Reactions between Benzocyclobutenone Tricarbonylchromium Complexes and Lithium Dialkylphosphides: A New Route to Isochromanones

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The reaction between *rac*-(benzocyclobutenone)tricarbonylchromium (*rac*-**1**) and lithium diisopropylphosphide (LDP) or lithium di-*tert*-butylphosphide, unlike its reaction with lithium diisopropylamide (LDA), results in a distal ring-opening, with formation of acylphosphane derivatives. The tricarbonylchromium complex *rac*-**6** of 2-methylbenzoyldiisopropylphosphane has been structurally characterized. The reaction proceeds through the corresponding benzylic anion intermediate, which was shown to react with ketones or aldehydes with formation of isochromanone derivatives. This indicates that a dialkylphosphide is a much better leaving group than an amide. The availability of **1** in enantiomerically pure form inspired an inspection of the diastereoselectivity of the cyclization with aldehydes. It was found that the reaction between the intermediate and benzaldehyde took place with complete diastereoselectivity, thus establishing a route to enantiomerically pure 3-phenylisochromanone.

Introduction

Benzocyclobutene and its derivatives are the basis for a number of syntheses of natural products and other important compounds, usually relying on the well investigated ring-opening to produce a reactive *ortho*-quinodimethane intermediate, which undergoes a [4+2] cycloaddition with reconstitution of the aromatic system.[1−11] We have contributed to the chemistry of benzocyclobutenes by investigation of their metal complexes, in most cases tricarbonylchromium(0) complexes; these investigations have recently been reviewed.[12,13]

Tricarbonylchromium complexes *rac*-**1** and **2** of benzocyclobutenone and of benzocyclobutenedione readily undergo reactions with nucleophiles attacking the ketone carbon atoms from the face opposite to the tricarbonylchromium moiety. In this context the *syn* diaddition of alkenylmetal reagents to **2** resulted in dianionic oxy-Cope rearrangements, taking place at −78 °C.[14−18]

The nucleophilic addition of amines to *rac*-**1** or **2** resulted neither in an isolable hemiaminal or imine nor in a distal ring-opening product. Instead, a proximal ring-opening occurred, resulting in complexes of phenylacetic acid derivatives such as **3** or **4**.[19,20]

Lithium diisopropylamide (LDA) is frequently used as a non-nucleophilic base. Treatment of *rac*-**1** with LDA resulted in unselective deprotonation of the aromatic ring. In contrast to LDA, the corresponding phosphorus compound, lithium diisopropylphosphide (LDP), should be softer and more nucleophilic. In the course of investigations directed towards the incorporation of additional ligand sites into the benzocyclobutene system, *rac*-**1** and **2** were treated with lithium phosphides. In contrast to the reaction with nitrogen nucleophiles, no proximal ring-opening reactions were observed. Instead, distal ring-opening reactions took place, and isochromanone (isocoumarin) complexes were subsequently formed. Isochromanone derivatives such as (*R*)-mellein [(*R*)-**5**] are found in some phytopathogenic fungi and play a role as pheromone precursors in some insects.[21]

Results and Discussion

When benzocyclobutenone complex *rac*-**1** was treated with a twofold excess of LDP at −78 °C in THF, TLC monitoring indicated the formation of a new product after a few minutes. Hydrolytic workup after two hours gave a product mixture, which was separated by column chromatography. Three fractions were obtained, consisting of acylphosphane *rac*-**6** (14%), the spiro anellated isochromanone *rac*-**7** (2:1 diastereomeric mixture) as the main product (62%), and − in one last fraction − oxidized phosphorus compounds *rac*-**8** and *rac*-**9** (18%).

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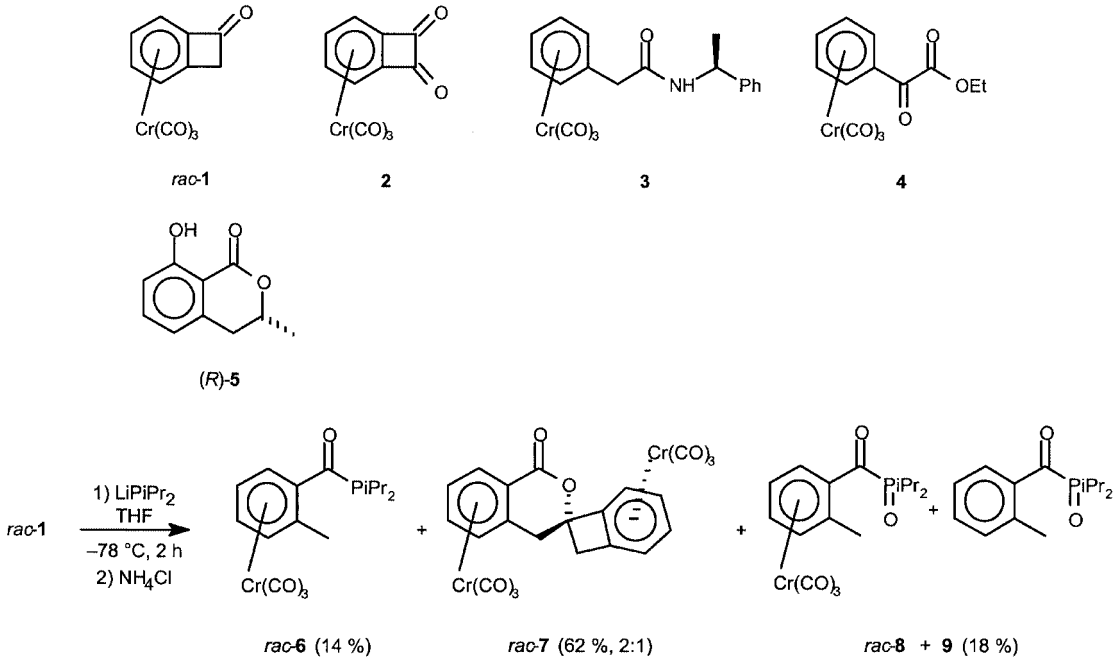


The acylphosphane complex *rac*-**6** was characterized spectroscopically. The ^{1}H NMR spectrum confirms the distal ring-opening, showing a singlet for the three benzylic protons at $\delta = 2.47$ ppm. Crystallization of *rac*-**6** from diethyl ether/pentane at −28 °C gave crystals that were believed to be suitable for an X-ray structure analysis (Figure 1), but the crystal quality was low and the *R* values of the X-ray analysis are unsatisfactory. However, the constitution of *rac*-**6** is confirmed, and the analysis shows that the phosphacyl carbonyl group adopts a conformation almost coplanar with the arene ring. Compound *rac*-**6** crystallizes in the space group $P\bar{1}$ with two independent, structurally rather similar molecules in the asymmetric unit; the data given refer to one of these molecules.

On the basis of the NMR spectroscopic data obtained for *rac*-**6** it was possible to carry out spectroscopic characterization of the mixture of *rac*-**8** and **9**, products of the oxidation and the decomplexation of *rac*-**6**, presumably formed during the workup. The formation of all three products clearly indicates that the reaction with lithium diisopropylphosphide is a distal ring-opening, in contrast to the earlier observations with nitrogen nucleophiles, which cause proximal ring-opening.

The most interesting reaction product is the spiro anellated isochromanone complex *rac*-**7**. Compound *rac*-**7** was characterized spectroscopically. The integrity of an anellated cyclobutane ring is indicated by the benzylic protons causing doublets in the ^{1}H NMR spectrum with geminal coupling constants of $^2J_{H,H} = -14.1$ Hz. The ^{13}C NMR signal of the quaternary carbon atom appears at $\delta = 81.8$.

The formation of the spiro anellated isochromanone *rac*-**7** is unexpected and can be explained by the assumption of a nucleophilic attack of the phosphide at the keto function, affording *rac*-**10**. Distal ring-opening gives benzylic anion *rac*-**11**, which adds diastereoselectively (only two out of three diastereomers of *rac*-**7** are formed) to another molecule of *rac*-**1** from the face opposite to the tricarbonylchromium moiety to give the bimetallic intermediate *rac*-**12**. Intramolecular nucleophilic substitution of the diisopropylphosphide by the alkoxide moiety finally produces *rac*-**7**. The diisopropylphosphide group serves as a leaving group, which also contrasts with the usual behavior of the nitrogen analogues (amides). In addition, we think that the reaction is entropically favored. The formation of *rac*-**6**, *rac*-**8**, and *rac*-**9** is easily explained by a protonation of the intermediate *rac*-**11**.

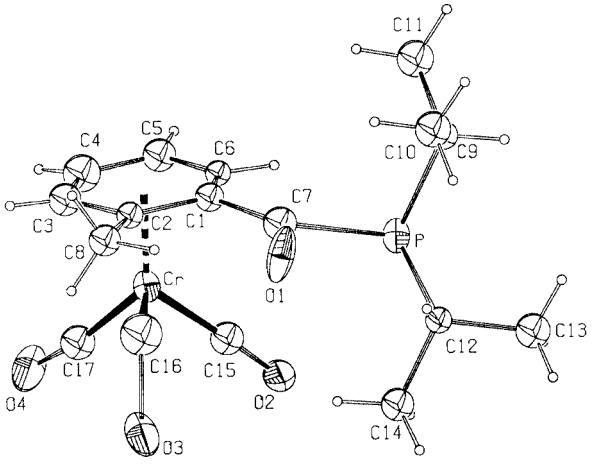
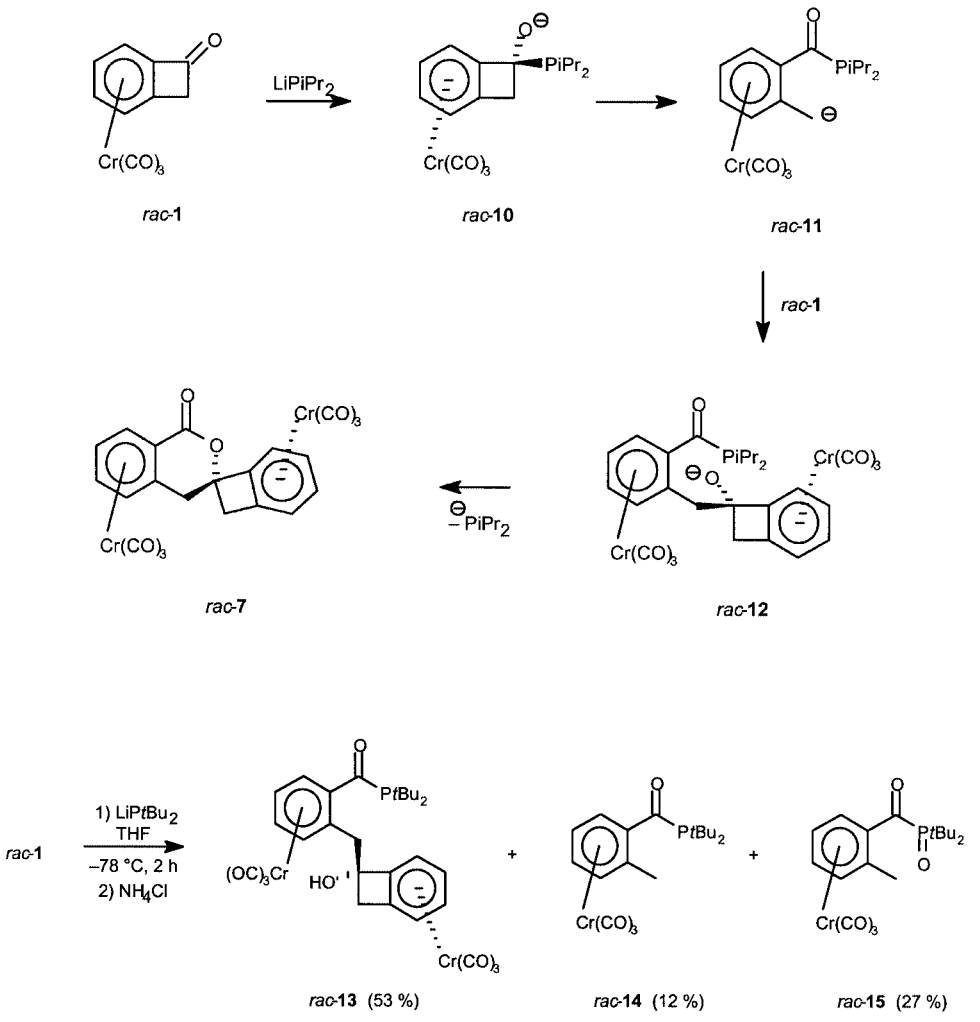


Figure 1. Structure of *rac*-**6** in the crystal;[22] selected bond lengths [Å], angles [°], and dihedral angles [°]: C1−C7 1.52(4), O1−C7 1.18(4), P−C7 2.05(4); O1−C7−C1 134(3), C1−C7−P 114(3), O1−C7−P 110(3); C2−C1−C7−O1 −1(5), C9−P−C7−O1 −86(3), C12−P−C7−O1 18(3)

In a similar way, *rac*-**7** was obtained from the reaction between *rac*-**1** and lithium diphenylphosphide in 72% yield,

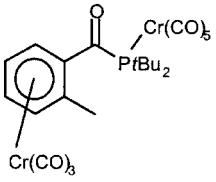


and also from the reaction between *rac*-**1** and lithium bis(trimethylsilyl)phosphide in 43% yield.

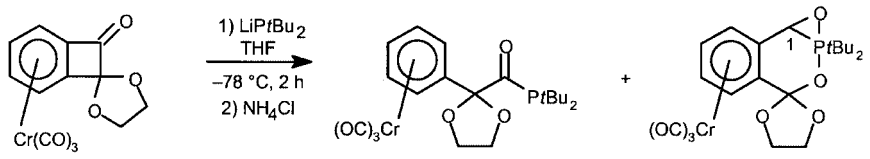
The intermediacy of *rac*-**12** is supported by the result of the reaction between *rac*-**1** and the sterically more hindered lithium di-*tert*-butylphosphide. After chromatographic separation of the product mixture, *rac*-**13** was obtained diastereomerically pure in 53% yield. Obviously the final cyclization step had not taken place, presumably as a result of the steric hindrance of the bulky phosphane substituents. Compounds *rac*-**14** and *rac*-**15** were obtained in 12% and 27% yields, respectively.

Compounds *rac*-**7** and *rac*-**13** are remarkable, since they are bis[(arene)tricarbonylchromium] complexes, a rare class of compounds. Our experience is that a dicomplexation of a bis(arene) is usually difficult to achieve and mostly takes place in poor yields. Here, coupling of two (arene)tricarbonylchromium units produces these complexes.

To test how far the lone electron pair at the phosphorus atom in *rac*-**14** is involved in a resonance with the neighboring carbonyl function − as in amides − or if it were available for complexation, a small amount of *rac*-**14** was treated with (THF)$Cr(CO)_5$ in THF at −15 °C. After having been warmed to 20 °C and stirred at this temperature for 2 h, the reaction mixture was worked up by filtration through a layer of kieselgur. The sensitive complex *rac*-**16** was detected spectroscopically (IR, ^1H, ^{31}P NMR, FAB-MS) in addition to unchanged *rac*-**14**, thus indicating the availability of the lone electron pair for complexation. This is in agreement with the crystal structure of *rac*-**6**, which showed a C−P bond length typical of a single bond.



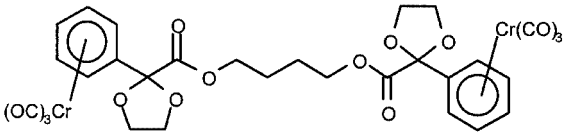
rac-**16**



rac-**17** **18** *rac*-**19**

In order to explore the scope of the reaction with respect to the benzocyclobutenone substrate, ketone acetal *rac*-**17** was tested next. Treatment with lithium *tert*-butylphosphide gave a mixture of two products, which were separated by column chromatography. In contrast to the preceding examples, a proximal ring-opening was observed, with formation of acylphosphane **18** in 21% yield. The second product, which was isolated in 38% yield, was difficult to identify. On the basis of spectroscopic studies the constitution of *rac*-**19** was finally assigned to this product.

The following observations explain the assignment of *rac*-**19**. The mass spectrum shows the molecular ion peak at *m*/*z* = 474. The NMR signals of the protons bound to the aromatic systems are an ABCD line system, indicating an unsymmetrically disubstituted arene. In addition, the ^{1}H NMR spectrum shows the signals for the ethylenedioxy and the *tert*-butyl substituents. The signal assigned to the benzylic proton 1-H appears at δ = 5.61 (d, *J* = 2.9 Hz). In the ^{13}C NMR spectrum (APT), the signal of C-1 is observed with negative phase (CH_3 or CH) at δ = 75.6 (*J* = 60.1 Hz), and the coupling constant is in agreement with a $^{1}J_{C,P}$ coupling in a small ring.[23] The ^{31}P NMR shift is δ = 59.7 ppm. NOE measurements indicate a strong interaction of 1-H with one of the *tert*-butyl groups and a weaker one with the other *tert*-butyl group. In addition, an interaction with one of the protons bound at the aromatic ring is observed. A 1D-TOCSY measurement confirms the assignment of the ^{1}H NMR signal at δ = 5.61 as 1-H. The observation of only one set of signals in the NMR spectra indicates the isolated compound to be diastereomerically pure.



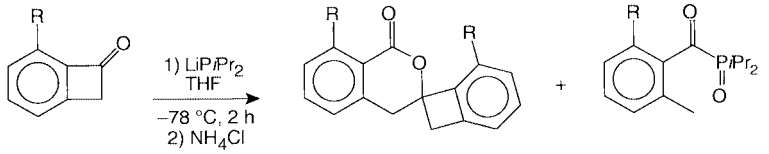
20

Interestingly, the corresponding reaction with use of lithium diphenylphosphide instead of lithium di-*tert*-butylphosphide under otherwise identical reaction conditions gives a completely different result, the dinuclear complex **20** being obtained as the only isolated product, in 63% yield, clearly as the result of incorporation of one molecule of the THF solvent.

The formation of isochromanone complexes *rac*-**7** upon treatment of *rac*-**1** with LDP raises the question of how far this reactivity might be observed when starting from the uncomplexed benzocyclobutenone. Indeed, when benzocyclobutenone (**21**) or 6-methoxybenzocyclobutenone (**22**) were treated with LDP under the usual reaction conditions, the spiro anellated isochromanones *rac*-**23** and *rac*-**24** were obtained in 79% and 83% yields, respectively. In the case of **21**, acylphosphorane **9** (14%) was obtained as a side product.

According to the proposed reaction mechanism, the reaction should also be possible with use of a catalytic amount of LDP. However, an attempt to achieve this by use of 0.1 equiv. of LDP only resulted in a yield of *rac*-**23** of less than 10%.

While the synthesis of spiro anellated isochromanones *rac*-**23** and *rac*-**24** proved to be possible through the use of two benzocyclobutenone building blocks **21** or **22**, the reaction conditions had to be modified when benzocyclobutenone and an aldehyde were used in order to construct isochromanones deriving from two different substrates. To achieve this, a dilute solution of **21** in THF was slowly added dropwise to a solution of LDP in THF. This caused almost complete reaction to give the benzyl anion intermediate without formation of *rac*-**23**. Subsequent addition of an aldehyde gave isochromanones *rac*-**25** and *rac*-**26** in 78% and 57% yield, respectively. There is a report of the synthesis of isochromanoles from benzocyclobutenols by

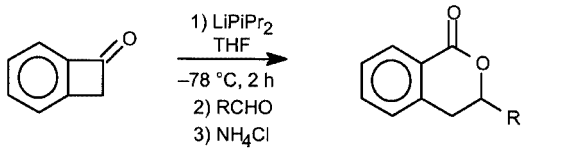


21 (R = H)
22 (R = OMe)

rac-**23** (R = H, 79 %)
rac-**24** (R = OMe, 83 %)

9 (R = H, 14 %)

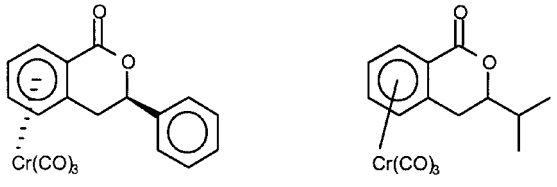
anionic ring-opening followed by cycloaddition with aldehydes. However, the isochromanoles have to be oxidized by chromium(VI) in order to obtain the isochromanones.[24] 3-Phenylisochromanone was obtained from (1-hydroxybenzocyclobutene)tricarbonylchromium by an anion-driven ring-opening followed by reaction with benzaldehyde and subsequent oxidation with pyridinium chlorochromate. The intermediate chromium complex was obtained in poor yield without stereochemical assignment.[25]



21 *rac*-**25** (R = *p*-O_2NPh, 78 %) *rac*-**26** (R = Pr, 57 %)

One incentive for investigating the chemistry of **1** is its planar chirality, which can be translated into reaction products through diastereoselective reduction or nucleophilic addition at the keto group, followed by cycloaddition or ring-expansion reactions.[13,16,26–30] As **1** is available in enantiomerically pure form, investigation of the diastereoselectivity of reactions between **1** and aldehydes in the presence of LDP is of interest. As the decomplexation is usually carried out under oxidative reaction conditions in quantitative yield, complete diastereoselectivity would correspond to a formal synthesis of the enantiopure isochromanone. There is one literature report of an asymmetric synthesis of isochromanoles by making use of chromium complexes of chiral benzaldehyde acetals, a final oxidation with pyridinium chlorochromate giving the respective isochromanones.[31]

When *rac*-**1** was treated with LDP followed by benzaldehyde, phenylisochromanone complex *rac*-**27** was obtained in 55% yield exclusively as the *exo* diastereomer. The full diastereoselectivity of the reaction makes this a formal total synthesis of enantiomerically pure 3-phenylisochromanone, which is known for its antifungal activity.[32,33] Remarkably, when 2-methylpropanal was used, the diastereoselectivity was lower, resulting in a 2:3 *endo*/*exo* mixture of *rac*-**28**, which could be separated by flash chromatography.



rac-**27** *rac*-**28** (*endo*/*exo* = 2:3)

The relative configuration of *rac*-**27** was established beyond any doubt through a crystal structure analysis (Figure 2).

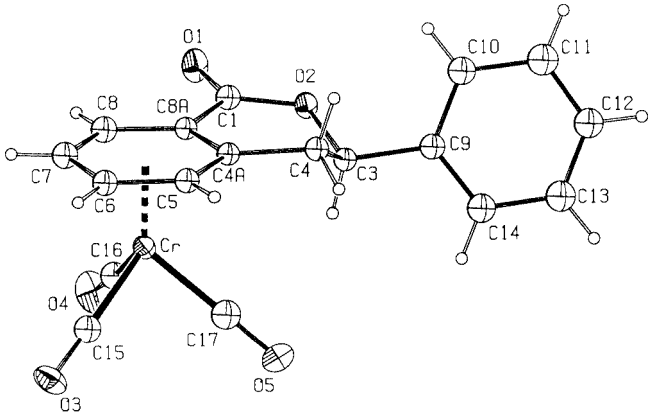


Figure 2. Structure of **27** in the crystal;[22] selected bond lengths [Å] and angles [°]: O(1)–C(1), 1.209(6), O(2)–C(1) 1.346(6), O(2)–C(3), 1.461(6), C(3)–C(4), 1.509(6), C(4)–C(4A), 1.521(6), C(4A)–C(5), 1.400(6), C(4A)–C(8A), 1.405(7), C(5)–C(6), 1.411(7), C(6)–C(7), 1.377(7), C(7)–C(8), 1.386(7), C(8)–C(8A), 1.408(6), Cr(1)–C(4A), 2.221(5), Cr(1)–C(5) 2.208(6), Cr(1)–C(6), 2.168(6), Cr(1)–C(7), 2.184(6), Cr(1)–C(8), 2.183(6), Cr(1)–C(8A), 2.204(6); C(1)–O(2)–C(3), 119.5(4), O(2)–C(3)–C(4) 111.0(4), C(3)–C(4)–C(4A)110.5(4)

In conclusion, the reaction between (benzocyclobutenone)tricarbonylchromium (**1**) and lithium phosphides has been shown to induce distal ring-opening, with formation of acylphosphane derivatives. In the presence of aldehydes or ketones a stepwise ring-expansion was observed, affording isochromanone complexes without further oxidation being necessary. The reaction sequence was diastereoselective when benzaldehyde was used. As enantiomerically **1** is available, this constitutes a formal total synthesis of enantiomerically pure 3-phenylisochromanone (**27**).

Experimental Section

General: See ref.[14] Melting points (uncorrected) were determined with a Büchi apparatus (Dr. Tottoli). *tert*-Butyl methyl ether (TBME), diethyl ether (DEE), petroleum ether (PE), and tetrahydrofuran (THF) were distilled from sodium–potassium alloy/benzophenone. Reagents were purchased and used without further purification.

General Working Procedure (GP): A solution of the benzocyclobutenone in THF was added dropwise at −78 °C to a cooled (−78 °C) solution of the lithiated phosphane[34] in THF. A change in color to deep brown was observed. After the mixture had been stirred for 2 h at −78 °C, a saturated aqueous solution of NH_4Cl (10 mL) or hydrochloric acid (1 N, 10 mL) was added. After warming to 20 °C the mixture was extracted with portions of TBME (15 mL) until the extract remained colorless. After drying of the collected organic layers over Na_2SO_4, the solvent was removed at reduced pressure and the crude product was purified by column chromatography on silica gel.

Treatment of *rac*-1 with Lithium Diisopropylphosphide: The GP was used, with *rac*-**1** (300 mg, 1.20 mmol) and lithium diisopropylphos-

phide (300 mg, 2.42 mmol) in THF (20 mL). During the addition the color changed to deep red. Hydrolysis was with aq. NH_4Cl. Column chromatography (280 × 30 mm, TBME/PE, 1:3) afforded: I: *rac*-tricarbonyl[η⁶-(1-diisopropylphosphanylcarbonyl-2-methyl)-benzene]chromium(0) (*rac*-**6**, 62 mg, 0.17 mmol, 14%), red oil. II: spiro-anellated isochromanone *rac*-**7** (189 mg, 0.37 mmol, 62%), mixture of diastereomers (2:1), orange solid. III: a mixture of tricarbonyl[η⁶-(1-diisopropylphosphorylcarbonyl-2-methyl-benzene)]chromium(0) (*rac*-**8**) and 1-diisopropylphosphorylcarbonyl-2-methylbenzene (**9**) (84 mg, 0.22 mmol, 18%).

***rac*-6:** IR ($CHCl_3$): $\tilde{\nu}$ = 3052 cm^{-1} (w), 2963 (m), 2869 (w), 1979 (s, CrCO), 1910 (s, CrCO), 1633 (m, CO), 1458 (w), 1386 (w), 1264 (s), 1098 (s), 1016 (s). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.14 (m, 12 H, PCHCH_3), 2.16 (m, $^3J_{P,H}$ = 14.1 Hz, 1 H, CHCH$_3$), 2.32 (m, 1 H, CHCH$_3$), 2.40 (s, 3 H, PCCH_3), 5.00 (d, ^3J = 6.4 Hz, 1 H, arom. H), 5.14 (dd, 1 H, arom. H), 5.65 (dd, 1 H, arom. H), 6.53 (dd, ^3J = 6.5 Hz, 1 H, arom. H). ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 18.4 (−, d, $^2J_{P,C}$ = 12.0 Hz, PCHCH$_3$), 20.5 (−, CCH$_3$), 23.7 (−, d, $^2J_{P,C}$ = 12.5 Hz, PCHCH$_3$), 24.3 (+, m, PCHCH$_3$), 86.6 (−, arom. CH), 91.6 (−, d, $^4J_{P,C}$ = 1.9 Hz, arom. CH), 95.6 (−, d, $^4J_{P,C}$ = 1.9 Hz, arom. CH), 97.7 (−, d, $^3J_{P,C}$ = 2.5 Hz, arom. CH), 102.6 (+, CCH$_3$), 110.4 [+, d, $^2J_{P,C}$ = 3.1 Hz, CC(O)P], 216.9 (+, d, $^1J_{P,C}$ = 46.6 Hz, CC(O)P], 231.0 (+, CO). $^{31}P\{^1H\}$ NMR (161.9 MHz, [D$_6$]acetone): δ = 31.4 (s). MS (70 eV, 80 °C): *m*/*z* (%) = 372 (3) [M$^+$], 344 (3) [M$^+$ − CO], 316 (15) [M$^+$ − 2CO], 288 (41) [M$^+$ − 3CO], 260 (16), 218 (19), 176 (33), 119 (100) [$H_3CC_6H_4CO^+$], 91 (36) [$C_7H_7^+$], 52 (43) [Cr$^+$]. HRMS ($C_{17}H_{21}CrO_4P$): calcd. 372.0583, found 372.0583.

***rac*-7 (Diastereomeric Mixture):** IR ($CHCl_3$): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2964 (w), 2932 (w), 1980 (s), 1912 (s), 1740 (m, ester), 1600 (w), 1520 (w), 1420 (w), 1096 (s), 1012 (m), 928 (w), 808 (m). MS (70 eV, 180 °C): *m*/*z* (%) = 508 (23) [M$^+$], 372 (29) [M$^+$ − 4CO − Cr], 340 [M$^+$ − 6CO], 288 (65), 244 (51), 202 (50), 150 (24), 136 (31), 91 (29), 52 (100) [Cr$^+$]. HRMS ($C_{22}H_{12}Cr_2O_8$): calcd. 507.9342, found 507.9340. $C_{22}H_{12}Cr_2O_8$ (508.32): calcd. C 50.98, H 2.38; found C 50.44, H 2.45.

***rac*-7 (Major Diastereomer):** ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.33 (d, $^2J_{H,H}$ = −14.1 Hz, 1 H, cyclobutane-CH_2), 3.46 (d, ^2J = −14.1 Hz, 1 H, cyclobutane-CH_2), 3.53 (m, 1 H, oxacyclohexane-CH_2), 3.68 (m, 1 H, oxacyclohexane-CH_2), 5.30 (m, 1 H, arom. H), 5.82 (m, 1 H, arom. H), 5.66−5.73 (m, 3 H, arom. H), 6.06 (dd, ^3J = 6.4 Hz, 1 H, arom. H), 6.21 (d, ^3J = 6.5 Hz, 1 H, arom. H), 6.38 (d, ^3J = 6.7 Hz, 1 H, arom. H next to C=O). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 34.1 (+, cyclobutane-CH$_2$), 44.8 (+, oxacyclohexyl-CH$_2$), 81.8 (+, spiro-C_q), 86.3 (+, arom C$_q$ next to C=O), 87.0 (−, arom. C), 88.2 (−, arom. C), 90.17 (−, arom. C), 90.21 (−, arom. C), 90.4 (−, arom. C), 95.15 (−, arom. C), 95.19 (−, arom. C), 96.1 (−, arom. C), 108.9 (+, arom. C$_q$), 113.31 (+, arom. C$_q$), 113.35 (+, arom. C$_q$), 162.0 (+, C=O), 231.0 (CO), 232.5 (CO).

***rac*-7 (Minor Diastereomer):** ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 5.99 (dd, ^3J = 6.40 Hz, 1 H, arom. H), 6.30 (d, ^3J = 6.65 Hz, 1 H, arom CH next to C=O). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 33.7 (+, cyclobutane-CH$_2$), 44.7 (+, oxacyclohexyl-CH$_2$), 82.0 (+, spiro-C_q), 86.7 [+, arom C$_q$ next to C=O], 86.9 (−, arom. C), 87.9 (−, arom. C), 91.3 (−, arom. C), 92.1 (−, arom. C), 93.1 (−, arom. C), 94.9 (−, arom C), 95.2 (−, arom. C), 96.1 (−, arom. C), 108.3 (+, arom. C$_q$), 113.5 (+, arom. C$_q$), 114.4 (+, arom. C$_q$), 162.1 (+, C=O), 231.2 (+, CO), 232.4 (+, CO).

***rac*-8 + 9:** IR ($CHCl_3$): $\tilde{\nu}$ = 2971 cm^{-1} (m), 2876 (w), 1987 (s, CrCO), 1918 (s, CrCO), 1632 (m, CO), 1462 (w), 1388 (w), 1176 (m), 1150 (m), 1026 (w), 882 (w). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.14−1.27 (m, 12 H, PCHCH_3), 2.26−2.38 (m, 2 H, PCHCH$_3$), 2.43 (s, 3 H, CCH_3), 4.96 (d, ^3J = 6.24 Hz, 1 H, arom H), 5.14 (m, 1 H, arom. H), 5.75 (m, 1 H, arom. H), 7.25 (d, ^3J = 6.2 Hz, 1 H, arom. H). ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 15.3 (−, CCH$_3$), 21.5 (−, m, PCHCH$_3$), 35.2 (−, m, PCHCH$_3$), 86.9 (−, arom. C), 91.3 (−, d, $^3J_{P,C}$ = 2.5 Hz, arom. C), 96.0 (−, arom. C), 97.2 (+, d, $^2J_{P,C}$ = 42.4 Hz, arom. C_qCH$_3$=O), 100.1 (−, arom. C), 110.7 (+, d, $^3J_{P,C}$ = 4.9 Hz, arom. C_qCH$_3$), 207.3 (+, d, $^1J_{P,C}$ = 63.2 Hz, C=O), 230.2 (+, CO). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ = 57.7 (s). MS (70 eV, 25 °C): *m*/*z* (%) = 252 (8) [M$^+$ − Cr(CO)$_3$], 134 (2) [P(O)(*i*Pr)$_2$], 119 (100), 84 (31), 52 (1) [Cr$^+$].

Crystal Structure Analysis of *rac*-6:[22] $C_{17}H_{21}CrO_4P$, M = 372.31, crystal: red, size 0.30 × 0.26 × 0.22 mm, a = 10.018(3), b = 13.233(4), c = 14.603(4) Å, α = 104.93(3), β = 90.01(3), γ = 93.54(3)°, V = 1866.7(9) Å^3, Z = 4, $d_{calcd.}$ = 1.325 g cm^{-3}, T = 300 K, crystal system triclinic, space group $P\bar{1}$, F(000) = 776 e, m = 0.713 mm^{-1}, Stoe IPDS area detector diffractometer, Mo-K_α = 0.71073 Å, 2θ$_{min}$ = 1.60, 2θ$_{max}$ = 21.01, 8407 measured reflections, 3732 independent, 856 observed reflections [$I > 2\sigma$], completeness of data 95.6%, $R(I)$ = 0.1566, no absorption correction, no extinction correction, refinement SHELXL-93, refinement according to least squares method (F^2), R = 0.145, wR_2 = 0.315, min./max. residual electron density −0.4/0.9 e·Å^{-3}.

Formation of *rac*-7 by Treatment of *rac*-1 with Lithium Diphenylphosphide: The GP was used, with *rac*-**1** (250 mg, 0.98 mmol) and lithium diphenylphosphide (230 mg, 1.20 mmol) in THF (20 mL). During addition the color changed to deep red. Hydrolysis was with aq. NH_4Cl. Column chromatography (280 × 30 mm, TBME/PE, 1:3) afforded *rac*-**7** (182 mg, 0.36 mmol, 73%).

Formation of *rac*-7 by Treatment of *rac*-1 with Lithium Bis(trimethylsilyl)phosphide: The GP was used, with *rac*-**1** (100 mg, 0.39 mmol) and lithium bis(trimethylsilyl)phosphide (74 mg, 0.40 mmol) in THF (20 mL). During addition the color changed to deep red. Hydrolysis was with aq. NH_4Cl. Column chromatography (140 × 20 mm, TBME/PE, 1:3), afforded *rac*-**7** (43 mg, 0.08 mmol, 43%).

Treatment of *rac*-1 with Lithium Di-*tert*-butylphosphide: The GP was used, with *rac*-**1** (150 mg, 0.60 mmol) and lithium di-*tert*-butylphosphide (180 mg, 1.20 mmol) in THF (20 mL). During addition the color changed to deep red. Hydrolysis was with aq. NH_4Cl. Column chromatography (250 × 30 mm, TBME/PE, 1:3) afforded: I: [η⁶-(1-di-*tert*-butylphosphanylcarbonyl-2-methylbenzene)]tricarbonylchromium(0) (*rac*-**14**, 29 mg, 0.07 mmol, 12%), red oil. II: *rac*-**13** (104 mg, 0.16 mmol, 53%), red oil. III: [η⁶-(1-di-*tert*-butylphosphorylcarbonyl-2-methylbenzene)]tricarbonylchromium(0) (*rac*-**15**, 67 mg, 0.16 mmol, 27%), red oil.

***rac*-14:** IR (ATR): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2864 (w), 1970 (s, CrCO), 1895 (s, CrCO), 1632 (m, CO), 1462 (w), 1365 (w), 1170 (m), 1031 (w), 895 (m). ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.21 [d, $^3J_{P,H}$ = 11.4 Hz, 9 H, C(CH_3)$_3$], 1.30 [d, $^3J_{P,H}$ = 12.2 Hz, 9 H, C(CH_3)$_3$], 2.47 (s, 3 H, CCH_3), 5.40 (d, $^3J_{4,5}$ = 6.4 Hz, 1 H, arom. H), 5.50 (m, 1 H, arom. H), 6.04 (m, 1 H, arom. H), 6.92 (d, $^3J_{7,6}$ = 7.0 Hz, 1 H, arom. H). $^{31}P\{^1H\}$ NMR (161.9 MHz, [D$_6$]acetone): δ = 44.7 (s).

***rac*-13:** IR ($CHCl_3$): $\tilde{\nu}$ = 2960 cm^{-1} (m), 2864 (w), 1981 (s, CrCO), 1900 (s, CrCO), 1629 (m), 1515 (w), 1471 (w), 1433 (w), 1366 (w), 1230 (w), 1166 (m), 1092 (m), 1060 (w), 1017 (m), 909 (m). ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.21 [d, $^3J_{P,H}$ = 11.4 Hz, 9

H, C(CH_3)$_3$], 1.28 [d, $^3J_{P,H}$ = 12.2 Hz, 9 H, C(CH_3)$_3$], 2.99 (d, ^2J = −14.4 Hz, 1 H, CH_2), 3.20 (d, ^2J = −13.9 Hz, 1 H, CH_2), 3.50 (d, ^2J = −13.7 Hz, 1 H, CH_2), 4.22 (d, ^2J = 14.4 Hz, 1 H, CH_2), 5.14 (m, 1 H, arom. H), 5.55 (m, 1 H, arom. H), 5.61−5.72 (m, 5 H, arom. H), 6.15 (m, 1 H, arom. H). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 30.2 [−, d, $^2J_{P,C}$ = 12.3 Hz, C(CH_3)$_3$], 32.7 [+, d, $^1J_{P,C}$ = 23.2 Hz, C(CH_3)$_3$], 34.2 [+, d, $^1J_{P,C}$ = 23.5 Hz, C(CH_3)$_3$], 40.5 (+, CH_2), 46.3 (+, CH_2), 78.6 (+, COH), 88.1(−, arom. CH), 88.7 (−, arom. CH), 89.0 (−, arom. CH), 90.4 (−, arom. CH), 92.7 (−, d, $^4J_{P,C}$ = 2.2 Hz, arom. CH), 95.1 (−, arom. CH), 97.7 (−, d, $^4J_{P,C}$ = 1.9 Hz, arom. CH), 100.8 (−, d, $^3J_{P,C}$ = 33.7 Hz, arom. CH), 102.5 (+, d, $^2J_{P,C}$ = 34.0 Hz, arom. C_qC=O), 111.4 (+, d, $^3J_{P,C}$ = 2.8 Hz, arom. C_q), 113.5 (+, arom. C_q), 121.8 (+, arom. C_q), 216.4 (+, d, $^1J_{P,C}$ = 53.6 Hz, C=O), 231.3 (+, CrCO), 233.3 (+, CrCO). ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone): δ = 41.0 (s). MS (70 eV, 150 °C): *m*/*z* (%) = 486 (3) [M$^+$ − 6CO], 462 (5), 434 (50), 406 (13), 378 (25), 350 (9), 314 (18), 289 (83), 245 (58), 198 (29), 146 (14), 119 (19), 92 (34), 57 (100) [*t*Bu$^+$], 52 (93) [Cr$^+$]. $C_{30}H_{31}Cr_2O_8P$ (654.533): calcd. C 53.05, H 4.77; found C 53.96, H 4.75.

***rac*-15:** IR ($CHCl_3$): $\tilde{\nu}$ = 2962 cm^{-1} (m), 2904 (w), 1983 (s, CrCO), 1909 (s, CrCO), 1628 (m, CO), 1474 (w), 1400 (w), 1230 (m), 1097 (s), 1016 (s). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.29 [d, $^3J_{P,H}$ = 13.7 Hz, 9 H, C(CH_3)$_3$], 1.40 [d, $^3J_{P,H}$ = 14.0 Hz, 9 H, C(CH_3)$_3$], 2.47 (s, 3 H, CCH_3), 5.39 (d, $^3J_{4,5}$ = 6.1 Hz, 1 H, arom. H), 5.47 (m, 1 H, arom. H), 6.13 (m, 1 H, arom. H), 7.88 (d, $^3J_{7,6}$ = 5.8 Hz, 1 H, arom. H). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 20.2 (−, 25.8, CCH_3) (−, d, $^2J_{P,C}$ = 24.3 Hz, C(CH_3)$_3$], 26.2 (−, d, $^2J_{P,C}$ = 24.0 Hz, C(CH_3)$_3$], 36.2 (+, m, C(CH_3)$_3$], 87.9 (−, arom. CH), 92.8 (−, d, $^3J_{P,C}$ = 1.9 Hz, arom. CH), 97.8 (−, arom. CH), 99.3 (+, d, $^3J_{P,C}$ = 2.5 Hz, C-3), 100.5 (−, d, $^4J_{P,C}$ = 1.4 Hz, arom. CH), 112.2 (+, d, $^2J_{P,C}$ = 4.7 Hz, arom. C_q), 208.9 (+, d, $^1J_{P,C}$ = 56.7 Hz, arom. C_q), 231.2 (+, CO). ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone): δ = 56.8 (s). MS (70 eV, 100 °C): *m*/*z* (%) = 360 (32) [M$^+$ − 2CO], 332 (100) [M$^+$ − 3CO], 305 (44), 249 (60), 189 (48), 119 (93), 91 (21), 52 (48) [Cr$^+$].

***rac*-16:** Compound *rac*-**14** (10 mg, 0.03 mmol) in THF (5 mL) was added at −15 °C to a freshly prepared solution of pentacarbonyl(tetrahydrofuran)chromium(0) in THF, which had been obtained by irradiation (Pyrex) of an excess of $Cr(CO)_6$ in THF for 15 min. The mixture was allowed to warm to 20 °C and was stirred for 2 h. After solvent removal at reduced pressure into a cold trap, the residue was taken up with DEE and filtered through a P4 frit covered with a 3 cm thick layer of kieselgur. After condensation of the DEE into the cold trap the filtering procedure was repeated with pentane. After solvent removal into a cold trap, a red product is obtained, in addition to starting material *rac*-**14** and its decomplexed ligand some *rac*-**16**. IR (ATR): $\tilde{\nu}$ = 2962 cm^{-1} (m), 2905 (w), 2060 (w), 1973 (m), 1933 (s), 1650 (w), 1413 (w), 1068 (s), 1016 (s), 864 (m), 795 (s), 660 (m). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.54 [d, $^3J_{P,H}$ = 13.2 Hz, 18 H, C(CH_3)$_3$] 2.38 (s, 3 H, CCH_3), 5.22 (d, $^3J_{4,5}$ = 6.52 Hz, 1 H, arom. H), 5.48 (m, 1 H, arom. H), 5.58 (m, 1 H, arom. H), 6.09 (d, $^3J_{7,6}$ = 7.4 Hz, 1 H, arom. H). ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone): δ = 115.9 (s). FAB-MS: *m*/*z* = 592 [M$^+$].

***rac*-Tricarbonyl(η^6-2-ethylenedioxybenzocyclobutenone)chromium(0) (*rac*-17):** Sulfuric acid (50%, 1.5 mL) was added to tricarbonyl-[η^6-1,2-bis(ethylenedioxy)benzocyclobutene]chromium(0)[15,18] (150 mg, 0.42 mmol) in acetone (10 mL). The mixture was stirred for 3 h at 25 °C, the yellow color changing to orange. TLC monitoring (TBME, R_f = 0.32) showed, in addition to a new spot, the presence of starting material and a small amount of **2**. Water (10 mL) and TBME (20 mL) were added. After separation of the layers the aqueous layer was extracted with portions (10 mL) of TBME until it remained colorless. The collected organic layers were washed with water, dried over Na_2SO_4, and filtered. The solvent was removed at reduced pressure, and the crude product was purified by column chromatography (400 × 30 mm, TBME/PE, 1:2), to afford *rac*-**17** (111 mg, 0.36 mmol, 85%), orange solid (m.p. 136 °C). IR ($CHCl_3$): $\tilde{\nu}$ = 2960 (w) cm^{-1}, 2932 (w) 1992 (s, CO), 1932 (s, CO), 1780 (m, C=O) 1120 (m), 1100 (w), 1076 (m),1012 (m), 948 (w), 860 (w), 612 (w). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 4.19 (m, 4 H, CH_2CH_2), 5.71 (dd, $^3J_{4,5}$ = 6.2, $^3J_{4,3}$ = 6.2 Hz, 1 H, 4-H), 5.9 (dd, 1 H, $^3J_{5,6}$ = 6.2 Hz, 5-H), 6.01 (d, 1 H, 3-H), 6.26 (d, 1 H, 6-H). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 67.2 (+, CH_2CH_2), 67.3 (+, CH_2CH_2), 85.9 (−, arom. CH), 87.3 (−, arom. CH), 93.3 (−, arom. CH), 94.7 (−, arom. CH), 107.9 (+, C-2), 120.1 (+, C-2a), 125.6 (+, C-6a), 190.0 (+, C-1), 229.8 (+, CO). MS (70 eV, 120 °C): *m*/*z* (%) = 312 (15) [M$^+$], 284 (8) [M$^+$ − CO], 256 (3) [M$^+$ − 2CO], 228 (28) [M$^+$ − 3CO], 200 (15), 148 (10), 128 (24), 104 (38), 52 (100) [Cr$^+$]. $C_{13}H_8CrO_6$ (312.2): calcd. C 50.01, H 2.58; found C 50.28, H 3.13.

Treatment of 17 with Lithium Di-*tert*-butylphosphide: The GP was used, with **17** (150 mg, 0.48 mmol) and lithium di-*tert*-butylphosphide (261 mg, 2.1 mmol) in THF (20 mL). Hydrolysis was with aq. NH_4Cl. Column chromatography (250 × 30 mm, TBME/PE, 1:1) afforded: I: tricarbonyl(η^6-2-ethylenedioxy-2-phenylacetyldi-*tert*-butylphosphide)chromium(0) (**18**, 46 mg, 0.10 mmol, 21%), yellow-orange solid (m.p. 132 °C). II: **17** (39 mg, 0.12 mol, 26%). III: of *rac*-**19** (86 mg, 0.18 mmol, 38%), yellow solid (m.p. 112 °C, dec.).

18: IR ($CHCl_3$): $\tilde{\nu}$ = 2925 cm^{-1} (m), 2860 (w), 1970 (s, CrCO), 1886 (s, CrCO), 1763 (m, C=O), 1608 (w), 1466 (m), 1315 (m), 1179 (w), 1105 (w), 1076 (m), 1020 (m), 945 (m), 810 (w), 664(m). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.16 (d, $^3J_{P,H}$ = 11.6 Hz, 9 H, CCH_3), 1.34 (d, $^3J_{P,H}$ = 11.6 Hz, 9 H, CCH_3) 4.27 (m, 4 H, CH_2CH_2), 5.43 (dd, ^3J = 6.4 Hz, 1 H, arom. H), 5.7 (m, 2 H, arom. H), 5.87 (dd, ^3J = 6.3 Hz, 1 H, arom. H), 6.15 (d, ^3J = 6.4 Hz, 1 H, arom. H). ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone): δ = 44.1 (s). MS (70 eV, 90 °C): *m*/*z* (%) = 460 (2) [M$^+$ + 2], 459 (5) [M$^+$ + 1], 458 (13) [M$^+$], 373 (19) [M$^+$ − 3CO], 302 (21), 246 (14), 177 (100) [M$^+$ − Cr(CO)$_3$ − C(O)P*i*Pr$_2$], 165 (50), 133 (26), 105 (14), 57 (43), 52 (10) [Cr$^+$]. HRMS ($C_{21}H_{27}CrPO_6$): calcd. 458.0950, found 458.0952.

***rac*-19:** IR ($CHCl_3$): $\tilde{\nu}$ = 2962 cm^{-1} (m), 2905 (w), 1964 (s, CrCO), 1896 (m, CrCO), 1874 (s, CrCO), 1697 (w), 1526(m), 1474 (m), 1318 (m), 1138 (m), 1109 (m), 1081 (m), 1041 (s, C−O), 1017 (m), 948 (m), 801 (m), 660 (m). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.21 [d, $^3J_{P,H}$ = 13.7 Hz, 9 H, C(CH_3)$_3$], 1.38 [d, $^3J_{P,H}$ = 13.3 Hz, 9 H, C(CH_3)$_3$] 4.30 (m, 4 H, CH_2CH_2), 5.48 (dd, ^3J = 6.0 Hz, 1 H, arom. H), 5.61 (d, ^3J = 2.9 Hz, 1 H, benzyl. H), 5.85 (dd, ^3J = 5.9 Hz, 1 H, arom. H), 6.16 (d, ^3J = 6.4 Hz, 1 H, arom. H), 6.20 (d, ^3J = 6.0 Hz, 1 H, arom. H). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 24.4 [−, C(CH_3)$_3$], 26.2 [−, C(CH_3)$_3$], 36.1 [+, d, $^1J_{P,C}$ = 55.3 Hz, C(CH_3)$_3$], 37.1 [+, d, $^1J_{P,C}$ = 54.2 Hz, C(CH_3)$_3$], 65.5 (+, CH_2), 66.3 (+, CH_2), 75.6 (−, d, ^1J = 60.1 Hz, benzyl. CH), 85.2 (−, arom. CH), 89.8 (−, arom. CH), 90.1 (−, arom. CH), 95.2 (−, arom. CH), 103.8 (+, arom. C_q), 114.6 (+, arom. C_q), 128.4 (+, d, $^2J_{P,C}$ = 3.0 Hz, benzyl. C_q), 232.3 (+). ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone): δ = 59.7 (s). MS (70 eV, 120 °C): *m*/*z* (%) = 476 (2) [M$^+$ + 2], 475 (8) [M$^+$ + 1], 474 (21) [M$^+$], 391 (37) [M$^+$ − 3CO], 335 (15), 303 (47), 247 (15), 177 (100) [M$^+$ − Cr(CO)$_3$ − C(O)P(O)*i*Pr$_2$], 133 (17), 105 (19), 57 (13), 52 (9) [Cr$^+$]. HRMS ($C_{21}H_{27}CrO_7P$): calcd. 474.0900, found 474.0902.

η^6:η^6-{Butane-1,4-bis[(ethylenedioxy)phenyl acetate]}bis(tricarbonylchromium) (20): The GP was used, with **17** (100 mg, 0.39 mmol) and lithium diphenylphosphide (173 mg, 0.90 mmol) in THF (15 mL). Hydrolysis was with aq. NH_4Cl. Column chromatography (200 × 30 mm, TBME/PE, 1:2) afforded **20** (88 mg, 0.13 mmol, 63%), yellow solid (m.p. 124 °C, dec.). IR (ATR): $\tilde{\nu}$ = 3070 cm^{-1} (w), 2903 (w), 1965 (s, CrCO), 1882 (s, CrCO), 1744 (m, C=O), 1592 (w), 1477 (w), 1435 (m), 1413 (w), 1110 (m), 1028 (m), 948 (w), 830 (w), 745 (w), 698 (w), 659 (w). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.35 (q, 4 H, CCH_2C), 4.19 (t, 4 H, OCH_2C), 4.23 (m, 8 H, OCH_2CH_2O), 5.52 (dd, 4 H, *m*-H), 5.76 (dd, 2 H, *p*-H), 5.87 (d, 4 H, *o*-H). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 32.6 (+, CCH_2C), 64.5 (+, OCH_2C), 66.4 (+, OCH_2CH_2O), 90.3 (−, arom. *C*H), 93.8 (−, arom. *C*H), 95.4 (−, arom. *C*H), 109.1 (+, benzyl. C_q), 116.7 (+, arom. C_q), 167.9 (+, *C*=O), 232.8 (+, CrCO). MS (70 eV, 180 °C): *m*/*z* (%) = 446 (3), 385 (20) [M^+ − (OC)$_3$CrPhC(OCH_2CH_2O)C(O)O], 357 (10) [1/2 M^+], 329 (38) [(OC)$_3$CrPhC(OCH_2CH_2O)C(O)O$^+$], 300 (100), 272 (15), 241 (27), 214 (49) [$C_6H_6Cr(CO)_3^+$], 173 (32), 149 (39) [PhC(OCH_2CH_2O)], 129 (43) [$CrC_5H_5^+$], 105 (28), 77 (19) [Ph^+], 52 (48) [Cr^+]. FAB: *m*/*z* = 714 [M^+].

***rac*-2:3,7:8-Dibenzo-6-oxo-5-oxaspiro[3.5]nonane (*rac*-23):** The GP was used, with benzocyclobutenone[35] (200 mg, 1.70 mmol) and lithium diisopropylphosphide (261 mg, 2.10 mmol) in THF (20 mL). Hydrolysis was with aq. NH_4Cl. Column chromatography (200 × 30 mm, TBME/PE, 1:2) afforded: I: *rac*-**23** (158 mg, 1.34 mmol, 79%), colorless solid (m.p. 119 °C). II: **9** (60 mg, 0.24 mmol, 14%).

***rac*-23:** IR ($CHCl_3$): $\tilde{\nu}$ = 3043 cm^{-1} (w), 2930 (w), 1718 (s, C=O), 1607 (w), 1459 (m), 1288 (s), 1119 (s), 1084 (m), 1031 (m), 934 (w). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.45 (m, 2 H, oxacyclohexane-CH_2), 3.48 (d, $^2J_{H,H}$ = 3.3 Hz, 2 H, cyclobutane-CH_2), 6.77 (d, ^3J = 7.4 Hz, 1 H, arom. H), 7.18 (dd, ^3J = 7.5 Hz, 1 H, arom. H), 7.25 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.35 (dd, ^3J = 7.5 Hz, 1 H, arom. H), 7.45 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.53 (dd, ^3J = 7.5 Hz, 1 H, arom. H), 7.67 (dd, ^3J = 7.5 Hz, 1 H, arom. H), 8.06 (d, ^3J = 7.8 Hz, 1 H, arom. H). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 35.5 (+, oxacyclohexane-*C*H$_2$), 43.9 (+, cyclobutane-*C*H$_2$), 84.3 (+, spiro-*C*), 120.6 (−, arom. *C*H), 123.8 (−, arom. *C*H), 124.4 (−, arom. *C*H), 125.5 (+, HCC_qC=O), 127.6 (−, arom. *C*H), 128.1 (−, arom. *C*H), 129.4 (−, arom. *C*H), 130.3 (−, arom. *C*H), 133.8 (−, arom. *C*H), 138.6 (+, cyclobutane-CH$_2C_q$CH), 141.1 (+, oxacyclohexane-CH$_2C_q$CH), 146.1 (+, cyclobutane-CH$_2C_qCq$CH), 164.0 (+, C=O). MS (70 eV, 25 °C): *m*/*z* (%) = 238 (5) [M^+ + 2], 237 (20) [M^+ + 1], 236 (100) [M^+], 208 (84) [M^+ − CO], 179 (38), 136 (37), 90 (60), 77 (8). HRMS ($C_{16}H_{12}O_2$): calcd. 236.0837, found 236.0836.

9: IR ($CHCl_3$): $\tilde{\nu}$ = 2972 cm^{-1} (m), 2876 (m), 1638 (s, CO), 1459 (m), 1291 (m), 1175 (m), 1149 (m), 1026 (w), 929 (w), 826 (w). ^{1}H NMR (200.1 MHz, [D$_6$]acetone): δ = 1.16 (m, $^3J_{P,H}$ = 7.2 Hz, 12 H, CHCH_3), 2.39 (m, 2 H, PC*H*CH$_3$), 2.52 (s, 3 H, CH_3), 7.39 (m, 2 H, arom. H), 7.55 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, arom. H), 8.98 (d, $^3J_{H,H}$ = 7.6 Hz, arom. H, 1 H). ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 15.3 [−, CH(*C*H$_3$)$_2$], 21.0 [−, m, PC*H*(CH$_3$)$_2$], 26.0 (−, m, C_q*C*H$_3$), 126.1 (−, arom. *C*H), 131.9 (−, d, $^3J_{P,C}$ = 2.5 Hz, arom. *C*H), 133.4 (−, arom. *C*H), 134.0 (−, arom. *C*H), 137.3 (+, d, $^2J_{P,C}$ = 39.1 Hz, arom. C_q), 138.8 (+, d, $^3J_{P,C}$ = 5.2 Hz, arom. C_q), 210.9 (+, d, $^1J_{P,C}$ = 60.1 Hz, C=O). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$): δ = 56.5 (s). MS (70 eV, 25 °C): *m*/*z* (%) = 253 (2) [M^+ + 1], 252 (11) [M^+], 236 (2) [M^+ − O], 149 (2), 136 (6), 119 (100) [P*i*Pr$_2$], 91 (27).

***rac*-24:** The GP was used, with 6-methoxybenzocyclobutenone[36] (**22**, 500 mg, 3.78 mmol) and lithium diisopropylphosphide (503 mg, 4.05 mmol) in THF (30 mL). Hydrolysis was with aq. NH_4Cl. Column chromatography (300 × 30 mm, TBME/PE, 1:2) afforded *rac*-**24**, 232 mg, 3.13 mmol, 83%), colorless solid (m.p. 132 °C). IR (ATR): $\tilde{\nu}$ = 2962 cm^{-1} (w), 2839 (w), 1726 (s, C=O), 1597 (m), 1585 (m), 1476 (s), 1368 (w), 1274 (s), 1238 (m), 1181 (w), 1084 (s), 1046 (s), 982 (m), 820 (w), 772 (m). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.17 (m, 2 H, oxacyclohexane-CH_2, cyclobutane-CH_2), 3.33 (d, ^2J = −14.1 Hz, 1 H, oxacyclohexane-CH_2), 3.58 (d, ^2J = −15.9 Hz, 1 H, cyclobutane-CH_2), 3.75 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3), 6.69 (d, ^3J = 8.4 Hz, 1 H, arom. H), 6.74 (d, ^3J = 7.15 Hz, arom. H), 6.82 (d, ^3J = 7.4 Hz, 1 H, arom. H), 6.96 (d, ^3J = 8.5 Hz, 1 H, arom. H), 7.27 (dd, ^3J = 8.4 Hz, 1 H, arom. H), 7.49 (dd, ^3J = 7.5 Hz, 1 H, arom. H). ^{13}C NMR (100.6 MHz, $CDCl_3$, BB): δ = 38.0 (cyclobutane-*C*H$_2$), 44.4 (oxacyclohexane-*C*H$_2$), 56.6 (O*C*H$_3$), 56.7 (O*C*H$_3$), 83.3 (spiro-*C*), 111.4 (arom. C), 112.2 (arom. C), 114.5 (arom. C), 116.3 (arom. C), 120.1 (arom. C), 130.6 (arom. C), 132.6 (arom. C), 135.1 (arom. C), 141.2 (arom. C), 143.2 (arom. C), 154.4 (arom. C), 161.6 (arom. C), 162.3 (*C*=O). MS (70 eV, 110 °C): *m*/*z* (%) = 298 (3) [M^+ + 2], 297 (16) [M^+ + 1], 296 (32) [M^+], 282 (17), 266 (41), 238 (24), 209 (37), 179 (53), 149 (84), 122 (100), 106 (44), 87 (37), 74 (31). HRMS ($C_{18}H_{16}O_4$): calcd. 296.1049, found 296.1046.

***rac*-3-(*p*-Nitrophenyl)isochroman-1-one (*rac*-25):** A cooled (−78 °C) solution of lithium diisopropylphosphide (201 mg, 1.62 mmol) in THF (50 mL) was added dropwise at −78 °C over 1.5 h to benzocyclobutenone (**21**, 126 mg, 1.07 mmol) in THF (15 mL). During the addition the solution became deep red. After completion of the addition the mixture was stirred for 30 min at −78 °C. *p*-Nitrobenzaldehyde (242 mg, 1.60 mmol) in THF (15 mL) was then added dropwise over 20 min, the solution becoming yellow. The mixture was stirred for 2 h at −78 °C and was then hydrolyzed at this temperature by addition of hydrochloric acid (1 N, 5 mL). After warming to 20 °C the mixture was extracted three times with TBME (10 mL each). The collected organic layers were washed with water (30 mL), separated, and dried over $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (270 × 30 mm, TBME/PE, 1:1) to afford *rac*-**25** (339 mg, 1.26 mmol, 78%), bright yellow oil.[37]

***rac*-3-Propylisochroman-1-one (*rac*-26):** A cooled (−78 °C) solution of lithium diisopropylphosphide (788 mg, 6.35 mmol) in THF (50 mL) was added dropwise over 2 h at −78 °C to benzocyclobutenone (**21**, 500 mg, 4.24 mmol) in THF (20 mL). During the addition the solution became deep red. After completion of the addition the mixture was stirred for 1 h at −78 °C. Butanal (310 mg, 4.31 mmol) in THF (15 mL) was then added dropwise, the solution becoming yellow. The mixture was stirred for 2 h at −78 °C and was then hydrolyzed at this temperature by addition of hydrochloric acid (1 N, 10 mL). After warming to 20 °C the mixture was extracted three times with TBME (20 mL each). The collected organic layers were washed with water (60 mL), separated, and dried over $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (330 × 30 mm, TBME/PE, 1:1) to afford *rac*-**26** (454 mg, 2.38 mmol, 57%), bright yellow oil.[38]

***rac*-(3-Phenylisochromanone)tricarbonylchromium (*rac*-27):** A cooled (−78 °C) solution of lithium diisopropylphosphide (195 mg, 1.6 mmol) in THF (40 mL) was added dropwise at −78 °C over 2 h to *rac*-(benzocyclobutenone)tricarbonylchromium (*rac*-**1**, 200 mg, 0.79 mmol) in THF (30 mL). During the addition the solution became dark brown. After completion of addition the mixture

was stirred for 30 min at −78 °C. Benzaldehyde (419 mg, 3.95 mmol) in THF (20 mL) was then added dropwise over 20 min, the solution becoming orange. The mixture was stirred for 2 h at −78 °C and was then hydrolyzed at this temperature by addition of sat. aq. NH_4Cl (40 mL). After warming to 20 °C the mixture was extracted three times with TBME (20 mL each). The collected organic layers were washed with water (60 mL), separated, and dried over $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (250 × 30 mm, TBME/PE, 1:1) to afford *rac*-**27** (155 mg, 0.43 mmol, 55%), yellow-orange solid (m.p. 158 °C, dec.). IR (ATR): $\tilde{\nu}$ = 3082 cm^{-1} (w), 2967 (m), 2924 (m), 2852 (m), 1965 (s, Cr−CO), 1886 (s, Cr−CO), 1704 (s, C=O, lactone), 1526 (m), 1259 (s), 1066 (s, C−O), 1010 (s, C−O), 795 (s), 771 (s), 758 (s). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.02 (dd, $^3J_{endo\text{-}4,3}$ = 2.6, $^2J_{endo\text{-}4,exo\text{-}4}$ = −16.4 Hz, 1 H, *endo*-4-H), 3.46 (m, $^3J_{exo\text{-}4,3}$ = 12.4, $^2J_{exo\text{-}4,endo\text{-}4}$ = −16.4 Hz, 1 H, *exo*-4-H), 5.62 (m, $^3J_{3,endo\text{-}4}$ = 2.6, $^3J_{3,exo\text{-}4}$ = 12.4 Hz, 1 H, 3-H), 5.71 (m, $^3J_{5,6}$ = 6.3 Hz, 1 H, 5-H), 5.77 (m, $^3J_{6,5}$ = 6.3 Hz, 1 H, 6-H), 6.07 (m, 1 H, arom. H), 6.26 (m, 1 H, arom. H). ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT/HMQC): δ = 34.6 (+, CH_2, C-4), 80.6 (−, CH, C-3), 87.1 (+, C_q, C-8a), 91.9 (−, CH, arom. CH), 92.2 (−, CH, arom. CH), 93.8 (−, CH, arom. CH), 96.7 (−, CH, arom. CH), 112.8 (+, C_q, C-4a), 127.0 [−, CH, C-10(14)], 129.5 [−, CH, C-11(13)], 129.6 (−, CH, C-12), 139.1 (+, C_q, C-9), 164.4 (+, C_q, C=O, C-1), 232.2 (+, C_q, CrCO). MS (70 eV, 170 °C): *m*/*z* (%) = 362 (17) [M^+ +2], 361 (40) [M^+ +1], 304 (18) [M^+ − 2CO], 276 (39) [M^+ − 3CO], 257 (13), 247 (27), 232 (100) [M^+ −3CO − CO_2], 207 (15), 178 (32), 149 (15), 127 (13), 105 (29), 91 (13) [$PhCH_2^+$]. HRMS ($C_{18}H_{12}CrO_5$): calcd. 360.0090, found 360.0089.

Crystal Structure Analysis of 27:[22] $C_{18}H_{12}CrO_5$, M = 360.28 g/mol, crystal: yellow needle, size 1.1 × 0.09 × 0.04 mm, triclinic, space group *P*-1, (No.2), a = 7.056(3), b = 7.253(4), c = 16.276(8) Å, α = 91.53(6), β = 99.07(5), γ = 105.71(5)°, V = 789.7(7) Å^3, Z = 2, $d_{calcd.}$ = 1.515 g cm^{-3}, T = 300(2) K, Stoe IPDS diffractometer, $\lambda_{Mo\text{-}K\alpha}$= 0.71073 Å, θ_{max}= 26.06°, 5088 measured, 2855 unique (R_{int} = 0.0855) and 869 observed ($I > 2\sigma_I$) reflections, completeness of data 92.5%, 127 refined parameters, $R_{gt}(F)$ = 0.0457, w$R(F^2)$ = 0.0869, min./max. residual electron density −0.24/0.41 e·Å^{-3}.

***rac*-(3-Isopropylisochromanone)tricarbonylchromium (*rac*-28):** A cooled (−78 °C) solution of lithium diisopropylphosphide (146 mg, 1.17 mmol) in THF (30 mL) was added dropwise at −78 °C over 2 h to *rac*-(benzocyclobutenone)tricarbonylchromium (*rac*-**1**, 150 mg, 0.59 mmol) in THF (20 mL). During the addition the solution became dark brown. After completion of addition the mixture was stirred for 30 min at −78 °C. 2-Methylpropanal (212 mg, 2.94 mmol) in THF (15 mL) was then added dropwise over 20 min, the solution becoming orange. The mixture was stirred at −78 °C for 2 h and was then hydrolyzed at this temperature by addition of sat. aq. NH_4Cl (30 mL). After warming to 20 °C the mixture was extracted three times with TBME (20 mL each). The collected organic layers were washed with water (60 mL), separated, and dried over $MgSO_4$. After solvent removal at reduced pressure the crude product was purified by column chromatography (300 × 30 mm, TBME/PE, 1:1) to afford: I: *rac-exo*-**28** (55 mg, 0.17 mmol, 29%), yellow-orange solid, m.p. 145 °C, and II: *rac-endo*-**28** (35 mg 0.11 mmol, 19%), yellow-orange solid, m.p. 142 °C.

Compound *rac-exo*-28: IR (ATR): $\tilde{\nu}$ = 3083 cm^{-1} (w), 2963 (m), 2929 (m), 1968 (s, CrCO), 1860 (s, CrCO), 1714 (s, C=O, lactone), 1601 (w), 1527 (m), 1270 (s), 1100 (s, C−O), 801 (m), 771 (m). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.06 (d, $^3J_{10/11-9}$ = 6.8 Hz, 3 H, 10-H or 11-H), 1.10 (d, $^3J_{10/11-9}$ = 6.8 Hz, 3 H, 10-H or 11-H), 2.06 (m, 1 H, 9-H), 2.59 (dd, $^2J_{endo\text{-}4,exo\text{-}4}$ = −16.0, $^3J_{endo\text{-}4,3}$ = 2.8 Hz, 1 H, *endo*-4-H), 2.93 (dd, $^3J_{exo\text{-}4,3}$ = 12.3 Hz, *exo*-4-H), 4.37 (m, $^3J_{3,endo\text{-}4}$ = 2.8 Hz, 1 H, 3-H), 5.13 (m, 1 H, arom. H), 5.33 (m, 1 H, arom. H), 5.61 (m, 1 H, arom. H), 6.13 (m, 1 H, arom. H). ^{13}C NMR (100.6 MHz, $CDCl_3$, APT/HMQC): δ = 18.1 (−, CH_3, C-10 or C-11), 18.2 (−, CH_3, C-10 or C-11), 29.6 (+, CH_2, C-4), 32.5 (−, CH, C-9), 83.4 (−, CH, C-3), 84.8 (+, C_q, C-4a), 88.2 (−, CH, arom. CH), 88.3 (−, CH, arom. CH), 94.9 (−, CH, arom. CH), 95.4 (−, CH, arom. CH), 110.5 (+, C_q, C-8a), 164.8 (+, C_q, C=O, C-1), 230.5 (+, C_q, CrCO). MS (70 eV, 60 °C): *m*/*z* (%) = 328 (5) [M^+ + 2], 327 (10) [M^+ + 1], 326 (18) [M^+], 270 (6) [M^+ − 2CO], 242 (100) [M^+ − 3CO], 224 (7), 196 (12), 142 (20), 119 (13), 91 (6) [$PhCH_2^+$], 72 (7). HRMS ($C_{15}H_{14}CrO_5$): calcd. 326.0246, found 326.0247.

Compound *rac-endo*-28: IR (ATR): $\tilde{\nu}$ = 3085 cm^{-1} (w), 2963 (m), 2928 (m), 2875 (m), 1965 (s, CrCO), 1903 (s, CrCO), 1866 (s, CrCO), 1713 (s, C=O, lactone), 1605 (w), 1525 (m), 1261 (s), 1109 (s, C−O), 1086 (s, C−O), 1003 (s, C−O), 799 (m), 766 (m). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.05 (d, $^3J_{10/11-9}$ = 6.9 Hz, 3 H, 10-H or 11-H), 1.08 (d, $^3J_{10/11-9}$ = 6.8 Hz, 3 H, 10-H or 11-H), 2.04 (m, 1 H, 9-H), 2.74 (dd, $^2J_{endo\text{-}4,exo\text{-}4}$ = −16.4, $^3J_{exo\text{-}4,3}$ = 2.4 Hz, 1 H, *exo*-4-H), 3.07 (dd, $^3J_{4endo,3}$ = 12.9 Hz, *endo*-4-H), 4.29 (m, $^3J_{3,exo\text{-}4}$ = 2.4 Hz, 1 H, 3-H), 5.15−5.20 (m, 2 H, arom. H), 5.63 (m, 1 H, arom. H), 6.33 (m, 1 H, arom. H). ^{13}C NMR (100.6 MHz, $CDCl_3$, APT/HMQC): δ = 18.1 (−, CH_3, C-10 or C-11), 18.3 (−, CH_3, C-10 or C-11), 29.3 (+, CH_2, C-4), 32.4 (−, CH, C-9), 83.2 (−, CH, C-3), 85.7 (+, C_q, C-4a), 89.3 (−, CH, arom. CH), 89.7 (−, CH, arom. CH), 92.8 (−, CH, arom. CH), 94.3 (−, CH, arom. CH), 111.1 (+, C_q, C-8a), 165.0 (+, C_q, C=O, C-1), 230.7 (+, C_q, CrCO). MS (70 eV, 100 °C): *m*/*z* (%) = 327 (19) [M^+ + 1], 326 (25) [M^+], 242 (100) [M^+ − 3CO], 210 (18), 186 (22), 155 (18), 117 (20). HRMS ($C_{15}H_{14}CrO_5$): calcd. 326.0246, found 326.0245.

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