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Synthesis of Enantiopure Tricarbonyl(indan-1,2-dione)chromium

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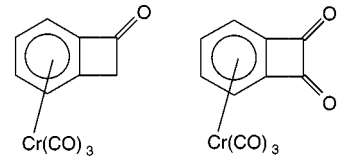
A multistep synthesis of the planar chiral tricarbonyl(η^6-indan-1,2-dione)chromium, based on acetal protection of the keto groups, is presented. Since common deacetalization procedures failed, an oxidative deprotection with triphenylcarbenium tetrafluoroborate was used. Tricarbonyl(η^6-indan-1,2-dione)chromium is regarded as a potential precursor for dianionic oxy-Cope rearrangements upon alkenyllithium diaddition. As an unexpected side product in the synthesis, an indan-1,2-dione complex with a triphenylmethyl substituent at C-3 was obtained. Attempts directed towards the formation of enantiomerically pure material include the first reported investigation into an enantioselective ketone reduction with two methoxy substituents present in the α position. Although enantiomeric excesses of up to 84.5 % were achieved, the chemical yields decreased with increasing *ee*. A classical resolution was therefore undertaken, giving access to the enantiomerically pure title compound (99.4 % *ee*). The absolute configuration was verified by an X-ray structure analysis of an intermediate. First experiments concerning the alkenyllithium addition showed that a single addition is possible while a second one does not occur, presumably due to enolate formation.

Introduction

The interest in the investigation of (arene)tricarbonylchromium complexes during the last 30 years is the result of their availability and stability on one hand and of the reactivity of the coordinated arene relative to the uncoordinated ligand on the other.[1–13] (Arene)tricarbonylchromium complexes have been the subjects of a number of review articles, the most recent of which give an excellent overview of the state of the art in this field.[14–21] We have contributed to this development in our investigations in the field of (arene)tricarbonylchromium complexes with functionalized anellated rings.[22–24] Key compounds in our research are complexes **1**–**4** of benzocyclobutenone,[22,25–31] benzocyclobutenedione,[27,29,30,32–37] 1,3-indandione,[38] and 1,2,3-indantrione.[38] In particular, chemistry relating to **1** and **2** has unveiled important oxy anion-accelerated reactions, such as anionic ring-opening reactions or dianionic oxy-Cope rearrangements, which take place under particularly mild reaction conditions. Here we wish to report the synthesis of the missing link in the series, tricarbonyl(indan-1,2-dione)chromium(0) (**5**), which shares with **1** the property of planar chirality. We include attempts directed towards an asymmetric synthesis of **5**, as well as a chiral resolution affording enantiomerically pure **5**. The synthesis of **5** is of interest for investigation of the possibility of dianionic oxy-Cope rearrangements upon diaddition of alkenyllithium reagents. This should produce benzanellated cyclononanediones, which would presumably be prone to transannular aldol reactions resulting in tricyclic systems consisting of anellated six- and five-membered rings. The option of starting from enantiomerically pure **5** would allow such tricycles to be prepared in enantiomerically pure form. Tricarbonylchromium complexes of indan-1-one[39] and of indan-2-one[40] were previously prepared by Jackson and by Gibson, respectively.



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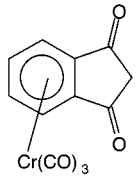

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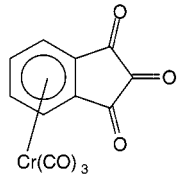

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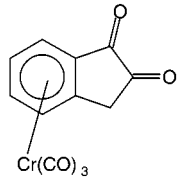

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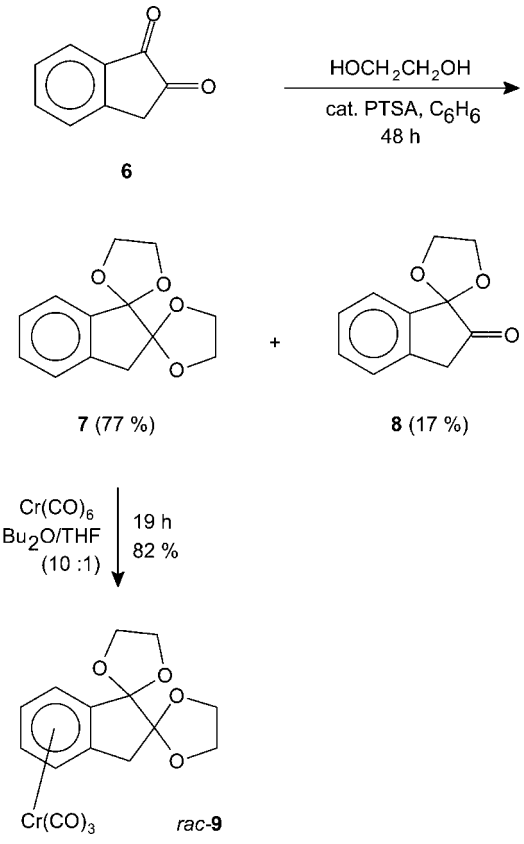
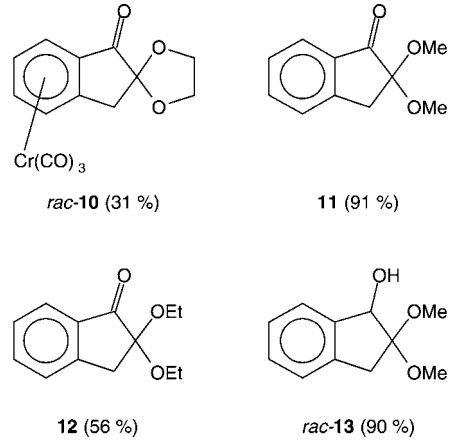
Results and Discussion

None of the complexes **1**–**5** is obtained in acceptable yield by direct complexation of the ligand with common complexation reagents. Complex **4** has been prepared, together with its hydrate tricarbonyl(ninhydrin)chromium(0), by oxidation of **3** with dimethyldioxirane, whereas complexes **1**–**3** have been obtained by protection of the keto groups as acetals, followed by complexation and subsequent acetal hydrolysis, and this route was therefore also envisaged for the synthesis of **5**. Indan-1,2-dione (**6**) was treated with ethane-1,2-diol in the presence of a catalytic amount of *p*-toluenesulfonic acid (PTSA) for 48 h, resulting in a 77% yield of the desired diacetal **7** along with monoacetal **8** (17%). Subsequent treatment of **7** with $Cr(CO)_6$ in Bu_2O/THF (10:1) afforded chromium complex *rac*-**9** in 82% yield as a bright yellow, air-sensitive material.



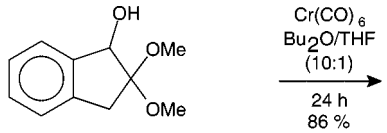
Next, *rac*-**9** was treated with acid in order to hydrolyze the acetal functions and to obtain *rac*-**5**. Unlike in the synthesis of **2**, however, use of 6 N hydrochloric or sulfuric acid did not effect the desired reaction. In order to circumvent solubility problems associated with water, dilute hydrochloric or sulfuric acid was added to solutions of *rac*-**9** in acetone or in THF. TLC monitoring indicated no reaction under these conditions; only addition of concentrated hydrochloric acid to a THF solution of *rac*-**9** caused an immediate reaction, with TLC indicating the formation of a number of colorless decomplexation products after only 1 min. The only chromium complex, isolated by column chromatography as a red oil in 10% yield, was a 2-hydroxyindan-1-one complex, which was not fully characterized. We suggest that the difference in reactivity of the diacetal of **2** relative to *rac*-**9** is due to the potential for enol formation in the hydrolysis products from *rac*-**9**, which is not the case for **2**. In order to avoid acidic reaction conditions we made recourse to an oxidative deacetalization with trityl tetrafluoroborate, introduced by Barton in 1971, which had already proven successful in the oxidative deacetalization of 1,2-[bis(ethylenedioxy)benzocyclobutene]tricarbonylchromium(0) in our group.[41] In the course of this reaction a hydride abstraction causes opening of the cyclic acetal with formation of an oxenium ion, which is finally hydrolyzed to give the deprotected ketone.[42,43] The reaction was only partly successful, however, resulting in the formation of a complex mixture of products, from which monoacetal *rac*-**10** was isolated in 31% yield and characterized spectroscopically. The formation of *rac*-**10** indicates that the oxidation with trityl tetrafluoroborate is compatible with the low-valent tricarbonylchromium group.



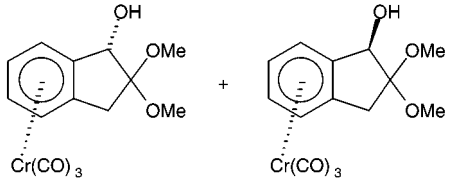
To facilitate the acetal cleavage, a new route using noncyclic acetals was envisaged. Indan-1,2-dione was treated with 2,2-dimethoxypropane or with triethyl orthoformate, in the presence of a catalytic amount of PTSA and in the corresponding alcohol as solvent to afford noncyclic monoacetals **11** and **12**, respectively, in 91% and 56% yield. Subsequent reduction of **11** with sodium borohydride gave the alcohol *rac*-**13** in 90% yield.

The complexation of *rac*-**13** with hexacarbonylchromium in dibutyl ether/THF (10:1) afforded a diastereomeric mixture of complexes *rac*-**14** and *rac*-**15** (72:28) in 86% overall yield. The assignment of the diastereomers was achieved on the basis of the ^{1}H NMR spectra. The chemical shifts of the benzylic protons next to the hydroxy substituent are δ(*rac*-**14**) = 4.98 ppm and δ(*rac*-**15**) = 4.65 ppm. The assignment for *rac*-**14** compares well with the values observed for the benzylic protons of compounds **16** (δ = 4.95 ppm), **17** (δ = 4.84 ppm), and *rac*-**18** (δ = 4.88 ppm).[38]

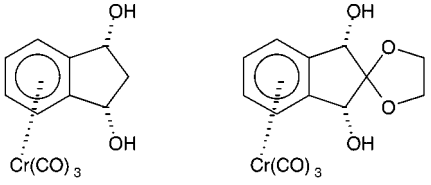
Complexation from the sterically more shielded *endo* face of the ligand system with predominant formation of *rac*-**14** demonstrates an effect first reported by Schmalz with the complexation of tetralol derivatives, which has been explained in terms of precomplexation of chromium to a lone electron pair of the hydroxy substituent.[44] In order to en-



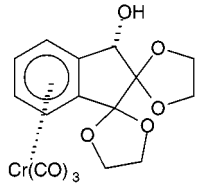
rac-**13**



rac-**14** 72:28 *rac*-**15**

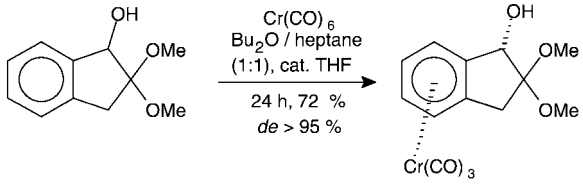


16 **17**



rac-**18**

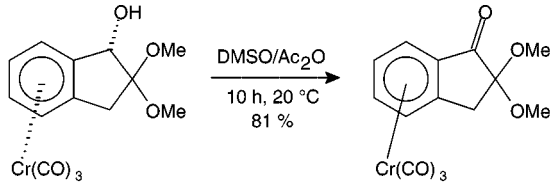
hance the diastereomeric excess, Schmalz used dibutyl ether/heptane/THF (30:30:1), which is less prone to occupy coordination sites at chromium and thus facilitates the precomplexation process. When we used a 1:1 mixture of dibutyl ether and heptane with a catalytic amount of THF as solvent, we were delighted to obtain *rac*-**14** as the only isolated diastereomer, with only traces of *rac*-**15** being detectable by TLC. In contrast to the tetralol ligands used by Schmalz, *rac*-**13** bears two methoxy substituents situated next to the hydroxy group, one at each face of the ligand. We regard it as remarkable that the precomplexation obviously takes place only at the benzylic hydroxy group and not at the methoxy substituents.



rac-**13** *rac*-**14**

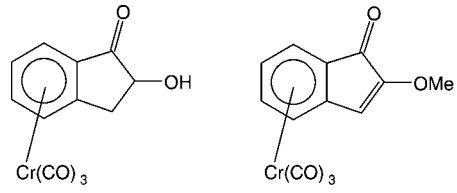
The final confirmation of the relative configuration of *rac*-**14** was achieved when we succeeded in obtaining crystals of *rac*-**14** suitable for X-ray structure analysis (see Experimental Section) from a diethyl ether/petroleum ether mixture.

Presumably for steric reasons, *rac*-**14** adopts a conformation with no CO ligand below the anellated five-membered ring. The arene C,C bond lengths alternate slightly as a result of the *trans* effect of the opposite CO ligands. As the next step in the synthesis of *rac*-**5**, oxidation of alcohol *rac*-**14** to the corresponding ketone was envisaged. To achieve this, an oxidation method compatible with the chromium in a formal oxidation state of zero was needed. While oxidation with DMSO/SO_3/pyridine[45] afforded the desired ketone in only 15% yield, together with 71% of starting material, a Swern oxidation with acetic anhydride/DMSO[46] was more successful and gave ketone *rac*-**19** in 81% yield. Remarkably, the acidic workup conditions did not cause acetal hydrolysis. This observation contrasts with the fact that the uncoordinated ligand **11** undergoes acetal hydrolysis in the presence of a catalytic amount of sulfuric acid in boiling ethanol.[47]



rac-**14** *rac*-**19**

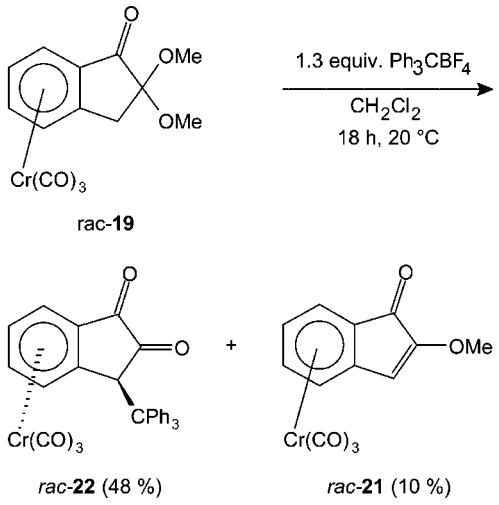
The deacetalization of *rac*-**19** turned out to be problematic. Treatment of *rac*-**19** with concentrated hydrochloric acid unexpectedly gave *rac*-**20** in 53% yield as a single diastereomer. With a number of other Brønsted or Lewis acids, either no reaction took place or decomplexation and in some cases decomposition occurred. Treatment with boron trifluoride–diethyl ether caused elimination of methanol resulting in a 77% yield of *rac*-**21**. Neither *rac*-**21** nor its ligand had been known previously.



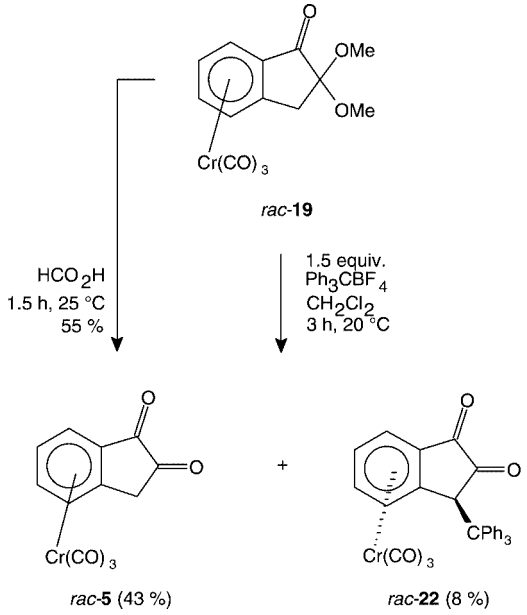
rac-**20** *rac*-**21**

The elimination of methanol from a dimethyl acetal on treatment with boron trifluoride–diethyl ether has so far been observed only once.[48] The only comparable reactions are methanol elimination from 2,2-dimethoxycyclopentanone on treatment with $FeCl_3/SiO_2$, affording 2-methoxy-2-cyclopentenone in 71% yield,[49] and an elimination caused by DMSO at elevated temperature.[50]

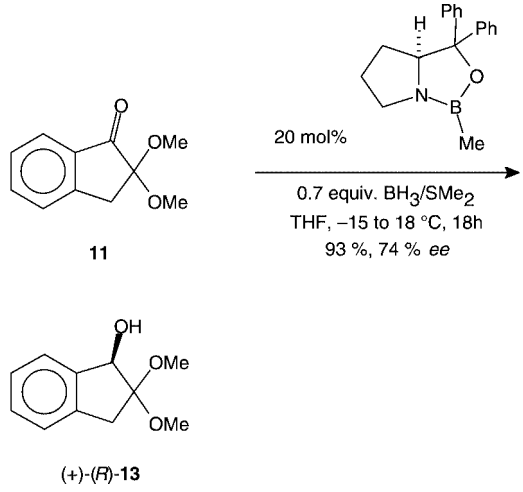
The oxidative deacetalization mentioned above was tried next.[42,43] When *rac*-**19** was treated with 1.3 equivalents of trityl tetrafluoroborate for 18 h, the substituted derivative *rac*-**22** of the target complex was obtained in 48% yield along with *rac*-**21**, which was formed in 10% yield. In accord with all analytical data we assign the *exo* configuration to *rac*-**22** for obvious steric reasons.



The formation of *rac*-**22** cannot be explained easily. The reaction mechanism does not necessarily have to be the same as with the cyclic acetals investigated by Barton.[42,43] Possibly *rac*-**21** is an intermediate, undergoing some type of electrophilic addition with formation of *rac*-**22**. Use of a larger excess of trityl tetrafluoroborate (1.5 equivalents) and a shorter reaction time (3 h) gave *rac*-**5** in 43% isolated yield along with *rac*-**22** (8%). Further investigation of the acetal hydrolysis finally showed that the dione *rac*-**5** could be obtained in 55% yield as a red-brown solid by treatment of *rac*-**19** with formic acid. The polarity of *rac*-**5** caused some difficulties in the chromatographic purification, resulting in a reduced yield.



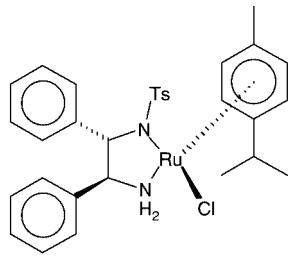
Although the synthesis of *rac*-**5** was finally successful, it appears somewhat redundant as it involves the reduction of the keto group in **11** and its later reoxidation. On the other hand, the high diastereoselectivity of the complexation of *rac*-**13** indicates the availability of enantiomerically pure **5** if **11** were to be enantioselectively reduced. This strategy has been pursued by Schmalz et al., who used the so-called CBS reduction[51,52] in the synthesis of enantiomerically highly enriched tetralol complexes.[44] The case of **11** is different, however, because the compound bears an acetal moiety next to the keto function to be enantioselectively reduced. The methoxy groups would be likely to cause a reduction in enantiomeric excess, because their lone electron pairs might coordinate a chiral reduction catalyst at either one of the enantiotopic faces of the keto group. In spite of this concern we attempted the CBS reduction of **11**. After some optimization we found that the reaction works with the borane/dimethyl sulfide complex as the reducing reagent to give a 93% yield of (+)-(*R*)-**13** with 74% *ee*. This value compares to a 90–94% yield and 97.8% *ee* for the CBS reduction of unsubstituted indan-1-one[53] and nicely reflects the influence of the 2,2-dimethoxy substitution. The absolute configuration was assigned on the basis of the accepted mechanism of the CBS reduction[54] and was later confirmed by a structural analysis of the corresponding chromium complex (vide infra).



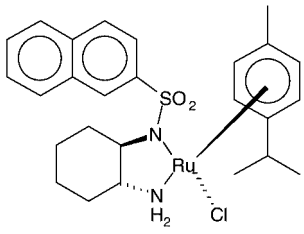
An attractive alternative to the CBS reduction is the asymmetric transfer hydrogenation of ketones catalyzed by enantiomerically pure chiral ruthenium or rhodium complexes.[55–58] So far there are no reports of enantioselective reductions of α-keto acetals catalyzed by these complexes. Ruthenium complex (*S*,*S*)-**23** has been shown by Noyori to catalyze the reduction of indan-1-one in >99% yield and 99% *ee*.[58] When **11** was treated with a 5:2 mixture of formic acid and triethylamine as the hydrogen source in the presence of 3 mol% of (*S*,*S*)-**23**, indanol acetal (–)-(*S*)-**13** was obtained in 82% yield and 75% *ee* as determined by ^{1}H NMR with Eu(hfc)$_3$ as the shift reagent. A reduction in the amount of catalyst to 0.85 mol% resulted in a chemical yield of only 34% and an improved *ee* of 82%.

In order to improve the enantiomeric excess further we decided to use the similar catalyst (*R*,*R*)-**24**, introduced by Knochel.[59] Here, the chemical yield decreased to only 27% of (+)-(*R*)-**13**, but with 84.5% *ee*.

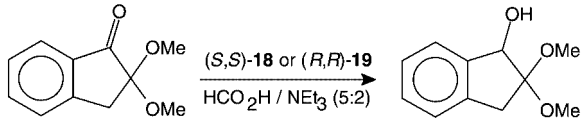
The results show that the methoxy substituents next to the keto group affect the enantioselective reduction of **11** in such a way that either the chemical yield is good with moderate enantiomeric excess or the enantiomeric excess is com-



(*S*,*S*)-**23**

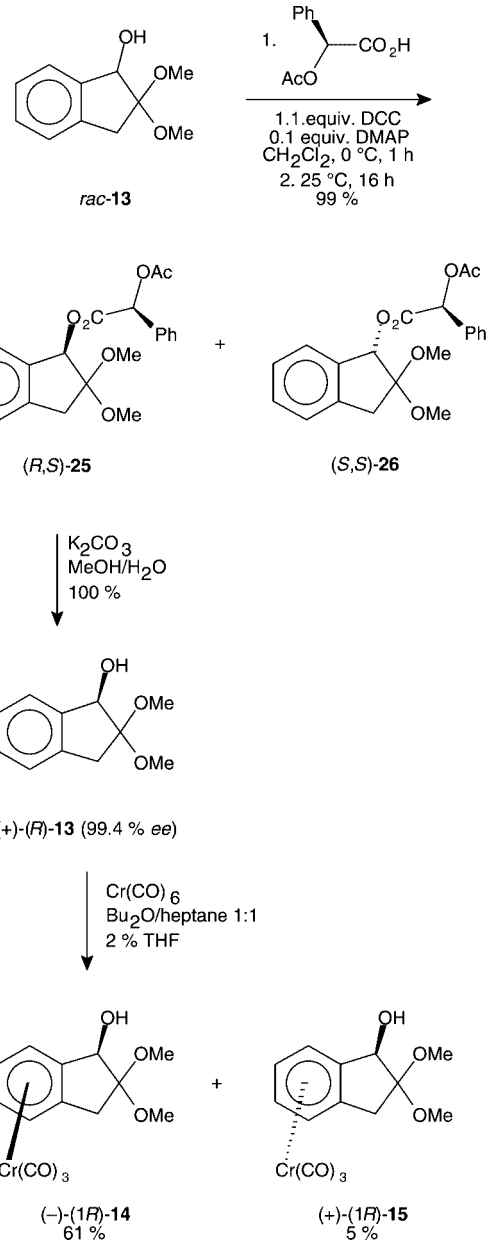


(*R*,*R*)-**24**



11 **13**

3.00 mol % of (*S*,*S*)-**23**: (–)-(*S*)-**13**, 82 % (75 % *ee*)
0.85 mol % of (*S*,*S*)-**23**: (–)-(*S*)-**13**, 34 % (82 % *ee*)
3.00 mol % of (*R*,*R*)-**24**: (+)-(*R*)-**13**, 27 % (84.5 % *ee*)



paratively high with poor chemical yield. For the first time, however, it has been shown that it is possible to achieve reasonable enantiomeric excesses in an enantioselective reduction of an α-keto acetal. In order to obtain reasonable amounts of enantiomerically pure material we therefore made recourse to a classical racemic resolution of *rac*-**13** by use of (*S*)-2-acetoxyphenylacetic acid as the chiral auxiliary. Esterification in the presence of 1.1 equivalents of dicyclohexylcarbodiimide (DCC) and 10 mol% of 4-(dimethylamino)pyridine (DMAP) afforded an almost quantitative yield of diastereomeric esters (*R*,*S*)-**25** and (*S*,*S*)-**26**. Separation by column chromatography was variable, giving 98 to 99.4% de (GC).

Subsequent quantitative hydrolysis and complexation of (+)-(*R*)-**13** with hexacarbonylchromium in a 1:1 mixture of dibutyl ether and heptane with 2% of added THF resulted in the formation of a diastereomeric mixture of (–)-(1*R*)-**14** (61%) and (+)-(1*R*)-**15** (5%), which were separated by column chromatography. Complex (–)-*endo*-(1*R*)-**14** was crystallized from *tert*-butyl methyl ether/petroleum ether to afford crystals suitable for an X-ray crystal structure analysis, which finally confirmed the absolute configuration (Figure 1) by refinement of the Flack *x* parameter.[60] The structure shows that the ligand adopts an envelope conformation with the acetal carbon atom bent towards the tricarbonylchromium group.

Swern oxidation of (–)-(1*R*)-**14** with dimethyl sulfoxide/acetic anhydride afforded the planar chiral indan-1,2-dione monoacetal complex (–)-p*R*-**19** in 76% yield, and oxidative deacetalization with triphenylcarbenium tetrafluoroborate finally gave (–)-p*R*-**5** in 36% yield. Note that the deacetalization with formic acid, which was carried out with racemic material, gives a 55% yield (vide supra). Assuming no reasonable racemization pathway from (+)-(*R*)-**13** we regard the *ee* of (–)-p*R*-**5** as 99.4%.

One reason for our interest in the indan-1,2-dione chromium complex was the potential to perform a dianionic oxy-Cope rearrangement upon alkenyllithium diaddition. This type of reaction starting from (benzocyclobutenedione)tricarbonylchromium has been investigated in depth by our group. The reaction sequence proved to be highly diastereoselective and makes highly substituted polycyclic systems available in a very efficient way.[22,23,33–37,61–63] It was also shown that the vinyllithium diaddition followed by a dianionic oxy-Cope rearrangement works with uncoordi-

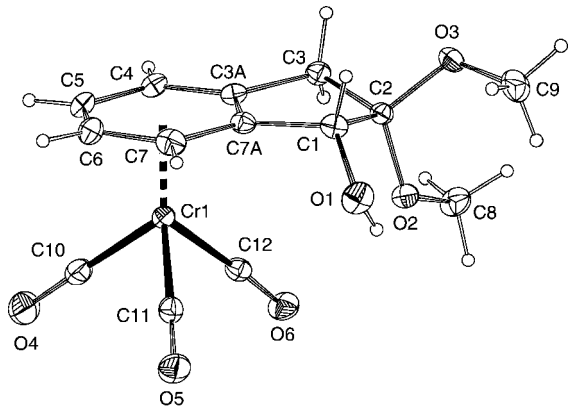
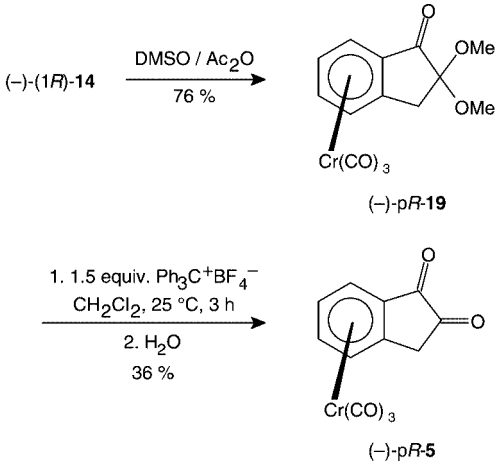
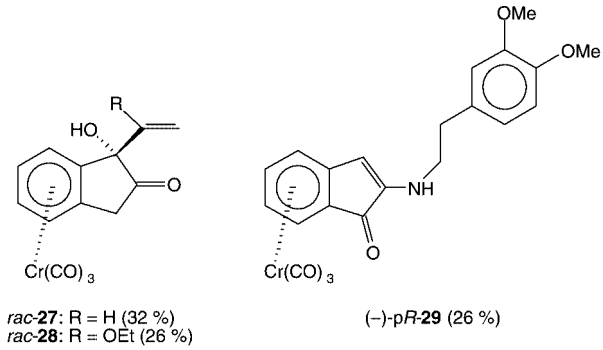


Figure 1. Structure of (–)-(1*R*)-**14** in the crystal. Selected bond lengths [pm]: C1–C2 1.555(3), C1–C7A 149.8(3), C1–O1 140.4(3), C2–C3 152.5(3), C2–O2 141.1(3), C2–O3 139.9(3), C3–C3A 149.6(3), C3A–C4 139.7(3), C3A–C7A 140.7(4), C4–C5 140.1(4), C5–C6 140.5(5), C6–C7 139.9(4), C7–C7A 141.5(3), Cr1–C3A 225.6(2), Cr1–C4 224.2(2), Cr1–C5 219.1(2), Cr1–C6 220.1(2), Cr1–C7 220.2(2), Cr1–C7A 223.6(2).



nated indan-1,2-dione, albeit in only moderate yield.[64] We envisaged the possibility that the electron withdrawal from the tricarbonylchromium group in **5** might help to improve the allkenyllithium diaddition yield and thereby allow the rearrangement to take place with better overall yield. However, treatment of *rac*-**5** with an excess of vinyllithium or 1-ethoxyvinyllithium resulted in the formation of the monoadducts *rac*-**27** and *rac*-**28** in moderate yields. This result contrasts with that obtained with the uncoordinated indan-1,2-dione and might be due to enolate formation as a result of the enhanced acidity of the benzylic protons in *rac*-**5**. This effect also became evident in the attempted synthesis of a spirobenzylisoquinoline[65] through a Pictet–Spengler reaction between (–)-p*R*-**5** and 2-(3,4-dimethoxyphenyl)ethylamine, which resulted in the formation of the enamine (–)-(p*R*)-**29** in 26% yield.

In conclusion, we report a synthesis of the title compound tricarbonyl(indan-1,2-dione)chromium (**5**) both in racemic and in enantiomerically pure form. A striking feature of the synthesis is the diastereoselective complexation of indanol **13** with the acetal methoxy substituents next to



rac-**27**: R = H (32 %)
rac-**28**: R = OEt (26 %)

(–)-p*R*-**29** (26 %)

the hydroxy group. An enantioselective reduction of an α-keto acetal has been achieved for the first time, giving up to 84.5% *ee*, although the chemical yields were unsatisfactory and a classical racemic resolution was therefore performed. Attempts directed towards diaddition of alkenyllithium reagents were unsuccessful, presumably due to enolate formation. In order to circumvent this difficulty we investigate nonenolizable indan-1,2-dione complexes.

Experimental Section

General: See ref.[36] Melting points were determined with a Büchi apparatus (Dr. Tottoli) without any correction. *tert*-Butyl methyl ether (TBME), diethyl ether (DEE), petroleum ether (PE), and tetrahydrofuran (THF) were distilled from sodium–potassium alloy and benzophenone. Reagents were purchased and used without further purification. In the ^{13}C NMR spectra, according to APT and DEPT measurements, "+" indicates signals of methylene or quaternary carbon atoms, whereas "–" indicates signals referring to methyl or methyne carbon atoms.

1,2-Bis(ethylenedioxy)indan (7) and 1-(Ethylenedioxy)indan-2-one (8): Indan-1,2-dione[66] (3280 mg, 22.5 mmol), ethane-1,2-diol (4180 mg, 3.75 mL, 67.4 mmol), and *p*-toluenesulfonic acid (20 mg) in benzene (125 mL) were heated at reflux with azeotropic water removal for 48 h. After solvent removal at reduced pressure the residue was purified by column chromatography (SiO_2, DEE/PE, 1:2, 20 × 3 cm). Fraction I: 750 mg (3.95 mmol, 17%) of 1-(ethylenedioxy)indan-2-one (**8**), colorless solid (m. p. 110 °C). Fraction II: 4050 mg (17.3 mmol, 77%) of 1,2-bis(ethylenedioxy)indane (**7**), colorless solid (m. p. 123 °C).

Compound 7: ^1H NMR (400 MHz, $CDCl_3$): δ = 3.12 (s, 2 H, 3-H), 3.63 + 3.73 [m, 2 × 2 H, 10(11)-H], 4.04–4.16 [m, 4 H, 8(9)-H], 7.25–7.44 (m, 4 H, arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.9 (+, C-3), 61.1 [+, C-8(9) or C-10(11)], 61.6 [+, C-8(9) or C-10(11)], 122.9 (–, C-5), 125.7 (–, C-6), 127.3 (–, C-4), 129.9 (–, C-7), 138.4 (+, C-3a), 139.6 (+, C-7a) ppm. IR (KBr): $\tilde{\nu}$ = 3087 (w), 2972 (w), 2944 (w), 2916 (w), 2876 (w), 1460 (w), 1300 (m), 1256 (w), 1140 (m), 1092 (s, acetal-C–O), 1052 (m), 1028 (m), 972 (s), 904 (w), 776 (m), 684 (w), 660 (w) cm^{-1}. MS (70 eV, 25 °C): *m*/*z* (%) = 236 (6) $[M + 2]^+$, 235 (40) $[M + 1]^+$, 234 (66) $[M]^+$, 206 (39), 189 (6), 174 (50), 162 (67), 146 (27), 135 (50), 118 (100) $[C_8H_6O]^+$, 105 (60), 90 (64), 77 (33). HRMS, $C_{13}H_{14}O_4$: calcd: 234.0892; found 234.0893. $C_{13}H_{14}O_4$ (234.09): calcd: C 66.66, H 6.02; found C 66.68, H 5.99.

Compound 8: ^1H NMR (400 MHz, $CDCl_3$): δ = 3.54 (s, 2 H, 3-H), 4.26–4.49 (m, 4 H, acetal-H), 7.30–7.56 (m, 4 H, arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.9 (CH_2, C-3), 66.0 [CH_2, C-8(9)], 104.2 (C_q, C-1), 125.3 (CH, C-4 or C-5 or C-6 or C-7), 125.5 (CH, C-4 or C-5 or C-6 or C-7), 128.2 (CH, C-4 or C-5 or C-6 or C-7),

131.2 (CH, C-4 or C-5 or C-6 or C-7), 136.8 (C_q, C-3a or C-7a), 137.8 (C_q, C-3a or C-7a), 212.0 (C_q, C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3063 (w), 2992 (w), 2952 (w), 2900 (w), 1756 (s, ketone), 1680 (w), 1612 (w), 1464 (m), 1396 (m), 1300 (m), 1232 (w), 1152 (w), 1072 (s), 1020 (m), 948 (m), 916 (m), 764 (s), 648 (w), 596 (w) cm^{-1}. MS (70 eV, 25 °C): *m*/*z* (%) = 190 (1) $[M]^+$, 162 (84), 135 (16), 105 (100) $[C_7H_5O]^+$, 90 (20), 77 (10). HRMS, $C_{11}H_{10}O_3$: calcd: 190.0630; found 190.0634. $C_{11}H_{10}O_3$ (190.06): calcd: C 69.46, H 5.30; found C 69.37, H 5.27.

***rac*-Tricarbonyl[η⁶-1,2-bis(ethylenedioxy)indane]chromium(0) (*rac*-9):** Compound **7** (500 mg, 2.1 mmol) and $Cr(CO)_6$ (705 mg, 3.2 mmol) in dibutyl ether (70 mL) and THF (7 mL) were heated at reflux for 19 h. After the mixture had cooled to 25 °C, the THF was removed at reduced pressure, and a yellow precipitate was obtained. After decanting of the almost colorless solvent and removal of residual solvent at 0.01 mbar, *rac*-**9** (640 mg, 1.7 mmol, 82%) was obtained as a yellow solid (m. p. 195 °C, dec.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.00 (d, $^2J_{exo\text{-}3,endo\text{-}3}$ = –16.1 Hz, 1 H, *exo*-3-H or *endo*-3-H), 3.11 (d, $^2J_{exo\text{-}3,endo\text{-}3}$ = –16.1 Hz, 1 H, *exo*-3-H or *endo*-3-H), 3.58–3.70 (m, 2 H, acetal-H), 3.80–3.88 (m, 1 H, acetal-H), 3.95–4.12 (m, 5 H, acetal-H), 5.27 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 5.8 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 5.8 Hz, 1 H, 5-H or 6-H), 5.58 (d, $^3J_{4,5}$ = 5.8 Hz or $^3J_{6,7}$ = 5.8 Hz, 1 H, 4-H or 7-H), 5.84 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 5.8 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 5.8 Hz, 1 H, 5-H or 6-H), 6.03 (d, $^3J_{4,5}$ = 5.8 Hz or $^3J_{6,7}$ = 5.8 Hz, 1 H, 4-H or 7-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 37.9 (+, C-3), 62.5 (+, C-8 or C-9 or C-10 or C-11), 63.0 (+, C-8 or C-9 or C-10 or C-11), 63.2 (+, C-8 or C-9 or C-10 or C-11), 63.4 (+, C-8 or C-9 or C-10 or C-11), 88.6 (–, C-4 or C-5), 89.0 (–, C-4 or C-5), 94.8 (–, C-6 or C-7), 98.0 (+, C-2), 99.1 (–, C-6 or C-7), 101.0 (+, C-1), 111.0 (+, C-3a), 116.9 (+, C-7a), 235.1 (+, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3076 (w), 2976 (w), 2940 (w), 2876 (w), 1964 (s, CO), 1868 (s, CO), 1452 (w), 1424 (w), 1300 (w), 1264 (w), 1232 (w), 1144 (m), 1096 (s), 1052 (w), 1028 (w), 972 (m), 668 (m), 632 (m), 536 (w) cm^{-1}. MS (70 eV, 60 °C): *m*/*z* (%) = 372 (2) $[M + 2]^+$, 371 (4) $[M + 1]^+$, 370 (11) $[M]^+$, 313 (15) $[M - 2\times CO]^+$, 286 (26) $[M - 3\times CO]^+$, 256 (24), 226 (100) $[(C_{11}H_{10}O_2)Cr]^+$, 174 (23), 162 (14), 118 (60), 90 (25). HRMS, $C_{16}H_{14}CrO_7$: calcd: 370.01446; found 370.01226. $C_{16}H_{14}CrO_7$ (370.01): calcd: C 51.90, H 3.81; found C 51.76, H 3.85.

***rac*-Tricarbonyl[η⁶-2-(ethylenedioxy)indan-1-one]chromium(0) (*rac*-10):** Compound *rac*-**9** (300 mg, 0.8 mmol) and triphenylcarbenium tetrafluoroborate (670 mg, 2.0 mmol) were stirred in anhydrous dichloromethane (10 mL) for 18 h at 20 °C, the color changing from yellow to deep red. After solvent removal at reduced pressure the residual dark oil was purified by column chromatography (SiO_2, DEE/PE, 1:1, 25 × 3 cm). Compound *rac*-**10** (80 mg, 0.24 mmol, 31%) was obtained as an orange solid (m. p. 128 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.22 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –17.2 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.40 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –17.2 Hz, 1 H, *endo*-3-H or *exo*-3-H), 4.04–4.50 (m, 4 H, acetal-H), 5.15–5.98 (ABCD line system, 4 H, arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.4 (+, C-3), 64.6 (+, C-8 or C-9), 64.8 (+, C-8 or C-9), 85.1 (–, C-4 or C-5 or C-6), 87.2 (–, C-4 or C-5 or C-6), 87.3 (–, C-4 or C-5 or C-6), 89.7 (+, C-2), 93.9 (–, C-7), 104.4 (+, C-3a), 116.4 (+, C-7a), 197.9 (+, C-1), 228.2 (+, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3075 (w), 2904 (w), 1992 (s, CO), 1928 (s, CO), 1720 (s, ketone), 1596 (w), 1524 (w), 1428 (w), 1316 (w), 1280 (w), 1228 (w), 1156 (m), 1136 (m), 1100 (m), 1016 (w), 648 (m), 612 (m) cm^{-1}. MS (70 eV, 100 °C): *m*/*z* (%) = 327 (3) $[M + 1]^+$, 326 (5) $[M]^+$, 325 (11), 270 (13) $[M - 2\times CO]^+$, 242 (13) $[M - 3\times CO]^+$, 214 (22), 198 (67) $[(C_9H_6O_2)Cr]^+$, 186 (5), 170 (7), 142 (13), 118 (5), 105 (6), 90 (5), 52 (100) $[^{52}Cr]^+$. HRMS, $C_{14}H_{10}CrO_6$: calcd: 325.9883; found 325.9888.

2,2-Dimethoxyindan-1-one (11): Indan-1,2-dione[66] (5.000 g, 34.2 mmol) and *p*-toluenesulfonic acid (0.030 g, 0.2 mmol) were dissolved in methanol (30 mL) and 2,2-dimethoxypropane (10 mL). The mixture was heated at reflux under argon for 23 h, the color becoming dark brown. After solvent removal at reduced pressure, the residual dark oil was purified by column chromatography (SiO_2, DEE/PE, 1:4, deactivation with triethylamine, 20 × 3 cm). After crystallization from DEE/PE (1:5), **11** (5.980 g, 31.1 mmol, 91%) was obtained as a colorless solid (m. p. 65 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26 (s, 2 H, 3-H), 3.48 [s, 6 H, 8(9)-H], 7.35–7.81 (ABCD line system, 4 H, arom.] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.1 (+, C-3), 51.3 [–, C-8(9)], 102.6 (+, C-2), 125.7 (–, C-4 or C-5 or C-6), 127.2 (–, C-4 or C-5 or C-6), 128.6 (–, C-4 or C-5 or C-6), 134.5 (+, C-3a), 136.4 (–, C-7), 150.0 (+, C-7a), 198.0 (+, C-1) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3080 (w), 3000 (w), 2964 (w), 2944 (m), 2836 (w), 1724 (s, ketone), 1608 (m), 1468 (m), 1304 (m), 1236 (m), 1140 (m), 1120 (m), 1048 (s), 852 (m) cm^{-1}. MS (70 eV, 20 °C): *m*/*z* (%) = 193 (3) $[M + 1]^+$, 192 (20) $[M]^+$, 161 (24), 149 (5), 132 (6), 118 (14), 104 (32), 91 (100). HRMS, $C_{11}H_{12}O_3$: calcd: 192.0786; found 192.0791. $C_{11}H_{12}O_3$ (192.21): calcd: C 68.73, H 6.29; found C 68.88, H 6.29.

2,2-Diethoxyindan-1-one (12): Indan-1,2-dione[66] (376 mg, 2.6 mmol) and *p*-toluenesulfonic acid (20 mg) were heated at reflux in anhydrous ethanol (5 mL) and triethyl orthoformate (5 mL) for 18 h, the mixture becoming dark. After hydrolysis with satd. aq. sodium hydrogen carbonate (20 mL), the mixture was extracted three times with DEE (each 3 mL). The collected organic layers were washed twice with water (5 mL) and dried with potassium carbonate. After filtration and solvent removal at reduced pressure the residual oil was crystallized from PE. Compound **12** (320 mg, 1.5 mmol, 56%) was obtained as a colorless solid (m. p. 62 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 [t, $^3J_{8,9}$ = 7.0 Hz, 6 H, 9(9′)-H], 3.30 (s, 2 H, 3-H), 3.75 [q, $^3J_{8,9}$ = 7.0 Hz, 4 H, 8(8′)-H], 7.35–7.82 (m, 4 H, arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 [–, C-9(9′)], 40.0 (+, C-3), 59.2 [+, C-8(8′)], 102.4 (+, C-2), 125.6 (–, C-4 or C-5 or C-6), 127.2 (–, C-4 or C-5 or C-6), 128.4 (–, C-4 or C-5 or C-6), 134.7 (+, C-7a), 136.3 (–, C-7), 150.2 (+, C-3a), 198.5 (+, C-1) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3061 (w), 2980 (m), 2928 (w), 2896 (w), 1724 (s, ketone), 1608 (m), 1468 (w), 1392 (w), 1304 (m), 1232 (w), 1192 (w), 1164 (m), 1132 (m), 1164 (w), 1132 (m), 1048 (s), 952 (m) cm^{-1}. MS (70 eV, 25 °C): *m*/*z* (%) = 221 (2) $[M + 1]^+$, 220 (11) $[M]^+$, 191 (2), 175 (6), 164 (5), 147 (29), 135 (21), 118 (20), 104 (48), 91 (100). HRMS, $C_{13}H_{16}O_3$: calcd: 220.1010; found 220.1010.

***rac*-2,2-Dimethoxyindan-1-ol (*rac*-13):** Sodium tetrahydridoborate (1.600 g, 42.2 mmol) was added to **11** (5.400 g, 28.1 mmol) in ethanol (75 mL). After the mixture had been stirred for 18 h at 20 °C, water 200 mL was added and the mixture was extracted ten times with DEE (50 mL). The collected organic layers were washed three times with water (100 mL each) and dried with potassium carbonate. After solvent removal at reduced pressure the remaining oil was crystallized from PE. Compound *rac*-**13** (4.920 g, 25.3 mmol, 90%) was obtained as a colorless solid (m. p. 56 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.92 (d, $^3J_{1,OH}$ = 8.8 Hz, 1 H, OH), 2.94 (d, $^2J_{3,3}$ = –16.5 Hz, 1 H, *cis*-3-H or *trans*-3-H), 3.26 (d, $^2J_{3,3}$ = –16.5 Hz, 1 H, *cis*-3-H or *trans*-3-H), 5.02 (d, $^3J_{1,OH}$ = 8.6 Hz, 1 H, 1-H), 7.14–7.43 (ABCD line system, 4 H, arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.3 (CH_2, C-3), 50.0 (CH_3, C-8 or C-9), 51.3 (CH_3, C-8 or C-9), 78.4 (CH, C-1), 109.8 (C_q, C-2), 125.3 (CH, C-4, C-5), 127.8 (CH, C-6 or C-7), 129.1 (CH, C-6 or C-7), 138.6 (C_q, C-7a), 143.5 (C_q, C-3a) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3552 (m, OH), 3076 (w), 3000 (m), 2964 (m), 2944 (m), 2840 (w), 1608 (w), 1460 (m), 1392 (m), 1324 (w), 1300 (w), 1268 (m), 1228 (m), 1184

(m), 1140 (s), 1120 (s), 1056 (s), 860 (w) cm^{-1}. MS (70 eV, 20 °C): *m*/*z* (%) = 196 (1) $[M + 2]^+$, 195 (8) $[M + 1]^+$, 194 (55) $[M]^+$, 163 (5), 147 (53), 131 (26), 119 (100), 103 (28), 91 (74), 75 (28). HRMS, $C_{11}H_{14}O_3$: calcd: 194.09429; found 194.09403. $C_{11}H_{14}O_3$ (194.09): calcd: C 68.02, H 7.26; found C 67.93, H 7.22.

(+)-(*R*)-2,2-Dimethoxyindan-1-ol [(+)-(*R*)-13] by Enantioselective Reduction: a) Borane–dimethyl sulfide (0.07 mL, 0.7 mmol) was added dropwise at –15 °C to **11** (200 mg, 1.1 mmol) and (*S*)-1-methyl-3,3-diphenyltetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*][1,3,2]oxazaborole (oxazaborolidine) (0.04 mL, 0.2 mmol) in THF (5 mL). The mixture was warmed to 25 °C over 14 h, and after addition of methanol (1 mL) the solvent was removed at reduced pressure. The crude product was purified by column chromatography (SiO_2, TBME/PE, 1:2, 20 × 3 cm) to provide (+)-(*R*)-**13** (1187 mg, 1.0 mmol, 93%, 74% *ee*) as a colorless oil. The *ee* was determined by NMR with europium(III)-tris[3-(heptafluoropropylhydroxymethylene)camphorate] as the chiral shift reagent and integration of the signals of the benzylic protons. b) Compound **11** (400 mg, 2.1 mmol), (*R*,*R*)-**24**[59] (39 mg, 0.063 mmol, 3 mol%), and potassium hydroxide (6 mg, 0.1 mmol, 5 mol%) were stirred in propan-2-ol (10 mL) at 25 °C for 60 h. After addition of water (100 mL) the mixture was extracted five times with TBME (each 50 mL). After drying over potassium carbonate, filtration, and solvent removal at reduced pressure, the crude product was purified by column chromatography (SiO_2, TBME/PE, 1:5, 20 × 3 cm) to provide (+)-(*R*)-**13** (110 mg, 0.6 mmol, 27%, 84.5% *ee*), $[\alpha]_D^{20}$ = +20.8 (*c* = 1, $CHCl_3$). The enantiomeric excess was determined by gas chromatography of the (*S*)-2-acetylphenylacetate.

(–)-(*S*)-2,2-Dimethoxyindan-1-ol [(–)-(*S*)-13] by Enantioselective Reduction: a) A suspension of **11** (400 mg, 2.1 mmol) and (*S*,*S*)-**23** (12 mg, 0.018 mmol, 0.85 mol%) in formic acid/triethylamine (5:2, 1 mL) was stirred at 25 °C for 60 h. After addition of water (100 mL) the mixture was extracted five times with TBME (each 50 mL). After drying over potassium carbonate, filtration, and solvent removal at reduced pressure the remaining crude product was purified by column chromatography (SiO_2, TBME/PE, 1:5, 20 × 3 cm) to provide (–)-(*S*)-**13** (139 mg, 0.71 mmol, 34%, 82% *ee*), $[\alpha]_D^{20}$ = –20.1 (*c* = 1, $CHCl_3$). The *ee* was determined by NMR with europium(III)-tris[3-(heptafluoropropylhydroxymethylene)camphorate] as the chiral shift reagent and integration of the signals of the benzylic protons. b) As a), with 3.0 mol% of (*S*,*S*)-**23**: Yield 82%, 75% *ee*.

***rac-endo*-Tricarbonyl(η⁶-2,2-dimethoxyindan-1-ol)chromium(0) (*rac*-14) and *rac-exo*-Tricarbonyl(η⁶-2,2-dimethoxyindan-1-ol)chromium(0) (*rac*-15):** a) Compound *rac*-**13** (4.200 g, 21.6 mmol) and hexacarbonylchromium (6.210 g, 28.1 mmol) in dibutyl ether (200 mL) and THF (20 mL) were heated at reflux for 24 h. The solvent was removed at reduced pressure, and the remaining green-yellow solid was purified by column chromatography (SiO_2, DEE/PE, 1:1, then DE, 30 × 5 cm). Fraction I: 4.340 g (13.2 mmol, 61%) of *rac*-**14**, bright yellow solid (m. p. 149 °C). Fraction II: 1.740 g (5.3 mmol, 25%) of *rac*-**15**, bright yellow solid (m. p. 128 °C). b) Compound *rac*-**13** (7.000 g, 27.7 mmol) and hexacarbonylchromium (6.700 g, 30.5 mmol) in dibutyl ether (120 mL), heptane (120 mL), and THF (4 mL) were heated at reflux for 24 h. After solvent removal at reduced pressure the remaining green-yellow solid was purified by column chromatography (SiO_2, TBME/PE, 1:4, then TBME, 25 × 5 cm) to provide *rac*-**14** (6.600 g, 19.9 mmol, 72%) as a bright yellow solid [m. p. 149 °C, de > 95% (NMR)].

Compound *rac*-14: ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.84 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –16.7 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.16 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –16.7 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.34 (d, *J* = 20.8 Hz, 1 H, OH), 3.35 (s, 3 H, 8-H or 9-H), 3.40 (s, 3 H, 8-H or 9-H), 4.98 (d, $^3J_{1,OH}$ = 10.3 Hz, 1 H, 1-H), 5.41 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 6.3 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 6.3 Hz, 1 H, 5-H or 6-H), 5.53 (d, $^3J_{4,5}$ = 6.6 Hz or $^3J_{6,7}$ = 6.6 Hz, 1 H, 4-H or 7-H), 5.65 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 6.4 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 6.4 Hz, 1 H, 5-H or 6-H), 5.75 (d, $^3J_{4,5}$ = 6.3 Hz or $^3J_{6,7}$ = 6.3 Hz, 1 H, 4-H or 7-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 37.1 (+, C-3), 49.7 (–, C-8 or C-9), 50.9 (–, C-8 or C-9), 77.7 (–, C-1), 89.1 (–, C-4 or C-5 or C-6 or C-7), 91.5 (–, C-4 or C-5 or C-6 or C-7), 96.1 (–, C-4 or C-5 or C-6 or C-7), 107.3 (+, C-2), 111.8 (+, C-7a), 116.0 (+, C-3a), 234.8 (+, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3500 (s, OH), 3085 (w), 2940 (w), 2908 (w), 2840 (w), 1956 (s, CO), 1856 (s, CO), 1448 (m), 1428 (w), 1388 (w), 1316 (w), 1260 (w), 1216 (m), 1180 (w), 1136 (m), 1052 (s), 1008 (w), 664 (s), 632 (m) cm^{-1}. MS (70 eV, 20 °C): *m*/*z* (%) = 331 (4) $[M + 1]^+$, 330 (14) $[M]^+$, 274 (19) $[M – 2\times CO]^+$, 246 (60) $[M – 3\times CO]^+$, 228 (7), 214 (54), 198 (13), 184 (65), 146 (100) $[C_9H_6O_2]^+$, 131 (28), 119 (16), 103 (67), 91 (23), 77 (19), 52 (67). HRMS, $C_{12}H_{14}CrO_4$ $[M – 2\times CO]^+$: calcd: 274.02929; found 274.02939. $C_{12}H_{14}CrO_4$ (330.05): calcd: C 50.92, H 4.27; found C 50.78, H 4.34.

Compound *rac*-15: ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.97 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –16.5 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.05 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –16.5 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.32 (s, 3 H, 8-H or 9-H), 3.35 (s, 3 H, 8-H or 9-H), 4.53 (d, $^3J_{1,OH}$ = 6.4 Hz, 1 H, OH), 4.65 (d, $^3J_{1,OH}$ = 7.2 Hz, 1 H, 1-H), 5.47 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 6.3 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 6.3 Hz, 1 H, 5-H or 6-H), 5.57 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 6.3 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 6.3 Hz, 1 H, 5-H or 6-H), 5.67 (d, $^3J_{4,5}$ = 6.4 Hz or $^3J_{6,7}$ = 6.4 Hz, 1 H, 4-H or 7-H), 5.84 (d, $^3J_{4,5}$ = 6.4 Hz or $^3J_{6,7}$ = 6.4 Hz, 1 H, 4-H or 7-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 37.4 (+, C-3), 50.0 (–, C-8 or C-9), 50.7 (–, C-8 or C-9), 77.7 (–, C-1), 90.8 (–, C-4 or C-5 or C-6 or C-7), 92.8 (–, C-4 or C-5 or C-6 or C-7), 93.3 (–, C-4 or C-5 or C-6 or C-7), 94.8 (–, C-4 or C-5 or C-6 or C-7), 108.9 (+, C-2), 112.6 (+, C-7a), 113.1 (+, C-3a), 234.5 (+, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3520 (m, OH), 3085 (w), 2976 (w), 2948 (w), 1968 (s, CO), 1876 (s, CO), 1452 (w), 1436 (w), 1356 (w), 1256 (w), 1212 (w), 1120 (m), 1076 (w), 1048 (m), 668 (m), 632 (m) cm^{-1}. MS (70 eV, 80 °C): *m*/*z* (%) = 332 (3) $[M + 2]^+$, 331 (9) $[M + 1]^+$, 330 (32) $[M]^+$, 274 (10) $[M – 2\times CO]^+$, 246 (62) $[M – 3\times CO]^+$, 228 (9), 214 (65), 198 (18), 184 (66), 171 (7), 147 (100) $[C_9H_7O_2]^+$, 131 (26), 119 (13), 103 (44), 91 (21), 77 (14), 52 (74). HRMS, $C_{12}H_{14}CrO_4$ $[M – 2\times CO]^+$: calcd.: 274.02972; found 274.02985. $C_{12}H_{14}CrO_4$ (330.05): calcd: C 50.92, H 4.27; found C 50.94, H 4.17.

Crystal Structure Analysis of *rac*-14:[67] $C_{14}H_{14}CrO_6$, molecular weight 330.25, crystal system monoclinic, space group P 21/n, *a* = 7.234(1), *b* = 18.707(3), *c* = 10.512(2) Å, α = 90°, β = 90.01(2)°, γ = 90.11(2)°, *V* = 1422.6(4) Å^3, *Z* = 4, $d_{calcd.}$ = 1.542 Mg m^{-3}, *F*(000) = 680, μ = 8.28 mm^{-1}, crystal size 1.37 × 0.26 × 0.15 mm, Stoe IPDS area detector diffractometer, *T* = 300(2) K, Mo-$K\alpha$ = 0.71073 Å, θ_{min} = 2.18, θ_{max} = 24.15°, $-8 \le h \le 8$, $-21 \le k \le 21$, $-12 \le l \le 12$, no absorption correction, no extinction correction, 10108 collected, 2182 unique reflections, 1638 observed reflections [$I > 2\sigma(I)$], 194 refined parameters, [*R*(int) = 0.0363], refinement program: SHELXL-93, refinement by full-matrix least-squares method (F_2), hydroxy H was found and refined, *R* indices: [$I > 2\sigma(I)$] R_1 = 0.0290, wR_2 = 0.0660, largest diff. peak and hole 0.222 and –0.159 eÅ^3

***rac*-Tricarbonyl(η⁶-2,2-dimethoxyindan-1-one)chromium(0) (*rac*-19):** Compound *rac*-**14** (1620 mg, 4.90 mmol) was stirred for 10 h at 25 °C in anhydrous DMSO (9.6 mL) and acetic acid anhydride (7.2 mL). After hydrolysis with water (200 mL) the mixture was extracted three times with diethyl ether (each 40 mL). The collected

organic layers were washed five times with satd. aq. sodium hydrogen carbonate and satd. aq. sodium chloride (each 30 mL). After drying over magnesium sulfate, filtration, and solvent removal, the crude product was purified by column chromatography (SiO_2, DEE/PE, 1:1, 20×3 cm) to provide *rac*-**19** (1.300 g, 4.0 mmol, 81%) as a red solid (m. p. 119 °C). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.19 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –16.7 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.33 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –16.7 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.39 (s, 3 H, 8-H or 9-H), 3.39 (s, 3 H, 8-H or 9-H), 5.59–6.13 (ABCD-system, 4 H, arom.) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 36.9 (+, C-3), 49.5 (–, C-8 or C-9), 49.9 (–, C-8 or C-9), 88.4 (–, C-4 or C-5 or C-6), 89.3 (–, C-4 or C-5 or C-6), 90.4 (–, C-4 or C-5 or C-6), 92.7 (+, C-2), 97.3 (–, C-7), 100.2 (+, C-3a), 119.2 (+, C-7a), 194.8 (+, C-1), 230.7 (+, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3061 (w), 2948 (w), 2924 (w), 2836 (w), 1996 (s, CO), 1924 (s, CO), 1892 (s, CO), 1716 (s, ketone), 1520 (w), 1276 (w), 1232 (w), 1136 (m), 1052 (w), 1028 (w), 896 (w), 656 (w), 612 (m) cm^{-1}. MS (70eV, 110 °C): *m*/*z* (%) = 330 (1) [*M* + 2]$^+$, 329 (4) [*M* + 1]$^+$, 328 (14) [*M*]$^+$, 297 (5), 272 (20) [*M* – 2×CO]$^+$, 244 (29) [*M* – 3×CO]$^+$, 229 (100), 213 (9), 199 (60), 184 (8), 171 (76), 143 (11), 118 (5), 91 (15). HRMS, $C_{14}H_{12}CrO_6$: calcd: 328.0039; found 328.0032. $C_{14}H_{12}CrO_6$ (328.00): calcd: C 51.23, H 3.68; found C 51.11, H 3.70.

Tricarbonyl(η^6-2-hydroxyindan-1-one)chromium(0) (*rac*-20): Conc. hydrochloric acid (30 mL) was slowly added to *rac*-**19** (240 mg, 0.7 mmol) in THF (30 mL). The solution immediately became dark red and lighter afterwards. After 5 min no starting material could be detected by TLC. Water (100 mL) was added, and the mixture was extracted three times with TBME (each 20 mL). The combined organic layers were washed three times with satd. aq. sodium hydrogen carbonate and three times with water (each 20 mL). After drying over potassium carbonate, filtration, and solvent removal at reduced pressure a brown oil was obtained and was purified by column chromatography (SiO_2, TBME/PE, 1:1, then TBME, 30×3 cm) to provide *rac*-**20** (110 mg, 0.39 mmol, 53%) as a red oil [(*de* > 95% (NMR)]. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.86 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –17.1 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.60 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –17.1 Hz, 1 H, *endo*-3-H or *exo*-3-H), 4.45 (br., 1 H, 2-H), 5.17 (br., 1 H, OH), 5.48–6.23 (ABCD line system, 4 H, arom.) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 34.6 (+, C-3), 71.2 (–, C-2), 88.7 (–, C-4 or C-5 or C-6), 89.6 (–, C-4 or C-5 or C-6), 90.0 (–, C-4 or C-5 or C-6), 95.5 (+, C-3a), 97.2 (–, C-7), 121.2 (+, C-7a), 202.9 (+, C-1), 231.0 (+, CO) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3555 (w, OH), 3032 (w), 2976 (w), 1988 (s, CO), 1928 (s, CO), 1716 (s, ketone), 1520 (w), 1428 (w), 1260 (w), 1100 (w), 1016 (w) cm^{-1}. MS (70 eV, 140 °C): *m*/*z* (%) = 286 (2) [*M* + 2]$^+$, 285 (4) [*M* + 1]$^+$, 284 (12) [*M*]$^+$, 228 (10) [*M* – 2×CO]$^+$, 220 (15), 200 (67) [*M* – 3×CO]$^+$, 182 (84) [(C$_9$H$_6$O)Cr]$^+$, 172 (19), 148 (17), 131 (6), 115 (4), 91 (9), 52 (42). HRMS, $C_{12}H_8CrO_5$: calcd: 283.9772; found 283.9773.

Tricarbonyl(η^6-2-methoxyinden-1-one)chromium(0) (*rac*-21): A solution of boron trifluoride–diethyl ether in DEE (50%, 10 mL) was added at 0 °C to *rac*-**19** (500 mg, 1.5 mmol). A blue-purple suspension formed, and the mixture was stirred at 0 °C for 1 h. After hydrolysis with ice water (100 mL) the mixture was extracted three times with TBME (each 30 mL). The collected organic layers were washed twice with water (50 mL each) and dried with magnesium sulfate. After solvent removal at reduced pressure the remaining purple-black crude product was purified by column chromatography (SiO_2, TBME/PE, 1:1, then TBME, 30×3 cm) to provide *rac*-**21** (347 mg, 1.2 mmol, 77%) as a purple solid (m. p. 132 °C). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.81 (s, 3 H, 8-H), 5.59 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 6.5 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 6.5 Hz, 1 H, 5-H or 6-H), 5.70 (d, $^3J_{4,5}$ = 6.5 Hz or $^3J_{6,7}$ = 6.5 Hz, 1 H, 4-H or 7-H), 6.09 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 6.5 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 6.5 Hz, 1 H, 5-H or 6-H), 6.31 (d, $^3J_{4,5}$ = 6.5 Hz or $^3J_{6,7}$ = 6.5 Hz, 1 H, 4-H or 7-H), 6.43 (s, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 57.4 (–, C-8), 87.1 (+, C-3a), 87.1 (–, C-4 or C-5 or C-6 or C-7), 87.8 (–, C-4 or C-5 or C-6 or C-7), 91.6 (–, C-4 or C-5 or C-6 or C-7), 94.6 (–, C-4 or C-5 or C-6 or C-7), 109.7 (–, C-3), 113.8 (+, C-7a), 156.3 (+, C-2), 187.2 (+, C-1), 232.2 (+, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3080 (m), 3060 (m), 2980 (m), 2936 (m), 1972 (s, CO), 1904 (s, CO), 1696 (s, ketone), 1600 (m), 1544 (m), 1520 (w), 1452 (w), 1404 (m), 1316 (w), 1260 (w), 1220 (m), 1160 (w), 1096 (w), 1028 (m), 804 (m), 652 (m), 620 (m) cm^{-1}. MS (70 eV, 110 °C): *m*/*z* (%) = 298 (4) [*M* + 2], 297 (10) [*M* + 1]$^+$, 296 (33) [*M*]$^+$, 268 (3) [*M* – CO]$^+$, 240 (23) [*M* – 2×CO]$^+$, 212 (97) [*M* – 3×CO]$^+$, 197 (100) [(C$_9$H$_5$O$_2$)Cr]$^+$, 169 (20), 160 (16), 141 (59), 131 (10), 108 (9), 89 (42), 81 (16), 52 (92) [^{52}Cr]$^+$. HRMS, $C_{13}H_8CrO_5$: calcd: 295.9777; found 295.9764. $C_{13}H_8CrO_5$ (295.98): calcd: C 52.72, H 2.72; found C 53.32, H 2.98.

Tricarbonyl[η^6-3-(triphenylmethyl)indan-1,2-dione]chromium(0) (*rac*-22): Compound *rac*-**19** (200 mg, 0.6 mmol) and triphenylmethylcarbenium tetrafluoroborate (262 mg, 0.8 mmol) were stirred at 20 °C for 18 h in anhydrous dichloromethane (10 mL). After solvent removal at reduced pressure the remaining black residue was purified by column chromatography (SiO_2, TBME/PE, 1:3, then TBME, 25×3 cm). Fraction I: 125 mg (0.6 mmol, 48%) of *rac*-**22** as a brown solid (m. p. 186 °C). Fraction II: 10 mg (0.03 mmol, 5%) of *rac*-**21** [*de* > 95% (NMR)].

Compound *rac*-22: ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 5.45 (d, $^3J_{4,5}$ = 7.0 Hz or $^3J_{6,7}$ = 7.0 Hz, 1 H, 4-H or 7-H), 5.63 (s, 1 H, 3-H), 5.69 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 7.0 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 7.0 Hz, 1 H, 5-H or 6-H), 6.05 (d, $^3J_{4,5}$ = 7.0 Hz or $^3J_{6,7}$ = 7.0 Hz, 1 H, 4-H or 7-H), 6.08 (t, $^3J_{4,5}$ = $^3J_{5,6}$ = 7.0 Hz or $^3J_{5,6}$ = $^3J_{6,7}$ = 7.0 Hz, 1 H, 5-H or 6-H), 7.13–7.52 (m, 15 H, trityl-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 49.6 (CH, C-3), 64.1 (C$_q$, C-8), 89.7 (CH, C-4 or C-5 or C-6), 90.4 (CH, C-4 or C-5 or C-6), 91.0 (CH, C-4 or C-5 or C-6), 97.1 (CH, C-7), 97.1 (CH, C-7), 97.3 (C$_q$, C-3a), 117.7 (C$_q$, C-7a), 126.7 (CH, C-12), 127.9 [CH, C-10 (11, 13, 14)], 129.8 (C$_q$, C-9), 179.0 (C$_q$, C-1), 195.9 (C$_q$, C-2), 229.7 (C$_q$, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3088 (w), 3056 (w), 3032 (w), 2924 (w), 2852 (w), 1988 (s, CO), 1928 (s, CO), 1756 (m, ketone), 1712 (s, ketone), 1524 (w), 1492 (w), 1448 (w), 1284 (w), 1252 (w), 1100 (w), 1032 (w), 704 (m), 648 (m), 608 (m) cm^{-1}. MS (70 eV, 150 °C): *m*/*z* (%) = 524 (1) [*M*]$^+$, 440 (20) [*M* – 3×CO]$^+$, 243 (100) [Ph$_3$C]$^+$, 228 (10), 215 (9), 197 (9), 165 (84), 141 (8), 115 (6), 91 (7), 77 (4), 52 (11). HRMS, $C_{31}H_{20}CrO_5$: calcd: 524.0716; found 524.0703.

***rac*-Tricarbonyl(η^6-indan-1,2-dione)chromium(0) (*rac*-5):** a) Compound *rac*-**19** (250 mg, 0.8 mmol) and triphenylcarbenium tetrafluoroborate (374 mg, 1.1 mmol) were stirred at 20 °C in anhydrous dichloromethane (10 mL) for 3 h. After addition of water (30 mL) the layer was extracted three times with dichloromethane (each 10 mL). The combined organic layers were dried with magnesium sulfate and filtered, and the solvent was removed at reduced pressure. The remaining black residue was purified by column chromatography (SiO_2, TBME/PE, 1:1, then TBME, 30×3 cm). Fraction I: 30 mg (0.1 mmol, 8%) of *rac*-**22**. Fraction II: 20 mg (0.1 mmol, 8%) of *rac*-**19**. Fraction III: 92 mg (0.3 mmol, 43%) of *rac*-**5** as a brown solid (m. p. 129 °C). b) Compound *rac*-**19** (4.000 g, 12.0 mmol) in formic acid (50 mL) was stirred at 25 °C for 1.5 h. After addition of water (200 mL) the layer was extracted three times with dichloromethane (each 20 mL). After drying over magnesium sulfate, filtration, and solvent removal at reduced pressure, the crude product was purified by column chromatography (SiO_2, TBME/PE, 1:11, then TBME, 25×30 cm) to provide *rac*-**5** (1.860 g, 6.6 mmol, 55%) as a red-brown solid (m. p. 127 °C).

Compound *rac*-5: ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.47 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –21.2 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.90 (d, $^2J_{endo\text{-}3,exo\text{-}3}$ = –21.2 Hz, 1 H, *endo*-3-H or *exo*-3-H), 5.77–6.41 (ABCD line system, 4 H, arom.) ppm. ^{13}C NMR (100 MHz, [D$_6$]-acetone): δ = 36.3 (+, C-3), 88.8 (–, C-4 or C-5 or C-6), 90.4 (–, C-4 or C-5 or C-6), 91.2 (–, C-4 or C- 5 or C-6), 97.9 (–, C-7), 97.0 (+, C-3a), 116.5 (+, C-7a), 182.4 (+, C-1), 195.3 (+, C-2), 230.3 (+, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3040 (w), 2960 (w), 2932 (w), 2860 (w), 2000 (s, CO), 1932 (s, CO), 1764 (w, ketone), 1708 (s, ketone), 1600 (w), 1524 (w), 1428 (w), 1280 (w), 1260 (w), 1100 (m), 1016 (m), 644 (m), 604 (m) cm^{-1}. MS (70 eV, 170 °C): *m*/*z* (%) = 282 (12) $[M]^+$, 280 (17), 198 (36) $[M - 3\times CO]^+$, 189 (9), 167 (42), 149 (100) $[C_9H_9O_2]^+$, 146 (8), 142 (12), 128 (17), 118 (11), 96 (21), 90 (12), 52 (59) $[^{52}Cr]^+$.

(*R*,*S*)-2,2-Dimethoxy-1-indanyl 2-Acetyl-2-phenylacetate [(*R*,*S*)-25] and (*S*,*S*)-2,2-Dimethoxy-1-indanyl 2-Acetyl-2-phenylacetate [(*S*,*S*)-26]: A solution of ***rac*-13** (1340 mg, 6.9 mmol), 2-acetyl-2-phenylacetic acid (1340 mg, 6.9 mmol), dicyclohexylcarbodiimide (1444 mg, 7.0 mmol), and 4-(dimethylamino)pyridine (84 mg, 0.69 mmol) in dichloromethane (50 mL) was stirred for 11 h at 0 °C and then for 16 h at 25 °C. Formed dicyclohexylurea was filtered off, and the filtrate was washed with satd. aq. sodium hydrogen carbonate (100 mL). After drying over magnesium sulfate the crude product was purified by column chromatography (SiO_2, TBME/PE, 1:10, 50 × 3 cm). Fraction I: 0.745 g (2.0 mmol, 29%) of (*S*,*S*)-**26** [*de* = 99.3%, GC], colorless solid. Fraction II: 1041 mg (2.8 mmol, 41%) of (*R*,*S*)-**25** [*de* = 99.4%, GC]. Fraction III 741 mg (2.0 mmol, 29%) mixture of (*R*,*S*)-**25** and (*S*,*S*)-**26**.

Compound (*R*,*S*)-25: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09 [s, 3 H, C(O)CH_3], 3.08–3.22 (AB line system, 2 H, 3-H), 3.25 (s, 3 H, OCH_3), 3.30 (s, 3 H, OCH_3), 5.91(s, 1 H, 1-H), 6.02 (s, 1 H, C*H*Ph), 7.07–7.47 (m, 9 H, arom.) ppm. MS (70 eV, 76 °C): *m*/*z* (%) = 373 (3) $[M + 3]^+$, 372 (5) $[M + 2]^+$, 371 (24) $[M + 1]^+$, 370 (100) $[M]^+$, 339 (6), 279 (3), 219 (3), 193 (62), 177 (26), 161 (50), 131 (8), 107 (22), 91 (7), 77 (9).

Compound (*S*,*S*)-26: ^{1}HNMR (400 MHz, $CDCl_3$): δ = 2.21 [s, 3 H, C(O)CH_3], 2.86 (s, 3 H, OCH_3), 3.06 (AB line system, 2 H, 3-H), 3.15 (s, 3 H, OCH_3), 5.93 (s, 1 H, 1-H), 6.06 (s, 1 H, C*H*Ph), 7.18–7.491 (m, 9 H, arom.) ppm. MS (70 eV, 70 °C): *m*/*z* (%) = 373 (3) $[M + 3]^+$, 372 (5) $[M + 2]^+$, 371 (24) $[M + 1]^+$, 370 (100) $[M]^+$, 339 (6), 279 (3), 219 (3), 193 (62), 177 (26), 161 (50), 131 (8), 107 (22), 91 (7), 77 (9).

(+)-(*R*)-2,2-Dimethoxyindan-1-ol [(+)-(*R*)-13] from (*R*,*S*)-25: A suspension of (*R*,*S*)-**25** (4.000 g, 10.8 mmol) and potassium carbonate (14.900 g, 108.0 mmol) in methanol/water (2:1) was stirred at 25 °C for 16 h. After addition of water (200 mL), the mixture was extracted five times with TBME (each 100 mL). After drying over potassium carbonate, filtration, and solvent removal at reduced pressure, the crude product was purified by column chromatography (SiO_2, TBME/PE, 1:5) to provide (+)-(*R*)-**13** (2.070 g, 10.7 mmol, 99%, 99.4% *ee*), $[\alpha]_D^{20}$ = +24.5 (*c* = 1, $CHCl_3$).

(–)-(1*R*)-*endo*-Tricarbonyl(η^6-2,2-dimethoxyindan-1-ol)chromium(0) [(–)-(1*R*)-14] and (+)-(1*R*)-Tricarbonyl(η^6-2,2-dimethoxyindan-1-ol)-chromium(0) [(+)-(1*R*)-15]: Compound (+)-(*R*)-**13** (1.950 g, 10.1 mmol, 99.4% *ee*) and hexacarbonylchromium (3.300 g, 15.0 mmol) in dibutyl ether (50 mL), heptane (50 mL), and THF (2 mL) were heated at reflux for 20 h under a light flow of argon. After cooling to 25 °C, the greenish reaction mixture was filtered through a frit covered with a 1 cm thick layer of silica gel. After solvent removal at reduced pressure, the crude product was purified by column chromatography (SiO_2, TBME/PE, 1:4, then TBME, 20 × 3 cm). Fraction I: 2.033 g (6.2 mmol, 61%) of (–)-(1*R*)-**14**, bright yellow solid {m. p. 161 °C, de >95% (NMR), 99.4% *ee*, $[\alpha]_D^{20}$ = –6.1 (*c* = 0.25, THF)}. Fraction II: 167 mg (0.51 mmol, 5%) of (+)-(1*R*)-**15**, bright yellow solid {m. p. 135 °C, de > 95% (NMR), 99.4% *ee*, $[\alpha]_D^{20}$ = +48.6 (*c* = 0.25, THF}.

Compound (–)-(1*R*)-14: $C_{14}H_{14}CrO_6$: calcd: C 50.93 H 4.24; found C 50.77 H 4.11.

Crystal Structure Analysis of (–)-(1*R*)-14:[67] $C_{14}H_{14}CrO_6$, molecular weight 330.25, crystal system monoclinic, space group P 21, *a* = 8.815(2) Å, *b* = 7.140(1) Å, *c* = 11.595(2) Å, α = 90°, β = 108.02(2)°, γ = 90°, *V* = 694.0(2) Å^3, *Z* = 2, $d_{calcd.}$ = 1.580 Mg m^{-3}, *F*(000) = 340, μ = 0.849 mm^{-1}, crystal size 0.52 × 0.24 × 0.22 mm, Stoe IPDS area detector diffractometer, *T* = 300(2) K, Mo-K_a = 0.71073 Å, θ_{min} = 2.43, θ_{max} = 26.14°, –10 ≤ *h* ≤ 10, –8 ≤ *k* ≤ 8, –14 ≤ *l* ≤ 14, no absorption correction, no extinction correction, 6155 collected, 2685 unique reflections, [*R*(int) = 0.0363], refinement program: SHELXL-93, refinement by least-squares method (F_2), F_2 = 1.109, *R* indices: [$I > 2\sigma(I)$] R_1 = 0.0257, wR_2 = 0.0541, *R* indices (all data): R_1 = 0.0324, wR_2 = 0.0551, residual electron density: –0.152 Å^{-3}, completeness of data 99.7%, Flack *x* parameter 0.00(2).

(–)-(p*R*)-Tricarbonyl(η^6-2,2-dimethoxyindan-1-one)chromium(0) [(–)-p*R*-19]: Dimethyl sulfoxide (12 mL) and acetic anhydride (9 mL) were added at 25 °C to (–)-(1*R*)-**14** (1.500 g, 4.5 mmol), the solution becoming dark red. After the mixture had been stirred for 15 h, water (200 mL) was added, and the mixture was extracted three times with TBME (each 50 mL). The combined organic layers were washed three times with satd. aq. sodium hydrogen carbonate and with satd. aq. sodium chloride (30 mL). After drying over magnesium sulfate and filtration through a frit covered with a 1 cm thick layer of silica gel the remaining material was purified by column chromatography (TBME/PE, 1:1, 20 × 3 cm) to provide (–)-(p*R*)-**19** (1.122 g, 3.4 mmol, 76%) as a red solid {m. p. 125 °C, 99.4% *ee*, $[\alpha]_D^{20}$ = –561.0 (*c* = 0.05, THF)}.

(–)-(p*R*)-Tricarbonyl(η^6-indan-1,2-dione)chromium(0) [(–)-(p*R*)-5]: Compound (–)-(p*R*)-**19** (1.000 g, 3.0 mmol) and triphenylcarbenium tetrafluoroborate (1.476 g, 4.5 mmol) were stirred for 3 h at 25 °C in anhydrous dichloromethane (50 mL). After addition of water (150 mL) the layer was extracted three times with dichloromethane (each 20 mL). After drying over magnesium sulfate, filtration through a frit, and solvent removal at reduced pressure, the remaining crude product was purified by column chromatography (SiO_2, TBME/PE, 1:1, then TBME, 25 × 3 cm) to provide (–)-(p*R*)-**5** (305 mg, 1.1 mmol, 36%) as a red brown solid {m. p. 132 °C, 99.4% *ee*, $[\alpha]_D^{20}$ = –36.0 (*c* = 0.017, THF)}.

***rac*-Tricarbonyl(η^6-*exo*-1-hydroxy-*endo*-1-vinylindan-2-one)chromium(0) (*rac*-27):** Compound *rac*-**5** (150 mg, 0.5 mmol) in DEE/THF (1:1, 20 mL) was added dropwise at –78 °C to a solution of vinyllithium in DEE (1.0 M, 3.19 mL, 3.2 mmol) in THF (10 mL). The mixture was stirred for 4 h at –78 °C and was then allowed to warm to 25 °C over 14 h. Sat. aq. ammonium chloride (20 mL) was added at –78 °C and the mixture was allowed to warm to 25 °C. After addition of water (10 mL) the aqueous layer was extracted three times with TBME (each 30 mL). After drying over magnesium sulfate, filtration through a frit, and solvent removal at reduced pressure, the crude product was purified by column chromatography (SiO_2, TBME/PE, 1:3, 25 × 3 cm) to provide *rac*-**27** (52 mg, 0.2 mmol, 32%) as a yellow solid (m. p. 145 °C). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 3.39 (d, $^2J_{gem}$ = –20.3 Hz, 1 H, *endo*-3-H or *exo*-3-H), 3.83 (d, $^2J_{gem}$ = –20.3 Hz, 1 H, *endo*-3-H or *exo*-3-H), 5.05 (s, 1 H, OH), 5.12–5.95 (m, 7 H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H) ppm. IR (ATR): $\tilde{\nu}$ = 3451 (w, br, OH), 3018 (w), 2986 (w), 2921 (w), 1963 (s, CO), 1865 (s, CO), 1765 (s, C=O, ketone),

1716 (m, C=O, ketone), 1633 (m), 1532 (m), 1439 (m), 1428 (m), 1382 (m), 1261 (m), 1050 (m, C–O), 819 (s), 667 (s), 633 (s) cm^{-1}. MS (70 eV, 90 °C): *m*/*z* (%) = 310 (16) $[M]^+$, 282 (20) $[M\text{-CO}]^+$, 254 (40) $[M\text{-}2\times\text{CO}]^+$, 226 (30) $[M\text{-}3\times\text{CO}]^+$, 174 (26) $[M\text{-Cr(CO)}_3]^+$, 149 (100), 132 (17), 115 (29), 91 (28), 77 (17), 53 (14), 52 (51).

***rac*-Tricarbonyl[η⁶-*exo*-1-hydroxy-*endo*-1-(1-ethoxyvinyl)indan-2-one]chromium(0) (*rac*-28):** A solution of *tert*-butyllithium in pentane (1.6 M, 2.0 mL, 3.2 mmol) was added at –78 °C to 360 mg (5.0 mmol) of ethoxyethene in THF (10 mL). The mixture was warmed to –5 °C over 2 h and was then stirred for another 45 min at this temperature, the color changing from yellow to colorless. A solution of *rac*-**5** (150 mg, 0.5 mmol) in DEE/THF (1:1, 20 mL) was then added dropwise at –78 °C. The mixture was stirred for 4 h at –78 °C and then allowed to warm to 25 °C over 14 h. Sat. aq. ammonium chloride (50 mL) was then added at –78 °C, and the mixture was allowed to warm to 25 °C. After addition of water (10 mL) the layer was extracted three times with TBME (each 30 mL). After drying over magnesium sulfate, filtration, and solvent removal at reduced pressure the crude product was purified by column chromatography (SiO_2, TBME/PE, 1:4, 25 × 3 cm) to provide *rac*-**28** (79 mg, 0.2 mmol, 42%) as a viscous, yellow oil. ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 1.15 (t, ^3J = 7.0 Hz, 3 H, CH_3), 3.29 (d, $^2J_{gem}$ = –20.5 Hz, 1 H, *endo*-3-H or *exo*-3-H) 3.70 (m, ^3J = 7.0 Hz, 2 H, CH_2CH_3), 3.83 (d, $^2J_{gem}$ = –20.5 Hz, 1 H, *endo*-3-H or *exo*-3-H), 4.20 (d, $^2J_{gem}$ = 2.9 Hz, 1 H, =CH_2), 4.60 (d, $^2J_{gem}$ = 2.9 Hz, 1 H, =CH_2), 5.43 (m, 1 H, 4-H or 5-H or 6-H or 7-H), 5.60 (s, 1 H, OH), 5.67 (m, 1 H, 4-H or 5-H or 6-H or 7-H), 5.75–5.90 (m, 2 H, 4-H or 5-H or 6-H or 7-H) ppm. IR (ATR): $\tilde{\nu}$ = 3416 (w, br, OH), 3015 (w), 2980 (w), 2932 (w), 1959 (s, CrCO), 1857 (s, CrCO), 1767 (s, C=O, ketone), 1713 (m, C=O, ketone), 1631 (m), 1537 (m), 1444 (m), 1428 (m), 1382 (m), 1261 (m), 1091 (s, C–O), 1050 (s, C–O), 819 (s), 661 (s), 623 (s) cm^{-1}. MS (70 eV, 120 °C): *m*/*z* (%) = 356 (24) $[M - 2]^+$, 354 (43) $[M]^+$, 298 (22) $[M - 2\times\text{CO}]^+$, 270 (40) $[M - 3\times\text{CO}]^+$, 252 (14), 226 (30), 218 (30) $[M - \text{Cr(CO)}_3]^+$, 208 (100), 191 (26), 172 (17), 149 (25), 132 (17), 115 (29), 91 (28), 77 (17), 53 (16), 51 (55).

(–)-(p*R*)-Tricarbonyl{η⁶-2-[2-(3,4-dimethoxyphenyl)ethylamino]-inden-1-one}chromium(0) [(–)-(p*R*)-29]: Hydrochloric acid (10%, 10 mL) was added to (–)-(p*R*)-**5** (150 mg, 0.5 mmol) and 2-(3,4-dimethoxyphenyl)ethylamine (100 mg, 0.6 mmol) in THF (10 mL). The mixture was stirred for 16 h, its color slowly changing from brown to deep purple. Water (100 mL) was added, and the mixture was extracted three times with TBME (30 mL each). After drying with magnesium sulfate, filtration, and solvent removal at reduced pressure, the crude product was purified by column chromatography (SiO_2, TBME/PE, 1:1, 25 × 3 cm) to provide (–)-(p*R*)-**29** (61 mg, 0.1 mmol, 26%) as a purple solid (m. p. 155 °C, dec.).

Compound (–)-p*R*-29: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.81 (t, 2 H, NCH_2CH_2), 3.31 (m, 2 H, NCH_2CH_2), 3.87 (2 × s, 6 H, OCH_3), 4.67 (t, 1 H, NH), 5.05–5.17 (m, 2 H, coord. arom. CH), 5.28 (s, 1 H, 3-H), 5.75 (m, 1 H, coord. arom. CH), 6.08 (d, 1 H, coord. arom. CH), 6.66–6.76 (m, 2 H, arom. CH), 6.82 (d, 1 H, arom. CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, APT/BB/HMQC): δ = 34.7 (+, NCH_2CH_2), 45.8 (+, NCH_2CH_2), 56.3 (–, OCH_3), 56.4 (–, OCH_3), 84.4 (–, coord. arom. CH), 84.6 (–, coord. arom. CH), 86.5 (+, C-3a), 91.9 (–, coord. arom. CH), 94.3 (–, coord. arom. CH), 97.9 (–, C-3), 112.1 (–, arom. CH), 112.5 (–, arom. CH), 121.1 (–, arom. CH), 129.3 (+, C-7a), 131.4 (+, quat. arom. C), 144.9 (+, C-2), 148.4 (+, quat. arom. C), 149.6 (+, quat. arom. C), 190.3 (+, C-1), 232.7 (+, CrCO) ppm. IR (ATR): $\tilde{\nu}$ = 3351 (w-m, br, NH), 3083 (w), 2961 (m), 2929 (m), 2837 (m), 1958 (s, CrCO), 1872 (s, CrCO), 1695 (s, C=O, ketone), 1615 (s), 1541 (m), 1514 (s), 1418 (m), 1259 (s), 1235 (s), 1139 (s), 1082 (s, C–O), 1024 (s, C–O), 801 (s), 782 (s), 762 (m) cm^{-1}. MS (EI+): *m*/*z* (%) = 361 (5) $[M - 3\times\text{CO}]^+$, 309 (14) $[M - \text{Cr(CO)}_3\text{=ligand}]^+$, 293 (10), 279 (6), 220 (43), 167 (22), 158 (44), 149 (100), 108 (9), 80 (13), 71 (25), 52 (60) $[^{52}\text{Cr}]^+$. $C_{22}H_{19}CrNO_6$: calcd: C 59.33 H 4.30 N 3.14; found C 59.55 H 4.99 N 2.49.

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