Supplementary Material (ESI) for Chemical Communications

Supporting data:

An outstanding catalyst for asymmetric transfer hydrogenation in aqueous solution and formic acid/triethylamine

Daljit S. Matharu, David J. Morris, Guy J. Clarkson[±] and Martin Wills

Synthesis of catalyst 11, enantiomeric excess determination for products, 1H-NMR spectrum of catalyst 11 and details of X-ray crystal structure.

*Synthesis of 2-(2,3,4,5-tetramethylcyclopentadienyl)-benzyl (1R,2R)-toluenesulfonyl-cyclohexyldiamine **13**;* 2-(2,3,4,5-Tetramethylcyclopentadienyl)-benzylaldehyde **12** (3.08g, 0.0136 mol) was dissolved in dry methanol (95 mL). To the solution was added R,R TsCYDN **3** (4.36 g, 0.0163 mol), followed by the addition of 6g of molecular sieves and 6 drops of glacial acetic acid. After formation of the imine was confirmed by TLC, sodium cyanoborohydride (1.11 g, 0.0177 mol) was added and the reaction left to stir overnight at room temperature. The molecular sieves were filtered through filter paper and the solution was concentrated under reduced pressure to remove the methanol. The residue was redissolved in ethyl acetate (80 mL). The organic layer was washed with saturated $NaHCO_3$ (80 mL) and saturated brine (80 mL) and then dried ($MgSO_4$). The solvent was removed to give a crude solid which was purified by silica gel column chromatography (0 → 30% v/v ethyl acetate/hexane) to afford the product **13** as a yellow solid (2.50 g, 5.23 mmol, 38%). mp 48-50 ^{0}C; $[\alpha]_D^{22}$ – 27 (*c* 0.3, $CHCl_3$); ν_{max} (neat)/cm^{-1}: 3261, 2926, 2855, 1599, 1446, 1325, 1159, 1092, 899, 813, 758, 662; δ_H (400MHz; $CDCl_3$)/ppm: 7.76-7.65 (2H, m, Ar*H*), 7.44-7.07 (5H, m, Ar*H*), 7.06-6.95 (1H, m, Ar*H*), 5.42 (1H, br s, N*H*Ts), 3.97-3.33 (2H, m, ArCH_2), 3.12-2.44 (2H, m, N*H*CH$_2$ + Cp*H*), 2.38 (3H, s, CH_3Ar), 2.25-0.70 (22H, m, 4 × CpCH_3 + C*H*NTs + C*H*NHCH$_2$ + 4 × CH_2 of cyclohexyl ring); δ_C (100.6 MHz; $CDCl_3$): 143.1, 140.3, 138.6, 138.0, 137.3, 130.1, 129.8, 129.6, 129.5, 128.7, 128.4, 127.3, 127.3, 126.7 (10 Ar-*C* and 4 Cp*C*), 60.2 (*C*H), 58.0 (*C*H), 57.7 (*C*H), 47.8 (*C*H$_2$), 32.7 (*C*H$_2$ of cyclohexyl ring), 31.3 (*C*H$_2$ of cyclohexyl ring), 24.6 (*C*H$_2$ of cyclohexyl ring), 24.3 (*C*H$_2$ of cyclohexyl ring), 21.5 (*C*H$_3$), 14.2 (Cp*C*H$_3$), 11.8 (Cp*C*H$_3$), 11.3 (Cp*C*H$_3$), 11.1 (Cp*C*H$_3$); *m/z* (LSIMS) 479 (MH$^+$, 100%), 211 (16%) HRMS (LSIMS) calc for MH$^+$ = 479.2732 found 479.2743 (2.3 ppm error).

*Synthesis of 2-(2,3,4,5-tetramethylcyclopentadienyl)-benzyl (1R,2R)-toluenesulfonyl-cyclohexyldiamine rhodium (III) chloride **11***; Rhodium (III) chloride hydrate (0.90 g, 4.31 mmol) was added to a stirred solution of 2-(2,3,4,5-tetramethylcyclopentadienyl)-benzyl (1R,2R)- toluenesulfonyl-cyclohexyldiamine **13** (2.06 g, 4.31 mmol) in methanol (90 mL). The reaction mixture was heated under reflux and stirred for 24 hours. Triethylamine (1.20 mL, 8.62 mmol) was added to the reaction mixture and the reactants were stirred at reflux temperature for a further 24 hours. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude residue was triturated with water (50 mL) for 10 minutes, collected by filtration (filter paper), washed with water (50 mL) and then allowed to dry on the filter paper. The red-brown solid was purified by silica gel column chromatography (50 → 100% v/v ethyl acetate/hexane and then 0 → 10% v/v methanol/ethyl acetate) to afford the product **11** as a dark red solid (1.14 g, 1.86 mmol, 43% yield); decomposition temperature 244-246^{0}C; $[\alpha]_D^{23}$ – 201.3 (*c* 0.3, $CHCl_3$); ν_{max} (neat)/cm^{-1}: 3450, 3230, 2927, 1448, 1264, 1252, 1139, 1129, 1098, 1022, 928, 899, 828, 769, 714, 667; δ_H (400 MHz; $CDCl_3$)/ppm: 7.95 (2H, d, *J* 8.2, Ar*H*), 7.55-7.46 (3H, m, Ar*H*), 7.40 (1H, d, *J* 7.0, Ar*H*), 7.16 (2H, d, *J* 8.2, Ar*H*), 4.36 (1H, dd, *J* 14.2 and 2.9, ArC*H*H), 4.24 (1H, br d, *J* 14.2, ArCH*H*), 4.01 (1H, br d, *J* 11.3, N*H*), 2.38-2.29 (2H, m, C*H*NTs + CH$_a$H$_b$C***H$_a$***H$_b$CHNTs), 2.34 (3H, s, CH_3Ar), 2.10-1.98 (2H, m, C*H*NHCH$_2$ + CH$_a$H$_b$C***H$_a$***H$_b$CHNHCH$_2$), 1.96 (3H, s, CpCH_3), 1.88 (3H, s, CpCH_3), 1.57 (3H, s, CpCH_3), 1.56-1.50 (1H, m, C***H$_a$***H$_b$CH$_a$H$_b$CHNTs), 1.49 (3H, s, CpCH_3), 1.44-1.36 (1H, m, C***H$_a$***H$_b$CH$_a$H$_b$CHNHCH$_2$), 1.03-0.73 (4H, m, CH$_a$H$_b$CH_a***H$_b$***CHNHCH$_2$ + CH$_a$H$_b$CH$_a$***H$_b$***CHNTs + CH$_a$***H$_b$***CH$_a$H$_b$CHNHCH$_2$ + CH$_a$***H$_b$***CH$_a$H$_b$CHNTs); δ_C (100.6 MHz; $CDCl_3$): 141.4, 140.1, 135.4, 131.1, 130.0, 129.9, 129.7, 128.6, 128.1, 126.9 (Ar-*C*), 104.2 (J^{RhC} 6.5, Cp*C*), 101.0 (J^{RhC} 6.9, Cp*C*), 97.4 (J^{RhC} 9.6, Cp*C*), 86.6 (J^{RhC} 9.2, Cp*C*), 81.0 (J^{RhC} 8.4, Cp*C*), 67.7 (*C*H), 63.5 (*C*H), 50.8 (*C*H$_2$), 35.5 (*C*H$_2$ of

cyclohexyl ring), 30.3 (*C*H_2 of cyclohexyl ring), 24.6 (*C*H_2 of cyclohexyl ring), 24.3 (*C*H_2 of cyclohexyl ring), 21.4 (*C*H_3Ar), 11.0 (Cp*C*H_3), 9.9 (Cp*C*H_3), 9.7 (Cp*C*H_3), 8.0 (Cp*C*H_3); *m/z* (FAB) 579 (M-Cl, 100%), 423 (13%), 154 (17%). HRMS (FAB) calc for M-Cl = 579.1553 found 579.1551 (0.2 ppm error).

Reduction of ketones using catalyst 11 in Formic acid/triethylamine

*Reduction of ketones using catalyst **11** in Formic acid:Triethylamine (5:2);* A solution of **11** (0.016 mmol) in formic acid : triethylamine 5 : 2 azeotrope (1.5 mL) was stirred in a flame dried schlenk tube at 28^{0}C for 15 minutes. The ketone substrate (3.2 mmol) was added and the reaction mixture was stirred at 25^{0}C for a period of time over which time the conversion was monitored by GC. After full conversion had been achieved the reaction was filtered (silica), washed (20% EtOAc/80% hexane) and concentrated under vacuum to give the reduction product. The residue was purified by flash column chromatography where necessary.

*Reduction of ketones using catalyst **11** in Water***;** To a solution of **11** (0.016 mmol) in water (5.5 mL) was added HCOONa (16.2 mmol) and stirred in a flame dried schlenk tube at 40^{0}C for 15 minutes. The ketone substrate (3.2 mmol) was added and the reaction mixture was stirred at 40^{0}C for a period of time over which time the conversion was monitored by GC. After full conversion had been achieved the reaction was filtered through silica and $MgSO_4$, washed (20% EtOAc/80% hexane) and concentrated under vacuum to give the reduction product. The residue was purified by flash column chromatography where necessary.

1-Phenylethanol 14: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 115 ^{0}C, P = 15 psi, ketone 9.7 min, R isomer 14.2 min., S isomer 15.1 min.); 96% ee (R) (lit.[1] $[\alpha]_D^{26}$ +45.4 (c 0.50 in $CHCl_3$) 98% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-(3'-Chlorophenyl)ethanol 15: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 150 ^{0}C, P = 10 psi, ketone 11.1 min, R isomer 16.3 min., S isomer 16.9 min.); 95% ee (R) (lit.[1] $[\alpha]_D^{24}$ +38.2 (c 0.9 in $CHCl_3$) 96% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-(3'-Trifluoromethylphenyl)ethanol 16: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 130 ^{0}C, P = 9 psi, ketone 8.5 min, R isomer 15.0min., S isomer 15.7 min.); 96% ee (R) (lit.[1] $[\alpha]_D^{26}$ +27.1 (c 1.60 in CH_3OH) 96% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-(3'-Methoxyphenyl)ethanol 17: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 140 ^{0}C, P = 15 psi, ketone 12.9 min, R isomer 17.9 min., S isomer 18.5 min.); Assigned as R configuration (see results for reductions in H_2O for $[\alpha]_D$ value and ^{1}H-NMR and ^{13}C-NMR data).

1-(2'-Trifluoromethylphenyl)ethanol 20: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 120 ^{0}C, P = 10 psi, ketone 11.1 min, R isomer 17.7 min., S isomer 18.7 min.); Assigned as R configuration (see results for reductions in H_2O for $[\alpha]_D$ value); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-(2'-Methoxyphenyl)ethanol 19: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 140 ^{0}C, P = 15 psi, ketone 12.5 min, S isomer 14.4 min., R isomer 14.8 min.); 94% ee (R) (lit.[1] $[\alpha]_D^{27}$ +37.7 (c 0.28 in toluene) 90% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-Phenylpropan-1-ol 22: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 115 ^{0}C, P = 15 psi, ketone 14.1 min, R isomer 21.2 min., S isomer 22.3 min.); $[\alpha]_D^{26}$ +46.9 (c 1.4 in $CHCl_3$) 96% ee (R) (lit.[2] $[\alpha]_D^{20}$ +47.0 (c 1.4 in $CHCl_3$) 95% ee (R)); δ_H (400 MHz; $CDCl_3$)/ppm: 7.36-7.24 (5H, m, Ar*H*), 4.57 (1H, t, *J* 6.5, PhC*H*(OH)CH_2), 2.00 (1H, br s, O*H*), 1.86-1.68 (2H, m, C*H*$_2$), 0.90 (3H, t, *J* 7.4, C*H*$_3$) ; δ_C (100.6MHz; $CDCl_3$)/ppm: 144.6, 128.4, 127.5, 126.0 (Ar-*C*), 76.0 (*C*H), 31.9 (*C*H_2), 10.2 (*C*H_3).

1-(1'-Naphthyl)ethanol 21: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 170 ^{0}C, P = 10 psi, ketone 23.0 min, S isomer 31.9 min., R isomer 32.7 min.); $[\alpha]_D^{22}$ +71.4 (c 0.35 in Et_2O) 84% ee (R) (lit.[3] $[\alpha]_D^{28}$ +77.2 (c 0.67 in Et_2O) 99% ee (R)); 8.09 (1H, d, *J* 8.0, Ar*H*), 7.87-7.83 (1H, m, Ar*H*), 7.76 (1H, d, *J* 8.3, Ar*H*), 7.65 (1H, d, *J* 7.0, Ar*H*), 7.53-7.43 (3H, m, Ar*H*), 5.64 (1H, q, *J* 6.4, C*H*(OH)CH_3), 2.05 (1H, br s, O*H*), 1.65 (3H, d, *J* 6.5, C*H*$_3$); δ_C (100.6MHz; $CDCl_3$)/ppm: 141.5, 133.8, 130.3, 128.9, 127.9, 126.0, 125.6, 125.5, 123.2, 122.1 (Ar-*C*), 67.1 (*C*H), 24.4 (*C*H_3).

2-Thienylethanol 26: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 125 ^{0}C, P = 9 psi, ketone 13.2 min, R isomer 15.6 min., S isomer 16.4 min.); $[\alpha]_D^{22}$ +25.6 (c 0.50 in $CHCl_3$) 97% ee (R) (lit.[3] $[\alpha]_D^{20}$ +15.2 (c 0.50 in $CHCl_3$) 52% ee (R)); δ_H (400 MHz; $CDCl_3$)/ppm: 7.24 (1H, dd, *J* 4.8 and 1.5, Ar*H*), 6.99-6.95 (2H, m, Ar*H*), 5.13 (1H, q, *J* 6.4, C*H*(OH)CH_3), 2.03 (1H, br s, O*H*) 1.60 (3H, d, *J* 6.5, C*H*$_3$); δ_C (100.6MHz; $CDCl_3$)/ppm: 149.9, 126.7, 124.5, 123.2 (Ar-*C*), 66.3 (*C*H), 25.3 (*C*H_3).

3-Thienylethanol 27: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 120 ^{0}C, P = 15 psi, ketone 10.1 min, R isomer 13.5 min., S isomer 14.2 min.); $[\alpha]_D^{24}$ +23.3 (c 0.78 in EtOH) 93% ee (R) (lit.[3] $[\alpha]_D^{24}$ +33.8 (c 0.43 in EtOH) 91% ee (R)); δ_H (400 MHz; $CDCl_3$)/ppm: 7.27 (1H, dd, *J* 4.9 and 2.9, Ar*H*), 7.16-7.14 (1H, m, Ar*H*), 7.07 (1H, dd, *J* 5.0 and 1.3, Ar*H*), 4.92 (1H, q, *J* 6.4, C*H*(OH)CH_3), 2.32 (1H, br s, O*H*), 1.49 (3H, d, *J* 6.5, C*H*$_3$); δ_C (100.6MHz; $CDCl_3$)/ppm: 147.4, 126.1, 125.7, 120.2 (Ar-*C*), 66.5 (*C*H), 24.5(*C*H_3).

2-Furylethanol 25: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 85 ^{0}C, P = 15 psi, ketone 10.5min, R isomer 15.1 min., S isomer 16.1 min.); $[\alpha]_D^{20}$ +18.9 (c 0.56 in $CHCl_3$) 98% ee (R) (lit.[4] $[\alpha]_D^{25}$ +20.8 (c 1.27 in $CHCl_3$) 99% ee (R)); δ_H (400 MHz; $CDCl_3$)/ppm: 7.37 (1H, dd, *J* 1.9 and 0.6, ArH), 6.33 (1H, dd, *J* 3.3 and 2.0, ArH), 6.23 (1H, d, *J* 3.3, Ar*H*), 4.88 (1H, q, *J* 6.5, C*H*(OH)CH_3), 1.96 (1H, br s, O*H*) 1.54 (3H, d, *J* 6.8, C*H*$_3$); δ_C (100.6MHz; $CDCl_3$)/ppm: 157.6, 141.9, 110.1, 105.1 (Ar-*C*), 63.7 (*C*H), 21.3 (*C*H_3).

4-Pyridylethanol 28: Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OD-H column, ethanol:hexane = 3:97 (0.5mL/min), ketone 28.4 min, S isomer 42.1 min., R isomer 46.0 min.) $[\alpha]_D^{20}$ +22.1 (c 0.14 in EtOH) 95% ee (R) (lit.[3] $[\alpha]_D^{21}$ +51.2 (c 0.122 in EtOH) 93% ee (R)); δ_H (400 MHz; $CDCl_3$)/ppm: 8.44 (2H, dd, *J* 4.5 and 1.5, Ar*H*), 7.30 (2H, dd, *J* 4.5 and 1.5, Ar*H*), 4.89 (1H, q, *J* 6.6, C*H*(OH)CH_3), 4.00 (1H, br s, O*H*), 1.48 (3H, d, *J* 6.5, C*H*$_3$); δ_C (100.6MHz; $CDCl_3$)/ppm: 155.5, 149.4, 120.6 (Ar-*C*), 68.5 (*C*H), 25.1 (*C*H_3).

1-(2'-Chlorophenyl)ethanol 18: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 150 ^{0}C, P = 15 psi, ketone 6.6 min, R isomer 9.8 min., S isomer 10.5 min.); 85% ee (R) (lit.[1] $[\alpha]_D^{26}$ +48.8 (c 1.0 in $CHCl_3$) 77% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-Cyclohexylethanol 32: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 92 ^{0}C, P = 9 psi, ketone 25.0 min, R isomer 40.5 min., S isomer 41.0 min.); $[\alpha]_D^{21}$ +2.07 (c 1.11 in $CHCl_3$) 87% ee (S) (lit.[3] $[\alpha]_D^{29}$ +1.82 (c 0.30 in $CHCl_3$) 68% ee (S)); δ_H (400 MHz; $CDCl_3$)/ppm: 3.54 (1H, quin, *J* 6.2, C*H*(OH)CH_3), 1.88-1.82 (1H, m, cyclohexyl C*H*), 1.80-1.72 (2H, m, CH_2), 1.71-1.63 (2H, m, CH_2), 1.49 (1H, br s, O*H*), 1.32-0.91 (6H, m, 3 × CH_2), 1.15 (3H, d, *J* 6.3, CH_3); δ_C (100.6MHz; $CDCl_3$)/ppm: 72.2 (*C*H(OH), 45.1 (cyclohexyl *C*H), 28.7 (*C*H_2), 28.4 (*C*H_2), 26.5 (*C*H_2), 26.2 (*C*H_2), 26.1 (*C*H_2), 20.4 (*C*H_3).

1-Tetralol 24: Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OD-H, 250 × 4.6mm column, Hexane/IPA 98:2, 0.5 mL/min, ketone 15.6 min, S isomer 29.7 min., R isomer 32.2 min.); 99.4% ee (R) (lit.[1] $[\alpha]_D^{27}$ -25 (c 0.114 in $CHCl_3$) 99.9% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

2-Chloro-1-phenylethanol 29: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 145 ^{0}C, P = 10 psi, ketone 18.3 min, S isomer 21.6 min., R isomer 22.4 min.); $[\alpha]_D^{25}$ +46.4 (c 1.43 in C_6H_{12}) 96% ee (S) (lit.[5] $[\alpha]_D^{25}$ -50.4 (c 1.78 in C_6H_{12}) 98% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

2-Phenoxy-1-phenylethanol 31: Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OD-H, 250 × 4.6mm column, Hexane/IPA,Et_2NH 90:10:0.1, 0.7 mL/min, ketone 18.3 min, R isomer 17.8 min., S isomer 31.0 min.); 92% ee (S)[6]; (Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

2-Hydroxy-1-phenylethanol 30: Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel OD-H, 250 × 4.6mm column, Hexane/EtOH,Et_2NH 95:5:0.1, 0.5 mL/min, ketone 18.3 min, R isomer 25.4 min., S isomer 27.2 min.); 99.5% ee (S)[7]; Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

Reduction of ketones using catalyst 11 in Water

1-Phenylethanol 14: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 115 ^{0}C, P = 15 psi, ketone 9.7 min, R isomer 14.2 min., S isomer 15.1 min.); 96% ee (R) (lit.[1] $[\alpha]_D^{26}$ +45.4 (c 0.50 in $CHCl_3$) 98% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-(3'-Trifluoromethylphenyl)ethanol 16: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 130 ^{0}C, P = 9 psi, ketone 8.5 min, R isomer 14.8 min., S isomer 15.5 min.); 96% ee (R) (lit.[1] $[\alpha]_D^{26}$ +27.1 (c 1.60 in CH_3OH) 96% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-(4'-Methylphenyl)ethanol 33: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 125 ^{0}C, P = 15 psi, ketone 11.9 min, R isomer 14.0 min., S isomer 14.6 min.); $[\alpha]_D^{22}$ +56.8 (c 0.41 in $CHCl_3$) 94% ee (R) (lit.[8] $[\alpha]_D^{25}$ +53.2 (c 0.236 in $CHCl_3$) 96% ee (R)); δ_H (300 MHz; $CDCl_3$)/ppm: 7.27 (2H, d (overlapping with the $CHCl_3$ peak, *J* 7.9, Ar*H*), 7.16 (2H, d, *J* 8.1, Ar*H*), 4.87 (1H, q, *J* 6.4, C*H*(OH)CH_3), 2.34 (3H, s, ArCH_3), 1.78 (1H, br s, O*H*), 1.48 (3H, d, *J* 6.6, CH_3); δ_C (75.5MHz; $CDCl_3$)/ppm: 142.6, 137.0, 129.0, 125.1 (Ar-*C*), 70.1 (*C*H), 24.9 (*C*H_3), 20.9 (Ar*C*H_3).

1-(4'-Bromophenyl)ethanol 34: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 150 ^{0}C, P = 15 psi, ketone 11.6 min, R isomer 17.9 min., S isomer 18.6 min.); $[\alpha]_D^{22}$ +33.4 (c 0.40 in

$CHCl_3$) 93% ee (R) (lit.[8] $[\alpha]_D^{26}$ +32.8 (c 1.600 in $CHCl_3$) 80% ee (R)); δ_H (400 MHz; $CDCl_3$)/ppm: 7.48-7.44 (2H, m, Ar*H*), 7.25-7.21 (2H, m, Ar*H*), 4.84 (1H, q, *J* 6.4, C*H*(OH)CH_3), 2.03 (1H, br s, O*H*), 1.45 (3H, d, *J* 6.5`, CH_3); δ_C (100.6MHz; $CDCl_3$)/ppm: 144.8 (Ar*C*-Br), 131.6, 127.2, 121.2 (Ar-*C*), 69.8 (*C*H), 25.3 (*C*H_3).

1-(3'-Methoxyphenyl)ethanol 17: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 140 ^{0}C, P = 15 psi, ketone 12.9 min, R isomer 18.1 min., S isomer 18.7 min.); $[\alpha]_D^{22}$ +32.9 (c 0.75 in MeOH) 97% ee (R) (lit.[5] $[\alpha]_D^{22}$ -34.9 (c 0.849 in MeOH) >99% ee (S)); δ_H (400 MHz; $CDCl_3$)/ppm: 7.26 (1H, dd, $J^1 = J^2$ 8.0, Ar*H*), 6.96-6.92 (2H, m, Ar*H*), 6.83-6.79 (1H, m, Ar*H*), 4.86 (1H, q, *J* 6.4, C*H*(OH)CH_3), 3.81 (3H, s, ArOCH_3), 1.94 (1H, br s, O*H*), 1.48 (3H, d, *J* 6.5, CH_3); δ_C (100.6MHz; $CDCl_3$)/ppm: 159.8 (Ar*C*-OMe), 147.6, 129.6, 117.7, 112.9, 110.9 (Ar-*C*), 70.4 (*C*H), 55.2 (O*C*H_3), 25.2 (*C*H_3).

1-(2'-Naphthyl)ethanol 35: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 155 ^{0}C, P = 15 psi, ketone 32.4 min, R isomer 40.1 min., S isomer 41.0 min.); 91% ee (R) (lit.[1] $[\alpha]_D^{25}$ +41.2 (c 0.50 in EtOH) 95% ee (R)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-Phenylpropan-1-ol 22: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 115 ^{0}C, P = 15 psi, ketone 14.1 min, R isomer 21.5 min., S isomer 22.6 min.); 96% ee (R). Refer to results of reductions in HCO_2H:Et_3N for $[\alpha]_D$, ^{1}H-NMR and ^{13}C-NMR data.

1-(2'-Trifluoromethylphenyl)ethanol 20: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 120 ^{0}C, P = 10 psi, ketone 10.7 min, R isomer 17.0 min., S isomer 18.0 min.); $[\alpha]_D^{24}$ +22.9 (c 0.46 in MeOH) 51% ee (R) (lit.[5] $[\alpha]_D^{22}$ -45.5 (c 0.661 in MeOH) 97% ee (S)); Refer to ref [1] for ^{1}H-NMR and ^{13}C-NMR data.

1-Cyclohexylethanol 32: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 92 ^{0}C, P = 9 psi, ketone 25.0 min, R isomer 40.5 min., S isomer 41.1 min.); 84% ee (S). Refer to results of reductions in HCO_2H:Et_3N for $[\alpha]_D$, ^{1}H-NMR and ^{13}C-NMR data.

2-Furylethanol 25: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 85 ^{0}C, P = 15 psi, ketone 10.5min, R isomer 15.0min., S isomer 15.9.); 98% ee (R). Refer to results of reductions in HCO_2H:Et_3N for $[\alpha]_D$, ^{1}H-NMR and ^{13}C-NMR data.

2-Thienylethanol 26: Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 125 ^{0}C, P = 9 psi, ketone 13.2 min, R isomer 15.6 min., S isomer 16.3 min.); 97% ee (R). Refer to results of reductions in HCO_2H:Et_3N for $[\alpha]_D$, ^{1}H-NMR and ^{13}C-NMR data.

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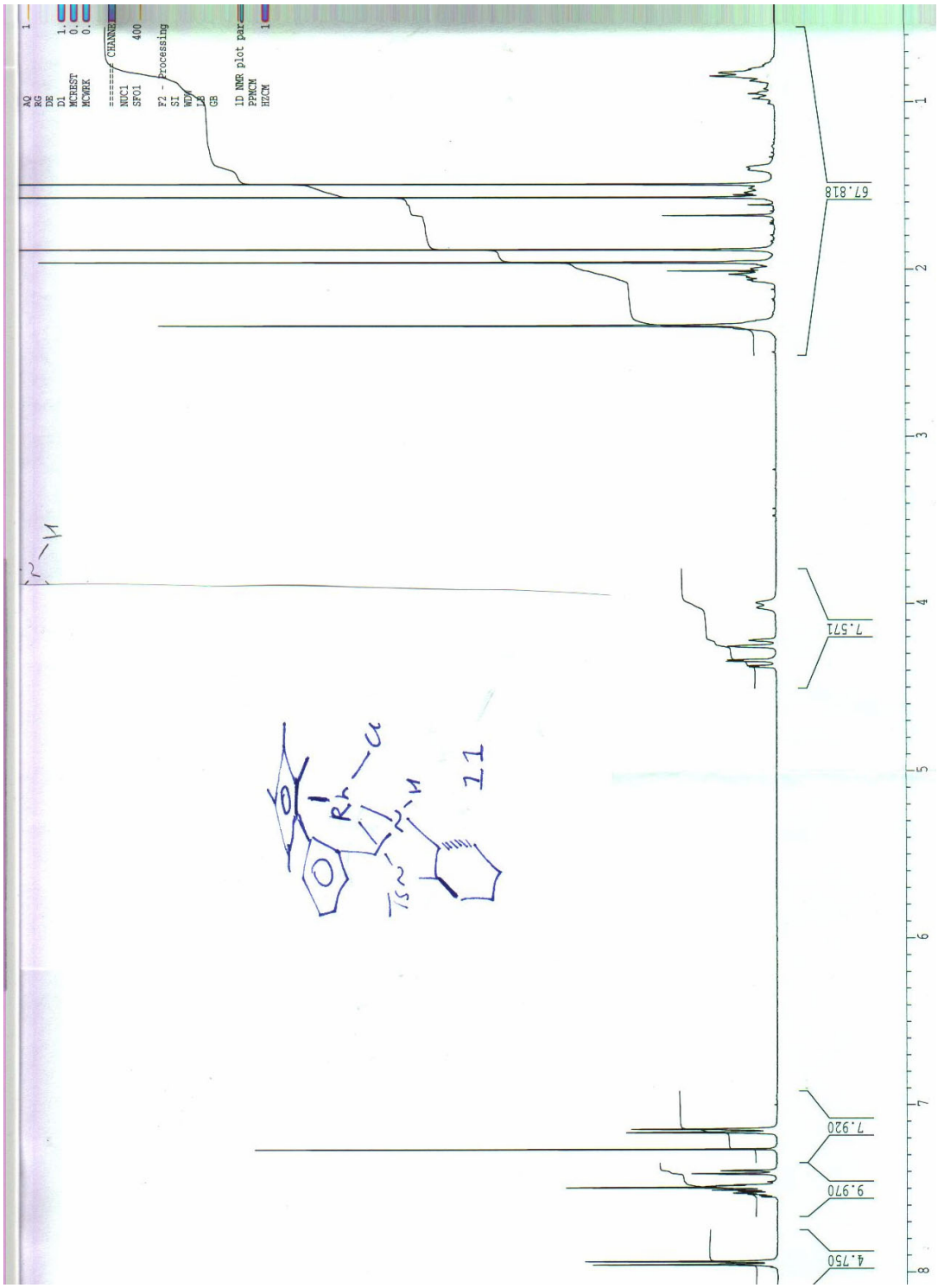
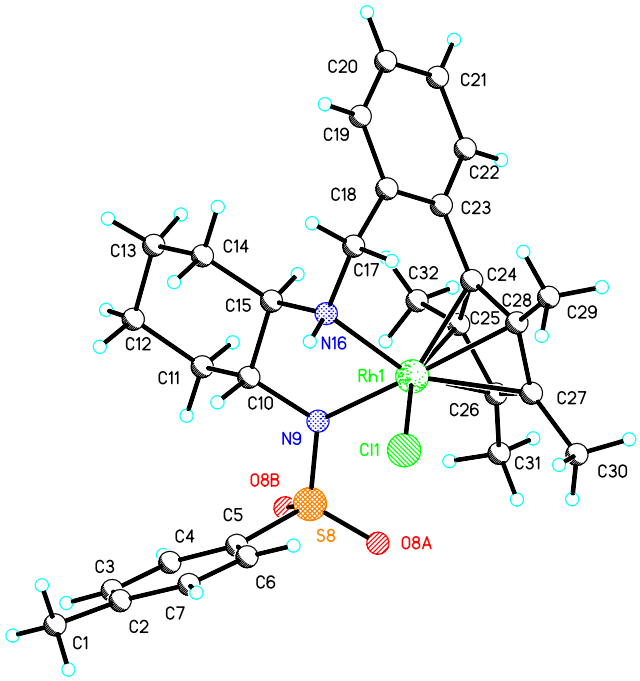
Proton NMR spectrum of Catalyst 11

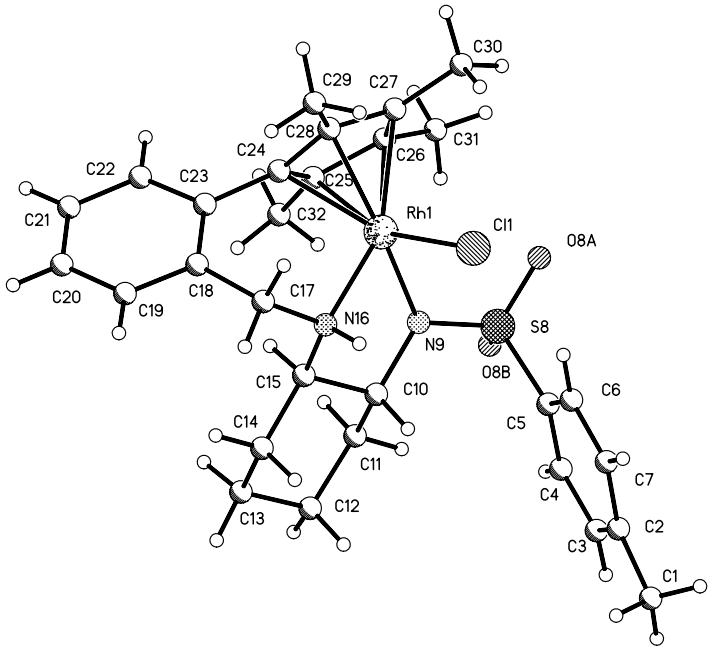


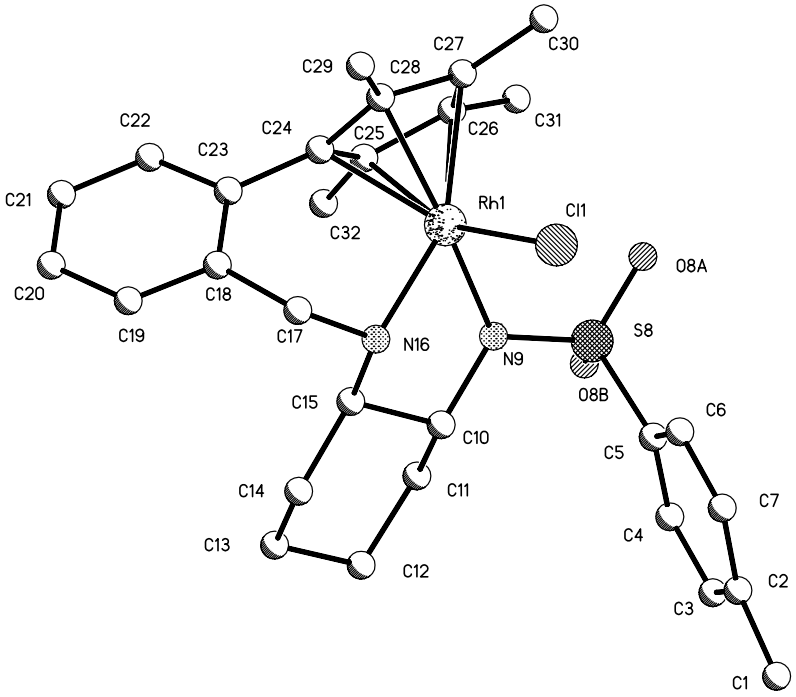
X-ray crystal structure data for 11

CCDC 603515 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif .

Solid state structure of DM3 with and without hydrogens







Experimental data for dm3

The asymmetric unit contains the complex. The hydrogen on the amine was located.

The angle between mean planes through the phenyl ring C18-C23 and the cyclopentenyl ring C24-C28 is 65.10 (0.10) degrees.
There are no other major factors in the crystal packing with no π stacking and only a few long (over 3A) CH-pi interactions.

Crystal Data
C29 H36 Cl N2 O2 Rh S, M = 615.02, Orthorhombic, space group P2(1)2(1)2(1)
a = 10.0963(12), b = 13.7861(16), c = 19.923(2) A ,
alpha = 90 deg., beta = 90 deg., gamma = 90 deg.,
U = 2773.1(6) A^3 (by least squares refinement on 7222 reflection positions),
T =180(2)K, lambda = 0.71073 A, Z = 4,
D(cal) = 1.473 Mg/m^3, F(000) = 1272.
mu(MoK-alpha) = 0.816 mm^-1.
Crystal character:orange block.
Crystal dimensions 0.40 x 0.30 x 0.08 mm,

Data Collection and Processing.
Siemens SMART (Siemens, 1994) three-circle system with CCD area detector.
The crystal was held at 180(2)
K with the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986).
Maximum theta was 29.21 deg.
The hkl ranges were -13/ 13, -18/ 18, -27/ 26.
27747 reflections measured, 6969 unique [R(int) = 0.0312].
Absorption correction by Semi-empirical from equivalents;
minimum and maximum transmission factors: 0.6990; 0.9376.
no crystal decay

Structure Analysis and Refinement.

Systematic absences indicated space group P2(1)2(1)2(1)
and shown to be correct by successful refinement.

**The structure was solved by direct methods
using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by
Fourier methods.**

**Hydrogen atoms were added at calculated positions and refined using a riding
model with freely rotating methyl groups except the N16-H16 which was located
in a Fourier map. Anisotropic displacement parameters were used for all non-H atoms;
H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for
methyl and NH hydrogen atoms) times the equivalent isotropic displacement parameter
of the atom to which the H-atom is attached.
The absolute structure of the individual crystal chosen was checked by
refinement of a delta-f" multiplier.
Absolute structure parameter x = 0.03(2).
The weighting scheme was calc w=1/[\s^2^(Fo^2^)+(0.0362P)^2^+1.0007P] where P=(Fo^2^+2Fc^2^)/3.
Goodness-of-fit on F^2 was 1.141,
R1[for 6772 reflections with
I>2sigma(I)] = 0.0294, wR2 = 0.0718.
Data / restraints / parameters 6969/ 0/ 327.
Largest difference Fourier peak and hole 0.623 and -0.735 e.A^-3 .**

Refinement used SHELXL 96 (Sheldrick, 1996).

**We thank EPSRC and Siemens Analytical Instruments for grants in support
of the diffractometer.**

**Additional material available from the Cambridge Crystallographic Data
Centre comprises H-atom coordinates, thermal parameters and the
remaining bond lengths and angles.**

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