**Electronic Supplementary Information (ESI)**

# Highly enantioselective metallation–substitution alpha to a chiral nitrile

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**Contents**

## 1. Experimental details

### 1.1 General

All reagents were obtained from commercial suppliers and were used without further purification unless otherwise specified. Solvents were purified using a Grubbs dry solvent system (model SPS-200-6). Petrol refers to petroleum ether (b.p. 40–60 °C). Reactions were carried out under $N_2$ using oven-dried and/or flame-dried glassware. Thin layer chromatography was performed on silica plates and visualised by UV irradiation at 254 nm or by staining with an alkaline $KMnO_4$ dip. Column chromatography was performed using silica gel (40–63 micron mesh). Infrared spectra were recorded on Perkin Elmer Spectrum RX Fourier Transform IR System. In situ ReactIR™ infra-red spectroscopic monitoring was performed on a Mettler-Toledo React-IR 4000 spectrometer equipped with a diamond-tipped (DiComp) probe. $^1$H NMR spectra were recorded on a Bruker AC400 (400 MHz) instrument. Chemical shifts are reported in ppm with respect to the residual solvent peaks, with multiplicities given as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, are quoted to the nearest 0.5 Hz. $^{13}$C NMR were recorded on the above instrument at 100 MHz. Low and high resolution (accurate mass) mass spectra were recorded on a Walters LCT instrument for Electro–Spray (ES). Chiral stationary phase (CSP) HPLC was performed on a Gilson instrument and a multiple wavelength, UV/Vis diode array detector; integration was performed at 254 nm. Gas chromatography (CSP GC) was performed on a Perkin Elmer Arnel Autosystem XL GC using an Astec CHIRALDEX Beta cyclodextrin, permethyl fused silica capillary column (30 m x 0.25 mm).

$^i$PrMgCl (2.0 M in THF or diethyl ether) was obtained commercially and used without further purification. TMPMgCl (0.5 M in THF or diethyl ether) was prepared by addition of $^i$PrMgCl to TMPH (2,2,6,6-tetramethylpiperidine) according to A. Krasovskiy, V. Krasovskaya, P. Knochel, *Angew. Chem. Int. Ed.* **2006**, *45*, 2958.

### 1.2 Experimental Procedures and Characterisation Data

#### General Procedure A: LDA mediated metallation–trapping

*n*-BuLi (2.5 M solution in hexanes, 1.1 eq) was added dropwise to a stirred solution of diisopropylamine (1.2 eq.) in THF at –25 °C under $N_2$. After 30 min, the mixture was cooled to –78 °C and the nitrile **4** (1.0 eq.) was added. After 10 min, the electrophile (1.2 eq.) was added. The resulting solution was stirred for 30 min, then warmed to room temperature. Saturated aqueous $NH_4Cl$ (2 mL) was added, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$) and evaporated under reduced pressure.

#### General Procedure B: TMPMgCl mediated *in situ* metallation–trapping

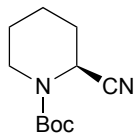
TMPMgCl (3.0 eq.) prepared in $Et_2O$ (2.5 mL) or THF–$Et_2O$ (2.5 mL, 1:1) was added via a syringe to a stirred solution of nitrile **4** (1 eq.) and electrophile (3 eq.) in $Et_2O$ (0.5 mL) at –104 °C under $N_2$. After 30 min, saturated aqueous $NH_4Cl$ (4 mL) was added. The resulting solution was allowed to

warm to room temperature and the layers were separated. The aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$) and evaporated under reduced pressure.

**General Procedure C: TMPMgCl mediated metallation–trapping**

TMPMgCl (3.0 eq.) prepared in $Et_2O$ (2.5 mL) or THF–$Et_2O$ (2.5 mL, 1:1) was added rapidly via a syringe to the nitrile **4** (1.0 eq.) in $Et_2O$ (0.5 mL) at –104 °C under $N_2$. After 10 sec, the electrophile (3.0 eq.) was added in one portion. After 30 min, saturated aqueous $NH_4Cl$ (4 mL) was added. The resulting solution was allowed to warm to room temperature and the layers were separated. The aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure.

***tert*-Butyl (*S*)-2-Cyanopiperidin-1-carboxylate 4**

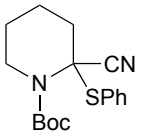



**4**

Ethyl chloroformate (4.2 mL, 44 mmol) was added to commercial (*S*)-*N*-Boc-pipecolic acid (4.5 g, 20 mmol) and triethylamine (2.7 mL, 20 mmol) in THF (30 mL) at −15 °C. After 1 h, 35% ammonia solution in water (8 mL) was added. After 16 h, the solvent was evaporated and the residue was taken up in EtOAc (100 mL) and washed with 10% citric acid (100 mL), $NaHCO_3$ (100 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent was evaporated to give the primary amide (4.15 g, 93%) as an amorphous solid; $[\alpha]^{D}_{23}$ −112 (1, $CHCl_3$); m.p. 89−91 °C; IR $\nu_{max}$ (film)/$cm^{-1}$ 3380, 3180, 2945, 1680; $^1$H NMR (400 MHz, $CDCl_3$) δ = 6.05 (1H, br s), 5.80 (1H, m), 4.81−4.69 (1H, m), 4.13−3.95 (1H, m), 2.87−2.76 (1H, m), 2.32−2.22 (1H, m), 1.68−1.56 (2H, m), 1.54−1.36 (3H, m), 1.47 (9H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 174.2, 155.5, 80.7, 54.2, 42.4 ($CH_2$), 28.5, 25.5, 25.0, 20.6; HRMS (ES) Found $MH^+$ 229.1560. $C_{11}H_{21}N_2O_3$ requires $MH^+$, 229.1552.

Trifluoroacetic anhydride (2.9 mL, 21 mmol) was added to the amide prepared as above (4.0 g, 17.5 mmol) and triethylamine (5.8 mL, 42 mmol) in THF (60 mL) at 0 °C. The mixture was stirred at room temperature for 18 h, then water (30 mL) was added and the solvent was evaporated. The residue was taken up in $CH_2Cl_2$ (100 mL), washed with aqueous HCl (100 mL, 0.1 M) and aqueous NaOH (100 mL, 0.1 M), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (4:1), gave nitrile **4** (2.98 g, 81%) as a solid; $[\alpha]^{D}_{21}$ −130 (1, $CHCl_3$); m.p. 79−80 °C; $R_f$ [petrol−EtOAc (4:1)] 0.74; $^1$H NMR (400 MHz, $CDCl_3$) δ = 5.40−5.08 (1H, m), 4.15−3.95 (1H, m), 3.04−2.83 (1H, m), 1.97−1.56 (6H, m), 1.47 (9H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 154.1, 117.8, 81.5, 44.2, 41.5, 28.6, 28.4, 24.7, 20.4; HRMS (ES) Found $MH^+$ 211.1438. $C_{11}H_{19}N_2O_2$ requires $MH^+$, 211.1447.

***tert*-Butyl 2-Cyano-2-(2-phenylsulfanyl)piperidin-1-carboxylate 5a**




**5a**

Racemic method (general procedure A):

*n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M in hexanes) was added dropwise to diisopropylamine (0.17 mL, 1.2 mmol) in THF (2 mL) at –78 °C under $N_2$. After 10 min, the nitrile **4** (0.21 g, 1 mmol) was added. After 10 min, $PhSSO_2Ph$ (0.275 g, 1.2 mmol) was added. The resulting solution was stirred for 30 min, then warmed to room temperature. Saturated aqueous $NH_4Cl$ (2 mL) was added, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$) and evaporated under reduced pressure. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5a** (251 mg, 79%) as an oil; $R_f$ [petrol−EtOAc (4:1)] 0.50; FT-IR $\nu_{max}$ (film)/$cm^{-1}$ 2930, 2865, 1705; $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.72–7.69 (2H, m), 7.48–7.35 (3H, m), 4.14−4.10 (1H, m), 3.23 (1H, td, *J* 13, 3), 2.30−2.12 (2H, m), 1.98−1.70 (2H, m), 1.58−1.52 (2H, m), 1.35 (9H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 153.5, 137.4, 130.4, 129.5, 129.3, 119.4, 83.0, 62.7, 40.4, 37.5, 27.9, 23.9, 19.1; HRMS (ES) Found $MH^+$ 319.1495. $C_{17}H_{22}N_2O_2S$ requires $MH^+$, 319.1480. The enantiomers were resolved by chiral stationary phase HPLC using an AD column with 0.5% $^i$PrOH in hexanes at 1 mL/min, detection at 254 nm, retention times 10.3 and 11.3 min.

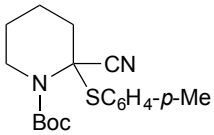
Asymmetric method (general procedure B):

TMPMgCl (1.6 mL, 0.75 mmol) was added to premixed nitrile **4** (54 mg, 0.25 mmol) and $PhSSO_2Ph$ (171 mg, 0.75 mmol) in $Et_2O$ (1 mL) at −104 °C. After 30 min, saturated aqueous $NH_4Cl$ (0.3 mL) was added. The mixture was extracted with $Et_2O$ (3 × 1 mL), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5a** (53 mg, 67%); $[\alpha]^{21}_D$ –21.6 (0.5, $CHCl_3$); data as above. The enantiomer ratio was determined to be 98:2 by CSP-HPLC (major enantiomer eluted at 11.7 min and minor enantiomer at 10.2 min).

Method from the sulfide **5c**

$^i$PrMgCl (0.375 mL, 0.75 mmol, 2 M in $Et_2O$) was added to the nitrile **5c** (87 mg, 0.25 mmol, er 85:15) in $Et_2O$ (2 mL) at −104 °C. After 10 sec, $PhSSO_2Ph$ (171 mg, 0.75 mmol) in $Et_2O$ (1 mL) was added at −104 °C. After 30 min, saturated aqueous $NH_4Cl$ (0.3 mL) was added. The mixture was extracted with $Et_2O$ (3 × 1 mL), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5a** (24 mg, 30%); $[\alpha]^{21}_D$ –16.0 (0.4, $CHCl_3$); data as above. The enantiomer ratio was determined to be 80:20 by CSP-HPLC.

***tert*-Butyl 2-Cyano-2-(*p*-tolylsulfanyl)piperidin-1-carboxylate 5b**




**5b**

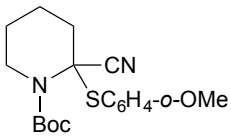
Racemic method (general procedure A):

*n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M in hexanes) was added dropwise to diisopropylamine (0.17 mL, 1.2 mmol) in THF (2 mL) at –78 °C under $N_2$. After 10 min, the nitrile **4** (0.21 g, 1 mmol) was added. After 10 min, *p*-Tolyl$SSO_2$Ph (316 mg, 1.2 mmol) was added. The resulting solution was stirred for 30 min, then warmed to room temperature. Saturated aqueous $NH_4Cl$ (2 mL) was added, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$) and evaporated under reduced pressure. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5b** (259 mg, 78%) as an oil; $R_f$ [petrol−EtOAc (4:1)] 0.50; FT-IR $\nu_{max}$ (film)/$cm^{-1}$ 2930, 2865, 1705; $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.59 (2H, d, *J* 8), 7.35–7.22 (2H, m), 4.14−4.10 (1H, m), 3.23 (1H, td, *J* 13, 3), 2.39 (3H, s), 2.29−2.24 (1H, m), 2.19–2.11 (1H, m), 2.00−1.70 (4H, m), 1.36 (9H, s); $^{13}$C NMR (100 MHz, CDCl3) δ = 152.6, 139.8, 136.3, 129.1, 124.9, 118.5, 81.9, 61.7, 39.3, 36.3, 28.7, 26.9, 22.9, 20.3; HRMS (ES) Found $MH^+$ 333.1634. $C_{18}H_{24}N_2O_2S$ requires $MH^+$, 333.1631. The enantiomers were resolved by chiral stationary phase HPLC using an AD column with 0.5% $^i$PrOH in hexanes at 1 mL/min, detection at 254 nm, retention times 10.3 and 12.0 min.

Asymmetric method (general procedure B):

TMPMgCl (1.6 mL, 0.75 mmol) was added to premixed nitrile **4** (54 mg, 0.25 mmol) and *p*-Tolyl$SSO_2$Ph (198 mg, 0.75 mmol) in $Et_2O$ (1 mL) at −104 °C. After 30 min, saturated aqueous $NH_4Cl$ (0.3 mL) was added. The mixture was extracted with $Et_2O$ (3 × 1 mL), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5b** (56 mg, 68%); $[\alpha]^{21}_D$ –24.9 (0.4, $CHCl_3$); data as above. The enantiomer ratio was determined to be 95:5 by CSP-HPLC (major enantiomer eluted at 12.8 min and minor enantiomer at 10.7 min).

***tert*-Butyl 2-Cyano-2-(*o*-methoxyphenylsulfanyl)piperidin-1-carboxylate 5c**




**5c**

Racemic method (general procedure A):

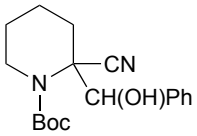
*n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M in hexanes) was added dropwise to diisopropylamine (0.17 mL, 1.2 mmol) in THF (2 mL) at –78 °C under $N_2$. After 10 min, the nitrile **4** (0.21 g, 1 mmol) was added. After 10 min, *o*-OMePh$SSO_2$Ph (336 mg, 1.2 mmol) was added. The resulting solution was stirred for 30 min, then warmed to room temperature. Saturated aqueous $NH_4Cl$ (2 mL) was added, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic

layers were dried ($Na_2SO_4$) and evaporated under reduced pressure. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5b** (254 mg, 73%) as an oil; $R_f$ [petrol−EtOAc (4:1)] 0.40; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2930, 2860, 1725; $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.79 (1H, dd, *J* 7.5, 1.5), 7.47 (1H, td, *J* 7.5, 1.5), 7.03 (1H, td, *J* 7.5, 1), 6.93 (1H, dd, *J* 7.5, 1), 4.13−4.10 (1H, m), 3.88 (3H, s), 3.39 (1H, td, *J* 13, 4), 2.38−2.32 (1H, m), 2.22 (1H, td, *J* 13, 4), 2.03–1.93 (1H, m), 1.82−1.71 (2H, m), 1.57−1.47 (1H, m), 1.32 (9H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 160.3, 152.6, 139.3, 131.4, 120.2, 118.4, 116.7, 81.7, 62.0, 54.6, 39.2, 37.3, 28.7, 26.8, 22.9; HRMS (ES) Found $MH^+$ 349.1581. $C_{18}H_{24}N_2O_3S$ requires $MH^+$, 349.1580. The enantiomers were resolved by chiral stationary phase HPLC using an AD column with 0.5% $^i$PrOH in hexanes at 1 mL/min, detection at 254 nm, retention times 14.9 and 17.0 min.

Asymmetric method (general procedure B):

TMPMgCl (1.6 mL, 0.75 mmol) was added to premixed nitrile **4** (54 mg, 0.25 mmol) and *o*-$OMePhSSO_2Ph$ (210 mg, 0.75 mmol) in $Et_2O$ (1 mL) at −104 °C. After 30 min, saturated aqueous $NH_4Cl$ (0.3 mL) was added. The mixture was extracted with $Et_2O$ (3 × 1 mL), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5c** (55 mg, 63%); $[\alpha]^{21}_D$ –22.0 (0.4, $CHCl_3$); data as above. The enantiomer ratio was determined to be 88:12 by CSP-HPLC (major enantiomer eluted at 17.2 min and minor enantiomer at 15.0 min).

***tert*-Butyl 2-Cyano-2-[hydroxy(phenyl)methyl]piperidine-1-carboxylate 5d**




**5d**

*n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M in hexanes) was added dropwise to diisopropylamine (0.17 mL, 1.2 mmol) in THF (2 mL) at –25 °C under $N_2$. After 30 min, the mixture was cooled to –78 °C and the nitrile **4** (0.21 g, 1 mmol) was added. After 10 min, benzaldehyde (0.116 g, 1.1 mmol) was added. The resulting solution was stirred for 30 min, then warmed to room temperature. Saturated aqueous $NH_4Cl$ (2 mL) was added, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$) and evaporated under reduced pressure. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitriles **5d** as separable diastereomers (diastereomer A: 126 mg, 40%, and diastereomer B: 132 mg, 42%) as amorphous solids;

**Diastereomer A** m.p. 147−149 °C; $R_f$ [petrol−EtOAc (4:1)] 0.30; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2975, 2115, 1700, 1680; $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.42−7.36 (5H, m), 5.60 (1H, s), 4.72 (1H, s), 3.71−3.65 (2H, m), 2.40−2.45 (1H, m), 2.04−1.96 (1H, m), 1.78−1.72 (4H, m), 1.61 (9H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 154.9, 137.5, 128.5, 128.2, 127.5, 119.8, 82.4, 74.1, 62.9, 39.7, 28.4, 27.4, 21.4, 16.6; HRMS (ES) Found $MNa^+$ 339.1682. $C_{18}H_{24}N_2O_3Na$ requires $MNa^+$, 339.1679. The enantiomers were resolved by chiral stationary phase HPLC using a Cellulose-2 column with 10% $^i$PrOH in hexanes at 1 mL/min, detection at 220 nm, retention times 5.6 and 6.6 min.

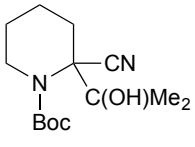
**Diastereomer 2** m.p. 139−141 °C; $R_f$ [petrol−EtOAc (4:1)] 0.27; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2975, 2115, 1695, 1680; $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.48 (2H, d, *J* 7.5), 7.40–7.33 (3H, m), 5.48 (1H, s), 3.91 (1H, s), 3.86−3.80 (1H, m), 3.00–2.93 (1H, m), 2.29−2.22 (1H, m), 1.82–1.59 (5H, m), 1.56 (9H,

s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 154.9, 137.5, 128.5, 128.2, 127.6, 119.8, 82.4, 74.1, 63.0, 39.8, 28.4, 27.4, 21.4, 16.6; HRMS (ES) Found $MNa^+$ 339.1683. $C_{18}H_{24}N_2O_3Na$ requires $MNa^+$, 339.1679. The enantiomers were resolved by chiral stationary phase HPLC using a Cellulose-1 column with 10% $^i$PrOH in hexanes at 1 mL/min, detection at 220 nm, retention times 6.1 and 10.1 min.

***tert*-Butyl 2-Cyano-2-(2-hydroxypropan-2-yl)piperidin-1-carboxylate 5e**

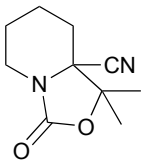
**and**

**1,1-Dimethyl-3-oxo-hexahydro-1H-[1,3]oxazolo[3,4-a]pyridine-8a-carbonitrile 5e'**




**5e**

and




**5e'**

Racemic method (general procedure A):

*n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M in hexanes) was added dropwise to diisopropylamine (0.17 mL, 1.2 mmol) in THF (2 mL) at –25 °C under $N_2$. After 30 min, the mixture was cooled to –78 °C and the nitrile **4** (0.21 g, 1 mmol) was added. After 10 min, acetone (0.088 mL, 1.2 mmol) was added. The resulting solution was stirred for 30 min, then warmed to room temperature. Saturated aqueous $NH_4Cl$ (2 mL) was added, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$) and evaporated under reduced pressure. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5e** (120 mg, 45%) as needles and the nitrile **5e'** (54 mg, 28%) as needles;

Data for **5e**:

m.p. 90−91 °C; $R_f$ [petrol−EtOAc (4:1)] 0.27; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2920, 2855, 1750; $^1$H NMR (400 MHz, $CDCl_3$) δ = 5.61 (1H, br s), 4.02−3.96 (1H, m), 3.07−2.95 (1H, m), 2.08−2.05 (1H, m), 1.94−1.82 (3H, m), 1.71−1.62 (2H, m), 1.52 (9H, s), 1.35 (3H, s), 1.27 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 156.6, 118.6, 82.9, 76.6, 67.1, 40.2, 29.8, 28.3, 26.2, 24.5, 20.7, 16.4; HRMS (ES) Found $MH^+$ 269.1854. $C_{14}H_{25}N_2O_3$ requires $MH^+$, 269.1865. The enantiomers were resolved by chiral stationary phase GC (CSP-GC) using a Perkin Elmer Arnel Autosystem XL GC using an Astec CHIRALDEX beta cyclodextrin, permethylated fused silica capillary column (30 m x 0.25 mm) at 160 °C and 1.40 mL/min, retention times 8.7 and 8.8 min (see GC trace below).

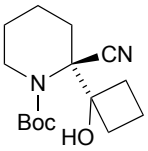
Data for **5e'**:

m.p. 81−84 °C; $R_f$ [petrol−EtOAc (4:1)] 0.14; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2950, 2860, 1750; $^1$H NMR (400 MHz, $CDCl_3$) δ = 3.92–3.86 (1H, m), 3.05 (1H, td, *J* 13, 3.5), 2.07–1.98 (1H, m), 1.94–1.65 (5H, m), 1.69 (3H, s), 1.43 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 154.9, 116.3, 81.5, 65.4, 40.5, 29.8, 25.5, 23.3, 22.2, 20.9; HRMS (ES) Found $MH^+$ 195.1126. $C_{10}H_{15}N_2O_2$ requires $MH^+$, 195.1134; LRMS *m/z* (ES) 195 (100%).

Asymmetric method (general procedure C):

TMPMgCl (1.6 mL, 0.75 mmol) was added to carbamate **4** (54 mg, 0.25 mmol) in $Et_2O$ (1 mL) at −104 °C. After 10 sec, acetone (0.088 mL, 1.2 mmol) was added. After 30 min, saturated aqueous $NH_4Cl$ (0.3 mL) was added. The mixture was extracted with $Et_2O$ (3 × 1 mL), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5e** (42 mg, 63%); $[\alpha]^{21}_D$ −12 (1.0, $CHCl_3$); data as above. The enantiomer ratio was determined to be 96:4 by CSP-GC (major enantiomer eluted at 8.6 min and minor at 9 min).

***tert*-butyl 2-cyano-2-(1-hydroxycyclobutyl)piperidine-1-carboxylate 5f**




**5f**

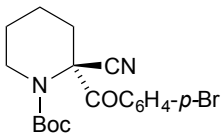
Racemic method (general procedure A):

*n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M in hexanes) was added dropwise to diisopropylamine (0.17 mL, 1.2 mmol) in THF (2 mL) at –25 °C under $N_2$. After 30 min, the mixture was cooled to –78 °C and the nitrile **4** (0.21 g, 1 mmol) was added. After 10 min, cyclobutanone (0.09 mL, 1.2 mmol) was added. The resulting solution was stirred for 30 min, then warmed to room temperature. Saturated aqueous $NH_4Cl$ (2 mL) was added, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$) and evaporated under reduced pressure. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5f** (118 mg, 42%) as needles; m.p. 95−98 °C; $R_f$ [petrol−EtOAc (4:1)] 0.31; FT-IR $\nu_{max}$ (film)/$cm^{-1}$ 2980, 2865, 1710; $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.88 (1H, br s), 3.96 (1H, dt, *J* 14, 4.5), 3.47 (1H, ddd, *J* 14, 10.5, 3.5) 2.69−2.61 (1H, m), 2.46–2.41 (1H, m), 2.25−1.81 (8H, m), 1.75−1.63 (2H, m), 1.48 (9H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 154.2, 119.2, 82.0, 78.7, 67.6, 44.9, 34.5, 32.7, 29.4, 28.2, 23.9, 20.4, 14.0; HRMS (ES) Found $MH^+$ 281.1860. $C_{15}H_{25}N_2O_3$ requires $MH^+$, 281.1860. The enantiomers were resolved by chiral stationary phase GC (CSP-GC) using a Perkin Elmer Arnel Autosystem XL GC using an Astec CHIRALDEX beta cyclodextrin, permethylated fused silica capillary column (30 m x 0.25 mm) at 178 °C and 1.40 mL/min, retention times 20.7 and 21.1 min (see GC trace below).

Asymmetric method (general procedure C):

TMPMgCl (1.6 mL, 0.75 mmol) was added to carbamate **4** (54 mg, 0.25 mmol) in $Et_2O$ (1 mL) at −104 °C. After 10 sec, cyclobutanone (0.056 mL, 0.75 mmol) was added. After 30 min, saturated aqueous $NH_4Cl$ (0.3 mL) was added. The mixture was extracted with $Et_2O$ (3 × 1 mL), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5f** (47 mg, 68%); $[\alpha]^{21}_D$ –25.7 (0.4, $CHCl_3$); data as above. The enantiomer ratio was determined to be 95:5 by CSP-GC (major enantiomer eluted at 21.0 min and minor at 21.4 min).

***tert*-Butyl 2-(4-Bromobenzoyl)-2-cyanopiperidin-1-carboxylate 5g**




**5g**

Racemic method (general procedure A):

*n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M in hexanes) was added dropwise to diisopropylamine (0.17 mL, 1.2 mmol) in THF (2 mL) at –25 °C under $N_2$. After 30 min, the mixture was cooled to –78 °C and the nitrile **4** (0.21 g, 1 mmol) was added. After 10 min, *p*-bromobenzoyl chloride (0.24 g, 1.1 mmol) was added. The resulting solution was stirred for 30 min, then warmed to room temperature. Saturated aqueous $NH_4Cl$ (2 mL) was added, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were dried ($Na_2SO_4$) and evaporated under reduced pressure. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5g** (333 mg, 85%) as a solid; m.p. 117−119 °C; $R_f$ [petrol−EtOAc (4:1)] 0.30; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2980, 2155, 1720, 1690; $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.06 (2H, d, *J* 8), 7.61 (2H, d, *J* 8), 4.21 (1H, br d, *J* 12.5), 3.12 (1H, td, *J* 12.5, 2.5), 2.17−2.14 (2H, m), 2.07–1.97 (2H, m), 1.86−1.60 (2H, m), 1.26 (9H, s); $^{13}$C NMR (100 MHz, $CDCl_3$, one aromatic C cannot be observed) δ = 188.8, 155.3, 131.8, 130.4, 128.4, 116.4, 84.1, 67.6, 43.6, 33.2, 27.7, 23.7, 20.3; HRMS (ES) Found $MNa^+$ 415.0629. $C_{18}H_{21}N_2O_3BrNa$ requires $MNa^+$, 415.0628. The enantiomers were resolved by chiral stationary phase HPLC using a cellulose 1 column with 1% $^i$PrOH in hexanes at 1 mL/min, detection at 254 nm, retention times 59 and 64 min.

Asymmetric method (general procedure C):

TMPMgCl (1.6 mL, 0.75 mmol) was added to the nitrile **4** (54 mg, 0.25 mmol) in $Et_2O$ (1 mL) at −104 °C. After 10 sec, *p*-bromobenzoyl chloride (165 mg, 0.75 mmol) in $Et_2O$ (1 mL) was added at −104 °C. After 30 min, saturated aqueous $NH_4Cl$ (0.3 mL) was added. The mixture was extracted with $Et_2O$ (3 × 1 mL), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5g** (71 mg, 72%); $[\alpha]^{21}_D$ –39.0 (0.4, $CHCl_3$); data as above. The enantiomer ratio was determined to be 83:17 by CSP-HPLC (major enantiomer eluted at 57 min and minor enantiomer at 65 min). Recrystallization gave er 99:1 by CSP HPLC. X-ray data deposited at CCDC 1477823.

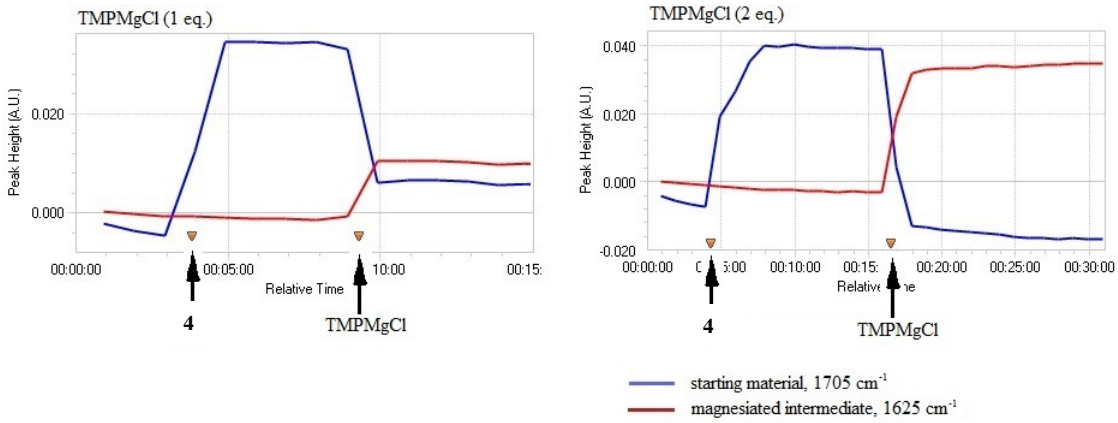
Method from the sulfide **5c**

$^i$PrMgCl (0.375 mL, 0.75 mmol, 2 M in $Et_2O$) was added to the nitrile **5c** (87 mg, 0.25 mmol, er 85:15) in $Et_2O$ (2 mL) at −104 °C. After 10 sec, *p*-bromobenzoyl chloride (165 mg, 0.75 mmol) in $Et_2O$ (1 mL) was added at −104 °C. After 30 min, saturated aqueous $NH_4Cl$ (0.3 mL) was added. The mixture was extracted with $Et_2O$ (3 × 1 mL), dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica gel, eluting with petrol−EtOAc (9:1), gave the nitrile **5g** (32 mg, 33%); $[\alpha]^{21}_D$ –35.0 (0.4, $CHCl_3$); data as above. The enantiomer ratio was determined to be 78:22 by CSP-HPLC.

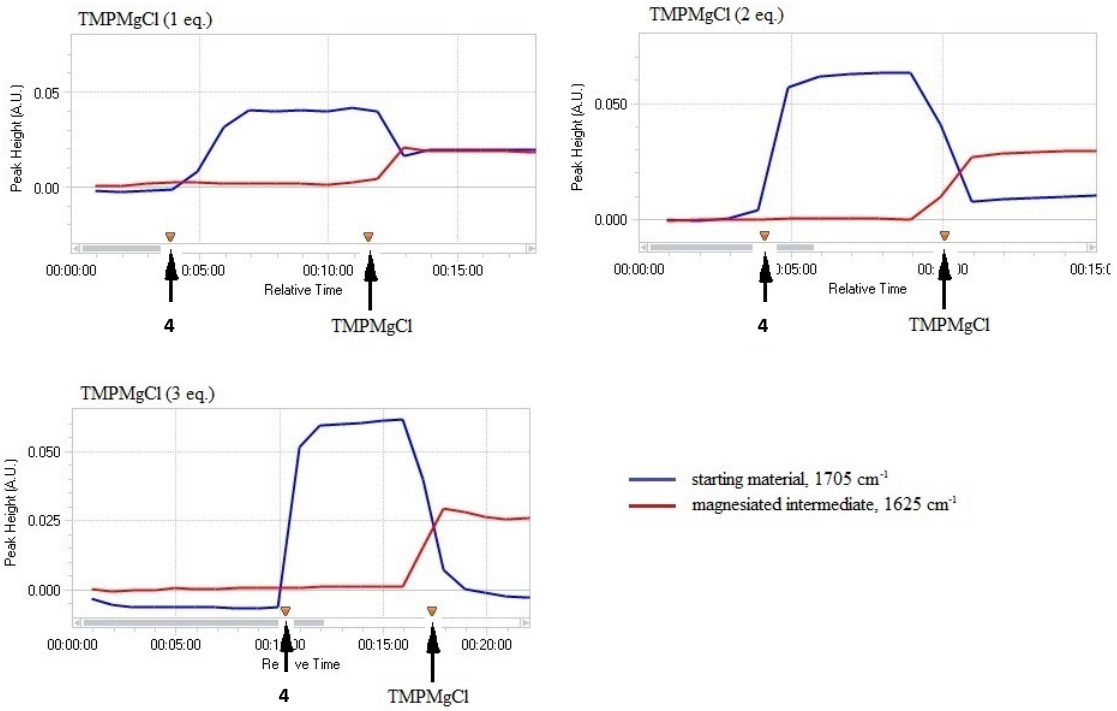
## 2. In situ IR spectra

A ReactIR probe was placed in THF/$Et_2O$ (10 mL) at the required temperature and a background scan was run. After about 5 min, the nitrile **4** (1 mmol) was added in THF/$Et_2O$ (2 mL). When the peak for the carbonyl group (at about 1705 $cm^{-1}$) had levelled out, TMPMgCl (1–3 molar equivalents) was added dropwise. After the metallated species had formed, the reaction was quenched by addition of MeOH or an electrophile.

At –78 °C the ReactIR traces are shown below. With 1 equiv. TMPMgCl, there is incomplete metallation. With two equiv. TMPMgCl, there is complete metallation within a few minutes.




At –107 °C the ReactIR traces are shown below. With 1 equiv. TMPMgCl, there is incomplete metallation. With two equiv. TMPMgCl, there is almost complete metallation within a few minutes. With three equiv. TMPMgCl, there is complete metallation.



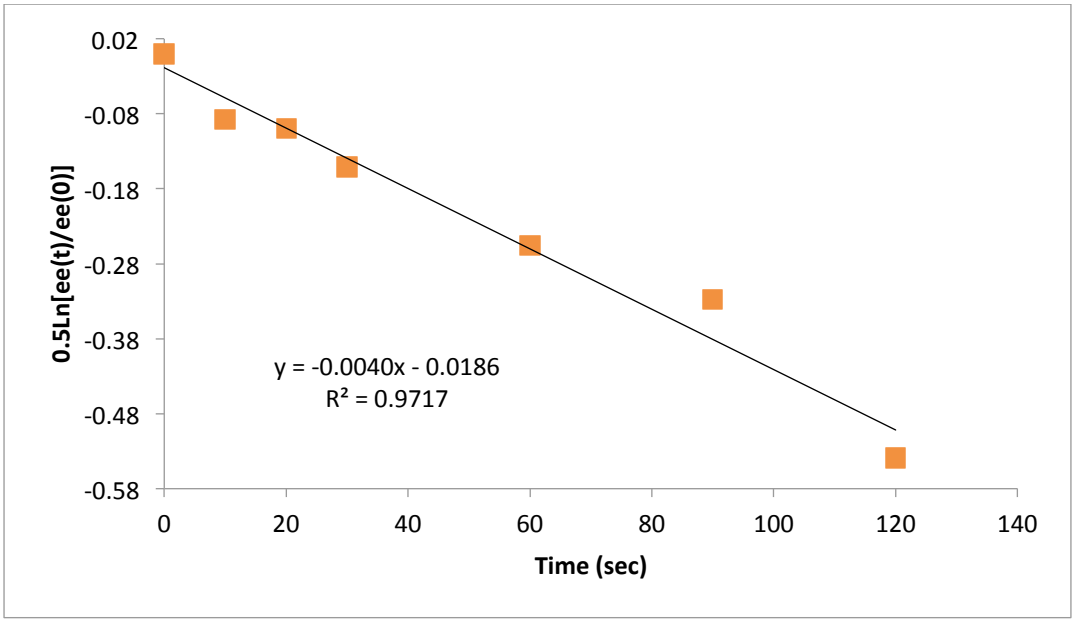
### 3. Kinetics of enantiomerization

#### (i) Kinetics of enantiomerization in $Et_2O$ as solvent

TMPMgCl (1.6 mL, 0.75 mmol, 0.47 M in $Et_2O$) was added to the nitrile (*S*)-*N*-Boc-2-cyanopiperidine **4** (54 mg, 0.25 mmol, er >99:1) in $Et_2O$ (1 mL) at –104 °C (total conc. 0.096 mM). The electrophile cyclobutanone (56 µL, 0.75 mmol) was added after various times as given below. The mixture was then quenched with aqueous $NH_4Cl$ (0.6 mL) at –104 °C and was allowed to warm to room temperature. The mixture was extracted with $Et_2O$ (5 mL) and the organic layer was evaporated. The enantiomer ratio was determined by using CSP-HPLC as described above.

| Time | er (*S*:*R*) (of product **5f**) | |
|---|---|---|
| 0 sec | 100:0 | (extrapolated for time zero) |
| 10 sec | 92:8 | |
| 20 sec | 91:9 | |
| 30 sec | 87:13 | |
| 60 sec | 80:20 | |
| 90 sec | 76:24 | |
| 120 sec | 67:33 | |

First order plot of 0.5ln(ee at time t/ee at time 0) against time (sec):




Gradient is –*k*(enantiomerization)

so enantiomerization (inversion) rate constant $k \approx 4 \times 10^{-3}$ $s^{-1}$

Half-life for enantiomerization, $t_{1/2} \approx 173$ sec (~2.9 min) at –104 °C

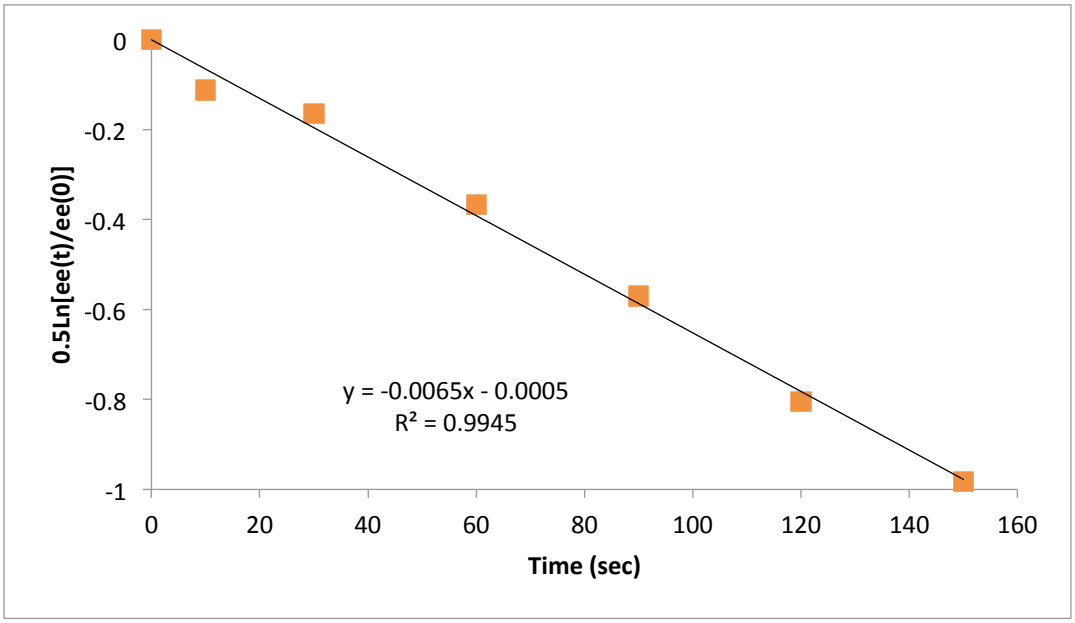
Barrier to enantiomerization, $\Delta G^{\ddagger} \approx 48.3$ kJ/mol (11.6 kcal/mol) at –104 °C

**(ii) Kinetics of enantiomerization in THF/$Et_2O$ mixture as solvent**

TMPMgCl (1.5 mL, 0.75 mmol, 0.5 M in THF) was added to the nitrile (*S*)-*N*-Boc-2-cyanopiperidine **4** (54 mg, 0.25 mmol, er >99:1) in $Et_2O$ (1.1 mL) at –104 °C (total conc. 0.096 mM). The electrophile $PhSSO_2Ph$ (188 mg, 0.75 mmol) was added after various times as given below. The mixture was then quenched with aqueous $NH_4Cl$ (0.6 mL) at –104 °C and was allowed to warm to room temperature. The mixture was extracted with $Et_2O$ (5 mL) and the organic layer was evaporated. The enantiomer ratio was determined by using CSP-HPLC as described above.

| Time | er (*R*:*S*) (of product **5a**) | |
|---|---|---|
| 0 sec | 100:0 | (extrapolated, although *in situ* quench gave er 91:9) |
| 10 sec | 90:10 | |
| 30 sec | 86:14 | |
| 60 sec | 74:26 | |
| 90 sec | 66:34 | |
| 120 sec | 60:40 | |
| 150 sec | 57:43 | |

First order plot of 0.5ln(ee at time t/ee at time 0) against time (sec):




so enantiomerization (inversion) rate constant $k \approx 6.5 \times 10^{-3}$ $s^{-1}$

Half-life for enantiomerization, $t_{1/2} \approx 107$ sec (~1.8 min) at –104 °C

Barrier to enantiomerization, $\Delta G^{\ddagger} \approx 47.7$ kJ/mol (11.4 kcal/mol) at –104 °C

## 4. X-ray data for compound 5g

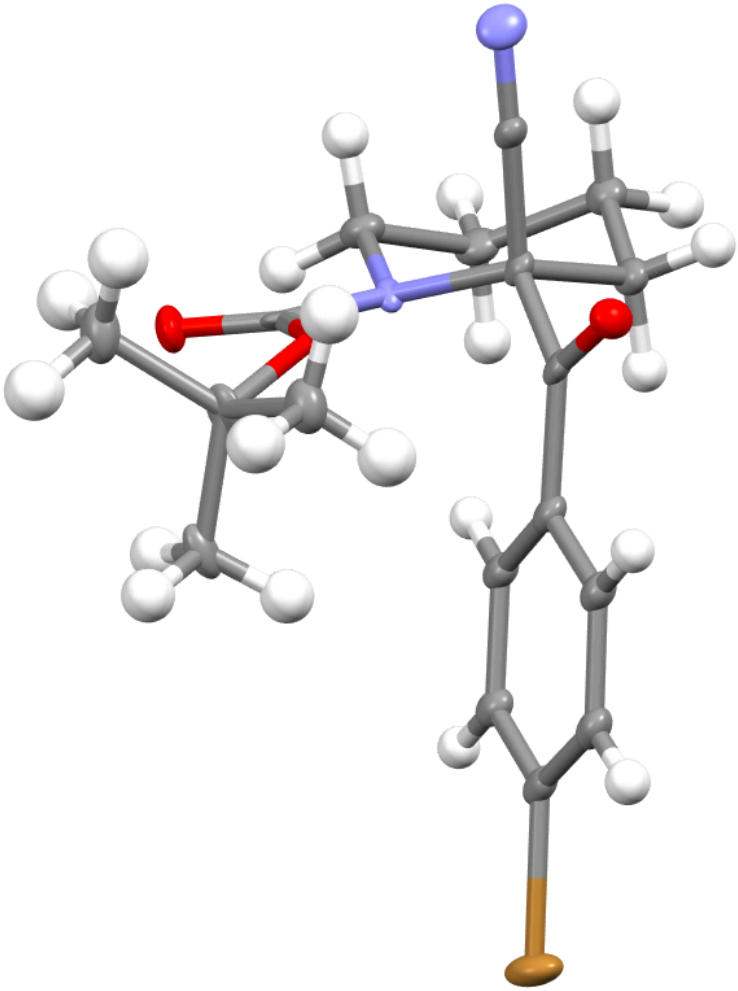


Table 1. Crystal data and structure refinement for compound **5g** (internal reference number: oic260redo_0m).

| | | |
|---|---|---|
| Identification code | shelx | |
| Empirical formula | C18 H21 Br N2 O3 | |
| Formula weight | 393.28 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1$ | |
| Unit cell dimensions | a = 8.8396(3) Å | a= 90°. |
| | b = 17.5572(7) Å | b= 94.347(2)°. |
| | c = 11.6494(4) Å | g = 90°. |
| Volume | 1802.77(11) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.449 $Mg/m^3$ | |

| | |
|---|---|
| Absorption coefficient | 3.259 $mm^{-1}$ |
| F(000) | 808 |
| Crystal size | 0.120 x 0.120 x 0.100 $mm^3$ |
| Theta range for data collection | 3.805 to 67.017°. |
| Index ranges | -10<=h<=10, -20<=k<=20, -13<=l<=13 |
| Reflections collected | 44389 |
| Independent reflections | 44389 [R(int) = ?] |
| Completeness to theta = 67.000° | 98.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.76 and 0.54 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 44389 / 261 / 440 |
| Goodness-of-fit on $F^2$ | 1.022 |
| Final R indices [I>2sigma(I)] | R1 = 0.0825, wR2 = 0.2026 |
| R indices (all data) | R1 = 0.1283, wR2 = 0.2326 |
| Absolute structure parameter | 0.040(14) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.757 and -0.621 e.$Å^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **5g**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 3794(2) | 2470(1) | 4326(2) | 27(1) |
| O(1) | 3707(14) | 5347(8) | 426(10) | 19(4) |
| O(2) | 6813(15) | 3466(8) | -1702(10) | 19(3) |
| O(3) | 4726(14) | 3986(7) | -990(10) | 17(3) |
| N(1) | 7026(17) | 4422(9) | -373(13) | 13(4) |
| N(2) | 5909(19) | 6063(11) | -1548(14) | 28(5) |
| C(1) | 4120(20) | 3200(12) | 3175(16) | 18(3) |
| C(2) | 3070(20) | 3743(12) | 2947(15) | 19(3) |
| C(3) | 3280(20) | 4296(12) | 2129(15) | 20(3) |
| C(4) | 4620(20) | 4282(12) | 1521(15) | 18(3) |
| C(5) | 5690(20) | 3726(11) | 1777(15) | 18(3) |
| C(6) | 5440(20) | 3162(12) | 2601(15) | 18(3) |
| C(7) | 4750(20) | 4913(12) | 642(15) | 18(3) |

| | | | | |
|---|---|---|---|---|
| C(8) | 6260(20) | 5071(12) | 132(16) | 18(3) |
| C(9) | 7310(20) | 5403(12) | 1137(14) | 18(3) |
| C(10) | 8910(20) | 5604(12) | 809(16) | 21(3) |
| C(11) | 9600(20) | 4870(12) | 346(15) | 21(3) |
| C(12) | 8630(20) | 4570(12) | -668(15) | 20(4) |
| C(13) | 6230(20) | 3914(11) | -1102(16) | 16(4) |
| C(14) | 3620(20) | 3378(11) | -1457(16) | 17(3) |
| C(15) | 3630(20) | 3340(12) | -2750(15) | 19(4) |
| C(16) | 2160(20) | 3692(12) | -1096(16) | 24(4) |
| C(17) | 3956(19) | 2597(12) | -904(14) | 20(4) |
| C(18) | 6000(20) | 5646(12) | -790(16) | 18(3) |
| Br(00) | 11167(2) | 7519(1) | 9656(2) | 28(1) |
| O(1A) | 11572(15) | 4752(8) | 5559(11) | 19(3) |
| O(2A) | 7898(15) | 6682(8) | 3624(10) | 21(3) |
| O(3A) | 10154(14) | 6110(7) | 4158(10) | 14(3) |
| N(1A) | 7980(17) | 5588(9) | 4674(12) | 12(4) |
| N(2A) | 9310(19) | 4112(11) | 3273(15) | 21(4) |
| C(1A) | 10910(20) | 6796(12) | 8464(15) | 17(3) |
| C(2A) | 9490(20) | 6686(11) | 7889(14) | 17(3) |
| C(3A) | 9290(20) | 6146(11) | 7020(15) | 17(3) |
| C(4A) | 10490(20) | 5734(12) | 6717(17) | 16(3) |
| C(5A) | 11970(20) | 5834(12) | 7299(15) | 18(3) |
| C(6A) | 12150(20) | 6366(12) | 8185(15) | 19(3) |
| C(7A) | 10450(20) | 5149(12) | 5763(15) | 15(3) |
| C(8A) | 8930(20) | 4930(11) | 5098(15) | 15(3) |
| C(9A) | 8130(20) | 4450(11) | 5957(15) | 18(3) |
| C(10A) | 6520(20) | 4234(12) | 5514(15) | 20(3) |
| C(11A) | 5620(20) | 4980(12) | 5251(15) | 20(3) |
| C(12A) | 6350(20) | 5441(12) | 4337(15) | 20(4) |
| C(13A) | 8650(20) | 6176(11) | 4093(16) | 15(4) |
| C(14A) | 11130(20) | 6795(11) | 3964(17) | 20(4) |
| C(15A) | 12690(20) | 6445(12) | 4168(17) | 26(4) |
| C(16A) | 10949(19) | 7420(14) | 4840(14) | 21(4) |
| C(17A) | 10900(20) | 7056(13) | 2740(16) | 27(4) |
| C(18A) | 9220(20) | 4464(11) | 4069(16) | 14(3) |

Table 3. Bond lengths [Å] and angles [°] for **5g**.

| | |
|---|---|
| Br(1)-C(1) | 1.891(19) |
| O(1)-C(7) | 1.21(2) |
| O(2)-C(13) | 1.20(2) |
| O(3)-C(13) | 1.35(2) |
| O(3)-C(14) | 1.52(2) |
| N(1)-C(13) | 1.39(2) |
| N(1)-C(8) | 1.47(2) |
| N(1)-C(12) | 1.50(2) |
| N(2)-C(18) | 1.14(2) |
| C(1)-C(2) | 1.34(3) |
| C(1)-C(6) | 1.39(2) |
| C(2)-C(3) | 1.38(3) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.42(3) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.38(3) |
| C(4)-C(7) | 1.52(3) |
| C(5)-C(6) | 1.41(3) |
| C(5)-H(5) | 0.9500 |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.53(3) |
| C(8)-C(18) | 1.48(3) |
| C(8)-C(9) | 1.55(3) |
| C(9)-C(10) | 1.54(2) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-C(11) | 1.54(3) |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.50(3) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(14)-C(15) | 1.51(2) |
| C(14)-C(16) | 1.49(3) |

| | |
|---|---|
| C(14)-C(17) | 1.54(3) |
| C(15)-H(15A) | 0.9800 |
| C(15)-H(15B) | 0.9800 |
| C(15)-H(15C) | 0.9800 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| Br(00)-C(1A) | 1.882(19) |
| O(1A)-C(7A) | 1.25(2) |
| O(2A)-C(13A) | 1.21(2) |
| O(3A)-C(13A) | 1.33(2) |
| O(3A)-C(14A) | 1.50(2) |
| N(1A)-C(13A) | 1.39(2) |
| N(1A)-C(8A) | 1.49(2) |
| N(1A)-C(12A) | 1.49(2) |
| N(2A)-C(18A) | 1.12(2) |
| C(1A)-C(6A) | 1.38(3) |
| C(1A)-C(2A) | 1.40(2) |
| C(2A)-C(3A) | 1.39(3) |
| C(2A)-H(2A) | 0.9500 |
| C(3A)-C(4A) | 1.35(3) |
| C(3A)-H(3A) | 0.9500 |
| C(4A)-C(5A) | 1.44(3) |
| C(4A)-C(7A) | 1.51(3) |
| C(5A)-C(6A) | 1.39(3) |
| C(5A)-H(5A) | 0.9500 |
| C(6A)-H(6A) | 0.9500 |
| C(7A)-C(8A) | 1.55(3) |
| C(8A)-C(18A) | 1.49(3) |
| C(8A)-C(9A) | 1.52(2) |
| C(9A)-C(10A) | 1.52(3) |
| C(9A)-H(9A1) | 0.9900 |
| C(9A)-H(9A2) | 0.9900 |
| C(10A)-C(11A) | 1.55(3) |
| C(10A)-H(10C) | 0.9900 |

| | |
|---|---|
| C(10A)-H(10D) | 0.9900 |
| C(11A)-C(12A) | 1.52(3) |
| C(11A)-H(11C) | 0.9900 |
| C(11A)-H(11D) | 0.9900 |
| C(12A)-H(12C) | 0.9900 |
| C(12A)-H(12D) | 0.9900 |
| C(14A)-C(17A) | 1.50(2) |
| C(14A)-C(15A) | 1.52(3) |
| C(14A)-C(16A) | 1.52(3) |
| C(15A)-H(15D) | 0.9800 |
| C(15A)-H(15E) | 0.9800 |
| C(15A)-H(15F) | 0.9800 |
| C(16A)-H(16D) | 0.9800 |
| C(16A)-H(16E) | 0.9800 |
| C(16A)-H(16F) | 0.9800 |
| C(17A)-H(17D) | 0.9800 |
| C(17A)-H(17E) | 0.9800 |
| C(17A)-H(17F) | 0.9800 |

| | |
|---|---|
| C(13)-O(3)-C(14) | 120.8(14) |
| C(13)-N(1)-C(8) | 121.0(15) |
| C(13)-N(1)-C(12) | 114.4(15) |
| C(8)-N(1)-C(12) | 115.4(15) |
| C(2)-C(1)-C(6) | 122.0(18) |
| C(2)-C(1)-Br(1) | 118.9(15) |
| C(6)-C(1)-Br(1) | 119.1(15) |
| C(1)-C(2)-C(3) | 120.5(19) |
| C(1)-C(2)-H(2) | 119.7 |
| C(3)-C(2)-H(2) | 119.7 |
| C(2)-C(3)-C(4) | 119(2) |
| C(2)-C(3)-H(3) | 120.3 |
| C(4)-C(3)-H(3) | 120.3 |
| C(5)-C(4)-C(3) | 119.3(18) |
| C(5)-C(4)-C(7) | 125.3(18) |
| C(3)-C(4)-C(7) | 115.4(18) |
| C(4)-C(5)-C(6) | 120.1(19) |
| C(4)-C(5)-H(5) | 119.9 |
| C(6)-C(5)-H(5) | 119.9 |

| | |
|---|---|
| C(1)-C(6)-C(5) | 118.6(19) |
| C(1)-C(6)-H(6) | 120.7 |
| C(5)-C(6)-H(6) | 120.7 |
| O(1)-C(7)-C(4) | 120.6(17) |
| O(1)-C(7)-C(8) | 118.5(18) |
| C(4)-C(7)-C(8) | 120.4(17) |
| N(1)-C(8)-C(18) | 106.8(15) |
| N(1)-C(8)-C(7) | 117.3(17) |
| C(18)-C(8)-C(7) | 108.4(16) |
| N(1)-C(8)-C(9) | 108.9(15) |
| C(18)-C(8)-C(9) | 110.0(17) |
| C(7)-C(8)-C(9) | 105.4(15) |
| C(10)-C(9)-C(8) | 114.2(14) |
| C(10)-C(9)-H(9A) | 108.7 |
| C(8)-C(9)-H(9A) | 108.7 |
| C(10)-C(9)-H(9B) | 108.7 |
| C(8)-C(9)-H(9B) | 108.7 |
| H(9A)-C(9)-H(9B) | 107.6 |
| C(9)-C(10)-C(11) | 106.8(16) |
| C(9)-C(10)-H(10A) | 110.4 |
| C(11)-C(10)-H(10A) | 110.4 |
| C(9)-C(10)-H(10B) | 110.4 |
| C(11)-C(10)-H(10B) | 110.4 |
| H(10A)-C(10)-H(10B) | 108.6 |
| C(12)-C(11)-C(10) | 110.7(17) |
| C(12)-C(11)-H(11A) | 109.5 |
| C(10)-C(11)-H(11A) | 109.5 |
| C(12)-C(11)-H(11B) | 109.5 |
| C(10)-C(11)-H(11B) | 109.5 |
| H(11A)-C(11)-H(11B) | 108.1 |
| C(11)-C(12)-N(1) | 111.8(14) |
| C(11)-C(12)-H(12A) | 109.3 |
| N(1)-C(12)-H(12A) | 109.3 |
| C(11)-C(12)-H(12B) | 109.3 |
| N(1)-C(12)-H(12B) | 109.3 |
| H(12A)-C(12)-H(12B) | 107.9 |
| O(2)-C(13)-O(3) | 126.0(18) |
| O(2)-C(13)-N(1) | 124.2(18) |

| | |
|---|---|
| O(3)-C(13)-N(1) | 109.8(16) |
| C(15)-C(14)-O(3) | 109.6(13) |
| C(15)-C(14)-C(16) | 111.6(16) |
| O(3)-C(14)-C(16) | 100.8(15) |
| C(15)-C(14)-C(17) | 111.3(16) |
| O(3)-C(14)-C(17) | 112.2(15) |
| C(16)-C(14)-C(17) | 110.8(15) |
| C(14)-C(15)-H(15A) | 109.5 |
| C(14)-C(15)-H(15B) | 109.5 |
| H(15A)-C(15)-H(15B) | 109.5 |
| C(14)-C(15)-H(15C) | 109.5 |
| H(15A)-C(15)-H(15C) | 109.5 |
| H(15B)-C(15)-H(15C) | 109.5 |
| C(14)-C(16)-H(16A) | 109.5 |
| C(14)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| C(14)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(14)-C(17)-H(17A) | 109.5 |
| C(14)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |
| C(14)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| N(2)-C(18)-C(8) | 174(2) |
| C(13A)-O(3A)-C(14A) | 120.1(14) |
| C(13A)-N(1A)-C(8A) | 119.2(15) |
| C(13A)-N(1A)-C(12A) | 116.1(15) |
| C(8A)-N(1A)-C(12A) | 117.6(16) |
| C(6A)-C(1A)-C(2A) | 120.7(19) |
| C(6A)-C(1A)-Br(00) | 119.3(14) |
| C(2A)-C(1A)-Br(00) | 120.0(15) |
| C(3A)-C(2A)-C(1A) | 120.1(19) |
| C(3A)-C(2A)-H(2A) | 120.0 |
| C(1A)-C(2A)-H(2A) | 120.0 |
| C(4A)-C(3A)-C(2A) | 119.9(19) |
| C(4A)-C(3A)-H(3A) | 120.0 |

| | |
|---|---|
| C(2A)-C(3A)-H(3A) | 120.0 |
| C(3A)-C(4A)-C(5A) | 121.0(19) |
| C(3A)-C(4A)-C(7A) | 125.4(19) |
| C(5A)-C(4A)-C(7A) | 113.6(18) |
| C(6A)-C(5A)-C(4A) | 118.6(19) |
| C(6A)-C(5A)-H(5A) | 120.7 |
| C(4A)-C(5A)-H(5A) | 120.7 |
| C(5A)-C(6A)-C(1A) | 119.7(18) |
| C(5A)-C(6A)-H(6A) | 120.2 |
| C(1A)-C(6A)-H(6A) | 120.2 |
| O(1A)-C(7A)-C(4A) | 123.1(18) |
| O(1A)-C(7A)-C(8A) | 115.9(18) |
| C(4A)-C(7A)-C(8A) | 120.5(17) |
| N(1A)-C(8A)-C(18A) | 106.6(14) |
| N(1A)-C(8A)-C(9A) | 111.5(15) |
| C(18A)-C(8A)-C(9A) | 110.1(16) |
| N(1A)-C(8A)-C(7A) | 114.8(16) |
| C(18A)-C(8A)-C(7A) | 110.0(16) |
| C(9A)-C(8A)-C(7A) | 103.9(14) |
| C(8A)-C(9A)-C(10A) | 112.6(15) |
| C(8A)-C(9A)-H(9A1) | 109.1 |
| C(10A)-C(9A)-H(9A1) | 109.1 |
| C(8A)-C(9A)-H(9A2) | 109.1 |
| C(10A)-C(9A)-H(9A2) | 109.1 |
| H(9A1)-C(9A)-H(9A2) | 107.8 |
| C(9A)-C(10A)-C(11A) | 108.1(17) |
| C(9A)-C(10A)-H(10C) | 110.1 |
| C(11A)-C(10A)-H(10C) | 110.1 |
| C(9A)-C(10A)-H(10D) | 110.1 |
| C(11A)-C(10A)-H(10D) | 110.1 |
| H(10C)-C(10A)-H(10D) | 108.4 |
| C(12A)-C(11A)-C(10A) | 110.3(16) |
| C(12A)-C(11A)-H(11C) | 109.6 |
| C(10A)-C(11A)-H(11C) | 109.6 |
| C(12A)-C(11A)-H(11D) | 109.6 |
| C(10A)-C(11A)-H(11D) | 109.6 |
| H(11C)-C(11A)-H(11D) | 108.1 |
| N(1A)-C(12A)-C(11A) | 111.3(15) |

| | |
|---|---|
| N(1A)-C(12A)-H(12C) | 109.4 |
| C(11A)-C(12A)-H(12C) | 109.4 |
| N(1A)-C(12A)-H(12D) | 109.4 |
| C(11A)-C(12A)-H(12D) | 109.4 |
| H(12C)-C(12A)-H(12D) | 108.0 |
| O(2A)-C(13A)-O(3A) | 126.8(18) |
| O(2A)-C(13A)-N(1A) | 121.6(18) |
| O(3A)-C(13A)-N(1A) | 111.6(16) |
| C(17A)-C(14A)-O(3A) | 110.6(15) |
| C(17A)-C(14A)-C(15A) | 109.1(17) |
| O(3A)-C(14A)-C(15A) | 100.3(15) |
| C(17A)-C(14A)-C(16A) | 114.0(18) |
| O(3A)-C(14A)-C(16A) | 112.9(15) |
| C(15A)-C(14A)-C(16A) | 109.1(16) |
| C(14A)-C(15A)-H(15D) | 109.5 |
| C(14A)-C(15A)-H(15E) | 109.5 |
| H(15D)-C(15A)-H(15E) | 109.5 |
| C(14A)-C(15A)-H(15F) | 109.5 |
| H(15D)-C(15A)-H(15F) | 109.5 |
| H(15E)-C(15A)-H(15F) | 109.5 |
| C(14A)-C(16A)-H(16D) | 109.5 |
| C(14A)-C(16A)-H(16E) | 109.5 |
| H(16D)-C(16A)-H(16E) | 109.5 |
| C(14A)-C(16A)-H(16F) | 109.5 |
| H(16D)-C(16A)-H(16F) | 109.5 |
| H(16E)-C(16A)-H(16F) | 109.5 |
| C(14A)-C(17A)-H(17D) | 109.5 |
| C(14A)-C(17A)-H(17E) | 109.5 |
| H(17D)-C(17A)-H(17E) | 109.5 |
| C(14A)-C(17A)-H(17F) | 109.5 |
| H(17D)-C(17A)-H(17F) | 109.5 |
| H(17E)-C(17A)-H(17F) | 109.5 |
| N(2A)-C(18A)-C(8A) | 174(2) |

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5g**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br(1) | 34(1) | 31(1) | 15(1) | 9(1) | 1(1) | -10(1) |
| O(1) | 18(9) | 23(9) | 15(8) | 4(6) | 5(7) | 3(7) |
| O(2) | 27(8) | 18(8) | 13(7) | -5(6) | 2(6) | 3(6) |
| O(3) | 25(8) | 13(8) | 14(7) | -4(5) | 5(6) | -10(6) |
| N(1) | 12(9) | 12(9) | 16(9) | -4(7) | -3(7) | 1(7) |
| N(2) | 15(10) | 39(13) | 30(11) | 12(9) | 4(8) | 3(9) |
| C(1) | 21(6) | 22(7) | 11(6) | 2(5) | 0(5) | -6(5) |
| C(2) | 20(6) | 25(7) | 13(6) | 3(5) | 1(5) | -6(5) |
| C(3) | 20(6) | 25(7) | 14(6) | 2(5) | 2(5) | -3(5) |
| C(4) | 20(6) | 23(6) | 10(5) | -1(4) | 2(5) | -1(5) |
| C(5) | 24(6) | 22(7) | 10(6) | 0(5) | 2(5) | -1(5) |
| C(6) | 23(6) | 22(7) | 10(6) | -1(5) | 0(5) | -2(5) |
| C(7) | 23(6) | 21(6) | 10(6) | -2(5) | 4(5) | 2(5) |
| C(8) | 22(6) | 22(6) | 10(5) | -1(5) | 5(5) | 3(5) |
| C(9) | 24(6) | 22(7) | 10(6) | -2(5) | 5(5) | 2(5) |
| C(10) | 26(6) | 26(7) | 12(6) | -3(5) | 4(5) | -2(6) |
| C(11) | 24(7) | 28(7) | 13(7) | -3(6) | 2(5) | 1(6) |
| C(12) | 23(8) | 25(8) | 12(7) | -2(6) | 5(6) | 1(7) |
| C(13) | 17(12) | 18(12) | 12(11) | 10(9) | 5(9) | 9(9) |
| C(14) | 19(8) | 14(8) | 18(7) | -1(6) | 6(7) | -11(7) |
| C(15) | 20(10) | 20(10) | 18(8) | -1(7) | 4(8) | -13(8) |
| C(16) | 26(9) | 20(10) | 25(10) | -5(8) | 6(8) | -5(8) |
| C(17) | 10(8) | 15(10) | 37(9) | 9(8) | 12(7) | -2(8) |
| C(18) | 19(8) | 22(8) | 13(7) | 2(6) | 4(6) | 3(7) |
| Br(00) | 36(1) | 32(1) | 17(1) | -10(1) | 4(1) | -11(1) |
| O(1A) | 16(8) | 19(9) | 21(8) | -2(6) | 0(6) | 3(7) |
| O(2A) | 28(9) | 14(8) | 22(8) | 6(6) | 1(6) | 5(6) |
| O(3A) | 18(8) | 12(7) | 11(7) | 2(5) | 1(6) | -1(6) |
| N(1A) | 16(10) | 10(9) | 11(8) | 1(6) | 6(7) | 5(7) |
| N(2A) | 12(10) | 30(12) | 21(10) | -3(8) | 6(8) | 4(8) |
| C(1A) | 19(6) | 20(7) | 11(6) | 4(5) | -1(5) | -6(5) |
| C(2A) | 19(6) | 20(7) | 12(6) | 2(5) | 1(5) | -4(5) |
| C(3A) | 20(6) | 19(6) | 11(6) | 2(5) | 0(5) | -3(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(4A) | 19(5) | 19(6) | 10(5) | 3(4) | -1(5) | -2(5) |
| C(5A) | 19(6) | 21(7) | 13(6) | 3(5) | -1(5) | -1(5) |
| C(6A) | 22(6) | 22(7) | 14(6) | 4(5) | -3(5) | -3(5) |
| C(7A) | 20(6) | 18(6) | 8(6) | 4(5) | -2(5) | -2(5) |
| C(8A) | 19(6) | 16(6) | 9(6) | 3(5) | 0(5) | -2(5) |
| C(9A) | 25(6) | 17(6) | 12(6) | 2(5) | 3(5) | -4(5) |
| C(10A) | 24(6) | 21(7) | 14(6) | 0(5) | 3(6) | -3(5) |
| C(11A) | 24(7) | 24(7) | 14(7) | -3(6) | 4(6) | -1(6) |
| C(12A) | 22(8) | 23(8) | 14(8) | -3(6) | 0(7) | -4(7) |
| C(13A) | 18(12) | 14(11) | 11(11) | -8(8) | -5(9) | 1(9) |
| C(14A) | 15(7) | 15(8) | 29(8) | 8(6) | 4(7) | -7(6) |
| C(15A) | 24(9) | 23(10) | 30(10) | 7(8) | 6(8) | 0(8) |
| C(16A) | 12(8) | 13(9) | 39(9) | 6(8) | 2(7) | 2(9) |
| C(17A) | 21(10) | 27(11) | 32(9) | 12(8) | 5(8) | 1(9) |
| C(18A) | 16(7) | 15(8) | 11(7) | 1(6) | -2(6) | -2(6) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for **5g**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 2176 | 3749 | 3351 | 23 |
| H(3) | 2544 | 4683 | 1974 | 23 |
| H(5) | 6605 | 3723 | 1397 | 22 |
| H(6) | 6151 | 2765 | 2761 | 22 |
| H(9A) | 6830 | 5868 | 1427 | 22 |
| H(9B) | 7391 | 5028 | 1772 | 22 |
| H(10A) | 9540 | 5791 | 1491 | 25 |
| H(10B) | 8865 | 6007 | 212 | 25 |
| H(11A) | 10630 | 4976 | 113 | 26 |
| H(11B) | 9679 | 4480 | 962 | 26 |
| H(12A) | 9073 | 4090 | -937 | 24 |
| H(12B) | 8616 | 4943 | -1305 | 24 |
| H(15A) | 2825 | 2996 | -3057 | 29 |

| | | | | |
|---|---|---|---|---|
| H(15B) | 4615 | 3149 | -2956 | 29 |
| H(15C) | 3456 | 3850 | -3076 | 29 |
| H(16A) | 1981 | 4197 | -1437 | 36 |
| H(16B) | 2209 | 3733 | -255 | 36 |
| H(16C) | 1324 | 3351 | -1358 | 36 |
| H(17A) | 3802 | 2622 | -80 | 30 |
| H(17B) | 5009 | 2454 | -1005 | 30 |
| H(17C) | 3271 | 2215 | -1272 | 30 |
| H(2A) | 8646 | 6981 | 8093 | 20 |
| H(3A) | 8316 | 6065 | 6639 | 20 |
| H(5A) | 12812 | 5544 | 7084 | 21 |
| H(6A) | 13106 | 6433 | 8598 | 23 |
| H(9A1) | 8089 | 4739 | 6684 | 22 |
| H(9A2) | 8719 | 3980 | 6128 | 22 |
| H(10C) | 6031 | 3932 | 6101 | 24 |
| H(10D) | 6541 | 3923 | 4806 | 24 |
| H(11C) | 4557 | 4855 | 4978 | 24 |
| H(11D) | 5592 | 5286 | 5963 | 24 |
| H(12C) | 6253 | 5160 | 3598 | 24 |
| H(12D) | 5809 | 5932 | 4222 | 24 |
| H(15D) | 13463 | 6823 | 4002 | 38 |
| H(15E) | 12775 | 6003 | 3662 | 38 |
| H(15F) | 12856 | 6282 | 4973 | 38 |
| H(16D) | 9907 | 7614 | 4761 | 32 |
| H(16E) | 11656 | 7836 | 4707 | 32 |
| H(16F) | 11170 | 7216 | 5617 | 32 |
| H(17D) | 9816 | 7063 | 2498 | 40 |
| H(17E) | 11423 | 6706 | 2246 | 40 |
| H(17F) | 11322 | 7569 | 2674 | 40 |

Table 6. Hydrogen bonds for **5g** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(17A)-H(17F)...O(2)#1 | 0.98 | 2.60 | 3.47(2) | 147.9 |
| C(17A)-H(17D)...O(2A) | 0.98 | 2.32 | 2.99(2) | 125.2 |
| C(16A)-H(16D)...O(2A) | 0.98 | 2.69 | 3.22(2) | 114.6 |
| C(6A)-H(6A)...N(2)#2 | 0.95 | 2.58 | 3.36(3) | 139.6 |
| C(17)-H(17B)...O(2) | 0.98 | 2.56 | 3.15(2) | 118.8 |
| C(15)-H(15B)...O(2) | 0.98 | 2.41 | 2.99(2) | 117.6 |
| C(15)-H(15A)...O(2A)#3 | 0.98 | 2.47 | 3.34(2) | 147.0 |
| C(2)-H(2)...N(2A)#4 | 0.95 | 2.61 | 3.44(3) | 145.9 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y+1/2,-z #2 x+1,y,z+1 #3 -x+1,y-1/2,-z

#4 x-1,y,z

## 5. DFT data

All calculations were performed as described in the main text of the paper. Optimizations were started from a number of chemically feasible magnesiated nitrile structures. It is noted that in particular for the non-bridged structures, the lability of coordinated diethylether means that a number of isomers are possible. As far as we can ascertain all these structures have been generated, although only the lowest energy structures are reported here. After convergence, frequencies were calculated in the harmonic approximation to confirm whether a minimum was found through the absence of imaginary frequencies.

### *4.1 1st rotamer of 4*

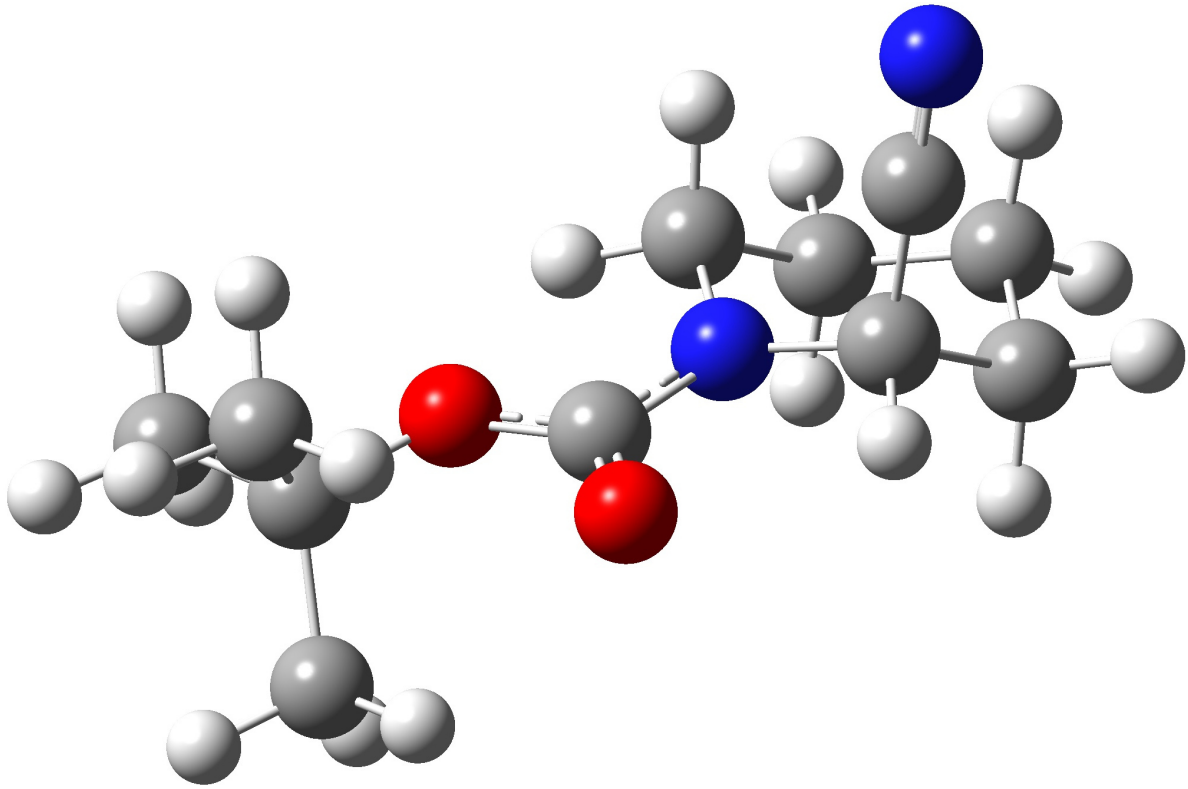

Figure S1: 1st rotamer of *4*

| | | |
|---|---|---|
| Route | : # opt freq b3lyp/6-311g(d,p) scrf=(solvent=diethylether) geom=connectivity empiricaldispersion=gd3bj int=ultrafine pop=(regular,mk) | |
| SMILES | : CC(C)(C)OC(=O)N1CCCCC1C#N | |
| Formula | : $C_{11}H_{18}N_2O_2$ | |
| Charge | : 0 | |
| Multiplicity | : 1 | |
| Dipole | : 13.6600 | Debye |
| Energy | : -690.23731225 | a.u. |
| Gibbs Energy | : -689.99801600 | a.u. |

*4.1.1 Cartesian Co-ordinates (XYZ format)*

33

| | | | |
|---|---|---|---|
| C | -2.08972311 | -1.44285202 | -1.08634698 |
| C | -1.75053704 | 0.99568301 | -0.71651202 |
| C | -2.34531808 | 0.87544602 | 0.69872200 |
| C | -2.14887094 | -0.53078002 | 1.26988399 |
| C | -2.70493293 | -1.58412504 | 0.30634999 |
| H | -2.56423092 | -2.11134791 | -1.79660201 |
| H | -1.02045095 | -1.69014704 | -1.05313802 |
| H | -1.89509296 | 1.63407195 | 1.34240103 |
| H | -3.41183400 | 1.10103202 | 0.61249900 |
| H | -1.08098698 | -0.71238798 | 1.43694401 |
| H | -2.63851595 | -0.60539901 | 2.24356103 |
| H | -2.50560999 | -2.59157300 | 0.68070501 |
| H | -3.79147696 | -1.47238803 | 0.22578099 |
| N | -2.24924397 | -0.06904600 | -1.57936502 |
| C | -2.58337092 | 0.26471099 | -2.87026095 |
| O | -2.58636189 | 1.41127801 | -3.28364706 |
| O | -2.91705799 | -0.82396001 | -3.58109593 |
| C | -3.34819293 | -0.71490300 | -4.99208689 |
| C | -4.62627077 | 0.11646300 | -5.08197880 |
| C | -2.21279597 | -0.14024501 | -5.83655596 |
| C | -3.61893511 | -2.16986489 | -5.36301088 |
| H | -5.38872290 | -0.29214299 | -4.41445780 |
| H | -4.43861294 | 1.15449703 | -4.81553316 |
| H | -5.01033878 | 0.07714500 | -6.10405111 |
| H | -1.30489898 | -0.73219901 | -5.69916821 |
| H | -2.49228501 | -0.18165600 | -6.89201880 |
| H | -2.00754309 | 0.89324200 | -5.56568813 |
| H | -3.94472098 | -2.23221803 | -6.40321398 |
| H | -2.71414399 | -2.76934910 | -5.24456596 |
| H | -4.40165615 | -2.58831596 | -4.72697401 |
| C | -0.27324501 | 0.96360302 | -0.67479402 |
| N | 0.87763798 | 0.91216701 | -0.63615602 |
| H | -2.03997898 | 1.94199097 | -1.17207694 |

*4.1.2 Frequencies*

| **Mode** | **IR frequency** | **IR intensity** |
|---|---|---|
| 1 | 13.62160000 | 1.48590000 |
| 2 | 37.79710000 | 1.29040000 |
| 3 | 67.47100000 | 4.82960000 |
| 4 | 104.75250000 | 3.16540000 |
| 5 | 114.95770000 | 1.45210000 |
| 6 | 125.10550000 | 1.38750000 |
| 7 | 140.73230000 | 3.24330000 |
| 8 | 204.55000000 | 0.19430000 |
| 9 | 228.64720000 | 6.77090000 |
| 10 | 242.69000000 | 1.15190000 |
| 11 | 252.84830000 | 0.51900000 |

| | | |
|---|---|---|
| 12 | 270.50240000 | 0.02010000 |
| 13 | 278.40110000 | 2.19320000 |
| 14 | 304.31950000 | 2.76450000 |
| 15 | 346.20480000 | 25.88200000 |
| 16 | 350.80720000 | 2.66320000 |
| 17 | 373.14210000 | 2.72460000 |
| 18 | 400.69800000 | 6.40600000 |
| 19 | 416.53700000 | 1.58520000 |
| 20 | 440.22450000 | 4.00210000 |
| 21 | 458.49780000 | 3.37910000 |
| 22 | 491.53890000 | 4.32330000 |
| 23 | 517.66110000 | 9.58440000 |
| 24 | 602.60090000 | 3.06130000 |
| 25 | 624.47610000 | 3.83390000 |
| 26 | 695.04060000 | 1.19450000 |
| 27 | 770.51140000 | 6.35880000 |
| 28 | 774.50680000 | 30.49840000 |
| 29 | 807.58290000 | 0.86900000 |
| 30 | 825.87490000 | 12.46580000 |
| 31 | 852.86060000 | 7.71370000 |
| 32 | 865.45460000 | 53.80030000 |
| 33 | 884.54060000 | 40.73970000 |
| 34 | 928.91820000 | 0.06510000 |
| 35 | 930.29350000 | 3.98860000 |
| 36 | 934.30930000 | 27.55310000 |
| 37 | 945.95460000 | 9.42240000 |
| 38 | 971.62100000 | 0.18040000 |
| 39 | 1005.46270000 | 17.77180000 |
| 40 | 1045.39900000 | 83.43710000 |
| 41 | 1052.65260000 | 0.58610000 |
| 42 | 1057.37290000 | 0.49920000 |
| 43 | 1082.94800000 | 13.25010000 |
| 44 | 1108.38720000 | 55.83840000 |
| 45 | 1152.11930000 | 67.00980000 |
| 46 | 1156.22430000 | 52.03160000 |
| 47 | 1180.70690000 | 514.64460000 |
| 48 | 1203.02730000 | 16.01840000 |
| 49 | 1269.95730000 | 18.97130000 |
| 50 | 1270.59620000 | 25.94150000 |
| 51 | 1277.33770000 | 163.26600000 |
| 52 | 1291.67330000 | 35.33420000 |
| 53 | 1294.72960000 | 137.23670000 |
| 54 | 1310.98440000 | 15.64560000 |
| 55 | 1355.18360000 | 80.63720000 |
| 56 | 1367.73940000 | 43.50500000 |
| 57 | 1385.58010000 | 14.64860000 |
| 58 | 1387.06260000 | 8.36380000 |
| 59 | 1396.07430000 | 29.07300000 |
| 60 | 1397.72160000 | 43.49210000 |
| 61 | 1404.30450000 | 56.53710000 |
| 62 | 1422.49850000 | 31.57030000 |
| 63 | 1434.06640000 | 366.81770000 |
| 64 | 1467.08140000 | 0.46000000 |
| 65 | 1475.77570000 | 5.42880000 |
| 66 | 1483.88940000 | 12.30480000 |

| | | |
|---|---|---|
| 67 | 1486.17860000 | 2.69840000 |
| 68 | 1486.94450000 | 0.07990000 |
| 69 | 1490.23770000 | 22.93750000 |
| 70 | 1493.05910000 | 3.44540000 |
| 71 | 1500.46530000 | 1.89830000 |
| 72 | 1507.90510000 | 5.84890000 |
| 73 | 1521.49850000 | 29.00810000 |
| 74 | 1730.28420000 | 540.88630000 |
| 75 | 2346.12740000 | 10.54030000 |
| 76 | 2998.36460000 | 37.60960000 |
| 77 | 3022.05230000 | 16.28150000 |
| 78 | 3029.20420000 | 48.88850000 |
| 79 | 3037.14560000 | 13.20100000 |
| 80 | 3039.36760000 | 34.52200000 |
| 81 | 3045.88510000 | 27.26000000 |
| 82 | 3046.01060000 | 16.98710000 |
| 83 | 3075.20590000 | 51.27490000 |
| 84 | 3078.83930000 | 59.92000000 |
| 85 | 3094.20740000 | 37.04230000 |
| 86 | 3101.00430000 | 10.00840000 |
| 87 | 3102.63200000 | 21.80280000 |
| 88 | 3108.53420000 | 12.62730000 |
| 89 | 3110.44670000 | 44.45730000 |
| 90 | 3115.35120000 | 61.82630000 |
| 91 | 3144.21240000 | 1.15330000 |
| 92 | 3147.24600000 | 22.11370000 |
| 93 | 3166.25310000 | 4.96030000 |

### *4.2 2nd rotamer of 4*

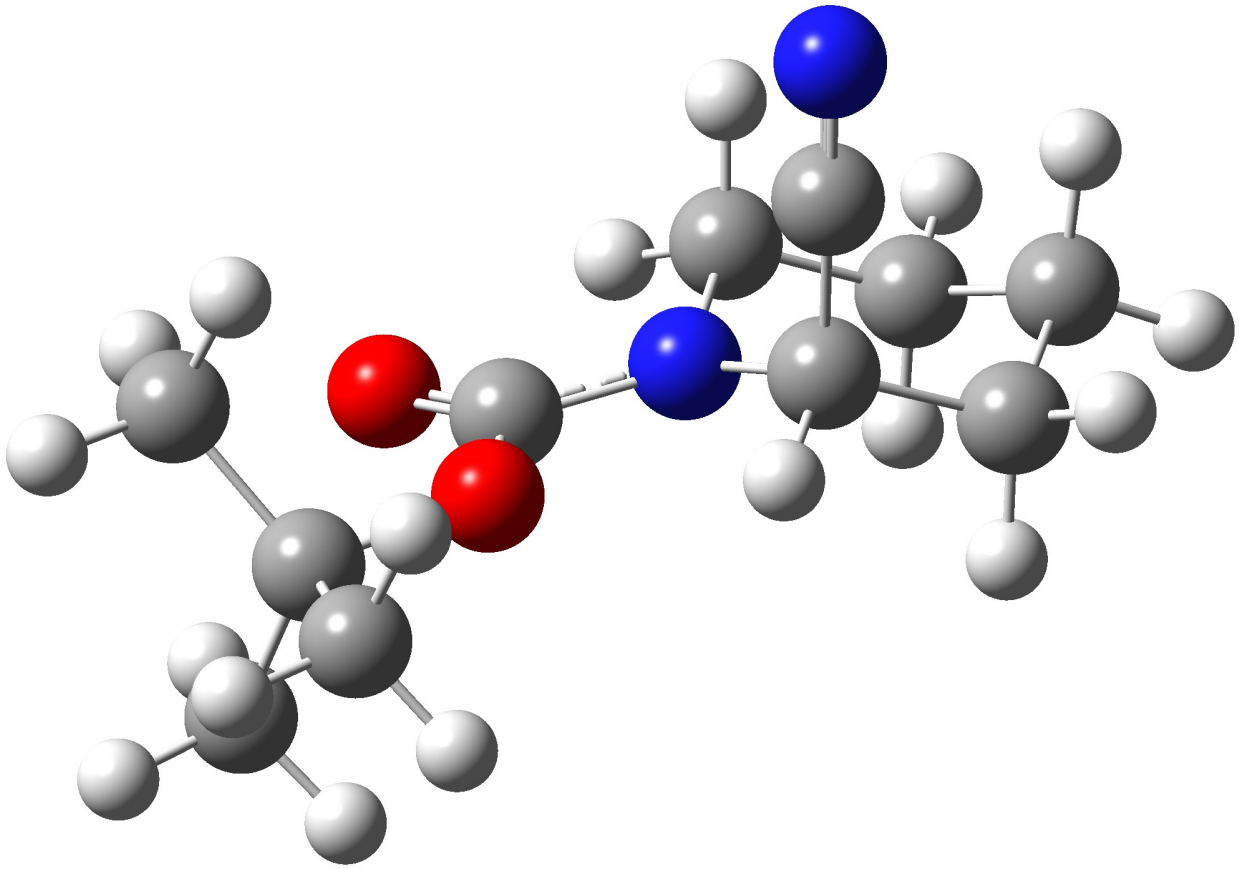

Figure S2: 2nd rotamer of **4**

| | | | |
|---|---|---|---|
| Route | : | # opt freq b3lyp/6-311g(d,p) scrf=(solvent=diethylether) geom=connectivity empiricaldispersion=gd3bj int=ultrafine pop=(regular,mk) | |
| SMILES | : | CC(C)(C)OC(=O)N1CCCCC1C#N | |
| Formula | : | $C_{11}H_{18}N_2O_2$ | |
| Charge | : | 0 | |
| Multiplicity | : | 1 | |
| Dipole | : | 10.6334 | Debye |
| Energy | : | -690.23722685 | a.u. |
| Gibbs Energy | : | -689.99767700 | a.u. |

*4.2.1 Cartesian Co-ordinates (XYZ format)*

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| | | | |
|---|---|---|---|
| C | -2.19942999 | -1.52823198 | -0.92590398 |
| C | -1.94777906 | 0.95107299 | -0.87313598 |
| C | -2.27751899 | 0.95040399 | 0.63196301 |

| | | | |
|---|---|---|---|
| C | -1.90434504 | -0.37582800 | 1.29566097 |
| C | -2.56467009 | -1.54303801 | 0.55610001 |
| H | -2.75032592 | -2.27977204 | -1.48428905 |
| H | -1.12793803 | -1.73520994 | -1.05171597 |
| H | -1.76865602 | 1.79247904 | 1.10586905 |
| H | -3.35433292 | 1.12121999 | 0.71689802 |
| H | -0.81543303 | -0.50029999 | 1.28295505 |
| H | -2.20956492 | -0.36143401 | 2.34446597 |
| H | -2.25435996 | -2.49817705 | 0.98728597 |
| H | -3.65309596 | -1.47519004 | 0.65666699 |
| N | -2.51416898 | -0.22607900 | -1.52752399 |
| C | -2.95725894 | -0.19089900 | -2.83110809 |
| O | -3.30607200 | -1.17983103 | -3.44632292 |
| O | -2.96652389 | 1.06978703 | -3.30195689 |
| C | -3.41425490 | 1.37583399 | -4.67815495 |
| C | -2.50219107 | 0.67633998 | -5.68374300 |
| C | -4.88149691 | 0.98711300 | -4.84534121 |
| C | -3.23972011 | 2.88989401 | -4.74771881 |
| H | -1.45884395 | 0.93410802 | -5.48766184 |
| H | -2.61727595 | -0.40431601 | -5.63214016 |
| H | -2.75472403 | 1.01163197 | -6.69242477 |
| H | -5.48753119 | 1.46014404 | -4.06891680 |
| H | -5.23798418 | 1.33643103 | -5.81729794 |
| H | -5.01006413 | -0.09183200 | -4.78951216 |
| H | -3.53340697 | 3.25150394 | -5.73511219 |
| H | -3.86184692 | 3.38251090 | -3.99752903 |
| H | -2.19723892 | 3.16276693 | -4.57223415 |
| C | -0.48745099 | 1.00675297 | -1.09986699 |
| N | 0.65114200 | 1.02595496 | -1.27871597 |
| H | -2.37563109 | 1.83588302 | -1.33799005 |

*4.2.2 Frequencies*

| **Mode** | **IR frequency** | **IR intensity** |
|---|---|---|
| 1 | 17.44460000 | 2.32220000 |
| 2 | 34.36320000 | 1.30730000 |
| 3 | 72.77520000 | 4.71620000 |
| 4 | 103.26300000 | 3.39250000 |
| 5 | 112.96120000 | 2.22780000 |
| 6 | 125.71570000 | 1.82510000 |
| 7 | 143.22420000 | 2.24360000 |
| 8 | 208.34870000 | 0.11310000 |
| 9 | 224.03990000 | 6.89590000 |
| 10 | 247.79120000 | 1.69400000 |
| 11 | 256.41560000 | 0.74470000 |
| 12 | 273.13770000 | 0.07830000 |
| 13 | 278.70440000 | 5.00200000 |
| 14 | 302.57820000 | 0.32860000 |
| 15 | 342.93710000 | 20.94630000 |
| 16 | 351.33130000 | 3.56860000 |
| 17 | 367.96540000 | 1.74380000 |
| 18 | 398.31090000 | 6.17490000 |
| 19 | 419.86940000 | 0.39060000 |

| | | |
|---|---|---|
| 20 | 443.46440000 | 3.06140000 |
| 21 | 458.70670000 | 3.87630000 |
| 22 | 500.46900000 | 0.43720000 |
| 23 | 511.74840000 | 9.10240000 |
| 24 | 570.46720000 | 7.18430000 |
| 25 | 625.67530000 | 5.29280000 |
| 26 | 721.33880000 | 9.18400000 |
| 27 | 764.50460000 | 8.01600000 |
| 28 | 776.79430000 | 32.34980000 |
| 29 | 808.40350000 | 5.46630000 |
| 30 | 825.51710000 | 4.70110000 |
| 31 | 857.02150000 | 5.17710000 |
| 32 | 868.13790000 | 41.87120000 |
| 33 | 877.07320000 | 47.19120000 |
| 34 | 929.55980000 | 0.16540000 |
| 35 | 930.23530000 | 1.60480000 |
| 36 | 937.50630000 | 17.56700000 |
| 37 | 946.41750000 | 3.52700000 |
| 38 | 972.01920000 | 0.15390000 |
| 39 | 1005.94360000 | 23.72770000 |
| 40 | 1049.61190000 | 68.88470000 |
| 41 | 1052.85700000 | 0.79100000 |
| 42 | 1058.02260000 | 0.91930000 |
| 43 | 1085.17330000 | 3.19730000 |
| 44 | 1110.88310000 | 77.35410000 |
| 45 | 1140.13320000 | 102.15560000 |
| 46 | 1154.43600000 | 19.38450000 |
| 47 | 1179.55690000 | 526.64760000 |
| 48 | 1204.64170000 | 17.60200000 |
| 49 | 1258.88350000 | 109.57610000 |
| 50 | 1270.67430000 | 21.65260000 |
| 51 | 1282.68800000 | 58.67620000 |
| 52 | 1292.42460000 | 8.62000000 |
| 53 | 1296.59390000 | 173.38470000 |
| 54 | 1309.49900000 | 7.82120000 |
| 55 | 1354.35270000 | 126.01730000 |
| 56 | 1365.12890000 | 22.70470000 |
| 57 | 1384.15510000 | 24.65430000 |
| 58 | 1388.45640000 | 0.97050000 |
| 59 | 1396.53880000 | 28.78480000 |
| 60 | 1398.48310000 | 32.88480000 |
| 61 | 1404.97780000 | 38.42350000 |
| 62 | 1423.07730000 | 45.00700000 |
| 63 | 1425.26150000 | 277.63870000 |
| 64 | 1467.66360000 | 0.42900000 |
| 65 | 1475.65040000 | 5.79040000 |
| 66 | 1483.87950000 | 12.27510000 |
| 67 | 1486.60530000 | 2.66810000 |
| 68 | 1487.30100000 | 0.03140000 |
| 69 | 1490.53320000 | 26.13810000 |
| 70 | 1493.06910000 | 6.45330000 |
| 71 | 1501.33780000 | 1.90000000 |
| 72 | 1507.22470000 | 9.87500000 |
| 73 | 1521.90510000 | 25.30290000 |
| 74 | 1744.01060000 | 566.24870000 |

| | | |
|---|---|---|
| 75 | 2345.33470000 | 9.42640000 |
| 76 | 2992.57200000 | 42.44280000 |
| 77 | 3021.95330000 | 17.34910000 |
| 78 | 3030.47400000 | 47.93360000 |
| 79 | 3036.96030000 | 13.60840000 |
| 80 | 3039.14740000 | 33.26650000 |
| 81 | 3045.23980000 | 21.26030000 |
| 82 | 3045.97840000 | 21.31550000 |
| 83 | 3076.09320000 | 52.09850000 |
| 84 | 3079.61940000 | 57.68560000 |
| 85 | 3093.12770000 | 35.64910000 |
| 86 | 3100.56710000 | 9.69180000 |
| 87 | 3103.37830000 | 21.18420000 |
| 88 | 3109.91510000 | 45.09180000 |
| 89 | 3115.75810000 | 61.67400000 |
| 90 | 3132.23090000 | 5.38800000 |
| 91 | 3143.62190000 | 1.17360000 |
| 92 | 3146.89210000 | 20.05720000 |
| 93 | 3147.36680000 | 7.42030000 |

### *4.3 1st rotamer of 4 with chelated bridged Mg dimer*

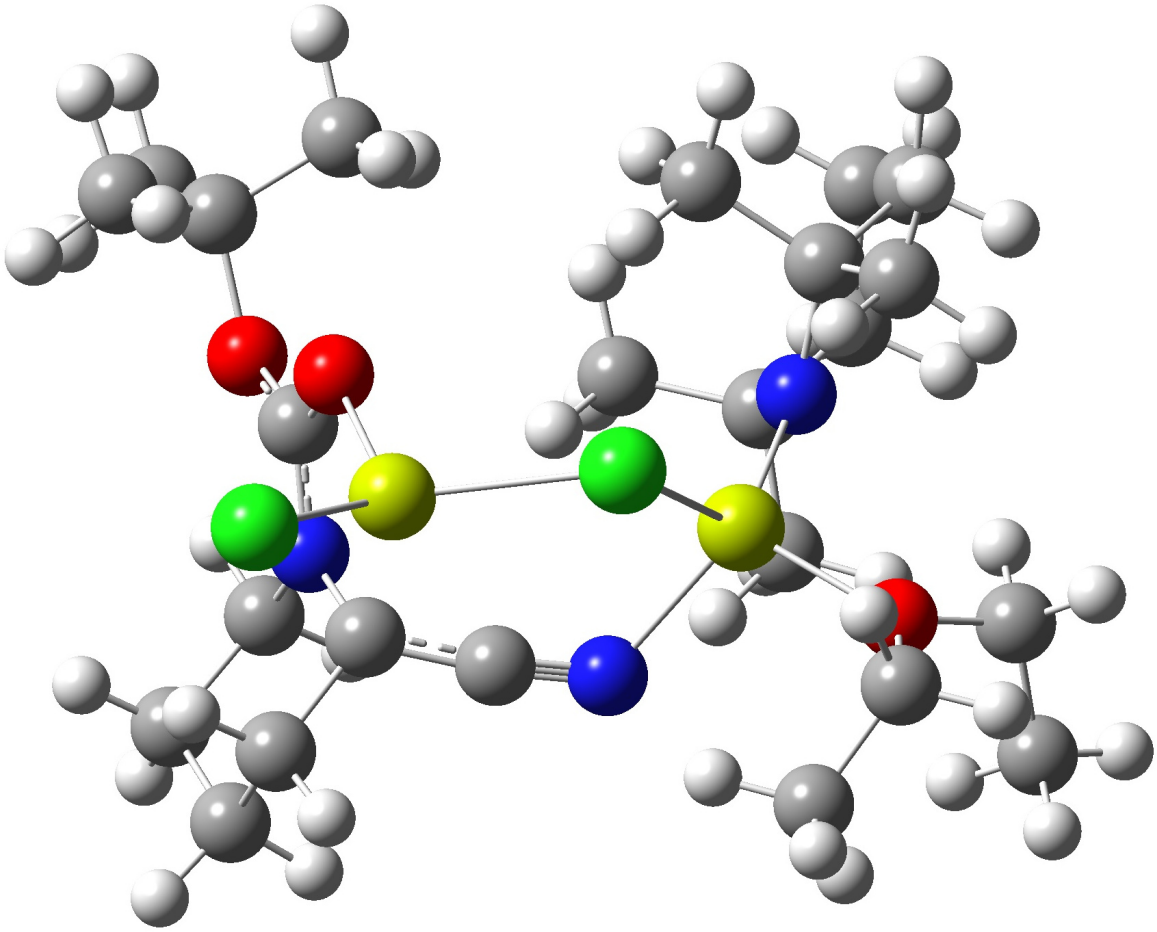

Figure S3: 1st rotamer of **4** with chelated bridged Mg dimer

| | | | |
|---|---|---|---|
| Route | : | # opt freq b3lyp/6-311g(d,p) scrf=(solvent=diethylether) geom=connectivity empiricaldispersion=gd3bj int=ultrafine pop=(regular,mk) | |
| SMILES | : | CCO(CC)[Mg]1(N=[C][C]2CCCCN2[C](O[Mg](Cl1)Cl)OC(C)(C)C)N3C(CCCC3(C)C)(C)C | |
| Formula | : | $C_{24}H_{45}Cl_2Mg_2N_3O_3$ | |
| Charge | : | 0 | |
| Multiplicity | : | 1 | |
| Dipole | : | 20.7324 | Debye |
| Energy | : | -2653.12437408 | a.u. |
| Gibbs Energy | : | -2652.52840400 | a.u. |

*4.3.1 Cartesian Co-ordinates (XYZ format)*

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| | | | |
|---|---|---|---|
| C | -2.91936994 | -0.15763500 | -2.52398491 |
| C | -1.85763097 | -1.68479395 | -0.84978002 |
| C | -2.68504000 | -2.86707211 | -1.35483694 |
| C | -3.10280299 | -2.67034006 | -2.81997991 |
| C | -3.79315591 | -1.31501806 | -3.01325893 |
| H | -3.44895005 | 0.78915799 | -2.57238007 |
| H | -2.01458812 | -0.07545400 | -3.13666010 |
| H | -2.11260796 | -3.78945804 | -1.23202503 |
| H | -3.57533908 | -2.96360302 | -0.72563499 |
| H | -2.21155596 | -2.71903992 | -3.45730805 |
| H | -3.76836610 | -3.47881103 | -3.13536906 |
| H | -4.03414106 | -1.15141106 | -4.06715822 |
| H | -4.73742104 | -1.30057096 | -2.45770502 |
| N | -2.50128889 | -0.39829099 | -1.13386905 |
| C | -2.71107507 | 0.46449500 | -0.11964700 |
| O | -2.37700796 | 0.20244300 | 1.05927801 |
| O | -3.28746200 | 1.59708905 | -0.47566399 |
| C | -3.70809197 | 2.63415909 | 0.51463097 |
| C | -4.72567511 | 2.03221512 | 1.47828496 |
| C | -2.47997999 | 3.19844389 | 1.21918595 |
| C | -4.35339403 | 3.68080592 | -0.38635701 |
| H | -5.54615593 | 1.57044899 | 0.92443800 |
| H | -4.26864290 | 1.28763199 | 2.12683296 |
| H | -5.14001417 | 2.82963395 | 2.09927011 |
| H | -1.75936306 | 3.56400490 | 0.48612899 |
| H | -2.78677893 | 4.03840399 | 1.84670103 |
| H | -1.99904299 | 2.45045304 | 1.84484994 |
| H | -4.70525789 | 4.51799011 | 0.21918400 |
| H | -3.63131595 | 4.05612087 | -1.11385298 |
| H | -5.20442915 | 3.25593591 | -0.92200100 |
| C | -0.50496602 | -1.64486897 | -1.20840394 |
| N | 0.65331900 | -1.55160201 | -1.35499597 |
| Mg | -1.67487204 | -1.65595102 | 1.44893003 |
| Mg | 1.91166103 | -0.61963600 | 0.06940300 |
| Cl | 0.66671097 | -1.53315496 | 2.00234103 |

| | | | |
|---|---|---|---|
| N | 2.36980891 | 1.29997396 | -0.07423600 |
| O | 3.58796692 | -1.76878905 | 0.19926800 |
| C | 2.02347589 | 2.05281806 | -1.29019701 |
| C | 2.56161404 | 2.04298902 | 1.18441999 |
| C | 3.68112397 | -3.09896398 | 0.77543402 |
| H | 3.30436993 | -3.01791406 | 1.79589498 |
| H | 4.73774195 | -3.36863804 | 0.81974399 |
| C | 4.79921007 | -1.23170900 | -0.39543799 |
| H | 4.59093904 | -0.16603200 | -0.50296801 |
| H | 5.61122417 | -1.35839605 | 0.32544699 |
| C | 5.11799479 | -1.87602603 | -1.73056495 |
| H | 5.33083677 | -2.94234991 | -1.62877202 |
| H | 4.28593922 | -1.75035906 | -2.42660403 |
| H | 6.00127411 | -1.39672196 | -2.16089296 |
| C | 2.87848306 | -4.10851622 | -0.02274200 |
| H | 3.24319911 | -4.18422222 | -1.04838896 |
| H | 2.96013188 | -5.09073496 | 0.45025799 |
| H | 1.82301402 | -3.83262396 | -0.04918600 |
| C | 1.23439300 | 2.42315507 | 1.89363098 |
| H | 0.60458398 | 1.53820801 | 2.00912189 |
| H | 1.42328095 | 2.83929110 | 2.88961697 |
| H | 0.66645700 | 3.16303802 | 1.33149803 |
| C | 3.40814400 | 3.32000208 | 0.98139799 |
| H | 3.43713307 | 3.89081907 | 1.91617501 |
| H | 4.43800306 | 3.01596308 | 0.75713903 |
| C | 2.86842895 | 3.33924794 | -1.44027805 |
| H | 2.49570298 | 3.92287397 | -2.28947806 |
| H | 3.89672494 | 3.04302192 | -1.68092501 |
| C | 0.51718801 | 2.41828990 | -1.38486004 |
| H | -0.09373800 | 1.52534103 | -1.22907400 |
| H | 0.22677200 | 3.15042710 | -0.63255799 |
| H | 0.26739499 | 2.83507299 | -2.36711597 |
| C | 2.34721088 | 1.16456604 | -2.50520897 |
| H | 3.39661407 | 0.85998201 | -2.47728610 |
| H | 1.72550297 | 0.26636699 | -2.52780390 |
| H | 2.17044806 | 1.70420599 | -3.44073892 |
| C | 3.34356689 | 1.13519204 | 2.15162492 |
| H | 3.54905009 | 1.65458405 | 3.09217906 |
| H | 2.78004909 | 0.23323800 | 2.41013503 |
| H | 4.29515505 | 0.83639300 | 1.70695400 |
| C | 2.89747405 | 4.18104076 | -0.16910499 |
| H | 1.89882600 | 4.57008791 | 0.05744400 |
| H | 3.54288912 | 5.05492496 | -0.30686599 |
| Cl | -3.05321789 | -3.10576296 | 2.58792901 |

*4.3.2 Frequencies*

| **Mode** | **IR frequency** | **IR intensity** |
|---|---|---|
| 1 | 16.89090000 | 1.21590000 |
| 2 | 22.27430000 | 0.77850000 |
| 3 | 27.12500000 | 0.88950000 |
| 4 | 32.93240000 | 0.82620000 |
| 5 | 38.81430000 | 0.66350000 |

| | | |
|---|---|---|
| 6 | 40.63350000 | 0.89550000 |
| 7 | 44.46440000 | 0.90580000 |
| 8 | 49.26080000 | 1.60250000 |
| 9 | 56.87480000 | 8.62970000 |
| 10 | 61.88990000 | 3.17160000 |
| 11 | 66.17880000 | 3.00810000 |
| 12 | 70.38280000 | 4.19300000 |
| 13 | 72.95720000 | 7.18590000 |
| 14 | 83.30870000 | 2.97080000 |
| 15 | 92.81140000 | 3.82840000 |
| 16 | 94.32800000 | 1.75400000 |
| 17 | 97.68270000 | 3.25770000 |
| 18 | 116.66800000 | 7.73940000 |
| 19 | 119.74820000 | 1.17280000 |
| 20 | 122.94850000 | 1.58750000 |
| 21 | 128.68100000 | 1.50900000 |
| 22 | 134.84590000 | 3.72900000 |
| 23 | 136.81810000 | 2.75230000 |
| 24 | 158.41640000 | 0.78010000 |
| 25 | 167.99510000 | 13.97600000 |
| 26 | 172.91820000 | 1.18920000 |
| 27 | 191.45370000 | 18.01740000 |
| 28 | 200.68370000 | 1.43110000 |
| 29 | 201.21840000 | 3.67150000 |
| 30 | 205.62190000 | 15.64140000 |
| 31 | 211.95470000 | 1.01360000 |
| 32 | 218.31230000 | 2.76870000 |
| 33 | 239.49870000 | 1.39820000 |
| 34 | 244.33900000 | 0.56720000 |
| 35 | 253.40550000 | 4.71210000 |
| 36 | 258.53600000 | 8.05560000 |
| 37 | 266.10860000 | 1.93660000 |
| 38 | 266.62200000 | 20.62470000 |
| 39 | 272.54870000 | 0.72030000 |
| 40 | 275.95710000 | 6.84940000 |
| 41 | 285.08200000 | 1.12950000 |
| 42 | 293.53600000 | 21.70010000 |
| 43 | 294.38420000 | 25.89960000 |
| 44 | 301.36870000 | 12.50690000 |
| 45 | 305.27950000 | 12.68570000 |
| 46 | 319.36060000 | 47.75460000 |
| 47 | 321.56660000 | 19.23680000 |
| 48 | 326.65970000 | 9.20220000 |
| 49 | 337.58750000 | 10.94080000 |
| 50 | 343.27040000 | 13.38600000 |
| 51 | 351.05300000 | 8.31420000 |
| 52 | 364.24440000 | 7.49370000 |
| 53 | 376.97010000 | 144.01020000 |
| 54 | 392.04540000 | 25.84330000 |
| 55 | 402.20560000 | 40.94910000 |
| 56 | 412.97540000 | 93.97470000 |
| 57 | 413.40600000 | 0.81320000 |
| 58 | 419.69010000 | 1.93620000 |
| 59 | 425.01630000 | 31.28870000 |
| 60 | 431.79260000 | 42.84470000 |

| | | |
|---|---|---|
| 61 | 441.55100000 | 35.51890000 |
| 62 | 456.53190000 | 3.66740000 |
| 63 | 469.57650000 | 2.73210000 |
| 64 | 475.08850000 | 80.54420000 |
| 65 | 491.39120000 | 29.17450000 |
| 66 | 496.70860000 | 0.68510000 |
| 67 | 510.33500000 | 33.37910000 |
| 68 | 517.05270000 | 36.34640000 |
| 69 | 527.56980000 | 25.25130000 |
| 70 | 540.19090000 | 57.59950000 |
| 71 | 549.48440000 | 16.78150000 |
| 72 | 590.71690000 | 5.75670000 |
| 73 | 620.83370000 | 10.81660000 |
| 74 | 653.56920000 | 11.60850000 |
| 75 | 696.52620000 | 36.55990000 |
| 76 | 739.57700000 | 43.34980000 |
| 77 | 744.50300000 | 18.87400000 |
| 78 | 759.99720000 | 0.91170000 |
| 79 | 773.99100000 | 40.10670000 |
| 80 | 786.59860000 | 47.87490000 |
| 81 | 803.53970000 | 12.41710000 |
| 82 | 811.16910000 | 14.11750000 |
| 83 | 823.88610000 | 9.37640000 |
| 84 | 844.00150000 | 59.31780000 |
| 85 | 846.87360000 | 11.28660000 |
| 86 | 859.89670000 | 11.56220000 |
| 87 | 860.18390000 | 5.28410000 |
| 88 | 866.39870000 | 4.25440000 |
| 89 | 908.83370000 | 4.12360000 |
| 90 | 909.80830000 | 42.76750000 |
| 91 | 910.93430000 | 2.28670000 |
| 92 | 911.29740000 | 17.53450000 |
| 93 | 915.72170000 | 3.59440000 |
| 94 | 920.65560000 | 42.47100000 |
| 95 | 924.58860000 | 16.92310000 |
| 96 | 931.20350000 | 0.16450000 |
| 97 | 935.30940000 | 8.40690000 |
| 98 | 953.16570000 | 13.87680000 |
| 99 | 961.74910000 | 4.27620000 |
| 100 | 975.36080000 | 0.39320000 |
| 101 | 976.37800000 | 7.35760000 |
| 102 | 1005.37030000 | 1.72680000 |
| 103 | 1008.26160000 | 0.32380000 |
| 104 | 1014.38080000 | 50.93400000 |
| 105 | 1036.15540000 | 58.07710000 |
| 106 | 1054.11540000 | 4.00370000 |
| 107 | 1054.48070000 | 21.98980000 |
| 108 | 1055.28080000 | 206.63280000 |
| 109 | 1057.83430000 | 46.09230000 |
| 110 | 1062.48310000 | 1.33310000 |
| 111 | 1068.29840000 | 2.02370000 |
| 112 | 1069.72760000 | 3.25810000 |
| 113 | 1090.17850000 | 20.49500000 |
| 114 | 1093.99740000 | 4.11280000 |
| 115 | 1108.87170000 | 27.78320000 |

| | | |
|---|---|---|
| 116 | 1114.36350000 | 13.74610000 |
| 117 | 1148.34710000 | 83.84020000 |
| 118 | 1151.72000000 | 7.71550000 |
| 119 | 1159.63880000 | 0.86680000 |
| 120 | 1177.95290000 | 37.92040000 |
| 121 | 1179.20000000 | 435.26650000 |
| 122 | 1190.96180000 | 15.89490000 |
| 123 | 1193.47050000 | 34.88110000 |
| 124 | 1213.76120000 | 0.17840000 |
| 125 | 1218.18000000 | 7.86220000 |
| 126 | 1220.49360000 | 14.61710000 |
| 127 | 1230.30470000 | 56.25190000 |
| 128 | 1244.39330000 | 3.53580000 |
| 129 | 1258.19120000 | 19.50260000 |
| 130 | 1258.52870000 | 55.08760000 |
| 131 | 1260.48770000 | 44.73210000 |
| 132 | 1274.89600000 | 26.07540000 |
| 133 | 1282.18410000 | 64.61110000 |
| 134 | 1306.70850000 | 121.88390000 |
| 135 | 1314.94690000 | 5.11340000 |
| 136 | 1318.87550000 | 8.75860000 |
| 137 | 1319.34510000 | 7.47480000 |
| 138 | 1347.99010000 | 6.15410000 |
| 139 | 1360.33630000 | 5.24050000 |
| 140 | 1364.18090000 | 0.38840000 |
| 141 | 1369.25320000 | 1.61950000 |
| 142 | 1372.02710000 | 5.55430000 |
| 143 | 1376.30790000 | 0.79580000 |
| 144 | 1382.19010000 | 2.04470000 |
| 145 | 1382.43270000 | 0.92360000 |
| 146 | 1389.66320000 | 30.16710000 |
| 147 | 1390.71590000 | 23.32970000 |
| 148 | 1400.32650000 | 9.21620000 |
| 149 | 1400.96340000 | 23.74520000 |
| 150 | 1402.34690000 | 20.54580000 |
| 151 | 1405.10590000 | 21.55610000 |
| 152 | 1408.79640000 | 3.61930000 |
| 153 | 1409.47750000 | 3.61000000 |
| 154 | 1422.97520000 | 19.84080000 |
| 155 | 1425.74630000 | 19.59750000 |
| 156 | 1426.20330000 | 15.83260000 |
| 157 | 1467.82200000 | 1.67680000 |
| 158 | 1470.15800000 | 1.30830000 |
| 159 | 1472.42620000 | 205.56860000 |
| 160 | 1475.77850000 | 43.53480000 |
| 161 | 1476.69100000 | 250.22370000 |
| 162 | 1478.28140000 | 8.22700000 |
| 163 | 1480.84670000 | 9.07180000 |
| 164 | 1482.34730000 | 2.23150000 |
| 165 | 1482.60460000 | 4.14230000 |
| 166 | 1483.32370000 | 4.74080000 |
| 167 | 1484.26620000 | 3.23160000 |
| 168 | 1486.31430000 | 0.86470000 |
| 169 | 1487.89290000 | 1.32550000 |
| 170 | 1489.79140000 | 43.50040000 |

| | | |
|---|---|---|
| 171 | 1490.55540000 | 26.59360000 |
| 172 | 1492.34320000 | 2.13140000 |
| 173 | 1493.48680000 | 7.61700000 |
| 174 | 1495.01920000 | 4.71970000 |
| 175 | 1499.54050000 | 5.11620000 |
| 176 | 1500.57300000 | 4.23710000 |
| 177 | 1502.73710000 | 7.68600000 |
| 178 | 1507.06200000 | 71.41680000 |
| 179 | 1507.90510000 | 58.21390000 |
| 180 | 1510.00140000 | 10.12570000 |
| 181 | 1511.09760000 | 9.09350000 |
| 182 | 1516.18390000 | 47.24860000 |
| 183 | 1519.39830000 | 16.52660000 |
| 184 | 1524.35430000 | 101.39910000 |
| 185 | 1623.63130000 | 561.10980000 |
| 186 | 2203.87380000 | 712.57250000 |
| 187 | 2995.99510000 | 34.62840000 |
| 188 | 2998.82080000 | 60.44240000 |
| 189 | 3010.64550000 | 29.66310000 |
| 190 | 3012.14300000 | 34.60210000 |
| 191 | 3013.04530000 | 40.33890000 |
| 192 | 3014.35320000 | 52.24530000 |
| 193 | 3018.98070000 | 17.42250000 |
| 194 | 3022.00530000 | 94.05440000 |
| 195 | 3023.28020000 | 16.04440000 |
| 196 | 3027.61930000 | 48.29910000 |
| 197 | 3033.05610000 | 21.07890000 |
| 198 | 3034.46130000 | 15.14080000 |
| 199 | 3036.57750000 | 80.16890000 |
| 200 | 3037.30910000 | 88.59780000 |
| 201 | 3040.96040000 | 27.54610000 |
| 202 | 3041.30360000 | 13.24600000 |
| 203 | 3041.63540000 | 23.27790000 |
| 204 | 3045.08000000 | 25.69200000 |
| 205 | 3050.35630000 | 115.91330000 |
| 206 | 3053.00080000 | 17.50060000 |
| 207 | 3060.51090000 | 34.33420000 |
| 208 | 3063.58550000 | 83.03670000 |
| 209 | 3072.73610000 | 57.18950000 |
| 210 | 3075.07450000 | 16.05680000 |
| 211 | 3076.65330000 | 23.92720000 |
| 212 | 3081.83200000 | 36.16780000 |
| 213 | 3082.40500000 | 129.08000000 |
| 214 | 3083.93400000 | 103.56720000 |
| 215 | 3090.14560000 | 9.01590000 |
| 216 | 3098.16370000 | 47.69900000 |
| 217 | 3099.79990000 | 45.69480000 |
| 218 | 3101.96980000 | 2.28910000 |
| 219 | 3102.16120000 | 39.62700000 |
| 220 | 3106.42930000 | 11.09600000 |
| 221 | 3108.19070000 | 34.84970000 |
| 222 | 3112.74120000 | 9.07080000 |
| 223 | 3113.96390000 | 22.35130000 |
| 224 | 3115.06210000 | 35.97590000 |
| 225 | 3115.79940000 | 40.02820000 |

| | | |
|---|---|---|
| 226 | 3120.60210000 | 59.41640000 |
| 227 | 3126.81430000 | 45.27930000 |
| 228 | 3133.72210000 | 51.43740000 |
| 229 | 3145.76820000 | 9.43790000 |
| 230 | 3153.89420000 | 8.80420000 |
| 231 | 3156.59220000 | 11.89650000 |

### *4.4 2nd rotamer of 4 with non-chelated bridged Mg dimer*

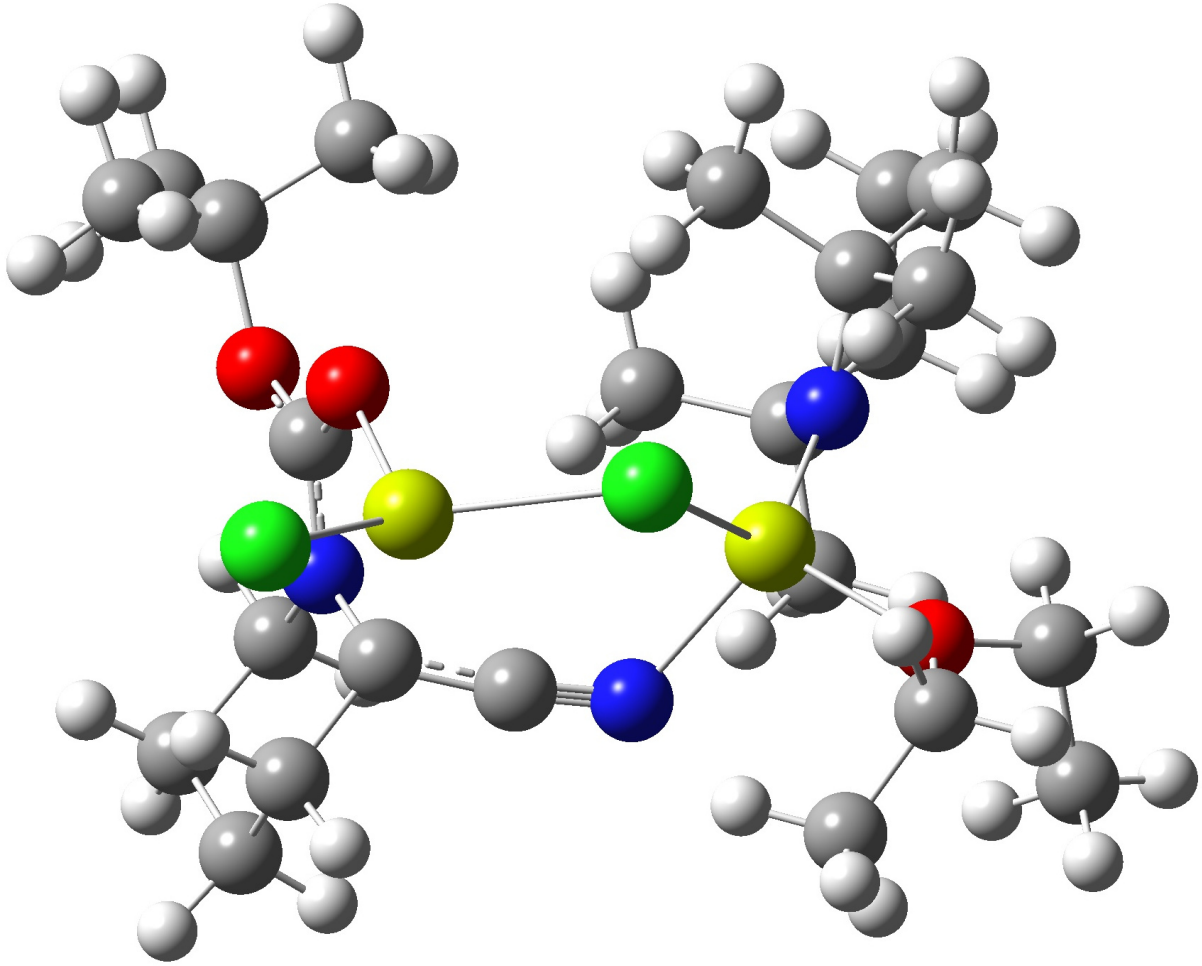

Figure S4: 2nd rotamer of **4** with non-chelated bridged Mg dimer

| | | | |
|---|---|---|---|
| Route | : | # opt freq b3lyp/6-311g(d,p) scrf=(solvent=diethylether) geom=connectivity empiricaldispersion=gd3bj int=ultrafine pop=(regular,mk) | |
| SMILES | : | CCO(CC)[Mg](Cl)Cl[Mg]([N][C][C]1CCCCN1C(=O)OC(C)(C)C)(N2C(CCCC2(C)C)(C)C)O(CC)CC | |
| Formula | : | $C_{28}H_{55}Cl_2Mg_2N_3O_4$ | |
| Charge | : | 0 | |
| Multiplicity | : | 1 | |
| Dipole | : | 37.8604 | Debye |
| Energy | : | -2886.87250936 | a.u. |
| Gibbs Energy | : | -2886.14305300 | a.u. |

*4.4.1 Cartesian Co-ordinates (XYZ format)*

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| | | | |
|---|---|---|---|
| C | -3.83969092 | 1.40514696 | 1.12875795 |
| C | -2.11899090 | 0.66254503 | -0.43640700 |
| C | -3.12154603 | 0.54623801 | -1.59571004 |
| C | -4.52029085 | 0.25569701 | -1.03518701 |
| C | -4.91840506 | 1.26903498 | 0.04745500 |
| H | -3.74675202 | 0.49037600 | 1.71946895 |
| H | -4.07146215 | 2.21526003 | 1.81486297 |
| H | -3.13703704 | 1.48952401 | -2.15812397 |
| H | -2.81519103 | -0.24036500 | -2.28857589 |
| H | -5.25604391 | 0.26301599 | -1.84462595 |
| H | -4.52376699 | -0.75131202 | -0.60786301 |
| H | -5.07313681 | 2.25267601 | -0.40953901 |
| H | -5.86609411 | 0.97910100 | 0.51139098 |
| N | -2.53813195 | 1.69379902 | 0.51409501 |
| C | -2.20226598 | 3.02567410 | 0.39010900 |
| O | -2.70745707 | 3.91497993 | 1.05317402 |
| O | -1.23810196 | 3.20019007 | -0.53240800 |
| C | -0.59475702 | 4.51052809 | -0.74166900 |
| C | -1.62614799 | 5.52896976 | -1.22475100 |
| C | 0.10632100 | 4.94768095 | 0.54260498 |
| C | 0.42058200 | 4.20685005 | -1.83972299 |
| H | -2.14951301 | 5.14463377 | -2.10386109 |
| H | -2.35364103 | 5.74915314 | -0.44675699 |
| H | -1.11522198 | 6.45252609 | -1.50825298 |
| H | 0.79886800 | 4.17187595 | 0.87480801 |
| H | 0.67659599 | 5.86007881 | 0.35168299 |
| H | -0.61528498 | 5.14291000 | 1.33378303 |
| H | 0.98250598 | 5.11077118 | -2.08457398 |
| H | 1.11688197 | 3.43539906 | -1.51150799 |
| H | -0.08625400 | 3.85539889 | -2.74100304 |
| C | -0.77456301 | 0.68422300 | -0.81249797 |
| N | 0.34313801 | 0.52633399 | -1.11887097 |
| Mg | -1.83989799 | -1.30967605 | 0.74046302 |
| Mg | 1.80675197 | -0.84441203 | -0.51397699 |
| Cl | -1.66291499 | -1.04820001 | 3.03084803 |
| Cl | 0.07208100 | -2.56310105 | -0.08270200 |
| N | 3.30015802 | -0.31987900 | 0.67442900 |
| O | -3.28869700 | -2.75503397 | 0.40332901 |
| O | 2.54906392 | -1.69477201 | -2.21970296 |
| C | 3.55533195 | 1.11039901 | 0.91570097 |
| C | 3.72177792 | -1.29389596 | 1.69702601 |
| C | 1.82150602 | -2.54150510 | -3.14659190 |
| H | 1.41671097 | -3.36727810 | -2.56009889 |
| H | 2.53761196 | -2.94746494 | -3.86293507 |
| C | 3.93877292 | -1.42610097 | -2.54635191 |
| H | 4.34933090 | -1.01260602 | -1.62383902 |
| H | 4.42700195 | -2.38266206 | -2.75190210 |
| C | 4.07555819 | -0.45641801 | -3.70398593 |
| H | 3.66629291 | -0.86443901 | -4.63093710 |
| H | 3.56500196 | 0.48226500 | -3.47935510 |
| H | 5.13406086 | -0.24027900 | -3.87122893 |
| C | 0.71384001 | -1.77238095 | -3.84075308 |
| H | 1.11417401 | -0.94207102 | -4.42499304 |

| | | | |
|---|---|---|---|
| H | 0.17080399 | -2.44253111 | -4.51266718 |
| H | 0.00693700 | -1.37192595 | -3.11277509 |
| C | -4.13779116 | -3.14217997 | 1.52667105 |
| H | -3.77376604 | -2.57283092 | 2.38001895 |
| H | -3.96213102 | -4.20139217 | 1.72835195 |
| C | -5.59726095 | -2.84546208 | 1.24368000 |
| H | -5.95618677 | -3.37076211 | 0.35572001 |
| H | -6.20253086 | -3.16965294 | 2.09397888 |
| H | -5.75374222 | -1.77477705 | 1.10221195 |
| C | -3.19265795 | -3.78062797 | -0.62595499 |
| H | -2.37475991 | -4.45086098 | -0.35066599 |
| H | -4.12655783 | -4.34416723 | -0.61680198 |
| C | -2.96873498 | -3.15831304 | -1.98750305 |
| H | -2.02891302 | -2.60596991 | -2.02589297 |
| H | -2.91318989 | -3.95438290 | -2.73398495 |
| H | -3.79175401 | -2.49350500 | -2.25353289 |
| C | 2.74865103 | -1.40451396 | 2.90111399 |
| H | 1.72927201 | -1.58283305 | 2.55046797 |
| H | 3.03023100 | -2.23394394 | 3.55979300 |
| H | 2.73329711 | -0.49755901 | 3.50456190 |
| C | 5.14488411 | -1.00015295 | 2.22242093 |
| H | 5.37950802 | -1.68377697 | 3.04589510 |
| H | 5.85836601 | -1.20881701 | 1.41540504 |
| C | 4.97430706 | 1.36106205 | 1.47664404 |
| H | 5.07550097 | 2.41652894 | 1.75288701 |
| H | 5.69626093 | 1.16859603 | 0.67322099 |
| C | 2.50811195 | 1.78179801 | 1.84350896 |
| H | 1.50113499 | 1.61002505 | 1.45409703 |
| H | 2.54083800 | 1.38666499 | 2.85798097 |
| H | 2.66848707 | 2.86427593 | 1.90383101 |
| C | 3.47723699 | 1.83664799 | -0.44000700 |
| H | 4.20245600 | 1.41221595 | -1.13854396 |
| H | 2.47991705 | 1.75462699 | -0.88012701 |
| H | 3.69179010 | 2.90355897 | -0.32542801 |
| C | 3.76014495 | -2.67951393 | 1.02679098 |
| H | 4.10226822 | -3.44497705 | 1.72953498 |
| H | 2.76676512 | -2.99066710 | 0.68580598 |
| H | 4.43621492 | -2.66941595 | 0.16895901 |
| C | 5.31500816 | 0.45319799 | 2.65376401 |
| H | 4.66939116 | 0.67644399 | 3.50975800 |
| H | 6.34217310 | 0.63405102 | 2.98797297 |

*4.4.2 Frequencies*

| **Mode** | **IR frequency** | **IR intensity** |
|---|---|---|
| 1 | 16.32510000 | 0.30200000 |
| 2 | 23.71730000 | 1.05840000 |
| 3 | 28.40010000 | 0.51530000 |
| 4 | 32.32260000 | 2.11380000 |
| 5 | 35.45070000 | 1.11630000 |
| 6 | 43.68810000 | 0.13790000 |
| 7 | 46.71200000 | 1.66780000 |
| 8 | 51.49540000 | 0.23330000 |

| | | |
|---|---|---|
| 9 | 55.51220000 | 0.75380000 |
| 10 | 58.01250000 | 1.60350000 |
| 11 | 60.91650000 | 0.91030000 |
| 12 | 67.11270000 | 0.57740000 |
| 13 | 71.29220000 | 3.44420000 |
| 14 | 74.27830000 | 1.85150000 |
| 15 | 81.60060000 | 3.28690000 |
| 16 | 87.63800000 | 2.78760000 |
| 17 | 93.30620000 | 6.44910000 |
| 18 | 94.80410000 | 4.00740000 |
| 19 | 101.36420000 | 1.50370000 |
| 20 | 108.41380000 | 2.18060000 |
| 21 | 116.87890000 | 4.04030000 |
| 22 | 118.42250000 | 5.66070000 |
| 23 | 123.42580000 | 1.13230000 |
| 24 | 126.36150000 | 1.87700000 |
| 25 | 129.87700000 | 2.98970000 |
| 26 | 132.97820000 | 13.65510000 |
| 27 | 139.67320000 | 4.49860000 |
| 28 | 144.28290000 | 4.70660000 |
| 29 | 151.37400000 | 7.62820000 |
| 30 | 163.02720000 | 5.98740000 |
| 31 | 168.46690000 | 2.36300000 |
| 32 | 172.63550000 | 1.38770000 |
| 33 | 181.25040000 | 14.33030000 |
| 34 | 194.29520000 | 7.35760000 |
| 35 | 196.66490000 | 2.27160000 |
| 36 | 205.84080000 | 4.41850000 |
| 37 | 207.62770000 | 0.18470000 |
| 38 | 214.68040000 | 2.47720000 |
| 39 | 224.25750000 | 11.59720000 |
| 40 | 232.63690000 | 5.11310000 |
| 41 | 236.50070000 | 4.42350000 |
| 42 | 242.15950000 | 0.51050000 |
| 43 | 248.91570000 | 0.51410000 |
| 44 | 264.40750000 | 20.40820000 |
| 45 | 267.83350000 | 8.08260000 |
| 46 | 271.66050000 | 0.02040000 |
| 47 | 275.11920000 | 8.49290000 |
| 48 | 282.46490000 | 5.95190000 |
| 49 | 291.26250000 | 57.66560000 |
| 50 | 293.08360000 | 23.48700000 |
| 51 | 304.65430000 | 16.03350000 |
| 52 | 307.87980000 | 6.09540000 |
| 53 | 310.70420000 | 5.76340000 |
| 54 | 313.89550000 | 51.59290000 |
| 55 | 325.67560000 | 18.49690000 |
| 56 | 327.16110000 | 47.01610000 |
| 57 | 328.42810000 | 22.18310000 |
| 58 | 330.04360000 | 36.74880000 |
| 59 | 344.45120000 | 10.28240000 |
| 60 | 348.29390000 | 23.32690000 |
| 61 | 350.22590000 | 2.46780000 |
| 62 | 353.88550000 | 20.38800000 |
| 63 | 364.76100000 | 23.20860000 |

| | | |
|---|---|---|
| 64 | 378.50850000 | 12.54670000 |
| 65 | 396.18330000 | 28.23140000 |
| 66 | 403.02660000 | 110.00490000 |
| 67 | 411.56650000 | 10.43410000 |
| 68 | 416.05910000 | 1.14050000 |
| 69 | 419.31700000 | 12.48170000 |
| 70 | 427.48810000 | 20.51690000 |
| 71 | 436.53600000 | 12.66940000 |
| 72 | 450.34800000 | 17.85860000 |
| 73 | 457.69530000 | 10.26240000 |
| 74 | 461.47450000 | 16.99310000 |
| 75 | 470.65220000 | 4.79420000 |
| 76 | 473.59280000 | 86.42520000 |
| 77 | 499.45290000 | 1.80140000 |
| 78 | 501.90910000 | 5.83810000 |
| 79 | 511.44580000 | 40.05460000 |
| 80 | 515.07570000 | 14.33350000 |
| 81 | 527.90790000 | 21.58470000 |
| 82 | 538.08390000 | 29.47000000 |
| 83 | 540.82160000 | 64.08560000 |
| 84 | 556.30620000 | 3.76550000 |
| 85 | 590.86620000 | 5.42590000 |
| 86 | 598.94490000 | 13.37110000 |
| 87 | 608.98490000 | 20.82760000 |
| 88 | 670.47030000 | 51.34670000 |
| 89 | 743.57360000 | 7.96180000 |
| 90 | 760.47040000 | 1.20460000 |
| 91 | 767.58070000 | 4.54680000 |
| 92 | 773.52360000 | 30.15980000 |
| 93 | 786.19070000 | 41.87510000 |
| 94 | 794.61970000 | 25.52390000 |
| 95 | 797.91110000 | 19.41100000 |
| 96 | 812.96650000 | 16.14650000 |
| 97 | 821.38140000 | 10.88670000 |
| 98 | 843.10550000 | 7.92940000 |
| 99 | 847.11720000 | 11.12330000 |
| 100 | 851.79340000 | 11.12560000 |
| 101 | 859.66960000 | 13.61030000 |
| 102 | 862.52950000 | 1.08530000 |
| 103 | 867.64130000 | 4.77190000 |
| 104 | 874.18670000 | 56.82460000 |
| 105 | 902.68700000 | 6.78780000 |
| 106 | 909.57640000 | 0.88520000 |
| 107 | 910.51790000 | 49.61290000 |
| 108 | 912.84940000 | 21.20160000 |
| 109 | 913.26630000 | 38.42620000 |
| 110 | 916.25730000 | 5.77700000 |
| 111 | 918.54950000 | 28.25620000 |
| 112 | 928.83630000 | 8.37250000 |
| 113 | 929.00040000 | 2.89970000 |
| 114 | 932.00430000 | 6.20590000 |
| 115 | 962.17060000 | 19.73820000 |
| 116 | 962.71230000 | 17.71930000 |
| 117 | 971.31260000 | 0.06290000 |
| 118 | 976.00250000 | 6.57930000 |

| | | |
|---|---|---|
| 119 | 1009.33780000 | 1.69140000 |
| 120 | 1013.13430000 | 0.49630000 |
| 121 | 1015.33280000 | 46.50020000 |
| 122 | 1021.95630000 | 85.91880000 |
| 123 | 1036.50620000 | 65.91150000 |
| 124 | 1039.79870000 | 41.79190000 |
| 125 | 1046.66200000 | 180.45440000 |
| 126 | 1052.67660000 | 0.39410000 |
| 127 | 1055.55680000 | 206.35250000 |
| 128 | 1060.96700000 | 3.65490000 |
| 129 | 1068.18380000 | 2.00520000 |
| 130 | 1071.71880000 | 5.46780000 |
| 131 | 1075.24590000 | 28.68710000 |
| 132 | 1095.08080000 | 4.31930000 |
| 133 | 1106.95800000 | 20.53470000 |
| 134 | 1107.78730000 | 4.23380000 |
| 135 | 1108.52990000 | 33.05300000 |
| 136 | 1114.75890000 | 12.72780000 |
| 137 | 1131.80500000 | 3.79380000 |
| 138 | 1137.34640000 | 117.47180000 |
| 139 | 1147.19780000 | 90.88330000 |
| 140 | 1164.53590000 | 77.41490000 |
| 141 | 1174.46450000 | 20.35070000 |
| 142 | 1177.99230000 | 47.94660000 |
| 143 | 1185.22690000 | 33.99580000 |
| 144 | 1186.86780000 | 411.89740000 |
| 145 | 1194.36270000 | 19.33540000 |
| 146 | 1214.68300000 | 0.12850000 |
| 147 | 1214.87440000 | 21.42220000 |
| 148 | 1217.56080000 | 7.90180000 |
| 149 | 1220.62960000 | 15.02070000 |
| 150 | 1238.69280000 | 32.23160000 |
| 151 | 1245.75910000 | 2.67910000 |
| 152 | 1258.24980000 | 84.12100000 |
| 153 | 1260.76910000 | 50.11120000 |
| 154 | 1270.12010000 | 19.12510000 |
| 155 | 1272.27890000 | 46.58260000 |
| 156 | 1278.72950000 | 78.61780000 |
| 157 | 1296.00310000 | 189.68650000 |
| 158 | 1310.76590000 | 22.72020000 |
| 159 | 1314.88550000 | 4.15370000 |
| 160 | 1320.25140000 | 17.42540000 |
| 161 | 1323.97870000 | 2.25310000 |
| 162 | 1332.42500000 | 11.45870000 |
| 163 | 1346.95090000 | 5.71810000 |
| 164 | 1354.83790000 | 5.54730000 |
| 165 | 1364.54900000 | 0.26560000 |
| 166 | 1371.92580000 | 5.06510000 |
| 167 | 1373.87490000 | 17.93200000 |
| 168 | 1376.56280000 | 0.66070000 |
| 169 | 1384.48720000 | 153.27150000 |
| 170 | 1385.97760000 | 0.88700000 |
| 171 | 1391.05340000 | 20.83140000 |
| 172 | 1394.19620000 | 25.90200000 |
| 173 | 1395.96210000 | 43.91720000 |

| | | |
|---|---|---|
| 174 | 1398.94030000 | 23.27170000 |
| 175 | 1400.19880000 | 1.42300000 |
| 176 | 1402.05490000 | 53.37200000 |
| 177 | 1406.54490000 | 5.25920000 |
| 178 | 1406.88500000 | 21.91070000 |
| 179 | 1408.46190000 | 1.65970000 |
| 180 | 1415.17380000 | 3.12260000 |
| 181 | 1415.55360000 | 9.29280000 |
| 182 | 1422.58810000 | 23.79540000 |
| 183 | 1422.80650000 | 24.13960000 |
| 184 | 1423.65070000 | 13.48020000 |
| 185 | 1427.49030000 | 16.94670000 |
| 186 | 1440.87730000 | 17.06330000 |
| 187 | 1467.33620000 | 0.70480000 |
| 188 | 1471.67150000 | 0.77580000 |
| 189 | 1477.59190000 | 2.67650000 |
| 190 | 1478.58020000 | 3.47650000 |
| 191 | 1478.70450000 | 5.51540000 |
| 192 | 1482.69740000 | 4.81110000 |
| 193 | 1483.33670000 | 3.59800000 |
| 194 | 1484.15550000 | 9.31630000 |
| 195 | 1484.84010000 | 1.66090000 |
| 196 | 1485.70390000 | 6.76790000 |
| 197 | 1486.04670000 | 1.54970000 |
| 198 | 1486.89670000 | 4.62170000 |
| 199 | 1488.85870000 | 3.59130000 |
| 200 | 1491.03270000 | 23.58470000 |
| 201 | 1493.49760000 | 1.94610000 |
| 202 | 1493.67860000 | 1.00560000 |
| 203 | 1494.77790000 | 7.57520000 |
| 204 | 1495.57210000 | 2.30680000 |
| 205 | 1499.26070000 | 4.19110000 |
| 206 | 1500.41700000 | 1.23970000 |
| 207 | 1501.42220000 | 5.71440000 |
| 208 | 1503.03370000 | 9.45110000 |
| 209 | 1507.52380000 | 7.61010000 |
| 210 | 1510.57310000 | 15.11480000 |
| 211 | 1510.99540000 | 2.75750000 |
| 212 | 1514.40600000 | 10.65560000 |
| 213 | 1516.13710000 | 11.11020000 |
| 214 | 1517.59620000 | 3.40450000 |
| 215 | 1520.48770000 | 12.25580000 |
| 216 | 1522.70060000 | 25.81500000 |
| 217 | 1523.71280000 | 9.62950000 |
| 218 | 1547.57300000 | 30.13200000 |
| 219 | 1566.88090000 | 6.95350000 |
| 220 | 1726.74000000 | 595.59660000 |
| 221 | 2220.41550000 | 781.40480000 |
| 222 | 2989.95290000 | 54.65410000 |
| 223 | 2995.44210000 | 28.51330000 |
| 224 | 2997.43160000 | 67.37670000 |
| 225 | 3011.47160000 | 33.42200000 |
| 226 | 3012.09290000 | 56.44370000 |
| 227 | 3015.10640000 | 55.68790000 |
| 228 | 3018.85160000 | 60.49950000 |

| | | |
|---|---|---|
| 229 | 3021.35800000 | 38.44680000 |
| 230 | 3024.39410000 | 47.57880000 |
| 231 | 3036.01760000 | 31.51530000 |
| 232 | 3036.27820000 | 65.53110000 |
| 233 | 3036.50360000 | 64.70270000 |
| 234 | 3036.86680000 | 10.02940000 |
| 235 | 3037.10700000 | 73.66160000 |
| 236 | 3039.19210000 | 33.89220000 |
| 237 | 3039.38440000 | 39.30930000 |
| 238 | 3041.11400000 | 18.84660000 |
| 239 | 3041.23580000 | 18.93870000 |
| 240 | 3047.50620000 | 29.72630000 |
| 241 | 3048.10810000 | 14.22500000 |
| 242 | 3050.87900000 | 16.40220000 |
| 243 | 3051.95160000 | 107.74830000 |
| 244 | 3058.61070000 | 47.20240000 |
| 245 | 3059.29320000 | 32.40190000 |
| 246 | 3061.45770000 | 35.82810000 |
| 247 | 3070.69350000 | 52.05210000 |
| 248 | 3076.08670000 | 37.22270000 |
| 249 | 3076.16080000 | 19.25890000 |
| 250 | 3080.10970000 | 33.36580000 |
| 251 | 3085.13200000 | 103.18450000 |
| 252 | 3088.05850000 | 82.36810000 |
| 253 | 3088.54840000 | 116.05220000 |
| 254 | 3089.62850000 | 8.58910000 |
| 255 | 3094.77190000 | 62.98170000 |
| 256 | 3097.24100000 | 15.98600000 |
| 257 | 3099.44110000 | 16.95800000 |
| 258 | 3101.16840000 | 21.82820000 |
| 259 | 3102.26400000 | 3.10460000 |
| 260 | 3102.69780000 | 59.49990000 |
| 261 | 3103.39970000 | 30.81640000 |
| 262 | 3107.21500000 | 16.48500000 |
| 263 | 3109.37190000 | 25.15610000 |
| 264 | 3110.73340000 | 68.07940000 |
| 265 | 3111.67720000 | 13.18560000 |
| 266 | 3112.46630000 | 43.53370000 |
| 267 | 3114.37860000 | 27.34100000 |
| 268 | 3117.21760000 | 24.69190000 |
| 269 | 3128.87150000 | 51.42160000 |
| 270 | 3131.36050000 | 60.23690000 |
| 271 | 3133.48250000 | 18.49710000 |
| 272 | 3133.52560000 | 17.46700000 |
| 273 | 3135.20670000 | 25.86370000 |
| 274 | 3141.91570000 | 5.18810000 |
| 275 | 3146.17820000 | 8.22550000 |
| 276 | 3147.41710000 | 15.07490000 |

### *4.5 1st rotamer of 4 with chelated Mg non-bridged dimer*

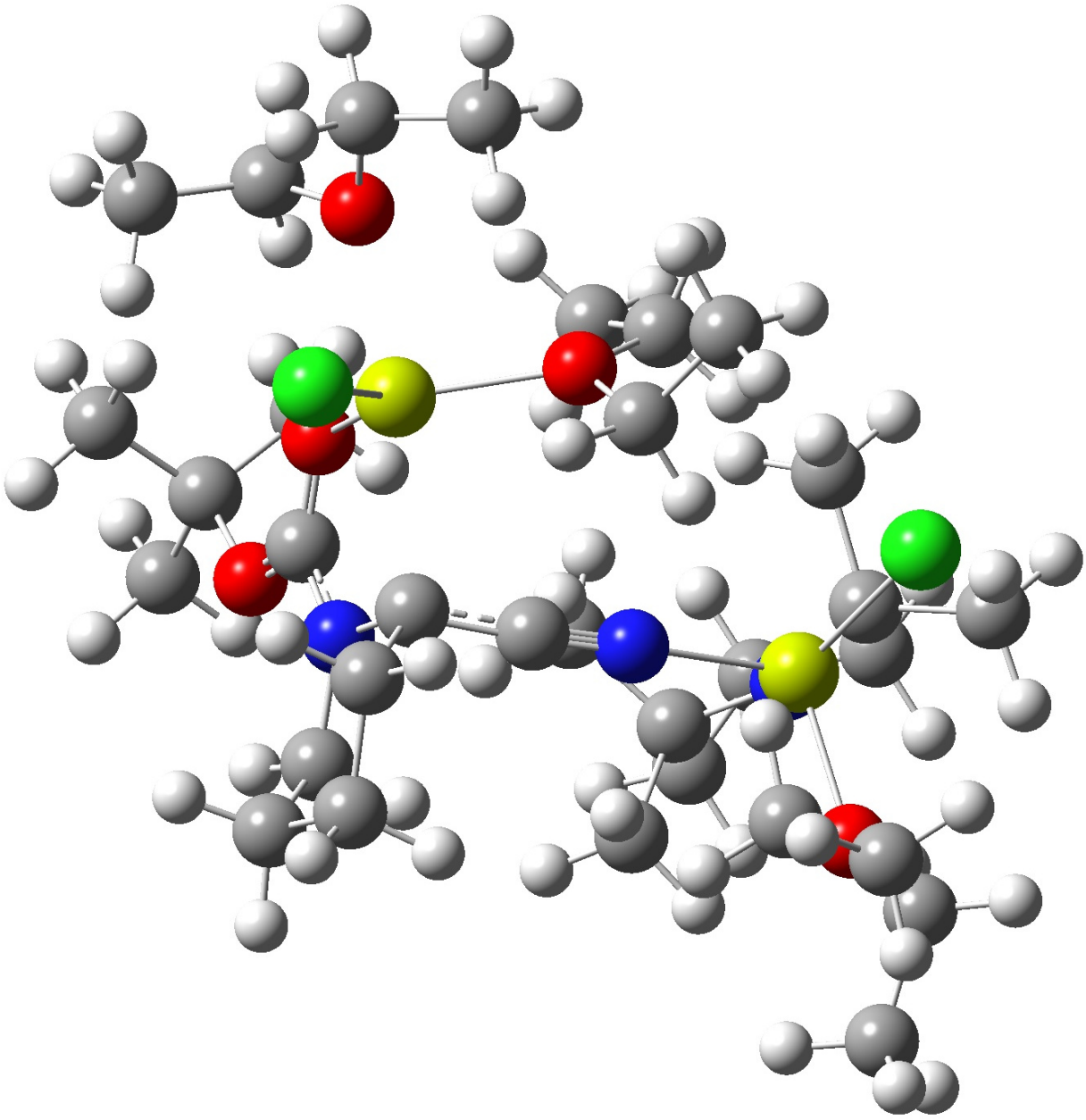

Figure S5: 1st rotamer of **4** with chelated non-bridged Mg dimer.

| | | |
|---|---|---|
| Route | : | # opt freq b3lyp/6-311g(d,p) scrf=(solvent=diethylether) geom=connectivity empiricaldispersion=gd3bj int=ultrafine pop=(regular,mk) |
| SMILES | : | CCO(CC)[Mg]([N]#C[C]1CCCCN1[C](OC(C)(C)C)O[Mg](O(CC)CC)(O(CC)CC)Cl)(N2C(CCCC2(C)C)(C)C)Cl |
| Formula | : | $C_{32}H_{65}Cl_2Mg_2N_3O_5$ |
| Charge | : | 0 |

| | | |
|---|---|---|
| Multiplicity | : 1 | |
| Dipole | : 20.9834 | Debye |
| Energy | : -3120.67341355 | a.u. |
| Gibbs Energy | : -3119.81296300 | a.u. |

*4.5.1 Cartesian Co-ordinates (XYZ format)*

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| | | | |
|---|---|---|---|
| C | 0.64409101 | 1.64736402 | 3.03396297 |
| C | 1.26434803 | -0.45389000 | 1.79915595 |
| C | 1.55721700 | -1.16510797 | 3.12176991 |
| C | 0.74979401 | -0.56085300 | 4.27939177 |
| C | 0.97166002 | 0.95381302 | 4.35806799 |
| H | 0.90323102 | 2.70169711 | 3.06589007 |
| H | -0.42580399 | 1.56628704 | 2.81505108 |
| H | 1.34775400 | -2.23129010 | 3.01080990 |
| H | 2.62726688 | -1.08609402 | 3.32870889 |
| H | -0.31703100 | -0.76441801 | 4.12348080 |
| H | 1.03054202 | -1.03015494 | 5.22702312 |
| H | 0.35458899 | 1.39722002 | 5.14465523 |
| H | 2.01795793 | 1.15715098 | 4.61262083 |
| N | 1.38743603 | 1.00576901 | 1.93747604 |
| C | 2.06157994 | 1.68178201 | 0.99585003 |
| O | 2.71560597 | 1.10383999 | 0.09526800 |
| O | 1.96739495 | 2.99877405 | 1.09956706 |
| C | 2.62373710 | 3.94573808 | 0.16041000 |
| C | 4.13596296 | 3.82645202 | 0.30784801 |
| C | 2.13625693 | 3.69719100 | -1.26448298 |
| C | 2.12618899 | 5.29373312 | 0.67140102 |
| H | 4.42909718 | 3.98777604 | 1.34741700 |
| H | 4.48583221 | 2.84794497 | -0.00808100 |
| H | 4.62113094 | 4.58736706 | -0.30752799 |
| H | 1.04610395 | 3.72000599 | -1.30026996 |
| H | 2.51839209 | 4.49041986 | -1.91099799 |
| H | 2.47787690 | 2.73877597 | -1.64726698 |
| H | 2.55405211 | 6.09595490 | 0.06720700 |
| H | 1.03814197 | 5.34967613 | 0.60534197 |
| H | 2.42360592 | 5.44338703 | 1.71091795 |
| C | -0.00255100 | -0.73088700 | 1.25738204 |
| N | -1.02145505 | -0.93404198 | 0.73247403 |
| Mg | 2.84048295 | -0.95600897 | 0.07246500 |
| Mg | -2.86516809 | -0.93978000 | -0.25265199 |
| Cl | 4.22001505 | -2.43611693 | 1.27389002 |
| Cl | -2.72081208 | -3.00766993 | -1.39674306 |
| N | -3.40314293 | 0.88285100 | -0.90035599 |
| O | 1.51036596 | -2.10561991 | -1.04718006 |
| O | -4.19635916 | -1.49982405 | 1.26944196 |
| C | -2.88121510 | 2.06371403 | -0.19025201 |
| C | -3.80493307 | 1.03701198 | -2.30957198 |
| C | -4.22736692 | -2.84585690 | 1.80681396 |
| H | -4.53024912 | -3.52341008 | 1.00380898 |
| H | -4.97708988 | -2.87688804 | 2.59909606 |

| | | | |
|---|---|---|---|
| C | -5.50852203 | -0.88751400 | 1.14269197 |
| H | -5.35118914 | -0.05825000 | 0.45096701 |
| H | -6.18333483 | -1.61236703 | 0.67635900 |
| C | -6.04064894 | -0.39491901 | 2.47613192 |
| H | -6.22278881 | -1.20839202 | 3.18132591 |
| H | -5.33994389 | 0.30819699 | 2.93015409 |
| H | -6.99007416 | 0.12244700 | 2.31402898 |
| C | -2.86525512 | -3.21510792 | 2.35472298 |
| H | -2.55275798 | -2.50876904 | 3.12665892 |
| H | -2.91756010 | -4.21348000 | 2.79631591 |
| H | -2.11254406 | -3.23168397 | 1.56720102 |
| C | 0.77157497 | -1.67155099 | -2.21718311 |
| H | -0.28775600 | -1.85550594 | -2.02980208 |
| H | 1.08562398 | -2.28376007 | -3.06626105 |
| C | 1.03986096 | -0.20663901 | -2.48286796 |
| H | 2.10095310 | -0.02823500 | -2.66363406 |
| H | 0.48424199 | 0.10309100 | -3.36998391 |
| H | 0.70759702 | 0.41511300 | -1.65051401 |
| C | 0.99265802 | -3.32848310 | -0.44574401 |
| H | 1.62705803 | -3.49558806 | 0.42492700 |
| H | -0.02698700 | -3.12561488 | -0.11907700 |
| C | 1.01790595 | -4.52801180 | -1.37464499 |
| H | 2.02143598 | -4.74098682 | -1.74337399 |
| H | 0.66834998 | -5.39851379 | -0.81366599 |
| H | 0.34359801 | -4.39611006 | -2.22174311 |
| C | -2.61211395 | 0.95993298 | -3.30124688 |
| H | -2.05677700 | 0.03268700 | -3.13782310 |
| H | -2.95587206 | 0.96916801 | -4.34205723 |
| H | -1.91703296 | 1.78993201 | -3.17352009 |
| C | -4.59066391 | 2.34407711 | -2.56636310 |
| H | -4.75803995 | 2.46155095 | -3.64277697 |
| H | -5.57737207 | 2.24513507 | -2.09741592 |
| C | -3.69665194 | 3.34389496 | -0.48835999 |
| H | -3.20478892 | 4.20495987 | -0.02148400 |
| H | -4.68066311 | 3.23981810 | -0.01510400 |
| C | -1.38198602 | 2.35934806 | -0.47327700 |
| H | -0.78755403 | 1.46206295 | -0.30155900 |
| H | -1.21616006 | 2.67406511 | -1.50349700 |
| H | -0.99987698 | 3.14963293 | 0.18229701 |
| C | -3.01320291 | 1.80598795 | 1.32212400 |
| H | -4.06224585 | 1.66482699 | 1.58641803 |
| H | -2.45861411 | 0.91871202 | 1.63546705 |
| H | -2.62519908 | 2.65301800 | 1.89674497 |
| C | -4.75261879 | -0.12367900 | -2.66252899 |
| H | -5.11507320 | -0.03213900 | -3.69133091 |
| H | -4.25375223 | -1.09278297 | -2.58043909 |
| H | -5.61546278 | -0.12140700 | -1.99158394 |
| C | -3.90406489 | 3.57224798 | -1.98084295 |
| H | -2.94563699 | 3.75223398 | -2.48023391 |
| H | -4.51187706 | 4.46758604 | -2.14993811 |
| O | 4.26357317 | -0.75765598 | -1.57265306 |
| C | 5.10545921 | -1.86999404 | -1.98311698 |
| H | 5.68053198 | -1.53165197 | -2.84945011 |
| H | 5.79234600 | -2.10513496 | -1.16882598 |
| C | 4.26974392 | -3.07586288 | -2.34154606 |

| | | | |
|---|---|---|---|
| H | 4.92857790 | -3.85494995 | -2.73384094 |
| H | 3.76400495 | -3.47157407 | -1.46449995 |
| H | 3.52960205 | -2.83084702 | -3.10521603 |
| C | 4.92766285 | 0.51587999 | -1.76186800 |
| H | 4.14837980 | 1.26414704 | -1.65946901 |
| H | 5.30564404 | 0.54301798 | -2.78814793 |
| C | 6.04106903 | 0.74851602 | -0.75527298 |
| H | 5.65309715 | 0.69846398 | 0.26410401 |
| H | 6.84070921 | 0.01298100 | -0.85551798 |
| H | 6.47517681 | 1.73920405 | -0.91234797 |

*4.5.2 Frequencies*

| Mode | IR frequency | IR intensity |
|---|---|---|
| 1 | -9.52770000 | 0.82300000 |
| 2 | 17.78970000 | 0.48620000 |
| 3 | 22.60170000 | 1.33210000 |
| 4 | 30.57210000 | 0.69770000 |
| 5 | 31.09910000 | 1.34120000 |
| 6 | 38.82870000 | 2.04940000 |
| 7 | 40.97240000 | 1.01600000 |
| 8 | 44.88660000 | 0.43130000 |
| 9 | 57.31480000 | 1.26710000 |
| 10 | 58.00330000 | 0.10700000 |
| 11 | 59.17340000 | 2.63110000 |
| 12 | 61.49300000 | 2.31550000 |
| 13 | 65.72930000 | 0.34730000 |
| 14 | 68.17040000 | 2.15050000 |
| 15 | 77.60230000 | 6.40830000 |
| 16 | 78.77120000 | 5.01400000 |
| 17 | 82.46780000 | 1.96860000 |
| 18 | 87.14590000 | 4.74990000 |
| 19 | 90.28510000 | 2.63450000 |
| 20 | 92.89830000 | 6.73150000 |
| 21 | 97.45470000 | 0.23630000 |
| 22 | 104.50530000 | 5.88440000 |
| 23 | 106.42030000 | 5.75130000 |
| 24 | 111.38730000 | 7.23480000 |
| 25 | 113.96320000 | 4.36700000 |
| 26 | 118.35310000 | 2.76080000 |
| 27 | 123.81140000 | 0.83120000 |
| 28 | 126.54500000 | 3.46420000 |
| 29 | 127.75400000 | 7.71230000 |
| 30 | 130.53320000 | 0.77890000 |
| 31 | 135.89430000 | 2.06830000 |
| 32 | 141.17750000 | 0.79810000 |
| 33 | 142.51730000 | 1.99460000 |
| 34 | 145.11880000 | 3.81240000 |
| 35 | 151.92660000 | 7.96560000 |
| 36 | 156.39400000 | 1.82480000 |
| 37 | 162.97810000 | 1.22910000 |
| 38 | 167.80430000 | 3.98170000 |
| 39 | 169.66390000 | 2.00380000 |

| | | |
|---|---|---|
| 40 | 180.78730000 | 9.16540000 |
| 41 | 184.94670000 | 6.73080000 |
| 42 | 187.79980000 | 9.14240000 |
| 43 | 189.84910000 | 1.67160000 |
| 44 | 196.38630000 | 0.41060000 |
| 45 | 210.12650000 | 5.19990000 |
| 46 | 211.43850000 | 5.59590000 |
| 47 | 215.44320000 | 4.24740000 |
| 48 | 228.47640000 | 5.54210000 |
| 49 | 233.09000000 | 1.55300000 |
| 50 | 238.72260000 | 0.56820000 |
| 51 | 242.10360000 | 1.30580000 |
| 52 | 252.09080000 | 0.18230000 |
| 53 | 253.19660000 | 1.97390000 |
| 54 | 261.53000000 | 0.16000000 |
| 55 | 265.49090000 | 0.28510000 |
| 56 | 271.65380000 | 7.06030000 |
| 57 | 273.59860000 | 2.28840000 |
| 58 | 275.25530000 | 12.58020000 |
| 59 | 283.86100000 | 103.34360000 |
| 60 | 289.35170000 | 2.15530000 |
| 61 | 296.69050000 | 27.54700000 |
| 62 | 297.07540000 | 1.41040000 |
| 63 | 300.80610000 | 34.70840000 |
| 64 | 302.78520000 | 23.02680000 |
| 65 | 312.20990000 | 4.47830000 |
| 66 | 313.49040000 | 4.15670000 |
| 67 | 321.24550000 | 15.87910000 |
| 68 | 326.74970000 | 8.19960000 |
| 69 | 335.75430000 | 16.18200000 |
| 70 | 340.00890000 | 34.34790000 |
| 71 | 342.23880000 | 86.03930000 |
| 72 | 351.73490000 | 1.48460000 |
| 73 | 352.84560000 | 35.99510000 |
| 74 | 354.87120000 | 8.31120000 |
| 75 | 361.64450000 | 44.91470000 |
| 76 | 375.02320000 | 41.25710000 |
| 77 | 386.45060000 | 50.91620000 |
| 78 | 394.14750000 | 55.33550000 |
| 79 | 399.92340000 | 53.98630000 |
| 80 | 408.19160000 | 25.23440000 |
| 81 | 416.28180000 | 12.66710000 |
| 82 | 419.20390000 | 25.17410000 |
| 83 | 426.38820000 | 37.40560000 |
| 84 | 432.10220000 | 25.17370000 |
| 85 | 441.48720000 | 11.58060000 |
| 86 | 456.38480000 | 27.27110000 |
| 87 | 457.16830000 | 33.34070000 |
| 88 | 469.85370000 | 4.22080000 |
| 89 | 477.36550000 | 47.42510000 |
| 90 | 499.37140000 | 0.76980000 |
| 91 | 503.73330000 | 22.40320000 |
| 92 | 508.13100000 | 18.21280000 |
| 93 | 518.31050000 | 11.63840000 |
| 94 | 523.55180000 | 16.82030000 |

| | | |
|---|---|---|
| 95 | 526.03600000 | 23.16620000 |
| 96 | 534.30720000 | 52.26720000 |
| 97 | 547.40210000 | 23.20380000 |
| 98 | 591.96450000 | 2.98270000 |
| 99 | 629.28430000 | 6.33810000 |
| 100 | 656.83870000 | 11.18080000 |
| 101 | 701.20350000 | 47.41770000 |
| 102 | 738.59480000 | 6.07080000 |
| 103 | 749.46660000 | 31.64100000 |
| 104 | 759.08900000 | 0.74980000 |
| 105 | 774.98670000 | 37.26030000 |
| 106 | 799.44620000 | 47.72650000 |
| 107 | 804.42740000 | 31.59230000 |
| 108 | 805.52170000 | 12.05660000 |
| 109 | 806.52130000 | 23.83940000 |
| 110 | 815.28780000 | 9.97820000 |
| 111 | 821.22880000 | 6.14390000 |
| 112 | 823.09870000 | 11.81050000 |
| 113 | 834.25340000 | 3.17990000 |
| 114 | 841.02280000 | 10.60810000 |
| 115 | 844.44860000 | 16.00090000 |
| 116 | 846.40950000 | 17.05910000 |
| 117 | 846.79260000 | 47.58950000 |
| 118 | 859.04570000 | 1.95280000 |
| 119 | 860.78450000 | 16.26030000 |
| 120 | 867.19630000 | 5.16320000 |
| 121 | 903.26440000 | 59.22700000 |
| 122 | 908.57540000 | 1.08430000 |
| 123 | 913.31840000 | 9.76240000 |
| 124 | 913.41110000 | 26.59790000 |
| 125 | 915.22260000 | 9.02120000 |
| 126 | 915.54540000 | 26.07210000 |
| 127 | 916.55580000 | 36.37890000 |
| 128 | 917.40330000 | 2.21840000 |
| 129 | 924.52630000 | 20.12710000 |
| 130 | 930.27300000 | 0.13810000 |
| 131 | 933.89180000 | 13.95430000 |
| 132 | 954.99130000 | 14.01070000 |
| 133 | 963.19420000 | 6.50190000 |
| 134 | 972.35090000 | 0.25250000 |
| 135 | 979.03850000 | 6.91040000 |
| 136 | 1007.51410000 | 1.91850000 |
| 137 | 1019.88530000 | 0.14870000 |
| 138 | 1027.51490000 | 49.79920000 |
| 139 | 1028.78980000 | 77.54400000 |
| 140 | 1033.20300000 | 16.93420000 |
| 141 | 1034.17540000 | 71.65400000 |
| 142 | 1049.49390000 | 30.39710000 |
| 143 | 1052.17780000 | 5.72850000 |
| 144 | 1054.51260000 | 8.56510000 |
| 145 | 1057.57100000 | 143.59990000 |
| 146 | 1057.80770000 | 162.57000000 |
| 147 | 1062.04860000 | 213.27180000 |
| 148 | 1062.41790000 | 33.41460000 |
| 149 | 1068.63220000 | 1.68850000 |

| | | |
|---|---|---|
| 150 | 1072.09200000 | 2.87970000 |
| 151 | 1089.88920000 | 29.43040000 |
| 152 | 1095.04060000 | 4.56020000 |
| 153 | 1106.35250000 | 18.80070000 |
| 154 | 1111.55060000 | 47.99570000 |
| 155 | 1113.51970000 | 24.22440000 |
| 156 | 1120.67940000 | 14.10080000 |
| 157 | 1127.37460000 | 11.92690000 |
| 158 | 1133.11930000 | 11.51500000 |
| 159 | 1146.81610000 | 97.27240000 |
| 160 | 1148.08410000 | 11.80680000 |
| 161 | 1155.92270000 | 0.79520000 |
| 162 | 1177.21870000 | 104.93130000 |
| 163 | 1179.84200000 | 148.30260000 |
| 164 | 1180.41090000 | 177.46210000 |
| 165 | 1180.72820000 | 20.78940000 |
| 166 | 1187.88360000 | 72.89390000 |
| 167 | 1192.32250000 | 33.30310000 |
| 168 | 1210.97500000 | 15.29260000 |
| 169 | 1212.01130000 | 18.06650000 |
| 170 | 1212.70710000 | 27.81950000 |
| 171 | 1215.09360000 | 1.19790000 |
| 172 | 1217.75920000 | 8.98960000 |
| 173 | 1226.21140000 | 61.73970000 |
| 174 | 1242.43750000 | 5.83240000 |
| 175 | 1252.60180000 | 3.23660000 |
| 176 | 1257.74670000 | 82.31970000 |
| 177 | 1261.19580000 | 48.77260000 |
| 178 | 1273.39700000 | 27.14520000 |
| 179 | 1280.12170000 | 45.65770000 |
| 180 | 1304.56630000 | 111.06580000 |
| 181 | 1308.85330000 | 13.73000000 |
| 182 | 1315.17310000 | 3.49130000 |
| 183 | 1317.60150000 | 1.22050000 |
| 184 | 1323.15780000 | 0.90070000 |
| 185 | 1325.39870000 | 3.89490000 |
| 186 | 1334.91000000 | 14.38750000 |
| 187 | 1341.18190000 | 9.54850000 |
| 188 | 1347.50730000 | 13.80170000 |
| 189 | 1355.02470000 | 2.61740000 |
| 190 | 1363.41450000 | 0.36980000 |
| 191 | 1366.47840000 | 0.68510000 |
| 192 | 1371.39160000 | 5.74930000 |
| 193 | 1376.00790000 | 0.76580000 |
| 194 | 1380.37440000 | 7.77090000 |
| 195 | 1382.90000000 | 1.01290000 |
| 196 | 1391.32070000 | 21.30020000 |
| 197 | 1394.34610000 | 21.08770000 |
| 198 | 1398.95250000 | 19.04840000 |
| 199 | 1401.52660000 | 1.56110000 |
| 200 | 1402.10960000 | 19.39740000 |
| 201 | 1402.52460000 | 13.97360000 |
| 202 | 1404.37600000 | 12.23430000 |
| 203 | 1405.37720000 | 6.25450000 |
| 204 | 1407.78300000 | 4.93020000 |

| | | |
|---|---|---|
| 205 | 1409.99550000 | 0.38330000 |
| 206 | 1415.61680000 | 5.19560000 |
| 207 | 1417.41640000 | 4.87190000 |
| 208 | 1424.05890000 | 9.17410000 |
| 209 | 1425.89720000 | 36.91570000 |
| 210 | 1428.21380000 | 17.24700000 |
| 211 | 1433.58640000 | 7.40070000 |
| 212 | 1435.86920000 | 22.18040000 |
| 213 | 1437.56650000 | 23.11460000 |
| 214 | 1445.78620000 | 7.52480000 |
| 215 | 1467.22560000 | 35.34490000 |
| 216 | 1467.60950000 | 13.82460000 |
| 217 | 1471.08180000 | 1.31690000 |
| 218 | 1476.76120000 | 1.52110000 |
| 219 | 1478.85580000 | 45.50900000 |
| 220 | 1480.14440000 | 320.25940000 |
| 221 | 1480.73770000 | 49.53830000 |
| 222 | 1481.48120000 | 10.73260000 |
| 223 | 1481.70790000 | 19.62210000 |
| 224 | 1482.01260000 | 4.41630000 |
| 225 | 1484.64750000 | 2.02110000 |
| 226 | 1485.22510000 | 1.13880000 |
| 227 | 1485.43150000 | 1.70240000 |
| 228 | 1485.94530000 | 12.64360000 |
| 229 | 1488.00020000 | 14.64240000 |
| 230 | 1488.84510000 | 9.31040000 |
| 231 | 1489.88830000 | 35.23880000 |
| 232 | 1490.19280000 | 7.19390000 |
| 233 | 1491.54390000 | 3.16890000 |
| 234 | 1493.38700000 | 30.89870000 |
| 235 | 1495.26350000 | 13.20290000 |
| 236 | 1495.81580000 | 5.25840000 |
| 237 | 1496.50370000 | 2.40350000 |
| 238 | 1497.33130000 | 5.99280000 |
| 239 | 1499.38040000 | 12.12650000 |
| 240 | 1500.35640000 | 7.97740000 |
| 241 | 1502.21710000 | 14.61860000 |
| 242 | 1502.77670000 | 6.45020000 |
| 243 | 1503.89480000 | 1.15670000 |
| 244 | 1507.88060000 | 62.77770000 |
| 245 | 1508.92270000 | 11.84700000 |
| 246 | 1511.01580000 | 5.01290000 |
| 247 | 1511.56410000 | 4.05140000 |
| 248 | 1512.32440000 | 20.78580000 |
| 249 | 1514.90270000 | 22.81150000 |
| 250 | 1518.26350000 | 37.46620000 |
| 251 | 1518.35040000 | 52.91770000 |
| 252 | 1520.17730000 | 7.72460000 |
| 253 | 1524.31750000 | 85.92730000 |
| 254 | 1531.52860000 | 8.82200000 |
| 255 | 1632.72570000 | 684.47370000 |
| 256 | 2258.42610000 | 729.68190000 |
| 257 | 2996.17230000 | 32.16970000 |
| 258 | 2997.93310000 | 58.59830000 |
| 259 | 3005.95090000 | 34.47000000 |

| | | |
|---|---|---|
| 260 | 3008.88040000 | 39.76660000 |
| 261 | 3012.45140000 | 40.13040000 |
| 262 | 3016.88810000 | 52.66980000 |
| 263 | 3019.43770000 | 60.95360000 |
| 264 | 3019.65610000 | 31.02640000 |
| 265 | 3026.32900000 | 72.13120000 |
| 266 | 3028.06660000 | 27.18920000 |
| 267 | 3034.27800000 | 104.79620000 |
| 268 | 3036.09670000 | 87.86150000 |
| 269 | 3036.68650000 | 18.67350000 |
| 270 | 3036.90540000 | 28.08320000 |
| 271 | 3037.11230000 | 16.91540000 |
| 272 | 3041.53930000 | 10.59630000 |
| 273 | 3041.72110000 | 26.90870000 |
| 274 | 3041.82160000 | 17.05130000 |
| 275 | 3042.77720000 | 18.18130000 |
| 276 | 3043.26410000 | 61.14000000 |
| 277 | 3043.93230000 | 47.25050000 |
| 278 | 3045.96990000 | 21.13880000 |
| 279 | 3046.88660000 | 12.59420000 |
| 280 | 3047.64440000 | 21.69320000 |
| 281 | 3048.93580000 | 117.20630000 |
| 282 | 3049.20240000 | 47.10700000 |
| 283 | 3052.77780000 | 15.34250000 |
| 284 | 3054.92890000 | 28.51660000 |
| 285 | 3059.37120000 | 91.29970000 |
| 286 | 3069.49970000 | 67.75570000 |
| 287 | 3073.54670000 | 32.16890000 |
| 288 | 3073.71590000 | 8.63550000 |
| 289 | 3080.87780000 | 113.41010000 |
| 290 | 3083.76020000 | 19.20500000 |
| 291 | 3085.76510000 | 46.24630000 |
| 292 | 3088.89770000 | 37.30070000 |
| 293 | 3090.58960000 | 23.61770000 |
| 294 | 3093.20390000 | 12.92520000 |
| 295 | 3094.45140000 | 26.08400000 |
| 296 | 3096.26360000 | 27.88330000 |
| 297 | 3096.51780000 | 70.73570000 |
| 298 | 3102.21310000 | 31.64700000 |
| 299 | 3106.22270000 | 11.87010000 |
| 300 | 3106.35910000 | 43.61440000 |
| 301 | 3106.54190000 | 17.06030000 |
| 302 | 3109.24590000 | 24.37530000 |
| 303 | 3110.58950000 | 58.23560000 |
| 304 | 3110.98700000 | 61.82300000 |
| 305 | 3113.71770000 | 28.65320000 |
| 306 | 3113.83100000 | 5.10180000 |
| 307 | 3115.88720000 | 15.50590000 |
| 308 | 3116.14490000 | 35.52780000 |
| 309 | 3117.56310000 | 40.74220000 |
| 310 | 3119.51520000 | 4.02760000 |
| 311 | 3119.66970000 | 16.51770000 |
| 312 | 3120.71130000 | 52.69810000 |
| 313 | 3129.97170000 | 51.56840000 |
| 314 | 3132.55590000 | 27.74960000 |

| | | |
|---|---|---|
| 315 | 3136.02190000 | 25.60810000 |
| 316 | 3140.66760000 | 23.34650000 |
| 317 | 3149.04240000 | 12.00680000 |
| 318 | 3156.70460000 | 18.45860000 |
| 319 | 3157.32740000 | 17.52120000 |
| 320 | 3167.51830000 | 8.90960000 |
| 321 | 3172.49760000 | 10.33820000 |

### *4.6 2nd rotamer of 4 with non-chelated non-bridged Mg dimer*

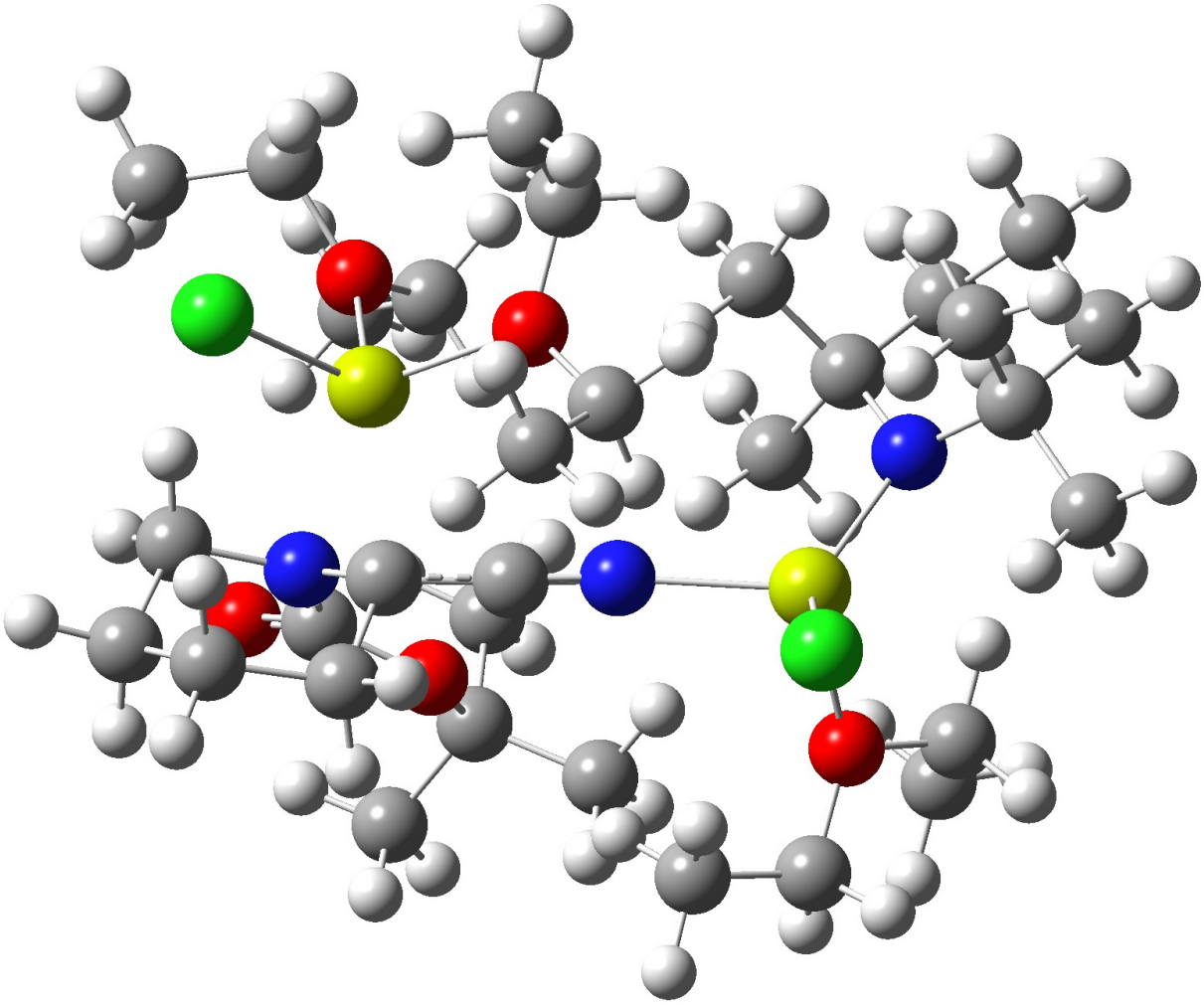


**Figure 6:** ***2nd rotamer of 4 with non-chelated non-bridged Mg dimer***

| | | | |
|---|---|---|---|
| Route | : | # opt freq b3lyp/6-311g(d,p) scrf=(solvent=diethylether) geom=connectivity empiricaldispersion=gd3bj int=ultrafine pop=(regular,mk) | |
| SMILES | : | CCO(CC)[Mg](O(CC)CC)Cl.CCO(CC)[Mg]([N]#C[C]1CCCCN1C(=O)OC(C)(C)C)(N2C(CCCC2(C)C)(C)C)Cl | |
| Formula | : | $C_{32}H_{65}Cl_2Mg_2N_3O_5$ | |
| Charge | : | 0 | |
| Multiplicity | : | 1 | |
| Dipole | : | 17.7328 | Debye |
| Energy | : | -3120.64945304 | a.u. |
| Gibbs Energy | : | -3119.78947500 | a.u. |

*4.6.1 Cartesian Co-ordinates (XYZ format)*

109

| | | | |
|---|---|---|---|
| C | -4.30285501 | 1.34812403 | -0.20562799 |
| C | -2.09233093 | 0.71177602 | -1.02565002 |
| C | -2.46830201 | 1.05754697 | -2.48167610 |
| C | -3.98376393 | 0.92986000 | -2.68394208 |
| C | -4.76258612 | 1.71351099 | -1.61976504 |
| H | -4.54775095 | 0.30526099 | 0.01347200 |
| H | -4.78910923 | 1.96455300 | 0.54472297 |
| H | -2.15278006 | 2.08583689 | -2.70375609 |
| H | -1.93394995 | 0.39773199 | -3.16976190 |
| H | -4.25139189 | 1.28475404 | -3.68293810 |
| H | -4.27225924 | -0.12523600 | -2.63278008 |
| H | -4.61354208 | 2.78948689 | -1.76389694 |
| H | -5.83462477 | 1.51872504 | -1.71248603 |
| N | -2.85083699 | 1.53492796 | -0.07462300 |
| C | -2.43517089 | 2.71025610 | 0.50381303 |
| O | -3.15350509 | 3.38960910 | 1.22090304 |
| O | -1.14727104 | 2.98513198 | 0.22637700 |
| C | -0.44943899 | 4.08932209 | 0.92440802 |
| C | -1.12994802 | 5.42547083 | 0.62988299 |
| C | -0.38473600 | 3.77634501 | 2.41786909 |
| C | 0.94206899 | 4.05962086 | 0.30537301 |
| H | -1.25247204 | 5.55087805 | -0.44872400 |
| H | -2.10427690 | 5.49121189 | 1.10652196 |
| H | -0.49431399 | 6.23571205 | 0.99597102 |
| H | 0.09554700 | 2.80870605 | 2.57834601 |
| H | 0.21079400 | 4.54052782 | 2.92277002 |
| H | -1.38033795 | 3.76278090 | 2.85733199 |
| H | 1.58616304 | 4.77455282 | 0.82090902 |
| H | 1.38459098 | 3.06829309 | 0.38320100 |
| H | 0.89767301 | 4.33690119 | -0.74856502 |
| C | -0.70288599 | 0.62614000 | -0.83212101 |
| N | 0.43853000 | 0.40712801 | -0.77843899 |
| Mg | -2.67145705 | -1.38626003 | -0.39716101 |
| Mg | 2.48802590 | -0.03167000 | -0.98433501 |
| Cl | -4.61259508 | -2.49929404 | -0.97242498 |
| Cl | 2.45936990 | -0.95751399 | -3.16565108 |
| N | 3.41215396 | -0.84963399 | 0.59937900 |
| O | -2.81775308 | -1.22119498 | 1.64471602 |
| O | 3.26736212 | 1.89366698 | -1.23549604 |
| C | 2.73999906 | -0.78158098 | 1.90691900 |
| C | 4.36333513 | -1.95337105 | 0.36666000 |
| C | 3.07893491 | 2.77116609 | -2.37289190 |
| H | 3.87304592 | 2.55691504 | -3.09565401 |
| H | 3.19506097 | 3.79990411 | -2.02586198 |
| C | 4.53443289 | 2.10198689 | -0.54954797 |
| H | 4.63612413 | 1.22028899 | 0.08508800 |
| H | 5.32919979 | 2.09527397 | -1.30231500 |
| C | 4.56101513 | 3.37175608 | 0.28133100 |
| H | 4.45802402 | 4.27617693 | -0.32095999 |
| H | 3.76924896 | 3.36015010 | 1.03125501 |
| H | 5.52142096 | 3.42792892 | 0.80080700 |
| C | 1.71168303 | 2.57380509 | -2.99305391 |
| H | 0.91900402 | 2.74537301 | -2.26636910 |

| | | | |
|---|---|---|---|
| H | 1.59527695 | 3.29160810 | -3.80925894 |
| H | 1.60367894 | 1.56988800 | -3.40178800 |
| C | -1.85067999 | -0.47554499 | 2.43503594 |
| H | -1.17368901 | -0.02911800 | 1.70923197 |
| H | -1.28055704 | -1.19885695 | 3.02240801 |
| C | -2.47025609 | 0.58964199 | 3.31677389 |
| H | -3.08541393 | 0.15804701 | 4.10784817 |
| H | -1.66385198 | 1.15067804 | 3.79551005 |
| H | -3.06937289 | 1.28975499 | 2.73533607 |
| C | -3.75411010 | -2.03409004 | 2.41409993 |
| H | -3.83321595 | -2.98278308 | 1.88304102 |
| H | -3.30060196 | -2.22137904 | 3.38963199 |
| C | -5.11676407 | -1.38023198 | 2.53018904 |
| H | -5.55892706 | -1.24911797 | 1.54237497 |
| H | -5.77526712 | -2.03209305 | 3.11082411 |
| H | -5.06265306 | -0.41244900 | 3.02829194 |
| C | 3.67569590 | -3.28858900 | -0.03075600 |
| H | 3.00400400 | -3.11593103 | -0.87525100 |
| H | 4.41333199 | -4.04140091 | -0.33124000 |
| H | 3.09026098 | -3.71009898 | 0.78672802 |
| C | 5.28998184 | -2.20105791 | 1.57993901 |
| H | 5.89328814 | -3.09748912 | 1.39857602 |
| H | 5.98541212 | -1.35583901 | 1.65387404 |
| C | 3.70567489 | -1.04206395 | 3.08596611 |
| H | 3.13709998 | -1.07717204 | 4.02238178 |
| H | 4.39215183 | -0.18967600 | 3.15813589 |
| C | 1.52788603 | -1.74417496 | 2.03197002 |
| H | 0.83866799 | -1.58207500 | 1.20070004 |
| H | 1.83370697 | -2.78940105 | 2.01204300 |
| H | 0.98501599 | -1.57886195 | 2.96939301 |
| C | 2.19611692 | 0.64713699 | 2.09233904 |
| H | 3.01001906 | 1.37139797 | 2.02426195 |
| H | 1.44732106 | 0.89727199 | 1.33820796 |
| H | 1.71844006 | 0.75860298 | 3.07108903 |
| C | 5.27799606 | -1.56022096 | -0.80816698 |
| H | 6.02184105 | -2.34075093 | -0.99591100 |
| H | 4.71309519 | -1.42464995 | -1.73365998 |
| H | 5.80758810 | -0.63189203 | -0.58222097 |
| C | 4.53003883 | -2.30975795 | 2.89649510 |
| H | 3.88228607 | -3.19330502 | 2.89546800 |
| H | 5.22734880 | -2.44101095 | 3.73079300 |
| O | -1.13653195 | -2.70865512 | -0.61747199 |
| C | -0.30742401 | -2.80500197 | -1.81817603 |
| H | 0.42880800 | -3.58972096 | -1.64231205 |
| H | 0.22507700 | -1.86239803 | -1.90034497 |
| C | -1.12749696 | -3.07628989 | -3.06366897 |
| H | -1.82652605 | -2.26139593 | -3.26947093 |
| H | -0.44859099 | -3.14823794 | -3.91687608 |
| H | -1.69435799 | -4.00472021 | -2.98422003 |
| C | -0.99278402 | -3.80439091 | 0.32443300 |
| H | -1.44363201 | -3.44342589 | 1.24903798 |
| H | 0.07412000 | -3.94375300 | 0.50795501 |
| C | -1.66367197 | -5.07688522 | -0.15507400 |
| H | -1.18590903 | -5.46710777 | -1.05569398 |
| H | -1.58399296 | -5.84049177 | 0.62318999 |

| | | | |
|---|---|---|---|
| H | -2.71964693 | -4.89915180 | -0.36588401 |

*4.6.2 Frequencies*

| Mode | IR frequency | IR intensity |
|---|---|---|
| 1 | 7.71980000 | 0.19460000 |
| 2 | 23.03210000 | 0.83910000 |
| 3 | 26.46080000 | 0.25930000 |
| 4 | 36.29190000 | 0.45150000 |
| 5 | 41.41640000 | 0.92090000 |
| 6 | 42.83610000 | 0.58150000 |
| 7 | 46.34940000 | 0.06760000 |
| 8 | 48.42410000 | 0.67800000 |
| 9 | 52.14360000 | 0.50320000 |
| 10 | 56.08900000 | 2.63940000 |
| 11 | 58.72600000 | 1.96140000 |
| 12 | 65.09300000 | 0.71750000 |
| 13 | 70.32210000 | 7.53040000 |
| 14 | 71.22280000 | 8.08490000 |
| 15 | 73.96380000 | 2.73030000 |
| 16 | 76.46630000 | 4.03840000 |
| 17 | 82.04050000 | 1.49310000 |
| 18 | 83.36900000 | 5.30410000 |
| 19 | 89.61320000 | 1.23880000 |
| 20 | 92.96320000 | 2.78370000 |
| 21 | 101.95960000 | 7.27100000 |
| 22 | 102.43000000 | 1.01820000 |
| 23 | 105.28130000 | 3.76950000 |
| 24 | 107.22910000 | 10.95660000 |
| 25 | 111.71000000 | 4.77110000 |
| 26 | 114.80760000 | 6.65640000 |
| 27 | 118.68240000 | 3.28970000 |
| 28 | 121.13610000 | 2.16110000 |
| 29 | 130.49750000 | 0.25200000 |
| 30 | 132.10910000 | 4.13110000 |
| 31 | 134.19470000 | 4.54380000 |
| 32 | 139.08860000 | 1.64590000 |
| 33 | 142.14310000 | 2.00530000 |
| 34 | 143.30150000 | 10.13930000 |
| 35 | 151.16520000 | 1.41460000 |
| 36 | 163.11580000 | 2.40570000 |
| 37 | 163.86170000 | 9.52950000 |
| 38 | 170.76860000 | 1.97720000 |
| 39 | 174.23900000 | 4.36180000 |
| 40 | 180.79770000 | 3.86150000 |
| 41 | 183.82970000 | 5.75100000 |
| 42 | 188.07970000 | 8.06230000 |
| 43 | 190.91660000 | 2.88920000 |
| 44 | 205.36320000 | 14.06320000 |
| 45 | 217.55240000 | 4.27730000 |
| 46 | 221.07100000 | 0.68860000 |
| 47 | 228.33220000 | 5.42420000 |
| 48 | 233.04270000 | 6.07430000 |
| 49 | 233.81250000 | 2.90650000 |

| | | |
|---|---|---|
| 50 | 241.90190000 | 2.29600000 |
| 51 | 255.87640000 | 1.30440000 |
| 52 | 259.39840000 | 3.45600000 |
| 53 | 262.20630000 | 3.97380000 |
| 54 | 265.24520000 | 3.65860000 |
| 55 | 270.56670000 | 0.77810000 |
| 56 | 284.58670000 | 1.72990000 |
| 57 | 286.17420000 | 13.58030000 |
| 58 | 294.53780000 | 1.04150000 |
| 59 | 296.28650000 | 0.69870000 |
| 60 | 299.36620000 | 8.77810000 |
| 61 | 300.28340000 | 43.47580000 |
| 62 | 303.76430000 | 40.40100000 |
| 63 | 313.79540000 | 3.01610000 |
| 64 | 316.32940000 | 18.61300000 |
| 65 | 322.03810000 | 18.02330000 |
| 66 | 324.79120000 | 3.30430000 |
| 67 | 327.26550000 | 33.33640000 |
| 68 | 337.03580000 | 47.96780000 |
| 69 | 339.81120000 | 18.45360000 |
| 70 | 344.44240000 | 43.02970000 |
| 71 | 345.13610000 | 6.61910000 |
| 72 | 356.21140000 | 12.82370000 |
| 73 | 358.13390000 | 9.69150000 |
| 74 | 364.92100000 | 56.97590000 |
| 75 | 386.91800000 | 22.65430000 |
| 76 | 389.28200000 | 30.09950000 |
| 77 | 396.36290000 | 29.48960000 |
| 78 | 401.69530000 | 32.64890000 |
| 79 | 405.07050000 | 5.54850000 |
| 80 | 413.85200000 | 0.26830000 |
| 81 | 417.99170000 | 25.07470000 |
| 82 | 426.52330000 | 108.36160000 |
| 83 | 432.51310000 | 13.25480000 |
| 84 | 440.38020000 | 21.55080000 |
| 85 | 455.24510000 | 21.41100000 |
| 86 | 461.29820000 | 6.94060000 |
| 87 | 468.84870000 | 5.02330000 |
| 88 | 483.28780000 | 72.43880000 |
| 89 | 495.88220000 | 0.34340000 |
| 90 | 511.28200000 | 14.64720000 |
| 91 | 512.61440000 | 2.74140000 |
| 92 | 521.14510000 | 38.78960000 |
| 93 | 523.70050000 | 22.06790000 |
| 94 | 527.21430000 | 16.49440000 |
| 95 | 535.96460000 | 50.67490000 |
| 96 | 537.34200000 | 1.52090000 |
| 97 | 544.29190000 | 43.66580000 |
| 98 | 582.63820000 | 5.59210000 |
| 99 | 589.31400000 | 4.53170000 |
| 100 | 604.04190000 | 29.63020000 |
| 101 | 667.51160000 | 53.62380000 |
| 102 | 736.80580000 | 8.19550000 |
| 103 | 756.98630000 | 0.61890000 |
| 104 | 763.59030000 | 15.26370000 |

| | | |
|---|---|---|
| 105 | 771.58040000 | 39.12390000 |
| 106 | 784.54650000 | 52.12450000 |
| 107 | 789.94160000 | 40.74990000 |
| 108 | 792.97480000 | 4.91240000 |
| 109 | 805.56780000 | 7.03480000 |
| 110 | 810.17680000 | 35.02580000 |
| 111 | 816.60890000 | 5.49010000 |
| 112 | 829.14180000 | 4.53490000 |
| 113 | 837.59470000 | 7.99160000 |
| 114 | 843.55170000 | 5.57580000 |
| 115 | 847.60510000 | 15.03510000 |
| 116 | 851.80360000 | 12.44490000 |
| 117 | 857.78660000 | 1.20870000 |
| 118 | 866.06300000 | 6.17030000 |
| 119 | 870.40270000 | 23.52640000 |
| 120 | 870.76790000 | 40.67380000 |
| 121 | 898.15320000 | 11.30230000 |
| 122 | 902.05610000 | 53.26420000 |
| 123 | 906.32040000 | 45.79570000 |
| 124 | 907.33070000 | 24.64350000 |
| 125 | 909.00040000 | 8.32990000 |
| 126 | 912.78120000 | 2.10750000 |
| 127 | 913.06240000 | 37.98150000 |
| 128 | 915.89760000 | 9.64070000 |
| 129 | 926.68420000 | 23.79050000 |
| 130 | 930.12930000 | 0.47860000 |
| 131 | 936.14360000 | 1.46090000 |
| 132 | 957.73770000 | 27.27230000 |
| 133 | 961.22990000 | 6.56610000 |
| 134 | 973.94210000 | 0.55880000 |
| 135 | 977.38950000 | 8.45760000 |
| 136 | 1005.81290000 | 1.24060000 |
| 137 | 1010.68960000 | 7.75110000 |
| 138 | 1014.44960000 | 58.67430000 |
| 139 | 1018.34640000 | 27.38190000 |
| 140 | 1031.77870000 | 50.43640000 |
| 141 | 1032.37660000 | 68.60440000 |
| 142 | 1032.90850000 | 49.54420000 |
| 143 | 1048.41750000 | 180.45820000 |
| 144 | 1052.57950000 | 14.50130000 |
| 145 | 1053.37640000 | 163.49280000 |
| 146 | 1061.27200000 | 183.21080000 |
| 147 | 1062.27470000 | 1.00320000 |
| 148 | 1068.83940000 | 4.76370000 |
| 149 | 1069.06380000 | 3.37390000 |
| 150 | 1076.23420000 | 20.90670000 |
| 151 | 1094.59620000 | 4.13510000 |
| 152 | 1101.94270000 | 34.20480000 |
| 153 | 1108.41380000 | 32.48630000 |
| 154 | 1111.81290000 | 22.99610000 |
| 155 | 1113.92120000 | 20.92550000 |
| 156 | 1115.98730000 | 31.41140000 |
| 157 | 1125.25960000 | 119.36210000 |
| 158 | 1128.67680000 | 7.67120000 |
| 159 | 1139.06410000 | 24.05070000 |

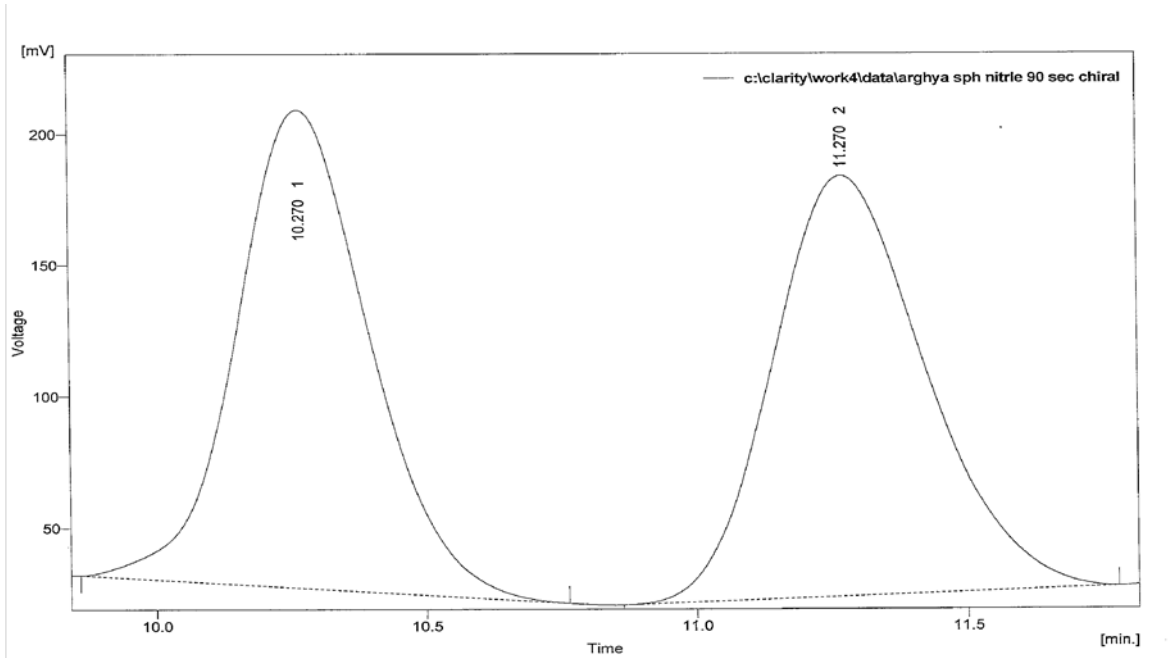
| | | |
|---|---|---|
| 160 | 1146.69880000 | 101.64350000 |
| 161 | 1154.82480000 | 51.35760000 |
| 162 | 1172.56520000 | 52.18800000 |
| 163 | 1173.49600000 | 51.06130000 |
| 164 | 1179.40430000 | 29.59810000 |
| 165 | 1184.28270000 | 83.73630000 |
| 166 | 1185.55190000 | 294.96100000 |
| 167 | 1193.01630000 | 30.75140000 |
| 168 | 1212.79580000 | 16.00140000 |
| 169 | 1213.75400000 | 8.22500000 |
| 170 | 1217.81840000 | 15.63330000 |
| 171 | 1221.02720000 | 10.30830000 |
| 172 | 1224.97090000 | 15.81950000 |
| 173 | 1230.07040000 | 18.10150000 |
| 174 | 1242.91050000 | 4.05710000 |
| 175 | 1257.69310000 | 90.25450000 |
| 176 | 1260.44630000 | 47.74680000 |
| 177 | 1270.35310000 | 18.80900000 |
| 178 | 1270.83570000 | 20.08880000 |
| 179 | 1280.78440000 | 128.14020000 |
| 180 | 1296.31140000 | 120.39290000 |
| 181 | 1303.74790000 | 15.41010000 |
| 182 | 1315.81730000 | 4.63630000 |
| 183 | 1318.80140000 | 7.56570000 |
| 184 | 1319.13910000 | 2.63770000 |
| 185 | 1331.42270000 | 12.70990000 |
| 186 | 1339.86590000 | 11.50700000 |
| 187 | 1347.84460000 | 6.61000000 |
| 188 | 1353.81160000 | 5.25830000 |
| 189 | 1363.75440000 | 0.40140000 |
| 190 | 1371.43390000 | 5.96620000 |
| 191 | 1372.54300000 | 10.72640000 |
| 192 | 1374.35710000 | 5.55020000 |
| 193 | 1376.41910000 | 0.58070000 |
| 194 | 1378.53030000 | 0.24670000 |
| 195 | 1379.95850000 | 17.48010000 |
| 196 | 1386.62450000 | 24.26030000 |
| 197 | 1390.93020000 | 27.61250000 |
| 198 | 1394.86200000 | 25.39220000 |
| 199 | 1396.03200000 | 95.44290000 |
| 200 | 1396.60030000 | 107.25030000 |
| 201 | 1401.54630000 | 13.33370000 |
| 202 | 1402.76470000 | 96.34640000 |
| 203 | 1405.29560000 | 8.98330000 |
| 204 | 1406.53380000 | 33.20360000 |
| 205 | 1407.13670000 | 7.18680000 |
| 206 | 1412.63730000 | 1.26750000 |
| 207 | 1413.28710000 | 8.65090000 |
| 208 | 1414.25510000 | 17.53420000 |
| 209 | 1420.84480000 | 26.62640000 |
| 210 | 1426.12930000 | 17.16330000 |
| 211 | 1426.74830000 | 19.52770000 |
| 212 | 1436.76960000 | 14.33810000 |
| 213 | 1436.91720000 | 7.11180000 |
| 214 | 1440.02290000 | 24.56200000 |

| | | |
|---|---|---|
| 215 | 1443.80680000 | 19.96510000 |
| 216 | 1468.93020000 | 3.20820000 |
| 217 | 1469.72750000 | 0.20050000 |
| 218 | 1477.59280000 | 4.36390000 |
| 219 | 1477.93000000 | 0.49230000 |
| 220 | 1478.04670000 | 8.65500000 |
| 221 | 1481.15830000 | 9.04610000 |
| 222 | 1483.44230000 | 3.49010000 |
| 223 | 1483.60910000 | 7.66680000 |
| 224 | 1484.14920000 | 10.41730000 |
| 225 | 1484.25180000 | 4.72800000 |
| 226 | 1484.94130000 | 10.66070000 |
| 227 | 1486.08480000 | 2.15910000 |
| 228 | 1487.64990000 | 5.37830000 |
| 229 | 1489.69630000 | 19.36780000 |
| 230 | 1491.13830000 | 12.13580000 |
| 231 | 1491.85750000 | 3.82710000 |
| 232 | 1492.87420000 | 2.57700000 |
| 233 | 1493.27230000 | 4.50280000 |
| 234 | 1493.81260000 | 6.48980000 |
| 235 | 1497.22090000 | 12.81180000 |
| 236 | 1497.76100000 | 2.10940000 |
| 237 | 1498.21910000 | 0.83540000 |
| 238 | 1499.19160000 | 2.61960000 |
| 239 | 1502.04690000 | 3.43260000 |
| 240 | 1505.19880000 | 11.75580000 |
| 241 | 1505.65380000 | 9.67210000 |
| 242 | 1507.16460000 | 10.91600000 |
| 243 | 1508.82380000 | 8.47740000 |
| 244 | 1510.84640000 | 3.19140000 |
| 245 | 1512.20430000 | 9.59800000 |
| 246 | 1515.66200000 | 4.46140000 |
| 247 | 1516.17650000 | 4.15080000 |
| 248 | 1517.96630000 | 14.25090000 |
| 249 | 1518.74100000 | 6.40740000 |
| 250 | 1523.52530000 | 6.47380000 |
| 251 | 1524.92190000 | 18.41530000 |
| 252 | 1525.31320000 | 46.30040000 |
| 253 | 1529.88830000 | 13.44440000 |
| 254 | 1611.44900000 | 6.58380000 |
| 255 | 1713.65400000 | 569.30330000 |
| 256 | 2266.17620000 | 744.81130000 |
| 257 | 2989.01090000 | 51.83120000 |
| 258 | 2995.58250000 | 29.84850000 |
| 259 | 2997.33670000 | 62.01030000 |
| 260 | 3010.09430000 | 40.08540000 |
| 261 | 3011.43070000 | 55.81470000 |
| 262 | 3013.46650000 | 47.71640000 |
| 263 | 3021.06850000 | 33.59580000 |
| 264 | 3021.31290000 | 47.76310000 |
| 265 | 3024.46070000 | 77.24730000 |
| 266 | 3025.69850000 | 9.28410000 |
| 267 | 3028.88140000 | 94.67990000 |
| 268 | 3032.26980000 | 25.20870000 |
| 269 | 3034.11610000 | 95.39580000 |

| | | |
|---|---|---|
| 270 | 3036.46110000 | 103.13430000 |
| 271 | 3038.51230000 | 17.41520000 |
| 272 | 3038.61150000 | 27.45020000 |
| 273 | 3040.90020000 | 11.58190000 |
| 274 | 3041.52400000 | 20.82620000 |
| 275 | 3042.99940000 | 7.09860000 |
| 276 | 3045.17450000 | 16.29680000 |
| 277 | 3047.87980000 | 17.54570000 |
| 278 | 3048.81080000 | 35.21720000 |
| 279 | 3049.14560000 | 31.34170000 |
| 280 | 3049.26440000 | 112.21870000 |
| 281 | 3054.47400000 | 30.38750000 |
| 282 | 3059.66130000 | 5.51240000 |
| 283 | 3061.86620000 | 51.47490000 |
| 284 | 3066.89510000 | 44.61330000 |
| 285 | 3067.72440000 | 29.36430000 |
| 286 | 3069.13320000 | 49.26200000 |
| 287 | 3075.37370000 | 31.40920000 |
| 288 | 3077.58980000 | 78.79580000 |
| 289 | 3079.33240000 | 36.05340000 |
| 290 | 3082.31740000 | 90.32430000 |
| 291 | 3082.99080000 | 28.78130000 |
| 292 | 3084.07490000 | 21.16650000 |
| 293 | 3084.51400000 | 48.41410000 |
| 294 | 3089.25650000 | 84.08730000 |
| 295 | 3098.03840000 | 20.20970000 |
| 296 | 3098.31190000 | 39.88300000 |
| 297 | 3102.17660000 | 18.43730000 |
| 298 | 3103.98980000 | 33.33060000 |
| 299 | 3104.16940000 | 37.96350000 |
| 300 | 3104.81130000 | 49.48200000 |
| 301 | 3106.46640000 | 9.78680000 |
| 302 | 3107.11250000 | 26.55350000 |
| 303 | 3110.66070000 | 55.24900000 |
| 304 | 3111.37510000 | 12.07130000 |
| 305 | 3111.55000000 | 11.22470000 |
| 306 | 3113.72210000 | 21.91960000 |
| 307 | 3116.76380000 | 34.67860000 |
| 308 | 3118.47690000 | 21.44140000 |
| 309 | 3119.94990000 | 28.32880000 |
| 310 | 3124.26900000 | 29.95950000 |
| 311 | 3128.15540000 | 50.70410000 |
| 312 | 3130.16590000 | 42.92180000 |
| 313 | 3130.66590000 | 15.36590000 |
| 314 | 3140.09290000 | 22.44450000 |
| 315 | 3141.92820000 | 10.04470000 |
| 316 | 3145.12270000 | 26.13660000 |
| 317 | 3146.96760000 | 9.81300000 |
| 318 | 3149.28890000 | 13.93910000 |
| 319 | 3149.62680000 | 9.10350000 |
| 320 | 3157.21740000 | 11.22190000 |
| 321 | 3164.67560000 | 5.32460000 |

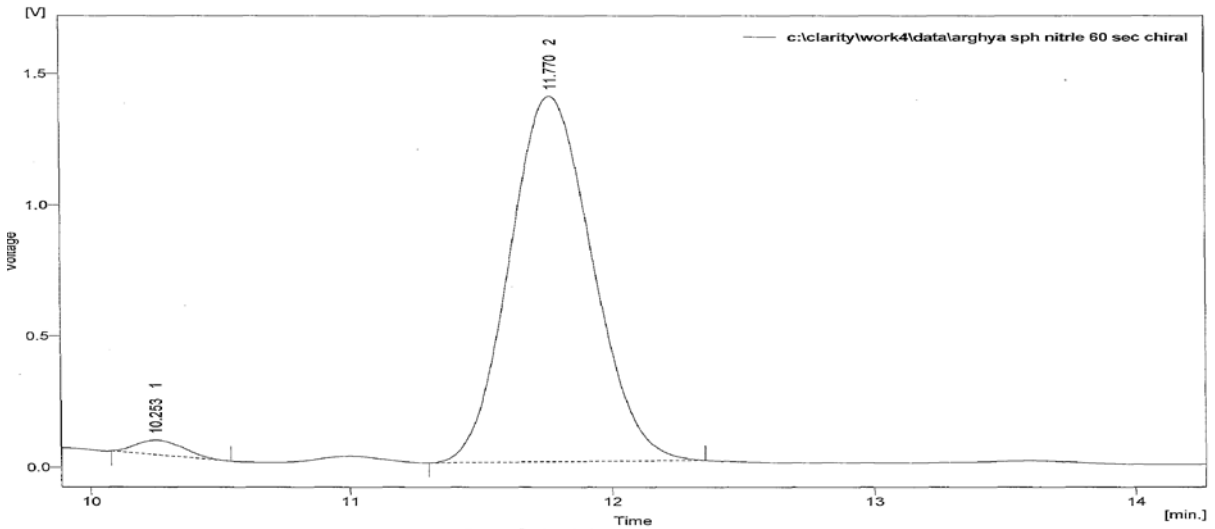
## 6. HPLC/GC traces

### *tert*-Butyl 2-Cyano-2-(2-phenylsulfanyl)piperidin-1-carboxylate 5a




*Result Table - Calculation Method Uncal*

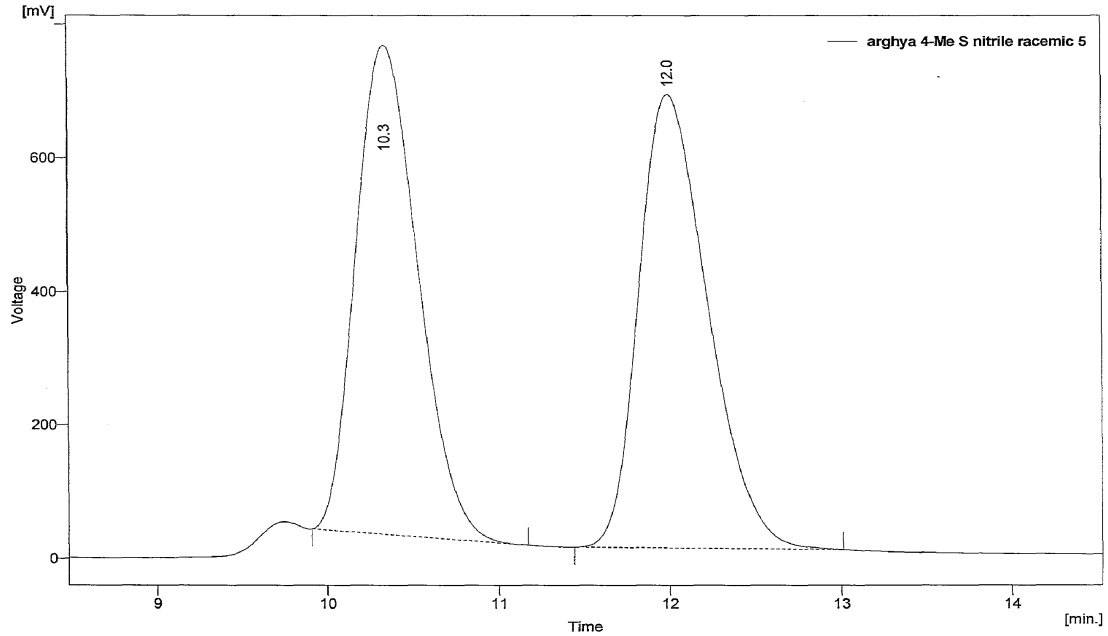
| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Response Factor |
|---|---|---|---|---|---|---|---|
| 1 | 10.270 | 3104.899 | 182.312 | 49.8 | 53.2 | 0.26 | 0.0 |
| 2 | 11.270 | 3129.136 | 160.583 | 50.2 | 46.8 | 0.31 | 0.0 |
| | Total | 6234.035 | 342.895 | 100.0 | 100.0 | | - |




*Result Table - Calculation Method Uncal*

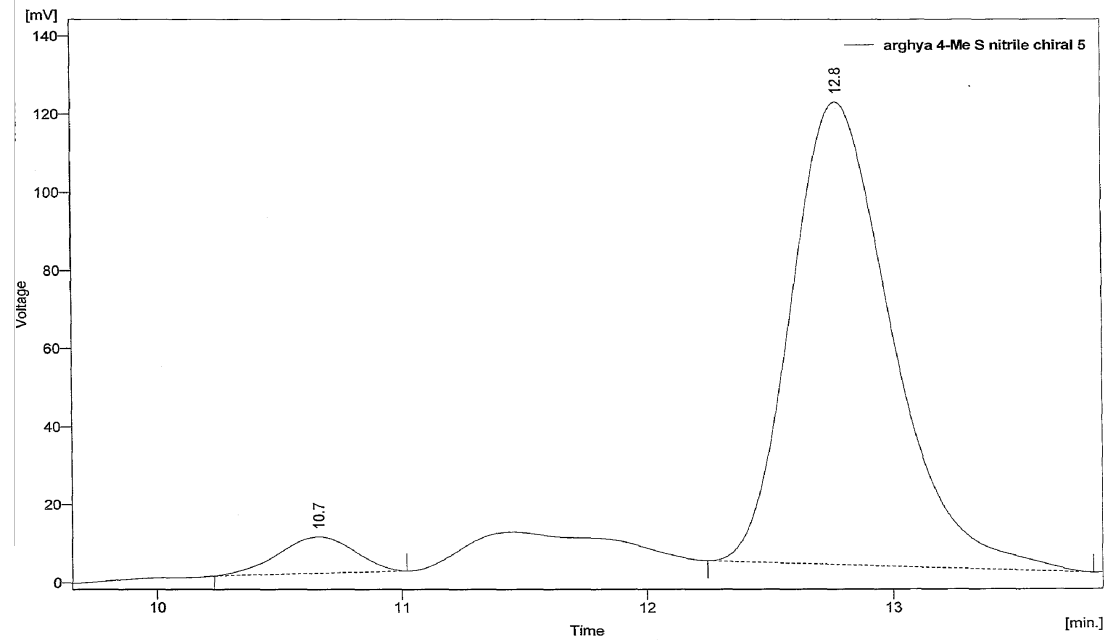
| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Response Factor |
|---|---|---|---|---|---|---|---|
| 1 | 10.253 | 716.416 | 55.254 | 2.3 | 3.8 | 0.21 | 0.0 |
| 2 | 11.770 | 30561.612 | 1392.200 | 97.7 | 96.2 | 0.35 | 0.0 |
| | Total | 31278.028 | 1447.454 | 100.0 | 100.0 | | - |

## *tert*-Butyl 2-Cyano-2-(*p*-tolylsulfanyl)piperidin-1-carboxylate 5b




*Result Table - Calculation Method Uncal*

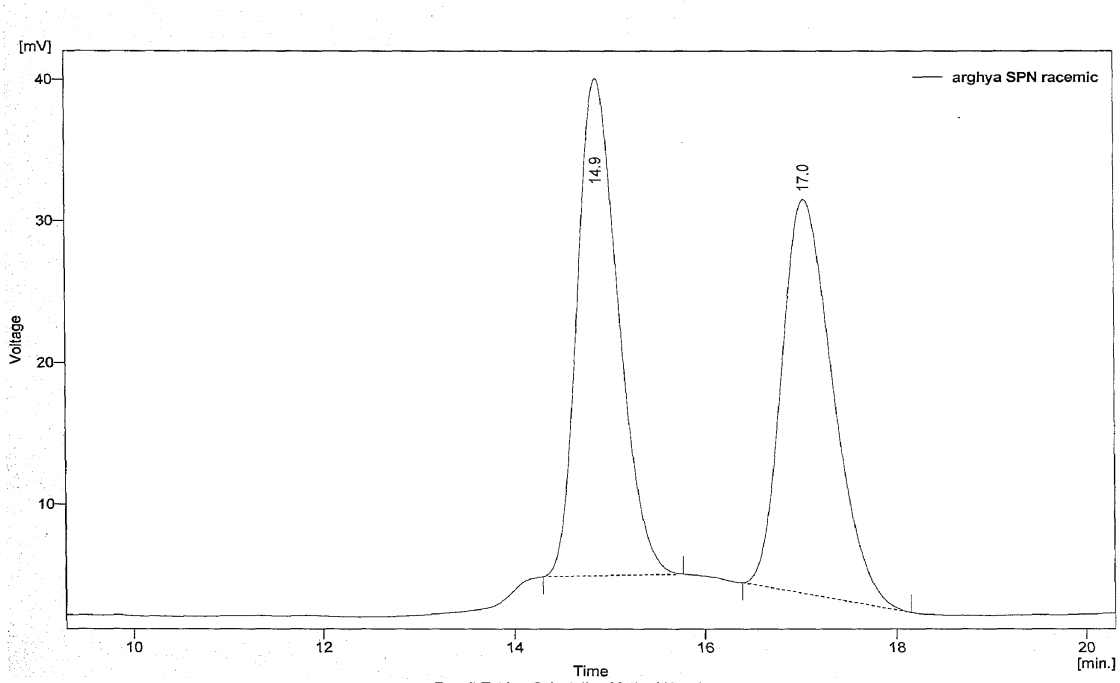
| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] |
|---|---|---|---|---|---|---|
| 1 | 10.337 | 18430.202 | 732.364 | 49.2 | 51.9 | 0.40 |
| 2 | 11.993 | 19007.543 | 678.906 | 50.8 | 48.1 | 0.44 |
| | Total | 37437.745 | 1411.269 | 100.0 | 100.0 | |




*Result Table - Calculation Method Uncal*

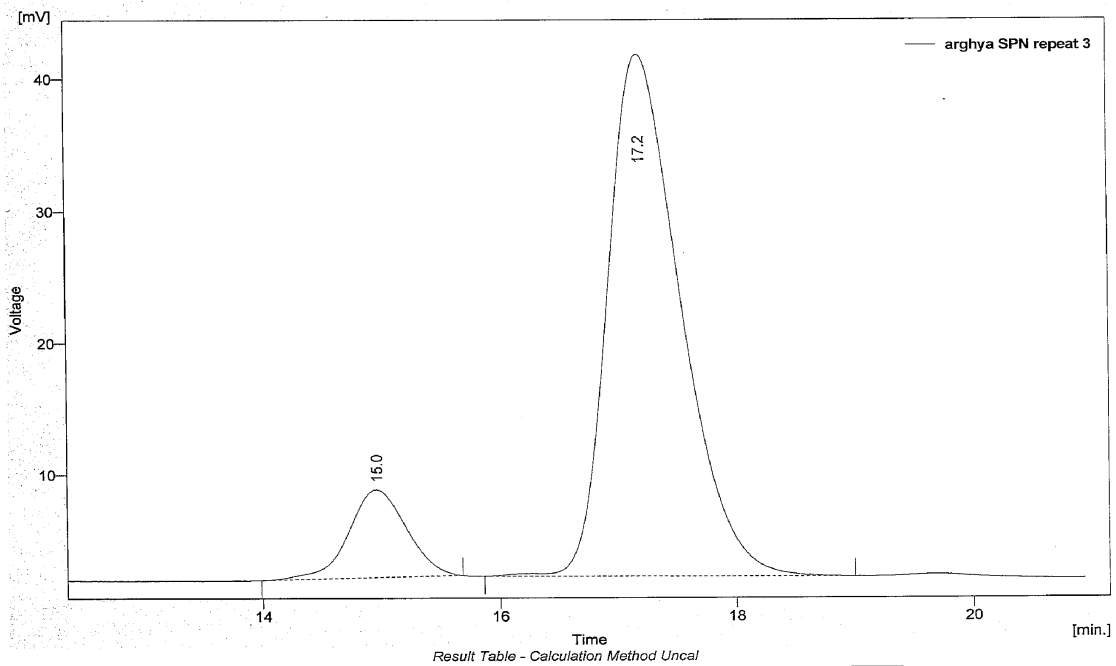
| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] |
|---|---|---|---|---|---|---|
| 1 | 10.663 | 199.629 | 9.298 | 5.6 | 7.3 | 0.35 |
| 2 | 12.773 | 3348.863 | 118.515 | 94.4 | 92.7 | 0.43 |
| | Total | 3548.492 | 127.813 | 100.0 | 100.0 | |

## *tert*-Butyl 2-Cyano-2-(*o*-methoxyphenylsulfanyl)piperidin-1-carboxylate 5c




*Result Table - Calculation Method Uncal*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] |
|---|---|---|---|---|---|---|
| 1 | 14.870 | 1051.692 | 35.167 | 50.5 | 55.8 | 0.47 |
| 2 | 17.040 | 1029.016 | 27.883 | 49.5 | 44.2 | 0.57 |
| | Total | 2080.708 | 63.050 | 100.0 | 100.0 | |




*Result Table - Calculation Method Uncal*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] |
|---|---|---|---|---|---|---|
| 1 | 14.963 | 225.980 | 6.643 | 11.8 | 14.4 | 0.52 |
| 2 | 17.200 | 1685.058 | 39.582 | 88.2 | 85.6 | 0.66 |
| | Total | 1911.038 | 46.225 | 100.0 | 100.0 | |

## *tert*-Butyl 2-Cyano-2-[hydroxy(phenyl)methyl]piperidine-1-carboxylate 5d

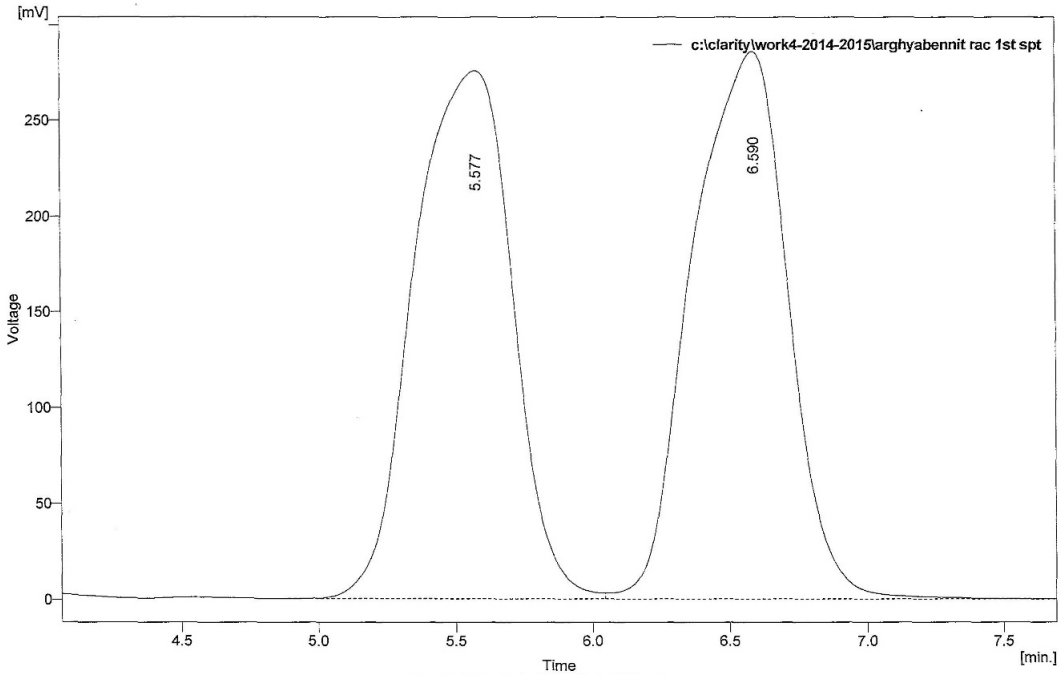
## Diastereomer A



| | | | |
|---|---|---|---|
| Created | : 20/03/2015 16:33:27 | By | : Clarity |
| Project | : WORK1 | Report Style | : Chromatogram |
| ISTD Amount | : 0 | Inj. Volume | : 10 |
| Sample ID | : arghyabennit rac 1st spt | Sample | : arghyabennit rac 1st spt |
| Calibration | : arghyabennit rac 1st spt | Chromatogram | : c:\clarity\work4-2014-2015\arghyabennit rac 1st spt |

| | | | |
|---|---|---|---|
| Method | : Cellulose-2 | By | : ch1rjh |
| Description | : arghyabennit rac 1st spt | | |
| Created | : 13/03/2001 08:37 | Modified | : 20/03/2015 17:33 |
| Column | : Cellulose-1 | Detection | : UV/Vis at 220nm |
| Mobile Phase | : 10% IPA in hexane | Temperature | : RT |
| Flow Rate | : 1mL/min | Pressure | : |
| Note | : | | |

| | | | |
|---|---|---|---|
| Autostop | : None | External Start | : Start Only, Down |
| Detector 1 | : Signal 1 | Range 1 | : Bipolar, 1250 mV, 10 Samp. per Sec. |
| Subtraction chromatogram | : (None) | Matching | : No Change |




*Result Table - Calculation Method Uncal*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Response Factor |
|---|---|---|---|---|---|---|---|
| 1 | 5.577 | 6866.274 | 275.830 | 49.9 | 49.1 | 0.41 | 0.0 |
| 2 | 6.590 | 6891.348 | 286.154 | 50.1 | 50.9 | 0.40 | 0.0 |
| | Total | 13757.622 | 561.984 | 100.0 | 100.0 | | - |

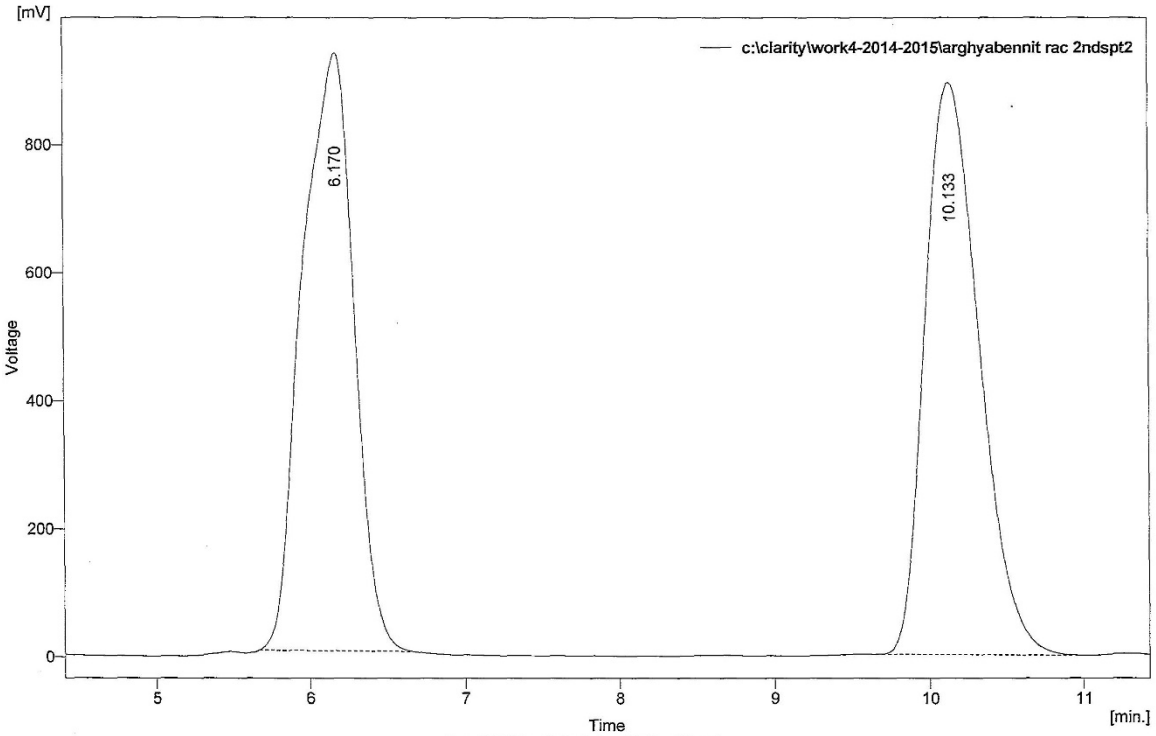
## Diastereomer B



| | | | |
|---|---|---|---|
| Created | : 20/03/2015 17:00:25 | By | : Clarity |
| Project | : WORK1 | Report Style | : Chromatogram |
| ISTD Amount | : 0 | Inj. Volume | : 10 |
| Sample ID | : arghyabennit rac 2ndspt2 | Sample | : arghyabennit rac 2ndspt2 |
| Calibration | : arghyabennit rac 2ndspt2 | Chromatogram | : c:\clarity\work4-2014-2015\arghyabennit rac 2ndspt2 |

| | | | |
|---|---|---|---|
| Method | : Cellulose-2 | By | : ch1rjh |
| Description | : arghyabennit rac 2ndspt2 | | |
| Created | : 13/03/2001 08:37 | Modified | : 20/03/2015 18:00 |
| Column | : Cellulose-1 | Detection | : UV/Vis at 220nm |
| Mobile Phase | : 10% IPA in hexane | Temperature | : RT |
| Flow Rate | : 1mL/min | Pressure | : |
| Note | : | | |

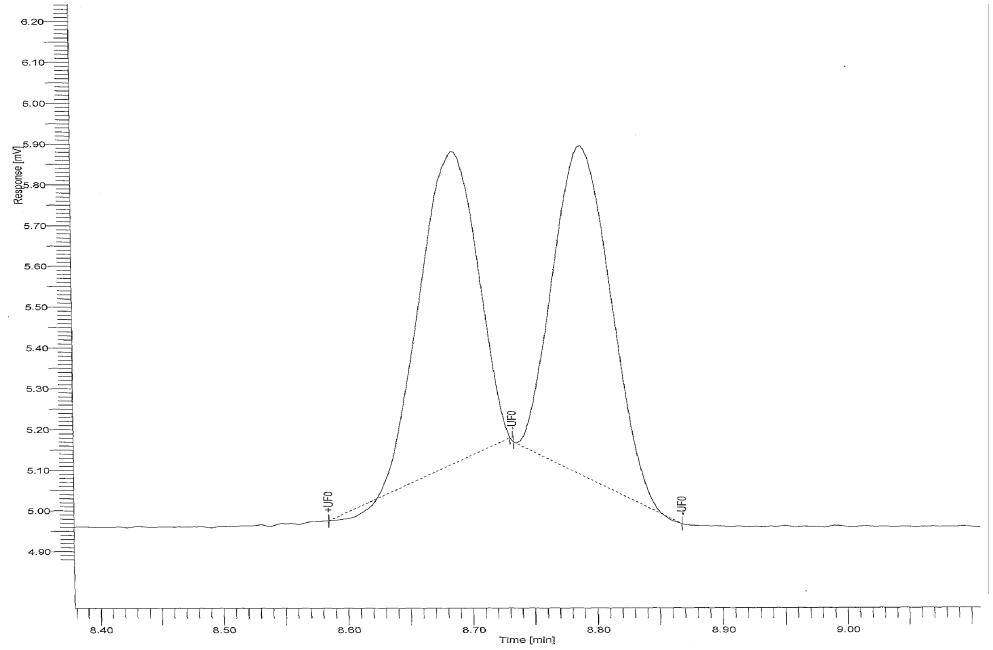
| | | | |
|---|---|---|---|
| Autostop | : None | External Start | : Start Only, Down |
| Detector 1 | : Signal 1 | Range 1 | : Bipolar, 1250 mV, 10 Samp. per Sec. |
| Subtraction chromatogram | : (None) | Matching | : No Change |



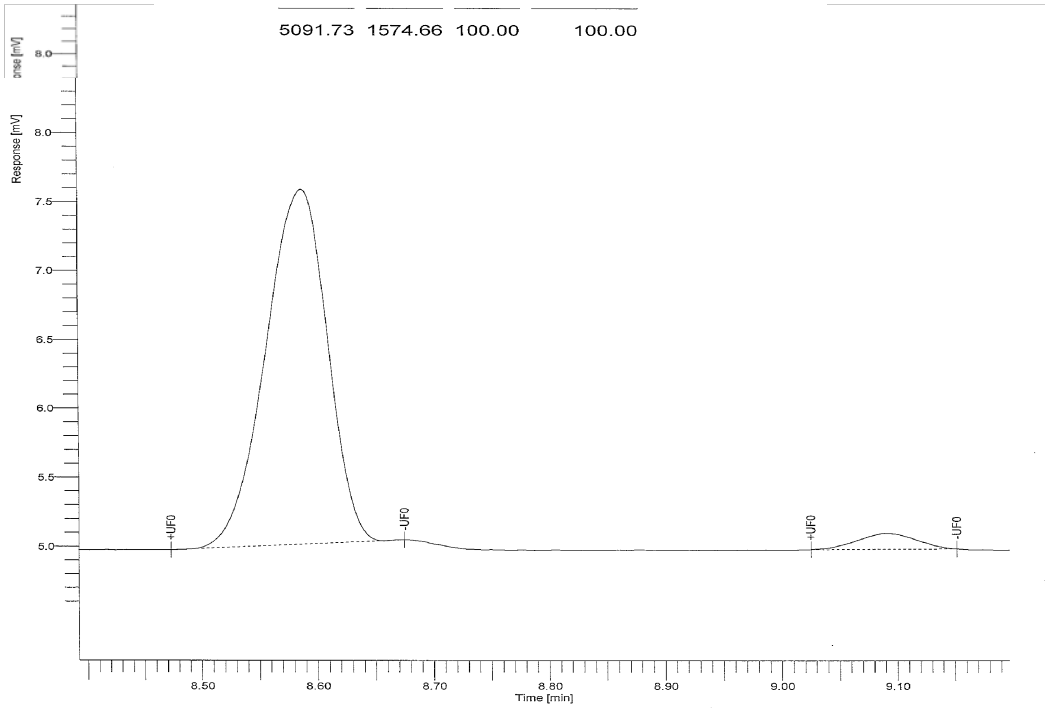

*Result Table - Calculation Method Uncal*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Response Factor |
|---|---|---|---|---|---|---|---|
| 1 | 6.170 | 21575.307 | 934.599 | 49.6 | 51.1 | 0.39 | 0.0 |
| 2 | 10.133 | 21927.637 | 893.946 | 50.4 | 48.9 | 0.39 | 0.0 |
| | Total | 43502.944 | 1828.545 | 100.0 | 100.0 | | - |

***tert*-Butyl 2-Cyano-2-(2-hydroxypropan-2-yl)piperidin-1-carboxylate 5e**

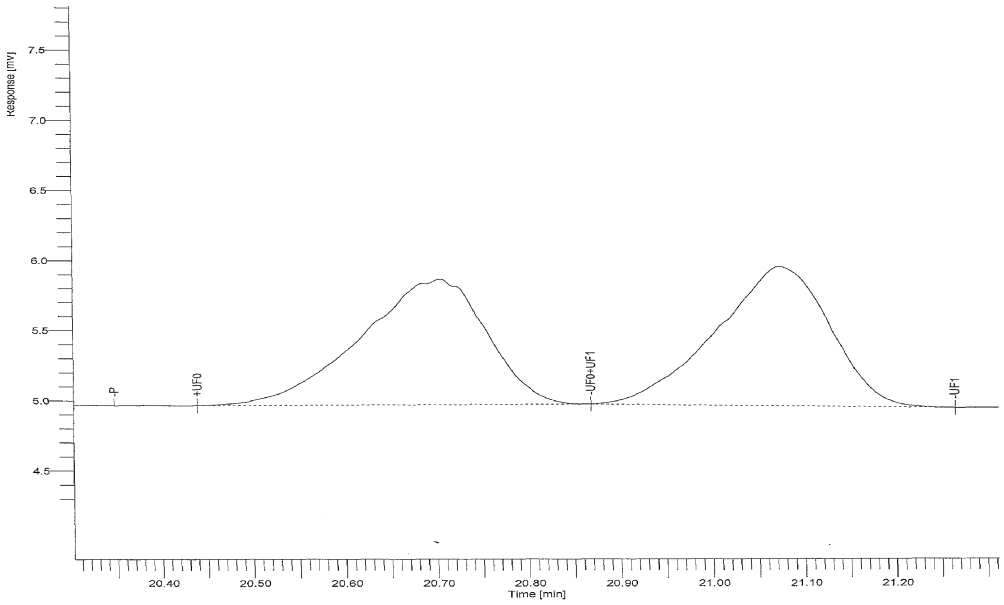



| Peak # | Time [min] | Area [µV·s] | Height [µV] | Area [%] | Norm. Area [%] | BL | Area/Height [s] |
|---|---|---|---|---|---|---|---|
| 1 | 8.685 | 2490.88 | 764.57 | 48.92 | 48.92 | *MM | 3.2579 |
| 2 | 8.789 | 2600.85 | 810.08 | 51.08 | 51.08 | *MM | 3.2106 |
| | | 5091.73 | 1574.66 | 100.00 | 100.00 | | |

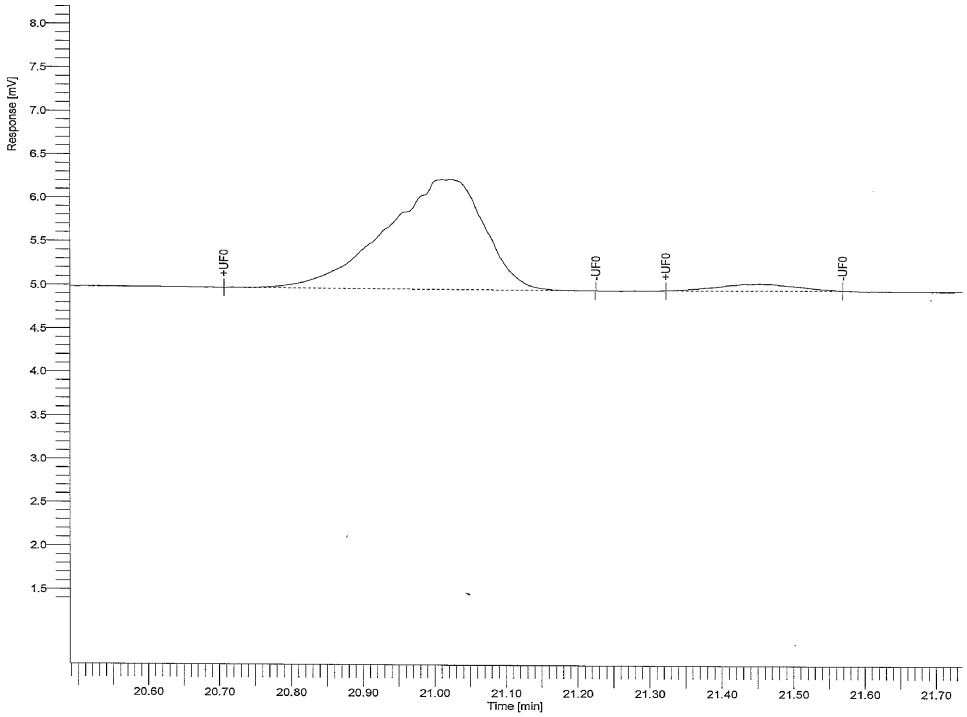



| Peak # | Time [min] | Area [µV·s] | Height [µV] | Area [%] | Norm. Area [%] | BL | Area/Height [s] |
|---|---|---|---|---|---|---|---|
| 1 | 8.587 | 9476.01 | 2575.19 | 95.93 | 95.93 | *MM | 3.6797 |
| 2 | 9.091 | 401.54 | 113.21 | 4.07 | 4.07 | *MM | 3.5470 |
| | | 9877.56 | 2688.40 | 100.00 | 100.00 | | |

***tert*-butyl 2-cyano-2-(1-hydroxycyclobutyl)piperidine-1-carboxylate 5f**

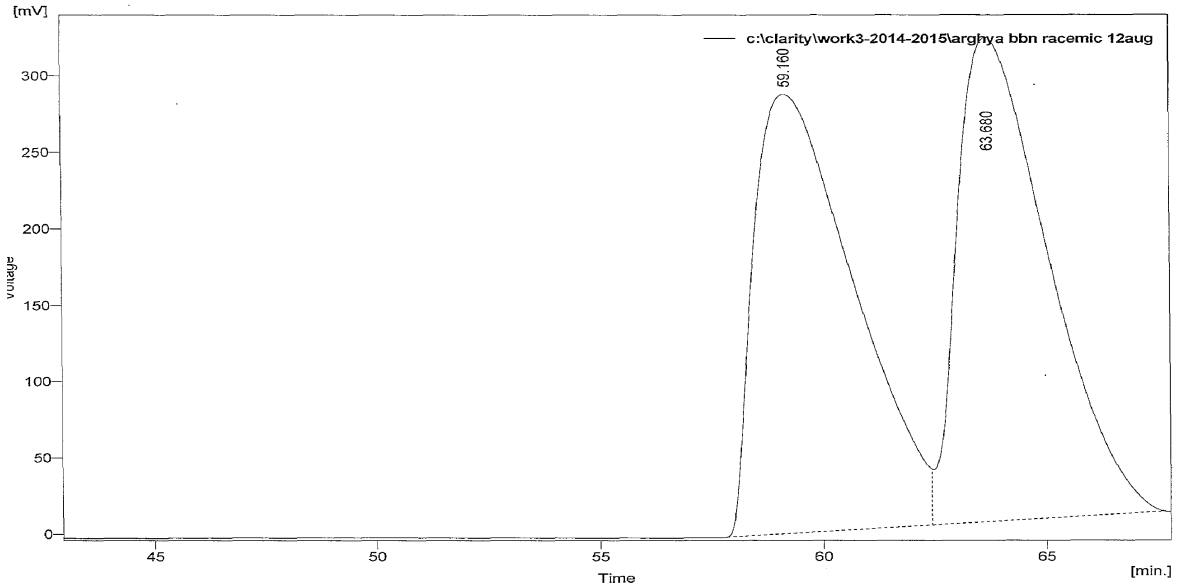



| Peak # | Time [min] | Area [µV·s] | Height [µV] | Area [%] | Norm. Area [%] | BL | Area/Height [s] |
|---|---|---|---|---|---|---|---|
| 1 | 20.704 | 8506.01 | 895.35 | 49.97 | 49.97 | *MM | 9.5002 |
| 2 | 21.075 | 8517.69 | 994.40 | 50.03 | 50.03 | *MM | 8.5657 |
| | | 17023.71 | 1889.75 | 100.00 | 100.00 | | |



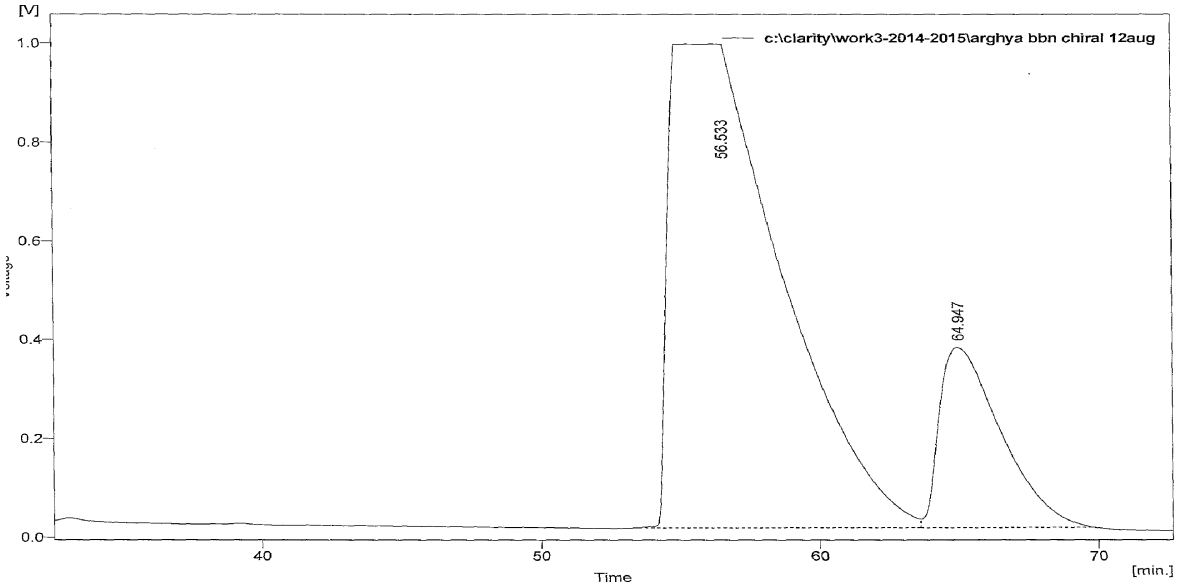

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 21.021 | 12045.92 | 1264.81 | 95.41 | 95.41 | | + | *MM | ---------- |
| 2 | | 21.451 | 579.54 | 77.21 | 4.59 | 4.59 | | | *MM | 0.0006 |
| | | | 12625.46 | 1342.02 | 100.00 | 100.00 | | | | 0.0006 |

## *tert*-Butyl 2-(4-Bromobenzoyl)-2-cyanopiperidin-1-carboxylate 5g




*Result Table - Calculation Method Uncal*

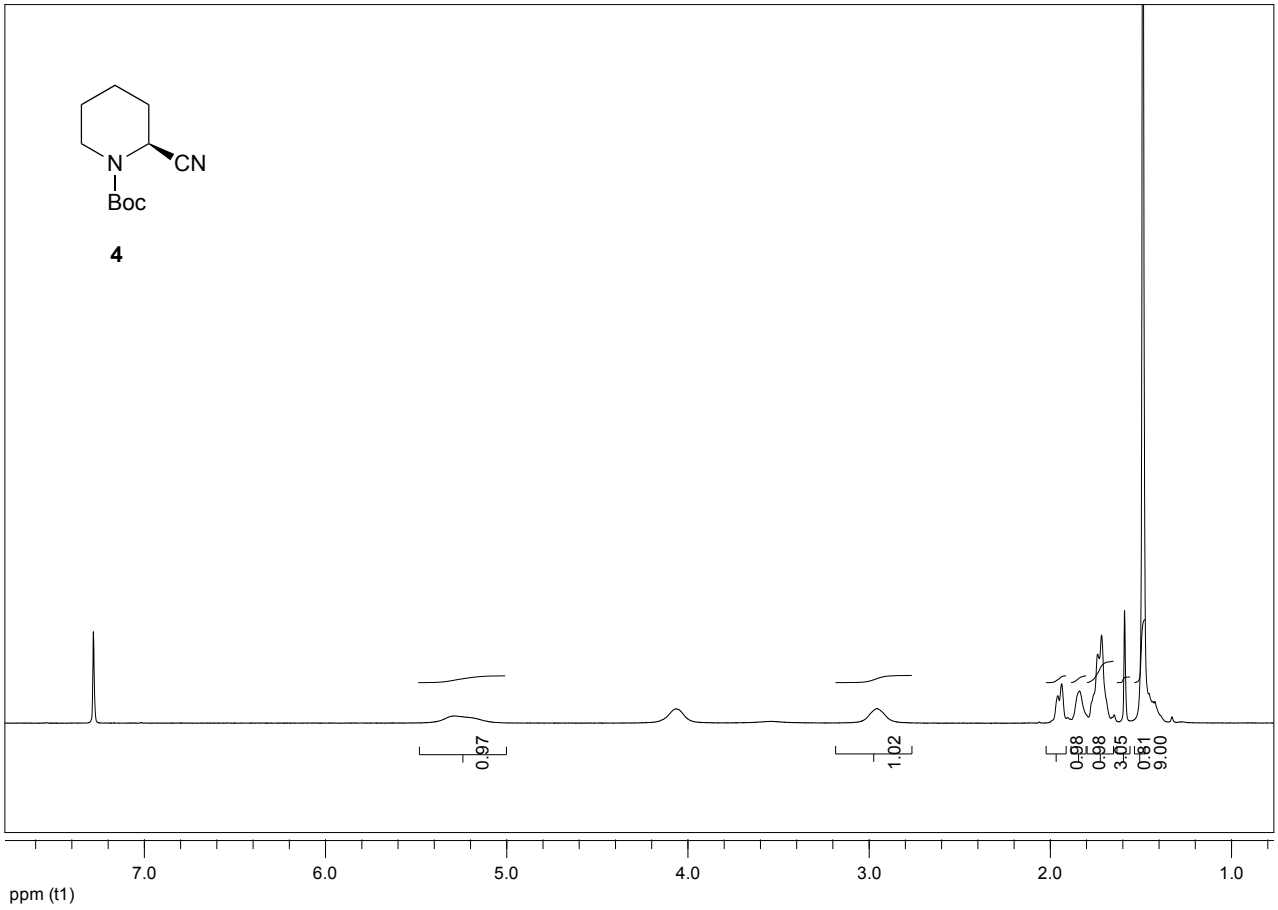
| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Response Factor |
|---|---|---|---|---|---|---|---|
| 1 | 59.160 | 44396.607 | 287.480 | 49.6 | 47.5 | 2.56 | 0.0 |
| 2 | 63.680 | 45042.678 | 317.305 | 50.4 | 52.5 | 2.27 | 0.0 |
| | Total | 89439.285 | 604.785 | 100.0 | 100.0 | | - |

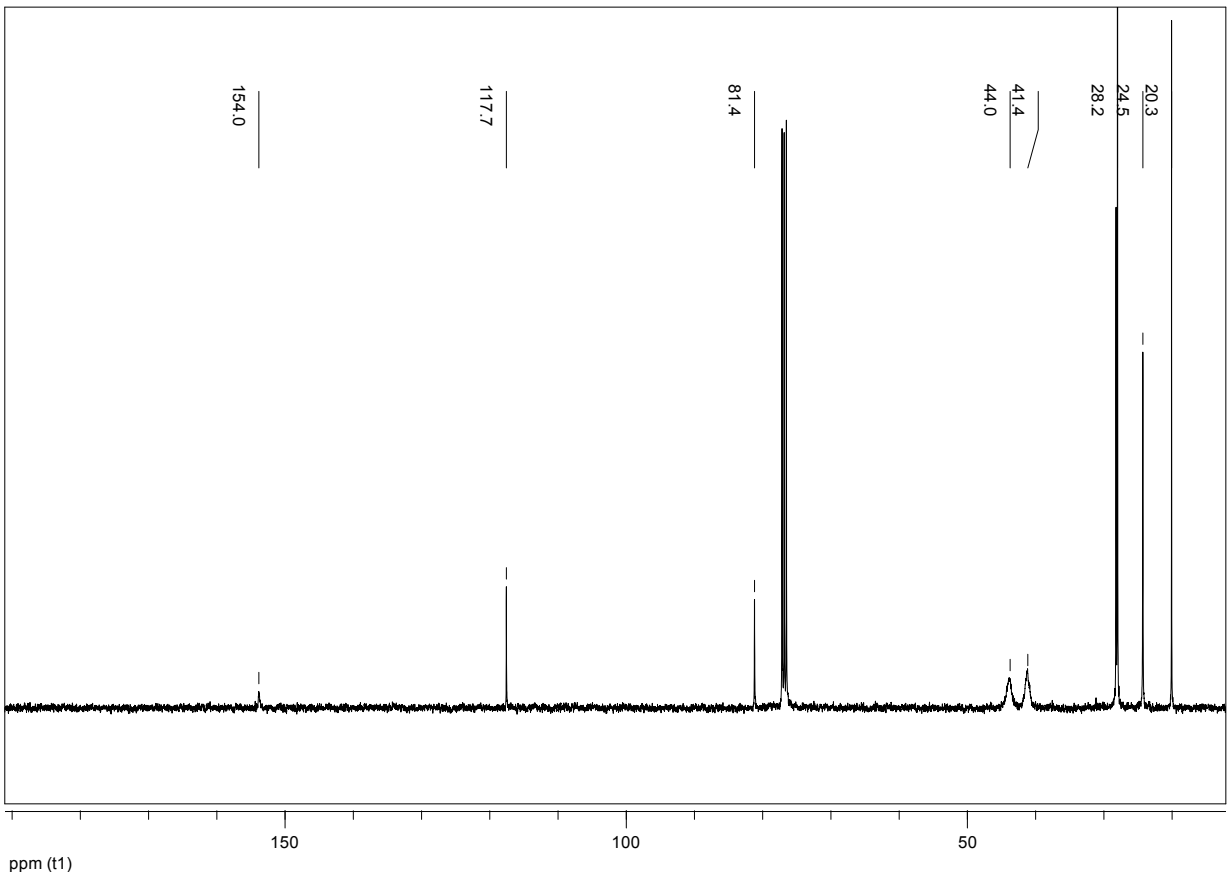


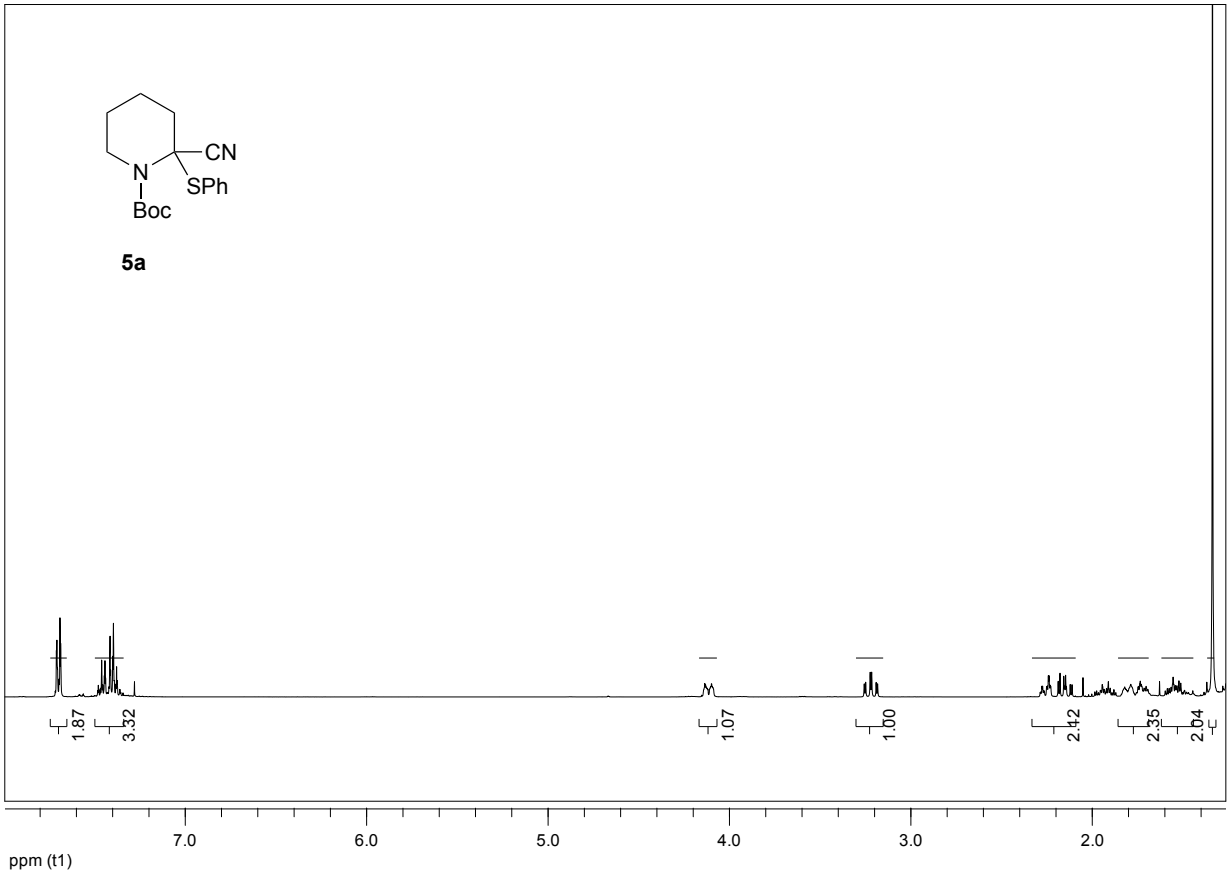

*Result Table - Calculation Method Uncal*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Response Factor |
|---|---|---|---|---|---|---|---|
| 1 | 56.533 | 271529.967 | 979.024 | 82.9 | 72.9 | 4.31 | 0.0 |
| 2 | 64.947 | 56169.594 | 363.539 | 17.1 | 27.1 | 2.41 | 0.0 |
| | Total | 327699.560 | 1342.563 | 100.0 | 100.0 | | - |

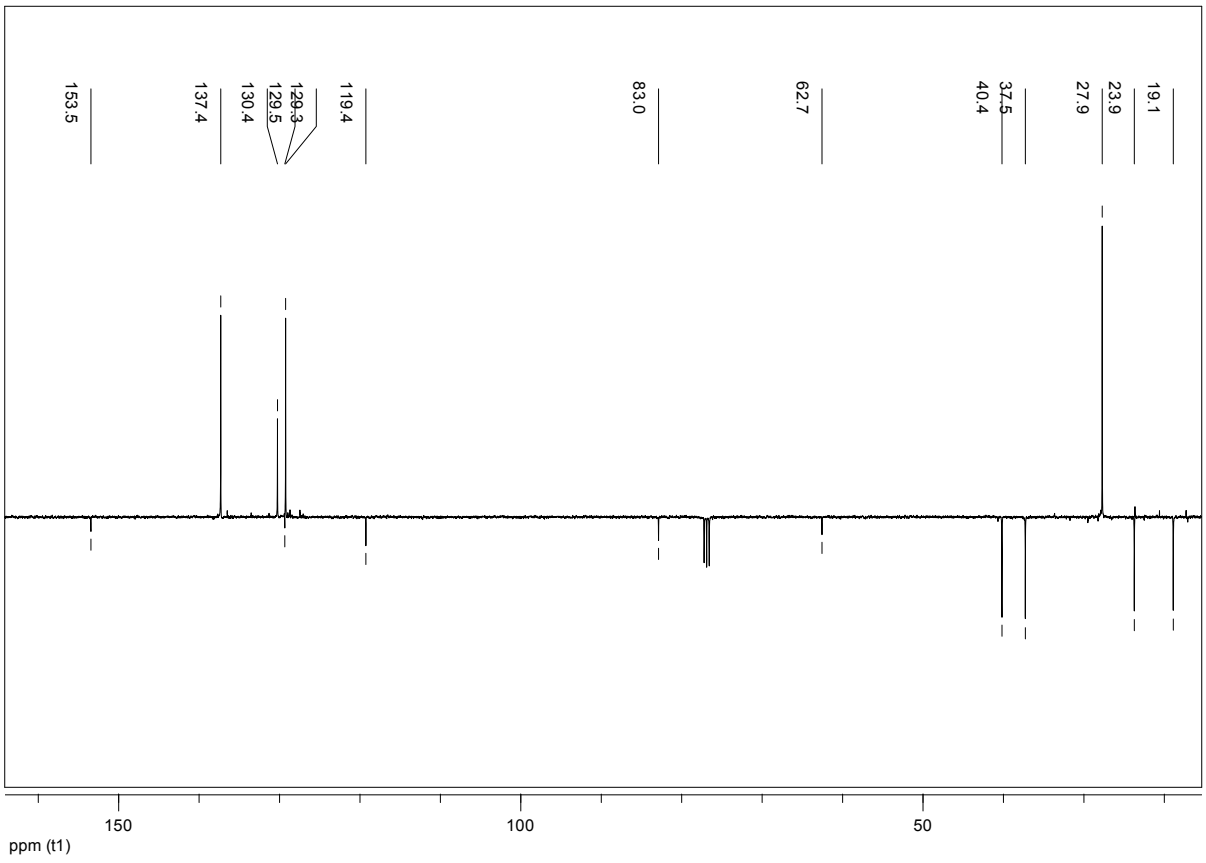
## 7. $^{1}H/^{13}C$ NMR spectra

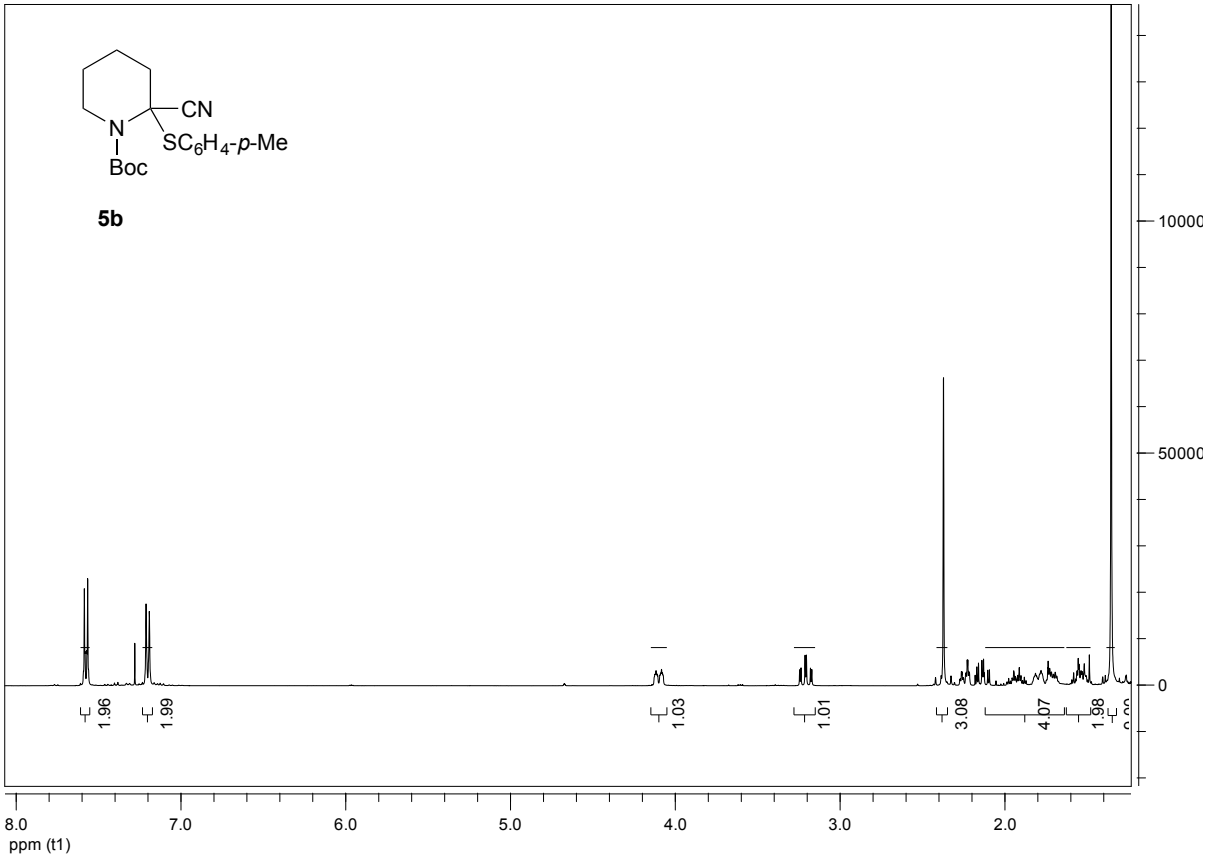


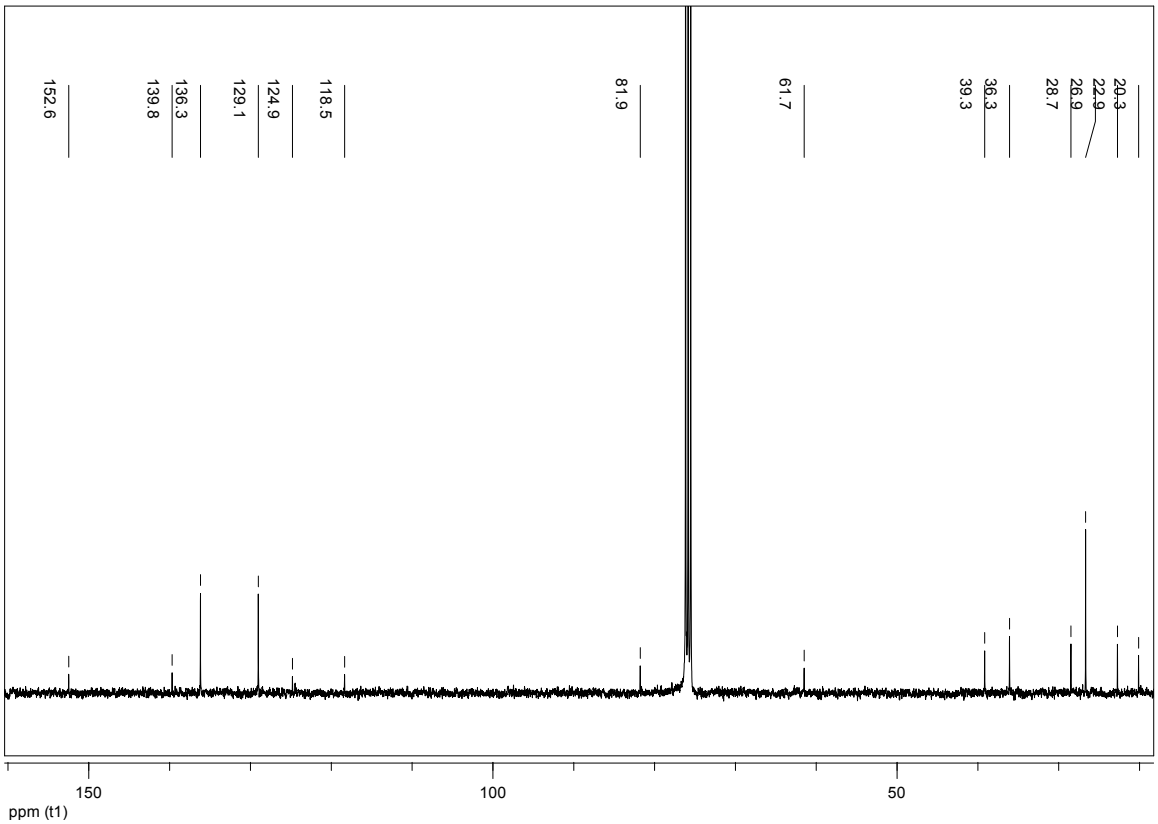



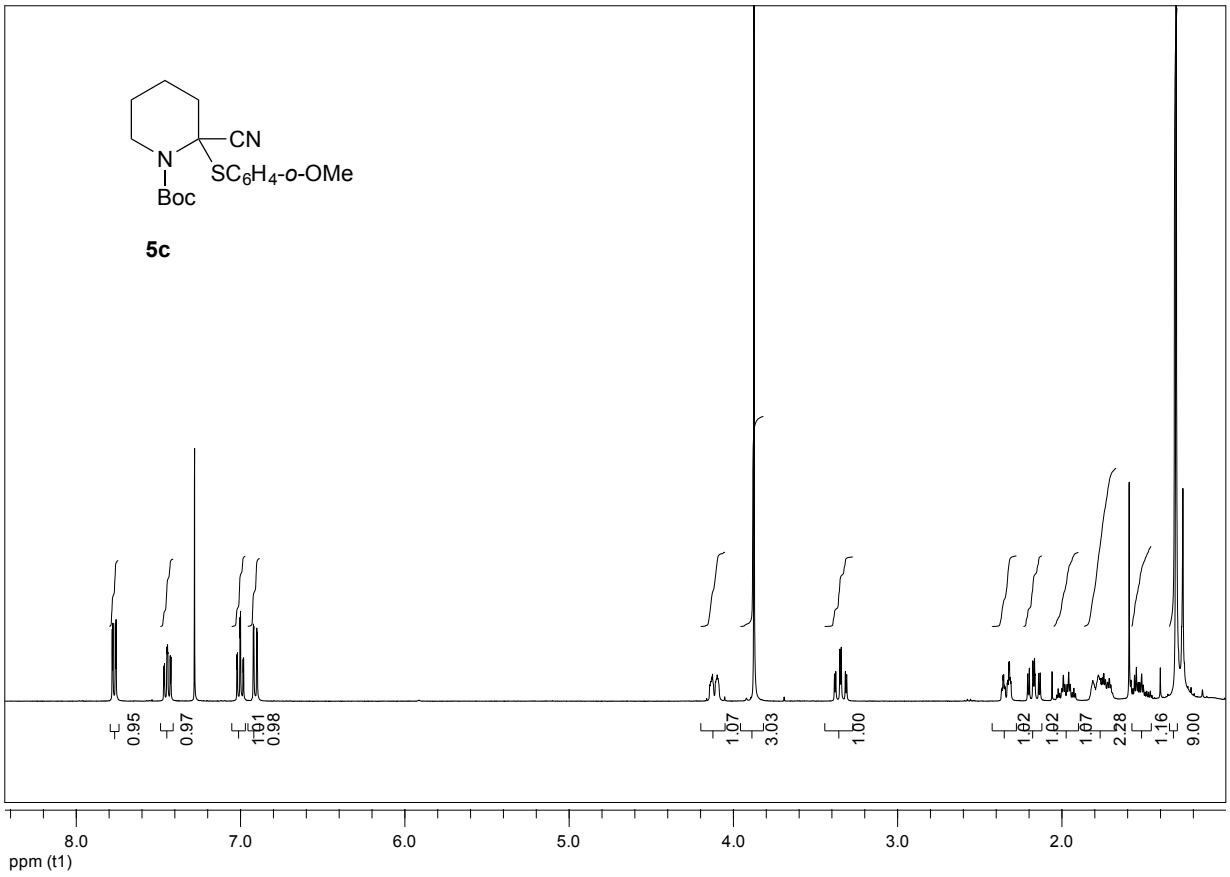

CN
N
SPh
Boc
1.87
3.32
1.07
1.00
2.12
2.35
2.04
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

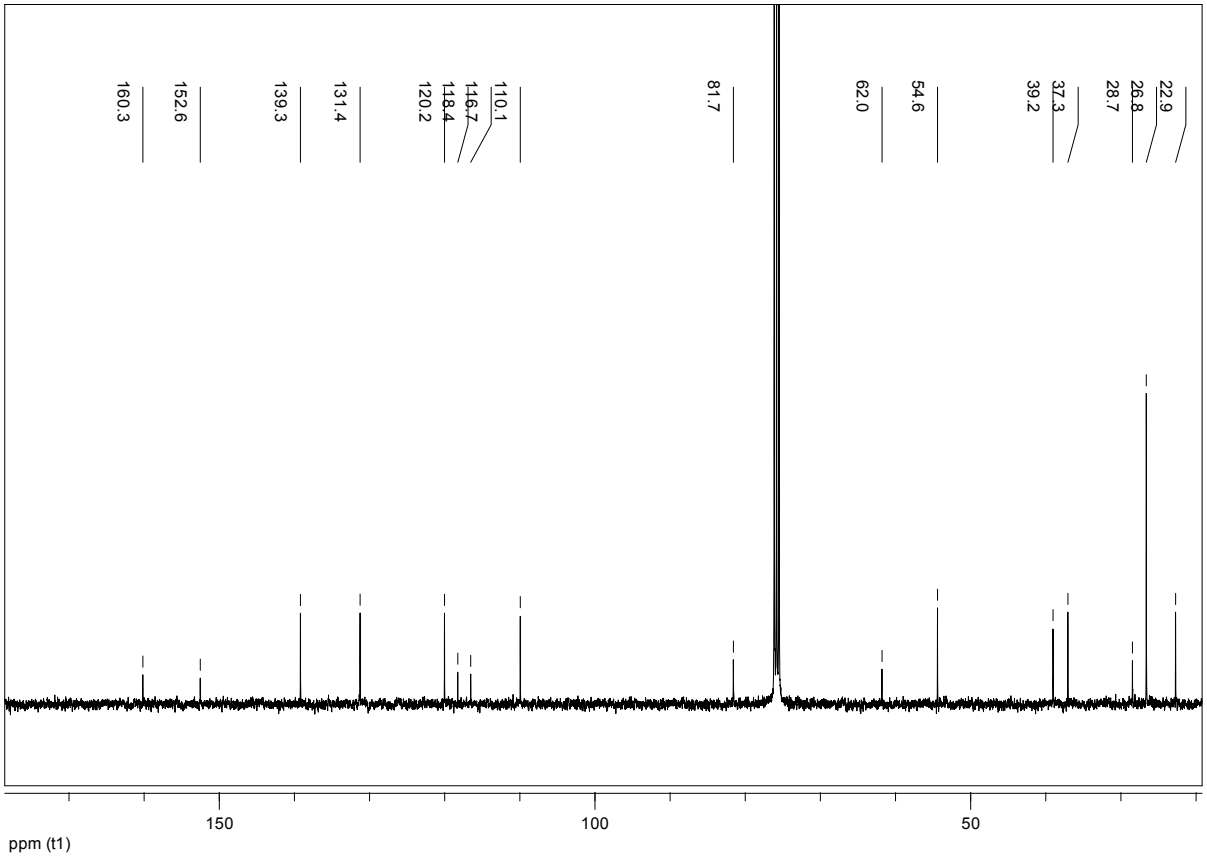
**5a**


153.5
137.4
130.4
129.5
129.3
119.4
83.0
62.7
40.4
37.5
27.9
23.9
19.1
150
100
50
ppm (t1)

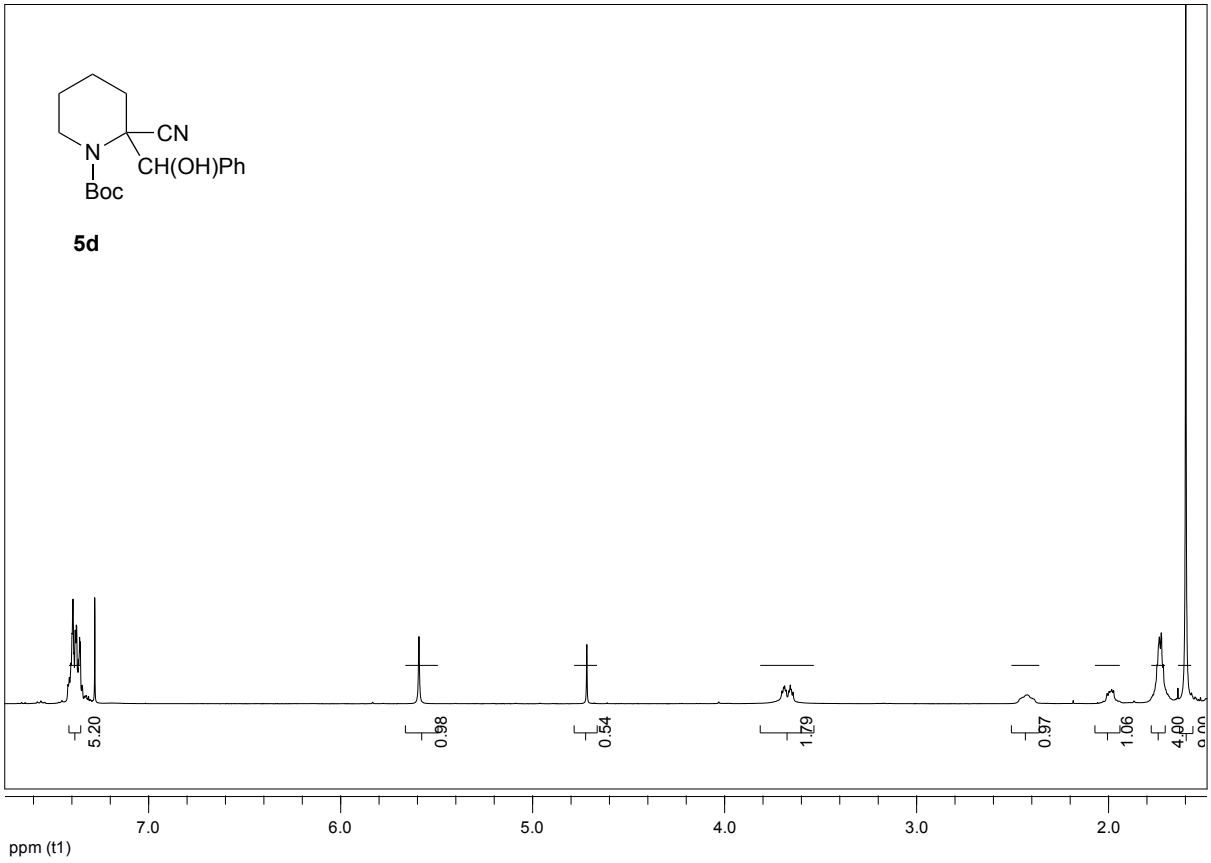

CN
N
SC6H4-p-Me
Boc
5b
10000
50000
0
1.96
1.99
1.03
1.01
3.08
4.07
1.88
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

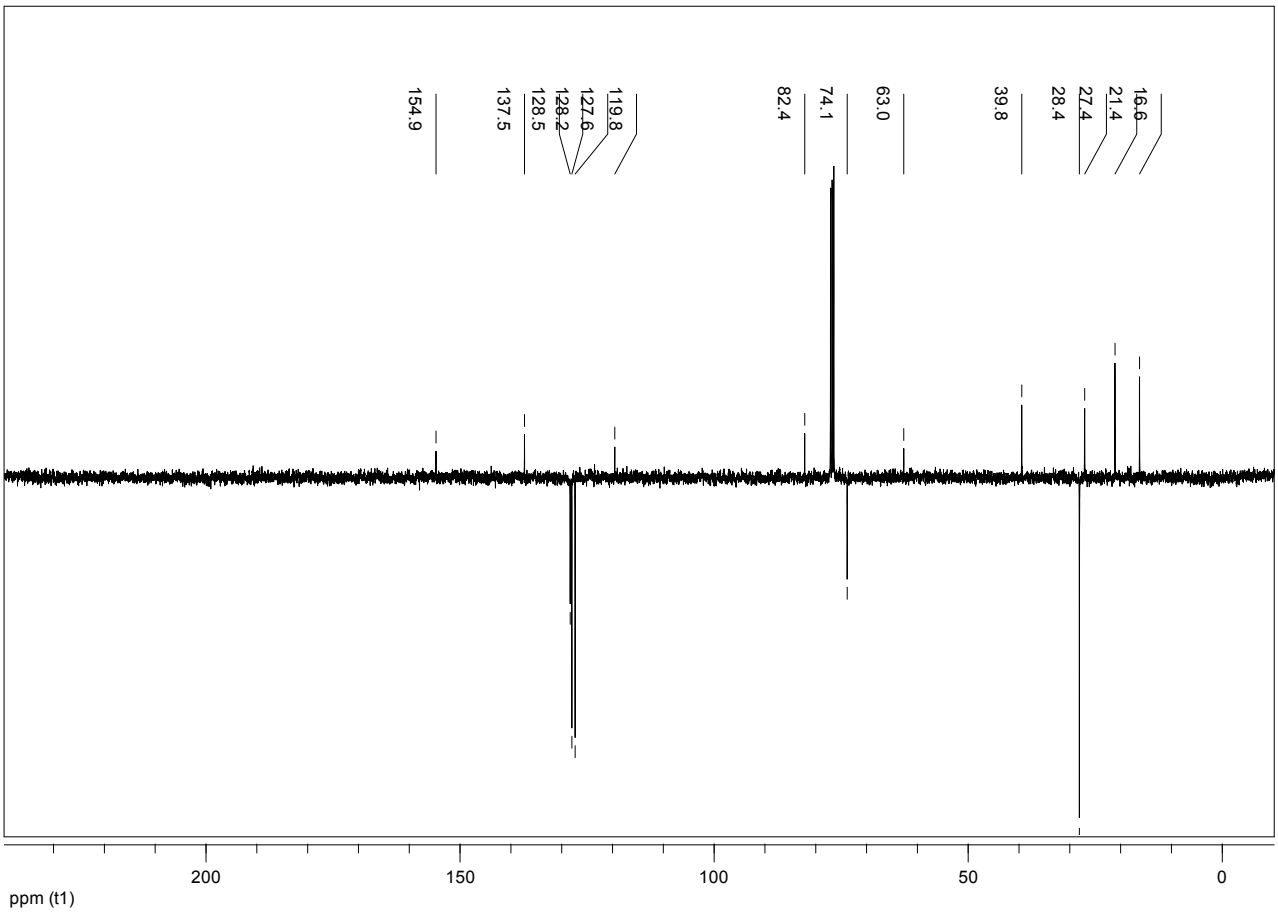

152.6
139.8
136.3
129.1
124.9
118.5
81.9
61.7
39.3
36.3
28.7
26.9
22.9
20.3
150
100
50
ppm (t1)


CN
N
SC6H4-o-OMe
Boc
5c
0.95
0.97
0.98
1.07
3.03
1.00
1.92
1.02
1.07
2.28
1.16
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

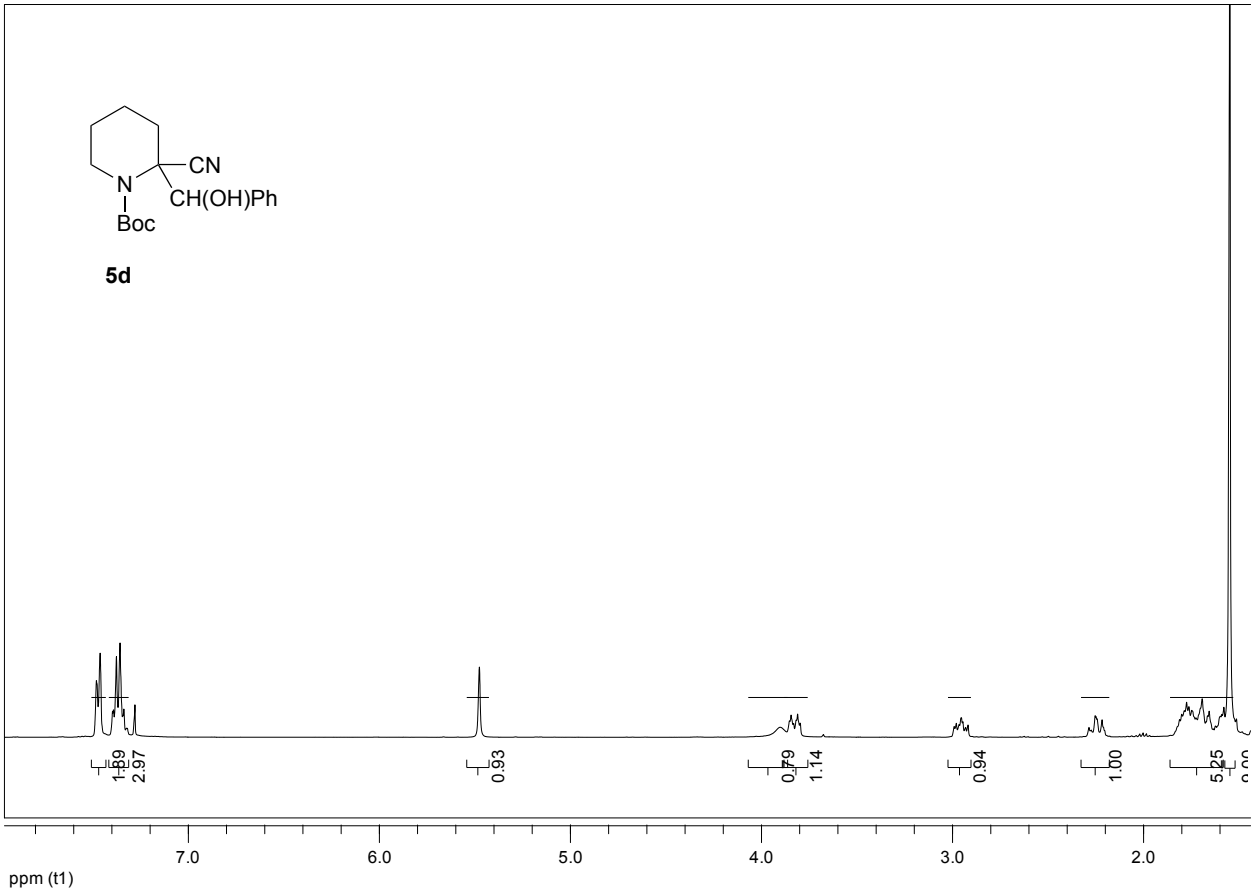

160.3
152.6
139.3
131.4
120.2
118.4
116.7
110.1
81.7
62.0
54.6
39.2
37.3
28.7
26.8
22.9
150
100
50
ppm (t1)

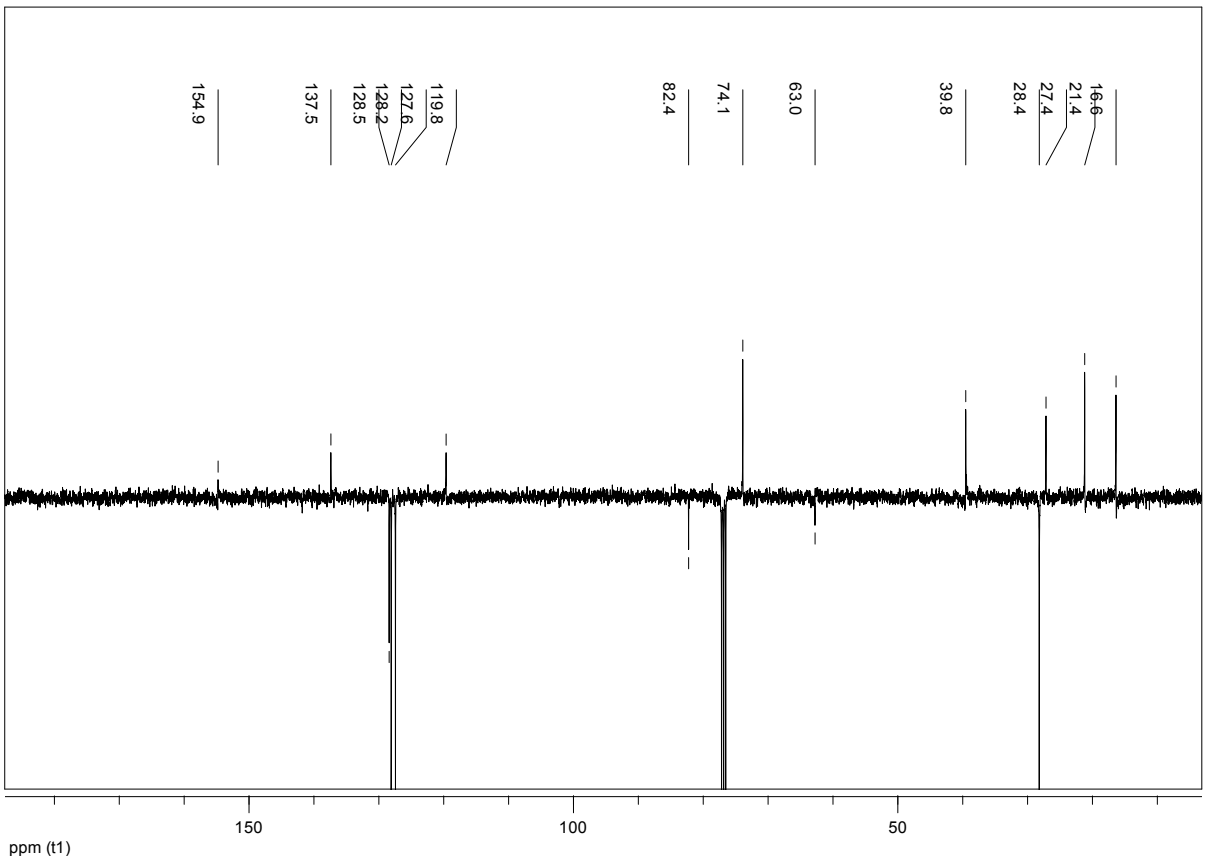
Diastereomer A

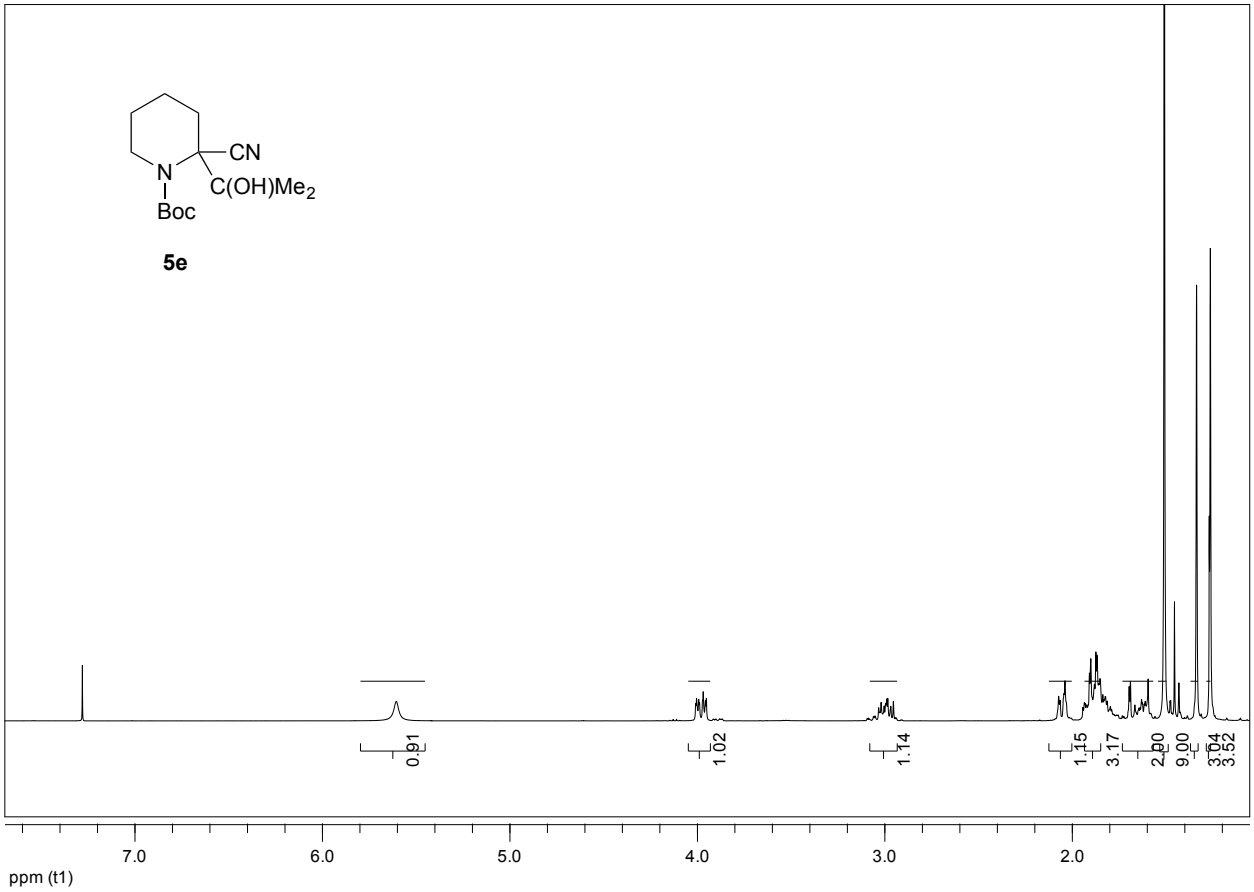


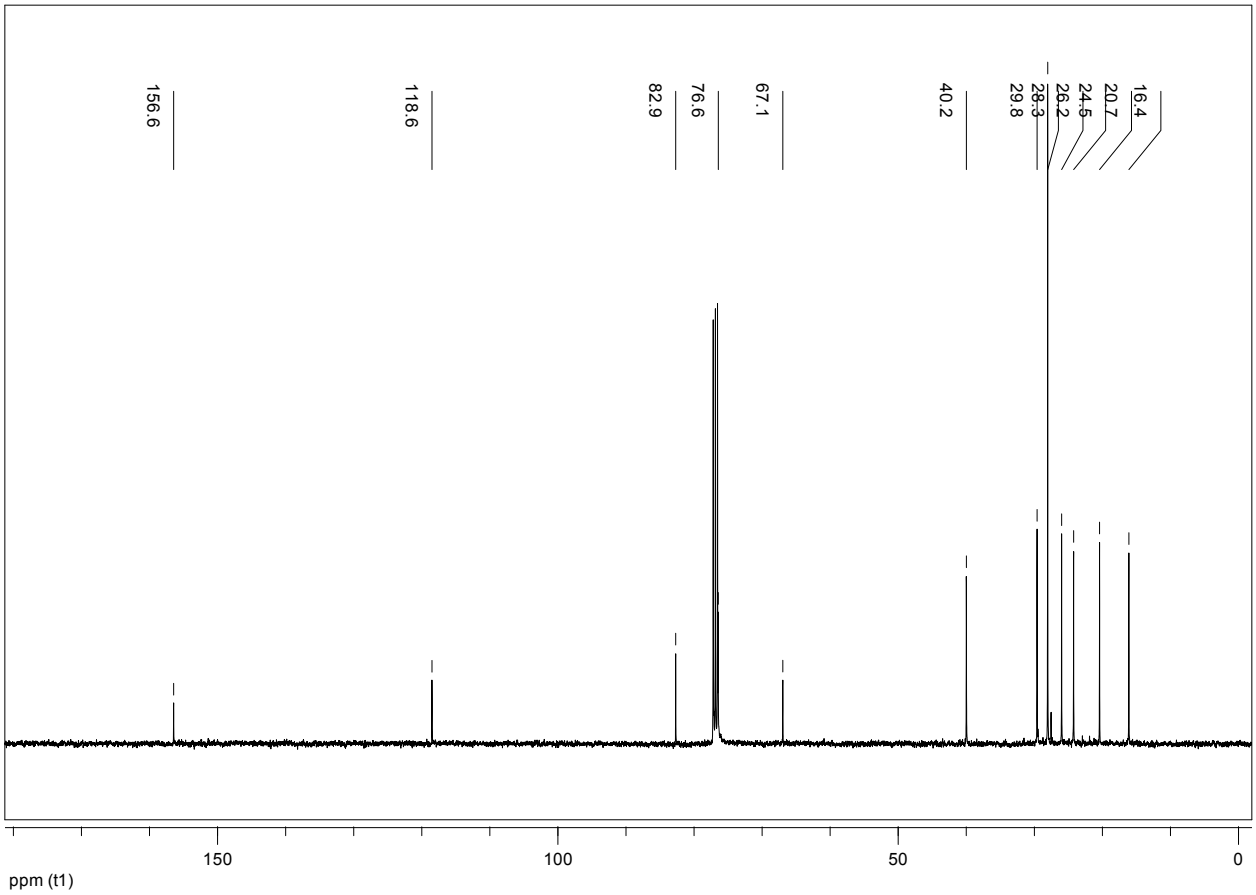



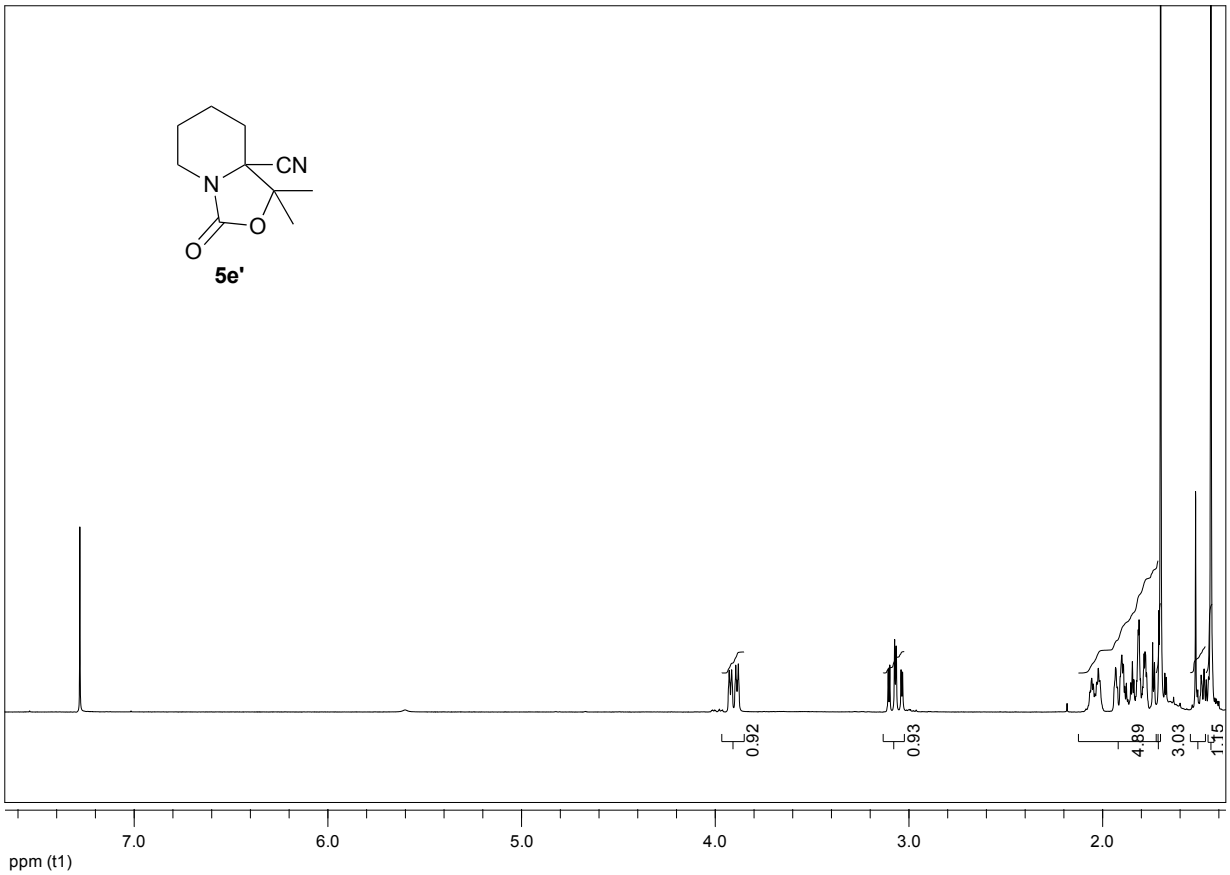
Diastereomer B

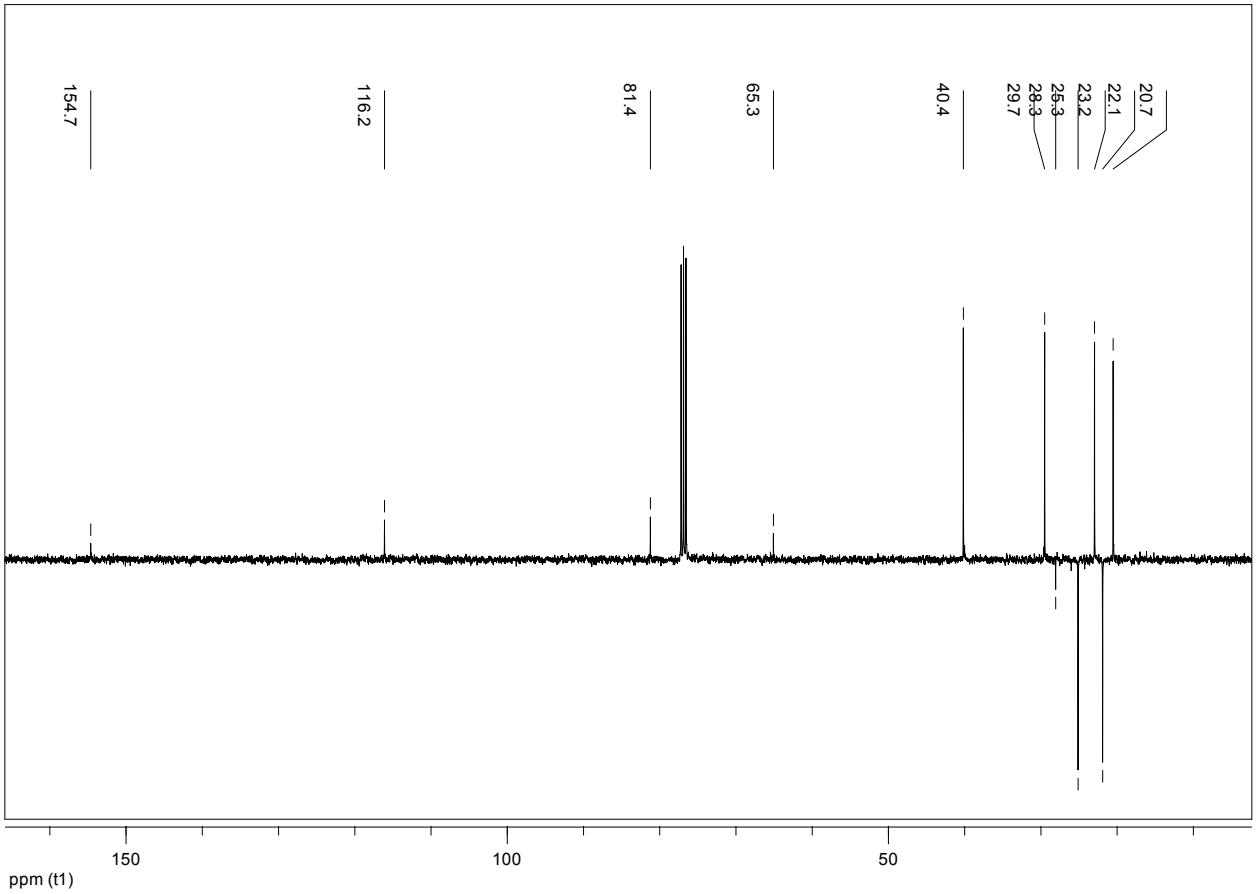


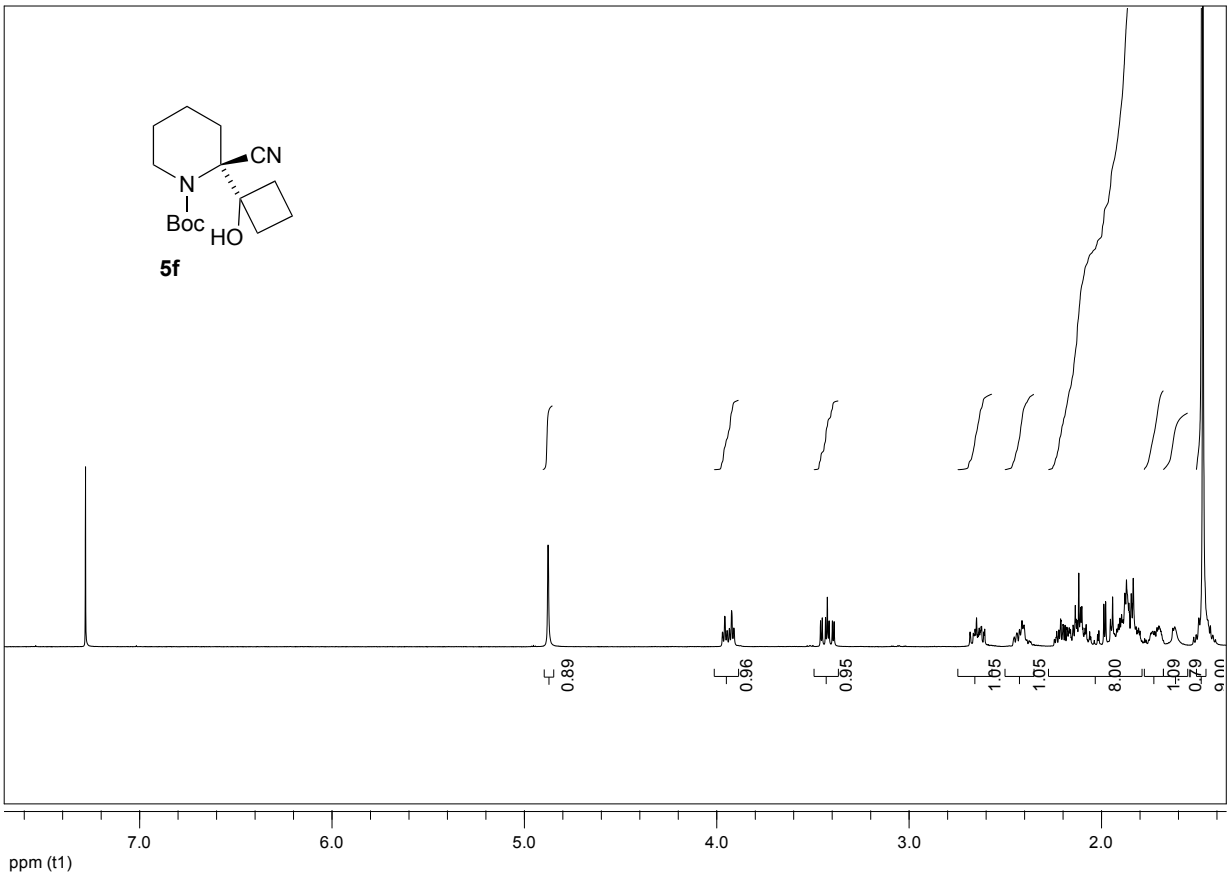



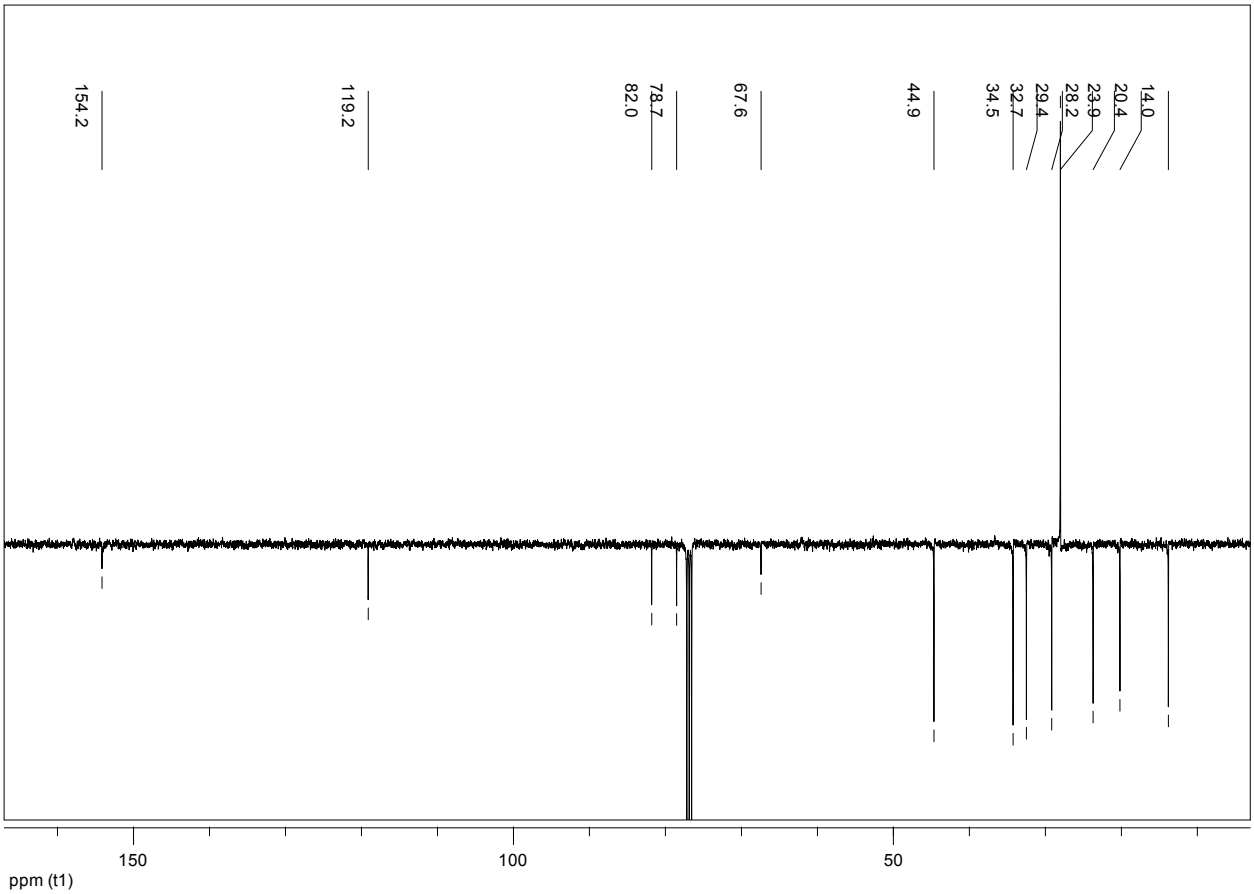

CN
N
C(OH)Me2
Boc
5e
0.91
1.02
1.14
1.15
3.17
2.00
9.00
3.04
3.52
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

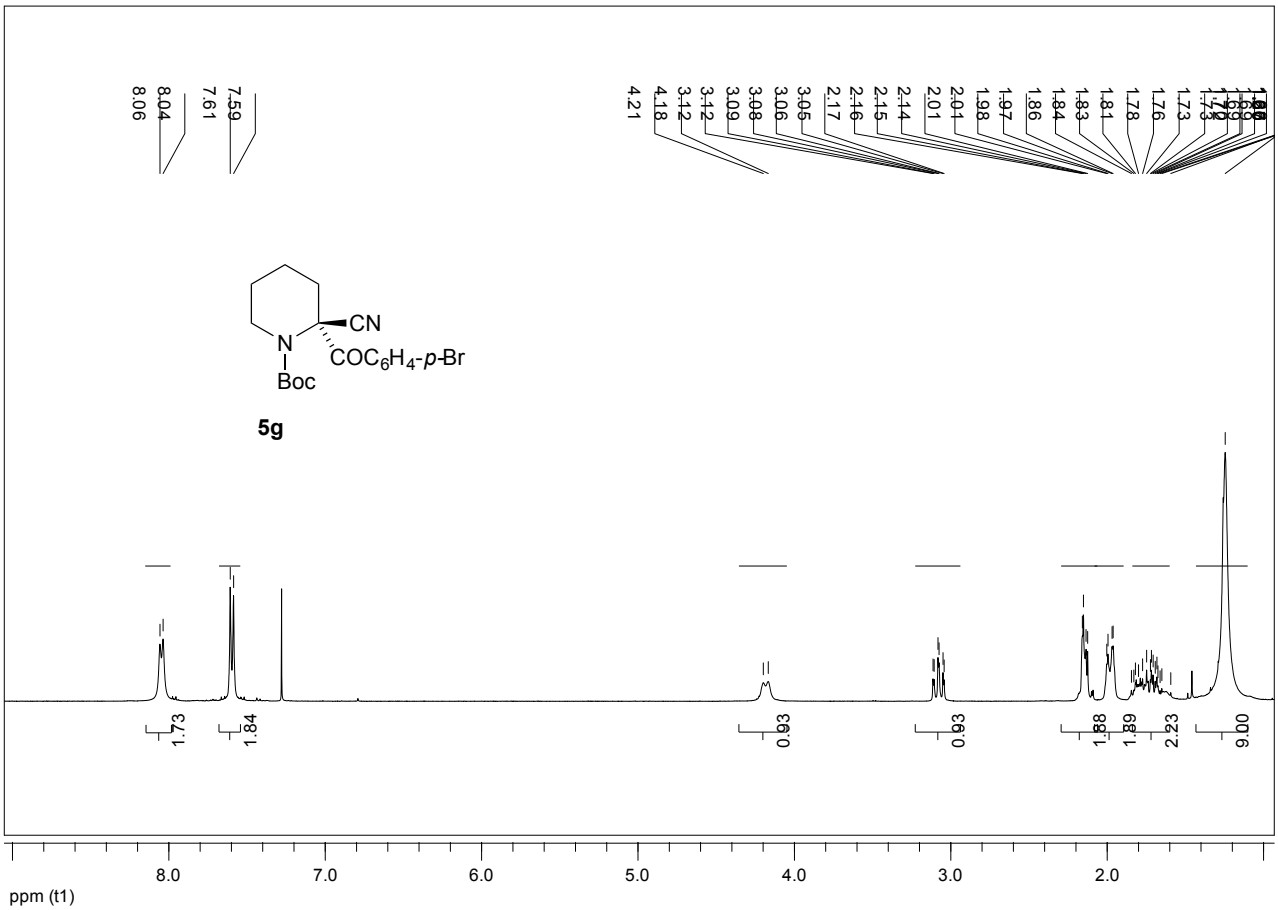

156.6
118.6
82.9
76.6
67.1
40.2
29.8
28.3
26.2
24.5
20.7
16.4
150
100
50
0
ppm (t1)

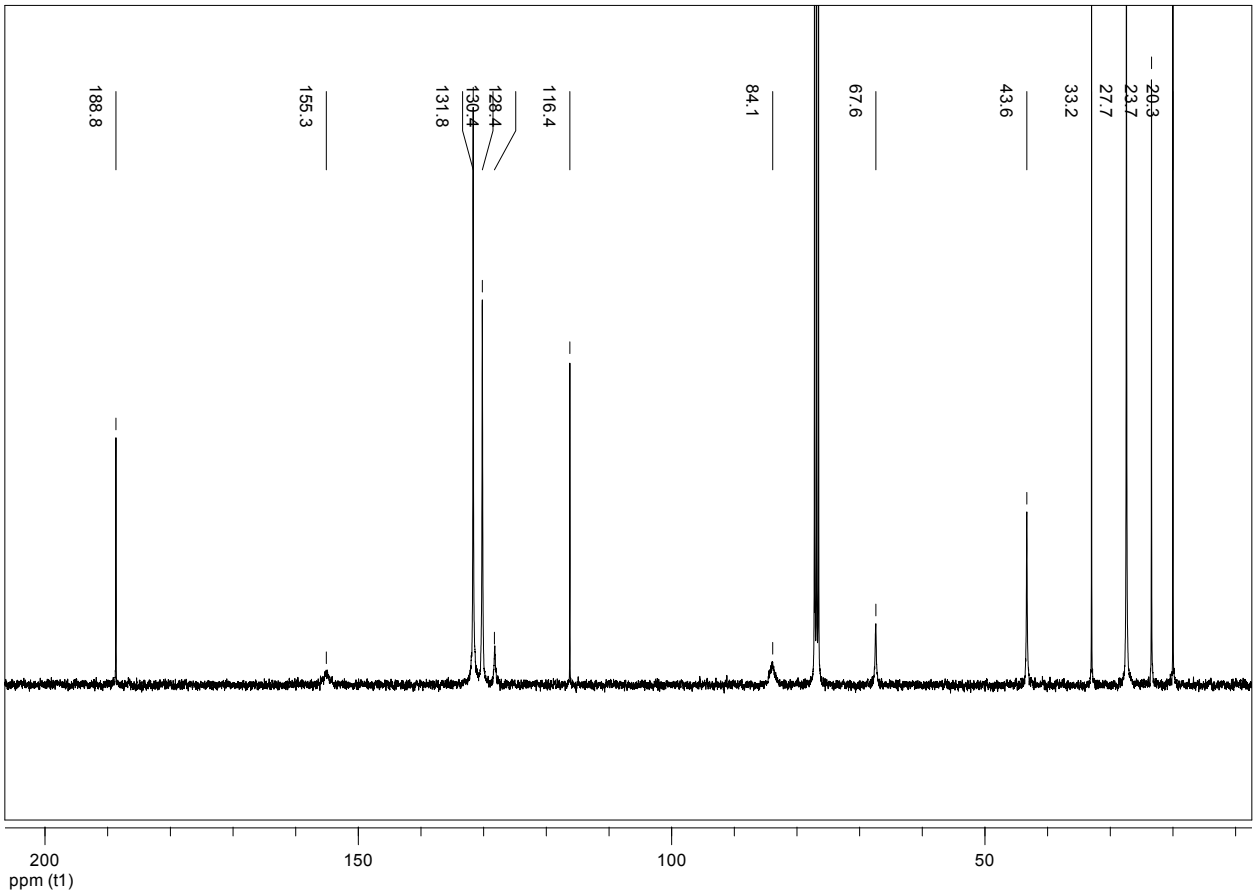

CN
N
O
O
5e'
0.92
0.93
4.89
3.03
1.15
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


154.7
116.2
81.4
65.3
40.4
29.7
28.3
25.3
23.2
22.1
20.7
150
100
50
ppm (t1)


CN
N
Boc
HO
5f
0.89
0.96
0.95
1.05
1.05
8.00
1.09
2.70
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


154.2
119.2
82.0
78.7
67.6
44.9
34.5
32.7
29.4
28.2
23.9
20.4
14.0
150
100
50
ppm (t1)


8.06
8.04
7.61
7.59
4.21
4.18
3.12
3.12
3.09
3.08
3.06
3.05
2.17
2.16
2.15
2.14
2.01
2.01
1.98
1.97
1.86
1.84
1.83
1.81
1.78
1.76
1.73
CN
N
COC6H4-p-Br
Boc
5g
1.73
1.84
0.93
0.93
1.88
1.89
2.23
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


188.8
155.3
131.8
130.4
128.4
116.4
84.1
67.6
43.6
33.2
27.7
23.7
20.3
200
150
100
50
ppm (t1)