β-Aminosubstituted α,β-Unsaturated Fischer Carbene Complexes as Precursors for Complex Oligocyclic Molecules

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Basics and Applications

DISSERTATION

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Meinem Lehrer, Herrn Prof. A. de Meijere, möchte ich an dieser Stelle für die Überlassung des interessanten, aufregenden Themas, seine vielen hilfreichen Anregungen und seine kontinuierliche Diskussionsbereitschaft während der Anfertigung dieser Arbeit ganz herzlich danken.

Meinen Eltern

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A. Introduction

Pharmaceutical and material chemistry are two most important areas in our life. The principle of pharmaceutical chemistry is devoted to the discovery and development of new agents for treating diseases.[1] One of the most fortuitous events in the history of science was the discovery of the antibiotic, penicillin, by Alexander Fleming in 1928. This kind of medicine help human against the bacterial infections. Unfortunately, the resistance of bacteria to antibiotics is easily induced after long-time or improper use. As the former wonder drug penicillin and other antibiotics became increasingly ineffective around the world, vancomycin is often recognized as the "antibiotic of last resort". After its introduction into hospitals more than forty years ago, the resistance of "Staph" (*Staphylococcus aureus* bacteria) to vancomycin increased dramatically during the 1990's, and several deaths were found.[2] Most of the research now underway has focused on finding other drug families that could take vancomycin's place. Providentially, ramoplanin, an antibiotic more active than vancomycin, was just synthesized in the laboratory last year.[3]

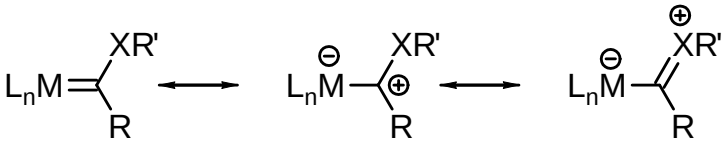
The other topic, material chemistry, has become an active area of investigation during the past two decades. Liquid crystals, conducting polymers, organic magnetic materials, nanosized and molecular devices, including electronic and nonlinear optical materials, are potential candidates of new materials in the future, although some of them are far from the practical applications.[4] One of these applications is conducting polymers, which are based on fully conjugated long-chain polymers and polyacetylene (PA) is the simplest form of them. In 1961, the first PA film was produced in Tokyo. Later, Shirakawa, McDiarmid and Heeger improved the conductivity of PA by modification their structures and addition of dopants.[5] Depending upon the types of dopants, such materials can be applied as light-emitting diodes (LEDs) and secondary batteries. The most popular application of LEDs is the traffic lights on the streets, at least in Taiwan. Organic conducting polymers have several advantages, such as light weight, higher potentials, longer lifetimes, lower toxicity and easy to be molded to the desired shape, over inorganic electroactive materials.[6] Lithium batteries of cellular phones are the best examples of these advantages. Due to their excellent contributions, the three scientists were awarded the Noble Prize in chemistry in 2000.[7]

Both pharmaceutical chemistry, which protects human's life, and material chemistry, which satisfies the need of human being, are based on the organic synthesis. In order to develop effective drugs and useful materials, chemists always look for easy and convenient synthetic methods. Homogeneous transition-metal-catalyzed or mediated reactions can be regarded as

useful tools for such applications.[8] Owing to the special properties of organometallic compounds, for instance: stabilization and/or activation of reactants, they make reactions more facile and effective. In contrast to the traditional procedures, they provide following advantages: a) reduction in required steps to achieve target molecules, b) simple introductions of functional groups, c) effortless control in stereochemistry and d) generally, provision of the mild reaction conditions.

Carbene complexes in organic synthesis are among the most promint examples. The first carbene complex was reported by E. O. Fischer et al. in 1964,[9] and it also exhibits the first examples of metal–carbon multiple bonds (Scheme 1). Complexes of this type, the so called Fischer carbene complexes, contain a low-valent transition metal and strong electron-withdrawing ligands. The combination of these two effects leads to a strong electrophilicity of carbene carbon, but the unshared electron pair(s) on the heteroatom enhances the stability of such kinds of compounds. This chemical property can be explained by the contribution of the canonical forms **1A** and **1B**. About 10 years later, Schrock carbene complexes **2** were discovered.[8a] Because of the good π-donation property of the metallic fragment in the Schrock-type complexes, the obvious nucleophilic character of the carbene carbon was detected. Since then, these classes of compounds have developed into an important branch in organometallics and organic synthesis.

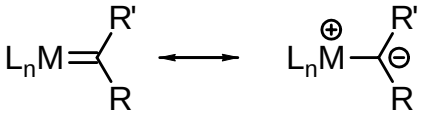
Fischer-Type :



1 **1A** **1B**

X = O, S, N
R,R' = Alkyl, Aryl
M = Tansition metal with lower oxidation state

Schrock-Type:

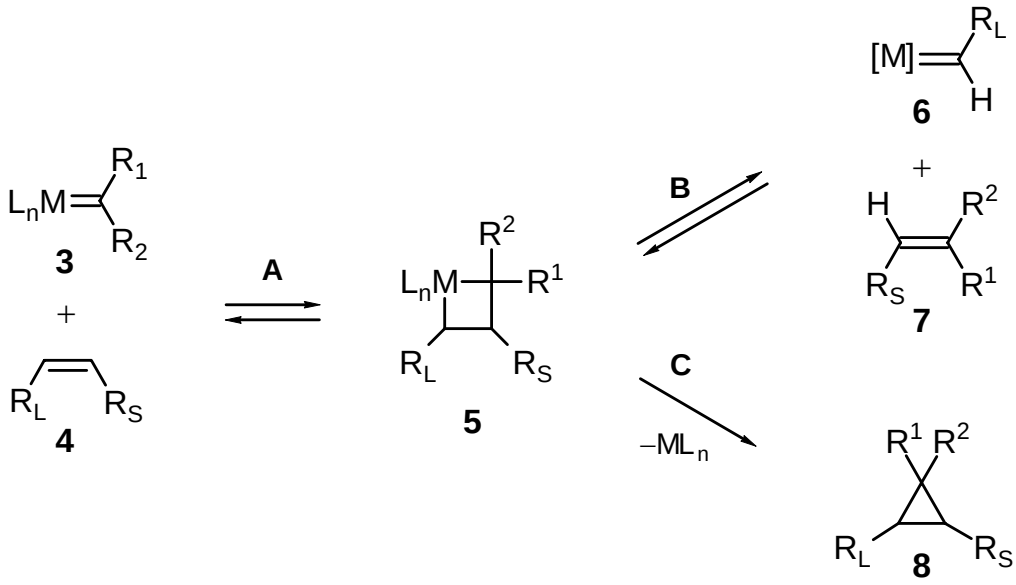


2 **2A**

R,R' = Alkyl, H
M = Transition metal with higher oxidation state

Scheme 1. Classification of transition-metal carbene complexes.

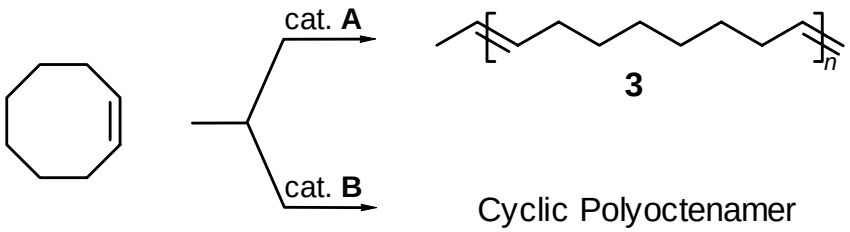
[2+2] Cycloaddition between alkenes **4** and carbene complexes **3**, either Fischer or Schrock types, was recognized as a key step to afford metathesis or cyclopropanation (Scheme 2).[11] The intermediate metallacyclobutane **5** undergoes [2+2] cycloreversion to give a carbene complex **6** and a new alkene **7**. This process via **A** and **B** is called olefin metathesis. On other hand, a cyclopropane **8** can be formed via the reductive elimination from the metalla-cyclobutane **5**. The selectivity of reaction routes depends upon the electronic properties of the alkene and carbene carbon (see later).

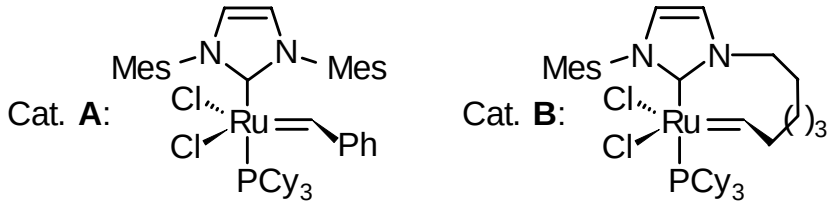


Scheme 2. Mechanism of olefin metathesis (via **A** and **B**) and cyclopropanation (via **A** and **C**). **A**: [2+2] cycloaddition between a carbene complex and an alkene; **B**: [2+2] cyclo-reversion; **C**: reductive elimination.

The term "olefin metathesis" was firstly defined in 1967,[12] although the phenomenon of ring-opening polymerization have already found before the discovery of carbene complexes.[13] From the mid-1950s to the early 1980s, these processes were carried out with the heterogeneous catalysts under harsh conditions and strong Lewis acids, which make them incompatible with most functional groups. Later, homogeneous carbene complexes, especially ruthenium-based catalysts, were recognized as efficient tools for olefin metathesis with high functional group tolerance.[14] Due to different chemical activities of complexes to olefins, reaction types could be in detail classified into ring-opening metathesis (ROM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis polymerization (ADMET), ring-closing metathesis (RCM) and cross-metathesis (CM). These new catalysts can be used for modification of fine chemicals and intermediates on the small scale or production of

functionalized polymers in industrial applications. Recently, Grubbs and coworkers discovered a new synthetic route to cyclic polymers by using a cyclic carbene complex as the catalyst (Scheme 3).[15] The catalyst **B** initiated the reaction with ROMP, and marcocyclic complex (not shown) was formed. After further propagation steps, this process was terminated by RCM and afforded cyclic polymers with number-average molecular weights up to 1200 kD. They showed very strong evidences by using of chemical and physical analysis methods to distinguish cyclic and linear polymers. More interesting, the reaction pathways to linear or cyclic polymers depend upon applied catalysts, not upon the concentration of monomers. This strategy for synthesis of cyclic polymers circumvents the traditional approaches which were carried out by usage of linear precursors in low contraction.

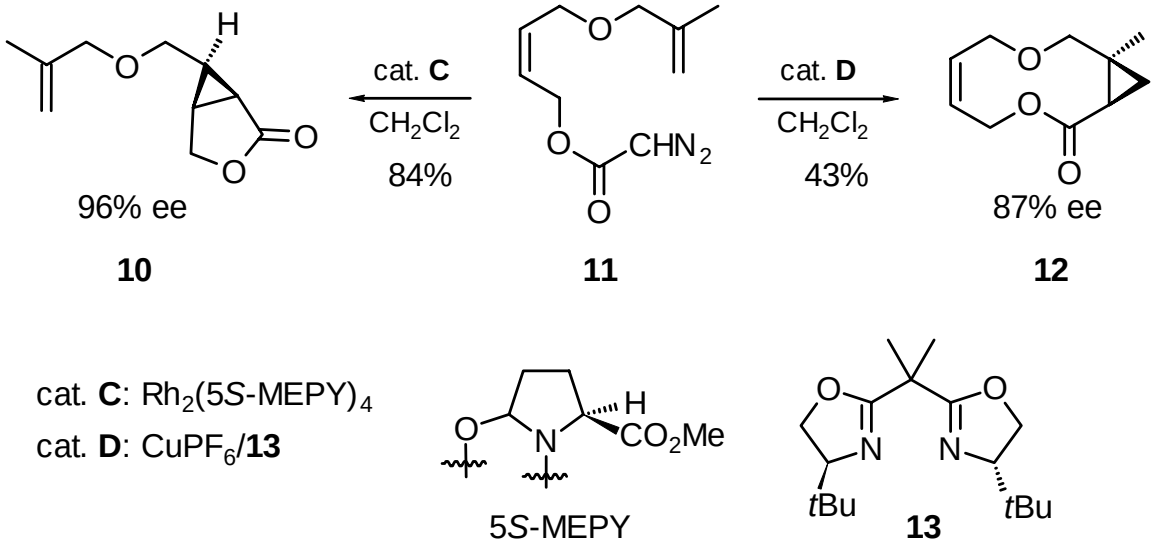




Scheme 3. Synthesis of cyclic and linear polymers with ruthenium carbene complexes.

Cyclopropanes are very important basic structures that can be as versatile intermediates in organic synthesis or exist in numerous natural products.[16] An extremely unusual example is the natural product, U-106305, which was isolated from *Streptomyces sp* by Upjohn's chemists in 1995.[17] The structure of this compound contains five continuous cyclopropyl groups and an additional one attached via a conjugated ethylene moiety. This novel U-106305 represents against atherosclerosis by inhabitating the action of the plasma protein CETP (cholesteryl ester transfer protein).

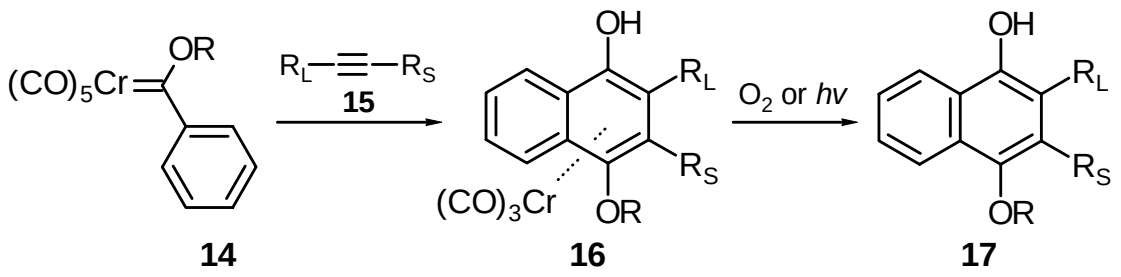
Cyclopropanation of alkenes by carbene complexes is one of the most common methods. These carbene catalysts can be generated *in situ* via decompositions of diazo compounds by numerous transition metals, especially copper and dirhodium complexes.[18] Doyle et al. showed the catalyst-induced chemoselectivity to produce cyclopropane moiety from **11** (scheme 4) and they proposed that the competition between the allylic intramolecular cyclopropanation (to **10**) and macrocyclization (to **12**) depends upon the electronic properties of olefins and a carbene carbon.[19] Excellent enantiocontrols could be achieved with chiral catalysts, either dirhodium with the pyrrolidine deviate (5*S*-MEPY) or copper with C_2-symmetric bis-oxazoline **13**.



Scheme 4. Chemo- and enantioselective cyclopropanation via *in situ* generated carbene catalysts.

As mentioned above and in Scheme 2, olefin metathesis and cyclopropanation are competitive in the reaction of carbene complexes with alkenes. This chemoselectivity can be easily explained by use of Fischer carbene complexes as reagents. The more electron-rich the olefin or the less electron-deficient the carbene carbon, the more favorable is the pathway to olefin metathesis.[11,20] In comparison to copper and dirhodium catalysts, cyclopropanation from Fischer complexes is not so widely applied, but they have played an important role in the elucidation of the mechanism of such cyclopropanations, since with Fischer carbene complexes the reations could not be proceed free carbenes and thus the activation property of carbene complexes were confirmed.[21]

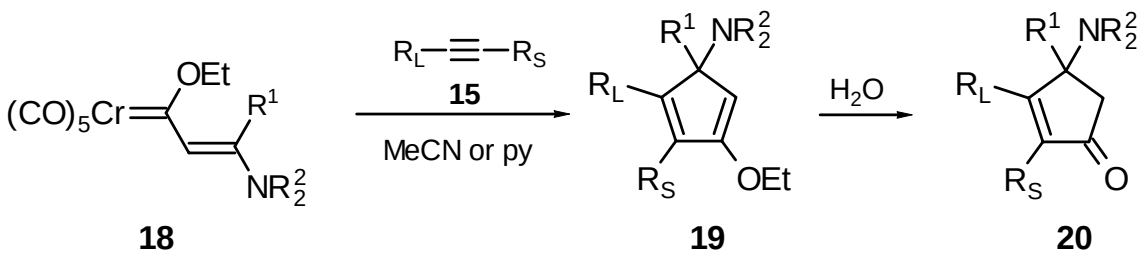
Another famous application of Fischer carbene complexes in organic syntheses is the Dötz reaction – the formal [3+2+1] cycloaddition of an α,β-unsaturated or α-aryl-substituted Fischer carbene complex **14**, an alkyne **15**, and a later inserted carbon monoxide moiety (Scheme 5).[22] Although the approximate mechanism of the Dötz reaction was established by many research groups,[23] there are still new surprising suggestions in each detail steps.[24] The key intermediate metallacyclobutene is generated via a [2+2] cycloaddition between carbene complex **14** and an alkyne **15**, closely related to the reaction route **A** in Scheme 2. Subsequent electrocyclic ring opening affords a 1-metalla-1,3,5-hexatriene complex. After the insertion of a carbon monoxide into the metal-carbene bond, the vinylketene complex undergoes an electronic ring closure to give a cyclohexadienone complex, which upon tautomerization accounts for the naphthol complex **16**.[25] The chromium fragment can be removed by treatment of oxidation agents or photolysis. This procedure was convincingly used towards the preparation of a variety of natural products, *i.e.* daunmycin,[26] desoxyfrenolycin,[27] fredericamycin,[28] vitamine E and K,[29] and other interesting molecules.



Scheme 5. The Dötz benzannulation.

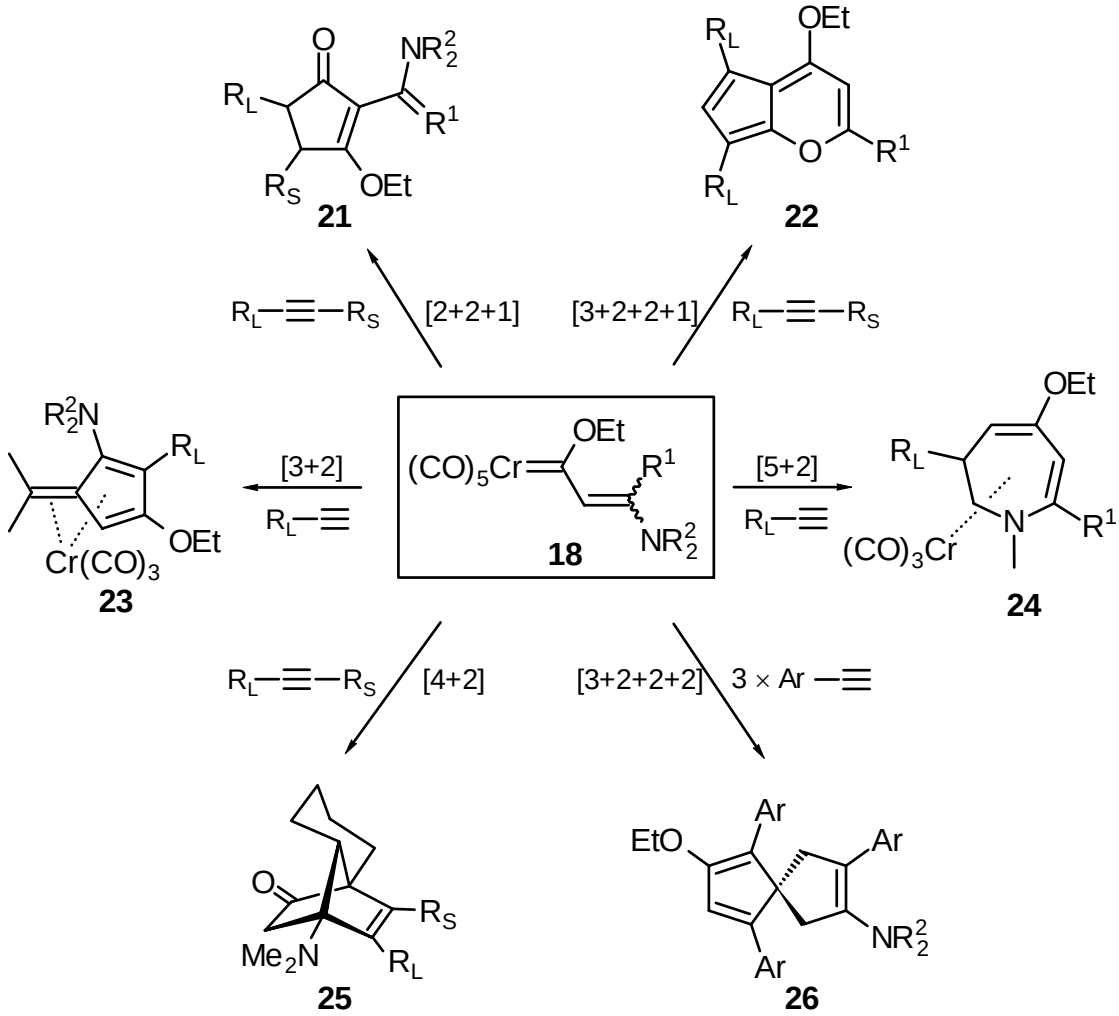
During the development of the Dötz reaction, indenes, the formal cycloaddition product without the insertion of carbon monoxide, were isolated as byproducts.[22] Lately, many research groups[30] have independently reduced the incorporation of a carbon monoxide in the Dötz reaction and compounds with five-membered ring were obtained as major product. Among so many different variations, including kinds of transition metals, solvents, reaction temperature, electronic properties of carbene complexes etc., de Meijere et al. found the most successful combination: introduction of the electron-donating substituents on α,β-unsaturated Fischer carbene complexes **18** and use of donor solvents, e.g. pyridine and acetonitrile.[31] In contrast to the Dötz reaction, highly substituted cyclopentadienes **19** or cyclopentenones **20**

(depending upon the hydrolysis) were formed with high chemoselectivity (Scheme 6). The importance of an simple access to cyclopentenones is not easily overstated to overstate.[32]



Scheme 6. Preparation of cyclopentadienes **19** and cyclopentenones **20** (depending upon the hydrolysis) according to the de Meijere protocol.

Furthermore, numerous interesting organic molecules and organometallic compounds, such as Clavulone-like cyclopentenones **21**,[33] cyclopenta[*b*]pyrans **22**,[34] a η^6-fulvene complex **23**,[35] η^5-dihydroazepine complexes **24**,[36] tricyclic compounds **25**[37] and spiro[4.4]nonan-trienes **26**[38] can be achieved by variations of substituents in carbene complexes of type **18** and reaction conditions (scheme 7). Formation of the unusual η^5-dihydroazepine complex **24** was proposed via a C–H activation and a formal [5+2] cycloaddition. After incorporation of an alkyne with a complex **18**, the chromium fragment activates a carbon–hydrogen bond in the dimethylamino functionality, inserts into it and makes an electronic ring closure to give **24**.[36] Treatment of dry or moisture pyridine to the complex **24** afford free dihydroazepines or methylenpyrrolidines, respectively. The novel spiro compound **26** is produced via formal [3+2+2+2] cocyclization with the participation of three alkyne molecules and the carbene complex **18**. Such triple reaction was firstly reported in 1999.[38a] The structure of the product was eventually determined by the X-ray crystal structure analysis. A control experiment was carried out with a ^{13}C-labeled carbene carbon, the ^{13}C label was only found at the spiro carbon. Due to the contribution of the conjugated diarylcyclopentadiene moiety in **26**, the molecule of this type showed the relative fluorescence quantum yield in 46%. According to above mentioned and many other applications, Fischer carbene complexes have been turned out to be useful building blocks for organic synthesis.[39]



Scheme 7. Cycloaddition products from carbene complexes **18**.

The targets of this thesis can be described in following terms:

- Confirmation of the mechanism of the formation of tricyclic compounds **25**.
- Investigation of the electronic and steric effects in the generations of cyclopentadienes **19** and tricyclo[5.2.2.0^{1,6}]undec-9-ones **25**.
- Synthesis of terpenoid and steroid-like compounds via use of cyclopentenones **20**.
- Looking for new applications of α,β-unsaturated Fischer carbene complexes **18** in organic synthesis.

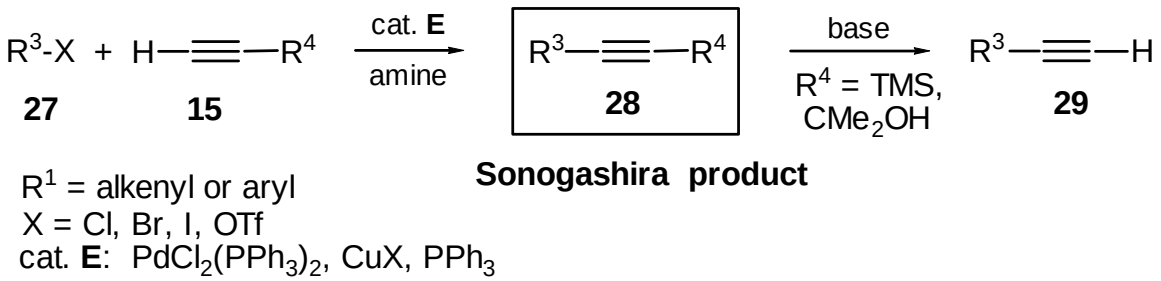
B. Main Part

1. Synthesis of Alkynes

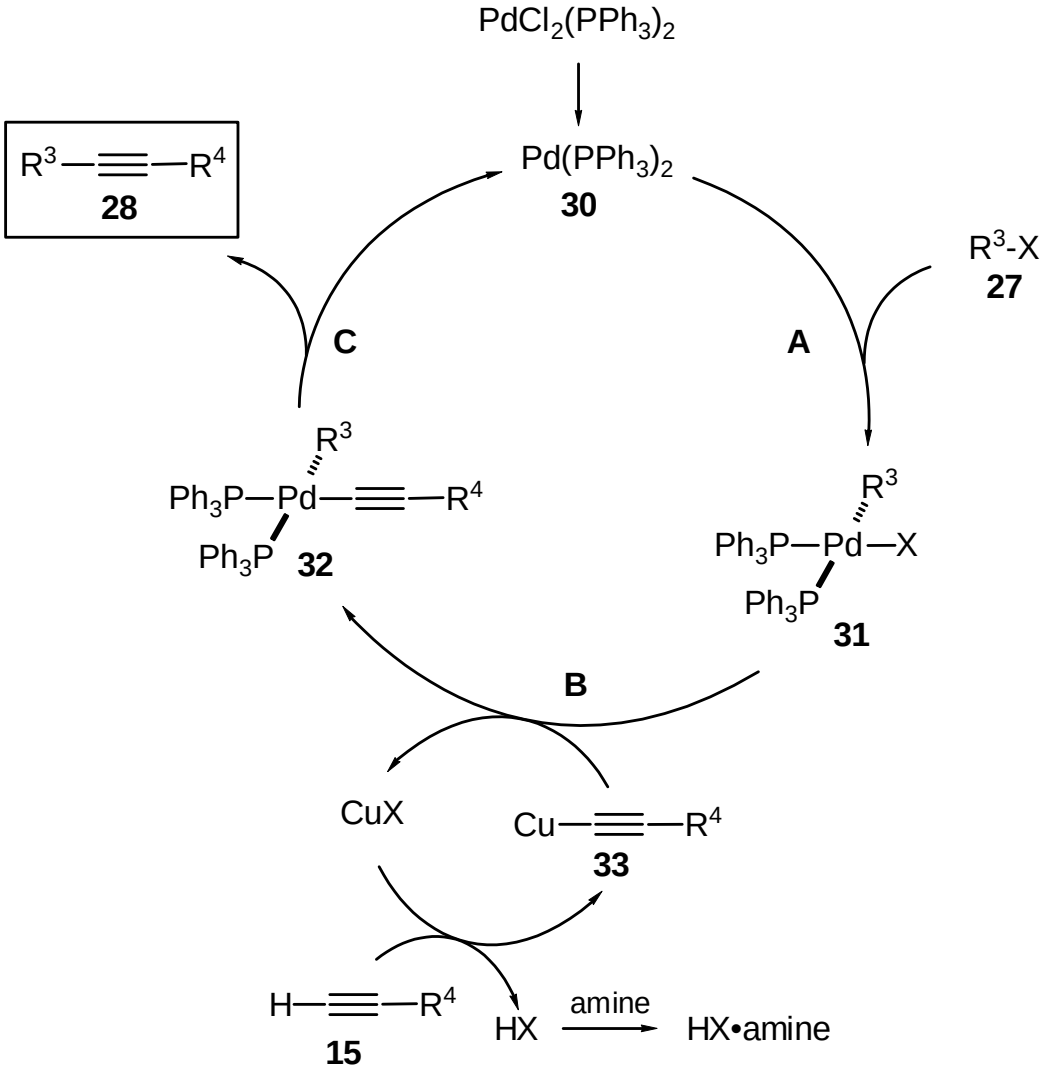
As mentioned in *Introduction*, (terminal) alkynes are necessary either as starting materials for synthesis of Fischer carbene complexes (chapter 2) or as a reaction partner for cocyclization with carbene complexes (chapter 3–6). Numerous methods for synthesis of acetylenic compounds will discussed below.

1.1. Preparation of Alkynes via the Sonogashira Reaction

The Sonogashira reaction provides a very useful tool to prepare enynes or arylalkynes **28** from a terminal alkyne **15** and an aryl or alkenyl halides (or enol triflates) **27** in an one-pot operation (Scheme 8).[40] This reaction processes under the combination of palladium and copper catalysts, and amine is used as solvent. The mechanism can be briefly described as following: the *cis*-alkenyl-coordinated complex **31** is formed via the insertion of an amine-activated palladium(0) catalyst **30** into an alkenyl halide **27** (step **A**) and a *trans-cis* isomerization (Scheme 9).[40b] In the subsequent transmetalltion step, an alkynyl moiety is transferred from alkynylcopper **33**, which is produced from a terminal alkyne **15** and copper halide, to the complex **31** affords palladium acetylide **32** (step **B**). Finally, an internal alkyne **28** is obtained after the reductive elimination of complex **32** (step **C**). The generated hydro halides or triflates can be converted to their salts by amine.



Scheme 8. The Sonogashira reaction. For more detail, see Table 1.



Scheme 9. Mechanism of the Sonogashira reaction. **A**: oxidative addition. **B**: transmetallation. **C**: reductive elimination.

Reaction of acetylene gas with alkenyl or aryl halides in this procedure only affords symmetric internal acetylenes, instead of terminal alkynes **29**, because of the higher reactivity of monosubstituted alkynes than that of acetylene gas.[40b] Hence, terminal alkynes should be synthesized via a transformation of masked disubstitued alkynes **28**. Trimethylsilylethyne (**15j**) and 3-butyn-2-ol (**15k**) as starting materials can satisfy this requirement. Upon treatment with a base, their coupling products convert to new terminal acetylenic compounds **29** (Scheme 8). Although the trimethylsilyl substituted internal alkynes of type **28** can be easily converted to terminal ones via desilylation under a mild condition, their starting material, trimethylsilylethyne (**15j**), is extremely expensive. On the contrary, cheaper 3-butyn-2-ol

(**15k**) provides the other possibility, but the cleavage of the 2-hydroxypropyl substituent with potassium hydroxide lacks tolerance of most functional groups (for instance, ester functionality). Later, such problems can be solved by employing a catalytic amount of sodium hydride.[41]

Table 1.

1	PhI (**27a**)	**15g**	*c*Pr	**28ag**	77
2	**27a**	**15h**^{2}	*n*Hex	**28ah**^{2}	84
3	**27a**	**15i**^{1}	1-cyclohexenyl	**28ai**^{1}	81
4	2-F_3C-C_6H_4-Br (**27a**^{1})	**15j**	TMS	**29a**^{1}	51[a]
5	3-F_3C-C_6H_4-Br (**27a**^{2})	**15j**	TMS	**29a**^{2}	81[a]
6	4-F_3C-C_6H_4-Br (**27a**^{3})	**15j**	TMS	**29a**^{3}	82[a]
7	**27a**^{3}	**29a**^{3}	4-F_3C-C_6H_4	**28a**^{3}**a**^{3}	89
8	4-MeO-C_6H_4-I (**27a**^{4})	**15k**	CMe_2OH	**29a**^{4}	47[a]
9	4-MeO_2C-C_6H_4-Br (**27a**^{5})	**15k**	CMe_2OH	**29a**^{5}	63[a]
10	**27a**^{5}	**29a**^{4}	4-MeO-C_6H_4	**28a**^{4}**a**^{5}	78
11	1-bromonaphthaline (**27b**)	**15k**	CMe_2OH	**29b**	75[a]
12	2-bromrothiophen(**27c**)	**15k**	CMe_2OH	**29c**	76[a]
13	1-bromo-2,4,6-triisopropyl-benzene (**27a**^{6})	**15k**	CMe_2OH	**28a**^{6}**k**	trace
14	(*E*)-1,2-dichloroethen (**27d**)	**15j**	TMS	**28dj**	77[b]
15	**27d**	**15a**	Ph	**28da**	81[b]
16	1,4-dibromobenzene(**27a**^{7})	**15k**	CMe_2OH	**29a**^{7}	65[a,c]
17	**27a**^{7}	**15g**	*c*Pr	**28a**^{7}**gg**	78[c]
18	**27a**^{7}	**15a**	Ph	**28a**^{7}**aa**	81[c]

Table 1. Continued.

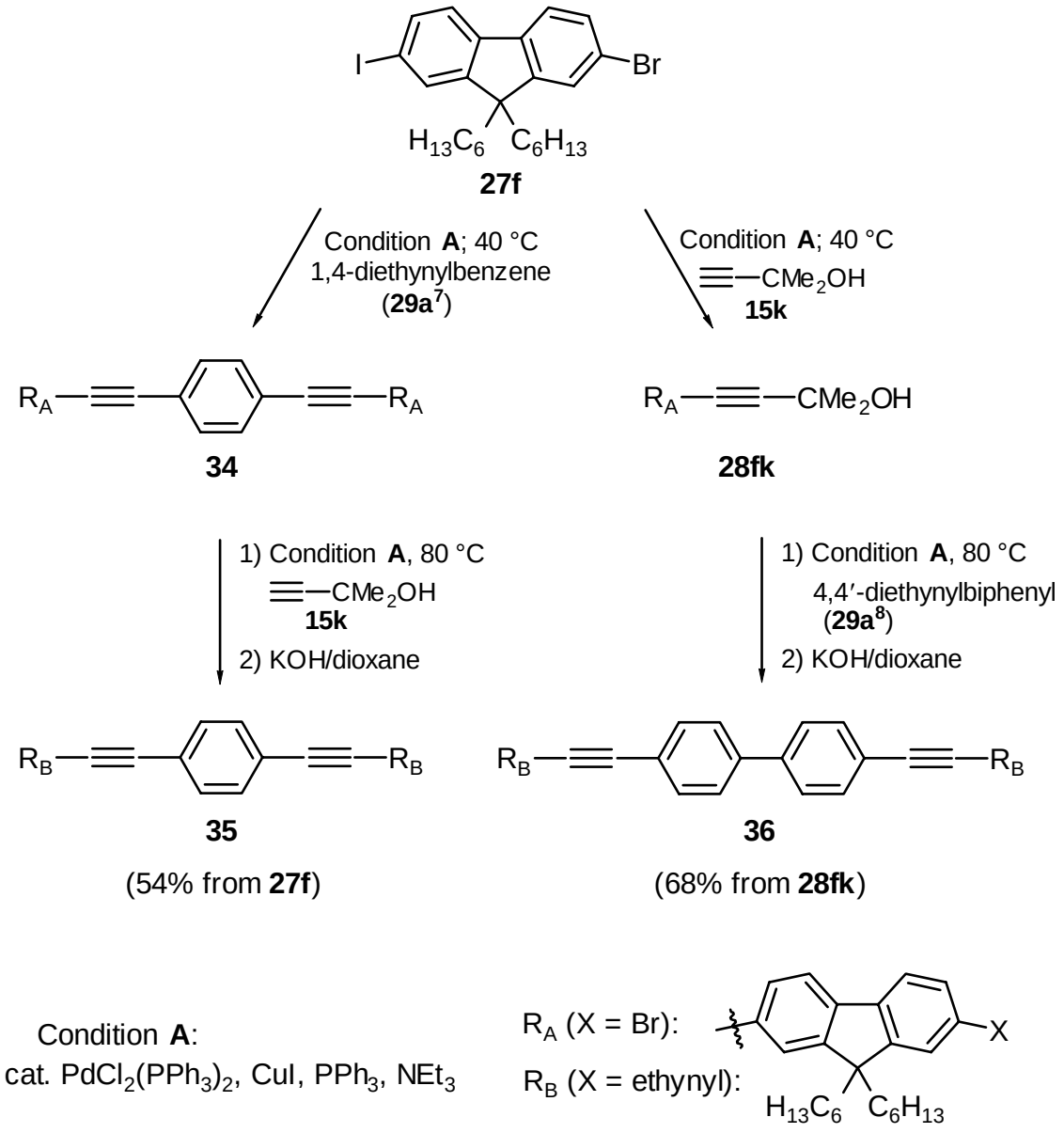
19	4,4′-dibromobiphenyl (**27a**^{8})	**15k**	CMe_2OH	**29a**^{8}	65[a,b]
20	4,4′-dibromobibenzyl (**27a**^{9})	**15k**	CMe_2OH	**29a**^{9}	69[a,c]
21	1,3,5-tribromobenzene (**27a**^{10})	**15k**	CMe_2OH	**29a**^{10}	55[a,d]
22	9,9-dihexyl-2-iodofluorene (**27e**)	**15k**	CMe_2OH	**29e**	71[a]
23	2-bromo-9,9-dihexyl-7-iodofluorene (**27f**)	**15k**	CMe_2OH	**28fk**	81[b]
24	**27f**	**15k**	CMe_2OH	**29f**	62[a,c]
25	**28fk**	**15a**	Ph	**29fa**	55[a]
26	1-bromo-1-cyclopentene (**27i**)	**15l**	2-isopropenyl	**28il**	81
27	**27i**	**15i**	1-cyclopentenyl	**28ii**	71
28	1-iodo-1-cyclohexene (**27i**^{1})	**15l**	2-isopropenyl	**28i**^{1}**l**	84
29	**27i**^{1}	**15i**^{1}	1-cyclohexenyl	**28i**^{1}**i**^{1}	92
30	1-bromo-1-cyclooctene (**27i**^{3})	**15l**	2-isopropenyl	**28i**^{3}**l**	66

[a] two steps to a terminal alkyne **29**. [b] mono-coupling product. [c] bis-coupling product. [d] tri-coupling product.

The reactivity order of this coupling reaction for leaving groups is RI>RBr>RCl, and for the same halides, vinyl groups are much more active than aryl substituents.[40] Due to these different chemical reactivities, chemoselectivity can be easily controlled by temperature to synthesize asymmetrical diynes or polyynes (Scheme 10).

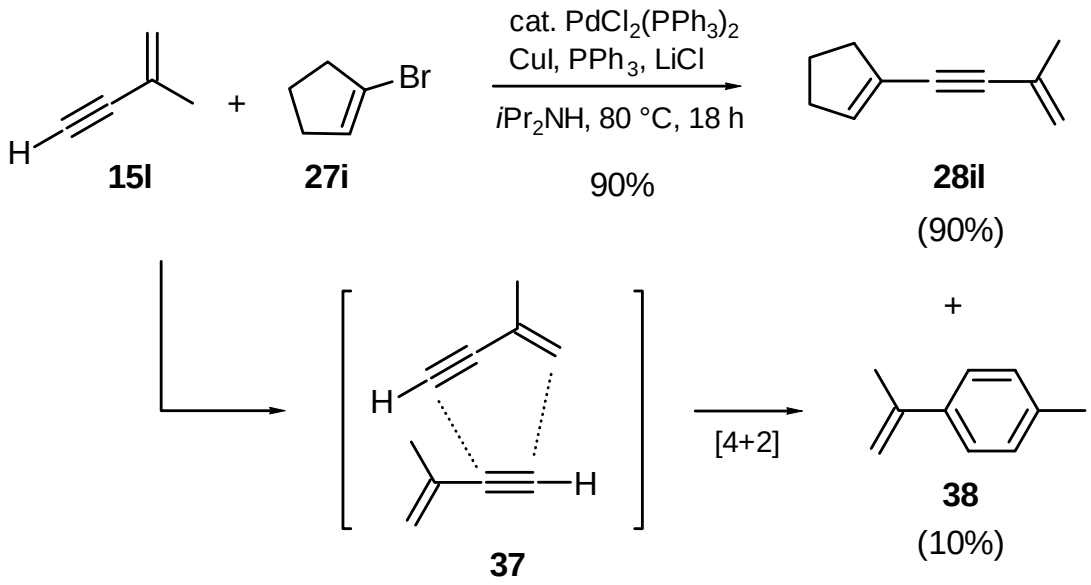
The electronic properties of aromatic compounds play also an important role on the reactivity. Although 4-iodoanisol (**27a**^{4}) should be more active than 4-bromo-benzoic acid methyl ester (**27a**^{5}) according to the above reactivity order of leaving groups, the coupling reaction from the former showed the worse chemical yield than it from the latter (Entries 8 and 9 in Table 1). In this case, the electron-withdrawing group (the ester functionality) accelerates the reaction and the electron-donating group (the methoxy moiety) reduces the reactivity. The steric hindrance on aryl halides is another factor in this coupling. Reactions of *o*-, *p*- and *m*-bromo(triflouromethyl)benzene with trimethylsilylethyne (**15j**) [entries 4 ,5 and 6 in Table 1] show clearly the tendency: the *o*-regioisomer would not give the product in good

yield. Moreover, the coupling reaction of 3-butyn-2-ol (**15k**) with 1-bromo-2,4,6-triisopropyl-benzene (**27a**[6]), which contains much more steric hindrance from two isopropyl groups at both *ortho* positions to the bromide, afforded only trace amount of the coupling product (entry 13 in Table 1). Therefore, acetylenes with large steric hindrance can not be access by utilizing this method.



Scheme 10. Temperature-controlled chemoselectivity of the Sonogashira reaction.

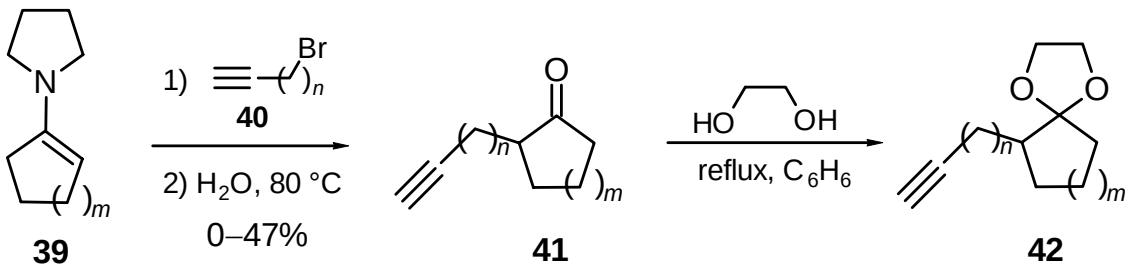
The Sonogashira reaction can be also applied for synthesis of conjugated yndienes of the type **28**. Unfortunately, sometimes the enyne cross-coupling product **38** was obtained as a byproduct (Scheme 11). Due to their similar polarity or boiling points, it is very difficult to separate both compounds, **28il** and **38**, by chromatography or distillation. Yamamoto et al reported that this formal [4+2] cycloaddition is favored under higher temperature (100 °C) without the presence of alkenyl bromide.[42] In order to reduce the reaction competition between cross- and the Sonogashira couplings and enhance the formation of conjugated dienynes **28**, the reaction should be carried out either in lower temperature and for shorter time, e.g. alkenyl iodides are suitable starting materials for this procedure.



Scheme 11. Competition between the Sonogashira reaction and the cross-coupling.

1.2. Synthesis of Alkynyl Substituted Cycloalkanones and their Acetal Derivatives

The preparation of alkynes **41** via the alkylation of Stock enamines **39** is one of the most well-known methods (Scheme 12). Enamines **34** are generated by the reaction of a secondary amine with a cycloalkanone, and they behave as nitrogen enolates, which can replace bromides in **40** by nucleophilic addition and form an α-alkyliminiun slats. Subsequent hydrolysis gave alkynyl substituted cycloalkanones **41**, which would be transformed to acetals **42** for the preparation of Fischer carbene complexes by treatment with *n*-butyllithium (Chapter 2).



Scheme 12. Synthesis of alkynyl cyclic ketones **41** via alkynyliation of enamines **39**. For more detail, see Table 2.

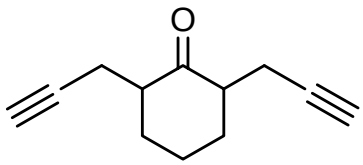
Table 2.

Entry	Enamine	Alkyne	Condition	Product	Yield (%)	Product	Yield (%)
1	**39a** (*m* = 1)	**40a** (*n* = 1)	**A**	**41a**	19[a]	**42a**	–[e]
2	**39b** (*m* = 2)	**40a** (*n* = 1)	**A**	**41b**	52[a], 47[b]	**42b**	87
3	**39b** (*m* = 2)	**40b** (*n* = 2)	**B**	**41c**	– [c]	**42c**	–[e]
4	**39b** (*m* = 2)	**40c** (*n* = 3)	**C**	**41d**	–	**42d**	26 [f]
5	**39c** (*m* = 3)	**40a** (*n* = 1)	**A** or **C**	**41e**	93[d], – [c]	**42e**	–[e]

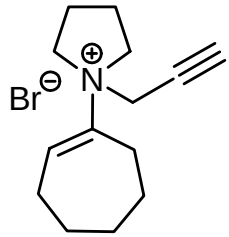
A: 1.5 eq. of alkynyl bromide **40** was dropwise added to the solution of enamine at ambient temperature, then refluxed for 18 h. **B**: addition of 0.5 equiv. of **40** to the enamine solution at 60 °C, then refluxed for 18 h. **C**: like **B**, but 1.5 equiv. of **40** was used. [a] lit. value, ref. 43. [b] in addition to **41b**, 9% bisalkynyl product **41b'** was isolated. [c] The chemical yield was very low and the product was not isolated. [d] lit. value, ref. 44. [e] due to the low yield of starting materials **41**, compounds **42** were synthesized from the other method (see Scheme 15, and Table 3). [f] chemical yield over two steps.

Formation of overalkylation byproducts, for instance **41b'**, is a serious problems of this reaction. In order to reduce this kind of byproducts, excess amount of enamines **39b** was used in the reaction, but none of alkyl substituted products was obtained (entry 3, Table 2). According to the report from Rossi et. al.,[44] alkyne **15e-e** was accessible in 42% yield. However, their procedure could not be reproduced. As the propagyl bromide **40a** was added to the solution of the enamine **39c** at room temperature, a strong exothermic reaction occurred and a massive solid was formed. Further heating this suspension under reflux would not afford desired product **41e** (entry 5 in Table 2). This massive salt should be the *N*-alkylation

product **43**. In order to reduce the reaction competition between *C*- and *N*-alkylations, an alkylation agents of type **40** were dropwise added to a solution of enamines **39** at higher temperature (60 °C). The reaction of the six-membered enamine **39b** with a excess amount of the inactive alkylation agent **40c** gave an acceptable yield (entry 4 in Table 2). Unfortunately, the alkyne **41e** could not be prepared under the same condition.



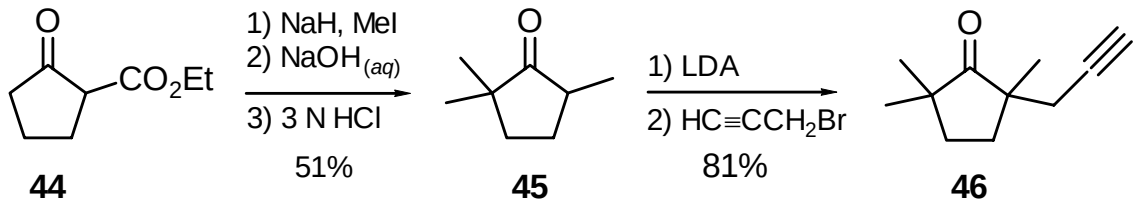
41b'



43

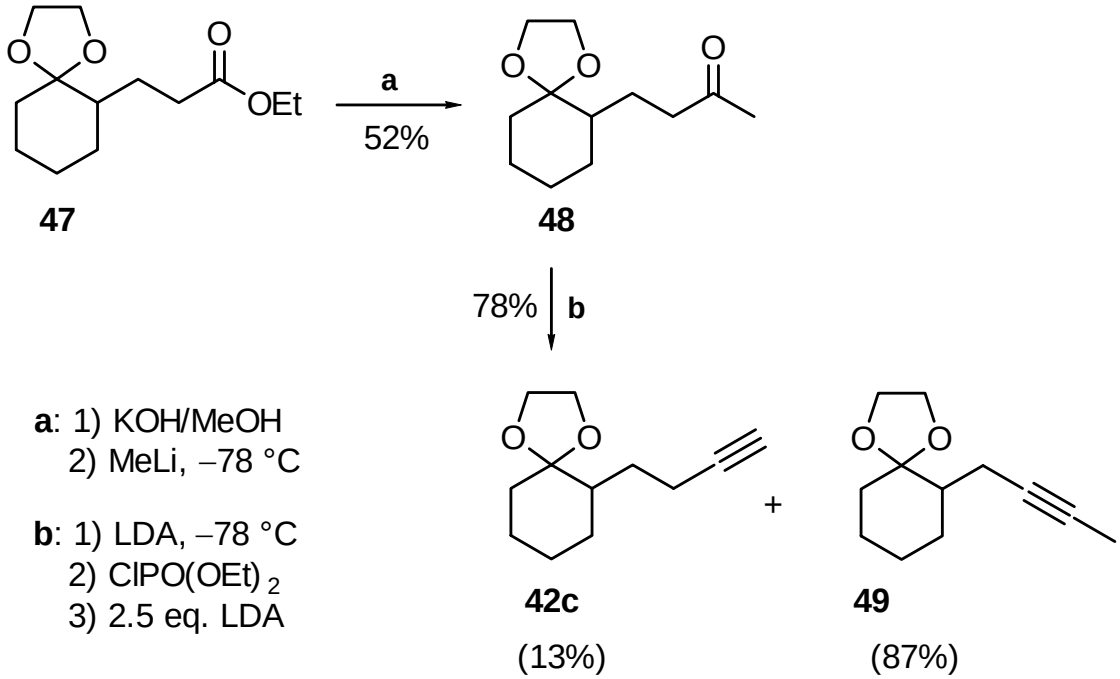
According to references[43,44] and the result in Table 2, some disadvantages can be summarized as following: a) Reaction should be carried out at higher temperature and it would enhance the formation of dialkylation compounds. b) A reaction competition between *C*- and *N*-alkylation that the latter would not afford desired products. c) Chemical yields depend dramatically upon the reactivity of alkylation agents **40** and the ring size of enamines **39**. d) Excess amount of alkyl agents are necessary for this reaction. e) Products are available in low yields. Hence, alkylation via the Stock enamines can not be regarded as a general method to prepare alkynyl cycloalkanones **41**.

Although direct monoalkylation of cycloalkanones can be achieved from either enol boranes[45] or β-keto esters,[46,47] the expensiveness of borane reagents or difficult cleavage of the ester functionality in the presence of the alkynyl moiety[47] should be the drawbacks of these methods. Reaction of lithium cyclopentenolate with propagyl bromide **40a** afforded the monoalkylation product **41a** in very low yield (less than 5%) and a large amount of residue with high-boiling points. The viscid remaining was not identified, but it is proposed as a multialkylation product. However, 2-(prop-2'-ynyl)-2,5,5-trimethylcyclopentanone (**46**) could be access from 2,2,5-trimethylcyclopentanone (**45**) in 81% yield under the same procedure (Scheme 13). This reaction should be a example to confirm the hypothesis of this overalkylation. Consequently, direct alkylation from lithium cyclopentenolate is not a suitable method to prepare alkynes of the type **41**.



Scheme 13. Synthesis of 2-(prop-2'-ynyl)-2,5,5-trimethylcyclopentanone (**46**).

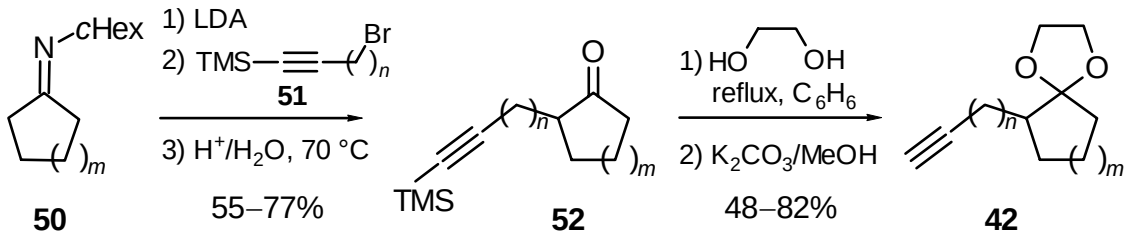
Negishi and coworkers reported a useful method to prepared a terminal alkyne from a methyl ketone under an one-pot operation with an excellent regioselectivity.[48] Seemingly, this functional group transformation is able to apply for synthesis of alkyne of the type **42** from the methyl ketone **48** (Scheme 14). However, a mixture of an internal and a terminal alkynes was obtained and the former was observed as the major product. Probably the existence of the 1,4-dioxlane group destroys the regioselectivity.



Scheme 14. Transformation of the methyl ketone **48** to alkynes **42c** and **49**.

Finally, a general procedure for preparation of alkynes of type **52** was found by using more reactive imines **50** with trimethylsilyl protected alkynyl bromides **51** (Scheme 15).[49] In

contrast to the alkylation via Stock's enamines, this process was operated at a lower temperature and none (with one exception) of overalkylnation products were detected. On the other hand, this reaction provided products **52** in 55–77% yields (Table 3). If unprotected propagyl bromide **40a** was used directly as a alkylation agent after treatment with LDA, the product **52a** was isolated in very low yield and further distillation of the residue made explosive (probably due to the formation of diynes or polyynes) !



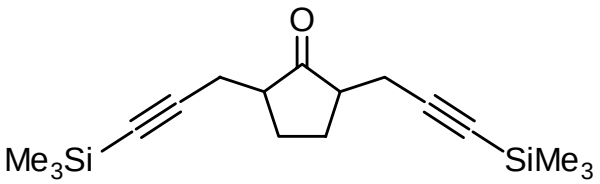
Scheme 15. Synthesis of alkynyl substituted cyclic acetales **42** under two-step operation. For more detail, see Table 3.

Table 3.

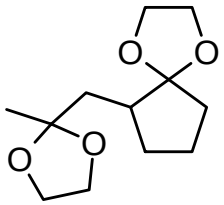
Entry	Imine	Alkyne	Product	Yield (%)	Product	Yield (%)
1	**50a** (*m* = 1)	**51a** (*n* = 1)	**52a**	55[a]	**42a**	48[b]
2	**50b** (*m* = 2)	**51b** (*n* = 2)	**52b**	77	**42c**	76
3	**50c** (*m* = 3)	**51a** (*n* = 1)	**52c**	67	**42e**	82

[a] in addition to **52a**, bisalkynyl product **52a'** was isolated in 19%. [b] in addition to **42a**, 30% of bisacetal product **53** was isolated in 43% yield.

Acetalization and desilylation of ketones of the type **52** afforded the terminal alkynes **42** in good yields. Unfortunately, the bisacetal compound **53** was obtained when longer reaction time was carried out in acetalization, although only one equivalent water was extracted. But 2-(4'-trimethylsilylbut-3'-yn-1'-yl)cyclohexanone (**52b**) would not give this kind byproduct under the same condition (entry 2 in Table 3).



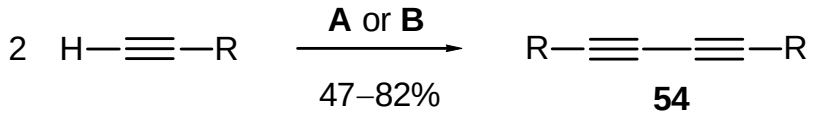
52a'



53

1.3. Synthesis of Symmetric Diynes

Symmetric diynes **54** can be generated by the reaction of terminal acetylene with copper(II) salts or copper(I) salts in the presence of oxygen.[40,50] There copper(II)-mediated or copper(I)-catalyzed reactions are called Glaser coupling (Method **A**, Scheme 16). Recently, Zhang et al. reported a new method to produce homocoupling products **54** via the combination of palladium(II) and copper(I) catalysts (Method **B**, Scheme 16).[51] Their new procedure is very similar to the Sonogashira coupling, but ethyl bromoacetate is used instead of alkenyl or aryl halides. In comparison with the Glaser coupling, the new procedure can be carried out in an inert atmosphere and under the mild conditions, i.e. at room temperature. The both advantages should be suitable for the preparation of unstable conjugated polyenynes.

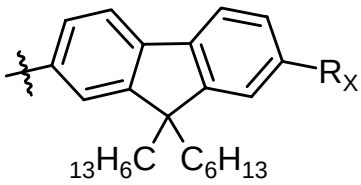
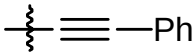


A: 4 eq. $Cu(OAc)_2$, 70 °C
Py/MeOH/THF (4/4/1).

B: cat. $PdCl_2(PPh_3)_2$, cat. CuI
$BrCh_2CO_2Et$, $EtN(iPr)_2$.

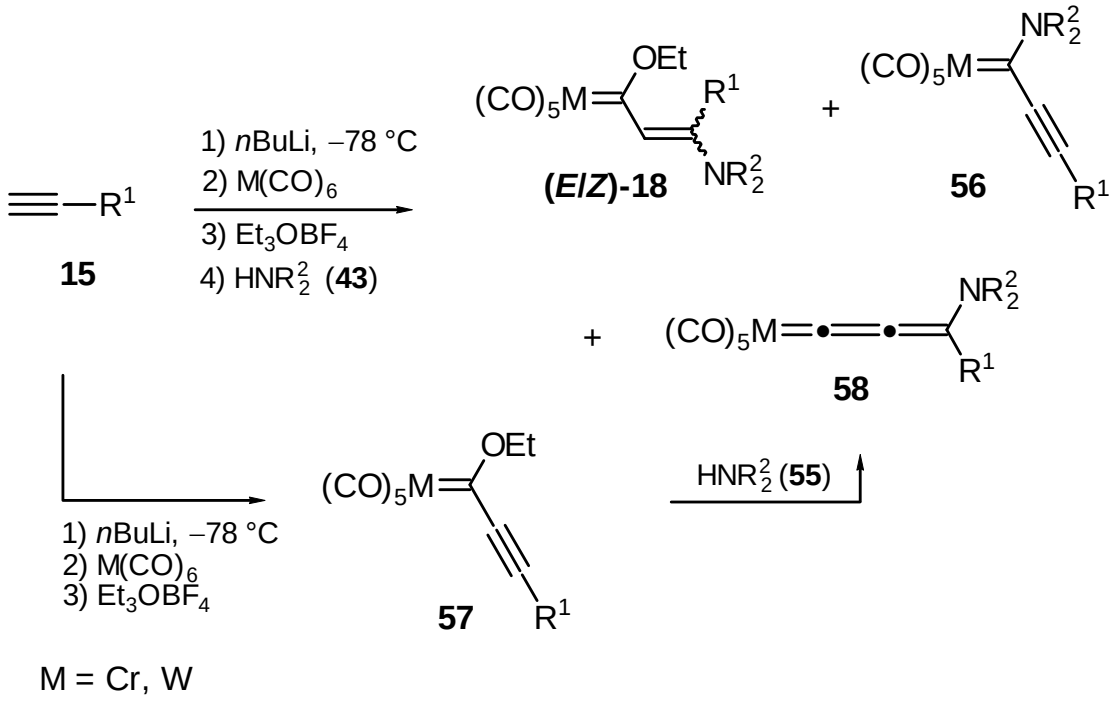
Scheme 16. Synthesis of symmetric diynes **54**. For more detail, see Table 4.

Table 4.

Entry	Alkyne	R	Condition	Product	Yield (%)
1	**29a**[3]	4-F_3C-C_6H_4	**A**	**54a**	57
2	**29a**[4]	4-MeO-C_6H_4	**A**	**54b**	47
3	**15i**[1]	1-cyclohexenyl	**B**	**54c**	81
					
4	**29e**	R_X = H	**A**	**54d**	82
5	**29fa**	R_X = 	**A**	**54e**	67

2. β-Aminosubstituted α,β-Unsaturated Fischer Carbene Complexes

The most convenient access to β-aminosubstituted α,β-unsaturated Fischer carbene complexes **18** certainly is by Michael type addition of secondary amines **55** to alkynylidene-carbene complexes **57**. The latter are easily obtained from lithiated terminal alkynes, hexa-carbonylchromium, triethyloxonium tetrafluoroborate (Scheme 17). In a previous systematic study of this Michael type reaction of complexes **57**, it was observed that in addition to the 1,4-addition products **18**, 1,2-addition-elimination (formal substitution) **56** and 1,4-addition-elimination products **58** can be formed.[52] The ratio of the three complexes **18**, **56** and **58** largely depends on the polarity of the solvent, the reaction temperature, and the substituents on the alkyne (R^1) and amine (R^2). The desired complexes **18** can be obtained as the only product (or at least as the major product) by careful choose of reaction conditions. Fortunately, the carbene complexes **18** have been easily access from terminal alkynes **15**, generally, in good to excellent yields by a new one-pot procedure (Table 5).[31,53] The configuration of complexes **18** are usually (*E*)-form besides existence of the bulky substitutes R^1, e.g. *tert*-butyl or trimethylsilyl groups.



Scheme 17. Synthesis of β-aminosubstituted α,β-unsaturated Fischer carbene complexes **18**. For more detail, see Table 5.

Table 5.

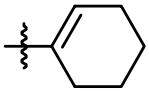
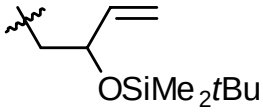
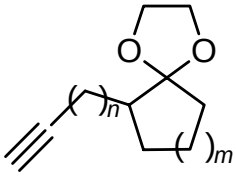
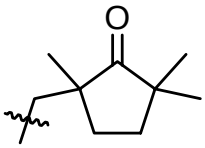
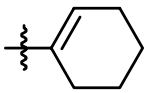
Entry	Alkyne	R^1	Product	Yield (%)[a]
M = Cr				
1	**15g**	*c*Pr	**18a**	91
2	**15h**	Me	**18b**	81
3	**15m**	*i*Pr	**18c**	72[b]
4	**15n**	*t*Bu	**18d**	93[c]
5	**15o**	$CMe_2(OSiMe_3)$	**18e**	82[c,d]
6	**15p**	$CHMe(OSiMe_2tBu)$	**18f**	79
7	**15i**[1]		**18g**	94
8	**15q**		**18h**	73
				
9	**42a**	(*m* = 1, *n* = 1)	**18i**	83
10	**42b**	(*m* = 2, *n* = 1)	**18j**	87
11	**42c**	(*m* = 2, *n* = 2)	**18k**	84
12	**42d**	(*m* = 2, *n* = 3)	**18l**	90
14	**42e**	(*m* = 3, *n* = 1)	**18m**	87
15	**46**		**18n**	50

Table 5. (continued)

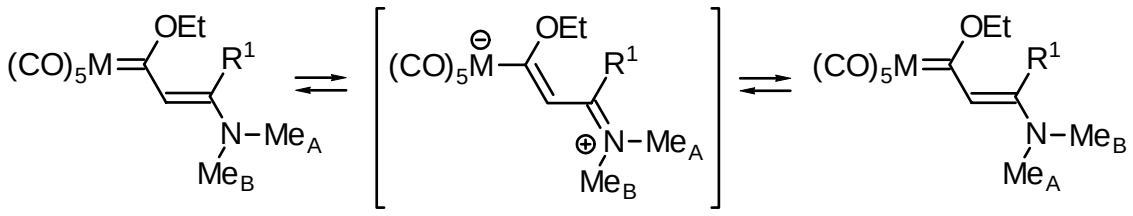
M = W				
16	**15i[1]**		**18o**	87

[a] All products were synthesized according the new one-pot procedure from the terminal alkynes, dimethylamine was used for the Michael type addition (R^2 = Me), and their configuration are (*E*)-form if not otherwise mentioned. [b] in addition to **18c**, 15% of **58c** was also isolated. [c] (*Z*)-form. [d] in addition to **18e**, 9% of **58e** was also isolated.

Acetalization of the ketone functionality with highly steric hindrance, e.g. alkyne **46**, by using normal methods would not give satisfactory results and it has to be carried out under high pressure (1.5 GPa).[54] Due to this inconvenience, the starting material **46** was directly used for the preparation of the carbene complex **18n** (entry 15 in Table 5). Although the lithium enolate of **46** can not be formed, *n*-butyllithium could attack the ketone moiety, even at –78 °C.[55] The optimized condition for this preparation was operated in a diluted solution, otherwise lower chemical yields were obtained.

Tungsten carbene complex **18o** is also accessible via this one-pot procedure, its chemical yield is similar to the chromium analogue (entry 7 and 16 in Table 5). These complexes prepared from the conjugated enynes are called 1-metalla-1,3,5-hexatrienes, and their solutions are not only air- but also temperature-sensitive, even at ambient temperature for a brief period. Hence, the more unstable molybdenum complex of this type, which was prepared from 1-ethynyl-1-cyclohexene (**15i[1]**), could not be isolated, although it was detected by TLC during the reaction progress.

In some cases, the two methyl groups in the dimethylamino functionality in complexes of the type **18** show broad signals not only in ^{1}H- but also ^{13}C-NMR spectra. This phenomenon can be explained by the degenerated rearrangement of two methyl groups.[56] Because of the strong electron-withdrawing property of the carbene fragment and electron-donating property of the dimethylamino group, the zwitterionic transition state **59** should be relatively stable and easily to formed (Scheme 18). It will enhance the rearrangement between both isomers **18-I** and **18-II** and therefore the signal(s) of the dimethylamino group in ^{13}C-NMR spectra would be observed as broad lines, instead of "peak(s)".

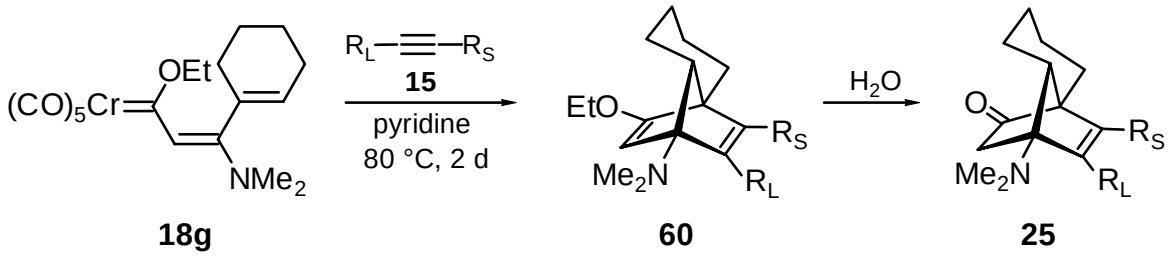


18-I **59** **18-II**

Scheme 18. Degenerated rearrangement of two methyl groups in the dimethylamino functionality.

3. Tricyclo[5.2.2.0^{1,6}]undec-9-ones

As mentioned in my diploma thesis, 7-dimethylaminotricyclo[5.2.2.0^{1,6}]undec-9-ones **25** were prepared from pentacarbonyl(3-cyclohexenyl-3-dimethylamino-1-ethoxy-2-propen-1-ylidene)chromium (**18g**) and alkynes (scheme 19).[37] The ethoxy groups of the initial cycloadducts **60** could be clearly observed in the ^{1}H- and ^{13}C-NMR spectra of the crude products, hydrolysis of **60** apparently occurred during chromatography, and the ketones **25** were the isolated products. At that time, the mechanism of the formation of compounds **60** was doubtful. It is well-known that alkyne insertion into the metal-carbon double bond is generally considered to be the first important step in reactions of Fischer carbene complexes with alkynes,[57] and the generation of the unstable intermediate **61** follows. Under this reaction condition, it was impossible to observe its existence. On the other hand, Aumann et al. reported another reaction mode, in which β-cyclopentenyl-substituted propenylidene-metal complexes undergo a rapid intramolecular insertion of the carbon-carbon into the metal-carbene double bond leading to ring-annulated pentacarbonyl-η^{1}-cyclopentadienyl-metal complexes, which upon heating in pyridine at 70 °C did not yield the uncomplexed cyclopentadiene, but eventually 4,5-ring-annelated 1-dimethylamino-cyclopent-1-en-3-ones.[56] In accordance with their result, the stable zwitterionic intermediate of the type **62** should be isolated. Unfortunately, the compound **62-Cr** was not observed. Hence, this doubtful possibility between the intermediates **61** and **62** has been studied in detail, and will be explained in the following sections.



Scheme 19. One-pot synthesis of 7-dimethylamino-tricyclo[5.2.2.0^{1,6}]undec-10-en-9-ones **25** from complex **18g** and alkynes. For details see Table 6.

Table 6.

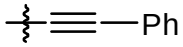
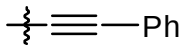
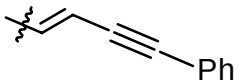
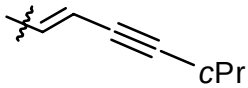
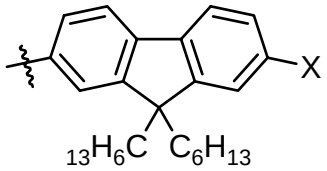
Entry	Alkyne	R_L	R_S	Product	Yield (%)
1	**15i**[1]	1-cyclohexenyl	H	**25a**	40[a,b]
2	**15i**	1-cyclopentenyl	H	**25b**	43[b]
3	**15i**[2]	1-cycloheptenyl	H	**25c**	26[b]
4	**15l**	2-isopropenyl	H	**25d**	73[a,b]
5	**15a**	Ph	H	**25e**	88[a,b]
6	**29c**	2-thienyl	H	**25f**	34
7	**15a**[12]	4-*n*Pr-C_6H_4	H	**25g**	87[a,b]
8	**15a**[13]	4-EtO-C_6H_4	H	**25h**	50[a,b]
9	**15a**[14]	4-*n*Pr-C_6H_4-C_6H_4	H	**25i**	15[a,b]
10	**29a**[5]	4-MeO_2C-C_6H_4	H	**25j**	91
11	**28aa**[15]	4-EtO_2C-C_6H_4	Ph	**25k**	66[b]
12	**29a**[1]	2-CF_3-C_6H_4	H	**25l**	44
13	**29a**[2]	3-CF_3-C_6H_4	H	**25m**	84
14	**29a**[3]	4-CF_3-C_6H_4	H	**25n**	85
15	**29b**	1-naphthyl	H	**25o**	52
16	**15j**[16]**j**		TMS	**25p**	47
17	**54f**		Ph	**25q**	60[a]
18	**28daa**		Ph	**25r**	48[a,b]
19	**28dgg**		*c*Pr	**25s**	46[a,b]
20	**29a**[7]	4-ethynyl-Ph	H	**25t**	69
21	**29a**[10]	3,5-diethynyl-Ph	H	**25u**	65

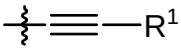
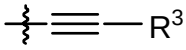
Table 6. Continued.

R^1 (X = H):

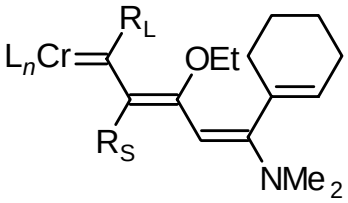
R^2 (X = ethynyl):

R^3 (X = phenylethynyl):

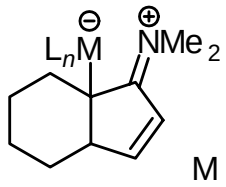


22	**29e**	R^1	H	**25v**	51
23	**54d**		R^1	**25w**	57
24	**29f**	R^2	H	**25x**	45
25	**54e**		R^3	**25y**	34

[a] ref. 37. [b] ref. 58.



61



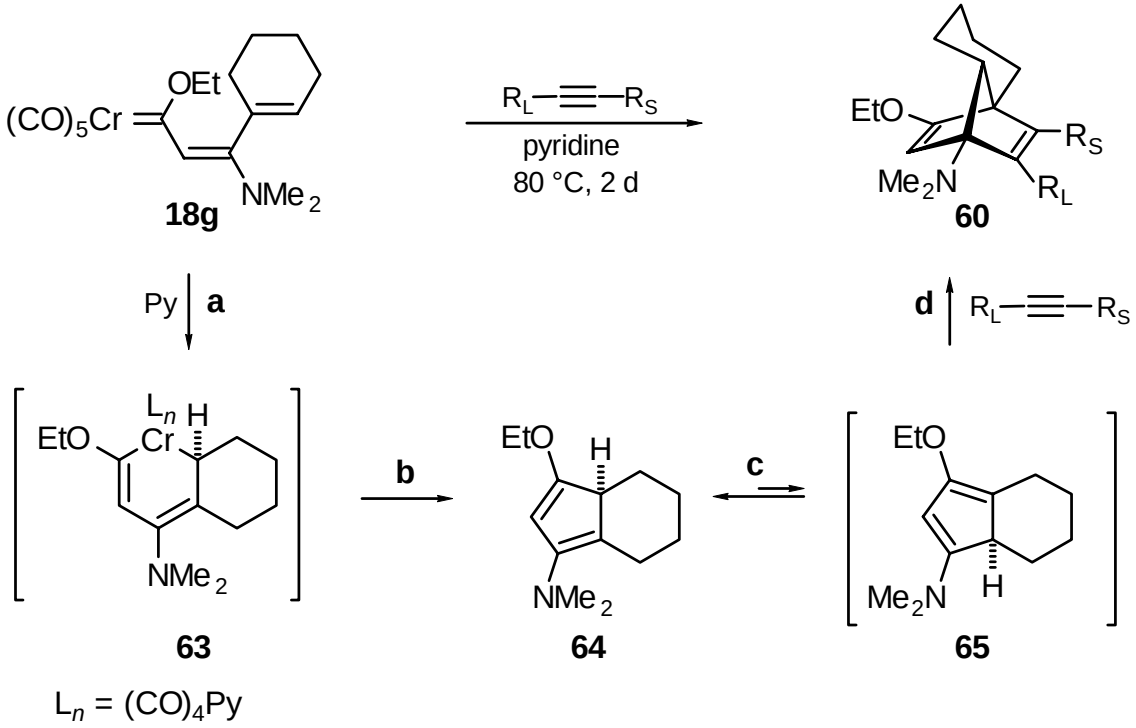
M = Cr, W

62

3.1. Mechanism

When the 1-chromahexa-1,3,5-triene **18g** without an added alkyne was kept in [D_5]-pyridine at room temperature for 16 h or at 80 °C for 1 h, it was completely converted to the cyclohexane-annulated cyclopentadiene **64**, the structure of which was assigned on the basis of a NOESY-2D-NMR spectrum. During this process, only signals of the complex **18g** and the cyclization product **64** were observed, and none of the intermediate, η^1-cyclohexadienyl complex **62-Cr**, was detected, even at the first 15 min. The results of this control experiment show that the formation of the cyclohexane-annelated cyclopentadiene **64** from **18g** in pyridine more probably occurs by 6π-electrocyclization of monodecarbonylated **18g** to the pyridine-stabilized chromacyclohexadiene **63**, which is subsequently followed by reductive elimination.[39] Signals of the isomeric diene **65** arising from **64** by a 1,5-hygrogen shift could not be detected by ^{1}H and ^{13}C NMR spectroscopy even at 80 °C.[59,60] Thus, **64** apparently

rapidly equilibrates with **65** even at room temperature, and the latter more rapidly than **64** preferentially reacts with the added alkynes to afford the [4+2] cycloadducts **60**.[61]



Scheme 20. Mechanism for the formation of cycloaddition products **60**. **a**: 6π-electro-cyclization; **b**: reductive elimination; **c**: 1,5-hydrogen shift; **d**: [4+2] cycloaddition.

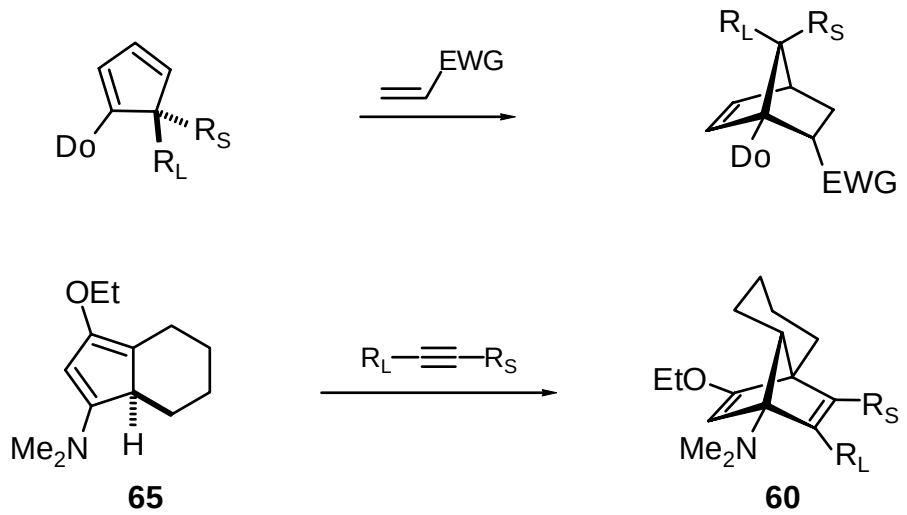
The high reactivity of the cyclopentadiene **65** can be confirmed that **25e** could be isolated in 36% yield after the introduction of complex **18g** with phenylethyne (**15a**) in a pyridine solution at room temperature for 2 d. Pyridine as a solvent is essential for this reaction, otherwise many byproducts and only traces of the cycloadduct **25e** were observed after 2 d at 60 °C, when either benzene or tetrahydrofuran even in the presence of triphenylphosphine were used. Without pyridine, pentacarbonyl[1-dimethylamino-3-ethoxy-3*a*H-tetrahydro-indene)-*N*]chromium would be formed after 6π-electrocyclization. The strong electron-withdrawing property of the pentacarbonyl-chromium fragment would reduce the reactivity of the cyclopentadiene **64** and **65** by decreasing its HOMO potential energy. Thus, the further Diels-Alder reaction would not easily happen.

As listen in Table 6, 24 out 25 examples were given only hydrolysis products **25**. However, only the reaction of complex **18g** with 1,4-diphenyl-1,3-butadiyne (**54f**) afforded not only

ketone **25q** but also the unhydrolysis product **60q** after chromatographic purification. Compounds of the type **60** have similar structures to norbornadiene, but their cyclohexane-annulated substituent would make the distance between two olefins much closer. Because of the through-space interaction between two olefins in norbornadiene, it has a lower first ionization potential than that of norbornaene.[62] Thus, this through-space interaction and the additional electron-donating properties of the ethoxy moiety in cycloaddition products **60** lead their HOMO potential energies obviously higher than these of normal enol ethers, and the formation of hydrolysis easily products **25** are enhanced. Phenylethynyl functionality in **60q** acts as a stronger electron-withdrawing group to reduces the hydrolysis rate.

3.2. Regio- and Stereoselectivity

The regional and facial selectivities in the above Diels-Alder reactions of **65** with dienophiles can be explained on the basis of a model proposed by Winterfeldt (Scheme 21).[63] The applied alkynes add onto the more reactive 1,3-diene **65** with *syn*-facial selectivity (with respect to the hydrogen in **65**) and the larger groups R_L obey the *ortho* selectivity (with respect to the dimethylamino group in **65**).[64] Energies, orbital phases and coefficients of LUMOs and HOMOs in the applied alkynes are similar to those in dienophiles with electron-withdrawing substituents.[65] The crystal structure of **25q** can be confirmed this regio- and stereoselectivity.



Scheme 21. Regional and facial selectivities in Diels-Alder reactions. Do: electron-donating group. R_L,R_S: Larger and smaller substituent. EWG: electron-withdrawing group.

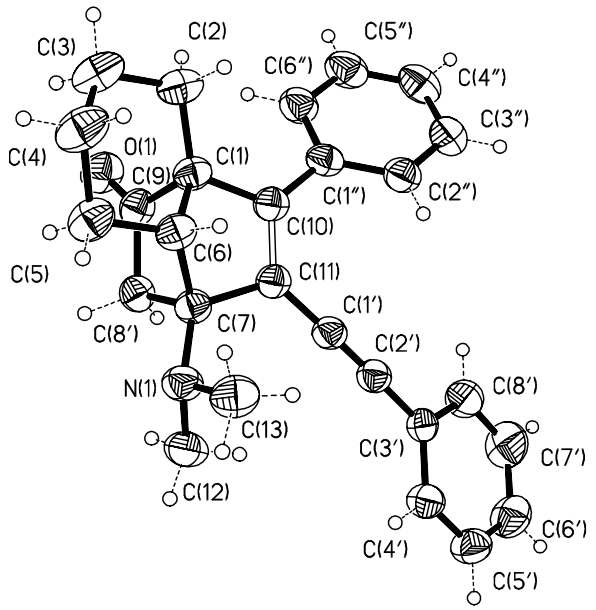


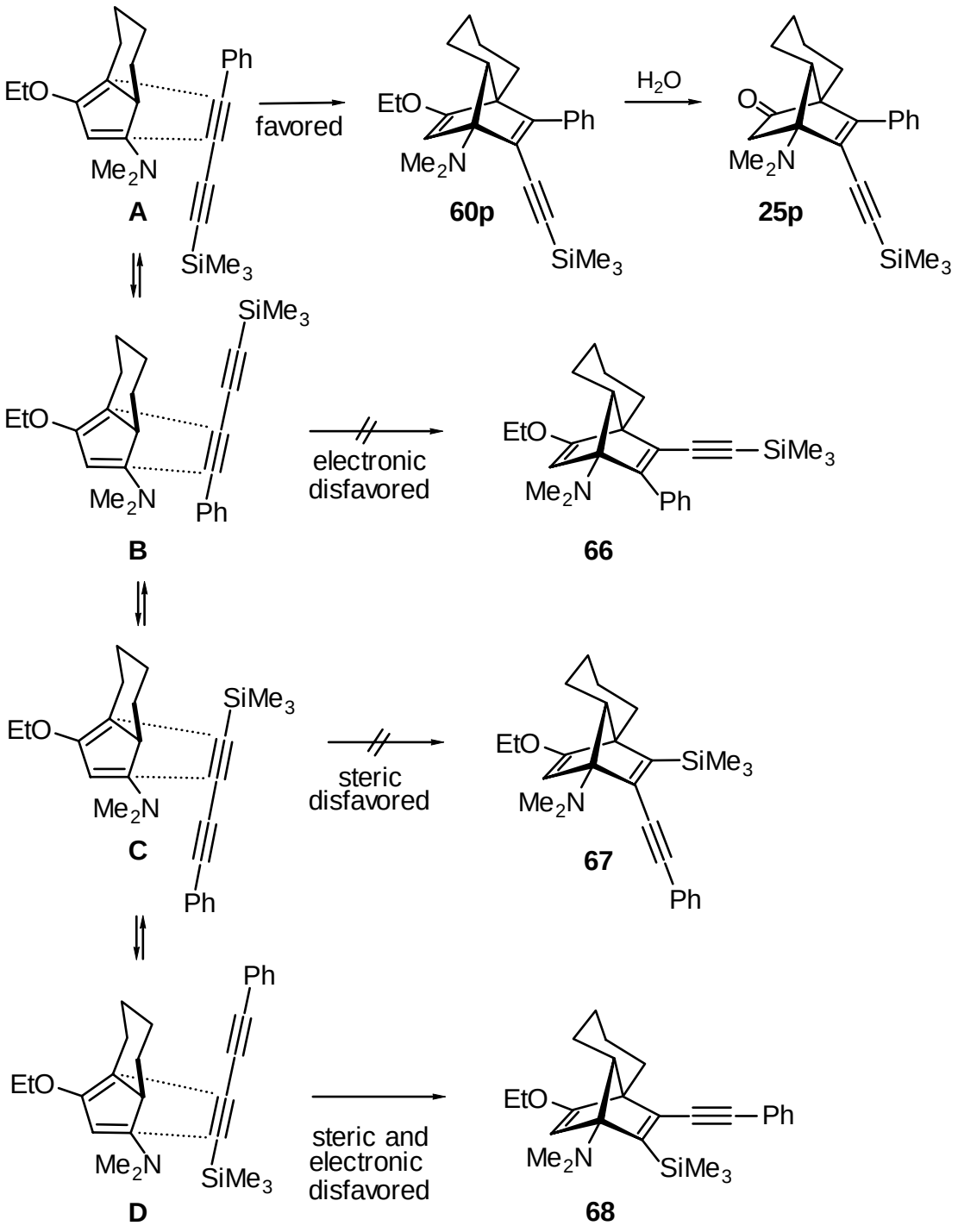
Figure 1. The crystal structure of **25q**: $C_{27}H_{27}NO$, triclinic crystals of space group *P*1, unit cell dimensions: $a = 10.13(3)$, $b = 15.01(4)$, $c = 15.10(3)$ Å, $\alpha = 99.2(2)$, $\beta = 107.8(2)$, $\gamma = 96.6(2)°$, $V = 12125(9)$ Å^3, 9865 reflections.

3.3. Electronic and Steric Effects of Dienophiles

It is well-known that the electronic and steric properties of dienophiles in the Diels-Alder reaction play important roles. As discussed in section *3.1*, cyclopentadiene **65** with two strong electron-donating groups behaves as an active diene to dienophiles, alkynes **15**. The more electron-deficient 4-phenyl benzoic acid methyl ester afforded much higher chemical yield than that of the electron-rich 4-ethoxyethynylbenzene (*cf.* entry 8 and 10 in Table 6). Thus, electron-withdrawing containing alkynes are suitable reaction partners for this kind of cycloaddition. Modification of the electronic property of the symmetric diphenylethyne to the 4-phenylethynyl benzoic acid ethyl ester (**28aa**[15]) did increase the chemical yields from 0 to 66% (entry 11 in Table 6).

Steric hindrance of the applied alkynes is the other limitation of this cycloaddition. Reaction of complex **18g** with *o*-, *m*- and *p*-(trifluoromethyl)ethynylbenzene (entries 12–14 in Table 6) showed that only the *ortho*-isomer gave the worse chemical yield. 1-Phenyl-4-trimethylsilylbuta-1,3-diyne (**15a**[16]**j)** as a dienophile affords. Only one cycloaddition product 25p was detected (Scheme 22). The reaction pathways **B** and **D** would not be followed because of the weaker electron-withdrawing property of the trimethylsilyl group, in contrast to phenyl functionality. On the other hand, the steric hindrance of the trimethylsilyl

substituent disfavor the reaction pathways **C** and **D**. This steric hindrance effect can also be confirmed by employing 3-(trimethylethynyl)benzotrifluoride as a dienophiles, which did not afford any tricyclic products, although the cycloaddition adduct **25m** was given in 84% yield from its terminal analogue **29a**[2] (entry 13 in Table 6).

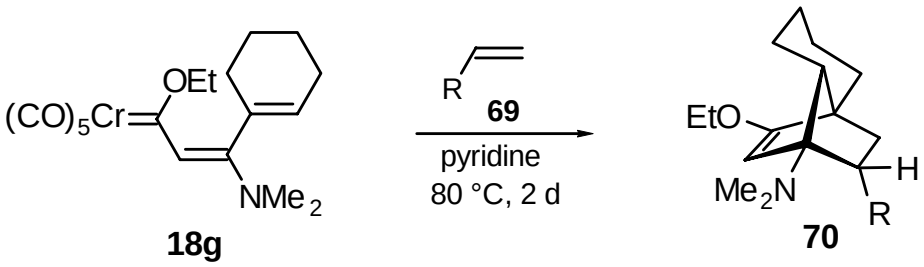


Scheme 22. Diels-Alder reaction between cyclopentadiene **53** and dienophile **15a**[16]**j**.

3.4. Alkenes as Dienophiles

Alkenes **69** can be also act as dienophiles for this [4+2] cycloaddition. They afford compounds **70**, which do not undergo subsequent hydrolysis (Scheme 22). In the absence of the through-space interaction, tricyclic products **70** are not hydrolyzed to ketones under the same purification process as the preparation of **25**. It is not surprising that the formation of the norbornene derivative **70a** does not give a good chemical yield, like that of **25e**. The LUMO potential energy of styrene **69a** is about 0.5 eV higher than it of phenylethyne (**15a**).[61] Slow diffusion crystallization of **70a** from pentane/diethyl ether afforded a single crystal for the X-ray structure analysis. Thus, the *endo*-structure was rigorously established (Figure 2).

Generally, the above used alkenes and alkynes were recognized as inactive dienophiles in the Diels-Alder reaction. More active dienophiles such as methyl propiolate, dimethyl acetylene dicarboxylate, maleic anhydride could not be employed as they react with the solvent pyridine and afford black solutions.



Alkene	R_L	Product	Yield (%)
69a	C_6H_5	**70a**	59
69b	3-CH_3-C_6H_4	**70b**	54
69c	4-CH_3-C_6H_4	**70c**	57

Scheme 23. Synthesis of 7-dimethylamino-9-ethoxytricyclo[5.2.2.0^{1,6}]undec-8-enes **70** from complex **18g** and alkenes **69**.

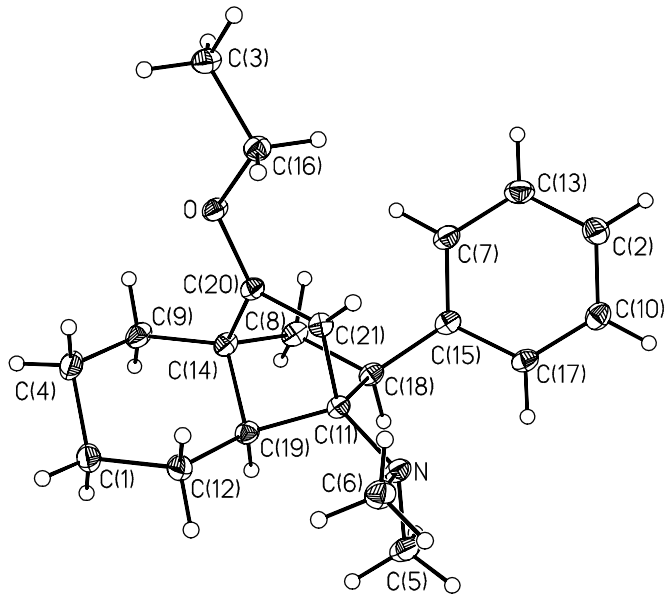


Figure 2. The crystal structure of **70a**: $C_{21}H_{29}NO$, triclinic crystals of space group *P*1, unit cell dimensions: a = 8.4438(8), b = 9.9685(9), c = 11.8828(11) Å, α = 97.698(7), β = 91.575(7)°, γ = 115.012(7)°, V = 894.28(14) Å^3.

3.5. Transitionmetal Effect

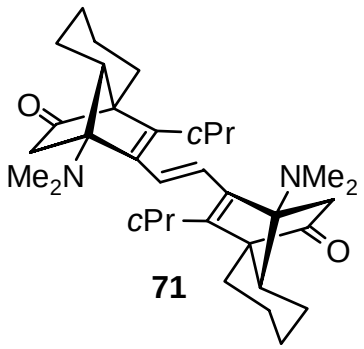
Tungsten complex **18o** was also applied for this kind of cycloaddition. However, the chemical yields for formation of tricyclic compounds **25** and **70** are much lower than these from its chromium analogue **18g** with only one exception (Table 7). In order to discuss this obvious difference, a control experiment of the tungsten complex **18o** in [D_5]-pyridine was carried out at room temperature. The intramolecular annulation went to completion very slowly: it had to take over 2 d. During this process, still no signal of the η^1-cyclohexadienyl complex **62-W** was detected. The bond strength between the transition metal in the VI group and the carbene carbon, M=C, increases with its series (W>Mo>Cr)[65]. Thus, the slower intramolecular cyclization of tungsten complex **18o** leads to lower yields of tricyclic products **25** and **70**. Unfortunately, the highly labile molybdenum analogue could not be isolated and the comparison of the transition metal effect in the VI group can not be completed.

Table 7. Influence of transition metal effect on synthesis of tricyclic compounds **25** and **70** from the tungsten complex **18o**.

Entry	Dienophile	R_L	R_S	Product	Yield (%)
1	**15h**[1]	1-cyclohexenyl	H	**25a**	24
2	**15h**	1-cyclopentenyl	H	**25b**	35
3	**15l**	2-isopropenyl	H	**25d**	44
4	**15a**	Ph	H	**25e**	58
5	**29a**[3]	4-CF_3-C_6H_4	H	**25n**	58
6	**29b**	1-naphthyl	H	**25o**	52
7	**29a**[7]	4-ethynyl-Ph	H	**25t**	62
8	**69c**	4-CH_3-C_6H_4	H	**70c**	19

3.6. Synthesis of Bis-cycloaddition Products.

Although several diynes, endiynes and oligoynes were used in this [4+2] cycloaddition, only the monoadducts **25** were obtained, even with a 2.2-fold excess of complex **18g** was employed (entry19 in Table 6). This hardly explainable result prompted me to study the possibility of the formation of bis-adducts of the type **72**.



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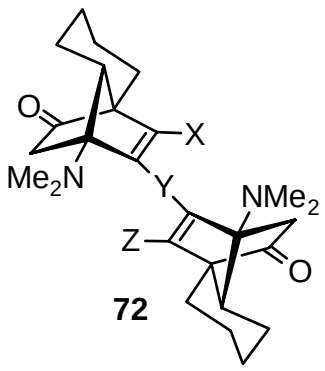
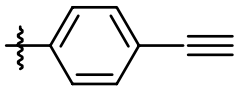


72

Utilization of phenyl substituted alkynes as dienophiles lead to higher chemical yields as shown above. Therefore, various conjugated and non-conjugated diynes of this type were applied for the this reaction. The competition between formation of the mono- and bis-adducts

depends upon the amount of the Fischer carbene complex **18g**. Over 1.5 equiv. of complex **18g** per alkyne is necessary, otherwise large amount of the monoadduct of type **25** was isolated. However, the bis-adduct **72a** was isolated in 8% yield, and none of the mono-adduct was observed (entry 1 in Table 8). Further control experiment from the monoadduct **25t** and complex **18g** did not give better chemical yield. This unsatisfactory result could arised by the much lower solubility of **72a** in organic solvents. Another dienophile, 1,4-diphenyl-1,3-butadiyne (**54f**), afforded only the monoadduct **25q**, even 3.5 equiv. of complex **18g** was used.

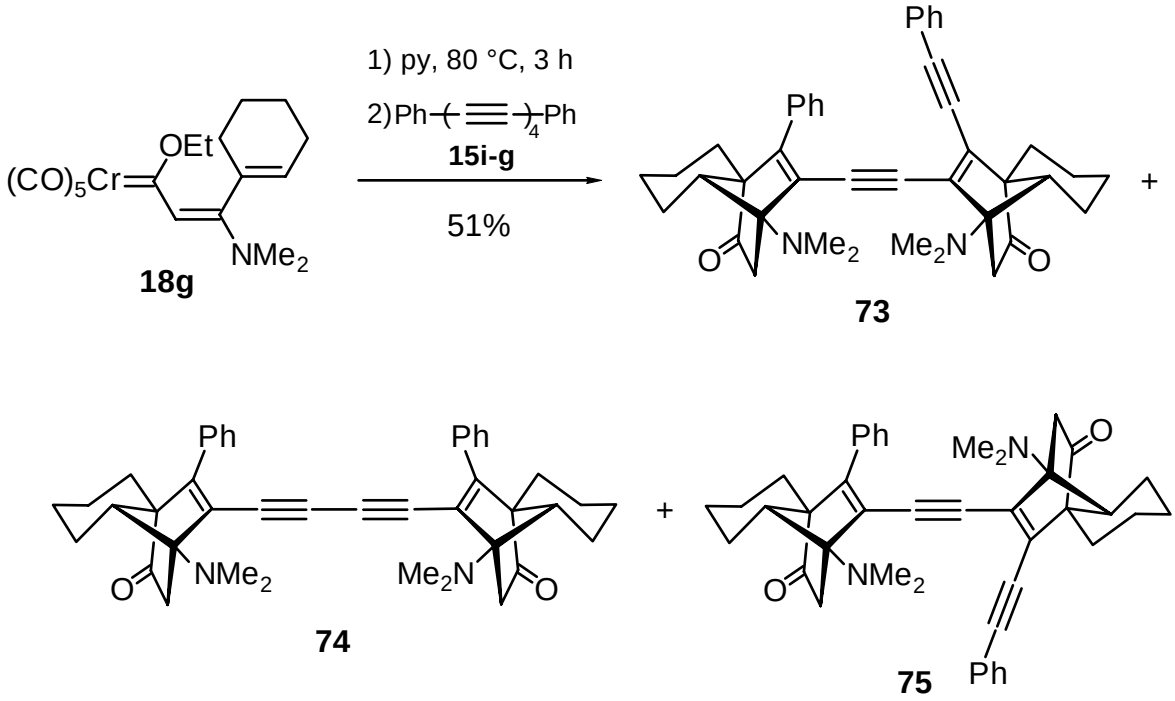
Table 8.

Entry	Alkyne	**18g**	X	Y	Z	product	Yield (%) [a]
1	R_A—≡—H **29a**[7]	3.1 eq.	H	C_6H_4	H	**72a**	8
2	R_A—R_A **29a**[8]	3.4 eq.	H	C_6H_4-C_6H_4	H	**72b**	51
3	R_A—⟍—R_A **29a**[9] R_A: 	2.2 eq.	H	C_6H_4-C_2H_6-C_6H_4	H	**72z**	14[b]
4	Ph—(≡)$_2$—Ph **54f**	3.5 eq.	Ph	—	Ph	**72c**	0[c]

[a] all reactions were undergone at 80 °C for 2 d, if not otherwise mentioned. [b] in addition to **72z**, monoadduct **25z** was isolated in 33% yield. [c] only monoadduct **25r** was isolated in 83%.

Due to the thermal instability of a highly reactive dienophile, 1,8-dipheny-1,3,5,7-octatertayne (**54g**), cyclopentadiene **64** was firstly generated from complex **18g** in pyridine at 80 °C for 3 h. Then, the reaction partner **54g** was introduced to this solution, and the mixture was stirred at ambient temperature for 3 d. After purification, only bis-adducts could be detected by the mass spectroscopy. Not only the dimethylamino functionalities but also the carbonyl groups show 5 signals (approximately in ratio 2:1:1:1:1) in their ^{1}H- and ^{13}C-NMR

spectra. Combination of these information, the regioselectivity and the electron-controlled principle, three regioisomers can be assigned as **73**, **74** and **75** (Scheme 24). Hence, the range of the formation of bisadducts depends upon the linkage Y in **72**, and it appears to be limited to phenyl derivatives or alkynyl functionalities.



Scheme 24. Synthesis of bis-cycloaddition products **73**, **74** and **75**.

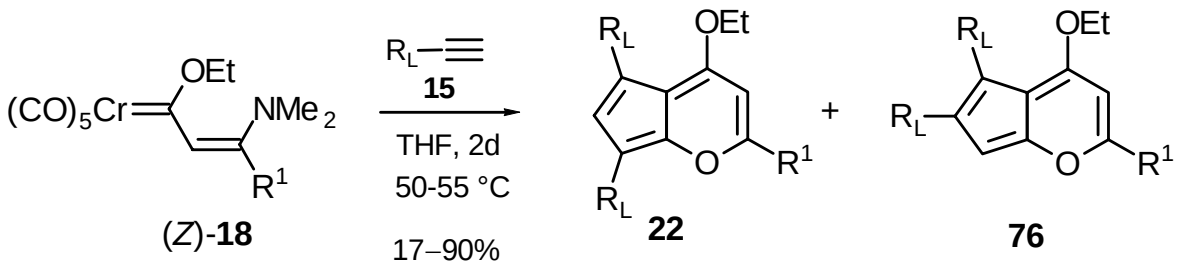
3.7. Photophysical property

Recently, oligo(9,9-dihexyl-2,7-fluoreneethynlene)s were reported as potential candidates of blue light-emitting diodes (LEDs) by modulation of their conjugation length.[66] In accordance with this information, the photophysical properties of fluorenyl substituted tricyclic compounds **25w** and their starting materials **54d** were examined.

Alkyne **54d** shows light absorption with a maximum peak at 375 nm and no signals over 392 nm in its UV spectra. However, the cycloaddition adduct **25w** exhibits light absorption with a maximum peak at 361 nm and a weaker peak at 410 nm. It means that the absorption band of the **25w** is bathochromically shifted by about 30 nm compared to that of **54d**, and part of it appears in the blue region. On the other hand, the absorption coefficient (ε) at the maximum peak of **25w** becomes approximate two-fold stronger than that of alkyne **54d**.

4. Cyclopenta[b]pyrans

Synthesis of cyclopenta[*b*]pyrans **22** and **76** from complexes (*Z*)-**18** and terminal alkynes **15** was first observed by Duetsch *et al*. in 1992 (Scheme 24).[34,67] Formation of cyclopenta[*b*]-pyrans was regarded as a formal [3+2+2+1] cycloaddition, including an Fischer carbene complex **18**, two molecules of alkyne **15**, and a latter inserted carbon monoxide moiety.[52c] The regioisomer **22** can be, generally, detected as a single or major product in this reaction. This new one-pot preparation of cyclopenta[*b*]pyrans from easily prepared starting materials is superior to previously developed accesses to these so-called pseudoazulenes. Due to the conjugation of the two aryl substituents R_L with cyclopenta[*b*]-pyrans, the molecule of these type showed unusual fluorescence characteristics. Unfortunately, the reaction conditions were mainly optimized as using a 8 fold excess of alkyne **15** in a 0.05 M solution of complex **18** in THF at 55 °C. Although it would give better chemical yields, too many byproducts in trace amounts make the purification process inconvenient.



Entry	Complex	R^1	R_L	Product	Yield (%)[a]
1	**18e**	CMe_2OSiMe_3	Ph	**22a**	90
				76a	0
2	**18e**	CMe_2OSiMe_3	*n*Pr	**22b**	0
				76b	16
3	**18f**	$CHMe(OSi\,tBuMe_2)$	Ph	**22d**	27
				76d	14

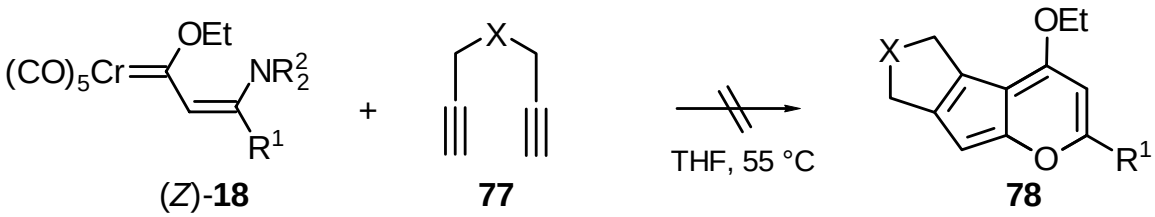
Scheme 25. Selected examples of synthesis of cyclopenta[*b*]pyrans **22** and **76**. [a] ref. 68.

4.1. Examination of optimal conditions

In order to decrease the needed amount of alkynes, a trivial reaction was carried out with 4 equiv. of phenylethyne **15a** in a 0.10 M solution of complex **18e**. Even after 5 d, large amount of the starting material **18e** could be detected on the TLC. Thus, 8 fold excess of reaction partner, **15**, seems necessary for complex **18** to complete this reaction. On other hand, solvent effect of the above described optimal condition was also studied, but instead of THF, hexane and acetonitrile were used. They afforded product **22a** in 28% and 29% yields, respectively. Although the chemicals became lower, both solvents decreased the amount of byproducts and impurities. Therefore, preparation of the sample for elemental analysis could be easily access.

4.2. Synthesis of derivatives of cyclopenta[b]pyrans

As shown in Scheme 25, the regioisomer **76b** was observed as product from the reaction complex **18e** with 1-pentyne (**15h**[1]). The reaction mode of this result seems able to prepare tricyclic compound of type **78** by using complexes **18** and heteroatom-substituted diynes **77** (Scheme 26). Unfortunately, TLC showed only starting materials and byproducts. The desired red-color product **78** were never detected.



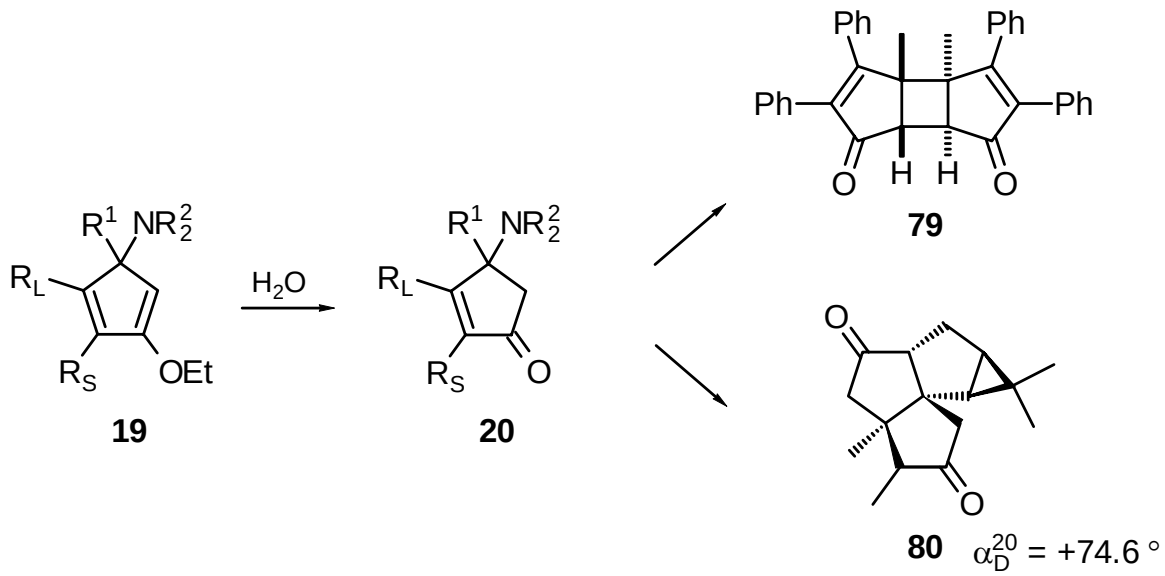
R_1 = *t*Bu, CMe_2OSiMe_3, $CHMe(OSi\,tBuMe_2)$

X = NMe (**77a**)
O (**77b**)

Scheme 26.

5. Highly Substituted Cyclopentadienes

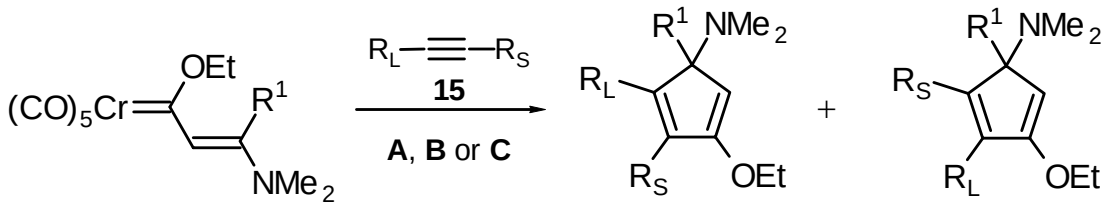
As mentioned in *Introduction*, highly substituted cyclopentadienes **19** and cyclopentenones **20** can be easy access by using de Meijere's protocol.[31,53] Formation of compound of the type **19** was regarded as a formal [3+2] cycloaddition, including an Fischer carbene complex **18** and one molecule of alkyne.[31] They offer various applications in organic synthesis and afford numerous interesting molecules, for example tricyclic compound **79** and natural-product analogues, for instance angular triquinane **80**.[69] Further development and application of this synthetic method are still in progress.



5.1. *Basic Study of Formation of Highly Substituted Cyclopentadienes*

Originally, cyclopentadienes **19** were easily prepared in good chemical yields only from the reaction of cyclopropyl substituted complex **18b** with alkynes in THF. Other complexes of the type **18** under the same condition would give unsatisfactory results (*cf.* entries 1 and 2 in Scheme 27).[30a] This dramatic difference was proposed due to the strong electron-donating property of the cyclopropyl functionality, which makes the insertion of carbon monoxide disfavored. After introduction of donor ligands as solvent, *e.g.* acetonitrile and pyridine, by Flynn et al., the range of complex **18** applicable in the cycloaddition with alkynes would not to be limited to the cyclopropyl substituted one anymore (*cf.* entries 3–6 in Scheme 27).[31] The reaction conditions were mainly optimized as using a twofold excess of alkyne in a

0.05 M solution of complex **18** in pyridine or acetonitrile at 80 °C.[70] Although acetonitrile using as a solvent can also give the cycloaddition products **19** as well as pyridine (or at least better than THF), because of its weaker electron-donating property, in relative to pyridine, alkynes should be dropwise added to the solution of complex **18** via a syringe pump over a long period. Otherwise, these successful procedures provide easy access for the preparation of highly substituted cyclopentadienes **19** with a comfortable purification process. As various functionalities were introduced in this reaction, the regioisomer **81** can be, sometimes, detected as a minor product. The factors of the formation competition between them will be discussed in the later section.



18 **19** **81**

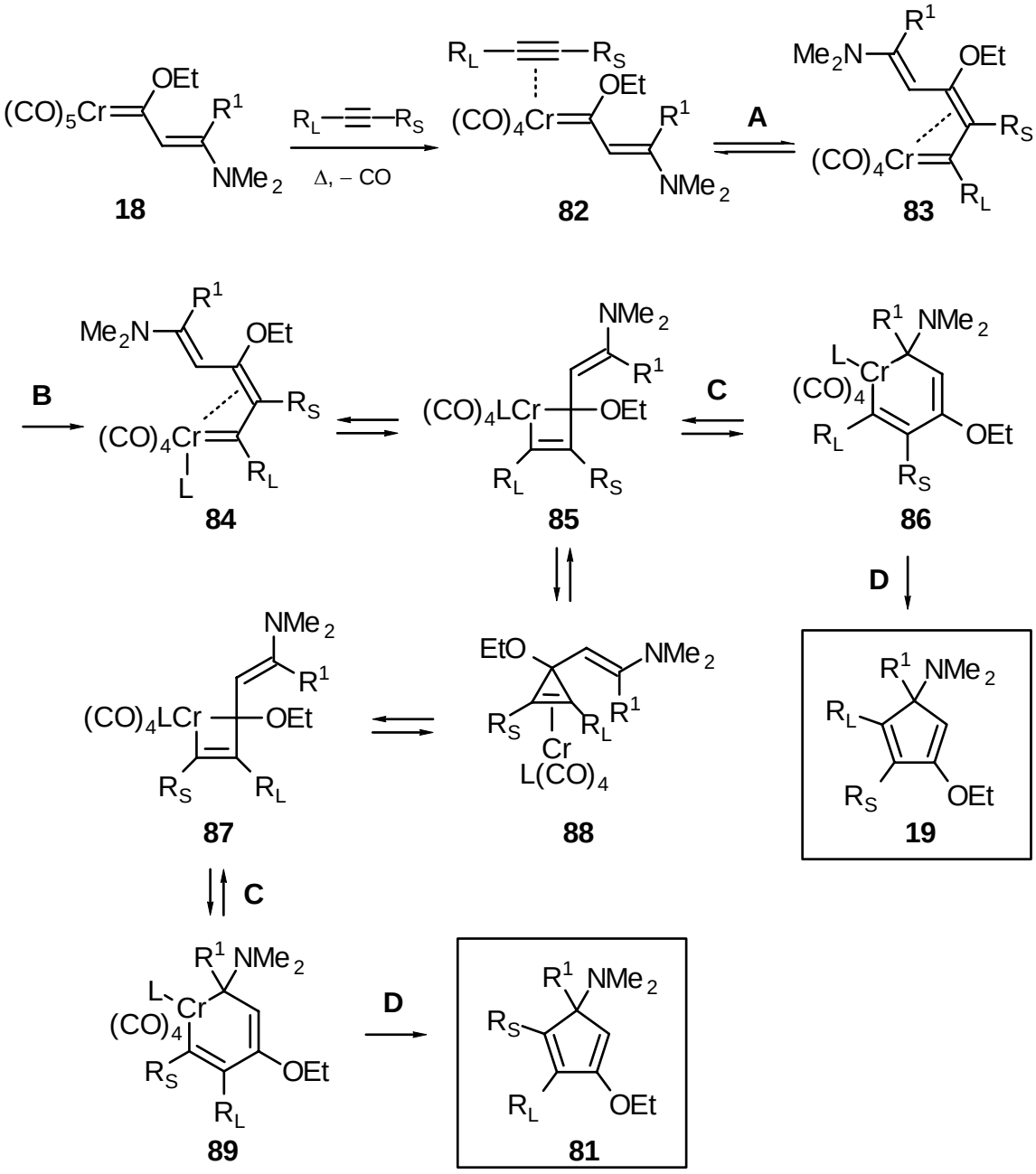
Entry	Starting Materials	R^1	Alkyne	R_L	R_S	Condition	Product	Yield (%)[a]
1	**18a**	*c*Pr	**15h**[1]	*n*Pr	H	**A**	**19a**	77[b]
2	**18b**	Me	**15a**	Ph	H	**A**	**19b**	2[b]
3	**18b**	Me	**15a**	Ph	H	**B**	**19c**	41[c]
4	**18b**	Me	**15hh**	Me	Me	**B**	**19d**	82[c]
5	**18p**	*n*Pr	**15hh**	Me	Me	**B**	**19e**	95[d]
6	**18p**	*n*Pr	**15a**	Ph	H	**C**	**19f**	80[d]

Scheme 27. Selected examples of synthesis of cyclopentadienes **19**. Condition **A**: THF, 52 °C. **B**: pyridine, 80 °C. **C**: MeCN, 80 °C. [a] only cyclopentadienes of the type **19** were isolated. [b] ref. 30a. [c] ref. 69. .[d] ref. 71.

5.1.1. Mechanism

The mechanism of the formation of the cyclopentadienes **19** and **81** can be rationalized in terms of the following sequence: Upon heating, complex **18** undergoes thermal, dissociative ligand exchange of a carbonyl for an alkyne to **82** (Scheme 28). In accordance with the calculations of Hofmann et al., carbene complex **82** then under undergoes insertion of the alkyne, in a concerted fashion, to give the carbene/π-chelate complex **83**.[23b] This pathway avoids the originally proposed 16-electron chromacyclobutene intermediate (not shown), which would be expected to be of much higher energy than the transition state along the concerted pathway. Recently, Wulff et al. presented that this alkyne-insertion process in the Dötz reaction between **82** and **83** are in equilibrium on the basis of kinetic studies.[24a] In the presence of a suitable coordinating agent or solvent, complex **83** is dechelated to give **84**. Complex **84** can now undergo 4π- and/or 6π-electrocyclization to give the vinylchromacyclobutene **85** and/or the chromacyclohexadiene **86**, respectively, which both would be formed as low energy 18-electron complexes. These two complexes, **85** and **86**, may interconvert via ring expansion and contraction. Reductive elimination from **86** gives the cyclopentadiene **19**. Reductive elimination from **85** gives the vinylcyclopropene **87**, which would be expected to undergo reinsertion of the chromium into the least congested cyclopropene single bond to give a regioisomeric vinylchromacyclobutene **88**.[72] Ring expansion of **88** to the chromacyclohexadiene **89** and reductive elimination than leads to the regioisomeric cyclopentadiene **81**.

A high concentration of the coordinating agent L relative to the alkyne is very important in favoring formation of cyclopentadienes **19** and **81** over carbonyl-inserted products.[70] In the presence of high concentrations of an alkyne, the group L in **84** can be replaced by an alkyne to give an alkyne complex (**84**, L = alkyne). Unlike the usual groups L, such as acetonitrile and pyridine, this alkyne ligand can act as a 4π-electron donor and induces carbonyl insertion to give an 18-electron ketene complex (not shown), which will ultimately lead to the formation of carbonyl-containing cocyclization products.



Scheme 28. Proposed mechanism for the formation of cyclopentadienes **19** and its regio-isomers **81**. **A**: alkyne insertion; **B**: coordination with a donor ligand; **C**: 6π-electro-cyclization; **D**: reductive elimination.

5.1.2. Regioselectivity between cyclopentadienes **19** *and* **81**

In order to understand the regioselectivity between cyclopentadienes **19** and **81**, the following factors should be studied: a) concentration of complexes **18** and applied alkynes in pyridine solution, b) steric effects of the substitutes in the complexes **18** and in alkynes, and c) electronic properties of alkynes. The concentration effect has been reported by Flynn et al. and this factor does not give obvious influence on the distribution of products.[70] However, the steric bulk of the substituents either in the complexes **18** (R^1) or in the applied alkynes (R_L) appears to have an important effect on the regioselectivity of the cocyclization, and in the former they have more influence than in the latter (Scheme 27 and Table 9).[53]

Table 9.

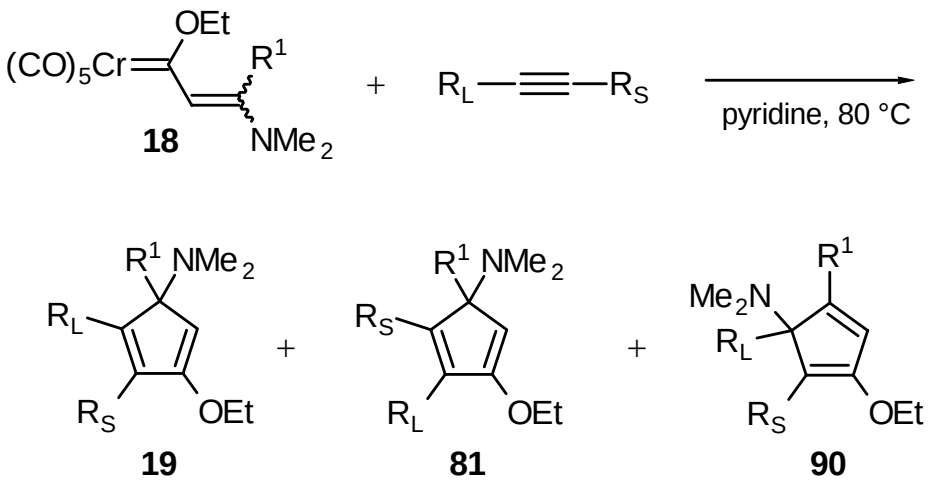
Entry	Starting Material	R^1	Alkyne	R_L	R_S	Product	Yield (%)	Combined Yield(%)[a]
1	**18p**	*n*Pr	**15j**	$SiMe_3$	H	**19f**	53	71[b]
						81f	18	
2	**18c**	*i*Pr	**15j**	$SiMe_3$	H	**19g**	21	44[c]
						81g	23	
3	**18c**	*i*Pr	**15a**	Ph	H	**19h**	28	48[c]
						81h	20	
4	**18c**	*i*Pr	**28ag**	Ph	*c*Pr	**19i**	39	68[d]
						81i	29	
5	**18c**	*i*Pr	**28ah**[2]	Ph	nC_6H_{13}	**19j**	49	70[d]
						81j	21	
6	**18c**	*i*Pr	**28aa**[15]	Ph	$4\text{-}EtO_2C\text{-}C_6H_4$	**19k**	16	36[e]
						81k	20	
7	**18c**	*i*Pr	**28a**[4]**a**[5]	$4\text{-}MeO_2C\text{-}C_6H_4$		**19l**	21	44[e]
					$4\text{-}MeO\text{-}C_6H_4$	**81l**	23	

[a] all reactions were run following the optimal condition (condition **B**, Scheme 26). [b] ref. 71. [c] ref. 69. [d] ref. 73. [e] ref. 74.

The internal alkynes 1-phenyl-1-octyne (**28ah**[2]) and cyclopropylphenylethyne (**28ag**), upon reaction with **18c**, gave higher proportions of the regioisomer **19** than phenyethyne (*cf.* entries 3–5 in Table 9). Variation of the electronic properties of the substituents on the phenyl groups of diphenylethyne does not influence the ratio between **19** and **81** greatly (*cf.* entries 6 and 7 in Table 9). Such results show regioselectivity depends much upon the steric effects of alkynes than the electronic effects of them.

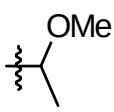
5.1.3. Migration of the Dimethylamino Group on the Cyclopentadienes **19**

Cocyclizations of internal alkynes and carbene complexes **18** with larger substitutes R^1 did not only lead to an increased formation of the regioisomer **81**, but also to yield another isomeric cyclopentadiene **90** which would result from **19** by 1,5-migration of the dimethylamino group (Scheme 29 and Table 10). Although cyclopentadienes **90** have been prepared by Funke[71] and Müller[75], they just assigned them as **19** (entries 2 and 3 in Table 10). Later Schirmer established rigorously the unusual structure of the correspondence ketone from **90m** by using X-ray structure analyses.[69] These 1,4,5-trisubstituted 5-dimethylamino-2-ethoxy-cyclopentadienes **90** have distinctly different NMR spectra compared to the isomers **19** and **81**. Due to the electron-donating effect of the ethoxy group, the signal of the olefinic proton in **19**/**81** appears more upfield than that of **90** (4.5–5 ppm versus 5.7–6.5 ppm). The same holds for the corresponding ^{13}C-NMR signals (95–100 ppm versus 110–120 ppm).



Scheme 29. Steric and electronic effects of applied alkynes on the distribution of cyclopentadienes **19**, **81** and **90**. For more detail, see Table 10.

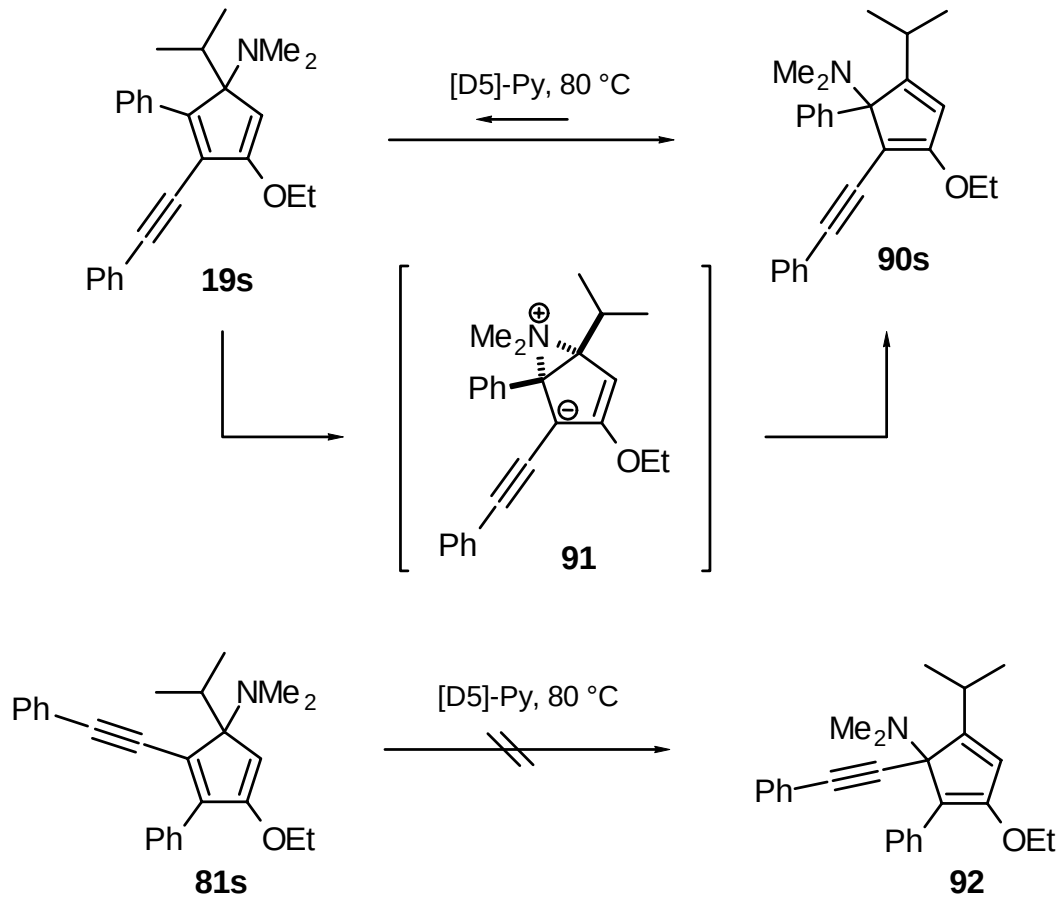
Table 10.

Entry	Starting Material	R^1	Alkyne	R_L	R_S	Product	Yield (%)	Ratio **90**/**19**	Combined Yield(%)
1	**18c**	*i*Pr	**15hh**	Me	Me	**19m**	38	1.02	77[a]
						90m	39		
2	**18r**		**15hh**	Me	Me	**19n**	0	∞	26[b]
						90n	26		
3	**18s**	$SiMe_3$	**15hh**	Me	Me	**19o**	0	∞	28[c]
						90o	28		
4	**18c**	*i*Pr	**15gg**	*c*Pr	*c*Pr	**19p**	78	0	78[d]
						90p	0		
5	**18c**	*i*Pr	**28a³a³**	4-F_3C-C_6H_4		**19q**	65	0	65
					4-F_3C-C_6H_4	**90q**	0		
6	**18c**	*i*Pr	**54a**	4-F_3C-C_6H_4		**19r**	7	2.43	73
					4-F_3C-C_6H_4-C≡C	**81r**	49		
						90r	17		
7	**18c**	*i*Pr	**54f**	Ph	PhC≡C	**19s**	22	0.41	68
						81s	37		
						90s	9		
8	**18c**	*i*Pr	**54b**	4-MeO-C_6H_4		**19t**	22	≤0.04	57
					4-MeO-C_6H_4C≡C	**81t**	35		
						90t	≤1		

[a] ref. 69. [b] ref. 75. [c] ref. 71. [d] isolated as a mixture of **19p** and its correspondence ketone **20p**.

In contrast to 2-butyne (**15hh**), the sterically more congested and more electron-rich dicyclopropylethyne (**15gg**) did not afford any product of type **90** (entry 4 in Table 10), complexes **18r** and **18s** with 2-butyne (**15hh**), gave only **90n** and **90o**, respectively. None of **81** could even be detected in the spectra of the crude products.

1,4-Diphenylbutadiyne (**54f**) can be regarded as an internal alkyne with a phenyl and a phenylethynyl substituent, and the latter is more strongly electron withdrawing than the former. With this acetylene, the cocyclization product **90s** was isolated in 9% yield (entry 7 in Table 10). In order to determine the mode of formation of **90s**, isolated samples of **19s** and **81s** in [D_5]-pyridine were heated at 80 °C. In the sample of **19s**, the signal of **90s** appeared slowly, after 17 days, 67% of **19s** converted to **90s**, while the isomer **81s** remained unchanged even upon prolonged heating (Scheme 30). This shift of the dimethylamino group is in equilibrium. But the rate coefficient for the transformation of **19s** to **90s** must be larger that that for the reverse reaction. When pure **90s** was heated in [D_5]-pyridine at 80 °C for 2 d, 21% of **19s** could be observed. Under the same condition, 40% of **19s** converted to **90s**.

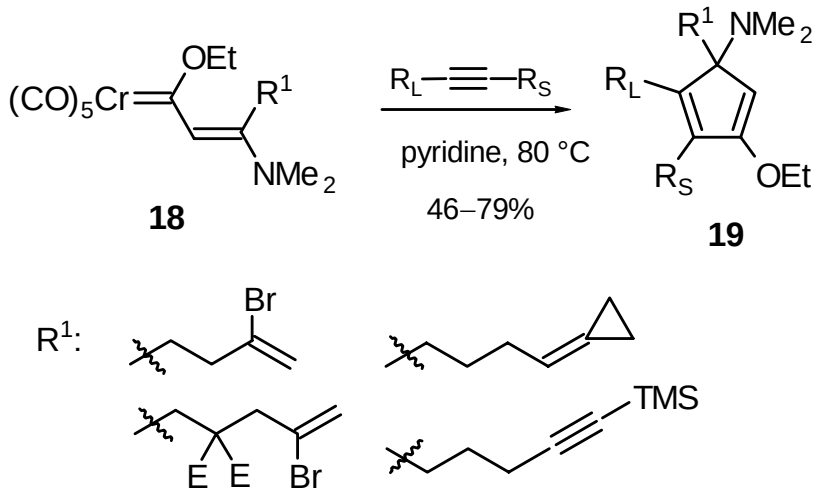


Scheme 30. A possible mode of formation of cyclopentadiene **90s** by 1,2-migration of the dimethylamino group in **19s** via a bridged zwitterionic intermediate **91**.

These results appear to indicate that **90s** is not formed by a 1,5-shift of the dimethylamino group, but rather a 1,2-migration via the bridged zwitterionic intermediate **91** which would be well stabilized by the strongly electron-withdrawing phenylethynyl and the electron-donating ethoxy group. Indeed, with the even more strongly electron-withdrawing *p*-trifluorophenyl-ethynyl substituent provided by 1,4-bis(*p*-trifluoromethylphenyl)butadiyne (**54a**) the ratio between formed **90r** and **19r** increased about sixfold. In contrast, the bis-donor-substituted diphenylbutadiyne **54b**, did afford only trace amount of product of type **90** (*cf.* entries 6 and 8 in Table 10). Bis(*p*-trifluoromethylphenyl)ethyne (**28a^{3}a^3**) also did not yield any of the product **90q**.

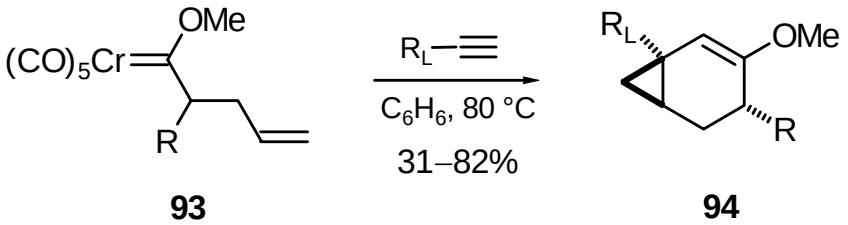
5.1.4. Intramolecular [2+1] Addition

Intramolecular diyne and enyne annulations of Fischer carbene complexes have developed by many research groups. After insertion of first alkynes by carbene complexes, the intermediates would undergo either cyclization with the second alkyne on the basis of the Dötz reaction[76] or cyclopropanation[77] with alkenes and finally, they give tricyclic compounds. On the other hand, Funke's studies have demonstrated that this de Meijere protocol offers an excellent chemoselectivity of formation of cyclopentadienes **19**.[53,71] None of intramolecular cyclization products was detected (Scheme 31).



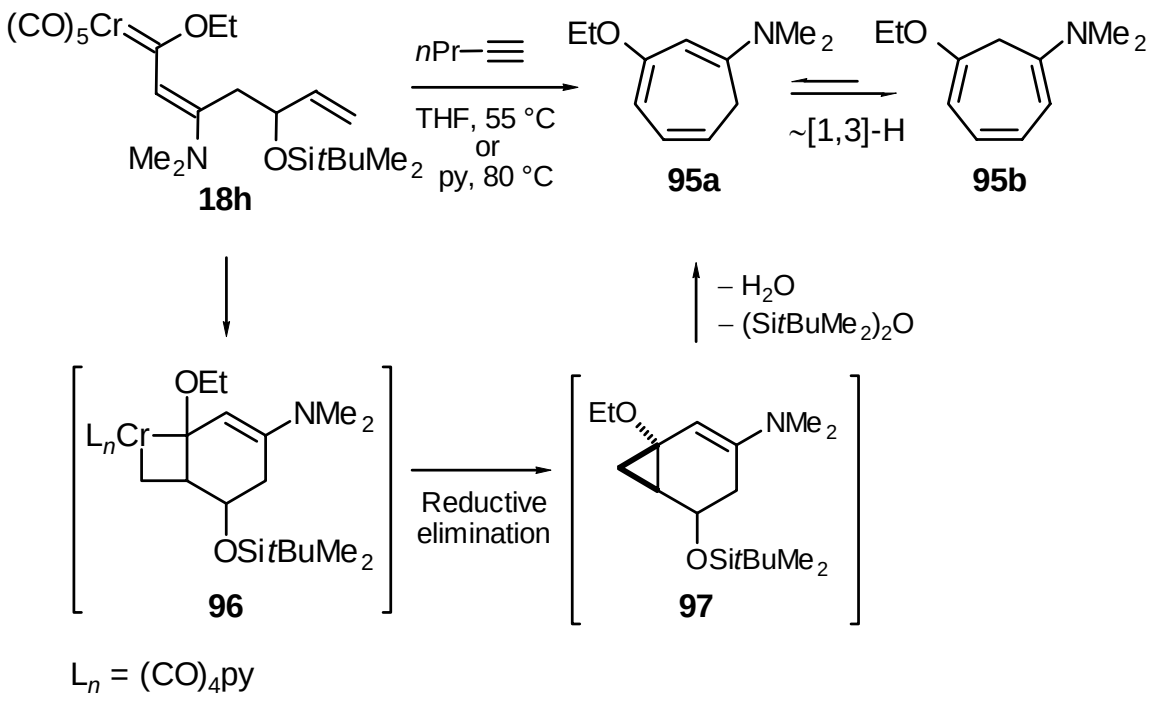
Scheme 31. Synthesis of alkynyl and alkenyl substituted cyclopentadienes **19.**

Furthermore, in accordance with the results of Hoye et al, the reaction of alkene-containing Fischer carbene complexes **93** with alkynes is an efficient and stereoselective route to functionalized bicyclo[4.1.0]heptane derivatives **94**, which are formed via an alkyne insertion and a subsequent intramolecular cyclopropanation (Scheme 32).[78]



Scheme 32. Synthesis of bicyclo[4.1.0]heptane derivatives **94**.

Following the conclusions of both reaction modes, either intermolecular or intermolecular-intramolecular cycloaddition products of type **19** or **94**, respectively, should be given from the reaction of complex **18h** with 1-pentyne. Instead, besides the byproduct, $Cr(CO)_5Py$, cycloheptatrienes **95a** and **95b** were formed, and the latter isomer was observed as a major product (Scheme 33). The intramolecular [2+1] cyclization seems apparently more rapid than alkyne insertion and the bicyclic intermediate **97** is generated, in which the strong electron-donating property of the dimethylamino functionality would enhances the ring opening of the three-membered ring and the cleavage of the silyloxy group. After further proton elimination and olefin isomerization, cycloheptatrienes **95a** is formed, which undergoes the 1,3-hydrogen migration to convent to **95b**. Without the presence of 1-pentyne, cyclization products **95a** and **95b** could be also reproduced. Unfortunately, these electron-rich products, like cyclopentadiene **64**, could not be isolated by the chromatographic purification. But ^{1}H-, ^{13}C-NMR, DEPT and mass spectra show strong evidences for this structure.

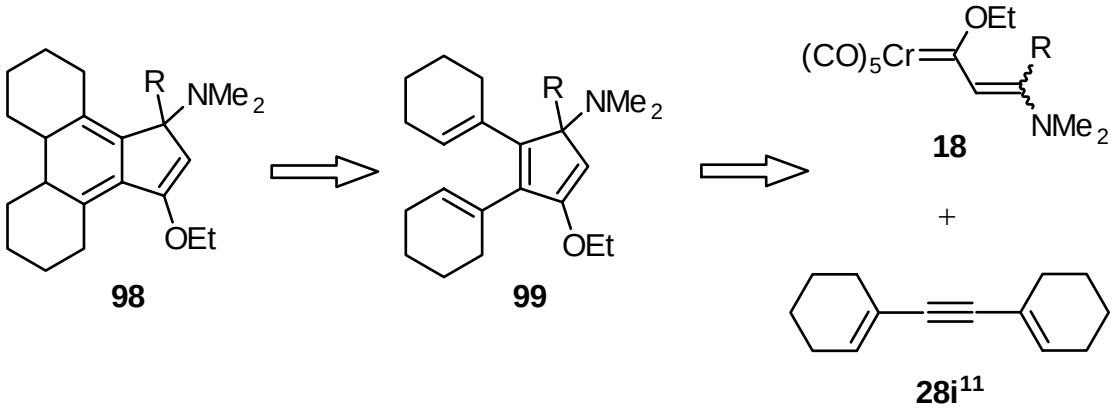


Scheme 33. Intramolecular [2+1] cyclization of complex **18h**.

5.3. Synthesis of Indenones and Their Derivatives

Construction of six-membered carbocycles via 6π-electrocyclizations from 1,3,5-hexatrienes have been well studied by de Meijere et al.[79] Symmetric 1,6-disubstiuted (*E*,*Z*,*E*)-1,3,5-hexatrienes were easy access by utilizing a twofold Heck coupling of 1,2-dibromocyclohexene with acrylates or styrene. Asymmetric ones have been prepared from the reaction of 2-bromocyclohex-1-enyl triflates with a variety of alkenylstannes and acrylates or styrene, the so-called a Still-Heck coupling. Further themal electrocyclization of them, afforded the corresponding 2,3-disubstituted 2,3,5,6,7,8-hexahydro- and/or 5,6,7,8-tetrahydronaphalene derivatives, generally, in good to excellent yields.[80]

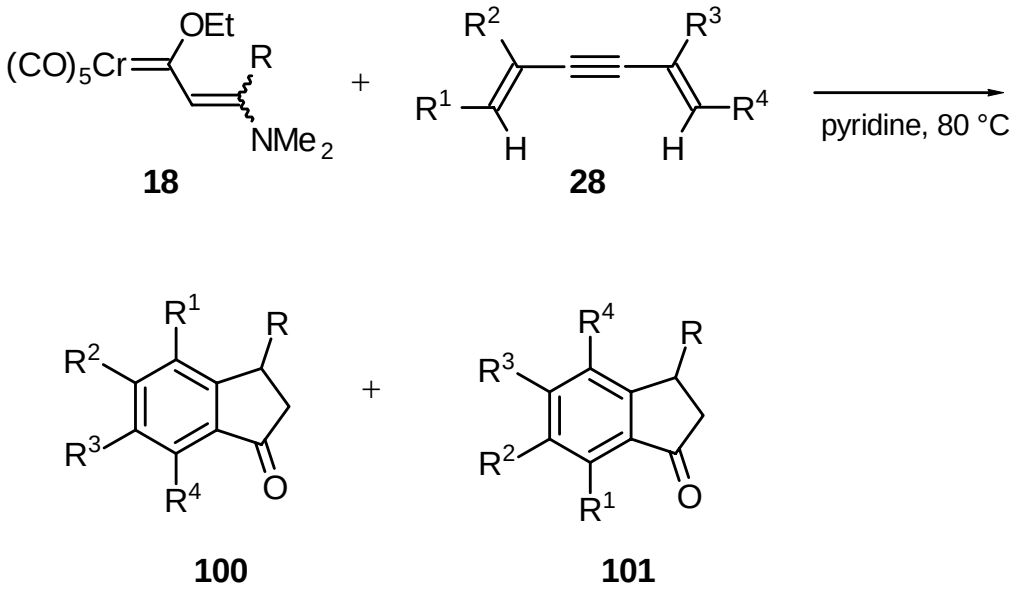
Synthesis of indene derivatives **98** was planned as a two-step operation. The cyclohexadienyl skeleton in the bicyclic compound **98** could be formed via a 6π-electrocyclization from the conjugated 1,3,5-hexatriene moiety in cyclopentadiene **99**, which should be easily prepared from the reaction of carbene complex **18** with dienyne **28i^{1}i^1**. (Scheme 34).



Scheme 34. The retro synthesis of indene derivatives **98**.

5.2.1. Synthesis of Indenone Derivatives

Upon heating complexes of the type **18** with conjugated dienynes **28** in pyridine at 80 °C, instead of the desired product **99**, only cycloaddition-cyclization compounds **100** and their regioisomers **101** were obtained, which can be regarded as products **98** with elimination of dimethylamino functionality and hydrolysis.



Scheme 35. Synthesis of indenone derivatives **100** and **101**. For more detail, see Table 11.

Table 11.

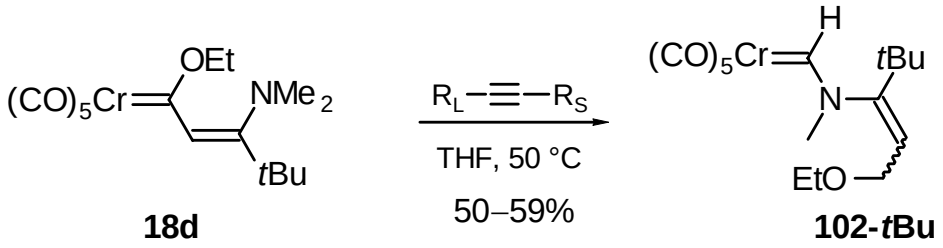
Entry	Starting Material	R	Alkyne	R^1	R^2	R^3	R^4	Product	Ratio (**100**/**101**)	Combined Yield(%)[a]
1	**18a**	*c*Pr	**15ll**	Me	H	Me	H	**100a**	—	22
2	**18c**	*i*Pr	**15ll**	Me	H	Me	H	**100b**	—	70
3	**18a**	*c*Pr	**28il**	$(CH_2)_3$		Me	H	**100c** **101c**	1.1:1	16
4	**18c**	*i*Pr	**28il**	$(CH_2)_3$		Me	H	**100d** **101d**	1.1:1	68
5	**18d**	*t*Bu	**28il**	$(CH_2)_3$		Me	H	**100e** **101e**	1.1:1	37
6	**18a**	*c*Pr	**28ii**	$(CH_2)_3$		$(CH_2)_3$		**100f**	—	19
7	**18b**	Me	**28ii**	$(CH_2)_3$		$(CH_2)_3$		**100g**	—	12
8	**18c**	*i*Pr	**28ii**	$(CH_2)_3$		$(CH_2)_3$		**100h**	—	75
9	**18c**	*i*Pr	**28i^{1}l**	$(CH_2)_4$		Me	H	**100i** **101i**	1.1:1	46
10	**18d**	*t*Bu	**28i^{1}l**	$(CH_2)_4$		Me	H	**100j** **101j**	1.1:1	21
11	**18c**	*i*Pr	**28i^{1}i^1**	$(CH_2)_4$		$(CH_2)_4$		**100k**	—	70[b]
12	**18d**	*t*Bu	**28i^{1}i^1**	$(CH_2)_4$		$(CH_2)_4$		**100l**	—	19[b]

[a] reaction for 3 d, if not otherwise mentioned. [b] reaction for 4 d.

As concluded in section *5.1.2*, the regioselectivity of formation of cyclopentadienes **19** depend upon the steric hindrance of applied alkynes, and the both substitutes of dienynes **28** have similar steric effect. Hence, it is not surprising that two isomers **100** and **101** were formed with lower regioselectivities, when asymmetric dienynes **28** were applied in this reaction. Unfortunately, the range of good chemical yields available in the cycloaddition to **100**/**101** appears to be limited to complex **18c** and sometimes **18d**. This result seems to indicate that this reaction depends upon the migration of the dimethylamino group, but no direct evidences can supply this propose. However, the "softer" the alkenyl substitutes in the dienynes **28**, the longer reaction time needed. When much "softer" cycloalkenyl substituted alkynes, e.g. 1-(1'-cyclooctenyl)-3-methyl-1-butyn-3-ene (**28i^{3}l**) and 1-(1'-cycloheptenyl)-2-

(1"-cyclooctenyl)ethyne, were applied for this reaction, none of cycloaddition products were observed, even cyclopentadienes of the type **19**. "Soft", here, means that flexibility of the cycloalkenyl moieties. As the ring size of cycloalkanes increases, the coplanar conformation of 1,3,5-hexatriene in **99** would not be easy to reach.

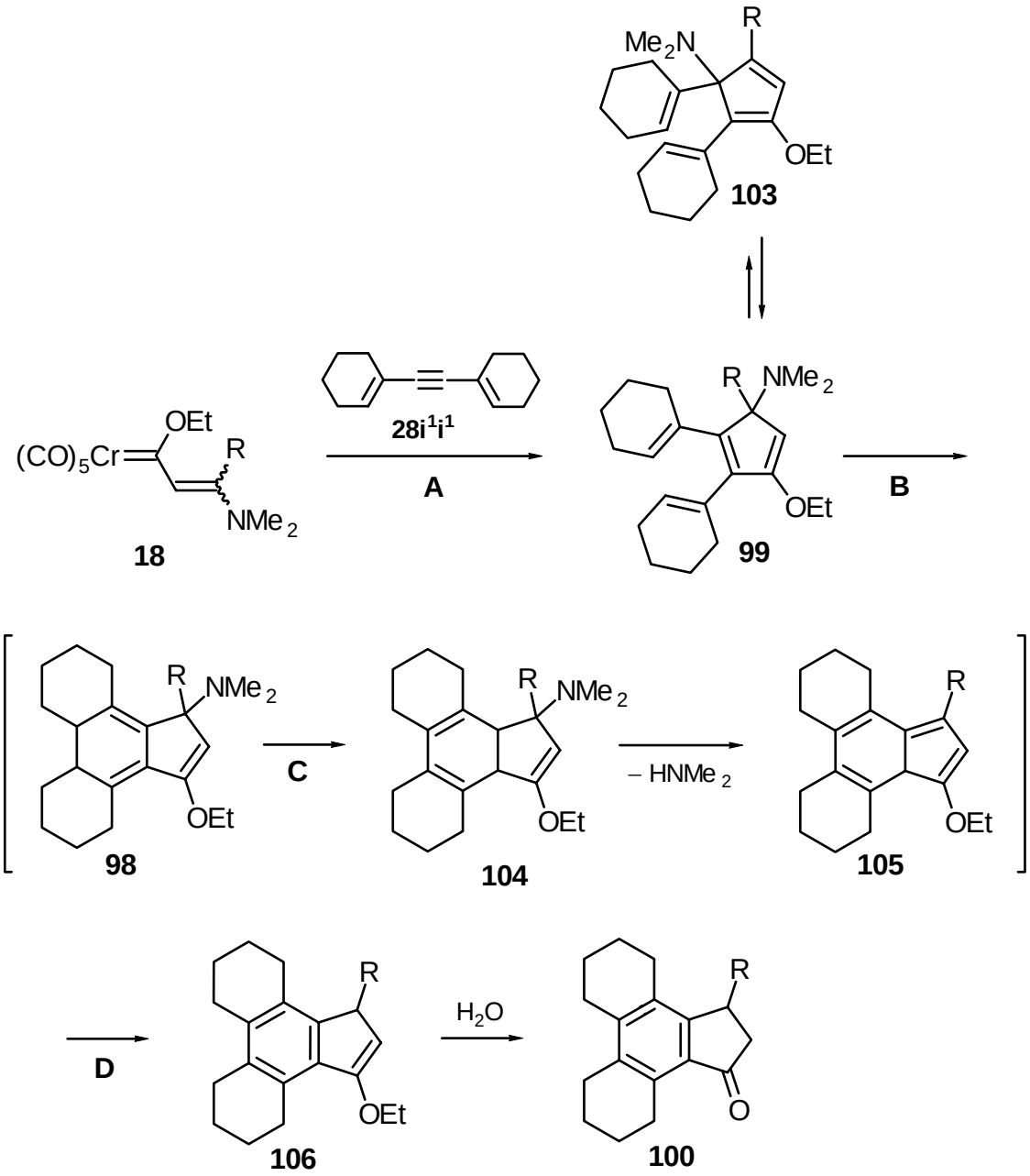
Besides the desired cycloaddition products **100**/**101**, complex **102-*t*Bu** was also obtained in this reaction, when the starting material **18d** and various dienynes were employed. The isomerization of Fischer complex **18d** to compound **102-*t*Bu** was first observed by Duetsch et al.[81] As "softer" dienynes were used as reaction partners of complex **18d**, isomerization reaction to complex **90-*t*Bu** would be favored, and lower chemical yields of cycloaddition products were given (*cf.* entries 5, 10 and 12 in Table 11).



Scheme 36. Isomerization of complex **18d** to **102-*t*Bu**.

5.2.2. Mechanism of Formation of Indanone Derivatives

The mechanism of the formation of the indene derivatives **100** can be rationalized in terms of following sequence: cyclopentadienes **99** and **102** are formed as a formal [3+2] cycloaddition from the reaction of complex **18** with dienynes **28** (Scheme 37). Apparently, the intermediates **91** apparently rapidly equilibrates with trienes **99**, and the latter preferentially undergo 6π-electrocyclization to afford **98**. After further hydrogen shifts and elimination of the dimethylamino functionality, the new unstable trienes **105** is given, which can be easy convent to the more stable aromatic compounds **106**.[82] The ethoxy groups in this cycloadducts **106** could be clearly observed in the ^{1}H- and ^{13}C-NMR spectra of the crude products, hydrolysis of **106** apparently occurred during chromatography, and the ketones **100** were the only isolated products.

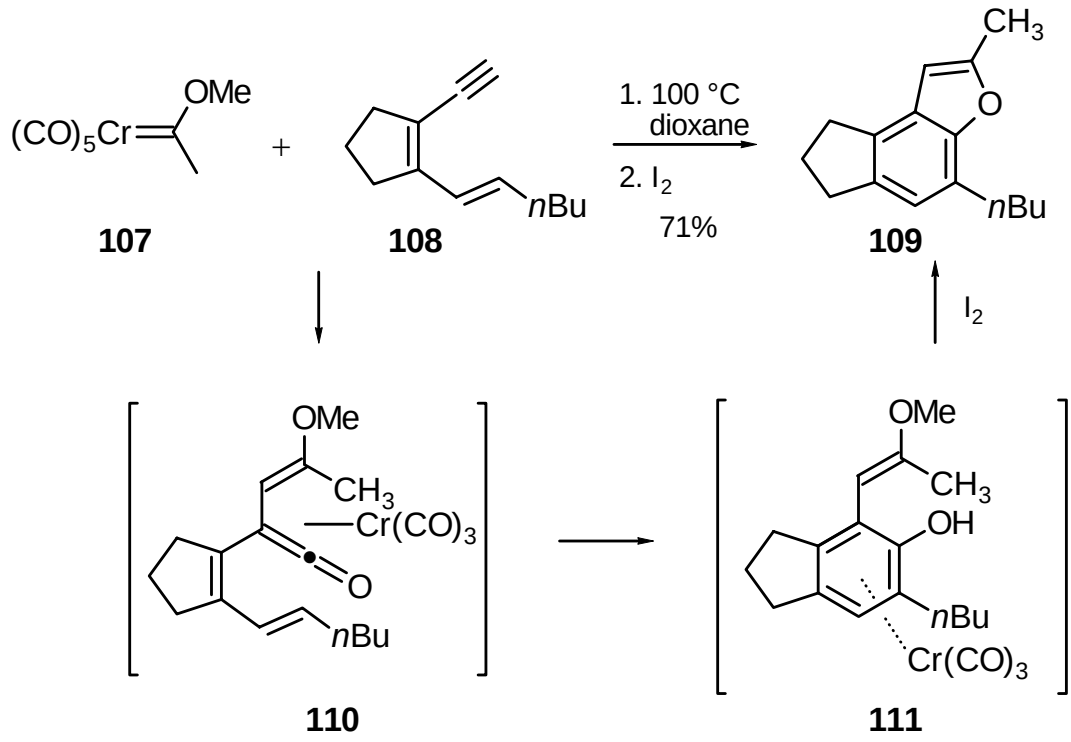


Scheme 37. Mechanism of formation of indanone derivatives **100**. **A**: formal [3+2] cyclo-addition. **B**: 6π-electrocyclization. **C**: twofold 1,*n*-hydrogen shift. **D**: 1,5-hydrogen shift.

In order to examine this mechanism, a control experiment of the reaction of complex **18c** with alkyne **28i^{1}i^1** in pyridine was carried out for *only* 40 h. After removal of $Cr(CO)_5Py$ and the starting material **28i^{1}i^1** by chromatographic purification, an inseparable mixture was afforded, in which the initial cocyclization adduct **99-*i*Pr** and the final cycloaddition product **100k** were detected as major products. Although cyclopentadiene **99-*i*Pr** has the same

molecular weight as the intermediates **98-*i*Pr** and **104-*i*Pr**, it can be distinguished from the latter two molecules by utilizing the ^{1}H- and ^{13}C-NMR spectroscopy.

Recently, Herndon et al. reported a synthetic route to the benzofuran derivative **109** though the coupling of a conjugated dienyne **108** and a Fischer carbene complex **107**.[83] This process is mechanistically related to the Dötz benzannulation reaction in that a chromium carbene-generated dienylketene complex **110** cyclizes to a complexed phenol **111**. Upon treatment with iodine, the complex **111** is converted to the benzofuran derivative **109** (Scheme 38). This reaction also shows that Fischer carbene complexes have highly chemoselectivity on an alkyne than an olefin.

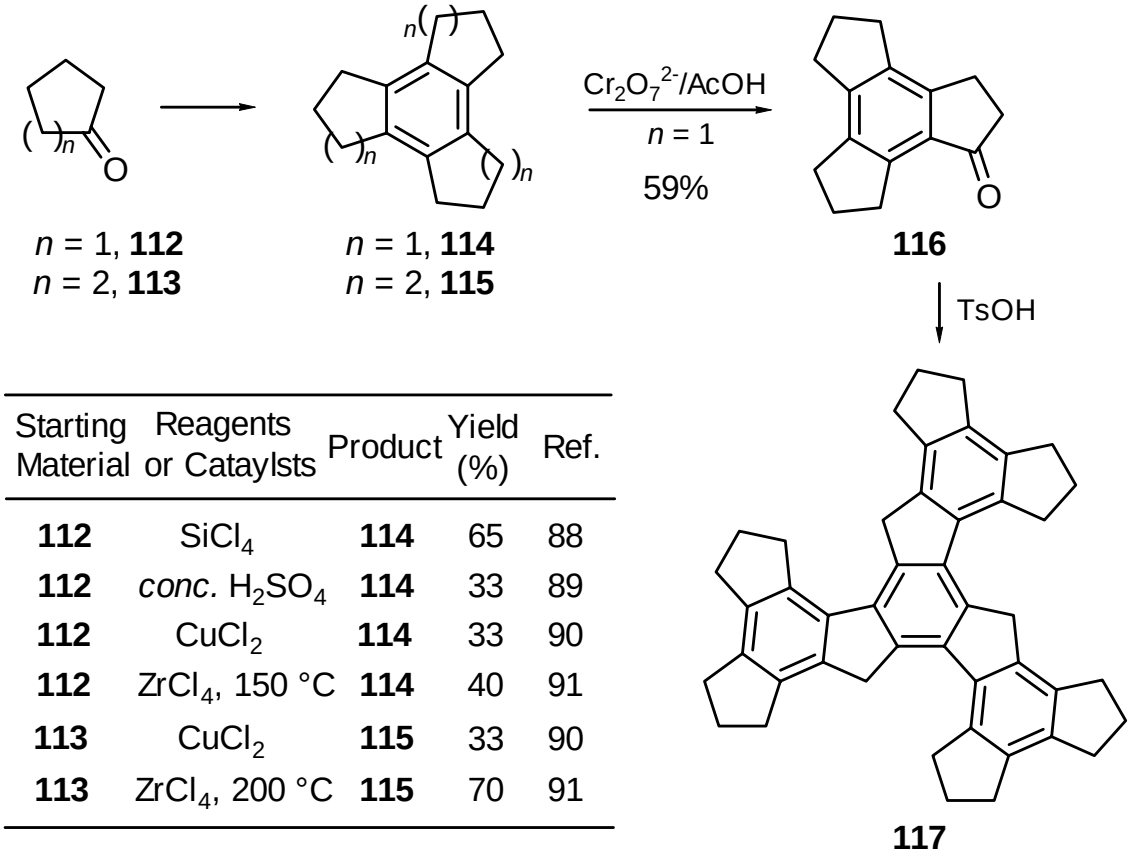


Scheme 38. Synthesis of benzofuran derivative **111** though the Dötz benzannulation reaction.

5.2.3. Remarks

Triannulated benzene derivatives, such as trindan (**114**) and dodecahydrotriphenylene (**115**), were first reported as minor products of acid-catalyzed condensation of cyclopentanone (**112**) and cyclohexanone (**113**), respectively (Scheme 39).[84] The chemical and physical properties of this kind of compounds and their analogues have been extensively studied to examine the bond length alternation.[85] Although serious perturbation of aromaticity is rarely

observed and the Mills-Nixon effect[86] is questioned, the interesting molecules of this type offer opportunities for synthesis of complex natural products.[87]

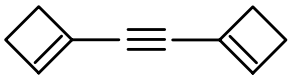


Starting Material	Reagents or Cataylsts	Product	Yield (%)	Ref.
112	$SiCl_4$	**114**	65	88
112	*conc.* H_2SO_4	**114**	33	89
112	$CuCl_2$	**114**	33	90
112	$ZrCl_4$, 150 °C	**114**	40	91
113	$CuCl_2$	**115**	33	90
113	$ZrCl_4$, 200 °C	**115**	70	91

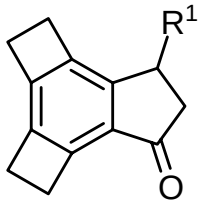
Scheme 39. Synthesis and application of trindanone **116** according to pervious studies.

However, very few procedures are available for preparation of the triannulated benzene derivatives and most of them are carried out either under harsh conditions or in strong acid solutions (Scheme 39). Such methods can not be applied for acid labile starting materials, e.g. cyclobutanone or thermal unstable adducts, as well as unsymmetrical molecules. Further oxidation of trindan (**114**) affords trindanone **116** in 59% yield, which has been regarded as a basic key intermediate for a rational fullerenes synthesis.[92] The insoluble cyclotrimerlization product **117** is generated from compound **116** that the former presents 75% of the carbon network of C_{60}.[93]

This new Fischer-carbene-complexes-mediated tandem reaction provides a direct synthetic route to symmetric and asymmetric trindanone and their analogues in a basic solvent, pyridine, and under a milder condition (*cf.* 80 °C and 150 °C). Due to these milder conditions, synthesis of the interesting molecule **119** from complexes **18** and dicyclobutenylethyne **118** should be reasonable.

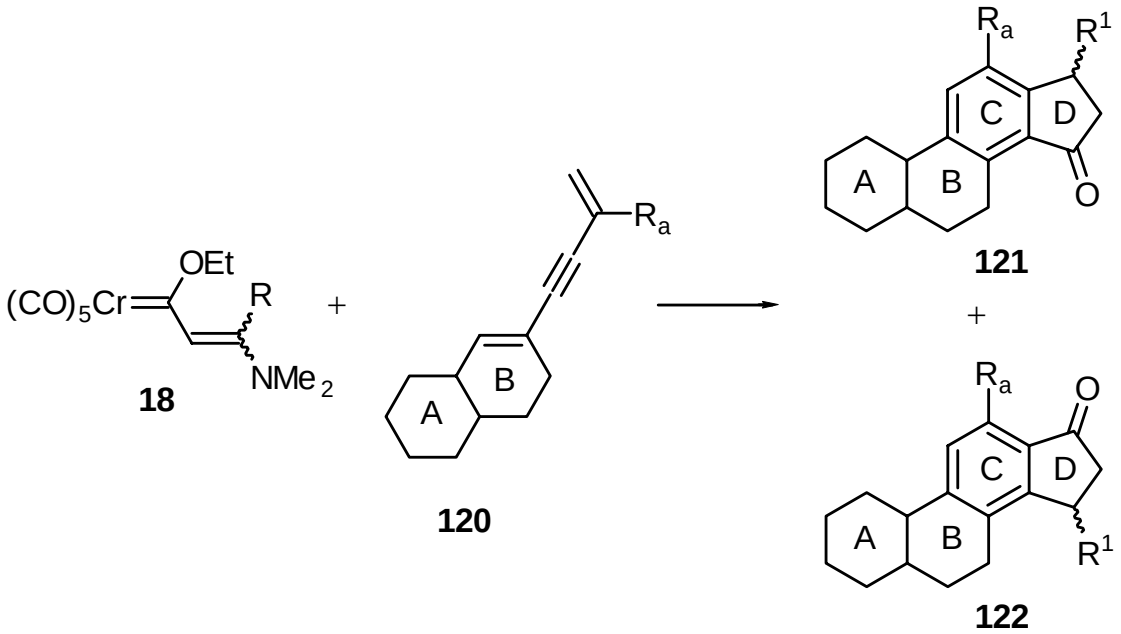


118



119

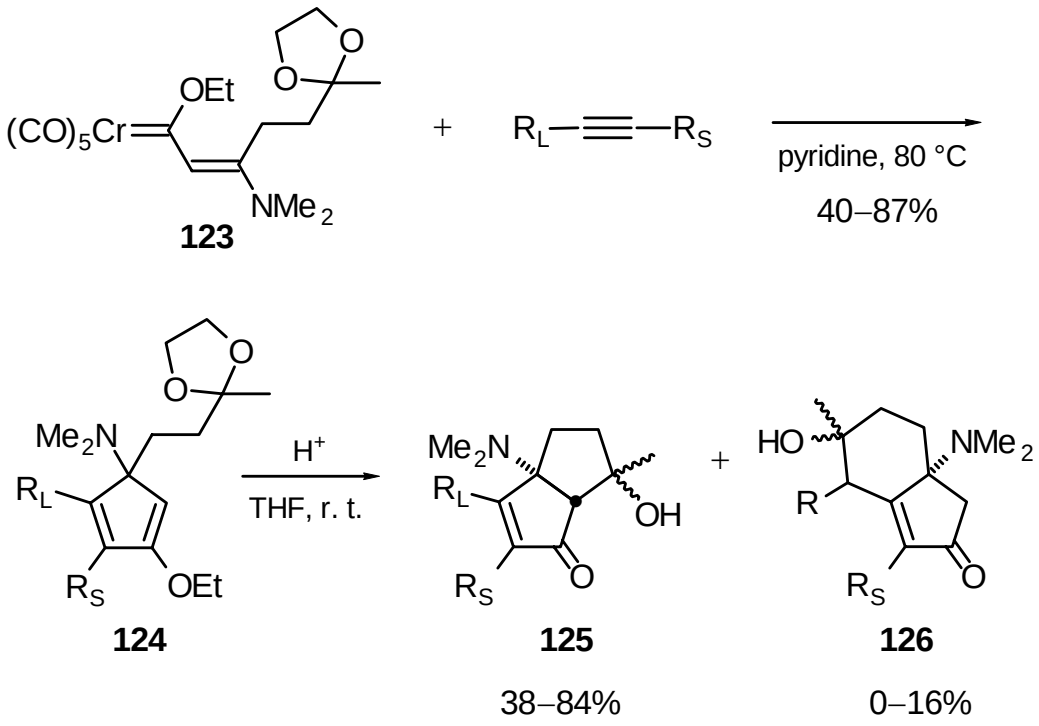
As shown in Scheme 35 and Table 11, the B-C-D ring moieties in the steroid-like compounds **100i**/**101i** and **100j**/**101j** have been achieved by using this cocyclization procedure. An one-pot operation to preparation of the steroid-like products **121**/**122** should be accessible from the reaction of complex **18** with bicyclic alkynes **120** (Scheme 40).



Scheme 40. A proposed synthesis of steroid-like compounds **121**/**122**.

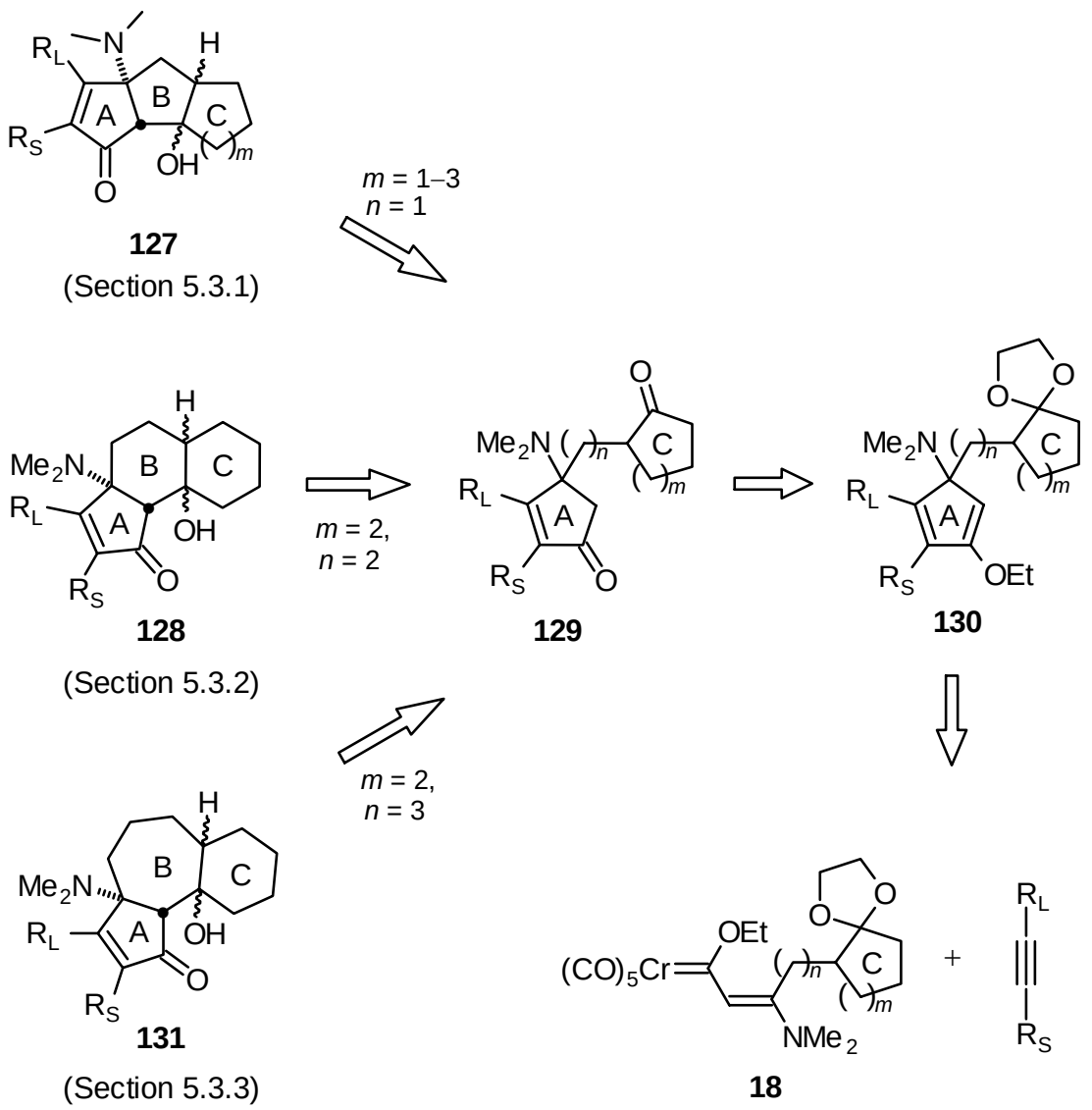
5.3. Synthesis of Basic Structures of Terpenoids

Recently, de Meijere and coworkers provided an useful tool to prepare bicyclo[3.3.0]oct-2-en-4-ones **125** via cyclopentadienes **124**, which were accessible from cocyclization of Fischer carbene complexes **123** with various alkynes (Scheme 41).[94] Under acid conditions, not only the acetal functionality but also the vinyl ethoxy groups in cyclopentdienes of the type **124** can be transfered to ketones, and further intramolecular aldol reaction clouses the second rings. Furthermore, this procedure can be run under an one-pot operation directly from complex **123** and alkynes. In some cases, bicyclic adducts **126** were also obtained as byproducts.



Scheme 40. Synthesis of bicyclo[3.3.0]oct-2-en-4-ones **125**.

In accordance with the above methodology, A-B-C rings of tricyclic molecules of types **127**, **128** and **131** could be constructed by an intramolecular aldol reaction from diketones **129**, which contain A and C rings. Variation of the ring size and chain length in complexes **18**, numerous compounds with tricyclic skeletions can be affored. Due to their different chemo- and stereoselectivies, these results will be divied into three subsections.



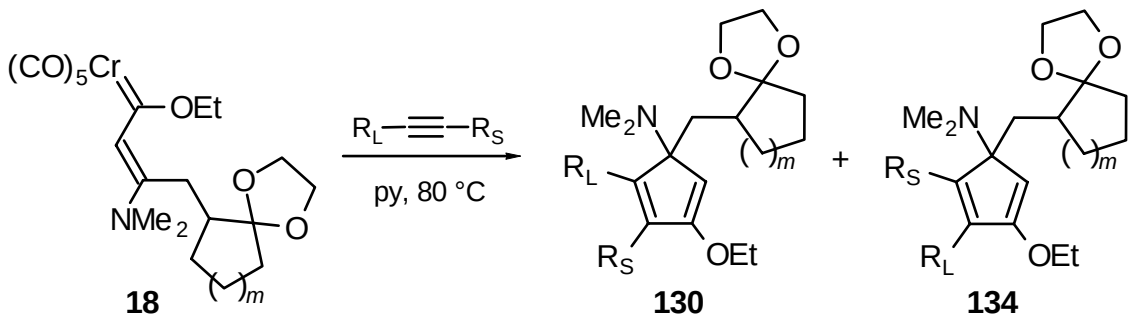
Scheme 41. Retrosynthetic analysis of tricyclic molecules **127**, **128** and **131**.

5.3.1. Synthesis of linear triquinanes and their derivatives

Triquinane is a generic name given to carbocyclic frames composed of three fused five membered rings, and can be divided into linear, angular and propellane structures. (–)-$\Delta^{3(12)}$-Capnellene (**132**) and (–)-hirsutene (**133**) are two examples of linear triquinanes. They have been suggested to act as significant antibiotic and/or antitumor agents.[95c] Due to their important roles in organic synthesis, preparation of tricyclic molecules of the type **127**, which have similar frameworks to linear triquinanes, should be an interesting project.

5.3.1.1. Preparation of Tirquinanes the Type **127**

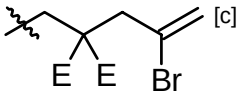
Upon heating complex of type **18** with various alkynes at 80 °C for 3 d, cyclopentadienes **130** were afforded in 38–81% yields. Alkynes **15** with a bulky substituents, e.g. 3,3-dimethyl-but-1-yne (**15n**) and trimethylsilylethyne (**15j**), gave low chemical yields. No obvious daisteremer selectivities were obtained in this reaction.



Scheme 42. Synthesis of cyclopentadienes **130** and **134**. For more deatail, see Table 12.

Cyclization products of the type **127** were afforded in good to excellent yields (77–93%) from cyclopentadienes **130** in dioxane by the treatment with *conc.* hydrochloric acid. From the ^{1}H-, ^{13}C-, and even 2D-NOESY-NMR spectra, it was not possible to unambiguously assign the stereochemistry of tricyclic molecules **127** with four stereogenic centers. Slow diffusion crystallization of **127a-II** and **127f-I** from benzene/dichloromethane afforded single crystals with good quality for X-ray structure analysis (Figure 3 and 4). Thus, their structures were rigorously established as *cis,anti,cis* (**127-I**), *cis,syn,cis* (**127-II**) and *cis,anti,trans* (**127-III**). Generally, *cis,anti,cis* isomers (**127-I**) were obtained as major products in 9 out of 11 examples. In accordance with the calculation of Osawa et al., the *cis,anti,cis* ring fusion of tricyclic[6.3.0.0^{2,6}]undecane is only slightly more stable than the hindered folded *cis,syn,cis* form, but much more stable than the third isomer (*cis,anti,trans*).[96]

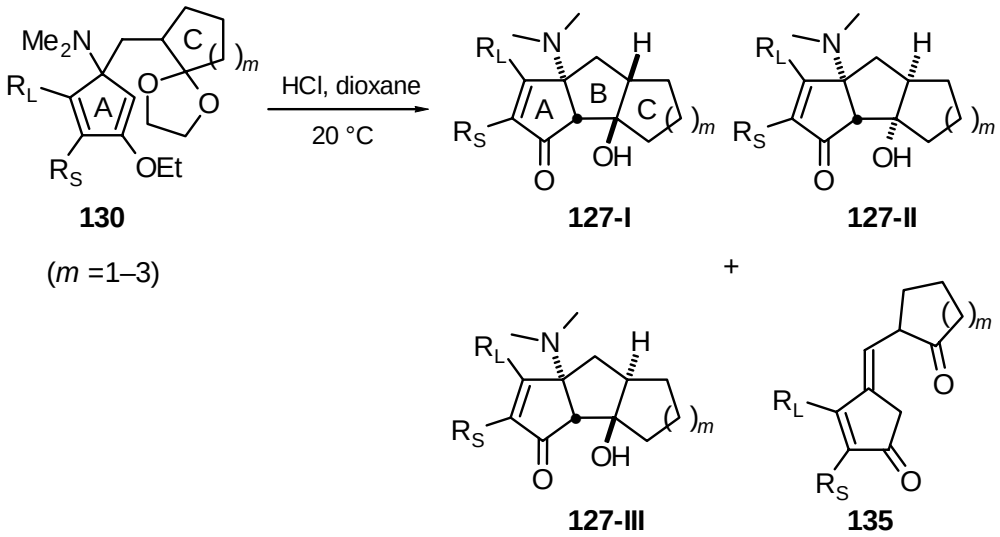
Table 12.

Entry	Starting Materials	Alkyne	R_L	R_S	Product	Yield (%)	d. r.[a]
	m = 1						
1	**18i**	**15aa**	Ph	Ph	**130a**	50	1.5 : 1
2	**18i**	**15j**	TMS	H	**130b**	45	1.3 : 1[b]
3	**18i**	**15h**[1]	*n*Pr	H	**130c**	68	1 : 1
4	**18i**	**15h**	Me	H	**130d**	75	2 : 1
5	**18i**	**15hh**	Me	Me	**130e**	67	1 : 1
	m = 2						
6	**18j**	**15aa**	Ph	Ph	**130f**	52	1 : 1
7	**18j**	**15hh**	Me	Me	**130g**	66	1 : 1
8	**18j**	**15n**	*t*Bu	H	**130h**	38	2 : 1
9	**18j**	**29a**[2]	3-CF_3-C_6H_4	H	**130i**	40	2 : 1
10	**18j**	**15r**	 [c]	H	**130j**	51	1.9 : 1
11	**18j**	**15g**	*c*Pr	H	**130k**	56	1.2:1
	m = 3						
12	**18m**	**15baa**	Ph	Ph	**130m**	81	1.3 : 1
13	**18m**	**15h**[1]	*n*Pr	H	**130n**	72	1.4 : 1

[a] all reactions were undergone at 80 °C for 4 d, if not otherwise mentioned. Diastereomeric ratio is basis on the ^{1}H NMR spectra. [b] trace amount of cyclopentadiene **134i** was also detected. [c] E = CO_2Et.

In the two cases, which did not agree with above calculation, *cis,syn,cis* isomers **127-II** were obtained either as major product or had equal proportion like its *cis,anti,cis* **127-I** (entries 3 and 4 in Table 13). Formation of them were more difficult than that of other examples: long reaction time and large amount of *conc.* hydrochloric acid were needed for this intramolecular aldol reactions. These results can be explained by two factors: electronic

effects of substituents R_L and ring size of C rings in the starting materials **130** or, eventually, their hydrolyzed-deprotective intermediates **129**. Three examples of diphenyl substituted tricyclic molecules with different ring size show that the triquinane **127a** was afforded under the same reaction condition in a slightly lower chemical yield (entries 1, 5 and 11 in Table 13). Phenyl moiety can be regarded as an electron-withdrawing group, and it will enhance the reactivity of the enone functionality for the aldol reaction. However, generation of dimethyl substituted triquinane **127e** were obviously controlled not only by ring size but also electronic effect.



Scheme 43. Synthesis of linear triquinanes **127**. For detail, see Table 13.

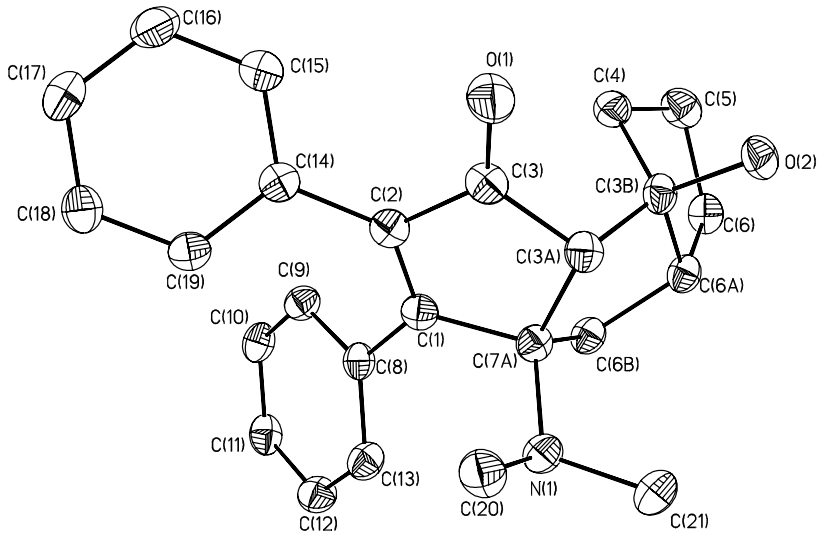


Figure 3. The structure of **127a-II** in the crystal: $C_{25}H_{27}NO_2$, monoclinic crystals of space group $P2_1/n$, unit cell dimensions: $a = 11.345(2)$, $b = 10.413(2)$, $c = 16.729(3)$ Å, $\alpha = 90$, $\beta = 94.56(3)$, $\gamma = 90°$, $V = 1970.0(7)$ Å^3, 2496 reflections. The distance of the hydrogen bonding between hydroxy and ketone groups: 3.45 Å.

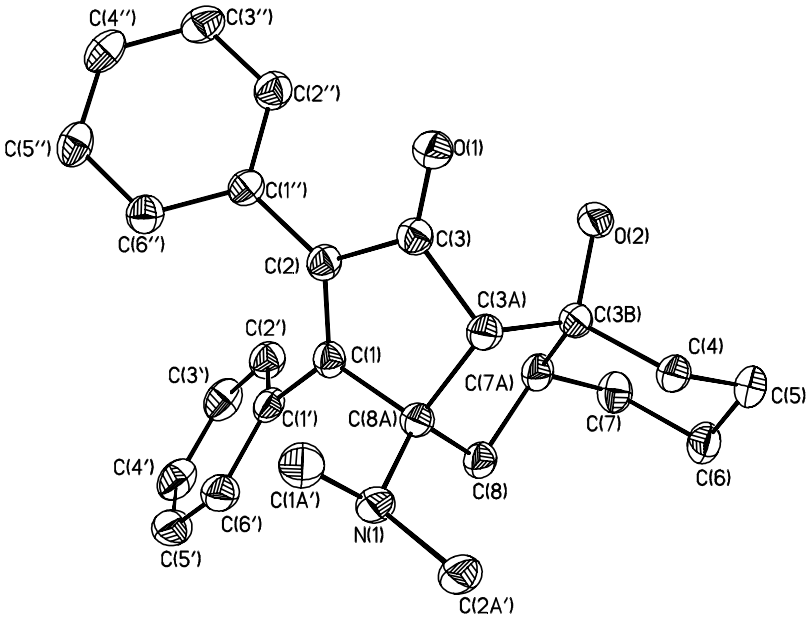
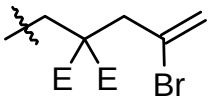


Figure 4. The structure of **127f-I** in the crystal: $C_{27}H_{27}NO$, triclinic crystals of space group $P1$, unit cell dimensions: $a = 10.13(3)$, $b = 15.01(4)$, $c = 15.10(3)$ Å, $\alpha = 99.2(2)$, $\beta = 107.8(2)$, $\gamma = 96.6(2)°$, $V = 12125(9)$ Å^3, 9865 reflections. The distance of the hydrogen bonding between hydroxy and ketone groups: 1.98 Å.

Table 13.

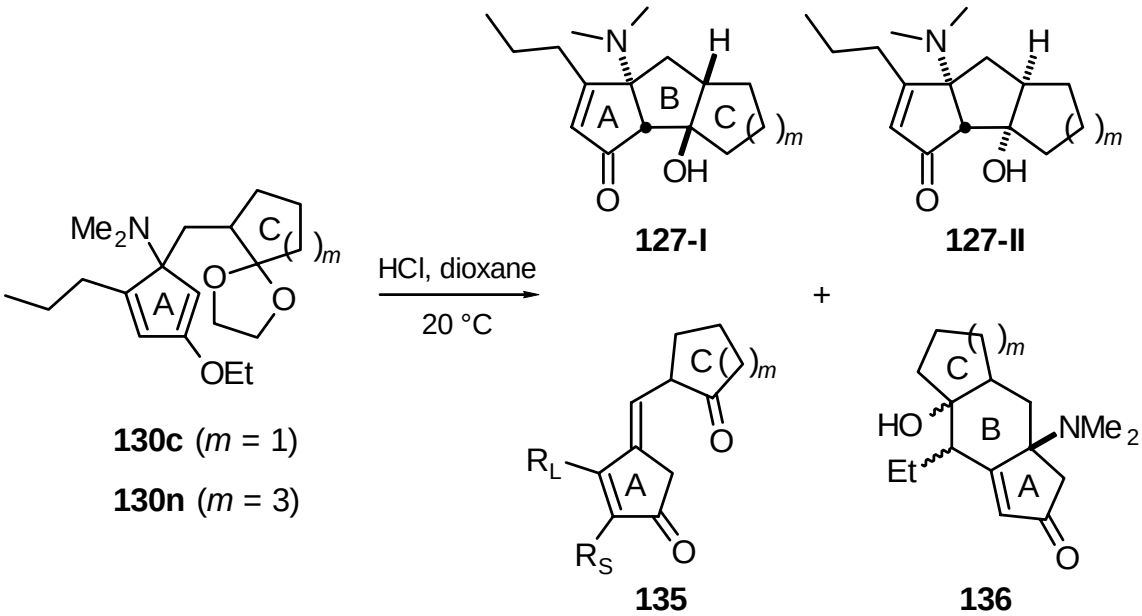
Entry	Starting Materials	R_L	R_S	Time (d)	Product	Yield (%) **I/II/III**	Combined Yield(%)
m = 1							
1	**130a**	Ph	Ph	2	**127a**	54/26/0	80
2	**130b**	$SiMe_3$	H	2	**127b**	47/24/0	74
3	**130d**	Me	H	4	**127d**	30/49/0	79
4	**130e**	Me	Me	4	**127e**	39/38/0	77
m = 2							
5	**130f**	Ph	Ph	2	**127f**	63/17/9	89
6	**130g**	Me	Me	2	**127g**	64/18/–[a]	82
7	**130h**	*t*Bu	H	2	**127h**	63/16/9	93
8	**130i**	3-CF_3-C_6H_4	H	2	**127i**	72/4/13	89
9	**130j**		H	2	**127j**	61/14/3	78[b]
10	**18k** + **15j**	$SiMe_3$	H	4+2	**127l**	29/9/2	40[c]
m = 3							
11	**130m**	Ph	Ph	2	**127m**	27/24/32	83

[a] traces of other stereoisomers were observed. [b] E = CO_2Et; in addition, 8% of the elimination product **135j** and 1% of the isomer **136j** were isolated. [c] one-pot operation from complex **18k** and trimethylsilylethyne (**15j**).

The selectivity among these three stereoisomers of type **127** does not depend on diastereomeric ratios in cyclopentadienes **130**, but on the ring size of C ring. Generally, starting materials **130** with a five-membered C ring gave only *cis,anti,cis* (**127-I**) and *cis,syn,cis* (**127-II**) isomers. But the ratios between them are lower than those of their six-membered C ring analogues. As the size of the C ring increases, the amounts the third isomers **127-III** also incases and low selectivity among three stereoisomers appear. While cyclopen-

tenones **129** equipped with a seven-membered C ring enhance the proportion of *cis,anti,trans* products of the type **127-III**. This result is caused due to the low ring strain energy of cycloheptane in *trans*-configuration. An one-pot operation to tricyclic molecules **127l** have been achieved directly from complex **18k** and alkyne **15j**, and this procedure did not effect the distribution of their three isomers.

The derivative of malonic acid diethyl ester **115j** gave, besides tricyclic molecule **127j**, not only the elimination product **135j** in 8% yield but also traces of a new structure isomer, which has completly different NMR spectra compared to **127j** (entries 9 in Table 13). Such kind of byproducts were not observed in other examples. Thus, formation of them should depend on the chain length, not the steric hindrance of the substituents R_L. Control experiments were carried out from *n*-propyl substituted cyclopentadiene **130c** and **130n**: besides **135** (and **127**), new cyclization products of the type **136** were also observed. Two diastereomers of tricyclic molecules **136** with four stereogenic centers were isolated, but, again, it was not so easy to assign their stereochemistry. On other hand, the formation of elimination products **135** is strongly enhanced by larger amounts of *conc.* hydrochloric acid.



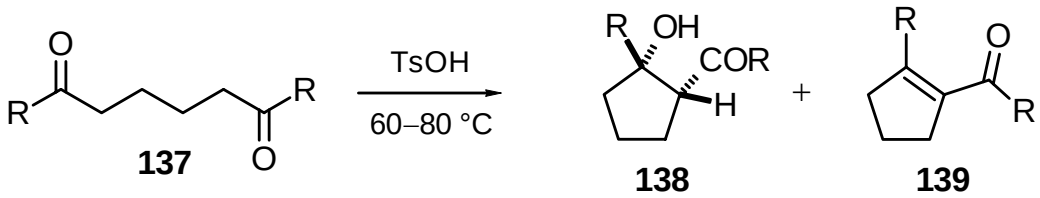
Scheme 44. Control experiments of formation of the elimination products **135** and the tricyclic adducts **136**. For detail, see Table 14.

Table 14.

Entry	Starting Material	Reagent	Time (d)	Product	Yield (%)	Combined Yield(%)
1	**130c** (*m* = 1)	3 N HCl	4	**135c** **136c**	7 59 + 9	75
2	**130n** (*m* = 3)	*conc*. HCl	2	**127n-I** **127n-II** **135n** **136n**	19 20 23 15 + 3	80

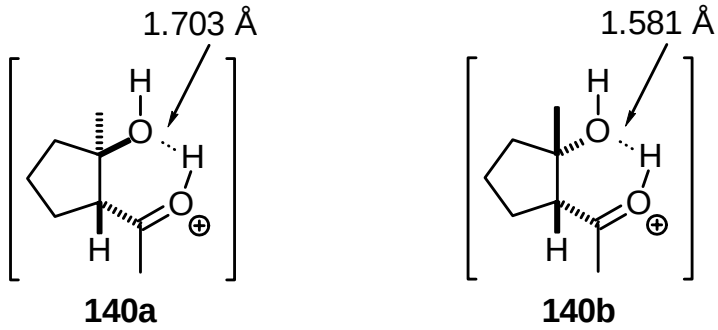
5.3.1.2. Mechanism

Intramolecular adol reaction of 1,6-disubstitued diones **137** under acidic conditions afford tertary alcohols **138** and/or their dehydrolysis derivatives **139**. When bulky hydrocarbon substituents next to the ketone functionalities in the starting material **137**, cyclization does not occur. The acetyl and hydroxy groups adapt the *cis*-configuration in the products **138**. Although acid-catalyzed adol reactions have been widely applied in organic synthesis since long time, only few theoretic studies about their mechanism were reported. In accordance with the calculations of Humbel et al., intermediates with *trans*-configuration (the hydroxy group with respect to the acetyl moiety in **140a**) are energetically higher than these of intermediates with *cis*-configuration **140b**.[97] In addition to the energetic viewpoint, the distance between the hydrogen of the protonated ketone functionality and the oxygen atom of the alcohol moiety in the former configuration is longer than that of the latter. Thus, the stereoselectivity with *cis*-form is established. Formation of the dehydrolysis derivative **139** is an endothermic reaction.



	138	139
R = $SiMe_3$	46%	16%
Me	–	57%
*t*Bu	–	–

Scheme 45. Intramolecular adol reaction of 1,6-disubstituted diketones **137**.



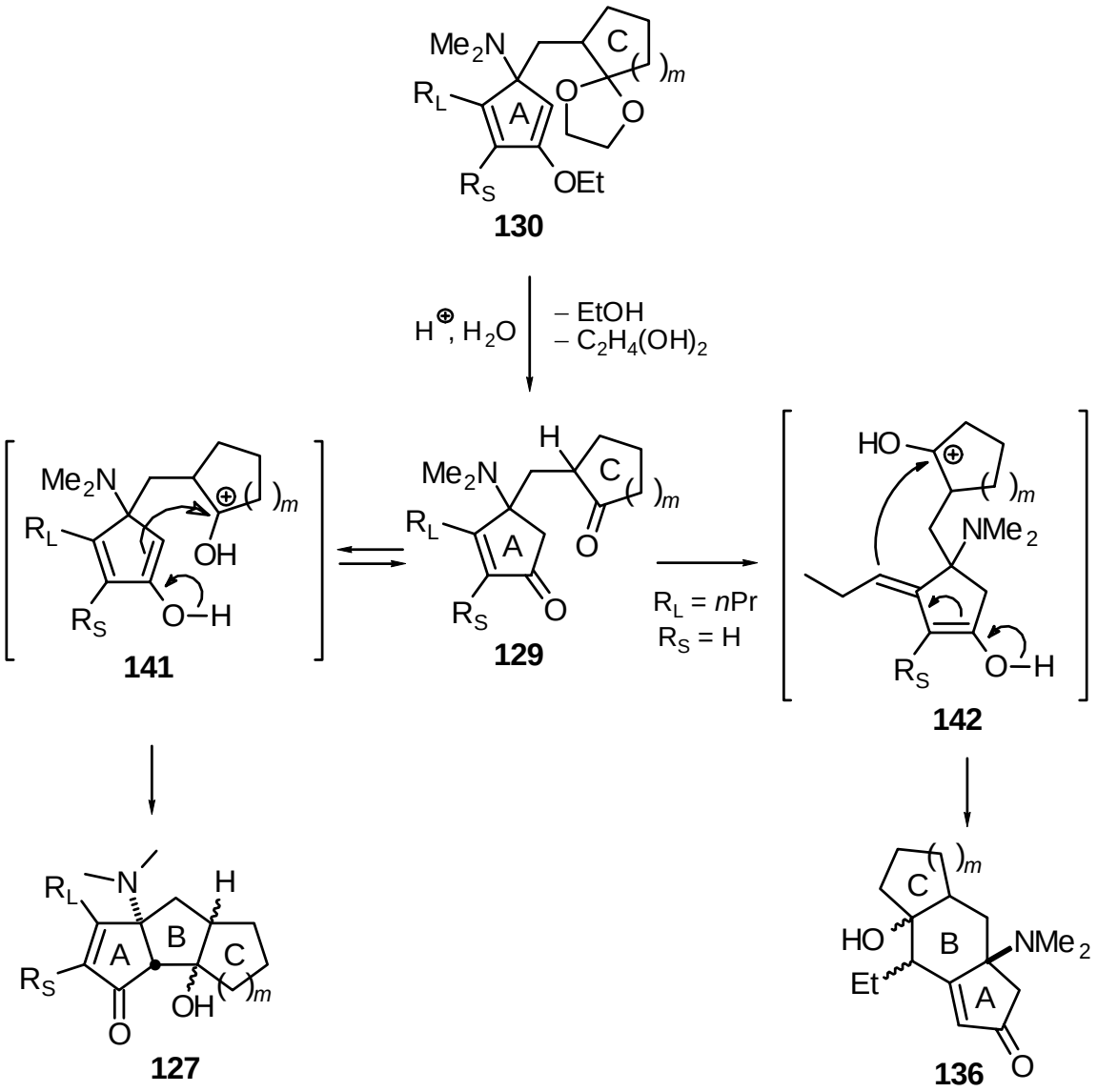
$\Delta E_{(\mathbf{140a–140b})}$ = 5.3 (kcal/mol)

$\Delta E_{(\mathbf{139\text{-}Me–140b})}$ = 16.2 (kcal/mol)

The mechanism of the formation of the tricyclic molecules **127** can be rationalized in terms of the following sequence: under acidic condition, cyclopentadienes **130** convent to cyclic diketone **127**. The intermediate **141** gives triquinanes and their derivatives **127**. However, when an electron-donating substituent (e. g. methyl and *n*-propyl) attached at R_L position in **130**, another intermediate **142** is favored. Further cyclization of **142** affords **136**. The ethyl substituted *exo* alkenyl group in **142**, which is generated from a *n*-propyl functionality, are more stable than the methylene one, which is produced from a methyl group. Therefore, none of product **136** was observed from methyl substituted cyclopentadienes **130**.

The stereochemistry of this reaction does not agree with the above calculations, e. g. the hydroxy and acetyl groups do not adopt the *cis*-configuration, but, eventually, the dimethyl-amino functionality is in the *cis*-position to the hydrogen next to the ketone moiety. It means ring strain energy here plays a more important role than the hydrogen bonding between the hydroxy and acetyl groups. Thus, *cis,anti,cis* and *cis,syn,cis* isomers are major adducts. On

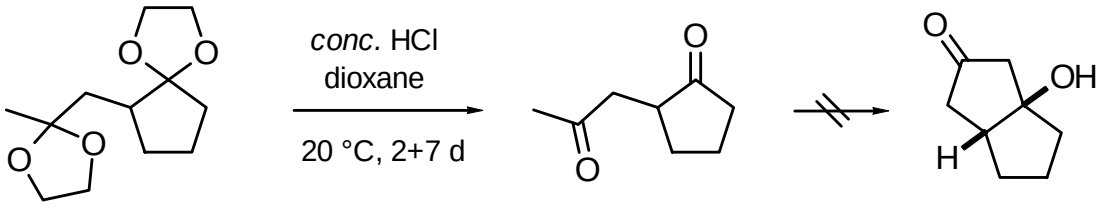
the other hand, it is doubtful whether, in some cases, formation of large proportions of the *cis,syn,cis* isomers are induced by the interaction (or hydrogen bonding) of the dimethylamino group and the hydrogen of alcohol moiety.



Scheme 46. Mechanism of formation of tricyclic products **127** and **136**.

In order to examine the ring strain effect in the intramolecular Aldol reaction, diacetal **53** was used as the starting material for this control experiment (Scheme 47). Only 2-(2'-oxoprop-yl)cyclopentanone (**143**) was obtained, but the cyclization to bicyclic product **144** did not happened, even in the presence of large amount of *conc.* hydrochloric acid for a long reaction time. Thus, the formation of the tricyclic molecules **127** (Scheme 46) shows that the

cyclopentenone moiety in the intermediates **129** are more active for this intramolecular Aldol reaction than the methyl ketone in **143**.



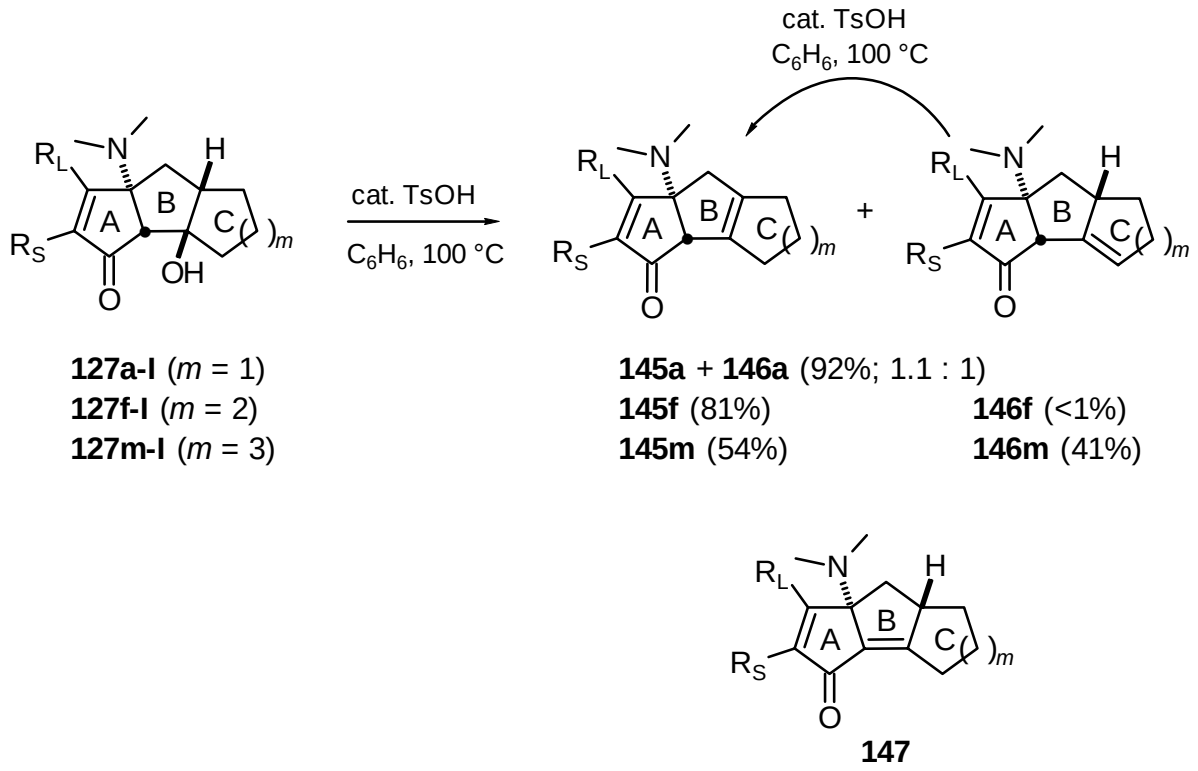
53 **143** **144**

Scheme 47.

Unfortunately, cyclization products **127** are not enantiomerically pure molecules. From the mechanistic analysis, formation of the stereogenic center attached to the dimethylamino group in the cyclopentadienes **130** is the key step for access to enantiomerically pure form. Despite numerous examples for the successful application of chiral auxiliaries derived from proline, e.g. in the SAMP/RAMP methodology developed by Enders et al.,[98] chiral pyrrolidinyl residues introduced into the α,β-unsaturated carbene complexes **18** did not give satisfactory results. But the research results of Müller showed that cocyclization of carbene complexes **18** with various alkynes at ambient temperature afford better stereoselectivity.[75] Recently, Sierana reported palladium-catalyzed Fischer-carbene-complexes transmetallations at room temperature with good chemical yields.[99] Furthermore, transition metal catalysts with the presence of chiral ligands have been widely utilized for asymmetric synthesis. Basis on the information, preparation of diastereomerically pure cyclopentadienes **130** should be reasonable. Stirring complex **18j** with cyclopropylethyne (**15g**) and catalytic amount of palladium(II) acetate [or palladium(II)chloride·bis(triphenylphosphine)] and triphenylphosphine in pyridine at ambient temperature afforded only a small amount of cocyclization product **130k** was observed by TLC, even after a week. However, this reaction process was very slow, and most of the starting material **18j** did not participate in this reaction.

Dehydroylsis is an endothermic reaction. Therefore, further heating cyclization products **127-I** in the presence of catalytic amount of *p*-toluenesulfonic acid in benzene using a Dean-Stark apparatus afforded dehydrolysis molecules **145** and **146** in excellent yields. None of products **147** was obtained. The ratio between two regioisomers **145** and **146** in this dehydroylsis process, again, depends upon the size of the C ring. Reaction of starting material

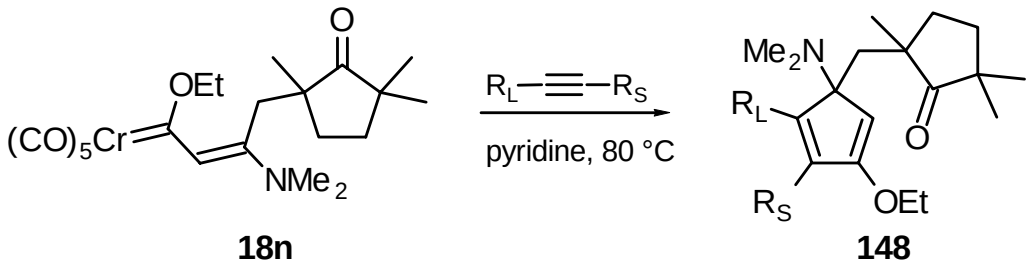
with a six-membered fused C-ring, **127f-I**, went much faster to completion with highly regioselectivity (entry 2 in Table 15). However, within the same reaction time, the five-membered-ring fused **127a-I** did not give any products. Further heating of it for another 17 h yielded a mixture of **145a** and **146a** in equal amount. The ratio between two isomers was changed from 1:1 to 2.1:1 after refluxing with catalytic amount of *p*-toluenesulfonic acid for an additional 36 h. Therefore, molecules **145** and **146** can be regarded as thermodynamic and kinetic products, respectively. The seven-membered-ring fused **127m-I** did not give better regioselectivity.



Scheme 48. Dehydration of tricyclic molecules **127-I**.

5.3.1.3. Preparation of Analogues of $\Delta^{3(12)}$-Capnellene (**132**)

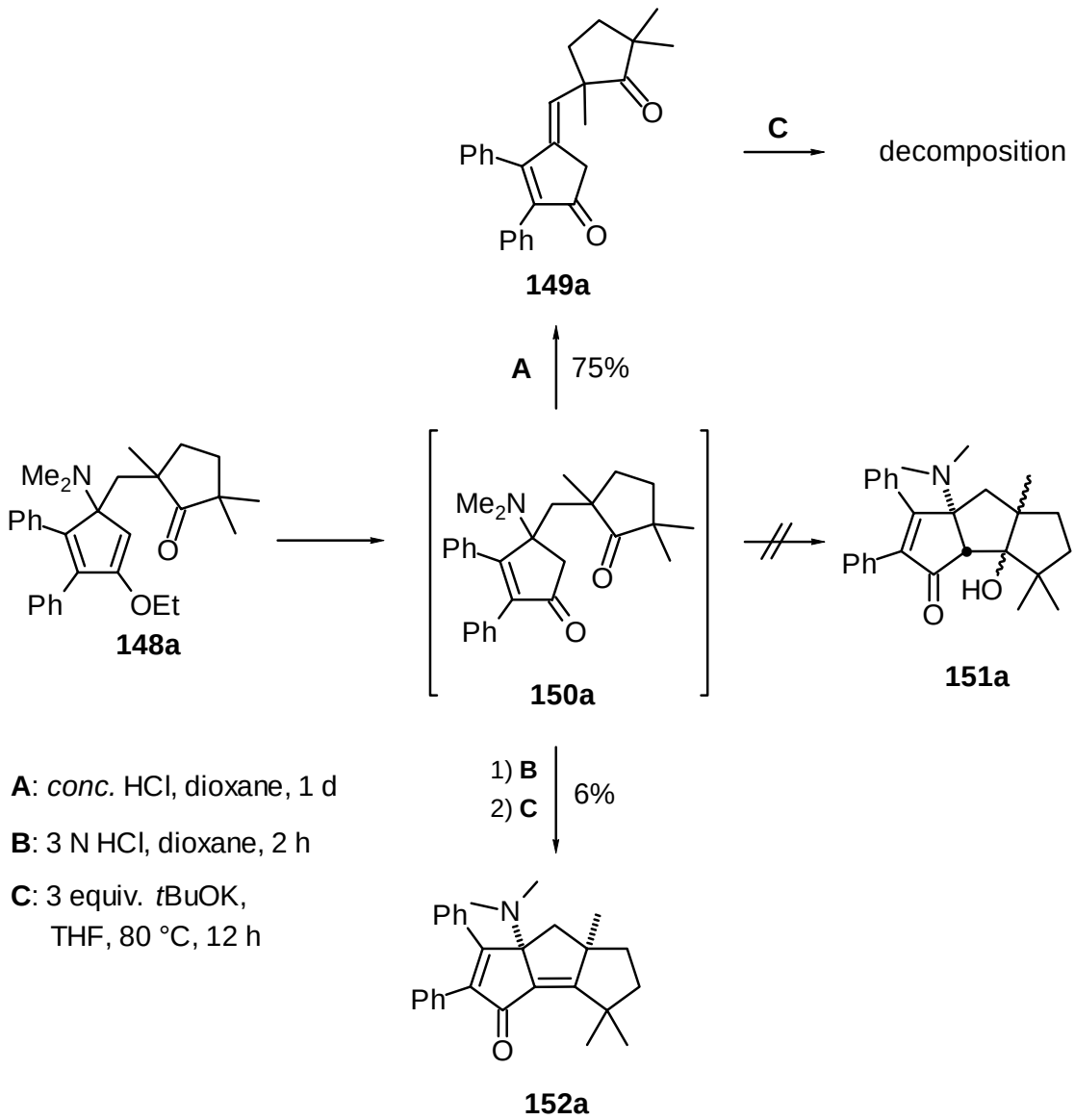
As shown in the subsection *5.3.1.1*, triquinanes of type **127** have been prepared in mediated to good yields. Thus, total synthesis of $\Delta^{3(12)}$-Capnellene (**132**) should be reasonable to achieve from cocyclization of complex **18n** and acetylene gas. Before starting this project, easily handled alkynes were used for test reaction, and cyclopentadienes of the type **148** were given in acceptable yields (Scheme 49).



Alkyne	R_L	R_S	Product	Yield (%)	d. r.
15aa	Ph	Ph	**148a**	47	1.2 : 1
15h[1]	*n*Pr	H	**148b**	57	1.5 : 1

Scheme 49.

Further hydrolysis of cocyclization products **148a** under strong acidic conditions did not afford tricyclic molecules **151a**, but, eventually, elimination products **149a**. This result seems to confirm the experiment of Humbel et al. that intramolecular Aldol reaction does not happen when a bulky hydrocarbon as a substituent in the neighborhood of a ketone (Scheme 43). Refluxing diketone **149a** with potassium *tert*-butoxide in THF leaded decomposition of starting materials. Treatment with diluted hydrochloric acid for a short time, and then, undergoing intramolecular cyclization in basic condition, gave triquinane **152a** in 6% yield from cyclopentadiene **148a**. The 2D-NOESY-NMR spectrum shows the dimethylamino and methyl groups adopt in *cis*-configuration.

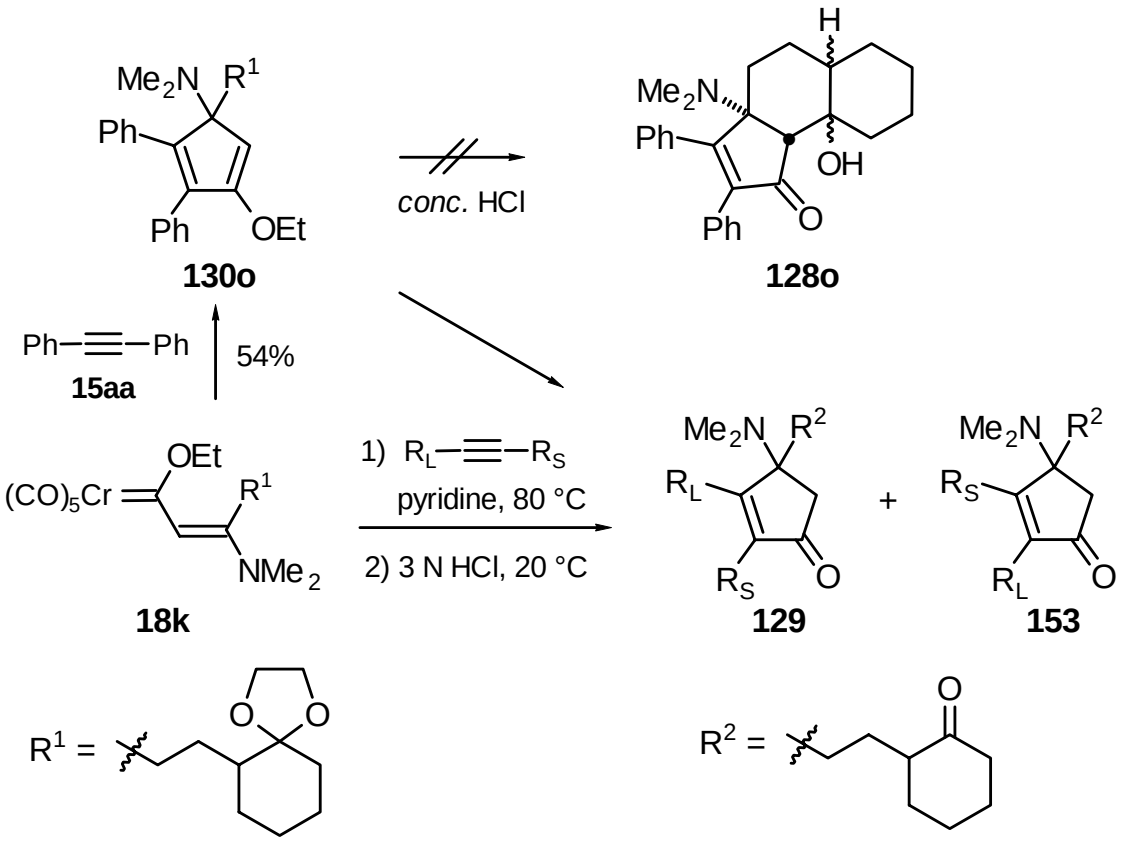


Scheme 50. Synthesis of triquinane **152a**.

This unsatisfactory results of these test experiments were caused by following reasons: a) In a steric hindrance environment and under acidic condition, elimination (to **149a**) easily happens than cyclization (to **151a**). b) The stereogenic center, which is attached by the methyl group, can not be converted to a suitable form via an enolization process for an intramolecular aldol reaction. Thus, the triquinane **152a** was isolated in very low yield, although with a high stereoselectivity.

5.3.2. Synthesis of B-C-D Rings of Steroid-like Molecules

By using the newly established method as mentioned in *5.3.1.* seems able to synthesize tricyclic compounds **128**, which contain *B-C-D* rings of steroids. Upon heating complex of **18k** with diphenylethyne (**15aa**) in pyridine, cyclopentadiene **130o** was afforded in 54% yield, from which **128o** was not yielded under a strong acidic condition, but eventually, cyclopentenone **129o**. Thus, access to diketones of the type **129** was modified as an one-pot operation directly from complex **18k** (Scheme 51).



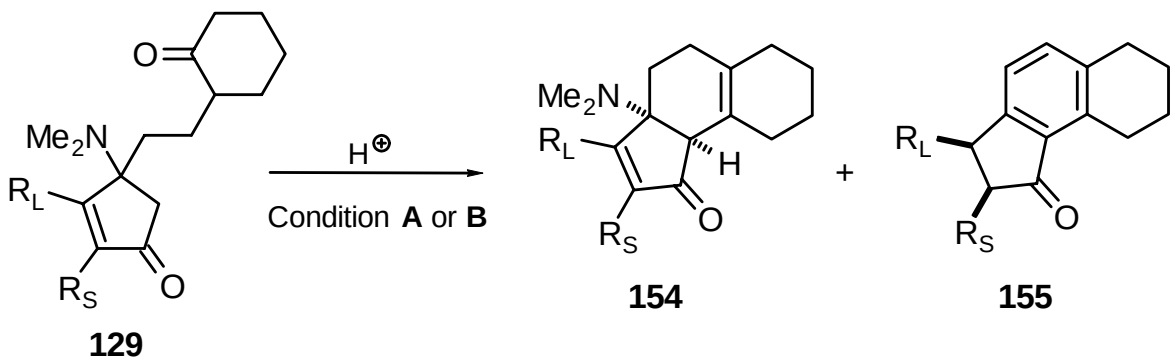
Scheme 51. For detail, see Table 15.

Table 15.

Entry	Alkyne	R_L	R_S	Product	Yield (%)	d. r.
1	**15j**	TMS	H	**129p**	49	1.5 : 1[a,b]
2	**15h**[1]	*n*Pr	H	**129q**	63	1.1 : 1[c]
3	**15h**	Me	H	**129r**	60	1.1 : 1[c]
4	**15hh**	Me	Me	**129s**	69	2.2 : 1[c]

[a] diastereomeric ratio based on the ^{1}H-NMR spectra. [b] traces of cyclopentadiene **153p** were also detected. [c] Diastereomeric ratio is basis on the ^{13}C-NMR spectra.

Further heating cyclopentenones **129** under acidic conditions afforded tricyclic products **154** and **155** in good to excellent yields (Scheme 52 and Table 16). The products distribution depends not only upon the reaction condition but also the substituents (R_L and R_S). Thus, this reaction was not optimized. As the reaction was carried out by utilizing condition **A** or by condition **B** for a short time, besides starting materials **129** and cyclization products **154** and/or **155**, another byproducts **157** were also observed in ^{1}H-NMR spectra of crude products. Reaction condition **A** for this aldol condensation is only suitable for the starting material **129q**, otherwise would give very low yields or even no convention at all. It is not surprising that under condition **B**, trimethylsilyl substituted cyclopentenone **129p** afforded only desilylation product **155p** in 86% yield.



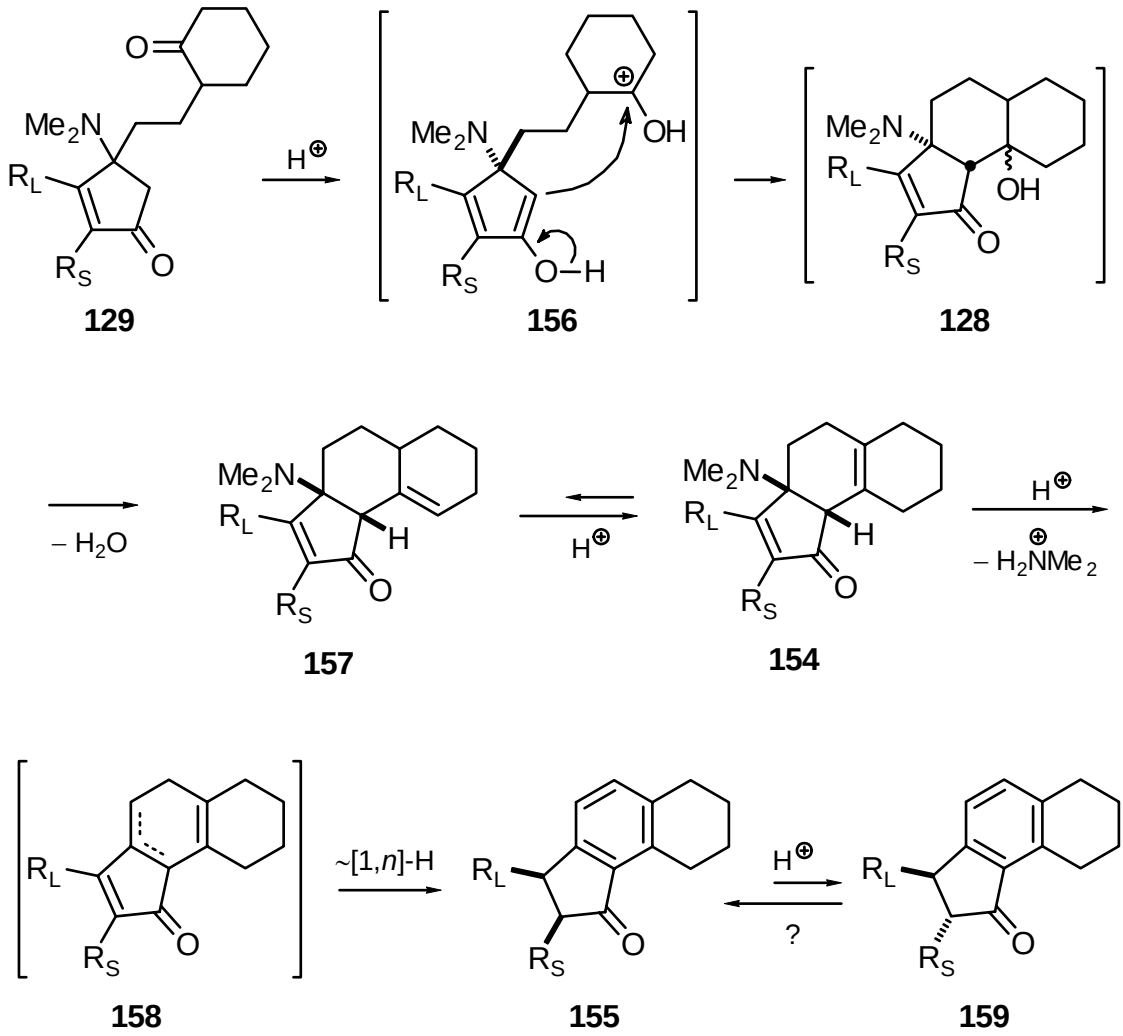
Scheme 52. Synthesis of tricyclic products **154** and **155**. **A**: Dean-Stark apparatus, catalytic amount of *p*-toluenesulfonic acid, C_6H_6, 100 °C, 24–36 h. **B**: *conc.* HCl, dioxane, 60 °C, 36 h. For detail, see Table 16.

Table 16.

Entry	Starting Material	R_L	R_S	Condition	Product	Yield (%)	Combined Yield(%)
1	**129p**	TMS	H	A	**154p**	0	0[a]
					155p	0	
2	**129p**	TMS	H	B	**154p**	0	86
					155p	86[b]	
3	**129q**	*n*Pr	H	A	**154q**	51	88
					155q	37	
4	**129r**	Me	H	A	**154r**	30[c]	30
					155r	0	
5	**129r**	Me	H	B	**154r**	0	77
					155r	77	
6	**18k** + **15h**	Me	H	B	**154r**	0	53[d]
					155r	53	
7	**129s**	Me	Me	A	**154s**	22	23[e]
					155s	1	
8	**129s**	Me	Me	B	**154s**	70	85
					155s	15	

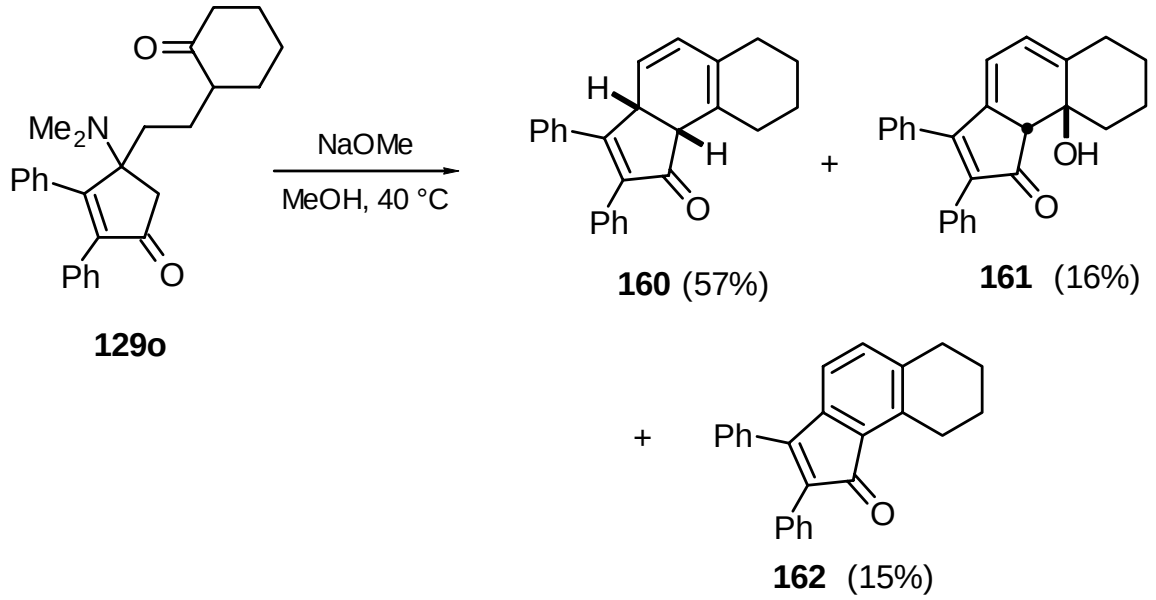
[a] only starting material was observed. [b] desilylation product. [c] NMR yield. [d] one-pot operation for complex **18k** and alkyne **15h**. [e] 62% of starting material **129s** was recovered.

Mechanistically, access to cyclization products **128** is similar to formation of tricyclic molecules **127** (Scheme 53). But, under high-temperate reaction conditions, an endothermic dehydrolysis process is favored to yield **154** and **157**, and the latter would be converted to the former. Acid-mediated removal of the dimethylamino group and olefin isomerization lead to indanone derivatives **155** with *cis*-configuration. However, it is very difficult to confirm that this stereoselectivity is caused by a stereospecific hydrogen migration during the olefin isomerization or by thermodynamic control via an enolation under acidic conditions.



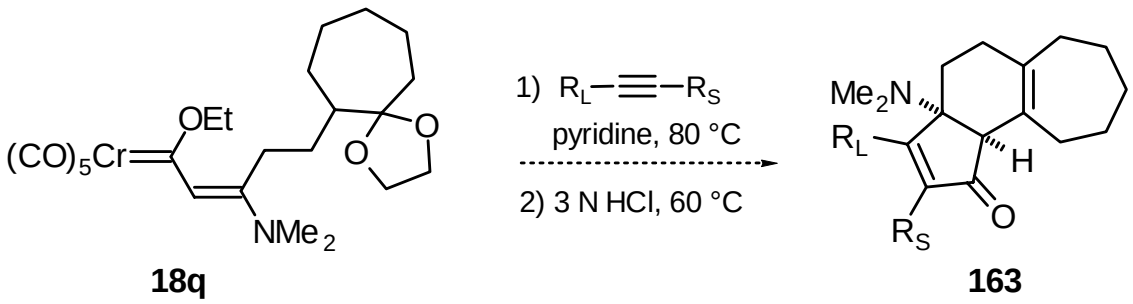
Scheme 53.

The intramolecular aldol condensation of cyclopentenone **129o** under basic conditions gave completely different products **160**, **161** and **162** (Scheme 54). All of them do not contain dimethylamino functionality. Tricyclic molecule **160** is probably yielded from cyclization adduct **157** via a base-mediated removal of dimethylamino group and olefin isomerization. In order to determine the mode of formation of **161** and **162**, the isolated sample of **160** in [D_4]-methanol was heated at 60 °C for 6 d, and it remained unchanged. However, as **160** stirring with sodium methylate in methanol at 40 °C for 18 h, the other adducts **161** and **162** were also observed besides the starting material.

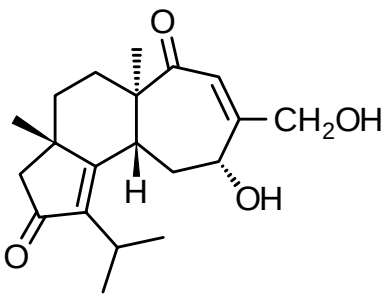


Scheme 54. Intramolecular aldol reaction of cyclopentenone **129o** under basic conditions.

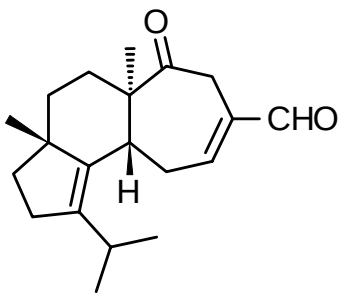
As shown above, it was possible to obtain tricyclic molecules of types **154** and **155** via an acid-mediated intermolecular aldol condensation. Therefore, cyclization products **163** with fused with five-six-seven-membered rings should be reasonable to achieve (Scheme 55). Cyathanes, a subgroup of diterpenoides, contain this angular five-six-seven-ring skeleton.[95a] 11,15-Dihydroxy-3,12-cyathadiene-2,14-dione (**164**) and 11-hydroxy-14-oxo-1,3,12-cyathatrien-15-al (**15**) are two examples of this kind of natural products. The former compound **164** severs as an efficient antibiotic.[100]



Scheme 55. A proposed synthesis of cyathanes-like molecules **163**.



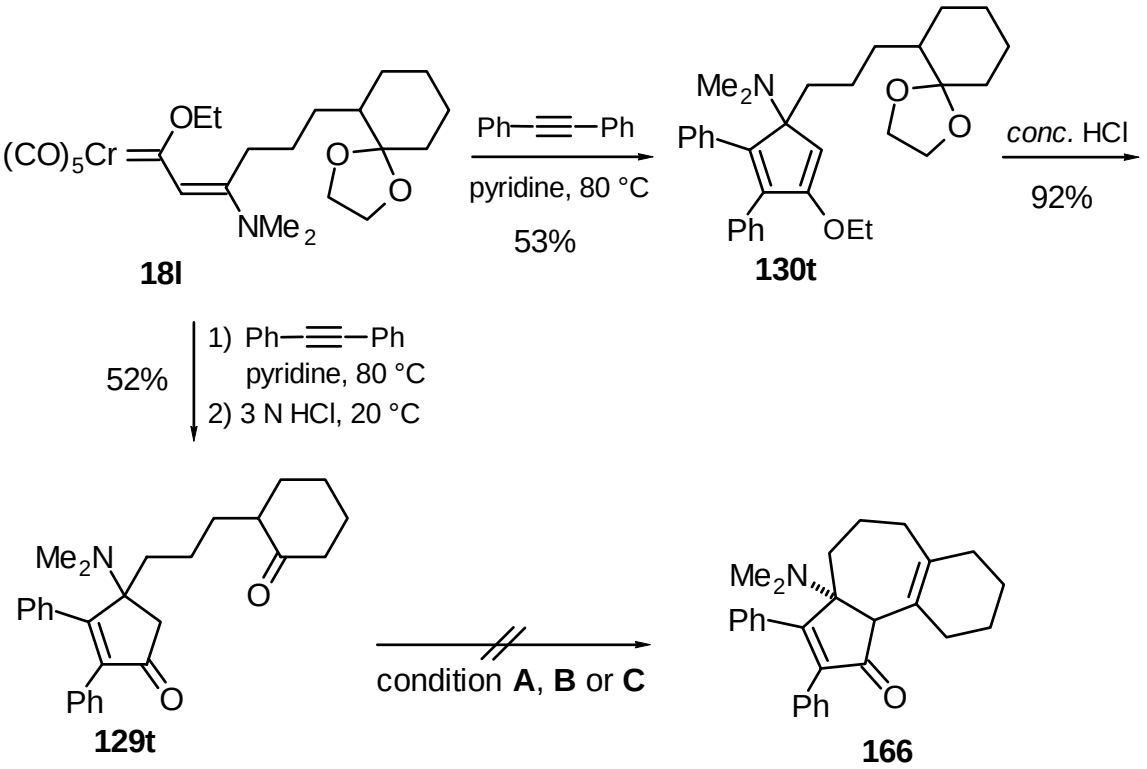
164



165

5.3.3. Synthesis of Tricyclic Molecules of the Type **131**

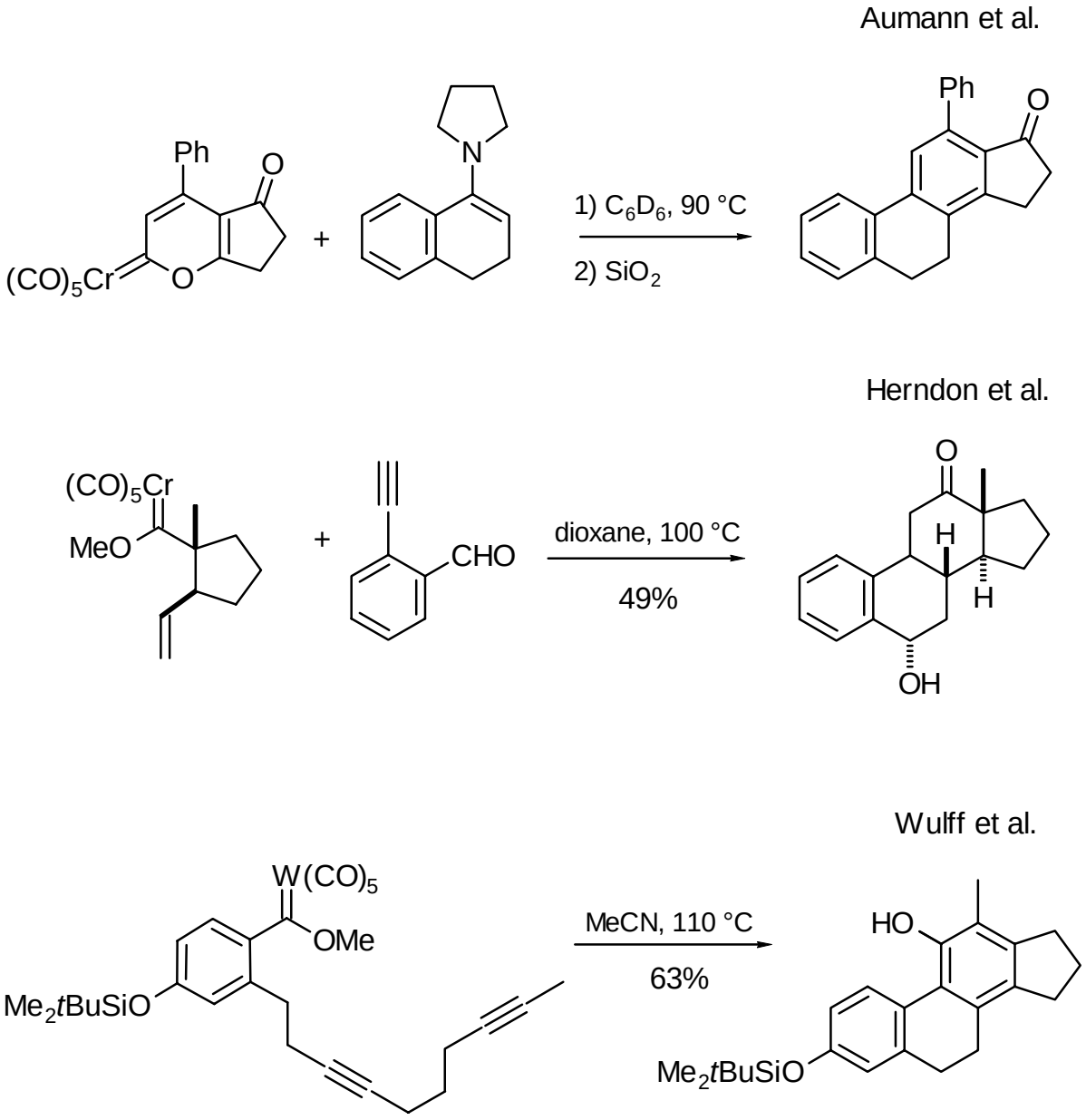
Although it is well-known that construction of a seven-member ring via an Aldol reaction is difficult, some examples were published.[101] Diketone **129t** could be prepared either via hydrolysis of cyclopentadiene **130t** or directly from the reaction of complex **18l** with diphenylethyne. Unfortunately, the seven-membered ring could not be closure either under acidic or basic conditions, and only decomposed products were obtained. Cyclization reaction with presence of catalytic amount of *p*-toluenesulfonic acid in benzene using a Dean-Stark apparatus also did not afford molecules **166**, but only starting material **129t** was recovered.



Scheme 56. **A**: Dean-Stark apparatus, catalytic amount of *p*-toluenesulfonic acid, C_6H_6. 100 °C. **B:** *conc.* HCl, dioxane, 60 °C. **C**: Sodium methylate, methanol, 40 °C.

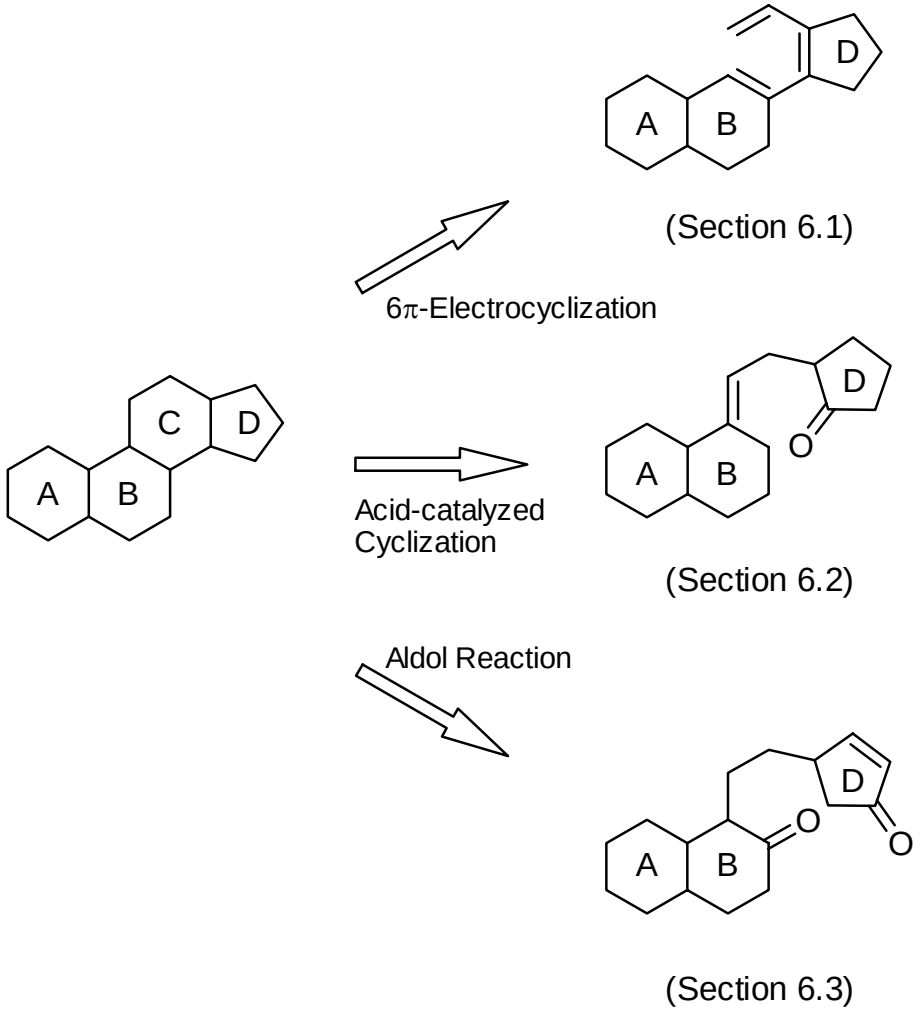
6. Synthesis of Steroid-like Molecules

The importance of steroids would not be described here again. Till now, three examples of preparation of steroid-like compounds via Fischer carbene complexes have been reported by Aumann,[102] Herndon[103] and Wulff[76a] et al. (Scheme 57). Despite these methodologies can not be widely used for organic synthesis. Therefore, these disadvantages promote me to develop a general access to this kind of important molecules.



Scheme 57. Synthesis of steroid-like molecules in accordance with the methodologies of Aumann, Herndon and Wulff.

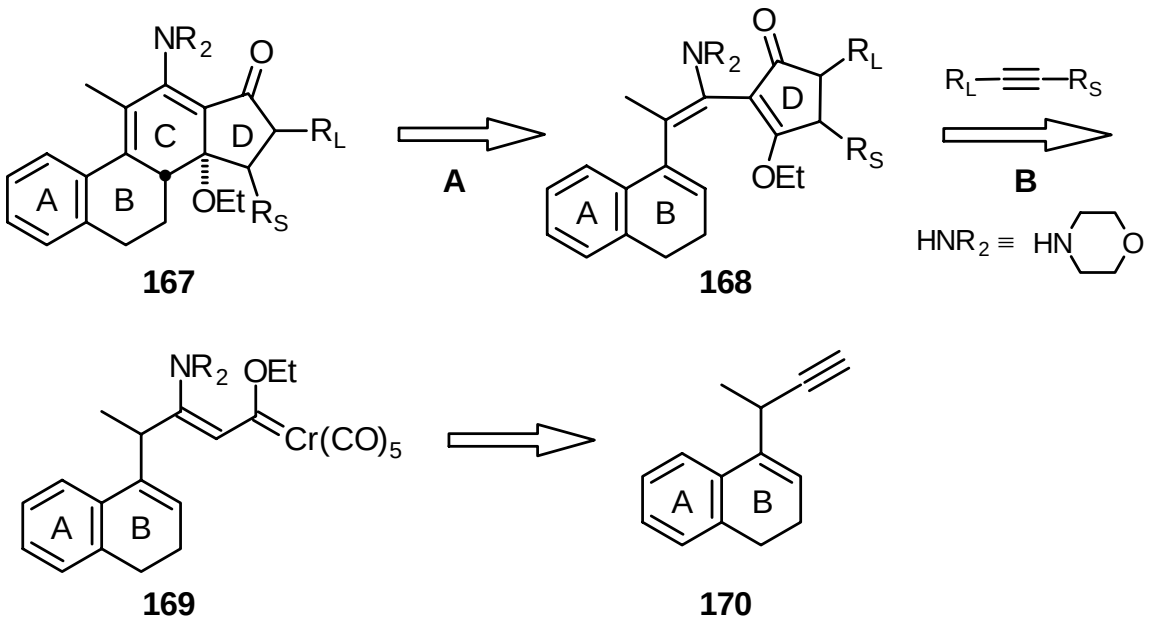
Synthesis of steroid-like molecules can be analyzed as shown in Scheme 58. The C ring of the steroid-like products could be closured via 6π-electrocyclization, acid-catalyzed cyclization or Aldol condensation.



Scheme 58. Retrosynthetic analysis of steroid-like molecules.

6.1. Ring Closure via 6π-Electrocyclization

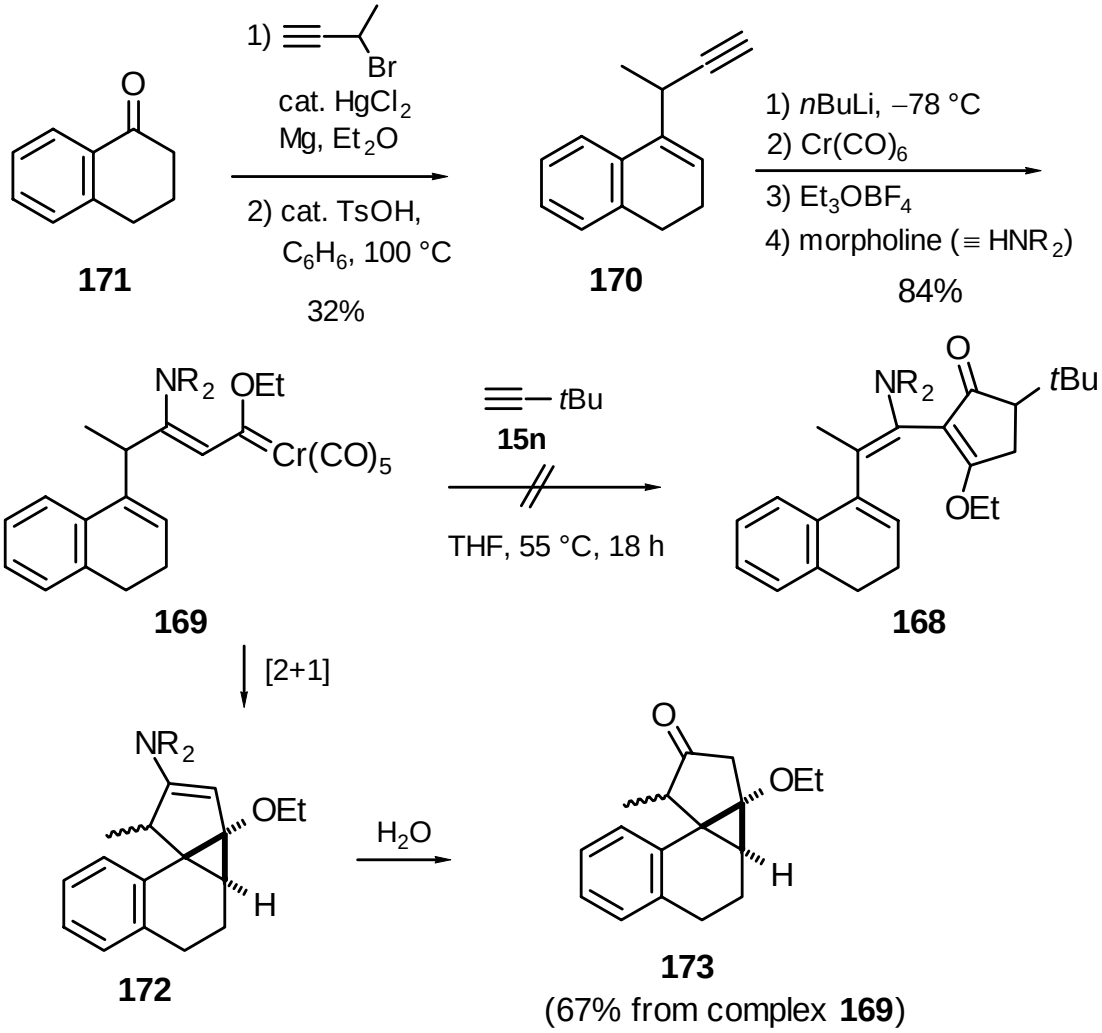
As shown in Scheme 53 (p. 50), the cyclohexadienyl skeleton in **98** could be formed via a 6π-electrocyclization from the conjugated 1,3,5-hexatriene moiety in cyclopentadiene **99**. Therefore, the C ring in the steroid-like molecules **167** should be closed via this method. The five-membered **D** ring in **167** could be generated by a formal [2+2+1] cycloaddition of complex **169** and alkynes (Scheme 59). This procedure to cyclopentenone moiety via the reaction of morpholino-substituted α,β-unsaturated Fischer carbene complexes with a molecule of alkynes have been developed by Flynn et al.[33]



Scheme 59. Retrosynthetic analysis of steroid-like molecules **167**. **A**: 6π-Electrocyclization. **B**: Formal [2+2+1] cyclization.

Alkyne **170** was prepared from the reaction of α-tetralone (**171**) with 1-methylallenyl-magnesium bromide, and then, by dehydration at 100 °C with catalytic amount of *p*-toluenesulfonic acid. These two steps gave **170** in 32% yield.

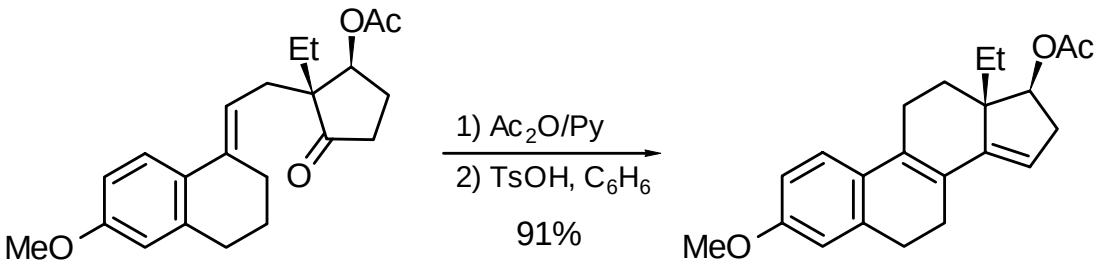
One-pot operation as mentioned in chapter 2 was applied for the access to complex **169** in good yield. However, it was not stable enough for characterization. Thus, further reaction of **169** with alkyne **15h**[1] was directly followed. Unfortunately, instead of the designed [2+2+1] cycloaddition, an intramolecular [2+1] cyclization happened, and a tertacyclic product **172** was isolated in 67% yield. Formally, cocyclization to **168** was blocked by the bulky substituent of 3,3-dimethyl-1-butyne (**15n**), but in the perilous study of formation of cyclopentenone via morpholino-substituted α,β-unsaturated Fischer carbene complexes did not show that steric hindrance of the applied alkynes would affect the reaction mode.[33,37]



Scheme 60. Synthesis of tetracyclic molecule **173**.

6.2. Ring Closure via Acid-Catalyzed Cyclization

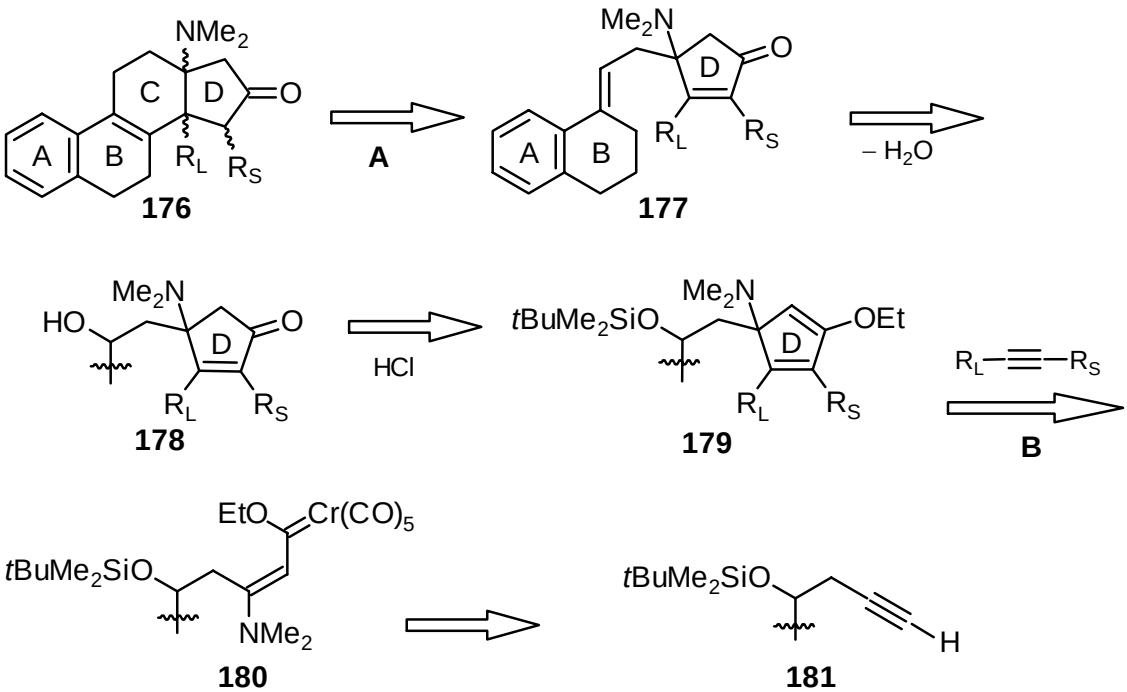
Smith reported a efficient methodology for the closure of C ring from enone **174** by an acid-catalyzed cyclization in excellent yield (Scheme 61).[104] This reaction did neither destroy the stereochemistry nor generate any new stereogenic centers. Under an acidic condition, the alkenyl moiety in the starting material **175** would migrate from the *exo* to the more stable *endo* position, where it reacts with the ketone functionality to undergo the ring closure process. The generated tertiary alcohol is easily removed by a sequential dehydrolysis to form a new olefin.



174 **175**

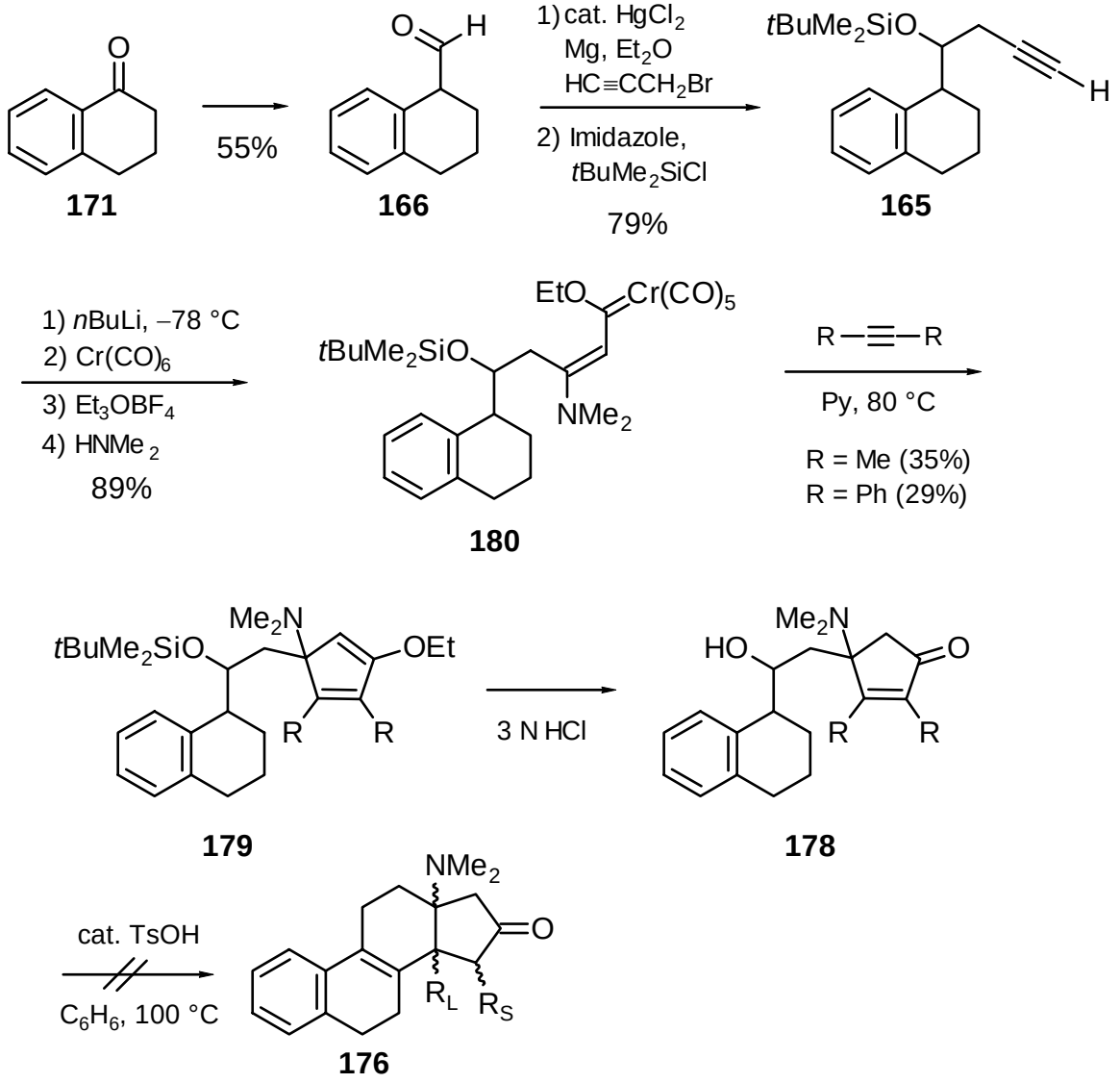
Scheme 61. Ring closure via acid-catalyzed cyclization.

Retrosynthetic analysis of steroid-like molecules **176** can be rationalized in terms of following the sequence: Access to **176** from **177** could be carried out via the C-ring closure by this acid-catalyzed methodology. Instead of a 2-oxo-cyclopentanyl-, a 3-oxo-1-cyclopentenyl substituent is used in this reaction, the electron density at the R_L-attached position of the latter compound should be similar to that of ketone in the former. In order to block the intramolecular cyclization of complex **180**, the olefinic moiety in **177** should be generated from a protected alcohol functionality, e. g. alkylsilyl ether. Under acid condition, not only the portative group can be removed, but also the enolether in **179** can be converted to ketone.



Scheme 62. Retrosynthetic analysis of steroid-like molecules **176**. **A**: Acid-catalyzed cyclization. **B**: Formal [2+2+1] cyclization.

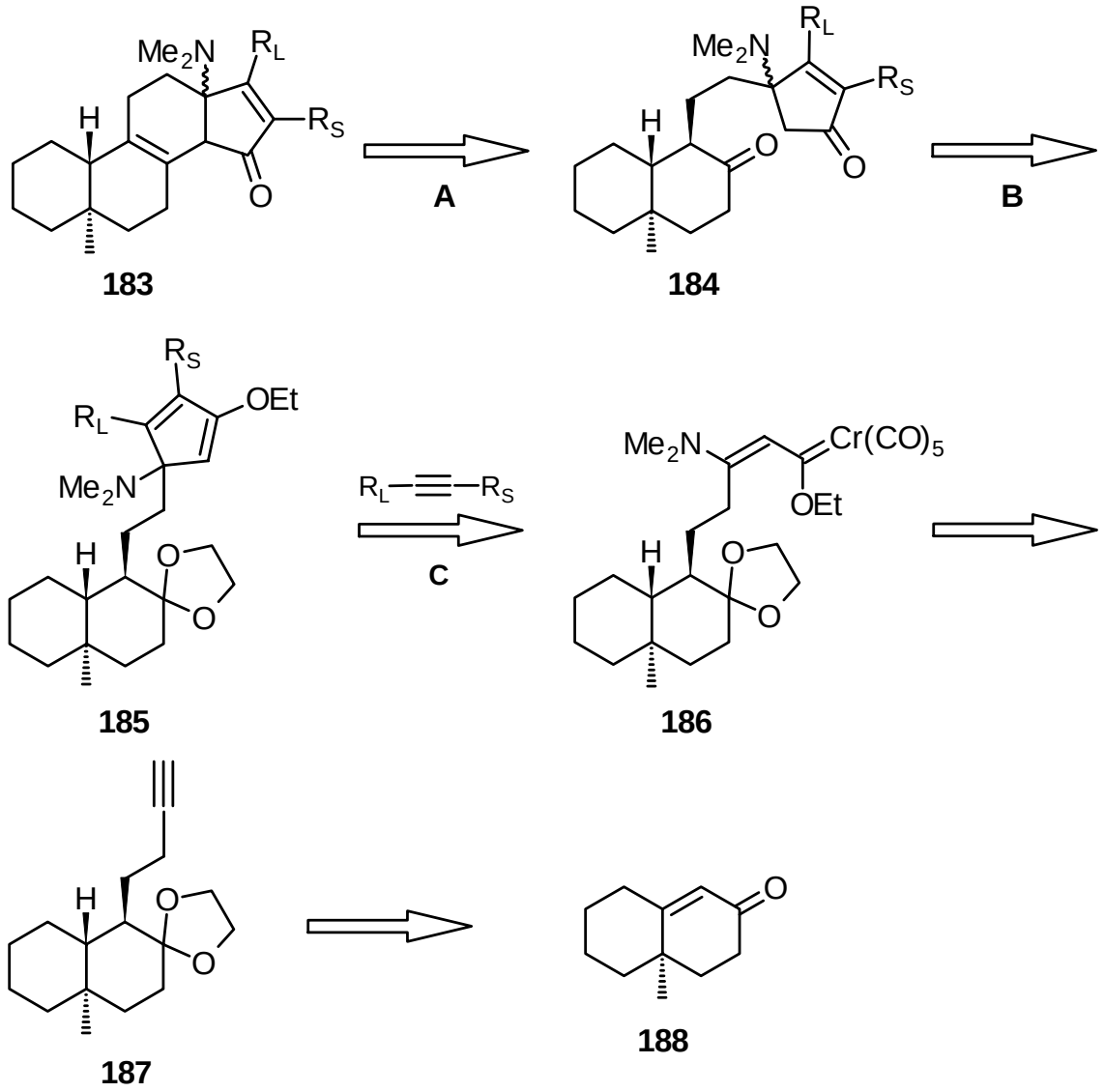
Due to the high-acid property of α-tetralone and uncomfortable purification process after the reaction of it with 4-trimethylsilyl-3-butynyl-1-magnesium bromide, alkyne **181** was prepared in 79% yield first from high active 1,2,3,4-tetrahydronaphthalene-1-carbaldehyde (**182**) by a nucleophilic addition of the allenylmagnesium bromide, and a following protective process by *tert*-butyldimethysilyl chloride and imidazole. Further transformation to complex **180** in an excellent yield (89%). Formation of cyclopentadienes of the type **179** gave unsatisfactory results. Desilylation and hydrolysis afforded adducts **178**, which were directly applied for dehydrolysis and cyclization by utilization of a Dean-Stark apparatus and catalytic amount of *p*-toluenesulfonic acid. Unfortunately, the alcohol functionality could not be removed, and thus, none of cyclization products **176** was obtained.



Scheme 63.

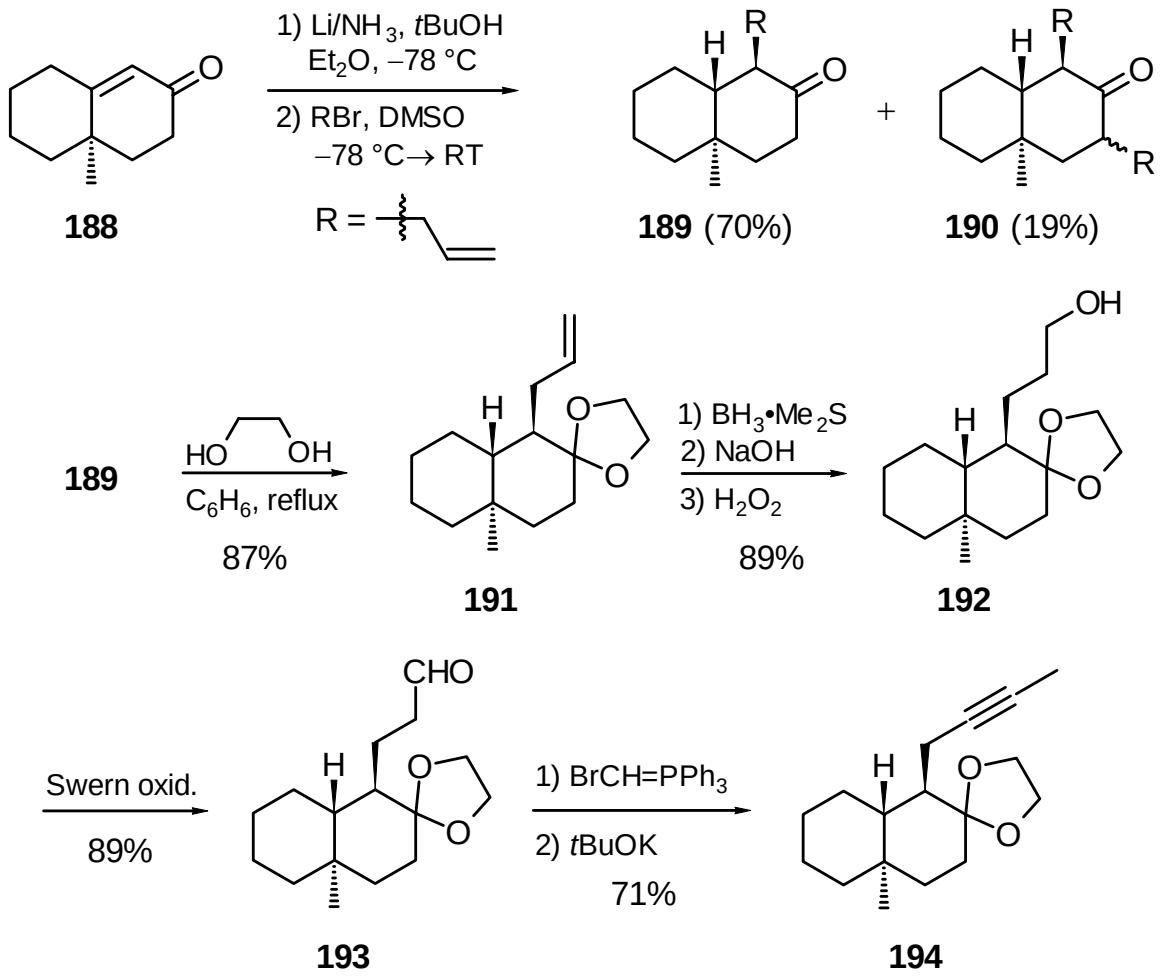
6.3. Ring Closure via Aldol Reaction

As shown in Scheme 52 (p. 73), the intramolecular aldol condensation has been successfully applied to prepare cyclization products **154** and **155**, which contain B-C-D-ring structures of steroids. Therefore, in order to synthesize steroid-like molecules of the type **183**, it is necessary to fuse a six-membered A ring to **154** (Scheme 64). However, a more convenient procedure is available directly from a bicyclic complex **186**. If it is lucky enough, access to **183** could be achieved under one-pot operation from the reaction complex **186** with alkynes. In order to reduce the number of the diastereomers of the desired molecules **183**, the original starting material **188** should be used in enantiomeric pure form.



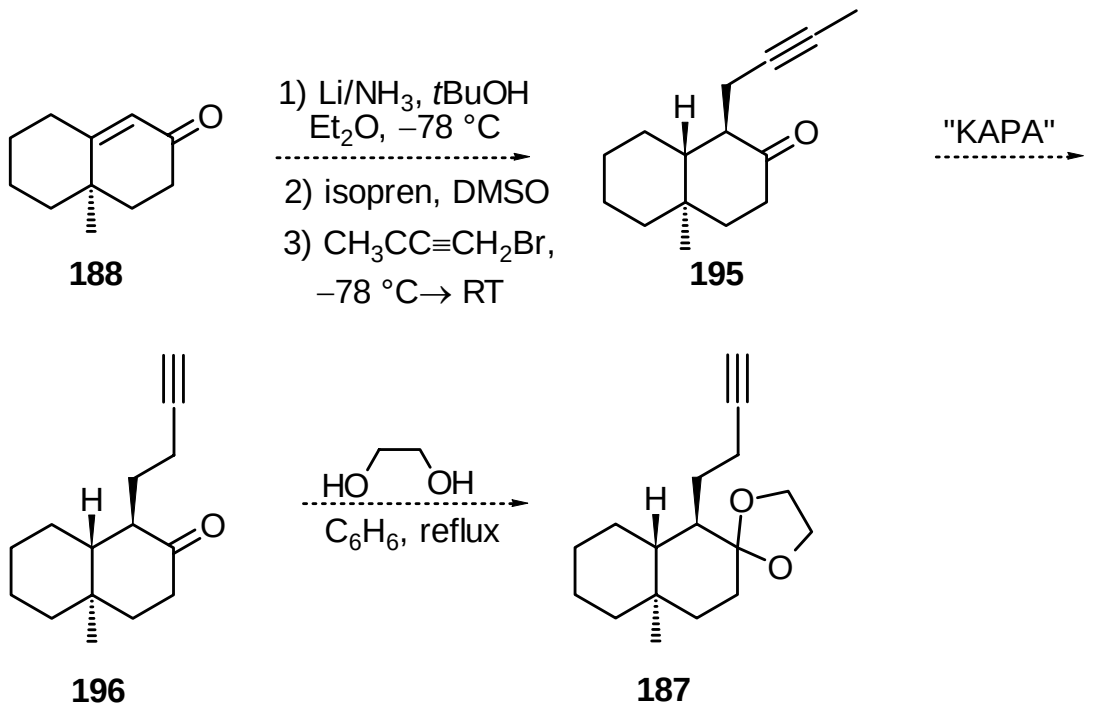
Scheme 64. Retrosynthetic analysis of steroid-like molecules **183**. **A**: Intramolecular Aldol condensation. **B**: Hydrolysis. **C**: Formal [2+2+1] cyclization.

It is not surprising that preparation of alkyne **187** from enone **188** was not successful by the reaction of Birch-reduction-generated lithium enolate with 1-bromo-3-butyne, which is regarded as an inactive alkylation agent.[105] Therefore, instead of it, much active allylic bromide was used for this reaction, and mono- and bis-alkylation products were isolated in 70% and 19% yields, respectively (Scheme 65). Both of them can be easily separated by chromatographic purification. After acetalization, the alkene **191** was easily transformed to alcohol **192** by a hydroboration and a sequential oxidation. The Swern oxidation was applied for the access to aldehyde **173** also in good yield. Unfortunately, further Wittig reaction and elimination would not give the desired product **187**, but, eventually, a pure internal alkyne **194**, which was probably converted by a alkyne isomerization from **187**. In contrast to Scheme 14 (p. 17), it can be concluded that in the presence of an acetal functionality, formation of a internal alkyne should be easier than that of a terminal one.



Scheme 65.

Thus, synthesis of alkyne **187** could be modified as a new four-step procedure (Scheme 66). Before addition of 1-bomo-2-butyne to birch-reduction-generated lithium enolate from ketone **188**, the excess amount of lithium should be quenched by addition of isoprene. Internal alkyne **195** without an acetal functionality could be easily transformed to the terminal one **196** by KAPA reagent. This step needs at least two equivalent of KAPA reagent due to the presence of ketone functionality, but the established 1-butynyl moiety can avoid formation of 1,3-dioxlane in the next step (*cf.* p.19). Further acetalization of ketone **196** is reasonable to afford the desired molecule **187**.



Scheme 66. Proposed synthesis of alkyne **187**.

Although, there are no successful examples available in this chapter to access steroid-like molecules, the 6π-electrocyclization (Scheme 40, p. 56) and the intramolecular aldol condensation (Scheme 64, p. 84) offer opportunities with highly potential to achieve this target. Applications of them toward these projects are still in process.

C. Experimental Section

General: – Melting points were determined with a Büchi melting point apparatus and are uncorrected. – IR spectroscopy: Bruker IFS 66 (FT-IR). – ^{1}H-NMR spectroscopy: Bruker AM 250 (250 MHz), Bruker AMX 300 (300 MHz), Varian VXR 500 (500 MHz). Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively. Benzene (δ = 7.15 for C_6D_6), chloroform (δ = 7.26 for $CDCl_3$) and pyridine (δ = 8.71 for [D_5]-pyridine) are used as internal standards. The signal multiplicity is abbreviated as following: s = singlets, d = doublets, t = triplets, q = quartets, qui = quintets, sxt = sextets, sep = septets, m = multiplets, dd = doublet of doublets, br = broad. First- and higher-order coupling in spectra are treated as AB and ABM for an AB and ABM spin systems, respectively. Abbreviations for identifications of Signals: *c*Pr-H = cyclopropyl, *i*Pr-H = isopropyl, *t*Bu-H = *tert*-butyl and Ph-H = phenyl protons. – ^{13}C-NMR spectroscopy: Bruker AM 250 (62.9 MHz), Bruker AMX 300 (75.5 MHz). Chemical shifts (δ) are expressed in ppm. Benzene (δ = 128.0 for C_6D_6) and chloroform (δ = 77.0 for $CDCl_3$) are used as internal standards. The signal multiplicity is determined by DEPT (DEPT = distortionless enhancement by polarization transfer) or APT (APT = attached proton test) spectra. DEPT: + = primary or tertiary (positive DEPT signal), – = secondary (negative DEPT signal), C_{quat} = quaternary carbon atom (no DEPT signal); APT: + = primary or tertiary (positive APT signal), – = secondary or quaternary (negative APT signal). Abbreviations for identifications of signals: *c*Pr-C = cyclopropyl, *i*Pr-C = isopropyl and C-Ph = phenyl Carbons. – Low-resolution EI MS: Varian MAT CH 7, MAT 731, ionizing voltage 70 eV. – High-resolution EI MS (HR EIMS): Varian MAT 311 A. – Elemental analysis: Mikroanalytisches Laboratorium der Georg-August-Universität Göttingen. – Chromatography: Merck silica gel 60 (230–400 mesh) or ICN neutral alumina (Super I, activity grade II). Solvents for chromatography are technical grade and freshly distilled before use. Diethylether (Et_2O) and tetrahydrofuran (THF) are distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) and pyridine are distilled from calcium hydride. – Thin-layer chromatography (TLC): Macherey-Nagel foils: Alugram SIL G/UV_{254} (0.25 mm silica gel with fluorescent indicator); Polygram Alox G/UV_{254} (0.20 mm aluminum oxide with fluorescent indicator). Developer: molybdenum phosphoric acid (10% in ethanol) and iodine vapor. – X-ray crystal structure determination: the data were collected by a Stoe-Siemens-AED or a Stoe-Siemens-Huber-Vierkreis diffractometers with a Siemens-CCD-Flächen detector. The structure is

solved by direct methods (SHELXL-97) and refined on F^2 by full-matrix least-squares techniques (SHELXL-90/97).[106] All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included in calculated positions and refined by using a riding model.

Triethyloxonium tetrafluoroborate,[107] phenylethyne (**15a**), 1-phenyl-4-trimethylsilyl-1,3-butadiyne (**15a^{16}j**),[108] 1-ethynyl-1-cyclopentene (**15i**),[109] 1-ethynyl-1-cyclohexene (**15i^{1}**),[109] 1-ethinyl-1-cycloheptene (**15i^{2}**),[109] trimethylsilylethyne (**15j**),[109] 2-methyl-buten-2-yne (**15l**)[109], 3,3-dimethylbutyne (**15n**),[109] pentacarbonyl[(2*E*)-3-cycloprop-yl-3-dimethylamino-1-ethoxy-2-propen-1-ylidene]chromium (**18a**),[69] pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-2-buten-1-yli-dene]chromium (**18b**),[69] pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-4-methyl-2-penten-1-ylidene]chromium (**18c**),[69] pentacarbonyl-[(2*Z*)-3-dimethylamino-4,4-dimethyl-1-ethoxy-2-penten-1-ylidene]chromium (**18d**),[69] pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-4-methyl-4-(trimethylsilyloxy)-2-penten-1-yliden]chromium (**18e**),[69] pentacarbonyl[(2*E*)-4-(*tert*-butyldimethylsilyloxy)-3-dimethyl-amino-1-ethoxy-penten-1-ylidene]chromium (**18f**),[70] pentacarbonyl[(2*E*)-3-cyclohexenyl-3-dimethyl-amino-1-ethoxy-2-prop-en-1-ylidene]-chromium (**18g**),[37] 4,4-bromobibenzyl (**27a^{9}**),[111a] 2-bromo-9,9-di-*n*-hexyl-7-iodofluorene (**27f**),[111b] 1-bromo-1-cyclopentene (**27i**),[112] 1-iodo-1-cyclohexene (**27i^{1}**),[112] 1-bromo-1-cyclooctene (**27i^{3}**),[112] (*E*)-1,2-di(phenylethynyl)ethene (**28daa**),[112] (*E*)-1,2-di(cyclopropylethynyl)ethene (**28dgg**),[112] 2-ethynylbenzotrifluoride (**29a^{1}**),[112] 3-ethynylbenzotrifluoride (**29a^{2}**),[112] 4-ethynyl-benzotrifluoride (**29a^{3}**),[112] 1,4-diethynyl-benzene (**29a^{7}**),[113] 1,3,5-triethynylbenzene (**29a^{10}**),[113] 1-ethynylnaphthaline (**29b**),[112] 2-ethynylthiophen (**29c**),[112] 9,9-di-*n*-hexyl-2-ethynylfluorene (**29e**),[66] 2,7-diethynyl-9,9-dihexylfluorene (**29f**),[66] 1-pyrrolidino-1-cyclo-hexene (**39c**),[114] 2-(2'-propynyl)-cyclohexanone (**41b**)[43], 2,2,5-trimethylcyclopentanone (**45**),[115] 1-bromo-3-trimethylsilyl-2-propyne (**51a**),[118] 1-bromo-4-trimethylsilyl-3-butyne (**51b**),[109] 1,4-diphenyl-1,3-butadiyne (**54f**),[112] 1,8-dipheny-1,3,5,7-octatertayne (**54g**),[118] 1,2,3,4-tetrahydronaphthalene-1-carbaldehyde (**182**),[119] (*R*)-(–)-10-methyl-1(9)-octa-2-one (**188**),[120] potassium 3-(2',2'-ethylene-dioxycyclohexan-1-yl)propionate,[120] allenyl-magnesium bromide[121], 1-methyl-allenylmagnesium bromide[121] and 2-bromo-3-butyn[109] were prepared according to published procedures. Cyclopropylethyne (**15g**) was a generous gift from Merck AG.

1. Synthesis of Alkynes

1.1. Preparation of Alkynes via the Sonogashira Reaction

General Procedure for the Preparation of Internal Alkynes **28** *by the Sonogashira Reaction:*
1) Alkynes with a Higher Boiling Point (GP1A): To a solution of a respective terminal alkyne (100 mmol) and alkenyl or aryl halide **27** (100 mmol) in an amine (50 mL) in a Schlenk flask is added 200 mg of palladium(II)chloride·bis(triphenylphosphane) [$PdCl_2(PPh_3)_2$], 500 mg of copper(I) iodide (CuI), and 150 mg of triphenylphosphane (PPh_3) at ambient temperature. The mixture is heated at 40–85 °C under argon for 4–18 h. After cooling to room temperature, the suspension is filtered off on a 3 cm thick layer of Celite and rinsed well with Et_2O (150 mL). The solvent of the filtrate is removed under reduced pressure and the residue is subjected to chromatography on silica gel (150 g). Elution with pentane/Et_2O affords the coupling product **28**.
2) Alkynes with a Lower Boiling Point (GP1B): Like GP1A, but the reaction is carried out in a screwed Pyrex bottle. Before heating the reaction mixture, a dry argon is bubbled through the solution for 5 min, and 1.1 eq. of the respective alkyne **15a** is added immediately.

General Procedure for Transformation of Internal Alkynes **28** *to Terminal Acetylenes* **29** *(GP2):* To a solution of a 2-hydroxypropyl substituted coupling product **28** (80 mmol) in dioxane or 2-propanol (100 mL) is treated with 5 g of powdered potassium hydroxide (KOH) and the mixture is heated under argon at 80 °C for 8 h. After cooling to room temperature, the suspension is filtered off on a 3 cm thick layer of Celite and rinsed well with Et_2O (100 mL). The solvent of the filtrate is removed under reduced pressure and the residue is subjected to chromatography on silica gel (100 g). Elution with pentane/Et_2O affords the terminal alkyne **29**.

1,4-Bis(cyclopropylethynyl)benzene (**28a^{7}gg**): In accordance with GP1A, to a solution of 11.8 g (50.0 mmol) of 1,4-dibromobeznene (**27a^7**) in 50 mL of triethylamine was added 7.27 g (110.0 mmol) of cyclopropylethyne (**15g**), $PdCl_2(PPh_3)_2$ (220 mg), PPh_3 (200 mg) and, CuI (500 mg), and the mixture was stirred at 85 °C for 12 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (200 g). Elution with pentane gave 8.04 g (78%) of **28a^{7}gg** [R_f = 0.84 (pentane)] as a colorless solid, m. p. 104–105 °C. – IR (KBr): ν = 3010 cm^{-1} (C–

H), 2227 (C≡C), 1505, 1444, 1051, 952, 844. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.77–0.90 (m, 8 H, *c*Pr-H), 1.40–1.50 (m, 2 H, *c*Pr-H), 7.27 (s, 4 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.21 (+, *c*Pr-C), 8.7 (–, *c*Pr-C), 75.6, 95.0 (C_{quat}, C-1,2), 122.9 (C_{quat}, C-Ar), 131.3 (+, C-Ar). – MS (70 eV), *m/z* (%): 206 (100) [M^+], 189 (22), 165 (12), 141 (10). – Elemental analysis calcd (%) for $C_{16}H_{14}$ (206.3): C 93.16, H 6.84; found: C 93.26, H 7.06.

1'-Cyclopentenyl-3-methylbut-3-en-1-yne (**28il**) and 4-Methyl-(2'-propenyl)benzene (**38**): According to GP1B, to a solution of 5.84 g (40.0 mmol) of 1-bromo-1-cyclopentene (**27q**) in 40 mL of diisopropylamine was added $PdCl_2(PPh_3)_2$ (100 mg), PPh_3 (100 mg), CuI (75 mg), LiCl (100 mg), and finally 5.00 mL (53.6 mmol) of 2-methylbut-1-en-3-yne (**15l**), and the mixture was heated at 60 °C for 16 h. The suspension was diluted with pentane (100 mL) and washed with water (50 mL). The aqueous phase was extracted pentane (50 mL). The combined organic phase was washed with water (30 mL) and hydrochloric acid (1 N, 3 × 30 mL). The solution was dried over $MgSO_4$. After filtration, the solvent was removed under normal pressure, and the residue was distilled under reduced pressure to afford 3.76 g of a colorless oil [b. p. 75 °C (20 Torr)], which contained **28il** (90%) and **35** (10%). The amount of **28il** equalized to 3.38 g (81%). **28il**: – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.40–1.70 (m, 5 H, CH_3, 4'-H), 1.90 (m, 4 H, 3',5'-H), 5.20–5.23 and 5.27–5.29 (m, 2 H, 4-H), 6.02 (m, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.3 (–, C-4'), 23.5. (+, CH_3), 33.3, 36.3 (–, C-3',4'), 85.7, 91.6 (C_{quat}, C-1,2), 121.2 (–, C-4), 124.4, 126.9 (C_{quat}, C-3,1'), 137.8 (+, C-2'). The NMR spectra of **38** agreed with those which have previously been reported.[122] – MS (70 eV), *m/z* (%): 132 (100) [M^+], 117 (78) [$M^+ – CH_3$], 115 (58), 91 (64), 77 (14), 65 (16), 51 (10).

Di(1'-cyclopentyl)ethyne (**28ii**): Following GP1A, to a solution of 5.84 g (40.0 mmol) of 1-bromo-1-cyclopentene (**27i**) in 40 mL of diisopropylamine was added 4.05 g (44.0 mmol) of 1-cyclopentyl-1-ethyne (**15i**), $PdCl_2(PPh_3)_2$ (100 mg), PPh_3 (100 mg), CuI (75 mg), and LiCl (100 mg), and the mixture was heated at 40 °C for 2 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 4.48 g (71%) of **28ii** [R_f = 0.63 (pentane)] as a colorless solid which became to a brown oil after exposure to air at ambient temperature for a short

time. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 ["qui", ^3J = 7.6, ^3J = 7.6 Hz, 4 H, 4'-H], 2.35–2.52 (m, 8 H, C-3',5'), 6.01–6.05 (m, 2 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.3, 33.3, 36.4 (–, cyclopentyl CH_2), 87.7 (C_{quat}, C-1,2), 124.6 (C_{quat}, C-1'), 137.4 (+, C-2'). – MS (70 eV), *m/z* (%): 158 (100) [M^+], 129 (35), 115 (21), 91 (16).

1'-Cyclohexenyl-3-methylbut-3-en-1-yne (**28i^{1}l**): In accordance with GP1B, to a solution of 8.32 g (40.0 mmol) of 1-iodo-1-cyclohexene (**27i^1**) in 40 mL of diisopropylamine was added PPh_3 (100 mg), CuI (75 mg), LiCl (100 mg), and $PdCl_2(PPh_3)_2$ (100 mg), and finally 5.0 mL (53.6 mmol) of 2-methylbut-1-en-3-yne (**15l**), and the mixture was heated at 40 °C for 2 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 4.91 g (84%) of **15l** [R_f = 0.61 (pentane)] as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.45–1.70 (br. m, 4 H, 4',5',6'-H), 1.90 ["t", ^4J = 1.3, ^4J = 1.3 Hz, 3 H, CH_3], 2.06–2.17 (br. m, 4 H, 3',6'-H), 5.12–5.18 and 5.23–5.60 (m, 2 H, 4-H), 6.08–6.11 (m, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 21.5, 22.3 (–, C-4',5'), 23.0. (+, CH_3), 25.7, 29.2, (–, C-3',6'), 87.9, 90.2 (C_{quat}, C-1,2), 120.8 (–, C-4), 120.6, 127.0 (C_{quat}, C-3,1'), 134.8 (+, C-2').

Di(1'-cyclohexyl)ethyne (**28i^{1}i^1**): Following GP1A, to a solution of 5.82 g (28.0 mmol) of 1-iodo-1-cyclohexene (**27i^1**) in 30 mL of diisopropylamine was added 3.19 g (30.0 mmol) of 1-cyclohexyl-1-ethyne (**15i^1**), $PdCl_2(PPh_3)_2$ (70.0 mg), PPh_3 (70 mg), CuI (50 mg), and LiCl (60 mg), and the mixture was heated at 40 °C for 5 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (70 g). Elution with pentane gave 4.80 g (92%) of **28i^{1}i^1** [R_f = 0.75 (pentane)] as a colorless oil. The ^{1}H- and ^{13}C-NMR spectra agreed with those which have previously been reported.[123]

1'-Cyclootenyl-3-methylbut-3-en-1-yne (**28i^{3}l**): Following GP1B, to a solution of 11.3 g (60.0 mmol) of 1-bromo-1-cyclooctene (**27i^3**) in 40 mL of diisopropylamine was added PPh_3 (100 mg), CuI (75 mg), LiCl (100 mg), $PdCl_2(PPh_3)_2$ (120 mg), and 7.50 mL (80.4 mmol) of 2-methylbut-1-en-3-yne (**15l**), and the mixture was heated at 70 °C for 3.5 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 6.89 g (66%) of **28i^{3}l**

[R_f = 0.69 (pentane)] as a colorless oil. – IR (film): ν = 3095 cm^{-1} (C–H), 3021, 2930, 2849, 2192 (C≡C), 1606, 1467, 1448, 1373, 1331, 889, 846. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.40–1.70 (br. m, 8 H, 4',5',6',7'-H), 1.90 (dd, ^4J = 1.1, ^4J = 1.0 Hz, 3 H, CH_3), 2.13–2.20 (m, 2 H, 3'-H), 2.30 (t, ^3J = 6.1 Hz, 2 H, 8'-H), 5.15–5.19 and 5.22–5.25 (m, 2 H, 4-H), 6.08 (t, ^3J = 8.4 Hz, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.6. (+, CH_3), 25.7, 26.3, 27.0, 28.4, 29.7, 29.9 (–, cyclooctenyl CH_2), 87.5, 91.0 (C_{quat}, C-1,2), 120.6 (–, C-4), 123.7, 127.1 (C_{quat}, C-3,1'), 137.6 (+, C-2'). – MS (70 eV), *m/z* (%): 174 (72) [M^+], 159 (19) [$M^+ – CH_3$], 146 (52), 131 (67), 117 (42), 105 (38), 91 (100), 79 (29), 77 (42), 67 (24), 65 (22), 53 (24), 41 (44).

2-Ethynyl-9,9-dihexyl-7-(phenylethynyl)fluorene (**29fa**): In accordance to GP1A, to a solution of 9.82 g (19.8 mmol) of 2-bromo-9,9-dihexyl-7-(3'-methylbut-1'-yn-3'-ol)fluorene (**28fk**) in 50 mL of triethylamine was added 2.55 g (25.0 mmol) of phenylethyne (**15a**), $PdCl_2(PPh_3)_2$ (100 mg), PPh_3 (100 mg) and, CuI (150 mg) and, the mixture was heated at 85 °C for 6 h. After filtration and evaporation of the solvent under reduced pressure, the residue was diluted with dioxane (100 mL), treated with KOH (2.50 g), and stirred at 80 °C for 4 h following GP2. Chromatography on silica gel (100 g) eluting with pentane/Et_2O (from 1 : 0 to 10 : 1) gave 5.38 (59%) of **29fa** [R_f = 0.40 (pentane)] as a white solid, m. p. 84–85.°C. – IR (KBr): ν = 3309 cm^{-1} (C≡C–H), 2953 (C–H), 2927, 2856, 2108 (C≡C), 1492, 1463, 896, 816, 754, 687. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.60–0.80 (br. m, 4 H), 0.85 (t, ^3J = 6.7 Hz, 6 H, CH_3), 1.05–1.20 (m, 12 H), and 2.00–2.10 (m, 4 H) [total 26 H, hexyl-H], 3.23 (s, 1 H, C≡CH), 7.35–7.45 (m, 3 H, Ar-H), 7.50–7.65 (m, 8 H, Ar-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_3), 22.5, 23.6, 29.6, 31.4, 40.2 (–, CH_2), 55.1 (C_{quat}, C-9), 77.4 (+, C≡*C*H), 84.5, 89.9, 90.4 (C_{quat}, *C*≡CH, *C*≡*C*Ph), 119.8, 120.0, 125.9, 126.4, 128.1, 128.3, 130.7, 131.2, 131.5 (+, C-Ar), 120.7, 122.1, 123.2, 140.3, 141.0, 150.9, 151.0 (C_{quat}, C-Ar). – MS (70 eV), *m/z* (%): 458 (100) [M^+], 358 (11), 303 (12), 289 (22), 204 (11).

1,4-Bis(7'-ethynyl-9',9'-di-n-hexylfluoren-2'-ylethynyl)benzene (**35**): According to GP1A, a mixture of 9.00 g (16.7 mmol) of 2-bromo-9,9-dihexyl-7-iodofluorene (**27f**), triethylamine (150 mL), 1.05 g (8.34 mmol) of 1,4-diethnylbenzene (**29a**[7]), PPh_3 (150 mg), CuI (300 mg), and $PdCl_2(PPh_3)_2$ (250 mg) was stirred at 40 °C for 4 h. 5.10 g (60.6 mmol) of 2-methyl-but-

3-yn-2-ol (**15k**) was added to the suspension, and the mixture was refluxed for an additional 8 h. Purification through a sort column [silica gel (50 g)] eluting with pentane/Et_2O (1 : 1) gave 5.42 g (68%) of the coupling product [R_f = 0.30, pentane/Et_2O (1 : 1)] as a pale-yellow semi-solid. This compound was diluted with dioxane (100 mL), treated with KOH (2.50 g), and stirred at 80 °C for 4 h following GP2. Chromatography on silica gel (100 g) eluting with pentane/Et_2O (from 1 : 0 to 5 : 1) gave 3.82 g (54% from **27f**) of **35** [R_f = 0.22 (pentane)] as a pale-yellow solid, m. p. 72–74 °C. – IR (KBr): ν = 3288 cm^{-1} (C≡C–H), 2928 cm^{-1} (C–H), 2956, 1508, 1464, 820. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.50–0.75 (br. m, 8 H), 0.78 (t, ^3J = 6.7 Hz, 12 H, CH_3), 1.00–1.20 (m, 24 H), and 1.90–2.05 (m, 8 H) [total 52 H, hexyl-H], 3.18 (s, 2 H, C≡CH), 7.49–7.70 (m, 16 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_3), 22.5, 23.7, 29.6, 31.5, 40.3 (–, CH_2), 55.2 (C_{quat}, C-9'), 77.4 (+, C≡*C*H), 84.5, 89.6, 92.4 (C_{quat}, *C*≡CH, Ar*C*≡*C*Ar), 119.9, 120.1, 125.9, 126.5, 130.8, 131.3, 131.5 (+, C-Ar), 120.7, 121.8, 123.1, 140.7, 141.0, 151.0, 151.1 (C_{quat}, C-Ar). – MS (70 eV), *m/z* (%): 838 (100) [M^+], 97 (10), 84 (18), 69 (27), 55 (63), 43 (100), 42 (83). – Elemental analysis calcd (%) for $C_{64}H_{70}$ (838.6): C 91.59, H 8.41; found: C 91.32, H 8.28.

4,4'-Bis(7''-ethynyl-9'',9''-di-n-hexylfluoren-2''-ylethynyl)biphenyl (**36**): Following GP1A, a mixture of 7.00 g (14.1 mmol) of 1.40 g (6.92 mmol) of 4,4'-diethynylbiphenyl (**29a**[3]), PPh_3 (100 mg), CuI (200 mg), $PdCl_2(PPh_3)_2$ (100 mg), benzene (50 mL), triethylamine (100 mL) and 2-bromo-9,9-dihexyl-7-(3'-methylbut-1'-yn-3'-ol)fluorene (**28fk**) was heated at 85 °C for 6 h. After filtration and evaporation of the solvent under reduced pressure, the residue was diluted with 100 mL of dioxane, treated with KOH (2.50 g) and stirred at 80 °C for 4 h according to GP2. Chromatography on silica gel (100 g) eluting with pentane/Et_2O (from 1 : 0 to 10 : 1) gave 4.28 g (68%) of **36** [R_f = 0.25 (pentane)] as a pale-yellow solid, m. p. 179–181 °C. – IR (KBr): ν = 3289 cm^{-1} (C≡C–H), 2952 (C–H), 2927, 2856, 1497, 1464, 823. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.50–0.70 (br. m, 8 H), 0.78 (t, ^3J = 6.9 Hz, 12 H, CH_3), 1.00–1.20 (m, 24 H), and 1.90–2.05 (m, 8 H) [total 52 H, hexyl-H], 3.16 (s, 2 H, C≡CH), 7.45–7.55 (m, 8 H, Ar-H), 7.62–7.70 (m, 12 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_3), 22.6, 23.7, 29.7, 31.5, 40.3 (–, CH_2), 55.2 (C_{quat}, C-9''), 77.2 (+, C≡*C*H), 84.6, 89.6, 91.4 (C_{quat}, *C*≡CH, Ar*C*≡*C*Ar), 119.9, 120.1, 125.9, 126.5, 126.9, 130.8, 131.2, 132.1 (+, C-Ar), 120.7, 122.0, 122.6, 139.9, 140.6, 141.1, 151.0, 151.1 (C_{quat}, C-Ar).

– MS (70 eV), *m/z* (%): 914 (8) [M^+], 309 (37), 178 (15), 151 (20), 84 (22), 69 (30), 55 (67), 43 (100), 42 (95). – Elemental analysis calcd (%) for $C_{70}H_{74}$ (914.6): C 91.93, H 8.16; found: C 91.69, H 8.41.

1.2 Synthesis of Alkynyl Substituted Cycloalkanones and their Acetal Derivatives

General Procedure for Preparation of Alkynyl Substituted Cycloalkanones **52** *(GP3):* To a solution of lithium diisopropylamide (LDA) [250 mmol; from diisopropylamine (36.0 mL, 257 mmol) and *n*-butyllithium (106 mL, 2.36 M in *n*-hexane, 250 mmol)] in 200 mL THF at –78 °C was dropwise added 300 mmol of a respective imine **50** for 15 min. The mixture is allowed to warm to ambient temperature and stirred for an additional 1 h. The respective alkynyl bromide **51** (300 mmol) is added to the above solution at –78 °C over a period of 10 min and stirred at this temperature for 30 min, at ambient temperature for 12 h and finally at 40 °C for 30 min. The reaction is cooled to room temperature, quenched with 250 mL of ice water, and the aqueous phase is extracted with Et_2O (3 × 200 mL). The solvent of the combined organic phase is removed under reduced pressure. To the residue at 0 °C is added a cold solution of 1 N hydrochloric acid (350 mL) over a period of 10 min. The mixture is washed with pentane (3 × 200 mL), in order to recover the alkyl bromide **51**. The pH value of the aqueous phase is modified between 5.5 and 6.0 by addition of a sat. aqueous solution of potassium carbonate at 0 °C and the mixture is refluxed at 70 °C for 1 h. The solution is extracted with Et_2O (3 × 200 mL) and the combined organic phase is dried over $MgSO_4$. After evaporation of the solvent, the reaming liquid is distilled under reduced pressure to afford **15h** as a colorless oil.

General Procedure for Synthesis of Alkynyl Substituted Acetals **42** *(GP4):* A mixture of 150 mmol of the respective alkynyl substituted cycloalkanone **52**, ethylene glycol (10 mL, 179 mmol), catalytic amount of TsOH (ca. 1 g) and benzene (250 mL) is refluxed for 4–12 h using a Dean-Stark apparatus. After cooling to ambient temperature, 100 mL of water is added to the mixture and the aqueous phase extracted with Et_2O (3 × 100 mL). The combined organic extract is dried over $MgSO_4$ The solvent is removed under reduced pressure and the residue is dissolved in 300 mL of MeOH. The solution, then, is treated with 20.0 g of

potassium carbonate and stirred at ambient temperature for 12 h. and distilled under reduced pressure to afford **42** as a colorless oil.

6-(Prop-2'-ynyl)-1,4-dioxaspiro[4.5]decane (**42b**): 20.0 g (147 mmol) of 2-(2'-propynyl)-cyclohexanone (**41b**) in benzene (200 mL) was refluxed with ethylene glycol (10 mL, 179 mmol) and catalytic amount TsOH for 4 h. The mixture was cooled to room temperature and washed with 100 mL water. The aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extract was dried over $MgSO_4$ and distilled under reduced pressure to afford 23.0 g (87%) of **42b** as a colorless oil, b. p. 78 °C (0.5 Torr). – IR (film): ν = 3300 cm^{-1} (C≡C–H), 2940 cm^{-1} (C–H), 2854, 2116 (C≡C), 1440, 1336, 1160, 1087, 1017, 952. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.18–2.04 (m, 11 H, 6,7,8,9,10,1'-H), 2.43, 2.50 (t, ^4J = 3.2 Hz, ratio = 1.4 : 1, 1 H, 3'-H), 3.84–3.97 (m, 4 H, 2,3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 17.9, 23.8, 24.5, 28.9, 34.6 (–, C-7,8,9,10,1'), 44.0 (+, C-6), 64.6, 64.7 (–, C-2,3), 68.4 (+, C-3'), 83.9 (C_{quat}, C-3'), 109.8 (C_{quat}, C-5). – MS (70 eV), *m/z* (%): 180 (6) [M^+], 165 (12), 152 (33), 137 (70), 126 (16), 99 (100), 86 (19). – Elemental analysis calcd (%) for $C_{11}H_{16}O_2$ (180.2): C 73.30, H 8.95; found: C 73.68, H 9.12.

6-(Pent-4'-yn-1'-yl)-1,4-dioxaspiro[4.5]decane (**42d**): To a solution 30.2 g (200 mmol) of 1-pyrrolidino-1-cyclohexene (**39c**) in dioxane (200 mL) at 60 °C was dropwise added 32.1 g (220 mmol) of 1-bromo-4-pentyne (**40c**) over a period of 30 min. Then, the mixture was kept at this temperature for an additional 30 min and refluxed at 100 °C for 12 h. After cooling to ambient temperature, the suspension was treated with 200 mL of water and stirred at 80 °C for 1 h. The aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extract was dried over $MgSO_4$ and the solvent was removed under reduced pressure. A mixture of the residue, ethylene glycol, (15 mL, 269 mmol), TsOH (ca. 1 g) and benzene (200 mL) was stirred at 100 °C for 4 h using a Dean-Stark apparatus. After cooling to ambient temperature, the solution was treated with 200 mL of water and washed with Et_2O (3 × 50 mL). The combined organic extract was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The pale-yellow oil was distilled by a *Kugelroh* apparatus (0.5 Torr, oven temperature: 85 °C). 11.0 g (26%) of **42d** was obtained as a colorless oil. – IR (KBr): ν = 3300 cm^{-1} (C≡C–H), 2936 (C–H), 2868, 2116 (C≡C), 1441,1281, 1159, 1089, 924, 635. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.97–1.70 (m, 12 H, 6,7,8,9,10,1',2'- H), 1.54, 1.85 (t, ^4J = 2.6 Hz, ratio = 1.3 : 1, 1 H, 5'-H), 2.02–2.09 (br. m, 2 H, 3'-H), 3.78–3.91 (m, 4 H, 2,3-

H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 18.6, 23.6, 24.3, 26.5, 27.3, 28.7, 34.4 (–, C-7,8,9,10,1',2',3'), 44.0 (+, C-6), 64.4, 64.5 (–, C-2,3), 68.0 (+, C-3'), 84.3 (C_{quat}, C-3'), 110.4 (C_{quat}, C-5). – MS (70 eV), *m/z* (%): 207 (6) [M^+], 165 (17), 152 (25), 125 (14), 113 (14), 99 (100), 86 (24), 55 (24), 41 (16). – Elemental analysis calcd (%) for $C_{13}H_{20}O_2$ (208.3): C 74.96, H 9.68; found: C 74.64, H 9.95.

2-(Prop-2'-ynyl)-2,5,5-trimethylcyclopentanone (**46**): To a solution of diisopropylamine (25.3 g, 250 mmol) and 2,2'-bipyridine (30.0 mg) in THF (300 mL) at –78 °C was dropwise added a solution of *n*-butyllithium (106 mL, 2.36 M in *n*-hexane, 250 mmol) over a period of 1 h and stirred at this temperature for an additional 1 h. The clear dark red solution was treated with 27.5 g (218 mmol) of 2,2,5-trimethylcyclopentanone (**45**), and warmed up to ambient temperature. After another 1 h, 41.0 g (80% in toluene, 276 mmol) of propagyl bromide was added at –60 °C. Then, the reaction mixture was stirred at ambient temperature overnight (ca. 12 h). This reaction was quenched at 0 °C with a cold solution of ammonia chloride (100 g) in water (300 mL). The aqueous phase was extracted with Et_2O (3 × 100 mL) and the combined organic phase was dried over $MgSO_4$. After evaporation of the solvent, the reaming liquid was distilled through a 10-cm Vigreux column under reduced pressure to afford 28.9 g (81%) of **46** as a colorless oil, b. p. 82 °C (14 Torr). The ^{1}H- and ^{13}C-NMR spectrum agreed with those which have previously been reported.[115]

4-(1',4'-Dioxaspiro[4.5]dec-6'-yl)butan-2-one (**48**): To a suspension of potassium 3-(2',2'-ethylenedioxycyclohexan-1yl)propionate (24.2 g, 95.9 mmol) in THF (150 mL) at –78 °C was added dropwise of a solution of methyllithium (38.5 mL, 2.20 M in Et_2O, 84.7 mmol). The mixture was allowed to warm to ambient temperature and stirred for an additional 1 h. The reaction was quenched with 250 mL ice water, and the aqueous phase is extracted with Et_2O (3 × 200 mL). The combined organic extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure. After crystallization in pentane/Et_2O (10 : 1) at –20 °C, 9.32 g (52%) of **48** was obtained as a colorless crystal, m. p. 43 °C. – IR (KBr):ν = 2924 cm^{-1} (C–H), 1710 (C=O), 1538, 1262, 1170, 1087, 1059, 1015, 922. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13–1.78 (m, 10 H, 4,7',8',9',10'-H), 1.80–1.91 (m, 1 H, 6'-H), 2.09 (s, 3 H, CH_3), 2.27–2.54 (m, 2 H, 3-H), 3.81–3.97 (m, 4 H, 2',3'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 29.7 (+, C-1), 22.5, 23.6, 24.4, 29.2, 34.5, 42.1 (–, C-3,4,7',8',9',10'), 43.9 (+,

C-6'), 64.5, 64.6 (C_{quat}, C-2',3'), 110.5 (C_{quat}, C-5'), 209.5 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 212 (40) [M^+], 169 (50), 155 (42), 113 (10), 99 (100), 86 (14). – Elemental analysis calcd (%) for $C_{12}H_{20}O_3$ (212.1): C 67.94, H 9.50; found: C 67.64, H 8.86.

6-(But-2'-yn-1'-yl)-1,4-dioxaspiro[4.5]decane (**42c**) and *6-(But-3'-yn-1'-yl)-1,4-dioxa-spiro-[4.5]decane* (**49**): To a solution of LDA [42.5 mmol; from diisopropylamine (4.30 g, 42.5 mmol) and *n*-butyllithium (27.3 mL, 1.56 M in *n*-hexane, 42.6 mmol)] in THF (150 mL) at –78 °C was dropwise added a solution of 8.21 g (38.7 mmol) of ketone **48** in THF (20 mL). After an additional 1.5 h, the solution was treated with $PO(OEt)_2Cl$ (6.16 mL, 42.6 mmol) and stirred at this temperature for 20 min. Then, the solution was raised to ambient temperature over 20 min. A solution of LDA [107 mmol; from diisopropylamine (10.8 g, 107 mmol) and *n*-butyllithium (68.3 mL, 1.56 M in *n*-hexane, 107 mmol)] in THF (50 mL) was transferred to this mixture at –78 °C via a double-ended needle over a period of 30 min. and the reaction was allowed to warm to ambient temperature overnight (ca. 12 h). This reaction was quenched with 250 mL of ice water, and the aqueous phase is extracted with Et_2O (3 × 100 mL). The solvent of the combined organic phase was distilled off is removed under reduced pressure. The residue was subjected to chromatography on silica gel (100 g). Elution with pentane/Et_2O (8 : 1) afforded a pale-yellow oil [R_f = 0.38 (pentane/Et_2O 6 : 1)], which was distilled by a *Kugelroh* apparatus (0.4 Torr, 105 °C) to give 5.89 g (78%) of **42c** and **49** (ratio = 5 : 1) as a colorless oil. – MS (70 eV), *m/z* (%): 194 (10) [M^+], 166 (41), 155 (14), 151 (41), 137 (11), 125 (11), 113 (24), 112 (20), 99 (100), 93 (18), 86 (22), 79 (26), 77 (14), 55 (75), 44 (21). **49**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15–1.70 (m, 8 H, 7,8,9,10-H), 1.73 (t, ^5J = 2.6 Hz, 1 H, 4'-H), 1.95–2.03 (m, 2 H, 6,1'-H), 2.39 [d"qui" (ddq), ^2J = 16.1 Hz, ^3J = 2.6 Hz, ^5J = 2.6 Hz, 1 H, 1'-H], 3.76–3.86 (m, 4 H, 2,3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 3.42 (+, CH_3), 18.1, 23.6, 24.4, 28.9, 34.5 (–, C-7,8,9,10,1'), 44.3 (+, C-6), 64.6, 64.7 (–, C-2,3), 75.5, 78.2 (C_{quat}, C-3',4'), 110.0 (C_{quat}, C-5).

2-(3'-Trimethylsilylprop-2'-ynyl)cyclopentanone (**52a**) and *cis/trans-2,5-di(3'-trimethylsilyl-prop-2'-ynyl)cyclopentanone* (**52a'**): Following GP3, a solution of LDA (250 mmol) in and the residue was distilled under reduced pressure to 200 mL THF was treated with imine **50a** (49.5 g, 299 mmol) and then, 60.0 g (314 mmol) of 1-bromo-3-trimethylsilyl-2-propyne (**51a**). After hydrolysis and evaporation of the solvent, afford 26.8 g (55%) of **52a** as a colorless oil, b. p. 76 °C (0.5 Torr). The residue was subjected to chromatography on silica

gel (100 g). Elution with pentane/Et_2O (5 : 1) afforded a pale-yellow oil (R_f = 0.80), which was distilled by a *Kugelroh* apparatus (0.5 Torr, 130 °C) to give 9.13 g (19%) of **52a'** as a colorless oil.

52a: IR (film): ν = 2962 cm^{-1} (C–H), 2176 (C≡C), 1746 (C=O), 1249, 1155, 839, 760. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 9 H, $Si(CH_3)_3$], 1.70–1.86 (m, 2 H) and 1.95–2.39 (m, 6 H) [total 8 H, 3,4,5,1'-H], 2.49–2.57 (m, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.1 [+, $Si(CH_3)_3$], 19.9, 20.4, 28.6, 38.0 (–, C-3,4,5,1'), 47.6 (+, C-2), 85.7, 104.2 (C_{quat}, C-2',3'), 218.7 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 194 (2) [M^+], 179 (52), 149 (13), 97 (12), 83 (10), 75 (100), 73 (22), 59 (10), 43 (13). – Elemental analysis calcd (%) for $C_{11}H_{18}OSi$ (194.4): C 67.98, H 9.34; found: C 67.68, H 9.09.

52a': – IR (film): ν = 2970 cm^{-1} (C–H), 2175 (C≡C), 1743 (C=O), 1246, 835, 759, 638. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.12, 0.13 [s, 18 H, $Si(CH_3)_3$, ratio=2.2 : 1], 1.61–1.77 (m, 1 H), and 1.97–2.65 (m, 9 H) [total 10 H, 3,4,5,1'-H]. – Major stereoisomer: ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.0 [+, $Si(CH_3)_3$], 20.1, 26.3 (–, C-3,4,1'), 48.1 (+, C-2,5), 86.1, 104.0 (C_{quat}, C-2',3'), 217.3 (C_{quat}, C-1). – Minor stereoisomer: ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.0 [+, $Si(CH_3)_3$], 20.1, 25.8 (–, C-3,4,1'), 46.7 (+, C-2,5), 85.7, 104.4 (C_{quat}, C-2',3'), 217.8 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 304 (11) [M^+], 289 (20) [$M^+ - CH_3$], 192 (24), 177 (52), 147 (16), 83 (12), 75 (26), 73 (100), 59 (10). – Elemental analysis calcd (%) for $C_{17}H_{28}OSi_2$ (304.6): C 67.04, H 9.27; found: C 66.84, H 9.48.

6-(2'-Propynyl)-1,4-dioxaspiro[4.4]nonane (**42a**) and *6-[1'-(2''-methyl[1'',3'']dioxolan-2''-*yl)methyl]-1,4-dioxaspiro[4.6]nonane (**53**): Following GP4, a mixture of **52a** (25.0 g, 129 mmol), ethylene glycol (10 mL, 179 mmol), catalytic amount TsOH and benzene (250 mL) was refluxed for 16 h. After aqueous work-up and evaporation of solvent, the residue was dissolved in 300 mL of MeOH. The solution was treated with K_2CO_3 (20.0 g) and stirred at ambient temperature overnight (ca. 12 h). The organic extract was dried over $MgSO_4$ and distilled under reduced pressure to afford 10.3 g (48%) of **42a** as a colorless oil, b. p. 57 °C (0.5 Torr). The dark residue was distilled again by a *Kugelroh* apparatus (0.5 Torr, oven temperature 110 °C) to gaive 8.76 g (43%) of **53** as a colorless oil.

42a: IR (film): ν = 3286 cm^{-1} (C≡C–H), 2961 cm^{-1} (C–H), 2875, 2117 (C≡C), 1329, 1199,

1153, 1046, 1024, 649. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.33–1.73 (m, 5 H) and 1.87-2.32 (m, 3 H) [total 8 H, 7,8,9,1'-H], 2.17–2.33 (m, 1 H, 6-H), 1.86 and 1.87 (t, ^4J = 2.5 Hz, ratio = 2.1 : 1, 1 H, 3'-H), 3.74–3.96 (m, 4 H, 2,3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 18.2, 20.3, 29.1, 35.5 (–, C-7,8,9,1'), 45.1 (+, C-6), 64.3, 64.6 (–, C-2,3), 68.0 (+, C-3'), 83.7 (C_{quat}, C-2'), 117.1 (C_{quat}, C-5). – DCI MS, *m/z* (%): 167 (100) [M^+ + H].

53: – IR (film): ν = 2938 cm^{-1} (C–H), 1653, 1558, 1520,1261. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, CH_3), 1.31–2.07 (m, 9 H, 6,7,8, 9,1'-H), 3.70–3.90 (m, 8 H, 2,3,4",5"-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.4, 30.1, 34.7, 37.3 (–, C-7,8,9,1'), 24.1 (+, CH_3), 41.2 (+, C-6), 64.1, 64.2, 64.4, 64.6 (–, C-2,3,4",5"), 110.0, 118.2 (C_{quat}, C-5,2"). – MS (70 eV), *m/z* (%): 213 (8) [M^+– CH_3], 183 (12), 141 (16), 99 (52), 87 (100), 55 (10), 43 (26), 41 (11). – Elemental analysis calcd (%) for $C_{12}H_{20}O_4$ (228.3): C 63.14, H 8.83; found: C 62.94, H 8.60.

2-(4'-trimethylsilylbut-3'-yn-1'-yl)cyclohexanone (**52b**): According to GP3, a solution of LDA (250 mmol) in THF (200 mL) was treated with 54.0 g (300 mmol) of imine **50b** and then, 97.0 g (473 mmol) of 1-bromo-4-trimethylsilyl-3-butyne (**51b**). After hydrolysis, the residue was distilled under reduced pressure to afford 42.8 g (77%) of **52b** as a colorless oil, b. p. 81–83 °C (0.5 Torr). 21.2 g of alkynyl bromide **51b** was recovered from the pentane extract. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 9 H, $Si(CH_3)_3$], 1.26–1.38 (2 H), 1.59–1.67 (2 H), 1.79–2.12 (4 H) and 2.27–2.44 (3 H) [m, 10 H, 2,3,4,5,6,1'-H], 2.22 (t, ^3J = 7.0 Hz, 2 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.0 [+, $Si(CH_3)_3$], 17.5, 25.1, 28.0, 28.1, 33.8, 42.1 (–, C-3,4,5,6,1',2'), 49.2 (+, C-2), 84.7, 106.8 (C_{quat}, C-3',4'), 212.6 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 222 (18) [M^+], 207 (30), 193 (16), 170 (28), 155 (16), 133 (18), 131 (16), 98 (100), 97 (20), 83 (30), 75 (84), 73 (46), 59 (16), 55 (16), 43 (10), 41 (11).

6-(But-3'-yn-1'-yl)-1,4-dioxaspiro[4.5]decane (**42c**): In accordance with GP4, a mixture of **52b** (42.5 g, 213 mmol), ethylene glycol (15 mL, 269 mmol), catalytic amount of TsOH, and benzene (200 mL) was refluxed for 12 h. After aqueous work-up and evaporation of the solvent, the residue was dissolved in 300 mL of MeOH. The solution was treated with K_2CO_3 (20.0 g) and stirred at ambient temperature overnight (ca. 12 h). The organic extract was dried over $MgSO_4$ and distilled under reduced pressure to afford 28.7 g (76%) of **42c** as a colorless oil, b. p. 80 °C (0.5 Torr). – IR (KBr): ν = 3291 cm^{-1} (C≡C–H), 2935 (C–H), 2870, 2116

(C≡C), 1443, 1282, 1158, 1088, 923. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.09–1.81 (m, 10 H, 6,7,8,9,10,1'-H), 1.84 (t, ^4J = 1.6 Hz, 1 H, 4'-H), 1.97–2.15 (m, 2 H, 2'-H), 3.76–3.86 (m, 4 H, 2,3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 16.2, 23.5, 24.2, 27.0, 28.5, 34.3 (–, C-7,8,9,10,1',2'), 43.2 (+, C-6), 64.3, 64.4 (–, C-2,3), 68.0 (+, C-4'), 84.4 (C_{quat}, C-3'), 110.3 (C_{quat}, C-5). – MS (70 eV), *m/z* (%): 194 (5) [M^+], 165 (12), 155 (92), 151 (12), 125 (11), 113 (24), 112 (24), 99 (100), 86 (17), 55 (16). – Elemental analysis calcd (%) for $C_{12}H_{18}O_2$ (194.3): C 74.19, H 9.34; found: C 73.95, H 9.12.

2-(3'-trimethylsilyl-prop-2'-ynyl)cycloheptanone (**52c**): Following GP4, to a solution of LDA (250 mmol) in THF (200 mL) was added 58.0 g (300 mmol) imine **50c** and, then 54.0 g (283 mmol) of 1-bromo-3-trimethylsilyl-2-propyne (**51a**). After aqueous work-up and hydrolysis, the residue was distilled under reduced pressure to afford 42.1 g (67%) of **52c** as a colorless oil, b. p. 105 °C (0.5 Torr). – IR (film): ν = 2910 cm^{-1} (C–H), 2853, 2177 (C≡C), 1700 (C=O), 1457, 1248, 837. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 9 H, $Si(CH_3)_3$],1.19–1.93 (m, 8 H, 3,4,5,6-H), 2.11–2.19 (1 H), 2.21–2.47 (3 H), and 2.53–2.64 (1 H) [m, 5 H, 2,7,1'-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.1 [+, $Si(CH_3)_3$], 22.0, 23.8, 28.6, 29.3, 30.0, 43.1 (–, C-3,4,5,6,7,1'), 50.7 (+, C-2), 85.5, 105.1 (C_{quat}, C-2',3'), 213.7 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 222 (7) [M^+], 207 (85), 189 (20), 179 (18), 170 (28), 149 (13), 131 (11), 83 (11), 75 (100), 73 (32), 59 (10), 43 (12). – Elemental analysis calcd (%) for $C_{13}H_{22}OSi$ (222.4): C 70.21, H 9.97; found: C 70.02, H 10.11.

6-(2'-Propynyl)-1,4-dioxaspiro[4.6]undecane (**42e**): According to GP4, 40.7 g (183 mmol) of 2-(3'-trimethylsilyl-2'-propynyl)cycloheptanone (**52c**) in benzene (250 mL) was refluxed with ethylene glycol (15 mL, 269 mmol), and catalytic amount of TsOH (2 g) for 8 h. After aqueous work-up and evaporation of the solvent, the residue was dissolved in 300 mL of MeOH. The solution was treated with K_2CO_3 (20.0 g) and stirred at ambient temperature overnight (ca. 12 h). The organic extract was dried over $MgSO_4$ and distilled under reduced pressure to afford 29.2 g (82%) **42e** as a colorless oil, b. p. 87 °C (0.5 Torr). – IR (film): ν = 3308 cm^{-1} (C≡C–H), 2929 (C–H), 2855, 2116 (C≡C), 1459, 1155, 1107. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23–2.07 (m, 13 H, 6,7,8,9,10,11,1'-H), 2.32 and 2.38 (t, ^4J = 2.6 Hz, ratio = 1.5 : 1, 1 H, 3'-H), 3.73–3.96 (m, 4 H, 2,3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 19.2, 21.3, 27.0, 27.3, 28.5, 36.7 (–, C-7,8,9,10,11,1'), 47.2 (+, C-6),

63.7, 64.9 (–, C-2,3), 68.1 (+, C-3'), 84.3 (C_{quat}, C-2'), 112.9 (C_{quat}, C-5). – MS (70 eV), *m/z* (%): 194 (1) [M^+], 155 (20), 137 (70), 113 (18), 99 (100), 86 (11), 55 (17), 41 (18). – Elemental analysis calcd (%) for $C_{12}H_{18}O_2$ (194.3): C 74.19, H 9.34; found: C 73.89, H 9.12.

1.2. Synthesis of Symmetric Diynes

General Procedure for Synthesis of 1,3-Butadiynes **54** *by the Glaser Coupling (GP5):* A solution of 10.0 mmol of a terminal alkyne in pyridine/THF/MeOH (40/40/10 mL) in a Schlenk flask is treated with 7.99 g (40 mmol) of copper(II) acetate monohydrate [$Cu(OAc)_2 \cdot H_2O$] at ambient temperature. The mixture is heated at 70 °C under argon for 12 h. After cooling to room temperature, the suspension is filtered off on a 5 cm thick layer of Celite and rinsed well with Et_2O (200 mL). The filtrate washed with water (2 × 50 mL) and a 3 N solution of hydrochloric acid (25 mL). The combined organic extract is dried over $MgSO_4$ and the solvent is removed under reduced pressure. The residue is subjected to chromatography on silica gel (100 g). Elution with pentane/Et_2O affords the coupling product **54**.

1,4-Di(9',9'-di-n-hexylfluoren-2'-ylethynyl)buta-1,3-diyne (**54d**): Following GP5, a mixture of 3.23 g (9.00 mmol) of 9,9-dihexyl-2-ethynylfluorene (**29e**), $Cu(OAc)_2 \cdot H_2O$ (7.99 g, 40 mmol) and pyridine/THF/MeOH (40/40/10 mL) was heated at 70 °C under argon for 12 h. After filtration, aqueous work-up and chromatography on silica gel (100 g, elution with pentane), 2.63 g (82%) of **54d** [R_f = 0.24 (pentane)] was obtained as a pale-yellow semi-solid. – UV (acetonitrile): λ_{max} (lg ε) = 338 nm (3.99), 349 (4.05), 375 (4.00). – IR (film): ν = 2928 cm^{-1} (C–H), 2957, 2854, 2138 (C≡C), 1465, 1450, 832, 793. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.60–0.78 (br. m, 8 H), 0.83 (t, ^3J = 6.5 Hz, 12 H, CH_3), 1.05–1.23 (m, 24 H), and 1.95–2.10 (m, 8 H) [total 52 H, hexyl-H], 7.34–7.42 (m, 6 H, Ar-H), 7.55–7.62 (m, 4 H, Ar-H), 7.68–7.72 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_3), 22.5, 23.7, 29.7, 31.5, 40.3 (–, CH_2), 55.1 (C_{quat}, C-9'), 74.3, 83.1 (C_{quat}, C-1,2,3,4), 119.7, 120.2, 122.9, 126.85, 126.92, 127.8, 131.5 (+, C-Ar), 119.9, 140.1, 142.3, 150.8, 151.1 (C_{quat}, C-Ar). – MS (70 eV), *m/z* (%): 714 (100) [M^+], 389 (9), 43 (11). – Elemental analysis calcd (%) for $C_{54}H_{66}$ (715.12): C 90.70, H 9.30; found: C 91.06, H 9.08.

1,4-Di[9',9'-di-n-hexyl-7'-(phenylethynyl)fluoren-2'-ylethynyl]buta-1,3-diyne (**54e**): Following GP5, a mixture of $Cu(OAc)_2{\cdot}H_2O$ (7.99 g, 40 mmol), pyridine/THF/MeOH (40/40/10 mL) and 4.58 g (10.0 mmol) of 2-ethynyl-9',9'-dihexyl-7-phenylethynylfluorene (**29fa**) was heated at 70 °C under argon for 12 h. After filtration, aqueous work-up and chromatography on silica gel [100 g, elution with pentane/CH_2Cl_2 (from 1 : 0 to 10 : 1)], 3.06 g (67%) of **54e** [R_f = 0.20 (pentane)] was obtained as a pale-yellow solid, m. p. 192–194 °C. – UV (acetonitrile): λ_{max} (lg ε) = 368 nm (4.82), 396 (4.68). – IR (KBr): ν = 2927 cm^{-1} (C–H), 2853, 2138, 1596, 1492, 1462, 1415, 823, 755. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.55–0.65 (br. m, 8 H), 0. 79 (t, ^3J = 6.5 Hz, 12 H, CH_3), 1.05–1.20 (m, 24 H), and 1.95–2.05 (m, 8 H) [total 52 H, hexyl-H], 7.30–7.40 (m, 6 H, Ar-H), 7.51–7.62 (m, 12 H, Ar-H), 7.68 (dd, ^3J = 8.4, ^4J = 3.3 Hz, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_3), 22.6, 23.7, 29.7, 31.5, 40.3 (–, CH_2), 55.2 (C_{quat}, C-9'), 74.5, 83.2, 89.9, 90.3 (C_{quat}, *C*≡*C*Ph, C-1,2,3,4), 120.0, 120.2, 126.0, 126.9, 128.3, 128.4, 130.8, 131.58, 131.64 (+, C-Ar), 120.3, 122.3, 123.3, 140.3, 141.6, 151.1, 151.3 (C_{quat}, C-Ar). – MS (70 eV), *m/z* (%): 914 (100) [M^+]. – Elemental analysis calcd (%) for $C_{70}H_{74}$ (915.4): C 91.85, H 8.15; found: C 91.88, H 8.44.

2. Synthesis of β-Amino-substituted α,β-Unsaturated Fischer Carbene Complexes

General Procedure for preparation of β-Amino-substituted α,β-Unsaturated Fischer Carbene Complexes **18** *(GP6):* To a solution of 20 mmol of a terminal alkyne in THF (100 mL) at –78 °C is added 20 mmol of a solution of *n*-butyllithium. The mixture is stirred at this temperature for an additional 1–3 h. After addition of hexacarbonylchromium (4.40 g, 20.0 mmol), the solution is warmed up to room temperature, stirred for another 30 min, and 20.5 mmol of triethyloxonium tetrafluoroborate (Et_3OBF_4) is added at 0 °C. After an additional 10 min, gaseous dimethylamine is added to the dark red solution in THF upon which the color changes to yellow or orange as the reaction goes to completion. After filtration through Celite and evaporation of solvent, the residue is purified by flash column chromatography.

Pentacarbonyl[(2E)-5-(tert-butyldimethylsilyloxy)-3-dimethylamino-1-ethoxy-2,6-heptdien-1-ylidene]chromium (**18h**): According to GP6, 4.62 g (22.0 mmol) of 3-(*tert*-butyldimethyl-

silyloxy)hex-1-en-5-yne (**15q**) in THF (100 mL) was treated with *n*-butyllithium (12.8 mL, 1.56 M in *n*-hexane, 20.0 mmol), hexacarbonylchromium (4.84 g, 22.0 mmol), Et_3OBF_4 (4.18 g, 22.0 mmol), and gaseous dimethylamine. Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 10 : 1 to 3 : 1) gave 7.63 g (73%) of **18h** [R_f = 0.56 (pentane/ Et_2O 3 : 1)] as a yellow solid, m. p. 85–86 °C (dec.). – IR (KBr): ν = 2929 cm^{-1} (C–H), 2046 (C=O), 1975 (C=O), 1949 (C=O), 1881 (C=O), 1533, 1479, 1227. – ^1H NMR (250 MHz, $CDCl_3$): δ = –0.04 [s, 3 H, $Si(CH_3)$], –0.01 [s, 3 H, $Si(CH_3)$], 0.85 [s, 9 H, $SiC(CH_3)_3$], 1.45 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.52–2.63 (m, 1 H, 4-H), 3.17–3.39 [m, 7 H, 4-H, $N(CH_3)_2$], 4.44–4.48 (m, 1 H, 5-H), 4.68–4.78 (m, 2 H, OCH_2CH_3), 5.14 (br. d, ^3J = 10.3 Hz, 7-H), 5.27 (br. d, ^3J = 17.0 Hz, 7-H), 5.82–5.96 (m, 1 H, 6-H), 6.41 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –4.9 [+, $Si(CH_3)$], –4.6 [+, $Si(CH_3)$], 15.8 (+, OCH_2CH_3), 18.1 [C_{quat},, $SiC(CH_3)_3$], 25.9 [+, $SiC(CH_3)_3$], 39.0 (–, C-4), 41.1, 41.7 [+, br., $N(CH_3)_2$], 73.8 (+, C-5), 74.1 (–, OCH_2CH_3), 114.5 (–, C-7), 118.0 (+, C-2), 140.9 (+, C-6), 156.7 (C_{quat}, C-3), 220.3, 224.8 (C_{quat}, CO), 284.4 (C_{quat}, C-1). – EI MS (70 eV), *m/z* (%):503 (1) [M^+ – 5 CO], 363 (100) [M^+ – 5 CO], 311 (29), 296 (40), 282 (25), 276 (114), 226 (12), 220 (26), 180 (47), 179 (46), 166 (26), 150 (29), 134 (22), 108 (20), 80 (29), 75 (100) [$OSi(CH_3)_2^+$], 52 (16) [Cr^+]. – Elemental analysis calcd (%) for $C_{22}H_{33}CrNO_7Si$ (503.1): C 52.51, H 6.61; found: C 52.23, H 6.43.

Pentacarbonyl[(2E)-4-(1',4'-dioxaspiro[4.4]non-6'-yl)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]chromium (**18i**): According to GP6, 3.58 g (21.5 mmol) of 6-(2'-propynyl)-1,4-dioxaspiro[4.5]nonane (**42a**) in THF (100 mL) was treated with *n*-butyllithium (13.5 mL, 1.56 M in *n*-hexane, 21.1 mmol), hexacarbonylchromium (4.73 g 21.5 mmol), Et_3OBF_4 (4.18 g, 22.0 mmol), and then, gaseous dimethylamine. Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 5 : 1 to 0 : 1) gave 8.07 g (83%) of **18i** [R_f = 0.63 (Et_2O)] as a yellow solid, m. p. 93–94 °C (dec.). – IR (KBr): ν = 2960 cm^{-1} (C–H), 2043 (C=O), 1970 (C=O), 1970 (C=O), 1920 (C=O), 1886 (C=O), 1538, 1281, 674, 650. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.48 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.41–1.82 (6 H) and 2.08–2.16 (1 H) [m, 7 H, 4,7',8',9'-H], 2.59 (AB, dd, ^2J = 13.6, ^3J = 4.3 Hz, 1 H, 4-H), 2.75–2.87 (m, 1 H, 6'-H), 3.16 [s, 6 H, $N(CH_3)_2$], 3.85–3.94 (m, 4 H, 2',3'-H), 4.72 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.35 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.5

(+, OCH_2CH_3), 20.3, 28.1, 28.9, 35.0 (–, C-4,7',8',9'), 40.7, 41.9 [+, br., $N(CH_3)_2$], 45.5 (+, C-6'), 64.3, 64.6 (–, C-2',3'), 73.8 (–, OCH_2CH_3), 117.5 (C_{quat}, C-5'), 118.1 (+, C-2), 159.3 (C_{quat}, C-3), 219.4, 224.5 (C_{quat}, CO), 285.4 (C_{quat}, C-1). – EI MS (70 eV), *m/z* (%): 459 (5) [M^+], 431 (21) [M^+ – CO], 403 (3) [M^+ – 2 CO], 375 (11) [M^+ – 3 CO], 347 (16) [M^+ – 4 CO], 319 (100) [M^+ – 5 CO], 257 (95), 227 (10), 213 (11), 206 (49), 162 (31), 150 (78), 52 (17) [Cr^+]. – Elemental analysis calcd (%) for $C_{20}H_{25}CrNO_8$ (459.4): C 52.29, H 5.48; found: C 52.33, H 5.25.

Pentacarbonyl[(2E)-4-(1',4'-dioxaspiro[4.5]dec-6'-yl)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]chromium (**18j**): According to GP6, 6.43 g (35.7 mmol) of 6-(2'-propynyl)-1,4-dioxa-spiro[4.5]decane (**42b**) in THF (175 mL) was treated with *n*-butyllithium (22.0 mL, 1.56 M in *n*-hexane, 34.3 mmol), hexacarbonylchromium (7.98 g, 36.3 mmol), Et_3OBF_4 (6.91 g, 36.4 mmol) and then, gaseous dimethylamine. Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 5 : 1 to 1 : 3) gave 14.1 g (87%) of **18j** [R_f = 0.33 (pentane/Et_2O = 1 : 1)] as a yellow solid, m. p. 91–92 °C (dec.). – IR (KBr): ν = 2945 cm^{-1} (C–H), 2932, 2041 (C=O), 1912 (C=O), 1898 (C=O), 1542, 1434, 1281, 1089, 668. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.13–1.86 (m, 10 H, 4,7',8',9',10'-H), 1.51 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.75–2.87 (m, 1 H, 6'-H), 3.15 [s, 6 H, $N(CH_3)_2$], 3.85–3.99 (m, 4 H, 2',3'-H), 4.72 (q, ^3J = 7.1 Hz, 1 H, OCH_2CH_3), 4.73 (q, ^3J = 7.1 Hz, 1 H, OCH_2CH_3), 6.40 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.5 (+, OCH_2CH_3), 23.7, 25.2, 28.2, 28.7, 34.8 (–, C-4,7',8',9',10'), 40.7 [+, br., $N(CH_3)_2$], 44.6 (+, C-6'), 64.6, 64.7 (–, C-2',3'), 73.9 (–, OCH_2CH_3), 110.1 (C_{quat}, C-5'), 119.0 (+, C-2), 158.8 (C_{quat}, C-3), 219.5, 224.6 (C_{quat}, CO), 286.6 (C_{quat}, C-1). – EI MS (70 eV), *m/z* (%): 473 (2) [M^+], 445 (8) [M^+ – CO], 417 (1) [M^+ – 2 CO], 389 (13) [M^+ – 3 CO], 361 (9) [M^+ – 4 CO], 333 (100) [M^+ – 5 CO], 271 (93), 220 (81), 176 (26), 164 (58), 52 (16) [Cr^+]. – Elemental analysis calcd (%) for $C_{21}H_{27}CrNO_8$ (473.4): C 53.28, H 5.75; found: C 53.43, H 5.53.

Pentacarbonyl[(2E)-4-(1',4'-dioxaspiro[4.6]undec-6'-yl)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]chromium (**18k**): Following GP6, 5.12 g (26.4 mmol) of 6-(2'-propynyl)-1,4-dioxa-spiro[4.6]undecane (**42c**) in THF (125 mL) was treated with *n*-butyllithium (16.7 mL, 1.56 M in *n*-hexane, 26.0 mmol), hexacarbonylchromium (6.16 g, 28.0 mmol), Et_3OBF_4 (6.91 g, 36.4 mmol), and then, gaseous dimethylamine. Flash chromatography on silica gel (150 g)

eluting with pentane/Et_2O (from 5 : 1 to 1 : 1) gave 6.90 g (54%) of **18k** [R_f = 0.33 (pentane/Et_2O = 1 : 1)] as a yellow solid, m. p. 104–105 °C (dec.). – IR (KBr): ν = 2927 cm^{-1} (C–H), 2042 (C=O), 1973 (C=O), 1913 (C=O) 1892 (C=O), 1541, 1576, 1431, 1271. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23–1.99 (m, 12 H, 4,7',8',9',10',11'-H), 1.50 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.54–2.60 (m 1 H, 6'-H), 3.15 [s, 6 H, $N(CH_3)_2$], 3.83–4.00 (m, 4 H, 2',3'-H), 4.72 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.41 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.6 (+, OCH_2CH_3), 21.2, 26.1, 27.8, 28.4, 29.8, 36.6 (–, C-4,7',8',9',10',11'), 40.7, 41.7 [+, br., $N(CH_3)_2$], 47.5 (+, C-6'), 63.9, 65.1 (–, C-2',3'), 73.9 (–, OCH_2CH_3), 113.7 (C_{quat}, C-5'), 119.4 (+, C-2), 159.0 (C_{quat}, C-3), 219.5, 224.5 (C_{quat}, CO), 287.5 (C_{quat}, C-1). – EI MS (70 eV), *m/z* (%): 487 (18) [M^+], 459 (5) [M^+ – CO], 431 (4) [M^+ – 2 CO], 403 (12) [M^+ – 3 CO], 375 (14) [M^+ – 4 CO], 347 (100) [M^+ – 5 CO], 285 (59), 234 (24), 190 (12), 178 (62), 57 (17), 52 (3) [Cr^+]. – Elemental analysis calcd (%) for $C_{22}H_{29}CrNO_8$ (487.5): C 54.21, H 6.00; found: C 54.68, H 5.76.

Pentacarbonyl[(2E)-5-(1',4'-dioxaspiro[4.5]dec-6'-yl)-3-dimethylamino-1-ethoxy-2-penten-1-ylidene]chromium (**18l**): Following GP6, 6.40 g (32.9 mmol) 6-(3'-butynyl)-1,4-dioxaspiro-[4.5]decane (**42d**) in THF (150 mL) was treated with *n*-butyllithium (22.0 mL, 1.56 M in *n*-hexane, 30.4 mmol), hexacarbonylchromium (7.04 g, 32.0 mmol), Et_3OBF_4 (6.91 g, 36.4 mmol) and gaseous dimethylamine. Flash chromatography on silica gel (140 g) eluting with pentane/Et_2O (from 5 : 1 to 1 : 3) gave 12.4 g (84%) of **18l** [R_f = 0.39 (pentane/Et_2O = 1 : 1)] as a yellow solid, m. p. 79–80 °C (dec.). – IR (KBr): ν = 2931 cm^{-1} (C–H), 2042 (C=O), 1942 (C=O), 1881 (C=O), 1539, 1480, 1433, 1274. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20–1.83 (11 H), 2.75–2.87 (2 H) [m, 13 H, 4,5, 6',7',8',9',10'-H), 1.50 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 3.13 [s, 6 H, $N(CH_3)_2$], 3.89–3.99 (m, 4 H, 2',3'-H), 4.74 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 6.32 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.6 (+, OCH_2CH_3), 23.6, 24.5, 26.1, 29.1, 29.8, 34.3 (–, C-4,5,7',8',9',10'), 39.8, 41.8 [+, br., $N(CH_3)_2$], 44.9 (+, C-6'), 64.46, 64.54 (–, C-2',3'), 73.9 (–, OCH_2CH_3), 110.3 (C_{quat}, C-5'), 117.7 (+, C-2), 159.7 (C_{quat}, C-3), 219.4, 224.5 (C_{quat}, CO), 286.1 (C_{quat}, br., C-1). – EI MS (70 eV), *m/z* (%): 487 (2) [M^+], 459 (5) [M^+ – CO], 431 (1) [M^+ – 2 CO], 403 (3) [M^+ – 3 CO], 375 (4) [M^+ – 4 CO], 347 (65) [M^+ – 5 CO], 190 (100), 178 (78), 52 (11) [Cr^+]. –

Elemental analysis calcd (%) for $C_{22}H_{29}CrNO_8$ (487.5): C 54.21, H 6.00; found: C 54.31, H 5.87.

Pentacarbonyl[(2E)-5-(1',4'-dioxaspiro[4.5]dec-6'-yl)-3-dimethylamino-1-ethoxy-2-hexen-1-ylidene]chromium (**18m**): Following GP6, 4.55 g (21.9 mmol) of 6-(5'-hexynyl)-1,4-dioxa-spiro[4.5]decane (**42e**) in THF (100 mL) was treated with *n*-butyllithium (12.8 mL, 1.56 M in *n*-hexane, 20.0 mmol), hexacarbonylchromium (4.84 g, 22.0 mmol), Et_3OBF_4 (4.18 g, 22.0 mmol) and gaseous dimethylamine. Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 5 : 1 to 1 : 3) gave 8.96 g (90%) of **18m** [R_f = 0.33 (pentane/Et_2O = 1 : 1)] as a yellow solid, m. p. 109–111 °C (dec.). – IR (KBr): ν = 2941 cm^{-1} (C–H), 2044 (C=O), 1972 (C=O), 1911 (C=O), 1887 (C=O), 1534, 1435, 1263, 1085, 671. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13–1.82 (13 H) and 2.64–2.73 (2 H) [m, 15 H, 4,5,6, 6',7',8',9',10'-H], 1.49 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 3.13 [s, 6 H, $N(CH_3)_2$], 3.87–4.01 (m, 4 H, 2',3'-H), 4.71 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.33 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.7 (+, OCH_2CH_3), 23.7, 24.6, 25.9, 28.5, 29.3, 32.0, 34.5 (–, C-4,5,6,7',8',9', 10'), 40.1, 41.8 [+, br., $N(CH_3)_2$], 44.7 (+, C-6'), 64.6, 64.7 (–, C-2',3'), 73.8 (–, OCH_2CH_3), 110.6 (C_{quat}, C-5'), 117.7 (+, C-2), 158.9 (C_{quat}, C-3), 219.4, 224.4 (C_{quat}, CO), 287.6 (C_{quat}, C-1). – EI MS (70 eV), *m/z* (%): 501 (1) [M^+], 473 (6) [M^+ – CO], 445 (7) [M^+ – 2 CO], 417 (4) [M^+ – 3 CO], 389 (4) [M^+ – 4 CO], 361 (81) [M^+ – 5 CO], 266 (24), 204 (100), 154 (38), 122 (11), 110 (31), 52 (14) [Cr^+].

Pentacarbonyl[(2E)-3-dimethylamino-1-ethoxy-4-(2',5',5'-trimethyl-2'-oxo-cyclopentyl)-2-buten-1-ylidene]chromium (**18n**): Variation A: According to GP6, 3.63 g (22.1 mmol) of 2-(2'-propynyl)-2,5,5-trimethylcyclopentanone (**46**) in THF (200 mL) was added *n*-butyl-lithium (8.50 mL, 2.36 M in *n*-hexane, 20.1 mmol) at –78 °C over a period of 15 min. The mixture was, then, treated with hexacarbonylchromium (4.73 g, 21.5 mmol), Et_3OBF_4 (4.18 g, 22.0 mmol), and gaseous dimethylamine. Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 5 : 1 to 2 : 1) gave 4.60 g (50%) of **18n** [R_f = 0.74 (Et_2O)] as a yellow solid, m. p. 111–113 °C (dec.). – IR (KBr): ν = 2964 cm^{-1} (C–H), 2046 (C=O), 1907 (C=O), 1885 (C=O), 1733 (C=O), 1525, 1265. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85, 1.06, 1.09 (s, 9 H, CH_3), 1.49 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.60–1.80 (m, 4 H, 3',4'-H), 1.90–2.05 (m, 1 H, 4, 2'-H), 2.92–3.30 (m, 2 H, 4-H), 3.08 [s, 6 H, $N(CH_3)_2$], 4.73 (q, ^3J = 7.0 Hz,

2 H, OC*H*$_2$CH$_3$), 6.48 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 15.9 (+, OCH$_2$*C*H$_3$), 23.1, 24.9, 25.0 (+, CH$_3$), 30.4, 34.6, 36.2 (–, C-4,3',4'), 41.9, 42.1 [+, br., N(CH$_3$)$_2$], 44.8, 49.9 (C$_{quat}$, C-2',5'), 73.9 (–, O*C*H$_2$CH$_3$), 120.2 (C$_{quat}$, C-2), 155.2 (C$_{quat}$, C-3), 219.2, 224.3, 225.2 (C$_{quat}$, CO), 289.1 (C$_{quat}$, C-1). – EI MS (70 eV), *m/z* (%): 457 (14) [M$^+$], 429 (1) [M$^+$ – CO], 401 (1) [M$^+$ – 2 CO], 373 (9) [M$^+$ – 3 CO], 345 (19) [M$^+$ – 4 CO], 317 (100) [M$^+$ – 5 CO], 303 (21), 288 (25), 264 (23), 257 (24), 204 (20), 193 (13), 177 (13), 149 (24), 96 (16), 52 (16) [Cr$^+$]. – HRMS (EI) calcd for C$_{21}$H$_{27}$CrNO$_7$: 457.1193 (correct HRMS).

Variation B: like variation A, but this reaction was carried out in THF (100 mL), and *n*-butyllithium (12.8 mL, 1.56 M in *n*-hexane, 20.0 mmol) was dropwise added over a period of 15 min. This procedure gave 2.74 g (30%) of **18n**.

Variation C: like variation B, but this reaction was carried out in THF (150 mL), and *n*-butyllithium was added via a syringe pump over a period of 30 min. This procedure gave 4.23 g (46%) of **18n**.

Pentacarbonyl[(2E)-3-cyclohexenyl-3-dimethylamino-1-ethoxy-2-propen-1-ylidene]tungsten (**18o**): According to GP6, 2.50 mL (21.3 mmol) of 1-ethynyl-1-cyclohexene (**15h^1**) in THF (100 mL) was treated with *n*-butyllithium (9.00 mL, 2.36 M in *n*-hexane, 21.2 mmol), hexacarbonyltungsten (8.01 g, 22.8 mmol), Et$_3$OBF$_4$ (4.18 g, 22.0 mmol), and dimethylamine. Flash chromatography on silica gel (120 g) eluting with pentane/Et$_2$O (from 10 : 1 to 4 : 1) gave 9.77 g (87%) of **18o** [R_f = 0.53 (pentane/Et$_2$O = 1 : 1)] as a yellow solid, m. p. 92–94 °C (dec.). – IR (KBr): ν = 2938 cm^{-1} (C–H), 2054 (C=O), 1910 (C=O), 1888 (C=O), 1653, 1558, 1520, 1261. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.39 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.60–1.80 (m, 4 H, 4',5'-H), 2.00–2.20 (m, 4 H, 3',6'-H), 3.06 [s, 6 H, N(CH$_3$)$_2$], 4.54 (q, ^3J = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 6.30 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 15.8 (+, OCH$_2$*C*H$_3$), 21.3, 22.0, 24.7, 27.2 (C-3',4',5',6'), 40.5 [–, N(CH$_3$)$_2$], 76.3 (–, O*C*H$_2$CH$_3$), 120.0 (+, C-2), 126.9 (+, C-2'), 134.9 (C$_{quat}$, C-1'), 161.1 (C$_{quat}$, C-3), 199.9 (C$_{quat}$, CO), 204.3 (C$_{quat}$, CO), 267.8 (C$_{quat}$, C-1). – MS (70 eV), *m/z* (%): 531 (1) [M$^+$], 475 (1) [M$^+$ – CO], 443 (1) [M$^+$ – 2 CO], 369 (2) [M$^+$ – 5 CO], 207 (28), 179 (72), 150 (27), 124 (100), 69 (27), 43(28). – Elemental analysis calcd (%) for C$_{18}$H$_{21}$NO$_6$W (531.2): C 40.70, H 3.98; found: C 40.72, H 3.82.

3. Synthesis of Tricyclo[5.2.2.0^{1,6}]undec-9-ones

General Procedure for Cocyclizations of Complexes **18** *with Alkynes or Alkenes* **69** *(GP7):* A thick-walled, screw-cap Pyrex bottle equipped with a magnetic stirring bar is charged with a 0.05 M solution of the complex **18** in anhydrous pyridine. Dry nitrogen is bubbled through the solution for 2 min, and two equiv. of an alkyne (or alkene **69**) are immediately added. The sealed bottle is kept in an oil bath at 80 °C for 2–3 days. The solvent is removed under reduced pressure, the residue is diluted with Et_2O (100 mL), and the solution exposed to air for 2 h. The suspension is filtered off on a 3 cm thick layer of Celite and rinsed well with Et_2O (50 mL). The solvent of the filtrate is evaporated and the residue is subjected to chromatography on aluminum oxide (activity grade, II). Elution with pentane/Et_2O (from 1 : 0 to 3 : 1) affords cocyclization products.

11-(1'-Cyclohexenyl)-7-dimethylaminotricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25a**):
Following GP7, to a solution of 531 mg (1.00 mmol) of complex **18o** in pyridine (20 mL) was added 159 mg (1.50 mmol) of 1-ethynyl-1-cyclohexene (**15ah^1**), and the mixture was stirred at 80 °C for 2 d. Chromatography on aluminum oxide (II, 25 g) eluting with pentane/Et_2O (from 1 : 0 to 5 : 1) gave 69.0 mg (24%) of **25a** [R_f = 0.80 (pentane/Et_2O 1 : 1)] as a colorless solid. The ^{1}H- and ^{13}C-NMR spectra agreed with those which have previously been reported.[58]

11-(1'-Cyclopentenyl)-7-dimethylaminotricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25b**):
Variation A: Following GP7, to a solution of 1.11 g (2.78 mmol) of complex **18g** in 50 mL of pyridine was added 0.51 g (5.54 mmol) of 1-ethynyl-1-cyclopentene (**15i**), and the mixture was stirred at 80 °C for 60 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 5 : 1) gave 323 mg (43%) of **25b** [R_f = 0.82 (pentane/Et_2O = 3 :1)] as a pale-yellow solid, m. p. 64 °C. – IR (KBr): ν = 2934 cm^{-1} (C–H), 2922 (C–H), 2829 (C–H), 1734 (C=O), 1653 (C=C), 1457, 1309, 1115. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.39, 1.53–1.91, 2.15–2.25, 2.30–2.47 (m, 15 H, 2,3,4,5,6,3',4', 5'-H), 1.92 (ABM, dd, ^2J = 16.3, ^4J =2.3 Hz, 1 H, 8-H), 2.39 [s, 6 H, $N(CH_3)_2$], 2.51 (AB, d, ^2J = 16.3 Hz, 1 H, 8-H), 5.42 (s, 1 H, 10-H), 6.57 (br. s, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.1, 22.3, 23.1, 24.5, 26.4, 33.3, 34.0 (–, C-2,3,4,5,3', 4',5'), 37.4 (–, C-8), 40.4 [+,

$N(CH_3)_2$], 59.5 (+, C-6), 61.8 (C_{quat}, C-1), 74.3 (C_{quat}, C-7), 126.7 (+, C-2'), 129.3 (+, C-10), 136.4 (C_{quat}, C-11), 153.1 (C_{quat}, C-1'), 212.2 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 271 (100) [M^+], 242 (29), 229 (45), 214 (22), 200 (32), 179 (14), 162 (12). – Elemental analysis calcd (%) for $C_{18}H_{25}NO$ (271.4): C 79.66, H 9.28; found C 79.32, H 9.02.

Variation B: Following GP7, to a solution of 531 mg (1.00 mmol) of complex **18o** in 20 mL of pyridine was added 138 mg (1.50 mmol) of 1-ethynyl-1-cyclopentene (**15i**), and the mixture was stirred at 80 °C for 2 d. After chromatography on aluminum oxide (II, 20 g), 95.0 mg (35%) of **25b** was obtained.

11-(1'-Cycloheptenyl)-7-dimethylaminotricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25c**):
Following GP7, to a solution of complex **18g** (1.13 g, 2.83 mmol) of in pyridine (50 mL) was added 0.67 g (5.57 mmol) of 1-ethynyl-1-cycloheptene (**15i^2**), and the mixture was stirred at 80 °C for 60 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 5 : 1) gave 220 mg (26%) of **25c** [R_f = 0.56 (pentane/Et_2O = 3 : 1)] as a pale-yellow solid, m. p. 59 °C. – IR (KBr): ν = 2930 cm^{-1} (C–H), 2918 (C–H), 2845 (C–H), 1734 (C=O), 1653 (C=C), 1457, 1304, 1114. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.04–1.80, 2.19–2.32 (m, 19 H, 2,3,4, 5,6,3',4',5',6', 7'-H), 1.99 (ABM, dd, ^2J = 16.3, ^4J = 2.2 Hz, 1 H, 8-H), 2.36 [s, 6 H, $N(CH_3)_2$], 2.58 (AB, d, ^2J = 16.3 Hz, 1 H, 8-H), 5.42 (s, 1 H, 10-H), 6.71 (t, ^3J = 7.0 Hz, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.3, 23.1, 24.5, 26.2, 26.6, 26.7, 28.5, 30.0, 32.6 (–, C-2,3,4,5,3',4',5',6',7'), 37.3 (–, C-8), 40.0 [+, $N(CH_3)_2$], 58.9 (+, C-6), 61.3 (C_{quat}, C-1), 74.3 (C_{quat}, C-7), 124.9 (+, C-2'), 129.5 (+, C-10), 139.0 (C_{quat}, C-11), 157.8 (C_{quat}, C-1'), 212.1 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 299 (60) [M^+], 284 (100) [$M^+ – CH_3$], 270 (14), 256 (49), 179 (23), 150 (10), 84 (23). – HRMS (EI) calcd for $C_{20}H_{29}NO$: 229.2249 (correct HRMS).

7-Dimethylamino-11-(2'-propenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25d**): According to GP7, a solution of 1.24 g (2.33 mmol) of complex **18o** in 30 mL of pyridine was treated with 0.70 mL(7.58 mmol) of 2-methylbut-1-en-3-yne (**15l**), and the mixture was stirred at 80 °C for 2 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 250 mg (44%) of **25d** [R_f = 0.88 (pentane/Et_2O = 3 : 1)] as a colorless solid. The ^1H- and ^{13}C-NMR spectrum agreed with those which have previously been reported.[58]

7-Dimethylamino-11-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25e**): Following GP7, to a solution of 1.00 g (1.89 mmol) of complex **18o** in pyridine (30 mL) was treated with 0.70 mL (6.37 mmol) of phenylethyne (**15a**), and the mixture was stirred at 80 °C for 2 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 309 mg (58%) of **25e** [R_f = 0.85 (pentane/Et_2O = 3 : 1)] as a colorless solid. The ^{1}H- and ^{13}C-NMR spectra agreed with those which have previously been reported.[58]

7-Dimethylamino-11-(2'-thienyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25f**): According to GP7, to a solution of 1.01 g (2.54 mmol) of complex **18g** in 45 mL of pyridine was added 412 mg (3.81 mmol) of 2-ethynylthiophen (**29c**), and the mixture stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 245 mg (34%) of **25f** [R_f = 0.67 (pentane/Et_2O = 3 : 1)] as a pale yellow solid, m. p. 104–105 °C. – IR (KBr): ν = 2928 cm^{-1} (C–H), 1728 (C=O), 1315, 850, 831. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.11–1.47 (m, 4 H, 2,3,4,5-H), 1.60–1.74 (m, 2 H, 3,4-H), 1.83–1.88 (m, 1 H, 5-H), 2.05 (ABM, dd, ^2J = 16.3, ^4J = 2.4 Hz, 1 H, 8-H), 2.24–2.31 (m, 1 H, 2-H), 2.40–2.43 (m, 1 H, 6-H), 2.46 [s, 6 H, $N(CH_3)_2$], 2.63 (AB, d, ^2J = 16.3 Hz, 1 H, 8-H), 5.91 (s, 1 H, 10-H), 6.98 (dd, ^3J = 5.1, ^3J = 3.5 Hz, 1 H, 4'-H), 7.24 (dd, ^3J = 5.1, ^3J = 1.0 Hz, 1 H, 3'-H), 7.45 (dd, ^3J = 3.5, ^3J = 1.0 Hz, 1 H, 5'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 22.9, 24.2, 25.7 (–, C-2,3,4,5), 37.1 (–, C-8), 40.4 [+, $N(CH_3)_2$], 59.5 (+, C-6), 62.1 (C_{quat}, C-1), 74.0 (C_{quat}, C-7), 124.4, 125.0, 126.5, 126.8 (+, C-10,3',4',5'), 136.1 (C_{quat}, C-2'), 150.3 (C_{quat}, C-11), 211.0 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 287 (100) [M^+], 259 (39) [M^+ – CO], 245 (52) [M^+ – C_3H_6], 230 (12), 215 (19), 179 (17), 162 (34), 150 (14). – Elemental analysis calcd (%) for $C_{17}H_{21}NOS$ (287.4): C 71.04, H 7.36; found C 70.78, H 7.23.

7-Dimethylamino-11-(4'-methoxycarbonylphenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25j**): According to GP7, a solution of 1.04 g (2.61 mmol) of complex **18g** in pyridine (52 mL) was treated with 500 mg (3.12 mmol) of *p*-methynyl benzoic acid methyl ester (**29aa**[5]), and the mixture stirred at 80 °C for 60 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1)] gave 805 mg (91%) of **25j** [R_f = 0.26 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 151–152 °C. – IR (KBr): ν = 2936 cm^{-1} (C–H), 1745 (C=O), 1715 (C=O), 1607, 1432, 1321, 1284, 1113, 765, 701. – ^{1}H NMR (250 MHz, $CDCl_3$): δ =

1.00–1.45 (m, 4 H, 2,3,4,5-H), 1.50–1.70 (m, 2 H, 3,4-H), 1.80–1.90 (m, 1 H, 5-H), 2.10–2.30 (m, 2 H, 2,8-H), 2.33 [s, 6 H, $N(CH_3)_2$], 2.41–2.57 (m, 1 H, 6-H), 2.76 (AB, d, ^2J = 14.4 Hz, 1 H, 8-H), 3.86 (s, 3 H, CO_2CH_3), 5.96 (s, 1 H, 10-H), 7.64 (d, ^3J = 8.0 Hz, 2 H, Ph-H), 7.92 (d, ^3J = 8.0 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT) δ = 22.2, 22.9, 24.3, 26.0 (–, C-2,3,4,5), 37.0 (–, C-8), 40.1 [+, $N(CH_3)_2$], 51.9 (+, OCH_3), 59.7 (+, C-6), 62.5 (C_{quat}, C-1), 74.6 (C_{quat}, C-7), 125.1 (+, Ph-C), 128.8 (C_{quat}, Ph-C), 129.3 (+, Ph-C), 131.7 (+, C-10), 140.0 (C_{quat}, Ph-C), 155.6 (C_{quat}, C-11), 166.9 (C_{quat}, CO_2Me), 211.6 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 339 (100) [M^+], 311 (92) [M^+ – CO], 297 (84) [$M^+ – C_3H_6$], 282 (12), 268 (24), 242 (10), 179 (23), 162 (22), 150 (16), 59 (10). – Elemental analysis calcd (%) for $C_{21}H_{25}NO_3$ (339.4): C 74.31, H 7.42; found C 74.62, H 7.13.

7-Dimethylamino-11-(4'-ethoxycarbonylphenyl)-10-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25k**): Following GP7, to a solution of complex **18g** (815 mg, 2.04 mmol) in pyridine (40 mL) was added 705 mg (2.82 mmol) of *p*-phenylethynyl benzoic acid ethyl ester (**28aa**[15]), and the mixture was stirred at 80 °C for 56 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave 581 mg (66%) of **25k** [R_f = 0.25 (pentane/ Et_2O = 3 : 1)] as a colorless solid, m. p. 78 °C. – IR (KBr): ν = 2934 cm^{-1} (C–H), 1738 (C=O), 1714 (C=O), 1603 (C=C), 1280, 1107, 701. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14–1.35 (m, 4 H, 2,3,4,5-H), 1.32 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.60–1.78 (m, 2 H, 3,4-H), 1.85–1.95 (m, 1 H, 5-H), 2.01–2.10 (m, 1 H, 2-H), 2.36 [s, 6 H, $N(CH_3)_2$], 2.55 (ABM, dd, ^2J = 16.5, ^4J = 2.3 Hz, 1 H, 8-H), 2.68–2.73 (m, 1 H, 6-H), 2.76 (AB, d, ^2J = 16.5 Hz, 1 H, 8-H), 4.30 (q, ^3J = 7.1 Hz, 2 H, CH_2CH_3), 6.85–6.92 (m, 2 H, Ph-H), 7.10–7.16 (m, 3 H, Ph-H), 7.22–7.28 (m, 2 H, Ph-H), 7.80–7.85 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.2 (+, CH_2CH_3), 22.3, 22.7, 24.1, 25.4 (–, C-2,3,4,5), 38.2 (–, C-8), 40.0 [+, $N(CH_3)_2$], 60.1 (+, C-6), 60.7 (–, CH_2CH_3), 65.9 (C_{quat}, C-1), 74.6 (C_{quat}, C-7), 127.3, 128.0 × 2, 128.67, 128.70 (+, Ph-C), 133.9 (C_{quat}, C-10), 140.5 (C_{quat}, Ph-C), 143.2 (C_{quat}, Ph-C), 151.5 (C_{quat}, C-11), 166.3 (C_{quat}, CO_2Et), 211.8 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 429 (22) [M^+], 401 (17) [M^+ – CO], 387 (100) [$M^+ – C_3H_6$], 178 (30), 150 (7), 91 (9). – HRMS (EI) calcd for $C_{28}H_{31}NO_3$: 429.2303 (correct HRMS).

7-Dimethylamino-11-(2'-trifluoromethylphenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25l**): According to GP7, to a solution of 840 mg (2.10 mmol) of complex **18g** in 42 mL of pyridine was added 537 mg (3.16 mmol) of 2-ethynyl-benzotrifluoride (**29a^1**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/ Et_2O (from 1 : 0 to 3 : 1) gave 320 mg (44%) of **25l** [R_f = 0.33 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 135–136 °C. – IR (KBr): ν = 2935 cm^{-1} (C–H), 1741 (C=O), 1444, 1312, 1160, 1110, 1034, 770. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.12–1.47 (m, 4 H, 2,3,4,5-H), 1.59–1.72 (m, 2 H, 3,4-H), 1.80–1.88 (m, 1 H, 5-H), 2.24–2.30 (m, 1 H, 2-H), 2.30 [s, 6 H, $N(CH_3)_2$], 2.50 (ABM, dd, ^2J = 16.5, ^4J = 2.5 Hz, 1 H, 8-H), 2.57–2.62 (m, 1 H, 6-H), 2.74 (AB, d, ^2J = 16.5 Hz, 1 H, 8-H), 5.88 (s, 1 H, 10-H), 7.26–7.44 (m, 3 H, Ph-H), 7.66 (d, ^3J = 7.8 Hz, 1 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 22.9, 24.1, 25.4 (–, C-2,3,4,5), 39.0 (–, C-8), 40.1 [+, $N(CH_3)_2$], 61.3 (+, C-6), 63.5 (C_{quat}, C-1), 75.6 (C_{quat}, C-7), 126.5 (+, q, $^3J_{C\text{-}F}$ = 5.6 Hz, C-3'), 127.0, 127.1, 135.4 (+, C-4',5',6'), 127.5 (C_{quat}, q, ^2J = 29.6 Hz, C-2'), 130.2 (+, C-10), 134.2 (C_{quat}, q, ^3J = 4.2 Hz, C-1'), 152.7 (C_{quat}, C-11), 212.4 (C_{quat}, C-9). The signal of CF_3 carbon was not detected. – EI MS (70 eV), *m/z* (%): 349 (100) [M^+], 321 (58) [M^+ – CO], 307 (64) [$M^+ – C_3H_6$], 292 (14), 278 (24), 252 (11), 179 (22), 162 (14). – Elemental analysis calcd (%) for $C_{20}H_{22}NOF_3$ (349.4): C 68.75, H 6.35; found C 68.40, H 6.02.

7-Dimethylamino-11-(3'-trifluoromethylphenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25m**): Following GP7, to a solution of complex **18g** (1.40 mg, 3.51 mmol) in 40 mL of pyridine was added 896 mg (5.27 mmol) of 3-ethynylbenzotrifluoride (**29a^2**), and the mixture was stirred at 80 °C for 2 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 1.03 g (84%) of **25m** [R_f = 0.70 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 88–89 °C. – IR (KBr): ν = 2942 cm^{-1} (C–H), 1739 (C=O), 1331, 1241, 1162, 1129, 1073, 799. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15–1.42 (m, 4 H, 2,3,4,5-H), 1.59–1.78 (m, 2 H, 3,4-H), 1.80–1.92 (m, 1 H, 5-H), 2.21 (ABM, dd, ^2J = 16.4, ^4J = 2.5 Hz, 1 H, 8-H), 2.27–2.35 (m, 1 H, 2-H), 2.36 [s, 6 H, $N(CH_3)_2$], 2.47–2.54 (m, 1 H, 6-H), 2.72 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 5.98 (s, 1 H, 10-H), 7.35–7.50 (m, 2 H, Ph-H), 7.80–7.90 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.1, 22.9, 24.3, 26.0 (–, C-2,3,4,5), 37.0 (–, C-8), 40.1 [+, $N(CH_3)_2$], 59.8 (+, C-6), 62.3 (C_{quat}, C-1), 74.4 (C_{quat}, C-7), 122.1, 124.0 (+,

$^3J_{C\text{-}F}$ = 3.9 Hz, C-2',4'), 128.34, 128.36, 128.42 (+, C-10,5',6'), 130.4 (C_{quat}, q, $^2J_{C\text{-}F}$ = 32.1 Hz, C-3'), 131.0 (+, C-10), 136.0 (C_{quat}, C-1'), 155.0 (C_{quat}, C-11), 211.7 (C_{quat}, C-9). The signal of CF_3 was not detected. – EI MS (70 eV), *m/z* (%): 349 (100) [M^+], 321 (89) [M^+ – CO], 307 (72) [$M^+ – C_3H_6$], 292 (16), 278 (30), 162 (12). – Elemental analysis calcd (%) for $C_{20}H_{22}NOF_3$: C 68.75, H 6.35; found C 68.52, H 6.14.

7-Dimethylamino-11-(4'-trifluoromethylphenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25n**): Variation A: Following GP7, to a solution of complex **18g** (958 mg, 2.40 mmol) in 48 mL of pyridine was added 612 mg (3.60 mmol) of 4-ethynylbenzotrifluoride (**29a^3**), and the mixture was stirred at 80 °C for 2 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 714 mg (85%) of **25n** [R_f = 0.25 (pentane/Et_2O = 6 : 1)] as a colorless solid, m. p. 88–89 °C. – IR (KBr): ν = 2930 cm^{-1} (C–H), 1744 (C=O), 1616, 1327, 1162, 1126, 1068, 1017, 851, 819. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10–1.45 (m, 4 H, 2,3,4, 5-H), 1.57–1.72 (m, 2 H, 3,4-H), 1.84–1.91 (m, 1 H, 5-H), 2.14–2.35 (m, 2 H, 2,8-H), 2.34 [s, 6 H, $N(CH_3)_2$], 2.44–2.54 (m, 1 H, 6-H), 2.75 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 7.51 (m, ^2J = 8.2 Hz, 2 H, Ph-H), 7.70 (d, ^2J = 8.2 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.1, 22.9, 24.3, 26.0 (–, C-2,3,4,5), 36.9 (–, C-8), 40.0 [+, $N(CH_3)_2$], 59.7 (+, C-6), 62.5 (C_{quat}, C-1), 74.5 (C_{quat}, C-7), 124.2 (C_{quat}, q, ^1J = 273.3 Hz, CF_3), 124.9 (+, q, ^3J = 3.7 Hz, C-3',5'), 125.4 (+, C-2',5'), 129.2 (C_{quat}, q, ^2J = 32.3 Hz, C-4'), 131.6 (+, C-10), 138.9 (C_{quat}, C-1'), 155.1 (C_{quat}, C-11), 211.6 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 349 (100) [M^+], 321 (79) [M^+ – CO], 307 (66) [$M^+ – C_3H_6$], 292 (12), 278 (24), 270 (38), 179 (14), 162 (17), 150 (7). – Elemental analysis calcd (%) for $C_{20}H_{22}NOF_3$ (349.4): C 68.75, H 6.35; found C 68.43, H 6.28.

Variation B: Following GP7, to a solution of 531 mg (1.00 mmol) of complex **18o** in 20 mL of pyridine was added 255 mg (1.50 mmol) of 4-ethynylbenzotrifluoride (**29a^3**), and the mixture was stirred at 80 °C for 2 d. After chromatography on aluminum oxide (II, 20 g), 204 mg (58%) of **25o** was obtained.

7-Dimethylamino-11-(1'-naphthyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25o**): According to GP7, a solution of complex **18g** (827 mg, 2.07 mmol) in pyridine (40 mL) was treated with 473 mg (3.12 mmol) of 1-ethynylnaphthaline (**29b**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to

3 : 1) gave 358 mg (52%) of **25o** [R_f = 0.30 (pentane/Et_2O 3 : 1)] as a colorless solid, m. p. 159–160 °C. – IR (KBr): ν = 2943 cm^{-1} (C–H), 1740 (C=O), 1448, 1305, 1117, 1073, 799, 781.– ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20–1.60 (m, 4 H, 2,3,4,5-H), 1.62–1.95 (m, 3 H, 3,4,5-H), 2.30 [s, 6 H, $N(CH_3)_2$], 2.35–2.43 (m, 1 H, 2-H), 2.65 (ABM, dd, ^2J = 16.0, ^4J = 2.1 Hz, 1 H, 8-H), 2.78 (AB, d, ^2J = 16.0 Hz, 1 H, 8-H), 2.73–2.80 (m, 1 H, 6-H), 5.96 (s, 1 H, C-10), 7.38–7.52 (m, 4 H, Ar-H), 7.76 (d, ^3J = 7.9 Hz, 1 H, Ar-H), 7.84–7.88 (m, 1 H, Ar-H), 8.23–8.27 (m, 1 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.3, 23.1, 24.3, 25.2 (–, C-2,3,4,5), 38.8 (–, C-8), 40.1 [+, $N(CH_3)_2$], 61.5 (+, C-6), 63.3 (C_{quat}, C-1), 75.5 (C_{quat}, C-7), 122.9, 124.5, 125.2, 125.4, 125.8, 127.3, 128.5 (+, Ar-C), 131.1, 133.7, 133.8 (C_{quat}, Ar-C), 133.9 (+, C-10), 154.6 (C_{quat}, C-11), 212.5 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 331 (100) [M^+], 303 (32) [M^+ – CO], 289 (42) [M^+ – C_3H_6], 179 (70), 162 (20), 150 (18). – Elemental analysis calcd (%) for $C_{23}H_{25}NO$ (331.5): C 83.34, H 7.60; found C 83.09, H 7.41.

Variation B: Following GP7, to a solution of 531 mg (1.00 mmol) of complex **18o** in 20 mL of pyridine was added 228 mg (1.50 mmol) of 1-ethynylnaphthaline (**29b**), and the mixture was stirred at 80 °C for 2 d. After chromatography on aluminum oxide (II, 20 g), 174 mg (52%) of **25o** was obtained.

7-Dimethylamino-11-(2'-trimethylsilylethynyl)-10-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25p**): Following GP7, to a solution of complex **18g** (1.38 g, 3.46 mmol) in pyridine (40 mL) was added 655 mg (5.19 mmol) of 1-phenyl-4-trimethylsilyl-1,3-butadiyne (**15a^{16}j**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 60 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 613 mg (49%) of **25p** [R_f = 0.26 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 92–94 °C. – IR (KBr): ν = 293 cm^{-1} (C–H), 2132 (C≡C), 1744 (C=O), 1248, 843, 761, 696. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 1.00–1.34 (m, 4 H, 2,3,4,5-H), 1.61–1.74 (m, 3 H, 3,4,5-H), 2.33–2.57 (m, 4 H, 2,6,8-H), 2.73 [s, 6 H, $N(CH_3)_2$], 7.19–7.39 (m, 4 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.52 [+, $Si(CH_3)_3$], 22.6, 22.7, 23.57, 23.62 (–, C-2,3, 4,5), 39.7 (–, C-8), 39.8 [+, $N(CH_3)_2$], 62.0 (+, C-6), 65.1 (C_{quat}, C-1), 73.8 (C_{quat}, C-7), 101.2, 107.3 (C_{quat}, C-1',2'), 127.5, 127.7, 127.8 (+, Ph-C), 132.1, 133.5 (C_{quat}, C-10, Ph-C), 152.5 (C_{quat}, C-11), 211.9 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 377 (26) [M^+], 349 (7) [M^+ – CO], 335

(100) [$M^+ - C_3H_6$], 178 (11), 150 (6), 73 (10). – Elemental analysis calcd (%) for $C_{24}H_{31}NOSi$ (377.2): C 76.42, H 8.28; found C 76.07, H 8.59.

7-Dimethylamino-11-phenylethynyl-10-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25q**): Following GP7, a solution of 799 mg (2.00 mmol) of complex **18g** in 40 mL of pyridine was treated with 117 mg (0.58 mmol) of 1,4-diphenyl-1,3-butadiyne (**54f**), and the mixture stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 23.0 mg of **48q** [R_f = 0.26 (pentane/Et_2O = 3 : 1)] as a pale-yellow oil, and 225 mg of a mixture (**25q** : **48q** = 10 : 1). Then, the both fractions were dissolved in Et_2O (50 mL), treated with a 2 N solution of hydrochloric acid (2 mL), and the mixture stirred overnight (ca. 8 h). The reaction was quenched with a solution of Na_2CO_3 (ca. 5 g in 10 mL of water), and extracted with Et_2O (3 × 50 mL). The combined organic phase was dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to chromato-graphy on aluminum oxide (II, 40 g). Elution with pentane/Et_2O (1 : 1) afforded 184 mg (83% from alkyne **54f**) of **25q** [R_f = 0.16 (pentane/Et_2O = 3 : 1)] as a colorless solid. The ^{1}H- and ^{13}C-NMR spectra agreed with those which have previously been reported.[58]

7-Dimethylamino-10-phenyl-11-(4'-phenyl-1'-buten-3'-ynyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25r**): Following GP7, to a solution of 958 mg (2.40 mmol) of complex **18g** in 50 mL of pyridine was added 535 mg (2.34 mmol) of (*E*)-1,2-di(phenyl-ethynyl)ethene (**28daa**), and the mixture was stirred at 80 °C for 56 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave 461 mg (48%) of **25r** [R_f = 0.55 (pentane/Et_2O = 3 : 1)] as a pale-yellow solid, m. p. 132 °C. – IR (KBr): ν = 2930 cm^{-1} (C–H), 1737 (C=O), 1488, 1443, 1314, 964, 753, 712, 687. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.04–1.31 (m, 4 H, 2,3,4,5-H), 1.58–1.72 (m, 2 H, 3,4-H), 1.87–1.92 (m, 1 H, 5-H), 2.15 (ABM, dd, ^2J = 16.5, ^4J = 4.0 Hz, 1 H, 8-H), 2.31–2.36 (m, 1 H, 2-H), 2.52 [s, 6 H, $N(CH_3)_2$], 2.52–2.60 (m, 1 H, 6-H), 2.78 (AB, d, ^2J = 16.5 Hz, 1 H, 8-H), 6.78 (d, ^3J = 15.9 Hz, 1 H, 1'-H), 7.10–7.42 (m, 11 H, 2'-H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.0, 22.2, 23.8, 26.0 (–, C-2,3,4,5), 36.9 (–, C-8), 39.9 [+, $N(CH_3)_2$], 58.4 (+, C-6), 64.5 (C_{quat}, C-1), 73.5 (C_{quat}, C-7), 90.3 (C_{quat}, C-4'), 93.3 (C_{quat}, C-3'), 111.1 (+, C-1'), 123.3 (C_{quat}, Ph-C), 127.4, 127.8, 128.0, 128.1 × 2, 131.2 (+, Ph-C), 133.8 (C_{quat}, Ph-

C), 133.9 (+, C-2'), 144.5 (C_{quat}, C-10), 145.8 (C_{quat}, C-11), 211.1 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 407 (53) [M^+], 365 (100) [$M^+ - C_3H_6$], 336 (14), 178 (48), 150 (12). – Elemental analysis calcd (%) for $C_{29}H_{29}NO$ (407.6): C 85.47, H 7.17; found C 85.60, H 7.04.

10-Cyclopropyl-11-(4'-cyclopropyl-1'-buten-3'-ynyl)-7-dimethylaminotricyclo[5.2.2.0^{1,6}]-undec-10-en-9-one (**25s**): Following GP7, to a solution of complex **18g** (1.41 g, 3.53 mmol) in pyridine (40 mL) was added 247 mg (1.58 mmol) of (*E*)-1,2-di(cyclopropylethynyl)ethene (**28dgg**), and the mixture was stirred at 80 °C for 60 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 251 mg (47%) of **25s** [R_f = 0.45 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 187 °C. – IR (KBr): ν = 2934 cm^{-1} (C–H), 1732 (C=O), 1458, 1311, 1026, 966, 891. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.40–0.55 (m, 2 H, *c*Pr-H), 0.62–0.85 (m, 6 H, *c*Pr-H), 1.02–1.29 (m, 4 H, 2,3,4,5-H), 1.33–1.45 (m, 2 H, *c*Pr-H), 1.57–1.67 (m, 2 H, 3,4-H), 1.75–1.80 (m, 1 H, 5-H), 1.93 (ABM, dd, ^2J = 16.2, ^4J = 2.2 Hz, 1 H, 8-H), 2.21–2.27 (m, 1 H, 2-H), 2.30–2.34 (m, 1 H, 6-H), 2.37 [s, 6 H, $N(CH_3)_2$], 2.55 (AB, d, ^2J = 16.2 Hz, 1 H, 8-H), 6.57 (ABM, dd, ^3J = 16.2, ^5J = 1.8 Hz, 1 H, 2'-H), 6.77 (AB, d, ^3J = 16.0 Hz, 1 H, 1'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.5 (+, *c*Pr-C), 5.0, 5.9 (–, *c*Pr-C), 8.1 (+, *c*Pr-C), 8.7 × 2 (–, *c*Pr-C), 22.25, 22.29, 24.3, 26.2 (–, C-2,3,4,5), 37.3 (–, C-8), 40.0 [+, $N(CH_3)_2$], 58.3 (+, C-6), 65.5 (C_{quat}, C-1), 72.9 (C_{quat}, C-7), 76.6 (C_{quat}, C-4'), 96.6 (C_{quat}, C-3'), 110.2 (+,C-1'), 132.4 (+, C-2'), 142.7 (C_{quat}, C-10), 147.0 (C_{quat}, C-11), 211.6 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 335 (43) [M^+], 320 (14), 293 (53) [$M^+ - C_3H_6$], 278 (46), 178 (100), 150 (26). – Elemental analysis calcd (%) for $C_{23}H_{29}NO$ (335.5): C 82.34, H 8.71; found C 82.58, H 8.66.

7-Dimethylamino-11-(4'-ethynylphenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25t**):
Following GP7, to a solution of complex **18g** (1.38 g, 3.46 mmol) in pyridine (40 mL) was added 655 mg (5.19 mmol) of 1,4-diethynylbenzene (**29a**[7]), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 728 mg (69%) of **25t** [R_f = 0.52 (pentane/Et_2O 3 : 1)] as a colorless solid, m. p. 138–139 °C. – IR (KBr): ν = 3286 cm^{-1} (C≡C–H), 2937 (C–H), 1742 (C=O), 1455, 1316, 1299, 847, 815. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.15–1.37 (m, 4 H, 2,3,4,5-

H), 1.54–1.74 (m, 2 H, 3,4-H), 1.78–1.85 (m, 1 H, 5-H), 2.15 (ABM, dd, ^2J = 16.4, ^4J = 2.3 Hz, 1 H, 8-H), 2.22–2.30 (m, 1 H, 2-H), 2.31 [s, 6 H, $N(CH_3)_2$], 2.41–2.50 (m, 1 H, 6-H), 2.70 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 3.09 (s, 1 H, C≡CH), 7.36 (d, ^2J = 8.3 Hz, 2 H, Ph-H), 7.56 (d, ^2J = 8.3 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.0, 22.8, 24.2, 25.9 (–, C-2,3,4,5), 36.8 (–, C-8), 39.9 [+, $N(CH_3)_2$], 59.4 (+, C-6), 62.1 (C_{quat}, C-1), 74.3 (C_{quat}, C-7), 77.5 (+, C≡*C*H), 83.6 (C_{quat}, C≡*C*H), 120.8 (C_{quat}, Ph-C), 125.0 (+, Ph-C), 130.2 (+, C-10), 131.6 (+, Ph-C), 135.6 (C_{quat}, Ph-C), 155.3 (C_{quat}, C-11), 211.5 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 305 (100) [M^+], 272 (56) [M^+ – CO], 263 (54) [$M^+ – C_3H_6$], 234 (17), 179 (19), 162 (19), 150 (14). – Elemental analysis calcd (%) for $C_{21}H_{23}NO$ (305.2): C 82.59, H 7.59; found C 82.33, H 7.46.

Variation B: Following GP7, to a solution of 1.06 g (2.00 mmol) of complex **18o** in 40 mL of pyridine was added 432 mg (3.42 mmol) of 1,4-diethynylbenzene (**29a**[7]), and the mixture was stirred at 80 °C for 2 d. After chromatography on aluminum oxide (II, 40 g), 377 mg (62%) of **25t** was obtained.

7-Dimethylamino-11-(3',5'-diethynylphenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25u**):

Following GP7, to a solution of complex **18g** (978 mg, 2.45 mmol) in pyridine (45 mL) was added 557 mg (3.71 mmol) of 1,3,5-triethynylbenzene (**29a**[10]), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (activity grade II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 525 mg (65%) of **25u** [R_f = 0.45 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 174–175 °C (dec.). – IR (KBr): ν = 3282 cm^{-1} (C≡C–H), 3258 (C≡C–H), 2933 (C–H), 2111 (C≡C), 1737 (C=O), 1313, 880, 829. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10–1.45 (m, 4 H, 2,3,4,5-H), 1.56–1.74 (m, 2 H, 3,4-H), 1.84–1.90 (m, 1 H, 5-H), 2.19 (ABM, dd, ^2J = 16.4, ^4J = 1.9 Hz, 1 H, 8-H), 2.25–2.35 (m, 2 H, 2,6-H), 2.37 [s, 6 H, $N(CH_3)_2$], 2.75 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 3.07 (s, 2 H, C≡CH), 5.94 (s, + 1 H, 10-H), 7.49 (s, 1 H, Ph-H), 7.71 (s, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.0, 22.8, 24.2, 25.9 (–, C-2,3,4,5), 36.9 (–, C-8), 40.1 [+, $N(CH_3)_2$], 59.8 (+, C-6), 62.3 (C_{quat}, C-1), 74.3 (C_{quat}, C-7), 77.7 (+, C≡*C*H), 82.6 (C_{quat}, C≡*C*H), 122.1 (C_{quat}, Ph-C), 129.1 (+, Ph-C), 131.1, 134.3 (+, C-10, Ph-C), 135.9 (C_{quat}, Ph-C), 154.5 (C_{quat}, C-11), 211.6 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 329 (100) [M^+], 301 (74) [M^+ – CO], 287

(70) [$M^+ - C_3H_6$], 258 (22), 179 (14), 162 (14), 150 (19). – Elemental analysis calcd (%) for $C_{23}H_{23}NO$ (329.2): C 83.86, H 7.04; found C 83.59, H 6.85.

7-Dimethylamino-11-(9',9'-di-n-hexyl-2'-fluorenyl)-10-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25v**): Following GP2, to a solution of complex **18g** (798 mg, 2.00 mmol) in pyridine (40 mL) was added 850 mg (2.25 mmol) of 9,9-dihexyl-2-ethynylfluorene (**29e**), and the mixture was red at 80 °C for 48 h. Chromatography on aluminum oxide (II, 50 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 546 mg (51%) of **25v** [R_f = 0.46 (pentane/Et_2O = 9 : 1)] as a pale-yellow oil. – IR (KBr): ν = 2930 cm^{-1} (C–H), 1742 (C=O), 1454, 1131, 1114, 817, 739. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70–0.84 (m, 10 H, hexyl-H), 1.00–1.49 [m, 16 H, 2,3,4,5-H (4 H), hexyl-H (12 H)], 1.64–1.78 (m, 2 H, 3,4-H), 1.89-2.02 [m, 5 H, 5-H (1 H), hexyl-H (4 H)], 2.43 (m, 2 H, 2,8-H), 2.43 [s, 6 H, $N(CH_3)_2$], 2.57–2.62 (m, 1 H, 6-H), 2.84 (d, ^2J = 16.4 Hz, 1 H, 8-H), 5.95 (s, 1 H, 10-H), 7.26–7.38 (m, 3 H, Ar-H), 7.57–7.71 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.86, 13.87 (+, hexyl CH_3), 22.2, 23.0, 24.3, 26.0 (–, C-2,3,4,5), 22.4, 22.5, 23.5, 23.6, 29.5, 29.7, 31.3, 31.4, 40.2 × 2 (–, C-hexyl), 37.2 (–, C-8), 40.0 [+, $N(CH_3)_2$], 54.8 (C_{quat}, C-9'), 59.7 (+, C-6), 62.0 (C_{quat}, C-1), 74.3 (C_{quat}, C-7), 119.1, 119.5, 119.6, 112.6, 124.1, 126.6, 126.8 (+, Ar-C), 128.4 (+, C-10), 134.2, 140.4, 140.7, 150.1, 150.8 (C_{quat}, Ar-C), 157.0 (C_{quat}, C-11), 211.8 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 537 (100) [M^+], 509 (37) [$M^+ - CO$], 495 (44) [$M^+ - C_3H_6$], 179 (12). – HRMS (EI) calcd for $C_{38}H_{51}NO$: 537.3971 (correct HRMS).

7-Dimethylamino-10-(9',9'-di-n-hexyl-2'-fluorenyl)-11-[(9'',9''-dihexyl-2''-fluorenyl)ethynyl]-tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25w**): Following GP7, to a solution of complex **18g** (799 mg, 2.00 mmol) in pyridine (40 mL) was added 1.45 g (2.03 mmol) of 1,4-bis(9',9'-dihexyl-2'-fluorenyl)-1,3-butadiyne (**54d**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 60 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave 1.03 g (57%) of **25w** [R_f = 0.36 (pentane/Et_2O = 3 : 1)] as a pale-yellow oil. – UV (CH_3CN): λ_{max} (lg ε) = 310 nm (4.34), 360 (4.25). – IR (film): ν = 2929 cm^{-1} (C–H), 1742 (C=O), 1451, 1310, 1131, 832, 740. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.67–0.83 (br. m, 20 H, hexyl-H), 1.00–1.49 [br. m, 28 H, 2,3,4,5-H (4 H), hexyl-H (24 H)], 1.64–2.05 (br. m, 11 H, 3,4,5-H (3 H), hexyl-H (8 H)], 2.50–2.90 (m, 4 H, 2,6,8-H), 2.90 [s, 6 H, $N(CH_3)_2$],

7.30–7.44 (m, 9 H, Ar-H), 7.53–7.77 (m, 5 H, Ar-H). – ^{13}C NMR (62.9 MHz $CDCl_3$, plus DEPT): δ = 14.0 × 4 (+, hexyl CH_3), 22.8, 23.0, 23.8, 24.0 (–, C-2,3,4,5), 22.6 × 4, 23.7 × 4, 29.6 × 3, 29.7, 31.5 × 3, 31.6, 40.1, 40.2 × 3, 40.4 (–, hexyl CH_2, C-8), 40.16 [+, $N(CH_3)_2$], 55.1 × 2 (C_{quat}, C-9',9''), 62.0 (+, C-6), 65.4 (C_{quat}, C-1), 74.1 (C_{quat}, C-7), 86.3, 101.7 (C_{quat}, C≡C), 119.0, 119.7, 119.7, 120.0, 121.6, 121.9, 122.87, 122.89, 125.1, 126.7 × 2, 126.9, 126.9, 127.1, 127.6 (+, Ar-C), 130.2, 131.7, 132.8, 140.3., 140.8 × 2, 141.7 (C_{quat}, C-10, Ar-C), 150.5, 150.9, 151.0 × 2, 151.6 (C_{quat}, C-11, Ar-C), 211.9 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 893 (38) [M^+], 852 (64), 851 (100) [$M^+ – C_3H_6$], 178 (10). – Elemental analysis calcd (%) for $C_{65}H_{83}NO$ (894.4): C 87.29, H 9.35; found C 87.39, H 9.04.

7-Dimethylamino-11-(9',9'-dihexyl-7'-ethynyl-2'-fluorenyl)tricyclo[5.2.2.0^{1,6}]-undec-10-en-9-one (**25x**): Following GP7, to a solution of complex **18g** (799 mg, 2.00 mmol) in pyridine (40 mL) was added 574 mg (3.00 mmol) of 2,7-diethynyl-9,9-dihexylfluorene (**29f**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 60 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 505 mg (45%) of **25x** [R_f = 0.63 (pentane/ Et_2O 3 : 1)] as a colorless semi-solid. – IR (KBr): ν = 3302 cm^{-1} (C≡C–H), 2930 (C–H), 2914 (C≡C), 1739 (C=O), 1607 (C=C), 1465, 1311, 1265, 1114, 816, 739. – ^{1}H NMR (250 MHz, $CDCl_3$): δ =0.55–0.70 (m, 4 H, hexyl-H), 0.76 (t, ^3J = 6.5 Hz, 3 H, hexyl CH_3), 0.77 (t, ^3J = 6.5 Hz, 3 H, hexyl CH_3), 1.00–1.43 [m, 16 H, 2,3,4,5-H (4 H), hexyl-H, (12 H)], 1.62–1.78 (m, 2 H, 3,4-H), 1.83–2.01 [m, 5 H, 5-H (1 H), hexyl-H (4 H)], 2.07–2.30 (m, 2 H, 2,8-H), 2.39 [s, 6 H, $N(CH_3)_2$], 2.52–2.63 (m, 1 H, 6-H), 2.80 (d, ^2J = 16.4 Hz, 1 H, 8-H), 3.14 (s, 1 H, C≡CH), 5.93 (s, 1 H, 10-H), 7.45–7.48 (m, 2 H, Ar-H), 7.57–7.63 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 × 2 (+, hexyl CH_3), 22.3, 23.1, 24.5, 26.1 (–, C-2,3,4,5), 22.5, 22.6, 23.6, 23.7, 29.6, 29.8, 31.5, 31.6, 40.3 × 2 (–, hexyl CH_2), 37.4 (–, C-8), 40.1 [+, $N(CH_3)_2$], 55.0 (C_{quat}, C-9'), 59.8 (+, C-6), 62.3 (C_{quat}, C-1), 74.3 (+, C≡*C*H), 84.7 (C_{quat}, *C*≡CH), 119.5, 119.65, 119.72, 124.4, 126.4, 129.0, 131.1 (+, C-10, Ar-C), 120.0, 135.0, 141.7, 139.6, 150.7, 151.0 (C_{quat}, Ar-C), 157.0 (C_{quat}, C-11), 212.2 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 561 (100) [M^+], 533 (24) [$M^+ – CO$], 519 (32) [$M^+ – C_3H_6$]. – HRMS (EI) calcd for $C_{40}H_{51}NO$: 561.3971 (correct HRMS).

7-Dimethylamino-10-(9',9'-di-n-hexyl-7'-phenylethynyl-2'-fluorenyl)-11-[(9'',9''-dihexyl-7''-phen-ylethynyl-2''-fluorenyl)ethynyl]tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25y**): Following GP7, to a solution of complex **18g** (336 mg, 0.84 mmol) in 40 mL of pyridine was added 770 mg (0.84 mmol) of 1,4-bis(7'-phenyl-ethynyl-9',9'-dihexyl-2'-fluorenyl)-1,3-butadiyne (**54e**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 50 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave 313 mg (34%) of **25y** [R_f = 0.77 (Et_2O)] as a pale-yellow solid, m. p. 107–108 °C.– UV (CH_3CN): λ_{max} (lg ε) = 339 nm (5.05). – IR (KBr): ν = 2927 cm^{-1} (C–H), 2851 (C–H), 1741 (C=O), 1492, 1464, 821, 754, 689. – ^{1}H NMR (250 MHz, $CDCl_3$): δ =0.65–0.82 (m, 20 H, hexyl-H), 1.00–1.20 [m, 28 H, 2,3,4,5-H (4 H), hexyl-H (24 H)], 1.64–2.10 [m, 11 H, 3,4,5-H (3 H), hexyl-H (8 H)], 2.45–2.80 (m, 4 H, 2,6,8-H), 2.89 [s, 6 H, $N(CH_3)_2$], 7.31–7.42 (m, 9 H, Ph-H), 7.53–7.72 (m, 13 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 × 4 (+, hexyl CH_3), 22.5, 22.6 × 3, 23.6 × 3, 23.7, 29.6 × 3, 29.7, 31.4 × 3, 31.6, 39.9, 40.17 × 3, 40.4 (–, C-8, hexyl CH_2), 22.7, 22.9, 23.8, 23.9 (–, C-2,3,4,5), 40.12 [+, $N(CH_3)_2$], 55.2 (C_{quat}, C-9',9''), 61.9 (+, C-6), 65.3 (C_{quat}, C-1), 74.1 (C_{quat}, C-7), 86.5, 89.5, 89.8, 90.3, 90.5, 101.6 (C_{quat}, C≡C), 119.4, 119.7, 119.9, 120.0, 121.8, 125.0, 125.9, 126.0, 126.8, 128.1, 128.2, 128.3 × 4, 130.3, 130.6, 130.7 131.5 × 4 (+, Ar-C), 121.5, 121.95, 122.02, 123.2, 123.3, 131.9, 133.2 × 2, 150.8, 151.0 × 3, 151.2 × 2, 151.5 (C_{quat}, C-10,11, Ar-C), 211.9 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 1094 (16) [M^+], 1052 (100) [$M^+ – C_3H_6$], 1037 (18), 526 (12). – Elemental analysis calcd (%) for $C_{81}H_{91}NO$ (1094.6): C 88.88, H 8.38; found C 88.59, H 8.60.

1-Dimethylamino-3-ethoxy-3aH-tetrahydroindene (**64**): Variation A: A solution of 10.0 mg of complex **18g** in 0.5 mL of [D_5]-pyridine under nitrogen was kept at ambient temperature for 16 h. – ^{1}H NMR (500 MHz, [D_5]-pyridine, plus CH COSY and HH NOESY): δ = 1.02 ("q"d, ^2J = 12.5, ^3J = 12.5, ^3J = 3.0 Hz, 1 H, 4-H), 1.08–1.19 (m, 1 H, 6-H), 1.24 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.27–1.33 (m, 1 H, 5-H), 1.63–1.78 (m, 2 H, 5,6-H), 1.90–2.03 (m, 1 H, 7-H), 2.25–2.33 (m, 1 H, 4-H), 2.60 [s, 6 H, $N(CH_3)_2$], 2.67 (dd, ^3J = 12.5, ^3J = 4.5 Hz, 1 H, 3*a*-H), 2.92–3.00 (m, 1 H, 7-H), 3.90 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.12 (s, 1 H, 2-H). – ^{13}C NMR (75 MHz, [D_5]-pyridine, plus APT): δ = 15.7 (+, OCH_2CH_3), 24.4, 26.3, 28.9, 32.6 (–, C-4,5,6,7), 41.1 [+, $N(CH_3)_2$], 47.2 (+, C-3*a*), 65.4 (–, OCH_2CH_3), 94.6 (+, C-2), 107.5 (–, C-7a), 150.0 (–, C-1), 160.9 (–, C-3).

Variation B: A solution of 14.0 mg of complex **18o** in 0.5 mL of [D_5]-pyridine under nitrogen was kept at ambient temperature over 2 d.

7-Dimethylamino-9-ethoxy-11-phenyltricyclo[5.2.2.0^{1,6}]undec-8-ene (**70a**): Following GP7, to a solution of 813 mg (2.04 mmol) of complex **18g** in 40 mL of pyridine was added 0.47 mL (4.06 mmol) of styrene (**69a**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 374 mg (66%) of **70a** [R_f = 0.60 (pentane/Et_2O 3 : 1)] as a colorless solid, m. p. 57 °C. – IR (KBr): ν = 2924 cm^{-1} (C–H), 1621 (C=C), 1446, 1347, 1245, 1081, 1036, 754. – ^{1}H NMR (250 MHz, $CDCl_3$, plus CH COSY and HH NOESY): δ = 0.95–1.36 (m, 3 H, 2,3,4-H), 1.45 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.47–1.72 (m, 5 H, 3,4,5,10-H), 1.87 (t, ^3J = 7.7 Hz, 3 H, 6-H), 2.02 (dd, ^2J = 11.9, ^3J = 9.5 Hz, 1 H, *10-endo*-H), 2.16–2.22 (m, 1 H, 2-H), 2.43 [s, 6 H, $N(CH_3)_2$], 3.70 (dd, ^3J = 9.5, ^3J = 4.8 Hz, 1 H, 11-H), 3.94 (q, ^3J = 7.0 Hz, 2 H, CH_2CH_3), 4.46 (s, 1 H, 8-H), 7.13–7.28 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.5 (+, CH_2CH_3), 23.4, 23.6, 24.5, 27.7 (–, C-2,3,4,5), 39.9 [+, $N(CH_3)_2$], 44.2 (–, C-10), 45.5 (+, C-11), 50.8 (C_{quat}, C-1), 59.9 (+, C-6), 64.1 (–, CH_2CH_3), 80.5 (C_{quat}, C-7), 93.3 (+, C-8), 125.4, 127.2, 129.1 (+, Ph-C), 144.9 (C_{quat}, Ph-C), 161.9 (C_{quat}, C-9). – DCI MS (70 eV), *m/z* (%): 329 (2) [M + NH_4^+], 312 (100) [M + H^+]. – Elemental analysis calcd (%) for $C_{21}H_{29}NO$ (331.5): C 80.98, H 9.38; found C 80.92, H 9.09.

7-Dimethylamino-9-ethoxy-11-(3'-methylphenyl)tricyclo[5.2.2.0^{1,6}]undec-8-ene (**70b**): Following GP7, to a solution of complex **18g** (839 mg, 2.10 mmol) in pyridine (42 mL) was added 0.55 mL (4.20 mmol) of 3-methylstyrene (**69b**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 370 mg (54%) of **70b** [R_f = 0.56 (pentane/Et_2O 3 : 1)] as a colorless solid, m. p. 56–58 °C – IR (KBr): ν = 2936 cm^{-1} (C–H), 1623 (C=C), 1444, 1346, 1220, 1084, 756. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.01–1.45 (m, 3 H, 2,3,4-H), 1.51 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.61–1.78 (m, 5 H, 3,4,5,10-H), 1.92 (t, ^3J = 7.5 Hz, 3 H, 6-H), 2.06 (dd, ^2J = 11.9, ^3J = 9.5 Hz, 1 H, 10-*endo*-H), 2.22–2.39 (m, 1 H, 2-H), 2.41 (s, 3 H, CH_3), 2.49 [s, 6 H, $N(CH_3)_2$], 3.71 (dd, ^3J = 9.5, ^3J = 4.7 Hz, 1 H, 11-H), 4.00 (q, ^3J = 7.0 Hz, 1 H, CH_2CH_3), 4.01 (q, ^3J = 7.0 Hz, 1 H, CH_2CH_3), 4.53 (s, 1 H, 8-H), 7.04–7.23 (m, 4 H, Ph-H). – ^{13}C

NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.8 (+, CH_2CH_3), 21.7 (+, CH_3), 23.7, 23.8, 24.7, 28.0 (–, C-2,3,4,5), 40.1 [+, $N(CH_3)_2$], 44.5 (–, C-10), 45.7 (+, C-11), 51.0 (C_{quat}, C-1), 60.1 (+, C-6), 64.3 (–, CH_2CH_3), 80.7 (C_{quat}, C-7), 93.7 (+, C-8), 126.4, 126.5, 127.3, 130.2 (+, Ph-C), 136.5, 145.0 (C_{quat}, Ph-C), 161.9 (C_{quat}, C-9). – DCI MS (70 eV), *m/z* (%): 326 (100) [M + H^+], 207 (28). – Elemental analysis calcd (%) for $C_{22}H_{31}NO$ (325.5): calcd C 81.18, H 9.60; found C 80.97, H 9.36.

7-Dimethylamino-9-ethoxy-11-(4'-methylphenyl)tricyclo[5.2.2.0^{1,6}]undec-8-ene (**70c**):
Following GP7, to a solution of complex **18g** (814 mg, 2.04 mmol) in pyridine (40 mL) was added 0.53 mL (4.01 mmol) of 4-methylstyrene (**69c**), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 378 mg (57%) of **70c** [R_f = 0.57 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 83–85 °C. – IR (KBr): ν = 2926 cm^{-1} (C–H), 1623 (C=C), 1457, 1242, 1083, 1033, 772. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.08–1.41 (m, 3 H, 2,3,4-H), 1.46 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.56–1.73 (m, 5 H, 3,4,5,10-H), 1.87 (t, ^3J = 7.6 Hz, 3 H, 6-H), 2.01 (dd, ^2J = 11.9, ^3J = 9.5 Hz, 1 H, 10-*endo*-H), 2.16–2.25 (m, 1 H, 2-H), 2.35 (s, 3 H, CH_3), 2.44 [s, 6 H, $N(CH_3)_2$], 3.66 (dd, ^3J = 9.5, ^3J = 4.7 Hz, 1 H, 11-H), 3.96 (q, ^3J = 7.0 Hz, 2 H, CH_2CH_3), 4.47 (s, 1 H, 8-H), 7.04–7.12 (br. s, 4 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.6 (+, CH_2CH_3), 20.9 (+, CH_3), 23.5, 23.6, 24.5, 27.7 (–, C-2,3,4,5), 40.0 [+, $N(CH_3)_2$], 44.3 (–, C-10), 45.2 (+, C-11), 50.8 (C_{quat}, C-1), 59.9 (+, C-6), 64.1 (–, CH_2CH_3), 80.4 (C_{quat}, C-7), 93.4 (+, C-8), 128.0, 129.0 (+, Ph-C), 134.7, 141.8 (C_{quat}, Ph-C), 161.9 (C_{quat}, C-9). – DCI MS (70 eV), *m/z* (%): 326 (100) [M + H^+], 208 (7). – Elemental analysis calcd (%) for $C_{22}H_{31}NO$ (325.5): C 81.18, H 9.60; found C 81.03, H 9.44.
Variation B: Following GP7, to a solution of 531 mg (1.00 mmol) of complex **18o** in 20 mL of pyridine was added 177 mg (1.50 mmol) of 4-methylstyrene (**69c**), and the mixture was stirred at 80 °C for 2 d. After chromatography on aluminum oxide (II, 20 g), 62.0 mg (19%) of **70c** was obtained.

1,4-Bis[7'-(dimethylamino)tricyclo[5.2.2.0^{1,6}]undec-10'-en-9'-oxo-11'-yl]benzene (**72a**):
Variation A: Following GP7, to a solution of 2.72 g (6.82 mmol) of complex **18g** in 45 mL of pyridine was added 280 mg (2.22 mmol) of 1,4-diethynyl-benzene (**29a**[7]), and the mixture

was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 2) gave 82.0 mg (8%) of **72a** [R_f = 0.20 (pentane/Et_2O = 1 : 1)] as a colorless solid, m. p. > 230 °C. – IR (KBr): ν = 2939 cm^{-1} (C–H), 1734 (C=O), 1450, 1309, 1122. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.17–1.41 (m, 8 H, 2',3',4',5'-H), 1.59–1.75 (m, 4 H, 3',4'-H), 1.84–1.90 (m, 2 H, 5'-H), 2.23 (ABM, dd, ^2J = 16.4, ^4J = 2.1 Hz, 1 H, 8'-H), 2.26–2.34 (m, 2 H, 2'-H), 2.37 [s, 6 H, $N(CH_3)_2$], 2.48–2.54 (m, 2 H, 6'-H), 2.73 (AB, d, ^2J = 16.4 Hz, 2 H, 8'-H), 5.86 (s, 2 H, 10'-H), 7.57 (br. s, 4 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 23.0, 24.4, 26.1 (–, C-2',3',4',5'), 37.2 (–, C-8'), 40.2 [+, $N(CH_3)_2$], 59.6 (+, C-6'), 62.2 (C_{quat}, C-1'), 74.4 (C_{quat}, C-7'), 125.0 (+, Ph-C), 129.1 (+, C-10), 134.6 (C_{quat}, Ph-C), 156.2 (C_{quat}, C-11'), 212.1 (C_{quat}, C-9'). – EI MS (70 eV), *m/z* (%): 484 (100) [M^+], 456 (29) [$M^+ - CO$], 442 (56) [$M^+ - C_3H_6$], 179 (11), 150 (11). – HRMS (EI) calcd for $C_{32}H_{40}NO$: 484.3090 (correct HRMS).

Variation B: According to GP7, to a solution of 458 mg (1.15 mmol) of complex **18o** in 23 mL of pyridine was added 350 mg (1.47 mmol) of alkyne **29a**[7], and the mixture stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 30 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 2) gave 45.0 mg (11%) of **72a** as a colorless solid.

4,4'-Bis[7''-(dimethylamino)tricyclo[5.2.2.0^{1,6}]undec-10''-en-9''-oxo-11''-yl]biphenyl (**72b**): Following GP7, a solution of 2.27 g (5.68 mmol) of complex **18g** in pyridine (40 mL) was treated with 344 mg (1.65 mmol) of 4,4'-diethynylbiphenyl (**29a**[8]), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 60 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave 476 mg (51%) of **72b** [R_f = 0.56 (pentane/Et_2O = 1 : 1)] as a colorless solid, m. p. > 230°C. – IR (KBr): ν = 2936 cm^{-1} (C–H), 1736 (C=O), 1492, 1305, 1114, 904, 810. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.13–1.48 (m, 4 H, 2'',3'',4'',5''-H), 1.65–1.76 (m, 2 H, 3'',4''-H), 1.82–1.92 (m, 1 H, 5''-H), 2.27 (ABM, dd, ^2J = 16.3, ^4J = 2.3 Hz, 1 H, 8''-H), 2.29–2.40 (m, 1 H, 2''-H), 2.41 [s, 6 H, $N(CH_3)_2$], 2.52–2.70 (m, 1 H, 6''-H), 2.77 (AB, d, ^2J = 16.3 Hz, 1 H, 8''-H), 5.92 (s, 1 H, 10''-H), 7.54 (d, ^2J = 8.5 Hz, 2 H, Ar-H), 7.77 (d, ^2J = 8.5 Hz, 2 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 23.0, 24.4, 26.1 (–, C-2'',3'',4'',5''), 37.2 (–, C-8''), 40.2 [+, $N(CH_3)_2$], 59.7 (+, C-6''), 62.2 (C_{quat}, C-1''), 74.5 (C_{quat}, C-7''), 125.7, 126.4 (+, Ar-C), 129.3.2 (+, C-10''), 134.5, 139.7 (C_{quat}, Ar-C), 156.0 (C_{quat}, C-11''), 212.1 (C_{quat}, C-9''). – EI MS (70 eV), *m/z* (%): 560

(72) [M^+], 532 (50) [M^+ – CO], 518 (100) [M^+ – C_3H_6], 490 (17), 179 (24), 162 (24), 150 (32). – Elemental analysis calcd (%) for $C_{38}H_{44}N_2O_2$ (560.8): C 81.39, H 7.91; found C 81.37, H 8.21.

1-{4'-[(7''-Dimethylamino)tricyclo[5.2.2.0^{1,6}]undec-10''-en-9''-oxo-11''-yl]phenyl}-2-(4-ethynylphenyl)ethane (**25z**) and *1,2-bis{4'-[7''-(dimethylamino)tricyclo[5.2.2.0^{1,6}]undec-10''-en-9''-oxo-11''-yl]phenyl}ethane* (**72z**): Following GP7, to a solution of complex **18g** (1.35 g, 3.38 mmol) in 40 mL of pyridine was added 354 mg (1.54 mmol) of 4,4′-diethynylbibenzylbenzene (**29a**[9]), and the mixture was stirred at 80 °C for 48 h. Chromatography on aluminum oxide (II, 50 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave 54.0 mg (15%) of alkyne **29a**[9] [R_f = 0.92 (pentane/Et_2O = 3 : 1)], 208 mg (33%) of monoadduct **25z** [R_f = 0.33 (pentane/Et_2O = 3 : 1)] as a pale-yellow oil, and 122 mg (14%) of bisadduct **72z** [R_f = 0.10, (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 190–191 °C.

25z: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15–1.45 (m, 4 H, 2",3",4",5"-H), 1.60–1.75 (m, 2 H, 3",4"-H), 1.82–1.90 (m, 1 H, 5"-H), 2.26 (ABM, dd, ^2J = 16.4, ^4J = 1.8 Hz, 1 H, 8"-H), 2.29–2.39 (m, 1 H, 2"-H), 2.40 [s, 6 H, $N(CH_3)_2$], 2.50–2.60 (m, 1 H, 6"-H), 2.75 (AB, d, ^2J = 16.4 Hz, 1 H, 8"-H), 2.90 (br. s, 4 H, bibenzyl CH_2CH_2), 3.07 (s, 1 H, C≡CH), 5.85 (s, 1 H, 10"-H), 7.09 (d, ^3J = 6.1 Hz, 2 H, Ph-H), 7.12 (d, ^3J = 6.1 Hz, 2 H, Ph-H), 7.42 (d, ^3J = 8.2 Hz, 2 H, Ph-H), 7.56 (d, ^3J = 8.2 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.1, 22.9, 24.3, 25.9 (–, C-2",3",4",5"), 37.1, 37.2, 37.5 (–, C-8", bibenzyl CH_2CH_2), 40.0 [+, $N(CH_3)_2$], 59.5 (+, C-6"), 61.9 (C_{quat}, C-1"), 74.2 (C_{quat}, C-7"), 76.7 (+, C≡*C*H), 83.6 (C_{quat}, C≡*C*H), 119.4 (C_{quat}, C-Ph), 125.2, 128.0, 128.3, 131.9 (+, Ph-C), 128.5 (+, C-10"), 133.4, 142.4, 140.5 (C_{quat}, Ph-C), 156.1 (C_{quat}, C-11"), 211.8 (C_{quat}, C-9). – EI MS (70 eV), *m/z* (%): 409 (100) [M^+], 381 (55) [M^+ – CO], 367 (57) [M^+ – C_3H_6], 266 (16), 179 (17), 115 (29). – Elemental analysis calcd (%) for $C_{29}H_{31}NO$ (409.6): C 85.05, H 7.63; found C 84.81, H 7.63.

72z: IR (KBr): ν = 2936 cm^{-1} (C–H), 1731 (C=O), 1505, 1457, 1307, 1114, 849, 816, 669. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.09–1.46 (m, 8 H, 2",3",4",5"-H), 1.60–1.80 (m, 4 H, 3",4"-H), 1.85–1.90 (m, 2 H, 5"-H), 2.24 (AB, d, ^2J = 16.4 Hz, 2 H, 8"-H), 2.27–2.32 (m, 2 H, 2"-H), 2.39 [s, 12 H, $N(CH_3)_2$], 2.45–2.55 (m, 2 H, 6"-H), 2.74 (AB, d, ^2J = 16.6 Hz, 2 H,

8''-H), 2.89 (br. s, 4 H, bibenzyl CH_2CH_2), 5.83 (s, 2 H, C-10''), 7.11 (d, ^2J = 8.1 Hz, 4 H, Ph-H), 7.55 (d, ^2J = 8.1 Hz, 4 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 23.0, 24.3, 26.0 (–, C-2'',3'',4'',5''), 37.2, 37.5 (–, C-8, bibenzyl CH_2CH_2), 40.1 [+, $N(CH_3)_2$], 59.6 (+, C-6''), 61.9 (C_{quat}, C-1''), 74.3 (C_{quat}, C-7''), 125.2, 128.0 (+, Ph-C), 128.5 (+, C-10''), 133.1, 141.0 (C_{quat}, Ph-C), 156.2 (C_{quat}, C-11''), 212.0 (C_{quat}, C-9''). – EI MS (70 eV), *m/z* (%): 588 (100) [M^+], 570 (20) [M^+ – CO], 546 (62) [$M^+ – C_3H_6$], 266 (16), 179 (13), 150 (13). – Elemental analysis calcd (%) for $C_{40}H_{48}N_2O_2$ (588.8): C 81.59, H 8.22; found C 81.73, H 8.08.

1-(7'-dimethylamino-10'-phenylethynyltricyclo[5.2.2.0^{1,6}]undec-10'-en-9'-oxo-11'-yl)-2-(7''-dimethylamino-10''-phenyltricyclo[5.2.2.0^{1,6}]undec-10''-en-9''-oxo-11''-yl)-ethyne (**73**), *1,4-Bis(7'-dimethylamino-10'-phenyltricyclo[5.2.2.0^{1,6}]undec-10'-en-9'-oxo-11'-yl)buta-1,3-diyne* (**74**), and *1-(7'-dimethylamino-10'-phenylethynyltricyclo[5.2.2.0^{1,6}]undec-10'-en-9'-oxo-11'-yl)-2-(7''-dimethylamino-11''-phenyltricyclo[5.2.2.0^{1,6}]undec-10''-en-9''-oxo-10''-yl)ethyne* (**75**): Like GP7, but a solution of complex **18g** (873 mg, 2.20 mmol) in pyridine (44 mL) was firstly heated at 80 °C for 3 h. After cooling to ambient temperature, the resultant cyclopentadiene **64** was treated with 110 mg (4.39 mmol) of 1,8-dipheny-1,3,5,7-octatertayne (**54g**), and the mixture stirred at this temperature for an additional 3 d. Chromatography on aluminum oxide (II, 50 g) eluting with pentane/Et_2O (from 8 : 1 to 1 : 3) gave 136 mg (51%) of bis-adducts [R_f = 0.65 (Et_2O)] as a yellow solid. – IR (KBr): ν = 2935 cm^{-1}, 2867 (C-H), 1739 (C=O), 1457, 1443, 1131. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.95–1.50 (m, 8 H), 1.60–1.80 (m, 6 H), 2.22–2.58 (m, 4 H), 2.37, 2.38, 2.66, 2.67, 2.70 [s, 12 H, ratio = 1 : 1 : 1 : 1 : 2, $N(CH_3)_2$], 7.15–7.41 (m, 10 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 21.7, 22.1, 22.46, 22.47, 22.6, 23.4, 23.5, 23.76, 23.82, 39.0, 39.1, 39.5, 39.6 (–), 39.7, 39.8, 39.99, 40.02 × 2, 40.1 [+, ratio 1 : 1 : 1 : 2 : 1, $N(CH_3)_2$], 61.5, 61.57, 61.60, 61.8 (+), 65.2, 65.3, 65.58, 65.63, (C_{quat}), 74.6, 74.7, 74.8, 75.1, 75.2 (C_{quat}), 81.3, 82.5, 84.8, 94.8, 100.2, 101.3, 101.4 (C_{quat}, C≡C), 127.2, 127.3, 127.6, 127.7, 127.8, 127.9, 128.0, 128.10, 128.14, 128.20, 128.23, 128.7, 131.5 (+, Ph-C), 122.51, 122.54, 130.88, 130.92, 132.0, 132.2, 133.4, 133.6, 133.7, 133.86, 133.92, 140.10, 140.12, 152.4, 152.9, 156.0, 156.1 (C_{quat}), 210.2, 210.3, 211.3 × 2, 211.7, 211.8 (C_{quat}, ratio 1 : 1 : 2 : 1 : 1, CO). – EI MS

(70 eV), *m/z* (%): 608 (76) [M^+], 566 (100), 524 (20), 304 (12), 178 (57), 150 (34). – HRMS calcd for $C_{42}H_{44}N_2O_2$: 608.3403 (correct HRMS).

4. Cyclopenta[*b*]pyrans

4-Ethoxy-2-[1'-methyl-1'-(trimethylsilyloxy)ethyl]-5,7-diphenylcyclopenta[b]pyran (**22a**):
Variation A: According to GP7, complex **18e** (898 mg, 2.00 mmol) in *n*-hexane (40 mL) was treated with 1.63 g (16.0 mmol) phenylethyne (**15a**), and the mixture was stirred at 60 °C for 2 d. After chromatography [40 g of silica gel, elution with pentane/Et_2O (10 : 1)], 251 mg (28%) of **22a** (R_f = 0.44) was obtained as a red crystal. The ^{1}H- and ^{13}C-NMR spectra agreed with those which have previously been reported.[52c] – Elemental analysis calcd for $C_{28}H_{32}O_3Si$ (444.6): C 75.63, H 7.25; found C 75.31, H 7.27.
Variation B: According to GP7, complex **18e** (898 mg, 2.00 mmol) in acetonitrile (40 mL) was treated with 1.63 g (16.0 mmol) of phenylethyne (**15a**), and the mixture was stirred at 60 °C for 2 d. 262 mg (29%) of **22a** was obtained after chromatography on 40 g of silica gel.

5. Highly Substituted Cyclopentadienes

5.1. Basic Study of Formation of Highly Substituted Cyclopentadienes

2-Cyclopropyl-5-dimethylamino-3-ethoxy-5-isopropyl-1-phenyl-1,3-cyclopentadiene (**19i**) and *1-Cyclopropyl-5-dimethylamino-3-ethoxy-5-isopropyl-2-phenyl-1,3-cyclopentadiene* (**81i**): Following GP7, to a solution of complex **18c** (723 mg, 2.00 mmol) in pyridine (40 mL) was added 356 mg (2.50 mmol) of cyclopropylphenylethyne (**28ag**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 20 : 1 to 1 : 1) gave 435 mg (70%) of **19i** and **81i** [R_f = 0.58 (pentane/Et_2O = 3 : 1), ratio 1.4 : 1] as colorless oils. After identification of the mixture and chromatography again on aluminum oxide [II, 40 g; elution with pentane/Et_2O (10 : 1)], **19i** was obtained as a colorless oil. – IR (film): ν = 2970 cm^{-1} (C–H), 1700, 1653 (C=C), 1457, 1383, 703, 668. – **19i** (Major stereoisomer): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.49–0.60 (m, 2 H, *c*Pr-H), 0.73 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.77–0.86 (m, 2 H, *c*Pr-H), 0.91 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.35 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.50–1.61 (m, 1 H, *c*Pr-H), 2.24 [s, 6 H, $N(CH_3)_2$], 2.43 (sep,

^3J = 6.8 Hz, 1 H, *i*Pr-H), 3.85 (q, ^3J = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.74 (s, 1 H, 4-H), 7.18–7.35 (m, 3 H, Ph-H), 7.72 (dd, ^3J = 8.5, ^4J = 1.5 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 6.1 × 2 (–, *c*Pr-C), 8.8 (+, *c*Pr-C), 14.5 (+, OCH$_2$*C*H$_3$), 17.0 (+, *i*Pr-C), 18.1 (+, *i*Pr-C), 29.6 (+, *i*Pr-C), 39.5 [+, N(CH$_3$)$_2$], 64.4 (–, O*C*H$_2$CH$_3$), 78.6 (C$_{quat}$, C-5), 98.9 (+, C-4), 126.3, 127.7, 129.5 (+, Ph-C), 138.9, 139.0 (C$_{quat}$, C-2, Ph-C), 143.7 (C$_{quat}$, C-1), 160.0 (C$_{quat}$, C-3). – **81i** (Minor stereoisomer): ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.25–0.37 (m, 1 H, *c*Pr-H), 0.38–0.47 (m, 1 H, *c*Pr-H), 0.49–0.60 (m, 1 H, *c*Pr-H), 0.77–0.86 (m, 1 H, *c*Pr-H), 1.01 (d, ^3J = 6.5 Hz, 3 H, *i*Pr-H), 1.03 (d, ^3J = 6.5 Hz, 3 H, *i*Pr-H), 1.25 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 1.25–1.33 (m, 1 H, *c*Pr-H), 2.43 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 2.45 [s, 6 H, N(CH$_3$)$_2$], 3.87 (q, ^3J = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.69 (s, 1 H, 4-H), 7.18–7.35 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 7.4 (–, *c*Pr-C), 8.1 (–, *c*Pr-C), 10.9 (+, *c*Pr-C), 14.3 (+, OCH$_2$*C*H$_3$), 17.1 (+, *i*Pr-C), 18.6 (+, *i*Pr-C), 30.4 (+, *i*Pr-C), 39.5 [+, N(CH$_3$)$_2$], 64.5 (–, O*C*H$_2$CH$_3$), 78.9 (C$_{quat}$, C-5), 97.3 (+, C-4), 126.7, 127.3, 129.9 (+, Ph-C), 134.5, 136.0 (C$_{quat}$, C-2, Ph-C), 148.1 (C$_{quat}$, C-1), 159.1 (C$_{quat}$, C-3). – MS (70 eV), *m/z* (%): 311 (20) [M$^+$], 282 (11) [M$^+$ – C$_2$H$_5$], 268 (100) [M$^+$ – C$_3$H$_7$]. – HRMS (EI) calcd for C$_{21}$H$_{29}$NO: 311.2249 (correct HRMS).

5-Dimethylamino-3-ethoxy-2-hexyl-5-isopropyl-1-phenyl-1,3-cyclopentadiene (**19j**) and *5-Dimethylamino-3-ethoxy-1-hexyl-5-isopropyl-2-phenyl-1,3-cyclopentadiene* (**81j**): Following GP7, to a solution of complex **18c** (553 mg, 1.53 mmol) in pyridine (31 mL) was added 295 mg (1.58 mmol) of 1-phenyl-1-octyne (**28ah^2**), and the mixture stirred at 80 °C for 3 d. Chromatography on aluminum oxide (activity grade II, 40 g) eluting with pentane/Et$_2$O (from 20 : 1 to 1 : 1) gave 382 mg (70%) of **19j** and **81j** [R_f = 0.59 (pentane/Et$_2$O = 3 : 1); ratio = 2.2 : 1] as colorless oils. After identification of the mixture and chromatography again on aluminum oxide [II, 40 g; elution with pentane/Et$_2$O (10 : 1)], **19j** was obtained as a colorless oil. – IR (film): ν = 2929 cm^{-1} (C–H), 2859, 2823, 1636 (C=C), 1601, 1586, 1457, 1373, 1192, 1139, 701. – **19j** (Major stereoisomer): ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.76 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.83 (t, ^3J = 6.5 Hz, 3 H, 6'-H), 0.92 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.13–1.30 (m, 8 H, 2',3',4',5'-H), 1.38 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 2.19 (t, ^3J = 7.7 Hz, 2 H, 1'-H), 2.25 [s, 6 H, N(CH$_3$)$_2$], 2.43 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 3.92 (q, ^3J = 7.0 Hz,

2 H, OCH_2CH$_3$), 4.76 (s, 1 H, 4-H), 7.22–7.38 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.0, 14.5 (+, OCH$_2$*C*H$_3$, C-6'), 17.1 (+, *i*Pr-C), 18.1 (+, *i*Pr-C), 22.5, 24.6, 29.0, 29.2 (–, C-2',3',4',5'), 29.6 (+, *i*Pr-C), 31.4 (–, C-1'), 39.7 [+, N(CH$_3$)$_2$], 64.4 (–, O*C*H$_2$CH$_3$), 79.4 (C$_{quat}$, C-5), 98.3 (+, C-4), 126.2, 127.8, 128.9 (+, Ph-C), 139.0, 140.0 (C$_{quat}$, C-2, Ph-C), 142.8 (C$_{quat}$, C-1), 159.8 (C$_{quat}$, C-3). – **81j** (Minor stereoisomer): ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.83 (t, ^3J = 6.5 Hz, 3 H, 6'-H), 0.98 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.02–1.25 (m, 11 H, 2',3',4',5'-H, *i*Pr-H), 1.27 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$CH_3), 2.19 (t, ^3J = 7.7 Hz, 2 H, 1'-H), 2.37 [s, 6 H, N(CH$_3$)$_2$], 2.43 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 3.92 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH$_3$), 4.68 (s, 1 H, 4-H), 7.22–7.38 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.0, 14.3 (+, OCH$_2$*C*H$_3$, C-6'), 17.3 (+, *i*Pr-C), 18.4 (+, *i*Pr-C), 22.5, 27.0, 28.0, 30.0 (–, C-2',3',4',5'), 30.4 (+, *i*Pr-C), 31.2 (–, C-1'), 39.5 [+, N(CH$_3$)$_2$], 64.5 (–, O*C*H$_2$CH$_3$), 78.4 (C$_{quat}$, C-5), 97.2 (+, C-4), 126.6, 127.6, 129.2 (+, Ph-C), 134.7, 137.2 (C$_{quat}$, C-2, Ph-C), 149.4 (C$_{quat}$, C-1), 158.9 (C$_{quat}$, C-3). – MS (70 eV), *m/z* (%): 355 (14) [M$^+$], 326 (13) [M$^+$ – C$_2$H$_5$], 312 (100) [M$^+$ – C$_3$H$_7$], 284 (10). – HRMS (EI) calcd for C$_{24}$H$_{37}$NO: 355.2875 (correct HRMS).

5-Dimethylamino-3-ethoxy-5-isopropyl-1-[4'-(ethoxycarbonyl)phenyl]-2-phenyl-1,3-cyclopentadiene (**19k**) and *5-Dimethylamino-3-ethoxy-5-isopropyl-2-[4'-(ethoxycarbonyl)phenyl]-2-phenyl-1,3-cyclopentadiene* (**81k**): According to GP7, a solution of complex **18c** (469 mg, 1.30 mmol) in pyridine (23 mL) was treated with 325 mg (1.30 mmol) of 4-phenylethynyl benzoic acid ethyl ester (**28aa**[15]), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et$_2$O (from 20 : 1 to 3 : 1) gave 194 mg (36%) of **19k** and **81k** [R_f = 0.53 (pentane/Et$_2$O = 3 : 1); ratio = 1.3 : 1] as yellow oils. – IR (film): ν = 2976 cm^{-1} (C–H), 1717 (C=O), 1635 (C=C), 1457, 1368, 1321, 1196, 1106, 1021. – Major stereoisomer: ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.76 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.80 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.35 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$CH_3), 1.36 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$CH_3), 2.37 [s, 6 H, N(CH$_3$)$_2$], 2.40–2.60 (m, 1 H, *i*Pr-H), 3.97 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH$_3$), 4.33 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH$_3$), 5.00 (s, 1 H, 4-H), 7.11–7.27 (m, 5 H, Ph-H), 7.39 (d, ^3J = 8.4 Hz, 2 H, Ph-H), 7.83 (d, ^3J = 8.4 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.3, 14.4 (+, OCH$_2$*C*H$_3$), 16.9 (+, *i*Pr-C), 18.0

(+, *i*Pr-C), 30.0 (+, *i*Pr-C), 39.6 [+, $N(CH_3)_2$], 60.7 (–, OCH_2CH_3), 64.9 (–, OCH_2CH_3), 79.6 (C_{quat}, C-5), 99.4 (+, C-4), 126.9, 128.0, 128.9, 129.7, 130.1 (+, Ph-C), 128.2, 138.5, 143.2, 144.7 (C_{quat}, C-2, Ph-C), 147.7 (C_{quat}, C-1), 158.2 (C_{quat}, C-3), 166.6 (C_{quat}, CO_2Et). – Minor stereoisomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.94 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.98 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.35 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.36 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.36 [s, 6 H, $N(CH_3)_2$], 2.40–2.60 (m, 1 H, *i*Pr-H), 3.97 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.33 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.97 (s, 1 H, 4-H), 7.11–7.27 (m, 5 H, Ph-H), 7.39 (d, ^3J = 8.4 Hz, 2 H, Ph-H), 7.86 (d, ^3J = 8.2 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3, 14.4 (+, OCH_2CH_3), 17.1 (+, *i*Pr-C), 17.8 (+, *i*Pr-C), 30.4 (+, *i*Pr-C), 39.8 [+, $N(CH_3)_2$], 60.7 (–, OCH_2CH_3), 64.9 (–, OCH_2CH_3), 79.6 (C_{quat}, C-5), 99.8 (+, C-4), 127.1, 127.8, 129.0, 129.6, 130.0 (+, Ph-C), 128.5, 137.8, 138.5, 137.9, 140.2 (C_{quat}, C-2, Ph-C), 143.2 (C_{quat}, C-1), 158.4 (C_{quat}, C-3), 166.6 (C_{quat}, CO_2Et). – MS (70 eV), *m/z* (%): 419 (20) [M^+], 390 (24) [$M^+ – C_2H_5$], 376 (100) [$M^+ – C_3H_7$], 348 (12), 347 (10), 250 (11), 211 (10). – HRMS (EI) calcd for $C_{27}H_{33}NO_3$: 419.2460 (correct HRMS).

5-Dimethylamino-3-ethoxy-5-isopropyl-1-[4'-(methoxycarbonyl)phenyl]-2-(4''-methoxy-phenyl)-1,3-cyclopentadiene (**19l**) and *5-Dimethylamino-3-ethoxy-5-isopropyl-2-[4''-(methoxycarbonyl)phenyl]-2-(4'-methoxyphenyl)-1,3-cyclopentadiene* (**81l**): Following GP7, a solution of complex **18c** (723 mg, 2.00 mmol) in pyridine (40 mL) was treated with 586 mg (2.20 mmol) of 4-(4'-methoxyphenylethynyl)benzoic acid methyl ester (**28a^{4}a^5**), and the mixture was stirred at 80 °C for 3 d. The alkyne **28a^{4}a^5** with very low solubility could not be completely removed. Twice chromatography on aluminum oxide (II, 60 g) eluting with pentane/Et_2O (first time: from 20 : 1 to 3 : 1, second time: from 6 : 1 to 3 : 1) gave 548 mg of a yellow solid, which contained **28a^{4}a^5** (30%) and cocyclization products **19l** and **81l** [70%; ratio = 1.1 : 1; R_f = 0.59 (pentane/Et_2O 3 : 1)]. The amount of products equalize to 384 mg (44% from complex **18c**). – Major stereoisomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.76 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.80 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.35 [s, 6 H, $N(CH_3)_2$], 2.40–2.60 (m, 1 H, *i*Pr-H), 3.75 (s, 3 H, CO_2CH_3), 3.87 (s, 3 H, OCH_3), 3.97 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.95 (s, 1 H, 4-H), 6.70 (d, ^3J = 8.8 Hz, 2 H, Ph-H), 7.17 (d, ^3J = 8.8 Hz, 2 H, Ph-H), 7.38 (d, ^3J = 8.4 Hz, 2 H, Ph-H), 7.85 (d, ^3J = 8.4 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+,

OCH_2CH_3), 17.1 (+, *i*Pr-C), 17.8 (+, *i*Pr-C), 30.4 (+, *i*Pr-C), 39.8 [+, $N(CH_3)_2$], 52.2, 55.3 (+, CO_2CH_3, OCH_3), 64.4 (–, OCH_2CH_3), 79.5 (C_{quat}, C-5), 99.7 (+, C-4), 113.3 (+, Ph-C), 114.7, 125.4, 127.7 (C_{quat}, C-2, Ph-C), 129.1, 129.8, 131.3 (+, Ph-C), 139.7, 143.6 (C_{quat}, C-1, Ph-C), 158.5, 158.6 (C_{quat}, C-3, Ph-C), 166.6 (C_{quat}, CO_2Me). – Minor stereoisomer: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.93 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.97 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.36 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.36 [s, 6 H, $N(CH_3)_2$], 2.40–2.60 (m, 1 H, *i*Pr-H), 3.75 (s, 3 H, CO_2CH_3), 3.87 (s, 3 H, OCH_3), 3.97 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.98 (s, 1 H, 4-H), 6.71 (d, ^3J = 8.8 Hz, 2 H, Ph-H), 7.05 (d, ^3J = 8.8 Hz, 2 H, Ph-H), 7.22 (d, ^3J = 8.4 Hz, 2 H, Ph-H), 7.83 (d, ^3J = 8.4 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 16.8 (+, *i*Pr-C), 17.9 (+, *i*Pr-C), 30.1 (+, *i*Pr-C), 39.6 [+, $N(CH_3)_2$], 52.2, 55.3 (+, CO_2CH_3, OCH_3), 64.4 (–, OCH_2CH_3), 79.5 (C_{quat}, C-5), 99.7 (+, C-4), 113.4 (+, Ph-C), 114.7, 125.4, 128.0 (C_{quat}, C-2, Ph-C), 128.9, 130.1, 130.8 (+, Ph-C), 138.9, 143.6 (C_{quat}, C-1, Ph-C), 158.3, 158.6 (C_{quat}, C-3, Ph-C), 166.6 (C_{quat}, CO_2Me). – MS (70 eV), *m/z* (%): 435 (28) [M^+], 406 (13) [$M^+ - C_2H_5$], 392 (60) [$M^+ - C_3H_7$], 266 (100) [M^+ of **28a⁴a⁵**]. – HRMS (EI) calcd for $C_{27}H_{33}NO_4$: 435.2410 (correct HRMS).

2,3-Dicyclopropyl-4-dimethylamino-4-isopropyl-2-cyclopentenone (**20p**): Following GP7, to a solution of 723 mg (2.00 mmol) complex **18c** in 40 mL of pyridine was added 319 mg (5.00 mmol) of dicyclopropylethyne (**15gg**) and the mixture was stirred at 80 °C for 2 d. Chromatography on aluminum oxide (II, 50 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave a colorless oil (407 mg), which consisted of cyclopenta-diene **19p** and cyclopentenone **20p** (ratio 1 : 1). Then, the mixture was dissolved in 20 mL of THF, treated with two drops of 2 N hydrochloric acid, stirred at ambient temperature for 1 d. The reaction was quenched with a solution of Na_2CO_3 (ca. 5 g in 10 mL of water), and extracted with Et_2O (3 × 50 mL). The combined organic extract was dried over $MgSO_4$ and the solvent was removed under reduced pressure. After chromatographic purification on aluminum oxide [II, 40 g; elution with pentane/Et_2O (1 : 1)], 325 mg (66%, from complex **18c**) of **20p** [R_f = 0.44 (pentane/Et_2O 1 : 1)] was obtained as a colorless oil. – IR (Film): ν = 2966 cm^{-1} (C–H), 2875, 2781, 1695 (C=O), 1610 (C=C), 1635, 1559, 1464, 1403, 1026 – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.51–0.57 (m, 2 H, *c*Pr-H), 0.64 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.90–1.10 (m, 5 H, *c*Pr-H), 1.02 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.21–1.27 (m, 1 H, *c*Pr-H), 1.47–1.55 (m, 1 H, *c*Pr-H), 1.69–1.77

(m, 1 H, *c*Pr-H),1.75 (AB, d, ^2J = 18.1 Hz, 1 H, 5-H), 2.10 [s, 6 H, $N(CH_3)_2$], 2.11 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 2.28 (AB, d, ^2J = 18.1 Hz, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 4.8, 5.2, 8.2, 8.6 (–, *c*Pr-C), 6.0, 12.5 (+, *c*Pr-C), 17.0, 17.9 (+, *i*Pr-C), 33.8 (+, *i*Pr-C), 38.2 (–, C-5), 38.9 [+, $N(CH_3)_2$], 71.5 (C_{quat}, C-4), 136.4 (C_{quat}, C-2), 175.8 (C_{quat}, C-3), 205.0 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 247 (1) [M^+], 204 (100) [M^+ – C_3H_7]. – HRMS (EI) calcd for $C_{16}H_{25}NO$: 247.1936 (correct HRMS).

5-Dimethylamino-3-ethoxy-5-isopropyl-1,2-di(p-trifluoromethyphenyl)-1,3-cyclopentadiene (**19q**): Following GP7, to a solution of complex **18c** (723 mg, 2.00 mmol) in pyridine (40 mL) was added 314 mg (2.50 mmol) of bis(*p*-triflouromethylphenyl)ethyne (**28a^{3}a^3**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 50 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 632 mg (65%) of **19q** [R_f = 0.81 (pentane/Et_2O = 3 : 1)] as a pale yellow solid. – IR (KBr): ν = 2984 cm^{-1} (C–H), 1700, 1653 (C=C), 1616, 1324, 1166, 1112, 1069, 1013. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.73 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.92 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.36 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.38 [s, 6 H, $N(CH_3)_2$], 2.43 (sep, ^3J = 6.8 Hz,, 1 H, *i*Pr-H), 3.96 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.04 (s, 1 H, 4-H), 7.24 (d, ^3J = 8.0 Hz, 2 H, Ph-H), 7.43 (s, 4 H, Ph-H), 7.47 (d, ^3J = 8.0 Hz, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3 (+, OCH_2CH_3), 17.0 (+, *i*Pr-C), 17.5 (+, *i*Pr-C), 30.5 (+, *i*Pr-C), 39.8 [+, $N(CH_3)_2$], 65.0 (–, OCH_2CH_3), 79.8 (C_{quat}, C-5), 100.1 (+, C-4), 124.2 × 2 (C_{quat}, q, $^1J_{C\text{-}F}$ = 272.0 Hz, CF_3), 124.76, 124.79 (+, m, Ph-C), 128.7, 129.0 (C_{quat}, q, $^2J_{C\text{-}F}$ = 32.3 Hz, C-4',4''), 130.0, 130.3 (+, Ph-C), 136.9, 138.9, 141.3 (C_{quat}, C-2, Ph-C), 145.8 (C_{quat}, C-1), 157.6 (C_{quat}, C-3). The signals of CF_3 carbons were not detected. – MS (70 eV), *m/z* (%): 483 (14) [M^+], 454 (14) [M^+ – C_2H_5], 440 (100) [M^+ – C_3H_7], 412 (16). – Elemental analysis calcd (%) for $C_{26}H_{27}F_6NO$ (483.2): C 64.63, H 5.63; found: C 64.39, H 5.83.

5-Dimethylamino-3-ethoxy-5-isopropyl-1-(4'-trifluoromethylphenyl)-2-[2''-(4'''-trifluoromethylphenyl)ethynyl]-1,3-cyclopentadiene (**19r**), *5-Dimethylamino-3-ethoxy-5-isopropyl-2-(4'-trifluoromethylphenyl)-1-[2''-(4'''-trifluoromethylphenyl)ethynyl]-1,3-cyclopentadiene* (**81r**) and *5-Dimethylamino-2-ethoxy-4-isopropyl-5-(4'-trifluoromethylphenyl)-1-[2''-(4'''-trifluoromethylphenyl)ethynyl]-1,3-cyclopentadiene* (**90r**): Following GP7, to a solution of 723 mg

(2.00 mmol) of complex **18c** in pyridine (40 mL) was added 713 mg (2.11 mmol) of 1,4-bis(*p*-trifluoro-methylphenyl)-1,3-butadiyne (**54a**) and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 60 g) eluting with pentane/Et_2O (from 20 : 1 to 1 : 1) gave 172 mg (17%) of **90r** [R_f = 0.89 (pentane/Et_2O = 3 : 1)] as a yellow oil, 68 mg (7%) of **19r** [R_f = 0.84 (pentane/Et_2O = 3 : 1)] as a yellow oil, and 501 mg (49%) of **81r** [R_f = 0.31 (pentane/Et_2O = 3 : 1)] as a yellow oil.

– **19r**: IR (film): ν = 2979 cm^{-1} (C–H), 2187 (C≡C), 1653 (C=C), 1616, 1559, 1457, 1323, 1126, 1062,. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.75 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.81 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.47 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.33 [s, 6 H, $N(CH_3)_2$], 2.37 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 4.03 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.98 (s, 1 H, 4-H), 7.50–7.64 (m, 6 H, Ph-H), 8.15 (d, ^3J = 8.2 Hz, 2 H, 2',6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 17.0 (+, *i*Pr-C), 17.4 (+, *i*Pr-C), 31.4 (+, *i*Pr-C), 40.1 [+, $N(CH_3)_2$], 65.3 (–, OCH_2CH_3), 80.9 (C_{quat}, C-5), 85.6, 94.0 (C_{quat}, C≡C), 99.4 (+, C-4), 121.7 (C_{quat}, C-Ph), 124.6, 125.2 (+, q, $^3J_{C-F}$ = 3.8 Hz, C-Ph), 126.9 (C_{quat}, C-Ph), 129.5, 130.0 (C_{quat}, d, $^2J_{C-F}$ = 32.3 Hz, C-4',4'''), 129.1, 131.8 (+, C-Ph), 140.4 (C_{quat}, C-2), 153.4 (C_{quat}, C-1), 156.5 (C_{quat}, C-3). The signals of CF_3 were not detected. – MS (70 eV), *m/z* (%): 507 (80) [M^+], 478 (38), 464 (100) [$M^+ – C_3H_7$], 462 (75), 436 (12), 338 (10). – HRMS (EI) calcd for $C_{28}H_{27}F_6NO$: 507.1997 (correct HRMS).

– **81r**: IR (film): ν = 2981 cm^{-1} (C–H), 2873 (C–H), 2782 (C–H), 2187 (C≡C), 1653 (C=C), 1617, 1559, 1457, 1324, 1127, 1067. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.98 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.17 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.42 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.57 [s, 6 H, $N(CH_3)_2$], 2.62 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 4.03 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.01 (s, 1 H, 4-H), 7.49 (d, ^3J = 8.3 Hz, 2 H, Ph-H), 7.59 (d, ^3J = 8.3 Hz, 2 H, Ph-H), 7.70 (d, ^3J = 8.2 Hz, 2 H, Ph-H), 7.99 (d, ^3J = 8.0 Hz, 2 H, 2',6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3 (+, OCH_2CH_3), 16.8 (+, *i*Pr-C), 18.6 (+, *i*Pr-C), 30.5 (+, *i*Pr-C), 39.4 [+, $N(CH_3)_2$], 65.4 (–, OCH_2CH_3), 79.1 (C_{quat}, C-5), 89.2, 99.1 (C_{quat}, C≡C), 104.0 (+, C-4), 123.9, 124.2 (C_{quat}, q, $^1J_{C-F}$ = 270.3 Hz, CF_3), 124.5, 125.3 (+, q, $^3J_{C-F}$ = 3.8 Hz, C-Ph), 127.2, (C_{quat}, C-Ph), 129.4 (+, C-Ph), 129.9 × 2 (C_{quat}, q, $^2J_{C-F}$ = 32.5 Hz, C-4'',4'''), 130.1 (C_{quat}, C-Ph), 131.2 (+, C-Ph), 132.5 (C_{quat}, C-2), 144.7 (C_{quat}, C-1), 157.3 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 507 (8) [M^+], 478 (7), 465 (26), 464 (100) [$M^+ – C_3H_7$], 436 (17). –

Elemental analysis calcd (%) for $C_{28}H_{27}F_6NO$ (507.2): C 66.31, H 5.37; found: C 66.05, H 5.15.

– **90r**: IR (film): ν = 2183 cm^{-1} (C≡C), 1653 (C=C), 1616, 1559, 1457, 1323, 1125, 1068. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.33 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.15 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.25 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2,45 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 2.48 [s, 6 H, $N(CH_3)_2$], 4.67 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 4.69 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 5.83 (s, 1 H, 3-H), 7.27 (d, ^3J = 8.0 Hz, 2 H, Ph-H), 7.46 (d, ^3J = 8.3 Hz, 2 H, Ph-H), 7.58 (d, ^3J = 8.3 Hz, 2 H, Ph-H), 7.76 (d, ^3J = 8.0 Hz, 2 H, 2''',6'''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.5 (+,OCH_2CH_3), 22.6 (+, *i*Pr-C), 24.7 (+, *i*Pr-C), 25.9 (+, *i*Pr-C), 40.3 [+, $N(CH_3)_2$], 66.4 (–, OCH_2CH_3), 83.0 (C_{quat}, C-5), 90.1, 94.7, 95.2 (C_{quat}, C-1, C≡C), 120.5 (+, C-3), 124.0, 124.3 (C_{quat}, q, $^1J_{C\text{-}F}$ = 271.9 Hz, CF_3), 125.1 (+, q, $^3J_{C\text{-}F}$ = 3.8 Hz, Ph-C), 125.2 (+, q, $^3J_{C\text{-}F}$ = 3.8 Hz, Ph-C), 125.2 (+, Ph-C), 128.46 (C_{quat}, Ph-C), 128.54, 129.4 (C_{quat}, q, $^2J_{C\text{-}F}$ = 32.5 Hz, C-4'',4'''), 130.1 (+, Ph-C), 144.3 (C_{quat}, Ph-C), 165.6 (C_{quat}, C-4), 167.4 (C_{quat}, C-2). – MS (70 eV), *m/z* (%): 507 (88) [M^+], 478 (40), 464 (100) [$M^+ - C_3H_7$], 436 (10), 342 (42), 340 (18), 237 (26), 185 (18), 159 (15). – Elemental analysis calcd (%) for $C_{28}H_{27}F_6NO$ (507.2): C 66.31, H 5.37; found: C 66.58, H 5.68.

5-Dimethylamino-3-ethoxy-5-isopropyl-1-phenyl-2-phenylethynyl-1,3-cyclopentadiene (**19s**), *5-Dimethylamino-3-ethoxy-5-isopropyl-2-phenyl-1-phenylethynyl-1,3-cyclopenta-diene* (**81s**) and *5-Dimethylamino-2-ethoxy-4-isopropyl-5-phenyl-1-(phenyl-ethynyl)-1,3-cyclopentadi-ene* (**90s**): According to GP7, a solution of 723 mg (2.00 mmol) of complex **18c** in pyridine (40 mL) was treated with 607 mg (3.00 mmol) 1,4-diphenyl-1,3-butadiyne (**54f**) and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 60 g) eluting with pentane/Et_2O (from 20 : 1 to 1 : 1) gave 67.0 mg (9%) of **90s** [R_f = 0.81 (pentane/Et_2O = 3 : 1)] as a yellow solid, 163 mg (22%) of **19s** [R_f = 0.67 (pentane/Et_2O 3 : 1)] as a yellow solid, and 278 mg (37%) of **81s** [R_f = 0.31 (pentane/Et_2O = 3 : 1)] as a yellow oil. The structures of all three compounds were assigned on the basis of HH COSY, HH NOESY and CH COSY spectra.

– **19s**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.90 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.51 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.38 [s, 6 H, $N(CH_3)_2$], 2.43 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 4.05 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.94 (s, 1 H, 4-H), 7.30–7.51 (m,

8 H, Ph-H), 8.06 (dd, ^3J = 7.0, ^4J = 1.5 Hz, 2 H, 2',6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 16.8 (+, *i*Pr-C), 17.5 (+, *i*Pr-C), 31.1 (+, *i*Pr-C), 40.0 [+, $N(CH_3)_2$], 65.0 (–, OCH_2CH_3), 80.5 (C_{quat}, C-5), 83.9, 94.6 (C_{quat}, C≡C), 98.2 (+, C-4), 120.5, 123.4 (C_{quat}, Ph-C), 127.5, 127.6, 128.0, 128.1, 128.9, 131.6 (+, Ph-C), 137.2 (C_{quat}, C-2), 154.1 (C_{quat}, C-1), 156.8 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 371.2 (100) [M^+], 356 (12), 342 (59), 328 (78) [$M^+ - C_3H_7$], 326 (90), 299 (16), 284 (17), 202 (13). – HRMS (EI) calcd for $C_{26}H_{29}NO$: 371.2349 (correct HRMS).

– **81s**: IR (Film): ν = 2978 cm^{-1} (C–H), 2870 (C–H), 2185 (C≡C), 1617 (C=C), 1576, 1485, 1443, 1211, 1054, 755. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.22 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.44 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.63 [s, 6 H, $N(CH_3)_2$], 2.67 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 4.06 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.97 (s, 1 H, 4-H), 7.30–7.51 (m, 8 H, Ph-H), 7.95 (dd, ^3J = 7.0, ^4J = 1.5 Hz, 2 H, 2''',6'''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 16.9 (+, *i*Pr-C), 18.7 (+, *i*Pr-C), 30.3 (+, *i*Pr-C), 39.3 [+, $N(CH_3)_2$], 65.0 (–, OCH_2CH_3), 78.3 (C_{quat}, C-5), 87.6, 99.7 (C_{quat}, C=C), 102.8 (+, C-4), 123.5, 128.2 (C_{quat}, Ph-C), 127.6, 127.9 × 2, 128.6, 129.0, 130.9 (+, Ph-C), 132.5 (C_{quat}, C-2), 144.6 (C_{quat}, C-1), 157.9 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 371 (17) [M^+], 342 (13), 328 (100) [$M^+ - C_3H_7$], 300 (17). – HRMS (EI) calcd for $C_{26}H_{29}NO$: 371.2349 (correct HRMS).

– **90s**: IR (Film): ν = 2964 cm^{-1} (C–H), 2868 (C–H), 2183 (C≡C), 1626 (C=C), 1569, 1488, 1333, 1070, 1030, 753. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.32 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.13 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.48 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.48 (sep, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 2.50 [s, 6 H, $N(CH_3)_2$], 4.67 (q, ^3J = 7.1 Hz, 1 H, OCH_2CH_3), 4.68 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 5.75 (d, ^4J = 0.7 Hz, 1 H, 3-H), 7.17–7.34 (m, 8 H, Ph-H), 7.61 –7.66 (m, 2 H, 2''',6'''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.6 (+, OCH_2CH_3), 22.6 (+, *i*Pr-C), 24.7 (+, *i*Pr-C), 25.7 (+, *i*Pr-C), 40.3 [+, $N(CH_3)_2$], 66.1 (–, OCH_2CH_3), 83.2 (C_{quat}, C-5), 87.4, 95.5, 95.8 (C_{quat}, C-1, C≡C), 119.9 (+, C-3), 124.9 (C_{quat}, Ph-C), 126.8, 126.9, 127.8, 128.1, 128.2, 130.1 (+, Ph-C), 139.9 (C_{quat}, Ph-C), 164.0 (C_{quat}, C-4), 167.0 (C_{quat}, C-2). – MS (70 eV), *m/z* (%): 371.2 (100) [M^+], 356 (12), 342

(52), 328 (80) [$M^+ - C_3H_7$], 326 (92), 299 (14), 284 (13), 202 (13). – HRMS (EI) calcd for $C_{26}H_{29}NO$: 371.2349 (correct HRMS).

5-Dimethylamino-3-ethoxy-5-isopropyl-1-(4'-methoxyphenyl)-2-[2''-(4'''-methoxyphenyl)-ethynyl]-1,3-cyclopentadiene (**19t**), *5-Dimethylamino-3-ethoxy-5-isopropyl-2-(4'-methoxyphenyl)-1-[2''-(4'''-methoxyphenyl)ethynyl]-1,3-cyclopentadiene* (**81t**) *and 5-Dimethylamino-2-ethoxy-4-isopropyl-5-(4'-methoxyphenyl)-1-[2''-(4'''-methoxyphenyl)ethynyl]-1,3-cyclopentdiene* (**90t**): According to GP7, a solution of 723 mg (2.00 mmol) of complex **18c** in 40 mL of pyridine was treated with 556 mg (2.12 mmol) of 1,4-bis(*p*-methoxyphenyl)-1,3-butadiyne (**54b**) and the mixture stirred at 80 °C for 3 d. In order to remove most part of **54b**, the residue was dissolved in pentane, in stead of Et_2O, and filtered over celite. Chromatography on aluminum oxide (II, 60 g) eluting with pentane/Et_2O from (20 : 1) to (1 : 1) gave 10.0 mg of a colorless oil which contained **54b** (29%) and **90t** [71%, 710 µg (1% from complex **18c**); R_f = 0.53 (pentane/Et_2O = 3 : 1)], 193 mg (22%) of **19t** [R_f = 0.47 (pentane/Et_2O = 3 : 1)] as a colorless oil, and 303 mg (35%) of **81t** [R_f = 0.49 (pentane/Et_2O = 1 : 1)] as a yellow oil.

– **19t**: IR (film): ν = 2205 cm^{-1} (C≡C), 1700, 1653 (C=C), 1635, 1559, 1506, 1457, 1248, 1031. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.79 (d, ^3J = 7.0 Hz, 3 H, *i*Pr-H), 0.82 (d, ^3J = 7.0 Hz, 3 H, *i*Pr-H), 1.46 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.31 [s, 6 H, $N(CH_3)_2$], 2.35 (sep, ^3J = 7.0 Hz, 1 H, *i*Pr-H), 3.80 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 4.01 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.86 (s, 1 H, 4-H), 6.83 (dd, ^3J = 8.4 Hz, 2 H, Ph-H), 6.90 (d, ^3J = 8.7 Hz, 2 H, Ph-H), 7.38 (d, ^3J = 8.4 Hz, 2 H, Ph-H), 8.00 (d, ^3J = 8.7 Hz, 2 H, 2',6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 16.8 (+, *i*Pr-C), 17.5 (+, *i*Pr-C), 31.3 (+, *i*Pr-C), 40.0 [+, $N(CH_3)_2$], 55.1, 55.2 (+, OMe), 65.0 (–, OCH_2CH_3), 80.3 (C_{quat}, C-5), 82.9, 94.6 (C_{quat}, C≡C), 97.4 (+, C-4), 112.9, 113.8 (+, Ph-C), 115.7, 119.2, 130.0 (C_{quat}, C-2, Ph -C), 130.3, 133.1 (+, Ph-C), 152.9, 157.1, 158.7, 159.0 (C_{quat}, C-1,3, Ph-C). – MS (70 eV), *m/z* (%): 431 (100) [M^+], 402 (30), 388 (56) [$M^+ - C_3H_7$], 386 (96), 262 (64), 247 (22). – HRMS (EI) calcd for $C_{28}H_{33}NO$: 431.2460 (correct HRMS).

– **81t**: IR (Film): ν = 2205 cm^{-1} (C≡C), 1700, 1653 (C=C), 1635, 1606, 1559, 1506, 1457, 1249, 1034. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.94 (d, ^3J = 6.5 Hz, 3 H, *i*Pr-H), 1.15 (d, ^3J = 6.5 Hz, 3 H, *i*Pr-H), 1.41 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.56 [s, 6 H, $N(CH_3)_2$], 2.60 (sep, ^3J = 6.5 Hz, 1 H, *i*Pr-H), 3.80 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 4.00 (q, ^3J = 7.0 Hz,

2 H, OCH_2CH$_3$), 4.88 (s, 1 H, 4-H), 6.85 (d, ^3J = 8.6 Hz, 2 H, Ph-H), 6.96 (d, ^3J = 8.6 Hz, 2 H, Ph-H), 7.35 (d, ^3J = 8.6 Hz, 2 H, Ph-H), 7.90 (d, ^3J = 8.6 Hz, 2 H, 2',6'-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.5 (+, OCH$_2$*C*H$_3$), 17.0 (+, *i*Pr-C), 18.7 (+, *i*Pr-C), 30.3 (+, *i*Pr-C), 39.4 [+, N(CH$_3$)$_2$], 55.2, 55.3 (+, OCH$_3$), 65.1 (–, O*C*H$_2$CH$_3$),78.2 (C$_{quat}$, C-5), 86.8, 99.6 (C$_{quat}$, C≡C), 102.4 (+, C-4), 113.1, 113.9 (+, Ph-C), 116.3, 125.4, 127.4 (C$_{quat}$, C-2, Ph-C), 130.4, 132.4 (+, Ph-C), 143.2, 158.1, 159.2, 159.4 (C$_{quat}$, C-1,3, Ph-C). – MS (70 eV), *m/z* (%): 431 (38) [M$^+$], 388 (100) [M$^+$ – C$_3$H$_7$], 386 (14), 84 (14). – HRMS (EI) calcd for C$_{28}$H$_{33}$NO$_3$: 431.2460 (correct HRMS).

– **90t**: ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.38 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.14 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.46 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 2.60 (sep, ^3J = 6.7 Hz, 1 H, *i*Pr-H), 2.65 [s, 6 H, N(CH$_3$)$_2$], 3.77 (s, 3 H, OCH$_3$), 3.80 (s, 3 H, OCH$_3$), 4.63 (q, ^3J = 7.0 Hz, 1 H, OC*H*$_2$CH$_3$), 4.65 (q, ^3J = 7.0 Hz, 1 H, OC*H*$_2$CH$_3$), 5.79 (s, 1 H, 3-H), 6.76 (d, ^3J = 8.5 Hz, 2 H, Ph-H), 6.87 (d, ^3J = 8.5 Hz, 2 H, Ph-H), 7.15 (d, ^3J = 8.5 Hz, 2 H, Ph-H), 7.59 (d, ^3J = 8.5 Hz, 2 H, 2',6'-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 15.6 (+, OCH$_2$*C*H$_3$), 22.8 (+, *i*Pr-C), 25.1 (+, *i*Pr-C), 25.7 (+, *i*Pr-C), 40.1 [+, N(CH$_3$)$_2$], 55.2, 55.3 (+, OMe), 66.2 (–, O*C*H$_2$CH$_3$), 82.7 (C$_{quat}$, C-5), 85.6, 94.9, 96.1 (C$_{quat}$, C-1, C≡C), 113.7 × 2 (+, C-3, Ph-C), 113.8, 129.0, 131.6 (+, Ph-C), 116.8, 120.6 (C$_{quat}$, Ph-C), 158.8, 158.9, 164.0, 165.8 (C$_{quart}$, C-2,4, Ph-C). – MS (70 eV), *m/z* (%): 431 (43) [M$^+$], 402 (12) [M$^+$ – C$_2$H$_5$], 388 (24) [M$^+$ – C$_3$H$_7$], 386 (37), 264 (24), 262 (100) [M$^+$ of **54b**]. – HRMS (EI) calcd for C$_{28}$H$_{33}$NO$_3$: 431.2460 (correct HRMS).

1-Dimethylamino-6-ethoxy-1,3,5-cycloheptatriene (**95b**): Variation A: a solution of 1.00 g (2.00 mmol) of complex **18h** in pyridine (40 mL) was kept at 80 °C for 1 d. After evaporation of solvent, the residue was dissolved in pentane (100 mL), and the solution exposed to air for 2 h. The suspension is filtered off on a 3 cm thick layer of Celite and rinsed well with pentane (50 mL). The solvent of the filtrate was removed under reduced pressure, and the spectra of the compounds were recorded. Besides of the major product **95b**, some weaker signals of its regioisomer **95a** were also detected in the ^{1}H- and ^{13}C-NMR spectra. **95b**: – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.23 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 2.59 (s, 2 H, 7-H), 2.75 [s, 6 H, N(CH$_3$)$_2$], 3.74 (q, ^3J = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 5.11 (d, ^3J = 6.3 Hz, 1 H, 2-H), 5.33 (d, ^3J = 6.1 Hz, 1 H, 5-H), 6.01 (dd, ^3J = 10.7, ^3J = 6.1 Hz, 1 H, 4-H), 6.22 (dd, ^3J = 10.7,

^3J = 6.3 Hz, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, OCH_2CH_3), 34.6 (–, C-7), 40.3 [+, $N(CH_3)_2$], 63.5 (–, OCH_2CH_3), 96.9 (+, C-2), 99.3 (+, C-5), 123.7, 124.5 (+, C-3,4), 139.8, 145.4 (C_{quat}, C-1,6), 157.6 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 179 (64) [M^+], 164 (16) [$M^+ – CH_3$], 150 (100) [$M^+ – C_2H_6$], 131 (25), 122 (16), 72 (13).

Variation B: Following GP7, to a solution of 1.00 g (2.00 mmol) of complex **18h** in THF (40 mL) was added 0.39 ml (4.00 mmol) of 1-pentyne, and the mixture was stirred at 80 °C for 3 d. Besides **95b**, none of cycloaddition products was detected.

5.2. Synthesis of Indenones and their Derivatives

3-Cyclopropyl-4,7-dimethylindan-1-one (**100a**): Following GP7, to a solution of complex **18a** (719 mg, 2.00 mmol) in pyridine (40 mL) was added 531 mg (5.00 mmol) of 2,5-dimethyl-hexa-1,5-dien-3-yne (**15ll**), and the mixture stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 87.0 mg (22%) of **100a** [R_f = 0.59 (pentane/Et_2O = 3 : 1)] as a colorless oil. – IR (film): ν = 3000 cm^{-1} (C–H), 2923 (C–H), 1705 (C=O), 1494, 1248, 820. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11–0.20 (m, 1 H, *c*Pr-H), 0.38–0.51 (m, 2 H, *c*Pr-H), 0.60–0.69 (m, 1 H, *c*Pr-H), 0.81–0.93 (m, 1 H, *c*Pr), 2.44 (s, 3 H, CH_3), 2.49 (AB, dd, ^2J = 18.5, ^3J = 1.6 Hz, 1 H, 2-H), 2.58 (s, 3 H, CH_3), 2.79 (AB, dd, ^2J = 18.5, ^3J = 7.9 Hz, 1 H, 2-H), 2.97 ["t"d, ^3J = 7.9, ^3J = 7.9, ^3J = 1.6 Hz, 1 H, 3-H], 7.02 (d, ^3J = 7.5 Hz, 1 H, 5-H), 7.25 (d, ^3J = 7.5 Hz, 1 H, 6-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.9, 6.8 (–, *c*Pr-C), 16.4 (+, *c*Pr-C), 18.1, 19.0 (+, CH_3), 40.5 (+, C-3), 44.5 (–, C-2), 129.5, 135.4 (+, C-5,6), 133.3, 133.9, 135.7, 156.8 (C_{quat}, C-3a,4,7,7a), 207.8 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 200 (100) [M^+], 172 (54) [M^+ – CO], 159 (88) [$M^+ – C_3H_5$], 157 (34), 141 (18), 129 (36), 128 (41), 115 (41), 91 (17). – Elemental analysis calcd (%) for $C_{14}H_{16}O$ (200.3): C 83.95, H 8.05; found: C 83.43, H 8.72.

3-Isopropyl-4,7-dimethylindan-1-one (**100b**): In accordance with GP7, to a solution of 723 mg (2.00 mmol) of complex **18c** in 40 mL of pyridine was added 531 mg (5.00 mmol) of 1,2-dimethylhexa-1,5-dien-3-yne (**15ll**), and the mixture stirred at 80 °C for 3 d. Chromato-

graphy on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 282 mg (70%) of **100b** [R_f = 0.65 (pentane/Et_2O = 3 : 1)] as a colorless oil. – IR (film): ν = 2984 cm^{-1} (C–H), 1705 (C=O), 1581, 1495, 1248, 821. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.37 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.02 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 2.23–2.37 (m, 1 H, *i*Pr-H), 2.31 (s, 3 H, CH_3), 2.44–2.47 (m, 2 H, 2-H), 2.53 (s, 3 H, CH_3), 3.35 ["qui", ^3J = 7.9, ^3J = 7.9, ^3J = 7.9 Hz, 1 H, 3-H], 6.94 (d, ^3J = 7.5 Hz, 1 H, 5-H), 7.16 (d, ^3J = 7.5 Hz, 1 H, 6-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.7 (+, *i*Pr-C), 17.7, 17.8 (+, CH_3), 21.6 (+, *i*Pr-C), 29.0 (+, *i*Pr-C), 38.2 (–, C-2), 42.5 (+, C-3), 129.2, 135.2 (+, C-5,6), 132.2, 134.3, 135.3, 156.6 (C_{quat}, C-3a,4,7,7a), 207.9 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 202 (48) [M^+], 160 (41), 159 (100) [$M^+ – C_3H_7$], 129 (10), 116 (12), 115 (16), 91 (10). – Elemental analysis calcd (%) for $C_{14}H_{18}O$ (202.3): C 83.12, H 8.97; found: C 82.80, H 8.69.

3-Cyclopropyl-4-methyl-3,6,7,8,-tetrahydro-2H-as-indacen-1-one (**100c**) and *1-Cyclopropyl-4-methyl-1,6,7,8,-tetrahydro-2H-as-indacen-3-one* **(101c)**: Following GP7, to a solution of complex **18a** (719 mg, 2.00 mmol) in pyridine (40 mL) was added 651 mg (4.43 mmol; purity 90%) of 4-(1'-cyclopentenyl)-2-methylbut-1-en-3-yne (**28il**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 72.0 mg (16%) of **100c** and **101c** [R_f = 0.47 (pentane/Et_2O = 3 : 1); ratio 1 : 1.1] as a colorless oil. – IR (film): ν = 2955 cm^{-1} (C–H), 1696, (C=O), 1559, 1243. – ^1H NMR (250 MHz, $CDCl_3$): 0.09–0.25 (m, 1 H, *c*Pr-H), 0.38–0.53 (m, 2 H, *c*Pr-H), 0.57–0.76 (m, 1 H, *c*Pr-H), 0.79–0.95 (m, 1 H, *c*Pr-H), 1.95–2.24 (m, 3 H, 2,7-H), 2.44, 2.59 (s, 3 H, CH_3), 2.45–2.57 (m, 1 H, 2-H), 2.63–3.20 (m, 5 H, 6,8-H, 3-H of **100c**, 1-H of **101c**), 7.00, 7.26 (s, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.7, 2.9, 6.8 × 2 (–, *c*Pr-C), 16.0, 16.5 (+, *c*Pr-H), 18.4, 19.3 (+, CH_3), 25.2, 25.4 (–, C-7), 30.7, 31.5, 31.6, 33.1 (–, C-6,8), 41.2, 41.8 (+, C-3 of **100c**, C-1 of **101c**), 44.2, 44.4 (–, C-2), 125.7, 131.7 (+, C-5), 132.4, 132.6, 133.6, 136.7, 138.8, 140.0, 144.8, 151.8, 154.5 × 2 (C_{quat}, Ar-C), 207.0, 207.5 (C_{quat}, CO). – MS (70 eV), *m/z* (%): 226 (100) [M^+], 198 (42) [$M^+ – CO$], 185 (53) [$M^+ – C_3H_5$], 183 (48), 169 (14), 155 (14), 141 (12), 115 (12). – Elemental analysis calcd (%) for $C_{16}H_{18}O$ (226.3): C 84.92, H 8.02; found: C 84.78, H 7.70.

3-Isopropyl-4-methyl-3,6,7,8,-tetrahydro-2H-as-indacen-1-one (**100d**) and *1-Isopropyl-4-methyl-1,6,7,8,-tetrahydro-2H-as-indacen-3-one* (**101d**): Following GP7, to a solution of 723 mg (2.00 mmol) of complex **18c** in 40 mL of pyridine was added 651 mg (4.43 mmol; 90% purity) of 4-(1'-cyclopentenyl)-2-methylbut-1-en-3-yne (**28il**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 231 mg (51%) of **100d** and **101d** [R_f = 0.64 (pentane/Et_2O = 3 : 1); ratio 1.1 : 1] as a pale-yellow oil. – IR (film): ν = 2960 cm^{-1} (C–H), 1706 (C=O), 1609, 1465, 1399, 1269, 736. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.41, 0.46 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.03, 1.04 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 2.00–2.57 (m, 5 H, 2,7-H and *i*Pr-H), 2.33, 2.56 (s, 3 H, CH_3), 2.78–2.92 (m, 3 H) and 3.12–3.18 (m, 1 H) [total 4 H, 6,8-H], 3.30–3.32, 3.39–3.41 (m, 1 H, 3-H of **100d** and C-1 of **101d**), 6.95, 7.20 (s, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.8, 14.9, 18.1, 18.3 (+, *i*Pr-C), 21.8, 22.1 (+, CH_3), 25.2, 25.3 (–, C-7), 28.7, 29.1 (+, *i*Pr-C), 30.5, 30.6, 31.5, 32.8 (–, C-6,8), 37.9, 38.0 (–, C-2), 42.8, 43.2 (+, C-3 of **100d** and 1-H of **101d**), 125.5, 131.6 (+, C-5), 132.7, 132.9, 133.1, 136.5, 138.1, 139.7, 144.5, 151.5, 154.3 × 2 (C_{quat}, Ar-C), 207.3, 207.8 (C_{quat}, CO). – MS (70 eV), *m/z* (%): 228 (40) [M^+], 186 (25), 185 (100) [$M^+ – C_3H_7$]. – Elemental analysis calcd (%) for $C_{16}H_{20}O$ (228.3): C 84.16, H 8.83; found: C 83.96, H 8.68.

3-tert-Butyl-4-methyl-3,6,7,8,-tetrahydro-2H-as-indacen-1-one (**100e**) and *1-tert-Butyl-4-methyl-1,6,7,8,-tetrahydro-2H-as-indacen-3-one* (**100e**): Following GP7, to a solution of 751 mg (2.00 mmol) of complex **18d** in 40 mL of pyridine added 651 mg (4.43 mmol; purity 90%) of 4-(1'-cyclopentenyl)-2-methylbut-1-en-3-yne (**28il**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide [II, 40 g; elution with pentane/Et_2O (from 1 : 0 to 3 : 1)] and later on silica gel [50 g, elution with pentane/Et_2O (5 : 1)] gave 178 mg (37%) of **100e** and **101e** [R_f = 0.73 (pentane/Et_2O = 3 : 1); ratio 1 : 1.1] as a colorless oil. Two yellow fractions of chromium complexes were also isolated [78.0 mg; R_f = 0.59 (pentane/Et_2O =3 : 1) and 148.0 mg; R_f = 0.32 (pentane/Et_2O =3 : 1)] that both of them show a signal between 10–11 ppm in their ^1H NMR spectra, and they were not stable enough to fully identifidy. – IR (film): ν = 2954 cm^{-1} (C–H), 1706 (C=O), 1758, 1467, 1366, 1241, 1100. – ^1H NMR (250 MHz, $CDCl_3$): 0.85, 0.87 (s, 9 H, *t*Bu-H), 1.19–2.16 (m, 2 H, 7-H), 2.36, 2.58 (s, 3 H, CH_3), 2.59–2.62 (m, 1 H, 2-H), 2.82–3.28 (m, 5 H, 2,6,8-H, 3-H of **100e**,

1-H of **101e**), 7.23, 7.26 (s, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 18.4, 20.1 (+, CH_3), 25.4, 26.1 (–, C-7), 28.0, 28.1 (+, *t*Bu-C), 30.7, 31.6, 32.8, 33.4 (–, C-6,8), 37.0, 37.2 (C_{quat}, C-*t*Bu), 44.1, 44.2 (–, C-2), 48.0, 48.4 (+, C-3 of **100e**, C-1 of **101e**), 125.8, 131.3 (+, C-5), 133.4, 133.6, 133.9, 136.2, 139.7, 139.8, 144.8, 151.2, 152.7, 153.1 (C_{quat}, Ar-C), 207.3, 207.6 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 242 (20) [M^+], 186 (100), 57 (10) [$C_4H_9^+$].– Elemental analysis calcd (%) for $C_{17}H_{22}O$ (242.4): C 84.25, H 9.15; found: C 84.04, H 8.97.

3-Cyclopropyl-2,3,4,5,6,7,8,9-octahydrotrinden-1-one (**100f**): Following GP7, to a solution of 719 mg (2.00 mmol) of complex **18a** in 40 mL of pyridine was added 633 mg (4.00 mmol) of di(1-cyclopentenyl)ethyne (**28ii**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 98.0 mg (19%) of **100f** [R_f = 0.45 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 97–98 °C. – IR (KBr): ν = 2839 cm^{-1} (C–H), 1701 (C=C), 1594, 1276, 1237, 1120, 1021. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.15–0.25 (m, 1 H, *c*Pr-H), 0.43–0.55 (m, 2 H, *c*Pr-H), 0.61–0.73 (m, 1 H, *c*Pr-H), 0.75–0.90 (m, 1 H, *c*Pr-H), 2.03–2.39 (m, 4 H, 5,8-H), 2.47 (AB, dd, ^2J = 18.1 Hz, ^3J = 2.2 Hz, 1 H, 2-H), 2.60–2.98 (m, 7 H) and 3.04–3.23 (m, 3 H) [total 10 H, 2,3,4,6,7,8-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.7, 6.8 (–, *c*Pr-C), 16.0 (+, *c*Pr-C), 25.1, 25.3 (–, C-5,8), 30.3, 30.9, 31.6, 31.7 (–, C-4,6,7,9), 42.5 (+, C-3), 44.0 (–, C-2), 131.6, 139.2, 140.2, 141.0, 147.5, 152.1 (C_{quat}, Ar-C), 206.7 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 252 (100) [M^+], 224 (56) [M^+ – CO], 211 (34) [M^+ – C_3H_5], 195 (14), 181 (12), 165 (22), 153 (16). – Elemental analysis calcd (%) for $C_{18}H_{20}O$ (252.4): C 85.67, H 7.99; found: C 85.32, H 7.51.

3-Methyl-2,3,4,5,6,7,8,9-octahydrotrinden-1-one (**100g**): Following GP7, to a solution of 667 mg (2.00 mmol) of complex **18b** in 40 mL of pyridine was added 633 mg (4.00 mmol) of di(1-cyclopentenyl)ethyne (**28ii**), and the mixture stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 54.0 mg (12%) of **100g** [R_f = 0.49 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 84–85 °C. – IR (KBr): ν = 2955 cm^{-1} (C–H), 1700 (C=O), 1596. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34 (d, ^3J = 7.1 Hz, 3 H, CH_3), 2.04–2.31 (m, 5 H, 2,5,8-H), 2.75–3.07 (m, 7 H) and 3.20 (t, ^3J = 7.5 Hz,

2 H) [total 9 H, 2,4,6,7,8-H], 3.37–3.43 (m, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.5 (+, CH_3), 25.3, 25.4 (–, C-5,8), 30.3 × 2, 30.9, 31.6 (–, C-4,6,7,9), 32.2 (+, C-3), 46.1 (–, C-2), 130.8, 138.6, 140.1, 141.2, 147.5, 153.9 (C_{quat}, Ar-C), 207.1 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 226 (100) [M^+], 211 (30) [$M^+ – CH_3$], 198 (8) [M^+ – CO], 183 (14), 115 (12). – Elemental analysis calcd (%) for $C_{16}H_{18}O$ (226.1): C 84.91, H 8.02; found: C 84.71, H 7.87.

3-Isopropyl-2,3,4,5,6,7,8,9-octahydrotrinden-1-one (**100h**): Following GP7, to a solution of 723 mg (2.00 mmol) of complex **18c** in 40 mL of pyridine was added 633 mg (4.00 mmol) of di(1-cyclopentenyl)ethyne (**28ii**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 382 mg (75%) of **100h** [R_f = 0.63 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 121–122 °C. – IR (KBr): ν = 2956 cm^{-1} (C–H), 1695 (C=O), 1588, 1448, 1281, 1126. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.43 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.98 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.94–2.22 (m, 4 H, 5,8-H), 2.23–2.48 (m, 3 H, *i*Pr-H, 2-H), 2.69 (t, ^3J = 7.6 Hz, 2 H), 2.76 (t, ^3J = 7.9 Hz, 2 H), 2.87 (t, ^3J = 7.7 Hz, 2 H), and 3.11 (t, ^3J = 7.4 Hz, 2 H) [total 8 H, 4,6,7,9-H], 3.20–3.35 (m, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.6, 21.6 (+, *i*Pr-C), 25.0 × 2 (–, C-5,8), 28.5 (+, *i*Pr-C), 30.0, 30.4, 30.6, 31.2 (–, C-4,6,7,9), 37.4 (–, C-2), 43.2 (+, C-3), 131.4, 138.2, 139.6, 140.6, 147.0, 151.7 (C_{quat}, Ar-C), 206.6 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 254 (26) [M^+], 211 (100) [$M^+ – C_3H_7$]. – Elemental analysis calcd (%) for $C_{18}H_{22}O$ (254.4): C 84.99, H 8.72; found: C 84.74, H 8.50.

3-Isopropyl-4-methyl-2,3,6,7,8,9-hexahydrocyclopenta[a]naphthalen-1-one (**100i**) and *1-Isopropyl-4-methyl-1,2,6,7,8,9-hexahydrocyclopenta[a]naphthalen-3-one* (**101i**): Following GP7, to a solution of 989 mg (2.74 mmol) of complex **18c** in 55 mL of pyridine was added 536 mg (3.68 mmol) of 4-(1'-cyclohexenyl)-2-methylbut-1-en-3-yne (**28i^{1}l**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 3 : 1) gave 302 mg (46%) of **100i** and **101i** [R_f = 0.74 (pentane/Et_2O = 3 : 1); ratio 1.1 : 1] as a colorless oil. – IR (film): ν = 2929 cm^{-1} (C–H), 1701 (C=O), 1576, 1464, 1248, 1116. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.37, 0.38 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.00 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.50–2.00 (m, 4 H, 7,8-H), 2.26, 2.48 (s, 3 H, CH_3),

2.40–2.50 (m, 3 H), 2.60–2.89 (m, 3 H), 3.05–3.15 (m, 1 H) and 3.25–3.33 (m, 1 H) [total 8 H, 2,6,9-H, *i*Pr-H, 3-H of **100d** and 1-H of **101d**], 6.74, 6.99 (s, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.5, 14.6, 17.6, 17.7 (+, *i*Pr-C), 21.8, 21.9 (+, CH_3), 22.3, 22.36, 22.38, 22.6, (–, C-7,8), 28.5, 28.9 (+, *i*Pr-C), 25.2, 25.4, 29.0, 29.6, (–, C-6,9), 38.2, 38.3 (–, C-2), 42.1, 42.2 (+, C-3 of **100i** and 1-H of **101i**), 130.4, 136.5 (+, C-5), 131.4, 131.6, 132.2, 133.9, 134.3 × 2, 136.1, 143.4, 154.8, 157.2 (C_{quat}, Ar-C), 207.2, 207.7 (C_{quat}, CO). – MS (70 eV), *m/z* (%): 242 (42) [M^+], 199 (100) [$M^+ – C_3H_7$], 43 (16) [$C_3H_7^+$]. – HRMS (EI) calcd for $C_{17}H_{22}O$: 242.1671 (correct HRMS).

3-tert-Butyl-4-methyl-2,3,6,7,8,9-hexahydrocyclopenta[a]naphthalen-1-one (**100j**) and *1-tert-Butyl-4-methyl-1,2,6,7,8,9-hexahydrocyclopenta[a]naphthalen-3-one* (**101j**): Following GP7, to a solution of 751 mg (2.00 mmol) of complex **18d** in 40 mL of pyridine was added 438 mg, 3.00 mmol) of 4-(1'-cyclohexenyl)-2-methylbut-1-en-3-yne (**28i^{1}l**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide [II, 40 g; elution with pentane/Et_2O (from 1 : 0 to 3 : 1)] and later on silica gel [50 g, elution with pentane/Et_2O (5 : 1)] gave 106 mg (21%) of **100j** and **101j** [R_f = 0.64 and 0.54 (pentane/Et_2O 3 : 1); ratio 1 : 1.1] as a pale-yellow colorless oil. – IR (film): ν = 2937 cm^{-1} (C–H), 1706 (C=O), 1573, 1480, 1277, 1113, 738. – ^{1}H NMR (250 MHz, $CDCl_3$): 0.84, 0.85 (s, 9 H, *t*Bu-H), 1.41–2.10 (m, 4 H, 7,8-H), 2.31, 2.54 (s, 3 H, CH_3), 2.50–2.60 (m, 2 H), 2.70–2.90 (m, 3 H) and 3.10–3.22 (m, 2 H) [total 7 H, 2,6,9-H, 3-H of **100j**, 1-H of **101j**], 6.84, 7.06 (s, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 17.9, 19.7 (+, CH_3), 22.47, 22.54, 22.6, 22.7 (–, C-7,8), 28.0, 28.2 (+, *t*Bu-C), 25.4, 27.5, 29.2, 29.7 (–, C-6,9), 37.1, 37.2 (C_{quat}, C-*t*Bu), 44.7, 44.8 (–, C-2), 47.0, 47.1 (+, C-3 of **100j**, C-1 of **101j**), 130.7, 136.3 (+, C-5), 132.8, 133.0, 133.8, 134.4, 134.5, 134.7, 136.5, 143.5, 153.5, 155.9 (C_{quat}, Ar-C), 207.3, 207.9 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 256 (28) [M^+], 200 (100), 57 (10) [$C_4H_9^+$]. – HRMS (EI) calcd for $C_{18}H_{24}O$:256.1827 (correct HRMS).

3-Isopropyl-2,3,4,5,6,7,8,9,10,11-decahydrocyclopenta[l]phenanthren-1-one (**100k**):
Following GP7, to a solution of 723 mg (2.00 mmol) of complex **18c** in 40 mL of pyridine was added 745 mg (4.00 mmol) of di(1-cyclohexenyl)ethyne (**28i^{1}i^1**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/

Et_2O (from 1 : 0 to 3 : 1) gave 382 mg (75%) of **100k** [R_f = 0.73 (pentane/Et_2O = 3 : 1)] as a colorless solid, m. p. 148–149 °C. – IR (KBr): ν = 2931 cm^{-1} (C–H), 1692 (C=C), 1571, 1546, 1278, 1124. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.41 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.04 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.50–2.10 (m, 8 H, 5,6,9,10-H), 2.22–2.82 (m, 9 H, *i*Pr-H, 4,7,8,11-H), 3.08–3.23 (m, 2 H, 2-H), 3.23–3.35 (m, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.6, 22.0 (+, *i*Pr-C), 21.8, 22.1, 22.6, 22.8, 25.9, 26.3, 26.4, 27.2 (–, C-4,5,6,7,8,9,10,11), 28.5 (+, *i*Pr-C), 38.4 (–, C-2), 42.0 (+, C-3), 131.4, 131.4, 134.1, 134.7, 142.3, 154.7 (C_{quat}, Ar-C), 207.8 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 282 (54) [M^+], 239 (100) [$M^+ – C_3H_7$]. – Elemental analysis calcd (%) for $C_{20}H_{26}O$ (282.4): C 85.06, H 9.28; found: C 84.84, H 9.34.

5-Dimethylamino-1,2-di(1'-cyclohexenyl)-3-ethoxy-5-isopropyl-1,3-cyclopentadiene (**99-*i*Pr**): Reaction condition like the experiment for preparation of **100k**, but reaction time only 2 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane to remove alkyne **28i^{1}i^1** and $Cr(CO)_5Py$, and then, washing with pentane/Et_2O (3 : 1) gave 211 mg of a mixture, which contained **99-*i*Pr** (major product), **100k** (first minor product), **102-*i*Pr** and other impurity. – MS (70 eV), *m/z* (%): 361 (1%) [M^+ (**102-*i*Pr**)], 355 (30) [M^+ (**99-*i*Pr**)], 326 (65) [M^+ (**99-*i*Pr**) – C_2H_5], 312 (100) [M^+ (**99-*i*Pr**) – C_3H_7], 310 (46), 282 (21) [M^+ (**100k**)], 239 (36) [M^+ (**100k**) – C_3H_7], 202 (18), 200 (90), 173 (33), 129 (30), 83 (41), 74 (46), 59 (100), 45 (47), 41 (28). Selected signals of **99-*i*Pr**: – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.39 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.00 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.28 (t, ^3J = 6.8 Hz, 2 H, OCH_2CH_3), 2.28 [s, 6 H, $N(CH_3)_2$], 3.80 (q, ^3J = 6.8 Hz, 2 H, OCH_2CH_3), 4.57 (s, 1 H, 4-H), 5.57, 5.65 (s, 2 H, 1'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.2, 14.6, 16.6 (+, *i*Pr-C, OCH_2CH_3), 42.0 [+, $N(CH_3)_2$], 64.1 (–, OCH_2CH_3), 78.5 (C_{quat}, C-5), 97.6 (+, C-4), 125.8, 126.3 (+, C-1'), 154.7, 158.8 (C_{quat}, C-1,3).

3-tert-Butyl-2,3,4,5,6,7,8,9,10,11-decahydrocyclopenta[l]phenanthren-1-one (**100l**): Following GP7, to a solution of 751 mg (2.00 mmol) of complex **18d** in 40 mL of pyridine was added 745 mg (4.00 mmol) of di(1-cyclophexenyl)ethyne (**28i^{1}i^1**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide [II, 40 g; elution with pentane/Et_2O (from 1 : 0 to 3 : 1)] and later on silica gel [50 g, elution with pentane/Et_2O

(5 : 1)] gave 110 mg (19%) of **100l** [R_f = 0.69 (pentane/Et_2O = 5 : 1)] as a colorless solid, m. p. 115 °C. – IR (KBr): ν = 2930 cm^{-1} (C–H), 1700 (C=O), 1567, 1448, 1364, 1291, 1253, 1120. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.86 (s, 9 H, *t*Bu-H), 1.38–2.10 (m, 8 H, 5,6,9,10-H), 2.45–2.90 (m, 8 H, *i*Pr-H, 4,7,8,11-H), 3.02–3.30 (m, 3 H, 2,3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.0, 22.4, 22.8, 23.0, 26.1, 26.7, 27.3, 28.4 (–, C-5,6,9,10), 28.2 (+, *t*Bu-C), 37.2 (C_{quat}, *t*Bu-C), 45.1 (–, C-2), 46.7 (+, C-3), 132.0, 133.3, 134.1, 135.1, 141.9, 153.5 (C_{quat}, Ar-C), 207.6 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 296 (22) [M^+], 240 (100). – Elemental analysis calcd (%) for $C_{21}H_{28}O$ (296.5): C 85.08, H 9.52; found: C 84.88, H 9.36.

5.3. Synthesis of Basic Structures of Terpenoids

General Procedure for the Adol Reaction

1) Reaction at Ambient Temperature (GP8A): To a solution of the respective ethoxycyclopentadiene **130** in dioxane (100-150 ml) is added a concentrated or 3 N solution of hydrochloric acid (5–10 ml), and the mixture is stirred at ambient temperature for 2–4 d. The reaction is quenched by addition of a sat. aqueous solution of potassium carbonate until no gas evaporation. The aqueous solution is extracted with CH_2Cl_2 (5 × 50 mL), and the combined organic phase is dried over $MgSO_4$. After removal of the solvent, the residue is purified by column chromatography on silica gel.

2) Reaction at High Temperature (GP8B): Like GP8A, but cyclopentenones **129** are used as starting materials, and reaction is carried out at 60 °C for 18–36 h.

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.4]non-6'-yl)methyl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (**130a**): According to GP7, a solution of complex **18i** (2.30 g, 5.01 mmol) in pyridine (100 mL) was treated with 1.34 g (7.52 mmol) of 1,2-diphenylethyne (**15baa**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (from 20 : 1 to 1 : 2) gave 1.11 g (50%) **10a** [R_f = 0.38 (pentane/ Et_2O =1 :1); d. r. = 1.5 : 1] as a pale-yellow oil. – IR (film): ν = 2970 cm^{-1} (C–H), 2874, 1710, 1630 (C=C), 1374, 1194, 1031, 764, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20–2.20 (m, 10 H, OCH_2CH_3, CCH_2CH, 7',8',9'-H), 2.35–2.45 (m, 1 H, 6'-H), 2.42 [s, 6 H,

$N(CH_3)_2$], 3.24–3.70 (m, 2 H, OCH_2CH_3), 3.80–4.12 (m, 4 H, 2',3'-H), 5.10, 5.11 (s, 1 H, 4-H), 7.11–7.35 (m, 8 H, Ph-H), 7.58–7.65 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major product: δ = 14.1 (+, OCH_2CH_3), 20.1, 32.6, 34.2, 35.2 (–, CCH_2CH, C-7',8',9'), 39.9 [+, $N(CH_3)_2$], 41.0 (+, C-6'), 64.0, 64.3, 64.4 (–, OCH_2CH_3, C-2',3'), 75.8 (C_{quat}, C-5), 98.0 (+, C-4), 118.5 (C_{quat}, C-5'), 126.3, 126.8, 127.2, 127.7, 129.3, 129.5 (+, Ph-C), 134.2, 135.3, 137.6 (C_{quat}, C-2, Ph-C), 145.7 (C_{quat}, C-1), 158.4 (C_{quat}, C-3). Minor product: δ = 14.2 (+, OCH_2CH_3), 20.9, 30.3, 34.2, 34.8 (–, CCH_2CH, C-7',8',9'), 39.9 [+, $N(CH_3)_2$], 41.4. (+, C-6'), 63.8, 64.0, 64.4 (–, OCH_2CH_3, C-2', 3'), 75.6 (C_{quat}, C-5), 97.7 (+, C-4), 118.4 (C_{quat}, C-5'), 126.3, 126.8, 127.3, 127.6, 129.5, 129.7 (+, Ph-C), 133.8, 135.2, 137.6 (C_{quat}, C-2, Ph-C), 145.5 (C_{quat}, C-1), 158.0 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 445 (18) [M^+], 416 (26) [$M^+ - C_2H_5$], 246 (16), 184 (13), 141 (36), 99 (100), 55 (17), 43 (20). – HRMS (EI) calcd for $C_{29}H_{35}NO_3$: 445.2617 (correct HRMS).

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.4]non-6'-yl)methyl]-3-ethoxy-1-trimethylsilyl-1,3-cyclopentadiene (**130b**): Following GP7, a solution of complex **18i** (2.19 g, 4.76 mmol) in pyridine (100 mL) was treated with 700 mg (7.13 mmol) of trimethylsilylethyne (**15j**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (+ 1% NEt_3, from 1 : 0 to 1 : 1) gave 230 mg of the first diastereomer [R_f = 0.59 (pentane/Et_2O = 1 : 1)] as a colorless oil, 353 mg of the mixture of the first and second diastereomers (ratio = 1.4 : 1) as a colorless oil, and 201 mg of the second diastereomer [R_f = 0.51, pentane/Et_2O = 1 : 1] as a pale yellow oil. The combined yield of this reaction: 784 mg (45%) and d. r. = 1.3 : 1. – First stereoisomer (major product): IR (film): ν = 2952 cm^{-1} (C–H), 1615 (C=C), 1327, 1246, 1192, 1039, 838, 756. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 1.31 [t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3], 1.00–1.09 (1 H), 1.34–1.65 (6 H), and 1.80–2.22 (2 H) [m, total 9 H, CCH_2CH, 6',7',8',9'-H], 2.16 [s, 6 H, $N(CH_3)_2$], 3.70–3.90 (m, 6 H, OCH_2CH_3, 2',3'-H), 4.96, (s, 1 H, 4-H), 6.25 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.4 [+, $Si(CH_3)_3$], 14.6 (+, OCH_2CH_3), 20.7, 31.9, 34.5, 34.9 (–, CCH_2CH, C-7',8',9'), 40.7 [+, $N(CH_3)_2$], 41.6 (+, C-6'), 64.4, 64.6, 64.7 (–, OCH_2CH_3, C-2',3'), 80.9 (C_{quat}, C-5), 103.0 (+, C-4), 118.9 (C_{quat}, C-5'), 138.9 (+, C-2), 157.2, 158.4 (C_{quat}, C-1,3). – MS (70 eV), *m/z* (%): 365 (37) [M^+], 336 (100) [M^+ –

C_2H_5], 238 (34), 73 (12) [$Si(CH_3)_3^+$]. – HRMS (EI) calcd for $C_{20}H_{35}NO_3Si$: 365.2386 (correct HRMS). – Second stereoisomer (minor product): IR (KBr): ν = 2952 cm^{-1} (C–H), 1613 (C=C), 1328, 1247, 1193, 836, 764. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 1.30 [t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3], 1.26–1.39 (2 H), 1.42–1.90 (6 H), 2.15–2.30 (1 H), [m, total 9 H, CCH_2CH, 6',7',8',9'-H], 2.22 [s, 6 H, $N(CH_3)_2$], 3.78–3.89 (m, 6 H, OCH_2CH_3, 2',3'-H), 4.99, (d, ^4J = 1.6 Hz, 1 H, 4-H), 6.25 (d, ^4J = 1.6 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.3 [+, $Si(CH_3)_3$], 14.5 (+, OCH_2CH_3), 20.1, 31.6, 33.8, 34.6 (–, CCH_2CH, C-1',7',8',9'), 40.3 [+, $N(CH_3)_2$], 41.5 (+, C-6'), 64.3, 64.7, 64.8 (–, OCH_2CH_3, C-2',3'), 81.0 (C_{quat}, C-5), 106.0 (+, C-4), 118.8 (C_{quat}, C-5'), 139.5 (+, C-2), 157.2, 158.0 (C_{quat}, C-1,3). – MS (70 eV), *m/z* (%): 365 (38) [M^+], 336 (100) [$M^+ – C_2H_5$], 238 (53), 169 (12), 99 (11), 73 (34) [$Si(CH_3)_3^+$]. – HRMS (EI) calcd for $C_{20}H_{35}NO_3Si$: 365.2386 (correct HRMS).

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.4]non-6'-yl)methyl]-3-ethoxy-1-propyl-1,3-cyclopentadiene (**130c**): According to GP7, a solution of complex **18i** (2.30 g, 5.01 mmol) in pyridine (100 mL) was treated with 681 mg (10.0 mmol) of 1-pentyne (**15h[1]**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (+ 1% NEt_3, from 1 : 0 to 0 : 1) gave 1.15 g (68%) of **130c** [R_f = 0.48 (Et_2O); d. r. = 1 : 1] as a pale-yellow oil. – IR (film): ν = 2956 cm^{-1} (C–H), 1635 (C=C), 1584, 1339, 1196, 1151, 1107, 1040. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.83 (t, ^3J = 7.0 Hz, 3 H, $CH_2CH_2CH_3$), 1.04–2.89 (m, 16 H, $CH_2CH_2CH_3$, CCH_2C, OCH_2CH_3, 6',7',8',9'-H), 2.02, 2.03 [s, 6 H, $N(CH_3)_2$], 3.60–3.85 (m, OCH_2CH_3, 2',3'-H), 4.53, 4.55 (s, 1 H, 4-H), 5.52, 5.57 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.96, 13.99, 14.2, 14.3 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 19.27, 19.33, 19.9, 20.4, 28.2, 29.4, 30.4, 31.8, 32.8, 33.8, 34.1, 34.5 (–, CCH_2CH, $CH_2CH_2CH_3$, C-7',8',9'), 39.6, 39.7 [+, $N(CH_3)_2$], 40.7, 40.9 (+, C-6'), 64.0, 64.10, 64.12, 64.17, 64.48, 64.51 (–, OCH_2CH_3, C-2',3'), 75.7, 75.8 (C_{quat}, C-5), 94.5, 95.3 (+, C-4), 118.4, 118.5 (C_{quat}, C-5'), 122.0, 122.3 (C_{quat}, C-2), 155.7, 156.6, 158.3, 158.4 (C_{quat}, C-1,3). – MS (70 eV), *m/z* (%): 335 (24) [M^+], 306 (100) [$M^+ – C_2H_5$], 194 (14), 178 (15), 99 (14). – HRMS (EI) calcd for $C_{20}H_{33}NO_3$: 335.2460 (correct HRMS).

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.4]non-6'-yl)methyl]-3-ethoxy-1-methyl-1,3-cyclopentadiene (**130d**): According to GP7, a solution of complex **18i** (2.30 g, 5.01 mmol) in pyridine (100 mL) was treated with 1-propyne (**15h**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (+ 1% NEt_3, from 1 : 0 to 1 : 2) gave 1.15 g (75%) of **130d** [R_f = 0.13 (pentane/Et_2O = 1 . 1); d. r. = 2 : 1] as a colorless oil. – IR (film): ν = 2948 cm^{-1} (C–H), 1638 (C=C), 1585, 1344, 1201, 1151, 1105, 1041. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.13–1.88 (m, 8 H, CCH_2CH, 7',8',9'-H), 1.27, 1.28 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.69, 1.71 (d, ^4J = 1.8 Hz, 3 H, CH_3), 2.08–2.18 (m, 1 H, 6'-H), 2.12, 2.14 [s, 6 H, $N(CH_3)_2$], 3.74–3.90 (m, 6 H, OCH_2CH_3, 2',3'-H), 4.62, 4.64 (d, ^4J = 1.8 Hz, 1 H, 4-H), 5.61, 5.66 ("qui", ^4J = 1.8, ^4J = 1.8 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major product: δ = 13.8, 14.4 (+, CH_3, OCH_2CH_3), 20.0, 30.7, 32.7, 34.3 (–, CCH_2CH, C-7',8',9'), 39.8 [+, $N(CH_3)_2$], 40.8 (+, C-6'), 64.2, 64.4, 64.7 (–, OCH_2CH_3, C-2',3'), 75.9 (C_{quat}, C-5), 95.7 (+, C-4), 118.6 (C_{quat}, C-5'), 124.5 (+, C-2), 151.9 (C_{quat}, C-1), 159.8 (C_{quat}, C-3). Minor product: δ = 12.5, 14.5 (+, OCH_2CH_3, CH_3,), 20.5, 32.0, 33.7, 34.6 (–, CCH_2CH, C-7',8',9'), 40.0 [+, $N(CH_3)_2$], 41.1 (+, C-6'), 64.3, 64.4, 64.8 (–, OCH_2CH_3, C-2',3'), 75.7 (C_{quat}, C-5), 94.9 (+, C-4), 118.7 (C_{quat}, C-5'), 124.7 (+, C-2), 151.0 (C_{quat}, C-1), 159.4 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 307 (36) [M^+], 278 (100) [$M^+ – C_2H_5$], 150 (26), 41 (12). – Elemental analysis calcd (%) for $C_{18}H_{29}NO_3$ (459.6): C 70.32, H 9.51; found: C 69.97, H 9.36.

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.4]non-6'-yl)methyl]-3-ethoxy-1,2-dimethyl-1,3-cyclopentadiene (**130e**): According to GP7, a solution of complex **18i** (2.30 g, 5.01 mmol) in pyridine (100 mL) was treated with 541 mg (10.0 mmol) of 2-butyne (**15hh**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O/EtOAc (+ 1% NEt_3, from 1/0/0 to 0/10/1) gave 1.08 g (67%) of **130e** [R_f = 0.21 (Et_2O); d. r. = 1 : 1] as a colorless oil. – IR (film): ν = 2946 cm^{-1} (C–H), 1664, 1593 (C=C), 1344, 1200, 1151, 1106, 1038. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.80 (m, 8 H, CCH_2CH, 7',8',9'-H), 1.18, 1.19 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.49, 1.51, 1.53, 1.56 (s, 6 H, CH_3), 1.96–2.06 (m, 1 H, 6'-H), 1.99, 2.01 [s, 6 H, $N(CH_3)_2$], 3.67–3.80 (m, 6 H, OCH_2CH_3, 2',3'-H), 4.49, 4.51 (s, 1 H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.50, 8.54, 9.06, 10.9 (+, CH_3), 14.2, 14.3 (+, OCH_2CH_3), 20.0, 20.4, 30.2, 31.8, 32.5,

33.7, 34.2, 34.5 (–, C*C*H$_2$CH, C-7',8',9'), 39.7, 39.8 [+, N(CH$_3$)$_2$], 40.8, 41.1 (+, C-6'), 64.01, 64.07, 64.11, 64.2, 64.5, 64.6 (–, O*C*H$_2$CH$_3$, C-2',3'), 74.2, 74.4 (C$_{quat}$, C-5), 93.6, 94.2 (+, C-4), 118.5, 118.6 (C$_{quat}$, C-5'), 130.4, 130.8 (C$_{quat}$, C-2), 141.8, 142.7 (C$_{quat}$, C-1), 160.0, 160.4 (C$_{quat}$, C-3). – MS (70 eV), *m/z* (%): 321 (58) [M$^+$], 292 (100) [M$^+$ – C$_2$H$_5$], 193 (12), 180 (60), 152 (26), 99 (19). – HRMS (EI) calcd for C$_{19}$H$_{31}$NO$_3$: 321.2204 (correct HRMS).

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.5]dec-6'-yl)methyl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (**130f**): According to GP7, a solution of complex **18j** (2.37 g, 5.01 mmol) in pyridine (100 mL) was treated with 1.34 g (7.50 mmol) of 1,2-diphenylethyne (**15aa**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et$_2$O (from 20 : 1 to 1 : 2) gave 1.20 g (52%) of **130f** [R_f = 0.37 (pentane/Et$_2$O = 3 :1); d. r. = 1 : 1] as a colorless solid. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.90–2.07 (m, 11 H, CC*H*$_2$CH, 6',7',8',9',10'-H), 1.35 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 2.36 [s, 6 H, N(CH$_3$)$_2$], 3.24–3.65 (m, 2 H, OC*H*$_2$CH$_3$), 3.91–4.01 (m, 4 H, 2',3'-H), 5.09, 5.11 (s, 1 H, 4-H), 7.14–7.36 (m, 8 H, Ph-H), 7.56–7.68 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.36, 14.42 (+, OCH$_2$*C*H$_3$), 23.5, 23.77, 23.83 × 2, 30.7, 31.7, 32.6, 32.7, 33.9, 34.3 (–, C*C*H$_2$CH, C-7',8',9',10'), 39.7 (+, C-6'), 40.26, 40.34 [+, N(CH$_3$)$_2$], 64.2, 64.3, 64.4, 64.6, 64.8 × 2 (–, O*C*H$_2$CH$_3$, C-2',3'), 76.1, 76.4 (C$_{quat}$, C-5), 98.1, 98.9 (+, C-4), 110.6, 111.2 (C$_{quat}$, C-5'), 126.4, 126.5, 127.09, 127.10, 127.4, 127.6, 128.0, 128.1, 129.5, 129.8, 129.9, 130.0 (+, Ph-C), 134.5, 134.6, 135.6, 135.7, 138.2 × 2 (C$_{quat}$, C-2, Ph-C), 145.7, 145.8 (C$_{quat}$, C-1), 158.3, 158.4 (C$_{quat}$, C-3). – MS (70 eV), *m/z* (%): 459 (100) [M$^+$], 430 (92) [M$^+$ – C$_2$H$_5$], 415 (30) [M$^+$ – N(CH$_3$)$_2$], 304 (32), 288 (14), 276 (13). – Elemental analysis calcd (%) for C$_{30}$H$_{37}$NO$_3$ (459.6): C 78.40, H 8.11; found: C 78.13, H 7.79.

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.5]dec-6'-yl)methyl]-3-ethoxy-1,2-dimethyl-1,3-cyclopentadiene (**130g**): According to GP7, a solution of complex **18j** (2.37 g, 5.01 mmol) in pyridine (100 mL) was treated with 541 mg (10.0 mmol) of 2-butyne (**15hh**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et$_2$O (from 10 : 1 to 1 : 2) gave 1.11 g (66%) of **130g** [R_f = 0.63 (Et$_2$O); d. r. = 1 : 1] and trace amount of its hydrolysis product as a colorless oil. – IR (film): ν = 2935 cm^{-1} (C–H), 1700, 1653 (C=C), 1446, 1382, 1155, 1088, 924. – ^{1}H NMR (250 MHz, CDCl$_3$):

δ = 1.00–1.70 (m, 17 H, 2 × CH_3, CC*H*$_2$CH, 6',7',8',9',10'-H), 1.29 (t, ^3J = 7.0 Hz,, 3 H, OCH$_2$C*H*$_3$), 2.09, 2.10 [s, 6 H, N(CH$_3$)$_2$], 3.70–3.90 (m, 6 H, OC*H*$_2$CH$_3$, 2',3'-H), 4.58, 4.62 (s, 1 H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.7 × 2, 9.1, 11.1 (+, CH_3), 14.4, 14.5 (+, OCH$_2$*C*H$_3$), 23.7 × 2, 23.8, 24.3, 30.8, 31.7, 32.7, 33.7 × 2, 34.3 (–, C*C*H$_2$CH, C-7',8',9',10'), 39.2 (+, C-6'), 39.9, 40.0 [+, N(CH$_3$)$_2$], 64.3, 64.4, 64.5 (–, O*C*H$_2$CH$_3$, C-2',3'), 74.9, 75.0 (C_{quat}, C-5), 93.7, 94.6 (+, C-4), 111.0, 111.1 (C_{quat}, C-5'), 130.8, 130.9 (C_{quat}, C-2), 142.2, 142.5 (C_{quat}, C-1), 160.3 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 335 (66) [M$^+$], 306 (100) [M$^+$ – C$_2$H$_5$], 291 (58) [M$^+$ – N(CH$_3$)$_2$], 180 (55), 164 (18), 152 (32). – HRMS (EI) calcd for $C_{20}H_{33}NO_3$: 335.2460 (correct HRMS).

1-tert-Butyl-5-dimethylamino-5-[(1',4'-dioxaspiro[4.5]dec-6'-yl)methyl]-3-ethoxy-1,3-cyclopentadiene (**130h**): According to GP7, a solution of complex **18j** (2.59 g, 5.48 mmol) in pyridine (100 mL) was treated with 823 mg (10.0 mmol) of 2,2-dimethyl-3-butyne (**15n**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et$_2$O (from 10 : 1 to 3 : 1) gave 747 mg (38%) of **130h** [R_f = 0.75 (pentane/Et$_2$O = 3 : 1); d. r. = 2 : 1] as a colorless oil. – IR (KBr): ν = 2936 cm^{-1} (C–H), 1696, 1653 (C=C), 1087, 924, 668. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02–1.79 (m, 10 H, CC*H*$_2$CH, 7',8',9',10'-H), 1.20, 1.23 [s, 9 H, C(CH$_3$)$_3$], 1.29, 1.30 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 2.11–2.20 (m, 1 H, 6'-H), 2.14, 2.16 [s, 6 H, N(CH$_3$)$_2$], 3.74–3.94 (m, 6 H, OC*H*$_2$CH$_3$, 2',3'-H), 4.63, 4.73 (d, ^4J = 1.8 Hz, 1 H, 4-H), 5.74, 5.83 (d, ^4J = 1.8 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major stereoisomer: δ = 14.5 (+, OCH$_2$*C*H$_3$), 23.7, 24.6, 31.9, 32.1, 34.9 (–, C*C*H$_2$CH, C-7',8',9',10'), 31.4 [+, C(*C*H$_3$)$_3$], 34.5 [C_{quat}, *C*(CH$_3$)$_3$], 40.7 [+, N(CH$_3$)$_2$], 41.78 (+, C-6'), 64.1, 64.40, 64.5 (–, O*C*H$_2$CH$_3$, C-2',3'), 79.2 (C_{quat}, C-5), 97.4 (+, C-4), 111.1 (C_{quat}, C-5'), 125.5 (+, C-2), 157.1 (C_{quat}, C-1), 162.4 (C_{quat}, C-3). Minor stereoisomer: δ = 14.5 (+, OCH$_2$*C*H$_3$), 23.8, 24.3, 32.0, 32.6, 34.9 (–, C*C*H$_2$CH, C-7',8',9',10'), 31.6 [+, C(*C*H$_3$)$_3$], 34.5 [C_{quat}, *C*(CH$_3$)$_3$], 41.0 [+, N(CH$_3$)$_2$], 41.84 (+, C-6''), 64.1, 64.44, 64.7 (–, O*C*H$_2$CH$_3$, C-2',3'), 78.3 (C_{quat}, C-5), 95.9 (+, C-4), 111.4 (C_{quat}, C-5'), 123.4 (+, C-2), 157.6 (C_{quat}, C-1), 164.0 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 363 (72) [M$^+$], 348 (18) [M$^+$ – CH$_3$], 334 (100) [M$^+$ – C$_2$H$_5$], 319 (26)

[M^+ – $N(CH_3)_2$], 318 (30), 306 (56) [M^+ – $C(CH_3)_3$], 221 (10), 192 (10). – Elemental analysis calcd (%) for $C_{22}H_{37}NO_3$ (363.5): C 72.69, H 10.26; found: C 72.59, H 9.95.

5-Dimethylamino-5-[(1'',4''-dioxaspiro[4.5]dec-6''-yl)methyl]-3-ethoxy-1-(3'-trifluoromethyl-phenyl)-1,3-cyclopentadiene (**130i**): Following GP7, a solution of complex **18j** (2.37 g, 5.01 mmol) in pyridine (100 mL) was treated with 1.70 g (10.0 mmol) of 3'-(triflouromethyl)-phenylethyne (**29a²**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (from 20 : 1 to 1 : 1) gave 893 mg (40%) of **130i** [R_f = 0.56 (pentane/Et_2O = 3 : 1); d. r. 2 : 1] as a colorless oil. – IR (film): ν = 2938 cm^{-1} (C–H), 1699, 1624 (C=C), 1333, 1278, 924, 803, 701. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.76–1.87 (m, 10 H, CCH_2CH, 7",8",9",10"-H), 1.38 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.22 [s, 6 H, $N(CH_3)_2$], 2.30–2.36 (m, 1 H, 6"-H), 3.45–3.58 (m, 1 H, OCH_2CH_3), 3.85–3.99 (m, 5 H, OCH_2CH_3, 2",3"-H), 5.04, 5.08 (d, ^4J = 1.8 Hz, 1 H, 4-H), 6.55, 6.56 (d, ^4J = 1.8 Hz, 1 H, 2-H), 7.39–7.44 (m, 2 H, Ar-H), 8.05 (d, ^3J = 6.9 Hz, 1 H, Ar-H), 8.20 (d, ^3J = 6.9 Hz, 1 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major product: δ = 14.4 (+, OCH_2CH_3), 23.56, 23.63, 30.7, 32.8, 33.5 (–, CCH_2CH, C-7",8",9",10"), 39.0 (+, C-6"), 40.07 [+, $N(CH_3)_2$], 64.2, 64.5, 64.7 (–, OCH_2CH_3, C-2",3"), 77.5 (C_{quat}, C-5), 100.5 (+, C-4), 111.0 (C_{quat}, C-5"), 122.7 (+, q, $^3J_{C-F}$ = 4.0 Hz, C-4'), 123.5 (+, q, $^3J_{C-F}$ = 3.7 Hz, C-2'), 124.3 (C_{quat}, q, $^1J_{C-F}$ = 272.3 Hz, CF_3), 126.3, 128.6 (+, C-5',6'), 129.1 (+, C-2), 130.5 (C_{quat}, q, $^2J_{C-F}$ = 31.9 Hz, C-3'), 135.6 (C_{quat}, C-1'), 148.7 (C_{quat}, C-1), 158.8 (C_{quat}, C-3). Minor product: δ = 14.37 (+, OCH_2CH_3), 23.4, 23.8, 33.2, 33.3, 34.1 (–, CCH_2CH, C-7",8",9",10"), 39.8 (+, C-6"), 40.14 [+, $N(CH_3)_2$], 63.9, 64.2, 64.7 (–, OCH_2CH_3, C-2",3"), 77.5 (C_{quat}, C-5), 99.4 (+, C-4), 110.4 (C_{quat}, C-5"), 123.2, 123.3 (+, q, $^3J_{C-F}$ = 4.3 Hz, C-2',4'), 124.4 (C_{quat}, q, $^1J_{C-F}$ = 272.3 Hz, CF_3), 126.0, 128.2 (+, C-5',6'), 129.6 (+, C-2), 130.1 (C_{quat}, q, $^2J_{C-F}$ = 31.7 Hz, C-3'), 135.4 (C_{quat}, C-1'), 149.3 (C_{quat}, C-1), 158.9 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 451 (100) [M^+], 422 (85) [M^+ – C_2H_5], 406 (14), 309 (24), 296 (18), 280 (34), 268 (12), 155 (14). – HRMS (EI) calcd for $C_{25}H_{32}F_3NO_3$: 451.2334 (correct HRMS).

5-Dimethylamino-5-[(1'',4''-dioxaspiro[4.5]dec-6''-yl)methyl]-3-ethoxy-1-[4'-bromo-2',2'-bis(ethoxycarbonyl)pent-4'-enyl]-1,3-cyclopentadiene (**130j**): According to GP7, a solution of

complex **18j** (2.85 g, 6.02 mmol) in pyridine (100 mL) was treated with 2.22 g (7.00 mmol) of 2-(2-bromo-allyl)-2-prop-2-ynylmalonic acid diethyl ester (**15r**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (from 10 : 1 to 1 : 4) gave 1.82 g (51%) of **130j** [R_f = 0.27 (pentane/Et_2O = 1 : 1); d. r. = 1.9 : 1] as a colorless oil. – IR (KBr): ν = 2937 cm^{-1} (C–H), 1732 (C=O), 1626 (C=C), 1446, 1269, 1220, 737. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.89–1.73 (m, 19 H, CCH_2CH, 7",8",9",10"-H, OCH_2CH_3, $CO_2CH_2CH_3$), 2.03, 2.10 [s, 6 H, $N(CH_3)_2$], 2.06–2.10 (m, 1 H, 6"-H), 2.68–2.95 (m, 2 H, 1'-H), 3.15–3.28 (m, 2 H, 3'-H), 3.70–4.17 (m, 10 H, 2",3"-H, OCH_2CH_3, $CO_2CH_2CH_3$), 4.61, 4.72 (d, ^4J = 1.6 Hz, 1 H, 4-H), 5.40–5.42 (m, 1 H, 5'-H), 5.40, 5.41 (d, ^4J = 1.8 Hz, 1 H, 5'-H), 5.56 (d, ^2J = 1.8 Hz, 5'-H), 5.62, 5.66 (d, ^4J = 1.6 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major stereoisomer: δ = 13.7 (+, $CO_2CH_2CH_3$), 14.3 (+, OCH_2CH_3), 23.53, 24.0, 30.2, 31.6, 33.4, 33.9 (–, CCH_2CH, C-1',7",8", 9",10"), 39.6 [+, $N(CH_3)_2$], 39.8 (+, C-6"), 43.2 (–, C-3'), 55.6 (C_{quat}, C-2'), 61.48, 61.51 (–, $CO_2CH_2CH_3$), 64.2, 64.3, 64.5 (–, OCH_2CH_3, C-2",3"), 76.8 (C_{quat}, C-5), 98.1 (+, C-4), 110.9 (C_{quat}, C-5"), 121.3 (–, C-5'), 122.6 (+, C-2), 127.3 (C-4'), 150.5 (C_{quat}, C-1), 157.9 (C_{quat}, C-3), 169.97, 169.99 (C_{quat}, $CO_2CH_2CH_3$). Minor stereoisomer: δ = 13.7 (+, $CO_2CH_2CH_3$), 14.3 (+, OCH_2CH_3), 23.47, 24.5, 30.6, 32.9, 33.4, 34.2 (–, CCH_2CH, C-1',7",8",9", 10"), 39.7 [+, $N(CH_3)_2$], 40.0 (+, C-6"), 43.9 (–, C-3'), 56.0 (C_{quat}, C-2'), 61.2, 61.4 (–, $CO_2CH_2CH_3$), 64.2, 64.3, 64.5 (–, OCH_2CH_3, C-2",3"), 76.9 (C_{quat}, C-5), 95.7 (+, C-4), 110.3 (C_{quat}, C-5"), 121.1 (–, C-5'), 123.7 (+, C-2), 127.6 (C-4'), 149.6 (C_{quat}, C-1), 158.7 (C_{quat}, C-3), 170.2, 170.3 (C_{quat}, $CO_2CH_2CH_3$). – MS (70 eV), *m/z* (%): 599 (20) [M^+], 597 (18), 507 (17) [$M^+ – CH_3$], 570 (20) [$M^+ – C_2H_5$], 568 (19), 518 (66), 473 (11), 320 (100), 178 (19). – HRMS (EI) calcd for $C_{28}H_{42}BrNO_7$: 597.2301 (correct HRMS).

1-Cyclopropyl-5-dimethylamino-5-[1(1',4'-dioxaspiro[4.5]dec-6'-yl)methyl]-3-ethoxy-1,3-cyclopentadiene (**130k**): According to GP7, a solution of 2.37 g (5.01 mmol) complex **18j** in 100 mL pyridine was treated with 661 mg (10.0 mmol) cyclopropylethyne (**15gg**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (+ 1% NEt_3, from 20 : 1 to 0 : 1) gave 977 mg (56%) of **115k** [R_f = 0.47 (Et_2O); d. r. = 1.2 : 1] a colorless oil. – IR (film): ν = 2936 cm^{-1} (C–H), 1695 (C=C), 1608, 1457, 1202, 1156, 1088, 1046, 925. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.22–0.30 (m, 1 H,

*c*Pr-H), 0.45–0.53 (m, 1 H, *c*Pr-H), 0.66–0.79 (m, 2 H, *c*Pr-H), 0.98–1.79 (m, 11 H, CCH_2CH, *c*Pr-H, 7',8',9',10'-H), 1.13 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$CH_3), 1.82–2.02 (m, 1 H, 6'-H), 2.07, 2.08 [s, 6 H, N(CH$_3$)$_2$], 3.62–3.77 (m, 6 H, OCH_2CH$_3$, 2',3'-H), 4.45, 4.46 (d, ^4J = 1.6 Hz, 1 H, 4-H), 5.12, 5.16 (br. s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): Major stereoisomer: δ = 8.8, 9.5, 12.9 (–, *c*Pr-C), 14.1 (+, OCH$_2$*C*H$_3$), 23.5 × 2, 32.2, 32.4, 33.5 (–, C*C*H$_2$CH, C-7',8',9',10'), 39.8 (+, C-6'), 40.03 [+, N(CH$_3$)$_2$], 64.0, 64.1, 64.21 (–, OCH$_2$*C*H$_3$, C-2',3'), 76.9 (C$_{quat}$, C-5), 95.2 (+, C-4), 110.8 (C$_{quat}$, C-5'), 116.4 (+, C-2), 158.99, 159.2 (C$_{quat}$, C-1,3). Minor stereoisomer: δ = 8.3, 8.9, 11.4 (–, *c*Pr-C), 14.2 (+, OCH$_2$*C*H$_3$), 23.5, 23.8, 30.9, 32.6, 34.0 (–, CCH_2CH, C-7',8',9',10'), 39.8 (+, C-6'), 39.96 [+, N(CH$_3$)$_2$], 64.1, 64.21, 64.25 (–, OCH$_2$*C*H$_3$, C-2',3'), 76.9 (C$_{quat}$, C-5), 94.8 (+, C-4), 110.6 (C$_{quat}$, C-5'), 117.0 (+, C-2), 158.97, 159.1 (C$_{quat}$, C-1,3). – MS (70 eV), *m/z* (%): 347 (21) [M$^+$], 318 (46) [M$^+$ – C$_2$H$_5$], 302 (12), 230 (18), 206 (28), 176 (100), 164 (21), 162 (20), 160 (14), 148 (12), 91 (11), 58 (29), 55 (12). – HRMS (EI) calcd for C$_{21}$H$_{33}$NO$_3$: 347.2460 (correct HRMS).

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.6]nona-6'-yl)methyl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (**130m**): Following GP7, a solution of complex **18m** (2.44 g, 5.00 mmol) in 100 mL pyridine was treated with 1.34 g (7.50 mmol) of 1,2-diphenylethyne (**15aa**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et$_2$O (+ 1% NEt$_3$, from 1 : 0 to 2 : 1) gave 1.91 g (81%) of **130m** [R_f = 0.39 (pentane/Et$_2$O = 3 :1); d. r. 1.3 : 1] as a colorless oil. – IR (film): ν = 2942 cm^{-1} (C–H), 1636 (C=C), 1440, 1348, 1188, 764, 700. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.19–2.00 (m, 12 H, CCH_2CH, 7',8',9',10',11'-H), 1.36, 1.37 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$CH_3), 2.29–2.41 (m, 1 H, 6'-H), 2.42 [s, 6 H, N(CH$_3$)$_2$], 3.84–4.06 (m, 6 H, 2',3'-H, OCH_2CH$_3$), 5.15, 5.17 [s, 1 H, 4-H], 7.06–7.18 (m, 3 H, Ph-H), 7.24–7.32 (m, 5 H, Ph-H), 7.62–7.66 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): Major product: δ = 14.2 (+, OCH$_2$*C*H$_3$), 21.5, 26.6, 27,8, 28.1, 33.2, 37.0 (–, C*C*H$_2$CH, C-7',8',9',10',11'), 40.1 [+, N(CH$_3$)$_2$], 41.8 (+, C-6'), 63.9, 64.4, 64.5 (–, O*C*H$_2$CH$_3$, C-2',3'), 76.5 (C$_{quat}$, C-5), 98.4 (+, C-4), 114.5 (C$_{quat}$, C-5'), 126.3, 127.0, 127.3, 127.9, 129.1, 129.6 (+, Ph-C), 134.5, 135.2, 138.0 (C$_{quat}$, C-2, Ph-C), 145.2 (C$_{quat}$, C-1), 158.21 (C$_{quat}$, C-3). Minor product: δ = 14.3 (+, OCH$_2$*C*H$_3$), 22.0, 28.1, 29.4, 30.7, 34.5, 37.6 (–, C*C*H$_2$CH, C-7',8',9',10',11'), 40.1 [+, N(CH$_3$)$_2$], 42.7 (+, C-6'), 63.2, 64.5,

64.6 (–, O*C*H$_2$CH$_3$, C-2',3'), 76.4 (C$_{quat}$, C-5), 97.3 (+, C-4), 114.2 (C$_{quat}$, C-5'), 126.1, 126.8, 127.8, 127.9, 129.6, 129.7 (+, Ph-C), 134.4, 135.5, 138.1 (C$_{quat}$, C-2, Ph-C), 145.4 (C$_{quat}$, C-1), 158.15 (C$_{quat}$, C-3). – MS (70 eV), *m/z* (%): 473 (56) [M$^+$], 444 (100) [M$^+$ – C$_2$H$_5$], 428 (18), 317 (14), 304 (16), 288 (73), 276 (18), 91 (12), 55 (19), 44 (16). – Elemental analysis calcd (%) for C$_{31}$H$_{39}$NO$_3$ (473.7): C 78.61, H 8.30; found: C 78.81, H 8.03.

5-Dimethylamino-5-[(1',4'-dioxaspiro[4.6]nona-6'-yl)methyl]-3-ethoxy-1-propyl-1,3-cyclopentadiene (**130n**): According to GP7, a solution of complex **18m** (2.44 g, 5.00 mmol) in pyridine (100 mL) was treated with 1.00 mL (10.1 mmol) of 1-pentyne (**15h^1**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et$_2$O (+ 1% NEt$_3$, from 10 : 0 to 0 : 1) gave 1.31 g (72%) of **130n** [R_f = 0.54 (Et$_2$O); d. r. = 1.4 : 1;] as a pale-yellow oil. – IR (film):ν = 2930 cm^{-1} (C–H), 1700, 1634 (C=C), 1583, 1457, 1340, 1046. – Major stereoisomer: ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.92 (t, ^3J = 7.5 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 1.01–2.15 (m, 17 H, C*C*H$_2$CH, C*H*$_2$C*H*$_2$CH$_3$, 6',7',8',9',10',11'-H), 1.28 (t, ^3J = 7.2 Hz, 3 H, OCH$_2$C*H*$_3$), 2.14 [s, 6 H, N(CH$_3$)$_2$], 3.73–3.89 (m, 6 H, OC*H*$_2$CH$_3$, 2',3'-H), 4.67 (br. s, 1 H, 4-H), 5.64 (d, ^4J = 1.8 Hz,, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.2, 14.4 (+, CH$_2$CH$_2$*C*H$_3$, OCH$_2$*C*H$_3$), 19.5, 21.5, 26.5, 28.0, 28.2, 29.7, 33.1, 37.1 (–, C*C*H$_2$CH, *C*H$_2$*C*H$_2$CH$_3$, C-7',8',9',10',11'), 39.9 [+, N(CH$_3$)$_2$], 41.4 (+, C-6'), 64.3, 64.4, 64.9 (–, OCH$_2$*C*H$_3$, C-2',3'), 76.7 (C$_{quat}$, C-5), 95.5 (+, C-4), 114.5 (C$_{quat}$, C-5'), 122.2 (+, C-2), 156.5, 159.6 (C$_{quat}$, C-1,3). – Minor stereoisomer: ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.93 (t, ^3J = 7.3 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 1.01–2.15 (m, 17 H, CC*H*$_2$CH, C*H*$_2$C*H*$_2$CH$_3$, 6',7',8',9',10', 11'-H), 1.28 (t, ^3J = 7.2 Hz, 3 H, OCH$_2$C*H*$_3$), 2.12 [s, 6 H, N(CH$_3$)$_2$], 3.73–3.89 (m, 6 H, OC*H*$_2$CH$_3$, 2',3'-H), 4.67 (br. s, 1 H, 4-H), 5.72 (d, ^2J = 1.9 Hz,, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.3, 14.5 (+, CH$_2$CH$_2$*C*H$_3$, OCH$_2$*C*H$_3$), 19.6, 21.9, 27.9, 28.0, 28.3, 32.1, 34.9, 37.4 (–, C*C*H$_2$CH, *C*H$_2$*C*H$_2$CH$_3$, C-7',8',9',10',11'), 40.0 [+, N(CH$_3$)$_2$], 42.2 (+, C-6'), 64.0, 64.3, 64.5 (–, OCH$_2$*C*H$_3$, C-2',3'), 76.7 (C$_{quat}$, C-5), 94.3 (+, C-4), 114.8 (C$_{quat}$, C-5'), 122.4 (+, C-2), 156.5, 159.4 (C$_{quat}$, C-1,3). – MS (70 eV), *m/z* (%): 363 (50) [M$^+$], 334 (100) [M$^+$ – C$_2$H$_5$],

319 (11), 208 (16), 194 (24), 178 (35), 166 (13). – Elemental analysis calcd (%) for $C_{22}H_{37}NO_3$ (363.5): C 72.69, H 10.26; found: C 72.39, H 10.05.

(*3aS,3bR,6aS,7aR*)/(*3aR,3bS,6aR,7aS*)-*7a-Dimethyamino-3b-hydroxy-1,2-diphenyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta[a]pentalen-3-one* (**127a-I**) and (*3aS,3bS,6aR,7aR*)/(*3aR,3bR,6aS,7aS*)-*7a-Dimethyamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta[a]pentalen-3-one* (**127a-II**): Following GP8A, to a solution of **130a** (623 mg, 1.40 mmol) in dioxane (150 mL) was added a conc. solution of hydrochloric acid (10 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (60 g). Elution with pentane/Et_2O (+ 10% CH_2Cl_2, from 5 : 1 to 1 : 1) gave 283 mg (54%) of **127a-I** [R_f = 0.57 (pentane/CH_2Cl_2 = 1 : 1)] as a colorless crystal (m. p. 156°C) and 136 mg (26%) of **127a-II** [R_f = 0.23 (pentane/CH_2Cl_2 = 1 : 1)] as a pale-yellow crystal (m. p. 214–216°C).

127a-I: IR (KBr): ν = 3445 cm^{-1} (O–H), 2958 (C–H), 1693 (C=O), 1340, 1175, 1122, 1009, 698. – ^1H NMR (250 MHz, $CDCl_3$, plus DEPT): δ = 1.39–1.44 (m, 1 H) and 1.63–1.99 (m, 7 H) [total 8 H, 4,5,6,7-H], 2.17–2.35 (m, 1 H, 6a-H), 2.40 [s, 6 H, $N(CH_3)_2$], 2.87 (s, 1 H, OH), 3.14 (s, 1 H, 3a-H), 7.17–7.32 (m, 8 H, Ph-H), 7.55–7.60 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.6, 26.5, 27.9, 40.9 (–, C-4,5,6,7), 40.4 [+, $N(CH_3)_2$], 47.1 (+, C-6a), 54.5 (+, C-3a), 80.2, 89.4 (C_{quat}, C-3b,7a), 127.8, 128.0, 128.1, 129.4, 129.8, 131.3 (+, Ph-C), 129.0, 134.2, 141.9 (C_{quat}, C-2, Ph-C), 169.7 (C_{quat}, C-1), 207.3 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 373 (100) [M^+], 344 (18), 312 (18), 290 (24), 277 (65), 178 (12), 164 (34), 138 (17). – Elemental analysis calcd (%) for $C_{25}H_{27}NO_2$ (373.5): C 80.40, H 7.29; found: C 80.75, H 7.10.

127a-II: IR (KBr): ν = 3254 cm^{-1} (O–H), 2783 (C–H), 1682 (C=O), 1342, 1216, 1170. – ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY and NOESY): δ = 1.36–1.48 (m, 1 H) and 1.79–2.00 (m, 5 H) [total 6 H, 4,5,6-H), 1.54 (dd, ^2J = 14.7, ^3J = 12.6 Hz, 1 H, 7-*exo*-H), 2.28 (dd, ^2J = 14.7, ^3J = 8.5 Hz, 1 H, 7-*endo*-H), 2.38 [s, 6 H, $N(CH_3)_2$], 2.65–2.73 (m, 1 H, 6a-H), 3.32 (s, 1 H, 3a-H), 3.36 (s, 1 H, OH), 7.15–7.34 (m, 8 H, Ph-H), 7.61–7.66 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 24.0, 28.7, 36.0 (–, C-4,5,6), 40.1 [+, $N(CH_3)_2$], 41.2 (–, C-7), 54.2 (+, C-6a), 55.6 (+, C-3a), 79.8, 90.4 (C_{quat}, C-3b,7a), 127.97, 128.04, 128.3, 129.5, 129.7, 130.0 (+, Ph-C), 131.7, 134.0, 138.6 (C_{quat}, C-2, Ph-C), 171.2 (C_{quat}, C-1), 206.1 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 373 (100) [M^+], 344 (12), 289 (26),

276 (89), 202 (14), 178 (14), 164 (24), 138 (18), 41 (21). – Elemental analysis calcd (%) for $C_{25}H_{27}NO_2$ (373.5): C 80.40, H 7.29; found: C 80.63, H 7.17.

(*3aS,3bR,6aS,7aR*)/(*3aR,3bS,6aR,7aS*)-*7a-Dimethyamino-3b-hydroxy-1-trimethylsilyl-3a,3b, 4,5,6,6a,7,7a-octahydrocyclopenta[a]pentalen-3-one* (**127b-I**) and (*3aS,3bS,6aR,7aR*)/(*3aR, 3bR,6aS,7aS*)-*7a-Dimethyamino-3b-hydroxy-1-trimethylsilyl-3a,3b,4,5,6,6a,7,7a-octahydro-cyclopenta[a]pentalen-3-one* (**127b-II**): Following GP8A, to a solution of **130b** (585 mg, 1.60 mmol) in dioxane (150 mL) was added a 3 N solution of hydrochloric acid (5 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography [first time on silica gel (60 g); second time on aluminum oxide (II, 50 g)].Elution with CH_2Cl_2/Et_2O (from 1 : 3 to 2 : 1) to afford 347 mg (74%) of a colorless oil [R_f = 0.17 (pentane/CH_2Cl_2 = 1 : 1); **127b-I**/**127b-II** = 2 : 1]. – IR (film): ν = 2953 cm^{-1} (C–H), 2780, 1700 (C=O), 1464, 1249, 1124, 1025, 1000, 840. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, $Si(Me_3)_3$ of **127b-II**], 0.19 [s, 9 H, $Si(Me_3)_3$ of **127b-I**], 1.27–1.45 and 1.60–2.20 (m, 18 H, 4,5,6, 6a,7-H of **127b-I**, 4,5,6,7-H and OH of **127b-II)**, 2.09 [s, 6 H, $N(CH_3)_2$ of **127b-I**], 2.10 [s, 6 H, $N(CH_3)_2$ of **127b-II**], 2.50–2.60 (m, 1 H, 6a-H of **127b-II**), 2.69 (s, 1 H, 3a-H of **127b-I**), 2.88 (s, 1 H, 3a-H of **127b-II**), 3.38 (br. s, 1 H, OH of **127b-I**), 5.98 (s, 1 H, 2-H of **127b-II**), 6.32 (s, 1 H, 2-H of **127b-I**). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **127b-I**: δ = –0.53 [+, $Si(CH_3)_3$], 22.9, 27.5, 37.5, 39.7 (–, C-4,5,6,7), 40.3 [+, $N(CH_3)_2$], 47.0 (+, C-6a), 54.3 (+, C-3a), 83.1, 88.5 (C_{quat}, C-3b,7a), 142.5 (+, C-2), 186.7 (C_{quat}, C-1), 209.6 (C_{quat}, C-3). **127b-II**:δ = –1.0 [+, $Si(CH_3)_3$], 24.2, 28.7, 36.1, 42.3 (–, C-4,5,6,7), 40.2 [+, $N(CH_3)_2$], 54.9, 55.0 (+, C-3a,6a), 84.2, 89.3 (C_{quat}, C-3b,7a), 138.0 (+, C-2), 189.2 (C_{quat}, C-1), 209.8 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 293 (100) [M^+], 378 (49) [$M^+ – CH_3$], 264 (81), 251 (44), 220 (47), 197 (14), 138 (21), 73 (26). – HRMS (EI) calcd for $C_{16}H_{27}NO_2Si$: 293.1811 (correct HRMS).

4-Dimethylamino-3-methyl-4-[(2'-oxo-1'-cyclopentyl)methyl]cyclopent-2-en-1-one (**129d**): Following GP8A, to a solution of **130d** (985 mg, 3.20 mmol) in dioxane (150 mL) was added a 3 N solution of hydrochloric acid (10 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on aluminum oxide (II, 60 g). Elution with Et_2O/MeOH (from 20 : 1 to 10 : 1) gave 653 mg (87%) of **294d** [R_f = 0.58 and 0.49 (Et_2O/MeOH = 10 : 1), d. r. = 1 : 1] as a colorless oil. – IR (film): ν = 2952 cm^{-1} (C–H)

1734 (C=O), 1684, 152, 1209, 1186. – First stereoisomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21–1.62 (m, 4 H, 4',5'-H), 1.77 (AB, d, ^2J = 18.8 Hz, 5-H), 1.78–2.23 (m, 5 H, CCH_2CH, 1',3'-H), 1.88 (d, ^4J = 1.2 Hz, 3 H, CH_3), 1.98 [s, 6 H, $N(CH_3)_2$], 2.42 (AB, d, ^2J = 18.8 Hz, 5-H), 5.84 (d, ^4J = 1.2 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.1 (+, CH_3), 20.4, 32.0, 36.3, 36.6, 36.8 (–, CCH_2CH, C-5,3',4',5'), 39.0 [+, $N(CH_3)_2$], 46.1 (+, C-1'), 70.2 (C_{quat}, C-4), 132.6 (+, C-2), 180.5 (C_{quat}, C-3), 205.7 (C_{quat}, C-1), 219.1 (C_{quat}, C-2''). – Second stereoisomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18–1.70 (m, 4 H, 4',5'-H), 1.78–2.23 (m, 5 H, CCH_2CH, 1',3'-H), 1.82 (AB, d, ^2J = 18.8 Hz, 5-H), 1.87 (d, ^4J = 1.2 Hz, 3 H, CH_3), 1.98 [s, 6 H, $N(CH_3)_2$], 2.34 (AB, d, ^2J = 18.8 Hz, 5-H), 5.80 (d, ^4J = 1.2 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.7 (+, CH_3), 20.0, 31.6, 36.0, 36.4, 36.8 (–, CCH_2CH, C-5,3',4',5'), 39.1 [+, $N(CH_3)_2$], 45.4 (+, C-1''), 70.2 (+, C-4), 132.6 (C_{quat}, C-2), 180.3 (C_{quat}, C-3), 205.3 (C_{quat}, C-1), 219.2 (C_{quat}, C-2''). – MS (70 eV), *m*/*z* (%): 235 (8) [M^+], 205 (9), 191 (12), 138 (100), 59 (9).

(*3aS,3bR,6aS,7aR)/(3aR,3bS,6aR,7aS)-7a-Dimethyamino-3b-hydroxy-1-methyl-3a,3b,4,5,6, 6a,7,7a-octahydrocyclopenta[a]pentalen-3-one* (**127d-I**) and (*3aS,3bS,6aR,7aR)/(3aR,3bR, 6aS,7aS)-7a-Dimethyamino-3b-hydroxy-1-methyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta-[a]pentalen-3-one* (**127d-II**): Following GP8A, to a solution of **130d** (972 mg, 3.16 mmol) in dioxane (150 mL) was added a conc. solution of hydrochloric acid (10 mL), and the mixture was stirred for 4 d. After aqueous work-up, the residue was subjected to chromatography on aluminum oxide (II, 60 g). Elution with Et_2O/MeOH (from 20 : 1 to 10 : 1) gave 212 mg (54%) of pure **127d-II** [R_f = 0.67 (Et_2O/MeOH = 10 : 1)] as a white solid (m. p. 121–122°C), 247 mg (33%) of a mixture of (**127d-I** : **127d-II** = 2 : 3) and 127 mg (17%) of **127a-I** [R_f = 0.58 (Et_2O/MeOH = 10 : 1)] as a white solid (m. p. 102–103 °C).

127d-I: IR (KBr): ν = 3417 cm^{-1} (O–H), 2964 (C–H), 1685 (C=O), 1627, 1282, 1191. – ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.37–1.59 (m, 2 H) and 1.69–2.08 (m, 7 H) [total 9 H, 4,5,6,6a,7-H], 1.95 (s, 3 H, CH_3), 2.40 [s, 6 H, $N(CH_3)_2$], 2.64 (s, 1 H, 3a-H), 3.20 (br. s, 1 H, OH), 5.88 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.1 (+, CH_3), 22.8, 27.5, 36.1, 40.0 (–, C-4,5,6,7), 39.9 [+, $N(CH_3)_2$], 47.2 (+, C-6a), 56.5 (+, C-3a), 79.6, 88.2 (C_{quat}, C-3b,7a), 132.4 (+, C-2), 179.1 (C_{quat}, C-1), 208.0 (C_{quat}, C-3). – MS (70 eV),

m/*z* (%): 235 (40) [M^+], 206 (21), 193 (13), 164 (15), 152 (100), 138 (82), 124 (12). – HRMS (EI) calcd for $C_{14}H_{21}NO_2$: 235.1572 (correct HRMS).

127d-II: IR (KBr): ν = 3235 cm^{-1} (O–H), 2956 (C–H), 1682 (C=O), 1622 (C=C), 1457, 1324, 1141. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.26–1.53 (m, 3 H), 1.67–2.00 (m, 4 H) and 2.12–2.22 (m, 1 H) [total 8 H, 4,5,6,7-H], 1.99 (s, 1 H, CH_3), 2.18 [s, 6 H, $N(CH_3)_2$], 2.62–2.71 (m, 1 H, 6a-H), 2.98 (s, 1 H, 3a-H), 3.58–3.65 (m, 1 H, OH), 5.68 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.5 (+, CH_3), 24.3, 29.0, 36.5, 40.7 (–, C-4,5,6,7), 40.0 [+, $N(CH_3)_2$], 54.4, 55.5 (+, C-3a, 6a), 81.0, 89.8 (C_{quat}, C-3b,7a), 128.6 (+, C-2), 182.0 (C_{quat}, C-1), 207.8 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 235 (100) [M^+], 192 (12), 164 (20), 152 (100), 138 (84), 124 (23), 108 (12), 91 (17), 77 (14), 55 (12), 41 (17). – Elemental analysis calcd (%) for $C_{14}H_{21}NO_2$ (235.3): C 71.46, H 8.99; found: C 71.31, H 8.72.

(*3aS,3bR,6aS,7aR*)/(*3aR,3bS,6aR,7aS*)-*7a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta[a]pentalen-3-one* (**127e-I**) and (*3aS,3bS,6aR,7aR*)/(*3aR,3bR,6aS,7aS*)-*7a-Dimethyamino-3b-hydroxy-1-methyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta-[a]pentalen-3-one* (**127e-II**): Following GP8A, to a solution of **130e** (870 mg, 2.71 mmol) in dioxane (150 mL) was added a solution of 3 N hydrochloric acid (10 mL), and the mixture was stirred for 2 d. After aqueous work-up, only diketone **129e** was detected. Then, the intermediate **129e** was diluted again in dioxane (150 mL), treated with a conc. solution of hydrochloric acid (20 mL), and kept at ambient temperature for an additional 4 d. Chromatography on aluminum oxide (II, 60 g) eluting with Et_2O/MeOH (from 1 : 0 to 10 : 1) gave an inseparable mixture of **127e-I** and **127e-II** [520 mg (77%); R_f = 0.61 (Et_2O/MeOH = 10 : 1); ratio = 1 : 1] as a colorless oil. This mixture was dissolved in pentane/Et_2O (10 : 1, 100 mL) and this solution was slowly concentrated at 0 °C under reduced pressure. As the solid was settled out, the solution was keep at this temperature under normal pressure for another 20 min. Separation from the reaming liquid (about 10 mL) and washing with pentane/Et_2O (10 : 1, 3 × 10 mL) afforded 210 mg of a white solid, which contained **127e-I** and **127e-II** in ratio 1 : 9.4). A colorless oil (310 mg; **127e-I**/**127e-II** = 3.3 : 1) was collected from the mother liquid and the washing solution. – IR (KBr): ν = 2959 cm^{-1} (C–H), 1692 (C=O), 1647, 1388, 1320, 1140, 1028. – ^1H NMR (250 MHz, $CDCl_3$, plus DEPT): δ = 1.13–1.26 (m, 2 H of **127e-I**, 3 H of **127e-II**), 1.47–1.90 (m, 6 H of **127e-I**, 4 H of **127e-II**) and

1.97–2.10 (m, 1 H of **127e-I** and 1 H of **127e-II**) [total 17 H, 4,5,6,6a,7-H of **127e-I**, 4,5,6,7-H of **127e-II**], 1.50 (s, 3 H, CH_3 of **127e-II**), 1.56 (s, 3 H, CH_3 of **127e-I**), 1.78 (s, 3 H, CH_3 of **127e-II**), 1.82 (s, 3 H, CH_3 of **127e-I**), 2.02 [s, 12 H, $N(CH_3)_2$ of **127e-I** and **127e-II**], 2.45-2.58 (m, 1 H, 6a of **127e-II**), 2.62 (s, 1 H, 3a-H of **127e-I**), 2.84 (s, 1 H, 3a-H of **127e-II**), 3.45 (br. s, 1 H, OH of **127a-I**), 4.43 (br. s, 1 H, OH of **127e-II**). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **127e-I**: δ = 7.7, 12.9 (+, CH_3), 22.9, 27.6, 36.0, 40.5 (–, C-4,5,6,7), 40.0 [+, $N(CH_3)_2$], 47.2 (+, C-6a), 55.1 (+, C-3a), 78.2, 88.4 (C_{quat}, C-3b,7a), 138.3 (C_{quat}, C-2), 170.2 (C_{quat}, C-1), 207.8 (C_{quat}, C-3). **127e-II**: δ = 7.4, 12.2 (+, CH_3), 24.0, 28.8, 36.0, 40.5 (–, C-4,5,6,7), 39.8 [+, $N(CH_3)_2$], 54.1, 54.5 (+, C-3a,6a), 79.5, 89.4 (C_{quat}, C-3b,7a), 134.3 (C_{quat}, C-2), 173.1 (C_{quat}, C-1), 207.7 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 249 (42) [M^+], 177 (14), 152 (100), 138 (16). – Elemental analysis calcd (%) for $C_{15}H_{23}NO_2$ (249.4): C 72.25, H 9.30; found: C 71.97, H 8.94.

(*3aS,3bR,7aS,8aR)/(3aR,3bS,7aR,8aS)-8a-Dimethylamino-3b-hydroxy-1,2-diphenyl-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127f-I**), (*3aS,3bS,7aR,8aR)/(3aR,3bR,7aS,8aS)-8a-Dimethylamino-3b-hydroxy-1,2-diphenyl-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127f-II**) and (*3aS,3bS,7aS,8aR)/(3aR,3bR,7aR,8aS)-8a-Dimethylamino-3b-hydroxy-1,2-diphenyl-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127f-III**): Following GP8A, to a solution of **130f** (924 mg, 2.01 mmol) in dioxane (200 mL) was added a conc. solution of hydrochloric acid (10 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (60 g). Elution with CH_2Cl_2/Et_2O (from 5 : 1 to 1 : 1) gave 73.0 mg (9%) of **127f-III** [R_f = 0.81 (CH_2Cl_2/Et_2O = 3 : 1)] as a pale-yellow oil, 487 mg (63%) of **127f-I** [R_f = 0.62 (CH_2Cl_2/Et_2O = 3 : 1)] as a colorless crystal (m. p. 204–205 °C) and 130 mg (17%) of **127f-II** [R_f = 0.35 (CH_2Cl_2/Et_2O = 3 : 1)] as a colorless crystal: (m. p. 181–183°C).

127f-I: IR (KBr): ν = 3047 cm^{-1} (O–H), 2932 (C–H), 1695 (C=O), 1166, 1092, 1021, 758, 695. – ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY and NOESY): δ = 1.18–2.02 (m, 9 H, 4,5,6,7,8-H), 1.97–2.06 (m, 1 H, 7a-H), 2.20 ["t" (dd), ^2J = 12.6, ^3J = 12.6 Hz, 1 H, 8-H], 2.41 [s, 6 H, $N(CH_3)_2$], 2.61 (s, 1 H, OH), 2.71 (s, 1 H, 3a-H), 7.15–7.34 (m, 8 H, Ph-H), 7.54–7.58 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.7, 21.6, 23.2, 31.9, 37.5 (–, C-4, 5,6,7,8), 40.3 (+, C-7a), 40.5 [+, $N(CH_3)_2$], 57.3 (+, C-3a), 76.9, 77.4 (C_{quat}, C-3b,8a), 128.0, 128.1 × 2, 129.2, 129.5, 129.8, 129.8 (+, Ph-C), 131.3, 134.4, 143.0

(C_{quat}, C-2, Ph-C), 171.5 (C_{quat}, C-1), 206.9 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 387 (100) [M^+], 370 (9) [M^+ – OH], 344 (15), 290 (12), 277 (28), 164 (18), 138 (10). – Elemental analysis calcd (%) for $C_{26}H_{29}NO_2$ (387.5): C 80.59, H 7.54; found: C 80.41, H 7.25.

127f-II: IR (film): ν = 3354 cm^{-1} (O–H), 2929 (C–H), 1700 (C=O), 1675, 1444, 1338, 1117. – ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY and NOESY): δ = 1.16–1.95 (m, 10 H, 4,5,6,7,8-H), 2.38 [s, 6 H, $N(CH_3)_2$], 2.40–2.55 (m, 1 H, 7a-H), 3.20 (s, 1 H, 3a-H), 3.23–3.42 (m, 1 H, OH), 7.16–7.31 (m, 8 H, Ph-H), 7.67–7.71 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 19.9, 21.1, 23.4, 30.8, 34.9 (–, C-4,5,6,7,8), 40.0 [+, $N(CH_3)_2$], 46.6 (+, C-7a), 58.4 (+, C-3a), 76.5, 78.3 (C_{quat}, C-3b,8a), 127.9, 128.0, 128.2, 129.4, 129.70, 129.74 (+, Ph-C), 131.6, 134.1, 139.4 (C_{quat}, C-2, Ph-C), 170.0 (C_{quat}, C-1), 206.5 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 387 (100) [M^+], 370 (9) [M^+ – OH], 344 (12), 290 (38), 277 (79), 164 (18), 138 (8). – HRMS (EI) calcd for $C_{26}H_{29}NO_2$: 387.2198 (correct HRMS).

127f-III: IR (film): ν = 2937 cm^{-1} (C–H), 1695 (C=O), 1444, 1343, 1173, 1015, 775, 702. – ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY and NOESY): δ = 1.18–2.02 (m, 11 H, 4,5,6,7,8-H, OH), 2.20–2.30 (m, 1 H, 7a-H), 2.34 [s, 6 H, $N(CH_3)_2$], 2.90 (s, 1 H, 3a-H), 7.15–7.28 (m, 8 H, Ph-H), 7.64–7.69 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.9, 24.8, 25.4, 36.5, 37.5 (–, C-4,5,6,7,8), 40.2 [+, $N(CH_3)_2$], 50.0, 55.6 (+, C-3a,7a), 77.2, 78.8 (C_{quat}, C-3b,8a), (–, C-4,5,6, 7,8), 127.8, 127.9, 128.2, 129.2, 129.8, 129.8 (+, Ph-C), 132.1, 134.8, 140.2 (C_{quat}, C-2, Ph-C), 169.9 (C_{quat}, C-1), 205.4 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 387 (78) [M^+], 370 (18) [M^+ – OH], 343 (10) [M^+ – $N(CH_3)_2$], 290 (43), 277 (100), 178 (18), 164 (27). – HRMS (EI) calcd for $C_{26}H_{29}NO_2$: 387.2198 (correct HRMS).

(3aS,3bR,7aS,8aR)/(3aR,3bS,7aR,8aS)-8a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3b,4,5,6, 7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one (**127g-I**) *3aS,3bS,7aR,8aR)/(3aR,3bR, 7aS,8aS)-8a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127g-II**): Following GP8A, to a solution of **130g** (728 mg, 2.17 mmol) in dioxane (100 mL) was added a conc. solution of hydrochloric acid (5 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (60 g). Elution with Et_2O/EtOAc/MeOH (from 1 : 0 : 0 to 1 : 0 : 1) gave 368 mg (64%) of **127g-I** [R_f = 0.37 (Et_2O/EtOAc = 1 : 1)] as a colorless crystal

(m. p. 102 °C) and 104 mg (18%) of **127g-II** [R_f = 0.16 (Et_2O/EtOAc = 1 : 1)] as a colorless crystal (m. p. 77–80 °C). Besides these compounds, two uncharacterized byproducts were also isolated: fraction I [25.0 mg; R_f = 0.87 (Et_2O/EtOAc = 1 : 1)] and fraction II [36.0 mg; R_f = 0.73 and 0.61 (Et_2O/EtOAc = 1 : 1), two isomers].

127g-I: IR (film): ν = 2932 cm^{-1} (C–H), 1700 (C=O), 1653 (C=C), 1172, 1030. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.44–1.80 (m, 10 H, 4,5,6,7,8-H), 1.71 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 2.05–2.17 (m, 1 H, 7a-H), 2.24 [s, 6 H, $N(CH_3)_2$], 2.31 (s, 1 H, 3a-H), 2.80 (s, 1 H, OH). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.4, 13.1 (+, CH_3), 20.2, 21.1, 22.6, 31.6, 36.0 (–, C-4,5,6,7,8), 39.8 [+, $N(CH_3)_2$], 40.1 (+, C-7a), 57.7 (+, C-3a), 75.3, 75.7 (C_{quat}, C-3b,8a), 139.1 (C_{quat}, C-2), 171.8 (C_{quat}, C-1), 207.5 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 263 (100) [M^+], 220 (7), 201 (7), 165 (8), 153 (100), 138 (13), 122 (9). – Elemental analysis calcd (%)) for $C_{16}H_{25}NO_2$ (263.4): C 72.97, H 9.57; found: C 73.27, H 9.35.

127g-II: IR (film): ν = 2940 cm^{-1} (C–H), 1696 (C=O), 1653, 1437, 1320, 1321, 1167. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.11–1.88 (m, 10 H, 4,5,6,7,8-H), 1.65 (s, 3 H, CH_3), 1.92 (s, 3 H, CH_3), 2.13 [s, 6 H, $N(CH_3)_2$], 2.39–2.48 (m, 1 H, 7a-H), 2.82 (s, 1 H, 3a-H), 2.95–3.10 (br. s, 1 H, OH). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.5, 13.4 (+, CH_3), 20.1, 21.2, 23.8, 30.9, 34.2 (–, C-4,5,6,7,8), 39.9 [+, $N(CH_3)_2$], 46.8 (+, C-7a), 57.5 (+, C-3a), 75.9, 77.4 (C_{quat}, C-3b,8a), 135.8 (C_{quat}, C-2), 172.0 (C_{quat}, C-1), 207.9 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 263 (29) [M^+], 153 (100), 152 (89), 138 (14). – Elemental analysis calcd (%) for $C_{16}H_{25}NO_2$ (263.4): C 72.97, H 9.57; found: C 73.38, H 9.19.

(3aS,3bR,7aS,8aR)/(3aR,3bS,7aR,8aS)-1-tert-Butyl-8a-dimethylamino-3b-hydroxy-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one (**127h-I**), (*3aS,3bS,7aR,8aR)/(3aR,3bR,7aS,8aS)-1-tert-Butyl-8a-dimethylamino-3b-hydroxy-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127h-II**) and (*3aS,3bS,7aS,8aR*)/(*3aR,3bR,7aR,8aS*)-*1-tert-Butyl-8a-dimethylamino-3b-hydroxy-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclo-penta[a]inden-3-one* (**127h-III**): Following GP8A, to a solution of **127h** (571 mg, 1.57 mmol) in dioxane (100 mL) was added a conc. solution of hydrochloric acid (5 mL), and the was mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (60 g). Elution with pentane/Et_2O (from 3 : 1 to 1 : 2) gave 43.0 mg (14%) **127h-III** [R_f = 0.44 (pentane/Et_2O = 1 : 1)] as a pale-yellow oil, 303 mg (66%) of **127h-I** [R_f = 0.29 (pentane/

Et_2O = 1 : 1); 95% diastereomeric purity] as a colorless crystal (m. p. 99–100 °C) and 74 mg (16%) of **127h-II** [R_f = 0.18 (pentane/Et_2O = 1 : 1)] as a colorless crystal (m. p. 97–99 °C).

127h-I: IR (KBr): ν = 3401 cm^{-1} (O–H), 2936 (C–H), 1692 (C=O), 1285 1177, 1031. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.27 [s, 9 H, $C(CH_3)_3$], 1.32–1.89 (m, 10 H, 4,5,6,7,8-H), 2.15 [s, 6 H, $N(CH_3)_2$], 2.19–2.26 (m, 1 H, 7a-H), 2.37 (s, 1 H, 3a-H), 2.78 (br. s, 1 H, OH), 6.17 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.6, 21.5, 23.0, 31.1, 36.5 (–, C-4,5,6,7,8), 31.2 [+, $C(CH_3)_3$], 36.2 [C_{quat}, $C(CH_3)_3$], 40.0 (+, C-7a), 40.6 [+, $N(CH_3)_2$], 56.1 (+, C-3a), 75.9, 79.6 (C_{quat}, C-3b,8a), 133.2 (C_{quat}, C-2), 192.5 (C_{quat}, C-1), 208.3 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 291 (100) [M^+], 274 (91) [M^+ – OH], 248 (65), 234 (64) [M^+ – $C(CH_3)_3$], 216 (34), 206 (11), 164 (42), 162 (29), 138 (30), 135 (11). – Elemental analysis calcd (%) for $C_{18}H_{29}NO_2$ (291.2): C 74.24, H 10.03; found: C 73.93, H 9.98.

127h-II: – IR (KBr): ν = 3367 cm^{-1} (O–H), 2936 (C–H), 1679 (C=O), 1457, 1365, 1284, 1169, 1026. – ^1H NMR (250 MHz, $CDCl_3$):δ = 1.20–1.69 (m, 9 H, 4,5,6,7,8-H),1.28 [s, 9 H, $C(CH_3)_3$], 1.86–2.11 (m, 2 H, 7a,8-H), 2.15 [s, 6 H, $N(CH_3)_2$], 2.87 (s, 1 H, 3a-H), 5.90 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.0, 21.1, 23.4, 30.9, 36.0 (–, C-4,5,6,7,8), 31.1 [+,$C(CH_3)_3$], 34.9 [C_{quat}, $C(CH_3)_3$], 40.0 [+, $N(CH_3)_2$], 47.3 (+, C-7a), 58.9 (+, C-3a), 76.8, 78.7 (C_{quat}, C-3b,8a), 130.0 (C_{quat}, C-2), 191.9 (C_{quat}, C-1), 208.2 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 291 (91) [M^+], 274 (44) [M^+ – OH], 248 (100), 234 (60) [M^+ – $C(CH_3)_3$], 216 (22), 180 (16), 178 (13), 164 (32), 138 (30), 125 (14). – HRMS (EI) calcd for $C_{18}H_{29}NO_2$: 291.2198 (correct HRMS).

127h-III: IR (film): ν = 3478 cm^{-1} (O–H), 2935 (C–H), 1648 (C=O), 1591, 1463, 1294, 1017, 736. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21–1.76 (m, 9 H, 4,5,6,7,8-H), 1.27 [s, 9 H, $C(CH_3)_3$], 1.88–2.28 (m, 3 H, 7a,8-H, OH), 2.12 [s, 6 H, $N(CH_3)_2$], 2.58 (s, 1 H, 3a-H), 5.89 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.9, 24.7, 25.5, 36.6, 37.2 (–, C-4,5,6,7,8), 31.1 [+, $C(CH_3)_3$], 36.0 [C_{quat}, $C(CH_3)_3$], 40.2 [+, $N(CH_3)_2$], 50.7 (+, C-7a), 55.9 (+, C-3a), 77.2, 80.1 (C_{quat}, C-3b,8a), 130.2 (C_{quat}, C-2), 192.1 (C_{quat}, C-1), 207.7 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 291 (24) [M^+], 274 (100) [M^+ – OH], 248 (12), 216 (19), 164 (9). – HRMS (EI) calcd for $C_{18}H_{29}NO_2$: 291.2198 (correct HRMS).

(3aS,3bR,7aS,8aR)/(3aR,3bS,7aR,8aS)-8a-Dimethylamino-3b-hydroxy-1-(3'-trifluoromethyl-phenyl)-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one (**127i-I**), (*3aS,3bS,7aR, 8aR)/(3aR,3bR,7aS,8aS)-8a-Dimethylamino-3b-hydroxy-1-(3'-trifluoromethylphenyl)-3b,4,5, 6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127i-II**) and (*3aS,3bS,7aS,8aR*)/(*3aR, 3bR,7aR,8aS*)*-8a-Dimethylamino-3b-hydroxy-1-(3'-trifluoromethyl-phenyl)-3b,4,5,6,7,7a,8, 8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127i-III**): Following GP8A, to a solution of **130i** (506 mg, 1.12 mmol) in dioxane (100 mL) was added a conc. solution of hydrochloric acid (5 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (60 g). Elution with pentane/Et_2O (from 3 : 1 to 1 : 2) gave 68.0 mg (16%) of **127i-III** [R_f = 0.26 (pentane/Et_2O = 1 : 1); 79% diastereomeric purity], 287 mg (67%) of **127i-I** [R_f = 0.14 (pentane/Et_2O = 1 : 1); 88% diastereomeric purity] and 74 mg (17%) of **127i-I**/**127i-II** [R_f = 0.12 (pentane/Et_2O = 1 : 1), ratio = 3 : 1] as a colorless oil. The combined yield of **112i-I** was equalized 72%. Further chromatography on silica gel (40 g) and collection of the first 60% of this product afforded pure **127i-I** as a colorless crystal (m. p. 134–135 °C).

127i-I: IR (KBr): ν = 2932 cm^{-1} (C–H), 1681 (C=O), 1429, 1338, 1318, 1077. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.28–1.90 (m, 10 H, 4,5,6,7,8-H), 2.24–2.38 (m, 1 H, 7a-H), 2.30 [s, 6 H, $N(CH_3)_2$], 2.64 (s, 1 H, OH), 2.83 (s, 1 H, 3a-H), 6.62 (s, 1 H, 2-H), 7.53 ["t", ^3J = 7.8, ^3J = 7.8 Hz, 1 H, 5'-H], 7.67 (d, ^3J = 7.8 Hz, 1 H, Ph-H), 8.25 (d, ^3J = 7.8 Hz, 1 H, Ph-H), 8.36 (s, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.6, 21.5, 22.9, 31.9, 36.7(–, C-4,5,6,7, 8), 40.3 [+, $N(CH_3)_2$], 57.0 × 2 (+, C-3a,7a), 76.2, 78.5 (C_{quat}, C-3b,8a), 123.8 (q, $^1J_{C\text{-}F}$ = 272.5 Hz, CF_3), 125.9 (+, q, $^3J_{C\text{-}F}$ = 3.9 Hz, C-4'), 127.2 (+, q, $^3J_{C\text{-}F}$ = 3.7 Hz, C-2'), 129.2, 131.4 (+, C-5',6'), 131.1 (C_{quat}, q, $^2J_{C\text{-}F}$ = 32.5 Hz, C-3'), 131.4 (C_{quat},C-1'), 133.7 (+, C-2), 174.8 (C_{quat}, C-1), 207.2 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 379 (21) [M^+], 362 (8) [M^+ – OH], 336 (11), 283 (11), 164 (100), 138 (25), 125 (19). – Elemental analysis calcd (%) for $C_{21}H_{24}F_3NO_2$ (379.4): C 66.48, H 6.38; found: C 66.39, H 6.07.

127i-II: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.28–2.10 (m, 11 H, 4,5,6,7,8-H, OH), 2.25 [s, 6 H, $N(CH_3)_2$], 2.48–2.54 (m, 1 H, 7a-H), 3.10 (s, 1 H, 3a-H), 6.41 (s, 1 H, 2-H), 7.53 ["t" (dd), ^3J = 7.8 Hz, 1 H, 5'-H], 7.67 (d, ^3J = 7.8 Hz, 1 H, Ph-H), 8.25 (d, ^3J = 7.8 Hz, 1 H, Ph-H), 8.36 (s, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 19.8, 21.1, 23.5, 31.2, 35.7 (–, C-4,5,6,7,8), 39.9 [+, $N(CH_3)_2$], 46.8 (+, C-7a), 59.4 (+, C-3a), 77.2, 78.5 (C_{quat}, C-

3b,8a), 123.8 (C_{quat}, q, $^1J_{C-F}$ = 272.5 Hz, CF_3), 125.9 (+, q, $^3J_{C-F}$ = 3.9 Hz, C-4'), 127.2 (+, q, $^3J_{C-F}$ = 3.7 Hz, C-2'), 127.9, 129.2 (+, C-5',6'), 131.1 (C_{quat}, q, $^2J_{C-F}$ = 32.5 Hz, C-3'), 131.4 (C_{quat}, C-1'), 133.1 (C_{quat}, C-2), 174.1 (C_{quat}, C-1), 206.9 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 379 (100) [M^+], 362 (28) [M^+ – OH], 336 (56), 323 (18), 282 (49), 269 (24), 268 (18), 164 (45), 138 (21), 125 (10).

127i-III and an unknown stereoisomer: – IR (film): ν = 2935 cm^{-1} (C–H), 1695 (C=O), 1334, 1168, 1127, 1077, 1019. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.11–1.97 (m, 9 H, 4,5,6,7,8-H), 2.13–2.17 (m, 1 H, 7*a*-H), 2.20, 2.38 [s, 6 H, $N(CH_3)_2$], 2.30 (s, 1 H, OH), 2.81, 2.87 (s, 1 H, 3a-H), 6.40, 6.56 (s, 1 H, 2-H), 7.47–7.69 (m, 2 H, Ph-H), 8.20–8.40 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **127i-III**: δ = 20.8, 24.7, 25.3, 36.3, 37.9 (–, C-4,5,6,7,8), 40.0 [+, $N(CH_3)_2$], 50.2 (+, C-7a), 56.2 (+, C-3a), 77.9, 78.9 (C_{quat}, C-3b,8a), 123.9 (C_{quat}, q, $^1J_{C-F}$ = 272.2 Hz, CF_3), 125.5 (+, q, $^3J_{C-F}$ = 4.0 Hz, C-4'), 130.4 (C_{quat}, C-1'), 127.1 (+, q, $^3J_{C-F}$ = 3.8 Hz, C-2'), 128.4, 129.0 (+, C-5',6'), 130.9 (C_{quat}, q, $^2J_{C-F}$ = 32.5 Hz, C-3'), 133.7 (+, C-2), 174.0 (C_{quat}, C-1), 206.5 (C_{quat}, C-3). The unknown stereoisomer: δ = 21.1, 24.4, 25.1, 33.7, 34.2 (–, C-4,5,6,7,8), 40.5 [+, $N(CH_3)_2$], 44.0 (+, C-7a), 58.2 (+, C-3a), 76.9, 80.0 (C_{quat}, C-3b,8a), 123.9 (C_{quat}, q, $^1J_{C-F}$ = 272.2 Hz, CF_3), 125.5 (+, q, $^3J_{C-F}$ = 4.0 Hz, C-4'), 127.2 (+, q, $^3J_{C-F}$ = 3.8 Hz, C-2'), 129.0, 129.2 (+, C-5',6'), 131.0 (C_{quat}, q, $^2J_{C-F}$ = 32.5 Hz, C-3'), 131.9 (+, C-2), 132.2 (C_{quat}, C-1'), 174.3 (C_{quat}, C-1), 206.0 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 379 (50) [M^+], 362 (100) [M^+ – OH], 282 (86), 269 (60), 268 (46), 164 (26), 138 (21).

(3aS,3bR,7aS,8aR)/(3aR,3bS,7aR,8aS)-1-[4'-Bromo-2',2'-di(ethoxycarbonyl)pent-4'-enyl]-8a-dimethylamino-3b-hydroxy-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one (**127j-I**), (*3aS,3bS,7aR,8aR)/(3aR,3bR,7aS,8aS)-1-[4'-Bromo-2',2'-di(ethoxycarbonyl)pent-4'-enyl]-8a-dimethylamino-3b-hydroxy-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127j-II**), (*3aS,3bS,7aS,8aR)/(3aR,3bR,7aR,8aS)-1-[4'-Bromo-2',2'-di(ethoxycarbonyl)-pent-4'-enyl]-8a-dimethylamino-3b-hydroxy-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta-[a]inden-3-one* (**127j-III**) and *3-[4'-Bromo-2',2'-di(ethoxycarbonyl)pent-4'-enyl]-4-[(2''-oxo-cyclohexanyl)methylen]cyclopent-2-enone* (**135j**) and *8a-Dimethylamino-4-[4'-Bromo-2',2'-di(ethoxycarbonyl)pent-4'-enyl]-4a-hydroxy-4,4a,5,6,7,7a,8,8a-octahydro-1H-s-indance-2-one* (**136j**): Following GP8A, to a solution of **130j** (1.40 g, 2.33 mmol) in dioxane (100 mL) was added a conc. solution of hydrochloric acid (5 mL), and the was mixture was stirred for

2 d. After aqueous work-up, the residue was subjected to chromatography (100 g). Elution with pentane/Et_2O/MeOH (+ 10% CH_2Cl_2 from 1 : 1 : 0 to 0 : 20 : 1) gave 126 mg of **127j-III**/**135j** [R_f = 0.57 (pentane/Et_2O 1 : 2), ratio = 1 : 2] as colorless oil, 749 mg (61%) of **127j-I** [R_f = 0.53 (Et_2O)] as a white solid (m. p. 110 °C) and 188 mg (15%) of **127j-II**/**136j** [R_f = 0.38 (Et_2O); ratio = 93 : 7] as a white solid (m. p. 136–137 °C).

127j-I: – IR(KBr): ν = 3432 cm^{-1} (O–H), 2938 (C–H), 1727 (C=O), 1648 (C=O), 1619, 1218, 1034, 894. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, 3 H, ^3J = 7.0 Hz, OCH_2CH_3), 1.25 (t, 3 H, ^3J = 7.0 Hz, OCH_2CH_3), 1.30–1.75 (m, 10 H, 4,5,6,7,8-H), 2.10–2.20 (m, 1 H, 7a-H), 2.28 [s, 7 H, 3a-H, $N(CH_3)_2$], 2.67 (s, 1 H, OH), 3.17 (s, 2 H, 3'-H), 3.26 (AB, d, ^2J = 15.3 Hz, 1 H, 1'-H), 3.40 (AB, d, ^2J = 15.3 Hz, 1 H, 1'-H), 4.22 (q, ^3J = 7.0 Hz, 4 H, OCH_2CH_3), 5.54 (AB, d, ^2J = 1.4 Hz, 5'-H), 5.60 (AB, d, ^2J = 1.4 Hz, 5'-H), 6.00 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.49, 13.52 (+, OCH_2CH_3), 20.1, 21.1, 22.5, 31.5, 32.1, 35.9, 42.7 (–, C-4,5,6,7,8,1',3'), 39.5 [+, $N(CH_3)_2$], 40.6 (+, C-7a), 55.2 (C_{quat}, C-2'), 58.7 (+, C-3a), 61.8, 61.9 (–, OCH_2CH_3), 75.7, 77.9 (C_{quat}, C-3b,8a), 121.9 (–, C-5'), 126.7 (C_{quat}, C-4'), 130.7 (+, C-2), 169.0, 169.3 (C_{quat}, CO_2Et), 178.0 (C_{quat}, C-1), 207.3 (C_{quat}, C-3).– MS (70 eV), *m*/*z* (%): 527/525 (5/5) [M^+], 446 (98) 248 (26), 191 (10), 164 (100), 138 (14). – HRMS (EI) calcd for $C_{25}H_{36}BrNO_6$: 525.1726 (correct HRMS).

127j-II and **136j**: IR (film): ν = 3506 cm^{-1} (O–H), 2938 (C–H), 1727 (C=O), 1690 (C=C), 1217, 1186, 1161. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, 3 H, ^3J = 7.0 Hz, OCH_2CH_3), 1.27 (t, 3 H, ^3J = 7.0 Hz, OCH_2CH_3), 1.19–1.93 (m, 11 H, 4,5,6,7,8-H, OH), 2.35–2.43 (m, 1 H, 7a-H), 2.14 [s, 6 H, $N(CH_3)_2$], 2.80 (s, 1 H, 3a-H), 3.03 (AB, d, ^2J = 20.8 Hz, 1 H, 3'-H), 3.29 (AB, d, ^2J = 20.8 Hz, 1 H, 3'-H), 3.30 (AB, d, ^2J = 15.3 Hz, 1 H, 1'-H), 3.43 (AB, d, ^2J = 15.3 Hz, 1 H, 1'-H), 4.13–4.26 (m, 4 H, OCH_2CH_3), 5.58 (AB, d, ^2J = 1.4 Hz, 5'-H), 5.61 (AB, d, ^2J = 1.4 Hz, 5'-H), 5.73 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.7, 13.8 (+, OCH_2CH_3), 19.9, 21.0, 23.3, 30.5, 30.9, 34.0, 43.1 (–, C-4,5,6,7,8,1',3'), 39.4 [+, $N(CH_3)_2$], 46.3 (+, C-7a), 55.2 (C_{quat}, C-2'), 57.3 (+, C-3*a*), 62.0, 62.1 (–, OCH_2CH_3), 77.0, 77.9 (C_{quat}, C-3b,8a), 121.9 (–, C-5'), 127.0 (C_{quat}, C-4'), 127.4 (+, C-2), 169.3, 169.5 (C_{quat}, CO_2Et), 178.6 (C_{quat}, C-1), 207.5 (C_{quat}, C-3). Selected signals of **136j**: – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.18 [s, 6 H, $N(CH_3)_2$]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 66.8 (C_{quat}, C-9a), 80.1 (C_{quat}, C-4a). – MS (70 eV), *m*/*z* (%): 527/525 (4/4) [M^+], 446

(100), 248 (50), 191 (10), 164 (26), 138 (10). – Elemental analysiscalcd (%) for $C_{25}H_{36}BrNO_6$ (525.2): C 57.04, H 6.89; found: C 57.39, H 6.64.

127j-III and **135j**: IR (film): ν = 3450 cm^{-1} (O–H), 2937 (C–H), 1735 (C=O), 1687 (C=O), 1220, 1188, 1018, 739. – Selected signals of **127j-III**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.07 [s, 6 H, $N(CH_3)_2$], 2.47 (s, 1 H, 3a-H), 2.76 (br. s, 2 H, 3'-H), 5.50 (AB, d, ^2J = 1.6 Hz, 5'-H), 5.65 (AB, d, ^2J = 1.6 Hz, 5'-H), 5.68 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 39.6 [+, $N(CH_3)_2$], 49.4 (+, C-7a), 54.5 (+, C-3a), 77.8, 79.7 (C_{quat}, C-3b,8a), 121.9 (–, C-5'), 127.0 (C_{quat}, C-4'), 127.4 (+, C-2), 169.5, 169.7 (C_{quat}, CO_2Et), 178.0 (C_{quat}, C-1), 206.8 (C_{quat}, C-3). Selected signals of **135j**: – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.30 (br. s, 2 H, 3'-H), 5.47 (AB, d, ^2J = 1.6 Hz, 5'-H), 5.53 (AB, d, ^2J = 1.6 Hz, 5'-H), 5.98 (s, 1 H, 2-H), 5.98 (s, 1 H, methylen-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 49.1 (+, C-1''), 121.5 (–, C-5'), 121.7 (+, methylen-C), 126.6, 126.7 (C_{quat}, C-4,4'), 131.9 (+, C-2), 168.5 (C_{quat}, CO_2Et), 172.5 (C_{quat}, C-3), 206.9 (C_{quat}, C-1), 210.2 (C_{quat}, C-2''). – MS (70 eV), *m*/*z* (%): 527/525 (4/4) [M^+ of **127j-III**], 482/480 (9/10) [M^+ of **135j**], 446 (100), 401 (38), 355 (11), 248 (26), 164 (20).

(3aS,3bR,7aS,8aR)/(3aR,3bS,7aR,8aS)-8a-Dimethylamino-3b-hydroxy-1-trimethylsilyl-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one (**127l-I**), (*3aS,3bS,7aR,8aR*)/(*3aR,3bR,7aS,8aS*)*-8a-Dimethylamino-3b-hydroxy-1-trimethylsilyl-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127l-II**) and (*3aS,3bS,7aS,8aR*)/(*3aR,3bR,7aR,8aS*)*-8a-Dimethylamino-3b-hydroxy-1-trimethylsilyl-3b,4,5,6,7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one* (**127l-III**):Following GP7 and GP8A, to a solution of complex **18j** (2.37 g, 5.01 mmol) in pyridine (100 mL) was added 737 mg (7.50 mmol) of trimethylsilylethyne (**15j**), and the mixture was kept at 80 °C for 4 d. After oxidation, filtration and evaporation of the solvent, the residue was directly dissolved dioxane (150 mL), treated with a conc. solution of hydrochloric acid (5 mL), and stirred for another 2 d according to GP8A. Chromatography on silica gel (60 g) eluting with pentane/Et_2O (from 3 : 1 to 1 : 2) gave 36.0 mg (2%) of **127l-III** [R_f = 0.49 (pentane/Et_2O = 1 : 1)] as a colorless oil, 441 mg (29%) of **127l-I** [R_f = 0.25 (pentane/Et_2O = 1 : 1)] as a colorless crystal (m. p. 94 °C) and 154 mg (10%) of **127l-II** [R_f = 0.15 (pentane/Et_2O = 1 : 1), 91% diastereomeric purity] as a colorless oil.

127l-I: IR (KBr): ν = 3419 cm^{-1} (O–H), 2931 (C–H), 1694 (C=O), 1289, 1238, 1171, 1024, 995, 904, 835. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.22 [s, 9 H, $Si(CH_3)_3$], 1.20–1.70 (m,

10 H, 4,5,6,7,8-H), 2.08 [s,6 H, $N(CH_3)_2$], 2.08–2.18 (m, 1 H, 7a-H), 2.24 (s, 1 H, OH), 3.03 (s, 1 H, 3a-H), 6.30 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.5 [+, $Si(CH_3)_3$], 20.4, 21.3, 22.8, 32.9, 36.0 (–, C-4,5,6,7,8), 39.8 (+, C-7a), 40.4 [+, $N(CH_3)_2$], 56.9 (+, C-3a), 76.4, 80.4 (C_{quat}, C-3b,8a), 143.4 (+, C-2), 188.3 (C_{quat}, C-1), 209.5 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 307 (73) [M^+], 290 (16) [M^+ – OH], 264 (100), 251 (10), 234 (38), 216 (14), 164 (12), 138 (24), 125 (10), 73 (27) [$Si(CH_3)_3^+$]. – Elemental analysis calcd (%) for $C_{17}H_{29}NO_2Si$ (307.5): C 66.40, H 9.51; found: C 66.71, H 9.25.

127l-II and an unknown stereoisomer: IR (film): ν = 3419 cm^{-1} (O–H), 2931 (C–H), 1694 (C=O), 1289, 1238, 1171, 1024, 995, 904, 835. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.18, 0.22 [s, 9 H, $Si(CH_3)_3$], 1.15–1.82 (m, 10 H, 4,5,6,7,8-H), 2.08 [s, 6 H, $N(CH_3)_2$], 2.15 (s, 1 H, OH), 2.35–2.43 (m, 1 H, 7a-H), 2.24 (s, 1 H, OH), 2.54, 2.77 (s, 1 H, 3a-H), 6.05, 6.25(s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **127l-II**: δ = –0.8 [+, $Si(CH_3)_3$], 19.9, 21.1, 23.5, 31.1, 35.7 (–, C-4,5,6,7,8), 40.1 [+, $N(CH_3)_2$], 47.4 (+, C-7*a*), 57.7 (+, C-3a), 77.2, 80.2 (C_{quat}, C-3b,8a), 139.6 (+, C-2), 187.8 (C_{quat}, C-1), 209.8 (C_{quat}, C-3). The unknown stereoisomer: δ = –0.3 [+, $Si(CH_3)_3$], 21.0, 24.4, 25.1, 33.9, 34.4 (–, C-4,5,6,7,8), 40.7 [+, $N(CH_3)_2$], 43.1 (+, C-7a), 57.5 (+, C-3a), 77.8, 82.3 (C_{quat}, C-3b,8a), 141.9 (+, C-2), 187.8 (C_{quat}, C-1), 209.4 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 307 (67) [M^+], 290 (25) [M^+ – OH], 264 (100), 251 (10), 234 (31), 216 (11), 197 (34), 138 (14), 99 (15), 73 (28) [$Si(CH_3)_3^+$].

127l-III: IR (film): ν = 2938 cm^{-1} (C–H), 1695 (C=O), 1246, 1016, 841. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.22 [s, 9 H, $Si(CH_3)_3$], 1.15–1.96 (m, 11 H, 4,5,6,7,8-H, OH), 2.11 [s, 6 H, $N(CH_3)_2$], 2.05–2.12 (m, 1 H, 7a-H), 2.51 (s, 1 H, 3a-H), 6.08 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.7 [+, $Si(CH_3)_3$], 20.9, 24.8, 25.5, 36.8, 38.0 (–, C-4,5, 6,7,8), 40.4 [+, $N(CH_3)_2$], 50.6 (+, C-7a), 54.7 (+, C-3a), 78.0, 81.7 (C_{quat}, C-3b,8a), 140.0 (+, C-2), 187.4 (C_{quat}, C-1), 209.0 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 307 (24) [M^+], 290 (100) [M^+ – OH], 216 (16), 197 (33), 164 (21), 101 (20), 87 (11), 73 (28) [$Si(CH_3)_3^+$], 55 (12), 43 (15). – HRMS (EI) calcd for $C_{17}H_{29}NO_2Si$: 307.1968 (correct HRMS).

(3aS,3bR,8aS,9aR)/(3aR,3bS,8aR,9aS)-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4, 5,6,7,8,8a,9,9a-decahydro-3H-cyclopenta[a]azulen-3-one (**127m-I**), (*3aS,3bS,8aR,9aR*)/ (*3aR,3bR,8aS,9aS*)*-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,7,8,8a,9,9a-decahydro-3H-cyclopenta[a]azulen-3-one* (**127m-II**) and (*3aS,3bS,8aS,9aR*)/(*3aR,3bR,8aR*,

9aS)-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,7,8,8a,9,9a-decahydro-3H-cyclopenta[a]azulen-3-one (**127m-III**): Following GP8A, to a solution of **130m** (1.20 g, 2.54 mmol) in dioxane (200 mL) was added a 3 N hydrochloric acid (5 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (60 g). Elution with pentane/Et_2O (+ 10% CH_2Cl_2, from 2 : 1 to 1 : 2) gave 323 mg (32%) of **127m-III** [R_f = 0.64 (pentane/Et_2O = 1 : 1)] as a white solid (m. p. 68 °C), 278 mg (27%) of **127m-I** [R_f = 0.36 (pentane/Et_2O = 1 : 1)] as a colorless crystal (m. p. 144–145 °C) and 248 mg (24%) of **127m-II** [R_f = 0.16 (pentane/Et_2O = 1 : 1)] as a colorless crystal (m. p. 183 °C).

127m-I: IR (KBr): ν = 3446 cm^{-1} (O–H), 2927 (C–H), 1695 (C=O), 1343, 699. – ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY and NOESY): δ = 1.19–1.38 (m, 2 H), 1.19–1.38 (m, 3 H) and 1.71–2.03 (m, 7 H) [total 12 H, 4,5,6,7,8,9-H], 2.06–2.20 (m, 1 H, 8a-H), 2.11 (s, 1 H, OH), 2.37 [s, 6 H, $N(CH_3)_2$], 2.79 (s, 1 H, 3a-H), 7.14–7.32 (m, 8 H, Ph-H), 7.53–7.57 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 21.1, 23.8, 29.6, 29.8, 36.5, 40.0 (–, C-4,5,6,7,8,9), 40.3 [+, $N(CH_3)_2$], 47.0 (+, C-8a), 60.0 (+, C-3a), 77.4, 82.2 (C_{quat}, C-3b,9a), 127.7, 128.0 × 2, 128.9, 129.3, 129.7 (+, Ph-C), 131.3, 134.4, 141.8 (C_{quat}, C-2, Ph-C), 170.0 (C_{quat}, C-1), 207.0 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 401 (100) [M^+], 384 (19) [M^+ – OH], 357 (13) [M^+ – $N(CH_3)_2$], 344 (17), 290 (16), 289 (17), 277/276 (38/33), 266 (22), 246 (10), 202 (14), 178 (38), 164 (42), 138 (26), 91 (12), 83 (10), 55 (11). – HRMS (EI) calcd for $C_{27}H_{31}NO_2$: 401.2355 (correct HRMS).

127m-II: IR (KBr): ν = 3513^{-1} (O–H), 2918 (C–H), 1678 (C=O), 1342, 1207, 1175, 772, 699. – ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY and NOESY): δ = 1.40–1.75 (12 H) and 2.12–2.32 (2 H) [m, total 14 H, 4,5,6,7,8,9, 8a-H, OH], 2.40 [s, 6 H, $N(CH_3)_2$], 2.93 (s, 1 H, 3a-H), 7.10–7.15 (m, 2 H, Ph-H), 7.24–7.31 (m, 6 H, Ph-H), 7.57–7.61 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.4, 25.2, 25.6, 27.2, 36.8, 39.1 (–, C-4,5, 6,7,8,9), 40.6 [+, $N(CH_3)_2$], 45.3 (+, C-8a), 61.2 (+, C-3a), 78.6, 81.1 (C_{quat}, C-3b,9a), 128.0, 128.16, 128.23, 129.2, 129.7, 129.8 (+, Ph-C), 131.7, 134.7, 142.1 (C_{quat}, C-2, Ph-C), 170.4 (C_{quat}, C-1), 205.7 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 401 (53) [M^+], 384 (32) [M^+ – OH], 290 (21), 277/276 (100/93), 178 (15). – Elemental analysis calcd for $C_{27}H_{31}NO_2$ (401.5): C 80.76, H 7.78; found: C 81.05, H 7.56.

127m-III: IR (KBr): ν = 2928 cm^{-1} (C–H), 1685 (C=O), 1342, 1172, 998, 775, 728, 699.

– ^{1}H NMR (250 MHz, $CDCl_3$, plus HH-,CH-COSY and NOESY): δ = 1.45–1.77 (m, 9 H, 5,6,7,8-H, OH), 1.91 ["t" (dd), ^2J = 13.6, ^3J = 13.6 Hz, 1 H, 9-H], 2.12 (dd, ^2J = 13.6, ^3J = 6.6 Hz, 1 H, 9-H), 2.34 [s, 6 H, $N(CH_3)_2$], 2.40–2.60 (m, 2 H, 4-H), 2.21–2.30 (m, 1 H, 8a-H), 2.97 (s, 1 H, 3a-H), 7.16–7.32 (m, 8 H, Ph-H), 7.65–7.70 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.5, 25.5, 25.7, 26.6, 41.1, 41.2 (–, C-4,5,6,7,8,9), 39.9 [+, $N(CH_3)_2$], 50.1, 58.0 (+, C-3a,8a), 77.5, 82.2 (C_{quat}, C-3b,9a), 127.5, 127.7, 128.0, 129.1, 129.7, 129.8 (+, Ph-C), 131.9, 134.4, 139.7 (C_{quat}, C-2, Ph-C), 170.4 (C_{quat}, C-1), 205.7 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 401 (93) [M^+], 384 (37) [M^+ – OH], 357 (29) [M^+ – $N(CH_3)_2$], 290 (30), 277 (100), 266 (14), 178 (14), 55 (10), 43 (30).

4-[(2'-oxocycloheptanyl)methylene]-3-propyl-cyclopent-2-enone (**135c**) and *8a-Dimethyl-amino-4-ethyl-4a-hydroxy-4,4a,5,6,7,7a,8,8a-octahydro-1H-s-indacen-2-one* (**136c**):

Following GP8A, to a solution of **130c** (978 mg, 2.92 mmol) in dioxane (200 mL) was added a 3 N solution of hydrochloric acid (15 mL), and the mixture was stirred for 4 d. After aqueous work-up, the residue was subjected to chromatography on aluminum oxide (II, 60 g). Elution with Et_2O/MeOH (from 1 : 0 to 10 : 1) gave 60.0 mg (9%) of **135c** [R_f = 0.60 (Et_2O)] as a colorless oil, 56.0 mg (7%) of the first stereoisomer of **136c** [R_f = 0.33 (Et_2O)] as a colorless oil and 451 mg (59%) of the second stereoisomer of **136c** [R_f = 0.18 (Et_2O)] as a white solid [m. p. 103–105 °C(dec.)].

135c: – IR (KBr): ν = 2964 cm^{-1} (C–H), 1734 (C=O), 1685 (C=O), 1576, 1155, 860. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (t, ^3J = 7.5 Hz, 3 H, $CH_2CH_2CH_3$), 1.40–2.43 (m, 10 H, $CH_2CH_2CH_3$, 3',4',5'-H), 2.89 (br. s, 2 H, 5-H), 2.96–3.05 (m, 1 H, 1'-H), 5.80 and 5.81 (t, ^3J = 1.5 Hz, 1 H, methylen-H), 6.00 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.5 (+, $CH_2CH_2CH_3$), 20.4, 23.4, 28.0, 29.9, 37.6, 37.9 (–, $CH_2CH_2CH_3$, C-5,3', 4',5'), 47.9 (+, C-1'), 129.1, 131.1 (+, methylen-C, C-2), 136.4 (C_{quat}, C-4), 171.9 (C_{quat}, C-3), 204.7 (C_{quat}, C-1), 219.0 (C_{quat}, C-2'). – MS (70 eV), *m*/*z* (%): 218 (100) [M^+], 161 (12), 135 (60), 119 (11), 107 (42), 91 (32), 79 (10), 57 (17), 41 (13).

First stereoisomer of **136c**: IR (film): ν = 3397 cm^{-1} (O–H), 2968 (C–H), 1780 (C=O), 1671 (C=O), 1607 (C=C), 1280, 1205, 1119, 1039. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (td, ^3J = 7.5, ^4J = 1.6 Hz, 1 H, 4-H), 0.97 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 1.20–1.82 (m, 7 H) and 2.01–2.35 (m, 4 H) [total 11 H, CH_2CH_3, OH, 5,6,7,8-H], 1.76 (AB, d, ^2J = 18.7 Hz, 1 H, 1-

H), 2.12 [s, 6 H, $N(CH_3)_2$], 2.62 (AB, d, ^2J = 18.7 Hz, 1 H, 1-H), 2.80–2.85 (m, 1 H, 7a-H), 5.85 (d, ^4J = 1.6 Hz, 1 H, 3-H).– ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 12.5 (+, CH_2CH_3), 18.7, 20.3, 28.5, 30.3, 37.9, 41.5 (–, CH_2CH_3, C-1,5,6,7,8), 38.5 [+, $N(CH_3)_2$], 43.0, 49.1 (+, C-4,7a), 67.3 (C_{quat}, C-8a), 86.9 (C_{quat}, C-4a), 127.2 (+, C-3), 185.6 (C_{quat}, C-3a), 206.8 (C_{quat}, C-2). – MS (70 eV), *m*/*z* (%): 263 (18) [M^+], 219 (37), 216 (14), 137 (38), 91 (14), 77 (14), 67 (16), 55 (39), 46 (73), 41 (100). – HRMS (EI) calcd for $C_{16}H_{25}NO_2$: 263.1855 (correct HRMS).

Second stereoisomer of **136c**: IR (KBr): ν = 3397 cm^{-1} (O–H), 2968 (C–H), 1671 (C=O), 1607, 1294, 1280, 1119, 1039. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.84 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.20–2.30 (m, 11 H, CH_2CH_3, 4,5,6,7,8-H), 1.68 (AB, d, ^2J = 18.6 Hz, 1 H, 1-H), 1.98 [s, 6 H, $N(CH_3)_2$], 2.48 (AB, d, ^2J = 18.6 Hz, 1 H, 1-H), 2.50 (s, 1 H, OH), 2.51–2.57 (m, 1 H, 7a-H), 5.85 (s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 12.2 (+, CH_2CH_3), 17.6, 21.1, 28.3, 35.8, 37.4, 38.8 (–, CH_2CH_3, C-1,5,6,7,8), 38.7 [+, $N(CH_3)_2$], 45.4, 46.4 (+, C-4,7a), 67.8 (C_{quat}, C-8a), 85.4 (C_{quat}, C-4a), 127.8 (+, C-3), 186.8 (C_{quat}, C-3a), 206.7 (C_{quat}, C-2). – MS (70 eV), *m*/*z* (%): 263 (100) [M^+], 245 (20), 234 (30), 219 (100), 201 (44), 166 (29), 150 (10), 136 (14), 46 (12). – Elemental analysis calcd for $C_{16}H_{25}NO_2$ (263.4): C 72.96, H 9.57; found: C 72.70, H 9.97.

(3aS,3bR,8aS,9aR)/(3aR,3bS,8aR,9aS)-9a-Dimethylamino-3b-hydroxy-1-propyl-3a,3b,4,5,6,7,8,8a,9,9a-decahydro-3H-cyclopenta[a]azulen-3-one (**127n-I**), (*3aS,3bS,8aR,9aR)/(3aR,3bR,8aS,9aS)-9a-Dimethylamino-3b-hydroxy-1-propyl-3a,3b,4,5,6,7,8,8a,9,9a-decahydro-3H-cyclopenta[a]azulen-3-one* (**127n-II**), *4-[(2'-oxocycloheptanyl)methylen]-3-propyl-cyclopent-2-enone* (**135n**) and *10a-Dimethylamino-4-ethyl-4a-hydroxy-3a-methyl-dodeca-hydrocyclohepta[f]inden-2one* (**136n**): Following GP8A, to a solution of **130n** (924 mg, 2.01 mmol) in dioxane (150 mL) was added a conc. solution of hydrochloric acid (10 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (70 g). Elution with pentane/Et_2O/MeOH (from 1 : 1 :0 to 0 : 10 :1) gave 161 mg (23%) of **135n** [R_f = 0.30 (pentane/Et_2O = 1 : 1)] as a white solid (m. p. 90–92°C), 182 mg (25%) of an inseparable mixture (**127n-II** and the first stereoisomer of **136n**) [R_f = 0.31 (pentane/Et_2O = 1 : 2); ratio = 6.3 : 1] as a white solid [m. p. 105–106 °C

(dec.)], 123 mg (17%) of the second stereoisomer of **136n** [R_f = 0.28 (Et_2O)] as a pale-yellow oil and 162 mg (22%) of **112n-I** [R_f = 0.24 (EtOAc)] as a colorless crystal (m. p. 105–106°C).

127n-I: IR (KBr): ν = 2953 cm^{-1} (C–H), 1683 (C=O), 1616, 1456, 1272, 1184, 1024. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.32–1.64 (m, 12 H, $CH_2CH_2CH_3$, 5,6,7,8-H), 1.96–2.12 (m, 3 H, 8a,9-H), 2.16 [s, 6 H, $N(CH_3)_2$], 2.27 (t, ^3J = 7.8 Hz, 2 H, 4-H), 2.39 (br. s, 1 H, OH), 2.51 (s, 1 H, 3a-H), 5.90 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, $CH_2CH_2CH_3$), 20.3, 21.6, 24.8, 25.3, 27.0, 30.9, 36.6, 37.9 (–, $CH_2CH_2CH_3$, C-4,5,6,7,8,9), 40.3 [+, $N(CH_3)_2$], 44.9 (+, C-8a), 61.7 (+, C-3a), 78.8, 80.3 (C_{quat}, C-3b,9a), 131.3 (+, C-2), 184.2 (C_{quat}, C-1), 206.6 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 291 (57) [M^+], 274 (100) [M^+ – OH], 262 (16), 248 (27), 230 (17), 167 (51), 166 (29), 138 (32), 125 (36). – Elemental analysis calcd for $C_{18}H_{29}NO_2$ (291.4): C 74.18, H 10.03; found: C 74.31, H 9.93.

127n-II and the first stereoisomer of **136n**: **127n-II**: – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.20–2.00 (m, 14 H, OH, $CH_2CH_2CH_3$, 5,6,7,8,9-H), 2.08 [s, 6 H, $N(CH_3)_2$], 2.13–2.38 (m, 4 H, C-4,8a,9). 2.60 (s, 1 H, 3a-H), 5.68 (t, ^4J = 1.6 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8 (+, $CH_2CH_2CH_3$), 19.7, 23.8, 25.5, 25.8, 26.4, 30.6, 40.5, 41.8 (–, $CH_2CH_2CH_3$, C-4,5,6,7,8,9), 39.9 [+, $N(CH_3)_2$], 49.8 (+, C-8a), 58.1 (+, C-3a), 78.3, 81.3 (C_{quat}, C-3b,9a), 127.4 (+, C-2), 185.9 (C_{quat}, C-1), 207.6 (C_{quat}, C-3). Selected signals of the first diastereomer of **136n**: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 2.06 [s, 6 H, $N(CH_3)_2$], 5.75 (d, ^4J = 1.5 Hz, 1 H, 3-H), – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): 12.8 (+, $CH_2CH_2CH_3$), 38.9 [+, $N(CH_3)_2$], 53.4 (+, C-9a), 66.8 (C_{quat}, C-4a), 81.3 (C_{quat}, C-10a), 126.7 (+, C-2). – MS (70 eV), *m*/*z* (%): 291 (30) [M^+], 262 (14), 247 (17), 244 (100), 229 (96), 199 (26), 150 (12), 135 (18), 91 (13), 55 (12), 46 (67), 41 (17).

135n: IR (KBr): ν = 2926 cm^{-1} (O–H), 1684 (C=O), 1574, 1230, 1141, 934, 864. – ^1H NMR (250 MHz, $CDCl_3$): δ =0.97 (t, ^3J = 7.5 Hz, 3 H, $CH_2CH_2CH_3$), 1.18–1.95 (m, 8 H), 2.08 ["qui", ^3J = 7.5, ^3J = 7.5 Hz, 2 H] and 2.27–2.57 (m, 3 H) [total 13 H, $CH_2CH_2CH_3$, 3',4',5',6',7'-H], 2.78–2.86 (m, 1 H, 3'-H), 2.81 (br. s, 2 H, 5-H), 2.85, 2.92 (d, ^3J = 7.4 Hz, 1 H, 1''-H), 5.75, 5.79 (d, ^3J = 7.4 Hz, 1 H, 1'-H), 5.85 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz,

$CDCl_3$, plus DEPT): δ = 13.3 (+, $CH_2CH_2CH_3$), 23.2, 23.6, 28.6, 28.9, 29.4, 31.0, 37.7, 43.0, (–, $CH_2CH_2CH_3$, C-5,3',4',5',6',7'), 49.5 (+, C-1'), 128.8, 130.5 (+, methylen-C, C-2), 136.4 (C_{quat}, C-4), 172.0 (C_{quat}, C-3), 204.5 (C_{quat}, C-1), 213.8 (C_{quat}, C-2'). – MS (70 eV), *m*/*z* (%): 246 (100) [M^+], 218 (9), 203 (17), 189 (9), 161 (10), 147 (12), 135 (36), 107 (22), 91 (26),77 (11), 41 (15). – Elemental analysis calcd (%) for $C_{16}H_{22}O_2$ (246.3): C 78.01, H 9.00; found: C 77.78, H 8.84.

Second of stereoisomer of **136n**: IR (film): ν = 3470 cm^{-1} (O–H), 2934 (C–H), 1684 (C=O), 1683, 1457, 1266, 737. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 0.93–1.17 (m, 1 H), 1.27–2.40 (m, 21 H) [total, 22 H, 4,5,6,7,8,9,9a,10-H, CH_2CH_3, $N(CH_3)_2$], 1.74 (AB, d, ^2J = 18.7 Hz, 1 H, 1-H), 2.50 (s, 1 H, OH), 2.59 (AB, d, ^2J = 18.7 Hz, 1 H, 1-H), 5.85 (d, ^2J = 1.4 Hz, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 12.5 (+, CH_2CH_3), 17.5, 20.7, 26.1, 26.8, 28.3, 38.3, 39.1, 43.4 (–, CH_2CH_3, C-1, 5,6,7,8,9,10), 38.7 [+, $N(CH_3)_2$], 41.3, 50.1 (+, C-4,9a), 67.4 (C_{quat}, C-8a), 77.9 (C_{quat}, C-4a), 128.3 (+, C-3), 186.4 (C_{quat}, C-3a), 206.6 (C_{quat}, C-2). – MS (70 eV), *m*/*z* (%): 291 (85) [M^+], 274 (34) [M^+ – OH], 247 (46), 229 (100), 199 (16), 166 (42), 135 (16), 115 (12), 91 (17), 55 (16), 46 (42),41 (19). – Elemental analysis calcd for $C_{18}H_{29}NO_2$ (291.4): C 74.18, H 10.03; found: C 74.30, H 9.95.

7a-Dimethyamino-1,2-diphenyl-3a,4,5,6,7,7a-hexahydrocyclopenta[a]pentalen-3-one (**145a**) and *7a-Dimethyamino-1,2-diphenyl-3a,5,6,6a,7,7a-hexahydrocyclopenta[a]pentalen-3-one* (**146a**): A solution of **127a-I** (200 mg, 0.54 mmol) in benzene (200 mL) was treated with catalytic amount of TsOH, and the mixture was refluxed for 2 h using a Dean-Stark apparatus. After cooling to the ambient temperature, a sat. solution of potassium carbonate (50 mL) was added to the solution, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extract was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was obtained as the starting material **127a-I**. Further heating this mixture as described above and aqueous work-up gave a pale-yellow oil, which was subjected to chromatography on aluminum oxide (II, 30 g). Elution with pentane/Et_2O (3 : 1) gave 175 mg (92%) of **145a**/**146a** [R_f = 0.35 (pentane/Et_2O = 3 : 1), ratio = 1.1 : 1] as a pale-yellow solid. When 102 mg (0.29 mmol) of these regioisomers were refluxed again with catalytic amount of TsOH in benzene (100 mL) for 36 h without using Dean-Stark apparatus,

94.0 mg (92%) of **145a**/**146a** (2.1 : 1) were isolated. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.19–1.56 (1 H) and 2.04–2.80 (4 H) [m, 8 H, 5,6,7-H, 4-H of **145a** and 6a-H of **146a**], 2.31, 2.39 [s, 6 H, $N(CH_3)_2$], 3.30–3.33, 3.58–3.62 (br. m, 1 H, 3a-H), 5.76 (br. s, 1 H, 4-H of **146a**), 7.11–7.35 (m, 8 H, Ph-H), 7.63–7.70 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **145a**: δ = 26.5, 28.1, 29.5 (–, C-4,5,6), 39.8 (–, C-7), 40.0 [+, $N(CH_3)_2$], 49.7 (+, C-3a), 85.2 (C_{quat}, C-7a), 127.8, 127.99, 128.20, 129.35, 129.9, 130.2 (+, Ph-C), 132.2, 133.9, 138.8, 141.0, 145.2 (C_{quat}, C-2,3b,6a, Ph-C), 169.2 (C_{quat}, C-1), 203.5 (C_{quat}, C-3). **146a**: δ = 32.3, 36.3, 43.6 (–, C-4,5,6), 44.7 (–, C-6a), 40.2 [+, $N(CH_3)_2$], 53.4 (+, C-3a), 85.2 (C_{quat}, C-7a), 120.8 (C_{quat}, C-3b), 127.8, 127.95, 128.16, 129.4, 129.9 × 2, 130.1 (+, C-4, Ph-C), 131.9, 134.2, 146.6 (C_{quat}, C-2, Ph-C), 170.1 (C_{quat}, C-1), 203.0 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 353 (100) [M^+], 327 (14), 310 (14), 250 (18), 149 (28), 162 (25). – HRMS (EI) calcd for $C_{25}H_{25}NO$: 355.1936 (correct HRMS).

8a-Dimethyamino-1,2-diphenyl-4,5,6,7,7a,8,8a-octahydrocyclopenta[a]inden-3-one (**145f**): A solution of **127f-I** (221 mg, 0.57 mmol) in benzene (150 mL) was treated with catalytic amount of TsOH, and the mixture was refluxed for 2 h using a Dean-Stark apparatus. After cooling to the ambient temperature, a sat. solution of potassium carbonate (50 mL) was added to the solution, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extract was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to chromatography on aluminum oxide (II, 30 g). Elution with pentane/Et_2O (3 : 1) gave 171 mg (81%) of **145f** [R_f = 0.67 (pentane/Et_2O = 3 : 1)] as a pale-yellow crystal (m. p. 155–156 °C). – IR (film): ν = 2722 cm^{-1} (C–H), 1695 (C=O), 1458, 1333, 1165, 1032. – ^{1}H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY, NOESY and HMBC): δ = 1.63–1.70 (m, 4 H), 1.84–2.42 (m, 4 H) [total 8 H, 4,5,6,7-H], 2.27 [s, 6 H, $N(CH_3)_2$], 2.72 (br. s, 2 H, 8-H), 3.57 (br. s, 1 H, 3a-H), 7.19–7.33 (m, 8 H, Ph-H), 7.63–7.69 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.5, 22.6, 23.7, 25.4 (–, C-4,5,6,7), 39.7 [+, $N(CH_3)_2$], 45.5 (–, C-8), 55.0 (+, C-3*a*), 77.2 (C_{quat}, C-8a), 127.7, 127.9, 128.1, 129.2,129.8, 130.1 (+, Ph-C), 131.2, 132.1, 133.8, 135.0, 138.5 (C_{quat}, C-2,7a,3b, Ph-C), 169.3 (C_{quat}, C-1), 203.9 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 369 (100) [M^+], 341 (14) [M^+ – CO], 163 (22), 162 (25), 135 (9). – Elemental analysis calcd (%) for $C_{26}H_{27}NO$ (369.5): C 84.52, H 7.36; found: C 84.35, H 7.05.

9a-Dimethylamino-1,2-diphenyl-3a,4,5,6,7,8,9,9a-octahydrocyclopenta[a]azulen-3-one (**145m**) and *9a-Dimethylamino-1,2-diphenyl-3a,5,6,7,8,8a,9,9a-octahydrocyclopenta-[a]azulen-3-one* (**146m**): A solution of **127m-I** (150 mg, 0.37 mmol) in benzene (80 mL) was treated with catalytic amount of TsOH, and the mixture was refluxed for 18 h using a Dean-Stark apparatus. After cooling to the ambient temperature, a sat. solution of potassium carbonate (50 mL) was added to the solution, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extract was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to chromatography on silica gel (40 g). Elution with pentane/Et_2O (from 3 : 1 to 1 : 1) gave 78.0 mg (54%) of **145m** [R_f = 0.33 (pentane/Et_2O = 3 : 1)] as a pale-yellow crystal (m. p. 173–174 °C) and 59.0 mg (41%) of **146m** [R_f = 0.16 (pentane/Et_2O = 3 : 1)] as a colorless solid (m. p. 171 °C).

145m: IR (KBr): ν = 2913 cm^{-1} (C–H), 1689 (C=O), 1444, 1341, 1170, 775, 728, 705. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.39–1.63 (m, 6 H), 1.98–2.11 (m, 2 H) and 2.10–2.43 (m, 2 H) [total 10 H, 4,5,6,7,8-H], 2.15 [s, 6 H, $N(CH_3)_2$], 2.68 (br. s, 2 H, 9-H), 3.47 (br. s, 1 H, 3a-H), 7.08–7.23 (m, 8 H, Ph-H), 7.48–7.54 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 27.1, 27.4, 28.2, 29.7, 30.8 (–, C-4,5,6,7,8), 39.8 [+, $N(CH_3)_2$], 48.1 (–, C-9), 57.1 (+, C-3a), 76.9 (C_{quat}, C-9a), 127.7, 128.0, 128.2, 129.3, 129.9, 130.1 (+, Ph-C), 132.3, 133.9, 134.6, 138.5, 138.7 (C_{quat}, C-2,3b,8b, Ph-C), 169.2 (C_{quat}, C-1), 204.6 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 383 (100) [M^+], 355 (7) [M^+ – CO], 338 (10), 177 (32). – Elemental analysis calcd (%) for $C_{27}H_{29}NO$ (383.5): C 84.55, H 7.62; found: C 84.32, H 7.32.

132m: IR (KBr): ν = 2916 cm^{-1} (C–H), 1703 (C=O), 1337, 1268, 1153, 1033, 766, 697. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.37–1.50 (m, 3 H) and 1.75–2.47 (m, 8 H) [total 11 H, 5,6,7,8, 9,8a-H], 2.39 [s, 6 H, $N(CH_3)_2$], 3.50 (br. s, 1 H, 3a-H), 7.10–7.35 (m, 8 H, Ph-H), 7.54–7.61 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 27.4, 28.5, 28.6, 33.0, 39.6 (–, C-5,6,7,8,9), 40.5 [+, $N(CH_3)_2$], 41.0 (–, C-9), 55.1 (+, C-3a), 78.0 (C_{quat}, C-9a), 127.6, 127.9, 128.1, 128.2, 129.0, 129.4, 129.8 (+, C-4, Ph-C), 131.7, 134.7, 141.0, 142.9 (C_{quat}, C-2,3b, Ph-C), 168.0 (C_{quat}, C-1), 205.0 (C_{quat}, C-3). – MS (70 eV), *m*/*z* (%): 383 (100) [M^+], 355 (28) [M^+ – CO], 340 (32), 177 (71), 148 (24), 123 (11), 91 (10), 84 (18). – HRMS (EI) calcd for $C_{27}H_{29}NO$: 383.2249 (correct HRMS).

5-Dimethylamino-5-[(1',3',3'-trimethyl-2'-oxocyclopentanyl)methyl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (**148a**): Following GP7, to a solution of complex **18n** (914 mg, 2.00 mmol) in pyridine (40 mL) was treated with 392 mg (2.20 mmol) of 1,2-diphenylethyne (**15aa**), and the mixture was stirred at 80 °C for 2 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave 429 g (47%) of **148a** [R_f = 0.47 (pentane/Et_2O = 3 :1); d. r. = 1.2 : 1] as a pale-yellow semi-solid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.57, 0.73, 0.96, 1.04 × 2, 1.09 (s, total 9 H, CH_3), 1.27, 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.60–2.05 (m, 5 H, CCH_2C, 4',5'-H), 2.36 [s, 6 H, $N(CH_3)_2$], 2.49 (d, ^2J = 13.8 Hz) and 2.59 (d, ^2J = 14.3 Hz) [total 1 H, CCH_2C], 3.84–3.98 (m, 2 H, OCH_2CH_3), 4.90, 5.12 (s, 1 H, 4-H), 7.09–7.30 (m, 8 H, Ph-H), 7.45–7.58 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3, 14.5 (+, OCH_2CH_3), 23.6, 24.3, 25.2, 25.35, 25.37, 27.1 (+, CH_3), 30.0, 31.8, 34.8, 35.0, 39.0, 40.5 (–, CCH_2C, C-4',5'), 40.0, 40.4 [+, $N(CH_3)_2$], 44.0, 44.2, 48.4, 49.0 (C_{quat}, C-1',3'), 64.8, 64.9 (–, OCH_2CH_3), 74.9, 75.6 (C_{quat}, C-5), 98.6, 98.8 (+, C-4), 126.7, 126.8, 127.28, 127.32, 127.6, 127.7, 128.1, 128.2, 129.53, 129.56, 129.61, 129.65 (+, Ph-C), 134.2, 134.7, 134.9, 135.2, 137.6, 137.9 (C_{quat}, C-2, C-Ph), 145.6, 146.9 (C_{quat}, C-1), 158.3, 158.8 (C_{quat}, C-3), 226.1, 226.4 (C_{quat}, C-2'). – MS (70 eV), *m/z* (%): 443 (100) [M^+], 414 (86) [$M^+ - C_2H_5$], 399 (27), 318 (90), 304 (12), 275 (18). – HRMS (EI) calcd for $C_{30}H_{37}NO_2$: 443.2824 (correct HRMS).

5-Dimethylamino-5-[(1',3',3'-trimethyl-2'-oxocyclopentanyl)methyl]-3-ethoxy-1-propyl-1,3-cyclopentadiene (**148b**): Following GP7, to a solution of complex **18n** (914 mg, 2.00 mmol) in pyridine (40 mL) was treated with 392 mg (2.20 mmol) of 1-pentyne (**15h^1**), and the mixture was stirred at 80 °C for 2 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et_2O (from 1 : 0 to 1 : 1) gave 491 g (57%) of **148b** [R_f = 0.48 (pentane/Et_2O = 1 :1); d. r. = 1.5 : 1] as a pale-yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.83, 0.86, 0.87, 0.90, 1.02 × 2 (s, total 9 H, CH_3), 0.97 (t, ^3J = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.26, 1.31 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.45–2.23 (m, 9 H, $CH_2CH_2CH_3$, CCH_2C, 4',5'-H), 2.09, 2.11 [s, 6 H, $N(CH_3)_2$], 2.40 (d, ^2J = 14.5 Hz, CCH_2C), 3.71–3.89 (m, 2 H, OCH_2CH_3), 4.53, 4.76 (s, 1 H, 4-H), 5.66, 5.68 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.2, 14.3, 14.4, 14.6 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 20.9 × 2 (–, $CH_2CH_2CH_3$), 24.6, 24.7, 24.9, 25.8 × 2, 26.7 (+, CH_3), 29.5 × 2, 30.0, 30.4, 32.1, 34.7 × 2, 35.1 (–, CCH_2C, $CH_2CH_2CH_3$,

C-4',5'), 39.6, 39.9 [+, $N(CH_3)_2$], 39.5, 40.9, 44.1, 44.2 (C_{quat}, C-1',3'), 64.4, 64.5 (–, OCH_2CH_3), 74.9, 75.6 (C_{quat}, C-5), 95.9, 96.7 (+, C-4), 123.1, 123.2 (+, C-2), 156.5, 157.1, 159.2, 159.7 (C_{quat}, C-1,3), 225.7, 226.0 (C_{quat}, C-2'). – MS (70 eV), *m/z* (%): 333 (32) [M^+], 304 (46) [$M^+ – C_2H_5$], 208 (100), 163 (15). – HRMS (EI) calcd for $C_{21}H_{35}NO_2$: 333.2668 (correct HRMS)

4-[(1',3',3'-trimethyl-2'-oxocyclopentanyl)methylen]-1,2-diphenylcyclopent-2-enone (**149a**): Following GP8A, to a solution of **148a** (400 mg, 0.90 mmol) in dioxane (100 mL) was added a conc. solution of hydrochloric acid (5 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel. Elution with pentane/Et_2O (from 3 : 1 to 0 : 1) gave 251 g (75%) of **149a** as a pale-yellow solid (m. p. 159–161 °C). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.02 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.78–2.16 (m, 4 H, 4',5'-H), 3.35 (d, ^4J = 1.5 Hz, 2 H, 5-H), 5.83 (t, ^4J = 1.5 Hz, 1 H, methylen-H), 7.10–7.24 (m, 8 H, Ph-H), 7.31–7.45 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.0, 25.0, 25.3 (+, CH_3), 34.4, 34.8, 38.7 (–, C-5,4',5'), 44.5, 51.2 (C_{quat}, C-1',3'), 127.6, 127.8, 128.4, 128.6, 128.9, 129.5 (+, C-Ph), 133.19 (+, C-methylen), 130.8, 133.22, 137.3, 139.7 (C_{quat}, C-Ph, C-2,4), 166.4 (C_{quat}, C-3), 202.7 (C_{quat}, C-1), 222.5 (C_{quat}, C-2'). – MS (70 eV), *m/z* (%): 370 (64) [M^+], 286 (100), 271 (22). – Elemental analysis calcd (%) for $C_{27}H_{29}NO$ (370.5): C 84.29, H 7.07; found: C 84.21, H 7.00.

7a-Dimethyamino-4,4,6a-trimethyl-1,2-diphenyl-4,5,6,6a,7,7a-hexahydrocyclopenta[a]-pentalen-3-one (**151a**): To a solution of **148a** (337 mg, 0.76 mmol) in dioxane (80 mL) was added a 3 n solution of hydrochloric acid (2 mL), and the mixture was stirred at the ambient temperature for 2 h. After addition of water (100 mL) and Et_2O (40 mL), the aqueous phase was extracted with Et_2O (4 × 30 mL). The combined organic extract was washed with a sat. solution of sodium carbonate (2 × 30 mL) and brine (2 × 30 mL). Before filtration and evaporation of the solvent, the solution was dried over $MgSO_4$. The residue, then, was diluted with dry THF (100 mL) and treated with potassium *tert*-butylate (632 mg, 5.63 mmol). This mixture was refluxed under argon at 80 °C for 12 h. After cooling to the ambient temperature, the solution was treated with water (50 mL), extracted with Et_2O (3 × 50 mL), and died with

dried over $MgSO_4$. Chromatography on silica gel (30 g) eluting with pentane/Et_2O (3 : 1) gave 19.0 mg (6%) of **151a** [R_f = 0.81 (pentane/Et_2O = 3 : 1)] as a yellow solid (m. p. 142–144 °C). – IR (film): ν = 2960 cm^{-1} (C–H), 2934, 1648 (C=O), 731, 696. – ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY and NOESY): δ = 1.22, 1.36, 1.62 (s, total 9 H, CH_3), 1.65–1.85 (m, 4 H, 5,6-H), 2.45 (d, ^2J = 12.0 Hz, 1 H, 7-*exo*-H), 2.66 (d, ^2J = 12.0 Hz, 1 H, 7-*endo*-H), 7.07–7.36 (m, 10 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 24.2, 25.2, 29.8 (+, CH_3), 38.4 (C_{quat}, C-4), 39.6 [+, $N(CH_3)_2$], 39.8, 44.0, (–, C-5,6), 49.6 (–, C-7), 63.3 (C_{quat}, C-6a), 83.8 (C_{quat}, C-7a), 127.4, 128.0, 128.29, 128.32, 128.6, 129.9 (+, Ph-C), 131.6, 136.0, 137.6, 142.9 (C_{quat}, C-2,3a, Ph-C), 158.9 (C_{quat}, C-3b), 169.3 (C_{quat}, C-1), 190.2 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 397 (77) [M^+], 369 (14) [M^+ – CO], 353 (100) [M^+ – $N(CH_3)_2$], 328 (32), 297 (35), 178 (26), 107 (34), 91 (42). 55 (12), 41 (22). – HRMS (EI) calcd for $C_{28}H_{31}NO$: 397.2406 (correct HRMS)

5-Dimethylamino-5-[2'-(1'',4''-dioxaspiro[4.6]dec-6''-yl)ethyl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (**130o**): Following GP7, to a solution of complex **18k** (2.44 g. 5.00 mmol) in pyridine (100 mL) was added 1.34 g (7.50 mmol) of 1,2-diphenylethyne (**15aa**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (+ 1% NEt_3, from 20 : 1 to 1 : 1) gave 1.29 g (54%) of **130o** [R_f = 0.28 (pentane/Et_2O = 3 :1); d. r. = 1 : 1] as a pale-yellow semi-solid. – IR (film): ν = 2936 cm^{-1} (C–H), 1630 (C=C), 1599, 1580, 1444, 1349, 1192, 1089, 1056. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.80–2.00 (m, 13 H, 1',2',6",7",8",9",10"-H), 1.36 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.38 [s, 6 H, $N(CH_3)_2$], 3.44–3.59 (m, 1 H, OCH_2CH_3), 3.71–4.03 (m, 5 H, 2",3"-H, OCH_2CH_3), 5.02, 5.06 [s, (1 : 1), 1 H, 4-H], 7.08–7.32 (m, 8 H, Ph-H), 7.43–7.49 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3 (+, OCH_2CH_3), 21.6, 22.3, 23.8 × 2, 24.2, 24.8, 28.9, 30.0, 32.4, 32.8, 34.8, 35.0 (–, C-1',2',7",8",9",10"), 40.08, 40.13 [+, $N(CH_3)_2$], 45.2 (+, C-6"), 64.3, 64.6, 64.7 (–, OCH_2CH_3, C-2",3"), 76.3, 76.4 (C_{quat}, C-5), 97.2, 97.3 (+, C-4), 110.8, 110.9 (C_{quat}, C-5"), 126.5, 126.9, 127.6 × 2, 127.8 × 2, 129.4, 129.5, 129.9 × 4 (+, Ph-C), 134.13, 134.16 (C_{quat}, C-Ph), 135.7, 135.9, 137.7, 137.8 (C_{quat}, C-2, Ph-C), 146.08, 146.13 (C_{quat}, C-1), 158.8, 158.9 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 473 (88) [M^+], 444 (100) [M^+ – C_2H_5], 429 (18), 304 (76), 276 (21), 259

(15), 215 (14), 202 (10), 155 (21), 131 (10), 99 (38), 91 (20), 72 (10), 55 (45), 42 (24). – HRMS (EI) calcd for $C_{31}H_{39}NO_3$: 473.2930 (correct HRMS).

5-Dimethylamino-5-[2'-(2''-oxo-1''-cyclohexanyl)ethyl]-3-trimethylsilyl-cyclopent-2-enone (**129p**): Following GP7, to a solution of complex **18k** (2.44 g. 5.00 mmol) in pyridine (100 mL) was added 737 mg (7.50 mmol) of trimethylsilylethyne (**15j**), and the mixture was stirred at 80 °C for 3 d. After oxidation, filtration and evaporation of the solvent, the residue was directly dissolved dioxane (125 mL), treated with a 3 N solution of hydrochloric acid (10 mL), and stirred for another 1 d according to GP8A. Chromatography on silica gel (60 g) eluting with pentane/Et_2O (from 1 : 1 to 1 : 2) gave 785 mg (49%) of **129p** [R_f = 0.25 (pentane/Et_2O = 1 :1); d. r. = 1.5 : 1] as a colorless oil. In addition, an unidentified regioisomer or byproduct [R_f = 0.30 (pentane/Et_2O = 1 :1)] was also observed. **129p**: IR (film): ν = 2936 cm^{-1} (C–H), 1710 (C=O), 1449, 1249, 1042, 984, 896, 841, 761. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.11, 0.15 [s, 9 H, $Si(CH_3)_3$], 0.57–0.70 (m, 1 H), 1.05–1.26 (m, 2 H) and 1.40–2.42 (m, 12 H) [total 15 H, 5,1',2',1'',3'',4'',5'',6''-H), 1.98, 1.99 [s, 6 H, $N(CH_3)_2$], 6.17 [s, 1 H, 2-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major stereoisomer: δ = –0.73 [+, $Si(CH_3)_3$], 24.9, 25.3, 27.8, 34.4, 35.2, 36.2, 40.9 (–, C-5,1',2',3'', 4'',5'',6''), 39.7 [+, $N(CH_3)_2$], 50.6 (+, C-1''), 74.1 (C_{quat}, C-4), 142.2 (+, C-2), 187.7 (C_{quat}, C-3), 208.1 (C_{quat}, C-1), 212.0 (C_{quat}, C-2''). Minor stereoisomer: δ = –0.73 [+, $Si(CH_3)_3$], 24.8, 25.2, 27.7, 34.0, 35.1, 36.5, 41.9 (–, C-5,1',2',3'',4'',5'', 6''), 39.7 [+, $N(CH_3)_2$], 50.8 (+, C-1''), 74.1 (C_{quat}, C-4), 141.9 (+, C-2), 188.6 (C_{quat}, C-3), 208.1 (C_{quat}, C-1), 211.9 (C_{quat}, C-2''). – MS (70 eV), *m/z* (%): 321 (16) [M^+], 224 (20), 211 (10), 196 (100), 179 (34), 138 (33), 85 (40), 73 (73), 55 (19), 41 (17). – Elemental analysis calcd (%) for $C_{18}H_{31}NO_2Si$ (321.5): C 67.24, H 9.72; found: C 67.52, H 9.65.

5-Dimethylamino-5-[2'-(2''-oxo-1''-cyclohexanyl)ethyl]-3-propyl-cyclopent-2-enone (**129q**): Following GP7, to a solution of complex **18k** (2.44 g. 5.00 mmol) in pyridine (100 mL) was added 1.00 mL (10.1 mmol) of 1-pentyne (**15h[1]**), and the mixture was stirred at 80 °C for 3 d. After oxidation, filtration and evaporation of the solvent, the residue was directly dissolved dioxane (125 mL), treated with a 3 N solution of hydrochloric acid (10 mL), and stirred for another 1 d according to GP8A. Chromatography on silica gel (50 g) eluting with Et_2O gave 915 mg (63%) of **129q** [R_f = 0.25 (Et_2O); d. r. 1.1 : 1] as a colorless oil. – IR (film): ν =

2935 cm^{-1} (C–H), 1708 (C=O), 1616, 1449, 1245. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.67 (t, ^3J = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 0.40–0.55 (m, 1 H) and 0.93–2.20 (m, 18 H) [total 19 H, $CH_2CH_2CH_3$, 5,1',2',1",3",4",5",6"-H), 1.77 [s, 6 H, $N(CH_3)_2$], 5.61 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major stereoisomer: δ = 13.3 [+, $CH_2CH_2CH_3$], 19.0, 23.92, 24.48, 27.4, 29.3, 33.7, 33.9, 35.51, 41.48 (–, $CH_2CH_2CH_3$, C-5,1',2',3",4",5",6"), 38.5 [+, $N(CH_3)_2$], 49.9 (+, C-1"), 69.90 (C_{quat}, C-4), 129.1 (+, C-2), 184.6 (C_{quat}, C-3), 205.4 (C_{quat}, C-1), 211.34 (C_{quat}, C-2"). Minor stereoisomer: δ = 13.3 [+, $CH_2CH_2CH_3$], 19.0, 23.88, 24.43, 27.3, 29.3, 33.4, 33.7, 35.45, 41.44 (–, $CH_2CH_2CH_3$, C-5,1',2',3",4",5",6"), 38.5 [+, $N(CH_3)_2$], 49.7 (+, C-1"), 69.95 (C_{quat}, C-4), 129.5 (+, C-2), 183.6 (C_{quat}, C-3), 205.4 (C_{quat}, C-1), 211.29 (C_{quat}, C-2"). – MS (70 eV), *m/z* (%): 291 (12) [M^+], 166 (100), 149 (18). – HRMS (EI) calcd for $C_{18}H_{29}NO_2$: 291.2198 (correct HRMS).

5-Dimethylamino-5-[2'-(2''-oxo-1''-cyclohexanyl)ethyl]-3-methyl-cyclopent-2-enone (**129r**): Following GP7, to a solution of complex **18k** (2.44 g. 5.00 mmol) in pyridine (100 mL) was added 1-propyne (**15h**), and the mixture was stirred at 80 °C for 3 d. After oxidation, filtration and evaporation of the solvent, the residue was directly dissolved dioxane (125 mL), treated with a 3 N solution of hydrochloric acid (10 mL), and stirred for another 1 d according to GP8A. Chromatography on silica gel (50 g) eluting with Et_2O gave 915 mg (63%) of **129r** [R_f = 0.25 (Et_2O); d. r. = 1.1 : 1] as a colorless oil. – IR (film): ν = 2935 cm^{-1} (C–H), 1700 (C=O), 1448, 1272, 734. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.38–0.47 (m, 1 H) and 0.85–2.05 (m, 13 H) [total 14 H, 5,1',2',1",3",4",5",6"-H), 1.62, 1.70 (s, 3 H, CH_3), 1.73 [s, 6 H, $N(CH_3)_2$], 2.77 (AB, d, ^2J = 18.6 Hz, 1 H, 5-H), 5.54 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major stereoisomer: δ = 13.8 (+, CH_3), 23.7, 24.33, 27.2, 33.2, 33.8, 35.14, 41.3 (–, C-5,1',2',3",4",5",6"), 38.4 [+, $N(CH_3)_2$], 49.5 (+, C-1"), 69.72 (C_{quat}, C-4), 131.4 (+, C-2), 180.2 (C_{quat}, C-3), 205.2 (C_{quat}, C-1), 211.4 (C_{quat}, C-2"). Minor stereoisomer: δ = 13.7 (+, CH_3), 23.8, 24.38, 27.3, 32.9, 33.6, 35.18, 41.4 (–, C-5,1',2',3",4",5",6"), 38.4 [+, $N(CH_3)_2$], 49.8 (+, C-1"), 69.68 (C_{quat}, C-4), 131.7 (+, C-2), 179.3 (C_{quat}, C-3), 205.2 (C_{quat}, C-1), 211.3 (C_{quat}, C-2"). – MS (DCI), *m/z* (%): 527 (16) [2M + H^+], 264 (100) [M + H^+].

5-Dimethylamino-5-[2'-(2''-oxo-1''-cyclohexanyl)ethyl]-2,3-dimethyl-cyclopent-2-enone (**129s**): Following GP7, to a solution of complex **18k** (2.44 g, 5.00 mmol) in pyridine (100 mL) was added 541 mg (10.0 mmol) of 2-butyne (**15hh**), and the mixture was stirred at 80 °C for 3 d. After oxidation, filtration and evaporation of the solvent, the residue was directly dissolved dioxane (125 mL), treated with a 3 N solution of hydrochloric acid (10 mL), and stirred for another 1 d according to GP8A. Chromatography on aluminum oxide (II, 50 g) eluting with pentane/Et_2O (from 1 : 1 to 0 : 1) gave 957 mg (69%) of **129s** [R_f = 0.25 (Et_2O); d. r. = 2.2 : 1] as a colorless oil. – IR (film): ν = 2943 cm^{-1} (C–H), 1700 (C=O), 1653 (C=C), 1659, 668. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.63–0.75 (m, 1 H), 1.18–1.37 (m, 2 H) and 1.42–2.45 (m, 12 H) [total 15 H, 5,1',2',1",3",4",5",6"-H], 1.64, 1.65, 1.87, 1.95 (s, total 6 H, CH_3), 2.05 [s, 6 H, $N(CH_3)_2$]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major stereoisomer: δ = 7.3, 11.9 (+, CH_3), 24.1, 24.67, 27.6, 33.8, 34.1, 34.7, 41.73 (–,C-5,1',2',3", 4",5",6"), 38.8 [+, $N(CH_3)_2$], 50.2 (+, C-1"), 68.47 (C_{quat}, C-4), 137.5 (+, C-2), 171.2 (C_{quat}, C-3), 206.0 (C_{quat}, C-1), 211.8 (C_{quat}, C-2"). Minor stereoisomer: δ = 7.3, 11.8 (+, CH_3), 24.0, 24.64, 27.5, 33.6, 33.9, 34.6, 41.68 (–, C-5,1',2',3",4",5",6"), 38.8 [+, $N(CH_3)_2$], 50.2 (+, C-1"), 68.49 (C_{quat}, C-4), 137.8 (+, C-2), 172.1 (C_{quat}, C-3), 206.0 (C_{quat}, C-1), 211.7 (C_{quat}, C-2"). – MS (70 eV), *m/z* (%): 277 (2) [M^+], 152 (100), 135 (17). – HRMS (EI) calcd for $C_{17}H_{27}NO_2$: .277.2043 (correct HRMS).

2,3,6,7,8,9-Hexahydrocyclopenta[a]naphthalen-1-one (**155p**): Variation A: Following GP8B, to a solution of **129p** (351 mg, 1.09 mmol) in dioxane (150 mL) was added a conc. solution of hydrochloric acid (10 mL), and the mixture was stirred at 60 °C for 36 h. After aqueous work-up, the residue was subjected to chromatography on silica gel (50 g). Elution with pentane/ Et_2O (from 5 : 1 to 3 : 1) gave 175 mg (87%) of **155q** [R_f = 0.70 (pentane/Et_2O = 3 : 1)] as a colorless oil. – IR (film): ν = 2924 cm^{-1} (C–H), 1696 (C=O), 1577, 1416, 1272, 1169, 1098, 838. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.70–1.78 (m, 4 H, 7,8-H), 2.52–2.58 (m, 2 H) and 2.91–2.97 (m, 2 H) [total 4 H, 2,3-H], 2.71 (br. s, 2 H) and 3.11 (br. s, 2 H) [total 4 H, 6,9-H], 7.09 (d, ^3J = 7.9 Hz, 1 H, 4-H), 7.17 (d, ^3J = 7.9 Hz, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.2, 22.3, 24.8, 25.5, 29.1, 36.8 (–, C-2,3,6,7,8,9), 123.0, 135.2 (+, C-4,5), 133.7, 135.9, 137.4, 153.7 (C_{quat}, C-3a,5a,9a,9b), 207.7 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 186 (100) [M^+], 171 (68) [$M^+ – CH_3$], 143 (28), 129 (44), 115 (24). – Elemental analysis calcd (%) for $C_{13}H_{14}O$ (186.3): C 83.83, H 7.58; found: C 83.56, H 7.36.

Variation B: a solution of **129p** (380 mg, 1.49 mmol) in benzene (150 mL) was treated with catalytic amount of TsOH, and the mixture was refluxed at 100 °C using a Dean-Stark apparatus under Ar for 12 h. After aqueous work-up, only starting material **129p** was observed.

3a-Dimethylamino-3-propyl-3a,4,5,6,7,8,9,9b-octahydrocyclopenta[a]naphthalen-1-one (**154q**) and *1-Propyl-2,3,6,7,8,9-octahydrocyclopenta[a]naphthalen-1-one* (**155q**): A mixture of diketone **129q** (368 mg, 1.26 mmol), catalytic amount of TsOH and benzene (150 mL) was refluxed at 100 °C using a Dean-Stark apparatus under Ar for 24 h. After cooling to the ambient temperature, a sat. solution of potassium carbonate (50 mL) was added to the solution, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic phase was dried over $MgSO_4$, and the solvent of the filtrate was removed under reduce pressure. The residue was subjected to chromatography on silica gel (50 g). Elution with eluting with pentane/Et_2O (from 5 : 1 to 0 : 1) gave 147 mg (51%) of **155q** [R_f = 0.50 (pentane/Et_2O = 5 : 1)] and 127 mg (37%) of **154q** [R_f = 0.18 (pentane/Et_2O = 1 : 1)] as colorless oils.

154q: IR (film): ν = 2935 cm^{-1} (C–H), 1696, 1621 (C=C), 1477, 1266, 1023, 737. 1324. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.40–1.85 (m, 12 H) and 2.06–2.45 (m, 4 H) [total 16 H, $CH_2CH_2CH_3$, 4,5,6,7,8,9-H), 2.11 [s, 6 H, $N(CH_3)_2$], 2.64 (br. s, 1 H, 9b-H), 5.96 (t, ^4J = 1.5 Hz, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, $CH_2CH_2CH_3$), 20.1, 22.6, 22.8, 27.0, 28.5, 28.8, 30.0, 30.6 (–, $CH_2CH_2CH_3$, C-4,5,6,7,8, 9), 39.5 [+, $N(CH_3)_2$], 49.5 (+, C-9b), 71.8 (C_{quat}, C-3a), 125.7, 132.0 (C_{quat}, C-5a,9a), 130.5 (+, C-2), 181.6 (C_{quat}, C-3), 204.7 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 273 (34) [M^+], 244 (100) [$M^+ - C_2H_5$]. – Elemental analysis calcd (%) for $C_{18}H_{27}NO$ (273.4): C 79.07, H 9.95; found: C 79.22, H 9.76.

155q: – IR (film): ν = 2930 cm^{-1} (C–H), 1700 (C=O), 1684 (C=C), 1103, 831, 813. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.33–1.45 (m, 3 H) and 1.76–1.89 (m, 5 H) [total 8 H, $CH_2CH_2CH_3$, 7,8-H], 2.11 [s, 6 H, $N(CH_3)_2$], 2.31 (dd, ^2J = 18.7 Hz, ^3J = 3.2 Hz, 1 H, 2-H), 2.80 (dd, ^2J = 18.7 Hz, ^3J = 7.5 Hz, 1 H, 2-H), 2.75–2.81 (m, 2 H) and 3.16–3.24 (m, 2 H) [total 4 H, 6,9-H], 7.20 (d, ^3J = 7.8 Hz, 1 H, 4-H), 7.27 (d, ^3J = 7.8 Hz, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.1 (+, $CH_2CH_2CH_3$), 20.8, 22.4, 22.6, 25.8, 29.4, 38.6, 43.9 (–, $CH_2CH_2CH_3$, C-2,6,7,8,9), 37.0 (+,

C-3), 122.2, 135.4 (+, C-4,5), 133.7, 136.4, 137.6, 158.0 (C_{quat}, C-3a,5a,9a,9b), 207.6 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 228 (100) [M^+], 185 (51), 129 (9), 115 (6). – Elemental analysis calcd (%) for $C_{16}H_{20}O$ (228.3): C 84.16, H 8.83; found: C 84.32, H 8.55.

3-Methyl-2,3,6,7,8,9-hexahydrocyclopenta[a]naphthalen-1-one (**155r**): Variation A: A mixture of diketone **129r** (605 mg, 2.30 mmol), *p*-toluenesulfonic acid monohydrate (655 mg, 1.5 eq), benzene (150 mL) was refluxed at 100 °C using a Dean-Stark apparatus under Ar for 18 h. After cooling to the ambient temperature, a sat. solution of potassium carbonate (50 mL) was added to the solution, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic phase was dried over $MgSO_4$, and the solvent of the filtrate was removed under reduce pressure. According to the ^{1}H-NMR spectrum of the crude product, 30% of **129r** was converted to **155r**.

Variation B: Following GP8B, to a solution of **129r** (453 mg, 1.72 mmol) in dioxane (150 mL) was added a conc. solution of hydrochloric acid (5 mL), and the mixture was stirred at 60 °C under Ar for 36 h. After aqueous work-up, the residue was subjected to the chromatography on aluminum oxide (II, 30 g). Elution with pentane/Et_2O (from 5 : 1 to 3 : 1) gave 265 mg (77%) of **155r** [R_f = 0.53 (pentane/Et_2O = 3 : 1)] as a colorless oil.

Variation C: Following GP7, to a solution of complex **18k** (1.02 g. 2.10 mmol) in pyridine (40 mL) was added 1-propyne (**15h**), and the mixture was stirred at 80 °C for 3 d. After oxidation, filtration and evaporation of the solvent, the residue was directly dissolved dioxane (125 mL), treated with a 3 N solution of hydrochloric acid (10 mL), and stirred at 60 °C for another 36 h according to GP8B. Chromatography on aluminum oxide (II, 30 g) eluting with pentane/Et_2O (from 5 : 1 to 3 : 1) gave 223 mg (53%) of **155r**.

155r: IR (film): ν = 2928 cm^{-1} (C–H), 1700 (C=O), 1481, 1103, 821, 812. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34 (d, ^3J = 7.1 Hz, 3 H, CH_3), 1.74–1.83 (m, 4 H, 7,8-H), 2.22 (ABM, dd, ^2J = 18.7, ^3J = 3.4 Hz, 1 H, 2-H), 2.87 (ABM, dd, ^2J = 18.7, ^3J = 7.6 Hz, 1 H, 2-H), 2.76–2.81 (m, 2 H) and 3.15–3.21 (m, 2 H) [total 4 H, 6,9-H], 3.26–3.35 (m, 1 H, 3-H). 7.09 (d, ^3J = 7.9 Hz, 1 H, 4-H), 7.26 (d, ^3J = 7.9 Hz, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 21.4 (+, CH_3), 22.3, 22.5, 25.7, 29.3, (–, C-6,7,8,9), 31.7 (+, C-3), 46.1 (–, C-2), 121.8, 135.5 (+, C-4,5), 133.3, 136.2, 137.4, 158.8 (C_{quat}, C-3a,5a,9a,9b), 207.3 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 200 (100) [M^+], 185 (42) [$M^+ - CH_3$], 157 (16), 129 (21), 115 (20), 41 (16).

3a-Dimethylamino-2,3-dimethyl-3a,4,5,6,7,8,9,9b-octahydrocyclopenta[a]naphthalen-1-one (**154s**) and *(trans)-2,3-Dimethyl-2,3,6,7,8,9-octahydrocyclopenta[a]naphthalen-1-one* (**155s**): Variation A: A mixture of diketone **129s** (353 mg, 1.27 mmol), catalytic amount of TsOH and benzene (150 mL) was refluxed at 100 °C using a Dean-Stark apparatus under Ar for 2 d. After cooling to the ambient temperature, a sat. solution of potassium carbonate (50 mL) was added to the solution, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic phase was dried over $MgSO_4$, and the solvent of the filtrate was removed under reduce pressure. The residue was subjected to chromatography on aluminum oxide (II, 50 g). Elution with eluting with pentane/Et_2O (from 5 : 1 to 2 : 1) gave 4.00 mg (1%) of **154s** [R_f = 0.71 (pentane/Et_2O = 3 : 1)], 71 mg (22%) of **155s** [R_f = 0.22 (pentane/Et_2O = 3 : 1)] as colorless oils, and 219 mg (62%) of the starting material **129s** was recovered.

Variation B: Following GP8B, to a solution of diketone **129s** (525 mg, 1.93 mmol) was added a conc. solution of hydrochloric acid (10 mL), and the mixture was stirred at 60 °C under Ar for 36 h. After aqueous work-up, the residue was subjected to the chromatography on aluminum oxide (II, 50 g). Elution with pentane/Et_2O (from 5 : 1 to 2 : 1) gave 60.0 mg (15%) of **155s** and 350 mg (70%) of **154s**.

154s: IR (film): ν = 2931 cm^{-1} (C–H), 1699 (C=O), 1657 (C=C), 1445, 1380, 1316, 1041, 736. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.83–1.93 (m, 11 H, 4,5,6,7,8,9), 1.40–1.85 (m, 11 H) and 2.18–2.38 (m, 1 H) [total 12 H, 4,5,6,7,8,9-H), 1.53, 1.77 (s, total 6 H, CH_3), 1.92 [s, 6 H, $N(CH_3)_2$], 2.45 (br. s, 1 H, 9b-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.7, 12.0 (+, CH_3), 22.4, 22.6, 26.8, 28.3, 28.4, 30.3 (–, C-4,5,6,7,8,9), 39.2 [+, $N(CH_3)_2$], 48.0 (+, C-9b), 69.9 (C_{quat}, C-3a), 125.8, 131.5, 138.0 (C_{quat}, C-3,5a,9a), 168.3 (C_{quat}, C-3), 204.2 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 259 (44) [M^+], 244 (16) [$M^+ – CH_3$], 214 (100), 199 (48), 185 (22), 91 (13), 46 (25). – HRMS (EI) calcd for $C_{17}H_{25}NO$: 259.1936 (correct HRMS).

155s: IR (film): ν = 2928 cm^{-1} (C–H), 1701 (C=O), 1581 (C=C), 1480, 1226, 936, 841. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.28 (d, ^3J = 7.2 Hz, 3 H, CH_3), 1.40 (d, ^3J = 6.9 Hz, 3 H, CH_3), 1.72–1.84 (m, 4 H, 7,8-H), 2.17 (dq, ^3J = 7.2, ^3J = 4.6 Hz, 1 H, 3-H), 2.72–2.87 (m, 3 H) and 3.07–3.28 (m, 2 H) [total 5 H, 2,7,8-H], 7.20 (d, ^3J = 7.9 Hz, 1 H, 4-H), 7.29 (d, ^3J = 7.9 Hz, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.2, 19.1 (+, CH_3), 22.3, 22.4, 25.6, 29.2 (–, C-6,7,8,9), 40.6, 51.7 (+, C-2,3), 121.2, 135.3 (+, C-4,5), 132.7,

136.3, 137.4, 156.3 (C_{quat}, C-3a,5a,9a, 9b), 209.3 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 214 (100) [M^+], 199 (64), 181 (13), 171 (12), 143 (14), 129 (21), 115 (19), 91 (10).

2,3-Diphenyl-3a,6,7,8,9,9b-hexahydrocyclopenta[a]naphthalen-1-one (**160**), *2,3-Diphenyl-6,7,8,9-tetra-hydrocyclopenta[a]naphthalen-1-one* (**162**) and *trans-9a-Hydroxy-2,3-diphenyl-6,7,8,9,9a,9b-hexahydrocyclopenta[a]naphthalen-1-one* (**161**) and: Following GP8A, to a solution of **130o** (910 mg, 1.92 mmol) in dioxane (200 mL) was added a conc. solution of hydrochloric acid (10 mL), and the mixture was stirred for 2 d. After aqueous work-up, only ketone **129o** was observed. Then, **129o** was diluted with dry methanol (100 mL), treated with a 30% solution of sodium methylate in methanol (2 mL), and this reaction mixture was stirred at 40 °C under Ar for 4 h. After cooling to the ambient temperature, a 3 N solution of hydrochloric acid (10 mL) was added to the solution, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic phase was dried over $MgSO_4$, and the solvent of the filtrate was removed under reduce pressure. The residue was subjected to chromatography on silica gel (50 g). Elution with eluting with pentane/Et_2O (from 10 : 1 to 0 : 1) gave 95.0 mg (15%) of **162** [R_f = 0.74 (pentane/Et_2O = 10 : 1)] as an orange solid (m. p. 174–175 °C), 358 mg (57%) of **160** [R_f = 0.52 (pentane/Et_2O = 10 : 1)] as a colorless oil and 106 mg (16%) of **161** [R_f = 0.35 (Et_2O)] as a white solid (m. p. 178–179 °C).

160: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.84–1.94 (m, 4 H, 7,8-H), 2.83–2.94 (m, 2 H) and 3.35–4.02 (m, 2 H) [total 4 H, 6,9-H], 3.83 (d, ^3J = 5.7 Hz, 1 H, 3a-H), 4.59 (d, ^3J = 5.7 Hz, 1 H, 9b-H), 7.03 (d, ^3J = 7.3 Hz, 1 H, 5-H), 7.10–7.23 (m, 4 H) and 7.25–7.42 (m, 7 H) [total 11 H, 5-H, Ph-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.3, 22.4, 25.7, 29.3 (–, C-6,7,8,9), 53.7, 64.9 (+, C-3a,9b), 123.2, 126.80, 126.81, 127.7, 128.2, 128.55, 128.63, 136.1 (+, C-Ph, C-4,5), 133.0, 137.2, 137.8, 138.9, 142.9, 154.9 (C_{quat}, C-Ph, C-5a, 9a), 205.8 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 338 (100) [M^+], 247 (15). – HRMS (EI) calcd for $C_{25}H_{22}O$: 338.1617 (correct HRMS).

161: IR (KBr): ν = 2933 cm^{-1} (C–H), 1695 (C=O), 1653 (C=C), 1599, 697. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.78–1.84 (m, 4 H, 7,8-H), 2.76–2.83 (m, 2 H) and 3.17–3.24 (m, 2 H) [total 4 H, 6,9-H], 6.89 (d, ^3J = 7.5 Hz, 1 H, 4-H), 7.05 (d, ^3J = 7.5 Hz, 1 H, 5-H), 7.25 (br. s, 5 H, Ph-H), 7.34–7.42 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.4, 22.8, 25.4, 29.8 (–, C-6,7,8,9), 118.9, 127.3, 127.9, 128.5, 128.6, 128.9, 130.0, 132.9 (+, C-4,5, C-Ph), 126.4, 131.1, 131.5, 133.0, 138.1, 139.9, 143.3, 156.3 (C_{quat}, C-3a,5a,9a,

9b), 197.9 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 336 (100) [M^+], 321 (10). – Elemental analysis calcd (%) for $C_{25}H_{20}O$ (336.4): C 89.25, H 5.99; found: C 89.55, H 6.21.

162: IR (KBr): ν = 3414 cm^{-1} (O–H), 2936 (C–H), 1704 (C=O), 1507, 699. – ^1H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY and NOESY): δ = 1.80–2.00 (m, 4 H, 7,8-H), 2.82–2.94 (m, 2 H, 6-H), 3.22 [ABM, "dt" (ddd), ^2J = 16.8, ^3J = 6.0, ^3J = 6.0 Hz, 1 H, 9-H], 3.24 (s, 1 H, OH), 3.41 [ABM, "dt"(ddd), ^2J = 16.8, ^3J = 6.0, ^3J = 6.0 Hz, 1 H, 9-H], 4.76 (s, 1 H, 9b-H), 6.78–7.05 (m, 11 H) and 7.33 (d, ^3J = 7.5 Hz, 1 H)[total 12 H, Ph-H, 4,5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.3, 22.5, 26.1, 29.4 (–, C-6,7,8,9), 58.5 (+, C-9b), 86.4 (C_{quat}, C-9a), 123.7, 126.4, 126.6, 127.2, 127.4, 127.6, 129.6, 136.7 (+, C-4,5, C-Ph), 133.0, 137.7, 137.9 × 2, 141.2, 152.1 (C_{quat}, C-3a,5a,9a, 9b), 207.7 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 354 (86) [M^+], 336 (10) [$M^+ – H_2O$], 263 (12), 249 (100), 232 (16), 207 (10), 105 (22). – Elemental analysis calcd (%) for $C_{25}H_{22}O_2$ (354.4): C 84.72, H 6.26; found: C 84.93, H 6.07.

5-Dimethylamino-5-[3'-(1'',4''-dioxaspiro[4.5]dec-6''-yl)prop-1'-yl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (**130t**): According to GP7, to a solution of complex **18l** (2.51 g, 5.01 mmol) in pyridine (100 mL) was added 1.34 g (7.50 mmol) of 1,2-diphenylethyne (**15aa**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 80 g) eluting with pentane/Et_2O (from 20 : 1 to 1 : 1) gave 1.20 g (52%) of **130t** [R_f = 0.28 (pentane/Et_2O = 3 :1); d. r. = 1.4 : 1] as a pale-yellow semi-solid. – IR (film): ν = 2936 cm^{-1} (C–H), 1714, 1635 (C=C), 1445, 1349, 1089, 924, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.85–2.10 (m, 15 H, 1',2',3',6'',7'',8'',9'',10''-H), 1.35 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.38, 2.39 [s, 6 H, $N(CH_3)_2$], 3.70–4.05 (m, 4 H, 2'',3''-H, OCH_2CH_3), 5.04, 5.06 (s, 1 H, 4-H), 7.14–7.30 (m, 8 H, Ph-H), 7.42–7.48 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major diastereomer: δ = 14.2 (+, OCH_2CH_3), 20.8, 23.7 × 2, 28.2, 28.6, 34.4, 34.6 (–, C-1',2',3',7'', 8'',9'',10''), 39.9 [+, $N(CH_3)_2$], 44.3 (+, C-6''), 64.41, 64.5, 64.6 (–, OCH_2CH_3, C-2'',3''), 76.1 (C_{quat}, C-5), 97.2 (+, C-4), 110.6 (C_{quat}, C-5''), 126.4, 127.51, 127.6 × 2, 129.8 × 2 (+, Ph-C), 133.9, 135.7, 137.6 (C_{quat}, C-2, Ph-C), 146.2 (C_{quat}, C-1), 158.8 (C_{quat}, C-3). Minor diastereomer: δ = 14.2 (+, OCH_2CH_3), 20.3, 24.25, 24.26, 28.1, 28.3, 34.1, 34.6 (–, C-1',2',3', 7'',8'',9'',10''), 39.9 [+, $N(CH_3)_2$], 43.6 (+, C-6''), 64.36, 64.41, 64.6 (–,

OCH_2CH_3, C-2",3"), 76.0 (C_{quat}, C-5), 97.3 (+, C-4), 110.6 (C_{quat}, C-5"), 126.7, 127.54, 127.7 × 2, 129.3 × 2 (+, Ph-C), 134.0, 135.5, 137.5 (C_{quat}, C-2, Ph-C), 146.0 (C_{quat}, C-1), 158.7 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 487 (<1) [M^+], 458 (<1) [$M^+ – C_2H_5$], 226 (30), 183 (31), 155 (25), 99 (100), 84 (49), 59 (36), 45 (26). – HRMS (EI) calcd for $C_{32}H_{41}NO_3$: 487.3086 (correct HRMS).

4-Dimethylamino-5-[3'-(2"-oxo-1"-cyclohexanyl)prop-1'-yl]-3-ethoxy-1,2-diphenylcyclopent-2-enone (**129t**): Variation A: Following GP8A, to a solution of **130t** (550 mg, 1.13 mmol) in dioxane (200 mL) was added a *conc.* solution of hydrochloric acid (10 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (50 g). Elution with pentane/Et_2O/CH_2Cl_2 (from 2 : 1 : 1 to 0 : 1 : 1) gave 429 mg (92%) of **129t** [R_f = 0.17 (pentane/Et_2O = 1 :1); d. r. = 1 : 1] as a pale-yellow oil. – IR (film): ν = 2930 cm^{-1} (C–H), 1700 (C=O), 1488 (C=C), 1447, 1342, 1164, 752, 698. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.80–1.10 (m, 4 H), 1.40–2.30 (m, 4 H) [total 16 H, 5,1',2',3',1",3",4", 5",6"-H], 2.35 [s, 6 H, $N(CH_3)_2$], 2.75, 2.76 (AB, d, ^2J = 19.2 Hz, 1 H, 5-H), 7.10–7.22 (m, 8 H, Ph-H), 7.60–7.82 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 21.1, 21.7, 24.5, 24.7, 27.5, 27.7, 28.9, 29.2, 32.9, 33.8, 35.9, 36.0, 36.5, 36.6 41.6, 41.8 (–, C-5,1', 2',3',3",4", 5",6"), 39.3 [+, $N(CH_3)_2$], 49.5, 49.8 (+, C-6"), 69.4 (C_{quat}, C-4), 127.5, 127.72, 127.73 × 2, 127.9 × 2, 128.8, 128.9, 129.5 × 2, 129.7, 129.8 (+, Ph-C), 131.37, 131.40, 134.07, 134.11 141.6 × 2 (C_{quat}, C-2, Ph-C), 170.2 (C_{quat}, C-3), 204.9 (C_{quat}, C-1), 212.5, 216.6 (C_{quat}, C-2"). – MS (70 eV), *m/z* (%): 415 (2) [M^+], 276 (100), 55 (14), 41 (19).

Variation B: According to GP7, to a solution of complex **18k** (2.51 g, 5.01 mmol) in pyridine (100 mL) was added 1.34 g (7.50 mmol) of 1,2-diphenylethyne (**15aa**), and the mixture was stirred at 80 °C for 4 d. After oxidation, filtration and evaporation of the solvent, the residue was directly dissolved dioxane (125 mL), treated with a 3 N solution of hydrochloric acid (10 mL), and stirred for another 1 d according to GP8A. Chromatography on silica gel (50 g) eluting with Et_2O gave 1.08 g (52%) of **129t**.

6. Synthesis of Steroid-like Molecules

1-(1'-methyl-prop-3'-ynyl)-3,4-dihydronaphthalene (**170**): To a solution of 1-methyl-allenylmagnesium bromide [from magnesium turning (12.2 g, 500 mmol), 2-bromo-3-butyn (59.8 g, 450 mmol), $HgCl_2$ (1.50 g),and 300 mL Et_2O] was added dropwise α-tetralone 43.9 g, 300 mmol) at 15 °C over a period of 15 min. The mixture was stirred at the ambient temperature for 12 h and then, this reaction was quenched with a sat. solution of ammonium chloride (50 mL). The aqueous phase was extracted with Et_2O (3 × 100 mL). The combined organic extract was dried over $MgSO_4$. After filtration and evaporation of the solvent, the remaining liquid was diluted with benzene (100 mL), treated with catalytic amount of TsOH, and the reaction mixture was refluxed at 100 °C using a using a Dean-Stark apparatus for 12 h. The solution was washed water (3 × 25 mL), dried over $MgSO_4$, filtrated, and removed of the solvent under reduced pressure, before the residue was subjected to chromatography on silica gel (300 g). Elution with pentane/Et_2O (from 1 : 0 to 10 : 1) gave 17.3 (32%) of **170** [R_f = 0.34 (pentane)] as a pale-yellow oil. – IR (film): ν = 3293 cm^{-1} (C–H), 2935, 1700, 1487, 1456, 767, 738. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.47 (d, ^3J = 7.0 Hz, 3 H, CH_3), 2.27 (d, ^4J = 2.5 Hz, 1 H, 3'-H), 2.27–2.36 (m, 2 H, 3-H), 2.76 (t, ^3J = 7.8 Hz, 2 H, 4-H), 3.75 –3.82 (m, 1 H, 1'-H), 6.32 (td, ^3J = 4.6, ^4J = 1.1 Hz, 1 H, 2-H), 7.15–7.27 (m, 3 H), 7.36 (d, ^3J = 7.3 Hz, 1 H) [total 4 H, Ar-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 21.3 (+, CH_3), 23.0, 28.2 (–, C-3,4), 27.8 (+, C-1'), 70.3 (+, C-3'), 87.1 (C_{quat}, C-2'), 122.4, 125.0, 126.2, 126.8, 127.7 (+, C-2, Ar-C), 133.3, 136.8, 136.9 (C_{quat}, Ar-C). – MS (70 eV), *m*/*z* (%): 182 (81) [M^+], 167 (49) [$M^+ – CH_3$], 165 (40), 152 (23), 129 (100) [$M^+ – C_4H_5$],

Pentacarbonyl[(2E)-4-(3',4'-dihydronaphthalen-1'-yl)-3-morpholino-1-ethoxy-2-penten-1-ylidene]chromium (**169**): According to GP6, alkyne **170** (1.92 g, 10.5 mmol) in THF (50 mL) was treated with *n*-butyllithium (6.40 mL, 1.56 M in *n*-hexane, 10.0 mmol), hexacarbonyl-chromium (2.42 g, 11.0 mmol), Et_3OBF_4 (2.09 g, 10.5 mmol). Then, to the reaction mixture was added morpholine (1.04 ml, 12.0 mmol) at –78 °C. Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 10 : 1 to 3 : 1) gave 4.35 g (84%) of **169** [R_f = 0.46 (pentane/Et_2O 3 : 1)] as a yellow solid, which was rashdecomposed to a purple oil. Therefore, there were no spectroscopic data available, and this compound was directly used for the cocyclization with alkynes.

3a-Ethoxy-1-methyl-3a,3b,4,5-tetrahydro-3H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalen-2-one (**173**): Following GP7, to a solution of 670 mg (1.30 mmol) of complex **18r** in 40 mL of THF was added 0.48 mL (3.90 mmol) of 2,2-dimethyl-3-butyne (**15n**), and the mixture was stirred at 60 °C for 18 h. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/ Et_2O (from 1 : 0 to 3 : 1) gave 220 mg (67%) of **173** [R_f = 0.50 (pentane/Et_2O = 3 : 1)] as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.00–1.04 (m, 1 H, 3b-H), 1.03 (d, ^3J = 6.9 Hz, 3 H, CH_3), 1.91–2.03 (m, 1 H), 2.15–2.25 (m, 1 H), 2.66–2.77 (m, 1 H) and 2.87–3.02 (m, 1 H) [total 4 H, 4,5-H], 2.64 (AB, d, ^2J = 18.0 Hz, 3-H), 3.16 (AB, d, ^2J = 18.0 Hz, 3-H), 3.24 (q, ^3J = 6.9 Hz, 1-H), 2.66–2.77 (m, 2 H, OCH_2CH_3), 7.14–7.27 (m, 3 H, Ar-H), 7.42 (d, ^3J = 7.5 Hz, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 9.8 (+, C-3b), 15.2 (+, OCH_2CH_3), 18.1 (–, C-4), 28.3 (–, C-5), 28.4 (+, CH_3), 35.4 (C_{quat}, C-9b), 44.0 (–, C-3), 48.5 (+, C-1), 63.6 (–, OCH_2CH_3), 70.8 (C_{quat}, C-3a), 125.4, 125.91, 125.93, 128.6 (+, C-2, Ar-C), 131.8 (C_{quat}, Ar-C), 213.6 (C_{quat}, C-2). – MS (70 eV), *m*/*z* (%): 256 (100) [M^+], 227 (18) [$M^+ – C_2H_5$], 210 (22), 200 (42), 183 (52), 157 (58), 129 (24), 115 (13).43 (11).

1-(1'-tert-Butyldimethylsiloxy-but-3'-ynyl)-1,2,3,4-tetrahydronaphthalene (**181**): To a solution of allenylmagnesium bromide [from magnesium turning (5.62 g, 226 mmol), $HgCl_2$ (0.50 g), 24.0 g (161 mmol) of propagyl bromide (80% in toluene) and 200 ml Et_2O] was dropwise added 9.83 g (61.4 mmol) of 1,2,3,4-tetrahydronaphthalene-1-carbaldehyde (**182**) at 5 °C in an ice-salt bath. The mixture was stirred at this temperature for 30 min and at room temperature for 2 h. Then, the solution was treated with a sat. solution of ammonium chloride (100 ml), and the aqueous phase was extracted with Et_2O (3 × 100 mL). The combined organic extract was washed with a sat. solution of brine (50 ml), and dried over $MgSO_4$. After evaporation of the solvent, the unpolar component of the residue was separated by chromatography on silica gel [50 g, elution with pentane/Et_2O (10 : 1)].

The oil was dissolved in DMF (200 ml), treated with DMSO (5 ml), a solution of *tert*-butyldimethylsilyl chloride (18.5 g, 50% in toluene, 61.4 mmol) and imidazole (6.37 g, 94.0 mmol), and the mixture was stirred at room temperature for 1 d. Then, to the solution was added H_2O (100 ml), and the aqueous phase was extracted with Et_2O (3 × 100 ml). The combined organic extracted was washed with a sat. solution of brine (50 ml), and dried with

$MgSO_4$. Chromatography on silica gel (100 g) eluting with pentane/Et_2O (10 : 1) gave 15.2 g (79%) of **181** [R_f = 0.41 (minor product) and R_f = 0.27 (major product); d. r. = 2.4 : 1] as a colorless oil. – IR (film): ν = 3311 cm^{-1} (C–H), 2929, 2967, 1653 (C=C), 1471, 1091, 933, 837, 776. – ^1H NMR (250 MHz, $CDCl_3$): Major diastereomer: δ = 0.02 (s, 3 H, $SiCH_3$), 0.15 (s, 3 H, $SiCH_3$), 0.97 [s, 9 H, $SiC(CH_3)_3$], 1.58–2.48 (m, 7 H, 2,3,4, 4'-H), 2.76 (t, ^3J = 6.3 Hz, 2 H, 2'-H), 3.11–3.19 (m, 1 H, 1-H), 4.28–4.35 (m, 1 H, 1-H), 7.11–7.33 (m, 4 H, Ph-H). Minor diastereomer: δ = –0.40 (s, 3 H, $SiCH_3$), –0.00 (s, 3 H, $SiCH_3$), 0.78 [s, 9 H, $SiC(CH_3)_3$], 1.58–2.48 (m, 7 H, 2,3,4,4'-H), 2.74 (t, ^3J = 6.3 Hz, 2 H, 2'-H), 3.11–3.19 (m, 1 H, 1-H), 4.28–4.35 (m, 1 H, 1-H), 7.11–7.33 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major diastereomer: δ = –5.0, –4.6 (+, $SiCH_3$), 18.1 [C_{quat}, $SiC(CH_3)_3$], 21.3, 23.1, 23.5 (–, C-2,3,4), 25.9 [+, $SiC(CH_3)_3$], 29.9 (–, C-2'), 43.3 (+, C-1), 69.4 (+, C-4'), 74.5 (+, C-1'), 82.9 (C_{quat}, C-4'), 125.6, 125.8, 129.0, 129.1 (+, Ar-C), 136.9, 138.0 (C_{quat}, Ar-C). Minor diastereomer: δ = –5.5, –4.9 (+, $SiCH_3$), 17.8 [C_{quat}, $SiC(CH_3)_3$], 21.5, 22.3, 25.3 (–, C-2,3,4), 25.6 [+, $SiC(CH_3)_3$], 30.1 (–, C-2'), 41.2 [+, C-1], 70.3 (+, C-4'), 75.6 (+, C-1), 81.8 (C_{quat}, C-4'), 125.5, 125.6, 128.6, 128.9 (+, Ar-C), 139.1, 139.3 (C_{quat}, Ar-C). – DCI MS (70 eV), *m/z* (%): 332 (100) [$M^+ + NH_4$], 315 (24) [$M^+ + H$].

Pentacarbonyl[(2E)-5-(tert-butyldimethylsiloxy)-3-dimethylamino-5-(3',4'-dihydronaphthal-en-1'-yl)-1-ethoxy-2-penten-1-ylidene]chromium (**180**): According to GP6, alkyne **181** (5.19 g, 16.5 mmol) in THF (80 mL) was treated with *n*-butyllithium (10.6 mL, 1.56 M in *n*-hexane, 16.5 mmol), hexacarbonylchromium (3.74 g, 17.0 mmol), Et_3OBF_4 (3.58 g, 18.8 mmol), and then, gaseous dimethylamine. Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 20 : 1 to 5 : 1) gave 8.92 g (89%) of **180** [R_f = 0.60 (pentane/Et_2O = 3 : 1); d. r. = 1.2 : 1] as a yellow solid, m. p. 95–96 °C (dec.). – IR (KBr): ν = 2929 cm^{-1} (C–H), 2044 (C=O), 1970 (C=O), 1885 (C=O), 1532, 1279, 1097, 672. – ^1H NMR (250 MHz, $CDCl_3$): δ = –0.08, –0.28, 0.05, 0.15 [s, total 6 H, $Si(CH_3)$], 0.79, 0.92 [s, 9 H, $SiC(CH_3)_3$], 0.95, 1.48 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.64–2.02 (m, 4 H), and 2.60–3.35 (m, 5 H) [total 9 H, 4,1',2',3',4'-H), 3.18 [s, 6 H, $N(CH_3)_2$], 4.25–4.70 (m, 2 H, OCH_2CH_3), 4.80–4.90 (m, 1 H, 5-H), 6.25, 6.41 (s, 1 H, 2-H), 7.07–7.28, 7.48–7.51 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –5.3, –5.2, –4.7, –4.6 [+, $Si(CH_3)_3$], 15.7, 16.3 (+, OCH_2CH_3), 18.86, 17.92 [C_{quat}, $SiC(CH_3)_3$], 22.0 × 2, 22.2, 22.5, 30.3, 30.5, 33.3, 36.3 (–,

4,2',3',4'), 25.7 [+, SiC(CH_3)$_3$], 41.6, 41.8, 42.6, 42.9 [+, br., N(CH_3)$_2$], 44.0, 44.5 (+, C-1'), 73.6, 73.3 (–, OCH_2CH_3), 77.3, 77.6 (–, C-5), 118.1, 118.2 (+, C-2), 125.7, 126.0, 126.1, 126.2, 128.2, 128.7, 129.3, 129.4 (+, C-Ar), 135.9, 136.9, 138.5, 139.1 (C_{quat}, C-Ar), 158.4, 159.6 (C_{quat}, C-3), 219.5, 219.6, 224.5, 224.6 (C_{quat}, CO), 284.2 (C_{quat}, C-1). – MS (DCI), *m/z* (%): 625 (2) [$M^+ + NH_3$], 614 (27), 608 (100) [$M^+ + H$], 311 580 (78), 569 (40), 514 (14), 423 (68), 416 (48), 360 (14), 284 (30), 240 (20228 (14), 181 (54), 164 (24), 158 (16). – Elemental analysis calcd (%) for $C_{30}H_{41}CrNO_7Si$ (607.2): C 59.34, H 6.81; found: C 59.19, H 7.06.

(9R,10R)-1-Allyl-10-methyl-2-decalon (**189**) and *1,3-Diallyl-10-methyl-trans-2-decalon* (**190**): Dry liquid ammonia (400 mL) at –78 °C was treated with 1.57 g (226 mmol) of lithium over 10 min. To the above deep blue solution was added a solution of 16.4 g (100 mmol) of (*R*)-(–)-10-methyl-1(9)-octal-2-one (**188**) in *tert*-butanol (5.83 g, 80.0 mmol) and dry Et_2O (150 ml) over a period of 20 min. The mixture was allowed to stir for another 45 min at this temperature, and then treated with allyl bromide (43.0 ml, 500 mmol) and dry DMSO (100 ml). A positive Ar stream was passed through the flask, and the dry ice bath and condenser were removed. The colorless solution was stirred overnight (ca. 12 h), and then, diluted with a sat. solution of ammonium chloride (150 ml). The aqueous phase was extracted with Et_2O (5 × 200 ml). The combined organic extracted was washed with water (3× 50 ml), dried over magnesium sulfate and concentrated to afford a yellow oil. Chromatography on silica gel (550 g) eluting with pentane/Et_2O (from 10 : 1 to 5 : 1) gave 4.59 g (19%) of **190** [R_f = 0.69 (pentane/Et_2O 15 : 1)] and 14.4 g (70%) of **188** [R_f = 0.39 (pentane/Et_2O 15 : 1)] as pale yellow oils, which were pure enough for the acetalization. Colorless samples for analytic purposes were prepared by the further Kugelrohr distillation.

189: IR (film): ν = 2925 cm^{-1} (C–H), 1709 (C=O), 1445, 1182, 999, 910. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.99 (s, 3 H, CH_3), 0.91–1.70 (11 H), 2.06–2.48 (5 H) [m, 16 H, 1,3,4,5,6, 7,8,9,3'-H), 4.82–4.95 (m, 2 H, 1'-H), 5.59–5.72 (m, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 16.0 (+, CH_3), 21.0, 25.2, 25.8, 29.3, 38.1, 40.7, 41.2 (–, C-3,4,5,6, 7,8,3'), 33.4 (C_{quat}, C-10), 47.7, 50.0 (+, C-1,9), 115.7 (–, C-1'), 136.3 (+, C-2'), 211.5 (C_{quat}, C-2). – MS (70 eV), *m/z* (%): 206 (49) [M^+], 165 (11), 149 (25), 109 (100), 96 (89), 81 (32), 67 (42), 55 (33), 41 (46). – HRMS (EI) calcd for $C_{14}H_{22}O$: 206.1671 (correct HRMS).

190: – IR (film): ν = 3075 cm^{-1} (C–H), 2925, 1706 (C=O), 1639 (C=C), 1437, 1382, 999, 910. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.94–2.56 (m, 17 H, 1,3,4,5,6,7,8,9,3', 3"-H), 1.07 (s, 3 H, CH_3), 4.87–5.03 (m, 4 H, 1',1"-H), 5.40–5.82 (m, 2 H, 2',3"-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 17.0 (+, CH_3), 21.0, 25.3, 25.9, 29.6, 33.9, 40.6, 48.7 (–, C-4, 5,6,7,8,3',3"), 33.6 (C_{quat}, C-10), 46.0, 49.6, 50.3 (+, C-1,3,9), 115.6, 115.9 (–, C-1',1"), 136.6, 136.8 (+, C-2',2"), 211.9 (C_{quat}, C-2). – MS (70 eV), *m/z* (%): 246 (28) [M^+], 231 (10) [$M^+ – CH_3$], 205 (20) [$M^+ – C_3H_5$], 149 (24), 109 (16), 95 (25), 81 (35), 67(51), 55 (46), 41 (100) [$C_3H_5^+$]. – Elemental analysis calcd (%) for $C_{17}H_{26}O$ (246.4): C 82.87, H 10.64; found: C 83.01, H 10.51.

(4a'R,8a'R)-1'-Allyl-4a-methyloctahydrospiro([1,3]dioxolane-2,2'-naphtalene) (**191**): A mixture of **189** (21.2 g, 103 mmol), ethylene glycol (15 mL, 269 mmol), TsOH (ca. 2 g) and benzene (300 mL) was stirred at 100 °C for 12 h using a Dean-Stark apparatus. After cooling to ambient temperature, the solution was treated with 100 mL of water, and extracted with Et_2O (5 × 100 mL). The combined organic extract was dried over $MgSO_4$, and the solvent of the filtrate was removed under reduced pressure. The residue was subjected to chromatography on silica gel (450 g). Elution with pentane/Et_2O (9 : 1) gave 22.4 g (87%) of **191** (R_f = 0.71) as pale yellow oils. Colorless samples for analytic purposes were prepared by the further Kugelrohr distillation. – IR (film): ν = 3073 cm^{-1} (C–H), 2923, 1706 (C=O), 1636 (C=C), 1437, 1183, 1156, 1105, 914. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.83 (s, 3 H, CH_3), 0.90–1.71 (m, 14 H, 1',3',4',5',6',7',8',8a'-H), 1.98–2.21 (m, 2 H, $CH_2CH=CH_2$), 3.82–3.95 (m, 4 H, 4,5-H), 4.78–4.91 (m, 2 H, $CH_2CH=CH_2$), 5.84 (ddd, ^3J = 17.0, ^3J = 10.2, ^3J = 9.4 Hz, 1 H, $CH_2CH=CH_2$). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 16.0 (+, CH_3), 21.0, 24.9, 26.6, 30.3, 30.7, 38.7, 41.3 (–, $CH_2CH=CH_2$, C-3',4',5',6',7',8'), 33.5 (C_{quat}, C-4a'), 43.8, 46.5 (+, C-1',8'a), 64.1, 64.3 (–, C-4,5), 111.6 (C_{quat}, C-2), 113.4 (–, $CH_2CH=CH_2$), 136.3 (+, $CH_2CH=CH_2$). – MS (70 eV), *m/z* (%): 250 (2) [M^+], 99 (100), 55 (10), 41 (15). – Elemental analysis calcd (%) for $C_{16}H_{26}O_2$ (250.4): C 76.75, H 10.47; found: C 76.56, H 10.27.

(4a'R,8a'R)-3-[4a'-methyl-octahydrospiro([1,3]dioxolane-2,2'-naphtalene)-1'-yl]propanol (**192**): To a solution of **191** (10.6 g, 42.3 mmol) in 30 ml THF at 0° C under Ar was

transferred a solution of borane-methylsulfide (11 mL, 2.00 M in THF, 22.0 mmol) in THF (100 mL) via a syringe pump over a period of 30 min. The solution was warmed to the ambient temperature, and stirred for another 90 min. The reaction flask was recooled to 0 °C, a 3 N solution of sodium hydroxide (15 ml) was added. Then, the mixture was treated with 10 ml of a 30% hydrogen peroxide solution, and stirred at the ambient temperature for an additional 1 h. The reaction was diluted with Et_2O (200 mL), washed with a sat. brine solution (2 × 50 mL), and died over $MgSO_4$. The solvent of the filtrate was removed under reduced pressure. The residue was subjected to chromatography on silica gel (200 g). Elution with pentane/Et_2O (from 1 : 1 to 0 : 1) gave 10.1 g (89%) of **192** [R_f = 0.50 (Et_2O)] as a colorless oil. – IR (film): ν = 3419 cm^{-1} (C–H), 2926, 1451, 1103, 1074, 918. – ^1H NMR (250 MHz, C_6D_6): δ = 0.79 (s, 3 H, CH_3), 0.80–1.82 (m, 18 H, 2,3,1',3',4',5',6',7',8',8a'-H), 2.49 (br. s, 1 H, OH), 3.44–3.63 (m, 6 H, OCH_2CH_2O, 1-H). – ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 16.2 (+, CH_3), 21.9, 22.7, 25.4, 27.3, 30.8, 32.9, 39.2, 41.8 (–, C-2,3,3',4',5', 6',7',8'), 33.9 (C_{quat}, C-4a'), 43.8, 47.8 (+, C-1',8'a), 62.7 (–, C-1), 64.1, 64.3 (–, OCH_2CH_2O), 112.2 (C_{quat}, C-2'). – MS (70 eV), *m/z* (%): 268 (10) [M^+], 99 (100). – HRMS (EI) calcd for $C_{16}H_{28}O_3$: 268.2038 (correct HRMS).

(4a'R,8a'R)-3-[4a'-Methyl-octahydrospiro([1,3]dioxolane-2,2'-naphtalene)-1'-yl]propion-aldehyde (**193**): To a solution of oxalic acid dichloride in dry CH_2Cl_2 (100 mL) at –78 °C under Ar was dropwise added a solution of DMSO (7.50 mL, 106 mmol) in dry CH_2Cl_2 (30 mL), and the mixture was stirred at this temperature for 30 min. A solution of **193** (9.83 g, 36.6 mmol) in dry CH_2Cl_2 (50 mL) was transferred to the mixture, and stirred for another 30 min. Then, the reaction was quenched with NEt_3 (30 mL), and the suspension was warmed to the ambient temperature. After dilution with water (100 mL), the aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extract was died over $MgSO_4$. The solvent of the filtrate was removed under reduced pressure. The residue was diluted in 300 ml of Et_2O, filtrated through Celite, and contracted. The remaining liquid was subjected to chromatography on silica gel (200 g). Elution with pentane/Et_2O (from 3 : 1 to 1 : 1) gave 8.64 g (89%) of **193** [R_f = 0.29 (pentane/Et_2O = 3 : 1)] as a colorless oil. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.79 (s, 3 H, CH_3), 0.82–1.73 (m, 16 H, 3,1',3',4',5',6',7',8',8a'-H), 2.26–2.56 (m, 2 H, 2-H), 3.78–3.96 (m, 4 H, OCH_2CH_2O), 9.63 (t, ^3J = 1.7 Hz, 1 H, 1-H). –

^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.9 (+, CH_3), 17.6, 21.2, 24.8, 26.6, 30.1, 38.5, 41.2, 43.2 (–, C-2,3,3',4',5', 6',7',8'), 33.4 (C_{quat}, C-4a'), 42.9, 46.1 (+, C-1',8'a), 63.9, 64.1 (–, O*C*H$_2$*C*H$_2$O), 111.6 (C_{quat}, C-2'), 203.0 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 266 (2) [M$^+$], 238 (13), 99 (100). – HRMS (EI) calcd for $C_{16}H_{26}O_3$: 266.1882 (correct HRMS).

(4a'R,8a'R)-1'-(2''-Betynyl)-4a'-methyl-3-octahydrospiro([1,3]dioxolane-2,2'-naphtalene) (**194**): To a suspension of triphenylbromomethylphosphsphonium bromide (65.0 g, 149 mmol) in dry THF (300 ml) at 0 °C was portionwise added potassium *tert*-butylate (17.0 g, 152 mmol) over a period of 10 min, and the mixture was stirred at the ambient temperature for 1 h. 18.9 g (71.1 mmol) of **193** was slowly added to this yellow suspension at 0 °C, and stirred at the ambient temperature for an additional 12 h. The reaction mixture was diluted with Et_2O (200 ml), washed with water (2 × 50 ml), and was dried over $MgSO_4$. The solvent of the filtrate was removed under reduced pressure, and the unpolar component of the residue was separated by chromatography on silica gel [200 g, elution with pentane/Et_2O (6 : 1)]. After evaporation of the solvent, the yellow oil was dissolved in dry THF (250 ml), treated with potassium *tert*-butylate (16.0 g, 143 mmol), and stirred under Ar at 60 °C for 1 h. Water (100 ml) was transferred to the solution at the ambient temperature, and the aqueous phase was extracted was extracted with Et_2O (3 × 100 ml). The combined organic extracted was washed with a sat. solution of brine (50 ml), and dried with over $MgSO_4$. The solvent of the filtrate was removed under reduced pressure. The remaining liquid was subjected to chromatography on silica gel (400 g). Elution with pentane/Et_2O (from 9 : 1 to 4 : 1) gave 13.21 g (71%) of **194** [R_f = 0.53 (pentane/Et_2O = 9 : 1)] as a colorless oil. – IR (film): ν = 2921 cm^{-1} (C–H), 1450, 1345, 1157, 1113, 1041, 920. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.76 (s, 3 H, CH_3), 0.86–1.70 (m, 15 H, 3,1',3',4',5',6',7',8',8a'-H), 1.61 (t, ^4J = 2.7 Hz, 3 H, 4'''-H), 1.85–1.96 (m, 1 H, 1'''-H), 2.08–2.18 (m, 1 H, 1'''-H), 3.74–3.86 (m, 4 H, OC*H*$_2$C*H*$_2$O). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 3.3 (+, C-4'''), 15.9 (+, CH_3), 15.3, 21.2, 24.9, 26.5, 30.6, 38.4, 41.1 (–, C-3',4',5',6',7',8',1'''), 33.3 (C_{quat}, C-4a'), 44.0, 46.5 (+, C-1',8a'), 64.2, 64.3 (–, C-4,5), 74.3, 78.9 (C_{quat}, C-2''',3'''), 110.7 (C_{quat}, C-2). – MS (70 eV), *m/z* (%): 262 (17) [M$^+$], 99 (100). – Elemental analysis calcd (%) for $C_{17}H_{26}O_2$ (262.4): C 77.82, H 9.99; found: C 78.13, H 9.69.

D. Conclusion

Under the recently developed optimized conditions, a wide range of β-Aminosubstituted α,β-unsaturated Fischer carbene complexes **18** are easily prepared in a four-step one-pot operation from terminal alkynes, hexacarbonylchromium, triethyloxonium tetrafluoroborate and secondary amines. Reaction of **18** with terminal and internal alkynes afford versatile adducts, from which complicated skeletons of natural product analogues and interesting molecules are accessible. Thus, Fischer carbene complexes have turned out to be useful building blocks for organic synthesis.

Tricyclic compounds **25** were prepared in 15–91% yields by the reaction of chromium complex **18g** or its tungsten analogues **18o** with alkynes. The highly regio- and diastereo-selective formation of **25** was accomplished by an intramolecular 6π-electro-cyclization of **18g** or **18o** and subsequent reduction elimination. The thus generated cyclopentadiene **64** would undergo 1,5-hydrogen shift to its more reactive isomer **65**. A subsequent Diels-Alder reaction of **65** with various alkynes affords cycloadducts **60**. Due to the through-space interaction between two olefin moieties in **60**, their hydrolyzed products **25** were, generally, isolated in most cases. In this procedure, the applied tungsten complex **18o** gave lower chemical yields, probably because of its high binding energy between tungsten and carbene carbon. Dienophiles with strong electron-withdrawing groups and minimal steric congestion are suitable as reaction partners for this cocyclization. The fluorenyl substituted tricyclic product **25w** exhibits strong bathochromic and high absorption intensities in the UV/Vis spectrum in comparison with its starting material **54d**. To understand the relationship between the structure and the unusual photo properties should be, potentially, useful for design LEDs. Biscycloaddition adducts **72** have been prepared under ambient conditions by modification of dienophiles.

Formation of cyclopenta[*b*]pyrans **22** and **76** was regarded as a formal [3+2+2+1] cycloaddition, incorporating a Fischer carbene complex **18**, two molecules of an alkyne, and a later inserted carbon monoxide. The optimized reaction conditions of synthesis of **22** and **76** were found to be with an eight-fold excess of alkyne in a 0.05 M solution of complex **18** in THF at 55 °C (16–99% yields). The tricyclic derivative of the type **78** could not be achieved from complex **18d**–**18f** and diynes **77**.

The formal [3+2] cycloadditions of complexes **18** with different alkynes, including diynes and enynes, performed in pyridine afforded highly substituted 5-dimethylamino-3-thoxy-cyclopentadienes **19** (sometimes also their regioisomers 81), generally in medium to good yields (36–78% yields). The product distribution between cyclopentadienes **19** and their regioisomer **81** depends upon the steric bulk of the substituents either in the complexes **18** (R^1) or in the applied alkynes (R_L), and in the former they have more influence than in the latter. However, electronic effects of applied alkynes does not play an important role. Cocyclizations of internal alkynes and carbene complexes **18** with larger substitutes R^1 did not only lead to an increased formation of the regioisomer **81**, but also to yield another isomeric cyclopentadiene **90**, which is formed from **19**. A control experiment of pure **19** in [D_5]-pyridine at 80 °C confirmed this hypothesis that the dimethylamino group shift is caused by a 1,2-migration via the bridged zwitterionic intermediate **91** in equilibrium between **19** and **81**, but the rate coefficient for the transformation of the former to the latter must be larger that that for the reverse reaction.

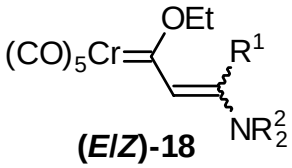
Although de Meijere protocol has highly chemoselectivity in the formation of cyclopentadienes **19**, the alkenyl-substituted complex **18i** underwent intramolecular [2+1] addition to afford bicyclic intermediate **97**, in which the strong electron-donating property of the dimethylamino functionality would enhance the ring opening of the three-membered ring and the removal of the silyloxy group. Further deprotonation and olefin isomerization yielded the cycloheptatriene **95b** as the major product. but this electron-rich compound could not be isolated.

Upon heating complexes **18** with conjugated dienynes **28** in pyridine at 80 °C, cycloaddition-cyclization-hydrolysis products **100** and their regioisomers **101** were isolated in 12–75% yields. However, the more flexible the alkenyl substitutes are in the dienynes **28**, the longer reaction times are needed to achieve good chemical yields. This new cascade reaction of Fischer carebene complexes provides a direct synthetic route to symmetric and asymmetric trindanone analogues under much milder condition than the traditional methods. Hence, synthesis of interesting molecules such as **119** by reaction of complex with dicyclobutenylethyne **118** appears to be possible.

Numerous compounds with [5-x-y] tricyclic skeletons (x = 5,6; y = 5,6,7) should were synthesized in 74–93% yields. Tricyclic molecules **127** were prepared in acidic conditions

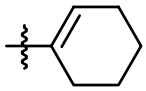
from protected (2'-oxo-cycloalknyl)methyl substituted cyclopentadienes **130**, which are cocyclization adducts of reaction of alkynes with corresponding complexes, namely **18i**, **18j** and **18m**. In spite of the four stereogenic centers, compounds **127** are not formed as a complicated mixture of diastereomers. Their structures were rigorously established as *cis,anti,cis* (**127-I**), *cis,syn,cis* (**127-II**) and *cis,anti,trans* (**127-III**). The *cis*-relationship between the dimethylamino functionality and the hydrogen in the vicinity of the ketone moiety apparently show in all three isomers. Generally, *cis,anti,cis* isomers (**127-I**) were obtained as major products. The ratios of three isomers strongly depend on the size of C ring. The intimidates **130** with the fused six-membered C ring give the thermodynamically more stable products **127-I** as dominating isomers with a proportion of about 75 : 20 :5. Cyclopentadienes **130** with *n*-propyl substituent at the R_L position did afford not only elimination products **135**, but also a new type of cyclization adducts **136**. Dehydration of **127-I** afforded the thermodynamically most stable products **145** along with the kinetic adducts **146**. The former became the only product when the starting material **127-I** contained a six-membered fused C ring. The triquinane **152a** was obtained from the diketone **150a** under basic conditions in low yield (6%). This unsatisfactory results can be explained by an unfavorable intramolecular aldol reaction due to the steric congestion environment and an unchangeable configuration at methyl-group substituted stereogenic center in **150a**. Aldol condensation of (2'-oxo-cycloalkanyl)ethyl substituted cyclopentenones **129** in presence of hydrochloric acid at 60 °C led to the cyclization products **154** and **155** in good to excellent yields (77–88%). Unfortunately, this procedure could not be applied to obtain the five-six-seven fused tricyclic molecule **163**.

Synthesis of the steroid-like molecules should be achievable by following methods: a) Formal [3+2] cycloaddition of complex **18** with bicyclic dienynes **120** and a sequential 6π-electrocyclization to afford **121** and **122** in a one-port operation. b) By intramolecular aldol condensation, the steroid-like molecules **183** could be prepared from (2'-oxo-decalenyl)butyl substituted cyclopentenones **184**, which are generated from cocyclization of complex **186** with various alkynes and subsequent hydrolysis. Other procedures did not produce the desired compounds. The tertacyclic product **173**, instead of the expected **167**, was isolated in 67% from attempted cocyclizations of complex **169** with alkynes. Apparently, complex **169** more rapidly undergoes the intramolecular [2+1] cycloaddition than the alkyne insertion. In the other example, the C ring in **178** could not be closed by treatment of the tricyclic molecule **176** by the acids.

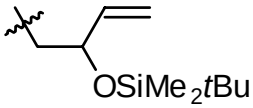


(*E*/*Z*)-18

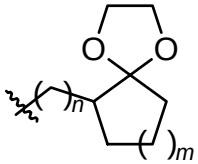
	a	**b**	**c**	**d**	**e**	**f**
R^1	*c*Pr	Me	*i*Pr	*t*Bu	$CMe_2(OSiMe_3)$	$CHMe(OSiMe_2tBu)$



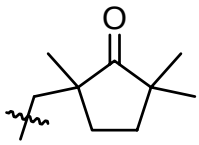
g



h



i (*m* = 1, *n* = 1)
j (*m* = 2, *n* = 1)
k (*m* = 2, *n* = 2)
l (*m* = 2, *n* = 3)
m (*m* = 3, *n* = 1)



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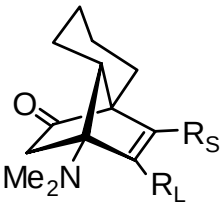

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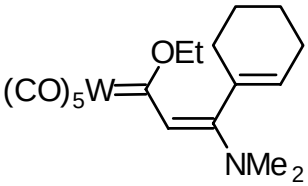
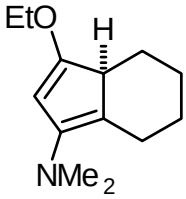
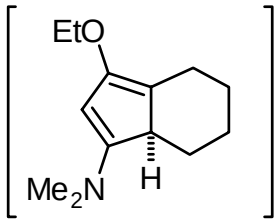


18o



64

R_L = aryl, alkynyl, alkenyl
R_S = aryl, H, *c*Pr



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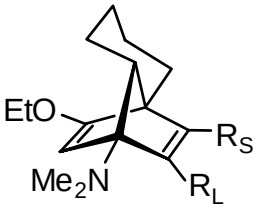

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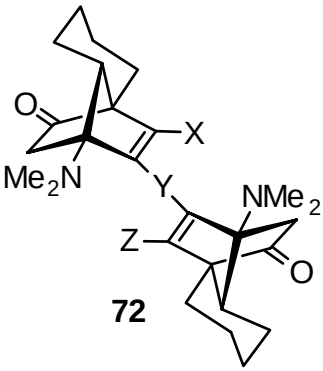

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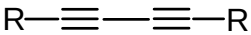
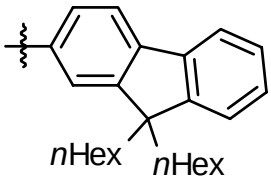
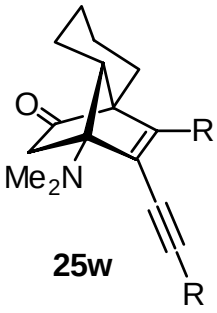


54d

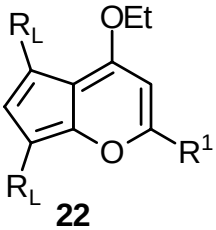
R:





25w

X, Z = H, alkynyl, Ph
Y = aryl, alkynyl



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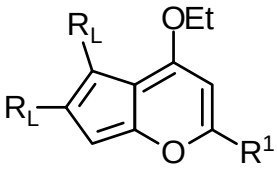

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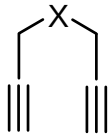

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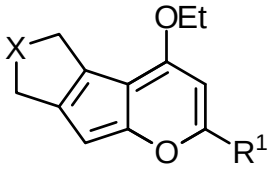
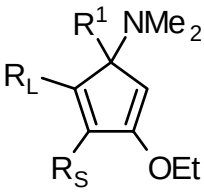


78

(X = NMe_2, O)



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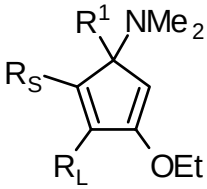

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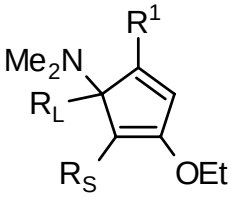

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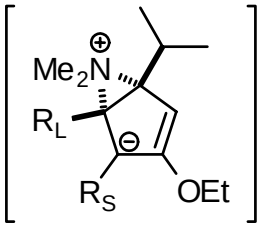
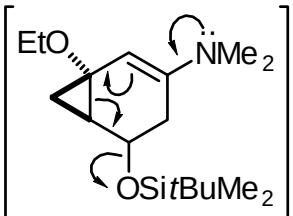


91

R_L = alkyl, aryl, cycloalkyl

R_S = alkyl, aryl, H, cycloalkyl



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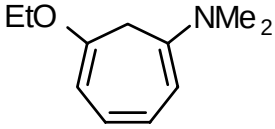
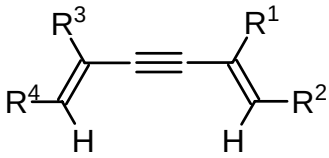
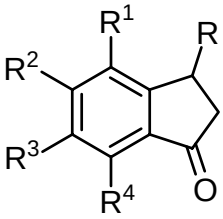


95b



28

R^2, R^3, R^4 = alkyl, cycloalkyl



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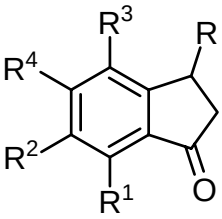

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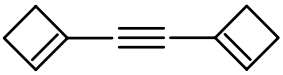

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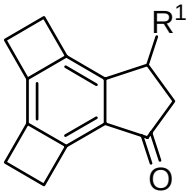

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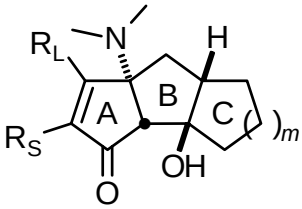
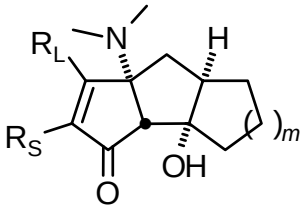
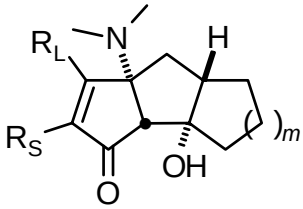


127-I



127-II

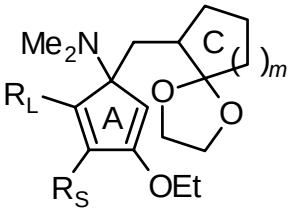


127-III

m = 1,2,3

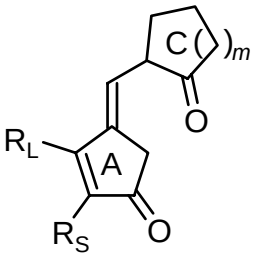
R_L = alkyl, aryl, $SiMe_3$

R_S = alkyl, H, Ph



130

m = 1,2,3



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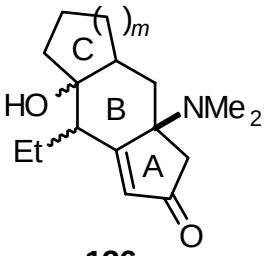

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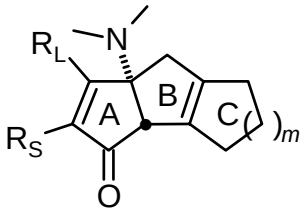

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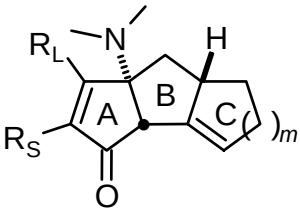

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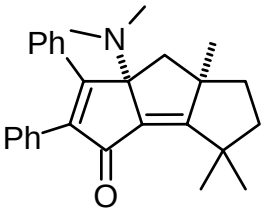

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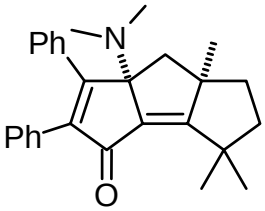
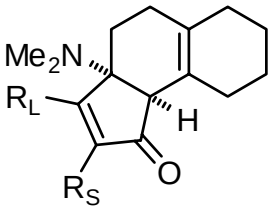


152a



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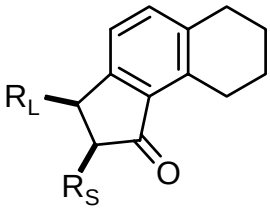

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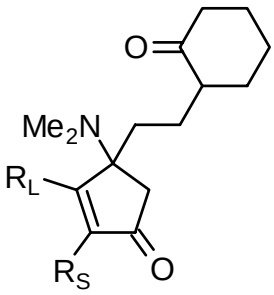
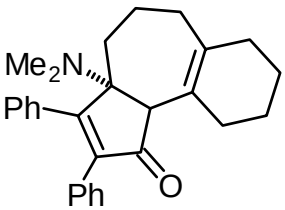


129

R_L = Me, *n*Pr, $SiMe_3$

R_S = H, Me



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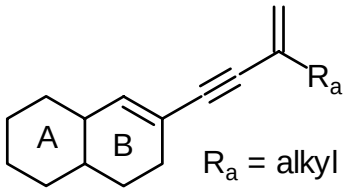
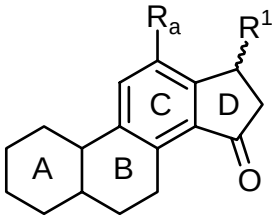


R_a = alkyl

120



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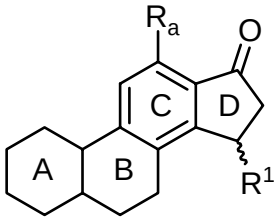

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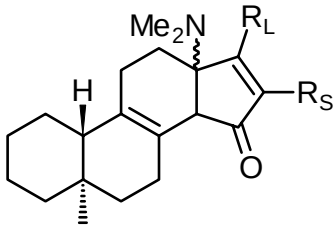

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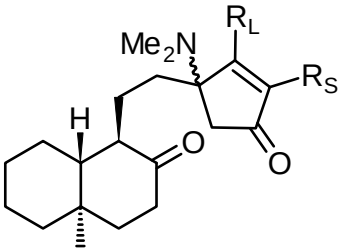

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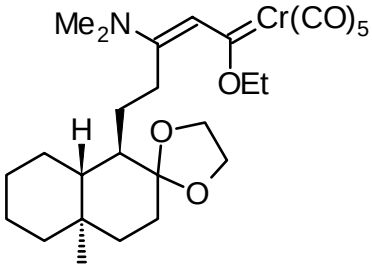

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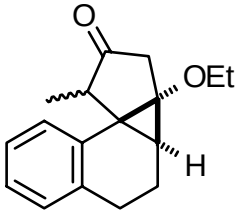

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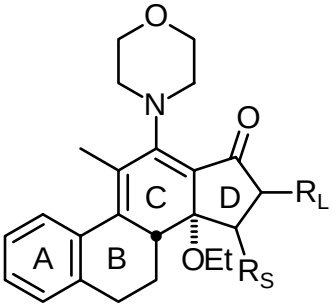

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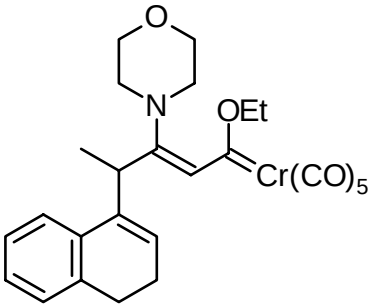

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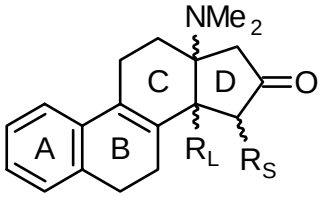

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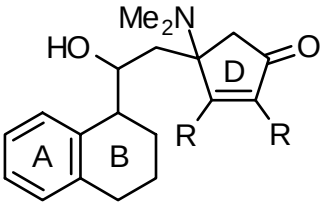

176

R = Me, Ph

E. Reference and Remarks

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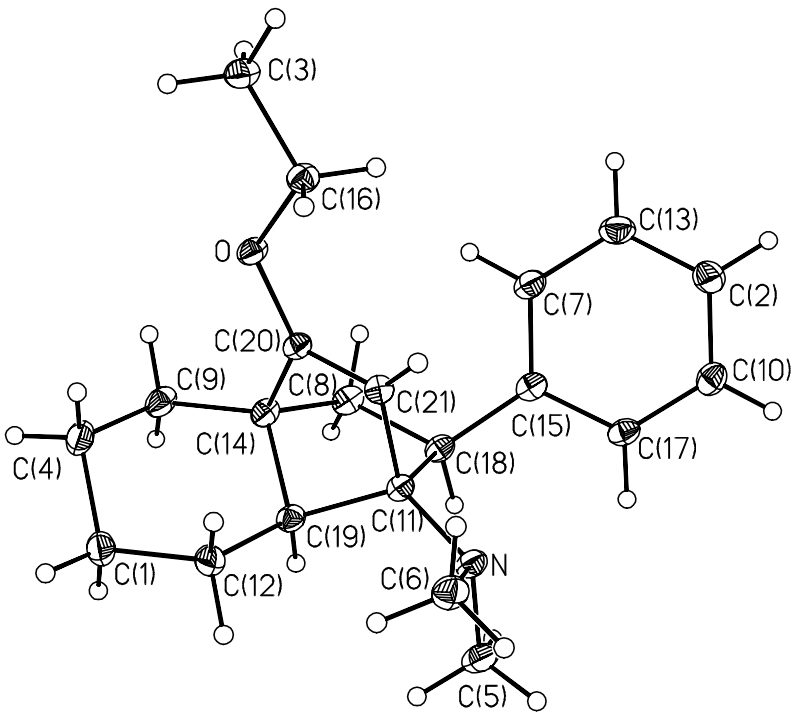
F. Crystal Data

1. 7-Dimethylamino-9-ethoxy-11-phenyltricyclo[5.2.2.0^{1,6}]undec-8-ene (**70a**).

2. (*3aS*,*3bS*,*6aR*,*7aR*)/(*3aR*,*3bR*,*6aS*,*7aS*)-7a-Dimethyamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,6a,7,7a-octahydrocyclo-penta[a]pentalen-3-one (**127a-II**).

3. (*3aS*,*3bR*,*7aS*,*8aR*)/(*3aR*,*3bS*,*7aR*,*8aS*)-8a-Dimethylamino-3b-hydroxy-1,2-diphenyl-3b,4,5,6, 7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one (**127f-I**).

1. 7-Dimethylamino-9-ethoxy-11-phenyltricyclo[5.2.2.0^{1,6}]undec-8-ene (**70a**).



Identification code	CP350
Empirical formula	$C_{21}H_{29}NO$
Formula weight	311.45
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, *P*1
Unit cell dimensions	a = 8.4438(8) Å alpha = 97.698(7)°.
	b = 9.9685(9) Å beta = 91.575(7)°.
	c = 11.8828(11) Å gamma = 115.012(7)°.
Volume	894.28(14) Å^3
Z, Calculated density	2, 1.157 mg/m^3
Absorption coefficient	0.070 mm^{-1}
F(000)	340
Theta range for data collection	1.74 to 24.72 deg.
Index ranges	-9<=h<=9, -11<=k<=11, -13<=l<=13
Reflections collected/unique	16770 / 3024 [R(int) = 0.0655]
Observed reflections	2703
Completeness to theta	24.72 99.3%

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3024 / 0 / 211
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0946
R indices (all data)	R1 = 0.0405, wR2 = 0.0969
Largest diff. peak and hole	0.280 and -0.160 $e.A^{-3}$

Table 1. Bond lengths

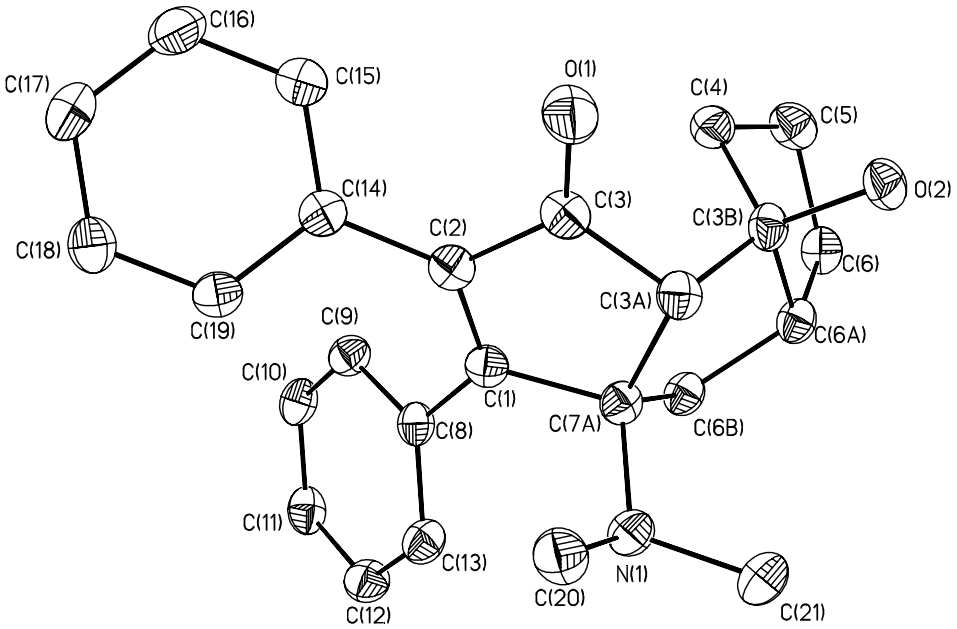
Bonding	Length [pm]	Bonding	Length [pm]	Bonding	Length [pm]
O(1)-C(9)	136.1(1)	C(2)-C(3)	153.0(2)	C(11)-C(12)	151.2(2)
O(1)-C(1")	144.2(1)	C(3)-C(4)	153.2(2)	C(12)-C(17)	139.6(2)
N(1)-C(2')	145.8(2)	C(4)-C(5)	153.5(2)	C(12)-C(13)	140.0(2)
N(1)-C(1')	146.5(2)	C(5)-C(6)	152.9(2)	C(13)-C(14)	138.8(2)
N(1)-C(7)	146.5(2)	C(6)-C(7)	155.8(2)	C(14)-C(15)	138.3(2)
C(1)-C(9)	151.5(2)	C(7)-C(8)	151.8(2)	C(15)-C(16)	138.9(2)
C(1)-C(2)	151.8(2)	C(7)-C(11)	160.3(2)	C(16)-C(17)	138.5(2)
C(1)-C(6)	154.3(2)	C(8)-C(9)	133.4(2)	C(1")-C(2")	150.4(2)
C(1)-C(10)	155.8(2)	C(10)-C(11)	155.8(2)		

Table 2. Bond angle

Bond angle	degree	Bond angle	degree
C(1)-C(6)-C(7)	94.01(9)	C(9)-O(1)-C(1")	113.98(9)
N(1)-C(7)-C(11)	112.76(9)	C(13)-C(12)-C(11)	119.61(11)
N(1)-C(7)-C(6)	121.12(10)	C(17)-C(16)-C(15)	120.46(12)
N(1)-C(7)-C(8)	115.12(10)	C(14)-C(13)-C(12)	121.73(12)
C(5)-C(6)-C(7)	119.60(10)	C(16)-C(17)-C(12)	121.30(12)
C(1')-N(1)-C(7)	114.34(9)	O(1)-C(1")-C(2")	108.46(10)
C(2')-N(1)-C(7)	114.24(10)	C(15)-C(14)-C(13)	119.98(12)
C(3)-C(4)-C(5)	111.81(11)	C(14)-C(15)-C(16)	119.31(12)
C(6)-C(5)-C(4)	110.63(11)	C(1)-C(2)-C(3)	110.74(11)
C(2)-C(3)-C(4)	111.42(11)	C(6)-C(1)-C(10)	100.28(9)
C(9)-C(1)-C(2)	117.42(10)	C(6)-C(7)-C(11)	99.41(9)
C(2)-C(1)-C(10)	117.27(11)	C(8)-C(7)-C(11)	104.88(9)

C(2)-C(1)-C(6)	114.53(10)	C(8)-C(7)-C(6)	101.22(9)
C(2')-N(1)-C(1')	109.10(10)	C(9)-C(1)-C(6)	100.17(9)
C(5)-C(6)-C(1)	112.18(10)	C(9)-C(1)-C(10)	104.48(10)
C(8)-C(9)-O(1)	131.65(11)	C(9)-C(8)-C(7)	106.30(10)
C(17)-C(12)-C(13)	117.21(12)	O(1)-C(9)-C(1)	118.16(10)
C(12)-C(11)-C(10)	117.38(10)	C(1)-C(10)-C(11)	104.00(9)
C(8)-C(9)-C(1)	109.61(10)	C(17)-C(12)-C(11)	123.11(11)
C(10)-C(11)-C(7)	101.97(9)	C(12)-C(11)-C(7)	113.14(10)

2. (*3aS,3bS,6aR,7aR*)/(*3aR,3bR,6aS,7aS*)-7a-Dimethyamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,6a,7,7a-octahydrocyclo-penta[a]pentalen-3-one (**127a-II**).



Identification code	CP1160-2
Empirical formula	$C_{25}H_{27}NO_2$
Formula weight	373.48
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 11.345(2) Å alpha = 90°.
	b = 10.413(2) Å beta = 94.56(3)°.
	c = 16.729(3) Å gamma = 90°.
Volume	1970.0(7) $Å^3$
Z, Calculated density	4, 1.259 mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	800
Theta range for data collection	2.09 to 24.66°.
Index ranges	-13<=h<=13, -11<=k<=12, -19<=l<=19
Reflections collected / unique	10152 / 3310 [R(int) = 0.0556]
Observed reflections	2496
Completeness to theta	24.66 99.1%

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3310 / 0 / 255
Goodness-of-fit on F^2	0.936
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.0922
R indices (all data)	R1 = 0.0560, wR2 = 0.0971
Largest diff. peak and hole	0.303 and -0.185 $e.A^{-3}$

Table 1. Bond lengths

Bonding	Length (pm)	Bonding	Length (pm)	Bonding	Length (pm)
O(2)-C(3B)	143.1(2)	C(9)-C(10)	138.5(2)	C(3)-C(3A)	151.3(2)
N(1)-C(21)	146.4(2)	C(9)-C(8)	140.4(2)	C(10)-C(11)	138.6(2)
N(1)-C(20)	147.0(2)	C(4)-C(3B)	153.3(2)	C(19)-C(18)	138.7(2)
N(1)-C(7A)	148.7(2)	C(4)-C(5)	153.8(2)	C(19)-C(14)	140.0(2)
C(1)-C(2)	135.9(2)	C(2)-C(3)	148.3(2)	C(13)-C(12)	139.0(2)
C(1)-C(8)	148.4(2)	C(2)-C(14)	148.4(2)	C(13)-C(8)	139.6(2)
C(1)-C(7A)	153.4(2)	C(6B)-C(6A)	153.4(2)	C(7A)-C(3A)	155.3(2)
O(1)-C(3)	122.4(2)	C(6B)-C(7A)	155.9(2)	C(12)-C(11)	139.1(2)
C(6A)-C(3B)	154.7(2)	C(3B)-C(3A)	155.3(2)	C(15)-C(16)	139.1(3)
C(6A)-C(6)	155.0(2)	C(6)-C(5)	154.3(2)	C(16)-C(17)	138.5(3)
C(14)-C(15)	139.8(2)	C(18)-C(17)	138.4(2)		

Table 2. Bond angles

Bond angle	degree	Bond angle	degree
C(21)-N(1)-C(20)	109.41(12)	C(21)-N(1)-C(7A)	113.29(13)
C(20)-N(1)-C(7A)	112.94(12)	C(2)-C(1)-C(8)	126.81(14)
C(2)-C(1)-C(7A)	112.65(13)	C(8)-C(1)-C(7A)	120.34(13)
C(10)-C(9)-C(8)	120.60(15)	C(3B)-C(4)-C(5)	102.61(13)
C(1)-C(2)-C(3)	109.21(14)	C(1)-C(2)-C(14)	128.76(14)
C(3)-C(2)-C(14)	121.92(13)	C(6A)-C(6B)-C(7A)	107.07(12)
O(1)-C(3)-C(3A)	125.11(14)	O(1)-C(3)-C(2)	126.27(15)
C(2)-C(3)-C(3A)	108.61(13)	C(9)-C(10)-C(11)	120.38(14)
C(18)-C(19)-C(14)	120.68(15)	C(12)-C(13)- C(8)	120.25(14)
N(1)-C(7A)-C(1)	109.70(12)	N(1)-C(7A)-C(3A)	115.97(11)

C(1)-C(7A)-C(3A)	103.12(12)	N(1)-C(7A)-C(6B)	111.00(12)
C(1)-C(7A)-C(6B)	111.35(11)	C(3A)-C(7A)-C(6B)	105.42(12)
C(13)-C(12)-C(11)	120.55(16)	C(13)-C(8)-C(9)	118.72(14)
C(13)-C(8)-C(1)	122.39(13)	C(9)-C(8)-C(1)	118.76(14)
C(6B)-C(6A)-C(3B)	103.77(12)	C(6B)-C(6A)-C(6)	114.35(12)
C(3B)-C(6A)-C(6)	105.61(13)	C(15)-C(14)-C(19)	118.49(15)
C(15)-C(14)-C(2)	121.71(14)	C(19)-C(14)-C(2)	119.68(14)
C(10)-C(11)-C(12)	119.48(14)	O(2)-C(3B)-C(4)	110.16(13)
O(2)-C(3B)-C(6A)	109.31(12)	C(4)-C(3B)-C(6A)	102.86(12)
O(2)-C(3B)-C(3A)	111.68(12)	C(4)-C(3B)-C(3A)	116.82(13)
C(6A)-C(3B)-C(3A)	105.32(12)	C(5)-C(6)-C(6A)	105.85(13)
C(3)-C(3A)-C(3B)	114.61(13)	C(3)-C(3A)-C(7A)	105.53(12)
C(3B)-C(3A)-C(7A)	107.03(12)	C(4)-C(5)-C(6)	104.80(13)
C(17)-C(18)-C(19)	120.35(16)	C(16)-C(15)-C(14)	120.41(16)
C(17)-C(16)-C(15)	120.43(16)	C(18)-C(17)-C(16)	119.62(16)

Table 3. Hydrogen bonding of cp1160-2 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2A)...O(1)	0.84	3.45	3.6347(17)	95.7

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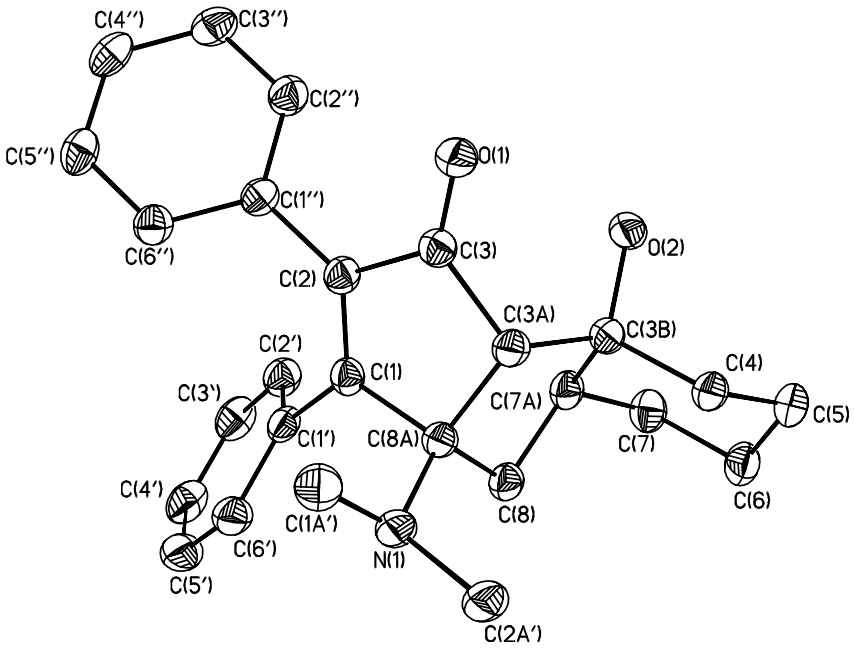
3. (*3aS,3bR,7aS,8aR*)/(*3aR,3bS,7aR,8aS*)-8a-Dimethylamino-3b-hydroxy-1,2-diphenyl-3b,4,5,6, 7,7a,8,8a-octahydro-3aH-cyclopenta[a]inden-3-one (**127f-I**)



Identification code	CP940i
Empirical formula	$C_{26}H_{29}NO_2$
Formula weight	387.50
Temperature	133(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.228(3) Å alpha = 90 deg.
	b = 9.0213(18) Å beta = 97.31(3) deg.
	c = 17.290(4) Å gamma = 90 deg.
Volume	2046.4(7) $Å^3$
Z, Calculated density	4, 1.258 mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	832
Theta range for data collection	2.38 to 24.77 deg.
Index ranges	-15<=h<=15, -10<=k<=10, -20<=l<=20
Reflections collected / unique	11386 / 3347 [R(int) = 0.0575]
Observed reflections	2664
Completeness to theta	24.77 95.3%

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3347 / 0 / 262
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0941
R indices (all data)	R1 = 0.0471, wR2 = 0.0970
Largest diff. peak and hole	0.235 and -0.176 $e.A^{-3}$

Table 1. Bond lengths

Bonding	Length (pm)	Bonding	Length (pm)	Bonding	Length (pm)
N(1)-C(1A')	146.3(2)	N(1)-C(2A')	146.7(2)	N(1)-C(8A)	148.1(2)
O(1)-C(3)	122.1(2)	O(2)-C(3B)	142.1(2)	C(1")-C(2")	139.5(2)
C(1")-C(6")	139.8(2)	C(1")-C(2)	148.7(2)	C(1')-C(6')	138.6(2)
C(1')-C(2')	140.1(2)	C(1')-C(1)	148.7(2)	C(1)-C(2)	134.8(2)
C(1)-C(8A)	154.3(2)	C(2")-C(3")	139.1(2)	C(2)-C(3)	148.7(2)
C(2')-C(3`)	138.8(2)	C(3)-C(3A)	151.4(2)	C(3B)-C(7A)	154.1(2)
C(3B)-C(4)	154.1(2)	C(3B)-C(3A)	156.8(2)	C(3")-C(4")	138.8(2)
C(3A)-C(8A)	156.3(2)	C(3`)-C(4')	137.8(3)	C(4)-C(5)	152.6(2)
C(4')-C(5')	138.6(3)	C(4")-C(5")	138.4(2)	C(5')-C(6')	139.3(2)
C(5")-C(6")	139.3(2)	C(5)-C(6)	152.7(2)	C(6)-C(7)	153.4(2)
C(7A)-C(8)	152.0(2)	C(7A)-C(7)	153.1(2)	C(8)-C(8A)	154.4(2)

Table 2. Bond anhles

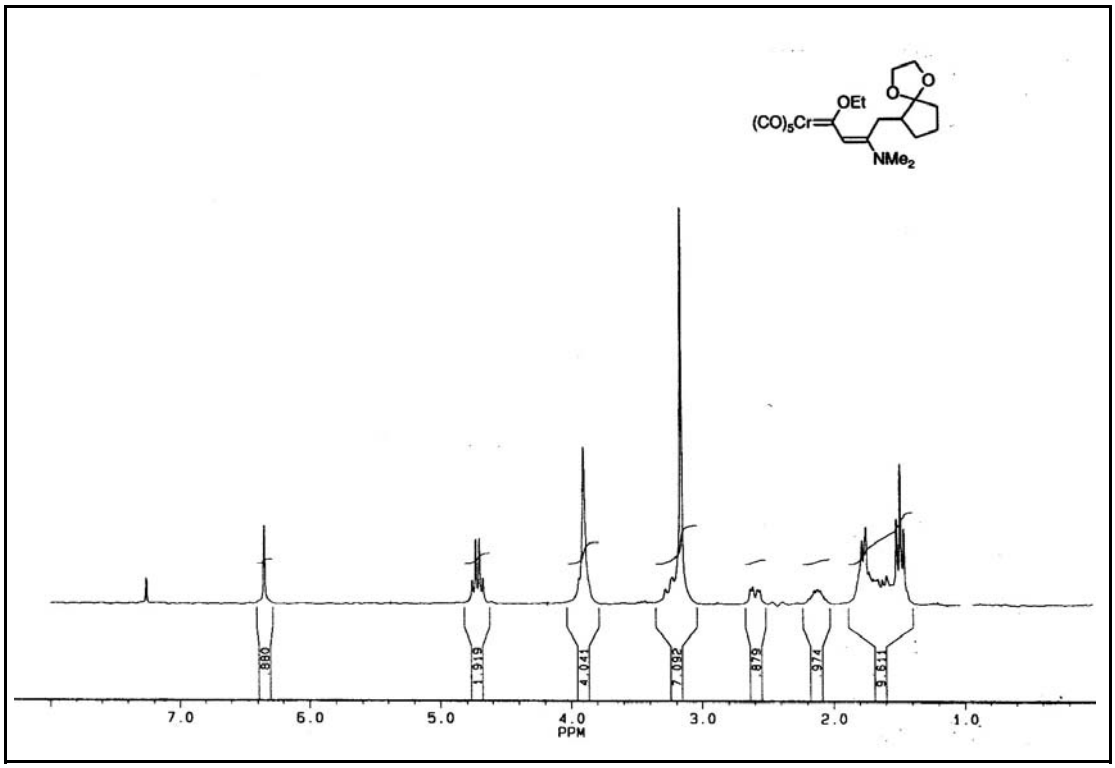
Bond angle	degree	Bond angle	degree
C(1A')-N(1)-C(2A')	109.32(12)	C(1A')-N(1)-C(8A)	112.76(11)
C(2A')-N(1)-C(8A)	113.01(12)	C(2")-C(1")-C(6")	118.82(13)
C(2")-C(1")-C(2)	120.39(13)	C(6")-C(1")-C(2)	120.78(13)
C(1A')-N(1)-C(2A')	109.32(12)	C(1A')-N(1)-C(8A)	112.76(11)
C(2")-C(1")-C(6")	118.82(13)	C(2A')-N(1)-C(8A)	113.01(12)
C(2")-C(1")-C(2)	120.39(13)	C(6")-C(1")-C(2)	120.78(13)
C(6')-C(1')-C(2')	118.74(13)	C(6')-C(1')-C(1)	123.12(13)
C(2')-C(1')-C(1)	118.05(14)	C(2)-C(1)-C(1')	126.42(12)
C(2)-C(1)-C(8A)	112.96(12)	C(1')-C(1)-C(8A)	120.50(11)

C(3")-C(2")-C(1")	120.61(14)	C(1)-C(2)-C(1")	128.32(13)
C(1)-C(2)-C(3)	109.27(12)	C(1")-C(2)-C(3)	122.40(12)
C(3`)-C(2')-C(1')	120.31(16)	O(1)-C(3)-C(2)	125.79(12)
O(1)-C(3)-C(3A)	125.79(12)	C(2)-C(3)-C(3A)	108.42(11)
O(2)-C(3B)-C(7A)	107.63(11)	O(2)-C(3B)-C(4)	110.99(12)
C(7A)-C(3B)-C(4)	111.69(11)	O(2)-C(3B)-C(3A)	113.50(11)
C(7A)-C(3B)-C(3A)	103.81(11)	C(4)-C(3B)-C(3A)	109.04(11)
C(4")-C(3")-C(2")	120.13(15)	C(3)-C(3A)-C(8A)	105.23(11)
C(3)-C(3A)-C(3B)	112.61(12)	C(8A)-C(3A)-C(3B)	105.86(11)
C(4')-C(3`)-C(2')	120.43(15)	C(5)-C(4)-C(3B)	112.62(12)
C(3`)-C(4')-C(5')	119.80(14)	C(5")-C(4")-C(3")	119.65(13)
C(4')-C(5')-C(6')	120.05(17)	C(4")-C(5")-C(6")	120.52(14)
C(4)-C(5)-C(6)	110.61(13)	C(1')-C(6')-C(5')	120.60(15)
C(5")-C(6")-C(1")	120.18(14)	C(5)-C(6)-C(7)	110.51(12)
C(8)-C(7A)-C(7)	116.82(12)	C(8)-C(7A)-C(3B)	104.02(12)
C(7)-C(7A)-C(3B)	113.24(12)	C(7A)-C(7)-C(6)	113.41(12)
C(7A)-C(8)-C(8A)	103.49(11)	N(1)-C(8A)-C(1)	109.19(11)
N(1)-C(8A)-C(8)	113.09(11)	C(1)-C(8A)-C(8)	109.20(11)
N(1)-C(8A)-C(3A)	117.07(11)	C(1)-C(8A)-C(3A)	102.17(10)
C(8)-C(8A)-C(3A)	105.41(11)		

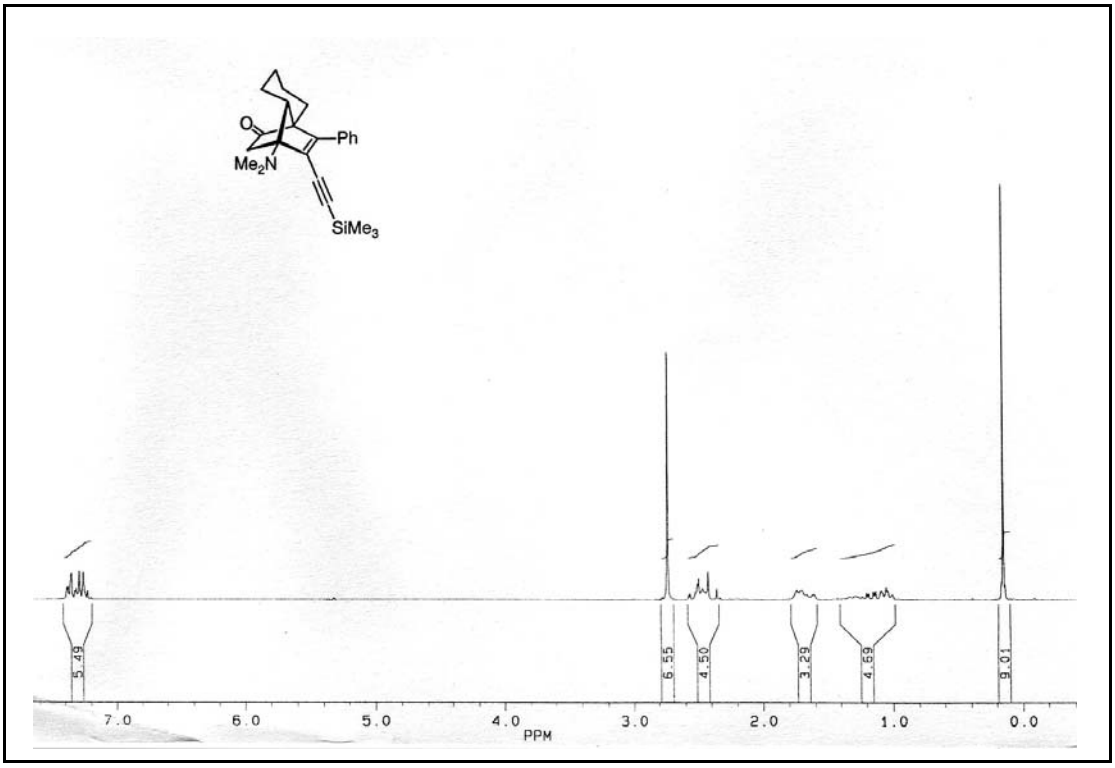
Table 3. Hydrogen bonding of CP940i [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2A)...O(1)	0.84	1.98	2.8144(15)	175.8

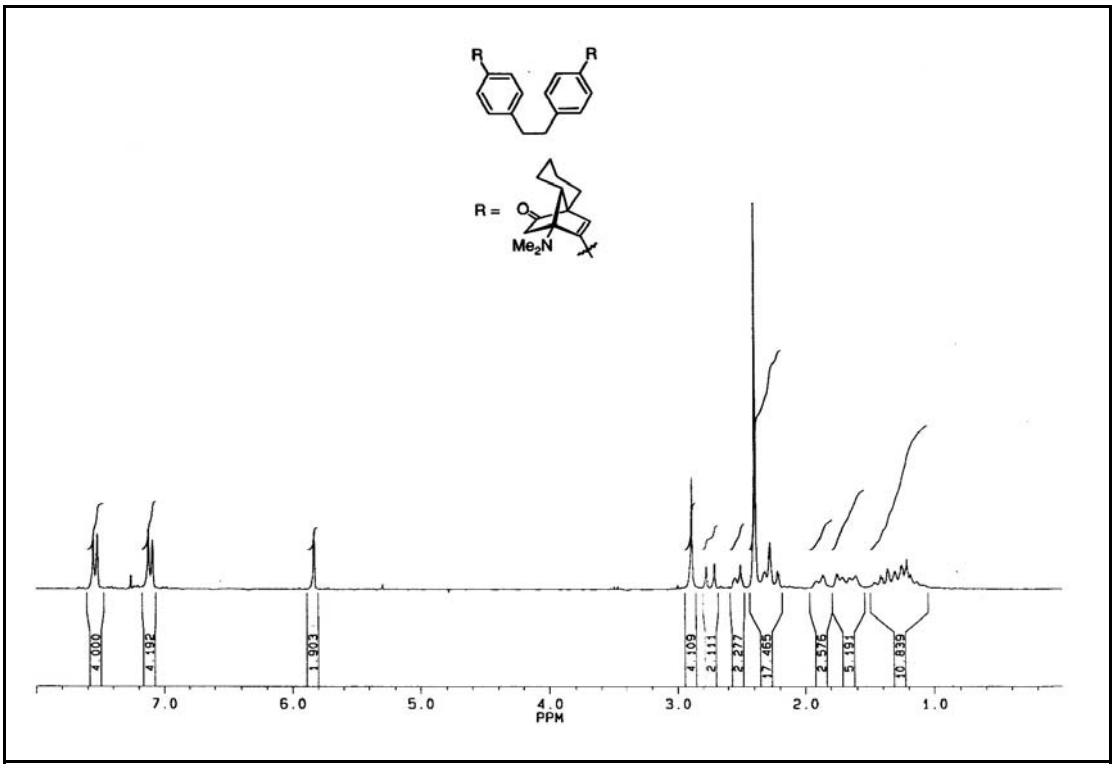
G. NMR Spectra



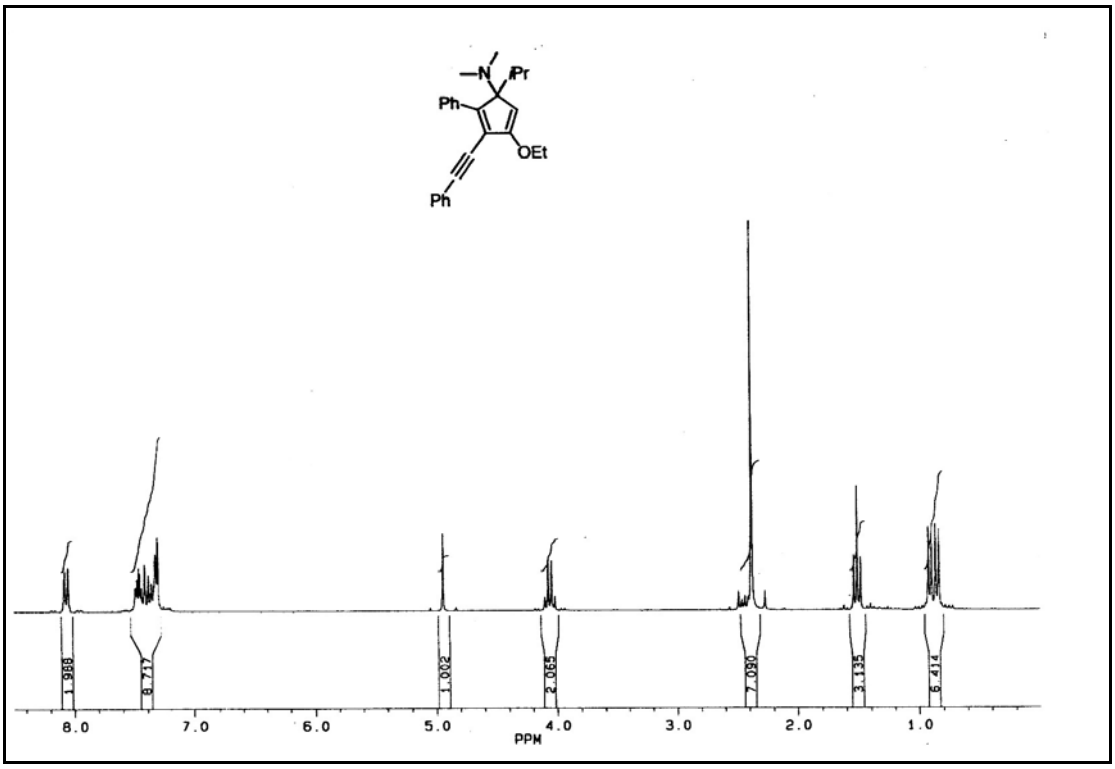
Pentacarbonyl[(2*E*)-4-(1',4'-dioxaspiro[4.4]non-6'-yl)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]chromium (**18i**), 250 MHz, $CDCl_3$



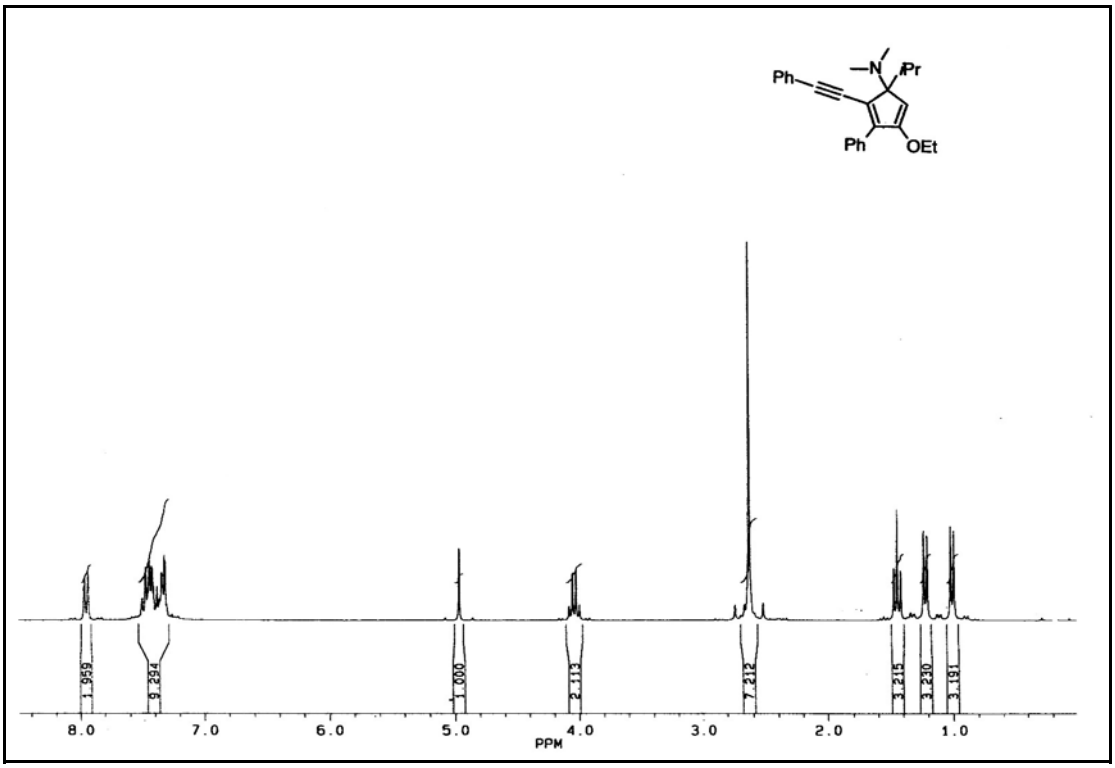
7-Dimethylamino-11-(2'-trimethylsilylethynyl)-10-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25p**), 250 MHz, $CDCl_3$



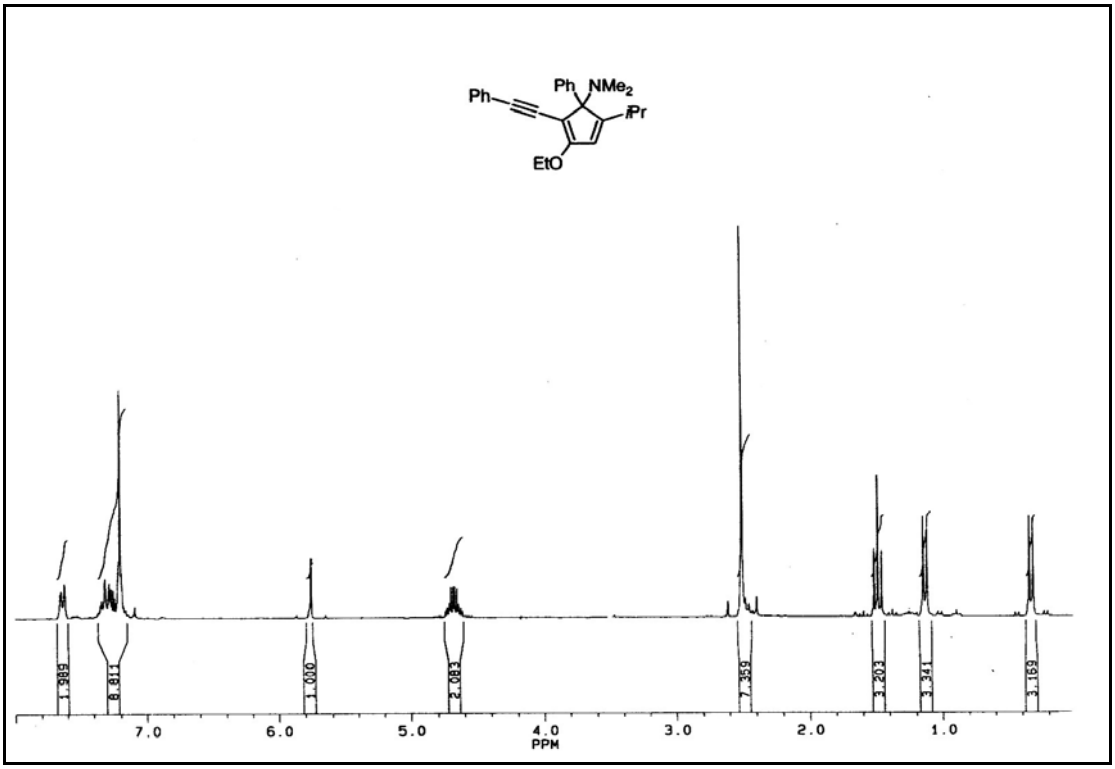
4,4'-Bis[7"-(dimethylamino)tricyclo[5.2.2.0^{1,6}]undec-10"-en-9"-oxo-11"-yl]bibenzyl (**72z)**, 250 MHz, $CDCl_3$



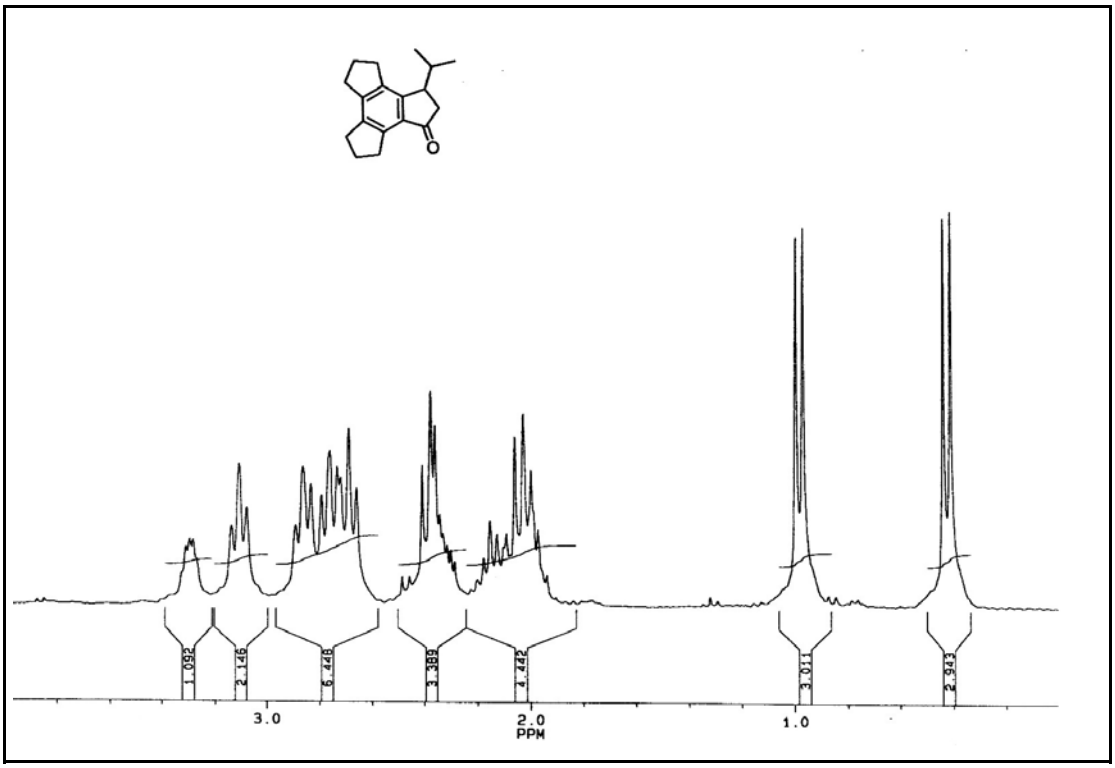
5-Dimethylamino-3-ethoxy-5-isopropyl-1-phenyl-2-phenylethynyl-1,3-cyclopenta-diene (**19s**), 250 MHz, $CDCl_3$



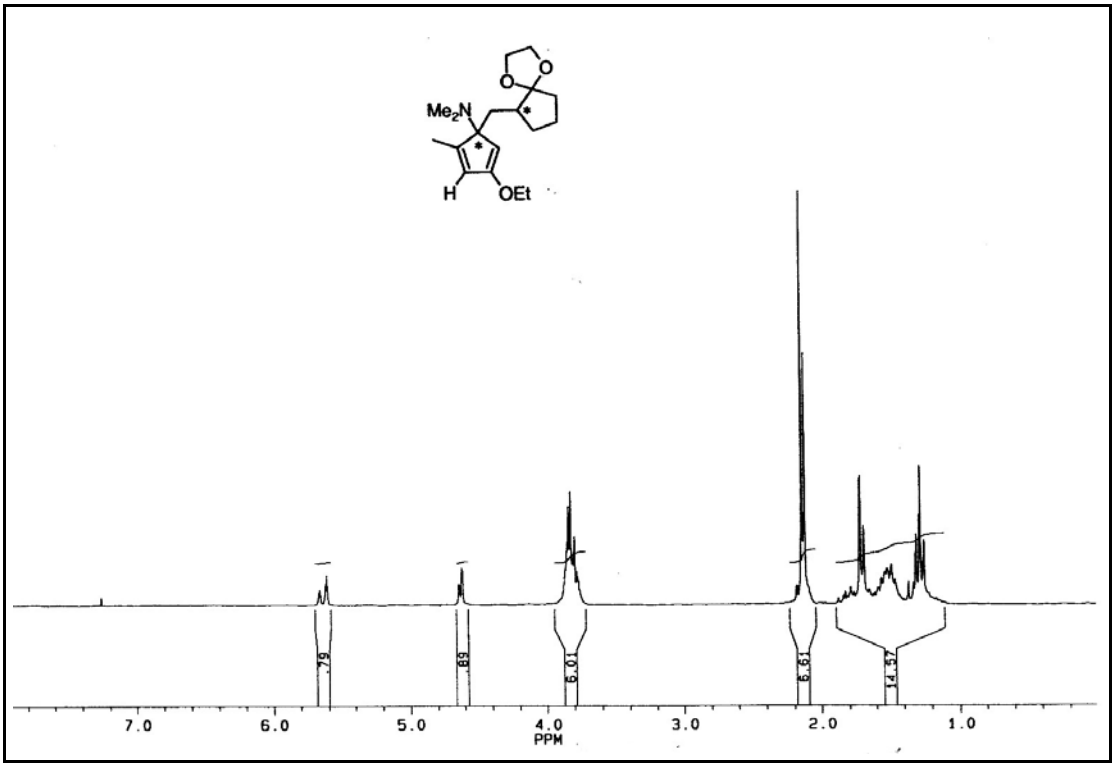
5-Dimethylamino-3-ethoxy-5-isopropyl-2-phenyl-1-phenylethynyl-1,3-cyclopenta-diene (**81s**), 250 MHz, $CDCl_3$



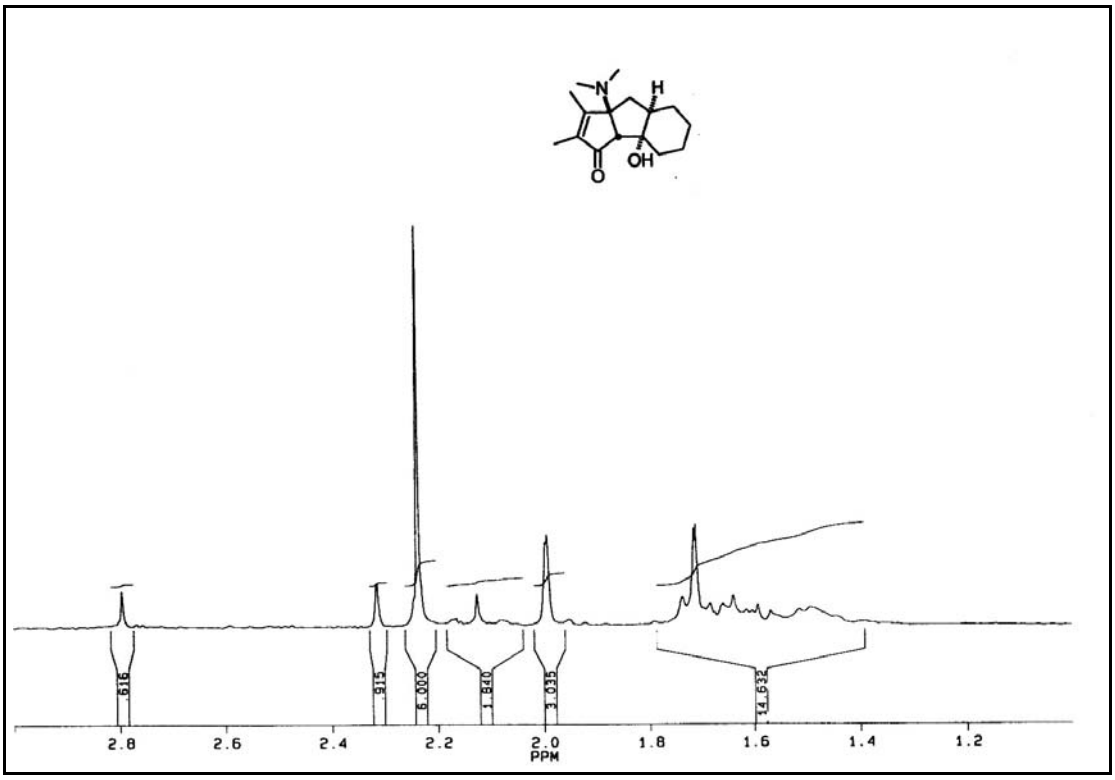
5-Dimethylamino-2-ethoxy-4-isopropyl-5-phenyl-1-(phenyl-ethynyl)-1,3-cyclopenta-diene (**90s**), 250 MHZ, $CDCl_3$



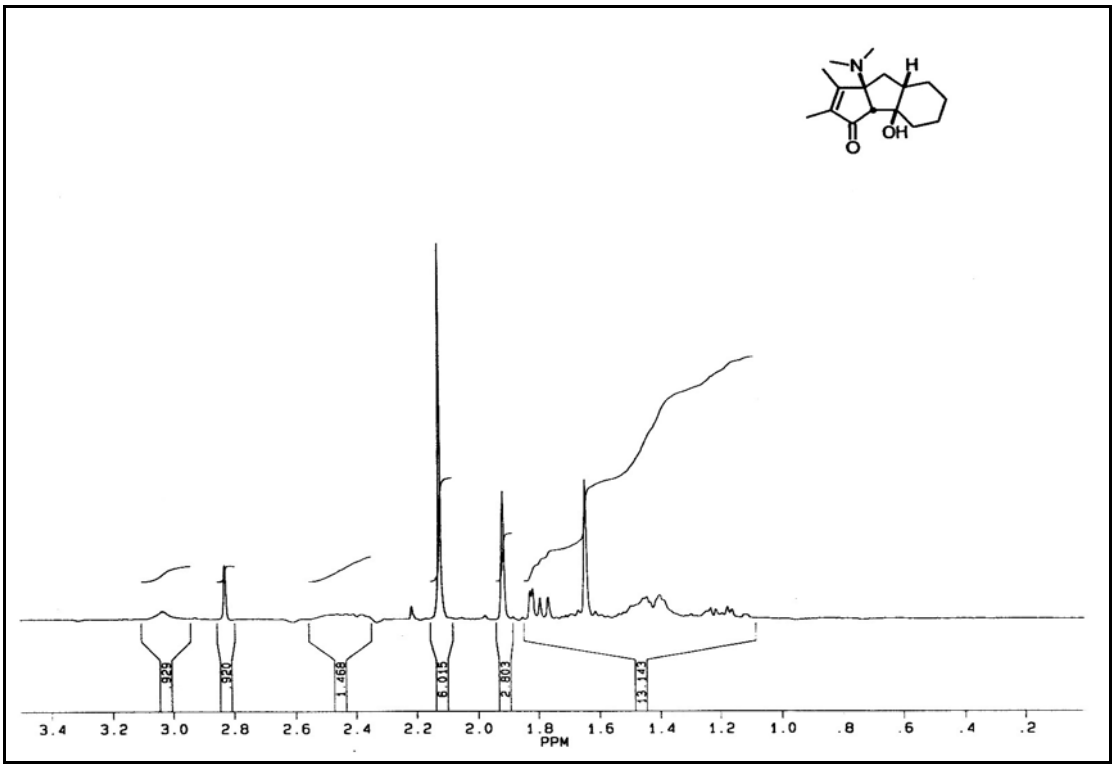
3-Isopropyl-2,3,4,5,6,7,8,9-octahydrotrinden-1-one (**100h**), 250 MHZ, $CDCl_3$



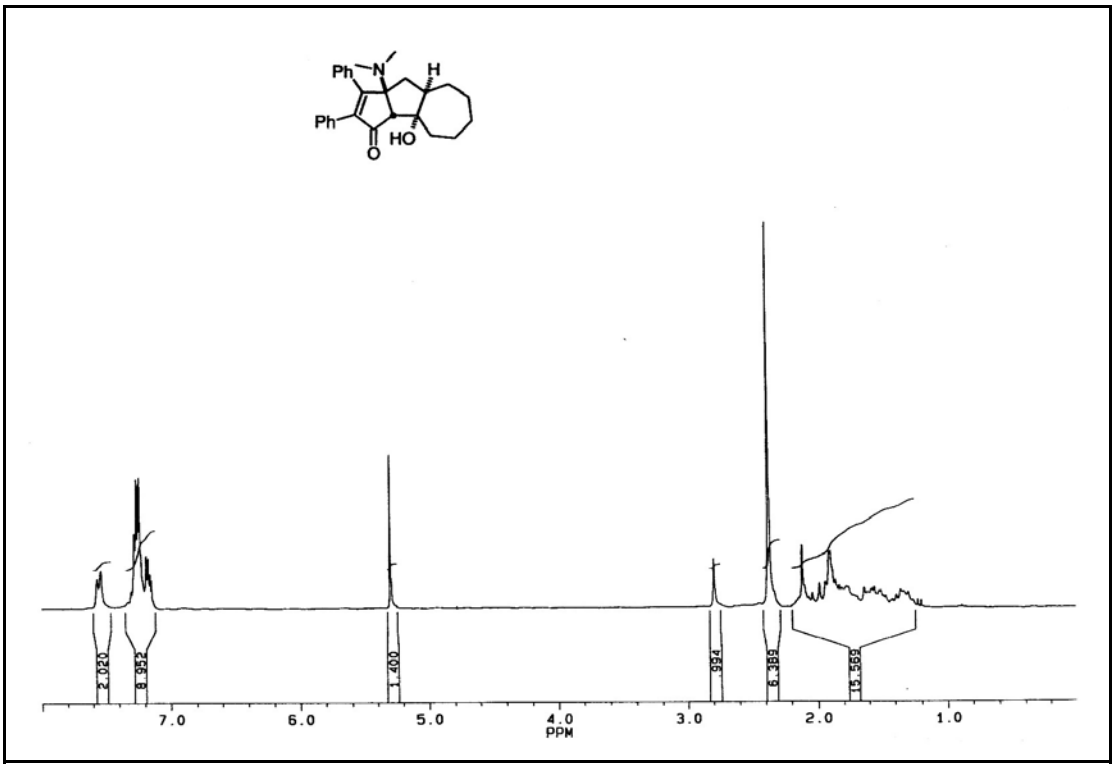
5-Dimethylamino-5-[(1',4'-dioxaspiro[4.4]non-6'-yl)methyl]-3-ethoxy-1-methyl-1,3-cyclo-pentadiene (**130d**), 250 MHz, $CDCl_3$



(3aS,3bR,7aS,8aR)/(3aR,3bS,7aR,8aS)-8a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (**127g-I**).

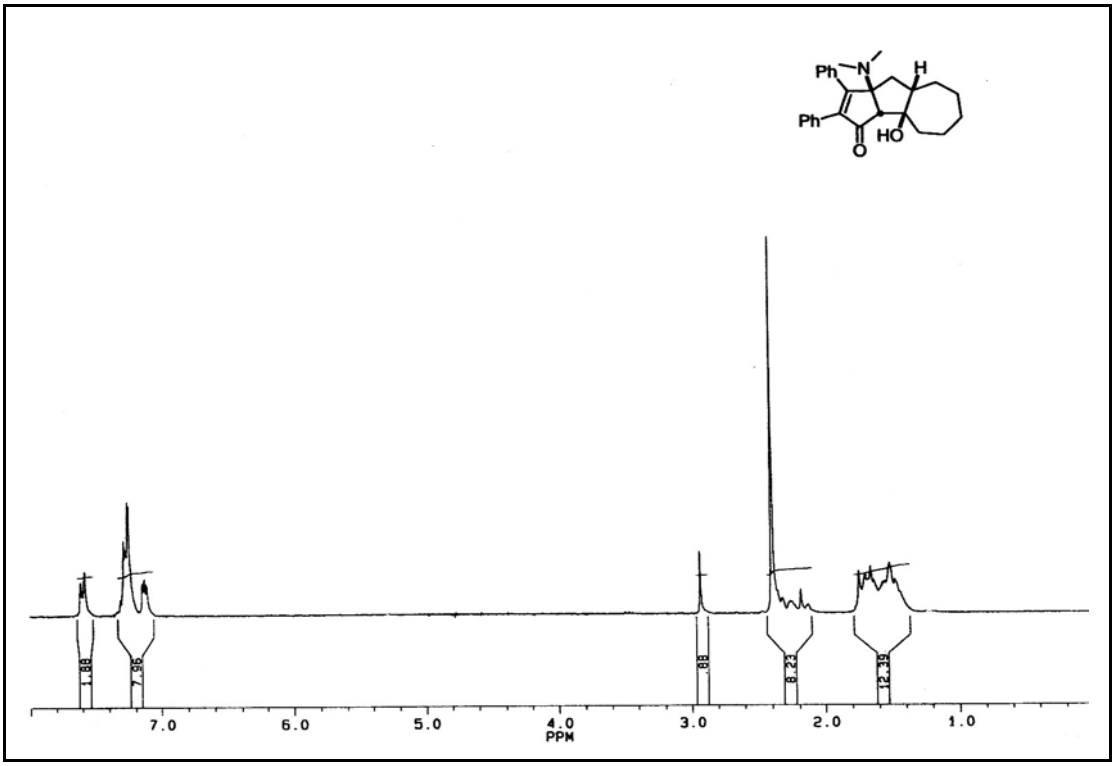


(3aS,3bS,7aR,8aR)/(3aR,3bR,7aS,8aS)-8a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (**127g-II**).

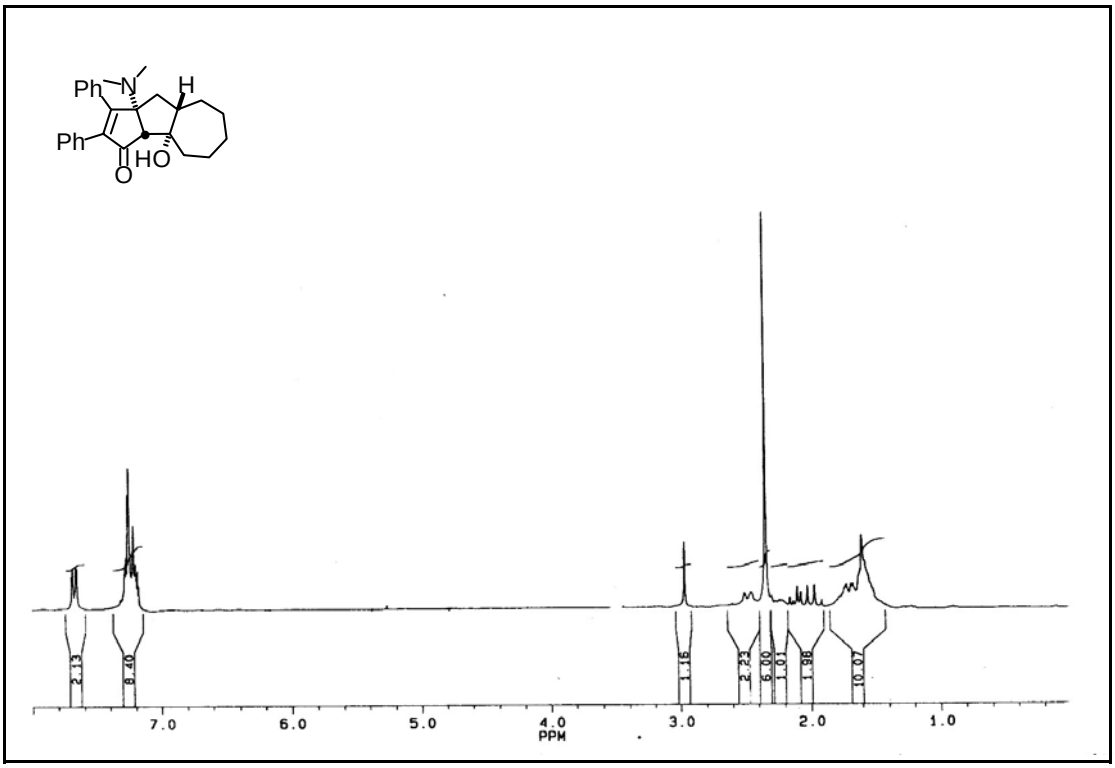


(3aS,3bR,8aS,9aR)/(3aR,3bS,8aR,9aS)-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4, 5,6,7,8,8a,9,9a-decahydro-3*H*-cyclopenta[*a*]azulen-3-one (**127m-I**)

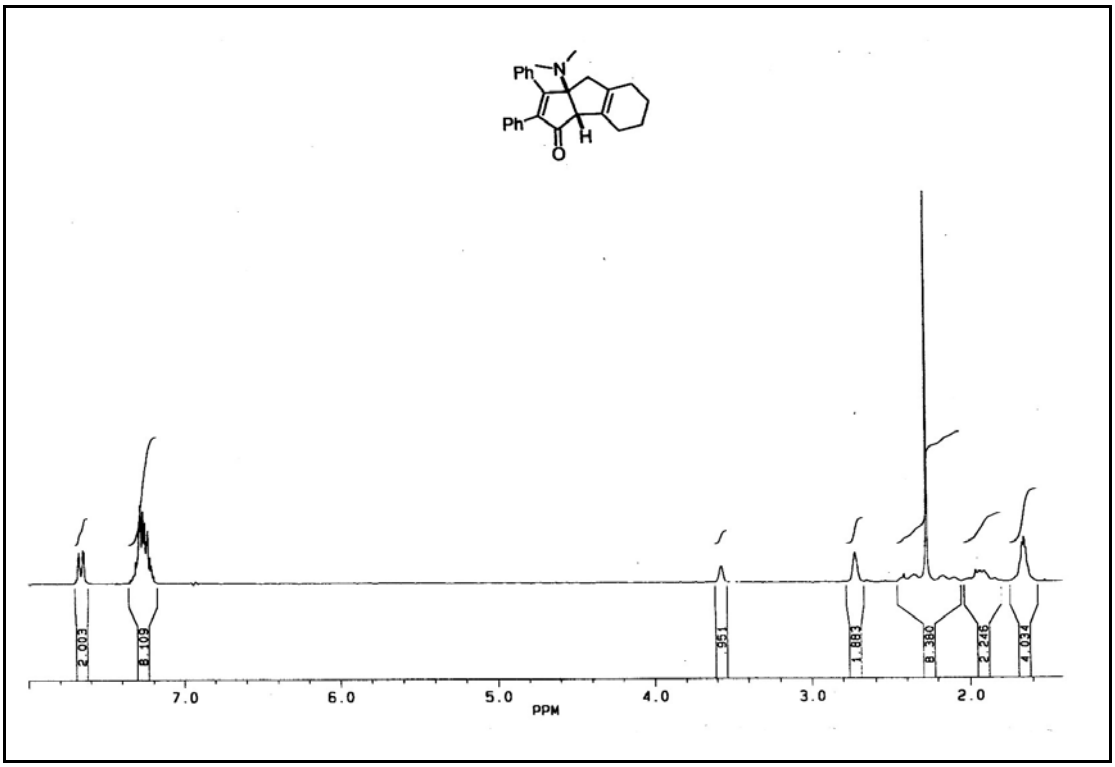
.



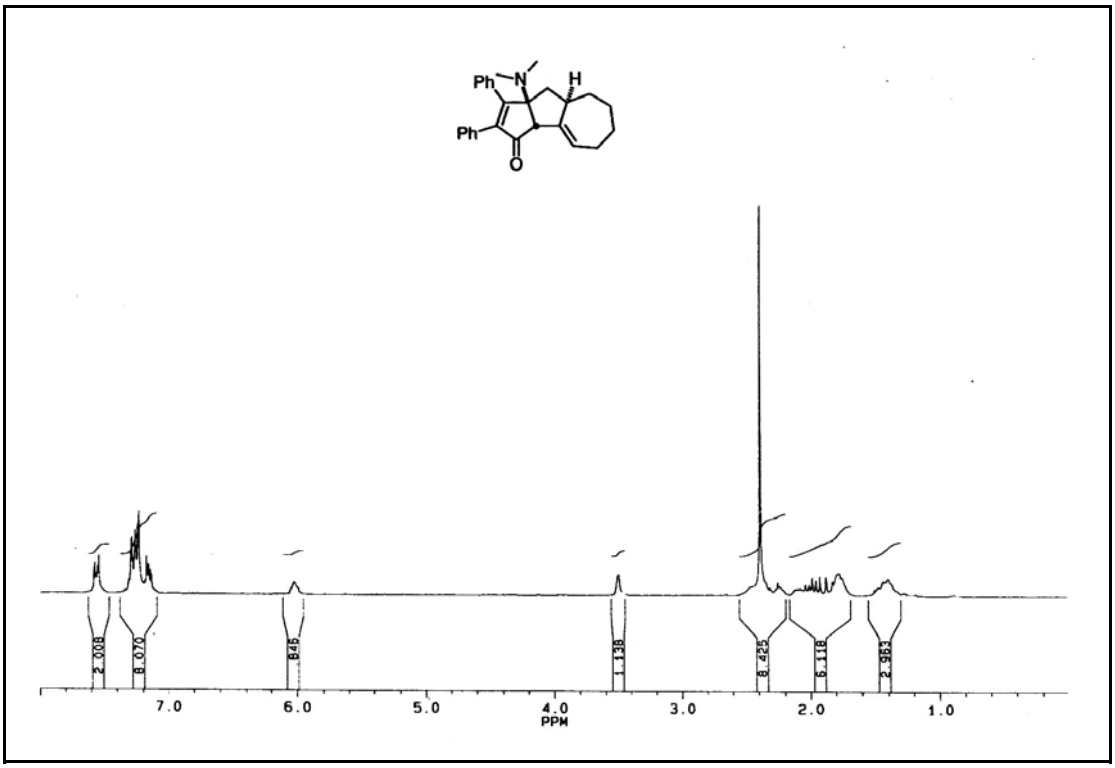
(*3aS,3bS,8aR,9aR)/(3aR,3bR,8aS,9aS)*-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,7,8,8a,9, 9a-decahydro-3*H*-cyclopenta[*a*]azulen-3-one (**127m-II**)



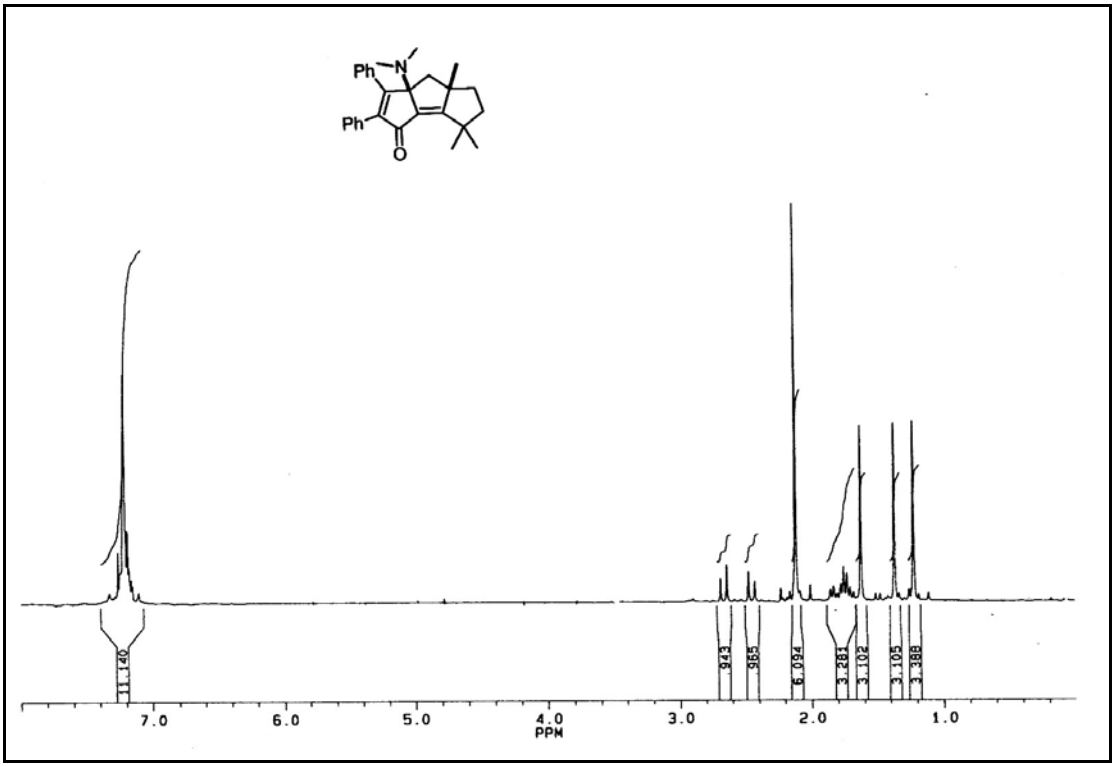
(*3aS*,*3bS*,*8aS*,*9aR*)/(*3aR*,*3bR*,*8aR*,*9aS*)-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,7,8,8a,9,9a-decahydro-3*H*-cyclopenta[*a*]azulen-3-one (**127m-III**).



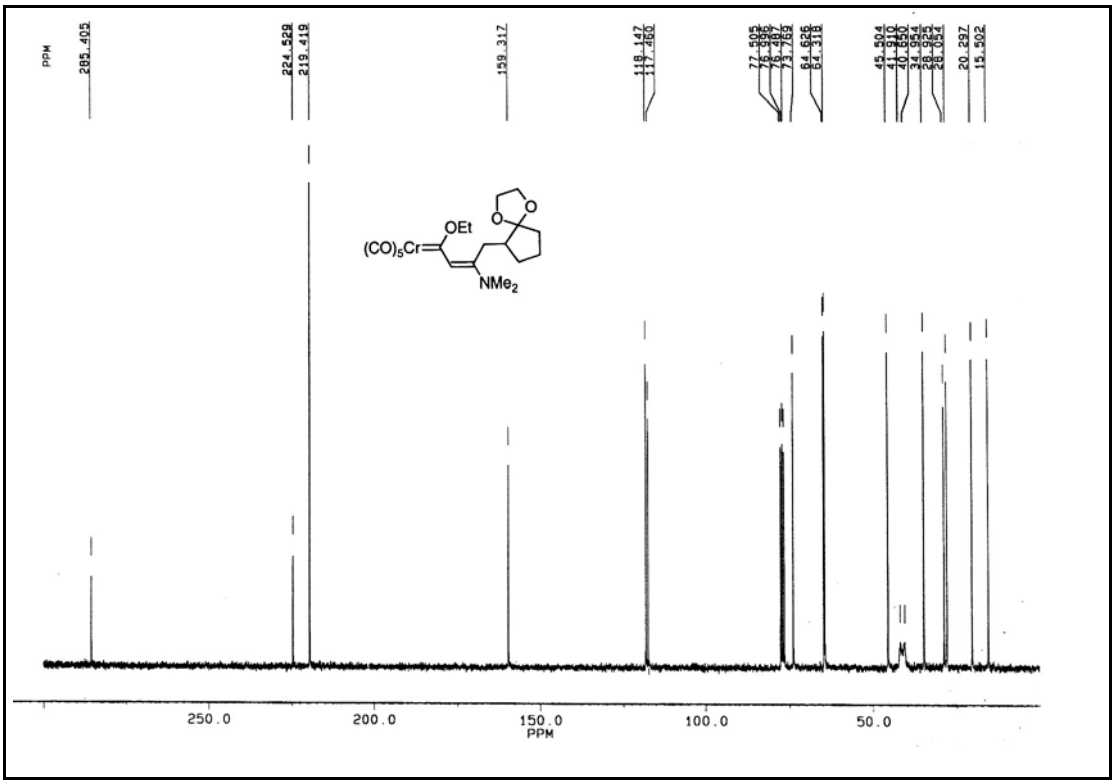
8a-Dimethyamino-1,2-diphenyl-4,5,6,7,7a,8,8a-octahydrocyclopenta[*a*]inden-3-one (**145f**), 250 MHz, $CDCl_3$



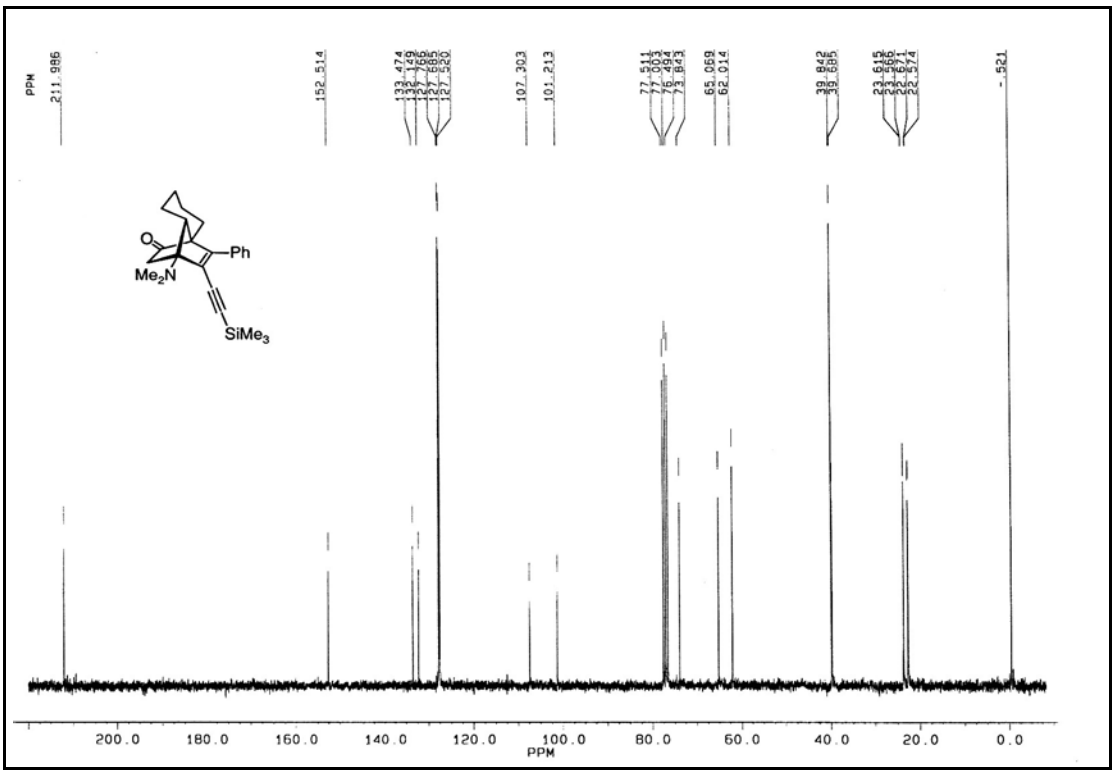
9a-Dimethylamino-1,2-diphenyl-3a,5,6,7,8,8a,9,9a-octahydrocyclopenta[*a*]azulen-3-one (**146m**), 250 MHZ, $CDCl_3$



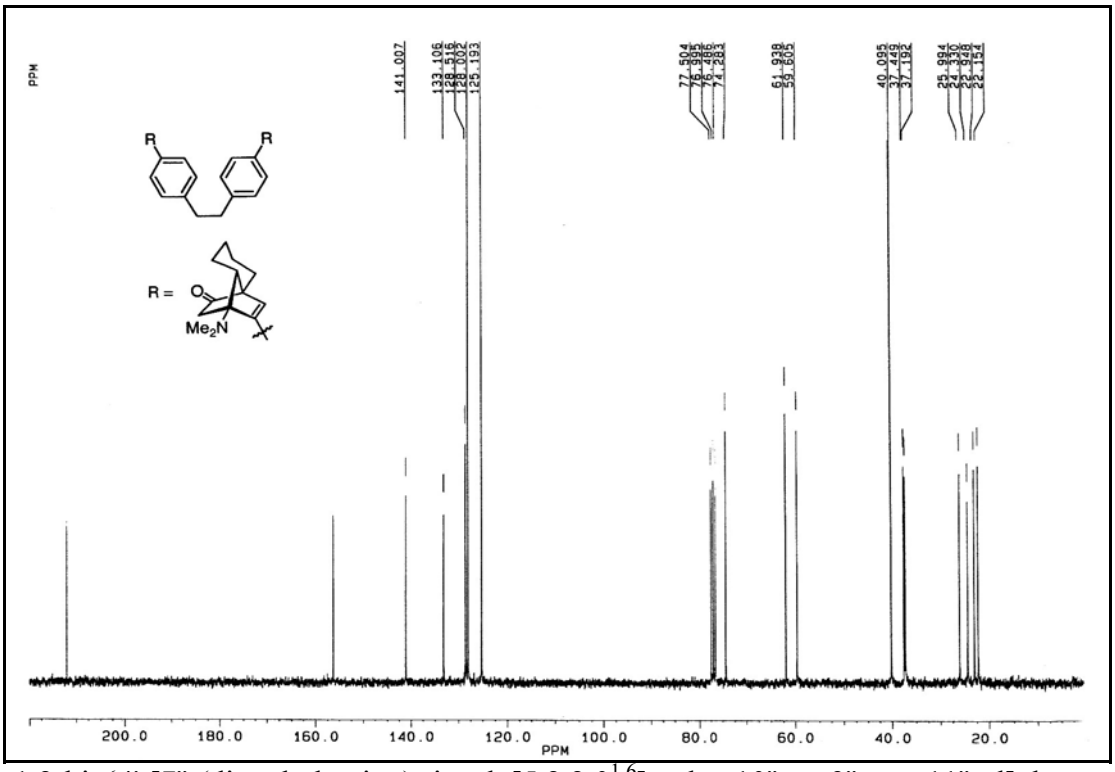
7a-Dimethyamino-4,4,6a-trimethyl-1,2-diphenyl-4,5,6,6a,7,7a-hexahydrocyclopenta-[*a*]pentalen-3-one (**151a**), 250 MHz, $CDCl_3$



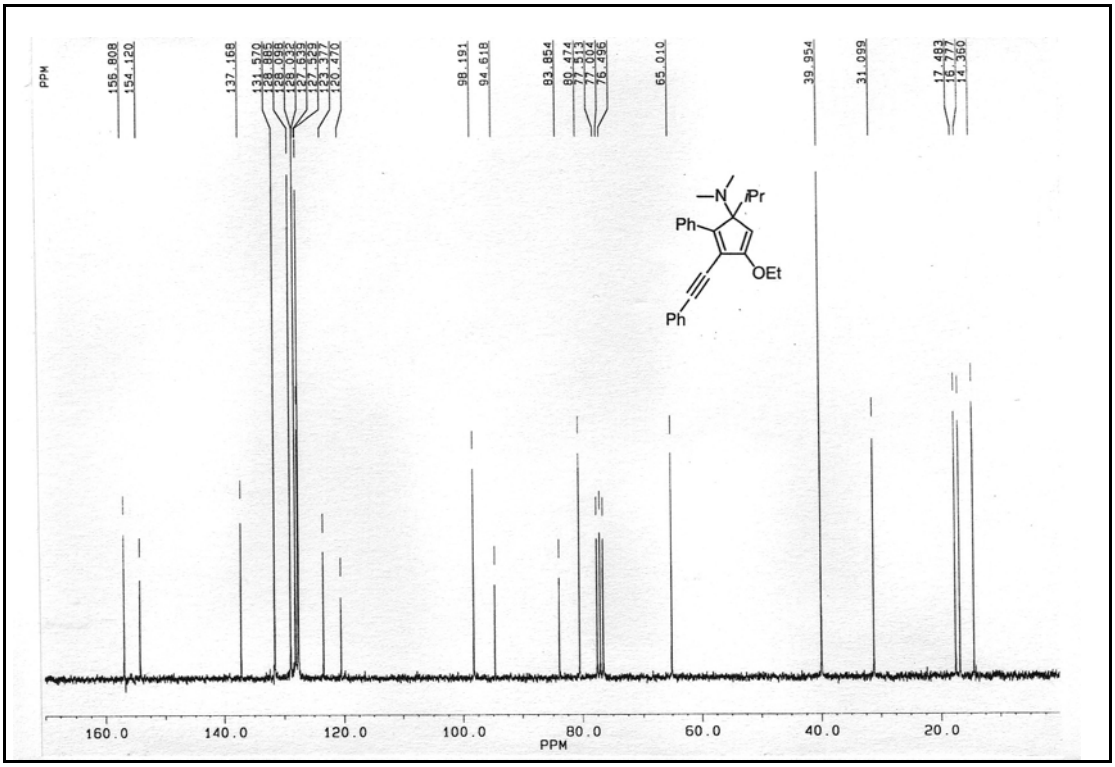
Pentacarbonyl[(2*E*)-4-(1',4'-dioxaspiro[4.4]non-6'-yl)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]chromium (**18i**), 62.9 MHz, $CDCl_3$



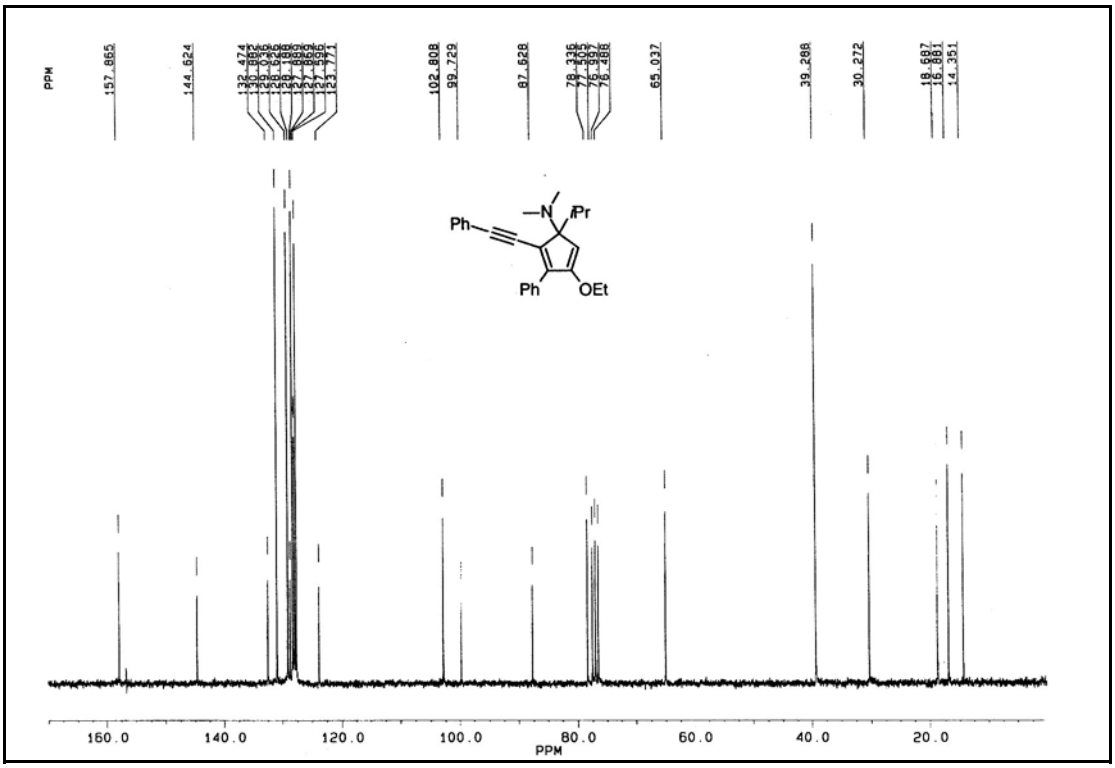
7-Dimethylamino-11-(2'-trimethylsilylethynyl)-10-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (**25p**), 62.9 MHz, $CDCl_3$



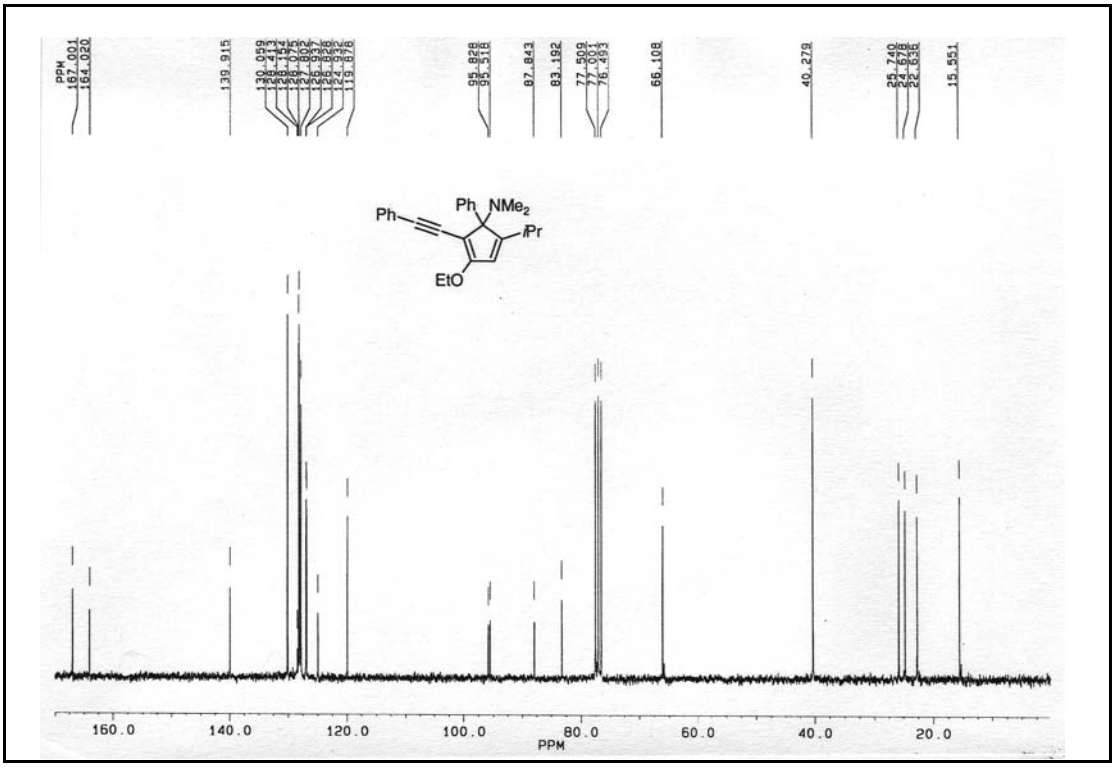
1,2-bis{4'-[7"-(dimethylamino)tricyclo[5.2.2.0^{1,6}]undec-10"-en-9"-oxo-11"-yl]phenyl}ethane (**72z**), 62.9 MHz, $CDCl_3$



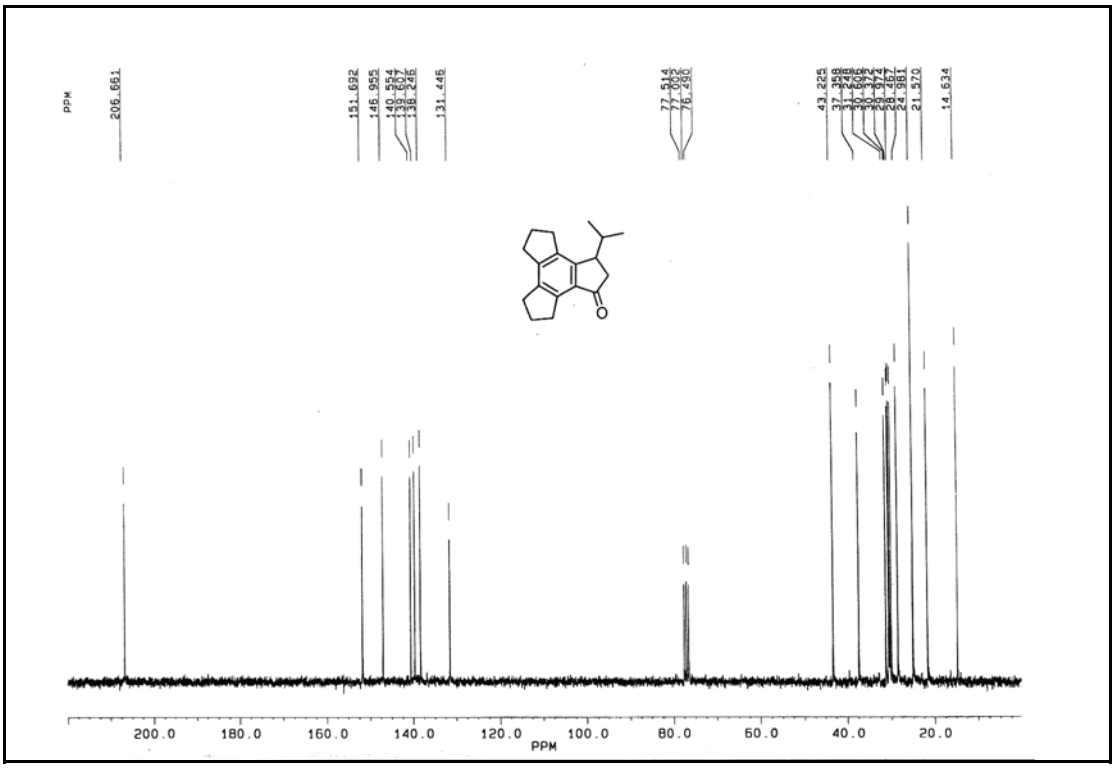
5-Dimethylamino-3-ethoxy-5-isopropyl-1-phenyl-2-phenylethynyl-1,3-cyclopentadiene (**19s**), 62.9 MHz, $CDCl_3$



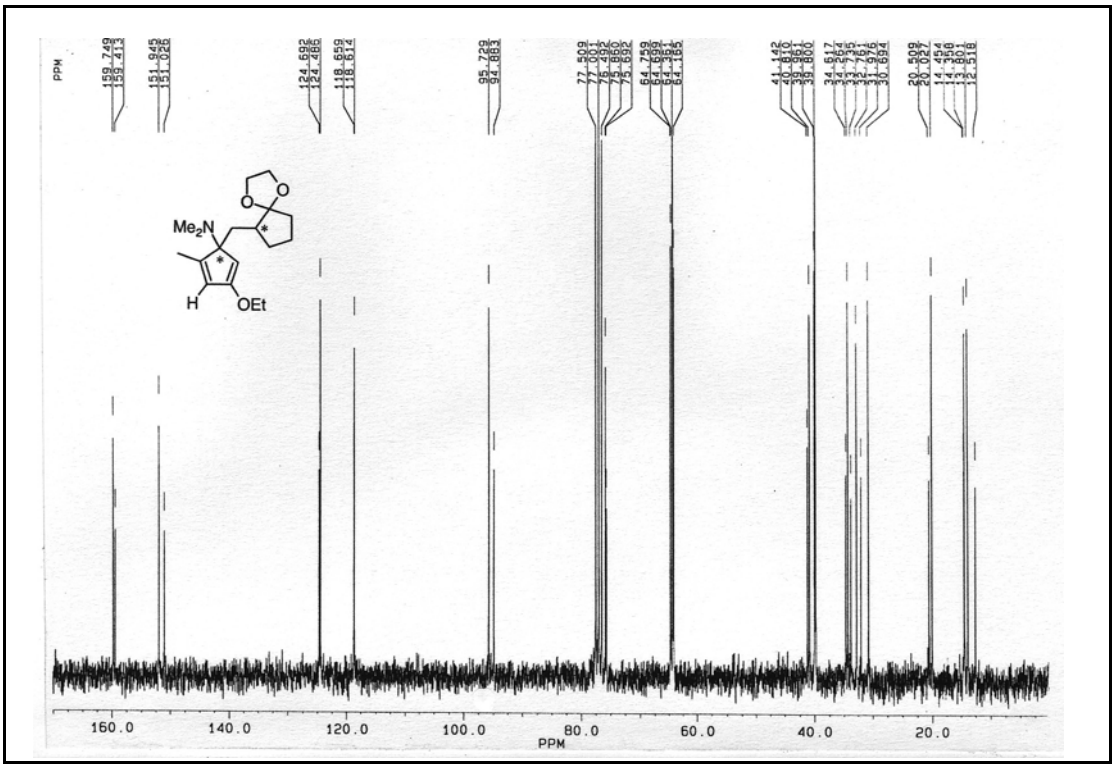
5-Dimethylamino-3-ethoxy-5-isopropyl-2-phenyl-1-phenylethynyl-1,3-cyclopentadiene (**81s**), 62.9 MHz, $CDCl_3$



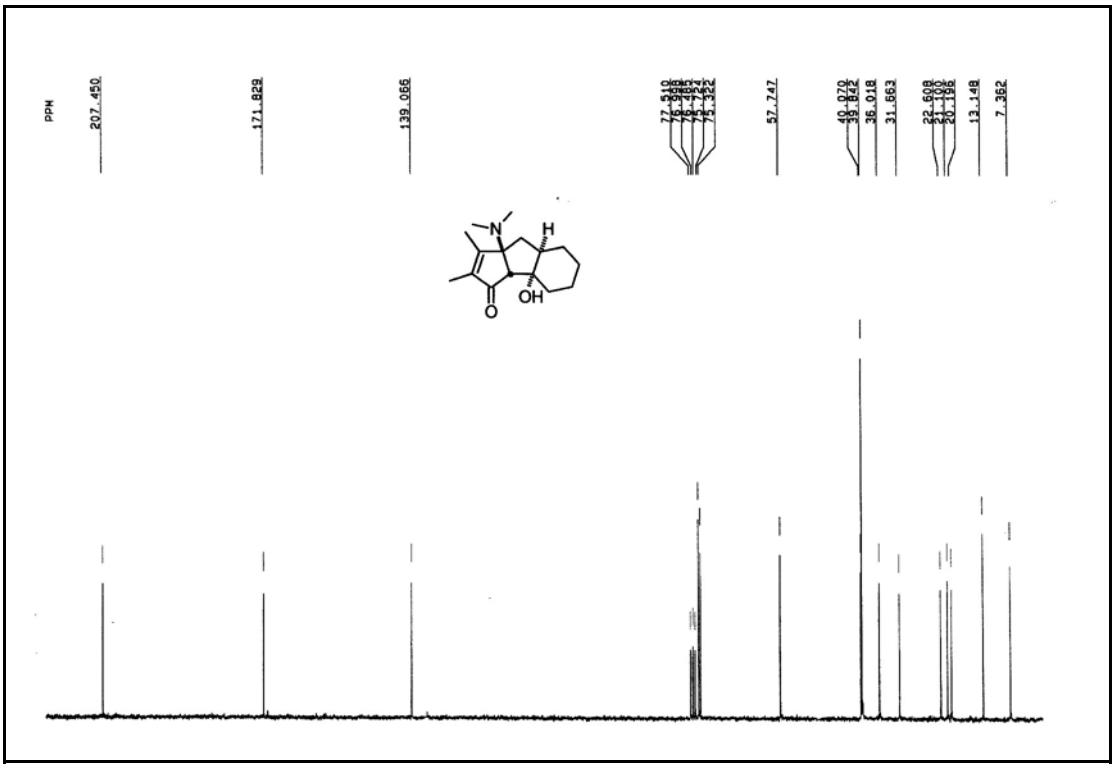
5-Dimethylamino-2-ethoxy-4-isopropyl-5-phenyl-1-(phenyl-ethynyl)-1,3-cyclopentadiene (**90s**), 62.9 MHz, $CDCl_3$



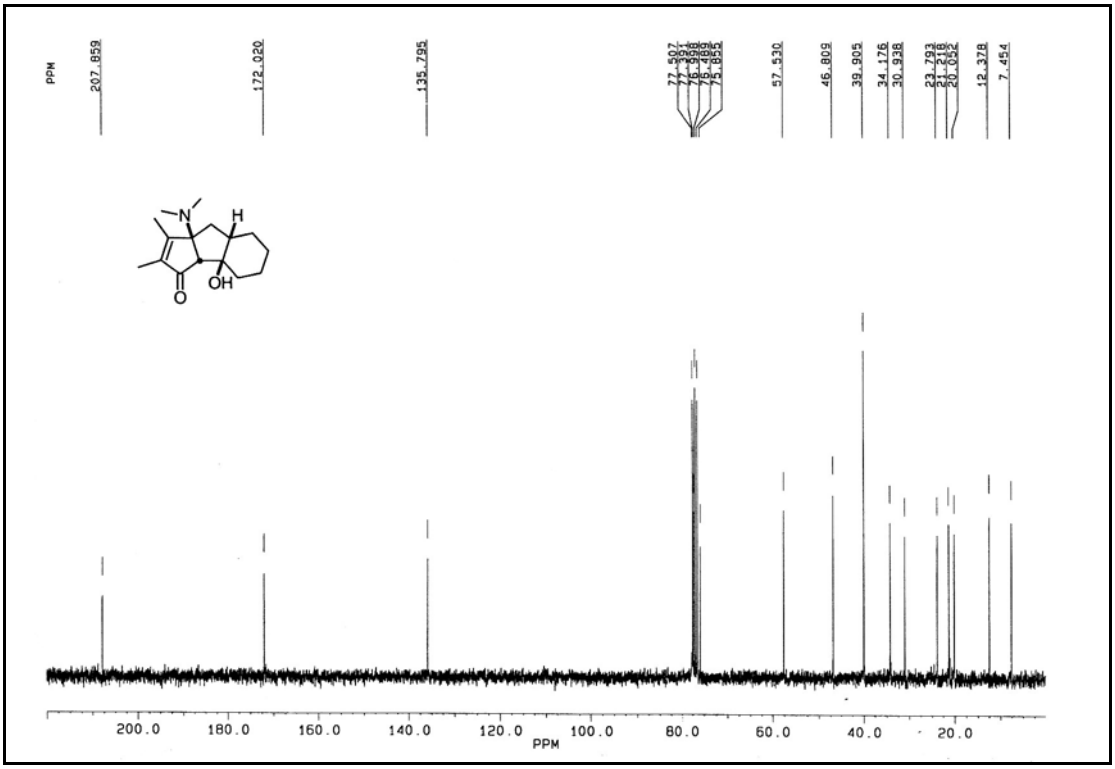
3-Isopropyl-2,3,4,5,6,7,8,9-octahydrotrinden-1-one (**100h**), 62.9 MHz, $CDCl_3$



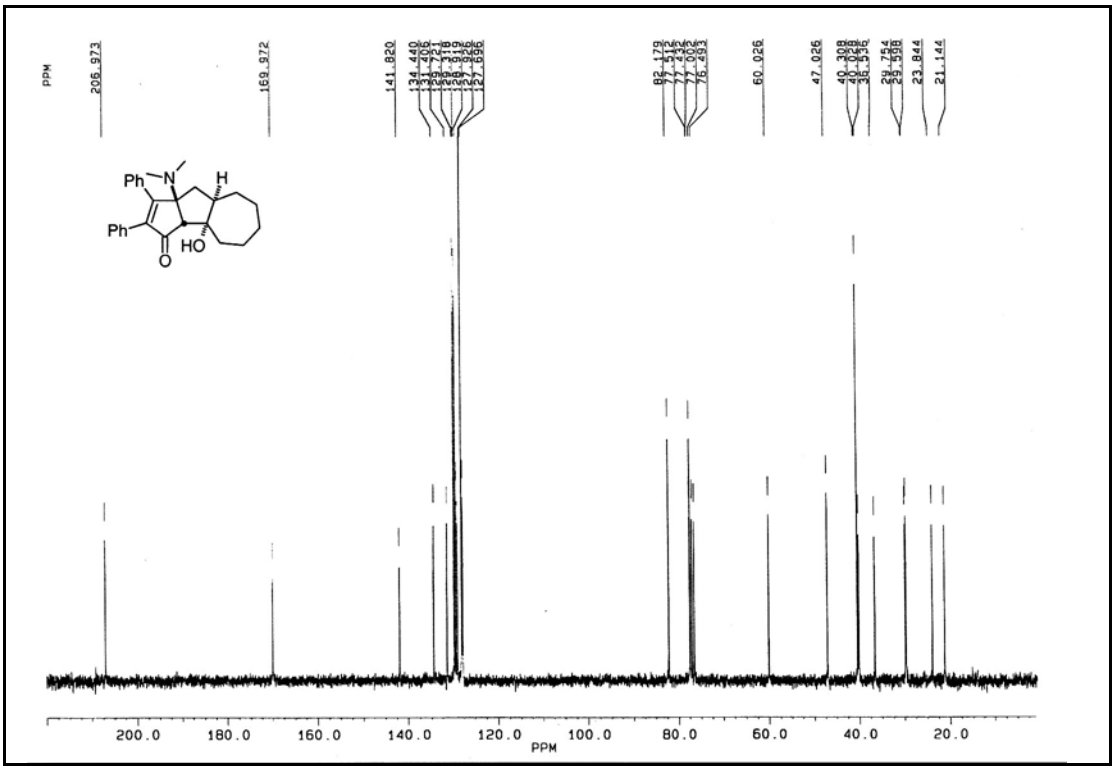
5-Dimethylamino-5-[(1',4'-dioxaspiro[4.4]non-6'-yl)methyl]-3-ethoxy-1-methyl-1,3-cyclopentadiene (**130d**), 62.9 MHz, $CDCl_3$



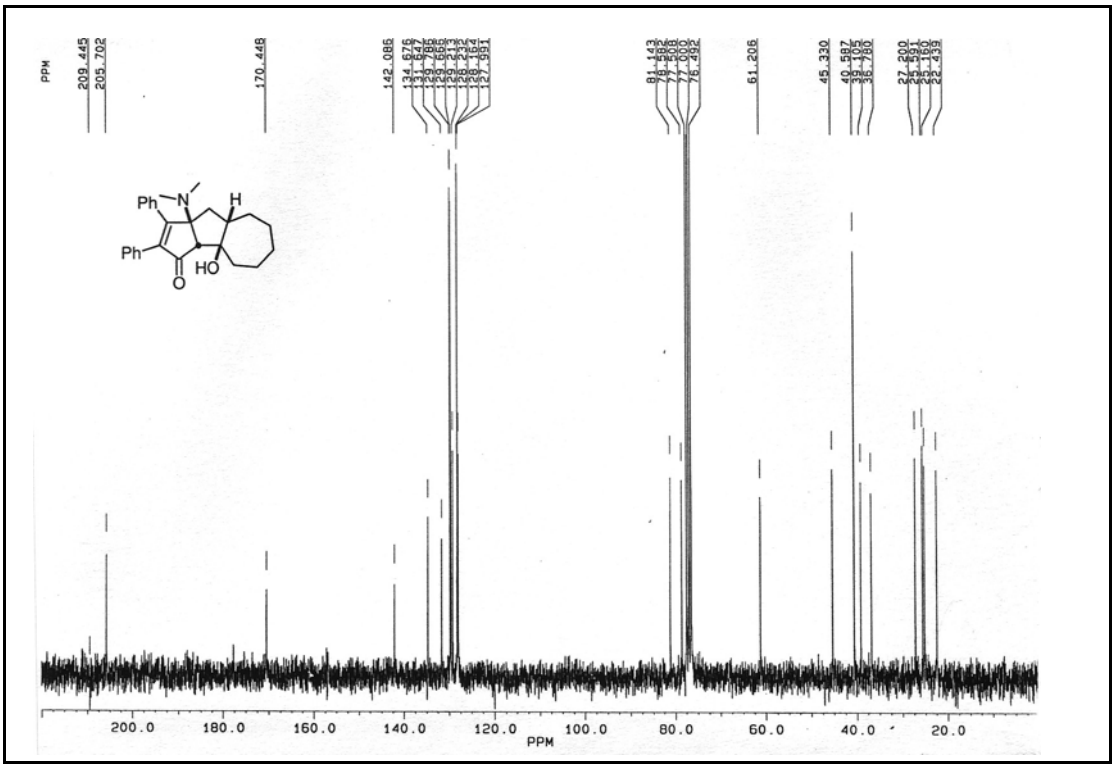
(3aS,3bR,7aS,8aR)/(3aR,3bS,7aR,8aS)-8a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (**127g-I**).



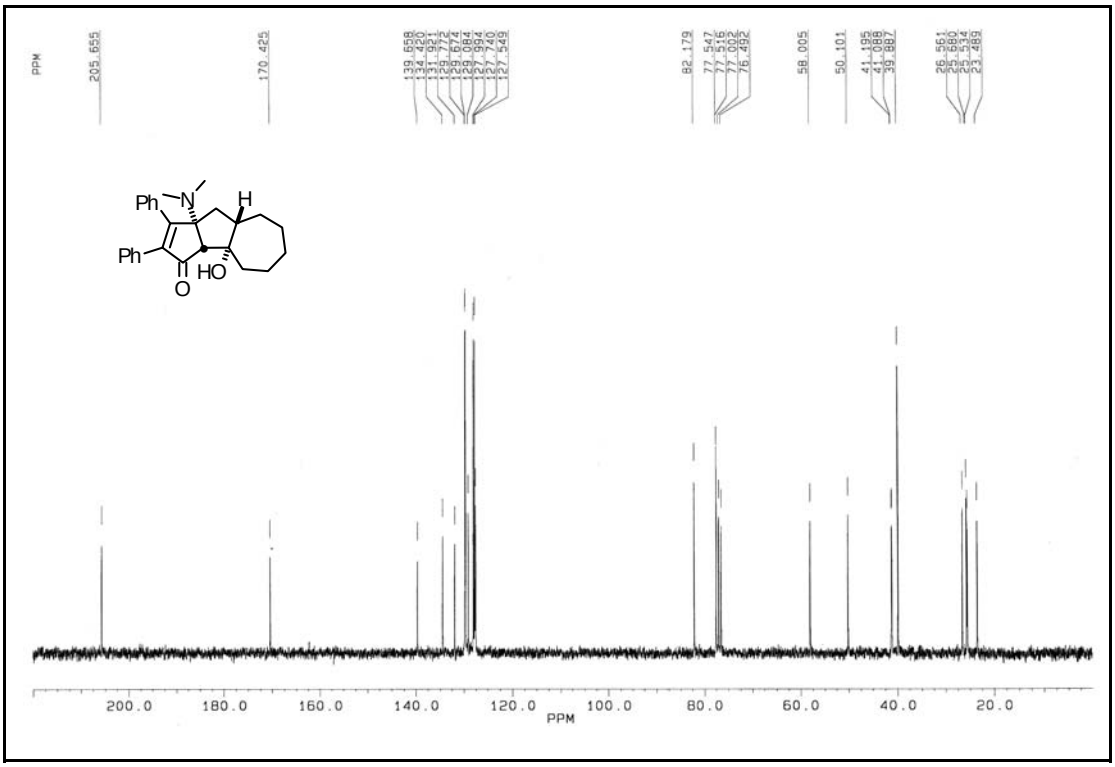
(3aS,3bS,7aR,8aR)/(3aR,3bR,7aS,8aS)-8a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (**127g-II**).



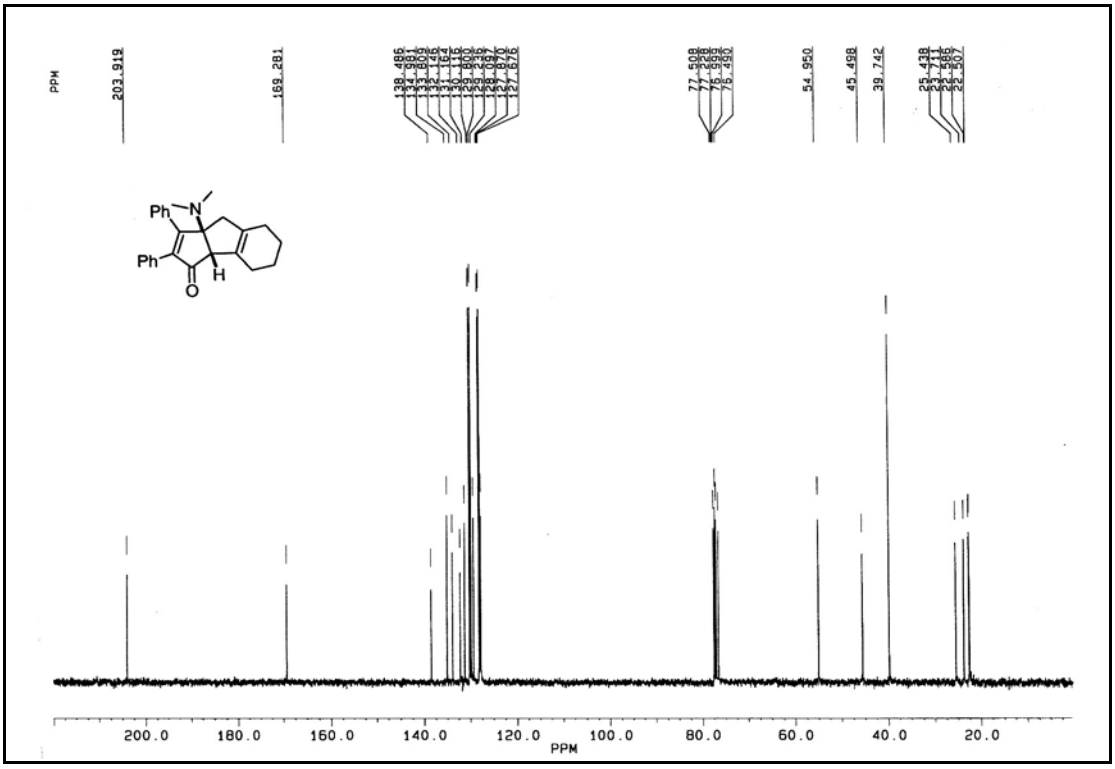
(3aS,3bR,8aS,9aR)/(3aR,3bS,8aR,9aS)-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4, 5,6,7,8,8a,9,9a-decahydro-3*H*-cyclopenta[*a*]azulen-3-one (**127m-I**).



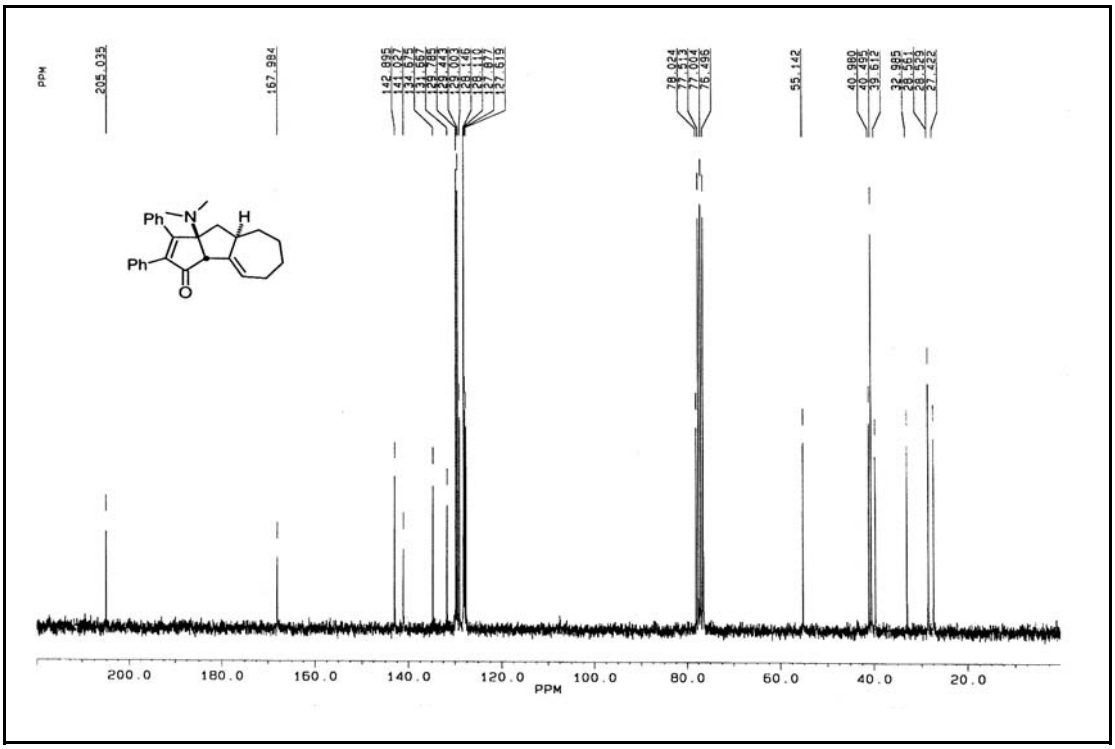
(3aS,3bS,8aR,9aR)/ (*3aR,3bR,8aS,9aS)*-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,7,8,8a,9,9a-decahydro-3*H*-cyclopenta[*a*]azulen-3-one (**127m-II**).



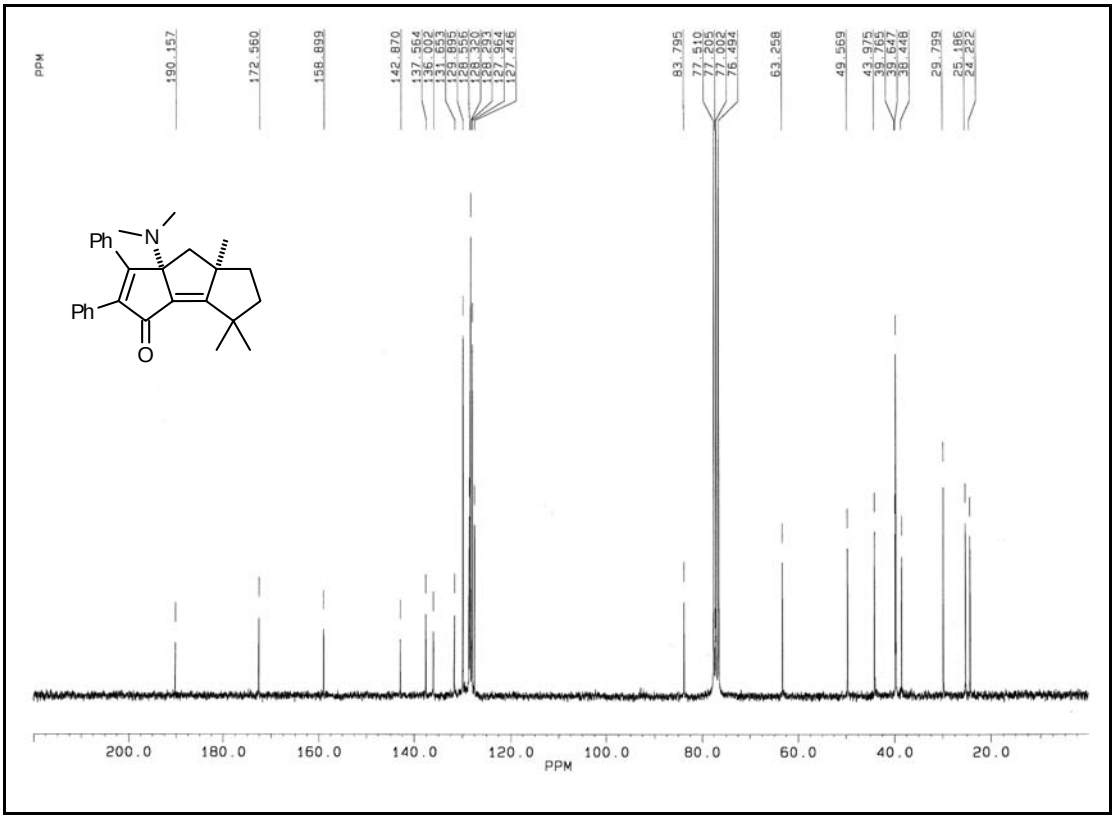
(*3aS*,*3bS*,*8aS*,*9aR*)/(*3aR*,*3bR*,*8aR*,*9aS*)-9a-Dimethylamino-1,2-diphenyl-3b-hydroxy-3a,3b,4,5,6,7,8,8a,9,9a-decahydro-3*H*-cyclopenta[*a*]azulen-3-one (**127m-III**).



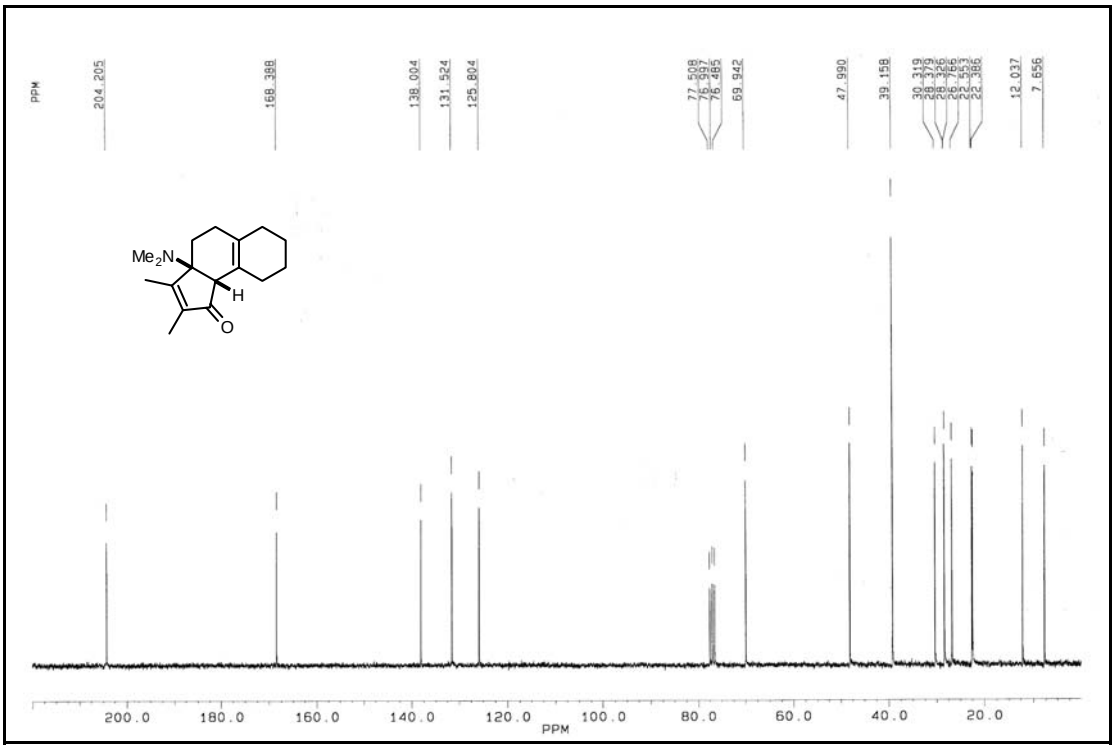
8a-Dimethyamino-1,2-diphenyl-4,5,6,7,7a,8,8a-octahydrocyclopenta[*a*]inden-3-one (**145f**), 62.9 MHz, $CDCl_3$



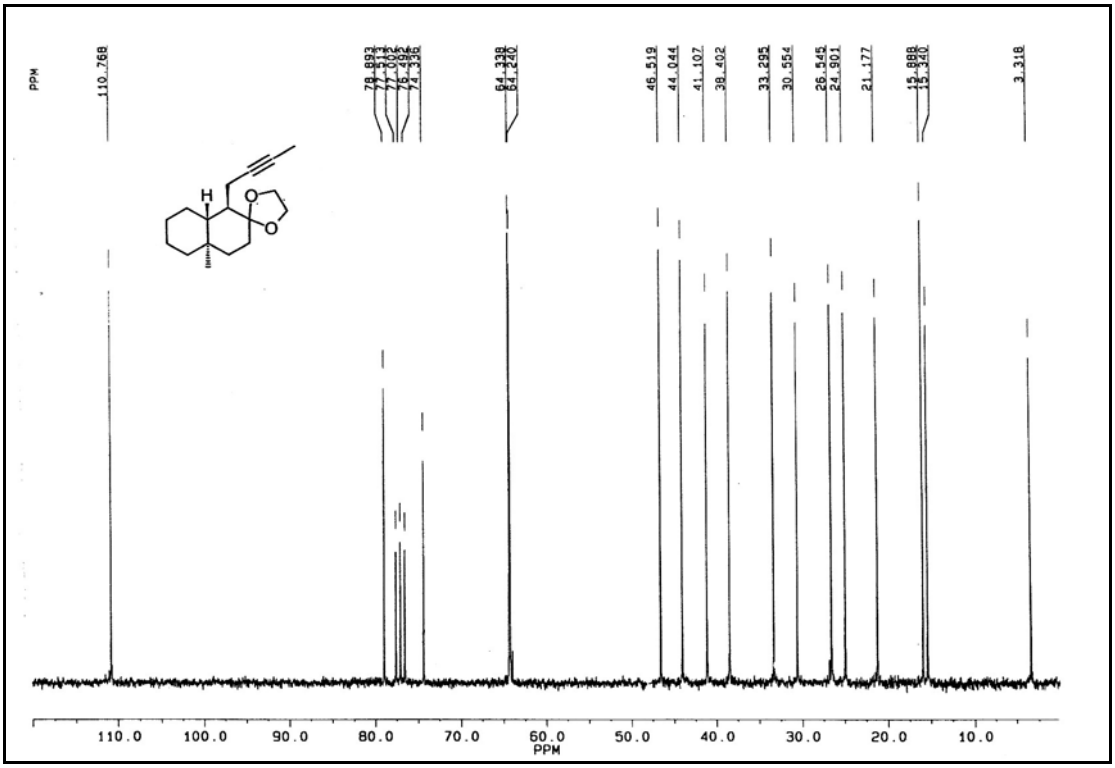
9a-Dimethylamino-1,2-diphenyl-3a,5,6,7,8,8a,9,9a-octahydrocyclopenta[*a*]azulen-3-one (**146m**), 62.9 MHz, $CDCl_3$



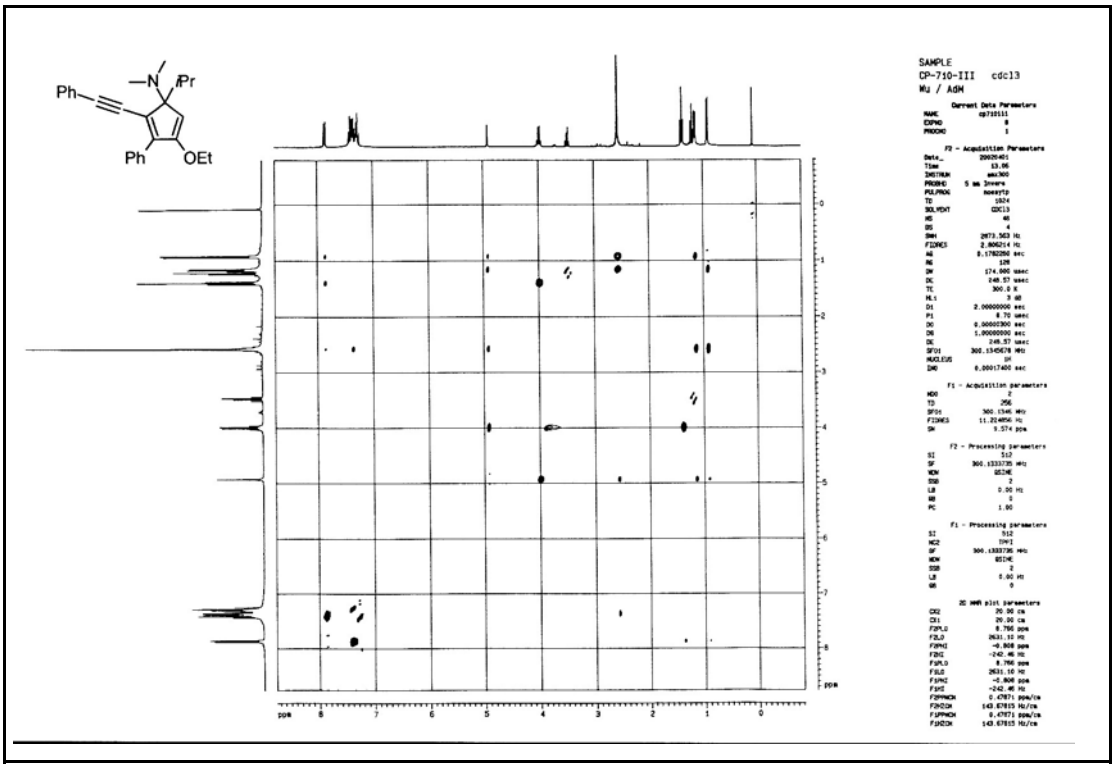
7a-Dimethyamino-4,4,6a-trimethyl-1,2-diphenyl-4,5,6,6a,7,7a-hexahydrocyclopenta-[*a*]pentalen-3-one (**151a**), 62.9 MHz, $CDCl_3$



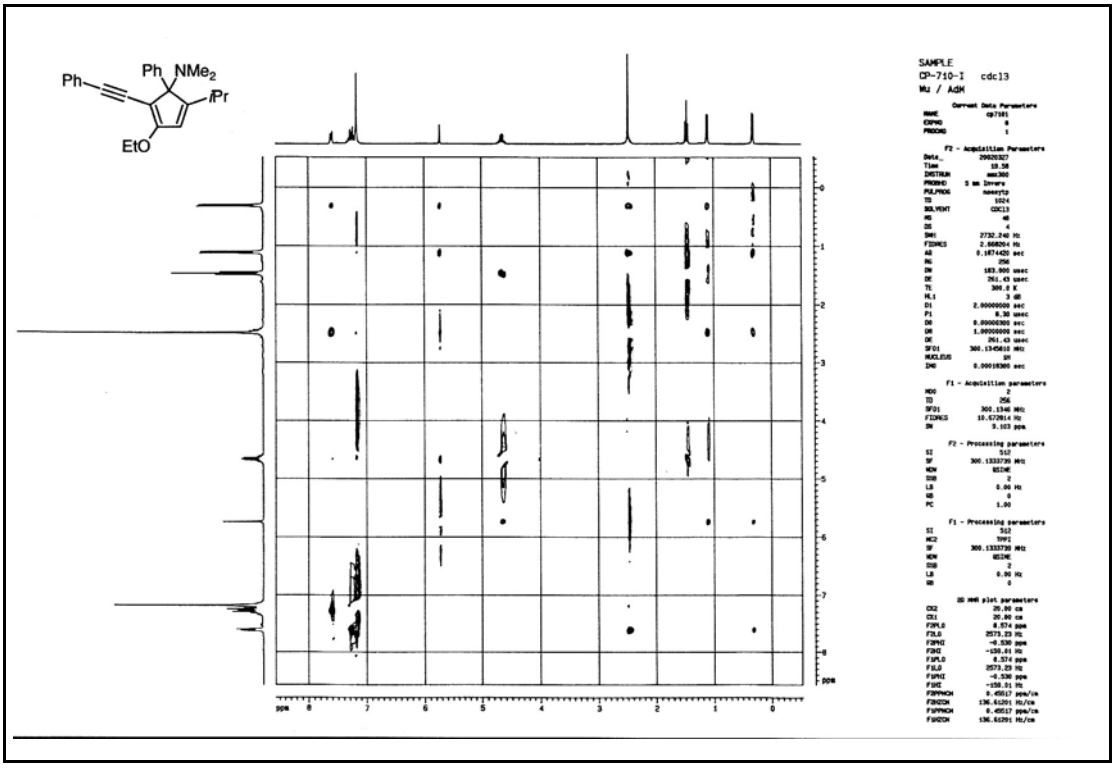
3a-Dimethylamino-2,3-dimethyl-3a,4,5,6,7,8,9,9b-octahydrocyclopenta[*a*]naphthalen-1-one (**154s**), 62.9 MHz, $CDCl_3$



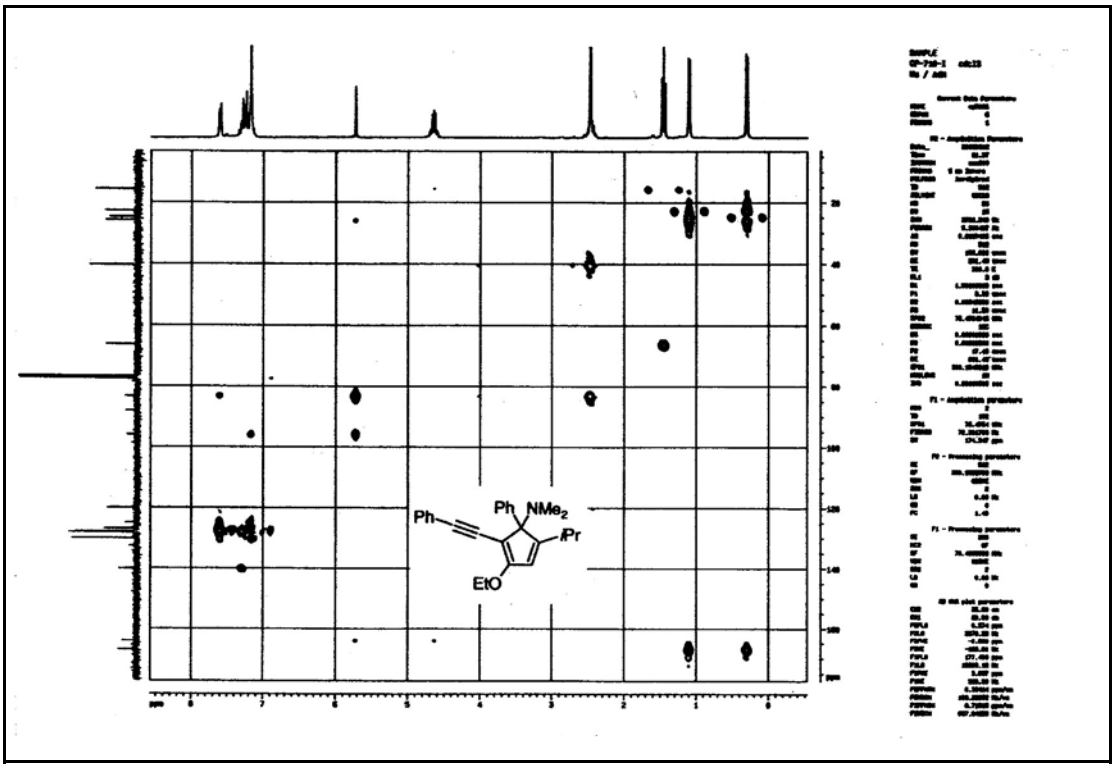
(4a'R,8a'R)-1'-(2"-Butynyl)-4a'-methyl-3-octahydrospiro([1,3]dioxolane-2,2'-naphtalene) (**194**), 62.9 MHz, $CDCl_3$



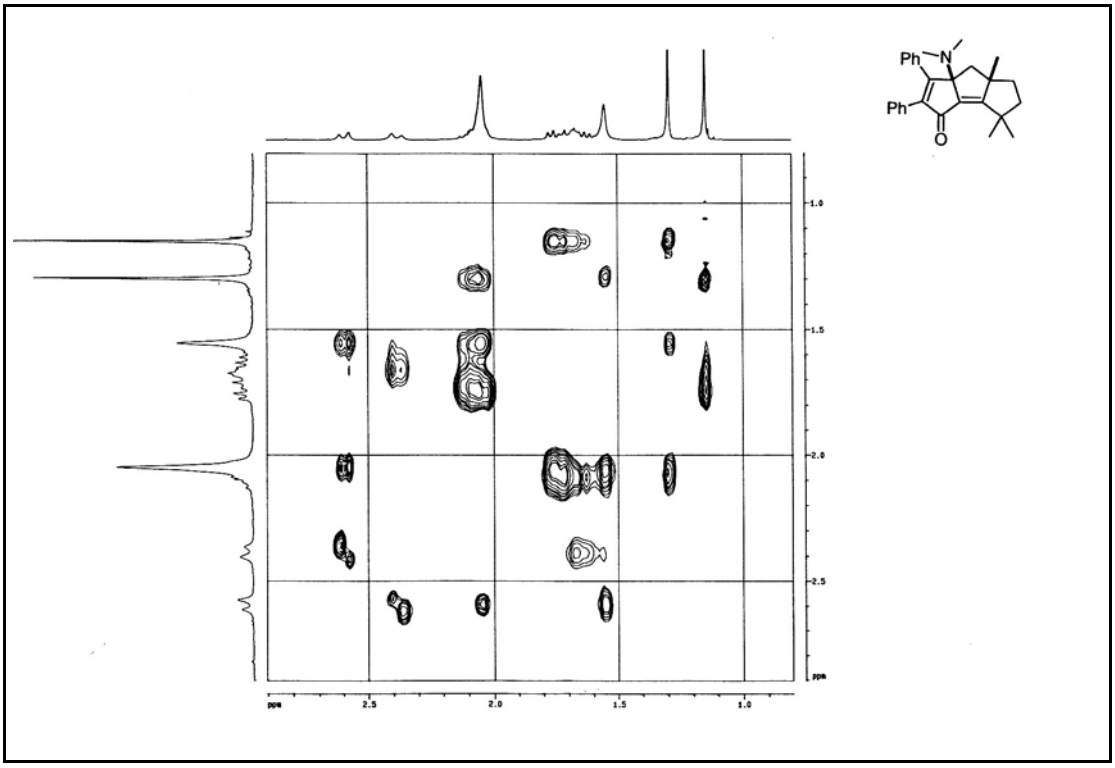
5-Dimethylamino-3-ethoxy-5-isopropyl-2-phenyl-1-phenylethynyl-1,3-cyclopentadiene (**81s**), 300 MHz, $CDCl_3$, HH NOESY.



5-Dimethylamino-2-ethoxy-4-isopropyl-5-phenyl-1-(phenyl-ethynyl)-1,3-cyclopentadiene (**90s**), 300 MHz, $CDCl_3$, HH NOESY.



5-Dimethylamino-2-ethoxy-4-isopropyl-5-phenyl-1-(phenyl-ethynyl)-1,3-cyclopenta-diene (**90s**), 300 MHz, $CDCl_3$, HMBC.



7a-Dimethyamino-4,4,6a-trimethyl-1,2-diphenyl-4,5,6,6a,7,7a-hexahydrocyclopenta-[*a*]pentalen-3-one (**151a**),, 300 MHz, $CDCl_3$, HH NOESY.

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Für den wissenschaftlichen Unterricht dank ich den Herrn Professoren K.-H. Hoyermann, U. Klingelbiel, A. de Meijere, J. Magull und G. F. Karl.

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Für die gute Gemeinschaft und den Spaß innerhalb und außerhalb des Lab P124 möchte ich mich bei André, Gerd und Hermann bedanken.

Lebenslauf

Am 27. Dezember 1972 wurde ich als ältester Sohn des Tierarztes Hsiung-Lung Wu und der Tierärztin Yuh-Yen Chen in Kaohsiung, Taiwan geboren.

Von 1978 bis 1985 besuchte ich die "Chauyung Elementary School" in Pingtung. Anschließend wechselte ich zur "Chengkwang Junior High School" in Tainan. Von 1998 bis 1991 besuchte ich die "Tainan First Senior High School". Anschließend bestand ich das "Joint College Entrance Examination 1991".

Im Jahr 1991 nahm ich das Studium der Chemie an der "National Cheng-Kung University" in Tainan, Taiwan auf. Am 28. Juni 1995 wurde mir der akademische Grad "B. Sc." Zugesprochen. Von Juli 1995 bis zum Juni 1997 leistete ich als Reserve Officer in der Taiwanische Armee meinen Dienst.

Zum Wintersemester 1997/1998 nahm ich das Studium der Chemie an der Georg-August Universität Göttingen auf. Von Februar 1999 bis zum Februar 2000 absolvierte ich unter der wissenschaftlichen Anleitung von Herrn Prof. de Meijere meine Diplomarbeit zum Thema "Neue β-amino-substituierte α,β-ungesättigte Carbenchrom Komplexe: Ein überraschender Zugang zu funktionalisierten 7-Dimethylaminotricyclo[5.2.2.0^{1,6}]undec-10-en-9-onen" an. Am 8. Mai 2000 wurde mir der akademische Grad "Diplom Chemiker" zuerkannt. Danach arbeitete ich in demselben Arbeitskreis an meiner Dissertation mit dem Titel "β-Aminosubstituted α,β-Unsaturated Fischer Carbene Complexes as Precursors for Complex Oligocyclic Molecules – Basics and Applications".

Am 14. Dezember 2000 bekam ich den Gustav-Tammann-Preis für die beste Diplomarbeit 2000 in der Fakultät für Chemie. Im Wintersemester 2002 absolvierte ich erfolgreich einen sechswöchigen Intensivkurs in Pharmakologie und Toxikologie.

Seit August 2000 bin ich als wissenschaftlicher Mitarbeiter angestellt und betreue Studenten im organisch-chemischen Fortgeschrittenpraktikum für Chemiker.

Publications

Journal Articles:

1. H. Schirmer, T. Labahn, B. Flynn, Y.-T. Wu, A. de Meijere, *Synlett* **1999**, 2004.
   "Tricarbonyl(dihydroazepinyl)chromium Complexes and Methylenepyrrolidines from (2'-Dimethylaminoethenyl)carbenechromium Complexes".
2. Y.-T. Wu, H. Schirmer, M. Noltemyer, A. de Meijere, *Eur. J. Org. Chem.* **2001**, 2501.
   "Facile Synthesis of 7-Dimethylaminotricyclo[5.2.2.0^{1,6}]undec-8-en-10-ones from 1-Ethynylcyclohexene via a β-Dimethylaminoethenylcarbenechromium Complex and Alkynes".
3. Y.-T. Wu, B. Flynn, H. Schirmer, F. Funke, S. Müller, T. Labahn, M. Nötzel, A. de Meijere, *Eur. J. Org. Chem.* **2004**, 724.
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