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A Stereocontrolled Approach to Ethers with Two α Stereocentres

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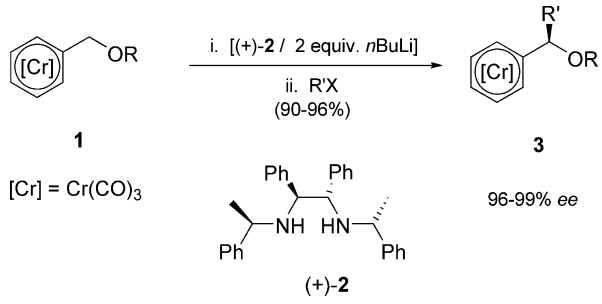
The stereocontrolled synthesis of enantiomeric pairs of four ethers, in which the oxygen atom is flanked by two α stereocentres, has been achieved using a chiral base/arene chromium tricarbonyl activation approach.

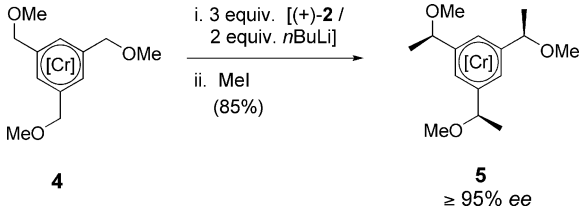
Introduction

Some time ago, we demonstrated that tricarbonylchromium(0) complexes of alkyl benzyl ethers (**1**) react with the chiral diamide derived from butyllithium/chiral diamine **2** and an electrophile to give the chiral ether complexes **3** in high yield and enantiomeric excess (Scheme 1).[1]



Scheme 1. Asymmetric functionalisation of alkyl benzyl ethers.

More recently we extended this chemistry to the C_3-symmetric tris-ether **4**, and found that it was possible to install three methyl groups in one pot in good yield and with good stereoselectivity to produce **5** (Scheme 2).[2]



Scheme 2. Formation of three stereocentres in one pot.

We subsequently employed this chemistry to make a range of enantiopure C_3-symmetric compounds[3] including the borane-protected tris(phosphane) **6**,[2b] the tris(pyridine) ligand **7**,[2b] and dendrimers with either a homochiral or a heterochiral relationship between their layers such as **8** (Figure 1).[4]

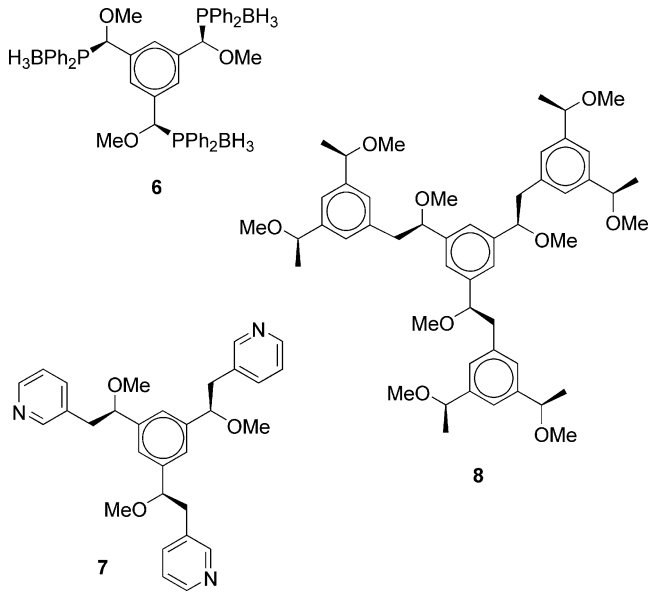


Figure 1. C_3-Symmetric molecules made using chiral base chemistry.

Pursuing the idea of using the chemistry described above to install more than one stereocentre in one pot, we elected to study the reactivity of the chromium complex **9** (Figure 2). Successful introduction of two stereocentres into this molecule would provide the foundation for a new route to

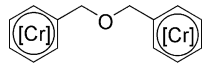


Figure 2. Hexacarbonyl(dibenzyl ether)dichromium(0).

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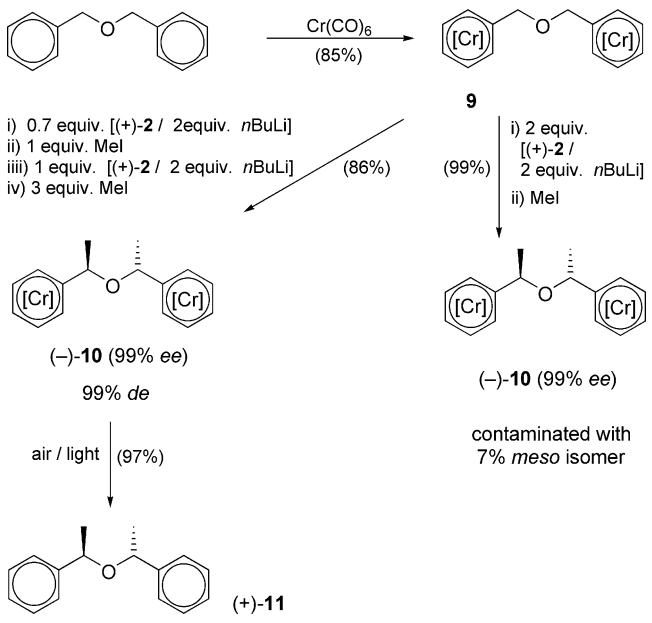
enantio-enriched ethers in which the oxygen atom is flanked by two chiral centres. The results of our study are presented here.

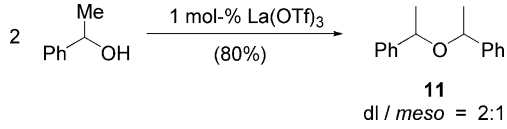
Results and Discussion

Hexacarbonyl(dibenzyl ether)dichromium(0) (**9**) was prepared according to a reported procedure.[5] Thermolysis of dibenzyl ether and hexacarbonylchromium(0) in a 5:1 mixture of di-*n*-butyl ether and THF, followed by work-up, gave **9** as a stable yellow solid in 85% yield (Scheme 3). To deprotonate the ether **9**, the diamine (+)-**2** (2 equiv.)[6] was treated with butyllithium and lithium chloride, and complex **9** was added to the resulting deep red solution. After the addition of iodomethane and work-up, a yellow solid was obtained that was identified as the dimethylated complex **10** on the basis of its elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and mass spectra. In order to establish the stereoisomeric composition of **10**, the reaction was repeated using diamine (–)-**2**. Analysis of both products by chiral HPLC revealed that the C_2-symmetric isomer had been formed in each case in ≥ 99% *ee*, but that the samples were contaminated with small amounts of the *meso* product (7%). The syntheses of (–)- and (+)-**10** were repeated but using the base/electrophile/base/electrophile sequence depicted for (–)-**10** in Scheme 3, and, pleasingly, this generated samples of (–)- and (+)-**10** that were essentially enantiopure (99% *ee*) and diastereomerically pure (99% *de*). The tricarbonylchromium(0) units were subsequently removed from the samples of (–)- and (+)-**10** by air/light oxidation to give the C_2-symmetric ethers (+)- and (–)-**11** respectively. These were both uncontaminated by the *meso* isomer, according to ^{1}H NMR spectroscopy, revealing that epimerisation had not occurred. It was therefore assumed that both samples were enantiomerically pure.



Scheme 3. Synthesis of (+)-(1*R*,1′*R*)-bis[1-(1-phenylethyl)] ether.

Attempts by others to synthesise the ether **11** have been based on nucleophilic substitution reactions. The stability of benzylic cations, however, imparts a considerable degree of S_N1 character to such reactions and renders them difficult to control. In a typical example, treatment of racemic α-methylbenzyl alcohol with a catalytic amount of lanthanum triflate gave a 2:1 mixture of the DL and *meso* isomers of ether **11** (Scheme 4).[7]



Scheme 4. A typical nucleophilic substitution approach to bis[1-(1-phenylethyl)] ether.

In an isolated solution to the problem of stereoselectivity in these reactions, a 1:2 inclusion crystal between (*S*)-(–)-1-phenylethanol and (*R*,*R*)-(–)-*trans*-4,5-bis[hydroxy(diphenyl)methyl]-2,2-dimethyl-1,3-dioxacyclopentane (**12**) (Figure 3), was treated with TsOH in the solid state. This gave enantiomerically and diastereoisomerically pure (*S*,*S*)-(–)-**11** in unreported yield.[8] It was proposed that the high degree of stereocontrol in this reaction originated from a well-defined and relatively rigid orientation of the two reaction partners in the solid state. Attack of one alcohol of the pair on the carbocation of the other alcohol was thus able to take place with complete retention of configuration.

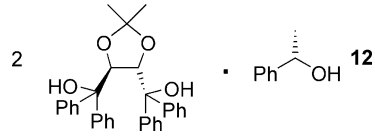
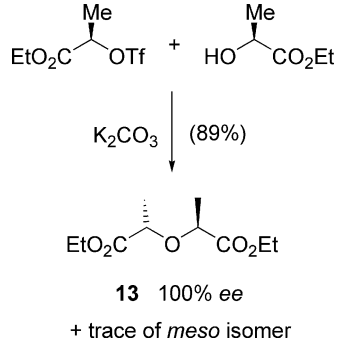


Figure 3. Inclusion compound used to generate stereochemically pure bis[1-(1-phenylethyl)] ether.

Attempts to synthesise enantio-enriched C_2-symmetric acyclic ethers with chiral centres α to the ether oxygen that lack an aromatic α-substituent have proven more amenable to the development of synthetically useful nucleophilic substitutions. For example, very careful control of the reaction conditions used for the synthesis of the bisester **13** from lactic acid derivatives led to an 89% yield of enantiomerically pure **13** accompanied by just a trace of the corresponding *meso* isomer (Scheme 5).[9]



Scheme 5. Non-aromatic chiral ethers can be generated from lactic acid derivatives.

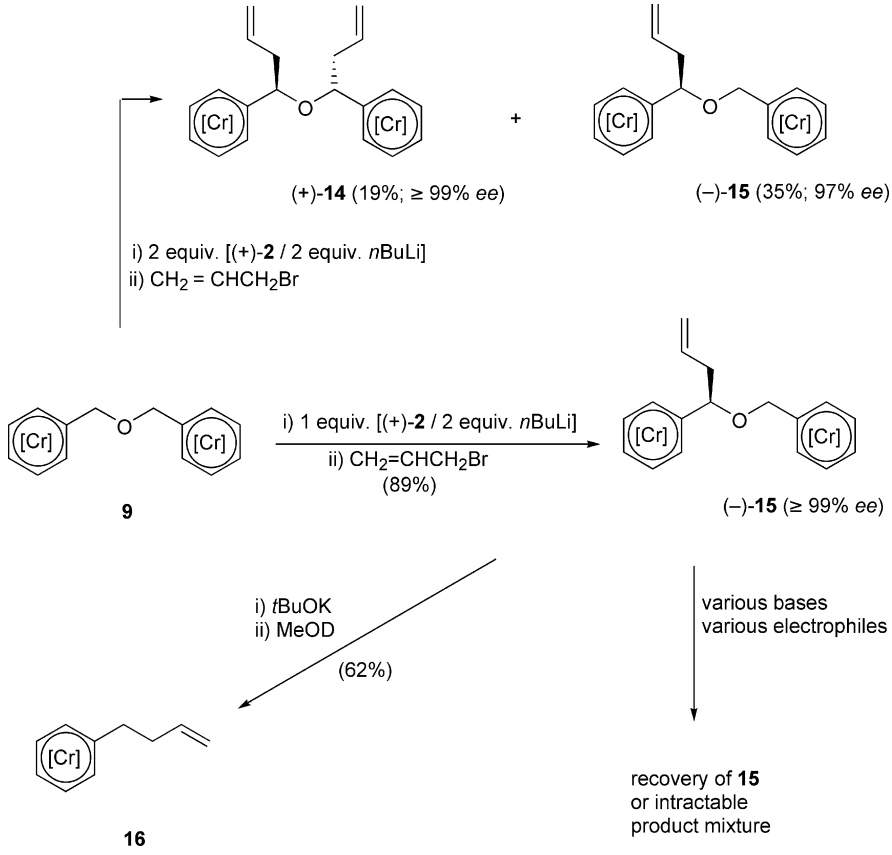
In view of the excellent stereoselectivity achieved in our deprotonation/alkylation approach to ether **11**, compared to that obtained through typical nucleophilic substitution routes to this compound, we decided to proceed to probe the scope and limitations of our synthesis.

Deprotonation of complex **9** with the base derived from (+)-**2** and quenching with allyl bromide was examined under a range of conditions. It was disappointing to discover, however, that all of these experiments led to a mixture of the diallylated complex **14** and the monoallylated complex **15** (Scheme 6). On one occasion, the mixture was separated by column chromatography to yield samples of (+)-**14** and (–)-**15** in 19 and 35% isolated yield respectively. Repetition of this reaction using the amine (–)-**2** provided samples of (–)-**14** and (+)-**15**, and chiral HPLC analysis revealed that both the diallyl and the monoallyl complexes had been generated in ≥ 97% *ee* in both reactions (the *meso* isomer of **14** was undetectable by NMR spectroscopy and HPLC analysis).

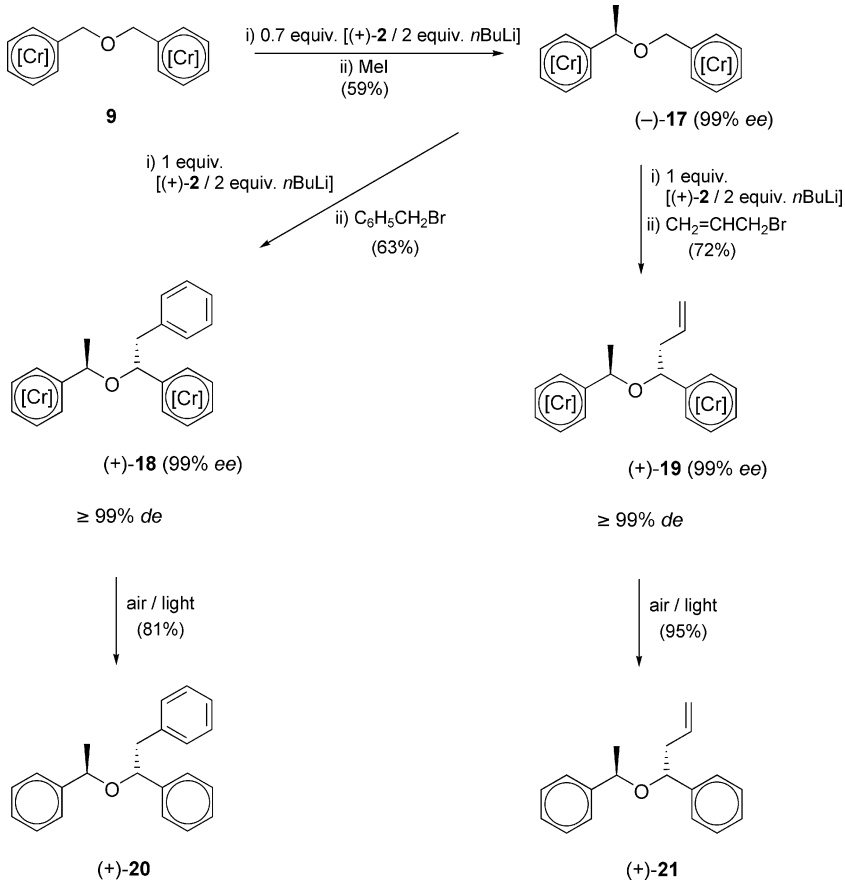
It was clear from these experiments, and similar results obtained using benzyl bromide as the electrophile (not documented here), that the introduction of the second allyl (or benzyl) substituent was problematic. In order to probe the second substitution further, a sample of (–)-**15** was prepared using one equivalent of the chiral base. This reaction proceeded smoothly to give an 89% yield of the monoallylated complex in ≥ 99% *ee*. Treatment of (–)-**15** with several bases (*t*BuLi, NaH, $LiNMe_2$, [(+)-**2**/*n*BuLi]) and electrophiles (MeOD, MeI, allyl bromide), however, consistently led either to the recovery of **15** or to an intractable mixture of products. (In contrast, treatment with *t*BuOK led to the rapid production of a black solution, which after quenching and work-up gave a yellow solid that was identified as the alkene complex **16**.[10] The mechanism for the formation of **16** is as yet undetermined, but its formation serves to underscore the difficulty in introducing a second electrophile into the monoallylated complex **15**.)

Having discovered that the monoallylated complex **15** could not be converted into disubstituted derivatives, our attention turned to the monomethylated complex **17** to see if this compound would afford ethers with two chiral centres α to the ether oxygen. Deprotonation of the dibenzyl ether complex **9** with 0.7 equiv. of the chiral amide followed by quenching with iodomethane led to (–)-**17** in satisfactory yield (59%) and excellent enantiopurity (98% *ee*) (Scheme 7). Pleasingly, the deprotonation of (–)-**17** followed by addition of benzyl bromide or allyl bromide led to the generation of the disubstituted complexes (+)-**18** and (+)-**19** in good yields and excellent enantiopurities (the *meso* isomers of **18** and **19** were undetectable by NMR spectroscopy and HPLC analysis). Oxidative removal of the chromium carbonyl groups proceeded efficiently to give the ethers (+)-**20** and (+)-**21**.

The ether **20** is a novel compound, whilst the ether **21** has been synthesised by the reaction of benzaldehyde with (*S*)-1-phenyl-1-(triethylsilyloxy)ethane followed by the ad-

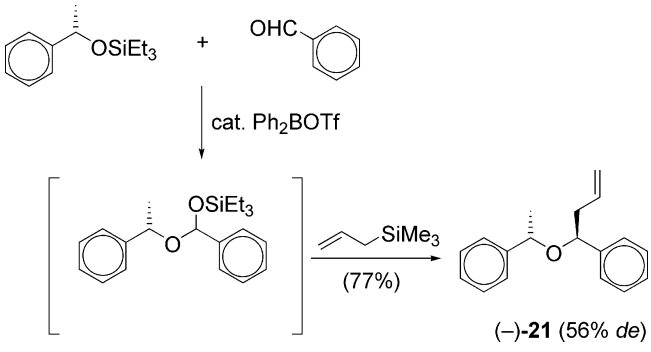


Scheme 6. Synthesis of allylated derivatives of ether complex **9**.



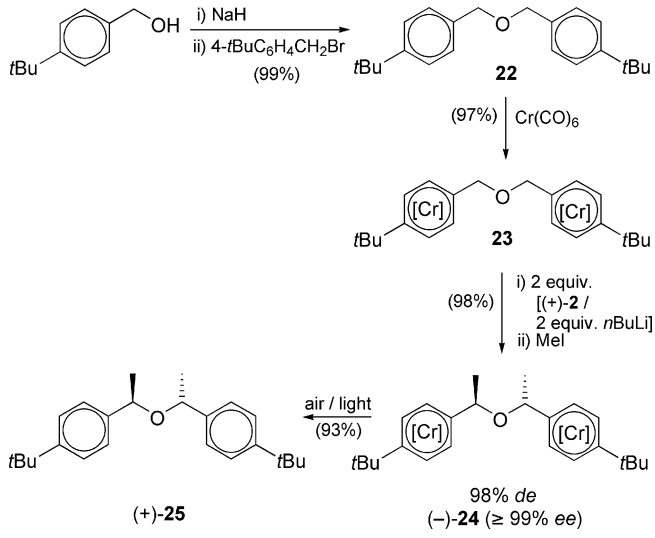
Scheme 7. Asymmetric synthesis of the ethers **20** and **21**.

dition of allyl(trimethyl)silane (Scheme 8).[11] Ether (–)-**21** was formed in 77% yield by this route, but was heavily contaminated with the *meso* isomer (56% *de*), an observation attributed to the ease of formation of a benzylic carbocation thus promoting an S_N1 type transition state during the allylation step.



Scheme 8. An alternative non-selective approach to ether **21**.

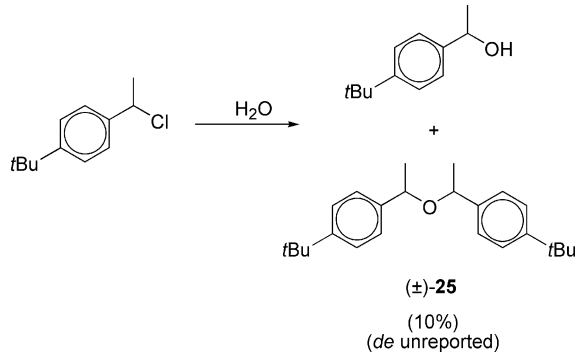
In order to start to access analogues of the C_2-symmetric ether **11**, in preparation for a study of applications of these ethers, we have synthesised both enantiomers of the *tert*-butyl analogue **25** (Scheme 9). The achiral ether **22**, required for asymmetric elaboration, has previously been synthesised by the action of catalytic amounts of Nafion-H® on the trimethylsilyl ether derivative of 4-*tert*-butylbenzyl alcohol,[12] but we chose to deprotonate the alcohol and



Scheme 9. Asymmetric synthesis of C_2-symmetric ether **25**.

react it with the corresponding bromide. Complexation of ether **22**, dimethylation using the bases derived from both (+)-**2** and (–)-**2**, and decomplexation all proceeded smoothly to generate samples of (+)- and (–)-**25** that were essentially enantiomerically and diastereoisomerically pure.

Racemic **25** has been observed previously as a byproduct of the hydrolysis of the corresponding chloride (Scheme 10).[13]



Scheme 10. An earlier approach to ether **25** is unselective.

Conclusions

We have developed a new approach to ethers with two α stereocentres. The method is limited by the constraint that the first electrophile introduced cannot be larger than iodomethane. On the other hand, the enantio- and diastereocontrol achieved in the new method is significantly superior to conventional approaches based on nucleophilic substitution reactions, especially for α-aryl-substituted ethers. It has thus proven possible to synthesise both enantiomers of the ethers **11**, **20**, **21**, and **25** for the first time in a highly stereocontrolled manner. In light of i) the success of the amine analogue of ether **11** in inducing stereoselectivity when used, for example, in its own right as a chiral base,[14] or when incorporated in a monodentate phosphoramidite ligand,[15] and ii) evidence that the presence of an ether can affect the outcome of a range of catalytic reactions,[16] it is anticipated that these molecules will find applications as chiral additives.

Experimental Section

General: All reactions and manipulations involving organometallic compounds were performed under dry nitrogen, using standard vacuum line and Schlenk techniques.[17] Reactions and operations involving the use of (arene)tricarbonylchromium(0) complexes were protected from light. Tetrahydrofuran was distilled from sodium benzophenone ketyl and used immediately. Dichloromethane was distilled from calcium hydride. The concentration of *n*-butyllithium was determined by titration against diphenylacetic acid in tetrahydrofuran.[18] All other chemicals were used as purchased from commercial sources. Thin-layer chromatography (TLC) was performed on Merck silica gel glass plates 60 (F254), using UV light (254 nm) as visualizing agent and/or vanillin or potassium permanganate as developing agents. Flash column chromatography was performed using BDH silica gel (particle size 33–70 μm). Melting points were recorded with a Sanyo Gallenkamp melting point apparatus in open capillaries and are uncorrected. Optical rotations were recorded with an AA 10 polarimeter from Index Instruments or with a Perkin–Elmer 241 polarimeter using a 1-dm path length; concentrations are given as g/100 mL. IR spectra were recorded with a Perkin–Elmer Spectrum RX FT-IR spectrometer. NMR spectra were recorded at room temperature with Bruker AC 300F, DRX 400, AV 400 or AV 500 instruments in $CDCl_3$, unless otherwise stated. *J* values are reported in Hertz and chemical shifts in ppm. Mass spectra were recorded with Micromass Platform II and Micromass AutoSpec-Q instruments by the mass spectrometry service at Imperial College London. Elemental analyses were performed by the London Metropolitan University microanalytical service. The diamines (+)- and (–)-**2** were prepared according to a literature method.[6]

Hexacarbonyl(dibenzyl ether)dichromium(0) (9):[5] Dibenzyl ether (2.25 mL, 11.8 mmol) and hexacarbonylchromium(0) (5.5 g, 24.9 mmol) were added to dry di-*n*-butyl ether (71 mL) and THF (14 mL) and the mixture was degassed 10 times and shielded from ambient light. The reaction mixture was heated under reflux for 72 h at 135 °C and then cooled to room temperature. The solvent was removed under reduced pressure and the crude mixture was pre-absorbed onto silica (30 g). Purification was carried out by flash column chromatography (SiO_2; hexane/ethyl acetate, 70:30) to yield complex **9** (4.73 g, 85%) as a yellow solid; m.p. 126–128 °C (ref.[5] 126–127 °C). R_f = 0.13 (SiO_2; hexane/ethyl acetate, 80:20). IR ($CHCl_3$): $\tilde{\nu}$ =1973 (s, υ_{CO}), 1899 (υ_{CO}, s) cm^{-1}. ^1H NMR (400 MHz): δ = 4.38 (s, 4 H, OCH_2×2), 5.28–5.32 (m, 2 H, $C_{Cr}H_{para}$×2), 5.38–5.43 (m, 8 H, $C_{Cr}H_{ortho}$×4, $C_{Cr}H_{meta}$×4). ^{13}C NMR (100 MHz): δ = 71.2 ($C_{Cr}CH_2$×2), 91.7 ($C_{Cr}H_{para}$×2), 91.8, 92.6 ($C_{Cr}H_{ortho}$×4, $C_{Cr}H_{meta}$×4), 106.9 (C_{Cr}×2), 232.6 ($C{\equiv}O$×6) ppm. MS (EI): *m*/*z* (%) = 470 (50) [M^+], 386 (26) [M^+ – 3CO], 302 (100) [M^+ – 6CO].

(–)-(1*R*,1′*R*)-Hexacarbonyl{bis[1-(1-phenylethyl) ether]}dichromium(0) [(–)-10]: *n*-Butyllithium (0.11 mL, 2.50 M in hexane, 0.27 mmol) was added dropwise to a stirred solution of the diamine (+)-**2** (59 mg, 0.14 mmol) in THF (4 mL) at –78 °C. The solution was warmed to room temperature over 30 min. The resulting deep red solution was then recooled to –78 °C. A solution of heat gun-dried lithium chloride (6 mg, 0.14 mmol) in THF (3 mL) was added through a cannula and the reaction mixture was stirred for a further 5 min before a precooled solution (–78 °C) of complex **9** (94 mg, 0.20 mmol) in THF (3 mL) was added dropwise through a cannula. The reaction was stirred at –78 °C for 40 min before iodomethane (12 μL, 0.20 mmol) was added through a micro-syringe into the reaction mixture. Stirring was continued for a further 15 min at –78 °C. Meanwhile, in another reaction flask, *n*-butyllithium (0.16 mL, 2.50 M in hexane, 0.40 mmol) was added dropwise to a stirred solution of the diamine (+)-**2** (84 mg, 0.20 mmol) in THF (4 mL) at –78 °C. The solution was warmed to room temperature over 30 min and the resulting deep red solution was then recooled to –78 °C. A solution of heat gun-dried lithium chloride (9 mg, 0.20 mmol) in THF (4 mL) was added through a cannula and the mixture was stirred for an additional 5 min. The bisamide solution was transferred through a cannula into the reaction mixture, which was stirred for a further 30 min. Addition of iodomethane (37 μL, 0.60 mmol) at –78 °C gave a yellow solution after stirring for 60 min. The reaction mixture was quenched using MeOH (1 mL) and the solvent was removed in vacuo to give a crude yellow solid. Purification by flash column chromatography (SiO_2; hexane/ethyl acetate, 100:0 → 80:20) yielded complex (–)-**10** (86 mg, 86%) as a yellow solid; m.p. 137–140 °C. R_f = 0.15 (SiO_2; hexane/ethyl acetate, 80:20). Enantio-

metric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min, 330 nm); (*S*)-enantiomer t_r = 15.0 min (minor); (*R*)-enantiomer t_r = 16.7 min (major): ≥ 99% *ee*. $[\alpha]_D^{20}$ = –13, (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 1953 (υ_{CO}, s), 1860 (υ_{CO}, s) cm^{-1}. ^1H NMR (400 MHz): δ = 1.50 (d, *J* = 7.0 Hz, 6 H, $CHCH_3$×2), 4.46 (q, *J* = 7.0 Hz, 2 H, $CHCH_3$), 5.27–5.69 (m, 10 H, C_6H_5×2). ^{13}C NMR (100 MHz): δ = 23.6 ($OCHCH_3$×2), 72.9 (OCH×2), 91.1 ($C_{Cr}H$×2), 91.2 ($C_{Cr}H$×2), 91.6 ($C_{Cr}H$×2), 92.1 ($C_{Cr}H$×2), 93.6 ($C_{Cr}H$×2), 113.8 (C_{Cr}×2), 232.9 ($C{\equiv}O$×6) ppm. MS (CI): *m*/*z* (%) = 516 (21) [MNH_4^+], 680 (12) [MNH_4^+ – Cr – 3CO], 241 (100) [MH^+ – $OCH_2(CH_3)Ph$ – Cr – 3CO]. $C_{22}H_{18}Cr_2O_7$ (498.37): calcd. C 53.01, H 3.61; found C 53.02, H 3.70.

(+)-(1*S*,1′*S*)-Hexacarbonyl{bis[1-(1-phenylethyl) ether]}dichromium(0) [(+)-10]: Complex (+)-**10** was prepared from **9** (94 mg, 0.20 mmol) and diamine (–)-**2** (143 mg, 1.06 mmol) following the procedure described for (–)-**10**. 82% yield, yellow solid. $[\alpha]_D^{20}$ = +12 (*c* = 1.00, $CHCl_3$). *ee* ≥ 99%. All other analytical data were identical to those obtained for (–)-**10**.

(+)-(1*R*,1′*R*)-Bis[1-(1-phenylethyl)] Ether [(+)-11]: Complex (–)-**10** (48.7 mg, 0.098 mmol) was dissolved in a mixture of DCM (20 mL) and Et_2O (2 mL) and left for 24 h by the window. The solvent was removed from the mixture under reduced pressure. Purification by column chromatography (SiO_2; hexane/diethyl ether, 98:2) gave a colourless oil (21.5 mg, 97%). R_f = 0.28 (SiO_2; hexane/diethyl ether, 98:2). $[\alpha]_D^{20}$ = +224 (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 1091 ($\upsilon_{C–O–C}$, s) cm^{-1}. ^1H NMR (400 MHz): δ = 1.41 (d, *J* = 6.5 Hz, 6 H, $CHCH_3$×2), 4.28 (q, *J* = 6.5 Hz, 2 H, $CHCH_3$×2), 7.28–7.41 (m, 10 H, $C_{Ar}H$×10) ppm. ^{13}C NMR (100 MHz): δ = 24.7 (CH_3×2), 74.6 ($CHCH_3$×2), 126.3 ($C_{Ar}H$×4), 127.4 ($C_{Ar}H$×2), 128.5 ($C_{Ar}H$×4), 144.2 (C_{Ar}×2) ppm. MS (CI): *m*/*z* (%) = 244 (100) [M + NH_4^+], 122 (13) [M – $C_6H_5CHCH_3$ + NH_4^+], 122 (75) [M – $C_6H_5CHCH_3$ + H^+], 105 (12) [$C_6H_5CHCH_3^+$]. HRMS (CI): calcd. for $C_{16}H_{22}NO^+$ (244.1701); found 244.1711.

(–)-(1*S*,1′*S*)-Bis[1-(1-phenylethyl)] Ether [(–)-11]: Ether (–)-**11** was prepared from (+)-**10** (39.5 mg, 0.079 mmol) following the procedure described for (+)-**11**. 98% yield, colourless oil. $[\alpha]_D^{20}$ = –234 (*c* = 1.00, $CHCl_3$). All other analytical data were identical to those obtained for (+)-**11**.

(–)-(1*S*,1′*S*)-Hexacarbonyl{bis[1-(1-phenylbut-3-enyl)] ether}dichromium(0) [(–)-14]: *n*-Butyllithium (0.32 mL, 2.50 M in hexane, 0.80 mmol) was added to a solution of the diamine (–)-**2** (168 mg, 0.40 mmol) in THF (2 mL) at –78 °C. The solution was warmed to room temperature over a period of 30 min. The deep red solution was recooled to –78 °C. A solution of heat gun-dried lithium chloride (17 mg, 0.40 mmol), dissolved in THF (2 mL) was added and the reaction mixture was stirred for a further 5 min before a precooled solution (–78 °C) of complex **9** (94 mg, 0.20 mmol) in THF (2 mL) was added. After stirring for 60 min at –78 °C, allyl bromide (0.10 mL, 1.20 mmol) was added. Stirring was continued for a further 2 h after which the reaction was quenched with methanol (1 mL). The solvent was removed in vacuo leaving a red residue. Purification by column chromatography (SiO_2; hexane/ethyl acetate, 95:5 → 80:20) afforded complex (–)-**14** as an orange solid (21 mg, 19%) and the monoallylated bischromium complex (+)-**15** (66 mg, 35%, 97% *ee*) as determined by HPLC analysis, ^1H and ^{13}C NMR spectroscopy; m.p. 105–107 °C. R_f = 0.27 (SiO_2; hexane/ethyl acetate, 80:20). Enantiometric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*PrOH, 90:10, 0.25 mL/min, 330 nm); (*S*)-enantiomer t_r = 32.5 min (major); (*R*)-enantiomer t_r = 35.1 min (minor): ≥ 99% *ee*. $[\alpha]_D^{20}$ = –18 (*c* = 0.82, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$= 1961 (υ_{CO}, s), 1868 (υ_{CO}, s) cm^{-1}. ^1H NMR (400 MHz): δ = 2.51–2.59 (m, 2 H, $OCHCH'H$×2), 2.63–2.70 (m, 2 H, $OCHCH'H$×2), 4.51 (t, *J* = 6.0 Hz, 2 H, OCH×2), 5.05 (dd, *J* = 1.0, 17.0 Hz, 2 H, $CH{=}CH'H$ x 2), 5.12 (dd, *J* = 1.0, 10.0 Hz, 2 H, $CH{=}CH'H$×2), 5.22–5.51 (m, 8 H, $C_{Ar}H$×8), 5.72–5.84 (m, 4 H, $C_{Ar}H$×2 and $CH{=}CH_2$×2) ppm. ^{13}C NMR (100 MHz): δ = 42.7 ($CH_2CH{=}CH_2$×2), 76.7 (OCH×2), 90.1 ($C_{Cr}H$×2), 90.4 ($C_{Cr}H$×2), 92.3 ($C_{Cr}H$×2), 93.5 ($C_{Cr}H$×2), 94.4 ($C_{Cr}H$×2), 111.5 (C_{Cr}×2), 119.2 ($CH{=}CH_2$×2), 132.6 ($CH{=}CH_2$×2), 232.9 ($C{\equiv}O$×6) ppm. MS (EI): *m*/*z* (%) = 550 (71) [M^+], 466 (44) [M^+ – 3CO], 382 (97) [M^+ – 6CO], 312 (100) [M^+ – Cr – 6CO], 278 (23) [M^+ – 2Cr – 6CO]. $C_{26}H_{22}Cr_2O_7$ (550.44): calcd. C 56.73, H 4.03; found C 56.78, H 4.04.

(+)-(1*R*,1′*R*)-Hexacarbonyl{bis[1-(1-phenylbut-3-enyl)] ether}dichromium(0) [(+)-14]: Complex (+)-**14** was prepared from **9** (188 mg, 0.4 mmol) and (+)-**2** (336 mg, 0.80 mmol) following the procedure described for (–)-**14**. 17% yield, orange solid. $[\alpha]_D^{20}$ = +18 (*c* = 0.82, $CHCl_3$). *ee* ≥ 99%. All other analytical data were identical to those obtained for (–)-**14**. Monoallylated complex (–)-**15** as a yellow oil (68 mg, 35%, ≥ 99% *ee*).

(–)-(*R*)-Hexacarbonyl{benzyl [1-(1-phenylbut-3-enyl)] ether}dichromium(0) [(–)-15]: *n*-Butyllithium (1.38 mL, 1.60 M in hexane, 2.20 mmol) was added to a solution of the diamine (+)-**2** (463 mg, 1.10 mmol) in THF (12 mL) at –78 °C. The solution was warmed to room temperature over 30 min. The deep red solution was recooled to –78 °C. A solution of heat gun-dried lithium chloride (47 mg, 1.10 mmol) in THF (6 mL) was added and the reaction mixture was stirred for a further 5 min before a precooled solution (–78 °C) of complex **9** (470 mg, 1.00 mmol) in THF (6 mL) was added. On addition of the complex, the reaction mixture slowly turned orange. After stirring for 40 min at –78 °C, allyl bromide (0.26 mL, 3.00 mmol) was added. Stirring was continued for a further 20 min before quenching with methanol (2 mL). The solvent was removed in vacuo leaving a yellow residue. Purification by column chromatography (SiO_2; hexane/ethyl acetate, 95:5 → 85:15) afforded complex (–)-**15** (451 mg, 89%) as a yellow oil. R_f = 0.25 (SiO_2; hexane/ethyl acetate, 80:20). Enantiometric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min, 330 nm); (*S*)-enantiomer t_r = 16.1 min (minor); (*R*)-enantiomer t_r = 19.7 min (major): ≥ 99% *ee*. $[\alpha]_D^{20}$ = –10 (*c* = 0.70 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$= 1974 (υ_{CO}, s), 1897 (υ_{CO}, s), 1642 ($\upsilon_{C=C}$, w) cm^{-1}. ^1H NMR (400 MHz): δ = 2.57–2.61 (m, 2 H, $CH_2CH{=}CH_2$), 4.24 (t, *J* = 6.0 Hz, 1 H, $OCHCH_2$), 4.38 (d, *J* = 11.5 Hz, 1 H, $OCH'H$), 4.59 (d, *J* = 11.5 Hz, 1 H, $OCH'H$), 5.10–5.18 (m, 2 H, $CH{=}CH_2$), 5.27–5.68 (m, 10 H, $C_{Cr}H$×10), 5.79–5.90 (m, 1 H, $CH{=}CH_2$) ppm. ^{13}C NMR (100 MHz): δ = 42.3 ($CH_2CH{=}CH_2$), 70.2 (OCH_2), 77.2 ($OCHCH_2$), 91.1 ($C_{Cr}H$), 91.4 ($C_{Cr}H$), 91.56 ($C_{Cr}H$), 91.61 ($C_{Cr}H$), 92.0 ($C_{Cr}H$), 92.1 ($C_{Cr}H$×2), 92.3 ($C_{Cr}H$×2), 93.2 ($C_{Cr}H$), 107.3 (C_{Cr}), 111.2 (C_{Cr}), 119.1 ($CH{=}CH_2$), 132.6 ($CH{=}CH_2$), 232.7 ($C{\equiv}O$×3), 232.9 ($C{\equiv}O$×3) ppm. MS (EI): *m*/*z* (%) = 510 (69) [M^+], 426 (39) [M^+ – 3CO], 398 (12) [M^+ – 4CO], 370 (16) [M^+ – 5CO], 342 (100) [M^+ – 6CO], 290 (55) [M^+ – Cr – 6CO], 238 (34) [M^+ – 2Cr – 6CO]. $C_{23}H_{18}Cr_2O_7$ (510.38): calcd. C 54.13, H 3.55; found C 54.06, H 3.43.

(+)-(*S*)-Hexacarbonyl{benzyl [1-(1-phenylbut-3-enyl)] ether}dichromium(0) [(+)-15]: Complex (+)-**15** was prepared from **9** (204 mg, 0.43 mmol) and (–)-**2** (200 mg, 0.43 mmol) following the procedure described for (–)-**15**. 86% yield, yellow oil. $[\alpha]_D^{20}$ = +6.4 (*c* = 1.85, $CHCl_3$). *ee* ≥ 99%. All other analytical data were identical to those obtained for (–)-**15**.

Tricarbonyl[1-phenylbut-3-ene]chromium(0) (16):[10] Potassium *tert*-butoxide (27 mg, 0.24 mmol) and THF (1 mL) were placed in a small Schlenk tube at room temperature. Complex (–)-**15** (95 mg, 0.91 mmol), dissolved in THF (2 mL), was added using a syringe.

The reaction mixture slowly darkened to red then black. After stirring for 19.5 h, MeOD was added and the solvent was removed under reduced pressure leaving a black residue. Purification by column chromatography (SiO_2; ethyl acetate/hexane, 80:20) gave complex **16** (32 mg, 62%) as a yellow oil. R_f = 0.50 (SiO_2; ethyl acetate/hexane, 80:20). IR ($CHCl_3$): $\tilde{\nu}$= 1970 (υ_{CO}, s), 1896 (υ_{CO}, s) cm^{-1}. ^1H NMR (400 MHz): δ = 2.36 (m, 2 H, CH_2CH=CH_2), 2.50 (t, J = 7.5 Hz, 2 H, CH_2CH_2CH=CH_2), 5.03–5.10 (m, 2 H, CH=CH_2), 5.19–5.24 (m, 3 H, $C_{Cr}H_{ortho}$×2, $C_{Cr}H_{para}$), 5.39–5.42 (m, 2 H, $C_{Cr}H_{meta}$×2), 5.78–5.89 (m, 1 H, CH=CH_2) ppm. ^{13}C NMR (100 MHz): δ = 34.5 (CH_2CH=CH_2), 35.1 (CH_2CH_2CH=CH_2), 90.4 (C_{Cr}), 92.7 ($C_{Cr}H_{meta}$×2), 93.7 ($C_{Cr}H_{ortho}$×2), 112.9 ($C_{Cr}H_{para}$), 116.3 (CH=CH_2), 136.4 (CH=CH_2), 232.1 (C≡O×3) ppm. MS (EI): m/z (%) = 268 (38) [M^+], 184 (100) [M^+ – 3CO].

(–)-(*R*)-Hexacarbonyl{benzyl [1-(1-phenylethyl)] ether}dichromium(0) [(–)-17]: *n*-Butyllithium (0.56 mL, 2.50 M in hexane, 1.40 mmol) was added to a solution of the diamine (+)-**2** (294 mg, 0.70 mmol) in THF (12 mL) at –78 °C. The solution was warmed to room temperature over 30 min and the resulting deep red solution was recooled to –78 °C. A solution of heat gun-dried lithium chloride (30 mg, 0.70 mmol) in THF (10 mL) was added and the reaction mixture was stirred for a further 10 min. A precooled solution (–78 °C) of complex **9** (470 mg, 1.0 mmol) in THF (10 mL) was added, upon which the reaction mixture slowly turned orange. After stirring the reaction mixture at –78 °C for 40 min, iodomethane (0.06 mL, 1.0 mmol) was added. Stirring was continued for 30 min and the reaction was quenched with methanol (2 mL). The solvent was removed in vacuo leaving a yellow residue. Purification by column chromatography (SiO_2; hexane/ethyl acetate, 95:5 → 80:20) afforded complex (–)-**17** (288 mg, 59%) as a yellow solid; m.p. 102–103 °C. R_f = 0.19 (SiO_2; hexane/ethyl acetate, 80:20). Enantiometric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/*i*PrOH, 80:20, 1.0 mL/min, 330 nm); (*S*)-enantiomer t_r = 31.6 min (minor); (*R*)-enantiomer t_r = 36.8 min (major): ≥ 99% *ee*. $[\alpha]_D^{20}$ = –15 (c = 1.20 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 1973 (υ_{CO}, s), 1898 (υ_{CO}, s) cm^{-1}. ^1H NMR (400 MHz): δ = 1.55 (d, J = 6.5 Hz, 3 H, CHCH_3), 4.34 (q, J = 6.5 Hz, 1 H, CHCH$_3$), 4.37 (d, J = 11.5 Hz, 1 H, OCHH′), 4.48 (d, J = 11.5 Hz, 1 H, OCHH′), 5.29–5.63 (m, 10 H, $C_{Cr}H$×10) ppm. ^{13}C NMR (100 MHz): δ = 22.9 (OCH$_2$CH_3), 69.3 (OCH_2), 75.9 (OCHCH$_3$), 91.1 (C_{Cr}H), 91.2 (C_{Cr}H), 91.7 (C_{Cr}H), 91.78, 91.83, 92.58 (C_{Cr}H×5), 92.60 (C_{Cr}H), 92.8 (C_{Cr}H), 107.7 (C_{Cr}), 113.1 (C_{Cr}), 232.7 (C≡O×3), 232.9 (C≡O×3) ppm. MS (EI): m/z (%) = 484 (35) [M^+], 400 (19) [M^+ – 2Cr – 3CO], 316 (100) [M^+ – 6CO], 264 (47) [M^+ – Cr – 6CO]. $C_{21}H_{16}Cr_2O_7$ (484.39): calcd. C 52.08, H 3.33; found C 52.15, H 3.36.

(+)-(*S*)-Hexacarbonyl{benzyl [1-(1-phenylethyl)] ether}dichromium(0) [(+)-17]: Complex (+)-**17** was prepared from **9** (470 mg, 1.00 mmol) and (–)-**2** (294 mg, 0.70 mmol) following the procedure described for (–)-**17**. 66% yield, yellow solid. $[\alpha]_D^{20}$ = +15 (c = 1.57, $CHCl_3$). *ee* ≥ 99%. All other analytical data were identical to those obtained for (–)-**17**.

(+)-(1*R*,1′*R*)-Hexacarbonyl{[1-(1,2-diphenylethyl)] [1-(1-phenylethyl)] ether}dichromium(0) [(+)-18]: *n*-Butyllithium (0.18 mL, 2.50 M in hexane, 0.44 mmol) was added to a solution of the diamine (+)-**2** (78 mg, 0.22 mmol) in THF (2 mL) at –78 °C. The solution was warmed to room temperature over 30 min before recooling to –78 °C. Heat gun-dried lithium chloride (10 mg, 0.22 mmol) in THF (2 mL) was added and the reaction mixture was stirred for a further 10 min before a precooled solution (–78 °C) of complex (–)-**17** (93 mg, 0.22 mmol) in THF (2 mL) was added. After stirring for 40 min at –78 °C, benzyl bromide (0.08 mL, 0.66 mmol) was added. Stirring was continued for a further 60 min before quenching with methanol (2 mL). The solvent was removed in vacuo leaving a yellow residue. Purification by column chromatography (SiO_2; hexane/ethyl acetate, 95:5 → 85:15) afforded (+)-**18** (95 mg, 63%) as a yellow solid; m.p. 134–136 °C. R_f = 0.27 (SiO_2; hexane/ethyl acetate, 80:20). Enantiometric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min, 330 nm); (*R*)-enantiomer t_r = 10.7 min (major); (*S*)-enantiomer t_r = 12.9 min (minor): 99% *ee*. $[\alpha]_D^{20}$ = +35 (c = 1.34 in $CHCl_3$). IR (film): $\tilde{\nu}$= 1964 (υ_{CO}, s), 1875 (υ_{CO}) cm^{-1}. ^1H NMR (400 MHz): δ = 1.54 (d, J = 6.5 Hz, 3 H, OCHCH_3), 2.90 (dd, J = 6.5, 13.5 Hz, 1 H, CHH′C$_6$H$_5$), 3.16 (dd, J = 7.0, 13.5 Hz, 1 H, CHH′C$_6$H$_5$), 4.42 (dd, J = 6.5, 7.0 Hz, 1 H, CHCH′HC$_6$H$_5$), 4.53 (q, J = 6.5 Hz, 1 H, CHCH$_3$), 5.04–5.72 (m, 10 H, $C_{Cr}H$×10), 7.06–7.09 (m, 2 H, $C_{Ar}H$×2), 7.23–7.31 (m, 3 H, $C_{Ar}H$×3) ppm. ^{13}C NMR (100 MHz): δ = 23.9 (OCHCH$_3$), 45.2 (OCHCH$_2$), 73.7 (OCHCH$_3$), 78.1 (OCHCH$_2$), 89.7 (C_{Cr}H), 90.2 (C_{Cr}H), 90.7 (C_{Cr}H), 90.9 (C_{Cr}H), 92.17 (C_{Cr}H), 92.23 (C_{Cr}H), 92.7 (C_{Cr}H), 93.5 (C_{Cr}H), 93.6 (C_{Cr}H), 94.7 (C_{Cr}H), 110.9 (C_{Cr}), 113.2 (C_{Cr}), 126.8 ($C_{Ar}H_{para}$) 128.5 ($C_{Ar}H_{ortho}$×2, $C_{Ar}H_{meta}$×2), 136.5 (C_{Ar}), 233.52 (C≡O×6) ppm. MS (EI): m/z (%) = 524 (19) [M^+], 440 (9) [M^+ – 3CO], 356 (35) [M^+ – 6CO], 304 (88) [M^+ – 6CO – Cr], 52 (100) [Cr^+]. $C_{28}H_{22}Cr_2O_7$ (574.46): calcd. C 58.54, H 3.86; found C 58.60, H 3.82.

(–)-(1*S*,1′*S*)-Hexacarbonyl{[1-(1,2-diphenylethyl)] [1-(1-phenylethyl)]} etherdichromium(0) [(–)-18]: Complex (–)-**18** was prepared from (+)-**17** (93 mg, 0.22 mmol) and (–)-**2** (78 mg, 0.22 mmol) following the procedure described for (+)-**18**. 70% yield, yellow oil. $[\alpha]_D^{20}$ = –35 (c = 1.48, $CHCl_3$). *ee* ≥ 99%. All other analytical data were identical to those obtained for (+)-**18**.

(+)-(1*R*,1′*R*)-Hexacarbonyl{[1-(1-phenylbut-3-enyl)] [1-(1-phenylethyl)] ether}dichromium(0) [(+)-19]: *n*-Butyllithium (0.32 mL, 2.50 M in hexane, 0.80 mmol) was added to a solution of the diamine (+)-**2** (168 mg, 0.40 mmol) in THF (4 mL) at –78 °C. The solution was warmed to room temperature over 30 min before recooling to –78 °C. Heat gun-dried lithium chloride (17 mg, 0.40 mmol) in THF (4 mL) was added and the reaction mixture was stirred for 10 min before a precooled solution (–78 °C) of complex (–)-**17** (194 mg, 0.40 mmol) in THF (4 mL) was added. After stirring for 40 min at –78 °C, allyl bromide (0.10 mL, 1.20 mmol) was added. Stirring was continued for a further 45 min before quenching with methanol (2 mL). The solvent was removed in vacuo leaving a yellow residue. Purification by column chromatography (SiO_2; hexane/ethyl acetate, 95:5 → 85:15) afforded complex (+)-**19** (152 mg, 72%) as a yellow oil. R_f = 0.28 (SiO_2; hexane/ethyl acetate, 80:20). Enantiometric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min, 330 nm); (*R*)-enantiomer t_r = 18.4 min (major); (*S*)-enantiomer t_r = 20.9 min (minor): *ee* ≥ 99%. $[\alpha]_D^{20}$ = +11 (c = 0.54 in $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 1961 (υ_{CO}, s), 1874 (υ_{CO}, s) cm^{-1}. ^1H NMR (400 MHz): δ = 1.55 (d, J = 6.5 Hz, 3 H, OCHCH_3), 2.48–2.64 (m, 2 H, CH_2CH=CH$_2$), 4.38 (t, J = 6.5 Hz, 1 H, OCHCH$_2$), 4.56 (q, J = 6.5 Hz, 1 H, OCHCH$_3$), 5.05 (dd, J = 1.5, 17.0 Hz, 1 H, CH=CH′H), 5.13 (dd, J = 1.4, 10.0 Hz, 1 H, CH=CH′H), 5.02–5.46 (m, 8 H, $C_{Cr}H$×8), 5.69–5.80 (m, 3 H, CH=CH$_2$, $C_{Cr}H$×2) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 23.9 (OCHCH$_3$), 42.5 (CH_2CH=CH$_2$), 73.8 (OCHCH$_3$), 76.6 (OCHCH$_2$), 90.1 (C_{Cr}H), 90.4 (C_{Cr}H), 90.9 (C_{Cr}×2), 91.6 (C_{Cr}H), 91.9 (C_{Cr}H), 92.1 (C_{Cr}H), 93.2 (C_{Cr}H), 93.6 (C_{Cr}H), 94.1 (C_{Cr}H), 111.5 (C_{Cr}), 113.4 (C_{Cr}), 119.0 (CH=CH$_2$), 132.8 (CH=CH$_2$), 233.47 (C≡O×3), 233.52 (C≡O×3) ppm. MS (EI): m/z (%) = 524 (19) [M^+], 440 (9) [M^+ – 3CO], 356 (35) [M^+ – 6CO], 304 (88) [M^+ – 6CO – Cr], 52 (100) [Cr^+]. $C_{24}H_{20}Cr_2O_7$ (524.40): calcd. C 54.97, H 3.84; found C 54.97, H 3.85.

(–)-(1*S*,1′*S*)-Hexacarbonyl{[1-(1-phenylbut-3-enyl)] [1-(1-phenylethyl)] ether}dichromium(0) [(–)-19]: Complex (–)-**19** was prepared from (+)-**17** (106 mg, 0.22 mmol) and (–)-**2** (93 mg, 0.22 mmol) following the procedure described for (+)-**19**. 72% yield, yellow oil. $[\alpha]_D^{20}$ = –10 (*c* = 0.86, $CHCl_3$). *ee* ≥ 99%. All other analytical data were identical to those obtained for (+)-**19**.

(+)-(1*R*,1′*R*)-[1-(1,2-Diphenylethyl)] [1-(1-Phenylethyl)] Ether [(+)-20]: Complex (+)-**18** (70 mg, 0.121 mmol) was dissolved in diethyl ether (100 mL) and left for 24 h by the window. The solvent was removed from the mixture under reduced pressure. Purification by column chromatography (SiO_2; hexane/diethyl ether, 98:2) gave a colourless oil (30 mg, 81%). R_f = 0.18 (SiO_2; hexane/diethyl ether, 98:2). $[\alpha]_D^{20}$ = +111 (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 1090 ($\upsilon_{C–O–C}$, m) cm^{-1}. ^1H NMR (400 MHz): δ = 1.36 (d, *J* = 6.5 Hz, 3 H, $CHCH_3$), 2.87 (dd, *J* = 8.0, 13.5 Hz, 1 H, $OCHCHH'$), 3.08 (dd, *J* = 5.5, 13.5 Hz, 1 H, $OCHCHH'$), 4.25 (q, *J* = 6.5 Hz, 1 H, $OCHCH_3$), 4.27 (dd, *J* = 5.5, 8.0 Hz, 1 H, $OCHCHH'$), 6.92–7.40 (m, 15 H, $C_{Ar}H\times15$) ppm. ^{13}C NMR (100 MHz): δ = 24.8 (CH_3), 45.3 ($OCHCH_2$), 74.6 ($OCHCH_3$), 79.9 ($OCHCHH'$), 126.0 ($C_{Ar}H$), 126.3 ($C_{Ar}H\times2$), 126.9 ($C_{Ar}H\times2$), 127.1 ($C_{Ar}H$), 127.5 ($C_{Ar}H$), 127.9 ($C_{Ar}H\times2$), 128.2 ($C_{Ar}H\times2$), 128.3 ($C_{Ar}H\times2$), 129.8 ($C_{Ar}H\times2$), 138.6 (C_{Ar}), 142.4 (C_{Ar}), 143.7 (C_{Ar}) ppm. MS (CI): *m*/*z* (%) = 320 (94) [M + NH_4^+], 198 (100) [M – $C_6H_5CHCH_3$ + H^+], 122 (54) [$C_6H_5CHCH_3^+$ + NH_3]. $C_{22}H_{22}O$ (302.41): calcd. C 87.38, H 7.33; found C 87.33, H 7.31.

(–)-(1*S*,1′*S*)-[1-(1,2-Diphenylethyl)] [1-(1-Phenylethyl)] Ether [(–)-20]: Ether (–)-**20** was prepared from (–)-**18** (70 mg, 0.121 mmol) following the procedure described for (+)-**20**. 84% yield, colourless oil. $[\alpha]_D^{20}$ = –116 (*c* = 1.00, $CHCl_3$). All other analytical data were identical to those obtained for (+)-**20**.

(+)-(1*R*,1′*R*)-[1-(1-Phenylbut-3-enyl)] [1-(1-Phenylethyl)] Ether [(+)-21]: Complex (+)-**19** (120 mg, 0.23 mmol) was dissolved in diethyl ether (100 mL) and left for 24 h by the window. The solvent was removed from the mixture under reduced pressure. Purification by column chromatography (SiO_2; hexane/diethyl ether, 98:2) gave a colourless oil (55 mg, 95%). R_f = 0.22 (SiO_2; hexane/diethyl ether, 98:2). $[\alpha]_D^{20}$ = +193 (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$= 1089 ($\upsilon_{C–O–C}$, s) cm^{-1}. ^1H NMR (400 MHz): δ = 1.41 (d, *J* = 6.5 Hz, 6 H, $CHCH_3\times2$), 2.34–2.01 (m, 1 H, $CHH'CH=CH_2$), 2.55–2.63 (m, 1 H, $CHH'CH=CH_2$), 4.15 (t, *J* = 6.0 Hz, 1 H, $OCHCH_2CH=CH_2$), 4.27 (q, *J* = 6.5 Hz, 1 H, $OCHCH_3$), 4.95–4.98 (m, 1 H, $CH=CHH'$), 4.98–5.02 (m, 1 H, $CH=CHH'$), 5.66–5.70 (m, 1 H, $CH=CH_2$) ppm. ^{13}C NMR (100 MHz): δ = 24.7 (CH_3), 43.0 ($CH_2CH=CH_2$), 74.6 ($CHCH_3$), 78.5 ($CHCH_2CH=CH_2$), 116.7 ($CH=CH_2$), 126.6 ($C_{Ar}H\times2$), 126.9 ($C_{Ar}H\times2$), 127.4 ($C_{Ar}H$), 127.6 ($C_{Ar}H$), 128.4 ($C_{Ar}H\times4$), 134.7 ($CH=CH_2$), 142.4 (C_{Ar}), 143.8 (C_{Ar}) ppm. MS (CI): *m*/*z* (%) = 270 (100) [M + NH_4^+], 252 (30) [M^+], 148 (60) [M – $C_6H_5CHCH_3$ + H^+], 122 (72) [M – $CH(CH_2CH=CH_2)C_6H_5$ + H^+]. HRMS (CI): calcd. for $C_{18}H_{24}NO^+$ (270.1851); found 270.1859.

(–)-(1*S*,1′*S*)-[1-(1-Phenylbut-3-enyl)] [1-(1-Phenylethyl)] Ether [(–)-21]: Ether (–)-**21** was prepared from (–)-**19** (72 mg, 0.127 mmol) following the procedure described for (+)-**21**. 92% yield, colourless oil. $[\alpha]_D^{20}$ = –208 (*c* = 1.00, $CHCl_3$). All other analytical data were identical to those obtained for (+)-**21**.

Bis(4-*tert*-butyl)benzyl Ether (22): 4-*tert*-Butylbenzyl alcohol (0.85 mL, 5 mmol) was added to a stirred and cooled (0 °C) suspension of sodium hydride (60% dispersion in mineral oil; 279 mg, 7 mmol, previously washed with hexane), in THF (20 mL). The reaction mixture was warmed to room temperature and then heated under reflux for 2 h. After cooling to room temperature, 4-*tert*-butylbenzyl bromide (0.91 mL, 5 mmol) was added. Stirring was continued at room temperature for 14 h. A saturated aqueous solution of ammonium chloride (5 mL) was added, the organic phase was separated and the aqueous phase extracted with diethyl ether (3×20 mL). The combined organic layers were washed with brine (60 mL), dried ($MgSO_4$) and concentrated in vacuo to afford ether **22** (1.54 g, 99%) as a colourless oil. R_f = 0.71 (SiO_2; hexane/diethyl ether). IR (neat): $\tilde{\nu}$ = 1090 ($\upsilon_{C–O–C}$, s) cm^{-1}. ^1H NMR (400 MHz): δ = 1.34 [s, 18 H, $C(CH_3)_3\times2$], 4.55 (s, 4 H, $OCH_2\times2$), 7.33 [d, *J* = 8.0 Hz, 4 H, ($OCH_2CC_{Ar}H\times4$)], 7.41 {d, *J* = 8.0 Hz, 4 H, $C_{Ar}HC[C(CH_3)_3]\times4$} ppm. ^{13}C NMR (400 MHz): δ = 31.4 [$C(CH_3)_3\times2$], 34.6 [$C(CH_3)_3\times2$], 71.8 ($CH_2\times2$), 125.3 [$C_{Ar}HC_{Ar}C(CH_3)_3\times4$], 127.6 ($OCH_2CC_{Ar}H\times4$), 135.4 ($OCH_2C_{Ar}\times2$), 150.6 [$C_{Ar}C(CH_3)_3\times2$] ppm. MS (EI): *m*/*z* (%) = 57 (100) [$C(CH_3)_3^+$], 133 (34) [$C_6H_4C(CH_3)_3^+$], 147 (86) [M^+ – $OCH_2C_6H_4C(CH_3)_3$], 163 (47) [M^+ – $CH_2C_6H_4C(CH_3)_3$], 295 (38) [M^+ – CH_3], 310 (3) [M^+]. HRMS (EI): calcd. for $C_{22}H_{30}O$ (310.2297); found 310.2297.

Hexacarbonyl[bis(4-*tert*-butyl)benzyl ether]dichromium(0) (23): Bis(4-*tert*-butyl)benzyl ether **22** (1.24 g, 4.00 mmol), hexacarbonylchromium(0) (2.64 g, 12.0 mmol), dry di-*n*-butyl ether (100 mL) and THF (20 mL) were degassed 10 times and shielded from ambient light. The reaction mixture was heated under reflux for 48 h at 140 °C and then cooled to room temperature. The solvent was removed under reduced pressure and the crude reaction mixture was pre-absorbed onto silica (30 g). Purification was carried out via column chromatography (SiO_2; hexane/ethyl acetate, 70:30) to yield complex **23** (2.25 g, 97% yield) as a yellow solid; m.p. 86–87 °C. R_f = 0.15 (SiO_2; hexane/ethyl acetate, 80:20). IR ($CHCl_3$): $\tilde{\nu}$ = 1958 (υ_{CO}, s), 1874 (υ_{CO}, s) cm^{-1}. ^1H NMR (400 MHz): δ = 1.31 [s, 18 H, $C(CH_3)_3\times2$], 4.40 (s, 4 H, $OCH_2\times2$), 5.31 [d, *J* = 6.0 Hz, 4 H, ($OCH_2CC_{Ar}H\times4$)], 5.59 {d, *J* = 8.0 Hz, 4 H, $C_{Ar}HC[C(CH_3)_3]\times4$} ppm. ^{13}C NMR (400 MHz): δ = 31.1 [$C(CH_3)_3\times2$], 33.7 [$C(CH_3)_3\times2$], 71.1 ($CH_2\times2$), 90.1 [$C_{Cr}HC_{Cr}C(CH_3)_3\times4$], 92.4 ($OCH_2CC_{Cr}H\times4$), 107.3 ($OCH_2C_{Cr}\times2$), 122.1 [$C_{Cr}C(CH_3)_3\times2$], 232.3 ($C\equiv O\times6$) ppm. MS (EI): *m*/*z* (%) = 582 (30) [M^+], 498 (19) [M^+ – 3CO], 414 (100) [M^+ – 6CO], 362 (35) [M^+ – Cr – 6CO]. $C_{28}H_{30}Cr_2O_7$ (582.53): calcd. C 57.73, H 5.19; found C 57.69, H 5.24.

(–)-(1*R*,1′*R*)-Hexacarbonyl(bis{1-[1-(4-*tert*-butylphenyl)ethyl]} ether)dichromium(0) [(–)-24]: *n*-Butyllithium (0.56 mL, 2.50 M in hexane, 1.40 mmol) was added to a solution of the diamine (+)-**2** (294 mg, 0.70 mmol) in THF (7 mL) at –78 °C. The solution was warmed to room temperature over 30 min and the resulting deep red solution was then recooled to –78 °C. Heat gun-dried lithium chloride (30 mg, 0.70 mmol) in THF (4 mL) was added and the reaction mixture was stirred for a further 5 min before a precooled solution (–78 °C) of complex **23** (204 mg, 0.35 mmol) in THF (7 mL) was added. After stirring for 60 min at –78 °C, iodomethane (0.13 mL, 2.10 mmol) was added. Stirring was continued for a further 1 h at –78 °C before MeOH (1 mL) was used to quench the reaction. The solvent was removed in vacuo. Purification by column chromatography (SiO_2; hexane/EtOAc, 100:0 → 80:20) yielded complex (–)-**24** (210 mg, 98%) as a yellow solid; m.p. 145–147 °C. R_f = 0.49 (SiO_2; hexane/ethyl acetate, 80:20). Enantiometric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min, 330 nm); (*R*)-enantiomer t_r = 6.1 min (major); (*S*)-enantiomer t_r = 7.4 min (minor): *ee* ≥ 99%, 97.4% *de*. $[\alpha]_D^{20}$ = –22 (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 1957 (υ_{CO}, s), υ_{CO} 1874(s) cm^{-1}. ^1H NMR (400 MHz): δ = 1.32 [s, 18 H, $C(CH_3)_3\times2$], 1.53 (d, *J* = 6.5 Hz, 6 H, $CHCH_3\times2$), 4.52 (q, *J* = 6.5 Hz, 2 H, $CHCH_3\times2$), 5.28 {dd, *J* = 7.0, 1.0 Hz, 2 H, $C_{Cr}[C(CH_3)_3]C_{Cr}HC_{Cr}H\times2$}, 5.50 {dd, *J* = 7.0, 1.0 Hz, 2 H, $C_{Cr}[C(CH_3)_3]C_{Cr}HC_{Cr}H\times2$}, 5.55 {dd, *J* = 7.0, 1.0 Hz, 2 H, $C_{Cr}[C(CH_3)_3]$

$C_{Cr}H'C_{Cr}H'\times2$}, 5.63 {dd, J = 7.0, 1.0 Hz, 2 H, $C_{Cr}[C(CH_3)_3]C_{Cr}H'C_{Cr}H'\times2$} ppm. ^{13}C NMR (100 MHz): δ = 23.7 ($OCHCH_3\times2$), 31.1 [$C(CH_3)_3\times2$], 34.0 [$C(CH_3)_3\times2$], 71.1 ($OCH\times2$), 90.1 ($C_{Cr}H\times4$), 92.4 ($C_{Cr}H\times4$), 114.5 [$C_{Cr}CH(CH_3)\times2$], 123.3 {$C_{Cr}[C(CH_3)_3]\times2$}, 233.7 ($C{\equiv}O\times6$) ppm. MS (EI): *m/z* (%) = 610 (44) [M$^+$], 526 (35) [M$^+$ – 3CO], 442 (100) [M$^+$ – 6CO], 390 (7) [M$^+$ – 6CO – Cr]. $C_{30}H_{34}Cr_2O_7$ (610.58): calcd. C 59.01, H 5.61; found C 59.07, H 5.57.

(+)-(1*S*,1′*S*)-Hexacarbonyl(bis{1-[1-(4-*tert*-butylphenyl)ethyl]}ether)dichromium(0) [(+)-24]: Complex (+)-**24** was prepared from **23** (150 mg, 0.26 mmol) and (–)-**2** (219 mg, 0.52 mmol) following the procedure described for (–)-**24**. 98% yield, yellow solid. $[\alpha]_D^{20}$ = +22 (*c* = 2.72, $CHCl_3$). *ee* ≥ 99%, 96% *de*. All other analytical data were identical to those obtained for (–)-**24**.

(+)-(1*R*,1′*R*)-Bis{1-[1-(4-*tert*-butylphenyl)ethyl]} Ether [(+)-25]: Complex (–)-**24** (159 mg, 0.26 mmol) was dissolved in DCM (20 mL) and the solution was left in direct sunlight for 24 h. The crude product mixture was filtered through a pad of Celite® and neutral alumina. The pad was thoroughly washed with diethyl ether and the filtrate was concentrated under reduced pressure to afford ether (+)-**25** (82 mg, 93%) as a white solid; m.p. 95–96 °C. R_f = 0.37 (SiO_2; hexane/diethyl ether, 80:20). $[\alpha]_D^{20}$ = +184 (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 1093 (υ_{C-O-C}, s) cm^{-1}. ^{1}H NMR (400 MHz): δ = 1.37 [s, 18 H, $C(CH_3)_3\times2$], 1.40 (d, J = 6.5 Hz, 6 H, $CHCH_3\times2$), 4.28 (q, J = 6.5 Hz, 2 H, $CHCH_3\times2$), 7.24 {d, J = 8.0 Hz, 4 H, $C_{Cr}[C(CH_3)_3]C_{Cr}HC_{Cr}H\times2$ and $C_{Cr}[C(CH_3)_3]C_{Cr}HC_{Cr}H\times2$}, 7.29 {d, J = 8.0 Hz, 4 H, $C_{Cr}[C(CH_3)_3]C_{Cr}H'C_{Cr}H'\times2$ and $C_{Cr}[C(CH_3)_3]C_{Cr}H'C_{Cr}H'\times2$} ppm. ^{13}C NMR (100 MHz): δ = 24.8 ($OCHCH_3\times2$), 31.1 [$C(CH_3)_3\times2$], 34.5 [$C(CH_3)_3\times2$], 74.2 ($OCH\times2$), 125.9 ($C_{Cr}H\times4$), 126.0 ($C_{Cr}H\times4$), 141.1 [$C_{Cr}CH(O)CH_3\times2$], 150.1 {$C_{Cr}[C(CH_3)_3]\times2$} ppm. MS (EI): *m/z* (%) = 338 (2) [M$^+$], 177 {37} [M$^+$ – $CH(CH_3)C_6H_4[C(CH_3)_3]$], 161 {100} [M$^+$ – $OCH(CH_3)C_6H_4[C(CH_3)_3]$], 57 (39) [$C(CH_3)_3^+$]. $C_{24}H_{34}O$ (338.53): calcd. C 85.15, H 10.12; found C 85.21, H 10.13.

(–)-(1*S*,1′*S*)-Bis{1-[1-(4-*tert*-butylphenyl)ethyl]} Ether [(–)-25]: Ether (–)-**25** was prepared from (+)-**24** (130 mg, 0.21 mmol), following the procedure described for (+)-**25**. 62 mg, 86% yield, white solid. $[\alpha]_D^{20}$ = –194 (*c* = 1.00, $CHCl_3$). All other analytical data were identical to those obtained for (+)-**25**.

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