An Efficient Synthesis of Bicyclo[3.3.0]oct-2-en-4-ones and 2-Azabicyclo[3.3.0]oct-7-en-6-ones via β-Amino-Substituted α,β-Unsaturated Fischer Carbene Complexes

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Dedicated to Professor Heindirk tom Dieck on the occasion of his 60th birthday

Keywords: Fischer carbene complexes, β-amino-substituted, α,β-unsaturated / Alkoxycyclopentadienes / Aldol reaction, diastereoselective / Bicyclo[3.3.0]octenones

The formal [3+2] cycloaddition of β-amino-substituted α,β-unsaturated Fischer carbenechromium complexes **2**, which are easily prepared in a one-pot procedure from terminal alkynes **1** via an initially formed alkynylidene complex by a Michael-type addition of a secondary amine, with a variety of alkynes **3** afford the 1,2,5-trisubstituted 3-alkoxy-5-dialkylamino-1,3-cyclopentadienes **4** with an acetal-protected aldehyde or ketone carbonyl group in either the 5-substituent R^1 or the N-substituent R^2. Under acidic conditions, both the enol ether moiety in the 5-membered ring as well as the acetals in the side chains are hydrolyzed, and the resulting cyclopentenones **6** with carbonyl-group containing side-chains undergo facile intramolecular aldol reactions to give bicyclo[3.3.0]oct-2-en-4-ones **8** and 8-azabicyclo[3.3.0]oct-2-en-4-ones **12**, respectively, in good to very good yields for most cases.

The chemistry of Fischer carbene complexes has become an important factor in the repertoire of organometallic transformations applied in organic synthesis.[1] The insertion of alkynes into (1-alkoxy-3-dialkylaminoalkenylidene)-pentacarbonylchromium complexes of type **2** and subsequent transformations of the resulting 1-chroma-1,3,5-hexatrienes has thoroughly been studied with respect to the effects of substituents, chelation, solvent, ligand additives, temperature and reagent concentrations.[2] Especially when carried out in the presence of donor solvents, the reaction proceeds without carbonyl insertion by 6π-electrocyclization and subsequent reductive elimination to give 5-dialkylamino-3-ethoxy-1,3-cyclopentadienes **4**, which correspond to a formal [3+2] cycloadduct of the carbene ligand in **2** to the alkyne **3**. Best yields of these products are generally obtained by performing the reactions in pyridine or acetonitrile, and the transformation is compatible with a large variety of functional groups R^1, R_L and R_S brought in with the alkynes **1** and **3**.[3] Functionally substituted cyclopentadienes of type **4** therefore offer themselves for further elaboration towards important skeletons of natural products or nonnatural biologically active compounds. In order to test the feasibility of such an approach to bicyclic skeletons, accesses to β-amino-substituted α,β-unsaturated Fischer carbene complexes of type **2** with an acetal-protected carbonyl group in the γ-position of R^1 or the β-position of R^2 were developed. The cyclopentenones of type **6** formed after hydrolysis of the ethoxycyclopentadienes of type **4** should be able to undergo intramolecular aldol reactions under acidic conditions to give bicyclo[3.3.0]oct-2-en-4-ones **8** and 8-azabicyclo[3.3.0]oct-2-en-4-ones **12**, respectively, by intramolecular aldol reactions[4] in analogy to previously published methodology.[5] We here report on the success of these recent developments.[6][7]

Results and Discussions

5-Dialkylamino-3-ethoxycyclopentadienes with Protected Carbonyl Groups in the 5- and the *N*-Substituent from (3-Aminoalkenylidene)-pentacarbonylchromium Complexes

Fischer-type β-amino-substituted α,β-unsaturated carbenechromium complexes **2** are easily available from terminal alkynes **1**, via initially formed alkynylcarbenechromium complexes by immediate Michael-type addition of a secondary amine;[8] all steps can actually be performed without isolation of any intermediate in a one-pot sequence giving high overall yields.[3] In most cases these complexes **2** are (*E*)-configured, only with bulky R groups like *tert*-butyl or groups of equivalent size are the (*Z*) isomers obtainable.[8b] The intermediate alkynylcarbenechromium complexes were previously prepared in diethyl ether with a small amount of tetrahydrofuran (THF) over a period of three hours.[8b,8c] When starting with the functionally sub-

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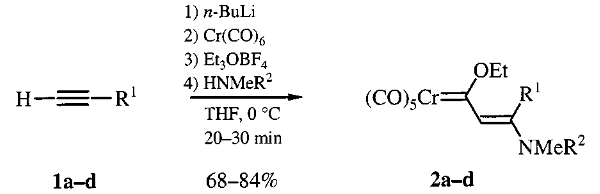
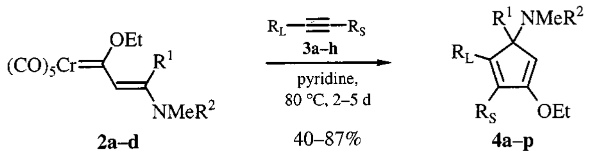
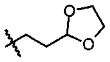
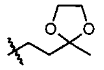
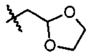
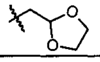


Scheme 1. For details see Table 1



Scheme 2. For details see Table 2

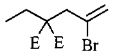
Table 1. Functionally substituted [3-(dialkylamino)-1-ethoxy-2-alken-1-ylidene]pentacarbonylchromium complexes **2a**–**d** from terminal alkynes **1a**–**d**

Alkyne	R^1	R^2	Product	(%)
1a		Me	**2a**	68
1b		Me	**2b**	72
1c	Me		**2c**	69
1d	*n*Pr		**2d**	84

stituted alkynes 2-(but-3′-ynyl)dioxolane (**1a**) and 2-(but-3′-ynyl)-2-methyldioxolane (**1b**), which were obtained by nucleophilic substitution with 1-lithio-2-trimethylsilylacetylene on the correspondingly functionalized alkyl iodide,[9][10] the long reaction times of this standard procedure led to partial decomposition of the alkynylcarbene complexes derived from **1a**,**b**. By using pure THF instead of diethyl ether from the beginning to enhance the solubility of hexacarbonylchromium, the reaction time could be shortened to 20–30 min at 0 °C.[11] The (3-amino-1-ethoxyalkenylidene)pentacarbonylchromium complexes **2a**–**d** were thus obtained in high purity and very good overall yields (68–84%) after simple filtration through silica gel (Scheme 1 and Table 1).

As had previously been shown, complexes of type **2** react with alkynes **3** in pyridine solution at 80°C[12] selectively to give 5-substituted 5-(dialkylamino)-3-ethoxycyclopentadienes **4** in good to very good yields.[3] Under these conditions, which are compatible with various functionalities at the vinylic terminus of complexes **2** and on the incoming alkyne **3**, the new complexes **2a**–**d** were treated with the alkynes **3a**–**h** to give the correspondingly substituted ethoxycyclopentadienes **4a**–**m** (Scheme 2 and Table 2). The yields ranged from 40 to 87%, depending mainly on the steric bulk of the substituents R_L and R_S on the alkyne **3**. Bulky groups like *tert*-butyl, TMS or TBDMS on the alkynes **3e**,**f**,**g** retard the insertion into the Cr=C bond. The resulting longer reaction times lead to increased decomposition of the carbenechromium complexes **2** and thus lower yields (entries 5–7, 11–13 in Table 2). The regioselectivity in the reactions of terminal alkynes was generally high yielding merely 1-substituted products such as **4e**–**h**,**k**,**l**,**p**, in only three cases, namely **4f**,**g**,**l**, was the second regioisomer obtained as a minor product (entries 6, 7, 12 in Table 2). Since the ethoxycyclopentadienes **4** are easily hydrolyzed even under mildly acidic conditions, e.g. in the presence of silica gel, to give the corresponding cyclopentenones **6**, they were all purified by chromatography on neutral alumina.

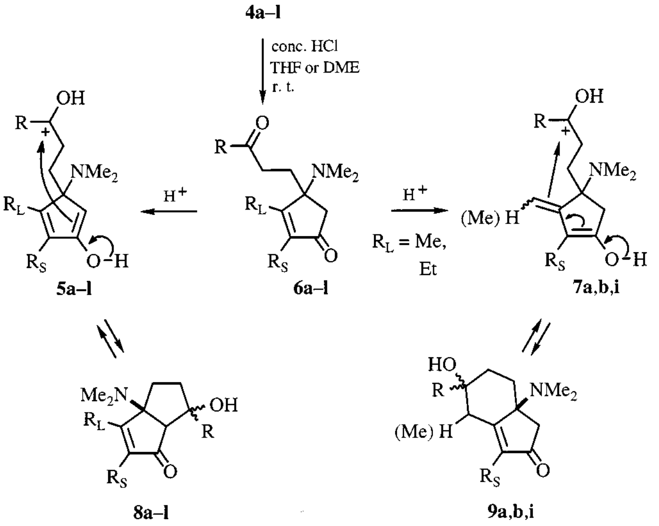
Table 2. Functionally substituted 5-dialkylamino-3-ethoxycyclopentadienes **4** from [(3-dialkylamino)-1-ethoxyalkenylidene]pentacarbonylchromium complexes **2**

Entry	Complex	Alkyne	R_L	R_S	Reaction Time	Product	Yield (%)
1	**2a**	**3a**	Me	Me	3 d	**4a**	87
2	**2a**	**3b**	Et	Et	4 d	**4b**	78
3	**2a**	**3c**	Ph	Ph	5 d	**4c**	81
4	**2a**	**3d**	*c*Pr	*c*Pr	4 d	**4d**	65
5	**2a**	**3e**	*t*Bu	H	3 d	**4e**	57
6	**2a**	**3f**	TMS	H	4 d	**4f**	40[a]
7	**2a**	**3g**	TBDMS	H	4 d	**4g**	42[b]
8	**2a**	**3h**		H	2 d	**4h**	48
9	**2b**	**3a**	Me	Me	3 d	**4i**	75
10	**2b**	**3c**	Ph	Ph	4 d	**4j**	51
11	**2b**	**3e**	*t*Bu	H	3 d	**4k**	59
12	**2b**	**3f**	TMS	H	4 d	**4l**	45[c]
13	**2c**	**3a**	Me	Me	6 d	**4m**	—[d]
14	**2c**	**3c**	Ph	Ph	7 d	**4n**	—[d]
15	**2d**	**3c**	Ph	Ph	3 d	**4o**	—[d]
16	**2d**	**3f**	TMS	H	40 h	**4p**	56

[a] In addition, 9% of the regioisomer of **4f** was obtained. – [b] In addition, 6% of the regioisomer of **4g** was obtained. – [c] In addition, 9% of the regioisomer of **4l** was obtained. – [d] The ethoxycyclopentadiene **4** was not isolated, but immediately subjected to strongly acidic conditions to set off the intramolecular aldol reaction to give **12** (see below).

Highly Substituted Bicyclo[3.3.0]oct-2-en-4-ones by Intramolecular Aldol Reaction

Intramolecular aldol reactions are well known and have often been used for the construction of oligocyclic systems. The ethoxycyclopentadienes **4a−l**, equipped with an acetal-protected 5-(3′-oxopropyl) or 5-(3′-oxobutyl) functionality, when treated with concentrated hydrochloric acid in tetrahydrofuran or dimethoxyethane solution at ambient temperature, are hydrolyzed both at the enol ether and the acetal moieties, and the resulting cyclopentenones **6a−l** undergo intramolecular aldol reactions to give 1-dimethylamino-6-hydroxybicyclo[3.3.0]oct-2-en-4-ones **8a−l** in good to very good yields (62−87%) except for **8d** (38% yield) (Scheme 3 and Table 3). In all these cases, the exocyclic carbonyl group reacts as such, while the endocyclic one reacts as the enol **5a−l**. In the case of **6a**,**b**,**i**, in which R_L and R_S are methyl or ethyl groups, a minor fraction reacts as the enol **7a**,**b**,**i** to give 1-dimethylamino-4-hydroxybicyclo[4.3.0]non-6-en-8-ones **9a**,**b**,**i** (5−16%). The bicyclic products **8** and **9** can easily be purified and separated by chromatography on silica gel.



Scheme 3. For details see Table 3

The required reaction times vary with the bulk of the substituents R_L and R_S. The conversion of the methyl-substituted cyclopentadienes **4a,i** is complete within 18 h, while those of cyclopentadienes with bulkier groups require up to 3 d. Whereas intramolecular aldol reactions, under thermodynamic control, normally yield *exo* diastereomers preferentially,[13] the *endo/exo* ratios for the products **8a−l** varied from 1:0 to 1:13 (see Table 3). The trialkylsilyl-substituted bicyclo[3.3.0]octenones **8f,g** were obtained with high *exo* selectivities (entries 6 and 7 in Table 3), whereas the phenyl- and *tert*-butyl-substituted products **8c,e** were mainly the *endo* isomers (entries 3 and 5 in Table 3). It is not surprising that the intramolecular aldol reactions of the 3′-oxobutyl-substituted cyclopentenones **6i−l** proceeded with lower diastereoselectivities. In all cases, the *exo* and *endo* diastereomers could easily be assigned on the basis of their ^1H-NMR spectra in which the coupling constants between the hydrogen atoms at C-5 and C-6 differ significantly according to their dihedral angles,[14] thus these $^3J_{HH}$ are 5 to 6 Hz larger for the *endo* than for the *exo* isomers. In addition, the ^{13}C signals of the bridgehead carbon atoms C-5 for the *endo* diastereomers, depending on the substituents R_L and R_S, are shifted downfield by up to 5−6 ppm compared to those of the *exo* isomers.

The configuration of the 6-hydroxy-6-methylbicyclo[3.3.0]oct-2-en-4-ones **8i−l** was assigned on the basis of the different chemical shifts of their bridgehead carbon atoms C-5 in the ^{13}C-NMR spectra (see above). The product **8l** crystallized well from chloroform, so that an X-ray crystal-structure analysis could be performed[15] which rigorously proves the *endo* orientation of the 6-hydroxy group in this bicyclo[3.3.0]octenone (Figure 1).

This facile production of highly functionalized bicyclo[3.3.0]oct-2-en-4-ones can also be carried out as a one-pot sequence, since the chromium salts, generated in the formal [3+2] cycloaddition of the β-amino-substituted α,β-unsaturated carbenechromium complexes **2** to alkynes **3**, do not disturb the intramolecular aldol reaction. Thus, in a one-pot operation, the product **8c** could be isolated in an overall yield of 65% starting from the complex **2a**.

Table 3. Highly substituted bicyclo[3.3.0]oct-2-en-4-ones **8** from functionally substituted 5-dialkylamino-3-ethoxycyclopentadienes **4a−l**

	Starting reaction			Bicyclo[3.3.0]octenones			Bicyclo[4.3.0]nonenones		
Entry	Material	Time	R	Product	*endo/exo*	(%)	Product	*endo/exo*	(%)
1	**4a**	18 h	H	**8a**	1:3	69	**9a**	1.4:1	16
2	**4b**	2 d	H	**8b**	8:1	84	**9b**	1:0	5
3	**4c**	3 d	H	**8c**	25:1	86			
4	**4d**	2 d	H	**8d**	2.5:1	38			
5	**4e**	2 d	H	**8e**	1:0	67			
6	**4f**	2 d	H	**8f**	1:13	87			
7	**4g**	3 d	H	**8g**	1:5.8	76			
8	**4h**	4 d	H	**8h**	1:0	62			
9	**4i**	18 h	Me	**8i**	1:3.2	76	**9i**	3:1	16
10	**4j**	2 d	Me	**8j**	1.8:1	81			
11	**4k**	3 d	Me	**8k**	1.6:1	81			
12	**4l**	2 d	Me	**8l**	2.6:1	80			

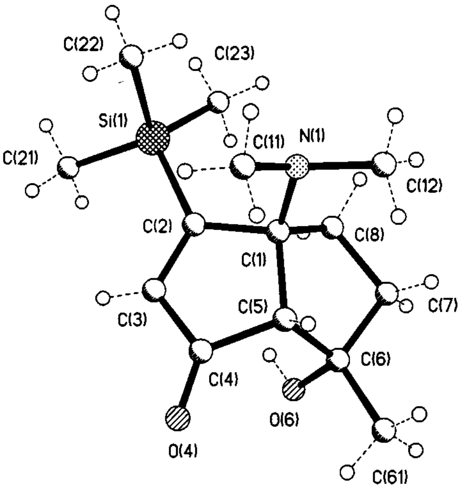
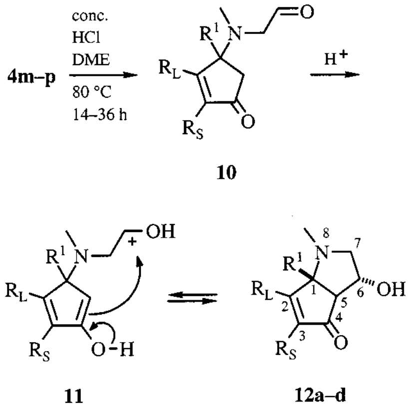


Figure 1. Structure of *endo*-**8l** in the crystal; $C_{14}H_{25}NO_2Si$, triclinic crystals of space group *P*1, cell dimensions: *a* = 1118.9(2), *b* = 1217.8(2), *c* = 1226.1(3) pm, α = 75.31(3), β = 80.12(3), γ = 74.84(3)°, *V* = 1.5500(5) nm³, 4060 reflections

8-Azabicyclo[3.3.0]octenones by Intramolecular Aldol Reactions

The 5-dialkylamino-3-ethoxycyclopentadienes **4m−p** with an acetal-protected 2′-oxoethyl group on the nitrogen atom, prepared from the correspondingly substituted carbenechromium complexes **2c,d** (Scheme 1), should be potential precursors to 8-azabicyclo[3.3.0]oct-2-en-4-ones **12**, just as the carbocyclic bicyclooctenones **8a−l** were obtained from the cyclopentadienes **4a−l**. The immediate precursor to the heterobicycles, the corresponding ethoxycyclopentadiene of type **4**, however, was isolated only in one case, namely **4p** (56%, Table 2). In all other cases, the formal [3+2] cycloaddition and the subsequent hydrolysis as well as intramolecular aldol reaction were carried out in the same flask. In all cases, the 6-hydroxy-8-azabicyclo[3.3.0]oct-2-en-4-ones **12** were isolated in moderate to good overall yield (36−50%) (Scheme 4 and Table 4). However, more stringent conditions, i. e. application of 50−60 equiv. of concentrated hydrochloric acid in dimethoxyethane (DME) at 80°C, were required. Apparently, the protonation of the amino group, which generates a positive charge in close proximity to the acetal moiety, severely retards the hydrolysis of the latter. On the other hand, the aldol reaction under these harsher conditions was highly diastereoselective and gave only the *endo* diastereomers *endo*-**12a−d** after chromatography on silica gel.



Scheme 4. For details see Table 4.

Experimental Section

^1H and ^{13}C NMR: Varian VXR 200 (200 and 50.3 MHz), Bruker AW 250 (250 and 62.9 MHz). Chemical shifts in $CDCl_3$ or $[D_6]$benzene are reported as δ values with chloroform (δ = 7.26) or benzene (δ = 7.15) as internal reference unless stated otherwise. − IR: Bruker IFS 66 (FT-IR). − Low-resolution EI MS: Varian MAT CH 7 with Aerograph 1740, ionizing voltage 70 eV. − High-resolution MS: VG-70−250S. − Elemental analyses: Mikroanalytisches Laboratorium der Universität Göttingen. − Melting points were determined with a Büchi melting-point apparatus and are uncorrected. − Solvents for extraction and chromatography were of technical grade and freshly distilled before use. − Chromatography: Merck silica gel 60 (230−400 mesh) or ICN neutral alumina (Super I, Activity II according to Brockmann). The concentrations of organolithium compounds were determined by titration according to the method of Suffert.[16] All reactions were carried out under nitrogen or argon in oven- and/or flame-dried glassware. Unless specified otherwise, solutions of NH_4Cl, $NaHCO_3$ and NaCl were saturated aqueous solutions. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, and pyridine was distilled from CaH_2.

General Procedure for the Preparation of β-Amino-Substituted α,β-Unsaturated Fischer Carbene Complexes 2 (GP 1): To a solution of 20 mmol of a terminal alkyne **1** in 100 mL of tetrahydrofuran was added 8.5 mL (20 mmol) of a 2.36 M solution of *n*-butyllithium in hexane over a period of 10 min at −78 °C. The solution was stirred at −78 °C for an additional 3 h. Then 4.4 g (20 mmol) of hexacarbonylchromium was added at −78 °C. The solution was warmed up to room temp. and stirred for another 30 min. Subsequently, 3.90 g (20.5 mmol) of Et_3OBF_4 was added at 0 °C. After 10 min, 1 equiv. of a secondary amine as a gas ($HNMe_2$) or a solution was added with vigorous stirring. The progress of the reaction was monitored by TLC. After filtration of the solution through Celite,

Table 4. 6-Hydroxy-8-azabicyclo[3.3.0]oct-2-en-4-ones **12** from 5-dialkylamino-3-ethoxycyclopentadienes **4**

Entry	Starting material	R_L	R_S	R^1	Time [h]	Product	d.r. (*endo/exo*)	(%)
1	**2c** + **3a**[a]	Me	Me	Me	14	**12a**	1:0	36[b]
2	**2c** + **3c**[a]	Ph	Ph	Me	36	**12b**	1:0	50[b]
3	**2d** + **3c**[a]	Ph	Ph	*n*Pr	20	**12c**	1:0	42[b]
4	**4p**	TMS	H	*n*Pr	20	**12d**	1:0	71

[a] The intermediate alkoxycyclopentadiene **4** was not isolated. − [b] Yield over two steps.

the solvent was evaporated in vacuo, and the residue was purified by column chromatography on flash silica gel.

General Procedure for the Preparation of Dialkylaminoethoxycyclopentadienes 4 (GP 2): A screw-cap Pyrex bottle was charged with a 0.05 M solution of a Fischer carbene complex **2** in anhydrous pyridine and 2−4 equiv. of an alkyne **3**. Dry nitrogen was bubbled through the solution for 5 min. The bottle was sealed with the screw cap and heated at 80 °C for 2 to 5 d. The solvent was removed under reduced pressure and diethyl ether was added to the residue. The mixture was exposed to air for 2 h. The diethyl ether was removed under reduced pressure and the residue was purified by column chromatography on neutral alumina (II).

General Procedure for the Preparation of Bicyclo[3.3.0]oct-2-en-4-ones 8 and Bicyclo[4.3.0]non-6-en-8-ones 9 (GP 3): To a 0.02 M solution of a 5-dialkylamino-3-ethoxycyclopentadiene **4** in tetrahydrofuran or dimethoxyethane was added 30 equiv. of concentrated HCl. The solution was stirred at room temp. or 80 °C for 1−3 d. After neutralization with 1 N KOH, the mixture was poured into CH_2Cl_2 and water, and the aqueous layer was extracted with three portions of CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel and/or recrystallization.

General Procedure for the Preparation of *endo*-6-Hydroxy-8-azabicyclo[3.3.0]oct-2-en-4-ones 12 (GP 4): A screw-cap Pyrex bottle was charged with a 0.05 M solution of pentacarbonyl{(2*E*)-3-[(1′,3′-dioxolan-2′-ylmethyl)methylamino]-1-ethoxy-2-alken-1-ylidene}chromium (**2**) in anhydrous pyridine and 3−6 equiv. of an alkyne **3**. Dry nitrogen was bubbled through the solution for 5 min. The bottle was sealed with the screw cap and heated at 80 °C for 2−6 d. The solvent was removed under reduced pressure, and diethyl ether was added to the residue. The mixture was exposed to air for 2 h. The diethyl ether was removed under reduced pressure, and the residue was filtered through Celite and the filtrate was concentrated. The filtrate was diluted with 10 mL of DME and 30 equiv. of conc. HCl. This solution was stirred at 80 °C for 14−36 h. The solution was poured into 50 mL of water. After neutralization with 2 N KOH, the aqueous layer was extracted with three portions of 50 mL of CH_2Cl_2 each. The combined organic layers were dried with $MgSO_4$, the solvent was evaporated in vacuo, and the residue purified by chromatography on silica gel and/or recrystallization.

Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(2′-methyl-1′,3′-dioxolan-2′-yl)-2-penten-1-ylidene]chromium (2b): 2-(But-3′-ynyl)-2-methyl-1,3-dioxolane (**1b**) (2.20 g, 15.7 mmol) in 100 mL of THF was treated with *n*-butyllithium (6.70 mL, 15.8 mmol), hexacarbonylchromium (3.45 g, 15.7 mmol), triethyloxonium tetrafluoroborate (3.4 g, 18 mmol) and dimethylamine (1 equiv. as a gas) according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 3:1, column 40 × 4 cm), 4.89 g (72%) of **2b** (R_f = 0.23, diethyl ether) was obtained as yellow crystals, m.p. 102 °C. − IR (KBr): $\tilde{\nu}$ = 2983 cm^{-1} (C−H), 2046 (C=O), 1904 (C=O), 1532, 1481, 1440, 1262, 1207, 1081, 1053, 1016, 920, 810, 694, 670. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, CH_3) 1.51 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.85 (t, ^3J = 8.2 Hz, 2 H, 5-H), 2.82 (t, ^3J = 8.2 Hz, 2 H, 4-H), 3.15 [s, 6 H, $N(CH_3)_2$], 3.96 (m_c, 4 H, OCH_2CH_2O), 4.75 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.34 (s, 1 H, 2-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.57 (+, OCH_2CH_3), 24.09 (+, CH_3), 25.84 (−, C-5), 36.52 (−, C-4), 40.73 [+, $N(CH_3)_2$], 64.91 (−, OCH_2CH_2O), 74.14 (−, OCH_2CH_3), 109.23 (C_{quat}, C-2′), 117.99 (+, C-2), 158.41 (C_{quat}, C-3), 219.38, 224.42 (C_{quat}, C=O), 286.87 (C_{quat}, C-1). − MS (70 eV); *m/z* (%): 433 (4) [M^+], 405 (10) [M^+ − CO], 377 (2) [M^+ − 2 CO], 349 (18) [M^+ − 3 CO], 321 (10) [M^+ − 4 CO], 293 (78) [M^+ − 5 CO], 261 (10), 233 (51) [M^+ − 5 CO − $(OCH_2)_2$], 231 (100), 221 (12), 202 (18), 188 (15), 180 (37), 152 (13), 136 (23), 124 (95), 95 (18), 87 (13), 52 (30) [Cr^+], 33 (15). − $C_{18}H_{23}CrNO_8$ (433.4): calcd. C 49.89, H 5.35, N 3.23; found C 50.08, H 5.33, N 3.21.

Pentacarbonyl{(2*E*)-3-[(1′,3′-dioxolan-2′-ylmethyl)methylamino]-1-ethoxy-2-buten-1-ylidene}chromium (2c): Propyne (**1c**) (1.40 g, 35.0 mmol) in 150 mL of THF was treated with *n*-butyllithium (12.7 mL, 30.0 mmol), hexacarbonylchromium (6.60 g, 30.0 mmol), triethyloxonium tetrafluoroborate (5.89 g, 31.0 mmol) and (1,3-dioxolan-2-ylmethyl)methylamine (3.63 g, 31.0 mmol) according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 3:1, column 40 × 4 cm), 8.39 g (69%) of **2c** (R_f = 0.13, diethyl ether) was obtained as yellow crystals, m.p. 72 °C. − IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1} (C−H), 2046, 1972, 1905 (C=O), 1522, 1442, 1255, 1030, 670. − ^1H NMR (250 MHz, C_6D_6): δ = 1.14 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.45 (s, 3 H, 4-H), 1.62−2.03 (m, 2 H, NCH_2), 2.35 (s, 3 H, NCH_3), 3.35 (m_c, 4 H, OCH_2CH_2O), 4.41 (m_c, 1 H, 2′-H), 4.70 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.61 (s, 1 H, 2-H). − ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 14.41 (+, OCH_2CH_3), 40.39 (+, C-4), 45.21 (−, NCH_2), 49.82 (+, NCH_3), 63.99 (−, OCH_2CH_2O), 73.05 (−, OCH_2CH_3), 100.88 (+, C-2′), 118.23 (+, C-2), 155.40 (C_{quat}, C-3), 219.17, 223.87 (C_{quat}, C=O), 286.17 (C_{quat}, C-1). − MS (70 eV); *m/z* (%): 405 (18) [M^+], 377 (8) [M^+ − CO], 349 (5) [M^+ − 2 CO], 321 (27) [M^+ − 3 CO], 293 (35) [M^+ − 4 CO], 265 (100) [M^+ − 5 CO], 208 (95), 168 (41), 123 (40), 52 (58) [Cr^+]. − $C_{16}H_{19}CrNO_8$ (405.3): 405.0515 (correct HRMS).

5-Dimethylamino-5-[2′-(1′′,3′′-dioxolan-2′′-yl)ethyl]-3-ethoxy-1,2-diphenyl-1,3-cyclopentadiene (4c): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(1′,3′-dioxolan-2′-yl)-2-penten-1-ylidene]chromium (**2a**) (1.05 g, 2.50 mmol) in 50 mL of pyridine was treated with diphenylethyne (**3c**) (891 mg, 5.00 mmol) and heated at 80 °C for 5 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 40:1 to 1:1, column 40 × 2.0 cm), 822 mg (81%) of **4c** (R_f = 0.40 on alumina, pentane/diethyl ether (1:1) was obtained as yellow crystals, m.p. 72 °C. − IR (KBr): $\tilde{\nu}$ = 2935 cm^{-1} (C−H), 2862 (C−H), 2822, 2779, 1629 (C=C), 1580 (C=C), 1485, 1443, 1403, 1370, 1347, 1307, 1192, 1144, 1054, 911, 762, 733, 701. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.39 (m_c, 2 H, 2′-H), 1.75 (m_c, 1 H, 1′-H), 2.10 (m_c, 1 H, 1′-H), 2.37 [s, 6 H, $N(CH_3)_2$], 3.72−4.01 (m, 6 H, OCH_2CH_2O, OCH_2CH_3) 4.64 (t, ^3J = 4.8 Hz, 1 H, 2′′-H), 5.04 (s, 1 H, 4-H), 7.11−7.26 (m, 8 H, Ph-H), 7.44−7.48 (m, 2 H, Ph-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.33 (+, OCH_2CH_3), 27.83, 28.17 (−, C-1′, C-2′), 40.13 [+, $N(CH_3)_2$], 64.60, 64.66, 64.82 (−, OCH_2CH_2O, OCH_2CH_3), 75.79 (C_{quat}, C-5), 96.77 (+, C-4), 104.89 (+, C-2′′), 126.72, 127.02, 127.75, 127.79, 129.40, 130.00 (+, Ph-C), 133.88, 135.42 (C_{quat}, Ph-C), 138.15 (C_{quat}, C-1), 145.61 (C_{quat}, C-2), 159.23 (C_{quat}, C-3). − MS (70 eV); *m/z* (%): 405 (26) [M^+], 376 (22) [M^+ − C_2H_5], 360 (8), 304 (20), 274 (27), 215 (9), 178 (18), 99 (100), 73 (47) [$CH(OCH_2)_2^+$], 47 (26). − $C_{26}H_{31}NO_3$ (405.5): calcd. C 77.01, H 7.71; found C 77.03, H 7.75.

1-*tert*-Butyl-5-dimethylamino-3-ethoxy-5-[2′-(2′′-methyl-1′′,3′′-dioxolan-2′′-yl)ethyl]-1,3-cyclopentadiene (4k): Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-5-(2′-methyl-1′,3′-dioxolan-2′-yl)-2-penten-1-ylidene]chromium (**2b**) (867 mg, 2.00 mmol) in 40 mL of pyridine was treated with 3,3-dimethylbutyne (**3e**) (492 mg, 6.00 mmol) and heated at 80 °C for 3 d according to GP 2. After column chromatography on neutral alumina (pentane/diethyl ether, 20:1 to 0:1, column 30 × 2.0 cm), 382 mg (59%) of **4k** (R_f = 0.59

on alumina, pentane/diethyl ether, 1:1) was obtained as a colorless oil. − IR (film): $\tilde{\nu}$ = 2954 cm^{-1} (C−H), 2870 (C−H), 2819, 2778, 1628 (C=C), 1570 (C=C), 1458, 1371, 1341, 1295, 1232, 1199, 1062, 974, 946, 859, 749, 717. − ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ = 1.20 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.22 (s, 3 H, $\mathrm{CH_3}$), 1.31 (t, ^{3}J = 7.0 Hz, 3 H, $\mathrm{OCH_2C}H_3$), 1.42 (m$_c$, 2 H, 2′-H), 1.93 (m$_c$, 1 H, 1′-H), 2.02 (m$_c$, 1 H, 1′-H), 2.19 [s, 6 H, $\mathrm{N(CH_3)_2}$], 3.76−3.95 (m, 6 H, $\mathrm{OCH_2}$-$\mathrm{CH_2O}$, $\mathrm{OC}H_2\mathrm{CH_3}$) 4.62 (d, ^{4}J = 1.7 Hz, 1 H, 4-H), 5.80 (d, ^{4}J = 1.7 Hz, 1 H, 2-H). − ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, plus DEPT): δ = 14.41 (+, $\mathrm{OCH_2C}H_3$), 23.84 (+, $\mathrm{CH_3}$), 28.04 (−, C-1′), 30.68 [+, $\mathrm{C(}C\mathrm{H_3)_3}$], 33.09 (−, C-2′), 34.61 [C$_{\mathrm{quat}}$, $C\mathrm{(CH_3)_3}$], 40.73 [+, $\mathrm{N(CH_3)_2}$], 64.19, 64.50 (−, $\mathrm{OCH_2CH_2O}$, $\mathrm{O}C\mathrm{H_2CH_3}$), 78.84 (C$_{\mathrm{quat}}$, C-5), 95.89 (+, C-4), 110.30 (C$_{\mathrm{quat}}$, C-2′′), 124.75 (+, C-2), 158.39 (C$_{\mathrm{quat}}$, C-1), 161.26 (C$_{\mathrm{quat}}$, C-3). − MS (70 eV); *m/z* (%): 323 (61) [M^{+}], 294 (100) [M^{+} − $\mathrm{C_2H_5}$], 266 (56), 192 (12), 177 (20), 126 (18), 98 (16), 87 (92) [$\mathrm{CH_3C(OCH_2)_2^{+}}$], 43 (17). − $\mathrm{C_{19}H_{33}NO_3}$ (323.5): calcd. C 70.55, H 10.28; found C 70.74, H 10.17.

***trans*-1-Dimethylamino-7-ethyl-4-hydroxy-5-methylbicyclo[4.3.0]non-6-en-8-one (9b), 1-Dimethylamino-2,3-diethyl-*endo*-6-hydroxybicyclo[3.3.0]oct-2-en-4-one (*endo*-8b) and 1-Dimethylamino-2,3-diethyl-*exo*-6-hydroxy[3.3.0]oct-2-en-4-one (*exo*-8b):** 5-Dimethylamino-5-[2′-(1′′,3′′-dioxolan-2′′-yl)ethyl]-3-ethoxy-1,2-diethyl-1,3-cyclopentadiene (**4b**) (487 mg, 1.57 mmol) in 75 mL of THF was treated with concentrated HCl (4.5 mL, 45 mmol) at room temp. for 2 d according to GP 3. After column chromatography on silica gel (diethyl ether/methanol, 20:1 to 5:1, column 40 × 4 cm), 18 mg (5%) of **9b** (R_{f} = 0.79, methanol), 254 mg (68%) of *exo/endo*-**8b** (1:6.5) (R_{f} = 0.70, 0.61, methanol), and 59 mg (16%) of *endo*-**8b** were obtained as colorless oils.

9b: IR (film): $\tilde{\nu}$ = 3446 cm^{-1} (OH), 2937 (C−H), 2872 (C−H), 2822, 2777, 1684 (C=O), 1633 (C=C), 1457, 1372, 1328, 1292, 1255, 1230, 1160, 1136, 1066, 1046, 1026, 988, 927. − ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ = 1.01 (t, ^{3}J = 7.5 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.17 (m$_c$, 1 H, 2-H), 1.45 (d, ^{3}J = 7.3 Hz, 3 H, $\mathrm{CH_3}$), 1.60 (m$_c$, 1 H, 2-H), 1.72 (AB, d, ^{2}J = 18.9 Hz, 1 H, 9-H), 2.08 [s, 6 H, $\mathrm{N(CH_3)_2}$], 2.14 (m$_c$, 2 H, 3-H), 2.24 (br. s, 1 H, OH), 2.34 (q, ^{3}J = 7.5 Hz, 1 H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.36 (q, ^{3}J = 7.5 Hz, 1 H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.55 (AB, d, ^{2}J = 18.9 Hz, 1 H, 9-H), 3.15 (dq, ^{3}J = 7.3, ^{3}J = 2.5 Hz, 1 H, 5-H), 3.99 (m$_c$, 1 H, 4-H). − ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, plus DEPT): δ = 14.82, 14.94 (+, $\mathrm{CH_3}$, $\mathrm{CH_2C}H_3$), 16.18 (−, $C\mathrm{H_2CH_3}$), 28.62, 32.16, 36.96 (−, C-3, C-2, C-9), 38.57 [+, $\mathrm{N(CH_3)_2}$], 38.83 (+, C-5), 66.04 (C$_{\mathrm{quat}}$, C-1), 73.57 (+, C-4), 142.86 (C$_{\mathrm{quat}}$, C-7), 174.00 (C$_{\mathrm{quat}}$, C-6), 207.26 (C$_{\mathrm{quat}}$, C-8). − MS (70 eV); *m/z* (%): 237 (75) [M^{+}], 220 (7) [M^{+} − OH], 208 (63) [M^{+} − $\mathrm{C_2H_5}$], 193 (100) [M^{+} − $\mathrm{N(CH_3)_2}$], 175 (94) [M^{+} − $\mathrm{N(CH_3)_2}$ − $\mathrm{H_2O}$], 165 (22), 146 (49), 130 (20), 105 (25), 84 (26), 55 (13), 44 (10) [$\mathrm{N(CH_3)_2^{+}}$].

***endo*-8b:** IR (film): $\tilde{\nu}$ = 3469 cm^{-1} (OH), 2963 (C−H), 2871 (C−H), 2823, 2776, 1684 (C=O), 1637 (C=C), 1461, 1377, 1354, 1304, 1253, 1211, 1155, 1105, 1021, 969, 903, 883, 834. − ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ = 0.99 (t, ^{3}J = 7.6 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.19 (t, ^{3}J = 7.6 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.24 (m$_c$, 1 H, 8-H), 1.76 (m$_c$, 1 H, 8-H), 1.90 (m$_c$, 2 H, 7-H), 2.12 [s, 6 H, $\mathrm{N(CH_3)_2}$], 2.18 (m$_c$, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.43 (m$_c$, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.66 (d, $^{3}J_{cis}$ = 9.1 Hz, 1 H, 5-H), 3.53 (br. s, 1 H, OH), 4.20 (ddd, $^{3}J_{cis}$ = 9.1, $^{3}J_{trans}$ = 4.5, $^{3}J_{cis}$ = 9.1 Hz, 1 H, 6-H). − ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, plus DEPT): δ = 12.77, 13.66 (+, $\mathrm{CH_2C}H_3$), 16.58, 20.47 (−, $C\mathrm{H_2CH_3}$), 28.47, 32.24 (−, C-8, C-7), 40.43 [+, $\mathrm{N(CH_3)_2}$], 47.39 (+, C-5), 73.04 (+, C-6), 78.29 (C$_{\mathrm{quat}}$, C-1), 144.83 (C$_{\mathrm{quat}}$, C-3), 177.86 (C$_{\mathrm{quat}}$, C-2), 208.85 (C$_{\mathrm{quat}}$, C-4). − MS (70 eV); *m/z* (%): 237 (68) [M^{+}], 220 (8) [M^{+} − OH], 208 (57) [M^{+} − $\mathrm{C_2H_5}$], 194 (19), 181 (100), 166 (41), 152 (18), 126 (15), 110 (26), 91 (11), 51 (7), 44 (6) [$\mathrm{N(CH_3)_2^{+}}$]. − $\mathrm{C_{14}H_{23}NO_2}$ (237.3): calcd. C 70.85, H 9.77; found C 70.87, H 9.72.

***exo*-8b:** ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ = 0.98 (t, ^{3}J = 7.6 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.19 (t, ^{3}J = 7.6 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.38 (m$_c$, 1 H, 8-H), 1.68 (m$_c$, 2 H, 7-H), 2.18 (m$_c$, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.20 [s, 6 H, $\mathrm{N(CH_3)_2}$], 2.33 (m$_c$, 1 H, 8-H), 2.40 (m$_c$, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.60 (s, 1 H, 5-H), 3.14 (br. s, 1 H, OH), 4.18 (d, ^{3}J = 3.5 Hz, 1 H, 6-H). − ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, plus DEPT): δ = 12.76, 13.51 (+, $\mathrm{CH_2C}H_3$), 16.67, 20.59 (−, $C\mathrm{H_2CH_3}$), 28.27, 32.19 (−, C-8, C-7), 40.82 [+, $\mathrm{N(CH_3)_2}$], 55.32 (+, C-5), 74.74 (+, C-6), 79.64 (C$_{\mathrm{quat}}$, C-1), 143.26 (C$_{\mathrm{quat}}$, C-3), 176.57 (C$_{\mathrm{quat}}$, C-2), 207.49 (C$_{\mathrm{quat}}$, C-4).

2-[2′,2′-Bis(ethoxycarbonyl)-4′-bromopent-4′-enyl]-1-dimethylamino-*endo*-6-hydroxybicyclo[3.3.0]oct-2-en-4-one (*endo*-8h): 1-[2′,2′-Bis(ethoxycarbonyl)-4′-bromopent-4′-enyl]-5-dimethylamino-[2′′-(1′′′,3′′′-dioxolan-2′′′-yl)ethyl]-3-ethoxycyclopenta-1,3-diene (**4h**) (364 mg, 0.67 mmol) in 30 mL of THF was treated with concentrated HCl (2.0 mL, 20 mmol) at room temp. for 4 d according to GP 3. After column chromatography on silica gel (pentane/diethyl ether, 2:1 to 0:1, column 40 × 4 cm), 197 mg (62%) of *endo*-**8h**, (R_{f} = 0.34, diethyl ether) was obtained as a colorless oil. − IR (film): $\tilde{\nu}$ = 3396 cm^{-1} (OH), 2980 (C−H), 1733, 1702 (C=O), 1618 (C=C), 1445, 1217, 1035, 859, 736. − ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ = 1.18 (t, ^{3}J = 7.1 Hz, 3 H, $\mathrm{CO_2CH_2C}H_3$), 1.21 (t, ^{3}J = 7.1 Hz, 3 H, $\mathrm{CO_2CH_2C}H_3$), 1.76−2.03 (m, 3 H, 7-H, 8-H), 2.12 (m$_c$, 1 H, 8-H), 2.14 [s, 6 H, $\mathrm{N(CH_3)_2}$], 2.71 (d, ^{3}J = 8.5 Hz, 1 H, 5-H), 3.08 (d, ^{2}J = 20.7 Hz, 1 H, 1′-H), 3.21 (br. s, 1 H, OH), 3.31 (s, 2 H, 3′-H), 3.37 (d, ^{2}J = 20.7 Hz, 1 H, 1′-H), 4.10−4.41 (m, 4 H, $\mathrm{CO_2C}H_2\mathrm{CH_3}$), 4.28 (m$_c$, 1 H, 6-H), 5.50 (d, ^{2}J = 1.7 Hz, 1 H, 5′-H), 5.58 (d, ^{2}J = 1.7 Hz, 1 H, 5′-H), 5.91 (s, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, plus DEPT): δ = 13.78 (+, 2 × $\mathrm{CO_2CH_2C}H_3$), 29.12 (−, C-8), 31.31 (−, C-1′), 33.12 (−, C-7), 39.59 [+, $\mathrm{N(CH_3)_2}$], 43.29 (−, C-3′), 48.66 (+, C-5), 55.29 (C$_{\mathrm{quat}}$, C-2′), 62.15 (−, $\mathrm{CO_2}C\mathrm{H_2CH_3}$), 72.62 (+, C-6), 80.33 (C$_{\mathrm{quat}}$, C-1), 122.24 (−, C-5′), 126.76 (+ C-3), 130.09 (C$_{\mathrm{quat}}$, C-4′), 169.36, 169.51 (C$_{\mathrm{quat}}$, $\mathrm{CO_2Et}$), 180.01 (C$_{\mathrm{quat}}$, C-2), 208.02 (C$_{\mathrm{quat}}$, C-4). − MS (70 eV); *m/z* (%): 473/471 (5/4) [M^{+}], 428/426 (6/5), 392 (100) [M^{+} − Br], 194 (81), 110 (38), 91 (10), 44 (6). − $\mathrm{C_{21}H_{30}BrNO_6}$ (472.4): calcd. C 53.40, H 6.40; found C 53.35, H 6.34.

1-Dimethylamino-*endo*-6-hydroxy-6-methyl-2,3-diphenylbicyclo[3.3.0]oct-2-en-4-one (*endo*-8j) and 1-Dimethylamino-*exo*-6-hydroxy-6-methyl-2,3-diphenylbicyclo[3.3.0]oct-2-en-4-one (*exo*-8j): 5-Dimethylamino-3-ethoxy-5-[2′-(2′′-methyl-1′′,3′′-dioxolan-2′′-yl)ethyl]-1,2-diphenyl-1,3-cyclopentadiene (**4j**) (484 mg, 1.15 mmol) in 50 mL of THF was treated with concentrated HCl (5.0 mL, 50 mmol) at room temp. for 2 d according to GP 3. After column chromatography on silica gel (pentane/diethyl ether, 2:1 to 0:1, column 40 × 4 cm), 105 mg (26%) of *endo*-**8j** (R_{f} = 0.50, diethyl ether) was obtained as colorless crystals, m.p. 158°C, 118 mg (30%) of *endo/exo*-**8j** (6:1) as colorless crystals and 100 mg (25%) of *exo*-**8j** (R_{f} = 0.32, diethyl ether) as colorless crystals, m.p. 174 °C.

***endo*-8j:** IR (KBr): $\tilde{\nu}$ = 3482 cm^{-1} (OH), 2968 (C−H), 2784 (C−H), 1678 (C=O), 1623 (C=C), 1488, 1446, 1371, 1348, 1282, 1212, 1170, 1123, 1030, 920, 766, 725, 695. − ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ = 1.60 (s, 3 H, $\mathrm{CH_3}$), 1.87 (m$_c$, 1 H, 8-H), 2.09 (m$_c$, 1 H, 8-H), 2.47 [s, 6 H, $\mathrm{N(CH_3)_2}$], 2.50 (m$_c$, 2 H, 7-H), 2.88 (s, 1 H, 5-H), 3.50 (br. s, 1 H, OH), 7.12−7.31 (m, 8 H, Ph-H), 7.53−7.62 (m, 2 H, Ph-H). − ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, plus DEPT): δ = 29.15 (+, $\mathrm{CH_3}$), 31.33 (−, C-8), 40.20 [+, $\mathrm{N(CH_3)_2}$], 40.90 (−, C-7), 55.78 (+, C-5), 78.19, 80.18 (C$_{\mathrm{quat}}$, C-6, C-1), 127.83, 127.99, 128.13, 129.21, 129.68, 129.77 (+, Ph-C), 131.65, 134.34 (C$_{\mathrm{quat}}$, Ph-C), 140.76 (C$_{\mathrm{quat}}$, C-3), 170.63 (C$_{\mathrm{quat}}$, C-2), 206.03 (C$_{\mathrm{quat}}$, C-4).

***exo*-8j:** IR (KBr): $\tilde{\nu}$ = 3483 cm^{-1} (OH), 2970 (C−H), 2784 (C−H), 1678 (C=O), 1623 (C=C), 1489, 1446, 1370, 1348, 1282, 1212, 1170, 1124, 1031, 920, 767, 726, 694. − ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.45$ (s, 3 H, CH_3), 1.47−1.79 (m, 3 H, 8-H, 7-H), 2.35 (m_c, 1 H, 8-H), 2.42 [s, 6 H, $N(CH_3)_2$], 2.89 (s, 1 H, 5-H), 3.45 (br. s, 1 H, OH), 7.10−7.27 (m, 8 H, Ph-H), 7.56−7.60 (m, 2 H, Ph-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): $\delta = 26.10$ (+, CH_3), 29.30 (−, C-8), 39.24 (−, C-7), 40.67 [+, $N(CH_3)_2$], 58.31 (+, C-5), 79.05, 80.81 (C_{quat}, C-6, C-1), 128.02, 128.16, 128.25, 129.28, 129.60, 129.75 (+, Ph-C), 131.54, 134.50 (C_{quat}, Ph-C), 141.37 (C_{quat}, C-3), 170.16 (C_{quat}, C-2), 205.79 (C_{quat}, C-4). − MS (70 eV); *m/z* (%): 347 (85) [M^+], 330 (17) [$M^+ - OH$], 290 (18), 276 (100), 152 (23), 126 (10), 44 (5) [$N(CH_3)_2{}^+$]. − $C_{23}H_{25}NO_2$ (347.5): calcd. C 79.51, H 7.25, N 4.03; found C 79.59, H 7.27, N 4.00.

***endo*-6-Hydroxy-1,8-dimethyl-2,3-diphenyl-8-azabicyclo[3.3.0]oct-2-en-4-one (12b):** Pentacarbonyl{(2*E*)-3-[(1′,3′-dioxolan-2′-ylmethyl)-methylamino]-1-ethoxy-2-buten-1-ylidene}chromium (**2c**) (600 mg, 1.48 mmol) and diphenylethyne (**3c**) (767 mg, 4.30 mmol) were treated for 7 d in anhydrous pyridine (30 mL) and then for 36 h in DME/HCl according to GP 4. After column chromatography on silica gel (diethyl ether/methanol, 1:0 to 10:1, column 1.5 × 15 cm), 237 mg (50%) of **12b** ($R_f = 0.10$, diethyl ether) was obtained as colorless crystals, m.p. 99 °C. − IR (KBr): $\tilde{\nu} = 3394\ cm^{-1}$ (OH), 2931, 2797 (C−H), 1700 (C=O), 1653 (C=C), 1437, 1266, 1031, 738. − ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.54$ (s, 3 H, CH_3), 2.08 (s, 3 H, NCH_3), 2.87 (br. s, 1 H, OH), 3.01 (d, $^3J = 7.7$ Hz, 1 H, 5-H), 3.02 (dd, $^2J = 10.3$, $^3J = 4.0$ Hz, 1 H, 7-H), 3.11 (dd, $^2J = 10.3$, $^3J = 4.5$ Hz, 1 H, 7-H), 4.52 (m_c, 1 H, 6-H), 7.03−7.25 (m, 6 H, Ph-H), 7.26−7.43 (m, 4 H, Ph-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, plus APT): $\delta = 18.98$ (+, CH_3), 36.36 (+, NCH_3), 63.10 (−, C-7), 63.36 (+, C-5), 69.54 (+, C-6), 70.88 (−, C-1), 127.68, 127.81, 128.02, 128.19, 128.28, 129.62 (+, Ph-C), 130.46, 130.47 (−, Ph-C), 140.28 (−, C-3), 172.34 (−, C-2), 204.57 (C-4). − MS (70 eV); *m/z* (%): 319 (79) [M^+], 304 (38) [$M^+ - CH_3$], 274 (18), 202 (82), 140 (100), 96 (71), 57 (17), 43 (16) [$NCH_3CH_2{}^+$]. − $C_{21}H_{21}NO_2$ (319.4): calcd. C 78.97, H 6.63; found C 78.89, H 6.74.

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