A New Access to Multifunctional Linear Triquinanes and Their Homologues via α,β-Unsaturated Fischer Carbene Complexes

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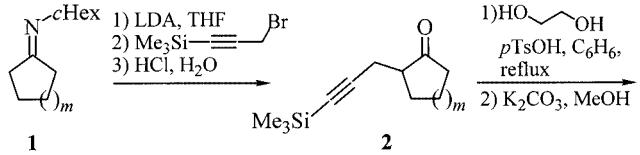
Twelve differently substituted tricyclic hydroxy ketones **7**, **8** with [5-5-x] (x = 5, 6, 7) combinations of ring sizes were prepared in a single step in 43–91 % yields (10 examples with 74–91 %) from the corresponding protected (2′-oxocycloalkyl)methyl-substituted cyclopentadienes **6**, which were obtained by cocyclization of the alkynes **5** with the β-dimethylamino-substituted α,β-unsaturated Fischer carbene complexes **4** in 38–81 % yield (6 examples with 66–81 %). In most cases, the *cis,anti,cis*-isomers *anti*-**7** were the major products. While the twofold *cis*-fusion is favored by minimal ring strain, hydrogen bonding between the hydroxy and the carbonyl group probably favors the *anti*-configuration of the tricyclic skeletons. Acid-catalyzed dehydration of the hydroxy ketones *anti*-**7aa**, *anti*-**7ba**, *anti*-**7ca** afforded the corresponding tricyclic dienes **15aa/16aa**, **15ba**, and **15ca/16ca**, respectively.

Introduction

Our recently published [3+2] cocyclization of β-dialkylamino-substituted α,β-unsaturated Fischer carbene chromium complexes and alkynes to yield 5-dialkylamino-3-ethoxycyclopentadienes, which essentially are protected cyclopentenones,[1,2] also provided facile access to highly substituted bicyclo[3.3.0]oct-2-en-4-ones (diquinanes) via such cyclopentadienes with a carbonyl-protected oxoalkyl side-chain, subsequent acid-catalyzed deprotection of both carbonyl groups and intramolecular aldol reaction.[3] This overall transformation can essentially be carried out in a one-pot operation. As an extrapolation of this methodology, linear triquinanes,[4] i.e. skeletons consisting of linearly annelated five-membered carbocycles, should be accessible from protected (2′-oxocycloalkyl)methyl-substituted Fischer carbene complexes and alkynes. Therefore, we embarked on a study of the chemo- and stereoselectivities in the formation of such tricycles as well as their homologues by this approach.

Results and Discussion

Adopting a published procedure,[5,6] 2-(trimethylsilylpropargyl)cycloalkanones **2a**–**c** were prepared from cycloalkanone *N*-cyclohexylimides **1a**–**c**, and converted in two steps into the 2-propargylcycloalkanone ethylene acetals **3a**–**c** (Scheme 1). According to the previously published one-pot procedure,[2,3] the terminal acetylenes **3a**–**c** were transformed to the β-dimethylamino-substituted α,β-unsaturated Fischer carbene complexes **4a**–**c** containing acetal-protected (2′-oxocycloalkyl)methyl substituents.



Entry	*m*	**2** (%)	**3** (%)	**4** (%)
a	1	55	48	83
b	2	47[a]	87	87
c	3	67	82	54

[a] Prepared according to ref. [6]

Scheme 1. Synthesis of β-dimethylamino-substituted α,β-unsaturated Fischer carbene complexes **4**.

Upon heating the complexes of type **4a**–**c** with various alkynes **5** in pyridine at 80 °C for 3 d, cyclopentadienes **6** were formed in 38–81 % yields (Scheme 2). Alkynes with bulky substituents like trimethylsilylethyne (**5b**) and 3,3-dimethylbut-1-yne (**5f**), gave low yields (45 and 38 %, respectively). The cocyclizations occurred without any significant diastereoselectivity. Upon treatment of these ethoxycyclopentadienes **6** with concd. hydrochloric acid in dioxane at ambient temperature, cleavage of the enol ether as well as

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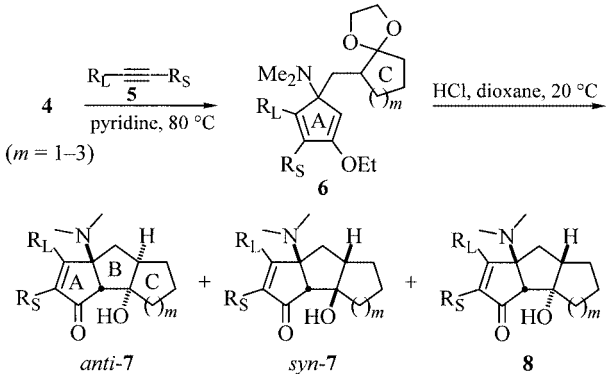
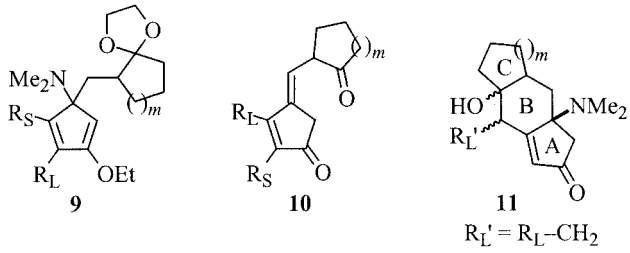
the dioxolane moieties and subsequent intramolecular aldol reactions occurred to give the tricyclic products *anti*-**7** and *syn*-**7** as well as **8** in good to excellent yields (74–91% for 10 out of 13 examples). From the ^1H, ^{13}C, and even 2D-NOESY NMR spectra, it was not possible to unambiguously assign the relative configurations of the tricyclic molecules **7** and **8** with their four stereogenic centers. Slow diffusion crystallization of *syn*-**7aa** and *anti*-**7ba** from benzene/dichloromethane afforded good quality single crystals for X-ray structure analysis (Figure 1),[7] and their structures were rigorously established as *cis*,*syn*,*cis* (*syn*-**7aa**), and *cis*,*anti*,*cis* (*anti*-**7ba**). Thus, the third stereoisomer was assigned as *cis*,*anti*,*trans* (**8**). Generally, the *cis*,*anti*,*cis*-stereoisomers (*anti*-**7**) were formed as the major products.



Scheme 2. Synthesis of triquinanes and homologous linearly annelated tricyclic skeletons. For details see Table 1.

The starting materials **6** with a five-membered ring C gave only *cis*,*anti*,*cis*- (*anti*-**7**) and *cis*,*syn*,*cis*-isomer (*syn*-**7**), but with a lower predominance of the *anti*-isomer than in the case of the analogues with a six-membered ring C. As the size of the ring C increases, the amounts of the third isomers *cis*,*anti*,*trans* **8** also increase, and the *anti*/*syn* selectivity decreases. This is an expression of the fact that *trans*-fusion of a five-membered to a larger ring does not cause a severe increase in ring strain. The tricycles **7bb/8bb** have been prepared in a one-pot operation directly from the complex **4b** and the alkyne **5b**. The derivative **6bh** with the diethyl malonate moiety in the side chain gave, besides the tricyclic molecules **7bh/8bh**, the elimination product **10bh** in 8% yield along with a trace of the new tricyclic structure **11bh** with a six-membered B-ring (Entry 10 in Table 1). Obviously, the tricycle of type **11** can only be formed, when the substituent R_L can provide a methylene group towards the ring closure. Thus, control experiments were carried out with *n*-propyl-substituted cyclopentadienes **6ac** and **6cc**, and indeed, cyclization products of type **11** were observed besides **7/8** and the elimination products **10**. Two diastereomers of the tricyclic molecules **11** with four stereogenic centers were isolated, but their relative configurations could not easily be assigned. The formation of the elimination products **10** appeared to be enhanced upon use of larger amounts of concd. hydrochloric acid.



While the tricycles **7/8** are formed by intramolecular aldol reactions from the diketones **12** via the protonated keto enols **13**, the ring-enlarged tricycles **11** must arise by cyclization of the protonated isomeric keto enols **14** (Scheme 3). This type of participation of an alkyl group attached at the β-position of a cyclopentenone has previously been observed.[3] Although such a participation would also be possible with a methyl substituent in the β-position, it was only observed for the *n*-propyl-substituted cases. Such methyl-substituted precursors **6** also reacted more slowly than others and gave products *anti*- and *syn*-**7** with lower diastereoselectivity.

According to molecular-mechanics calculations, the *cis*,*anti*,*cis*-tricyclo[6.3.0.0^{2,6}]undecane is only slightly more stable than the *cis*,*syn*,*cis*-isomer, but much more stable than the third isomer with *cis*,*anti*,*trans*-configuration.[8] On the other hand, Humbel et al. reported that the intramolecular aldol reaction of octane-2,7-dione under acidic conditions yielded predominantly *cis*-1-(2-hydroxy-2-methylcyclopentynyl)ethanone due to a favorable hydrogen bonding in the transition structure leading to this stereoisomer in

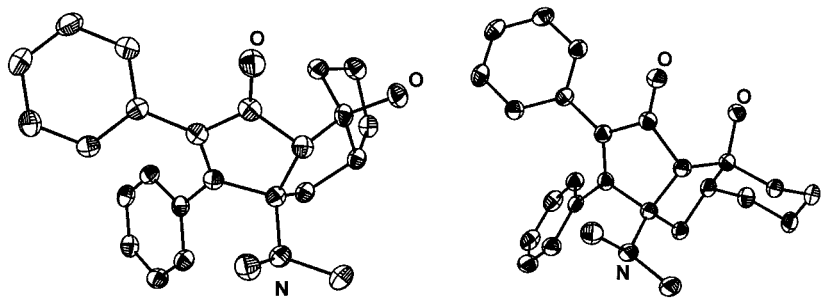
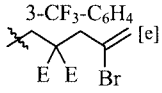
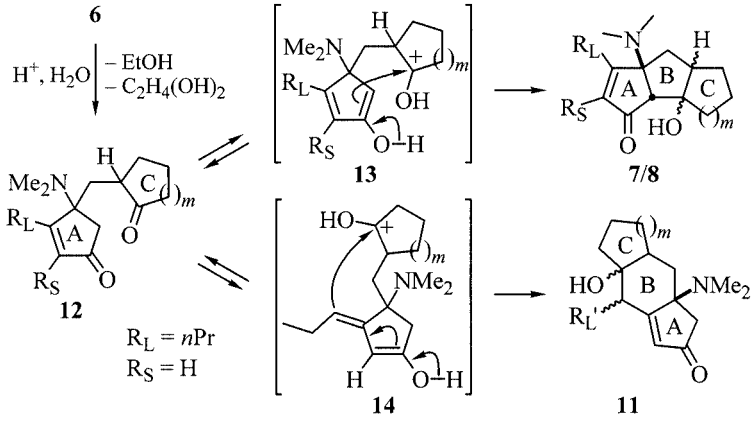


Figure 1. The molecular structures of *syn*-**7aa** (left) and *anti*-**7ba** (right) in the crystals. *syn*-**7aa**: Monoclinic crystals of space group $P2_1/n$, the distance between the hydroxy hydrogen and the carbonyl oxygen is 3.45 Å. *anti*-**7ba**: Monoclinic crystals of space group $P2_1/c$; the distance between the hydroxy hydrogen and the carbonyl oxygen is 1.98 Å.[7]

Table 1. Cocyclizations of dioxolane-protected [1-ethoxy-3-dimethylamino-3-(oxocycloalkylmethyl)propenylidene]pentacarbonylchromium complexes **4** with alkynes **5** and subsequent transformations of the resulting 3-ethoxycyclopentadienes **6** to tricyclic compounds **7/8**.

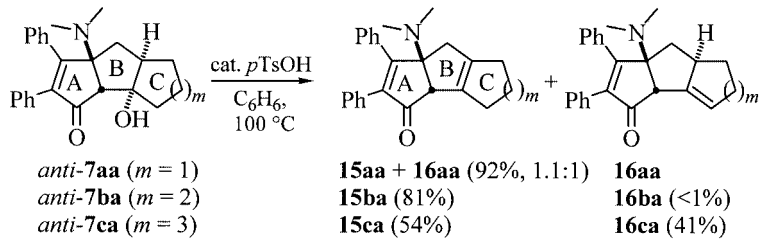
Entry	Starting material	Alkyne	R_L	R_S	Product	Yield (%)	d. r.[a]	Time [d]	Products	Yield (%)	Ratio
1	**4a**	**5a**	Ph	Ph	**6aa**	50	1.5:1	2	*anti-/syn*-**7aa**	80	54/26
2	**4a**	**5b**	$SiMe_3$	H	**6ab**	45	1.3:1[b]	2	*anti-/syn*-**7ab**	74	47/24
3	**4a**	**5c**	*n*Pr	H	**6ac**	68	1:1	4	*anti-/syn*-**7ac**	0[c]	—
4	**4a**	**5d**	Me	H	**6ad**	75	2:1	4	*anti-/syn*-**7ad**	79	40/39
5	**4a**	**5e**	Me	Me	**6ae**	67	1:1	6	*anti-/syn*-**7ae**	77	39/38
6	**4b**	**5a**	Ph	Ph	**6ba**	52	1:1	2	*anti-/syn*-**7ba/8ba**	89	63/17/9
7	**4b**	**5e**	Me	Me	**6be**	66	1:1	2	*anti-/syn*-**7be/8be**	82	64/18/–[d]
8	**4b**	**5f**	*t*Bu	H	**6bf**	38	2:1	2	*anti-/syn*-**7bf/8bf**	91	66/16/9
9	**4b**	**5g**	3-CF_3-C_6H_4	H	**6bg**	40	2:1	2	*anti-/syn*-**7bg/8bg**	89	72/4/13
10	**4b**	**5h**	 [e]	H	**6bh**	51	1.9:1	2	*anti-/syn*-**7bh/8bh**	78[f]	61/14/3
11	**4b**	**5b**	$SiMe_3$	H	—[g]	—	—	4+2	*anti-/syn*-**7bb/8bb**	40[g]	29/9/2
12	**4c**	**5a**	Ph	Ph	**6ca**	81	1.3:1	2	*anti-syn*-**7ca/8ca**	83	27/24/32
13	**4c**	**5c**	*n*Pr	H	**6cc**	72	1.4:1	2	*anti-/syn*-**7cc/8cc**	43[h]	22/21/–

[a] All reactions were carried out at 80 °C for 4 d. The diastereomeric ratios are based on ^1H NMR spectra. [b] A trace of the regioisomeric cyclopentadiene **9ab** was also detected. [c] Instead, 9% of the elimination product **10ac** and 66% (59 + 7%) of the isomer **11ac** were isolated. [d] Traces of other stereoisomers were observed. [e] E = CO_2Et. [f] In addition, 8% of the elimination product **10bh** and 1% of the isomer **11bh** were isolated. [g] One-pot operation from complex **4b** and trimethylsilylethyne (**5b**). [h] In addition, 22% of the elimination product **10cc** and 20% (17 + 3%) of the two diastereomers of **11cc** were isolated.



Scheme 3. Mechanistic rationalization of the formation of tricycles **7/8** and **11**.

which the hydroxy and the keto carbonyl group end up on the same side of the ring.[9] The stereochemical outcome of the intramolecular aldol reactions reported here is in agreement with the calculated relative stabilities of the stereoisomeric triquinanes. Hydrogen bonding between the developing hydroxy and the remaining keto group in the transition structure apparently favors the formation of the *anti*-configured bicyclo[7.3.0.$0^{3,7}$]dodecanes.[10] The X-ray structure of *anti*-**7ba** does indeed show a hydrogen bond between the keto carbonyl and hydroxy groups with a distance of



Scheme 4. Dehydration of tricyclic hydroxy ketones *anti*-**7**.

1.98 Å between them,[11] whereas the X-ray structure of *syn*-**7aa** displays a distance of 3.45 Å between the hydroxy hydrogen and the carbonyl oxygen.

Upon heating the cyclization products *anti*-**7** in the presence of a catalytic amount of *p*-toluenesulfonic acid in benzene using a Dean–Stark apparatus, the dehydration products **15** and **16** were formed in excellent yields (Scheme 4). The regioisomeric triquinadiene derivatives **15aa** and **16aa** were obtained as an inseparable 1:1 mixture after 17 h, while the homologous tricyclic diene with a fused six-membered C-ring, **15ba**, was formed much more rapidly (within 2 h) and as a single isomer. Further heating for an additional 36 h of the mixture of **15aa** and **16aa** in the presence of *p*-toluenesulfonic acid changed the ratio between the two isomers from 1:1 to 2.1:1.

The tricyclic dienes **15ca** and **16ca** with a fused seven-membered ring were formed in a ratio of 1.3:1, but could be separated by column chromatography.

Experimental Section

General: ^{1}H and ^{13}C NMR: Bruker AM 250 (250 and 62.9 MHz) and Bruker AMX 300 (300 and 75.5 MHz). IR: Bruker IFS 66 (FT-IR). EI-MS: Finnigan MAT 95 spectrometer (70 eV). High-resolution mass data (HRMS) were obtained by preselected-ion peak matching at $R \approx 10000$ to be within ± 2 ppm of the exact mass. X-ray crystal structure determination: The data were collected with a Stoe–Siemens-AED diffractometer. Melting points were determined with a Büchi 510 capillary melting point apparatus and are uncorrected. Elemental analyses: Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie 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. *p*-Toluenesulfonic acid monohydrate is abbreviated as *p*TsOH.

General Procedure for the Preparation of Alkynyl-Substituted Cycloalkanones 2 (GP1):[5] 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 of THF at –78 °C is added dropwise 300 mmol of the respective imine **1** within 15 min. The mixture is warmed to ambient temperature and stirred for an additional 1 h. 3-Trimethylsilylpropargyl bromide[12] (300 mmol) is added to this solution at –78 °C over a period of 10 min, and the mixture stirred at this temperature for 30 min, at ambient temperature for 12 h and finally at 40 °C for 30 min. The mixture is cooled to room temperature, the reaction quenched with 250 mL of ice water, and the aqueous phase is extracted with Et_2O (3 × 200 mL). The solvents of the combined organic phases are removed under reduced pressure. To the residue is added at 0 °C a cold solution of 1 N hydrochloric acid (350 mL) over a period of 10 min. The mixture is washed with pentane (3 × 50 mL) in order to recover the propargyl bromide. The pH value of the aqueous phase is adjusted to 5.5 to 6.0 by addition at 0 °C of a satd. aqueous solution of potassium carbonate, and the mixture is heated under reflux at 70 °C for 1 h. The solution is extracted with Et_2O (3 × 200 mL), and the combined organic phases are dried with $MgSO_4$. After evaporation of the solvent, the remaining liquid is distilled under reduced pressure to afford **2** as a colorless oil.

General Procedure for the Synthesis of Alkynyl-Substituted Acetals 3 (GP2): A mixture of 150 mmol of the respective alkynyl-substituted cycloalkanone **2**, ethylene glycol (10.0 mL, 179 mmol), a catalytic amount of *p*TsOH (1.00 g) and benzene (250 mL) is heated under reflux 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 is extracted with Et_2O (3 × 100 mL). The combined organic extracts are dried with $MgSO_4$, the solvent is removed under reduced pressure, and the residue dissolved in MeOH (300 mL). To this solution is added 20.0 g of potassium carbonate, and the mixture stirred at ambient temperature for 12 h. After filtration through Celite, washing with Et_2O (3 × 50 mL) and evaporation of the solvents, the residue is distilled under reduced pressure to afford **3** as a colorless oil.

2-(3′-Trimethylsilylprop-2′-ynyl)cyclopentanone (2a) and *cis*-/*trans*-2,5-Bis(3′-trimethylsilylprop-2′-ynyl)cyclopentanone: According to GP1, a solution of LDA (250 mmol) in 200 mL of THF was treated with 49.5 g (299 mmol) of *N*-cyclohexylcyclopentylideneamine (**1a**)[13] and then 60.0 g (314 mmol) of 1-bromo-3-trimethylsilyl-2-propyne.[12] After hydrolysis and evaporation of the solvent, the residue was distilled under reduced pressure to afford 26.8 g (55%) of **2a** 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 in a kugelrohr (0.5 Torr, 130 °C) to give 9.13 g (19%) of *cis*-/*trans*-2,5-di(3′-trimethylsilylprop-2′-ynyl)cyclopentanone as a colorless oil.

2a: IR (film): $\tilde{\nu}$ = 2962 cm^{-1} (C–H), 2176 (C≡C), 1746 (C=O), 1249, 1155, 839, 760. ^{1}H 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) ppm. ^{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) ppm. MS (70 eV): *m*/*z* (%) = 194 (2) [M^+], 179 (52), 149 (13), 97 (12), 83 (10), 75 (100), 73 (22) [$Si(CH_3)_3^+$], 59 (10), 43 (13). $C_{11}H_{18}OSi$ (194.4): calcd. C 67.98, H 9.34; found C 67.68, H 9.09.

***cis*- and *trans*-2,5-Bis(3′-trimethylsilylprop-2′-ynyl)cyclopentanone:** IR (film): $\tilde{\nu}$ = 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, 2,3,4,5,1′-H). Major isomer: ^{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) ppm. Minor isomer: ^{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) ppm. 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) [$Si(CH_3)_3^+$], 59 (10). $C_{17}H_{28}OSi_2$ (304.6): calcd. C 67.04, H 9.27; found C 66.84, H 9.48.

6-(2′-Propynyl)-1,4-dioxaspiro[4.4]nonane (3a) and 6-[(2′-Methyl-1′,3′-dioxolan-2′-yl)methyl]-1,4-dioxaspiro[4.4]nonane: According to GP2, a mixture of **2a** (25.0 g, 129 mmol), ethylene glycol (10 mL, 179 mmol), *p*TsOH (2.00 g) and benzene (250 mL) was heated under reflux for 16 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 with $MgSO_4$, concentrated, and the product distilled under reduced pressure to afford 10.3 g (48%) of **3a** as a colorless oil, b.p. 57 °C (0.5 Torr). The dark residue was distilled again in a kugelrohr apparatus (0.5 Torr, oven temperature 110 °C) to give 6-[(2′-methyl-1′,3′-dioxolan-2′-yl)methyl]-1,4-dioxaspiro[4.4]nonane [8.76 g (43%)] as a colorless oil.

3a: IR (film): $\tilde{\nu}$ = 3286 cm^{-1} (C≡C–H), 2961 (C–H), 2875, 2117 (C≡C), 1329, 1199, 1153, 1046, 1024, 649. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33–1.73 (5 H) and 1.87–2.32 (3 H) [m, 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) ppm. ^{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) ppm.

6-[(2′-Methyl-1′,3′-dioxolan-2′-yl)methyl]-1,4-dioxaspiro[4.4]-nonane: IR (film): $\tilde{\nu}$ = 2938 cm^{-1} (C–H), 1653, 1558, 1520, 1261. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, CH_3), 1.31–2.07 (m, 9 H, $CHCH_2C$, 6,7,8,9-H), 3.70–3.90 (m, 8 H, 2,3,4′,5′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.4, 30.1, 34.7, 37.3 (–, $CHCH_2C$, C-7,8,9), 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′) ppm. MS (70 eV): *m*/*z* (%) = 213 (8) [$M^+ - CH_3$], 183 (12), 141 (16), 99 (52), 87 (100), 55 (10), 43 (26), 41 (11). $C_{12}H_{20}O_4$ (228.3): calcd. C 63.14, H 8.83; found C 62.94, H 8.60.

6-(Prop-2′-ynyl)-1,4-dioxaspiro[4.5]decane (3b): 20.0 g (147 mmol) of 2-(2′-propynyl)cyclohexanone in benzene (200 mL) was heated under reflux with ethylene glycol (10 mL, 179 mmol) and *p*TsOH (2.00 g) for 4 h. The mixture was cooled to ambient temperature and washed with 100 mL water. The aqueous phases were extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried with $MgSO_4$ and distilled under reduced pressure to afford 23.0 g (87%) of **3b** as a colorless oil, b.p. 78 °C (0.5 Torr). IR (film): $\tilde{\nu}$ = 3300 cm^{-1} (C≡C–H), 2940 (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) ppm. ^{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-2′), 109.8 (C_{quat}, C-5) ppm. MS (70 eV): *m*/*z* (%) = 180 (6) [M^+], 165 (12), 152 (33), 137 (70), 126 (16), 99 (100), 86 (19). $C_{11}H_{16}O_2$ (180.2): calcd. C 73.30, H 8.95; found C 73.68, H 9.12.

2-(3′-Trimethylsilylprop-2′-ynyl)cycloheptanone (2c): According to GP1, to a solution of LDA (250 mmol) in THF (200 mL) was added 58.0 g (300 mmol) of cycloheptylidenecyclohexylamine (**2c**),[13] and then 54.0 g (283 mmol) of 1-bromo-3-trimethylsilyl-2-propyne. After aqueous work-up and hydrolysis, the residue was distilled under reduced pressure to afford 42.1 g (67%) **2c** as a colorless oil, b.p. 105 °C (0.5 Torr). IR (KBr): $\tilde{\nu}$ = 2910 cm^{-1} (C–H), 2853, 2177 (C≡C), 1700 (C=O), 1457, 1248, 837. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 9 H, $Si(CH_3)_3$], 1.19–1.93 (m, total 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] ppm. ^{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) ppm. 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) [$Si(CH_3)_3^+$], 59 (10), 43 (12). $C_{13}H_{22}OSi$ (222.4): calcd. C 70.21, H 9.97; found C 70.02, H 10.11.

6-(2′-Propynyl)-1,4-dioxaspiro[4.6]undecane (3c): According to GP2, 40.7 g (183 mmol) of 2-(3′-trimethylsilyl-2′-propynyl)cycloheptanone (**2c**) in benzene (250 mL) was heated under reflux with ethylene glycol (15 mL, 269 mmol) and a catalytic amount of *p*TsOH (2.0 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 with $MgSO_4$ and distilled under reduced pressure to afford 29.2 g (82%) of **3c** as a colorless oil, b.p. 87 °C (0.5 Torr). IR (film): $\tilde{\nu}$ = 3308 cm^{-1} (C≡C–H), 2929 (C–H), 2855, 2116 (C≡C), 1459, 1155, 1107. ^1H 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) ppm. ^{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) ppm. MS (70 eV): *m*/*z* (%) = 194 (1) [M^+], 155 (20), 137 (70), 113 (18), 99 (100), 86 (11), 55 (17), 41 (18). $C_{12}H_{18}O_2$ (194.3): calcd. C 74.19, H 9.34; found C 73.89, H 9.12.

General Procedure for the Preparation of β-Amino-substituted α,β-Unsaturated Fischer-Carbene Complexes 4 (GP3): To a solution of the respective terminal alkyne **3** (20 mmol) in THF (100 mL) at –78 °C is added a solution of *n*-butyllithium (20 mmol). The mixture is stirred at this temperature for an additional 30 min. 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 the solvent, the residue is purified by flash column chromatography.

Pentacarbonyl[(2*E*)-4-(1′,4′-dioxaspiro[4.4]non-6′-yl)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]chromium (4a): According to GP3, 3.58 g (21.5 mmol) of 6-(2′-propynyl)-1,4-dioxaspiro[4.4]-nonane (**3a**) 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 **4a** [R_f — 0.63 (Et_2O)] as a yellow solid, m.p. 93–94 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (C–H), 2043 (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, total 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) ppm. ^{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) ppm. 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^+]. $C_{20}H_{25}CrNO_8$ (459.4): calcd. C 52.29, H 5.48; found C 52.33, H 5.25.

Pentacarbonyl[(2*E*)-4-(1′,4′-dioxaspiro[4.5]dec-6′-yl)-3-dimethylamino-1-ethoxy-2-buten-1-ylidene]chromium (4b): According to GP3, 6.43 g (35.7 mmol) of 6-(2′-propynyl)-1,4-dioxaspiro[4.5]decane (**3b**) 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 **4b** [R_f = 0.33 (pentane/Et_2O, 1:1)] as a yellow solid, m.p. 91–92 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1} (C–H), 2932, 2041 (C=O), 1912 (C=O), 1898 (C=O), 1542, 1434, 1281, 1089, 668. ^{1}H 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) ppm. ^{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) ppm. 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^+]. $C_{21}H_{27}CrNO_8$ (473.4): calcd. C 53.28, H 5.75; found C 53.43, H 5.53.

General Procedure for Cocyclizations of Complexes 4 with Alkynes 5 (GP4): A thick-walled, screw-cap Pyrex bottle equipped with a magnetic stirring bar is charged with a 0.05 M solution of the complex **4** in anhydrous pyridine. Dry nitrogen is bubbled through the solution for 2 min, and two equiv. of the respective alkyne **5** is immediately added. The sealed bottle is kept in an oil bath at 80 °C for 4 d. 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 through a 3 cm thick layer of Celite and the solids 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 the cocyclization products **6**.

5-Dimethylamino-5-[(1′,4′-dioxaspiro[4.4]non-6′-yl)methyl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (6aa): According to GP4, a solution of complex **4a** (2.30 g, 5.01 mmol) in pyridine (100 mL) was treated with 1.34 g (7.52 mmol) 1,2-diphenylethyne (**5a**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (80 g) eluting with pentane/Et_2O (from 20:1 to 1:2) gave 1.11 g (50%) of **6aa** [R_f = 0.38 (pentane/Et_2O, 1:1); *dr* = 1.5:1] as a pale-yellow oil. IR (film): $\tilde{\nu}$ = 2970 cm^{-1} (C–H), 2874 (C–H), 1710, 1630 (C=C), 1347, 1194, 1031, 764, 700. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20–2.20 (m, 11 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) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major diastereomer: 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 diastereomer: 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) ppm. 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 (6ab): According to GP4, a solution of complex **4a** (2.19 g, 4.76 mmol) in pyridine (100 mL) was treated with 700 mg (7.13 mmol) of trimethylsilylethyne (**5b**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (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 a mixture of the first and the second diastereomer (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 yields were 784 mg (45%) and *dr* = 1.3:1. Major (first) diastereomer: IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (C–H), 1615 (C=C), 1327, 1246, 1192, 1039, 838, 756. ^{1}H 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) ppm. ^{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) ppm. 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). Minor (second) diastereomer: IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (C–H), 1613 (C=C), 1328, 1247, 1193, 836, 764. ^{1}H 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) ppm. ^{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-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) ppm. 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 (6ac): According to GP4, a solution of complex **4a** (2.30 g, 5.01 mmol) in pyridine (100 mL) was treated with 681 mg (10.0 mmol) of 1-pentyne (**5c**), 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 0:1) gave 1.15 g (68%) of **6ac** [R_f = 0.48 (Et_2O); *dr* = 1:1] as a pale-yellow oil. IR (film): $\tilde{\nu}$ = 2956 cm^{-1} (C–H), 1635 (C=C), 1584,

1339, 1196, 1151, 1107, 1040. ^{1}H 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, $N(CH_3)_3$], 3.60–3.85 (m, 6 H, OCH_2CH_3, 2′,3′-H), 4.53, 4.55 (s, 1 H, 4-H), 5.52, 5.57 (s, 1 H, 2-H) ppm. ^{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 [+, $N(CH_2)_2$], 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-2), 155.7, 156.6, 158.3, 158.4 (C_{quat}, C-1,3) ppm. 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 (6ad): According to GP4, a solution of complex **4a** (2.30 g, 5.01 mmol) in pyridine (100 mL) was treated with 1-propyne (**5d**) (2 mL) at –78 °C, then the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (80 g) eluting with pentane/Et_2O (+ 1% NEt_3, from 1:0 to 1:2) gave 1.15 g (75%) of **6ad** [R_f = 0.13 (pentane/Et_2O, 1:1); *dr* = 2:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2948 cm^{-1} (C–H), 1638 (C=C), 1585, 1344, 1201, 1151, 1105, 1041. ^{1}H 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″ (dq), ^4J = 1.8, ^4J = 1.8 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major diastereomer: 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 diastereomer: 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) ppm. MS (70 eV): *m*/*z* (%) = 307 (36) [M^+], 278 (100) [$M^+ - C_2H_5$], 150 (26), 41 (12). $C_{18}H_{29}NO_3$ (307.4): calcd. C 70.32, H 9.51; found C 69.97, H 9.36.

5-Dimethylamino-5-[(1′,4′-dioxaspiro[4.5]dec-6′-yl)methyl]-3-ethoxy-1,2-dimethyl-1,3-cyclopentadiene (6be): According to GP4, a solution of complex **4b** (2.37 g, 5.01 mmol) in pyridine (100 mL) was treated with 541 mg (10.0 mmol) of 2-butyne (**5e**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (80 g) eluting with pentane/Et_2O (from 10:1 to 1:2) gave 1.11 g (66%) of **6be** [R_f = 0.63 (Et_2O); *dr* = 1:1] and traces of its hydrolysis product as colorless oils. IR (film): $\tilde{\nu}$ = 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, CCH_2CH, 6′,7′,8′,9′,10′-H), 1.29 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.09, 2.10 [s, 6 H, $N(CH_3)_2$], 3.70–3.90 (m, 6 H, OCH_2CH_3, 2′,3′-H), 4.58, 4.62 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.7×2, 9.09, 11.1 (+, CH_3), 14.4, 14.5 (+, OCH_2CH_3), 23.7×2, 23.8, 24.3, 30.8, 31.7, 32.7, 33.7×2, 34.3 (–, CCH_2CH, C-7′,8′,9′,10′), 39.2 (+, C-6′), 39.9, 40.0 [+, $N(CH_3)_2$], 64.3, 64.4, 64.5 (–, OCH_2CH_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) ppm. MS (70 eV): *m*/*z* (%) = 335 (66) [M^+], 306 (100) [$M^+ - C_2H_5$], 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).

5-Dimethylamino-5-[(1″,4″-dioxaspiro[4.5]dec-6″-yl)methyl]-3-ethoxy-1-(3′-trifluoromethylphenyl)-1,3-cyclopentadiene (6bg): According to GP3, a solution of complex **4b** (2.37 g, 5.01 mmol) in pyridine (100 mL) was treated with 1.70 g (10.0 mmol) of 3′-(trifluoromethyl)phenylethyne (**5g**),[14] 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 **6bg** [R_f = 0.56 (pentane/Et_2O, 3:1); *dr* = 2:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2938 cm^{-1} (C–H), 1699, 1624 (C=C), 1333, 1278, 924, 803, 701. ^{1}H 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) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): Major diastereomer: 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 diastereomer: δ = 14.4 (+, 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) ppm. 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).

General Procedure for Intramolecular Adol Reactions (GP5): To a solution of the respective ethoxycyclopentadiene **6** 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 satd. aqueous solution of potassium carbonate, until the gas evolution ceases. The aqueous solution is extracted with CH_2Cl_2 (5×50 mL), and the combined organic phases are dried with $MgSO_4$. After removal of the solvent, the residue is purified by column chromatography on silica gel.

(3a*S*,3b*R*,6a*S*,7a*R*)/(3a*R*,3b*S*,6a*R*,7a*S*)-7a-Dimethyamino-3b-hydroxy-1,2-diphenyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta[*a*]pentalen-3-one (*anti*-7aa) and (*syn*-7aa): According to GP5, concd. hydrochloric acid (10 mL) was added to a solution of **6aa** (623 mg, 1.40 mmol) in dioxane (150 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 *anti*-**7aa** [R_f = 0.57 (pentane/CH_2Cl_2, 1:1)] as colorless crystals (m.p. 156 °C) and 136 mg (26%) of *syn*-**7aa** [R_f = 0.23 (pentane/CH_2Cl_2, 1:1)] as pale-yellow crystals (m.p. 214–216 °C).

***anti*-7aa:** IR (KBr): $\tilde{\nu}$ = 3445 cm^{-1} (O–H), 2958 (C–H), 1693 (C=O), 1340, 1175, 1122, 1009, 698. ^{1}H 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) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 23.6, 27.9, 26.5, 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) ppm. MS (70 eV): *m*/*z* (%) = 373 (100) [M^+], 344 (18), 312 (18), 290 (24), 277 (65), 178 (12), 164 (34), 138 (17). $C_{25}H_{27}NO_2$ (373.5): calcd. C 80.40, H 7.29; found C 80.75, H 7.10.

***syn*-7aa:** IR (KBr): $\tilde{\nu}$ = 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) ppm. ^{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) ppm. MS (70 eV): *m*/*z* (%) = 373 (100) [M^+], 344 (12), 289 (26), 276 (89), 202 (14), 178 (14), 164 (24), 138 (18), 41 (21). $C_{25}H_{27}NO_2$ (373.5): calcd. C 80.40, H 7.29; found C 80.63, H 7.17.

(3a*S*,3b*R*,6a*S*,7a*R*)/(3a*R*,3b*S*,6a*R*,7a*S*)-7a-Dimethyamino-3b-hydroxy-1-trimethylsilyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta[*a*]-pentalen-3-one (*anti*-7ab) and (3a*S*,3b*S*,6a*R*,7a*R*)/(3a*R*,3b*R*,6a*S*,7a*S*)-7a-Dimethyamino-3b-hydroxy-1-trimethylsilyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta[*a*]pentalen-3-one (*syn*-7ab): According to GP5, a 3 N solution of hydrochloric acid (5 mL) was added to a solution of **6ab** (585 mg, 1.60 mmol) in dioxane (150 mL), and the mixture was stirred for 2 d. After aqueous work-up, the residue was subjected to chromatography on silica gel (60 g) followed by chromatography on aluminum oxide (activity grade II, 50 g). Elution with CH_2Cl_2/Et_2O (from 1:3 to 2:1) gave 347 mg (74%) of a colorless oil [R_f = 0.17 (pentane/CH_2Cl_2, 1:1); *anti*-/*syn*-**7ab** = 2:1]. IR (film): $\tilde{\nu}$ = 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, $Si(CH_3)_3$ of *syn*-**7ab**], 0.19 [s, 9 H, $Si(CH_3)_3$ of *anti*-**7ab**], 1.27–1.45 and 1.60–2.20 (m, 18 H, 4,5,6,6a,7-H of *anti*-**7ab**, 4,5,6,7-H and OH of *syn*-**7ab**), 2.09 [s, 6 H, $N(CH_3)_2$ of *anti*-**7ab**], 2.10 [s, 6 H, $N(CH_3)_2$ of *syn*-**7ab**], 2.50–2.60 (m, 1 H, 6a-H of *syn*-**7ab**), 2.69 (s, 1 H, 3a-H of *anti*-**7ab**), 2.88 (s, 1 H, 3a-H of *syn*-**7ab**), 3.38 (br. s, 1 H, OH of *anti*-**7ab**), 5.98 (s, 1 H, 2-H of *syn*-**7ab**), 6.32 (s, 1 H, 2-H of *anti*-**7ab**) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): ***anti*-7ab:** δ = –0.53 *ppm*[+, $Si(CH_3)_3$], 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). ***syn*-7ab:** 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) ppm. 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 (12ad): According to GP5, a 3 N solution of hydrochloric acid (10 mL) was added to **6ad** (985 mg, 3.20 mmol) in dioxane (150 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 **12ad** [R_f = 0.58 and 0.49 (Et_2O/MeOH, 10:1), *dr* = 1:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (C–H), 1734 (C=O), 1684 (C=O), 1521, 1209, 1186. First diastereomer: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21–1.62 (m, 4 H, 4′,5′-H), 1.77 (AB, d, ^2J = 18.8 Hz, 1 H, 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, 1 H, 5-H), 5.84 (d, ^4J = 1.2 Hz, 1 H, 2-H) ppm. ^{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 diastereomer: ^1H 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, 1 H, 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, 1 H, 5-H), 5.80 (d, ^4J = 1.2 Hz, 1 H, 2-H) ppm. ^{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_{quat}, C-4), 132.6 (+, C-2), 180.3 (C_{quat}, C-3), 205.3 (C_{quat}, C-1), 219.2 (C_{quat}, C-2′′) ppm. MS (70 eV): *m*/*z* (%) = 235 (8) [M^+], 205 (9), 191 (12), 138 (100), 59 (9).

(3a*S*,3b*R*,6a*S*,7a*R*)/(3a*R*,3b*S*,6a*R*,7a*S*)-7a-Dimethyamino-3b-hydroxy-1-methyl-3a,3b,4, 5,6,6a,7,7a-octahydrocyclopenta[*a*]pentalen-3-one (*anti*-7ad) and (3a*S*,3b*S*,6a*R*,7a*R*)/(3a*R*,3b*R*,6a*S*,7a*S*)-7a-Dimethyamino-3b-hydroxy-1-methyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta[*a*]pentalen-3-one (*syn*-7ad): According to GP5, concd. hydrochloric acid (10 mL) was added to a solution of 6ad (972 mg, 3.16 mmol) in dioxane (150 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 (29%) of *syn*-**7ad** [R_f = 0.67 (Et_2O/MeOH, 10:1)] as a colorless solid (m.p. 121–122 °C), 249 mg (33%) of a mixture of (*anti*-/*syn*-**7ad** = 2.2:1) and 127 mg (17%) of *anti*-**7ad** [R_f = 0.58 (Et_2O/MeOH, 10:1)] as a colorless solid (m.p. 102–103 °C).

***anti*-7ad:** IR (KBr): $\tilde{\nu}$ = 3417 cm^{-1} (O–H), 2964 (C–H), 1685 (C=O), 1627, 1282, 1191. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.37–1.59 (2 H) and 1.69–2.08 (7 H) [m, 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) ppm. ^{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) ppm. 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).

***syn*-7ad:** IR (KBr): $\tilde{\nu}$ = 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 (3 H), 1.67–2.00 (4 H) and 2.12–2.22 (1 H) [m, total 8 H, 4,5,6,7-H], 1.99 (s, 3 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) ppm. ^{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) ppm. 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). $C_{14}H_{21}NO_2$ (235.3): calcd. C 71.46, H 8.99; found C 71.31, H 8.72.

(3a*S*,3b*R*,6a*S*,7a*R*)/(3a*R*,3b*S*,6a*R*,7a*S*)-7a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3a,3b,4, 5,6,6a,7,7a-octahydrocyclopenta[*a*]pentalen-3-one (*anti*-7ae) and (3a*S*,3b*S*,6a*R*,7a*R*)/(3a*R*,3b*R*,6a*S*,7a*S*)-7a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3a,3b,4,5,6,6a,7,7a-octahydrocyclopenta[*a*]pentalen-3-one (*syn*-7ae): According to GP5, a solution of 3 N hydrochloric acid (10 mL) was added to a solution of **6ae** (870 mg, 2.71 mmol) in dioxane (150 mL), and the mixture was stirred for 2 d. After aqueous work-up, only the diketone **12ae** was detected. Then, the intermediate **12ae** was taken-up again with

dioxane (150 mL), the solution treated with concd. hydrochloric acid (20 mL), and the mixture 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 *anti*- and *syn*-**7ae** [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 a solid precipitated, the mixture was kept at this temperature under normal pressure for another 20 min. Separation from the remaining liquid (about 10 mL) and washing with pentane/Et_2O, (10:1, 3 × 10 mL) afforded 210 mg of a colorless solid (m.p. 130–134 °C) of *anti*-/*syn*-**7ae** in ratio 1:9.4. A colorless oil (310 mg; *anti*-/*syn*-**7ae** = 3.3:1) was collected upon evaporation of the mother liquor and the washing solution. IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} (C–H), 1692 (C=O), 1647 (C=C), 1388, 1320, 1140, 1028. ^1H NMR (250 MHz, $CDCl_3$, plus DEPT): δ = 1.13–1.26 (2 H of *anti*-**7ae**, 3 H of *syn*-**7ae**), 1.47–1.90 (6 H of *anti*-**7ae**, 4 H of *syn*-**7ae**) and 1.97–2.10 (1 H of *anti*-**7ae** and 1 H of *syn*-**7ae**) [m, total 17 H, 4,5,6,6a,7-H of *anti*-**7ae**, 4,5,6,7-H of *syn*-**7ae**], 1.50 (s, 3 H, CH_3 of *syn*-**7ae**), 1.56 (s, 3 H, CH_3 of *anti*-**7ae**), 1.78 (s, 3 H, CH_3 of *syn*-**7ae**), 1.82 (s, 3 H, CH_3 of *anti*-**7ae**), 2.02 [s, 12 H, $N(CH_3)_2$ of *anti*- and *syn*-**7ae**], 2.45–2.58 (m, 1 H, 6a of *syn*-**7ae**), 2.62 (s, 1 H, 3a-H of *anti*-**7ae**), 2.84 (s, 1 H, 3a-H of *syn*-**7ae**), 3.45 (br. s, 1 H, OH of *anti*-**7ae**), 4.43 (br. s, 1 H, OH of *syn*-**7ae**) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): ***anti*-7ae:** 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). *syn*-7ae: 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) ppm. MS (70 eV): *m*/*z* (%) = 249 (42) [M^+], 177 (14), 152 (100), 138 (16). $C_{15}H_{23}NO_2$ (249.4): calcd. C 72.25, H 9.30; found C 71.97, H 8.94.

(3a*S*,3b*R*,7a*S*,8a*R*)/(3a*R*,3b*S*,7a*R*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1,2-diphenyl-3b,4, 5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta-[*a*]inden-3-one (*anti*-7ba), (3a*S*,3b*S*,7a*R*,8a*R*)/(3a*R*,3b*R*,7a*S*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1,2-diphenyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (*syn*-7ba) and (3a*S*,3b*S*,7a*S*,8a*R*)/(3a*R*,3b*R*,7a*R*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1,2-diphenyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (8ba): According to GP5, to a solution of **6ba** (924 mg, 2.01 mmol) in dioxane (200 mL) was added concd. 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 mg (9%) of **8ba** [R_f = 0.81 (CH_2Cl_2/Et_2O, 3:1)] as a pale-yellow oil, 487 mg (63%) of *anti*-**7ba** [R_f = 0.62 (CH_2Cl_2/Et_2O, 3:1)] as colorless crystals (m.p. 204–205 °C) and 130 mg (17%) of *syn*-**7ba** [R_f = 0.35 (CH_2Cl_2/Et_2O, 3:1)] as colorless crystals (m.p. 181–183 °C).

***anti*-7ba:** IR (KBr): $\tilde{\nu}$ = 3407 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) ppm. ^{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, (+, 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) ppm. MS (70 eV): *m*/*z* (%) = 387 (100) [M^+], 370 (9) [M^+/OH], 344 (15), 290 (12), 277 (28), 164 (18), 138 (10). $C_{26}H_{29}NO_2$ (387.5): calcd. C 80.59, H 7.54; found C 80.41, H 7.25.

***syn*-7ba:** IR (KBr): $\tilde{\nu}$ = 3345 cm^{-1} (O–H), 2929 (C–H), 1700 (C=O), 1675, 1444, 1338, 1171. ^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) ppm. ^{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) ppm. 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).

8ba: IR (film): $\tilde{\nu}$ = 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) ppm. ^{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), 127.8, 127.9, 128.2, 129.2, 129.80, 129.84 (+, 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) ppm. 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).

(3a*S*,3b*R*,7a*S*,8a*R*)/(3a*R*,3b*S*,7a*R*,8a*S*)-8a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta-[*a*]inden-3-one (*anti*-7be), and (3a*S*,3b*S*,7a*R*,8a*R*)/(3a*R*,3b*R*,7a*S*,8a*S*)-8a-Dimethyamino-3b-hydroxy-1,2-dimethyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (*syn*-7be): According to GP5, concd. hydrochloric acid (5 mL) was added to a solution of **6be** (728 mg, 2.17 mmol) in dioxane (100 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 *anti*-**7be** [R_f = 0.37 (Et_2O/EtOAc, 1:1)] as colorless crystals (m.p. 102 °C) and 104 mg (18%) of *syn*-**7be** [R_f = 0.16 (Et_2O/EtOAc, 1:1)] as colorless crystals (m.p. 77–80 °C). Besides these compounds, two uncharacterized fractions were also isolated: fraction I [25 mg; R_f = 0.87 (Et_2O/EtOAc, 1:1)] and fraction II [36 mg; R_f = 0.73 and 0.61 (Et_2O/EtOAc, 1:1)].

***anti*-7be:** IR (KBr): $\tilde{\nu}$ = 2932 cm^{-1} (C–H), 1700 (C=O), 1653, 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) ppm. ^{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) ppm. MS (70 eV): *m*/*z* (%) = 263 (100) [M^+], 220 (7), 201 (7), 165 (8), 153 (100), 138 (13), 122 (9). $C_{16}H_{25}NO_2$ (263.4): calcd. C 72.97, H 9.57; found C 73.27, H 9.35.

***syn*-7be:** IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (C–H), 1696 (C=O), 1653, 1437, 1320, 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) ppm. ^{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) ppm. MS (70 eV): *m/z* (%) = 263 (29) [M^+], 153 (100), 152 (89), 138 (14). $C_{16}H_{25}NO_2$ (263.4): calcd. C 72.97, H 9.57; found C 73.38, H 9.19.

(3a*S*,3b*R*,7a*S*,8a*R*)/(3a*R*,3b*S*,7a*R*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1-(3′-trifluoromethylphenyl)-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (*anti*-7bg), (3a*S*,3b*S*,7a*R*,8a*R*)/(3a*R*,3b*R*,7a*S*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1-(3′-trifluoromethylphenyl)-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (*syn*-7bg) and (3a*S*,3b*S*,7a*S*,8a*R*)/(3a*R*,3b*R*,7a*R*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1-(3′-trifluoromethylphenyl)-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (8bg): According to GP5, concd. hydrochloric acid (5 mL) was added to a solution of **6bg** (506 mg, 1.12 mmol) in dioxane (100 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 mg of a mixture of **8bg** [R_f = 0.26 (pentane/Et_2O, 1:1) and an unidentified diastereomer (ratio 79:21), corresponding to 16% yield of **8bg**, 287 mg of a mixture of *anti*-**7bg** [R_f = 0.14 (pentane/Et_2O, 1:1)] and an unidentified diastereomer (ratio 88:12), corresponding to 67% yield of *anti*-**7bg** and 74 mg (17%) of *anti*-/*syn*-**7bg** [R_f = 0.12 (pentane/Et_2O, 1:1), ratio = 3:1] as colorless oils. The combined yields of *anti*-**7bg** were 72%. Repeated chromatography on silica gel (40 g) and collection of the first 60% fraction of this product afforded pure *anti*-**7bg** as colorless crystals (m.p. 134–135 °C).

***anti*-7bg:** IR (KBr): $\tilde{\nu}$ = 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′′ (dd), ^3J = 7.8 Hz, 1 H, Ar-H], 7.67 (d, ^3J = 7.8 Hz, 1 H, Ar-H), 8.25 (d, ^3J = 7.8 Hz, 1 H, Ar-H), 8.36 (s, 1 H, Ar-H) ppm. ^{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, $^1J_{C,F}$ = 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′), 129.2, 131.4 (+, C-5′,6′), 131.1 (C_{quat}, q, $^2J_{C,F}$ = 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) ppm. MS (70 eV): *m/z* (%) = 379 (21) [M^+], 362 (8) [M^+ – OH], 336 (11), 283 (11), 164 (100), 138 (25), 125 (19). $C_{21}H_{24}F_3NO_2$ (379.4): calcd. C66.48, H 6.38; found C 66.39, H 6.07.

***syn*-7bg:** ^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, Ar-H], 7.67 (d, ^3J = 7.8 Hz, 1 H, Ar-H), 8.25 (d, ^3J = 7.8 Hz, 1 H, Ar-H), 8.36 (s, 1 H, Ar-H) ppm. ^{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) ppm. 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).

8bg and an Unknown Diastereomer: IR (film): $\tilde{\nu}$ = 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, 10 H, 4,5,6,7,8-H), 2.13–2.17 (m, 1 H, 7a-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, Ar-H), 8.20–8.40 (m, 2 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **8bg:** 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 Diastereomer:** 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) ppm. MS (70 eV): *m/z* (%) = 379 (50) [M^+], 362 (100) [M^+ – OH], 282 (86), 269 (60), 268 (46), 164 (26), 138 (21).

(3a*S*,3b*R*,7a*S*,8a*R*)/(3a*R*,3b*S*,7a*R*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1-trimethylsilyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta-[*a*]inden-3-one (*anti*-7bb), (3a*S*,3b*S*,7a*R*,8a*R*)/(3a*R*,3b*R*,7a*S*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1-trimethylsilyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (*syn*-7bb) and (3a*S*,3b*S*,7a*S*,8a*R*)/(3a*R*,3b*R*,7a*R*,8a*S*)-8a-Dimethylamino-3b-hydroxy-1-trimethylsilyl-3b,4,5,6,7,7a,8,8a-octahydro-3a*H*-cyclopenta[*a*]inden-3-one (8bb): According to GP4, to a solution of complex **4b** (2.37 g, 5.01 mmol) in pyridine (100 mL) was added 737 mg (7.50 mmol) of trimethylsilylethyne (**5b**), and the mixture was kept at 80 °C for 4 d. After exposure to air, filtration and evaporation of the solvent, the residue was directly dissolved in dioxane (150 mL), treated with concd. hydrochloric acid (5 mL), and stirred for another 2 d according to GP5. Finally, chromatography on silica gel (60 g) eluting with pentane/Et_2O (from 3:1 to 1:2) gave 36 mg (2%) of **8bb** [R_f = 0.49 (pentane/Et_2O, 1:1)] as a colorless oil, 441 mg (29%) of *anti*-**7bb** [R_f = 0.25 (pentane/Et_2O, 1:1)] as colorless crystals (m.p. 94 °C) and 154 mg (10%) of *syn*-**7bb** [R_f = 0.15 (pentane/Et_2O, 1:1), including an unknown diastereomer (9%)] as a colorless oil.

***anti*-7bb:** IR (KBr): $\tilde{\nu}$ = 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 = 0.22 [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) ppm. ^{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) ppm. 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) [$Si(CH_3)_3^+$]. $C_{17}H_{29}NO_2Si$ (307.5): calcd. C 66.40, H 9.51; found C 66.71, H 9.25.

***syn*-7bb and an Unknown Diastereomer:** IR (film): $\tilde{\nu}$ = 2937 cm^{-1} (C–H), 1700 (C=O), 1248, 909, 841. ^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) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): *syn*-**7bb**: 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 diastereomer: 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) ppm. 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) [$Si(CH_3)_3^+$].

8bb: IR (film): $\tilde{\nu}$ = 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) ppm. ^{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) ppm. 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).

General Procedure for the Dehydration of Hydroxy Ketones *anti*-7a–c (GP6): A solution of the respective *anti*-**7** in benzene (150 mL) was treated with a catalytic amount (15 mg) of *p*TsOH, and the mixture was heated under reflux using a Dean–Stark apparatus. After cooling to ambient temperature, a satd. solution of potassium carbonate (50 mL) was added to the mixture, and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried with $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel [or aluminum oxide (activity grade II)].

7a-Dimethyamino-1,2-diphenyl-3a,4,5,6,7,7a-hexahydrocyclopenta[*a*]pentalen-3-one (15aa) and 7a-Dimethyamino-1,2-diphenyl-3a,5,6,6a,7,7a-hexahydrocyclopenta[*a*]pentalen-3-one (16aa): According to GP6, a solution of *anti*-**7aa** (200 mg, 0.54 mmol) in benzene (200 mL) was treated with a catalytic amount (20 mg) of *p*TsOH, and the mixture was heated under reflux for 2 h. After work-up, the obtained residue was the starting material *anti*-**7aa**. Upon prolonged (17 h) heating of this mixture, a pale-yellow oil was obtained, which was subjected to chromatography on aluminum oxide (II, 30 g). Elution with pentane/Et_2O, (3:1) gave 175 mg (92%) of **15aa/16aa** [R_f = 0.35, ratio = 1.1:1] as a pale-yellow solid. When the mixture of 102 mg (0.29 mmol) of these regioisomers was heated under reflux again with a catalytic amount (20 mg) of *p*TsOH in benzene (100 mL) for 36 h without using a Dean–Stark apparatus, 94 mg (92%) of the mixture of **15aa/16aa** (ratio 2.1:1) was isolated. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.19–1.56 (1 H) and 2.04–2.80 (7 H) [m, 8 H, 4,5,6,7-H of **15aa** and, 5,6,6a,7-H of **16aa**], 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 **16aa**), 7.11–7.35 (m, 8 H, Ph-H), 7.63–7.70 (m, 2 H, Ph-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): 15aa: 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). 16aa: δ = 32.3, 36.3, 43.6 (–, C-5,6,7), 40.2 [+, $N(CH_3)_2$], 44.7 (+, C-6a), 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) ppm. MS (70 eV): *m*/*z* (%) = 355 (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 (15ba): A solution of *anti*-**7ba** (221 mg, 0.57 mmol) in benzene (150 mL) was treated with a catalytic amount (20 mg) of *p*TsOH, and the mixture was heated under reflux for 2 h. Chromatography on aluminum oxide (II, 30 g) eluting with pentane/Et_2O (3:1) gave 171 mg (81%) of **15ba** [R_f = 0.67 (pentane/Et_2O, 3:1)] as a pale-yellow solid (m.p. 155–156 °C). IR (KBr): $\tilde{\nu}$ = 2722 cm^{-1} (C–H), 1695 (C=O), 1458, 1333, 11 165, 1032. ^{1}H NMR (250 MHz, $CDCl_3$, plus HH-, CH-COSY, NOESY and HMBC): δ = 1.63–1.70 (4 H), 1.84–2.42 (4 H) [m, 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) ppm. ^{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-3a), 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) ppm. MS (70 eV): *m*/*z* (%) = 369 (100) [M^+], 341 (14) [M^+ – CO], 163 (22), 162 (25), 135 (9). $C_{26}H_{27}NO$ (369.5): calcd. 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 (15ca) and 9a-Dimethylamino-1,2-diphenyl-3a,5,6,7,8,8a,9,9a-octahydrocyclopenta[*a*]azulen-3-one (16ca): A solution of *anti*-**7ca** (150 mg, 0.37 mmol) in benzene (80 mL) was treated with a catalytic amount (15 mg) of *p*TsOH, and the mixture was heated under reflux for 18 h. Chromatography on silica gel (40 g) eluting with pentane/Et_2O (from 3:1 to 1:1) gave 78 mg (54%) of **15ca** [R_f = 0.33 (pentane/Et_2O, 3:1)] as a pale-yellow solid (m.p. 173–174 °C), and 59 mg (41%) of **16ca** [R_f = 0.16 (pentane/Et_2O, 3:1)] as a colorless solid (m.p. 171 °C).

15ca: IR (KBr): $\tilde{\nu}$ = 2913 cm^{-1} (C–H), 1689 (C=O), 1444, 1341, 1170, 775, 728, 705. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39–1.63 (6 H), 1.98–2.11 (2 H) and 2.10–2.43 (2 H) [m, 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) ppm. ^{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) ppm. MS (70 eV): *m*/*z* (%) = 383 (100) [M^+], 355 (7) [M^+ – CO], 338 (10), 177 (32). $C_{27}H_{29}NO$ (383.5): calcd. C 84.55, H 7.62; found C 84.32, H 7.32.

16ca: IR (KBr): $\tilde{\nu}$ = 2916 cm^{-1} (C–H), 1703 (C=O), 1444, 1337, 1268, 1153, 1033, 766, 697. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37–1.50 (3 H) and 1.75–2.47 (8 H) [m, 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), 5.99 (m, 1 H, 4-H), 7.10–7.35 (m, 8 H, Ph-H), 7.54–7.61 (m, 2 H, Ph-H) ppm. ^{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-8a), 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) ppm. 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).

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