Supporting information

Ether- Tethered Ru(II)/TsDPEN Complexes; Synthesis and Applications to Asymmetric Transfer Hydrogenation.

Vimal Parekh,[a] James Ramsden[b] and Martin Wills.*[a]

Contents:

1. General experimental details.

All air sensitive reactions were carried out under an argon or nitrogen atmosphere. Room temperature (rt) refers to ambient temperature (20-22 °C), 0 °C refers to an ice slush bath and -78 °C refers to a dry ice acetone bath. Heated experiments were conducted using thermostatically controlled oil baths or Asynt aluminium heating blocks. Reactions were monitored by Thin Layer Chromatography (TLC) using aluminium backed silica gel 60 (F_{254}) plates, visualised using $UV_{254\ nm,}$ PMA, iodine, potassium permanganate and ninhydrin dips as appropriate. ^{13}C-NMR spectra were recorded on a Bruker DPX-300 (300 MHz) or a Bruker DPX-400 (400 MHz). All chemical shifts are reported in ppm downfield from TMS (Me_4Si). Coupling constants (*J*) are reported in Hz. Multiplicity in ^{1}H-NMR is reported as singlet (s), doublet (d), quartet (q), quintet (quin), octet (oct), sextet (sext), double doublet (dd), double triplet (dt), triple triplet (tt), broad singlet (br s), broad multiplet (br m) and multiplet (m). Mass spectra were recorded on an Esquire 2000. High resolution mass spectra were recorded on Bruker Micro ToF. Infrared spectra were recorded on PerkinElmer spectrum100. The optical rotations were measured on Optical Activity Ltd. AA-1000 Polarimeter. The Chiral HPLC measurements were carried out on HPLC consisting of a Gilson 811B Dynamic Mixer, a Gilson 805 Monometer Module, a Gilson 305 Piston Pump, Merck-Hitachi L-4000 UV detector linked to HEWLETT PACKARD 3396 Series II integrator with CHIRAL PAK IA/IB column (0.46 cm x 25 cm) or CHIRAL CEL OD-H/OD column (0.46 cm x 25 cm). The chiral GC measurements were done on HEWLETT PACKARD 5890 linked to HEWLETT PACKARD HP3396A integrator or PERKIN-ELMER 8500 chromatography linked to PC running DataApex Clarity software with Chrompak CP-Chirasil Dex Cβ column. Melting points were determined on a Stuart scientific melting point apparatus and are uncorrected. Purification of compounds was carried out by using flash column chromatography using silica gel of mesh size 230-400/ Florisil of mesh 100-200 or Kugelrohr distillation using BÜCHI GKR-51.

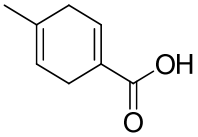
2. Experimental data for novel compounds and ketone/imine reduction products.

The following compounds have been reported and fully characterised, and were prepared as previously described; **(**2-hydroxyethylamino)TsDPEN **35** and its aminal precursor,[1a] 3-((*tert*-butyldiphenylsilyl)oxy)propan-1-ol and 3-((*tert*-butyldiphenylsilyl)oxy)propanal, the precursors of **43**,[1b] 4-((*tert*-

butyldiphenylsilyl)oxy)butan-1-ol and 4-((*tert*-butyldiphenylsilyl)oxy)butanal, the precursors of **44**,[1c] o-phenoxy acetophenone,[2] *tert*-butyl benzyl(2-oxo-2-phenylethyl)carbamate,[3] 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline.[4] All other ketone substrates were used as purchased.

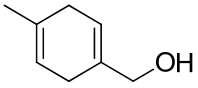
Synthesis of catalyst precursors and alcohol products.

Synthesis of 4-methylcyclohexa-1,4-dienecarboxylic acid (7).[5] (VRP275).



To a solution of propiolic acid (25.0 g, 22.0 cm^3, 357 mmol) in toluene was added, isoprene (25.3 g, 37.1 cm^3, 371 mmol) and hydroquinone (0.55 g, 5.01 mmol). The reaction was fitted with a condenser and heated to 130 °C overnight. The reaction mixture was cooled to room temperature, and a solid precipitate was filtered off and washed with cold toluene to give carboxylic acid **(7)** (26.5 g, 0.193 mol, 54 %) as a white crystalline solid; Mp 181-184 °C; ν_{max} 3675, 2963, 2882, 2631, 2532, 1701, 1666, 1645, 1425, 1282, 1161, 1097, 1035, 1027, 957, 922, 800, 780, 736 and 716 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.10 (1 H, br s, C*H*=CCO_2H), 5.48 (1 H, br s, C*H*=CCH_3), 2.98-2.88 (2 H, m, CH_2C=CH), 2.82-2.72 (2 H, m, C=CCH_2) and 1.70 (3 H, s, CH_3); δ_C (101 MHz, $CDCl_3$) 172.44 (*C*OOH), 139.17 (*C*H), 129.23 (*C*), 127.07 (*C*), 118.55 (*C*H), 31.99 (CH_2), 25.48 (CH_2), 22.76 (CH_3); *m/z* (ESI-MS) 137.0 $[M-H]^+$. Found (ESI-HR-MS): 137.0620 $[M-H]^+$, $C_8H_9O_2$ requires 137.0608 (-8.6 ppm error).

Synthesis of (4-methylcyclohexa-1,4-dien-1-yl)methanol (8).[6] (VRP 420).

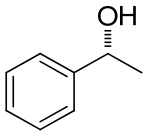


4-Methylcyclohexa-1,4-dienecarboxylic acid **(7)** (5.64 g, 40.8 mmol) in THF (50 cm^3) was added dropwise to a solution of $LiAlH_4$ (4.64 g, 123 mmol) in THF (250 cm^3) with stirring at 0 °C. After addition, the solution was allowed to stir at r.t. over the weekend. The solution was then cooled to 0 °C and quenched with a 50 : 50 mixture of water and THF (50 cm^3: 50 cm^3), followed by water (50 cm^3). Rochelle salt (40 g, 142.12 mmol) was then added followed by DCM (75 cm^3) and was further allowed to stir for 3 hrs. As the Rochelle salt absorbs all the water, the remaining solution was

then filtered off through celite, dried ($MgSO_4$), filtered and concentrated to give the alcohol (**8)** as a white solid (4.1 g, 33.1 mmol, 81 %); Mp 39-43 °C; ν_{max} 3361, 2963, 2908, 2818, 1429, 1338, 1185, 1140, 1065, 1001, 949, 904, 835 and 783 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.70 (1 H, s, C*H*=CCH_2OH), 5.45 (1 H, s, C*H*=CCH_3), 4.03 (2 H, s, CH_2OH), 2.72-2.65 (2 H, m, CH_2C=CH), 2.64-2.58 (2 H, m, C=CCH_2) and 1.68 (3 H, s, CH_3); δ_C (101 MHz, $CDCl_3$) 134.85 (*C*), 131.11 (*C*), 120.30 (*C*H), 118.25 (*C*H), 67.08 (CH_2), 31.26 (CH_2), 27.43 (CH_2) and 23.02 (CH_3); *m/z* (ESI-MS) 271.2 $[2M+Na]^+$. Found (ESI-HR-MS): 271.1673 $[2M+Na]^+$, $C_{16}H_{24}NaO_2$ requires 271.1669 (-1.6 ppm error).

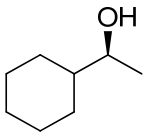
Reduction product analysis.

(*R*)-1-Phenylethanol (12) (VRP 343).



Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 115 °C, P = 15 psi, G = H_2, *R* isomer 15.0 min., *S* isomer 16.7 min.); $[\alpha]_D^{28}$ +56.0 (*c* 1.0, $CHCl_3$) 99% ee (*R*) (lit.[7] $[\alpha]_D^{22}$ +49.0 (*c* 1.0, $CHCl_3$) 98% ee (*R*)); δ_H (400 MHz, $CDCl_3$) 7.39-7.24 (5 H, m, 5 x Ar-*H*), 4.88 (1 H, q, *J* 6.4, C*H*OH), 2.03 (1 H, br s, O*H*) and 1.49 (3 H, d, *J* 6.4, CH_3); δ_C (101 MHz, $CDCl_3$) 145.83 (*C*), 128.52 (2 x *C*H), 127.49 (*C*H), 125.41 (2 x *C*H), 70.43 (*C*H) and 25.16 (CH_3).

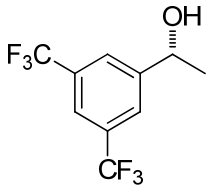
(*S*)-1-Cyclohexylethanol (30) (VRP 472 AND VRP 330).



Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, (Product was converted to (*S*)-1-cyclohexylethyl acetate for GC separation) T = 115 °C, P = 15 psi, G = He, *S* isomer 24.6 min., *R* isomer 27.6 min.); $[\alpha]_D$ not recorded as shown to be 0% ee by GC analysis (lit.[8] $[\alpha]_D^{22}$ +2.7 (*c* 0.5, $CHCl_3$) 75% ee (*S*)); δ_H (400 MHz, $CDCl_3$) 3.58-3.51 (1 H, m, C*H*OH), 1.90-1.62 (5 H, m, cyclohexyl), 1.50 (1 H, br s, O*H*), 1.32-0.91 (6 H, m, cyclohexyl) and 1.16 (3

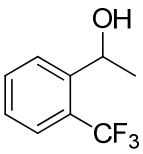
H, d, *J* 6.3, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 72.22 (*C*H), 45.13 (*C*H), 28.71 (*C*H$_2$), 28.37 (*C*H$_2$), 26.53 (*C*H$_2$), 26.24 (*C*H$_2$), 26.15 (*C*H$_2$) and 20.37 (*C*H$_3$).

(*R*)-1-(3,5-Bis(trifluoromethyl)phenyl)ethanol (25) (VRP298).



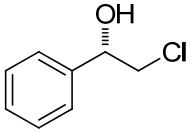
Enantiomeric excess and conversion by GC analysis (CP-Chirasil-Dex CB, 25 m, 0.25 mm, 0.25 µm, T = 100 °C for 10 minutes then ramp at 10 °C/minute to 200 °C, P = 20 psi, G = He, *S* isomer 11.0 min., *R* isomer 12.0 min.); $[\alpha]^{546}_{28}$ +11.2 (*c* 1.0, $CHCl_3$) 60% ee (*R*) (lit.[9] $[\alpha]^{546}_{22}$ +16.0 (*c* 1.2, $CHCl_3$) >99% ee (*R*)); δ_H (400 MHz, $CDCl_3$) 7.85 (2 H, s, 2 x Ar-*H o* to CHOH), 7.79 (1 H, s, Ar-*H p* to CHOH), 5.05 (1 H, q, *J* 6.5, C*H*OH), 2.02 (1 H, br s, O*H*) and 1.55 (3 H, d, *J* 6.5, C*H*$_3$); δ_C (101 MHz, $CDCl_3$) 148.22 (*C*), 131.92 (*C*), 131.59 (*C*), 125.66 (2 x *C*H), 124.71 (*C*), 121.94 (*C*), 121.31 (*C*H), 69.28 (*C*H) and 25.60 (*C*H$_3$).

1-(2-(Trifluoromethyl)phenyl)ethanol (26) (VRP299 AND VRP 460).



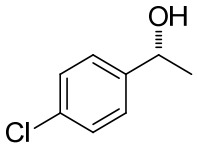
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 110 °C, P = 15 psi, G = H_2, *R* isomer 18.3 min., *S* isomer 20.0 min.) 17% ee; (lit.[10] $[\alpha]_D^{29}$ -30.4 (*c* 1.41, $CHCl_3$) 96% ee (*R*)); δ_H (300 MHz, $CDCl_3$) 7.82 (1 H, d, *J* 7.8 , Ar-*H o* to CF_3), 7.63-7.55 (2 H, m, Ar-*H o* to $CHOHCH_3$ and Ar-*H p* to $CHOHCH_3$), 7.40-7.32 (1 H, m, Ar-*H m* to $CHOHCH_3$ and *p* to CF_3), 5.37-5.27 (1 H, m, C*H*OH), 2.10 (1 H, d, *J* 3.0, O*H*) and 1.48 (3 H, d, *J* 6.3, C*H*$_3$); δ_C (75 MHz, $CDCl_3$) 144.41 (*C*), 131.77 (*C*H), 126.72 (*C*H), 126.47 (*C*H), 125.57 (*C*), 124.71 (*C*H), 121.94 (*C*), 65.06 (*C*H) and 24.79 (*C*H$_3$).

(*S*)-2-Chloro-1-phenylethanol (21) (VRP 302)



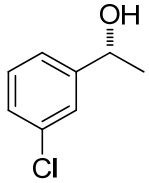
Novelty. Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β- 236M-19 50m, T = 140 °C, P = 10 psi, G = H_2, *S* isomer 29.9 min., *R* isomer 31.7 min.); $[\alpha]_D^{28}$ +43.4 (*c* 1.0, cyclohexane) 98% ee (*S*) (lit.[7] $[\alpha]_D^{25}$ +51.5 (*c* 1.1, cyclohexane) 95% ee (*S*)); δ_H (300 MHz, $CDCl_3$) 7.33-7.15 (5 H, m, 5 x Ar-*H*), 4.76 (1 H, dd, *J* 8.7, 3.4, C*H*OH), 3.61 (1 H, dd, *J* 3.4, 11.2, $CH_{(1)}H_{(2)}Cl$), 3.51 (1 H, dd, *J* 8.7, 11.2, $CH_{(1)}H_{(2)}Cl$) and 2.60 (1 H, br s, O*H*); δ_C (75 MHz, $CDCl_3$) 139.27 (*C*), 128.07 (2 x *C*H), 127.87 (*C*H), 125.44 (2 x *C*H), 73.46 (*C*H) and 50.31 (CH_2).

(*R*)-1-(4-Chlorophenyl)ethanol (13) (VRP 311).



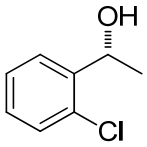
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 130 °C, P = 15 psi, G = H_2, *R* isomer 27.9 min., *S* isomer 31.4 min.); $[\alpha]_D^{20}$ +50.4 (*c* 1.0, $CHCl_3$) 96% ee (*R*) (lit.[11] $[\alpha]_D^{22}$ +45.6 (*c* 1.0, $CHCl_3$) 91% ee (*R*)); δ_H (400 MHz, $CDCl_3$) 7.33-7.25 (4 H, m, 4 x Ar-*H*), 4.87 (1 H, q, *J* 6.5, C*H*OH), 2.73 (1 H, br s, O*H*) and 1.47 (3 H, d, *J* 6.5, CH_3); δ_C (101 MHz, $CDCl_3$) 144.17 (*C*), 133.12 (*C*), 128.80 (2 x *C*H), 126.82 (2 x *C*H), 69.81 (*C*H) and 25.24 (CH_3).

(*R*)-1-(3-Chlorophenyl)ethanol (14) (EXP VRP301).



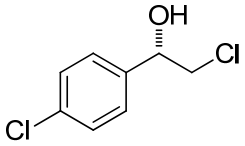
Enantiomeric excess and conversion by GC analysis (CP-Chirasil-Dex CB, 25 m, 0.25 mm, 0.25 µm, T = 120 °C for 20 minutes then ramp at 15 °C/minute to 200 °C, P = 20 psi, G = He, *R* isomer 19.2 min., *S* isomer 21.1 min.); $[\alpha]_D^{29}$ +34.8 (*c* 1.0, $CHCl_3$) 94% ee (*R*) (lit.[12] $[\alpha]_D^{22}$ +43.3 (*c* 1.0, $CHCl_3$) 90% ee (*R*)); δ_H (300 MHz, $CDCl_3$) 7.37-7.32 (1 H, m, Ar-*H o* to Cl and $CHOHCH_3$), 7.30-7.19 (3 H, m, 1 x Ar-*H m* to Cl/$CHOHCH_3$ and 1 x Ar-*H p* to Cl and 1 x Ar-*H p* to $CHOHCH_3$), 4.85 (1 H, q, *J* 6.5, C*H*OH), 2.50 (1 H, br s, O*H*) and 1.46 (3 H, d, *J* 6.5, CH_3); δ_C (75 MHz, $CDCl_3$) 147.18 (*C*), 133.74 (*C*), 129.18 (*C*H), 126.92 (*C*H), 125.02 (*C*H), 122.93 (*C*H), 69.29 (*C*H) and 24.59 (CH_3).

(*R*)-1-(2-Chlorophenyl)ethanol (17) (VRP314).



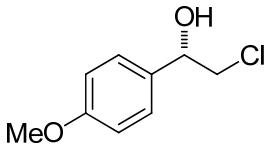
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 130 °C, P = 15 psi, G = H_2, *R* isomer 22.9 min., *S* isomer 28.8 min.); $[\alpha]_D^{29}$ +49.2 (*c* 1.0, $CHCl_3$) 87% ee (*R*) (lit.[11] $[\alpha]_D^{22}$ +40.8 (*c* 1.0, $CHCl_3$) 77% ee (*R*)); δ_H (300 MHz, $CDCl_3$) 7.59 (1 H, dd, *J* 1.8, 1.8, Ar-*H o* to Cl), 7.34-7.25 (2 H, m, 1 x Ar-*H o* to $CHOHCH_3$ and 1 x Ar-*H p* to $CHOHCH_3$), 7.19 (1 H, ddd, *J* 1.8, 1.8, 1.8, Ar-*H p* to Cl), 5.29 (1 H, q, *J* 6.4, C*H*OH), 2.20 (1 H, br s, O*H*) and 1.49 (3 H, d, *J* 6.4, C*H*$_3$); δ_C (75 MHz, $CDCl_3$) 142.41 (*C*), 131.02 (*C*), 128.79 (*C*H), 127.79 (*C*H), 126.60 (*C*H), 125.79 (*C*H), 66.36 (*C*H) and 22.88 (CH_3).

(*S*)-2-Chloro-1-(4-chlorophenyl)ethanol (22) (VRP309).



Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 160 °C, P = 11 psi, G = H_2, *S* isomer 38.2 min., *R* isomer 40.9 min.); $[\alpha]_D^{31}$ +44.8 (*c* 1.0, $CHCl_3$) 96% ee (*S*) (lit.[7] $[\alpha]_D^{25}$ +47.0 (*c* 1.1, $CHCl_3$) 93% ee (*S*)); δ_H (400 MHz, $CDCl_3$) 7.37-7.30 (4 H, m, 4 x Ar-*H*), 4.88 (1 H, dd, *J* 3.5, 8.6, C*H*OH), 3.71 (1 H, dd, *J* 3.5, 11.3, C*H*$_{(1)}$H$_{(2)}$Cl), 3.61 (1 H, dd, *J* 8.6, 11.3, CH$_{(1)}$*H*$_{(2)}$Cl) and 2.95 (1 H, br s, O*H*); δ_C (101 MHz, $CDCl_3$) 138.37 (*C*), 134.26 (*C*), 128.86 (2 x *C*H), 127.47 (2 x *C*H), 73.39 (*C*H) and 50.67 (CH_2).

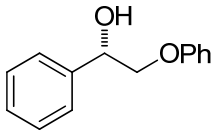
(*S*)-2-Chloro-1-(4-methoxyphenyl)ethanol (23) (VRP 310).



Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 160 °C, P = 14 psi, G = H_2, *S* isomer 33.2 min., *R* isomer 34.6 min.); $[\alpha]_D^{31}$ +50.0 (*c* 1.0, $CHCl_3$) 97% ee (*S*) (lit.[7] $[\alpha]_D^{24}$ +52.9 (*c* 1.1, $CHCl_3$) 95% ee (*S*)); δ_H (400 MHz, $CDCl_3$) 7.34-7.27 (2 H, m, 2 x Ar-*H o* to $CHOHCH_2Cl$), 6.93-

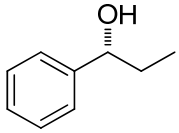
6.87 (2 H, m, 2 x Ar-*H o* to MeO), 4.85 (1 H, dd, *J* 3.6, 8.7, C*H*OH), 3.81 (3 H, s, CH_3O), 3.70 (1 H, dd, *J* 3.6, 11.2, C$H_{(1)}$H$_{(2)}$Cl), 3.63 (1 H, dd, *J* 8.7, 11.2, CH$_{(1)}$$H_{(2)}$Cl) and 2.65 (1 H, br s, O*H*); δ_C (101 MHz, $CDCl_3$) 159.72 (*C*-OMe), 132.06 (*C*), 127.35 (2 x *C*H), 114.09 (2 x *C*H), 73.75 (*C*H), 55.33 (*C*H_3) and 50.92 (*C*H_2).

(*S*)-2-Phenoxy-1-phenylethanol (24) (EXP VRP 334).



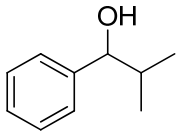
Enantiomeric excess by HPLC analysis and conversion by GC analysis (ChiralPak IA Column: 0.46 cm^3 x 25 cm, hexane:isopropanol = 95:5, flow rate 0.5 ml/min, 254 nm, 24 °C: t_R = 28.9 min (minor), t_S = 36.4 (major)); $[\alpha]_D^{30}$ +58.8 (*c* 1.0, $CHCl_3$) 95% ee (*S*) (lit.[13] $[\alpha]_D^{20}$ +50.0 (*c* 1.7, $CHCl_3$) 98% ee (*S*)); δ_H (400 MHz, $CDCl_3$) 7.47-7.23 (7 H, m, 5 x Ar-*H* and 2 x Ar-*H m* to CH_2O), 6.97 (1 H, t, *J* 7.4, Ar-*H p* to CH_2O), 6.91 (2 H, d, *J* 7.8, 2 x Ar-*H o* to CH_2O), 5.12 (1 H, dd, *J* 3.2, 8.8, C*H*OH), 4.10 (1 H, dd, *J* 3.2, 9.6, C$H_{(1)}$H$_{(2)}$OPh), 4.01 (1 H, dd, *J* 9.6, 8.8, CH$_{(1)}$$H_{(2)}$OPh) and 2.90 (1 H, br s, O*H*); δ_C (101 MHz, $CDCl_3$) 158.41 (*C*), 139.66 (*C*), 129.60 (2 x *C*H), 128.61 (2 x *C*H), 128.23 (*C*H), 126.32 (2 x *C*H), 121.35 (*C*H), 114.68 (2 x *C*H), 73.32 (*C*H_2) and 72.63 (*C*H).

(*R*)-1-Phenylpropan-1-ol (18) (VRP 319).



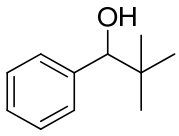
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 110 °C, P = 15 psi, G = H_2, *R* isomer 31.1 min., *S* isomer 33.8 min.); $[\alpha]_D^{26}$ +53.6 (*c* 1.0, $CHCl_3$) >99% ee (*R*) (lit.[14] $[\alpha]_D^{26}$ -40.0 (*c* 0.85, $CHCl_3$) 66% ee (*S*)); δ_H (400 MHz, $CDCl_3$) 7.38-7.24 (5 H, m, 5 x Ar-*H*), 4.59 (1 H, t, *J* 6.5, C*H*OH), 2.40 (1 H, br s, O*H*), 1.90-1.68 (2 H, m, CH_2) and 0.91 (3 H, t, *J* 7.4, CH_3); δ_C (101 MHz, $CDCl_3$) 144.55 (*C*), 128.43 (2 x *C*H), 127.54 (*C*H), 125.99 (2 x *C*H), 76.09 (*C*H), 31.88 (*C*H_2) and 10.15 (*C*H_3).

2-Methyl-1-phenylpropan-1-ol (19) (VRP318).



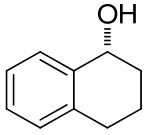
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 110 °C, P = 15 psi, G = H_2, *R* isomer 39.4 min., *S* isomer 40.8 min.), $[\alpha]_D$ not recorded due to low conversion), 27% ee; (lit.[15] $[\alpha]_D^{20}$ +34.6 (*c* 1.0, $CHCl_3$) 68.5% ee (*R*)); δ_H (400 MHz, $CDCl_3$) 7.36-7.22 (5 H, m, 5 x Ar-*H*), 4.33 (1 H, d, *J* 6.8, C*H*OH), 1.97 (1 H, br s, O*H*), 1.94 (1 H, oct, *J* 6.8, C*H*$(CH_3)_2$), 0.99 (3 H, d, *J* 6.8, CH_3) and 0.78 (3 H, d, *J* 6.8, CH_3); δ_C (101 MHz, $CDCl_3$) 143.68 (*C*), 127.94 (2 x *C*H), 127.01 (*C*H), 126.60 (2 x *C*H), 80.05 (*C*H), 35.09 (*C*H), 19.02 (*C*H_3) and 18.28 (*C*H_3).

2,2-Dimethyl-1-phenylpropan-1-ol (20) (VRP 324 AND VRP 322).



Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 125 °C, P = 15 psi, G = H_2, *S* isomer 29.5 min., *R* isomer 30.5 min.), $[\alpha]_D$ not recorded due to low conversion), 14% ee; (lit.[16] $[\alpha]_D^{20}$ +12.2 (*c* 1.0, $CHCl_3$) 45% ee (*R*)); δ_H (400 MHz, $CDCl_3$) 7.34-7.22 (5 H, m, 5 x Ar-*H*), 4.38 (1 H, s, C*H*OH), 1.92 (1 H, br s, O*H*) and 0.92 (9 H, s, 3 x CH_3); δ_C (101 MHz, $CDCl_3$) 142.23 (*C*), 127.64 (2 x *C*H), 127.57 (2 x *C*H), 127.29 (*C*H), 82.41 (*C*H), 35.64 (*C*) and 25.96 (3 x *C*H_3).

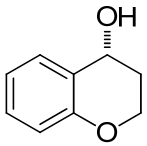
(*R*)-1,2,3,4-Tetrahydronaphthalen-1-ol (15) (VRP 325).



Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 115 °C, P = 15 psi, G = H_2, *S* isomer 74.1 min., *R* isomer 74.3 min.); $[\alpha]_D^{29}$ -19.2 (*c* 1.0, $CHCl_3$) >99% ee (*R*) (lit.[17] $[\alpha]_D^{20}$ +38.9 (*c* 1.45, $CHCl_3$) 99% ee (*S*)); δ_H (300 MHz, $CDCl_3$) 7.45-7.36 (1 H, m, 1 x Ar-*H*), 7.22-7.04 (3 H, m, 3 x Ar-*H*), 4.77 (1 H, t, *J* 4.4, C*H*OH), 2.88-2.62 (2 H, m, CH_2 *p* to CHOH), 2.50 (1 H, br s, O*H*) and 2.05-1.69 (4 H, m, 2 x CH_2 *o* and *m* to CHOH); δ_C (75 MHz, $CDCl_3$)

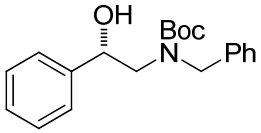
138.10 (*C*), 136.52 (*C*), 128.42 (*C*H), 128.06 (*C*H), 127.00 (*C*H), 125.58 (*C*H), 67.57 (*C*H), 31.62 (CH_2), 28.63 (CH_2) and 18.16 (CH_2).

(*R*)-Chroman-4-ol (16) (VRP 335).



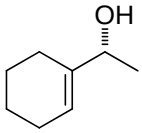
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 160 °C, P = 15 psi, G = H_2, *S* isomer 13.4 min., *R* isomer 13.6 min.); $[\alpha]_D^{30}$ +77.6 (*c* 1.0, $CHCl_3$) >99% ee (*R*) (lit.[17] $[\alpha]_D^{20}$ -62.0 (*c* 1.8, $CHCl_3$) 98% ee (*S*)); δ_H (400 MHz, $CDCl_3$) 7.32 (1 H, dd, *J* 7.6, 1.6, Ar-*H*), 7.21 (1 H, dt, *J* 7.4, 1.6, Ar-*H*), 6.93 (1 H, dt, *J* 7.4, 1.1, Ar-*H*), 6.85 (1 H, d, *J* 8.3, Ar-*H*), 4.80 (1 H, t, *J* 4.0, C*H*OH), 4.31-4.24 (2 H, m, CH_2 *m* to CHOH), 2.18-2.09 (1 H, m, $CH_{(1)}H_{(2)}$ *o* to CHOH), 2.08-2.00 (1 H, m, $CH_{(1)}H_{(2)}$ *o* to CHOH) and 1.80 (1 H, br s, O*H*); δ_C (101 MHz, $CDCl_3$) 154.45 (*C*), 129.76 (*C*H), 129.64 (*C*H), 124.42 (*C*), 120.62 (*C*H), 117.11 (*C*H), 63.29 (*C*H), 61.93 (CH_2) and 30.84 (CH_2).

(*S*)-*tert*-Butyl benzyl(2-hydroxy-2-phenylethyl)carbamate (27) (VRP 368 AND VRP353).



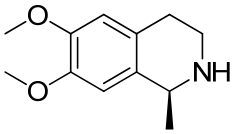
Enantiomeric excess by HPLC analysis and conversion by NMR analysis (ChiralPak IA Column: 0.46 cm^3 x 25 cm, hexane:isopropanol = 98:2, flow rate 0.5 ml/min, 254 nm, 21 °C: t_R = 49.6 min (minor), t_S = 64.9 (major)); $[\alpha]_D^{29}$ +2.4 (*c* 0.5, ethanol) >99% ee (*S*) (lit.[3] $[\alpha]_D^{20}$ +3.3 (*c* 2.0, ethanol) 80% ee (*S*)); δ_H (400 MHz, $CDCl_3$) 7.34-7.15 (10 H, m, 10 x Ar-*H*), 4.92-4.86 (1 H, m, C*H*OH), 4.51-4.41 (2 H, m, $CH_{(1)}H_{(2)}$-Ar and O*H*), 4.19 (1 H, d, *J* 14.4, $CH_{(1)}H_{(2)}$-Ar), 3.64-3.49 (1 H, m, CH(OH)$CH_{(1)}H_{(2)}$), 3.33 (1 H, d, *J* 13.0, CH(OH)$CH_{(1)}H_{(2)}$) and 1.49 (9 H, s, CH_3); δ_C (101 MHz, $CDCl_3$) 155.91 (*C*=O) 142.39 (*C*), 137.96 (*C*), 128.62 (4 x *C*H), 128.41 (*C*H), 127.51 (*C*H), 127.38 (*C*H), 127.34 (*C*H), 125.80 (2 x *C*H), 81.51 ($(CH_3)_3C$), 74.23 (*C*H(OH)), 57.30 (CH_2), 52.53 (CH_2) and 28.42 ($(CH_3)_3C$); *m/z* (ESI-MS) 350.2 $[M+Na]^+$.

(*R*)-1-(Cyclohex-1-en-1-yl)ethanol (31) (VRP 360).



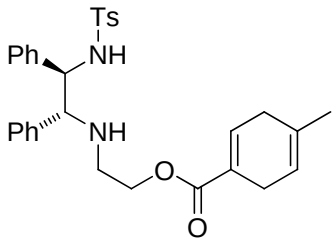
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 115 ^{o}C, P = 15 psi, G = H_2, *S* isomer 13.5 min., *R* isomer 13.9 min.); $[\alpha]_D^{30}$ +26.4 (*c* 0.5, $CHCl_3$) 71% ee (*R*) (lit.[18] $[\alpha]_{589}^{20}$ +19.7 (*c* 1.69, $CHCl_3$) 83% ee (*R*)); δ_H (400 MHz, $CDCl_3$) 5.66 (1 H, s, C*H*=C), 4.16 (1 H, q, *J* 6.4, C*H*OH), 2.10-1.90 (4 H, m, 2 x CH_2), 1.72-1.49 (5 H, m, 2 x CH_2 + OH) and 1.25 (3 H, d, *J* 6.4, CH_3); δ_C (101 MHz, $CDCl_3$) 141.27 (*C*), 121.49 (*C*H), 72.14 (*C*H), 24.89 (*C*H_2), 23.67 (*C*H_2), 22.66 (*C*H_2), 22.60 (*C*H_2) and 21.50 (*C*H_3).

(*S*)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (50) (VRP273, VRP282 AND VRP473).



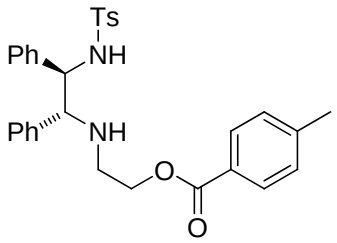
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 170 ^{o}C, P = 15 psi, G = He, *S* isomer 35.5 min., *R* isomer 36.1 min.); $[\alpha]_D^{27}$ -40.0 (*c* 0.5, $CHCl_3$) 87% ee (*S*) (lit.[19] $[\alpha]_D^{28}$ -32.9 (*c* 0.3, $CHCl_3$) 84% ee (*S*)); δ_H (400 MHz, $CDCl_3$) 6.63 (1 H, s, Ar-*H*), 6.57 (1 H, s, Ar-*H*), 4.05 (1 H, q, *J* 6.6, C*H*NH), 3.85 (6 H, s, 2 x CH_3O), 3.29-3.21 (1 H, m, C$H_{(1)}$H$_{(2)}$ *p* to CH(CH_3)), 3.04-2.95 (1 H, m, CH$_{(1)}$$H_{(2)}$ *p* to CH(CH_3)), 2.85-2.73 (1 H, m, C$H_{(1)}$H$_{(2)}$ *m* to CH(CH_3)), 2.69-2.60 (1 H, m, CH$_{(1)}$$H_{(2)}$ *m* to CH(CH_3)), 1.73 (1 H, br s, N*H*) and 1.44 (3 H, d, *J* 6.6, CH_3); δ_C (101 MHz, $CDCl_3$) 147.30 (*C*), 147.22 (*C*), 132.52 (*C*), 126.85 (*C*), 111.77 (*C*H), 109.04 (*C*H), 56.00 (1 x *C*H_3O), 55.86 (1 x *C*H_3O), 51.25 (*C*H), 41.89 (*C*H_2), 29.61 (*C*H_2) and 22.90 (*C*H_3).

Synthesis of 2-(((1*R*,2*R*)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)amino)ethyl 4-methylcyclohexa-1,4-dienecarboxylate (39) (EXP VRP 385).



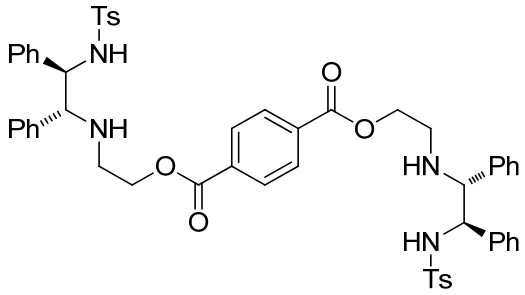
4-Methylcyclohexa-1,4-diene carboxylic acid (18 mg, 0.13 mmol) was added to a solution of *N*-((1*R*, 2*R*)-2-((2-hydroxyethyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide **35** (53 mg, 0.13 mmol) in DCM (2 cm^3) at r.t, followed by addition of DCC (165 mg, 0.80 mmol) and DMAP (16 mg, 0.13 mmol). The resulting mixture was stirred overnight and the concentrated under reduced pressure. The crude white residue was then purified by flash chromatography (10→30 % v/v ethyl acetate/hexane) giving **(39)** as a colourless gum (58 mg, 0.109 mmol, 84 %); $[\alpha]_D^{22}$ -10.4 (*c* 0.5, $CHCl_3$); ν_{max} 3663, 3259, 2902, 1712, 1690, 1651, 1600, 1495, 1454, 1395, 1327, 1304, 1252, 1185, 1157, 1092, 1048, 960, 920, 812, 756, 719, 699 and 668 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.38 (2 H, d, *J* 8.3, 2 x Ar-*H*), 7.16-7.10 (3 H, m, 3 x Ar-*H*), 7.09-7.03 (3 H, m, 3 x Ar-*H*), 7.02-6.94 (6 H, m, 6 x Ar-*H*), 6.90-6.85 (1 H, m, C*H*=C(CO_2)), 6.04 (1 H, d, *J* 3.3, N*H*Ts), 5.50-5.45 (1 H, m, C*H*=C(CH_3)), 4.30 (1 H, dd, *J* 7.3, 3.3, C*H*NHTs), 4.25-4.17 (1 H, m, C$H_{(1)}H_{(2)}$OC=O), 4.09-4.02 (1 H, m, C$H_{(1)}H_{(2)}$OC=O), 3.74 (1 H, d, *J* 7.3, C*H*NH), 2.87-2.75 (4 H, m, CH_2C=CCH_2), 2.75-2.67 (1 H, m, C$H_{(1)}H_{(2)}$NH), 2.62-2.53 (1 H, m, C$H_{(1)}H_{(2)}$NH), 2.32 (3 H, s, CH_3Ts) and 1.72 (3 H, s, CH_3); δ_C (101 MHz, $CDCl_3$) 166.85 (*C*=O), 142.67 (*C*), 138.78 (2 x *C*), 138.36 (2 x *C*), 137.03 (*C*H), 129.39 (*C*), 129.10 (2 x *C*H), 128.42 (2 x *C*H), 128.04 (2 x *C*H), 127.64 (*C*H), 127.44 (2 x *C*H), 127.35 (3 x *C*H), 127.03 (2 x *C*H), 118.55 (*C*H), 67.14 (*C*H), 63.13 (CH_2), 63.07 (*C*H), 45.66 (CH_2), 31.89 (CH_2), 26.07 (CH_2), 22.83 (CH_3) and 21.42 (CH_3); *m/z* (ESI-MS) 531.1 $[M+H]^+$, 553.1 $[M+Na]^+$. Found (ESI-HR-MS): 531.2330 $[M+H]^+$, $C_{31}H_{35}N_2O_4S$ requires 531.2312 (-3.2 ppm error).

Synthesis of 2-(((1*R*,2*R*)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)amino)ethyl 4-methylbenzoate (40) (VRP 432).



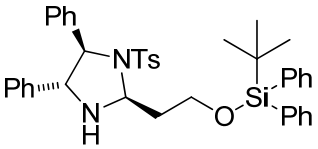
p-Toluic acid (18 mg, 0.13 mmol) was added to a solution of *N*-((1*R*, 2*R*)-2-((2-hydroxyethyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide **35** (53 mg, 0.13 mmol) in DCM (2 cm^3) at r.t., followed by addition of DCC (165 mg, 0.80 mmol) and DMAP (16 mg, 0.13 mmol). The resulting mixture was stirred overnight and then concentrated under reduced pressure. The crude white residue was then purified by flash chromatography (10→30 % v/v ethyl acetate/hexane) giving **(40)** as white crystals (58 mg, 0.109 mmol, 85 %); Mp 61-64 °C; $[\alpha]_D^{23}$ -17.6 (*c* 0.5, $CHCl_3$); ν_{max} 3266, 3031, 1712, 1611, 1495, 1453, 1406, 1327, 1271, 1178, 1156, 1093, 1020, 917, 841, 812, 753, 698 and 666 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.83 (2 H, d, *J* 8.1, 2 x Ar-*H*), 7.33 (2 H, d, *J* 8.1, 2 x Ar-*H*), 7.25 (2 H, d, *J* 7.7, 2 x Ar-*H*), 7.18-7.09 (3 H, m, 3 x Ar-*H*), 7.08-7.01 (3 H, m, 3 x Ar-*H*), 6.98 (6 H, d, *J* 7.7, 6 x Ar-*H*), 6.07 (1 H, br s, N*H*Ts), 4.40-4.28 (1 H, m, C$H_{(1)}$H$_{(2)}$OC=O), 4.31 (1 H, d, *J* 7.3, C*H*NHTs), 4.26-4.17 (1 H, m, CH$_{(1)}H_{(2)}$OC=O), 3.77 (1 H, d, *J* 7.3, C*H*NH), 2.84-2.75 (1 H, m, C$H_{(1)}$H$_{(2)}$NH), 2.71-2.62 (1 H, m, CH$_{(1)}H_{(2)}$NH), 2.44 (3 H, s, CH_3Ts), 2.30 (3 H, s, CH_3) and 1.76 (1 H, br s, N*H*); δ_C (101 MHz, $CDCl_3$) 166.53 (*C*=O), 143.79 (*C*), 142.68 (*C*), 138.80 (*C*), 138.37 (*C*), 137.01 (*C*), 129.69 (2 x *C*H), 129.15 (2 x *C*H), 129.11 (2 x *C*H), 128.43 (2 x *C*H), 128.06 (2 x *C*H), 127.66 (*C*H), 127.46 (2 x *C*H), 127.35 (3 x *C*H), 127.20 (*C*), 127.04 (2 x *C*H), 67.29 (*C*H), 63.72 (CH_2), 63.11 (*C*H), 45.73 (CH_2), 21.72 (CH_3) and 21.41 (CH_3); *m/z* (ESI-MS) 529.1 $[M+H]^+$, 551.2 $[M+Na]^+$. Found (ESI-HR-MS): 529.2159 $[M+H]^+$, $C_{31}H_{33}N_2O_4S$ requires 529.2156 (-0.6 ppm error).

Synthesis of bis(2-(((1*R*,2*R*)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)amino)ethyl) terephthalate (41) (VRP 407).



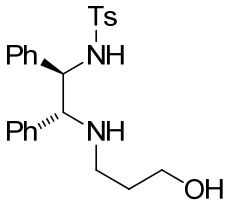
Terephthalic acid (11 mg, 0.065 mmol) was added to a solution of *N*-((1*R*, 2*R*)-2-((2-hydroxyethyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide **35** (53 mg, 0.13 mmol) in DCM (2 cm^3) at r.t, followed by addition of EDC (150 mg, 0.80 mmol) and DMAP (16 mg, 0.13 mmol). The resulting mixture was stirred overnight and then water (2 cm^3) was added. The organic phase was separated from the aqueous, and then DCM (2 x 2 cm^3) was further added to extract the remaining product from the aqueous layer. The organic layers were then combined, dried ($MgSO_4$), filtered and concentrated under reduced pressure giving the crude product, which was then purified by flash chromatography (10→30 % v/v ethyl acetate/hexane) giving **(40)** as white crystals (14.5 mg, 0.0304 mmol, 24 %); Mp 80-83 °C; $[\alpha]_D^{22}$ -54.4 (*c* 0.25, $CHCl_3$); ν_{max} 3272, 1716, 1599, 1495, 1454, 1408, 1325, 1267, 1155, 1092, 1018, 918, 876, 812, 767, 731, 698 and 667 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.10 (4 H, s, 4 x CO_2Ar-*H*), 7.36 (4 H, d, *J* 8.2, 4 x Ar-*H*), 7.21-7.06 (6 H, m, 6 x Ar-*H*), 7.05-6.91 (14 H, m, 14 x Ar-*H*), 6.91-6.84 (4 H, m, 4 x Ar-*H*), 6.20 (2 H, br s, 2 x N*H*Ts), 4.51-4.28 (2 H, m, 2 x C$H_{(1)}$H$_{(2)}$OC=O), 4.35-4.21 (4 H, m, 2 x CH$_{(1)}H_{(2)}$OC=O + C*H*NHTs), 3.81 (2 H, d, *J* 7.9, 2 x C*H*NH), 2.86-2.76 (2 H, m, 2 x C$H_{(1)}$H$_{(2)}$NH), 2.76-2.66 (2 H, m, 2 x CH$_{(1)}H_{(2)}$NH) and 2.29 (6 H, s, 2 x CH_3Ts); δ_C (101 MHz, $CDCl_3$) 165.61 (2 x *C*), 142.83 (2 x *C*), 138.76 (2 x *C*), 138.26 (2 x *C*), 136.96 (2 x *C*), 133.90 (2 x *C*), 129.77 (4 x *C*H), 129.14 (5 x *C*H), 128.38 (4 x *C*H), 128.01 (4 x *C*H), 127.63 (5 x *C*H), 127.30 (6 x *C*H), 127.09 (4 x *C*H), 67.44 (2 x *C*H), 64.24 (2 x *C*H_2), 63.52 (2 x *C*H), 45.74 (2 x *C*H_2) and 21.42 (2 x *C*H_3); *m/z* (ESI-MS) 951.1 $[M+H]^+$, 973.1 $[M+Na]^+$. Found (ESI-HR-MS): 476.1755 $[M+2H]^{2+}$, $C_{54}H_{56}N_4O_8S_2$ requires 476.1764 (2.6 ppm error).

Synthesis of (2*S*, 4*R*, 5*R*)-2-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,5-diphenyl-1-tosylimidazolidine (43) (VRP 439).



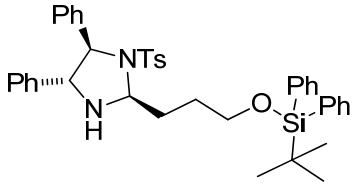
To a suspension of powdered molecular sieves (4 Å, 1.2 g) in dry methanol (70 cm^3) was added 3-((*tert*-butyldiphenylsilyl)oxy)propanal (1.53 g, 4.90 mmol), (1*R*, 2*R*)-TsDPEN (2.0 g, 5.44 mmol) and glacial acetic acid (14 drops). The reaction mixture was stirred at r.t. and monitored by TLC. After 2 hrs, the imine had formed, and sodium cyanoborohydride (0.92 g, 14.70 mmol) was added. The reaction was left to stir overnight at r.t. Molecular sieves were removed by filtration, and the solution was concentrated under reduced pressure. The residue was re-dissolved in DCM (90 cm^3). The organic phase was washed with saturated $NaHCO_3$ (90 cm^3) and brine (90 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure to give **(43)** as a white solid (1.12 g, 1.69 mmol, 35 %); Mp 64-67 °C; $[\alpha]_D^{22}$ -64 (*c* 0.5, $CHCl_3$); ν_{max} 3322, 3030, 2930, 2856, 1600, 1495, 1472, 1450, 1428, 1349, 1305, 1258, 1163, 1091, 1028, 949, 821, 736, 698 and 664 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.72-7.66 (4 H, m, 4 x Ar-*H*), 7.60 (2 H, d, *J* 8.2, 2 x Ar-*H*), 7.46-7.33 (6 H, m, 6 x Ar-*H*), 7.31-7.12 (10 H, m, 10 x Ar-*H*), 6.94 (2 H, d, *J* 6.6, 2 x Ar-*H*), 5.18 (1 H, d, *J* 7.2, NTsC*H*NH), 4.62 (1 H, d, *J* 6.3, C*H*NTs), 4.21 (1 H, br s, C*H*NH), 4.02-3.93 (1 H, m, $CH_{(1)}H_{(2)}OSi$), 3.92-3.84 (1 H, m, $CH_{(1)}H_{(2)}OSi$), 2.54 (1 H, br s, N*H*), 2.49-2.37 (1 H, m, $CHCH_{(1)}H_{(2)}$), 2.40 (3 H, s, CH_3Ts), 2.09-1.98 (1 H, m, $CHCH_{(1)}H_{(2)}$) and 1.06 (9 H, s, 3 x CH_3); δ_C (101 MHz, $CDCl_3$) 143.57 (*C*), 140.41 (*C*), 138.45 (*C*), 135.65 (2 x *C*H), 135.61 (2 x *C*H), 134.52 (*C*), 133.63 (*C*), 133.58 (*C*), 129.71 (*C*H), 129.69 (*C*H), 129.59 (2 x *C*H), 128.59 (2 x *C*H), 128.45 (2 x *C*H), 127.79 (2 x *C*H), 127.72 (4 x *C*H), 127.64 (*C*H), 127.43 (*C*H), 126.84 (2 x *C*H), 126.49 (2 x *C*H), 76.22 (*C*H), 71.05 (*C*H), 69.90 (*C*H), 60.98 (CH_2), 38.63 (CH_2), 26.88 (3 x CH_3), 21.55 (CH_3) and 19.21 ($(CH_3)_3C$); *m/z* (ESI-MS) 661.2 $[M+H]^+$, 683.2 $[M+Na]^+$. Found (ESI-HR-MS): 661.2920 $[M+H]^+$, $C_{40}H_{45}N_2O_3SSi$ requires 661.2915 (0.1 ppm error).

Synthesis of *N*-((1*R*, 2*R*)-2-((3-hydroxypropyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (36) (VRP 447).



(2*S*, 4*R*, 5*R*)-2-(2-((*tert*-Butyldiphenylsilyl)oxy)ethyl)-4,5-diphenyl-1-tosylimidazolidine **43** (143 mg, 0.22 mmol) in THF (0.32 cm^3) was added dropwise to a solution of $LiAlH_4$ (25 mg, 0.65 mmol) in THF (1.4 cm^3) with stirring at 0 °C. After addition, the solution was allowed to stir at r.t. over the weekend. The solution was then cooled to 0 °C and quenched with a 50 : 50 mixture of water and THF (0.32 cm^3: 0.32 cm^3), followed by water (0.32 cm^3). Rochelle salt (216 g, 0.77 mmol) was then added followed by DCM (0.40 cm^3) and was further allowed to stir for 3 hrs. The remaining solution was then filtered off through celite, dried ($MgSO_4$), filtered and concentrated to give the crude product, which was then purified by flash chromatography (10→30 % v/v ethyl acetate/pet ether) to give **(36)** as a white solid (22 mg, 0.52 mmol, 24 %); Mp 110-113 °C; $[\alpha]_D^{27}$ -12.8 (*c* 0.25, $CHCl_3$); ν_{max} 3274, 3029, 2922, 1599, 1495, 1454, 1321, 1184, 1153, 1091, 1052, 922, 845, 812, 758, 698 and 667 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.40 (2 H, d, *J* 8.3, 2 x Ar-*H*), 7.16-7.11 (3 H, m, 3 x Ar-*H*), 7.05-6.92 (7 H, m, 7 x Ar-*H*), 6.84 (2 H, dd, *J* 8.0, 1.2, 2 x Ar-*H*), 4.35 (1 H, d, *J* 8.0, C*H*NHTs), 3.74 (1 H, d, *J* 8.0, C*H*NH), 3.73-3.64 (2 H, m, CH_2OH), 2.58-2.52 (2 H, m, CH_2NH), 2.31 (3 H, s, CH_3Ts) and 1.76-1.56 (2 H, m, CH_2CH_2OH); δ_C (101 MHz, $CDCl_3$) 142.80 (*C*), 138.56 (*C*), 137.91 (*C*), 137.11 (*C*), 129.14 (2 x *C*H), 128.37 (2 x *C*H), 127.94 (2 x *C*H), 127.75 (2 x *C*H), 127.65 (*C*H), 127.49 (2 x *C*H), 127.30 (*C*H), 127.09 (2 x *C*H), 67.94 (*C*H), 63.05 (*C*H), 62.34 (CH_2), 45.70 (CH_2), 31.72 (CH_2) and 21.42 (CH_3); *m/z* (ESI-MS) 425.1 $[M+H]^+$. Found (ESI-HR-MS): 425.1895 $[M+H]^+$, $C_{24}H_{29}N_2O_3S$ requires 425.1893 (-0.3 ppm error).

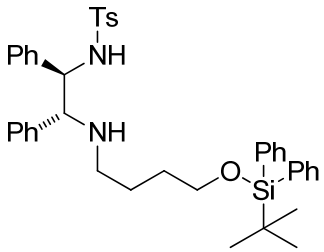
(2*S*, 4*R*, 5*R*)-2-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-4,5-diphenyl-1-tosylimidazolidine (44) (VRP 422).



To a stirred solution of (*R*, *R*)-TsDPEN (117 mg, 0.32 mmol) and molecular sieves (4 Å, 221 g) in dry methanol (2.5 cm^3) was added a solution of 4-((*tert*-butyldiphenylsilyl)oxy)butanal (125 mg, 0.38 mmol) in methanol (1.0 cm^3) followed by the addition of glacial acetic acid (0.022 cm^3). The reaction was stirred for 4 hrs during which time a white precipitate formed. The precipitate (molecular sieves and the product) was filtered off and washed with cold methanol. The remaining solid was

washed thoroughly with DCM to separate the product from molecular sieves, and was then concentrated *in vacuo*. Aminal (**44)** was obtained as a white solid (78 mg, 0.115 mmol, 30 %); Mp 45-47 °C; $[\alpha]_D^{25}$ -45.6 (*c* 0.5, $CHCl_3$); ν_{max} 3069, 2930, 2857, 1600, 1495, 1472, 1449, 1428, 1349, 1304, 1163, 1091, 1029, 867, 821, 758, 741, 698 and 664 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.71-7.65 (4 H, m, 4 x Ar-*H*), 7.60 (2 H, d, *J* 8.2, 2 x Ar-*H*), 7.46-7.32 (6 H, m, 6 x Ar-*H*), 7.27-7.14 (10 H, m, 10 x Ar-*H*), 6.88 (2 H, d, *J* 6.7, 2 x Ar-*H*), 5.01 (1 H, dd, *J* 8.5, 5.2, NTsC*H*NH), 4.59 (1 H, d, *J* 6.8, C*H*NTs), 4.22 (1 H, d, *J* 6.8, C*H*NH), 3.77 (2 H, t, *J* 6.1, CH_2OSi), 2.40 (3 H, s, CH_3Ts), 2.31-2.13 (2 H, m, $CH_{(1)}H_{(2)}CH_2OSi$ + N*H*), 2.02-1.88 (1 H, m, $CH_{(1)}H_{(2)}CH_2OSi$), 1.87-1.76 (2 H, m, $CHCH_2$) and 1.06 (9 H, s, 3 x CH_3); δ_C (101 MHz, $CDCl_3$) 143.62 (*C*), 140.10 (*C*), 138.15 (*C*), 135.63 (3 x *C*H), 135.03 (*C*), 133.99 (*C*), 133.93 (*C*), 129.64 (2 x *C*H), 129.59 (*C*H), 128.71 (2 x *C*H), 128.43 (2 x *C*H), 127.88 (*C*H), 127.76 (2 x *C*H), 127.68 (3 x *C*H), 127.67 (3 x *C*H), 127.40 (*C*H), 126.90 (2 x *C*H), 126.45 (2 x *C*H), 78.75 (*C*H), 70.81 (*C*H), 70.48 (*C*H), 63.48 (CH_2), 33.20 (CH_2), 29.22 (CH_2), 26.92 (3 x CH_3), 21.55 (CH_3) and 19.27 ($(CH_3)_3C$); *m/z* (ESI-MS) 675.2 $[M+H]^+$, 697.2 $[M+Na]^+$. Found (ESI-HR-MS): 675.3082 $[M+H]^+$, $C_{41}H_{47}N_2O_3SSi$ requires 675.3071 (-1.5 ppm error).

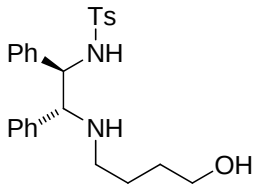
Synthesis of *N*-((1*R*, 2*R*)-2-((4-((*tert*-butyldiphenylsilyl)oxy)butyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (38) (VRP 440).



To a suspension of powdered molecular sieves (4 Å, 0.8 g) in dry methanol (48 cm^3) was added 4-((*tert*-butyldiphenylsilyl)oxy)butanal **(44)** (1.1 g, 3.35 mmol), (1*R*, 2*R*)-TsDPEN (1.36 g, 3.72 mmol) and glacial acetic acid (10 drops). The reaction mixture was stirred at r.t. and monitored by TLC. After 2 hrs, the imine had formed, and sodium cyanoborohydride (0.63 g, 10.05 mmol) was added. The reaction was left to stir overnight at r.t. Molecular sieves were removed by filtration, and the solution was concentrated under reduced pressure. The residue was re-dissolved in DCM (64 cm^3). The organic phase was washed with saturated $NaHCO_3$ (64 cm^3) and brine (64 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure to give the crude

product, which after purification by flash chromatography (10→30 % v/v ethyl acetate/pet ether) gave **(38)** as a colourless gum (0.9 g, 1.33 mmol, 40 %); $[\alpha]_D^{23}$ -8.8 (*c* 0.5, $CHCl_3$); ν_{max} 3262, 3030, 2930, 2857, 1737, 1600, 1495, 1472, 1455, 1428, 1390, 1328, 1185, 1154, 1108, 1091, 1027, 998, 927, 812, 771, 740, 698 and 667 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.63 (4 H, d, *J* 7.5, 4 x Ar-*H*), 7.47-7.33 (8 H, m, 8 x Ar-*H*), 7.18-6.98 (8 H, m, 8 x Ar-*H*), 6.94 (2 H, d, *J* 7.5, 2 x Ar-*H*), 6.91-6.85 (2 H, m, 2 x Ar-*H*), 6.30 (1 H, br s, N*H*Ts), 4.23 (1 H, d, *J* 7.9, C*H*NHTs), 3.64-3.54 (3 H, m, C*H*NH + CH_2OSi), 2.42-2.34 (1 H, m, C$H_{(1)}$H$_{(2)}$NH), 2.32 (3 H, s, CH_3Ts), 2.30-2.22 (1 H, m, CH$_{(1)}H_{(2)}$NH), 1.54-1.38 (4 H, m, CH_2CH_2CH$_2$OSi) and 1.03 (9 H, s, 3 x CH_3); δ_C (101 MHz, $CDCl_3$) 142.67 (*C*), 139.35 (*C*), 138.40 (*C*), 137.10 (*C*), 135.57 (4 x *C*H), 133.99 (2 x *C*), 129.58 (2 x *C*H), 129.08 (2 x *C*H), 128.32 (2 x *C*H), 127.91 (2 x *C*H), 127.64 (4 x *C*H), 127.59 (2 x *C*H), 127.45 (*C*H), 127.38 (2 x *C*H), 127.26 (*C*H), 127.15 (2 x *C*H), 67.79 (*C*H), 63.61 (*C*H_2), 63.06 (*C*H), 47.00 (*C*H_2), 30.11 (*C*H_2), 26.90 (3 x *C*H_3), 26.45 (*C*H_2), 21.45 (*C*H_3) and 19.23 ((CH$_3$)$_3$*C*); *m/z* (ESI-MS) 677.2 $[M+H]^+$, 699.2 $[M+Na]^+$. Found (ESI-HR-MS): 677.3231 $[M+H]^+$, $C_{41}H_{49}N_2O_3SSi$ requires 677.3228 (-0.3 ppm error).

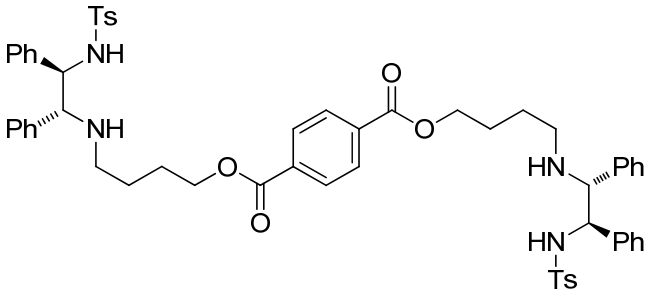
Synthesis of *N*-((1*R*, 2*R*)-2-((4-hydroxybutyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (37) (VRP 442).



To a solution of *N*-((1*R*, 2*R*)-2-((4-((*tert*-butyldiphenylsilyl)oxy)butyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide **38** (730 mg, 1.08 mmol) in dry THF (7 cm^3) was added TBAF (1 M solution in THF, 1.62 cm^3, 1.62 mmol) at 0 °C. The resulting mixture was stirred at r.t for 24 hrs. The reaction mixture was then concentrated under reduced pressure to give a residue. The residue was purified by flash chromatography (10→100 % v/v ethyl acetate/pet ether) to give **(37)** as a white solid (360 mg, 0.82 mmol, 76 %); Mp 135-138 °C; $[\alpha]_D^{22}$ -12.8 (*c* 0.25, $CHCl_3$); ν_{max} 3278, 3091, 2836, 1598, 1495, 1450, 1429, 1350, 1333, 1259, 1215, 1189, 1181, 1156, 1090, 1060, 1046, 1030, 1011, 996, 962, 922, 903, 843, 832, 820, 773, 757, 727, 698 and 668 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.39 (2 H, d, *J* 8.2, 2 x Ar-*H*), 7.15-7.10 (3 H, m, Ar-*H*), 7.08-6.97 (5 H, m, 5 x Ar-*H*), 6.96-6.91 (2 H, m, 2 x Ar-*H*), 6.88 (2

H, d, *J* 6.9, 2 x Ar-*H*), 4.30 (1 H, d, *J* 8.0, C*H*NHTs), 3.67 (1 H, d, *J* 8.0, C*H*NH), 3.64-3.55 (2 H, m, CH_2OSi), 2.50-2.34 (2 H, m, CH_2NH), 2.32 (3 H, s, CH_3Ts) and 1.60-1.40 (4 H, m, CH_2CH_2CH$_2$OSi); δ_C (101 MHz, $CDCl_3$) 142.80 (*C*), 138.98 (*C*), 138.13 (*C*), 137.04 (*C*), 129.13 (2 x *C*H), 128.31 (2 x *C*H), 127.93 (2 x *C*H), 127.59 (2 x *C*H), 127.52 (3 x *C*H), 127.29 (*C*H), 127.14 (2 x *C*H), 67.82 (*C*H), 63.04 (*C*H), 62.62 (*C*H_2), 47.01 (*C*H_2), 30.72 (*C*H_2), 26.79 (*C*H_2) and 21.44 (*C*H_3); *m/z* (ESI-MS) 439.1 $[M+H]^+$, 461.1 $[M+Na]^+$. Found (ESI-HR-MS): 439.2050 $[M+H]^+$, $C_{25}H_{31}N_2O_3S$ requires 439.2050 (-0.5 ppm error).

Synthesis of bis(4-(((1*R*, 2*R*)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)amino)butyl) terephthalate (43) (VRP 445).



Novelty? Terephthalic acid (11 mg, 0.065 mmol) was added to a solution of *N*-((1*R*, 2*R*)-2-((4-hydroxybutyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (**37)** (57 mg, 0.13 mmol) in DCM (2 cm^3) at r.t, followed by addition of EDC (153 mg, 0.80 mmol) and DMAP (16 mg, 0.13 mmol). The resulting mixture was stirred overnight and then water (2 cm^3) was added. The organic phase was separated from the aqueous, and then DCM (2 x 2 cm^3) was further added to extract the remaining product from the aqueous. The organic layers were then combined, dried ($MgSO_4$), filtered and concentrated under reduced pressure giving the crude product, which was then purified by flash chromatography (10→30 % v/v ethyl acetate/pet ether) giving **(42)** as white crystals (20 mg, 0.040 mmol, 31 %); Mp 199-202 °C; $[\alpha]_D^{27}$ -12.8 (*c* 0.25, $CHCl_3$); ν_{max} 3267, 2931, 1716, 1600, 1495, 1454, 1408, 1325, 1269, 1184, 1154, 1117, 1093, 1018, 928, 875, 843, 812, 762, 731, 698 and 666 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.04 (4 H, s, 4 x CO_2Ar-*H*), 7.37 (4 H, d, *J* 8.0, 2 x Ar-*H*), 7.16-7.08 (6 H, m, 6 x Ar-*H*), 7.07-6.97 (10 H, m, 10 x Ar-*H*), 6.96-6.88 (8 H, m, 8 x Ar-*H*), 4.34-4.24 (6 H, m, 2 x C*H*NHTs + 2 x CH_2OC=O), 3.65 (2 H, d, *J* 8.0, 2 x C*H*NH), 2.52-2.42 (2 H, m, 2 x C$H_{(1)}$H$_{(2)}$NH), 2.41-2.33 (2 H, m, 2 x CH$_{(1)}H_{(2)}$NH), 2.31 (6 H, s, 2 x CH_3Ts), 1.80-1.65 (4 H, m, 2 x CH$_2$CH_2CH$_2$OC=O) and 1.63-1.45 (4 H, m, 2 x

$CH_2CH_2CH_2OC{=}O$); δ_C (101 MHz, $CDCl_3$) 165.82 (2 x *C*=O), 142.74 (2 x *C*), 139.16 (2 x *C*), 138.24 (2 x *C*), 137.06 (2 x *C*), 134.10 (2 x *C*), 129.57 (4 x *C*H), 129.10 (4 x *C*H), 128.36 (4 x *C*H). 127.93 (4 x *C*H), 127.55 (6 x *C*H), 127.42 (4 x *C*H), 127.29 (2 x *C*H), 127.12 (4 x *C*H), 67.87 (2 x *C*H), 65.17 (2 x CH_2), 63.11 (2 x *C*H), 46.76 (2 x CH_2), 26.58 (2 x CH_2), 26.37 (2 x CH_2) and 21.43 (2 x CH_3); *m/z* (ESI-MS) 1007.2 $[M+H]^+$, 1029.1 $[M+Na]^+$. Found (ESI-HR-MS): 504.2095 $[M+2H]^{2+}$, $C_{58}H_{64}N_4O_8S_2$ requires 504.2077 (-2.1 ppm error).

3. References.

1) (a) S. Gosiewska, R. Soni, G. J. Clarkson and M. Wills, *Tetrahedron Lett.* 2010, **51**, 4214-4217. (b) V. Druais, M. J. Hall, C. Corsi, S. V. Wendeborn, C. Meyer and J. Cossy, *Org. Lett*. 2009, **11**, 935-938. (c) J. Luo, H. Li, J. Wu, X. Xing and W.-M. Dai, *Tetrahedron* 2009, **65**, 6828-6833.

2) A. Banerjee, K. Lee and D. E. Falvey, *Tetrahedron* 1999, **55**, 12699-12710.

3) A. M. Kawamoto and M. Wills, M. *J. Chem. Soc., Perkin Trans. 1*, **2001**, 1916-1928.

4) R. Soni, F. K. Cheung, G. C. Clarkson, J. E. D. Martins, M. A. Graham and M. Wills, *Org. Biomol. Chem*. 2011, **9**, 3290-3294.

5) A. Hoppmann and P. Weyerstahl, *Chem. Ber.* 1974, **107**, 1102-1107.

6) (a) R. K. Dolor and P. Vogel, *J. Mol. Catal.* 1990, **60**, 59-63. F. Sugawara, T. Sugiyama, A. Kobayashi and K. Yamashita, *Agricult. Biol. Chem.* 1978, **42**, 847-850.

7) F. K. Cheung, C. Lin, F. Minissi, A. L. Crivillé, M. A, Graham, D. J. Fox and M. Wills, *Org. Lett*. 2007, **9**, 4659-4662.

8) G. Li and G. W. Kabalka, *J. Organomet. Chem.* 1999, **581,** 66-69.

9) R. P. Singh, B. Twamley, L. Fabry-Asztalos, D. S. Matteson and J. M. Shreeve, *J. Org. Chem*. 2000, **65**, 8123-8125.

10) K. Murata and T. Ikariya, *J. Org. Chem.* 1999, **64**, 2186-2187.

11) M. Bandini, A. Bottoni, P. G. Cozzi, G. P. Miscione, M. Monari, R. Pierciaccante and A. Umani-Ronchi, *Eur. J. Org. Chem.* 2006, 4596-4608.

12) K. Nakamura and T. Matsuda, T. *J. Org. Chem.* 1998, **63**, 8957-8964.

13) K. Huang, M. Ortiz-Marciales, W. Correa, E. Pomales and X. Y. López, *J. Org. Chem*. 2009, **74**, 4195-4202.

14) J. E. D. Martins, D. J. Morris and M. Wills, *Tetrahedron Lett.* 2009, **50**, 688-692.

15) F. Wang, H. Liu, L. Cun, J. Zhu, J. Deng and Y. Jiang, *J. Org. Chem.* 2005, **70**, 9404-9429.

16) D. Zhu and L. Hua, L. *J. Org. Chem.* 2006, **71**, 9484-9486.

17) D. R. Li, A. He and J. R. Falck, *Org. Lett*. 2010, **12**, 1756-1759.

18) R. Moser, Ž. V. Bošković, C. S. Crowe and B. H. Lipshutz, *J. Am. Chem. Soc*. 2010, **132**, 7852-7853.

19) J. E. D. Martins, M. A. C. Redondo and M. Wills, *Tetrahedron: Asymmetry* 2010, **21**, 2258-2264.

4. Monitoring reactions over time to confirm ee does not deteriorate:

The reductions in Table 1 were monitored over time for conversion and ee in order to determine whether the ee deteriorated (S/C= 0.5 mol%, ketone (1 mmol), FA/TEA (5:2, 0.5 ml), 28^{o}C;

Catalyst **45** **(VRP416)**
After 1 hr > 1.3% conv., -
After 5 hrs 40 mins > 6.4% conv., 92% ee
After 24 hrs 10 mins > 28% conv., 92% ee
After 48 hrs 40 mins > 63% conv., 93% ee
After 72 hrs 40 mins > 88% conv., 93% ee

Catalyst **46** **(VRP478)**
After 16 hrs 40 mins > 87% conv., 94% ee
After 25 hrs 10 mins > 96% conv., 95% ee
After 42 hrs 10 mins > >99% conv., 94% ee

Catalyst **47** **(VRP479)**
After 16 hrs 40 mins > 93% conv., 95% ee
After 25 hrs 10 mins > 98% conv., 95% ee
After 42 hrs 10 mins > >99% conv., 95% ee

Catalyst **48** **(VRP480)**
After 16 hrs 40 mins > 94% conv., 95% ee
After 25 hrs 10 mins > 98% conv., 96% ee
After 42 hrs 10 mins > >99% conv., 95% ee

Ligand **35** **(VRP394)**
After 2 hrs 50 mins > -
After 23 hrs 5 mins > 7.8% conv., 91% ee
After 94 hrs 20 mins > 60% conv., 90.4% ee
After 141 hrs 50 mins > 89% conv., 91% ee
After 311 hrs 50 mins > >99% conv., 92% ee

Ligand **36** **(VRP455)**
After 17 hrs 45 mins > 10% conv., 93% ee
After 41 hrs 45 mins > 20.5% conv., 93% ee
After 116 hrs 45 mins > 30% conv., 92% ee
After 138 hrs 45 mins > 30% conv., 92% ee
After 185 hrs 45 mins > 31% conv., 92% ee

Ligand **37** **(VRP454)**
After 17 hrs 45 mins > 25% conv., 93% ee
After 41 hrs 45 mins > 67.3% conv., 94% ee
After 116 hrs 45 mins > 93% conv., 94% ee
After 138 hrs 45 mins > 93% conv., 94% ee
After 185 hrs 45 mins > 93% conv., 94% ee

Ligand **38** **(VRP456)**

After 17 hrs 45 mins > 24% conv., 94% ee
After 41 hrs 45 mins > 73.4% conv., 95% ee
After 116 hrs 45 mins > >99% conv., 95% ee
After 138 hrs 45 mins > >99% conv., 95% ee

Ligand **39** **(VRP403)**
After 16 hrs > 51% conv., 96% ee
After 41 hrs > 88% conv., 97% ee
After 113 hrs > 98% conv., 95% ee

Ligand **40** **(VRP404)**
After 16 hrs > 46% conv., 96% ee
After 41 hrs > 86% conv., 95% ee
After 113 hrs > 97% conv., 96% ee

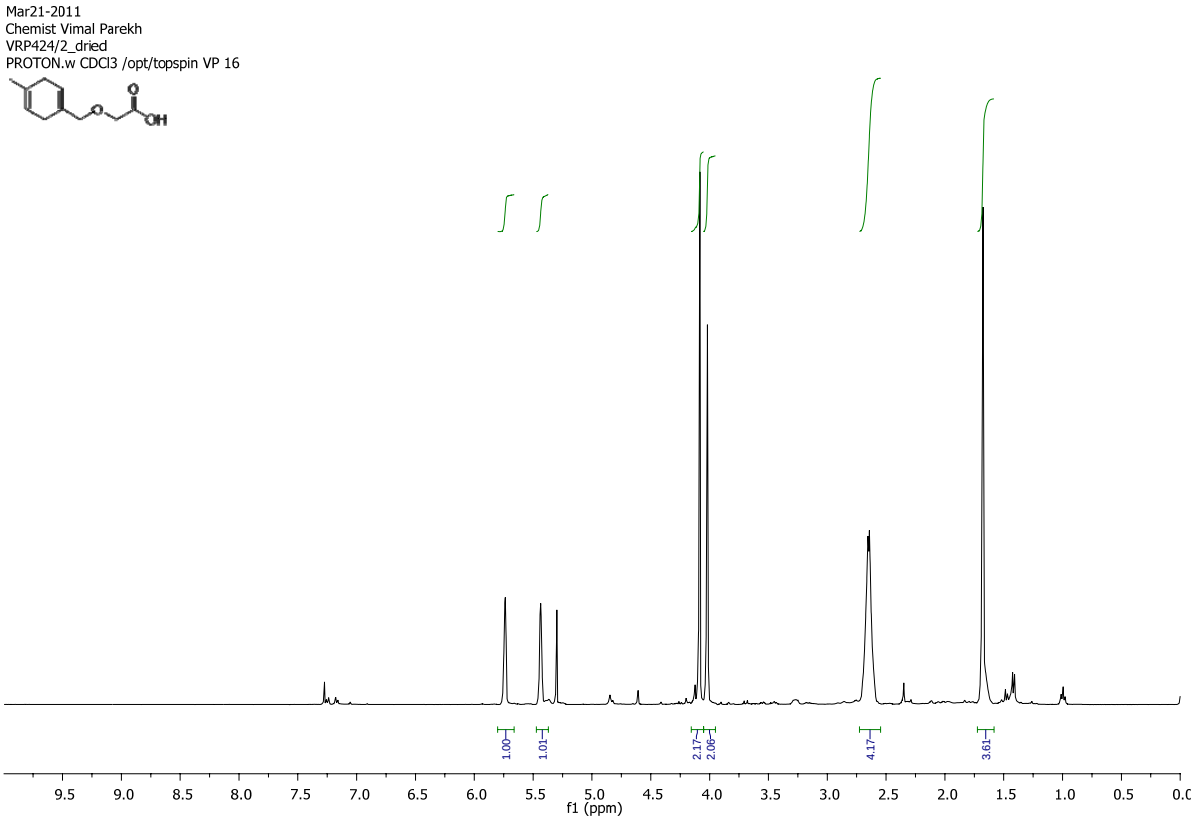
Ligand **41** **(VRP408)**
After 4 hrs > 4% conv., conv. too low to assess ee accurately.
After 23 hrs > 48% conv., 95% ee
After 46 hrs 30 mins > 78% conv., 97% ee
After 119 hrs 30 mins > 92% conv., 96% ee

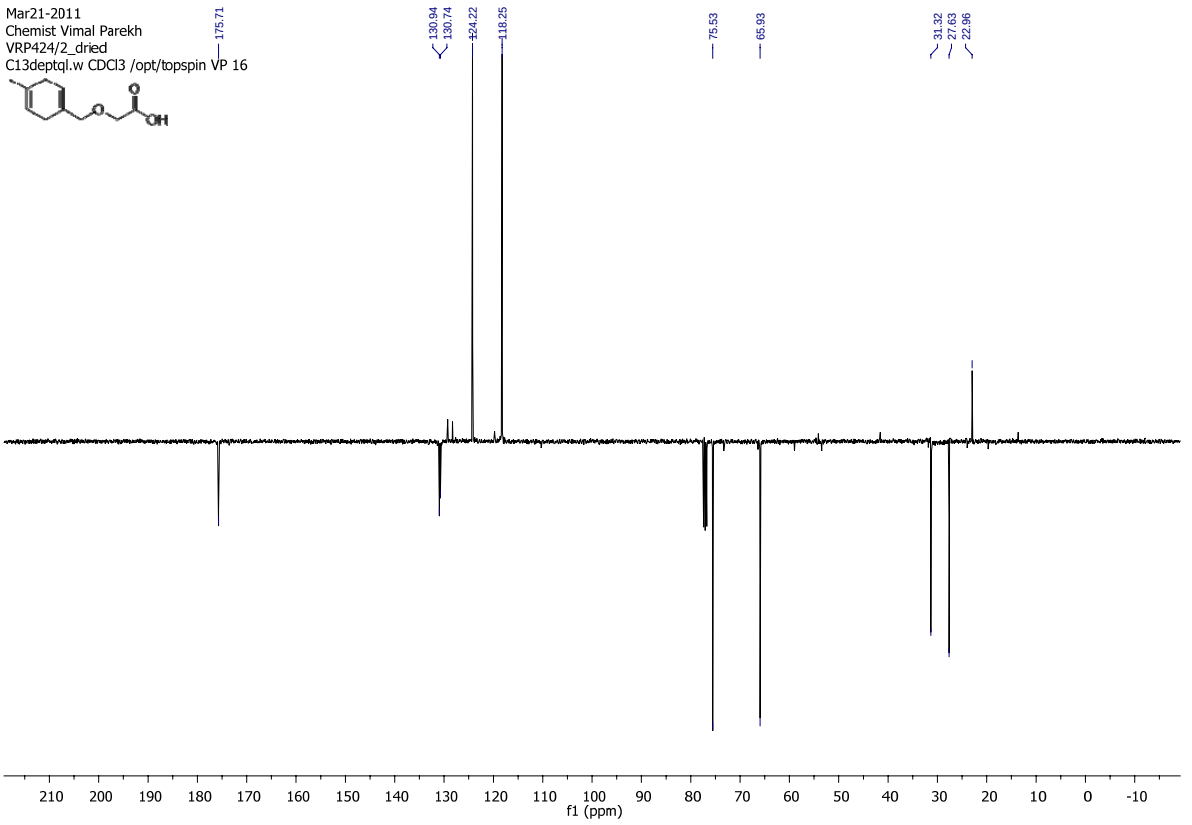
Ligand **42** **(VRP457)**
After 17 hrs 45 mins > 11% conv., 94% ee
After 41 hrs 45 mins > 40.1% conv., 95% ee
After 116 hrs 45 mins > 93% conv., 95% ee
After 138 hrs 45 mins > 96% conv., 95% ee
After 185 hrs 45 mins > >99% conv., 95% ee

In all cases the measured ee did not vary by more than 1% from the final measured value.

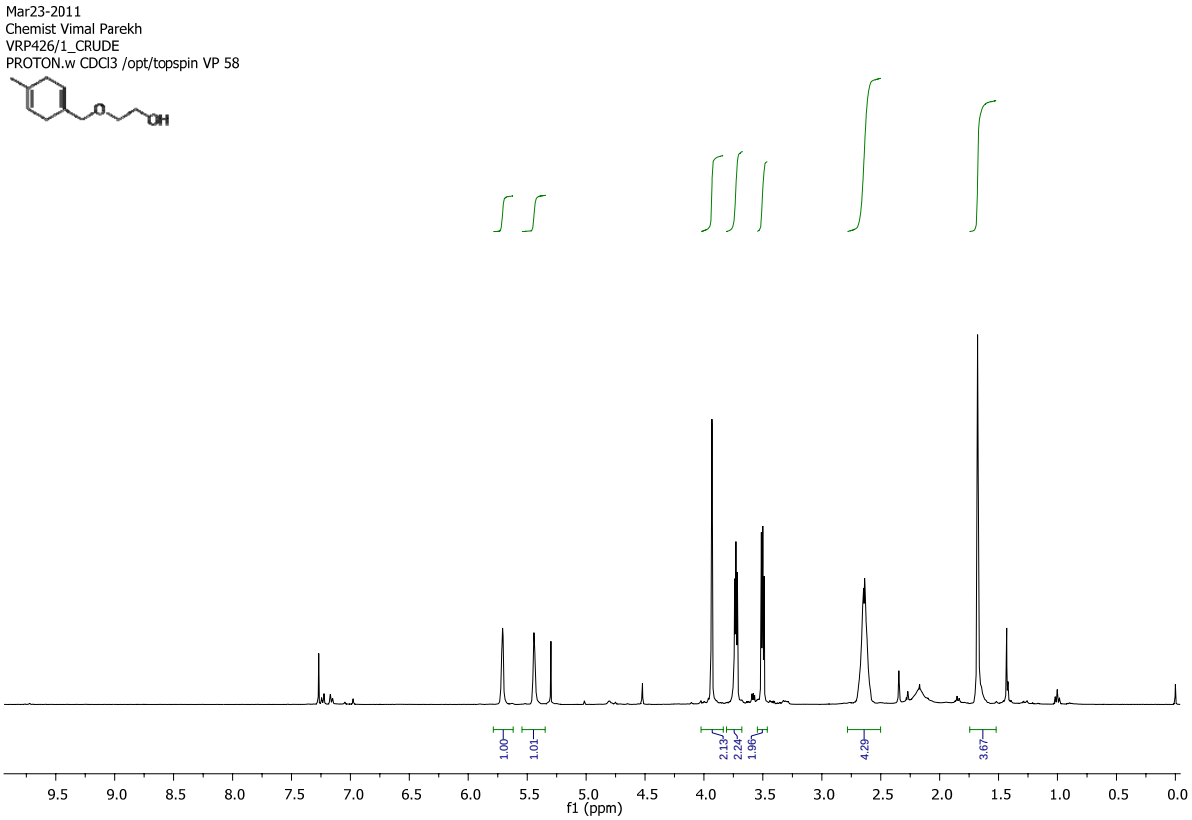
5. 1H and 13C NMR spectra of novel catalysts and precursors.

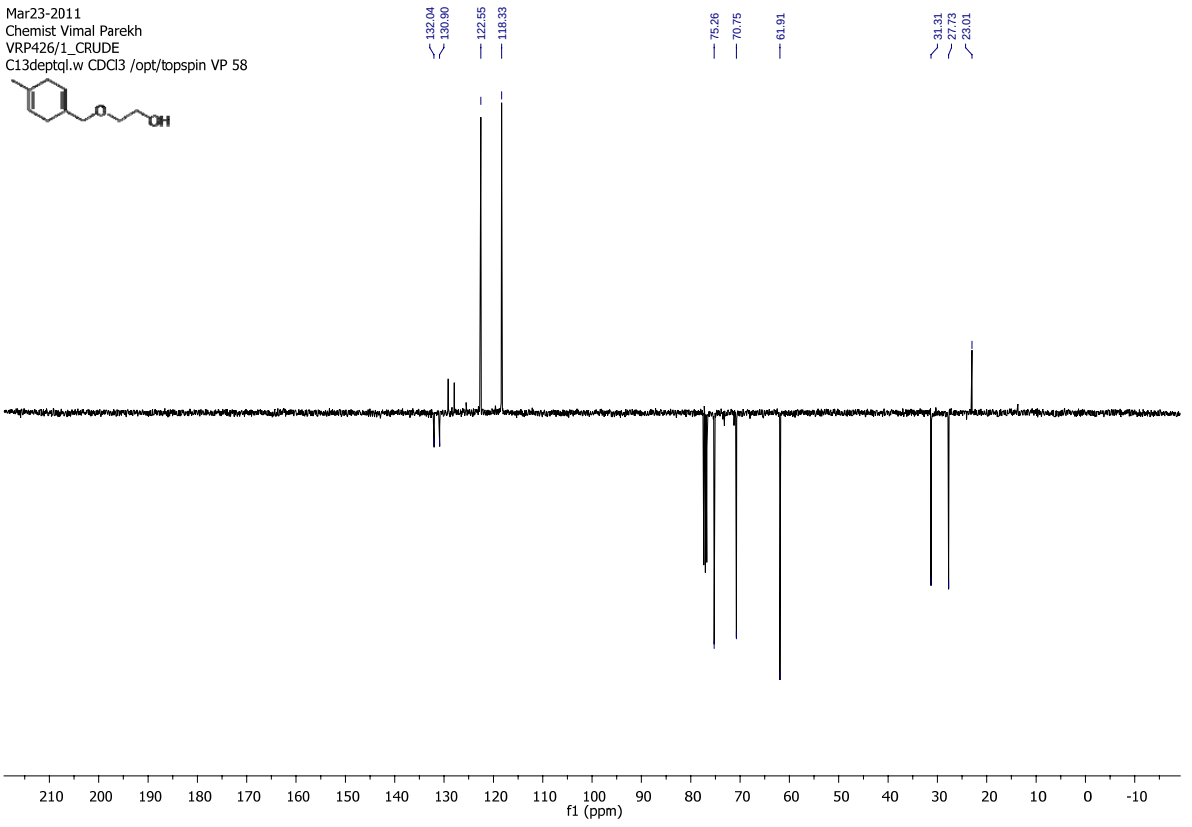
…



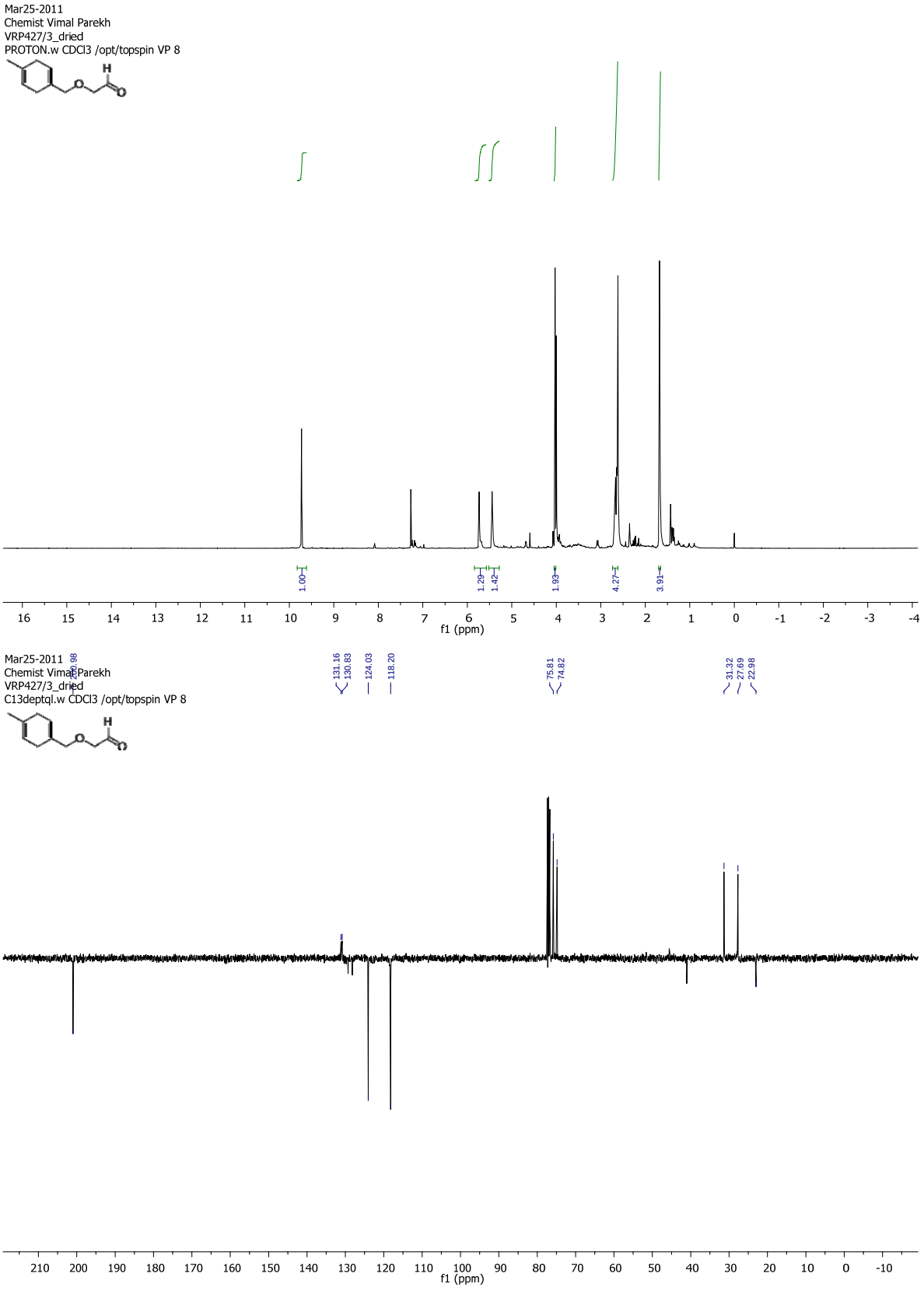


2-((4-methylcyclohexa-1,4-dien-1-yl)methoxy)acetic acid

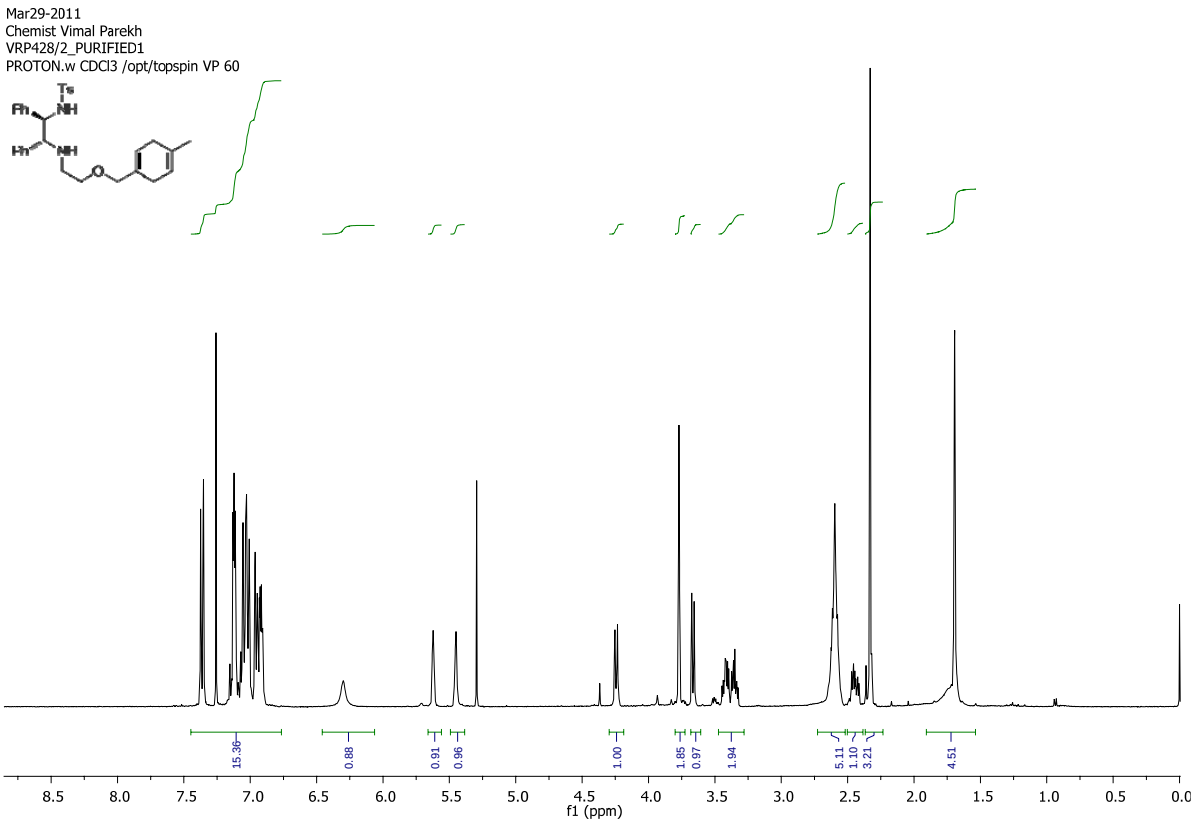


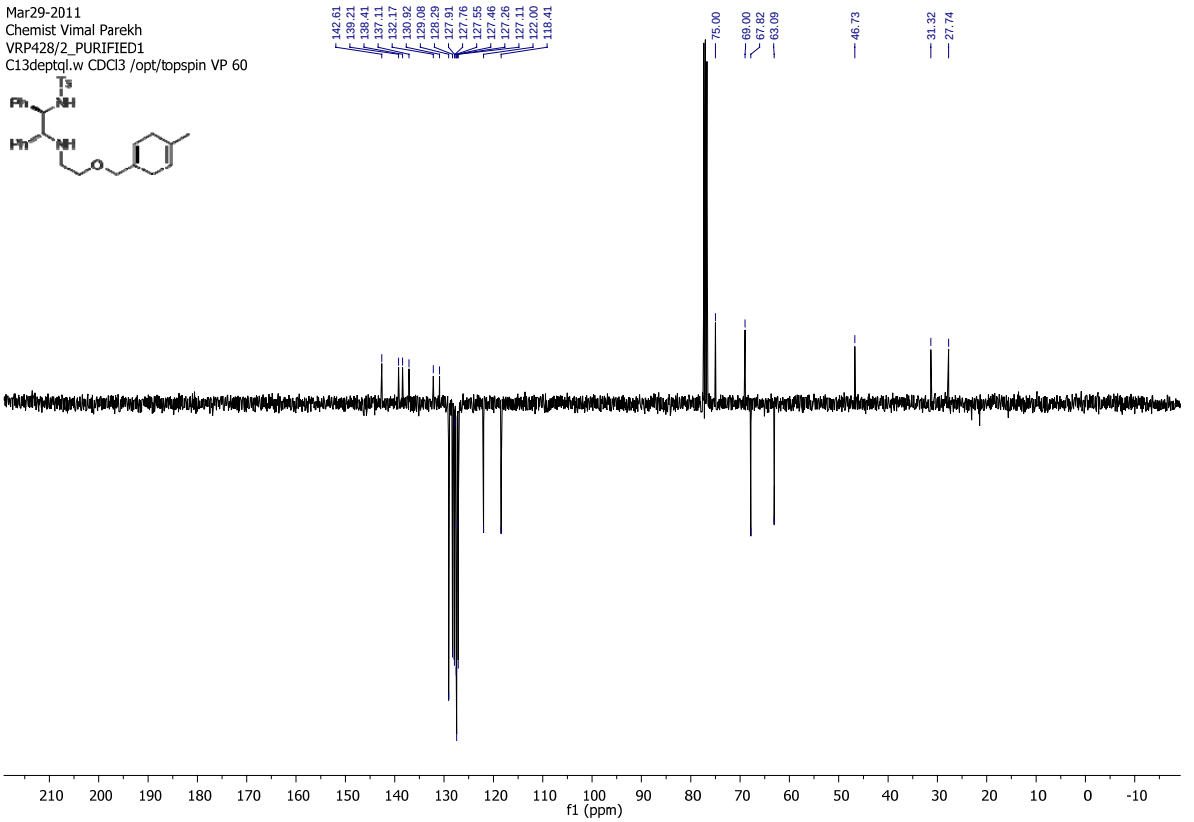


2-((4-methylcyclohexa-1,4-dien-1-yl)methoxy)ethanol (9)

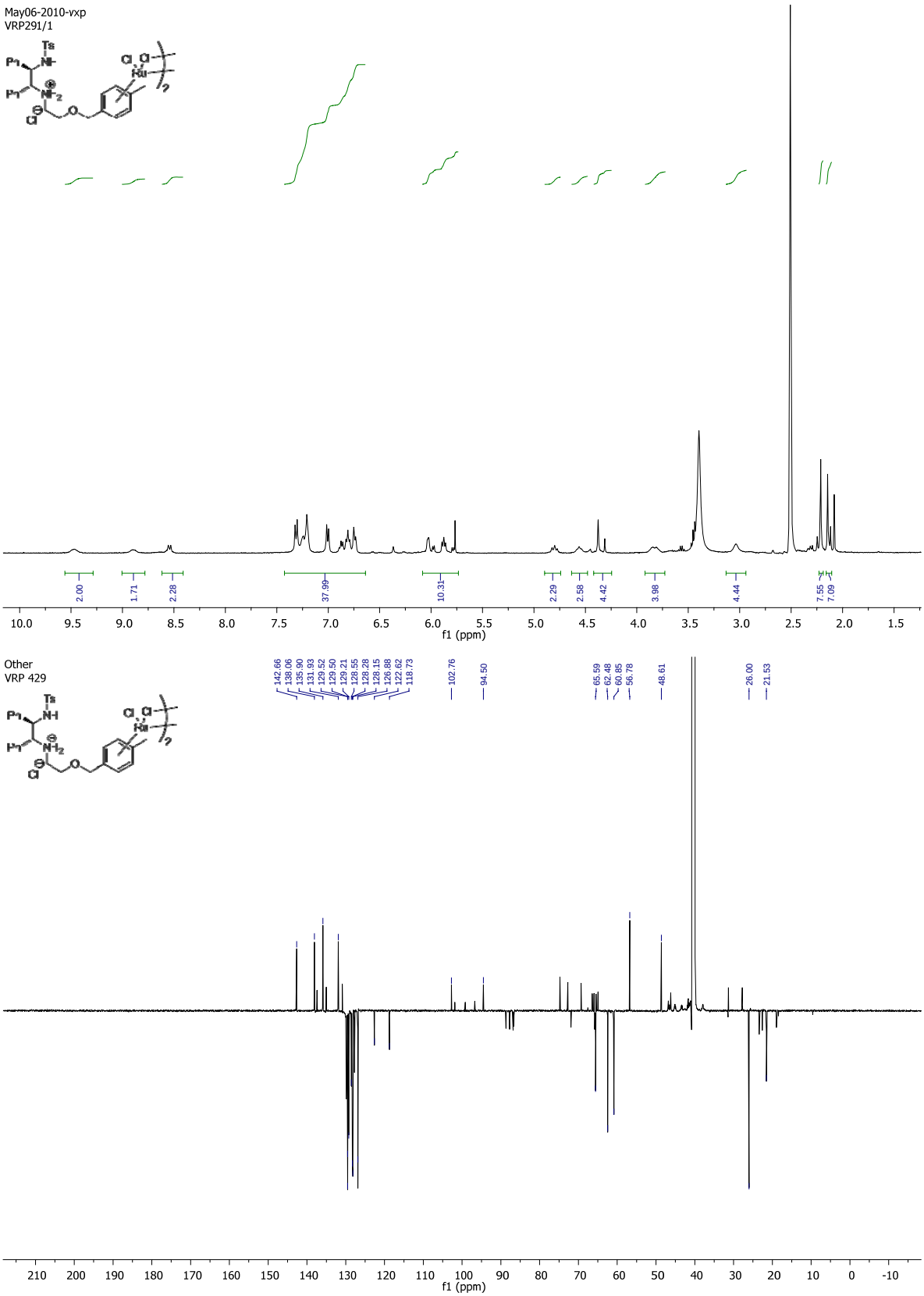


2-((4-methylcyclohexa-1,4-dien-1-yl)methoxy)acetaldehyde

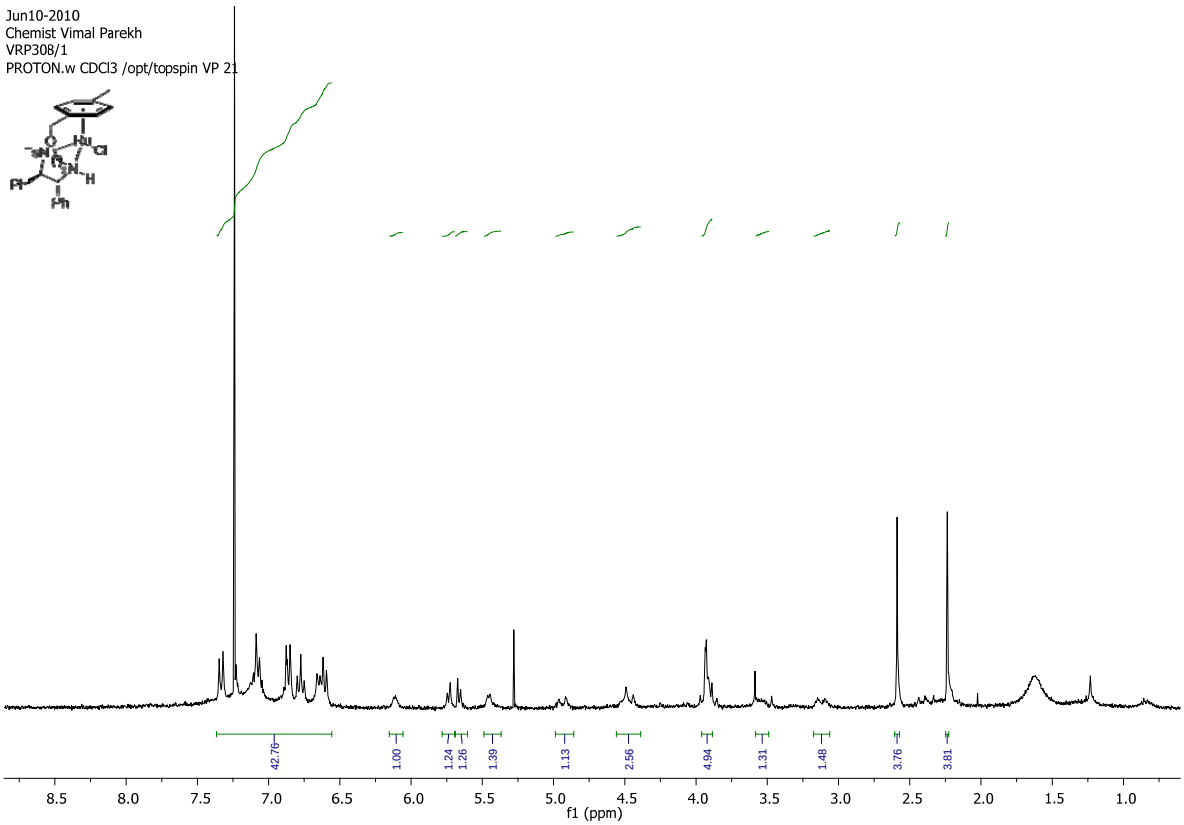




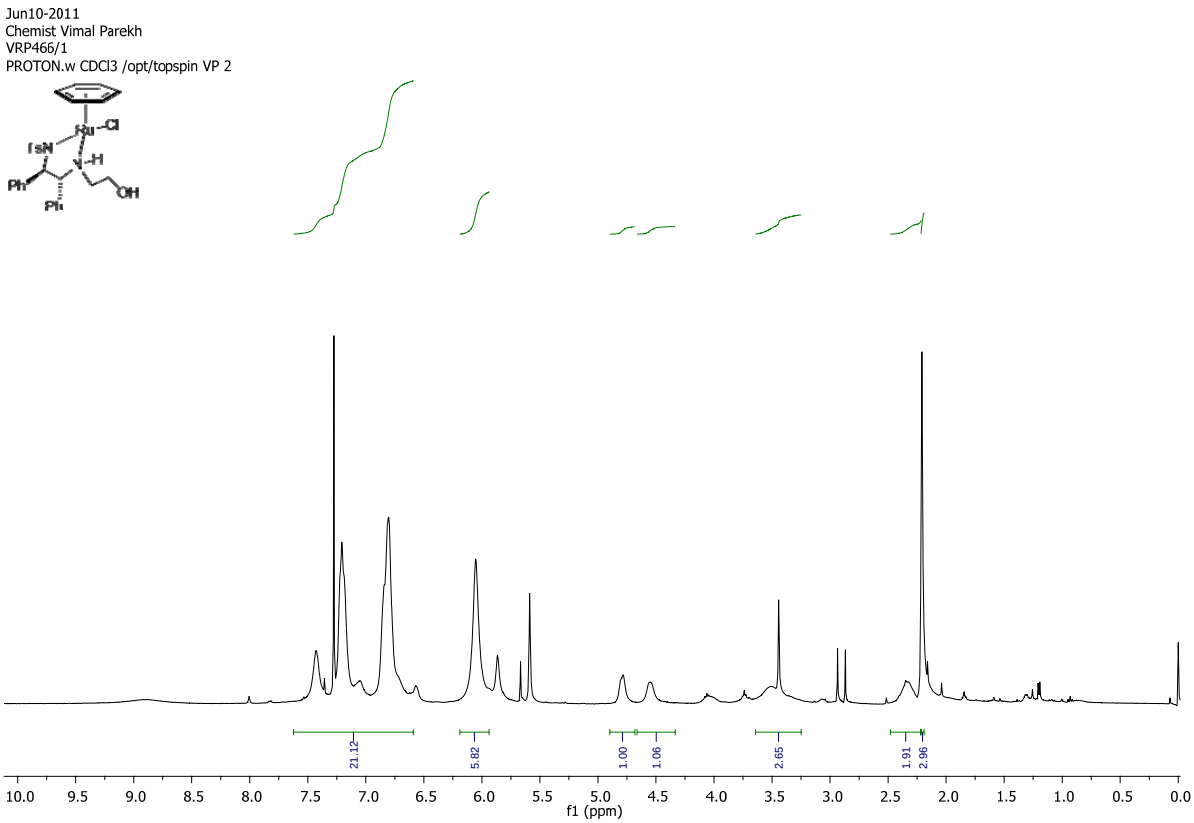
4-methyl-*N*-((1*R*, 2*R*)-2-((2-((4-methylcyclohexa-1, 4-dien-1-yl)methoxy)ethyl)amino)-1, 2-diphenylethyl)benzenesulfonamide (10)

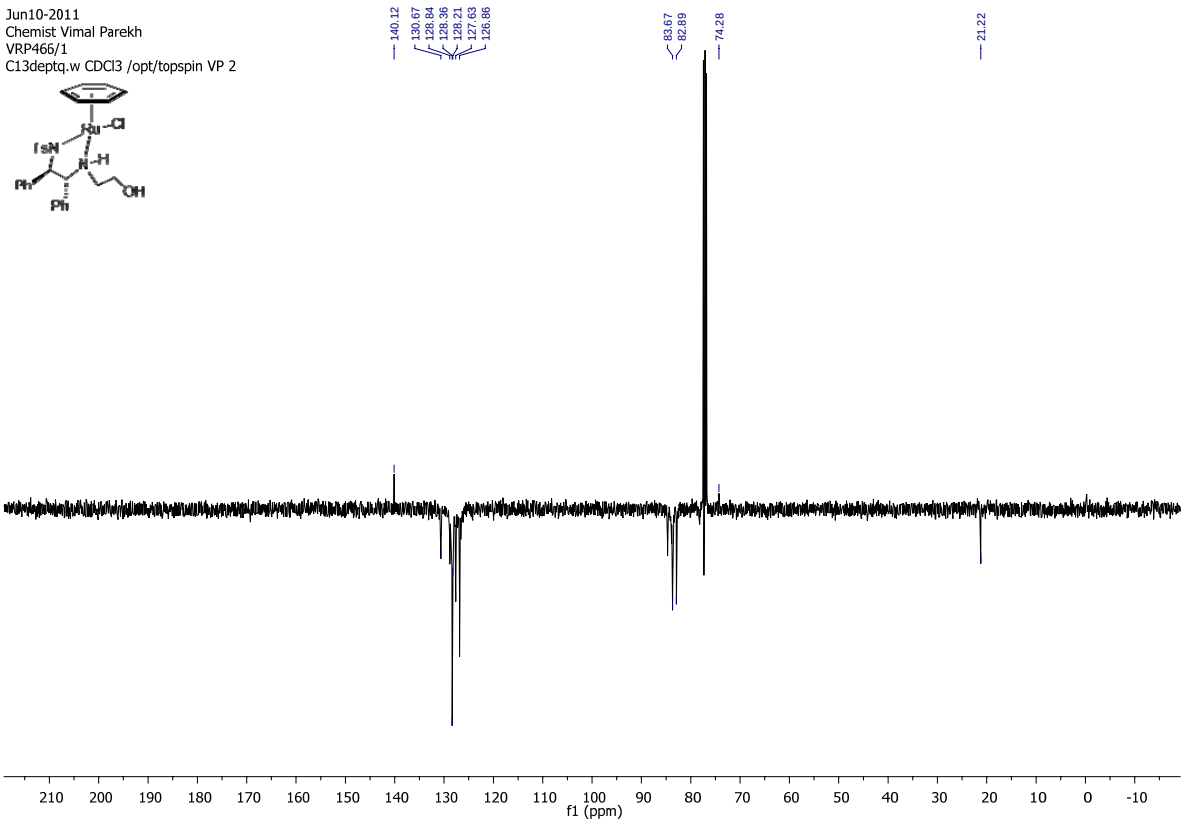


Synthesis of ether linked “tethered” dimer (11)

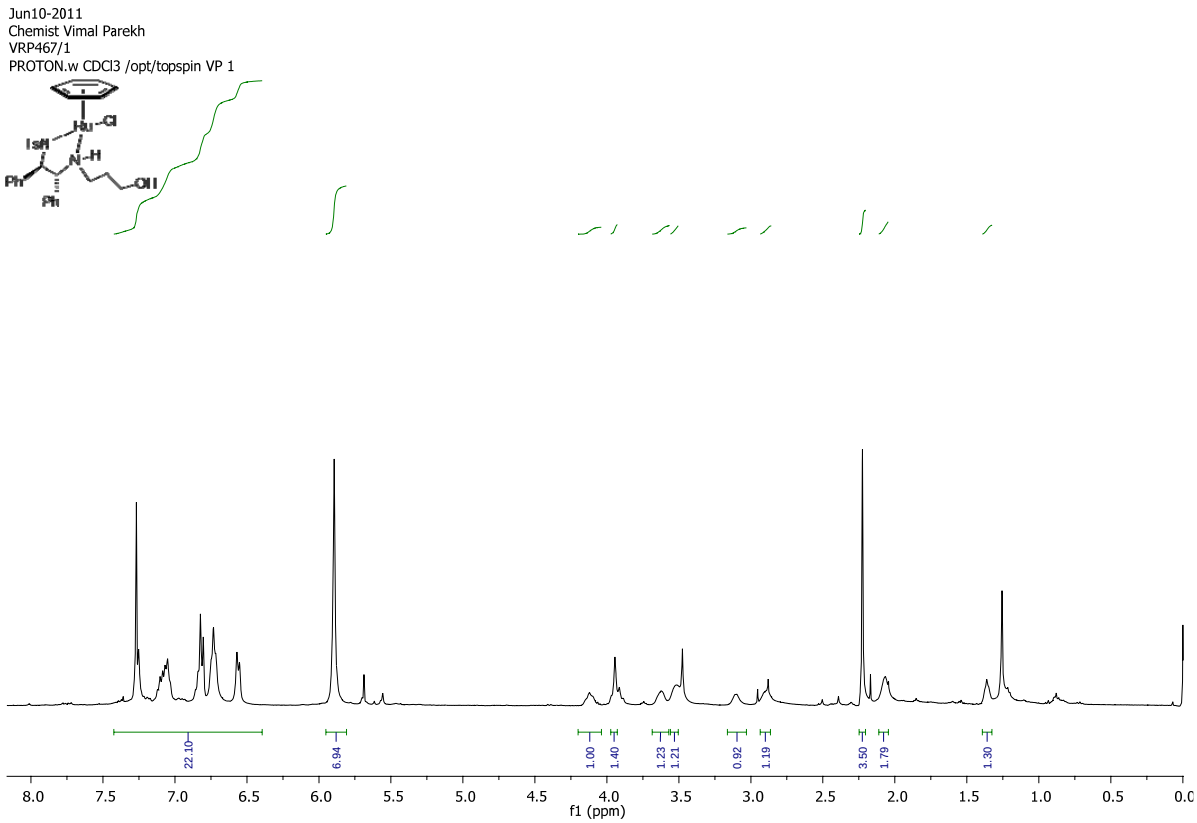


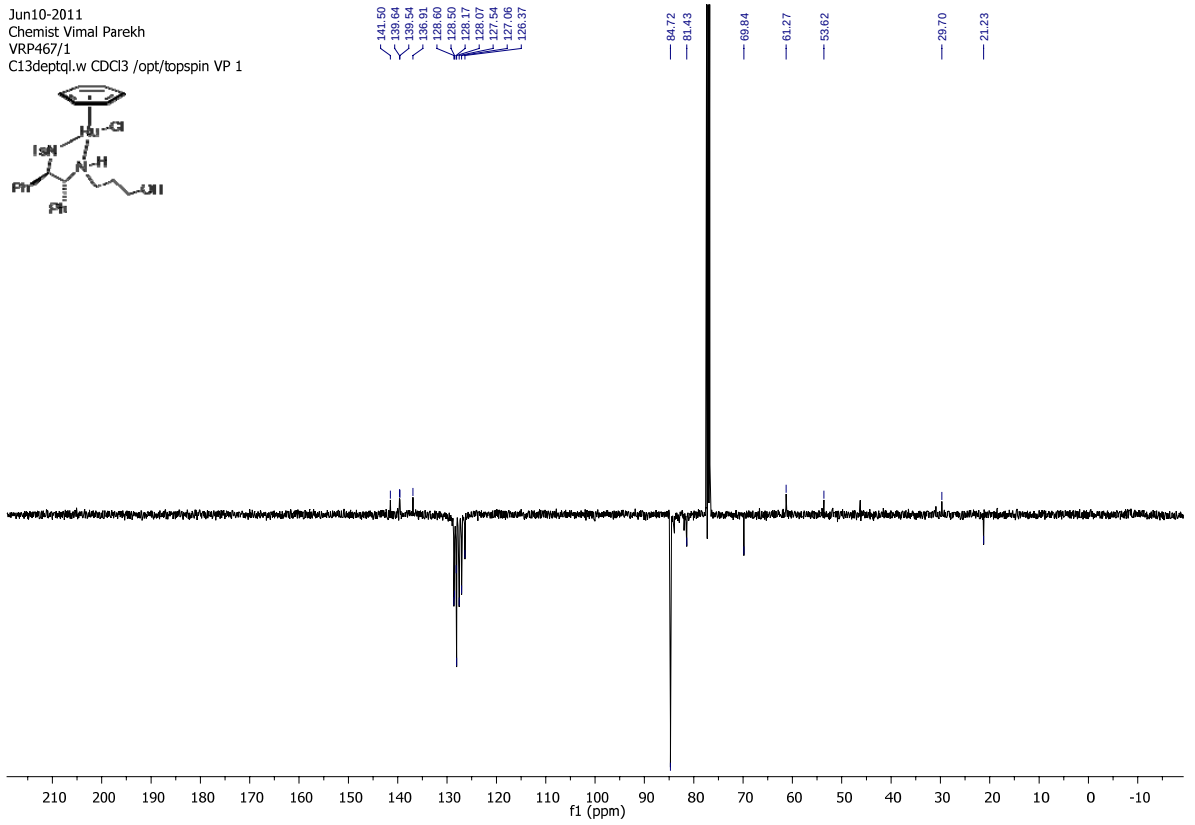
Synthesis of ether linked “tethered” monomer (5)



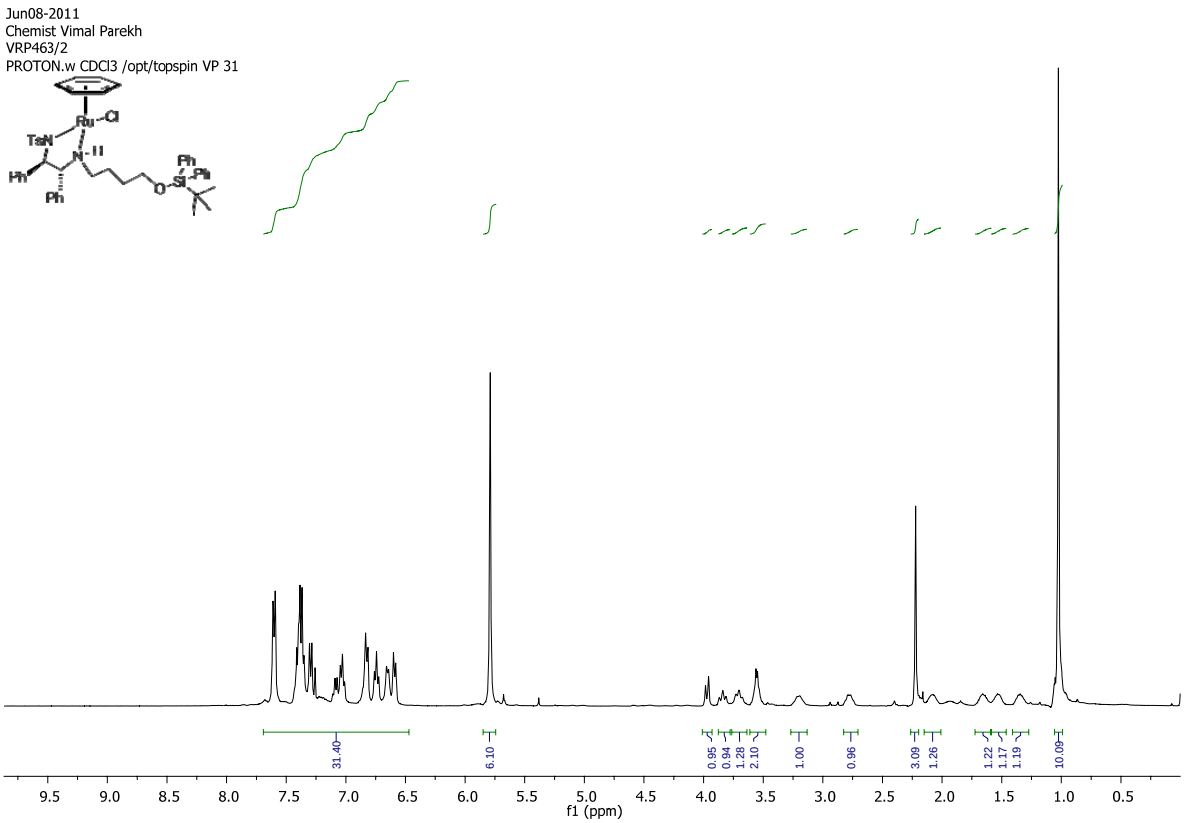


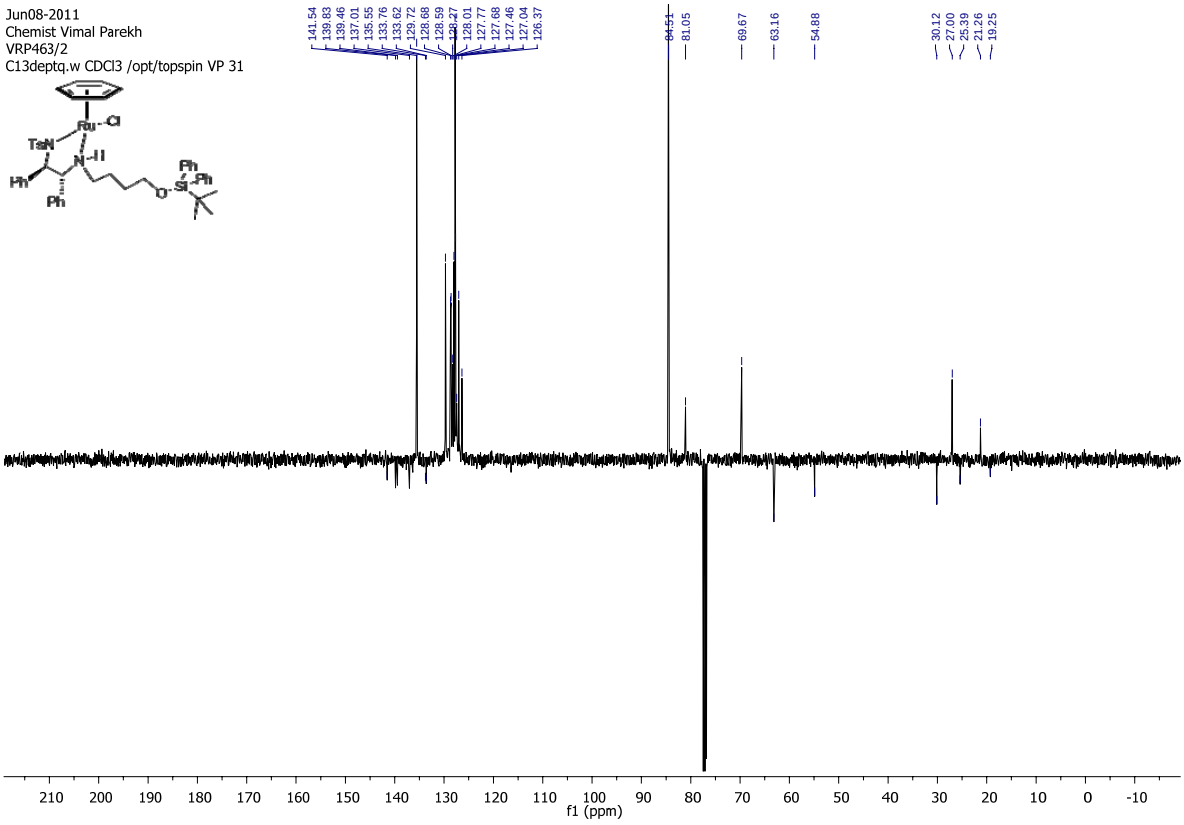
Synthesis of catalyst (45)



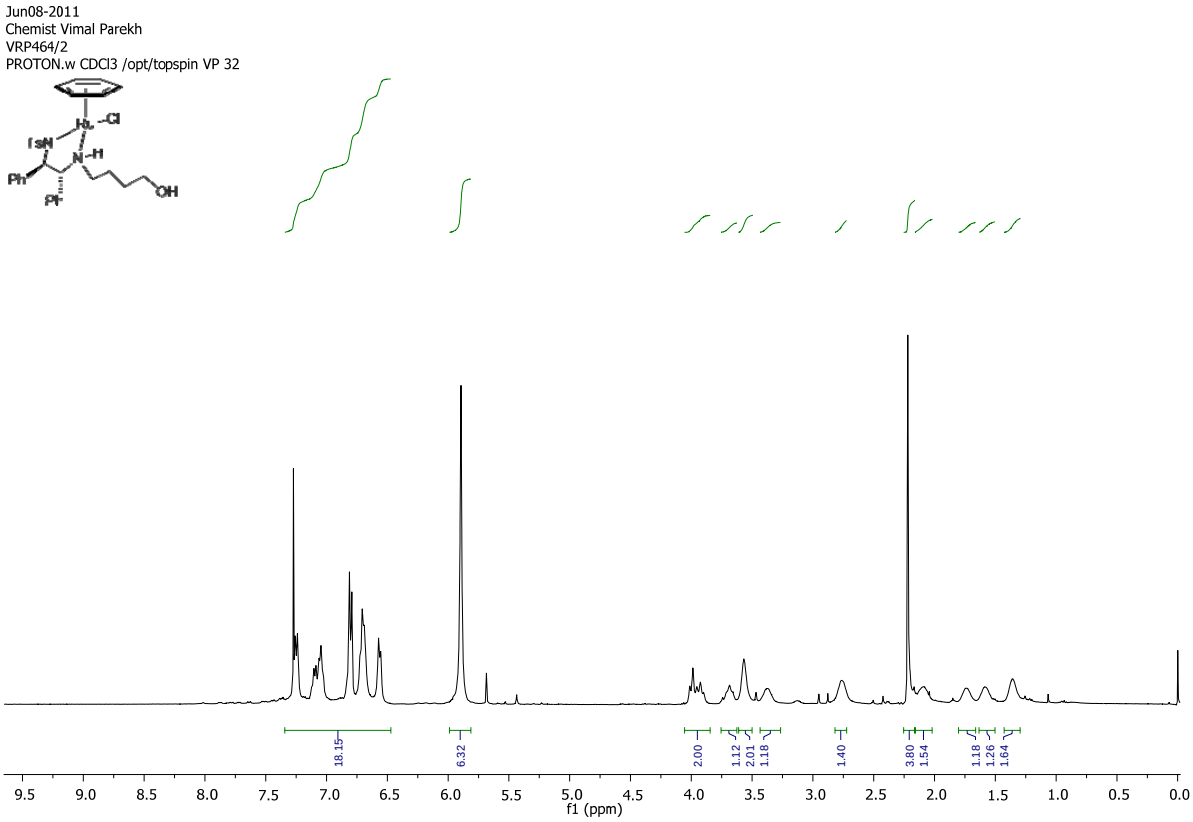


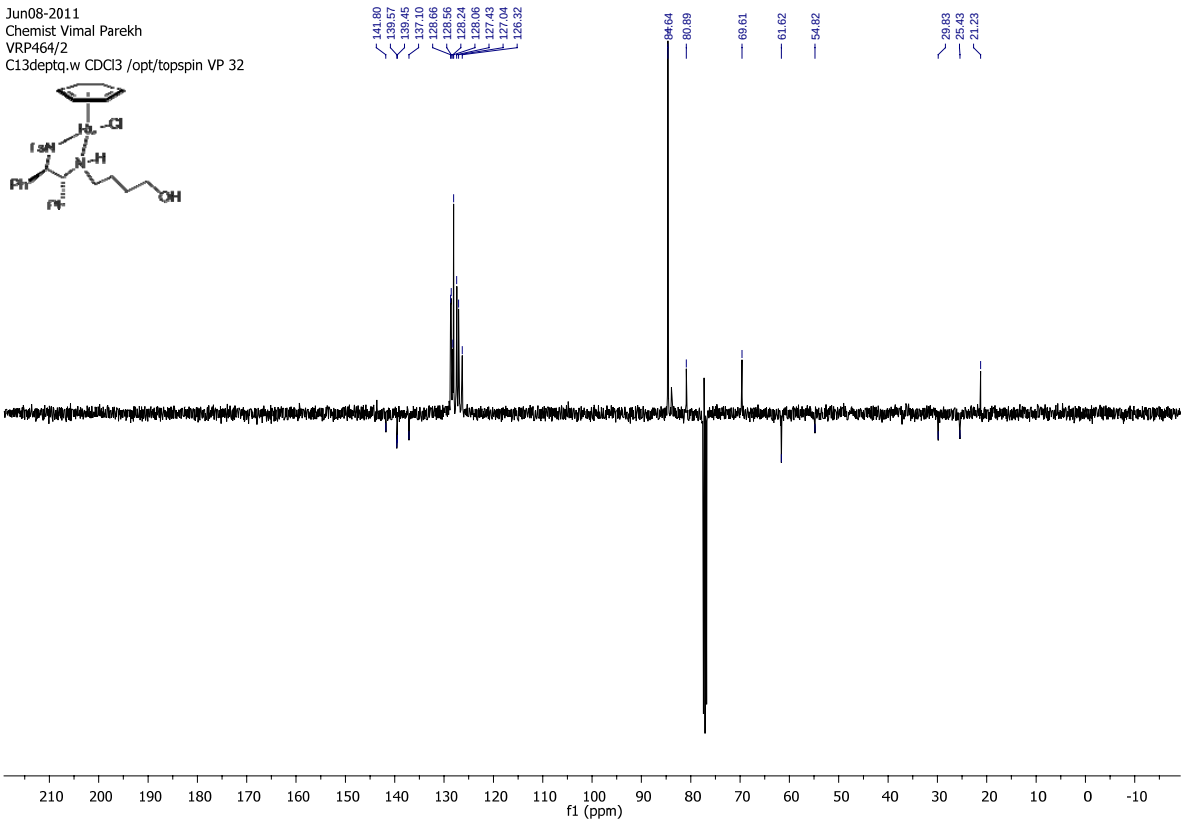
Synthesis of catalyst (46)



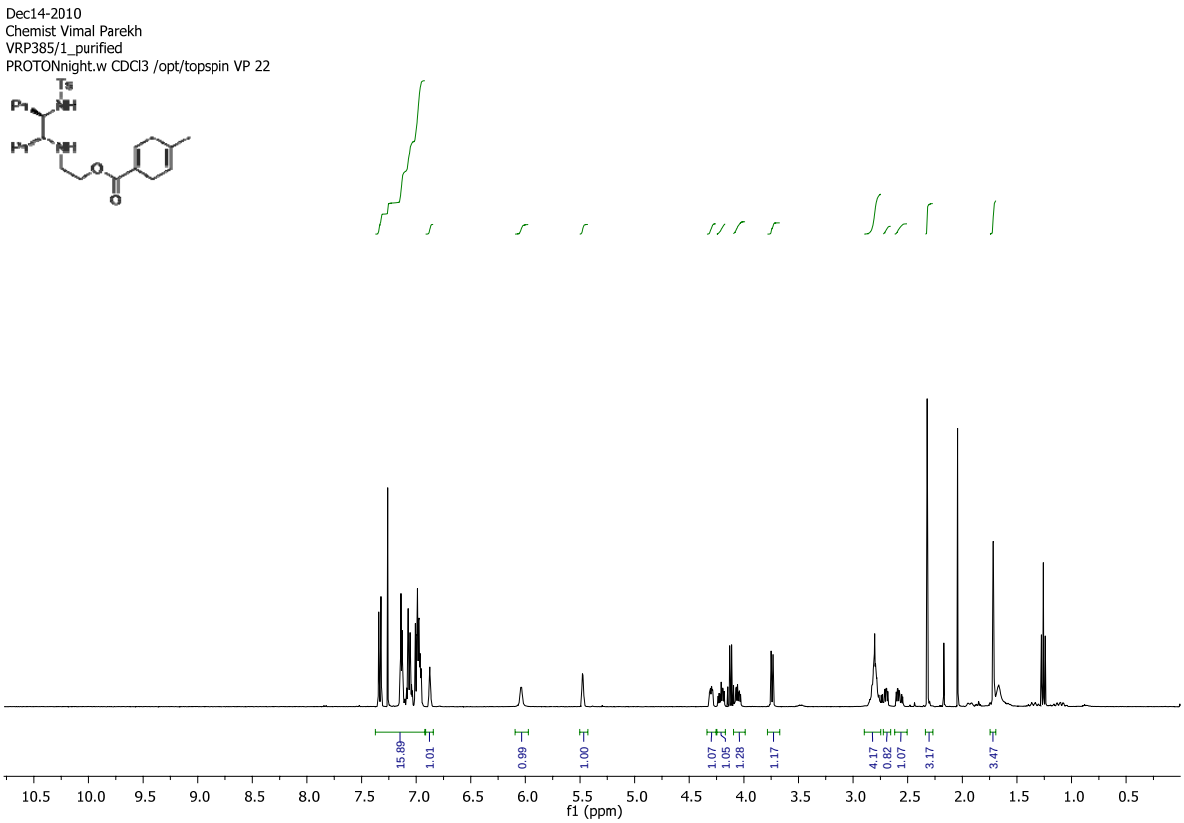


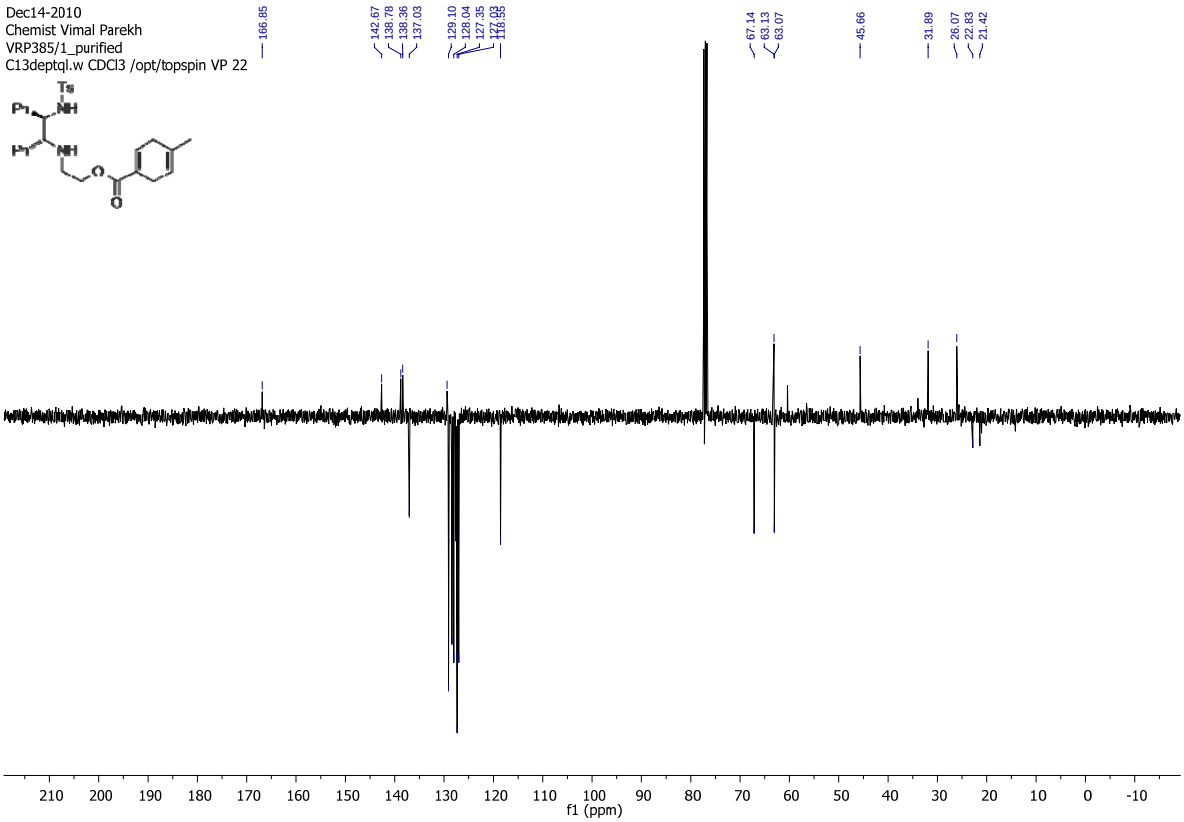
Synthesis of catalyst (48)



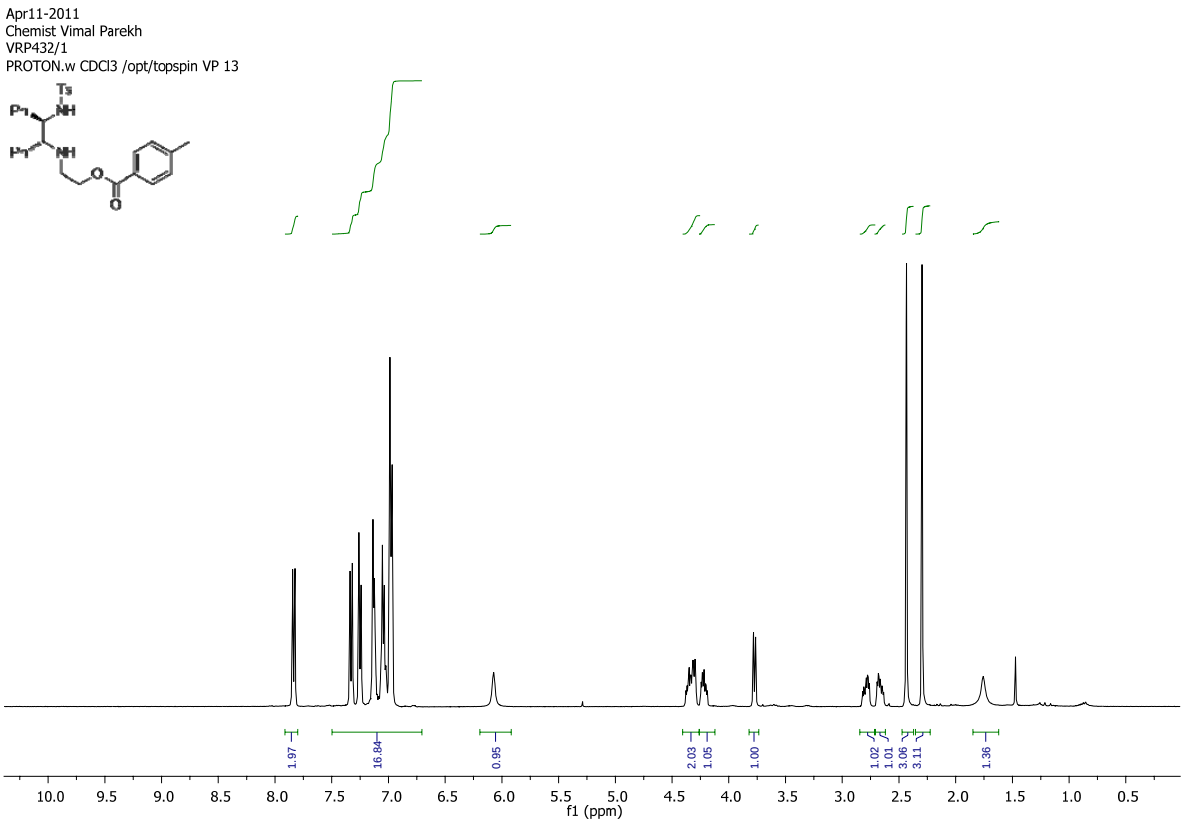


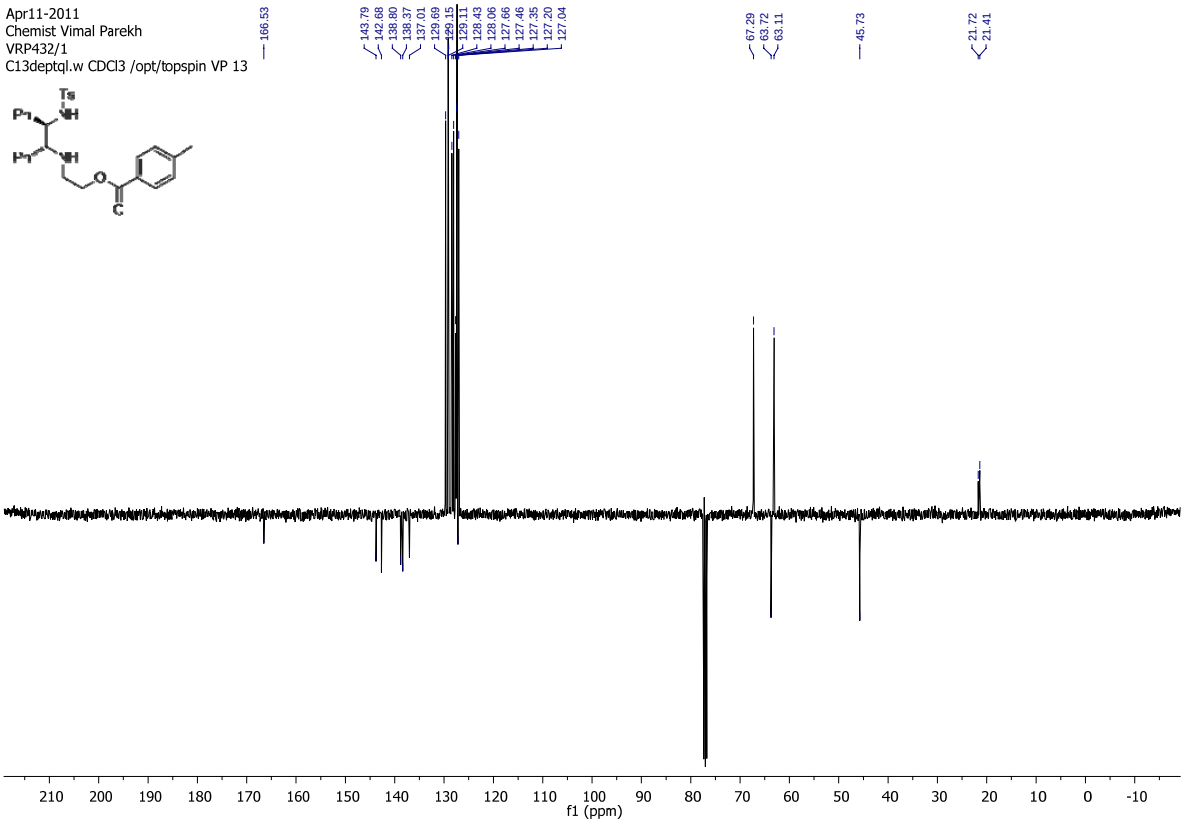
Synthesis of catalyst (47)



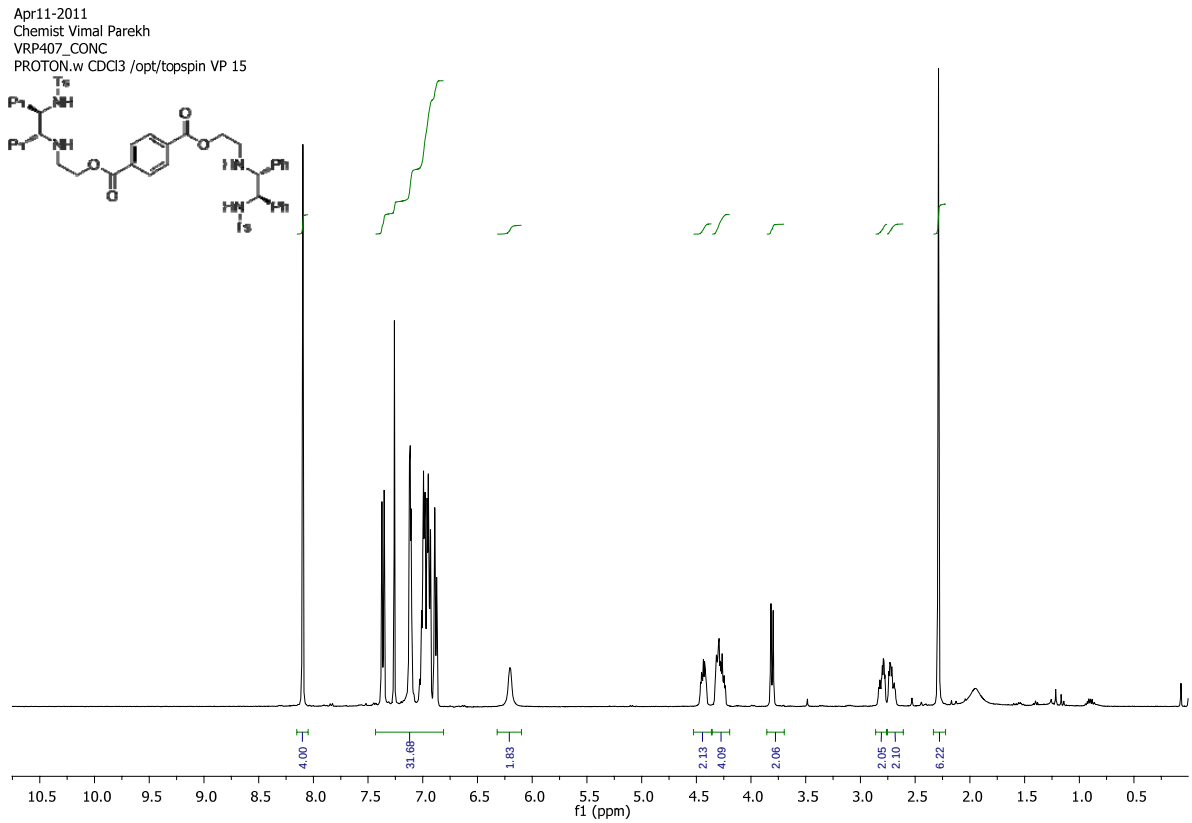


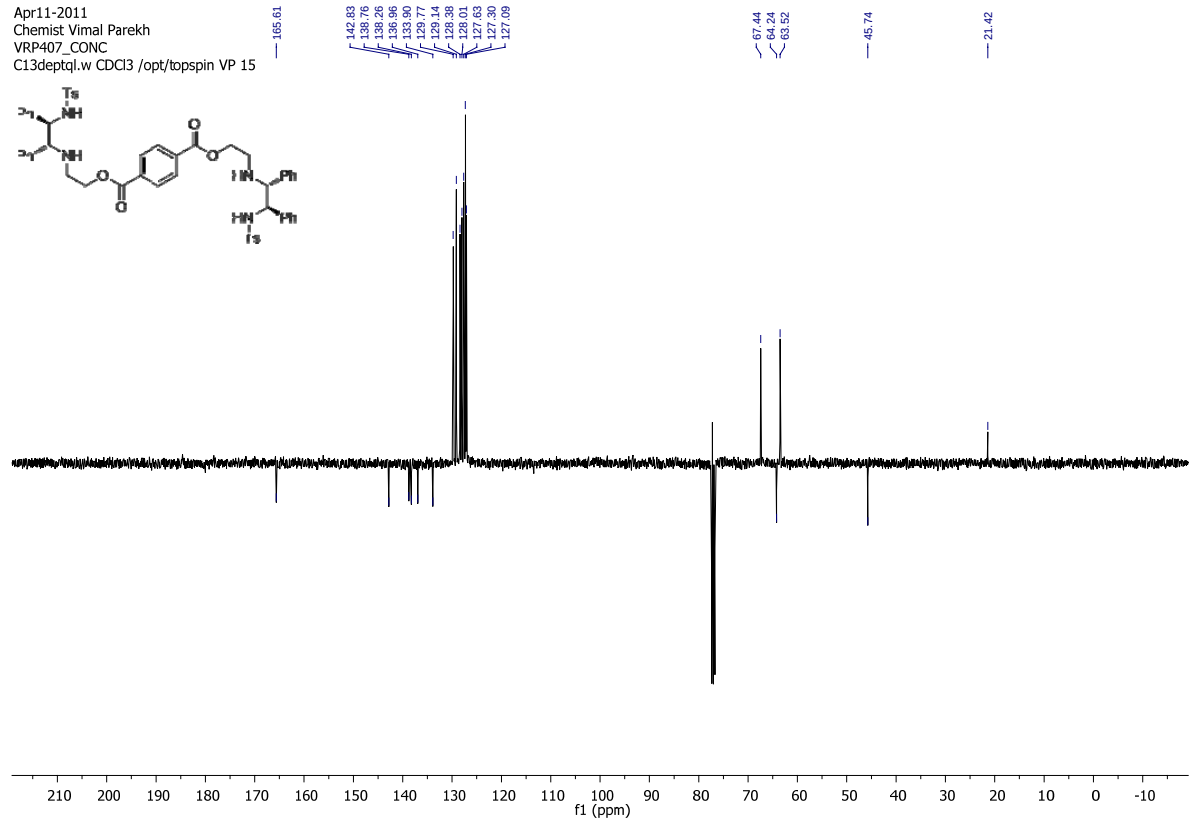
2-(((1*R*,2*R*)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)amino)ethyl 4-methylcyclohexa-1,4-dienecarboxylate (39)



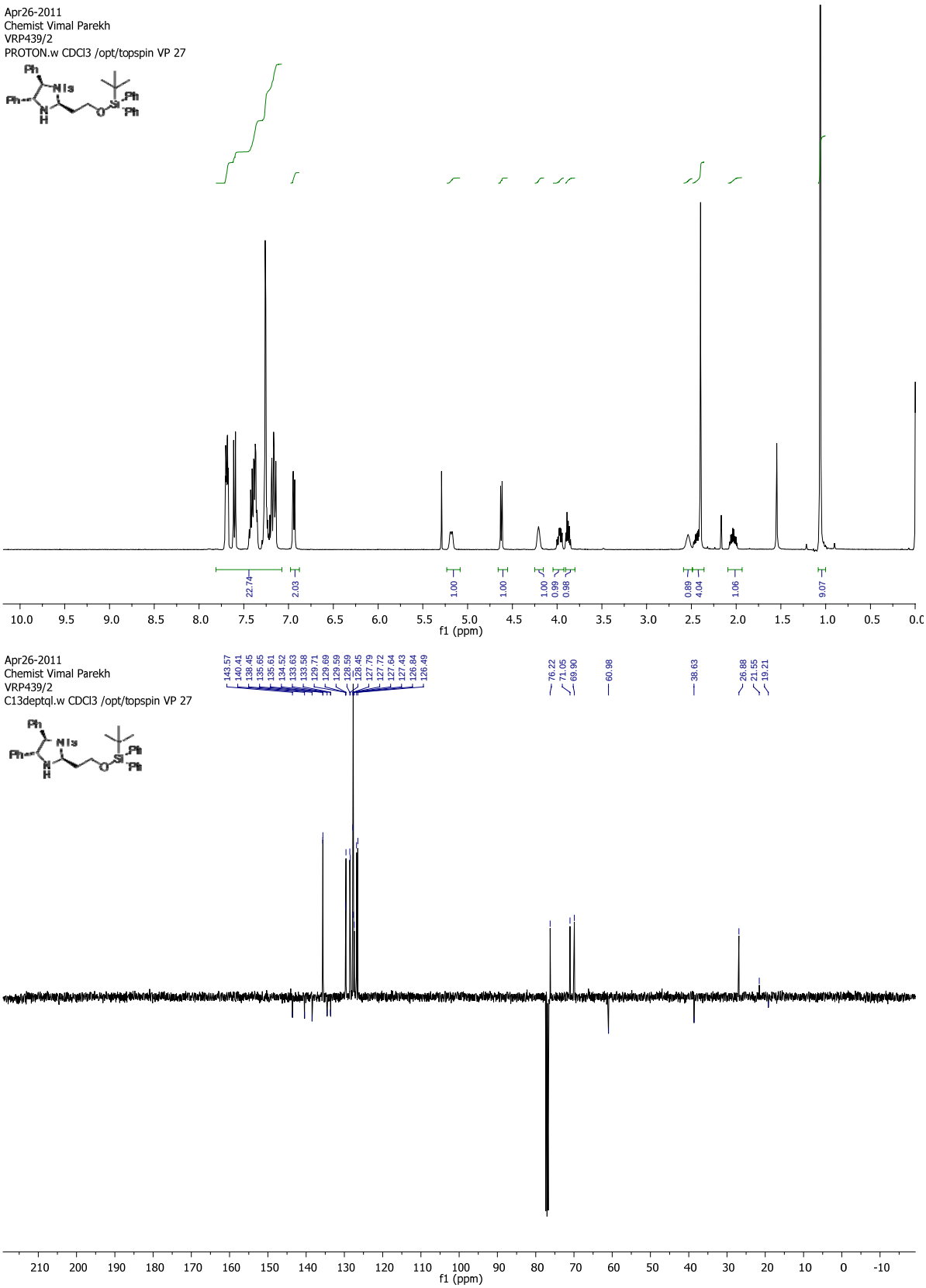


2-(((1*R*,2*R*)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)amino)ethyl 4-methylbenzoate (40)

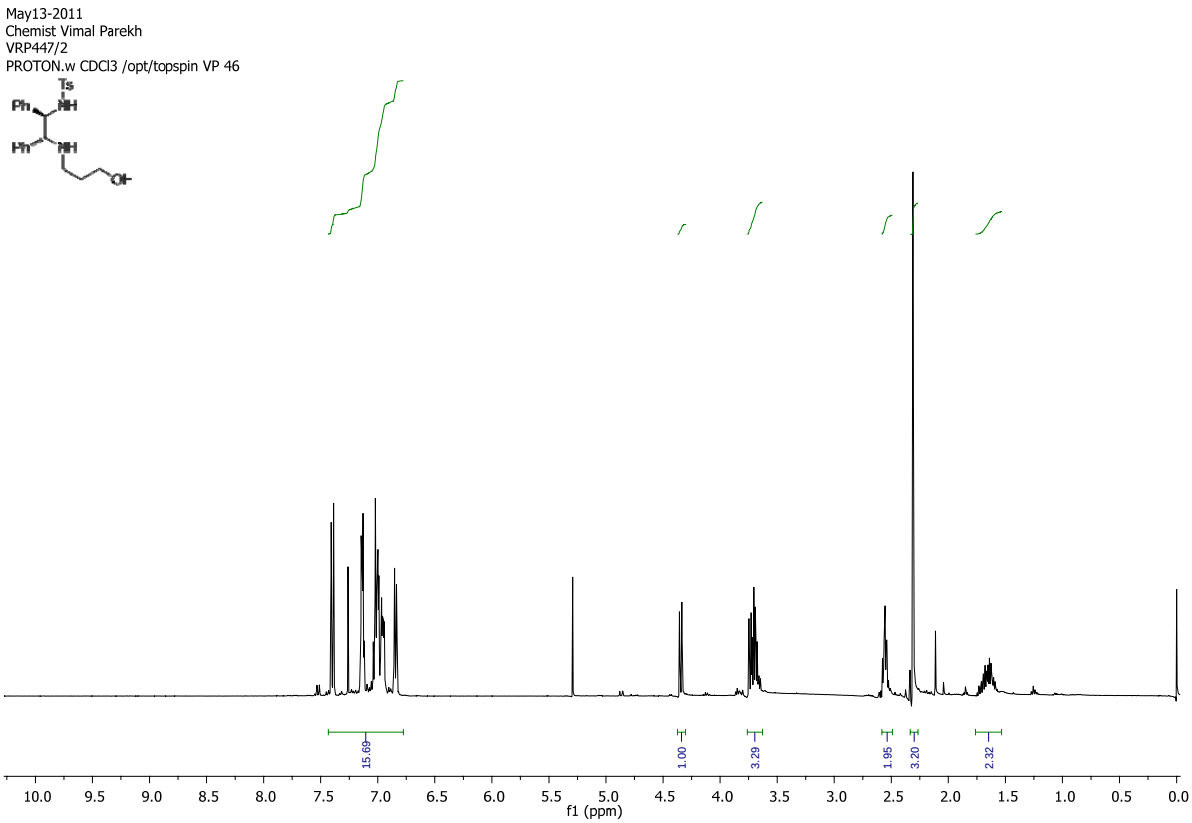


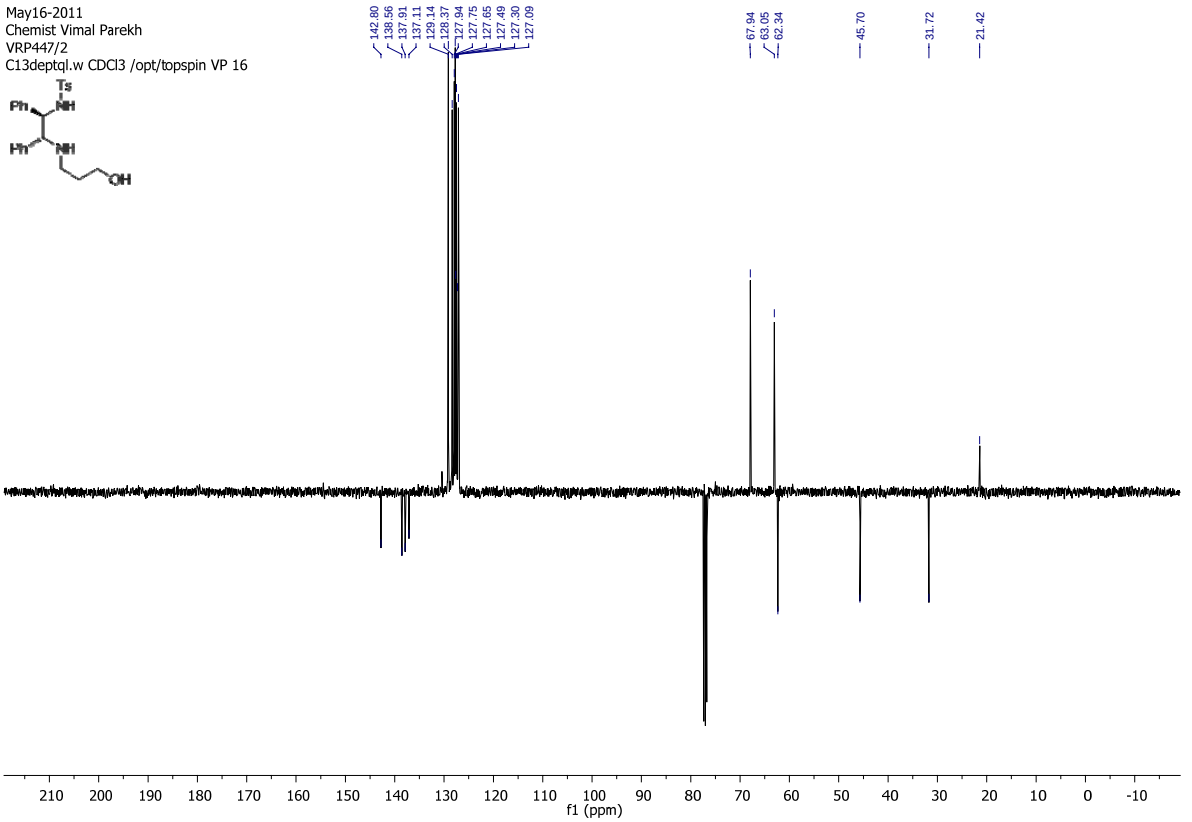


bis(2-(((1*R*,2*R*)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)amino)ethyl) terephthalate (41)

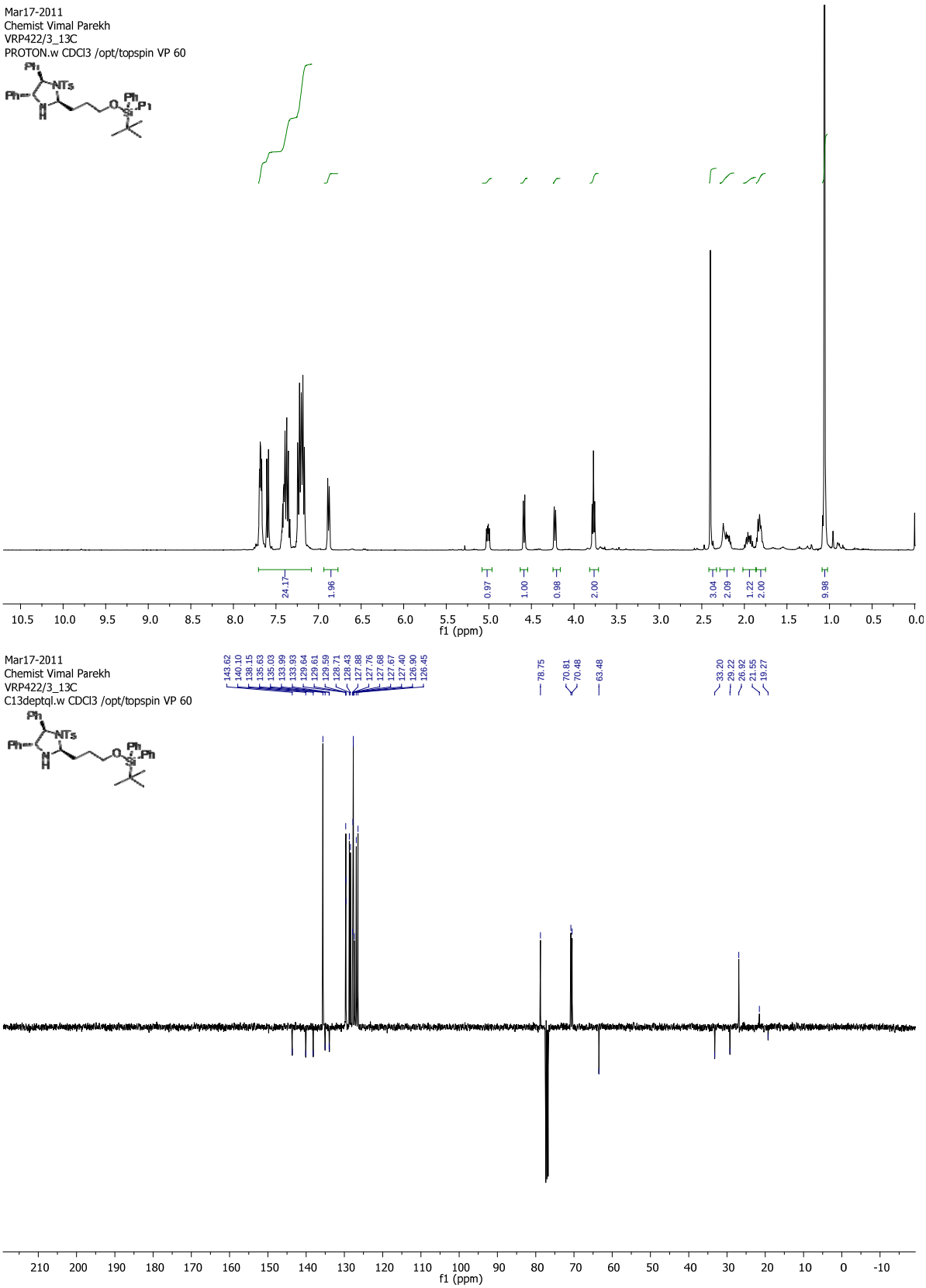


(2*S*, 4*R*, 5*R*)-2-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,5-diphenyl-1-tosylimidazolidine (43)

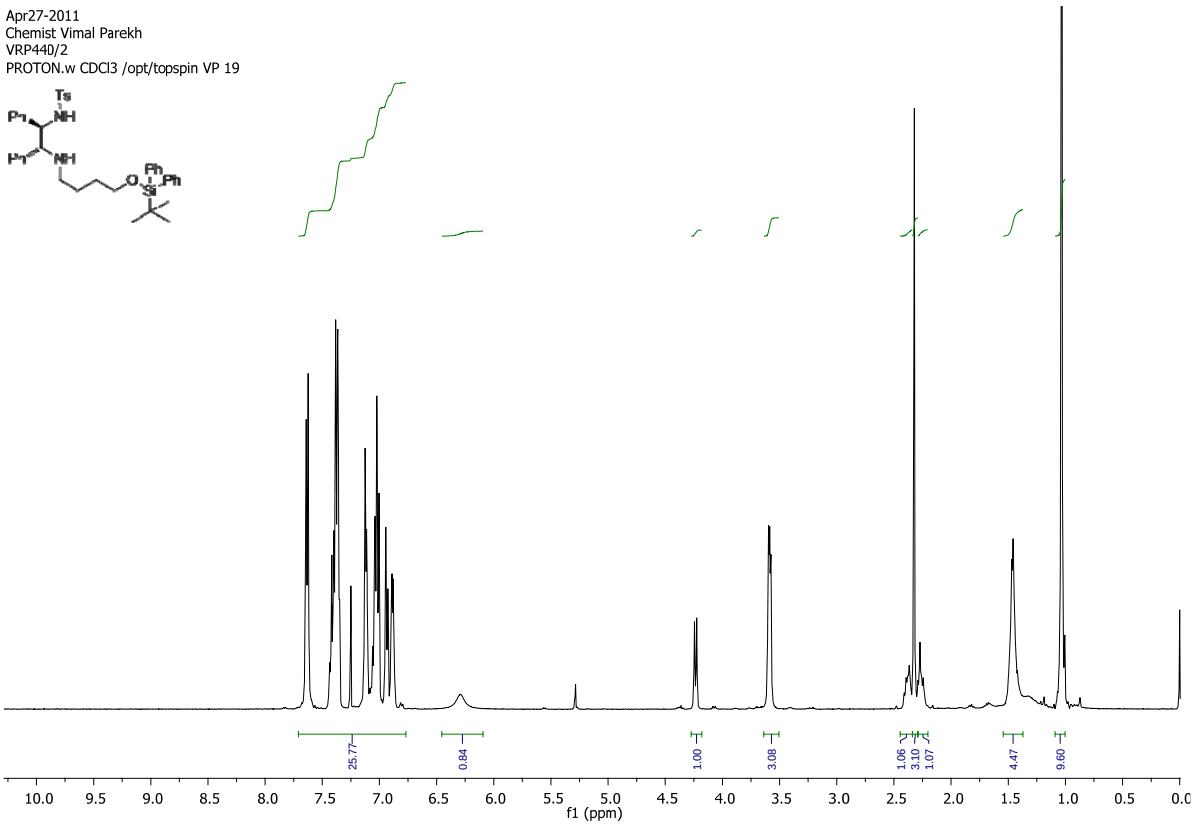


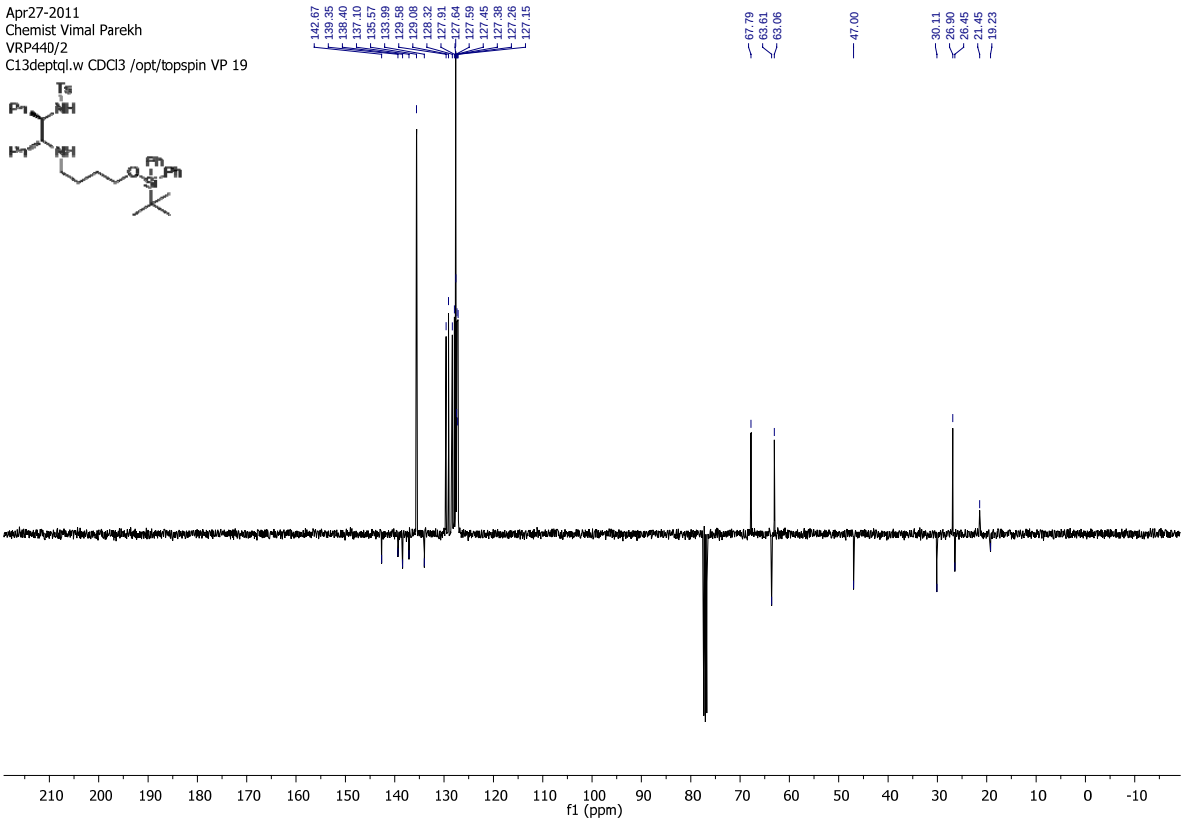


_N_-((1_R_, 2_R_)-2-((3-hydroxypropyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (36)

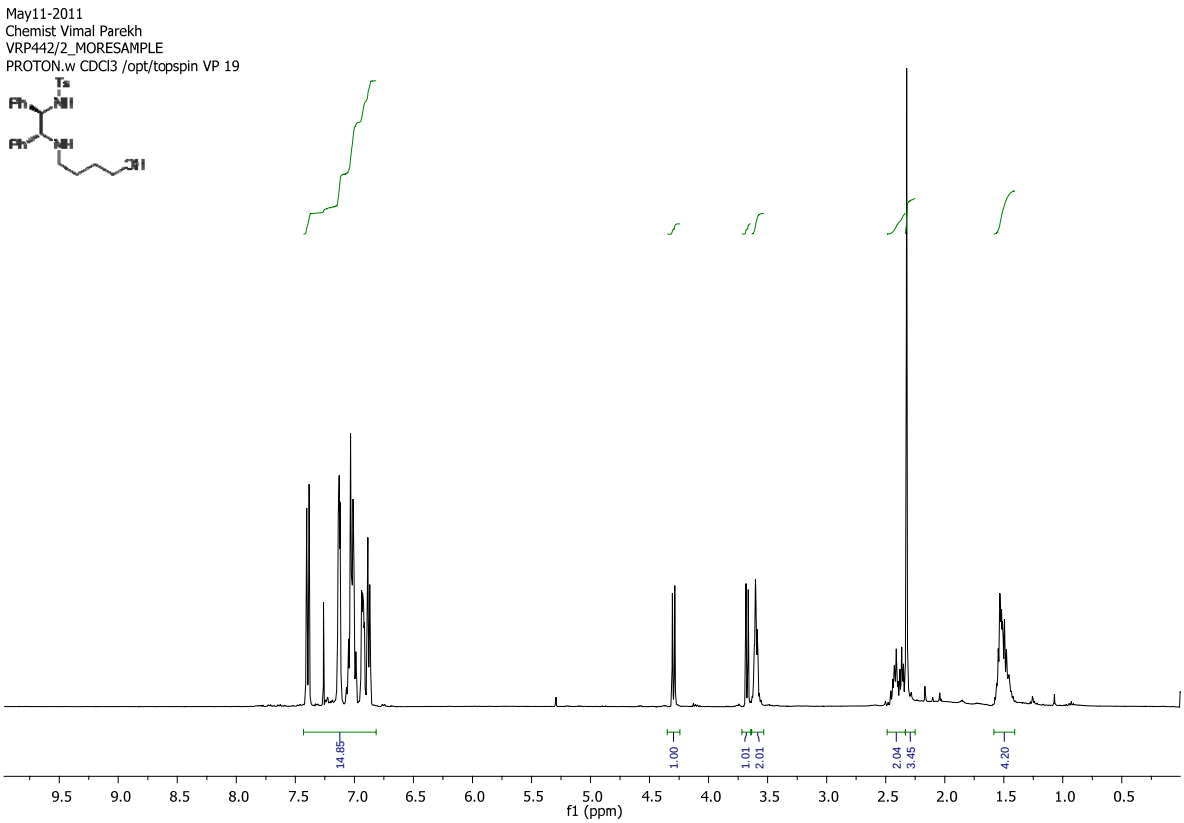


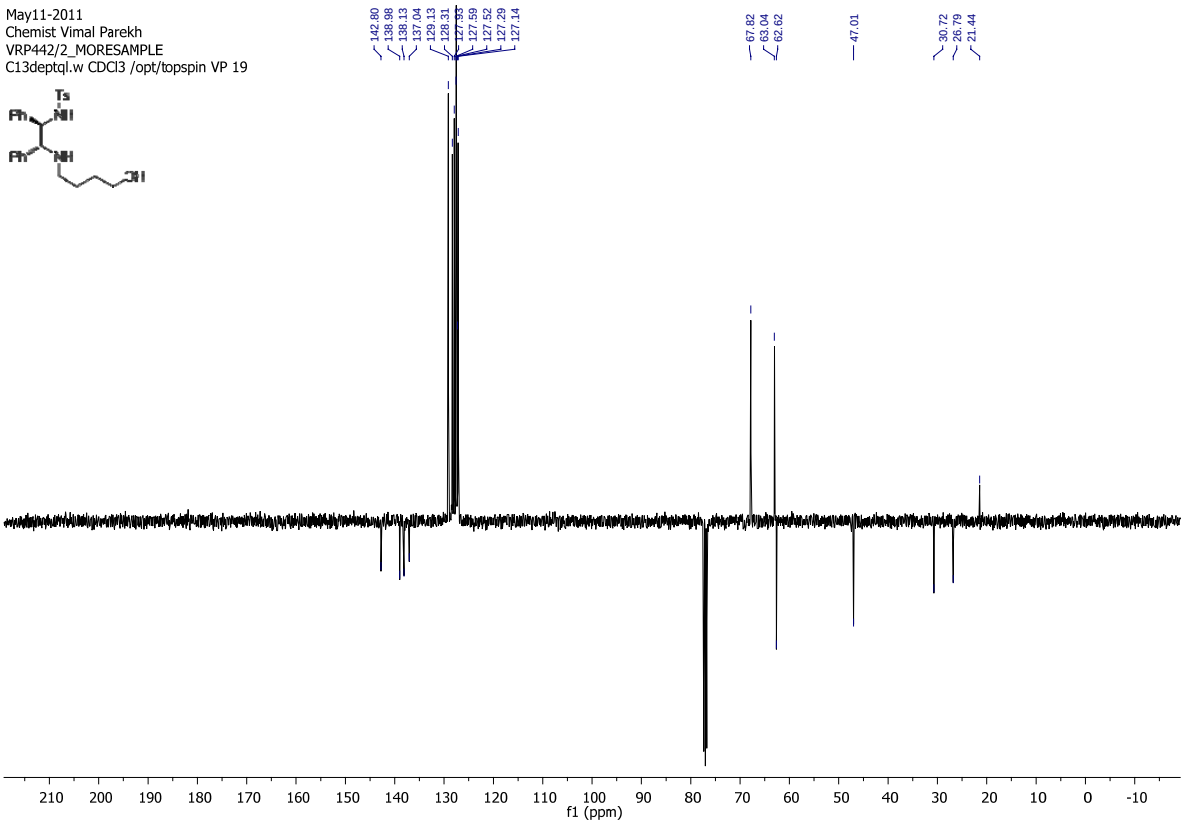
(2*S*, 4*R*, 5*R*)-2-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-4,5-diphenyl-1-tosylimidazolidine (44)



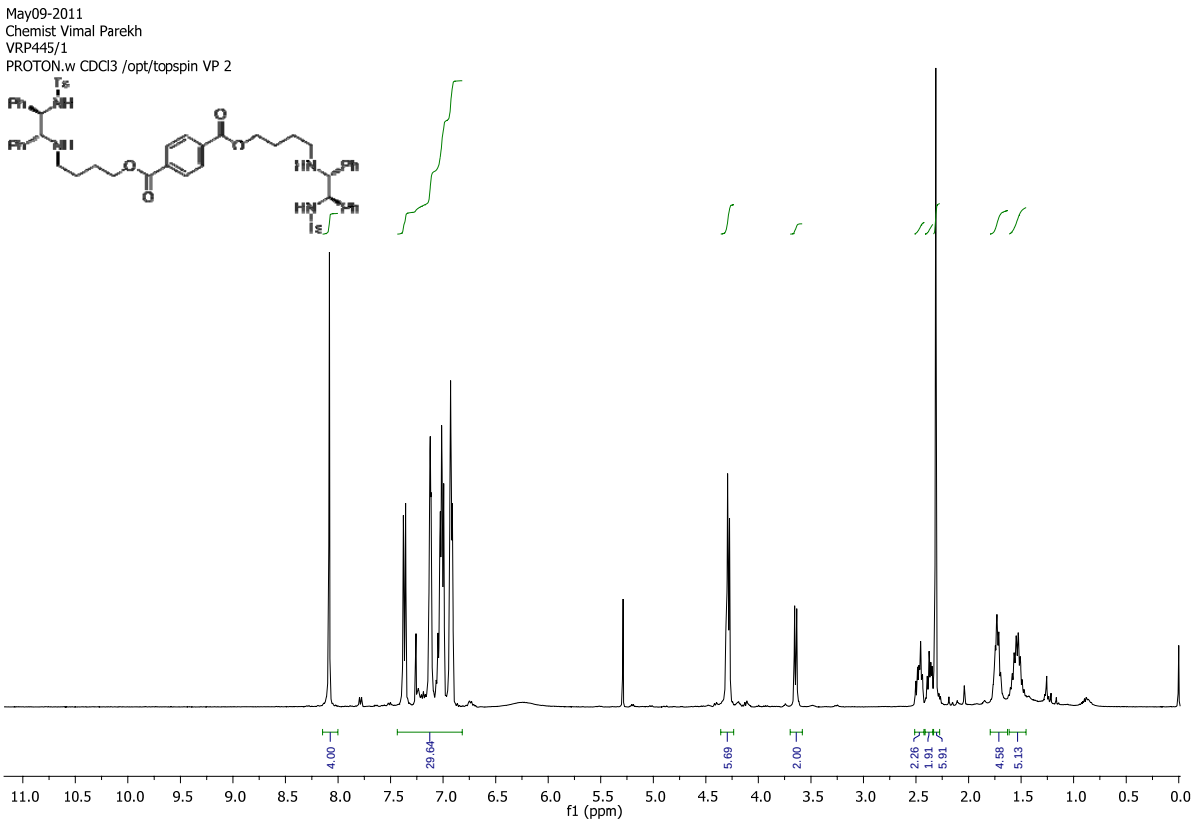


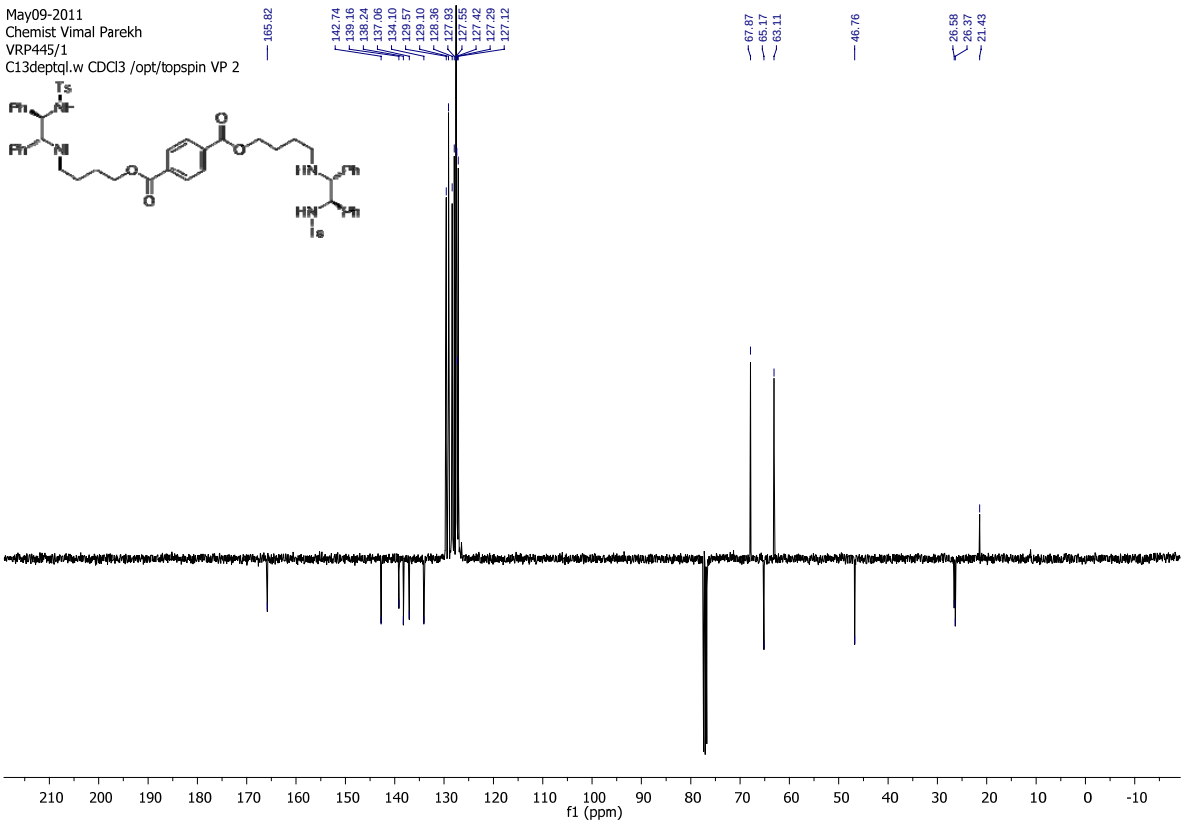
_N_-((1_R_, 2_R_)-2-((4-((*tert*-butyldiphenylsilyl)oxy)butyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (38)





_N_-((1_R_, 2_R_)-2-((4-hydroxybutyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (37)





bis(4-(((1*R*, 2*R*)-2-(4-methylphenylsulfonamido)-1,2-diphenylethyl)amino)butyl) terephthalate (43)