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The stereodivergent asymmetric synthesis of a range of 2-(1′-hydroxyalkyl)-phenols

Stephen G. Davies *, W. Ewan Hume, Paul M. Roberts, James E. Thomson

Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, UK

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ABSTRACT

The use of the (*S*)-α-methylbenzyl group as a chiral auxiliary has allowed the diastereoselective *ortho*-deprotonation of a chromium tricarbonyl complexed phenoxy ring. When the resultant *ortho*-anion is treated with an aldehyde two diastereoisomeric complexes are formed, in relatively poor dr, which differ in the configuration of the newly formed benzylic stereogenic centre. However, both *ortho*-formylation followed by treatment with Grignard reagents and *ortho*-acylation followed by reduction with Super-Hydride® were found to be completely diastereoselective, giving access to either epimer of the corresponding benzylic alcohol complexes in >99:1 dr. Subsequent oxidative removal of the chromium tricarbonyl unit, followed by cleavage of the *O*-α-methylbenzyl chiral auxiliary gives enantiopure 2-(1′-hydroxyalkyl)phenols. Following this stereodivergent procedure, either enantiomer of the product may be accessed from a single antipode of [(α-methylbenzyloxy)benzene]Cr(CO)$_3$.

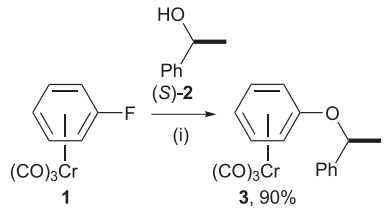
1. Introduction

Chromium tricarbonyl complexes of benzaldehyde and phenyl ketones each possessing an *ortho*-substituent are chiral and have been shown to undergo a variety of diastereoselective addition reactions[1] making them attractive building blocks for asymmetric synthesis. This has led to a number of approaches being developed for their preparation in homochiral form. Resolution procedures have involved the separation of diastereoisomers[2] and kinetic resolutions via oxazolidines[3] and enantioselective yeast reductions.[4] Asymmetric syntheses have been achieved via stereoselective complexation of chiral aminals,[5] and the stereoselective *ortho*-metallation of phenyl complexes bearing homochiral side-chains,[6] homochiral acetals,[7] homochiral aminals[8] and homochiral sulphoxides.[9] Homochiral lithium amide bases have been used to enantioselectively *ortho*-deprotonate prochiral substrates, such as anisole chromium tricarbonyl,[10] phenyl chromium tricarbonyl carbamates[11] and benzaldehyde acetal chromium tricarbonyl complexes.[10,11] As part of our ongoing research program concerning the utility of arene chromium tricarbonyl complexes in synthesis,[12,13] we became interested in the stereoselective *ortho*-deprotonation of [(*S*)-(α-methylbenzyloxy)-benzene]Cr(CO)$_3$ followed by alkylation with a range of electrophiles. We describe herein the conversion of the resultant *ortho*-substituted complexes into either enantiomer of the corresponding 2-(1′-hydroxyalkyl)-phenols via a stereodivergent acylation/nucleophilic addition procedure. Part of this work has been communicated previously.[14]

2. Results and discussion

2.1. *ortho*-Deprotonation studies

[(*S*)-(α-Methylbenzyloxy)benzene]Cr(CO)$_3$ **3** was produced via treatment of the sodium salt of (*S*)-α-methylbenzyl alcohol **2** with (fluorobenzene)Cr(CO)$_3$ **1**, giving (*S*)-**3** in 90% isolated yield (Scheme 1). It is known that treatment of (anisole)Cr(CO)$_3$ with BuLi results in regiospecific removal of an *ortho*-proton from the complexed aryl ring via chelation of the base with the methoxy group,[15] hence it was expected that treatment of (*S*)-**3** with base would result in preferential removal of one of the diastereotopic *ortho*-protons. It was anticipated that the preferred conformation of **3** would involve minimisation of *syn*-pentane-type interactions between the complexed arene ring and the α-methylbenzyl chiral auxiliary giving rise to two possible conformations **4A** and **4B**. Within **4A**, unfavourable steric interactions are experienced between the Cr(CO)$_3$ unit and the phenyl group of the auxiliary; therefore **4B**, in which the pro-*S ortho*-



Scheme 1. Reagents and conditions: (i) NaH, THF, rt, 16 h.

* Corresponding author. E-mail address: steve.davies@chem.ox.ac.uk (S.G. Davies).

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proton is shielded by the auxiliary, was expected to be the favoured conformation (Fig. 1). In support of this hypothesis, the two diastereotopic *ortho*-protons within **3** were found to have significantly different chemical shifts by ^{1}H NMR spectroscopic analysis (δ_H 4.86 and 5.27 ppm), consistent with one of these protons being significantly more shielded by the phenyl ring of the auxiliary than the other.

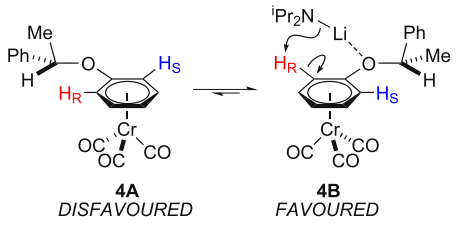
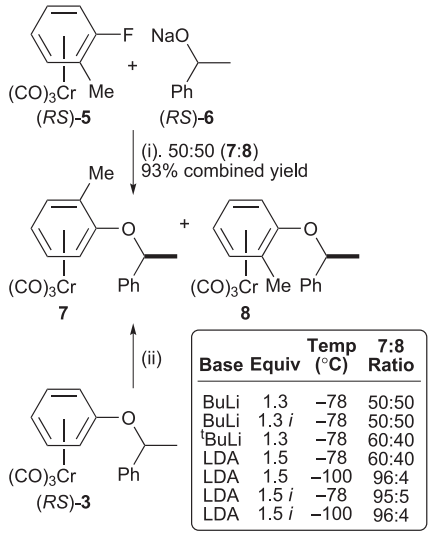


Figure 1. Diastereoselective deprotonation of the pro-*R ortho*-proton within (*S*)-**3** with LDA. [H_R=pro-*R* proton. H_S=pro-*S* proton].

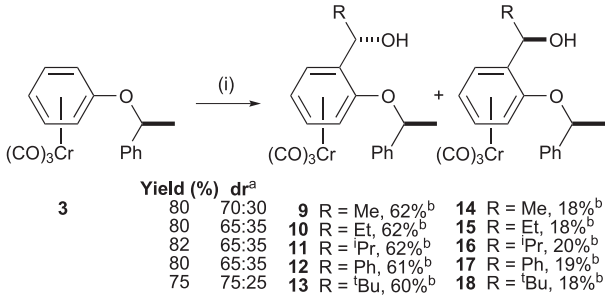
An *ortho*-deprotonation/methylation sequence was initially carried out with a variety of bases in order to assess the effectiveness of the α-methylbenzyl chiral auxiliary in controlling the diastereoselective deprotonation of (*S*)-**3**. In order to asses the extent of enantiorecognition phenomena[16] within this system, and to provide authentic samples of the two possible diastereoisomers **7** and **8** that could be derived from *ortho*-methylation of (*S*)-**3**, (*RS*)-**5** was reacted with (*RS*)-**6** to give racemic **7** and **8** in approximately 50:50 dr; this result indicates that enantiorecognition phenomena are not occurring to an appreciable extent in this system. Deprotonation and subsequent methylation of (*RS*)-**3** was next undertaken. The requisite base was added to a solution of (*RS*)-**3** in THF at −78 °C. After stirring at −78 °C for 3 h (during which time a colour change from yellow to orange was observed)[17] excess methyl iodide was added. The reaction mixture was then allowed to warm up to 0 °C over a period of 16 h. The ratios of **7**:**8** obtained from deprotonation with the alkyl lithium bases were found to be low, presumably due to their high reactivity. However, with the less reactive lithium amide base LDA high levels of diastereoselectivity were obtained. Lower temperatures (−100 °C) and following an inverse addition procedure, where a solution of (*RS*)-**3** was added dropwise to a solution of the base in THF, were both found to increase the diastereoselectivity of this process, i.e., the deprotonation is under kinetic rather than thermodynamic control (Scheme 2).



Base	Equiv	Temp (°C)	7:8 Ratio
BuLi	1.3	−78	50:50
BuLi	1.3 *i*	−78	50:50
^{t}BuLi	1.3	−78	60:40
LDA	1.5	−78	60:40
LDA	1.5	−100	96:4
LDA	1.5 *i*	−78	95:5
LDA	1.5 *i*	−100	96:4

Scheme 2. Reagents and conditions: (i) THF, rt, 16 h; (ii) Base then MeI (see table). [*i*=inverse addition].

In order to exploit this diastereoselective *ortho*-deprotonation protocol for the generation of new benzylic stereogenic centres, it was envisaged that the *ortho*-anions derived from (*S*)-**3** could be reacted with prochiral electrophiles such as aldehydes. Thus, a solution of (*S*)-**3** in THF was added dropwise to a solution of LDA at −78 °C in THF. The resultant mixture was stirred at −78 °C for 3 h then 5.0 equiv of the requisite aldehyde (as a solution in THF) was added and the reaction mixture was allowed to warm up to 0 °C over a period of 16 h to give mixtures of the corresponding *ortho*-substituted complexes **9**–**18** in ≥65:35 dr after work-up. Purification allowed separation of the diastereoisomers to give **9**–**18** in >99:1 dr (Scheme 3). In each case ^{1}H NMR spectroscopic analysis of **9**–**18** revealed diagnostic peaks at δ_H 4.73–4.89 ppm, corresponding to the C(6)*H* protons, confirming that the deprotonation occurred with complete diastereoselectivity. The relative configuration within the minor product **17** was unambiguously established by single crystal X-ray analysis of the racemate, with the absolute configuration within (1*pR*,1′*R*,α*S*)-**17** being assigned from the known configuration of the (*S*)-α-methylbenzyl stereocentre (Fig. 2). The absolute configuration within the major diastereoisomer **12** could therefore be unambiguously assigned and the absolute configurations within the major products **9**–**11** and **13** were therefore assigned by analogy.



Scheme 3. Reagents and conditions: (i) LDA, THF, −78 °C, 3 h, RCHO, 16 h. [[a]Crude; [b]Isolated in >99:1 dr].

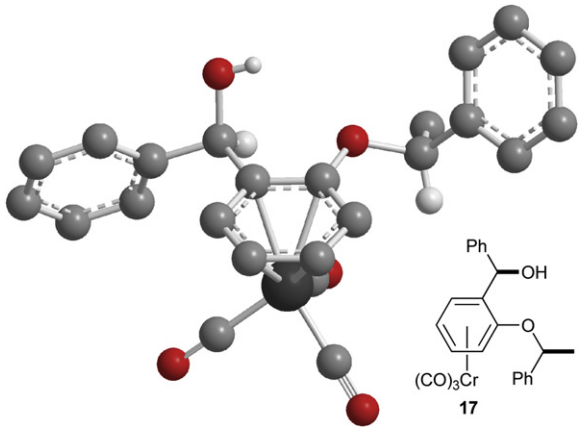


Figure 2. Chem3D representation of the single crystal X-ray structure of (1*pRS*,1′*RS*,α*SR*)-**17** (some H atoms have been omitted for clarity).

We have previously shown that the addition of nucleophiles to chromium tricarbonyl complexes of *ortho*-anisaldehyde and *ortho*-methoxyphenyl ketones occurs with very high levels of diastereoselectivity.[18] In each case the nucleophile adds to the carbonyl group in the *anti* conformation **19A**, presumably owing to lone pair–lone pair repulsions between the oxygen atoms, on the face distal to the chromium tricarbonyl moiety (Fig. 3). We therefore envisaged that nucleophilic addition to a range of homochiral *ortho*-acyl complexes derived from (*S*)-**3** would lead to the diastereoselective formation of the corresponding benzylic alcohol complexes.

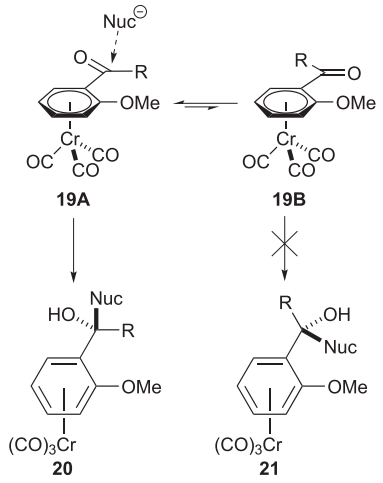
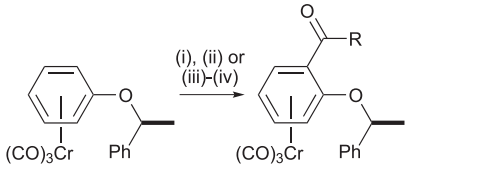


Figure 3. Diastereoselective nucleophilic addition to *ortho*-acyl substituted chromium tricarbonyl complexed arenes.

ortho-Benzoyl **26** and *ortho*-pivaloyl **27** complexes were obtained as single diastereoisomers (>99:1 dr)[19] in 67 and 65% yield, respectively, via direct acylation of the *ortho*-anion derived from (*S*)-**3** with benzyl chloride and pivaloyl chloride. Additionally, treatment of the *ortho*-anion derived from (*S*)-**3** with DMF gave, after work-up and chromatographic purification, *ortho*-formyl **22** in 82% yield and >99:1 dr. Repeated attempts at formation of the corresponding acetyl, propanoyl and isobutanoyl derivatives **23**–**25** via treatment of the *ortho*-anion derived from (*S*)-**3** with the requisite acyl chloride, chloroformate, *N*,*N*-dimethylamide or Weinreb amide reagents failed to yield the desired products. Therefore, the crude reaction mixtures resulting from treatment of the *ortho*-anion derived from (*S*)-**3** with acetaldehyde, propanaldehyde and isobutyraldehyde were subjected to an oxidation protocol with Ac_2O and DMSO to give the corresponding *ortho*-acyl derivatives **23**–**25** as single diastereoisomers (>99:1 dr) in 62–77% yield (Scheme 4).

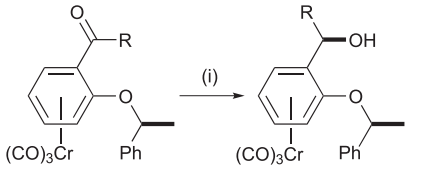


22 R = H, (ii). 82%, >99:1 dr
23 R = Me, (iii)-(iv). 63%,[a] >99:1 dr
24 R = Et, (iii)-(iv). 77%,[a] >99:1 dr
25 R = ^{i}Pr, (iii)-(iv). 62%,[a] >99:1 dr
26 R = Ph, (i). 67%, >99:1 dr
27 R = ^{t}Bu, (i). 65%, >99:1 dr

Scheme 4. Reagents and conditions: (i) LDA, THF, −78 °C, 3 h, then RCOCl, THF, −78 °C, 16 h; (ii) LDA, THF, −78 °C, 3 h, then DMF, THF, −78 °C, 16 h; (iii) LDA, THF, −78 °C, 3 h, RCHO, 16 h; (iv) DMSO, Ac_2O, rt, 16 h. [[a]Combined yield after two steps].

2.2. Reduction of *ortho*-acyl substituted complexes

The reduction of ketone complexes **23**–**27** was achieved with Super-Hydride®. Thus, 3.0 equiv of Super-Hydride® was added to solutions of the ketone complexes **23**–**27** in THF at −78 °C. Upon addition, the red colour of the solution, which is diagnostic of a conjugated *ortho*-acyl substituted arene chromium tricarbonyl complex, changed to yellow except when R=^{t}Bu as this complex was yellow in colour initially.[20] ^{1}H NMR spectroscopic analysis of the crude reaction mixtures following reduction with Super-Hydride® revealed that **14**–**17** were all formed in >99:1 dr. Purification of the crude reaction mixtures gave **14**–**17** as single diastereoisomers in ≥92% isolated yield. In the case of *ortho*-pivaloyl **27** a mixture of benzylic alcohols **13** and **18** was obtained in 58:42 dr; purification of this mixture gave **18** in 54% yield and **13** in 40% yield as single diastereoisomers (>99:1 dr) in each case (Scheme 5).



23 R = Me, >99:1 dr
24 R = Et, >99:1 dr
25 R = ^{i}Pr, >99:1 dr
26 R = Ph, >99:1 dr
27 R = ^{t}Bu, >99:1 dr

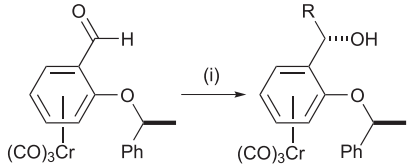
14 R = Me, 97%, >99:1 dr
15 R = Et, 96%, >99:1 dr
16 R = ^{i}Pr, 96%, >99:1 dr
17 R = Ph, 92%, >99:1 dr
18 R = ^{t}Bu, 54%, >99:1 dr[a]

Scheme 5. Reagents and conditions: (i) $LiBHEt_3$, THF, −78 °C, 2 h. [[a]Crude 42:58 dr (**13**:**18**); **13** was also isolated in 40% yield from this reaction].

The stereochemical outcome of these reactions is consistent with nucleophilic addition to the complexes in the *anti* conformation (see **19A**, Fig. 3) onto the face distal to the chromium tricarbonyl moiety. The poor diastereoselectivity (42:58 dr) observed for reduction of **27** is thought to arise from the fact that the carbonyl group of the ketone is not able to adopt a geometry which is coplanar with the complexed aryl ring and is consistent with the higher carbonyl absorption frequency in the infrared spectrum of **27** (1700 cm^{-1}) compared to that observed in the other acyl complexes **22**–**26** (~1670 cm^{-1}), and the fact that the solution of **27** in THF is not the diagnostic red colour which was observed for **22**–**26**.

2.3. Grignard addition to *ortho*-formyl substituted complexes

The epimeric alcohols **9**–**13** were accessed by an analogous procedure involving the addition of Grignard reagents to *ortho*-formyl **22**. Thus, treatment of **22** with the requisite Grignard reagents gave complexes **9**–**13** in >99:1 dr in each case; purification of the crude reaction mixtures gave **9**–**13** in good yield and >99:1 dr. However, the use of Grignard reagents containing a β-hydrogen also brought about concomitant reduction of the aldehyde moiety giving **28** in 24, 28 and 10% yield upon treatment of **22** with EtMgBr, ^{i}PrMgBr and ^{t}BuMgBr, respectively, although in each case the desired 1-(α-methylbenzyloxy)-2-(1′-hydroxyalkyl)benzene chromium tricarbonyl complexes were formed as the major products and were isolated in ≥70% yield and >99:1 dr (Scheme 6). The stereochemical outcome of these reactions is again consistent with nucleophilic addition to the complexes in the *anti* conformation (see **19A**, Fig. 3) onto the face distal to the chromium tricarbonyl moiety.



22, >99:1 dr

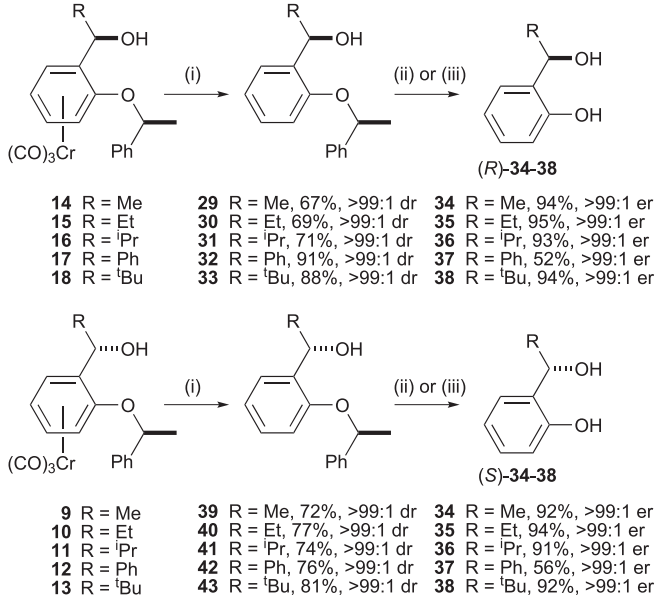
9 R = Me, 88%, >99:1 dr
10 R = Et, 76%, >99:1 dr
11 R = ^{i}Pr, 70%, >99:1 dr
12 R = Ph, 92%, >99:1 dr
13 R = ^{t}Bu, 83%, >99:1 dr
28 R = H[a]

Scheme 6. Reagents and conditions: (i) RMgX, THF, −78 °C, 2 h. [[a]Isolated in 10–28% yield and >99:1 dr upon reaction with EtMgBr, ^{i}PrMgBr and ^{t}BuMgBr].

2.4. Deprotection and decomplexation

Having developed methodology for the synthesis of single diastereoisomers of 1-(α-methylbenzyloxy)-2-(1′-hydroxyalkyl)benzene chromium tricarbonyl complexes, the removal of the chiral

auxiliary was investigated. However all attempts at this, while at the same time trying to retain the chromium tricarbonyl unit, were unsuccessful. Hydrogenolysis, using 5% Pd/C under four atmospheres of H_2, resulted in only starting material being recovered. Sodium/liquid ammonia reduction[21] also failed, even upon the addition of excess Na. Removal of the chromium tricarbonyl unit was therefore carried out prior to cleavage of the auxiliary. Solutions of complexes **14**–**18** and **9**–**13** in Et_2O were therefore allowed to stand in air and direct sunlight for two days to give decomplexed arenes **29**–**33** and **39**–**43**, respectively, in 67–91% yield as single diastereoisomers in each case after chromatographic purification. Subsequent cleavage of the auxiliary from **29**–**31**, **33**, **39**–**41** and **43** was achieved via hydrogenolysis to give the corresponding phenolic alcohols **34**–**36** and **38** in ≥91% isolated yield.[22] For substrates **32** and **42** it was decided that the auxiliary should be removed using Na in liquid NH_3, owing to the presence of two benzylic groups in each case. Thus, liquid NH_3 was added to a solution of the requisite ether at −78 °C. Sodium was subsequently added and the solution turned from yellow to an intense blue colour. Stirring was continued at −78 °C for 15 min, after which time MeOH was carefully added. The desired phenolic alcohols (*R*)-**37** and (*S*)-**37** were isolated in 52 and 56% yield, respectively, after purification by flash column chromatography. In each case the enantiopurity of the 2-(1′-hydroxyalkyl)phenols was determined to be >99:1 er (Scheme 7).[23]



Scheme 7. Reagents and conditions: (i) hν, O_2, Et_2O, rt, 48 h; (ii) H_2 (4 atm), Pd/C, EtOH, rt, 16 h; (iii) Na, NH_3, −78 °C, 15 min.

3. Conclusion

The use of the α-methylbenzyl group as a chiral auxiliary has allowed the diastereoselective *ortho*-deprotonation of [(*S*)-(α-methylbenzyloxy)benzene]Cr(CO)$_3$. When the resultant *ortho*-anions are treated with aldehydes two epimeric alcohol complexes are formed in relatively low dr. However, sequential *ortho*-acylation, followed by nucleophilic addition of either Super-Hydride® or Grignard reagents proceeds with high levels of diastereoselectivity. Subsequent removal of the chromium tricarbonyl unit followed by cleavage of the *O*-α-methylbenzyl group provides access to either antipode of the corresponding the 2-(1′-hydroxyalkyl)phenols in good yield and >99:1 er.

4. Experimental

4.1. General experimental

All reactions involving organometallic or other moisture-sensitive reagents were carried out under a nitrogen or argon atmosphere using standard vacuum line techniques and glassware that was flame dried and cooled under nitrogen before use. Solvents were dried according to the procedure outlined by Grubbs and co-workers.[24] Water was purified by a Millipore Elix® UV-10 system. All other solvents were used as supplied (analytical or HPLC grade) without prior purification. Organic layers were dried over $MgSO_4$. Thin layer chromatography was performed on aluminium plates coated with 60 F_{254} silica. Plates were visualised using UV light (254 nm), iodine, 1% aq $KMnO_4$, or 10% ethanolic phosphomolybdic acid. Flash column chromatography was performed on Kieselgel 60 silica.

Elemental analyses were recorded by the microanalysis service of the Inorganic Chemistry Laboratory, University of Oxford, U.K. Melting points were recorded on a Gallenkamp Hot Stage apparatus and are uncorrected. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter with a water-jacketed 10 cm cell. Specific rotations are reported in 10^{-1} deg cm^2 g^{-1} and concentrations in g/100 mL. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Selected characteristic peaks are reported in cm^{-1}. NMR spectra were recorded on Bruker Avance spectrometers in the deuterated solvent stated. The field was locked by external referencing to the relevant deuteron resonance. Low-resolution mass spectra were recorded on either a VG MassLab 20-250 or a Micromass Platform 1 spectrometer. Accurate mass measurements were run on either a Bruker MicroTOF, which was internally calibrated with polyalanine, or a Micromass GCT instrument fitted with a Scientific Glass Instruments BPX5 column (15 m×0.25 mm) using amyl acetate as a lock mass.

4.2. General procedure 1: diastereoselective *ortho*-deprotonation and alkylation

A solution of **3** (1.0 equiv) in THF was added to a solution of LDA (1.5 equiv) in THF at −78 °C and the resultant solution was stirred at −78 °C for 3 h. A solution of the requisite electrophile (5.0 equiv) in THF at −78 °C was then added. The reaction mixture was then allowed to warm to 0 °C over a period of 16 h. After this time satd aq $NaHCO_3$ was added and the organic layer was concentrated in vacuo. The residue was dissolved in CH_2Cl_2. The resultant solution was filtered through Al_2O_3 (eluent CH_2Cl_2) and the filtrate was concentrated in vacuo.

4.3. General procedure 2: oxidation of benzylic alcohols

The mixture of diastereoisomeric benzylic alcohols was dissolved in DMSO and Ac_2O was added slowly whilst N_2 was bubbled through the reaction mixture. The resultant solution was then allowed to stir at rt, in the dark, for 16 h. The reaction mixture was then diluted with benzene, cooled to 0 °C, and sequentially washed with 20% aq NaOH, water and brine, then concentrated in vacuo.

4.4. General procedure 3: reduction of *ortho*-acyl complexes with Super-Hydride®

$LiBHEt_3$ (1.0 M in THF, 3.0 equiv) was added to a solution of the requisite *ortho*-acyl complex (1.0 equiv) in THF at −78 °C and the resultant solution was stirred at −78 °C for 2 h. After this time MeOH was added and the reaction mixture was allowed to warm to rt. The reaction mixture was then concentrated in vacuo and the residue was redissolved in CH_2Cl_2. The resultant solution was

filtered through Al_2O_3 (eluent CH_2Cl_2) and the filtrate was concentrated in vacuo.

4.5. General procedure 4: reaction of *ortho*-formyl complexes with Grignard reagents

The requisite Grignard reagent (4.0 equiv) was added dropwise to a solution of *ortho*-formyl complex **22** (1.0 equiv) in THF at −78 °C and the resultant mixture was stirred at −78 °C for 2 h. After this time MeOH was added and the reaction mixture was allowed to warm to rt. The reaction mixture was then concentrated in vacuo and the residue was redissolved in CH_2Cl_2. The resultant solution was filtered through Al_2O_3 (eluent CH_2Cl_2) and the filtrate was concentrated in vacuo.

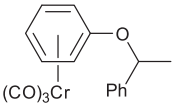
4.6. General procedure 5: decomplexation

A solution of the requisite complex in Et_2O was left open to the air and allowed to stand in direct sunlight for 2 days. After this time the reaction mixture was filtered through Al_2O_3 (eluent Et_2O) and the filtrate was concentrated in vacuo.

4.7. General procedure 6: O-deprotection via hydrogenolysis

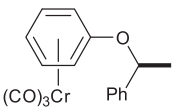
Pd/C (30% w/w) was added to a solution of the requisite *O*-α-methylbenzyl ether (1.0 equiv) in EtOH and the resultant mixture was vigorously stirred under H_2 (4 atm) for 16 h. After this time the reaction mixture was filtered through Celite (eluent MeOH) and the filtrate was concentrated in vacuo.

4.7.1. (RS)-[(α-Methylbenzyloxy)benzene]tricarbonylchromium(0) ***3****.*



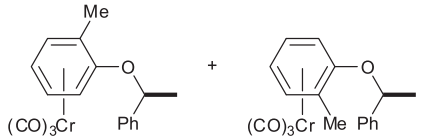
A solution of (*RS*)-α-methylbenzylalcohol **2** (578 mg, 4.74 mmol) in THF (20 mL) was added dropwise to a suspension of NaH (207 mg, 60% dispersion in mineral oil, 5.17 mmol) in THF (20 mL) at rt. The reaction mixture was stirred for 2 h at rt then a solution of (fluorobenzene)tricarbonylchromium(0) (1.00 g, 4.31 mmol) in THF (20 mL) was added and the resultant mixture was stirred at rt for 16 h before being concentrated in vacuo. The yellow residue was then dissolved in CH_2Cl_2 and the resultant solution was filtered through Al_2O_3 (eluent CH_2Cl_2) and concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 10:1) gave (*RS*)-**3** as a yellow oil (1.30 g, 90%); $C_{17}H_{14}CrO_4$ requires C, 61.1; H, 4.2%; found C, 61.1; H, 4.5%; mp 64–66 °C (pentane); ν_{max} ($CHCl_3$) 3090, 2960, 2930, 2870, 1990, 1840, 1470, 1465, 1455, 1440, 1375, 1155, 1090, 1080, 1075, 1070, 610; δ_H (300 MHz, $CDCl_3$) 1.63 (3H, d, *J* 6.4, C(α)*Me*), 4.80 (1H, t, *J* 6.1, C(4)*H*), 4.86 (1H, dd, *J* 7.0, 2.1, C(6)*H*), 5.10 (1H, q, *J* 6.4, C(α)*H*), 5.27 (1H, ddd, *J* 6.9, 2.5, 0.9, C(2)*H*), 5.37 (1H, dt, *J* 7.5, 1.3, C(5)*H*), 5.54 (1H, dt, *J* 7.3, 1.3, C(3)*H*), 7.29–7.42 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 24.5 (C(α)*Me*), 77.9 (*C*(α)), 78.0 (*C*(6)), 82.1 (*C*(2)), 85.3 (*C*(4)), 94.7 (*C*(5)), 95.8 (*C*(3)), 125.4, 128.4, 129.3 (*o*,*m*,*p*-*Ph*), 141.9 (*i*-*Ph*), 142.2 (*C*(1)), 192.3 (Cr(*CO*)$_3$); *m*/*z* (EI^+) 335 ($[M+H]^+$, 3%), 334 ($[M]^+$, 16%), 250 ($[M-C_3O_3]^+$, 41%).

4.7.2. (S)-[(α-Methylbenzyloxy)benzene]tricarbonylchromium(0) ***3****.*



A solution of (*S*)-α-methylbenzylalcohol **2** (578 mg, 4.74 mmol) in THF (20 mL) was added dropwise to a suspension of NaH (207 mg, 60% dispersion in mineral oil, 5.17 mmol) in THF (20 mL) at rt. The reaction mixture was stirred for 2 h at rt then a solution of (fluorobenzene)tricarbonylchromium(0) (1.00 g, 4.31 mmol) in THF (20 mL) was added and the resultant mixture was stirred at rt for 16 h before being concentrated in vacuo. The yellow residue was then dissolved in CH_2Cl_2 and the resultant solution was filtered through Al_2O_3 (eluent CH_2Cl_2) and concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 10:1) gave (*S*)-**3** as a yellow oil (1.25 g, 87%, >99:1 er); $[\alpha]_D^{24}$ −305 (*c* 0.3 in CH_2Cl_2).

4.7.3. (1pRS,αSR)- and (RS,RS)-[1-(α-Methylbenzyloxy)-2-methylbenzene]tricarbonylchromium(0) ***7*** *and* ***8****.*

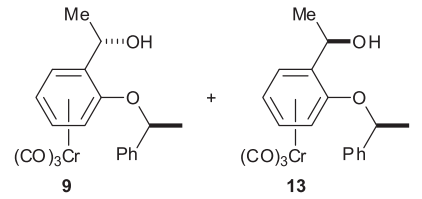


A solution of (*RS*)-α-methylbenzylalcohol **2** (55 mg, 0.45 mmol) THF (10 mL) was added dropwise to a suspension of NaH (20 mg, 60% dispersion in mineral oil, 0.49 mmol) in THF (10 mL) at rt. The reaction mixture was stirred for 2 h at rt then a solution of (*RS*)-(2-methyl-1-fluorobenzene)tricarbonylchromium(0) **5** (100 mg, 0.41 mmol) in THF (10 mL) was added and the resultant mixture was stirred at rt for 16 h before being concentrated in vacuo. The yellow residue was dissolved in CH_2Cl_2 and the resultant solution was filtered through Al_2O_3 (eluent CH_2Cl_2) and then concentrated in vacuo to give a 50:50 mixture of **7** and **8**. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 10:1) gave **7** as a yellow solid (69 mg, 49%) and **8** as a yellow oil (63 mg, 44%).

Data for **7**: $C_{18}H_{16}CrO_4$ requires C, 62.1; H, 4.6%; found C, 62.25; H, 4.6%; mp 66–67 °C (from 30–40 °C petroleum ether); ν_{max} ($CHCl_3$) 2890, 2880, 1970, 1880, 1470, 1385, 1175, 1080, 1020, 625; δ_H (500 MHz, $CDCl_3$) 1.66 (3H, d, *J* 6.5, C(α)*Me*), 2.27 (3H, s, C(6)*Me*), 4.85 (1H, t, *J* 6.1, C(4)*H*), 4.87 (1H, d, *J* 6.1, C(2)*H*), 5.11 (1H, q, *J* 6.5, C(α)*H*), 5.20 (1H, dt, *J* 6.1, 1.5, C(5)*H*), 5.50 (1H, dd, *J* 6.1, 1.3, C(3)*H*), 7.30–7.41 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 16.3 (C(6)*Me*), 24.8 (C(α)*Me*), 77.9 (*C*(α)), 78.3 (*C*(6)), 79.8 (*C*(2)), 86.2 (*C*(4)), 93.2 (*C*(5)), 97.3 (*C*(3)), 125.2, 128.2, 129.3 (*o*,*m*,*p*-*Ph*), 141.0 (*i*-*Ph*), 142.1 (*C*(1)), 195.7 (Cr(*CO*)$_3$); *m*/*z* (CI^+) 349 ($[M+H]^+$, 100%), 348 ($[M]^+$, 34%), 264 ($[M-C_3O_3]^+$, 47%).

Data for **8**: $C_{18}H_{16}CrO_4$ requires C, 62.1; H, 4.6%; found C, 62.2; H, 4.7%; ν_{max} ($CHCl_3$) 2930, 2920, 2910, 2890, 2870, 2860, 1965, 1880, 1480, 1455, 1385, 1155, 1100, 1070, 620; δ_H (200 MHz, $CDCl_3$) 1.63 (3H, d, *J* 6.4, C(α)*Me*), 2.23 (3H, s, *C*(6)*Me*), 4.94 (1H, t, *J* 6.3, C(4)*H*), 5.07–5.11 (2H, m, C(α)*H*, C(2)*H*), 5.22 (1H, dt, *J* 6.3, 1.4, C(3)*H*), 5.37 (1H, d, *J* 6.2, C(5)*H*), 7.33–7.44 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 16.2 (C(6)*Me*), 23.7 (C(α)*Me*), 78.5 (*C*(α)), 79.9 (*C*(2)), 88.1 (*C*(4)), 91.5 (*C*(5)), 95.3 (*C*(3)), 98.7 (*C*(6)), 126.0, 128.5, 129.0 (*o*,*m*,*p*-*Ph*), 140.8 (*i*-*Ph*), 142.1 (*C*(1)), 198.0 (Cr(*CO*)$_3$); *m*/*z* (EI^+) 348 ($[M]^+$, 7%), 264 ($[M-C_3O_3]^+$, 19%).

4.7.4. (1pR,1′S,αS)- and (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxyethyl)benzene]tricarbonylchromium(0) ***9*** *and* ***13****.*



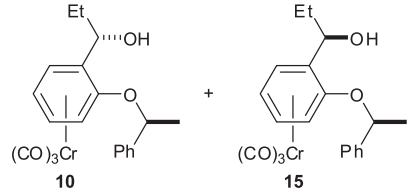
Following *general procedure* 1, treatment of (*S*)-**3** (100 mg, 1.50 mmol) with LDA (0.6 mL, 0.60 mmol) followed by acetaldehyde

(66 mg, 1.50 mmol) gave a 70:30 mixture of **9** and **13**, respectively. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1) gave **9** as a yellow oil (70 mg, 62%, >99:1 dr) and **13** as a yellow oil (20 mg, 18%, >99:1 dr).

Data for **9**: ν_{max} (CH_2Cl_2) 3600, 2940, 2930, 2870, 1960, 1880, 1530, 1495, 1430, 1380, 1350, 1265, 1210, 1175, 1155, 1110, 1075, 1030, 1010, 1000, 930, 895, 640, 630; δ_H (200 MHz, $CDCl_3$) 1.57 (3H, d, *J* 6.4, C(2′)H_3), 1.70 (3H, d, *J* 6.3, C(α)*Me*), 2.27 (1H, br s, O*H*), 4.82–4.88 (2H, m, C(6)*H*, C(4)*H*), 5.13–5.17 (2H, m, C(α)*H*, C(1′)*H*), 5.33–5.37 (1H, m, C(5)*H*), 5.96 (1H, dd, *J* 6.9, 1.1, C(3)*H*), 7.30–7.47 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 23.9 (*C*(2′)), 24.8 (C(α)*Me*), 63.9 (*C*(1′)), 76.7 (*C*(α)), 78.2 (*C*(6)), 85.5 (*C*(4)), 92.4 (*C*(5)), 94.4 (*C*(3)), 107.3 (*C*(2)), 125.1, 128.4, 129.4 (*o*,*m*,*p*-*Ph*), 140.1 (*C*(1)), 142.0 (*i*-*Ph*), 234.1 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 378 ($[M]^+$, 5%), 361 ($[M-OH]^+$, 100%), 274 ($[M-C_8H_8]^+$, 13%), 255 ($[M-C_8H_{10}O]^+$, 3%); HRMS (CI^+) $C_{19}H_{18}CrO_5^+$ ($[M]^+$) requires 378.0554; found 378.0550.

Data for **13**: ν_{max} (CH_2Cl_2) 3600, 2950, 2940, 2920, 2880, 1970, 1880, 1530, 1465, 1380, 1270, 1070, 1030, 1010, 1000, 930, 640, 635; δ_H (300 MHz, $CDCl_3$) 1.61 (3H, d, *J* 6.6, C(2′)*Me*), 1.69 (3H, d, *J* 6.5, C(α)*Me*), 2.54 (1H, br d, *J* 4.6, O*H*), 4.78–4.83 (2H, m, C(6)*H*, C(4)*H*), 5.10–5.13 (1H, m, C(1′)*H*), 5.18 (1H, q, *J* 6.5, C(α)*H*), 5.38 (1H, dt, *J* 5.9, 1.3, C(5)*H*), 5.82 (1H, dd, *J* 6.5, 1.3, C(3)*H*), 7.30–7.43 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 21.9 (*C*(2′)), 24.7 (C(α)*Me*), 64.6 (*C*(1′)), 76.0 (*C*(α)), 78.4 (*C*(6)), 83.9 (*C*(4)), 94.1 (*C*(5)), 94.6 (*C*(3)), 103.6 (*C*(2)), 124.9, 128.3, 129.2 (*o*,*m*,*p*-*Ph*), 140.5 (*C*(1)), 141.4 (*i*-*Ph*), 233.1 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 378 ($[M]^+$, 5%), 361 ($[M-OH]^+$, 100%), 225 ($[M-C_3HCrO_4]^+$, 7%); HRMS (CI^+) $C_{19}H_{18}CrO_5^+$ ($[M]^+$) requires 378.0554; found 378.0556.

4.7.5. (1pR,1′S,αS)- and (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxypropyl)benzene]tricarbonylchromium(0) ***10*** *and* ***15****.*

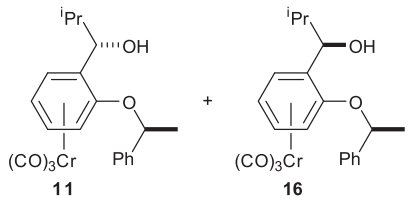


Following *general procedure* 1, treatment of (*S*)-**3** (100 mg, 1.50 mmol) with LDA (0.6 mL, 0.60 mmol) followed by propionaldehyde (87 mg, 1.50 mmol) gave a 65:35 mixture of **10** and **15**, respectively. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1) gave **10** as a yellow oil (73 mg, 62%, >99:1 dr) and **15** as a yellow oil (21 mg, 18%, >99:1 dr).

Data for **10**: ν_{max} (CH_2Cl_2) 3600, 2940, 2880, 1960, 1880, 1530, 1495, 1430, 1380, 1270, 1225, 1210, 1080, 1070, 930, 645, 630; δ_H (200 MHz, $CDCl_3$) 1.10 (3H, t, *J* 7.3, C(3′)H_3), 1.65 (3H, d, *J* 6.4, C(α)*Me*), 1.80–1.84 (2H, m, C(2′)H_2), 1.90 (1H, d, *J* 3.0, O*H*), 4.79 (1H, d, *J* 6.6, C(6)*H*), 4.87 (1H, t, *J* 6.3, C(4)*H*), 4.96–5.00 (1H, m, C(1′)*H*), 5.10 (1H, q, *J* 6.4, C(α)*H*), 5.34 (1H, dt, *J* 6.7, 1.4, C(5)*H*), 5.90 (1H, dd, *J* 6.3, 1.3, C(3)*H*), 7.26–7.45 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 10.1 (*C*(3′)), 24.8 (C(α)*Me*), 30.8 (*C*(2′)), 68.3 (*C*(1′)), 74.4 (*C*(α)), 78.33 (*C*(6)), 85.4 (*C*(4)), 92.8 (*C*(5)), 94.5 (*C*(3)), 106.5 (*C*(2)), 125.1, 128.4, 129.4 (*o*,*m*,*p*-*Ph*), 140.5 (*C*(1)), 142.1 (*i*-*Ph*), 234.0 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 392 ($[M]^+$, 9%), 375 ($[M-OH]^+$, 100%), 239 ($[M-C_3HCrO_4]^+$, 3%); HRMS (CI^+) $C_{20}H_{20}CrO_5^+$ ($[M]^+$) requires 392.0710; found 392.0703.

Data for **15**: ν_{max} (CH_2Cl_2) 3600, 2950, 2940, 2930, 2880, 1965, 1880, 1530, 1430, 1225, 1070, 900, 650, 640, 630; δ_H (200 MHz, $CDCl_3$) 1.17 (3H, t, *J* 7.4, C(3′)H_3), 1.68 (3H, d, *J* 6.4, C(α)*Me*), 1.82–1.87 (2H, m, C(2′)H_2), 2.73 (1H, d, *J* 5.9, O*H*), 4.61–4.66 (1H, m, C(1′)*H*), 4.75–4.79 (2H, m, C(6)*H*, C(4)*H*), 5.17 (1H, q, *J* 6.4, C(α)*H*), 5.38 (1H, dt, *J* 5.9, 1.3, C(5)*H*), 5.82 (1H, dd, *J* 6.5, 1.3, C(3)*H*), 7.27–7.45 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 11.3 (*C*(3′)), 24.7 (C(α)*Me*), 29.5 (*C*(2′)), 70.6 (*C*(1′)), 76.07 (*C*(α)), 78.3 (*C*(6)), 83.9 (*C*(4)), 94.6 (*C*(5)), 95.0 (*C*(3)), 103.8 (*C*(2)), 124.9, 128.2, 129.2 (*o*,*m*,*p*-*Ph*), 140.1 (*C*(1)), 141.4 (*i*-*Ph*), 233.2 (Cr(*C*O)$_3$); *m*/*z* (EI^+) 392 ($[M]^+$, 1%), 290 ($[M-C_8H_8]^+$, 10%); HRMS (CI^+) $C_{20}H_{20}CrO_5^+$ ($[M]^+$) requires 392.0710; found 392.0710.

4.7.6. (1pR,1′S,αS)- and (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′-methylpropyl)benzene]tricarbonylchromium(0) ***11*** *and* ***16****.*

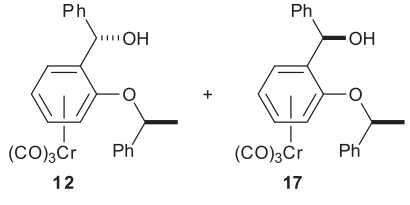


Following *general procedure* 1, treatment of (*S*)-**3** (100 mg, 1.50 mmol) with LDA (0.6 mL, 0.60 mmol) followed by isobutyraldehyde (108 mg, 1.50 mmol) gave a 65:35 mixture of **11** and **16**, respectively. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1) gave **11** as a yellow oil (75 mg, 62%, >99:1 dr) and **16** as a yellow oil (24 mg, 20%, >99:1 dr).

Data for **11**: ν_{max} (CH_2Cl_2) 3620, 3580, 2960, 2930, 2280, 1965, 1880, 1530, 1430, 1265, 1070, 1030, 1010, 1000, 930, 640, 630; δ_H (200 MHz, $CDCl_3$) 1.07 (6H, t, *J* 7.1, C(2′)Me_2), 1.65 (3H, d, *J* 6.4, C(α)*Me*), 1.79 (1H, d, *J* 3.0, O*H*), 1.99–2.02 (1H, m, C(2′)*H*), 4.76–4.79 (1H, d, *J* 6.8, C(1′)*H*), 4.86–4.89 (2H, m, C(6)*H*, C(4)*H*), 5.09 (1H, q, *J* 6.4, C(α)*H*), 5.35 (1H, dt, *J* 6.7, 1.4, C(5)*H*), 5.89 (1H, dd, *J* 6.2, 1.2, C(3)*H*), 7.27–7.45 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 14.3 (C(2′)Me_A), 17.1 (C(2′)Me_B), 25.0 (C(α)*Me*), 34.5 (*C*(2′)), 70.9 (*C*(1′)), 76.0 (*C*(α)), 78.5 (*C*(6)), 85.1 (*C*(4)), 93.4 (*C*(5)), 94.6 (*C*(3)), 106.1 (*C*(2)), 124.8, 128.1, 129.1 (*o*,*m*,*p*-*Ph*), 140.8 (*C*(1)), 141.9 (*i*-*Ph*), 233.4 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 389 ($[M-OH]^+$, 100%), 253 ($[M-C_3HCrO_4]^+$, 22%), 149 ($[M-C_{11}H_9CrO_4]^+$, 22%), 105 ($[M-C_{14}H_{17}CrO_4]^+$, 50%); HRMS (CI^+) $C_{21}H_{22}CrO_5^+$ ($[M]^+$) requires 406.0867; found 406.0869.

Data for **16**: ν_{max} (CH_2Cl_2) 3620, 3580, 2960, 2940, 2880, 1965, 1880, 1700, 1530, 1430, 1220, 1070, 1030, 650, 645, 630; δ_H (200 MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.8, C(2′)Me_A), 1.19 (3H, d, *J* 6.6, C(2′)Me_B), 1.69 (3H, d, *J* 6.4, C(α)*Me*), 2.19–2.22 (1H, m, C(2′)*H*), 2.99 (1H, d, *J* 9.0, O*H*), 3.93 (1H, t, *J* 8.0, C(1′)*H*), 4.74–4.76 (2H, m, C(6)*H*, C(4)*H*), 5.18 (1H, q, *J* 6.4, C(α)*H*), 5.35 (1H, dt, *J* 6.9, 1.3, C(5)*H*), 5.55 (1H, dd, *J* 6.2, 1.2, C(3)*H*), 7.28–7.46 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 19.1 (C(2′)Me_A), 20.3 (C(2′)Me_B), 24.9 (C(α)*Me*), 34.1 (*C*(2′)), 76.1 (*C*(1′)), 78.4 (*C*(α)), 79.1 (*C*(6)), 83.6 (*C*(4)), 94.1 (*C*(5)), 97.1 (*C*(3)), 103.5 (*C*(2)), 124.8, 128.3, 129.2 (*o*,*m*,*p*-*Ph*), 139.3 (*C*(1)), 141.3 (*i*-*Ph*), 233.0 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 252 ($[M-C_3HCrO_4]^+$, 6%); HRMS (CI^+) $C_{21}H_{22}CrO_5^+$ ($[M]^+$) requires 406.0867; found 406.0886.

4.7.7. (1pR,1′S,αS)- and (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-1′-phenylmethyl)benzene]tricarbonylchromium(0) ***12*** *and* ***17****.*



Following *general procedure* 1, treatment of (*S*)-**3** (100 mg, 1.50 mmol) with LDA (0.6 mL, 0.60 mmol) followed by benzaldehyde (159 mg, 1.50 mmol) gave a 65:35 mixture of **12** and **17**, respectively.

Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1) gave **12** as a yellow oil (80 mg, 61%, >99:1 dr) and **17** as a yellow oil (25 mg, 19%, >99:1 dr).

Data for **12**: $C_{24}H_{20}CrO_5$ requires C, 65.3; H, 4.5%; found C, 65.3; H, 4.6%; mp 127–128 °C (pentane); ν_{max} ($CHCl_3$) 3600, 3470, 2940, 2880, 2860, 1965, 1885, 1605, 1600, 1495, 1490, 1460, 1455, 1450, 1445, 1380, 1080, 1070, 1065, 1020, 1010, 620; δ_H (300 MHz, $CDCl_3$) 1.67 (3H, d, *J* 6.4, C(α)*Me*), 2.35 (1H, d, *J* 3.0, O*H*), 4.77 (1H, d, *J* 6.8, C(6)*H*), 4.87 (1H, t, *J* 6.3, C(4)*H*), 5.13 (1H, q, *J* 6.4, C(α)*H*), 5.32–5.35 (1H, m, C(5)*H*), 6.07 (1H, d, *J* 2.8, C(1′)*H*), 6.11–6.14 (1H, m, C(3)*H*), 6.66–6.68 (2H, m, *Ph*), 6.94–6.97 (3H, m, *Ph*), 7.09–7.11 (3H, m, *Ph*), 7.39–7.42 (2H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 24.8 (C(α)*Me*), 69.5 (*C*(6)), 75.4, 77.9 (*C*(α), C(1′)), 84.9 (*C*(4)), 92.6 (*C*(2)), 94.5 (*C*(5)), 104.9 (*C*(3)), 125.0, 127.0, 128.3, 128.4, 128.8, 129.2 (*o*,*m*,*p*-*Ph*), 139.7 (*C*(1)), 141.6, 142.1 (*i*-*Ph*), 235.1 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 440 ($[M]^+$, 4%), 423 ($[M-OH]^+$, 100%).

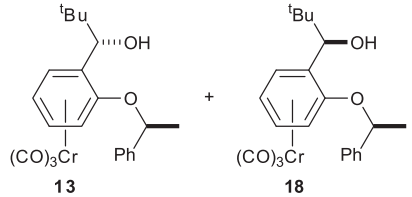
Data for **17**: $C_{24}H_{20}CrO_5$ requires C, 65.3; H, 4.5%; found C, 65.35; H, 4.5%; mp 117–121 °C (dec, pentane); ν_{max} ($CHCl_3$) 3600, 2960, 2940, 2930, 1965, 1890, 1495, 1460, 1450, 1380, 1180, 1160, 1090, 860, 635, 625; δ_H (300 MHz, $CDCl_3$) 1.74 (3H, d, *J* 6.5, C(α)*Me*), 3.10 (1H, d, *J* 4.6, O*H*), 4.66 (1H, t, *J* 6.0, C(4)*H*), 4.78 (1H, d, *J* 6.6, C(6)*H*), 5.13 (1H, dd, *J* 6.3, 1.3, C(3)*H*), 5.20 (1H, q, *J* 6.4, C(α)*H*), 5.34 (1H, dt, *J* 6.6, 1.3, C(5)*H*), 6.05 (1H, d, *J* 4.5, C(1′)*H*), 7.22–7.48 (8H, m, *Ph*), 7.58–7.60 (2H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 24.8 (C(α)*Me*), 71.2 (*C*(6)), 75.8, 78.5 (*C*(α), *C*(1′)), 84.1 (*C*(4)), 94.7 (*C*(2)), 95.9 (*C*(5)), 103.5 (*C*(3)), 125.1, 127.1, 128.4, 128.6, 128.8, 129.4 (*o*,*m*,*p*-*Ph*), 139.6 (*C*(1)), 141.0, 141.6 (*i*-*Ph*), 233.3 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 423 ($[M-OH]^+$, 17%).

*4.7.7.1. X-ray crystal structure determination for (1pRS,1′RS,αSR)-**17**.* Data were collected using an Enraf–nonius CAD4 diffractometer with graphite monochromated Cu Kα radiation using standard procedures at 190 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[25]

X-ray crystal structure data for (1*pRS*,1′*RS*,α*SR*)-**17** [$C_{24}H_{20}CrO_5$]: *M*=440.4, monoclinic, space group *P* $2_1/n$, *a*=10.6255(7) Å, *b*=6.6609(6) Å, *c*=29.424(2) Å, β=95.54(1)°, *V*=2072.8(1) Å^3, *Z*=4, yellow block, crystal dimensions=0.20×0.20×0.20 mm^3. The final parameters were wR_2=0.033 and R_1=0.028 [$I>3.0\sigma(I)$].

Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 776717. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

*4.7.8. (1pR,1′S,αS)- and (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′, 2′-dimethylpropyl)benzene]tricarbonylchromium(0) **13** and **18**.*



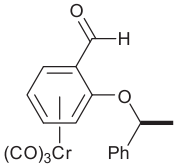
13 **18**

Following *general procedure* 1, treatment of (*S*)-**3** (100 mg, 1.50 mmol) with LDA (0.6 mL, 0.60 mmol) followed by pivalaldehyde (129 mg, 1.50 mmol) gave a 75:25 mixture of **13** and **18**, respectively. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1) gave **13** as a yellow oil (75 mg, 60%, >99:1 dr) and **18** as a yellow oil (19 mg, 15%, >99:1 dr).

Data for **13**: $C_{22}H_{24}CrO_5$ requires C, 62.9; H, 5.7%; found C, 63.0; H, 5.6%; mp 143–144 °C (dec, pentane/Et_2O); ν_{max} ($CHCl_3$) 3590, 2950, 2940, 2930, 1920, 2880, 1960, 1885, 1605, 1590, 1485, 1460, 1390, 1380, 1370, 1350, 1170, 1155, 1095, 1085, 1080, 1070, 1010, 900, 645, 620; δ_H (300 MHz, $CDCl_3$) 1.08 (9H, s, CMe_3), 1.64 (1H, d, *J* 2.7, O*H*), 1.66 (3H, d, *J* 6.4, C(α)*Me*), 4.73 (1H, d, *J* 6.6, C(6)*H*), 4.80 (1H, d, *J* 2.6, C(1′)*H*), 4.88 (1H, t, *J* 6.3, C(4)*H*), 5.07 (1H, q, *J* 6.4, C(α)*H*), 5.36 (1H, dt, *J* 6.7, 1.4, C(5)*H*), 5.88 (1H, dd, *J* 6.3, 1.3, C(3)*H*), 7.28–7.43 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 25.1 (C(α)*Me*), 26.0 (CMe_3), 36.6 (*C*Me_3), 72.6 (*C*(1′)), 75.6 (*C*(α)), 79.0 (*C*(6)), 84.8 (*C*(4)), 94.6 (*C*(2)), 95.2 (*C*(5)), 106.0 (*C*(3)), 125.1, 128.3, 129.4 (*o*,*m*,*p*-*Ph*), 142.3 (*i*-*Ph*), 138.7 (*C*(1)), 232.7 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 421 ($[M+H]^+$, 9%), 403 ($[M-OH]^+$, 100%).

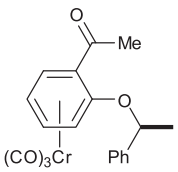
Data for **18**: $C_{22}H_{24}CrO_5$ requires C, 62.9; H, 5.7%; found C, 62.7; H, 5.6%; mp 186–190 °C (dec, Et_2O); ν_{max} ($CHCl_3$) 3570, 2950, 2915, 2905, 2870, 1965, 1890, 1590, 1470, 1460, 1395, 1380, 1370, 1175, 1095, 1070, 1015, 900, 620; δ_H (300 MHz, $CDCl_3$) 1.08 (9H, s, CMe_3), 1.71 (3H, d, *J* 6.4, C(α)*Me*), 3.85 (1H, d, *J* 3.4, C(1′)*H*), 4.74 (1H, dt, *J* 6.2, 0.5, C(4)*H*), 4.78 (1H, d, *J* 6.8, C(6)*H*), 5.19 (1H, q, *J* 6.4, C(α)*H*), 5.32–5.34 (1H, m, C(5)*H*), 5.47 (1H, dd, *J* 6.2, 1.2, C(3)*H*), 7.31–7.45 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 25.0 (C(α)*Me*), 26.8 (CMe_3), 38.2 (*C*Me_3), 73.3 (*C*(1′)), 76.0 (*C*(α)), 79.7 (*C*(6)), 83.9 (*C*(4)), 94.3 (*C*(2)), 98.0 (*C*(5)), 101.1 (*C*(3)), 125.1, 128.6, 129.5 (*o*,*m*,*p*-*Ph*), 140.1 (*C*(1)), 141.7 (*i*-*Ph*), 233.0 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 438 ($[M+NH_4]^+$, 8%), 420 ($[M]^+$, 13%), 403 ($[M-OH]^+$, 100%).

*4.7.9. (1pR,αS)-[1-(α-Methylbenzyloxy)-2-formylbenzene]tricarbonylchromium(0) **22**.*



Following *general procedure* 1, treatment of (*S*)-**3** (500 mg, 1.50 mmol) with LDA (3.0 mL, 3.00 mmol) followed by DMF (548 mg, 7.50 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 2:1), **22** as a red solid (445 mg, 82%, >99:1 dr); $C_{18}H_{14}CrO_5$ requires C, 59.7; H, 3.9%; found C, 59.45; H, 3.7%; mp 89–93 °C (pentane); $[\alpha]_D^{24}$ +642 (*c* 0.8 in CH_2Cl_2); ν_{max} ($CHCl_3$) 2930, 2890, 2880, 1985, 1910, 1680, 1495, 1455, 1450, 1380, 1175, 1155, 1090, 1065, 610; δ_H (300 MHz, $CDCl_3$) 1.70 (3H, d, *J* 6.4, C(α)*Me*), 4.84 (1H, d, *J* 6.9, C(6)*H*), 4.91 (1H, t, *J* 6.4, C(4)*H*), 5.25 (1H, q, *J* 6.4, C(α)*H*), 5.65 (1H, dt, *J* 7.3, 1.3, C(5)*H*), 6.22 (1H, dd, *J* 6.4, 1.3, C(3)*H*), 7.30–7.44 (5H, m, *Ph*), 10.22 (1H, s, C(1′)*H*); δ_C (50 MHz, $CDCl_3$) 24.5 (C(α)*Me*), 75.1 (*C*(6)), 78.7 (*C*(α)), 84.1 (*C*(4)), 92.6 (*C*(5)), 95.2 (*C*(3)), 125.2, 128.7, 129.6 (*o*,*m*,*p*-*Ph*), 141.2 (*i*-*Ph*), 144.6 (*C*(1)), 186.0 (*C*(1′)), 231.7 (Cr(*C*O)$_3$); *m*/*z* (CI^+) 363 ($[M+H]^+$, 18%), 278 ($[M-C_3O_3]^+$, 5%).

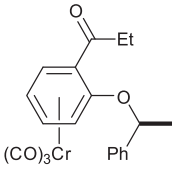
*4.7.10. (1pR,αS)-[1-(α-Methylbenzyloxy)-2-acetylbenzene]tricarbonylchromium(0) **23**.*



Following *general procedure* 1, treatment of (*S*)-**3** (500 mg, 1.50 mmol) with LDA (3.00 mL, 3.00 mmol) followed by acetaldehyde (330 mg, 7.50 mmol) gave a 70:30 mixture of **9** and **14**, respectively. Following *general procedure* 2, this mixture was treated with Ac_2O (15 mL, 0.16 mmol) and DMSO (22.5 mL) to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 2:1), **23** as a red oil (355 mg, 63%, >99:1 dr); $C_{19}H_{16}CrO_5$ requires C, 60.6; H, 4.3%; found C, 60.6; H, 4.05%; $[\alpha]_D^{25}$ +237 (*c* 0.2 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 2960, 2940, 2870, 1975, 1900,

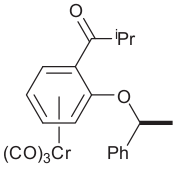
1675, 1520, 1430, 1220, 1110, 1065, 1030, 1010, 1000, 930, 650, 630; δ_H (200 MHz, $CDCl_3$) 1.70 (3H, d, *J* 6.4, C(α)*Me*), 2.19 (3H, s, C(2′)H_3), 4.81–4.85 (2H, m, C(4)*H*, C(6)*H*), 5.29 (1H, q, *J* 6.3, C(α)*H*), 5.60 (1H, t, *J* 6.5, C(5)*H*), 6.24 (1H, d, *J* 6.9, C(3)*H*), 7.29–7.42 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 24.4 (C(α)*Me*), 31.3 (*C*(2′)), 75.7 (*C*(α)), 78.6 (*C*(6)), 84.3 (*C*(4)), 90.1 (*C*(2)), 95.9 (*C*(5)), 96.1 (*C*(3)), 125.1, 128.6, 129.4 (*o*,*m*,*p*-*Ph*), 141.1 (*C*(1)), 143.3 (*i*-*Ph*), 166.7 (*C*(1′)), 195.7 ($Cr(CO)_3$); *m*/*z* (EI^+) 376 ($[M]^+$, 3%).

4.7.11. (1pR,αS)-[1-(α-Methylbenzyloxy)-2-propanoylbenzene]tricarbonylchromium(0) ***24****.*



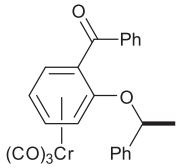
Following *general procedure* 1, treatment of (*S*)-**3** (500 mg, 1.50 mmol) with LDA (3.0 mL, 3.0 mmol) followed by propionaldehyde (436 mg, 7.50 mmol) gave a 65:35 mixture of **10** and **15**, respectively. Following *general procedure* 2, this mixture was treated with Ac_2O (15 mL, 0.16 mmol) and DMSO (22.5 mL) to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 2:1), **24** as a red solid (450 mg, 77%, >99:1 dr); $C_{20}H_{18}CrO_5$ requires C, 61.5; H, 4.6%; found C, 61.2; H, 4.2%; mp 108–109 °C (pentane/Et_2O); $[\alpha]_D^{25}$ +203 (*c* 0.1 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 2960, 2940, 2920, 2870, 1975, 1890, 1675, 1520, 1430, 1380, 1350, 1230, 1220, 1070, 925, 650, 645, 625; δ_H (200 MHz, $CDCl_3$) 1.26 (3H, t, *J* 7.1, C(3′)H_3), 1.72 (3H, d, *J* 6.4, C(α)*Me*) 3.11 (2H, q, *J* 7.2, C(2′)H_2), 4.82–4.86 (2H, m, C(4)*H*, C(6)*H*), 5.28 (1H, q, *J* 6.4, C(α)*H*), 5.58 (1H, t, *J* 6.5, C(5)*H*), 6.24 (1H, dt, *J* 6.7, 1.4, C(3)*H*), 7.26–7.46 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 8.5 (*C*(3′)), 24.5 (C(α)*Me*), 36.4 (*C*(2′)), 75.8 (*C*(α)), 78.5 (*C*(6)), 84.3 (*C*(4)), 90.6 (*C*(2)), 96.0 (*C*(5)), 96.1 (*C*(3)), 125.2, 128.6, 129.4 (*o*,*m*,*p*-*Ph*), 141.2 (*C*(1)), 142.9 (*i*-*Ph*), 199.2 (*C*(1′)), 232.1 ($Cr(CO)_3$); *m*/*z* (EI^+) 390 ($[M]^+$, 75%), 306 ($[M-C_3O_3]^+$, 18%), 201 ($[M-C_{11}H_9O_3]^+$, 64%).

4.7.12. (1pR,αS)-[1-(α-Methylbenzyloxy)-2-(2′-methylpropanoyl) benzene]tricarbonylchromium(0) ***25****.*



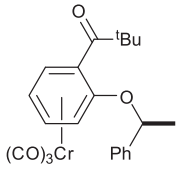
Following *general procedure* 1, treatment of (*S*)-**3** (500 mg, 1.50 mmol) with LDA (3.0 mL, 3.0 mmol) followed by isobutyraldehyde (541 mg, 7.50 mmol) gave a 65:35 mixture of **11** and **16**, respectively. Following *general procedure* 2, this mixture was treated with Ac_2O (15 mL, 0.16 mmol) and DMSO (22.5 mL) to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 2:1), **25** as a red solid (376 mg, 62%, >99:1 dr); $C_{21}H_{20}CrO_5$ requires C, 62.4; H, 5.0%; found C, 62.5; H, 5.1%; mp 137–138 °C (pentane/Et_2O); $[\alpha]_D^{25}$ +193 (*c* 0.2 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 2950, 2940, 2930, 1975, 1900, 1675, 1520, 1220, 1215, 1065, 985, 925, 645, 625; δ_H (200 MHz, $CDCl_3$) 0.88 (6H, t, *J* 6.1, C(2′)Me_2), 1.70 (3H, d, *J* 6.4, C(α)*Me*), 3.65 (1H, sep, *J* 6.7, C(2′)*H*), 4.81–4.84 (2H, m, C(4)*H*, C(6)*H*), 5.29 (1H, q, *J* 6.4, C(α)*H*), 5.59 (1H, dt, *J* 6.2, 1.4, C(5)*H*), 6.10 (1H, dd, *J* 6.5, 1.4, C(3)*H*), 7.27–7.45 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 19.4 (C(2′)Me_A), 19.8 (C(2′)Me_B), 24.5 (C(α)*Me*), 39.3 (*C*(2′)), 75.1 (*C*(α)), 78.5 (*C*(6)), 83.9 (*C*(4)), 91.2 (*C*(2)), 95.6 (*C*(5)), 96.0 (*C*(3)), 124.9, 128.4, 129.2 (*o*,*m*,*p*-*Ph*), 141.0 (*C*(1)), 142.6 (*i*-*Ph*), 204.2 (*C*(1′)), 231.6 ($Cr(CO)_3$); *m*/*z* (CI^+) 405 ($[M+H]^+$, 7%), 301 ($[M-C_8H_9]^+$, 15%), 165 ($[M-C_{11}H_9CrO_3]^+$, 53%).

4.7.13. (1pR,αS)-[1-(α-Methylbenzyloxy)-2-benzoylbenzene]tricarbonylchromium(0) ***26****.*



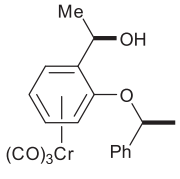
Following *general procedure* 1, treatment of (*S*)-**3** (100 mg, 0.30 mmol) with LDA (0.6 mL, 0.60 mmol) followed by benzoyl chloride (210 mg, 1.50 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 2:1), **26** as a red oil (88 mg, 67%, >99:1 dr); $C_{23}H_{18}CrO_5$ requires C, 65.75; H, 4.1%; found C, 65.95; H, 4.0%; mp 110–111 °C (pentane); $[\alpha]_D^{25}$ −200 (*c* 0.3 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 2950, 2940, 2930, 1980, 1900, 1670, 1650, 1600, 1585, 1520, 1380, 1095, 1070, 1030, 915, 635, 625; δ_H (300 MHz, $CDCl_3$) 1.24 (3H, d, *J* 6.4, C(α)*Me*), 4.81–4.86 (2H, m, C(6)*H*, C(4)*H*), 5.07 (1H, q, *J* 6.4, C(α)*H*), 5.51 (1H, dt, *J* 6.6, 1.3, C(5)*H*), 5.95 (1H, dd, *J* 6.4, 1.3, C(3)*H*), 7.11–7.14 (2H, m, *Ph*), 7.31–7.35 (3H, m, *Ph*), 7.50 (2H, t, *J* 7.7, *Ph*), 7.61 (1H, t, *J* 7.4, *Ph*), 7.91 (2H, dd, *J* 8.8, 1.4, *Ph*); δ_C (50 MHz, $CDCl_3$) 24.0 (C(α)*Me*), 74.7 (*C*(6)), 78.4 (*C*(α)), 82.9 (*C*(4)), 95.0 (*C*(5)), 96.4 (*C*(2)), 97.2 (*C*(3)), 125.3, 125.8, 128.4, 129.2, 129.3, 133.0 (*o*,*m*,*p*-*Ph*), 138.6 (*C*(1)), 140.5, 141.7 (*i*-*Ph*), 192.9 (*C*(1′)), 230.2 ($Cr(CO)_3$); *m*/*z* (CI^+) 439 ($[M+H]^+$, 29%), 354 ($[M-C_3O_3]^+$, 68%).

4.7.14. (1pR,αS)-[1-(α-Methylbenzyloxy)-2-(2′,2′-dimethylpropanoyl)benzene]tricarbonylchromium(0) ***27****.*



Following *general procedure* 1, treatment of (*S*)-**3** (100 mg, 0.30 mmol) with LDA (0.6 mL, 0.60 mmol) followed by pivaloyl chloride (180 mg, 1.50 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 2:1), **27** as a yellow solid (81 mg, 65%, >99:1 dr); $C_{22}H_{22}CrO_5$ requires C, 63.15; H, 5.3%; found C, 63.4; H, 5.2%; mp 146–148 °C (hexane); $[\alpha]_D^{25}$ −157 (*c* 0.1 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 2940, 2930, 2910, 2880, 1970, 1900, 1710, 1605, 1520, 1480, 1380, 1370, 1175, 1070, 1030, 925, 630; δ_H (300 MHz, $CDCl_3$) 1.33 (9H, s, CMe_3), 1.59 (3H, d, *J* 6.5, C(α)*Me*), 4.70–4.72 (2H, m, C(6)*H*, C(4)*H*), 5.12 (1H, q, *J* 6.4, C(α)*H*), 5.33 (1H, dt, *J* 6.7, 1.2, C(5)*H*), 5.49 (1H, dd *J* 6.2, 1.3, C(3)*H*), 7.31–7.44 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 24.6 (C(α)*Me*), 27.2 (CMe_3), 45.1 (*C*Me_3), 73.8 (*C*(6)), 79.4 (*C*(α)), 81.7 (*C*(4)), 94.0 (*C*(5)), 94.3 (*C*(3)), 106.3 (*C*(2)), 125.2, 128.5, 129.4 (*o*,*m*,*p*-*Ph*), 139.0 (*C*(1)), 142.0 (*i*-*Ph*), 206.4 (*C*(1′)), 232.7 ($Cr(CO)_3$); *m*/*z* (CI^+) 419 ($[M+H]^+$, 3%), 334 ($[M-C_3O_3]^+$, 50%).

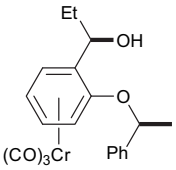
4.7.15. (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxyethyl) benzene]tricarbonylchromium(0) ***14****.*



Following *general procedure* 3, treatment of **23** (50 mg, 0.133 mmol) with $LiBHEt_3$ (1.0 M in THF, 0.40 mL, 0.40 mmol) gave,

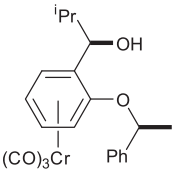
after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **14** as a yellow oil (49 mg, 97%, >99:1 dr).

4.7.16. (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxypropyl) benzene]tricarbonylchromium(0) ***15****.*



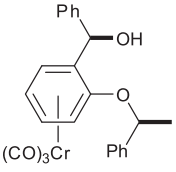
Following *general procedure* 3, treatment of **24** (50 mg, 0.133 mmol) with $LiBHEt_3$ (1.0 M in THD, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **15** as a yellow oil (48 mg, 96%, >99:1 dr).

4.7.17. (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′-methylpropyl)benzene]tricarbonylchromium(0) ***16****.*



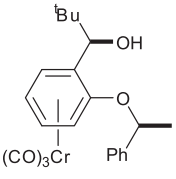
Following *general procedure* 3, treatment of **25** (50 mg, 0.133 mmol) with $LiBHEt_3$ (1.0 M in THD, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **16** as a yellow oil (48 mg, 96%, >99:1 dr).

4.7.18. (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-1′-phenylmethyl)benzene]tricarbonylchromium(0) ***17****.*



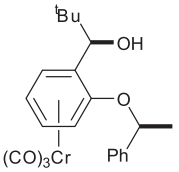
Following *general procedure* 3, treatment of **26** (50 mg, 0.133 mmol) with $LiBHEt_3$ (1.0 M in THD, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **17** as a yellow oil (46 mg, 92%, >99:1 dr).

4.7.19. (1pR,1′R,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′,2′-dimethylpropyl)benzene]tricarbonylchromium(0) ***18****.*



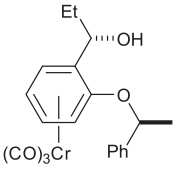
Following *general procedure* 3, treatment of **27** (50 mg, 0.133 mmol) with $LiBHEt_3$ (1.0 M in THF, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **13** as a yellow oil (20 mg, 40%, >99:1 dr) and **18** as a yellow oil (27 mg, 54%, >99:1 dr).

4.7.20. (1pR,1′S,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxyethyl) benzene]tricarbonylchromium(0) ***9****.*



Following *general procedure* 4, treatment of **22** (50 mg, 0.133 mmol) with MeMgBr (1.0 M in THF, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **9** as a yellow oil (46 mg, 88%, >99:1 dr).

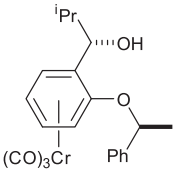
4.7.21. (1pR,1′S,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxypropyl) benzene]tricarbonylchromium(0) ***10****.*



Following *general procedure* 4, treatment of **22** (50 mg, 0.133 mmol) with EtMgBr (1.0 M in THF, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **10** as a yellow oil (41 mg, 76%, >99:1 dr) and (1*pR*,α*S*)-[1-(α-methylbenzyloxy)-2-(hydroxymethyl)benzene] tricarbonylchromium(0) **28** as a yellow oil (12 mg, 24%, >99:1 dr).

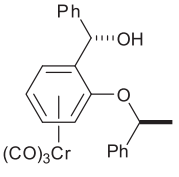
Data for **28**: δ_H (300 MHz, $CDCl_3$) 1.66 (3H, d, *J* 6.4, C(α)*Me*), 2.05 (1H, br s, O*H*), 4.52 (1H, br d, *J* 14.0, C(1′)H_A), 4.76 (1H, br d, *J* 14.0, C(1′)H_B), 4.85 (2H, m, C(4)*H*, C(6)*H*), 5.13 (1H, q, *J* 6.4, C(α)*H*), 5.34 (1H, app t, *J* 6.5, C(3)*H*), 5.78 (1H, app d, *J* 6.0, C(5)*H*), 7.31–7.44 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 24.7 (C(α)*Me*), 59.9 (*C*(1′)), 76.8 (*C*(α)), 78.5 (*C*(6)), 85.0 (*C*(4)), 94.2 (*C*(5)), 95.3 (*C*(3)), 100.4 (*C*(2)), 125.1, 128.4, 129.4 (*o*,*m*,*p*-*Ph*), 140.7 (*C*(1)), 141.9 (*i*-*Ph*), 233.7 (Cr(*CO*)$_3$); *m*/*z* (CI^+) 382 ($[M+NH_4]^+$, 5%), 364 ($[M]^+$, 25%), 334 ($[M-OH]^+$, 100%); HRMS (CI^+) $C_{18}H_{16}CrO_5^+$ ($[M]^+$) requires 364.0397; found 364.0400.

4.7.22. (1pR,1′S,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′-methylpropyl)benzene]tricarbonylchromium(0) ***11****.*



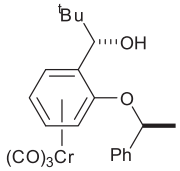
Following *general procedure* 4, treatment of **22** (50 mg, 0.133 mmol) with ^iPrMgCl (1.0 M in THF, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **11** as a yellow oil (39 mg, 70%, >99:1 dr) and **28** as a yellow oil (14 mg, 28%, >99:1 dr).

4.7.23. (1pR,1′S,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-1′-phenylmethyl)benzene]tricarbonylchromium(0) ***12****.*



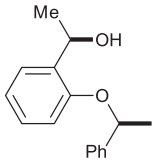
Following *general procedure* 4, treatment of **22** (50 mg, 0.133 mmol) with PhMgCl (1.0 M in THF, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **12** (56 mg, 92%, >99:1 dr).

4.7.24. (1pR,1′S,αS)-[1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′,2′-dimethylpropyl)benzene]tricarbonylchromium(0) ***13***.



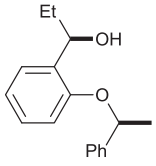
Following *general procedure* 4, treatment of **22** (50 mg, 0.133 mmol) with ^{t}BuMgCl (1.0 M in THF, 0.40 mL, 0.40 mmol) gave, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **13** as a yellow oil (48 mg, 83%, >99:1 dr) and **28** as a yellow oil (5 mg, 10%, >99:1 dr).

4.7.25. (1′R,αS)-1-(α-Methylbenzyloxy)-2-(1′-hydroxyethyl)benzene ***29***.



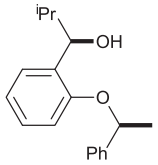
Following *general procedure* 5, **14** (200 mg, 0.53 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **29** as a colourless oil (86 mg, 67%, >99:1 dr); $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%; found C, 79.4; H, 7.4%; $[\alpha]_D^{25}$ +75.3 (*c* 0.3 in CH_2Cl_2), ν_{max} (CH_2Cl_2) 3600, 2960, 2930, 2870, 1600, 1590, 1490, 1225, 1080, 1010, 935; δ_H (200 MHz, $CDCl_3$) 1.62 (3H, d, *J* 6.5, C(2′)H_3), 1.71 (3H, d, *J* 6.4, C(α)*Me*), 2.91 (1H, br s, O*H*), 5.26 (1H, q, *J* 6.5, C(1′)*H*), 5.41 (1H, q, *J* 6.4, C(α)*H*), 6.76 (1H, d, *J* 8.1, *Ar*), 6.93 (1H, dt, *J* 7.0, 0.6, *Ar*), 7.11 (1H, dt, *J* 7.8, 1.7, *Ar*), 7.25–7.78 (6H, m, *Ar*); δ_C (50 MHz, $CDCl_3$) 23.1 (*C*(2′)), 24.4 (C(α)*Me*), 66.7 (*C*(1′)), 76.1 (*C*(α)), 113.1, 120.8, 125.4, 126.2, 127.7, 128.0, 128.8 (*Ar, o,m,p-Ph*), 134.0 (*C*(2)), 142.8 (*i-Ph*), 154.7 (*C*(1)); *m/z* (CI^+) 242 ($[M]^+$, 27%), 225 ($[M-OH]^+$, 100%), 121 ($[M-C_8H_9O]^+$, 45%).

4.7.26. (1′R,αS)-1-(α-Methylbenzyloxy)-2-(1′-hydroxypropyl)benzene ***30***.



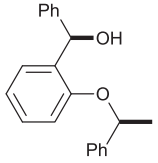
Following *general procedure 5*, **15** (200 mg, 0.51 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **30** as a colourless oil (90 mg, 69%, >99:1 dr); $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.9%; found C, 79.9; H, 7.9%; $[\alpha]_D^{25}$ +80.8 (*c* 0.3 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3600, 3560, 2960, 2940, 2930, 2880, 1600, 1590, 1490, 1225, 1070, 1010; δ_H (200 MHz, $CDCl_3$) 1.03 (3H, t, *J* 7.5, C(3′)H_3), 1.68 (3H, d, *J* 6.4, C(α)*Me*), 1.93 (2H, quin, *J* 7.0, C(2′)H_2), 2.79 (1H, br s, O*H*), 4.95 (1H, br t, *J* 6.3, C(1′)*H*), 5.38 (1H, q, *J* 6.4, C(α)*H*), 6.73 (1H, d, *J* 7.7, *Ar*), 6.90 (1H, dt, *J* 7.4, 1.0, *Ar*), 7.09 (1H, dt, *J* 7.7, 1.8, *Ar*), 7.26–7.41 (6H, m, *Ar*); δ_C (50 MHz, $CDCl_3$) 10.5 (*C*(3′)), 24.4 (C(α)*Me*), 30.4 (*C*(2′)), 65.8 (*C*(1′)), 76.0 (*C*(α)), 113.0, 120.6, 125.4, 127.1, 127.6, 127.6, 128.7 (*Ar, o,m,p-Ph*), 132.8 (*C*(2)), 142.9 (*i-Ph*), 154.7 (*C*(1)); *m/z* (CI^+) 256 ($[M]^+$, 21%), 239 ($[M-OH]^+$, 100%), 135 ($[M-C_8H_9O]^+$, 45%), 105 ($[M-C_{10}H_{15}O]^+$, 25%).

4.7.27. (1′R,αS)-1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′-methylpropyl)benzene ***31***.



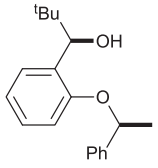
Following *general procedure 5*, **16** (200 mg, 0.49 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **31** as a colourless oil (95 mg, 71%, >99:1 dr); $C_{18}H_{22}O_2$ requires C, 80.0; H, 8.2%; found C, 80.0; H, 8.0%; $[\alpha]_D^{25}$ +84.3 (*c* 0.3 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3610, 3560, 2960, 2940, 2930, 2880, 1600, 1590, 1490, 1230, 1070, 1020; δ_H (200 MHz, $CDCl_3$) 0.91 (3H, d, *J* 6.8, C(2′)*Me*), 1.13 (3H, d, *J* 6.6, C(2′)*Me*), 1.69 (3H, d, *J* 6.4, C(α)*Me*), 2.22 (1H, sextet, *J* 6.8, C(2′)*H*), 2.63 (1H, br s, O*H*), 4.69 (1H, d, *J* 7.2, C(1′)*H*), 5.38 (1H, q, *J* 6.4, C(α)*H*), 6.73 (1H, d, *J* 8.0, *Ar*), 6.90 (1H, dt, *J* 7.4, 0.9, *Ar*), 7.09 (1H, dt, *J* 7.9, 1.8, *Ar*), 7.28–7.40 (6H, m, *Ar*); δ_C (50 MHz, $CDCl_3$) 18.5, 19.7 (C(2′)Me_2), 24.5 (C(α)*Me*), 34.4 (*C*(2′)), 76.0 (*C*(1′)), 76.8 (*C*(α)), 113.0, 120.4, 125.4, 127.6, 127.8, 128.2, 128.7 (*Ar, o,m,p-Ph*), 132.0 (*C*(2)), 142.9 (*i-Ph*), 154.8 (*C*(1)); *m/z* (CI^+) 270 ($[M]^+$, 7%), 253 ($[M-OH]^+$, 22%), 149 ($[M-C_8H_9O]^+$, 18%), 105 ($[M-C_{11}H_{16}O]^+$, 100%).

4.7.28. (1′R,αS)-1-(α-Methylbenzyloxy)-2-(1′-hydroxy-1′-phenylmethyl)benzene ***32***.



Following *general procedure 5*, **17** (200 mg, 0.46 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **32** as a colourless oil (126 mg, 91%, >99:1 dr); $C_{21}H_{20}O_2$ requires C, 82.9; H, 6.6%; found C, 83.0; H, 6.6%; $[\alpha]_D^{25}$ +154 (*c* 0.1 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3600, 3560, 2940, 2930, 2920, 1600, 1590, 1490, 1400, 1220, 1180, 1110, 1070, 1020, 940; δ_H (300 MHz, $CDCl_3$) 1.58 (3H, d, *J* 6.3, C(α)*Me*), 3.29 (1H, br d, O*H*), 5.34 (1H, q, *J* 6.4, C(α)*H*), 6.09 (1H, br d, C(1′)*H*), 6.71 (1H, d, *J* 8.2, *Ar*), 6.92 (1H, d, *J* 7.4, *Ar*), 7.08–7.12 (3H, m, *Ar*), 7.27–7.48 (9H, m, *Ar*); δ_C (50 MHz, CD_2Cl_2) 24.1 (C(α)*Me*), 72.7 (*C*(α)), 75.8 (*C*(1′)), 113.3, 120.7, 125.7, 126.1, 126.7, 127.1, 127.5, 128.0, 128.5, 128.8 (*Ar, o,m,p-Ph*), 132.8 (*C*(2)), 142.9, 144.4 (*i-Ph*), 154.9 (*C*(1)); *m/z* (CI^+) 287 ($[M-OH]^+$, 100%), 182 ($[M-C_8H_{10}O]^+$, 41%).

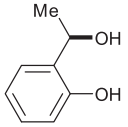
4.7.29. (1′R,αS)-1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′,2′-dimethylpropyl)benzene ***33***.



Following *general procedure 5*, **18** (200 mg, 0.48 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **33** as

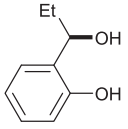
a white solid (119 mg, 88%, >99:1 dr); $C_{19}H_{24}O_2$ requires C, 80.2; H, 8.5%; found C, 80.4; H, 8.55%; mp 73–74 °C (pentane); $[\alpha]_D^{25}$ +40.9 (*c* 0.1 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3610, 3550, 2950, 2930, 2900, 2680, 1690, 1605, 1580, 1490, 1225, 1110, 1070, 1045, 1010, 935, 645, 610; δ_H (200 MHz, CD_2Cl_2) 1.10 (9H, s, C*Me*$_3$), 1.71 (3H, d, *J* 6.5, C(α)*Me*), 2.95 (1H, br s, O*H*), 4.97 (1H, br s, C(1′)*H*), 5.37 (1H, q, *J* 6.4, C(α)*H*), 6.77 (1H, d, *J* 8.2, *Ar*), 6.96 (1H, t, *J* 7.4, *Ar*), 7.13 (1H, t, *J* 6.4, *Ar*), 7.33–7.47 (6H, m, *Ar*); δ_C (50 MHz, CD_2Cl_2) 24.5 (C(α)*Me*), 26.1 (C*Me*$_3$), 36.7 (*C*Me$_3$), 76.9 (*C*(α)), 77.1 (*C*(1′)), 113.2, 120.1, 125.6, 127.7, 127.9, 128.9, 129.7 (*Ar*, *o*,*m*,*p*-*Ph*), 131.1 (*C*(2)), 143.7 (*i*-*Ph*), 155.7 (*C*(1)); *m*/*z* (CI^+) 266 ([M−OH]$^+$, 4%), 162 ([M−$C_8H_{10}O$]$^+$, 33%), 105 ([M−$C_{12}H_{19}O$]$^+$, 100%).

4.7.30. (R)-2-(1′-Hydroxyethyl)phenol ***34****.*



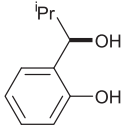
Following *general procedure 6*, hydrogenolysis of (1′*R*,α*S*)-**29** (86 mg, 0.36 mmol) gave (*R*)-**34** as a yellow oil (46 mg, 94%, >99:1 er); $C_8H_{10}O_2$ requires C, 69.55; H, 7.3%; found C, 69.5; H, 7.4%; $[\alpha]_D^{20}$ +20.5 (*c* 0.2 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3590, 3380, 2940, 2910, 2880, 1620, 1590, 1490, 1225, 645; δ_H (200 MHz, $CDCl_3$) 1.56 (3H, d, *J* 6.5, C(2′)*H*$_3$), 5.02 (1H, q, *J* 6.5, C(1′)*H*), 6.86–6.96 (2H, m, *Ar*), 6.98 (1H, d, *J* 6.8, *Ar*), 7.17 (1H, t, *J* 7.7, *Ar*); δ_C (50 MHz, $CDCl_3$) 23.3 (*C*(2′)), 71.2 (*C*(1′)), 116.9, 120.0, 126.5, 128.6. 128.8 (*Ar*), 155.1 (*C*(1)); *m*/*z* (EI^+) 138 ([M]$^+$, 23%), 120 ([M−OH]$^+$, 100%), 91 ([M−C_2H_6O]$^+$, 35%).

4.7.31. (R)-2-(1′-Hydroxypropyl)phenol ***35****.*



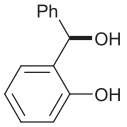
Following *general procedure 6*, hydrogenolysis of (1′*R*,α*S*)-**30** (94 mg, 0.38 mmol) gave (*R*)-**35** as a colourless oil (55 mg, 95%, >99:1 er); $C_9H_{12}O_2$ requires C, 71.0; H, 7.9%; found C, 70.8, H, 7.9%; $[\alpha]_D^{25}$ +23.5 (*c* 0.7 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3590, 3370, 2960, 2950, 2940, 2880, 1620, 1590, 1490, 1225, 1220, 650; δ_H (200 MHz, $CDCl_3$) 0.94 (3H, t, *J* 7.4, C(3′)*H*$_3$), 1.86–1.90 (2H, m, C(2′)*H*$_2$), 4.68 (1H, t, *J* 6.8, C(1′)*H*), 5.63 (1H, br s, O*H*), 6.85–6.91 (2H, m, *Ar*), 6.94 (1H, dd, *J* 8.1, 1.9, *Ar*), 7.15 (1H, dt, *J* 7.6, 1.8, *Ar*); δ_C (50 MHz, $CDCl_3$) 10.1 (*C*(3′)), 30.1 (*C*(2′)), 76.9 (*C*(1′)), 116.8, 119.7, 127.4, 128.4, 128.7 (*Ar*), 155.2 (*C*(1)); *m*/*z* (EI^+) 152 ([M]$^+$, 15%), 134 ([M−OH]$^+$, 52%).

4.7.32. (R)-2-(1′-Hydroxy-2′-methylpropyl)phenol ***36****.*



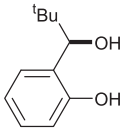
Following *general procedure 6*, hydrogenolysis of (1′*R*,α*S*)-**31** (95 mg, 0.35 mmol) gave (*R*)-**36** as a colourless oil (54 mg, 93%, >99:1 er); $C_{10}H_{14}O_2$ requires C, 72.3; H, 8.5%; found C, 72.2; H, 8.6%; $[\alpha]_D^{25}$ +24.1 (*c* 0.2 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3590, 3370, 2940, 2930, 2910, 2880, 1620, 1590, 1490, 1430, 1230, 1000, 650, 640; δ_H (200 MHz, $CDCl_3$) 0.85 (3H, d, *J* 6.8, C(2′)*Me*$_A$), 1.04 (3H, d, *J* 6.6, C(2′)*Me*$_B$), 1.83 (1H, sextet, *J* 3.5, C(2′)*H*), 4.47 (1H, d, *J* 7.1, C(1′)*H*), 6.86–6.90 (3H, m, *Ar*), 7.15 (1H, dt, *J* 8.9, 1.9, *Ar*); δ_C (50 MHz, $CDCl_3$) 18.1, 19.1 (C(2′)*Me*$_2$), 34.4 (*C*(2′)), 81.5 (*C*(1′)), 117.0, 119.6, 128.4, 128.5, 128.8 (*Ar*), 155.8 (*C*(1)); *m*/*z* (EI^+) 166 ([M]$^+$, 15%), 148 ([M−OH]$^+$, 40%), 133 ([M−CH_4O]$^+$, 51%), 123 ([M−C_2H_7O]$^+$, 100%), 105 ([M−C_3H_8O]$^+$, 25%).

4.7.33. (R)-2-(1′-Hydroxy-1′-phenylmethyl)phenol ***37****.*



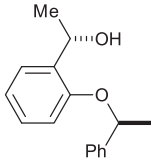
NH_3 (2 mL) was condensed and added to a flask containing a solution of (1′*R*,α*S*)-**32** (126 mg, 0.414 mmol) in THF (2 mL) at −78 °C. Sodium (24 mg, 1.03 mmol) was then added and stirring was continued at −78 °C for 15 min. After this time MeOH (0.5 mL) was added and the reaction mixture was allowed to warm to rt before being concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1) gave (*R*)-**37** as a colourless oil (43 mg, 52%, >99:1 er); $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.0%; found C, 78.3; H, 6.1%; $[\alpha]_D^{25}$ −35.1 (*c* 0.6 in CH_2Cl_2); δ_H (200 MHz, CD_2Cl_2) 3.18 (1H, br s, O*H*), 6.01 (1H, s, C(1′)*H*), 6.83–6.90 (3H, m, *Ar*), 7.19 (1H, t, *J* 6.6, *Ar*), 7.61–7.65 (5H, m, *Ar*), 7.90 (1H, br s, O*H*); δ_C (50 MHz, $CDCl_3$) 77.2 (*C*(1′)), 117.5, 120.2, 127.0, 127.3, 128.5, 128.6, 129.0, 129.5 (*Ar*, *o*,*m*,*p*-*Ph*), 142.6 (*i*-*Ph*), 155.9 (*C*(1)); *m*/*z* (CI^+) 183 ([M−OH]$^+$, 100%), 105 ([M−C_6H_6O]$^+$, 4%).

4.7.34. (R)-2-(1′-Hydroxy-2′,2′-dimethylpropyl)phenol ***38****.*



Following *general procedure 6*, hydrogenolysis of (1′*R*,α*S*)-**33** (119 mg, 0.42 mmol) gave (*R*)-**38** as a colourless oil (71 mg, 94%, >99:1 er); $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.95%; found C, 73.6; H, 8.6%; mp 83–84 °C (pentane); $[\alpha]_D^{25}$ +10.0 (*c* 0.1 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3600, 3370, 2950, 2920, 2880, 1620, 1590, 1490, 1470, 1400, 1370, 1220, 1160, 1100, 1030, 1000, 645; δ_H (200 MHz, $CDCl_3$) 1.00 (9H, s, C*Me*$_3$), 1.68 (1H, br s, O*H*), 4.55 (1H, s, C(1′)*H*), 6.85–6.89 (3H, m, *Ar*), 7.21–7.25 (1H, m, *Ar*); δ_C (50 MHz, $CDCl_3$) 26.0 (C*Me*$_3$), 37.3 (*C*Me$_3$), 85.1 (*C*(1′)), 117.3, 118.6, 123.6, 128.7, 129.7 (*Ar*), 156.2 (*C*(1)); *m*/*z* (CI^+) 180 ([M]$^+$, 9%), 163 ([M−OH]$^+$, 100%).

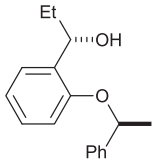
4.7.35. (S,S)-1-(α-Methylbenzyloxy)-2-(1′-hydroxyethyl)benzene ***39****.*



Following *general procedure 5*, **9** (200 mg, 0.53 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **39** as a colourless oil (92 mg, 72%, >99:1 dr); $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%; found C, 79.0; H, 7.3%; $[\alpha]_D^{24}$ +40.8 (*c* 0.1 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3600, 2940, 2900, 2880, 1600, 1590, 1490, 1220, 1080, 1010, 935, 610; δ_H (200 MHz, $CDCl_3$) 1.62 (3H, d, *J* 6.4, C(2′)*H*$_3$), 1.71 (3H, d, *J* 6.4, C(α)*Me*), 2.96 (1H, br s, O*H*), 5.27 (1H, q, *J* 6.4, C(1′)*H*), 5.41 (1H, q, *J* 6.4, C(α)*H*), 6.75 (1H, d, *J* 8.2, *Ar*), 6.94 (1H, dt, *J* 7.4, 1.0, *Ar*), 7.12 (1H, dt, *J* 7.5, 1.8, *Ar*), 7.28–7.40 (6H, m, *Ar*); δ_C (50 MHz, $CDCl_3$) 23.1 (*C*(2′)), 24.5 (C(α)*Me*), 66.6 (*C*(1′)), 76.1 (*C*(α)), 113.0, 120.7, 125.3, 126.1, 127.6, 128.0, 128.8 (*Ar*, *o*,*m*,*p*-*Ph*), 133.9 (*C*

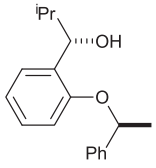
(2)), 142.8 (*i-Ph*), 154.7 (*C*(1)); *m/z* (CI^+) 225 ($[M-OH]^+$, 41%), 120 ($[M-C_8H_{10}O]^+$, 100%).

4.7.36. (S,S)-1-(α-Methylbenzyloxy)-2-(1′-hydroxypropyl)benzene ***40***.



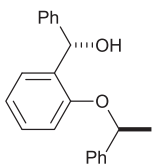
Following *general procedure 5*, **10** (200 mg, 0.51 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **40** as a colourless oil (101 mg, 77%, >99:1 dr); $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.9%; found C, 79.8; H, 8.1%; $[\alpha]_D^{24}$ +45.5 (*c* 0.1 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3600, 3570, 2950, 2940, 2880, 2860, 1600, 1590, 1490, 1225, 1090, 1070, 1010, 940; δ_H (200 MHz, $CDCl_3$) 1.03 (3H, t, *J* 7.4, C(3′)*H*$_3$), 1.68 (3H, d, *J* 6.5, C(α)*Me*), 1.92 (2H, app quin, *J* 7.2, C(2′)*H*$_2$), 2.80 (1H, br s, O*H*), 4.94 (1H, t, *J* 6.6, C(1′)*H*), 5.37 (1H, q, *J* 6.5, C(α)*H*), 6.72 (1H, d, *J* 8.2, *Ar*), 6.92 (1H, t, *J* 7.4, *Ar*), 7.09 (1H, dt, *J* 7.7, 1.8, *Ar*), 7.27–7.39 (6H, m, *Ar*); δ_C (50 MHz, $CDCl_3$) 10.6 (*C*(3′)), 24.5 (C(α)*Me*), 30.3 (*C*(2′)), 65.8 (*C*(1′)), 76.2 (*C*(α)), 113.1, 120.6, 125.3, 127.1, 127.6, 127.9, 128.7 (*Ar*, *o*,*m*,*p-Ph*), 132.7 (*C*(2)), 142.9 (*i-Ph*), 154.8 (*C*(1)); *m/z* (CI^+) 134 ($[M-C_8H_{10}O]^+$, 100%).

4.7.37. (S,S)-1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′-methylpropyl) benzene ***41***.



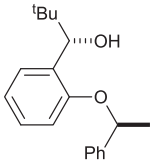
Following *general procedure 5*, **11** (200 mg, 0.49 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **41** as a colourless oil (98 mg, 74%, >99:1 dr); $C_{18}H_{22}O_2$ requires C, 80.0; H, 8.2%; found C, 79.8; H, 7.9%; $[\alpha]_D^{25}$ +51.0 (*c* 0.3 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3610, 3560, 2960, 2940, 2880, 1600, 1590, 1490, 1225, 1070, 1010; δ_H (200 MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.8, C(2′)*Me*$_A$), 1.15 (3H, d, *J* 6.8, C(2′)*Me*$_B$), 1.70 (3H, d, *J* 6.4, C(α)*Me*), 2.23 (1H, app sextet, *J* 6.8, C(2′)*H*), 2.91 (1H, br s, O*H*), 4.74 (1H, d, *J* 6.8, C(1′)*H*), 5.37 (1H, q, *J* 6.4, C(α)*H*), 6.75 (1H, d, *J* 8.1, *Ar*), 6.94 (1H, t, *J* 7.0, *Ar*), 7.11 (1H, dt, *J* 8.0, 1.6, *Ar*), 7.32–7.42 (6H, m, *Ar*); δ_C (50 MHz, $CDCl_3$) 18.4, 19.8 (C(2′)*Me*$_2$), 24.6 (C(α)*Me*), 34.4 (*C*(2′)), 76.4 (*C*(1′)), 76.4 (*C*(α)), 113.1, 120.5, 125.3, 127.6, 127.9, 128.2, 128.8 (*Ar*, *o*,*m*,*p-Ph*), 132.2 (*C*(2)), 143.0 (*i-Ph*), 154.9 (*C*(1)); *m/z* (CI^+) 270 ($[M]^+$, 5%), 253 ($[M-OH]^+$, 21%), 149 ($[M-C_8H_9O]^+$, 22%), 105 ($[M-C_{11}H_{16}O]^+$, 100%).

4.7.38. (S,S)-1-(α-Methylbenzyloxy)-2-(1′-hydroxy-1′-phenylmethyl) benzene ***42***.



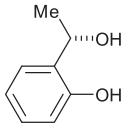
Following *general procedure 5*, **12** (200 mg, 0.46 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **42** as a colourless oil (105 mg, 76%, >99:1 dr); $C_{21}H_{20}O_2$ requires C, 82.9; H, 6.6%; found C, 82.5; H, 6.7%; $[\alpha]_D^{25}$ −226 (*c* 0.2 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3600, 2950, 2940, 2920, 1600, 1590, 1490, 1400, 1225, 1165, 1160, 1070, 1015, 940, 610; δ_H (300 MHz, $CDCl_3$) 1.53 (3H, d, *J* 6.4, C(α)*Me*),3.05 (1H, br s, O*H*), 5.30 (1H, q, *J* 6.4, C(α)*H*), 6.13 (1H, s, C(1′)*H*), 6.69 (1H, d, *J* 8.2, *Ar*), 6.93 (1H, *J* 7.4, *Ar*), 7.10–7.15 (2H, m, *Ar*), 7.25–7.46 (10H, m, *Ar*); δ_C (50 MHz, CD_2Cl_2) 24.2 (C(α)*Me*), 72.1 (*C*(α)), 76.0 (*C*(1′)), 113.1, 120.7, 125.7, 127.3, 127.4, 127.6, 127.7, 128.1, 128.4, 128.8 (*Ar*, *o*,*m*,*p-Ph*), 133.0 (*C*(2)), 143.2, 144.3 (*i-Ph*), 154.8 (*C*(1)); *m/z* (CI^+) 287 ($[M-OH]^+$, 100%), 182 ($[M-C_8H_{10}O]^+$, 47%).

4.7.39. (S,S)-1-(α-Methylbenzyloxy)-2-(1′-hydroxy-2′,2′-dimethylpropyl)benzene ***43***.



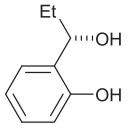
Following *general procedure 5*, **13** (200 mg, 0.48 mmol) was decomplexed to give, after purification by flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1), **43** as a colourless oil (110 mg, 81%, >99:1 dr); $C_{19}H_{24}O_2$ requires C, 80.2; H, 8.5%; found C, 80.1; H, 8.7%; $[\alpha]_D^{25}$ +90.4 (*c* 0.1 in CH_2Cl_2); ν_{max} (CH_2Cl_2) 3610, 3540, 2950, 2940, 2930, 2880, 1600, 1580, 1490, 1395, 1225, 1070, 1045, 1010, 1005; δ_H (200 MHz, $CDCl_3$) 1.01 (9H, s, C*Me*$_3$), 1.66 (3H, d, *J* 6.4, C(α)*Me*), 2.44 (1H, br s, O*H*), 4.98 (1H, br s, C(1′)*H*), 5.38 (1H, q, *J* 6.4, C(α)*H*), 6.74 (1H, d, *J* 8.2, *Ar*), 6.89 (1H, t, *J* 6.9, *Ar*), 7.08 (1H, dt, *J* 7.4, 1.8, *Ar*), 7.28–7.43 (6H, m, *Ar*); δ_C (50 MHz, $CDCl_3$) 24.1 (C(α)*Me*), 25.8 (C*Me*$_3$), 36.5 (*C*Me$_3$), 75.9 (*C*(α)), 76.0 (*C*(1′)), 112.7, 119.9, 125.7, 127.7, 127.8, 128.8, 129.3 (*Ar*, *o*,*m*,*p-Ph*), 131.2 (*C*(2)), 143.5 (*i-Ph*), 155.3 (*C*(1)); *m/z* (CI^+) 284 ($[M]^+$, 6%), 267 ($[M-OH]^+$, 15%), 163 ($[M-C_8H_9O]^+$, 24%), 105 ($[M-C_{12}H_{18}O]^+$, 100%).

4.7.40. (S)-2-(1′-Hydroxyethyl)phenol ***34***.



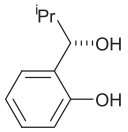
Following *general procedure 6*, hydrogenolysis of (*S*,*S*)-**39** (92 mg, 0.38 mmol) gave (*S*)-**34** as a colourless oil (48 mg, 92%, >99:1 er); $[\alpha]_D^{25}$ −23.9 (*c* 0.3 in CH_2Cl_2).

4.7.41. (S)-2-(1′-Hydroxypropyl)phenol ***35***.



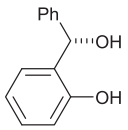
Following *general procedure 6*, hydrogenolysis of (*S*,*S*)-**40** (101 mg, 4.0 mmol) gave (*S*)-**35** as a colourless oil (56 mg, 94%, >99:1 er); $[\alpha]_D^{25}$ −24.0 (*c* 0.2 in CH_2Cl_2).

4.7.42. (S)-2-(1′-Hydroxy-2′-methylpropyl)phenol ***36***.



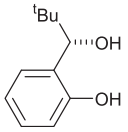
Following *general procedure 6*, hydrogenolysis of (*S*,*S*)-**41** (98 mg, 0.36 mmol) gave (*S*)-**36** as a colourless oil (55 mg, 91%, >99:1 er); $[\alpha]_D^{26}$ −27.4 (*c* 0.3 in CH_2Cl_2).

4.7.43. (S)-2-(1′-Hydroxy-1′-phenylmethyl)phenol ***37***.



NH_3 (2 mL) was condensed and added to a flask containing a solution of (*S*,*S*)-**42** (105 mg, 0.35 mmol) in THF (2 mL) at −78 °C. Sodium (24 mg, 0.86 mmol) was then added and stirring was continued at −78 °C for 15 min. After this time MeOH (0.5 mL) was added and the reaction mixture was allowed to warm to rt before being concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petroleum ether/Et_2O, 5:1) gave (*S*)-**37** as a colourless oil (39 mg, 56%, >99:1 er); $[\alpha]_D^{26}$ +36.1 (*c* 1.2 in CH_2Cl_2).

*4.7.44. (S)-2-(1′-Hydroxy-2′,2′-dimethylpropyl)phenol **38**.*



Following *general procedure 6*, hydrogenolysis of (*S*,*S*)-**43** (110 mg, 0.387 mmol) gave (*S*)-**38** as a colourless oil (64 mg, 92%, >99:1 er); $[\alpha]_D^{25}$ −10.5 (*c* 0.1 in CH_2Cl_2).

Acknowledgements

The authors would like to thank the EPSRC for a studentship (W.E.H.), and Dr. Alexander N. Chernega and the Oxford Chemical Crystallography Service for X-ray crystal structure determination and the use of their diffractometers.

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