Addition and Ring Expansion Reactions of Tricarbonyl-(1,2-dioxobenzocyclobutene)chromium(0) with Carbon Nucleophiles – Unexpected Formation of Benzocycloheptene Derivatives and the First Head-to-Head Coupling of Two Methoxyallene Molecules

Beate Voigt[a], Michael Brands[b], Richard Goddard[b], Rudolf Wartchow[c], and Holger Butenschön*[a]

Institut für Organische Chemie der Universität Hannover[a],
Schneiderberg 1B, D-30167 Hannover, Germany
Fax: (internat.) + 49(0)511/762-4616
E-mail: holger.butenschoen@mbox.oci.uni-hannover.de

Max-Planck-Institut für Kohlenforschung[b],
Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

Institut für Anorganische Chemie der Universität Hannover[c],
Callinstraße 9, D-30167 Hannover, Germany

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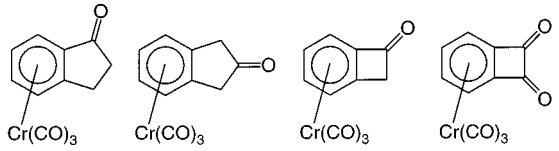
Addition of carbon nucleophiles to (benzocyclobutenedione)tricarbonylchromium(0) (**4**) results in the formation of *exo* mono- and diadducts as well as 1,2-diketones as the consequence of proximal ring-opening reactions. In one case the unexpected formation of benzocycloheptenedione complexes is observed. Treatment of **4** with an excess of 1-ethoxy-1-lithioethene gives the product of a dianionic oxy-Cope rearrangement followed by an intramolecular aldol addition. This is also the case with lithiated methoxyallene, and as the result the first head-to-head coupling product **12** of two methoxyallene molecules is isolated in good yield. **12** is used as a diene in Diels-Alder cycloadditions, and its molecular structure is compared to that of the similar molecule **13**, lacking the two *exo* methylene substitutents.

The chemistry of chromium arene complexes containing functionalized anellated rings shows interesting differences from that of the uncoordinated ligands. These differences have their origin in the electronic and steric effects of the tricarbonylchromium group.[1][2][3][4][5] The steric bulk causes external reagents to attack from the face opposite to the tricarbonylchromium group, and the electron withdrawing effect deactivates the aromatic ring towards electrophilic attack and increases the electrophilicity of carbonyl groups in the anellated ring. In addition, the plane of symmetry present in the aromatic system of most arenes is eliminated upon complexation. As a consequence of the facial differentiation complexes of prochiral arenes like 1-oxobenzocyclobutene or 1-indanone are chiral. The tricarbonylchromium complex **1** of 1-indanone was prepared as a racemate[6] in 1965 and in enantiopure form ten years later.[7] The transfer of the planar chirality of the complex to the novel asymmetric centre by diastereoselective alkylation of the enolate from the *anti* face represents now a textbook example for the use of tricarbonylchromium complexes in stereoselective organic synthesis.[8][9]

The tricarbonylchromium complexes **3**[10][11] and **4**[12][13] bear funtionalized benzocyclobutene ligands and are, in contrast to the indanone complexes **1** and **2**[14], strained complexes. Their chemical reactivity is characterized by



1 **2** **3** **4**

stereoselective additions and ring-opening reactions under mild reaction conditions. Important examples are the reduction of the keto functionality of **3** and subsequent oxyanion accelerated distal ring opening reactions of the resulting alcohol leading to *ortho*-quinodimethane intermediates which can be trapped by cycloaddition reactions with dienophiles.[10][11][15][16][17] However, in addition to this distal ring opening a proximal ring opening is frequently observed, which, less interestingly, usually leads to phenylacetic acid derivatives.[11][18] The most important reaction of the 1,2-dioxobenzocyclobutene complex **4** is the double nucleophilic addition to both keto groups which usually leads to decomposition products when uncoordinated 1,2-dioxobenzocyclobutene is used. *Cis*-selective double addition of vinyl lithium or vinyl Grignard reagents paves the way for an immediately occuring dianionic oxy-Cope rearrangement resulting in benz-anellated cyclooctenedione

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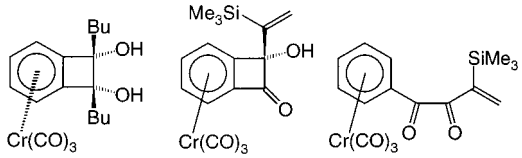
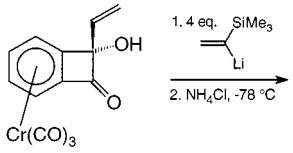
derivatives, which often undergo a subsequent intramolecular aldol addition.[12][13][19] Similar chemistry has been undertaken by Paquette with diisopropylsquarate. However, in contrast to **4**, both faces of the squarate are easily accessible by nucleophiles, and thus *trans* diaddition usually predominates over a *cis* diaddition, and not only dianionic oxy-Cope pathways are followed.[20] In some cases, a preference of a *cis* diaddition was indeed effected, and consequently products of dianionic oxy-Cope rerrangements were obtained.[21] Here we report on the addition of carbon nucleophiles to **4** resulting in the formation of mono and diadducts, ring opening, as well as ring expansion products. Among the latter are the unexpected formation of cycloheptenedione derivatives and an unprecedented coupling product of two methoxyallene molecules.

Uncoordinated benzocyclobutenedione does not usually undergo a nucleophilic diaddition to both ketone functionalities; instead decomposition usually is observed. There is however one brief report of a phenyllithium diaddition to benzocyclobutenedione,[22][23] and addition of ethyl acetate enolate to benzocyclobutenedione resulted in a 85% yield of a 5:4 mixture of the *cis* and the *trans* diadduct.[12] We earlier reported the successful diaddition of ethylmagnesium iodide to complex **4** to obtain a 60% yield of the *cis-endo* diadduct.[12] One drawback was that an over all 17fold excess of the Grignard reagent was necessary to obtain complete diaddition. We now observed that under optimized reaction conditions a diaddition of butyllithium to **4** is possible with similar yield using only 6 equivalents of the nucleophile. Diadduct **5** was obtained in 56% yield as the only detected diastereomer. In contrast to earlier work, shorter reaction times were used, and hydrolysis was carried out just after complete addition at low temperature. Best results were obtained with anion concentrations between 0.1 and 0.2 mol/l. The diaddition was not observed when sterically more hindered nucleophiles were employed. With *tert*-butyllithium, decomposition was observed, and with 1-lithio-1-(trimethylsilyl)ethene only monoaddition took place giving **6** in 63% yield, when 6 equivalents of the alkylating agent were used. With only 4 equivalents of the nucleophile, 44% of **6**, in addition to 25% of the proximal ring opening product **7**, were obtained. **6** and **7** were separated by column chromatography.



5 **6** **7**

Although proximal ring-opening reactions of benzocyclobutenone and benzocyclobutenedione complexes are known, this is the first example of such a reaction taking place by treatment of **4** with a carbon nucleophile.[18][24] Thus in contrast to O or N nucleophiles, not an acetic acid derivative but a 1,2-diketone is formed. Presumably the steric bulk of the trimethylsilyl group in **6** prevents the second addition to the remaining keto group. It appears that under the basic reaction conditions, the system resorts to the much less strained ring opening product **7**. In order to allow the second addition step, monovinyl adduct **8**[12] was used instead of diketone **4** and it was treated with 1-lithio-1-(trimethylsilyl)ethene. The vinyl substituent is much less sterically demanding than the trimethylsilyl-substituted vinyl residue in **6**, facilitating the second addition step. Based on our earlier work a dianionic oxy-Cope rearrangment was expected, which would lead to a benzocyclooctenedione derivative presumably accompanied by the transannular aldol adducts.[12][13][19] In contrast to our prior experience the reaction yields 73% of a 1:1 regioisomeric mixture of the benzocycloheptenedione complexes **9** and **10**.



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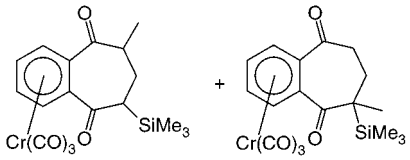
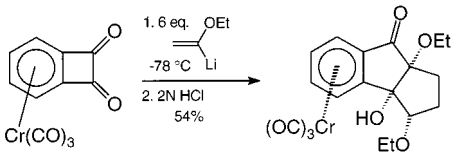


9 (34%) **10** (39%)

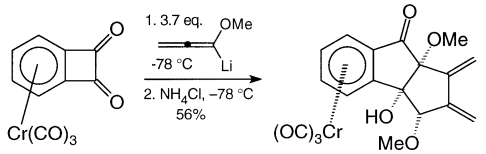
9 and **10** were obtained as pure diastereomers and have been characterized by all usual spectroscopic methods as well as correct elemental analyses; the relative configurations of the products could not yet be elucidated. To explain the formation of cycloheptenediones **9** and **10** one has to envisage an addition of 1-lithio-1-(trimethylsilyl)ethene to the keto group of **8**. In the adduct, the terminal vinyl carbon atoms apparently attack the internal vinyl carbon atom of the opposite vinyl substituents. To our knowledge, there is no literature precedence for such a reaction pathway.

1-Ethoxy-1-lithioethene[25][26] is another 1-substituted vinyllithium derivative with less steric crowding than the silyl compound used above. It is easily obtained by treatment of ethoxyethene with *tert*-butyllithium. In contrast to the reaction with 1-lithio-1-(trimethlsilyl)ethene a double nucleophilic addition took place, followed by a dianionic oxy-Cope rearrangement and an intramolecular aldol addition. As a result of this reaction sequence, the tricyclic chromium complex **11** is obtained in 54% yield as red solid. **11** was characterized spectroscopically, the assignment of the relative configuration being based on literature precedence.[12][13][19]



4 **11**

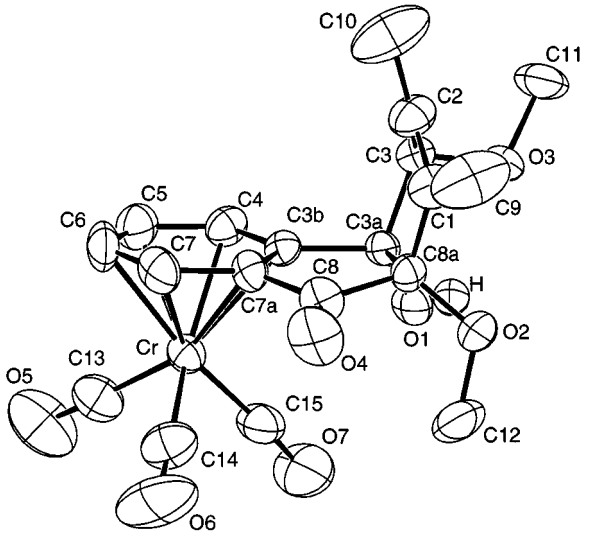
According to our experience, 2-substituted vinyllithium derivatives react much less cleanly than those with a substituent at C-1, unless one uses cyclic vinyllithium derivatives.[12][19][27] We assume that this can be explained by steric factors. As an interesting sterically less demanding class of vinyllithium derivatives, 1-alkoxy-1-lithioallenes were examined next. However, as the central carbon atom is *sp* hybridized in opposite to sp^2 in normal alkenes, it was a priori unpredictable, as to how the corresponing reaction would follow the regularly observed pathway of diaddition/dianionic oxy-Cope rearrangement.



4 **12**

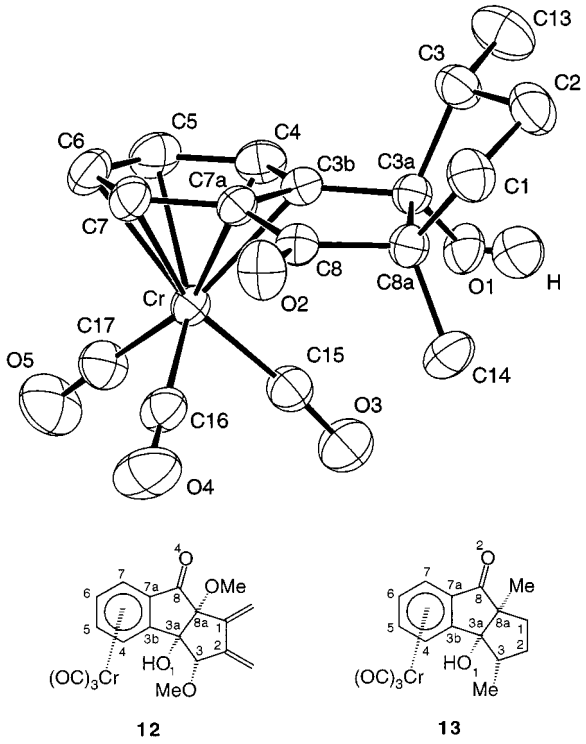
Methoxyallene, the simplest representative of the alkoxyallene class of compounds is easily available, can be metallated at C-1 by treatment with butyllithium between −78°C and −30°C, and has been used in organic synthesis for many years.[28][29][30] Treatment of **4** with 3.7 equiv. of 1-lithio-1-methoxyallene at −78°C followed by hydrolysis with aqueous ammonium chloride gave a 56% yield of **12** as the result of a dianionic oxy-Cope rearrangement followed by an intramolecular aldol addition. **12** is the only diastereomer observed and nicely demonstrates the potential of the reaction sequence to give access to highly functionalized polycycles. **12** was completely characterized by spectroscopic methods and an elemental analysis. However, in order to determine the relative configuration it was necessary to perform an X-ray structure analysis. Suitable crystals were grown from diethyl ether/petroleum ether (4:1), allowing to determine the structure depicted in Figure 1.

Figure 1. Structure of **12** in the crystal



The structure clearly shows that the intramolecular aldol addition took place in such a way, that the enolate attacked the ketone functionality from the face opposite from the chromium atom.[12] This configuration is also observed for the similar tricyclic complex **13**, which results from the reaction of **4** with an excess of 2-propenyllithium.[12] We have now suceeded in preparing crystals of **13**, and its crystal structure (Figure 2) reveals that both compounds have the same relative configuration. Table 1 gives a comparison of selected bond lengths of **12** and **13**. The data show that both structures are rather similar to one another, if one takes into account the different substitution patterns. Both complexes have an *anti* conformation of the tricarbonylchromium group with respect to the anellated ring. In both cases the anellated ring is almost coplanar with the arene ring, and the C3a−C8a bond is rather long [1.579(3) and 1.577(2) Å, respectively].

Figure 2. Structure of **13** in the crystal

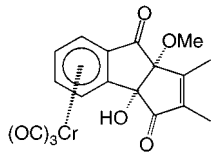


12 **13**

Table 1. Selected bond lengths [Å] in **12** and in **13**

12	[Å]	**13**
1.465(3)	C1−C2	1.513(3)
1.518(3)	C1−C8a	1.555(3)
1.490(3)	C2−C3	1.529(3)
1.538(3)	C3−C3a	1.549(3)
1.517(3)	C3a−C3b	1.511(2)
1.579(3)	C3a−C8a	1.577(2)
1.394(3)	C3a−O1	1.407(2)
1.408(3)	C3b−C4	1.408(3)
1.398(3)	C3b−C7a	1.407(2)
1.390(3)	C4−C5	1.402(3)
1.401(4)	C5−C6	1.421(3)
1.396(4)	C6−C7	1.392(3)
1.412(3)	C7−C7a	1.417(3)
1.477(3)	C7a−C8	1.481(2)
1.542(3)	C8−C8a	1.520(2)
1.203(3)	C8−O4/2	1.215(2)

In contrast to earlier investigations of the dianionic oxy-Cope rearrangement[12][13][19] we did not observe formation of the benzocyclooctenedione complex. Attempts to trap this presumably highly strained complex (6 sp^2 centers in the eight-membered ring) by rapid quenching with trifluoromethane sulfonic acid or with 6 N hydrochloric acid at −78°C resulted in reduced yields of **12** (17%, 28%, respectively) in addition to **14** (18%, 23%, respectively), which is the product of a partial ether hydrolysis in combination with a double bond migration. **12** can be transformed into **14** under acidic reaction conditions in over 90% yield. In addition, in some experiments a small amount of a product containing one *exo* methylene group, one methyl, and two methoxy substituents was obtained (see Experimental Section).



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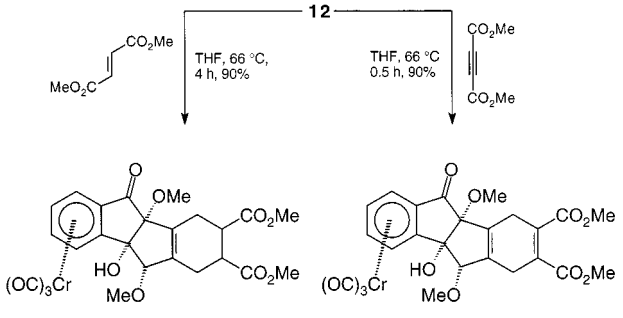
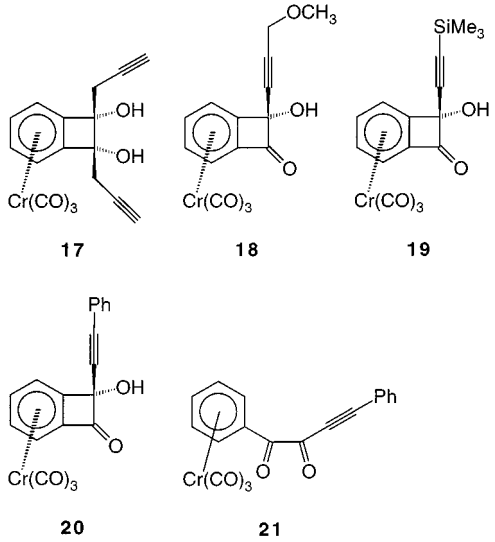
To our knowledge the reaction is the first example of a head-to-head coupling of two methoxyallene building blocks, and as a consequence of the formation of the exocyclic 1,3-diene substructure potential for further Diels-Alder cycloaddition reactions is opened up. In addition, the two allyl ether substructures deserve interest regarding allyl transition metal complexes and their reactions.[9][31]

To test the possibility of a Diels-Alder reaction, **12** was then treated with dimethyl fumarate. Although no reaction was observed in boiling diethyl ether, the reaction did indeed take place in THF at 66°C and gave [4+2] cycloadduct **15** as a mixture of two diastereomers (9:1) in 90% yield after a reaction time of 4 h. Treatment of **12** with dimethyl butynedioate in THF at 66°C gave cycloadduct **16** in 90% yield after only 30 min.



15 (9:1) **16**

Allenylmagnesium bromide, which can be obtained by treatment of propargyl bromide with magnesium was used as another example of an allenyl anion.[32] However, treatment of the benzocyclobutenedione complex **4** with 6 equivalents of allenylmagnesium bromide did not result in the desired rearrangement but instead gave the diadduct **17** in 90% yield. The reaction of **4** with 5.5 equiv. of 1-lithio-3-methoxypropyne, an isomer of the lithiated methoxyallene, only resulted in a single addition to **18** (48%). Single additions to **4** were also observed with 5.5 equiv. of 1-lithio-2-(trimethylsilyl)ethyne to give **19** in 52% yield and with 5.5 equiv. of 1-lithio-2-phenylethyne to give **20** (58%). When only 2.5 equiv. of 1-lithio-2-phenylethyne were used, 1,4-diphenylbut-3-yne-1,2-dione complex **21** was obtained in 75% yield as the result of a proximal ring opening similar to that leading to **7**.



We are currently investigating further reactions of **4** and will report on reactions with other nucleophiles in due course.

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Experimental Section

General: All operations were performed in flame-dried reaction vessels in an argon atmosphere using the Schlenk technique. Diethyl ether and THF were distilled from sodium-potassium alloy/benzophenone. Petroleum ether and chlorinated solvents were distilled from P_4O_{10}. − ^{1}H NMR: Bruker WP 80 (80 MHz), WP 200 SY (200.1 MHz), AM 400 (400.1 MHz). ^{13}C NMR: Bruker WP 200 SY (50.3 MHz), AM 400 (100.1 MHz). Signal multiplicities were determined with APT and DEPT techniques. Signals with negative phase are labelled with "−", those with positive phase with "+". Chemical shifts refer to $\delta_{TMS} = 0$ or to residual solvent signals.[33][34] Air sensitive samples were prepared and sealed under argon. − IR: Perkin-Elmer FT-IR 580 and 1710. Only selected diagnostic bands are reported. − MS: Finnigan MAT 112, 312, SSQ 7000 at 70 eV. − HRMS: Finnigan MAT 312, VG Autospec, peak matching with PFK. − Combustion analyses: Heraeus CHN Rapid, Elementar Vario EL (Analysensysteme GmbH). − Melting points: Thermal Sciences PL Gold DSC. − Column chromatography: Silica gel was degassed by heating it with a heat gun at reduced pressure followed by setting it under normal pressure with argon. This sequence was repeated five times.

General Procedure 1 (GP1): A −78°C cold solution of alkenyllithium in diethyl ether or THF (c = 0.1−0.2 M) is added dropwise at −78°C to a solution of tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0) (**4**)[12][13] in diethyl ether/THF (1:1). During the addition the red solution first becomes bright red and then changes ist color to deep brown. After complete addition at −78°C, 20 ml of a saturated aqueous solution of ammonium chloride or 20 ml of 2 N hydrochloric acid is added. After warming to 25°C the layers are separated, and the aqueous layer is extracted with 15-ml portions of diethyl ether until the extract remains colorless. The combined organic layers are dried with Na_2SO_4, filtered and the solvent is condensed into a cold trap. The crude product is purified by column chromtography on silica gel or by fractional crystallization.

General Procedure 2 (GP2): A solution of tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0) (**4**)[12][13] in diethyl ether/THF (1:1) is added dropwise at −78°C to a solution of an alkenyllithium in diethyl ether or THF (c = 0.1−0.2 M). During the addition the solution becomes deep brown. After complete addition 20 ml of a saturated aqueous solution of ammonium chloride or 20 ml of hydrochloric acid is added at −78°C. After warming to 25°C the layers are separated, and the aqueous layer is extracted with 15-ml portions of diethyl ether until the extract remains colorless. The collected organic layers are dried with Na_2SO_4, filtered, and the solvent is condensed into a cold trap. The crude product is purified by column chromatography on silica gel or by fractional crystallization.

Tricarbonyl(η^6-1,2-di-exo-butyl-1,2-di-endo-hydroxybenzocyclobutene)chromium(0) (**5**): GP2, 3.5 ml (5.60 mmol) of butyllithium (1.6 M in hexane) is dissolved in 20 ml of diethyl ether at −78°C. 250 mg (0.93 mmol) of **4** in 50 ml of diethyl ether/THF (1:1), 20 ml of a sat., aqu. soln. of ammonium chloride. Column chromatography on silica gel (400 × 30 mm, diethyl ether/petroleum ether, 1:1). 201 mg (0.52 mmol, 56%) of **5**, yellow solid (m.p. 65°C, R_f = 0.56). − IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} (s, br, OH), 3090 (w, arom. CH), 1976 (s, CO), 1888 (s, CO) − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.95 (t, 6 H, CH_3, ^3J = 6.0 Hz), 1.41 (m, 6 H, CH_2), 1.75 (m, 6 H, CH_2), 2.94 (s, 2 H, OH), 5.15 + 5.47 [AA′BB′ line system, 2× 2 H, 3(6)-H, 4(5)-H]. − ^{13}C NMR (400 MHz, $CDCl_3$, APT): δ = 13.8 (−, CH_3), 23.0 (+, CH_2), 26.6 (+, CH_2), 33.6 (+, CH_2), 83.4 [+, C-1(2)], 86.9 [−, C-4(5)], 91.2 [-, C-3(6)], 121.7 [+, C-2a(6a)], 232.0 (+, CO). − MS (70 eV, 130°C): *m/z* (%) = 384 (4) [M^+], 329 (4) [M^+ − 2 CO, ^{53}Cr], 328 (12) [M^+ − 2 CO], 300 (25) [M^+ − 3 CO], 299 (80), 282 (24), 257 (12), 240 (51), 238 (23), 230 (24), 214 (100) [M^+ − 3 CO, − OH, − C_5H_9], 187 (30), 53 (12) [^{53}Cr], 52 (78) [^{52}Cr]. − HRMS ($C_{19}H_{24}CrO_5$): calcd. 384.102884; found 384.1028. − $C_{19}H_{24}CrO_5$ (384.39): calcd. C 59.37, H 6.29; found C 60.66, H 7.08.

Tricarbonyl{η^6-2-endo-hydroxy-2-exo-1-[(trimethylsilyl)vinyl]-benzocyclobuten-1-one}chromium(0) (**6**): GP2, 2.2 ml (3.48 mmol) of *tert*-butyllithium (1.6 M in pentane) is added dropwise to a −78°C cold solution of 620 mg (3.48 mmol) of 1-bromo-1-(trimethylsilyl)ethene and stirred for 60 min. The solution is diluted by addition of 60 ml of diethyl ether at −78°C. 250 mg (0.93 mmol) of **4** in 60 ml of diethyl ether/THF (2:1), 20 ml of a sat. aqu. soln. of ammonium chloride. Column chromatography on silica gel (400 × 30 mm, diethyl ether/petroleum ether, 1:1). 215 mg (0.58 mmol, 63%) of **6**, orange solid (m.p. 94°C, R_f = 0.18). − IR ($CDCl_3$): $\tilde{\nu}$ = 3380 cm^{-1} (m, br, OH), 3080 (w, arom. CH), 1996 (s, CO), 1932 (s, CO), 1776 (s, CO, ketone), 1160 (m), 1120 (m), 1096 (m), 844 (s), 612 (m), 520 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.22 [s, 9 H, Si(CH_3)$_3$], 2.85 (s, 1 H, OH), 5.38 (dd, 1 H, 4-H or 5-H, ^3J = 6.2 Hz, ^3J = 6.0 Hz), 5.49 (dd, 1 H, 4-H or 5-H, ^3J = 6.0 Hz, ^3J = 6.2 Hz), 5.60 (m, 3 H, *E*-8-H, *Z*-8-H + 3-H or 6-H), 5.81 (dd, 1 H, 3-H or 6-H, ^3J = 6.0 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = −0.01 [−, Si(CH_3)$_3$], 84.6 (−, C-3 or C-4 or C-5 or C-6), 86.5 (−, C-3 or C-4 or C-5 or C-6), 92.2 (−, C-3 or C-4 or C-5 or C-6), 92.3 (−, C-3 or C-4 or C-5 or C-6), 99.7 (+, C-2), 104.9 (+, C-6a), 128.6 (+, C-2a), 150.8 (+, C-8), 188.3 (+, C-1), 229.4 (+, CO). − MS (70 eV, 110°C): *m/z* (%) = 368 (9) [M^+], 312 (6) [M^+ − 2 CO], 311 (15), 285 (30) [M^+ − 3 CO, ^{53}Cr], 284 (43) [M^+ − 3 CO], 232 (16), 225 (30), 217 (28), 141 (28), 127 (30), 126 (43), 77 (30), 53 (32) [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{16}H_{16}CrO_5Si$): calcd. 368.029325; found 368.0261. − $C_{16}H_{16}CrO_5Si$ (368.38): calcd. C 52.17, H 4.38; gef C 53.30, H 4.72.

Tricarbonyl{η^6-2-endo-hydroxy-2-exo-1-[(trimethylsilyl)vinyl]-benzocyclobuten-1-one}chromium(0) (**6**) *and Tricarboyl[η^6-1-phenyl-3-(trimethylsilyl)-3-buten-1,2-dione]chromium(0)* (**7**): GP1. 2.4 ml (3.72 mmol) of *tert*-butyllithium (1.6 M in pentane) is added dropwise at −78°C to a −78°C cold solution of 660 mg (3.72 mmol) of 1-bromo-1-(trimethylsilyl)ethene in 20 ml of diethyl ether. After stirring 60 min at −78°C the solution is diluted with 60 ml of diethyl ether. 250 mg (0.93 mmol) of **4** in 60 ml of diethyl ether/THF (2:1), 20 ml of a sat. aqu. soln. of ammonium chloride.The crude product is obtained as a red oil and is purified two times by column chromatography on silica gel (400 × 30 mm, diethyl ether/petroleum, ether 1:1). Fraction I (R_f = 0.18): 150 mg (0.40 mmol, 44%) of **6**. − Fraction II (R_f = 0.12): 86 mg (0.23 mmol, 25%) of **7**, red oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 3040 cm^{-1} (w, arom. CH), 1984 (s, CO), 1920 (s, CO), 1684 (m, C=O, ketone), 1600 (m, C=O, ketone), 1516 (m), 1448 (m), 1412 (m), 1252 (s), 1228 (s), 1144 (m), 1076 (m), 988 (m), 944 (m), 640 (s), 616 (m), 532 (s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 [s, 9 H, Si(CH_3)$_3$], 5.23 [dd, 2 H, 7(9)-H, ^3J = 6.2 Hz, ^3J = 6.5], 5.78 (dd, 1 H, 8-H, ^3J = 6.2 Hz, ^3J = 6.5 Hz), 6.08 [d, 2 H, 6(10)-H, ^3J = 6.2 Hz]. − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = − 1.21 [−, Si(CH_3)$_3$], 88.3 [−, C-6(10)], 90.4 (+,C-5), 95.8 [−, C-7(9)], 96.5 (−, C-8), 146.1 (+, C-4), 148.3 (+, C-3), 189.0 (+, C-2), 197.7 (+, C-1), 230.0 (+, CO). − MS (70 eV, 200°C): *m/z* (%) = 368 (4) [M^+], 340 (6) [M^+ − CO], 313 (18) [M^+ − 2 CO, ^{53}Cr], 312 (28) [M^+ − 2 CO], 285 (35), [M^+ − 3 CO, ^{53}Cr], 284 (62) [M^+ − 3 CO], 296 (53), 217 (32), 158 (40), 126 (54), 77 (38), 53 (39) [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{16}H_{16}CrO_5Si$): calcd. 368.017212; found 368.0166.

Tricarbonyl[η^6-6-methyl-8-(trimethylsilyl)-7,8-dihydro-6H-benzocyclohepten-5,9-dione]chromium(0) (**9**) *and Tricarbonyl[η^6-6-methyl-6-(trimethylsilyl)-7,8-dihydro-6H-benzocyclohepten-5,9-dione)]chromium(0)* (**10**): GP2. 1.7 ml (2.70 mmol) of *tert*-butyllithium (1.6 M in pentane) is added dropwise at −78°C to a solution of 481 mg (2.70 mmol) of 1-bromo-1-(trimethylsilyl)ethene in 20 ml of diethyl ether. The mixture is stirred at −78°C for 60 min and is then diluted with 40 ml of diethyl ether. 200 mg (0.67 mmol) of **8**[12] in 50 ml of diethyl ether/THF (2:1), 20 ml of a sat. aqu. soln. of ammonium chloride. The crude product is a red oil, which is purified two times by column chromatography on silica gel (400 × 30 mm, diethyl ether/petroleum ether, 1:1).

Fraction I (R_f = 0.45): 90 mg (0.22 mmol, 34%) of **9**, orange solid (m.p. 126°C). IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w, arom. CH), 1988 (s, CO), 1920 (s, CO), 1896 (s, CO), 1696 (m, CO, ketone), 1676 (m, CO, ketone), 616 (m), 524 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.10 [s, 9 H, Si(CH_3)$_3$], 1.26 (d, 3 H, CH_3, ^3J = 5.3 Hz), 1.65 (m, 1 H, aliph. H), 1.95 (m, 1 H, aliph. H), 2.48 (m, 1 H, aliph. H), 3.20 (m, 1 H, aliph. H), 5.42 (dd, 1 H, 2-H or 3-H, ^3J = 6.8 Hz, ^3J = 6.0 Hz), 5.56 (dd, 1 H, 2-H or 3-H, ^3J = 6.0 Hz, ^3J = 6.8 Hz), 5.75 (d, 1 H, 1-H or 4-H, ^3J = 6.8 Hz), 5.79 (d, 1 H, 1-H or 4-H, ^3J = 6.0 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ =

−2.5 (−, Si(CH_3)$_3$), 15.5 (−, CH_3), 29.8 (+, CH_2), 44.4 (−, CH), 45.1 (−, CH), 89.4 (−, C-1 or C-2 or C-3 or C-4), 91.0 (−, C-1 or C-2 or C-3 or C-4), 91.2 (−, C-1 or C-2 or C-3 or C-4), 93.0 (−, C-1 or C-2 or C-3 or C-4), 98.2 (+, C-4a or C-9a), 108.5 (+, C-4a or C-9a), 201.3 (+, C-5 or C-9), 203.9 (+, C-5 or C-9), 229.9 (+, CO). − MS (70 eV, 80°C): *m/z* (%) = 396 (7) [M^+], 340 (13) [M^+ − 2 CO], 312 (21) [M^+ − 3 CO], 311 (59) [M^+ − 3 CO, − H], 297 (13), 222 (37), 171 (64), 155 (10), 125 (47), 53 (10) [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{18}H_{20}CrO_5Si$): calcd. 396.048512; found 396.0489. − $C_{18}H_{20}CrO_5Si$ (396.43): calcd. C 54.54, H 5.08; found C 55.43, H 5.35.

II (R_f = 0.40): 105 mg (0.26 mmol, 39%) of **10**, orange solid (m.p. 119°C). − IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1} (w, arom. CH), 2952 (w, -CH_2-), 2904 (w, -CH_2-), 2872 (w), 1972 (s, CO), 1900 (s, CO), 1688 (s, CO-ketone), 1680 (s, CO-ketone), 1516 (w), 1480 (w), 1456 (w), 1428 (w), 1404 (w), 1316 (w), 1252 (s), 1232 (m), 1168 (w), 1048 (w), 956 (w), 840 (m), 756 (w), 648 (m), 620 (w), 520 (w). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.18 [s, 9 H, Si(CH_3)$_3$], 1.23 (s, 3 H, CH_3), 1.80 (m, 1 H, aliph. H), 2.30 (m, 1 H, aliph. H), 2.85 (m, 2 H, aliph. H), 5.48 (dd, 1 H, 2-H or 3-H, ^3J = 6.3 Hz, ^3J = 6.5 Hz), 5.57 (dd, 1 H, 2-H or 3-H, ^3J = 6.5 Hz, ^3J = 6.3 Hz), 5.69 (d, 1 H, 1-H or 4-H, ^3J = 6.3 Hz), 5.91 (d, 1 H, 1-H or 4-H, ^3J = 6.5 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = -2.4 [-, Si(CH_3)$_3$], 22.7 (−, CH_3), 27.9 (+, CH_2), 40.3 (+, CH_2), 43.2 (+, C-6), 90.1 (−, C-1 or C-2 or C-3 or C-4), 91.51 (−, C-1 or C-2 or C-3 or C-4), 91.57 (−, C-1 or C-2 or C-3 or C-4), 94.1 (−, C-1 or C-2 or C-3 or C-4), 95.7 (+, C-4a or C-9a), 104.7 (+, C-4a or C-9a), 199.0 (+, C-5 or C-9), 207.2 (+, C-5 or C-9), 229.9 (+, CO). − MS (70 eV, 80°C): *m/z* (%) = 396 (3) [M^+], 340 (7) [M^+ − 2 CO], 312 (12) [M^+ − 3 CO], 311 (37) [M^+ − 3 CO, − H), 240 (20), 170 (24), 161 (18), 159 (33), 146 (20), 115 (21), 73 (100) [Si(CH_3)$_3$], 53 (5) [^{53}Cr], 52 (60) [^{52}Cr]. − HRMS ($C_{18}H_{20}CrO_5Si$): calcd. 396.048512; found 396.0488. − $C_{18}H_{20}CrO_5Si$ (396.43): calcd. C 54.54, H 5.08; found C 54.23, H 5.13.

Tricarbonyl(η^6-3,8a-di-endo-ethoxy-3a-endo-hydroxy-2,3,3a,8a-tetrahydro-1H-cyclopenta[a]inden-8-one)chromium(0) (**11**): GP2. 3.5 ml (5.60 mmol) of *tert*-butyllithium (1.6 M in pentane) is added dropwise at −78°C to a solution of 500 mg (7.03 mmol) of ethoxyethene in 5 ml of THF. The mixture is warmed to −5°C, stirred at this temperature for 40 min cooled to −78°C and diluted with THF to a volume of 40 ml. 250 mg (0.93 mmol) of **4** in 50 ml of diethyl ether/THF (1:1), 10 ml of 2 N hydrochloric acid. The crude product is a red oil which is purified by column chromoatography on silica gel (400 × 30 mm, diethyl ether/petroleum ether, 2:1). 207 mg (0.50 mmol, 54%) of **11**, red solid (m.p. 152°C, dec., R_f = 0.20). − IR (KBr): $\tilde{\nu}$ = 3484 cm^{-1} (s, br, OH), 1984 (s, CO), 1900 (s, CO), 1708 (s, CO, ketone), 1268 (w, C-O), 1196 (m), 1160 (m), 1224 (m), 1100 (m), 1068 (m), 1020 (m), 956 (m), 904 (m), 652 (m), 616 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, 3 H, CH_3, ^3J = 6.9 Hz), 1.28 (t, 3 H, CH_3, ^3J = 6.9 Hz), 1.88 (m, 1 H, aliph. H), 2.15 (m, 2 H, aliph. H), 3.56 (m, 1 H, aliph. H), 3.68 (m, 4 H, OCH_2CH_3), 3.98 (m, 1 H, aliph. H), 4.03 (s, 1 H, OH), 5.30 (dd, 1 H, 4H or 5 H, ^3J = 6.0 Hz, ^3J = 6.0 Hz), 5.58 (d, 1 H, 3H or 6 H, ^3J = 6.0 Hz), 5.64 (dd, 1 H, 4H or 5 H, ^3J = 6.0 Hz, ^3J = 6.0 Hz), 5.71 (d, 1 H, 3H or 6 H, ^3J = 6.0 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 15.2 (−, CH_3), 15.5 (−, CH_3), 25.4 (+, C-2), 32.5 (+, C-1), 61.8 (+, CH_2), 66.0 (+, CH_2), 82.2 (+, C-8a), 85.3 (−, C-3), 85.3 (−, C-4 or C-5 or C-6 or C-7), 85.3 (−, C-4 or C-5 or C-6 or C-7), 87.3 (+, C-3a), 90.3 (−, C-4 or C-5 or C-6 or C-7), 93.3 (−, C-4 or C-5 or C-6 or C-7), 95.4 (+, C-7a), 123.8 (+, C-3b), 202.0 (+, C-8), 229.6 (+, CO). − MS (70 eV, 130°C) *m/z* (%) = 412 (8) [M^+], 357 (9) [M^+ − 2 CO, ^{53}Cr], 356 (32) [M^+ − 2 CO], 328 (30) [M^+ − 3 CO], 327 (100) [M^+ − 3 CO, − H], 264 (12), 238 (42), 220 (74) [M^+ − 3 CO, − OH, − 2 OCH_2CH_3] , 168 (62), 141 (26), 115 (29), 77 (5), 53 (12) [^{53}Cr], 52 (79) [^{52}Cr]. − HRMS ($C_{19}H_{20}CrO_7$): calcd. 412.061412; found 412.0614. − $C_{19}H_{20}CrO_7$ (412.35): calcd. C 55.33, H 4.85; found C 54.83, H 5.35.

Tricarbonyl(η^6-3a-endo-hydroxy-3,8a-endo-dimethoxy-1,2-dimethylene-2,3,3a,8a-tetrahydrocyclopenta[a]inden-8-one)chromium(0) (**12**): GP1. 2.1 ml (3.40 mmol) of butyllithium (1.6 M in hexan) is added dropwise at −30°C to a solution of 260 mg (3.72 mmol) of methoxyallene in 20 ml of diethyl ether.[35][36] 250 mg (0.93 mmol) of **4** in 10 ml of diethyl ether/THF (1:1), 20 ml of a sat. aqu. soln. of ammonium chloride. The crude product is a red oil which is purified by column chromatography on silica gel [400 × 30 mm, diethyl ether/petroleum ether (1:1)]. 212 mg (0.52 mmol, 56%) of **12**, orange solid (m. p. 130°C, dec., R_f = 0.12). **12** is recrystallized from diethyl ether/petroleum ether (1:4) as transparent orange crystals. − IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} (s, br, OH), 3080 (w, alkene CH), 2936 (w, −CH_2−), 2936 (w, −CH_2−), 2836 (w), 1984 (s, CO), 1912 (s, CO), 1712 (s, CO ketone), 1640 (m), 1600 (m), 1516 (m), 1448 (m), 1368 (m), 1268 (m, C-O), 1132 (m), 1084 (m), 992 (m), 924 (m), 892 (m), 648 (s), 616 (s), 572 (m), 528 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.39 (s, 3 H, CH_3), 3.46 (s, 3 H, CH_3), 3.64 (s, 1 H, 3-H), 4.25 (s, 1 H, OH), 5.08 (s, 1 H, =C*H*), 5.34 (dd, 1 H, 5-H or 6-H, ^3J = 6.2 Hz, ^3J = 5.8 Hz), 5.50 (s, 1 H, =C*H*), 5.57 (dd, 1 H, 5-H or 6-H, ^3J = 5.8 Hz, ^3J = 6.2 Hz), 5.60 (s, 1 H, =C*H*), 5.69 (m, 3 H, 4-H, 7-H, =C*H*). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 52.6 (−, OCH_3), 57.0 (−, OCH_3), 82.8 (+, C-3a), 86.4 (−, C-4 or C-5 or C-6 or C-7), 87.3 (−, C-4 or C-5 or C-6 or C-7), 87.9 (−, C-3), 90.5 (C-8a), 91.9 (−, C-4 or C-5 or C-6 or C-7), 93.4 (−, C-4 or C-5 or C-6 or C-7), 97.7 (+, C-7a), 115.9 (+, =CH_2), 116.4 (+, =CH_2), 121.9 (+, C-3b), 141.5 (+, C-1 or C-2), 146.3 (+, C-1 or C-2), 198.0 (+, C-8), 230.6 (+, CO). − MS (70 eV, 110°C): *m/z* (%) = 408 (4) [M^+], 352 (11) [M^+ − 2 CO, ^{53}Cr], 352 (25) [M^+ − 2 CO], 324 (27) [M^+ − 3 CO], 292 (10), 260 (22), 246 (9), 194 (45), 193 (95), 165 (89), 152 (26), 115 (18), 77 (21), 53 (15) [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{19}H_{16}CrO_7$): calcd. 408.030113, found 408.0304. − $C_{19}H_{16}CrO_7$ (408.32) calcd. C 55.88 H 3.92; found C 55.79 H 4.03.

Crystal Data for **12***:* $C_{19}H_{16}CrO_7$, 408.33 g/mol, crystal size 0.67 × 0.18 × 0.09 mm, *a* = 8.908(2), *b* = 9.410(2), *c* = 11.934(2) Å, α = 75.77(2), β = 78.74(2), γ = 76.50(2)°, *V* = 932.7 Å^3, d_{calc} = 1.45 gcm^{-1}, μ = 6.50 cm^{-1}, *Z* = 2, crystal system triclinic, space group $P\bar{1}$ (Nr. 2), Stoe IPDS Diffractometer, λ = 0.71073 Å, data collecting mode 160 exposures, Δφ = 2.0°, 14322 reflections measured, 4156 independent and 2511 observed reflections [$I > 2\sigma(I)$], 249 refined parameters, H-1 atom position found and included in the refinement, all other H atoms in geometrically calculated positions, *R* = 0.038, R_w = 0.084, residual electron density 0.25 e Å^{-3}.

Crystal Data for **13**: $C_{17}H_{16}CrO_5$, M_r = 352.3, orange plate, crystal size 0.07 × 0.39 × 0.70 mm, *a* = 7.281(1), *b* = 11.342(1), *c* = 18.895(1) Å, β = 91.686(5)°, *V* = 1559.7(3) Å^3, *T* = 293 K, monoclinic, space group $P2_1/n$ [No. 14], *Z* = 4, D_c = 1.50 g cm^{-3}, μ = 0.756 mm^{-1}. Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation, λ = 0.71069 Å. 6162 measured reflections, 3570 unique, 3048 observed [$I > 2.0\sigma(F_o^2)$]. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares on F^2 (SHELXL-97) for all data with Chebyshev weights to *R* = 0.036 (obs.), *wR* = 0.100 (all data), *S* = 1.09, H atoms riding (OH isotropic), max shift/error 0.001, residual ρ_{max} = 0.521 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101370 (**12**) and CCDC-101306 (**13**). Copies of the data can be obtained free

of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223/ 336-033; E-mail: deposit@ccdc.cam.ac.uk].

Tricarbonyl(η^6-3a-endo-hydroxy-8a-endo-methoxy-1,2-dimethyl-3,3a,8,8a-tetrahydrocyclopenta[a]inden-3,8-dion)chrom(0) (**14**)

a) GP2, 4.5 ml (7.20 mmol) of a 1.6 M solution of butyllithium in hexane is added at −30°C to 522 mg (7.45 mmol) of methoxyallene in 60 ml of diethyl ether. 500 mg (1.86 mmol) of **4** in 70 ml of diethyl ether/THF (1:1), 2 ml of trifluormethane sulfonic acid, 20 ml of water. The crude product mixture is a red oil which is separated by column chromatography (silica gel, 400 × 30 mm, diethyl ether/petroleum ether, 1:1). Fraction I: 135 mg (0.32 mmol, 18%) of **14** as a red solid [m. p. 170°C (dec.) R_f = 0.22]. Fraction II: 131 mg (0.32 mmol, 17%) of **12** (R_f = 0.12).

14: IR (KBr): $\tilde{\nu}$ = 3428 cm^{-1} (s, br, OH), 3084 (w, arom. CH), 2976 (w, $-CH_2-$), 2940 (w, $-CH_2-$), 1984 (s, CO), 1916 (s, CO), 1712 (s, CO ketone), 1640 (m), 1268 (m, C−O), 1196 (m), 644 (m), 612 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 3.67 (s, 3 H, OCH_3), 4.05 (s, 1 H, OH), 5.37 (dd, 1 H, 5-H or 6-H, ^3J = 5.8 Hz, ^3J = 6.6 Hz), 5.66 (dd, 1 H, 5-H or 6-H, ^3J = 6.6 Hz, ^3J = 5.8 Hz), 5.68 (d, 1 H, 4-H or 7-H, ^3J = 6.6 Hz), 5.81 (d, 1 H, 4-H or 7-H, ^3J = 5.8 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 9.1 (−, CH_3), 13.2 (−, CH_3), 56.4 (−, OCH_3), 78.6 (+, C-3a or C-8a), 86.8 (−, C-4 or C-5 or C-6 or C-7), 87.1 (−, C-4 or C-5 or C-6 or C-7), 88.9 (+, C-3a or C-8a), 91.5 (−, C-4 or C-5 or C-6 or C-7), 94.0 (−, C-4 or C-5 or C-6 or C-7), 120.0 (+, C-3b), 136.7 (+, C-1), 166.2 (+, C-2), 195.4 (+, C-3 or C-8), 202.9 (+, C-3 or C-8), 230.1 (+, CO). − MS (70 eV, 120°C): *m/z* (%) = 394 (14) [M^+], 338 (24) [M^+ − 2 CO], 310 (1) [M^+ − 3 CO], 309 (64), 260 (42), 250 (23), 154 (8), 100 (13), 77 (8), 53 (13) [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{18}H_{14}CrO_7$): calcd. 394.014463; found 394.0121. − $C_{18}H_{14}CrO_7$ (394.30): calcd. C 54.82, H 3.58; found C 54.87, H 3.80.

b) GP2, 2.7 ml (4.40 mmol) of a 1.6 M solution of butyllithium in hexane is added at −30°C to 333 mg (4.75 mmol) of methoxyallene in 20 ml of diethyl ether. 300 mg (1.11 mmol) of **4** in 50 ml of diethyl ether/THF (1:1), 5 ml of 6 N hydrochloric acid. The crude product is a red oil and is purified twice by column chromatography on silica gel [400 × 30 mm, diethyl ether/pertroleum ether (1:1)]. Fraction I: 100 mg (0.25 mmol, 23%) of **12** (R_f = 0.22). Fraction II: 129 mg (0.31 mmol, 28%) of **14** (R_f = 0.12). Fraction III: 26 mg (0.06 mmol, 6%) of a red solid (m.p. 122°C, dec.), tentatively characterized as tricarbonyl(η^6-3*a-endo*-hydroxy-3,8a-*endo*-dimethoxy1-methylene-2-methyl-1,3a,8,8a-tetrahydrocyclopenta[*a*]inden-8-one)chromium(0).

IR (KBr): $\tilde{\nu}$ = 3428 cm^{-1} (m, br, OH), 3084 (w, arom. CH), 2936 (w, $-CH_2-$), 2826 (w), 2360 (w), 2340 (w), 1968 (s, CO), 1904 (s, CO), 1720 (w), 1664 (m, CO ketone), 1276 (m), 1244 (m, C−O), 1196 (m), 1076 (m), 1000 (m), 908 (m), 656 (m), 620 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, CH_3), 3.04 (s, 1 H, OH), 3,55 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 5.28 (dd, 1 H, 5-H or 6-H, ^3J = 6.0 Hz, ^3J = 6.4 Hz), 5.62 (dd, 1 H, 5-H or 6-H, ^3J = 6.4 Hz, ^3J = 6.0 Hz), 5.88 (d, 1 H, 4-H or 7-H, ^3J = 6.0 Hz), 5.92 (s, 2 H, olefin. H), 5.99 (dd, 1 H, 4-H or 7-H, ^3J = 6.4 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 13.2 (−, CH_3), 57.9 (−, OCH_3), 60.4 (−, OCH_3), 73.9 (+, C-3a), 87.5 (−, C-4 or C-5 or C-6 or C-7), 91.9 (−, C-4 or C-5 or C-6 or C-7), 95.9 (+, C-8a), 96.5(−, C-4 or C-5 or C-6 or C-7), 97.20 (−, C-4 or C-5 or C-6 or C-7), 97.26 (+, C-7a), 144.5 (+, C-3b), 137.2 (+, C-3), 145.6 (+, C-2), 150.3 (+, C=CH_2), 181.9 (+, C-1), 199.8 (+, C-8), 234.0 (+, CO). − MS (70 eV, 130°C): *m/z* (%) = 408 (11) [M^+], 380 (3) [M^+ − CO], 353 (7) [M^+ − 2 CO, ^{53}Cr], 352 (19) [M^+ − 2 CO], 324 (17) [M^+ − 3 CO], 308 (20), 293 (19), 278 (23), 258 (14), 240 (19), 105 (22), 77 (22), 53 (14) [^{53}Cr], 52 (100) [^{52}Cr]. HRMS ($C_{19}H_{16}CrO_7$): calcd. 408.030113; found 408.0292.

c) At 25°C 5 ml of 6 N hydrochloric acid is added to 212 mg (0.52 mmol) of **12** in 50 ml of diethyl ether. The mixture is stirred for 60 min, diluted with 100 ml of water, and the layers are separated. The aqueous layer is extracted three times wih portions of 30 ml of diethyl ether, and the collected organic layers are washed with a saturated aqueous solution of $NaHCO_3$. The organic layer is separated, dried with $MgSO_4$, and the solvent is removed into a cold trap. 188 mg (0.48 mmol, 92%) of **14**.

Tricarbonyl{η^6-9b-hydroxy-4b,10-di-endo-methoxy-2,3-di(methoxycarbonyl)-5-oxo-1,2,3,4,4b,5,9b,10-octahydroindeno[2,1-a]indene}chromium(0) (**15**): 116 mg (0.80 mmol) of dimethylfumarate is added to 33 mg (0.08 mmol) of **12** in 5 ml of THF. The mixture is heated at reflux for 4 h. After removal of the solvent into a cold trap the solid residue is purified by column chromatography on silica gel (diethyl ether/petroleum ether, 1:1, 200 × 20 mm). 40 mg (0.07 mmol, 90%) of **15** as an orange solid (m. p. 156°C, R_f = 0.43). − IR (KBr): $\tilde{\nu}$ = 3428 cm^{-1} (m, br, OH), 3084 (w, arom. CH), 2996 (w, -CH_2-), 2836 (w), 1984 (s, CO); 1912 (s, CO), 1736 (s, CO ketone), 1436 (m), 1364 (m), 1232 (m), 1196 (m), 1072 (m), 1044 (m), 1008 (m), 936 (s), 908 (m), 884 (m), 816 (m), 648 (m), 616 (m), 568 (m), 524 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.55 (m, 2 H, aliph. H), 2.75 (m, 1 H, aliph. H), 2.85 (m, 3 H, aliph. H), 3.51 (s, OCH_3), 3.62 (s, OCH_3), 3.67 (s, OCH_3), 3.71 (s, OCH_3), 4.08 (s, 1 H, 10-H), 4.47 (s, 1 H, OH), 5.71 (dd, 1 H, 7-H or 8-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz), 5.91 (m, 2 H, 6-H, 9-H), 6.04 (dd, 1 H, 7-H or 8-H, ^3J = 6.0 Hz, ^3J = 6.2 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 25.3 (+, C-1 or C-4), 27.2 (+, C-1 or C-4), 42.3 (−, C-2 or C-3), 42.5 (−, C-2 or C-3), 52.46 (−, COOCH_3), 52.48 (−, COOCH_3), 55.0 (−, OCH_3), 61.6 (−, OCH_3), 84.0 (+, C-9b), 88.3 (−, C-6 or C-7 or C-8 or C-9), 88.7 (−, C-6 or C-7 or C-8 or C-9), 92.1 (−, C-10), 93.4 (+, C-4b), 93.6 (−, C-6 or C-7 or C-8 or C-9), 96.5 (−, C-6 or C-7 or C-8 or C-9), 97.3 (+, C-9a), 126.7 (+, C-5a), 136.3 (+, C-4a or C-10a), 139.2 (+, C-4a or C-10a), 175.1 (+, 2 -*C*OOCH$_3$), 197.0 (+, C-5), 232.1 (+, CO). − MS (70 eV, 180°C): *m/z* (%) = 552 (3) [M^+], 468 (8) [M^+ − 3 CO], 467 (20) [M^+ − 3 CO, − H), 435 (31), 406 (100) [M^+ − 3 CO, − 2 OCH_3], 352 (18), 293 (29), 277 (43), 245 (49), 218 (43), 189 (30), 165 (19), 105 (10), 53 (7) [^{53}Cr], 52 (52) [^{52}Cr]. − HRMS ($C_{25}H_{24}CrO_{11}$): calcd. 552.072372; found 552.0699. − $C_{25}H_{24}CrO_{11}$ (552.46): calcd. C 54.35, H 4.38; found C 53.71, H 4.50.

Tricarbonyl[η^6-2,3-di(methoxycarbonyl)-9b-hydroxy-4b,10-dimethoxy-5-oxo-1,4,4b,5,9b,10-hexahydroindeno[2,1-a]indene]chromium(0) (**16**): 116 mg (0.80 mmol) of dimethyl butynedioate is added to a solution of 33 mg (0.08 mmol) of **12** in 5 ml of THF. The mixture is heated at reflux for 30 min, and the solvent is condensed into a cold trap. The solid crude product is purified by column chromatography (silica gel, 200 × 20 mm, petroleum ether/diethyl ether, 1:1). 41 mg (0.07 mmol, 90%) of **16**, orange solid (m. p. 151°C, R_f = 0.23). − IR (KBr): $\tilde{\nu}$ = 3432 cm^{-1} (m, br, OH), 3080 (w, arom. CH), 1984 (s, CO), 1916 (s, CO), 1720 (s, CO ketone), 1648 (m), 1520 (m), 1436 (m), 1348 (m), 1268 (s), 1196 (m), 1144 (m), 1076 (m), 992 (m), 968 (m), 944 (m), 648 (m), 616 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.80−3.22 (m, 4 H, 1-H, 4-H), 3.55 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.83 (s, 1 H, 10-H), 3.89 (s, 1 H, OH), 5.35 (dd, 1 H, 7-H or 8-H, ^3J = 5.8 Hz, ^3J = 6.5 Hz), 5.49 (d, 1 H, 6-H or 9-H, ^3J = 6.5 Hz), 5.66 (dd, 1 H, 7-H or 8-H, ^3J = 5.8 Hz, ^3J = 6.5 Hz), 5.74 (d, 1 H, 6-H or 9-H, ^3J = 6.5 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 25.2 (+, C-1 or C-4), 27.1 (+,

C-1 or C-4), 52.37 (−, COO*C*H$_3$), 52.38 (−, COO*C*H$_3$), 54.9 (−, O*C*H$_3$), 61.1 (−, O*C*H$_3$), 82.1 (+, C-9b), 85.2 (−, C-6 or C-7 or C-8 or C-9), 86.2 (−, C-6 or C-7 or C-8 or C-9), 90.4 (−, C-6 or C-7 or C-8 or C-9), 90.6 (−, C-10), 91.9 (+, C-4b), 93.1 (−, C-6 or C-7 or C-8 or C-9), 94.4 (+, C-9a), 123.0 (+, C-5a), 130.8 (+, C-4a or C-10a), 133.2 (+, C-4a or C-10a), 134.2 (+, C-2 or C-3), 134.6 (+, C-2 or C-3), 167.6 (+, -*C*OOCH$_3$), 167.7 (+, -*C*OOCH$_3$), 194.9 (+, C-5), 229.4 (+, CO). − MS (70 eV, 190°C): *m/z* (%) = 550 (8) [M$^+$], 467 (20) [M$^+$ − 3 CO, ^{53}Cr], 466 (60) [M$^+$ − 3 CO], 438 (33), 402 (29), 350 (70), 303 (80), 275 (46), 233 (58), 190 (60), 53 (14) [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{25}H_{22}CrO_{11}$): calcd. 550.056722; found 552.0560. − $C_{25}H_{22}CrO_{11}$ (550.44): calcd. C 54.55, H 4.03, found 53.66, H 4.50.

Tricarbonyl[η^6-1,2-di-exo-(2-propyn-1-yl)-1,2-di-endo-hydroxybenzocyclobutene]chromium(0) (**17**): GP2; 10 mg of $HgCl_2$ is added to a suspension of 214 mg (8.95 mmol) of Mg filings in 5 ml of diethyl ether. The mixture is stirred for 30 min at 20°C.[32] The mixture is cooled to 0°C, and a few drops of 527 mg (4.47 mmol) of propargyl bromide is added. Then the mixture is cooled to −78°C, and the rest of the propargyl bromide is added over 1 h. After stirring for 1 h 200 mg (0.74 mmol) of **4** in 50 ml of diethyl ether/THF (1:1) is added. 5 ml of 4 N hydrochloric acid. The crude yellow brown oil is purified by column chromatography (silica gel, 400 × 30 mm, diethyl ether/petroleum ether, 1:1). 231 mg (0.66 mmol, 90%) of **17**, yellow solid (m.p. 145°C, R_f = 0.48). − IR ($CDCl_3$): ṽ = 3304 cm^{-1} (m, OH), 2240 (w, C≡C), 1980 (s, CO), 1908 (s, CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.16 (t, 2 H, *J* = 2.1 Hz), 2.94 (t, 4 H, *J* = 2.1 Hz), 3.41 (s, 2 H, OH), 5.18 + 5.56 [AA′BB′ line system, 2× 2 H, 3(6)-H, 4(5)-H]. − ^{13}C NMR (50 MHz, [D$_6$]acetone, APT): δ = 24.9 (+, CH_2), 72.7 [, C-1(2)], 80.4 (+, C≡C), 82.3 (+, C≡C), 88.2 [−, C-3(6) or C-4(5)], 93.0 [−, C-3(6) or C-4(5)], 121.7 [+, C-2a(6a)], 233.5 (+, CO). - MS (70 eV, 100°C): *m/z* (%) = 348 (21 [M$^+$], 292 (77) [M$^+$ − 2CO], 264 (99) [M$^+$ − 3CO], 246 (20), 220 (19), 207 (11), 176 (14), 165 (19), 105 (12), 77 (20), 53 (19) [^{53}Cr], 52 (100) [^{52}Cr]. - HRMS ($C_{17}H_{12}CrO_5$): calcd. 348.008984; found 348.0090. − $C_{17}H_{12}CrO_5$ (348.28): calcd. C 58.62, H 3.45, found C 59.71, H 3.72.

Tricarbonyl[η^6-2-endo-hydroxy-2-exo-(3-methoxy-1-propynyl)benzocyclobuten-1-one]chromium(0) (**18**): GP2; 3.2 ml (5.12 mmol) of butyllithium (1.6 M in hexane) is added dropwise at −78°C to 391 mg (5.59 mmol) of 3-methoxypropyne in 20 ml of THF. The mixture is stirred for 5 min. 250 mg (0.93 mmol) of **4** in 50 ml of diethyl ether/THF, 20 ml sat. aqu. solution of NH_4Cl. The crude product is a red oil, which is purified by column chromtography (silica gel, 400 × 30 mm, diethyl ether). 150 mg (0.44 mmol, 48%) of **18**, orange solid (m.p. 130°C, dec., R_f = 0.40). − IR (KBr): ṽ = 3340 cm^{-1} (m, br, OH), 3092 (w, arom. CH), 2220 (w, C≡C), 1988 (s, CO), 1920 (s, CO), 1744 (s, CO ketone), 1652 (m), 1496 (m), 1448 (m), 1424 (m), 1252 (m, C-O), 1188 (m), 1124 (m), 1088 (m), 1044 (m), 936 (m), 876 (m), 660 (s), 644 (s), 612 (s), 564 (m), 524 (s). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 3.28 (s, 3 H, C*H*$_3$), 4.16 (s, 2 H, C*H*$_2$), 5.66 (dd, 1 H, 4-H or 5-H, ^3J = 6.4 Hz, ^3J = 6.2 Hz), 5.89 (dd, 1 H, 4-H or 5-H, , ^3J = 6.2 Hz, ^3J = 6.4 Hz), 5.96 (d, 1 H, 3-H or 6-H, ^3J = 6.4 Hz), 6.16 (d, 1 H, 3-H or 6-H, ^3J = 6.2 Hz), 6.82 (s, 1 H, OH). − ^{13}C NMR (50 MHz, [D$_6$]acetone, APT): δ = 56.4 (−, *C*H$_3$), 58.7 (+, *C*H$_2$), 81.8 (+, C-7 or C-8), 85.3 (+, C-7 or C-8), 85.5 (−, C-3 or C-4 or C-5 orC-6), 85.5 (−, C-3 or C-4 or C-5 orC-6), 86.1 (+, C-2), 92.4 (−, C-3 or C-4 or C-5 orC-6), 94.1 (−, C-3 or C-4 or C-5 orC-6), 104.4 (+, C-6a), 128.4 (+, C-2a), 183.5 (+, C-1), 229.9 (+, CO). - MS (70 eV, 100°C): *m/z* (%) = 338 (4) [M$^+$], 282 (5) [M$^+$ − 2 CO], 254 (12) [M$^+$ − 3 CO], 224 (12), 196 (17), 167 (7), 158 (10), 149 (22), 129 (11), 105 (13), 77 (15), 52 (100) [^{52}Cr]. - HRMS ($C_{15}H_{10}CrO_6$): calcd. 337.988248; found 337.9885. − $C_{15}H_{10}CrO_6$ (338.26): calcd. C 53.26, H 2.98; found C 53.79, H 3.40.

Tricarbonyl{η^6-2-endo-hydroxy-2-exo-[2-(trimethylsilyl)-1-ethynyl]benzocyclobuten-1-one}chromium(0) (**19**): GP2; 3.2 ml (5.12 mmol) of butyllithium (1.6 M in hexane) is added dropwise at −20°C to 548 mg (5.59 mmol) of trimethylsilylethyne in 15 ml of THF.[37] The mixture is stirred for 35 min. 250 mg (0.93 mmol) of **4** in 50 ml of diethyl ether/THF, 20 ml sat. aqu. solution of NH_4Cl. The crude product is a red oil, which is purified twice by column chromtography (silica gel, 400 × 30 mm, diethyl ether). 177 mg (0.48 mmol, 52%) of **19**, orange red solid (m.p. 98°C, dec., R_f = 0.47). − IR (KBr): ṽ = 3380 cm^{-1} (m, br, OH), 3088 (m, arom. CH), 2960 (m), 2900 (m), 2080 (w, C≡C), 1996 (s, CO), 1924 (s, CO), 1796 (s), 1756 (s, CO ketone), 1676 (m), 1656 (m), 1588 (m), 1496 (m), 1424 (m), 1400 (m), 1332 (m), 1252 (s, C−O), 1176 (m), 1160 (m), 1124 (s), 1024 (m), 892 (m), 848 (s), 764 (s), 736 (m), 700 (m), 652 (s), 608 (s), 564 (m), 520 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, -Si(C*H*$_3$)$_3$], 3.60 (s, 1 H, OH), 5.29 (dd, 1 H, 4-H or 5-H, ^3J = 6.3 Hz, ^3J = 6.2 Hz), 5.50 (dd, 1 H, 4-H or 5-H, ^3J = 6.2 Hz, ^3J = 6.3 Hz), 5.60 (d, 1 H, 3-H or 6-H, ^3J = 6.3 Hz), 5.82 (d, 1 H, 3-H or 6-H, ^3J = 6.2 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = −0.5 [−, -Si(*C*H$_3$)$_3$], 84.5 (−, C-3 or C-4 or C-5 or C-6), 84.6 (−, C-3 or C-4 or C-5 or C-6), 85.8 (+, C-7 or C-8), 91.0 (−, C-3 or C-4 or C-5 or C-6), 92.3 (−, C-3 or C-4 or C-5 or C-6), 97.2 (+, C-2), 99.0 (+, C-7 or C-8), 103.9 (+, C-6a), 126.0 (+, C-2a), 183.3 (+, C-1), 228.8 (+, CO). - MS (70 eV, 120°C): *m/z* (%) = 366 (4) [M$^+$], 283 (10) [M$^+$ − 3 CO, ^{53}Cr], 282 (33) [M$^+$ − 3 CO], 267 (18), 266 (40), 233 (53), 216 (18), 215 (80), 187 (26), 159 (10), 155 (15), 77 (27), 53 (12) [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{16}H_{14}CrO_5Si$): calcd. 365.988986; found 365.9880.

Tricarbonyl[η^6-2-endo-hydroxy-2-exo-(2-phenyl-1-ethynyl)-benzocyclobuten-1-one]chromium(0) (**20**): GP2; 3.2 ml (5.12 mmol) of butyllithium (1.6 M in hexane) is added dropwise at −20°C to 570 mg (5.59 mmol) of phenylethyne in 5 ml of THF. The mixture is warmed to 20°C and stirred for 10 min. Then the solution is diluted with THF to a volume of 35 ml and cooled to −78°C. 250 mg (0.93 mmol) of **4** in 50 ml of diethyl ether/THF, 20 ml sat. aqu. solution of NH_4Cl. The crude product is a red oil which is purified by column chromtography (silica gel, 400 x 30 mm, diethyl ether/petroleum ether1:1). 200 mg (0.54 mmol, 58%) of **20**, orange solid (m.p. 140°C, dec., R_f = 0.35).

IR (KBr): ṽ = 3380 cm^{-1} (m, br, OH), 3092 (w, arom. CH), 2220 (w, C≡C), 1992 (s, CO), 1928 (s, CO), 1796 (m), 1744 (s, CO ketone), 1488 (m), 1252 (w, C−O), 1176 (m), 1160 (m), 1124 (m), 896 (m), 756 (m), 688 (m), 656 (s), 640 (s), 600 (s), 544 (m), 512 (m). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 5.68 (dd, 1 H, 4-H or 5-H, ^3J = 6.4 Hz, ^3J = 6.2 Hz), 5.91 (dd, 1 H, 4-H or 5-H, ^3J = 6.2 Hz, ^3J = 6.4 Hz), 5.98 (d, 1 H, 3-H or 6-H, ^3J = 6.4 Hz), 6.22 (d, 1 H, 3-H or 6-H, ^3J = 6.2 Hz), 6.91 (s, 1 H, OH), 7.33−7.49 (m, 5 H, arom.-H). − ^{13}C NMR (50 MHz, [D$_6$]acetone, APT): δ = 85.0 (+, C-7 or C-8), 85.6 (+, C-7 or C-8) 85.7 (−, C-3 or C-4 or C-5 or C-6), 85.8 (−, C-3 or C-4 or C-5 or C-6), 89.2 (+, C-2), 92.4 (−, C-3 or C-4 or C-5 or C-6), 94.1 (−, C-3 or C-4 or C-5 or C-6), 104.6 (+, C-6a), 121.2 (+, C-2a), 128.3 (−, *o*-C), 128.5 (+, *ipso*-C), 129.0 (−, *p*-C), 131.2 (−, *m*-C), 183.7 (+, C-1), 229.9 (+, CO). − MS (70 eV, 130°C): *m/z* (%) = 370 (4) [M$^+$], 287 (14) [M$^+$ − 3 CO, ^{53}Cr], 286 (47) [M$^+$ − 3 CO), 233 (9), 167 (19), 149 (49), 104 (11), 77 (10), 53 (11), [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{19}H_{10}CrO_5$): calcd. 369.993333; found 369.9917. − $C_{19}H_{10}CrO_5$ (370.28): calcd. C 61.63, H 2.27; found C 61.76, H 2.81.

Tricarbonyl(η^6-1,4-diphenyl-3-butyne-1,2-dione)chromium(0) (**21**): GP1; 300 mg (2.99 mmol) of phenylethyne is added quickly

dropwise to 1.5 ml (2.33 mmol) of butyllithium (1.6 M in hexane) in 1.5 ml of diethyl ether at −78°C. 250 mg (0.93 mmol) of **4** in 50 ml of diethyl ether/THF (1:1), 20 ml of sat. aqu. solution of NH_4Cl. The crude product is a red oil, which is purified twice by column chromatography (silica gel, 400 × 30 mm, diethyl ether/petroleum ether1:1). 258 mg (0.69 mmol, 75%) of **21**, dark red oil (R_f = 0.46). − IR ($CDCl_3$): $\tilde{\nu}$ = 3092 cm^{-1} (w, arom. CH), 1992 (s, CO), 1932 (s, CO), 1656 (s, CO ketone), 1596 (m), 1512 (m), 1196 (m), 1104 (m), 1072 (m), 1004 (w), 920 (m), 640 (m), 604 (m), 564 (w), 524 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.28 [dd, 2 H, 3(5)-H, ^3J = 6.0 Hz, 6.4 Hz), 5.78 (dd, 1 H, 4-H, ^3J = 6.0 Hz), 6.32 [d, 2 H, 2(6)-H, ^3J = 6.4 Hz], 7.50 (m, 3 H, arom. H), 7.65 (d, 2 H, *o*-H, ^3J = 6.8 Hz]. − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 86.8 (+, C-9 or C-10), 88.3 (+, C-9 or C-10), 88.9 [−, C-2(6) or C-3(5)], 95.4 [−, C-2(6) or C-3(5), C-4], 100.0 (+, C-1), 118.9 (+, C-11), 128.7 (−, *m*-C), 131.8 (−, *p*-C), 133.8 (−, *o*-C), 176.2 (+, C-8), 184.2 (+, C-7), 229.5 (+, CO). − MS (70 eV, 150°C): *m/z* (%) = 370 (2) [M^+], 314 (4) [M^+ − 2 CO], 313 (12) [M^+ − 2 CO, − H), 286 (75) [M^+ − 3 CO], 258 (30), 178 (7), 153 (7), 129 (16), 105 (26), 105 (26), 77 (20), 53 (13) [^{53}Cr], 52 (100) [^{52}Cr].

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