Supporting Information for

Dynamic Thermodynamic and Dynamic Kinetic Resolution of 2-Lithiopyrrolidines

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General

All experiments were carried out under an inert atmosphere of argon or nitrogen and using freshly distilled solvents. Diethyl ether (Et_2O) and THF were distilled from sodium/benzophenone or by using a Grubbs solvent purification system.[1] All chiral ligands and electrophiles were distilled prior to use. Commercial *sec*-BuLi (solution in cyclohexane) and *n*-BuLi (solution in hexanes) were titrated prior to use, against *N*-pivaloyl-*o*-toluidine, according to the published procedure.[2]

Column chromatography was performed on silica gel (230-400 mesh). Optical rotations were recorded on an AA–1000 polarimeter using either a 0.5 or 0.1 dm path-length cell. Infrared spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were run on a Brucker AM250 (250 MHz), AC300 (300 MHz) or DRX400 (400 MHz) instrument. Chemical shifts are reported in parts per million (ppm) relative to solvent signals and coupling constants, *J*, are given

in Hz (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet). ^{13}C NMR spectra were run on the above instruments at 62.5, 75 or 100 MHz. Mass spectra were run on a Micromass GCT instrument or Micromass LCT. Low resolution mass spectra were recorded using a Thermoquest CE Trace GCMS2000 series instrument fitted with a Restek RTX-5MS (Cross bond 5% diphenyl- 95% dimethyl polysiloxane 15 m column) with helium as the carrier gas using either EI or CI mode. Microanalysis was performed on a Carlo Erba 1110 instrument. Analytical high pressure liquid chromatography (HPLC) was performed using Beckman Gold system equipped with a Chiralpak AD, Chiralcel OD or OJ column (250 × 4.6 mm i.d.) with visualisation by a Gilson UV detector. Chiral GC analysis was performed on Perkin Elmer Auto system XL with flame ionization detector. When an elemental analysis was not obtained then the purity was established on the basis of ^{1}H and ^{13}C NMR spectra and HRMS. For all enantiomer ratio (er) analyses, authentic racemic compounds were used to establish the method of separation of the enantiomers and these racemic compounds were prepared under the same reaction conditions as for the enantiomerically enriched compounds except using TMEDA or no ligand to coordinate to the organolithium intermediate.

Experimental

For the preparation of *N*-butyl-2-tributylstannylpyrrolidine **3**, R=$CH_2CH_2CH_3$, *N*-ethyl-2-tributylstannylpyrrolidine **3**, R=CH_3 and *N*-isobutyl-2-tributylstannylpyrrolidine **3**, R=$CH(CH_3)_2$ and their spectroscopic data, see previous published procedures.[3]

The chiral ligand (–)-α-isosparteine was prepared in low yield according to the literature method.[4] The chiral ligand **6** was prepared by alkylation of 1,2-diaminocyclohexane with 1,4-dibromobutane.[5] The chiral ligand **7** was prepared from *N*-Cbz-L-proline.[6] The ligands **8**–**11**, **13** and **15** are available commercially. The ligands **12** and **14** were prepared by *O*-methylation (with KH, THF, heat then MeI) from (1*S*,2*S*)-*N*-methylpseudoephedrine or (1*R*,2*S*)-*N*,*N*-diethylnorephedrine.[7] The diproline ligand **16** is commercially available but was prepared from L-proline methyl ester and *N*-Cbz-L-proline according to

the literature method.[6] Simple *O*-methylation of **16** with NaH, MeI gave the ligand **17**.[6]

*General procedure for the dynamic thermodynamic resolution of the organolithium derived from N-isobutyl-2-tributylstannylpyrrolidine **3**, R=CH(CH$_3$)$_2$ using (–)-sparteine **4** (Table 1, entry 3):*

N-*(2-Methylpropyl)-2-trimethylsilylpyrrolidine* **19**, R=CH(CH$_3$)$_2$

n-BuLi (0.46 mL, 1.15 mmol, 2.5 M in hexanes) was added to the stannane **3**, R=CH(CH$_3$)$_2$ (400 mg, 0.96 mmol) in hexane (1 mL) and (–)-sparteine **4** (338 mg, 1.44 mmol) at room temperature. After 30 min TMSCl (0.20 mL, 1.62 mmol) was added at 0 °C. After 10 min water (15 mL) was added. The mixture was acidified to pH 3 with HCl$_{(aq)}$ (2 mL, 2 M) and the aqueous layer was washed with Et$_2$O (2 × 25 mL). The aqueous layer was basified to pH 12 with NaOH$_{(aq)}$ (4 mL, 2 M) and the mixture was extracted with Et$_2$O (3 × 25 mL). The latter combined Et$_2$O extracts were dried (Na$_2$SO$_4$), filtered and evaporated. Purification by column chromatography on silica gel, eluting with CH$_2$Cl$_2$–MeOH–NH$_{3(aq)}$ (10:1:0.1), gave the pyrrolidine (*R*)-**19**, R=CH(CH$_3$)$_2$ (149 mg, 78 %) as an oil; $[\alpha]_D^{25}$ –77.8 (1.0, CHCl$_3$). The enantiomer ratio of **19**, R=CH(CH$_3$)$_2$ was determined to be 85:15 by inducing non equivalence in the ^{1}H NMR spectrum for the Si(CH$_3$)$_3$ singlet by use of (*S*)-(+)-mandelic acid (8 mg) as a chiral solvating agent with the pyrrolidine **19**, R=CH(CH$_3$)$_2$ (5 mg) in C$_6$D$_6$. The absolute configuration of **19**, R=CH(CH$_3$)$_2$ was determined by comparison with an authentic sample prepared from (*S*)-*N*-Boc-2-trimethylsilylpyrrolidine[8] by replacing the *N*-Boc group with *N*-isobutyl (using *B*-bromocatecholborane, then *i*PrCOCl, then LiAlH$_4$) to give (*S*)-**19**, R=CH(CH$_3$)$_2$ $[\alpha]_D^{25}$ +105.4 (1.5, CHCl$_3$). The spectroscopic data for *N*-(2-methylpropyl)-2-trimethylsilylpyrrolidine **19**, R=CHMe$_2$, for *N*-butyl-2-trimethylsilylpyrrolidine **19**, R=CH$_2$CH$_2$CH$_3$ and for *N*-ethyl-2-trimethylsilylpyrrolidine **19**, R=Me corresponded with the literature.[3]

The general procedure for use of ligands **5–7** matches that using (–)-sparteine **4**. The ligands **8**, **10**, **11**, **13–16** were pre-treated with *n*-BuLi prior to addition to the organolithium generated from the stannane

3.

*General procedure for the dynamic thermodynamic resolution of the organolithium derived from N-isobutyl-2-tributylstannylpyrrolidine **3**, R=CH(CH$_3$)$_2$ using the ligand **16** (Table 1, entry 16):*

*(*S*)*-N-*(2-Methylpropyl)-2-trimethylsilylpyrrolidine* **19**, R=CH(CH$_3$)$_2$

n-BuLi (0.35 mL, 0.86 mmol, 2.5 M in hexanes) was added to the stannane **3**, R=CH(CH$_3$)$_2$ (300 mg, 0.72 mmol) in Et$_2$O (0.7 mL) at room temperature. After 1 h, the deprotonated ligand **16** [prepared by adding *n*-BuLi (0.52 mL, 1.3 mmol) to **16** (215 mg, 1.1 mmol) in Et$_2$O (0.7 mL) at –30 °C then warming to room temperature] was added. After 1 h at room temperature, the mixture was cooled to –20 °C and TMSCl (0.38 mL, 3.0 mmol) was added. After 30 min water (10 mL) was added. The mixture was acidified to pH 3 with HCl$_{(aq)}$ (2 mL, 2 M) and the aqueous layer was washed with Et$_2$O (2 × 25 mL). The aqueous layer was basified to pH 12 with NaOH$_{(aq)}$ (4 mL, 2 M) and the mixture was extracted with Et$_2$O (3 × 25 mL). The latter combined Et$_2$O extracts were dried (Na$_2$SO$_4$), filtered and evaporated. Purification as above gave the pyrrolidine (*S*)-**19**, R=CH(CH$_3$)$_2$ (108 mg, 75 %) as an oil; $[\alpha]_D^{25}$+110.7 (0.5, CHCl$_3$). Spectroscopic data as reported.[3] The enantiomer ratio of **19**, R=CH(CH$_3$)$_2$ was determined to be ≥97:3 by the method described above.

*(*R*)*-N-*(2-Methylpropyl)pyrrolidine-2-carboxylic acid phenylamide* **20**

Using the general procedure described above, *n*-BuLi (0.35 mL, 0.86 mmol, 2.5 M in cyclohexane), the stannane **3**, R=CH(CH$_3$)$_2$ (300 mg, 0.72 mmol), the ligand **16** [prepared by adding *n*-BuLi (0.52 mL, 1.3 mmol) to **16** (215 mg, 1.1 mmol)] and phenylisocyanate (0.38 mL, 3.0 mmol) gave, after purification by column chromatography on silica gel, eluting with petrol–EtOAc (7:3), the amide (*R*)-**20** (108 mg, 61%); $[\alpha]_D^{25}$ +154.8 (0.78, CHCl$_3$). Spectroscopic data as reported.[3] The enantiomer ratio of **20** was determined to be 97:3 by chiral HPLC [Chiralpak AD column (250 mm × 4.6 mm i.d.) with hexane:EtOH (90:10 v/v), flow rate 1.0 mL min^{-1}, detection by UV absorbance at 235 nm, injection

volume 20 μL of the sample prepared in a 1 mg mL^{-1} solution of EtOH, retention times 6.3 min (major) and 9.2 min (minor)].

*(*S*)*-N-*(2-Methylpropyl)-2-tributylstannylpyrrolidine* **3**

Using the general procedure described above, *n*-BuLi (0.7 mL, 1.73 mmol, 2.5 M in cyclohexane), the stannane **3**, R=$CH(CH_3)_2$ (600 mg, 1.44 mmol), the ligand **16** [prepared by adding *n*-BuLi (1.04 mL, 2.6 mmol) to **16** (430 mg, 2.2 mmol)] and tributyltin chloride (1.62 mL, 6.0 mmol) gave, after purification by column chromatography on basic alumina, eluting with petrol–EtOAc (98:2), the stannane (*S*)-**3** (423 mg, 71%); $[\alpha]_D^{24}$ +83.8 (1.3, $CHCl_3$). Spectroscopic data as reported.[3] The enantiomer ratio of (*S*)-**3** was determined to be 96:4 by comparison of the specific rotation with that of the stannane (*S*)-**3** ($[\alpha]_D^{24}$ +86.2) prepared from the *N*-Boc stannane (*S*)-**1** (er 97:3)[8] by removal of the *N*-Boc group, acylation and reduction.[3]

*(*R*)-2-[*N*-(2-Methylpropyl)pyrrolidin-2-yl]propan-2-ol* **21**

Using the general procedure described above, *n*-BuLi (0.35 mL, 0.86 mmol, 2.5 M in cyclohexane), the stannane **3**, R=$CH(CH_3)_2$ (300 mg, 0.72 mmol), the ligand **16** [prepared by adding *n*-BuLi (0.52 mL, 1.3 mmol) to **16** (215 mg, 1.1 mmol)] and acetone (0.22 mL, 3.0 mmol) gave, after purification by column chromatography on silica gel, eluting with CH_2Cl_2–MeOH–NH_3 (10:1:0.1), the alcohol (*R*)-**21** (108 mg, 75%); $[\alpha]_D^{25}$ +33.5 (0.9, $CHCl_3$). Spectroscopic data as reported.[3] The enantiomer ratio of (*R*)-**21** was determined to be ≥97:3 by inducing non-equivalence in the ^1H NMR spectrum for the two diastereotopic $CH(CH_3)_2$ doublets by use of (*R*)-(–)-1-(9-anthryl)-2,2,2-trifluoroethanol (30 mg) as a chiral solvating agent with the pyrrolidine (*R*)-**21** (4 mg) in $CDCl_3$.

*(*S*)*-N-*(2-Methylpropyl)-2-methylpyrrolidine* **22**

Using the general procedure described above, *n*-BuLi (1.15 mL, 2.88 mmol, 2.5 M in cyclohexane), the

stannane **3**, R=$CH(CH_3)_2$ (1.0 g, 2.4 mmol), the ligand **16** [prepared by adding *n*-BuLi (1.7 mL, 4.3 mmol) to **16** (0.71 g, 3.6 mmol)] and dimethyl sulfate (0.95 mL, 10.0 mmol) (added at –70 °C) gave, after purification by column chromatography on silica gel, eluting with CH_2Cl_2–MeOH–NH_3 (10:1:0.1), the pyrrolidine (*S*)-**22** (220 mg, 65%) as an oil; $[\alpha]_D^{26}$ +125.7 (1.4, $CHCl_3$); R_f 0.41 [CH_2Cl_2–MeOH–NH_3 (10:1:0.1)]; ν_{max} (film)/cm^{-1} 2960, 2870 & 2785 (C–H); ^{1}H NMR (400 MHz, C_6D_6) δ = 3.18–3.13 (1H, m, NCH), 2.43 (1H, t, *J* 11.0, NCH), 2.26–2.24 (1H, m, NCH), 2.02–1.97 (2H, m, 2 × NCH), 1.83–1.77 [3H, m, C*H*$(CH_3)_2$ & CH_2], 1.62–1.58 (1H, m, CH), 1.44–1.39 (1H, m, CH), 1.15 [3H, d, *J* 6.5, $CH(CH_3)^A(CH_3)^B$], 1.13 [3H, d, *J* 6.5, $CH(CH_3)^A(CH_3)^B$], 0.98 (3H, d, *J* 7.0, NCHCH_3); ^{13}C NMR (100 MHz, C_6D_6) δ = 62.8 (CH_2), 60.1 (CH), 54.2 (CH_2), 33.0 (CH_2), 27.7 (CH), 22.1 (CH_2), 21.4 (CH_3), 20.6 (CH_3), 19.4 (CH_3); HRMS (ES) Found: MH^+, 142.1595. $C_9H_{20}N$ requires MH^+, 142.1595; GCMS *m*/*z* (CI) 142 (100%, MH^+); Found: C, 76.80; H, 13.98; N, 9.96. $C_9H_{19}N$ requires C, 76.53; H, 13.56; N, 9.92. The enantiomer ratio of (*S*)-**22** was determined to be 97:3 by inducing non-equivalence in the ^{1}H NMR spectrum for the CH(CH_3) doublet by use of (*R*)-(–)-1-(9-anthryl)-2,2,2-trifluoroethanol (30 mg) as a chiral solvating agent with the pyrrolidine (*S*)-**22** (5 mg) in $CDCl_3$. The absolute configuration of (*S*)-**22** was determined by preparation of an authentic sample from (*S*)-**1** (er 97:3), which was converted to (*S*)-*N*-Boc-2-methylpyrrolidine according to the literature,[8] and then converted to (*S*)-**22** by removal of the *N*-Boc group with *B*-bromocatechol borane and acylation with 2-methylpropanoyl chloride, followed by reduction with $LiAlH_4$; this method gave (*S*)-**22**, $[\alpha]_D^{26}$ +124.8 (1.2, $CHCl_3$).

N-*(2-Methylpropyl)pyrrolidin-2-yl-phenylmethanol* **23**

Using the general procedure described above, *n*-BuLi (1.15 mL, 2.88 mmol, 2.5 M in cyclohexane), the stannane **3**, R=$CH(CH_3)_2$ (1.0 g, 2.4 mmol), the ligand **16** [prepared by adding *n*-BuLi (1.7 mL, 4.3 mmol) to **16** (0.71 g, 3.6 mmol)] and benzaldehyde (1.0 mL, 10 mmol) (added at –70 °C) gave, after purification by column chromatography on silica gel, eluting with petrol–EtOAc (1:1), the pyrrolidines **23** as separable diastereomers:

23a (190 mg, 34%) as an oil; $[\alpha]_D^{27}$ +13.3 (0.45, $CHCl_3$); R_f 0.66 [CH_2Cl_2–MeOH–NH_3 (20:1:0.1)]; ν_{max} (film)/cm^{-1} 3435 (O–H), 2955, 2870 & 2800 (C–H); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38–7.31 (4H, m, Ph), 7.26–7.23 (1H, m, Ph), 4.85 (1H, d, *J* 3.2, C*H*OH), 3.70 (1H, br, OH), 3.25–3.22 (1H, m, NCH), 2.71–2.58 (1H, m, NCH), 2.56 (1H, t, *J* 11.0, NCH), 2.32–2.23 (2H, m, 2 × NCH), 1.84–1.82 [1H, m, C*H*(CH_3)$_2$], 1.67–1.61 (3H, m, CH_2 & CH), 1.26–1.24 (1H, m, CH), 0.99 (3H, d, *J* 6.5, CH_3), 0.94 (3H, d, *J* 6.5, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7 (C), 128.1 (CH), 126.6 (CH), 125.4 (CH), 69.9 (CH), 69.8 (CH), 62.5 (CH_2), 54.3 (CH_2), 27.5 (CH), 23.7 (CH_2), 23.3 (CH_2), 21.3 (CH_3), 20.3 (CH_3); HRMS (ES) Found: MH^+, 234.1858. $C_{15}H_{24}NO$ requires MH^+, 234.1858; GCMS *m*/*z* (CI) 234 (100%, MH^+), 126 (39). The enantiomer ratio of **23a** was determined to be 85:15 by chiral HPLC [Chiralcel OD column (250 mm × 4.6 mm i.d.) with hexane:^{i}PrOH (99.5:0.5 v/v), flow rate 0.5 mL min^{-1}, detection by UV absorbance at 236 nm, injection volume 20 μL of the sample prepared in a 1 mg mL^{-1} solution of hexane, retention times 11.0 min (minor) and 11.5 min (major)], and

23b (195 mg, 35%) as an oil; $[\alpha]_D^{27}$ –12.8 (0.16, $CHCl_3$); R_f 0.48 [CH_2Cl_2–MeOH–NH_3 (20:1:0.1)]; ν_{max} (film)/cm^{-1} 3420 (O–H), 2955, 2870 & 2800 (C–H); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38–7.31 (4H, m, Ph), 7.27–7.25 (1H, m, Ph), 4.65 (1H, br, OH), 4.29 (1H, d, *J* 4.4, C*H*OH), 3.20–3.13 (1H, m, NCH), 2.90–2.86 (1H, m, NCH), 2.37–2.27 (2H, m, 2 × NCH), 2.20–2.12 (1H, m, NCH), 1.85–1.68 [4H, m, CH_2, CH and C*H*(CH_3)$_2$], 1.69–1.66 (1H, m, CH), 0.99 (3H, d, *J* 6.5, CH_3), 0.81 (3H, d, *J* 6.5, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5 (C), 128.2 (CH), 127.1 (CH), 125.4 (CH), 75.4 (CH), 71.8 (CH), 66.2 (CH_2), 54.2 (CH_2), 28.7 (CH_2), 27.8 (CH), 24.5 (CH_2), 21.1 (CH_3), 20.2 (CH_3); HRMS (ES) Found: MH^+, 234.1861. $C_{15}H_{24}NO$ requires MH^+, 234.1858; GCMS *m*/*z* (CI) 234 (100%, MH^+), 126 (39). The enantiomer ratio of **23b** was determined to be 85:15 by chiral HPLC [Chiralcel OD column (250 mm × 4.6 mm i.d.) with hexane:^{i}PrOH (99.5:0.5 v/v), flow rate 0.5 mL min^{-1}, detection by UV absorbance at 236 nm, injection volume 20 μL of the sample prepared in a 1 mg mL^{-1} solution of hexane, retention times 12.8 min (major) and 13.4 min (minor)].

N-*(2-Methylpropyl)pyrrolidin-2-yl-4-methoxyphenylmethanol* **24**

Using the general procedure described above, *n*-BuLi (0.35 mL, 0.86 mmol, 2.5 M in cyclohexane), the stannane **3**, R=$CH(CH_3)_2$ (300 mg, 0.72 mmol), the ligand **16** [prepared by adding *n*-BuLi (0.52 mL, 1.3 mmol) to **16** (0.21 g, 1.1 mmol)] and 4-methoxybenzaldehyde (0.16 mL, 0.86 mmol) (added at –70 °C) gave, after purification by column chromatography on silica gel, eluting with petrol–EtOAc (1:1), the pyrrolidines **24** as separable diastereomers:

24a (67 mg, 35%) as needles; $[\alpha]_D^{25}$ +67.6 (0.15, $CHCl_3$); m.p. 30–31 ºC; R_f 0.82 [CH_2Cl_2–MeOH–NH_3 (10:1:0.1)]; ν_{max} (KBr)/cm^{-1} 3435 (O–H), 2955, 2870, 2835 & 2805 (C–H); ^{1}H NMR (400 MHz, C_6D_6) δ = 7.51–7.47 (2H, m, Ph), 6.98–6.95 (2H, m, Ph), 4.93 (1H, d, *J* 3.0, C*H*OH), 3.93 (1H, br, OH), 3.46 (3H, s, OCH_3), 3.07–3.03 (1H, m, NCH), 2.61–2.57 (1H, m, NCH), 2.46 (1H, t, *J* 11.0, NCH), 2.13 (1H, dd, *J* 11.5, 4.5, NCH), 2.04–1.99 (1H, m, NCH), 1.87–1.83 (1H, m, CH), 1.73–1.69 [1H, m, C*H*$(CH_3)_2$], 1.58–1.55 (1H, m, CH), 1.47–1.43 (1H, m, CH), 1.26–1.23 (1H, m, CH), 1.00 (3H, d, *J* 6.5, CH_3), 0.91 (3H, d, *J* 6.5, CH_3); ^{13}C NMR (100 MHz, C_6D_6) δ = 158.8 (C), 134.2 (C), 126.6 (CH), 113.7 (CH), 70.4 (CH), 69.5 (CH), 62.5 (CH_2), 54.5 (CH_3), 54.4 (CH_2), 27.4 (CH), 23.8 (CH_2), 23.3 (CH_2), 21.2 (CH_3), 20.2 (CH_3); HRMS (ES) Found: MH^+, 264.1965. $C_{16}H_{26}NO_2$ requires MH^+, 264.1963; GCMS *m/z* (CI) 264 (100%, MH^+), 126 (77); Found: C, 72.59; H, 9.97; N, 4.97. $C_{16}H_{25}NO_2$ requires C, 72.96; H, 9.57; N, 5.32. The enantiomer ratio of **24a** was determined to be 97:3 by chiral HPLC [Chiralpak AD column (250 mm × 4.6 mm i.d.) with hexane:^{i}PrOH (99.5:0.5 v/v), flow rate 0.5 mL min^{-1}, detection by UV absorbance at 269 nm, injection volume 20 μL of the sample prepared in a 1 mg mL^{-1} solution of hexane, retention times 18.8 min (major) and 20.2 min (minor)], and

24b (66 mg, 35%) as an oil; $[\alpha]_D^{25}$ –22.7 (0.18, $CHCl_3$); R_f 0.77 [CH_2Cl_2–MeOH–NH_3 (10:1:0.1)]; ν_{max} (film)/cm^{-1} 3410 (O–H), 2955, 2870 & 2835 (C–H); ^{1}H NMR (400 MHz, C_6D_6) δ = 7.44–7.42 (2H, m, Ph), 6.94–6.91 (2H, m, Ph), 4.42 (1H, d, *J* 6.0, C*H*OH), 4.40 (1H, br, OH), 3.44 (3H, s, OCH_3), 3.01–2.98 (1H, m, NCH), 2.83–2.82 (1H, m, NCH), 2.27 (1H, dd, *J* 11.5, 10.5, NCH), 2.19–2.17 (2H, m, 2 × NCH), 1.67–1.52 [5H, m, 2 × CH_2 & C*H*$(CH_3)_2$], 1.03 (3H, d, *J* 6.5, CH_3), 0.81 (3H, d, *J* 6.5, CH_3); ^{13}C

NMR (100 MHz, C_6D_6) δ = 159.1 (C), 136.1 (C), 127.8 (CH), 113.6 (CH), 75.1 (CH), 71.9 (CH), 66.2 (CH_2), 54.6 (CH_3), 54.2 (CH_2), 28.3 (CH_2), 27.9 (CH), 24.4 (CH_2), 21.0 (CH_3), 20.2 (CH_3); HRMS (ES) Found: MH^+, 264.1961. $C_{16}H_{26}NO_2$ requires MH^+, 264.1963; GCMS *m/z* (CI) 264 (100%, MH^+), 126 (41); Found: C, 72.73; H, 10.18; N, 5.27. $C_{16}H_{25}NO_2$ requires C, 72.96; H, 9.57; N, 5.32. The enantiomer ratio of **24a** was determined to be 97:3 by chiral HPLC [Chiralcel OJ column (250 mm × 4.6 mm i.d.) with hexane:^{i}PrOH (90:10 v/v), flow rate 0.7 mL min^{-1}, detection by UV absorbance at 264 nm, injection volume 20 μL of the sample prepared in a 1 mg mL^{-1} solution of hexane, retention times 9.2 min (minor) and 10.7 min (major)].

*(*S*)*-N-*(2-Methylpropyl)pyrrolidine-2-carboxylic acid phenylamide* **20**

Using the general procedure described above, *n*-BuLi (0.58 mL, 1.2 mmol, 2.5 M in cyclohexane), the stannane **3**, R=$CH(CH_3)_2$ (500 mg, 1.2 mmol), the ligand **25** [prepared by adding *n*-BuLi (0.87 mL, 2.16 mmol) to **25** (360 mg, 1.8 mmol)] and phenylisocyanate (0.54 mL, 5.0 mmol) gave, after purification by column chromatography on silica gel, eluting with petrol–EtOAc (7:3), the amide (*S*)-**20** (108 mg, 74%); $[\alpha]_D^{25}$ –157.7 (1.1, $CHCl_3$). Spectroscopic data as reported.[3] The enantiomer ratio of **20** was determined to be 96:4 by chiral HPLC [Chiralpak AD column (250 mm × 4.6 mm i.d.) with hexane:EtOH (90:10 v/v), flow rate 1.0 mL min^{-1}, detection by UV absorbance at 235 nm, injection volume 20 μL of the sample prepared in a 1 mg mL^{-1} solution of EtOH, retention times 6.7 min (minor) and 10.4 min (major)].

*(*R*)*-N-*(3-Methylbut-2-enyl)pyrrolidine-2-carboxylic acid phenylamide* **27**

n-BuLi (0.21 mL, 0.5 mmol, 2.5 M in hexanes) was added to the stannane **26**[9] (184 mg, 0.4 mmol) in Et_2O (0.5 mL) at 0 °C. After 1 h, the deprotonated ligand **16** [prepared by adding *n*-BuLi (0.31 mL, 0.77 mmol) to **16** (128 mg, 0.64 mmol) in Et_2O (1 mL) at 0 °C] was added. After 30 min, the mixture was cooled to –78 °C and phenylisocyanate (0.16 mL, 1.5 mmol) was added. After 1 h, the mixture was

absorbed onto silica and purified by column chromatography on silica gel, eluting with CH_2Cl_2–MeOH–NH_3 (10:0.2:0.1), to give the amide **27** (80 mg, 72%) which was recrystallised from hot EtOAc to give plates; m.p. 60–62 °C; $[\alpha]_D^{25}$ +62.5 (1.9, $CHCl_3$); R_f 0.5 [CH_2Cl_2–MeOH–NH_3 10:1:0.1]; ν_{max} (KBr)/cm^{-1} 3260 (NH), 2950–2850 (CH), 1675 (C=O); δ_H(400 MHz, $CDCl_3$) 9.40 (1H, br s, NH), 7.55–7.05 (5H, m, Ph), 5.22–5.18 (1H, m, CH=), 3.19–3.09 (4H, m, 4 × NCH), 2.40–1.54 [11H, m, NCH, $(CH_3)_2C$ and 2 × CH_2]; δ_C(100 MHz, $CDCl_3$) 172.0 (C), 137.6 (C), 136.3 (C), 127.5 (CH), 119.2 (CH), 118.1 (CH), 117.9 (CH), 65.7 (CH), 52.6 (CH_2), 51.1 (CH_2), 29.3 (CH_2), 24.4 (CH_3), 22.9 (CH_2), 16.6 (CH_3); Found (CI): MH^+, 259.1817. $C_{16}H_{22}N_2O$ requires *MH*, 259.1810; *m/z* (CI) 259 (100%, MH^+), 191 (28). The enantiomer ratio of **27** was determined to be 87:13 by chiral HPLC [Chiralpak AD column (250 mm × 4.6 mm i.d.) with hexane:^{i}PrOH (95:5 v/v), flow rate 0.7 mL min^{-1}, detection by UV absorbance at 254 nm, injection volume 20 μL of the sample prepared in a 1 mg mL^{-1} solution of ^{i}PrOH, retention times 12.4 min (major) and 14.6 min (minor)].

Compounds **28** and **30** and **31** were prepared as reported in the literature.[6]

*(*S*)*-N-*(2-Cyclopentyl-ethyl)pyrrolidin-2-yl-methanol* **29**

Cyclopentylacetyl chloride (1.45 g, 9.9 mmol) in THF (6 mL) was added to (*S*)-prolinol (1 g, 9.8 mmol) and *N*-methylmorpholine (1.3 mL, 11.8 mmol) in THF (30 mL) at 0 °C. After 1 h, the mixture was warmed to rt. After a further 1 h, the mixture was filtered and the solvent was evaporated under reduced pressure to give the amide as an oil (1.98 g, 95%). This amide (1 g, 4.7 mmol) in THF (7 mL) was added to a suspension of $LiAlH_4$ (360 mg, 9.4 mmol) in THF (20 mL) at 0 °C. After 1 h, EtOAc (10 mL) then water was added until a white precipitate formed. The mixture was filtered and the precipitate was washed with Et_2O (3 × 15mL). The aqueous layer was extracted with Et_2O (3 × 15 mL) and the solvent was evaporated to give the amine **29** (0.65 g, 70%) as an oil; R_f 0.21 [CH_2Cl_2–MeOH–NH_3 10:1:0.1]; $[\alpha]_D^{27}$ –56.2 (*c* 0.9, $CHCl_3$); ν_{max}(film)/cm^{-1} 3400 (OH), 2950 (CH); δ_H(400 MHz, $CDCl_3$) 3.61

(1H, dd, *J* 4.5 & 2.0, C*H*^{A}H^{B}OH), 3.37 (1H, dd, *J* 4.5 & 1.5, CH^{A}*H*^{B}OH), 3.19–3.15 (1H, m, NCH), 3.09–2.86 (1H, br s, OH), 2.76–2.69 (1H, m, NCH), 2.58–2.53 (1H, m, NCH), 2.26–2.18 (2H, m, 2 × NCH), 1.90–1.42 (13H, m, 6 × CH_2 & CH), 1.14–1.02 (2H, m, CH_2); δ_C(100 MHz, $CDCl_3$) 65.0 (CH), 61.9 (CH_2), 54.3 (CH_2), 53.9 (CH_2), 38.2 (CH), 35.5 (CH_2), 33.1 (CH_2), 32.6 (CH_2), 27.8 (CH_2), 25.2 (CH_2), 23.7 (CH_2); Found (CI): MH^+, 198.1855. $C_{12}H_{24}NOSi$ requires *MH*, 198.1858; *m/z* (CI) 198 (100%, MH^+), 166 (37).

N-*(2,3-Dimethylbut-2-enyl)-2-tributylstannylpyrrolidine* **32**

B-Bromocatecholborane (5.2 mL, 5.2 mmol, 1 M in CH_2Cl_2) was added to the stannane **1** (2.0 g, 4.3 mmol) in CH_2Cl_2 (50 mL). After 10 min, $NaOH_{(aq)}$ (50 mL, 2 M) and 1-bromo-2,3-dimethylbut-2-ene[10] (710 mg, 4.3 mmol) were added. After 2 h, the two layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layers were dried ($MgSO_4$), evaporated and purified by flash chromatography on basic alumina, eluting with petrol–EtOAc (9:1), to give the amine **32** (1.45 g, 75%) as an oil; R_f 0.3 [CH_2Cl_2–MeOH–NH_3 (100:10:1)]; ν_{max}(film)/cm^{-1} 2955–2775 (CH); δ_H(400 MHz, C_6D_6) 3.10 (1H, d, *J* 12, NCH), 2.84 (1H, d, *J* 12, NCH), 2.82–2.74 (1H, m, NCH), 2.41–2.29 (1H, m, NCH), 2.08–1.61 [20H, m, $NCHCH_2CH_2$, 3 × CH_3 and $Sn(CH_2CH_2CH_2CH_3)_3$], 1.54–1.44 [6H, m, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.40–1.25 [6H, m, $Sn(CH_2CH_2CH_2CH_3)_3$], 0.90 [9H, t, *J* 7.5, $Sn(CH_2CH_2CH_2CH_3)_3$]; δ_C(100 MHz, C_6D_6) 126.8 (C), 126.5 (C), 59.0 (CH_2), 57.6 (CH), 53.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 27.6 (CH_2), 24.7 (CH_2), 20.9 (CH_3), 20.3 (CH_3), 17.5 (CH_3), 13.7 (CH_3), 9.1 (CH_2); Found (CI): MH^+, 444.2659. $C_{22}H_{45}N^{120}Sn$ requires *MH*, 444.2652; *m/z* (CI) 444 (100%, MH^+), 152 (84).

*(*R*)*-N-*(2,3-Dimethylbut-2-enyl)pyrrolidine-2-carboxylic acid phenylamide* **33**, E=CONHPh

n-BuLi (0.2 mL, 0.5 mmol, 2.5 M in hexanes) was added to the stannane **32** (180 mg, 0.4 mmol) and TMEDA (0.075 mL, 0.5 mmol) in Et_2O (0.5 mL) at 0 °C. After 1 h, the deprotonated ligand **16** [prepared by adding *n*-BuLi (0.25 mL, 0.6 mmol) to **16** (121 mg, 0.6 mmol) in Et_2O (1 mL) at 0 °C] was added. After 90 min, the mixture was cooled to –78 °C and phenylisocyanate (0.13 mL, 1.2 mmol) was added. After 1 h, the mixture was acidified with 10% aqueous citric acid solution (10 mL) and the aqueous layer was washed with Et_2O (2 × 15 mL). The aqueous layer was basified to pH 11 with aqueous NaOH (2M) and was extracted with Et_2O (3 × 25mL). The latter Et_2O extracts were combined, dried ($MgSO_4$), filtered and evaporated. Purification by column chromatography on silica gel, eluting with CH_2Cl_2–MeOH–NH_3 (200:2:1), gave the amide **33**, E=CONHPh (57 mg, 51%) which was recrystallised from hot EtOAc to give plates; m.p. 69–71 °C; $[\alpha]_D^{25}$ +68.8 (3.1, EtOH); $[\alpha]_D^{25}$ +96.0 (0.5, $CHCl_3$); R_f 0.52 [CH_2Cl_2–MeOH–NH_3 (200:10:1)]; ν_{max} (KBr)/cm^{-1} 2950–2850 (CH), 1675 (C=O); δ_H(400 MHz, $CDCl_3$) 9.53 (1H, br, NH), 7.59 (2H, d, *J* 5.0, Ph), 7.32 (2H, t, *J* 5.0, Ph), 7.09 (1H, t, *J* 5.0, Ph), 3.40–3.37 (1H, m, NCH), 3.20–3.09 (3H, m, 3 × NCH), 2.42–2.35 (1H, m, NCH), 2.30–2.24 (1H, m, CH), 2.02–1.98 (1H, m, CH), 1.85–1.66 (11H, m, 3 × CH_3 & CH_2); δ_C(100 MHz, $CDCl_3$) 173.3 (C=O), 137.8 (C), 128.9 (CH), 124.5 (C), 123.8 (CH), 119.0 (CH), 67.8 (CH), 58.1 (CH_2), 53.9 (CH_2), 30.7 (CH_2), 24.3 (CH_2), 20.9 (CH_3), 20.4 (CH_3), 17.9 (CH_3); Found (CI): MH^+, 273.1968. $C_{17}H_{24}N_2O$ requires *MH*, 273.1967; *m/z* (CI) 273 (100%, MH^+), 191 (68), 152 (84). The enantiomer ratio of **33**, E=CONHPh was determined to be 96:4 by chiral HPLC [Chiralpak AD column (250 mm × 4.6 mm i.d.) with hexane:^{i}PrOH (95:5 v/v), flow rate 0.7 mL min^{-1}, detection by UV absorbance at 254 nm, injection volume 20 μL of the sample prepared in a 1 mg mL^{-1} solution of ^{i}PrOH, retention times 8.7 min (major) and 9.6 min (minor)]. The absolute configuration was determined by comparison with the literature of the specific rotation of the compound **34**, obtained by removing the *N*-2,3-dimethylbut-2-enyl group (see below).

*(*S*)*-N-*(2,3-Dimethylbut-2-enyl)pyrrolidine-2-carboxylic acid phenylamide* **33**, E=CONHPh

In the same way as (*R*)-**33**, E=CONHPh, the stannane **32** (183 mg, 0.41 mmol), TMEDA (0.074 mL, 0.49 mmol), *n*-BuLi (0.2 mL, 0.49 mmol), the ligand **25** [prepared by adding *n*-BuLi (0.25 mL, 0.61 mmol) to **25** (122 mg, 0.61 mmol) in Et_2O (1 mL) at 0 °C] and phenylisocyanate (0.2 mL, 1.65 mmol) gave, after purification as above, the amide (*S*)-**33**, E=CONHPh (66 mg, 58 %) as plates; $[\alpha]_D^{25}$ –71.0 (3, EtOH); data as above. The enantiomer ratio was determined to be 96:4 by chiral HPLC as above.

*(*S*)*-N-*(2,3-Dimethylbut-2-enyl)-2-trimethylsilylpyrrolidine* **33**, E=$SiMe_3$

In the same way as the amide **33**, E=CONHPh, the stannane **32** (139 mg, 0.31 mmol), TMEDA (0.057 mL, 0.38 mmol), *n*-BuLi (0.15 mL, 0.38 mmol), the ligand **16** (93 mg, 0.47 mmol) and TMSCl (0.119 mL, 0.94 mmol) gave, after purification by column chromatography on silica gel, eluting with CH_2Cl_2–MeOH–NH_3 (200:3:1), the silane **33**, E=$SiMe_3$ (44 mg, 62%) as an oil; $[\alpha]_D^{24}$ +72.1 (0.86, $CHCl_3$); R_f 0.52 [CH_2Cl_2–MeOH–NH_3 (200:10:1)]; ν_{max} (film)/cm^{-1} 2960–2705 (CH), 840 (Si–C); δ_H(400 MHz, $CDCl_3$) 3.12 (1H, d, *J* 12, NCH), 2.93–2.85 (1H, m, NCH), 2.83 (1H, d, *J* 12, NCH), 1.89–1.59 (15H, m, 3 × CH_3 & 3 × CH_2), 0.05 (9H, s, $SiMe_3$); δ_C(100 MHz, $CDCl_3$) 120.6 (C), 59.1 (CH_2), 55.5 (CH_2), 50.7 (CH), 27.3 (CH_2), 24.0 (CH_2), 20.9 (CH_3), 20.3 (CH_3), 17.7 (CH_3), –2.4 (CH_3); Found (CI): MH^+, 226.1993. $C_{13}H_{28}NSi$ requires *MH*, 226.1991; *m/z* (CI) 226 (55%, MH^+), 210 (100). The enantiomer ratio of **33**, E=$SiMe_3$ was determined to be 95:5 by inducing non equivalence in the ^1H NMR spectrum for one of the CH_3 singlets by use of *S*-(+)-mandelic acid (3.7 mg) as a chiral solvating agent with the pyrrolidine **33**, E=$SiMe_3$ (3.7 mg) in $CDCl_3$ (0.5 mL). Alternatively, the enantiomer ratio of **33**, E=$SiMe_3$ was determined by removing the *N*-2,3-dimethylbut-2-enyl group and replacing with *N*-Boc to give **35**, followed by the use of chiral GC analysis (see below). The absolute configuration was determined by comparison with the literature of the specific rotation of the compound **35** (see below). This was confirmed by the preparation of an authentic sample of (*S*)-**33**, E=$SiMe_3$ from the known silane (*S*)-**35**[8] (er 95:5 based on its specific rotation, formed by asymmetric deprotonation of

36 with *sec*-BuLi and (–)-sparteine) (230 mg, 0.94 mmol) in CH_2Cl_2 (15 mL) by adding *B*-bromocatecholborane (1.1 mL, 1.13 mmol, 1.0 M in CH_2Cl_2); after 10 min, $NaOH_{(aq)}$ (15 mL, 2 M) and 1-bromo-2,3-dimethylbut-2-ene (154 mg, 0.94 mmol) were added. After stirring for 2 h, the two layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layers were dried ($MgSO_4$), filtered and evaporated. Purification as above gave the silane (*S*)-**33**, E=$SiMe_3$ (149 mg, 70%) as an oil; $[\alpha]_D^{24}$ +71.8 (0.85, $CHCl_3$); other spectroscopic data as above.

(S)-N-*(2,3-Dimethylbut-2-enyl)-2-methylpyrrolidine* **33**, E=Me

In the same way as the amide **33**, E=CONHPh, the stannane **32** (200 mg, 0.45 mmol), TMEDA (0.082 mL, 0.54 mmol), *n*-BuLi (0.22 mL, 0.54 mmol), the ligand **16** [prepared by adding *n*-BuLi (0.27 mL, 0.68 mmol) to **16** (135 mg, 0.68 mmol) in Et_2O (1 mL) at 0 °C] and Me_2SO_4 (0.18 mL, 1.9 mmol) gave, after purification by column chromatography on silica gel, eluting with CH_2Cl_2–MeOH–NH_3 (200:4:1), the pyrrolidine **33**, E=Me [46 mg, 59%, although this contained a small amount of *N*-(2,3-Dimethylbut-2-enyl)pyrrolidine that was difficult to remove by column chromatography] as an oil; $[\alpha]_D^{24}$ –83.4 (3.2, CH_2Cl_2); R_f 0.50 [CH_2Cl_2–MeOH–NH_3 (20:2:1)]; ν_{max} (film)/cm^{-1} 2865 (C–H); δ_H(400 MHz, $CDCl_3$) 3.23 (1H, d, *J* 12, NCH), 3.08–2.99 (1H, m, CH), 2.84 (1H, d, *J* 12, CH), 2.40–2.30 (1H, m, CH), 2.19–2.07 (1H, m, CH), 1.99–1.87 (1H, m, CH), 1.83–1.38 (3H, m, 3 × CH), 1.72 (6H, s, 2 × CH_3), 1.68 (3H, s, CH_3), 1.15 (3H, d, *J* 6.0, CH_3); δ_C(125 MHz, $CDCl_3$) 60.6 (CH), 56.6 (CH_2), 54.2 (CH_2), 32.6 (CH_2), 21.5 (CH_2), 20.9 (CH_3), 20.3 (CH_3), 18.9 (CH_3), 18.2 (CH_3) (quaternary alkene carbon atoms not observed); Found (ES): MH^+, 168.1758. $C_{11}H_{22}N$ requires *MH*, 168.1752; GCMS *m/z* (ES) 168 (100, MH^+). The enantiomer ratio of **33**, E=Me was determined to be 94:6 by chiral stationary phase GC using γ-Dex 120 fused silica capillary column 30 m x 0.25 mm i.d. (20% permethylated γ-cyclodextrin in SPB-35 poly(35% diphenyl/65% dimethyl)siloxane, nitrogen carrier at 10 psi), 2.7 mL/min, retention times 36.83 (major) and 38.11 min (minor) (at 150 °C). The absolute configuration was determined by conversion to *N*-Boc-2-methylpyrrolidine (using 1-chloroethyl chloroformate followed by *N*-protection

using Boc_2O) and comparison with the literature value of the specific rotation [Found, $[\alpha]_D^{24}$ +30.0 (0.2, $CHCl_3$); Lit. $[\alpha]_D^{24}$ +31.2 (2.76, $CHCl_3$)[8]].

(R)-N-(2,3-Dimethylbut-2-enyl)-pyrrolidin-2-yl]cyclohexanol **33**, E=$C(OH)C_5H_{10}$

In the same way as the amide **33**, E=CONHPh, the stannane **32** (200 mg, 0.45 mmol), TMEDA (0.082 mL, 0.54 mmol), *n*-BuLi (0.22 mL, 0.54 mmol), the ligand **16** [prepared by adding *n*-BuLi (0.27 mL, 0.68 mmol) to **16** (135 mg, 0.68 mmol) in Et_2O (1 mL) at 0 °C] and cyclohexanone (0.21 mL, 2.0 mmol) gave, after purification by column chromatography on silica gel, eluting with CH_2Cl_2–MeOH–NH_3 (200:3:1), the pyrrolidine **33**, E=$C(OH)C_5H_{10}$ (55 mg, 48%) as an oil; $[\alpha]_D^{24}$ +54 (1.1, $CHCl_3$); R_f 0.50 [CH_2Cl_2–MeOH–NH_3 (20:1:1)]; ν_{max} (film)/cm^{-1} 3348 (O–H), 2927 & 2857–2835 (C–H); δ_H(400 MHz, $CDCl_3$) 3.43 (1H, d, *J* 12.5, NCH), 3.00–2.93 (2H, m, CH_2), 2.75–2.58 (2H, m, CH_2), 2.49–2.40 (1H, m, CH), 1.82–1.14 (13H, m, CH & 6 × CH_2), 1.75 (3H, s, CH_3), 1.71 (3H, s, CH_3), 1.67 (3H, s, CH_3); δ_C(125 MHz, $CDCl_3$) 126.9 (C), 126.8 (C), 72.7 (C), 72.3 (CH), 60.7 (CH_2), 53.5 (CH_2), 37.3 (CH_2), 33.5 (CH_2), 27.0 (CH_2), 26.0 (CH_2), 25.0 (CH_2), 22.2 (CH_2), 22.1 (CH_2), 20.9 (CH_3), 20.3 (CH_3), 16.9 (CH_3); Found (ES): MH^+, 252.2335. $C_{16}H_{30}NO$ requires *MH*, 252.2327; GCMS *m/z* (ES) 252 (100, MH^+). The enantiomer ratio of **33**, E=$C(OH)C_5H_{10}$ was determined to be 95:5 by chiral stationary phase GC using γ-Dex 120 fused silica capillary column 30 m x 0.25 mm i.d. (20% permethylated γ-cyclodextrin in SPB-35 poly(35% diphenyl/65% dimethyl)siloxane, nitrogen carrier at 10 psi), 2.7 mL/min, retention times 36.4 (minor) and 37.1 min (major) (at 150 °C).

*(*R*)-pyrrolidine-2-carboxylic acid phenylamide* **34**

1-Chloroethyl chloroformate (0.033 mL, 0.3 mmol) was added to the amide (*R*)-**33**, E=CONHPh (40 mg, 0.14 mmol) in PhMe (2 mL) and the mixture was heated under reflux. After 4 h, HCl (3 mL, 0.1 M) was added and the mixture was extracted with CH_2Cl_2. The organic layers were dried ($MgSO_4$) and

evaporated. The resulting carbamate was dissolved in MeOH (3 mL) and heated under reflux. After 16 h, the solvent was evaporated and the mixture was purified by column chromatography, eluting with petrol–EtOAc (1:1 to 0:1), to give the amide (*R*)-**34** (16 mg, 60%) as a solid; m.p. 74–77 °C; $[\alpha]_D^{24}$ +63.0 (1.0, EtOH) [Lit. for (*S*)-**34** –71.0 (1.0, EtOH)][6a]; other spectroscopic data corresponds to that reported.[6a]

*(*S*)-pyrrolidine-2-carboxylic acid phenylamide* **34**

In the same way as the amide (*R*)-**34**, the amine (*S*)-**33**, E=CONHPh (60 mg, 0.22 mmol) gave the amide (*S*)-**34** (23 mg, 55%) as a solid; m.p. 75–77 °C (Lit. m.p. 76–77 °C)[6a]; $[\alpha]_D^{24}$ –63.0 (1.0, EtOH) [Lit. –71.0 (1.0, EtOH)][6a]; other spectroscopic data corresponds to that reported.[6a]

*(*S*)-*N*-Boc-2-trimethylsilylpyrrolidine* **35**

1-Chloroethyl chloroformate (0.06 mL, 0.554 mmol) was added to the amide (*R*)-**33**, E=$SiMe_3$ (50 mg, 0.22 mmol) in PhMe (3 mL) and the mixture was heated under reflux. After 5 h, HCl (3 mL, 0.1 M) was added and the mixture was extracted with CH_2Cl_2. The organic layers were dried ($MgSO_4$) and evaporated. The resulting carbamate was dissolved in MeOH (3 mL) and heated under reflux. After 16 h, the solvent was evaporated and the mixture was dissolved in dry CH_2Cl_2 (3 mL) and cooled to 0 °C. Et_3N (0.12 mL, 0.88 mmol) and di-*tert*-butyl dicarbonate (0.126 mL, 0.55 mmol) were added. After 16 h, the solvent was evaporated and mixture was purified by column chromatography, eluting with petrol–EtOAc (97:3), to give the silane (*S*)-**35** (42 mg, 78%) as an oil; $[\alpha]_D^{24}$ +67.3 (1.0, $CHCl_3$) [Lit. +71.8 (2.62, $CHCl_3$)][8]; other spectroscopic data as reported.[11] The enantiomer ratio of **35** was determined to be 95:5 by chiral GC [β-cyclodextrin 120 fused silica column (30 × 0.25 mm, i.d.), flow rate 2.7 mL/min, nitrogen carrier at 10 psi, retention times: 47.0 min for *S*-**35** and 48.3 min for *R*-**35** at 100 °C].

Alternatively, (*S*)-**35** was prepared by dynamic kinetic resolution from *N*-Boc-2-lithiopyrrolidine:

sec-Butyllithium (2.8 mL, 3.1 mmol, 1.1 M in cyclohexane) was added to the ligand **16** (352 mg, 1.77

mmol) in Et_2O (2 mL) at –78 °C. After 20 min, *N*-Boc-pyrrolidine **36**[11] (0.2 mL, 1.2 mmol) was added. After 6 h, *n*-BuLi (5.6 mL, 11.8 mmol, 2.1 M) was added. The mixture was warmed to –20 °C and TMSCl (2.5 mL, 20.1 mmol) was added slowly (over 30 min) using a syringe pump. The mixture was quenched with MeOH (2 mL), evaporated and purified by column chromatography on silica, eluting with petrol–EtOAc (97:3), to give the silane (*S*)-**35** (164 mg, 57%), as an oil; $[\alpha]_D^{22}$ +71.8 (4.0, $CHCl_3$). The enantiomer ratio of **35** was determined to be 95:5 by chiral GC as described above.

*(*R*)*-N-*Boc-2-trimethylsilylpyrrolidine* **35**

In the same way as the silane (*S*)-**35**, *N*-Boc-pyrrolidine **36**[11] (0.2 mL, 1.2 mmol), *sec*-butyllithium (2.8 mL, 3.1 mmol, 1.1 M in cyclohexane), the ligand **25** (352 mg, 1.77 mmol), excess *n*-BuLi (5.9 mL, 11.8 mmol, 2.0 M) and TMSCl (2.5 mL, 20.1 mmol) gave the silane (*R*)-**35** (181 mg, 63%), as an oil; $[\alpha]_D^{22}$ –64.5 (2.8, $CHCl_3$). The enantiomer ratio of **35** was determined to be 91:9 by chiral GC as described above.

Computational Details

All geometries presented herein were geometry optimized using the non-local gradient corrected B3LYP functional and the 6-311G** split-valence basis set. Additionally, a counterpoise-corrected MP2 energy was calculated. Gaussian03 rev. C2 software was used for all presented calculations.

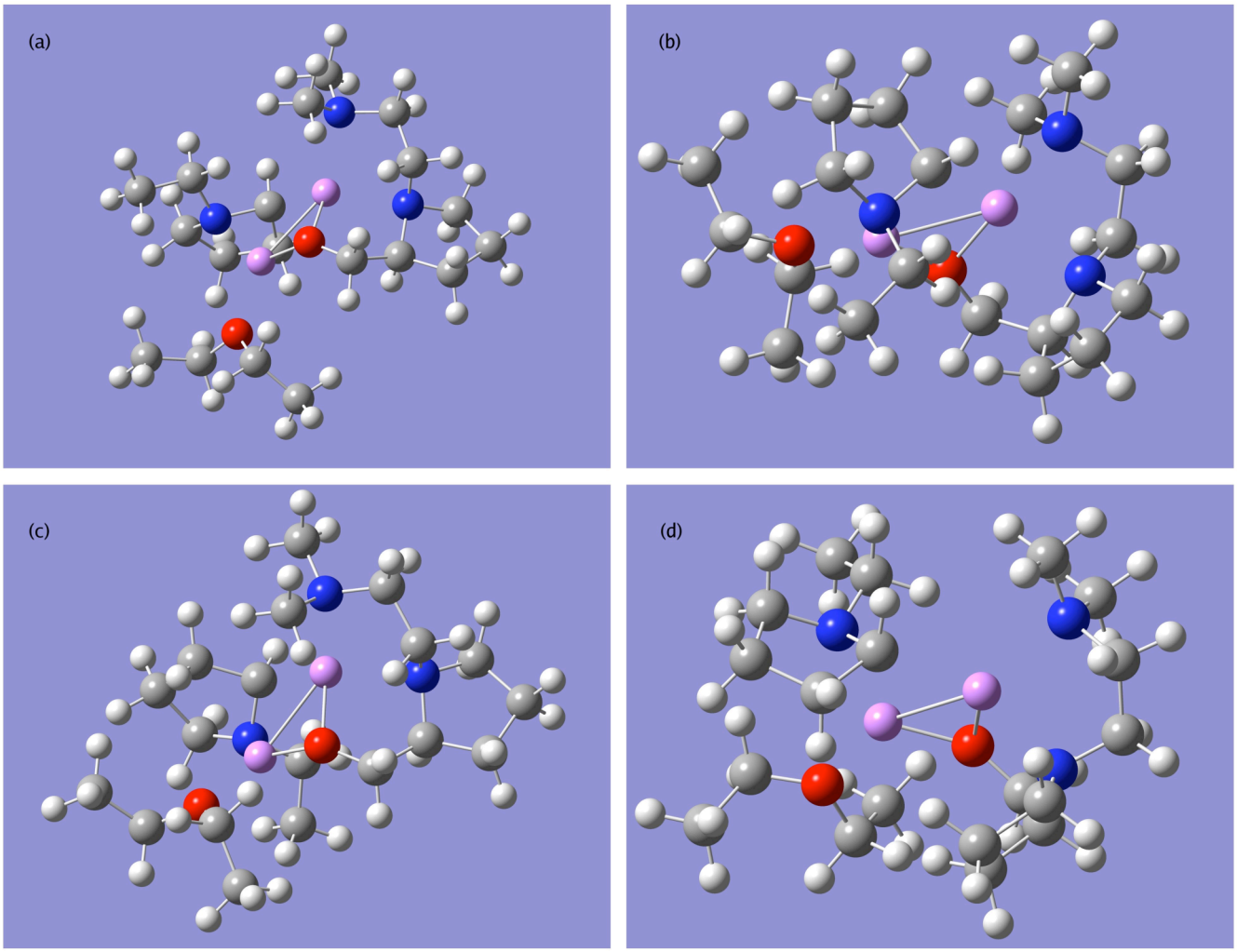

Figure. Final calculated structure of *N*-ethyl-2-lithiopyrrolidine complexed with ligand **16** and complexed with Et_2O: Pictures (a) and (b) with (*S*)-enantiomer of the 2-lithiopyrrolidine with different conformations of the ligand (carbon substituents at N and C-2 of the prolinol ligand *cis* or *trans*); Pictures (c) and (d) with (*R*)-enantiomer of the 2-lithiopyrrolidine with different conformations of the ligand (carbon substituents at N and C-2 of the prolinol ligand *cis* or *trans*).

Table. Calculated relative energies and ratios of the 2-lithiopyrrolidine·**16** complexes, in which the carbon substituents at N and C-2 of the prolinol ligand are *cis* or *trans*.

	ΔE (kJ/mol)	ratio
N-ethyl (cis)	1.37	36:64

N-isobutyl (cis)	5.91	8:92
N-dimethylallyl (cis)	1.56	35:65
N-trimethylallyl (cis)	5.48	10:90
N-ethyl (trans)	2.26	29:71
N-isobutyl (trans)	-0.187	52:48
N-dimethylallyl (trans)	2.77	25:75
N-trimethylallyl (trans)	-0.099	51:49

Computed electronic structures and energies

N-ethyl substituted organolithium cis-substituted ligand 1st stereoisomer and Et_2O

B3LYP Energy : -1078.837281920
MP2 Energy (Counterpoise Corrected) : -1075.489744013

C	3.101729	2.131534	1.187124
C	2.797976	1.506036	2.564822
C	1.357119	0.929045	2.409732
C	0.781633	1.533590	1.119013
O	2.040090	1.629670	0.284132
H	4.103637	1.882834	0.819769
H	3.527343	0.733257	2.829002
H	0.724689	1.153466	3.273549
H	0.490916	2.579926	1.366514
C	1.871353	2.466843	-0.900635
H	1.644899	3.508279	-0.597994
H	0.991180	2.099396	-1.437909
H	2.844476	2.268967	3.346110
H	1.421234	-0.169029	2.357923
H	3.036686	3.232130	1.246942
Li	-1.020312	0.705024	0.180009
O	-2.478886	2.130487	-0.652272
O	-2.802436	-0.588406	0.574759
C	-3.768588	1.471792	-0.387770
H	-4.553938	1.847075	-1.067107
H	-4.076429	1.731679	0.628750
C	-3.667490	-0.050014	-0.499001
H	-4.680344	-0.477247	-0.473756
H	-3.246476	-0.316709	-1.467926
C	-3.606382	-0.981076	1.751172
H	-2.953125	-0.987229	2.627795
H	-4.401417	-0.256934	1.939858
C	-2.112299	-1.870455	0.238930
H	-1.416239	-2.028683	1.073743
C	-3.210365	-2.948856	0.331753
H	-3.750572	-3.029063	-0.616974
H	-2.798856	-3.935449	0.554893
C	-4.137911	-2.419512	1.460272

H	-4.087153	-3.039658	2.357983
H	-5.183472	-2.404418	1.143748
C	-1.235923	-1.773801	-1.016843
H	-0.730647	-2.757225	-1.115029
H	-1.886129	-1.713607	-1.914146
N	-0.359922	-0.713126	-0.921956
Li	1.237868	-0.234203	-0.167378
C	-2.420927	3.459991	-0.038069
H	-2.567284	3.374837	1.040321
H	-1.436248	3.897749	-0.208539
H	-3.185081	4.144308	-0.444668
C	-2.204145	2.221554	-2.090748
H	-2.968104	2.817837	-2.618596
H	-1.231284	2.691007	-2.245240
H	-2.160777	1.227141	-2.535322
C	3.074776	2.466064	-1.845081
H	3.965547	2.887134	-1.372063
N	2.632257	-1.681043	-0.283600
C	4.036026	-1.444816	-0.094362
H	4.135476	-0.364172	0.010208
H	4.582877	-1.745951	-0.996018
C	2.307761	-2.894079	-0.986502
H	3.053522	-3.660972	-0.749674
H	1.350545	-3.226623	-0.582891
H	2.859255	3.066878	-2.733696
H	3.312523	1.450322	-2.174576
C	2.198738	-2.666188	-2.487404
H	1.933000	-3.600845	-2.991074
H	1.421310	-1.926696	-2.689088
H	3.143781	-2.314549	-2.910714
C	4.579824	-2.155591	1.138376
H	5.642073	-1.925269	1.264799
H	4.047976	-1.826298	2.033494
H	4.480495	-3.241340	1.059149

N-ethyl substituted organolithium cis-substituted ligand 2nd stereoisomer and Et_2O

B3LYP Energy : -1078.839895820
MP2 Energy (Counterpoise Corrected) : -1075.490406084

C	2.914355	1.406159	2.270756
C	3.177048	2.475329	1.190656
C	1.896874	2.442404	0.299284
C	0.850092	1.606391	1.057428
O	1.748235	0.631571	1.787813
H	2.655710	1.891237	3.228107
H	3.323997	3.454683	1.653140
H	2.157208	1.998613	-0.673436
C	1.057029	-0.061604	2.872801
H	0.751434	0.665797	3.649517
H	0.133623	-0.477957	2.458500
H	4.083126	2.255108	0.616362
H	1.521923	3.447112	0.081824
H	3.782420	0.763273	2.451776
Li	-0.923747	0.787052	0.038416
O	-1.954859	2.056156	-1.404296
O	-2.912816	-0.184939	0.339085
C	-3.347477	1.584750	-1.332679
H	-3.890106	1.800765	-2.269910
H	-3.849103	2.145025	-0.538701

C	-3.438348	0.090777	-1.016327
H	-4.483088	-0.231796	-1.135747
H	-2.855966	-0.470845	-1.745340
C	-3.987969	-0.134659	1.351392
H	-3.535159	0.072077	2.325042
H	-4.687143	0.676228	1.137433
C	-2.371028	-1.563240	0.533489
H	-1.871574	-1.522477	1.510714
C	-3.612118	-2.467406	0.675984
H	-3.958204	-2.796141	-0.309162
H	-3.401220	-3.364610	1.261592
C	-4.658930	-1.542645	1.354982
H	-4.888798	-1.859692	2.374676
H	-5.602578	-1.538146	0.804314
C	-1.285428	-1.931159	-0.487663
H	-0.859323	-2.898813	-0.153973
H	-1.771391	-2.161753	-1.459369
N	-0.343255	-0.928191	-0.591017
Li	1.262370	-0.341795	0.052639
H	0.417103	2.276388	1.833624
C	-1.321024	1.701302	-2.679425
H	-1.849024	2.145149	-3.540817
H	-0.290611	2.061301	-2.679484
H	-1.286259	0.618075	-2.795097
C	-1.865867	3.500065	-1.173250
H	-0.818307	3.805362	-1.183227
H	-2.408121	4.082752	-1.937528
H	-2.278971	3.744157	-0.192525
C	1.876850	-1.180738	3.517414
H	2.772712	-0.797299	4.012731
C	2.287428	-1.972687	-2.150095
H	2.856783	-1.737053	-3.056439
H	1.242764	-1.703747	-2.306761
C	4.127788	-0.943726	-0.920833
H	4.628733	-1.913829	-1.015363
H	4.262181	-0.601963	0.106880
N	2.712237	-1.111494	-1.076363
H	1.280790	-1.701600	4.272779
H	2.192340	-1.913781	2.768866
C	2.402607	-3.450035	-1.796098
H	2.030388	-4.057165	-2.626900
H	3.434241	-3.754306	-1.600901
H	1.800827	-3.675964	-0.913186
C	4.715759	0.067556	-1.898267
H	4.236941	1.041486	-1.777337
H	5.787060	0.185428	-1.709379
H	4.595167	-0.249894	-2.936915

N-isobutyl substituted organolithium cis-substituted ligand 1st stereoisomer and Et_2O

B3LYP Energy : -1157.485230780
MP2 Energy (Counterpoise Corrected) : -1153.883775978

C	2.881514	0.904330	2.165465
C	2.244667	-0.045170	3.203263
C	0.777627	-0.221139	2.707058
C	0.529550	0.885361	1.670260
O	1.907356	0.988585	1.050563
H	3.862458	0.559788	1.819894
H	2.779762	-0.998856	3.267885
H	0.053174	-0.173647	3.525061

H	0.372955	1.824282	2.247153
C	2.066401	2.214449	0.272452
H	1.947115	3.091536	0.939027
H	1.240801	2.257889	-0.448276
H	2.277909	0.405100	4.198501
H	0.671448	-1.228266	2.271234
H	3.019809	1.906776	2.606129
Li	-1.186149	0.682303	0.328433
O	-2.257192	2.458983	-0.406363
O	-3.151841	-0.317071	0.289425
C	-3.656550	2.001742	-0.400069
H	-4.275649	2.605322	-1.087086
H	-4.054360	2.156277	0.606854
C	-3.780539	0.519798	-0.757076
H	-4.843142	0.277821	-0.902951
H	-3.289008	0.331982	-1.710879
C	-4.146011	-0.746574	1.293959
H	-3.616280	-0.997135	2.217008
H	-4.842123	0.062326	1.524843
C	-2.615532	-1.626783	-0.188865
H	-2.048702	-2.014968	0.667893
C	-3.856244	-2.523074	-0.380025
H	-4.273673	-2.391584	-1.383456
H	-3.616807	-3.582327	-0.265487
C	-4.842368	-2.012773	0.706874
H	-5.017624	-2.756799	1.487153
H	-5.816759	-1.769650	0.276424
C	-1.599648	-1.483460	-1.329721
H	-1.217056	-2.506889	-1.525736
H	-2.134965	-1.207324	-2.262279
N	-0.607917	-0.581572	-1.000459
Li	0.960187	-0.507570	-0.048544
C	-2.086327	3.664628	0.408834
H	-2.398928	3.464501	1.435483
H	-1.031999	3.945242	0.428103
H	-2.669357	4.518528	0.023310
C	-1.767923	2.690336	-1.770276
H	-2.358389	3.461198	-2.294689
H	-0.728466	3.019929	-1.729463
H	-1.791892	1.765230	-2.345911
C	3.396145	2.358133	-0.489274
C	3.469621	3.741225	-1.150724
C	3.591213	1.243809	-1.523647
H	4.215462	2.296424	0.237429
H	3.375440	4.543869	-0.413306
H	4.420124	3.878312	-1.674588
H	2.666807	3.867197	-1.886081
H	3.548514	0.257784	-1.057813
H	2.806194	1.285710	-2.287801
H	4.555604	1.342658	-2.031994
N	2.130796	-2.104618	-0.511012
C	3.049656	-2.792336	0.349543
H	3.890311	-3.177063	-0.238059
H	3.442809	-2.026869	1.020632
C	1.836307	-2.750373	-1.764012
H	1.608294	-3.808175	-1.589120
H	0.927480	-2.258186	-2.108910
C	2.389001	-3.909807	1.148641
H	1.991903	-4.696132	0.501997
H	3.121772	-4.369237	1.818833
H	1.570518	-3.515900	1.754949

C	2.950601	-2.597460	-2.792541
H	3.879101	-3.081513	-2.479273
H	2.640654	-3.059903	-3.734519
H	3.158365	-1.542595	-2.982110

N-isobutyl substituted organolithium cis-substituted ligand 2nd stereoisomer and Et_2O

B3LYP Energy : -1157.487990980
MP2 Energy (Counterpoise Corrected) : -1153.886028748

C	2.869137	0.670818	-2.361777
C	2.987945	-0.826062	-2.710446
C	1.636875	-1.441069	-2.230828
C	0.706306	-0.263444	-1.888691
O	1.715103	0.775270	-1.440168
H	2.659119	1.255983	-3.274031
H	3.136648	-0.955722	-3.785508
H	1.832001	-2.082915	-1.359175
C	1.145107	2.121115	-1.422530
H	0.848507	2.410496	-2.449743
H	0.221645	2.081656	-0.832763
H	3.846911	-1.288515	-2.212972
H	1.190226	-2.091049	-2.989596
H	3.783465	1.076566	-1.914755
Li	-1.096189	-0.541874	-0.652863
O	-2.275773	-2.352983	-0.984040
O	-3.007709	0.373339	-0.001633
C	-3.638244	-1.937622	-0.611610
H	-4.246395	-2.802321	-0.293350
H	-4.117456	-1.523838	-1.503079
C	-3.634735	-0.874175	0.488753
H	-4.666779	-0.718015	0.835871
H	-3.071071	-1.241593	1.345369
C	-4.011661	1.283108	-0.590664
H	-3.500646	1.955371	-1.285396
H	-4.755319	0.725370	-1.163312
C	-2.399838	1.229984	1.060211
H	-1.836272	1.990994	0.504240
C	-3.592031	1.931923	1.742328
H	-3.991899	1.306296	2.546529
H	-3.305748	2.887467	2.186446
C	-4.624986	2.091628	0.593564
H	-4.771477	3.137291	0.313984
H	-5.603698	1.700207	0.880959
C	-1.374113	0.479356	1.921834
H	-0.885372	1.241842	2.561009
H	-1.918378	-0.175061	2.635533
N	-0.483547	-0.220939	1.133907
Li	1.133777	-0.169781	0.284935
H	0.294157	0.102120	-2.855562
C	-1.717204	-3.316830	-0.029408
H	-2.310500	-4.246379	0.013309
H	-0.697431	-3.567971	-0.327088
H	-1.667098	-2.876436	0.966378
C	-2.230743	-2.896098	-2.343921
H	-1.199111	-3.139580	-2.602985
H	-2.844669	-3.806338	-2.454248
H	-2.588758	-2.147406	-3.053466
C	2.055135	3.221339	-0.847037
C	2.461006	2.938635	0.604441
H	1.578057	2.890817	1.252130

H	2.988404	1.986473	0.691847
H	3.114941	3.726561	0.991125
C	1.359694	4.584361	-0.966882
H	2.003187	5.389987	-0.601399
H	1.097467	4.809893	-2.004766
H	0.436106	4.605624	-0.377426
H	2.968271	3.262262	-1.453825
N	2.493013	-1.024830	1.484908
C	3.889802	-1.242535	1.245148
H	4.470678	-0.914473	2.114524
H	4.143841	-0.583875	0.412697
C	2.005120	-1.411620	2.785112
H	2.397000	-2.401786	3.044141
H	0.925480	-1.479846	2.650542
C	4.214704	-2.689249	0.891004
H	5.283692	-2.786461	0.678530
H	3.975984	-3.374329	1.708080
H	3.658971	-3.001783	0.004543
C	2.338627	-0.388827	3.863839
H	1.903305	-0.705559	4.816514
H	3.415243	-0.274396	4.014966
H	1.919504	0.585691	3.604703

N-3,3-dimethylallyl substituted organolithium cis-substituted ligand 1st stereoisomer and Et_2O

B3LYP Energy : -1195.580745550
MP2 Energy (Counterpoise Corrected) : -1191.861461750

C	-2.535441	-0.270940	2.332424
C	-1.613022	0.441060	3.340642
C	-0.178567	0.220603	2.760287
C	-0.310993	-0.809915	1.624871
O	-1.698852	-0.476332	1.128365
H	-3.446968	0.290363	2.101334
H	-1.857549	1.504900	3.430750
H	0.531593	-0.113302	3.522376
H	-0.381500	-1.808081	2.112676
C	-2.249949	-1.503999	0.243425
H	-2.353139	-2.457681	0.788196
H	-1.501675	-1.681186	-0.541100
H	-1.722895	0.003399	4.336190
H	0.203869	1.189056	2.396964
H	-2.845129	-1.252443	2.731352
Li	1.373580	-0.815912	0.233247
O	2.077149	-2.625449	-0.786005
O	3.479435	-0.203586	0.263269
C	3.537008	-2.436939	-0.793889
H	4.010060	-3.021445	-1.602805
H	3.928944	-2.825266	0.150470
C	3.929761	-0.964091	-0.923339
H	5.017222	-0.899111	-1.073722
H	3.469432	-0.542538	-1.815787
C	4.538226	-0.134388	1.290111
H	4.066682	0.052036	2.258852
H	5.073353	-1.083360	1.363350
C	3.194577	1.241746	0.016752
H	2.706211	1.581787	0.939743
C	4.579001	1.918376	-0.061301
H	4.965738	1.885318	-1.084935
H	4.537274	2.968660	0.234740
C	5.455797	1.063332	0.894827

H	5.767713	1.622349	1.779839
H	6.366923	0.721258	0.398242
C	2.175831	1.468569	-1.108139
H	1.959647	2.557401	-1.112205
H	2.667409	1.280874	-2.085796
N	1.050930	0.689243	-0.921442
Li	-0.523873	0.796980	0.003950
C	1.705736	-3.896031	-0.158512
H	2.085785	-3.928411	0.864403
H	0.618221	-3.976036	-0.114521
H	2.099101	-4.768617	-0.707813
C	1.506252	-2.531636	-2.134662
H	1.932480	-3.286961	-2.817048
H	0.427070	-2.685957	-2.079107
H	1.668067	-1.535583	-2.546516
C	-4.699766	-1.765870	-0.476550
N	-1.542981	2.411193	-0.620113
C	-2.513590	3.145325	0.138701
H	-3.278103	3.551912	-0.532614
H	-2.996742	2.406878	0.780463
C	-1.160333	2.986298	-1.882577
H	-1.002346	4.064721	-1.764572
H	-0.203483	2.518108	-2.112106
C	-1.881882	4.250320	0.976952
H	-1.382628	4.997500	0.354911
H	-2.652265	4.762624	1.561190
H	-1.147492	3.833852	1.670137
C	-2.172198	2.697014	-2.984463
H	-3.152664	3.131507	-2.772714
H	-1.819465	3.120085	-3.929910
H	-2.293684	1.619611	-3.117176
C	-3.547940	-1.088956	-0.395196
C	-5.892503	-1.175963	-1.190316
H	-6.214265	-1.818323	-2.019146
H	-6.751105	-1.088593	-0.513450
H	-5.674591	-0.185179	-1.593979
C	-4.941647	-3.138486	0.100727
H	-5.167579	-3.857135	-0.696484
H	-4.094084	-3.522089	0.666981
H	-5.815122	-3.125892	0.763268
H	-3.511304	-0.102713	-0.856135

N-3,3-dimethylallyl substituted organolithium cis-substituted ligand 2nd stereoisomer and Et_2O

B3LYP Energy : -1195.582771060
MP2 Energy (Counterpoise Corrected) : -1191.862055453

C	-2.860293	-0.180814	2.051486
C	-2.448016	-1.491391	2.749752
C	-0.923074	-1.627330	2.442809
C	-0.465787	-0.282150	1.847491
O	-1.735897	0.152121	1.145909
H	-2.975568	0.623244	2.798310
H	-2.643315	-1.428495	3.823386
H	-0.783209	-2.461943	1.740205
C	-1.723305	1.573713	0.791756
H	-1.674125	2.189416	1.705502
H	-0.788140	1.756641	0.247809
H	-3.016256	-2.348505	2.373005
H	-0.345795	-1.883569	3.336482
H	-3.806365	-0.256654	1.505571

Li	1.405305	-0.091159	0.694660
O	3.198240	-1.038572	1.492539
O	2.808276	1.349261	-0.270994
C	4.285457	-0.187329	0.982882
H	5.235148	-0.747267	0.921225
H	4.439482	0.622178	1.701676
C	3.953880	0.419761	-0.381836
H	4.854829	0.910196	-0.778588
H	3.701339	-0.375845	-1.081566
C	3.262886	2.731993	-0.017628
H	2.445094	3.282594	0.455486
H	4.107807	2.744036	0.673961
C	2.007950	1.512690	-1.522028
H	1.119684	2.074642	-1.203859
C	2.850624	2.438235	-2.422700
H	3.558377	1.852690	-3.018278
H	2.230448	3.004063	-3.120879
C	3.595651	3.351035	-1.410246
H	3.257161	4.388114	-1.463993
H	4.671900	3.358253	-1.598249
C	1.491973	0.180080	-2.081700
H	0.804838	0.434271	-2.913329
H	2.334903	-0.353386	-2.570021
N	0.892708	-0.571788	-1.090582
Li	-0.703974	-0.908560	-0.269752
H	-0.330533	0.411066	2.707420
C	3.193051	-2.361832	0.858848
H	4.131219	-2.912702	1.043946
H	2.361932	-2.946260	1.257834
H	3.036477	-2.265207	-0.215475
C	3.256226	-1.168985	2.950512
H	2.404360	-1.756581	3.296713
H	4.183363	-1.659755	3.293080
H	3.194243	-0.181786	3.412759
C	-3.740141	2.989112	0.070325
N	-1.598311	-2.447466	-1.166281
C	-2.986208	-2.803880	-1.115221
H	-3.331026	-2.483794	-0.130890
H	-3.089610	-3.893646	-1.164098
C	-0.791425	-3.173786	-2.113254
H	0.080673	-2.535243	-2.258784
H	-1.328357	-3.260116	-3.064838
C	-3.806865	-2.129403	-2.208314
H	-4.860598	-2.406035	-2.106194
H	-3.729215	-1.042992	-2.128979
H	-3.479851	-2.426478	-3.207821
C	-0.375712	-4.544379	-1.593235
H	0.268261	-5.037076	-2.328139
H	0.184130	-4.445016	-0.660621
H	-1.232111	-5.199249	-1.412296
C	-2.884056	1.970917	-0.079095
C	-4.831356	3.234286	-0.944274
H	-5.821214	3.192711	-0.473795
H	-4.739930	4.232832	-1.388773
H	-4.805933	2.499856	-1.751704
C	-3.722164	3.976705	1.210522
H	-4.698981	4.004423	1.707691
H	-2.966936	3.751595	1.962175
H	-3.534841	4.990999	0.837531
H	-3.013022	1.333816	-0.953693

N-2,3,3-trimethylallyl substituted organolithium cis-substituted ligand 1st stereoisomer and Et_2O

B3LYP Energy : -1234.900868910
MP2 Energy (Counterpoise Corrected) : -1231.057588062

C	-2.583803	-0.069870	2.152925
C	-1.711337	0.702928	3.160520
C	-0.250037	0.441601	2.673653
C	-0.331581	-0.643955	1.584581
O	-1.693591	-0.339204	1.000295
H	-3.486698	0.470719	1.849865
H	-1.953287	1.771038	3.170663
H	0.412017	0.136143	3.488967
H	-0.430459	-1.614915	2.119730
C	-2.189955	-1.442730	0.167983
H	-2.238199	-2.361892	0.769781
H	-1.425982	-1.624491	-0.599596
H	-1.877131	0.331151	4.174915
H	0.168013	1.387766	2.291343
H	-2.905643	-1.026616	2.597643
Li	1.386560	-0.848157	0.251389
O	1.924361	-2.750482	-0.700747
O	3.541720	-0.447175	0.312560
C	3.395499	-2.714195	-0.661904
H	3.830129	-3.376322	-1.431639
H	3.713651	-3.103248	0.309416
C	3.945567	-1.296790	-0.829865
H	5.037802	-1.352881	-0.943156
H	3.562762	-0.864385	-1.753287
C	4.579037	-0.434482	1.363813
H	4.105222	-0.165977	2.311868
H	5.020851	-1.425311	1.487728
C	3.403501	1.007189	-0.000005
H	2.933572	1.432861	0.896590
C	4.848901	1.540257	-0.074569
H	5.251795	1.413095	-1.084468
H	4.905827	2.604055	0.165336
C	5.614291	0.655625	0.947741
H	5.947780	1.225814	1.817651
H	6.505757	0.210420	0.499669
C	2.432097	1.284827	-1.155165
H	2.342676	2.389678	-1.217651
H	2.912864	0.994021	-2.112729
N	1.223995	0.647818	-0.953374
Li	-0.344978	0.897251	-0.033836
C	1.406382	-3.959042	-0.053897
H	1.742958	-3.996187	0.984018
H	0.315455	-3.933425	-0.052440
H	1.733694	-4.881762	-0.562901
C	1.413150	-2.642574	-2.072535
H	1.783990	-3.458364	-2.716466
H	0.322740	-2.685243	-2.054609
H	1.690442	-1.681907	-2.505669
C	-4.639963	-1.862424	-0.310166
C	-3.387659	-0.069488	-1.569199
H	-2.871707	0.790357	-1.135241
H	-2.777261	-0.403825	-2.418579
H	-4.342131	0.277691	-1.961291
N	-1.122532	2.710302	-0.499955
C	-2.017321	3.495915	0.300876
H	-2.711407	4.041826	-0.347385

H	-2.601218	2.771859	0.871288
C	-0.597471	3.354402	-1.675956
H	-0.245888	4.360261	-1.418962
H	0.264587	2.747161	-1.949068
C	-1.287136	4.449651	1.239223
H	-0.686115	5.180350	0.692422
H	-2.012720	5.001761	1.844170
H	-0.628872	3.898354	1.914175
C	-1.596747	3.402950	-2.825418
H	-2.485165	3.991892	-2.583676
H	-1.124144	3.862729	-3.698644
H	-1.915086	2.395555	-3.100869
C	-3.507892	-1.169121	-0.537147
C	-5.927703	-1.650717	-1.076668
H	-6.303137	-2.610496	-1.451126
H	-6.709365	-1.251219	-0.418398
H	-5.832948	-0.981781	-1.929434
C	-4.793186	-2.949695	0.731054
H	-4.983876	-3.918094	0.251491
H	-3.933810	-3.062232	1.387090
H	-5.666010	-2.741768	1.361411

N-2,3,3-trimethylallyl substituted organolithium cis-substituted ligand 2nd stereoisomer and Et_2O

B3LYP Energy : -1234.903414780
MP2 Energy (Counterpoise Corrected) : -1231.059677152

C	2.838445	0.237661	1.965482
C	2.407935	1.518319	2.706456
C	0.873455	1.621375	2.436869
C	0.442226	0.287195	1.798290
O	1.711088	-0.092558	1.062661
H	2.979518	-0.583060	2.688416
H	2.630697	1.434081	3.773309
H	0.692997	2.478515	1.772586
C	1.716564	-1.512092	0.683856
H	1.625455	-2.129704	1.588355
H	0.802512	-1.686633	0.102512
H	2.944987	2.399330	2.339361
H	0.308696	1.822926	3.352369
H	3.777180	0.349767	1.412435
Li	-1.447894	0.023101	0.690086
O	-3.267825	0.800813	1.601274
O	-2.804343	-1.470696	-0.288205
C	-4.324025	-0.078883	1.073488
H	-5.302239	0.432472	1.065690
H	-4.417931	-0.932449	1.750123
C	-3.994619	-0.593709	-0.329579
H	-4.879419	-1.104143	-0.737801
H	-3.791915	0.250285	-0.987823
C	-3.186209	-2.882320	-0.077216
H	-2.329869	-3.410460	0.351190
H	-4.009146	-2.962059	0.635900
C	-2.033042	-1.549280	-1.565210
H	-1.111518	-2.079684	-1.290828
C	-2.855317	-2.480570	-2.478678
H	-3.604046	-1.907624	-3.035136
H	-2.227730	-2.990852	-3.212140
C	-3.530754	-3.463141	-1.483216
H	-3.149241	-4.481396	-1.586167
H	-4.610597	-3.511142	-1.642522

C	-1.595292	-0.175067	-2.089830
H	-0.918721	-0.367238	-2.946441
H	-2.474524	0.333185	-2.539063
N	-1.006317	0.570768	-1.088392
Li	0.587259	0.984778	-0.290310
H	0.339131	-0.440031	2.634874
C	-3.379908	2.165133	1.074429
H	-4.330981	2.643130	1.365435
H	-2.555316	2.767907	1.459416
H	-3.301373	2.158558	-0.012924
C	-3.259445	0.818381	3.066387
H	-2.427996	1.432176	3.416862
H	-4.195887	1.221559	3.488393
H	-3.114004	-0.194379	3.447324
C	2.979796	-1.157065	-1.463739
H	2.020655	-1.208789	-1.992551
H	3.162636	-0.097064	-1.262348
H	3.753834	-1.505770	-2.144430
C	3.776296	-2.896599	0.183361
N	1.255833	2.709584	-1.074145
C	2.555482	3.304227	-0.963338
H	3.022564	2.806034	-0.112523
H	2.458360	4.365610	-0.708872
C	0.289321	3.424445	-1.869437
H	-0.491530	2.684602	-2.048997
H	0.737557	3.705826	-2.828771
C	3.408207	3.123073	-2.214582
H	4.407169	3.534198	-2.040859
H	3.511730	2.064072	-2.460683
H	2.985765	3.637399	-3.080988
C	-0.281215	4.643112	-1.154033
H	-1.049357	5.106774	-1.780401
H	-0.743211	4.349883	-0.208672
H	0.476283	5.403198	-0.946299
C	2.905606	-1.929308	-0.164996
C	4.934585	-3.350725	-0.678680
H	5.888332	-3.121099	-0.187467
H	4.908712	-4.439779	-0.804163
H	4.958967	-2.904777	-1.670588
C	3.732527	-3.670718	1.483285
H	4.704491	-3.611621	1.987532
H	2.976328	-3.326604	2.184059
H	3.551618	-4.735156	1.287956

N-ethyl substituted organolithium trans-substituted ligand 1st stereoisomer and Et_2O

B3LYP Energy : -1078.847203840
MP2 Energy (Counterpoise Corrected) : -1075.498347935

C	-2.663170	1.779466	2.036182
C	-2.708354	2.834718	0.912431
C	-1.417285	2.561584	0.081862
C	-0.536534	1.624760	0.928565
O	-1.604075	0.821822	1.640567
H	-3.626342	1.280565	2.188683
H	-3.616168	2.743522	0.307085
H	-0.891788	3.486971	-0.172103
H	-0.056580	2.263348	1.704146
C	-1.080972	0.074829	2.781878
H	-0.704382	0.776711	3.551249
H	-0.214535	-0.492512	2.429906

H	-2.708810	3.841793	1.337221
H	-1.705634	2.102527	-0.876013
H	-2.382907	2.255416	2.992065
Li	1.132013	0.546013	-0.049076
O	2.439452	1.853786	-1.271945
O	3.008724	-0.707675	0.128491
C	3.788140	1.281051	-1.129183
H	4.226425	1.686675	-0.213436
H	4.445495	1.591287	-1.960226
C	3.763173	-0.246194	-1.036887
H	3.298537	-0.659146	-1.934396
H	4.800195	-0.623309	-1.019369
C	3.784501	-0.735048	1.375444
H	4.740959	-1.268624	1.225634
H	4.021018	0.275055	1.720404
C	2.424123	-2.065899	-0.014274
H	3.184637	-2.759423	-0.419194
C	2.084233	-2.470584	1.437424
H	1.011270	-2.367004	1.606797
H	2.349443	-3.514822	1.615136
C	2.883454	-1.504318	2.348172
H	3.466574	-2.021868	3.112562
H	2.210393	-0.813510	2.860391
C	1.203097	-2.051951	-0.963348
H	1.585438	-1.984098	-2.004378
H	0.751880	-3.063716	-0.897087
N	0.320584	-1.041973	-0.668403
Li	-1.191146	-0.275390	-0.052595
C	1.926075	1.715352	-2.639350
H	1.881831	0.664749	-2.927616
H	0.910370	2.111808	-2.685538
H	2.549300	2.257486	-3.371206
C	2.416829	3.261426	-0.863693
H	3.073496	3.889702	-1.489546
H	1.398192	3.644639	-0.934215
H	2.737299	3.350497	0.176047
C	-2.092633	-0.880058	3.417921
H	-2.943854	-0.345496	3.847359
H	-1.621306	-1.450214	4.224033
H	-2.476910	-1.590710	2.679958
H	-4.173845	-0.218207	0.130144
C	-4.136835	-0.602182	-0.890453
N	-2.751789	-0.883258	-1.133959
H	-4.714029	-1.533704	-0.916712
C	-4.710557	0.419979	-1.864760
C	-2.475284	-1.825229	-2.186708
H	-5.754195	0.629320	-1.611168
H	-4.150116	1.355628	-1.812347
H	-4.685244	0.060363	-2.896402
H	-1.443364	-1.621133	-2.471318
H	-3.124955	-1.617516	-3.044447
C	-2.617472	-3.269862	-1.725023
H	-2.369379	-3.947733	-2.547412
H	-1.932420	-3.469690	-0.898703
H	-3.634820	-3.502210	-1.399084

N-ethyl substituted organolithium trans-substituted ligand 2nd stereoisomer and Et_2O

B3LYP Energy : -1078.846868300
MP2 Energy (Counterpoise Corrected) : -1075.499209120

C	-2.503916	2.544146	1.202366
C	-2.333362	1.818700	2.552638
C	-1.005586	1.015838	2.387616
C	-0.327780	1.542822	1.111437
O	-1.546556	1.889650	0.281978
H	-2.234789	3.609847	1.307664
H	-2.271253	2.543267	3.368629
H	-1.249362	-0.055586	2.314965
C	-1.223717	2.722821	-0.873462
H	-0.821850	3.697918	-0.534656
H	-0.416102	2.224621	-1.419482
H	-3.184631	1.165307	2.770617
H	-0.350188	1.116496	3.257840
H	-3.530958	2.501012	0.823273
Li	1.253590	0.415399	0.079571
O	3.015886	1.580686	-0.615115
O	2.747489	-1.205739	0.378826
C	4.159220	0.739006	-0.224563
H	4.359379	0.922211	0.834583
H	5.073076	1.023693	-0.775108
C	3.879315	-0.751755	-0.429371
H	3.652659	-0.940323	-1.480514
H	4.793451	-1.325112	-0.199768
C	3.099069	-1.592945	1.751123
H	3.940289	-2.310125	1.751049
H	3.403364	-0.725368	2.342833
C	1.989985	-2.349480	-0.195281
H	2.693936	-3.112832	-0.574513
C	1.212317	-2.922921	1.013992
H	0.150710	-2.686585	0.926684
H	1.310472	-4.010250	1.046078
C	1.821125	-2.254824	2.271687
H	2.027687	-2.963932	3.075961
H	1.143801	-1.493390	2.663848
C	1.084169	-1.880475	-1.359213
H	1.737047	-1.666599	-2.231879
H	0.496426	-2.771547	-1.668713
N	0.306628	-0.803022	-1.014832
Li	-1.154838	-0.066503	-0.253557
H	0.143243	2.513222	1.388541
C	3.098141	2.905631	0.006748
H	3.996613	3.462317	-0.310387
H	2.215539	3.488961	-0.259239
H	3.114964	2.803942	1.093281
C	2.905062	1.711679	-2.072040
H	2.030389	2.317261	-2.315366
H	3.796057	2.191596	-2.512276
H	2.766872	0.735583	-2.537166
C	-2.400953	2.962009	-1.820662
H	-3.208099	3.518702	-1.337490
H	-2.076161	3.541526	-2.689994
H	-2.810385	2.013646	-2.180874
N	-2.774260	-1.220454	-0.444188
C	-2.657499	-2.404305	-1.253759
H	-1.685337	-2.831130	-1.007780
H	-3.428828	-3.124324	-0.958118
C	-4.115640	-0.829092	-0.116287
H	-4.065196	0.243808	0.072788
H	-4.766922	-0.984640	-0.984419
C	-2.731417	-2.089618	-2.741372
H	-2.624905	-3.009972	-3.323776

H	-3.685876	-1.630727	-3.013386
H	-1.921561	-1.411415	-3.016427
C	-4.650539	-1.563669	1.106686
H	-5.659295	-1.211318	1.342402
H	-4.703987	-2.642963	0.942231
H	-4.011183	-1.379261	1.972651

N-isobutyl substituted organolithium trans-substituted ligand 1st stereoisomer and Et_2O

B3LYP Energy : -1157.494977280
MP2 Energy (Counterpoise Corrected) : -1153.893921702

C	-2.632201	0.401913	-2.469125
C	-2.491265	-1.075793	-2.887451
C	-1.123267	-1.515668	-2.283587
C	-0.399659	-0.230521	-1.841146
O	-1.582321	0.631936	-1.449077
H	-3.630180	0.641067	-2.085275
H	-3.321511	-1.684162	-2.513829
H	-0.524973	-2.084286	-3.001882
H	0.024627	0.223853	-2.764604
C	-1.219831	2.043634	-1.345479
H	-0.877302	2.409729	-2.333446
H	-0.357258	2.114037	-0.673099
H	-2.498766	-1.163628	-3.976881
H	-1.311429	-2.195263	-1.439108
H	-2.446658	1.059250	-3.336271
Li	1.324642	-0.386738	-0.455055
O	2.820943	-1.902857	-1.056374
O	3.111397	0.577692	0.561076
C	4.117689	-1.340535	-0.644803
H	4.452525	-0.665325	-1.436770
H	4.885621	-2.128698	-0.553264
C	4.022743	-0.561855	0.668637
H	3.660834	-1.221239	1.459745
H	5.034177	-0.239394	0.969872
C	3.729286	1.790888	0.009611
H	4.671372	2.021622	0.539826
H	3.968444	1.669355	-1.050273
C	2.482362	0.988534	1.842756
H	3.249918	1.038952	2.637451
C	1.954169	2.410404	1.549835
H	0.875016	2.375727	1.393581
H	2.146707	3.071916	2.396988
C	2.683515	2.881759	0.266251
H	3.145984	3.864910	0.374529
H	1.987450	2.937515	-0.573260
C	1.382954	-0.011504	2.271920
H	1.888959	-0.914141	2.677700
H	0.879468	0.444401	3.149433
N	0.520750	-0.317084	1.247427
Li	-1.011505	-0.330897	0.291031
C	2.467008	-3.097017	-0.281078
H	2.405630	-2.860182	0.781271
H	1.484163	-3.452002	-0.595811
H	3.197258	-3.912397	-0.421806
C	2.808971	-2.209550	-2.489572
H	3.559798	-2.971201	-2.761146
H	1.821972	-2.576266	-2.773465
H	3.008995	-1.303268	-3.064485
C	-2.328431	2.982448	-0.835482

H	-3.182709	2.907100	-1.519602
H	-3.981363	-0.884427	0.121449
C	-3.782134	-1.582122	0.936628
N	-2.412825	-1.357284	1.297484
H	-4.435541	-1.308768	1.773258
C	-4.048817	-3.013270	0.484573
C	-2.027246	-1.802414	2.612126
H	-5.094391	-3.116205	0.178814
H	-3.415072	-3.270716	-0.366525
H	-3.864601	-3.736064	1.283123
H	-0.942801	-1.892892	2.557881
H	-2.455864	-2.792434	2.803670
C	-2.419703	-0.811633	3.700464
H	-2.073741	-1.175231	4.672827
H	-1.954666	0.158257	3.512811
H	-3.501997	-0.671934	3.764975
C	-2.810784	2.604107	0.570134
H	-3.613480	3.269578	0.903078
H	-3.185161	1.578835	0.600508
H	-1.993072	2.681292	1.295637
C	-1.835127	4.435584	-0.872875
H	-1.523313	4.725970	-1.880473
H	-2.619563	5.127581	-0.552750
H	-0.977842	4.575301	-0.205010

N-isobutyl substituted organolithium trans-substituted ligand 2nd stereoisomer and Et_2O

B3LYP Energy : -1157.494422020
MP2 Energy (Counterpoise Corrected) : -1153.893850444

C	-2.524518	1.499933	2.053134
C	-2.128145	0.473709	3.136320
C	-0.741592	-0.060715	2.665434
C	-0.242127	0.910935	1.585611
O	-1.557270	1.307901	0.946138
H	-2.425248	2.525148	2.449548
H	-2.058186	0.961706	4.111733
H	-0.870770	-1.081476	2.273523
C	-1.425390	2.501974	0.114239
H	-1.103987	3.355839	0.743469
H	-0.615883	2.318049	-0.602678
H	-2.871000	-0.325312	3.233748
H	-0.027914	-0.143247	3.490447
H	-3.559103	1.380462	1.712488
Li	1.384043	0.384249	0.204552
O	2.935716	1.945079	-0.115148
O	3.095883	-1.024625	-0.066211
C	4.200596	1.193630	-0.044681
H	4.447893	1.057335	1.011567
H	5.031218	1.765085	-0.494776
C	4.097231	-0.177751	-0.714845
H	3.818271	-0.052137	-1.762902
H	5.091029	-0.656792	-0.711410
C	3.596784	-1.770344	1.095370
H	4.527122	-2.310588	0.840871
H	3.820858	-1.101397	1.930663
C	2.457904	-2.025504	-0.960859
H	3.226378	-2.509288	-1.591136
C	1.859946	-3.069407	0.013532
H	0.772566	-2.983951	0.036678
H	2.108797	-4.080615	-0.315926

C	2.465727	-2.754386	1.403637
H	2.830106	-3.643070	1.923205
H	1.722077	-2.275788	2.044334
C	1.407326	-1.353981	-1.877629
H	1.951563	-0.770887	-2.650007
H	0.928350	-2.179541	-2.447726
N	0.516225	-0.582415	-1.173531
Li	-0.957011	-0.341405	-0.150946
H	0.124380	1.812942	2.126069
C	2.888197	2.996374	0.905571
H	3.686464	3.746385	0.771440
H	1.923321	3.503321	0.862452
H	2.987816	2.553296	1.898025
C	2.717586	2.523302	-1.445776
H	1.756173	3.039358	-1.463350
H	3.507118	3.245562	-1.715749
H	2.684711	1.741806	-2.205284
C	-2.686806	2.919682	-0.663018
H	-3.491207	3.100565	0.060630
N	-2.355577	-1.770028	-0.444312
C	-2.173692	-2.621897	-1.590186
H	-1.115886	-2.533895	-1.833938
H	-2.376092	-3.661796	-1.309484
C	-3.515571	-2.044169	0.355288
H	-3.725486	-1.115280	0.887699
H	-4.371855	-2.252988	-0.295739
C	-3.026313	-2.199302	-2.779820
H	-2.824641	-2.859555	-3.628775
H	-4.096183	-2.256045	-2.563521
H	-2.787368	-1.176588	-3.077479
C	-3.293985	-3.183744	1.343022
H	-4.193340	-3.328286	1.949251
H	-3.079778	-4.128185	0.836589
H	-2.462579	-2.954883	2.012792
C	-3.154811	1.830747	-1.635297
H	-3.363286	0.894536	-1.114034
H	-4.063363	2.137886	-2.162840
H	-2.383842	1.627967	-2.387418
C	-2.426602	4.239681	-1.402075
H	-3.321665	4.579285	-1.931315
H	-2.125734	5.032662	-0.710880
H	-1.628860	4.122318	-2.144220

N-3,3-dimethylallyl substituted organolithium trans-substituted ligand 1st stereoisomer and Et_2O

B3LYP Energy : -1195.590249160
MP2 Energy (Counterpoise Corrected) : -1191.870040666

C	2.589929	0.198011	-2.211346
C	2.029739	1.432660	-2.942218
C	0.528035	1.480104	-2.516045
C	0.223926	0.152601	-1.794523
O	1.578122	-0.141388	-1.185075
H	3.575744	0.364887	-1.764932
H	2.563055	2.346140	-2.659615
H	-0.134775	1.628479	-3.373902
H	0.069080	-0.608462	-2.592340
C	1.706548	-1.528969	-0.734117
H	1.631195	-2.214068	-1.595481
H	0.836496	-1.736059	-0.099211
H	2.143553	1.320432	-4.023557

H	0.376525	2.351244	-1.861018
H	2.687459	-0.645036	-2.916814
Li	-1.565897	-0.002980	-0.492463
O	-3.420441	0.787678	-1.412331
O	-3.007506	-1.300850	0.663281
C	-4.495426	-0.075803	-0.896326
H	-4.550562	-0.957955	-1.539661
H	-5.477216	0.425254	-0.959997
C	-4.240226	-0.522130	0.544812
H	-4.158379	0.354755	1.189888
H	-5.112672	-1.094287	0.904737
C	-3.163583	-2.725956	0.344374
H	-4.017369	-3.156016	0.899336
H	-3.353472	-2.877010	-0.721606
C	-2.375676	-1.254041	2.006777
H	-3.142309	-1.421549	2.786338
C	-1.395371	-2.447997	1.989187
H	-0.377040	-2.087421	1.836830
H	-1.420179	-2.977123	2.943985
C	-1.844591	-3.351165	0.811928
H	-1.975075	-4.395745	1.101723
H	-1.109623	-3.324684	0.004592
C	-1.697558	0.113335	2.258622
H	-2.497241	0.848166	2.493911
H	-1.131435	0.004813	3.206881
N	-0.917447	0.516119	1.202213
Li	0.591138	0.891502	0.286775
C	-3.523040	2.158848	-0.900543
H	-3.463959	2.167244	0.188122
H	-2.686185	2.748101	-1.279415
H	-4.464328	2.645294	-1.209254
C	-3.405422	0.795771	-2.877961
H	-4.339866	1.199051	-3.304413
H	-2.571534	1.404511	-3.229565
H	-3.261759	-0.219537	-3.252680
C	2.963491	-1.770960	0.057057
H	3.263645	2.254554	0.137735
C	2.784726	3.006227	0.767326
N	1.515532	2.442976	1.126341
H	3.401903	3.129759	1.664655
C	2.650787	4.324488	0.013981
C	0.900071	2.980866	2.311683
H	3.641320	4.691642	-0.271172
H	2.060599	4.187615	-0.894419
H	2.172931	5.096109	0.622743
H	-0.156578	2.737446	2.203632
H	1.012684	4.070872	2.320336
C	1.455070	2.359069	3.586597
H	0.940275	2.777189	4.456996
H	1.293000	1.279317	3.580121
H	2.524279	2.550976	3.709879
C	3.868653	-2.747872	-0.077661
C	5.057266	-2.831568	0.849746
H	5.997922	-2.779554	0.288118
H	5.054096	-2.025339	1.586056
H	5.069584	-3.786067	1.389924
C	3.815118	-3.840830	-1.116049
H	4.750079	-3.871287	-1.687889
H	3.712262	-4.822133	-0.636943
H	2.992127	-3.724708	-1.819922
H	3.125312	-1.044353	0.852965

N-3,3-dimethylallyl substituted organolithium trans-substituted ligand 2nd stereoisomer and Et_2O

B3LYP Energy : -1195.589742810
MP2 Energy (Counterpoise Corrected) : -1191.871096302

C	2.546989	-0.358445	2.138395
C	1.778576	0.447886	3.203172
C	0.292338	0.388056	2.725626
C	0.229733	-0.656353	1.597143
O	1.610028	-0.485466	0.998594
H	2.784953	-1.364337	2.525143
H	1.908642	-0.001984	4.190818
H	-0.003954	1.390916	2.380423
C	1.980211	-1.583343	0.102429
H	2.029607	-2.531082	0.665255
H	1.159884	-1.694168	-0.618538
H	2.143937	1.477838	3.271066
H	-0.394079	0.136151	3.539506
H	3.491835	0.106416	1.837219
Li	-1.459806	-0.691616	0.186219
O	-2.301415	-2.671917	-0.338337
O	-3.568305	0.001206	-0.054929
C	-3.757337	-2.461221	-0.273663
H	-4.055903	-2.534008	0.775650
H	-4.301262	-3.254986	-0.815499
C	-4.171918	-1.092184	-0.817580
H	-3.859790	-1.002784	-1.859726
H	-5.272779	-1.022554	-0.815234
C	-4.334713	0.405713	1.130954
H	-5.391816	0.590546	0.865950
H	-4.317262	-0.372024	1.899103
C	-3.328247	1.244520	-0.834132
H	-4.218331	1.482301	-1.445494
C	-3.144963	2.329229	0.253041
H	-2.091000	2.599383	0.335660
H	-3.701870	3.230882	-0.010999
C	-3.653305	1.702670	1.575690
H	-4.339699	2.354190	2.120500
H	-2.815378	1.476264	2.238069
C	-2.105248	1.086147	-1.768388
H	-2.404573	0.429611	-2.612712
H	-1.948242	2.081006	-2.238086
N	-0.999739	0.611948	-1.106960
Li	0.459667	0.855000	-0.072401
H	0.228019	-1.652709	2.094761
C	-1.881004	-3.735591	0.578795
H	-2.327335	-4.711230	0.321013
H	-0.794756	-3.832101	0.552256
H	-2.167982	-3.478975	1.600112
C	-1.850071	-2.971761	-1.701804
H	-0.766146	-3.098603	-1.704248
H	-2.310665	-3.893982	-2.095934
H	-2.083518	-2.147090	-2.375311
C	3.256048	-1.322125	-0.651649
N	1.360678	2.601948	-0.447453
C	0.850311	3.393545	-1.535751
H	-0.234234	3.380072	-1.426358
H	1.188087	4.429504	-1.420378
C	2.670387	2.966019	0.014340
H	3.079010	2.062103	0.467427

H	3.302994	3.224965	-0.843074
C	1.250218	2.825946	-2.890269
H	0.839139	3.446684	-3.692414
H	2.336478	2.797936	-3.013000
H	0.854275	1.814305	-2.997197
C	2.630511	4.102813	1.027625
H	3.642775	4.328426	1.376533
H	2.213826	5.017047	0.597077
H	2.024054	3.822526	1.891590
C	4.346608	-2.091574	-0.753605
C	4.530611	-3.427509	-0.077492
H	4.637025	-4.225149	-0.822758
H	5.452856	-3.431610	0.515263
H	3.705107	-3.691962	0.581689
C	5.521290	-1.659072	-1.598016
H	5.730229	-2.392468	-2.386306
H	5.346073	-0.691857	-2.073237
H	6.433116	-1.584009	-0.993193
H	3.257250	-0.377668	-1.195000

N-2,3,3-trimethylallyl substituted organolithium trans-substituted ligand 1st stereoisomer and Et_2O

B3LYP Energy : -1234.910734190
MP2 Energy (Counterpoise Corrected) : -1231.067635130

C	-2.527870	0.212010	2.146613
C	-1.934446	1.400941	2.925119
C	-0.421915	1.393569	2.536245
C	-0.163233	0.082762	1.766710
O	-1.516368	-0.124329	1.119459
H	-3.503108	0.427358	1.697096
H	-2.419750	2.344080	2.653909
H	0.225898	1.474989	3.414271
H	-0.060422	-0.715828	2.535542
C	-1.683389	-1.493365	0.615052
H	-1.579301	-2.205476	1.446182
H	-0.836490	-1.684660	-0.055475
H	-2.081577	1.266226	3.999852
H	-0.212554	2.282367	1.922214
H	-2.660882	-0.648224	2.824113
Li	1.660830	-0.092472	0.517795
O	3.518685	0.488139	1.576129
O	3.074467	-1.361026	-0.711959
C	4.557181	-0.398875	1.026737
H	4.515939	-1.340664	1.580487
H	5.566657	0.019602	1.185240
C	4.347772	-0.685393	-0.461502
H	4.355738	0.252888	-1.019040
H	5.197987	-1.279863	-0.837407
C	3.124298	-2.819698	-0.543570
H	3.976910	-3.245359	-1.103634
H	3.249517	-3.095191	0.507052
C	2.511568	-1.128512	-2.066951
H	3.302229	-1.261158	-2.828881
C	1.458943	-2.247954	-2.220293
H	0.460714	-1.835624	-2.065212
H	1.491994	-2.669813	-3.226890
C	1.794739	-3.302454	-1.135166
H	1.877529	-4.314895	-1.535419
H	1.023508	-3.318180	-0.362236
C	1.929727	0.299171	-2.192763

H	2.783715	1.002475	-2.299198
H	1.414346	0.335355	-3.174922
N	1.115052	0.629263	-1.137278
Li	-0.414093	0.980394	-0.239009
C	3.730962	1.888212	1.192006
H	3.711075	1.995581	0.107234
H	2.922410	2.499143	1.596959
H	4.691132	2.279489	1.570229
C	3.441863	0.370489	3.035071
H	4.381336	0.671701	3.529378
H	2.634364	1.001400	3.408320
H	3.217859	-0.661407	3.312281
C	-2.967286	-1.726444	-0.165046
H	-3.000318	2.546139	0.021454
C	-2.470032	3.288943	-0.576780
N	-1.247721	2.651242	-0.972106
H	-3.081279	3.499092	-1.462159
C	-2.239300	4.557278	0.236502
C	-0.588266	3.214407	-2.122490
H	-3.200445	4.977349	0.548001
H	-1.654235	4.337707	1.131950
H	-1.713928	5.322883	-0.339721
H	0.446374	2.885870	-2.028514
H	-0.618759	4.308108	-2.063560
C	-1.183691	2.716607	-3.432947
H	-0.630060	3.141543	-4.275721
H	-1.111892	1.628633	-3.490256
H	-2.232686	3.002534	-3.547275
C	-3.025279	-0.905111	-1.434519
H	-3.983957	-0.948609	-1.947480
H	-2.816329	0.144055	-1.208318
H	-2.250671	-1.230813	-2.140379
C	-3.922708	-2.601352	0.203686
C	-5.161776	-2.898324	-0.613614
H	-5.266781	-3.980626	-0.754834
H	-6.063413	-2.569342	-0.081936
H	-5.168217	-2.438051	-1.599287
C	-3.900565	-3.416603	1.478534
H	-4.841184	-3.279261	2.025253
H	-3.831641	-4.487484	1.249511
H	-3.087479	-3.165167	2.154732

N-2,3,3-trimethylallyl substituted organolithium trans-substituted ligand 2nd stereoisomer and Et_2O

B3LYP Energy : -1234.910055650
MP2 Energy (Counterpoise Corrected) : -1231.067597301

C	2.502483	-0.148116	2.081250
C	1.702726	0.650213	3.129196
C	0.217609	0.499006	2.670454
C	0.200450	-0.574681	1.567983
O	1.566567	-0.354041	0.951934
H	2.790855	-1.127109	2.499252
H	1.865141	0.237941	4.128420
H	-0.139299	1.475147	2.306520
C	1.973082	-1.479206	0.099978
H	1.995063	-2.401846	0.698090
H	1.174966	-1.615021	-0.641588
H	2.015255	1.699189	3.165046
H	-0.445848	0.228914	3.497395
H	3.421631	0.352604	1.758478

Li	-1.482989	-0.771840	0.170145
O	-2.138487	-2.842975	-0.327259
O	-3.642555	-0.294284	-0.066970
C	-3.606968	-2.765838	-0.249076
H	-3.888047	-2.849134	0.804300
H	-4.080625	-3.614574	-0.773169
C	-4.149825	-1.449138	-0.808718
H	-3.853948	-1.346469	-1.854449
H	-5.252441	-1.480423	-0.798079
C	-4.426732	0.051275	1.125884
H	-5.500091	0.135288	0.875231
H	-4.326952	-0.712124	1.902217
C	-3.530797	0.955528	-0.865308
H	-4.441013	1.091481	-1.477711
C	-3.456553	2.072319	0.203632
H	-2.442462	2.470877	0.258480
H	-4.126164	2.894227	-0.059019
C	-3.859114	1.409425	1.544578
H	-4.584543	1.996549	2.111600
H	-2.980473	1.265223	2.176698
C	-2.298966	0.905449	-1.799693
H	-2.524640	0.200053	-2.627237
H	-2.251713	1.899733	-2.294874
N	-1.148951	0.570435	-1.129466
Li	0.305050	0.911663	-0.112690
H	0.251491	-1.556398	2.091437
C	-1.613821	-3.848655	0.601663
H	-1.977000	-4.864053	0.367866
H	-0.523825	-3.851253	0.559553
H	-1.907762	-3.598939	1.622658
C	-1.677582	-3.126192	-1.691087
H	-0.586701	-3.151687	-1.706867
H	-2.054840	-4.094929	-2.061568
H	-1.996315	-2.340882	-2.376779
C	3.278003	-1.270923	-0.651379
N	1.028325	2.767643	-0.425228
C	0.464033	3.509502	-1.522123
H	-0.493728	3.029295	-1.716559
H	0.274366	4.542051	-1.207362
C	2.042139	3.448614	0.328959
H	2.618830	2.659287	0.813282
H	2.715381	3.979786	-0.353321
C	1.336993	3.468429	-2.769971
H	0.850877	4.024802	-3.577103
H	2.319188	3.917914	-2.602643
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C	1.462263	4.399494	1.369151
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H	0.874456	5.198065	0.909675
H	0.821847	3.859127	2.069307
C	3.185057	-0.142955	-1.654960
H	2.819607	0.763115	-1.164156
H	4.128472	0.099500	-2.140361
H	2.455228	-0.385408	-2.437902
C	4.373936	-2.035007	-0.479837
C	4.498059	-3.152324	0.533443
H	4.613728	-4.119456	0.028034
H	5.403400	-3.010378	1.135531
H	3.657374	-3.228981	1.218214
C	5.645792	-1.886029	-1.286761
H	5.569312	-1.185239	-2.115245

H 6.474511 -1.560976 -0.645359
H 5.942313 -2.856587 -1.702190

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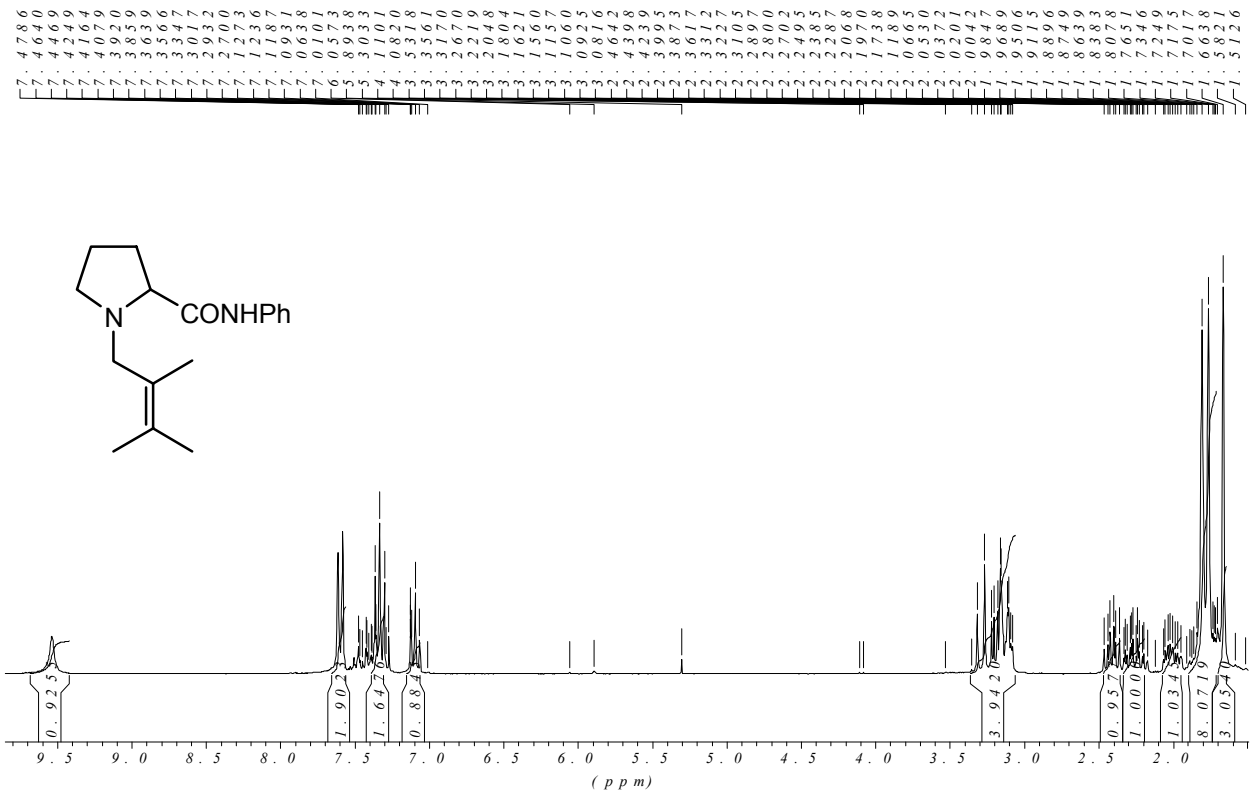
(18) Gaussian 03, Revision C.02, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A.; Vreven, T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; and Pople, J.A.; Gaussian, Inc., Wallingford CT, 2004.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1.642
0.884
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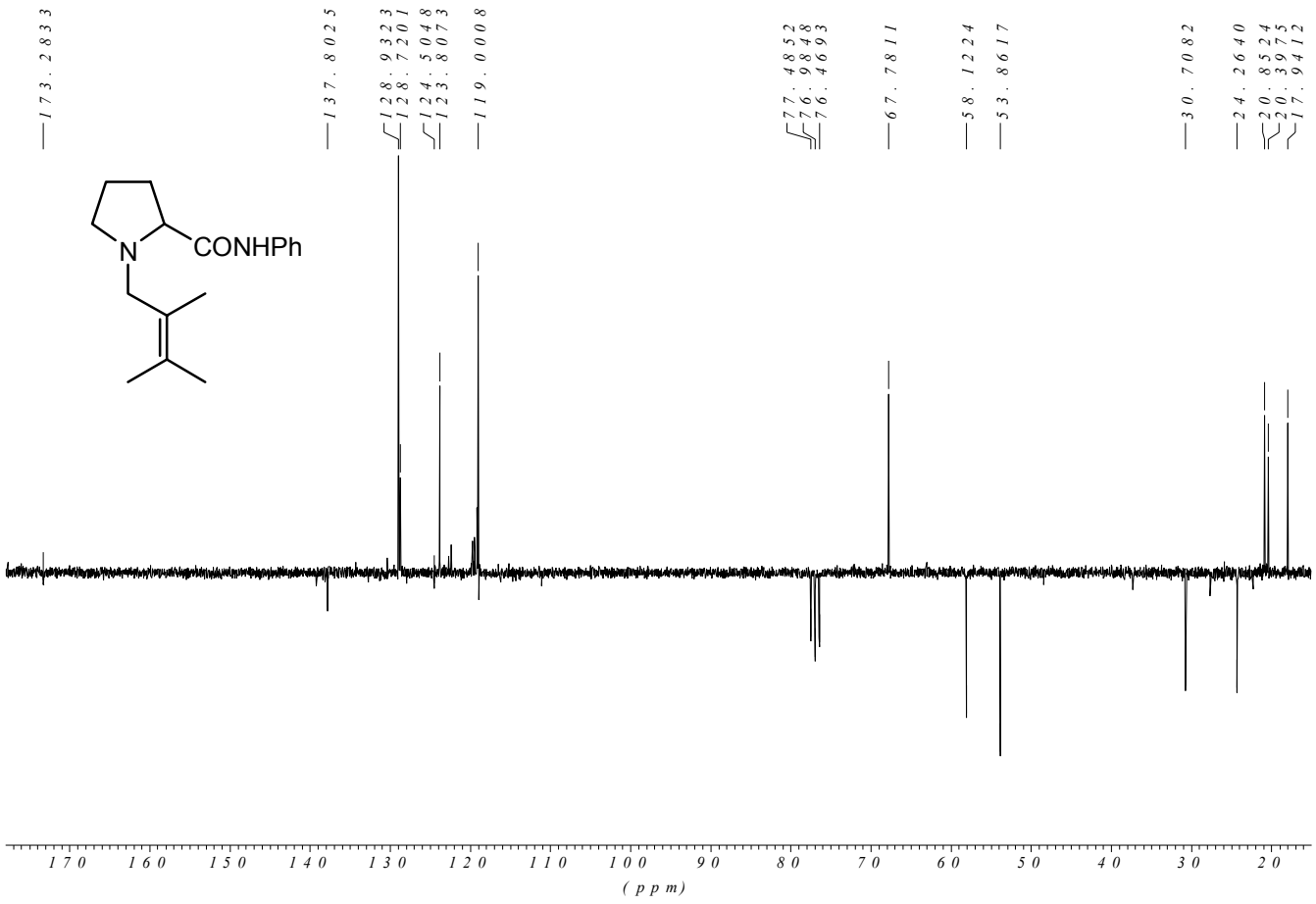
0.957
1.000
1.034
8.071
3.054
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
(ppm)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137.8025
128.9323
128.7201
124.5048
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119.0008
77.4852
76.9848
76.4693
67.7811
58.1224
53.8617
30.7082
24.2640
20.8524
20.3975
17.9412
CONHPh
N
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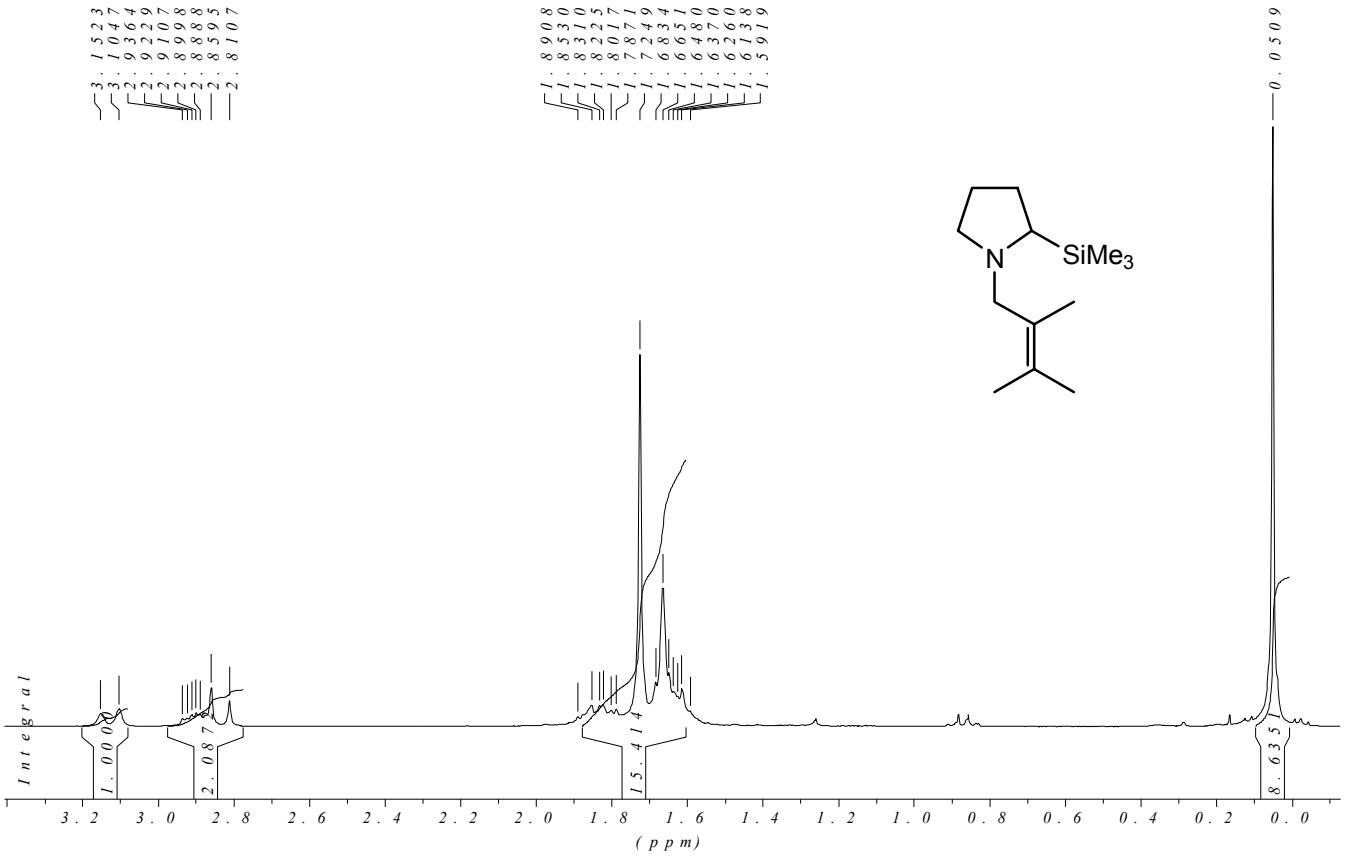
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)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3.1047
2.9364
2.9229
2.9107
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2.8888
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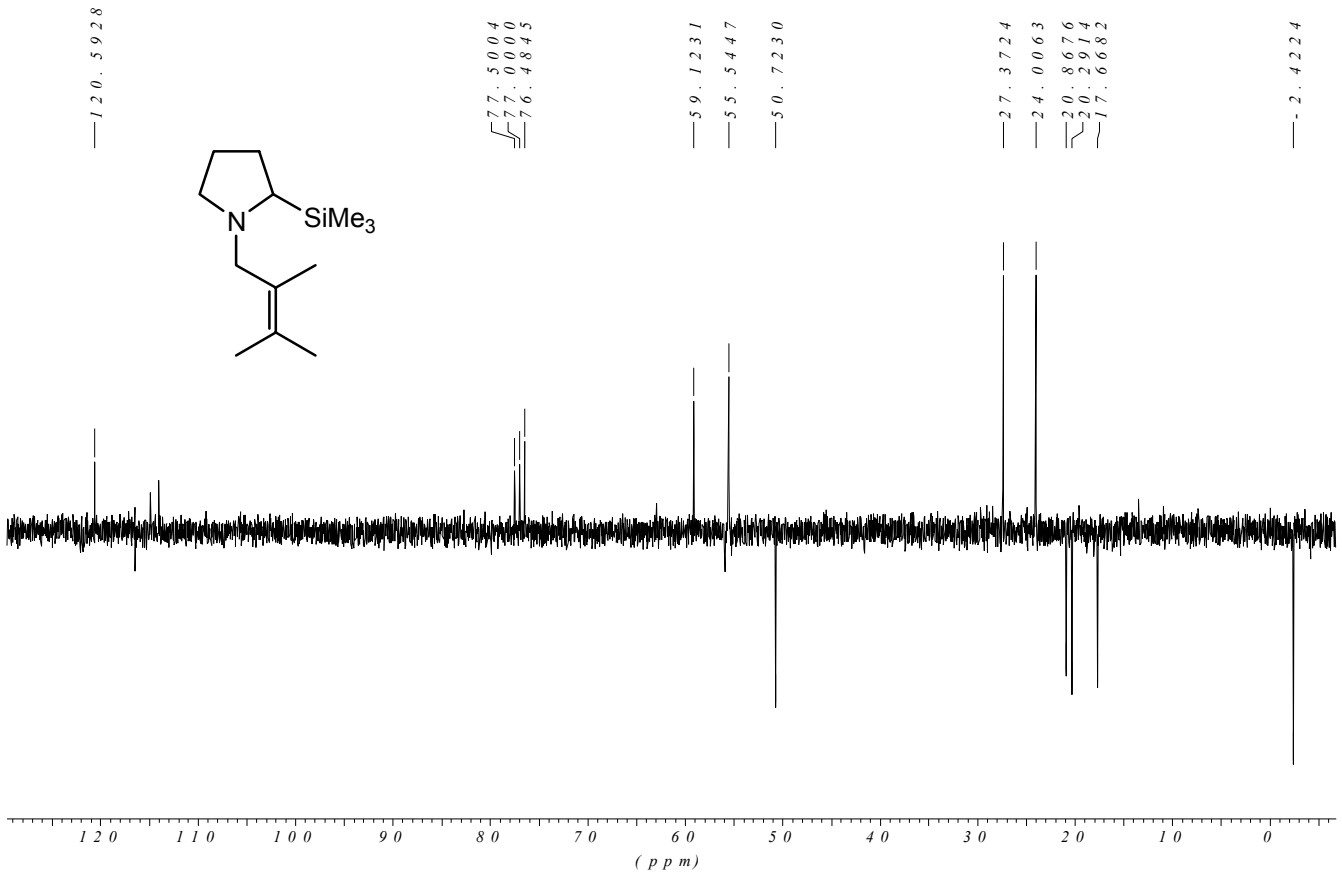
2.8107
1.8908
1.8530
1.8310
1.8225
1.8017
1.7871
1.7249
1.6834
1.6651
1.6480
1.6370
1.6260
1.6138
1.5919
0.0509
N
SiMe3
Integral
1.000
2.087
15.414
8.635
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
(ppm)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77.0000
76.4845
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20.8676
20.2914
17.6682
-2.4224
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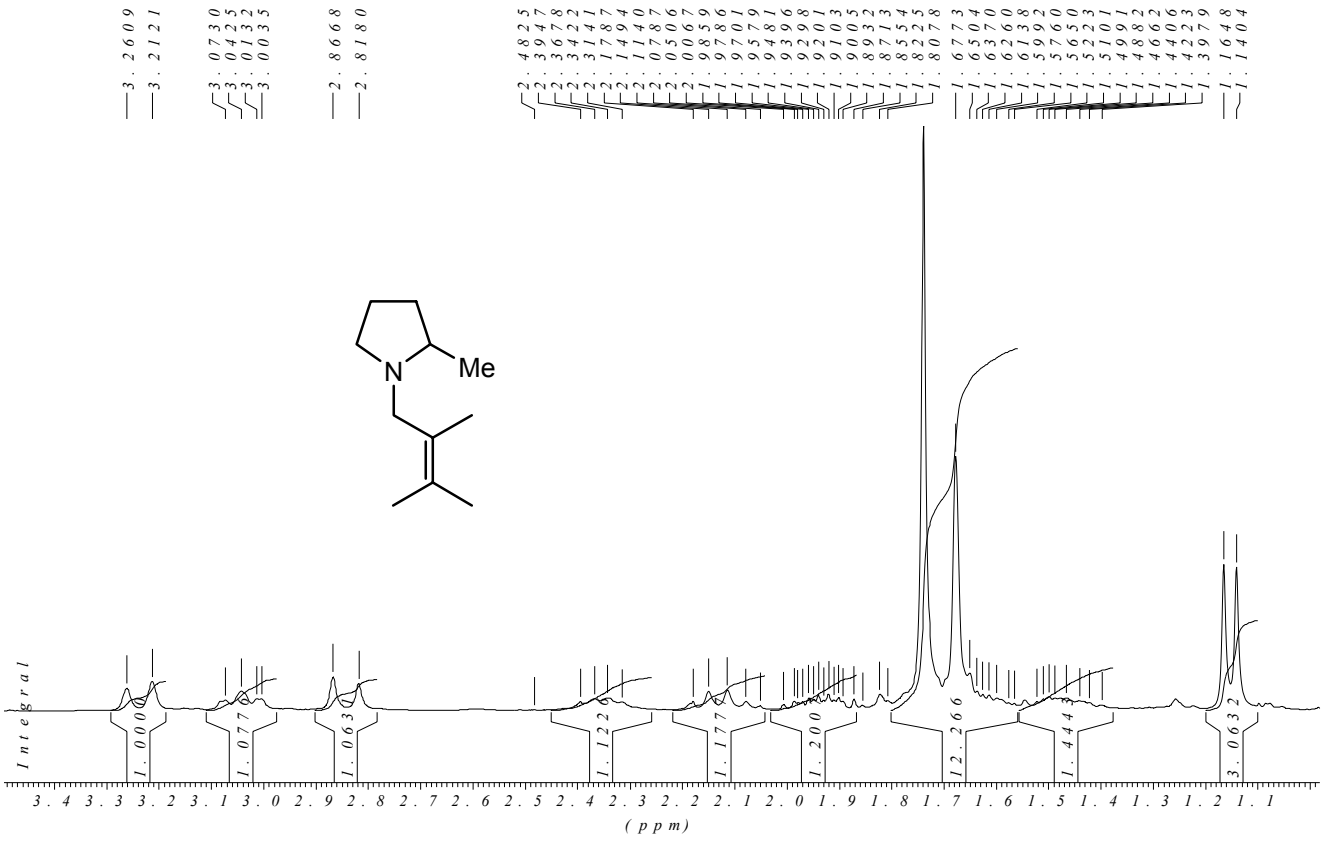
SiMe3
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)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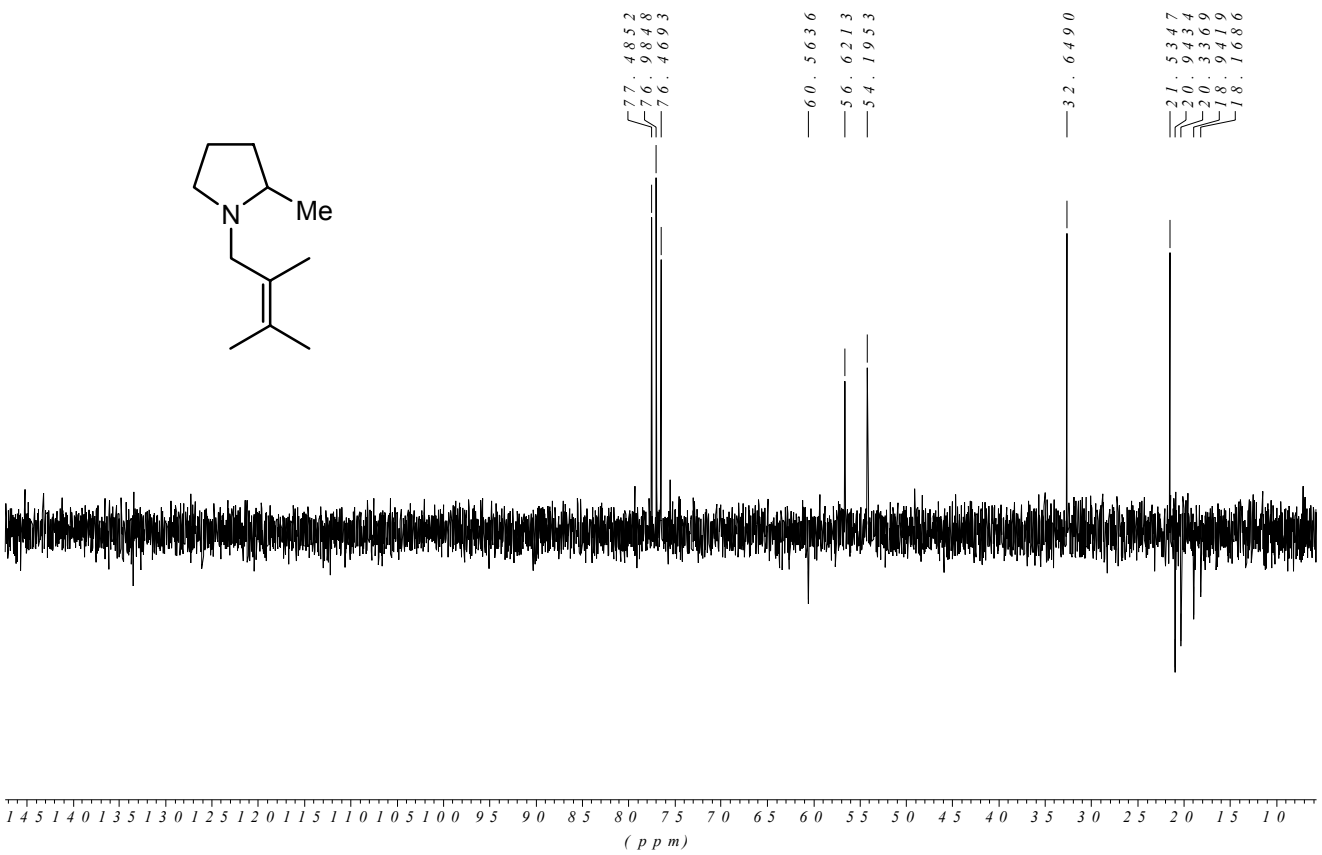
2.3422
2.3141
2.1787
2.1494
2.1140
2.0787
2.0506
2.0067
1.9859
1.9786
1.9701
1.9579
1.9481
1.9396
1.9298
1.9201
1.9103
1.9005
1.8932
1.8713
1.8554
1.8225
1.8078
1.6773
1.6504
1.6370
1.6260
1.6138
1.5992
1.5760
1.5650
1.5223
1.5101
1.4991
1.4882
1.4662
1.4406
1.4223
1.3979
1.1648
1.1404
N
Me
Integral
1.000
1.077
1.063
1.122
1.177
1.200
12.266
1.443
3.063
3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1
(ppm)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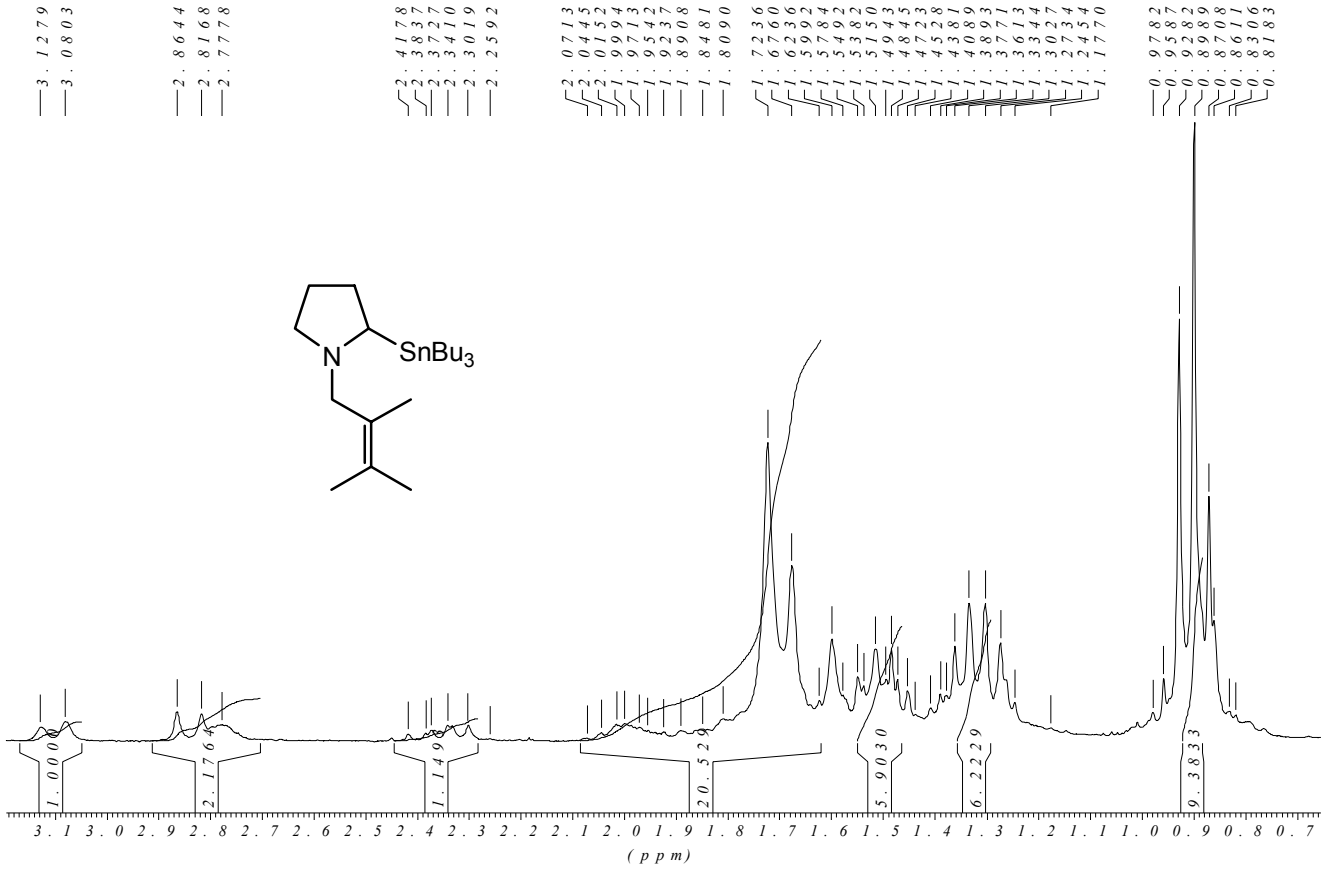
20.9434
20.3369
18.9419
18.1686
N
Me
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
(ppm)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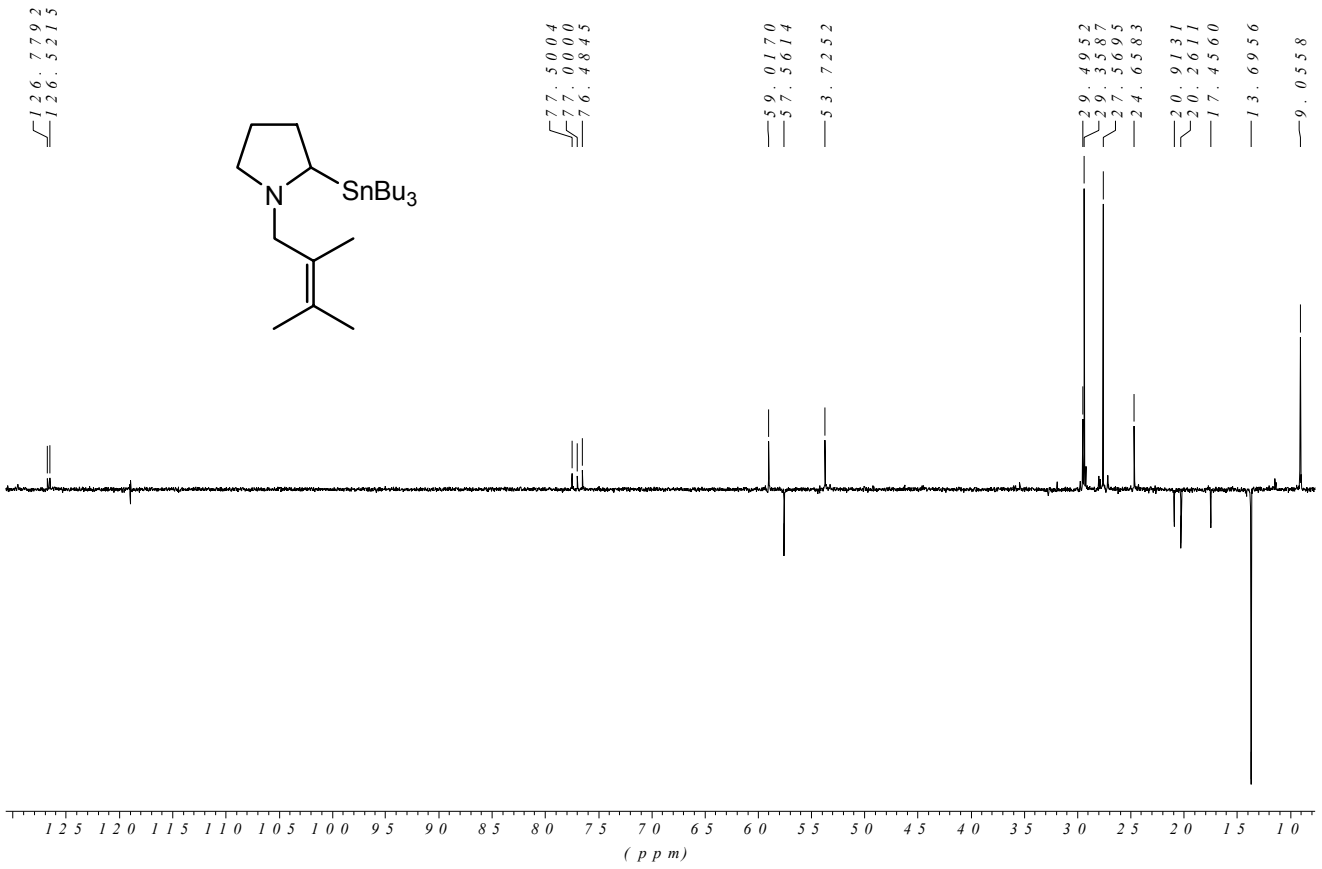
2.0713
2.0445
2.0152
1.9994
1.9713
1.9542
1.9237
1.8908
1.8481
1.8090
1.7236
1.6760
1.6236
1.5992
1.5784
1.5492
1.5382
1.5150
1.4943
1.4845
1.4723
1.4528
1.4381
1.4089
1.3893
1.3771
1.3613
1.3344
1.3027
1.2734
1.2454
1.1770
0.9782
0.9587
0.9282
0.8989
0.8708
0.8611
0.8306
0.8183
SnBu3
N
1.000
2.176
1.149
20.529
5.9030
6.2229
9.3833
3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7
(ppm)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57.5614
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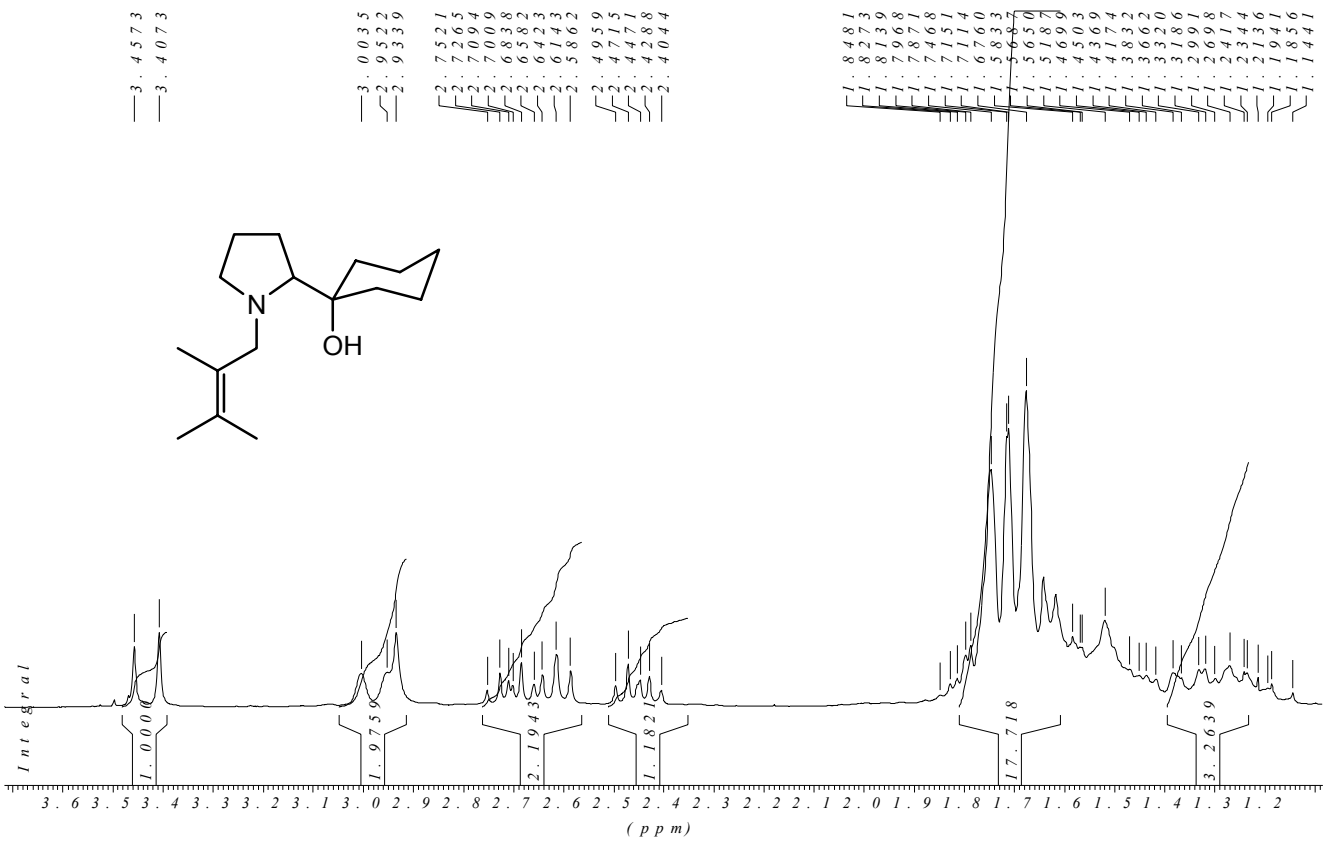
29.4952
29.3587
27.5695
24.6583
20.9131
20.2611
17.4560
13.6956
9.0558
N
SnBu3
125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
(ppm)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2.6423
2.6143
2.5862
2.4959
2.4715
2.4471
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2.4044
1.8481
1.8273
1.8139
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1.5687
1.5650
1.5187
1.4699
1.4503
1.4369
1.4174
1.3832
1.3662
1.3320
1.3186
1.2991
1.2698
1.2417
1.2344
1.2136
1.1941
1.1856
1.1441
N
OH
Integral
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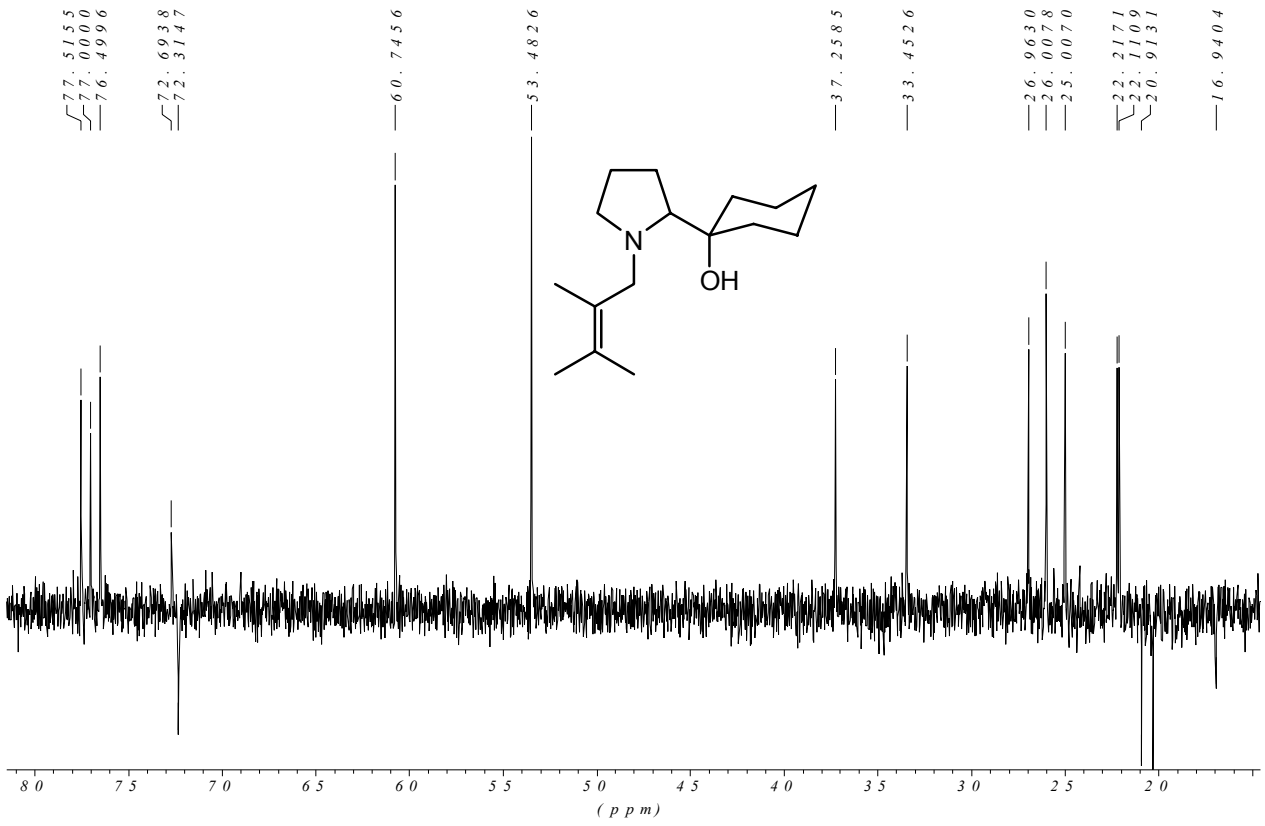
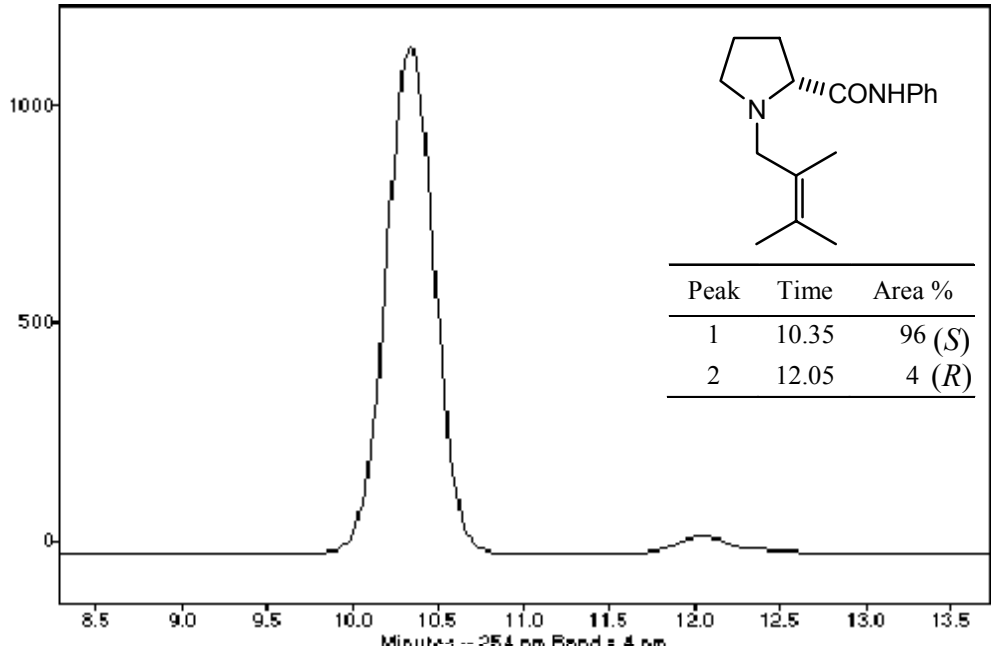
1.975
2.193
1.182
17.718
3.2639
3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2
(ppm)



(Quaternary carbons of alkene observed at 126.9 and 126.8 *ppm*)



Peak	Time	Area %
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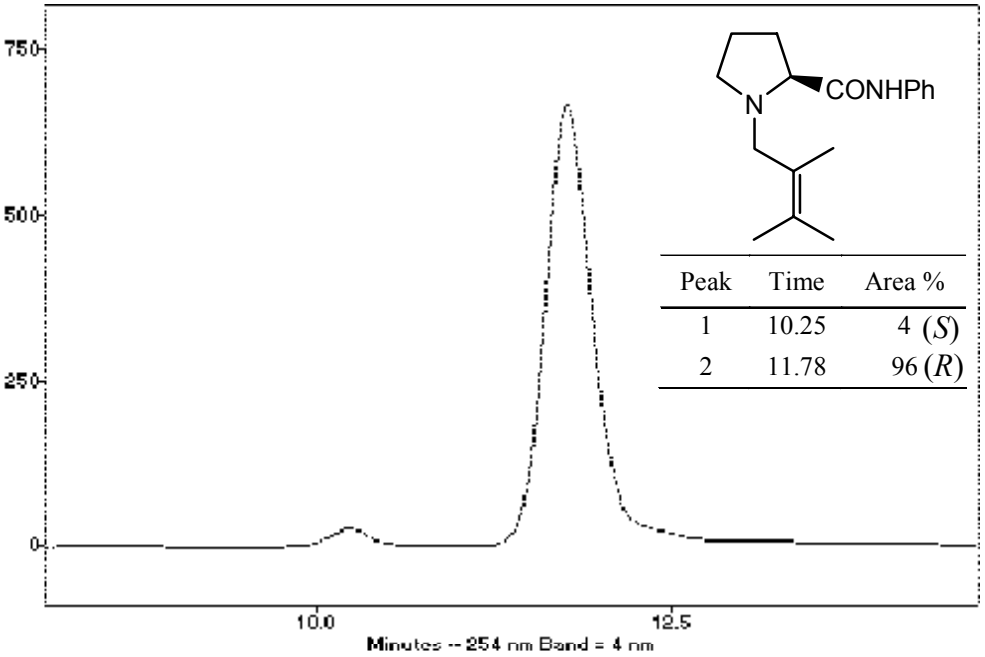
2	12.05	4 (*R*)



Peak	Time	Area %
1	10.25	4 (*S*)
2	11.78	96 (*R*)

Chromatogram

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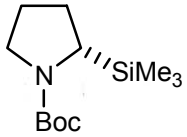
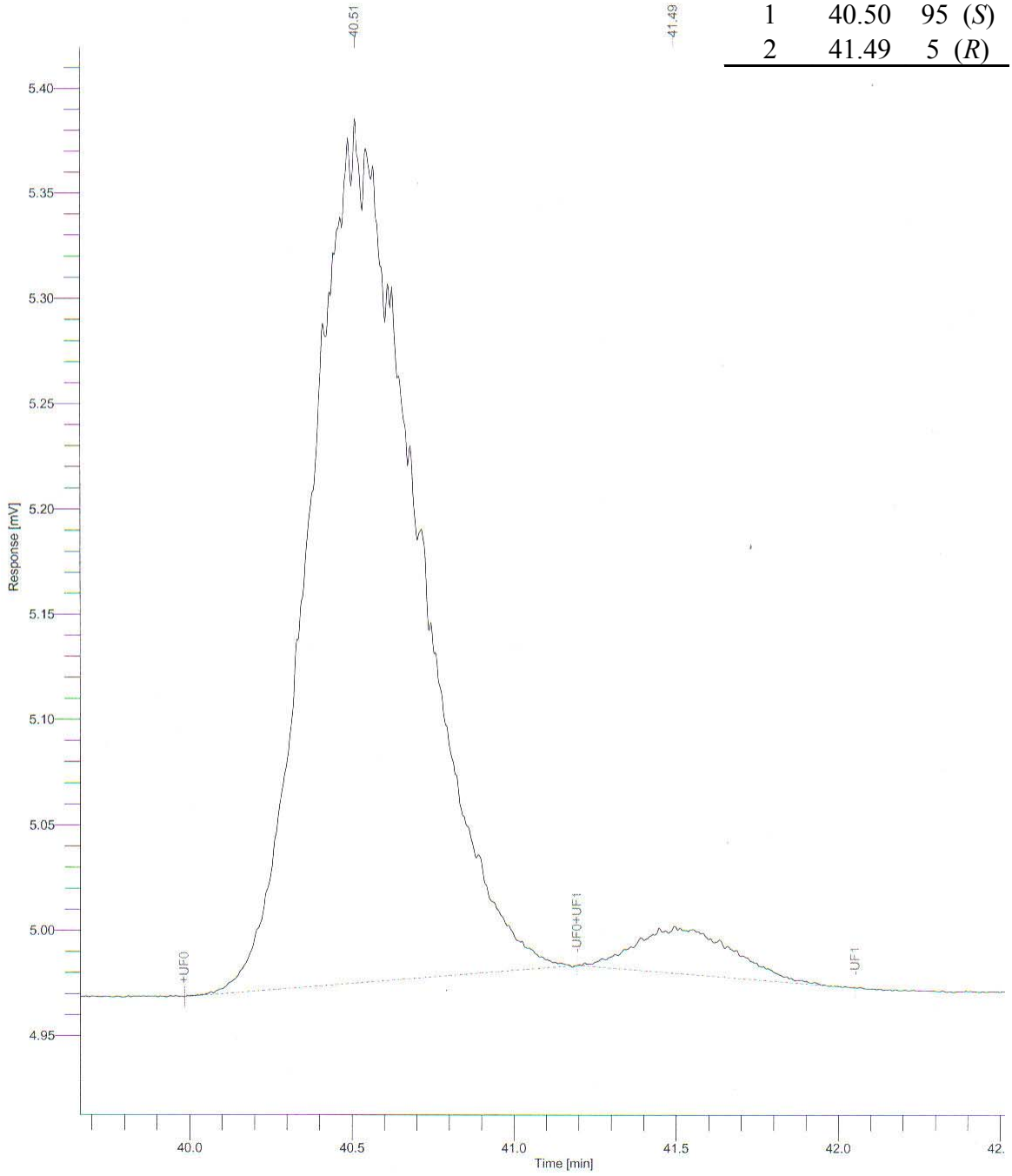
Plot Offset: 4.94 mV Plot Scale: 0.5 mV



Peak	Time	Area %
1	40.50	95 (*S*)
2	41.49	5 (*R*)



Chromatogram

Sample Name : Jingesh-Exp-131 Sample #: 001 Page 1 of 1
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Date : 14/03/2006 15:01:49
Method : Time of Injection: 08/02/2005 12:24:54
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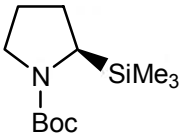
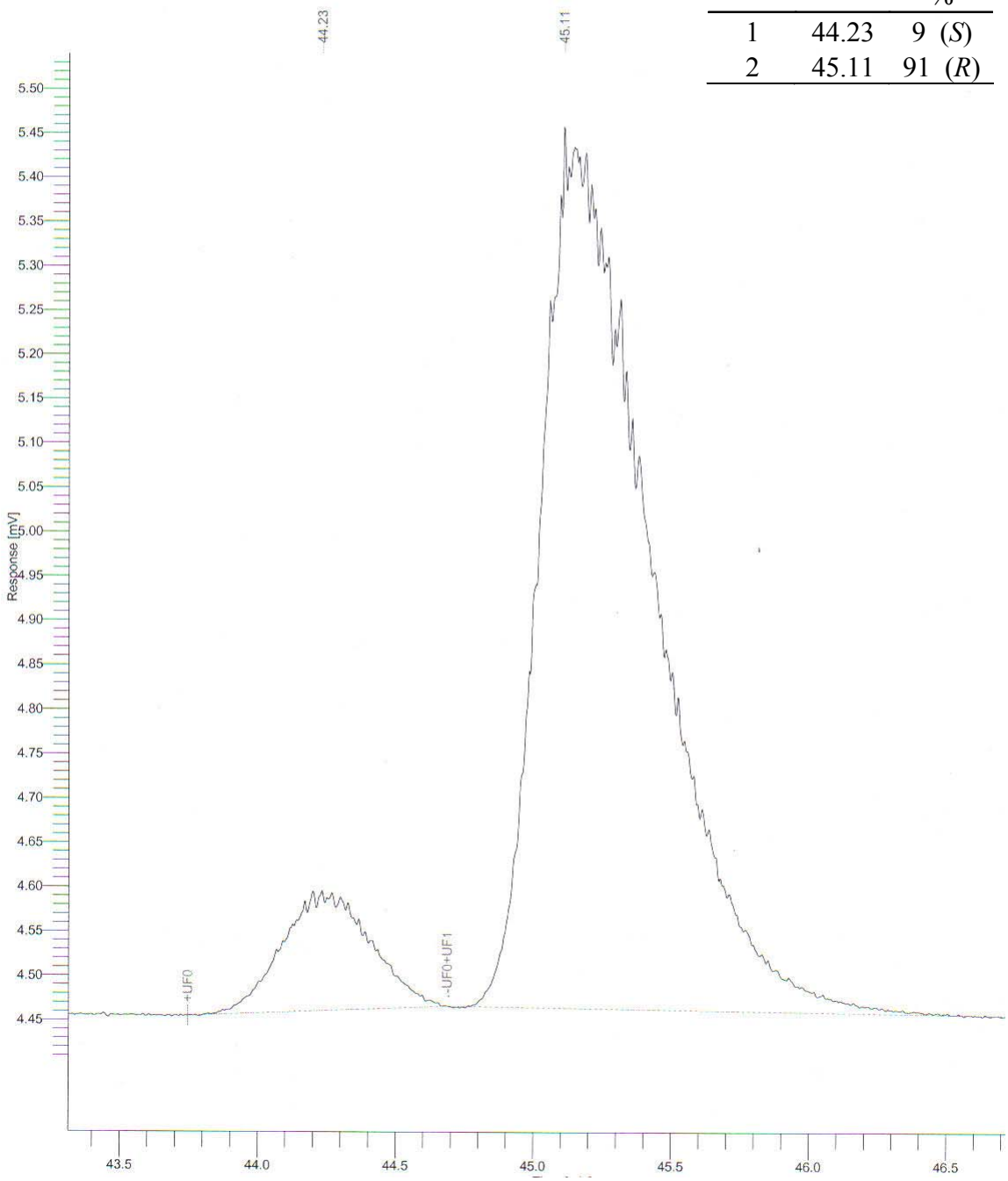
Plot Offset: 4.40 mV Plot Scale: 1.1 mV



Peak	Time	Area %
1	44.23	9 (*S*)
2	45.11	91 (*R*)



Chromatogram

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Method : Time of Injection: 11/17/04 4:40:17 PM
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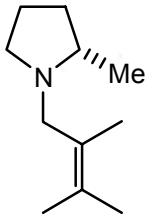
Plot Offset: 4.93 mV Plot Scale: 1.8 mV



Peak	Time	Area %
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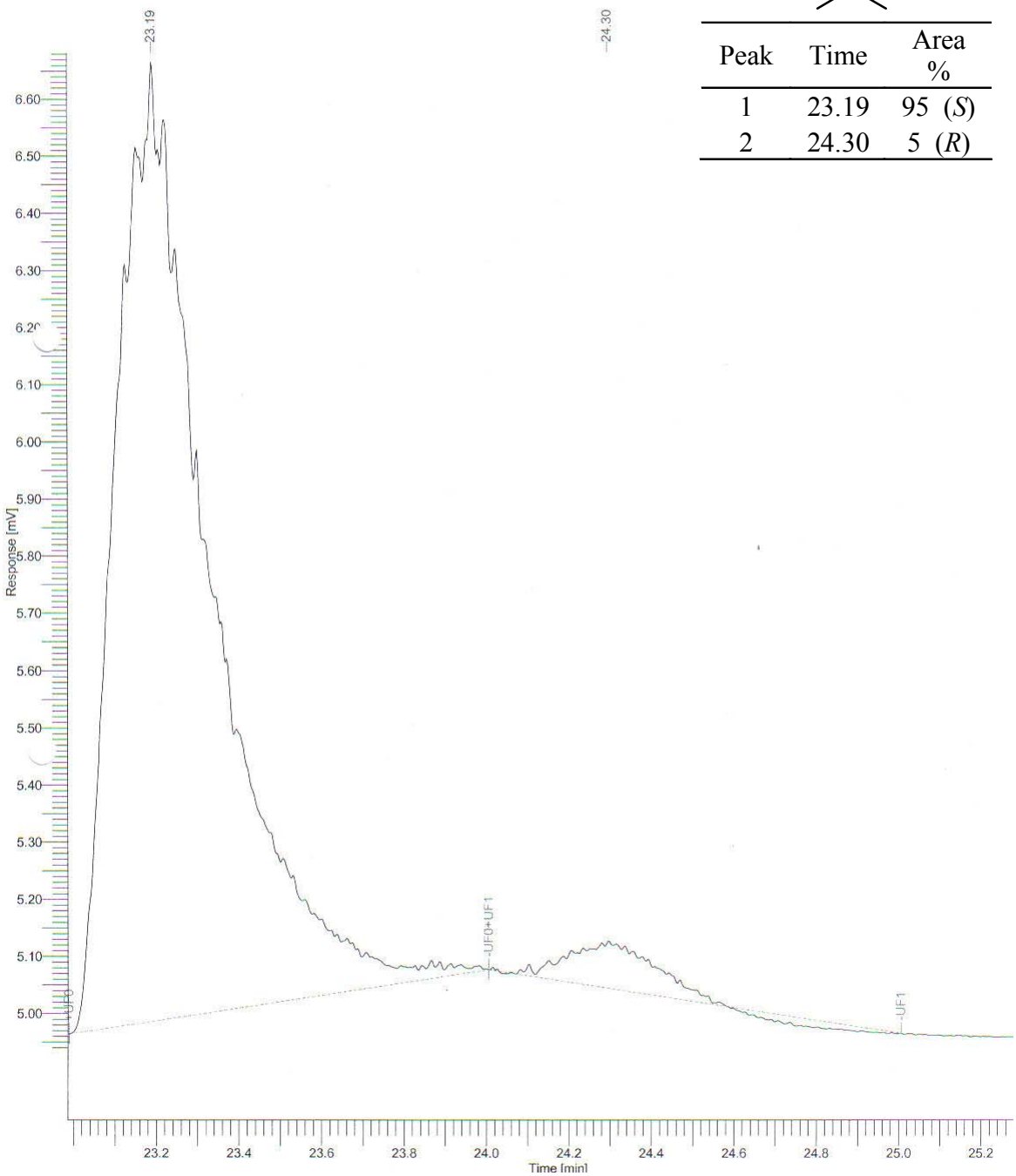
2	24.30	5 (*R*)



Chromatogram

Sample Name : Exp-253 Sample #: 001 Page 1 of 1
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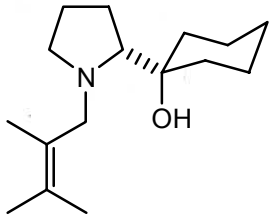
Time of Injection: 11/11/05 2:04:58 PM
Start Time : 35.77 min End Time : 38.12 min Low Point : 4.92 mV High Point : 5.47 mV
Plot Offset: 4.92 mV Plot Scale: 0.5 mV



Peak	Time	Area %
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2	37.10	95 (*R*)