Supporting Information for

Ammonium-Directed Oxidation of Cyclic Allylic and Homoallylic Amines

Christopher W. Bond, Alexander J. Cresswell, Stephen G. Davies,* Ai M. Fletcher, Wataru Kurosawa, James A. Lee, Paul M. Roberts, Angela J. Russell, Andrew D. Smith and James E. Thomson

Department of Chemistry, Chemistry Research Laboratory,
University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K.

steve.davies@chem.ox.ac.uk

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1. Experimental

General Experimental

*m*CPBA was supplied as a 70-77% slurry in water and titrated according to the procedure of Swern[1] immediately before use. Et_2O was dried according to the procedure outlined by Grubbs and co-workers.[2] Cl_3CCO_2H and TsOH were dried according to the procedure outlined by Armaregeo and Chai.[3] All other solvents were used as supplied (analytical or HPLC grade) without prior purification. Organic layers were dried over $MgSO_4$. Thin layer chromatography was performed on aluminium plates coated with 60 F_{254} silica. Plates were visualised using UV light (254 nm), iodine, 1% aq $KMnO_4$, or 10% ethanolic phosphomolybdic acid. Flash column chromatography was performed either on Kieselgel 60 silica on a glass column, or on an automated flash column chromatography platform.

Melting points are uncorrected. IR spectra were recorded as either a thin film on NaCl plates (film) or a KBr disc (KBr), as stated. Selected characteristic peaks are reported in cm^{-1}. NMR spectra were recorded in the deuterated solvent stated. The field was locked by external referencing to the relevant deuteron resonance. In cases where methylene protons of carbocyclic ring systems could not be unambiguously assigned to a specific carbon atom, the descriptor "CH_2" is employed throughout. ^{1}H-^{1}H COSY and ^{1}H-^{13}C HMQC analyses were used to establish atom connectivity.

General Procedure for Transesterification of Acetate and Trichloroacetate Esters

K_2CO_3 was added to a stirred solution of the requisite trichloroacetate or acetate ester in MeOH or MeOH/THF mixture, as stated, at rt. After 12 h the mixture was concentrated *in vacuo*. The residue was dissolved in Et_2O (or CH_2Cl_2), washed three times with brine, dried and concentrated *in vacuo*.

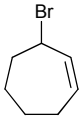
Cycloheptene 9

A mixture of bromocycloheptane (38.8 mL, 282 mmol) and powdered KOH (50.0 g, 891 mmol) in EtOH (125 mL) was heated at reflux for 18 h. After being allowed to cool to rt, the mixture was diluted with H_2O (1 L) and extracted with pentane (300 mL). The organic extracts were dried and concentrated *in vacuo* (300 mbar, 40 ºC) to give a 95:5 mixture of **9** and ethylcycloheptyl ether. Purification *via* fractional distillation at

[1] Swern, D. *Org. React.* **1953**, VII, 392.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
[3] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, Fifth Edition, Elsevier, 2003.

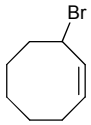
atmospheric pressure using a 15 cm Vigreux column gave **9** as a colourless oil (16.8 g, 62%) and ethylcycloheptyl ether as a colourless oil (1.90 g, 5%). Data for **9**: bp 112-115 ºC (760 mmHg); {lit.[4] bp 113-116 ºC (774 mmHg)}; δ_H (400 MHz, $CDCl_3$) 1.48-1.56 (4H, m, CH_2), 1.70-1.77 (2H, m, CH_2), 2.09-2.17 (4H, m, CH_2), 5.76-5.84 (2H, m, C(1)*H*, C(2)*H*). Data for ethylcycloheptyl ether: bp 171-180 ºC; {lit.[4] bp 172-181 ºC (774 mmHg)}; ν_{max} (film) 2974, 2928, 2859 (C–H), 1459, 1372, 1089; δ_H (400 MHz, $CDCl_3$) 1.17 (3H, t, *J* 7.1, OCH_2CH_3), 1.31-1.41 (2H, m, CH_2), 1.48-1.59 (6H, m, CH_2), 1.59-1.69 (2H, m, CH_2), 1.84-1.93 (2H, m, CH_2), 3.35-3.42 (1H, m, C(1)*H*), 3.45 (2H, q, *J* 7.1, OCH_2CH_3); δ_C (100 MHz, $CDCl_3$) 15.7 (OCH_2CH_3), 23.1, 28.4, 34.0 (*C*(2)-*C*(7)), 63.4 (OCH_2CH_3), 79.9 (*C*(1)).

(*RS*)-3-Bromocyclohept-1-ene 12



A mixture of **9** (16.8 g, 175 mmol), NBS (31.1 g, 175 mmol) and benzoyl peroxide (70%, 606 mg, 1.75 mmol) in CCl_4 (112 mL) was heated at reflux for 1 h. The reaction mixture was cooled to 0 ºC then filtered through a pad of Celite® (eluent CCl_4). The filtrate was washed with 5% aq. $NaHCO_3$ (50 mL) then dried and concentrated *in vacuo*. Purification *via* fractional distillation at reduced pressure (1.7 mmHg) using a 10 cm Vigreux column gave **12** as a colourless oil (16.0 g, 52%);[5] bp 42 ºC (1.7 mmHg); {lit.[5] bp 59 ºC (5.2 mmHg)}; δ_H (400 MHz, $CDCl_3$) 1.44-1.55 (1H, m, CH_2), 1.76-1.92 (2H, m, CH_2), 1.95-2.10 (2H, m, CH_2), 2.15-2.27 (3H, m, CH_2), 4.92-4.97 (1H, m, C(3)*H*), 5.82-5.89 (1H, m, C*H*=CH), 5.91-5.97 (1H, m, CH=C*H*).

(*RS,Z*)-3-Bromocyclooct-1-ene 13



A mixture of **10** (40.0 mL, 309 mmol), NBS (54.8 g, 309 mmol), and benzoyl peroxide (70%, 200 mg, 0.58 mmol) in CCl_4 (200 mL) was heated at reflux for 1 h. The reaction mixture was cooled to 0 ºC then filtered through a pad of Celite® (eluent CCl_4). The filtrate was washed with 5% aq. $NaHCO_3$ (100 mL) then dried and concentrated *in vacuo*. Purification *via* fractional distillation at reduced pressure (1.6 mmHg) using a 10

[4] Vogel, A. I. *J. Chem. Soc.* **1938**, 1323.
[5] Cope, A. C.; Liss, T. A.; Wood, G. W. *J. Am. Chem. Soc.* **1957**, *79*, 6287; Sellén, M.; Bäckvall, J.-E., Helquist, P. *J. Org. Chem* **1991**, *56*, 835.

cm Vigreux column gave **13** as a colourless oil (32.9 g, 56%);[6] bp 59-62 ºC (1.6 mmHg); {lit.[6] bp 77-79 ºC (5 mmHg)}; δ_H (400 MHz, $CDCl_3$) 1.24-1.74 (6H, m, CH_2), 1.93-2.28 (4H, m, CH_2), 4.90-4.98 (1H, m, C(3)*H*), 5.55-5.64 (1H, m, C*H*=CH), 5.71-5.83 (1H, m, CH=C*H*).

(*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopent-1-ene 14

A mixture of **8** (119 mL, 1.35 mol), NBS (60.0 g, 337 mmol) and benzoyl peroxide (70%, 1.17 g, 3.37 mmol) in CCl_4 (216 mL) was heated at reflux for 1 h. The reaction mixture was cooled to 0 ºC then filtered through a pad of Celite® (eluent CCl_4) to give a yellow solution. Concentration of an aliquot *in vacuo* gave a 98:1:1 mixture of **11**, *cis*-3,5-dibromocyclopentene, and *trans*-3,5-dibromocyclopentene, respectively.

Data for **11**:[7] δ_H (400 MHz, $CDCl_3$) 2.32-2.43 (3H, m, CH_2), 2.58-2.70 (1H, m, CH_2), 5.17 (1H, d, *J* 2.7, C(3)*H*), 6.00-6.09 (2H, m, C(1)*H*, C(2)*H*).

Data for *cis*-3,5-dibromocyclopentene:[8] δ_H (400 MHz, $CDCl_3$) 2.76 (1H, app d, *J* 16.7, C(4)H_AH_B), 3.03 (1H, dt, *J* 16.7, 6.8, C(4)H_AH_B), 5.06 (2H, dt, *J* 6.8, 1.4, C(3)*H*, C(5)*H*), 6.15 (2H, d, *J* 1.4, C(1)*H*, C(2)*H*).

Data for *trans*-3,5-dibromocyclopentene:[9] δ_H (400 MHz, $CDCl_3$) 2.96 (2H, t, *J* 5.1, C(4)H_2), 5.12 (2H, dt, *J* 5.1, 1.0, C(3)*H*, C(5)*H*), 6.11 (2H, d, *J* 1.0, C(1)*H*, C(2)*H*).

Dibenzylamine (162 mL, 843 mmol) was added to the crude solution of bromides at 0 ºC and the mixture then warmed to rt and stirred for 30 min. The reaction mixture was then filtered, heated to 40 ºC, and stirred at this temperature for 1 h, then filtered and stirred at rt for 12 h. The mixture was then filtered and concentrated *in vacuo*, and the residue was dissolved in CH_2Cl_2 (1 L) and washed sequentially with 10% aq. citric acid (3 × 500 mL) and sat. aq. $NaHCO_3$ (3 × 500 mL) then concentrated *in vacuo*. The residue was dissolved in 1 M aq. HCl (1 L) and washed with Et_2O (3 × 200 mL). The aqueous layer was then slowly basified to pH >10 by the portionwise addition of solid $NaHCO_3$, then extracted with CH_2Cl_2 (3 × 300 mL). The combined organic extracts were dried and concentrated *in vacuo*. Purification *via* flash column chromatography (gradient elution, 1%→5% Et_2O in 30-40 ºC petrol) gave **14** as a pale yellow oil (36.3 g, 41%); R_f 0.29 (30-40 ºC petrol/Et_2O, 96:4); ν_{max} (film) 3084, 3060, 3027, 2942, 2848, 2798 (C–H), 1715 (C=C), 1602, 1493, 1452; δ_H (400 MHz, $CDCl_3$) 1.92-2.09 (2H, m, C(4)H_2), 2.34-2.58 (2H, m, C(5)H_2),

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[6] Cope, A. C.; Estes, J., L. L. *J. Am. Chem. Soc.* **1950**, *72*, 1128; Sellén, M.; Bäckvall, J.-E., Helquist, P. *J. Org. Chem* **1991**, *56*, 835.

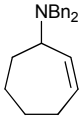
[7] Ikeda, H.; Namai, H.; Taki, H.; Miyashi, T. *J. Org. Chem.* **2005**, *70*, 3806.

[8] Begley, M. J.; Madeley, J. P.; Pattenden, G.; Smith, G. F. *J. Chem. Soc. Perkin Trans. 1*, **1992**, 57.

[9] Heasley, G. E.; Heasley, V. L.; Manatt, S. L.; Day, H. A.; Hodges, R. V.; Kroon, P. A.; Redfield, D. A.; Rold, T. L.; Williamson, D. E.. *J. Org. Chem.* **1973**, *38*, 4109.

3.59 (2H, d, *J* 14.0, N(C*H*$_A$H$_B$Ph)$_2$), 3.81 (2H, d, *J* 14.0, N(CH$_A$*H*$_B$Ph)$_2$), 4.17-4.25 (1H, m, C(3)*H*), 5.88-5.95 (1H, m, C(1)*H*), 5.99-6.05 (1H, m, C(2)*H*), 7.32-7.58 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 23.4 (*C*(4)), 31.9 (*C*(5)), 54.5 (N(*C*H$_2$Ph)$_2$), 66.1 (*C*(3)), 126.8 (*p-Ph*), 128.3, 128.8 (*o*-, *m-Ph*), 132.1 (*C*(1)), 133.3 (*C*(2)), 140.8 (*i-Ph*); *m/z* (ESI$^+$) 264 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{19}H_{22}N^+$ ([M+H]$^+$) requires 264.1747; found 264.1747.

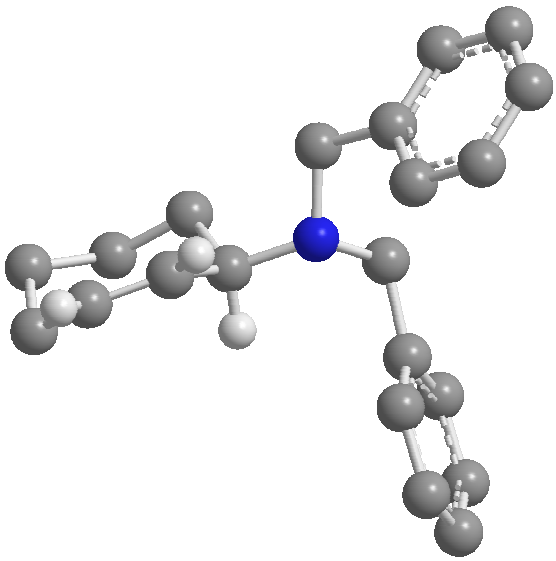
(*RS*)-3-(*N,N*-Dibenzylamino)cyclohept-1-ene 15



A mixture of **12** (16.0 g, 91.4 mmol), dibenzylamine (43.9 mL, 228 mmol) and K_2CO_3 (15.2 g, 110 mmol) was stirred at 60 ºC for 35 h. The mixture was then diluted with H_2O (1 L) and CH_2Cl_2 (1 L). The organic layer was separated and washed sequentially with 10% aq. citric acid (3 × 500 mL) and sat. aq. $NaHCO_3$ (500 mL). The resultant solution was dried and concentrated *in vacuo*. Purification *via* recrystallisation (^{i}PrOH) gave **15** as a white crystalline solid (21.6 g, 81%);[10] mp 54-55 ºC (^{i}PrOH); ν_{max} (KBr) 3084, 3062, 3025, 2923, 2851, 2800 (C–H), 1645 (C=C), 1602, 1494, 1453; δ_H (400 MHz, $CDCl_3$) 1.26-1.74 (4H, m, C*H*$_2$), 1.89-2.10 (3H, m, C*H*$_2$), 2.13-2.23 (1H, m, C*H*$_2$), 3.35 (1H, app d, *J* 10.4, C(3)*H*), 3.59 (2H, d, *J* 14.2, N(C*H*$_A$H$_B$Ph)$_2$), 3.74 (2H, d, *J* 14.2, N(CH$_A$*H*$_B$Ph)$_2$), 5.80-5.89 (1H, m, C(1)*H*), 5.93-6.00 (1H, m, C(2)*H*), 7.20-7.42 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 26.9, 28.5, 28.5, 28.6 (*C*(4)-*C*(7)), 54.0 (N(*C*H$_2$Ph)$_2$), 59.0 (*C*(3)), 126.6 (*p-Ph*), 128.2, 128.6 (*o*-, *m-Ph*), 131.1 (*C*(1)), 136.2 (*C*(2)), 140.7 (*i-Ph*); *m/z* (ESI$^+$) 292 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{26}N^+$ ([M+H]$^+$) requires 292.2060; found 292.2058.

[10] For the preparation of (*S*)-**15**, see: Uozumi, Y.; Tanaka, H.; Shibatomi, K. *Org. Lett.* **2004**, *6*, 281.

X-ray Crystal Structure Determination for 15

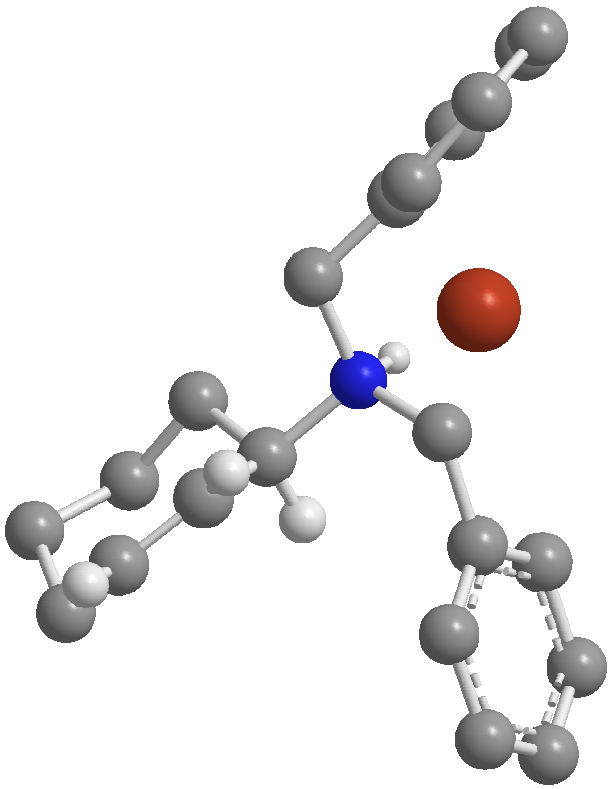


Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[11]

X-ray crystal structure data for **15** [$C_{21}H_{25}N$]: M = 291.44, monoclinic, space group $P\ 2_1/c$, a = 15.7454(3) Å, b = 6.33680(10) Å, c = 17.3225(4) Å, β = 93.0165(10) °, V = 1725.97(6) Å^3, Z = 4, μ = 0.064 mm^{-1}, colourless block, crystal dimensions = 0.3 × 0.3 × 0.3 mm^3. A total of 3899 unique reflections were measured for $5 < \theta < 27$ and 2751 reflections were used in the refinement. The final parameters were wR_2 = 0.102 and R_1 = 0.048 [$I>3.0\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733888. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

[11] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

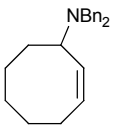
X-ray Crystal Structure Determination for 15•HBr



Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[11]

X-ray crystal structure data for **15•HBr** [$C_{21}H_{26}BrN$]: M = 372.35, monoclinic, space group $P\ 2_1/n$, a = 10.0731(2) Å, b = 13.6453(3) Å, c = 14.6931(4) Å, β = 109.8180(8) °, V = 1899.96(8) Å^3, Z = 4, μ = 2.16 mm^{-1}, colourless plate, crystal dimensions = 0.05 × 0.05 × 0.2 mm^3. A total of 4309 unique reflections were measured for 5 < θ < 27 and 2536 reflections were used in the refinement. The final parameters were wR_2 = 0.082 and R_1 = 0.038 [I>3.0$\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733889. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

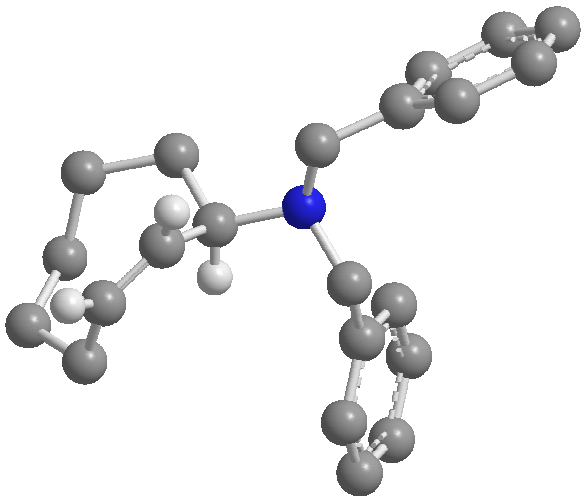
(*RS*,*Z*)-3-(*N*,*N*-Dibenzylamino)cyclooct-1-ene 16



A mixture of **13** (31.1 g, 165 mmol), dibenzylamine (79.0 mL, 412 mmol) and K_2CO_3 (27.4 g, 198 mmol) was stirred at 60 ºC for 35 h. The mixture was then diluted with H_2O (1 L) and CH_2Cl_2 (1 L). The organic

layer was separated and washed sequentially with 10% aq. citric acid (3 × 500 mL) and sat. aq. $NaHCO_3$ (500 mL). The resultant solution was dried and concentrated *in vacuo*. Purification *via* recrystallisation (^{i}PrOH) gave **16** as a white crystalline solid (43.2 g, 86%); mp 49-50 ºC; ν_{max} (KBr) 3084, 3061, 3025, 2925, 2853, 2799 (C–H), 1644 (C=C), 1603, 1493, 1453; δ_H (400 MHz, $CDCl_3$) 1.38-1.54 (4H, m, CH_2), 1.57-1.81 (3H, m, CH_2), 1.94-2.07 (2H, m, CH_2), 2.09-2.18 (1H, m, CH_2), 3.71 (2H, d, *J* 13.8, N(CH_AH$_B$Ph)$_2$), 3.80 (1H, ddd, *J* 11.6, 7.3, 3.8, C(3)*H*), 3.97 (2H, d, *J* 13.8, N(CH$_A$$H_B$Ph)$_2$), 5.89-6.00 (2H, m, C(1)*H*, C(2)*H*), 7.35-7.60 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 25.1, 26.3, 26.6, 29.4, 33.7 (*C*(4)-*C*(8)), 54.7 (N(*C*H$_2$Ph)$_2$), 55.8 (*C*(3)), 126.7 (*p-Ph*), 128.1, 128.7 (*o*-, *m-Ph*), 129.7, 130.8 (*C*(1), *C*(2)), 140.8 (*i-Ph*); *m/z* (ESI$^+$) 306 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{22}H_{28}N^+$ ([M+H]$^+$) requires 306.2216; found 306.2203.

X-ray Crystal Structure Determination for 16



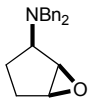
Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-*Kα* radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[12]

X-ray crystal structure data for **16** [$C_{22}H_{27}N$]: M = 305.46, monoclinic, space group *P* $2_1/n$, *a* = 10.7783(2) Å, *b* = 14.9377(4) Å, *c* = 11.3867(3) Å, *β* = 92.8387(10) °, *V* = 1831.04(8) Å^3, *Z* = 4, μ = 0.063 mm^{-1}, colourless block, crystal dimensions = 0.2 × 0.2 × 0.2 mm^3. A total of 4167 unique reflections were measured for 5 < *θ* < 27 and 2409 reflections were used in the refinement. The final parameters were wR_2 = 0.145 and R_1 = 0.062 [$I>3.0\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733890. Copies

[12] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

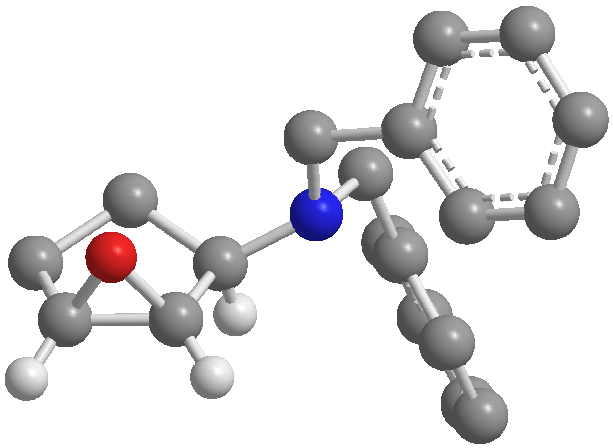
of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 20



Cl_3CCO_2H (31.0 g, 190 mmol) was added to a stirred solution of **14** (10 g, 38.0 mmol) in CH_2Cl_2 (127 mL, 0.3 M w.r.t. **14**) and the resultant mixture was stirred at rt for 5 min. *m*CPBA (73%, 9.43 g, 39.9 mmol) was then added in one portion and the reaction mixture was stirred at rt for 3.5 h. The mixture was diluted with CH_2Cl_2 (100 mL) and sat. aq. Na_2SO_3 was added until starch-iodide paper indicated no remaining peracid. Sat. aq. $NaHCO_3$ (200 mL) was added and the layers were separated. The organic layer was washed with sat. aq. $NaHCO_3$ (2 × 200 mL) then dried, filtered through a short plug of silica gel (eluent CH_2Cl_2), and concentrated *in vacuo* to give **20** in >99:1 dr. Purification *via* recrystallisation (^{i}PrOH) gave **20** as a white crystalline solid. Concentration of the mother liquors and purification of the residue *via* flash column chromatography (gradient elution, 1%→8% EtOAc in 40-60 ºC petrol) gave **20** as a colourless oil that solidified on standing to a white crystalline solid (10.5 g combined, 99%, >99:1 dr); R_f 0.12 (40-60 ºC petrol/EtOAc, 96:4); $C_{19}H_{21}NO$ requires C, 81.7; H, 7.6; N, 5.0%; found C, 81.5; H, 7.7; N, 4.9%; mp 58-60 ºC (^{i}PrOH); ν_{max} (KBr) 3084, 3061, 3027, 2951, 2802 (C–H), 1602, 1494, 1453; δ_H (400 MHz, $CDCl_3$) 1.45-1.59 (3H, m, C(4)H_A, C(5)H_2), 2.00-2.11 (1H, m, C(4)H_B), 3.25-3.31 (1H, m, C(3)*H*), 3.34 (1H, app d, *J* 2.7, C*H*, epoxide), 3.47 (1H, app d, *J* 2.7, C*H*, epoxide), 3.74 (2H, d, *J* 14.3, N(C$H_A$$H_B$Ph)$_2$), 3.86 (2H, d, *J* 14.3, N(C$H_A$$H_B$Ph)$_2$), 7.22-7.46 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 17.9 (*C*(5)), 25.7 (*C*(4)), 53.7, 55.5, 56.4 (*C*(1), *C*(2), N(*C*H_2Ph)$_2$), 61.4 (*C*(3)), 126.8 (*p*-*Ph*), 128.2, 128.5 (*o*-, *m*-*Ph*), 140.4 (*i*-*Ph*); *m/z* (ESI$^+$) 280 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{19}H_{22}NO^+$ ([M+H]$^+$) requires 280.1696; found 280.1692.

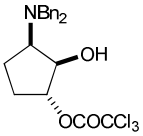
X-ray Crystal Structure Determination for 20



Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[13]

X-ray crystal structure data for **20** [$C_{19}H_{21}NO$]: M = 558.76, monoclinic, space group $P\ 2_1$, a = 12.444(3) Å, b = 7.8733(16) Å, c = 16.766(3) Å, β = 109.74(3)º, V = 1546.1(6) Å^3, Z = 4, μ = 0.073 mm^{-1}, colourless block, crystal dimensions = 0.2 × 0.2 × 0.2 mm^3. A total of 3651 unique reflections were measured for 5 < θ < 27 and 3651 reflections were used in the refinement. The final parameters were wR_2 = 0.214 and R_1 = 0.092 [I>–3.0σ(I)]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733891. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(1*RS*,2*RS*,3*RS*)-1-Trichloroacetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cyclopentane 21



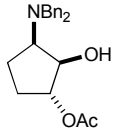
Anhydrous Cl_3CCO_2H (292 mg, 1.79 mmol) was added to a stirred solution of **20** (100 mg, 0.36 mmol) in CH_2Cl_2 (5 mL) and the resultant mixture was heated at 40 °C for 12 h. The mixture was allowed to cool to rt then diluted with CH_2Cl_2 (15 mL) and washed with sat. aq. $NaHCO_3$ (3 × 10 mL). The resultant solution was dried and concentrated *in vacuo* to give **21** (>95%), along with trace amounts of unidentifiable species, as a colourless oil, which solidified on standing to a white solid (111 mg, 70%); ν_{max} (film) 3426 (O–H), 3085,

[13] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

3062, 3029, 2944, 2848 (C–H), 1767 (C=O), 1602, 1494, 1454; *m/z* (ESI$^+$) 444 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{23}{}^{35}Cl_3NO_3{}^+$ ([M+H]$^+$) requires 442.0738; found 442.0743.

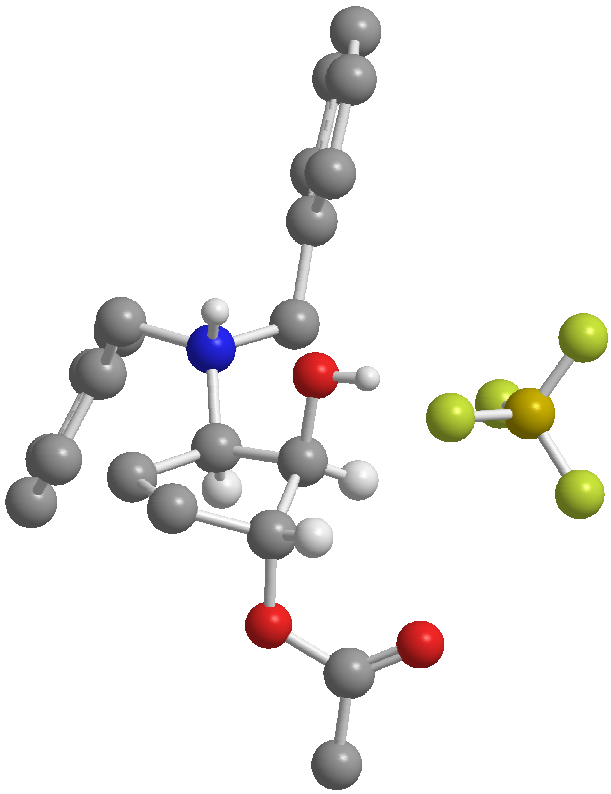
Data for **21**: δ_H (400 MHz, $CDCl_3$) 1.72 (1H, app ddd, *J* 14.2, 8.6, 3.0, C(5)H_A), 1.82 (1H, app t, *J* 10.7, C(4)H_A), 1.96-2.06 (1H, m, C(4)H_B), 2.41-2.52 (1H, m, C(5)H_B), 3.31 (1H, ddd, *J* 10.7, 6.8, 4.1, C(3)*H*), 3.76 (4H, A_2, N(CH_2Ph)$_2$), 4.17 (1H, app d, *J* 4.1, C(2)*H*), 5.20 (1H, app dd, *J* 7.3, 3.0, C(1)*H*), 7.25-7.36 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 26.9, 28.6 (*C*(4), *C*(5)), 55.5 (N(*C*H$_2$Ph)$_2$), 65.2 (*C*(3)), 73.9 (*C*(2)), 83.7 (*C*(1)), 89.9 (*C*Cl$_3$), 127.4 (*p-Ph*), 128.5, 129.0 (*o*-, *m-Ph*), 137.9 (*i-Ph*), 161.1 (*C*OCCl$_3$).

(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-hydroxy-3-(*N,N*-dibenzylamino)cyclopentane 22



A solution of **20** (5.26 g, 18.8 mmol) in glacial AcOH (53 mL) was stirred at 50 ºC for 66 h. The reaction mixture was then allowed to cool to rt and concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (200 mL) and the resultant solution was washed with sat. aq. $NaHCO_3$ (3 × 200 mL), then dried and concentrated *in vacuo*. Purification *via* recrystallisation (MeOH) gave **22** as a white crystalline solid (5.27 g, 83%, >99:1 dr); $C_{21}H_{25}NO_3$ requires C, 74.3; H, 7.4; N, 4.1%; found C, 74.3; H, 7.4; N, 4.15%; mp 121-123 ºC (MeOH); ν_{max} (KBr) 3448 (O–H), 3062, 3028, 2944 (C–H), 1734 (C=O), 1602, 1494, 1454; δ_H (400 MHz, $CDCl_3$) 1.49-1.60 (1H, m, C(5)H_A), 1.68-1.80 (1H, m, C(4)H_A), 1.90-1.99 (1H, m, C(4)H_B), 2.05 (3H, s, CO*Me*), 2.37 (1H, dddd, *J* 14.3, 9.4, 7.3, 2.4, C(5)H_B), 3.24 (1H, ddd, *J* 10.9, 6.8, 4.4, C(3)*H*), 3.66 (1H, s, O*H*), 3.74 (4H, AB system, J_{AB} 14.3, N(CH_2Ph)$_2$), 4.04 (1H, app d, *J* 4.4, C(2)*H*), 5.02 (1H, ddd, *J* 7.3, 4.4, 1.3, C(1)*H*), 7.24-7.37 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 21.2 (CO*Me*), 26.9, 29.2 (*C*(4), *C*(5)), 55.6 (N(*C*H$_2$Ph)$_2$), 65.6 (*C*(3)), 74.5 (*C*(2)), 79.2 (*C*(1)), 127.3 (*p-Ph*), 128.5, 129.0 (*o*-, *m-Ph*), 138.4 (*i-Ph*), 170.3 (*C*OMe); *m/z* (ESI$^+$) 340 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{25}NNaO_3{}^+$ ([M+Na]$^+$) requires 362.1727; found 362.1726.

X-ray Crystal Structure Determination for 22•HBF_4

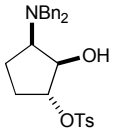


Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[14]

X-ray crystal structure data for **22•HBF_4** [$C_{21}H_{26}BF_4NO_3$]: M = 427.25, triclinic, space group P –1, a = 8.8068(2) Å, b = 10.2538(2) Å, c = 11.8459(2) Å, α = 106.3042(9) °, β = 91.0410(8) °, γ = 95.2761(9) °, V = 1021.27(4) Å^3, Z = 2, μ = 0.115 mm^{-1}, colourless plate, crystal dimensions = 0.3 × 0.3 × 0.5 mm^3. A total of 4629 unique reflections were measured for 5 < θ < 27 and 3546 reflections were used in the refinement. The final parameters were wR_2 = 0.051 and R_1 = 0.039 [I>3.0$\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733892. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

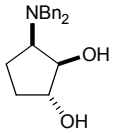
[14] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

(1*RS*,2*RS*,3*RS*)-1-*p*-Toluenesulfonyloxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cyclopentane 23



Anhydrous TsOH (664 mg, 3.86 mmol) was added to a stirred solution of **20** (216 mg, 0.77 mmol) in CH_2Cl_2 (12.8 mL) and the resultant mixture was heated at reflux for 4.5 h. The reaction mixture was then allowed to cool to rt and was diluted with CH_2Cl_2 (20 mL), washed with sat. aq. $NaHCO_3$ (3 × 30 mL), then dried and concentrated *in vacuo* to give **23** in >99:1 dr. Purification *via* flash column chromatography (gradient elution, 5%→40% EtOAc in 30-40 ºC petrol) gave **23** as a colourless gum (305 mg, 88%, >99:1 dr); R_f 0.25 (30-40 ºC petrol/EtOAc, 80:20); ν_{max} (film) 3412 (O–H), 3062, 3028, 2946, 2828 (C–H), 1599, 1494, 1454, 1362 (S=O), 1190 (C–O), 1177 (S=O); δ_H (400 MHz, $CDCl_3$) 1.61-1.79 (2H, m, C(4)H_A, C(5)H_A), 1.90-2.00 (1H, m, C(4)H_B), 2.20-2.30 (1H, m, C(5)H_B), 2.46 (3H, s, Ar*Me*), 3.26 (1H, ddd, *J* 10.6, 6.8, 4.3, C(3)*H*), 3.66 (2H, d, *J* 14.2, N(CH_AH$_B$Ph)$_2$), 3.72 (2H, d, *J* 14.2, N(CH$_A$$H_B$Ph)$_2$), 4.04 (1H, app d, *J* 4.3, C(2)*H*), 4.71 (1H, app dd, *J* 7.1, 2.5, C(1)*H*), 7.20-7.38 (12H, m, *Ar*, *Ph*), 7.79-7.84 (2H, m, *Ar*); δ_C (100 MHz, $CDCl_3$) 21.7 (Ar*Me*), 26.7, 29.4 (*C*(4), *C*(5)), 55.6 (N(*C*H$_2$Ph)$_2$), 65.3 (*C*(3)), 74.3 (*C*(2)), 85.8 (*C*(1)), 127.4, 127.9, 128.5, 129.0, 130.0, 133.7, 138.1, 144.9 (*Ar*, *Ph*); *m/z* (ESI$^+$) 452 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{26}H_{30}NO_4S^+$ ([M+H]$^+$) requires 452.1890; found 452.1888.

(1*RS*,2*RS*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 24

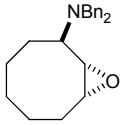


*From **20**:* 3 M aq. H_2SO_4 (3 mL) was added to a stirred solution of **20** (500 mg, 1.79 mmol) in THF (9 mL) and the resultant mixture was stirred at 40 ºC for 20 h. The reaction mixture was then allowed to cool to rt and was concentrated *in vacuo*. The residue was dissolved in Et_2O (50 mL) and washed with sat. aq. $NaHCO_3$ (3 × 20 mL), then dried and concentrated *in vacuo* to give a 96:4 mixture of **24**:**35**. Purification *via* flash column chromatography (eluent 40-60 ºC petrol/EtOAc, 50:50) gave a 96:4 mixture of **24**:**35** as a colourless oil which solidified on standing to a white crystalline solid (504 mg, 96%).

*From **21**:* Following the *General Procedure*, K_2CO_3 (152 mg, 1.1 mmol) and **21** (97 mg, 0.22 mmol) in MeOH (2 mL) gave a 97:3 mixture of **24**:**35**. Purification *via* flash column chromatography (eluent 40-60 ºC petrol/EtOAc, 50:50) gave a 97:3 mixture of **24**:**35** as a colourless oil which solidified on standing to a white crystalline solid (58 mg, 89%).

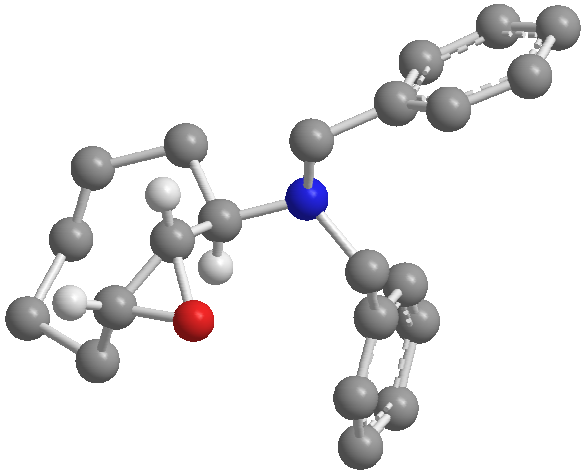
*From **22**:* following the *General Procedure*, K_2CO_3 (1.63 g, 11.8 mmol) and **22** (800 mg, 2.36 mmol) in MeOH (8 mL) gave, after purification *via* flash column chromatography (gradient elution, 12%→100% EtOAc in 40-60 ºC petrol), **24** as a colourless oil which solidified on standing to a white crystalline solid (678 mg, 97%, >99:1 dr); *Rf* 0.21 (40-60 ºC petrol/EtOAc, 50:50); mp 65-67 ºC; ν_{max} (KBr) 3400 (O–H), 3085, 3062, 3028, 2938 (C–H), 1602, 1494, 1453; δ_H (400 MHz, $CDCl_3$) 1.51 (1H, dddd, *J* 13.7, 9.1, 9.0, 4.0, C(5)H_A), 1.66-1.77 (1H, m, C(4)H_A), 1.92-2.01 (1H, m, C(4)H_B), 2.27 (1H, dddd, *J* 13.7, 9.4, 7.1, 2.4, C(5)H_B), 3.30-3.37 (1H, m, C(3)*H*), 3.37 (4H, A_2, N(CH_2Ph)$_2$), 3.91 (1H, app d, *J* 4.3, C(2)*H*), 4.19-4.24 (1H, m, C(1)*H*), 7.22-7.34 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 26.9 (*C*(4)), 31.4 (*C*(5)), 55.7 (N(*C*H_2Ph)$_2$), 65.5 (*C*(3)), 77.0 (*C*(1)), 77.2 (*C*(2)), 127.2 (*p-Ph*), 128.4, 129.0 (*o*-, *m-Ph*), 138.5 (*i-Ph*); *m/z* (ESI^+) 298 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{19}H_{24}NO_2^+$ ($[M+H]^+$) requires 298.1802; found 298.1810.

(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclooctane 25



Cl_3CCO_2H (26.7 g, 164 mmol) was added to a stirred solution of **16** (10 g, 32.7 mmol) in CH_2Cl_2 (109 mL, 0.3 M w.r.t. **16**) and the resultant mixture was stirred at rt for 5 min. *m*CPBA (74%, 8.02 g, 34.4 mmol) was then added in one portion and the reaction mixture was stirred at rt for 3.5 h. The mixture was diluted with CH_2Cl_2 (100 mL) and sat. aq. Na_2SO_3 was added until starch-iodide paper indicated no remaining peracid. Sat. aq. $NaHCO_3$ (200 mL) was added and the layers were separated. The organic layer was washed with sat. aq. $NaHCO_3$ (2 × 200 mL) then dried, filtered through a short plug of silica gel (eluent CH_2Cl_2), and concentrated *in vacuo* to give **25** as a white crystalline solid (10.4 g, quant, >99:1 dr); mp 103-105 ºC (EtOH); ν_{max} (KBr) 2972, 2926, 2854 (C–H), 1602, 1493, 1454; δ_H (400 MHz, $CDCl_3$) 0.85-0.99 (1H, m, C(8)H_A), 1.11-1.21 (1H, m, CH_2), 1.34-1.61 (5H, m, CH_2), 1.65-1.75 (2H, m, C(4)H_2), 2.10 (1H, app dq, *J* 13.7, 3.9, C(8)H_B), 2.68 (1H, app td, *J* 9.5, 6.7, C(3)*H*), 2.89 (1H, app dt, *J* 10.4, 4.4, C(1)*H*), 3.08 (1H, dd, *J* 9.5, 4.4, C(2)*H*), 3.79 (4H, AB system, J_{AB} 13.7, N(CH_2Ph)$_2$), 7.19-7.46 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 25.2, 25.5, 26.8, 27.1, 31.2 (*C*(4)-*C*(8)), 53.4 (*C*(1)), 54.6 (N(*C*H_2Ph)$_2$), 55.7 (*C*(2)), 55.8 (*C*(3)), 126.7 (*p-Ph*), 128.1, 128.7 (*o*-, *m-Ph*), 140.5 (*i-Ph*); *m/z* (ESI^+) 322 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{22}H_{28}NO^+$ ($[M+H]^+$) requires 322.2165; found 322.2161.

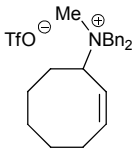
X-ray Crystal Structure Determination for 25



Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[15]

X-ray crystal structure data for **25** [$C_{22}H_{27}NO$]: M = 642.93, monoclinic, space group $P\ 2_1/c$, a = 14.8507(4) Å, b = 14.8824(4) Å, c = 16.6996(4) Å, β = 94.0401(18) °, V = 3681.67(17) Å^3, Z = 8, μ = 0.070 mm^{-1}, colourless plate, crystal dimensions = 0.2 × 0.2 × 0.3 mm^3. A total of 8288 unique reflections were measured for 5 < θ < 27 and 3748 reflections were used in the refinement. The final parameters were wR_2 = 0.133 and R_1 = 0.151 [I>3.0$\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733893. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(*RS*,*Z*)-3-(*N*,*N*-Dibenzyl-*N*-methylammonio)cyclooct-1-ene trifluoromethanesulfonate 26

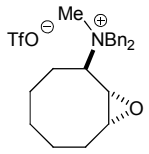


MeOTf (207 μL, 1.83 mmol) was added to a solution of **16** (559 mg, 1.83 mmol) in anhydrous Et_2O (5 mL) and the resultant mixture was stirred at rt for 2 h. The precipitate was collected *via* filtration and dissolved in CH_2Cl_2 (5 mL), then washed with sat. aq. $NaHCO_3$ (2 × 5 mL) and concentrated *in vacuo*. The residue was triturated with Et_2O and the precipitate was collected *via* filtration and dried *in vacuo* to give **26** as a white

[15] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

crystalline solid (202 mg, 23%); mp 131-133 ºC (Et_2O); ν_{max} (KBr) 3013, 2935, 2860 (C–H), 1255, 1153 (S=O); δ_H (400 MHz, $CDCl_3$) 1.17-1.35 (2H, m, CH_2), 1.44-1.66 (5H, m, CH_2), 1.70-1.83 (1H, m, CH_2), 1.98-2.10 (1H, m, CH_2), 2.41-2.53 (1H, m, CH_2), 2.82 (3H, s, N*Me*), 4.08 (1H, ddd, *J* 12.0, 8.7, 3.0, C(3)*H*), 4.42 (1H, d, *J* 13.1, N(CH_AH$_B$Ph)$_A$), 4.49 (1H, d, *J* 12.9, N(CH_AH$_B$Ph)$_B$), 4.66 (1H, d, *J* 12.9, N(CH$_A$$H_B$Ph)$_B$), 4.91 (1H, d, *J* 13.1, N(CH$_A$$H_B$Ph)$_A$), 5.94-6.10 (2H, m, C(1)*H*, C(2)*H*), 7.35-7.58 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$)[16] 24.3, 25.8, 26.6, 28.5, 28.9 (*C*(4)-*C*(8)), 46.8 (N*Me*), 63.0 (N(*C*H$_2$Ph)$_2$), 69.2 (*C*(3)), 121.6 (*C*(2)), 126.9, 127.0 (*i-Ph*), 129.3, 129.4, 130.7, 130.9, 133.2, 133.3 (*o*-, *m*-, *p-Ph*), 136.5 (*C*(1)); *m/z* (ESI$^+$) 320 ([M–OTf]$^+$, 100%); HRMS (ESI$^+$) $C_{23}H_{30}N^+$ ([M–OTf]$^+$) requires 320.2373; found 320.2377.

(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzyl-*N*-methylammonio)cyclooctane trifluoromethanesulfonate 27



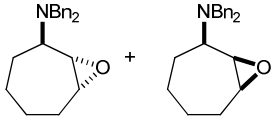
*From **25**:* MeOTf (195 μL, 1.72 mmol) was added to a solution of **25** (553 mg, 1.72 mmol) in anhydrous Et_2O (5 mL) and the resultant mixture was stirred at rt for 2 h. The precipitate was collected *via* filtration and dissolved in CH_2Cl_2 (5 mL), then washed with sat. aq. $NaHCO_3$ (2 × 5 mL) and concentrated *in vacuo*. The residue was triturated with Et_2O and the precipitate was collected *via* filtration and dried *in vacuo* to give **27** as a white crystalline solid (64 mg, 8%, >98% de); mp 186-188 ºC (Et_2O); ν_{max} (KBr) 3015, 2938, 2867 (C–H), 1253, 1153 (S=O); δ_H (400 MHz, $CDCl_3$) 0.58-0.72 (1H, m, CH_2), 1.21-1.57 (5H, m, CH_2), 1.65-1.79 (1H, m, CH_2), 1.88-2.10 (2H, m, CH_2), 2.66-2.78 (1H, m, CH_2), 2.87 (3H, s, N*Me*), 2.99-3.10 (2H, m, C(1)*H*), C(3)*H*), 3.55 (1H, dd, *J* 9.4, 4.6, C(2)*H*), 4.24 (1H, d, *J* 13.5, N(CH_AH$_B$Ph)$_A$), 4.79 (1H, d, *J* 12.6, N(CH_AH$_B$Ph)$_B$), 4.91 (1H, d, *J* 12.6, N(CH$_A$$H_B$Ph)$_B$), 5.19 (1H, d, *J* 13.5, N(CH$_A$$H_B$Ph)$_A$), 7.31-7.49 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$)[17] 25.5, 25.8, 27.1 (*C*(4)-*C*(8)), 47.2 (N*Me*), 51.5, 55.7 (*C*(1), *C*(2)), 62.7 (N(*C*H$_2$Ph)$_A$), 64.2 (N(*C*H$_2$Ph)$_B$), 71.8 (*C*(3)), 126.7, 127.0 (*i-Ph*), 129.3, 129.4, 130.7, 131.0, 132.8, 133.7 (*o*-, *m*-, *p-Ph*); *m/z* (ESI$^+$) 336 ([M–OTs$^-$]$^+$, 100%); HRMS (ESI$^+$) $C_{23}H_{30}NO^+$ ([M–OTs$^-$]$^+$) requires 336.2322; found 336.2322.

*From **26**:* Cl_3CCO_2H (177 mg, 1.08 mmol) was added to a solution of **26** (102 mg, 0.22 mmol) in CH_2Cl_2 (0.73 mL, 0.3 M w.r.t. **26**) and the resultant mixture was stirred at rt for 5 min. *m*CPBA (69%, 56.8 mg, 0.23

[16] The quartet associated with the CF_3 group was not observed within the ^{13}C NMR spectrum of **26** due to low signal intensity.
[17] The quartet associated with the CF_3 group was not observed within the ^{13}C NMR spectrum of **27** due to low signal intensity.

mmol) was then added in one portion and the reaction mixture was stirred at rt for 3.5 h. The mixture was then diluted with CH_2Cl_2 and sat. aq. Na_2SO_3 was added until starch-iodide paper indicated no remaining peracid. Sat. aq. $NaHCO_3$ (5 mL) was then added and the layers separated. The organic layer was washed with sat. aq. $NaHCO_3$ (2 × 5 mL), then dried and concentrated *in vacuo* to give 4% conversion to a 96:4 mixture of **26**:**27** as a colourless gum (103 mg).

(1*RS*,2*SR*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cycloheptane 28 and 29

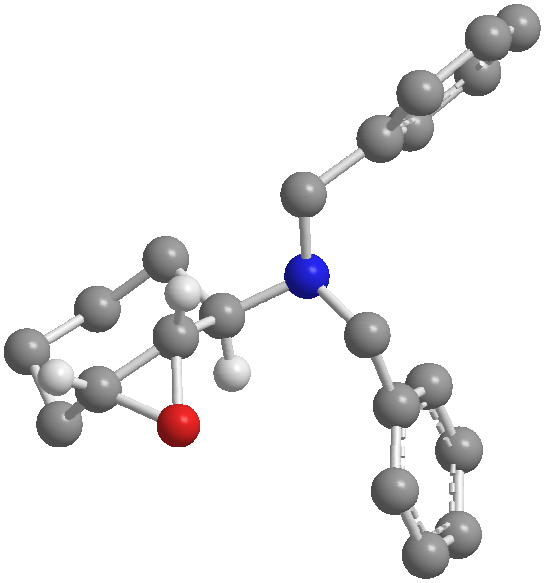


28 29

Cl_3CCO_2H (5.74 g, 35.2 mmol) was added to a stirred solution of **15** (2.05 g, 7.03 mmol) in CH_2Cl_2 (23 mL, 0.3 M w.r.t. **15**) and the resultant mixture was stirred at rt for 5 min. *m*CPBA (74%, 1.72 g, 7.38 mmol) was then added in one portion and the reaction mixture was stirred at rt for 3.5 h. The mixture was diluted with CH_2Cl_2 (25 mL) and sat. aq. Na_2SO_3 was added until starch-iodide paper indicated no remaining peracid. Sat. aq. $NaHCO_3$ (25 mL) was added and the layers were separated. The organic layer was washed with sat. aq. $NaHCO_3$ (2 × 25 mL) then dried, filtered through a short plug of silica gel (eluent CH_2Cl_2), and concentrated *in vacuo* to give a 94:6 mixture of **28**:**29**. Purification *via* flash column chromatography (gradient elution, 2%→20% Et_2O in 40-60 ºC petrol) gave **29** as a colourless oil which solidified on standing to a white crystalline solid (94 mg, 4%, >99:1 dr); R_f 0.28 (40-60 ºC petrol:Et_2O, 90:10); mp 53-55 ºC; ν_{max} (film) 3084, 3062, 3027, 2926, 2849, 2803 (C–H), 1603, 1494, 1453; δ_H (400 MHz, $CDCl_3$) 0.59-0.70 (1H, m, CH_2), 1.26-1.65 (4H, m, CH_2), 1.74-1.82 (1H, m, CH_2), 1.84-1.91 (1H, m, CH_2), 2.22-2.31 (1H, m, CH_2), 2.89 (1H, app dd, *J* 11.6, 2.8, C(1)*H*), 3.06 (1H, app t, *J* 5.3, C(3)*H*), 3.35 (1H, dd, *J* 4.8, 1.0, C(2)*H*), 3.59 (2H, d, *J* 13.9, N(CH_AH$_B$Ph)$_2$), 3.90 (2H, d, *J* 13.9, N(CH$_A$$H_B$Ph)$_2$), 7.21-7.42 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 23.4, 24.1, 27.1, 28.0 (*C*(4)-*C*(7)), 53.3 (*C*(3)), 54.3 (N(*C*H$_2$Ph)$_2$), 58.4 (*C*(1)), 60.7 (*C*(2)), 126.7 (*p*-*Ph*), 128.1, 128.5 (*o*-, *m*-*Ph*), 140.4 (*i*-*Ph*); *m/z* (ESI$^+$) 308 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{26}NO^+$ ([M+H]$^+$) requires 308.2009; found 308.2005. Further elution gave **28** as a colourless oil which solidified on standing to a white crystalline solid (1.49 g, 69%, >99:1 dr); R_f 0.17 (40-60 ºC petrol/Et_2O, 90:10); mp 69-70 ºC; ν_{max} (KBr) 3084, 3061, 3028, 2926, 2851, 2804 (C–H), 1602, 1494, 1454; δ_H (400 MHz, $CDCl_3$) 1.02-1.12 (1H, m, C(7)H_A), 1.15-1.34 (2H, m, CH_2), 1.60-1.73 (2H, m, C(4)H_2), 1.83-1.92 (2H, m, CH_2), 2.22 (1H, app ddd, *J* 13.7, 6.8, 6.5, C(7)H_B), 2.66 (1H, app dd, *J* 10.4, 7.5, C(3)*H*), 3.00 (1H, ddd, *J* 8.0, 6.5, 5.0, C(1)*H*), 3.24 (1H, dd, *J* 7.5, 5.0, C(2)*H*), 3.77 (4H, AB system, J_{AB} 13.9, N(CH_2Ph)$_2$), 7.21-7.46 (10H, m,

Ph); δ_C (100 MHz, $CDCl_3$) 24.0, 29.3, 29.8, 31.2 (*C*(4)-*C*(7)), 52.7 (*C*(3)), 54.6 (N($CH_2Ph)_2$), 55.6 (*C*(1)), 60.7 (*C*(2)), 126.8 (*p-Ph*), 128.1, 128.8 (*o-*, *m-Ph*), 140.1 (*i-Ph*); *m/z* (ESI^+) 308 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{21}H_{26}NO^+$ ($[M+H]^+$) requires 308.2009; found 308.2006.

X-ray Crystal Structure Determination for 28

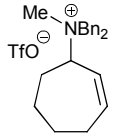


Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[18]

X-ray crystal structure data for **28** [$C_{21}H_{25}NO$]: M = 307.44, monoclinic, space group $P\ 2_1/c$, a = 9.6786(2) Å, b = 15.6935(4) Å, c = 11.6781(4) Å, β = 92.0417(10) °, V = 1772.67(8) $Å^3$, Z = 4, μ = 0.070 mm^{-1}, colourless block, crystal dimensions = 0.1 × 0.1 × 0.1 mm^3. A total of 4010 unique reflections were measured for $5 < \theta < 27$ and 1988 reflections were used in the refinement. The final parameters were wR_2 = 0.035 and R_1 = 0.034 [$I>3.0\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733894. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

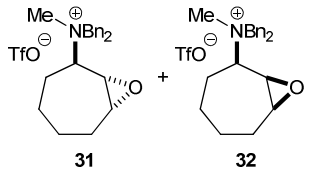
[18] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

(*RS*)-3-(*N*,*N*-Dibenzyl-*N*-methylammonio)cyclohept-1-ene trifluoromethanesulfonate 30



MeOTf (191 μL, 1.68 mmol) was added to a solution of **15** (491 mg, 1.68 mmol) in anhydrous Et_2O (5 mL) and the resultant mixture was stirred at rt for 2 h. The precipitate was collected *via* filtration and dissolved in CH_2Cl_2 (5 mL), then washed with sat. aq. $NaHCO_3$ (2 × 5 mL) and concentrated *in vacuo*. The residue was triturated with Et_2O and the precipitate was collected *via* filtration and dried *in vacuo* to give **30** as a white crystalline solid (164 mg, 21%); mp 135-137 ºC; ν_{max} (KBr) 3014, 2941, 2858 (C–H), 1256, 1153 (S=O); δ_H (400 MHz, $CDCl_3$) 1.13-1.27 (1H, m, CH_2), 1.39-1.53 (1H, m, CH_2), 1.54-1.72 (2H, m, CH_2), 1.79-1.91 (1H, m, CH_2), 2.07-2.25 (2H, m, CH_2), 2.46 (1H, app d, *J* 13.4, CH_2), 2.91 (3H, s, N*Me*), 3.84 (1H, dd, *J* 10.7, 4.2, C(3)*H*), 4.38 (1H, d, *J* 13.1, N(CH_AH$_B$Ph)$_A$), 4.52 (1H, d, *J* 13.1, N(CH_AH$_B$Ph)$_B$), 4.76 (1H, d, *J* 13.1, N(CH$_A$$H_B$Ph)$_A$), 4.81 (1H, d, *J* 13.1, N(CH$_A$$H_B$Ph)$_B$), 6.14-6.23 (1H, m, C(1)*H*), 6.38-6.48 (1H, m, C(2)*H*), 7.35-7.61 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$)[19] 24.2, 27.0, 27.2, 28.6 (*C*(4)-*C*(7)), 46.5 (N*Me*), 62.8 (N(*C*H$_2$Ph)$_A$), 63.0 (N(*C*H$_2$Ph)$_B$), 71.1 (*C*(3)), 126.0 (*C*(2)), 126.6, 126.8 (*i-Ph*), 129.3, 129.4, 130.8, 130.8, 133.1, 133.4 (*o*-, *m*-, *p-Ph*), 135.6 (*C*(1)); *m/z* (ESI$^+$) 306 ([M–OTf]$^+$, 100%); HRMS (ESI$^+$) $C_{22}H_{28}N^+$ ([M–OTf]$^+$) requires 306.2216; found 306.2218.

(1*RS*,2*SR*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzyl-*N*-methylammonio)cycloheptane trifluoromethanesulfonate 31 and 32



31 **32**

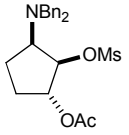
*From **28**:* MeOTf (166 μL, 1.47 mmol) was added to a solution of **28** (452 mg, 1.47 mmol) in anhydrous Et_2O (5 mL) and the resultant mixture was stirred at rt for 2 h. The precipitate was collected *via* filtration and dissolved in CH_2Cl_2 (5 mL), then washed with sat. aq. $NaHCO_3$ (2 × 5 mL), dried and concentrated *in vacuo*. The residue was triturated with Et_2O and the precipitate was collected *via* filtration and dried *in vacuo* to give **31** as a white crystalline solid (187 mg, 27%, >99:1 dr); mp 184-186 ºC; ν_{max} (KBr) 3020, 2930, 2860 (C–H), 1224, 1151 (S=O); δ_H (400 MHz, $CDCl_3$) 0.73 (1H, td, *J* 13.3, 8.8, CH_2), 1.03-1.29 (2H, m, CH_2), 1.54-1.65 (1H, m, CH_2), 1.70-1.82 (1H, m, CH_2), 1.89 (1H, app d, *J* 13.6, CH_2), 2.15-2.25 (1H, m, CH_2),

[19] The quartet associated with the CF_3 group was not observed within the ^{13}C NMR spectrum of **30** due to low signal intensity.

2.76 (1H, app d, *J* 14.4, CH_2), 2.89-2.97 (1H, m, C(3)*H*) overlapping 2.93 (3H, s, N*Me*), 3.06-3.13 (1H, m, C(1)*H*), 3.67 (1H, dd, *J* 7.7, 5.2, C(2)*H*), 4.26 (1H, d, *J* 13.4, N(CH_AH$_B$Ph)$_A$), 4.77 (1H, d, *J* 12.8, N(CH_AH$_B$Ph)$_B$), 4.94 (1H, d, *J* 12.8, N(CH$_A$$H_B$Ph)$_B$), 5.06 (1H, d, *J* 13.4, N(CH$_A$$H_B$Ph)$_A$), 7.28-7.50 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$)[20] 22.7, 26.3, 27.5, 29.0 (*C*(4)-*C*(7)), 46.3 (N*Me*), 52.3, 54.0 (*C*(1), *C*(2)), 62.0 (N(*C*H$_2$Ph)$_A$), 64.4 (N(*C*H$_2$Ph)$_B$), 73.0 (*C*(3)), 126.6, 127.0 (*i-Ph*), 129.4, 129.5, 130.8, 131.0, 133.0, 133.8 (*o*-, *m*-, *p-Ph*); *m/z* (ESI$^+$) 322 ([M–OTf]$^+$, 100%); HRMS (ESI$^+$) $C_{22}H_{28}NO^+$ ([M–OTf]$^+$) requires 322.2165; found 322.2163.

*From **30**:* Cl_3CCO_2H (92.2 mg, 0.56 mmol) was added to a solution of **30** (51 mg, 0.11 mmol) in CH_2Cl_2 (0.37 mL, 0.3 M w.r.t **30**) and the resultant mixture was stirred at rt for 5 min. *m*CPBA (69%, 30 mg, 0.12 mmol) was then added in one portion and the reaction mixture was stirred at rt for 3.5 h. The mixture was then diluted with CH_2Cl_2 and sat. aq. Na_2SO_3 was added until starch-iodide paper indicated no remaining peracid. Sat. aq. $NaHCO_3$ (5 mL) was then added, and the layers were separated. The organic layer was washed with sat. aq. $NaHCO_3$ (2 × 5 mL), then dried, filtered and concentrated *in vacuo* to give a 66:17:17 mixture of **30**:**31**:**32** as a yellow gum (49 mg). Data for **31**: δ_H (400 MHz, $CDCl_3$) [selected peaks] 5.19 (1H, d, *J* 13.3, N(CH_AH$_B$Ph)$_A$).

(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-methanesulfonyloxy-3-(*N*,*N*-dibenzylamino)cyclopentane 33

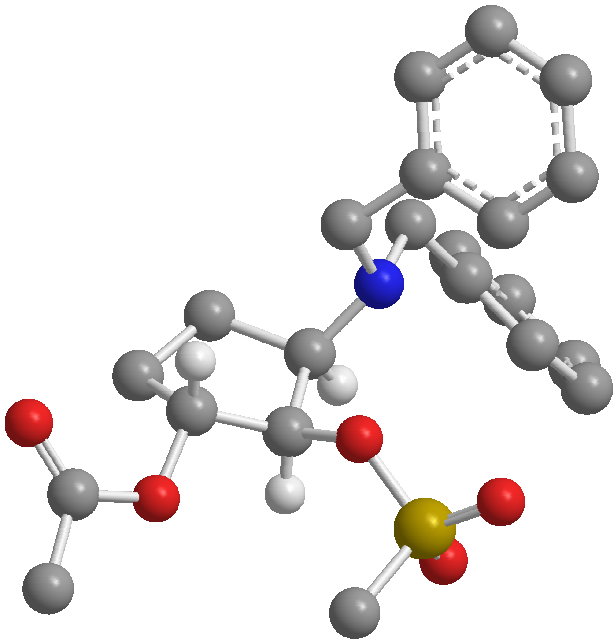


MsCl (1.32 mL, 17.1 mmol) was added dropwise to a stirred solution of **22** (4.83 g, 14.2 mmol), Et_3N (5.95 mL, 47.2 mmol) and DMAP (174 mg, 1.42 mmol) in CH_2Cl_2 (100 mL) at 0 ºC, and the resultant mixture was stirred at 0 ºC for 1 h. The reaction mixture was then allowed to warm to rt and was stirred for a further 1 h. The mixture was then washed sequentially with H_2O (100 mL) and sat. aq. $CuSO_4$ (3 × 100 mL) then dried, filtered through a short plug of silica (eluent CH_2Cl_2) and concentrated *in vacuo* to give **33** as a colourless oil which solidified on standing to a white crystalline solid (5.64 g, 93%, >99:1 dr). Recrystallisation of an aliquot (40-60 ºC petrol/$CHCl_3$, 80:20) gave an analytical sample; R_f 0.15 (40-60 ºC petrol/EtOAc, 80:20); mp 94-95 ºC (dec); ν_{max} (KBr) 3085, 3062, 3028, 2962, 2883, 2807 (C–H), 1737 (C=O), 1602, 1494, 1454, 1357 (S=O), 1238 (C–O), 1176 (S=O); δ_H (400 MHz, $CDCl_3$) 1.50-1.60 (1H, m, C(5)H_A), 1.89-1.98 (2H, m, C(4)H_2), 2.00 (3H, s, CO*Me*), 2.24-2.35 (1H, m, C(5)H_B), 3.15 (3H, s, SO_2*Me*), 3.33 (1H, app td, *J* 9.4, 5.3, C(3)*H*), 3.86 (4H, AB system, J_{AB} 14.2, N(CH_2Ph)$_2$), 5.00 (1H, dd, *J* 5.3, 1.8,

[20] The quartet associated with the CF_3 group was not observed within the ^{13}C NMR spectrum of **31** due to low signal intensity.

C(2)*H*), 5.14 (1H, ddd, *J* 6.9, 4.8, 1.8, C(1)*H*), 7.21-7.43 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 20.9 (CO*Me*), 24.2, 27.3 (*C*(4), *C*(5)), 38.8 (SO_2*Me*), 55.5 (N(*C*H_2Ph)$_2$), 61.0 (*C*(3)), 77.2 (*C*(2)), 83.8 (*C*(1)), 126.9 (*p*-*Ph*), 128.3, 128.6 (*o*-, *m*-*Ph*), 139.7 (*i*-*Ph*), 170.2 (*C*OMe); *m/z* (ESI$^+$) 418 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{22}H_{27}NNaO_5S^+$ ([M+Na]$^+$) requires 440.1502; found 440.1500.

X-ray Crystal Structure Determination for 33

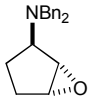


Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-*Kα* radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[21]

X-ray crystal structure data for **33** [$C_{22}H_{27}NO_5S$]: M = 417.53, monoclinic, space group $P\ 2_1/n$, a = 9.6265(2) Å, b = 7.4403(2) Å, c = 29.2042(7) Å, β = 90.7608(11) °, V = 2091.54(9) Å^3, Z = 4, μ = 0.188 mm^{-1}, colourless plate, crystal dimensions = 0.1 × 0.1 × 0.2 mm^3. A total of 4598 unique reflections were measured for 5 < θ < 27 and 2231 reflections were used in the refinement. The final parameters were wR_2 = 0.056 and R_1 = 0.049 [I>2.0σ(I)]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733895. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

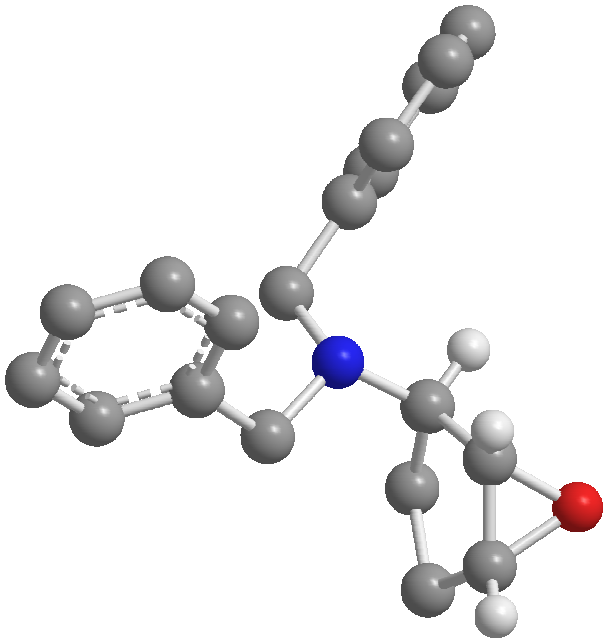
[21] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 34



A mixture of **33** (3.99 g, 9.56 mmol) and K_2CO_3 (1.59 g, 11.5 mmol) in MeOH/THF (v:v 7:3, 70 mL) was stirred at rt for 2 h then concentrated *in vacuo*. The residue was partitioned between CH_2Cl_2 (100 mL) and H_2O (100 mL) and the organic layer was washed with H_2O (2 × 100 mL), then dried, filtered through a short plug of silica (eluent CH_2Cl_2) and concentrated *in vacuo* to give **34** as a white crystalline solid (2.67 g, quant, >99:1 dr); mp 66-69 ºC; ν_{max} (KBr) 3087, 3062, 3027, 2931, 2801 (C–H), 1602, 1494, 1453; δ_H (400 MHz, $CDCl_3$) 1.44-1.56 (1H, m, C(4)H_A), 1.75-1.84 (1H, m, C(5)H_A), 1.89-1.96 (1H, m, C(4)H_B), 2.01-2.09 (1H, m, C(5)H_B), 3.44 (2H, d, *J* 13.7, N(CH_AH$_B$Ph)$_2$), 3.47 (1H, app d, *J* 2.1, C*H*), 3.50 (1H, app d, *J* 7.9, C*H*), 3.54-3.56 (1H, m, C*H*), 3.73 (2H, d, *J* 13.7, N(CH$_A$$H_B$Ph)$_2$), 7.23-7.42 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 21.6 (*C*(4)), 27.5 (*C*(5)), 55.0 (N(*C*H$_2$Ph)$_2$), 58.9 (*C*(3)), 59.2, 59.4 (*C*(1), *C*(2)), 127.0 (*p-Ph*), 128.3, 128.1 (*o-*, *m-Ph*), 139.7 (*i-Ph*); *m/z* (ESI$^+$) 280 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{19}H_{22}NO^+$ ([M+H]$^+$) requires 280.1696; found 280.1696.

X-ray Crystal Structure Determination for 34

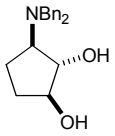


Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-*Kα* radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[22]

[22] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

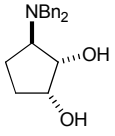
X-ray crystal structure data for **34** [$C_{19}H_{21}NO$]: M = 279.38, orthorhombic, space group $P\ n\ 2_1\ a$, a = 8.38070(10) Å, b = 8.5672(2) Å, c = 21.6908(4) Å, V = 1557.38(5) Å^3, Z = 4, μ = 0.073 mm^{-1}, colourless plate, crystal dimensions = 0.1 × 0.1 × 0.2 mm^3. A total of 1886 unique reflections were measured for $5 < \theta < 27$ and 1582 reflections were used in the refinement. The final parameters were wR_2 = 0.072 and R_1 = 0.035 [$I>3.0\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733896. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(1*RS*,2*RS*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 35



3 M aq. H_2SO_4 (1.4 mL) was added to a stirred solution of **34** (139 mg, 0.50 mmol) in THF (4.2 mL) and the resultant mixture was stirred at 40 ºC for 24 h. The reaction mixture was then allowed to cool to rt and was concentrated *in vacuo*. The residue was dissolved in Et_2O (10 mL) and washed with sat. aq. $NaHCO_3$ (3 × 10 mL), then dried and concentrated *in vacuo*. Purification *via* flash column chromatography (gradient elution, 12%→100% EtOAc in 40-60 ºC petrol) gave **35** as a colourless oil which solidified on standing to a white crystalline solid (124 mg, 83%, >99:1 dr); R_f 0.13 (40-60 ºC petrol/EtOAc, 50:50); mp 55-57 ºC; ν_{max} (KBr) 3383 (O–H), 3085, 3062, 3028, 2960, 2877, 2837, 2804 (C–H), 1602, 1494, 1454; δ_H (400 MHz, $CDCl_3$) 1.51-1.62 (1H, m, CH_2), 1.68-1.86 (2H, m, CH_2), 1.91-2.01 (1H, m, CH_2), 2.26 (2H, br s, 2 × O*H*), 3.00 (1H, app q, J 8.8, C(3)*H*), 3.54 (2H, d, J 13.9, N(CH_AH$_B$Ph)$_2$), 3.83 (2H, d, J 13.9, N(CH$_A$$H_B$Ph)$_2$), 3.85-3.90 (2H, m, C(1)*H*, C(2)*H*), 7.22-7.39 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 19.2, 28.3 (*C*(4), *C*(5)), 54.6 (N(*C*H$_2$Ph)$_2$), 64.1 (*C*(3)), 75.9 (*C*(2)), 79.5 (*C*(1)), 127.0 (*p-Ph*), 128.4, 128.6 (*o*-, *m-Ph*), 139.9 (*i-Ph*); *m/z* (ESI$^+$) 298 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{19}H_{24}NO_2^+$ ([M+H]$^+$) requires 298.1802; found 298.1801.

(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 39

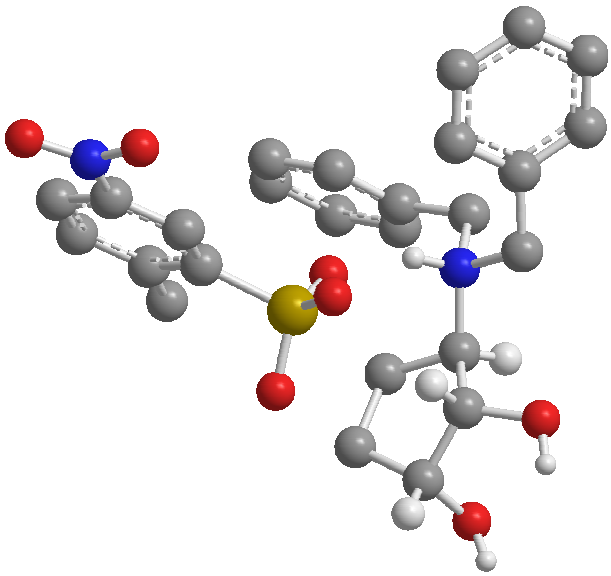


*From **33**:* KOAc (353 mg, 3.59 mmol) was added to a stirred solution of **33** (1.00 g, 2.40 mmol) in AcOH/H_2O (v:v 6:1, 40 mL) and the resultant mixture was heated at 80 °C for 18 h. The reaction mixture

was allowed to cool to rt then concentrated *in vacuo*. The residue was dissolved in Et_2O (50 mL) and the resultant solution was washed with sat. aq. $NaHCO_3$ (3 × 50 mL), then dried and concentrated *in vacuo* to give a 34:12:54 mixture of **36**:**37**:**38**. Following the *General Procedure*, transesterification with K_2CO_3 (1.64 g, 12 mmol) in MeOH (10 mL) gave a 54:46 mixture of **38**:**39**. Purification *via* flash column chromatography (gradient elution, 0%→20% EtOAc in 40-60 ºC petrol) gave **38** as a yellow oil (175 mg, 37%);[10] R_f 0.35 (40-60 ºC petrol/EtOAc, 50:50); δ_H (400 MHz, $CDCl_3$) 1.73 (1H, br s, N*H*), 3.87 (4H, s, CH_2), 7.29-7.43 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 53.2 (*C*H_2), 127.0 (*p-Ph*), 128.2, 128.5 (*o*-, *m-Ph*), 140.4 (*i-Ph*); *m/z* (ESI^+) 198 ($[M+H]^+$, 100%). Further elution (gradient elution, 20→50% EtOAc in 40-60 ºC petrol) gave **39** as a pale brown crystalline solid (311 mg, 44%, >99:1 dr). Trituration of an aliquot using Et_2O gave an analytical sample as a white crystalline solid; R_f 0.26 (40-60 ºC petrol/EtOAc, 50:50); $C_{19}H_{23}NO_2$ requires C, 76.7; H, 7.8; N, 4.7%; found C, 76.5; H, 7.7; N, 4.8%; mp 73-74 ºC; ν_{max} (KBr) 3385 (O–H), 3084, 3062, 3027, 2930 (C–H), 1602, 1494, 1453; δ_H (400 MHz, $CDCl_3$) 1.52-1.75 (2H, m, CH_2), 1.83-1.96 (2H, m, CH_2), 2.52 (2H, br s, 2 × O*H*), 3.27 (1H, app q, *J* 8.4, C(3)*H*), 3.57 (2H, d, *J* 13.9, N(C$H_A$$H_B$Ph)$_2$), 3.78 (2H, d, *J* 13.9, N(C$H_A$$H_B$Ph)$_2$), 3.92 (1H, dd, *J* 8.2, 5.2, C(2)*H*), 3.99-4.05 (1H, m, C(1)*H*), 7.22-7.43 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 19.6, 29.0 (*C*(4), *C*(5)), 55.0 (N(*C*H_2Ph)$_2$), 65.1 (*C*(3)), 71.1, 74.6 (*C*(1), *C*(2)), 127.1 (*p-Ph*), 128.4, 128.7 (*o*-, *m-Ph*), 139.9 (*i-Ph*); *m/z* (ESI^+) 298 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{19}H_{24}NO_2^+$ ($[M+H]^+$) requires 298.1802; found 298.1803.

*Dihydroxylation of **14**:* OsO_4 (52.8 mg, 1 mol%) was added to a stirred solution of **14** (5.47 g, 20.8 mmol) and NMO (7.30 g, 62.3 mmol) in acetone/H_2O (v:v 4:1, 160 mL) and the resultant mixture was stirred at rt for 4 h. Sat. aq. Na_2SO_3 (10 mL) was then added and the solution was stirred for an additional 30 min. The reaction mixture was then concentrated *in vacuo* and dissolved in CH_2Cl_2 (100 mL). The resultant solution was filtered through a short plug of silica (eluent CH_2Cl_2), dried and concentrated *in vacuo* to give a 91:9 mixture of **39**:**47**. Purification *via* flash column chromatography (gradient elution, 12%→100% EtOAc in 40-60 ºC petrol) gave **39** as a white crystalline solid (2.86 g, 46%, >99:1 dr).

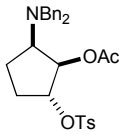
X-ray Crystal Structure Determination for 39•$MeC_6H_3(NO_2)SO_3H$



Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[23]

X-ray crystal structure data for **39•$MeC_6H_3(NO_2)SO_3H$** [$C_{26}H_{30}N_2O_7S$]: M = 514.60, triclinic, space group P –1, a = 9.2056(2) Å, b = 10.1292(2) Å, c = 14.5600(3) Å, α = 93.3862(8) °, β = 104.3284(9) °, γ = 108.7909(8) °, V = 1230.97(5) Å^3, Z = 2, μ = 0.181 mm^{-1}, colourless plate, crystal dimensions = 0.05 × 0.1 × 0.3 mm^3. A total of 5611 unique reflections were measured for 5 < θ < 27 and 5611 reflections were used in the refinement. The final parameters were wR_2 = 0.110 and R_1 = 0.059 [I>–3.0$\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733897. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(1*RS*,2*RS*,3*RS*)-1-*p*-Toluenesulfonyloxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 44

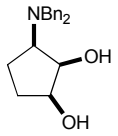


Ac_2O (370 μL, 3.96 mmol) was added to solution of **23** (1.49 g, 3.23 mmol), Et_3N (550 μL, 3.96 mmol) and DMAP (40.0 mg, 0.32 mmol) in CH_2Cl_2 (30 mL), and the resultant mixture was stirred at rt for 6 h. The

[23] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

reaction mixture was then diluted with CH_2Cl_2 (70 mL) and washed sequentially with sat. aq. $NaHCO_3$ (3 × 50 mL) and sat. aq. $CuSO_4$ (3 × 50 mL). The organic layer was then dried and concentrated *in vacuo*. Purification *via* flash column chromatography (eluent 40-60 ºC petrol/EtOAc, 80:20) gave **44** as a colourless oil which solidified on standing to a white solid (1.48 g, 93%, >99:1 dr); R_f 0.13 (40-60 ºC petrol/EtOAc, 80:20); mp 82-83 ºC (dec); ν_{max} (KBr) 3062, 3028, 2952, 2805 (C–H), 1743 (C=O), 1599, 1494, 1453, 1366 (S=O), 1231 (C–O), 1190 (C–O), 1177 (S=O); δ_H (400 MHz, $CDCl_3$) 1.63-1.74 (1H, m, CH_2), 1.75-1.86 (1H, m, CH_2), 1.87-1.96 (1H, m, CH_2) overlapping 1.93 (3H, s, CO*Me*), 2.12-2.21 (1H, m, CH_2), 2.45 (3H, s, Ar*Me*), 3.36 (1H, ddd, *J* 10.2, 7.8, 6.3, C(3)*H*), 3.65 (4H, A_2, N(CH_2Ph)$_2$), 4.76 (1H, ddd, *J* 7.2, 5.4, 3.3, C(1)*H*), 5.19 (1H, dd, *J* 6.3, 3.3, C(2)*H*), 7.19-7.32 (10H, m, *Ar*, *Ph*), 7.34 (2H, d, *J* 8.2, *Ar*), 7.76 (2H, d, *J* 8.2, *Ar*); δ_C (100 MHz, $CDCl_3$) 21.1, 21.7 (CO*Me*, Ar*Me*), 23.7, 28.5 (*C*(4), *C*(5)), 56.0 (N(*C*H_2Ph)$_2$), 60.2 (*C*(3)), 76.5 (*C*(2)), 84.3 (*C*(1)), 126.9, 127.9, 128.3, 129.9, 133.8, 139.5, 144.8 (*Ar*, *Ph*), 169.5 (*C*OMe); *m/z* (ESI$^+$) 494 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{28}H_{32}NO_5S^+$ ([M+H]$^+$) requires 494.1996; found 494.2005.

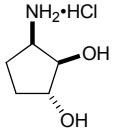
(1*RS*,2*SR*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 47



KOAc (244 mg, 2.49 mmol) was added to a stirred solution of **44** (818 mg, 1.66 mmol) in EtOH/H_2O (v:v 6:1, 30 mL) and the resultant mixture was heated at 80 °C for 6 h. The reaction mixture was allowed to cool to rt then concentrated *in vacuo*. The residue was dissolved in Et_2O (50 mL) and the resultant solution was washed with sat. aq. $NaHCO_3$ (3 × 50 mL), then dried and concentrated *in vacuo* to give a 69:31 mixture of **45**:**46** as a colourless oil (563 mg, quant). Data for **45**: δ_H (400 MHz, $CDCl_3$) 1.67-2.10 (4H, m, CH_2), 2.12 (3H, s, CO*Me*), 3.09-3.16 (1H, app td, *J* 8.5, 3.8, C(3)*H*), 3.73 (4H, A_2, N(CH_2Ph)$_2$), 4.26 (1H, app t, *J* 3.8, C(2)*H*), 4.99-5.05 (1H, m, C(1)*H*), 7.21-7.37 (10H, m, *Ph*). Data for **46**: δ_H (400 MHz, $CDCl_3$) 1.67-2.10 (4H, m, CH_2), 2.18 (3H, s, CO*Me*), 3.24 (1H, ddd, *J* 10.2, 8.2, 4.9, C(3)*H*), 3.76 (4H, A_2, N(CH_2Ph)$_2$), 4.16 (1H, app td, *J* 7.3, 4.2, C(1)*H*), 5.29 (1H, app t, *J* 4.6, C(2)*H*), 7.21-7.37 (10H, m, *Ph*). Following the *General Procedure*, transesterification with K_2CO_3 (1.15 g, 8.3 mmol) in MeOH (6 mL) gave **47** in >99:1 dr. Purification *via* flash column chromatography (gradient elution, 12%→100% EtOAc in 40-60 ºC petrol) gave **47** as a brown oil which solidified on standing to a brown solid (465 mg, 94%, >99:1 dr); R_f 0.34 (40-60 ºC petrol/EtOAc, 50:50); mp 38-40 ºC; ν_{max} (film) 3401 (O–H), 3084, 3062, 3027, 2939 (C–H), 1602, 1494, 1453; δ_H (400 MHz, $CDCl_3$) 1.74-1.95 (4H, m, CH_2), 3.09-3.17 (1H, m, C(3)*H*), 3.69 (2H, d, *J* 14.2, N(CH_AH$_B$Ph)$_2$), 3.81 (2H, d, *J* 14.2, N(CH$_A$*H*$_B$Ph)$_2$), 3.95-3.99 (1H, m, C(2)*H*), 4.10-4.15 (1H, m, C(1)*H*),

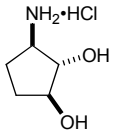
7.25-7.38 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 25.4, 31.0 (*C*(4), *C*(5)), 55.4 (N(*C*H_2Ph)$_2$), 64.2 (*C*(3)), 71.1, 72.2 (*C*(1), *C*(2)), 127.3 (*p-Ph*), 128.5, 128.9 (*o*-, *m-Ph*), 138.5 (*i-Ph*); *m/z* (ESI^+) 298 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{19}H_{24}NO_2^+$ ($[M+H]^+$) requires 298.1802; found 298.1799.

(1*RS*,2*RS*,3*RS*)-3-Aminocyclopentane-1,2-diol hydrochloride 48



$Pd(OH)_2$/C (125 mg, 50% w/w) was added to a vigorously stirred solution of **24** (250 mg, 0.84 mmol) in degassed MeOH (5 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 4 h. The suspension was filtered through a pad of Celite® (eluent MeOH), the filtrate was acidified to pH 1 with conc. aq. HCl and concentrated *in vacuo* to give **48** as a yellow gum (122 mg, 95%, >99:1 dr);[24] ν_{max} (film) 3385 (O–H, N–H); δ_H (400 MHz, d_6-DMSO) 1.32-1.44 (1H, m, C(5)H_A), 1.50-1.62 (1H, m, C(4)H_A), 1.93-2.05 (2H, m, C(4)H_B, C(5)H_B), 3.36-3.49 (1H, m, C(3)*H*), 3.81 (1H, app s, C(2)*H*), 3.89 (1H, app s, C(1)*H*), 4.96 (1H, br s, O*H*), 5.65 (1H, d, *J* 3.8, O*H*), 7.95 (3H, br s, NH_3); δ_C (100 MHz, $CDCl_3$) 26.3, 30.6 (*C*(4), *C*(5)), 52.4 (*C*(3)), 76.3, 76.5 (*C*(1), *C*(2)); *m/z* (ESI^+) 118 ($[M-Cl]^+$, 100%); HRMS (ESI^+) $C_5H_{12}NO_2^+$ ($[M-Cl]^+$) requires 118.0863; found 118.0865.

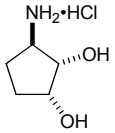
(1*RS*,2*RS*,3*SR*)-3-Aminocyclopentane-1,2-diol hydrochloride 49



$Pd(OH)_2$/C (50 mg, 50% w/w) was added to a vigorously stirred solution of **35** (100 mg, 0.34 mmol) in degassed MeOH (2 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 4 h. The suspension was filtered through a pad of Celite® (eluent MeOH), the filtrate was acidified to pH 1 with conc. aq. HCl and concentrated *in vacuo* to give **49** as a yellow gum (52 mg, quant, >99:1 dr);[24] ν_{max} (film) 3383, 2957, 2063 (O–H, N–H); δ_H (DMSO-d_6) 1.48-1.59 (1H, m, C(5)H_A), 1.60-1.72 (1H, m, C(4)H_A), 1.76-1.98 (2H, m, C(4)H_B, C(5)H_B), 3.09 (1H, app q, *J* 7.4, C(3)*H*), 3.69-3.79 (2H, m, C(1)*H*, C(2)*H*), 5.15 (1H, br s, O*H*), 5.45 (1H, d, *J* 3.5, O*H*), 8.24 (3H, br s, NH_3); δ_C (100 MHz, $CDCl_3$) 25.6, 30.1 (*C*(4), *C*(5)), 56.4 (*C*(3)), 76.2, 81.1 (*C*(1), *C*(2)); *m/z* (ESI^+) 118 ($[M-Cl]^+$, 100%); HRMS (ESI^+) $C_5H_{12}NO_2^+$ ($[M-Cl]^+$) requires 118.0863; found 118.0867.

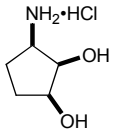
[24] Whitten, J. P.; McCarthy, J. R.; Whalon, M. R. *J. Org. Chem.* **1985**, *50*, 4399.

(1*RS*,2*SR*,3*RS*)-3-Aminocyclopentane-1,2-diol hydrochloride 50



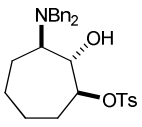
$Pd(OH)_2$/C (125 mg, 50% w/w) was added to a vigorously stirred solution of **39** (250 mg, 0.84 mmol) in degassed MeOH (5 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 4 h. The suspension was filtered through a pad of Celite® (eluent MeOH), the filtrate was acidified to pH 1 with conc. aq. HCl and concentrated *in vacuo* to give **50** as a white crystalline solid (126 mg, 97%, >99:1 dr);[25] mp 151-155 ºC; ν_{max} (KBr) 3356, 2950, 2046 (O–H, N–H); δ_H (400 MHz, d_6-DMSO); 1.42-1.59 (2H, m, C(4)H_A, C(5)H_A), 1.78-1.91 (1H, m, C(5)H_B), 1.96-2.09 (1H, m, C(4)H_B), 3.23 (1H, app q, *J* 7.8, C(3)*H*), 3.75-3.82 (1H, m, C(2)*H*), 3.85-3.92 (1H, app s, C(1)*H*), 4.69 (1H, d, *J* 3.0, O*H*), 5.18 (1H, d, *J* 5.6, O*H*), 8.29 (3H, br s, NH_3); δ_C (100 MHz, $CDCl_3$) 25.3, 29.7 (*C*(4), *C*(5)), 55.9 (*C*(3)), 71.5 (*C*(1)), 77.2 (*C*(2)); *m/z* (ESI^+) 118 ($[M-Cl]^+$, 100%); HRMS (ESI^+) $C_5H_{12}NO_2^+$ ($[M-Cl]^+$) requires 118.0863; found 118.0868.

(1*RS*,2*SR*,3*SR*)-3-Aminocyclopentane-1,2-diol hydrochloride 51



$Pd(OH)_2$/C (144 mg, 50% w/w) was added to a vigorously stirred solution of **47** (288 mg, 0.97 mmol) in degassed MeOH (5 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 4 h. The suspension was filtered through a pad of Celite® (eluent MeOH), the filtrate was acidified to pH 1 with conc. aq. HCl and concentrated *in vacuo* to give **51** as a yellow gum (176 mg, quant, >99:1 dr);[25] ν_{max} (film) 3310, 3230, 3140 (O–H, N–H); δ_H (400 MHz, d_6-DMSO) 1.57-1.75 (3H, m, CH_2), 1.82-1.92 (1H, m, CH_2), 3.28-3.38 (1H, m, C(3)*H*), 3.80-3.85 (1H, m, C(2)*H*), 3.89-3.95 (1H, m, C(1)*H*), 7.83 (3H, br s, NH_3); δ_C (100 MHz, $CDCl_3$) 26.3, 29.6 (*C*(4), *C*(5)), 51.9 (*C*(3)), 72.4 (*C*(2)), 72.8 (*C*(1)); *m/z* (ESI^+) 118 ($[M-Cl]^+$, 100%); HRMS (ESI^+) $C_5H_{12}NO_2^+$ ($[M-Cl]^+$) requires 118.0863; found 118.0865.

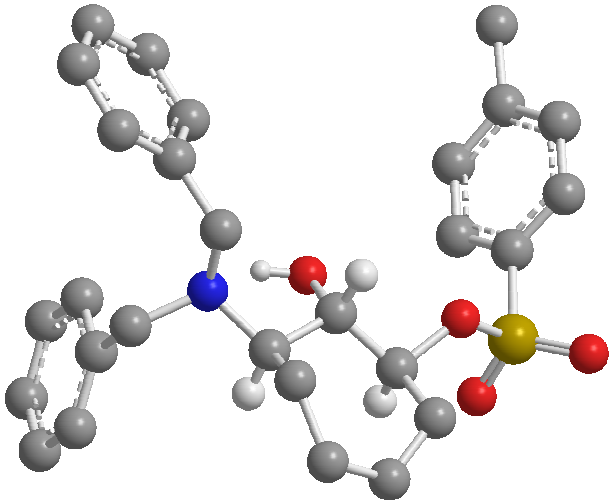
(1*RS*,2*RS*,3*SR*)-1-*p*-Toluenesulfonyloxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cycloheptane 52



[25] Whitten, J. P.; McCarthy, J. R.; Whalon, M. R. *J. Org. Chem.* **1985**, *50*, 4399.

Anydrous TsOH (280 mg, 1.63 mmol) was added to a stirred solution of **28** (100 mg, 0.33 mmol) in CH_2Cl_2 (5.2 mL) and the resultant mixture was heated at reflux for 4 h. The reaction mixture was allowed to cool to rt then diluted with CH_2Cl_2 (15 mL). The resultant solution was washed with sat. aq. $NaHCO_3$ (3 × 10 mL) then dried and concentrated *in vacuo* to give **52** as a white crystalline solid (158 mg, quant, >99:1 dr); mp 94-96 ºC (dec); ν_{max} (KBr) 3356 (O–H), 3086, 3063, 3028, 2934, 2863 (C–H), 1600, 1495, 1454, 1356 (S=O), 1175 (S=O); δ_H (400 MHz, $CDCl_3$) 1.20-1.47 (2H, m, CH_2), 1.60-1.70 (2H, m, CH_2), 1.76-1.86 (2H, m, CH_2), 1.98-2.05 (1H, m, CH_2), 2.38-2.47 (1H, m, C(4)H_A) overlapping 2.41 (3H, s, Ar*Me*), 3.28 (2H, d, *J* 13.3, N(CH_AH$_B$Ph)$_2$), 3.60 (1H, app dd, *J* 9.7, 5.3, C(3)*H*), 3.74 (2H, d, *J* 13.3, N(CH$_A$$H_B$Ph)$_2$), 4.31 (1H, app s, C(2)*H*), 4.54 (1H, ddd, *J* 7.9, 5.3, 2.2, C(1)*H*), 7.19-7.34 (12H, m, *Ar*, *Ph*), 7.81-7.85 (2H, m, *Ar*); δ_C (100 MHz, $CDCl_3$) 20.7 (*C*H$_2$), 21.7 (Ar*Me*), 22.2, 25.9, 29.3 (*C*H$_2$), 53.1 (N(*C*H$_2$Ph)$_2$), 59.9 (*C*(3)), 74.2 (*C*(2)), 87.0 (*C*(1)), 127.5, 127.8, 128.6, 129.1, 129.6, 134.4, 138.3, 144.3 (*Ar*, *Ph*); *m/z* (ESI$^+$) 480 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{28}H_{34}NO_4S^+$ ([M+H]$^+$) requires 480.2203; found 480.2186.

X-ray Crystal Structure Determination for 52



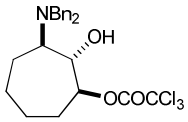
Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-*Kα* radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[26]

X-ray crystal structure data for **52** [$C_{28}H_{33}NO_4S$]: M = 479.64, monoclinic, space group *P* $2_1/n$, *a* = 9.8999(2) Å, *b* = 12.3140(3) Å, *c* = 20.6999(6) Å, *β* = 91.4895(9) º, *V* = 2522.62(11) Å^3, *Z* = 4, μ = 0.162 mm^{-1}, colourless block, crystal dimensions = 0.1 × 0.1 × 0.1 mm^3. A total of 5723 unique reflections were measured for 5 < *θ* < 27 and 3124 reflections were used in the refinement. The final parameters were *wR*$_2$ =

[26] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

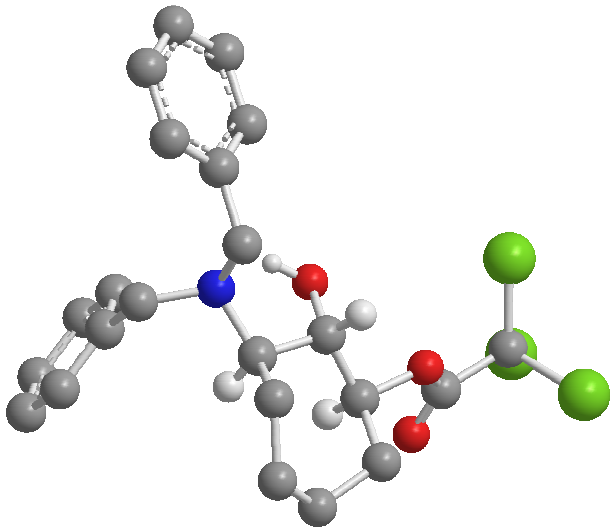
0.126 and R_1 = 0.062 [I>2.3σ(I)]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733898. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(1*RS*,2*RS*,3*SR*)-1-Trichloroacetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cycloheptane 53



Anhydrous Cl_3CCO_2H (266 mg, 1.63 mmol) was added to a stirred solution of **28** (100 mg, 0.33 mmol) in CH_2Cl_2 (5 mL) and the resultant mixture was heated at reflux for 12 h. The reaction mixture was allowed to cool to rt then diluted with CH_2Cl_2 (15 mL). The resultant solution was washed with sat. aq. $NaHCO_3$ (3 × 10 mL) then dried and concentrated *in vacuo*. Purification *via* recrystallisation (40-60 ºC petrol/$CHCl_3$, 80:20) gave **53** as a white crystalline solid (135 mg, 87%, >99:1 dr); mp 119-121 ºC; ν_{max} (KBr) 3375 (O–H), 3086, 3063, 3028, 2936, 2864 (C–H), 1761 (C=O), 1603, 1495, 1454; δ_H (400 MHz, $CDCl_3$) 1.32-1.54 (3H, m, CH_2), 1.62-1.75 (2H, m, CH_2), 1.77-1.91 (2H, m, CH_2), 2.05-2.16 (1H, m, CH_2), 2.56 (1H, app t, *J* 9.4, C(3)*H*), 3.35 (2H, d, *J* 13.2, N(CH_AH$_B$Ph)$_2$), 3.76 (1H, dd, *J* 9.9, 6.5, C(2)*H*), 3.85 (2H, d, *J* 13.2, N(CH$_A$$H_B$Ph)$_2$), 4.64 (1H, br s, O*H*), 4.78-4.85 (1H, m, C(1)*H*), 7.25-7.37 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 20.7, 21.8, 25.2, 27.7 (*C*(4)-*C*(7)), 53.2 (N(*C*H$_2$Ph)$_2$), 59.4 (*C*(3)), 73.6 (*C*(2)), 84.5 (*C*(1)), 90.3 (*C*Cl$_3$), 127.6 (*p*-*Ph*), 128.7, 129.1 (*o*-, *m*-*Ph*), 138.2 (*i*-*Ph*), 161.1 (*C*OCCl$_3$); *m/z* (ESI$^+$) 470 ([M+H]$^+$, 45%), 326 (100); HRMS (ESI$^+$) $C_{23}H_{26}{}^{35}Cl_3NNaO_3^+$ ([M+Na]$^+$) requires 492.0870; found 492.0867.

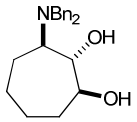
X-ray Crystal Structure Determination for 53



Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[27]

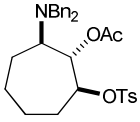
X-ray crystal structure data for **53** [$C_{23}H_{26}Cl_3NO_3$]: M = 470.82, monoclinic, space group $P\ 2_1/n$, a = 9.3961(4) Å, b = 14.0160(6) Å, c = 18.0227(9) Å, β = 99.271(2) °, V = 2342.51(18) Å^3, Z = 4, μ = 0.415 mm^{-1}, colourless block, crystal dimensions = 0.1 × 0.1 × 0.1 mm^3. A total of 5073 unique reflections were measured for $5 < \theta < 27$ and 3687 reflections were used in the refinement. The final parameters were wR_2 = 0.078 and R_1 = 0.047 [$I>3.0\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733899. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(1*RS*,2*RS*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cycloheptane-1,2-diol 54



Following the *General Procedure*, K_2CO_3 (138 mg, 1.0 mmol) and **53** (95.3 mg, 0.2 mmol) in MeOH (1 mL) gave **54** as a colourless oil that solidified on standing to a white crystalline solid (53.9 mg, 83%, >99:1 dr); mp 90-92 ºC; ν_{max} (KBr) 3406 (O–H), 3086, 3064, 3028, 2934, 2863 (C–H), 1603, 1495, 1454; δ_H (400 MHz, $CDCl_3$) 1.35-1.59 (4H, m, CH_2), 1.62-1.72 (1H, m, CH_2), 1.74-1.84 (2H, m, CH_2), 1.94-2.01 (1H, m, CH_2), 2.40-2.47 (1H, m, C(3)*H*), 2.85 (1H, s, O*H*), 3.24-3.30 (1H, m, C(1)*H*), 3.34 (2H, d, *J* 13.3, N(CH_AH$_B$Ph)$_2$), 3.36-3.41 (1H, m, C(2)*H*), 3.85 (2H, d, *J* 13.3, N(CH$_A$$H_B$Ph)$_2$), 4.69 (1H, br s, O*H*), 7.23-7.38 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 20.8, 21.5, 23.9, 29.9 (*C*(4)-*C*(7)), 53.2 (N(*C*H$_2$Ph)$_2$), 60.0 (*C*(3)), 75.9, 76.0 (*C*(1), (*C*(2)), 127.4 (*p-Ph*), 128.6, 129.1 (*o*-, *m-Ph*), 138.7 (*i-Ph*); *m/z* (ESI$^+$) 326 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{28}NO_2^+$ ([M+H]$^+$) requires 326.2115; found 326.2120.

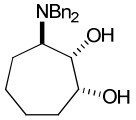
(1*RS*,2*RS*,3*SR*)-1-*p*-Toluenesulfonyloxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)cycloheptane 55



[27] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

Ac_2O (345 μL, 3.65 mmol) was added to solution of **52** (876 mg, 1.83 mmol), Et_3N (305 μL, 2.19 mmol) and DMAP (22.3 mg, 0.18 mmol) in CH_2Cl_2 (20 mL), and the resultant mixture was stirred at rt for 18 h. The reaction mixture was then diluted with CH_2Cl_2 (30 mL) and washed sequentially with sat. aq. $NaHCO_3$ (3 × 50 mL) and sat. aq. $CuSO_4$ (3 × 50 mL). The organic layer was dried and concentrated *in vacuo*. Purification *via* trituration from EtOH gave **55** as a white crystalline solid (765 mg, 80%, >99:1 dr); mp 119-120 ºC (dec); ν_{max} (KBr) 3085, 3062, 3028, 2932, 2864, 2805 (C–H), 1739 (C=O), 1599, 1495, 1454, 1371 (S=O), 1236 (C–O), 1177 (S=O); δ_H (400 MHz, $CDCl_3$) 1.08-1.20 (1H, m, CH_2), 1.47-1.78 (5H, m, CH_2), 1.88-2.02 (2H, m, CH_2) overlapping 1.94 (3H, s, CO*Me*), 2.25 (3H, s, Ar*Me*), 2.63 (1H, app dd, *J* 9.9, 8.4, C(3)*H*), 3.22 (2H, d, *J* 13.6, N(CH_AH$_B$Ph)$_2$), 3.50 (2H, d, *J* 13.6, N(CH$_A$$H_B$Ph)$_2$), 4.66 (1H, app dd, *J* 8.1, 4.6, C(1)*H*), 5.03 (1H, dd, *J* 8.4, 4.6, C(2)*H*), 7.17-7.32 (12H, m, *Ar*, *Ph*), 7.79-7.83 (2H, m, *Ar*); δ_C (100 MHz, $CDCl_3$) 21.1, 21.5 (CO*Me*, Ar*Me*), 21.8, 22.2, 27.0, 28.6 (*C*(4)-*C*(7)), 53.5 (N(*C*H$_2$Ph)$_2$), 62.6 (*C*(3)), 74.8 (*C*(2)), 81.9 (*C*(1)), 126.9, 127.6, 128.1, 128.9, 129.9, 134.4, 139.7, 144.8 (*Ar*, *Ph*), 169.6 (*C*OMe); *m/z* (ESI$^+$) 522 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{30}H_{36}NO_5S^+$ ([M+H]$^+$) requires 522.2309; found 522.2298.

(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cycloheptane-1,2-diol 58

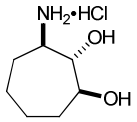


*From **52**:* KOAc (53.4 mg, 0.54 mmol) was added to a stirred solution of **55** (189 mg, 0.36 mmol) in EtOH/H_2O (v:v 6:1, 7.6 mL) and the resultant mixture was heated at reflux for 12 h. The reaction mixture was allowed to cool to rt then concentrated *in vacuo*. The residue was dissolved in Et_2O (20 mL) and the resultant solution was washed with sat. aq. $NaHCO_3$ (3 × 10 mL), then dried and concentrated *in vacuo* to give a 75:25 mixture of **56**:**57** as a colourless oil (132 mg). Data for **56**: δ_H (400 MHz, $CDCl_3$) 1.20-2.13 (8H, m, CH_2) overlapping 1.74 (3H, s, CO*Me*), 2.91 (1H, app td, *J* 9.5, 3.1, C(3)*H*), 3.37 (2H, d, *J* 13.2, N(CH_AH$_B$Ph)$_2$), 3.66 (1H, dd, *J* 9.5, 2.4, C(2)*H*), 3.83 (2H, d, *J* 13.2, N(CH$_A$$H_B$Ph)$_2$), 3.83 (1H, s, O*H*), 5.29-5.33 (1H, m, C(1)*H*), 7.21-7.39 (10H, m, *Ph*). Data for **57**: δ_H (400 MHz, $CDCl_3$) 1.20-2.13 (8H, m, CH_2) overlapping 2.08 (3H, s, CO*Me*), 2.79 (1H, ddd, *J* 10.2, 7.3, 2.7, C(3)*H*), 3.39 (2H, d, *J* 13.7, N(CH_AH$_B$Ph)$_2$), 3.74 (2H, d, *J* 13.7, N(CH$_A$$H_B$Ph)$_2$), 3.94-3.99 (1H, m, C(1)*H*), 5.41-5.46 (1H, m, C(2)*H*), 7.21-7.39 (10H, m, *Ph*). Following the *General Procedure*, transesterification with K_2CO_3 (249 mg, 1.8 mmol) in MeOH (2 mL) gave **58** in >99:1 dr. Purification *via* flash column chromatography (gradient elution, 5%→40% EtOAc in 40-60 ºC petrol) gave **58** as a colourless oil (115 mg, quant, >99:1 dr); R_f 0.18 (40-60 ºC petrol/EtOAc, 80:20); ν_{max} (film) 3425 (O–H), 3085, 3062, 3028, 2929, 2859 (C–H), 1603, 1495,

1454, 1260, 1104, 1073, 1030; δ_H (400 MHz, $CDCl_3$) 1.30-1.84 (7H, m, CH_2), 1.97-2.05 (1H, m, CH_2), 2.46 (1H, s, O*H*), 2.85 (1H, app td, *J* 9.8, 2.1, C(3)*H*), 3.37 (2H, d, *J* 13.2, N(C$H_A$$H_B$Ph)$_2$), 3.50 (1H, dd, *J* 9.8, 3.6, C(2)*H*), 3.82 (2H, d, *J* 13.2, N(C$H_A$$H_B$Ph)$_2$), 4.08-4.13 (1H, m, C(1)*H*), 4.99 (1H, br s, O*H*), 7.24-7.36 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 18.9, 22.1, 24.6, 28.6 (*C*(4)-*C*(7)), 53.4 N(*C*H_2Ph)$_2$), 56.7 (*C*(3)), 68.8 (*C*(1)), 73.7 (*C*(2)), 127.4 (*p-Ph*), 128.6, 129.2 (*o*-, *m-Ph*), 138.6 (*i-Ph*); *m/z* (ESI^+) 326 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{21}H_{28}NO_2^+$ ($[M+H]^+$) requires 326.2115; found 326.2115.

*Dihydroxylation of **15**:* OsO_4 (4.4 mg, 1 mol%) was added to a stirred solution of **15** (500 mg, 1.72 mmol) and NMO (603 mg, 5.15 mmol) in acetone/H_2O (v:v 4:1, 13.2 mL) and the resultant mixture was stirred at rt for 4 h. Sat. aq. Na_2SO_3 (10 mL) was then added and the solution was stirred for an additional 30 min. The reaction mixture was then concentrated *in vacuo* and dissolved in CH_2Cl_2 (100 mL). The resultant solution was filtered through a short plug of silica (eluent CH_2Cl_2) then dried and concentrated *in vacuo* to give an 83:17 mixture of **58**:**97**. Purification *via* flash column chromatography (gradient elution, 5%→40% EtOAc in 40-60 ºC petrol) gave **97** as a yellow oil (21 mg, 4%, >99:1 dr); R_f 0.08 (40-60 ºC petrol/EtOAc, 80:20); ν_{max} (film) 3418 (O–H), 3104, 3084, 3062, 3027, 3004, 2931, 2862, 2800 (C–H), 1602, 1493, 1453; δ_H (400 MHz, $CDCl_3$) 1.15-1.29 (1H, m, CH_2), 1.41-1.79 (6H, m, CH_2), 2.02-2.13 (1H, m, CH_2), 2.77 (1H, ddd, *J* 11.2, 3.9, 2.0, C(3)*H*), 3.51-3.58 (1H, m, C*H*), 3.76 (4H, AB system, J_{AB} 14.4, N(CH_2Ph)$_2$), 4.23 (1H, app s, C*H*), 7.20-7.41 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 21.6, 22.4, 24.9, 32.2 (*C*(4)-*C*(7)), 54.9 (N(*C*H_2Ph)$_2$), 56.8 (*C*(3)), 74.4, 75.2 (*C*(1), *C*(2)), 126.8 (*p-Ph*), 128.3, 128.5 (*o*-, *m-Ph*), 140.5 (*i-Ph*); *m/z* (ESI^+) 326 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{21}H_{28}NO_2^+$ ($[M+H]^+$) requires 326.2115; found 326.2113. Further elution gave **58** as a yellow oil (137 mg, 24%, >99:1 dr).

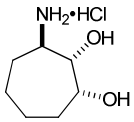
(1*RS*,2*RS*,3*SR*)-3-Aminocycloheptane-1,2-diol hydrochloride 59



$Pd(OH)_2$/C (125 mg, 50% w/w) was added to a vigorously stirred solution of **54** (250 mg, 0.84 mmol) in degassed MeOH (5 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 4 h. The suspension was filtered through a pad of Celite® (eluent MeOH), the filtrate was acidified to pH 1 with conc. aq. HCl and concentrated *in vacuo* to give **59** as a white crystalline solid (129 mg, 93%, >99:1 dr); mp 168-171 ºC; ν_{max} (KBr) 3356 (O–H, N–H), 2938 (C–H); δ_H (400 MHz, d_6-DMSO) 1.29-1.90 (8H, m, CH_2), 2.85 (1H, app s, C(3)*H*), 3.22-3.31 (1H, m, C(2)*H*), 3.33-3.45 (1H, m, C(1)*H*), 4.94 (1H, d, *J* 3.0, O*H*), 5.61 (1H, d, *J* 4.3, O*H*), 7.96 (3H, br s, NH_3); δ_C (100 MHz, $CDCl_3$) 21.6, 24.2, 28.2, 31.7 (*C*(4)-*C*(7)), 55.0 (*C*(3)),

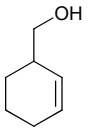
74.3 (*C*(1)), 78.3 (*C*(2)); *m/z* (ESI$^+$) 146 ([M–Cl]$^+$, 100%); HRMS (ESI$^+$) $C_7H_{16}NO_2^+$ ([M–Cl]$^+$) requires 146.1176; found 146.1178.

(1*RS*,2*SR*,3*RS*)-3-Aminocycloheptane-1,2-diol hydrochloride 60



$Pd(OH)_2$/C (61 mg, 50% w/w) was added to a vigorously stirred solution of **58** (123 mg, 0.38 mmol) in degassed MeOH (5 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 4 h. The suspension was filtered through a pad of Celite® (eluent MeOH), the filtrate was acidified to pH 1 with conc. aq. HCl and concentrated *in vacuo* to give **60** as a yellow gum (69 mg, quant, >99:1 dr); ν_{max} (film) 3385 (O–H, N–H), 2933 (C–H); δ_H (400 MHz, d_6-DMSO) 1.31-1.92 (8H, m, CH_2), 3.03-3.14 (1H, m, C(3)*H*), 3.48 (1H, app dd, *J* 9.1, 1.9, C(2)*H*), 3.92 (1H, app d, *J* 6.8, C(1)*H*), 3.92 (3H, br s, NH_3); δ_C (100 MHz, $CDCl_3$) 22.9, 23.7, 29.2, 31.3 (*C*(4)-*C*(7)), 54.2 (*C*(3)), 72.0 (*C*(1)), 75.8 (*C*(2)); *m/z* (ESI$^+$) 146 ([M–Cl]$^+$, 100%); HRMS (ESI$^+$) $C_7H_{16}NO_2^+$ ([M–Cl]$^+$) requires 146.1176; found 146.1178.

(*RS*)-3-(Hydroxymethyl)cyclohex-1-ene 62

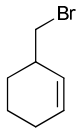


BuLi (1.6 M in hexanes, 200 mL, 320 mmol) was added to a degassed suspension of KO^{t}Bu (33.9 g, 302 mmol) in cyclohexene **61** (270 mL, 2.7 mol) under an atmosphere of nitrogen. The reaction mixture was kept below 15 ºC over a period of 2 h, and then allowed to warm to rt over 16 h. The resultant suspension was cooled to 0 °C and $(CH_2O)_n$ (9.98 g, 332 mmol) was added (*Exothermic!*). The reaction mixture was heated to 60 ºC for 3 h, then cooled to 0 °C and quenched with sat. aq. $NaHCO_3$ (200 mL). The mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (200 mL) and brine (200 mL), dried and concentrated *in vacuo* to give **62** as a yellow oil (29.2 g, 86%) that was used without purification. Purification of an aliquot *via* flash column chromatography (gradient elution, 1%→70% Et_2O in 30-40 °C petrol) gave an analytical sample;[28] δ_H (400 MHz, $CDCl_3$) 1.25-1.33 (1H, m, C(6)H_A), 1.42-1.51 (1H, m, C(6)H_B), 1.63-1.75 (2H, m, C(5)H_2), 1.86-1.92 (2H, m,

[28] Clausen, R. P.; Bols, M. *J. Org. Chem.* **2000**, *65*, 2797.

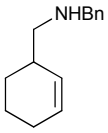
C(4)H_2), 2.20-2.21 (1H, m, C(3)*H*), 3.40 (2H, d, *J* 6.4, CH_2OH), 5.52-5.55 (1H, m, C*H*=CH), 5.69-5.72 (1H, m, CH=C*H*).

(*RS*)-3-(Bromomethyl)cyclohex-1-ene 63



NBS (25.5 g, 143 mmol) was added to a stirred solution of **62** (11.1 g, 99 mmol) and PPh_3 (36.3 g, 138 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The resultant mixture was stirred for 17 h at rt and then concentrated *in vacuo*. The residue was dissolved in 30-40 °C petrol/Et_2O (v:v 1:1) and filtered through a short plug of silica gel (eluent 30-40 °C petrol/Et_2O) to give **63** as a colourless oil (13 g, 74%) that was used without purification;[29] δ_H (400 MHz, $CDCl_3$) 1.36-1.91 (6H, m, C(4)H_2, C(5)H_2, C(6)H_2), 2.44-2.57 (1H, m, C(3)*H*), 3.27-3.41 (2H, m, CH_2Br), 5.56-5.64 (1H, m, C*H*=CH), 5.78-5.87 (1H, m, CH=C*H*).

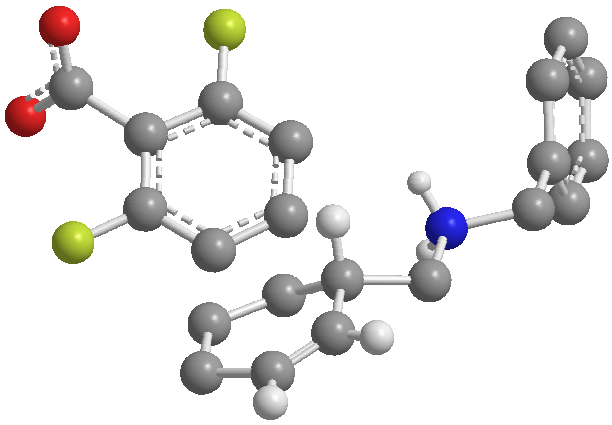
(*RS*)-3-(*N*-Benzylamino)methyl-cyclohex-1-ene 64



A stirred mixture of **63** (1.0 g, 5.71 mmol), benzylamine (5 mL, 45.7 mmol) and NaI (85 mg, 0.57 mmol) was heated at 50 °C for 20 h. The reaction mixture was cooled to rt and diluted with EtOAc (100 mL). The mixture was washed with 1 M aq. NaOH (100 mL) and the aqueous layer was extracted with EtOAc (2 × 100 mL). The combined organic extracts were dried and concentrated *in vacuo*. Purification *via* flash column chromatography (eluent 30-40 °C petrol/Et_2O, 85:15) gave **64** as a yellow oil (700 mg, 61%);[30] ν_{max} (film) 2931 (N–H), 1449 (C=C); δ_H (400 MHz, $CDCl_3$) 1.32-1.37 (1H, m, C(6)H_A), 1.52-1.58 (1H, m, C(5)H_A), 1.71-1.79 (1H, m, C(5)H_B), 1.80-1.86 (1H, m, C(6)H_B), 1.97-2.03 (2H, m, C(4)H_2), 2.30-2.36 (1H, m, C(3)*H*), 2.53-2.63 (2H, m, C(3)CH_2N), 3.79-3.86 (2H, m, NCH_2Ph), 5.60-5.63 (1H, m, C*H*=CH), 5.72-5.76 (1H, m, CH=C*H*), 7.25-7.35 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 21.2, 25.4, 27.2 (*C*(4), *C*(5), *C*(6)), 35.5 (*C*(3)), 54.0 (C(3)*C*H_2N), 54.6 (N*C*H_2Ph), 126.9 (*p-Ph*), 128.1, 128.4, 128.5, 129.7 (*C*(1), *C*(2), *o*-, *m-Ph*), 140.3 (*i-Ph*); *m/z* (ESI$^+$) 202 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{14}H_{20}N^+$ ([M+H]$^+$) requires 202.1590; found 202.1596.

[29] Walton, J. C. *J. Chem. Soc.*, *Perkin Trans. 2*, **1986**, 1641.
[30] Solé, D.; Cancho, Y.; Llebaria, A.; Moretó, J. M.; Delgado, A. *J. Org. Chem.* **1996**, *61*, 5895.

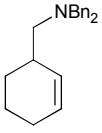
X-ray Crystal Structure Determination for 64•2,6-$F_2C_6H_3CO_2H$



Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[31]

X-ray crystal structure data for **64•2,6-$F_2C_6H_3CO_2H$** [$C_{28}H_{27}F_4NO_4$]:[32] M = 517.52, monoclinic, space group *P* 21/*n*, *a* = 10.37900(10) Å, *b* = 13.8632(2) Å, *c* = 18.1137(2) Å, β = 102.1347(5)°, *V* = 2548.08(5) Å^3, *Z* = 4, μ = 0.109 mm^{-1}, colourless plate, crystal dimensions = 0.05 × 0.2 × 0.2 mm^3. A total of 5832 unique reflections were measured for 5 < θ < 27 and 3342 reflections were used in the refinement. The final parameters were wR_2 = 0.072 and R_1 = 0.066 [I>3.0$\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733900. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohex-1-ene 65



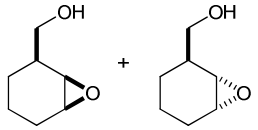
^{i}Pr$_2$NEt (1.1 mL, 6.26 mmol) and BnBr (0.74 mL, 6.26 mmol) were added sequentially to a stirred solution of **64** (840 mg, 4.17 mmol) in CH_2Cl_2 (10 mL) at rt. The resultant solution was heated to 40 °C for 2 h and allowed to cool to rt. The reaction mixture was diluted with 2 M aq. KOH (20 mL) and extracted with Et_2O (2 × 20 mL). The combined organic extracts were washed with brine (50 mL), dried and concentrated *in*

[31] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

[32] Compound **64•2,6-$F_2C_6H_3CO_2H$** co-crystallised with an additional molecule of 2,6-difluorobenzoic acid in the asymmetric unit.

vacuo. Purification *via* flash column chromatography (eluent 30-40 °C petrol/Et_2O, 98:2) gave **65** as a colourless oil (1.05 g, 87%); Found C, 86.6; H, 8.7; N, 4.8%; $C_{21}H_{25}N$ requires C, 86.55; H, 8.65; N, 4.8%; ν_{max} (film) 1451 (C=C); δ_H (400 MHz, $CDCl_3$) 1.28-1.35 (1H, m, C(6)H_A), 1.48-1.61 (2H, m, C(5)H_2), 1.86-1.90 (1H, m, C(6)H_B), 1.93-1.99 (2H, m, C(4)H_2), 2.32-2.37 (2H, m, C(3)CH_2N), 2.40-2.45 (1H, m, C(3)*H*), 3.51 (2H, d, *J* 13.6, N(C$H_A$$H_B$Ph)$_2$), 3.68 (2H, d, *J* 13.6, N(C$H_A$$H_B$Ph)$_2$), 5.69-5.74 (2H, m, C(1)*H*, C(2)*H*), 7.24-7.43 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 21.0 (*C*(6)), 25.5 (*C*(4)), 27.4 (*C*(5)), 33.4 (*C*(3)), 58.7 (N(*C*H_2Ph)$_2$), 59.3 (C(3)*C*H_2N), 126.8 (*p-Ph*), 127.6 (*C*H=CH), 128.1, 128.9 (*o-*, *m-Ph*), 130.2 (CH=*C*H), 139.9 (*i-Ph*); *m/z* (ESI^+) 292 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{21}H_{26}N^+$ ($[M+H]^+$) requires 292.2060; found 292.2060.

(1*RS*,2*SR*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-hydroxymethyl-cyclohexane 66 and 67



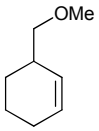
66 **67**

*m*CPBA (70%, 2.45 g, 9.94 mmol) was added to a stirred solution of **62** (744 mg, 6.63 mmol) in CH_2Cl_2 (16 mL) at 0 °C. The reaction mixture was allowed to warm to rt over 1 h and then quenched with 10% aq. Na_2SO_3 (10 mL) and sat. aq. $NaHCO_3$ (10 mL). The mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried and concentrated *in vacuo* to give a 76:24 mixture of **66**:**67**. Purification *via* flash column chromatography (gradient elution, 10%→90% Et_2O in 30-40 °C petrol) gave a 76:24 mixture of **66**:**67** as a colourless oil (579 mg, 68%); ν_{max} (film) 3386 (N−H), 2935, 2864 (C−H), 1445, 1024; *m/z* (CI^+) 129 ($[M+H]^+$, 60%), 111 (100); $C_7H_{13}O_2^+$ ($[M+H]^+$) requires 129.0910; found 129.0908.

Data for **66**: δ_H (400 MHz, C_6D_6) 0.95-0.98 (1H, m, C(5)H_A), 1.12-1.22 (2H, m, C(4)H_2), 1.35-1.53 (2H, m, C(5)H_B, C(6)H_A), 1.70-1.76 (1H, m, C(6)H_B), 1.83-1.86 (1H, m, C(3)*H*), 2.94 (1H, m, C(1)*H*), 3.16 (1H, m, C(2)*H*), 3.60-3.62 (1H, m, C(3)C$H_A$$H_B$OH), 3.75-3.80 (1H, m, C(3)$H_B$$H_B$OH); δ_C (100 MHz, C_6D_6) 19.5, 21.9, 24.1 (*C*(4), *C*(5), *C*(6)), 37.6 (*C*(3)), 51.9 (*C*(1)), 53.4 (*C*(2)), 65.1 (C(3)*C*H_2OH).

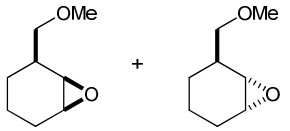
Data for **67**: δ_H (400 MHz, C_6D_6) [selected peaks] 2.92-2.96 (1H, m, C(1)*H*), 3.30-3.49 (2H, m, C(3)CH_2OH); δ_C (100 MHz, C_6D_6) 17.5, 24.1, 30.1 (*C*(4), *C*(5), *C*(6)), 37.9 (*C*(3)), 52.3 (*C*(1)), 53.9 (*C*(2)), 65.0 (C(3)*C*H_2OH).

(*RS*)-3-(Methoxymethyl)cyclohex-1-ene 68



NaH (60% dispersion in mineral oil, 803 mg, 20.1 mmol) was added to a stirred solution of **62** (1.0 g, 8.92 mmol) in THF/DMF (v:v 4:1, 12.5 mL) at 0 °C. After 30 min, the reaction mixture was diluted with THF/DMF (v:v 11 mL/4.5 mL) and MeI (1.24 mL, 19.9 mmol) was added dropwise. The mixture was allowed to warm to rt and stirred for 48 h. The reaction was cooled to 0 °C, quenched with 2 M aq. KOH (20 mL) and allowed to warm to rt over 3 h. The mixture was extracted with Et_2O (2 × 50 mL), and the combined organic extracts were washed sequentially with H_2O (2 × 100 mL) and brine (50 mL), dried and concentrated *in vacuo*. Purification *via* flash column chromatography (gradient elution, 2%→50% Et_2O in 30-40 °C petrol) gave **68** as a colourless oil (942 mg, 84%); ν_{max} (film) 3019, 2979, 2862 (C–H), 1449 (C=C); δ_H (400 MHz, $CDCl_3$) 1.31-1.37 (1H, m, C(4)H_A), 1.50-1.56 (1H, m, C(5)H_A), 1.70-1.79 (2H, m, C(4)H_B, C(5)H_B), 1.93-1.99 (2H, m, C(6)H_2), 2.36-2.39 (1H, m, C(3)*H*), 3.25-3.27 (2H, m, C(3)CH_2O), 3.35 (3H, s, O*Me*), 5.56-5.63 (1H, m, C*H*=CH), 5.73-5.77 (1H, m, CH=C*H*); δ_C (100 MHz, $CDCl_3$) 20.1 (*C*(5)), 25.3 (*C*(6)), 25.9 (*C*(4)), 35.7 (*C*(3)), 58.8 (O*Me*), 77.1 (C(3)*C*H_2O), 128.3, 128.6 (*C*(1), *C*(2)).[33]

(1*RS*,2*SR*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-methoxymethyl-cyclohexane 69 and 70



69 **70**

*From a 76:24 mixture of **66**:**67**:* NaH (60% dispersion in mineral oil, 356 mg, 8.9 mmol) was added to a stirred solution of a 76:24 mixture of **66**:**67** (571 mg, 4.45 mmol) in THF/DMF (v:v 3:1, 20 mL) at 0 °C. After 30 min, MeI (0.64 mL, 10.3 mmol) was added dropwise. The mixture was allowed to warm to rt and stirred for 48 h. The reaction was cooled to 0 °C, quenched with 2 M aq. KOH (6 mL) and allowed to warm to rt over 3 h. The mixture was extracted with Et_2O (3 × 50 mL), and the combined organic extracts were washed sequentially with H_2O (2 × 100 mL) and brine (50 mL), dried and concentrated *in vacuo* to give a 76:24 mixture of **69**:**70**. Purification *via* flash column chromatography (gradient elution, 2%→50% Et_2O in 30-40 °C petrol) gave a 76:24 mixture of **69**:**70** as a colourless oil (591 mg, 93%); ν_{max} (film) 2981, 2934, 2865 (C–H), 872 (C–O, epoxide), 771 (C–O epoxide); *m/z* (CI^+) 143 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_8H_{15}O_2^+$ ($[M+H]^+$) requires 143.1067; found 143.1069.

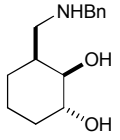
[33] Compound **68** did not yield to analysis by mass spectrometry under a range of ionisation conditions.

Data for **69**: δ_H (400 MHz, C_6D_6) [selected peaks] 2.00-2.09 (1H, m, C(3)*H*), 2.92-2.95 (1H, m, C(1)*H*), 3.16-3.21 (1H, m, C(2)*H*), 3.24 (3H, s, O*Me*), 3.25-3.31 (1H, m, C(3)C$H_A$$H_B$O), 3.49-3.55 (1H, m, C(3)C$H_A$$H_B$O); δ_C (100 MHz, C_6D_6) 19.6, 22.2, 24.2 (*C*(4), *C*(5), *C*(6)), 35.9 (*C*(3)), 51.7, 53.0 (*C*(1), *C*(2)), 58.6 (O*Me*), 75.2 (C(3)*C*H_2O).

Data for **70**: δ_H (400 MHz, C_6D_6) [selected peaks] 2.14-2.24 (1H, m, C(3)*H*), 2.98-3.01 (1H, m, C(1)*H*), 3.07-3.14 (3H, m, C(2)*H*, C(3)CH_2O), 3.15 (3H, s, O*Me*); δ_C (100 MHz, C_6D_6) 17.5, 24.4, 25.2 (*C*(4), *C*(5), *C*(6)), 35.5 (*C*(3)), 52.0, 53.9 (*C*(1), *C*(2)), 58.5 (O*Me*), 75.1 (C(3)*C*H_2O).

*From **68**: m*CPBA (72%, 413 mg, 1.72 mmol) was added to a stirred solution of **68** (145 mg, 1.15 mmol) in CH_2Cl_2 (3.2 mL) at 0 °C. The reaction mixture was allowed to warm to rt over 2.5 h and then quenched with 10% aq. Na_2SO_3 (5 mL) and sat. aq. $NaHCO_3$ (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (2 × 10 mL) and brine (10 mL), dried and concentrated *in vacuo* to give a 58:42 mixture of **69**:**70**. Purification *via* flash column chromatography (gradient elution, 2%→50% Et_2O in 30-40 °C petrol) gave a 58:42 mixture of **69**:**70** as a colourless oil (66 mg, 40%).

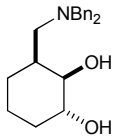
(1*RS*,2*RS*,3*SR*)-3-(*N*-Benzylamino)methyl-cyclohexane-1,2-diol 71



Cl_3CCO_2H (486 mg, 2.98 mmol) was added to a stirred solution of **64** (150 mg, 0.75 mmol) in CH_2Cl_2 (2.1 mL) and the resultant mixture was stirred at rt for 5 min. *m*CPBA (74%, 486 mg, 2.98 mmol) was then added in one portion and the reaction mixture was stirred at rt for 21 h. The mixture was then diluted with CH_2Cl_2 (10 mL) and sat. aq. Na_2SO_3 was added until starch-iodide paper indicated no remaining peracid. Sat. aq. $NaHCO_3$ (10 mL) was then added and the layers were separated. The organic extracts were washed with sat. aq. $NaHCO_3$ (2 × 10 mL), dried and concentrated *in vacuo*. Following the *General Procedure*, transesterification with K_2CO_3 (1.02 g, 7.4 mmol) in MeOH (5 mL) gave **71** (95:5 dr) as a yellow oil; ν_{max} (film) 3373 (O–H, N–H), 2931 (C–H), 1657, 1452, 1149; δ_H (500 MHz, $CDCl_3$) 1.22-1.40 (2H, m, C(4)H_A, C(5)H_A), 1.47-1.50 (1H, m, C(6)H_A), 1.55-1.57 (2H, m, C(5)H_B, C(6)H_B), 1.95-1.98 (1H, m, C(4)H_B), 2.23-2.27 (1H, m, C(1)*H*), 2.75 (1H, dd, *J* 14.5, 1.5, C(3)C$H_A$$H_B$N), 3.02 (1H, dd, *J* 14.5, 11.5, C(3)C$H_A$$H_B$N), 3.52 (1H, dd, *J* 8.2, 4.4, C(2)*H*), 3.64-3.68 (1H, m, C(3)*H*), 3.66 (1H, d, *J* 13.1, NC$H_A$$H_B$Ph), 3.81 (1H, d, *J* 13.1, NC$H_A$$H_B$), 7.25-7.35 (5H, m, *Ph*); δ_C (125 MHz, $CDCl_3$) 20.0 (*C*(5)), 27.6 (*C*(6)), 31.1 (*C*(4)), 37.0 (*C*(1)), 51.4 (C(3)*C*H_2N), 53.9 (N*C*H_2Ph), 71.1 (*C*(3)), 77.9 (*C*(2)), 127.4 (*p-Ph*), 128.2, 128.6 (*o-*, *m-Ph*),

138.8 (*i-Ph*); *m/z* (ESI$^+$) 236 ([M+H]$^+$, 100%); HRMS (CI$^+$) $C_{14}H_{22}NO_2^+$ ([M+H]$^+$) requires 236.1645; found 236.1646.

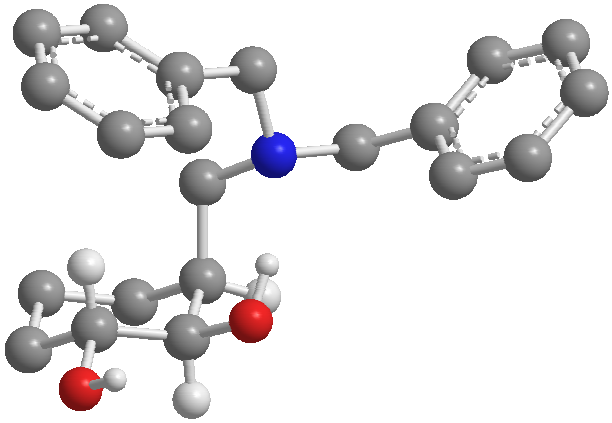
(1*RS*,2*RS*,3*SR*)-3-(*N,N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 75



*Dihydroxylation of **65**:* Cl_3CCO_2H (4.20 g, 25.7 mmol) was added to a stirred solution of **65** (1.5 g, 5.15 mmol) in CH_2Cl_2 (14 mL) and the resultant mixture was stirred at rt for 30 min. *m*CPBA (70%, 1.90 g, 7.71 mmol) was then added in one portion and the reaction mixture was stirred at rt for 21 h. The mixture was then diluted with CH_2Cl_2 (20 mL) and sat. aq. Na_2SO_3 was added until starch-iodide paper indicated no remaining peracid. Sat. aq. $NaHCO_3$ (150 mL) was then added and the layers were separated. The organic layer was washed with sat. aq. $NaHCO_3$ (2 × 100 mL), dried and concentrated *in vacuo*. Following the *General Procedure*, transesterification with K_2CO_3 (3.55 g, 25.7 mmol) in MeOH (80 mL) gave **75** in 90:10 dr. Purification *via* exhaustive flash column chromatography (gradient elution, 7%→60% EtOAc in 30-40 °C petrol) gave **75** as a white solid (916 mg, 55%, >99:1 dr) and a sample of **76** contaminated with trace amounts (<5%) of unknown impurities (63 mg, ~4%).

Data for **75**: mp 83-85 °C; ν_{max} (film) 3356 (O–H); δ_H (400 MHz, $CDCl_3$) 1.09-1.14 (2H, m, C(5)H_2), 1.26-1.29 (1H, m, C(6)H_A), 1.43-1.49 (2H, m, C(4)H_2), 1.71-1.78 (1H, m, C(6)H_B), 2.20-2.24 (1H, m, C(3)*H*), 2.55-2.60 (1H, br s, O*H*), 2.60-2.70 (2H, m, C(3)CH_2N), 3.07-3.15 (3H, m, C(1)*H*, N(CH_AH$_B$Ph)$_2$), 3.36-3.39 (1H, m, C(2)*H*), 4.05-4.09 (2H, m, N(CH$_A$$H_B$Ph)$_2$), 6.78-6.99 (1H, br s, O*H*), 7.27-7.42 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 19.9 (*C*(5)), 28.5 (*C*(4)), 31.7 (*C*(6)), 33.7 (*C*(3)), 54.7 (C(3)*C*H$_2$N), 58.9 (N(*C*H$_2$Ph)$_2$), 70.6 (*C*(1)), 76.7 (*C*(2)), 127.7 (*p-Ph*), 128.6, 129.6 (*o-*, *m-Ph*), 137.4 (*i-Ph*); *m/z* (ESI$^+$) 326 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{28}NO_2^+$ ([M+H]$^+$) requires 326.2115; found 326.2114.

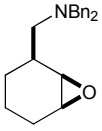
X-ray Crystal Structure Determination for 75



Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[34]

X-ray crystal structure data for **75** [$C_{21}H_{27}NO_2$]: M = 325.45, monoclinic, space group *P* 21/n, a = 10.9893(3) Å, b = 13.7910(3) Å, c = 12.2178(4) Å, β = 102.4024(11) °, V = 1808.44(9) Å^3, Z = 4, μ = 0.076 mm^{-1}, colourless block, crystal dimensions = 0.3 × 0.3 × 0.3 mm^3. A total of 4097 unique reflections were measured for $5 < \theta < 27$ and 2235 reflections were used in the refinement. The final parameters were wR_2 = 0.037 and R_1 = 0.038 [$I>3.0\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733901. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 79



Anhydrous TsOH (8.95 g, 52 mmol) was added to a stirred solution of **65** (5.05 g, 17.3 mmol) in CH_2Cl_2 (48 mL) at rt and stirred for 30 min. *m*CPBA (72%, 6.65 g, 27.7 mmol) was added in one portion and the reaction mixture was stirred at rt for a further 22 h. The reaction was quenched with 10% aq. Na_2SO_3 (50 mL) and sat. aq. $NaHCO_3$ (100 mL). The mixture was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (300 mL) and brine (300 mL), dried, and concentrated *in vacuo* to give a 10:75:15 mixture of **75**:**77**:**78** as an oil (6.46 g) which was used

[34] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

without purification. The 10:75:15 mixture of **75**:**77**:**78** (6.46 g) was dissolved in CH_2Cl_2 (100 mL) and the solution was cooled to 0 °C. DBU (2.9 mL, 19.4 mmol) was added and the reaction mixture was stirred for 15 h. The reaction was quenched with 10% aq. $CuSO_4$ (100 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic extracts were washed sequentially with 10% aq. $CuSO_4$ (200 mL) and brine (200 mL), dried, and concentrated *in vacuo* to give a 10:4:75:11 mixture of **75**:**78**:**79**:**80**. Purification *via* exhaustive flash column chromatography (gradient eluent, 1%→10% Et_2O in 30-40 °C petrol) gave **79** as a white solid (877 mg, 17%, >99:1 dr) and an 86:14 mixture of **79**:**80** as a white solid (1.67 g, 31%).

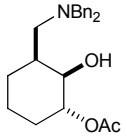
Data for **79**: Found C, 81.8; H, 8.2; N, 4.6%; $C_{21}H_{25}NO$ requires C, 82.0; H, 8.2; N, 4.6%; mp 43-45 °C; ν_{max} (KBr) 912, 746 (C–O); δ_H (400 MHz, $CDCl_3$) 1.09-1.15 (2H, m, C(5)H_2), 1.39-1.44 (2H, m, C(4)H_2), 1.78-1.88 (2H, m, C(6)H_2), 2.06-2.09 (1H, m, C(3)*H*), 2.46-2.50 (1H, m, C(3)C$H_A$$H_B$N), 2.65-2.69 (1H, m, C(3)C$H_A$$H_B$N), 3.17-3.18 (1H, m, C(1)*H*), 3.26-3.28 (1H, m, C(2)*H*), 3.62-3.69 (4H, m, N(CH_2Ph)$_2$), 7.25-7.42 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 19.7 (*C*(5)), 23.4 (*C*(4)), 24.0 (*C*(6)), 33.7 (*C*(3)), 52.7 (*C*(1)), 54.9 (*C*(2)), 57.1 (C(3)*C*H_2N), 59.0 (N(*C*H_2Ph)$_2$), 126.9 (*p-Ph*), 128.2, 128.8 (*o-*, *m-Ph*), 139.5 (*i-Ph*); *m/z* (ESI^+) 308 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{21}H_{26}NO^+$ ($[M+H]^+$) requires 308.2009; found 308.2013.

*Ring-opening of **79** with Cl_3CCO_2H:* Anhydrous Cl_3CCO_2H (265 mg, 1.63 mmol) was added to a stirred solution of **79** (100 mg, 0.33 mmol) in CH_2Cl_2 (1.5 mL) at rt and stirred for 2 h. The reaction was quenched with sat. aq. $NaHCO_3$ (1.5 mL) and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (30 mL) and brine (30 mL), dried and concentrated *in vacuo*. Following the *General Procedure*, transesterification with K_2CO_3 (225 mg, 1.63 mmol) in MeOH (4 mL) gave a 95:5 mixture of **75**:**76**. Purification *via* flash column chromatography (gradient elution, 20%→60% EtOAc in 30-40 °C petrol) gave a 95:5 mixture of **75**:**76** as a colourless oil (106 mg, quant).

*Ring-opening of **79** with TsOH:* Anhydrous TsOH (168 mg, 0.98 mmol) was added to a stirred solution of **79** (100 mg, 0.33 mmol) in CH_2Cl_2 (1.5 mL) at rt and stirred for 3 h. The reaction was quenched with sat. aq. $NaHCO_3$ (1.5 mL) and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (30 mL) and brine (30 mL), dried and concentrated *in vacuo* to give **77** in >99:1 dr. Purification *via* flash column chromatography (gradient elution, 5%→30% EtOAc in 30-40 °C petrol) gave **77** as a colourless oil (150 mg, 96%, >99:1 dr); ν_{max} (film) 3347 (O–H); δ_H (400 MHz, $CDCl_3$) 1.28-1.78 (4H, m, C(4)H_2, C(5)H_2), 2.11-2.15 (2H, m, C(3)CH_2N), 2.26-2.33 (1H, m, C(6)H_A), 2.43 (3H, s, Ar*Me*), 2.56-2.64 (1H, m, C(6)H_B), 3.12-4.11 (4H, m, N(CH_2Ph)$_2$), 3.20-3.27 (1H, m, C(3)*H*), 3.90-3.93 (1H, m, C(2)*H*), 4.48-4.51 (1H, m, C(1)*H*), 7.23-7.45 (14H, m, *Ph*, *Ar*); δ_C (100 MHz, $CDCl_3$) 19.5

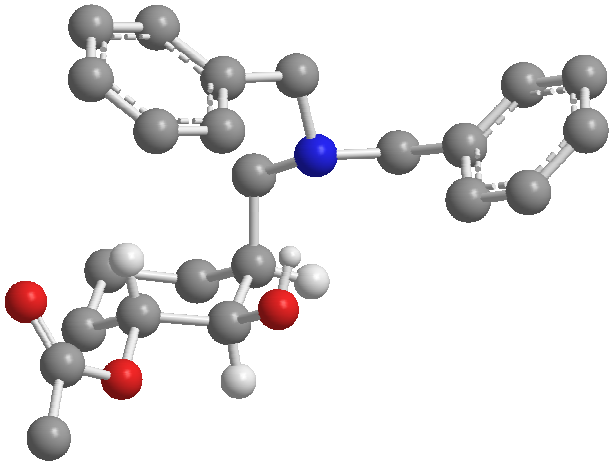
(*C*(4)), 21.7 (Ar*Me*), 27.0 (*C*(5)), 33.7 (*C*(6)), 52.7 (C(3)*C*H_2N), 54.8 (N(*C*H_2Ph)$_2$), 58.7 (*C*(3)), 70.6 (*C*(2)), 80.7 (*C*(1)), 127.5, 127.8, 128.5, 129.1, 129.7, 134.3, 138.7, 144.4 (*Ph*, *Ar*); *m/z* (ESI$^+$) 480 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{28}H_{34}NO_4S^+$ ([M+H]$^+$) requires 480.2203; found 480.2208.

(1*RS*,2*RS*,3*SR*)-1-Acetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 81



A solution of **79** (100 mg, 0.33 mmol) in AcOH (2 mL) was stirred at rt for 12 h. The reaction was quenched with sat. aq. $NaHCO_3$ (5 mL) and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (30 mL) and brine (30 mL), dried and concentrated *in vacuo* to give **81** in 95:5 dr. Purification *via* flash column chromatography (eluent 30-40 °C petrol/EtOAc, 4:1) gave **81** as a white solid (108 mg, 90%, >99:1 dr); mp 77-80 °C; ν_{max} (film) 3409 (O–H), 1733 (C=O); δ_H (400 MHz, $CDCl_3$) 1.32-1.34 (2H, m, C(4)H_2), 1.40-1.45 (2H, m, C(6)H_2), 1.82-1.87 (2H, m, C(5)H_2), 2.05 (3H, s, CO*Me*), 2.25-2.30 (1H, m, C(3)CH_AH$_B$N), 2.34-2.37 (1H, m, C(3)*H*), 2.86-2.92 (1H, m, C(3)CH$_A$$H_B$N), 3.24-3.27 (2H, m, N(CH_AH$_B$Ph)$_2$), 3.80-3.83 (1H, m, C(2)*H*), 3.87-3.90 (2H, m, N(CH$_A$$H_B$Ph)$_2$), 4.54-4.59 (1H, m, C(1)*H*), 4.82-5.10 (1H, br s, O*H*), 7.27-7.37 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 19.8 (*C*(4)), 21.4 (*C*(6)), 26.6 (CO*Me*), 28.1 (*C*(5)), 34.7 (*C*(3)), 55.2 (C(3)*C*H_2N), 58.9 (N(*C*H_2Ph)$_2$), 72.1 (*C*(2)), 73.4 (*C*(1)), 127.4 (*p-Ph*), 128.6, 129.2 (*o*-, *m-Ph*), 138.2 (*i-Ph*), 170.4 (*C*OMe); *m/z* (ESI$^+$) 368 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{23}H_{30}NO_3^+$ ([M+H]$^+$) requires 368.2220; found 368.2226.

X-ray Crystal Structure Determination for 81



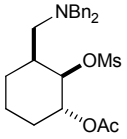
Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-*Kα* radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-

hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[35]

X-ray crystal structure data for **81** [$C_{23}H_{29}NO_3$]: M = 367.49, triclinic, space group P –1, a = 6.1629(4) Å, b = 10.0202(7) Å, c = 16.9326(13) Å, α = 96.357(3) °, β = 93.842(2) °, γ = 103.221(3) °, V = 1007.06(12) Å^3, Z = 2, μ = 0.079 mm^{-1}, colourless plate, crystal dimensions = 0.05 × 0.1 × 0.3 mm^3. A total of 3963 unique reflections were measured for 5 < θ < 27 and 2525 reflections were used in the refinement. The final parameters were wR_2 = 0.049 and R_1 = 0.050 [I>2.0σ(I)]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733902. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

*Transesterification of **81**:* Following the *General Procedure*, K_2CO_3 (197 mg, 1.43 mmol) and **81** (105 mg, 0.29 mmol) in MeOH (2 mL) gave the crude reaction mixture. Purification *via* flash column chromatography (gradient elution, 7%→60% EtOAc in 30-40 °C petrol) gave **75** as a white solid (73 mg, 79%, >99:1 dr).

(1*RS*,2*RS*,3*SR*)-1-Acetoxy-2-methanesulfonyloxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 82

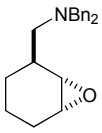


MsCl (0.1 mL, 1.29 mmol) was added to a stirred solution of **81** (319 mg, 0.87 mmol), Et_3N (0.4 mL, 2.87 mmol) in CH_2Cl_2 (5 mL) at 0 °C and the resultant solution was stirred for 1 h. The reaction was quenched with sat. aq. $NaHCO_3$ (5 mL) and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (30 mL) and brine (30 mL), dried and concentrated *in vacuo*. Purification via flash column chromatography (gradient elution, 5%→40% EtOAc in 30-40 °C petrol) gave **82** as colourless oil (374 mg, 97%, >99:1 dr); ν_{max} (film) 1740 (C=O); δ_H (400 MHz, $CDCl_3$) 1.20-1.31 (1H, m, C(5)H_A), 1.32-1.42 (1H, m, C(5)H_B), 1.47-1.65 (3H, m, C(4)H_2, C(6)H_A), 1.78-1.89 (1H, m, C(6)H_B), 2.04 (3H, s, CO*Me*), 2.18-2.29 (1H, m, C(3)*H*), 2.49 (1H, dd, *J* 12.7, 9.1, C(3)CH_AH$_B$N), 2.57 (1H, dd, *J* 12.7, 5.3, C(3)CH$_A$$H_B$N), 2.88 (3H, s, SO_2*Me*), 3.43 (2H, d, *J* 13.6, N(CH_AH$_B$Ph)$_2$), 3.74 (2H, d, *J* 13.6, N(CH$_A$$H_B$Ph)$_2$), 4.73 (1H, dd, *J* 6.0, 3.4, C(2)*H*), 4.97-5.02 (1H, m, C(1)*H*), 7.23-7.40 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 18.8 (*C*(5)), 21.2 (CO*Me*), 24.6, 27.0 (*C*(4), *C*(6)), 35.8 (*C*(3)), 38.2 (SO_2*Me*), 53.5 (C(3)*C*H$_2$N), 59.0 (N(*C*H$_2$Ph)$_2$), 69.6 (*C*(1)), 80.0 (*C*(2)), 127.0 (*p*-*Ph*),

[35] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

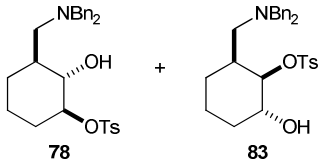
128.3, 129.0 (*o*-, *m*-*Ph*), 139.4 (*i*-*Ph*), 169.8 (*C*OMe); *m/z* (ESI^+) 446 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{24}H_{32}NO_5S^+$ ($[M+H]^+$) requires 446.1996; found 446.2013.

(1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 80



Following the *General Procedure*, K_2CO_3 (1.54 g, 11.1 mmol) and **82** (1.66 g, 3.73 mmol) in MeOH (20 mL) gave **80** in >99:1 dr. Purification *via* flash column chromatography (gradient elution, 3%→40% Et_2O in 30-40 °C petrol) gave **80** as a white solid (971 mg, 85%, >99:1 dr); mp 75-76 °C; ν_{max} (KBr) 873, 746 (C–O); δ_H (400 MHz, $CDCl_3$) 0.71-0.81 (1H, m, C(4)H_A), 1.29-1.32 (2H, m, C(5)H_2), 1.56-1.66 (2H, m, C(6)H_A, C(4)H_B), 2.02-2.06 (1H, m, C(6)H_B), 2.13-2.21 (1H, m, C(3)*H*), 2.33-2.49 (2H, m, C(3)CH_2N), 3.04-3.06 (2H, m, C(1)*H*, C(2)*H*), 3.50-3.69 (4H, m, N(CH_2Ph)$_2$), 7.24-7.39 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 17.2 (C(5)), 24.9 (*C*(4)), 25.8 (*C*(6)), 32.6 (*C*(3)), 52.7 (*C*(1)), 54.9 (*C*(2)), 57.0 (C(3)*C*H_2N), 58.6 (N(*C*H_2Ph)$_2$), 126.8 (*p*-*Ph*), 128.2, 129.0 (*o*-, *m*-*Ph*), 139.6 (*i*-*Ph*); *m/z* (ESI^+) 308 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{21}H_{26}NO^+$ ($[M+H]^+$) requires 308.2009; found 308.2014.

(1*RS*,2*RS*,3*RS*)-1-(*p*-Toluenesulfonyloxy)-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 78 and (1*RS*,2*RS*,3*SR*)-1-hydroxy-2-(*p*-toluenesulfonyloxy)-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 83

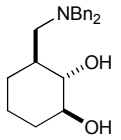


78 **83**

Anhydrous TsOH (123 mg, 0.71 mmol) was added to a stirred solution of **80** (73 mg, 0.24 mmol) in CH_2Cl_2 (1 mL) at rt and the resultant solution was stirred for 2 h. The reaction was quenched with sat. aq. $NaHCO_3$ (1 mL) and the mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (10 mL) and brine (10 mL), dried and concentrated *in vacuo* to give a 64:36 mixture of **78**:**83**. Purification *via* flash column chromatography (gradient elution, 3%→35% EtOAc in 30-40 °C petrol) gave **78** as a white solid (65 mg, 57%, >99:1 dr); mp 105-108 °C; ν_{max} (KBr) 3350 (O–H), 2934, 2860 (C–H), 1559, 1452, 1357, 1175, 939; δ_H (400 MHz, $CDCl_3$) 0.75-0.79 (1H, m, C(4)H_A), 1.29-1.44 (3H, m, C(4)H_B, C(5)H_A, C(6)H_A), 1.66-1.77 (2H, m, C(3)*H*, C(5)H_B), 2.04-2.08 (1H, m, C(6)H_B), 2.33 (1H, dd, *J* 12.7, 3.4, C(3)CH_AH$_B$N), 2.46 (3H, s, Ar*Me*), 2.61 (1H, dd, C(3)CH$_A$$H_B$N), 3.21 (2H, d, *J* 12.7, N(CH_AH$_B$Ph)$_2$), 3.22 (1H, t, *J* 9.3, C(2)*H*), 3.90 (2H, d, *J* 12.7, N(CH$_A$$H_B$Ph)$_2$), 4.40-4.42 (1H, m,

C(1)*H*), 7.40-7.65 (12H, m, *Ar*, *Ph*), 6.31-6.55 (1H, br s, O*H*), 7.85-7.90 (2H, d, *J* 8.5, *Ar*); δ_C (100 MHz, $CDCl_3$) 21.7 (Ar*Me*), 23.0 (*C*(5)), 27.8 (*C*(4)), 30.7 (*C*(6)), 39.1 (*C*(3)), 58.6 (N(*C*H_2Ph)$_2$), 59.7 (C(3)*C*H_2N), 77.8 (*C*(2)), 85.7 (*C*(1)), 127.4, 128.0, 128.5, 129.3, 129.4, 134.9, 137.3, 144.0 (*Ar*, *Ph*); *m/z* (ESI^+) 480 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{28}H_{33}NNaO_4S^+$ ($[M+Na]^+$) requires 502.2023; found 502.2020. Further elution gave **83** as a white solid (31 mg, 27%, >99:1 dr); mp 116-118 °C; ν_{max} (KBr) 3359 (O–H), 1568, 1494, 1356, 1188; δ_H (400 MHz, $CDCl_3$) 1.00-1.04 (1H, m, C(5)H_A), 1.27-1.75 (5H, m, C(4)H_2, C(5)H_B, C(6)H_2), 2.13-2.17 (1H, m, C(3)CH_AH$_B$N), 2.20-2.23 (1H, m, C(3)*H*), 2.31-2.36 (1H, m, C(3)H$_A$$H_B$N), 2.41 (3H, s, Ar*Me*), 3.06 (2H, d, *J* 13.6, N(CH_AH$_B$Ph)$_2$), 3.68 (2H, d, *J* 13.6, N(CH$_A$$H_B$Ph)$_2$), 3.75-3.90 (1H, m, C(1)*H*), 4.45-4.55 (1H, m, C(2)*H*), 7.21-7.32 (12H, m, *Ar*, *Ph*), 7.75 (2H, d, *J* 8.4, *Ar*); δ_C (100 MHz, $CDCl_3$) 18.2 (*C*(5)), 21.6 (Ar*Me*), 24.9 (*C*(4)), 30.0 (*C*(6)), 35.0 (*C*(3)), 52.7 (C(3)*C*H_2N), 58.7 (N(*C*H_2Ph)$_2$), 67.5 (*C*(1)), 85.1 (*C*(2)), 126.9, 127.7, 128.2, 128.9, 129.9, 134.0, 139.5, 144.8 (*Ar*, *Ph*); *m/z* (ESI^+) 480 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{28}H_{34}NO_4S^+$ ($[M+H]^+$) requires 480.2203; found 480.2204.

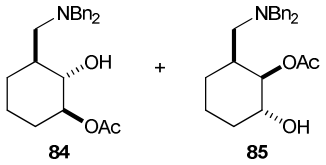
(1*RS*,2*RS*,3*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 76



Anhydrous Cl_3CCO_2H (283 mg, 1.73 mmol) was added to a stirred solution of **80** (106 mg, 0.34 mmol) in CH_2Cl_2 (1 mL) at rt and stirred for 14 h. The reaction was quenched with sat. aq. $NaHCO_3$ (1 mL) and the mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (10 mL) and brine (10 mL), dried and concentrated *in vacuo* to give a crude reaction mixture. Following the *General Procedure*, transesterification with K_2CO_3 (239 mg, 1.73 mmol) in MeOH (4 mL) gave a 56:44 mixture of **76**:**75**. Purification *via* flash column chromatography (gradient elution, 7%→60% EtOAc in 30-40 °C petrol) gave **76** as a colourless oil (59 mg, 52%, >99:1 dr); ν_{max} (film) 3406 (O–H); δ_H (400 MHz, $CDCl_3$) 1.02-1.20 (2H, m, C(5)H_2), 1.32-1.53 (2H, m, C(4)H_2), 1.67-1.83 (2H, m, C(6)H_2), 1.90-1.94 (1H, m, C(3)*H*), 2.19-2.37 (2H, m, C(3)CH_2N), 2.85-2.90 (1H, br s, O*H*), 2.95-3.01 (1H, m, C(1)*H*), 3.06-3.16 (2H, m, N(CH_AH$_B$Ph)$_2$), 3.45-3.52 (1H, m, C(2)*H*), 4.05-4.09 (2H, m, N(CH$_A$$H_B$Ph)$_2$), 6.95-7.96 (1H, br s, O*H*), 7.27-7.39 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 23.1 (*C*(4)), 28.5 (*C*(6)), 31.1 (*C*(5)), 37.9 (*C*(3)), 54.7 (C(3)*C*H_2N), 59.0 (N(*C*H_2Ph)$_2$), 74.8 (*C*(1)), 81.8 (*C*(2)), 127.5 (*p-Ph*), 128.6, 129.2 (*o*-, *m-Ph*), 137.4 (*i-Ph*); *m/z* (ESI^+) 326 ($[M+H]^+$, 100%); HRMS (ESI^+) $C_{21}H_{27}NNaO_2^+$ ($[M+Na]^+$) requires 348.1934; found 348.1936. Further elution gave **75** as a colourless oil (43 mg, 38%, >99:1 dr).

(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 84

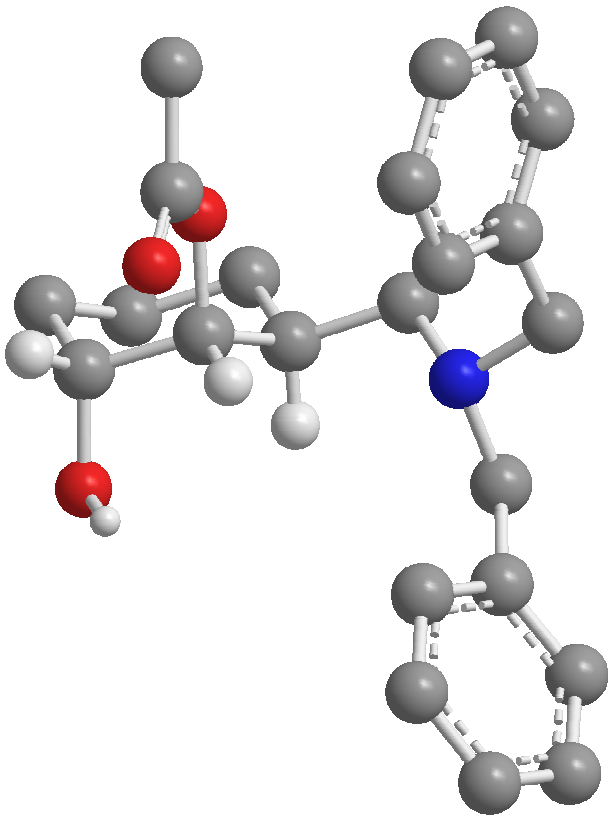
and (1*RS*,2*RS*,3*SR*)-1-hydroxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 85



84 **85**

A solution of **80** (350 mg, 1.14 mmol) in AcOH (3 mL) was stirred at rt for 13 h. The reaction was quenched with sat. aq. $NaHCO_3$ (20 mL) and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed sequentially with sat. aq. $NaHCO_3$ (30 mL) and brine (30 mL), dried and concentrated *in vacuo* to give an 18:24:58 mixture of **80**:**84**:**85**. Purification *via* exhaustive flash column chromatography (gradient elution, 5%→40% EtOAc in 30-40 °C petrol) gave **84** as a colourless oil (8.5 mg, 2%, >99:1 dr); ν_{max} (film) 3374 (O–H), 3028, 2935, 2860 (C–H), 1713 (C=O), 1452, 1248; δ_H (400 MHz, $CDCl_3$) 0.80-0.92 (1H, m, C(4)H_A), 1.13-1.20 (1H, m, C(6)H_A), 1.38-1.40 (1H, m, C(5)H_A), 1.45-1.49 (1H, m, C(4)H_B), 1.62-1.70 (1H, m, C(5)H_B), 1.86-1.88 (1H, m, C(3)*H*), 2.00-2.05 (1H, m, C(6)H_B), 2.12 (3H, s, CO*Me*), 2.37 (1H, dd, *J* 11.4, 9.0, C(3)CH_AH$_B$N), 2.68 (1H, dd, *J* 11.4, 11.3, C(3)CH$_A$$H_B$N), 3.16 (2H, d, *J* 13.4, N(CH_AH$_B$Ph)$_2$), 3.29 (1H, app t, *J* 9.0, C(2)*H*), 4.01 (2H, d, *J* 13.4, N(CH$_A$$H_B$Ph)$_2$), 4.65-4.74 (1H, m, C(1)*H*), 6.88-6.95 (1H, br s, O*H*), 7.25-7.40 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 21.6 (CO*Me*), 23.0, 28.2, 29.5 (*C*(4), *C*(5), *C*(6)), 38.7 (*C*(3)), 58.8 (N(*C*H$_2$Ph)$_2$), 60.4 (C(3)*C*H$_2$N), 77.1 (*C*(1)), 78.4 (*C*(2)), 127.5 (*p*-*Ph*), 128.5, 129.0 (*o*-, *m*-*Ph*), 137.2 (*i*-*Ph*); 171.1 (*C*OMe); *m/z* (ESI$^+$) 368 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{23}H_{29}NNaO_3^+$ ([M+Na]$^+$) requires 390.2040; found 390.2038. Further elution gave **85** as a white solid (42 mg, 10%, >99:1 dr); mp 110-113 °C; ν_{max} (KBr) 3484 (O–H), 2935 (C–H), 1717 (C=O), 1452, 1243; δ_H (400 MHz, $CDCl_3$) 1.25-1.67 (6H, m, C(4)H_2, C(5)H_2, C(6)H_2), 1.78 (3H, s, CO*Me*), 2.02 (1H, br s, O*H*), 2.18 (1H, dd, *J* 12.2, 6.8, C(3)CH_AH$_B$N), 2.28-2.39 (1H, m, C(3)*H*), 2.46 (1H, dd, *J* 12.2, 7.8, C(3)CH$_A$$H_B$N), 3.41 (2H, d, *J* 13.4, N(CH_AH$_B$Ph)$_2$), 3.60 (2H, d, *J* 13.4, N(CH$_A$$H_B$Ph)$_2$), 3.85 (1H, app br s, C(1)*H*), 4.88-4.97 (1H, m, C(2)*H*), 7.22-7.42 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 19.0 (*C*H$_2$), 21.1 (CO*Me*), 25.2, 29.0 (*C*H$_2$), 32.9 (*C*(3)), 54.0 (C(3)*C*H$_2$N), 59.1 (N(*C*H$_2$Ph)$_2$), 66.6 (*C*(1)), 74.0 (*C*(2)), 126.8 (*p*-*Ph*), 128.2, 129.0 (*o*-, *m*-*Ph*), 139.7 (*i*-*Ph*), 170.7 (*C*OMe); *m/z* (ESI$^+$) 368 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{23}H_{30}NO_3^+$ ([M+H]$^+$) requires 368.2220; found 368.2225. A mixed fraction containing both **84** and **85** was also obtained (284 mg, 68%).

X-ray Crystal Structure Determination for 85

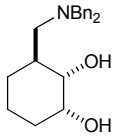


Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[36]

X-ray crystal structure data for **85** [$C_{23}H_{29}NO_3$]: M = 367.49, monoclinic, space group P 21/a, a = 8.7731(2) Å, b = 22.3043(6) Å, c = 10.5826(3) Å, β = 98.2573(11) °, V = 2049.31(9) Å^3, Z = 4, μ = 0.078 mm^{-1}, colourless plate, crystal dimensions = 0.05 × 0.2 × 0.2 mm^3. A total of 4631 unique reflections were measured for 5 < θ < 27 and 2475 reflections were used in the refinement. The final parameters were wR_2 = 0.048 and R_1 = 0.045 [I>2.5σ(I)]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733903. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

[36] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

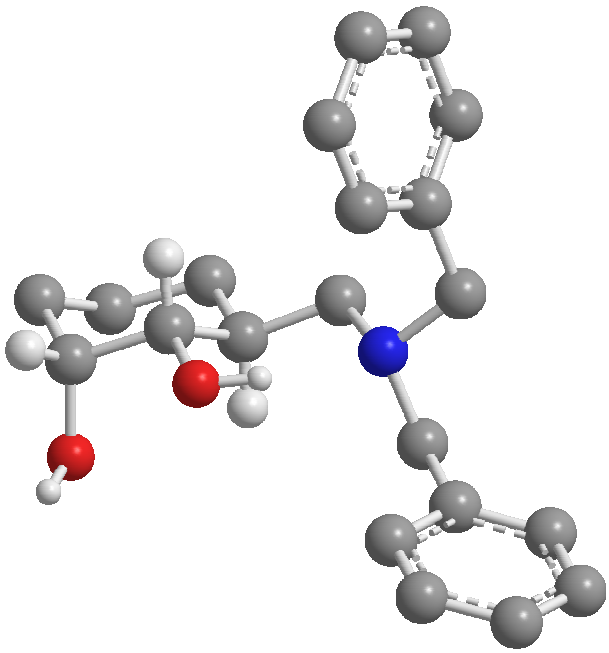
(1*RS*,2*SR*,3*SR*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 88



*From **82**:* KOAc (122 mg, 1.24 mmol) was added to a stirred solution of **82** (370 mg, 0.83 mmol) in EtOH/H_2O (v:v 6:1, 7 mL) and the resultant mixture was heated at 80 °C for 12 h. The reaction mixture was allowed to cool to rt then concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (10 mL) and the resultant solution was washed sequentially with sat. aq. $NaHCO_3$ (3 × 10 mL) and brine (10 mL), then dried and concentrated *in vacuo* to give a 75:25 mixture of **86**:**87**. Following the *General Procedure*, transesterification with K_2CO_3 (574 mg, 4.15 mmol) in MeOH (3 mL) gave **88** in >99:1 dr. Purification *via* flash column chromatography (gradient elution, 7%→60% EtOAc in 30-40 °C petrol) gave **88** as a white solid (221 mg, 82%, >99:1 dr); mp 137-139 °C; ν_{max} (KBr) 3396 (O–H); δ_H (400 MHz, $CDCl_3$) 0.68-0.82 (1H, m, C(4)H_A), 1.21-1.34 (1H, m, C(6)H_A), 1.36-1.50 (2H, m, C(4)H_B, C(5)H_A), 1.60-1.73 (1H, m, C(5)H_B), 1.88-1.98 (1H, m, C(6)H_B), 2.08-2.20 (1H, m, C(3)*H*), 2.29-2.39 (1H, dd, *J* 12.5, 2.8 C(3)C$H_A$$H_B$N), 2.62 (1H, app t, *J* 6.3, C(3)C$H_A$$H_B$N), 3.09-3.20 (3H, m, C(2)*H*, N(C$H_A$$H_B$Ph)$_2$), 3.86-3.91 (1H, m, C(1)*H*), 4.07 (2H, d, *J* 13.0, N(C$H_A$$H_B$Ph)$_2$), 7.26-7.43 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 19.1 (*C*(5)), 28.1 (*C*(4)), 29.3 (*C*(6)), 33.3 (*C*(3)), 59.0 (N(*C*H_2Ph)$_2$), 60.4 (C(3)*C*H_2N), 68.4 (*C*(1)), 78.7 (*C*(2)), 127.5 (*p-Ph*), 128.6, 129.3 (*o*-, *m-Ph*), 137.4 (*i-Ph*); *m/z* (ESI$^+$) 326 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{28}NO_2^+$ ([M+H]$^+$) requires 326.2115; found 326.2117.

*Dihydroxylation of **65**:* A solution of OsO_4 (92 mg, 0.36 mmol) in CH_2Cl_2 (1 mL) was added *via* syringe to a stirred solution of **65** (100 mg, 0.34 mmol) and TMEDA (0.1 mL, 0.38 mmol) in CH_2Cl_2 (3 mL) at −78 °C. After 2 h the mixture was allowed to warm to rt and then concentrated *in vacuo*. The residue was dissolved in MeOH (10 mL) and conc. HCl (5 drops) was added. After stirring at rt for 24 h, sat. aq. $NaHCO_3$ (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were washed with brine (50 mL), dried and concentrated *in vacuo*. Purification *via* flash column chromatography (eluent 30-40 °C petrol/EtOAc, 85:15) gave **88** as a white solid (93 mg, 83%, >99:1 dr).

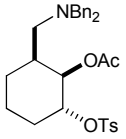
X-ray Crystal Structure Determination for 88



Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 190 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[37]

X-ray crystal structure data for **88** [$C_{21}H_{27}NO_2$]: M = 650.90, triclinic, space group P –1, a = 9.80800(10) Å, b = 12.7341(2) Å, c = 15.9205(3) Å, α = 100.7822(6)°, β = 93.3074(7)°, γ = 109.7640(10)°, V = 1822.44(5) Å^3, Z = 4, μ = 0.075 mm^{-1}, colourless block, crystal dimensions = 0.2 × 0.2 × 0.2 mm^3. A total of 8196 unique reflections were measured for 5 < θ < 27 and 8195 reflections were used in the refinement. The final parameters were wR_2 = 0.114 and R_1 = 0.079 [I>–10.0σ(I)]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733904. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(1*RS*,2*RS*,3*SR*)-1-(*p*-Toluenesulfonyloxy)-2-acetoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 89

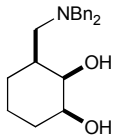


Ac_2O (34 μL, 0.3 mmol) was added to solution of **77** (114 mg, 0.24 mmol), pyridine (97 μL, 1.26 mmol) and DMAP (6 mg) in CH_2Cl_2 (2 mL), and the resultant mixture stirred at rt for 2 h. The reaction mixture was

[37] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. CRYSTALS, 2001, Issue 11, Chemical Crystallography Laboratory, University of Oxford, UK.

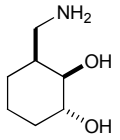
then diluted with CH_2Cl_2 (5 mL) and washed sequentially with sat. aq. $NaHCO_3$ (3 × 5 mL) and sat. aq. $CuSO_4$ (3 × 5 mL). The organic layer was dried and concentrated *in vacuo*. Purification *via* flash column chromatography (gradient elution, 3%→30% EtOAc in 30-40 °C petrol) gave **89** as a colourless oil (74 mg, 60%, >99:1 dr); ν_{max} (film) 1732 (C=O); δ_H (400 MHz, $CDCl_3$) 1.19-1.30 (1H, m, C(4)H_A), 1.40-1.51 (2H, m, C(4)H_B, C(5)H_A), 1.53-1.69 (2H, m, C(5)H_B, C(6)H_A) overlapping 1.64 (3H, s, CO*Me*), 1.72-1.86 (1H, m, C(6)H_B), 2.07 (1H, dd, *J* 12.2, 6.1, C(3)CH_AH$_B$N), 2.16-2.26 (1H, m, C(3)*H*), 2.40 (1H, dd, *J* 12.2, 8.8, C(3)CH$_A$$H_B$N), 2.45 (3H, s, Ar*Me*), 3.23 (2H, d, *J* 13.4, N(CH_AH$_B$Ph)$_2$), 3.62 (2H, d, *J* 13.4, N(CH$_A$$H_B$Ph)$_2$), 4.65-4.70 (1H, m, C(1)*H*), 4.86-4.91 (1H, m, C(2)*H*), 7.20-7.34 (12H, m, *Ar*, *Ph*), 7.80 (2H, d, *J* 8.3, *Ar*); δ_C (100 MHz, $CDCl_3$) 19.0 (*C*(5)), 20.7 (CO*Me*), 21.8 (Ar*Me*), 24.2, 26.8 (*C*(4), *C*(6)), 32.8 (*C*(3)), 54.1 (C(3)*C*H$_2$N), 58.8 (N(*C*H$_2$Ph)$_2$), 69.4 (*C*(2)), 76.2 (*C*(1)), 126.8, 127.7, 128.2, 128.9, 129.8, 133.9, 139.4, 144.6, (*Ar*, *Ph*), 169.7 (*C*OMe); *m/z* (ESI$^+$) 522 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{30}H_{36}NO_5S^+$ ([M+H]$^+$) requires 522.2309; found 522.2315.

(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 92



KOAc (218 mg, 2.22 mmol) was added to a stirred solution of **89** (772 mg, 1.48 mmol) in EtOH/H_2O (v:v 6:1, 10 mL) and the resultant mixture was heated at 80 °C for 12 h. The reaction mixture was allowed to cool to rt then concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (10 mL) and the resultant solution was washed sequentially with sat. aq. $NaHCO_3$ (3 × 10 mL) and brine (10 mL), then dried and concentrated *in vacuo* to give a 55:45 mixture of **90**:**91**. Following the *General Procedure*, transesterification with K_2CO_3 (2.05 g, 14.8 mmol) in MeOH (5 mL) gave **92** in >99:1 dr. Purification *via* flash column chromatography (gradient elution, 5%→60% EtOAc in 30-40 °C petrol) gave **92** as a colourless oil (135 mg, 28%, >99:1 dr); ν_{max} (film) 3378 (O–H); δ_H (400 MHz, $CDCl_3$) 1.14-1.35 (3H, m, C(4)H_2, C(5)H_A), 1.50-1.74 (4H, m, C(3)*H*, C(5)H_B, C(6)H_2), 2.32 (1H, dd, *J* 12.5, 4.8, C(3)CH_AH$_B$N), 2.50 (2H, br s, O*H*), 2.72 (1H, dd, *J* 12.5, 10.4, C(3)CH$_A$$H_B$N), 3.34 (2H, d, *J* 13.1, N(CH_AH$_B$Ph)$_2$), 3.51 (1H, app dt, *J* 10.1, 3.5, C(1)*H*), 3.79 (2H, d, *J* 13.1, N(CH$_A$$H_B$Ph)$_2$), 4.04 (1H, app br s, C(2)*H*), 7.20-7.41 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 22.4 (*C*(5)), 24.4 (*C*(4)), 29.4 (*C*(6)), 38.2 (*C*(3)), 55.7 (C(3)*C*H$_2$N), 59.2 (N(*C*H$_2$Ph)$_2$), 70.8 (*C*(2)), 71.8 (*C*(1)), 127.3 (*p-Ph*), 128.5, 129.1 (*o*-, *m-Ph*), 139.5 (*i-Ph*); *m/z* (ESI$^+$) 326 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{28}NO_2^+$ ([M+H]$^+$) requires 326.2115; found 326.2120.

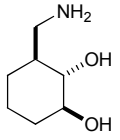
(1*RS*,2*RS*,3*SR*)-3-Aminomethyl-cyclohexane-1,2-diol 93



*From **71**:* $Pd(OH)_2/C$ (75 mg, 50% w/w) was added to a vigorously stirred solution of **71** (150 mg, 0.64 mmol, 95:5 dr) in degassed MeOH (2 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 6 h. The suspension was filtered through a pad of Celite® (eluent MeOH) and the filtrate was concentrated *in vacuo* to give **93** as a colourless oil (89 mg, 96%, 95:5 dr).

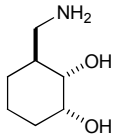
*From **75**:* $Pd(OH)_2/C$ (40 mg, 50% w/w) was added to a vigorously stirred solution of **75** (80 mg, 0.24 mmol) in degassed MeOH (3 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 6 h. The suspension was filtered through a pad of Celite® (eluent MeOH) and the filtrate was concentrated *in vacuo* to give **93** as a colourless oil (35 mg, 99%, >99:1 dr); ν_{max} (film) 3355 (O–H), 2932 (C–H); δ_H (400 MHz, d_4-MeOH) 1.45-1.55 (4H, m, C(4)H_A, C(5)H_2, C(6)H_A), 1.61-1.65 (1H, m, C(4)H_B), 1.80-1.95 (2H, m, C(3)*H*, C(6)H_B), 2.63 (1H, dd, *J* 12.6, 6.6, C(3)CH_AH$_B$N), 2.83 (1H, dd, *J* 12.6, 6.8, C(3)CH$_A$$H_B$N), 3.65-3.69 (1H, m, C(2)*H*), 3.69-3.74 (1H, m, C(1)*H*); δ_C (100 MHz, d_4-MeOH) 19.5, 24.5, 28.7 (*C*(4), *C*(5), *C*(6)), 39.0 (*C*(3)), 42.9 (C(3)*C*H$_2$N), 69.5 (*C*(1)), 72.2 (*C*(2)); *m/z* (ESI$^+$) 146 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_7H_{16}NO_2^+$ ([M+H]$^+$) requires 146.1176; found 146.1174.

(1*RS*,2*RS*,3*RS*)-3-Aminomethyl-cyclohexane-1,2-diol 94



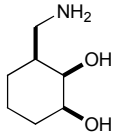
$Pd(OH)_2/C$ (24 mg, 50% w/w) was added to a vigorously stirred solution of **76** (48 mg, 0.15 mmol) in degassed MeOH (3 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 6 h. The suspension was filtered through a pad of Celite® (eluent MeOH) and the filtrate was concentrated *in vacuo* to give **94** as a colourless oil (21 mg, 99%, >99:1 dr); ν_{max} (film) 3345 (O–H), 2961, 2930 (C–H); δ_H (400 MHz, d_4-MeOH) 0.98-1.23 (1H, m, C(4)H_A), 1.25-1.47 (3H, m, C(3)*H*, C(4)H_B, C(6)H_A), 1.73-1.76 (2H, m, C(5)H_2), 1.92-1.95 (1H, m, C(6)H_B), 2.68 (1H, dd, *J* 12.6, 5.8, C(3)CH_AH$_B$N), 2.94 (1H, dd, *J* 12.6, 5.8, C(3)CH$_A$$H_B$N), 3.08 (1H, app t, *J* 9.4, C(2)*H*), 3.31-3.37 (1H, m, C(1)*H*); δ_C (100 MHz, d_4-MeOH) 23.3, 28.6, 33.1 (*C*(4), *C*(5), *C*(6)), 43.3 (*C*(3)), 45.1 (C(3)*C*H$_2$N), 75.0 (*C*(1)), 78.9 (*C*(2)); *m/z* (ESI$^+$) 146 ([M+H]$^+$, 100%); HRMS (ESI$^+$) $C_7H_{16}NO_2^+$ ([M+H]$^+$) requires 146.1176; found 146.1177.

(1*RS*,2*SR*,3*SR*)-3-Aminomethyl-cyclohexane-1,2-diol 95



$Pd(OH)_2$/C (36 mg, 50% w/w) was added to a vigorously stirred solution of **88** (72 mg,0.23 mmol) in degassed MeOH (3 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 6 h. The suspension was filtered through a pad of Celite® (eluent MeOH) and the filtrate was concentrated *in vacuo* to give **95** as a colourless oil (32 mg, 99%, >99:1 dr); ν_{max} (film) 3357 (O–H), 2931 (C–H), 1574, 1456, 1326, 1067; δ_H (400 MHz, d_4-MeOH) 0.94-1.07 (1H, m, C(4)H_A), 1.39-1.51 (2H, m, C(5)H_A, C(6)H_A), 1.59-1.77 (2H, m, C(4)H_B, C(5)H_B), 1.77-1.88 (2H, m, C(3)*H*, C(6)H_B), 2.63-2.74 (1H, m C(3)CH_AH$_B$N), 2.89-2.92 (1H, m, C(3)CH$_A$$H_B$N), 3.30-3.37 (1H, m, C(2)*H*), 3.86-3.91 (1H, m, C(1)*H*); δ_C (100 MHz, d_4-MeOH) 19.1 (*C*(5)), , 28.3 (*C*(4)), 33.1 (*C*(6)), 39.1 (*C*(3)), 45.3 (C(3)*C*H$_2$N), 69.8 (*C*(1)), 76.6 (*C*(2)); HRMS (ESI$^+$) $C_7H_{16}NO_2^+$ ([M+H]$^+$) requires 146.1176; found 146.1172.

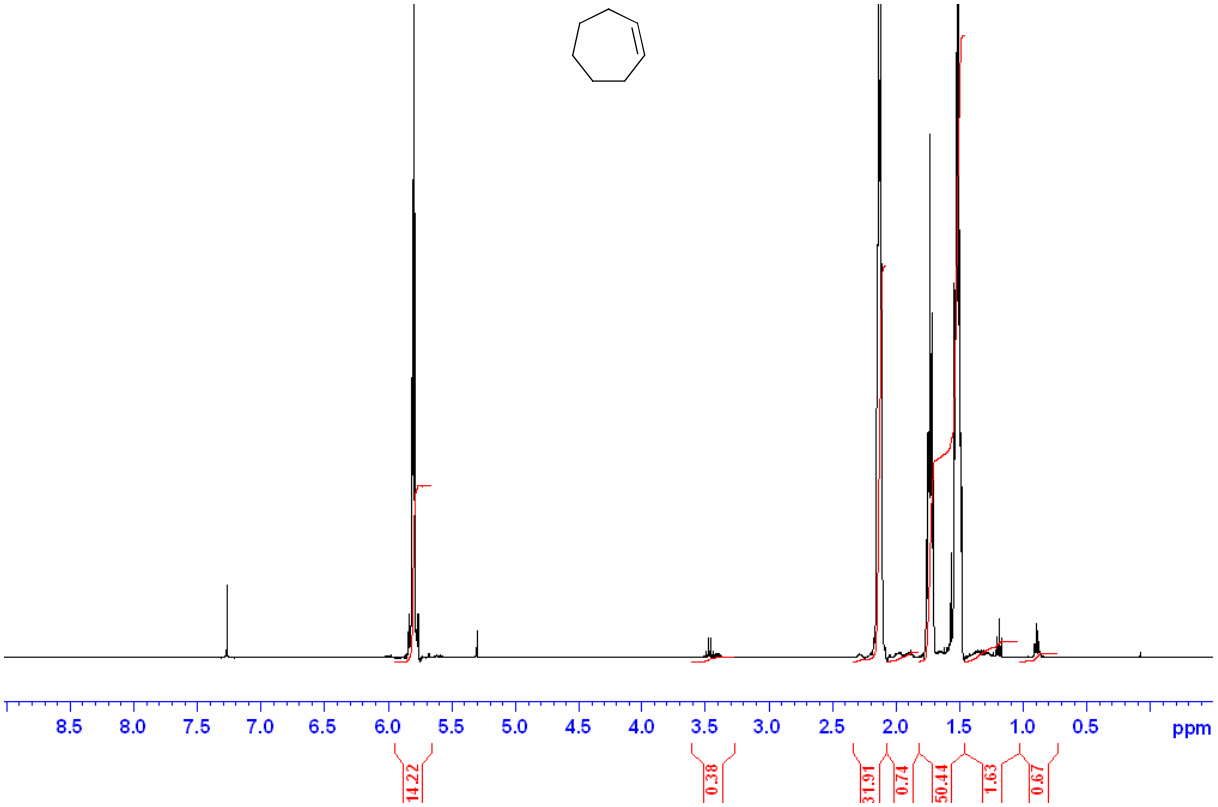
(1*RS*,2*SR*,3*RS*)-3-Aminomethyl-cyclohexane-1,2-diol 96



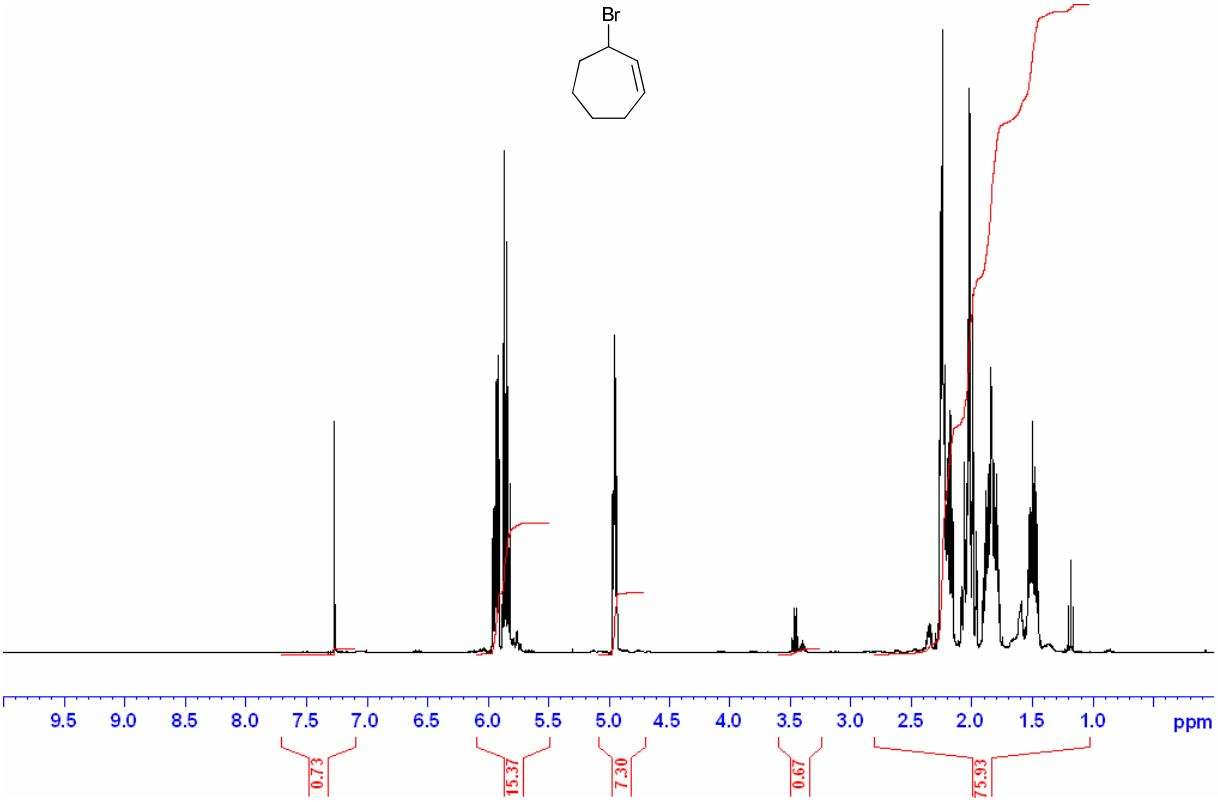
$Pd(OH)_2$/C (44 mg, 50% w/w) was added to a vigorously stirred solution of **92** (88 mg, 0.28 mmol) in degassed MeOH (3 mL) and the resultant suspension was stirred at rt under H_2 (1 atm) for 6 h. The suspension was filtered through a pad of Celite® (eluent MeOH) and the filtrate was concentrated *in vacuo* to give **96** as a colourless oil (39 mg, 98%, >99:1 dr); ν_{max} (film) 3357 (O–H), 2933 (C–H), 1593, 1448; δ_H (400 MHz, d_4-MeOH) 1.22-1.42 (3H, m, C(4)H_2, C(5)H_A), 1.43-1.53 (1H, m, C(3)*H*), 1.57-1.67 (2H, m, C(6)H_2), 1.78-1.80 (1H, m, C(5)H_B), 2.64 (1H, dd, *J* 7.6, 12.6, C(3)CH_AH$_B$N), 2.78 (1H, dd, *J* 5.8, 12.6, C(3)CH$_A$$H_B$N), 3.44-3.53 (1H, m, C(1)*H*), 3.88-3.93 (1H, m, C(2)*H*); δ_C (100 MHz, d_4-MeOH) 23.1 (*C*(4)) , 23.5 (*C*(5)), 28.1 (*C*(6)), 43.0 (*C*(3)), 43.7 (C(3)*C*H$_2$N), 69.5 (*C*(2)), 72.5 (*C*(1)); HRMS (ESI$^+$) $C_7H_{16}NO_2^+$ ([M+H]$^+$) requires 146.1176; found 146.1175.

2. Copies of ^{1}H and ^{13}C Spectra

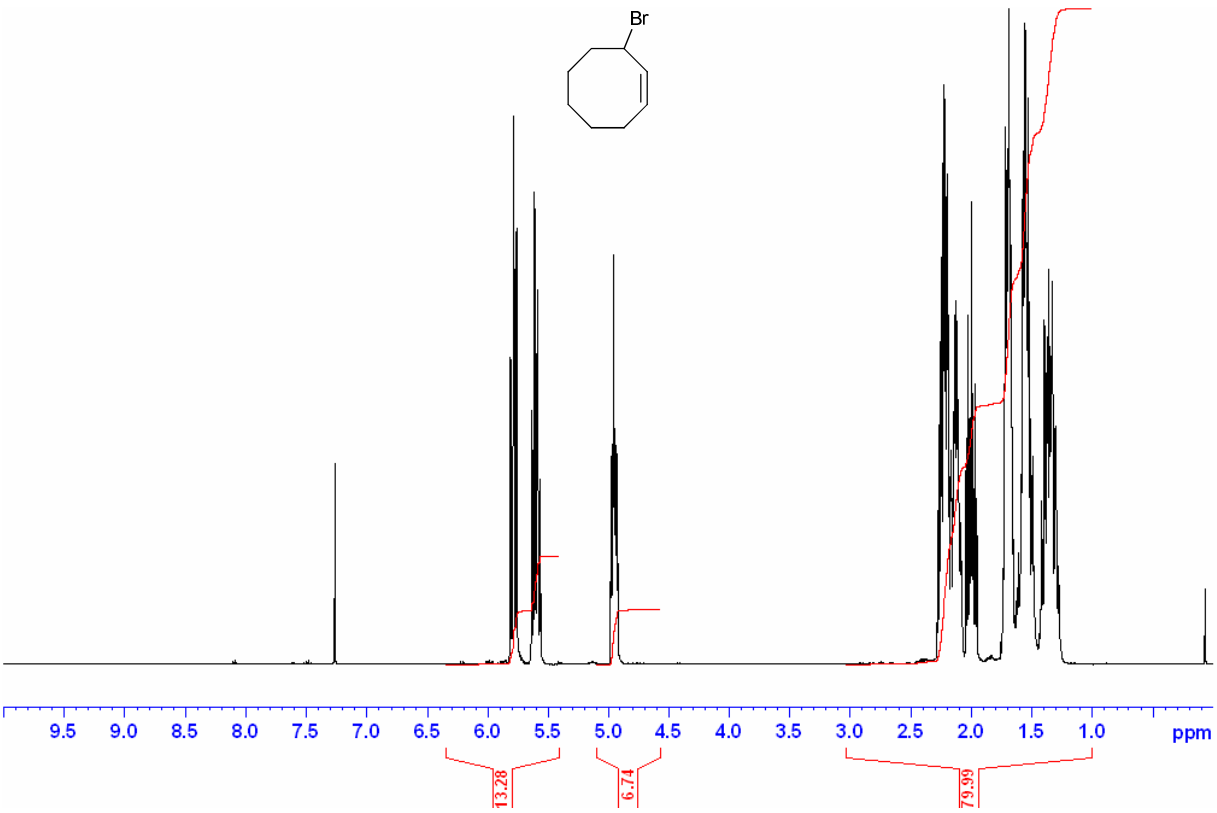
Cycloheptene 9 (400 MHz ^{1}H, $CDCl_3$)



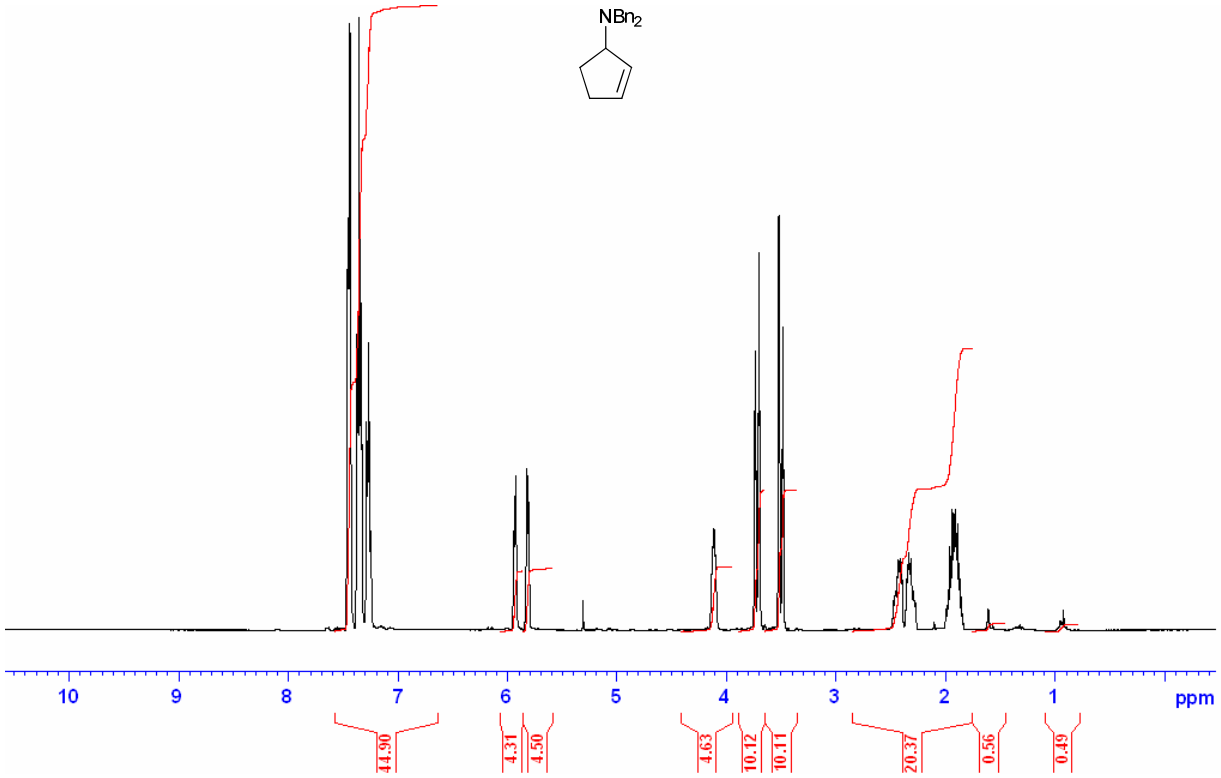
(*RS*)-3-Bromocyclohept-1-ene 12 (400 MHz ^{1}H, $CDCl_3$)



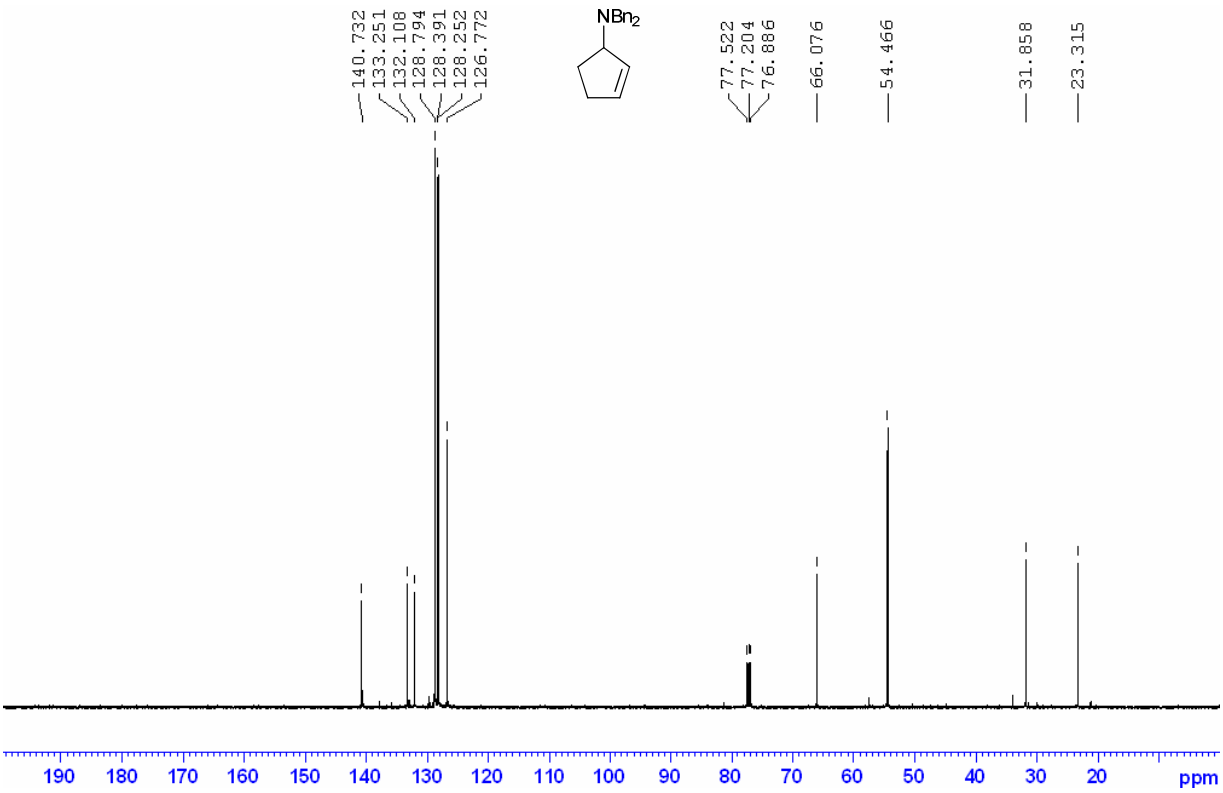
(*RS*,*Z*)-3-Bromocyclooct-1-ene 13 (400 MHz ^{1}H, $CDCl_3$)



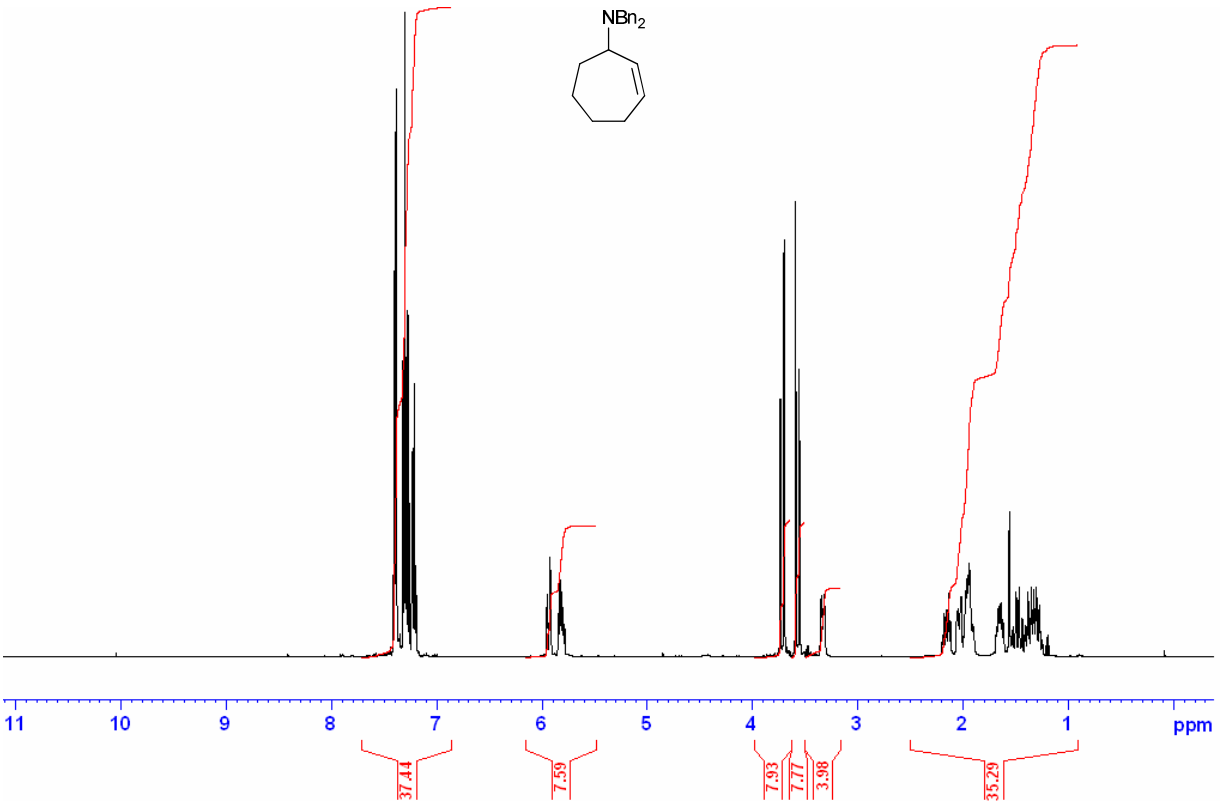
(*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopent-1-ene 14 (400 MHz ^{1}H, $CDCl_3$)



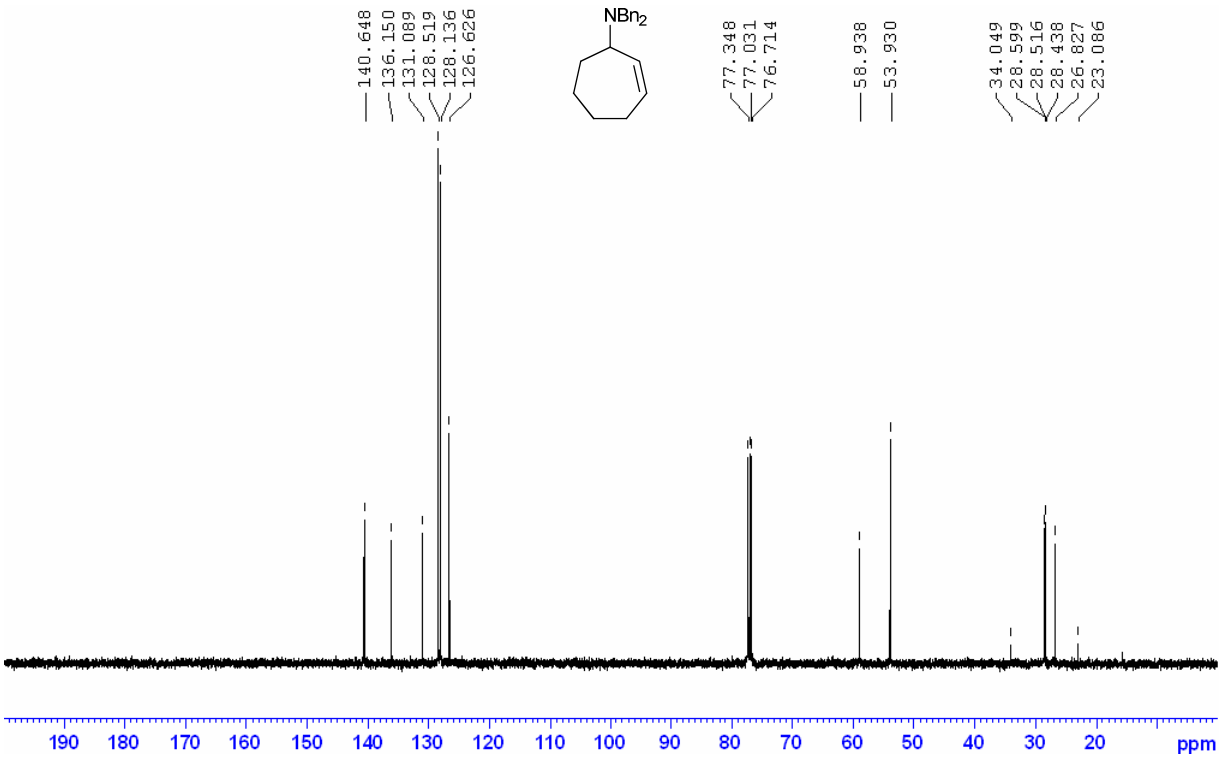
(*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopent-1-ene 14 (100 MHz ^{13}C, $CDCl_3$)



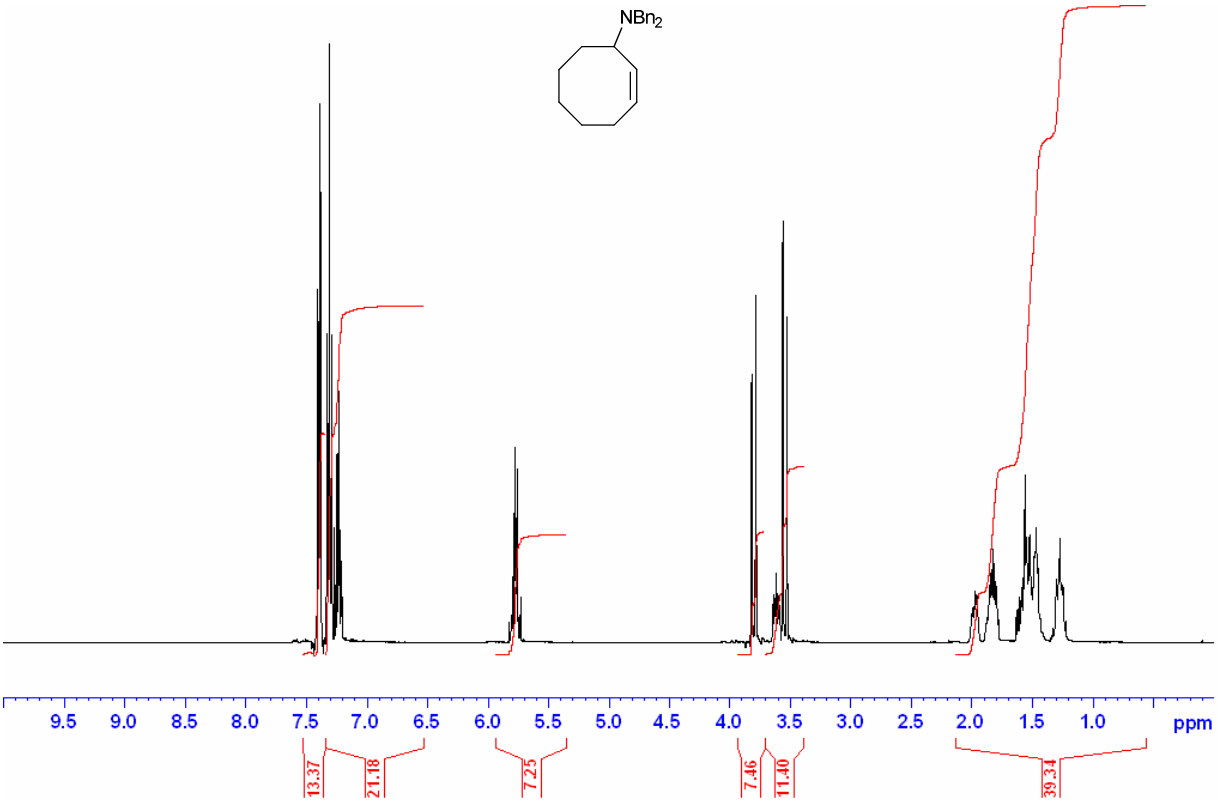
(*RS*)-3-(*N*,*N*-Dibenzylamino)cyclohept-1-ene 15 (400 MHz ^{1}H, $CDCl_3$)



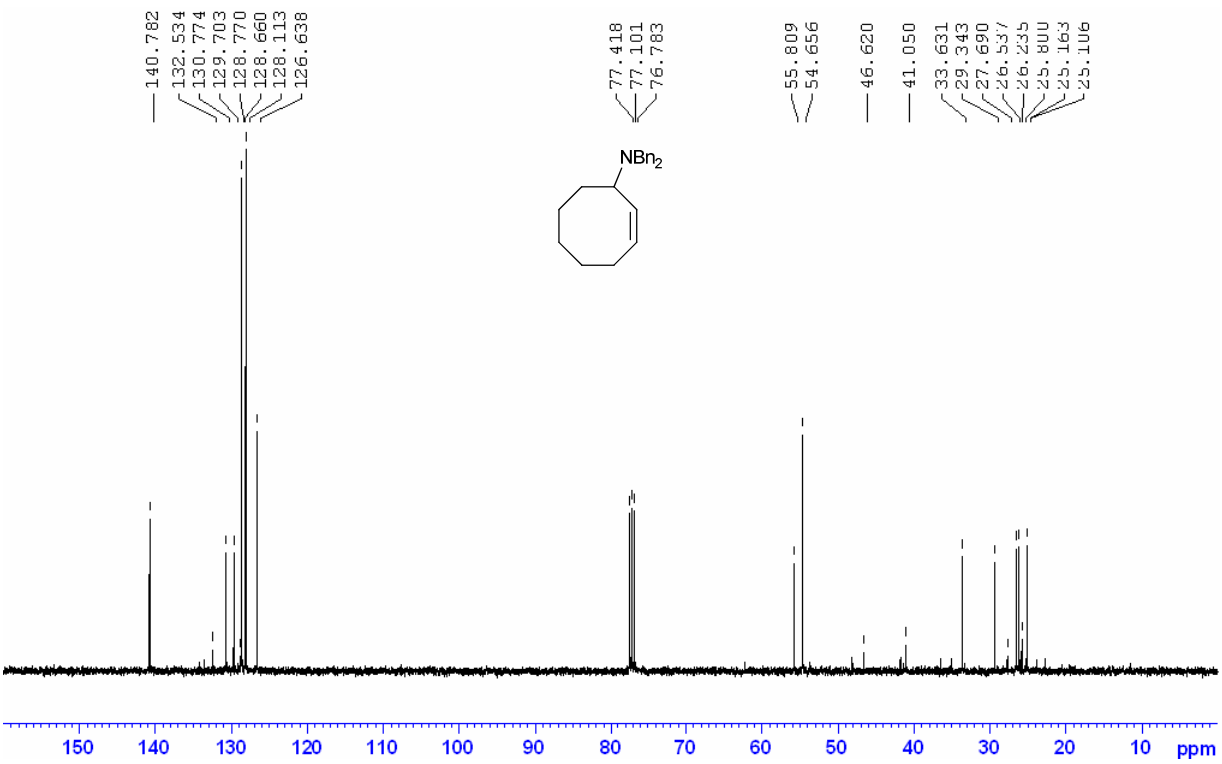
(*RS*)-3-(*N*,*N*-Dibenzylamino)cyclohept-1-ene 15 (100 MHz ^{13}C, $CDCl_3$)



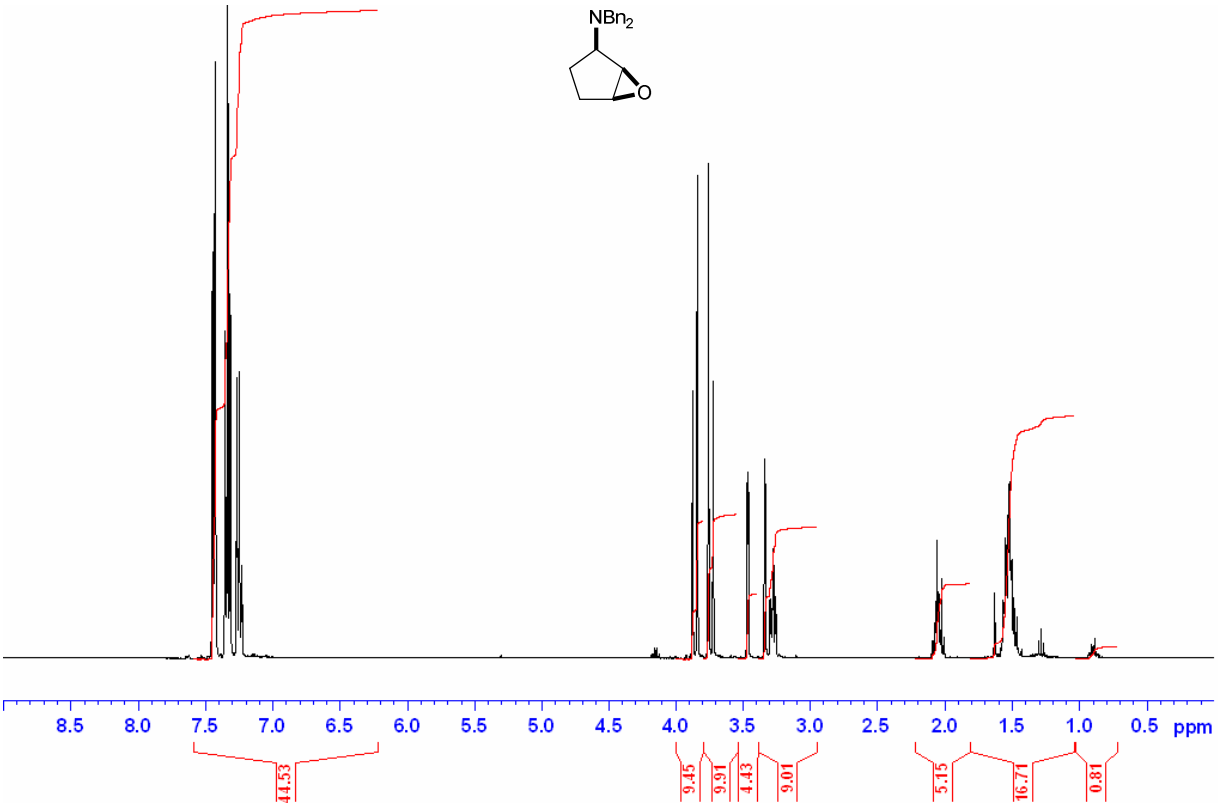
(*RS*,*Z*)-3-(*N*,*N*-Dibenzylamino)cyclooct-1-ene 16 (400 MHz ^{1}H, $CDCl_3$)



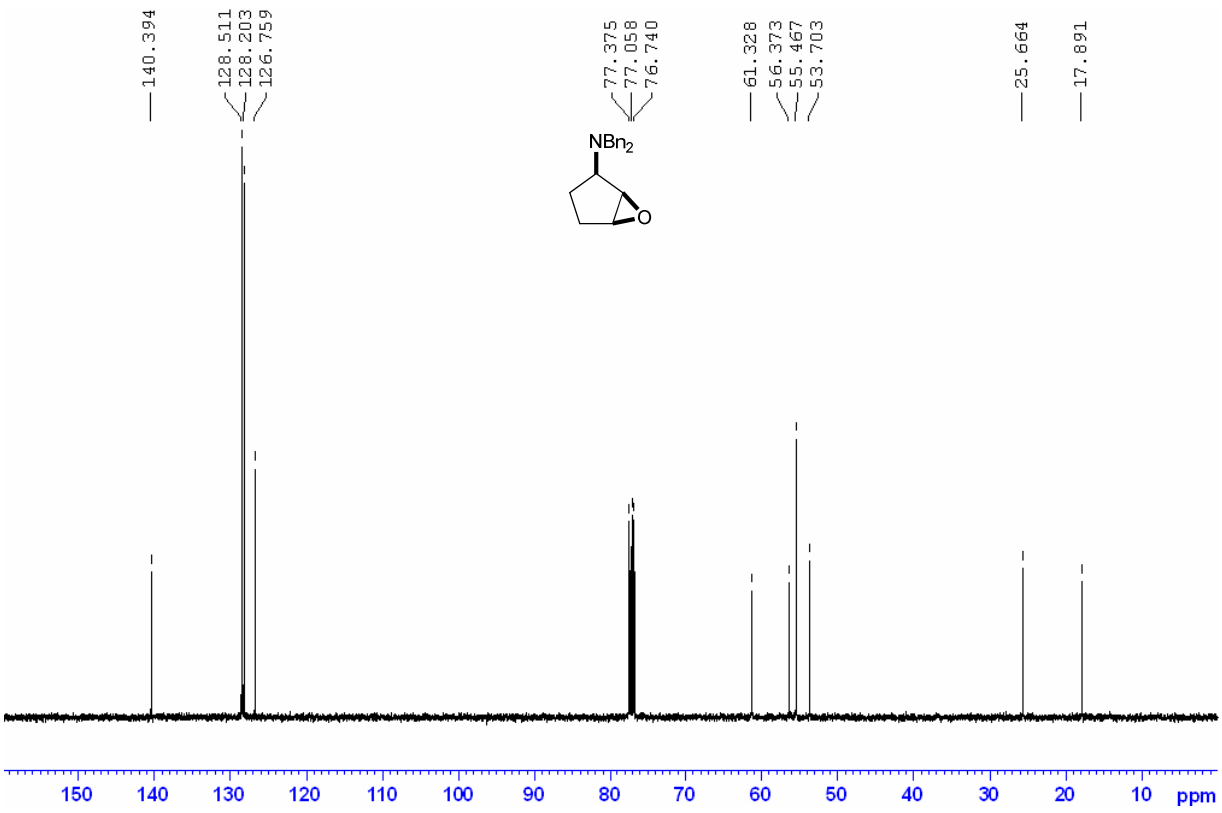
(*RS*,*Z*)-3-(*N*,*N*-Dibenzylamino)cyclooct-1-ene 16 (100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 20 (400 MHz ^{1}H, $CDCl_3$)

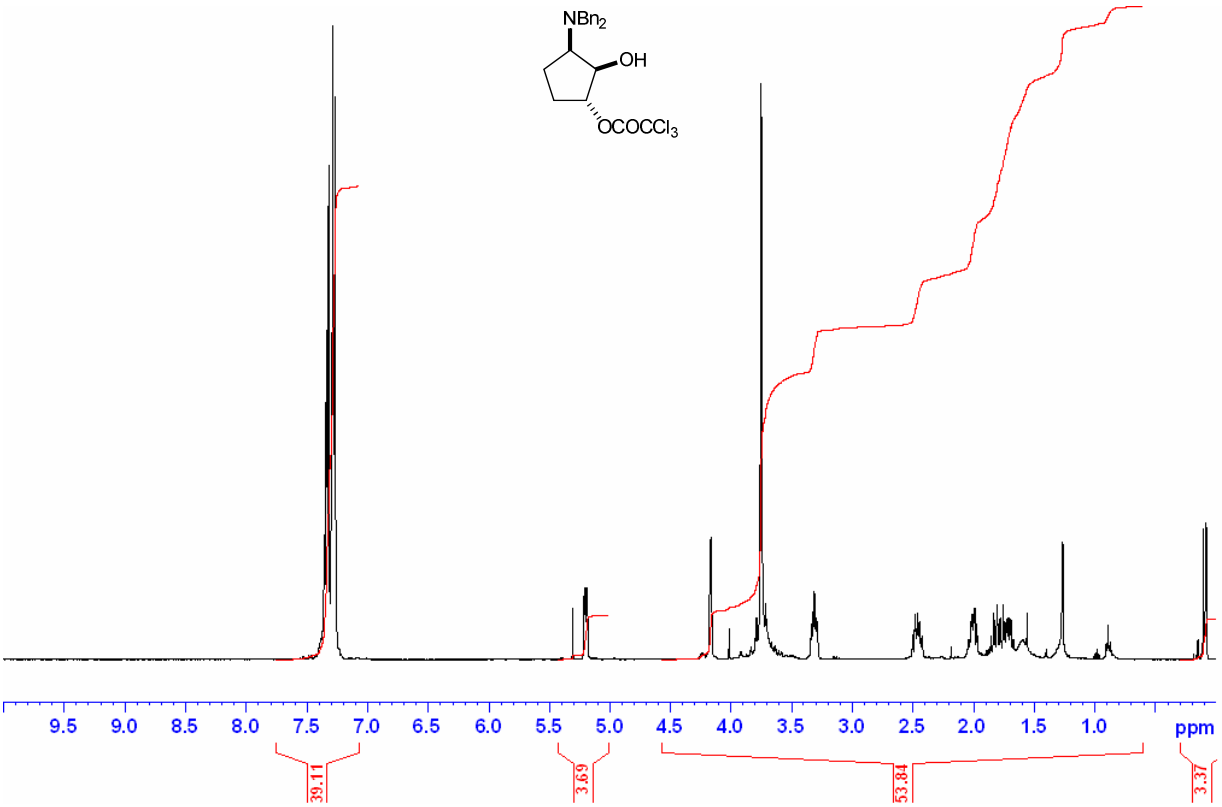


(1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 20 (100 MHz ^{13}C, $CDCl_3$)



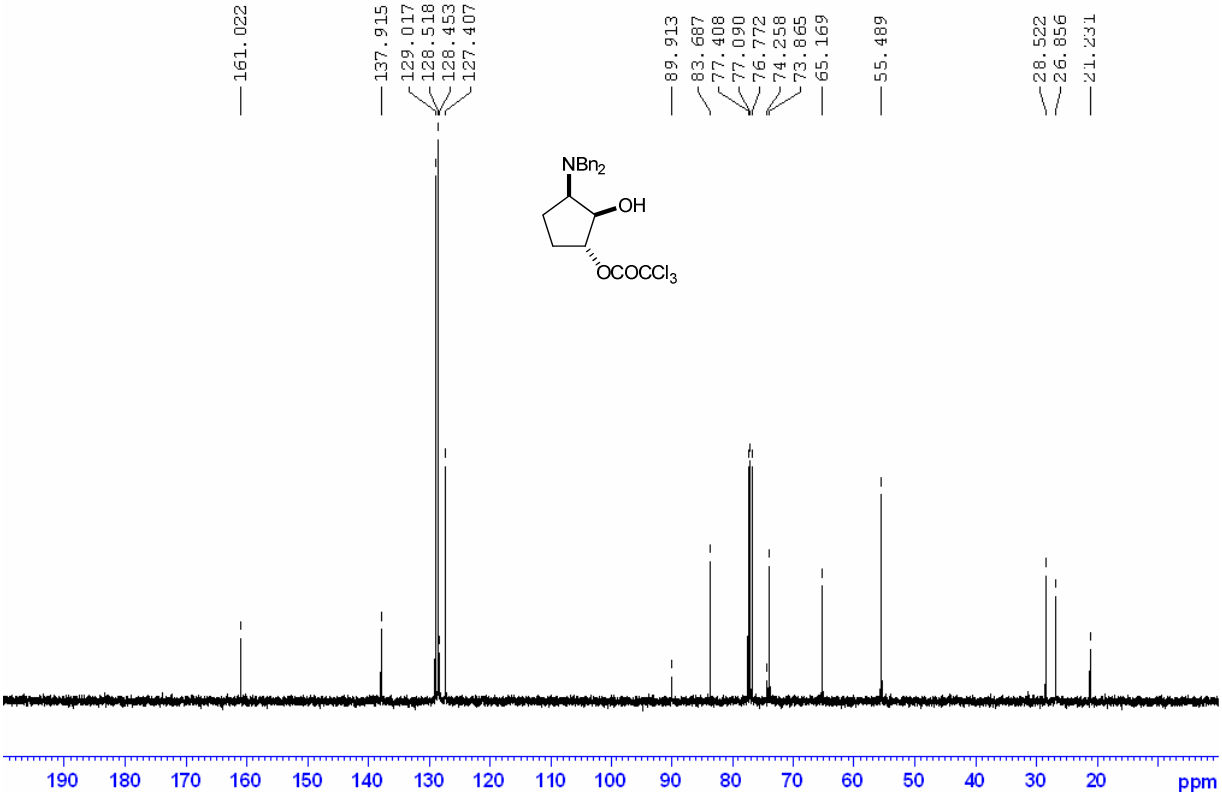
(1*RS*,2*RS*,3*RS*)-1-Trichloroacetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cyclopentane 21

(400 MHz ^{1}H, $CDCl_3$)

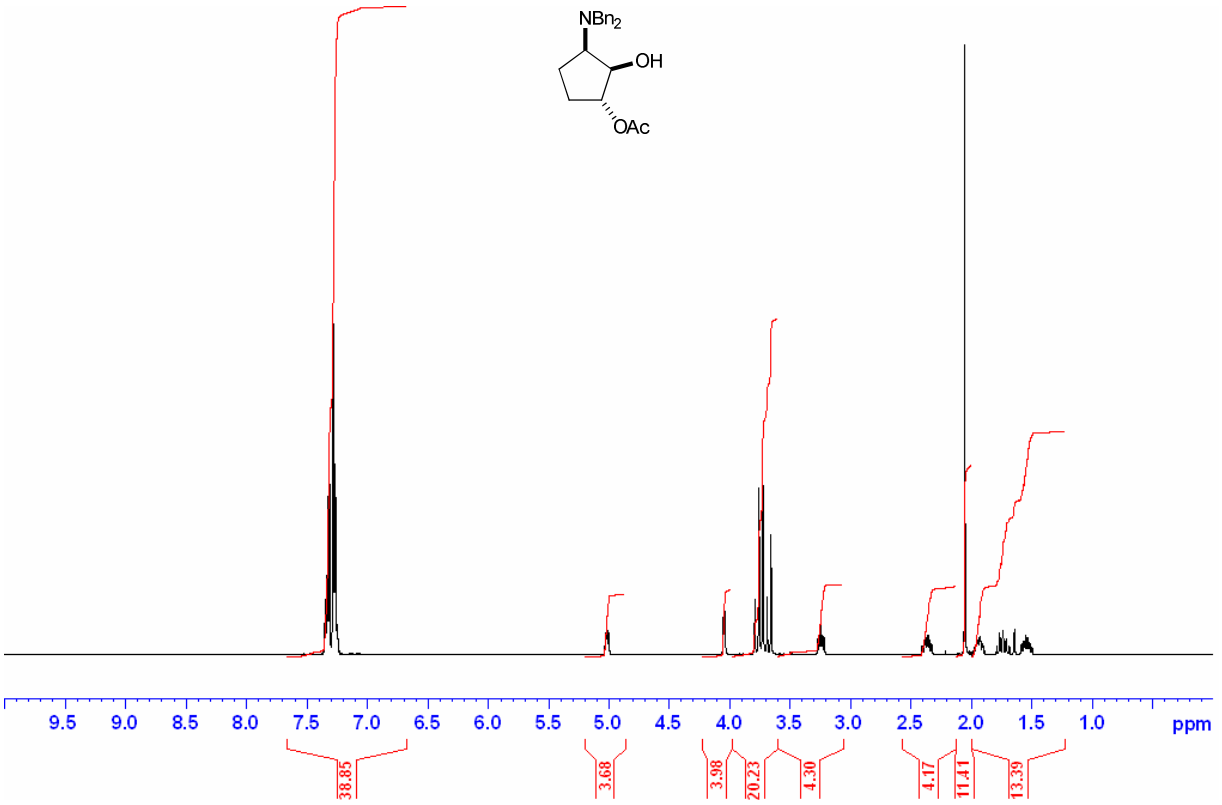


(1*RS*,2*RS*,3*RS*)-1-Trichloroacetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cyclopentane 21

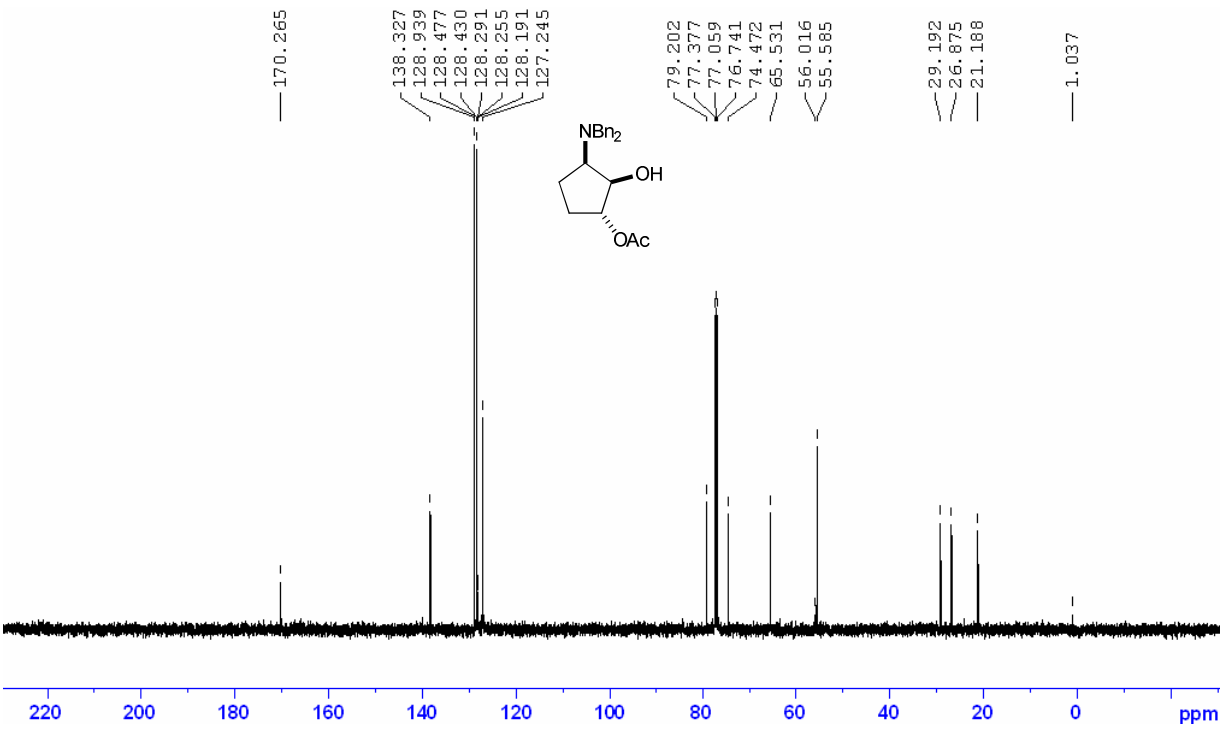
(100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cyclopentane 22 (400 MHz ^{1}H, $CDCl_3$)

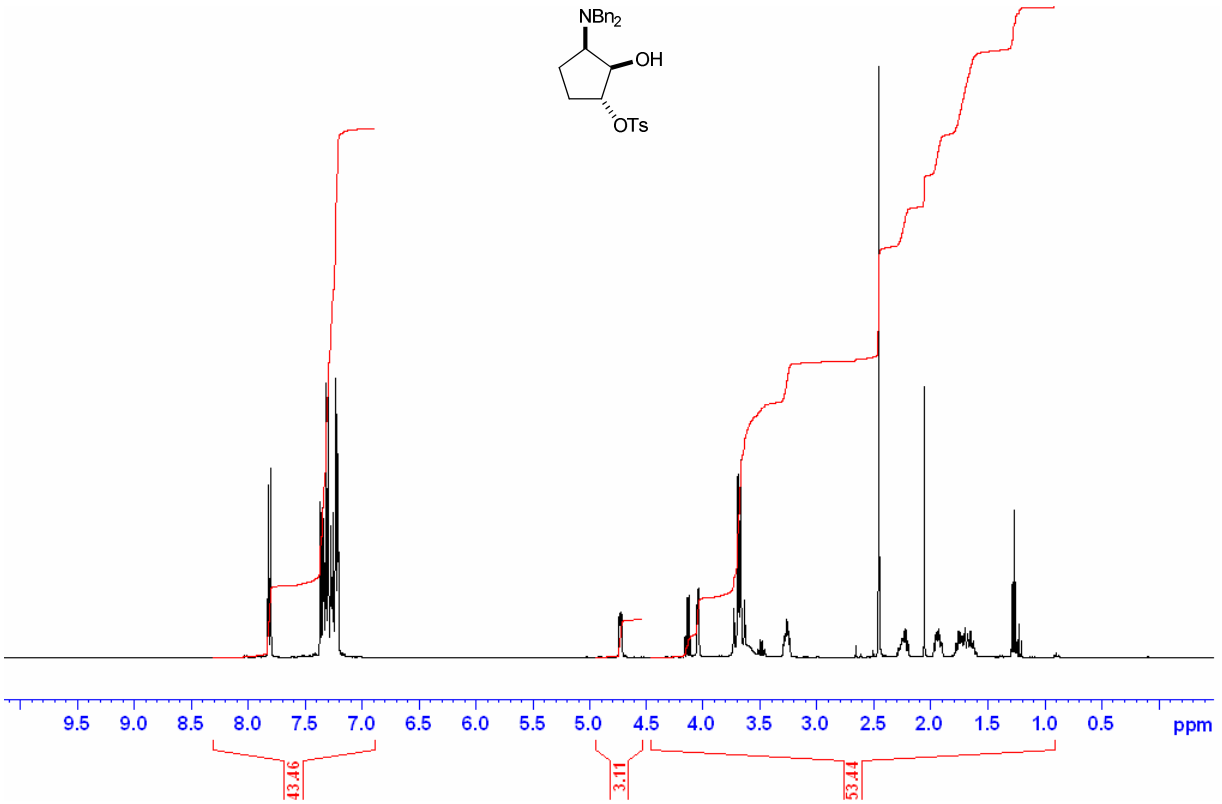


(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cyclopentane 22 (100 MHz ^{13}C, $CDCl_3$)



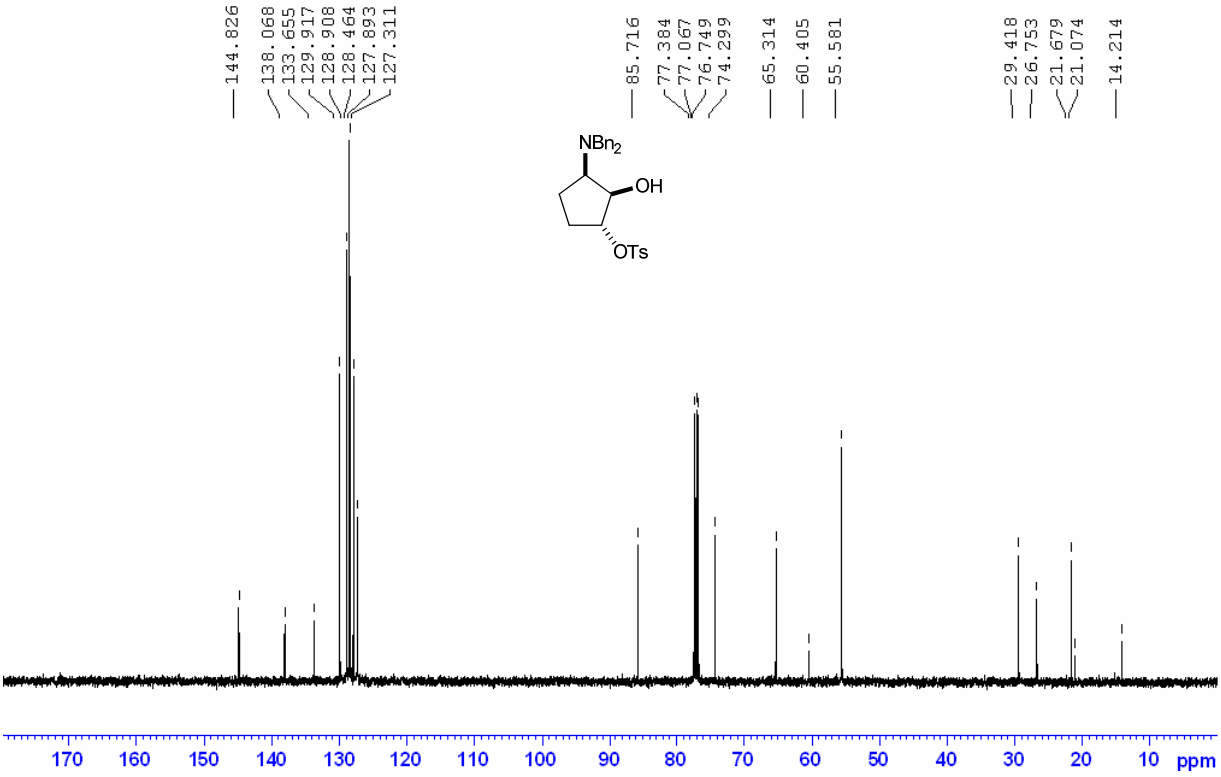
(1*RS*,2*RS*,3*RS*)-1-*p*-Toluenesulfonyloxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cyclopentane 23

(400 MHz ^{1}H, $CDCl_3$)

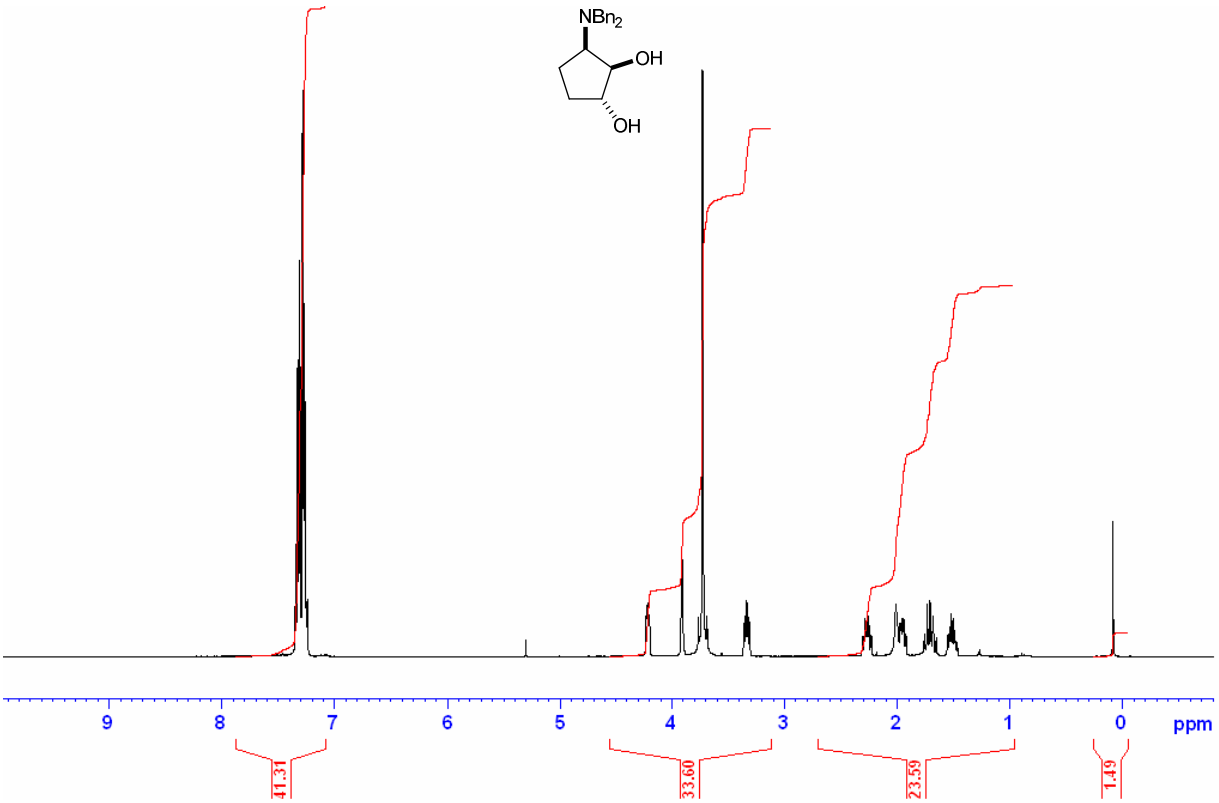


(1*RS*,2*RS*,3*RS*)-1-*p*-Toluenesulfonyloxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cyclopentane 23

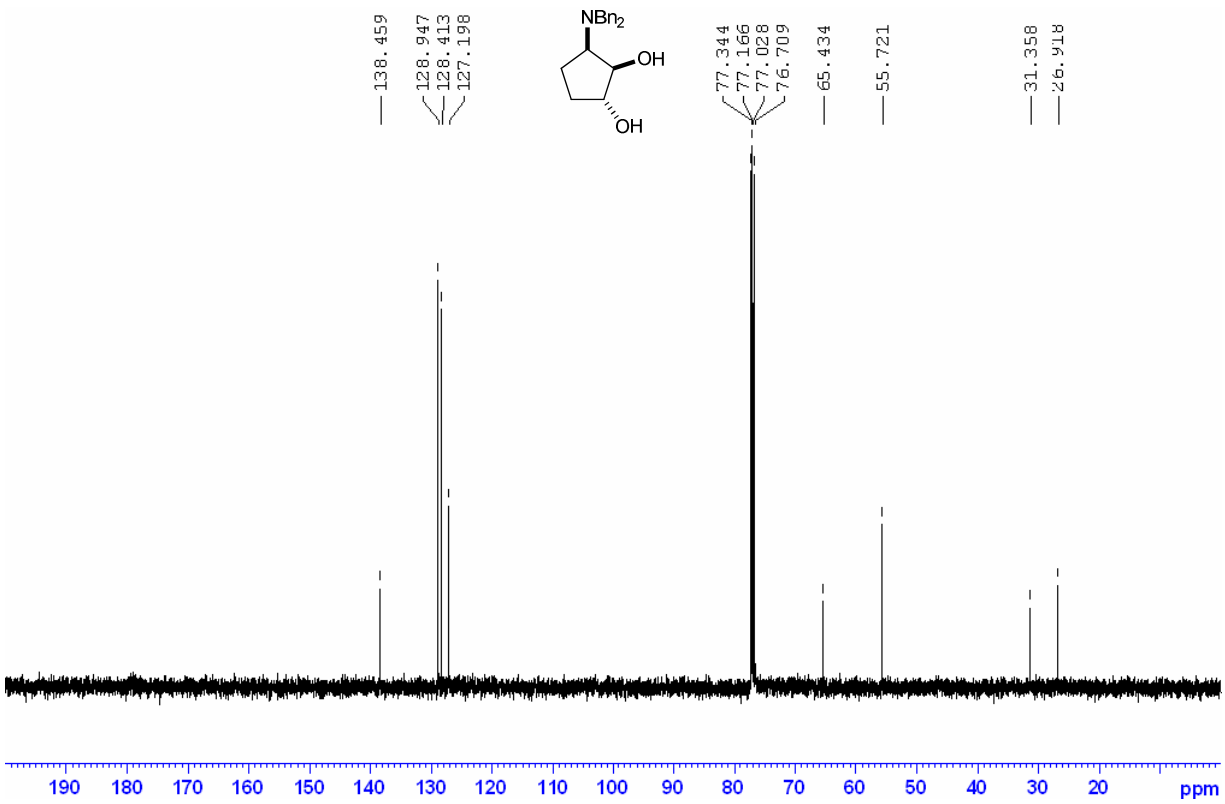
(100 MHz ^{13}C, $CDCl_3$)



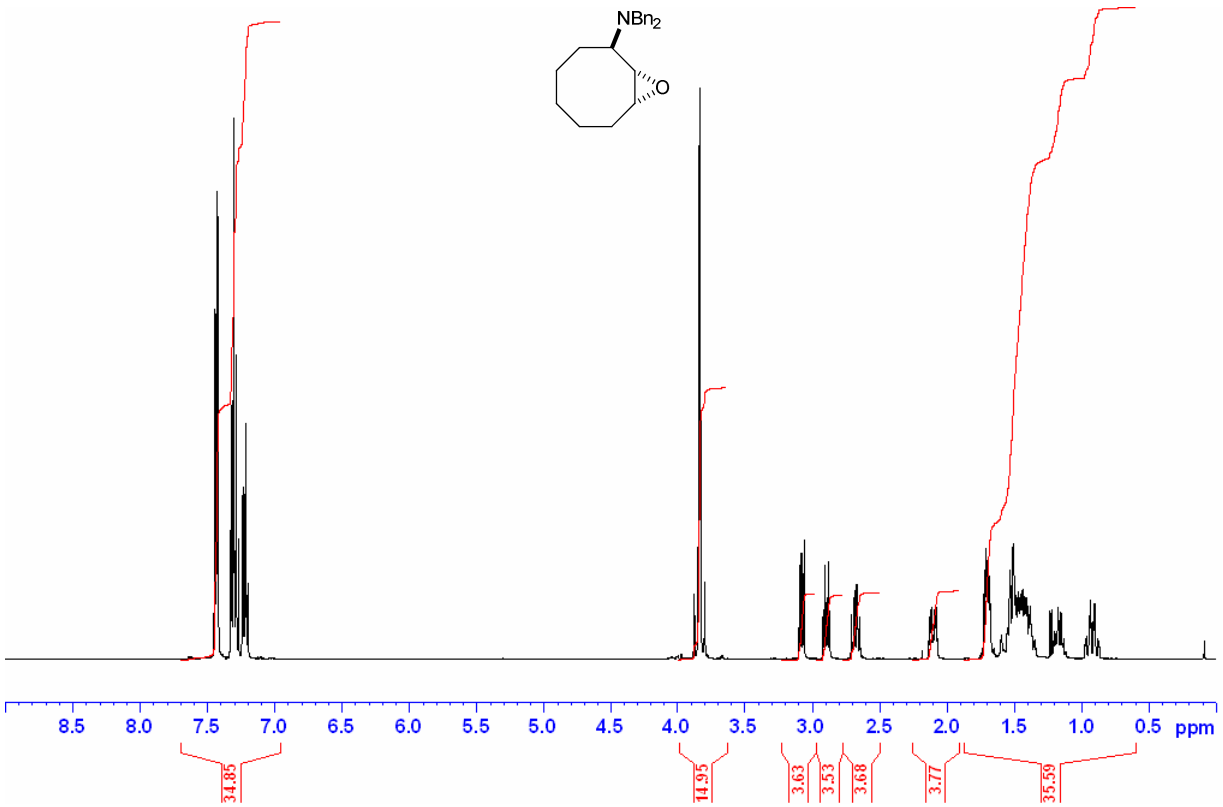
(1*RS*,2*RS*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 24 (400 MHz ^{1}H, $CDCl_3$)



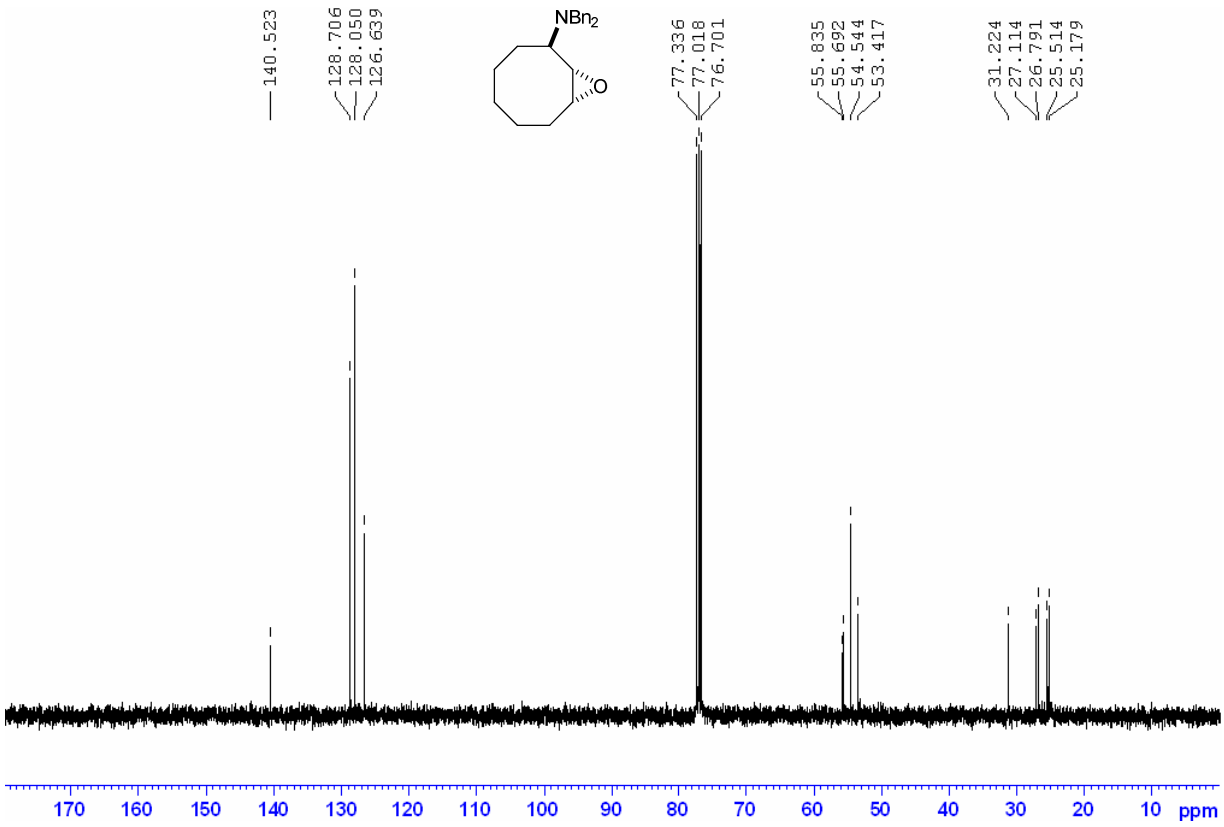
(1*RS*,2*RS*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 24 (100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclooctane 25 (400 MHz ^{1}H, $CDCl_3$)

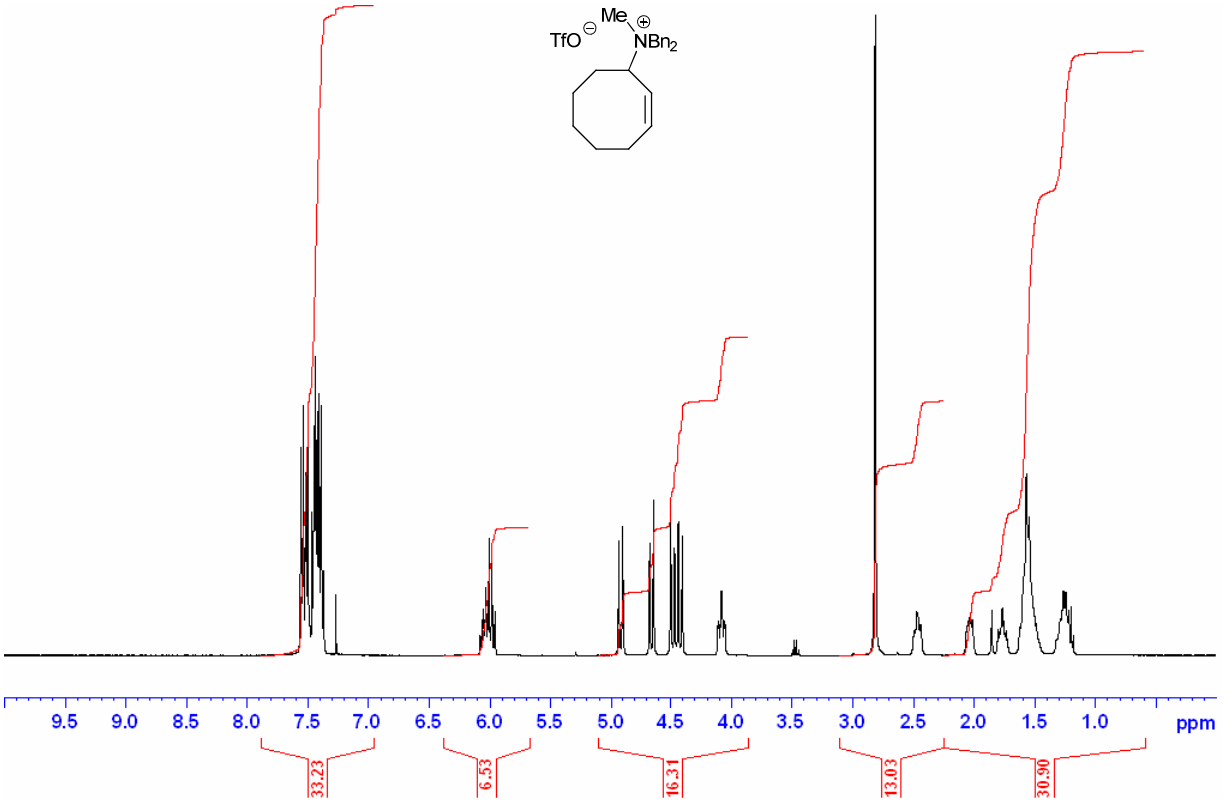


(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclooctane 25 (100 MHz ^{13}C, $CDCl_3$)



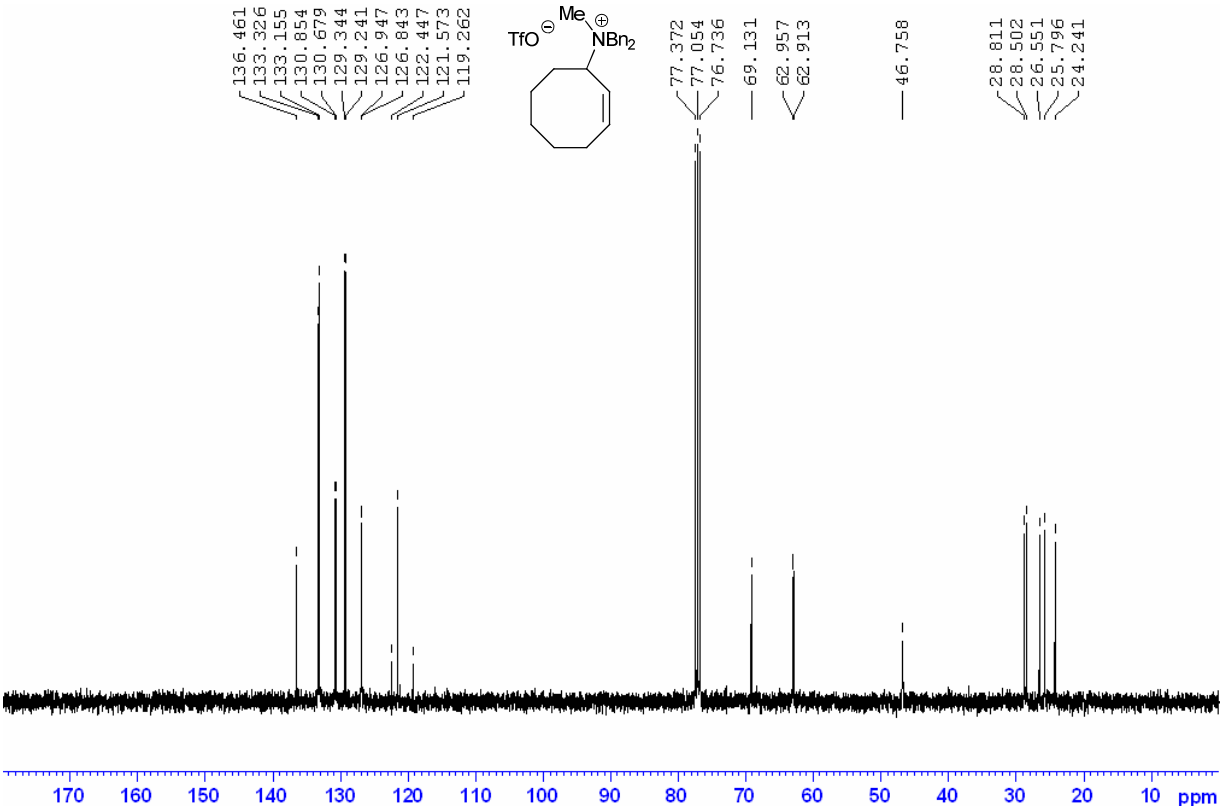
(*RS*,*Z*)-3-(*N*,*N*-Dibenzyl-*N*-methylammonio)cyclooct-1-ene trifluoromethanesulfonate 26

(400 MHz ^{1}H, $CDCl_3$)

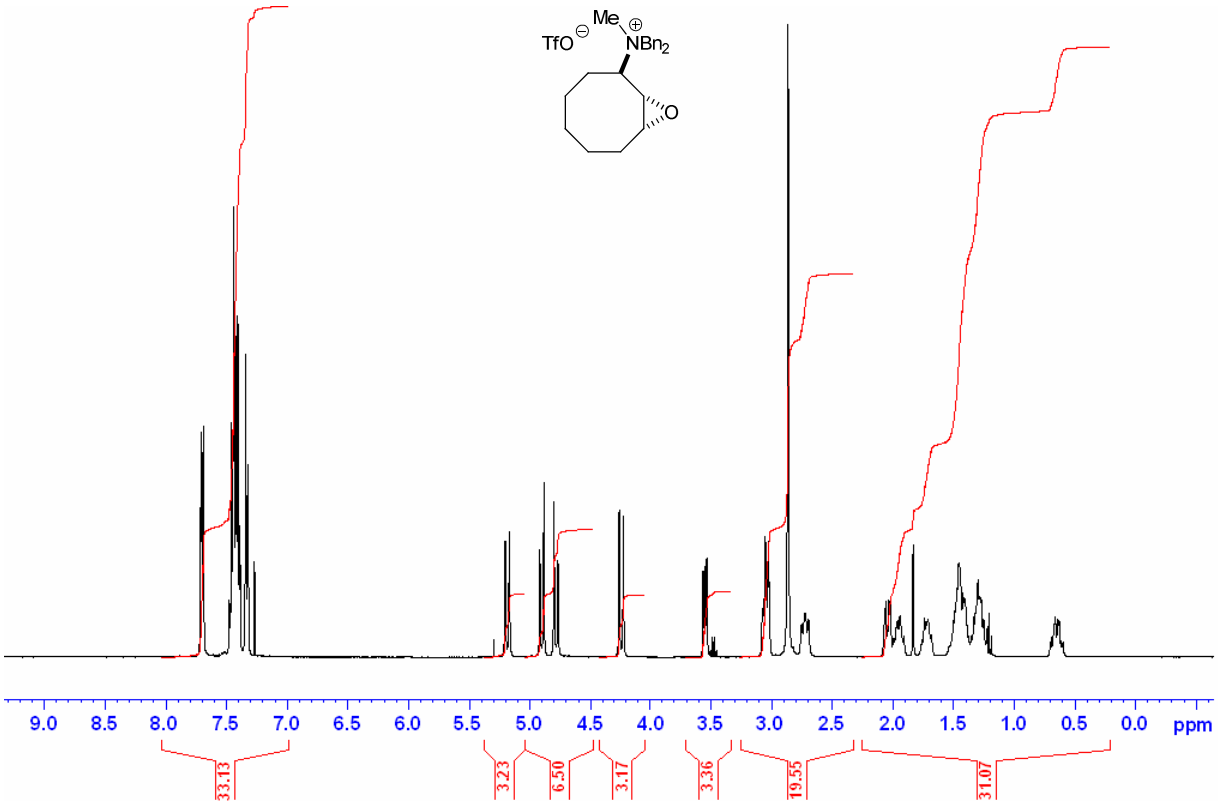


(*RS*,*Z*)-3-(*N*,*N*-Dibenzyl-*N*-methylammonio)cyclooct-1-ene trifluoromethanesulfonate 26

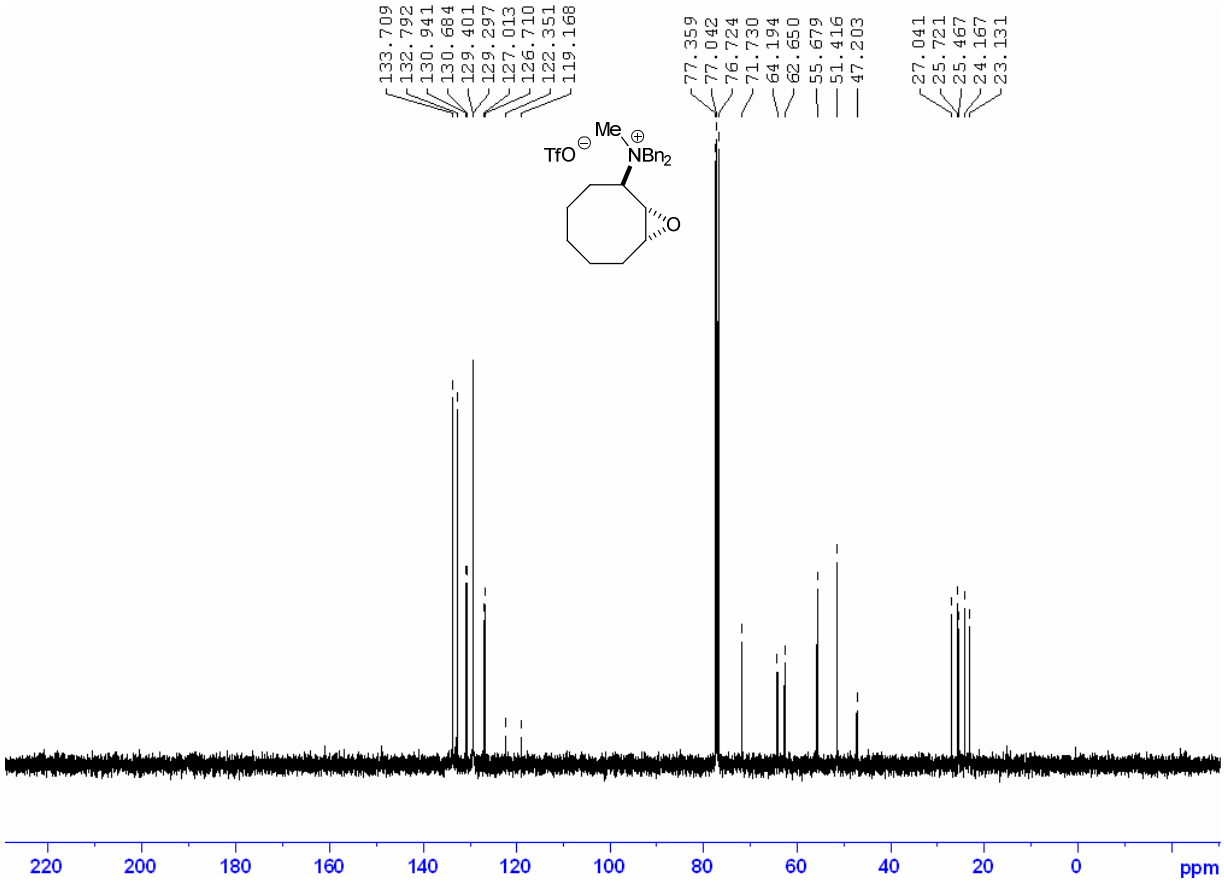
(100 MHz ^{13}C, $CDCl_3$)



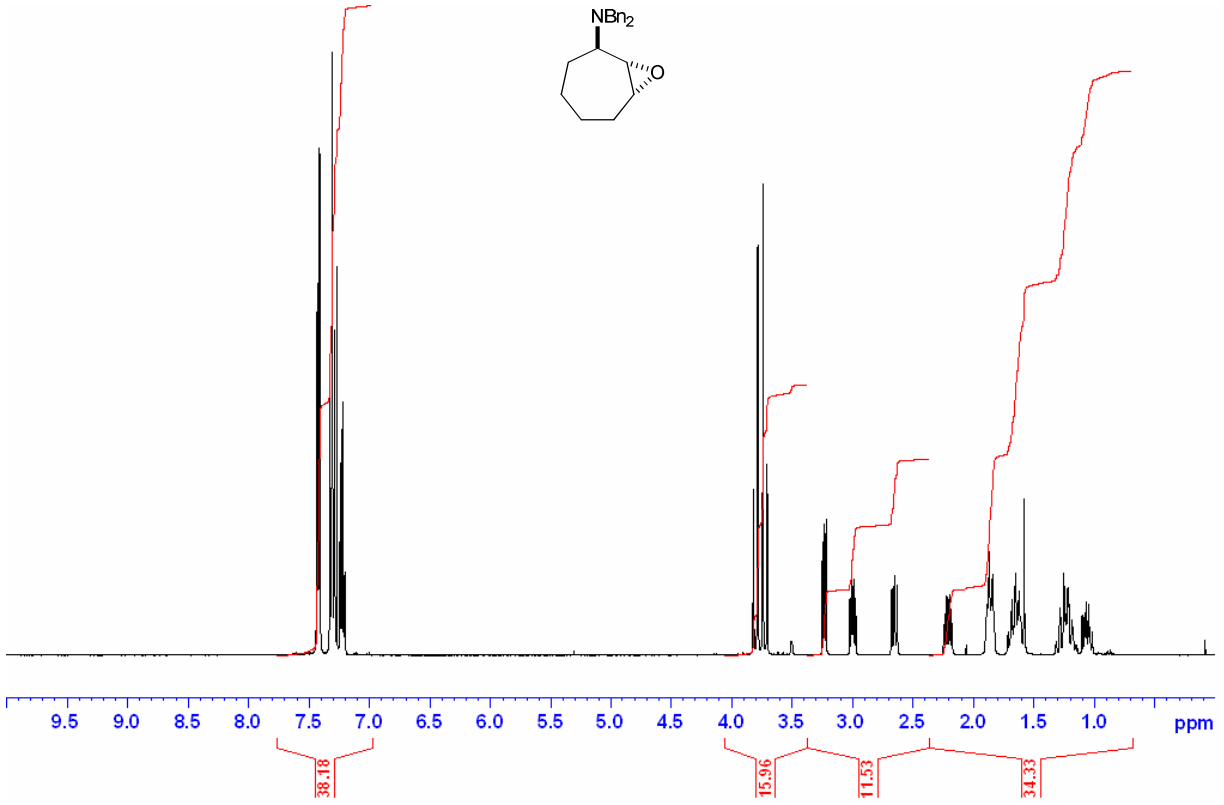
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzyl-*N*-methylammonio)cyclooctane trifluoromethanesulfonate 27 (400 MHz ^{1}H, $CDCl_3$)



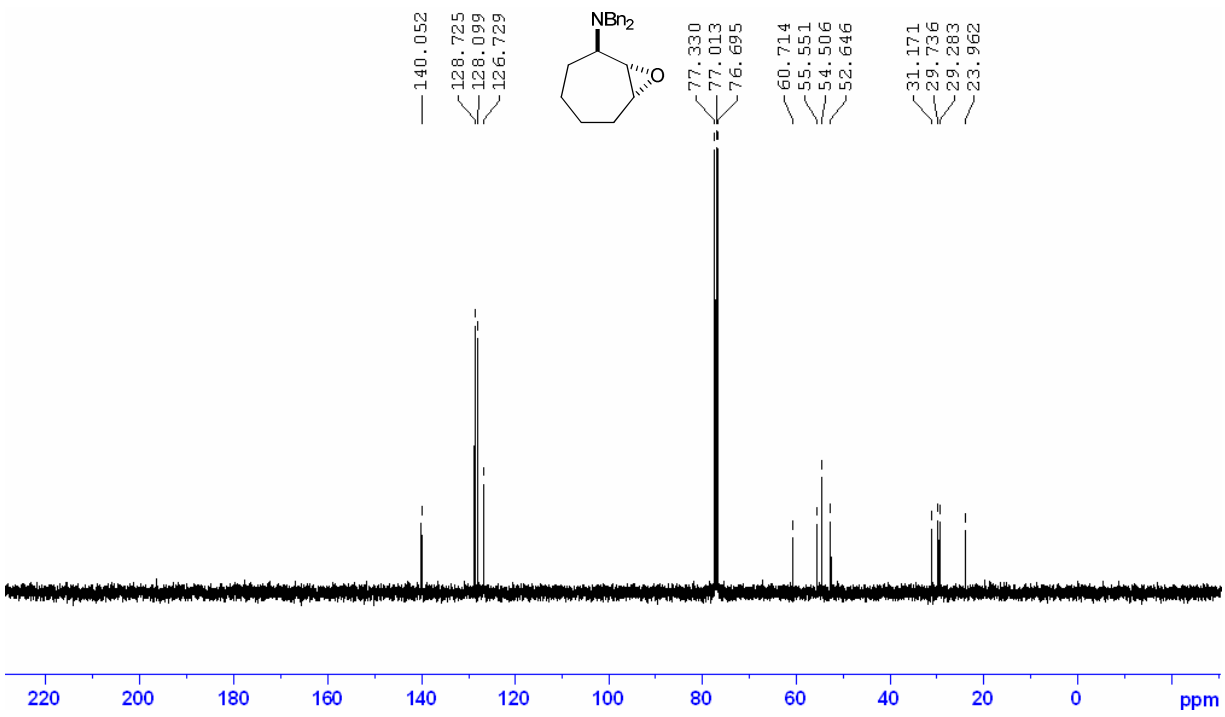
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzyl-*N*-methylammonio)cyclooctane trifluoromethanesulfonate 27 (100 MHz ^{13}C, $CDCl_3$)



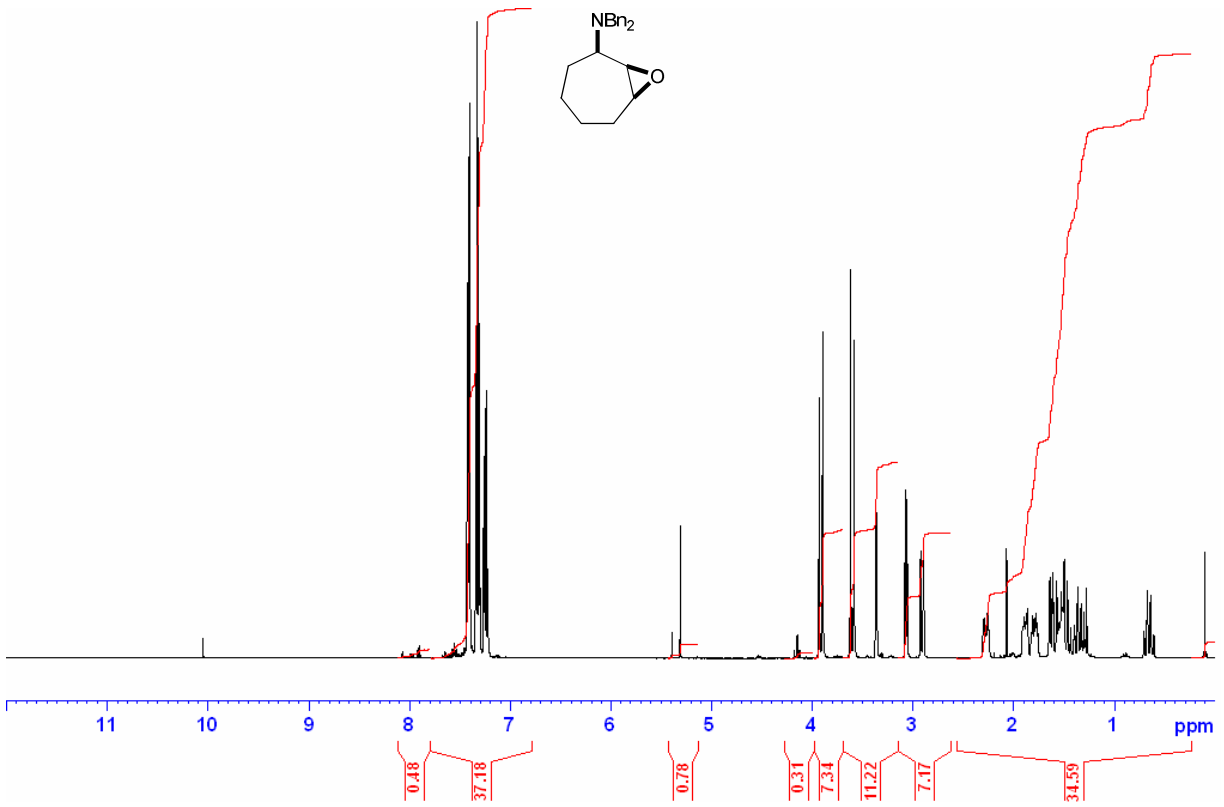
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cycloheptane 28 (400 MHz ^{1}H, $CDCl_3$)



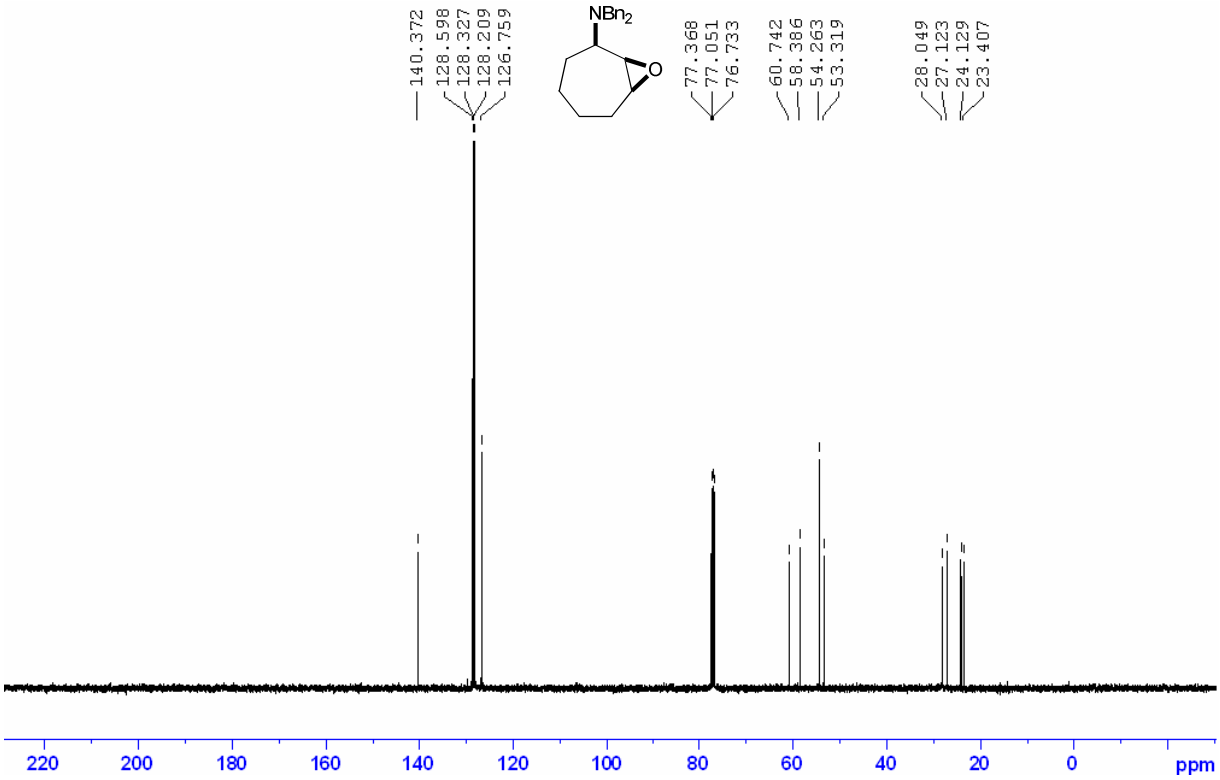
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cycloheptane 28 (100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cycloheptane 29 (400 MHz ^{1}H, $CDCl_3$)

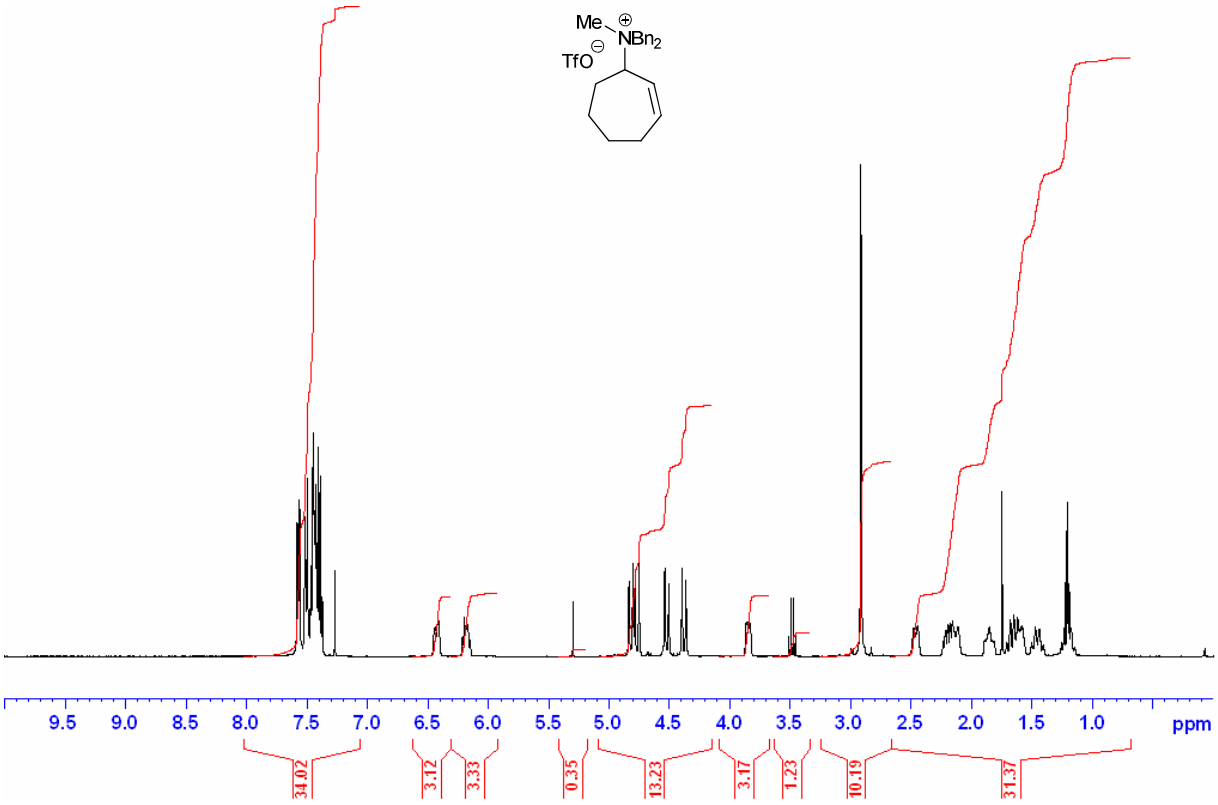


(1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cycloheptane 29 (100 MHz ^{13}C, $CDCl_3$)



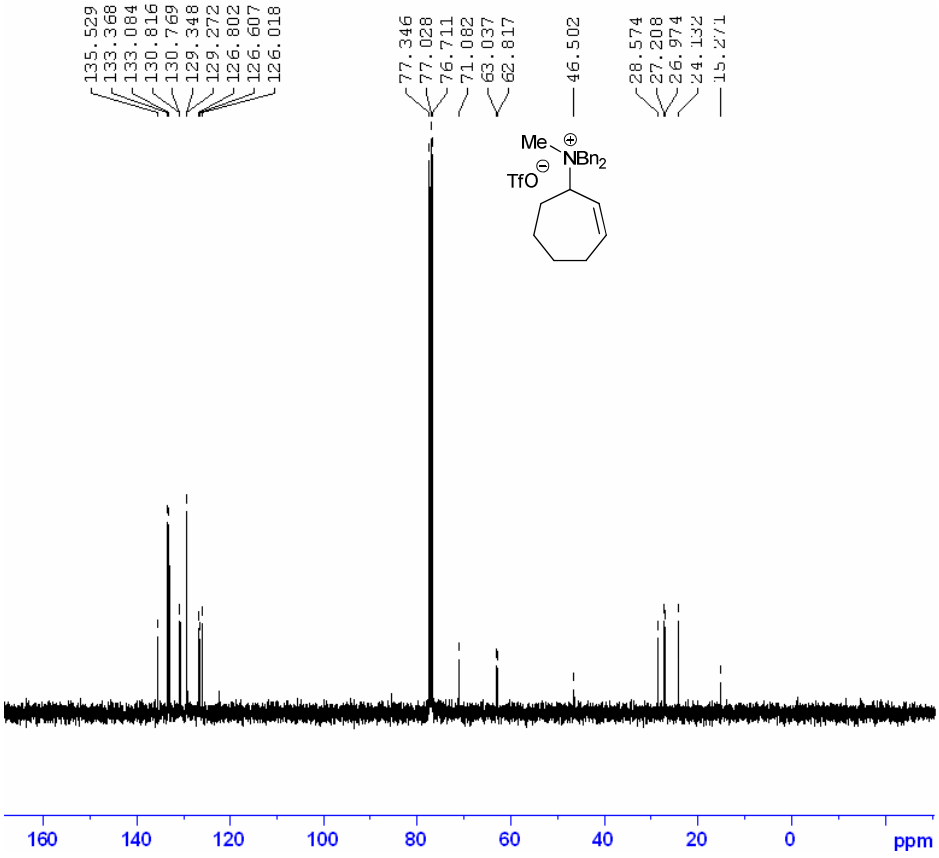
(*RS*)-3-(*N*,*N*-Dibenzyl-*N*-methylammonio)cyclohept-1-ene trifluoromethanesulfonate 30

(400 MHz ^{1}H, $CDCl_3$)

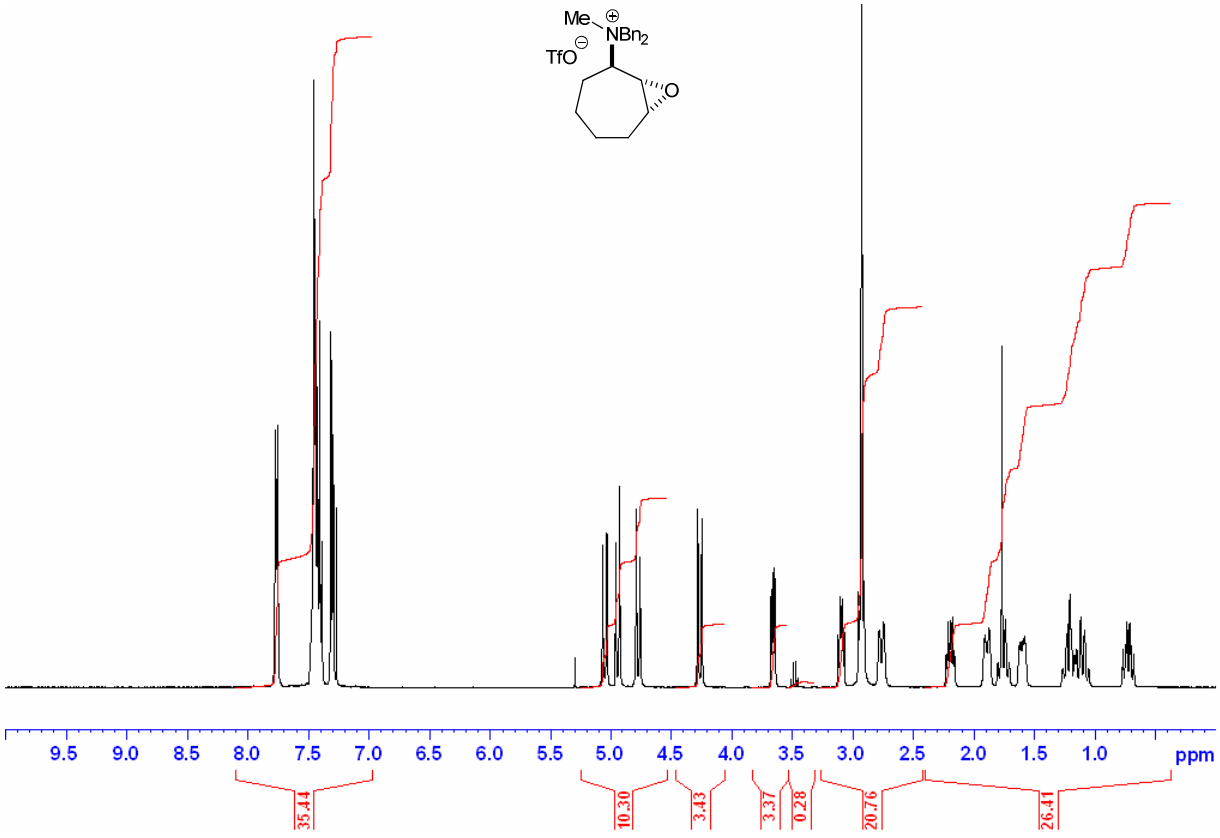


(*RS*)-3-(*N*,*N*-Dibenzyl-*N*-methylammonio)cyclohept-1-ene trifluoromethanesulfonate 30

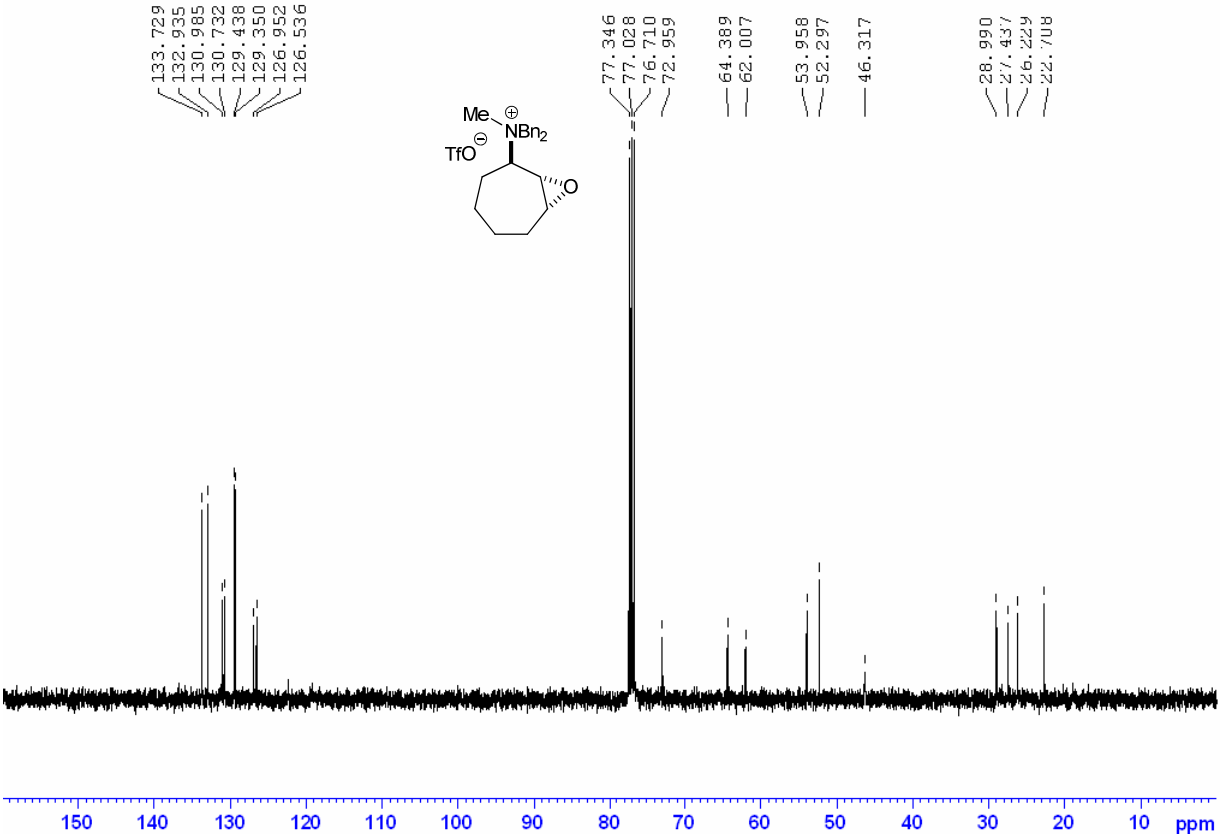
(100 MHz ^{13}C, $CDCl_3$)



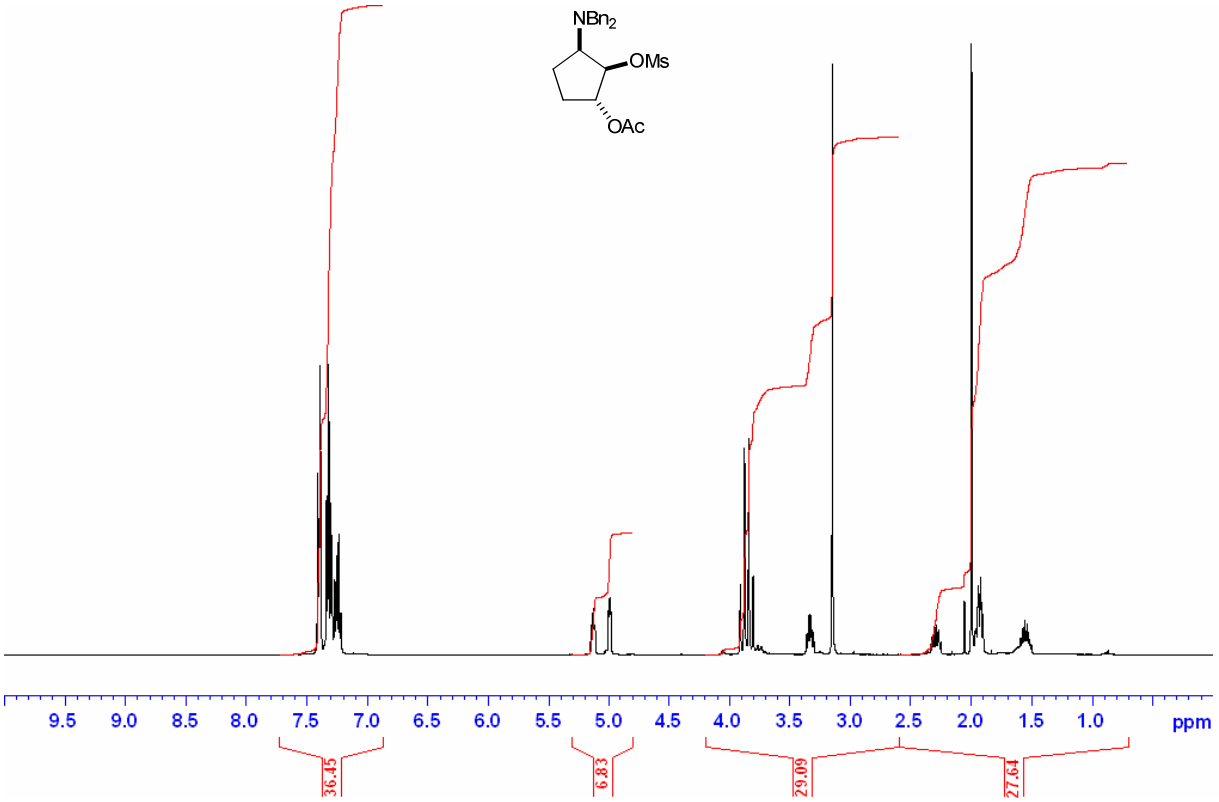
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzyl-*N*-methylammonio)cycloheptane trifluoromethanesulfonate 31 (400 MHz ^{1}H, $CDCl_3$)



(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzyl-*N*-methylammonio)cycloheptane trifluoromethanesulfonate 31 (100 MHz ^{13}C, $CDCl_3$)

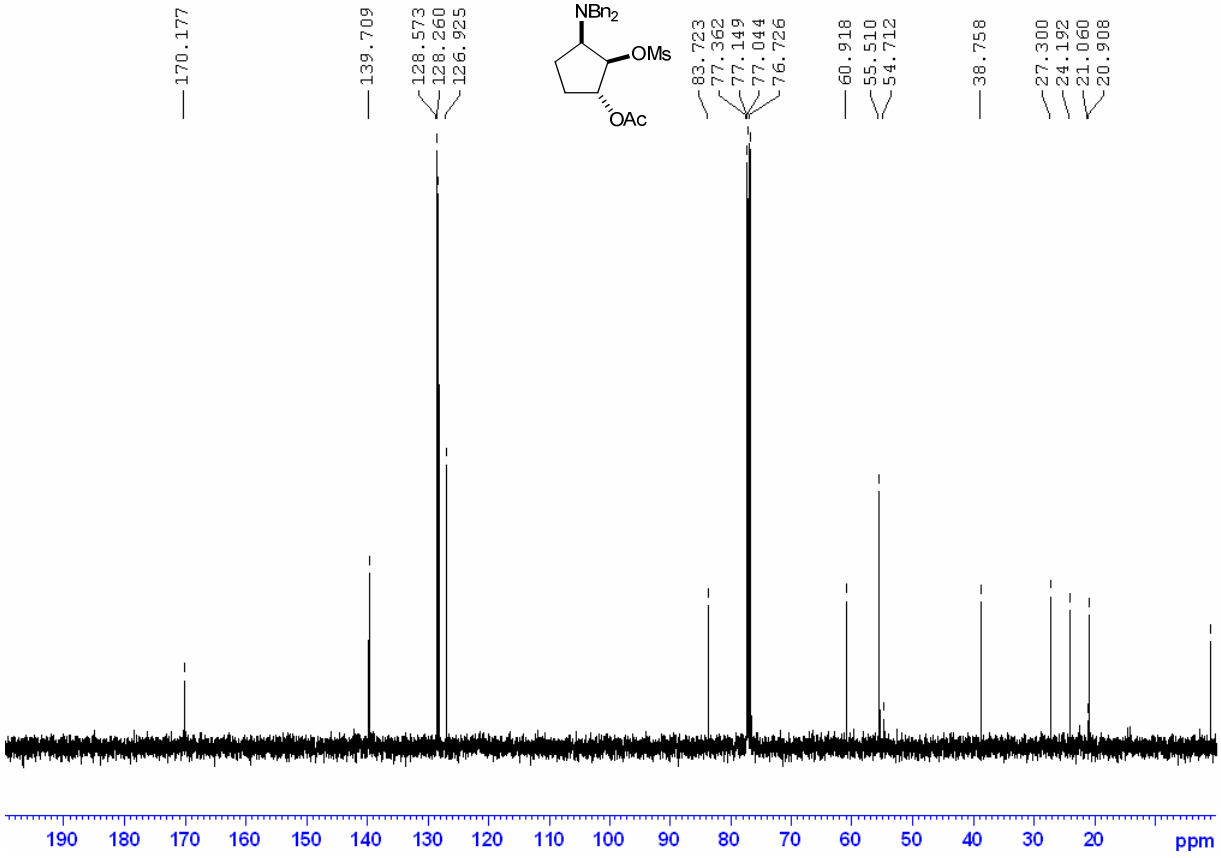


(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-methanesulfonyloxy-3-(*N*,*N*-dibenzylamino)cyclopentane 33 (400 MHz ^{1}H, $CDCl_3$)

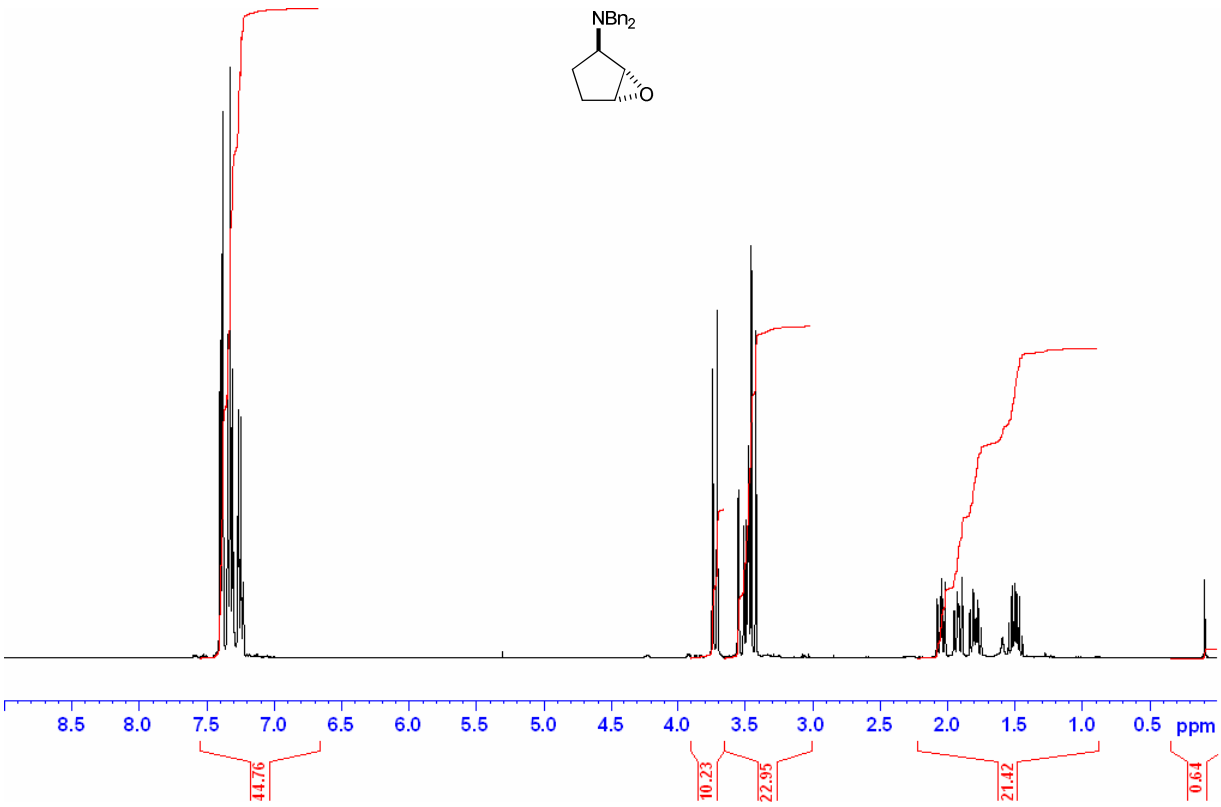


(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-methanesulfonyloxy-3-(*N*,*N*-dibenzylamino)cyclopentane 33

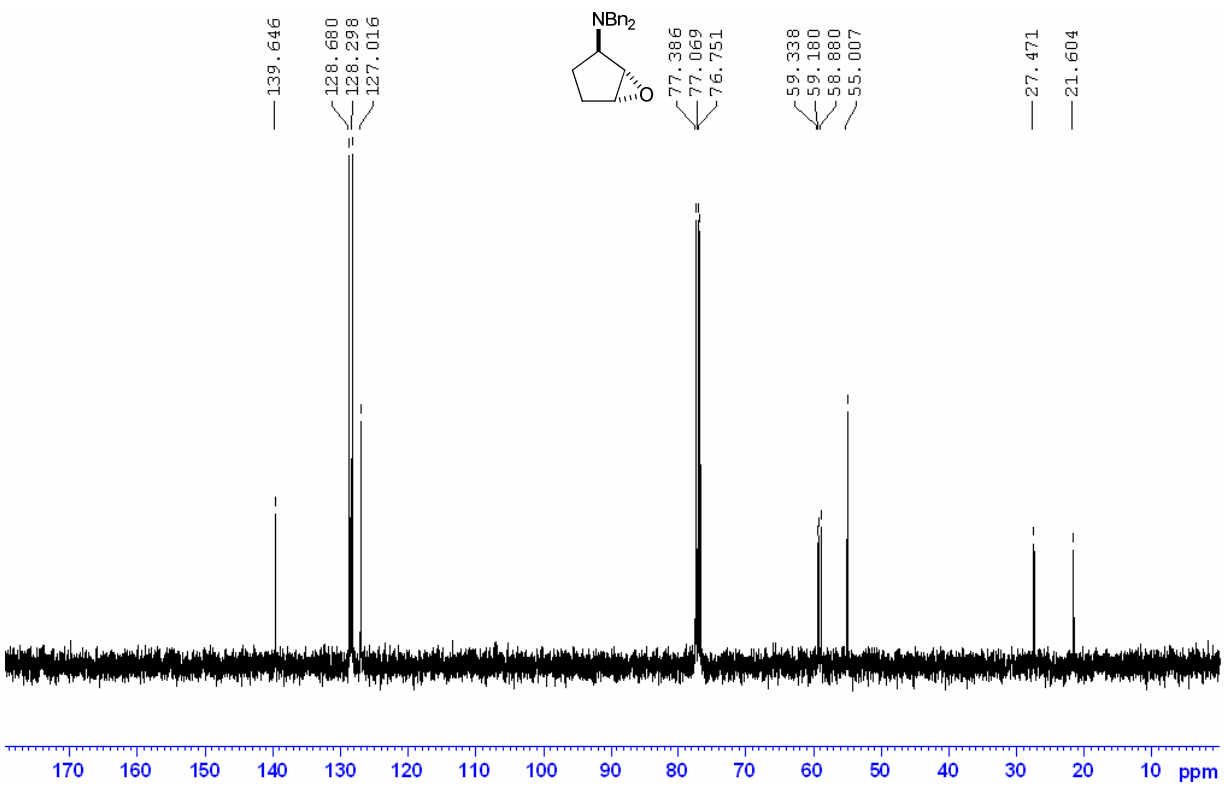
(100 MHz ^{13}C, $CDCl_3$)



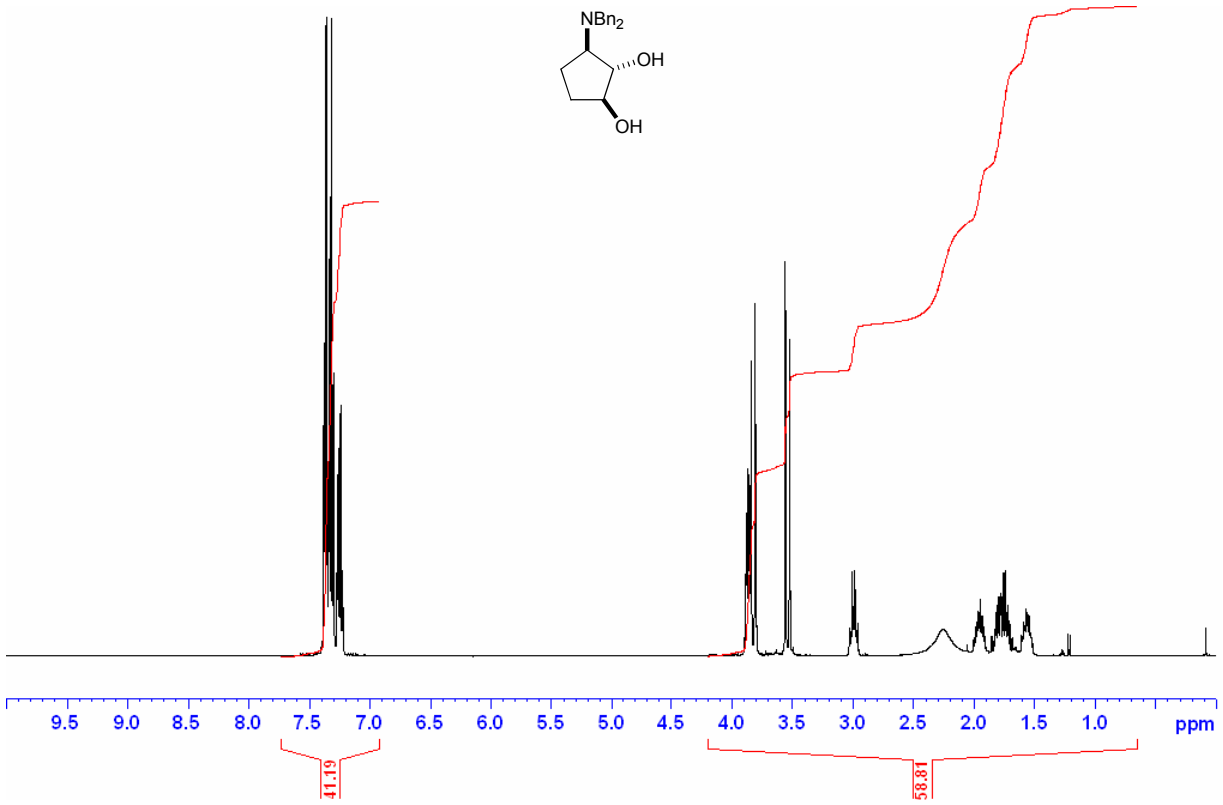
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 34 (400 MHz ^{1}H, $CDCl_3$)



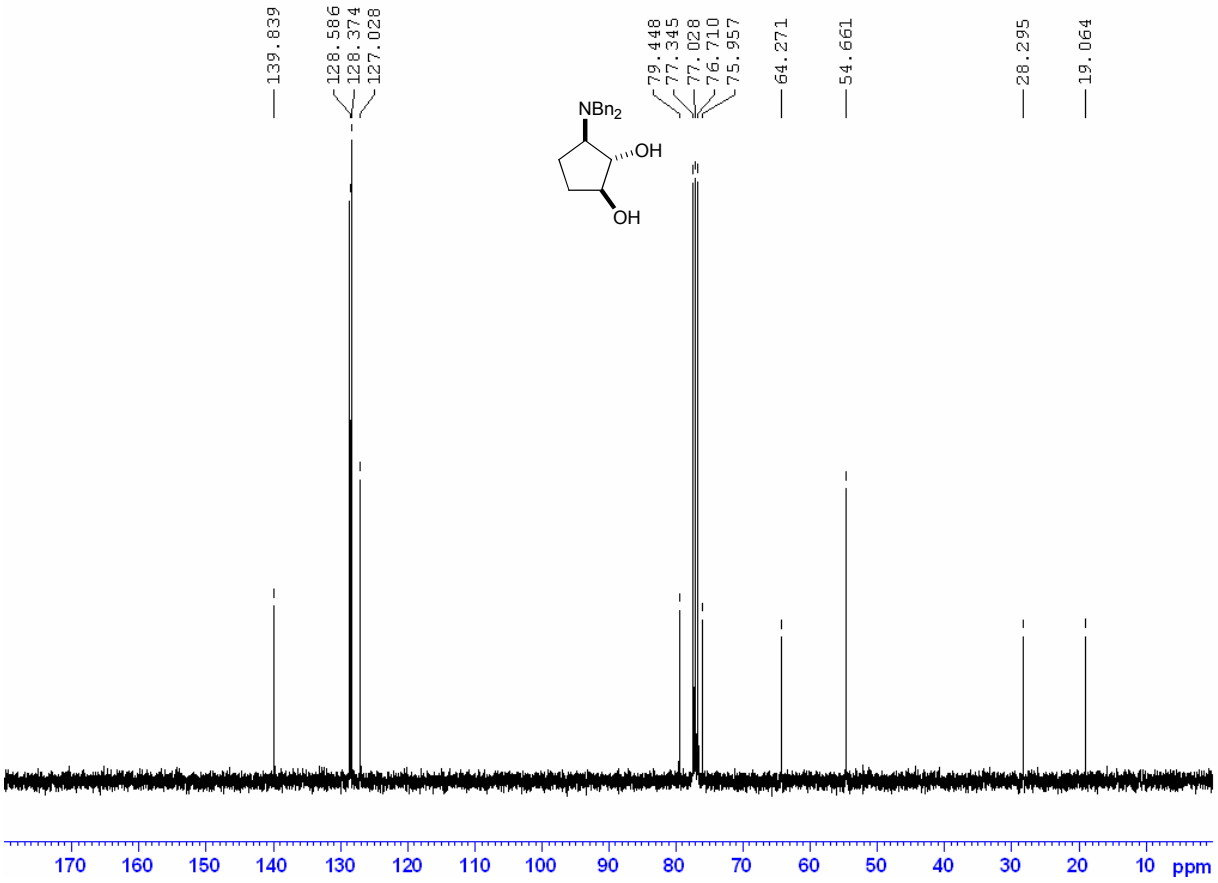
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 34 (100 MHz ^{13}C, $CDCl_3$)



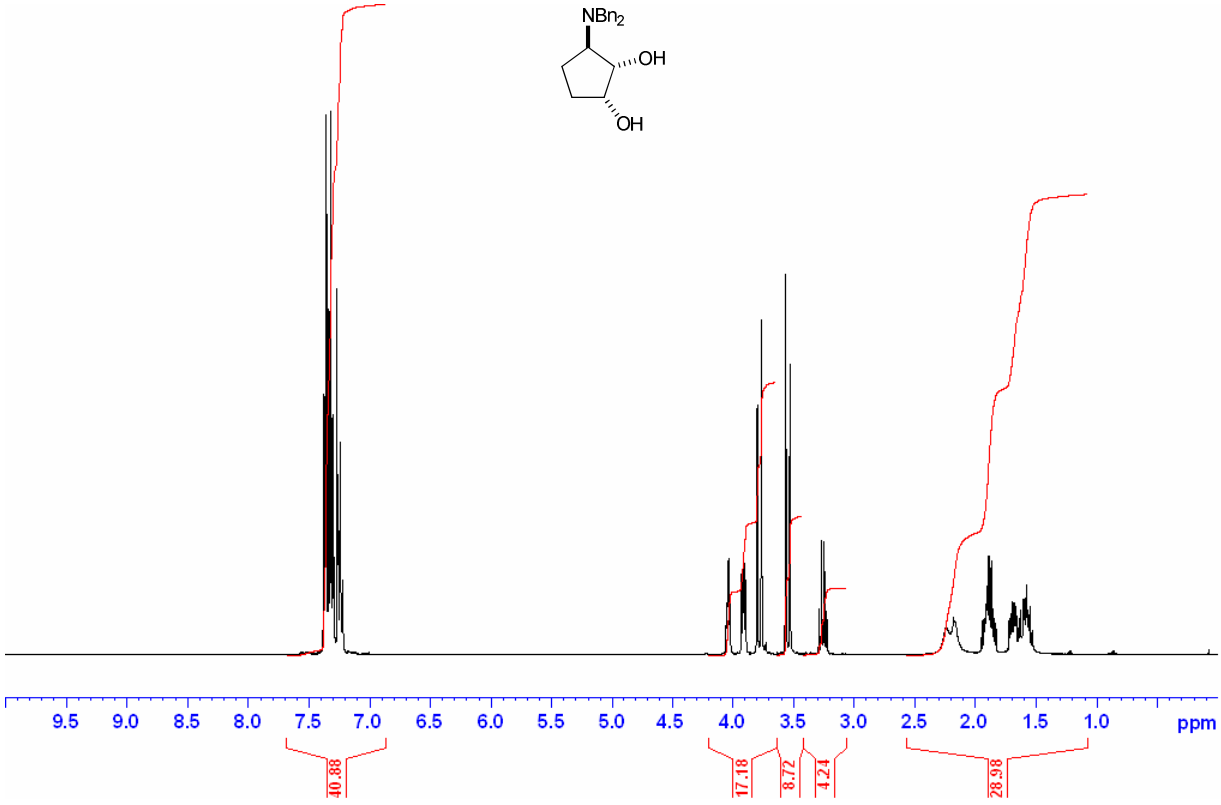
(1*RS*,2*RS*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 35 (400 MHz ^{1}H, $CDCl_3$)



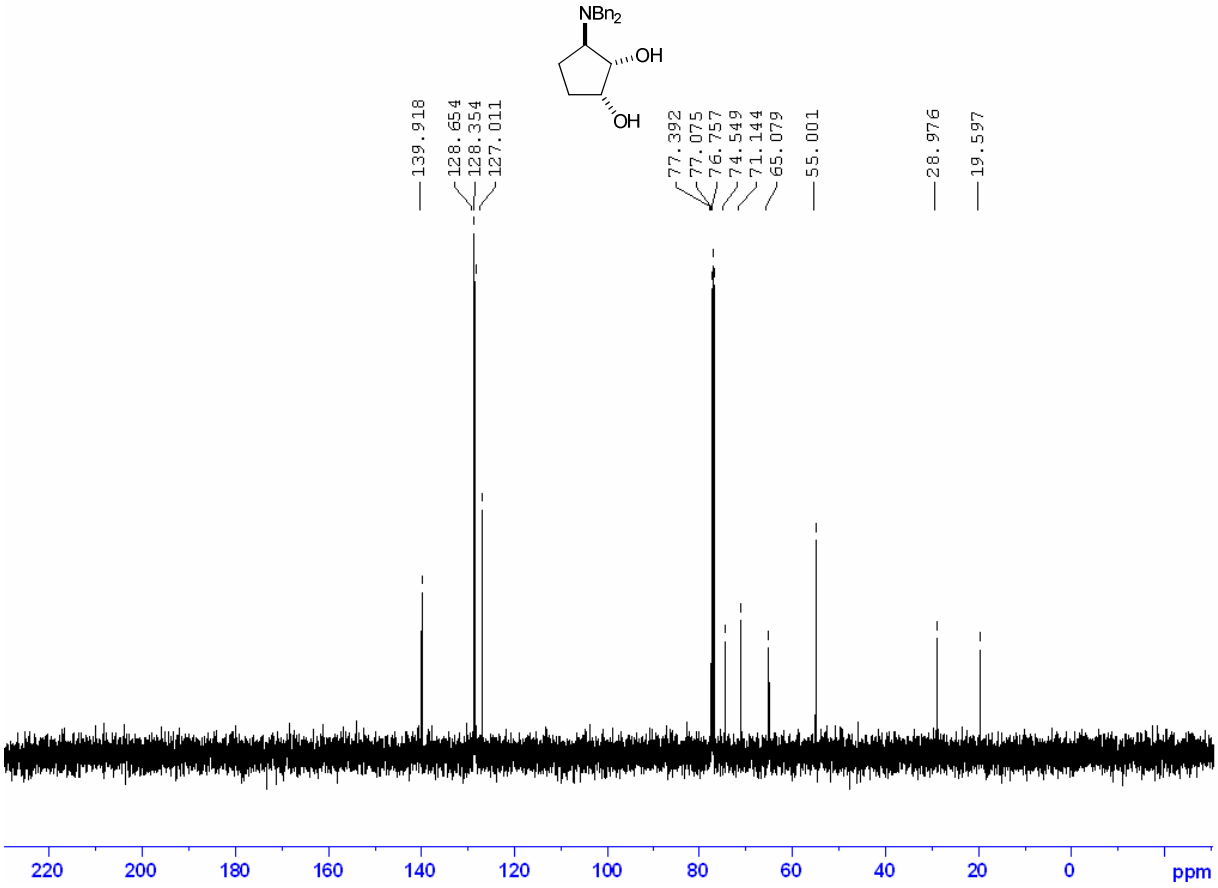
(1*RS*,2*RS*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 35 (100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 39 (400 MHz ^{1}H, $CDCl_3$)

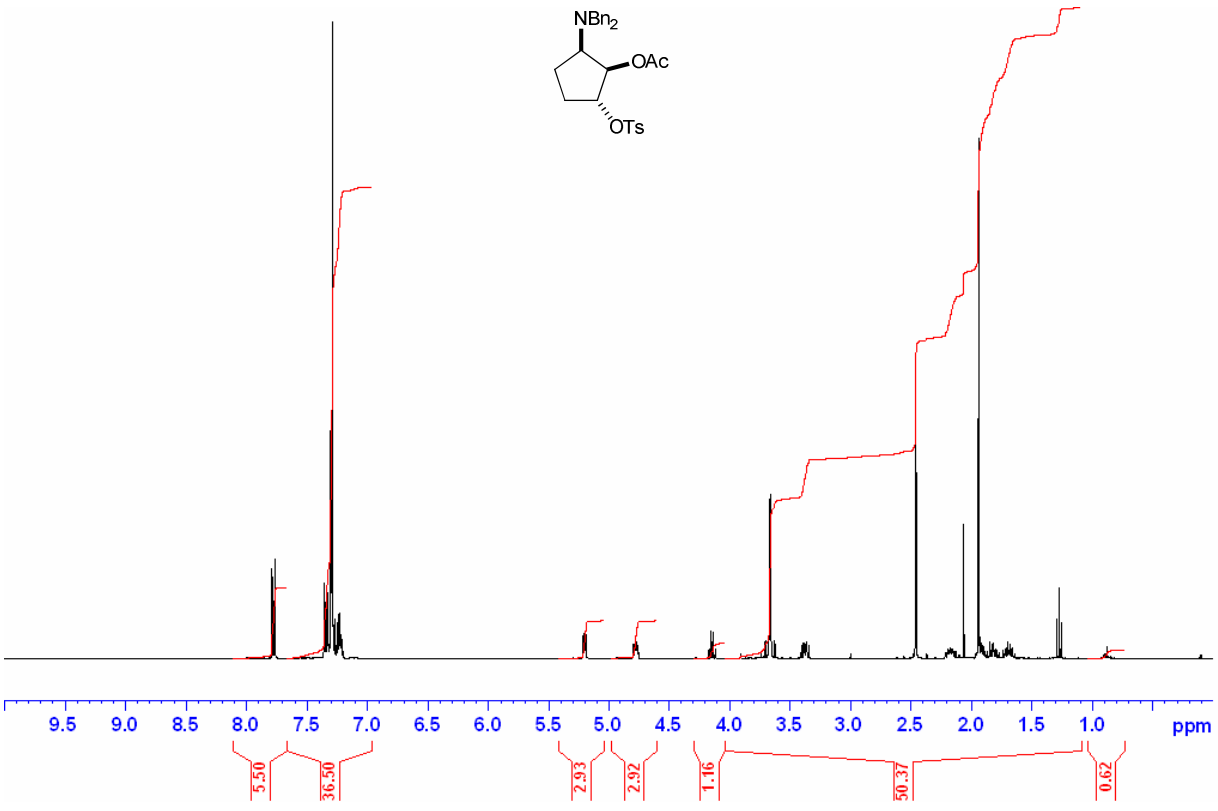


(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 39 (100 MHz ^{13}C, $CDCl_3$)



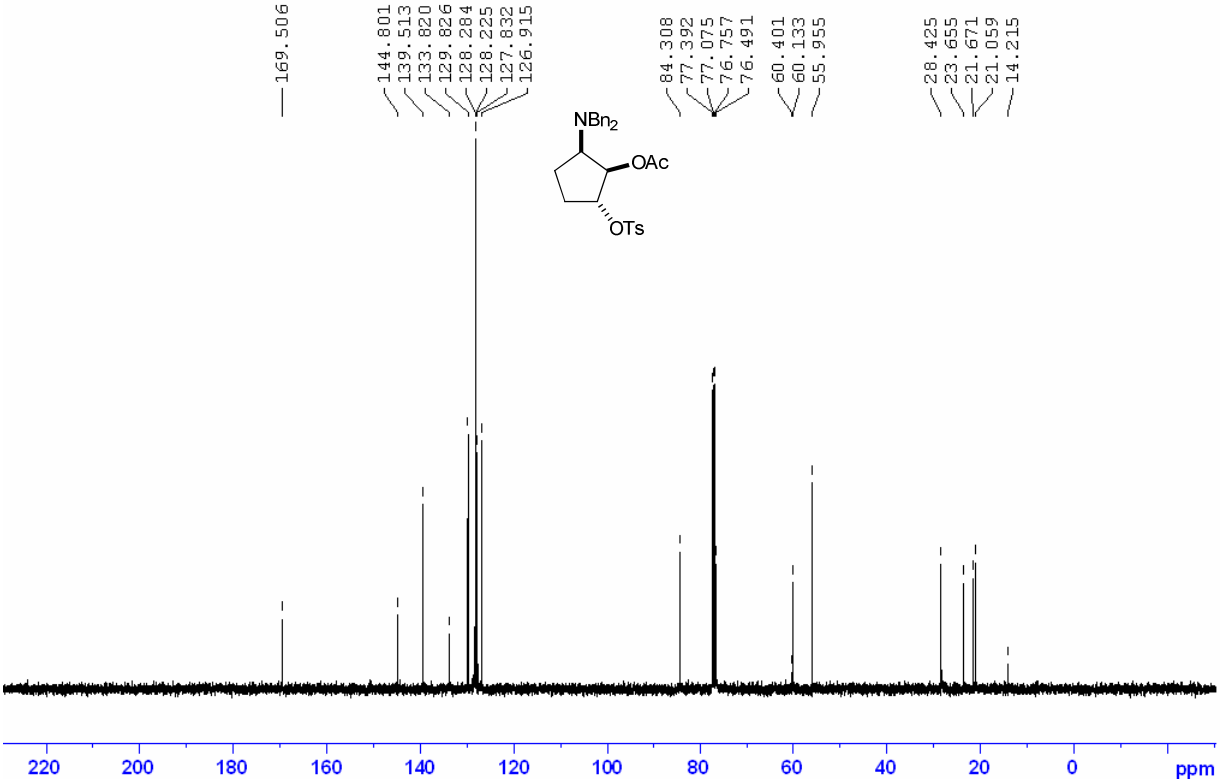
(1*RS*,2*RS*,3*RS*)-1-*p*-Toluenesulfonyloxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 44

(400 MHz ^{1}H, $CDCl_3$)

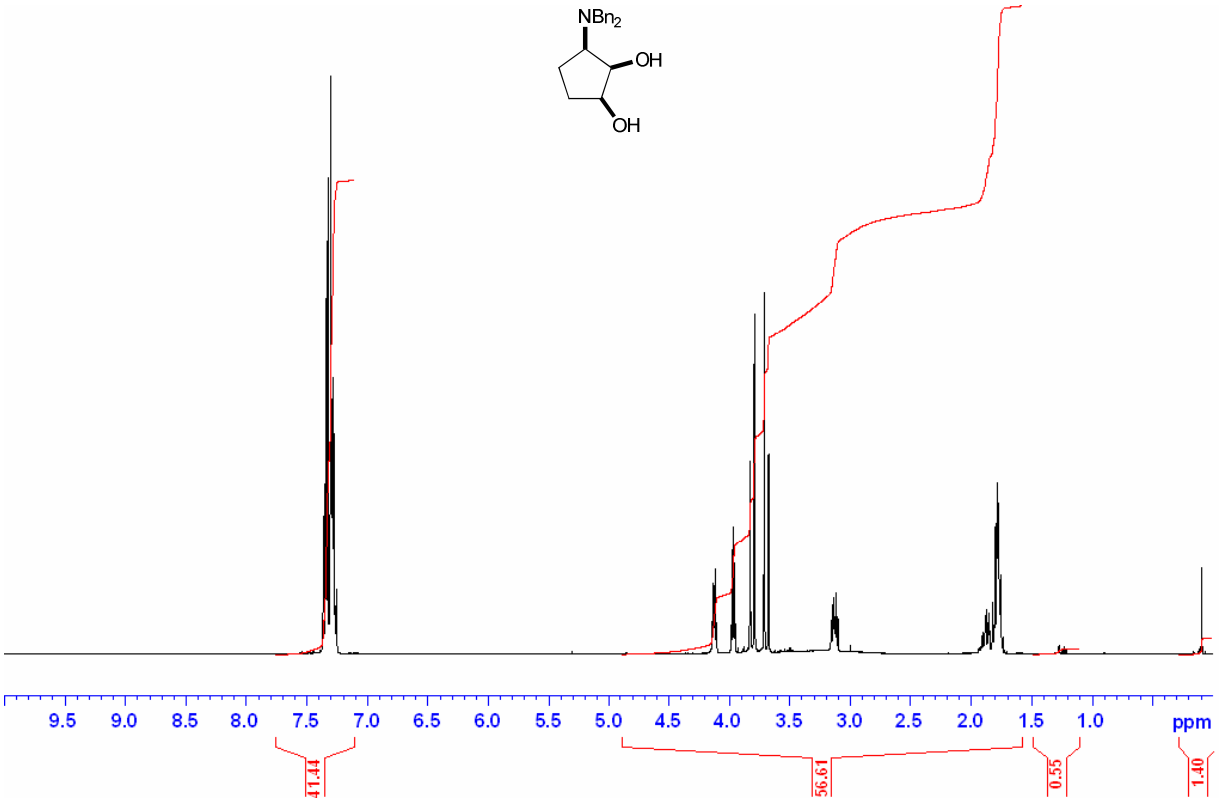


(1*RS*,2*RS*,3*RS*)-1-*p*-Toluenesulfonyloxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)cyclopentane 44

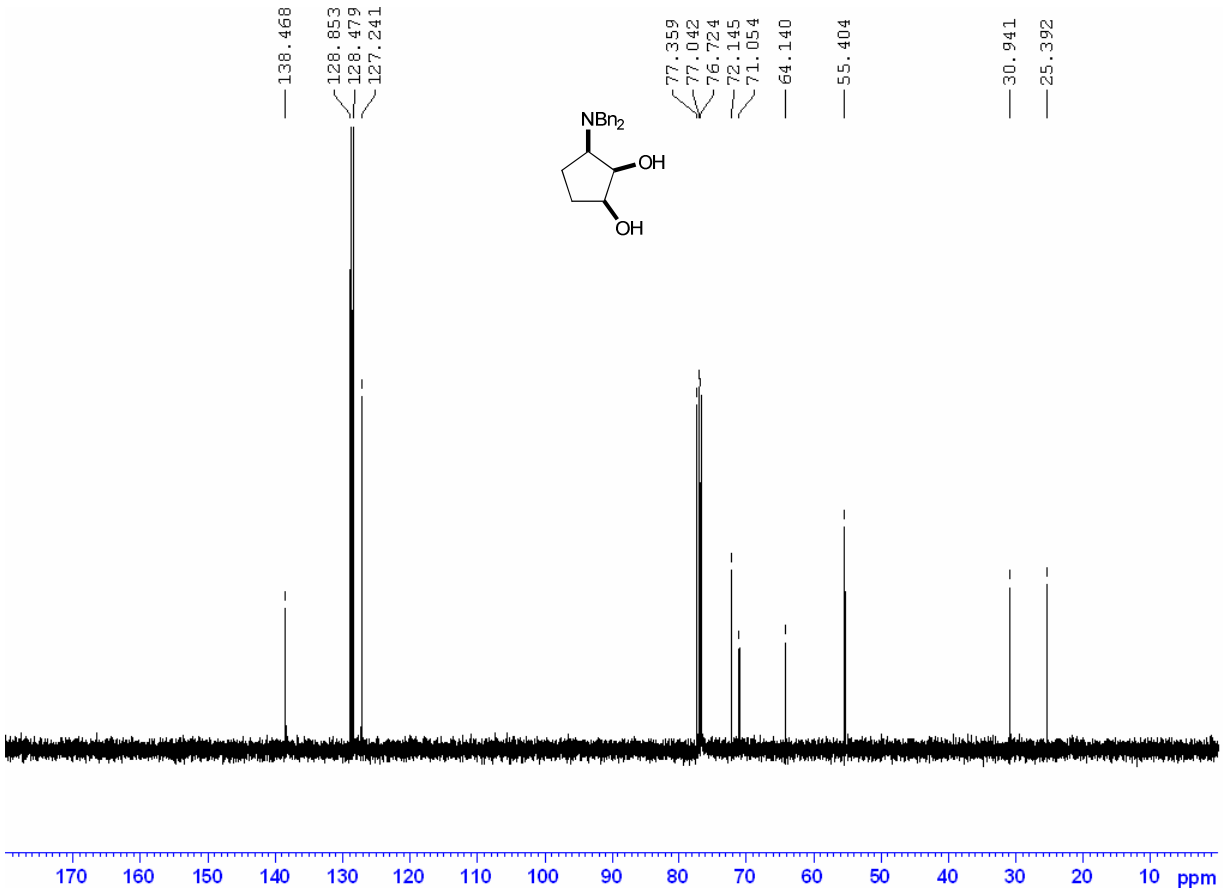
(100 MHz ^{13}C, $CDCl_3$)



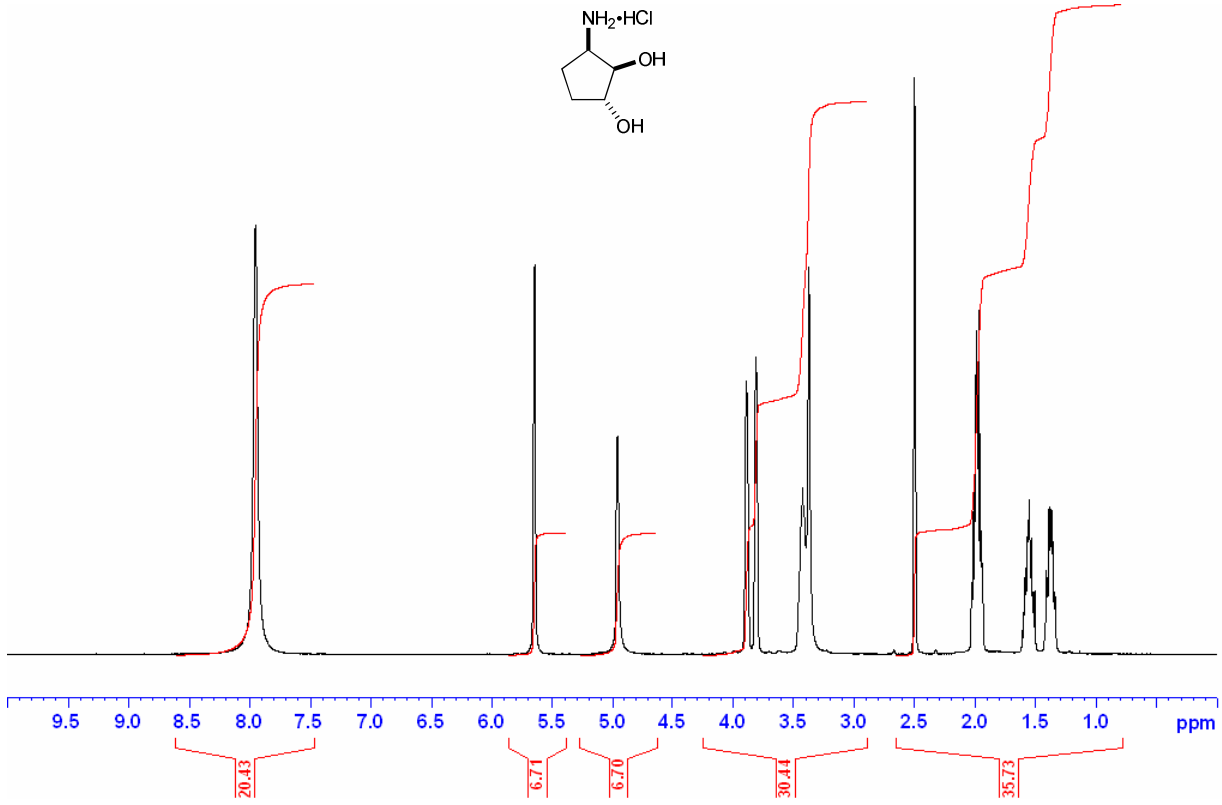
(1*RS*,2*SR*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 47 (400 MHz ^{1}H, $CDCl_3$)



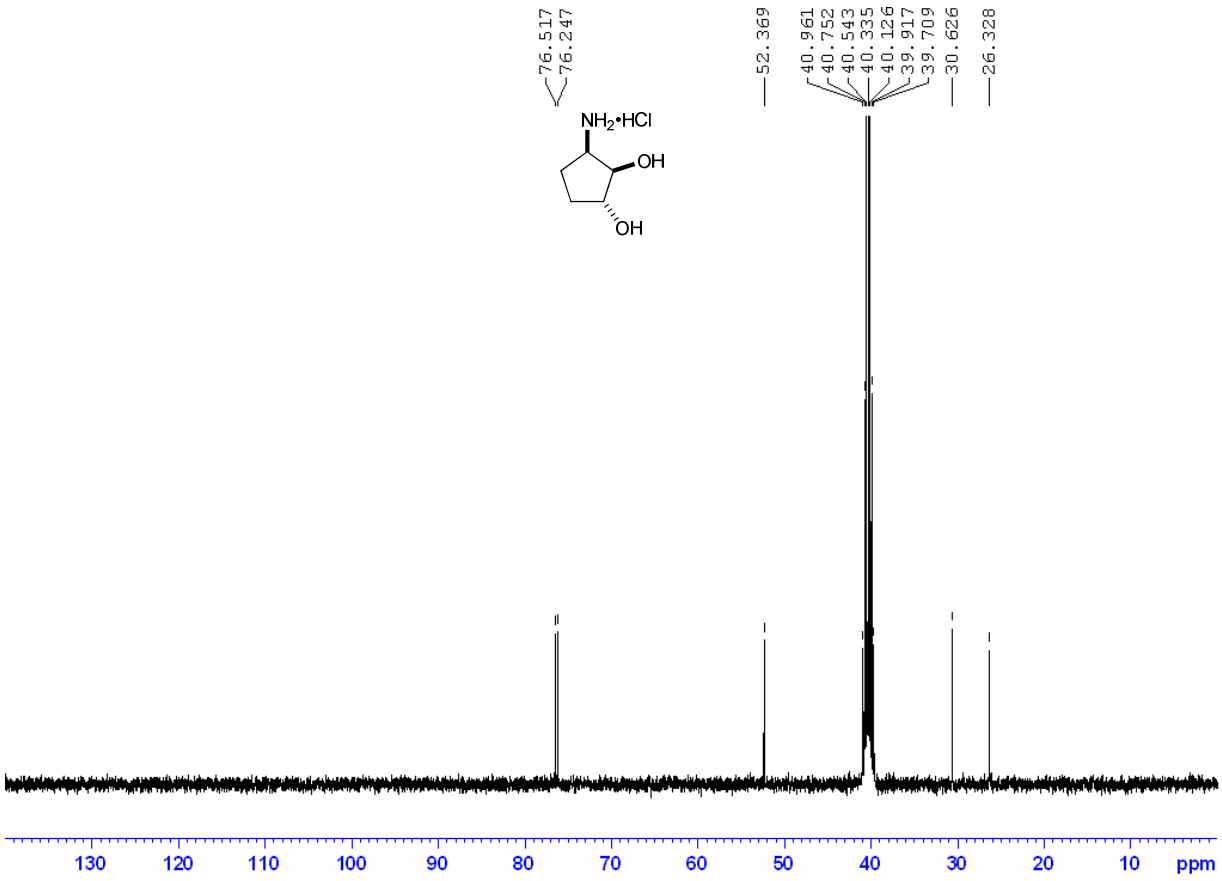
(1*RS*,2*SR*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cyclopentane-1,2-diol 47 (100 MHz ^{13}C, $CDCl_3$)



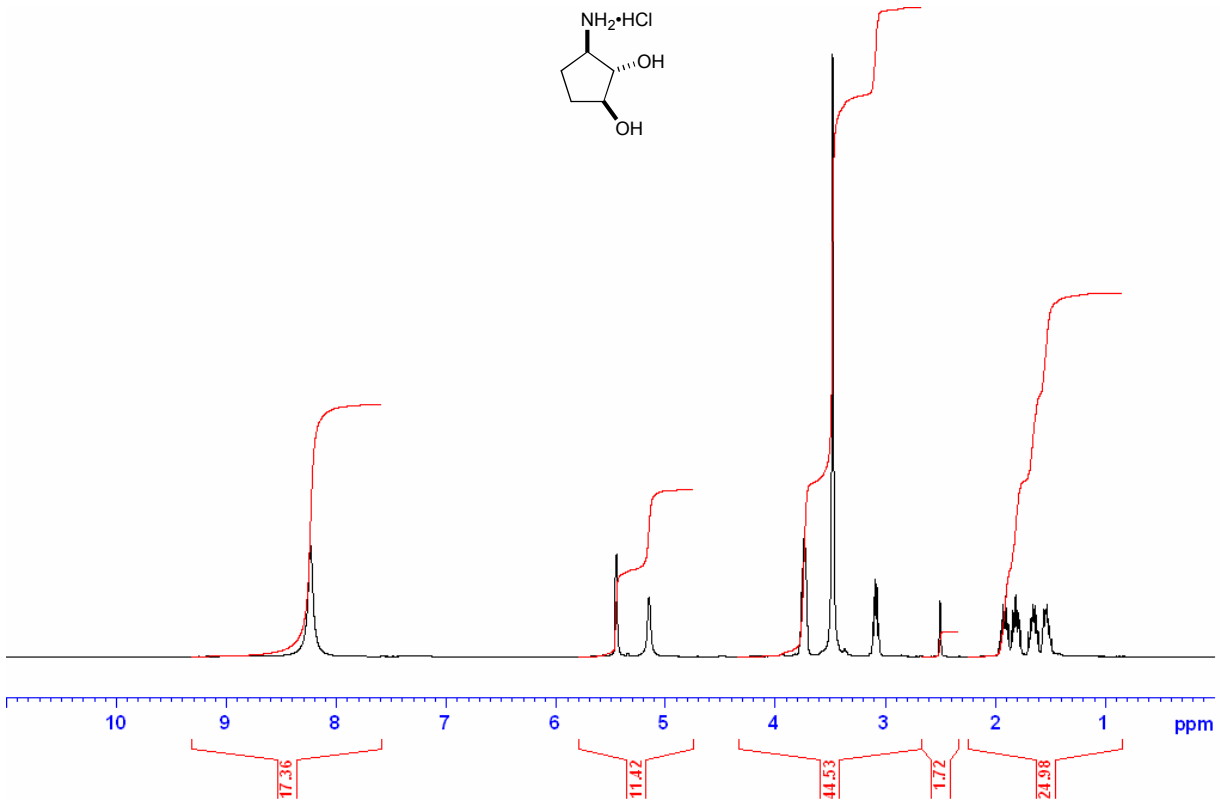
(1*RS*,2*RS*,3*RS*)-3-Aminocyclopentane-1,2-diol hydrochloride 48 (400 MHz ^{1}H, d_6-DMSO)



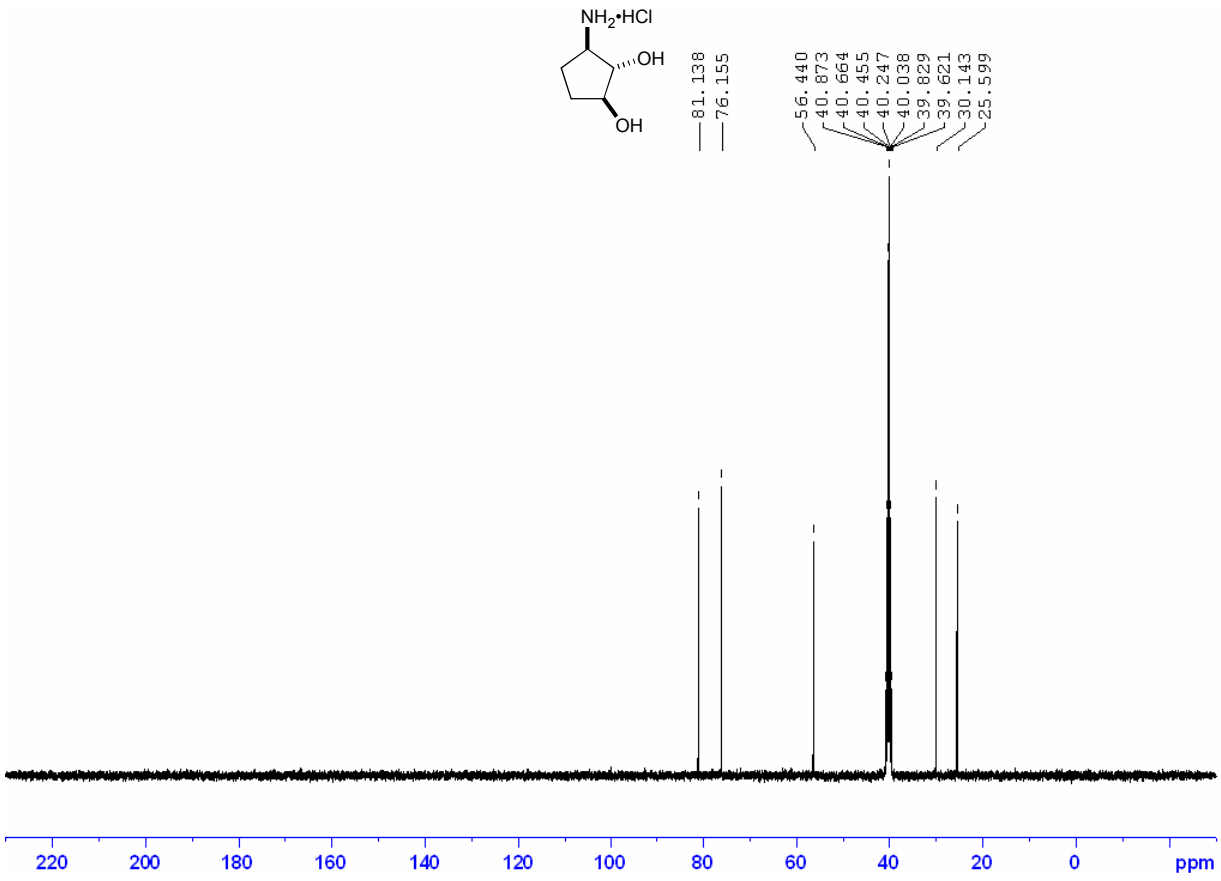
(1*RS*,2*RS*,3*RS*)-3-Aminocyclopentane-1,2-diol hydrochloride 48 (100 MHz ^{13}C, $CDCl_3$)



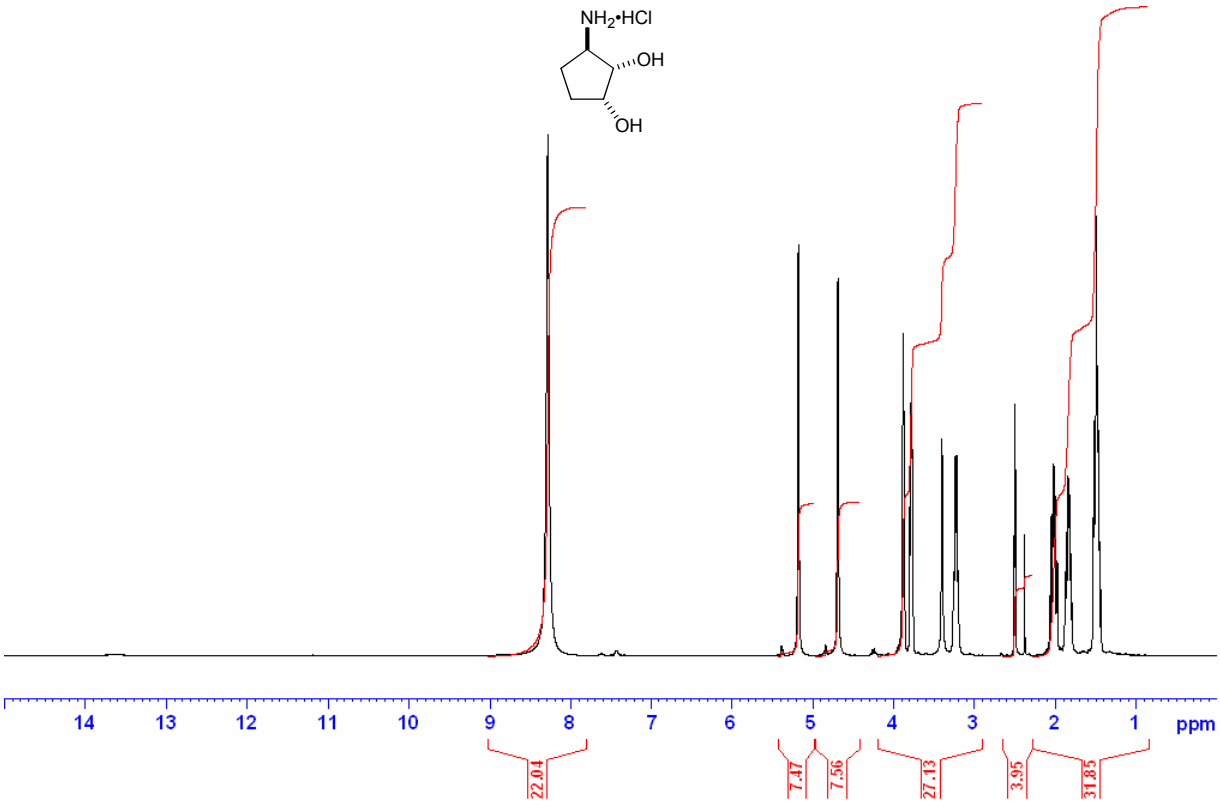
(1*RS*,2*RS*,3*SR*)-3-Aminocyclopentane-1,2-diol hydrochloride 49 (400 MHz ^{1}H, d_6-DMSO)



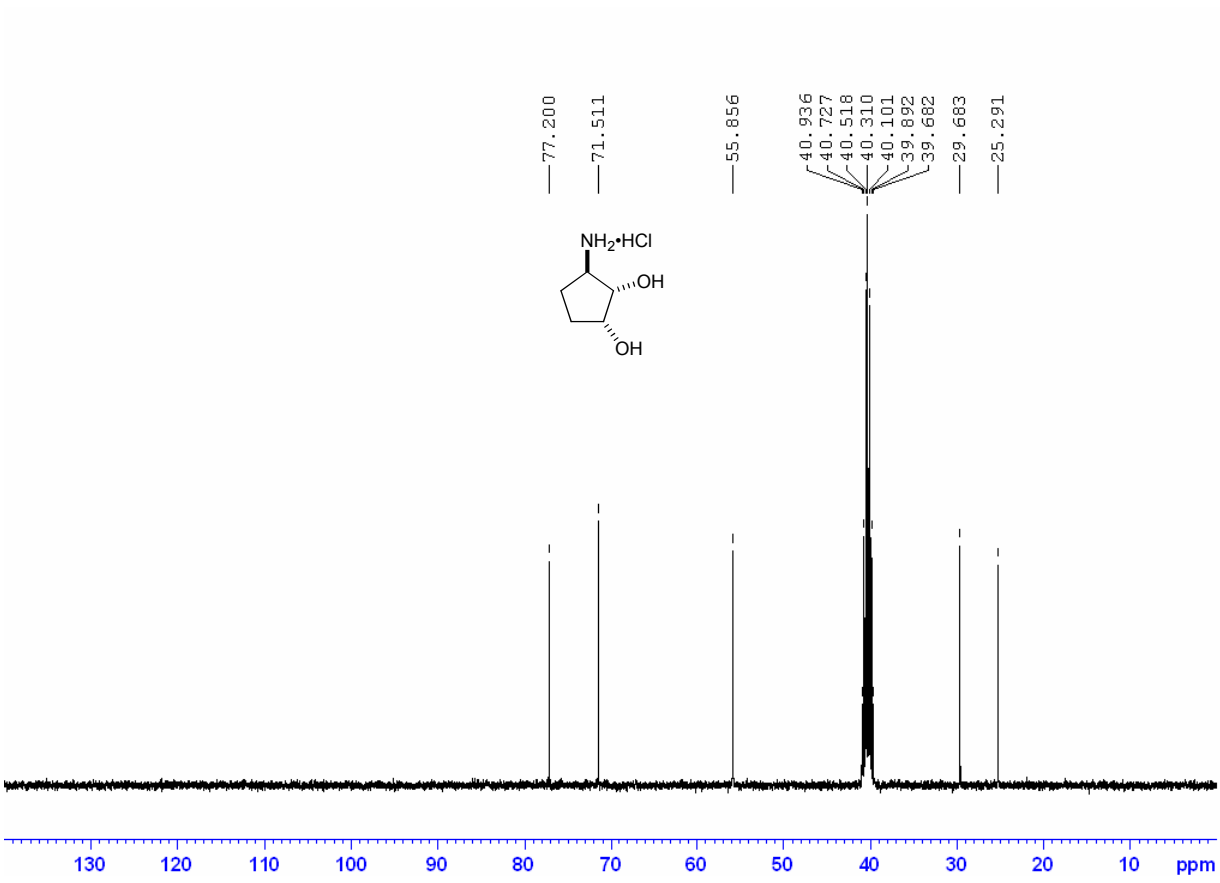
(1*RS*,2*RS*,3*SR*)-3-Aminocyclopentane-1,2-diol hydrochloride 49 (100 MHz ^{13}C, $CDCl_3$)



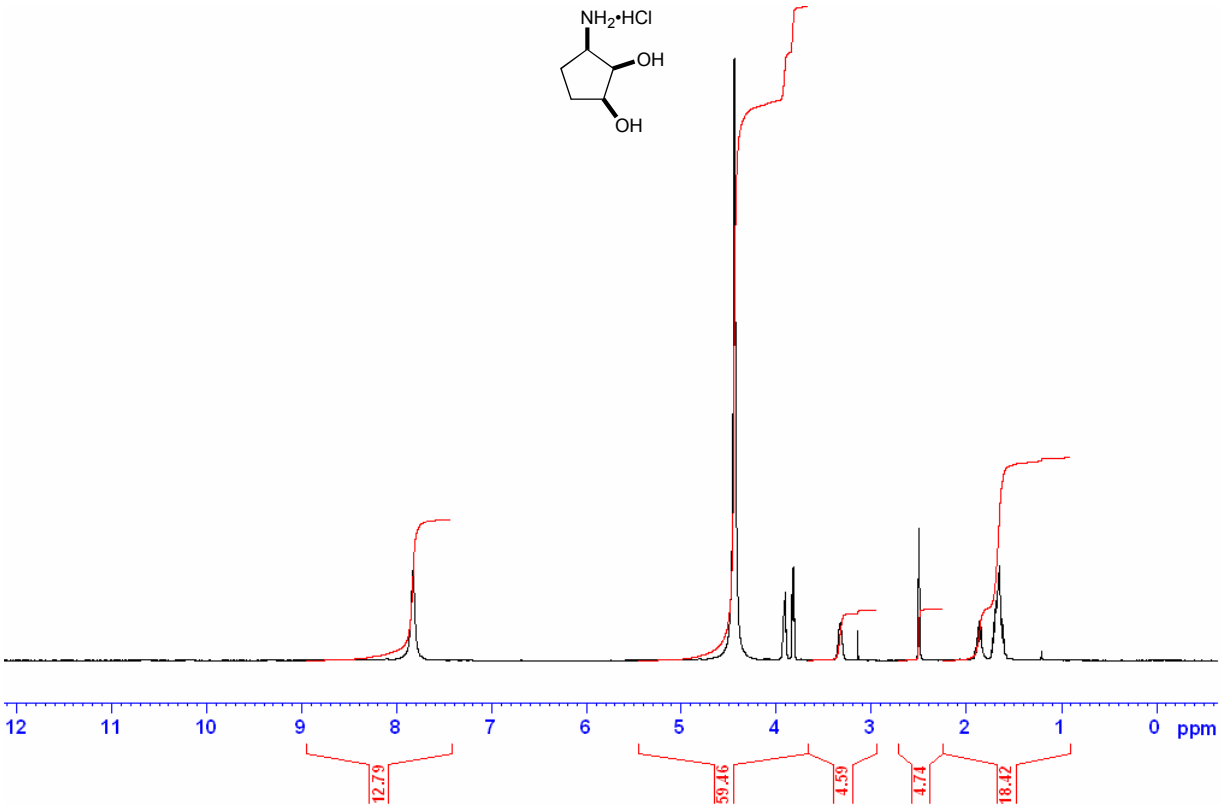
(1*RS*,2*SR*,3*RS*)-3-Aminocyclopentane-1,2-diol hydrochloride 50 (400 MHz ^{1}H, d_6-DMSO)



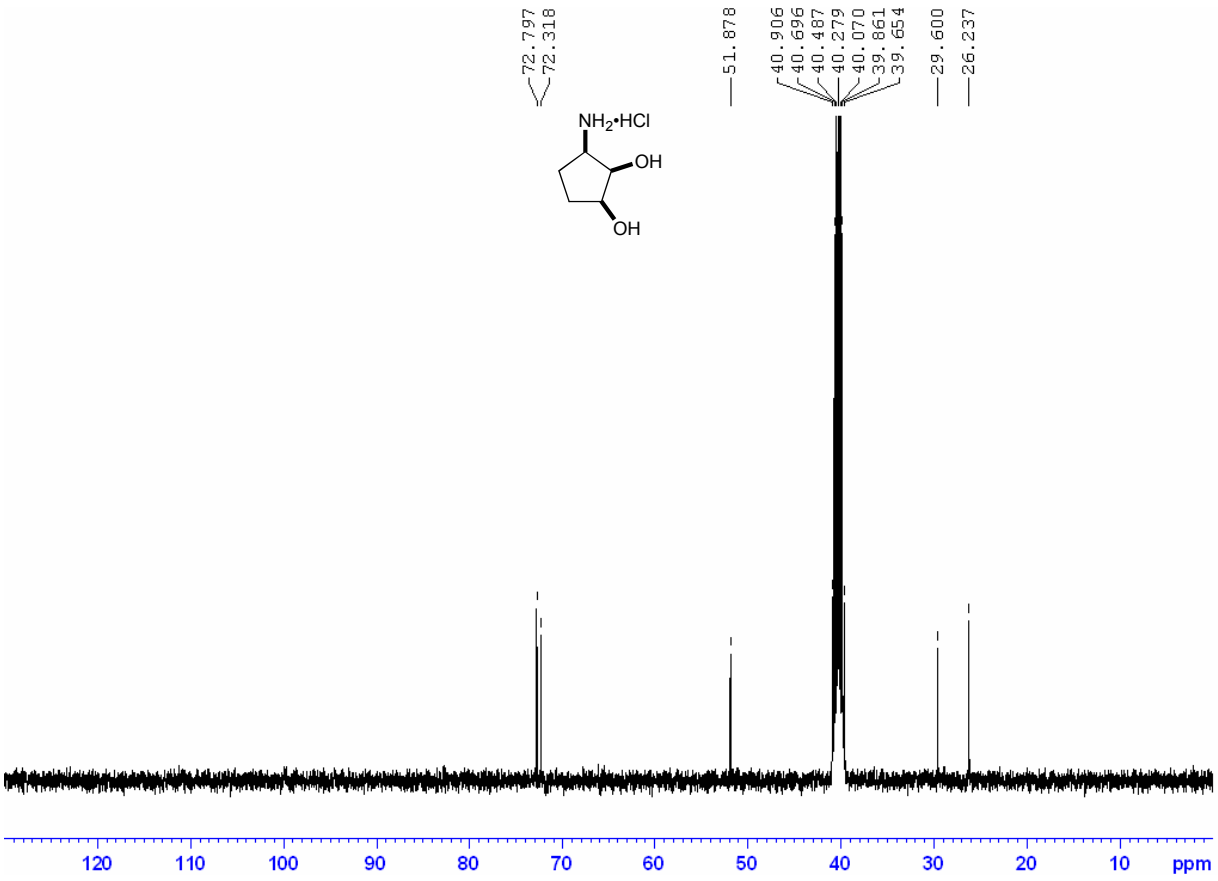
(1*RS*,2*SR*,3*RS*)-3-Aminocyclopentane-1,2-diol hydrochloride 50 (100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*SR*,3*SR*)-3-Aminocyclopentane-1,2-diol hydrochloride 51 (400 MHz ^{1}H, d_6-DMSO)

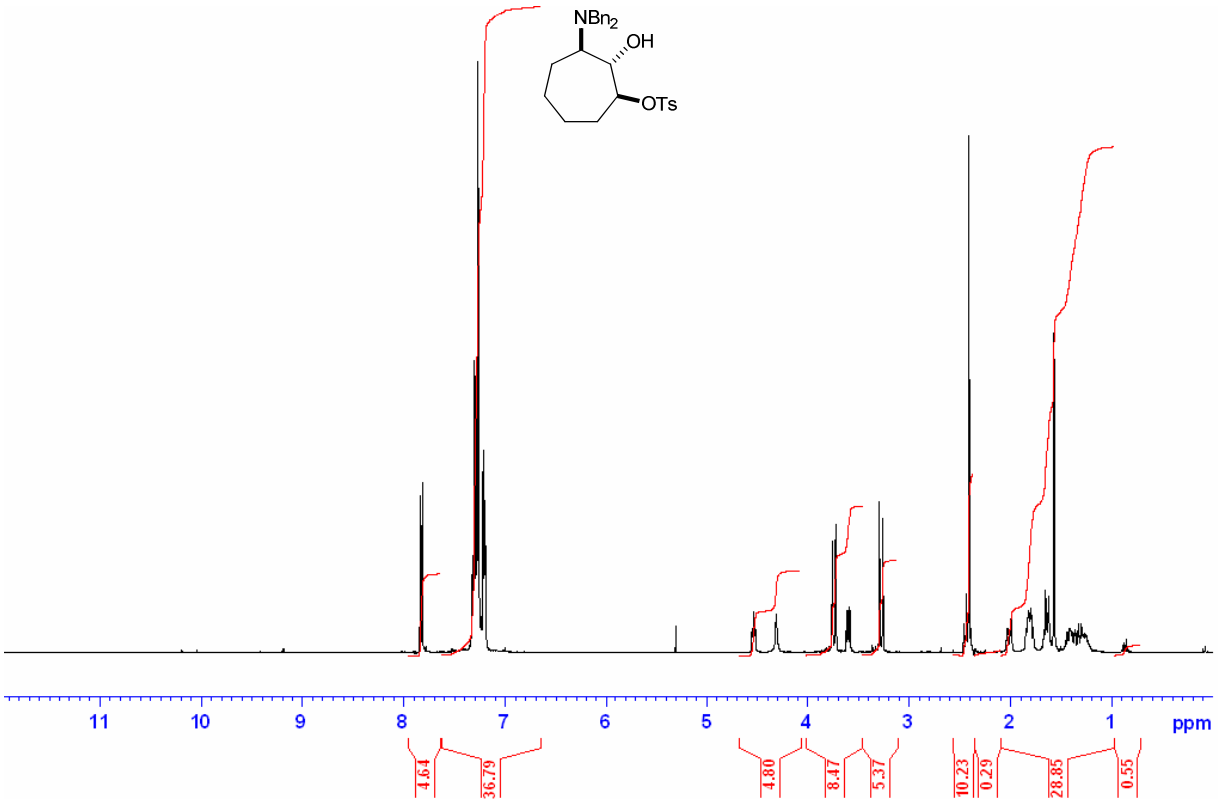


(1*RS*,2*SR*,3*SR*)-3-Aminocyclopentane-1,2-diol hydrochloride 51 (100 MHz ^{13}C, $CDCl_3$)



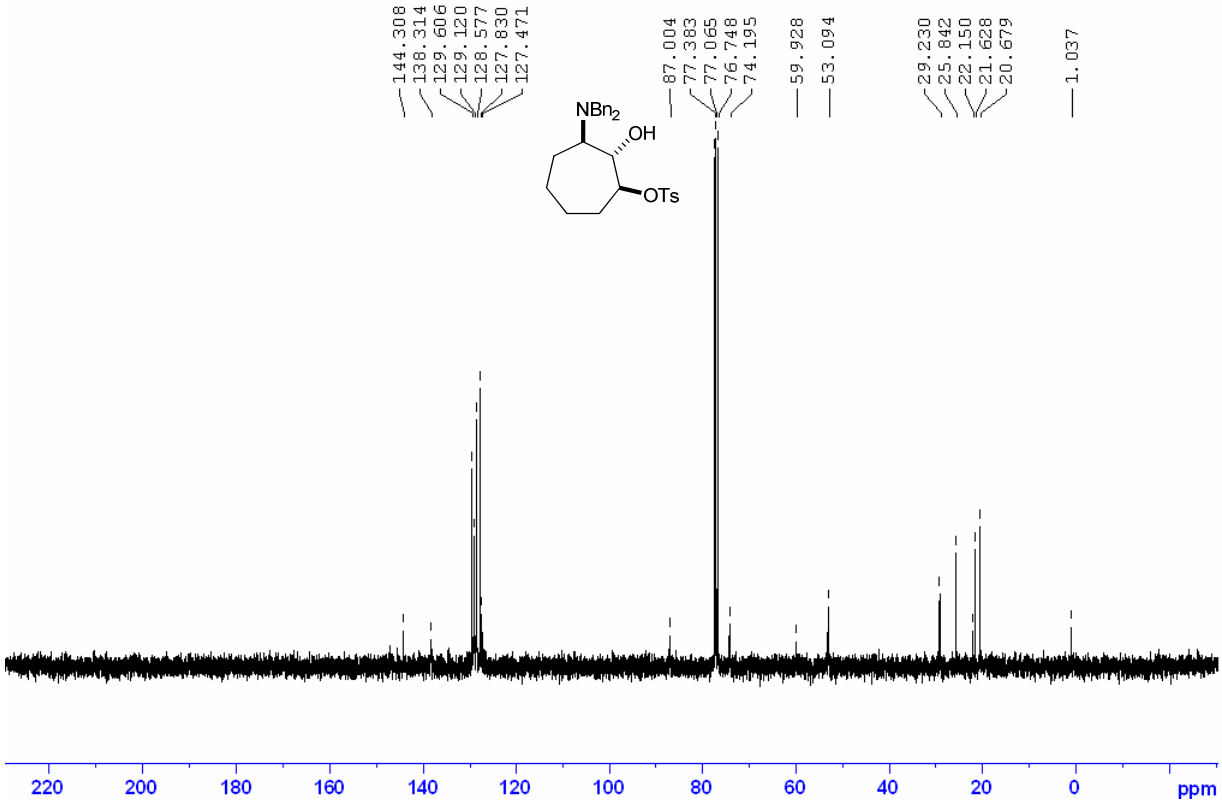
(1*RS*,2*RS*,3*SR*)-1-*p*-Toluenesulfonyloxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cycloheptane 52

(400 MHz ^{1}H, $CDCl_3$)



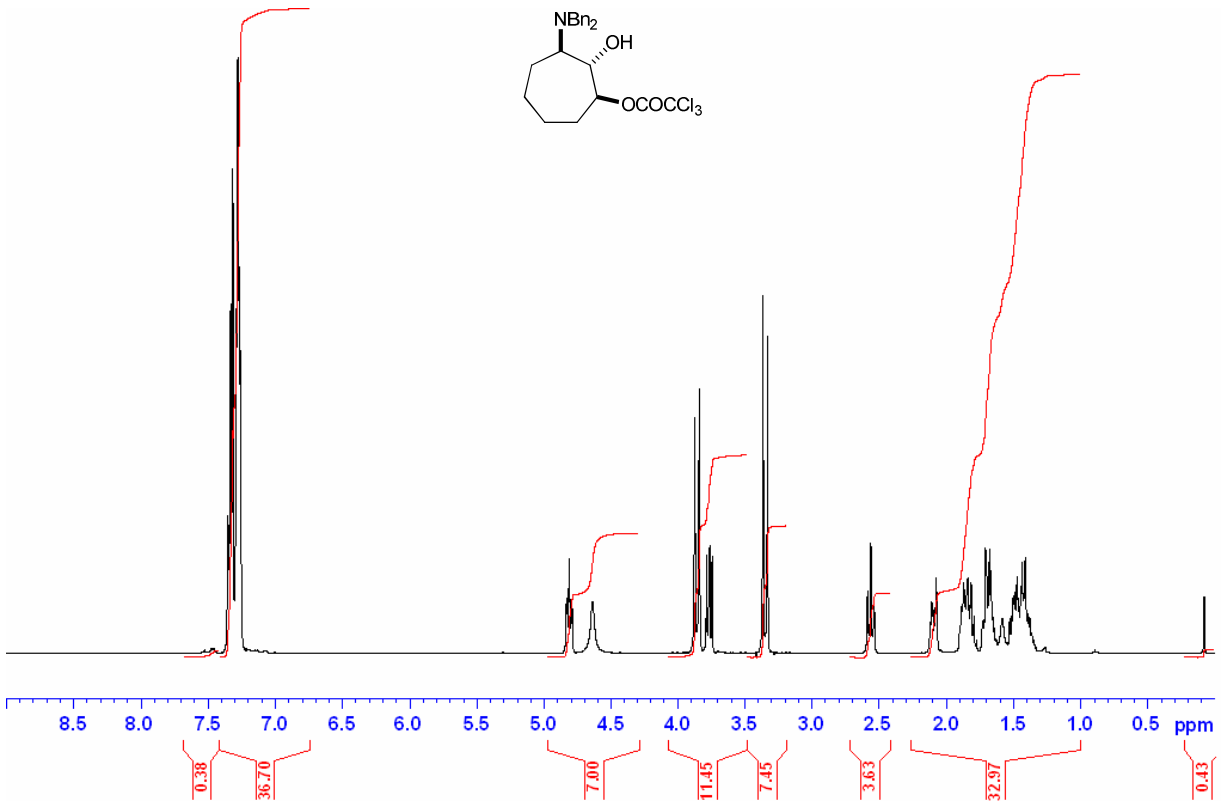
(1*RS*,2*RS*,3*SR*)-1-*p*-Toluenesulfonyloxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cycloheptane 52

(100 MHz ^{13}C, $CDCl_3$)



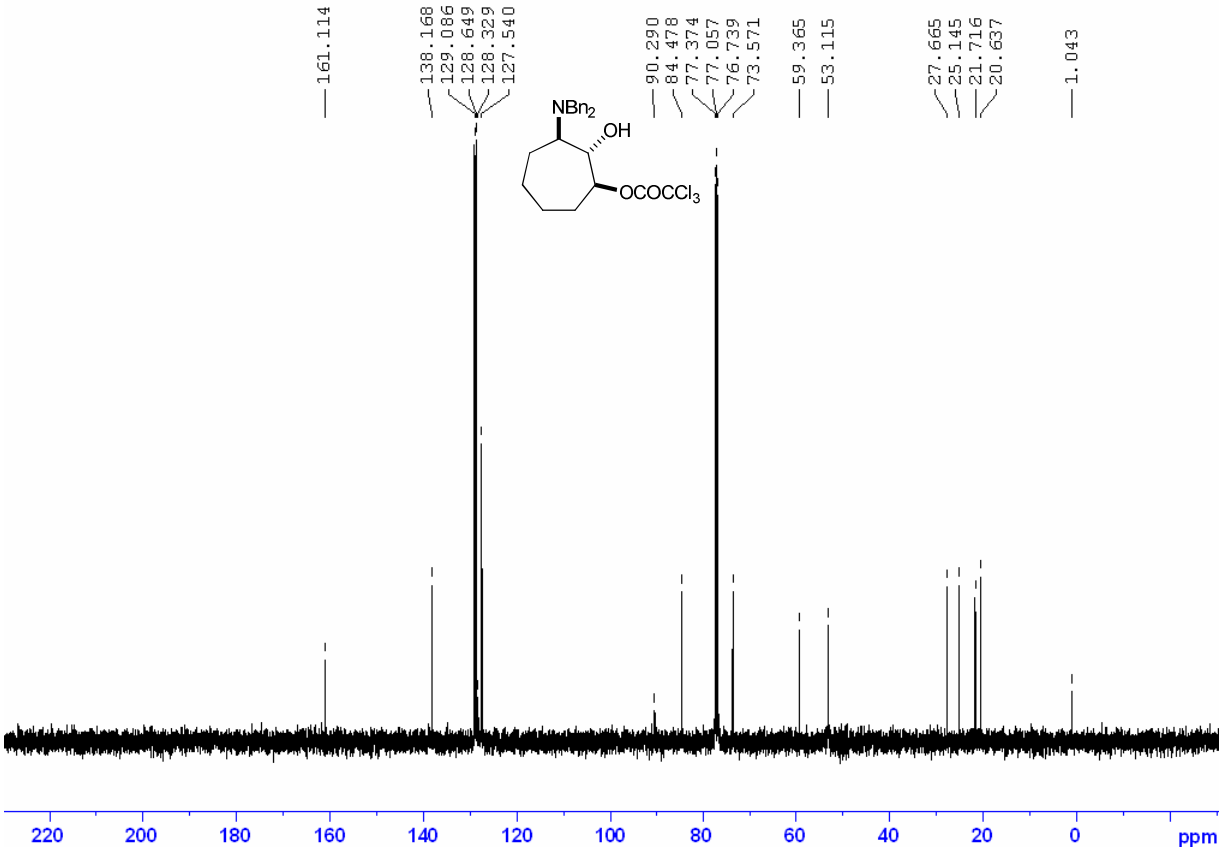
(1*RS*,2*RS*,3*SR*)-1-Trichloroacetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cycloheptane 53

(400 MHz ^{1}H, $CDCl_3$)

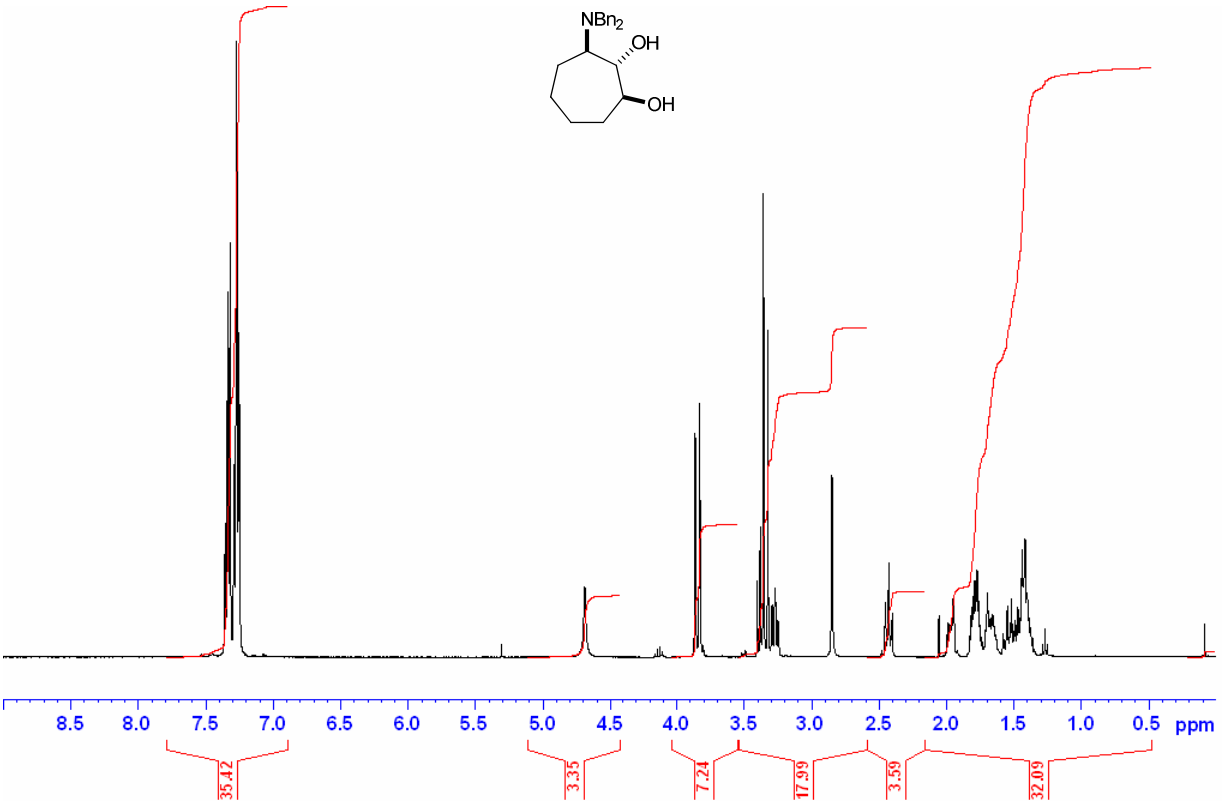


(1*RS*,2*RS*,3*SR*)-1-Trichloroacetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)cycloheptane 53

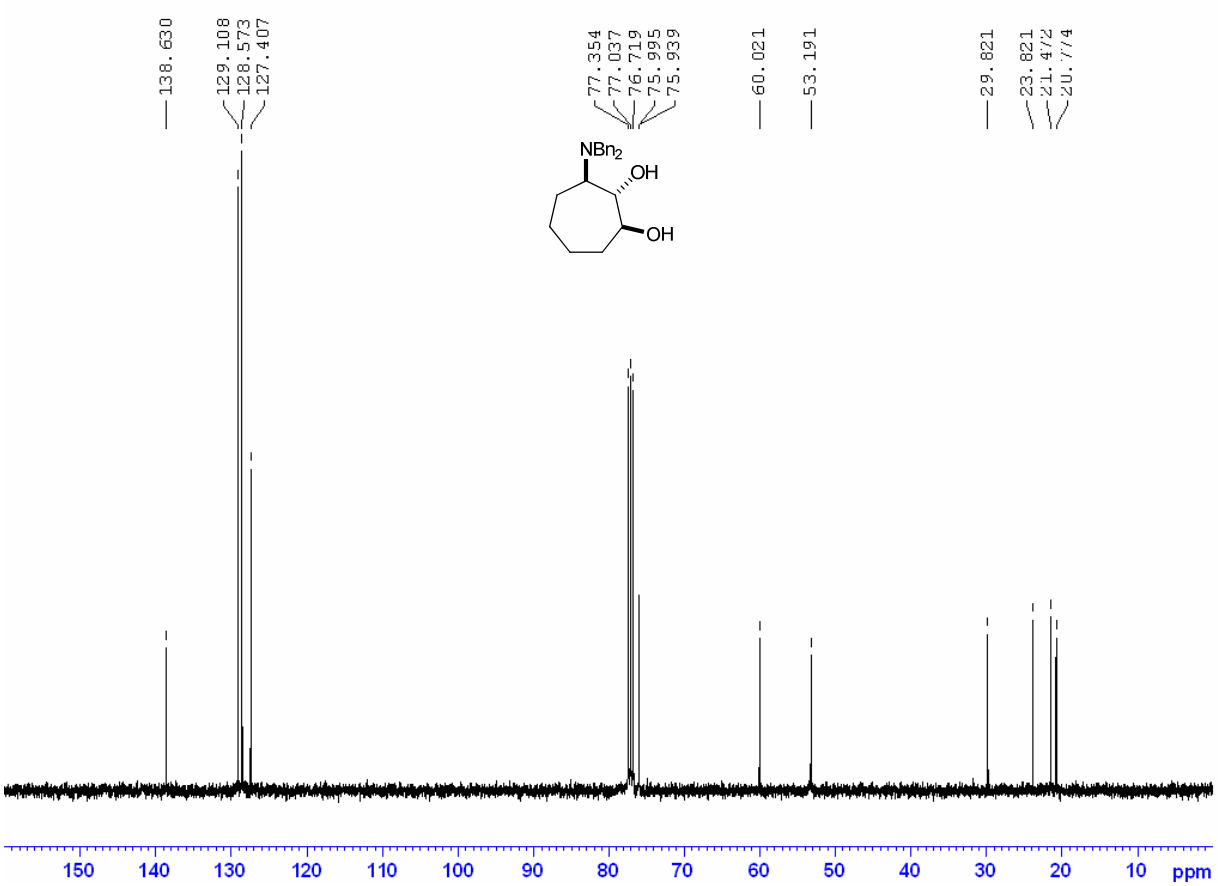
(100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*RS*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cycloheptane-1,2-diol 54 (400 MHz ^{1}H, $CDCl_3$)

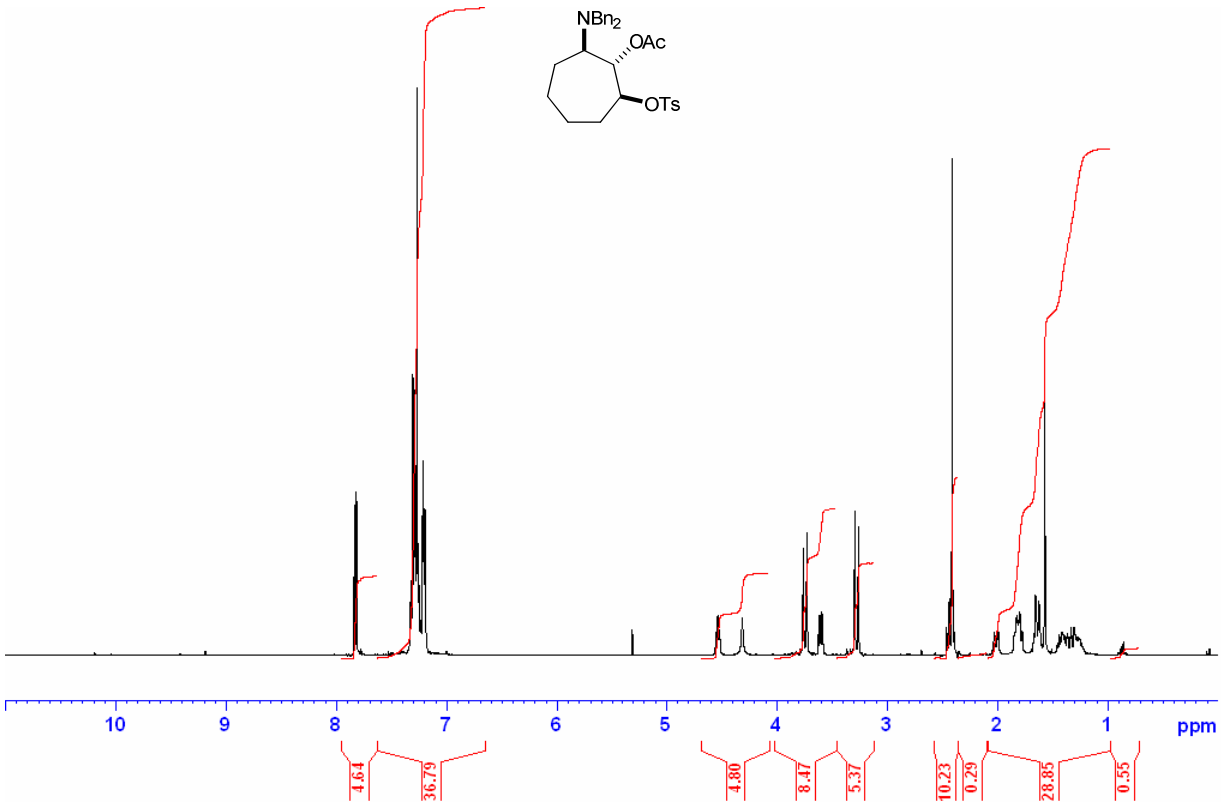


(1*RS*,2*RS*,3*SR*)-3-(*N*,*N*-Dibenzylamino)cycloheptane-1,2-diol 54 (100 MHz ^{13}C, $CDCl_3$)



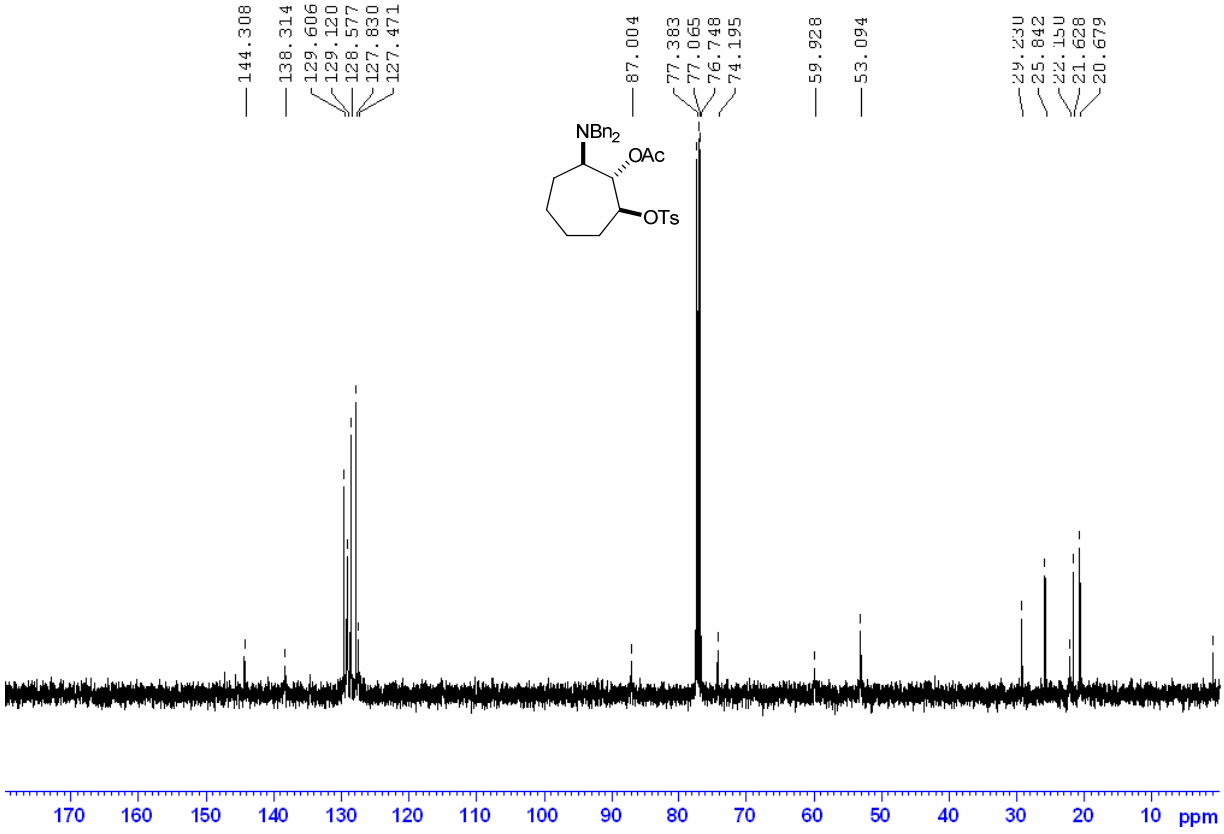
(1*RS*,2*RS*,3*SR*)-1-*p*-Toluenesulfonyloxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)cycloheptane 55

(400 MHz ^{1}H, $CDCl_3$)

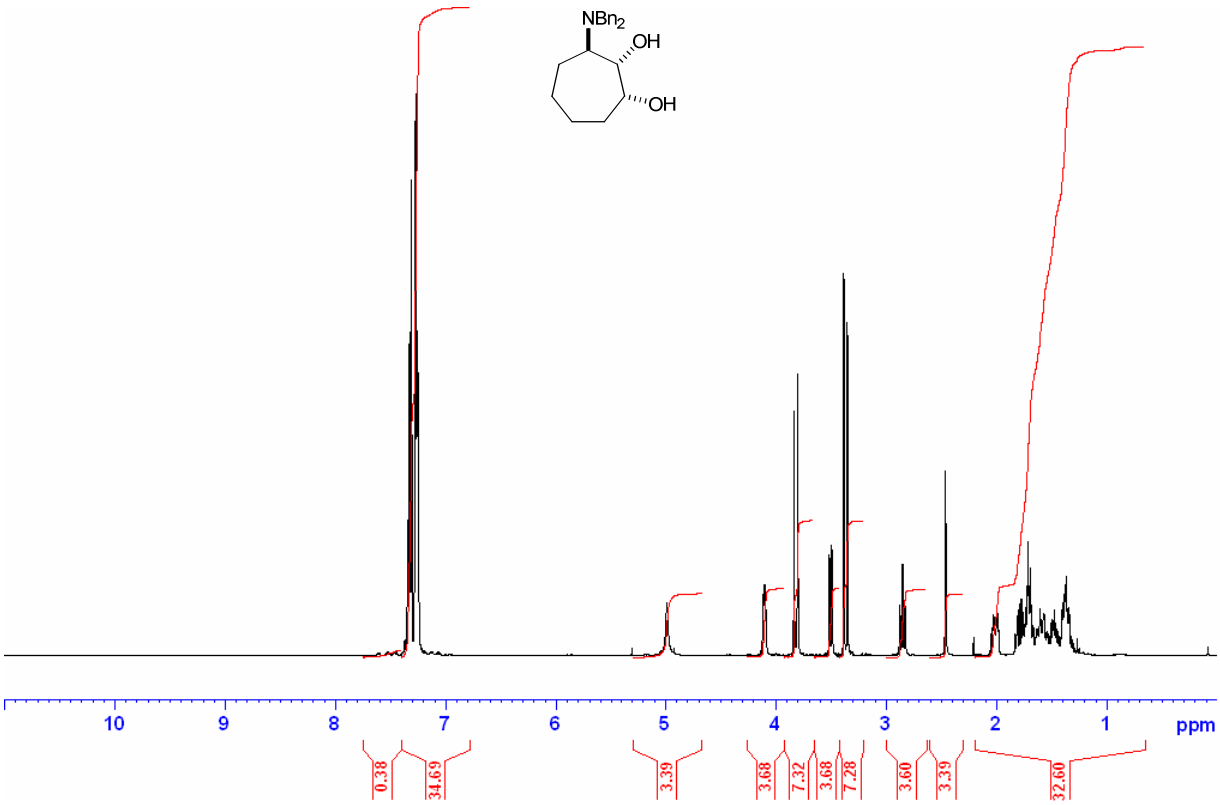


(1*RS*,2*RS*,3*SR*)-1-*p*-Toluenesulfonyloxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)cycloheptane 55

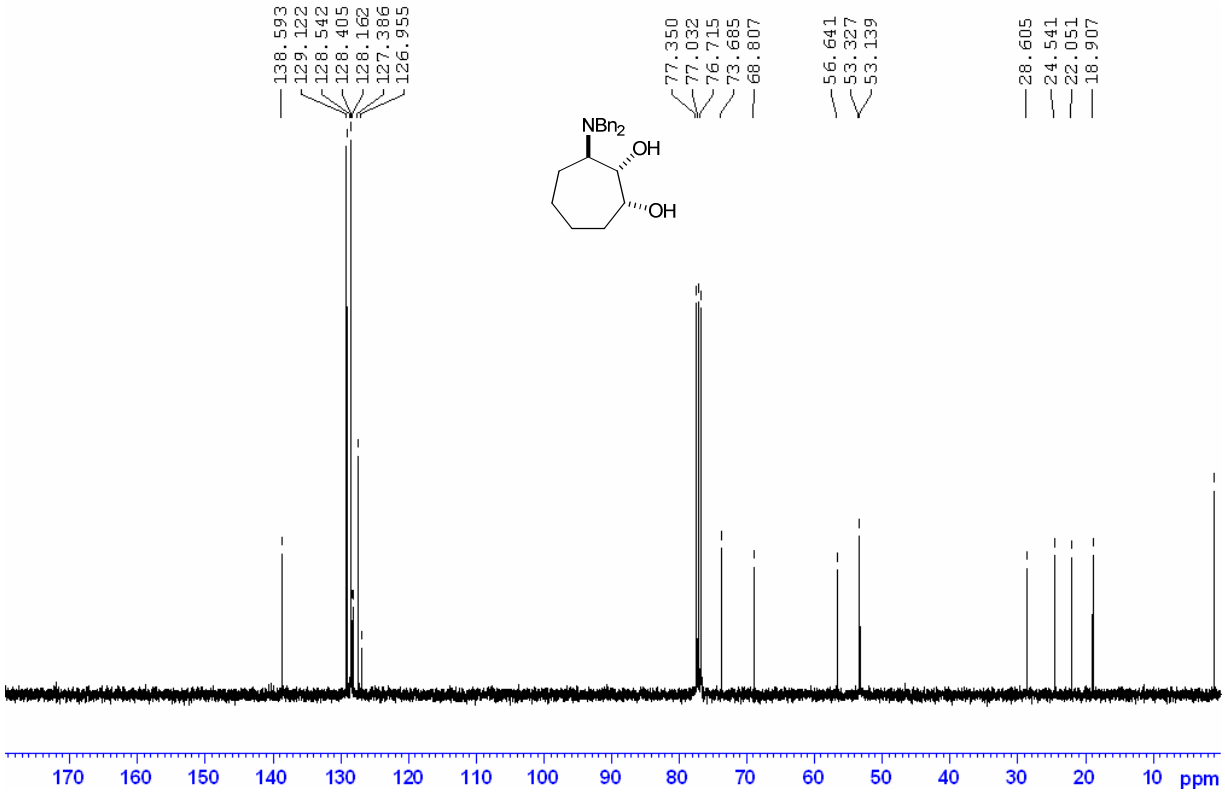
(100 MHz ^{13}C, $CDCl_3$)



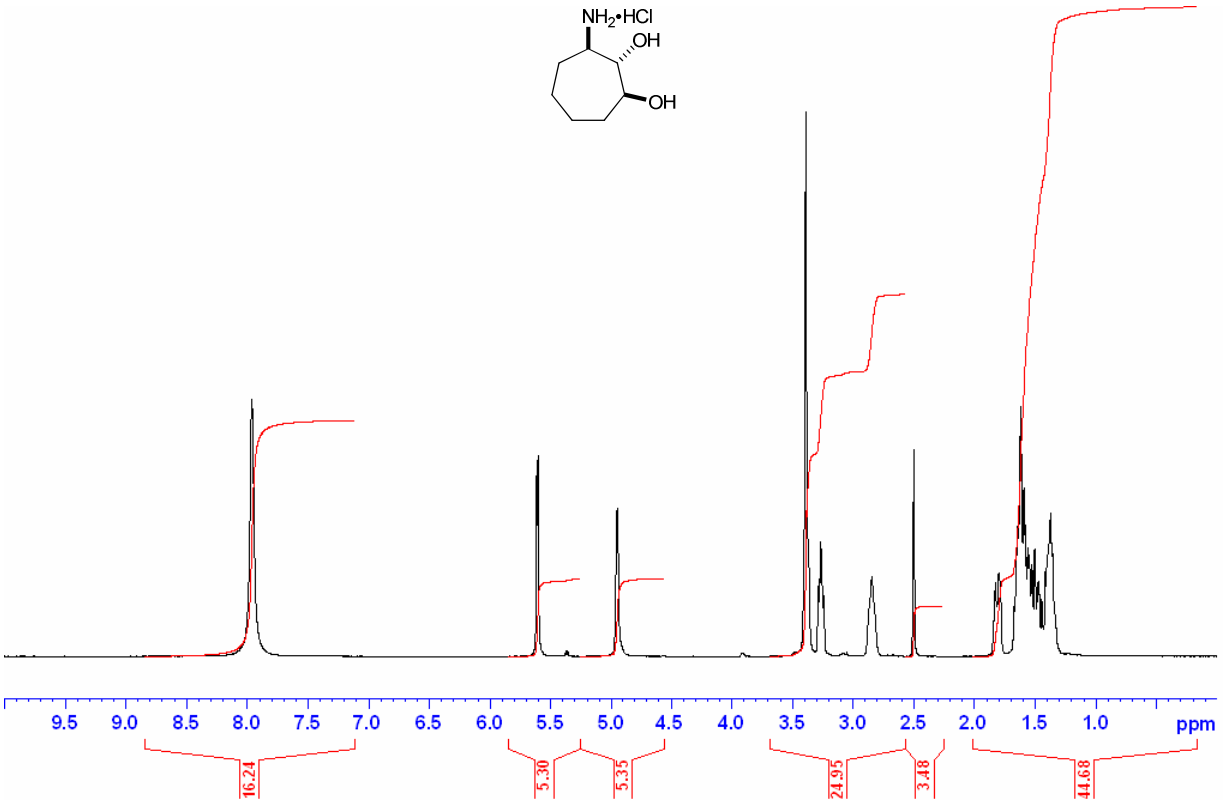
(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cycloheptane-1,2-diol 58 (400 MHz ^{1}H, $CDCl_3$)



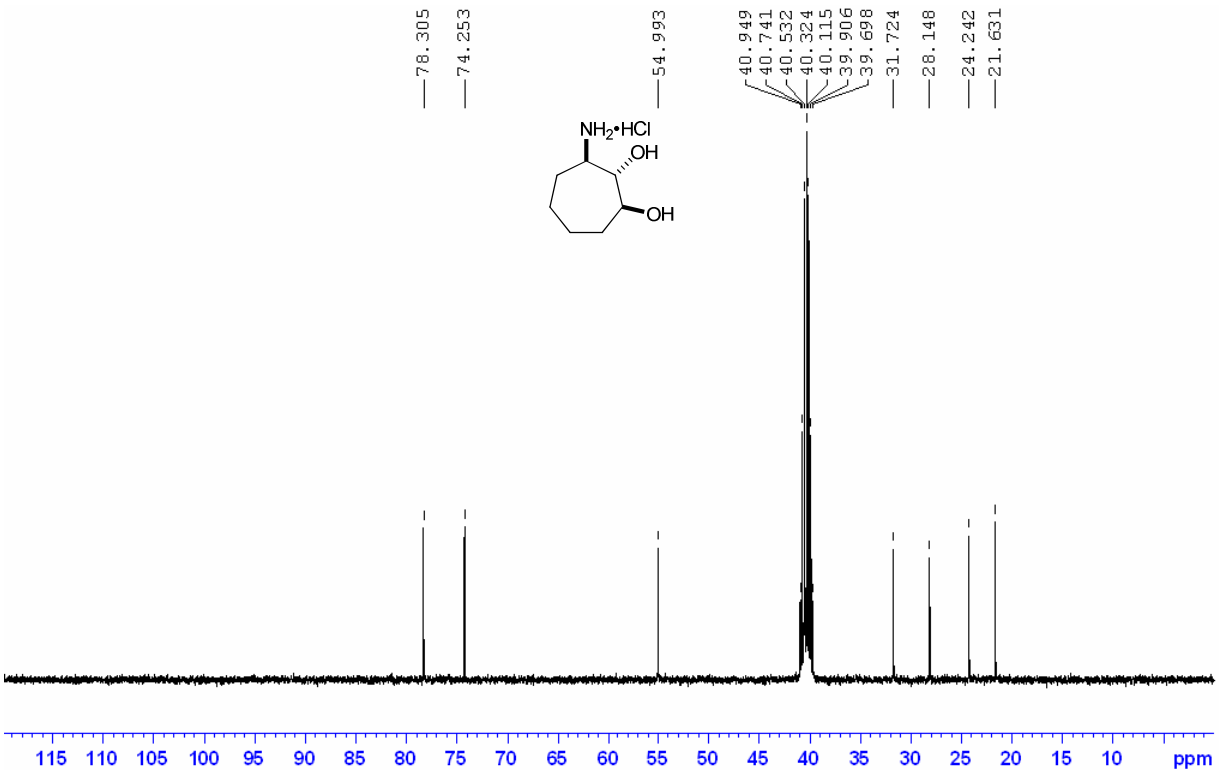
(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)cycloheptane-1,2-diol 58 (100 MHz ^{13}C, $CDCl_3$)



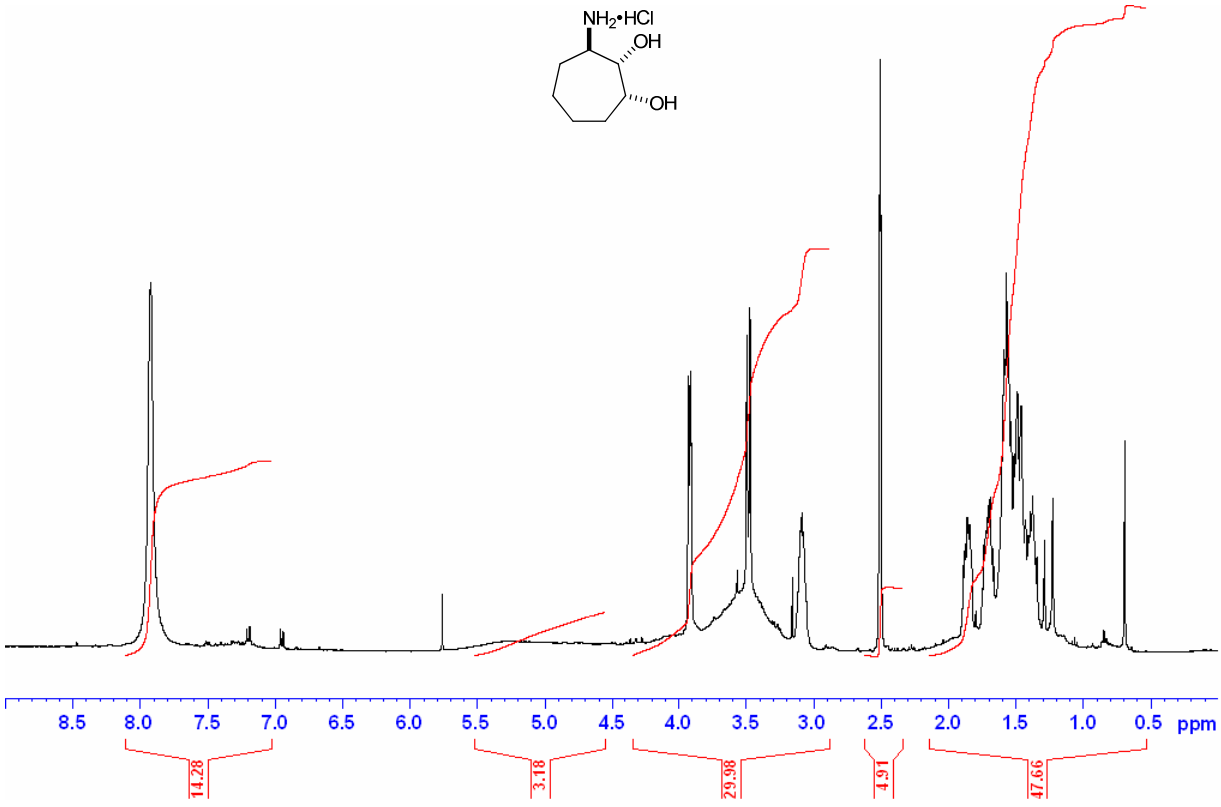
(1*RS*,2*RS*,3*SR*)-3-Aminocycloheptane-1,2-diol hydrochloride 59 (400 MHz ^{1}H, d_6-DMSO)



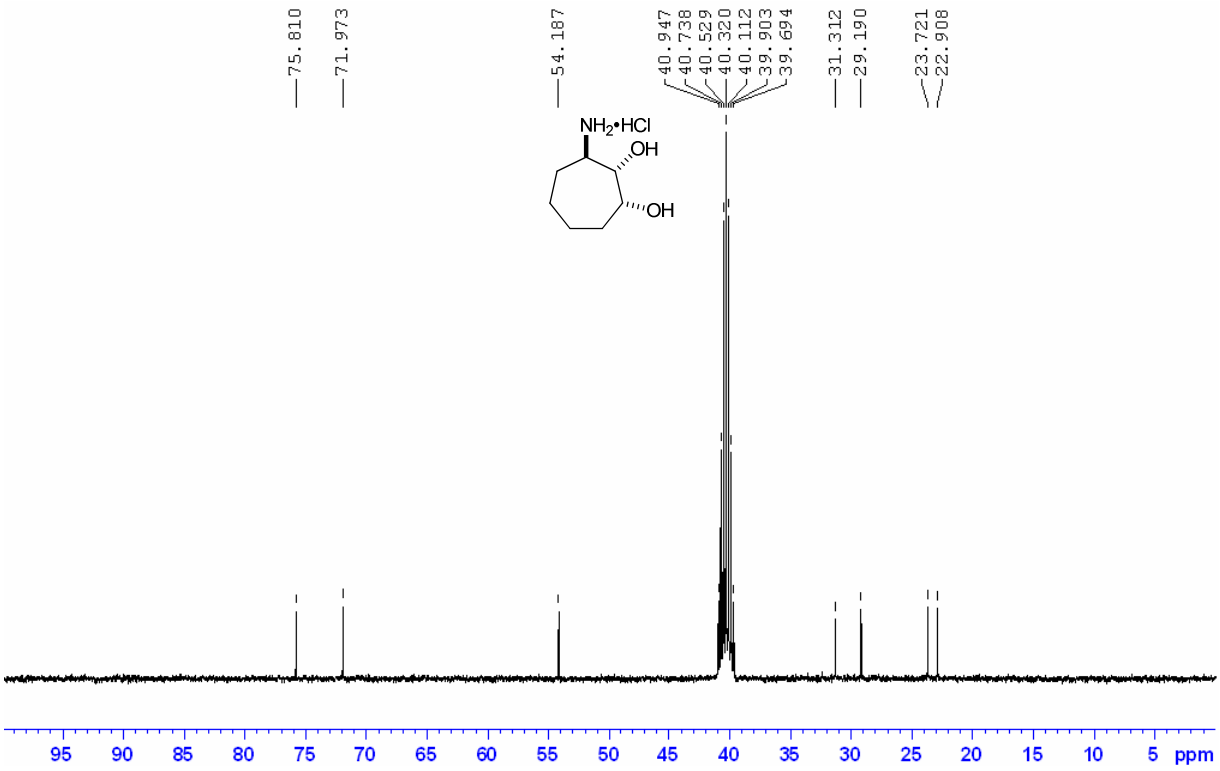
(1*RS*,2*RS*,3*SR*)-3-Aminocycloheptane-1,2-diol hydrochloride 59 (100 MHz ^{13}C, $CDCl_3$)



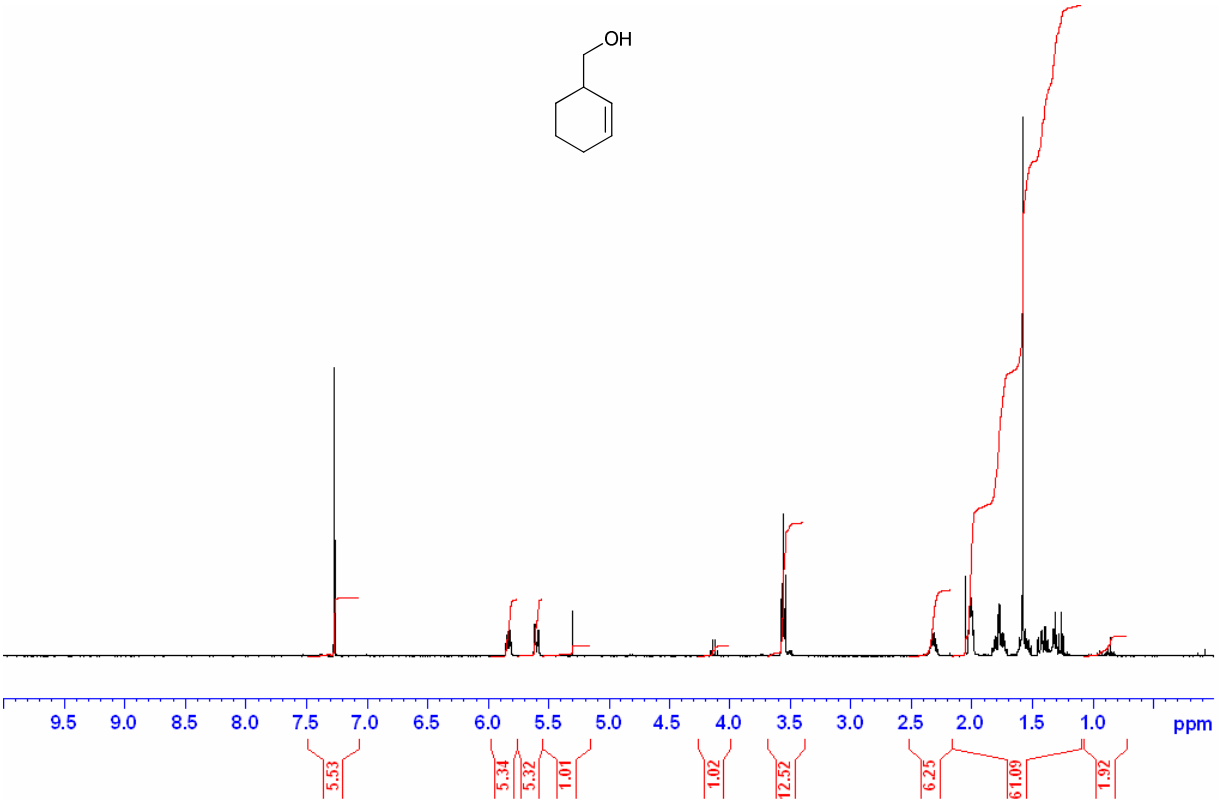
(1*RS*,2*SR*,3*RS*)-3-Aminocycloheptane-1,2-diol hydrochloride 60 (400 MHz ^{1}H, d_6-DMSO)



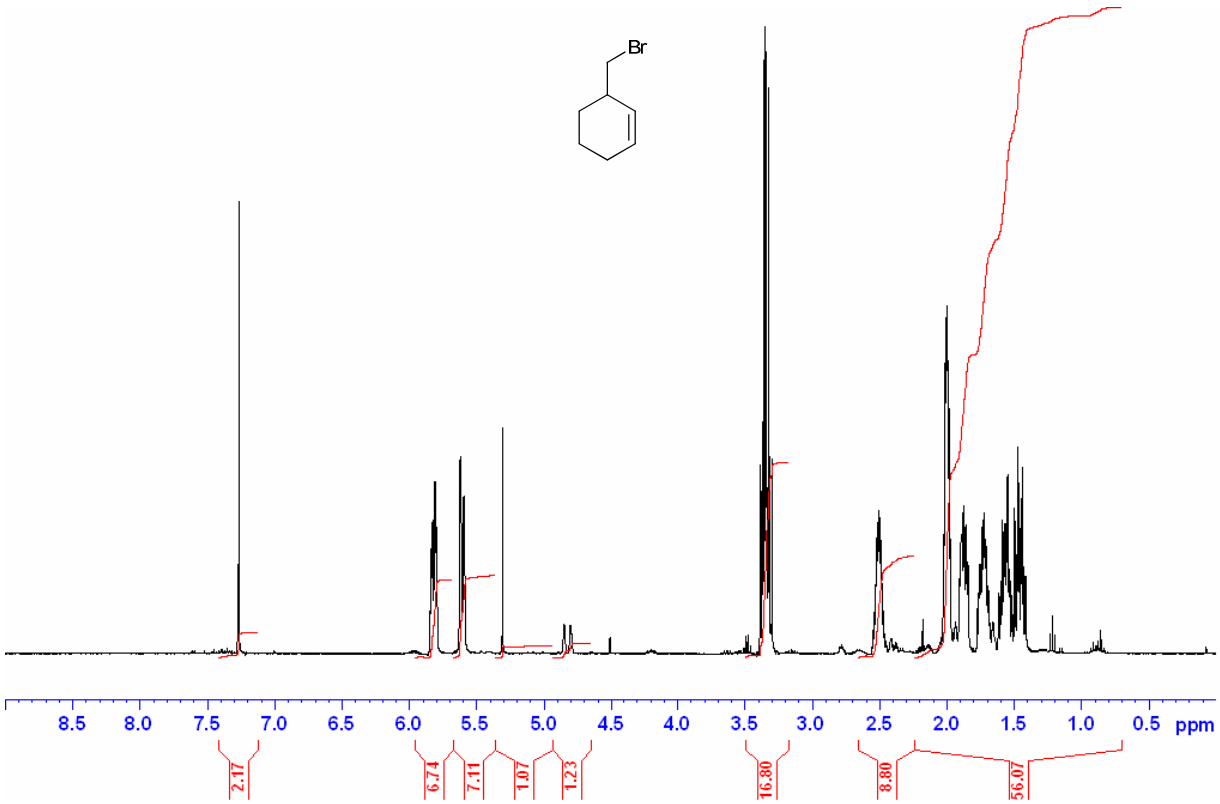
(1*RS*,2*SR*,3*RS*)-3-Aminocycloheptane-1,2-diol hydrochloride 60 (100 MHz ^{13}C, $CDCl_3$)



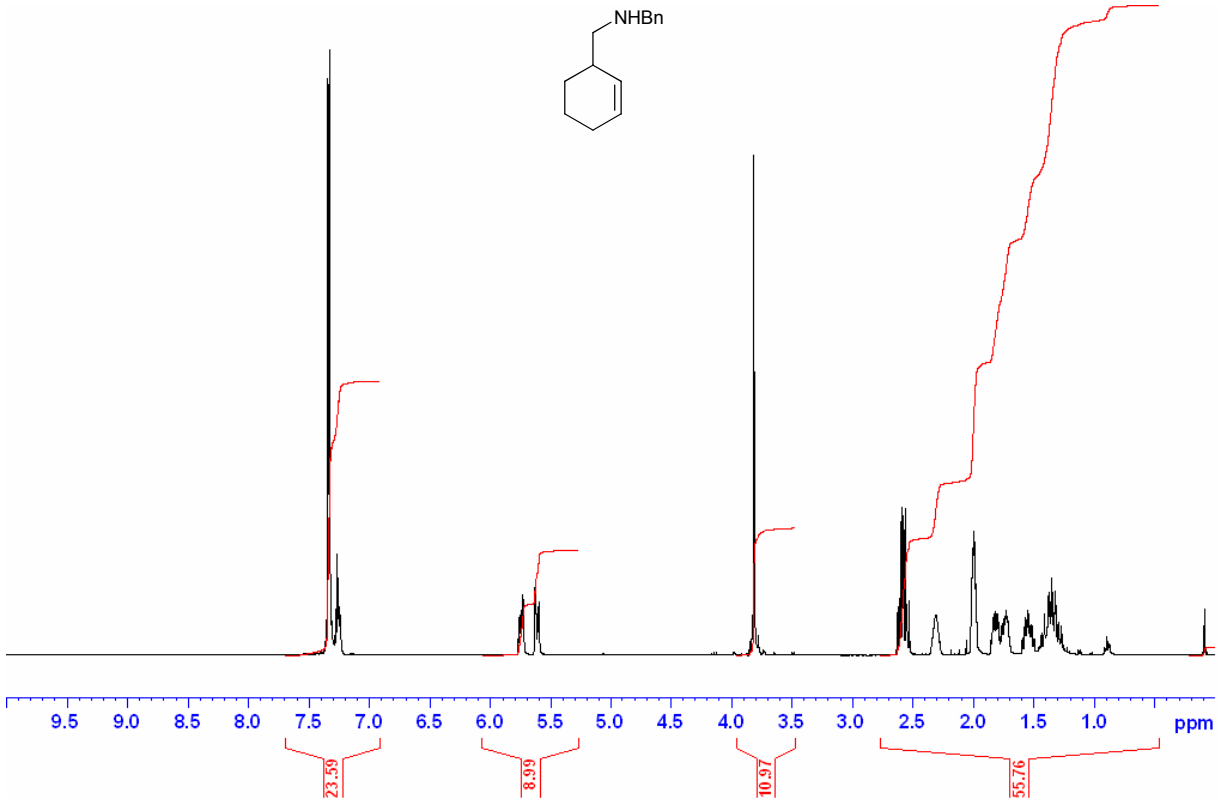
(*RS*)-3-(Hydroxymethyl)cyclohex-1-ene 62 (400 MHz ^{1}H, $CDCl_3$)



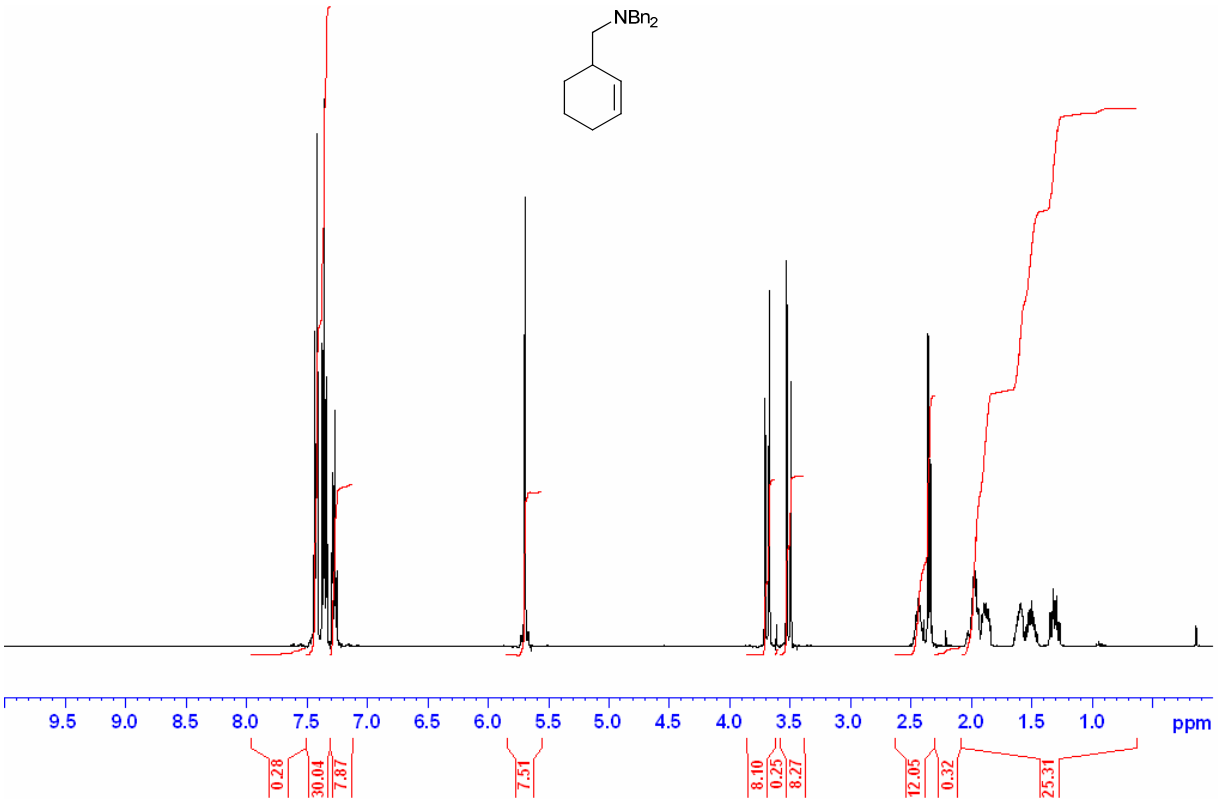
(*RS*)-3-(Bromomethyl)cyclohex-1-ene 63 (400 MHz ^{1}H, $CDCl_3$)



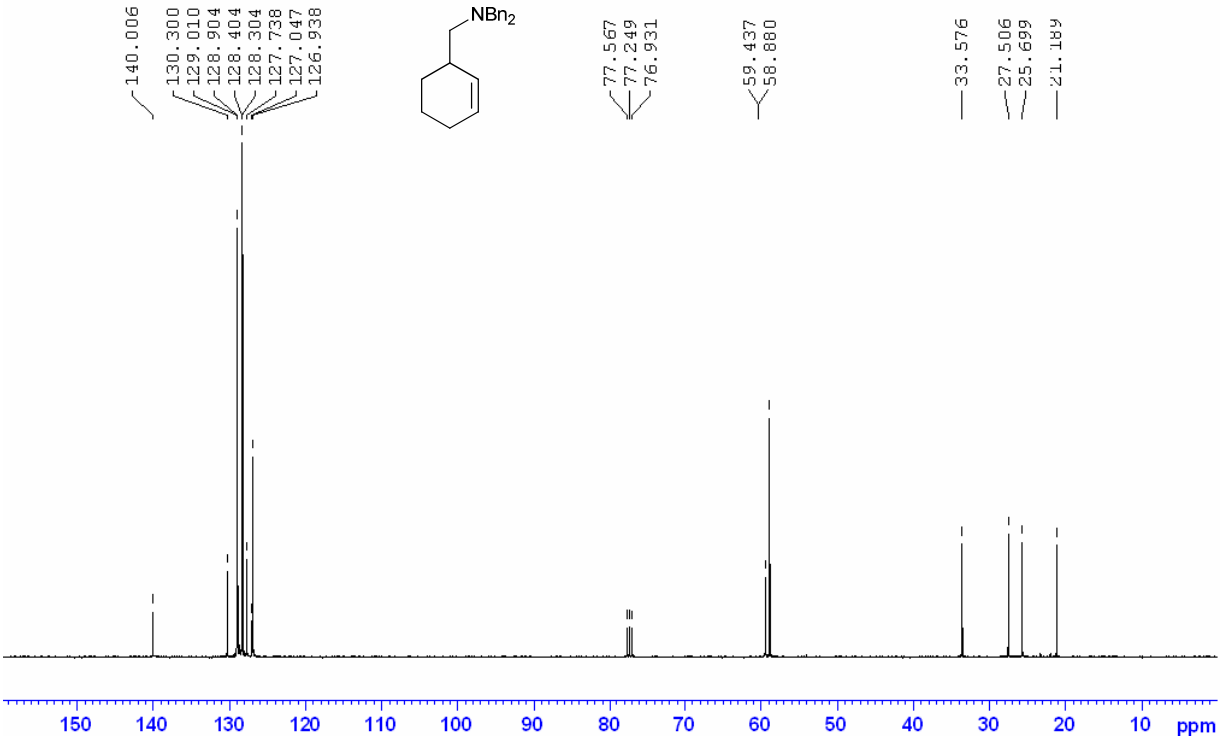
(*RS*)-3-(*N*-Benzylamino)methyl-cyclohex-1-ene 64 (400 MHz ^{1}H, $CDCl_3$)



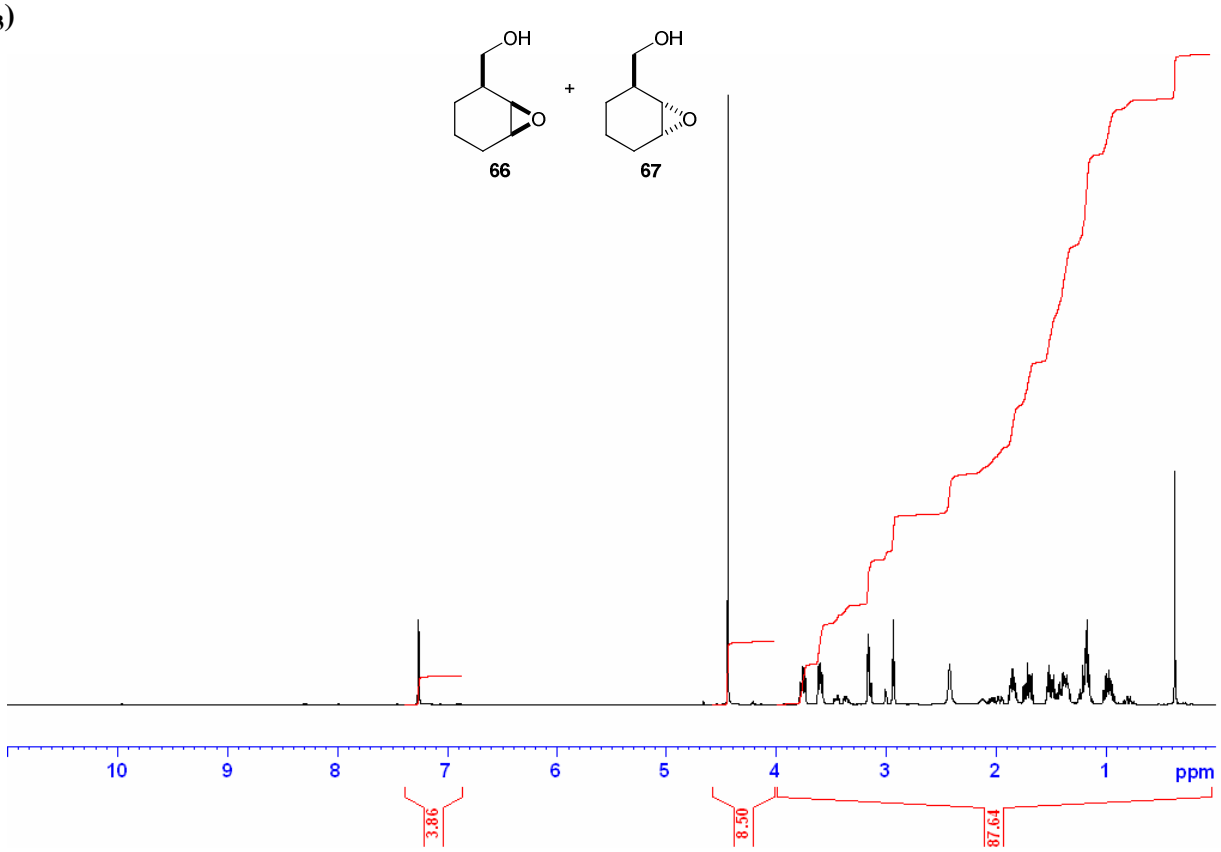
(*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohex-1-ene 65 (400 MHz ^{1}H, $CDCl_3$)



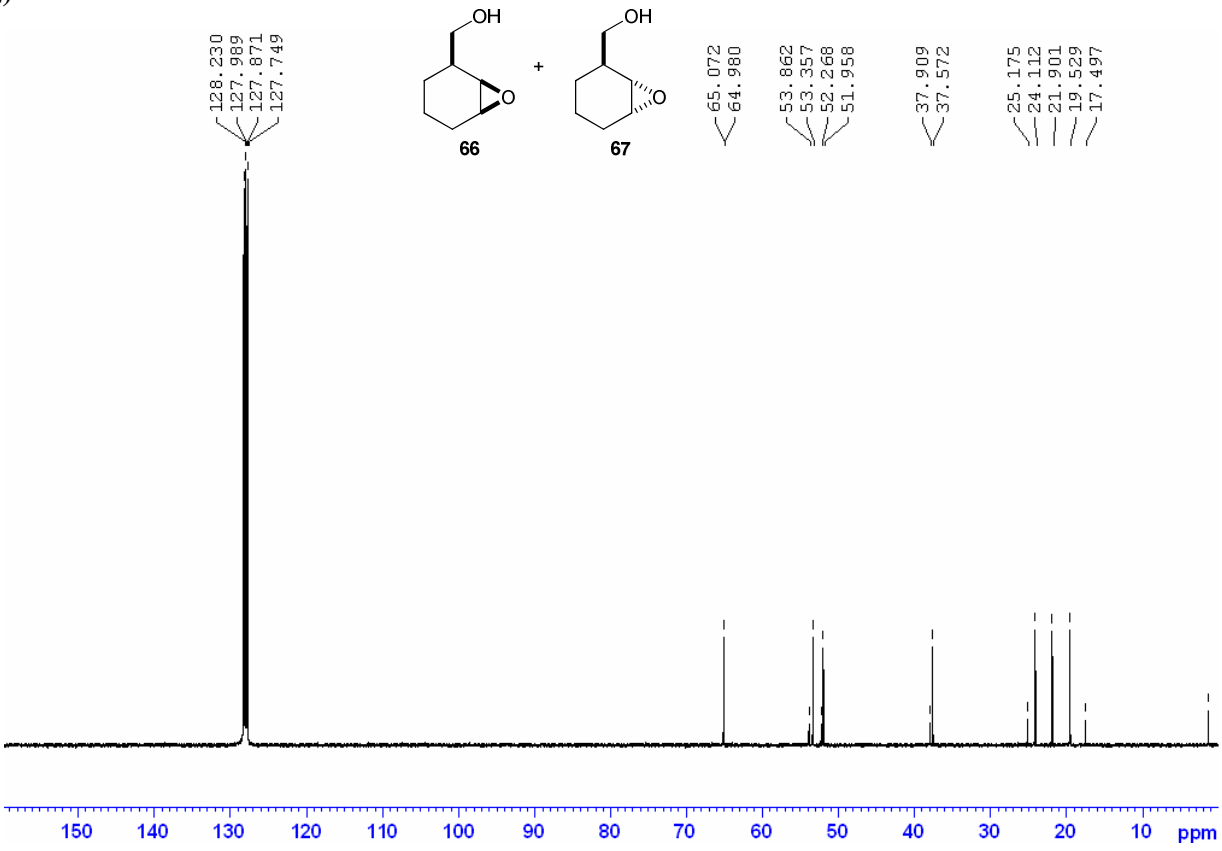
(*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohex-1-ene 65 (100 MHz ^{13}C, $CDCl_3$)



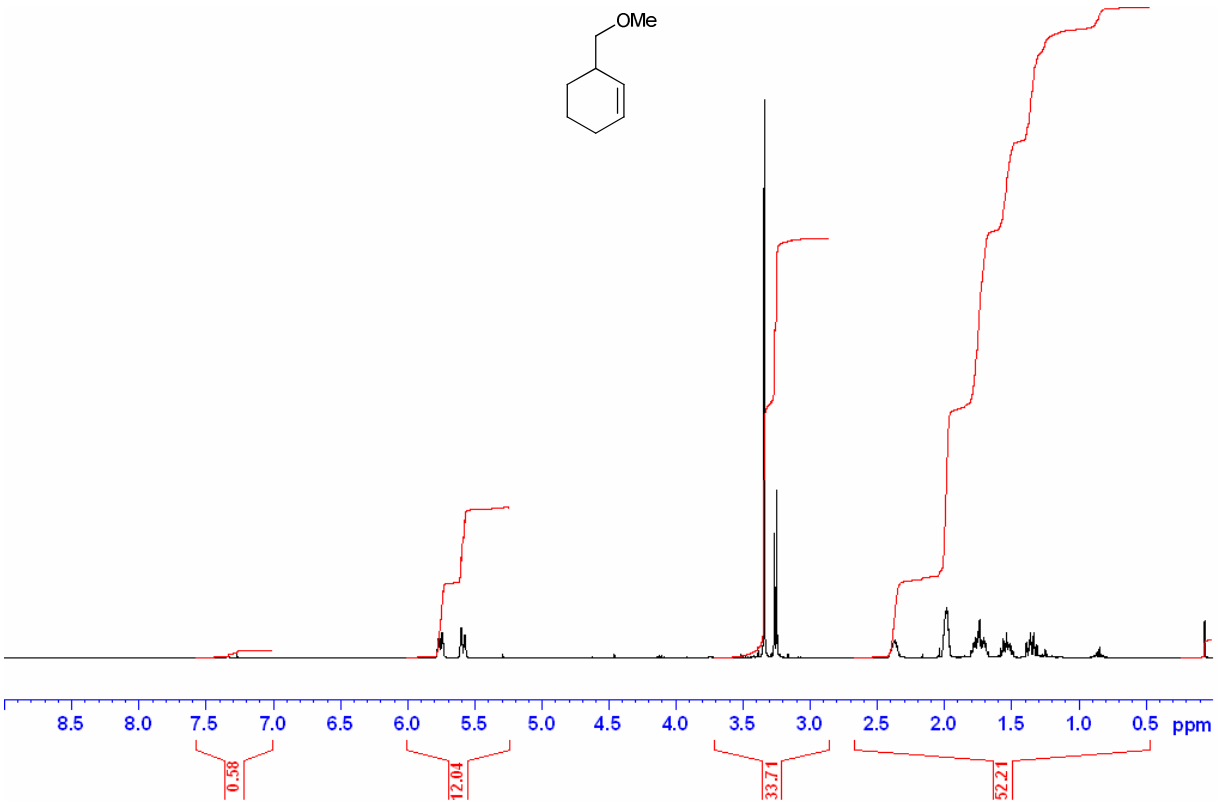
(1*RS*,2*SR*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-hydroxymethyl-cyclohexane 66 and 67 (400 MHz ^{1}H, $CDCl_3$)



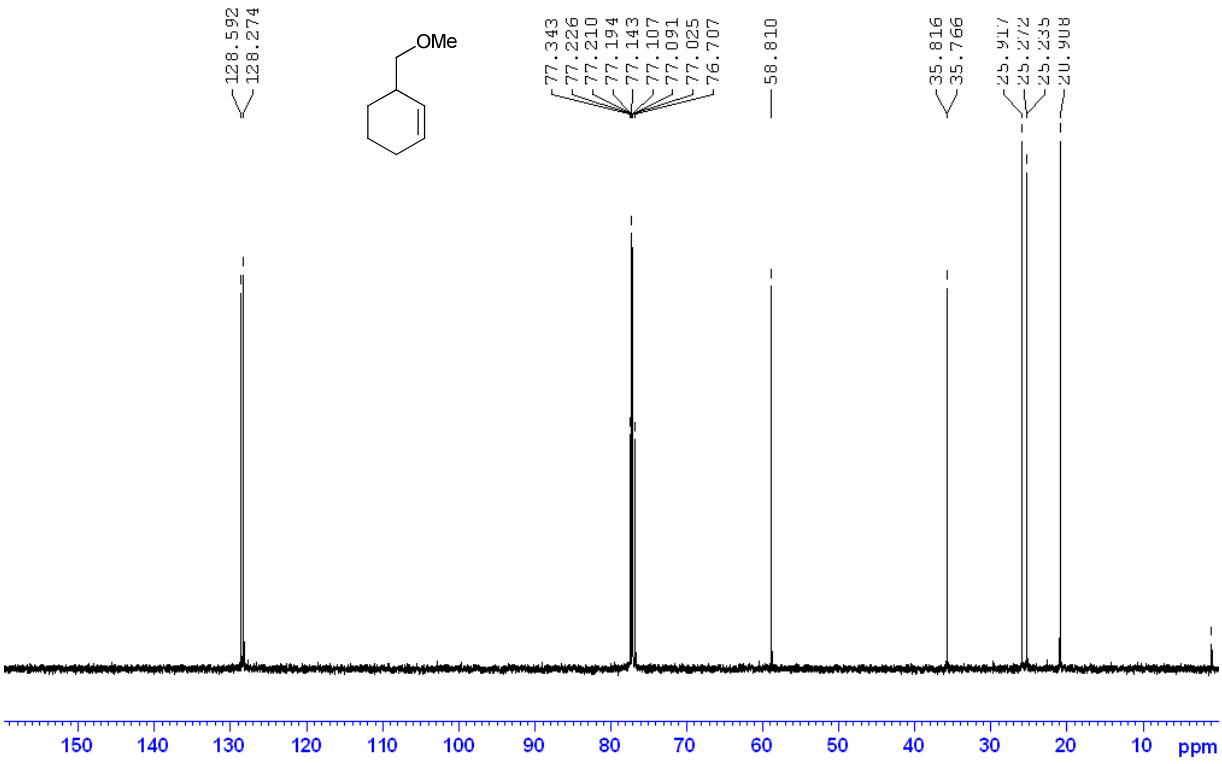
(1*RS*,2*SR*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-hydroxymethyl-cyclohexane 66 and 67 (100 MHz ^{13}C, $CDCl_3$)



(*RS*)-3-(Methoxymethyl)cyclohex-1-ene 68 (400 MHz ^{1}H, $CDCl_3$)

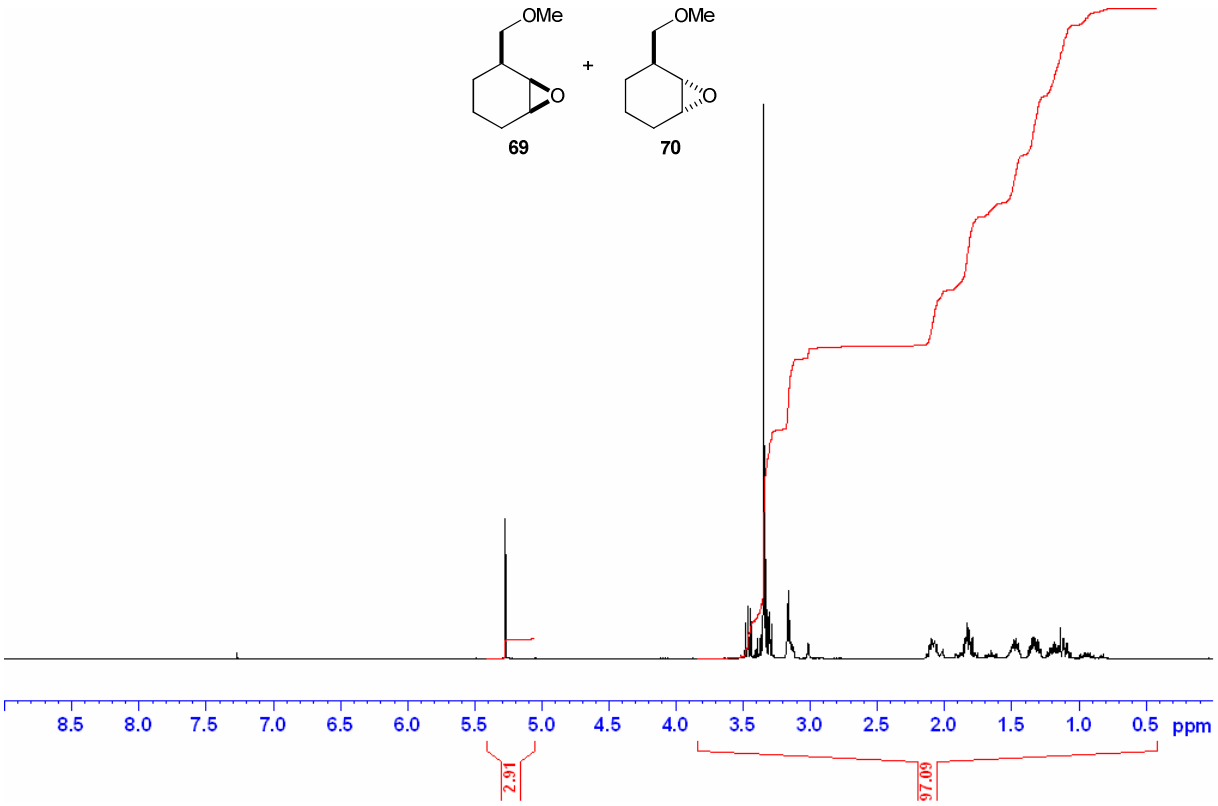


(*RS*)-3-(Methoxymethyl)cyclohex-1-ene 68 (100 MHz ^{13}C, $CDCl_3$)



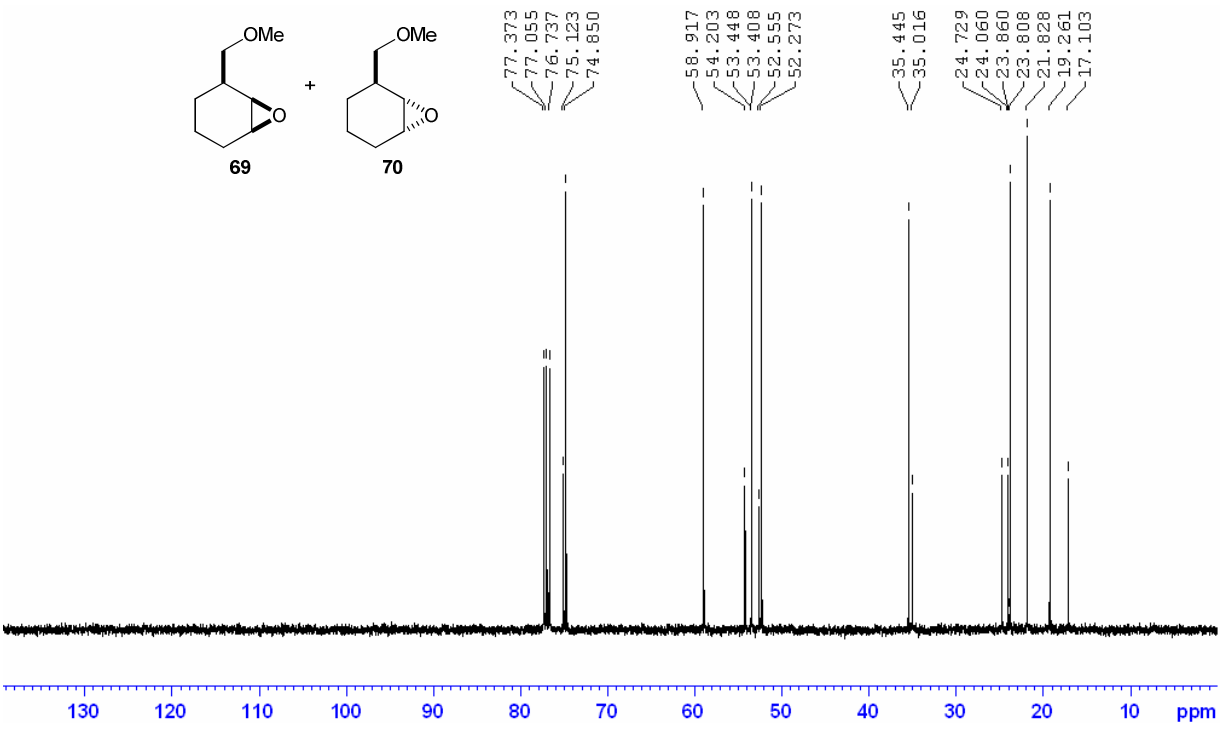
(1*RS*,2*SR*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-methoxymethyl-cyclohexane 69 and 70

(400 MHz, ^{1}H, $CDCl_3$)

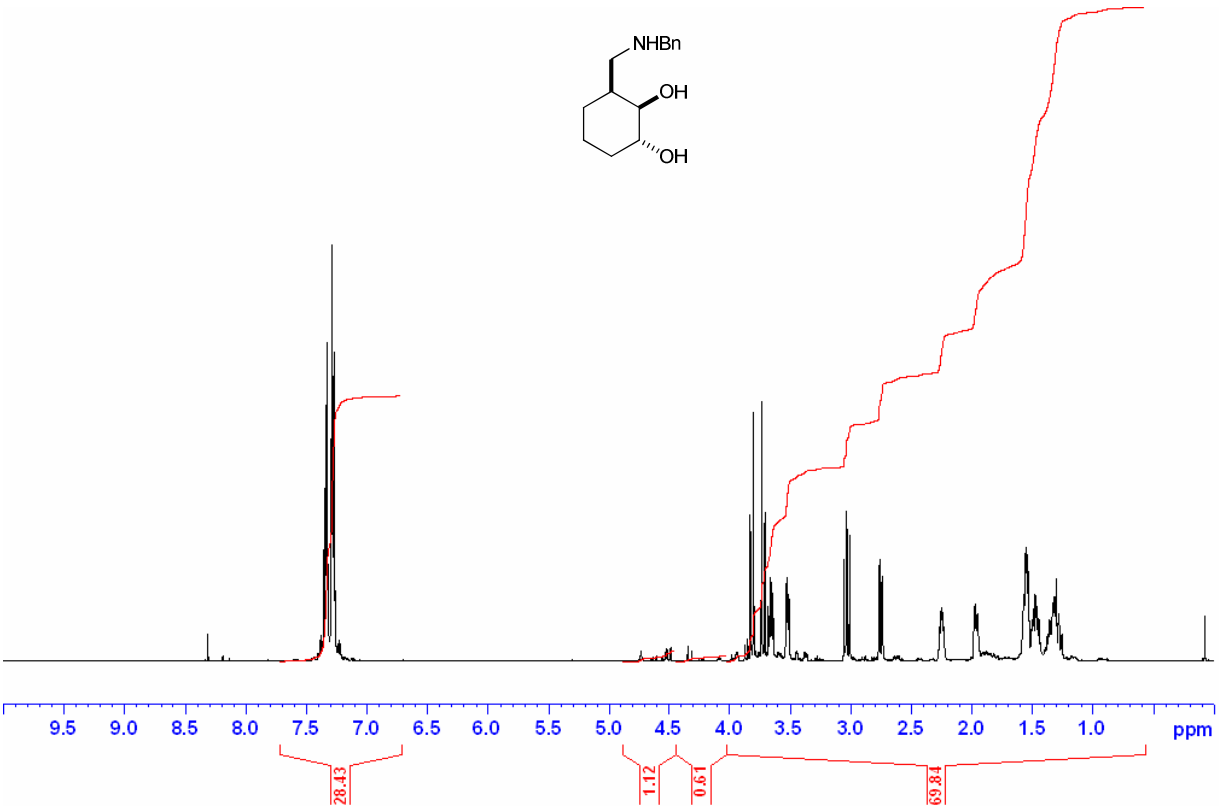


(1*RS*,2*SR*,3*RS*)- and (1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-methoxymethyl-cyclohexane 69 and 70

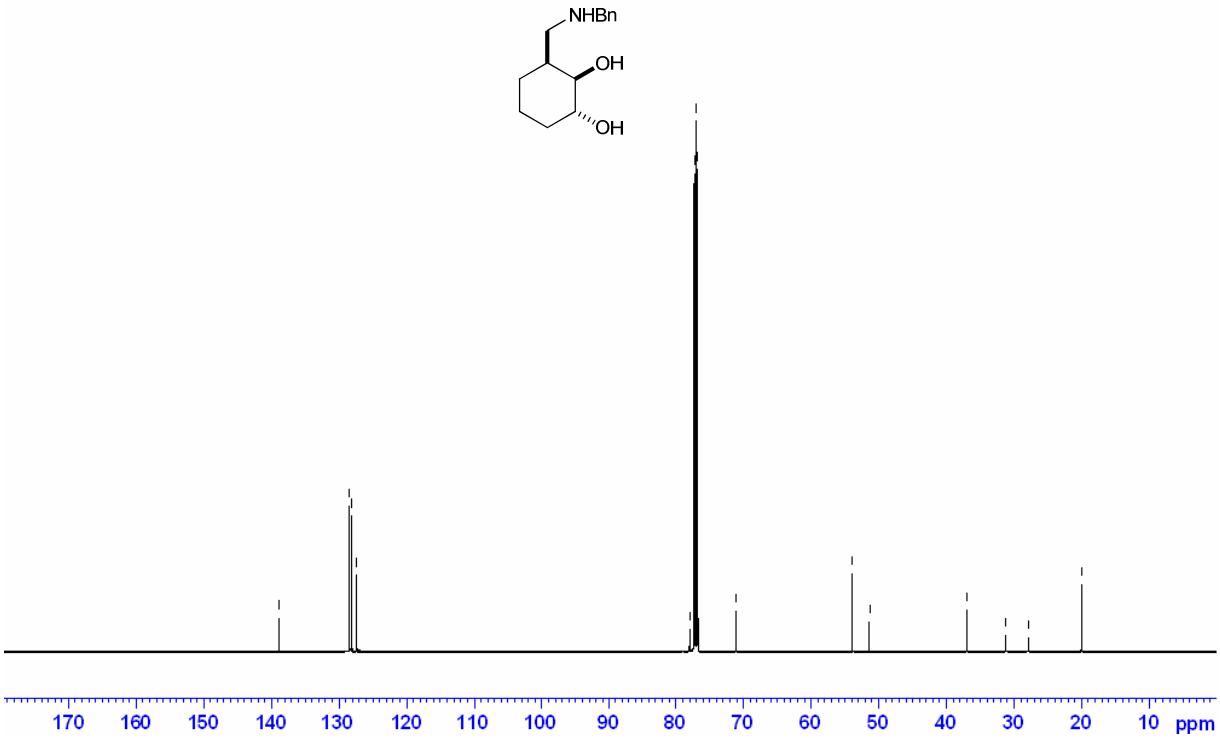
(100 MHz, ^{13}C, $CDCl_3$)



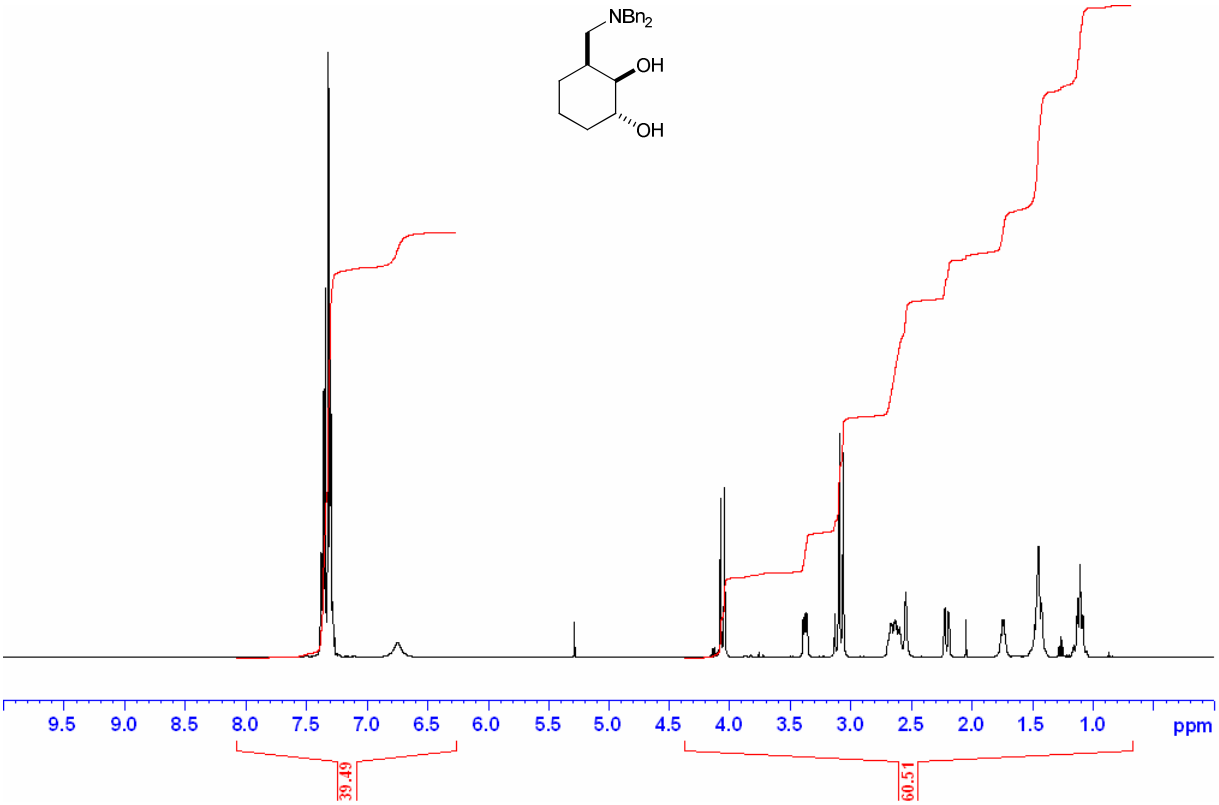
(1*RS*,2*RS*,3*SR*)-3-(*N*-Benzylamino)methyl-cyclohexane-1,2-diol 71 (400 MHz, ^{1}H, $CDCl_3$)



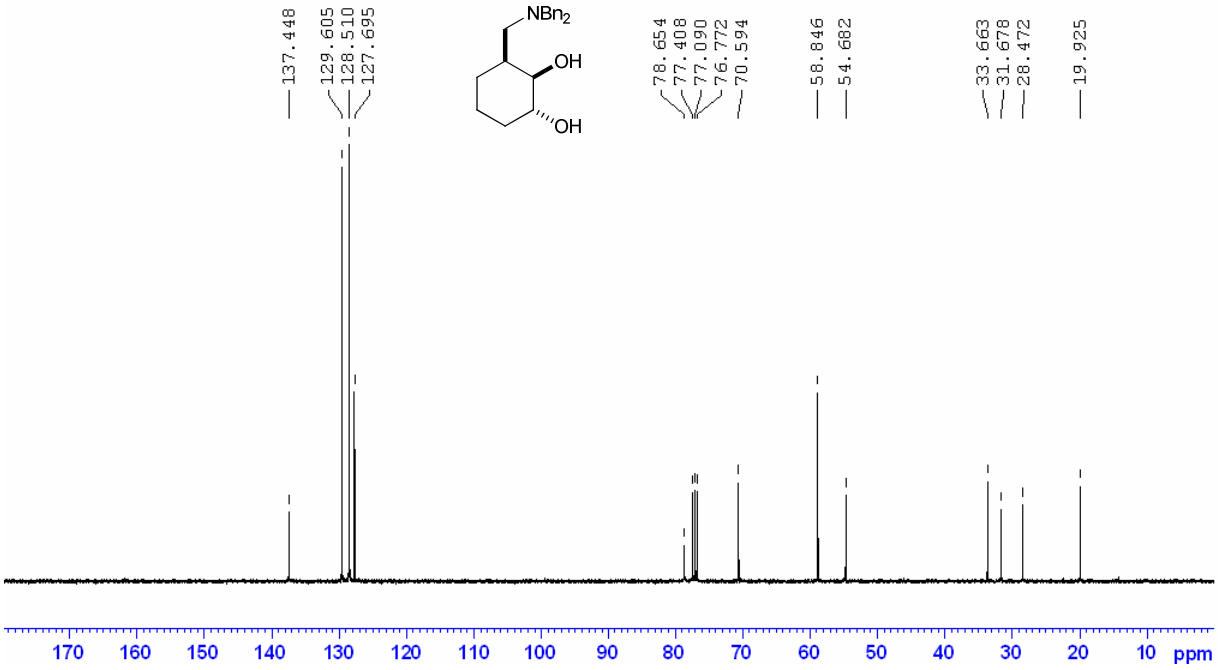
(1*RS*,2*RS*,3*SR*)-3-(*N*-Benzylamino)methyl-cyclohexane-1,2-diol 71 (100 MHz, ^{13}C, $CDCl_3$)



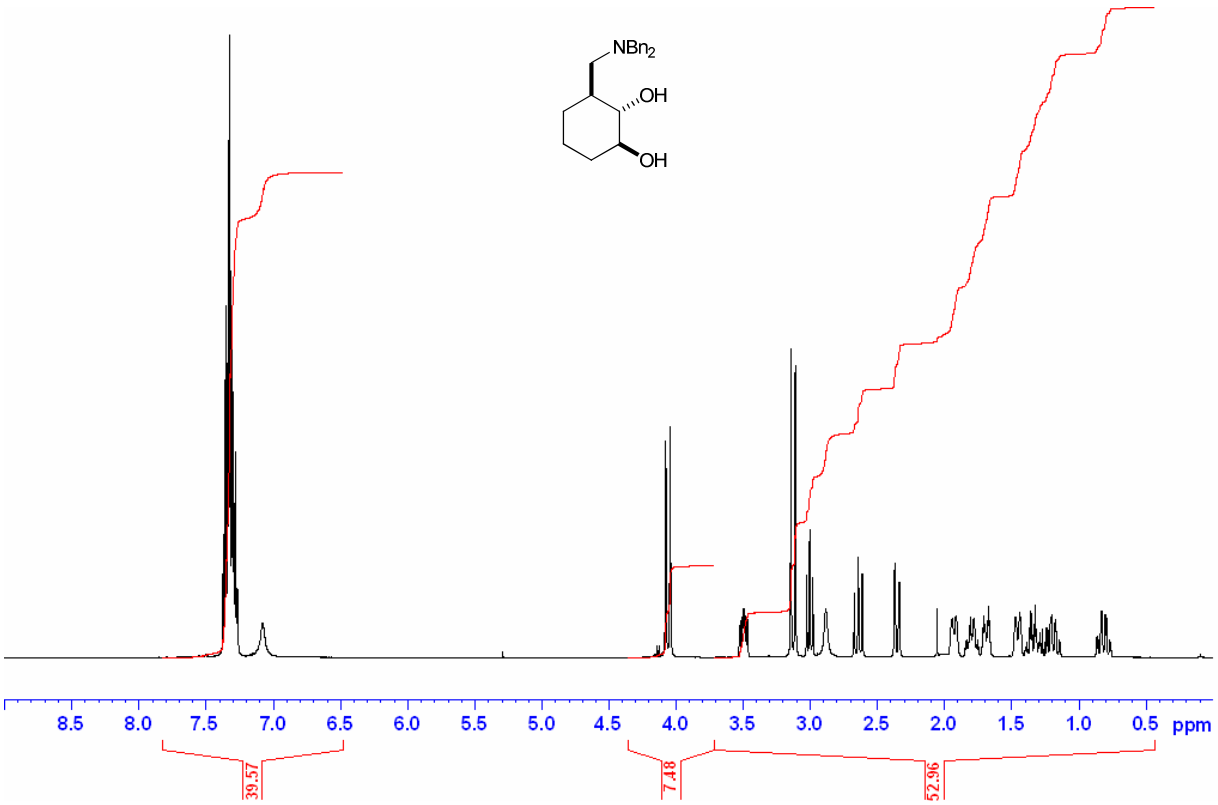
(1*RS*,2*RS*,3*SR*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 75 (400 MHz ^{1}H, $CDCl_3$)



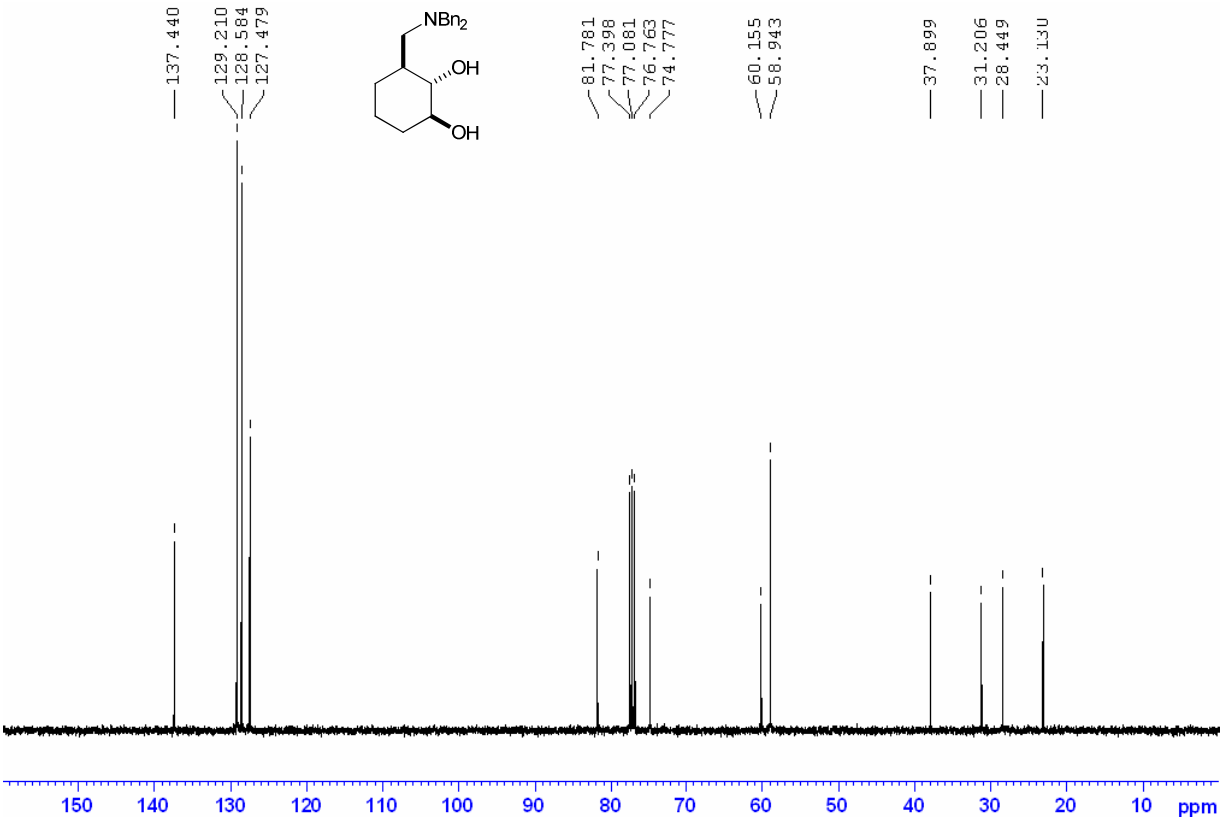
(1*RS*,2*RS*,3*SR*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 75 (100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*RS*,3*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 76 (400 MHz ^{1}H, $CDCl_3$)

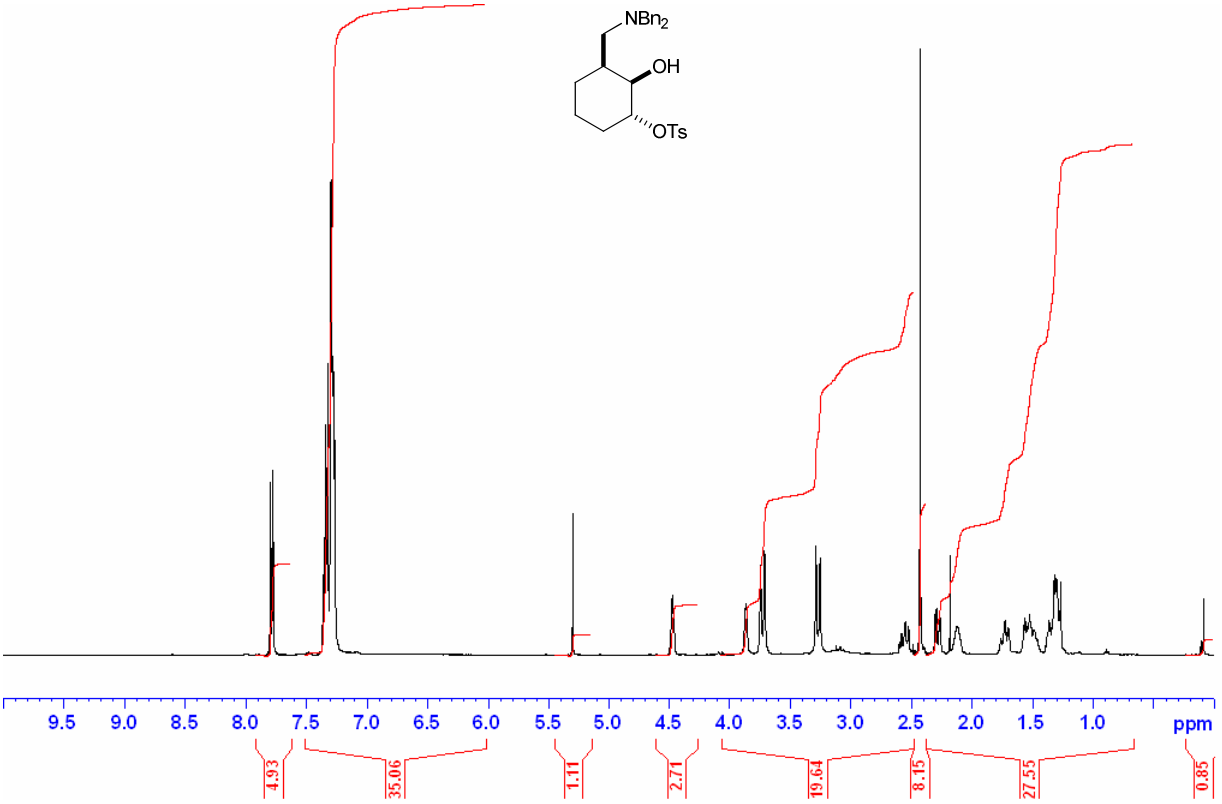


(1*RS*,2*RS*,3*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 76 (100 MHz ^{13}C, $CDCl_3$)



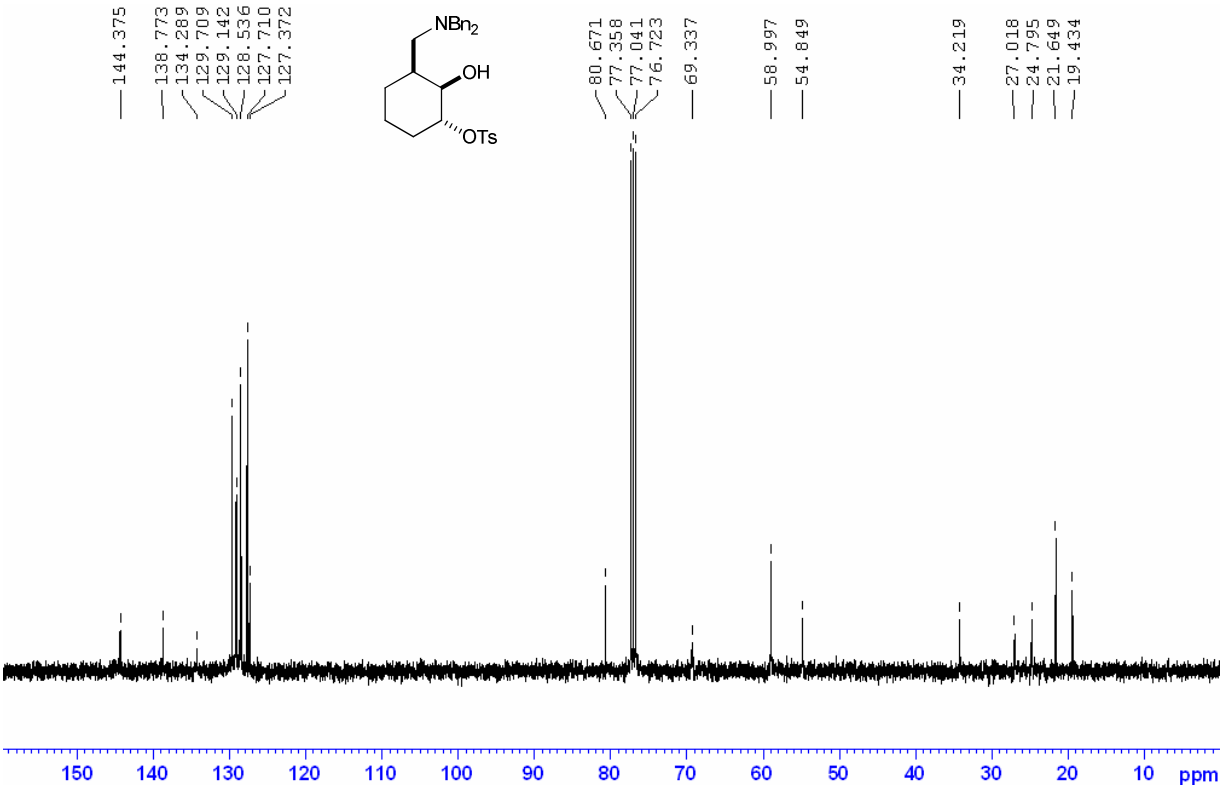
(1*RS*,2*RS*,3*SR*)-1-(*p*-Toluenesulfonyloxy)-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 77

(400 MHz ^{1}H, $CDCl_3$)



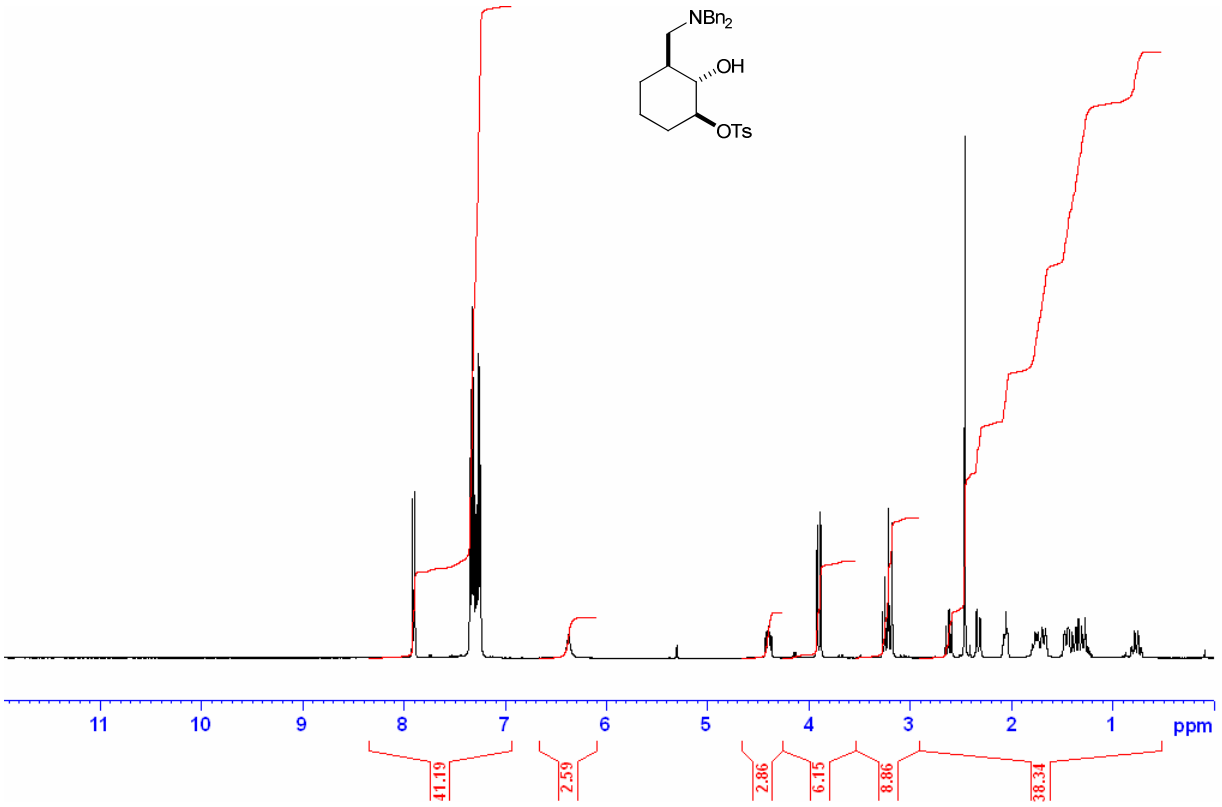
(1*RS*,2*RS*,3*SR*)-1-(*p*-Toluenesulfonyloxy)-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 77

(100 MHz ^{13}C, $CDCl_3$)



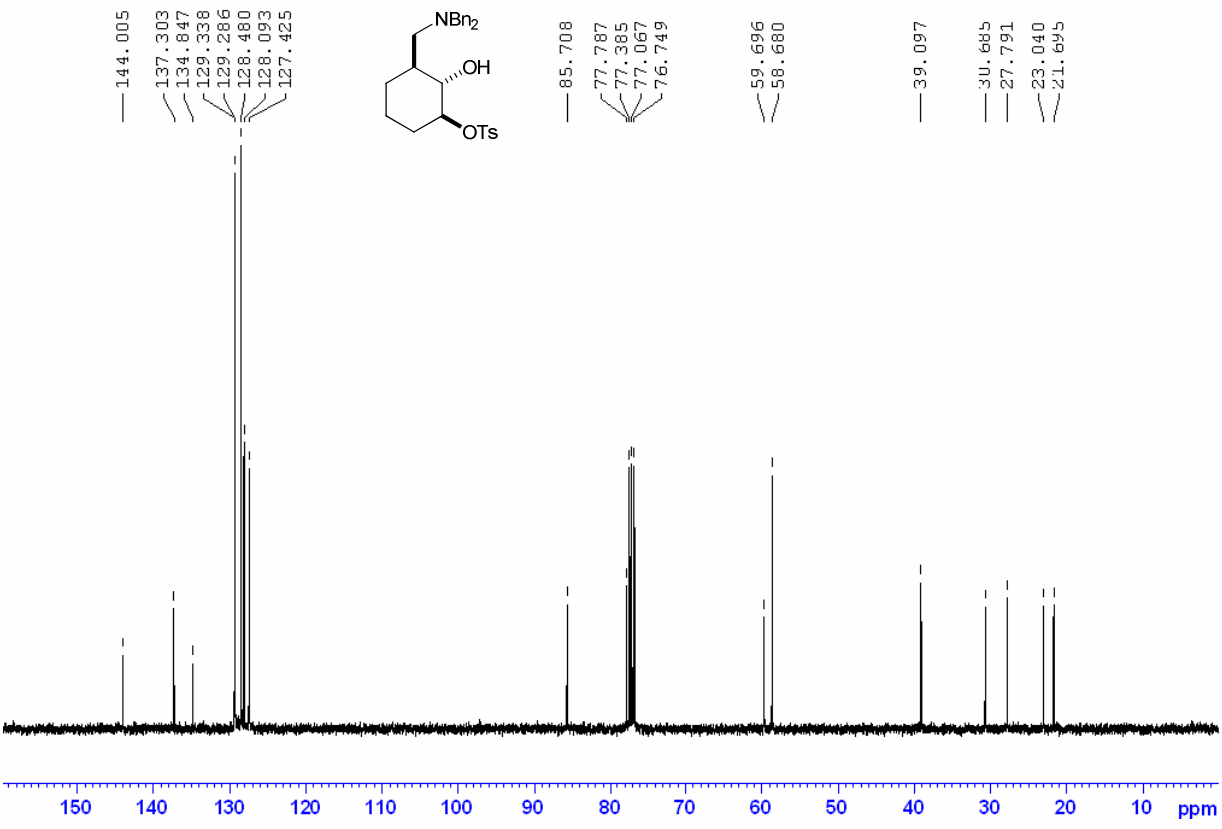
(1*RS*,2*RS*,3*RS*)-1-(*p*-Toluenesulfonyloxy)-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 78

(400 MHz ^{1}H, $CDCl_3$)

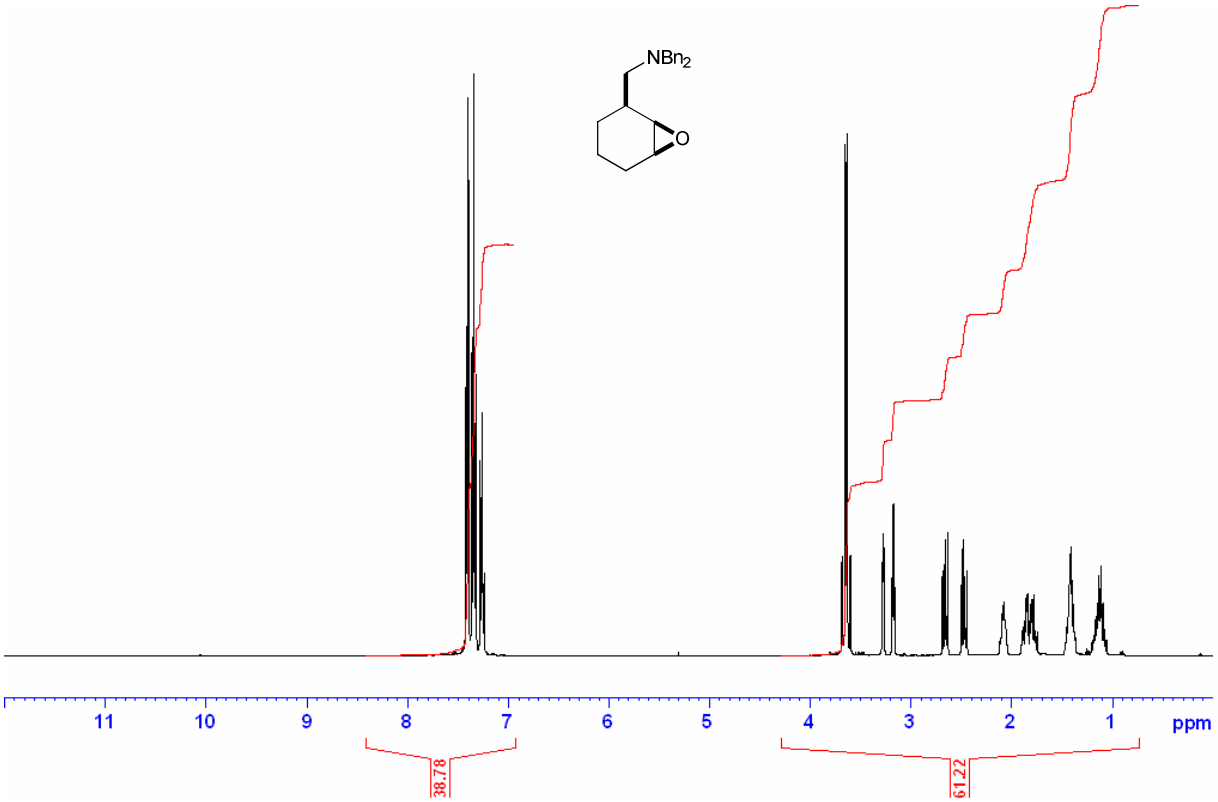


(1*RS*,2*RS*,3*RS*)-1-(*p*-Toluenesulfonyloxy)-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 78

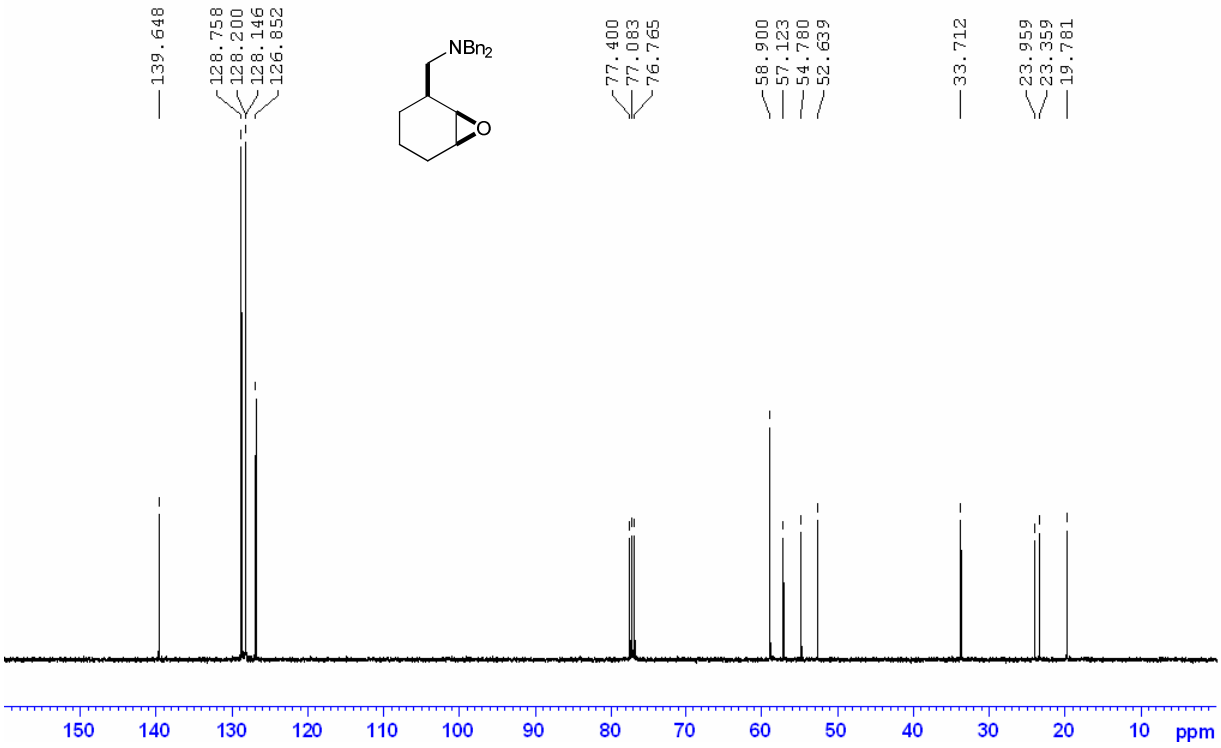
(100 MHz ^{13}C, $CDCl_3$)



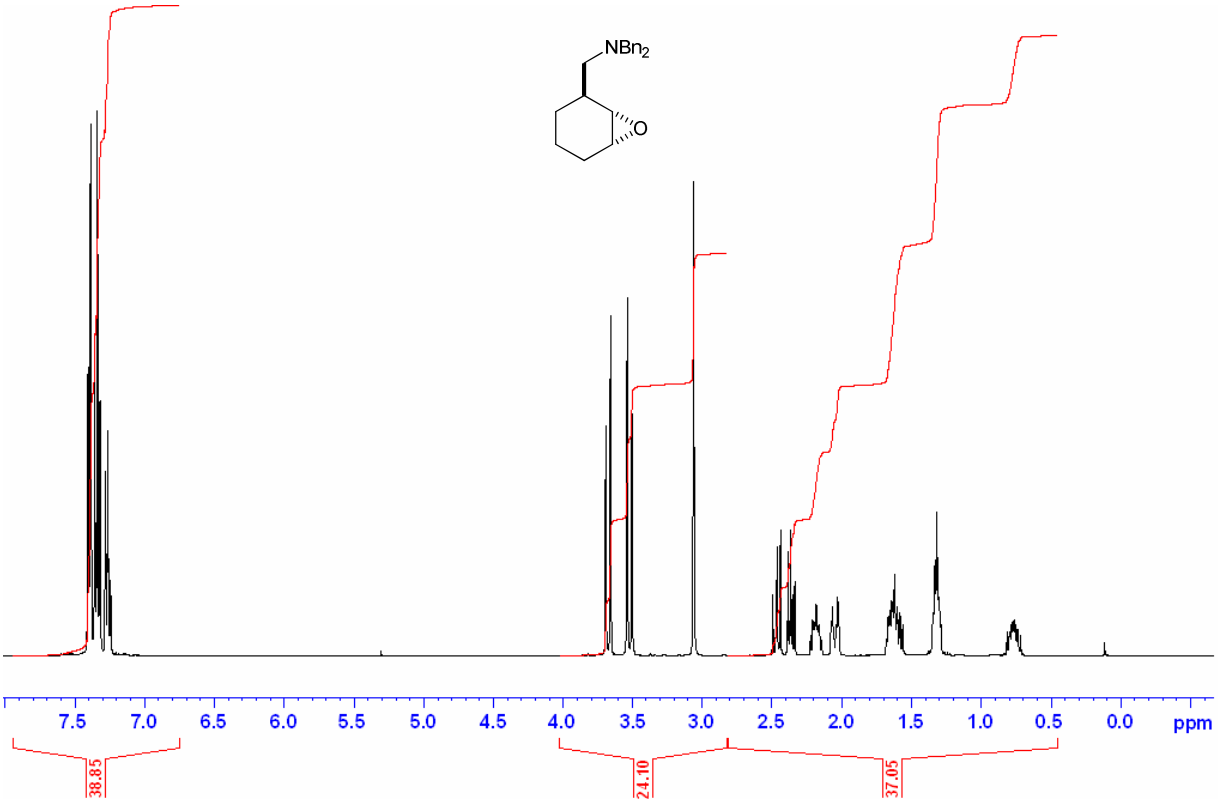
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 79 (400 MHz ^{1}H, $CDCl_3$)



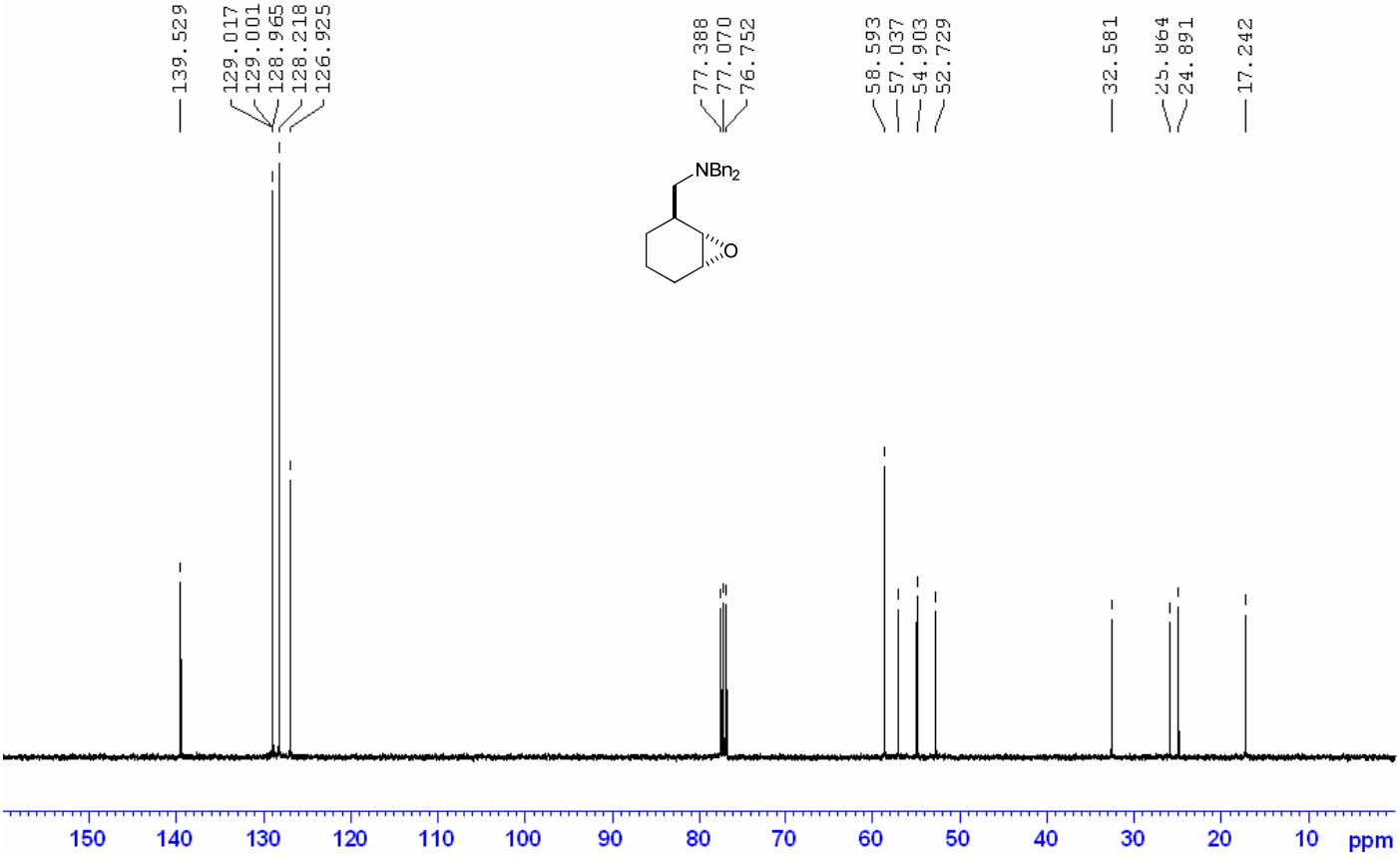
(1*RS*,2*SR*,3*RS*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 79 (100 MHz ^{13}C, $CDCl_3$)



(1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 80 (400 MHz ^{1}H, $CDCl_3$)

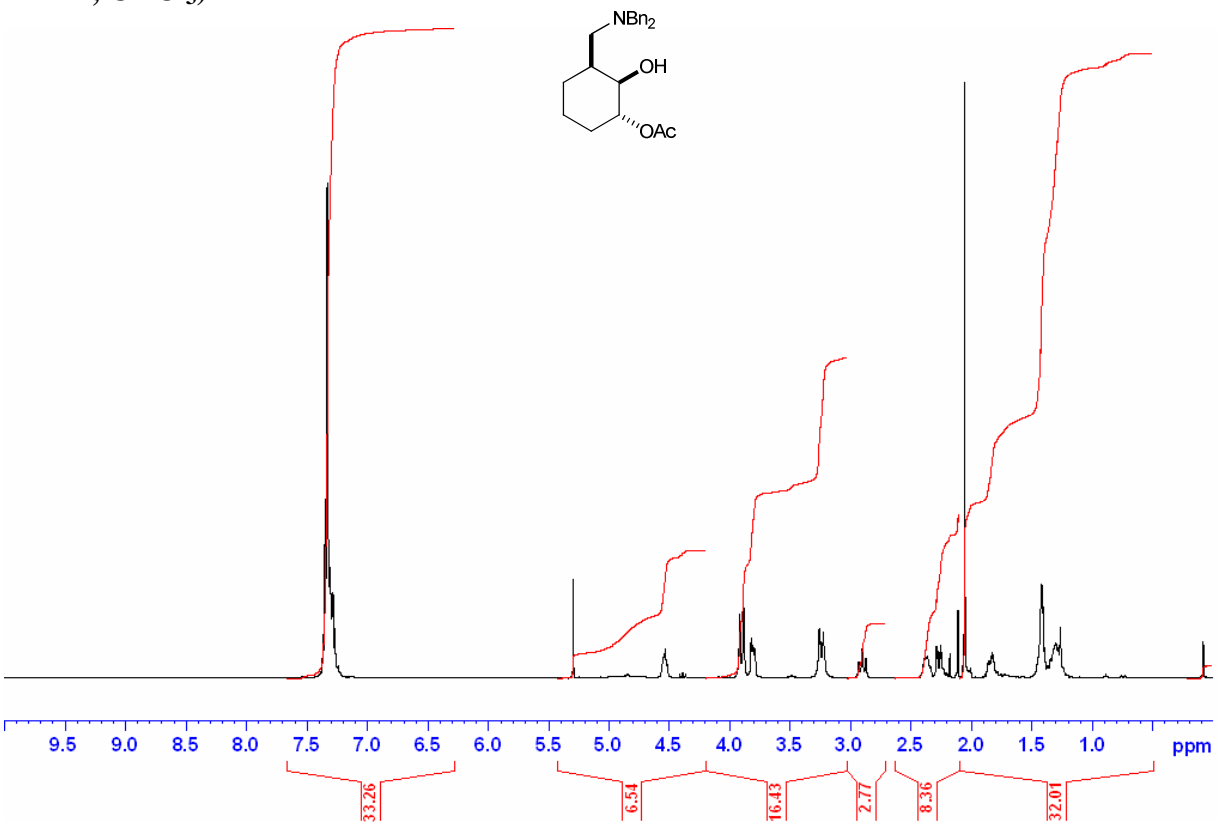


(1*RS*,2*SR*,3*SR*)-1,2-Epoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 80 (100 MHz ^{13}C, $CDCl_3$)



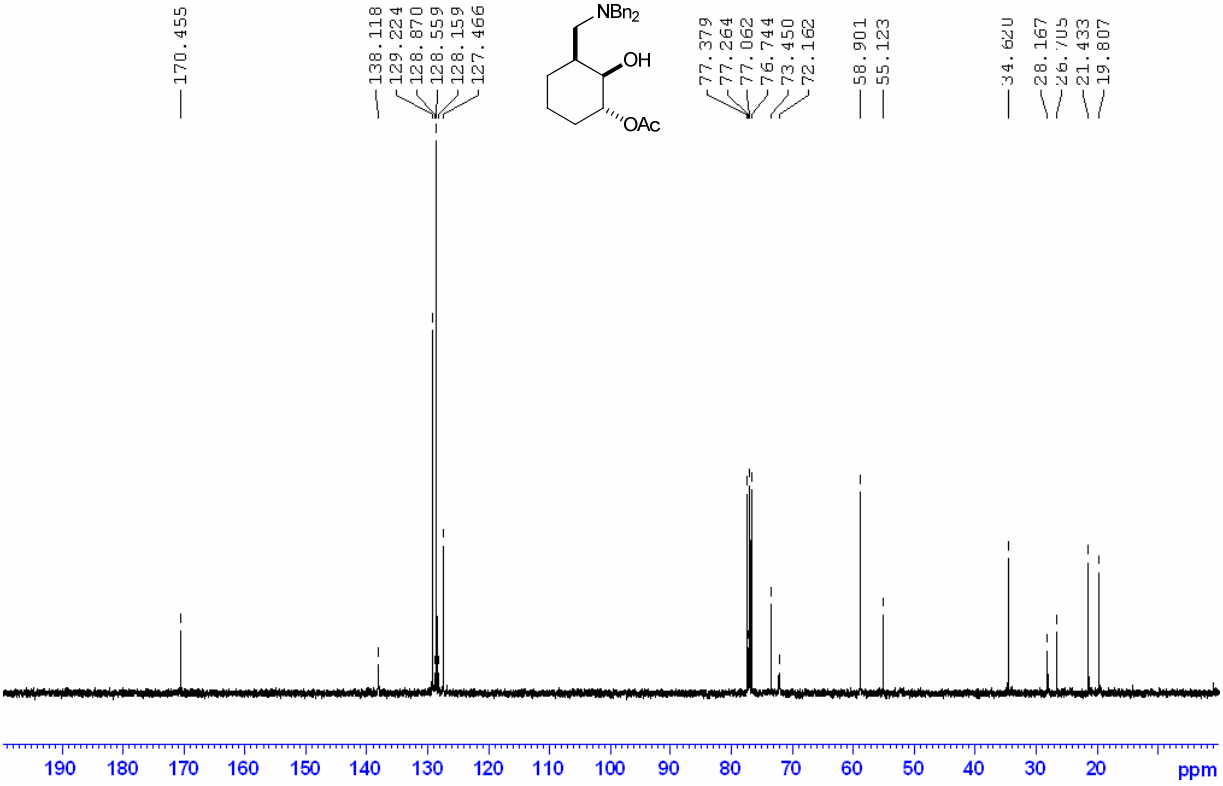
(1*RS*,2*RS*,3*SR*)-1-Acetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 81

(400 MHz ^{1}H, $CDCl_3$)



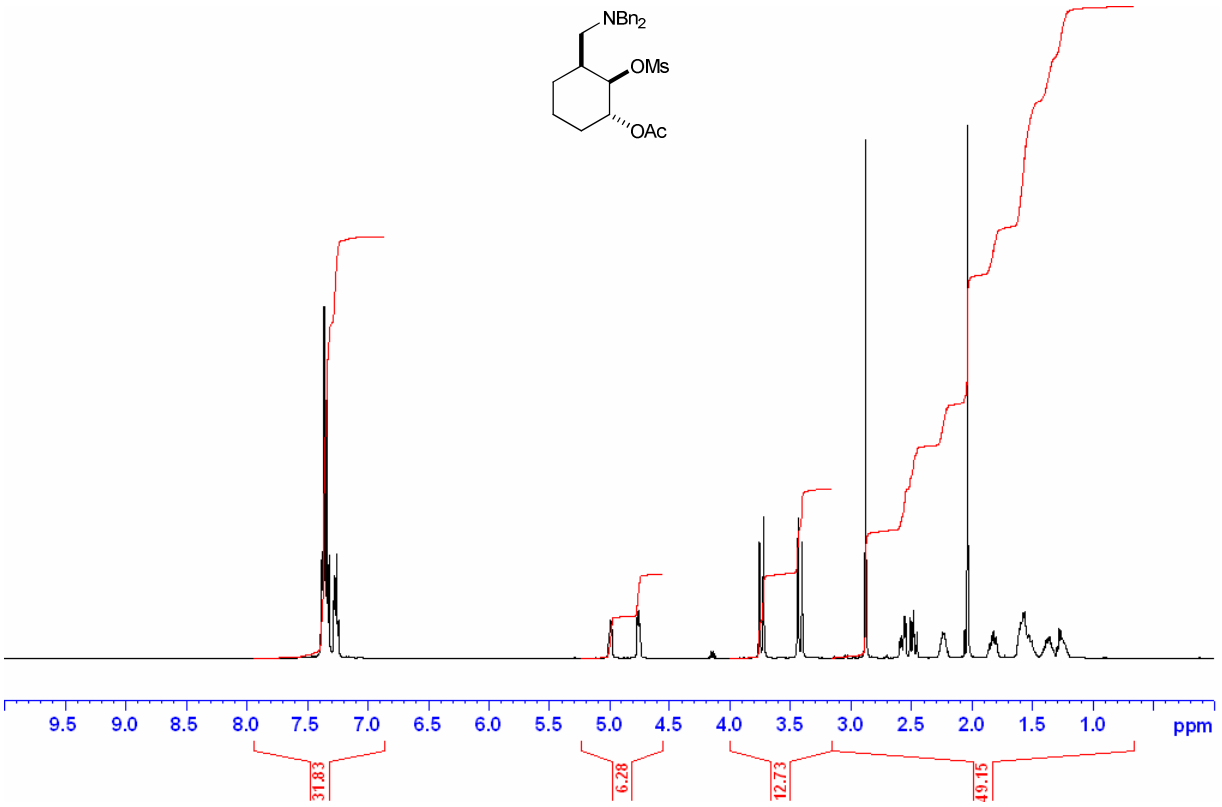
(1*RS*,2*RS*,3*SR*)-1-Acetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 81

(100 MHz ^{13}C, $CDCl_3$)



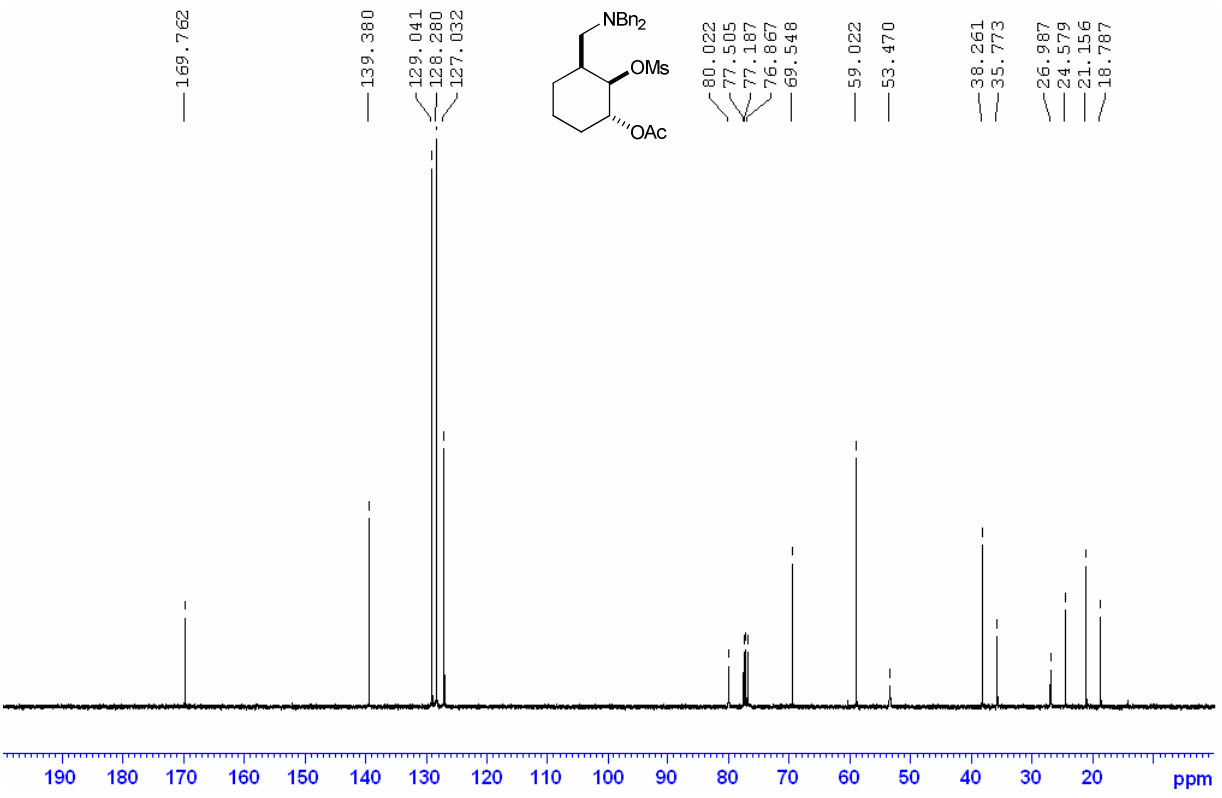
(1*RS*,2*RS*,3*SR*)-1-Acetoxy-2-methanesulfonyloxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 82

(400 MHz, ^{1}H, $CDCl_3$)



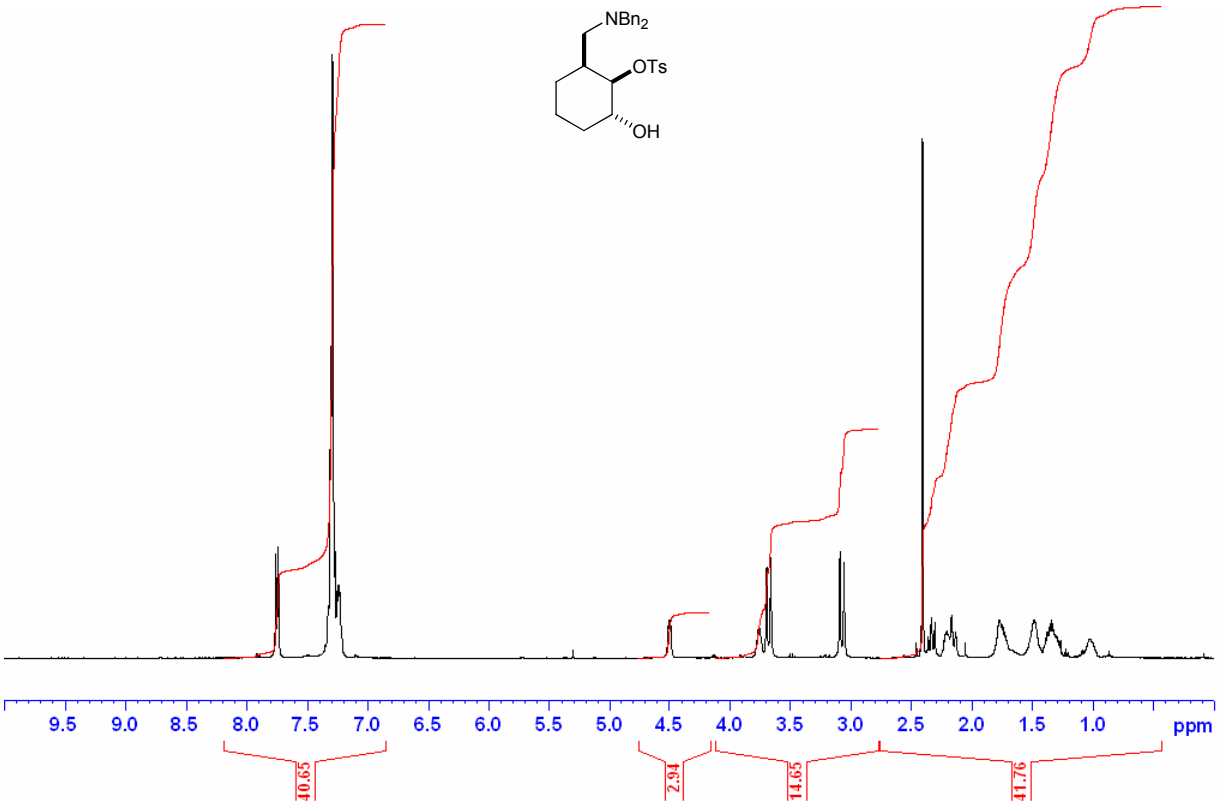
(1*RS*,2*RS*,3*SR*)-1-Acetoxy-2-methanesulfonyloxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 82

(100 MHz, ^{13}C, $CDCl_3$)



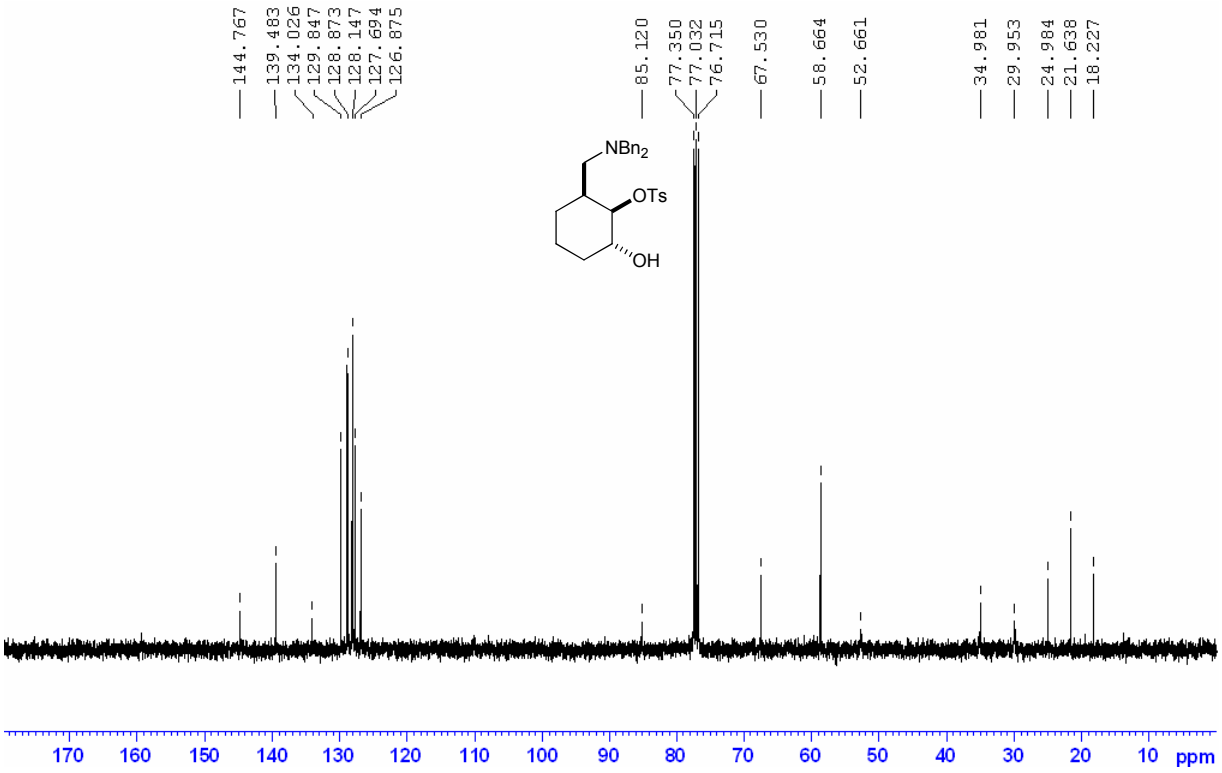
(1*RS*,2*RS*,3*SR*)-1-Hydroxy-2-(*p*-toluenesulfonyloxy)-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 83

(400 MHz, ^{1}H, $CDCl_3$)



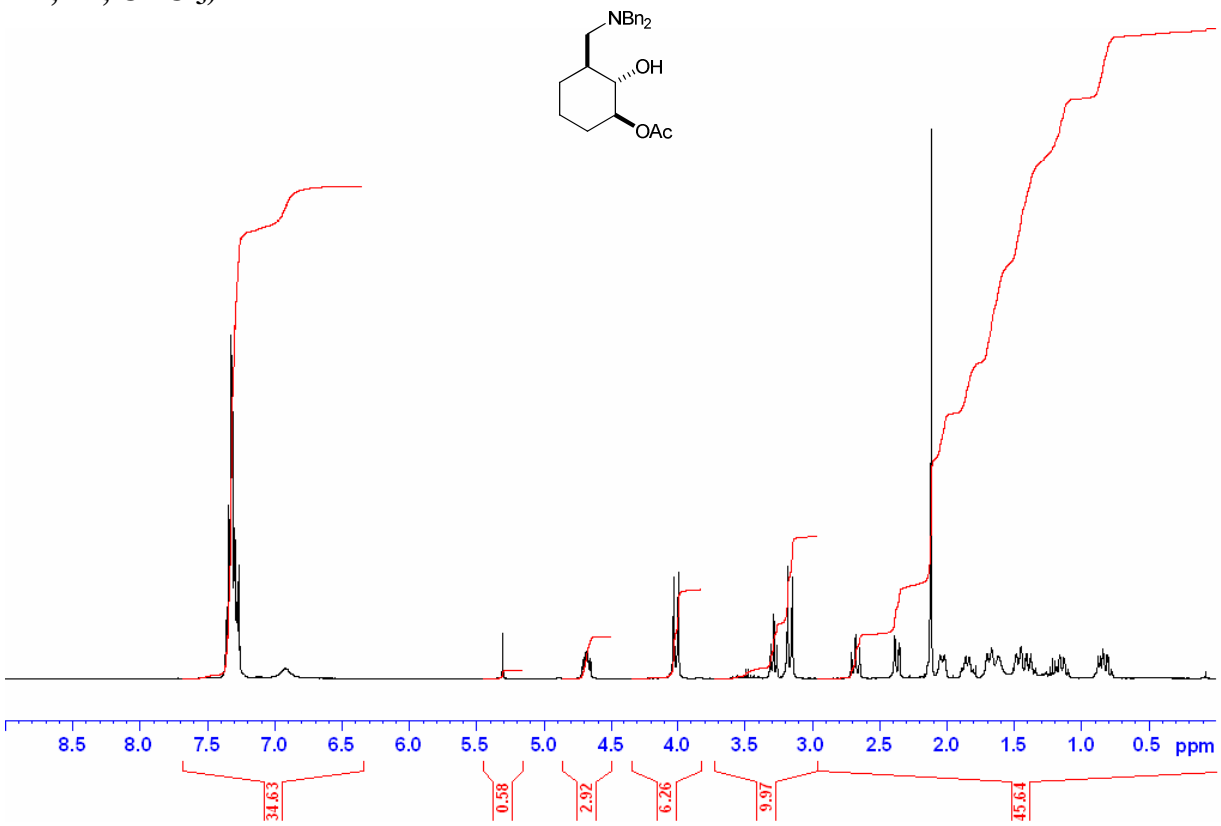
(1*RS*,2*RS*,3*SR*)-1-Hydroxy-2-(*p*-toluenesulfonyloxy)-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 83

(100 MHz, ^{13}C, $CDCl_3$)



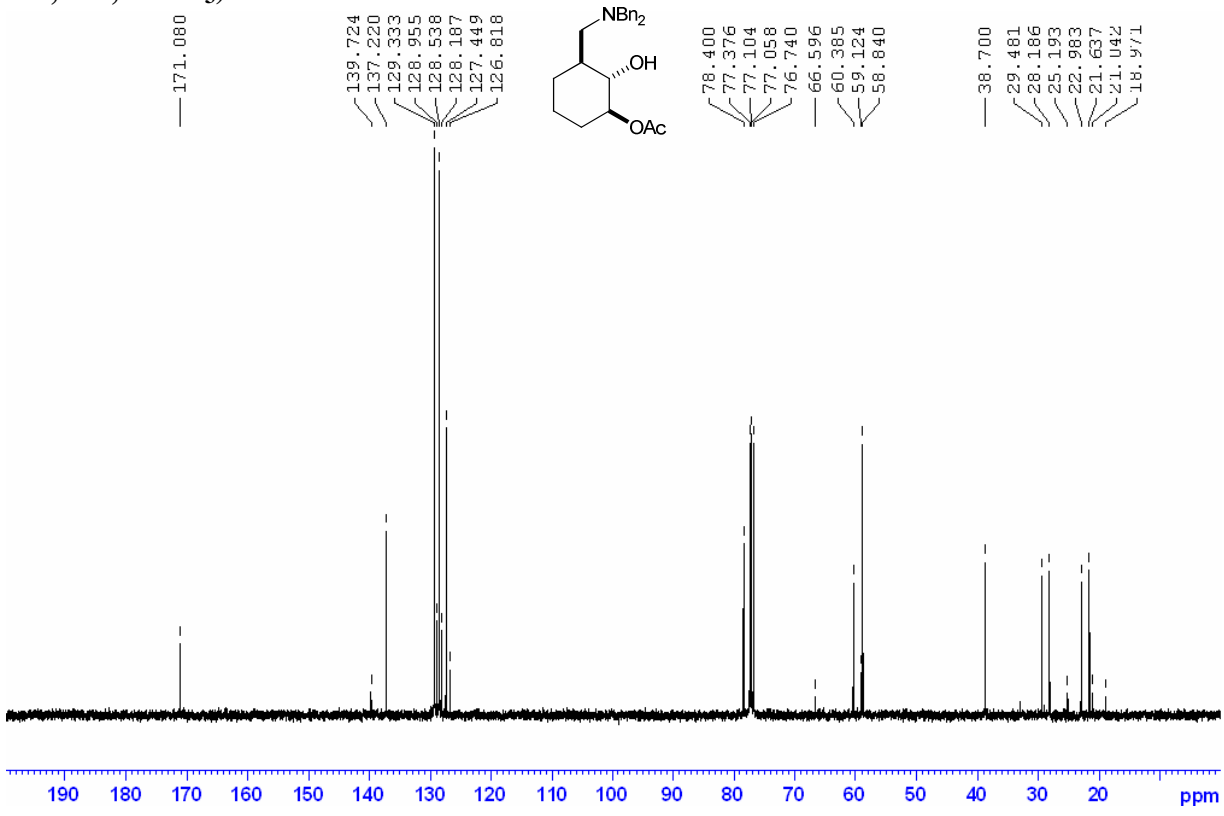
(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 84

(400 MHz, ^{1}H, $CDCl_3$)



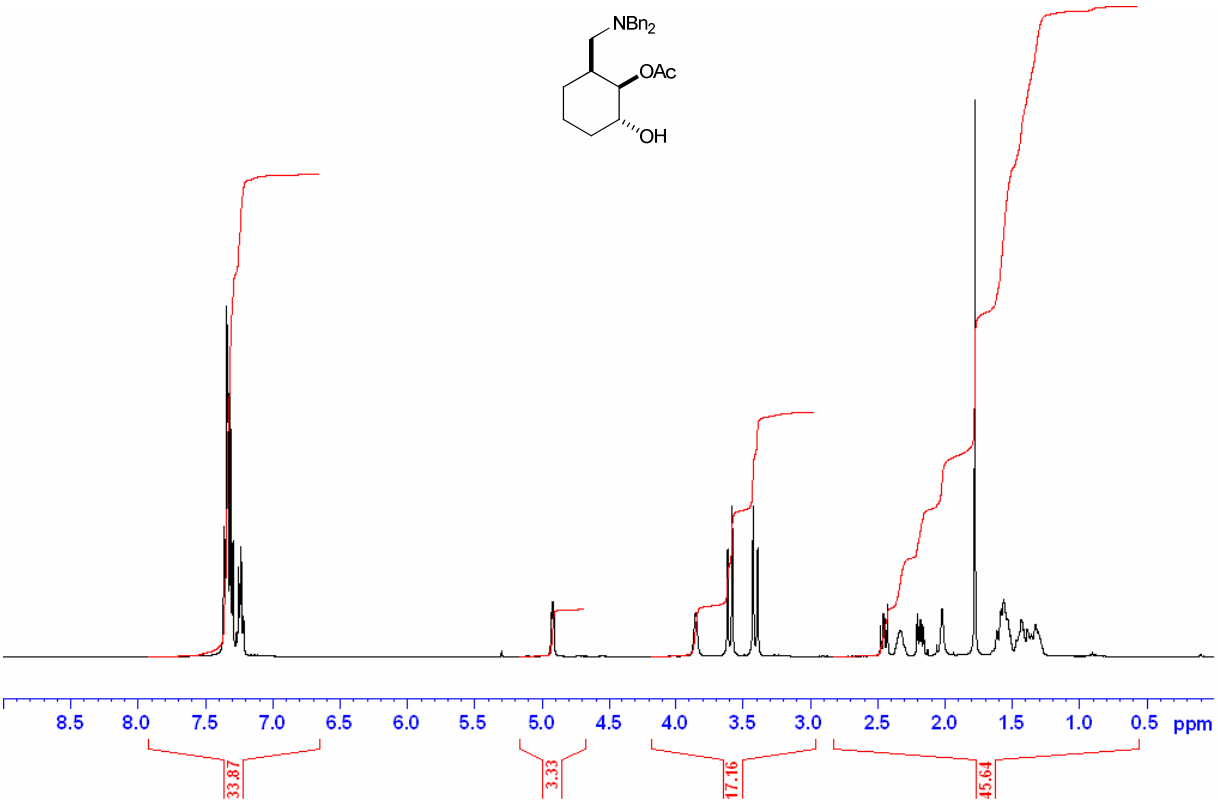
(1*RS*,2*RS*,3*RS*)-1-Acetoxy-2-hydroxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 84

(100 MHz, ^{13}C, $CDCl_3$)



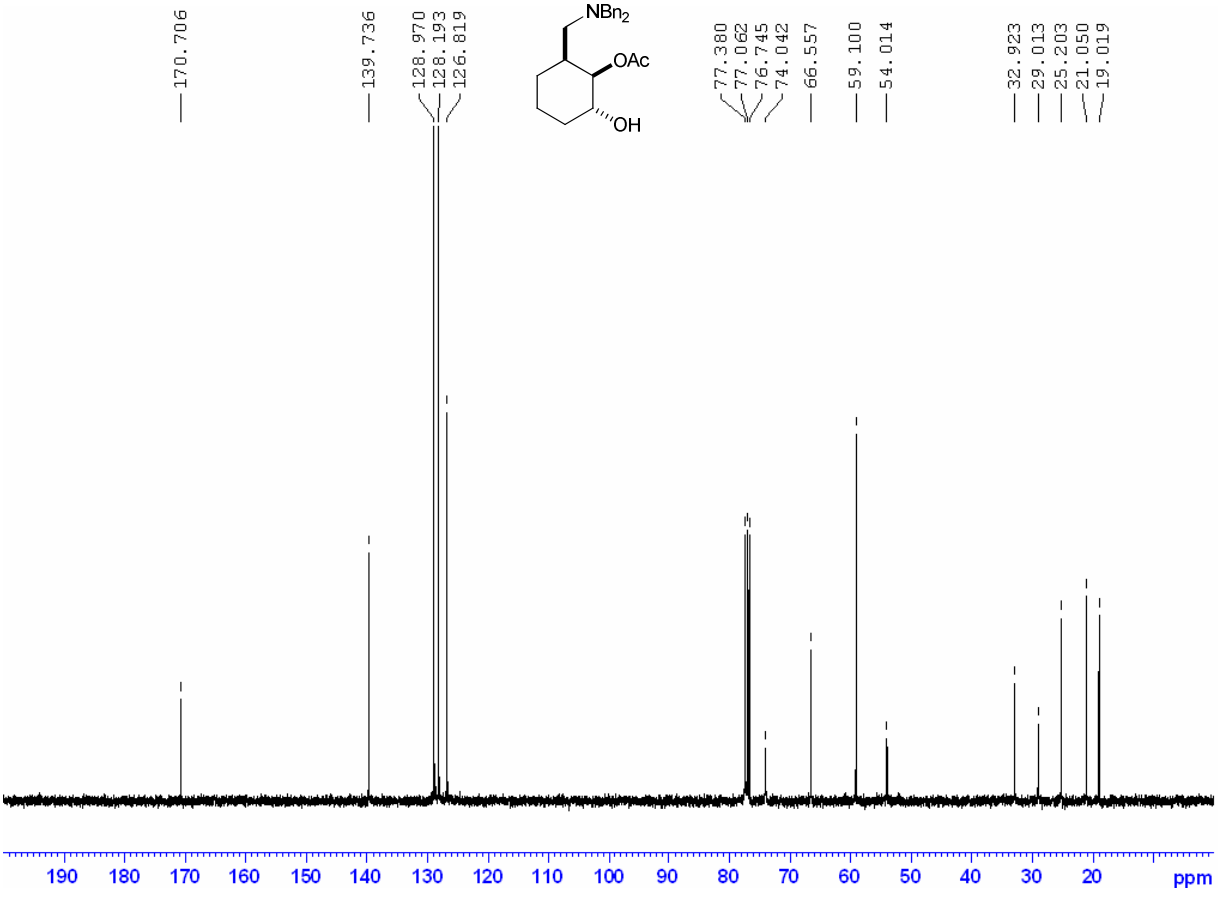
(1*RS*,2*RS*,3*SR*)-1-hydroxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 85

(400 MHz, ^{1}H, $CDCl_3$)

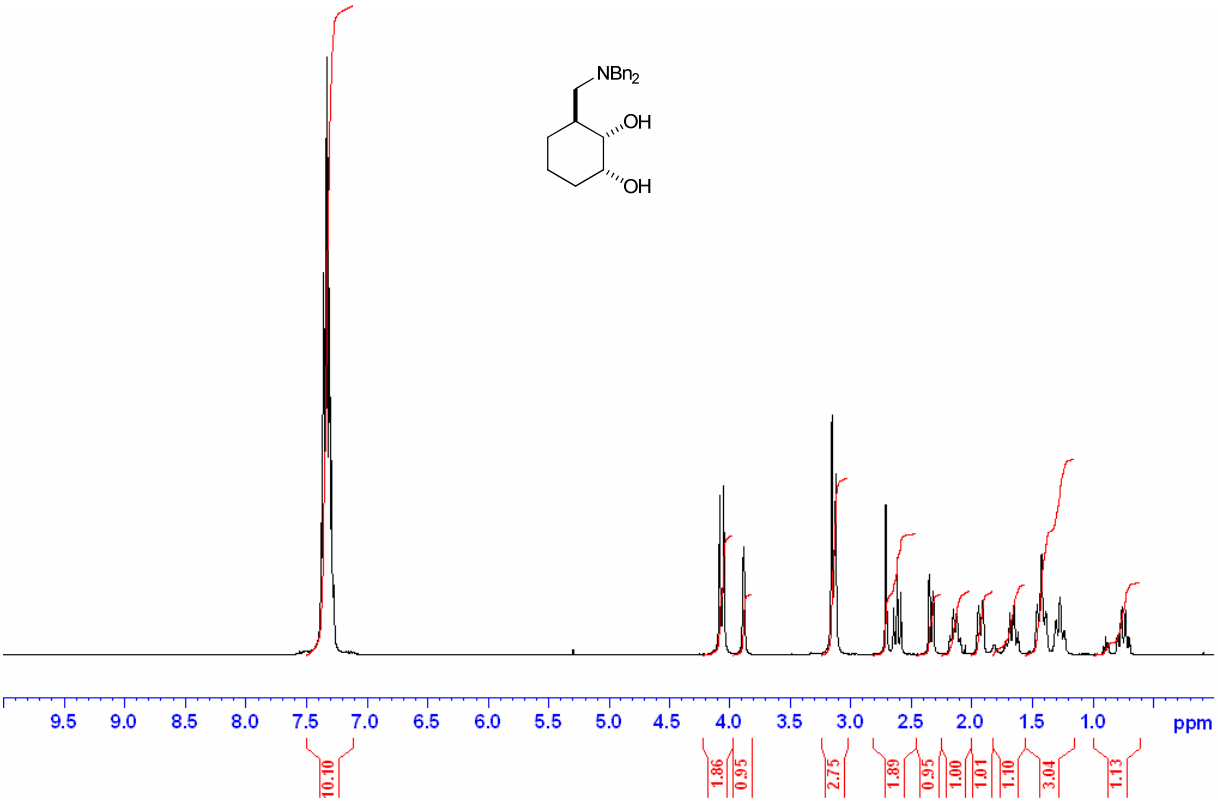


(1*RS*,2*RS*,3*SR*)-1-hydroxy-2-acetoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 85

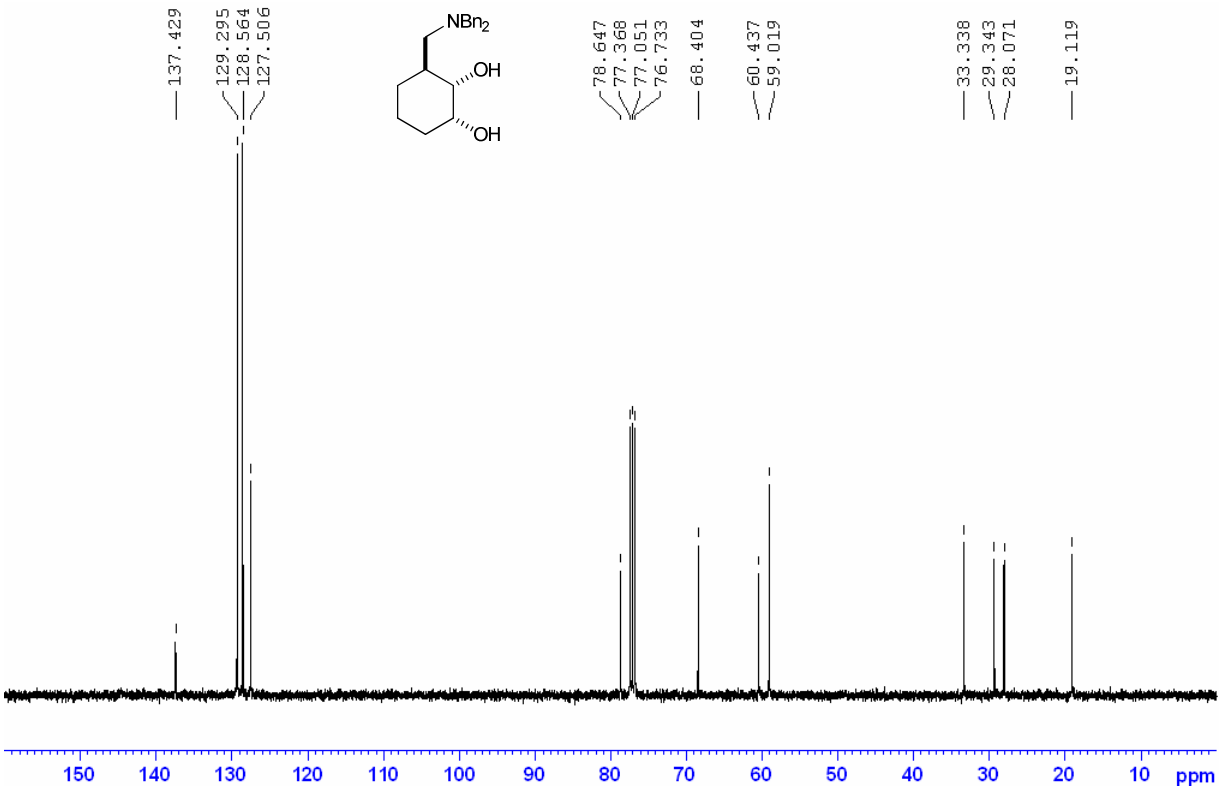
(100 MHz, ^{13}C, $CDCl_3$)



(1*RS*,2*SR*,3*SR*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 88 (400 MHz, ^{1}H, $CDCl_3$)

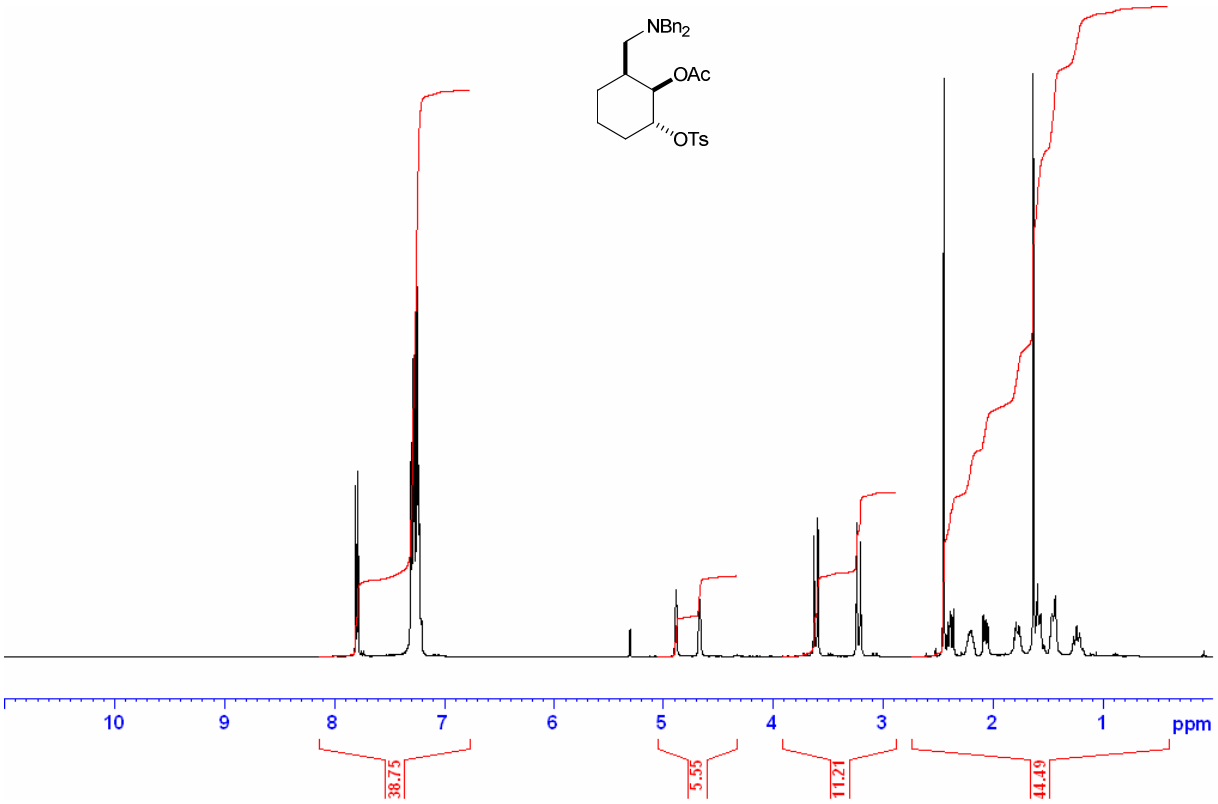


(1*RS*,2*SR*,3*SR*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 88 (100 MHz, ^{13}C, $CDCl_3$)



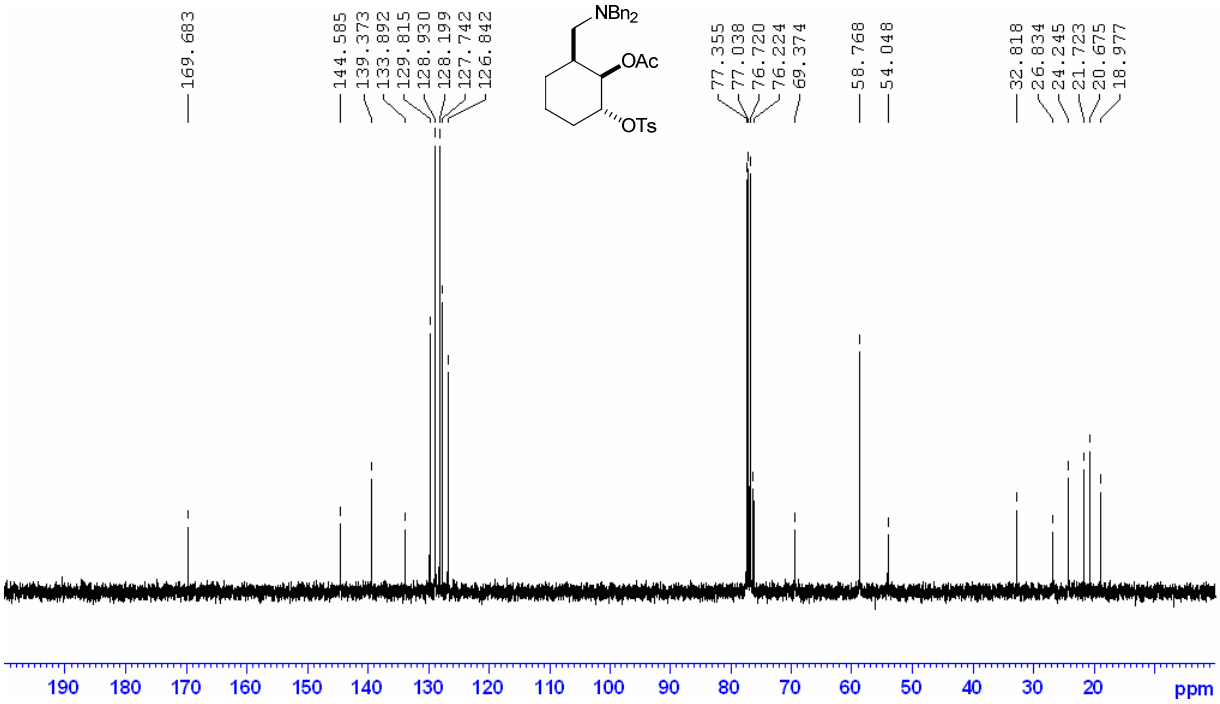
(1*RS*,2*RS*,3*SR*)-1-(*p*-Toluenesulfonyloxy)-2-acetoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 89

(400 MHz, ^{1}H, $CDCl_3$)

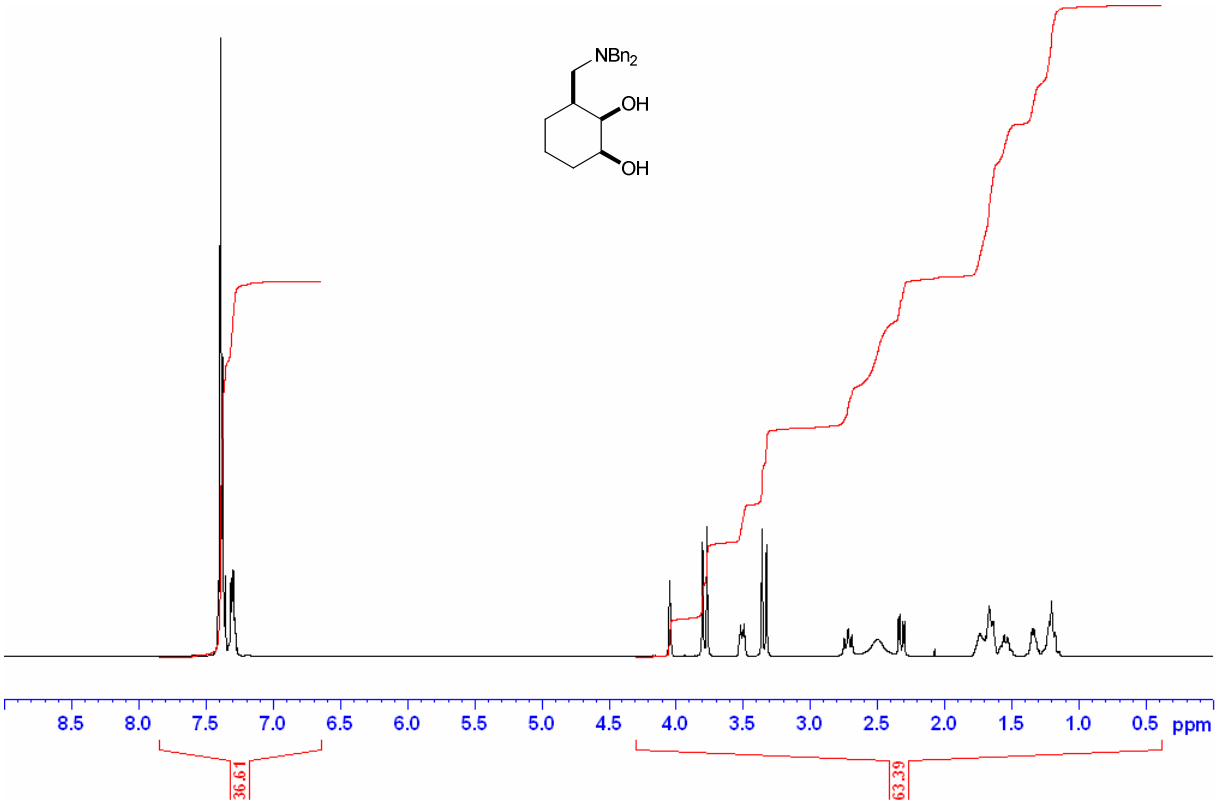


(1*RS*,2*RS*,3*SR*)-1-(*p*-Toluenesulfonyloxy)-2-acetoxy-3-(*N*,*N*-dibenzylamino)methyl-cyclohexane 89

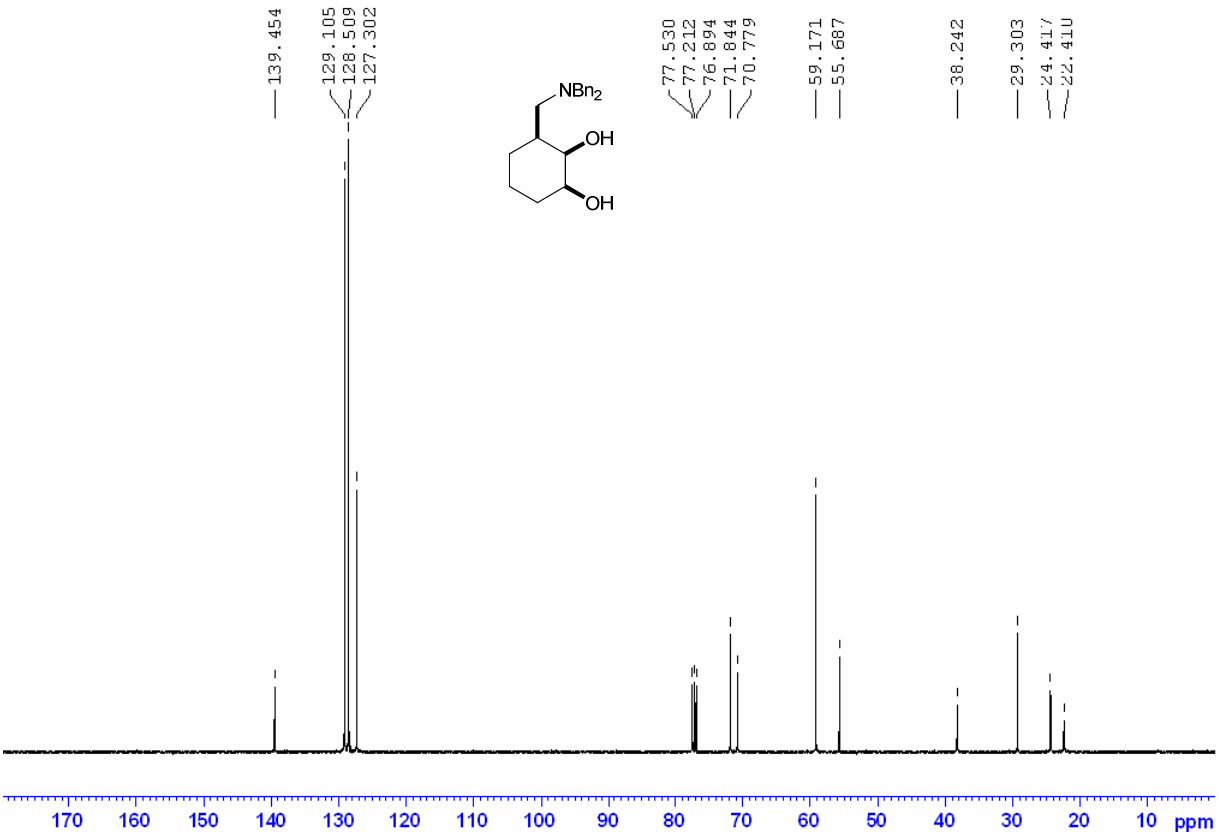
(100 MHz, ^{13}C, $CDCl_3$)



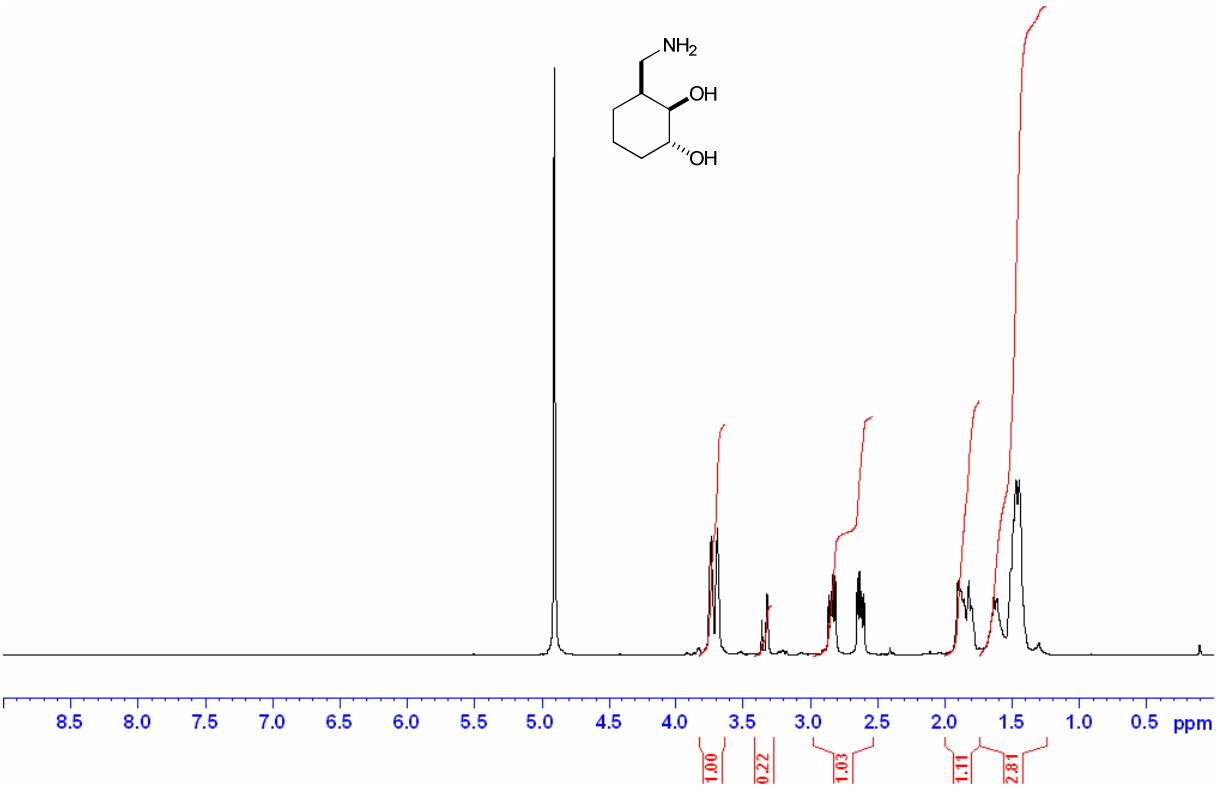
(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 92 (400 MHz, ^{1}H, $CDCl_3$)



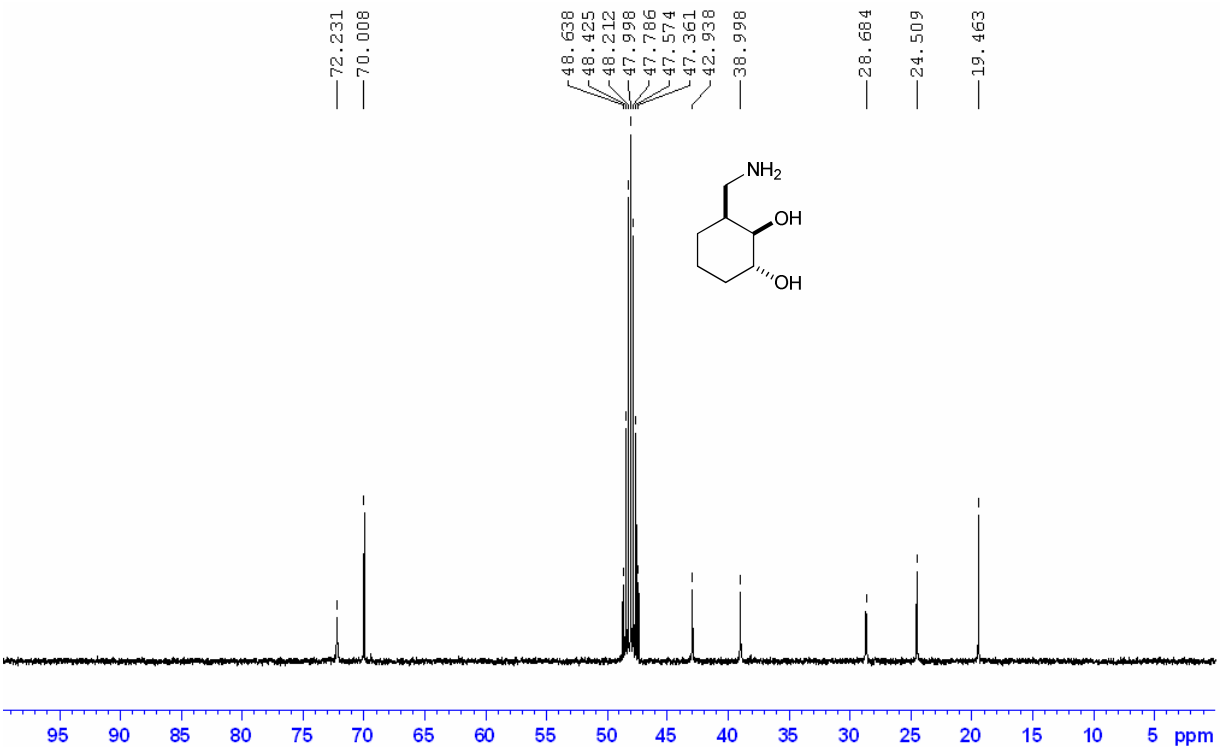
(1*RS*,2*SR*,3*RS*)-3-(*N*,*N*-Dibenzylamino)methyl-cyclohexane-1,2-diol 92 (100 MHz, ^{13}C, $CDCl_3$)



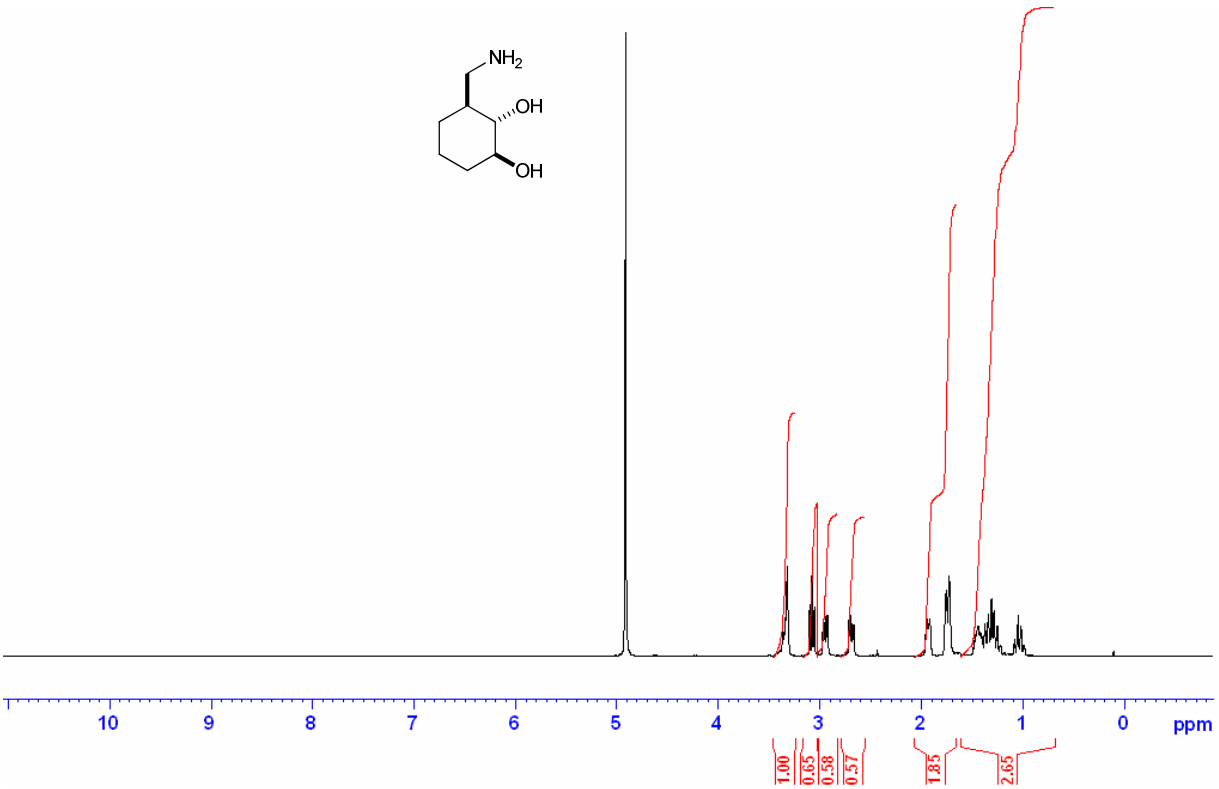
(1*RS*,2*RS*,3*SR*)-3-Aminomethyl-cyclohexane-1,2-diol 93 (400 MHz, ^{1}H, CH_3OD)



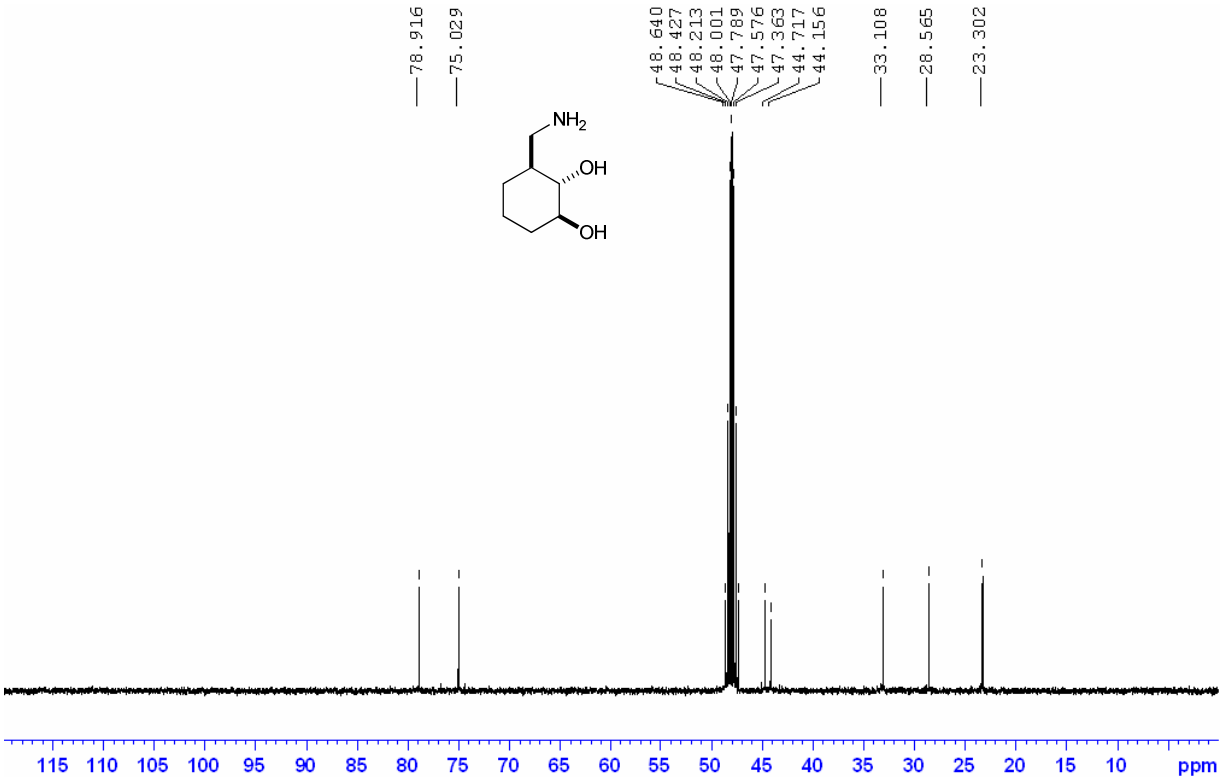
(1*RS*,2*RS*,3*SR*)-3-Aminomethyl-cyclohexane-1,2-diol 93 (100 MHz, ^{13}C, CH_3OD)



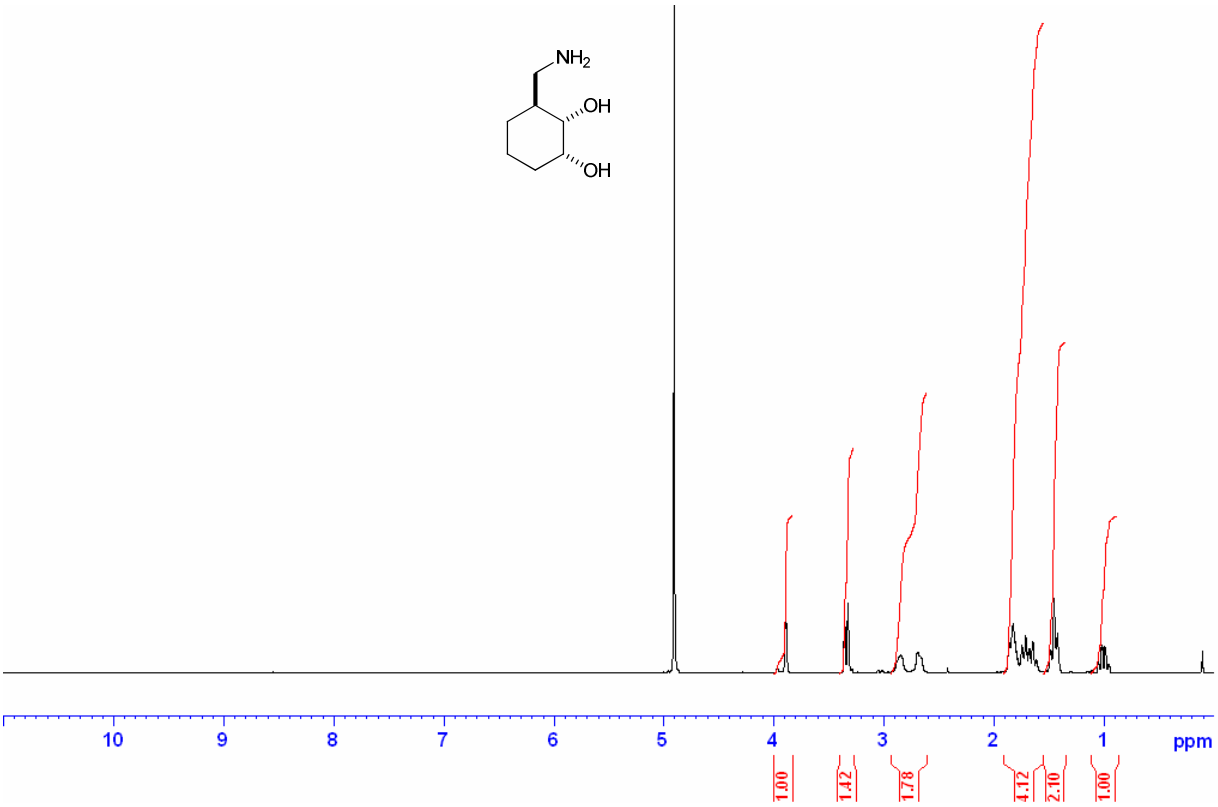
(1*RS*,2*RS*,3*RS*)-3-Aminomethyl-cyclohexane-1,2-diol 94 (400 MHz, ^{1}H, CH_3OD)



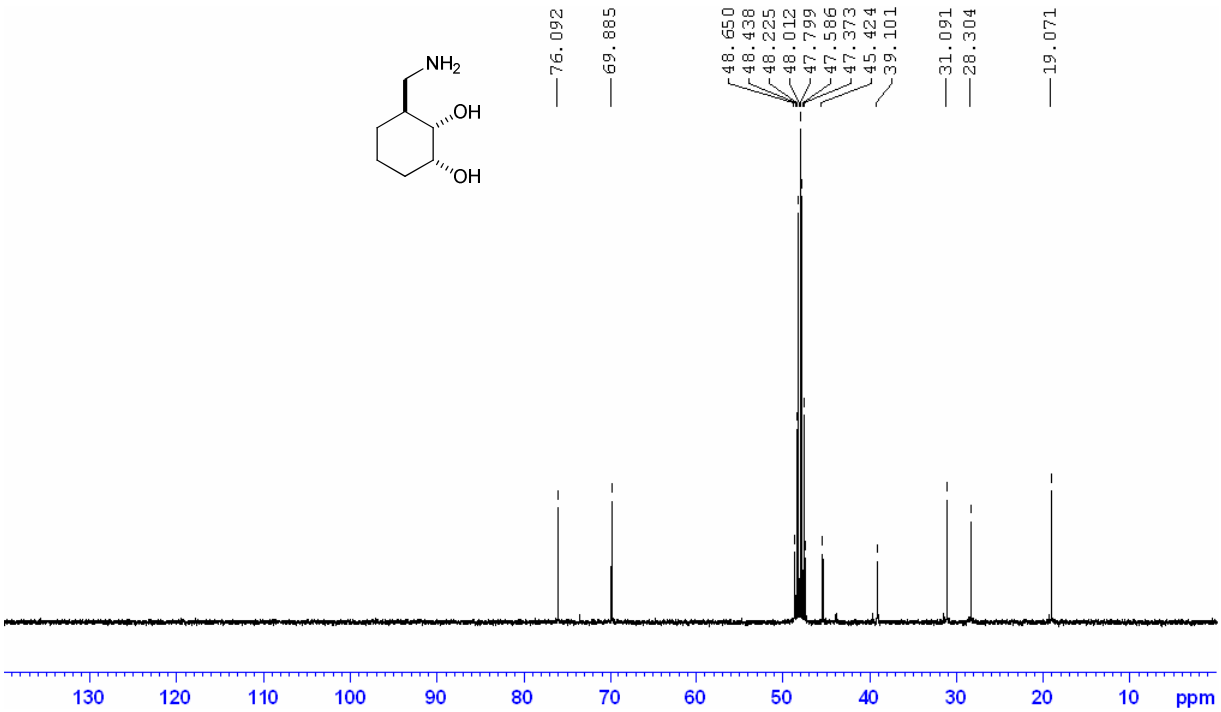
(1*RS*,2*RS*,3*RS*)-3-Aminomethyl-cyclohexane-1,2-diol 94 (100 MHz, ^{13}C, CH_3OD)



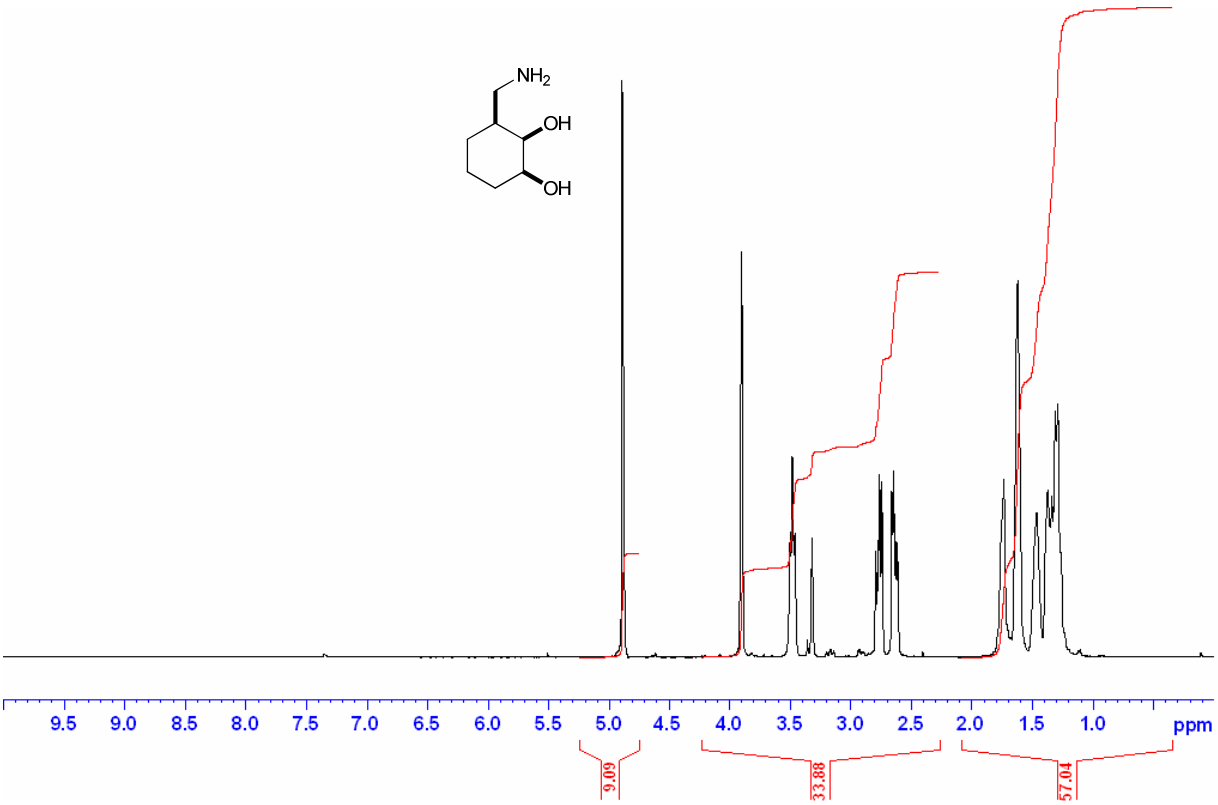
(1*RS*,2*SR*,3*SR*)-3-Aminomethyl-cyclohexane-1,2-diol 95 (400 MHz, ^{1}H, CH_3OD)



(1*RS*,2*SR*,3*SR*)-3-Aminomethyl-cyclohexane-1,2-diol 95 (100 MHz, ^{13}C, CH_3OD)



(1*RS*,2*SR*,3*RS*)-3-Aminomethyl-cyclohexane-1,2-diol 96 (400 MHz, ^{1}H, CH_3OD)



(1*RS*,2*SR*,3*RS*)-3-Aminomethyl-cyclohexane-1,2-diol 96 (100 MHz, ^{13}C, CH_3OD)