Facile Synthesis of 7-Dimethylamino-*endo*-tricyclo[5.2.2.0^{1,6}]-undec-10-en-9-ones

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Dedicated to Professor Herbert W. Roesky on the occasion of his 65th birthday

Keywords: Carbene complexes / Cyclization / Electrocyclic reactions / Alkynes

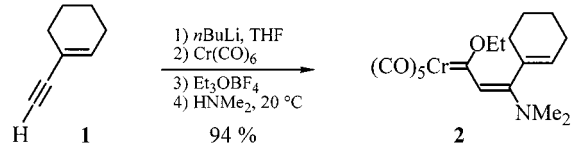
Pentacarbonyl[(2*E*)-3-cyclohexenyl-3-dimethylamino-1-ethoxy-2-propen-1-ylidene]chromium (**2**) yields 7-dimethylamino-*endo*-tricyclo[5.2.2.0^{1,6}]undec-10-en-9-ones **5** (15–88%, 12 examples) upon treatment with alkynes **3** in pyridine, most probably by a 6π-electrocyclization followed by a subsequent reductive elimination/intermolecular Diels–Alder reaction with the alkyne and eventual hydrolysis. The direct cyclization of **2** to the cyclohexane-annelated cyclopentadiene **6** is faster than the usual alkyne insertion of α,β-unsaturated Fischer carbene complexes. The [4+2] cycloadditions of **7** and the added alkynes **3** occur with high degrees of regio- and complete diastereoselectivity.

Introduction

There is now ample evidence that β-amino-substituted, α,β-unsaturated Fischer carbene complexes can serve as versatile reactive building blocks for organic synthesis.[1,2] Many of their reactions are unprecedented in that they do not occur with other α,β-unsaturated Fischer carbenes and/or lead to unusual structures.[3−12] Recently, this repertoire of transformations has been enlarged by Aumann et al. with yet another reaction mode in which β-cycloalkenyl-substituted β-dialkylaminopropenylidene metal complexes undergo a rapid intramolecular insertion of the carbon−carbon into the metal−carbon double bond leading to ring-annelated pentacarbonyl-η^1-cyclopentadienyl metal complexes, which upon heating in pyridine at 70 °C did not yield the uncomplexed alkoxydimethylaminocyclopentadiene, but eventually gave 4,5-ring-annelated 1-dimethylaminocyclopent-1-en-3-ones.[13] This prompted us to report our own results on the reaction of pentacarbonyl(3-cyclohexenyl-3-dimethylamino-1-ethoxypropenylidene)-chromium (**2**) with various alkynes **3**.

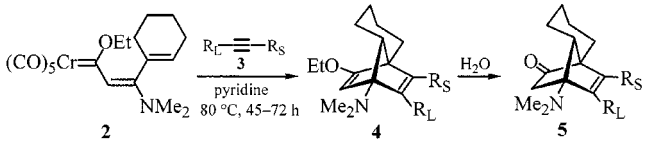
Results and Discussion

The β-dimethylamino-substituted, α,β-unsaturated complex **2** was readily prepared by the new one-pot procedure[4] in excellent yield (overall 94%) from 1-ethynyl-1-cyclohexene (**1**), hexacarbonylchromium, triethyloxonium tetrafluoroborate and dimethylamine in tetrahydrofuran solution (Scheme 1).



Scheme 1. Preparation of the Fischer carbene complex **2** in a one-pot sequence

Upon heating the complex **2** with two equivalents of an alkyne **3** in pyridine[14] at 80 °C for two days, rather nonpolar cycloaddition products **5** were obtained after purification by chromatography (Scheme 2 and Table 1). From the IR, ^{1}H, ^{13}C NMR and mass spectra, it was not possible to assign the structures of these compounds unambiguously. Slow diffusion crystallization of **5d** and **5i** from pentane/diethyl ether afforded good quality single crystals for X-ray structure analyses, and thus their structures were rigorously established (Figure 1).[15]



Scheme 2. For details see Table 1

When the 1-chromahexa-1,3,5-triene **2** without an added alkyne was kept in pyridine at room temperature for 16 h, or at 80 °C for 1 h, it was completely converted into the cyclohexane-annelated cyclopentadiene **8**, the structure of which was assigned on the basis of a NOESY-2D NMR spectrum. No sign of the isomeric diene **9** arising from **8** by a 1,5-hydrogen shift could be detected by ^{1}H and ^{13}C NMR spectroscopy, even at 80 °C.[16] On the other hand, the transformation of complex **2** with added phenylacetylene

[‡] X-ray crystal structure analysis
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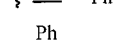
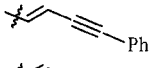
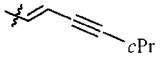
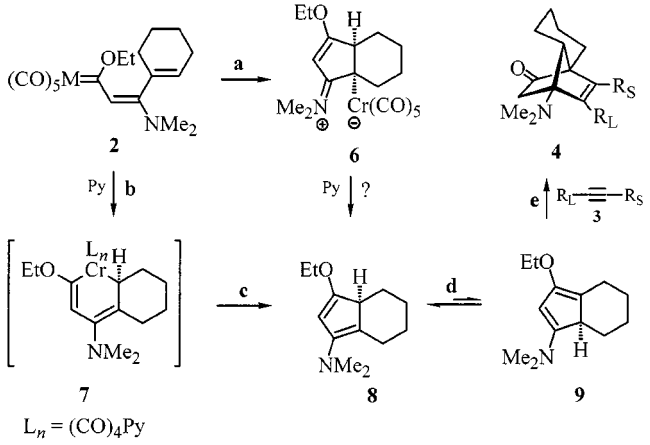
Table 1. Reaction of complex **2** with various alkynes in pyridine at 80 °C

Entry	Alkyne	R_L	R_S	Time [h]	Product	Yield (%)[a]
1	**3a** ≡ **1**	1-cyclohexenyl	H	60	**5a**	40
2	**3b**	1-cyclopentenyl	H	60	**5b**	43
3	**3c**	1-cycloheptenyl	H	60	**5c**	26
4	**3d**	isopropenyl	H	45	**5d**	73
5	**3e**	Ph	H	68	**5e**	88
6	**3f**	4-*n*Pr-C_6H_4	H	64	**5f**	87
7	**3g**	4-EtO-C_6H_4	H	52	**5g**	50
8	**3h**	4-*n*Pr-C_6H_4-C_6H_4	H	60	**5h**	15
9	**3i**		Ph	72	**5i**	60
10	**3j**	Ph	Ph	60	**5j**	0
11	**3k**	4-EtO_2C-C_6H_4	Ph	56	**5k**	66
12	**3l**		Ph	56	**5l**	48
13	**3m**		cPr	60	**5m**	47

[a] Non-optimized isolated yields of purified products based on the complex **2**

(**3e**) in pyridine solution occurred even at room temperature, and 36% of **5e** could be isolated after 68 h, 57% after 68 h at 40 °C, and 71% after 68 h at 60 °C. Thus, **8** apparently rapidly equilibrates with **9** even at room temperature, and the latter preferentially reacts more rapidly than **8** with the added alkynes **3** to afford the [4+2] cycloadducts **4**[17] (Scheme 3). The ethoxy groups of the initial cycloadducts **4** could be clearly observed in the ^1H and ^{13}C NMR spectra of the crude products; hydrolysis of **4** apparently occurred during chromatography, and the ketones **5** were the only isolated products. The other isomers or by-products, with the exception of those of **5i**, were not detected in the ^1H NMR spectra of the crude products, but trace amounts were observed in the thin layer chromatogram.



Scheme 3. On the mechanism for the formation of cycloaddition products **4**; **a**: 1,5-cyclization; **b**: 6π-electrocyclization; **c**: reductive elimination; **d**: 1,5-hydrogen shift; **e**: [4+2] cycloaddition

Aumann et al. have shown that Fischer carbene complexes of type **2** with tungsten undergo 1,5-cyclization to yield η^1-cyclopentadienyl complexes of type **6**, which upon heating in pyridine at 70 °C do not liberate the cyclopentadiene ligand of type **8**. The formation of the cyclohexane-annelated cyclopentadiene **8** from **2** in pyridine thus most probably occurs by 6π-electrocyclization of monodecarbonylated **2** to the pyridine-stabilized chroma-cyclohexadiene **7**, followed by reductive elimination.[1,4] Pyridine is essential as the solvent for this reaction mode of **2** to occur: many by-products and only a trace amount of the cycloadduct **5e** from **2** and phenylacetylene (**3e**) were observed after two days at 60 °C, either in benzene or in tetrahydrofuran, even in the presence of triphenylphosphane.

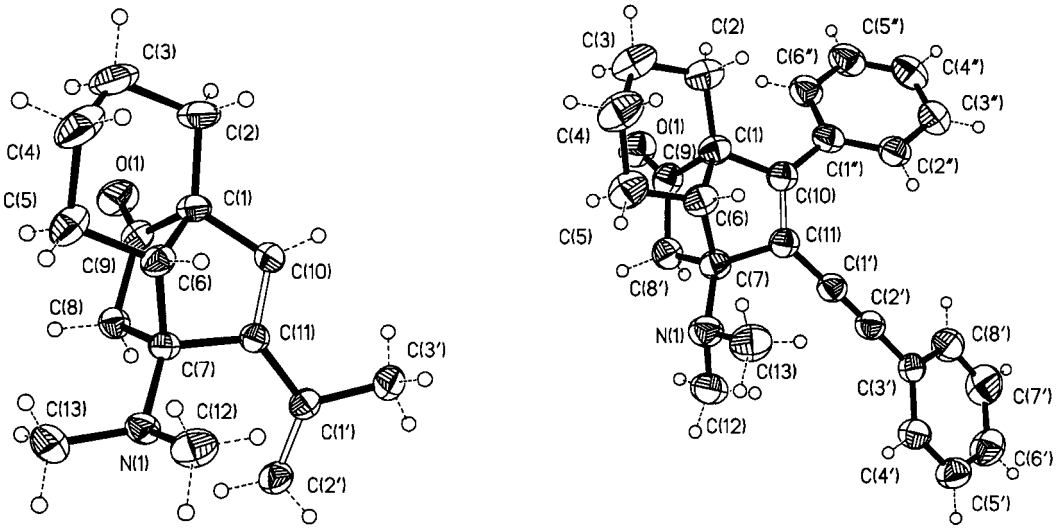
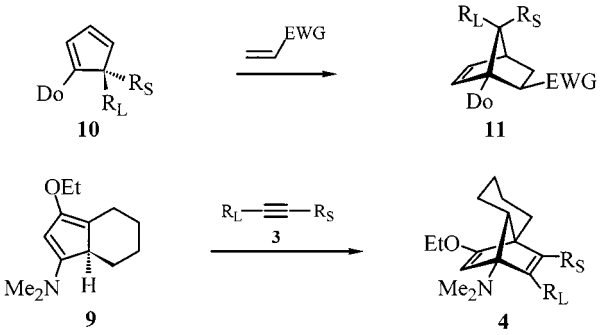


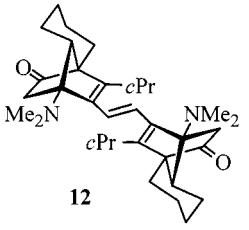
Figure 1. Structures of **5d** (left) and **5i** (right) in the crystals; **5d**: $C_{16}H_{23}NO$, monoclinic crystals of space group $P2_1/c$, unit cell dimensions: a = 9.618(2), b = 10.817(2), c = 13.411(3) Å, β = 98.75(3)°, V = 1379.0(5) Å^3, 3405 reflections; **5i**: $C_{27}H_{27}NO$, triclinic crystals of space group $P\bar{1}$, unit cell dimensions: a = 10.13(3), b = 15.01(4), c = 15.10(3) Å, α = 99.2(2), β = 107.8(2), γ = 96.6(2)°, V = 12125(9) Å^3, 9865 reflections

The regional and facial selectivities in the above Diels−Alder reactions of **8** can be explained on the basis of a model proposed by Winterfeldt (Scheme 4).[18] The applied alkynes **3** add to the more reactive 1,3-diene **9** with *syn*-facial selectivity (with respect to the hydrogen in **9**) and the larger groups R_L obey the *ortho* selectivity (with respect to the dimethylamino group in **9**).[19] The energies, orbital phases and coefficients of LUMOs and HOMOs in the applied alkynes are similar to those in dienophiles with electron-withdrawing substituents.[17]



Scheme 4. Regional and facial selectivities in Diels−Alder reactions; Do: electron-donating group; R_L,R_S: larger and smaller substituent; EWG: electron-withdrawing group

Unfortunately, the range of dienophiles applicable in the cycloaddition to **9** appears to be limited to unsymmetrical alkenyl- and alkynyl-substituted alkynes. Several terminal acetylenes [trimethylsilyl-, *n*-propyl-, isopropyl-, cyclopropyl-, 2′-methoxyethenyl-, and (1′-trimethylsilyl)cyclopropylacetylene] and the symmetrically disubstituted diphenylacetylene (**3j**) did not yield any cycloadduct of type **5**. However, the *p*-phenylethynyl benzoic acid ethyl ester (**3k**) *did* give the tricyclic product **5k** in 66% yield. The enediyne **3m**, even with a 2.2-fold excess of **2**, only gave the monoadduct **5m** (46% yield), and none of the bisadduct **12** could be detected. More typical dienophiles such as methyl propiolate, dimethyl acetylenedicarboxylate and maleic anhydride could not be employed as they react with the pyridine.



Conclusion

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.[20] In pyridine solution, however, the cyclohexenyl-substituted β-dimethylaminopropenylidenechromium complex **2** as a 1-chromahexa-1,3,5-triene apparently undergoes 6π-electrocyclization more rapidly than alkyne insertion. A subsequent reductive elimination then forms the cyclohexane-annelated cyclopentadiene **8**, which equilibrates with **9** by 1,5-hydrogen shift, and the latter preferentially reacts with alkynes **3** to afford single [4+2] cycloadducts **4** in a highly regio- and diastereoselective manner.

Experimental Section

General: ^{1}H and ^{13}C NMR: Bruker AM 250 (250 and 62.9 MHz), Bruker AMX 300 (300 and 75 MHz) and Varian VXR 500 (500 and 125.7 MHz). − IR: Bruker IFS 66 (FT-IR). − Low-resolution EI MS: Varian MAT CH 7, MAT 731, ionizing voltage 70 eV. − High-resolution EI-MS (HR EIMS): Varian MAT 311 A. − X-ray crystal structure determination: the data were collected on a Stoe-Siemens-AED diffractometer. − Melting points were determined with a Büchi melting point apparatus and are uncorrected. − Elemental analysis: Mikroanalytisches Laboratorium der Georg-August-Universität Göttingen. − Chromatography: Merck silica gel 60 (230−400 mesh) or ICN neutral alumina (Super I, Activity II). Solvents for chromatography were technical grade and freshly distilled before use. Tetrahydrofuran was distilled from sodium benzophenone ketyl and pyridine was distilled from calcium hydride. − 1-Ethynyl-1-cyclohexene (**1**),[21] 1-ethynyl-1-cyclopentene (**3b**),[21] 1-ethynyl-1-cycloheptene (**3c**),[21] 2-methylbuten-3-yne (**3d**),[21] 1,4-diphenylbuta-1,3-diyne (**3i**),[21] *p*-phenylethynylbenzoic acid ethyl ester (**3k**),[22] (*E*)-1,2-di(phenylethynyl)ethene (**3l**)[22] and (*E*)-1,2-di(cyclopropylethynyl)ethene (**3m**),[22] were prepared according to published procedures. *p*-Propylphenylethyne (**3f**), *p*-ethoxyphenylethyne (**3g**) and 4-ethynyl-4′-propylbiphenyl (**3h**) were generous gifts from Merck AG.

Pentacarbonyl[(2*E*)-3-cyclohexenyl-3-dimethylamino-1-ethoxy-2-propen-1-ylidene]chromium (2): Complex **2** was prepared adapting a previously published procedure[4] from 1-ethynyl-1-cyclohexene (**1**; 2.50 mL, 21.3 mmol), *n*-butyllithium (2.36 M in *n*-hexane; 8.50 mL, 20.1 mmol), hexacarbonylchromium (4.60 g, 20.9 mmol), triethyloxonium tetrafluoroborate (4.17 g, 21.9 mmol) and gaseous dimethylamine in THF (100 mL). Chromatography on silica gel with pentane to pentane/Et_2O (1:1) afforded 7.56 g (94%) of **2** (R_f = 0.85, Et_2O) as a yellow solid, m.p. (dec.) 85 °C. − IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (C−H), 2045 (C=O), 1893 (C=O), 1426, 1259, 1104, 931, 668. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.47 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.60−1.80 (m, 4 H, 4′,5′-H), 2.00−2.20 (m, 4 H, 3′,6′-H), 3.05 [s, 6 H, $N(CH_3)_2$], 4.66 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.52−5.64 (br. s, 1 H, 2-H), 6.26 (s, 1 H, 2′-H). − ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 15.9 (+, OCH_2CH_3), 21.6, 22.2, 24.8, 27.3 (−, C-3′,4′,5′,6′), 39.5 [+, $N(CH_3)_2$], 74.0 (−, OCH_2CH_3), 117.8 (+, C-2), 126.8 (+, C-2′), 135.2 (C_{quat}, C-1′), 158.4 (C_{quat}, C-3), 220.3 (C_{quat}, CO), 225.0 (C_{quat}, CO), 288.3 (C_{quat}, C-1). − MS (70 eV): *m*/*z* (%) = 399 (16) [M$^+$], 343 (7) [M$^+$ − 2 CO], 315 (4) [M$^+$ − 3 CO], 287 (50) [M$^+$ − 4 CO], 259 (88) [M$^+$ − 5 CO], 229 (18), 220 (32), 213 (78), 207 (100) [M$^+$ − 5 CO − Cr], 178 (72) [M$^+$ − 5 CO − Cr − C_2H_5], 160 (34), 150 (22), 135 (14), 108 (26), 80 (53), 52 (32) [Cr$^+$]. − $C_{18}H_{21}CrNO_6$ (399.4): calcd. C 54.14, H 5.30; found C 53.94, H 5.30.

General Procedure for the Cocyclization of Complexes 2 with Alkynes 3: A thick-walled, screw-cap Pyrex bottle equipped with a magnetic stirring bar was charged with a 0.05 M solution of the complex **2** in anhydrous pyridine. Dry nitrogen was bubbled through the solution for 2 min, and two equiv. of the alkyne **3** were immediately added. The sealed bottle was kept in an oil bath at 80 °C for 2−3 days. The solvent was removed under reduced pressure,

the residue was diluted with Et_2O, and the solution exposed to air for 2 h. The mixture was then filtered, concentrated under reduced pressure, diluted again with pentane/Et_2O (20:1), and kept at −20 °C for 12−24 h in order to crystallize $Cr(CO)_6$ and $Cr(CO)_3Py_3$. The solution was decanted, the solvents were removed under reduced pressure, and the ^1H NMR spectra of these crude products were recorded. Chromatography on aluminum oxide (II) (column 2.5 × 30 cm) with pentane to pentane/Et_2O (3:1) afforded compounds **5**.

11-(1′-Cyclohexenyl)-7-dimethylaminotricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (5a): 1-Ethynyl-1-cyclohexene (**3a**; 0.60 mL, 5.10 mmol) was added to a solution of complex **2** (915 mg, 2.29 mmol) in 50 mL of pyridine, and the mixture was stirred at 80 °C for 60 h. After chromatographic purification, **5a** [257 mg (40%), R_f = 0.80, pentane/Et_2O = 1:1] was obtained as a pale-yellow solid, m.p. 63 °C. − IR (KBr): $\tilde{\nu}$ = 2938 cm^{-1} (C−H), 2862 (C−H), 2826 (C−H), 1739 (C=O), 1653 (C=C), 1457, 1315, 1301, 1114. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.08−2.20 (m, 16 H, 2,3,4,5,3′,4′,5′,6′-H), 1.99 (ABM, dd, ^2J = 16.3, ^4J = 2.4 Hz, 1 H, 8-H), 2.25−2.35 (m, 1 H, 6-H), 2.35 [s, 6 H, $N(CH_3)_2$], 2.57 (AB, d, ^2J = 16.3 Hz, 1 H, 8-H), 5.14 (s, 1 H, 10-H), 6.74 (m, 1 H, 2′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.1, 22.3, 22.8, 23.1, 24.5, 25.72, 25.76, 26.3 (−, C-2,3,4,5,3′,4′,5′,6′), 37.4 (−, C-8), 40.1 [+, $N(CH_3)_2$], 59.2 (+, C-6), 61.2 (C_{quat}, C-1), 74.5 (C_{quat}, C-7), 124.5 (+, C-2′), 125.7 (+, C-10), 131.2 (C_{quat}, C-11), 156.5 (C_{quat}, C-1′), 212.1 (C_{quat}, C-9). − MS (70 eV): *m/z* (%) = 285 (84) [M^+], 270 (76) [$M^+ - CH_3$], 256 (26) [$M^+ - C_2H_5$], 242 (100) [$M^+ - NC_2H_5$], 228 (24), 214 (36), 200 (19), 179 (26), 162 (20), 150 (19), 129 (11), 115 (10), 91 (13), 56 (26), 41 (43). − $C_{19}H_{27}NO$ (285.4): calcd. C 79.96, H 9.54; found C 80.00, H 9.47.

11-(1′-Cyclopentenyl)-7-dimethylaminotricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (5b): 1-Ethynyl-1-cyclopentene (**3b**; 0.51 g, 5.54 mmol) was added to a solution of complex **2** (1.11 g, 2.78 mmol) in 50 mL of pyridine, and the mixture was stirred at 80 °C for 60 h. After chromatographic purification, **5b** [323 mg (43%), R_f = 0.82, pentane/Et_2O = 3:1] was obtained as a pale-yellow solid, m.p. 64 °C. − IR (KBr): $\tilde{\nu}$ = 2934 cm^{-1} (C−H), 2922 (C−H), 2829 (C−H), 1734 (C=O), 1653 (C=C), 1457, 1309, 1115. − ^1H 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). − MS (70 eV): *m/z* (%) = 271 (100) [M^+], 242 (29), 229 (45), 214 (22), 200 (32), 179 (14), 162 (12). − $C_{18}H_{25}NO$ (271.4): calcd. C 79.66, H 9.28; found C 79.32, H 9.02.

11-(1′-Cycloheptenyl)-7-dimethylaminotricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (5c): 1-Ethynyl-1-cycloheptene (**3c**; 0.67 g, 5.57 mmol) was added to a solution of complex **2** (1.13 g, 2.83 mmol) in 50 mL of pyridine, and the mixture was stirred at 80 °C for 60 h. After chromatographic purification, **5c** [220 mg (26%), R_f = 0.56, pentane/Et_2O = 3:1] was obtained as a pale-yellow solid, m.p. 59 °C. − IR (KBr): $\tilde{\nu}$ = 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). − MS (70 eV): *m/z* (%) = 299 (60) [M^+], 284 (100) [$M^+ - CH_3$], 270 (14), 256 (49), 179 (23), 150 (10), 84 (23). − $C_{20}H_{29}NO$: calcd. 299.2249; found 299.2249 (HR EIMS).

7-Dimethylamino-11-(2′-propenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (5d): 2-Methylbuten-3-yne (**3d**; 0.56 mL, 6.01 mmol) was added to a solution of complex **2** (1.21 g, 3.03 mmol) in 60 mL of pyridine, and the mixture was stirred at 80 °C for 45 h. After chromatographic purification, **5d** [538 mg (73%), R_f = 0.80, pentane/Et_2O = 1:1] was obtained as a colorless solid, m.p. 79 °C. − IR (KBr): $\tilde{\nu}$ = 2932 cm^{-1} (C−H), 1734 (C=O), 1670 (C=C), 1447, 1305, 1114, 1077, 900, 845. − ^1H NMR (250 MHz, $CDCl_3$, plus CH and HH COSY): δ = 1.03−1.36 (m, 4 H, 2,3,4,5-H), 1.51−1.59 (m, 1 H, 3-H), 1.59−1.66 (m, 1 H, 4-H), 1.77 (s, 3 H, CH_3), 1.76−1.84 (m, 1 H, 5-H), 1.97 (ABM, dd, ^2J = 16.3, ^4J = 2.4 Hz, 1 H, 8-H), 2.15−2.21 (m, 1 H, 2-H), 2.28−2.36 (m, 1 H, 6-H), 2.36 [s, 6 H, $N(CH_3)_2$], 2.58 (AB, d, ^2J = 16.3 Hz, 1 H, 8-H), 4.90 (AB, d, ^2J = 2.8 Hz, 1 H, 1′-H), 5.58 (s, 1 H, 10-H), 5.92 (AB, d, ^2J = 2.8 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **δ** = 21.2 (+, CH_3), 22.0, 23.0, 24.4, 26.3 (−, C-2,3,4,5), 37.0 (−, C-8), 40.1 [+, $N(CH_3)_2$], 59.3 (+, C-6), 61.6 (C_{quat}, C-1), 74.5 (C_{quat}, C-7), 114.1 (−, C-1′), 128.1 (+, C-10), 137.2 (C_{quat}, C-11), 156.1 (C_{quat}, C-2′), 212.0 (C_{quat}, C-9). − MS (70 eV): *m/z* (%) = 245 (64) [M^+], 230 (58) [$M^+ - CH_3$], 216 (18) [$M^+ - C_2H_5$], 202 (100) [$M^+ - NC_2H_5$], 188 (26), 174 (18), 150 (16), 115 (10), 91 (14). − $C_{16}H_{23}NO$ (245.4): calcd. C 78.32, H 9.45; found C 78.26, H 9.52.

7-Dimethylamino-11-phenyltricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (5e): Phenylethyne (**3e**; 0.78 mL, 7.10 mmol) was added to a solution of complex **2** (1.41 g, 3.53 mmol) in 70 mL of pyridine, and the mixture stirred at 80 °C for 68 h. After purification, **5e** [869 mg (88%), R_f = 0.68, pentane/Et_2O = 2:1] was obtained as a colorless solid, m.p. 120 °C. − IR (KBr): $\tilde{\nu}$ = 2936 cm^{-1} (C−H), 1734 (C=O), 1653 (C=C), 1461, 1442, 1303, 1044, 754, 693. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.13−1.47 (m, 4 H, 2,3,4,5-H), 1.60−1.70 (m, 1 H, 3-H), 1.70−1.78 (m, 1 H, 4-H), 1.82−1.91 (m, 1 H, 5-H), 2.26 (ABM, dd, ^2J = 16.4, ^4J = 2.4 Hz, 1 H, 8-H), 2.30−2.38 (m, 1 H, 2-H), 2.38 [s, 6 H, $N(CH_3)_2$], 2.46−2.57 (m, 1 H, 6-H), 2.74 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 5.86 (s, 1 H, 10-H), 7.23−7.33 (m, 3 H, Ph-H), 7.60−7.64 (m, 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 (−, C-8), 40.0 [+, $N(CH_3)_2$], 59.6 (+, C-6), 62.0 (C_{quat}, C-1), 74.3 (C_{quat}, C-7), 125.1 (+, Ph-C), 127.3 (+, Ph-C), 127.9 (+, Ph-C), 129.2 (+, C-10), 135.4 (C_{quat}, C-11), 156.3 (C_{quat}, C-Ph), 211.8 (C_{quat}, C-9). − MS (70 eV): *m/z* (%) = 281 (100) [M^+], 253 (72) [$M^+ - CO$], 239 (77) [$M^+ - C_3H_6$], 224 (18), 210 (38), 179 (22), 162 (24), 150 (18), 115 (14), 91 (10). − $C_{19}H_{23}NO$ (281.4): calcd. C 81.10, H 8.24; found C 81.06, H 8.03.

7-Dimethylamino-11-(4′-propylphenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (5f): *p*-Propylphenylethyne (**3f**; 0.90 mL, 5.62 mmol) was added to a solution of complex **2** (1.15 g, 2.88 mmol) in 60 mL of pyridine, and the mixture stirred at 80 °C for 64 h. After purification, **5f** [810 mg (87%), R_f = 0.70, pentane/Et_2O = 2:1] was obtained as a colorless solid, m.p. 52 °C. − IR (KBr): $\tilde{\nu}$ = 2835 cm^{-1} (C−H), 1738 (C=O), 1503, 1458, 1306, 1237, 905, 814, 804. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.5 Hz, 3 H, Pr-CH_3), 1.25−1.45 (m, 4 H, 2,3,4,5-H), 1.57−1.74 (m, 2 H, 3,4-H), 1.65

(sex, ^3J = 7.4 Hz, 2 H, Pr-CH_2), 1.80−1.90 (m, 1 H, 5-H), 2.24 (ABM, dd, ^2J = 16.5, ^4J = 2.2 Hz, 1 H, 8-H), 2.27−2.35 (m, 1 H, 2-H), 2.39 [s, 6 H, N(CH_3)$_2$], 2.49−2.55 (m, 1 H, 6-H), 2.57 (t, ^3J = 7.4 Hz, 2 H, Pr-CH_2), 2.73 (AB, d, ^2J = 16.5 Hz, 1 H, 8-H), 5.82 (s, 1 H, 10-H), 7.11 (d, ^3J = 8.2 Hz, 2 H, Ph-H), 7.57 (d, ^3J = 8.2 Hz, 2 H, Ph-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.6 (+, Pr-CH_3), 22.0, 22.8, 24.2 × 2, 25.9 (−, C-2,3,4,5, Pr-CH_2), 36.9 (−, Pr-CH_2), 37.6 (−, C-8), 39.9 [+, N(CH_3)$_2$], 59.4 (+, C-6), 61.7 (C_{quat}, C-1), 74.1 (C_{quat}, C-7), 124.9, 127.8 (+, C-2′,3′), 128.1 (+, C-10), 132.6 (C_{quat}, C-11), 141.7 (C_{quat}, C-4′), 156.1 (C_{quat}, C-1′), 211.3 (C_{quat}, C-9). − MS (70 eV): *m*/*z* (%) = 323 (94) [M$^+$], 295 (100) [M$^+$ − CO], 281 (82) [M$^+$ − C_3H_6], 252 (27), 209 (23), 162 (30), 154 (25), 150 (13), 70 (18). − $C_{22}H_{29}NO$ (323.5): calcd. C 81.69, H 9.04; found C 80.77, H 9.09.

7-Dimethylamino-11-(4′-ethoxyphenyl)tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (5g): *p*-Ethoxyphenylethyne (**3g**; 0.45 mL, 4.77 mmol) was added to a solution of complex **2** (0.99 g, 2.48 mmol) in 50 mL of pyridine, and the mixture stirred at 80 °C for 52 h. After purification, **5g** [401 mg (50%), R_f = 0.60, pentane/Et_2O = 2:1] was obtained as a yellow solid, m.p. 101 °C. − IR (KBr): $\tilde{\nu}$ = 2928 cm^{-1} (C−H), 1738 (C=O), 1609 (C=C), 1565 (C=C), 1508, 1249, 1046, 811. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.16−1.47 (m, 4 H, 2,3,4,5-H), 1.39 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$CH_3), 1.55−1.64 (m, 1 H, 3-H), 1.64−1.75 (m, 1 H, 4-H), 1.80−1.91 (m, 1 H, 5-H), 2.22 (ABM, dd, ^2J = 16.4, ^4J = 2.3 Hz, 1 H, 8-H), 2.24−2.32 (m, 1 H, 2-H), 2.38 [s, 6 H, N(CH_3)$_2$], 2.44−2.53 (m, 1 H, 6-H), 2.71 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 4.01 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH$_3$), 5.75 (s, 1 H, 10-H), 6.81 (d, ^3J = 8.6 Hz, 2 H, Ph-H), 7.58 (d, ^3J = 8.6 Hz, 2 H, Ph-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.7 (+, OCH$_2$CH_3), 22.2, 23.0, 24.4, 26.1 (−, C-2,3,4,5), 37.2 (−, C-8), 40.0 [+, N(CH_3)$_2$], 59.6 (+, C-6), 61.7 (C_{quat}, C-1), 63.2 (−, OCH_2CH$_3$), 74.2 (C_{quat}, C-7), 113.9, 126.5 (+, C-2′,3′), 126.9 (+, C-10), 127.8 (C_{quat}, C-4′), 155.9 (C_{quat}, C-1′), 158.5 (C_{quat}, C-11), 211.9 (C_{quat}, C-9). − MS (70 eV): *m*/*z* (%) = 325 (100) [M$^+$], 297 (66) [M$^+$ − CO], 283 (66) [M$^+$ − C_3H_6], 268 (18), 254 (20), 207 (18), 179 (26), 162 (26), 149 (24), 91 (16), 84 (26), 57 (13), 41 (13). − $C_{21}H_{27}NO_2$ (325.5): calcd. C 77.50, H 8.36; found C 77.16, H 8.10.

7-Dimethylamino-11-(4′′-propylbiphenyl-4′-yl)tricyclo[5.2.2.0^{1,6}]-undec-10-en-9-one (5h): 4-Ethynyl-4′-propylbiphenyl (**3h**; 898 mg, 4.08 mmol) was added to a solution of complex **2** (1.10 g, 2.75 mmol) in 55 mL of pyridine, and the mixture stirred at 80 °C for 60 h. After purification, **5h** [165 mg (15%), R_f = 0.73, pentane/Et_2O = 10:1] was obtained as a yellow solid, m.p. 113 °C. − IR (KBr): $\tilde{\nu}$ = 2933 cm^{-1} (C−H), 1734 (C=O), 1653 (C=C), 1496 (C=C), 1457, 1306, 1245, 804. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00 (t, ^3J = 7.3 Hz, 3 H, CH$_2$CH_3), 1.15−1.46 (m, 4 H, 2,3,4,5-H), 1.66−1.78 (m, 2 H, 3,4-H), 1.70 (sex, ^3J = 7.3 Hz, 2 H, CH$_2$CH_2CH$_3$), 1.89−1.95 (m, 1 H, 5-H), 2.29 (ABM, dd, ^2J = 16.4, ^4J = 2.3 Hz, 1 H, 8-H), 2.33−2.43 (m, 1 H, 2-H), 2.44 [s, 6 H, N(CH_3)$_2$], 2.50−2.62 (m, 1 H, 6-H), 2.65 (t, ^3J = 7.3 Hz, 2 H, CH_2CH$_2$CH$_3$), 2.79 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 5.93 (s, 1 H, 10-H), 7.26 (d, ^3J = 8.2 Hz, 2 H, Ph-H), 7.54 (d, ^3J = 8.2 Hz, 2 H, Ph-H), 7.55 (d, ^3J = 8.2 Hz, 2 H, Ph-H), 7.59 (d, ^3J = 8.2 Hz, 2 H, Ph-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **δ** = 13.9 (+, CH$_2$CH$_2$CH_3), 22.3, 23.1, 24.5, 26.2 (−, C-2,3,4,5), 24.6 (−, CH$_2$CH_2CH$_3$), 37.1 (−, C-8), 37.7 (−, CH_2CH$_2$CH$_3$), 40.3 [+, N(CH_3)$_2$], 59.8 (+, C-6), 62.2 (C_{quat}, C-1), 74.5 (C_{quat}, C-7), 125.7 (+, Ph-C), 126.5 (+, Ph-C), 126.7 (+, Ph-C), 128.9 (+, Ph-C), 129.2 (+, C-10), 134.2 (C_{quat}, Ph-C), 138.1 (C_{quat}, Ph-C), 140.2 (C_{quat}, Ph-C), 141.9 (C_{quat}, Ph-C), 156.1 (C_{quat}, C-11), 212.0 (C_{quat}, C-9). − MS (70 eV): *m*/*z* (%) = 399 (100) [M$^+$], 371 (90) [M$^+$ − CO], 357 (73) [M$^+$ − C_3H_6], 328 (18), 279 (10), 191 (18), 179 (32), 162 (32), 149 (75), 91 (10), 74 (14), 59 (22), 41 (18). − $C_{28}H_{33}NO$ (399.6): calcd. C 84.17, H 8.32; found C 84.07, H 8.33.

7-Dimethylamino-10-phenyl-11-phenylethinyltricyclo[5.2.2.0^{1,6}]-undec-10-en-9-one (5i): 1,4-Diphenylbuta-1,3-diyne (**3i**; 825 mg, 4.08 mmol) was added to a solution of complex **2** (1.05 g, 2.63 mmol) in 50 mL of pyridine, and the mixture was stirred at 80 °C for 72 h. After chromatography, a mixture of **4i**, **5i** and their regioisomers [814 mg (81%)] was obtained as a pale yellow oil. Crystallization from pentane/Et_2O (20:1) at −20 °C afforded 603 mg (60%) of **5i** (R_f = 0.09, pentane/Et_2O = 10:1) as colorless crystals (m.p. 119 °C). − IR (KBr): $\tilde{\nu}$ = 2927 cm^{-1} (C−H), 1741 (C=O), 1598 (C=C), 1442, 1310, 1131, 1026, 767, 756, 691. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06−1.39 (m, 4 H, 2,3,4,5-H), 1.62−1.78 (m, 3 H, 3,4,5-H), 2.46 (AB, d, ^2J = 16.4 Hz, 1 H, 8-H), 2.50−2.56 (m, 2 H, 2,6-H), 2.59 (ABM, dd, ^2J = 16.4, ^4J = 2.1 Hz, 1 H, 8-H), 2.81 [s, 6 H, N(CH_3)$_2$], 7.24−7.46 (m, 10 H, Ph-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 22.6, 22.7, 23.6, 23.7 (−, C-2,3,4,5), 39.8 (−, C-8), 40.1 [+, N(CH_3)$_2$], 61.8 (+, C-6), 65.2 (C_{quat}, C-1), 74.0 (C_{quat}, C-7), 85.8 (C_{quat}, C-1′), 100.0 (C_{quat}, C-2′), 123.3 (+, Ph-C), 127.6 (+, Ph-C), 127.8 (+, Ph-C), 127.9 (+, Ph-C), 128.3 (+, Ph-C), 128.4 (C_{quat}, C-10), 131.0 (+, Ph-C), 132.3 (C_{quat}, Ph-C), 133.9 (C_{quat}, Ph-C), 151.4 (C_{quat}, C-11), 212.0 (C_{quat}, C-9). − MS (70 eV): *m*/*z* (%) = 381 (25) [M$^+$], 353 (11) [M$^+$ − CO], 339 (100) [M$^+$ − C_3H_6], 178 (10). − $C_{27}H_{27}NO$ (381.5): calcd. C 85.00, H 7.13; found C 85.35, H 7.06.

7-Dimethylamino-11-(4′-ethoxycarbonylphenyl)-10-phenyltricyclo-[5.2.2.0^{1,6}]undec-10-en-9-one (5k): *p*-Phenylethynyl benzoic acid ethyl ester (**3k;** 705 mg, 2.82 mmol) was added to a solution of complex **2** (815 mg, 2.04 mmol) in 40 mL of pyridine, and the mixture stirred at 80 °C for 56 h. After purification, **5k** [581 mg (66%), R_f = 0.25, pentane/Et_2O = 3:1] was obtained as a colorless solid, m.p. 78 °C. − IR (KBr): $\tilde{\nu}$ = 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$_2$CH_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$_2$CH_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). − MS (70 eV): *m*/*z* (%) = 429 (22) [M$^+$], 401 (17) [M$^+$ − CO], 387 (100) [M$^+$ − C_3H_6], 178 (30), 150 (7), 91 (9). − $C_{28}H_{31}NO_3$: calcd. 429.2304; found 429.2303 (HR EIMS).

7-Dimethylamino-10-phenyl-11-(4′-phenyl-1′-buten-3′-ynyl)-tricyclo[5.2.2.0^{1,6}]undec-10-en-9-one (5l): (*E*)-1,2-Di(phenylethynyl)ethene (**3l**; 535 mg, 2.34 mmol) was added to a solution of complex **2** (958 mg, 2.40 mmol) in 50 mL of pyridine, and the mixture stirred at 80 °C for 56 h. After purification, **5l** [461 mg (48%), R_f = 0.55, pentane/Et_2O = 3:1] was obtained as a pale-yellow solid, m.p. 132 °C. − IR (KBr): $\tilde{\nu}$ = 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). − MS (70 eV): *m*/*z* (%) = 407 (53) [M^+], 365 (100) [$M^+ - C_3H_6$], 336 (14), 178 (48), 150 (12). − $C_{29}H_{29}NO$ (407.6): calcd. 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 (5m): (*E*)-1,2-Di(cyclopropylethynyl)ethene (**3m**; 247 mg, (1.58 mmol) was added to a solution of complex **2** (1.41 g, 3.53 mmol) in 40 mL of pyridine, and the mixture stirred at 80 °C for 60 h. After purification, **5m** [251 mg (47%), R_f = 0.45, pentane/Et_2O = 3:1] was obtained as a colorless solid, m.p. 187 °C. − IR (KBr): $\tilde{\nu}$ = 2934 cm^{-1} (C−H), 1732 (C=O), 1458, 1311, 1026, 966, 891. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.40−0.55 (m, 2 H, *c*Pr), 0.62−0.85 (m, 6 H, *c*Pr), 1.02−1.29 (m, 4 H, 2,3,4,5-H), 1.33−1.45 (m, 2 H, *c*Pr), 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). − MS (70 eV): *m*/*z* (%) = 335 (43) [M^+], 320 (14), 293 (53) [$M^+ - C_3H_6$], 278 (46), 178 (100), 150 (26). − $C_{23}H_{29}NO$ (335.5): calcd. C 82.34, H 8.71; found C 82.58, H 8.66.

1-Dimethylamino-3-ethoxy-3a*H*-tetrahydroindene (8): A solution of complex **2** (10 mg) in 0.5 mL of [D_5]pyridine under nitrogen was kept at room temp. 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, 3a-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-3a), 65.4 (−, OCH_2CH_3), 94.6 (+, C-2), 107.5 (−, C-7a), 150.0 (−, C-1), 160.9 (−, C-3).

Acknowledgments

This work was supported by the Volkswagen-Stiftung and the Fonds der Chemischen Industrie. Generous gifts of chemicals by BASF, Bayer, Degussa-Hüls and Merck AG have been provided. The authors are grateful to Dr. Burkhard Knieriem for his careful proofreading of the final manuscript.

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Received January 18, 2001
[O01023]