

Supporting Information

for

Stereoselective nucleophilic addition reactions to cyclic *N*-acyliminium ions using the indirect cation pool method: Elucidation of stereoselectivity by spectroscopic conformational analysis and DFT calculations

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Experimental details, ORTEP drawings of **1a**, **1b**, **1d–1f**, theoretical calculations of **C1–C6**, and NMR spectra of all new compounds and **C1–C6**.

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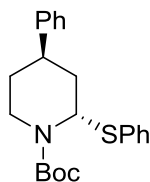
General remarks

GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused silica capillary. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS400 (^1H 400 MHz, ^{13}C 100 MHz), Varian VNMRS-400 (^1H 400 MHz, ^{13}C 100 MHz), Varian VNMRS-600 (^1H 600 MHz, ^{13}C 150 MHz), or JEOL ECA-600P (^1H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or residual CHCl_3 in CDCl_3 (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to residual CDCl_3 (δ 77.0 ppm). IR spectra were measured using a JASCO FT/IR-4100 spectrometer. Thin-layer chromatography (TLC) was carried out on Merck pre-coated silica gel F_{254} plates (thickness 0.25 mm). Flash chromatography was carried out on KANTO CHEMICAL Silica Gel 60N (40–50 μm). All reactions were carried out under Ar atmosphere unless otherwise noted.

Materials

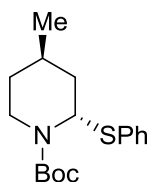
Dichloromethane was washed with water, distilled from P_2O_5 , redistilled from dried K_2CO_3 to remove trace amounts of acid, and stored over molecular sieves 4 Å. Trifluoromethanesulfonic acid was purchased from Tokyo Chemical Industries (TCI) and used without further purification. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was purchased from TCI and dried over P_4O_{10} under reduced pressure. Dry diethyl ether (Et_2O) and tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries. ArSSAr ($\text{Ar} = p\text{-FC}_6\text{H}_4$) was prepared according to the procedure in the literature.¹

Preparation of *N*-acyliminium ion precursors

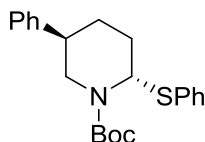


***N*-Boc-*trans*-4-phenyl-2-phenylthiopiperidine (1a).** To a solution of *N*-Boc-4-phenylpiperidine (2.61 g, 10.0 mmol) in dry Et_2O (18 mL) was slowly added TMEDA (1.94 mL, 1.15 g, 13.0 mmol) at -78°C . To this mixture was added dropwise *sec*-BuLi (1.03 M in cyclohexane, 12.6 mL, 13.0 mmol) at the same temperature. The mixture was slowly warmed to -40°C , stirred for 30 min, and then cooled again to -78°C . To this mixture was added dropwise diphenyl disulfide (PhSSPh , 4.37 g, 20.0 mmol) in Et_2O (17 mL). Then the mixture was slowly allowed to warm to room temperature and stirred for 3 h. The reaction mixture was quenched with saturated aqueous NaHCO_3 (20 mL), extracted with Et_2O (3×10 mL). The combined organic phase was dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/ EtOAc 30:1) and subsequent recrystallization from hexane to afford the title compound as a colorless solid (2.52 g, 6.82 mmol, 68% yield); ^1H NMR (600 MHz, CDCl_3) (rotamer) δ 7.57–7.49 (m, 2H), 7.34–7.20 (m, 8H), 6.17 and 5.90 (d, $J = 4.1$ Hz, 1H), 4.22 and 4.00 (d, $J = 13.4$ Hz, 1H), 3.48 (ddd, $J = 2.8, 13.2, 13.2$ Hz, 1H), 3.25 and 3.20 (dddd, $J = 3.4, 3.4, 12.7, 12.7$ Hz, 1H), 2.19 and 2.14 (d, $J = 13.4$ Hz, 1H), 2.08–2.00 (m, 1H), 1.95 and 1.89 (d, $J = 13.0$ Hz, 1H), 1.68 and 1.64 (dddd, $J = 4.5, 12.7, 12.7, 12.7$ Hz, 1H), 1.33 and 1.18 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) (rotamer) δ 153.9 and 153.7, 145.1 and 145.0, 135.1 and 134.1, 133.6 and 133.1, 129.0, 128.8, 128.6, 128.2 and 127.7,

126.8 and 126.5, 80.2 and 80.1, 64.1 and 61.9, 39.6 and 38.6, 38.3 and 37.6, 37.4 and 37.3, 33.0 and 32.9, 28.2 and 27.9; IR (KBr) 2978, 1682, 1412, 1171 cm^{-1} ; HRMS (FAB⁺) calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 370.1841, found: 370.1843. mp 71.9–72.3 °C.

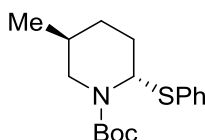


***N*-Boc-*trans*-4-methyl-2-phenylthiopiperidine (1b).** To a solution of 4-methylpiperidine (1.98 g, 20.0 mmol) and DMAP (0.0999 g, 0.818 mmol) in toluene (30 mL) was added slowly $(\text{Boc})_2\text{O}$ (4.59 mL, 4.80 g, 22.0 mmol) at 0 °C. After being stirred at room temperature for 30 min, the reaction was quenched with water. The solvent was removed under reduced pressure. The residue was quickly filtered through a short column of alumina. The combined solution was concentrated to give crude *tert*-butyl 4-methylpiperidinecarboxylate (3.35 g, 12.9 mmol, 65%) which was used directly for the next step. To a solution of *tert*-butyl 4-methylpiperidinecarboxylate (3.35 g, 12.9 mmol) in dry Et_2O (17 mL) was slowly added TMEDA (2.51 mL, 1.95 g, 16.8 mmol) at -78 °C, followed by dropwise addition of *sec*-BuLi (1.02 M in hexane, 16.5 mL, 16.8 mmol) at the same temperature. Then the mixture was slowly warmed to -40 °C, stirred for 30 min, and then cooled again to -78 °C. To this mixture was added dropwise diphenyl disulfide (PhSSPh , 11.3 g, 51.6 mmol) in Et_2O (22 mL). Then the mixture was slowly allowed to warm to room temperature and stirred for 24 h. The reaction mixture was quenched with water (30 mL), extracted with Et_2O (3×30 mL). The combined organic phase was washed with saturated aqueous NaHCO_3 (30 mL), dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/ EtOAc 30:1 to 10:1) to obtain the title compound (9.90 g, 3.22 mmol, 25%) as a colorless solid; ^1H NMR (600 MHz, CDCl_3) δ 7.50–7.47 (m, 2H), 7.29–7.22 (m, 3H), 6.05 and 5.78 (d, $J = 4.2$ Hz, 1H) (rotamer), 4.07 and 3.85 (d, $J = 12.6$ Hz, 1H) (rotamer), 3.33 (ddd, $J = 13.2, 13.2, 2.4$ Hz, 1H), 2.09–1.95 (m, 1H), 1.72 and 1.65 (d, $J = 12.6$ Hz, 1H), 1.51 (ddd, $J = 13.8, 13.2, 6.0$ Hz, 1H), 1.30 and 1.13 (s, 9H) (rotamer), 1.14–1.06 (m, 1H), 0.94–0.92 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 153.7, 139.4, 128.9, 128.0, 79.8, 64.1, 39.6, 38.0, 33.9, 28.2, 27.9, 26.3, 21.9; IR (KBr) 2929, 1698, 1404, 1159, 1088 cm^{-1} ; HRMS (FAB⁺) calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$ 330.1504, found 330.1508; mp 79.9–80.8 °C.

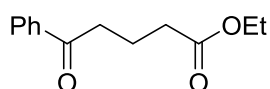


***N*-Boc-*trans*-5-phenyl-2-phenylthiopiperidine (1c).** A solution of 3-phenylpiperidine (1.00 g, 6.2 mmol) and trimethylamine (0.86 mL, 1.0 equiv) in dry THF (6.2 mL) was cooled to 0 °C, and $(\text{Boc})_2\text{O}$ (1.42 mL, 6.2 mmol) was added in portions. The mixture was stirred for 10 min, and warmed to room temperature. After being stirred for 4 h at room temperature, the mixture was diluted with water (5 mL), and extracted with Et_2O (3×10 mL). The combined organic phase was dried over MgSO_4 and the solvent removed to obtain *N*-Boc-3-phenylpiperidine (1.78 g, 6.7 mmol, >98% yield) which was used without further

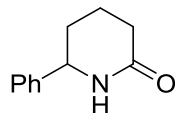
purification. To a solution of *N*-Boc-3-phenylpiperidine (1.98 g, 7.6 mmol) in dry Et₂O (14 mL) was slowly added TMEDA (1.5 mL, 1.15 g, 9.9 mmol) at -78°C followed by dropwise addition of *sec*-BuLi (1.07 M in cyclohexane, 9.3 mL, 9.9 mmol) at the same temperature. The mixture was slowly warmed to -40°C , stirred for 30 min, and then cooled again to -78°C . To this mixture was added dropwise diphenyl disulfide (PhSSPh, 3.34 g, 15.3 mmol) in Et₂O (13 mL). Then the mixture was slowly allowed to warm to room temperature and stirred for 24 h. The reaction mixture was quenched with water (20 mL), extracted with Et₂O (3×10 mL). The combined organic phase was washed with saturated aqueous NaHCO₃ (20 mL), dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc/Et₃N 30:1:0.03) and subsequent recrystallization from hexane to afford the title compound (1.02 g, 2.77 mmol, 41% yield, 2 steps) as a colorless solid; ¹H NMR (400 MHz, CDCl₃) δ 7.53–7.51 (m, 2H), 7.32–7.23 (m, 7H), 7.18–7.12 (t, $J = 7.2$ Hz, 1H), 5.90 (s, 1H), 4.39 (d, $J = 14.0$ Hz), 3.74 (dd, $J = 14.0, 4.4$ Hz, 1H), 3.12 (s, 1H), 2.42 (tt, $J = 13.9$ Hz, 4.7 Hz, 1H), 2.05–1.85 (m, 2H), 1.77 (d, $J = 14.0$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 154.1, 143.3, 134.7, 133.8, 128.9, 128.8, 127.8, 127.6, 126.0, 80.2, 63.1, 41.6, 37.4, 31.8, 28.1, 26.2, 25.8; IR (KBr) 2982, 2882, 1697, 1364, 1169 cm⁻¹, mp 54.3–54.8 $^{\circ}\text{C}$.



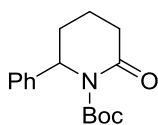
***N*-Boc-*trans*-5-methyl-2-phenylthiopiperidine (1d).** To a solution of 3-methylpiperidine (2.92 mL, 2.48 g, 25.0 mmol) in dry Et₂O (25 mL) was added slowly (Boc)₂O (5.61 mL, 5.33 g, 23.1 mmol) at 0°C . After being stirred at room temperature for 1 h, the reaction was quenched with water. The mixture was extracted with Et₂O (3×20 mL) and the combined organic phase was washed with saturated aqueous NaHCO₃, and drying over MgSO₄. After removal of solvent, *tert*-butyl 3-methylpiperidinecarboxylate (4.56 g, 22.8 mmol, 99%) was obtained. To a solution of *tert*-butyl 3-methylpiperidinecarboxylate (1.99 g, 10.0 mmol) in dry Et₂O (18.5 mL) was slowly added TMEDA (1.95 mL, 1.51 g, 13.0 mmol) at -78°C followed by dropwise addition of *sec*-BuLi (1.07 M in cyclohexane, 12.1 mL, 13.0 mmol) at the same temperature. The mixture was slowly warmed to -40°C , stirred for 30 min, and then cooled again to -78°C . To this mixture was added dropwise diphenyl disulfide (PhSSPh, 6.55 g, 30.0 mmol) in Et₂O (25 mL). Then the mixture was slowly allowed to warm to room temperature and stirred for 24 h. The reaction was quenched with water and extracted with Et₂O. The combined organic phase was washed with saturated aqueous NaHCO₃, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 10:1) and subsequent recrystallization to afford the title compound (1.29 g, 4.20 mmol, 42%) as a colorless solid; ¹H NMR (400 MHz, CDCl₃, 60°C) δ 7.52–7.40 (m, 2H), 7.31–7.15 (m, 3H), 5.89 (s, 1H), 3.70 (d, $J = 14.0$ Hz, 1H), 3.50 (dd, $J = 13.2, 3.2$ Hz, 1H), 2.20–2.12 (m, 2H), 2.20–1.98 (m, 2H), 1.81–1.64 (m, 1H), 1.51–1.34 (m, 1H), 0.98 (d, $J = 6.8$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 60°C) δ 154.6, 134.2, 134.1, 128.8, 127.6, 79.7, 62.9, 43.8, 28.2, 27.7, 25.7, 25.6, 16.3; IR (KBr) 2970, 1683, 1408, 862, 754 cm⁻¹; HRMS (FAB⁺) calcd for C₁₇H₂₅NO₂SNa [M + Na]⁺ 330.1500, found 330.1504, mp 79.9–80.8 $^{\circ}\text{C}$.



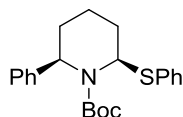
Ethyl 5-oxo-5-phenylpentanoate (S1).² A mixture of glutaric anhydride (3.42 g, 30.0 mmol) and Fe(acac)₃ (0.32 g, 0.90 mmol, 3 mol %) and dry THF (36.0 mL) was cooled to 0 °C, and PhMgBr (1.1 M in THF, 25.9 mL, 28.5 mmol) was added over a period of 60 min with the aid of syringe pump. The reaction mixture was stirred overnight at the same temperature. Then the mixture was acidified with 2 M HCl aqueous solution (20 mL) and extracted with Et₂O (3 × 10 mL). The combined organic phase was extracted with a 1 M aqueous NaOH solution (3 × 15 mL), discarding the organic layer. The combined aqueous basic phase was acidified with 2 M aqueous HCl in order to obtain pH around 1, and this mixture was extracted with Et₂O (3 × 20 mL). The combined organic phase was dried over MgSO₄. After removal of solvent, the crude (5.0 mmol) was dissolved in EtOH (25.0 mL), concentrated H₂SO₄ (0.79 mL, 15.0 mmol) was added at room temperature, and then the reaction mixture was refluxed overnight. After evaporation of the solvent, H₂O (10 mL) was added, and the mixture was neutralized with a 2 M aqueous NaOH solution (5 mL) and extracted with Et₂O (3 × 20 mL). The combined organic phase was dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 10:1) to afford **S1** (2.2158 g, 2.45 mmol, 49% yield, 2 steps) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.95 (m, 2H), 7.54 (m, 1H), 7.50–7.37 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.06 (quin, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.4, 173.2, 136.8, 133.0, 128.5, 130.0, 60.3, 37.4, 33.3, 19.3, 14.1; IR (neat) 2974, 1680, 1416, 1366, 1169 cm⁻¹.



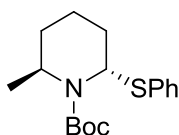
6-Phenyl-2-piperidone (S2).³ A mixture of **S1** (2.78 g, 12.6 mmol), HCO₂NH₄ (2.39 g, 37.8 mmol), AcOH (0.72 mL, 12.6 mmol), and chloro[*N*-[4-(dimethylamino)phenyl]-2-pyridinecarboxamidato](pentamethylcyclopentadienyl)iridium(III) (15.1 mg, 0.025 mmol, 0.2 mol %) in CH₂Cl₂ (126 mL) was heated to 60 °C. After being stirred at 60 °C for 8 h, the mixture was quenched by saturated aqueous NaHCO₃ (20 mL), and extracted with CH₂Cl₂ (3 × 20 mL). To the combined organic phase was added TsOH·H₂O (0.60 g, 2.9 mmol) at room temperature, and then the mixture was stirred overnight. The reaction mixture was quenched by saturated aqueous NaHCO₃ (20 mL), and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phase was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by filtration to afford **S2** (1.77 g, 10.1 mmol, 80% yield, 2 steps) as a colorless solid: ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.29 (m, 2H), 7.29–7.16 (m, 3H), 5.94 (brs, 1H), 4.51 (dd, *J* = 8.7, 4.6 Hz, 1H), 2.53–2.29 (m, 2H), 2.17–1.99 (m, 1H), 1.97–1.82 (m, 1H), 1.82–1.71 (m, 1H), 1.70–1.56 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 172.2, 142.5, 128.8, 127.9, 126.0, 57.7, 32.1, 31.2, 19.6; IR (KBr) 3065, 1645, 1402, 1306, 1150 cm⁻¹.



***N*-Boc-6-phenyl-2-piperidone (S3).**³ To a solution of **S2** (1.76 g, 10.1 mmol) in dry tetrahydrofuran (100 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 12.5 mL, 20.0 mmol) at $-78\text{ }^{\circ}\text{C}$. After 10 min, a solution of (Boc)₂O (4.6 mL, 20.0 mmol) in tetrahydrofuran (40 mL) was transferred via syringe. After stirring at $-78\text{ }^{\circ}\text{C}$ for 2 h, the reaction mixture was quenched with saturated aqueous NH₄Cl (20 mL). The reaction mixture was extracted with Et₂O (3 $\times$ 20 mL). The combined organic phase was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 3:1) to afford **S3** (2.6635 g, 9.7 mmol, 96% yield) as a colorless solid: ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.28–7.23 (m, 1H), 7.23–7.15 (m, 2H), 5.20 (t, *J* = 5.3 Hz, 1H), 2.70–2.49 (m, 2H), 2.23–2.08 (m, 1H), 1.99–1.82 (m, 1H), 1.82–1.62 (m, 2H), 1.29–1.16 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 151.9, 142.5, 128.5, 127.2, 125.7, 82.9, 60.7, 34.5, 3.6, 27.5, 17.4; IR (KBr) 3049, 1757, 1668, 1296, 1142 cm⁻¹.



***N*-Boc-*cis*-6-phenyl-2-phenylthiopiperidine (1e).**^{4,5} To a solution of **S3** (0.5509 g, 2.0 mmol) in dry THF (4 mL) was added dropwise DIBAL (1.0 M in hexane, 3.0 mL, 3.0 mmol) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 2 h and then quenched with a saturated potassium acetate solution (4.0 mL) at $-78\text{ }^{\circ}\text{C}$. To the mixture was added saturated NH₄Cl/ether 1:3 (30 mL). The solution was warmed to room temperature and stirred until a thick white gel formed at the bottom, and the mixture was then filtered through a Celite. The aqueous layer was extracted with Et₂O (3 $\times$ 10 mL), and the combined organic phase was washed with saturated aqueous NH₄Cl (10 mL) and dried over MgSO₄, and concentrated under reduced pressure to afford crude intermediate, which was used directly in the next step. The solution of a mixture of the crude (2.0 mmol), thiophenol (2.0 mL, 20.0 mmol, 10.0 equiv), *p*-toluenesulfonate acid monohydrate (50.2 mg, 0.2 mmol, 0.1 equiv), PPTS (38.2 mg, 0.2 mmol, 0.1 equiv) in anhydrous CH₂Cl₂ (2.0 mL) was stirred at room temperature for 24 h. The reaction was quenched with 3 M aqueous NaOH solution (1 mL) and the mixture was extracted with CH₂Cl₂ (3 $\times$ 10 mL). The combined organic phase was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc/Et₃N 30:1:0.03) and subsequent recrystallization to afford **1e** (0.18 g, 0.50 mmol, 25% yield, 2 steps) as a colorless solid: ¹H NMR (400 MHz, CDCl₃) δ 7.53–7.53 (m, 2H), 7.32–7.23 (m, 7H), 7.18–7.12 (m, 1H), 6.06 and 5.82 (s, 1H) (rotamer), 5.29 and 4.98 (t, *J* = 4.8 Hz, 1H) (rotamer), 2.59–2.36 (m, 1H), 2.24–2.08 (m, 1H), 2.08–1.80 (m, 3H), 1.72–1.57 (m, 1H), 1.39 and 1.17 (s, 9H) (rotamer); ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 144.4 and 142.6 (rotamer), 136.0 and 135.5 (rotamer), 133.6 and 133.0 (rotamer), 128.9 and 128.7 (rotamer), 128.1 and 128.1 (rotamer), 127.3 and 127.0 (rotamer), 126.6, 126.2, 125.5, 80.7, 64.3 and 62.0 (rotamer), 55.7 and 53.6 (rotamer), 30.9 and 29.4 (rotamer), 27.8, 15.9 and 14.5 (rotamer); IR (KBr) 2968, 1688, 1481, 1366, 1161 cm⁻¹; HRMS (ESI⁺) calcd for C₂₂H₂₈NO₂S [M + H]⁺ 302.2115, found 302.2114, mp 68.9–69.4 $^{\circ}\text{C}$.



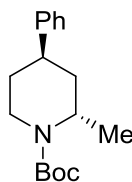
***N*-Boc-*trans*-6-methyl-2-phenylthiopiperidine (1f).** To a solution of 2-methylpiperidine (5.86 mL, 4.96 g, 50.0 mmol) in dry Et₂O (50 mL) was added slowly (Boc)₂O (11.0 mL, 10.5 g, 48.0 mmol) at 0 °C. After being stirred at room temperature for 1 h, the reaction was quenched with water. The mixture was extracted with Et₂O (3 × 20 mL) and the combined organic phase was washed with saturated aqueous NaHCO₃ and dried over MgSO₄. After removal of solvent, *tert*-butyl 2-methylpiperidinecarboxylate (9.00 g, 45.0 mmol, 94%) was obtained. To a solution of *tert*-butyl 2-methylpiperidinecarboxylate (1.99 g, 10.0 mmol) in dry Et₂O (18.5 mL) was slowly added TMEDA (1.95 mL, 1.51 g, 13.0 mmol) at –78 °C followed by dropwise addition of *sec*-BuLi (1.07 M in cyclohexane, 12.1 mL, 13.0 mmol) at the same temperature. The mixture was slowly warmed to –40 °C, stirred for 30 min, and then cooled again to –78 °C. To this mixture was added dropwise diphenyl disulfide (PhSSPh) (4.36 g, 20.0 mmol) in Et₂O (16.7 mL). Then the mixture was slowly allowed to warm to room temperature and stirred for 24 h. The reaction was quenched with water and extracted with ether. The combined organic phase was washed with saturated aqueous NaHCO₃, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 10/1) and subsequent recrystallization to afford the title compound (1.73 g, 5.64 mmol, 56%) as a colorless solid; ¹H NMR (400 MHz, CDCl₃, 60 °C) δ 7.54 (d, *J* = 7.2, Hz, 2H), 7.36–7.16 (m, 3H), 5.74 (brs, 1H), 4.39–4.25 (m, 1H), 2.13 (qt, *J* = 13.3, 4.2 Hz, 1H), 1.96 (dt, *J* = 13.7, 1.6, 1H), 1.84–1.56, (m, 2H), 1.56–1.33, (m, 14H); ¹³C NMR (100 MHz, CDCl₃, 60 °C) δ 154.4, 136.2, 133.4, 128.9, 127.3, 80.2, 63.0, 46.7, 31.2, 30.1, 28.4, 19.9, 14.4; IR (KBr) 2943, 1699, 1087, 752, 478 cm^{–1}; HRMS (FAB⁺) calcd for C₁₇H₂₆NO₂S [M + H]⁺ 308.1684, found 308.1709, mp 56.3–57.0 °C.

Electrochemical generation and accumulation of ArS(ArSSAr)⁺ (Ar = *p*-FC₆H₄). Analogous as described in our previous report.⁶ The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mmHg for 1 h before use) and a platinum plate cathode (40 mm × 20 mm). In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-FC₆H₄) (101.9 mg, 0.401 mmol) in 0.3 M Bu₄NBF₄/CH₂Cl₂ (8.0 mL). In the cathodic chamber were placed 0.3 M Bu₄NBF₄/CH₂Cl₂ (8.0 mL) and trifluoromethanesulfonic acid (41.0 mg, 0.273 mmol). The constant current electrolysis (8 mA) was carried out at –78 °C with magnetic stirring until 0.67 F/mol of electricity was consumed. The solution of ArS(ArSSAr)⁺ (0.0377 M at –80 °C) thus obtained was used for the subsequent reaction.

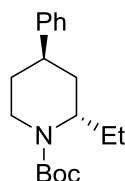
Generation of *N*-acyliminium ions and reactions with carbon nucleophiles

Typical procedure of the indirect cation pool method. To a solution of a cation precursor (0.150 mmol) in 0.3 M Bu₄NBF₄/CH₂Cl₂ (1.0 mL) was added a solution of ArS(ArSSAr)⁺ (0.0377 M, 5.0 mL, 0.189 mmol) at –78 °C and the reaction mixture was stirred for 10 min. To the “cation pool” thus generated, was added the corresponding nucleophile at –78 °C and the reaction mixture was stirred for 5 min and immediately quenched by the addition of Et₃N (1 mL) at the same temperature. Then the mixture was warmed to room temperature and the solvent was removed under reduced pressure. The residue was quickly filtered through a

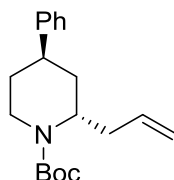
short column (2 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with Et_2O (50 mL). The combined solution was concentrated to give the crude product, which was purified by flash chromatography.



***N*-Boc-*trans*-2-methyl-4-phenylpiperidine (2aa).** Prepared from **1a** (57.5 mg, 0.156 mmol) and trimethylaluminum (1.08 M in toluene, 0.722 ml, 0.156 mmol) following the typical procedure; isolated yield 85% (colorless oil, 36.6 mg, 0.132 mmol, purified with flash chromatography, hexane/EtOAc = 20/1); ^1H NMR (600 MHz, CDCl_3) δ 7.23–7.20 (m, 1H), 4.62 and 4.47 (s, 1H), (rotamer), 4.14 and 4.02 (d, J = 13.2 Hz, 1H) (rotamer), 3.18–2.92 (m, 1H), 2.89 (dd, J = 12.8, 12.4 Hz, 1H), 1.83 (ddd, J = 12.8, 9.6, 5.6 Hz, 2H), 1.74–1.68 (m, 1H), 1.64–1.50 (m, 1H), 1.49 (s, 9H), 1.23 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0 and 154.7 (rotamer), 145.8, 128.4, 126.8, 126.2, 79.2, 46.9 and 45.5 (rotamer), 39.3 and 38.3 (rotamer), 38.0 and 37.7 (rotamer), 33.3 and 33.0 (rotamer), 16.2 and 15.9 (rotamer); IR (neat) 2973, 1690, 1411, 1167, 699 cm^{-1} ; Anal Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2$ C, 74.14; H, 9.15; O, 5.09. Found C, 74.34; H, 8.92; O, 4.95.

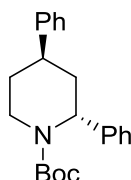


***N*-Boc-*trans*-2-ethyl-4-phenylpiperidine (2ab).** Prepared from **1a** (55.1 mg, 0.149 mmol) and diethyl zinc (1.0 M in hexane, 0.450 ml, 0.450 mmol) following the typical procedure; isolated yield 89% (colorless oil, 38.6 mg, 0.135 mmol, purified with flash chromatography, hexane/EtOAc = 20/1); ^1H NMR (600 MHz, CDCl_3) δ 7.32–7.29 (m, 2H), 7.22–7.19 (m, 3H), 4.37–4.04 (m, 2H), (rotamer), 2.98–2.82 (m, 2H), 1.85–1.74 (m, 4H), 1.62–1.52 (m, 2H), 1.49 (s, 9H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.9, 128.5, 126.8, 126.3, 79.2 and 79.1 (rotamer), 39.5, 38.2, 36.8, 36.3 and 35.3 (rotamer), 33.4 and 33.1 (rotamer), 28.4, 23.3 and 22.8 (rotamer), 11.0 and 10.8 (rotamer); IR (neat) 2927, 1689, 1417, 1163, 1074 cm^{-1} ; Anal Calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2$ C, 74.70; H, 9.40; N, 4.84. Found C, 74.36; H, 9.64; N, 4.76.

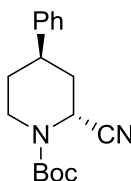


***N*-Boc-*trans*-2-allyl-4-phenylpiperidine (2ac).** Prepared from **1a** (55.4 mg, 0.150 mmol) and (allyl)tributyltin (115 μL , 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield >99% (colorless oil, 43.7 mg, 0.144 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.28 (m, 2H), 7.24–7.16 (m, 3H), 5.87–5.70 (m, 1H), 5.10 (dd, J = 17.4, 1.4 Hz, 1H), 5.04 (d, J = 10.1 Hz, 1H), 4.53 and 4.36 (dddm, J = 6.4, 6.4, 6.4 Hz, 1H) (rotamer), 4.21 and 4.05 (dm, J =

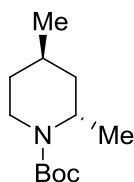
12.8 Hz, 1H) (rotamer), 3.05–2.81 (m, 2H), 2.56–2.44 (m, 1H), 2.43–2.26 (m, 1H), 1.92–1.69 (m, 3H), 1.69–1.56 (m, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0 and 154.9 (rotamer), 145.7, 135.4 and 135.3 (rotamer), 128.5, 126.8, 126.3, 117.0 and 116.7 (rotamer), 79.4 and 79.3 (rotamer), 50.9 and 49.6 (rotamer), 39.6 and 38.5 (rotamer), 36.6, 35.7, 35.0 and 34.6 (rotamer), 33.1 and 32.9 (rotamer), 28.4; IR (neat) 2982, 2066, 1705, 1418, 1167 cm^{-1} ; HRMS (FAB^+) m/z calcd for $\text{C}_{19}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 302.2120, found 302.2124.



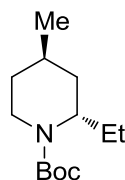
***N*-Boc-*trans*-2,4-diphenylpiperidine (2ad).** Prepared from **1a** (55.1 mg, 0.149 mmol) and PhMgBr (1.0 M in Et_2O , 300 μL , 0.300 mmol, 2.0 equiv) following the typical procedure. Isolated yield 87% (colorless solid, 44.0 mg, 0.130 mmol, purified with flash chromatography, hexane/ EtOAc = 20/1); ^1H NMR (500 MHz, CDCl_3) δ 7.39 (t, J = 7.5 Hz, 2H), 7.35–7.26 (5H), 7.23–7.20 (m, 3H), 5.71 and 5.55 (brs, 1H) (rotamer), 4.29 and 4.15 (brs, 1H) (rotamer), 2.93 (brs, 1H), 2.73 (brs, 1H), 2.56 (brs, 1H), 2.09 (ddd, J = 13.5, 13.0, 3.3 Hz 1H), 1.74 (br, 2H), 1.62–1.35 (m, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.7, 128.7, 128.5, 126.7, 126.5, 126.4, 79.8, 53.9 and 52.5 (rotamer), 40.8 and 39.7 (rotamer), 37.1 and 36.9 (rotamer), 35.7 and 35.1 (rotamer), 33.4 and 33.0 (rotamer), 28.5 and 28.4 (rotamer); IR (neat) 2959, 1701, 1457, 1377, 724 cm^{-1} ; Anal Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_2$ C, 78.30; H, 8.06; N, 4.15. Found C, 78.03; H, 8.39; N, 4.17, mp 68.1–68.7 $^\circ\text{C}$.



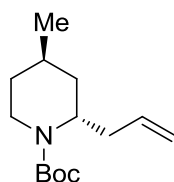
***N*-Boc-*trans*-2-cyano-4-phenylpiperidine (2ae).** Prepared from **1a** (111 mg, 0.301 mmol) and trimethylsilylcyanide (149 mg, 0.188 ml, 1.50 mmol) following the typical procedure. Isolated yield 99% (colorless oil, 85.2 mg, 0.299 mmol, purified by flash chromatography, hexane/ EtOAc = 20/1); ^1H NMR (600 MHz, CDCl_3) δ 7.35–7.32 (m, 2H), 7.27–7.24 (m, 1H), 7.23–7.20 (m, 2H), 5.46 and 5.28 (s, 1H) (rotamer), 4.33–4.15 (m, 1H), 3.23–3.05 (m, 1H), 3.02 (dd, J = 12.6, 12.0 Hz, 1H), 2.12 and 2.10 (d, J = 13.2 Hz, 1H) (rotamer), 1.90 (ddd, J = 13.2, 13.2, 5.4 Hz, 1H), 1.65 (dddd, J = 12.6, 12.6, 4.8, 4.2 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 153.8, 143.6, 128.7, 126.9, 126.7, 81.7, 43.9, 41.8, 38.5, 35.4, 32.1, 28.2; IR (neat) 2977, 1698, 1393, 1024, 700 cm^{-1} ; Anal Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$ C, 71.30; H, 7.74; N, 9.76. Found C, 71.61; H, 7.84; N, 9.78.



***N*-Boc-*trans*-2,4-dimethylpiperidine (2ba).** Prepared from **1b** (46.4 mg, 0.151 mmol) and trimethylaluminum (1.08 M in toluene, 0.722 ml, 0.156 mmol) following the typical procedure. Isolated yield 86% (colorless oil, 27.5 mg, 0.129 mmol, purified with flash chromatography, hexane/EtOAc = 20/1); ^1H NMR (400 MHz, CDCl_3) δ 4.39 (brs, 1H), 3.92 (brs, 1H), 2.82 (t, J = 13.0 Hz, 1H), 1.80–1.63 (m, 1H), 1.52–1.41 (m, 12H), 1.26 (td, J = 12.8, 5.6 Hz, 1H), 1.11 (d, J = 6.8 Hz, 3H), 1.01 (qd, J = 13.3, 4.4 Hz, 1H), 0.89 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 154.6, 79.0, 46.5, 39.1, 38.8, 34.4, 28.6, 25.1, 22.2, 16.3; IR (neat) 2972, 2621, 2351, 1693, 1410 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{12}\text{H}_{23}\text{NO}_2\text{Na} [\text{M} + \text{H}]^+$ 236.1621, found 236.1625.

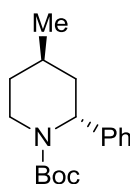


***N*-Boc-*trans*-2-ethyl-4-methylpiperidine (2bb).** Prepared from **1b** (46.4 mg, 0.151 mmol) and diethylzinc (1.0 M in hexane, 0.450 ml, 0.450 mmol) following the typical procedure. Isolated yield 95% (colorless oil, 32.7 mg, 0.144 mmol, purified with flash chromatography, hexane/EtOAc = 20/1); ^1H NMR (600 MHz, CDCl_3) δ 4.20 and 4.07 (s, 1H) (rotamer), 4.07 and 3.90 (s, 1H) (rotamer), 2.81–2.66 (m, 1H), 1.71–1.63 (m, 2H), 1.60–1.49 (m, 2H), 1.44 (s, 9H), 1.41–1.34 (m, 1H), 1.19 (ddd, J = 13.2, 12.6, 5.4 Hz, 1H), 1.07–0.96 (m, 1H), 0.87 (d, J = 6.6 Hz, 3H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0 and 154.6 (rotamer), 80.5 and 79.8 (rotamer), 79.8 and 79.5 (rotamer), 62.1 and 61.6 (rotamer), 39.1 and 39.0 (rotamer), 38.8 and 37.8 (rotamer), 33.8 and 33.6 (rotamer), 28.4 and 28.3 (rotamer), 25.0 and 24.9 (rotamer), 22.0, 15.2 and 15.1 (rotamer); IR (neat) 2927, 2872, 1700, 1404, 1160 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{13}\text{H}_{26}\text{NO}_2 [\text{M} + \text{H}]^+$ 228.1964, found 228.1988.

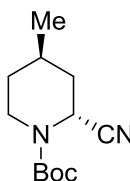


***N*-Boc-*trans*-2-allyl-4-methylpiperidine (2bc).** Prepared from **1b** (46.3 mg, 0.151 mmol) and allyltributyltin (149.0 mg, 0.450 mmol) following the typical procedure. Isolated yield 95% (pale yellow oil, 34.4 mg, 0.144 mmol, purified by flash chromatography hexane/EtOAc 20:1); ^1H NMR (600 MHz, CDCl_3) δ 5.80–5.68 (m, 1H), 5.02 (d, J = 17.4 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 4.38 and 4.22 (s, 1H) (rotamer), 4.04 and 3.90 (d, J = 10.8 Hz, 1H) (rotamer), 2.83–2.70 (m, 1H), 2.36 (ddd, J = 14.4, 8.4, 7.2 Hz, 1H), 2.24–2.14 (m, 1H), 1.74–1.66 (m, 1H), 1.64–1.55 (m, 2H), 1.49 (s, 9H), 1.19 (ddd, J = 12.6, 7.2, 5.4 Hz, 1H), 1.08–0.98 (m, 1H), 0.89 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 135.6, 116.6 and 116.4 (rotamer), 79.1, 50.9 and 49.6 (rotamer), 39.5 and 38.3 (rotamer), 36.7 and 36.1 (rotamer), 35.3 and 34.9

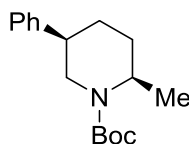
(rotamer), 34.2 and 33.9 (rotamer), 28.4, 25.1, 22.2; IR (neat) 2980, 1680, 1363, 1178, 744 cm^{-1} ; HRMS (FAB⁺) calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 240.1964, found 240.1975.



***N*-Boc-*trans*-4-methyl-2-phenylpiperidine (2bd).** Prepared from **1b** (46.3 mg, 0.151 mmol) and PhMgBr (1.0 M in Et₂O, 375 μL , 0.375 mmol) following the typical procedure. Isolated yield 93% (pale yellow oil, 38.5 mg, 0.140 mmol, purified by flash chromatography hexane/EtOAc = 20/1); ¹H NMR (400 MHz, CDCl₃) δ 7.34 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.7 Hz, 1H), 7.21 (d, J = 7.7, 2H), 5.46 (brs, 1H), 4.09 (brs, 1H) 2.76 (td, J = 13.2, 2.4 Hz, 1H), 2.29 (d, J = 10.8 Hz, 1H), 1.56–1.50 (m, 3H), 1.47 (s, 9H), 1.04 (qd, J = 13.3, 4.8 Hz, 1H), 0.92 (d, J = 5.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 60 °C) δ 155.5, 140.9, 128.4, 126.5, 126.3, 79.4, 53.5, 40.3, 36.9, 34.2, 28.5, 25.7, 22.1; IR (neat) 2951, 2357, 1695, 1414, 1157 cm^{-1} ; HRMS (ESI⁺) calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_2$ $[\text{M} + \text{Na}]^+$ 298.1778, found 298.1789.

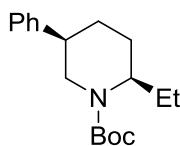


***N*-Boc-*trans*-2-cyano-4-methylpiperidine (2be).** Prepared from **1b** (46.1 mg, 0.150 mmol) and trimethylsilylcyanide (74.4 mg, 93 μL , 0.750 mmol) following the typical procedure. Isolated yield 89% (colorless oil, 85.2 mg, 0.134 mmol, purified by flash chromatography hexane/EtOAc 20:1); ¹H NMR (400 MHz, CDCl₃) δ 5.32 and 5.16 (brs, 1H) (rotamer), 4.05 (brs, 1H), 2.97 (brs, 1H), 2.00–1.79 (m, 2H), 1.71 (brd, J = 12.8 Hz, 1H), 1.48 (s, 9H), 1.36 (td J = 13.6, 5.2 Hz, 1H), 1.10 (qd, J = 13.6, 5.2 Hz, 1H), 0.99 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 60 °C) δ 153.9, 117.8, 81.4, 44.4, 41.4, 36.5, 33.2, 28.3, 27.3, 21.3; IR (neat) 2957, 2874, 2255, 1697, 1395 cm^{-1} ; Anal Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$ C, 71.30; H, 7.74; N, 9.76. Found C, 71.61; H, 7.84; N, 9.78.

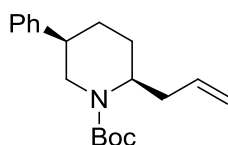


***N*-Boc-*cis*-2-methyl-5-phenylpiperidine (2ca).** Prepared from **1c** (55.4 mg, 0.150 mmol) and trimethylaluminum (1.08 M in toluene, 0.69 mL, 0.75 mmol) following the typical procedure. Isolated yield 89% (colorless solid, 36.8 mg, 0.134 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, J = 7.3 Hz, 2H), 7.28–7.17 (m, 3H), 4.50 (s, 1H), 4.10 (d, J = 12.5 Hz, 1H), 2.89 (t, J = 12.5 Hz, 1H), 2.71–2.57 (m, 1H), 1.95–1.75 (m, 3H), 1.67 (dd, J = 8.9, 2.5 Hz, 1H), 1.51 (s,

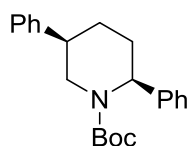
9H), 1.23 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 143.9, 128.5, 127.0, 126.6, 79.3, 45.5, 45.0, 43.0, 30.3, 28.6, 26.2, 15.7; IR (KBr) 2970, 1688, 1342, 1165, 1136 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{17}\text{H}_{26}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 276.1958, found 276.1967, mp 99.7–100.2 $^\circ\text{C}$.



***N*-Boc-*cis*-2-ethyl-5-phenylpiperidine (2cb).** Prepared from **1c** (55.4 mg, 0.150 mmol) and diethyl zinc (1.0 M in hexane, 0.750 mL, 0.750 mmol) following the typical procedure. Isolated yield >99% (colorless solid, 43.7 mg, 0.144 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 7.33 (t, $J = 7.1$ Hz, 2H), 7.29–7.18 (m, 3H), 4.24 (d, $J = 11.9$ Hz, 1H), 4.17 (s, 1H), 2.82 (t, $J = 11.9$ Hz, 1H), 2.74–2.58 (m, 1H), 1.90–1.71 (m, 5H), 1.68–1.53 (m, 1H), 1.49 (s, 9H), 0.94 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 155.2, 143.9, 128.5, 128.2, 127.0, 126.5, 79.2, 51.6, 45.5, 42.9, 28.6, 26.5, 22.8, 10.8; IR (KBr) 3003, 2864, 1694, 1396, 1130 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 290.2115, found 290.2125, mp 65.5–66.0 $^\circ\text{C}$.

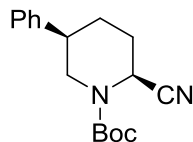


***N*-Boc-*cis*-2-allyl-5-phenylpiperidine (2cc).** Prepared from **1c** (55.4 mg, 0.150 mmol) and allyltributylstannane (1.0 M in Et_2O , 375 μL , 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 97% (pale yellow oil, 43.7 mg, 0.145 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 7.33 (t, $J = 7.5$ Hz, 2H), 7.28–7.20 (m, 4H), 5.90–5.72 (m, 1H), 5.09 (dd, $J = 16.0, 1.4$ Hz, 1H), 5.06 (dd, $J = 10.1, 1.4$ Hz, 1H), 4.39 (brs, 1H), 4.16 (brs, 1H), 2.84 (t, $J = 12.1$ Hz, 1H), 2.74–2.58 (m, 1H), 2.56–2.42 (m, 1H), 2.42–2.24 (m, 1H), 1.88–1.76 (m, 4H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 155.0, 143.8, 135.5, 128.5, 127.1, 126.6, 116.7, 79.4, 49.7, 45.3, 42.7, 34.5, 28.6, 27.8, 26.3; IR (neat) 3003, 2934, 2864, 1682, 1173 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{19}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 302.2115, found 302.2143.

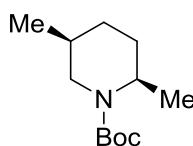


***N*-Boc-*cis*-2,5-diphenylpiperidine (2cd).** Prepared from **1c** (55.4 mg, 0.150 mmol) and PhMgBr (1.0 M in Et_2O , 375 μL , 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 97% (colorless solid, 48.9 mg, 0.145 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 7.37 (t, $J = 7.4$ Hz, 2H), 7.31–7.20 (m, 6H), 7.17 (t, $J = 7.4$ Hz, 1H), 7.11 (d, $J = 7.4$ Hz, 2H), 5.52 (s, 1H), 4.21 (d, $J = 6.9$ Hz, 1H), 2.88–2.70 (m, 2H), 2.49 (dd, $J = 14.2, 4.8$ Hz, 1H), 2.19–1.97 (dddd, $J =$

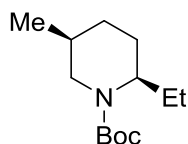
14.2, 10.8, 4.0, 3.7 Hz, 1H), 1.87 (dd, $J = 13.0, 3.7$ Hz, 1H), 1.72 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , 60 °C) δ 155.6, 143.6, 140.3, 128.7, 128.5 (2), 127.0, 126.6 (2), 79.8, 52.7, 46.5, 42.8, 28.6, 28.2, 26.9; IR (KBr) 2976, 1688, 1452, 1366, 1146 cm^{-1} ; HRMS (ESI $^{+}$) calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^{+}$ 338.2115, found 338.2123, mp 107.5–108.0 °C.



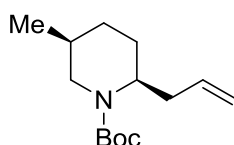
***N*-(*tert*-Butyloxycarbonyl)-*cis*-2-cyano-5-phenylpiperidine (2ce).** Prepared from **1c** (55.4 mg, 0.150 mmol) and trimethylsilylcyanide (74.4 mg, 0.093 mL, 0.750 mmol) following the typical procedure. Isolated yield 96% (colorless solid, 41.2 mg, 0.144 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ^1H NMR (400 MHz, CDCl_3 , 60 °C) δ 7.34 (t, $J = 7.3$ Hz, 2H), 7.29–7.21 (m, 3H), 5.32 (s, 1H), 4.19 (d, $J = 12.7$ Hz, 1H), 3.03 (t, $J = 12.7$ Hz, 1H), 2.75–2.60 (m, 1H), 2.13–1.97 (m, 3H), 1.97–1.84 (m, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , 60 °C) δ 153.8, 142.2, 128.8, 127.1 (2), 117.5, 81.7, 47.5, 43.8, 42.0, 28.7, 28.3, 27.8; IR (KBr) 2976, 2862, 1694, 1366, 1155 cm^{-1} ; HRMS (ESI $^{+}$) calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^{+}$ 287.1754, found 287.1754, 140.9–141.4 °C.



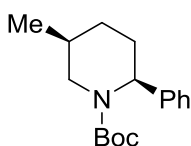
***N*-Boc-*cis*-2,5-dimethylpiperidine (2da).** Prepared from **2d** (46.1 mg, 0.150 mmol) and trimethylaluminum (1.08 M in toluene, 0.69 mL, 0.75 mmol) following the typical procedure. Isolated yield 73% (colorless oil, 23.4 mg, 0.110 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3 , 60 °C) δ 4.17 (dd, $J = 6.0$ Hz, 1H), 3.87 (brd, $J = 12.8$ Hz, 1H), 2.40 (t, $J = 12.4$ Hz, 1H), 1.59–1.43 (m, 12H), 1.33–1.16 (m, 1H), 1.10 (d, $J = 6.4$ Hz, 3H), 0.89 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 60 °C) δ 155.0, 79.0, 45.7, 45.5, 31.4, 30.2, 28.6, 27.8, 19.2, 15.6; IR (neat) 2934, 2864, 1682, 1416, 1146 cm^{-1} ; HRMS (ESI $^{+}$) calcd for $\text{C}_{12}\text{H}_{23}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^{+}$ 236.1621, found 236.1631.



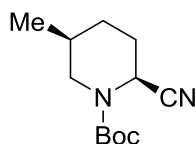
***N*-Boc-*cis*-2-ethyl-5-methylpiperidine (2db).** Prepared from **2d** (46.1 mg, 0.150 mmol) and diethyl zinc (1.0 M in hexane, 0.750 mL, 0.750 mmol) following the typical procedure. Isolated yield 82% (colorless oil, 27.9 mg, 0.123 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 4.15 and 4.02 (s, 1H) (rotamer), 3.96 and 3.77 (d, J = 12.4 Hz, 1H) (rotamer), 2.34 and 2.26 (t, J = 12.4 Hz, 1H) (rotamer), 1.43 (s, 9H), 1.84–1.10(m, 7H), 0.85–0.80 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 155.3, 78.9, 51.7 and 50.5 (rotamer), 46.3 and 44.7 (rotamer), 31.2, 28.2, 27.9, 22.7 and 20.2 (rotamer), 19.3, 10.9; IR (neat) 2965, 1692, 1418, 1152, 880 cm^{-1} , HRMS (ESI^+) calcd for $\text{C}_{13}\text{H}_{25}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 250.1778, found 250.1784.



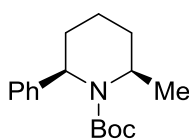
***N*-Boc-*cis*-2-allyl-5-methylpiperidine (2dc).** Prepared from **1d** (46.1 mg, 0.150 mmol) and allyltributyltin (230 μL , 248.0 mg, 0.750 mmol) following the typical procedure. Isolated yield 90% (pale yellow oil, 32.4 mg, 0.135 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 5.80–5.64 (m, 1H), 5.02 (d, J = 17.6 Hz, 1H), 4.98 (d, J = 10.4 Hz, 1H), 4.35 and 4.20 (s, 1H) (rotamer), 3.96 and 3.79 (d, J = 11.6 Hz, 1H) (rotamer), 2.42–2.26 (m, 2H), 2.26–2.10 (m, 1H), 1.61–1.60 (m, 4H), 1.43 (s, 9H), 1.24–1.12 (m, 1H), 0.87 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 155.1, 135.6, 116.6, 79.1, 50.0 and 48.6 (rotamer), 46.4 and 45.2 (rotamer), 34.5, 34.1, 31.1, 28.4, 27.7, 19.3; IR (neat) 2927, 1693, 1411, 1151, 983 cm^{-1} ; HRMS (FAB^+) calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 262.1786, found 262.1783.



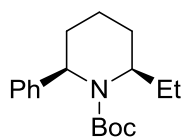
***N*-Boc-*cis*-5-methy-2-phenylpiperidine (2dd).** Prepared from **1d** (55.4 mg, 0.150 mmol) and PhMgBr (1.0 M in Et_2O , 375 μL , 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 83% (colorless oil, 34.1 mg, 0.124 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 7.28–7.19 (m, 2H), 7.19–7.06 (m, 3H), 5.32 (brs, 1H), 3.91 (brd, J = 13.2 Hz, 1H), 2.36–2.14 (m, 2H), 1.84 (dddd, J = 13.7, 13.7, 5.5, 3.4 Hz, 1H), 1.65–1.45 (m, 2H), 1.45–1.28 (m, 9H), 1.11–0.90 (m, 1H), 0.72 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 155.6, 140.6, 128.5, 126.6, 126.3, 79.5, 52.8, 47.2, 31.3, 28.5, 28.2, 19.1; IR (neat) 2976, 1688, 1452, 1366, 1146 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 298.1778, found 298.1782.



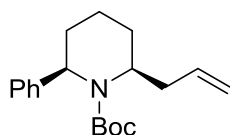
***N*-Boc-*cis*-2-cyano-5-methylpiperidine (2de).** Prepared from **1d** (46.1 mg, 0.150 mmol) and trimethylsilylcyanide (74.4 mg, 0.093 ml, 0.750 mmol) following the typical procedure. Isolated yield 98% (colorless oil, 32.9 mg, 0.147 mmol, purified by flash chromatography hexane/EtOAc = 10/1); ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 5.20 (s, 1H), 3.98 (d, J = 12.7 Hz, 1H), 2.55 (dd, J = 12.7 Hz, 1H), 1.98–1.88 (m, 1H), 1.86–1.65 (m, 2H), 1.60–1.30 (m, 11H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 153.8, 117.6, 81.4, 48.2, 43.8, 30.6, 29.1, 28.7, 28.3, 18.8; IR (neat) 3394, 2978, 2234, 1699, 1395 cm^{-1} ; HRMS (FAB $^+$) calcd for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{O}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 247.1422, found 247.1426.



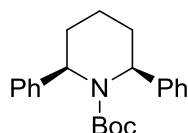
***N*-Boc-*cis*-2-methyl-6-phenylpiperidine (2ea).** Prepared from **1e** (55.8 mg, 0.151 mmol) and trimethylaluminum (1.08 M in hexane, 347 μL , 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 40% (pale yellow oil, *cis/trans* = 63/37, 30.8 mg, 0.102 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 7.38–7.25 (m, 6H), 7.24–7.09 (m, 6H), 5.38 (s, 1H, *trans*) and 4.98 (t, J = 4.8 Hz, 1H, *cis*), 4.48 (t, J = 5.3 Hz, 1H, *trans*) and 4.29–4.11 (m, 1H, *cis*), 2.36 (d, J = 10.5 Hz, 1H), 2.24–2.08 (m, 1H), 2.07–1.93 (m, 1H), 1.92–1.70 (m, 4H), 1.70–1.56 (m, 2H), 1.56–1.37 (m, 16H), 1.37–1.20 (m, 17H), 0.90 (d, J = 6.9 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 156.0, 144.7 and 143.7, 128.1 and 128.0, 126.6, 126.2 and 126.0, 125.7, 79.4 and 79.3, 55.0 and 52.1, 47.8 and 46.6, 30.5, 28.5 and 28.4, 28.5 and 27.5, 20.9 and 20.6, 15.5 and 14.7; IR (neat) 2972, 1682, 1454, 1366, 1173 cm^{-1} ; HRMS (ESI $^+$) calcd for $\text{C}_{17}\text{H}_{26}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 276.1958, found 276.1971.



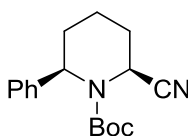
***N*-Boc-*cis*-2-ethyl-6-phenylpiperidine (2eb).** Prepared from **1e** (56.1 mg, 0.152 mmol) and diethylzinc (1.0 M in heptane, 354 μL , 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 90% (colorless oil, *cis/trans* = 76/24, 31.4 mg, 0.131 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 7.40 (d, J = 7.3 Hz, 2H), 7.35–7.23 (m, 14H), 7.22–7.14 (m, 4H), 5.44 (d, J = 4.1 Hz, 1H, *trans*), 5.01 (t, J = 4.6 Hz, 3H, *cis*), 4.26–4.13 (m, 1H, *trans*), 3.95–3.83 (m, 3H, *cis*), 2.35 (d, J = 14.2 Hz, 1H), 2.21–1.99 (m, 6H), 1.96–1.80 (m, 4H), 1.80–1.53 (m, 16H), 1.53–1.39 (m, 14H), 1.39–1.22 (m, 27H), 1.19–1.01 (m, 1H), 0.97 (t, J = 6.9 Hz, 9H), 0.73 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 156.3 and 156.1, 144.3 and 143.7, 128.1 and 128.0, 126.8 and 126.3, 126.0 and 125.8, 79.4 and 79.2, 55.1 and 54.1, 53.1 and 51.8, 28.5 and 28.0, 28.3, 27.7 and 27.3, 23.9, 15.8 and 15.0, 11.6 and 11.4; IR (neat): 2976, 2862, 1694, 1366, 1155 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 290.2115, found 290.2129.



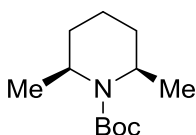
***N*-Boc-*cis*-2-allyl-6-phenylpiperidine (2ec).** Prepared from **1e** (56.0 mg, 0.15 mmol) and (allyl)tributyltin (115 μ L, 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 94% (pale yellow oil, *cis/trans* = 72/28, 42.5 mg, 0.141 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 7.35 (d, J = 7.3 Hz, 2H), 7.31–7.23 (m, 8H), 7.23–7.07 (m, 8H), 5.92–5.71 (m, 2H), 5.62 (d, J = 6.9 Hz, 1H), 5.41 (d, J = 3.4 Hz, 1H), 5.18–4.94 (m, 7H), 4.89 (d, J = 10.5 Hz, 1H), 4.79 (d, J = 16.9 Hz, 1H), 4.41–4.26 (m, 1H), 4.14–3.96 (m, 2H), 2.71–2.52 (m, 2H), 2.44–2.22 (m, 3H), 2.21–1.97 (m, 5H), 1.92–1.50 (m, 13H), 1.50–1.37 (m, 14H), 1.32 (s, 20H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 156.0 and 155.9, 144.3 and 143.4, 136.4 and 136.1, 128.1 and 128.1, 126.8 and 126.4, 126.0 and 125.7, 79.6 and 79.4, 55.0 and 51.1, 52.1 and 51.8, 39.1 and 38.8, 28.5 and 28.3, 28.2, 27.3 and 27.2, 23.6, 15.5 and 14.6; IR (neat) 2974, 1693, 1416, 1366, 1168 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{19}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 302.2115, found 302.2143.



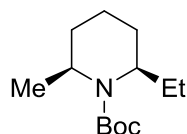
***N*-Boc *cis*-2,6-diphenylpiperidine (2ed).** Prepared from **1e** (55.2 mg, 0.149 mmol) and phenylmagnesium bromide (3.0 M in Et_2O , 340 μ L, 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 56% (colorless solid, 29.2 mg, 0.077 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 7.32–7.22 (m, 7H), 7.22–7.10 (m, 3H), 5.22 (s, 2H), 2.19–2.03 (m, 2H), 2.03–1.88 (m, 2H), 1.47–1.32 (m, 3H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 156.2, 144.9, 128.3, 126.1, 125.8, 79.6, 55.6, 28.3, 28.1, 14.7; IR (KBr) 2955, 2941, 1450, 1364, 1173 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 338.2115, found 338.2115, mp 71.4–71.9 $^\circ\text{C}$.



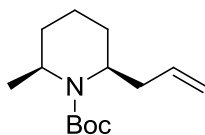
***N*-Boc-*cis*-2-cyano-6-phenylpiperidine (2ee).** Prepared from **1e** (55.2 mg, 0.149 mmol) and trimethylsilyl cyanide (93 μ L, 0.75 mmol, 5.0 equiv) following the typical procedure. Isolated yield 85% (colorless solid, *cis/trans* = 64/36, 36.5 mg, 0.127 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.22 (m, 4H), 7.22–7.14 (m, 1H), 5.31–5.21 (m, 2H), 2.33 (dd, J = 10.7, 3.4 Hz, 1H), 1.94 (dt, J = 9.1, 2.1 Hz, 1H), 1.88–1.71 (m, 3H), 1.63 (d, J = 3.2 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.6, 139.9, 128.4, 127.2, 126.6, 118.8, 81.8, 53.4, 40.8, 28.6, 28.2, 27.4, 16.1; IR (KBr) 2963, 1678, 1393, 1368, 1163 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 287.1754, found 287.1768, mp 88.8–89.3 $^\circ\text{C}$.



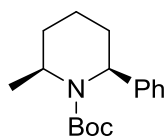
***N*-Boc-*cis*-2,6-dimethylpiperidine (2fa).** Prepared from **1f** (46.1 mg, 0.150 mmol) and trimethylaluminium (1.08 M in hexane, 347 μ L, 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 49% (colorless oil, 15.8 mg, 0.074 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ^1H NMR (400 MHz, CDCl_3) δ 4.34–4.15(m, 2H), 1.85–1.65 (m, 1H), 1.65–1.48 (m, 3H), 1.45 (s, 9H), 1.38–1.23, (m, 1H), 1.16 (d, J = 6.8 Hz, 6H), 0.95–0.85 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 155.3, 78.9, 45.8, 30.3, 28.6, 20.8, 14.0; IR (neat) 2960, 2932, 1728, 1275, 1123 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{12}\text{H}_{23}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 236.1621 found 236.1631.



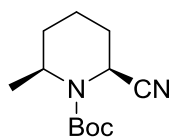
***N*-Boc-*cis*-2-ethyl-6-methylpiperidine (2fb).** Prepared from **1f** (46.1 mg, 0.150 mmol) and diethyl zinc (1.0 M in hexane, 230 μ L, 0.750 mmol) following the typical procedure. Isolated yield 46% (colorless oil, 15.7 mg, 0.069 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3 , 60 $^\circ\text{C}$) δ 4.35–4.18 (m, 1H), 4.03–3.88 (m, 1H), 1.73–1.59 (m, 3H), 1.59–1.48 (m, 4H), 1.45 (s, 9H), 1.43–1.36 (m, 1H), 1.14 (d, J = 6.8 Hz, 3H), 0.88 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.5, 78.8, 52.1, 45.8, 30.5, 28.6, 28.1, 27.2, 20.5, 14.4, 11.9; IR (neat) 2965, 2932, 1694, 1368, 1173 cm^{-1} ; HRMS (FAB^+) calcd for $\text{C}_{13}\text{H}_{26}\text{NO}_2$ [$\text{M} + \text{H}^+$] 228.1958, found 228.1958.



***N*-Boc-*cis*-2-allyl-6-methylpiperidine (2fc).** Prepared from **1f** (46.1 mg, 0.150 mmol) and (allyl)tributyltin (230 μ L, 248.0 mg, 0.750 mmol) following the typical procedure. Isolated yield 87% (pale yellow oil, 31.4 mg, 0.131 mmol, purified by flash chromatography hexane/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3) δ 5.74 (ddt, J = 17.4, 10.2, 7.2 Hz, 1H), 5.02 (dd, J = 17.4, 1.2 Hz, 1H), 4.99 (dd, J = 1.2 Hz, 1H), 4.28–4.24 (m, 1H), 4.12–4.07 (m, 1H), 2.30–2.24 (m, 2H), 1.44 (s, 9H), 1.70–1.39 (m, 6H), 1.15 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.3, 136.8, 116.6, 79.1, 50.0, 45.6, 39.6, 30.2, 28.6, 26.7, 20.5, 13.9; IR (neat) 3075, 2936, 1688, 1458, 1080 cm^{-1} ; HRMS (FAB^+) calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 262.1756, found 262.1729.



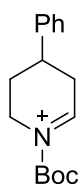
***N*-Boc-*cis*-6-methy-2-phenylpiperidine (2fd).** Prepared from **1f** (55.4 mg, 0.150 mmol) and PhMgBr (1.0 M in Et₂O, 375 μ L, 0.375 mmol, 2.5 equiv) following the typical procedure. Isolated yield 87% (pale yellow oil, 35.9 mg, 0.131 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ¹H NMR (400 MHz, CDCl₃) δ : 7.32–7.19 (m, 4H), 7.19–7.09 (m, 1H), 5.39 and 5.31 (brs, 1H) (rotamer), 4.45 and 4.43 (dq, *J* = 6.9, 2.2 Hz, 1H) (rotamer), 2.41–2.28 (m, 1H), 1.84–1.64 (m, 3H), 1.54–1.36 (m, 11H), 0.79 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 60 °C) δ : 155.9, 143.6, 128.0, 126.6, 126.2, 79.4, 52.1, 46.6, 30.5, 28.5, 27.5, 20.9, 15.4; IR (neat) 2972, 1682, 1404, 1175, 1069 cm⁻¹; HRMS (ESI⁺) calcd for C₁₇H₂₆NO₂ [*M* + *H*]⁺ 276.1958, found 276.1958.



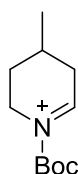
***N*-Boc-*cis*-2-cyano-6-methylpiperidine (2fe).** Prepared from **1f** (55.4 mg, 0.150 mmol) and trimethylsilylcyanide (74.4 mg, 0.093 ml, 0.750 mmol) following the typical procedure. Isolated yield 90% (colorless oil, 30.2 mg, 0.135 mmol, purified by flash chromatography hexane/EtOAc = 30/1): ¹H NMR (400 MHz, CDCl₃) δ 5.05(d, *J* = 4.4 Hz, 1H), 4.39–4.27 (m, 1H), 2.06–1.96 (m, 1H), 1.96–1.82 (m, 1H), 1.74–1.59 (m, 4H), 1.48 (s, 9H), 1.33 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 60 °C) δ 154.8, 120.2, 81.3, 47.0, 40.7, 29.4, 28.3, 28.0, 17.3, 15.3; IR (neat) 2976, 2943, 1697, 1368, 1173 cm⁻¹; HRMS (ESI⁺) calcd for C₁₂H₂₁N₂O₂ [*M* + *H*]⁺ 225.1598, found 225.1608.

NMR analysis of *N*-acyliminium ion generated by the indirect cation pool method.

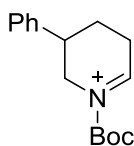
Typical procedure of NMR analysis of *N*-acyliminium ions. Analogous as described in our previous report.⁶ The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-FC₆H₄) (75 μ L, 0.401 mmol) in 4.0 mL of 0.3 M Bu₄NBF₄/CH₂Cl₂. In the cathodic chamber were placed trifluoromethanesulfonic acid (24 μ L, 0.273 mmol) and 0.3 M Bu₄NBF₄ in CH₂Cl₂ (4.0 mL). The constant current electrolysis (8.0 mA) was carried out at –78 °C with magnetic stirring until 0.67 F/mol of electricity was consumed. To the solution of the cation precursor (13.0 mg, 0.0352 mmol) in CD₂Cl₂ (0.35 mL) which was placed in a 5 mm $\varnothing$ NMR tube equipped with a septum cap was transferred the reaction mixture of the anodic chamber (0.35 mL) under Ar atmosphere at –78 °C. After the mixture was quickly shaken at –78 °C, the NMR measurement was carried out at –60 °C. Exclusively ion **C1** was measured at –80 °C



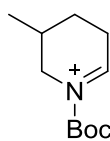
NMR analysis of 4-Ph-N-acyliminium ion (C1). ^1H NMR (600 MHz, CD_2Cl_2) δ 9.46 (s, 1H), 4.32 (d, J = 11.3 Hz, 1H), 3.86 (t, J = 12.7 Hz, 1H), 3.47 (d, J = 20.9 Hz, 1H), 3.22–3.08 (m, 2H), 2.27–2.10 (m, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 186.4, 144.8, 141.5, 91.1, 47.6, 36.4, 32.4, 26.7, 26.3; Other signals could not be assigned because of overlap with the signals of Bu_4NBF_4 used as the electrolyte or the signals of ArSSAr ($\text{Ar} = p\text{-FC}_6\text{H}_4$).



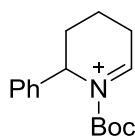
NMR analysis of 4-Me-N-acyliminium ion (C2). ^1H NMR (400 MHz, CD_2Cl_2) δ 9.32 (s, 1H), 4.10 (d, J = 13.2 Hz, 1H), 3.66 (t, J = 13.2 Hz, 1H), 3.21 (d, J = 22.8 Hz, 1H), 2.54 (dd, J = 22.8, 8.5 Hz, 1H), 1.99–1.84 (m, 2H), 0.94 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 186.6, 144.7, 91.2, 53.8, 47.1, 36.4, 27.0, 26.0, 21.5, 19.3; Other signals could not be assigned because of overlap with the signals of Bu_4NBF_4 used as the electrolyte or the signals of ArSSAr ($\text{Ar} = p\text{-FC}_6\text{H}_4$).



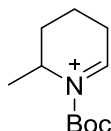
NMR analysis of 5-Ph-N-acyliminium ion (C3). ^1H NMR (400 MHz, CD_2Cl_2) δ 9.49 (s, 1H), 4.25 (d, J = 12.2 Hz, 1H), 3.73 (t, J = 12.2 Hz, 1H), 3.41 (d, J = 23.3 Hz, 1H), 3.25–3.09 (m, 2H), 2.07 (q, J = 11.1 Hz, 1H), 2.00–1.89 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 186.4, 144.6, 91.1, 53.8, 51.5, 36.3, 30.3, 26.1, 21.2; Other signals could not be assigned because of overlap with the signals of Bu_4NBF_4 used as the electrolyte or the signals of ArSSAr ($\text{Ar} = p\text{-FC}_6\text{H}_4$).



NMR analysis of 5-Me-N-acyliminium ion (C4). ^1H NMR (400 MHz, CD_2Cl_2) δ 9.36 (s, 1H), 4.05 (d, J = 11.4 Hz, 1H), 3.27–3.14 (m, 2H), 1.94 (m, 1H), 1.74 (m, 1H), 0.96 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 187.1, 144.7, 91.2, 52.0, 29.7, 26.2, 25.5, 22.3, 17.4; Other signals could not be assigned because of overlap with the signals of Bu_4NBF_4 used as the electrolyte or the signals of ArSSAr ($\text{Ar} = p\text{-FC}_6\text{H}_4$).



NMR analysis of 6-Ph-*N*-acyliminium ion (C5). ^1H NMR (400 MHz, CD_2Cl_2) δ 9.72 (s, 1H), 3.42 (d, J = 23.6 Hz, 1H), 3.25 (dt, J = 23.6, 7.0 Hz, 1H), 2.32 (t, J = 12.9 Hz, 1H), 1.99 (d, J = 12.9 Hz, 1H), 1.83–1.70 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 189.8, 144.5, 91.6, 60.8, 29.7, 27.9, 25.8, 11.1; Other signals could not be assigned because of overlap with the signals of Bu_4NBF_4 used as the electrolyte or the signals of ArSSAr ($\text{Ar} = p\text{-FC}_6\text{H}_4$).



NMR analysis of 6-Me-*N*-acyliminium ion (C6). ^1H NMR (400 MHz, CD_2Cl_2) δ 9.44 (s, 1H), 4.58 (s, 1H), 3.28 (d, J = 23.8 Hz, 1H), 3.09 (dt, J = 23.8, 8.8 Hz, 1H), 1.99–1.82 (m, 2H), 1.82–1.67 (m, 2H), 1.34 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 188.2, 144.1, 91.5, 53.8, 29.4, 26.0, 24.8, 18.4, 10.4; Other signals could not be assigned because of overlap with the signals of Bu_4NBF_4 used as the electrolyte or the signals of ArSSAr ($\text{Ar} = p\text{-FC}_6\text{H}_4$).

2. X-ray crystallography

Details of the crystal data and a summary of the intensity data collection parameters for cation precursors **1a**, **1b**, and **1d–f** are listed in Table S1–S5 and Figure S1–S5. X-ray single crystal analysis was conducted using a Rigaku VariMax with Saturn. Graphite-monochromated MoK α radiation ($\lambda = 0.71075$ Å) was used. The structures were solved by direct methods with SIR2014⁷ or SHELXT⁸ and refined by full-matrix least-squares techniques against F^2 (SHELXL).⁸ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. In the subsequent refinement, the function $\sum w(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$. All calculations were performed by using Yadokari-XG⁹ and illustrations were drawn by using ORTEP-3¹⁰ and colored by Adobe Illustrator. These cif data can also be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif (**1a**: CCDC-1813600, **1b**: CCDC-1813582, **1d**: CCDC-1813594, **1e**: CCDC-1813595, **1f**: CCDC-1813596).

Table S1. Crystal data and structure refinement for **1a**

Empirical formula	$C_{22}H_{27}NO_2S$	
Formula weight	369.50	
Temperature	100 K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	P-1 (#2)	
Unit cell dimensions	$a = 6.334(6)$ Å	$\alpha = 89.62(3)^\circ$.
	$b = 9.919(8)$ Å	$\beta = 88.65(3)^\circ$.
	$c = 16.374(16)$ Å	$\gamma = 75.52(2)^\circ$.
Volume	$995.8(16)$ Å ³	
Z	2	
Density (calculated)	1.232 Mg/m ³	
Absorption coefficient	0.178 mm ⁻¹	
F(000)	396	
Crystal size	0.09 x 0.08 x 0.05 mm ³	
Theta range for data collection	1.244 to 31.404°.	
Index ranges	-9 ≤ h ≤ 8, -14 ≤ k ≤ 14, -22 ≤ l ≤ 23	
Reflections collected	13987	
Independent reflections	5818 [R(int) = 0.0905]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.567	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5818 / 0 / 238	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	$R_1 = 0.0753$, $wR_2 = 0.1651$	
R indices (all data)	$R_1 = 0.1455$, $wR_2 = 0.2375$	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.429 and -0.578 e.Å ⁻³	

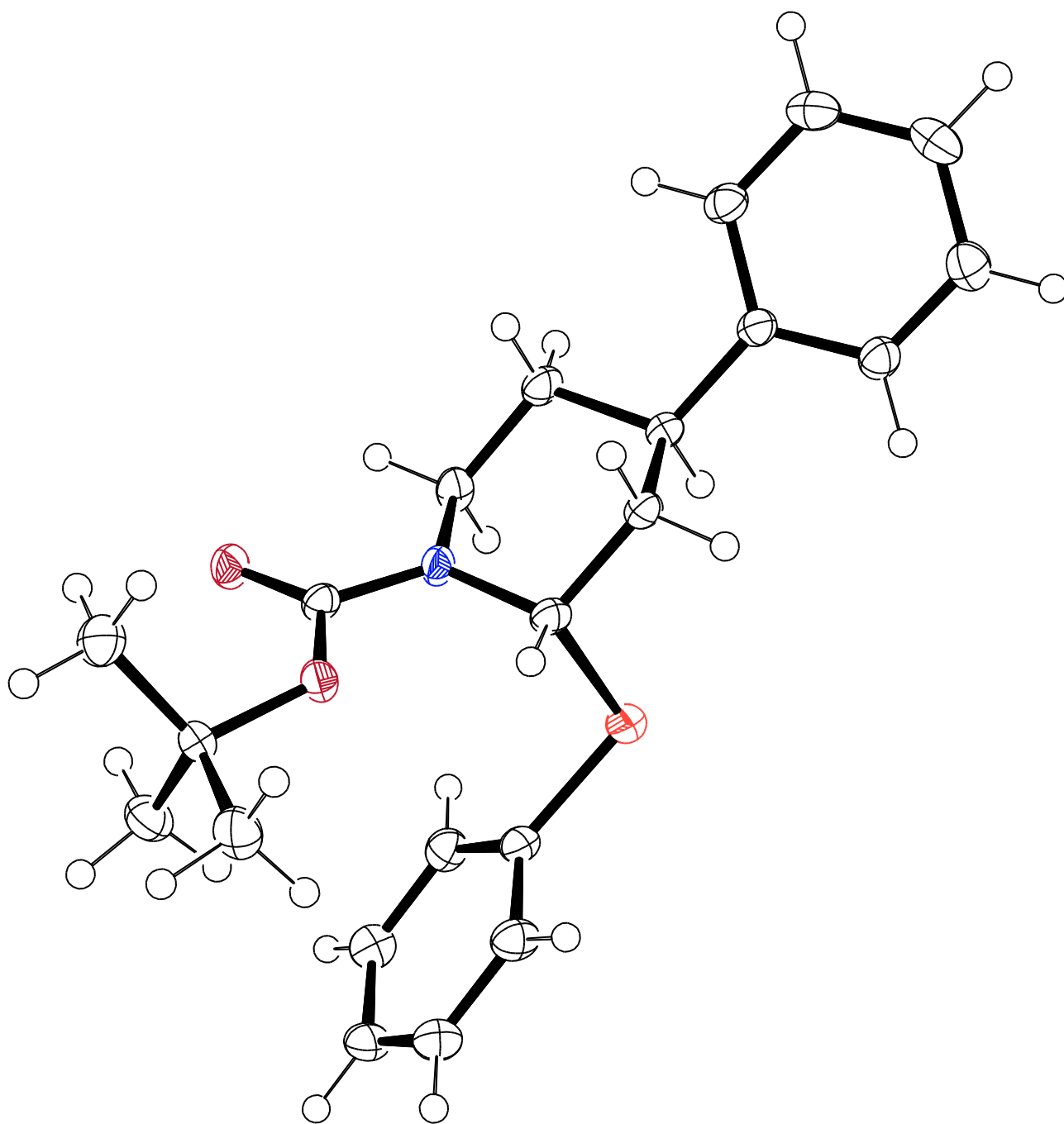


Figure S1. ORTEP drawing of **1a** with 50% thermal ellipsoids.

Table S2. Crystal data and structure refinement for **1b**

Empirical formula	$C_{17}H_{25}NO_2S$	
Formula weight	307.44	
Temperature	100(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	$a = 10.541(4)$ Å	$\alpha = 90^\circ$.
	$b = 16.901(6)$ Å	$\beta = 90^\circ$.
	$c = 18.710(6)$ Å	$\gamma = 90^\circ$.
Volume	$3333(2)$ Å ³	
Z	8	
Density (calculated)	1.225 Mg/m ³	
Absorption coefficient	0.199 mm ⁻¹	
F(000)	1328	
Crystal size	0.200 x 0.200 x 0.200 mm ³	
Theta range for data collection	2.177 to 27.495°.	
Index ranges	-13 ≤ h ≤ 11, -20 ≤ k ≤ 19, -24 ≤ l ≤ 13	
Reflections collected	12485	
Independent reflections	3720 [R(int) = 0.0451]	
Completeness to theta = 25.242°	98.3 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3720 / 0 / 194	
Goodness-of-fit on F ²	1.161	
Final R indices [I > 2sigma(I)]	R1 = 0.0564, wR2 = 0.1343	
R indices (all data)	R1 = 0.0686, wR2 = 0.1421	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.685 and -0.444 e.Å ⁻³	

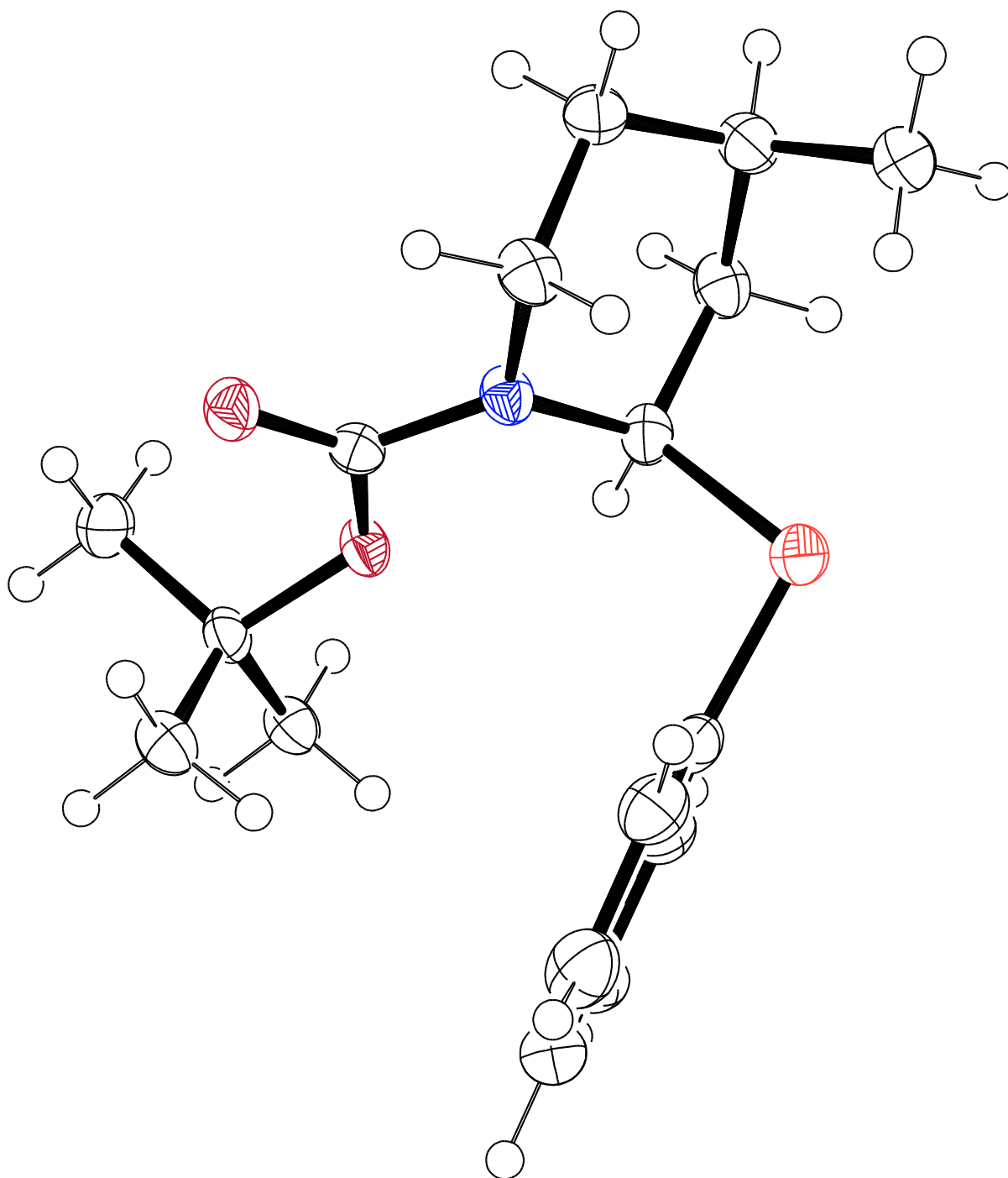


Figure S2. ORTEP drawing of **1b** with 50% thermal ellipsoids.

Table S3. Crystal data and structure refinement for **1d**

Empirical formula	$C_{17}H_{25}NO_2S$	
Formula weight	307.44	
Temperature	100(2) K	
Wavelength	0.71075 Å	
Crystal system	Trigonal	
Space group	$P3_1$	
Unit cell dimensions	$a = 10.154(4)$ Å	$\alpha = 90^\circ$.
	$b = 10.154(4)$ Å	$\beta = 90^\circ$.
	$c = 14.189(5)$ Å	$\gamma = 120^\circ$.
Volume	$1267.0(10)$ Å ³	
Z	3	
Density (calculated)	1.209 Mg/m ³	
Absorption coefficient	0.196 mm ⁻¹	
F(000)	498	
Crystal size	0.580 x 0.320 x 0.200 mm ³	
Theta range for data collection	3.690 to 27.437°.	
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-18 \leq l \leq 18$	
Reflections collected	20112	
Independent reflections	3847 [R(int) = 0.0350]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3847 / 1 / 194	
Goodness-of-fit on F ²	0.987	
Final R indices [I > 2sigma(I)]	R1 = 0.0255, wR2 = 0.0653	
R indices (all data)	R1 = 0.0278, wR2 = 0.0662	
Absolute structure parameter	-0.020(19)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.160 and -0.137 e.Å ⁻³	
Largest diff. peak and hole	0.159 and -0.138 e.Å ⁻³	

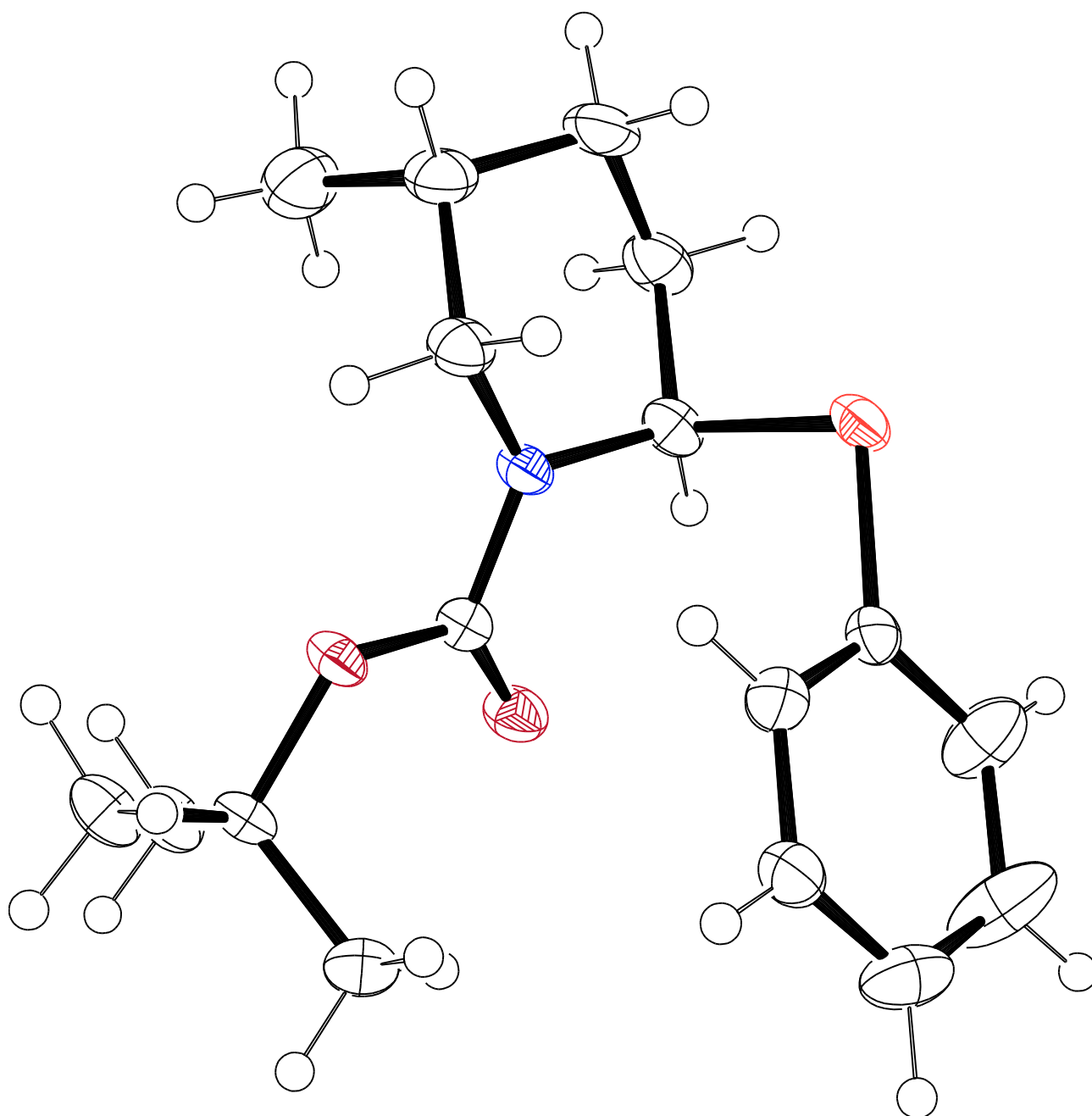


Figure S3. ORTEP drawing of **1d** with 50% thermal ellipsoids.

Table S4. Crystal data and structure refinement for **1e**

Empirical formula	$C_{22}H_{27}NO_2S$	
Formula weight	369.50	
Temperature	110(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	$a = 10.555(2)$ Å	$\alpha = 90^\circ$.
	$b = 21.275(4)$ Å	$\beta = 90^\circ$.
	$c = 17.615(3)$ Å	$\gamma = 90^\circ$.
Volume	3955.6(13) Å ³	
Z	8	
Density (calculated)	1.241 Mg/m ³	
Absorption coefficient	0.179 mm ⁻¹	
F(000)	1584	
Crystal size	0.220 x 0.180 x 0.130 mm ³	
Theta range for data collection	1.914 to 27.500°.	
Index ranges	-13 ≤ h ≤ 13, -27 ≤ k ≤ 27, -22 ≤ l ≤ 22	
Reflections collected	60370	
Independent reflections	4540 [R(int) = 0.0541]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4540 / 0 / 238	
Goodness-of-fit on F ²	1.300	
Final R indices [I > 2sigma(I)]	$R_1 = 0.0500$, wR2 = 0.1426	
R indices (all data)	$R_1 = 0.0581$, wR2 = 0.1601	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.427 and -0.545 e.Å ⁻³	

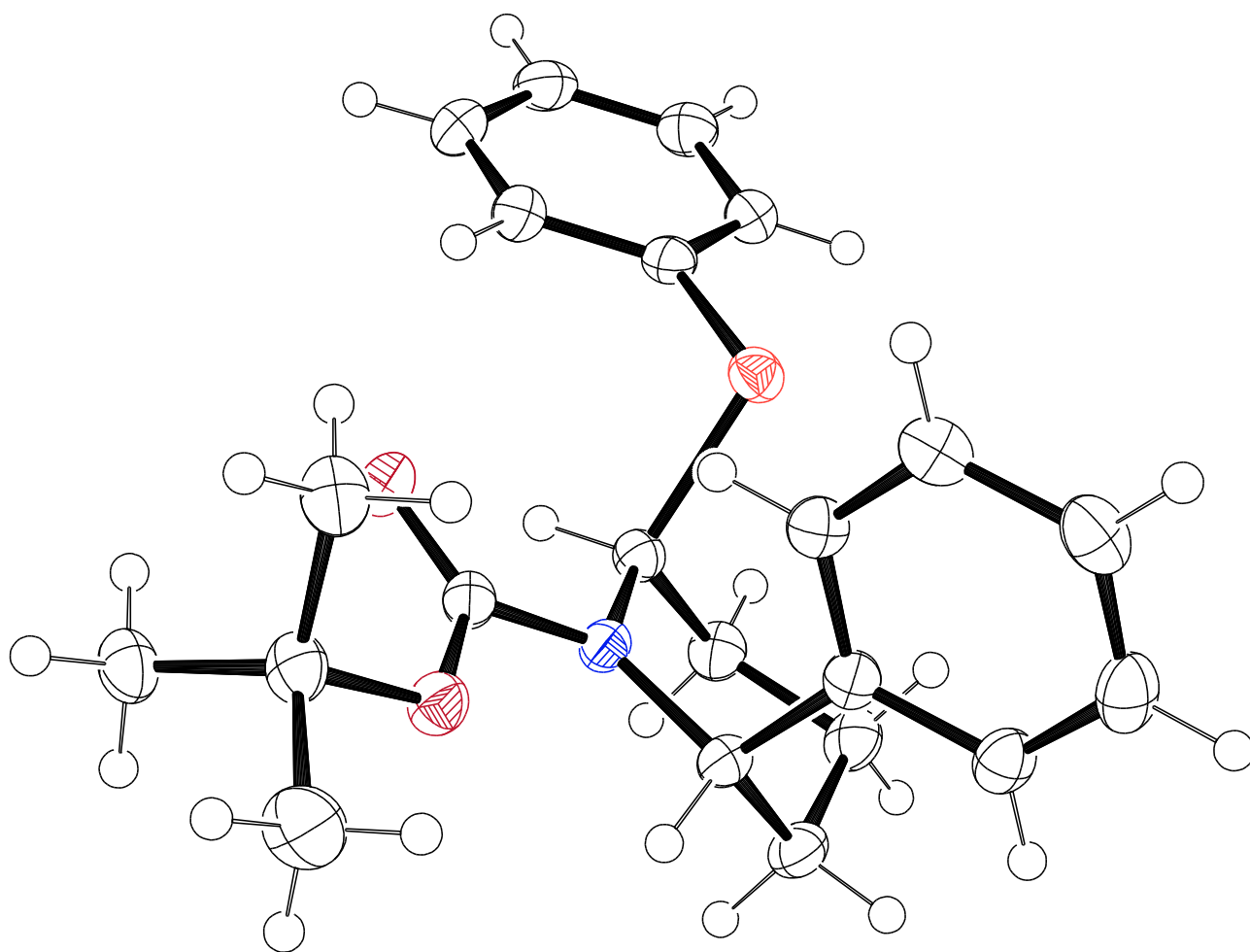


Figure S4. ORTEP drawing of **1e** with 50% thermal ellipsoids.

Table S5. Crystal data and structure refinement for **1f**

Empirical formula	$C_{17}H_{25}NO_2S$	
Formula weight	307.44	
Temperature	100(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	Pna2 ₁	
Unit cell dimensions	a = 27.491(19) Å	$\alpha = 90^\circ$.
	b = 5.651(4) Å	$\beta = 90^\circ$.
	c = 21.462(14) Å	$\gamma = 90^\circ$.
Volume	3334(4) Å ³	
Z	8	
Density (calculated)	1.225 Mg/m ³	
Absorption coefficient	0.199 mm ⁻¹	
F(000)	1328	
Crystal size	0.190 x 0.060 x 0.050 mm ³	
Theta range for data collection	1.481 to 27.498°.	
Index ranges	-32 ≤ h ≤ 35, -7 ≤ k ≤ 7, -27 ≤ l ≤ 19	
Reflections collected	21267	
Independent reflections	6444 [R(int) = 0.0864]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6444 / 1 / 387	
Goodness-of-fit on F ²	1.158	
Final R indices [I > 2σ(I)]	R ₁ = 0.0694, wR ₂ = 0.1637	
R indices (all data)	R ₁ = 0.0817, wR ₂ = 0.1822	
Absolute structure parameter	0.31(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.338 and -0.423 e.Å ⁻³	

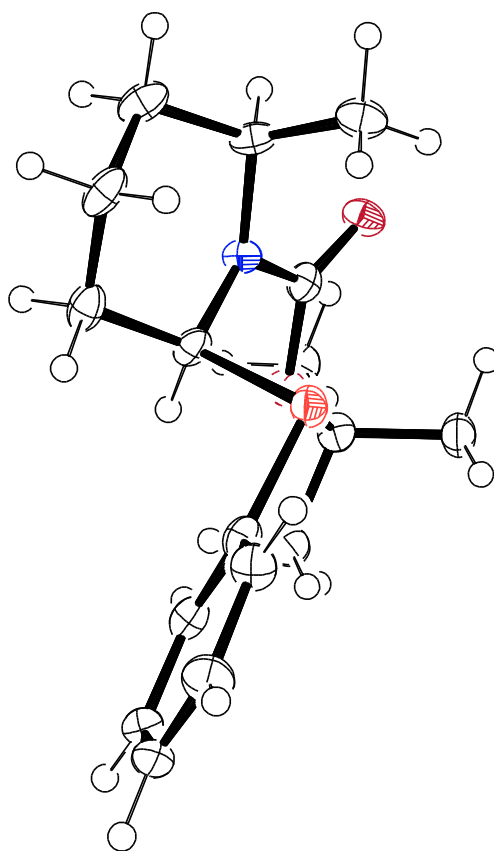
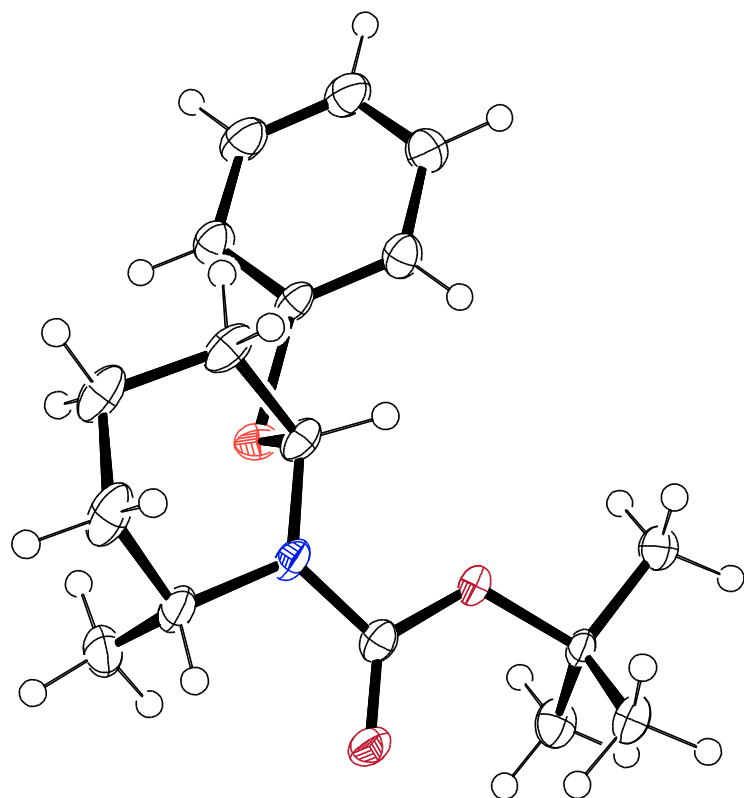


Figure S5. ORTEP drawing of **1f** with 50% thermal ellipsoids.

3. Theoretical calculations

Density functional theory (DFT) calculations were performed using the Gaussian 09 program.¹¹ Geometries were optimized at the B3LYP/6-31G(d) level of theory.¹² Thermochemical corrections were obtained from frequency calculations at the same level of theory. The data were summarized in Figure S6. Calculated structures are illustrated using ChemDraw and CYLView.¹³

Underneath the Cartesian coordinates for the optimized geometries are listed the following energies:

B3LYP/6-31G(d) electronic energy (E)

B3LYP/6-31G(d) enthalpy at 298.15 K (H)

B3LYP/6-31G(d) Gibbs free energy at 298.15 K (G),

Otherwise noted, all energies are given in Hartree.

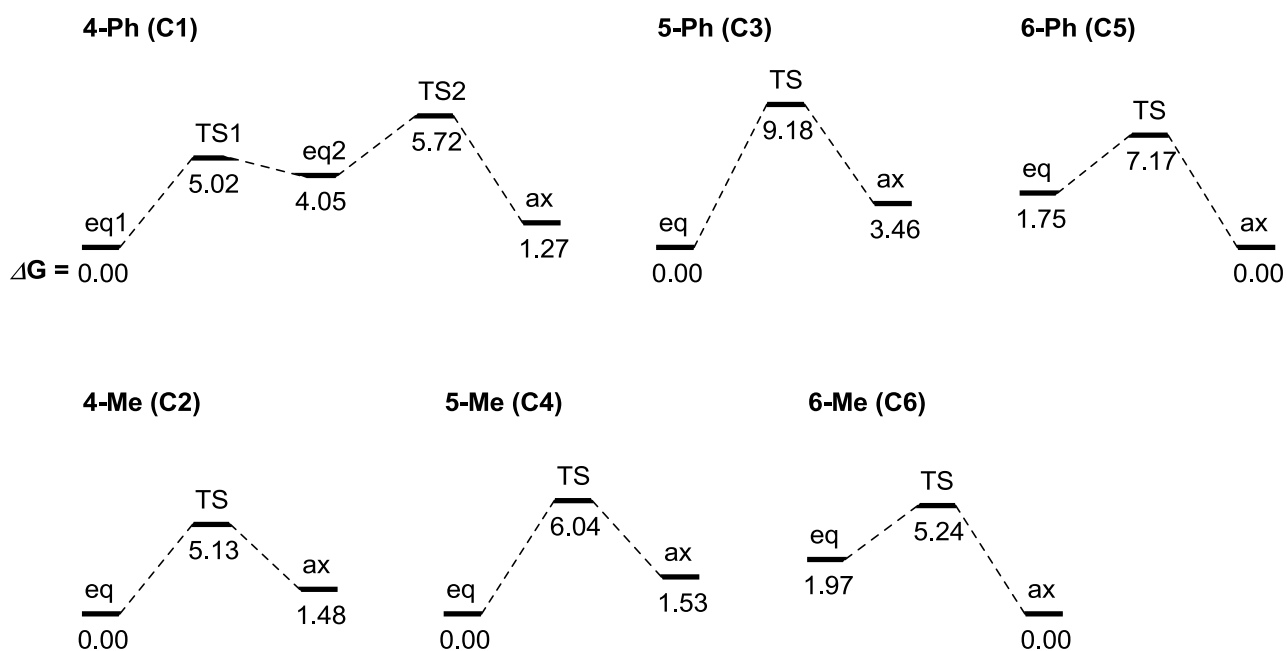
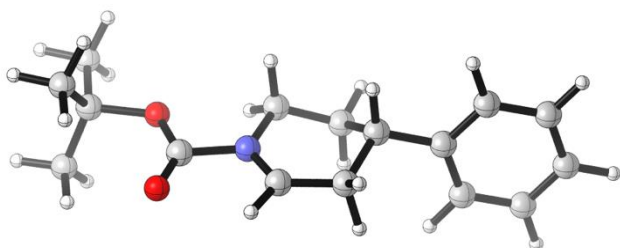


Figure S6. Energy diagram of flipping of *N*-acyliminium ions. The values of ΔG are given in kcal/mol

Computed Geometries and Energies

C1 (equatorial 1)



C	0.389375386580	-0.925826268684	0.266307212243
C	-1.089482583195	-1.092909892558	-0.075066307855
C	-1.932433912162	0.088991677650	0.441751597215
C	-1.382846334846	1.385140238545	-0.187974548971
C	0.091833287239	1.444555156692	-0.292946937300
N	0.882950843623	0.440793679462	-0.086430903721
H	-1.775624563540	0.161167234928	1.525924354019
H	-1.716304819198	2.284515613828	0.348760073010
H	-1.766724785615	1.530303611549	-1.212321016625
H	0.593973473332	2.374103686592	-0.559881721060
H	-1.208652719791	-1.196092204902	-1.160445113716
C	2.365341933239	0.713156196941	-0.199433090422
O	2.731690793504	1.812414296464	-0.514612586780
O	3.005018271918	-0.376870428768	0.097191621979
C	4.545801085063	-0.434055040051	0.089633144794
H	-1.435419038547	-2.030412659231	0.370570758003
H	1.016987324721	-1.632377839726	-0.276915852733
H	0.587170001095	-1.062159253609	1.334402605200
C	5.059557682653	0.557096941741	1.128062353759
H	6.146210649762	0.446705304285	1.203858338007
H	4.843939076428	1.590485878649	0.849146432396
H	4.633552864804	0.348481768859	2.114606543451
C	5.021368431176	-0.137230908466	-1.328279467006
H	6.106129862527	-0.280350893266	-1.366736453628
H	4.568136482602	-0.827239225426	-2.047128031163
H	4.805983501585	0.891143341435	-1.625669005695
C	4.798199134117	-1.880756646257	0.495450099415
H	5.877371754263	-2.057455210628	0.533837966244
H	4.383187218682	-2.092227188169	1.485402193279
H	4.365456647831	-2.577261267852	-0.229003931456
C	-3.423188251995	-0.078159259985	0.197329245241
C	-4.307887487369	-0.127572893449	1.280769269824

C	-3.938614144004	-0.192877343833	-1.101927086076
C	-5.678968320322	-0.288605937294	1.073924495441
H	-3.924529368562	-0.039917088299	2.295040486816
C	-5.307990135274	-0.353583330842	-1.310896215456
H	-3.275095583457	-0.163466749243	-1.964689429008
C	-6.181649154118	-0.401598371902	-0.222353202743
H	-6.351543681309	-0.324333669127	1.925822521427
H	-5.692114381929	-0.442412486499	-2.322871857946
H	-7.247972441514	-0.526071569553	-0.385389552404

0 imaginary frequencies

E = -827.951452

H = -827.575528

G = -827.642879

C1 (TS1)



C	-1.087406044671	1.047326087886	0.579894247943
C	-2.506669226381	1.421324584947	0.072332352530
C	-3.382267108218	0.230438916485	-0.380661347300
C	-2.983133942468	-1.047565432760	0.423742553229
C	-1.544411028341	-1.308927547592	0.220034511502
N	-0.678946717090	-0.344037290359	0.240638736651
H	-3.149094889679	0.013038761833	-1.429300345688
H	-3.570886805625	-1.919897903392	0.129216580114
H	-3.170828971846	-0.879284564122	1.495684950617
H	-1.140832901043	-2.293423055969	-0.010910641127
H	-3.008281901468	1.956972013447	0.882638153693
C	0.761099111323	-0.711526739770	-0.020117385382
O	1.024020324318	-1.851107006153	-0.293280931878
O	1.495233453684	0.350594776455	0.117357532733
C	3.023397033734	0.303885931597	-0.078201508581
H	-2.417642426892	2.126883669421	-0.758161660566
H	-1.029636257296	1.113879998098	1.671413086482
H	-0.322443330873	1.705425633211	0.175580059555

C	3.301170138725	-0.103838566292	-1.520926349517
H	4.380052722919	-0.042499461986	-1.696745976058
H	2.984183797452	-1.128701363786	-1.724826356999
H	2.809445590378	0.576968407811	-2.223030900982
C	3.603703102360	-0.657934006975	0.952925761878
H	4.695958260347	-0.607252031252	0.896611374972
H	3.308694428193	-0.370787629994	1.967188930041
H	3.303248173115	-1.690568098939	0.764784742110
C	3.409399195849	1.751482271604	0.199705192631
H	4.493136740333	1.858374802036	0.093281698868
H	2.929549748050	2.432759652164	-0.509493337509
H	3.136232173302	2.045743430560	1.217454222074
C	-4.873839478528	0.503547487656	-0.288920982638
C	-5.661582423776	0.455300292553	-1.445064742616
C	-5.488173820484	0.796104316612	0.937348311812
C	-7.034246389686	0.701555136389	-1.381328035023
H	-5.200563429829	0.228378843995	-2.403771502766
C	-6.859224746451	1.039084042993	1.003531585889
H	-4.901049992777	0.839702621936	1.853131179489
C	-7.635593936283	0.992923346066	-0.157137678197
H	-7.630501463930	0.664618049534	-2.288191260682
H	-7.321224607199	1.264793582752	1.960104938192
H	-8.703465093251	1.182800961304	-0.105191309494

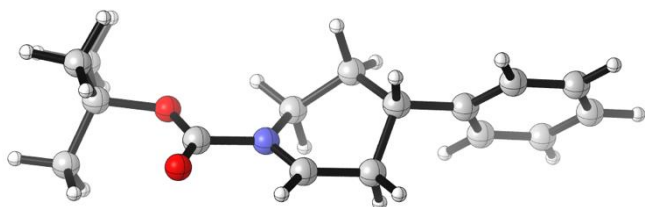
1 imaginary frequency

E = -827.944177

H = -827.568899

G = -827.634877

C1 (equatorial 2)



C	-0.248761581977	0.927106277350	-0.139707483561
C	0.988574579207	0.789476763755	0.768635488868
C	1.906006542683	-0.420372453360	0.420618806263
C	1.373466264268	-1.165101462064	-0.857800792991
C	-0.083318885928	-1.380312188062	-0.761933154943

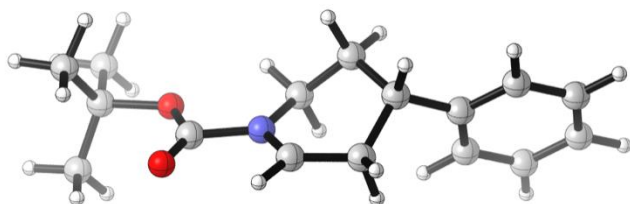
N	-0.857860206811	-0.402151407639	-0.406239718538
H	1.828124489362	-1.145009663191	1.236996480317
H	1.895777331864	-2.110293299141	-1.016447404300
H	1.572206304520	-0.533703879887	-1.738174424733
H	-0.573387973718	-2.335450699185	-0.942265987546
H	1.544848597312	1.727503308713	0.692096883600
C	-2.332552579211	-0.680806384943	-0.300081675634
O	-2.724561705735	-1.792276534246	-0.531869894569
O	-2.942327114349	0.413252009222	0.043221232622
C	-4.471942735195	0.458158904211	0.225719571216
H	0.655074054666	0.706081037306	1.807318760078
H	0.019600231148	1.345730444464	-1.116044102894
H	-1.013221780262	1.560915326698	0.301776934410
C	-4.843235772065	-0.505764948918	1.347276154536
H	-5.912617532209	-0.398189018720	1.555979810470
H	-4.655566567484	-1.545615007369	1.072355091205
H	-4.298449428425	-0.267115646610	2.266265039471
C	-5.115780732719	0.117239970070	-1.113739384373
H	-6.198734438141	0.248874832527	-1.021391769019
H	-4.763433515800	0.791117677460	-1.901083116255
H	-4.925626987935	-0.916977289517	-1.408004936883
C	-4.688534758074	1.914425204128	0.618436472398
H	-5.757243495067	2.086031446460	0.778835173465
H	-4.162585497205	2.156826520673	1.546839460873
H	-4.349934148773	2.591834589530	-0.171206555223
C	3.376691746838	-0.076220969276	0.251694738651
C	4.339869752368	-0.745986838955	1.014688617820
C	3.797380757468	0.892183164396	-0.671391019183
C	5.696633170899	-0.451351613260	0.865219047378
H	4.029919146830	-1.499227813186	1.735591015251
C	5.151364993668	1.186732637880	-0.823431008147
H	3.069546724662	1.429663148702	-1.277346178416
C	6.104692833181	0.514483392815	-0.054114059263
H	6.431151558316	-0.976388038167	1.468607976555
H	5.462364730719	1.941085155987	-1.540171803723
H	7.159270627103	0.744815343350	-0.171895285250

0 imaginary frequencies

E = -827.944675

H = -827.568486

G = -827.636432

C1 (TS2)

C	-0.109988722594	0.658891349062	0.268832577035
C	1.007554879021	0.358395095034	1.272089380025
C	2.018568487792	-0.719924479192	0.787103827628
C	1.371941727138	-1.669717258728	-0.278041744954
C	-0.104828836782	-1.678961376062	-0.314139305224
N	-0.801692701494	-0.609160230470	-0.091086029025
H	2.243970497018	-1.349827264205	1.652469008164
H	1.743169351189	-2.694362755278	-0.191535810363
H	1.677303571392	-1.337255255839	-1.286363041448
H	-0.679107867567	-2.568020581161	-0.570254322858
H	1.530112930163	1.293923102122	1.488644696398
C	-2.299039065798	-0.719743859192	-0.219445756312
O	-2.775107015346	-1.785010561681	-0.504346727794
O	-2.825001696960	0.443728915914	0.016306653174
C	-4.349980021454	0.663134253133	-0.036010910281
H	0.537283260055	0.030383747539	2.206211323324
H	0.273504841180	1.094313091219	-0.659738836982
H	-0.857885075260	1.333551360007	0.677999130253
C	-4.991184874811	-0.225100391834	1.024520687255
H	-6.060675849120	0.005077836279	1.068351279862
H	-4.883283710399	-1.285970603582	0.789825801992
H	-4.566169200596	-0.025007692626	2.013273318037
C	-4.820385370892	0.361315111910	-1.454481813692
H	-5.883251839559	0.613710506266	-1.528122998651
H	-4.280924128761	0.972121905209	-2.185299733890
H	-4.705704701533	-0.694817312440	-1.706513200881
C	-4.456367080864	2.143877761412	0.307036510325
H	-5.510629542056	2.436916223513	0.300251568717
H	-4.053126244855	2.350137686551	1.303164469355
H	-3.927357826228	2.759296261791	-0.426754449802
C	3.339836535651	-0.148889974747	0.289489436112
C	4.511877557025	-0.391114814552	1.015149706871

C	3.418044493689	0.638494804916	-0.869416396604
C	5.733894448717	0.139577976807	0.597007088516
H	4.472208131133	-1.000646163090	1.915087360693
C	4.636916222475	1.171260476784	-1.288604688441
H	2.527712400916	0.845616383664	-1.461051358630
C	5.799058752893	0.922499007878	-0.555191776333
H	6.632927175639	-0.062855055291	1.171553767874
H	4.679026882250	1.779111492338	-2.187705695639
H	6.748621227591	1.334708280622	-0.882912993806

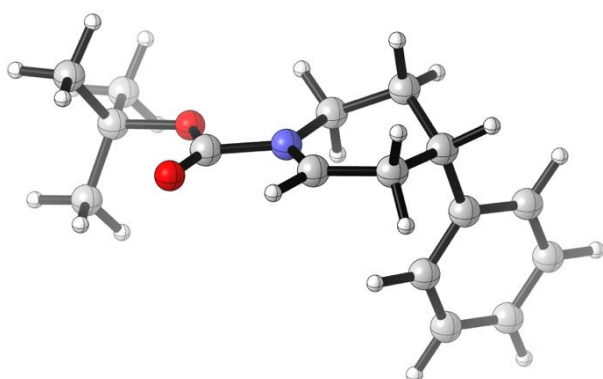
1 imaginary frequency

E = -827.944054

H = -827.568990

G = -827.633759

C1 (axial)



C	0.025754355738	-0.007572516180	1.219630979347
C	1.173008936232	-0.691199581459	1.957096552907
C	2.190007960186	-1.319970241068	0.976503921052
C	1.433571237555	-2.336959402641	0.103417460909
C	0.057719717379	-1.943959029269	-0.275887770462
N	-0.581493555078	-0.929713978072	0.214426267605
H	2.917672853897	-1.881225464963	1.571903499785
H	1.321573100201	-3.301233494226	0.628531892757
H	1.975691657096	-2.593662579044	-0.816854445606
H	-0.504135687595	-2.531439586633	-1.001254452547
H	1.661515770200	0.057677521443	2.587072759607
C	-1.973456956052	-0.687842900624	-0.316703446235
O	-2.433114561721	-1.459656431597	-1.114161695967
O	-2.439134727445	0.395188558386	0.227247802027

C	-3.844093689722	0.926461901366	-0.114553265391
H	0.770507719201	-1.463755558785	2.624982898604
H	0.364446069719	0.876293418328	0.669117134554
H	-0.774092495613	0.296317819847	1.893401728168
C	-4.862447183078	-0.127854956170	0.305710523918
H	-5.866865252425	0.284670681740	0.165219056583
H	-4.783405806771	-1.035986152832	-0.295364131157
H	-4.750756394545	-0.380256016810	1.364949382246
C	-3.876923887819	1.250994482236	-1.604162853769
H	-4.833552772616	1.731834073794	-1.832867532790
H	-3.079061408879	1.951616828237	-1.870227544182
H	-3.794252542030	0.353657019621	-2.220779290323
C	-3.915127041832	2.178029833910	0.751643316781
H	-4.882650922067	2.665025958124	0.596702986093
H	-3.825317336719	1.930491186619	1.813693143838
H	-3.128290252334	2.889425281183	0.483842695424
C	2.954361645709	-0.262949263192	0.186417786720
C	4.043851929076	0.370176168423	0.804902195718
C	2.605623586002	0.131347800231	-1.112286421248
C	4.757357405386	1.371113124679	0.149311058692
H	4.342508780601	0.068645455142	1.806814529016
C	3.319067446752	1.135939943939	-1.772637528489
H	1.785453265029	-0.349286542325	-1.642298494433
C	4.395220322633	1.758769570765	-1.143349967483
H	5.601868476875	1.842140347744	0.643593656907
H	3.036527179671	1.421059539356	-2.781848779817
H	4.954950059203	2.533669180777	-1.658262609362

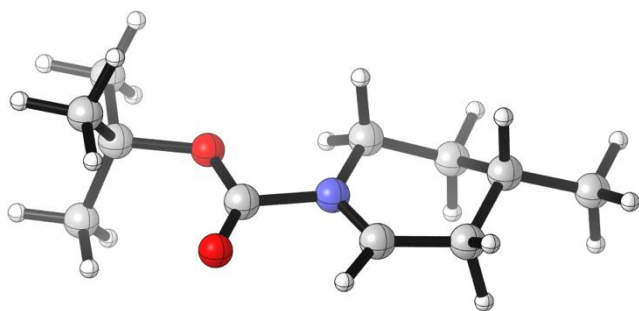
0 imaginary frequencies

E = -827.950390

H = -827.574353

G = -827.640861

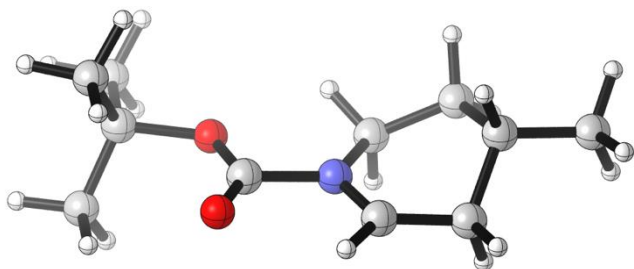
C2 (equatorial)



C	-1.066825608949	1.120341641434	0.004046430355
C	-2.527167677793	1.295312991725	0.414270145768
C	-3.459320468031	0.359132088304	-0.368727763692
C	-3.009039492695	-1.090836482186	-0.121146614163
C	-1.542156397868	-1.284738359994	-0.063641483415
N	-0.677553672871	-0.323045795548	-0.017654052082
H	-3.333037412161	0.568507750511	-1.440242140160
H	-3.405646746491	-1.791825525981	-0.869486029099
H	-3.398226452820	-1.475144143543	0.839091332117
H	-1.112876193696	-2.286181053429	-0.052697956567
H	-2.632309006185	1.111916473607	1.491919815732
C	0.781324439329	-0.724555204486	-0.001409374094
O	1.060432486618	-1.892184284266	0.012823867273
O	1.501842420048	0.354554281771	-0.014729552466
C	3.043713035064	0.294604542832	-0.011019051498
H	-2.798482114749	2.342441634181	0.244599990576
H	-0.383772308156	1.616003586066	0.693619177303
H	-0.867485829088	1.512133137080	-0.998518127072
C	-4.934252746853	0.555022354310	-0.005407360854
H	-5.258765612958	1.572988164815	-0.242302360334
H	-5.574836283260	-0.136616232678	-0.562663108546
H	-5.104455853241	0.387123811835	1.064865976701
C	3.489342765982	-0.425789352804	-1.278550809250
H	4.581636428442	-0.379498771543	-1.336950827712
H	3.196408097235	-1.477745251070	-1.276410228224
H	3.086433028657	0.063722949800	-2.170878067093
C	3.484577709099	-0.396557249038	1.274417527438
H	4.576778715819	-0.349665511036	1.335094688307
H	3.079659665166	0.114248686405	2.153867562228
H	3.190323766000	-1.447831148759	1.295923847366
C	3.404876404226	1.774646119986	-0.027000234940
H	4.494354697110	1.875896979170	-0.026427615428
H	3.017792908658	2.267376209232	-0.923846480661

H 3.015411310413 2.286963963293 0.857895876185
 0 imaginary frequencies
 E = -636.216332
 H = -635.896457
 G = -635.954971

C2 (TS)



C	-1.079112146074	1.081009599490	0.500002880323
C	-2.491459937009	1.390085329793	-0.066249297208
C	-3.369943948278	0.156022029575	-0.364076370004
C	-2.956109998081	-1.024757451607	0.558017018652
C	-1.514933227556	-1.299596452675	0.375336545125
N	-0.657237441940	-0.332362356622	0.298957343014
H	-3.172897597465	-0.170423457009	-1.392923050847
H	-3.535496600092	-1.930500344758	0.362419357092
H	-3.134391240649	-0.749138299028	1.610811558726
H	-1.104989491882	-2.300348106081	0.249134469974
H	-2.994593352444	2.027571729679	0.668379269120
C	0.789012631466	-0.714325284218	0.079666026628
O	1.058654242596	-1.874869336184	-0.068878635676
O	1.512894375768	0.362215846848	0.102782018322
C	3.044219569301	0.307479487523	-0.085450196314
H	-2.389596134188	1.984044209580	-0.978773132916
H	-1.044835548352	1.248215185513	1.581618738851
H	-0.311424697005	1.705957577333	0.051016340855
C	-4.865009328038	0.464060109040	-0.235623666644
H	-5.142898448186	1.289659538105	-0.898747278444
H	-5.473511717184	-0.403086111073	-0.511533648114
H	-5.123152939211	0.753064854073	0.789838553591
C	3.327255899361	-0.261786557913	-1.470953724169
H	4.405195054069	-0.205137166565	-1.654270894989
H	3.025331034625	-1.307913163557	-1.552849908343

H	2.825490228152	0.325099010108	-2.246793036779
C	3.628388240557	-0.524730635800	1.050508598426
H	4.720400368171	-0.479362817213	0.985914984704
H	3.334823413128	-0.121066480507	2.024680198100
H	3.330024193211	-1.573050576533	0.985461858955
C	3.415703936642	1.780966121091	0.024612433429
H	4.499202206820	1.885029198214	-0.087157541604
H	2.935002316091	2.371034006201	-0.761544895275
H	3.133837083676	2.189004765177	0.999888083441

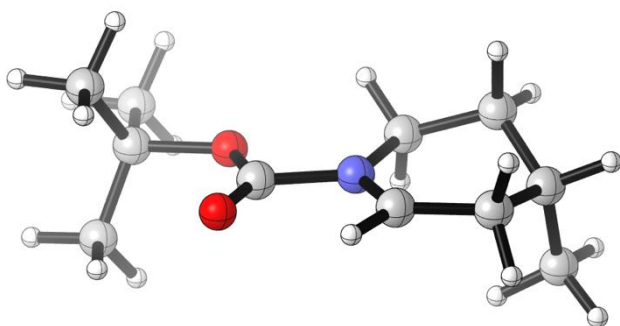
1 imaginary frequency

E = -636.208696

H = -635.889371

G = -635.946794

C2 (axial)



C	-1.219836722836	1.078650825075	-0.374570483905
C	-2.627694835133	1.214725952961	-0.953304374243
C	-3.623917466286	0.234413176115	-0.308172665227
C	-3.094881991586	-1.195481932603	-0.528038334063
C	-1.627539984119	-1.339479351989	-0.385663938049
N	-0.793787647025	-0.351748617182	-0.316140619280
H	-4.577246466362	0.320584888612	-0.839804070008
H	-3.327192617228	-1.570111845252	-1.540431310520
H	-3.563907043873	-1.928817209317	0.143120986664
H	-1.168469208155	-2.326837123960	-0.345316145033
H	-2.950872970735	2.249998526732	-0.804403914843
C	0.666199444464	-0.710313183679	-0.146416405008
O	0.980664835766	-1.868988992426	-0.134903784438
O	1.345746812491	0.388972252248	-0.029238839440
C	2.875895380460	0.371958873470	0.168493359769

H	-2.589157819941	1.048278289618	-2.037119662121
H	-1.143471167017	1.469468241188	0.644401291741
H	-0.479585822423	1.600286942273	-0.980973677956
C	-3.877720578673	0.523507197599	1.179708284353
H	-4.236292039346	1.548524579449	1.318227455773
H	-4.639887553369	-0.151254679192	1.582875023085
H	-2.975349217222	0.398616141393	1.791453329744
C	3.501217041528	-0.287862681364	-1.055461545494
H	4.590047316863	-0.207214277986	-0.973700758071
H	3.245843007286	-1.347207593365	-1.125483703880
H	3.197399033924	0.222519196058	-1.974949788337
C	3.173335761574	-0.353697797984	1.476010117938
H	4.246961846413	-0.278319826546	1.676874655188
H	2.644179055176	0.112651422968	2.313128973047
H	2.913571862368	-1.413099993397	1.425543920677
C	3.188330601576	1.861029722155	0.248087637711
H	4.264896831257	1.992084103098	0.393158985221
H	2.904710009883	2.375252464192	-0.675110384481
H	2.671510310300	2.329635311037	1.090847383486

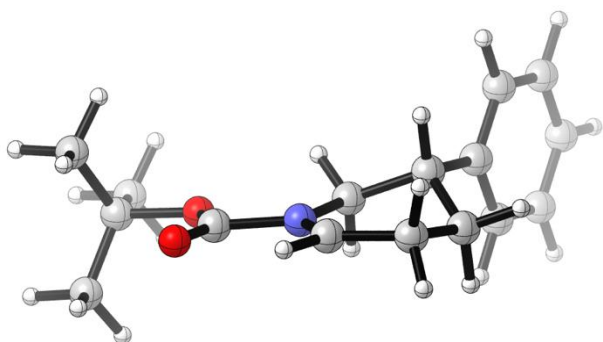
0 imaginary frequencies

E = -636.214309

H = -635.894322

G = -635.952616

C3 (equatorial)



C	0.312549910145	0.268867295578	-0.073157143066
C	1.644586665402	0.816552365792	-0.610681844140
C	1.944782915524	2.186015561616	0.025052433894
C	0.804267930352	3.168742886862	-0.267180996245
C	-0.546400248632	2.565506058711	-0.211311395821
N	-0.776045859422	1.296039528688	-0.113353376289

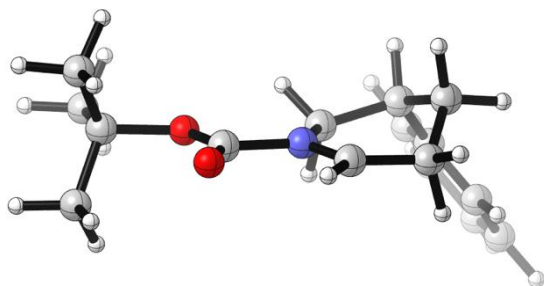
H	2.885905375088	2.583696870490	-0.363211731780
H	0.803691681215	4.036100150252	0.408327841140
H	-1.437249424084	3.191069013203	-0.255494455940
C	-2.227878884170	0.878104504552	-0.030532350400
O	-3.080061581588	1.720698468471	-0.107157865108
O	-2.273960178950	-0.408927493764	0.129248518165
C	-3.615344946479	-1.156627728980	0.262757232841
H	1.521719854617	0.967487028302	-1.691906406748
C	-4.402781066980	-0.946635982150	-1.025820149810
H	-5.307620631875	-1.561592452622	-0.982572600424
H	-4.707712804258	0.093947941995	-1.154002497414
H	-3.822852529841	-1.267152017361	-1.897112380552
C	-4.325481643650	-0.633197264422	1.506378169445
H	-5.225004452308	-1.235462146500	1.670135124052
H	-3.690644662064	-0.733902269871	2.392417841459
H	-4.632678820670	0.408672418959	1.394861804142
C	-3.144476291261	-2.596370137395	0.426920068165
H	-4.017187508257	-3.247965495483	0.532001520365
H	-2.574793140555	-2.928386819761	-0.446222562242
H	-2.524114112244	-2.710502332180	1.320807162006
H	2.069036638558	2.079876190717	1.108608742264
H	-0.035200864161	-0.579148667077	-0.662494848949
H	0.889590712767	3.613948995368	-1.273611969377
H	0.395544957461	-0.062984241962	0.965980530002
C	2.745596456505	-0.213161632631	-0.406739259660
C	3.343521762005	-0.824143225971	-1.515771508831
C	3.177919685624	-0.572078632100	0.878429510696
C	4.355274041741	-1.770475662581	-1.347537370107
H	3.020907403380	-0.555321638789	-2.519247980807
C	4.188407617680	-1.518358090270	1.048139484537
H	2.734894960987	-0.111166018871	1.759089109406
C	4.779460860987	-2.119533750712	-0.065003773233
H	4.811448393843	-2.231930058250	-2.218361077600
H	4.515417439020	-1.783655795516	2.049229919209
H	5.567505388548	-2.854760724339	0.067677532757

0 imaginary frequencies

E = -827.951768

H = -827.575720

G = -827.642924

C3 (TS)

C	1.344400138405	0.817488479400	0.024918180380
C	2.841235681933	0.956055440284	0.476687377154
C	3.502287595344	-0.401256689791	0.795296793059
C	3.026990968402	-1.545124120319	-0.118496390390
C	1.551363793023	-1.622902700887	-0.133571622062
N	0.804534956467	-0.572840458226	-0.025351519031
H	3.271347369473	-0.684709408041	1.827819484385
H	3.351287035505	-1.387183930536	-1.160041424827
H	1.013987160596	-2.566074795228	-0.220076636633
C	-0.692303169028	-0.808489903679	-0.051285230964
O	-1.097729789434	-1.936280459512	-0.122927816966
O	-1.293273800337	0.339735615807	0.008991848563
C	-2.831624074407	0.445008247242	0.000744512952
H	2.808988895932	1.508801412266	1.421220729858
C	-3.361697190399	-0.286213430348	1.229108848008
H	-4.442822875699	-0.123777823877	1.288569143383
H	-3.184585392385	-1.362259677832	1.174014860859
H	-2.914044171473	0.110661170088	2.145851942114
C	-3.335773301033	-0.127443187841	-1.319594586701
H	-4.415997351730	0.040453597103	-1.379438720578
H	-2.871407280262	0.381249959770	-2.170393271553
H	-3.157132942508	-1.201990215271	-1.396058679464
C	-3.032954986213	1.952539687552	0.091797747966
H	-4.105358249224	2.169704292532	0.087755128843
H	-2.608195605264	2.353869036489	1.016862572638
H	-2.578391886966	2.464606203467	-0.761480151232
H	4.589034462607	-0.309192882180	0.731845949454
H	0.675454724256	1.373703836774	0.678925471357
H	3.433632869943	-2.516061833868	0.180859164596
H	1.214547944867	1.216904725641	-0.984886142221
C	3.595845860715	1.840523673555	-0.516310093475

C	3.381742438666	3.226305184205	-0.465094042190
C	4.469155948547	1.336997873008	-1.488527689650
C	4.013750175455	4.083992317332	-1.364593383998
H	2.726823480478	3.642703570571	0.298059551152
C	5.106889097061	2.194145202308	-2.388370540631
H	4.685158055095	0.273819597097	-1.548077700082
C	4.878142095708	3.568629147509	-2.332143140025
H	3.840818306895	5.154307078398	-1.300942798369
H	5.786734205923	1.784082216953	-3.129501305047
H	5.377304315065	4.234299822086	-3.029765330630

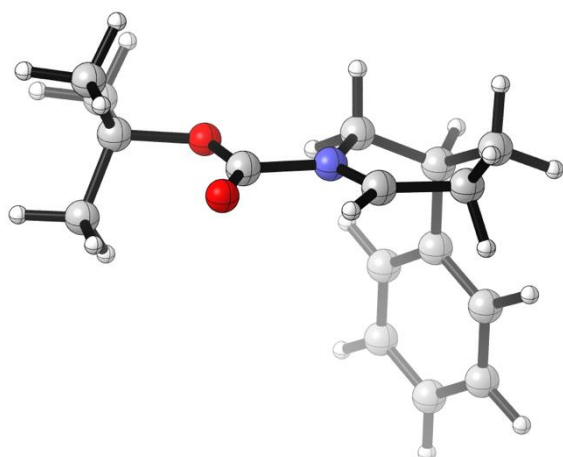
1 imaginary frequency

E = -827.939885

H = -827.939885

G = -827.628297

C3 (axial)



C	0.191844944326	0.352873448071	-1.362480743163
C	1.704981857313	0.635200639541	-1.427029998175
C	1.906142154628	2.162452385368	-1.449942478377
C	1.256114405291	2.842576282727	-0.234932820525
C	0.021081352812	2.189311426101	0.246965555738
N	-0.464538085442	1.096229049604	-0.244564936963
H	1.452271217396	2.558249141052	-2.365160339257
H	1.922217285134	2.885622845395	0.640529843003
H	-0.549992906301	2.619098052859	1.068925742480
C	-1.760319358778	0.605090930499	0.357453348315
O	-2.242418265053	1.215763773906	1.272195281399
O	-2.139417357554	-0.456266906684	-0.287174260906

C	-3.444114099947	-1.192442547379	0.072573012228
H	2.019225003940	0.249433032224	-2.405896954208
C	-4.605238244175	-0.229931359320	-0.151488229969
H	-5.541991436973	-0.775436053300	0.002145629208
H	-4.583513109311	0.606811513814	0.549661147542
H	-4.606086997956	0.152800914598	-1.177059198647
C	-3.327704477867	-1.687422817184	1.509979856260
H	-4.201758954783	-2.307502033252	1.734327204237
H	-2.435371340428	-2.307887569406	1.640453666531
H	-3.305257035328	-0.863457895737	2.225997715739
C	-3.436344588439	-2.334683270319	-0.935995626614
H	-4.333590793091	-2.944313467233	-0.792519671372
H	-3.442314922174	-1.956364356078	-1.962568205956
H	-2.562619948429	-2.978841635477	-0.798158680405
H	2.966538185297	2.420729782146	-1.496907977957
H	-0.313442998562	0.661986378119	-2.283391846867
H	1.006451192721	3.896298136906	-0.431002621965
H	-0.028548080619	-0.698600495979	-1.199536896873
C	2.490309697784	-0.128752951853	-0.352304314073
C	2.314448797725	-1.517825734802	-0.235094138695
C	3.434658125332	0.484219309330	0.480856364096
C	3.033981259201	-2.261013709080	0.698219744215
H	1.628313605344	-2.040167238787	-0.898543907734
C	4.157907319307	-0.257360162654	1.419339666765
H	3.645606057631	1.545689312278	0.396586021543
C	3.955241659056	-1.630437615504	1.537212353379
H	2.883410011534	-3.334776115538	0.761906733154
H	4.885218142580	0.243954957002	2.051176510434
H	4.518361726858	-2.207422375975	2.264425452431

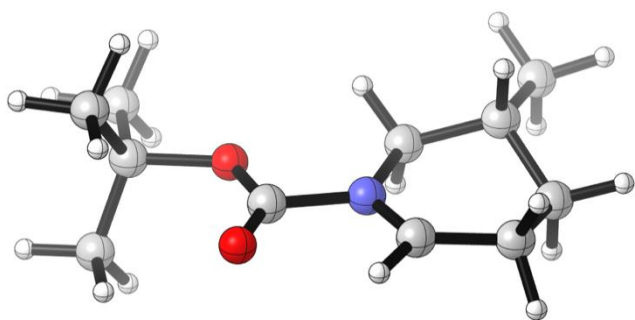
0 imaginary frequencies

E = -827.946431

H = -827.946431

G = -827.946431

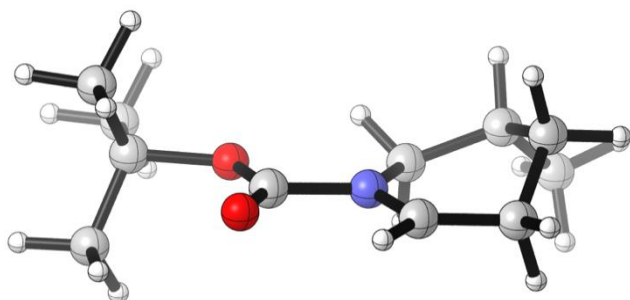
C4 (equatorial)



C	1.338442716751	0.764192643883	-0.009664186169
C	2.805211940740	0.793648101755	0.433098474890
C	3.594119485897	-0.301394277769	-0.298580538603
C	2.982069304184	-1.679991480708	-0.023106901884
C	1.502397787170	-1.684458424184	0.020562005259
N	0.768833461857	-0.618738796293	0.016472932956
H	4.641297005475	-0.296157702273	0.016968229200
H	3.291670304224	-2.440906814281	-0.753426806284
H	0.948890892819	-2.621885829755	0.063336371828
C	-0.730032289096	-0.832257513084	0.026236102501
O	-1.154579697720	-1.954100738267	0.078487904006
O	-1.308858527065	0.327217607159	-0.036689478078
C	-2.846333339354	0.459396677342	-0.060469742185
H	2.831996676486	0.578224949094	1.511265927461
C	-3.389313666158	-0.121078366041	1.240517435354
H	-4.467520961863	0.065486860816	1.278890806600
H	-3.230983534947	-1.199475919958	1.305081977315
H	-2.935446930848	0.367434701251	2.108622699262
C	-3.359744321755	-0.249121155841	-1.309003607895
H	-4.436902442538	-0.070622509597	-1.389775784391
H	-2.886586922301	0.151904765414	-2.210958364330
H	-3.199506539335	-1.328282060254	-1.262805969838
C	-3.019806428883	1.970880366655	-0.138348659235
H	-4.088143935380	2.206271244942	-0.163193429069
H	-2.583547412247	2.465347854994	0.734803456560
H	-2.560764288671	2.376448506965	-1.044854338592
H	3.587942736386	-0.103430713325	-1.377961916486
H	0.707721502200	1.370974199000	0.640075790500
H	3.309170140786	-2.091303473931	0.947539337493
C	3.387680717934	2.193303086202	0.201944956736
H	2.808073679362	2.960793915275	0.725794323545
H	4.415505811964	2.242402894847	0.573926296387
H	3.403578561665	2.446299663434	-0.864587464693

H 1.214449512260 1.135911736531 -1.032819840119
 0 imaginary frequencies
 E = -636.216270
 H = -635.896331
 G = -635.954871

C4 (TS)



C	-1.091441727158	1.058035885696	0.449278266626
C	-2.545545195649	1.427127264510	0.016010874861
C	-3.360460399016	0.209729960409	-0.465420626696
C	-2.989981688437	-1.074709854107	0.306471512109
C	-1.538938623402	-1.322626640143	0.161561786873
N	-0.685789568011	-0.349481327254	0.172004128700
H	-3.188561043607	0.028564961753	-1.531918032812
H	-3.214001258833	-0.956842991750	1.379366183510
H	-1.115255294474	-2.312872059006	0.002026861231
C	0.770281982552	-0.722483904981	-0.016369459083
O	1.046675749350	-1.873863809257	-0.214332568644
O	1.490959654394	0.351230278675	0.085610237162
C	3.028060255425	0.306694906193	-0.055481559421
H	-2.455180760646	2.113823877668	-0.832126452265
C	3.357125122826	-0.194278275325	-1.457164975467
H	4.440616689017	-0.131088785830	-1.601504135655
H	3.058009516955	-1.234576312589	-1.600921591539
H	2.882045606117	0.430971482650	-2.219760636650
C	3.576214142827	-0.579648869622	1.057181057004
H	4.669706770286	-0.531114446569	1.030436542705
H	3.250640478187	-0.223433216050	2.039686868653
H	3.281518877698	-1.623445263560	0.931580768839
C	3.392608418688	1.773059173544	0.138313095611
H	4.478631139329	1.883380658347	0.063102489768
H	2.933759362282	2.401068097237	-0.631347027037

H	3.081810076540	2.131688074552	1.124090867230
H	-4.429849806971	0.404350816459	-0.345675293920
H	-0.351774855468	1.692211148285	-0.033988335422
H	-3.548259325059	-1.950690543265	-0.033805456200
C	-3.244860640126	2.177963870200	1.160334814059
H	-2.646925865019	3.029320316549	1.503516304246
H	-4.211495857522	2.566766339679	0.826332002234
H	-3.422975948954	1.525714475793	2.024780502674
H	-0.969243804116	1.186126241109	1.530555126716

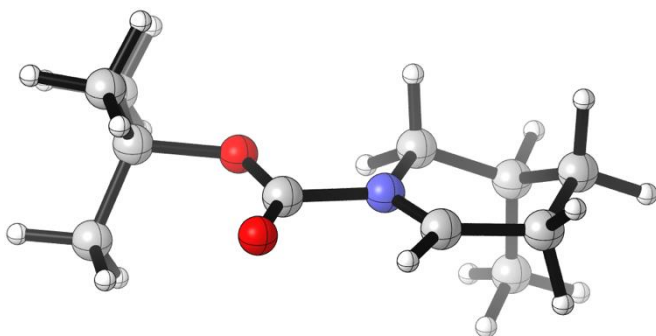
1 imaginary frequency

E = -636.207129

H = -635.887930

G = -635.945242

C4 (axial)



C	1.296603570671	0.925077515673	0.558927545792
C	2.795072421524	1.138618825882	0.301032201717
C	3.584015455206	-0.057964903871	0.863082694352
C	3.111493760825	-1.371912381039	0.226535638914
C	1.651870855392	-1.437933999912	-0.008075017740
N	0.843814944311	-0.437691415591	0.136100988793
H	3.446794733953	-0.114138018752	1.949297827313
H	3.579290959266	-1.557726660269	-0.754984441708
H	1.180912616688	-2.365206533533	-0.332843318314
C	-0.622482211633	-0.714171527488	-0.120926797840
O	-0.949381080052	-1.810120493448	-0.486345569775
O	-1.293579701785	0.367055286974	0.131836339519
C	-2.828887141367	0.416849197149	-0.016240392125
H	3.068418262376	2.029419047377	0.878643049759
C	-3.427455504025	-0.589124816794	0.960438414971
H	-4.517562412223	-0.490346334608	0.934329802345

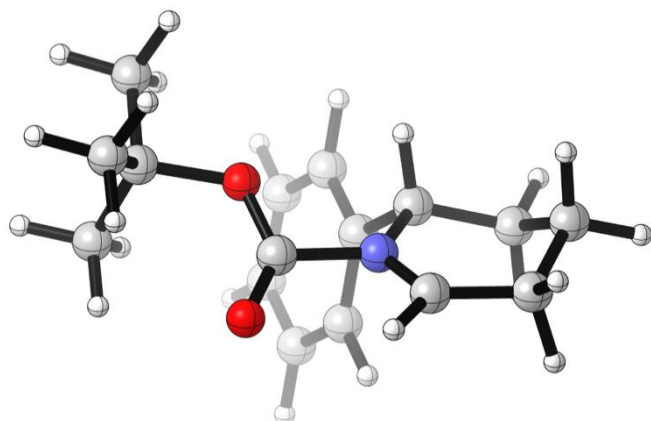
H	-3.175857908619	-1.617800626002	0.694387548241
H	-3.098400907682	-0.385592337928	1.984394141631
C	-3.172019901737	0.135030324569	-1.474808711575
H	-4.249507574128	0.275056894021	-1.609513828002
H	-2.659087050296	0.835402572492	-2.141600160478
H	-2.926735165062	-0.888915658564	-1.764226524676
C	-3.124798267177	1.857382273381	0.381336992290
H	-4.203888755551	2.028860727291	0.322799939603
H	-2.803124014430	2.058908486273	1.407405599242
H	-2.631304388766	2.564069206381	-0.292664985085
H	4.655450261328	0.070055230548	0.686195721311
H	1.042881011626	1.019020138849	1.619674957612
H	3.388110072414	-2.253698799086	0.821860932389
C	3.096434336247	1.420966871241	-1.180242255368
H	2.574175175259	2.321265056019	-1.519902529059
H	4.168559613258	1.586081752097	-1.326029222710
H	2.796208472131	0.598584698693	-1.840689930636
H	0.683446462058	1.637374401978	0.007391349297

0 imaginary frequencies

E = -636.213751

H = -635.893765

G = -635.952439

C5 (equatorial)

C	1.123980556411	-0.812675419547	0.762865818159
C	2.432420645405	-1.617033218956	0.863051316023
C	2.196204674064	-3.124184561842	0.971915821858
C	1.443477071985	-3.604030623628	-0.273175441846
C	0.336538858248	-2.695434011824	-0.659215485617
N	0.159466405615	-1.507966334925	-0.178510278598
H	1.611901984342	-3.360053709450	1.869584860310
H	1.016158040081	-4.609334614813	-0.159087377135
H	-0.412424612366	-3.017104079612	-1.381973298499
H	3.052103213867	-1.398321910988	-0.014835319309
C	-1.112041369751	-0.806479878231	-0.611928061832
O	-1.588356662824	-1.082851156752	-1.678557222348
O	-1.491567848827	-0.024268265198	0.350521712442
C	-2.734374248703	0.870854326298	0.211393005365
H	2.978099602124	-1.234839141641	1.730879646050
H	0.609273651608	-0.800557353494	1.727801327632
C	-3.953974311333	-0.029738135375	0.045861755210
H	-4.851897176179	0.596658047379	0.057835994334
H	-3.934665458075	-0.574686351327	-0.900079783638
H	-4.031835692808	-0.740467989431	0.874840723814
C	-2.505126212257	1.814709078547	-0.964464341293
H	-3.328832128842	2.535425520647	-0.996328276758
H	-1.571545528747	2.372235238375	-0.841044714899
H	-2.486532703009	1.282084464784	-1.917787172273
C	-2.735691694342	1.602334068572	1.548360570607
H	-3.592519487120	2.282058873780	1.583324628566
H	-2.824378732992	0.899474089941	2.382339626337
H	-1.823585736647	2.192535773091	1.674187246696
H	3.146259353777	-3.657692055790	1.060973949589

H	2.108542678671	-3.682729878201	-1.149696695614
C	1.367673341635	0.613949630593	0.301900544873
C	1.290364588417	1.657346067965	1.231489074201
C	1.729896028929	0.896621108548	-1.021933519998
C	1.573659148519	2.967402335403	0.843826765265
H	1.012309699579	1.446268414223	2.261336925020
C	1.996659215851	2.209535146181	-1.412354364971
H	1.804761398728	0.098548831168	-1.757538916872
C	1.921149734967	3.246227027226	-0.479950142749
H	1.520601364184	3.768883389216	1.574619917004
H	2.270228822076	2.419876546716	-2.441880077237
H	2.136845525739	4.266407712374	-0.782717737870

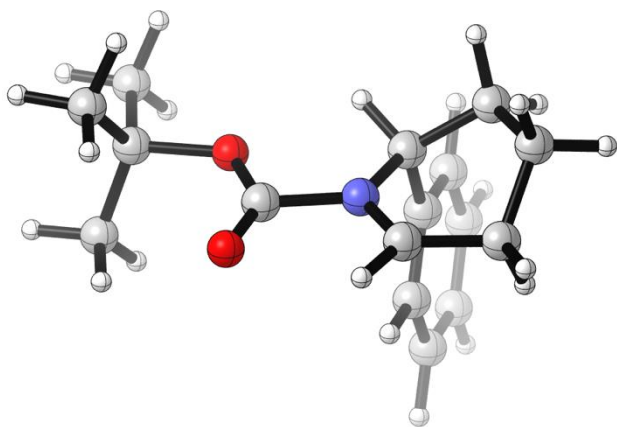
0 imaginary frequencies

E = -827.950776

H = -827.574869

G = -827.641063

C5 (TS)



C	-1.396528137570	1.056192724126	-0.007839380656
C	-2.690732924757	1.249808830912	-0.866117745247
C	-3.630280086906	0.027371166213	-0.944621959791
C	-3.342334586056	-1.005925564004	0.169694974443
C	-1.895639669931	-1.316381815303	0.180922568335
N	-1.007605542322	-0.382728711804	0.051374650285
H	-3.516934522493	-0.475652732185	-1.909984967720
H	-3.919584466047	-1.925273867623	0.046921074990
H	-1.501156972625	-2.327728526444	0.265989531151
H	-3.218788332051	2.105548547675	-0.440202980231
C	0.440527307215	-0.814712617734	0.073254282010

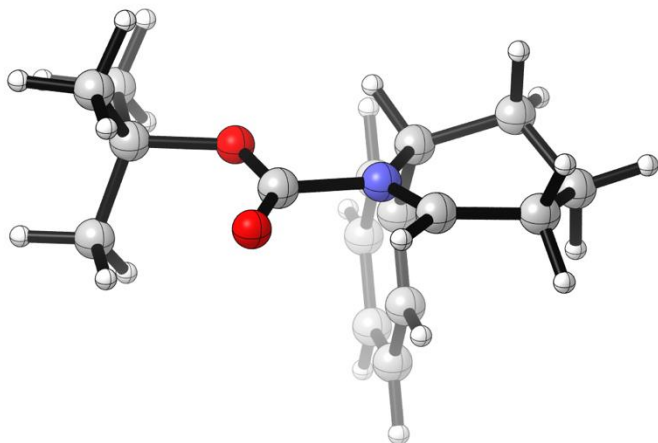
O	0.689606465487	-1.977067910726	0.246853541285
O	1.192551702358	0.224928331326	-0.116353777793
C	2.729121989988	0.118784687519	-0.117776319806
H	-2.390874872884	1.534184784654	-1.878723890449
H	-0.568918830905	1.544589576951	-0.519848204103
C	3.139439565816	-0.797875642929	-1.264842171762
H	4.231831049556	-0.792774067733	-1.338414789494
H	2.816125952377	-1.827723686255	-1.100665119937
H	2.738988719613	-0.437291390349	-2.217687701263
C	3.166128345430	-0.382065898099	1.254544805952
H	4.259551916097	-0.352650859743	1.302261643277
H	2.778326909978	0.263997166671	2.048449509380
H	2.848023187079	-1.411055339333	1.434243549953
C	3.133212628082	1.567896606318	-0.360081425164
H	4.225193796678	1.636364290460	-0.376703513087
H	2.755435167207	1.928402920308	-1.321702572946
H	2.762230876130	2.220011155852	0.436228973471
H	-4.675404797822	0.338027071020	-0.873060672067
H	-3.605875364244	-0.582973924852	1.151057517147
C	-1.481844390344	1.649369213659	1.404934665768
C	-1.563886521235	3.047106648798	1.498870266813
C	-1.469191526134	0.893635079993	2.581152771178
C	-1.655099465867	3.670789387459	2.740907185239
H	-1.553966415347	3.654044674511	0.596303641662
C	-1.559272695631	1.520966147447	3.827792535766
H	-1.378412988762	-0.188929735004	2.556787452741
C	-1.656152075914	2.907978300291	3.911552668175
H	-1.719675525072	4.753443244854	2.793931801841
H	-1.549862204600	0.917721200339	4.730683516642
H	-1.725517783569	3.393554362760	4.880042104014

l imaginary frequency

E = -827.942131

H = -827.566711

G = -827.632432

C5 (axial)

C	0.843355382779	-0.789647365689	0.907249765212
C	1.887981432217	-1.796118036232	1.429121200873
C	2.644084151842	-2.480559513225	0.288623731085
C	1.648017742108	-3.207086342856	-0.621585276217
C	0.360979364216	-2.496474441413	-0.806313060617
N	-0.009537822352	-1.450919099599	-0.138845002410
H	3.373484182277	-3.193775015288	0.681169970859
H	1.376440415437	-4.200407891100	-0.223478580357
H	-0.362981707355	-2.851154225096	-1.539059268549
H	2.574223041592	-1.250336827460	2.082346553402
C	-1.363318506159	-0.875174998244	-0.495169286402
O	-1.949208904095	-1.321580834286	-1.444102422515
O	-1.660763833330	0.049697811295	0.363801118763
C	-2.959145477133	0.866552346937	0.249826787756
H	1.380669688630	-2.546813232607	2.049289192271
H	0.150281584460	-0.549528806480	1.714763333391
C	-4.136096574676	-0.090539573868	0.404020984167
H	-5.060096744268	0.496440313988	0.426009869647
H	-4.201990153562	-0.793634050904	-0.428805858826
H	-4.070204815407	-0.645282771250	1.345378960967
C	-2.938338870031	1.601485222485	-1.086266268902
H	-3.798701165903	2.277602841948	-1.123535821358
H	-2.031255637202	2.205838208170	-1.185557399996
H	-3.012184846277	0.914704686884	-1.932001601170
C	-2.825192104952	1.816568427674	1.433863318311
H	-3.700940272129	2.471753806525	1.467835250895
H	-2.775929850794	1.266093145710	2.378356243008
H	-1.932523189850	2.441830364002	1.338441561917
H	3.202207459412	-1.736338073452	-0.289076268620

H	2.053384023295	-3.422126254082	-1.620257232756
C	1.424438870993	0.511329825578	0.369034322534
C	1.589143779861	1.575044731589	1.267237406486
C	1.843482923346	0.669279346318	-0.957833464586
C	2.178878037141	2.767209914983	0.850912901783
H	1.260381736148	1.468364463134	2.298552363846
C	2.427004770103	1.867762367936	-1.376158862887
H	1.711285152611	-0.128639323399	-1.684333703166
C	2.598371117999	2.916665698079	-0.473338906542
H	2.305079190698	3.580986952812	1.558733218637
H	2.744696222415	1.978021025032	-2.408638599487
H	3.052166205896	3.847492175450	-0.799558170447

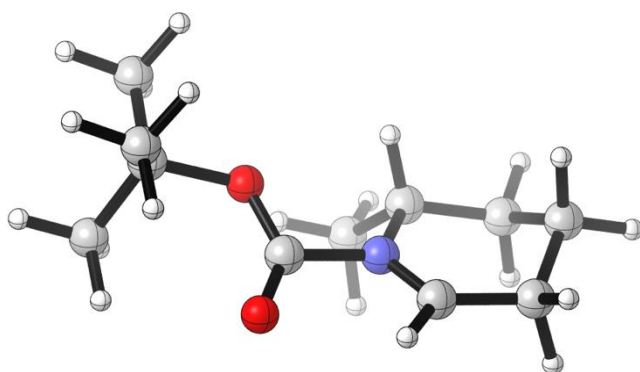
0 imaginary frequencies

E = -827.952556

H = -827.576636

G = -827.643854

C6 (equatorial)



C	-1.473436100426	1.084551878025	0.016386150798
C	-2.998880573343	1.202473754450	-0.147189659170
C	-3.612525163671	0.089385471742	-0.995910985290
C	-3.291888833238	-1.261770506936	-0.348924087262
C	-1.861947635551	-1.371625574397	0.025865249499
N	-1.052540068449	-0.366336924685	0.126873397538
H	-3.212056010229	0.111902627908	-2.016568296514
H	-3.529628064551	-2.118111197263	-0.992843765441
H	-1.407649135443	-2.345907400037	0.201877265312
H	-3.464559953717	1.199135121559	0.846833556472
C	0.406173171249	-0.732936531574	0.326054533349
O	0.675468908329	-1.809438383483	0.783221619954

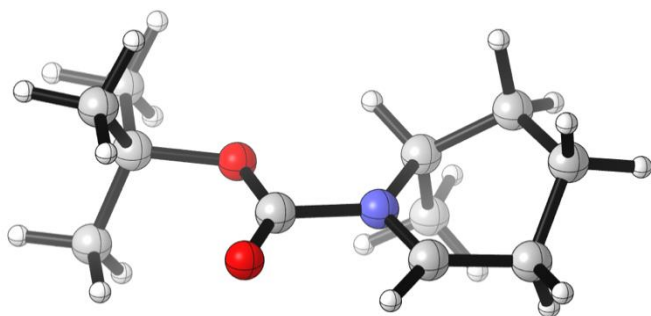
O	1.141146410769	0.243205941208	-0.114691244344
C	2.682009619166	0.151676792644	-0.114813410300
H	-3.202081275902	2.185766819648	-0.582790081717
H	-0.957724985090	1.451206168550	-0.875410516694
C	3.083408617739	-1.008416151388	-1.019195816789
H	4.174021277293	-1.011226883038	-1.115369943316
H	2.779129900600	-1.973057217823	-0.607888522113
H	2.660749181905	-0.888510296958	-2.021844818416
C	3.149902104295	-0.007590391635	1.327487328870
H	4.244180253047	0.027771535147	1.341467164911
H	2.783174773559	0.811481531641	1.954506783872
H	2.837341010604	-0.961632581242	1.756608884990
C	3.066485531901	1.502856605167	-0.704728810062
H	4.156829719740	1.565058005526	-0.772585355174
H	2.655121695913	1.626683603647	-1.710890823876
H	2.718383327973	2.326243239976	-0.073764053083
H	-4.695156900294	0.217693541334	-1.074178250351
H	-3.883108798395	-1.424421228288	0.567966710096
C	-1.002466726245	1.859451479630	1.253339302384
H	-1.429554897575	1.433778044656	2.167443676800
H	0.083548604370	1.889101382302	1.342373469904
H	-1.361181986336	2.889621723986	1.164769345161

0 imaginary frequencies

E = -636.213410

H = -635.893441

G = -635.951698

C6 (TS)

C	-1.002669416476	1.171784629179	0.256604588599
C	-2.350079201544	1.403171781135	-0.480347120562
C	-3.317545366818	0.196048300220	-0.516876326449
C	-2.895766899992	-0.954384386984	0.428305441633
C	-1.447257516936	-1.228580913259	0.293119851511
N	-0.586723590408	-0.269449262813	0.171033895192
H	-3.363414823758	-0.209855636465	-1.531761750407
H	-3.461606751079	-1.870256166598	0.239908062301
H	-1.034163851085	-2.235775583361	0.265937042939
H	-2.826714821095	2.259361840461	0.005504432000
C	0.862173677532	-0.676583535164	0.026020104518
O	1.130607004632	-1.846572973537	-0.006744081839
O	1.595188782979	0.393322208791	-0.036172104463
C	3.127360382199	0.310466082605	-0.199073891555
H	-2.132739102083	1.713276901756	-1.506239259574
H	-0.214555598019	1.719914075481	-0.255433147362
C	3.424461946076	-0.395435113404	-1.517436809477
H	4.504423813934	-0.358035483493	-1.693655263632
H	3.121778517170	-1.444250792815	-1.498380550049
H	2.932443741050	0.111573449879	-2.353580157473
C	3.692034096935	-0.407258097028	1.021637470389
H	4.785036477222	-0.378748134657	0.964918661601
H	3.392890598652	0.095938993802	1.946646266953
H	3.382954649520	-1.453758688960	1.059998406917
C	3.509043404404	1.784991184826	-0.233337095272
H	4.594364328205	1.870005184599	-0.343703039552
H	3.040611255040	2.296372063876	-1.079744444968
H	3.220806429723	2.290614707246	0.693160851252
H	-4.333754151871	0.502687444271	-0.258338514646
H	-3.088730360444	-0.681794495234	1.477709807024
C	-1.008352415997	1.596942580965	1.732724696390

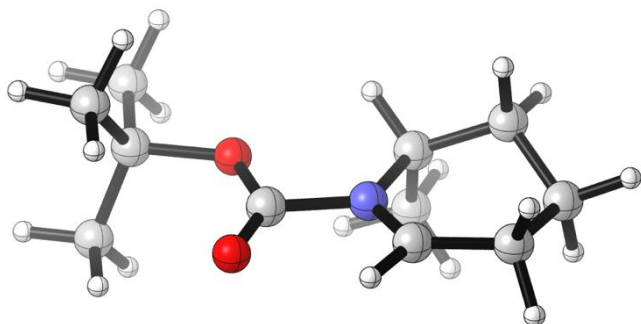
H	-1.779677237746	1.081588566611	2.313475736880
H	-0.036025595454	1.411765705633	2.198202534428
H	-1.208708404468	2.670984562438	1.787604706753

1 imaginary frequency

E = -636.208822

H = -635.889329

G = -635.946476

C6 (axial)

C	-1.409022020951	1.023009635186	-0.231318066058
C	-2.791266532039	1.052858918310	-0.899731386614
C	-3.811155296791	0.181597708213	-0.158122117575
C	-3.300562893695	-1.262382777749	-0.078686583884
C	-1.831641391812	-1.392305660090	0.054711141477
N	-0.989449668744	-0.412385615626	-0.023763974339
H	-4.776996642040	0.202086309061	-0.669551025466
H	-3.556621139158	-1.841268721609	-0.983161125965
H	-1.381942826605	-2.372633903999	0.208649515408
H	-3.124712605151	2.094318188640	-0.937280558486
C	0.472608883434	-0.784897256280	0.108155173362
O	0.758581055996	-1.921927662346	0.368009094768
O	1.195771252592	0.271412518178	-0.109335292645
C	2.736834206429	0.213682945106	-0.067097698568
H	-2.696005820569	0.713462567813	-1.939010829452
H	-0.662170118896	1.430653736918	-0.913529914788
C	3.202889786508	-0.754977369529	-1.148484407816
H	4.295943207399	-0.717094211338	-1.198764847141
H	2.910514627222	-1.784049637968	-0.930276563646
H	2.813960842108	-0.464977031996	-2.129737135123
C	3.155426458247	-0.193441942223	1.341254292713
H	4.246480282944	-0.132773243454	1.409501784735
H	2.736850181447	0.488393725955	2.088507268798
H	2.859047805734	-1.217680818832	1.576188480303
C	3.103689803104	1.657468745285	-0.386760335840
H	4.193452001573	1.756183309393	-0.389352426283
H	2.733222918250	1.951021947419	-1.373531170454
H	2.702138243708	2.344664474508	0.364054092209
H	-3.983847887289	0.568461254267	0.851462869143
H	-3.758541635485	-1.836251735163	0.739634259464
C	-1.332790309469	1.773064578890	1.104013216210

H	-2.049795046080	1.384008772052	1.833339689775
H	-0.330954180254	1.715940426720	1.536416189259
H	-1.561648541667	2.828421826289	0.927884392519

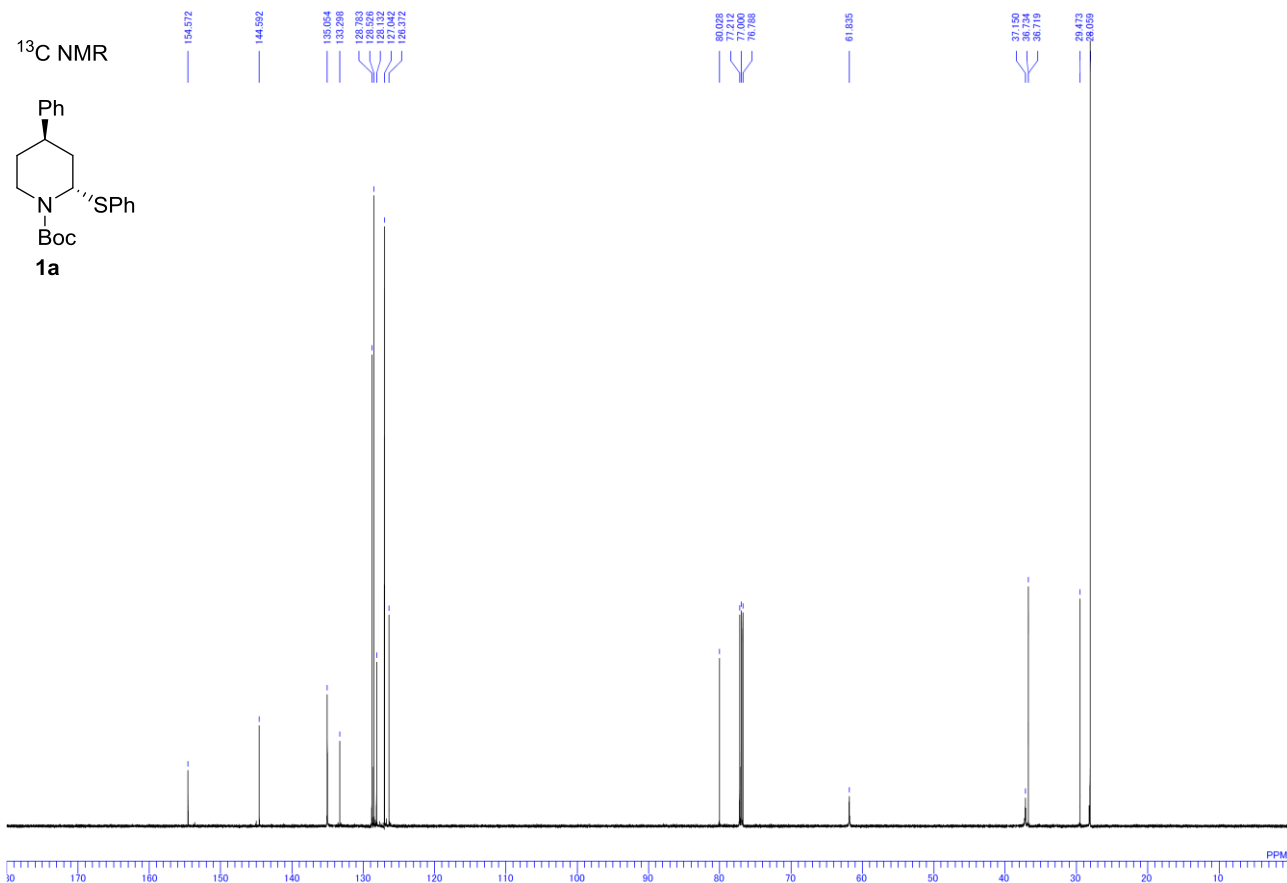
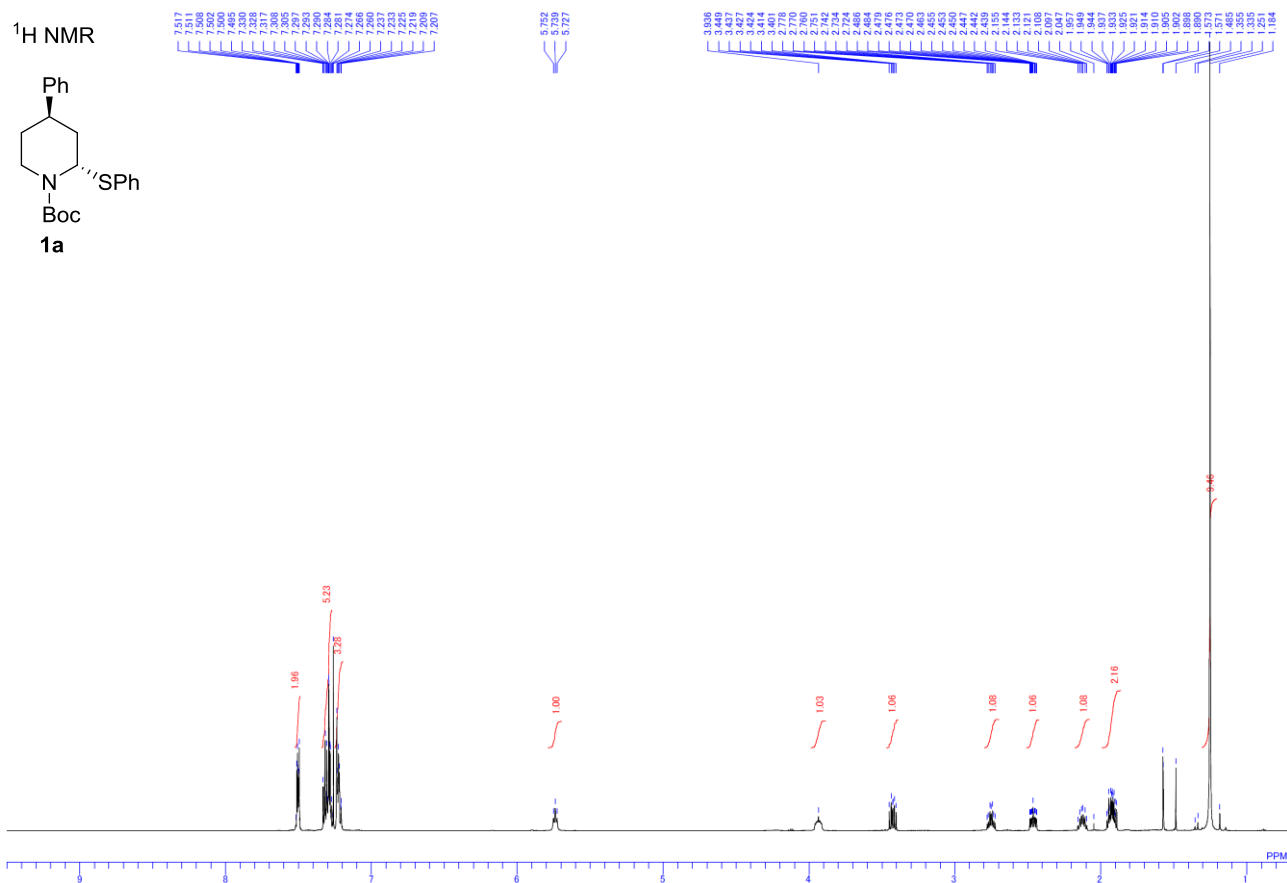
0 imaginary frequencies

E = -636.216746

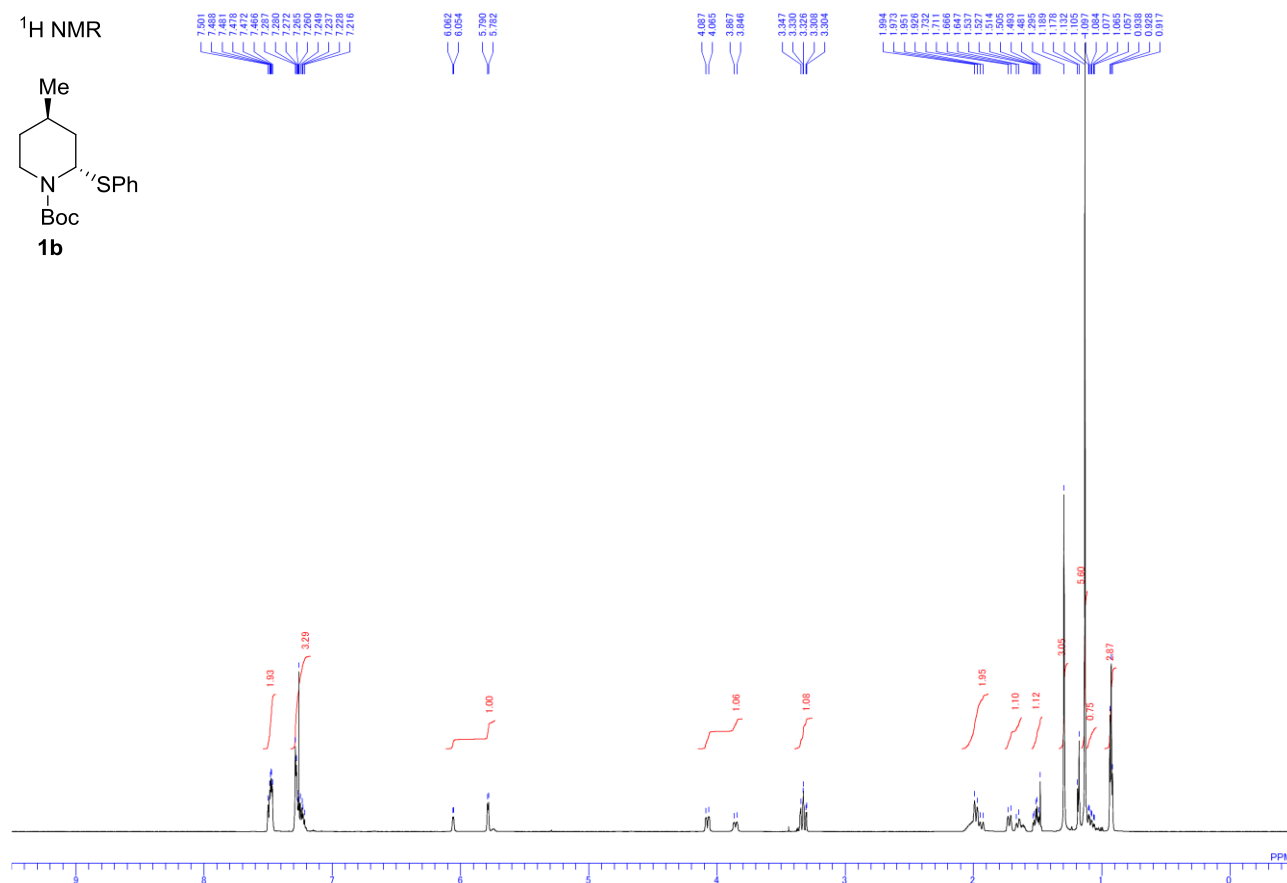
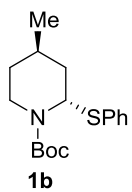
H = -635.896753

G = -635.954832

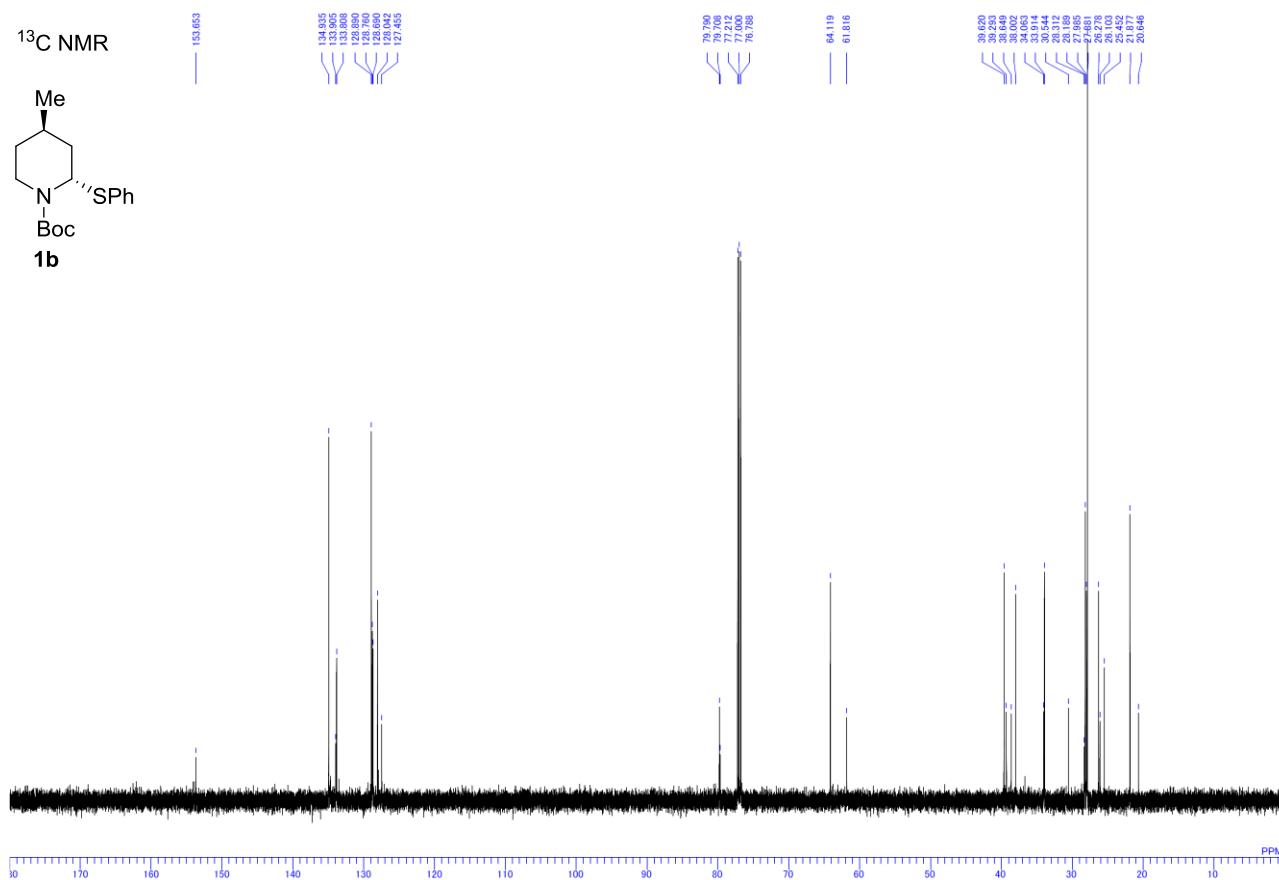
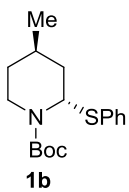
NMR spectra of products and *N*-acyliminium ions

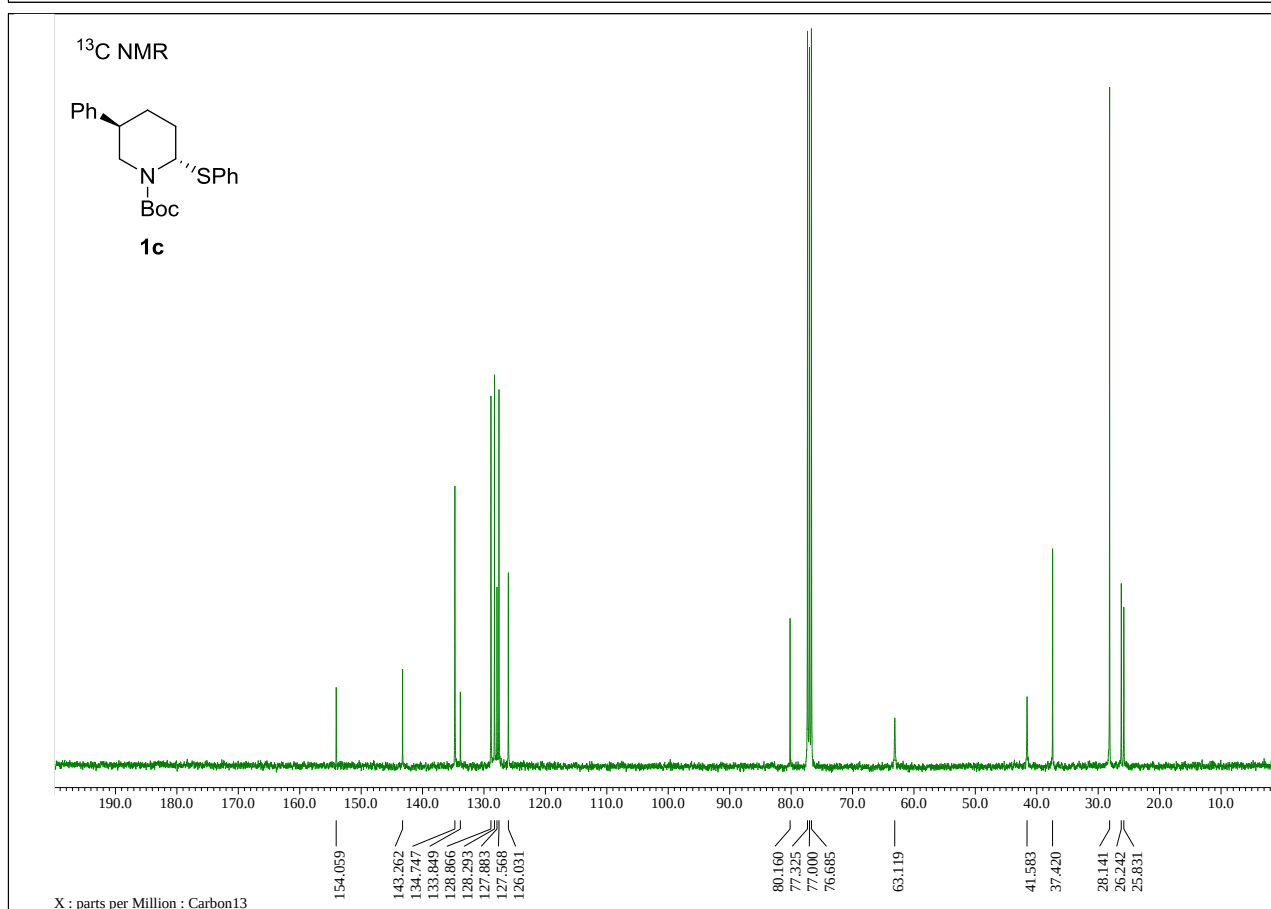
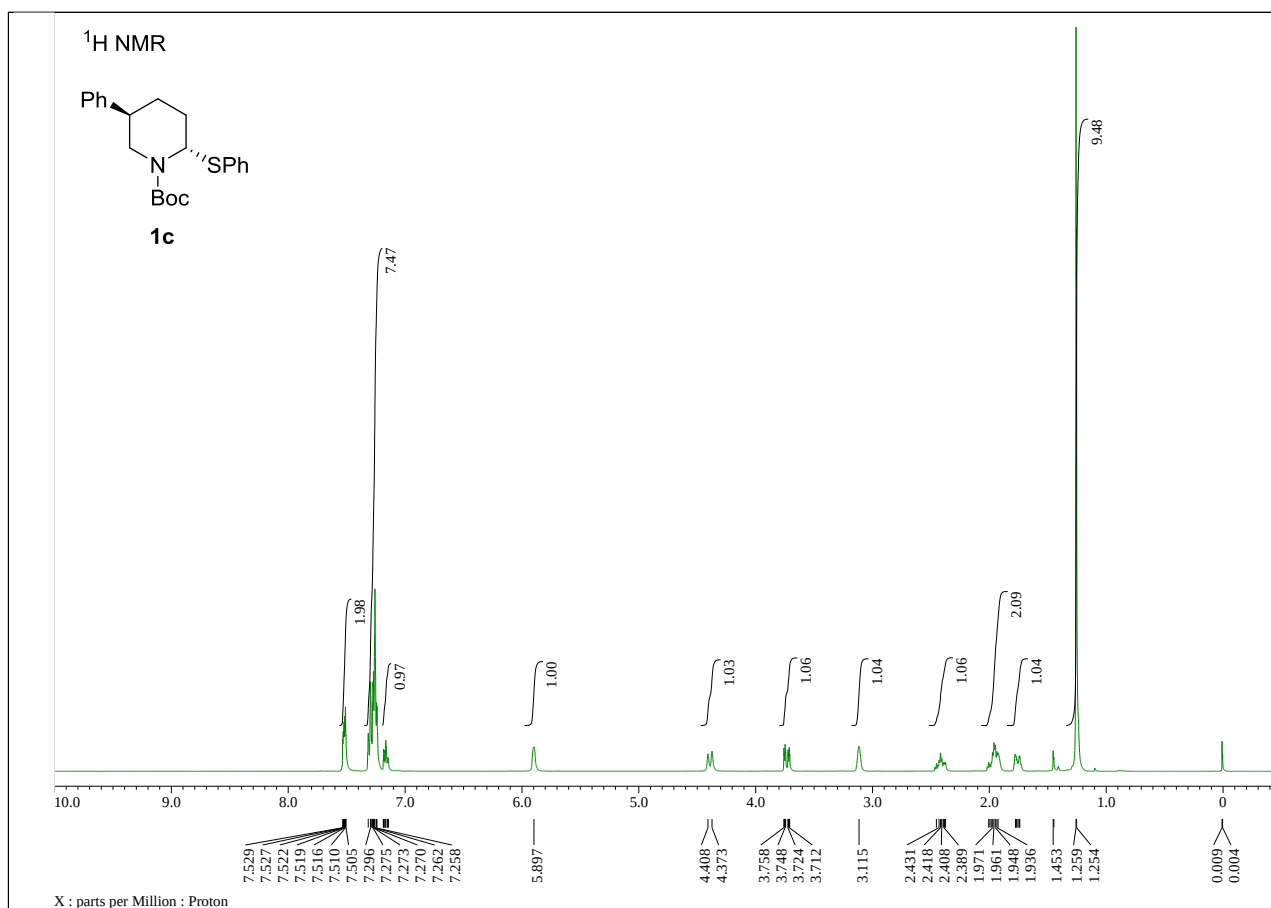


¹H NMR



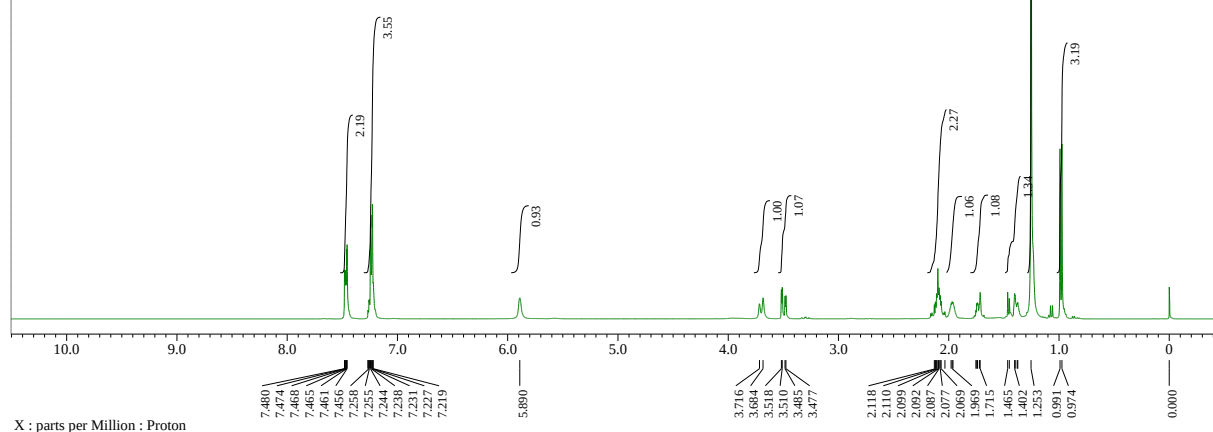
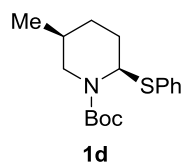
¹³C NMR





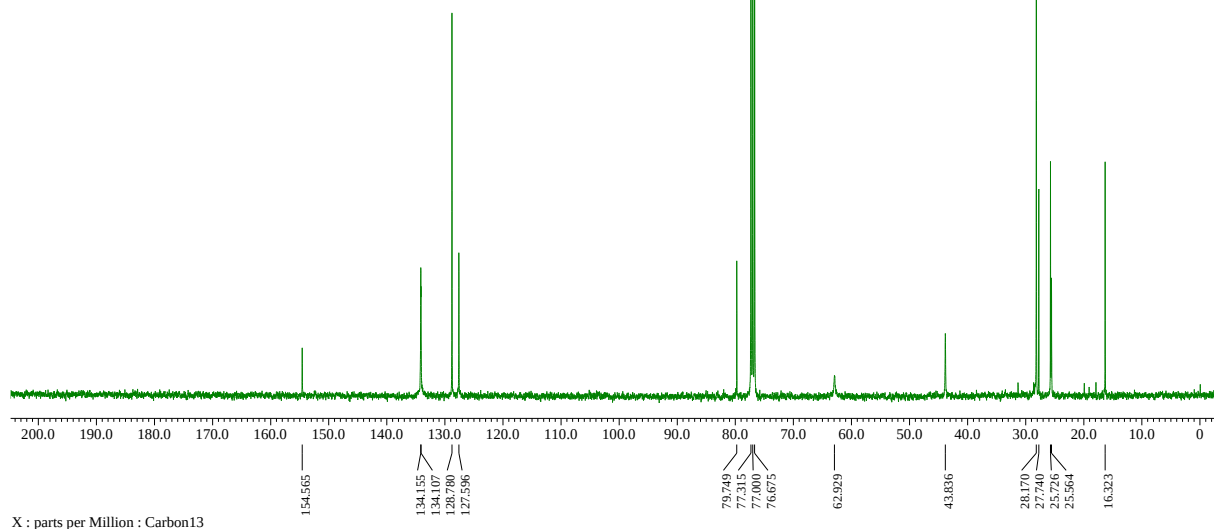
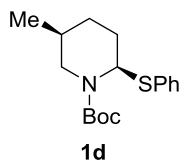
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¹H NMR

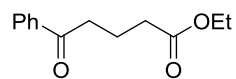


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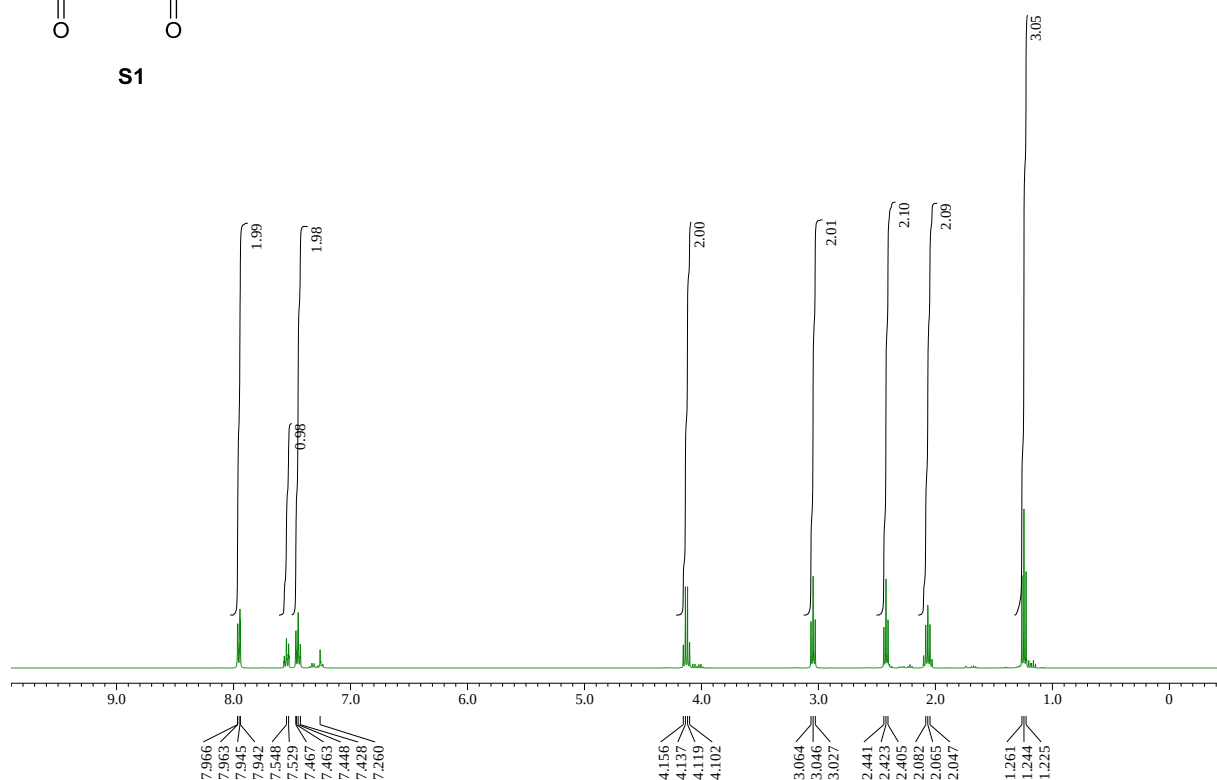
¹³C NMR



¹H NMR

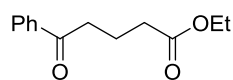


S1

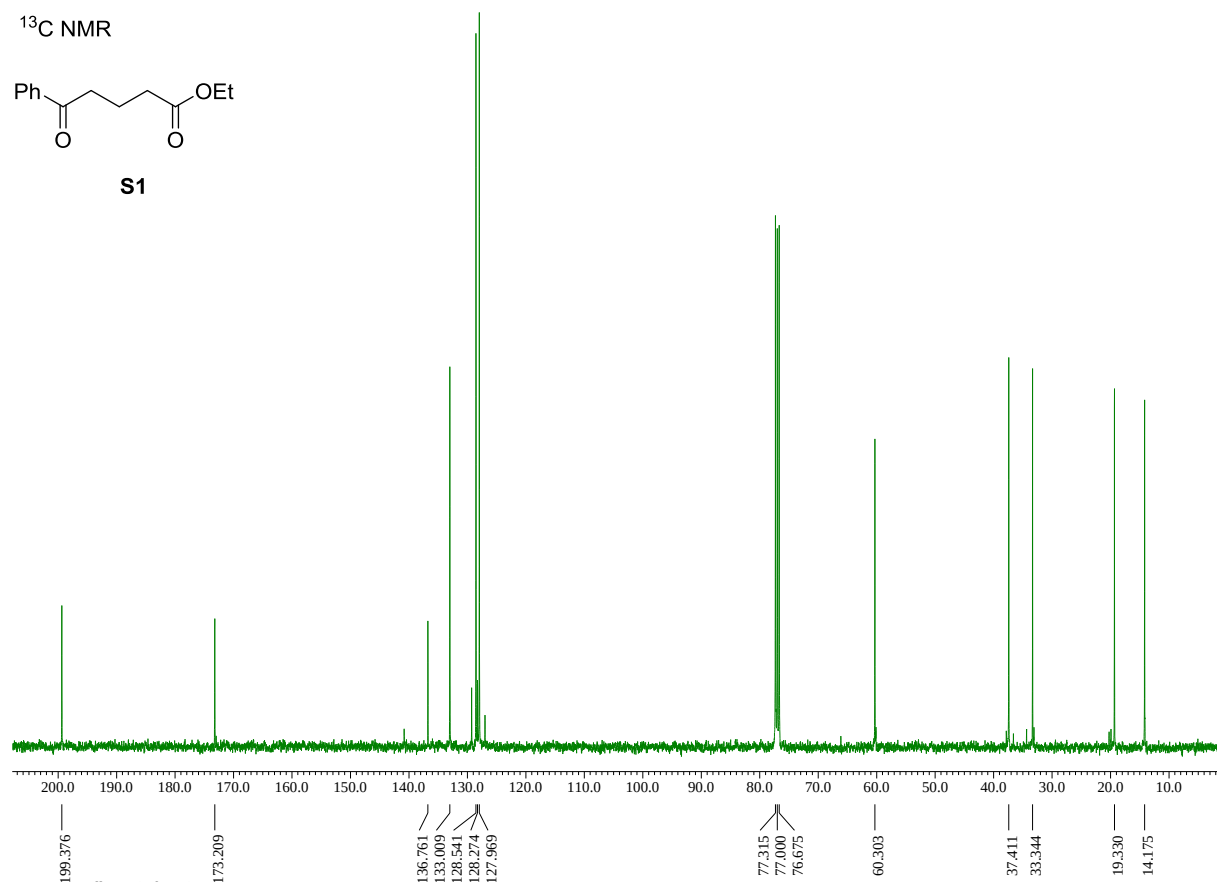


X : parts per Million : Proton

¹³C NMR

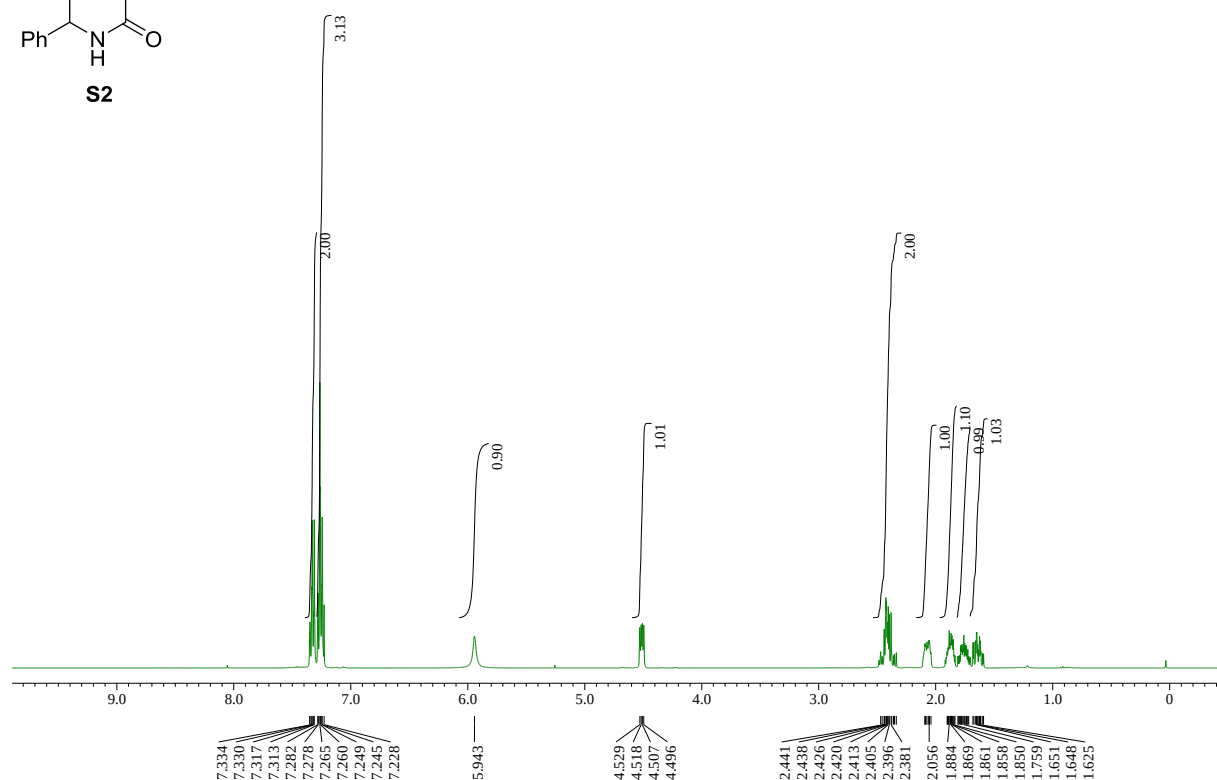
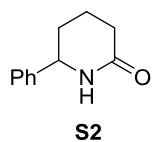


S1



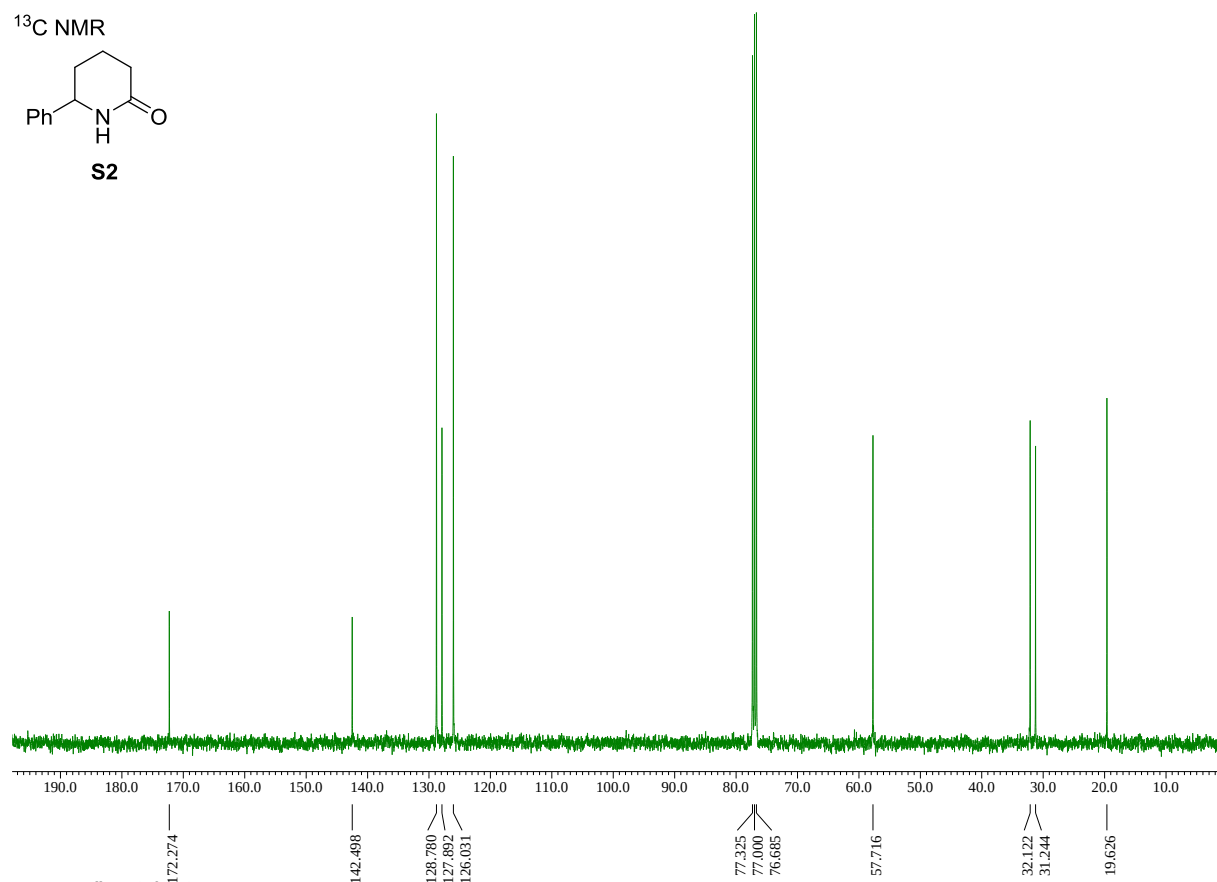
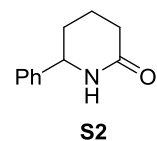
X : parts per Million : Carbon13

¹H NMR



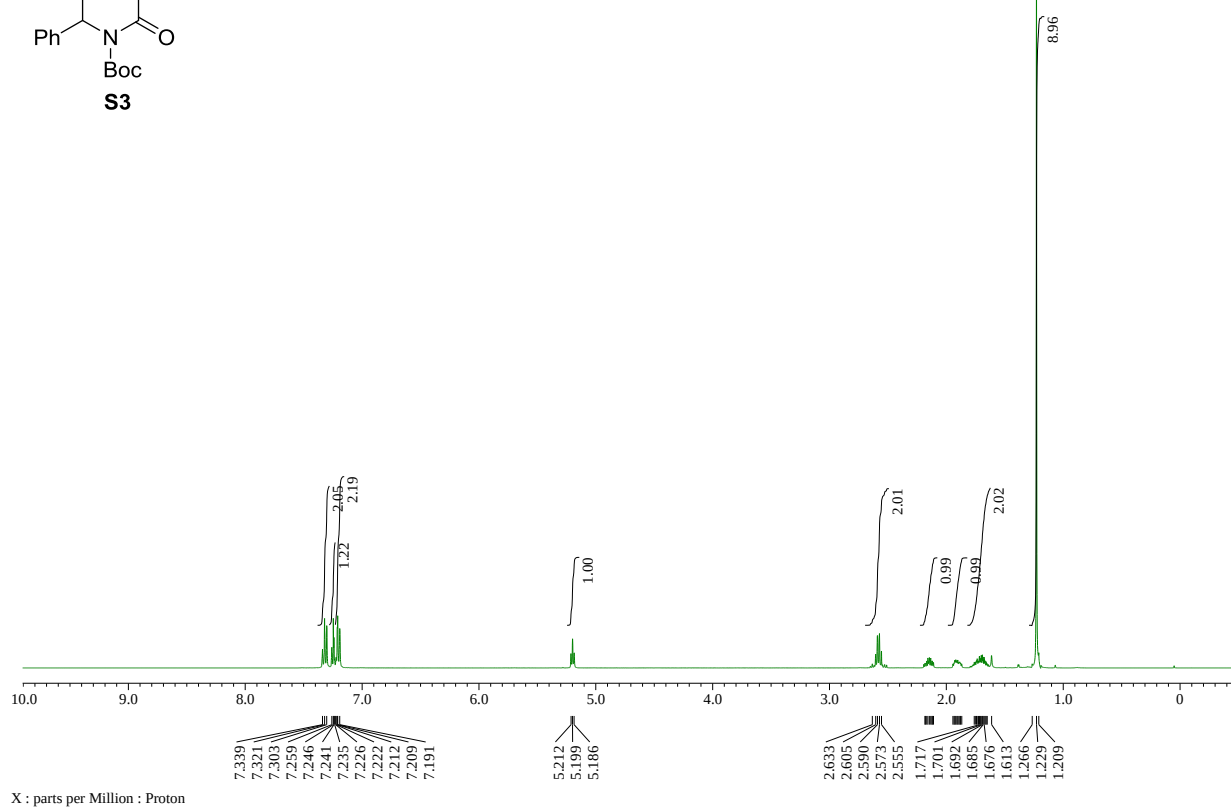
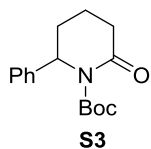
X : parts per Million : Proton

¹³C NMR

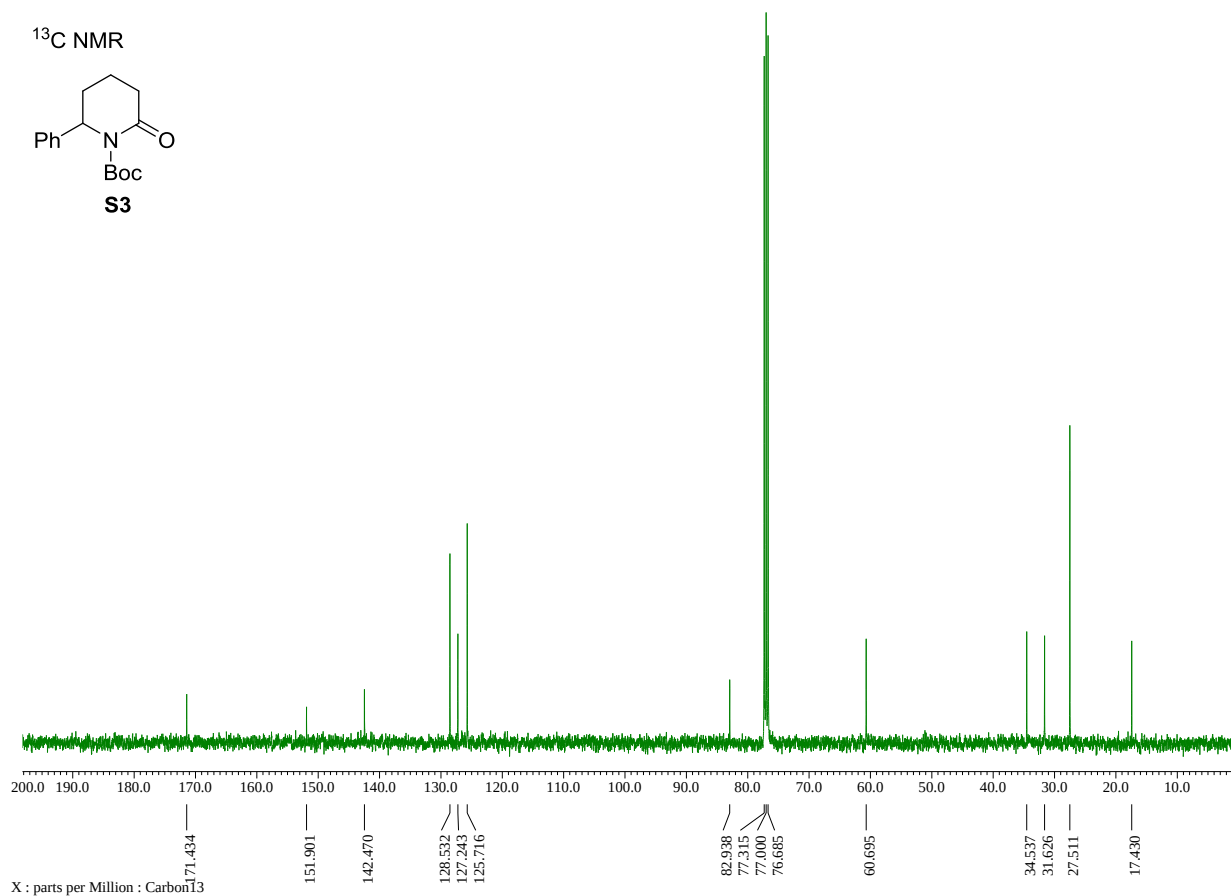
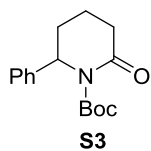


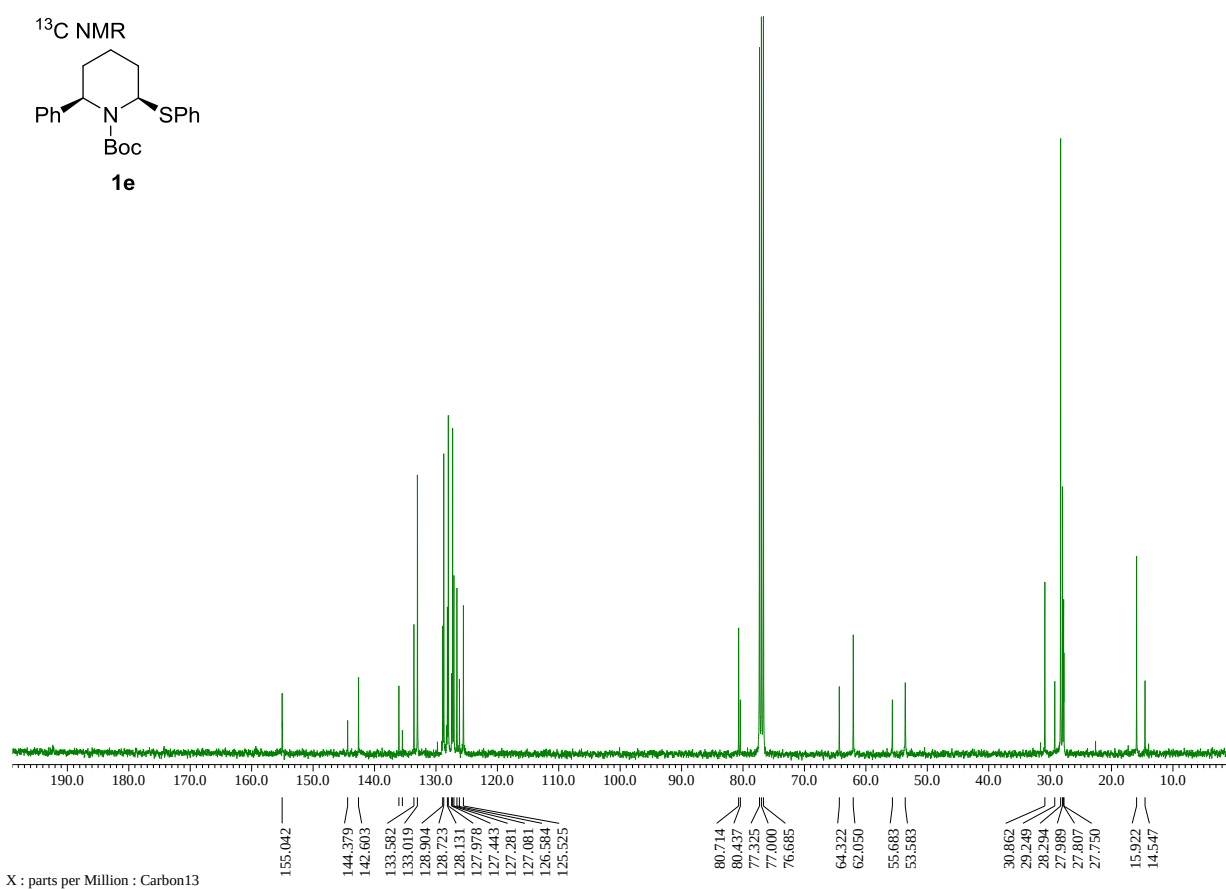
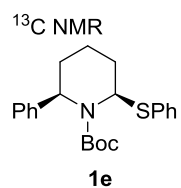
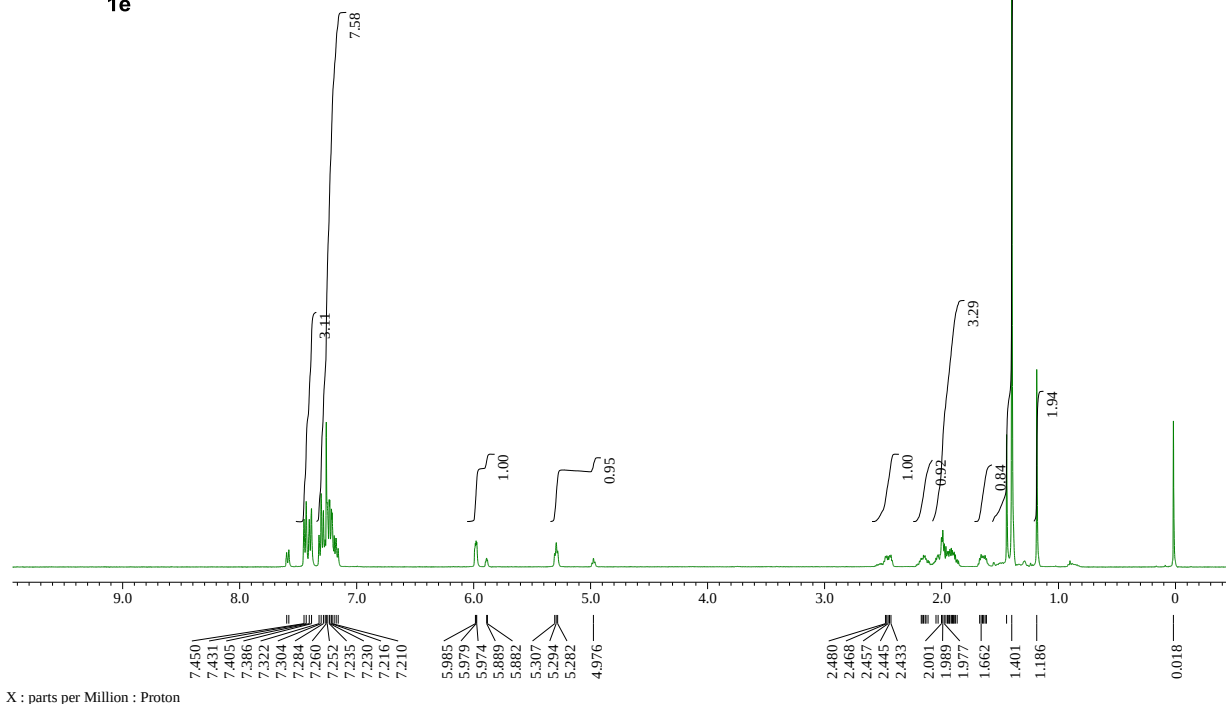
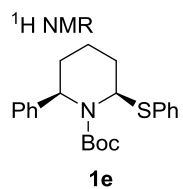
X : parts per Million : Carbon13

¹H NMR



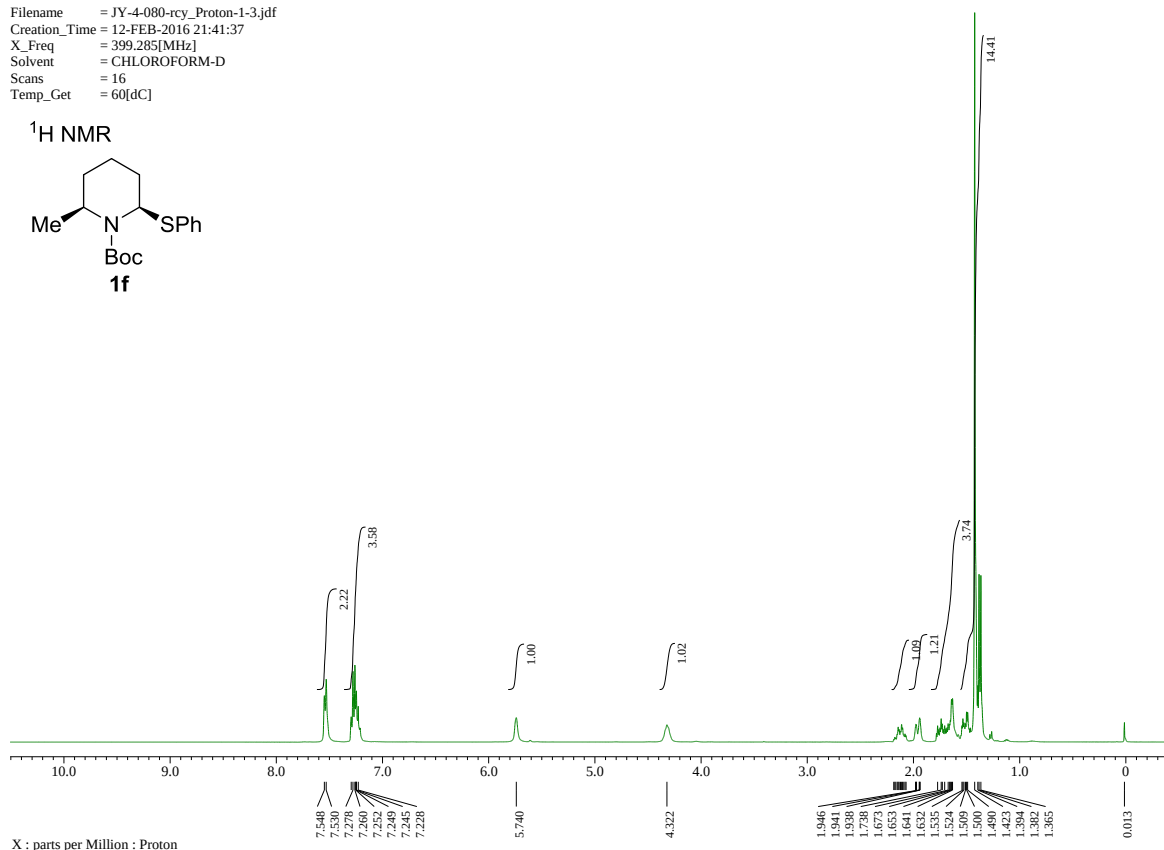
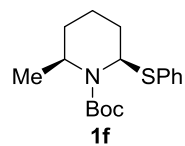
¹³C NMR





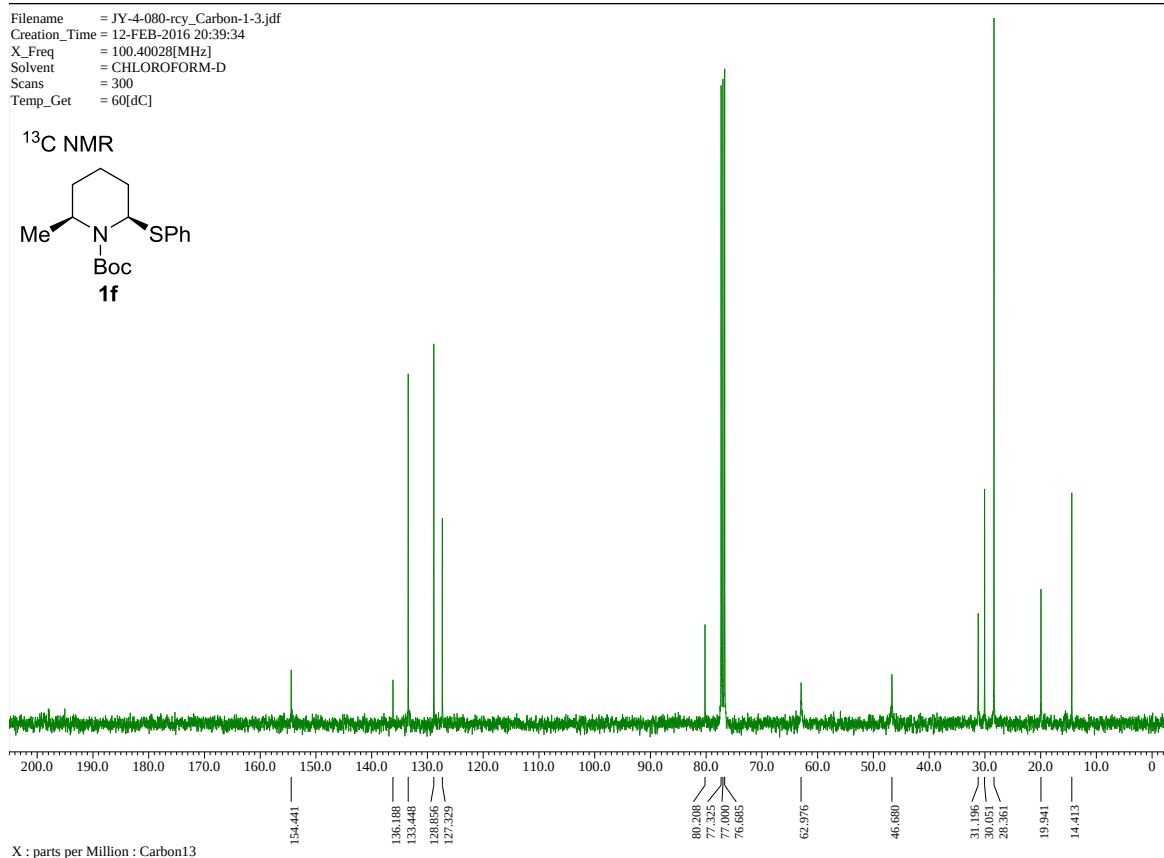
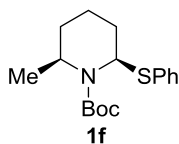
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 Solvent = CHLOROFORM-D
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¹H NMR

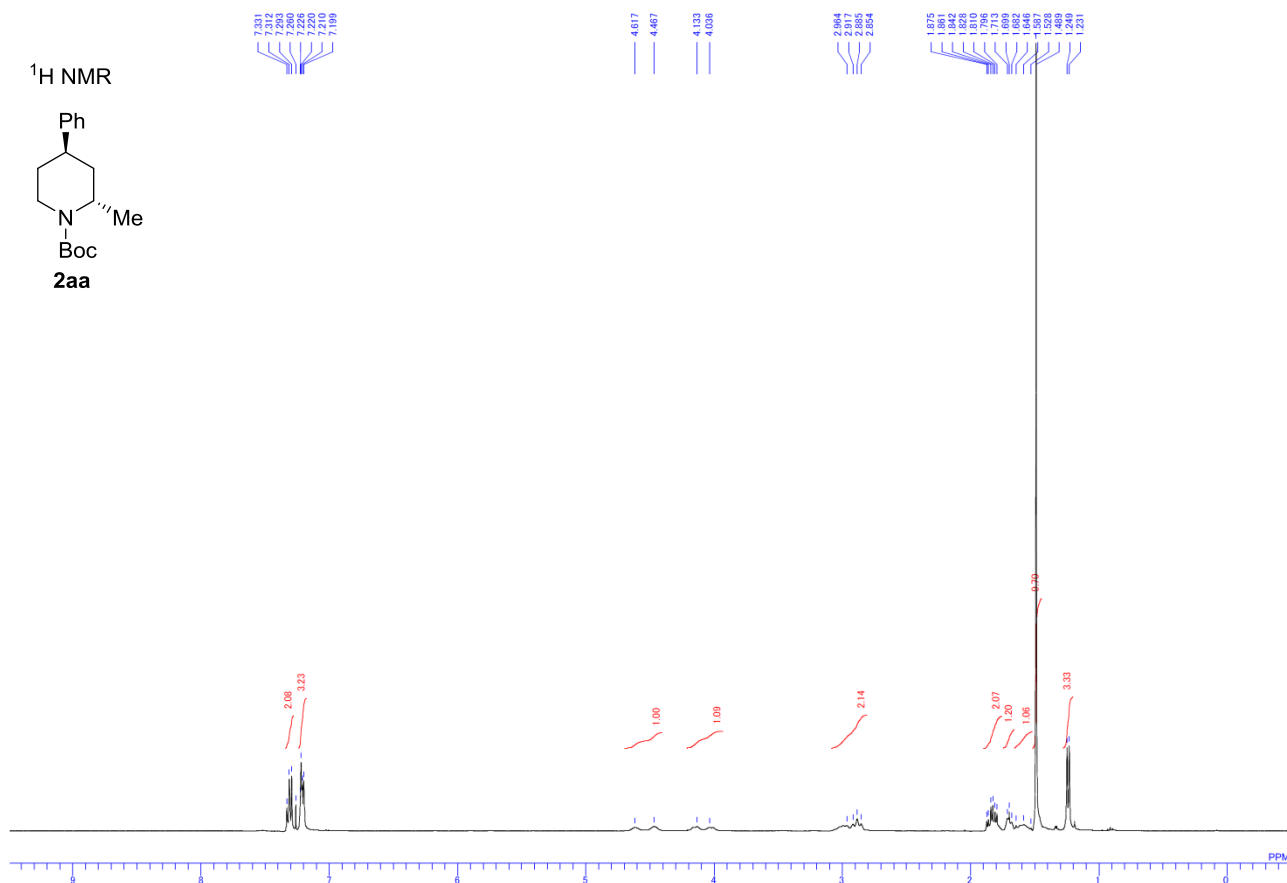
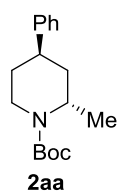


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 Creation_Time = 12-FEB-2016 20:39:34
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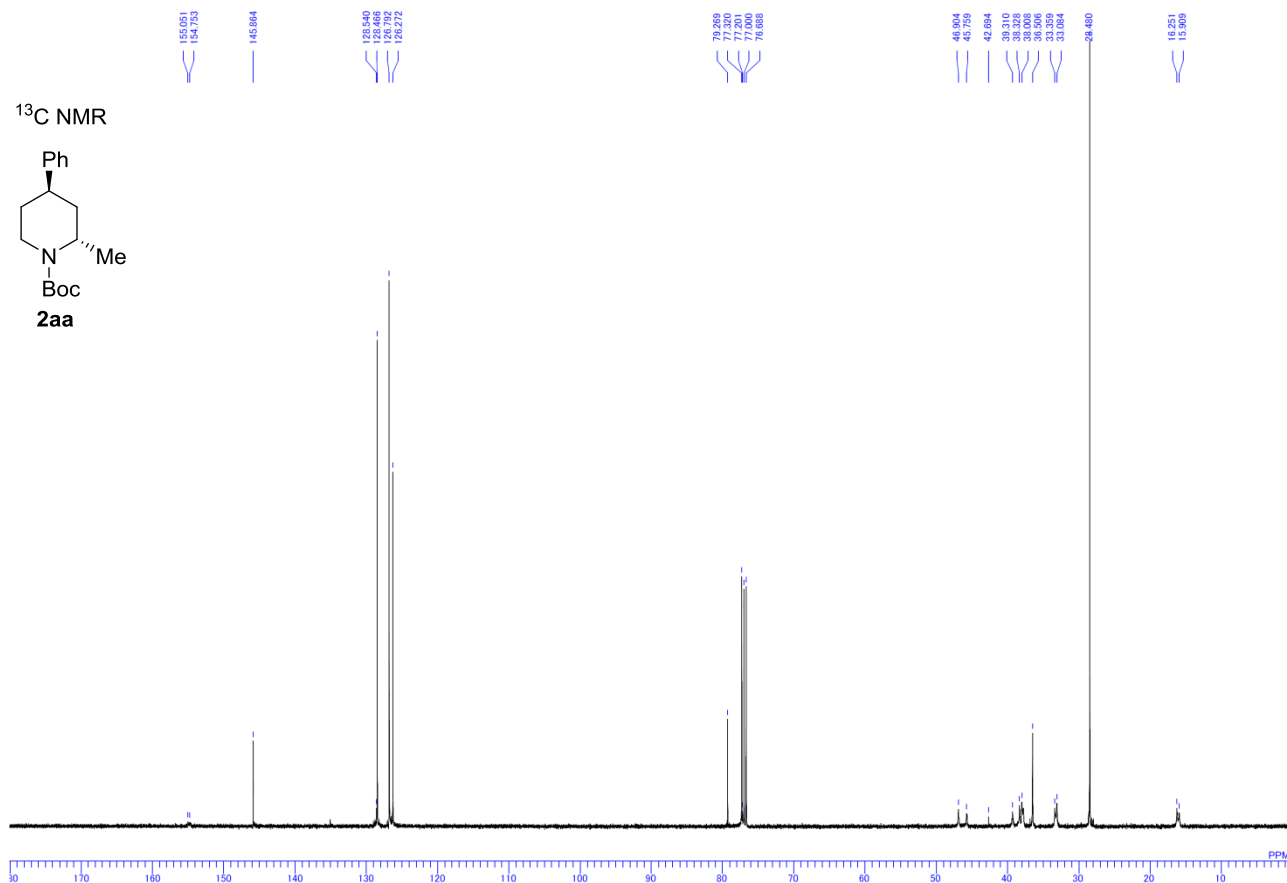
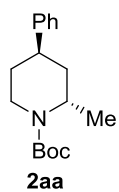
¹³C NMR



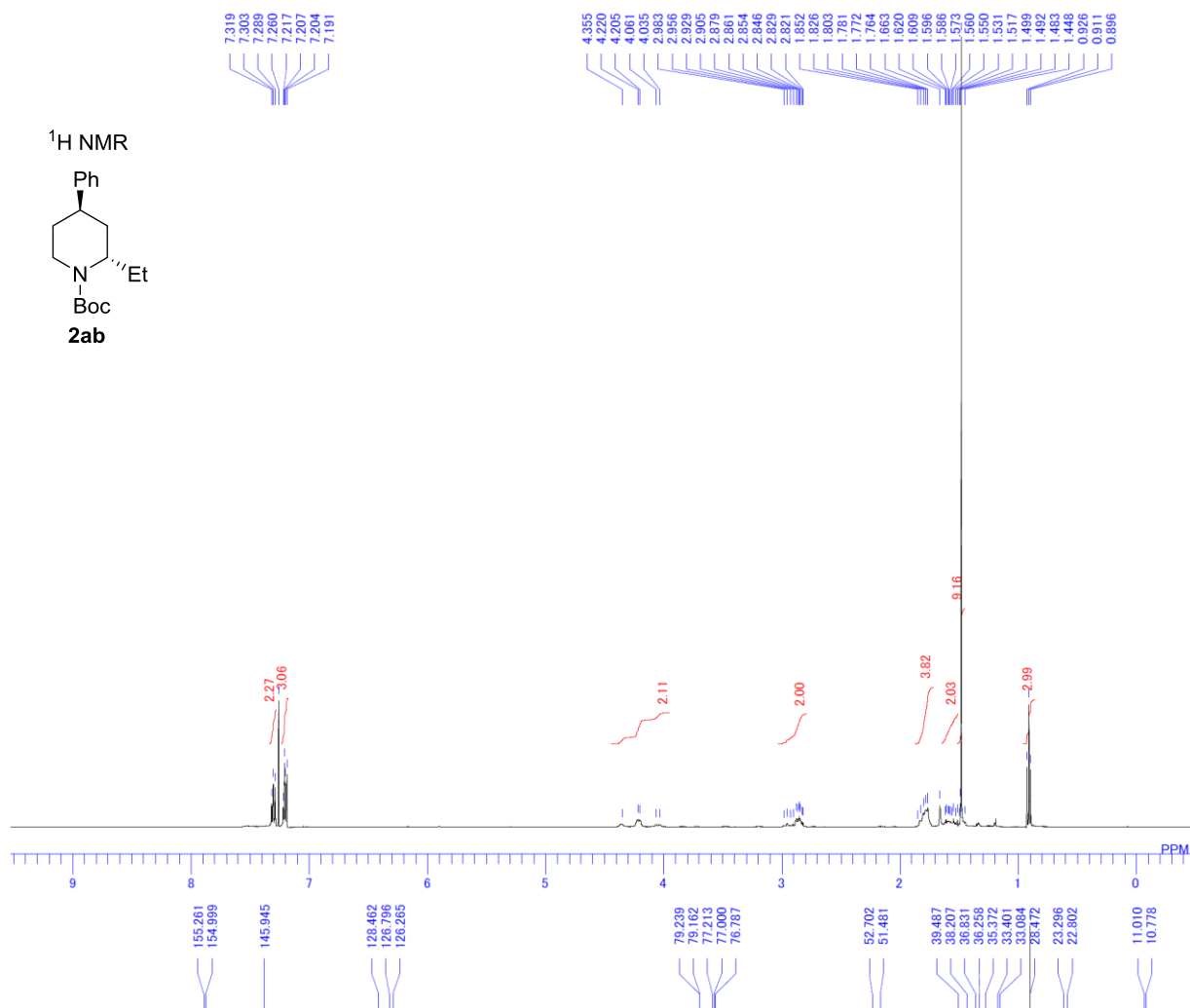
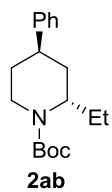
¹H NMR



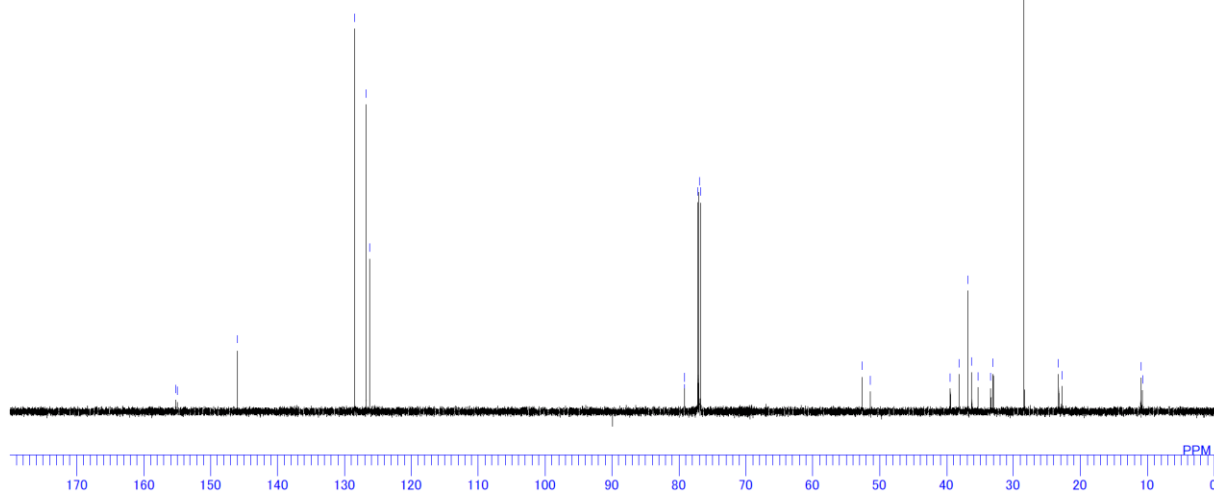
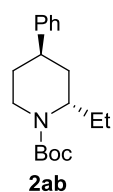
¹³C NMR



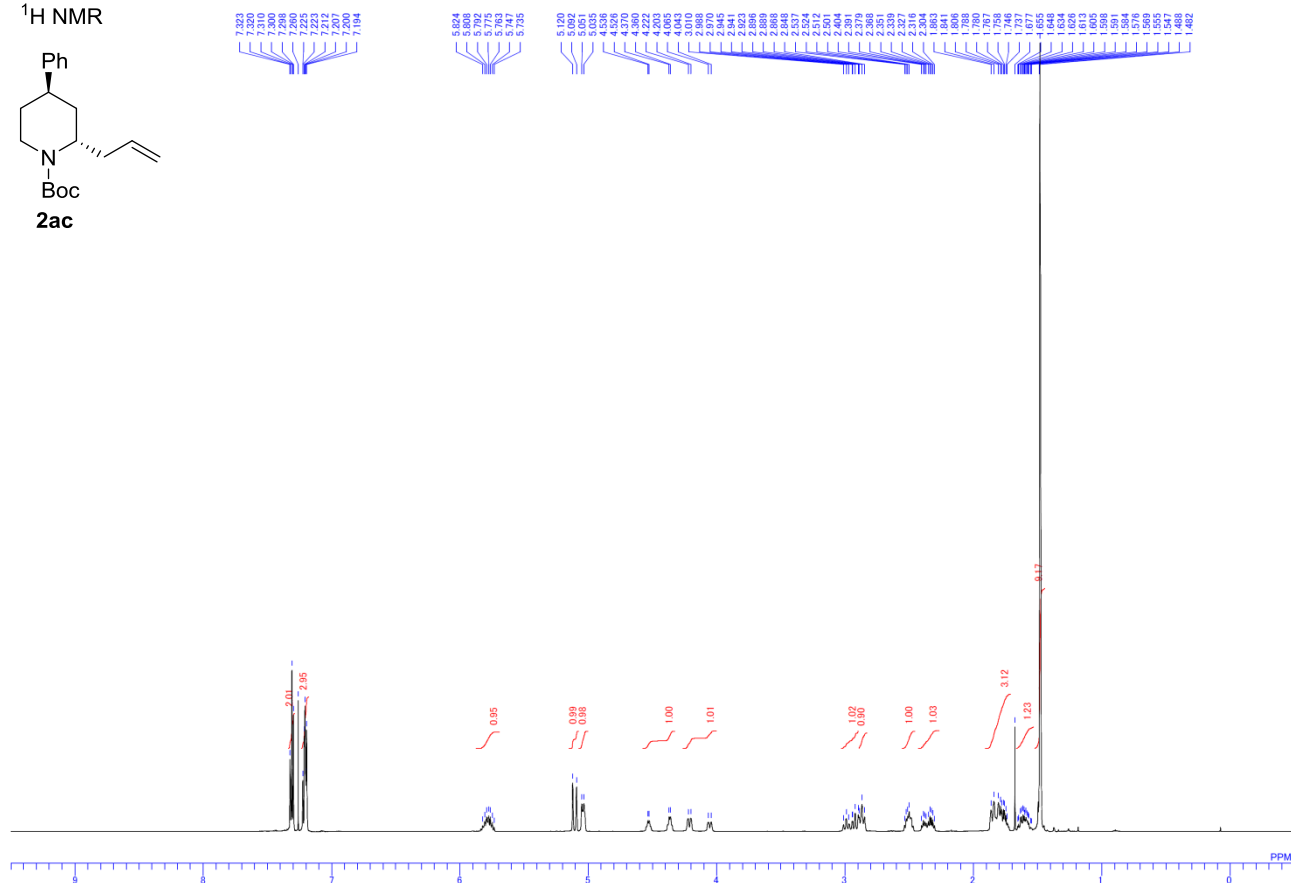
¹H NMR



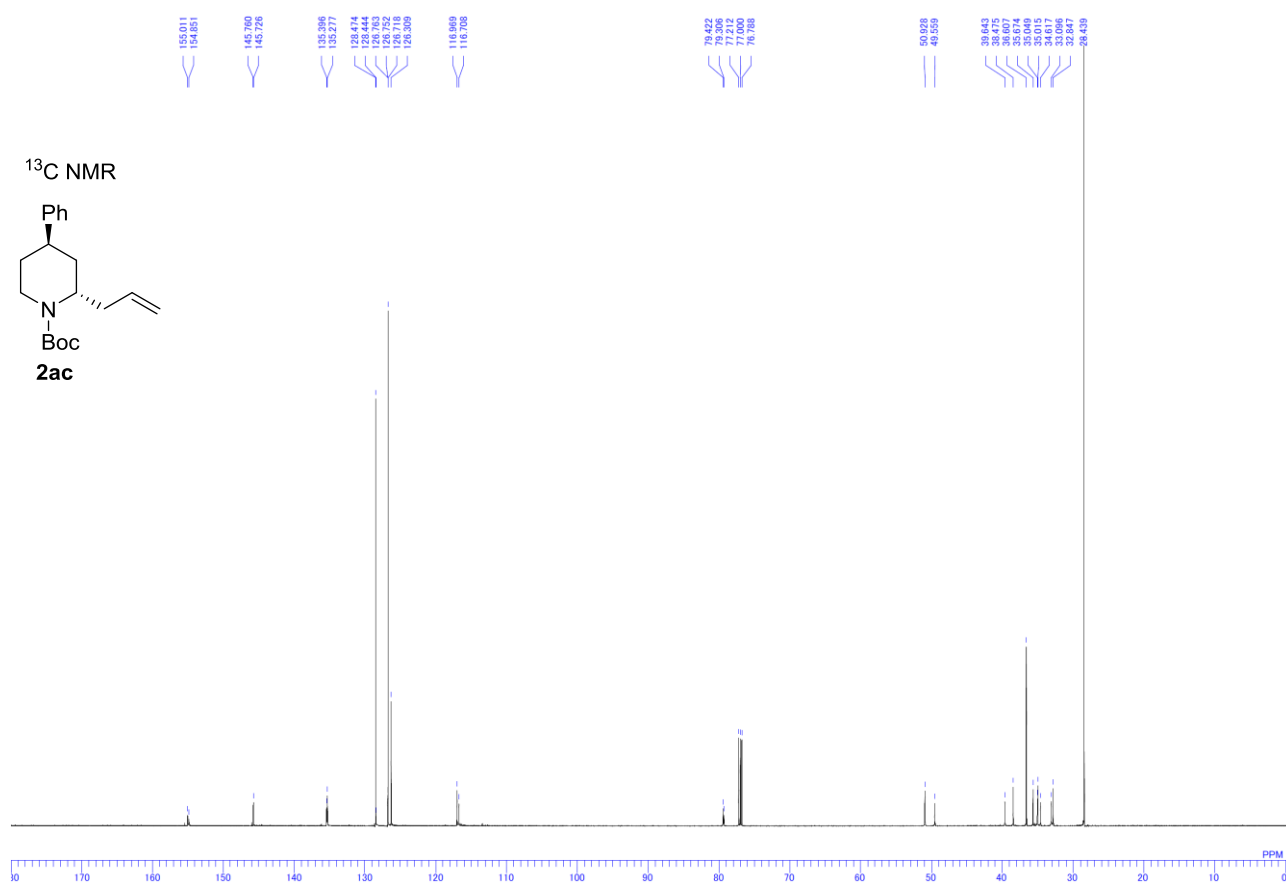
¹³C NMR



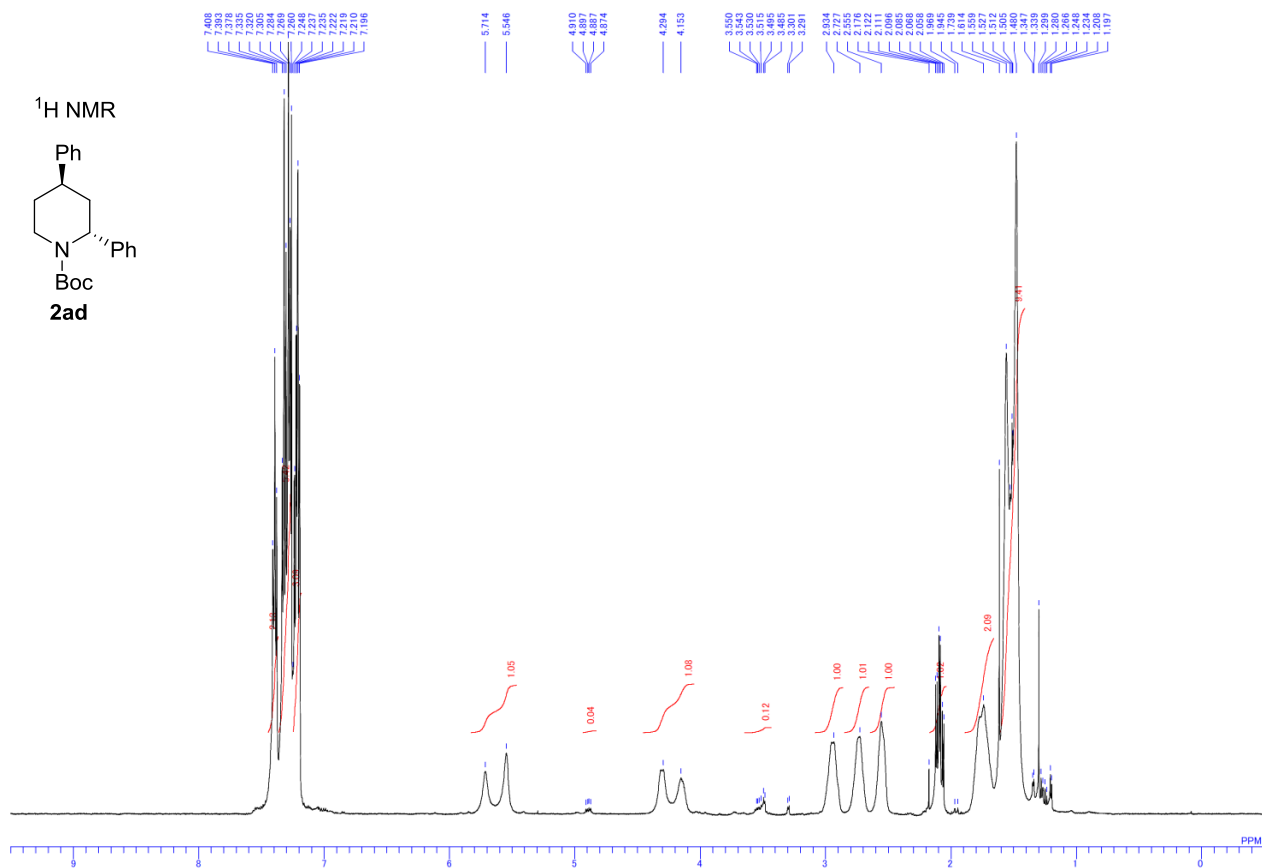
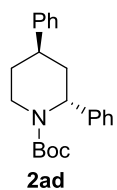
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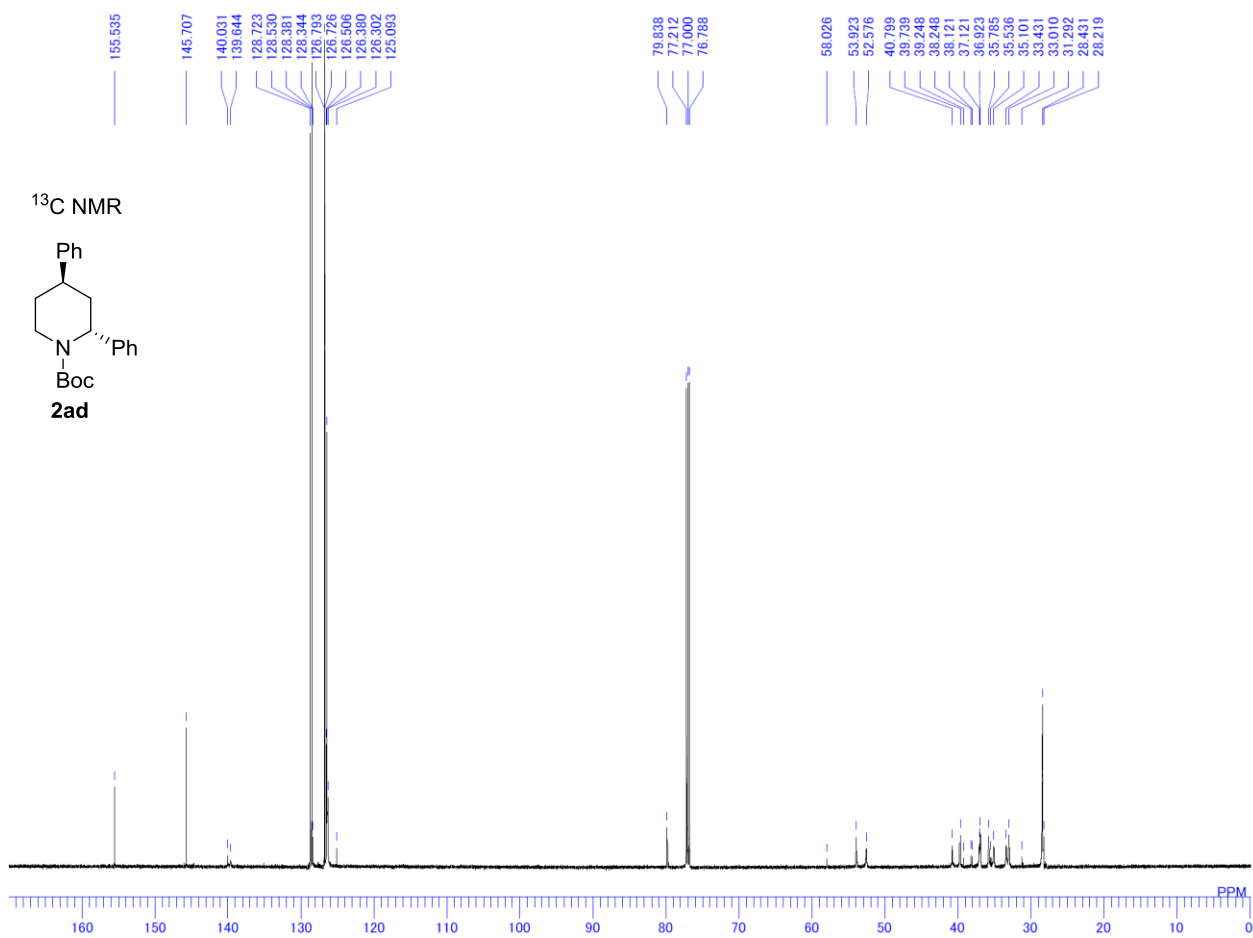
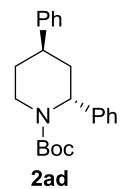
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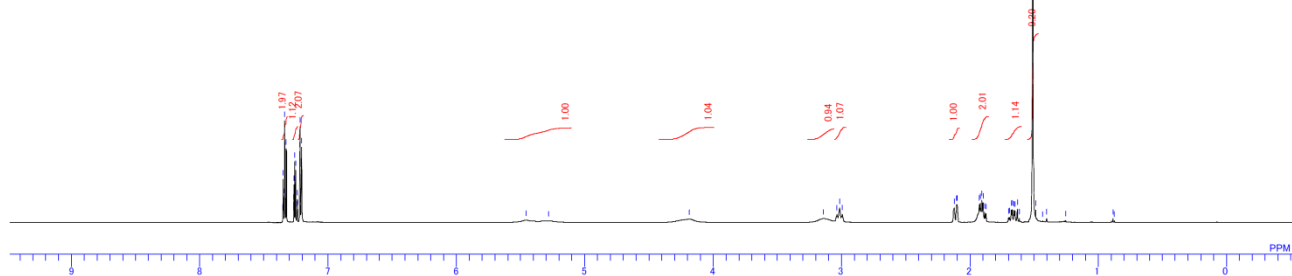
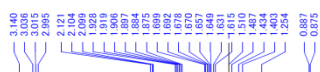
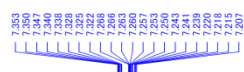
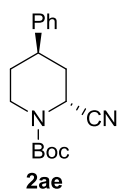
¹H NMR



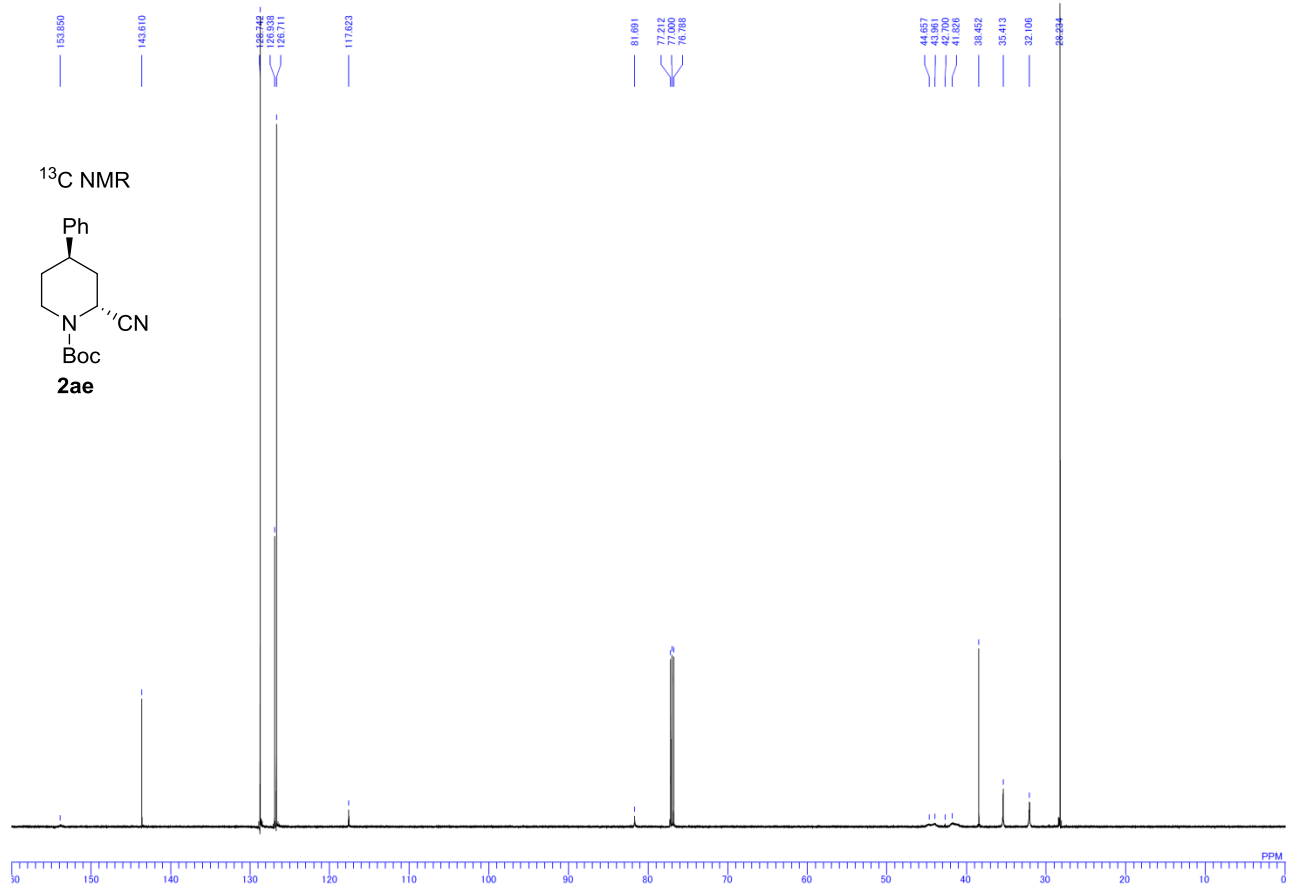
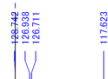
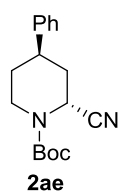
¹³C NMR



¹H NMR

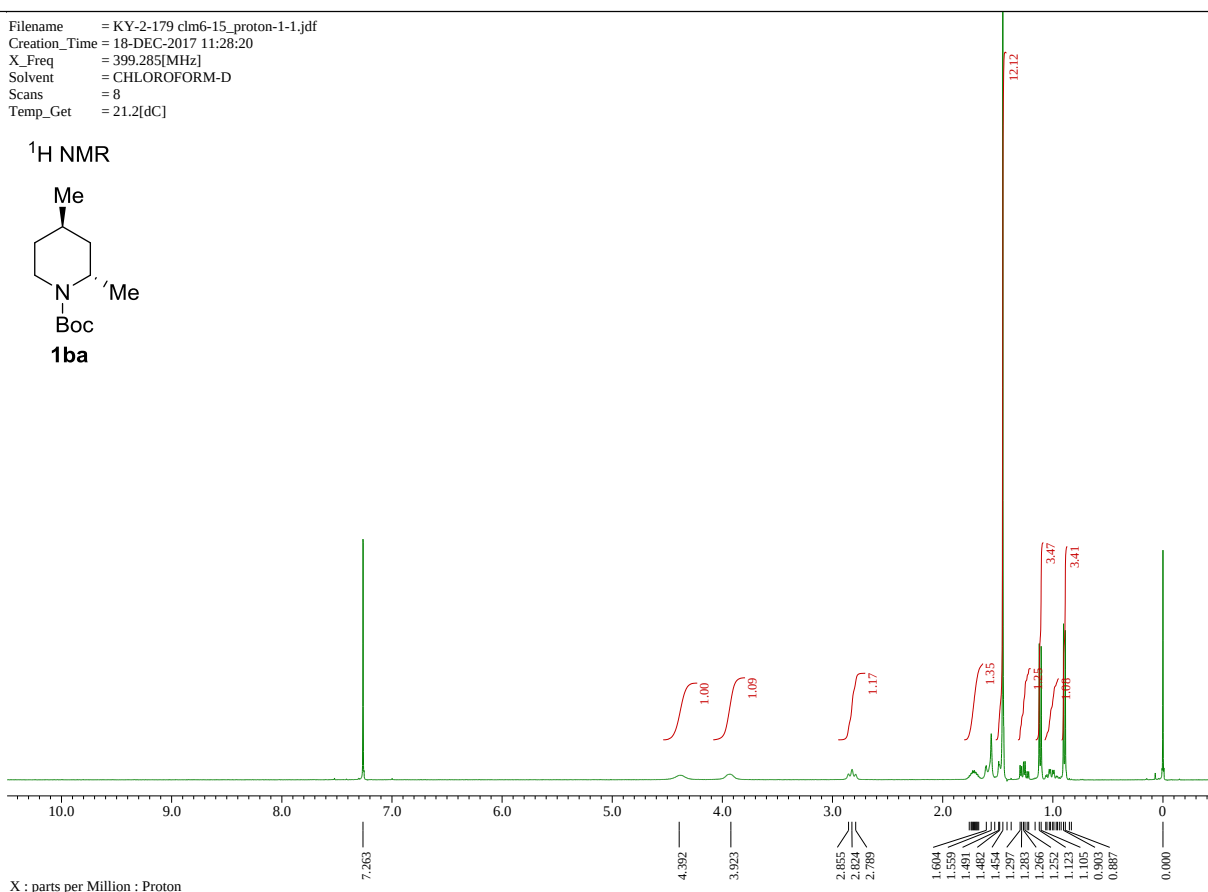
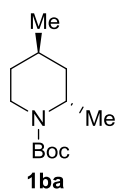


¹³C NMR



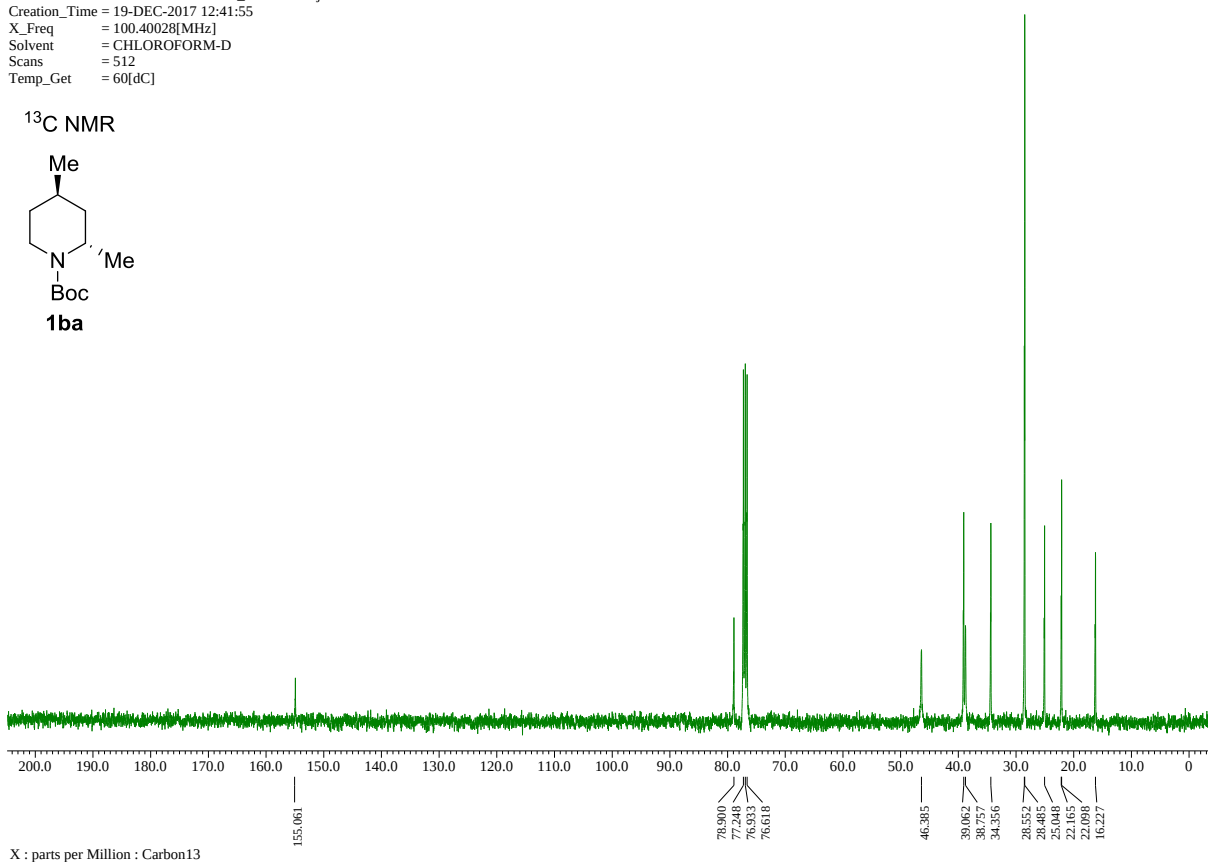
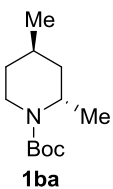
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 X_Freq = 399.285[MHz]
 Solvent = CHLOROFORM-D
 Scans = 8
 Temp_Get = 21.2[dC]

¹H NMR

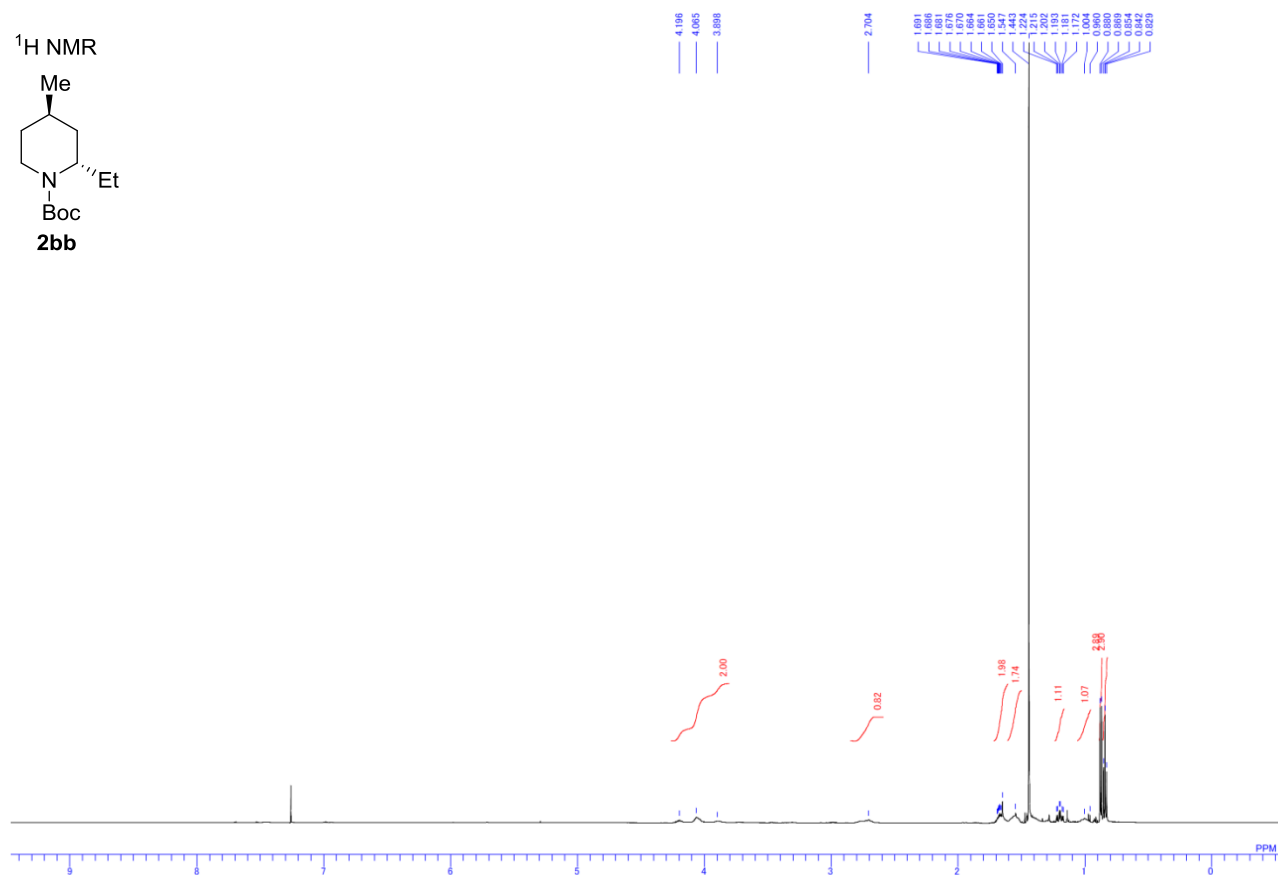
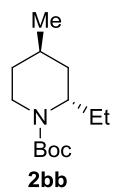


Filename = KY-2-179 clm6-15_1_Carbon-1-1.jdf
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 X_Freq = 100.40028[MHz]
 Solvent = CHLOROFORM-D
 Scans = 512
 Temp_Get = 60[dC]

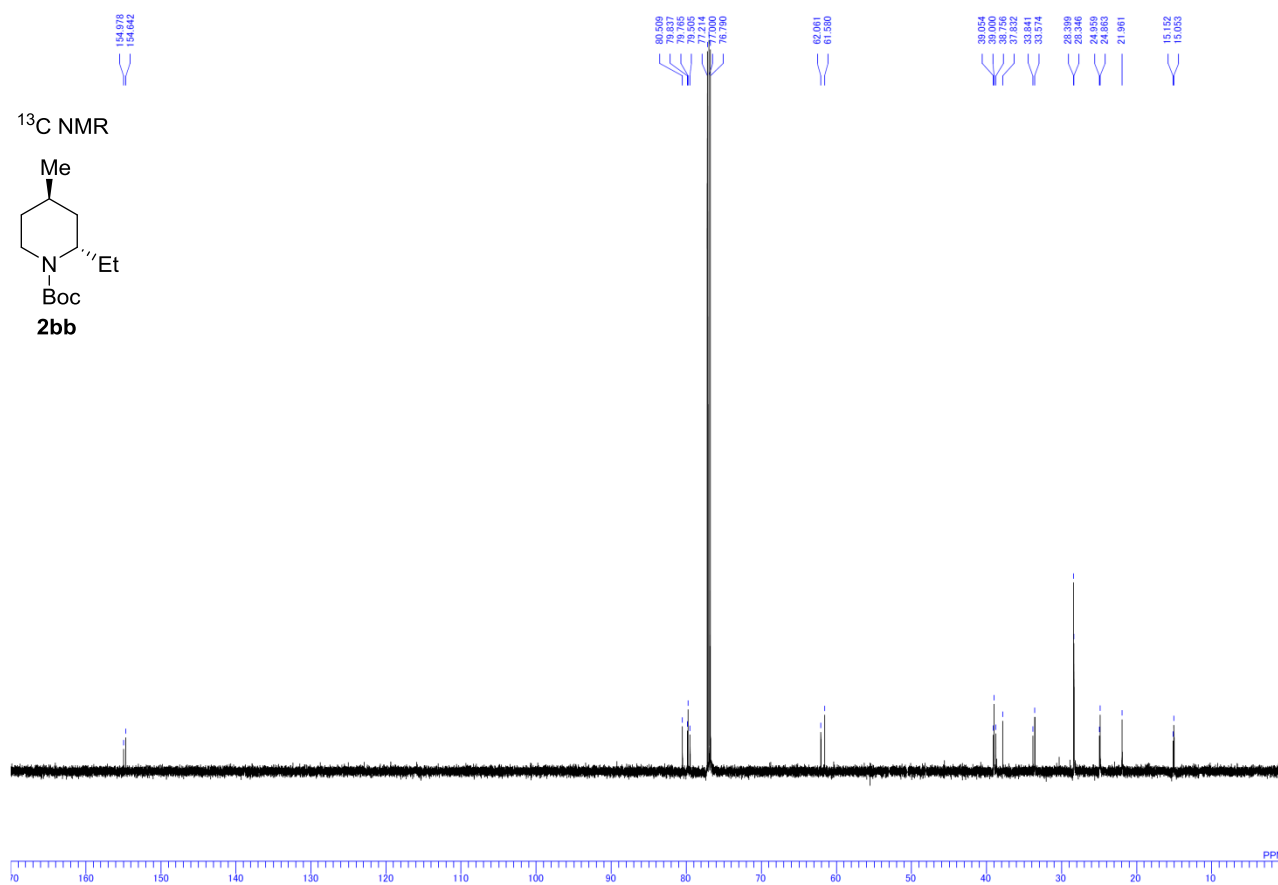
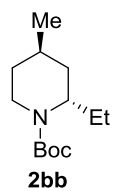
¹³C NMR



¹H NMR

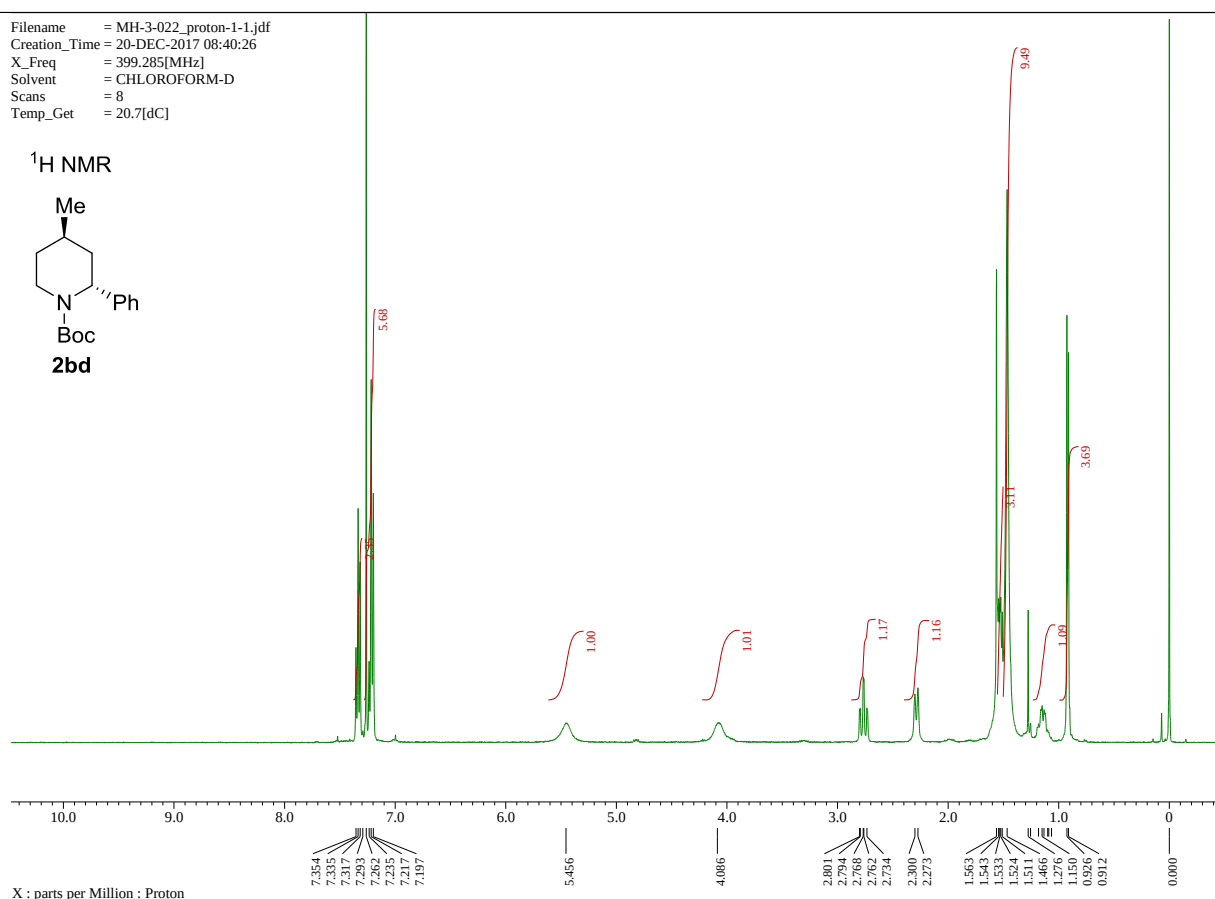
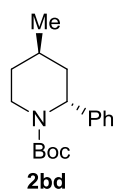


¹³C NMR



Filename = MH-3-022_proton-1-1.jdf
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 X_Freq = 399.285[MHz]
 Solvent = CHLOROFORM-D
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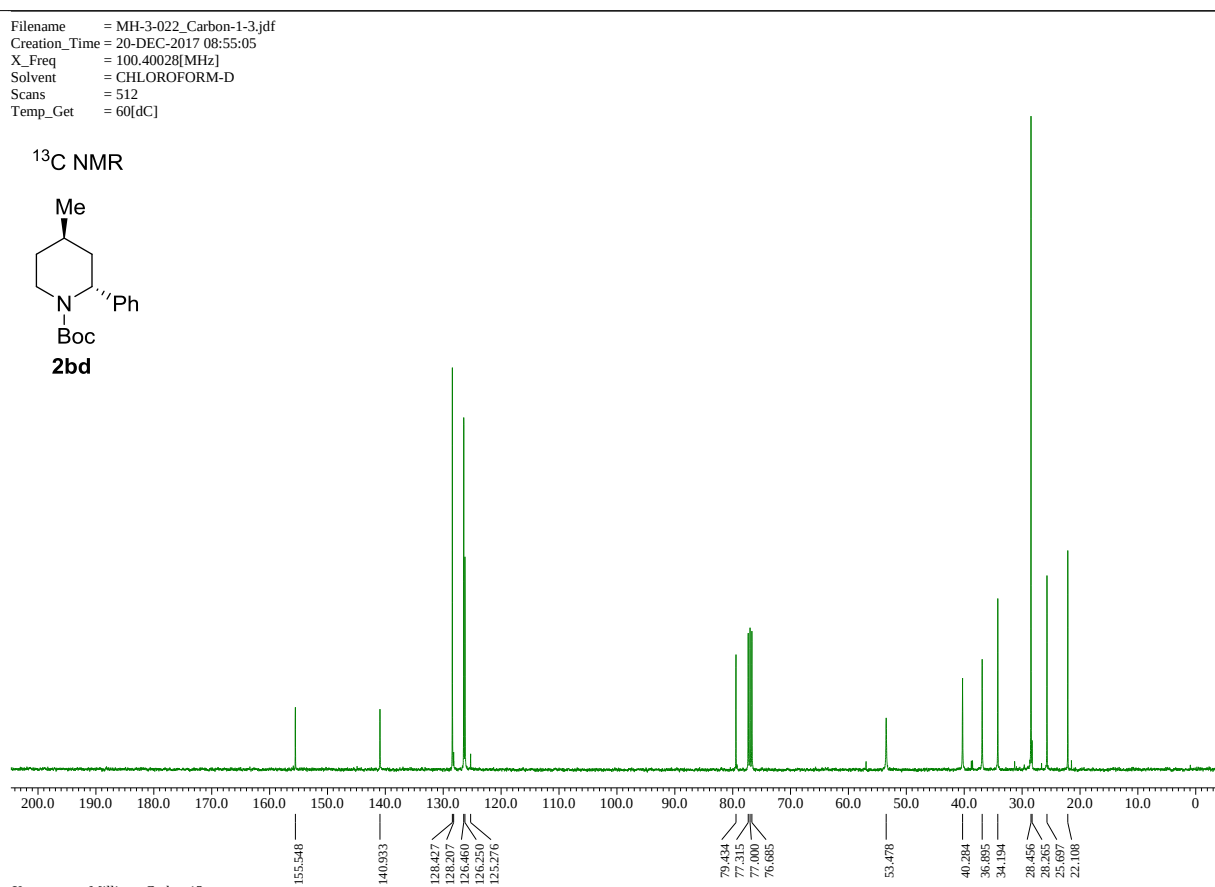
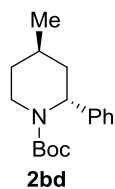
¹H NMR



X : parts per Million : Proton

Filename = MH-3-022_Carbon-1-3.jdf
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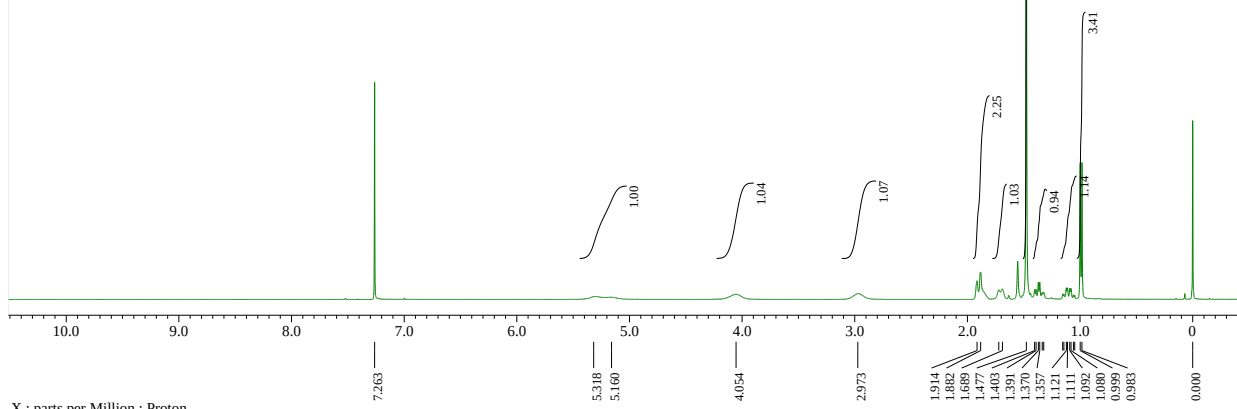
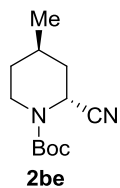
¹³C NMR



X : parts per Million : Carbon13

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 Solvent = CHLOROFORM-D
 Scans = 8
 Temp_Get = 21[dC]

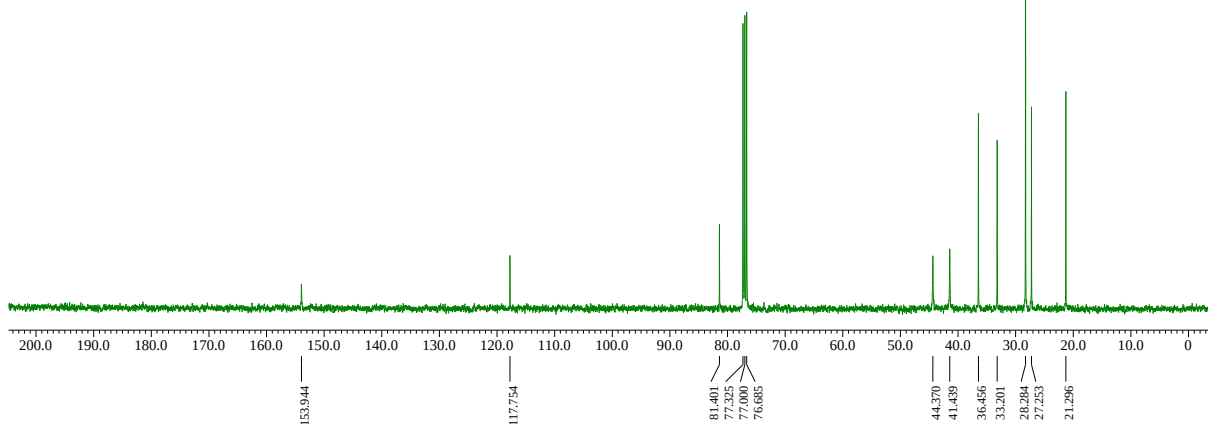
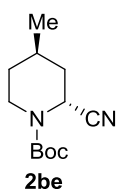
¹H NMR



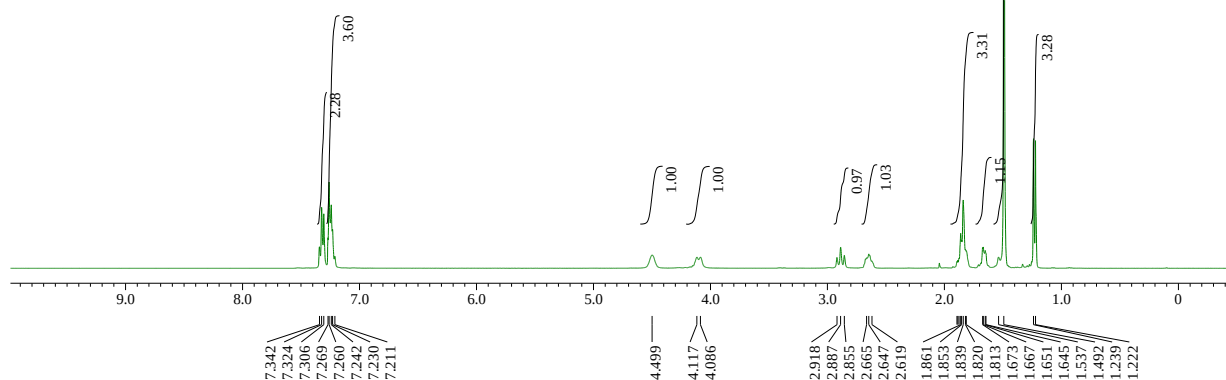
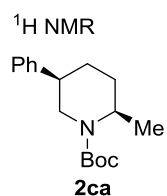
X : parts per Million : Proton

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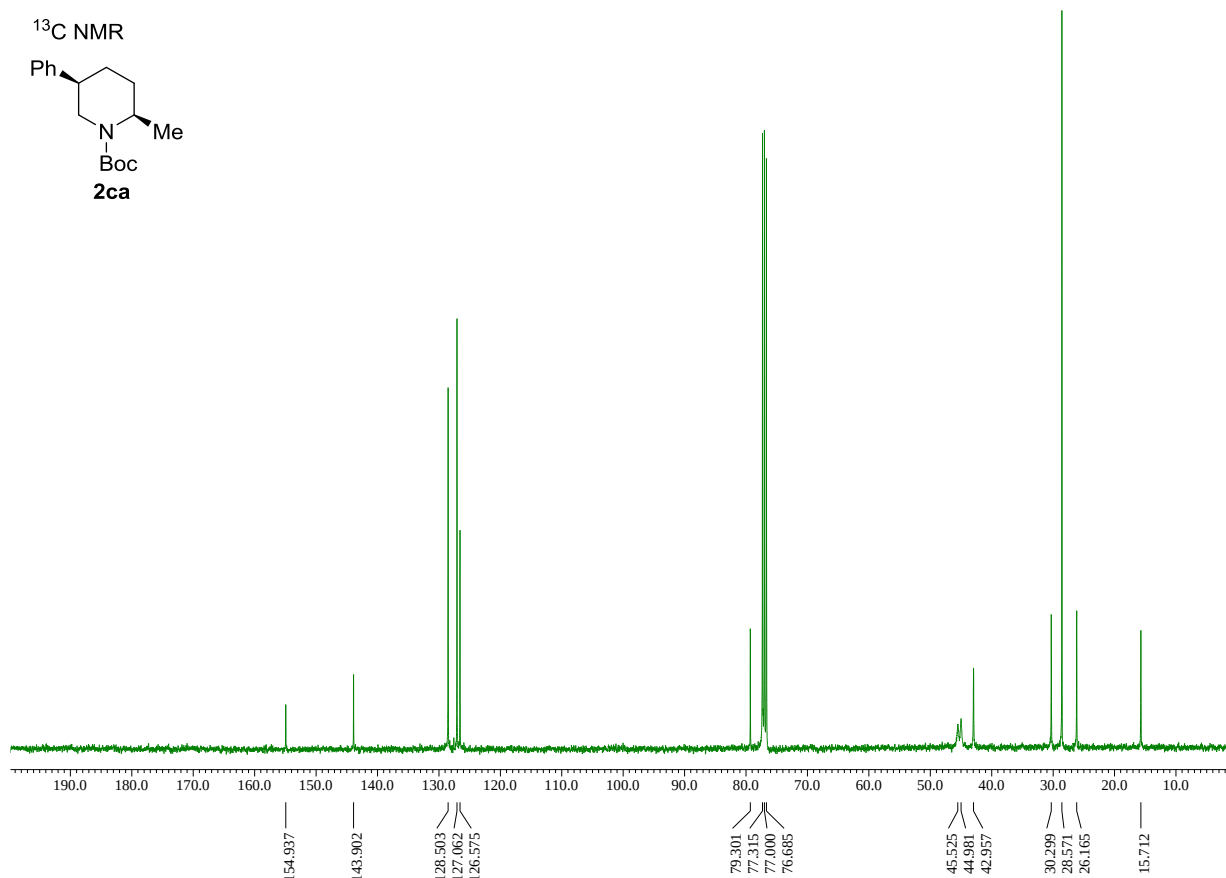
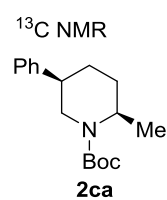
¹³C NMR



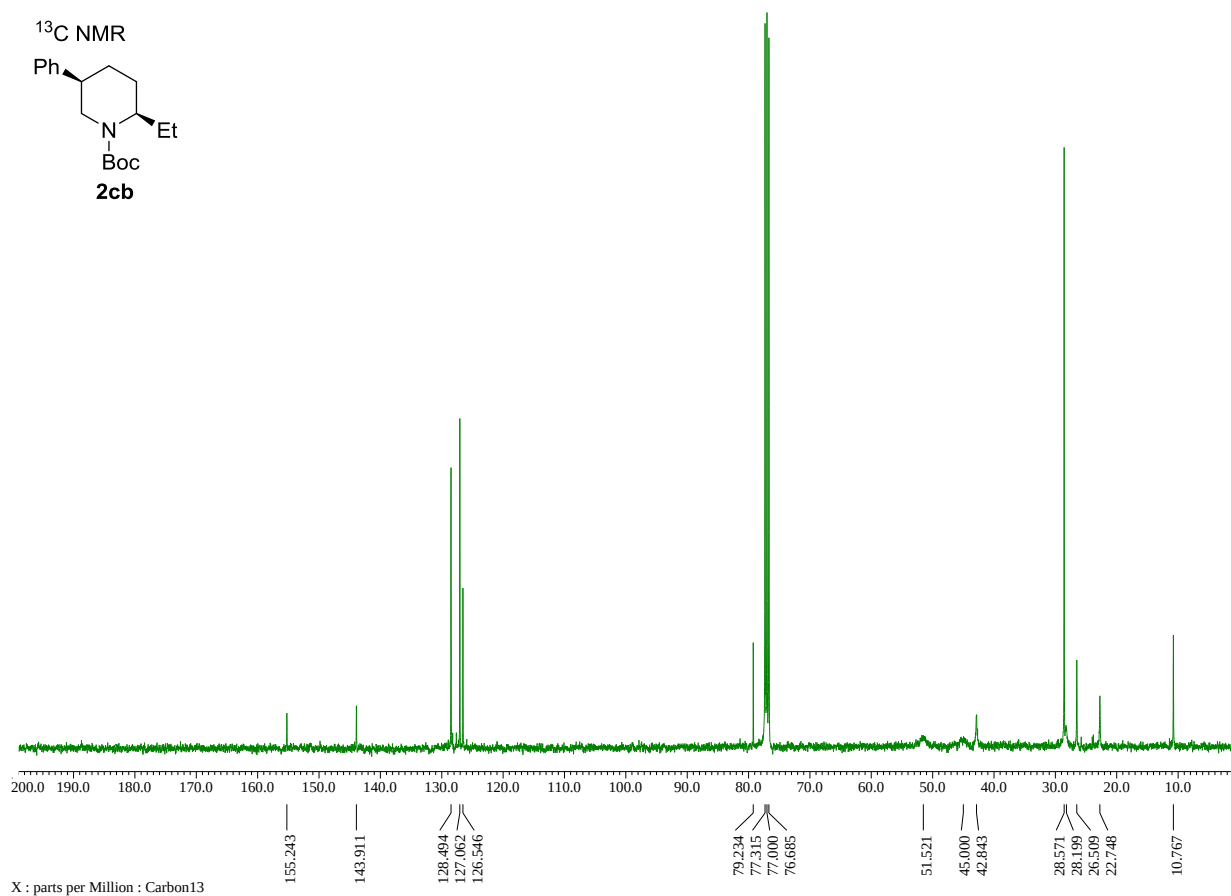
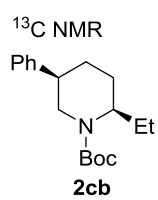
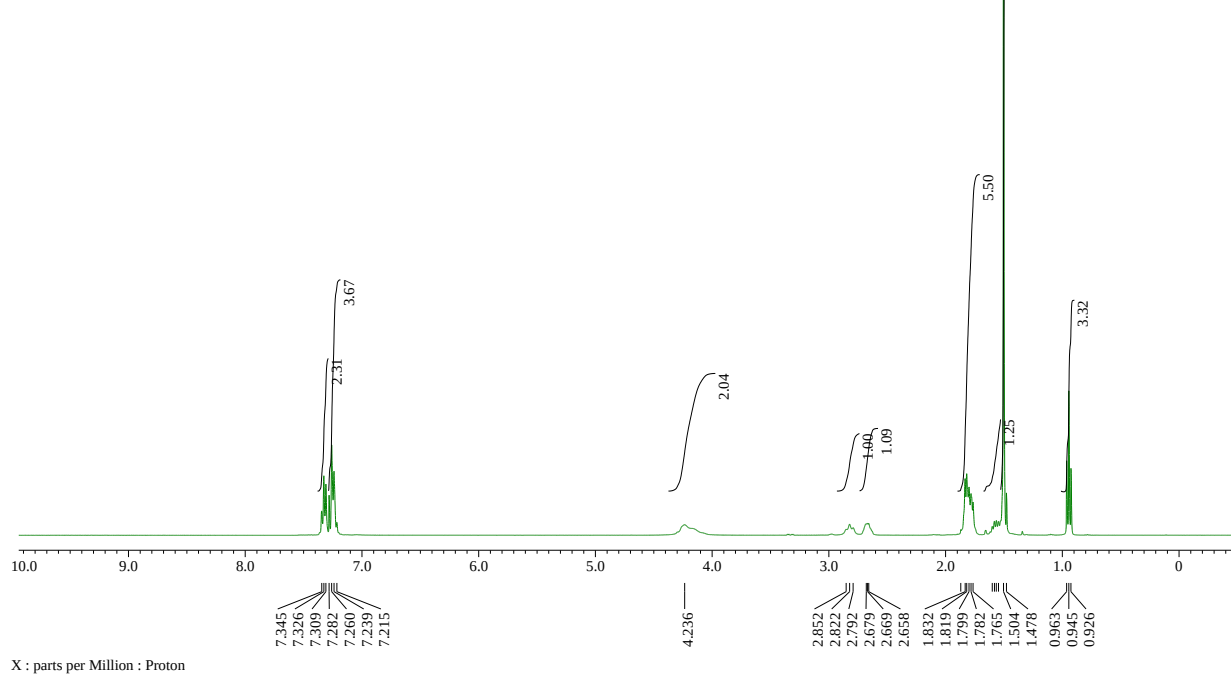
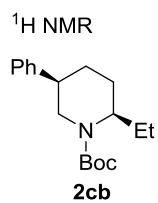
X : parts per Million : Carbon13

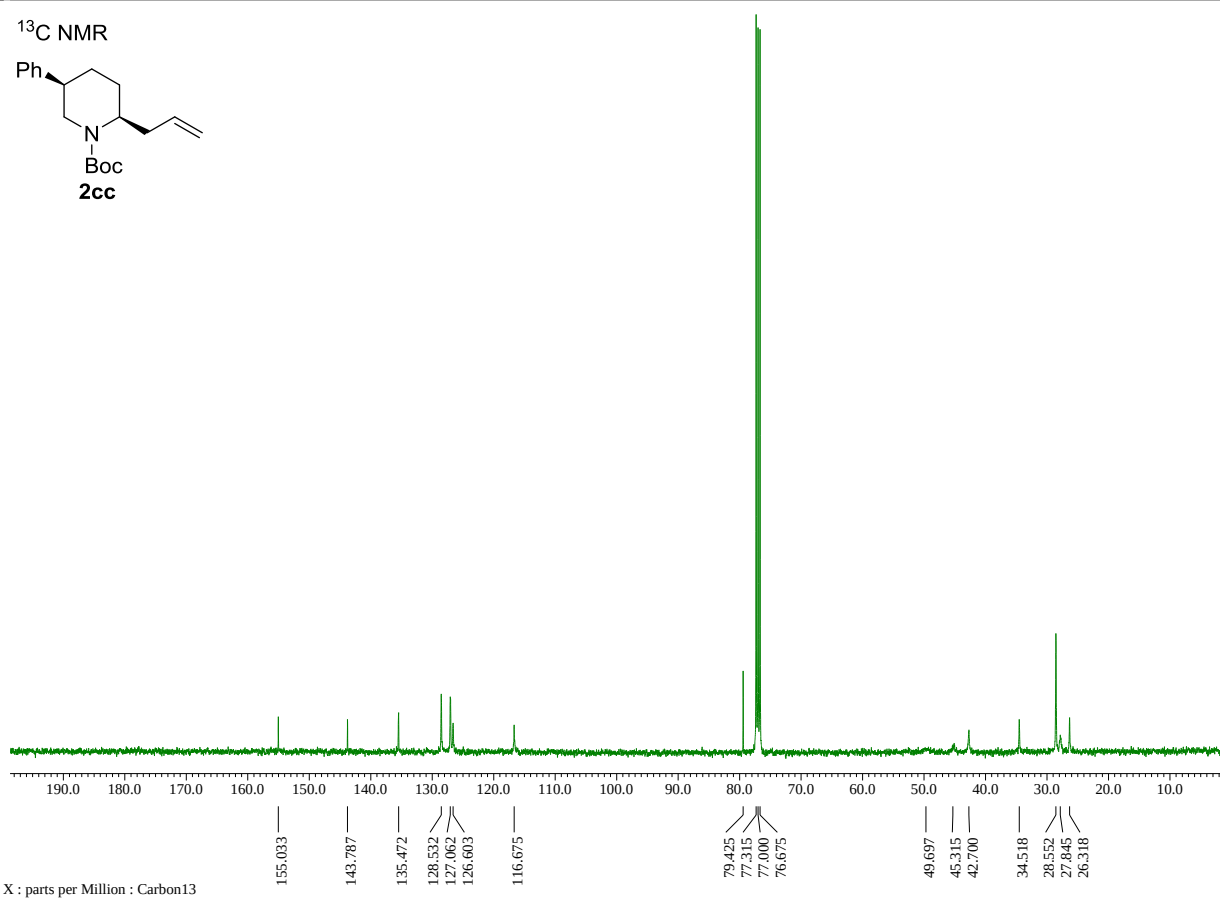
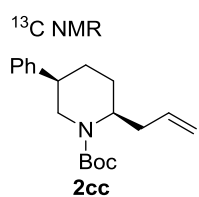
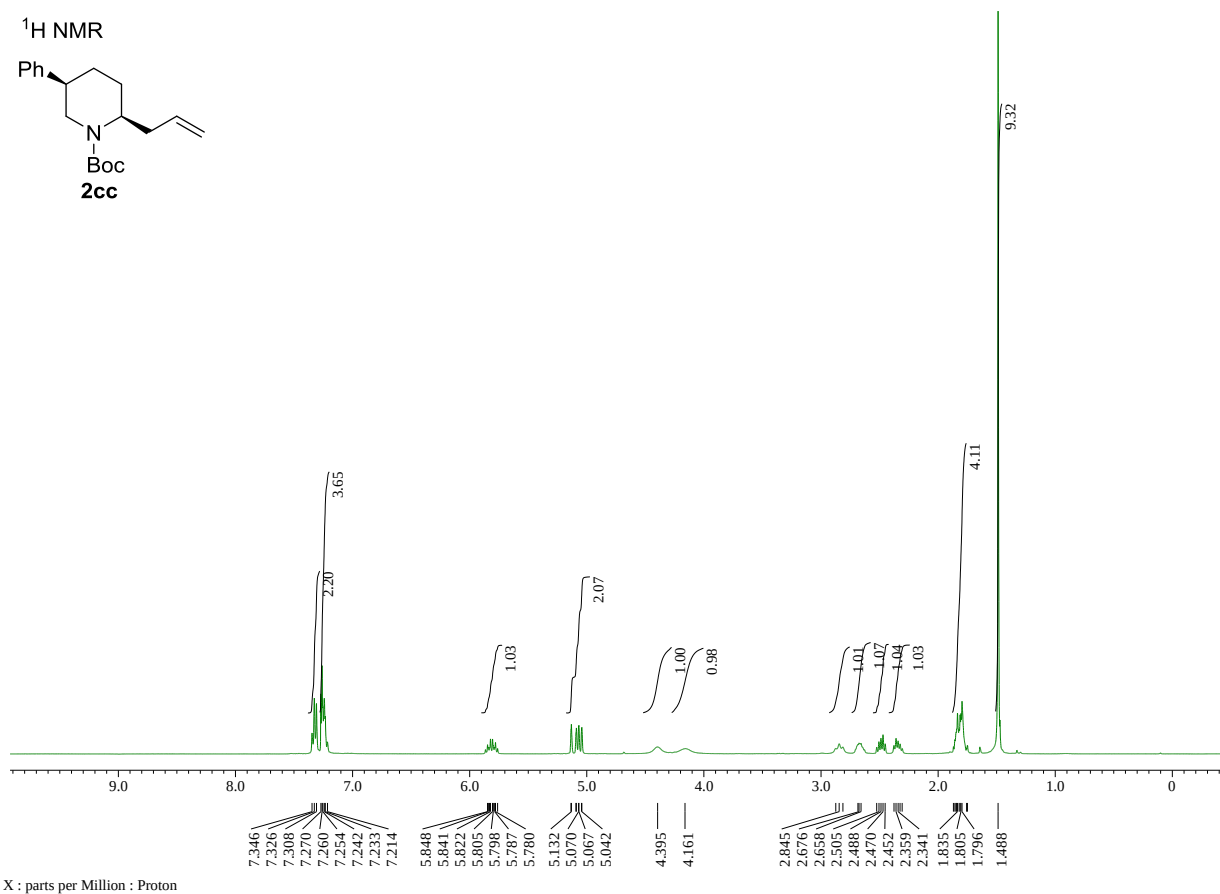
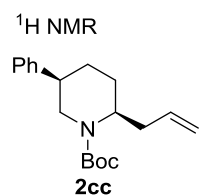


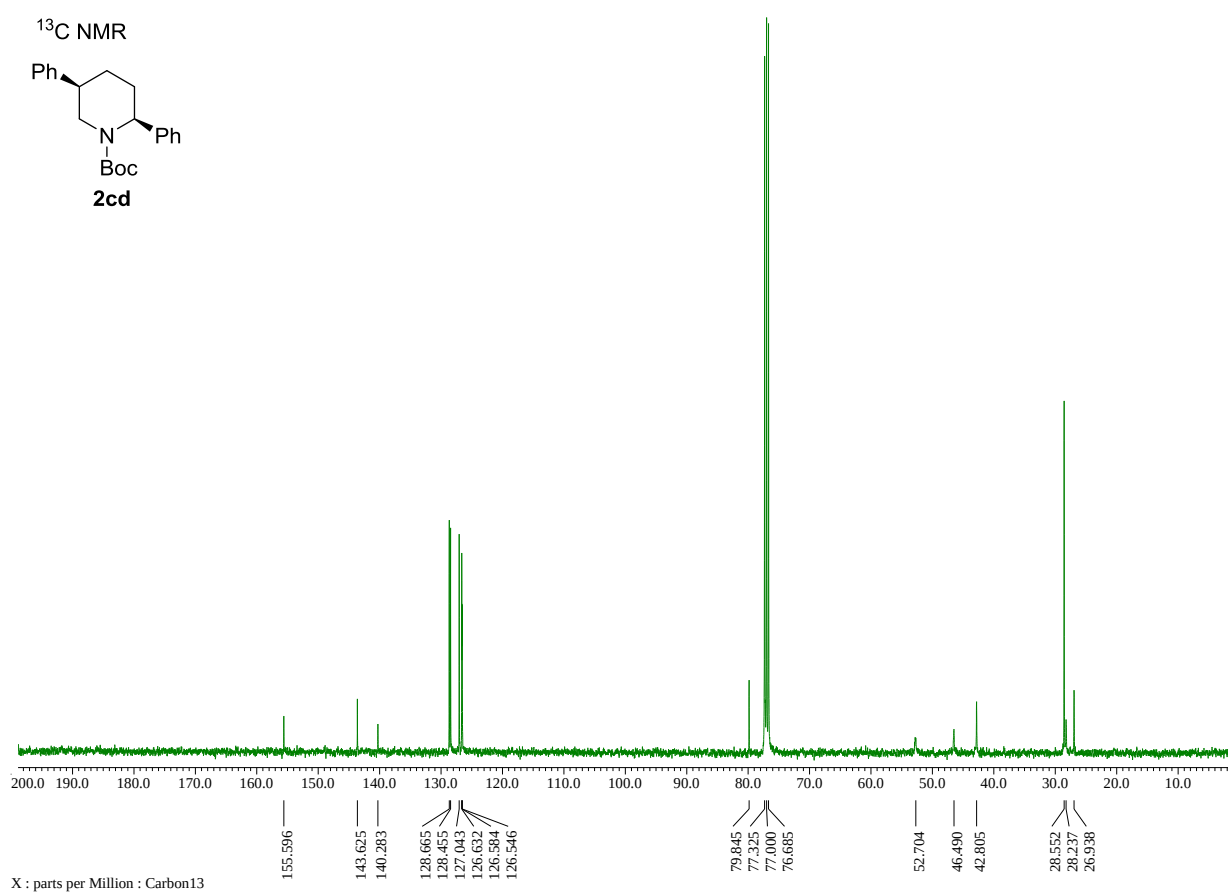
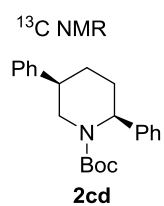
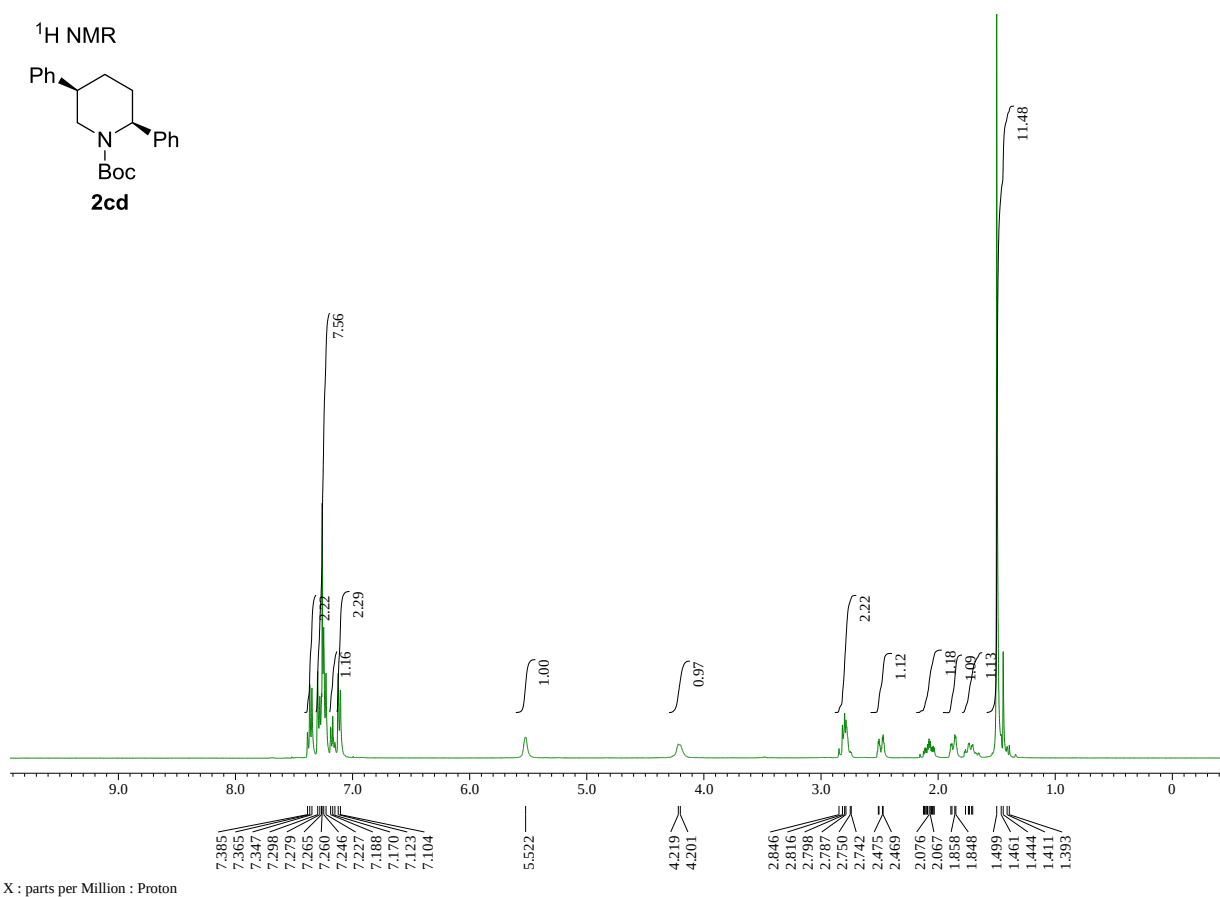
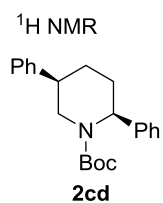
X : parts per Million : Proton

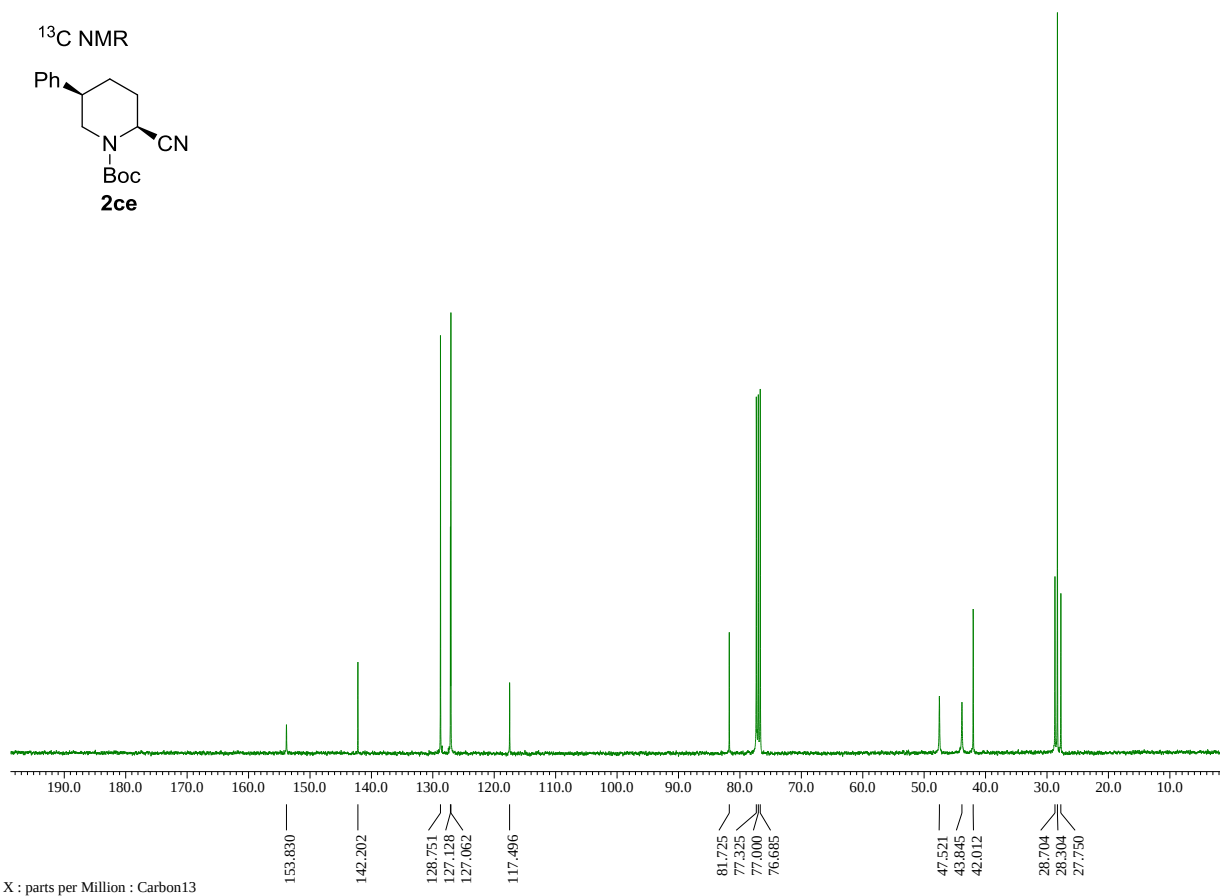
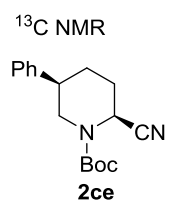
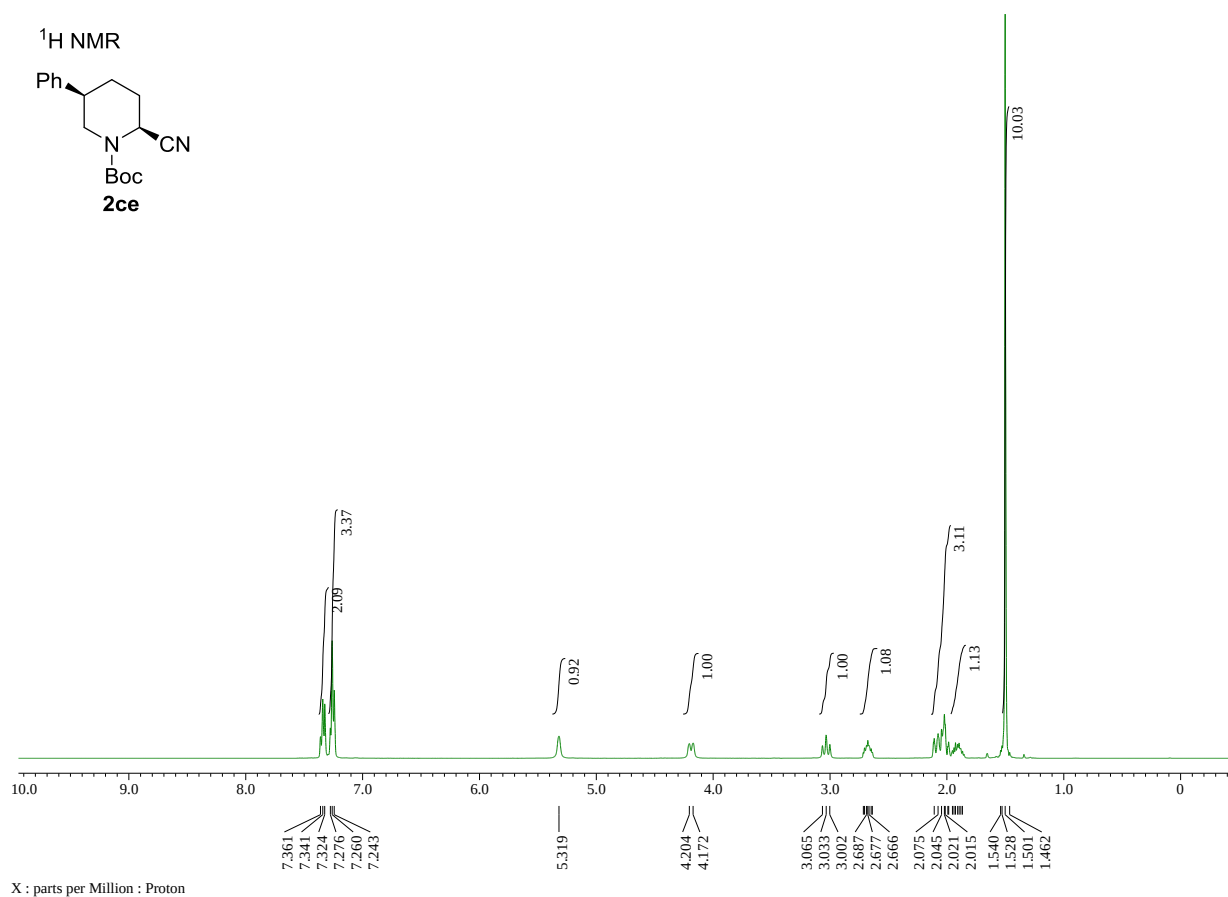
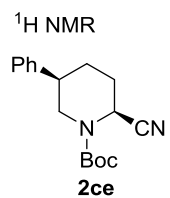


X : parts per Million : Carbon13



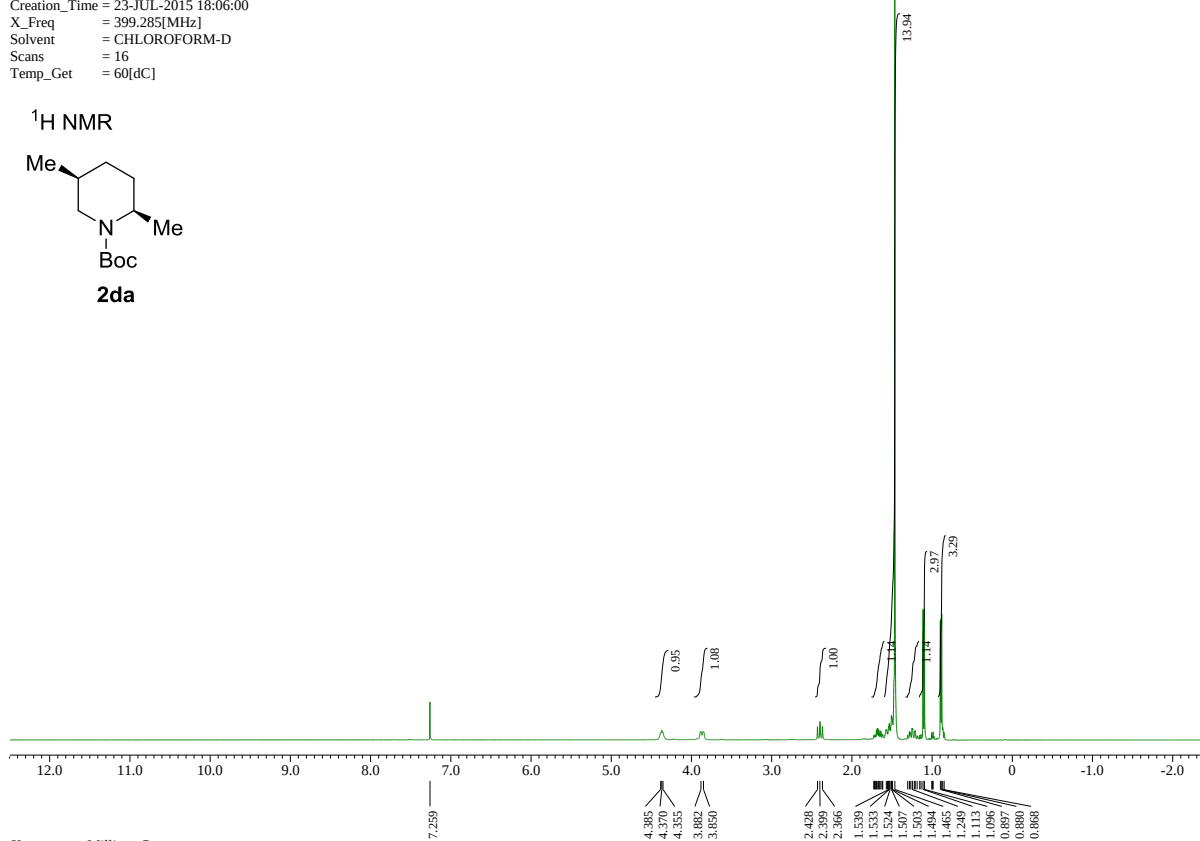
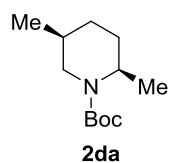






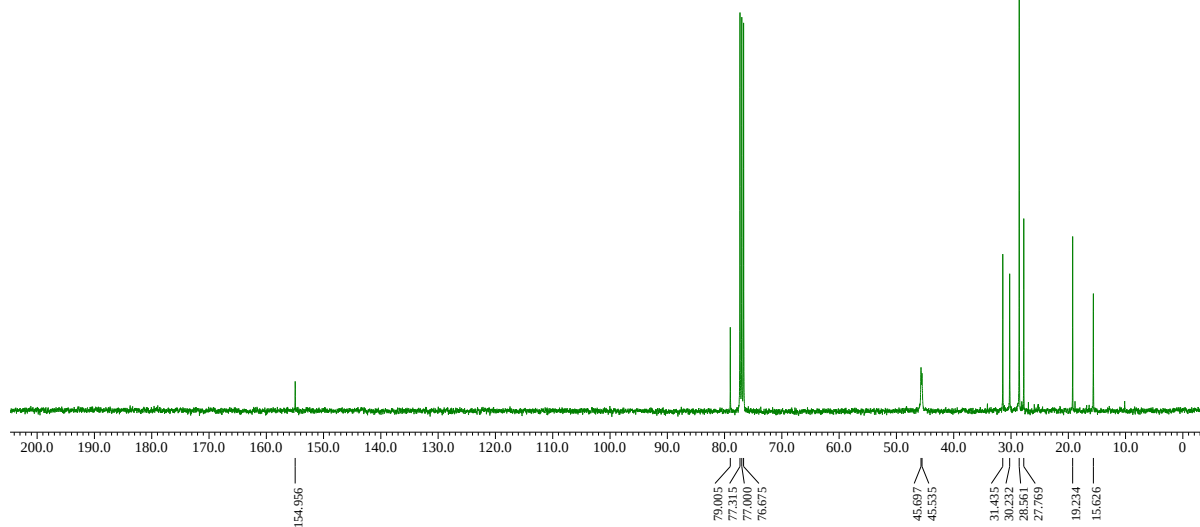
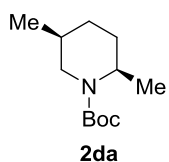
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¹H NMR



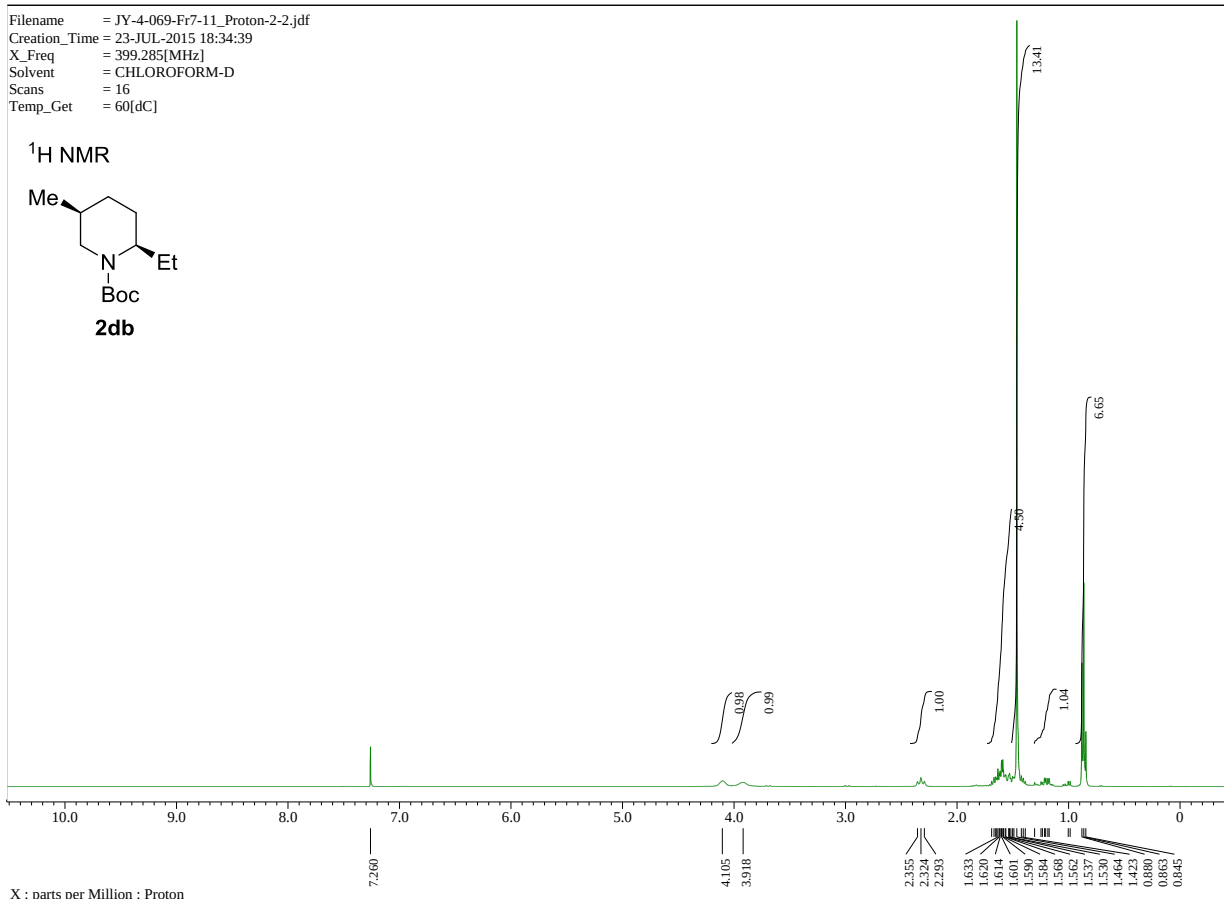
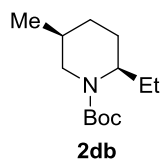
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¹³C NMR



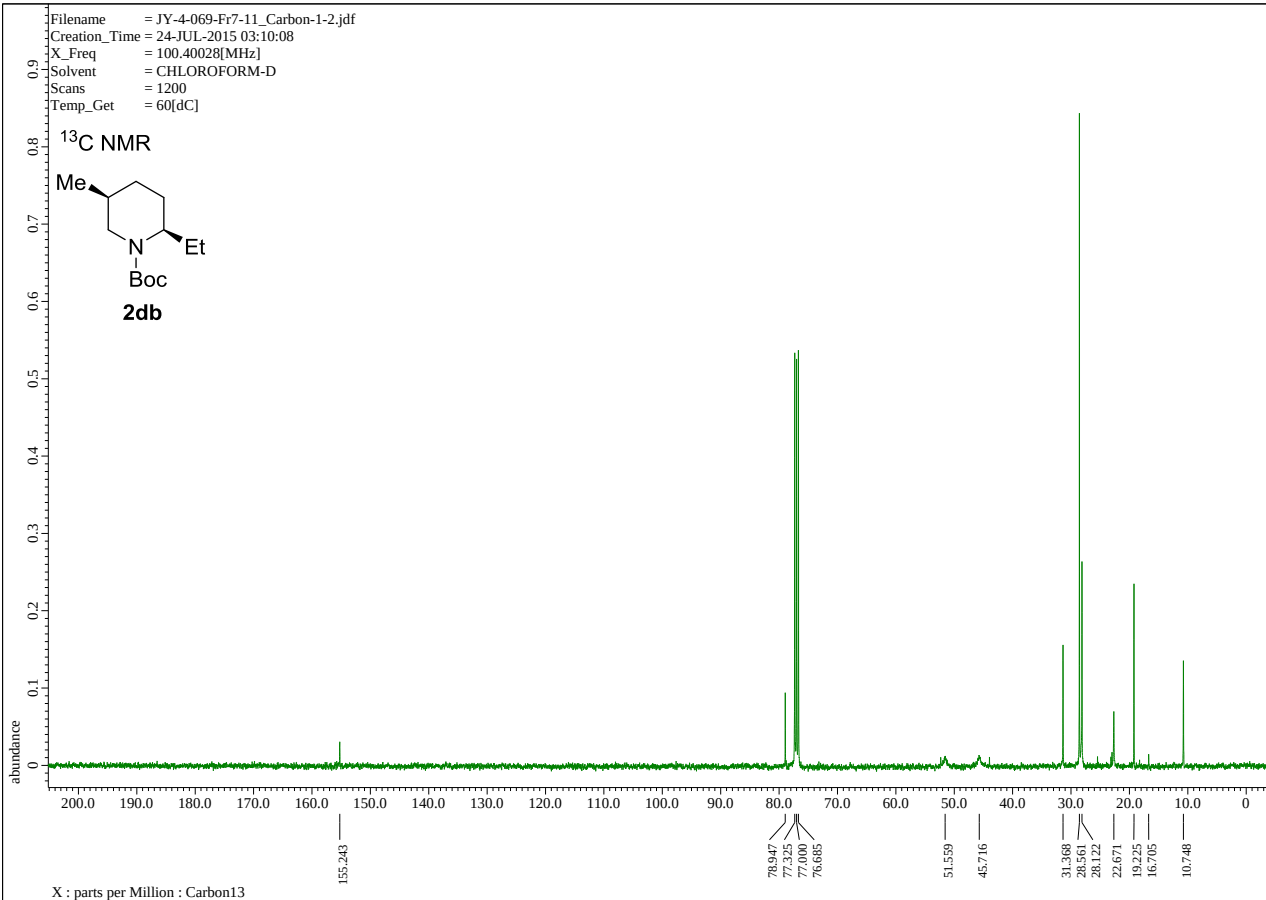
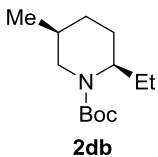
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¹H NMR



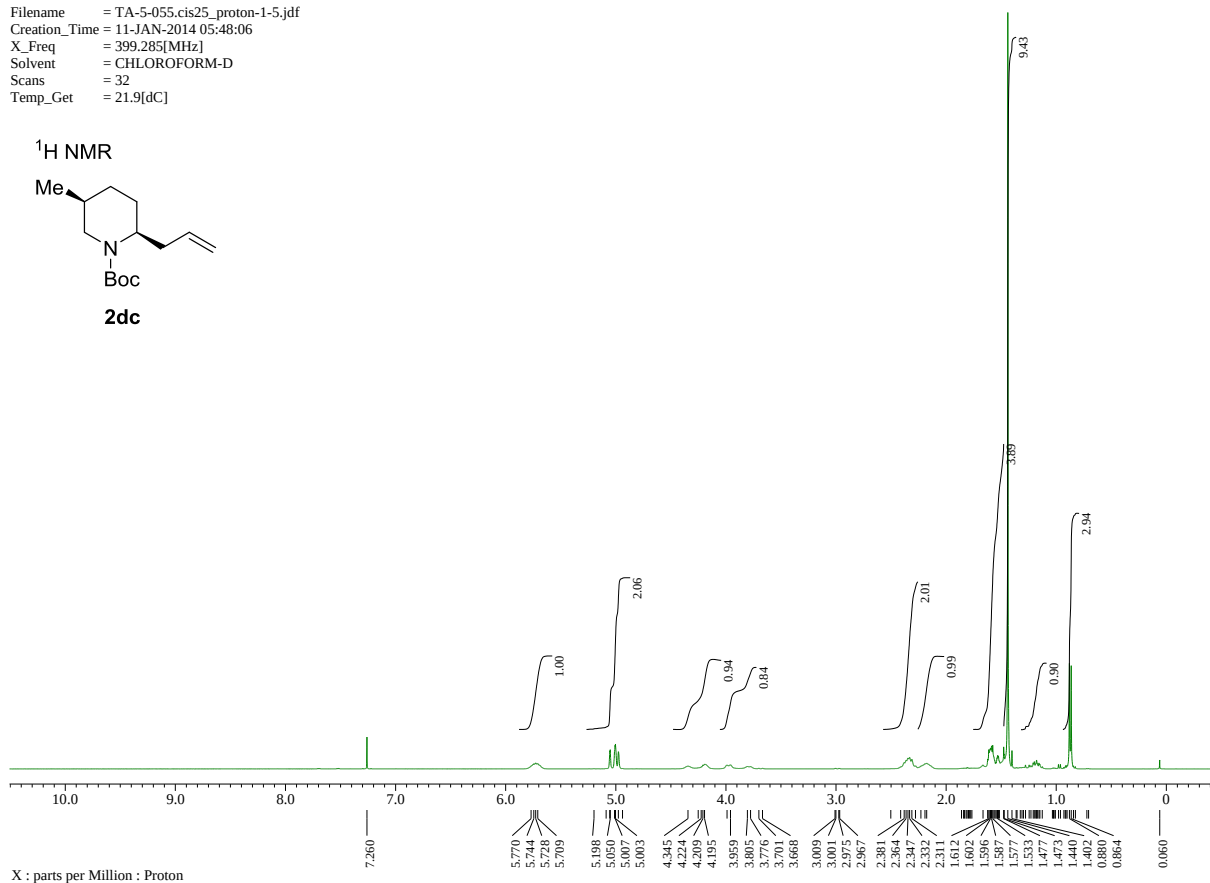
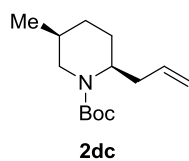
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¹³C NMR



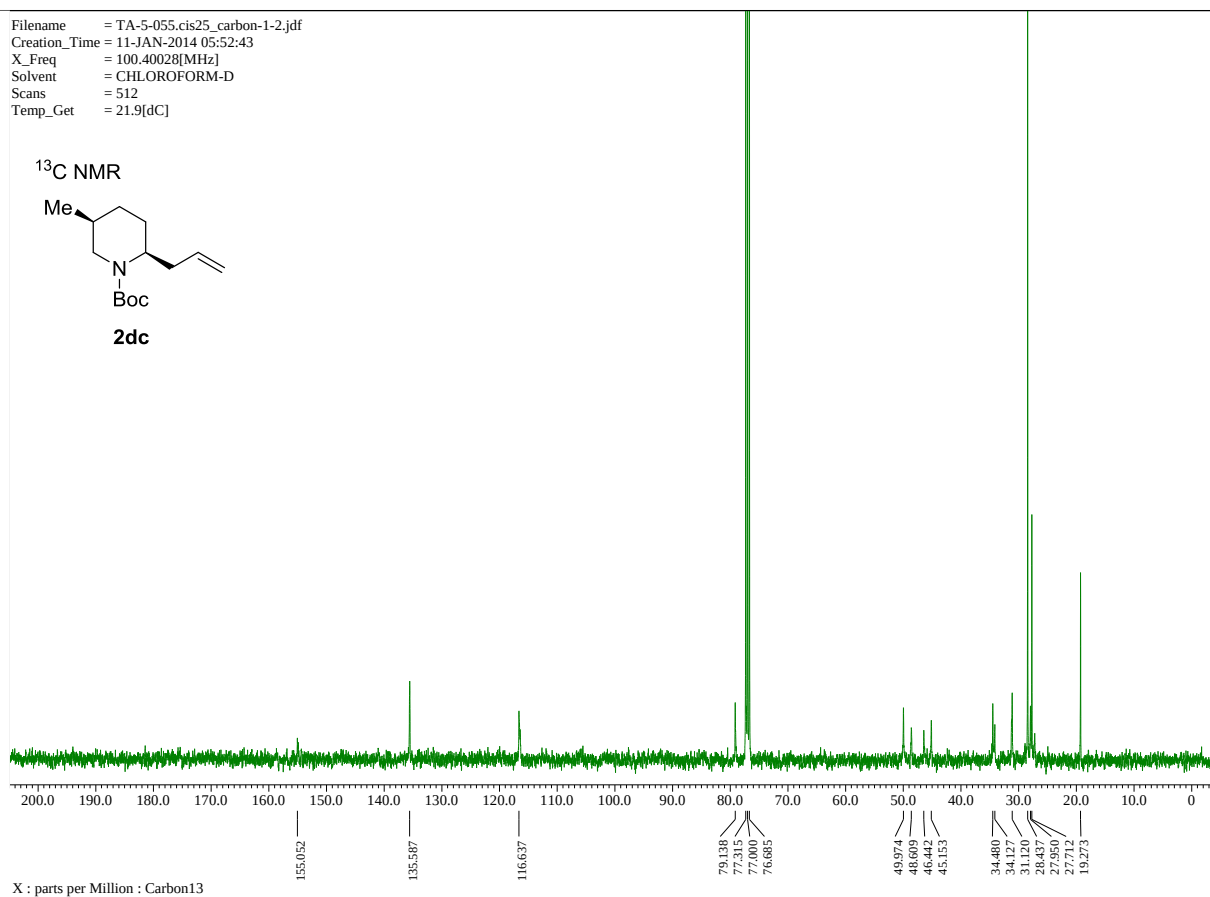
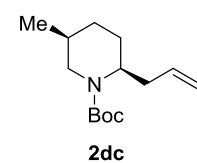
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¹H NMR



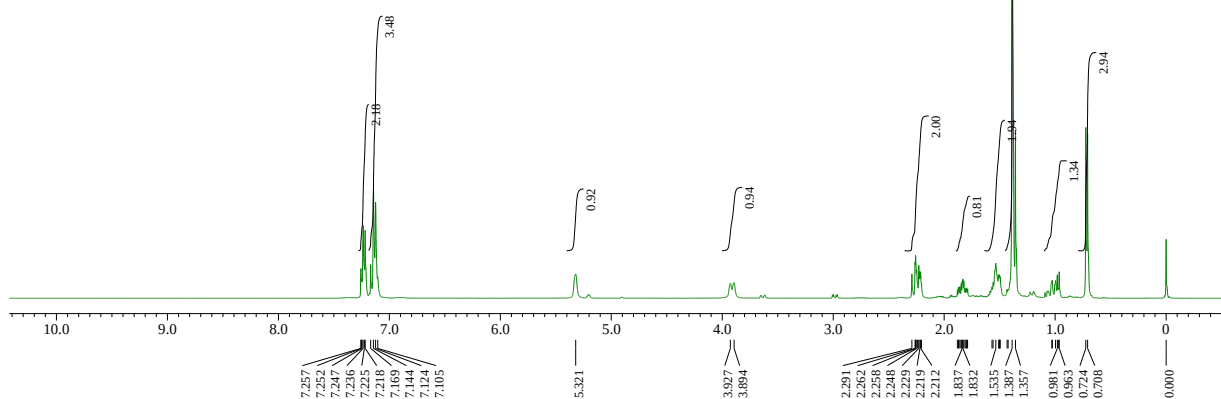
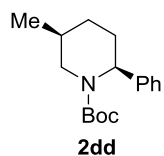
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¹³C NMR



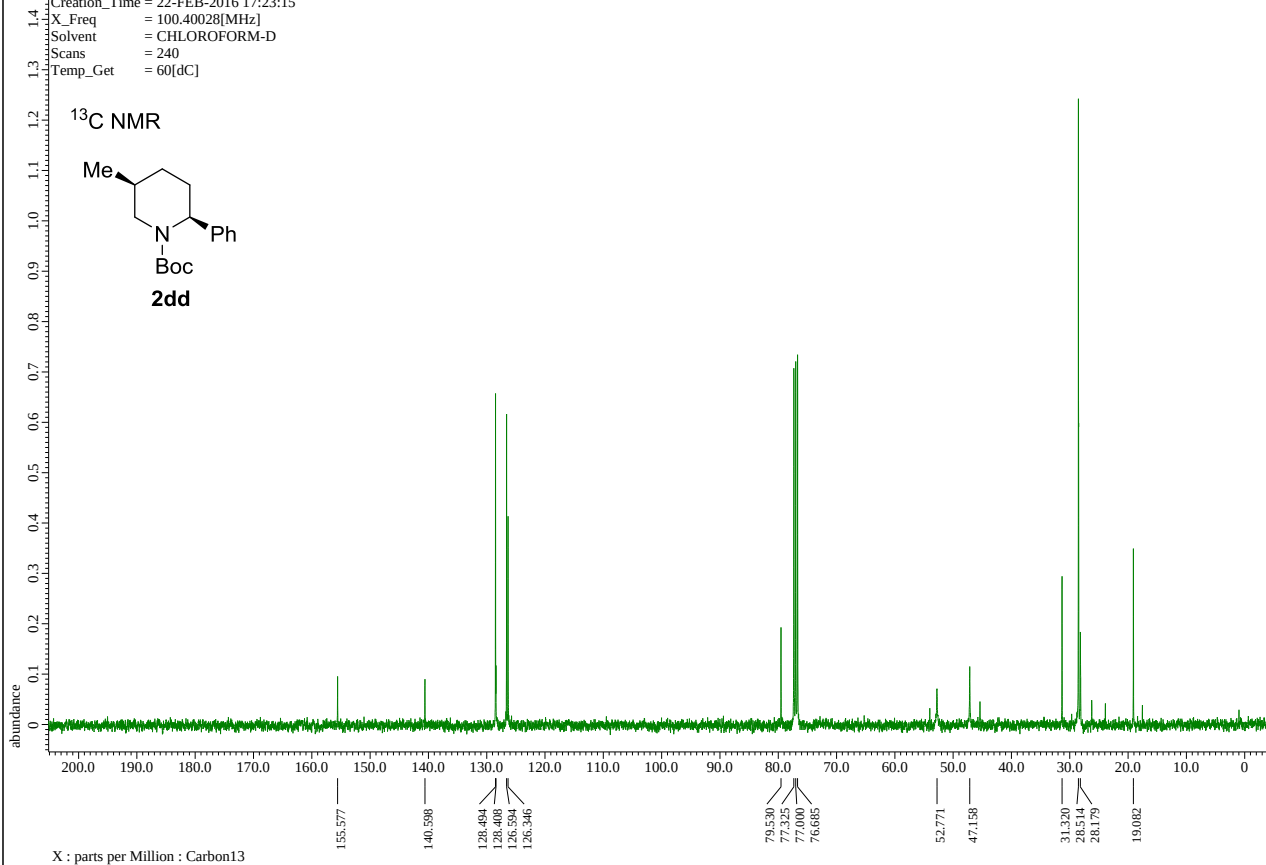
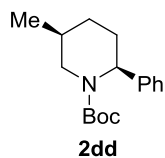
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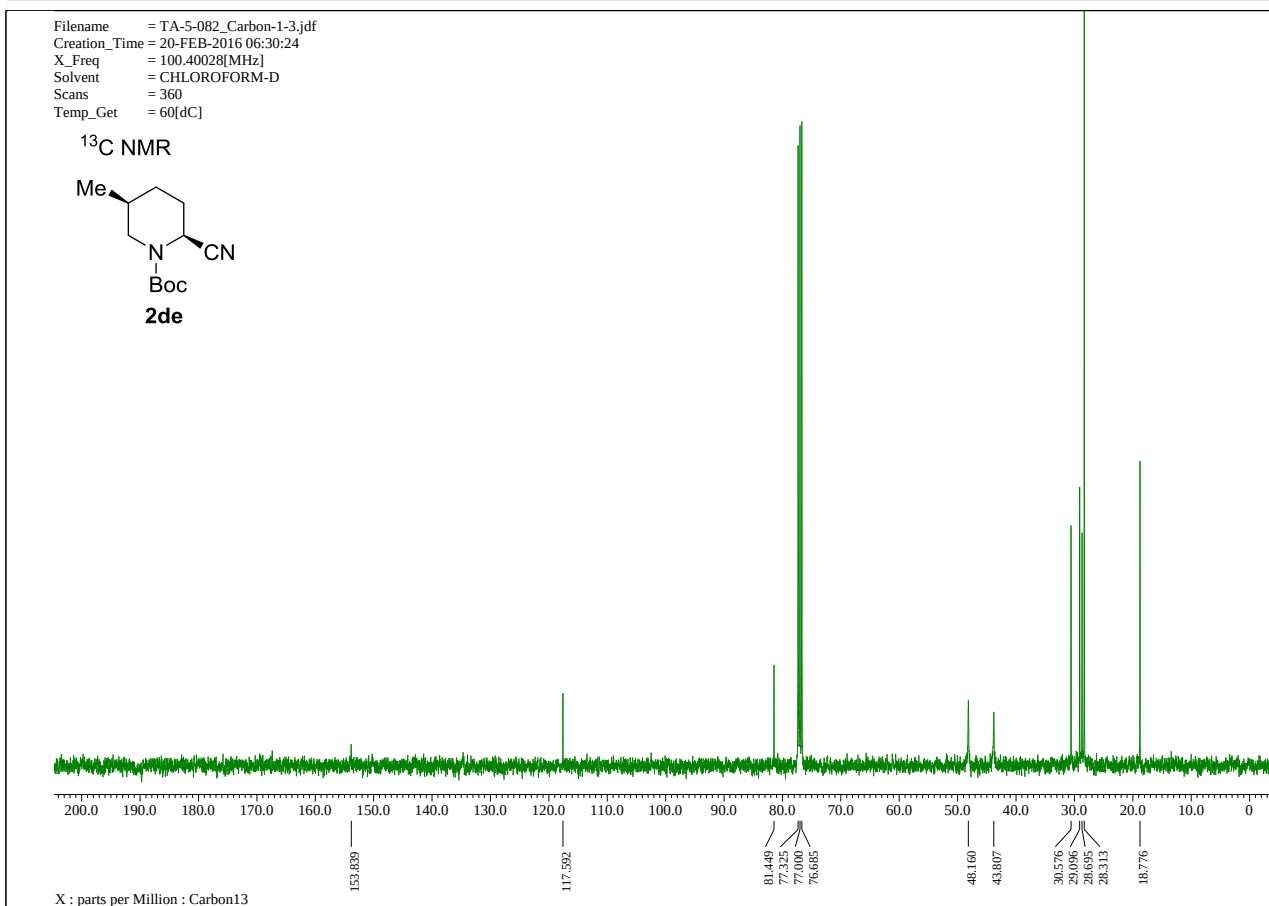
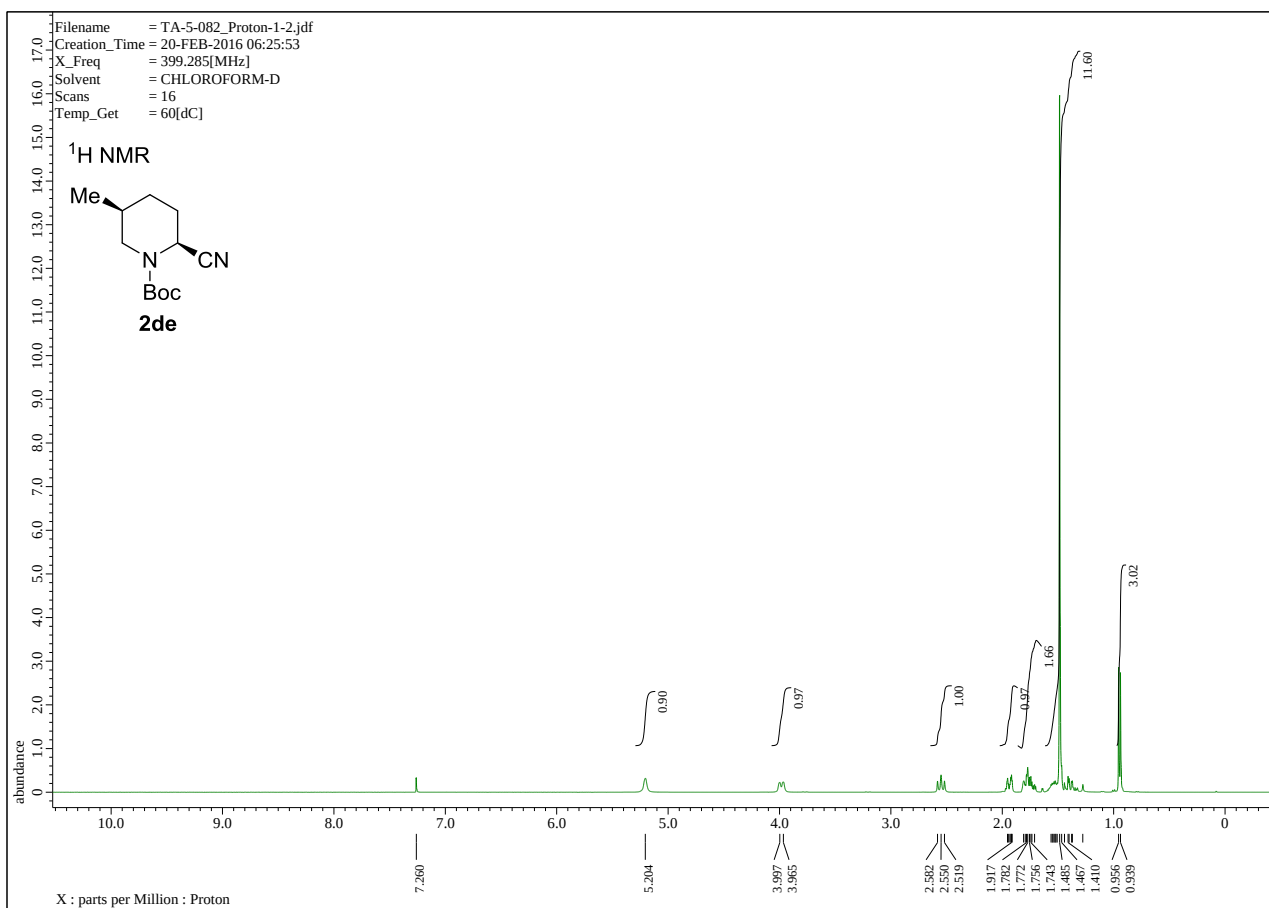
¹H NMR



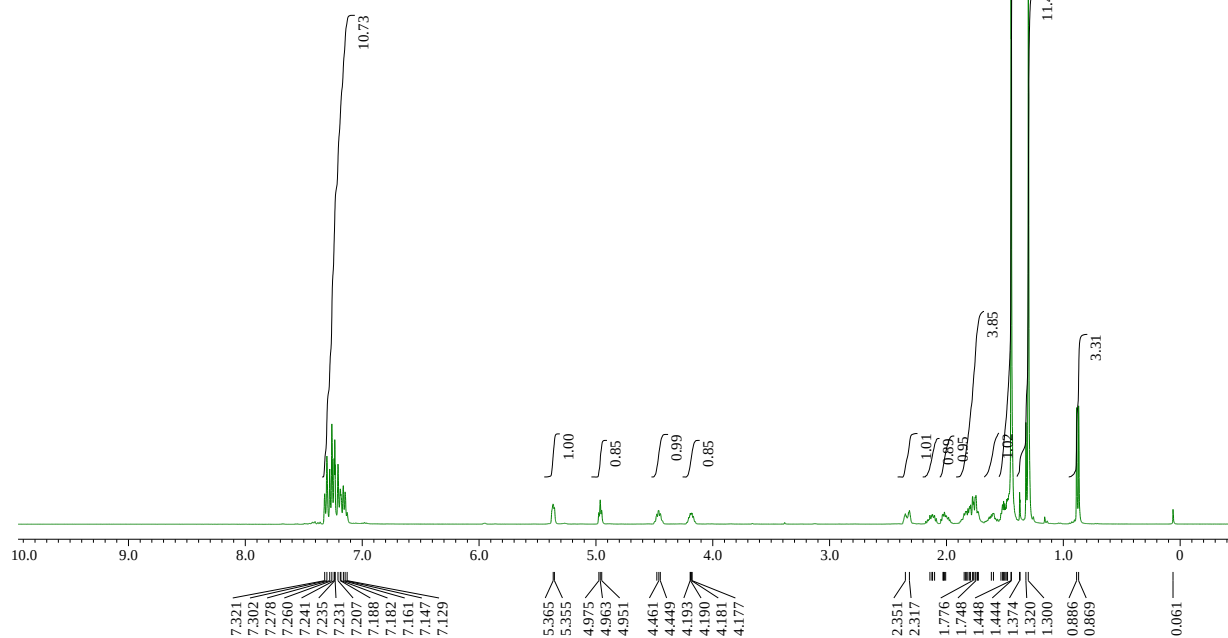
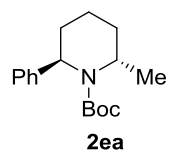
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¹³C NMR



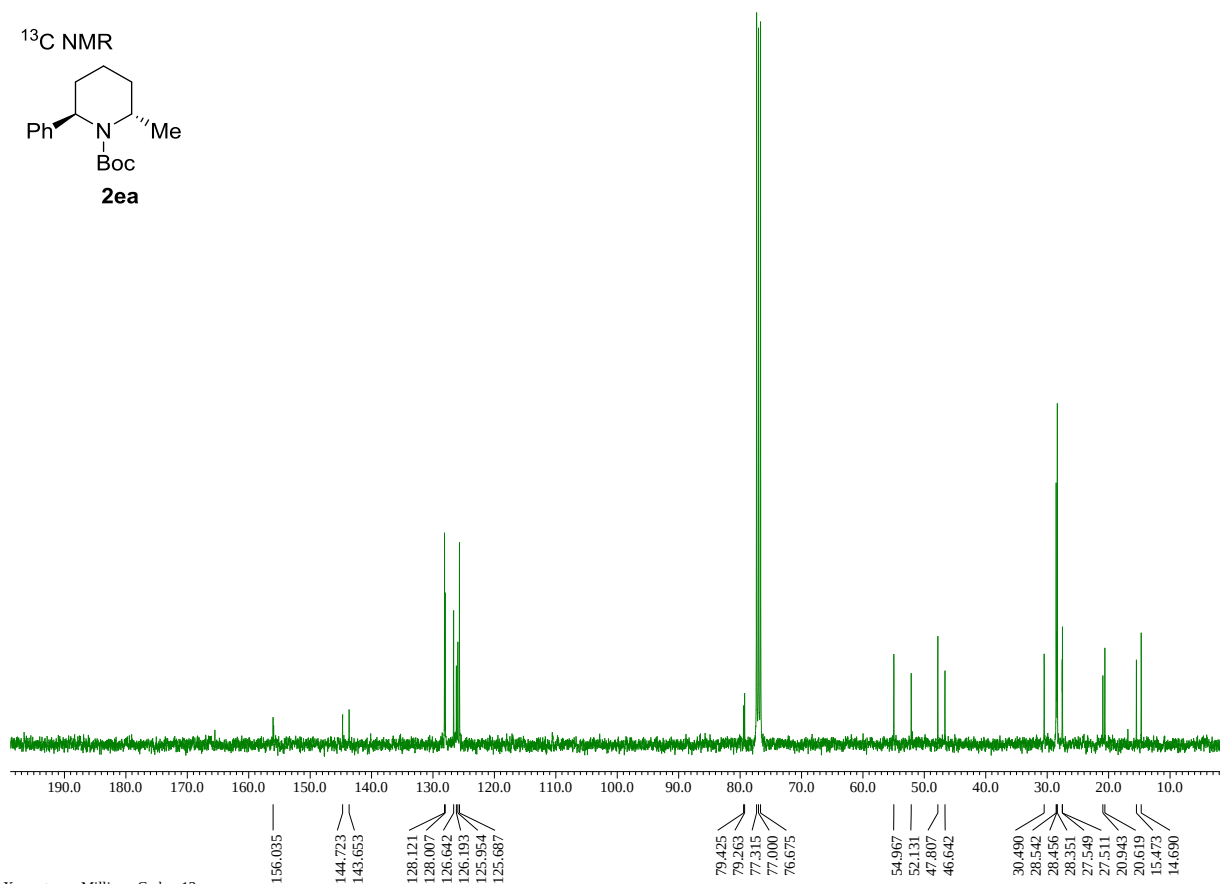
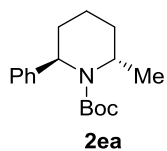


¹H NMR



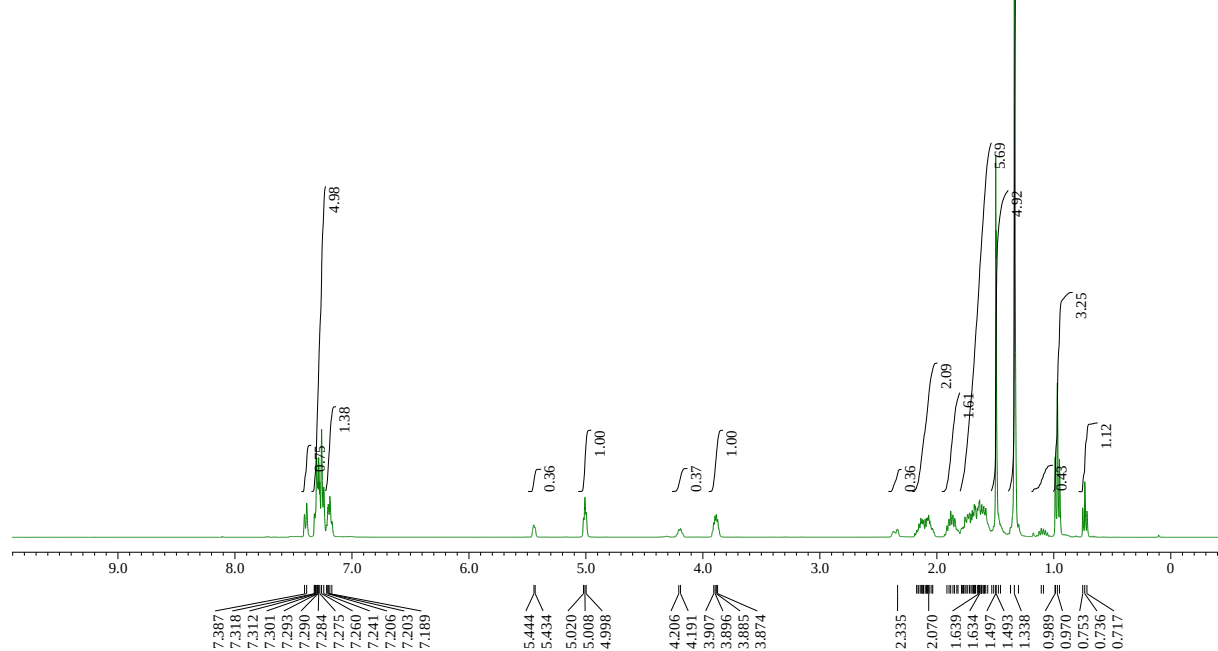
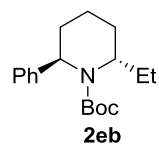
X : parts per Million : Proton

¹³C NMR



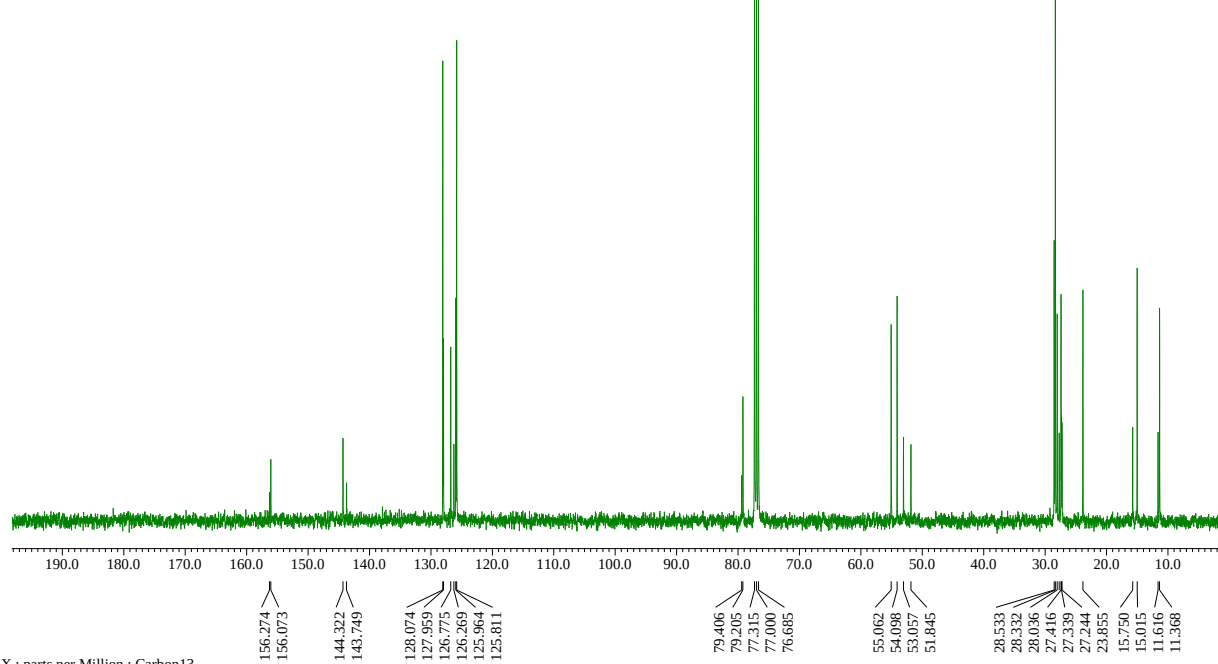
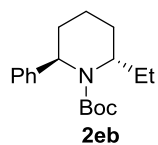
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¹H NMR

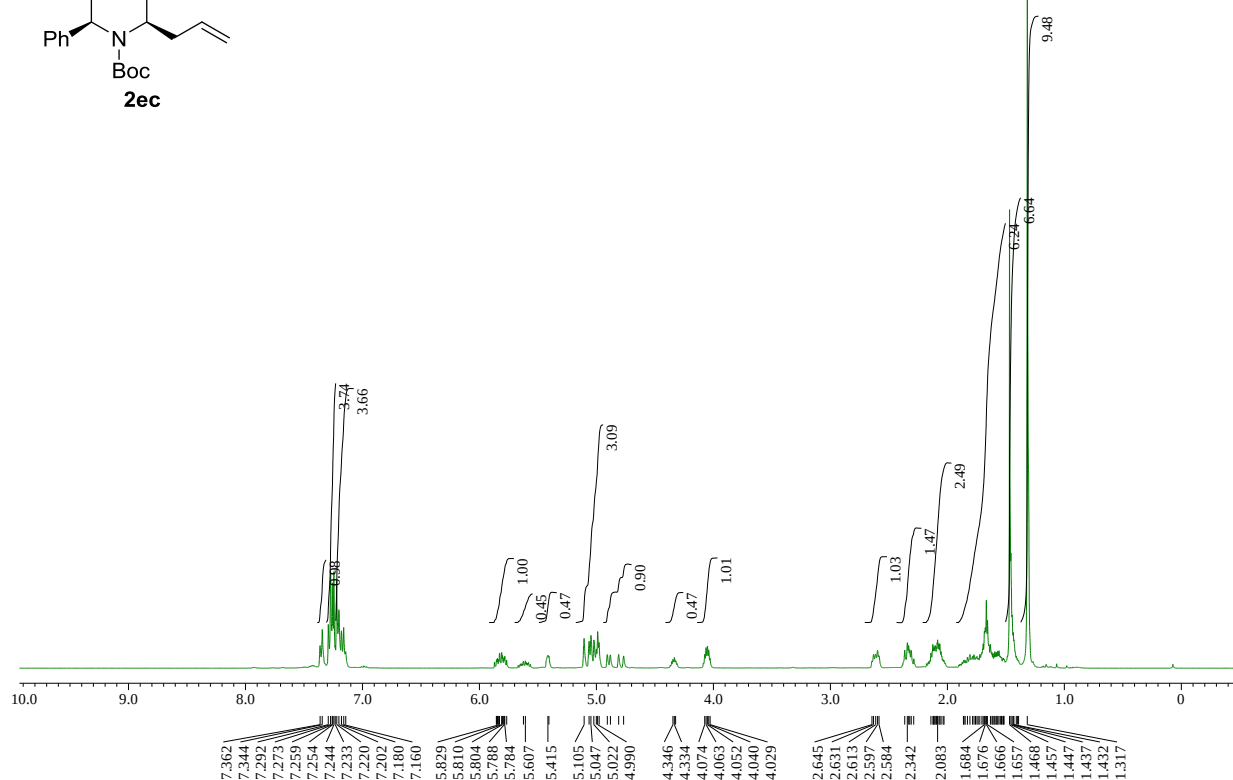
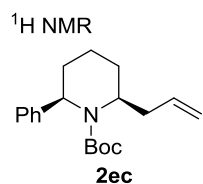


X : parts per Million : Proton

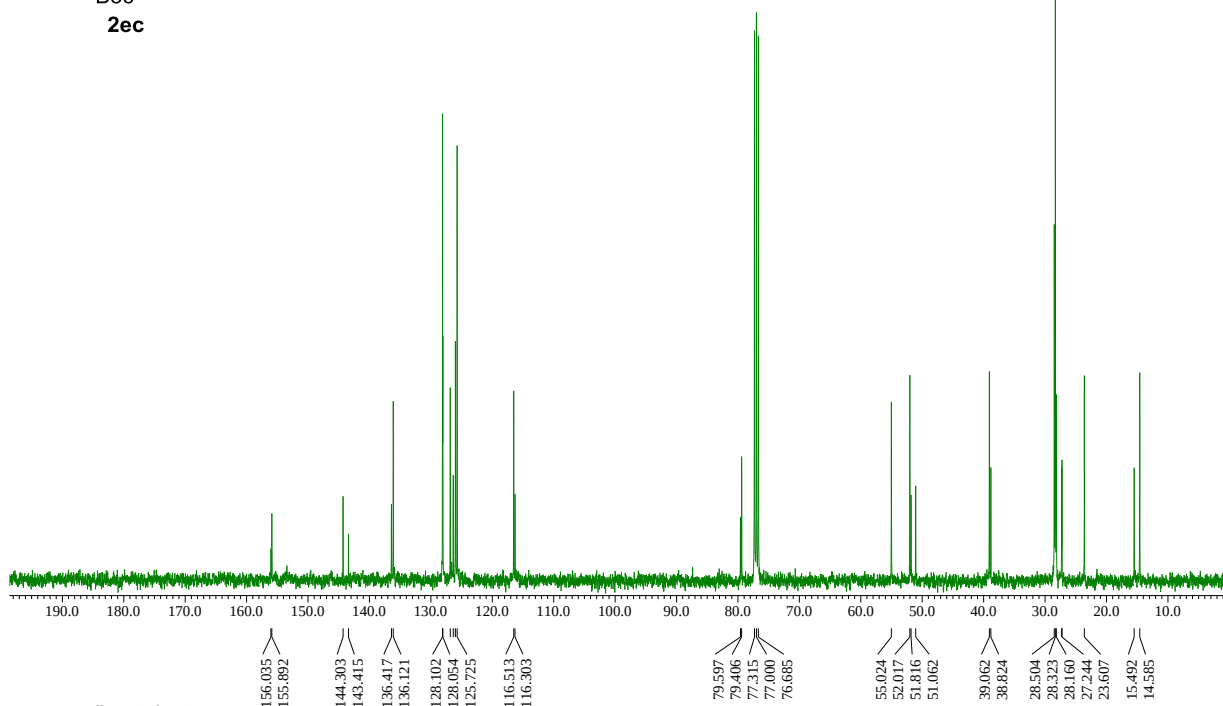
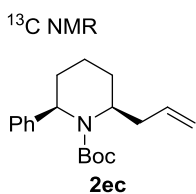
¹³C NMR



X : parts per Million : Carbon13

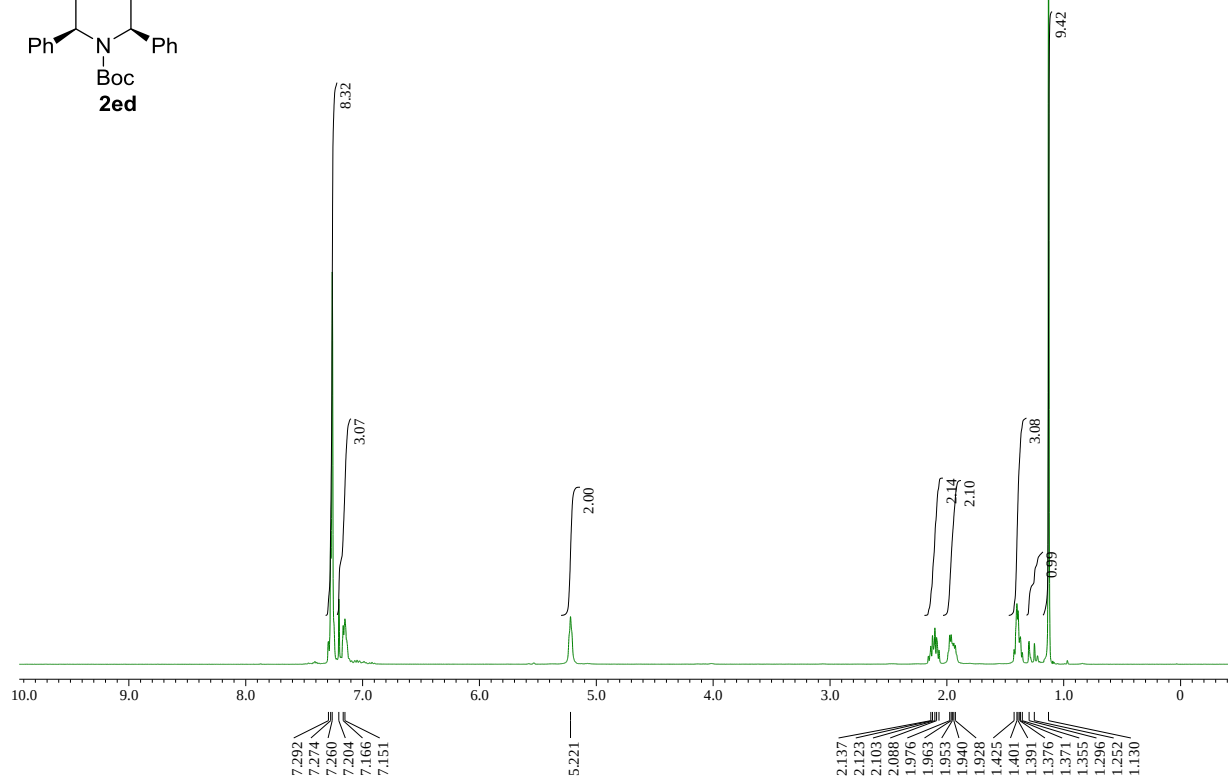
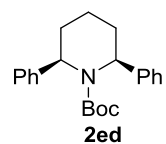


X : parts per Million : Proton

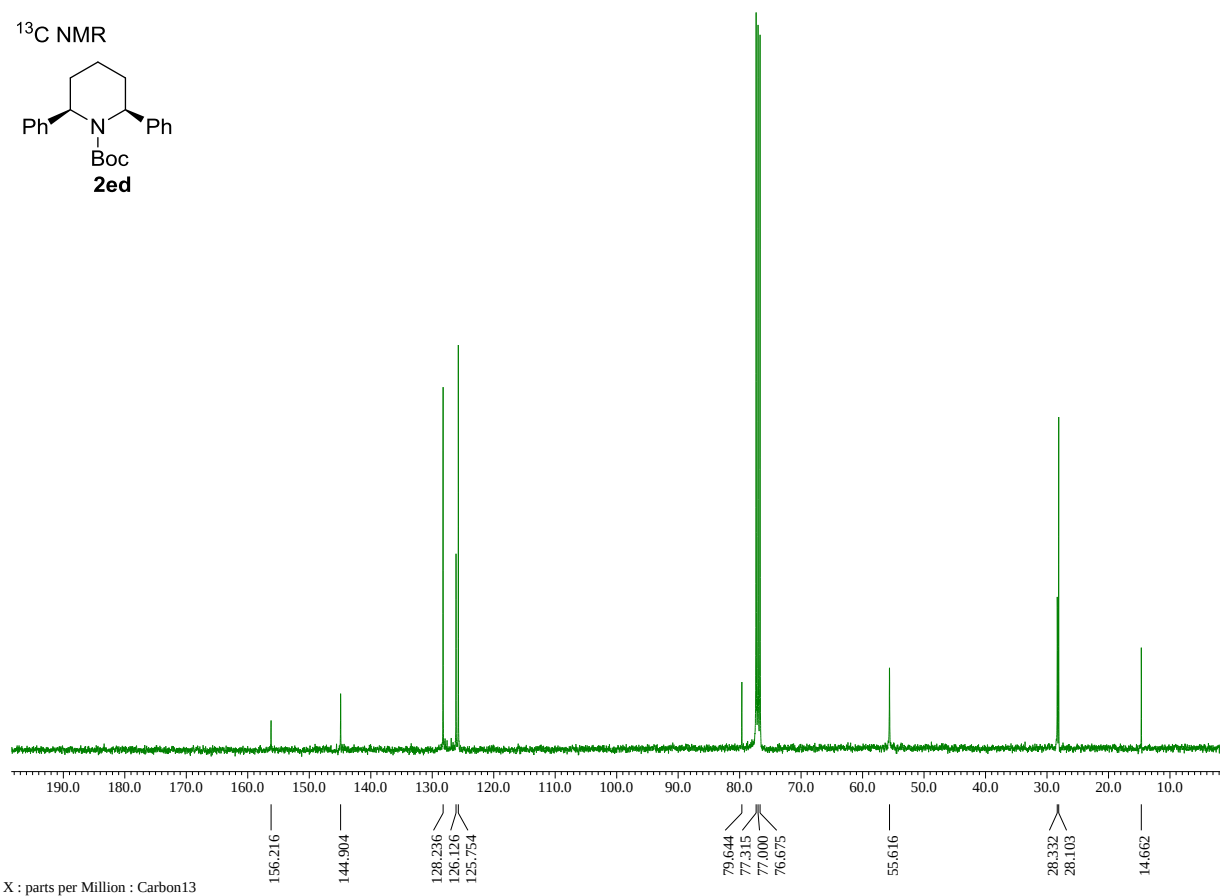
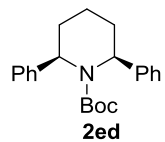


X : parts per Million : Carbon13

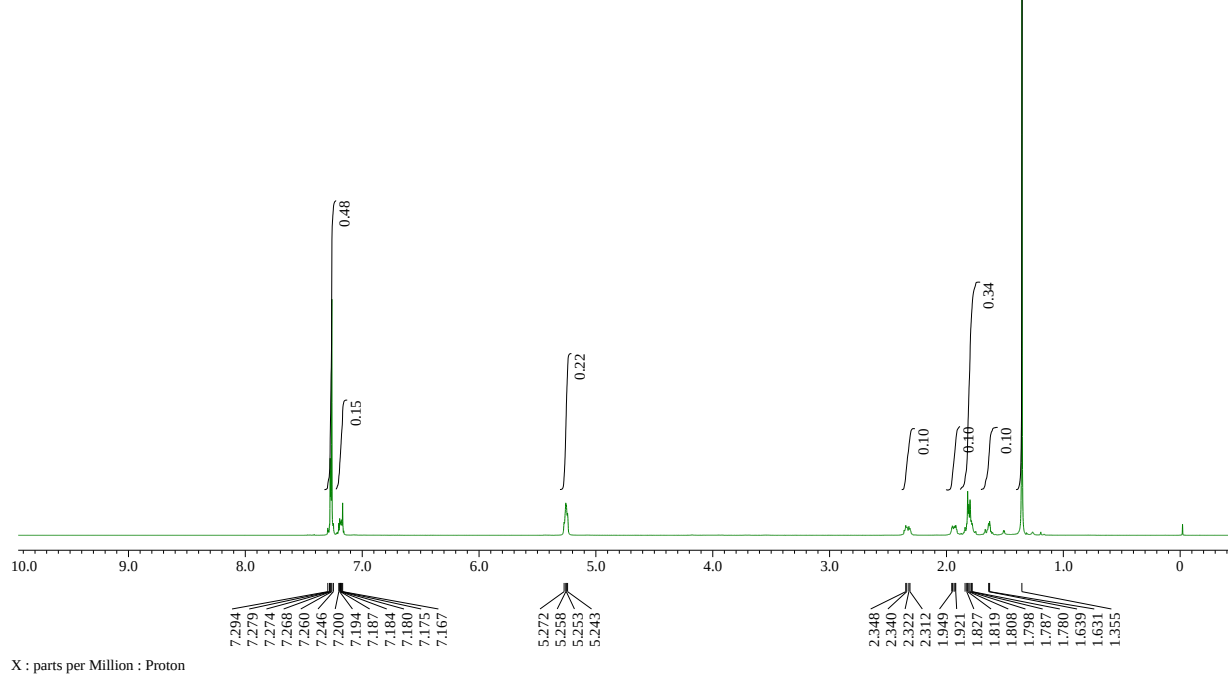
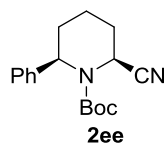
¹H NMR



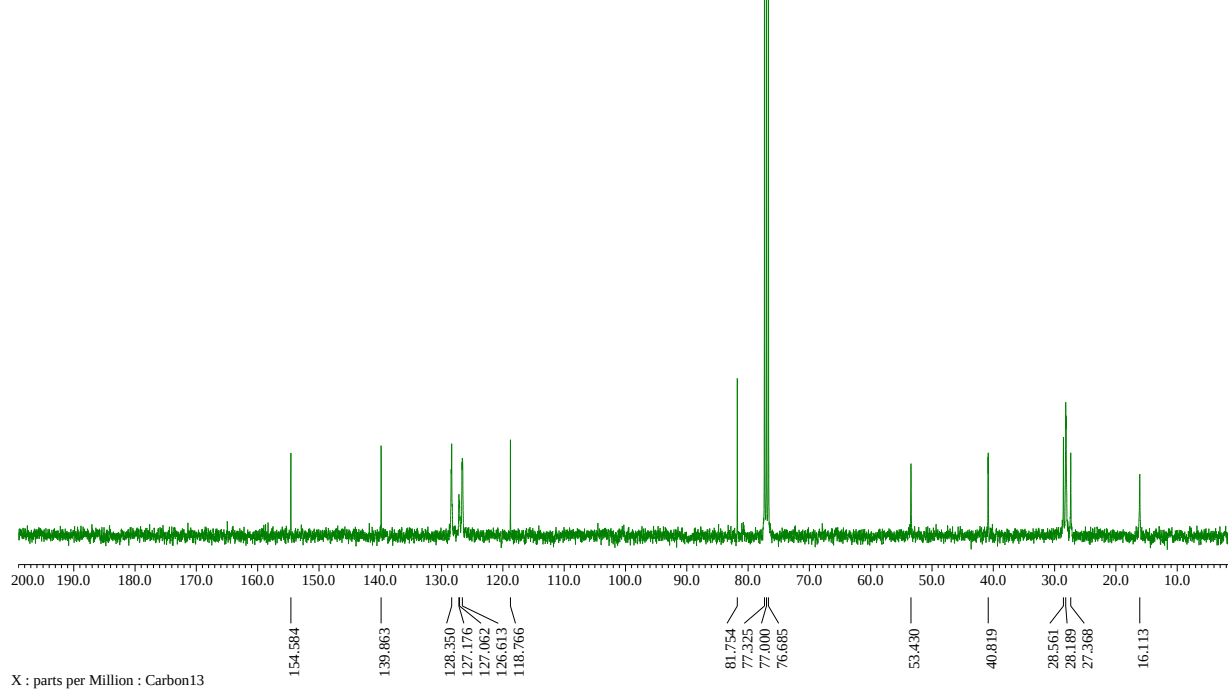
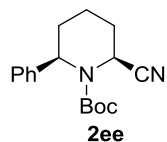
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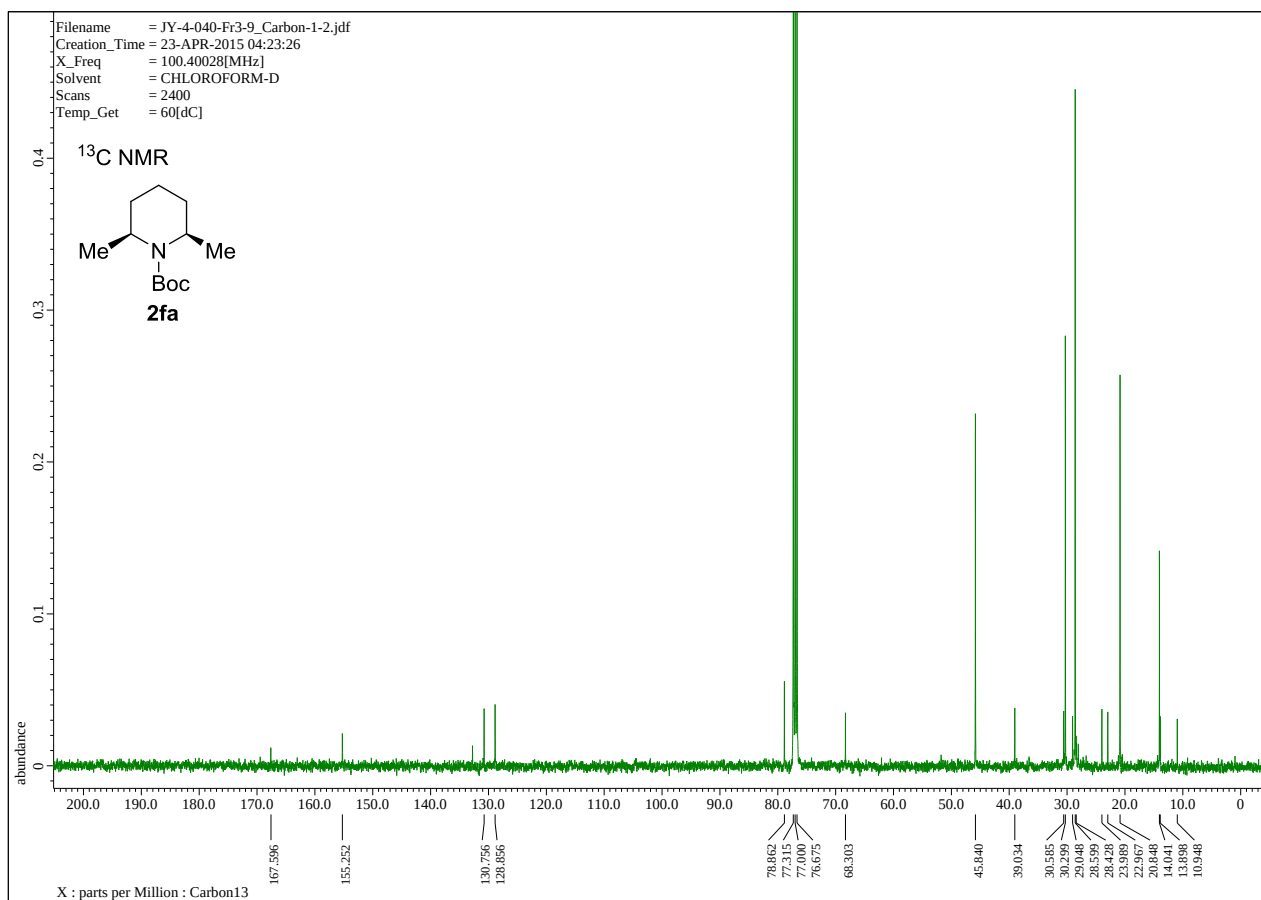
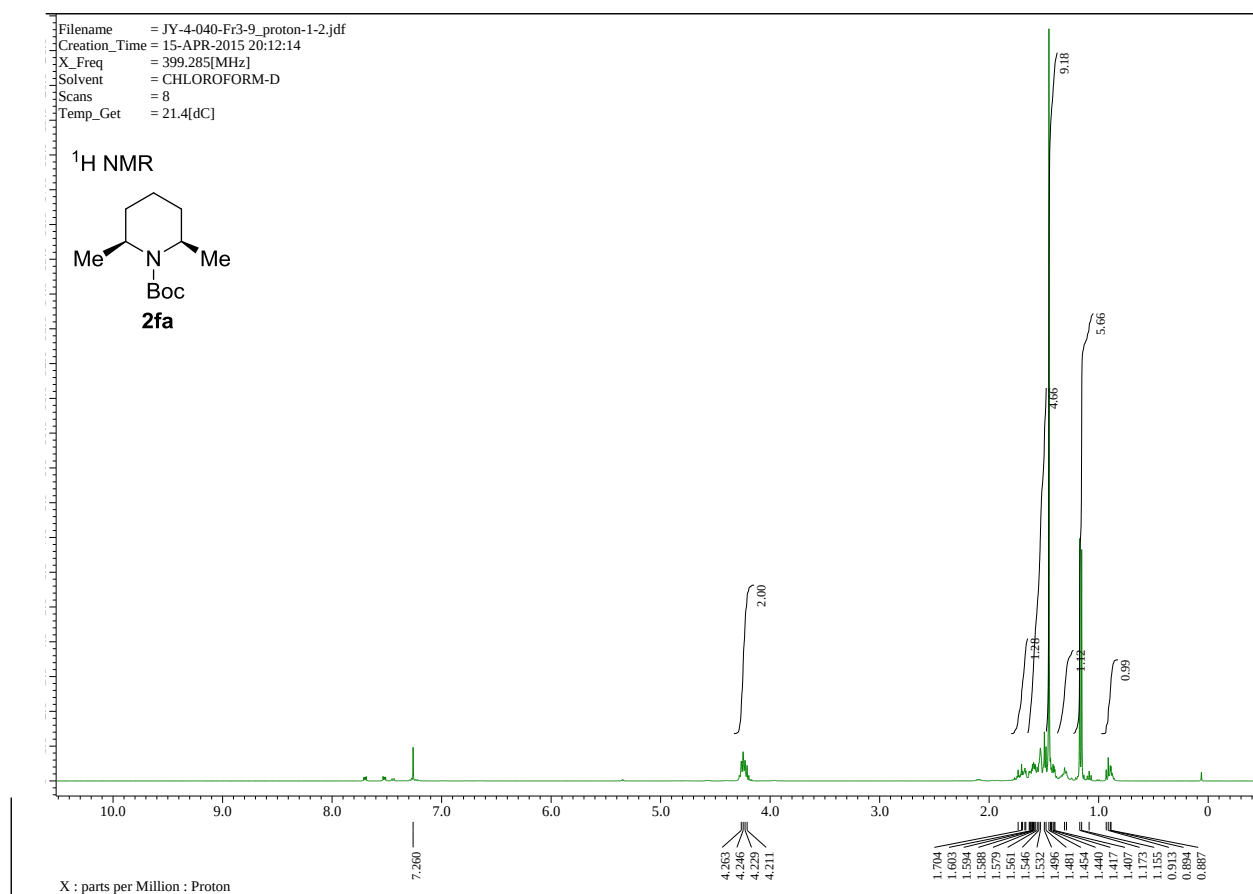


¹H NMR



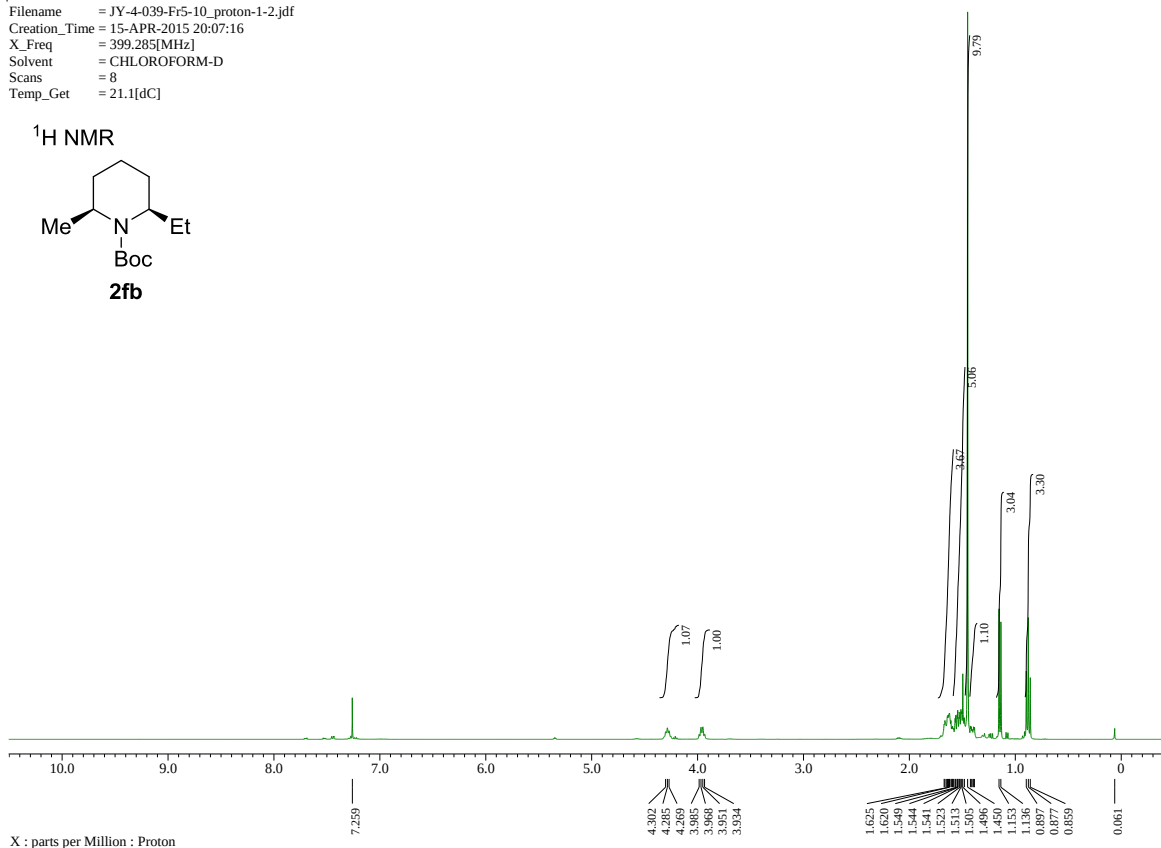
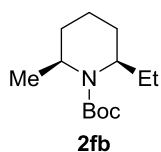
¹³C NMR





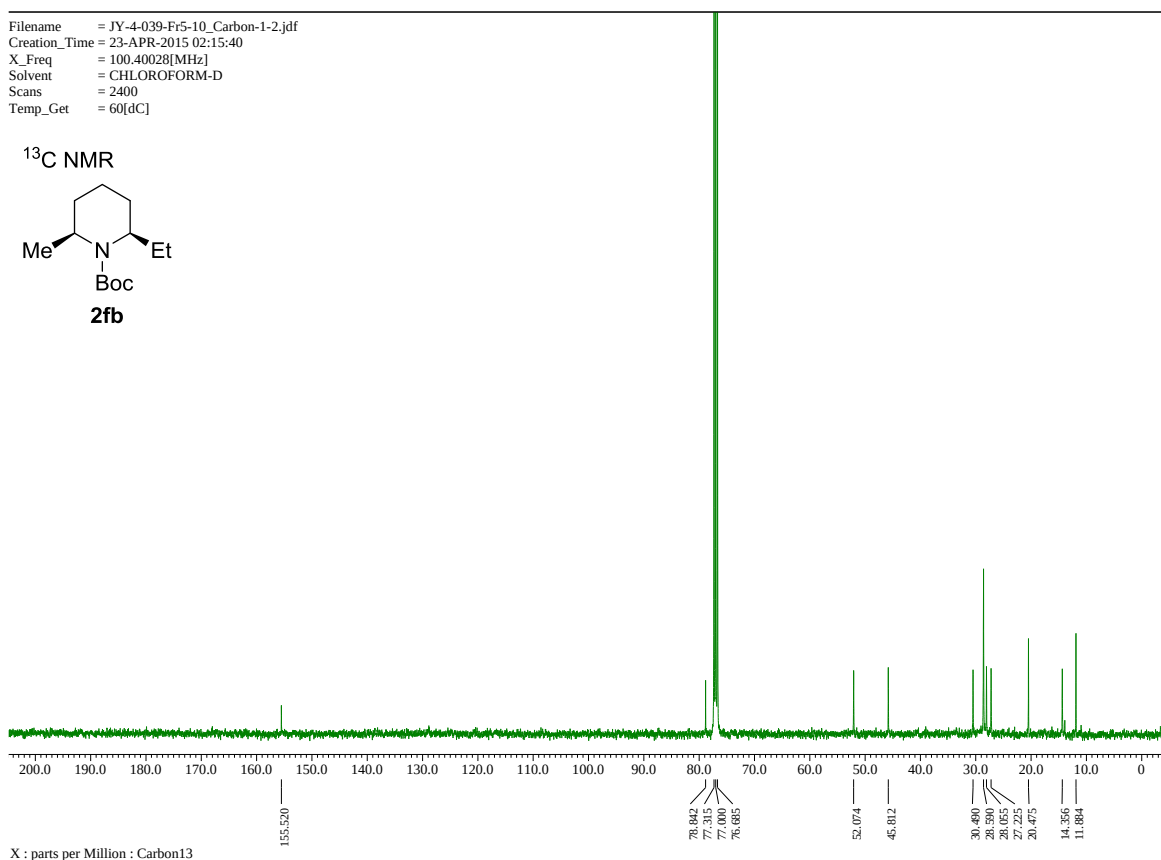
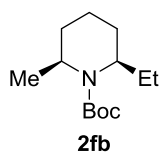
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¹H NMR



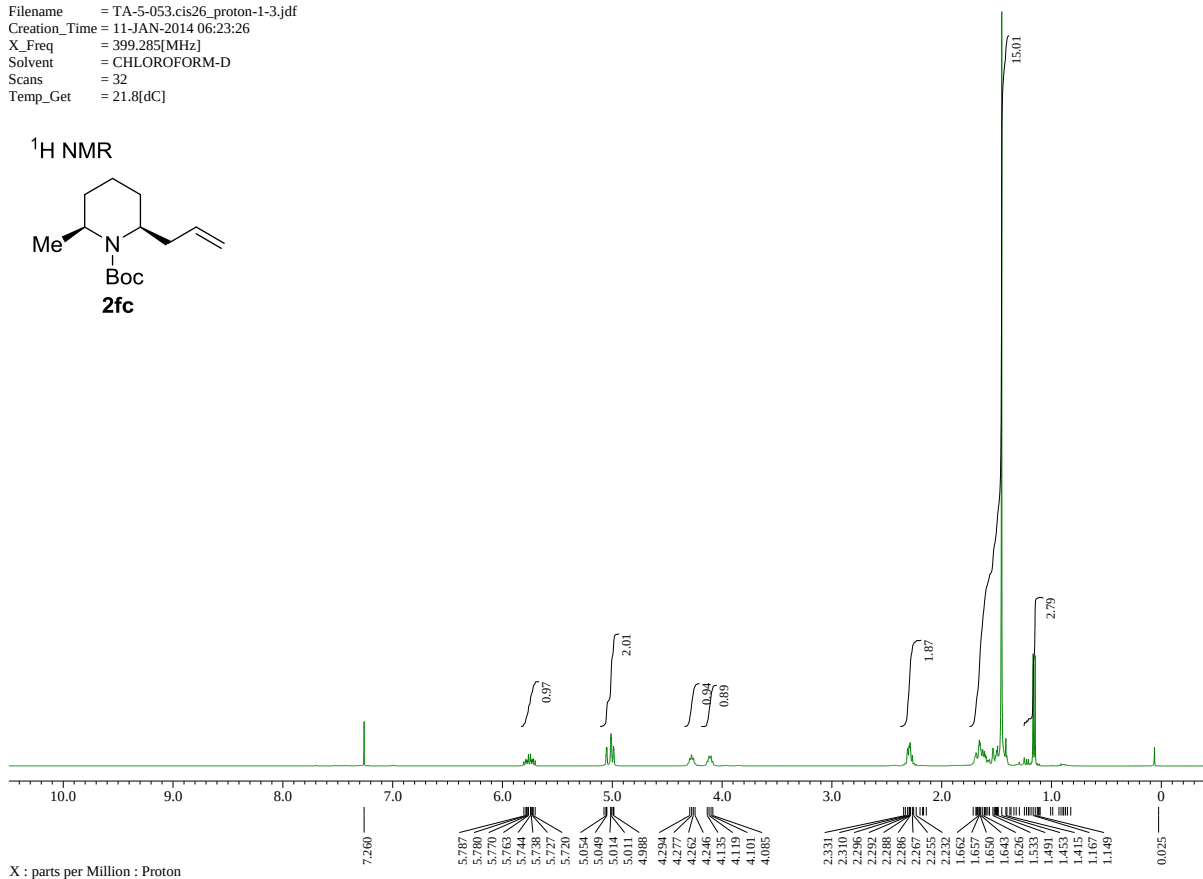
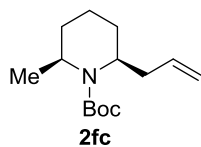
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¹³C NMR



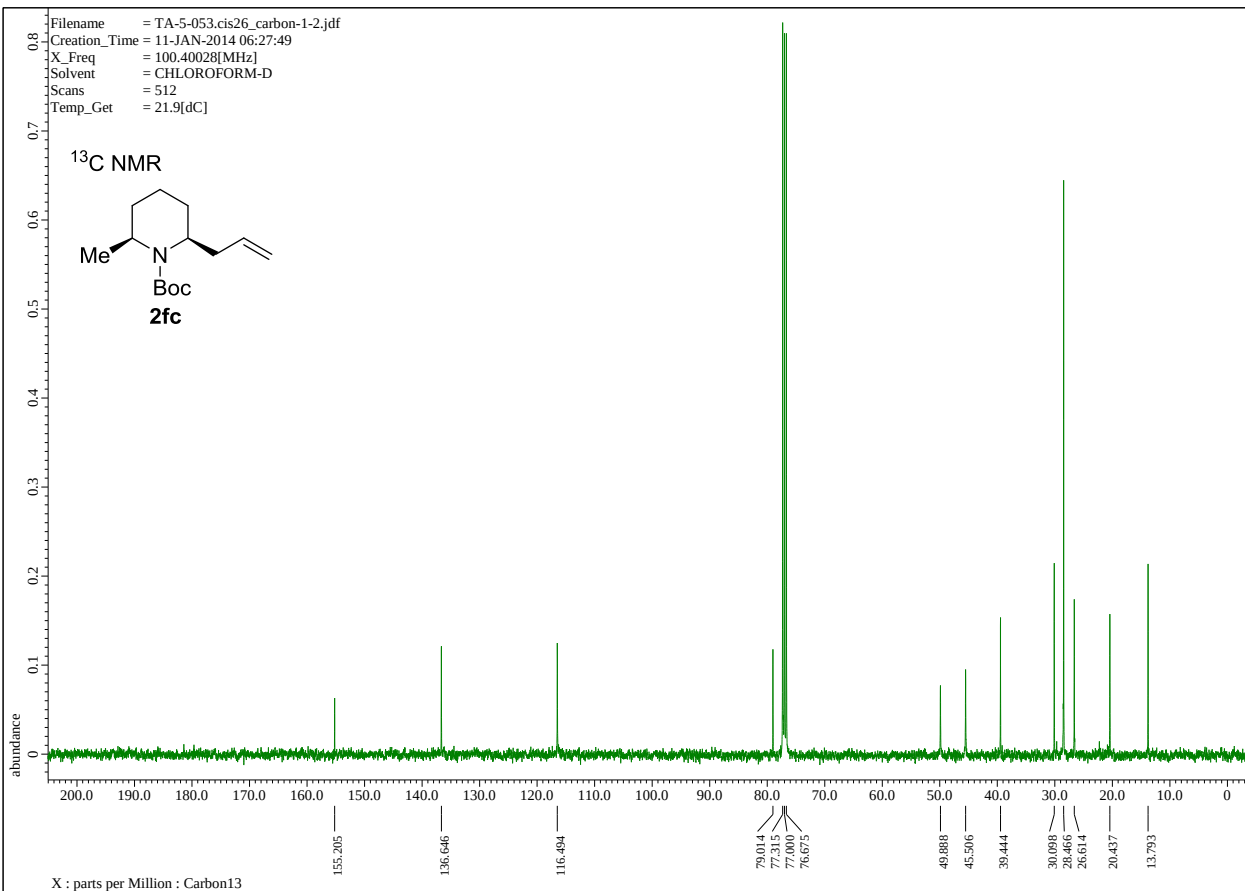
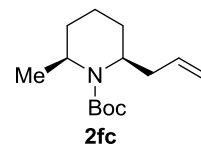
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¹H NMR



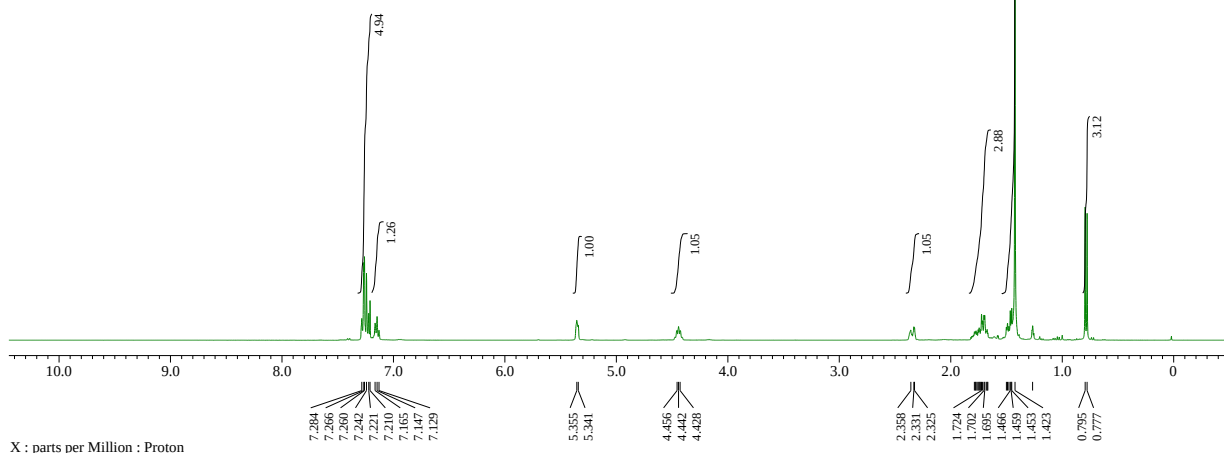
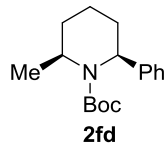
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¹³C NMR



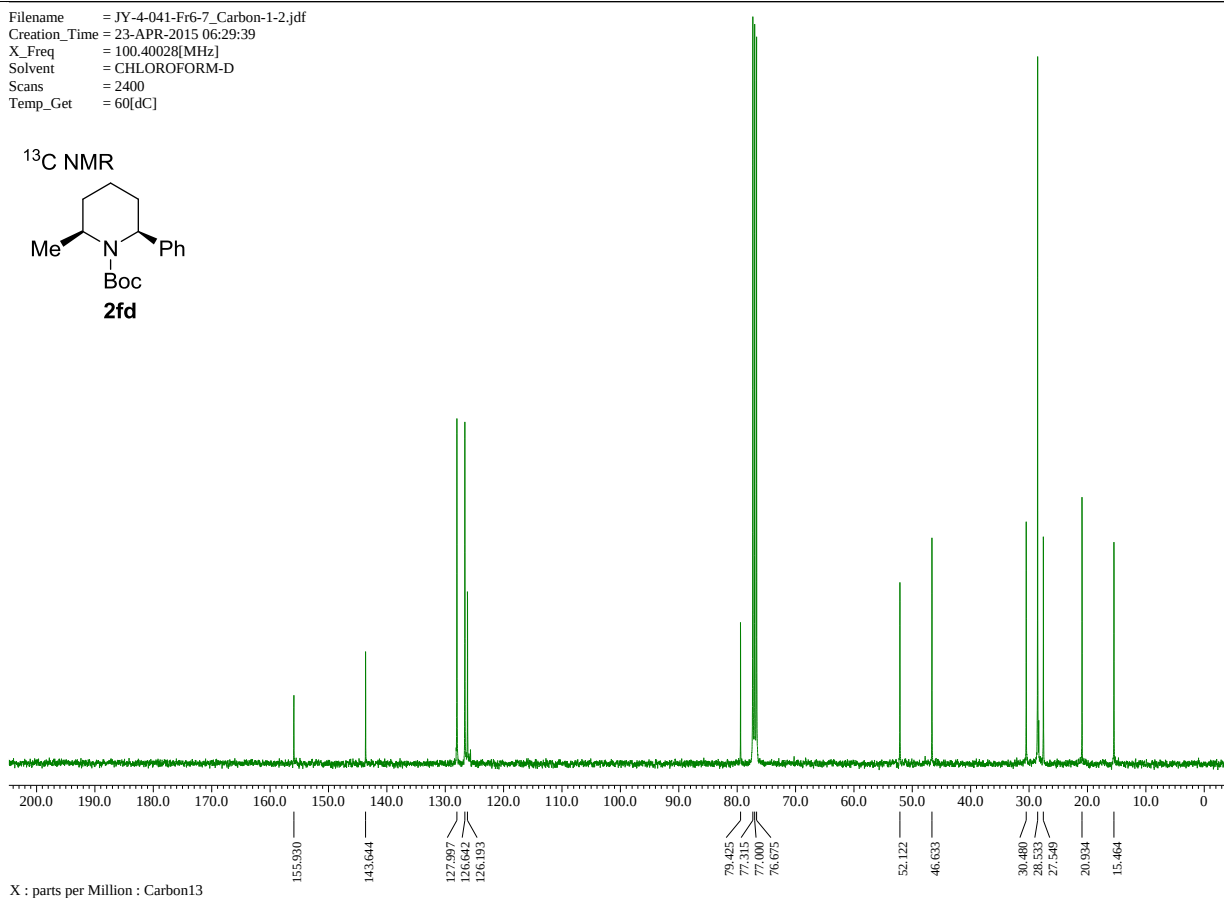
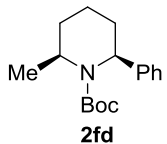
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¹H NMR



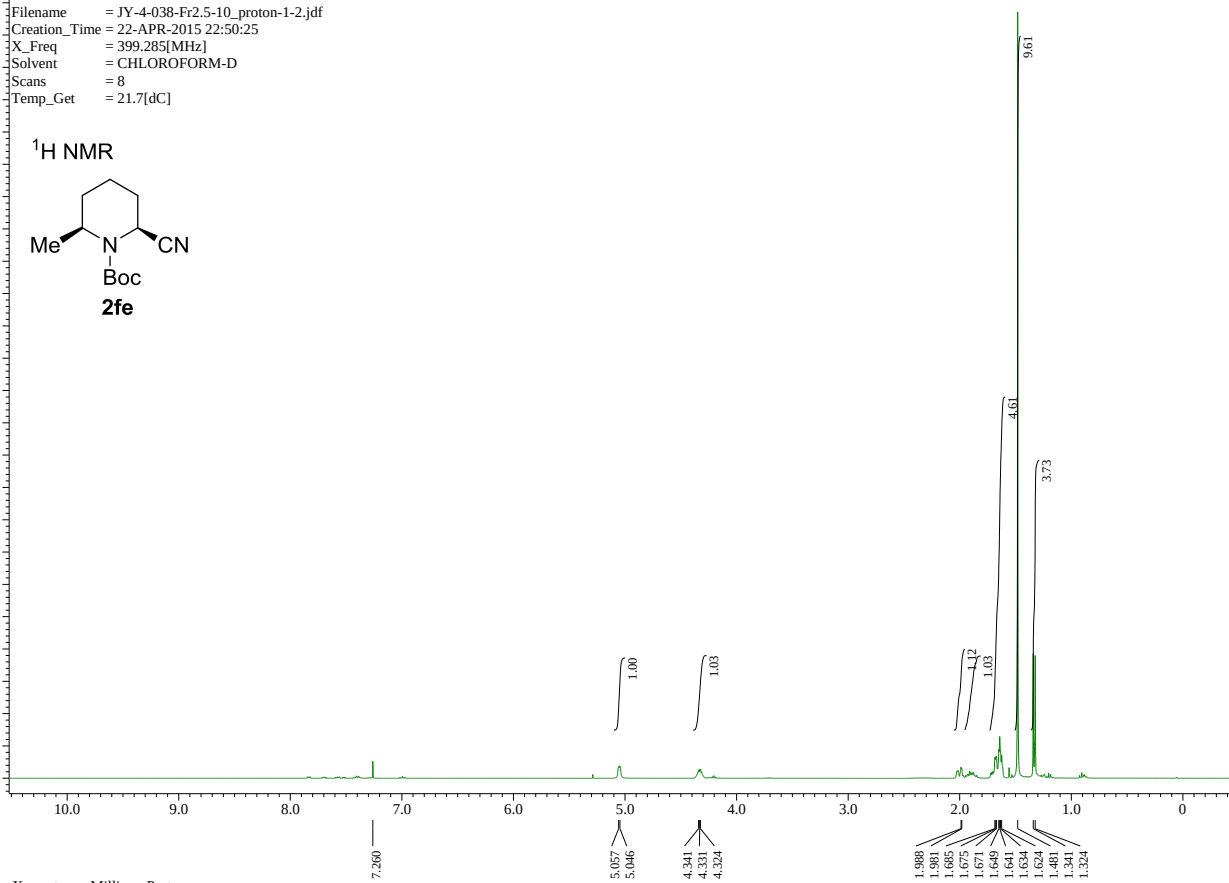
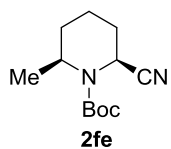
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¹³C NMR



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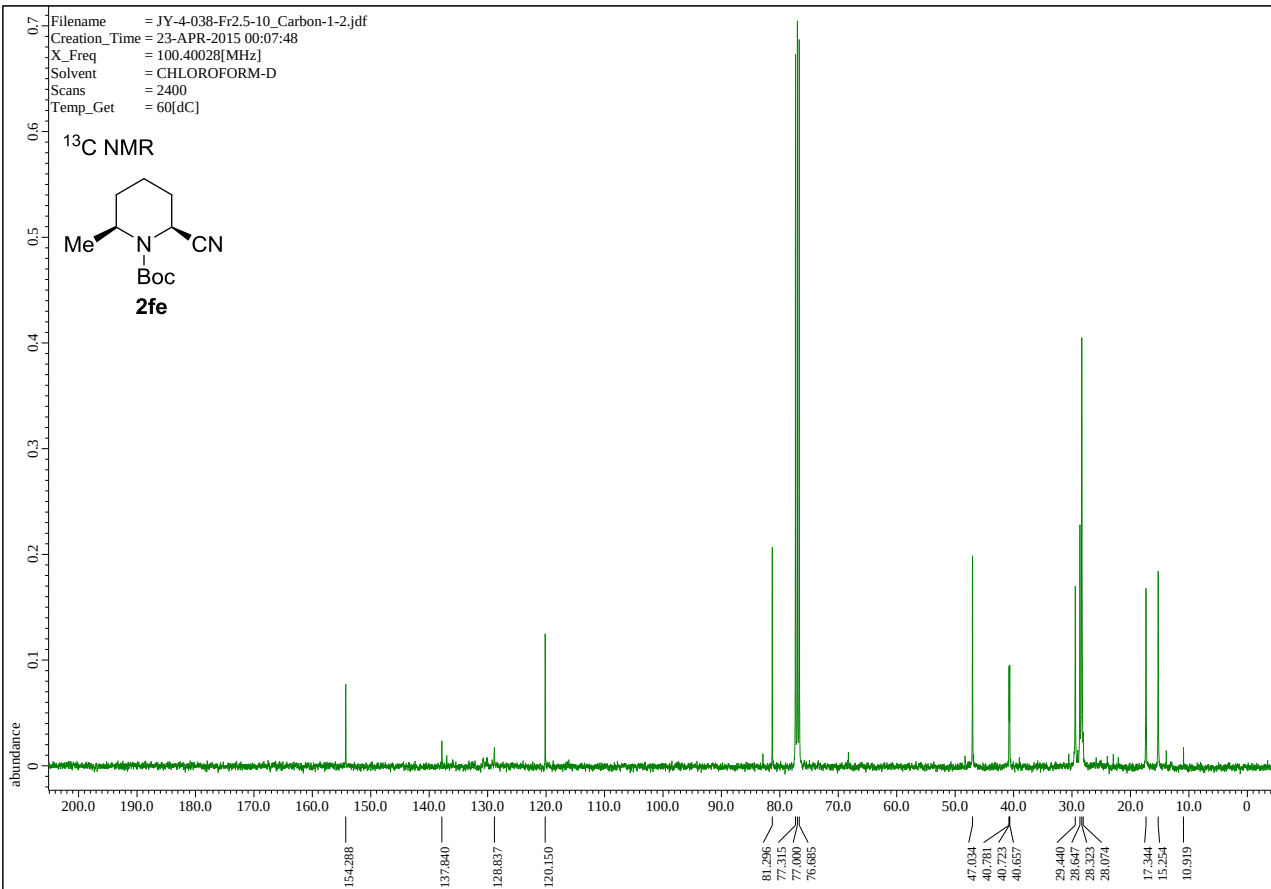
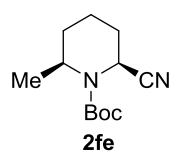
¹H NMR



X : parts per Million : Proton

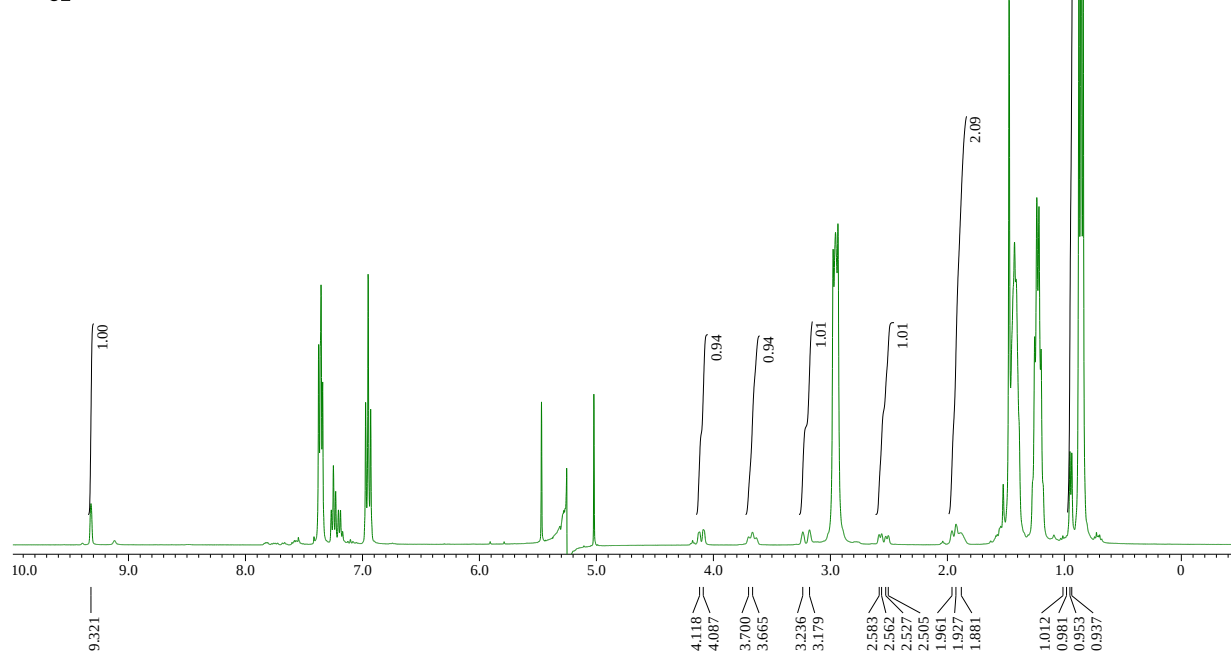
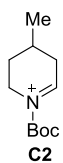
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¹³C NMR

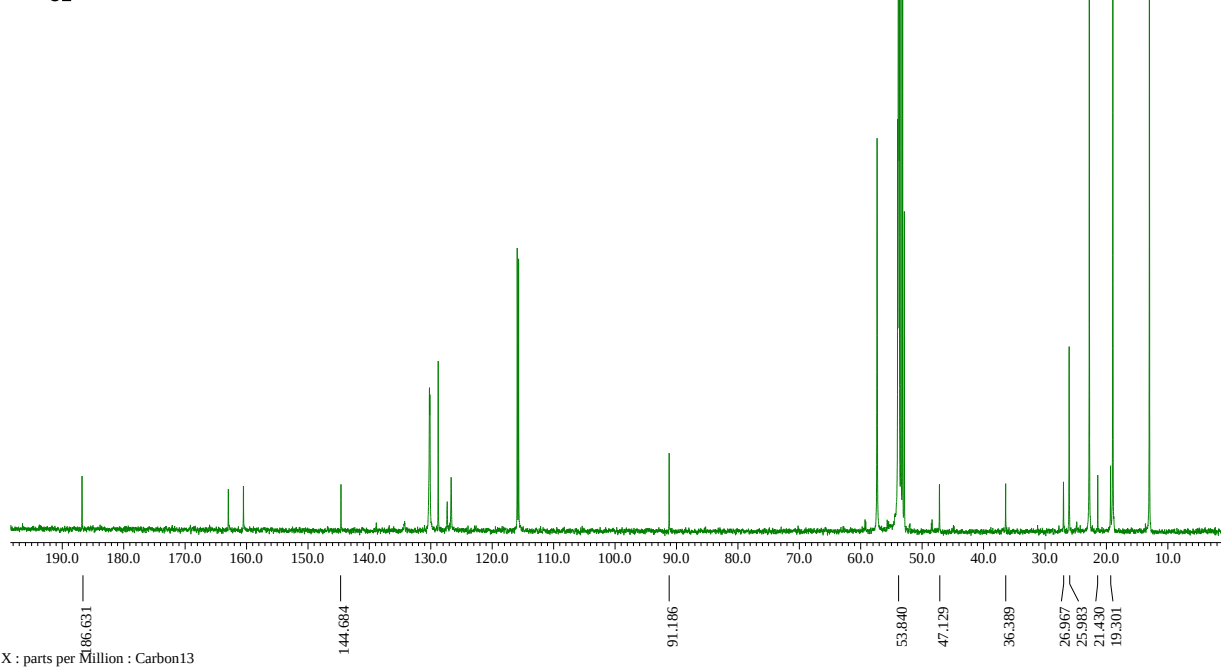
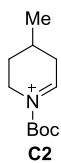


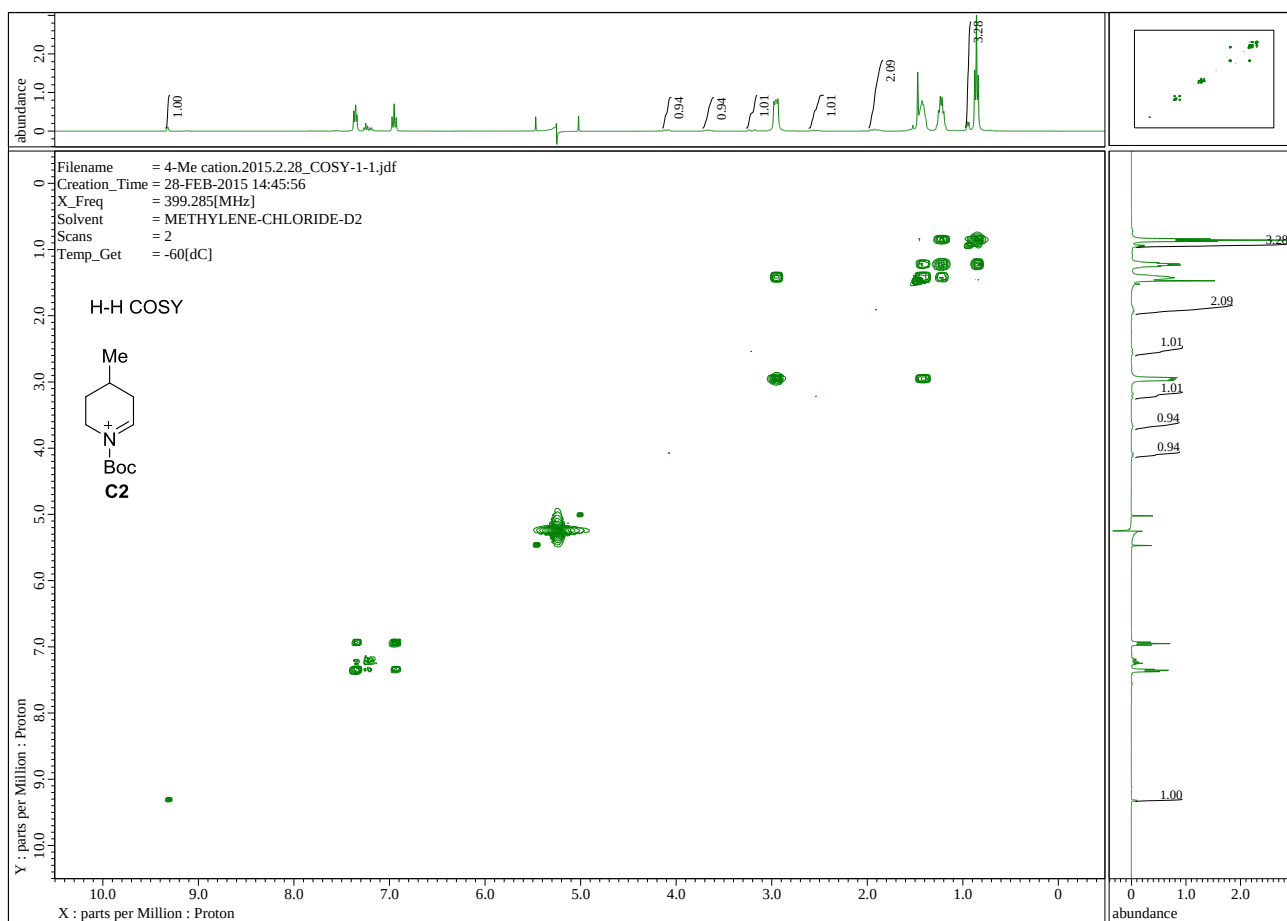
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¹H NMR

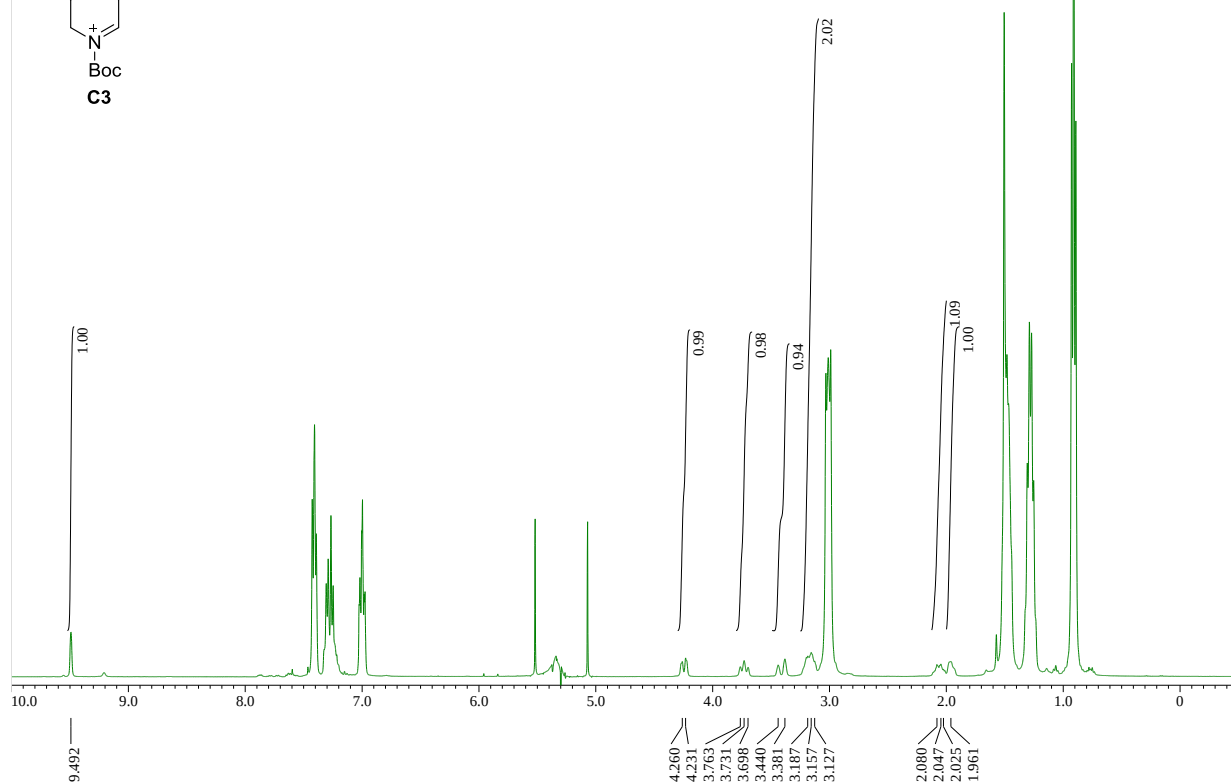
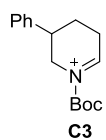


¹³C NMR

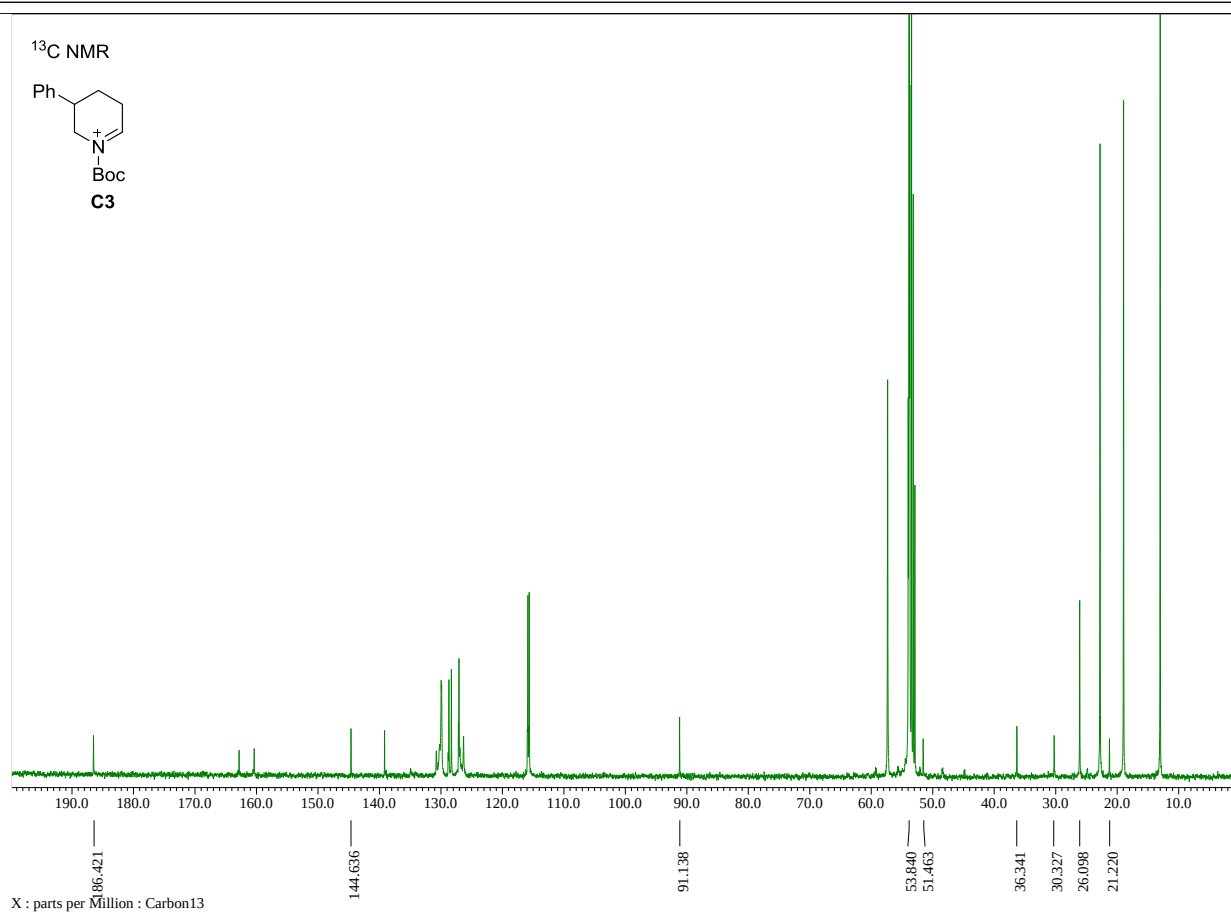
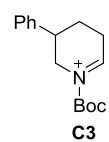




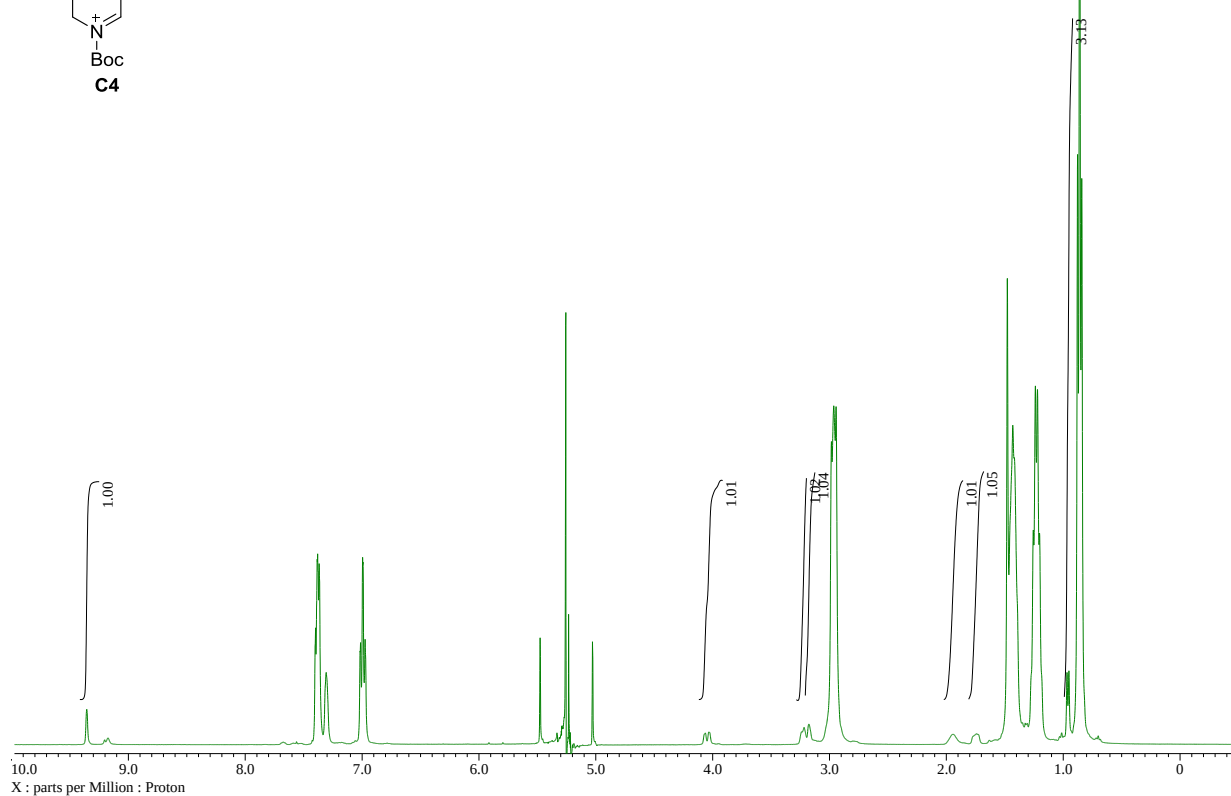
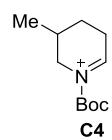
¹H NMR



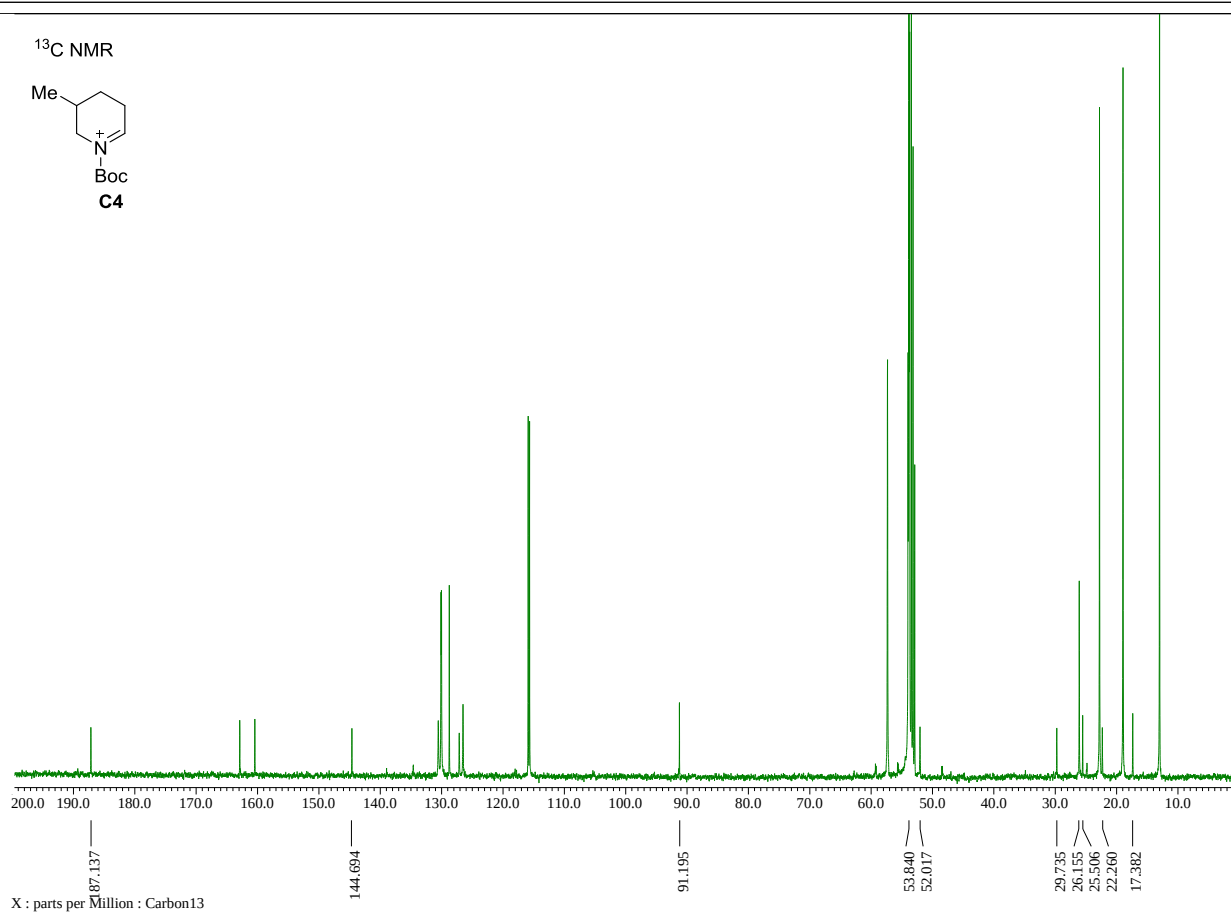
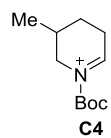
¹³C NMR



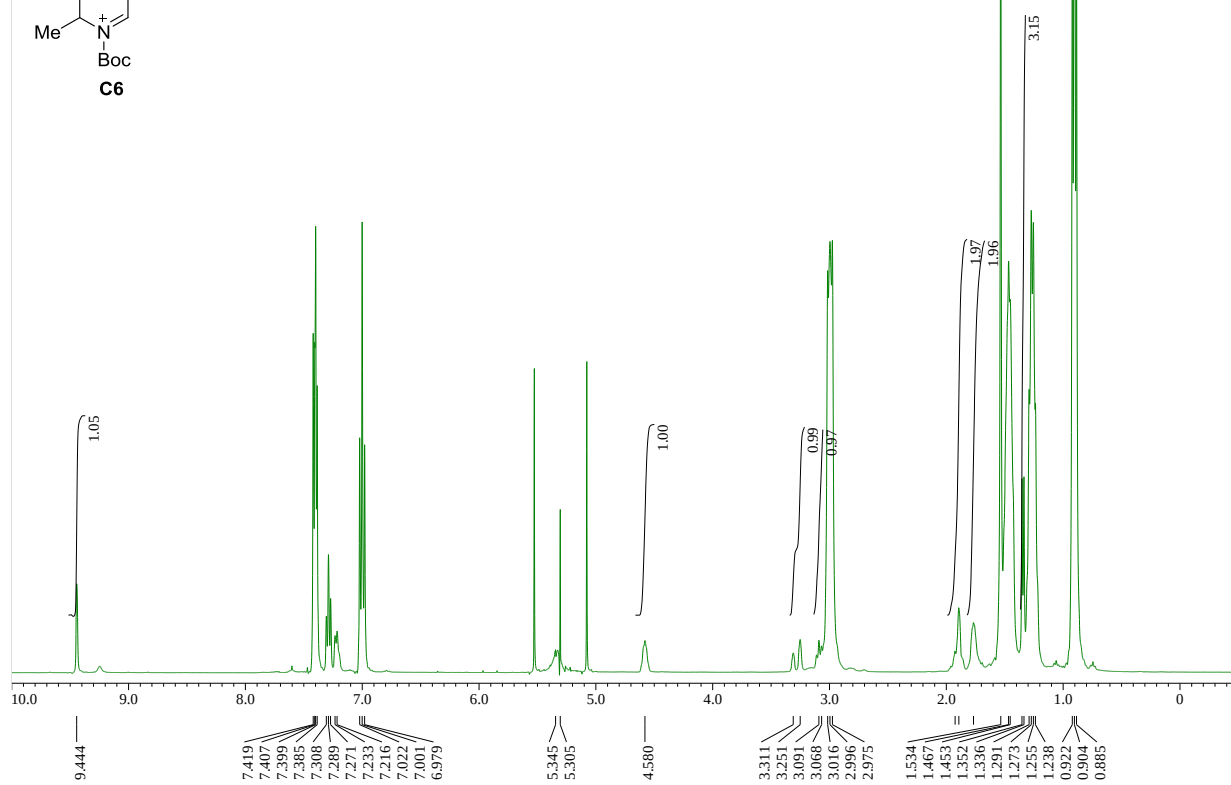
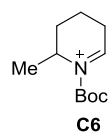
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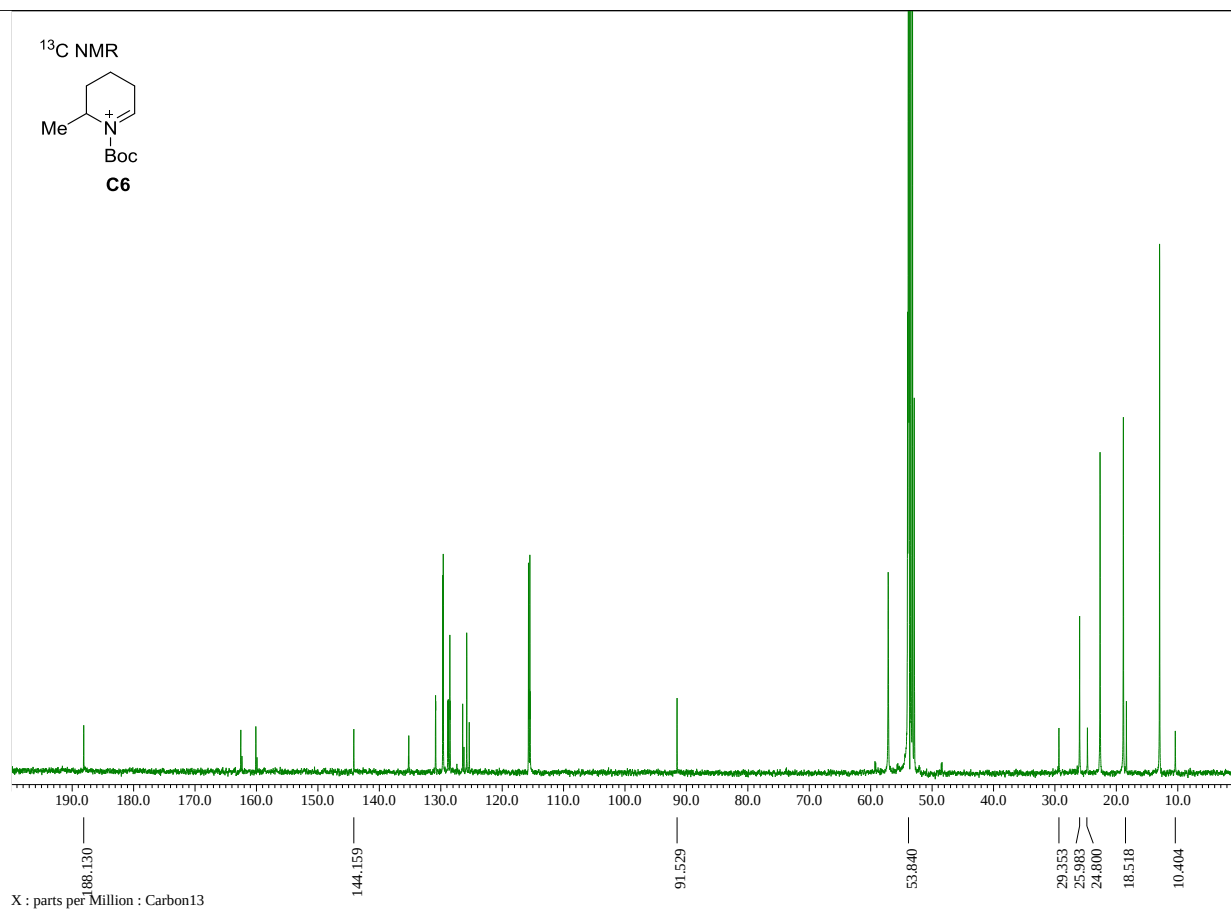
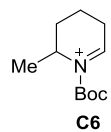
¹³C NMR

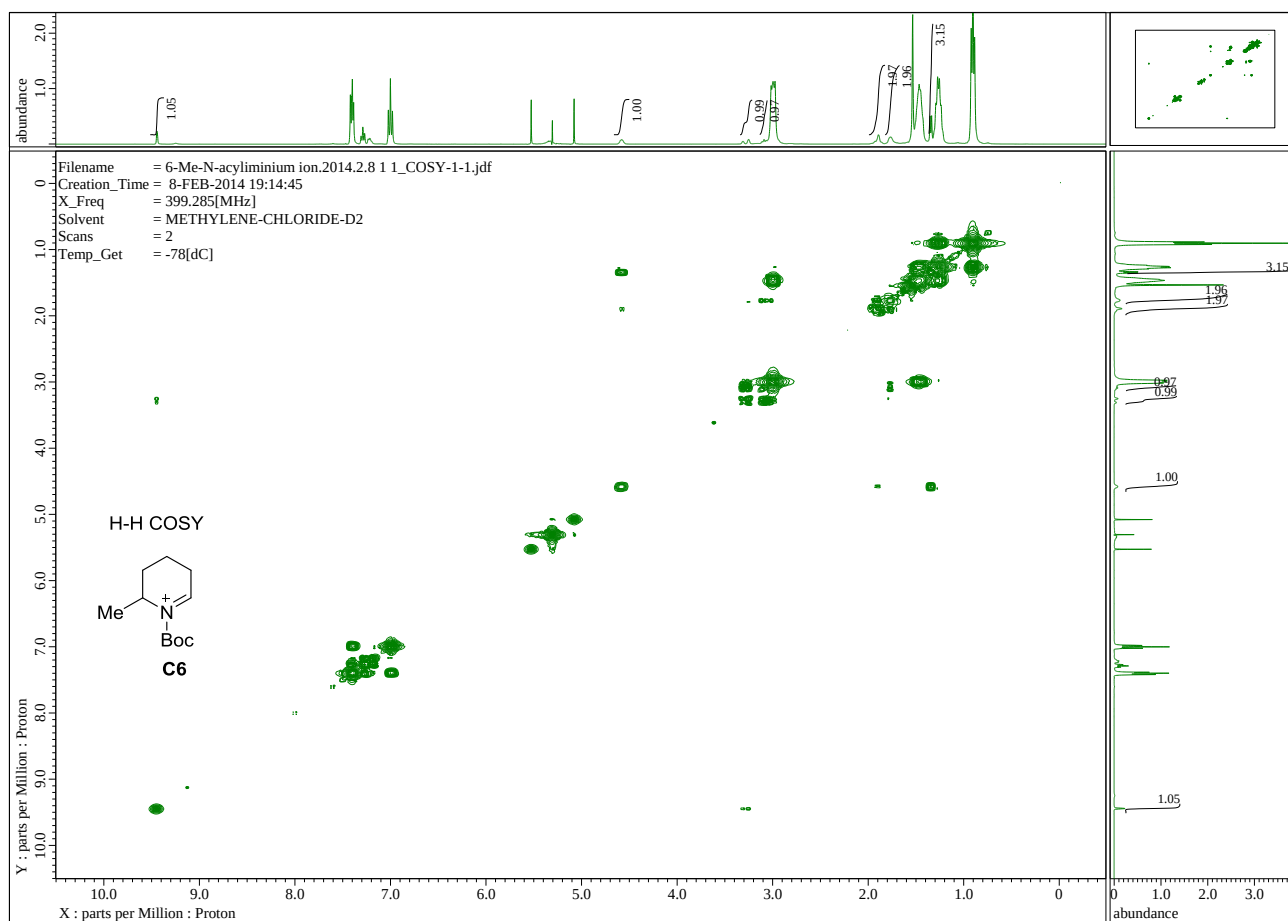


¹H NMR



¹³C NMR





5. References

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