Synthesis of (*R*)-{η⁶-[*O*-methyl-*N*-(α-methylbenzyl)hydroxyamino]-benzene} chromium tricarbonyl *via* nucleophilic aromatic substitution of (η⁶-fluorobenzene) chromium tricarbonyl

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Chiral hydroxylamine chromium tricarbonyl complexes may be prepared in satisfactory to reasonable yield *via* nucleophilic aromatic substitution of the anion derived from *N*,*O*-substituted hydroxylamines and (η⁶-fluorobenzene) chromium tricarbonyl. The enantiomerically pure complex (*R*)-{η⁶-[*O*-methyl-*N*-(α-methylbenzyl)hydroxyamino]-benzene} chromium tricarbonyl **6a** was characterised by X-ray crystallography.

Introduction

Optically active molecules containing nitrogen have an important position among biologically active substances. Thus, there is great interest in developing new methods to control the stereochemical outcome of synthesis involving these compounds.[1] Many chiral hydroxylamines bearing a stereogenic centre α to nitrogen are biologically active and are also precursors of chiral ligands used in asymmetric synthesis.[2] In particular, they have found applications as chiral auxiliaries, in the preparation of cyclic compounds containing N–O bonds, such as isoxazolidinones,[3,4] isoxazolidines[4,5] or hydroxymethylchromanes.[6] Chiral hydroxylamines are also used as key intermediates in the synthesis of optically active amines,[7] allylic alcohols,[8] α-[9] and β-amino acids,[10] α,β-diamino acids,[11] 3-amino-1,2-diols[12] and therapeutic chiral hydroxyureas.[13] This makes these molecules attractive targets for synthesis.

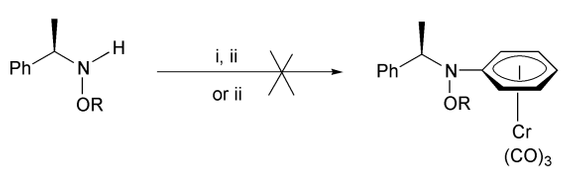
Chromium tricarbonyl complexes of aryl halides undergo nucleophilic replacement of halide by an extensive list of nucleophiles such as stabilised carbanions, $^{-}NR_2$, ^{-}OR and ^{-}SR under conditions where the uncomplexed arenes are inert.[14] Although the aromatic nucleophilic substitution of halide in (haloarene) chromium tricarbonyl complexes by nitrogen substituents has recently been extended to the preparation of arylpiperazines[15] and *N*-arylindoles,[16] the number of methods for the introduction of nitrogen bearing functional groups onto a chromium tricarbonyl complexed arene is quite limited[17] and, to the best of our knowledge, no chiral *N*-aryl chromium tricarbonyl hydroxylamine complexes have been previously described.

The first example of organometallic complexes of chiral hydroxylamines was reported in 1984 by Martin *et al.*,[18] who prepared chiral *N*-(ferrocenylalkyl)hydroxylamines starting from *S*-(ferrocenylalkyl)mercaptoethanoic acids. Baldoli *et al.*[19] have reported the preparation of *O*-arylhydroxylamine derivatives by aromatic nucleophilic substitution on (haloarene) chromium tricarbonyl complexes with *N*-(*tert*-butyloxycarbonyl), and Gibson *et al.*[20] have shown that *N*-hydroxycarbamate chromium tricarbonyl complexes may be prepared *via* addition of a nitrogen nucleophile (*tert*-butyl-*N*-hydroxycarbamate) to chiral benzyl ether chromium tricarbonyl complexes.

A process for the synthesis of chiral hydroxylamine chromium tricarbonyl complexes was envisaged through an *ipso*-substitution reaction using (η⁶-fluorobenzene) chromium tricarbonyl and a suitable hydroxylamine derivative and the results are reported herein.

Results and discussion

The first attempts to obtain *N*-aryl chromium tricarbonyl hydroxylamine complexes involved the reaction of (*R*)-*N*-(α-methylbenzyl)hydroxylamine **1a**[21] or its *O*-silylated derivatives **1b**,**c** with (η⁶-fluorobenzene) chromium tricarbonyl[22] alone or after prior treatment with base (NaH, BuLi). However, the ^{1}H NMR spectra of the crude materials indicated only the presence of starting materials and none of the required complexes (*R*)-**2** (Scheme 1).



(*R*)-**1a** R=H (*R*)-**2a** R=H
(*R*)-**1b** R=$SiMe_3$ (*R*)-**2b** R=$SiMe_3$
(*R*)-**1c** R=$SiMe_2Bu^t$ (*R*)-**2c** R=$SiMe_2Bu^t$

Scheme 1 *Reagents and conditions*: i, base; ii, (η⁶-fluorobenzene)-$Cr(CO)_3$.

As this approach was unsuccessful, the synthesis of *O*-alkyl protected hydroxylamines and reaction of these with (η⁶-fluorobenzene) chromium tricarbonyl was investigated. For this purpose a series of *N*,*O*-substituted hydroxylamines **5a**–**c** were easily prepared in two steps in high yields, starting from *O*-substituted hydroxylamine hydrochlorides **3a**–**c**, according

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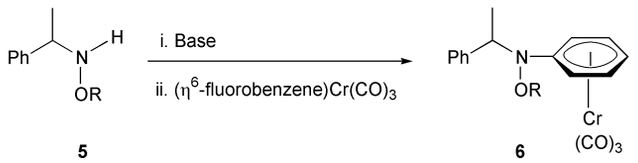
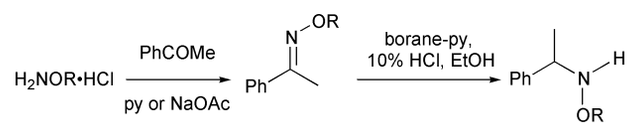
Table 1 Preparation of [*O*-alkyl-*N*-(α-methylbenzyl)hydroxyamino]-benzene chromium tricarbonyl complexes



5 6

R	Substrate	Base	Product	Yield (%)
Me	**5a**	BuLi	**6a**	56
Bu^t	**5b**	BuLi	**6b**	—
CH_2Ph	**5c**	BuLi	**6c**	50
Allyl	**5d**	NaHMDS	**6d**	23



3 4 5

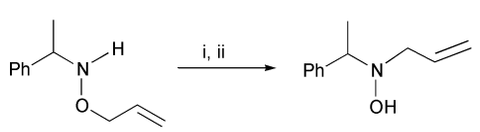
Compound	Compound	Yield	Compound	Yield
3a R = Me	**4a** R = Me	97%	**5a** R = Me[23]	98%
3b R = Bu^t [24]	**4b** R = Bu^t	89%	**5b** R = Bu^t [25]	93%
3c R = CH_2Ph	**4c** R = CH_2Ph	100%	**5c** R = CH_2Ph[26]	41%
3d R = allyl	**4d** R = allyl	99%	**5d** R = allyl	91%

Scheme 2

to known procedures (Scheme 2).[23,25,26] Oxime **4d**, although known,[27] is synthesised here by a different route. Upon reduction with pyridine–borane complex in 10% HCl and EtOH, oxime **4d** gave the new hydroxylamine **5d** in good yield (Scheme 2).

(η6-Fluorobenzene) chromium tricarbonyl was added to the anion derived from the *N*,*O*-dialkylhydroxylamines **5**, generated by different bases, to give the *N*-(phenyl chromium tricarbonyl)-*N*,*O*-dialkylhydroxylamine complexes **6** in moderate yields (Table 1). In the reaction of hydroxylamine **5b** none of the required complex was formed. Presumably, the increased steric bulk in this hydroxylamine is not compatible with the nucleophilic displacement of fluoride by addition/elimination in the synthesis of hydroxylamine chromium tricarbonyl complexes.

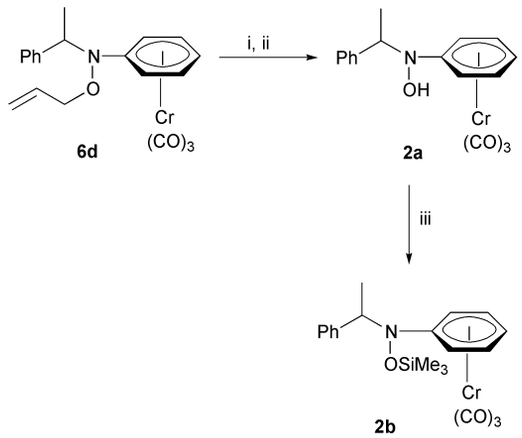
On deprotonation of hydroxylamine **5d** with BuLi at 0 °C, followed by addition of (η6-fluorobenzene) chromium tricarbonyl only **7**, the product of a [2,3]-sigmatropic rearrangement,[28] was observed and no reaction with (η6-fluorobenzene) chromium tricarbonyl was observed (Scheme 3).



5d 7

Scheme 3 *Reagents and conditions*: i, BuLi, −78 °C, 0 °C; ii, (η6-fluorobenzene)$Cr(CO)_3$.

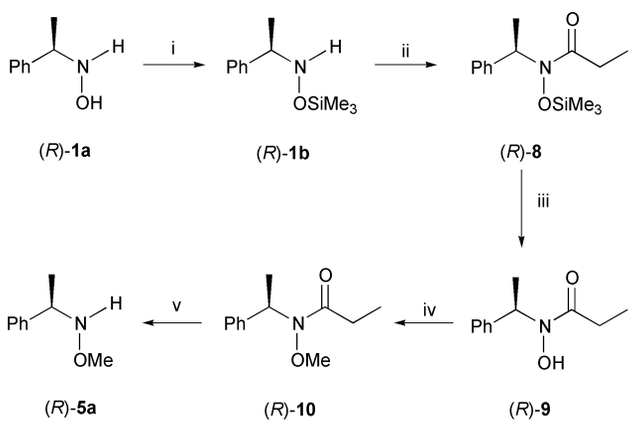
With complex **6d** in hand (Table 1), we envisaged that the allyl group may be easily removed and thus allow the preparation of hydroxylamine complex **2a**. Using the Guibé procedure[29] for deallylation of allylamines, complex **6d** was deprotected using tetrakis(triphenylphosphine)palladium(0) and *N*,*N*-dimethylbarbituric acid (NDMBA) in dichloromethane. However, all attempts at the isolation of complex **2a** resulted in rapid reduction to the known [η6-*N*-(α-methylbenzylamine)benzene] chromium tricarbonyl.[30] The proposed intermediate hydroxylamine complex **2a** could however be trapped *in situ* as its *O*-trimethylsilyl derivative on addition of TMSCl and triethylamine prior to work-up to give a yellow oil. Column chromatography followed by recrystallisation led to the isolation of **2b** as yellow crystals (37%) (Scheme 4).



6d 2a 2b

Scheme 4 *Reagents and conditions*: i, $Pd(PPh_3)_4$, CH_2Cl_2; ii, NDMBA; iii, TMSCl–NEt_3.

With this methodology developed for the preparation of racemic hydroxylamine complex **2b**, extension to enantiomerically pure hydroxylamine (*R*)-**5a** was investigated to confirm that no racemisation would occur during the nucleophilic substitution reaction. The enantiomerically pure hydroxylamine (*R*)-**5a** was prepared in five steps, starting from hydroxylamine (*R*)-**1a**.[21] Silylation afforded hydroxylamine (*R*)-**1b**, which was directly acylated with propionic anhydride to produce (*R*)-**8** (Scheme 5). Work-up removed the TMS group

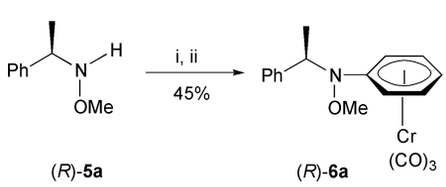


(*R*)-**1a** (*R*)-**1b** (*R*)-**8** (*R*)-**9** (*R*)-**10** (*R*)-**5a**

Scheme 5 *Reagents and conditions*: i, py–TMSCl; ii, $EtCO_2COMe$; iii, HCl; iv, MeI, K_2CO_3; v, MeMgBr.

to afford compound (*R*)-**9** as white crystals in 92% yield. Subsequent alkylation of compound (*R*)-**9** by treatment with methyl iodide and K_2CO_3 gave compound (*R*)-**10** as a colourless oil, in quantitative yield. To remove the propionyl group, a THF solution of compound (*R*)-**10** was treated with an excess of methylmagnesium bromide[31] to afford hydroxylamine (*R*)-**5a** in 76% yield (Scheme 5).

As in the racemic series, deprotonation of (*R*)-**5a** with BuLi followed by addition of (η6-fluorobenzene) chromium tricarbonyl gave the enantiomerically pure hydroxylamine complex (*R*)-**6a** as yellow crystals in 45% yield (Scheme 6).



(*R*)-**5a** (*R*)-**6a**

Scheme 6 *Reagents and conditions*: i, BuLi, −78 °C, 0 °C; ii, (η6-fluorobenzene)$Cr(CO)_3$.

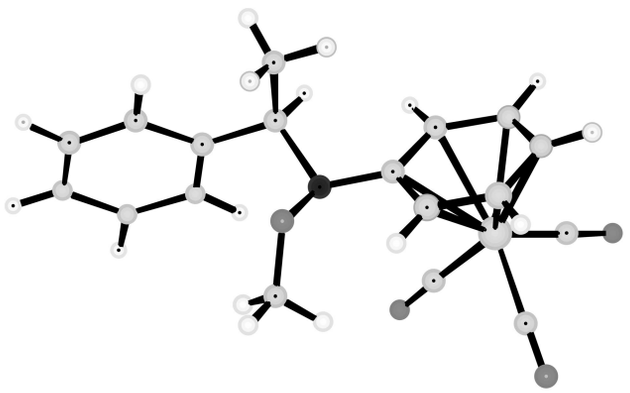


Fig. 1 X-Ray crystal structure of (*R*)-**6a** (only one of two independent conformers is depicted).

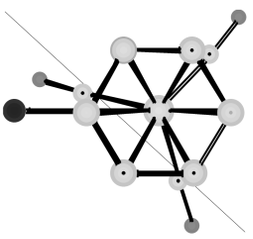


Fig. 2 The relative positions of carbonyl ligands to the arene ring at (*R*)-**6a** [for clarity hydrogen atoms and the *N*-(α-methylbenzyl) and *N*-methoxy substituents were omitted].

Crystals of complex (*R*)-**6a** were suitable for an X-ray single crystal structure analysis, which unambiguously established the absolute configuration (Fig. 1).

Two crystallographically distinct molecules were observed: their superposition confirmed that while they were the same enantiomer, they adopted slightly differing conformations. The dihedral angles O–N–C_{ipso}–C_{ortho} in these two conformers were +2.0 and +16.9°. A view of the structure from the uncomplexed side of arene (*R*)-**6a** shows the carbonyl groups nearly eclipsed with the electron-donating hydroxylamine substituent (Fig. 2), which is in agreement with previous structures of chromium tricarbonyl complexes bearing an electron donating substituent.[32]

Conclusions

Novel chiral hydroxylamine chromium tricarbonyl complexes have been synthesised and isolated for the first time in reasonable yield, by *ipso*-substitution reactions. Using the same methodology employed in the racemic series, the enantiomerically pure complex (*R*)-{η⁶-[*O*-methyl-*N*-(α-methylbenzyl)hydroxyamino]benzene} chromium tricarbonyl **6a** was isolated and its absolute configuration was determined by X-ray structural analysis. Since no racemisation was observed during this synthesis, this procedure should be useful for the preparation of a broad range of enantiomerically pure *N*,*N*,*O*-substituted hydroxylamines derived from (η⁶-fluorobenzene) chromium tricarbonyl.

Experimental

All the reactions involving air sensitive reagents and organometallic complexes, as well as their purifications, were performed under an atmosphere of dry nitrogen and all solvents were degassed before use. All solvents were distilled under a nitrogen atmosphere. Diethyl ether (referred to as ether) and THF were distilled from sodium–benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Petroleum ether refers to the fraction distilling between 40 and 60 °C and was redistilled before use. Reagents were used as purchased and when necessary were purified according to standard procedures.[33] BuLi was used as a 1.3–1.6 M solution in hexane and was titrated immediately before use. Sodium hexamethyldisilazide (NaHMDS) was used as a 1 M solution in THF. Borane–pyridine complex contained an excess of pyridine and the borane concentration was approximately 8 M. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh) with petroleum ether–ether 9 : 1 (v/v) as eluent, unless otherwise stated. Melting points were determined on a Reichert Thermovar or on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 172SX Fourier Transform or a Perkin-Elmer 781 instrument. ^{1}H NMR spectra were recorded at 200 MHz on a Varian Gemini 200 or a Bruker AC 200, at 300 MHz on a General Electrical QE-300 and at 500 MHz on a Bruker AMX 500 instrument. ^{13}C NMR spectra were recorded at 50 MHz on a Bruker AC 200 and at 125 MHz on a Bruker AMX 500 instrument. NMR spectra were recorded in $CDCl_3$, using tetramethylsilane (δ_H 0.00 ppm) or residual chloroform (δ_H 7.26 ppm; δ_C 77.0 ppm) as internal standard. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Since some hydroxylamine complexes were unstable, it was not possible to record their ^{13}C NMR spectra. Mass spectra (*m*/*z*) were recorded on a Kratos 25 RF, a VG MicromassLab ZAB 1F, a VG MassLab 20–250 or an APCI Plataform spectrometer. High resolution mass spectra (HRMS) were obtained on a VG AutoSpect instrument. Elemental analysis were performed on a Carlo Erba 1106 elemental analyser by the Dyson Perrins Laboratory Analytical Department.

(η⁶-Fluorobenzene) chromium tricarbonyl,[22] enantiomerically pure oxalate salt of (*R*)-*N*-(α-methylbenzyl)hydroxylamine **1a**,[21] *O*-*tert*-butylhydroxylamine hydrochloride **3b**,[24] acetophenone *O*-methyloxime **4a**,[23] *O*-methyl-*N*-(α-methylbenzyl)-hydroxylamine **5a**,[23] acetophenone *O*-*tert*-butyloxime **4b**,[25] *O*-*tert*-butyl-*N*-(α-methylbenzyl)hydroxylamine **5b**,[25] acetophenone *O*-benzyloxime **4c**[26] and *O*-benzyl-*N*-(α-methylbenzyl)hydroxylamine **5c** [26] were prepared according to the literature and the spectroscopic data were identical with those reported.

Preparation of (*R*)-*O*-*tert*-butyldimethylsilyl-*N*-(α-methylbenzyl)hydroxylamine 1c

A mixture of hydroxylamine (*R*)-**1a** (379 mg, 2.76 mmol), imidazole (376 mg, 5.523 mmol) and TBDMSCl (499 mg, 3.31 mmol) in DMF (2 cm^3) was stirred overnight at room temperature. The reaction mixture was washed with 0.1 M hydrochloric acid (50 cm^3), extracted with ethyl acetate (4 × 100 cm^3), dried with magnesium sulfate, filtered and the solvent evaporated *in vacuo* to afford a pale yellow oil. Purification by column chromatography [petroleum ether–ether (19 : 1)] gave compound (*R*)-**1c** as a colourless oil (398 mg, 57%); bp 165 °C; $[\alpha]_D^{23}$ +12.0 (*c* 1.69 in $CHCl_3$); ν_{max} (film)/cm^{-1} 3326 (N–H), 3086, 3064, 3031 (C–H)Ar, 2957, 2930, 2885, 2857 (C–H), 1605, 1586, 1495 (C=C); δ_H (300 MHz, $CDCl_3$) 0.05 (3H, s, OSiCH_3), 0.13 (3H, s, OSiCH_3), 0.96 [9H, s, OSiC(CH_3)$_3$], 1.44 (3H, d, *J* 6.6, CHCH_3), 4.13 (1H, q, *J* 6.6, C*H*CH_3), 5.13 (1H, br s, N*H*), 7.27–7.39 (5H, m, Ph*H*); δ_C (50 MHz, $CDCl_3$) −5.4 [OSi(*C*H$_3$)], −5.3 [OSi(*C*H$_3$)], 18.1 [OSi*C*(CH$_3$)$_3$], 19.4 (CH*C*H$_3$), 26.3 [OSiC(*C*H$_3$)$_3$], 62.2 (*C*HCH$_3$), 127.4, 127.6, 128.2 (Ph: C_{ortho}, C_{meta}, C_{para}), 142.5 (Ph: C_{ipso}); *m*/*z* (APCI$^+$) 252 (MH^+, 56%), 120 (MH^+ − OSiMe$_2$Bu^t, 94), 105 (PhCHCH$_3^+$, 100) [HRMS: found (CI, NH_3) MH^+, 252.1780. $C_{14}H_{25}NOSi$ requires MH^+, 252.1784].

General procedure: reactions of hydroxylamines with (η⁶-fluorobenzene) chromium tricarbonyl

BuLi was added dropwise to a solution of the required hydroxylamine in THF at −78 °C. After stirring at −78 °C for 30 min, the reaction mixture was warmed to 0 °C and a solution of

(η⁶-fluorobenzene) chromium tricarbonyl in THF at 0 °C was added slowly to the mixture. The reaction mixture was allowed to warm to room temperature and stirred overnight. After quenching by addition of methanol (0.5 cm^3), the solvent was removed under reduced pressure. The residue was redissolved in ethyl acetate, the solution was filtered through a plug of magnesium sulfate and silica and the solvent removed *in vacuo*.

Preparation of {η⁶-[*O*-methyl-*N*-(α-methylbenzyl)hydroxyamino]benzene} chromium tricarbonyl 6a

Compound **5a** (2.32 g, 15.34 mmol) in THF (50 cm^3), BuLi (8.7 cm^3, 1.5 M in hexane, 13.05 mmol) and (η⁶-fluorobenzene) chromium tricarbonyl (2.75 g, 11.85 mmol) in THF (50 cm^3) were added according to the general procedure to give an orange oil. Column chromatography, followed by recrystallisation from *n*-hexane–ether gave complex **6a** as yellow crystals (2.41 g, 56%); mp 99–100 °C (decomp.) (Found: C, 59.31; H, 4.39; N, 3.63. $C_{18}H_{17}CrNO_4$ requires C, 59.51; H, 4.71; N, 3.86%); ν_{max} (KBr)/cm^{-1} 3089 (C–H)Ar, 2976, 2938, 2817 (C–H), 1970, 1887, 1842 (C≡O), 1527, 1456 (C=C); δ_H (300 MHz, $CDCl_3$) 1.58 (3H, d, *J* 6.6, $CHCH_3$), 3.61 (3H, s, OCH_3), 4.49 (1H, q, *J* 6.6, $CHCH_3$), 4.98 (1H, t, *J* 6.0, Ar*H*, 4-H), 5.16 (1H, d, *J* 6.3, Ar*H*, 6-H), 5.25 (1H, d, *J* 6.3, Ar*H*, 2-H), 5.37 (2H, app. t, *J* 6.3, Ar*H*, 3-H and 5-H), 7.27–7.34 (5H, m, Ph*H*); δ_C (125 MHz, $CDCl_3$) 16.4 ($CHCH_3$), 62.9 (OCH_3), 66.3 ($CHCH_3$), 80.9, 88.1, 93.0 (Ar: C_{ortho}, C_{meta}, C_{para}), 127.8, 128.4 (Ph: C_{ortho}, C_{meta}, C_{para}), 131.1 (Ar: C_{ipso}), 140.3 (Ph: C_{ipso}), 233.7 (CO); *m*/*z* (EI) 363 (M^+, 7%), 333 ($M^+ - CH_2O$, 11), 307 ($M^+ - 2CO$, 2), 279 ($M^+ - 3CO$, 15), 249 (279 − CH_2O, 31), 197 (249 − Cr, 24), 182 (197 − Me, 56), 105 ($PhCHCH_3^+$, 100).

Preparation of {η⁶-[*O*-benzyl-*N*-(α-methylbenzyl)hydroxyamino]benzene} chromium tricarbonyl 6c

Compound **5c** (2.65 g, 11.66 mmol) in THF (50 cm^3), BuLi (8.5 cm^3, 1.5 M in hexane, 12.8 mmol) and (η⁶-fluorobenzene) chromium tricarbonyl (2.71 g, 11.66 mmol) in THF (50 cm^3) were added according to the general procedure to afford an orange oil. Column chromatography, followed by recrystallisation from petroleum ether–ether gave complex **6c** as yellow crystals (2.56 g, 50%); mp 86–88 °C (Found: C, 65.6; H, 4.7; N, 3.1. $C_{24}H_{21}NO_4Cr$ requires C, 65.6; H, 4.8; N, 3.2%); ν_{max} (KBr)/cm^{-1} 3094, 3030 (C–H)Ar, 2973, 2887 (C–H), 1959, 1918, 1896 (C≡O), 1604, 1524, 1497, 1457 (C=C); δ_H (300 MHz, $CDCl_3$) 1.57 (3H, d, *J* 6.6, $CHCH_3$), 4.55 (2H, m, $CHCH_3$ and OCH_2Ph), 4.80 (1H, AB system, J_{AB} 9.9, OCH_2Ph), 5.00 (1H, m, Ar*H*), 5.27 (1H, d, *J* 6.6, Ar*H*), 5.34 (3H, m, Ar*H*), 7.24–7.35 (10H, m, Ph*H*); *m*/*z* (EI) 439 (M^+, 3%), 355 ($M^+ - 3CO$, 6), 303 [$M^+ - Cr(CO)_3$, 1], 212 (303 − CH_2Ph, 7), 197 (303 − $PhCH_2O + H^+$, 28), 182 (197 − Me, 46), 105 ($PhCHCH_3^+$, 100).

Preparation of acetophenone *O*-allyloxime 4d

To a solution of *O*-allylhydroxylamine hydrochloride hydrate **3d** (976 mg, 8.91 mmol) in ethanol (10 cm^3) was added dropwise acetophenone (1.04 cm^3, 8.91 mmol) and sodium acetate (585 mg, 7.13 mmol) and the reaction mixture was refluxed overnight. After cooling, the mixture was basified with saturated aqueous sodium hydrogen carbonate solution and extracted with ether (3 × 100 cm^3). The combined extracts were dried with magnesium sulfate, filtered and the solvent evaporated *in vacuo* to afford a colourless oil. Purification by column chromatography gave oxime **4d** as colourless oil (1.54 g, 99%); ν_{max} (film)/cm^{-1} 3082, 3022 (C–H)Ar and (C–H)allyl, 2922, 2867 (C-H), 1646 (C=C)allyl, 1612, 1573, 1497, 1445 [(C=N), (C=C)]; δ_H (200 MHz, $CDCl_3$) 2.28 (3H, s, CH_3), 4.71–4.75 (2H, m, $OCH_2CH=CH_2$), 5.22–5.28 (1H, m, $OCH_2CH=CH_2$), 5.31–5.41 (1H, m, $OCH_2CH=CH_2$), 6.10 (1H, ddt, *J* 17.3, 10.3 and 5.9, $OCH_2CH=CH_2$), 7.27–7.43 (3H, m, Ph*H*), 7.64–7.69 (2H, m, Ph*H*); δ_C (50 MHz, $CDCl_3$) 12.9 (CH_3), 75.1 ($OCH_2CH=CH_2$), 117.4 ($OCH_2CH=CH_2$), 126.1, 128.4, 129.1 (Ph: C_{ortho}, C_{meta}, C_{para}), 134.5 ($OCH_2CH=CH_2$), 136.7 (Ph: C_{ipso}), 154.8 [$PhC(CH_3)N$]; *m*/*z* (GC-MS, CI/NH_3) 176 (MH^+, 47%), 160 ($M^+ - CH_3$, 8), 120 [$MH^+ - OCH_2CH=CH_2 + H^+$ or $PhC(CH_3)(NH) + H^+$, 100] [HRMS: found (CI/NH_3) MH^+, 176.1077. $C_{11}H_{13}NO$ requires MH^+, 176.1075].

Preparation of *O*-allyl-*N*-(α-methylbenzyl)hydroxylamine 5d

10% Hydrochloric acid (30 cm^3) was added dropwise over 15 min to a stirred solution of oxime **4d** (1.52 g, 8.67 mmol) and borane–pyridine (3.6 cm^3, 8 M in py, 28.71 mmol) in ethanol (25 cm^3) at −5 °C. After stirring for 30 min at room temperature, the reaction mixture was made alkaline with saturated aqueous sodium hydrogen carbonate solution and then extracted with dichloromethane (3 × 100 cm^3). The combined extracts were dried with magnesium sulfate, filtered and the solvent evaporated *in vacuo* to afford hydroxylamine **5d** as a colourless oil (1.40 g, 91%) (Found: C, 74.2; H, 8.8; N, 7.8. $C_{11}H_{15}NO$ requires C, 74.5; H, 8.5; N, 7.9%); ν_{max} (film)/cm^{-1} 3252 (N–H), 3064, 3029 (C–H)Ar and (C–H)allyl, 2978, 2865 (C–H), 1645 (C=C)allyl, 1605, 1495, 1454 (C=C); δ_H (200 MHz, $CDCl_3$) 1.42 (3H, d, *J* 6.6, $CHCH_3$), 4.09–4.26 (3H, m, $CHCH_3$ and $OCH_2CH=CH_2$), 5.16–5.32 (2H, m, $OCH_2CH=CH_2$), 5.66 (1H, br s, N*H*), 5.94 (1H, ddt, *J* 17.3, 10.7 and 5.9, $OCH_2CH=CH_2$), 7.26–7.50 (5H, m, Ph*H*); δ_C (50 MHz, $CDCl_3$) 19.9 ($CHCH_3$), 60.6 ($CHCH_3$), 75.6 ($OCH_2CH=CH_2$), 117.5 ($OCH_2CH=CH_2$), 127.2, 127.4, 128.4 (Ph: C_{ortho}, C_{meta}, C_{para}), 134.5 ($OCH_2CH=CH_2$), 142.8 (Ph: C_{ipso}); *m*/*z* (CI, NH_3) 178 (MH^+, 100%), 120 ($M^+ - OCH_2CH=CH_2$, 16), 105 ($PhCHCH_3^+$, 20).

Preparation of *N*-allyl-*N*-(α-methylbenzyl)hydroxylamine 7 by rearrangement of *O*-allyl-*N*-(α-methylbenzyl)hydroxylamine 5d

Compound **5d** (111 mg, 0.63 mmol) in THF (10 cm^3), BuLi (0.46 cm^3, 1.5 M in hexane, 0.680 mmol) and (η⁶-fluorobenzene) chromium tricarbonyl (146 mg, 0.629 mmol) in THF (10 cm^3) were added according to the general procedure to afford a yellow oil. The crude reaction mixture was redissolved in ether (10 cm^3) and acidified with 10% hydrochloric acid. The aqueous layer was made alkaline with saturated aqueous sodium hydrogen carbonate solution and then extracted with ether (3 × 50 cm^3). The combined extracts were dried with magnesium sulfate, filtered and the solvent evaporated *in vacuo* to afford hydroxylamine **7** as a colourless oil (90 mg, 81%); ν_{max} (film)/cm^{-1} 3241 (N–H), 3081, 3030 (C–H)Ar and (C–H)allyl, 2977, 2934 (C–H), 1645 (C=C)allyl, 1603, 1494, 1454 (C=C); δ_H (200 MHz, $CDCl_3$) 1.50 (3H, d, *J* 6.6, $CHCH_3$), 3.23–3.37 (2H, m, $NCH_2CH=CH_2$), 3.85 (1H, q, *J* 6.6, $CHCH_3$), 5.13–5.21 (2H, m, $NCH_2CH=CH_2$), 5.89–6.09 (1H, m, $NCH_2CH=CH_2$), 7.27–7.35 (5H, m, Ph*H*); δ_C (50 MHz, $CDCl_3$) 19.6 ($CHCH_3$), 60.0 ($CHCH_3$), 66.4 ($NCH_2CH=CH_2$), 118.3 ($NCH_2CH=CH_2$), 127.4, 128.0, 128.4 (Ph: C_{ortho}, C_{meta}, C_{para}), 134.3 ($NCH_2CH=CH_2$), 142.3 (Ph: C_{ipso}); *m*/*z* (CI, NH_3) 178 (MH^+, 100%), 105 ($PhCHCH_3^+$, 32) [HRMS: found (CI/NH_3) MH^+, 178.1230. $C_{11}H_{15}NO$ requires MH^+, 178.1232].

Preparation of {η⁶-[*O*-allyl-*N*-(α-methylbenzyl)hydroxyamino]-benzene} chromium tricarbonyl 6d

NaHMDS (0.31 cm^3, 1.0 M in THF, 0.31 mmol) was added dropwise to a solution of compound **5d** (50 mg, 0.282 mmol) in THF (10 cm^3), at −78 °C. After stirring at −78 °C for 30 min, the resultant solution was warmed to 0 °C and stirred for 30 min. Then a solution of (η⁶-fluorobenzene) chromium tricarbonyl (52 mg, 0.224 mmol) in THF (10 cm^3) at 0 °C was added slowly to the mixture. The reaction mixture was stirred for 1 h at 0 °C, then slowly warmed to room temperature overnight, quenched by addition of saturated aqueous sodium hydrogen carbonate solution (0.1 cm^3) and the solvent concentrated *in vacuo*. The residue was redissolved in ether, filtered

through a plug of magnesium sulfate and silica and the solvent removed *in vacuo* to afford an orange oil. Column chromatography [petroleum ether–ether (19 : 1)], followed by recrystallisation from petroleum ether–ether gave complex **6d** as yellow crystals (20 mg, 23%); mp 78–79 °C (Found: C, 62.0; H, 4.7; N, 3.9. $C_{20}H_{19}CrNO_4$ requires C, 61.7; H, 4.9; N, 3.6%); ν_{max} (KBr)/cm^{-1} 3080 (C–H)Ar, 2972, 2935, 2876 (C–H), 1977, 1883, 1861 (C≡O), 1645 (C=C)allyl, 1604, 1522, 1498, 1462 (C=C); δ_H (500 MHz, $CDCl_3$) 1.59 (3H, d, *J* 6.9, CHC*H*$_3$), 4.31–4.34 (1H, m, OC*H*$_2$CH=CH$_2$), 4.53 (1H, q, *J* 6.9, C*H*CH$_3$), 4.99 (1H, t, *J* 6.1, Ar*H*), 5.19–5.37 (7H, m, Ar*H*, OCH$_2$CH=C*H*$_2$, OC*H*$_2$CH=CH$_2$), 5.86 (1H, br m, OCH$_2$C*H*=CH$_2$), 7.26–7.34 (5H, m, Ph*H*); *m*/*z* (EI) 389 (M$^+$, 3%), 333 (M$^+$ − 2CO, 5), 305 (M$^+$ − 3CO, 3), 249 (305 − OCH$_2$CH=CH$_2$ + H$^+$, 24), 197 (249 − Cr, 20), 105 (PhCHCH$_3^+$, 81), 52 (Cr$^+$, 100).

Preparation of {η^6-[*O*-trimethylsilyl-*N*-(α-methylbenzyl)-hydroxyamino]benzene} chromium tricarbonyl 2b

A solution of complex **6d** (50 mg, 0.128 mmol), $Pd(PPh_3)_4$ (1.5 mg, 0.013 mmol) and *N*,*N*-dimethylbarbituric acid (60 mg, 0.385 mmol) in dichloromethane (20 cm^3) was stirred at 40 °C for 16 h. After cooling to room temperature, triethylamine (1 cm^3) and TMSCl (0.1 cm^3, 0.788 mmol) were added to the reaction mixture. After stirring at room temperature overnight, the solvent was removed *in vacuo*. The crude product was extracted with ether (3 × 50 cm^3), filtered through silica and the solvent removed *in vacuo* to afford an orange oil. Purification by column chromatography, followed by recrystallisation from petroleum ether–ether gave complex **2b** as yellow crystals (20 mg, 37%); mp 62–63 °C (Found: C, 57.2; H, 5.6; N, 3.2. $C_{20}H_{23}CrNO_4Si$ requires C, 57.0; H, 5.5; N, 3.3%); ν_{max} (KBr)/cm^{-1} 2964 (C–H), 1960, 1876 (C≡O), 1603, 1525, 1455 (C=C); δ_H (200 MHz, $CDCl_3$) 0.14 [9H, s, OSi(C*H*$_3$)$_3$], 1.53 (3H, d, *J* 6.8, CHC*H*$_3$), 4.55 (1H, q, *J* 6.9, C*H*CH$_3$), 5.02–5.08 (2H, m, Ar*H*), 5.23–5.43 (3H, m, Ar*H*), 7.35–7.36 (5H, m, Ph*H*); *m*/*z* (EI) 421 (M$^+$, 2%), 337 (M$^+$ − 3CO, 3), 322 (337 − Me, 5), 249 (337 − OSiMe$_3$ + H$^+$, 6), 197 (249 − Cr, 11), 182 (197 − Me, 23), 105 (PhCHCH$_3^+$, 100).

Preparation of (*R*)-*N*-hydroxy-*N*-(α-methylbenzyl)propanamide 9[33]

TMSCl (8.5 cm^3, 66.97 mmol) was added dropwise to a stirred solution of (*R*)-**1a** (2.53 g, 11.14 mmol) in dry pyridine (34 cm^3) at −10 °C. After 2 h at −10 °C propionic anhydride (1.6 cm^3, 12.48 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The residue was acidified with 2 M hydrochloric acid until pH 2 and was extracted with ethyl acetate (2 × 30 cm^3). The combined extracts were washed successively with 0.5 M hydrochloric acid (30 cm^3), water (60 cm^3) and saturated aqueous sodium hydrogen carbonate solution (3%) (30 cm^3), dried with magnesium sulfate, filtered and the solvent was evaporated *in vacuo*. Recrystallisation from *n*-hexane–ethyl acetate gave compound (*R*)-**9** as white crystals (1.97 g, 92%); mp 70 °C; $[\alpha]_D^{23}$ +63.6 (*c* 1.02 in $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 1.17 (3H, t, *J* 7.5, CH$_2$C*H*$_3$), 1.69 (3H, br d, *J* 5.8, CHC*H*$_3$), 2.46 (2H, q, *J* 7.5, C*H*$_2$CH$_3$), 5.21 (1H, br s, C*H*CH$_3$), 7.30–7.36 (5H, m, Ph*H*).

Preparation of (*R*)-*N*-methoxy-*N*-(α-methylbenzyl)propanamide 10[33]

A solution of compound (*R*)-**9** (1.03 g, 5.33 mmol), methyl iodide (1.3 cm^3, 20.88 mmol) and potassium carbonate (1.48 g, 10.71 mmol) in chloroform (5 cm^3) was refluxed for 48 h. Then the solvent was removed and the residue was redissolved with ether, filtered through silica and the solvent removed *in vacuo* to afford compound (*R*)-**10** as colourless oil (1.11 g, 100%), which was distilled in a Kugelrohr apparatus at 160 °C under vacuum; $[\alpha]_D^{23}$ +117.7 (*c* 1.09 in $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 1.15 (3H, t, *J* 7.5, CH$_2$C*H*$_3$), 1.61 (3H, d, *J* 7.1, CHC*H*$_3$), 2.31–2.57 (2H, m, C*H*$_2$CH$_3$), 3.44 (3H, s, OC*H*$_3$), 5.69 (1H, q, *J* 7.1, C*H*CH$_3$), 7.27–7.45 (5H, m, Ph*H*).

Preparation of (*R*)-*O*-methyl-*N*-(α-methylbenzyl)hydroxylamine 5a[23]

Methylmagnesium bromide (2.9 cm^3, 3.0 M in ether, 8.67 mmol) was added dropwise to a solution of compound (*R*)-**10** (600 mg, 2.89 mmol) in THF (50 cm^3) at room temperature. After stirring for 3 h, 10% hydrochloric acid (5 cm^3) was added and the solvent was removed *in vacuo*. The residue was basified with saturated aqueous sodium hydrogen carbonate solution, extracted with ether (3 × 50 cm^3), dried with magnesium sulfate, filtered and the solvent removed *in vacuo* to afford a colourless oil. Distillation in a Kugelrohr apparatus gave hydroxylamine (*R*)-**5a** (333 mg, 76%); bp 190 °C; $[\alpha]_D^{23}$ +44.6 (*c* 1.15 in $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 1.38 (3H, d, *J* 6.6, CHC*H*$_3$), 3.50 (3H, s, OC*H*$_3$), 4.16 (1H, q, *J* 6.6, C*H*CH$_3$), 7.23–7.40 (5H, m, Ph*H*).

Preparation of (*R*)-{η^6-[*O*-methyl-*N*-(α-methylbenzyl)hydroxy-amino]benzene} chromium tricarbonyl 6a

Hydroxylamine (*R*)-**5a** (212 mg, 1.40 mmol) in THF (20 cm^3), BuLi (1.2 cm^3, 1.4 M in hexane, 1.68 mmol) and (η^6-fluorobenzene) chromium tricarbonyl (326 mg, 1.40 mmol) in THF (20 cm^3) were added according to the general procedure to give an orange oil. Column chromatography, followed by recrystallisation from *n*-hexane–ether gave complex (*R*)-**6a** as yellow crystals (229 mg, 45%); mp 93 °C; $[\alpha]_D^{23}$ +0.8 (*c* 1.01 in $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 1.59 (3H, d, *J* 6.6, CHC*H*$_3$), 3.61 (3H, s, OC*H*$_3$), 4.50 (1H, q, *J* 6.6, C*H*CH$_3$), 4.99 (1H, t, *J* 6.1, Ar*H*, 4-H), 5.17 (1H, d, *J* 6.3, Ar*H*, 6-H), 5.26 (1H, d, *J* 6.5, Ar*H*, 2-H), 5.38 (2H, app. t, *J* 6.5, Ar*H*, 3-H and 5-H), 7.33 (5H, m, Ph*H*).

Details of the crystal structure determination for (*R*)-{η^6-[*O*-methyl-*N*-(α-methylbenzyl)hydroxyamino]benzene} chromium tricarbonyl 6a.† *Crystal data.* 2 × ($C_{18}H_{17}CrNO_4$), *M* = 363.83, crystal system: monoclinic, *a* = 12.876(1), *b* = 8.464(1), *c* = 15.239(2) Å, *β* = 91.29(9)°, *U* = 1660.16 Å^3 (by least squares refinement using 250 recorded reflections), space group $P2_1$, *Z* = 4, D_c = 1.45 g cm^{-3}, *F*(000) = 752, *μ* = 0.69 cm^{-1}, crystal dimensions 0.24 × 0.07 × 0.11 mm.

Data collection and processing. Enraf-Nonius F.A.S.T. diffractometer, Ω scan mode, graphite monochromated Mo-Kα radiation (*λ* = 0.71069 Å), *T* = 150 K. A total of 7037 reflections were measured (0 < *θ* < 20.00°), of which 2070 unique with $I > 3\sigma(I)$ (Sheldrick merging *R* = 0.11).

Structure analysis and refinement. Direct methods (SIR92[34]), full-matrix least-squares refinement with all non-hydrogen atoms in anisotropic approximation (434 parameters, observations/parameters = 4.9). Hydrogen atoms were positioned geometrically. The Flack Parameter was refined to −0.1(1). The data were corrected for Lorenz and polarisation effects, and a Chebychev[35] weighting scheme were also applied. Final *R* and R_w values are 0.0529 and 0.0555, goodness of fit = 0.9521. Maximum and minimum peaks in the final difference synthesis are 1.75 and −2.58 e Å^3. Crystallographic calculations were carried out using the CRYSTALS[36] package on a PC computer. Neutral atom scattering factors were taken from the usual sources.[37]

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