

Hexafluoroisopropanol-assisted selective intramolecular synthesis of heterocycles by single-electron transfer

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1. General considerations

General experimental details

Unless otherwise indicated, reactions were conducted under an argon-filled glove box (mBraun Unilab 4420) with concentrations of O₂ and H₂O < 0.1 ppm or using Schlenk techniques under argon atmosphere. All the glassware was oven-dried at 100 °C overnight and cooled under vacuum prior use. Synthesis grade solvents were used as purchased. Anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (40-63 µm). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 F₂₅₄) were employed. Unless otherwise noted, visualization of developed plates was performed under UV light and/or using basic aqueous potassium permanganate (KMnO₄) stain.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV 400 spectrometer at 400MHz (¹H NMR), 100MHz (¹³C NMR), and 375MHz (¹⁹F NMR) using CDCl₃ as solvent. ¹H, ¹³C and ¹⁹F NMR chemical shifts are reported in parts per million (ppm), relative to tetramethylsilane (TMS) for ¹H and ¹³C with the residual solvent peak used as an internal reference (CDCl₃: δ_H = 7.26 ppm, δ_C = 77.16 ppm), and relative to CFC₃ (Freon) for ¹⁹F. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), triplets of triplets (tt) and multiplet (m). NMR yields for optimization studies were obtained by ¹H NMR analysis of the crude reaction mixture using mesitylene or 1,1,2,2-tetrachloroethane as an internal standard.

High Resolution Mass Spectrometry (HRMS) data was recorded on a LCT-Premier (Waters) or a MicroTOF Focus (Bruker Daltonics) mass spectrometers using ESI ionization technique and methanol as solvent.

UV-Vis measurements were carried out on a Shimadzu UV-1800PC spectrophotometer equipped with a photomultiplier detector, double beam optics and D² and W light sources.

Continuous wave (CW) EPR spectra were acquired at room temperature on a Bruker EMX Micro X-band spectrometer operating at 9.86GHz using a Bruker ER 1164 HS cavity. Individual EPR tubes were placed at the same position of the resonant cavity for EPR spectral acquisition.

The emission spectra were carried out on a Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with a photomultiplier detector, a double monochromator, and a 350W xenon light source.

Cyclic voltammetry studies were performed with a Biologic SP-150 potentiostat at rt. The working electrode: glassy carbon disk (0.07 cm² of surface area); the counter electrode: platinum; the reference electrode: SCE (Saturated Calomel electrode).

Materials

Commercial grade reagents and solvents were purchased from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, SynQuest used without further purification, unless otherwise stated.

Experimental setup

– **Set-up 1** (for 5-membered ring formation under light irradiation)

For reactions performed using a blue LED strip as the light source, a 3D-printed photoreactor was used, consisting of a 9 cm diameter crystallizing dish with a 3D printed support of 10 positions and a hole of 5 cm in the middle to allow ventilation (Figure S1, left). A commercial 1-meter LED strip was wrapped around the crystallizing dish, while a fan was used to cool down the reactor (the reaction temperature within the reaction vessel was measured to be between 35-40 °C). Each of the positions could be used to fit a standard 16 mm diameter vial with a Teflon screw cap. Experiments at 465 nm were conducted using a 1m strip, 14.4W “LEDXON MODULAR 9009083 LED, SINGLE 5050” purchased from Farnell, catalog number 9009083. The emission spectrum of these LEDs is shown in Figure S1, right panel.

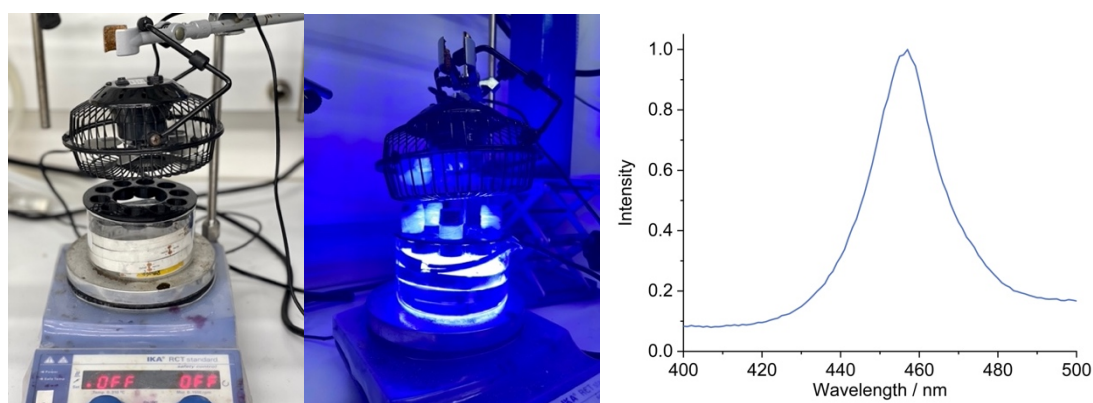


Figure S1: *Left and middle panel:* Blue LEDs photoreactor used for reactions. *Right panel:* Emission spectrum of the 465 nm LED strip used in this reactor.

– **Set-up 2** (for 6-membered ring formation under light irradiation)

The vials were placed into a parallel photoreactor with 8 positions, fitted with 470 nm OSRAM Oslon SSL 8o blue LEDs on star as controlled by an external power supply. The temperature was kept at 5 °C with a chiller connected to the irradiation plate (the setup is detailed in Figure S2).

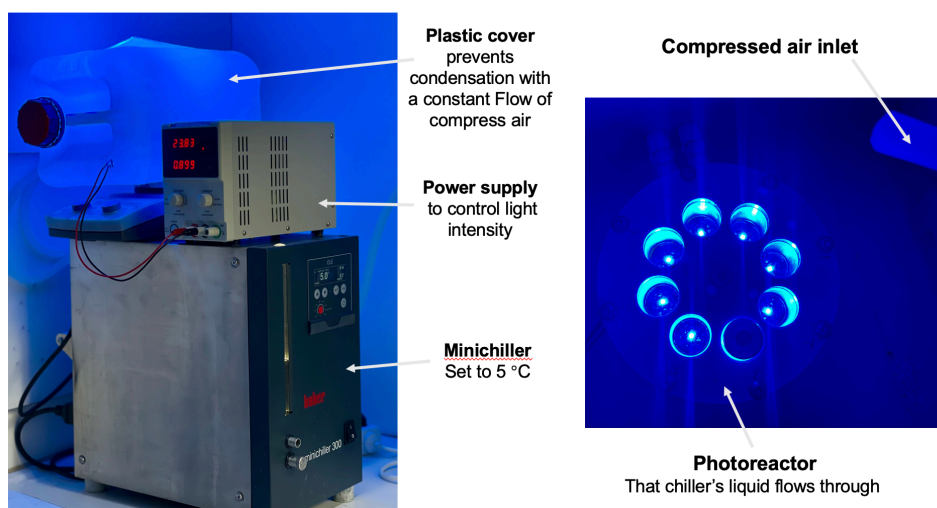
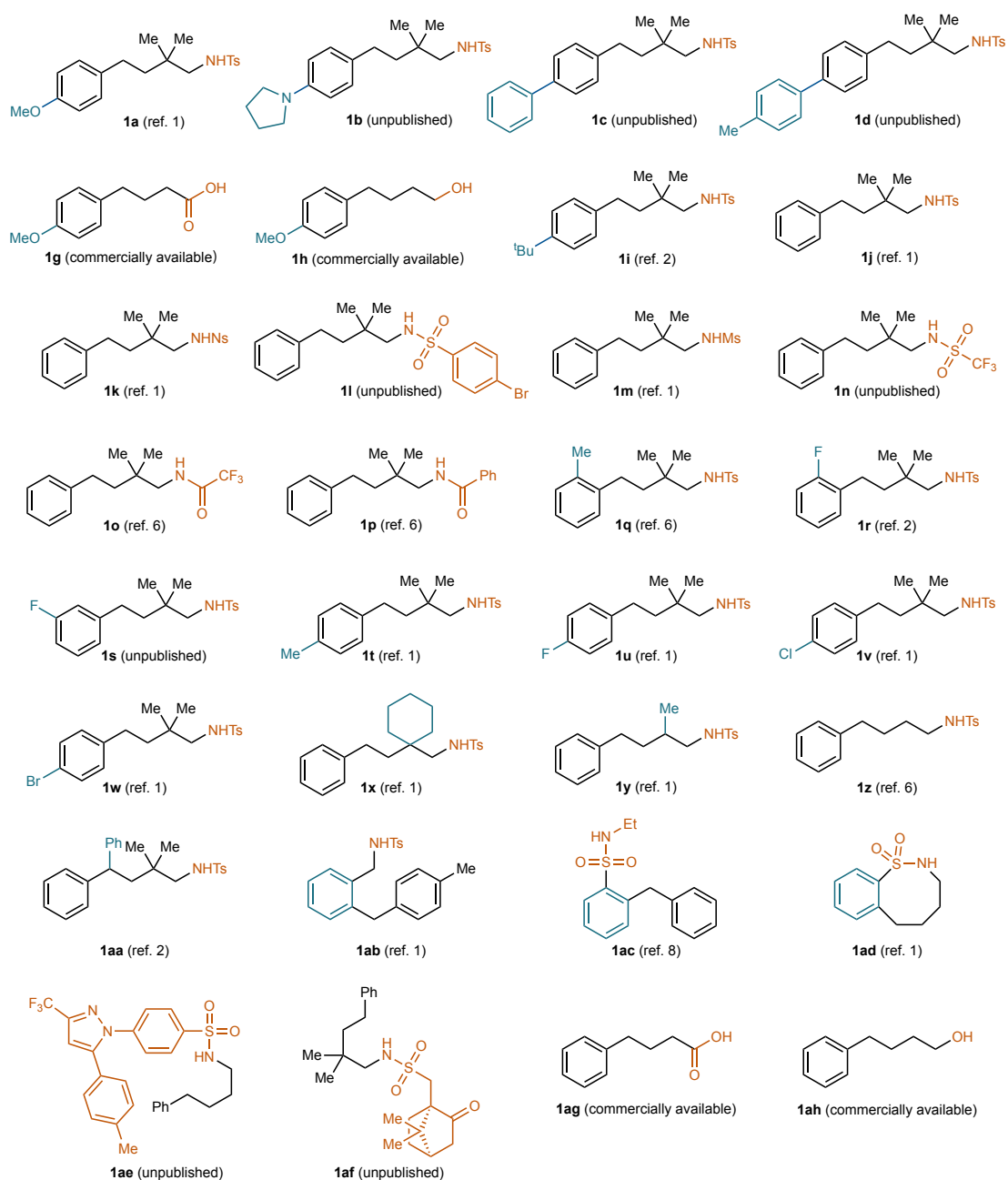
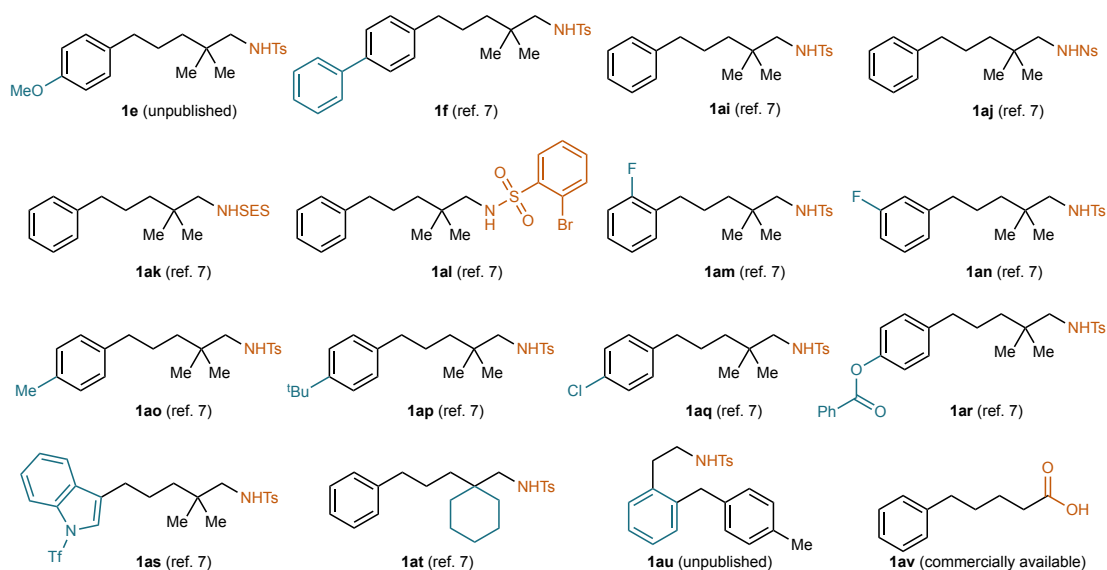


Figure S2. Detailed photoreactor setup with 8 parallel reactors. The light source for illuminating the reaction vessel consisted of 470 nm OSRAM Oslon SSL 8o blue LEDs on star.

2. Preparation of starting materials

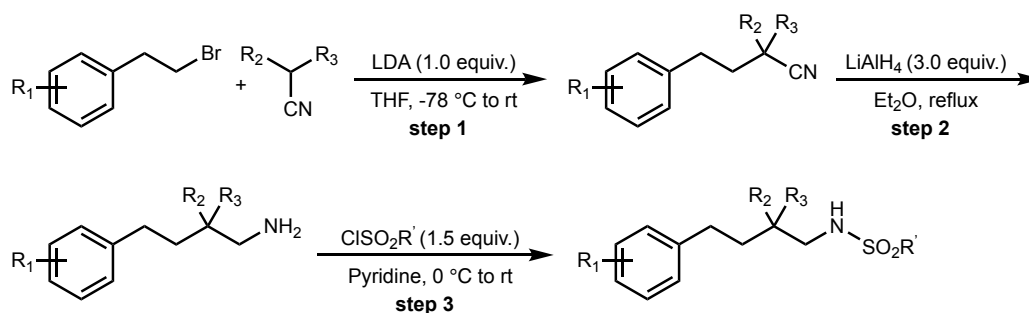
The substrates for 5-membered ring formation





2.1 General procedure for the synthesis of the starting materials for 5-membered ring formation

General procedure 1 (GP1) for the corresponding starting materials (1a, 1j-1q, 1s-1z, 1ab, 1ad) was performed following the procedure reported in literature¹ as outlined below.



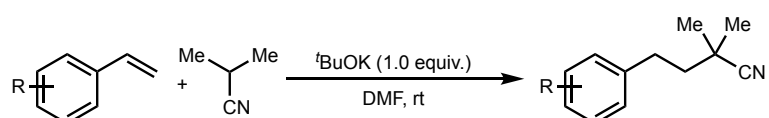
Step 1: The corresponding nitrile compound (1 equiv.) was dissolved in dry THF (0.4 M) under an argon atmosphere. The solution was then cooled to -78 °C, and lithium diisopropylamide (LDA) (2 M, 1.0 equiv.) was added dropwise at this temperature. The reaction mixture was stirred for 30 minutes at -78 °C. Following this, the corresponding bromide compound (1.2 equiv.) was added, and the reaction mixture was warmed to room temperature and stirred for an additional 12 hours. To quench the reaction, a saturated solution of NH₄Cl was added, and the resulting mixture was extracted with DCM (3 x). The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The resulting crude product was used in the subsequent step without further purification.

Step 2: A two-neck flask equipped with a stirring bar and a reflux condenser was charged with LiAlH₄ (3 equiv. based on the nitrile obtained from step 1). Subsequently, Et₂O (0.25 M based on nitrile) was added carefully, and the resulting suspension was cooled to 0 °C.

The crude product obtained from step 1 was dissolved in a small volume of Et₂O and added dropwise to the suspension. Then, the reaction mixture was refluxed for 2 hours. After refluxing, the reaction was cooled again to 0 °C and quenched by adding a 10% aqueous solution of NaOH. The mixture was filtered over a pad of anhydrous Na₂SO₄ and the solvent was removed under reduced pressure to yield the crude amine in quantitative yields.

Step 3: The crude amine from step 2 (1 equiv.) was dissolved in pyridine (0.4 M) and the resulting solution was cooled to 0 °C. Subsequently, the corresponding sulfonyl chloride was added in one portion, and the reaction mixture was stirred at room temperature for 12 hours. Then, the mixture was diluted with DCM and washed with a 5% aqueous solution of HCl (3 x). The organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. The resulting crude product was further purified by column chromatography on silica gel, employing hexane and EtOAc as eluents.

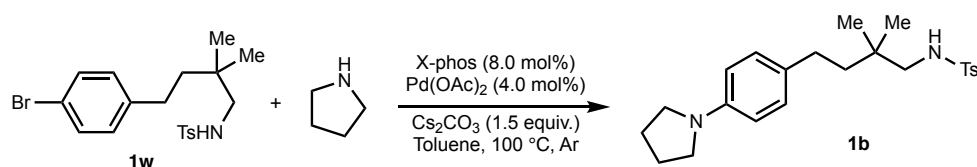
General procedure 2 (GP2) for the corresponding starting materials (**1c**, **1i**, **1r**, **1aa**) was performed following the procedure reported in literature² as outlined below.



For the synthesis of the required nitriles the first step of GP1 was replaced. A solution of ^tBuOK (1.0 equiv.) in DMF (0.5 M) was prepared, to which the corresponding vinyl-substituted substrate (1.0 equiv.) was added. Subsequently, 1.5 equiv. of the nitrile was added to the reaction. The resulting solution exhibited a distinct color and was stirred at room temperature overnight. The reaction mixture was then poured into cold water (5-fold excess to the DMF volume) and extracted with diethyl ether (3 x). The combined organic phase was washed with water and brine, dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The resulting crude product was used in the subsequent step without further purification.

2.2 Characterization of new starting materials for 5-membered ring formation

N-(2,2-dimethyl-4-(4-(pyrrolidin-1-yl)phenyl)butyl)-4-methylbenzenesulfonamide (**1b**)



According to a previously reported literature procedure³, to a 50 mL Schlenk flask equipped with a magnetic stirrer, Pd(OAc)₂ (13.5 mg, 0.06 mmol, 4.0 mol%), 2-dicyclohexylphosphino-2',4',6'-tri-iso-propylbiphenyl (57.2 mg, 0.12 mmol, 8.0 mol%), Cs₂CO₃ (0.73 g, 2.25 mmol, 1.5 equiv.), and *N*-(4-(4-bromophenyl)-2,2-dimethylbutyl)-4-methylbenzenesulfonamide **1w** (0.61 g, 1.50 mmol, 1.0 equiv.) were added. The Schlenk flask was connected to a vacuum condenser and the total system was purged with an

argon atmosphere. Then, toluene (7.5 mL) and pyrrolidine (0.21 g, 3.0 mmol, 2.0 equiv.) were added to the mixture, and the reaction flask was stirred at 100 °C for 16 hours. After cooling to room temperature, the reaction mixture was filtration over celite and extracted with EtOAc (3 x). The combined organic layers were dried over anhydrous Na₂SO₄ and the solvents were evaporated under reduced pressure. The resulting crude product was purified by chromatography on silica gel (hexane/EtOAc: 10:1 v/v) to afford the title compound **1b** as a white solid in 76% yield.

mp: 135–137 °C; TLC (hexane/EtOAc: 6:1 v/v): R_f = 0.19.

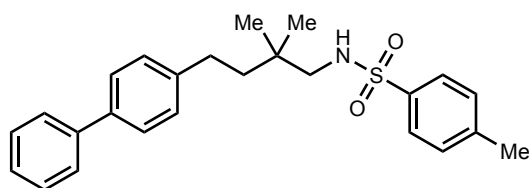
¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 8.2 Hz, 2H), 4.43 (t, *J* = 6.9 Hz, 1H), 3.26 (t, *J* = 6.6 Hz, 4H), 2.71 (d, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 2.41–2.36 (m, 2H), 2.02–1.97 (m, 4H), 1.48–1.42 (m, 2H), 0.91 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 143.4, 137.2, 129.8, 129.0, 127.2, 112.0, 53.0, 48.0, 42.1, 34.1, 29.3, 25.6, 25.1, 21.6.

IR ν(cm⁻¹): 3263, 2924, 1521, 1319, 1070, 886, 800, 661.

HRMS(ESI) *m/z*: Calcd. for [C₂₃H₃₃N₂O₂S]⁺: 401.2257; Found: 401.2256.

***N*-(4-([1,1'-biphenyl]-4-yl)-2,2-dimethylbutyl)-4-methylbenzenesulfonamide (1c)**



Following GP2, **1c** was obtained as a white solid in 65% yield.

mp: 133–135 °C; TLC (hexane/EtOAc: 6:1 v/v): R_f = 0.18.

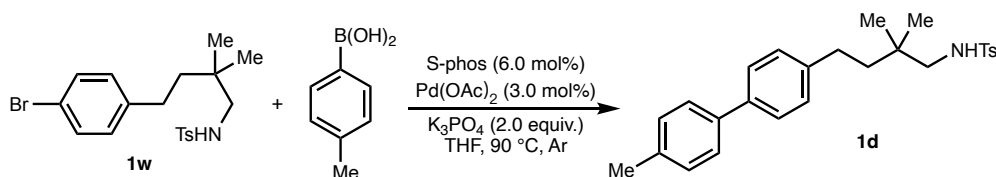
¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.60–7.55 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.36–7.31 (m, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 4.49 (t, *J* = 6.9 Hz, 1H), 2.76 (d, *J* = 6.9 Hz, 2H), 2.59–2.51 (m, 2H), 2.41 (s, 3H), 1.60–1.49 (m, 2H), 0.95 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 143.5, 141.8, 141.2, 138.9, 137.2, 129.9, 128.9, 128.9, 127.3, 127.2, 127.2, 127.1, 53.0, 41.6, 34.2, 30.0, 25.1, 21.7.

IR ν(cm⁻¹): 3261, 1424, 1319, 1160, 1071, 810, 755, 697.

HRMS(ESI) *m/z*: Calcd. for [C₂₅H₂₉NNaO₂S]⁺: 430.1811; Found: 430.1822.

***N*-(2,2-dimethyl-4-(4'-methyl-[1,1'-biphenyl]-4-yl)butyl)-4-methylbenzenesulfonamide (1d)**



According to a previously reported literature procedure⁴, in a 25 mL Schlenk flask equipped with a magnetic stir bar, *N*-(4-(4-bromophenyl)-2,2-dimethylbutyl)-4-methylbenzenesulfo-

namide **1w** (0.61 g, 1.50 mmol, 1.0 equiv.), Pd(OAc)₂ (10.1 mg, 0.045 mmol, 3.0 mol%), S-Phos (37.0 mg, 0.09 mmol, 6 mol%), 4-methylphenyl boronic acid (0.24 g, 1.8 mmol, 1.2 equiv.) and K₃PO₄ (0.64 g, 3.0 mmol, 2.0 equiv.) were added. The reaction mixture was connected to a vacuum condenser and purged with an argon atmosphere. This process was repeated three times. Then, 4.5 mL of THF was added to the mixture under argon. The reaction mixture was stirred for 24 hours at 90 °C. After cooling to room temperature, the mixture was filtered through a celite and extracted with EtOAc (3 ×). The filtrate was collected and dried over anhydrous Na₂SO₄, the solvents were then evaporated under reduced pressure. The resulting crude product was purified by chromatography on silica gel (hexane/EtOAc: 10:1 v/v) to afford the pure compound **1d** as a white solid in 75% yield. mp: 152–154 °C; TLC (hexane/EtOAc: 6:1 v/v): R_f = 0.19.

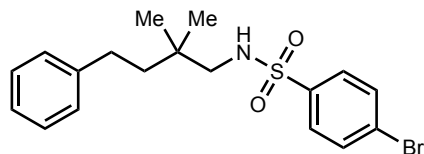
¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 4H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.46 (t, *J* = 7.1 Hz, 1H), 2.76 (d, *J* = 6.9 Hz, 2H), 2.59–2.49 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 1.57–1.51 (m, 2H), 0.94 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 143.5, 141.5, 138.8, 138.3, 137.1, 136.9, 129.9, 129.6, 128.8, 127.2, 127.1, 127.0, 53.0, 41.6, 34.2, 30.0, 25.1, 21.7, 21.2.

IR ν(cm⁻¹): 3265, 2924, 1497, 1422, 1319, 1068, 809, 660.

HRMS(ESI) *m/z*: Calcd. for [C₂₆H₃₁NNaO₂S]⁺: 444.1968; Found: 444.1958.

4-bromo-*N*-(2,2-dimethyl-4-phenylbutyl)benzenesulfonamide (**1l**)



Following GP1, **1l** was obtained as a white solid in 63% yield.

mp: 108–110 °C; TLC (hexane/EtOAc: 8:1 v/v): R_f = 0.20.

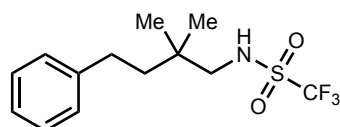
¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.30–7.24 (m, 2H), 7.21–7.15 (m, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 4.64 (t, *J* = 6.8 Hz, 1H), 2.75 (d, *J* = 6.8 Hz, 2H), 2.56–2.47 (m, 2H), 1.54–1.46 (m, 2H), 0.93 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 142.5, 139.2, 132.5, 128.7, 128.6, 128.4, 127.7, 126.0, 53.1, 41.6, 34.2, 30.4, 25.0.

IR ν(cm⁻¹): 3273, 2964, 1573, 1323, 1154, 819, 739, 697.

HRMS(ESI) *m/z*: Calcd. for [C₁₈H₂₃BrNO₂S]⁺: 396.0627; Found: 396.0630.

N-(2,2-dimethyl-4-phenylbutyl)-1,1,1-trifluoromethanesulfonamide (**1n**)



Following GP1, **1n** was obtained as a white solid in 56% yield.

mp: 68–70 °C; TLC (hexane/EtOAc: 10:1 v/v): R_f = 0.27.

¹H NMR (400 MHz, CDCl₃): δ 7.33–7.27 (m, 2H), 7.23–7.16 (m, 3H), 4.92 (t, *J* = 6.5 Hz, 1H), 3.12 (d, *J* = 6.4 Hz, 2H), 2.62–2.56 (m, 2H), 1.63–1.50 (m, 2H), 1.02 (s, 6H).

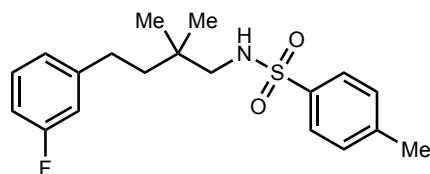
¹³C NMR (100 MHz, CDCl₃): δ 142.2, 128.7, 128.4, 126.1, 119.9 (q, *J* = 319.6 Hz), 54.23, 41.45, 34.37, 30.36, 24.68.

¹⁹F NMR (375 MHz, CDCl₃): δ -76.94 (s, 3F).

IR ν(cm⁻¹): 3306, 2948, 1602, 1438, 1361, 857, 737 699.

HRMS(ESI) *m/z*: Calcd. for [C₁₃H₁₈F₃NNaO₂S]⁺: 332.0903; Found: 332.0890.

***N*-(4-(3-fluorophenyl)-2,2-dimethylbutyl)-4-methylbenzenesulfonamide (1s)**



Following GP1, **1s** was obtained as a yellow solid in 68% yield.

mp: 114–116 °C; TLC (hexane/EtOAc: 6:1 v/v): *R*_f = 0.19.

¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.21 (td, *J* = 7.9, 6.1 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.88–6.78 (m, 2H), 4.53 (t, *J* = 6.8 Hz, 1H), 2.74 (d, *J* = 7.2 Hz, 2H), 2.52–2.45 (m, 2H), 2.42 (s, 3H), 1.52–1.44 (m, 2H), 0.92 (s, 6H).

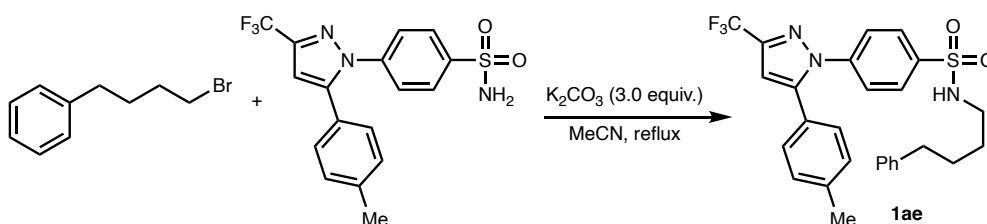
¹³C NMR (100 MHz, CDCl₃): δ 163.0 (d, *J* = 244.0 Hz), 145.3 (d, *J* = 7.2 Hz), 143.6, 137.1, 129.9 (d, *J* = 8.3 Hz), 129.9, 127.2, 124.1 (d, *J* = 2.7 Hz), 115.2 (d, *J* = 20.8 Hz), 112.7 (d, *J* = 21.0 Hz), 53.0, 41.2, 34.1, 30.2 (d, *J* = 1.7 Hz), 25.0, 21.6.

¹⁹F NMR (375 MHz, CDCl₃): δ -113.89 (td, 1F).

IR ν(cm⁻¹): 3267, 2941, 1587, 1424, 1320, 1066, 870, 662.

HRMS(ESI) *m/z*: Calcd. for [C₁₉H₂₄FNNaO₂S]⁺: 372.1404; Found: 372.1412.

***N*-(4-phenylbutyl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (1ae)**



According to a previously reported literature procedure⁵, to a solution of (4-bromobutyl)benzene (0.21 g, 1.0 mmol, 1.0 equiv.) in MeCN (4.0 mL), K₂CO₃ (0.42 g, 3.0 mmol, 3.0 equiv.) was added, followed by the addition of benzenesulfonamide (0.76 g, 2.0 mmol, 2.0 equiv.). The resulting solution was heated to reflux and stirred for 5 hours. After completion of the reaction, the mixture was filtrated through Celite and concentrated in vacuo. The desired product **1ae** was afforded after purification by flash column chromatography using silica gel (hexane/EtOAc: 4:1 v/v) as a white solid in 82% yield.

mp: 142–144 °C; TLC (hexane/EtOAc: 4:1 v/v): *R*_f = 0.18.

¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.29–7.21 (m, 2H), 7.20–7.14 (m, 3H), 7.14–7.08 (m, 4H), 6.75 (s, 1H), 4.56 (s, 1H), 2.96 (q, *J* = 6.4 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.65–1.55 (m, 2H), 1.54–1.44 (m, 2H).

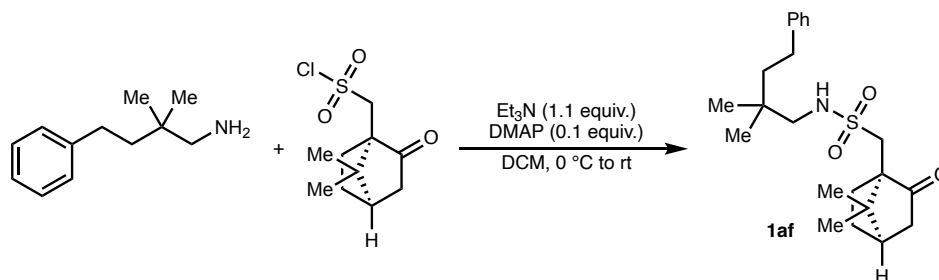
¹³C NMR (100 MHz, CDCl₃): δ 145.4, 144.2 (q, *J* = 38.2 Hz), 142.6, 141.7, 139.9, 139.6, 129.9, 128.8, 128.5, 128.5, 128.2, 126.1, 125.8, 125.7, 120.1 (q, *J* = 267.7 Hz), 106.4, 43.3, 35.3, 29.2, 28.3, 21.4.

¹⁹F NMR (375 MHz, CDCl₃): δ -62.54 (s, 3F).

IR ν(cm⁻¹): 3254, 2927, 1596, 1235, 1094, 974, 814, 698.

HRMS(ESI) *m/z*: Calcd. for [C₂₇H₂₆F₃N₃NaO₂S]⁺: 536.1590; Found: 536.1577.

1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-(2,2-dimethyl-4-phenylbutyl)methane-sulfonamide (1af)



According to a previously reported literature procedure⁶, the third step of GP1 was adjusted. 2,2-dimethyl-4-phenylbutan-1-amine (0.89 g, 5.0 mmol, 1.0 equiv.) was dissolved in DCM (25 mL). Then, Et₃N (0.76 mL, 5.5 mmol, 1.1 equiv.) and DMAP (61.1 mg, 0.5 mmol, 0.1 equiv.) were added to the solution. The solution was cooled to 0 °C, and sulfonyl chloride (1.9 g, 7.5 mmol, 1.5 equiv.) was added dropwise. After stirring at room temperature for 12 hours, the solution was diluted with DCM and washed with saturated NaHCO₃ solution and water. The organic phase was dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The product **1af** was isolated as a white solid in 74% yield by flash column chromatography using a hexane/EtOAc: 4:1 as the eluent.

mp: 109–111 °C; TLC (hexane/EtOAc: 4:1 v/v): R_f = 0.21.

¹H NMR (400 MHz, CDCl₃): δ 7.31–7.23 (m, 2H), 7.22–7.13 (m, 3H), 5.32 (dd, *J* = 8.8, 5.2 Hz, 1H), 3.35 (d, *J* = 14.8 Hz, 1H), 3.04 (dd, *J* = 12.1, 8.8 Hz, 1H), 2.93 (dd, *J* = 12.1, 5.2 Hz, 1H), 2.92 (d, *J* = 14.8 Hz, 1H), 2.66–2.52 (m, 2H), 2.45–2.34 (m, 1H), 2.25–2.15 (m, 1H), 2.13 (t, *J* = 4.4 Hz, 1H), 2.08–1.96 (m, 2H), 1.93 (d, *J* = 18.6 Hz, 1H), 1.65–1.53 (m, 2H), 1.50–1.39 (m, 1H), 1.02 (s, 3H), 1.02 (s, 3H), 1.02 (s, 3H), 0.92 (s, 3H).

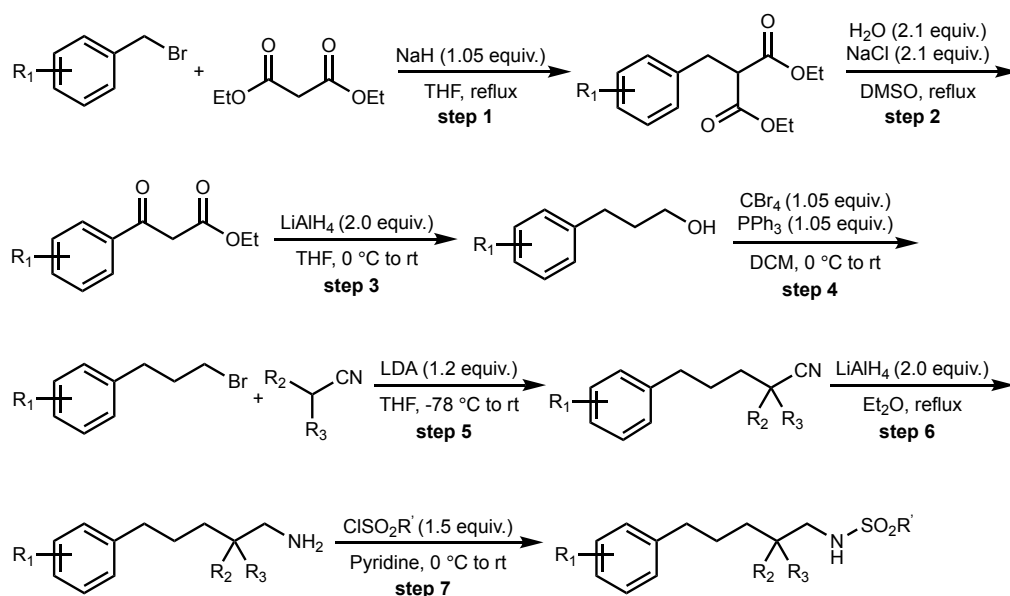
¹³C NMR (100 MHz, CDCl₃): δ 217.4, 142.8, 128.4, 128.4, 125.7, 59.4, 53.3, 49.4, 49.0, 43.0, 42.8, 41.8, 34.2, 30.4, 27.1, 27.0, 25.0, 25.0, 20.0, 19.5.

IR ν(cm⁻¹): 3239, 2964, 1727, 1455, 1324, 1073, 838, 742.

HRMS(ESI) *m/z*: Calcd. for [C₂₂H₃₃NNaO₃S]⁺: 414.2073; Found: 414.2083

2.3 General procedure for the synthesis of the starting materials for 6-membered ring formation

General procedure 3 (GP3) for the synthesis of corresponding starting materials (**1e**, **1f**, **1ai–1at**): it was performed following the procedure reported in literature^{1,7} and as outlined below.



Step 1: Diethyl malonate (1.05 equiv.) was added dropwise to a suspension of NaH (60% on mineral oil, 1.05 equiv.) in dry THF at 0 °C and stirred for 15 minutes. Subsequently, the corresponding benzyl bromide was added in one portion, resulting in a milky mixture, which was then stirred at reflux for 1 hour. The reaction mixture was cooled and quenched by the addition of water. The THF solvent was removed under reduced pressure, and the resulting crude product was dissolved in Et₂O and washed with water. The aqueous layer was extracted with Et₂O (4 x), and the combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and filtered. The solvent was evaporated under reduced pressure, and the crude product was directly used for the subsequent step without further purification.

Step 2: A solution containing the diester (1.0 equiv.), NaCl (2.1 equiv.), and H₂O (2.1 equiv.) in DMSO (30 mL) was heated at reflux for 8 hours. After completion of the reaction, the mixture was cooled to 25 °C and diluted with a 3M HCl solution. The resulting mixture was extracted with EtOAc (3 x 20 mL). The combined organic layer was washed with water (5 x 50 mL), followed by brine (1 x 100 mL) and dried over anhydrous Na₂SO₄. The crude product, appearing as a brown oil, was then filtered through a pad of silica to obtain the desired ester in a quantitative yield.

Step 3: A solution of the ester (1.0 equiv.) in THF was prepared and maintained at 0 °C. To this solution, LiAlH₄ (2.0 equiv.) was slowly added, followed by stirring at room temperature for 2 hours. After that, a solution of NaOH (10% in water) was added carefully until a white solid precipitated. The reaction mixture was then filtered over anhydrous Na₂SO₄, and the solvent was evaporated to yield the crude amine in quantitative yields.

Step 4: A solution of propanol (1.0 equiv.) in CH₂Cl₂ was prepared and cooled to 0 °C. To this solution, CBr₄ (1.05 equiv.) was added, followed by the portion wise addition of triphenylphosphine (1.05 equiv.). The reaction mixture was allowed to warm up to 25 °C and monitored by TLC. After 3 hours, no starting material was detected. The organic layer was dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was purified using chromatography on silica gel with hexane as the eluent to afford bromides.

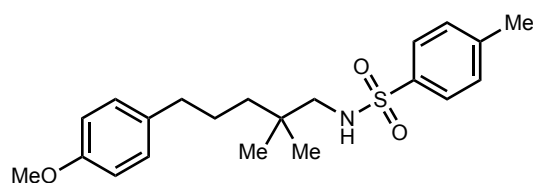
Step 5: A Schlenk tube equipped with a stirrer bar was charged with the corresponding nitrile compound (1.2 equiv.) and THF (20 mL). Then LDA (1.2 equiv.) was added dropwise at -78 °C and the solution was stirred for 30 minutes. After this period, the corresponding bromide (1.0 equiv.) was added in a single portion, and the mixture was stirred at room temperature for 12 hours. To quench the reaction, a saturated aqueous solution of NH₄Cl was added, and the resulting mixture was extracted with DCM (3 x). The organic layer was then dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The resulting crude product was utilized directly for the subsequent reduction step.

Step 6: A flame dried Schlenk flask equipped with a stirrer bar and a reflux condenser was charged with LiAlH₄ (3 equiv.), Et₂O was carefully added while the mixture was cooled to 0 °C with an external ice/water cooling bath. The crude nitrile (1 equiv.) was dissolved in a small volume of Et₂O and added carefully to the suspension of LiAlH₄. The mixture was then heated to reflux for 2 hours and cooled back to 0 °C afterwards. A solution of NaOH (10% in water) was added carefully until a white solid precipitated. After filtration over anhydrous Na₂SO₄ and evaporation of the solvent, the crude amine was obtained in quantitative yields.

Step 7: The crude amine obtained from step 6 (1 equiv.) was dissolved in pyridine (20 mL) and the respective sulfonyl chloride (1.5 equiv.) was added to the solution at 0 °C. The resulting solution was stirred overnight at 25 °C. DCM was subsequently added, and the mixture was washed three times with a hydrochloride solution (10% HCl in water). The organic layer was dried over anhydrous Na₂SO₄ and the solvent was then evaporated under reduced pressure. The crude material was purified by chromatography (silica gel, hexane/EtOAc) to give the pure product.

2.4 Characterization of new starting materials for 6-membered ring formation

N-(5-(4-methoxyphenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide (**1e**)



Following GP3, **1e** was obtained as a white solid in 56% yield.

mp: 72–74 °C; TLC (hexane/EtOAc: 6:1 v/v): R_f = 0.19.

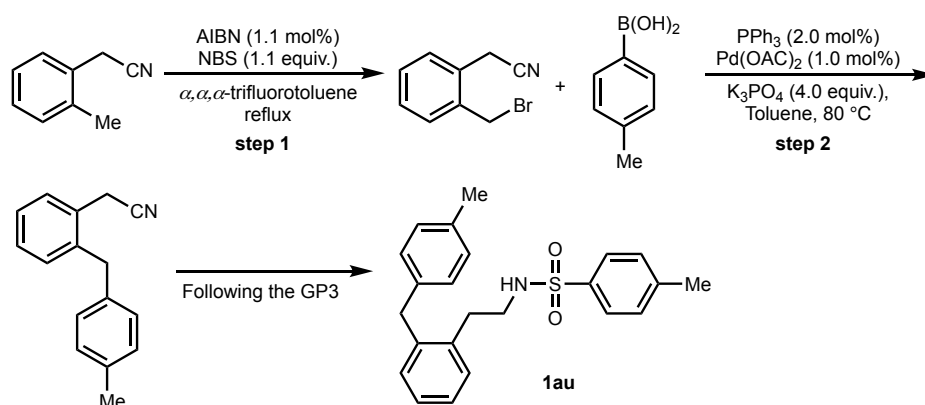
¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.40 (s, 1H), 3.79 (s, 3H), 2.66 (d, *J* = 6.0 Hz, 2H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.50–1.39 (m, 2H), 1.23–1.17 (m, 2H), 0.82 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 157.9, 143.4, 137.2, 134.6, 129.8, 129.3, 127.2, 113.9, 55.4, 53.0, 39.0, 35.7, 33.9, 26.0, 25.0, 21.6.

IR ν(cm⁻¹): 3273, 2930, 1610, 1509, 1320, 1246, 818, 676.

HRMS(ESI) *m/z*: Calcd. for [C₂₁H₂₉NNaO₃S]⁺: 398.1760; Found: 398.1763.

***N*-(5-(4-methoxyphenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide (1au)**



For the synthesis of the corresponding nitrile for the preparation of compound **1au**, steps 1-4 of GP3 were replaced⁶.

Step 1: In a flame-dried Schlenk tube, 2-(2-methylphenyl)acetonitrile (1 mL, 7.7 mmol, 1 equiv.) was dissolved in α,α,α -trifluorotoluene (20 mL). To this solution were added *N*-bromosuccinimide (NBS) (1.5 g, 1.1 equiv.) and azobisisobutyronitrile (AIBN) (14 mg). The mixture was heated under reflux for 2 hours. Subsequently, water was added to quench the reaction and the organic phase was extracted. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product obtained was directly used in the subsequent step without further purification.

Step 2: $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.05 mmol, 1.0 mol%), PPh_3 (26.2 mg, 0.1 mmol, 2.0 mol%), arylboronic acid (1.5 equiv.) and K_3PO_4 (4.25 g, 20.0 mmol, 4.0 equiv.) were added to a pre-dried flask. After protecting the reaction mixture with argon, dry toluene (15 mL) followed by 2-(bromomethyl)benzonitrile (980.3 mg, 5.0 mmol, 1.0 equiv.) were added. The mixture was stirred at 80 °C until all starting material was consumed (9 hours) and then quenched with water. The solution was extracted with Et_2O and the organic phase was washed with water, NaOH solution (1 M), brine and dried over anhydrous Na_2SO_4 . The solvent was removed and the product was isolated by flash column chromatography (hexane/ EtOAc : 4:1 v/v).

Subsequently, the corresponding nitrile was submitted to GP3 affording **1au** as a white solid in 37% yield.

mp: 99–101 °C; TLC (hexane/ EtOAc : 6:1 v/v): R_f = 0.14.

^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 7.20–7.09 (m, 3H), 7.08–7.01 (m, 3H), 6.92 (d, J = 8.2 Hz, 2H), 4.24 (s, 1H), 3.89 (s, 2H), 3.05 (q, J = 7.0 Hz, 2H), 2.75 (t, J = 7.3 Hz, 2H), 2.41 (s, 3H), 2.30 (s, 3H).

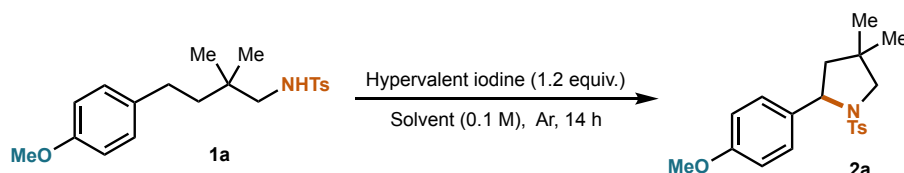
^{13}C NMR (100 MHz, CDCl_3): δ 143.5, 139.2, 137.5, 137.1, 136.2, 135.8, 131.1, 129.8, 129.8, 129.3, 128.6, 127.2, 127.2, 127.0, 43.5, 38.7, 33.0, 21.7, 21.1.

IR ν (cm^{-1}): 3264, 2853, 1430, 1324, 1153, 1094, 811, 771.

HRMS(ESI) m/z : Calcd. for $[\text{C}_{21}\text{H}_{29}\text{NNaO}_3\text{S}]^+$: 380.1679; Found: 380.1684.

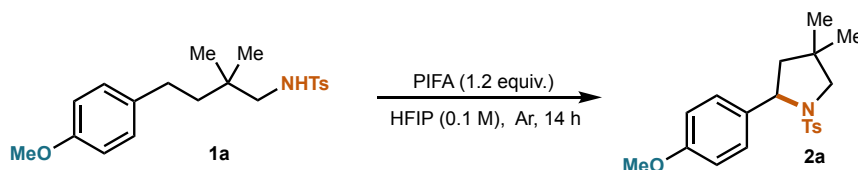
3. Experimental section for C(sp³)–H functionalization without light irradiation

3.1 Optimization studies



The sulfonamide **1a** (0.05 mmol, 1.0 equiv.) and hypervalent iodine (0.06 mmol, 1.2 equiv.) were added to a reaction vial equipped with a stir bar. This reaction vial was then brought into an argon-filled glovebox. Inside the glovebox, 0.5 mL of dry solvent were added to the mixture, and the reaction vial was sealed with a cap equipped with a Teflon-septa. The sealed vial was removed from the glovebox and stirred at room temperature for 14 hours. After completion of the reaction, volatiles were evaporated under reduced pressure and the residue was dissolved in CDCl₃ and analyzed by ¹H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

Table S1. Optimization for C(sp³)–H functionalization without light

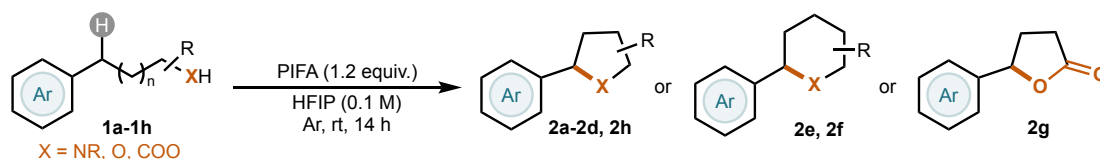


Entry	Variation from standard condition	Yield 2a [%] ^a
1	none	72
2	PIDA instead of PIFA	NR
3	DCM instead of HFIP	NR
4	2-Propanol instead of HFIP	NR
5	MeCN instead of HFIP	15
6	PhCF ₃ instead of HFIP	trace
7	1,4-Dioxane instead of HFIP	NR
8	DMSO instead of HFIP	NR

Standard reaction condition: **1a** (0.05 mmol), PIFA (1.2 equiv.), HFIP (0.5 mL) under argon atmosphere for 14 hours,

^a Yield determined by ¹H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

3.2 General synthetic procedure (GP4)

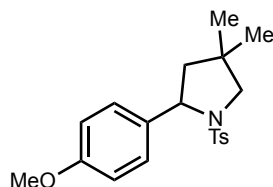


The sulfonamide **1a-1h** (0.15 mmol, 1.0 equiv.) and PIFA (0.18 mmol, 1.2 equiv.) were added to a reaction vial equipped with a stir bar. This reaction vial was then brought into

an argon-filled glovebox. Inside the glovebox, 1.5 mL of dry HFIP were added to the mixture, and the reaction vial was sealed with a cap equipped with a Teflon-septa. The sealed vial was removed from the glovebox and stirred at room temperature for 14 hours. After completion of the reaction, volatiles were evaporated under reduced pressure and the resulting crude product was purified by chromatography (silica gel, hexane/EtOAc) to obtain the pure product **2a-2h**.

3.3 Characterization of the resulting products following GP4

2-(4-methoxyphenyl)-4,4-dimethyl-1-tosylpyrrolidine (**2a**)

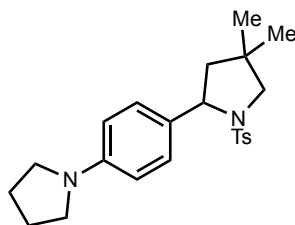


Following GP4, **2a** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (33.7 mg, 0.094 mmol, 62% yield). TLC (hexane/EtOAc: 8:1 v/v): R_f = 0.21. The NMR spectra match those previously described in literature.¹

¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, J = 8.4 Hz, 2H), 7.23–7.15 (m, 4H), 6.79 (d, J = 8.7 Hz, 2H), 4.66 (dd, J = 9.5, 7.2 Hz, 1H), 3.79 (s, 3H), 3.43 (dd, J = 10.3, 1.5 Hz, 1H), 3.32 (d, J = 10.3 Hz, 1H), 2.39 (s, 3H), 1.99 (ddd, J = 12.8, 7.2, 1.5 Hz, 1H), 1.71 (dd, J = 12.8, 9.5 Hz, 1H), 1.05 (s, 3H), 0.77 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 158.8, 143.0, 136.1, 135.0, 129.4, 127.9, 127.5, 113.8, 63.4, 61.9, 55.4, 51.6, 38.1, 26.3, 25.8, 21.6.

4,4-dimethyl-2-(4-(pyrrolidin-1-yl)phenyl)-1-tosylpyrrolidine (**2b**)



Following GP4, **2b** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (24.7 mg, 0.062 mmol, 41% yield).

mp: 115–117 °C; TLC (hexane/EtOAc: 8:1 v/v): R_f = 0.13.

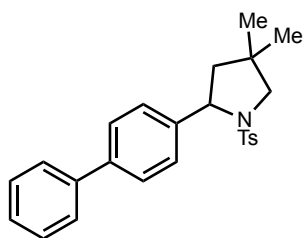
¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 8.6 Hz, 2H), 4.60 (dd, J = 9.5, 7.1 Hz, 1H), 3.41 (dd, J = 10.2, 1.5 Hz, 1H), 3.31 (d, J = 10.2 Hz, 1H), 3.29–3.21 (m, 4H), 2.38 (s, 3H), 2.03–1.92 (m, 5H), 1.74 (dd, J = 12.8, 9.5 Hz, 1H), 1.06 (s, 3H), 0.78 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 147.4, 142.6, 136.3, 129.3, 129.1, 127.8, 127.5, 111.5, 63.8, 61.9, 51.5, 47.8, 37.8, 26.4, 25.9, 25.6, 21.6.

IR ν (cm⁻¹): 2877, 1495, 1335, 1155, 1092, 1054, 756, 687.

HRMS(ESI) m/z : Calcd. for [C₂₃H₃₁N₂O₂S]⁺: 399.2101; Found: 399.2105.

2-([1,1'-biphenyl]-4-yl)-4,4-dimethyl-1-tosylpyrrolidine (2c)



Following GP4, **2c** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (51.9 mg, 0.128 mmol, 85% yield).

mp: 176–178 °C; TLC (hexane/EtOAc: 8:1 v/v): R_f = 0.23.

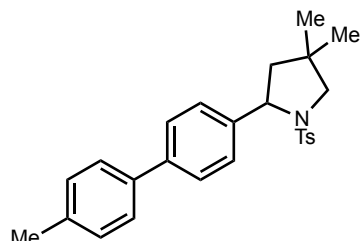
^1H NMR (400 MHz, CDCl_3): δ 7.61–7.52 (m, 4H), 7.50–7.40 (m, 4H), 7.37–7.30 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 4.76 (dd, J = 9.4, 7.3 Hz, 1H), 3.48 (dd, J = 10.4, 1.4 Hz, 1H), 3.37 (d, J = 10.4 Hz, 1H), 2.39 (s, 3H), 2.06 (ddd, J = 12.8, 7.3, 1.4 Hz, 1H), 1.77 (dd, J = 12.8, 9.4 Hz, 1H), 1.08 (s, 3H), 0.80 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.1, 142.1, 141.1, 140.2, 136.0, 129.4, 128.8, 127.5, 127.3, 127.2, 127.2, 127.1, 63.7, 62.0, 51.6, 38.3, 26.2, 25.8, 21.6.

IR $\nu(\text{cm}^{-1})$: 3028, 2866, 1593, 1485, 1340, 1150, 1053, 771.

HRMS(ESI) m/z : Calcd. for $[\text{C}_{25}\text{H}_{27}\text{NNaO}_2\text{S}]^+$: 428.1655; Found: 428.1652.

4,4-dimethyl-2-(4'-methyl-[1,1'-biphenyl]-4-yl)-1-tosylpyrrolidine (2d)



Following GP4, **2d** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (49.1 mg, 0.117 mmol, 78% yield).

mp: 131–133 °C; TLC (hexane/EtOAc: 8:1 v/v): R_f = 0.18.

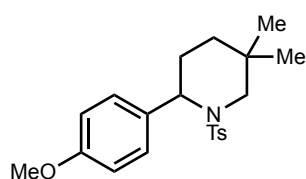
^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, J = 8.3 Hz, 2H), 7.50–7.42 (m, 4H), 7.31 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 7.7 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 4.75 (dd, J = 9.4, 7.3 Hz, 1H), 3.48 (dd, J = 10.4, 1.4 Hz, 1H), 3.37 (d, J = 10.4 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 2.05 (ddd, J = 12.8, 7.3, 1.4 Hz, 1H), 1.77 (dd, J = 12.8, 9.4 Hz, 1H), 1.08 (s, 3H), 0.80 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.1, 141.7, 140.1, 138.2, 137.1, 136.1, 129.6, 129.4, 127.5, 127.1, 127.0, 127.0, 63.7, 62.0, 51.6, 38.3, 26.2, 25.8, 21.6, 21.2.

IR $\nu(\text{cm}^{-1})$: 2876, 1496, 1342, 1154, 1092, 808, 687, 659.

HRMS(ESI) m/z : Calcd. for $[\text{C}_{26}\text{H}_{29}\text{NNaO}_2\text{S}]^+$: 442.1811; Found: 442.1815.

2-(4-methoxyphenyl)-5,5-dimethyl-1-tosylpiperidine (2e)



Following GP4, **2e** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (35.1 mg, 0.095 mmol, 63% yield).

mp: 104–106 °C; TLC (hexane/EtOAc: 8:1 v/v): R_f = 0.21.

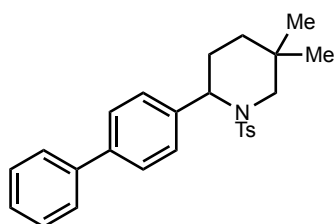
^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 5.16 (t, J = 4.0 Hz, 1H), 3.77 (s, 3H), 3.37 (d, J = 13.6 Hz, 1H), 2.84 (d, J = 13.6 Hz, 1H), 2.39 (s, 3H), 2.10–1.99 (m, 2H), 1.33–1.15 (m, 2H), 0.79 (s, 3H), 0.78 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 158.5, 142.8, 138.7, 130.9, 129.5, 128.3, 127.1, 113.9, 55.3, 55.1, 52.5, 32.6, 30.5, 28.7, 25.8, 24.3, 21.6.

IR $\nu(\text{cm}^{-1})$: 2924, 1508, 1324, 1154, 1093, 976, 907, 749.

HRMS(ESI) m/z : Calcd. for $[\text{C}_{21}\text{H}_{28}\text{NO}_3\text{S}]^+$: 374.1784; Found: 374.1776.

2-([1,1'-biphenyl]-4-yl)-5,5-dimethyl-1-tosylpiperidine (**2f**)

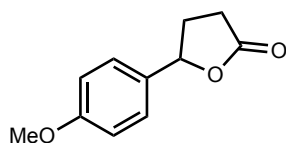


Following GP, **2f** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (50.5 mg, 0.120 mmol, 80% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.24. The NMR spectra match those previously described in literature.⁷

^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, J = 8.3 Hz, 2H), 7.56 (dd, J = 8.4, 1.3 Hz, 2H), 7.49–7.40 (m, 4H), 7.36–7.31 (m, 1H), 7.25–7.19 (m, 4H), 5.26 (t, J = 4.4 Hz, 1H), 3.44 (d, J = 13.6 Hz, 1H), 2.91 (d, J = 13.6 Hz, 1H), 2.40 (s, 3H), 2.16–2.05 (m, 2H), 1.33–1.20 (m, 2H), 0.82 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 142.9, 140.8, 139.7, 138.7, 138.2, 129.6, 128.9, 127.6, 127.4, 127.2, 127.2, 127.1, 55.4, 52.7, 32.7, 30.5, 28.8, 25.9, 24.3, 21.6.

5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (**2g**)



Following GP4, **2g** was isolated by column chromatography on silica (hexane/EtOAc: 5:1 v/v) as a colorless liquid (22.3 mg, 0.116 mmol, 77% yield).

mp: 53–55 °C; TLC (hexane/EtOAc: 2:1 v/v): R_f = 0.34.

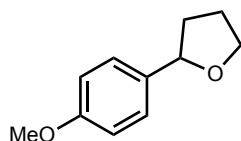
^1H NMR (400 MHz, CDCl_3): δ 7.26 (d, J = 8.3 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 5.45 (dd, J = 8.5, 6.1 Hz, 1H), 3.81 (s, 3H), 2.68–2.54 (m, 3H), 2.27–2.13 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 177.1, 159.9, 131.3, 127.1, 114.2, 81.5, 55.5, 31.0, 29.3.

IR $\nu(\text{cm}^{-1})$: 3502, 1609, 1514, 1246, 1176, 1014, 833, 804.

HRMS(ESI) m/z : Calcd. for $[\text{C}_{11}\text{H}_{12}\text{NaO}_3]^+$: 215.0679; Found: 215.0678.

2-(4-methoxyphenyl)tetrahydrofuran (2h)



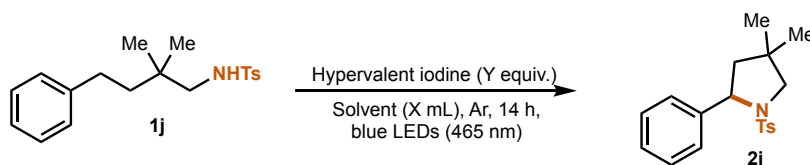
Following GP4, **2h** was isolated by column chromatography on silica (hexane/EtOAc: 10:1 v/v) as a colorless liquid, (16.04 mg, 0.090 mmol, 60% yield). TLC (hexane/EtOAc: 4:1 v/v): R_f = 0.32. The NMR spectra match those previously described in literature⁸.

¹H NMR (400 MHz, CDCl₃): δ 7.26 (d, J = 8.3 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.83 (t, J = 7.2 Hz, 1H), 4.12–4.04 (m, 1H), 3.95–3.87 (m, 1H), 3.80 (s, 3H), 2.32–2.22 (m, 1H), 2.10–1.93 (m, 2H), 1.85–1.73 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 159.0, 135.5, 127.1, 113.8, 80.6, 68.6, 55.4, 34.6, 26.2.

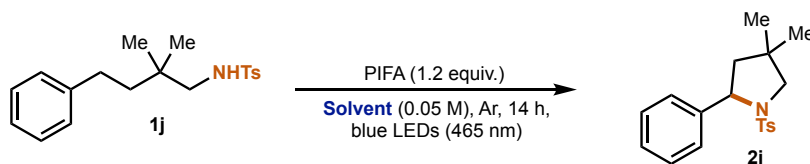
4. Experimental section for C(sp³)-H functionalization under light irradiation

4.1 Optimization studies for the 5-membered ring formation



Reactions performed using **set-up 1** in Figure S1. The sulfonamide **1j** (0.05 mmol, 1.0 equiv.) and hypervalent iodine (Y equiv.) were added to a reaction vial equipped with a stir bar. Subsequently, this reaction vial was brought into an argon-filled glovebox, X mL of dry solvent were added to the mixture, and the reaction vial was sealed with a Teflon-septa equipped cap. The vial was carefully taken outside of the glovebox and subjected to irradiation under stirring for 14 hours. After completion of the reaction, volatiles were evaporated under reduced pressure and the residue was dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy using mesitylene as the internal standard.

Table S2. Solvent optimization

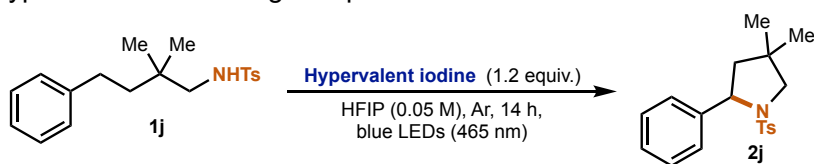


Entry	Solvent	Yield 2j [%] ^a
1	HFIP	86
2	TFE	35
3	2-Propanol	NR
4	MeCN	trace
5	DCE	19

6	Toluene	NR
7	Me-HFIP	trace
8	PFTB	33
9	PhCF ₃	5
10	1,4-Dioxane instead of HFIP	NR
11	DMSO instead of HFIP	21

Reaction condition: **1j** (0.05 mmol), PIFA (1.2 equiv.), solvent (1 mL) under argon atmosphere for 14 hours, blue LEDs, 465 nm, 30~40 °C ^aYield determined by ¹H NMR analysis of the crude mixture using mesitylene as the internal standard. HFIP = Hexafluoroisopropanol, TFE = 2,2,2-Trifluoroethanol, Me-HFIP = 1,1,1,3,3,3-Hexafluoro-2-methyl-2-propanol PFTB = Perfluoro-tert-butanol.

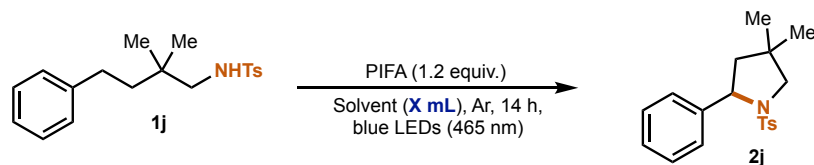
Table S3. Hypervalent iodine reagent optimization



Entry	Hypervalent iodine reagent	Yield 2j [%] ^a
1	PIFA	86
2	PIDA	9
3	PhI(<i>m</i> CBA) ₂	7

Reaction condition: **1j** (0.05 mmol), Hypervalent iodine (1.2 equiv.), HFIP (1 mL) under argon atmosphere for 14 hours, blue LEDs, 465 nm, 30~40 °C ^aYield determined by ¹H NMR analysis of the crude mixture using mesitylene as the internal standard.

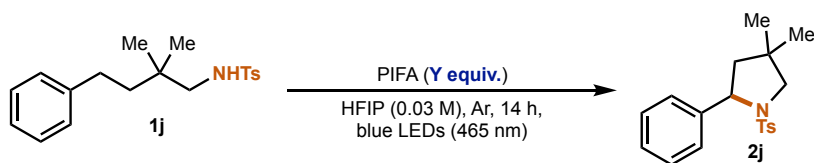
Table S4. Concentration optimization



Entry	HFIP (X mL)	Yield 2j [%] ^a
1	0.25	82
2	0.5	84
3	1.0	86
4	1.5	88
5	2.0	88

Reaction condition: **1j** (0.05 mmol), PIFA (1.2 equiv.), HFIP (X mL) under argon atmosphere for 14 hours, blue LEDs, 465 nm, 30~40 °C ^aYield determined by ¹H NMR analysis of the crude mixture using mesitylene as the internal standard.

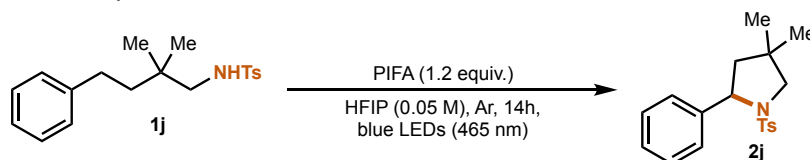
Table S5. PIFA optimization



Entry	PIFA (Y equiv.)	Yield 2j [%] ^a
1	0.6	49
2	1.2	88
3	1.5	88

Reaction condition: **1j** (0.05 mmol), PIFA (Y equiv.), HFIP (1.5 mL) under argon atmosphere for 14 hours, blue LEDs, 465 nm, 30~40 °C ^aYield determined by ¹H NMR analysis of the crude mixture using mesitylene as the internal standard.

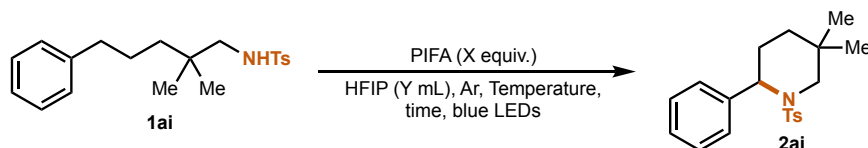
Table S6. Control experiments



Entry	Variation from standard condition	Yield 2j [%] ^a
1	none	86
2	Without <i>hν</i> , rt	trace
3	Without <i>hν</i> , 40 °C	trace
4	Without PIFA	NR
5	Under air	14

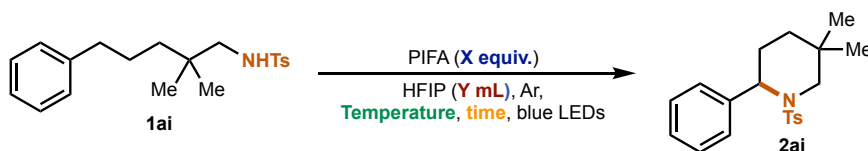
Standard reaction condition: **1j** (0.05 mmol), PIFA (1.2 equiv.), HFIP (1.0 mL) under argon atmosphere for 14 hours, blue LEDs, 465 nm, 30~40 °C ^aYield determined by ¹H NMR analysis of the crude mixture using mesitylene as the internal standard.

4.2 Optimization studies for the 6-membered ring formation



Reactions performed using **set-up 1** or **set-up 2** in Figure S1, Figure S2. The sulfonamide **1ai** (0.05 mmol, 1.0 equiv.) and PIFA (X equiv.) were added to a reaction vial equipped with a stir bar. Subsequently, this reaction vial was brought into an argon-filled glovebox, Y mL of dry HFIP were added to the mixture, and the reaction vial was sealed with a Teflon-septa equipped cap. The vial was carefully taken outside of the glovebox and subjected to irradiation under stirring different temperature for some hours. After completion of the reaction, volatiles were evaporated under reduced pressure and the residue was dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy using mesitylene as the internal standard.

Table S7. Optimization studies

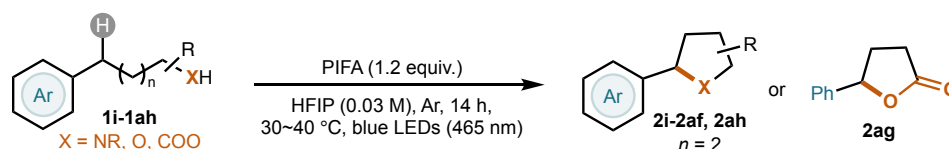


Entry	Temperature (°C)	Time (h)	PIFA (X equiv.)	HFIP (Y mL)	Yield 2ai [%] ^c
1 ^a	30-40	14	1.2	1.5	65
2 ^a	30-40	14	1.2	1.0	65
3 ^b	10	24	1.2	1.0	71
4 ^b	5	30	1.2	1.0	72
5 ^b	5	30	1.3	1.0	78

6^b	5	30	1.4	1.0	72
7^b	5	18	1.3	1.0	75

Reaction condition: **1ai** (0.05 mmol), PIFA (X equiv.), HFIP (1.0 mL) under argon atmosphere. ^a The reaction was performed using the illumination *set-up 1* in Figure S1. ^b The reaction was performed using the illumination *set-up 2* in Figure S2. ^c Yield determined by ¹H NMR analysis of the crude mixture using mesitylene as the internal standard.

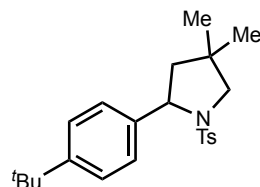
4.3 General procedure (GP5) for the 5-membered ring formation



Reactions performed using **set-up 1** in Figure S1. The sulfonamide **1i-1ah** (0.15 mmol, 1.0 equiv.) and PIFA (0.16 mmol, 1.2 equiv.) were added to a reaction vial equipped with a stir bar. Subsequently, this reaction vial was brought into an argon-filled glovebox, 4.5 mL of dry HFIP was added to the mixture, and the reaction vial was sealed with a Teflon-septa equipped cap. The vial was carefully taken outside of the glovebox and subjected to irradiation under stirring for 14 hours. After completion of the reaction, volatiles were evaporated under reduced pressure and the resulting crude product was purified by chromatography (silica gel, hexane/EtOAc) to obtain the pure product **2i-2ah**.

4.4 Characterization of 5-membered ring products

2-(4-(tert-butyl)phenyl)-4,4-dimethyl-1-tosylpyrrolidine (**2i**)

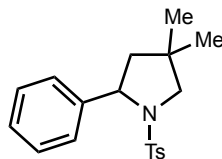


Following GP5, **2i** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (43.6 mg, 0.113 mmol, 75% yield). TLC (hexane/EtOAc: 9:1 v/v): R_f = 0.38. The NMR spectra match those previously described in literature.²

¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.1 Hz, 4H), 4.71 (dd, J = 9.5, 7.2 Hz, 1H), 3.49 (dd, J = 10.3, 1.5 Hz, 1H), 3.33 (d, J = 10.3 Hz, 1H), 2.37 (s, 3H), 2.02 (ddd, J = 12.8, 7.2, 1.5 Hz, 1H), 1.74 (dd, J = 12.8, 9.5 Hz, 1H), 1.30 (s, 9H), 1.06 (s, 3H), 0.82 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 150.0, 142.8, 139.6, 136.4, 129.3, 127.4, 126.5, 125.2, 63.5, 61.9, 51.6, 38.2, 34.5, 31.5, 26.2, 25.8, 21.6.

4,4-dimethyl-2-phenyl-1-tosylpyrrolidine (**2j**)

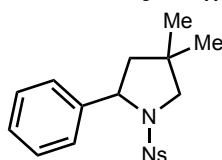


Following GP5, **2j** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (42.4 mg, 0.129 mmol, 86% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.31. The NMR spectra match those previously described in literature¹.

¹H NMR (400 MHz, CDCl₃): δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.30–7.24 (m, 4H), 7.23–7.17 (m, 3H), 4.70 (dd, *J* = 9.4, 7.3 Hz, 1H), 3.44 (dd, *J* = 10.3, 1.5 Hz, 1H), 3.34 (d, *J* = 10.4 Hz, 1H), 2.39 (s, 3H), 2.02 (ddd, *J* = 12.8, 7.3, 1.5 Hz, 1H), 1.72 (dd, *J* = 12.8, 9.4 Hz, 1H), 1.05 (s, 3H), 0.76 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 143.1, 143.0, 135.9, 129.4, 128.4, 127.5, 127.1, 126.6, 63.9, 62.0, 51.6, 38.2, 26.2, 25.8, 21.6.

4,4-dimethyl-1-((4-nitrophenyl)sulfonyl)-2-phenylpyrrolidine (2k)

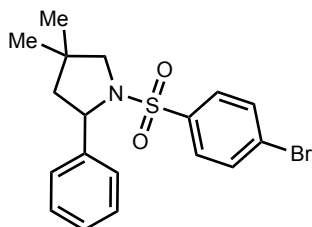


Following GP5, **2k** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (40.8 mg, 0.113 mmol, 75% yield). TLC (hexane/EtOAc: 9:1 v/v): *R_f* = 0.21. The NMR spectra match those previously described in literature¹.

¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.22–7.14 (m, 3H), 7.13–7.07 (m, 2H), 4.86 (dd, *J* = 9.8, 7.2 Hz, 1H), 3.65 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.30 (d, *J* = 10.0 Hz, 1H), 2.14 (ddd, *J* = 12.9, 7.2, 1.7 Hz, 1H), 1.78 (dd, *J* = 12.9, 9.8 Hz, 1H), 1.13 (s, 3H), 1.02 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 149.5, 145.9, 141.4, 128.5, 128.1, 127.7, 127.2, 123.8, 64.1, 61.8, 51.3, 38.5, 25.7, 25.7.

1-((4-bromophenyl)sulfonyl)-4,4-dimethyl-2-phenylpyrrolidine (2l)



Following GP5, **2l** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (48.8 mg, 0.124 mmol, 83% yield).

mp: 113–115 °C; TLC (hexane/EtOAc: 8:1 v/v): *R_f* = 0.28.

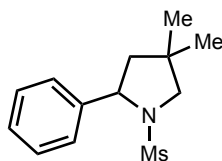
¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.25–7.14 (m, 5H), 4.76 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.52 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.31 (d, *J* = 10.2 Hz, 1H), 2.08 (ddd, *J* = 12.9, 7.2, 1.6 Hz, 1H), 1.75 (dd, *J* = 12.9, 9.6 Hz, 1H), 1.09 (s, 3H), 0.90 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 142.2, 138.6, 131.9, 128.7, 128.4, 127.4, 127.1, 126.8, 64.0, 61.9, 51.5, 38.3, 25.9, 25.8.

IR ν(cm⁻¹): 3257, 2958, 1573, 1465, 1349, 1088, 817, 756.

HRMS(ESI) *m/z*: Calcd. for [C₁₈H₂₁BrNO₂S]⁺: 394.0471; Found: 394.0475.

4,4-dimethyl-1-(methylsulfonyl)-2-phenylpyrrolidine (2m)

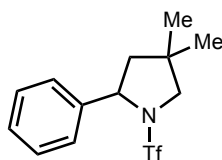


Following GP5, **2m** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (32.1 mg, 0.127 mmol, 84% yield). TLC (hexane/EtOAc: 9:1 v/v): R_f = 0.17. The NMR spectra match those previously described in literature.⁶

¹H NMR (400 MHz, CDCl₃): δ 7.39–7.30 (m, 4H), 7.30–7.23 (m, 1H), 4.90 (dd, J = 9.8, 7.3 Hz, 1H), 3.66 (dd, J = 10.2, 1.7 Hz, 1H), 3.28 (d, J = 10.2 Hz, 1H), 2.52 (s, 3H), 2.19 (ddd, J = 12.8, 7.3, 1.7 Hz, 1H), 1.83 (dd, J = 12.8, 9.7 Hz, 1H), 1.18 (s, 3H), 1.14 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 142.6, 128.8, 127.8, 126.9, 63.6, 61.5, 51.6, 40.7, 38.5, 25.8, 25.8.

4,4-dimethyl-2-phenyl-1-((trifluoromethyl)sulfonyl)pyrrolidine (2n)



Following GP5, **2n** was isolated by column chromatography on silica (hexane/EtOAc: 10:1 v/v) as a pale yellow oil (36.4 mg, 0.118 mmol, 79% yield). TLC (hexane/EtOAc: 10:1 v/v): R_f = 0.40.

¹H NMR (400 MHz, CDCl₃): δ 7.38–7.32 (m, 2H), 7.32–7.26 (m, 3H), 5.07 (dd, J = 9.7, 7.3 Hz, 1H), 3.68 (dd, J = 10.4, 1.8 Hz, 1H), 3.45 (d, J = 10.5 Hz, 1H), 2.27 (ddd, J = 13.0, 7.3, 1.8 Hz, 1H), 1.91 (dd, J = 12.8, 9.8 Hz, 1H), 1.21 (s, 3H), 1.18 (s, 3H).

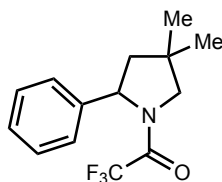
¹³C NMR (100 MHz, CDCl₃): δ 141.3, 128.7, 128.1, 126.8, 119.9 (q, J = 321 Hz), 65.2, 62.8, 51.2, 39.0, 25.5, 25.4.

¹⁹F NMR (375 MHz, CDCl₃): δ -77.6 (s, 3F).

IR ν (cm⁻¹): 2962, 1467, 1378, 1223, 1137, 1050, 770, 698.

HRMS(ESI) m/z : Calcd. for [C₁₃H₁₆F₃NNaO₂S]⁺: 330.0746; Found: 330.0741.

1-(4,4-dimethyl-2-phenylpyrrolidin-1-yl)-2,2,2-trifluoroethan-1-one (2o)



Following GP5, **2o** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (23.1 mg, 0.085 mmol, 57% yield). Traces of the other diastereomeric species were visible by NMR spectroscopy. TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.31. The NMR spectra match those previously described in literature.⁶

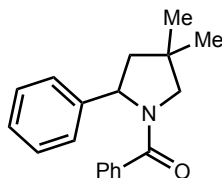
¹H NMR (400 MHz, CDCl₃): δ 7.36–7.30 (m, 2H), 7.27–7.22 (m, 1H), 7.25–7.18 (m, 2H), 5.11 (dd, J = 9.9, 7.7 Hz, 1H), 3.71 (dt, J = 10.9, 1.9 Hz, 1H), 3.51 (d, J = 10.9 Hz, 1H), 2.23 (ddd, J = 13.0, 7.8, 1.7 Hz, 1H), 1.74 (dd, J = 13.0, 9.8 Hz, 1H), 1.19 (s, 3H), 1.12 (s,

3H).

¹³C NMR (100 MHz, CDCl₃): δ 155.9 (d, J = 36.4 Hz), 141.7, 128.9, 127.5, 125.7, 116.4 (q, J = 288.0 Hz), 62.7, 60.6 (d, J = 2.9 Hz), 48.6, 39.0, 25.6, 25.5.

¹⁹F NMR (375 MHz, CDCl₃): δ -72.00 (d, J = 2.4 Hz, 3F).

(4,4-dimethyl-2-phenylpyrrolidin-1-yl)(phenyl)methanone (2p)

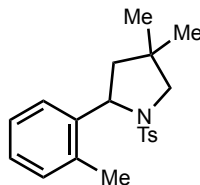


Following GP5, **2p** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (35.5 mg, 0.127 mmol, 85% yield). Traces of another diastereomeric species were visible by NMR spectroscopy. TLC (hexane/EtOAc: 9:1 v/v): R_f = 0.12. The NMR spectra match those previously described in literature.⁶

¹H NMR (400 MHz, CDCl₃): δ 7.65–7.57 (m, 2H), 7.47–7.37 (m, 3H), 7.37–7.27 (m, 4H), 7.24–7.18 (m, 1H), 5.33 (dd, J = 10.2, 7.7 Hz, 1H), 3.58 (d, J = 10.4 Hz, 1H), 3.37 (dd, J = 10.4, 1.9 Hz, 1H), 2.23 (ddd, J = 12.8, 7.6, 1.9 Hz, 1H), 1.77 (dd, J = 12.7, 10.2 Hz, 1H), 1.10 (s, 3H), 1.03 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 170.3, 143.7, 136.8, 130.4, 128.7, 128.3, 127.9, 126.9, 125.8, 64.2, 60.9, 49.4, 39.1, 25.7, 25.5.

4,4-dimethyl-2-(o-tolyl)-1-tosylpyrrolidine (2q)

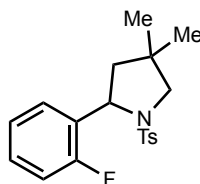


Following GP5, **2q** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (34.9 mg, 0.102 mmol, 68% yield). TLC (hexane/EtOAc: 9:1 v/v): R_f = 0.35. The NMR spectra match those previously described in literature.²

¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, J = 8.3 Hz, 2H), 7.32–7.27 (m, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.13–7.02 (m, 3H), 4.99 (dd, J = 9.4, 7.4 Hz, 1H), 3.49 (dd, J = 10.4, 1.5 Hz, 1H), 3.34 (d, J = 10.5 Hz, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 2.06 (ddd, J = 12.7, 7.4, 1.5 Hz, 1H), 1.61 (dd, J = 12.7, 9.4 Hz, 1H), 1.07 (s, 3H), 0.80 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 143.1, 141.2, 136.1, 134.2, 130.3, 129.4, 127.5, 126.8, 126.4, 126.3, 61.8, 60.6, 50.0, 38.4, 26.2, 25.9, 21.6, 19.4.

2-(2-fluorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2r)



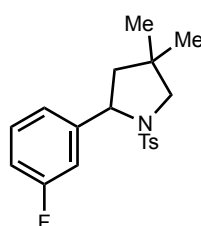
Following GP5, **2r** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (26.1 mg, 0.075 mmol, 50% yield). TLC (hexane/EtOAc: 9:1 v/v): R_f = 0.31. The NMR spectra match those previously described in literature.²

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, J = 8.3 Hz, 2H), 7.48 (td, J = 7.7, 1.9 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 7.21–7.15 (m, 1H), 7.09 (td, J = 7.5, 1.2 Hz, 1H), 6.93 (ddd, J = 10.8, 8.1, 1.2 Hz, 1H), 4.96 (dd, J = 9.1, 7.5 Hz, 1H), 3.37 (s, 2H), 2.40 (s, 3H), 2.05 (dd, J = 12.7, 7.5 Hz, 1H), 1.74 (dd, J = 12.7, 9.0 Hz, 1H), 1.05 (s, 3H), 0.70 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 160.2 (d, J = 246.5 Hz), 143.3, 135.3, 130.0 (d, J = 12.2 Hz), 129.53, 128.8 (d, J = 4.2 Hz), 128.7 (d, J = 8.3 Hz), 127.56, 124.2 (d, J = 3.5 Hz), 115.3 (d, J = 21.7 Hz), 61.6, 58.0 (d, J = 2.6 Hz), 49.3, 38.4, 26.2, 25.8, 21.6.

¹⁹F NMR (375 MHz, CDCl₃): δ -119.52–119.74 (m, 1F).

2-(3-fluorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (**2s**)



Following GP5, **2s** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (31.8 mg, 0.092 mmol, 61% yield).

mp: 83–85 °C; TLC (hexane/EtOAc: 8:1 v/v): R_f = 0.25.

¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, J = 8.4 Hz, 2H), 7.25–7.18 (m, 3H), 7.06 (d, J = 7.7 Hz, 1H), 6.96–6.84 (m, 2H), 4.69 (dd, J = 9.3, 7.3 Hz, 1H), 3.44 (dd, J = 10.4, 1.5 Hz, 1H), 3.33 (d, J = 10.5 Hz, 1H), 2.40 (s, 3H), 2.02 (ddd, J = 12.8, 7.3, 1.5 Hz, 1H), 1.68 (dd, J = 12.8, 9.3 Hz, 1H), 1.05 (s, 3H), 0.75 (s, 3H).

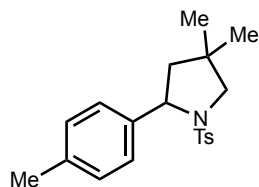
¹³C NMR (100 MHz, CDCl₃): δ 163.0 (d, J = 245.6 Hz), 145.9 (d, J = 6.9 Hz), 143.4, 135.7, 129.9 (d, J = 8.2 Hz), 129.5, 127.5, 122.2 (d, J = 2.7 Hz), 114.1 (d, J = 21.3 Hz), 113.5 (d, J = 22.2 Hz), 63.4 (d, J = 2.0 Hz), 62.0, 51.5, 38.3, 26.2, 25.8, 21.6.

¹⁹F NMR (375 MHz, CDCl₃): δ -113.45 (td, 1F).

IR ν (cm⁻¹): 3066, 2960, 1592, 1341, 1156, 1089, 776, 691.

HRMS(ESI) m/z : Calcd. for [C₁₉H₂₃FNO₂S]⁺: 348.1428; Found: 348.1433.

4,4-dimethyl-2-(p-tolyl)-1-tosylpyrrolidine (**2t**)



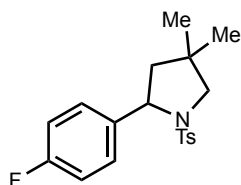
Following GP5, **2t** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (41.6 mg, 0.121 mmol, 81% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.25. The NMR spectra match those previously described in literature.¹

¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 4.65 (dd, J = 9.4, 7.2 Hz, 1H), 3.42 (dd, J = 10.4,

1.4 Hz, 1H), 3.34 (d, $J = 10.4$ Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H), 1.99 (ddd, $J = 12.8, 7.2, 1.4$ Hz, 1H), 1.72 (dd, $J = 12.8, 9.4$ Hz, 1H), 1.05 (s, 3H), 0.74 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.1, 140.0, 136.8, 135.9, 129.4, 129.1, 127.5, 126.6, 63.7, 62.0, 51.6, 38.1, 26.2, 25.8, 21.6, 21.2.

2-(4-fluorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2u)



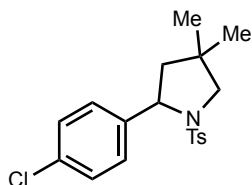
Following GP5, **2u** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (44.5 mg, 0.128 mmol, 85% yield). TLC (hexane/EtOAc: 19:1 v/v): $R_f = 0.27$. The NMR spectra match those previously described in literature.¹

^1H NMR (400 MHz, CDCl_3): δ 7.53 (d, $J = 8.3$ Hz, 2H), 7.25–7.19 (m, 4H), 6.94 (t, $J = 8.7$ Hz, 2H), 4.67 (dd, $J = 9.4, 7.2$ Hz, 1H), 3.43 (dd, $J = 10.4, 1.5$ Hz, 1H), 3.33 (d, $J = 10.4$ Hz, 1H), 2.40 (s, 3H), 2.00 (ddd, $J = 12.8, 7.2, 1.5$ Hz, 1H), 1.68 (dd, $J = 12.8, 9.4$ Hz, 1H), 1.05 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 162.0 (d, $J = 245.1$ Hz), 143.3, 138.8 (d, $J = 3.2$ Hz), 135.8, 129.5, 128.2 (d, $J = 8.1$ Hz), 127.5, 115.2 (d, $J = 21.4$ Hz), 63.3, 61.9, 51.7, 38.2, 26.2, 25.8, 21.6.

^{19}F NMR (375 MHz, CDCl_3): δ -115.96 (tt, 1F).

2-(4-chlorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2v)

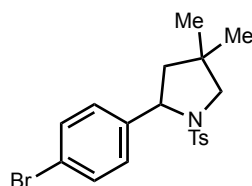


Following GP5, **2v** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (43.2 mg, 0.119 mmol, 79% yield). TLC (hexane/EtOAc: 19:1 v/v): $R_f = 0.23$. The NMR spectra match those previously described in literature.¹

^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, $J = 8.4$ Hz, 2H), 7.25–7.18 (m, 6H), 4.65 (dd, $J = 9.3, 7.3$ Hz, 1H), 3.42 (dd, $J = 10.4, 1.4$ Hz, 1H), 3.33 (d, $J = 10.4$ Hz, 1H), 2.40 (s, 3H), 1.99 (ddd, $J = 12.8, 7.3, 1.4$ Hz, 1H), 1.66 (dd, $J = 12.9, 9.5$ Hz, 1H), 1.04 (s, 3H), 0.73 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.4, 141.7, 135.6, 132.8, 129.5, 128.5, 128.0, 127.5, 63.3, 62.0, 51.5, 38.2, 26.2, 25.7, 21.6.

2-(4-bromophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2w)

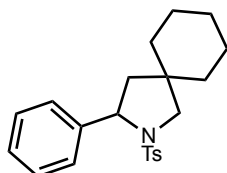


Following GP5, **2w** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (42.8 mg, 0.105 mmol, 70% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.23. The NMR spectra match those previously described in literature.¹

¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 4.63 (dd, J = 9.3, 7.3 Hz, 1H), 3.42 (dd, J = 10.4, 1.4 Hz, 1H), 3.33 (d, J = 10.5 Hz, 1H), 2.41 (s, 3H), 2.00 (ddd, J = 12.8, 7.3, 1.4 Hz, 1H), 1.66 (dd, J = 12.8, 9.4 Hz, 1H), 1.04 (s, 3H), 0.74 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 143.4, 142.2, 135.6, 131.5, 129.5, 128.3, 127.5, 120.9, 63.3, 62.0, 51.4, 38.2, 26.2, 25.7, 21.6.

3-phenyl-2-tosyl-2-azaspiro[4.5]decane (2x)

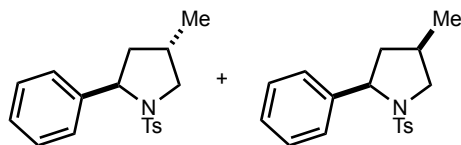


Following GP5, **2x** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (47.9 mg, 0.130 mmol, 86% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.23. The NMR spectra match those previously described in literature.¹

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, J = 8.3 Hz, 2H), 7.35–7.27 (m, 4H), 7.27–7.20 (m, 3H), 4.64 (dd, J = 9.4, 7.3 Hz, 1H), 3.64 (dd, J = 10.7, 1.4 Hz, 1H), 3.33 (d, J = 11.0 Hz, 1H), 2.42 (s, 3H), 2.13 (ddd, J = 13.0, 7.3, 1.4 Hz, 1H), 1.68 (dd, J = 12.9, 9.4 Hz, 1H), 1.53–1.40 (m, 3H), 1.39–1.23 (m, 5H), 1.12 – 0.94 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 143.2, 143.1, 135.6, 129.4, 128.4, 127.5, 127.1, 126.5, 63.1, 59.4, 49.6, 42.1, 36.4, 34.0, 26.0, 23.9, 22.9, 21.6.

4-methyl-2-phenyl-1-tosylpyrrolidine (2y)



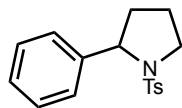
Following GP5, **2y** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (39.1 mg, 0.123 mmol, 83% yield, $d.r.$ = 2:1). TLC (hexane/EtOAc: 9:1 v/v): R_f = 0.21. The NMR data of the major diastereoisomer (*anti*) is given which match those previously reported.¹

¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, J = 8.3 Hz, 0.69H), 7.61 (d, J = 8.3 Hz, 1.31H), 7.34–7.19 (m, 7H), 4.85 (dd, J = 8.4, 2.5 Hz, 0.33H), 4.64 (dd, J = 9.5, 7.2 Hz, 0.67H), 3.84 (ddd, J = 11.1, 7.3, 1.4 Hz, 0.67H), 3.74 (ddd, J = 9.4, 6.9, 0.8 Hz, 0.34H), 3.09 (t, J = 10.8 Hz,

0.66H), 2.88 (t, $J = 9.2$ Hz, 0.34H), 2.43 (s, 1H), 2.41 (s, 2H), 2.40–2.30 (m, 1H), 1.93–1.76 (m, 1H), 1.62–1.55 (m, 0.34H), 1.55–1.42 (m, 0.69H), 0.95 (d, $J = 6.5$ Hz, 2H), 0.88 (d, $J = 6.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.4, 143.1, 135.7, 129.6, 128.4, 127.5, 127.2, 126.4, 64.7, 56.8, 45.7, 33.5, 21.6, 16.6.

2-phenyl-1-tosylpyrrolidine (**2z**)

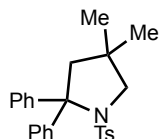


Following GP5, **2z** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (32.6 mg, 0.108 mmol, 72% yield). TLC (hexane/EtOAc: 8:1 v/v): $R_f = 0.33$. The NMR spectra match those previously described in literature.¹

^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 8.3$ Hz, 2H), 7.35–7.19 (m, 7H), 4.79 (dd, $J = 8.0, 3.6$ Hz, 1H), 3.66–3.57 (m, 1H), 3.47–3.38 (m, 1H), 2.42 (s, 3H), 2.03–1.93 (m, 1H), 1.90–1.77 (m, 2H), 1.71–1.61 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.4, 143.2, 135.3, 129.7, 128.4, 127.6, 127.1, 126.3, 63.4, 49.5, 35.9, 24.1, 21.6.

4,4-dimethyl-2,2-diphenyl-1-tosylpyrrolidine (**2aa**)

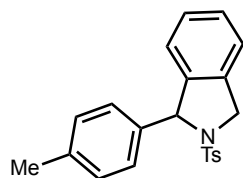


Following GP5, **2aa** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (53.6 mg, 0.132 mmol, 88% yield). TLC (hexane/EtOAc: 9:1 v/v): $R_f = 0.38$. The NMR spectra match those previously described in literature.²

^1H NMR (400 MHz, CDCl_3): δ 7.38–7.31 (m, 4H), 7.28–7.20 (m, 6H), 6.99 (d, $J = 7.8$ Hz, 2H), 6.82 (d, $J = 8.3$ Hz, 2H), 3.52 (s, 2H), 2.69 (s, 2H), 2.35 (s, 3H), 1.06 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 144.5, 142.3, 136.7, 129.7, 128.8, 127.5, 127.3, 126.9, 76.9, 63.5, 61.3, 37.1, 28.1, 21.6.

1-(p-tolyl)-2-tosylisoindoline (**2ab**)

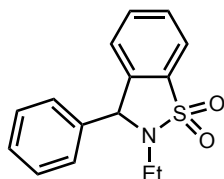


Following GP5, **2ab** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (44.0 mg, 0.121 mmol, 81% yield). TLC (hexane/EtOAc: 9:1 v/v): $R_f = 0.31$. The NMR spectra match those previously described in literature.⁶

^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, $J = 8.3$ Hz, 2H), 7.24–7.20 (m, 2H), 7.19–7.13 (m, 3H), 7.13–7.03 (m, 4H), 6.88 (d, $J = 7.6$ Hz, 1H), 5.86 (s, 1H), 4.88–4.76 (m, 2H), 2.36 (s, 3H), 2.32 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 143.3, 141.3, 139.1, 137.7, 135.5, 135.2, 129.6, 129.3, 128.1, 128.0, 127.7, 127.6, 123.8, 122.5, 69.4, 54.1, 21.6, 21.3.

2-ethyl-3-phenyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2ac)

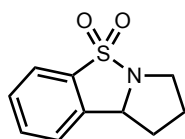


Following GP5, **2ac** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (35.0 mg, 0.128 mmol, 85% yield). TLC (hexane/EtOAc: 6:1 v/v): R_f = 0.18. The NMR spectra match those previously described in literature.⁹

¹H NMR (400 MHz, CDCl₃): δ 7.88–7.78 (m, 1H), 7.54–7.45 (m, 2H), 7.43–7.30 (m, 5H), 7.10–6.99 (m, 1H), 5.40 (s, 1H), 3.39 (dq, J = 14.7, 7.4 Hz, 1H), 3.17 (dq, J = 14.2, 7.1 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 138.4, 137.5, 134.3, 133.0, 129.4, 129.3, 129.1, 128.1, 125.1, 121.1, 64.9, 37.0, 13.6.

1,2,3,9b-tetrahydrobenzo[d]pyrrolo[1,2-b]isothiazole 5,5-dioxide (2ad)

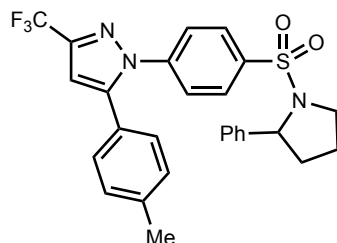


Following GP5, **2ad** was isolated by column chromatography on silica (hexane/EtOAc: 10:1 v/v) as a white solid (15.1 mg, 0.072 mmol, 48% yield). TLC (hexane/EtOAc: 4:1 v/v): R_f = 0.30. The NMR spectra match those previously described in literature.¹

¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, J = 7.8 Hz, 1H), 7.60 (td, J = 7.5, 1.2 Hz, 1H), 7.53–7.48 (m, 1H), 7.36 (dd, J = 7.7, 0.9 Hz, 1H), 4.99 (t, J = 6.8 Hz, 1H), 3.86–3.74 (m, 1H), 3.39–3.36 (m, 1H), 2.52–2.36 (m, 1H), 2.07–1.80 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 140.1, 136.4, 133.3, 129.5, 124.0, 121.7, 65.2, 48.5, 32.6, 26.2.

1-(4-((2-phenylpyrrolidin-1-yl)sulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole (2ae)



Following GP5, **2ae** was isolated by column chromatography on silica (hexane/EtOAc: 10:1 v/v) as a white solid (65.5 mg, 0.127 mmol, 85% yield). TLC (hexane/EtOAc: 6:1 v/v): R_f = 0.26. The NMR spectra match those previously described in literature.¹⁰

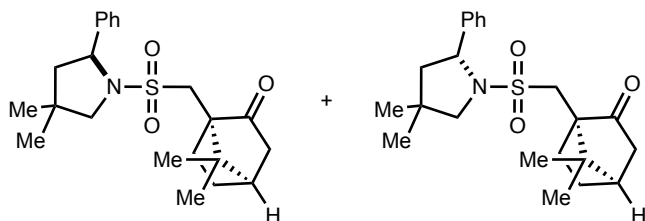
¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 8.9 Hz, 2H), 7.43 (d, J = 8.9 Hz, 2H), 7.33–7.21

(m, 5H), 7.17 (d, $J = 7.9$ Hz, 2H), 7.09 (d, $J = 8.3$ Hz, 2H), 6.75 (s, 1H), 4.79 (dd, $J = 7.9$, 3.8 Hz, 1H), 3.66–3.56 (m, 1H), 3.49–3.38 (m, 1H), 2.38 (s, 3H), 2.10–1.98 (m, 1H), 1.98–1.79 (m, 2H), 1.78–1.65 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 145.4, 144.2 (q, $J = 38.6$ Hz), 142.6, 142.5, 139.9, 138.0, 129.8, 128.8, 128.5, 128.5, 127.4, 126.3, 125.8, 125.6, 121.2 (q, $J = 269.0$ Hz), 106.3, 63.7, 49.5, 36.0, 24.2, 21.4.

^{19}F NMR (375 MHz, CDCl_3): δ -62.49 (s, 3F).

1-(((4,4-dimethyl-2-phenylpyrrolidin-1-yl)sulfonyl)methyl)-7,7-dimethylbicyclo-[2.2.1]heptan-2-one (2af)



Following GP5, **2af** was isolated by column chromatography on silica (hexane/EtOAc: 15:1 v/v) as a white solid (50.3 mg, 0.129 mmol, 86% yield, *d.r.* = 1:1).

mp: 94–96 °C; TLC (hexane/EtOAc: 6:1 v/v): $R_f = 0.19$.

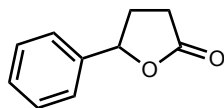
^1H NMR (400 MHz, CDCl_3): δ 7.41–7.30 (m, 4H), 7.29–7.21 (m, 1H), 4.99–4.88 (m, 1H), 3.72–3.62 (m, 1H), 3.30 (d, $J = 10.4$ Hz, 1H), 3.17 (d, $J = 14.4$ Hz, 0.5H), 2.96 (d, $J = 14.4$ Hz, 0.5H), 2.63 (d, $J = 14.8$ Hz, 0.5H), 2.44–2.13 (m, 3H), 2.15 (d, $J = 14.8$ Hz, 0.5H), 2.01–1.76 (m, 3.5H), 1.62–1.52 (m, 0.5H), 1.38–1.23 (m, 2H), 1.18 (s, 3H), 1.15 (s, 1.5H), 1.14 (s, 1.5H), 0.98 (s, 1.5H), 0.82 (s, 1.5H), 0.75 (s, 1.5H), 0.48 (s, 1.5H).

^{13}C NMR (100 MHz, CDCl_3): δ 215.2, 214.9, 142.7, 142.6, 128.7, 128.7, 127.8, 127.7, 127.6, 127.3, 63.5, 63.5, 61.6, 61.4, 58.4, 51.4, 51.2, 50.4, 49.7, 47.8, 47.7, 43.0, 42.7, 42.6, 42.5, 38.6, 38.5, 27.1, 27.0, 25.8, 25.7, 25.6, 25.0, 24.8, 20.1, 19.9, 19.7, 19.5.

IR $\nu(\text{cm}^{-1})$: 2954, 1741, 1457, 1049, 1024, 964, 770, 702.

HRMS(ESI) m/z : Calcd. for $[\text{C}_{22}\text{H}_{32}\text{NO}_3\text{S}]^+$: 390.2097; Found: 390.2098.

5-phenyldihydrofuran-2(3H)-one (2ag)

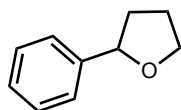


Following GP5, **2ag** was isolated by column chromatography on silica (hexane/EtOAc: 10:1 v/v) as a colorless liquid (19.5 mg, 0.129 mmol, 80% yield). TLC (hexane/EtOAc: 6:1 v/v): $R_f = 0.15$. The NMR spectra match those previously described in literature.¹¹

^1H NMR (400 MHz, CDCl_3): δ 7.43–7.37 (m, 2H), 7.36–7.30 (m, 3H), 5.57–5.46 (m, 1H), 2.72–2.61 (m, 3H), 2.27–2.12 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 177.0, 139.5, 128.9, 128.6, 125.4, 81.3, 31.1, 29.1.

2-phenyltetrahydrofuran (2ah)

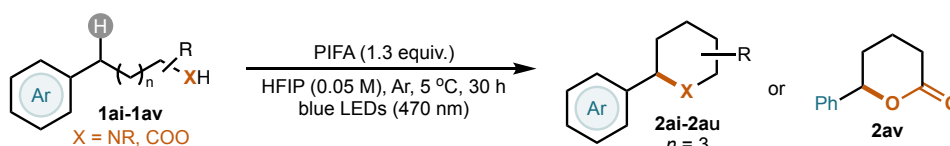


Following GP5, **2ah** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a colorless liquid (8.2 mg, 0.056 mmol, 37% yield). TLC (hexane/EtOAc: 10:1 v/v): R_f = 0.31. The NMR spectra match those previously described in literature.¹¹

¹H NMR (400 MHz, CDCl₃): δ 7.37–7.30 (m, 4H), 7.29–7.23 (m, 1H), 4.90 (t, J = 7.2 Hz, 1H), 4.16–4.06 (m, 1H), 4.00–3.90 (m, 1H), 2.39–2.27 (m, 1H), 2.06–1.96 (m, 2H), 1.87–1.76 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 143.6, 128.4, 127.2, 125.8, 80.8, 68.8, 34.7, 26.2.

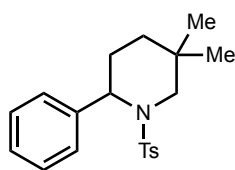
4.5 General procedure (GP6) for 6-membered ring formation



Reactions performed using **set-up 2** in Figure S2. The sulfonamide **1ai-1av** (0.15 mmol, 1.0 equiv.) and PIFA (0.195 mmol, 1.3 equiv.) were added to a reaction vial equipped with a stir bar. Subsequently, this reaction vial was brought into an argon-filled glovebox, 3.0 mL of dry HFIP were added to the mixture, and the reaction vial was sealed with a Teflon-septa equipped cap. The vial was carefully taken outside of the glovebox and subjected to irradiation under stirring at 5 °C for 30 hours. After completion of the reaction, volatiles were evaporated under reduced pressure and the resulting crude product was purified by chromatography (silica gel, hexane/EtOAc) to obtain the pure product **2ai-2av**.

4.6 Characterization of 6-membered ring products

5,5-dimethyl-2-phenyl-1-tosylpiperidine (2ai)

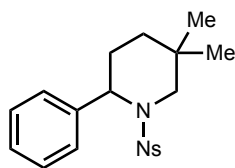


Following GP6, **2ai** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (39.1 mg, 0.116 mmol, 76% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.23. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, J = 8.3 Hz, 2H), 7.28–7.14 (m, 7H), 5.23 (t, J = 4.1 Hz, 1H), 3.42 (d, J = 13.5 Hz, 1H), 2.86 (d, J = 13.5 Hz, 1H), 2.40 (s, 3H), 2.14–2.06 (m, 2H), 1.28–1.20 (m, 2H), 0.80 (s, 3H), 0.79 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 142.9, 139.0, 138.7, 129.5, 128.5, 127.1, 127.0, 126.8, 55.5, 52.7, 32.6, 30.4, 28.7, 25.8, 24.2, 21.6.

5,5-dimethyl-1-((4-nitrophenyl)sulfonyl)-2-phenylpiperidine (2aj)

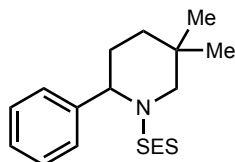


Following GP6, **2aj** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (41.2 mg, 0.110 mmol, 73% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.18. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.24–7.14 (m, 3H), 7.12–7.03 (m, 2H), 5.24 (t, J = 4.4 Hz, 1H), 3.47 (d, J = 13.3 Hz, 1H), 2.94 (d, J = 13.3 Hz, 1H), 2.14–2.05 (m, 2H), 1.34–1.21 (m, 2H), 0.85 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 149.6, 147.0, 138.5, 128.7, 128.2, 127.3, 126.9, 124.1, 56.2, 53.2, 32.4, 30.6, 28.6, 26.2, 24.4.

5,5-dimethyl-2-phenyl-1-((2-(trimethylsilyl)ethyl)sulfonyl)piperidine (2ak)

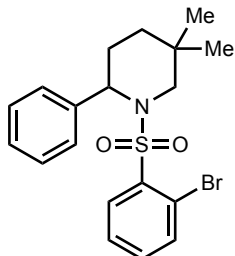


Following GP6, **2ak** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a yellow oil (24.8 mg, 0.070 mmol, 47% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.25. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 7.41–7.33 (m, 4H), 7.30–7.23 (m, 1H), 5.08 (dd, J = 5.8, 3.0 Hz, 1H), 3.38 (d, J = 13.5 Hz, 1H), 3.00 (d, J = 13.5 Hz, 1H), 2.84–2.73 (m, 2H), 2.28–2.17 (m, 1H), 2.14–2.06 (m, 1H), 1.40–1.29 (m, 2H), 1.10 (s, 3H), 1.07–1.00 (m, 1H), 1.00–0.92 (m, 1H), 0.87 (s, 3H), -0.03 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ 139.9, 128.8, 127.2, 127.1, 55.8, 53.2, 49.7, 32.8, 30.6, 28.8, 26.4, 24.4, 10.6, -1.9.

1-((2-bromophenyl)sulfonyl)-5,5-dimethyl-2-phenylpiperidine (2al)



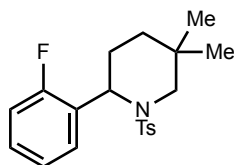
Following GP6, **2al** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (44.2 mg, 0.108 mmol, 72% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.23. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 8.10 (dd, J = 7.6, 2.1 Hz, 1H), 7.72 (dd, J = 7.3, 1.8 Hz, 1H), 7.39–7.27 (m, 6H), 7.22–7.15 (m, 1H), 5.31 (dd, J = 5.5, 2.9 Hz, 1H), 3.30 (d, J = 13.6 Hz,

1H), 3.01 (d, $J = 13.5$ Hz, 1H), 2.44–2.30 (m, 1H), 2.23–2.13 (m, 1H), 1.33–1.20 (m, 2H), 0.79 (s, 3H), 0.74 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 139.9, 139.1, 135.5, 133.3, 132.4, 128.7, 127.6, 127.0, 126.9, 120.5, 56.4, 53.4, 32.8, 30.7, 28.7, 25.6, 23.9.

2-(2-fluorophenyl)-4,4-dimethyl-1-tosylpiperidine (2am)



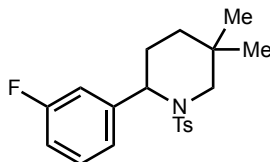
Following GP6, **2am** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a yellow oil (14.6 mg, 0.0405 mmol, 27% yield). TLC (hexane/EtOAc: 19:1 v/v): $R_f = 0.21$. The NMR spectra match those previously described in literature.⁷

^1H NMR (400 MHz, CDCl_3): δ 7.52 (d, $J = 8.3$ Hz, 2H), 7.20–7.12 (m, 3H), 7.11–7.04 (m, 1H), 7.00–6.82 (m, 2H), 5.25 (t, $J = 5.1$ Hz, 1H), 3.37 (d, $J = 13.0$ Hz, 1H), 3.17 (d, $J = 12.9$ Hz, 1H), 2.37 (s, 3H), 2.09–1.91 (m, 2H), 1.30–1.17 (m, 2H), 0.94 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 160.0 (d, $J = 246.2$ Hz), 142.9, 137.6, 129.4, 129.1 (d, $J = 4.2$ Hz), 128.6 (d, $J = 8.5$ Hz), 128.1 (d, $J = 12.6$ Hz), 127.2, 123.7 (d, $J = 3.5$ Hz), 115.8 (d, $J = 22.7$ Hz), 54.4, 52.2, 33.3, 30.5, 28.2, 27.3 (d, $J = 3.9$ Hz), 24.9, 21.6.

^{19}F NMR (375 MHz, CDCl_3): δ -115.06–115.31 (m, 1F).

2-(3-fluorophenyl)-4,4-dimethyl-1-tosylpiperidine (2an)



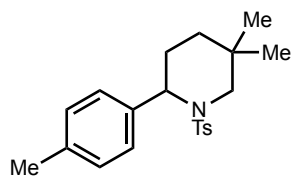
Following GP6, **2an** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a yellow oil (14.9 mg, 0.0412 mmol, 29% yield). TLC (hexane/EtOAc: 19:1 v/v): $R_f = 0.21$. The NMR spectra match those previously described in literature.⁷

^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J = 8.3$ Hz, 2H), 7.28–7.16 (m, 3H), 6.97–6.93 (m, 1H), 6.91–6.84 (m, 1H), 6.83–6.74 (m, 1H), 5.21 (t, $J = 4.0$ Hz, 1H), 3.42 (d, $J = 13.5$ Hz, 1H), 2.82 (d, $J = 13.5$ Hz, 1H), 2.40 (s, 3H), 2.13–2.00 (m, 2H), 1.27–1.15 (m, 2H), 0.80 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 163.2 (d, $J = 245.5$ Hz), 143.2, 142.0 (d, $J = 6.4$ Hz), 138.5, 130.1 (d, $J = 8.1$ Hz), 129.6, 127.1, 122.7 (d, $J = 2.7$ Hz), 114.2 (d, $J = 22.6$ Hz), 113.8 (d, $J = 21.0$ Hz), 55.1 (d, $J = 1.8$ Hz), 52.7, 32.6, 30.4, 28.8, 25.9, 24.1, 21.6.

^{19}F NMR (375 MHz, CDCl_3): δ -110.97–117.19 (m, 1F).

4,4-dimethyl-2-(p-tolyl)-1-tosylpiperidine (**2ao**)

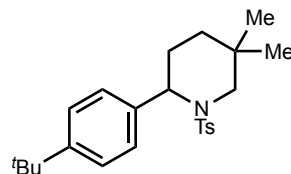


Following GP6, **2ao** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (37.3 mg, 0.104 mmol, 70% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.25. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.04 (m, 4H), 5.19 (t, J = 4.0 Hz, 1H), 3.39 (d, J = 13.5 Hz, 1H), 2.85 (d, J = 13.5 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.15–1.98 (m, 2H), 1.32–1.15 (m, 2H), 0.80 (s, 3H), 0.79 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 142.8, 138.7, 136.4, 135.9, 129.5, 129.2, 127.1, 127.0, 55.3, 52.6, 32.6, 30.5, 28.7, 25.8, 24.2, 21.6, 21.0.

2-(4-(tert-butyl)phenyl)-4,4-dimethyl-1-tosylpiperidine (**2ap**)

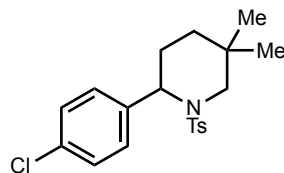


Following GP6, **2ap** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a pale yellow oil (46.7 mg, 0.117 mmol, 78% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.27. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 5.18 (t, J = 4.2 Hz, 1H), 3.40 (d, J = 13.4 Hz, 1H), 2.88 (d, J = 13.4 Hz, 1H), 2.39 (s, 3H), 2.11–2.02 (m, 2H), 1.29 (s, 9H), 1.38–1.17 (m, 2H), 0.81 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 149.7, 142.7, 138.7, 136.1, 129.4, 127.2, 126.8, 125.4, 55.4, 52.7, 34.5, 32.7, 31.5, 30.5, 28.8, 25.9, 24.3, 21.6.

2-(4-chlorophenyl)-4,4-dimethyl-1-tosylpiperidine (**2aq**)

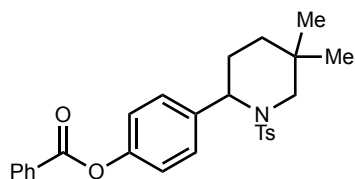


Following GP6, **2aq** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a yellow solid (45.3 mg, 0.120 mmol, 80% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.24. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 7.64 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 5.17 (t, J = 4.0 Hz, 1H), 3.39 (d, J = 13.4 Hz, 1H), 2.80 (d, J = 13.5 Hz, 1H), 2.41 (s, 3H), 2.11–1.99 (m, 2H), 1.25–1.15 (m, 2H), 0.79 (s, 3H), 0.77 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 143.1, 138.5, 137.6, 132.8, 129.6, 128.7, 128.6, 127.1, 55.1, 52.7, 32.6, 30.5, 28.7, 25.8, 24.2, 21.6.

4-(5,5-dimethyl-1-tosylpiperidin-2-yl)phenyl benzoate (**2ar**)

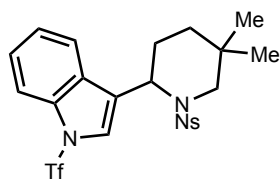


Following GP6, **2ar** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (43.1 mg, 0.093 mmol, 62% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.17. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 8.19 (dd, J = 8.5, 1.4 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 5.24 (t, J = 4.2 Hz, 1H), 3.43 (d, J = 13.6 Hz, 1H), 2.86 (d, J = 13.5 Hz, 1H), 2.41 (s, 3H), 2.16–2.07 (m, 2H), 1.31–1.19 (m, 2H), 0.82 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 165.2, 149.8, 143.0, 138.6, 136.7, 133.8, 130.3, 129.6, 129.6, 128.7, 128.2, 127.1, 121.7, 55.1, 52.6, 32.6, 30.5, 28.7, 25.8, 24.2, 21.6.

3-(5,5-dimethyl-1-((4-nitrophenyl)sulfonyl)piperidin-2-yl)-1-((trifluoromethyl)sulfonyl)-1H-indole (**2as**)



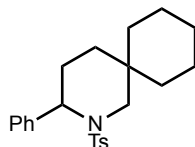
Following GP6, **2as** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a pale yellow oil (25.4 mg, 0.046 mmol, 31% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.19. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, J = 8.7 Hz, 2H), 7.83 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 7.2 Hz, 1H), 7.50–7.35 (m, 2H), 6.74 (s, 1H), 5.55 (d, J = 4.2 Hz, 1H), 3.56 (d, J = 12.7 Hz, 1H), 2.97 (d, J = 12.8 Hz, 1H), 2.32–2.18 (m, 1H), 2.06–1.97 (m, 1H), 1.42–1.27 (m, 2H), 1.04 (s, 3H), 0.99 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 150.0, 146.0, 135.2, 129.4, 128.1, 126.7, 125.2, 124.1, 123.0, 122.9, 120.5, 119.5 (q, J = 320.8 Hz), 114.1, 53.5, 49.4, 32.5, 30.7, 28.8, 26.2, 23.7.

¹⁹F NMR (375 MHz, CDCl₃): δ -75.05 (s, 3F).

3-phenyl-2-tosyl-2-azaspiro[5.5]undecane (**2at**)



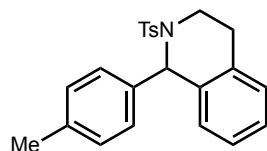
Following GP6, **2at** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a yellow oil (39.1 mg, 0.102 mmol, 68% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f =

0.19. The NMR spectra match those previously described in literature.⁷

¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, J = 8.3 Hz, 2H), 7.25–7.12 (m, 7H), 5.21 (t, J = 4.3 Hz, 1H), 3.73 (d, J = 13.2 Hz, 1H), 2.78 (d, J = 13.6 Hz, 1H), 2.39 (s, 3H), 2.09–1.99 (m, 2H), 1.43–1.24 (m, 8H), 1.21–1.02 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): δ 142.8, 139.2, 138.7, 129.5, 128.5, 127.2, 127.1, 126.8, 56.1, 50.3, 38.0, 32.7, 32.0, 30.9, 26.6, 25.1, 21.7, 21.6, 21.5.

1-(p-tolyl)-2-tosyl-1,2,3,4-tetrahydroisoquinoline (2au)

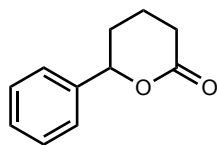


Following GP6, **2au** was isolated by column chromatography on silica (hexane/EtOAc: 20:1 v/v) as a white solid (44.8 mg, 0.119 mmol, 79% yield). TLC (hexane/EtOAc: 19:1 v/v): R_f = 0.19. The NMR spectra match those previously described in literature.¹²

¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, J = 8.3 Hz, 2H), 7.15–7.10 (m, 2H), 7.10–7.05 (m, 6H), 7.01–6.94 (m, 2H), 6.20 (s, 1H), 3.80–3.71 (m, 1H), 3.38–3.24 (m, 1H), 2.73–2.61 (m, 1H), 2.60–2.51 (m, 1H), 2.32 (s, 3H), 2.31 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 143.1, 138.8, 137.9, 137.5, 134.4, 133.9, 129.4, 129.1, 129.0, 128.8, 128.5, 127.2, 127.1, 126.2, 59.1, 39.1, 26.8, 21.6, 21.2.

6-phenyltetrahydro-2H-pyran-2-one (2av)



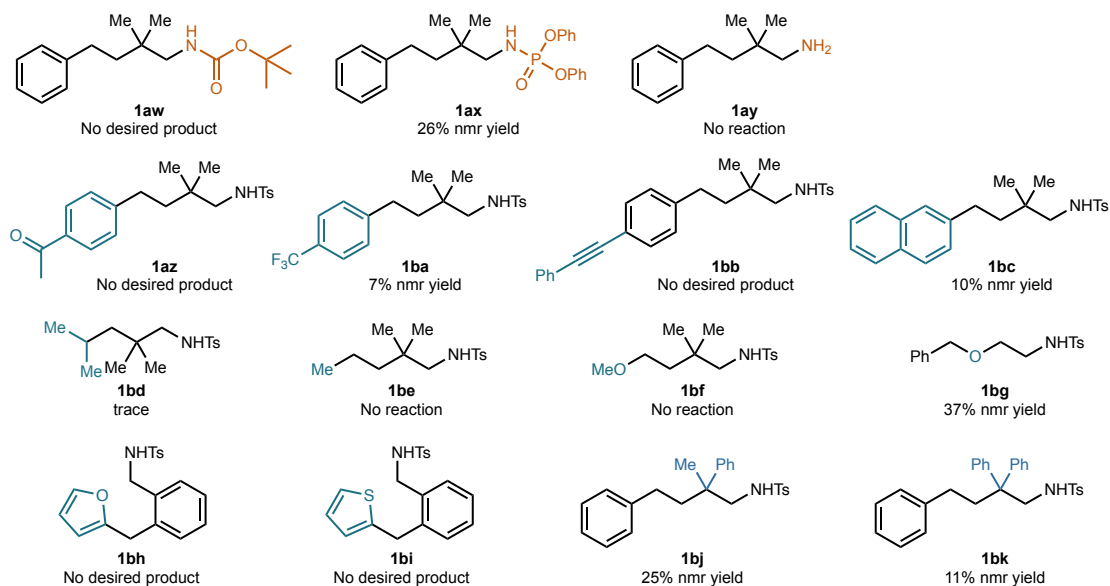
Following GP6, **2av** was isolated by column chromatography on silica (hexane/EtOAc: 8:1 v/v) as a yellow liquid (19.0 mg, 0.108 mmol, 72% yield). TLC (hexane/EtOAc: 6:1 v/v): R_f = 0.15. The NMR spectra match those previously described in literature.¹³

¹H NMR (400 MHz, CDCl₃): δ 7.42–7.29 (m, 5H), 5.36 (dd, J = 10.4, 3.4 Hz, 1H), 2.77–2.67 (m, 1H), 2.64–2.51 (m, 1H), 2.22–2.13 (m, 1H), 2.04–1.95 (m, 2H), 1.91–1.82 (m, 1H).

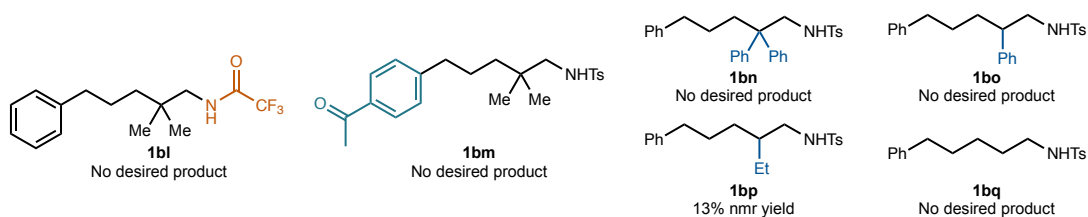
¹³C NMR (100 MHz, CDCl₃): δ 171.5, 139.9, 128.7, 128.4, 125.8, 81.8, 30.7, 29.6, 18.7.

5. Moderately successful and unsuccessful examples

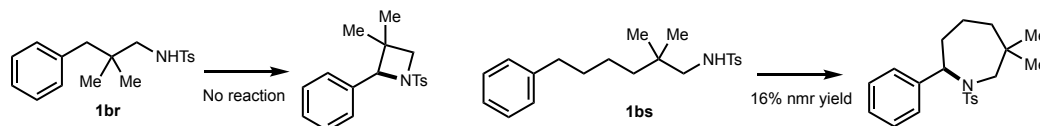
The substrates for 5-membered ring formation



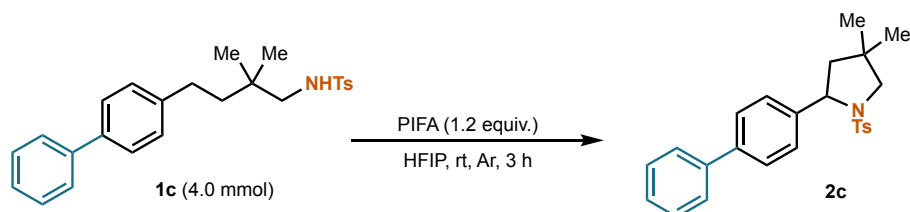
The substrates for 6-membered ring formation



The substrates for 4 or 7-membered ring formation

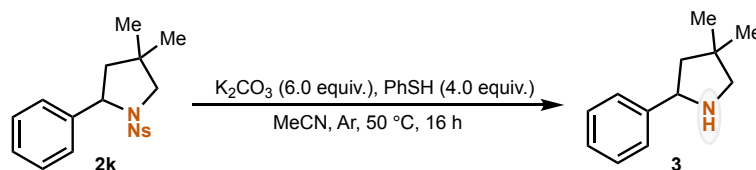


6. Gram-scale synthesis of 2c



In a Schlenk flask equipped with a magnetic stir bar, *N*-(4-([1,1'-biphenyl]-4-yl)-2,2-dimethylbutyl)-4-methylbenzenesulfonamide **1c** (1.63 g, 4.0 mmol) and PIFA (2.06 g, 4.8 mmol) were added. The reaction mixture was connected to a vacuum condenser, and the entire system was purged with an argon atmosphere. Subsequently, 40 mL of HFIP was added to the reaction mixture under an inert atmosphere. The reaction mixture was stirred for 3 hours, and then the solvent was evaporated. The crude product was purified by chromatography using silica gel and a mixture of hexane and EtOAc as the eluent. This purification step afforded product **2c** as a white solid (1.31 g, 81% yield).

7. Deprotection of 2k to free pyrrolidine 3



A flame-dried pressure tube equipped with a magnetic stir bar was charged with compound **2k** (54.0 mg, 0.15 mmol, 1.0 equiv.) and K_2CO_3 (124.4 mg, 0.9 mmol, 6.0 equiv.). The reaction tube was purged with argon atmosphere, then MeCN (2.5 mL) and PhSH (61 μ L, 0.6 mmol, 4.0 equiv.) was added via syringe. The tube was sealed, and the reaction mixture was stirred at 50 °C for 16 hours. DCM was added and the resulting solution was washed with saturated aqueous solutions of $NaHCO_3$ and extracted with DCM (3 x). The combined organic layers were dried over anhydrous Na_2SO_4 and solvents were evaporated under reduced pressure. The crude product was purified by chromatography (silica gel, hexane/EtOAc: 2/1 v/v) to give the pure product **3** as colorless liquid with a yield of 90% (25.8 mg, 0.135 mmol). TLC (hexane/EtOAc: 4:1 v/v): R_f = 0.21. The NMR spectra match those previously described in literature.¹⁴

1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.35 (m, 2H), 7.34–7.28 (m, 2H), 7.25–7.19 (m, 1H), 4.30 (dd, J = 9.7, 7.1 Hz, 1H), 2.92 (d, J = 10.1 Hz, 1H), 2.80 (d, J = 10.1 Hz, 1H), 2.11 (s, 1H), 1.98 (dd, J = 12.5, 7.1 Hz, 1H), 1.55 (dd, J = 12.5, 9.7 Hz, 1H), 1.15 (s, 3H), 1.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 128.5, 126.8, 126.6, 62.6, 61.4, 50.2, 39.8, 28.7, 28.0.

8. X-Ray crystallography

Crystal preparation: Crystals of compound **2ac** was obtained by slow diffusion of hexane into a saturated dichloromethane solution room temperature. The crystals used for structure determination were selected using a Zeiss stereomicroscope using polarized light and prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

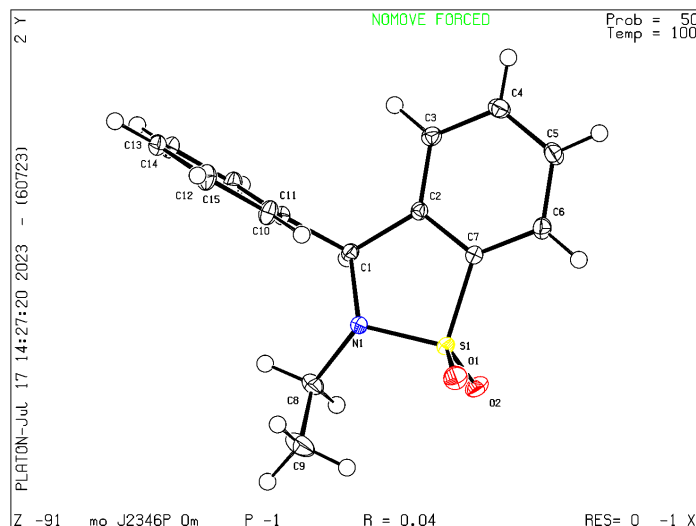


Figure S3. ORTEP drawing (thermal ellipsoids set at 50% probability) of **2ac**

Table S8. Crystal data and structure refinement for **2ac** (CCDC: 2282188)

Identification code	mo_J2346P_0m	
Empirical formula	C ₁₅ H ₁₅ NO ₂ S	
Formula weight	273.34	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.4061(15)Å	a = 107.475(3)°.
	b = 9.3059(16)Å	b = 105.031(3)°.
	c = 10.2652(18)Å.	g = 109.077(3)°.
Volume	664.5(2) Å ³	
Z	2	
Density (calculated)	1.366 Mg/m ³	
Absorption coefficient	0.240 mm ⁻¹	
F(000)	288	
Crystal size	0.500 x 0.500 x 0.400 mm ³	
Theta range for data collection	2.266 to 32.066°.	

Index ranges	-12<=h<=12,-13<=k<=13,-15<=l<=15
Reflections collected	12709
Independent reflections	4521[R(int) = 0.0406]
Completeness to theta =32.066°	97.2%
Absorption correction	Multi-scan
Max. and min. transmission	0.74 and 0.68
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4521/ 0/ 173
Goodness-of-fit on F ²	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0974
R indices (all data)	R1 = 0.0414, wR2 = 0.1012
Largest diff. peak and hole	0.469 and -0.440 e.Å ⁻³

9. Mechanistic experiments

9.1 Absorption spectroscopy analysis (UV-vis)

- *Absorption spectra of the substrates **1a**, PIFA and the mixture*

For the solutions of PIFA: A 10 mL glass vial containing PIFA (25.8 mg, 0.06 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (10 mL) was added via syringe ($6 \cdot 10^{-3}$ M solution). A 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

For the solutions of substrate **1a**: A 10 mL volumetric flask containing substrate **1a** (18.1 mg, 0.05 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (10 mL) was added via syringe ($5 \cdot 10^{-3}$ M solution). 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

For the solution containing a mixture of substrate **1a** and PIFA: following the completion of substrate **1a** measurement, a 10 µL of the 0.3 M PIFA solution was injected into the argon filled quartz cuvette using a Hamilton microliter syringe. The resulting mixture was then thoroughly mixed.

For the solutions of substrate **2a**: A 10 mL volumetric flask containing substrate **2a** (18.0 mg, 0.05 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (10 mL) was added via syringe ($5 \cdot 10^{-3}$ M solution). 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

For the solution containing a mixture of substrate **2a** and PIFA: following the completion of substrate **2a** measurement, a 60 µL of the 0.3 M PIFA solution was injected into the argon filled quartz cuvette using a Hamilton microliter syringe. The resulting mixture was then thoroughly mixed.

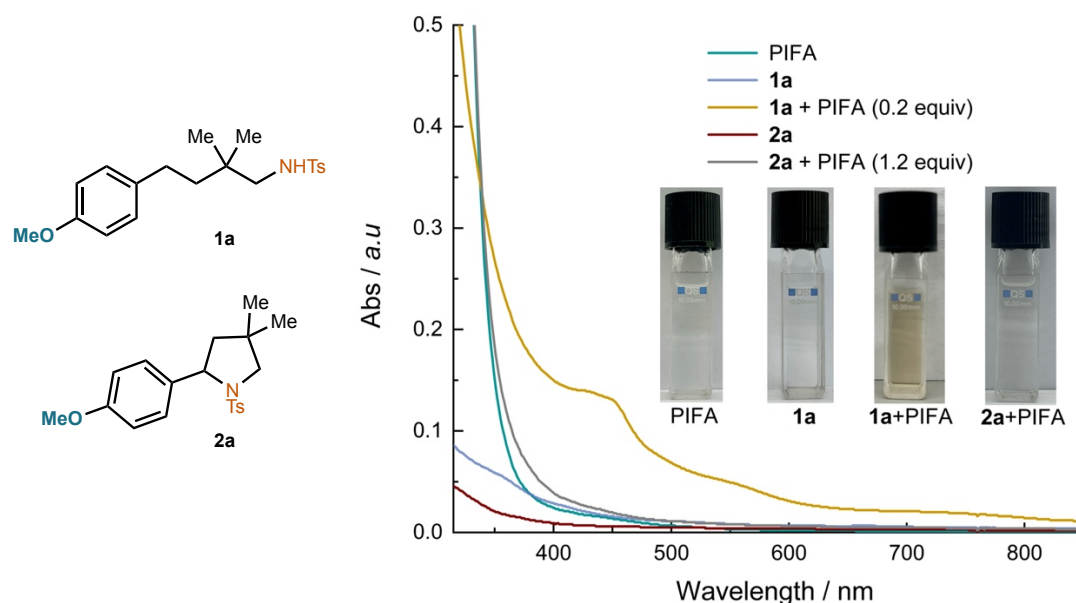


Figure S4: Absorption spectra of the substrates **1a**, product **2a**, PIFA, and the mixtures in HFIP. [**1a**] = $5 \cdot 10^{-3}$ M, [**2a**] = $5 \cdot 10^{-3}$ M, [PIFA] = $6 \cdot 10^{-3}$ M.

- Solvent influence of PIFA absorption spectra*

For the solutions of PIFA: A 5 mL glass vial containing PIFA (86.0 mg, 0.2 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed DCM (5 mL), *i*PrOH (5 mL), MeCN (5 mL), PhCF₃ (5 mL) or HFIP (5 mL) was added via syringe ($4 \cdot 10^{-2}$ M solution). 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

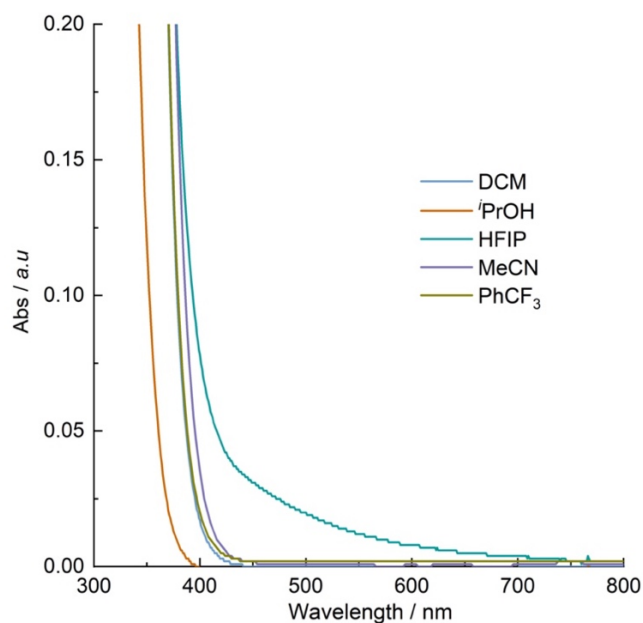


Figure S5: Absorption spectra of PIFA in DCM, *i*PrOH, MeCN, PhCF₃, and HFIP. [PIFA] = $4 \cdot 10^{-2}$ M.

- *Absorption spectra of the substrates **1j**, PIFA and the mixture*

For the solutions of PIFA: A 5 mL glass vial containing PIFA (86.0 mg, 0.2 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (5 mL) was added via syringe ($4 \cdot 10^{-2}$ M solution). A 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

For the solutions of substrate **1j**: A 5 mL volumetric flask containing substrate **1j** (55.2 mg, 0.16 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (5 mL) was added via syringe ($3.3 \cdot 10^{-2}$ M solution). 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

For the solutions of the mixture of **1j** and PIFA: A 5 mL glass vial containing substrate **1j** (55.2 mg, 0.16 mmol) and PIFA (86.0 mg, 0.2 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (5 mL) was added via syringe ($6 \cdot 10^{-3}$ M solution). The resulting mixture was then thoroughly mixed. 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

For the solutions of substrate **2j**: A 5 mL volumetric flask containing substrate **2j** (52.7 mg, 0.16 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (5 mL) was added via syringe ($3.3 \cdot 10^{-2}$ M solution). 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

For the solutions of the mixture of **2j** and PIFA: A 5 mL glass vial containing substrate **2j** (52.7 mg, 0.16 mmol) and PIFA (86.0 mg, 0.2 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (5 mL) was added via syringe ($6 \cdot 10^{-3}$ M solution). The resulting mixture was then thoroughly mixed. 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

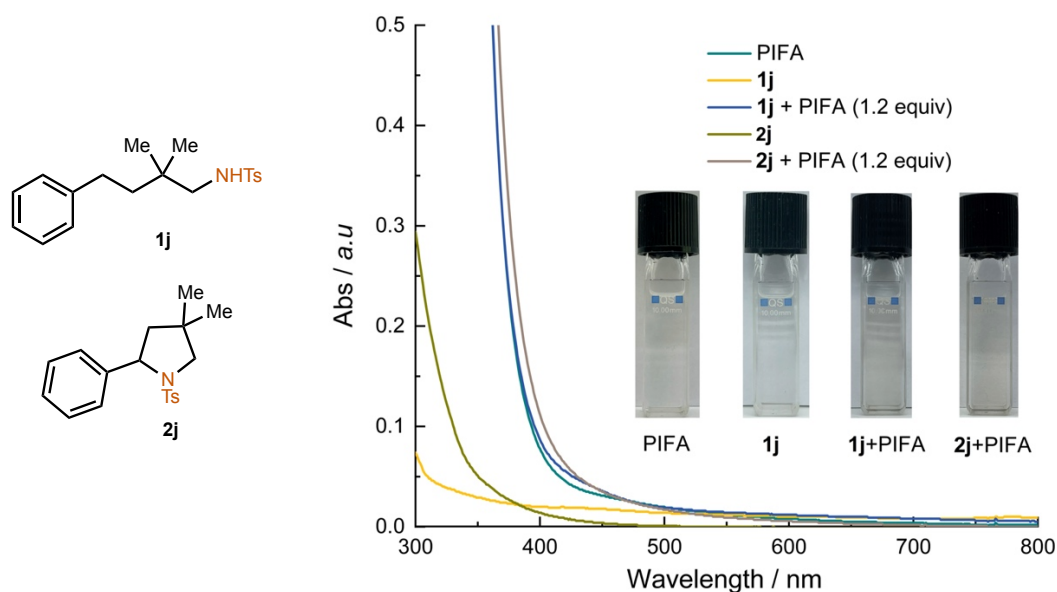


Figure S6: Absorption spectra of the substrates **1j**, product **2j**, PIFA, and the mixtures in HFIP. $[1j] = 3.3 \cdot 10^{-2}$ M, $[2j] = 3.3 \cdot 10^{-2}$ M, $[PIFA] = 4 \cdot 10^{-2}$ M.

- Absorption spectra evolution of the mixture of **1j** and PIFA upon irradiation*

A 3 mL glass vial containing substrate **1j** (33.1 mg, 0.1 mmol) and PIFA (51.6 mg, 0.12 mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (3 mL) was added via syringe ($6 \cdot 10^{-3}$ M solution). The resulting mixture was then thoroughly mixed. Subsequently, 3 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a stirring bar and a septum. The cuvette was then subjected to irradiation using **set-up 1** in Figure S1 and the absorption spectra were recorded over time.

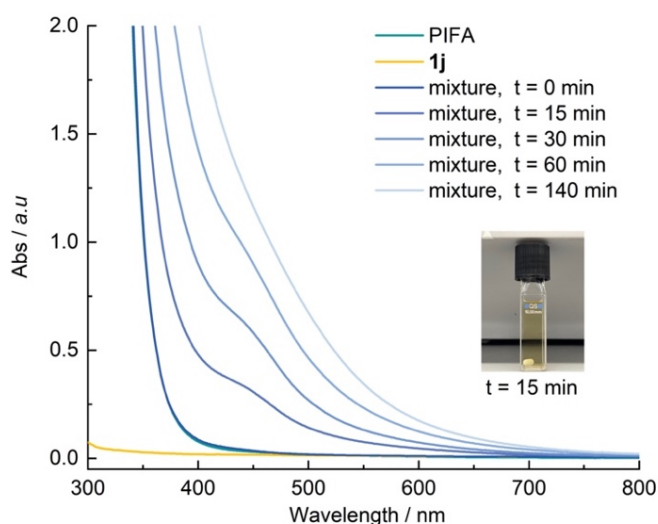


Figure S7: Absorption spectra of the substrates **1j**, PIFA, and the mixture of **1j** and PIFA (1.2 equiv.) upon irradiation in HFIP. $[1j] = 3 \cdot 10^{-2}$ M, $[PIFA] = 4 \cdot 10^{-2}$ M. The cuvette was irradiated at 465 nm and the absorption spectra were recorded over time.

- *Absorption spectra of PIFA in HFIP with low concentration.*

A 5 mL glass vial containing PIFA (2.1 mg, $5 \cdot 10^{-3}$ mmol) was sealed with a rubber plug, vacuumed and backfilled with argon for 3 times, then degassed HFIP (5 mL) was added via syringe. A 0.1 mL of the solution was transferred into an argon filled quartz cuvette (10 x 10 mm light path) equipped with a septum and degassed HFIP (2.9 mL) was added via syringe ($3.3 \cdot 10^{-5}$ M solution).

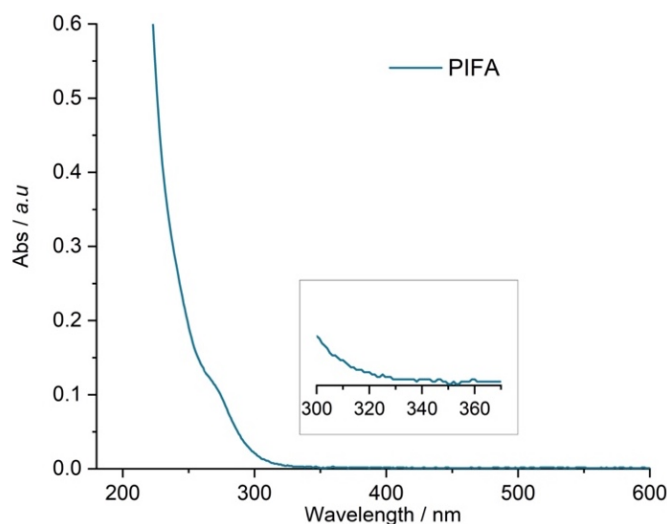
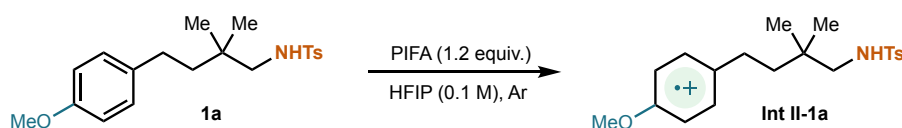


Figure S8: Absorption spectra of PIFA in HFIP. [PIFA] = $3.3 \cdot 10^{-5}$ M

9.2 Electron paramagnetic resonance (EPR) experiments

To gain further understanding of the mechanism, electron paramagnetic resonance (EPR) experiments were conducted (Figure S9). A single clean signal at 3516.3 G was observed with a g -value of 2.0028, which provided conclusive evidence for the existence of radicals. Interestingly, the peak shape and g -value of the observed signal differed from the nitrogen radical signal previously reported in the literature.¹⁵ The result suggests that the experimental mechanism likely involves a radical cation **Int-II-1a**.^{16,17}



In two reaction vials were added respectively the sulfonamide **1a** (18.08 mg, 0.05 mmol, 1.0 equiv.) in the first, and PIFA (25.80 mg, 0.06 mmol, 1.2 equiv.) in the second. The reaction vials were then brought into an argon-filled glovebox, and dry HFIP (0.5 mL) followed by PIFA was added to the first vial. Immediately the stock solution was transferred to the capillary via a Hamilton 100 μ L syringe, and then placed the capillary in the EPR tube. The spectral data was collected at 298 K with the following spectrometer settings: g -factor = 1.999000, microwave power = 2.066 mW; center field = 3510.25 G, sweep width = 200.0 G, sweep time = 30.00 s, modulation frequency = 100.00 KHz, modulation amplitude = 1.00 G, power attenuation = 20.00 dB, time constant = 0.01 ms, conversion time = 15.00 ms, gain = 30.00 dB.

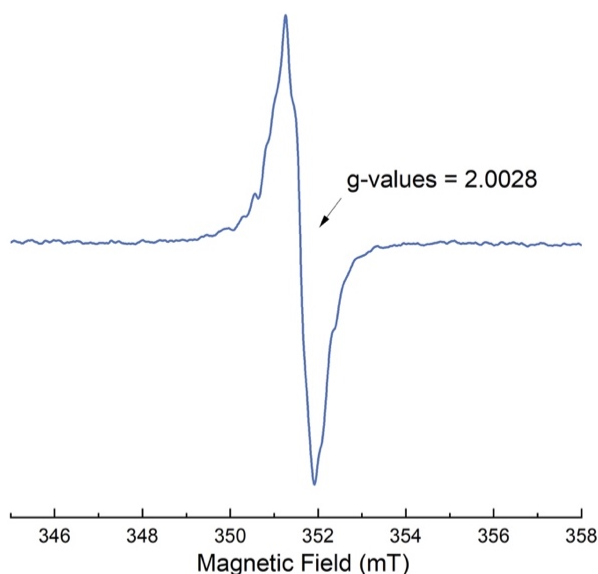


Figure S9: EPR experiment of sulfonamide **1a** (g-factor 2.0028)

9.3 Cyclic voltammetry studies (CV)

For all cyclic voltammetry (CV) measurements of sulfonamide substrate **1a**, **1c**, **1i**, **1j** and **1v** were performed in a 3-electrode cell set up consisting of a glassy carbon disk (0.07 cm² of surface area) as working electrode and platinum as a counter electrode and SCE (Saturated Calomel Electrode) as the reference electrode. The electrodes were previously polished with diamond abrasive slurries (DIAPAT-M, 39-321-M, Netkon) in an order of 3 μ m and 1 μ m diameter particle-based slurries (2 minutes in each). Synthetic nap based polishing pads (METAPO-B, polishing cloth, self-adhesive back, diamond 3-1 μ m, Netkon) were used for diamond polishing.

The substrates were measured at concentration of 3 mM in HFIP with TBAPF₆ (0.1 M) as electrolyte at the scan rate is 100 mV/s with Fc/Fc⁺ as a reference.

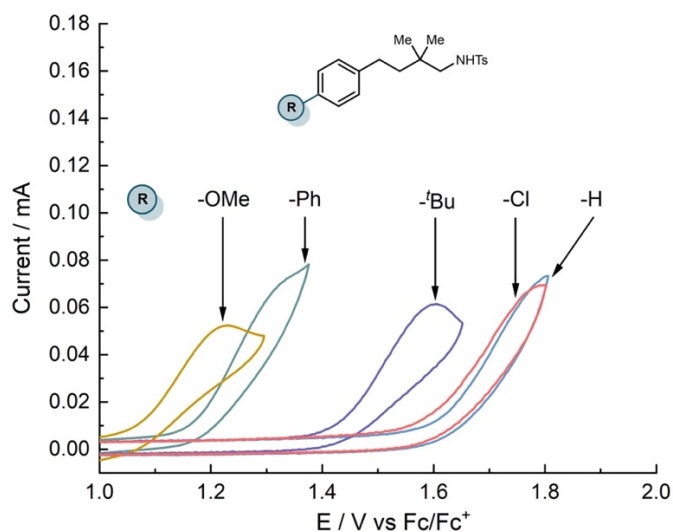
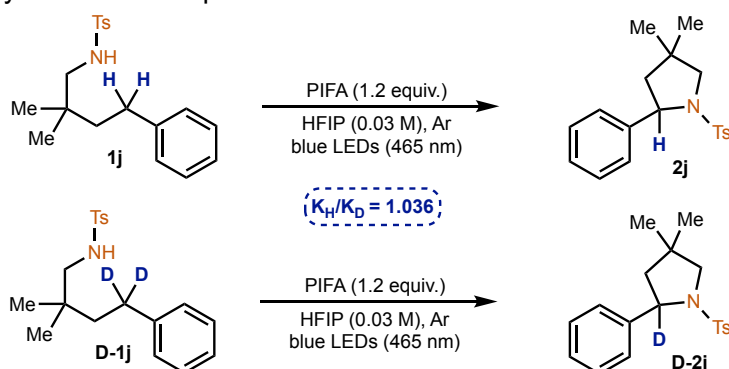


Figure S10. Cyclic voltammetry of **1a** (yellow line), **1c** (green line), **1i** (purple line), **1j** (blue line) and **1v** (red line).

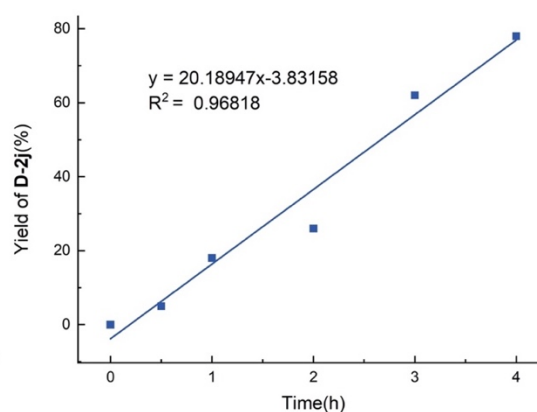
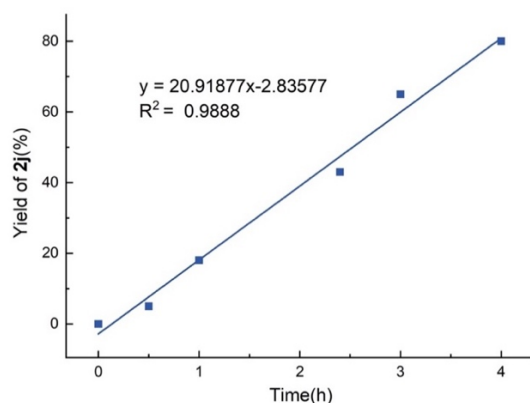
9.4 Kinetic isotope effect (KIE) studies

Reactions performed using **set-up 1** in Figure S1. In the reaction vials with previously placed stir bars were charged **1j** (16.6 mg, 0.05 mmol, 1.0 equiv.) or **D-1j** (16.7 mg, 0.05 mmol, 1.0 equiv.), PIFA (25.8 mg, 0.06 mmol, 1.2 equiv.). The reaction vials were then brought into an argon-filled glovebox. Inside the glovebox, 1.5 mL of dry HFIP were added to the mixture, and the reaction vials were sealed with a Teflon-septa equipped cap. The vials were carefully taken outside of the glovebox and subjected to irradiation under stirring for different time. After completion of the reaction, volatiles were evaporated under reduced pressure, and the yield of **2j** and **D-2j** were determined by crude ^1H NMR using mesitylene as internal standard to determine the intermolecular KIE value. The KIE value of the C–H activation process was 1.036, suggesting that the C–H cleavage is not involved in the rate-determining step.

Table S9. Study of kinetic isotope effect.



Time (h)	2j yield (%)	D-2j yield (%)
0	0	0
0.5	5	5
1	18	18
2		26
2.4	43	
3	65	62
4	80	78



9.5 Emission spectrum and Stern-Volmer quenching studies

– Emission spectrum of [PIFA]*

The emission spectra were recorded in a Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with a photomultiplier detector, a double monochromator, and a 350W xenon light source. In the glovebox, 3 mL of a 0.033 mM solution of PIFA in degassed HFIP were placed in a 10 x10 mm light path quartz fluorescence cuvette equipped with Silicone/PTFE 3.2 mm septum under an argon atmosphere. The excitation wavelength was fixed at 332 nm (incident light slit regulated to 5 mm), while the emission light was acquired from 342 nm to 549 nm (emission light slit regulated to 5 mm).

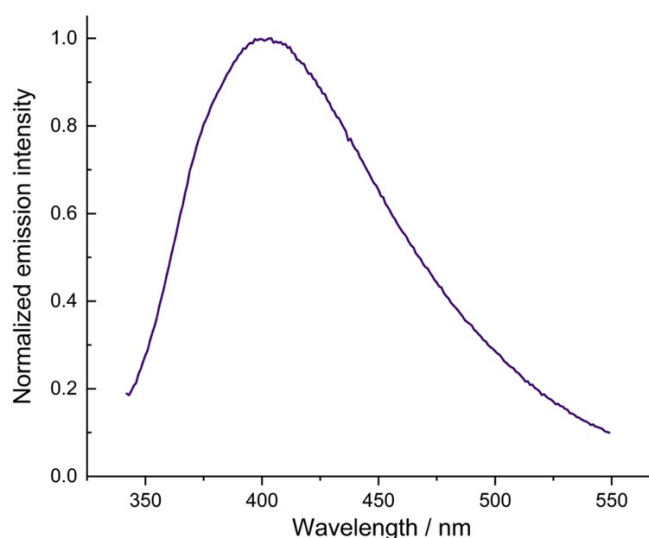


Figure S11. Emission spectrum of [PIFA]* upon 332 nm irradiation in HFIP.

– Stern-Volmer Quenching Studies using **1j** as the quencher

In the glovebox, a solution of sulfonamide **1j** in HFIP was prepared with a concentration of 1.6 mM. This stock solution, 12 μ L were added to the solution of PIFA, prepared as described above. The addition of this solution of **1j** was repeated five consecutive times. After each addition, an absorption spectrum and an emission spectrum of the solution were recorded. The excitation wavelength was fixed at 332 nm (incident light slit regulated to 5 mm); the emission light was acquired from 342 nm to 549 nm (emission light slit regulated to 5 mm). The excitation wavelength was chosen in order to avoid saturation of the emission detector. The results, showed in Figure S12, clearly demonstrate that sulfonamide **1j** effectively quenches the excited state of PIFA and its emission.

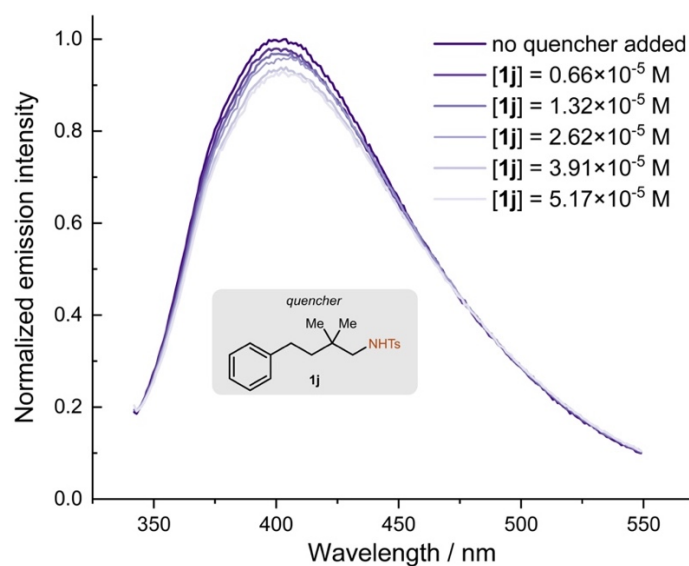


Figure S12. Quenching of the emission of [PIFA]* (0.033 mM in HFIP) in the presence of increasing amounts of **1j**.

The Stern-Volmer plot, reported in Figure S13, shows a linear correlation between the amounts of **1j** and the ratio I^0/I . Based on the following Equation 1, it is possible to calculate the Stern-Volmer constant K_{SV} .¹⁸

$$I^0/I = 1 + K_{SV}[Q] \quad [\text{Eq. 1}]$$

We calculated a Stern-Volmer quenching constant of **1595 M⁻¹**.

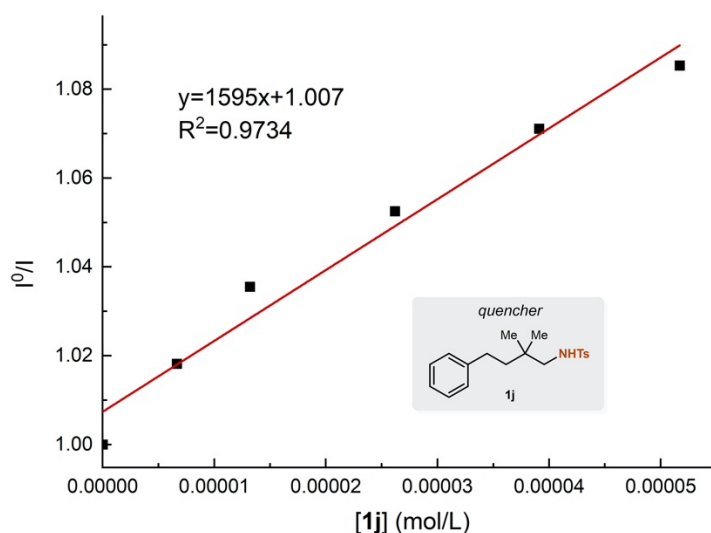


Figure S13. Stern-Volmer quenching plot using **1j** as a quencher.

9.6 Evaluation of the excited-state potential of [PIFA]*

Using the data from the absorption spectra (Figure S8) of **PIFA** and the cyclic voltammetry (CV) studies those previously described in literature¹⁹, the oxidation potential relative to its excited state [PIFA]* could be estimated, by means of the following Equation 2²⁰:

$$E(\text{PIFA}^{\bullet-}/[\text{PIFA}]^*) = E(\text{PIFA}^{\bullet-}/\text{PIFA}) + E_{0-0}([\text{PIFA}]^*)/\text{PIFA} \quad [\text{Eq. 2}]$$

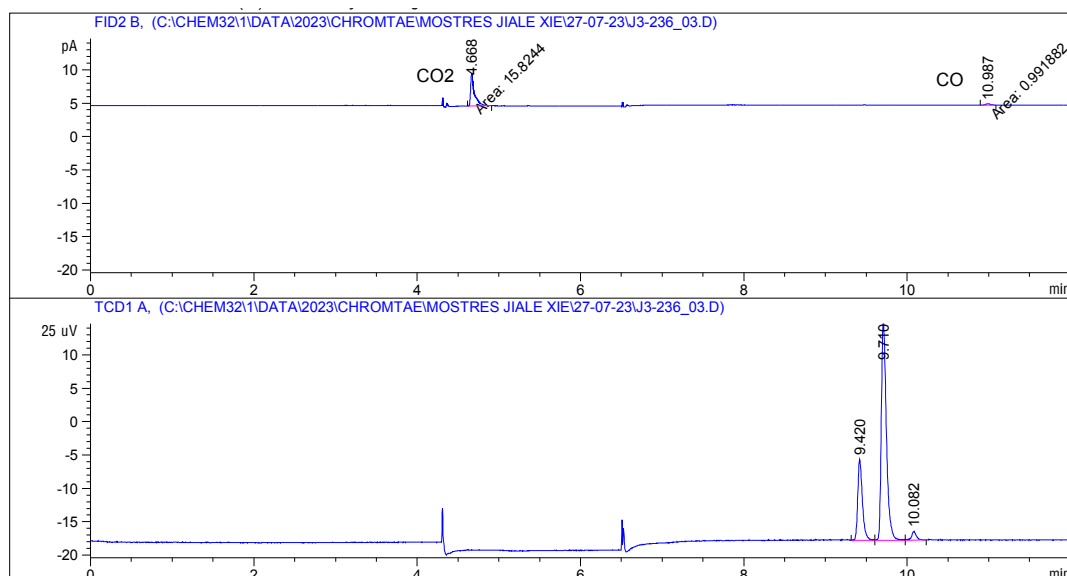
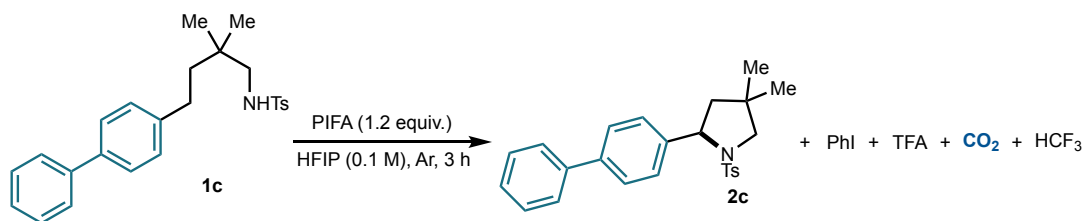
$E(\text{PIFA}^{\bullet-}/\text{PIFA})$ was provided by the reported cyclic voltammetry (CV) studies¹⁹, is -0.45 V vs. Fc/Fc^+ in HFIP. $E_{0-0}([\text{PIFA}]^*)/\text{PIFA}$, which is the excited state energy of **PIFA**, was estimated spectroscopically from the position of the long wavelength tail of the absorption spectrum recorded in degassed HFIP (354 nm, Figure S8), which translates into an $E_{0-0}([\text{PIFA}]^*)/\text{PIFA}$ of 3.54 eV.

$$E(\text{PIFA}^{\bullet-}/[\text{PIFA}]^*) = -0.45 + 3.54 = 3.09\text{ V (vs Fc/ Fc}^+)$$

9.7 Detection of CO_2

(1) Protocol without light irradiation

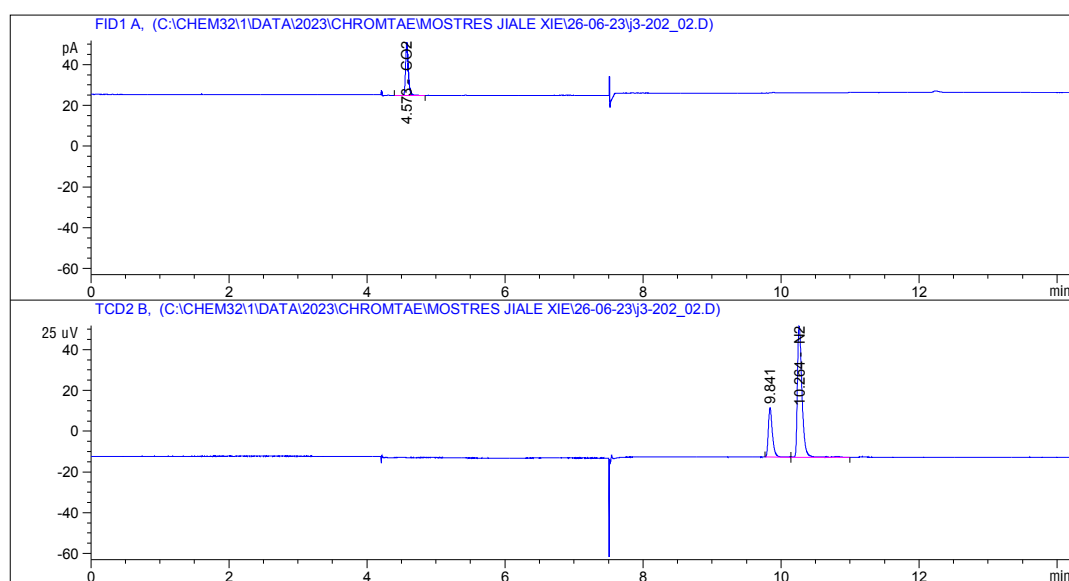
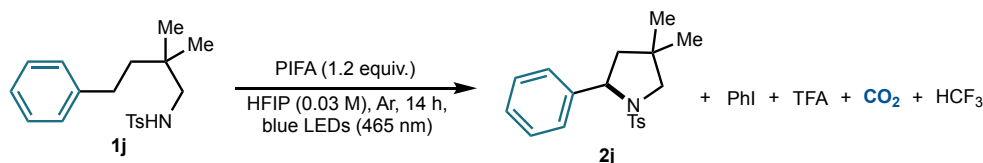
The sulfonamide **1c** (20.4 mg, 0.05 mmol, 1.0 equiv.) and PIFA (25.8 mg, 0.06 mmol, 1.2 equiv.) were added to a reaction vial equipped with a stir bar. This reaction vial was then brought into an argon-filled glovebox. Inside the glovebox, the reaction vial was sealed with a cap equipped with a Teflon-septa and 0.5 mL of dry HFIP were added. The sealed vial was removed from the glovebox and stirred at room temperature. After 3 hours, a gas sample was taken from the head space of the sealed reaction vial via a syringe with valve for GC-FID-TCD analysis. (Column: Gas carrier: Ar; Flux: 8 mL/min; T injector: 200 °C; Mode: Split (ratio 1:3); T oven: 50 °C for 5 min, 50-80 °C at 25 °C /min, 80 °C for 8 min; T detector FID: 250 °C; T detector TCD: 200 °C).



(2) Protocol under light irradiation

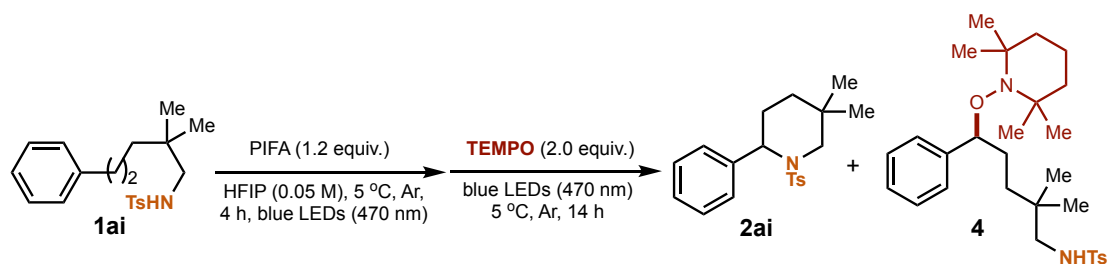
The sulfonamide **1j** (16.6 mg, 0.05 mmol, 1.0 equiv.) and PIFA (25.8 mg, 0.06 mmol, 1.2 equiv.) were added to a reaction vial equipped with a stir bar. This reaction vial was then brought into an argon-filled glovebox. Inside the glovebox, 1.5 mL of dry HFIP were added

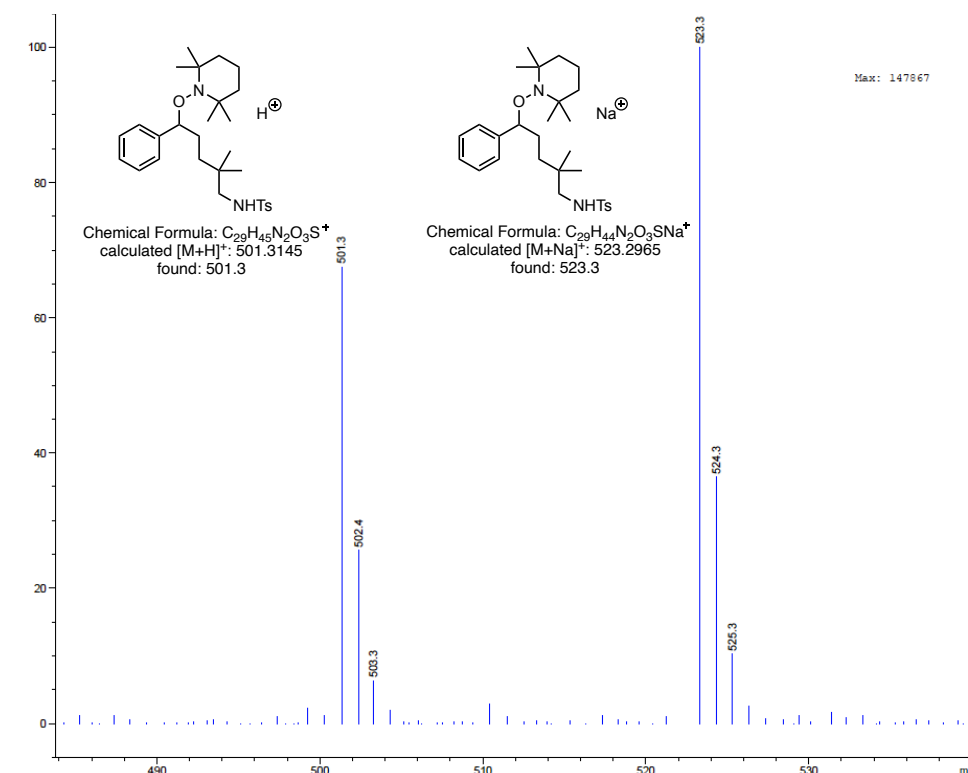
to the mixture, and the reaction vial was sealed with a cap equipped with a Teflon-septa. The sealed vial was removed from the glovebox and stirred at room temperature. After 14 hours, a gas sample was taken from the head space of the sealed reaction vial via a syringe with valve for GC-FID-TCD analysis. (Column: Gas carrier: Ar; Flux: 8 mL/min; T injector: 200 °C; Mode: Split (ratio 1:3); T oven: 50 °C for 5 min, 50-80 °C at 25 °C /min, 80 °C for 8 min; T detector FID: 250 °C; T detector TCD: 200 °C).



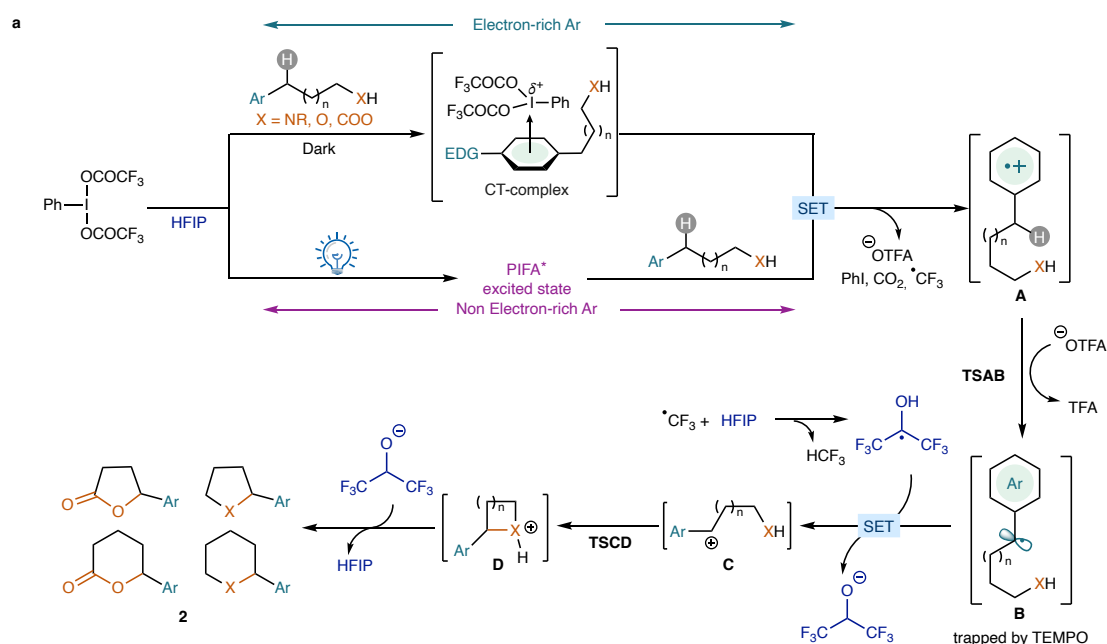
9.8 Detection of TEMPO-adduct 4

The sulfonamide **1ai** (17.3 mg, 0.05 mmol, 1.0 equiv.) and PIFA (27.9 mg, 0.06 mmol, 1.2 equiv.) were added to a reaction vial equipped with a stirrer. This reaction vial was then brought into an argon-filled glovebox. Inside the glovebox, 1.0 mL of dry HFIP were added to the mixture, and the reaction vial was sealed with a cap equipped with a Teflon-septa. The sealed vial was removed from the glovebox and stirred at 5 °C under irradiation. After 4 hours, the reaction was taken into the glovebox and TEMPO (15.6 mg, 0.1 mmol, 2.0 equiv.) was added. The vial was sealed and removed from the glovebox and stirred at 5 °C under irradiation for another 14 hours. Then the sample was injected to HPLC-MS analysis (Column: Sunfire-C18 100*4.6 mm, 5μm; H₂O/MeOH 1:1, 50% MeOH up to 100% in 10', hold 5'; 1 mL/min; ESI +/-). TEMPO-adduct **4** was detected indicate that the benzylic radical was involve in the reaction.





9.9 Proposed mechanisms



Scheme S1: Proposed mechanism of HFIP-assisted intramolecular C(sp³)-H functionalization.

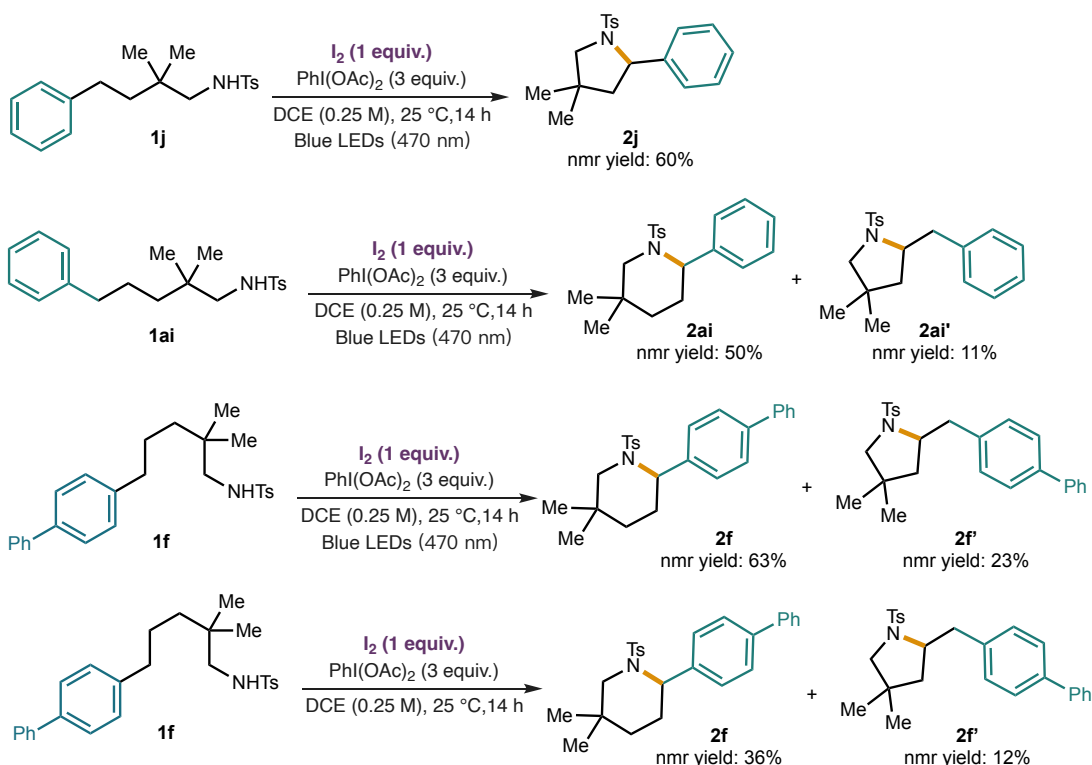
The reaction commences with the substrate undergoing a SET process with PIFA, resulting in the formation of the aromatic radical cation **A**. In the case of the electron-rich substrate, **A** is formed through an intracomplex SET of the CT-complex in the ground state. On the other hand, PIFA oxidizes substrate into the aromatic radical cation **A**. And PIFA acquires one electron from the substrate **1a**, leading to the generation of OTFA anion, CF₃ radical,

PhI, and CO₂. Next, rapid deprotonation occurs, facilitated by the *in-situ* generated OTFA anion, resulting in the formation of the benzylic radical **B**. Subsequently, intermediate **B** undergoes further single-electron oxidation by the HFIP radical, which is formed through a HAT process involving the CF₃ radical and HFIP. The oxidation of intermediate **B** leads to the formation of the benzylic cation **C**, which is then captured by the nucleophilic tosylamide, resulting in the formation of the desired product.

9.10 Comparison to HLF Modifications

- PIDA/I₂ system^{21, 22}

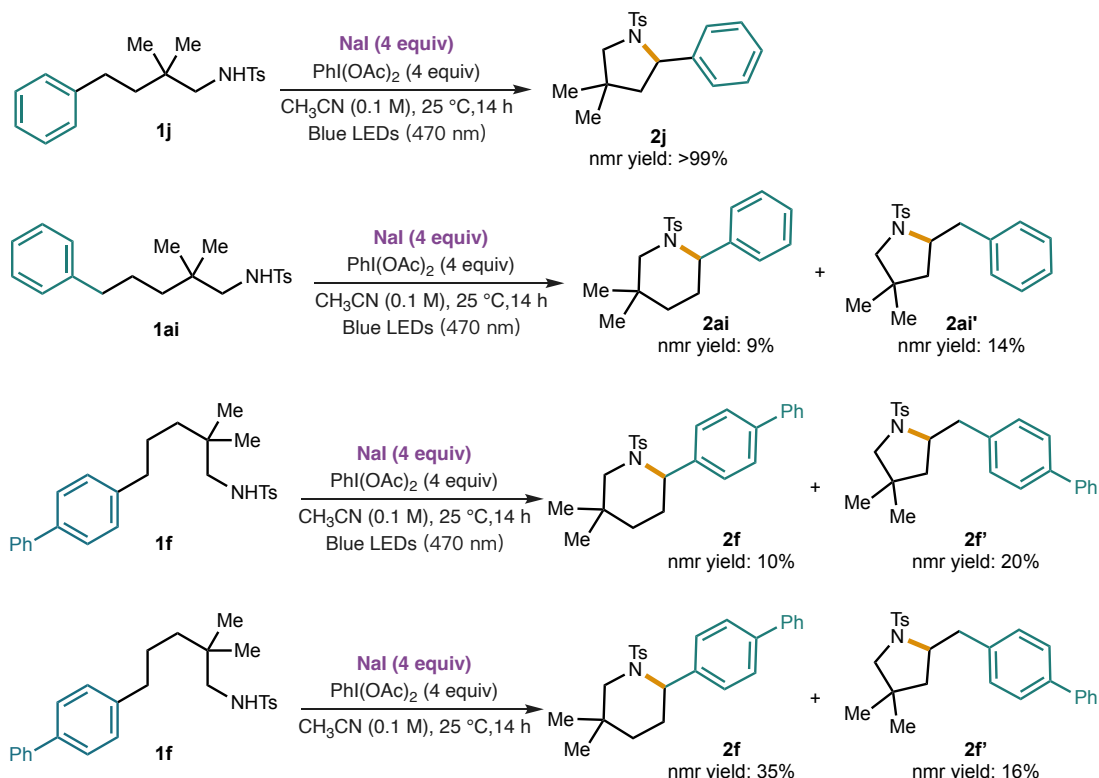
Reactions performed using **set-up 2** in Figure S2. The sulfonamide (0.05 mmol, 1.0 equiv.), I₂ (0.05 mmol, 1.0 equiv.) PIDA (0.15 mmol, 3.0 equiv.) were added to a reaction vial equipped with a stir bar. Subsequently, this reaction vial was brought into an argon-filled glovebox, 0.2 mL of dry DCE were added to the mixture, and the reaction vial was sealed with a Teflon-septa equipped cap. The vial was carefully taken outside of the glovebox and subjected to irradiation under stirring at 25 °C for 14 hours. After completion of the reaction, volatiles were evaporated under reduced pressure and the residue was dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.



- PIDA/NaI system²³

Reactions performed using **set-up 2** in Figure S2. The sulfonamide (0.05 mmol, 1.0 equiv.), NaI (0.2 mmol, 4.0 equiv.) PIDA (0.2 mmol, 4.0 equiv.) were added to a reaction vial equipped with a stir bar. Subsequently, this reaction vial was brought into an argon-filled glovebox, 0.5 mL of dry MeCN were added to the mixture, and the reaction vial was sealed with a Teflon-septa equipped cap. The vial was carefully taken outside of the glovebox and subjected to irradiation under stirring at 25 °C for 14 hours. After completion

of the reaction, volatiles were evaporated under reduced pressure and the residue was dissolved in CDCl_3 and analyzed by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.



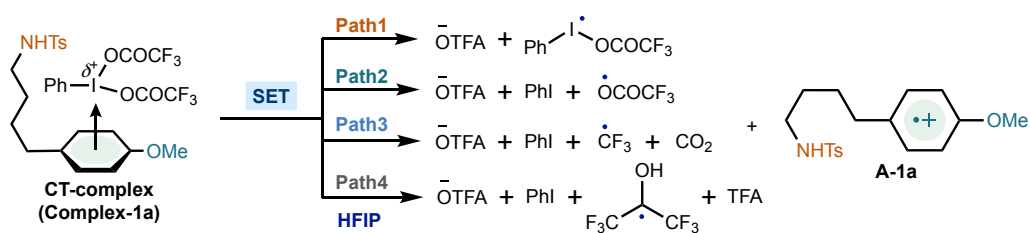
10. DFT calculations

10.1 Computational details

DFT calculations were performed using the Gaussian16²⁴ package with the M06-D3 functional²⁵, where D3 stands for Grimme's empirical dispersion²⁶. Geometry optimizations of all the compounds and transition states were carried out with LANL2DZ as the basis set for iodine,²⁷ and 6-31G(d)²⁸⁻³⁰ for the remaining atoms. Implicit solvent was modeled through the SMD method.³¹ As the solvent, hexafluoroisopropanol, is not included in Gaussian, we defined the solvent by including the dielectric constant and the refracting index. The keywords used were: (solvent=generic, eps=16.7, epsinf=1.625625). Frequencies were computed at the same level of theory to obtain the free energies and to confirm whether the structures are minima (no imaginary frequency) or transition states (only one imaginary frequency). All the potential energies were refined with single-point calculations with a larger def2-TZVP³² and the same functional and solvation models. The CYL View software was employed to show the 3D structures of the studied species³³.

10.2 Possible reaction pathways for SET

To investigate the single electron transfer (SET) process in detail, we explored four possible sets of resulting intermediates (Scheme S2). The results indicate that Path3 is the most probable among the four, where PIFA acquires one electron from the electron-rich substrate **1a**, leading to the generation of OTFA anion, CF₃ radical, PhI, and CO₂. The corresponding free energies are shown in Figure S14.



Scheme S2: Potential pathways for SET process to generate the radical cation **A-1a**.

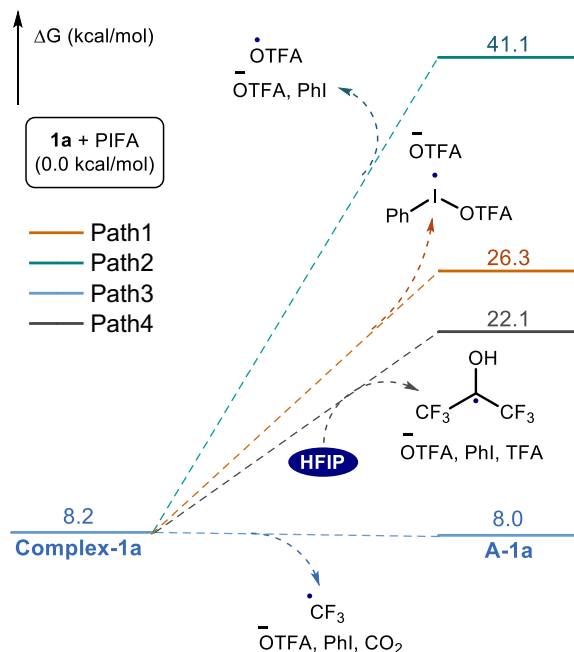


Figure S14: Free energy profile of the potential pathways for single electron transfer process to generate the radical cation **A-1a**.

10.3 Comparing the SET process of substrate **1a** and substrate **1j**

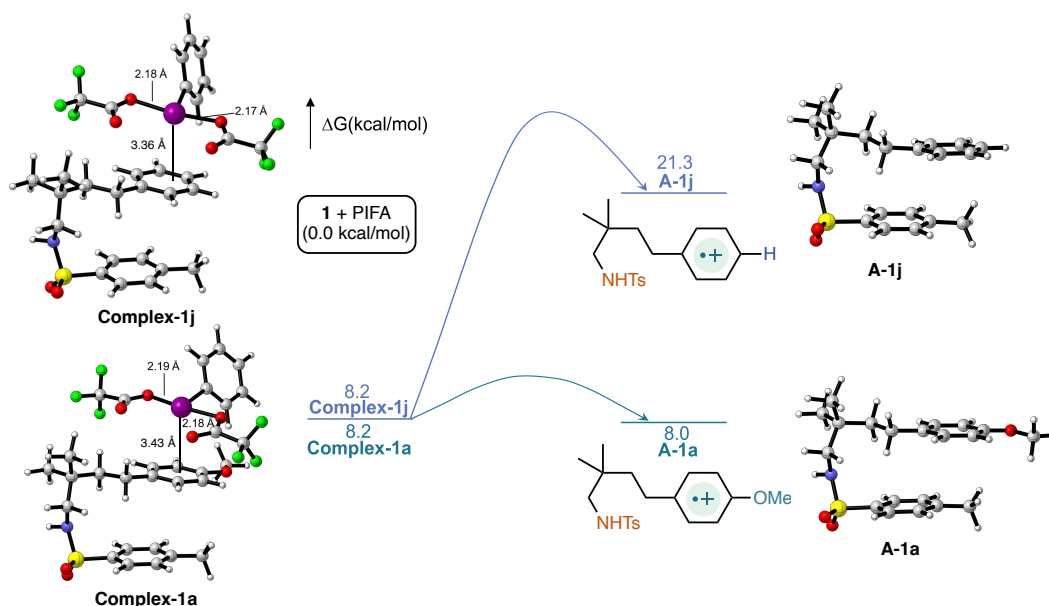


Figure S15: Free energy profile of complex and aromatic radical cation species of substrate **1a** and substrate **1j**.

Figure S15 presents the comparison for the SET step corresponding to systems **1a** and **1j**. We did not compute the barriers, but we can assume that they would involve a minimum of 10 kcal/mol, which would render the process for **1j** inaccessible. This is why photoactivation is necessary for **1j**, but not for **1a**.

10.4 The fate of the CF₃ radical

For the CF₃ radical, we propose it undergoes a HAT process with HFIP, resulting in the formation of HFIP radical and HCF₃. The corresponding free energies are shown in Figure S16.

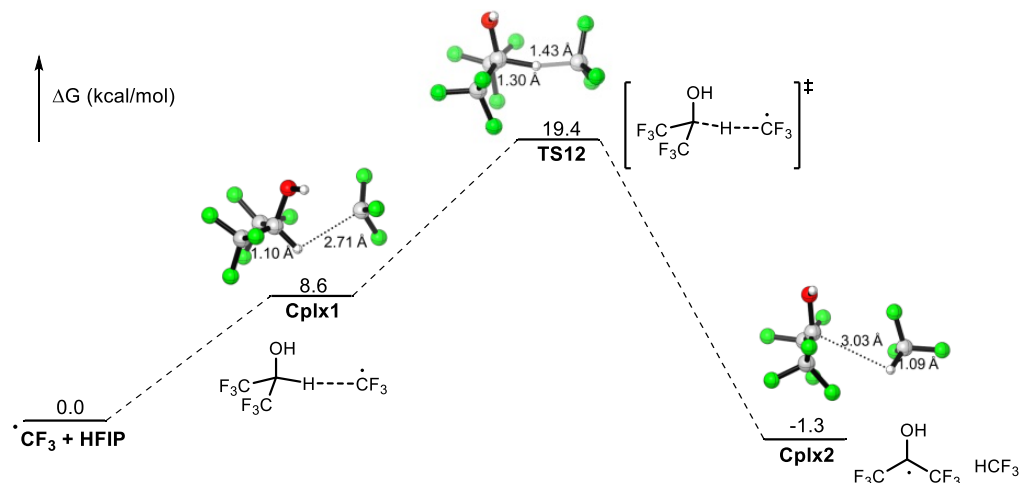


Figure S16: Free energy profile of the process of converting CF₃ radical into HCF₃.

10.5 Reaction mechanism: computational analysis

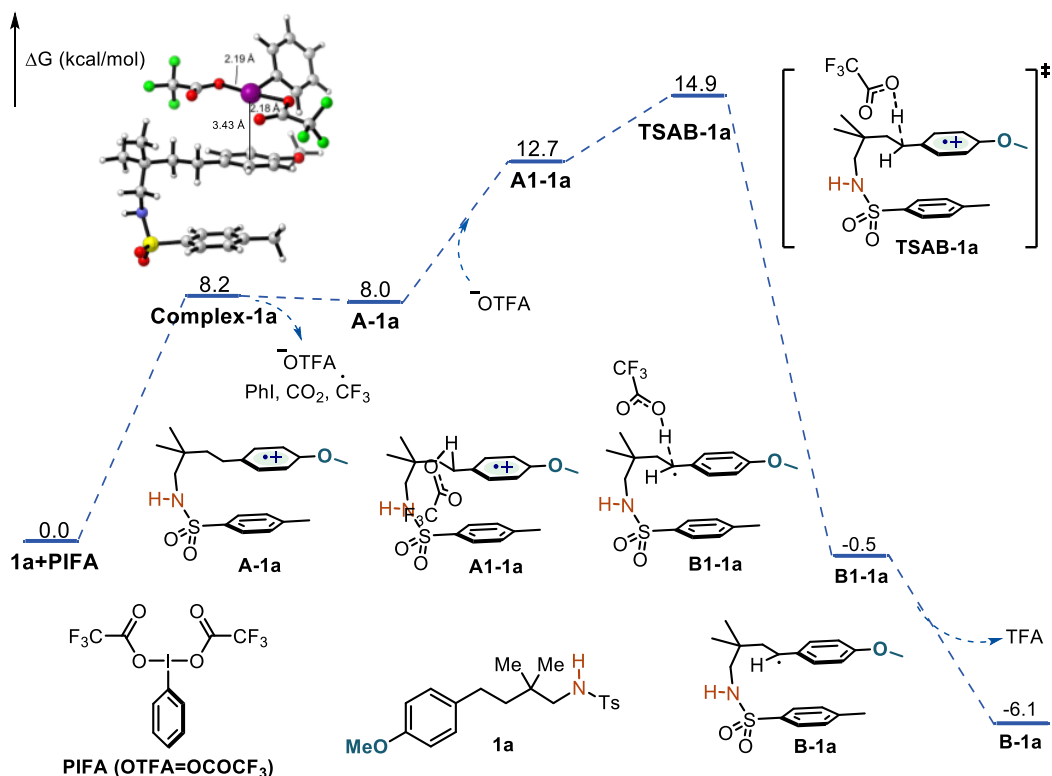


Figure S17: Free energy profile of the C(sp³)-H functionalization with substrate **1a** and PIFA in HFIP (part1).

OTFAradical	-525.916940	-526.1438540	None
CO₂	-188.505639	-188.5917025	None
CF₃radical	-337.450997	-337.6048109	None
HFIP	-789.497551	-789.8416152	None
HFIPradical	-788.851118	-789.1946534	None
TFA	-526.589326	-526.8211115	None
A1-1a	-1981.75997	-1982.466729	None
TSAB-1a	-1981.753904	-1982.463188	-601.22
B1-1a	-1981.775748	-1982.487823	None
B-1a	-1455.192016	-1455.675633	None
HCF₃	-338.118409	-338.2727126	None
HFIPanion	-789.003297	-789.3602762	None
HFIPanion1	-788.976470	-789.3360898	None
C-1a	-1455.042386	-1455.520035	None
TSCD-1a	-1455.039641	-1455.514041	-101.24
D-1a	-1455.056189	-1455.529069	None
D1-1a	-2244.132777	-2244.944739	None
TSBE-1a	-1455.142892	-1455.614800	-861.46
E-1a	-1455.198279	-1455.668292	None
Cplx1	-1126.939246	-1127.432769	None
TS12	-1126.921957	-1127.415438	-1983.34
Cplx2	-1126.955269	-1127.448525	None

11. References

1. Martínez, C. & Muñiz, K. An Iodine-Catalyzed Hofmann–Löffler Reaction. *Angew. Chem. Int. Ed.* **54**, 8287-8291 (2015).
2. Nikolaienko, P., Jentsch, M., Kale, A. P., Cai, Y. & Rueping, M. Electrochemical and Scalable Dehydrogenative C(sp³)–H Amination via Remote Hydrogen Atom Transfer in Batch and Continuous Flow. *Chem. Eur. J.* **25**, 7177-7184 (2019).
3. Miyake, Y., Nakajima, K. & Nishibayashi, Y. Visible Light-Mediated Oxidative Decarboxylation of Arylacetic Acids into Benzyl Radicals: Addition to Electron-Deficient Alkenes by Using Photoredox Catalysts. *Chem. Commun.* **49**, 7854-7856 (2013).
4. Deb, A., Hazra, A., Peng, Q., Paton, R. S. & Maiti, D. Detailed Mechanistic Studies on Palladium-Catalyzed Selective C–H Olefination with Aliphatic Alkenes: A Significant Influence of Proton Shuttling. *J. Am. Chem. Soc.* **139**, 763-775 (2017).
5. Yin, Z., Zhang, Y., Zhang, S. & Wu, X.-F. Copper-catalyzed intra- and intermolecular carbonylative transformation of remote C(sp³)–H bonds in N-fluoro-sulfonamides. *J. Catal.* **377**, 507-510 (2019).
6. Becker, P., Duhamel, T., Stein, C. J., Reiher, M. & Muñiz, K. Cooperative Light-Activated Iodine and Photoredox Catalysis for the Amination of C(sp³)–H Bonds. *Angew. Chem. Int. Ed.* **56**, 8004-8008 (2017).
7. Zhang, H. & Muñiz, K. Selective Piperidine Synthesis Exploiting Iodine-Catalyzed Csp³–H Amination under Visible Light. *ACS Catal.* **7**, 4122-4125 (2017).
8. Liu, D., Liu, C., Li, H. & Lei, A. Direct Functionalization of Tetrahydrofuran and 1,4-Dioxane: Nickel-Catalyzed Oxidative C(sp³)–H Arylation. *Angew. Chem. Int. Ed.* **52**, 4453-4456 (2013).
9. Duhamel, T., Stein, C. J., Martínez, C., Reiher, M. & Muñiz, K. Engineering Molecular Iodine Catalysis for Alkyl–Nitrogen Bond Formation. *ACS Catal.* **8**, 3918-3925 (2018).
10. Murray, P. R. D., Leibler, I. N., Hell, S. M., Villalona, E., Doyle, A. G. & Knowles, R. R. Radical Redox Annulations: A General Light-Driven Method for the Synthesis of Saturated Heterocycles. *ACS Catal.* **12**, 13732-13740 (2022).
11. Herold, S., Bafaluy, D. & Muñiz, K. Anodic benzylic C(sp³)–H amination: unified access to pyrrolidines and piperidines. *Green Chem.* **20**, 3191-3196 (2018).
12. Zhang, J., Zhang, Z. M., Wu, Q. & Zhang, J. Synthesis of 1,2,3,4-Tetrahydroisoquinolines via Palladium-Catalyzed Cyclization of *N*-Tosylhydrazones with *ortho*-Bromophenethyl Tosylamides. *Adv. Synth. Catal.* **364**, 4075-4079 (2022).
13. Bergamaschi, E., Lunic, D., McLean, L. A., Hohenadel, M., Chen, Y. K. & Teskey, C. J. Controlling Chemoselectivity of Catalytic Hydroboration with Light. *Angew. Chem. Int. Ed.* **61**, e202114482 (2022).
14. Yuan, Q., Liu, D. & Zhang, W. Iridium-Catalyzed Asymmetric Hydrogenation of beta,gamma-Unsaturated gamma-Lactams: Scope and Mechanistic Studies. *Org. Lett.* **19**, 1144-1147 (2017).
15. Bosnidou, A. E., Duhamel, T. & Muñiz, K. Detection of the Elusive Nitrogen-Centered Radicals from Catalytic Hofmann–Löffler Reactions. *Eur. J. Org. Chem.* **2020**, 6361-6365 (2019).
16. Ito, M., Ogawa, C., Yamaoka, N., Fujioka, H., Dohi, T. & Kita, Y. Enhanced reactivity

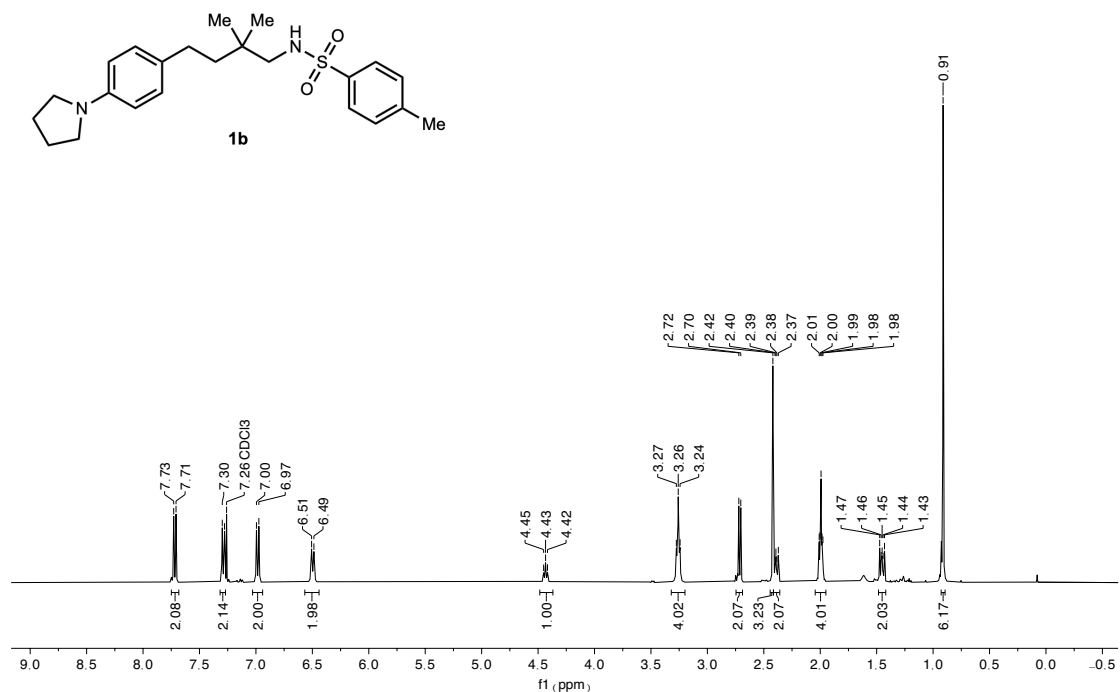
- of [hydroxy(tosyloxy)iodo]benzene in fluoroalcohol media. Efficient direct synthesis of thienyl(aryl)iodonium salts. *Molecules* **15**, 1918-1931 (2010).
17. Dohi, T., Ito, M., Yamaoka, N., Morimoto, K., Fujioka, H. & Kita, Y. Unusual ipso substitution of diaryliodonium bromides initiated by a single-electron-transfer oxidizing process. *Angew. Chem. Int. Ed.* **49**, 3334-3337 (2010).
 18. Lakovicz, J. R. *Principles of Fluorescence Spectroscopy* (Springer, 2006).
 19. Colomer, I., Batchelor-McAuley, C., Odell, B., Donohoe, T. J. & Compton, R. G. Hydrogen Bonding to Hexafluoroisopropanol Controls the Oxidative Strength of Hypervalent Iodine Reagents. *J. Am. Chem. Soc.* **138**, 8855-8861 (2016).
 20. Kavarnos, G. J. Energetics of photoinduced electron transfer. In *Fundamentals of Photoinduced Electron Transfer*; VCH: New-York, Weinheim, 29-37 (1993).
 21. de Armas, P., Carrau, R., Concepcio'n, J.I., Francisco, C.G., Herná'ndez, R., Sua' rez, T.L. Synthesis of 1, 4-epimine compounds. Iodosobenzene diacetate, an efficient reagent for neutral nitrogen radical generation. *Tetrahedron Lett.* **26**, 2493-2496 (1985).
 22. Fan, R., Pu, D., Wen, F. & Wu, J. δ and α sp^3 C-H Bond Oxidation of Sulfonamides with $PhI(OAc)_2/I_2$ under Metal-Free Conditions. *J. Org. Chem.* **72**, 8994-8997 (2007).
 23. Wappes, E. A., Fosu, S. C., Chopko, T. C. & Nagib, D. A. Triiodide-Mediated δ -Amination of Secondary C-H Bonds. *Angew. Chem. Int. Ed.* **55**, 9974-9978 (2016).
 24. Gaussian 16, Revision A. 03, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J. A. Jr., Peralta, J. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B., Fox, D. J. & Gaussian, Inc. Wallingford CT, 2016.
 25. Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Account.* **120**, 215-241 (2008).
 26. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **27**, 1787-1799 (2006).
 27. Dunning Jr., T. H. & Hay, P. J. *Modern Theoretical Chemistry*, Ed. Schaefer III, H. F. Vol. 3 (Plenum, New York, 1977) 1-28
 28. Hehre, W. J., Ditchfield, R. & Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **56**, 2257-2261 (1972).
 29. Dill, J. D. & Pople, J. A. Self-consistent molecular orbital methods. XV. Extended Gaussian-type basis sets for lithium, beryllium, and boron. *J. Chem. Phys.* **62**, 2921-

2923 (1975).

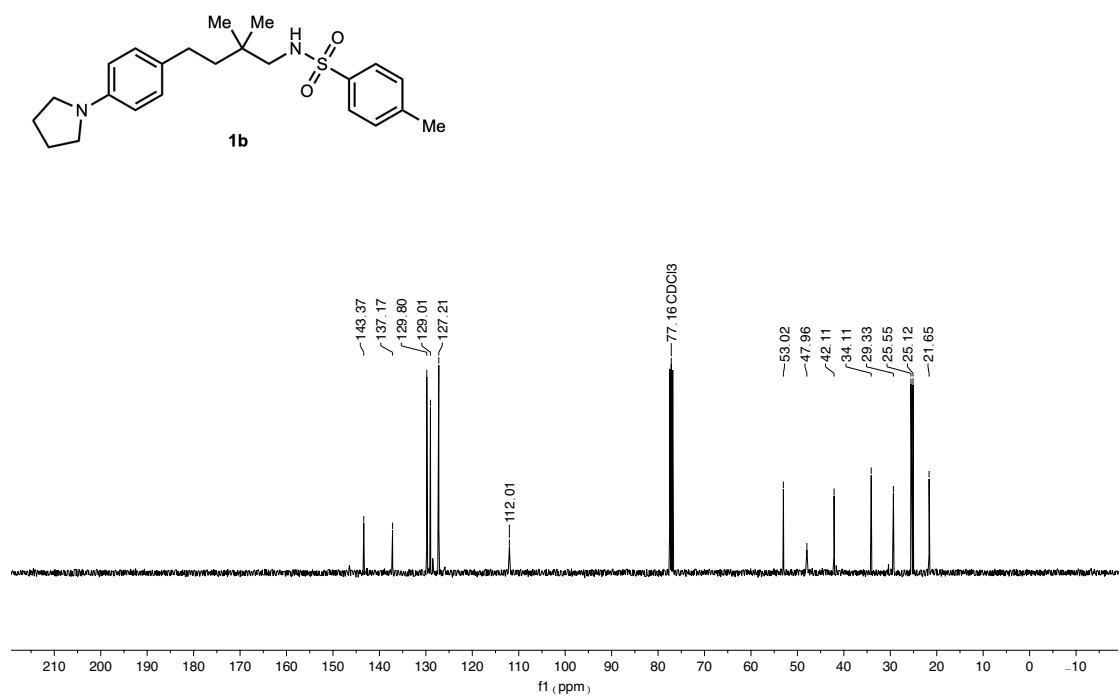
30. Francl, M. M., Pietro, W. J., Hehre, W. J., Binkley, J. S., Gordon, M. S., DeFrees, D.J. & Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **77**, 3654-3665 (1982).
31. Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **113**, 6378-6396 (2009).
32. Weigend, F. & Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **7**, 3297-3305 (2005).
33. C. Y. Legault, CYLview, 1.0b. Université de Sherbrooke. (<http://www.cylview.org>) (2009).

12. NMR spectra

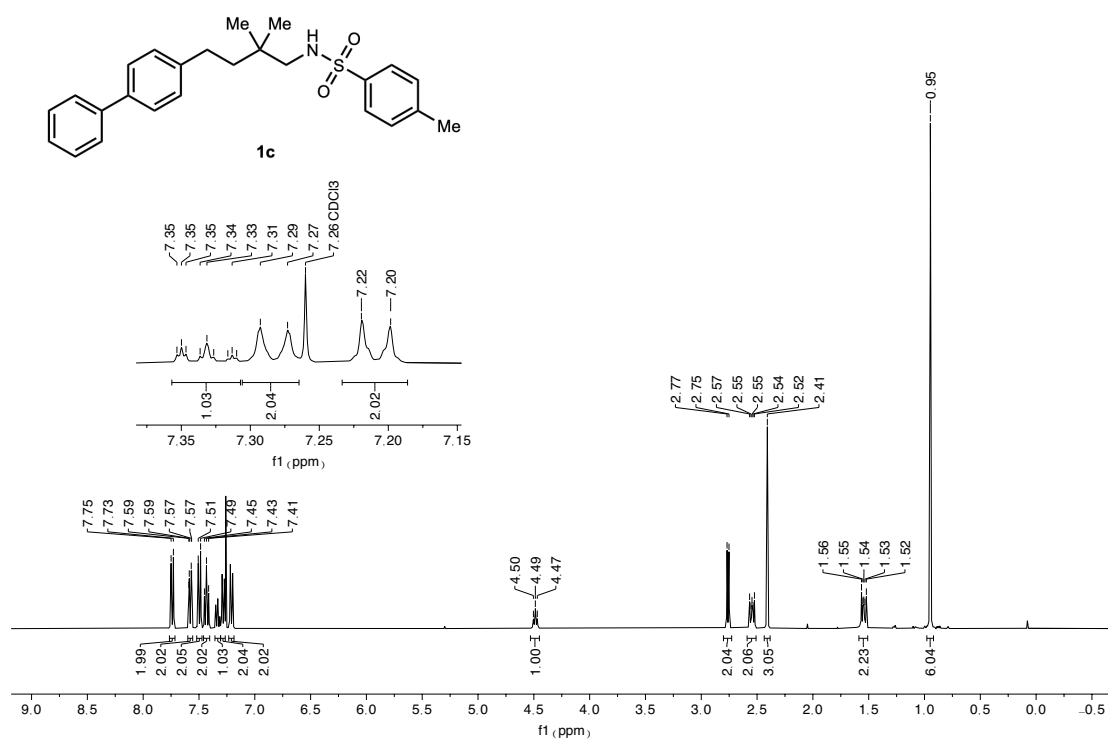
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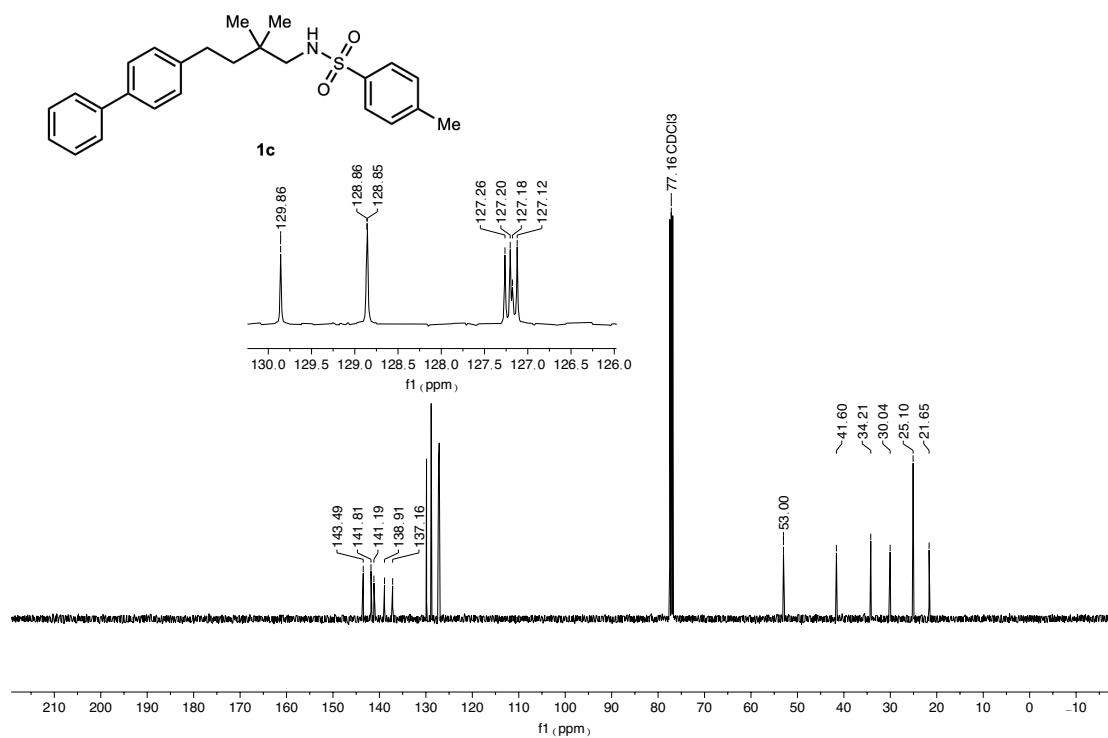
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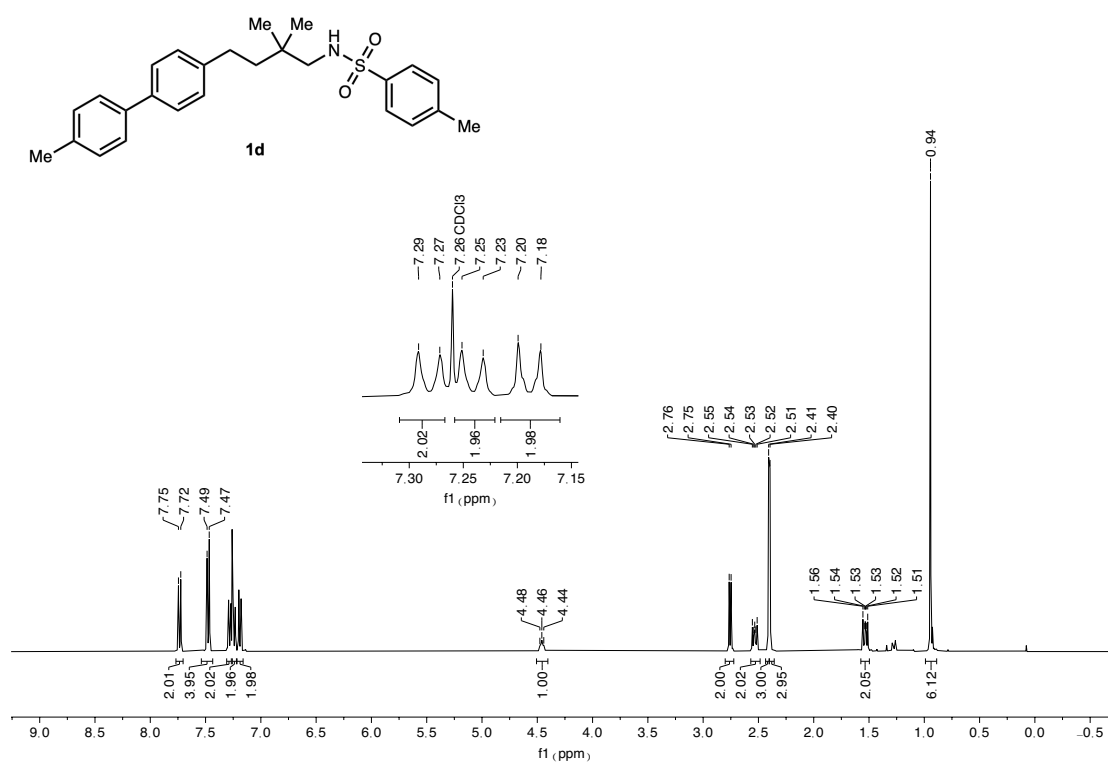
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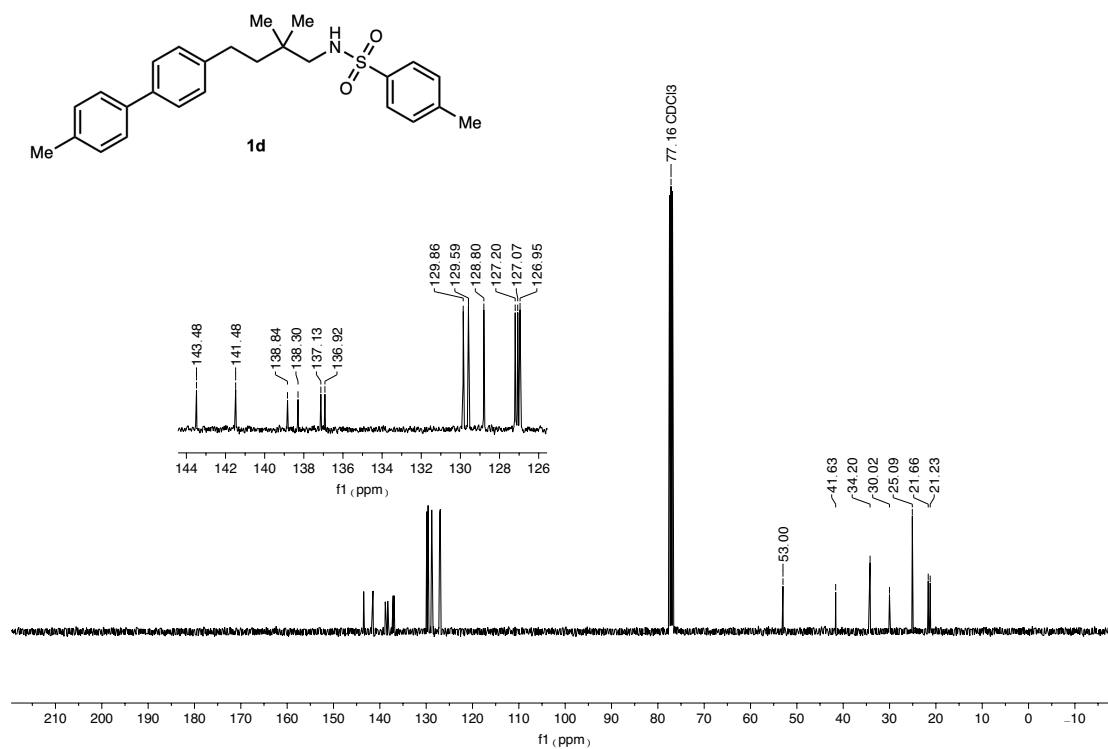
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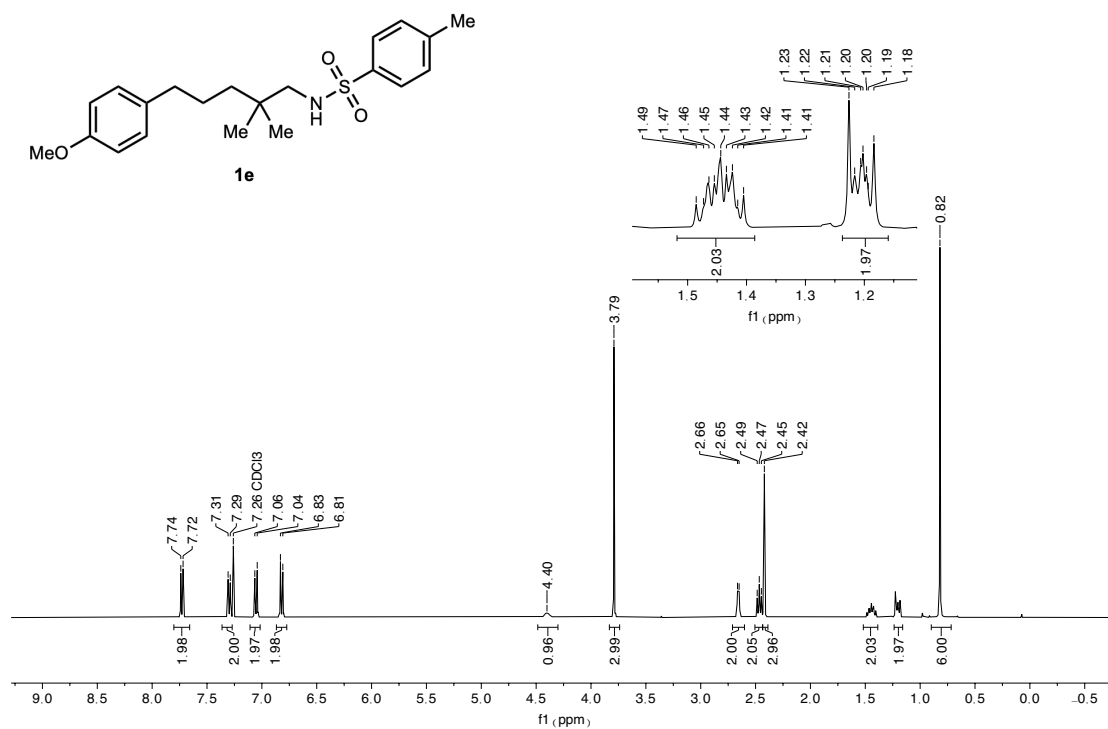
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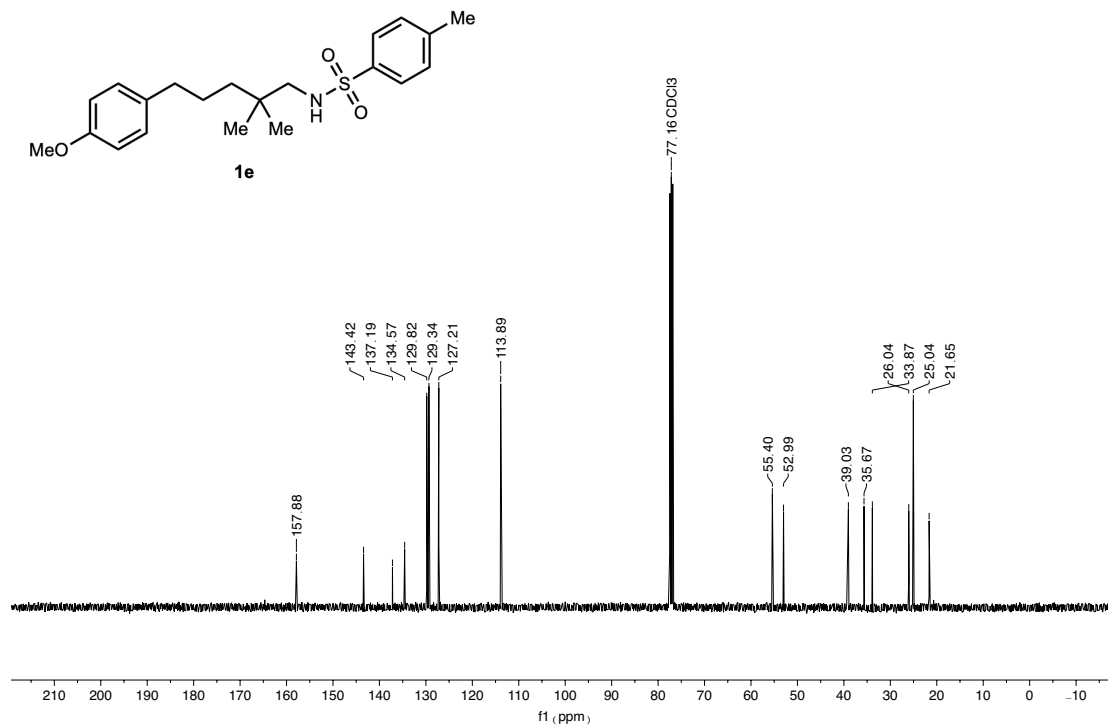
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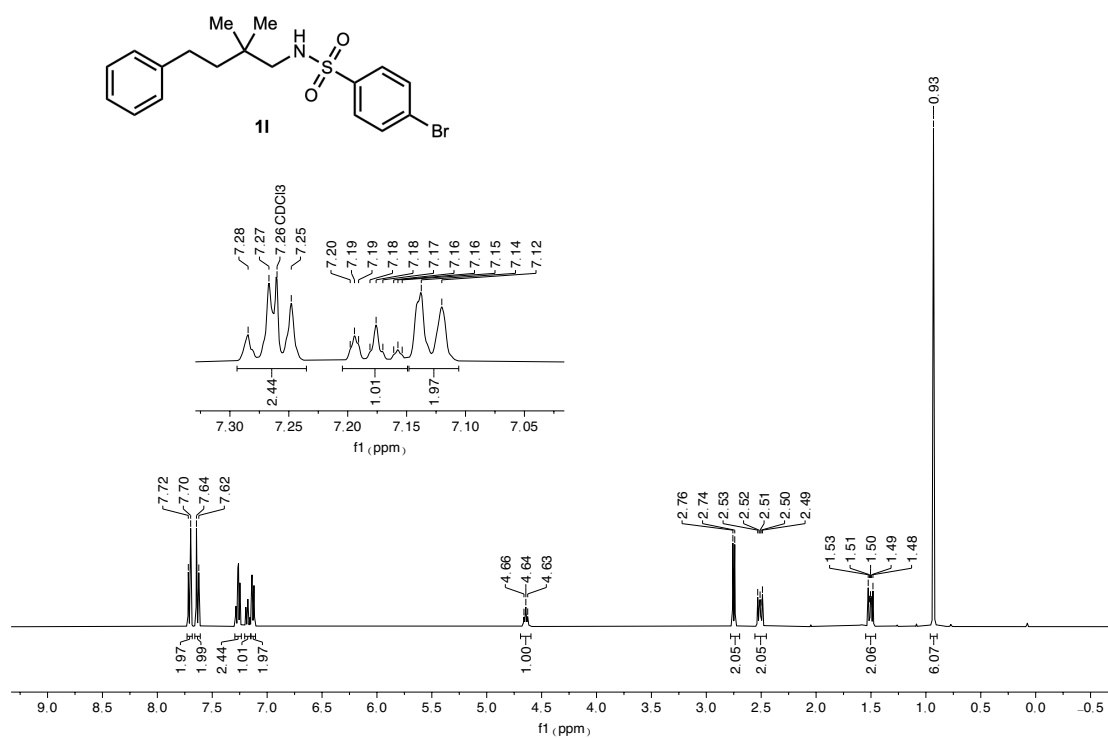
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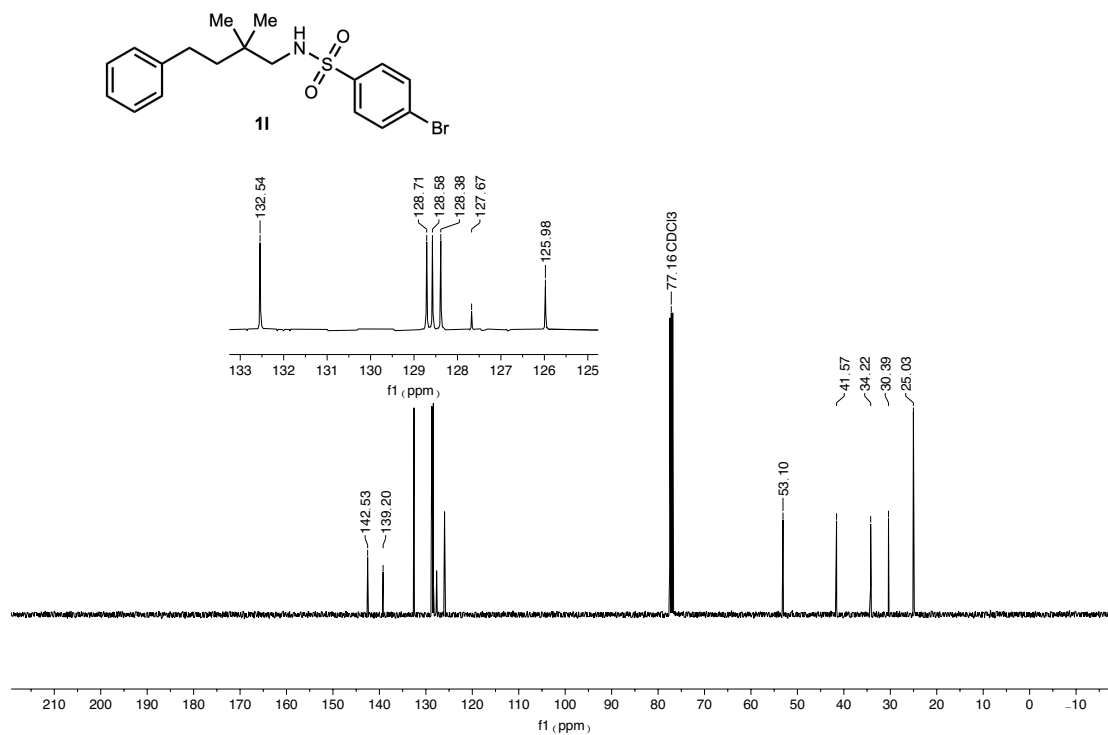
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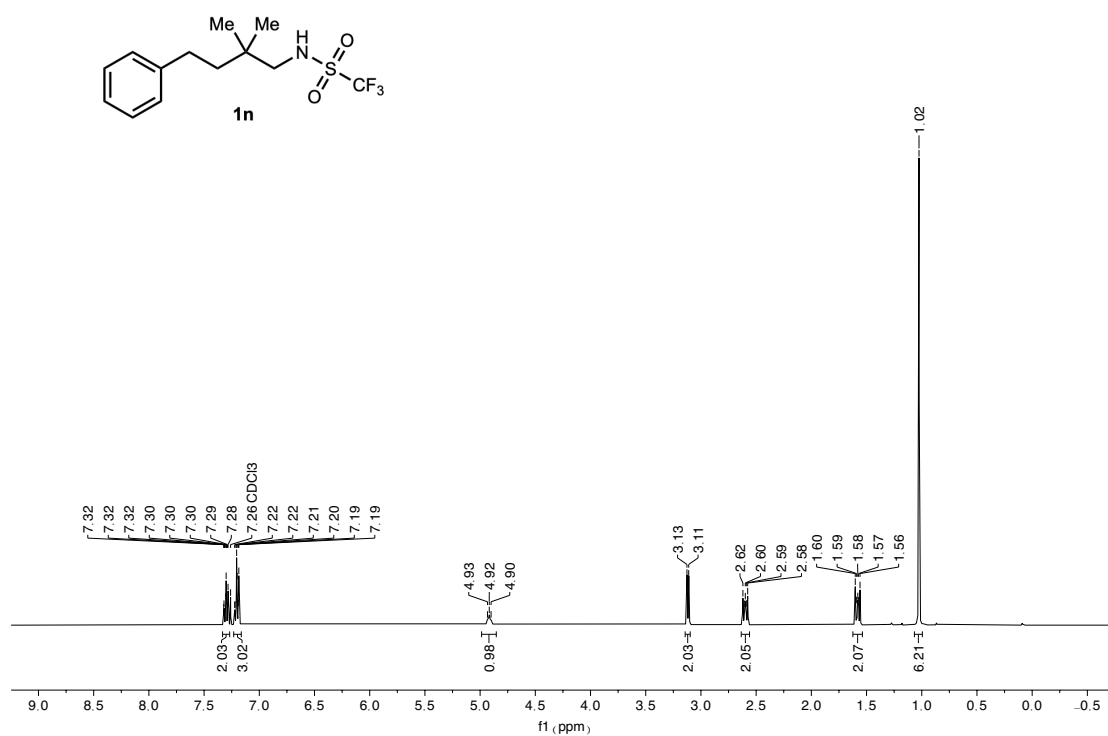
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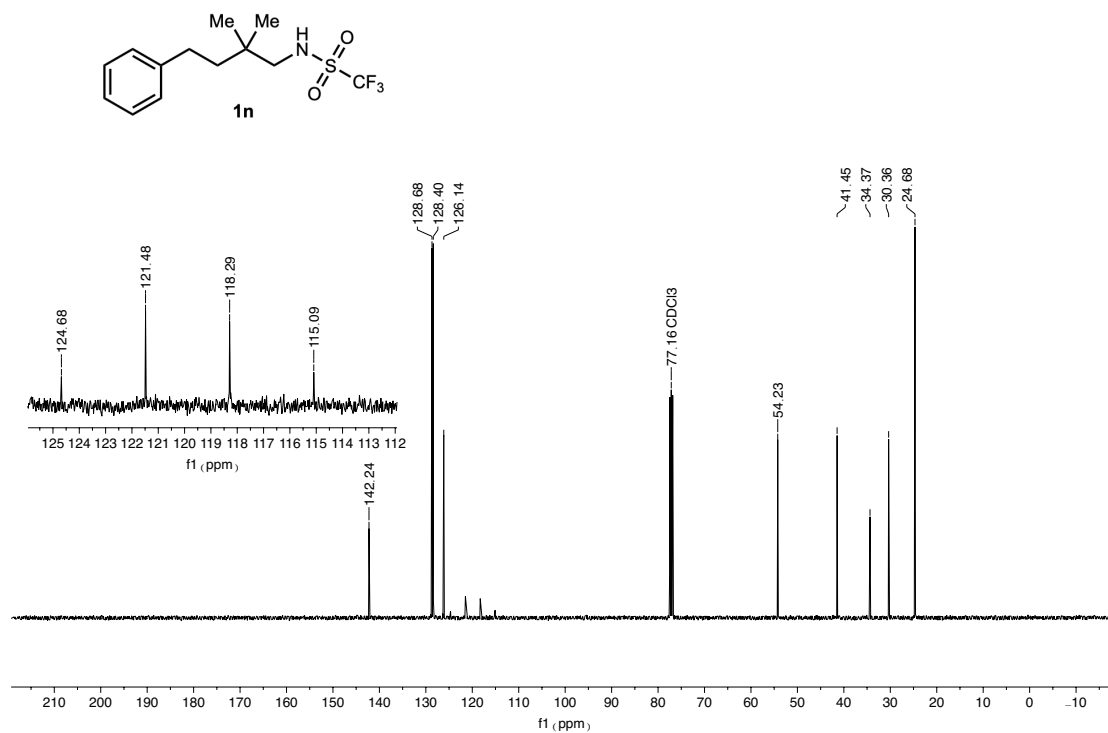
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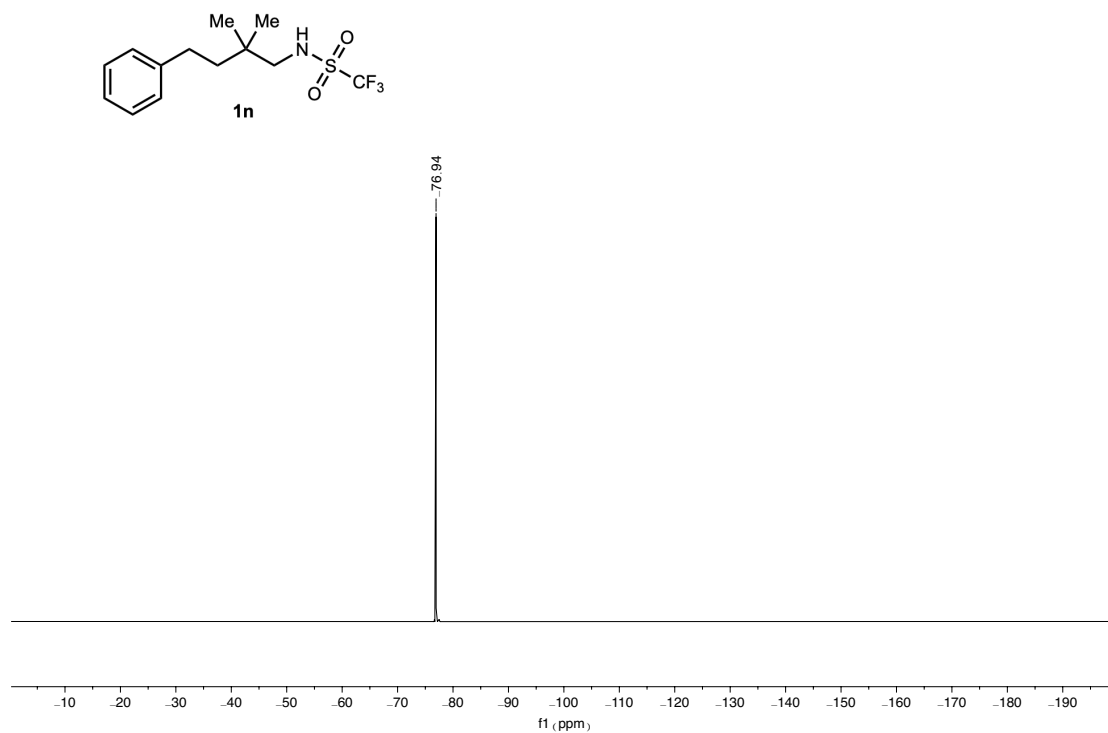
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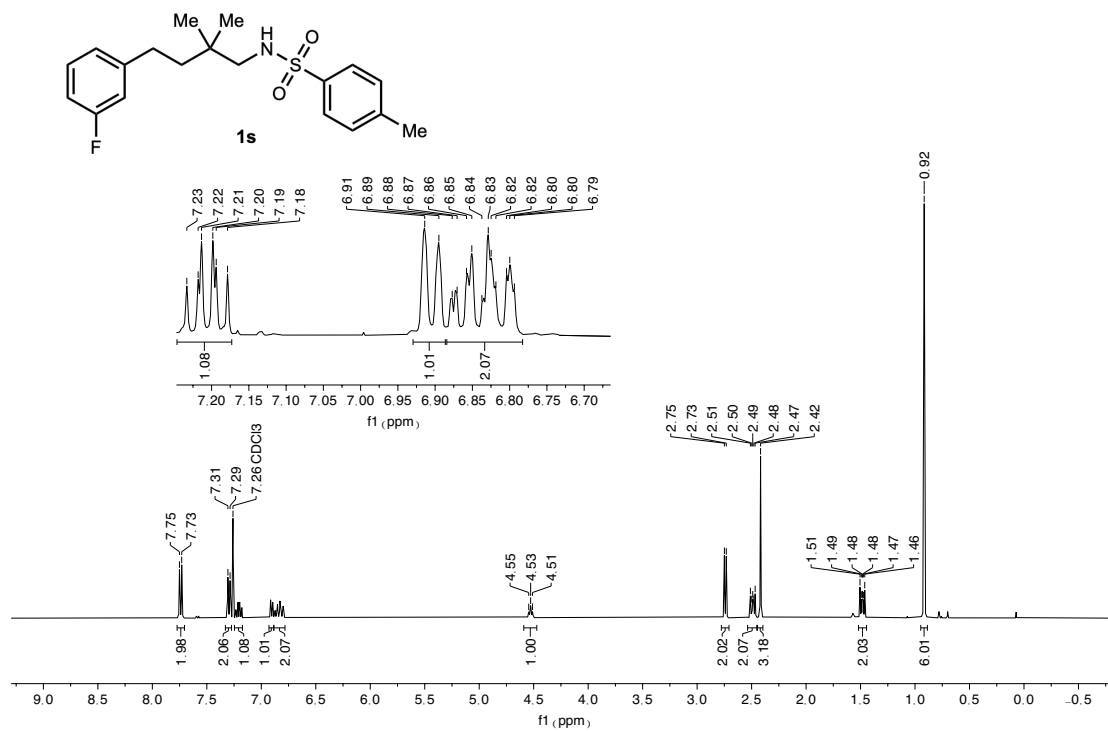
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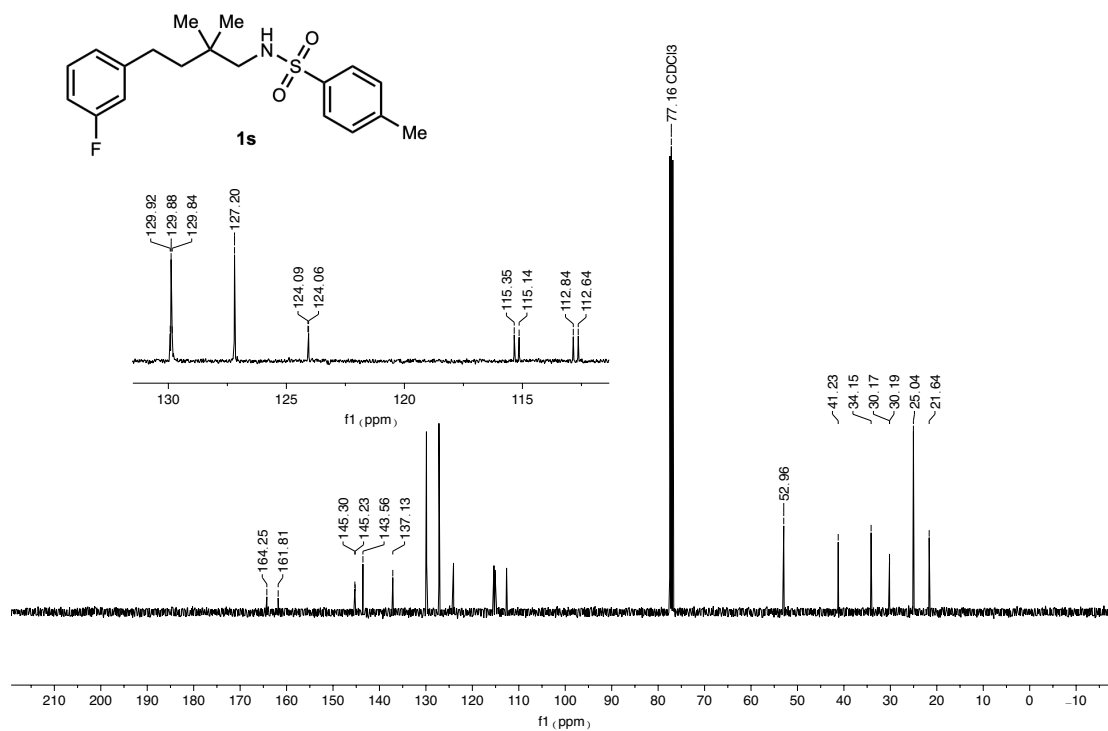
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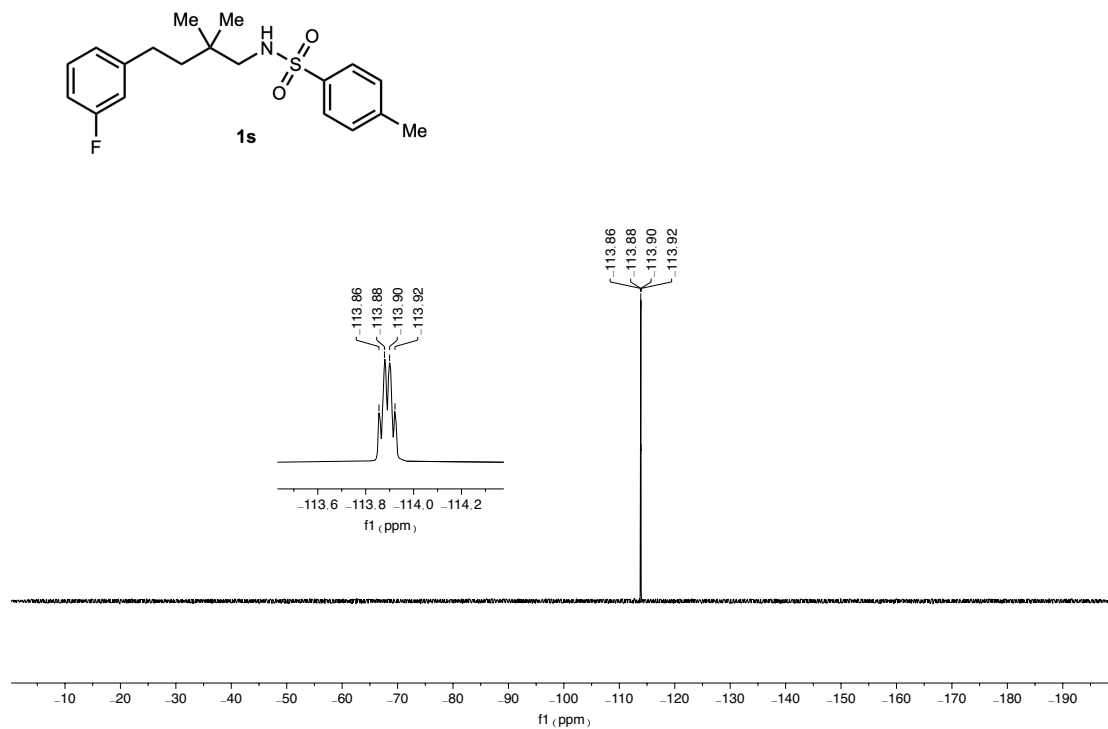
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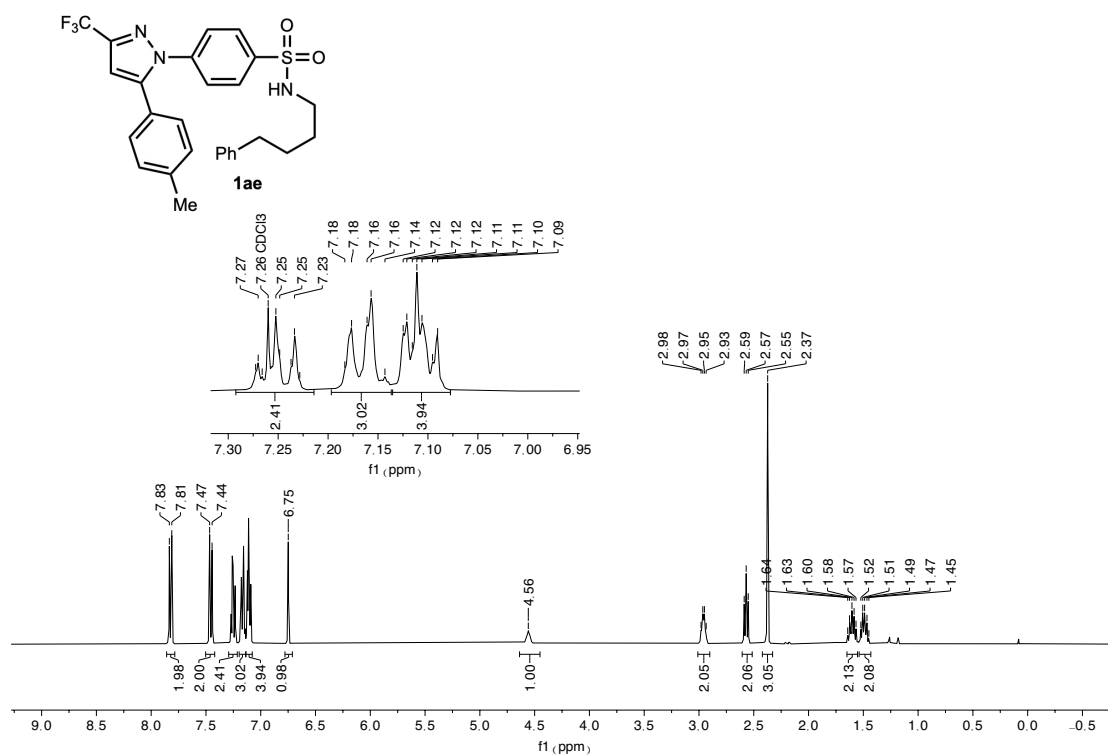
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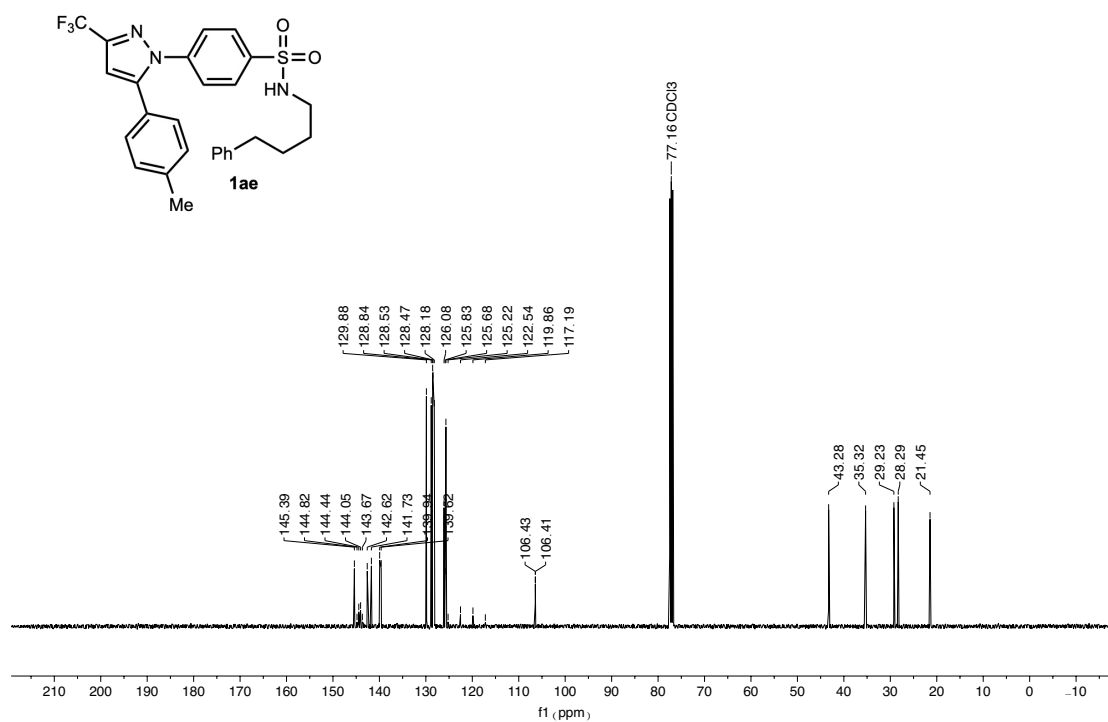
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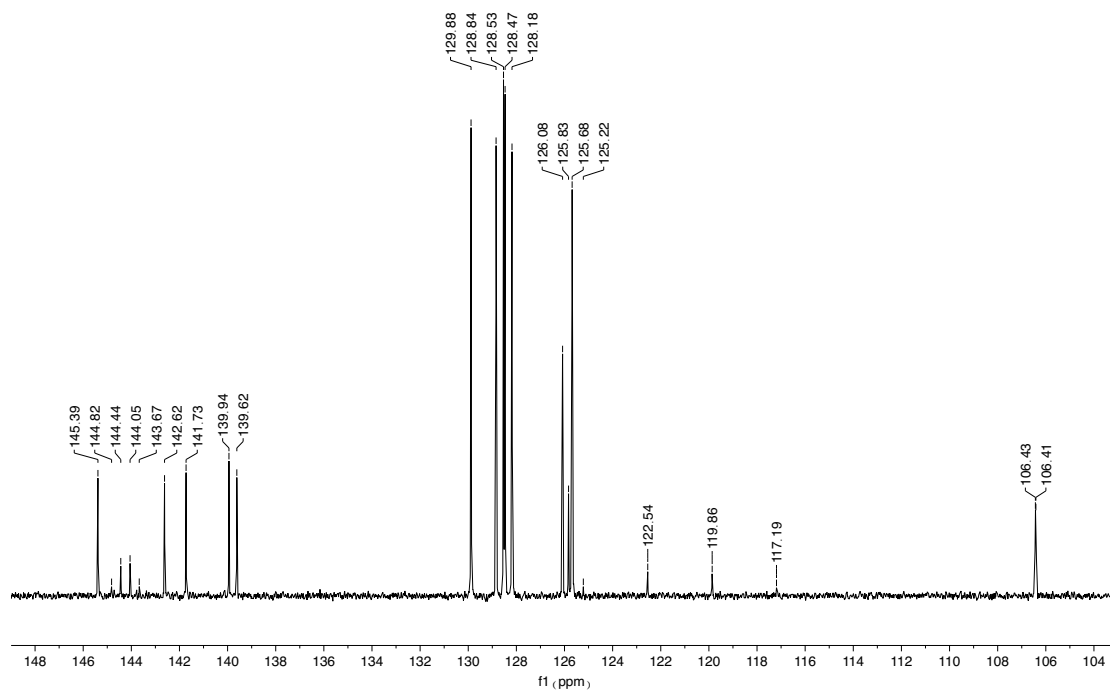


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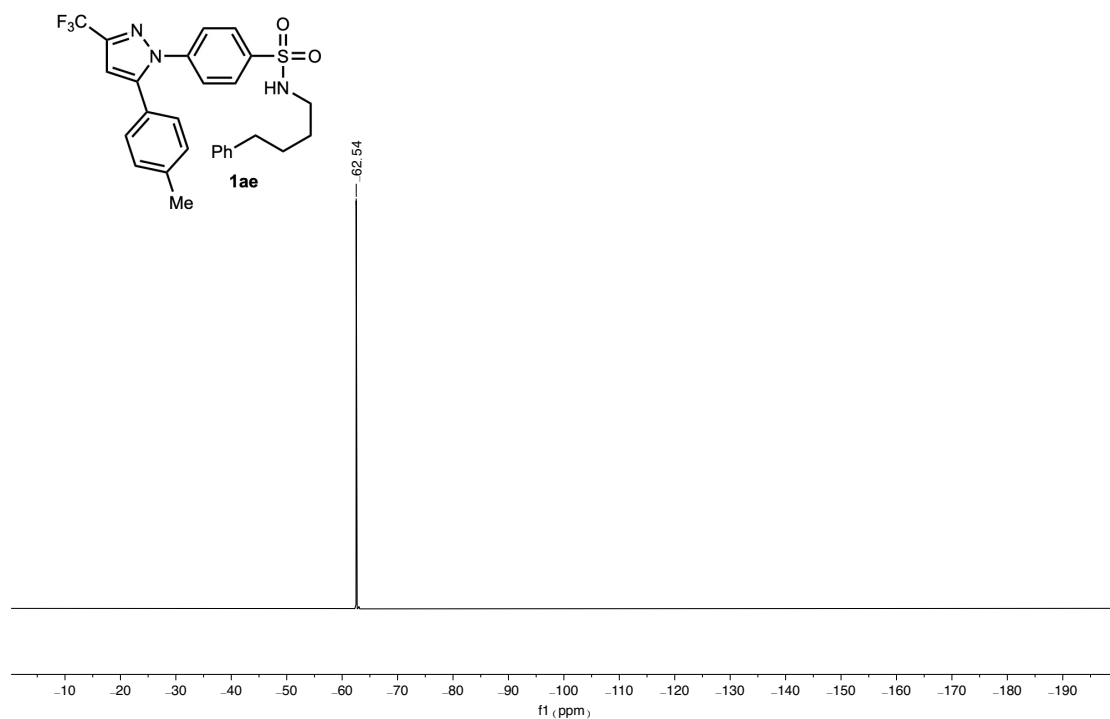


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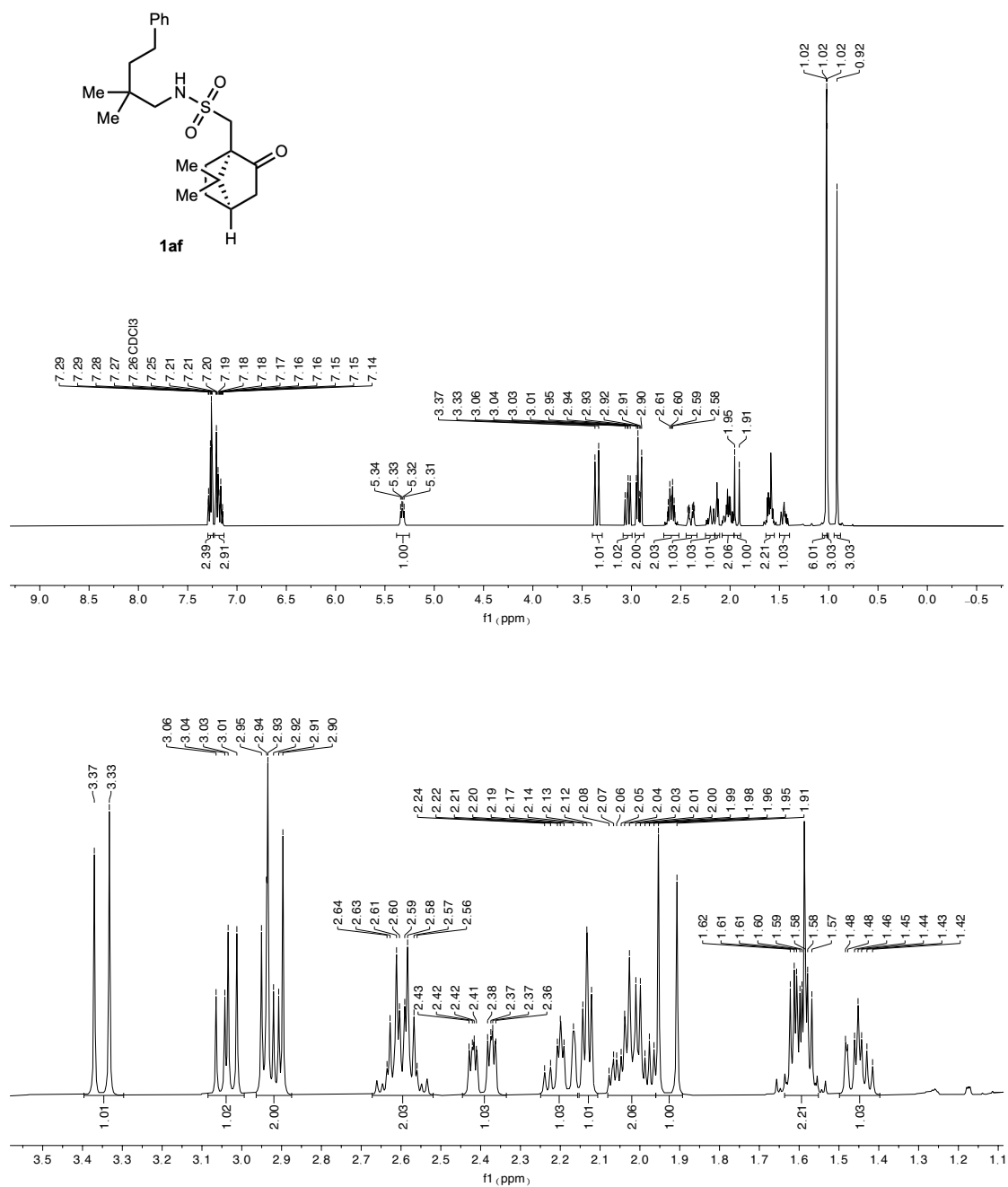




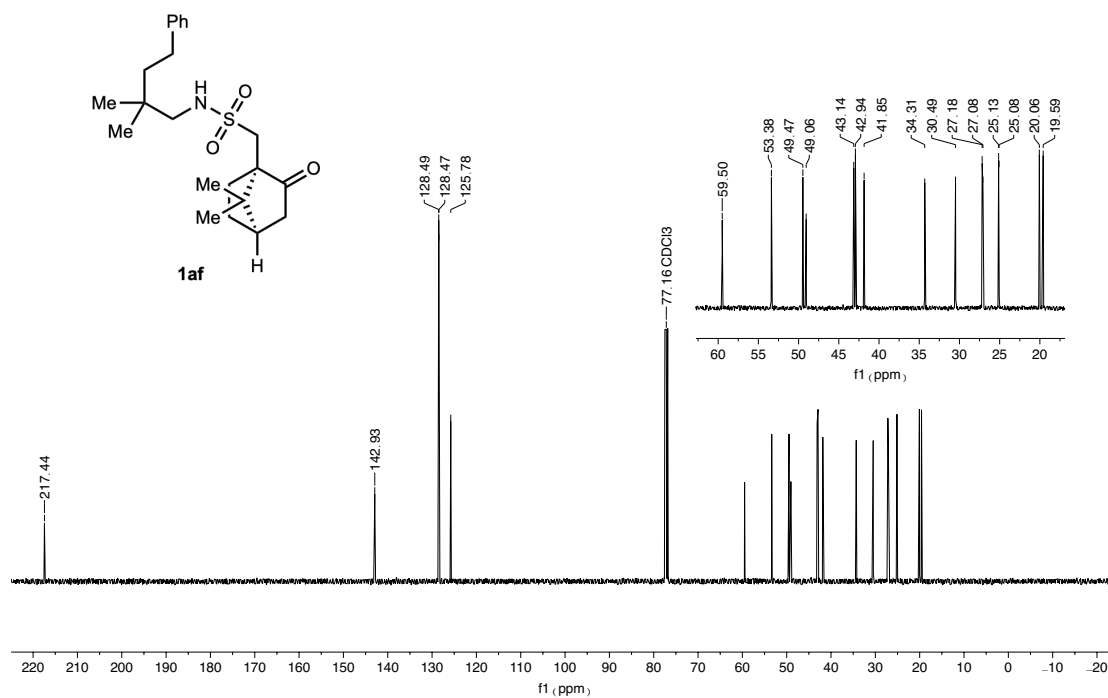
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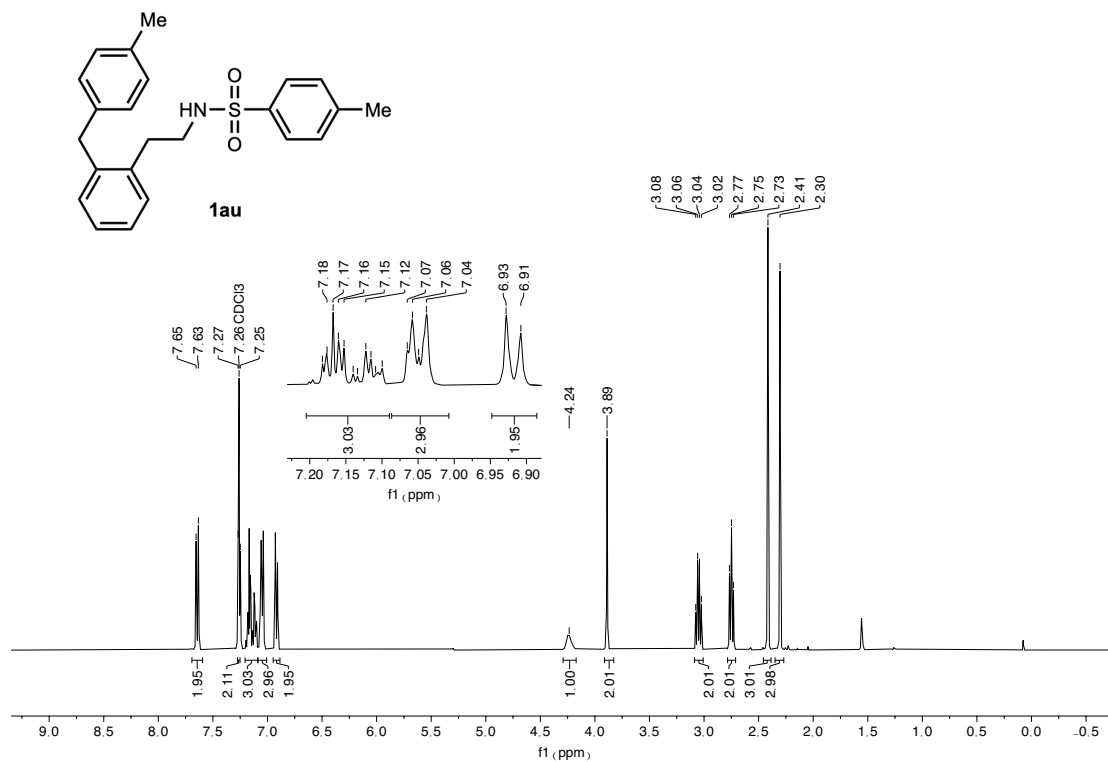
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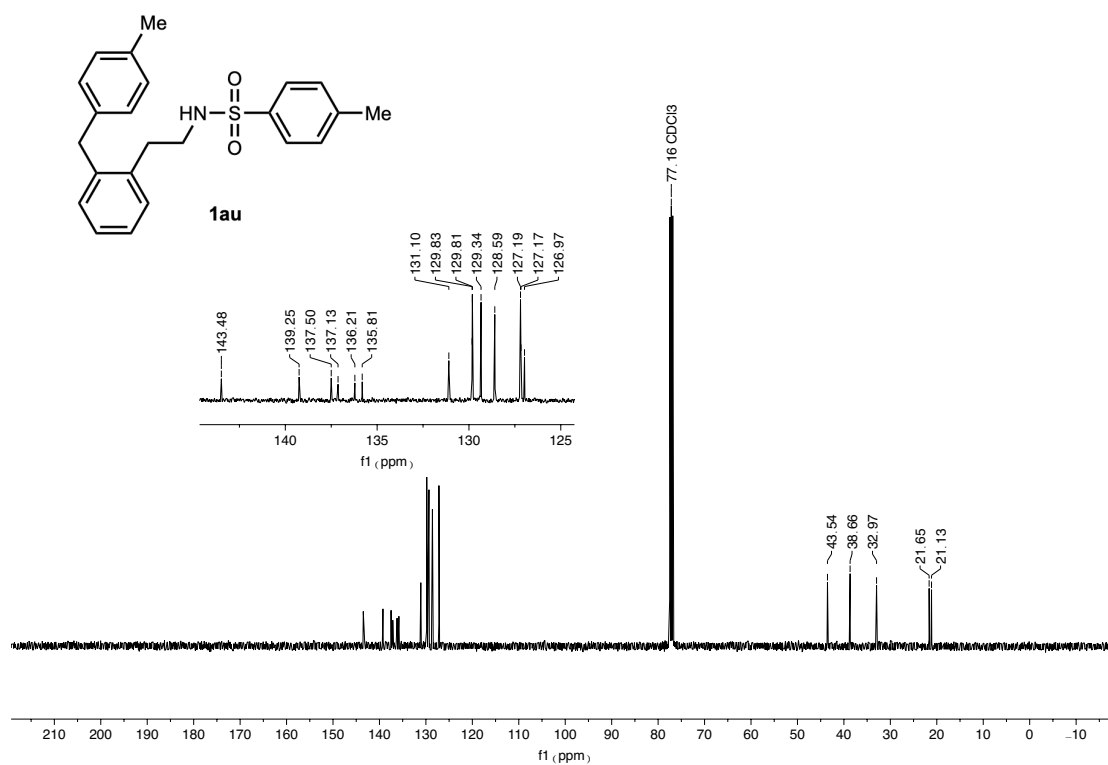
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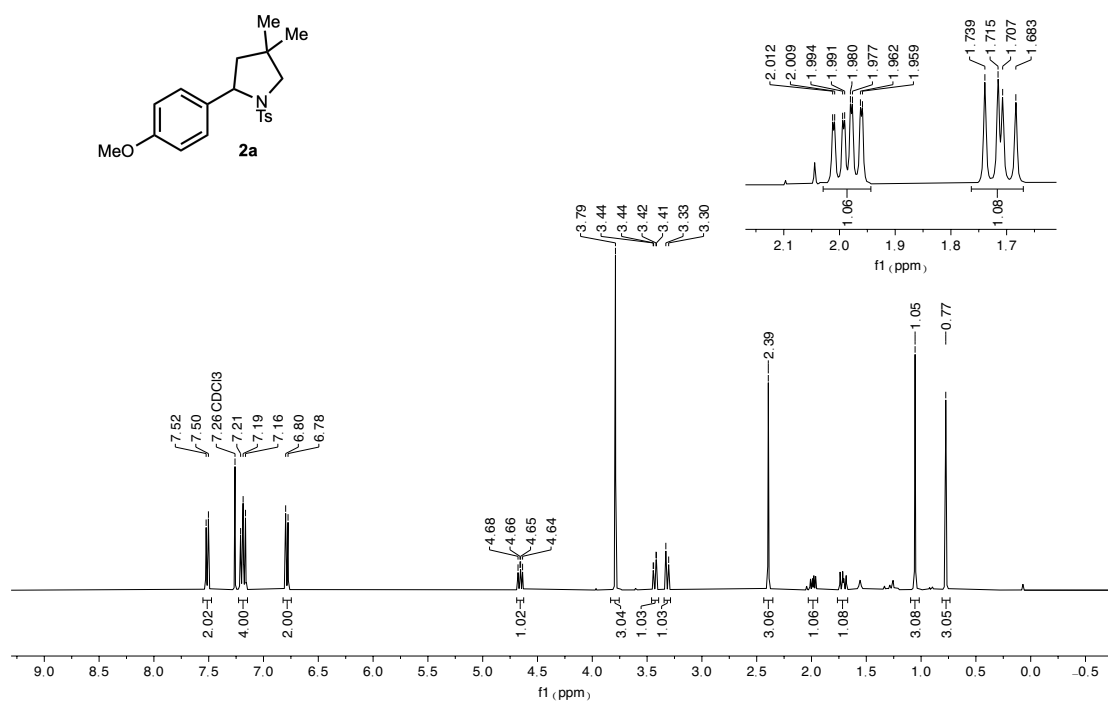
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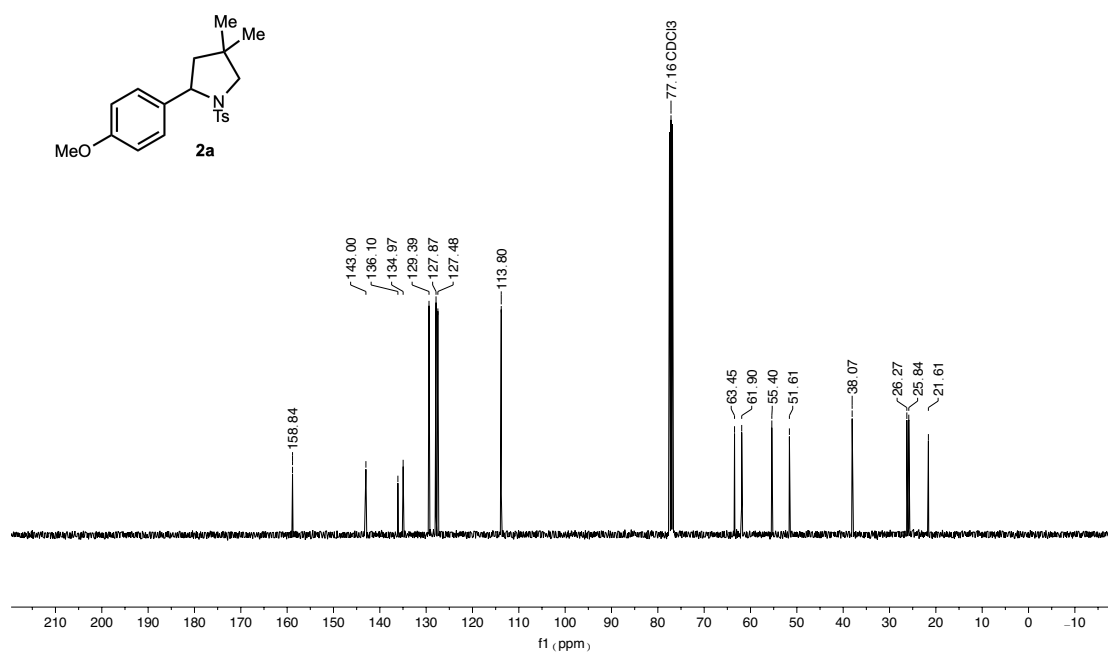
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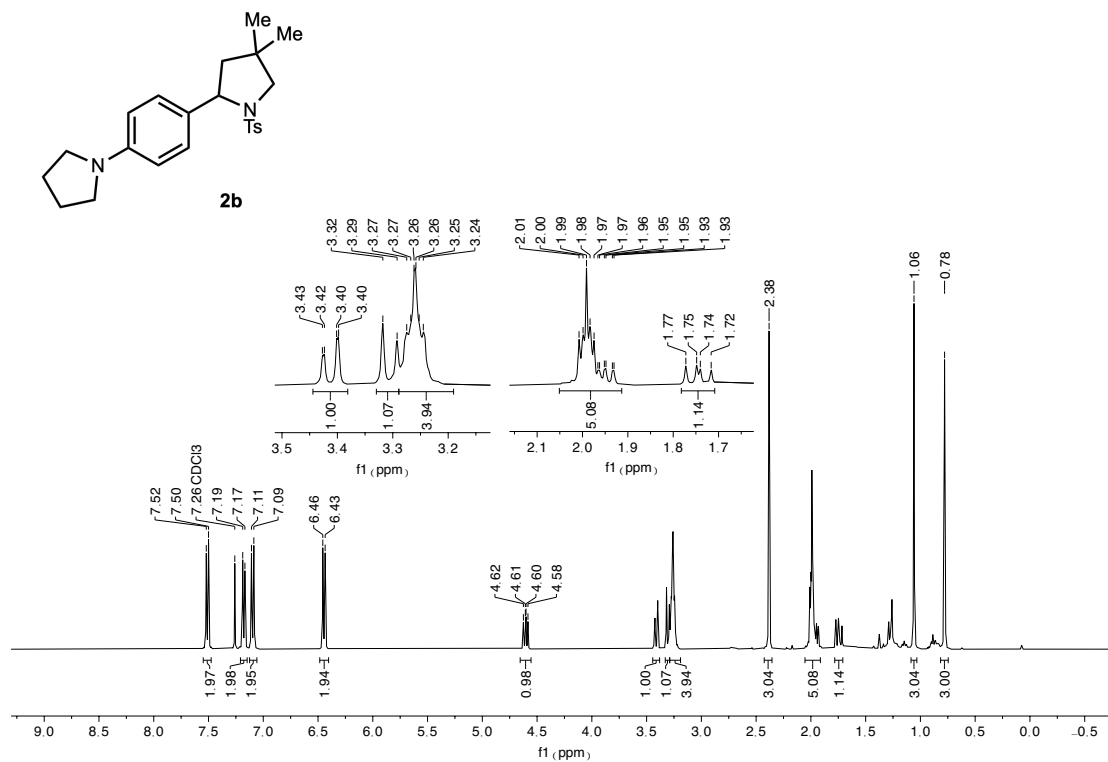
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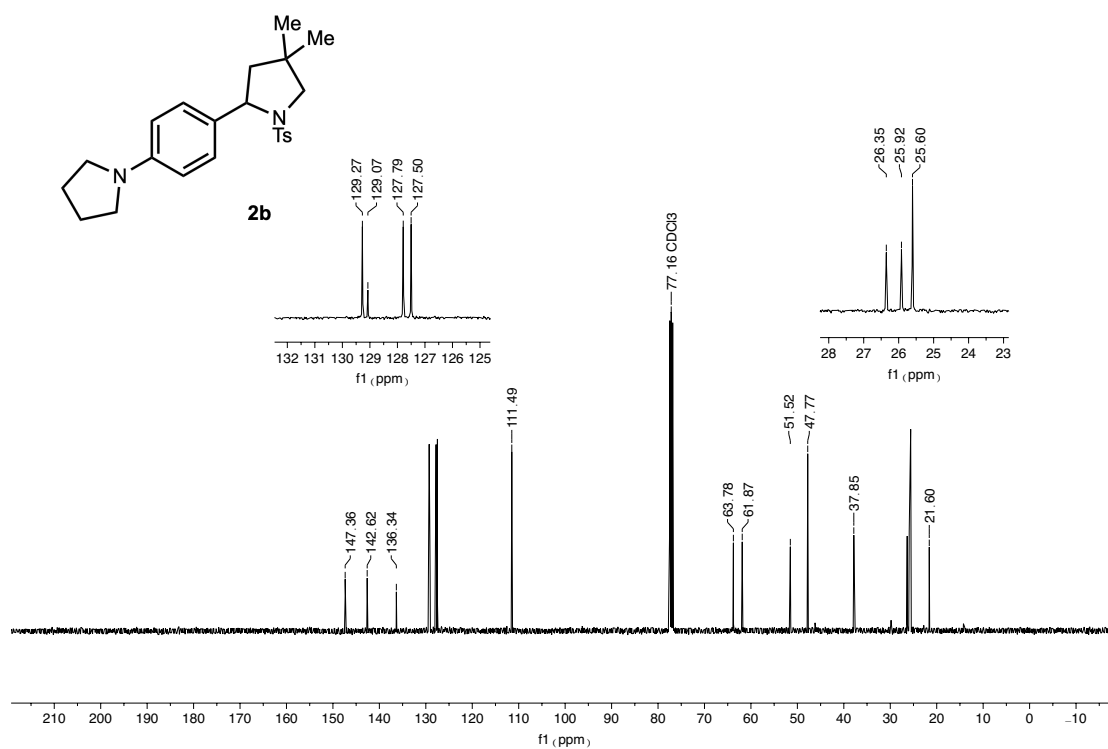
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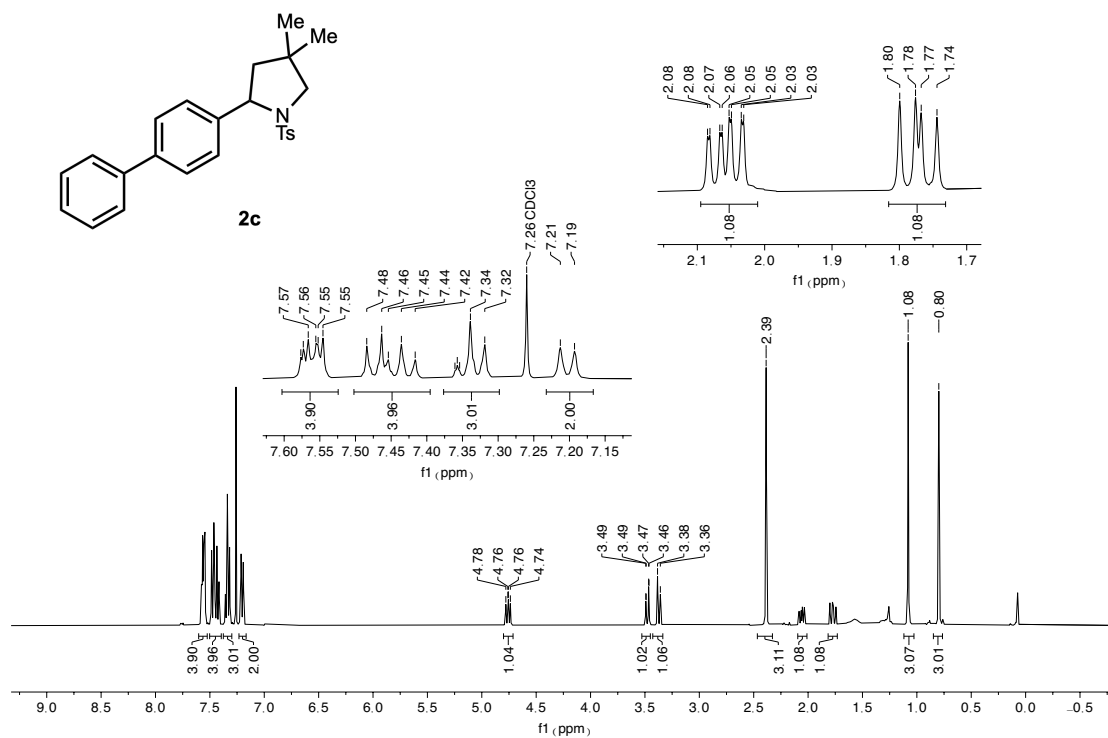
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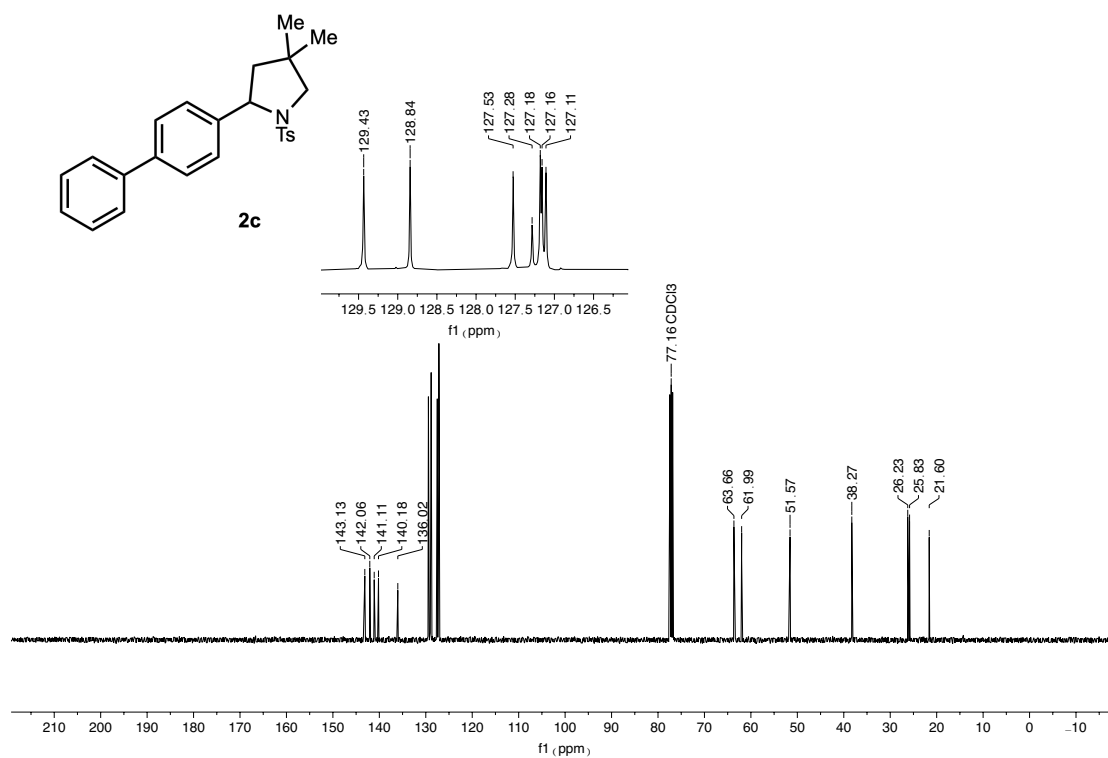
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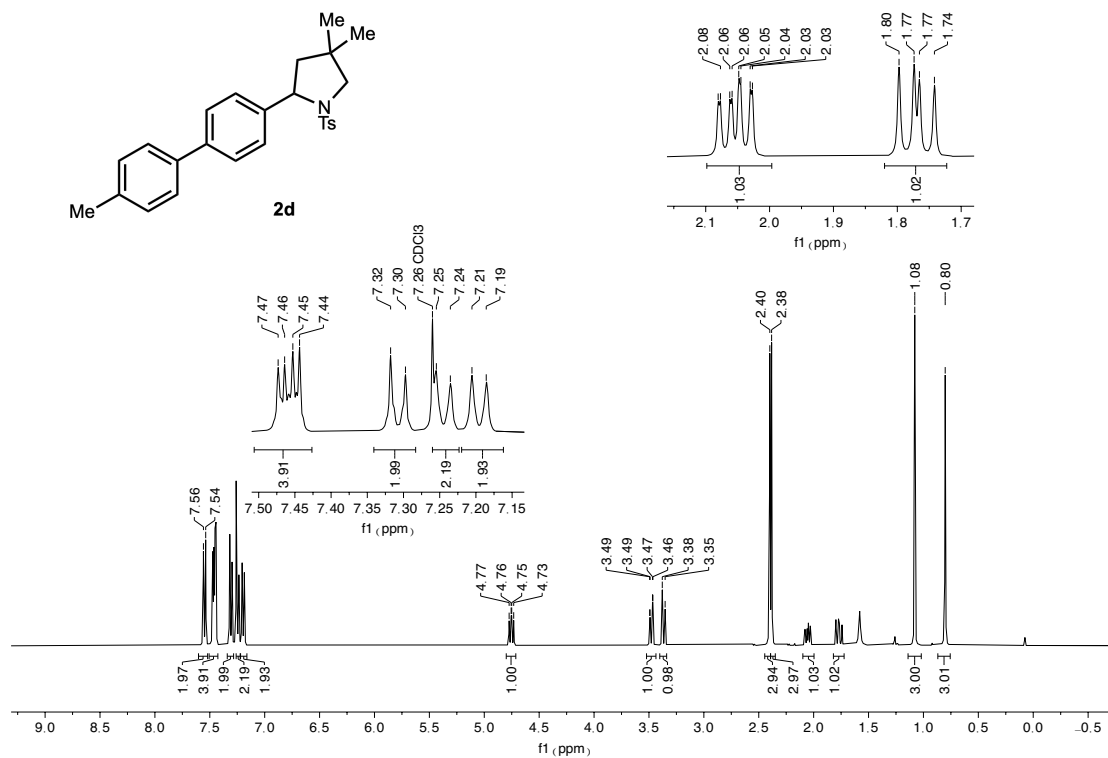
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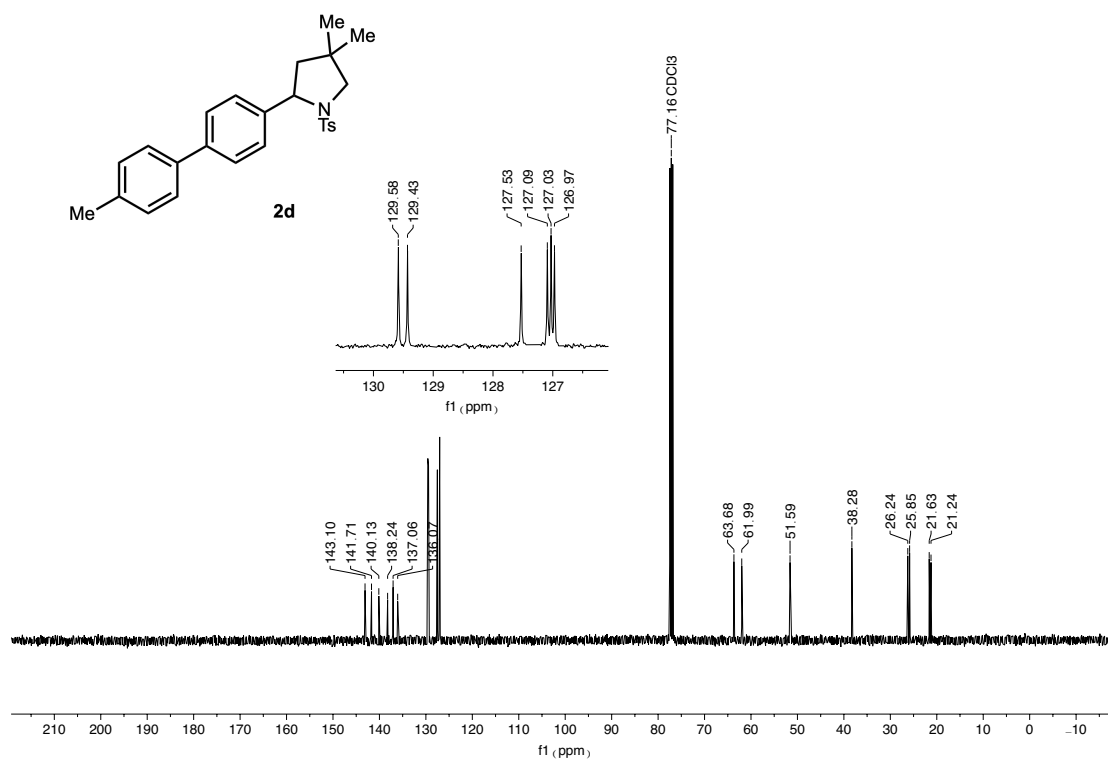
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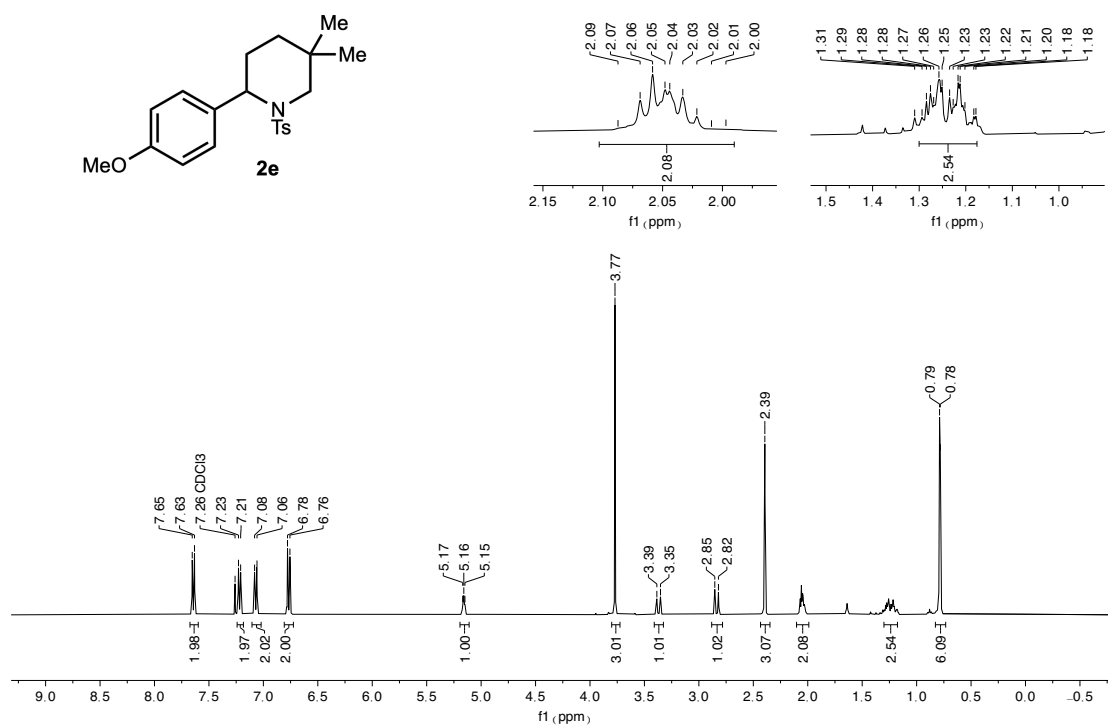
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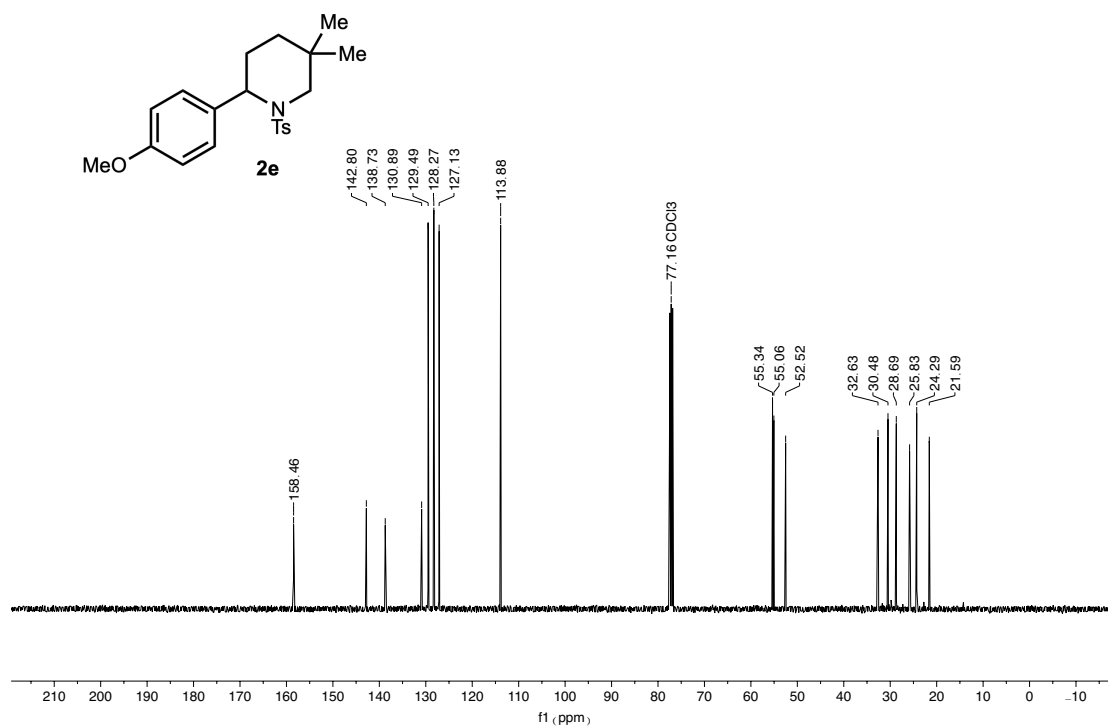
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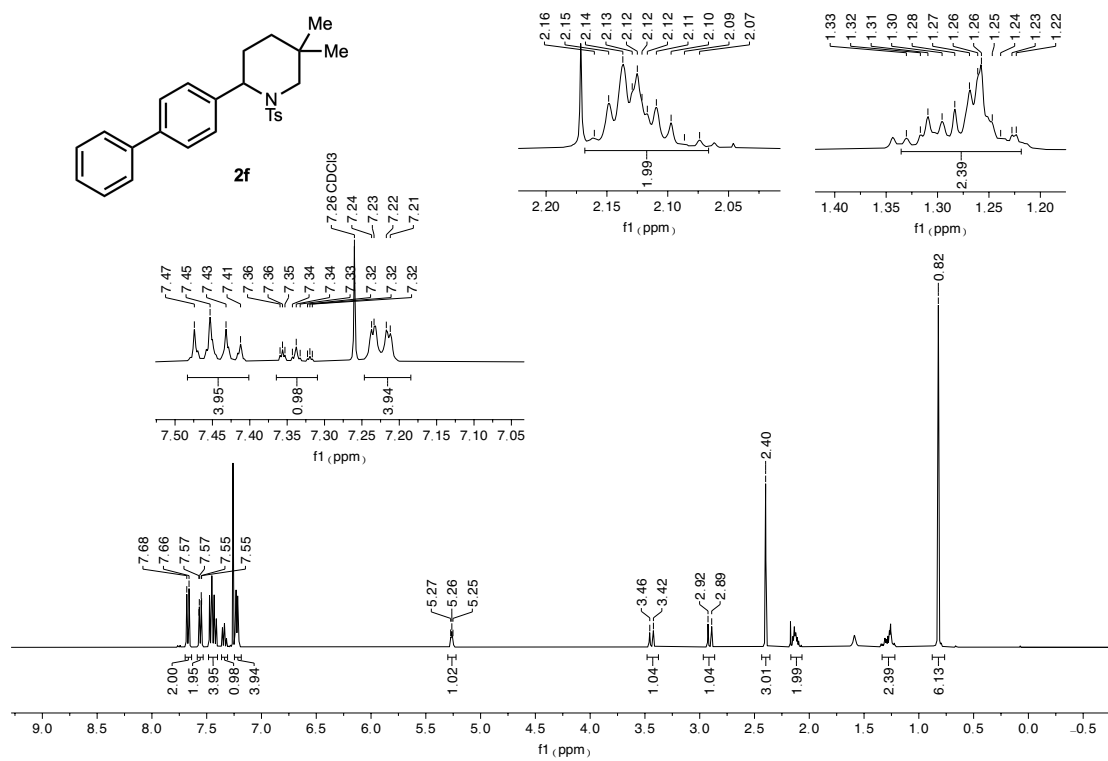
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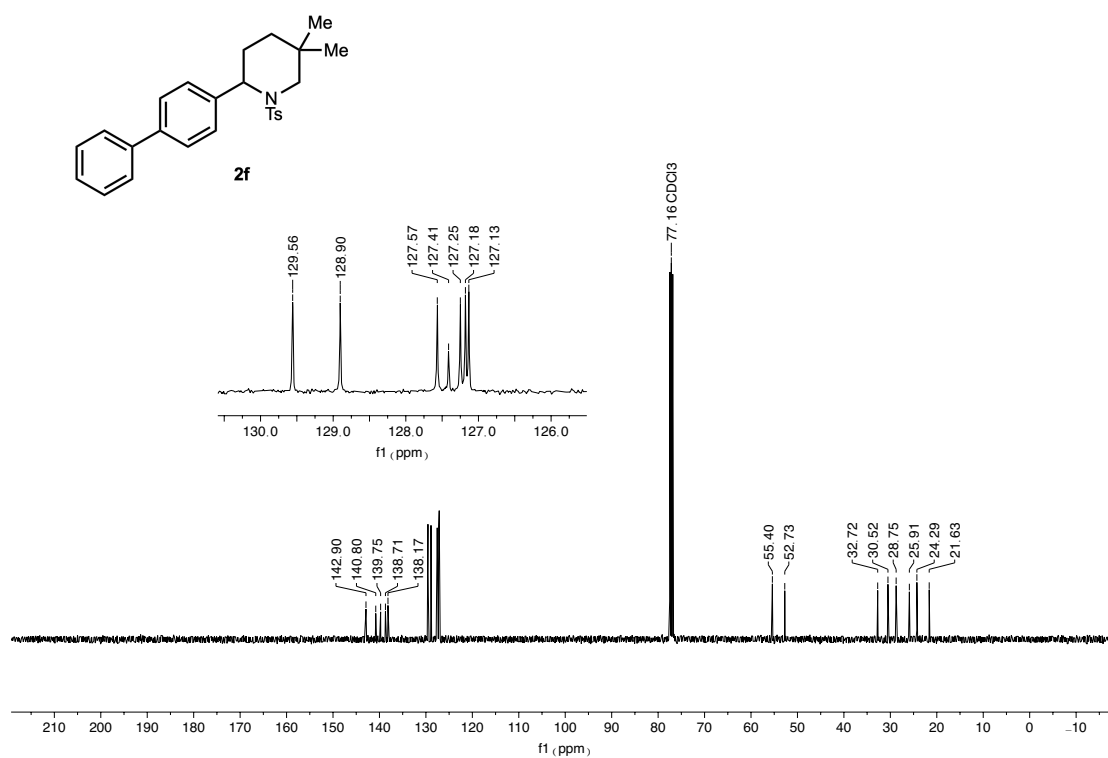
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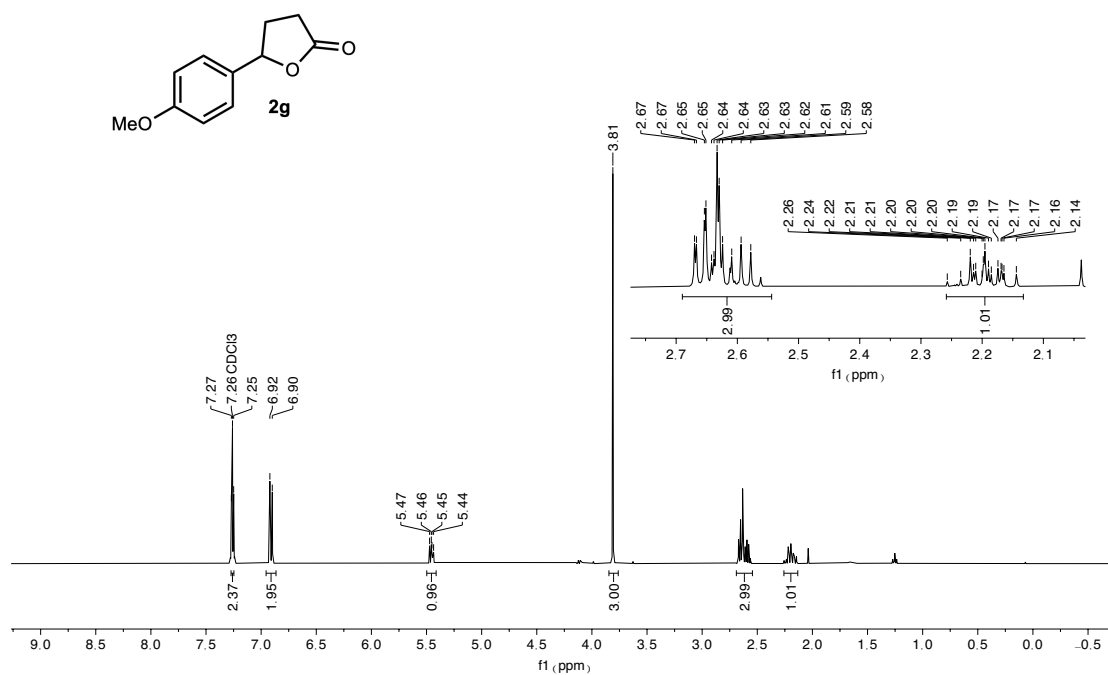
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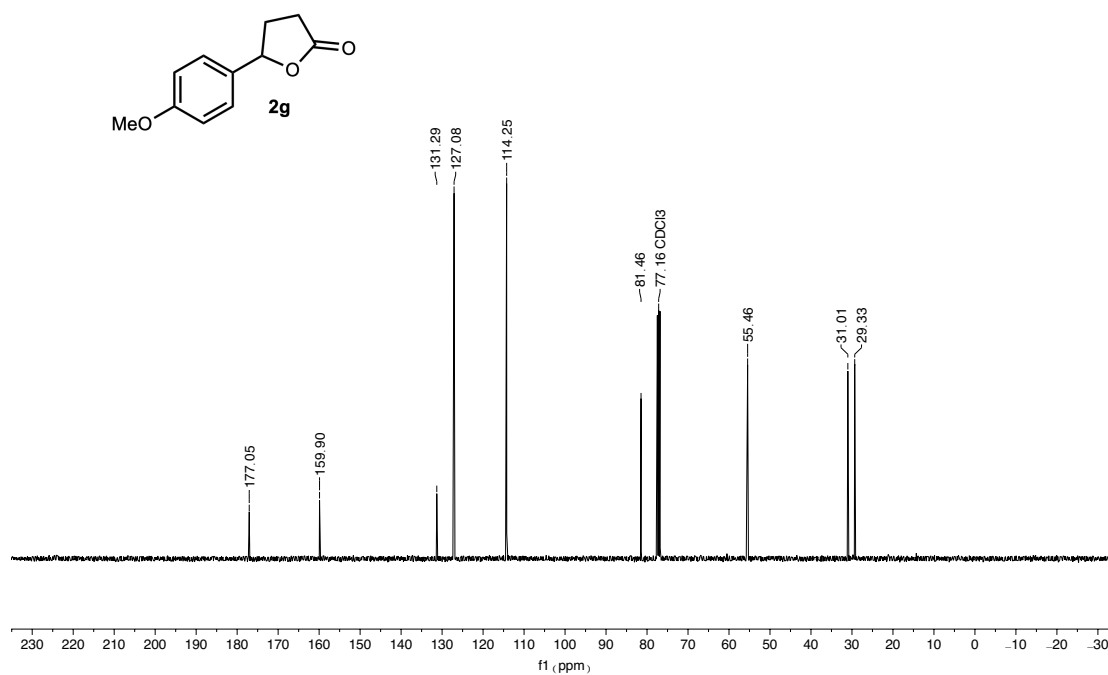
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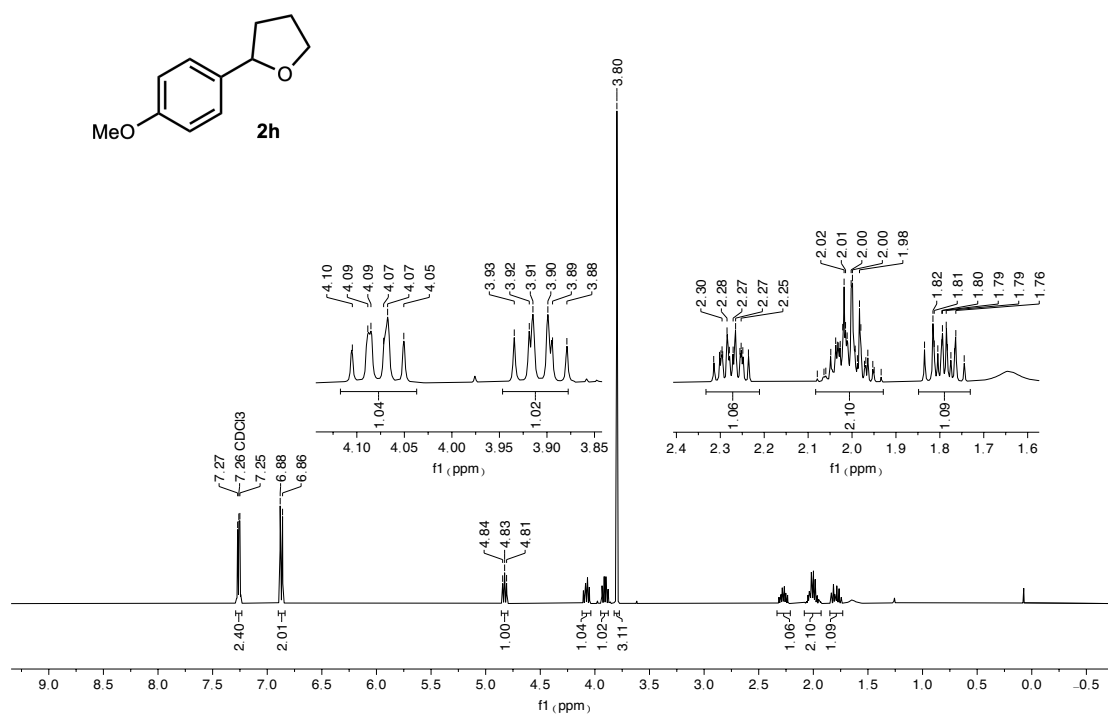
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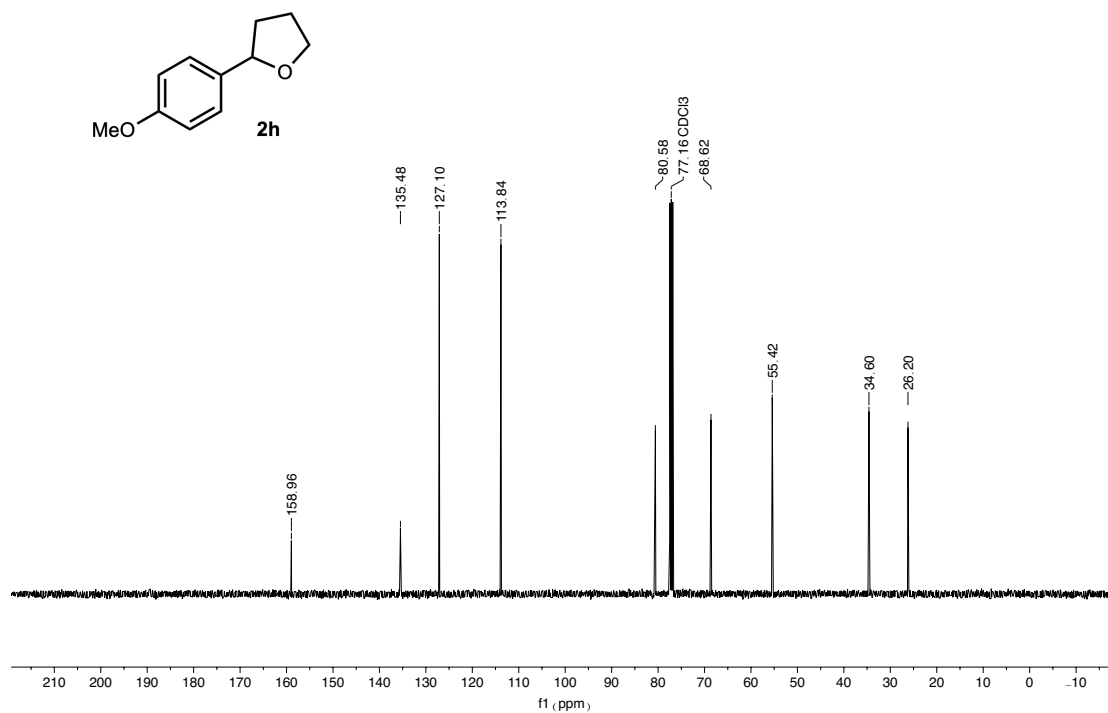
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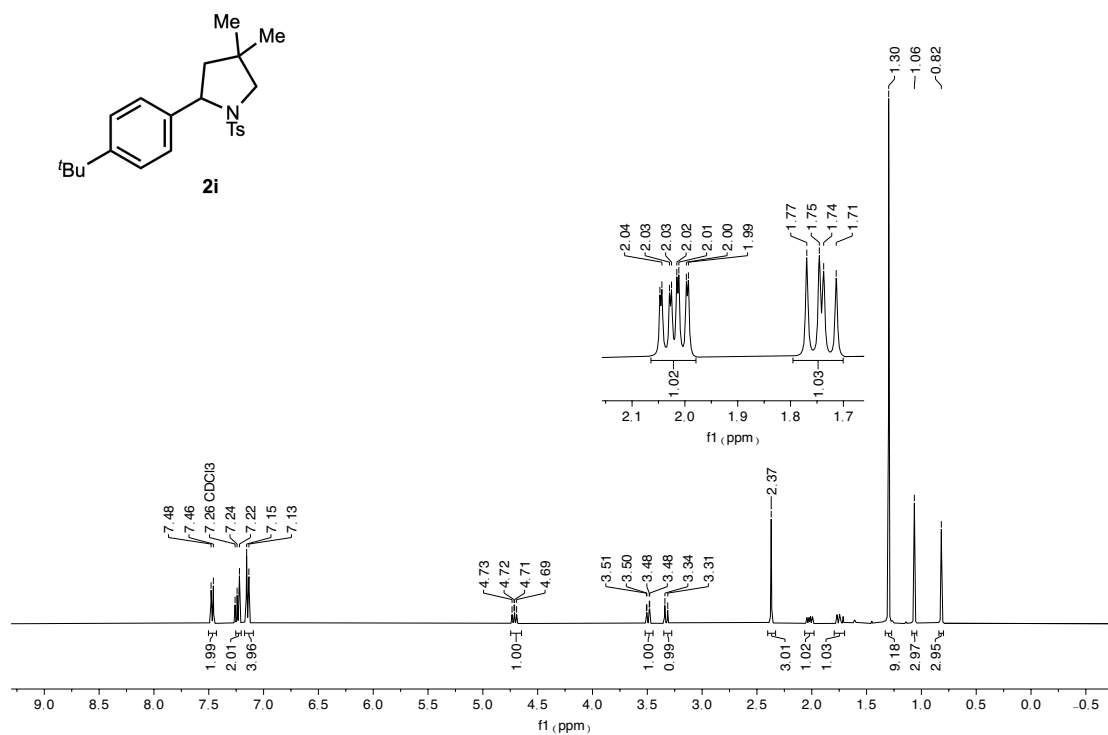
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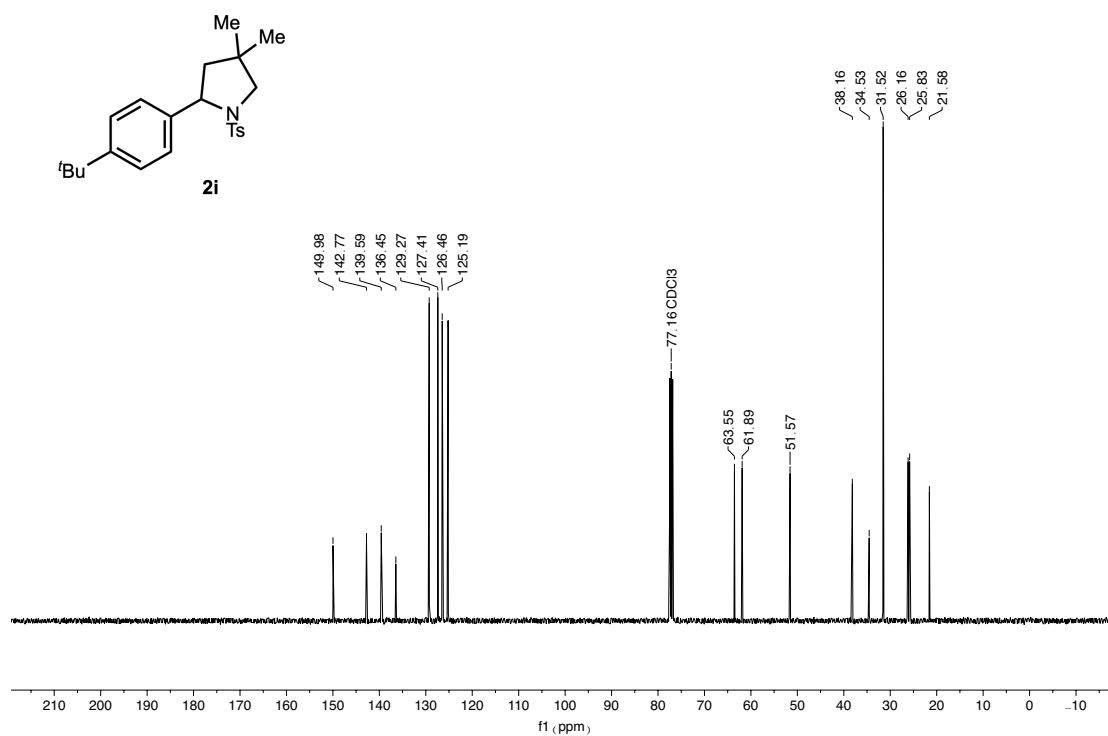
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2h**



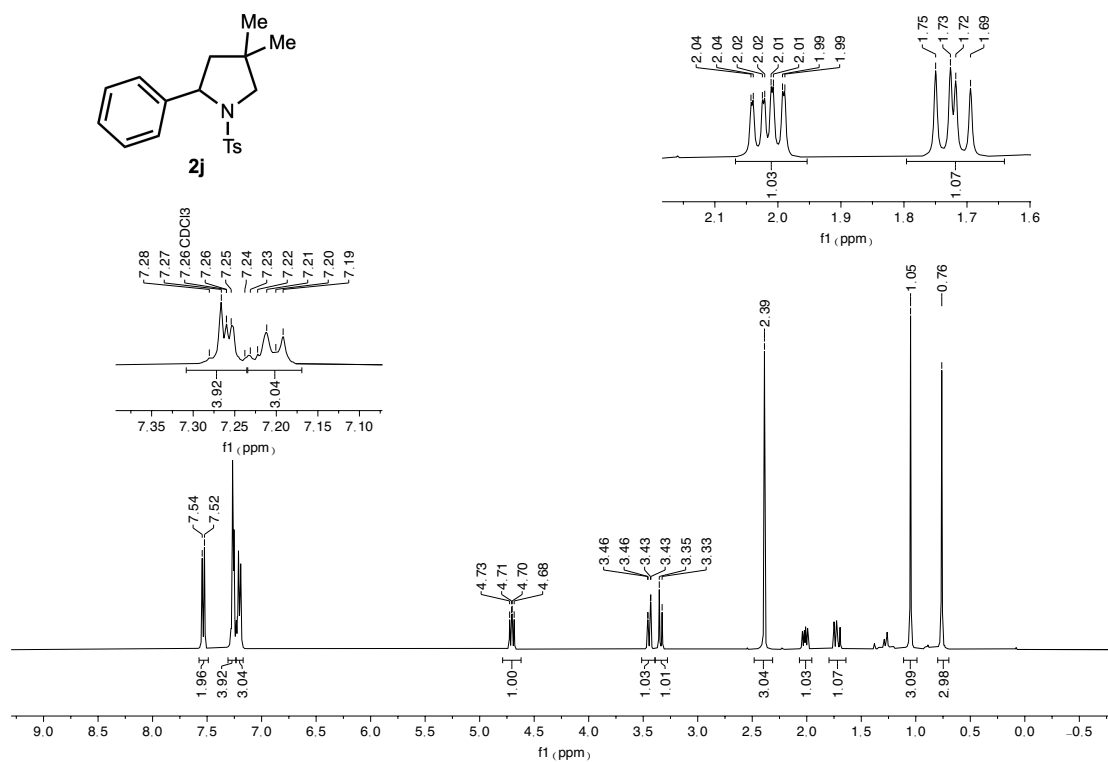
^1H NMR spectrum (400 MHz, CDCl_3) of **2i**



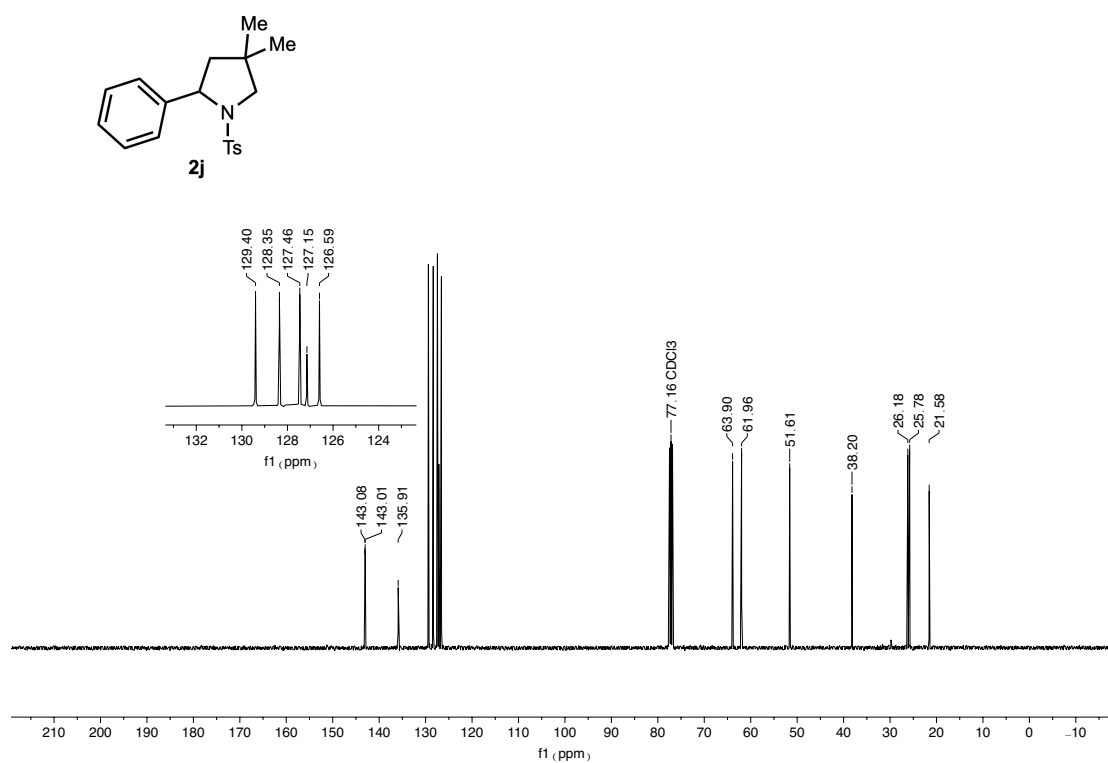
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2i**



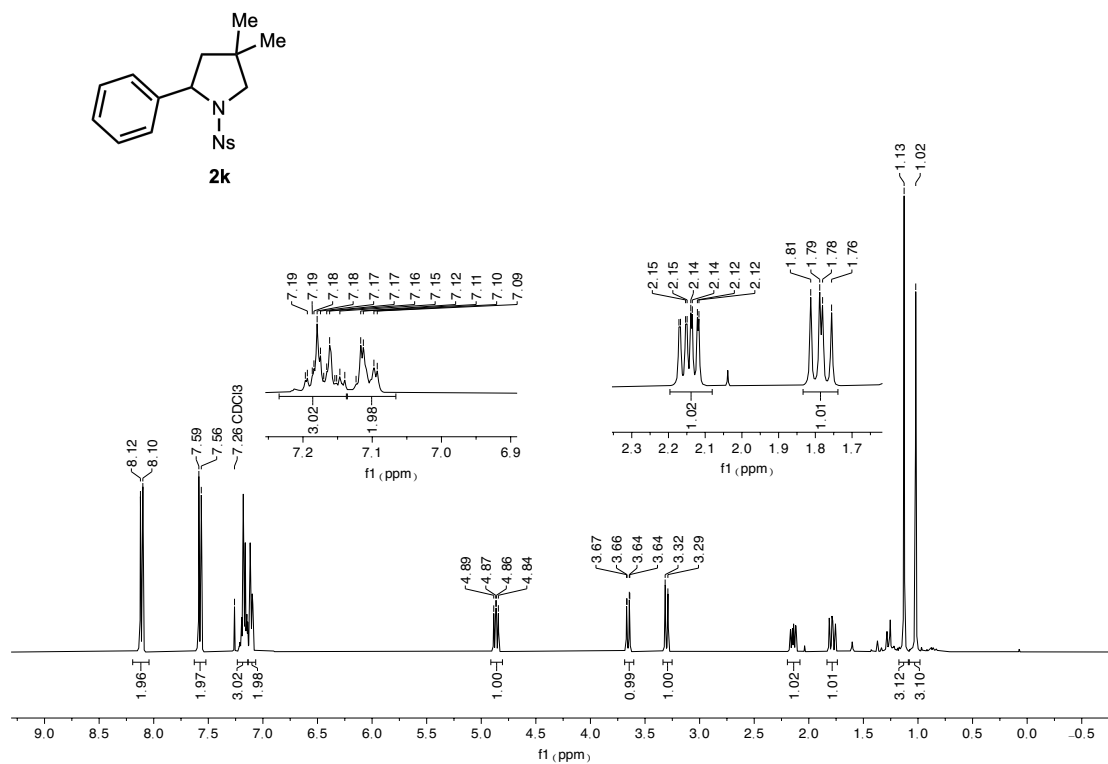
^1H NMR spectrum (400 MHz, CDCl_3) of **2j**



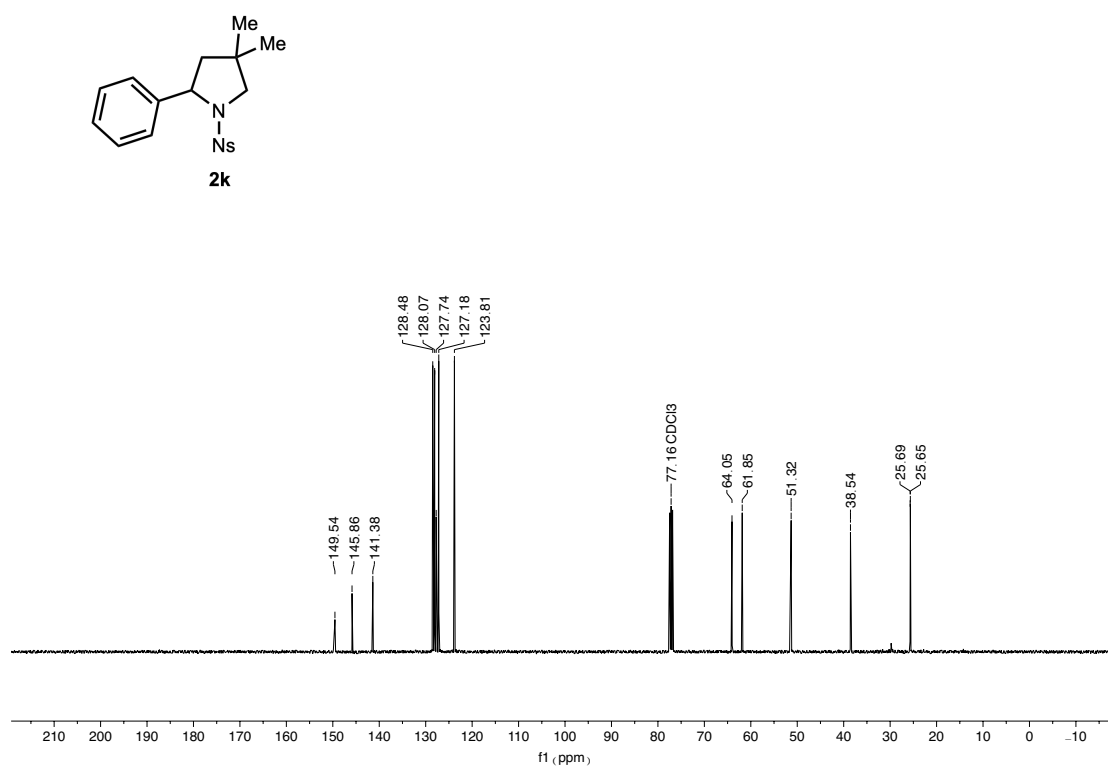
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2j**



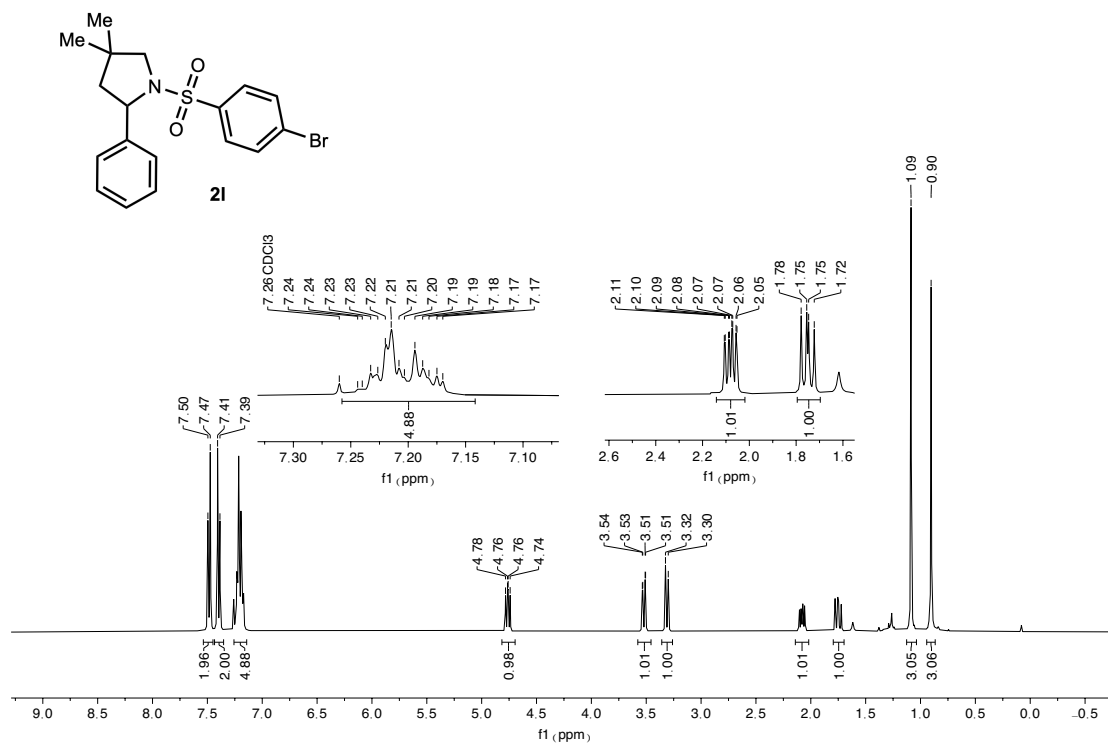
^1H NMR spectrum (400 MHz, CDCl_3) of **2k**



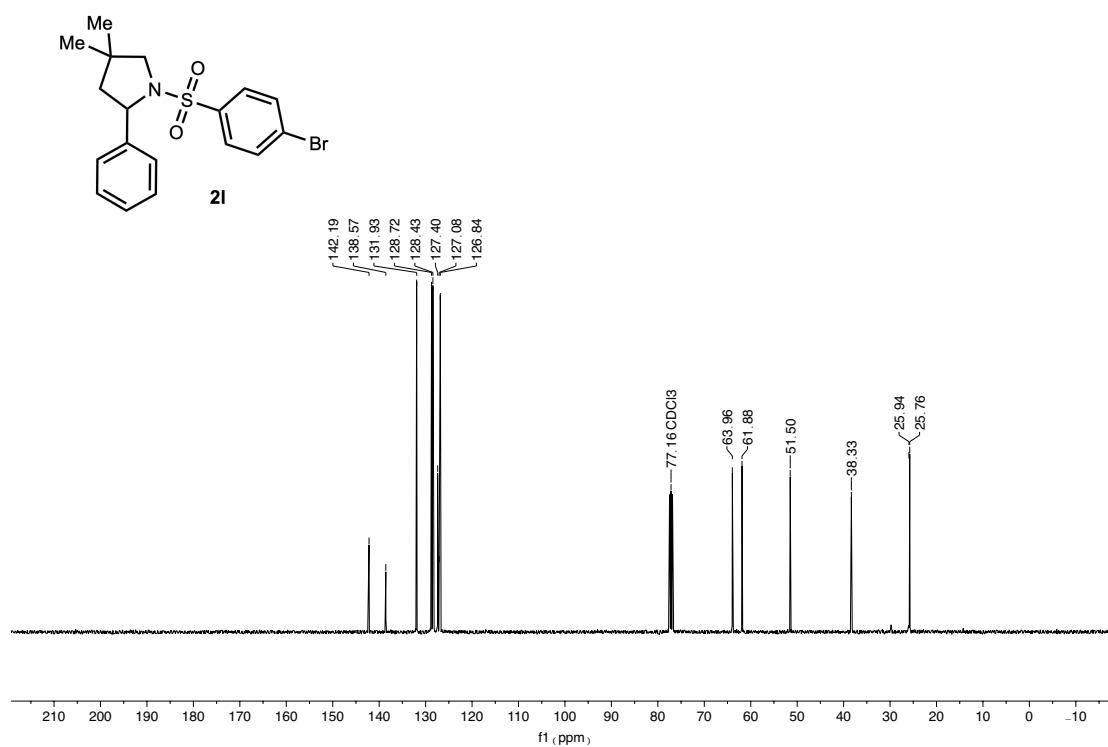
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2k**



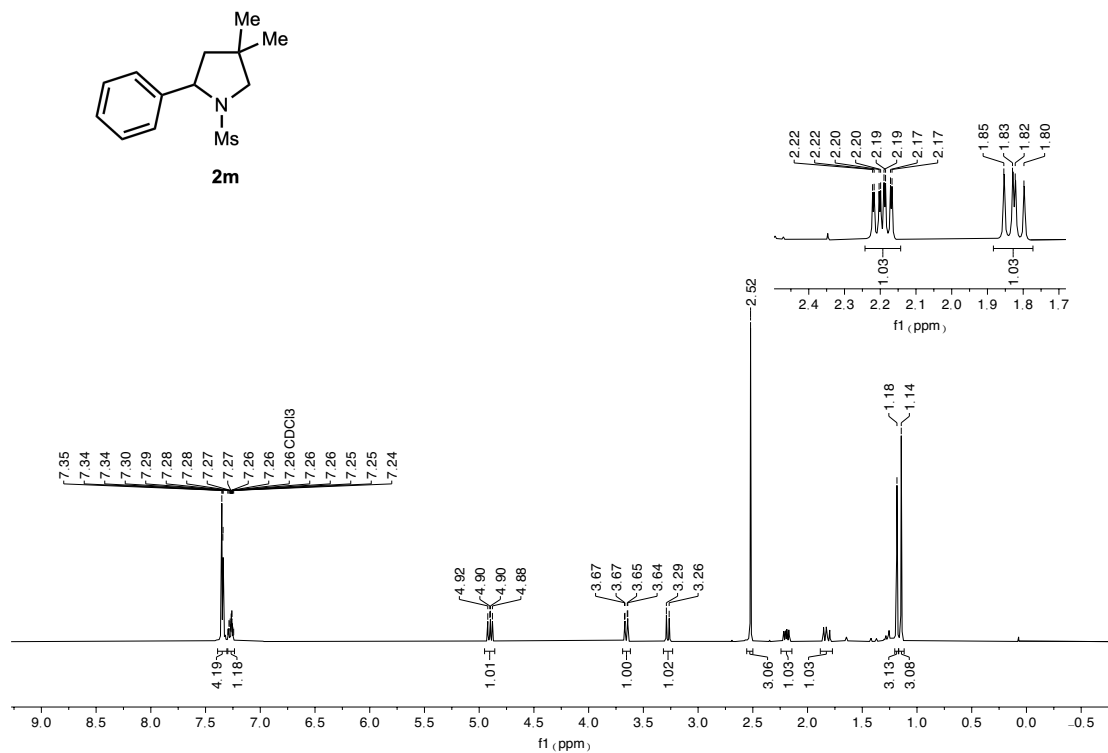
^1H NMR spectrum (400 MHz, CDCl_3) of **2l**



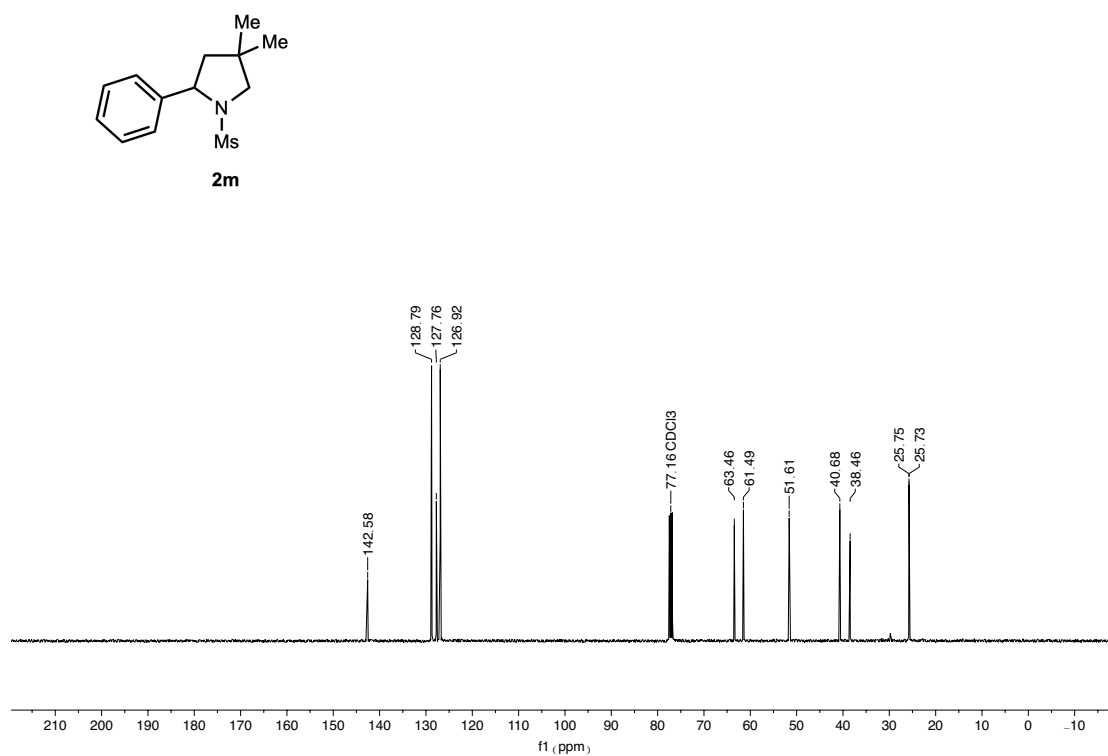
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2l**



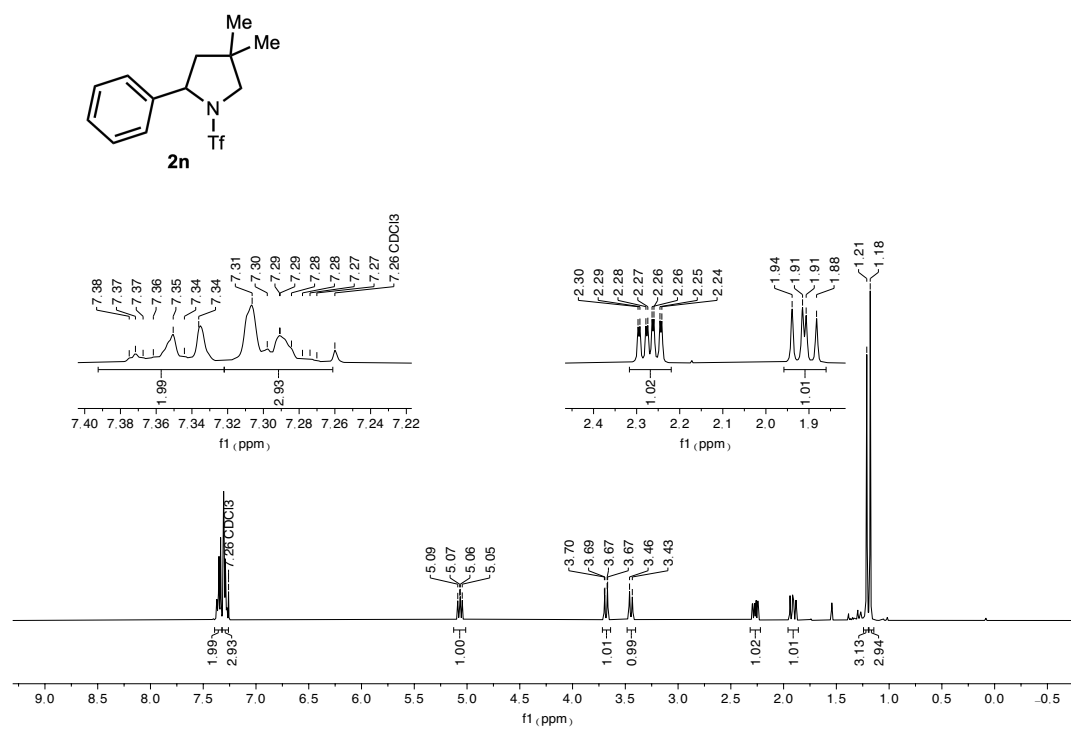
^1H NMR spectrum (400 MHz, CDCl_3) of **2m**



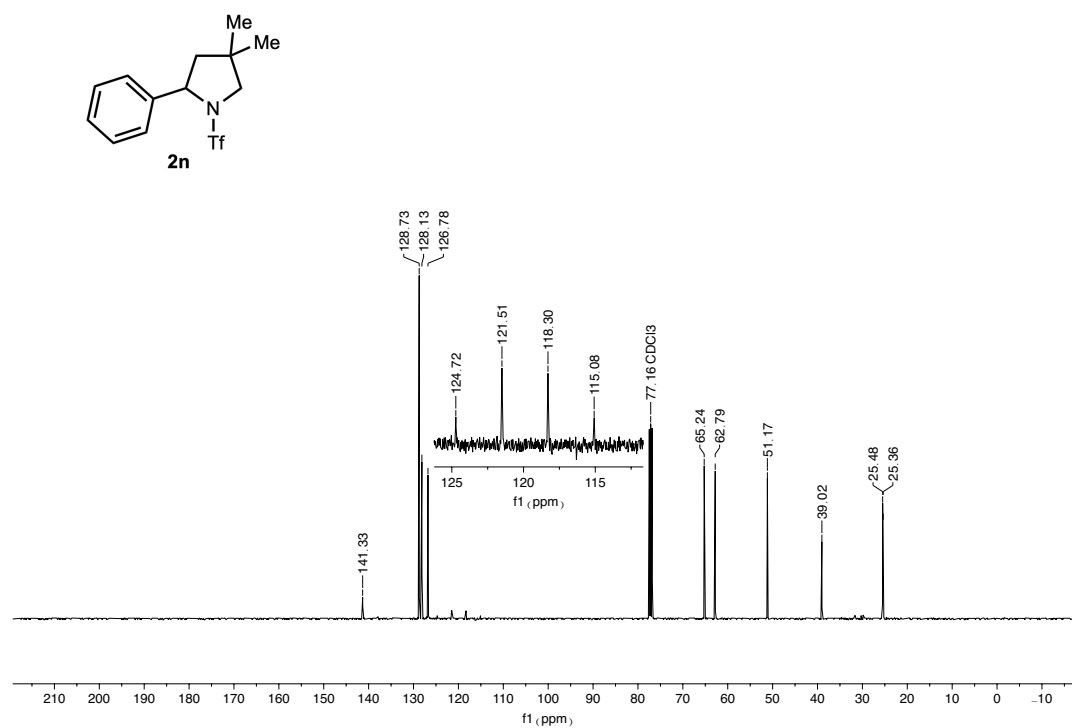
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2m**



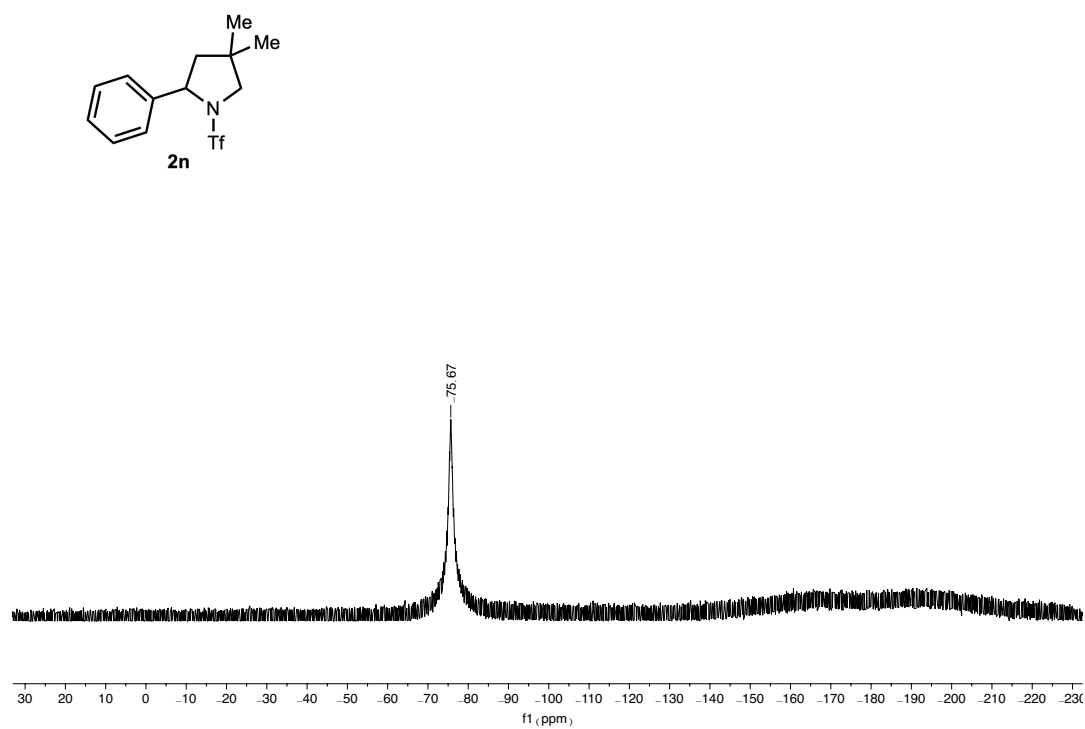
^1H NMR spectrum (400 MHz, CDCl_3) of **2n**



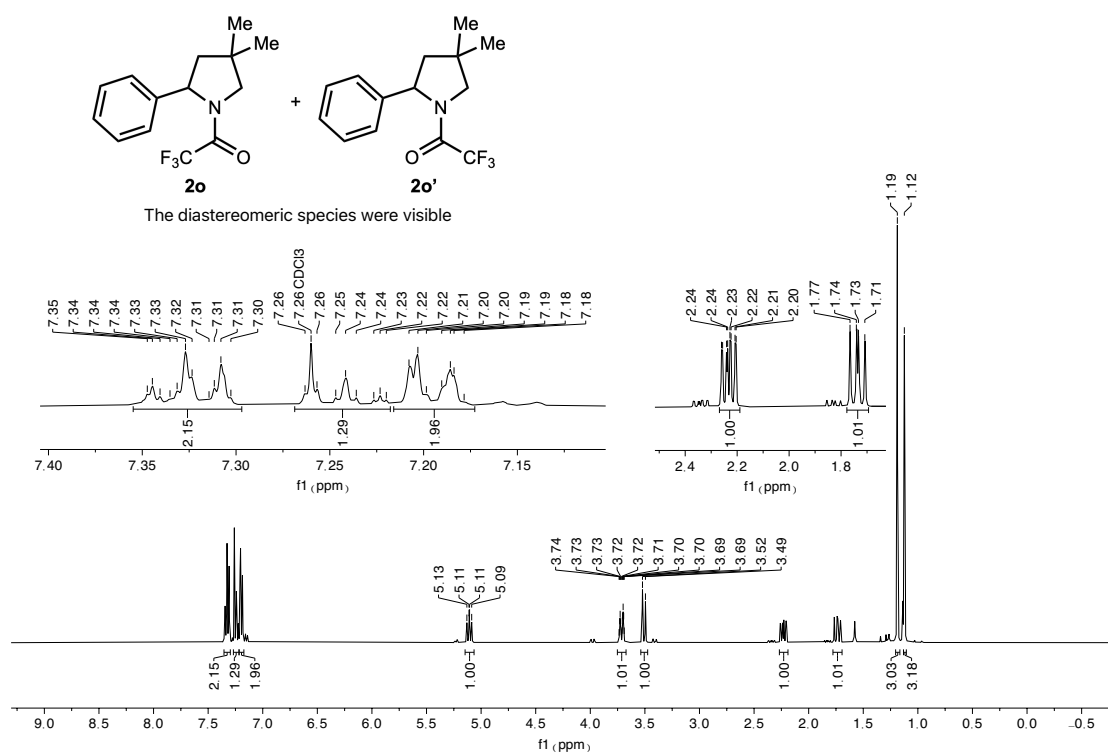
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2n**



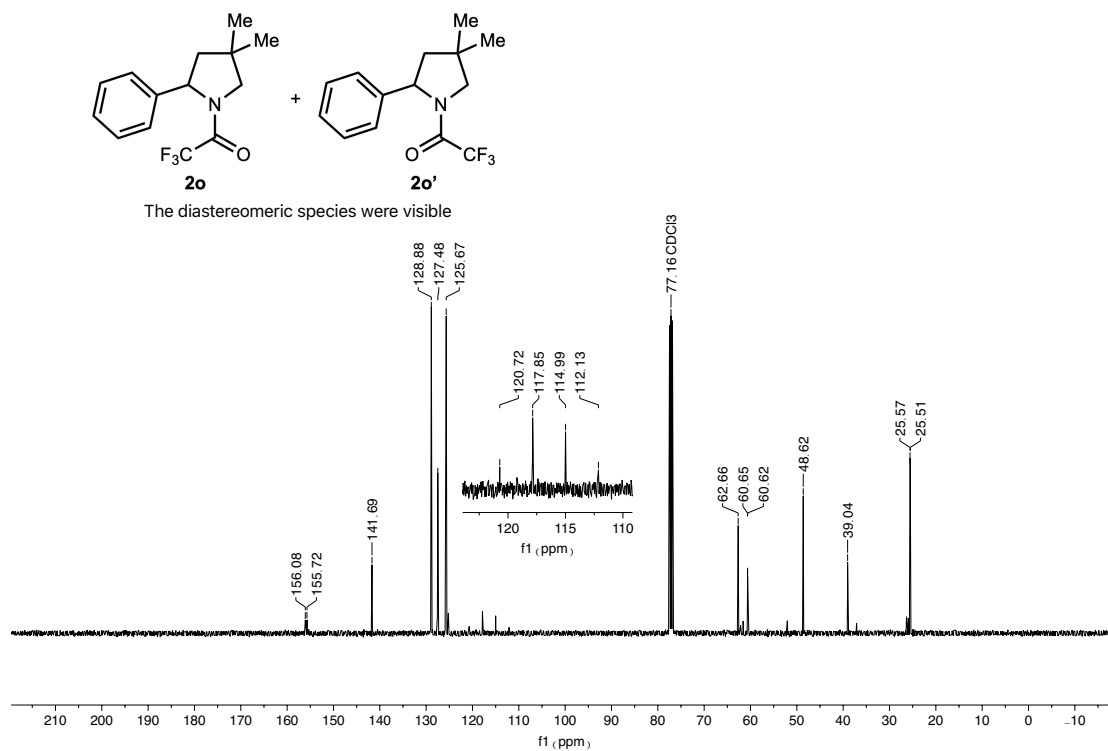
^{19}F NMR spectrum (375 MHz, CDCl_3) of **2n**



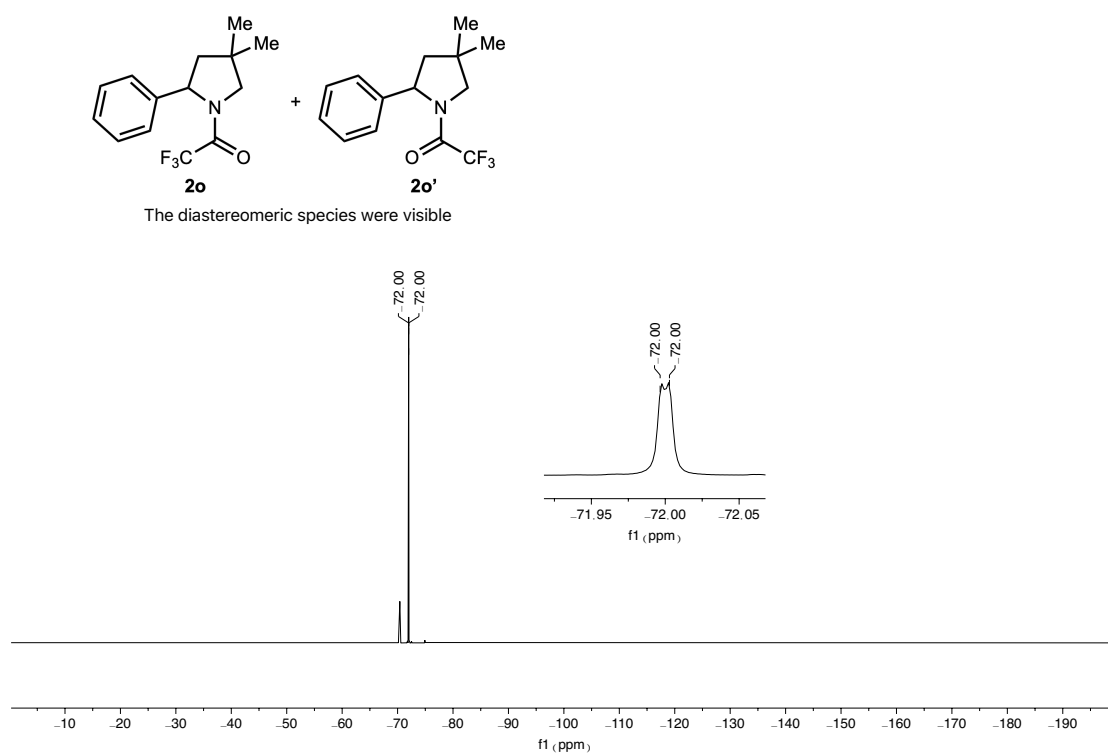
¹H NMR spectrum (400 MHz, CDCl₃) of **2o**



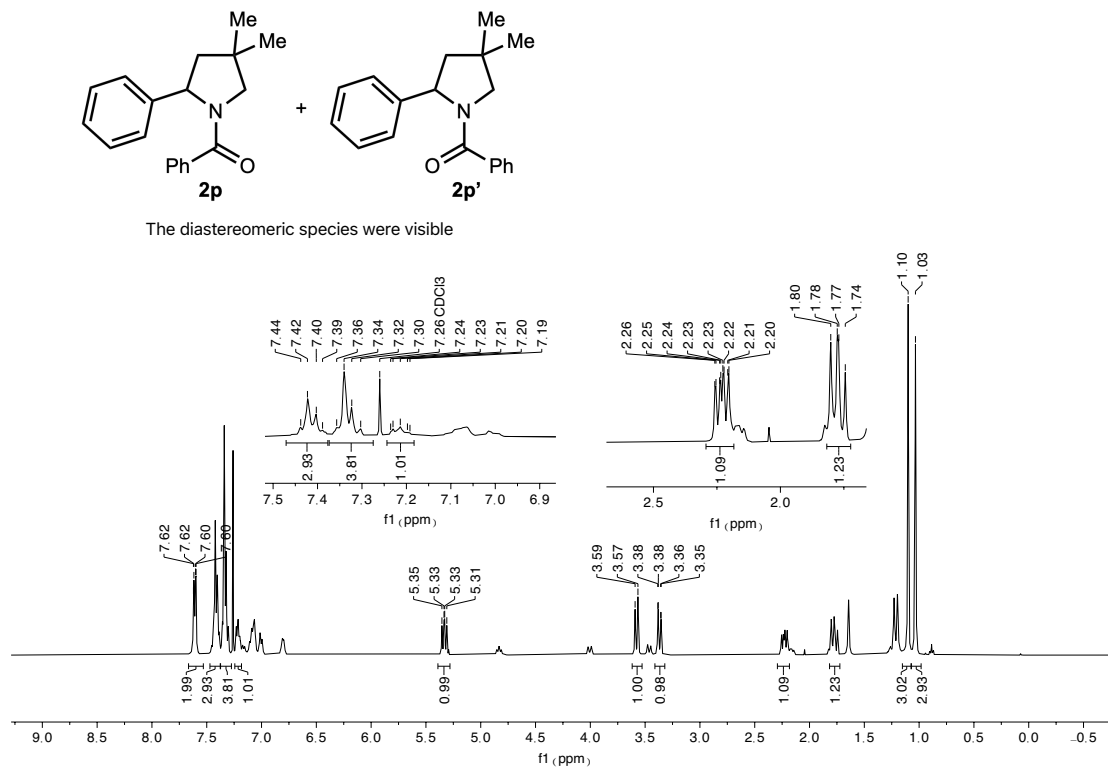
¹³C NMR spectrum (100 MHz, CDCl₃) of **2o**



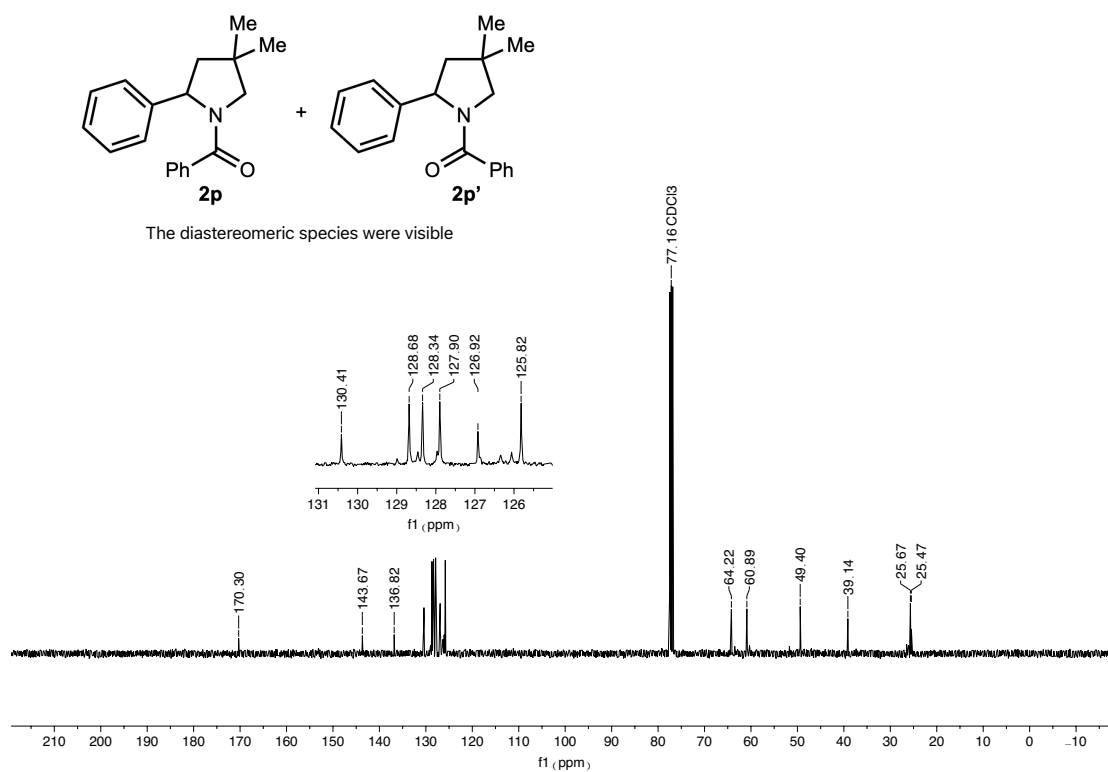
^{19}F NMR spectrum (375 MHz, CDCl_3) of **2o**



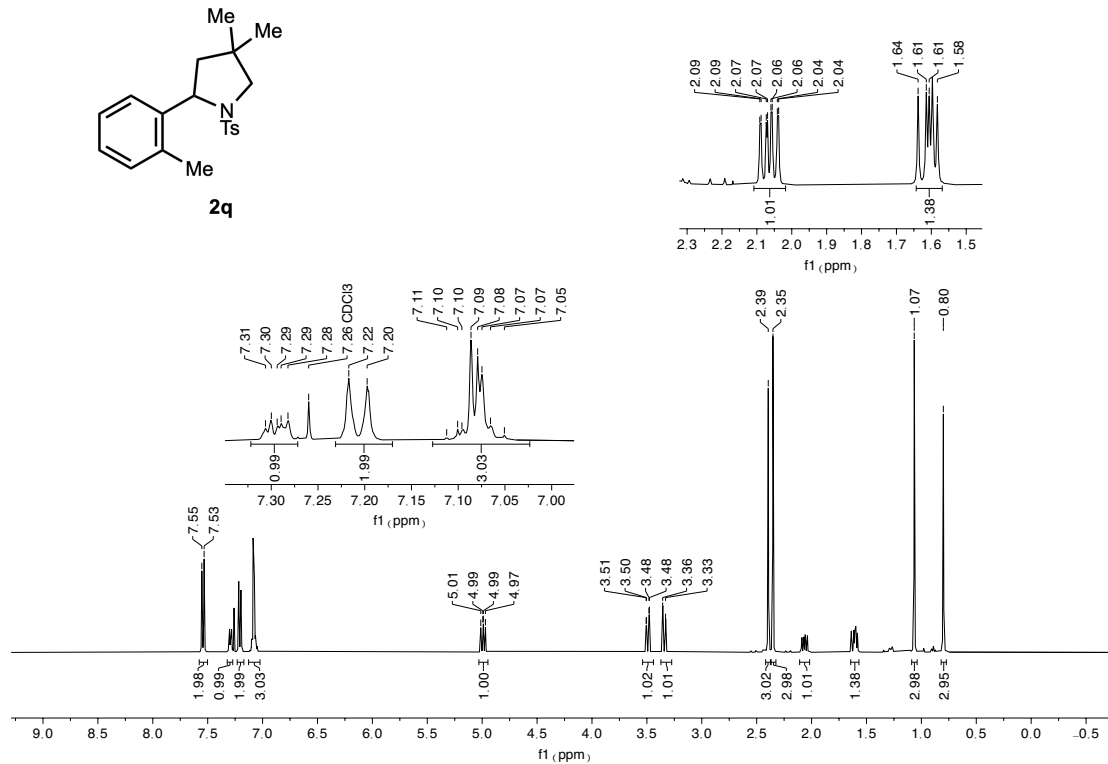
^1H NMR spectrum (400 MHz, CDCl_3) of **2p**



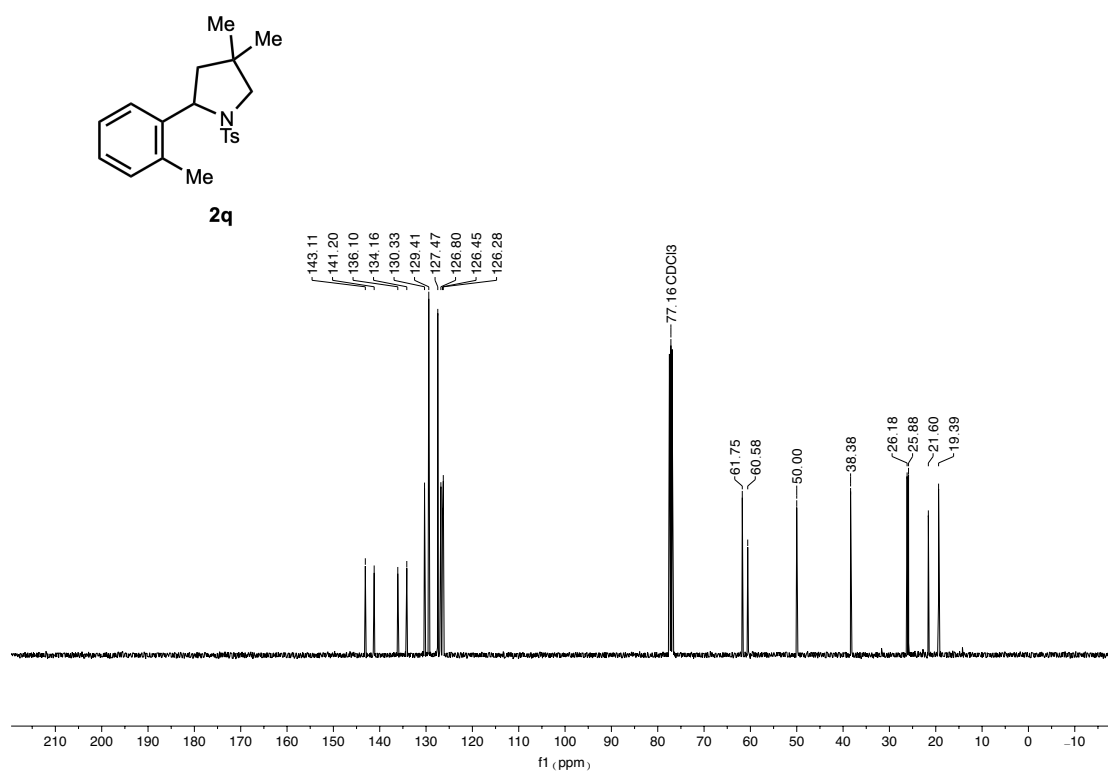
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2p**



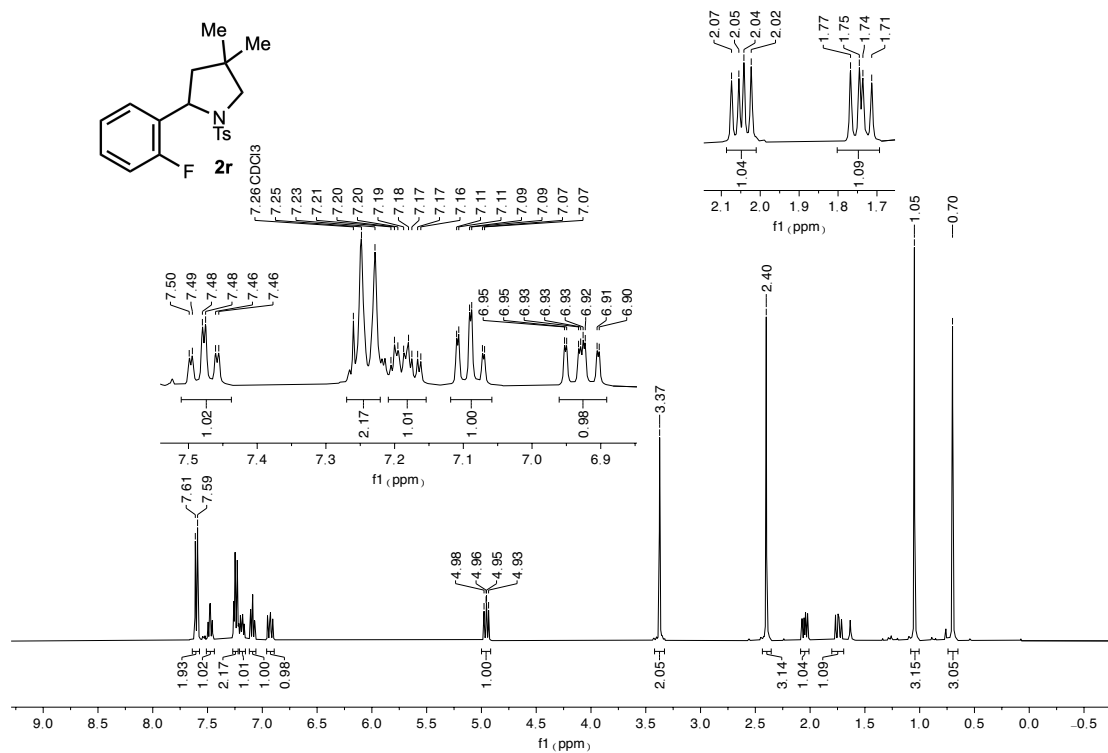
^1H NMR spectrum (400 MHz, CDCl_3) of **2q**



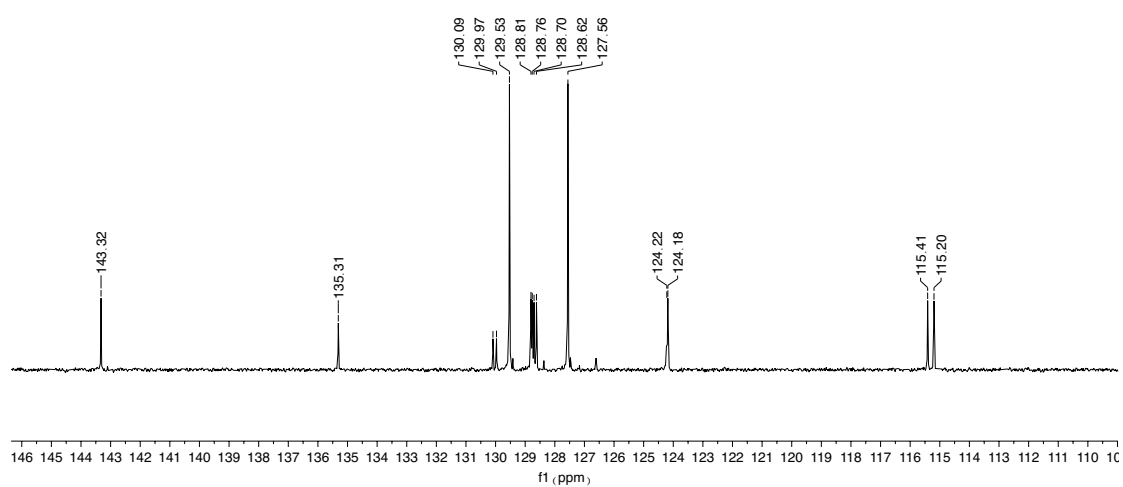
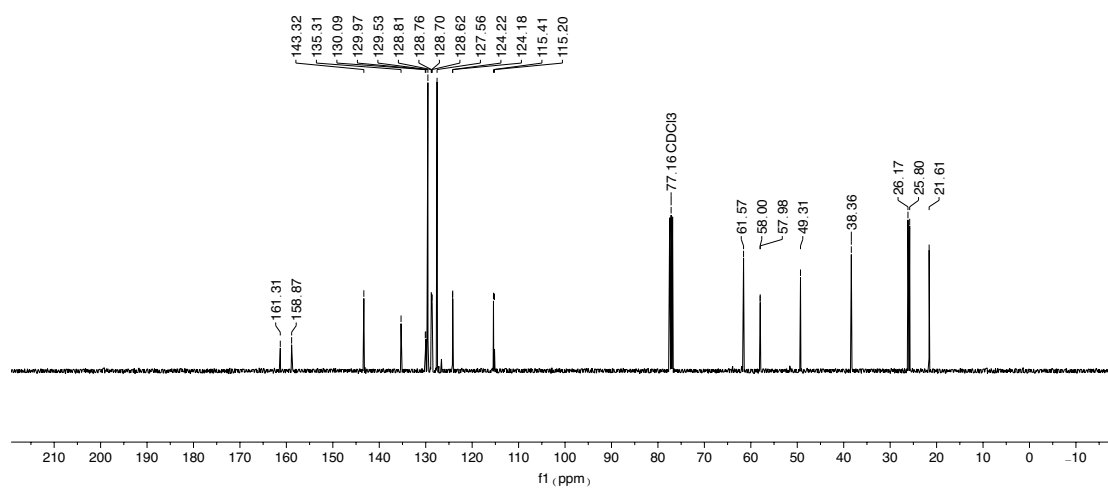
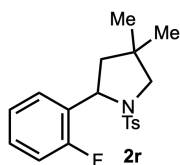
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2q**



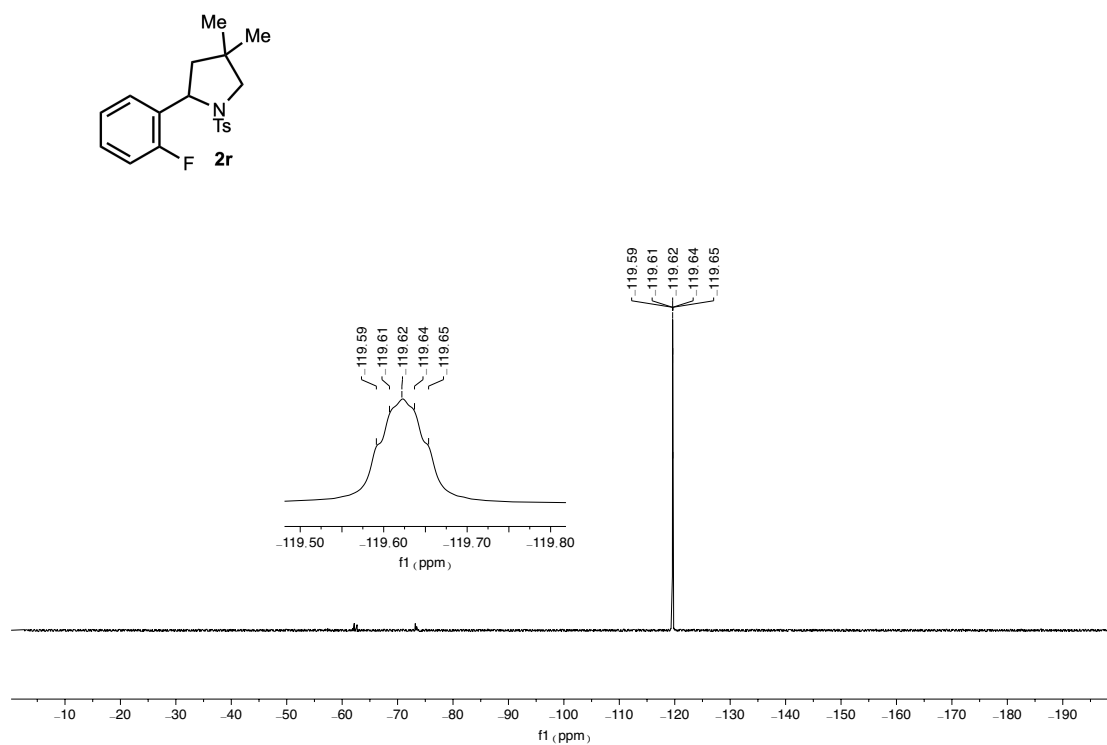
^1H NMR spectrum (400 MHz, CDCl_3) of **2r**



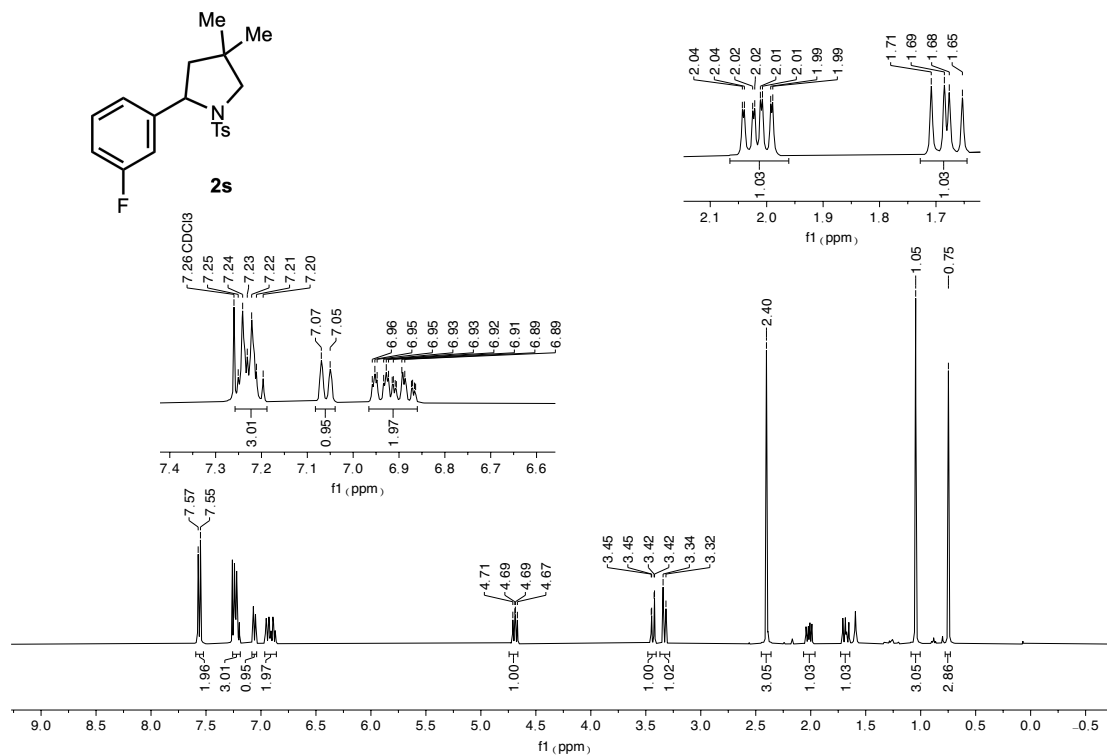
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2r**



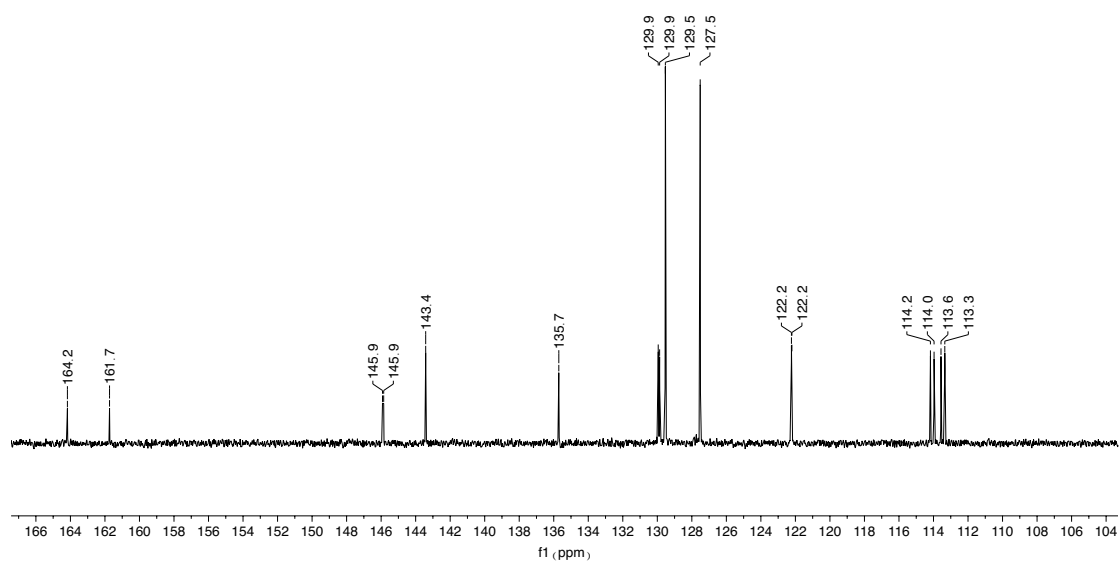
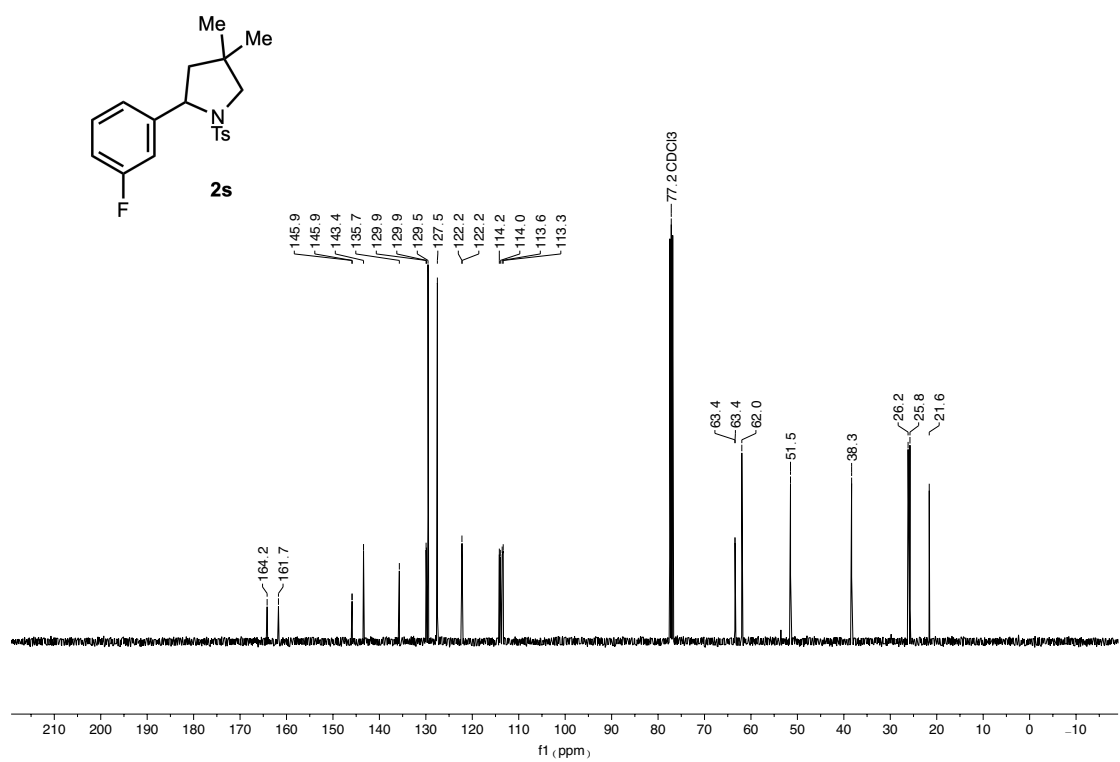
^{19}F NMR spectrum (375 MHz, CDCl_3) of **2r**



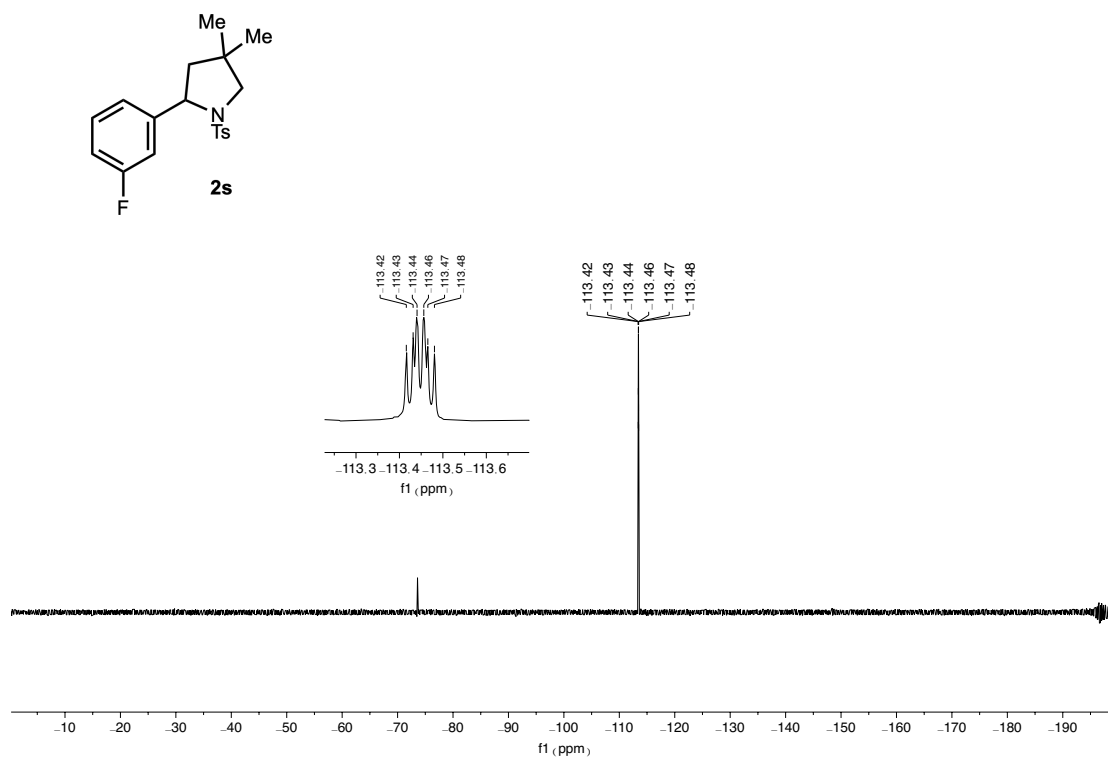
^1H NMR spectrum (400 MHz, CDCl_3) of **2s**



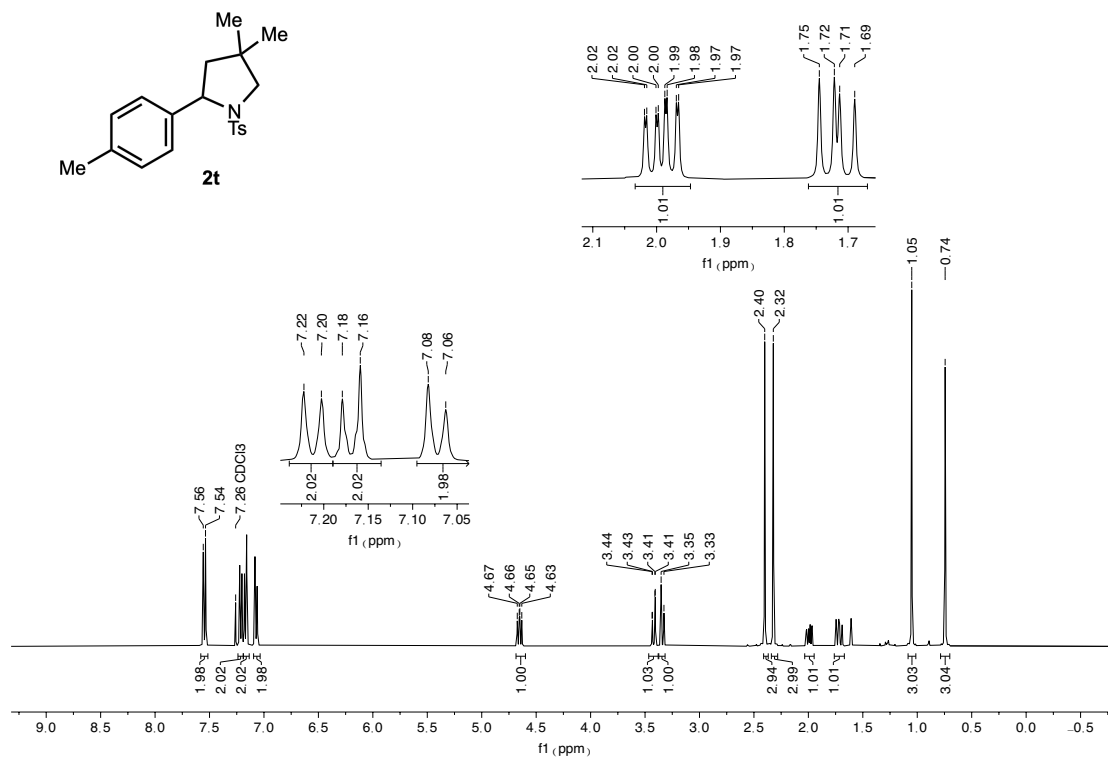
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2s**



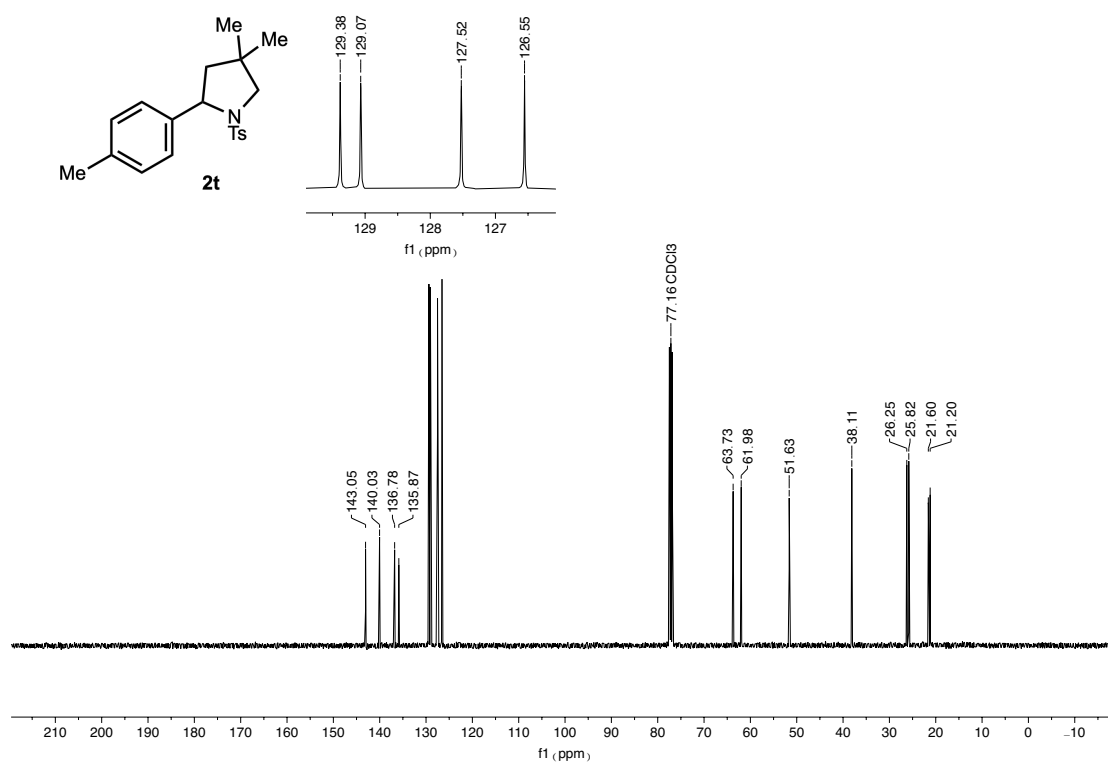
^{19}F NMR spectrum (375 MHz, CDCl_3) of **2s**



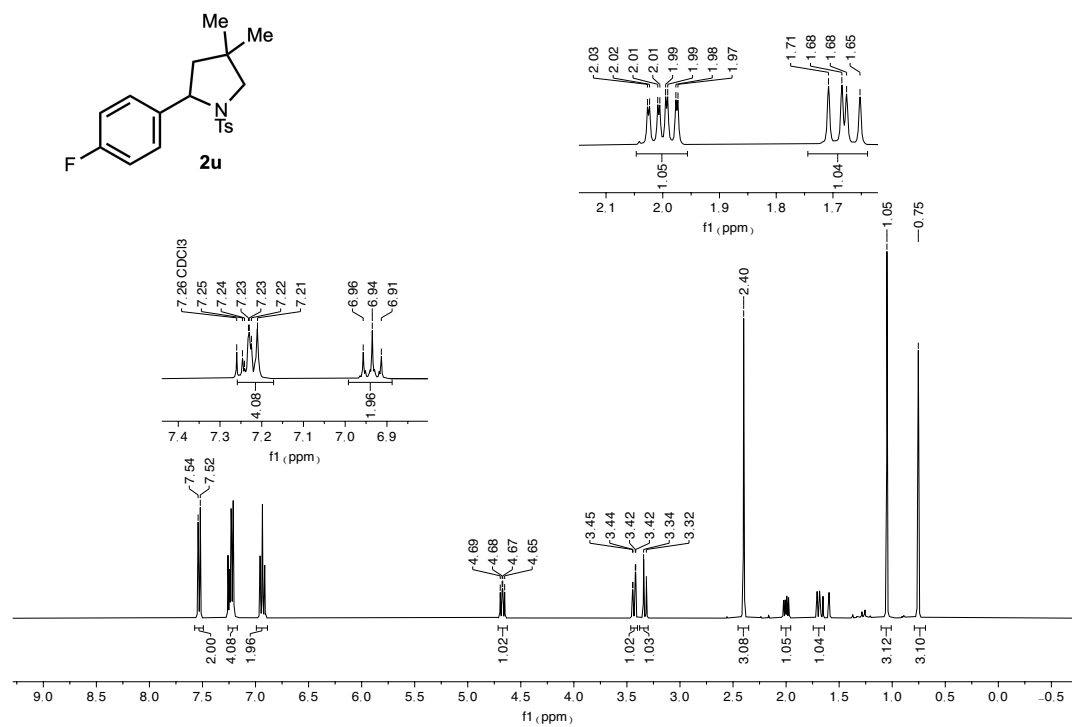
^1H NMR spectrum (400 MHz, CDCl_3) of **2t**



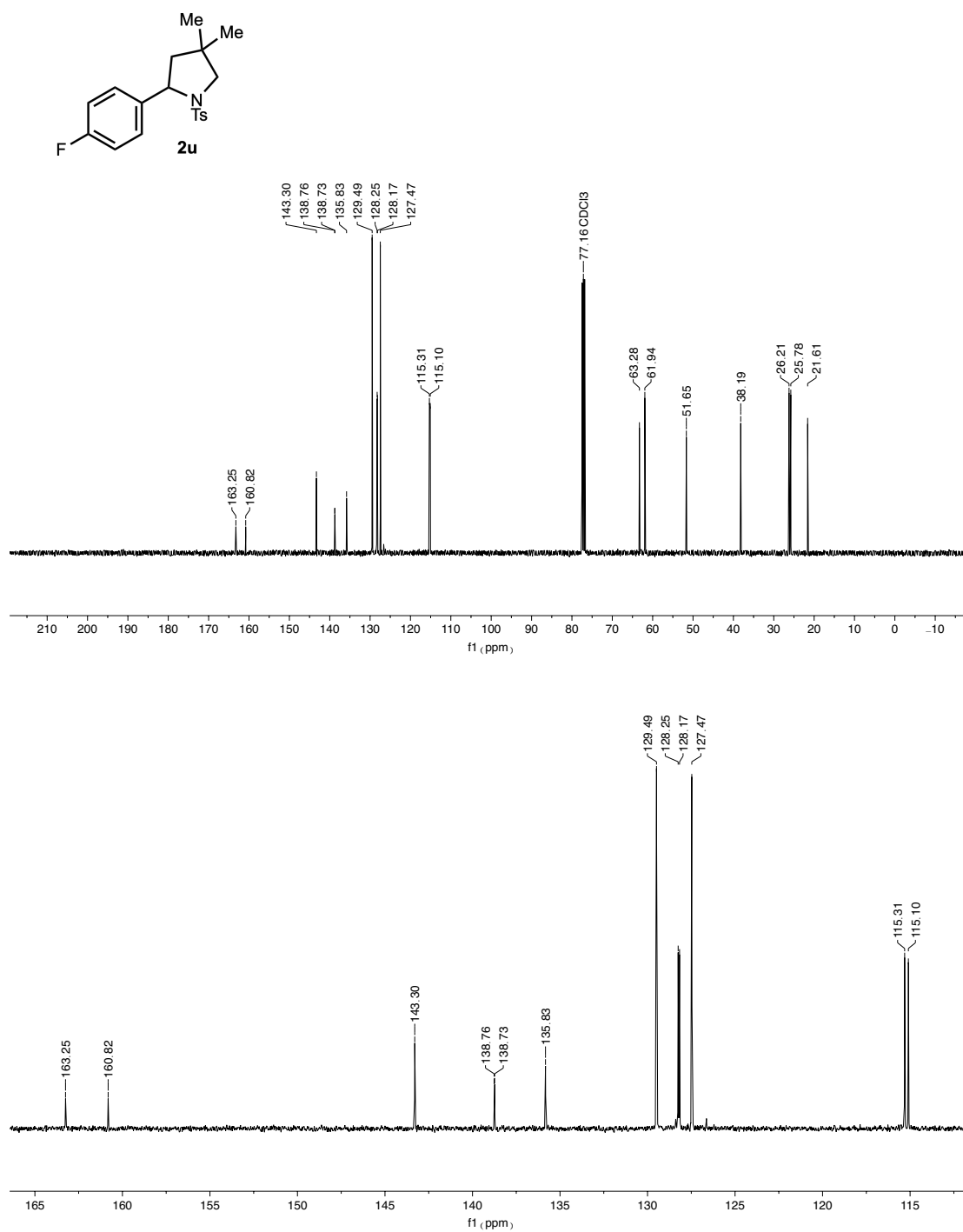
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2t**



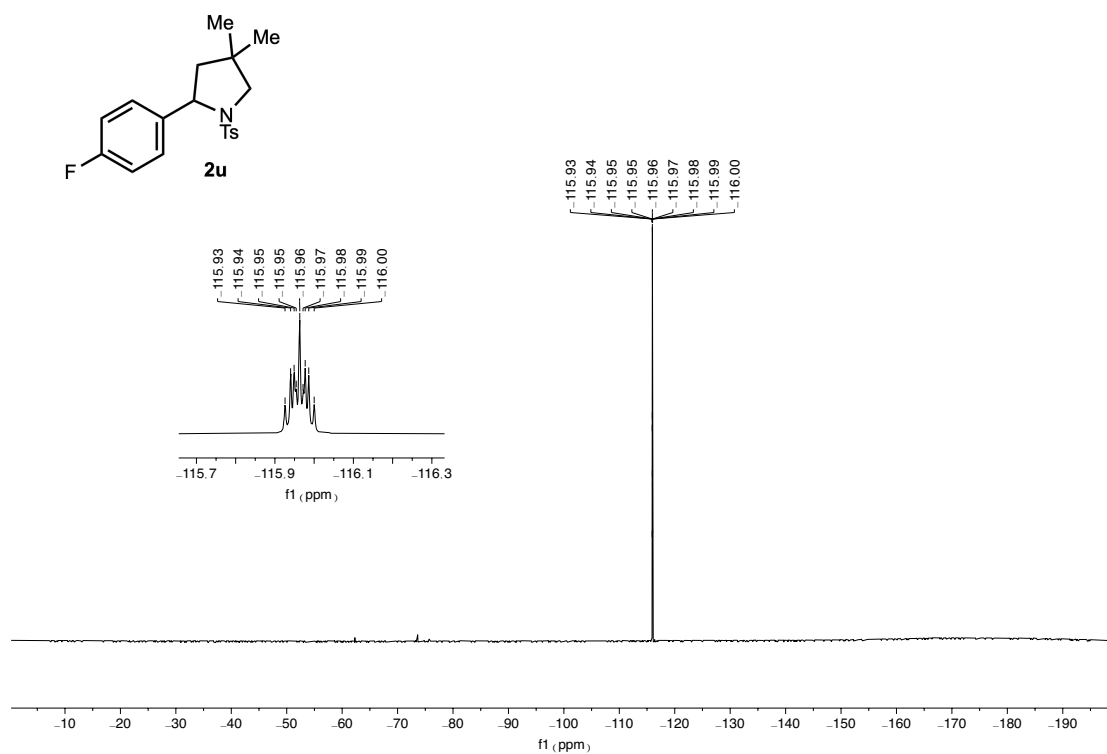
^1H NMR spectrum (400 MHz, CDCl_3) of **2u**



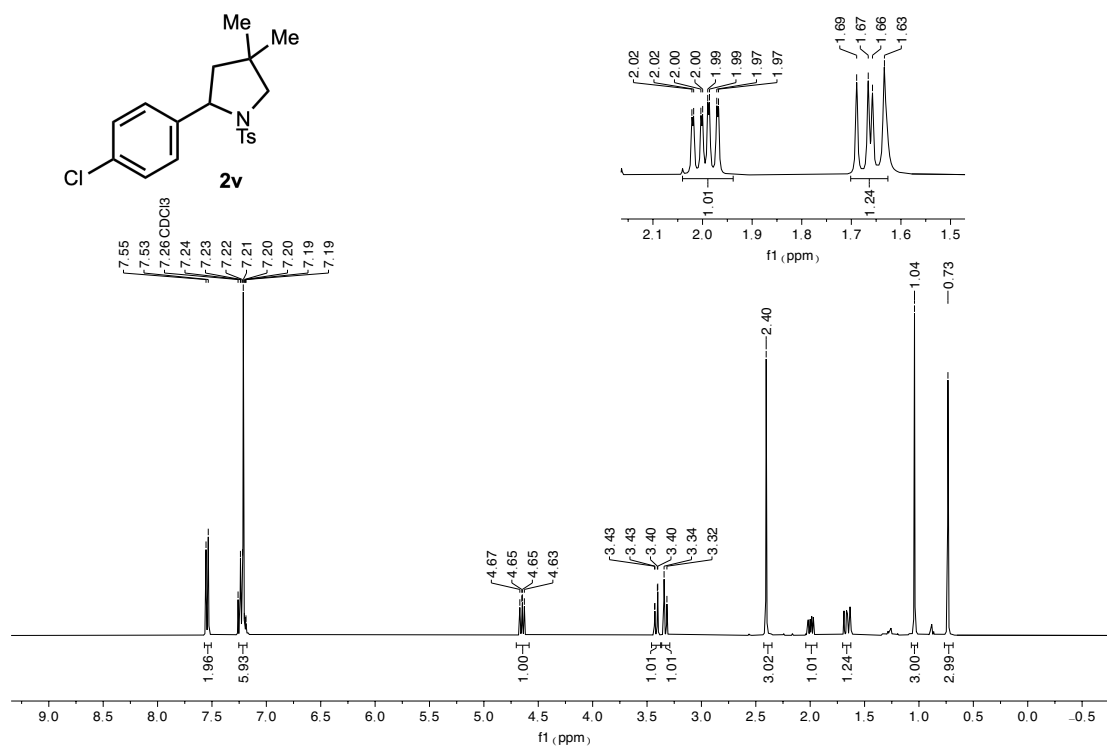
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2u**



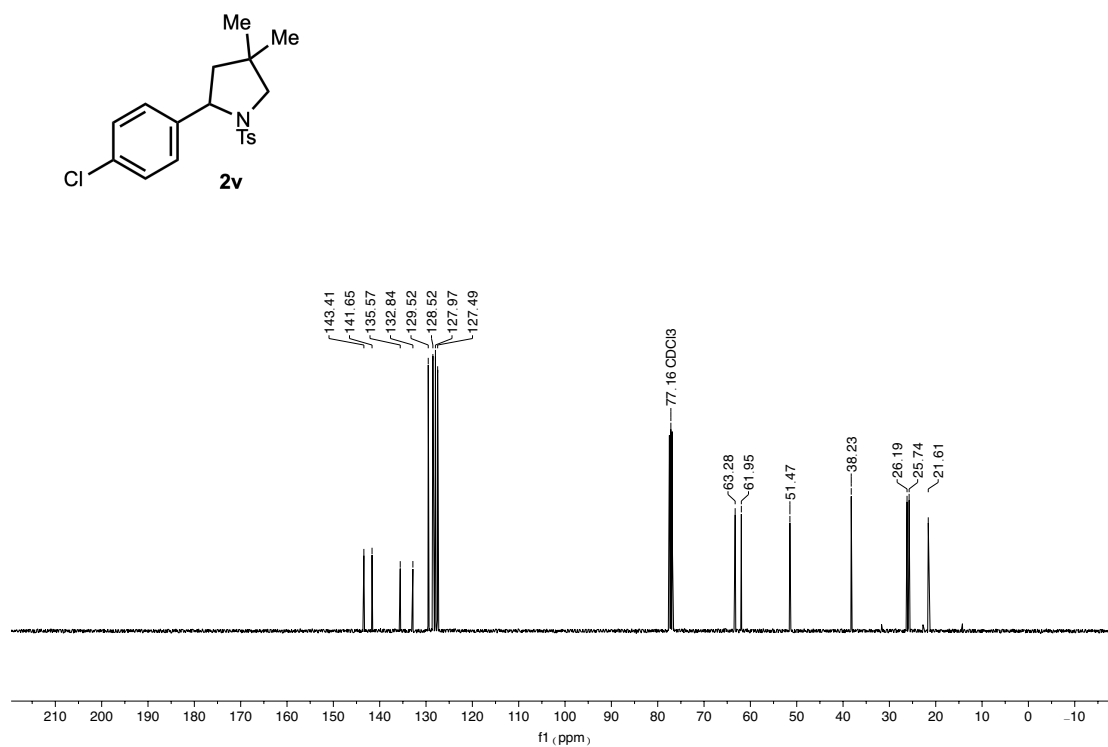
^{19}F NMR spectrum (375 MHz, CDCl_3) of **2u**



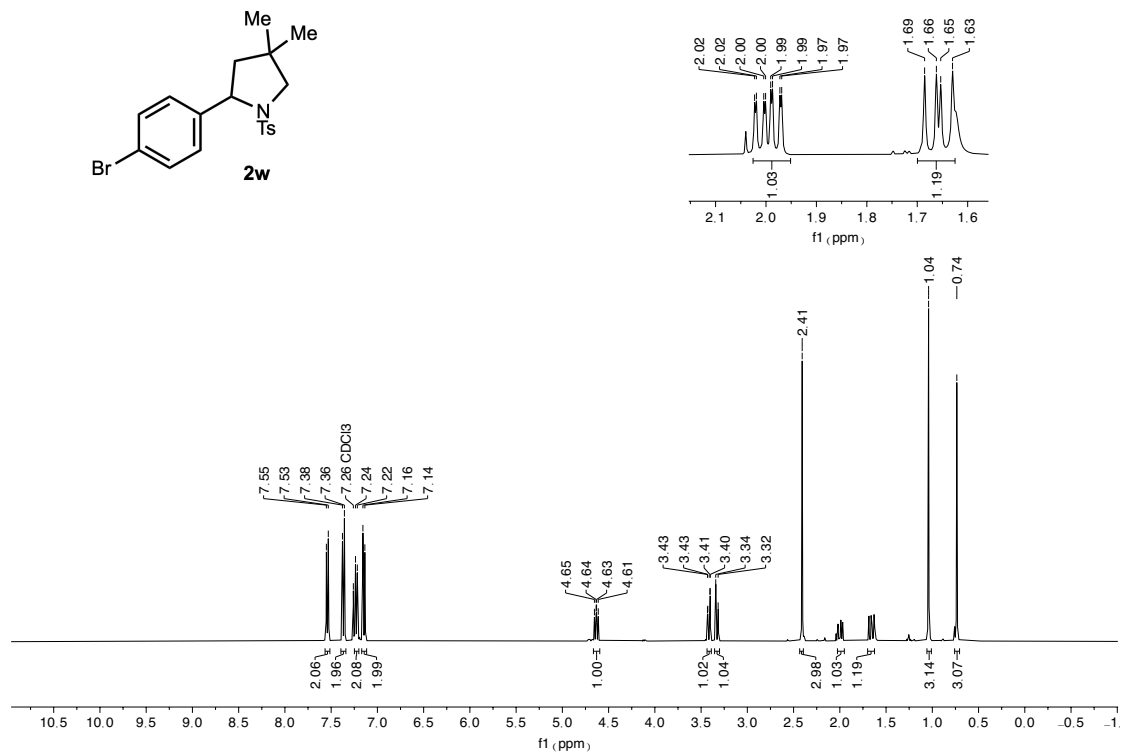
^1H NMR spectrum (400 MHz, CDCl_3) of **2v**



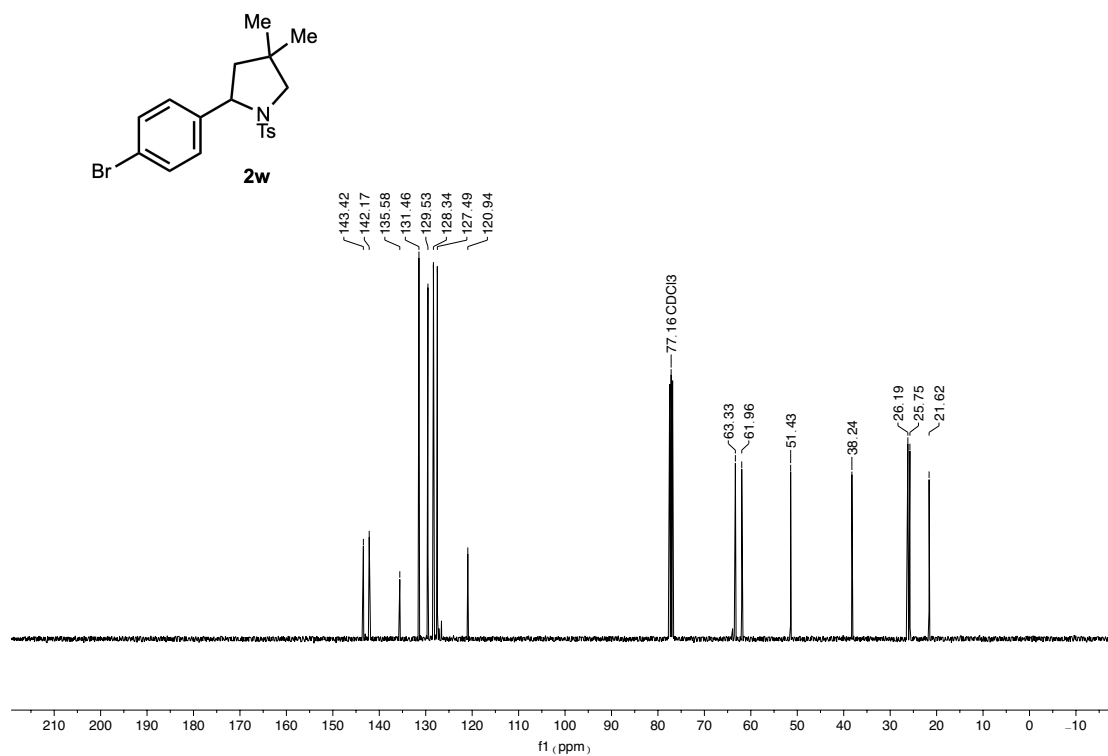
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2v**



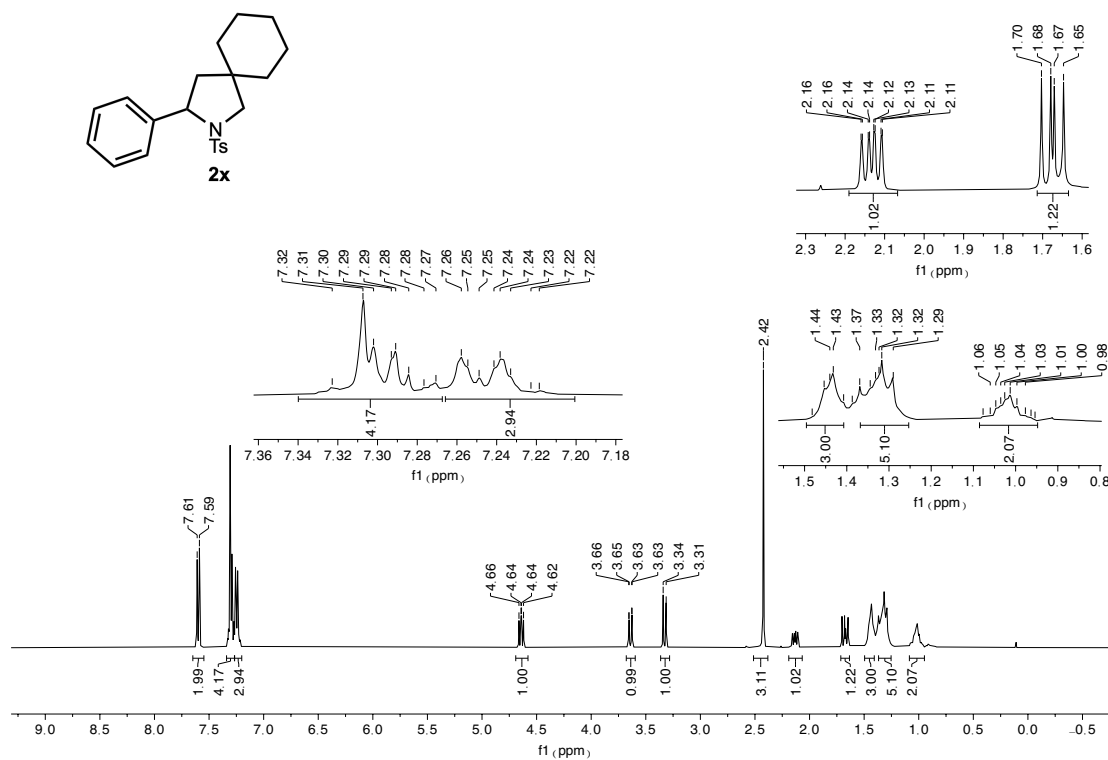
^1H NMR spectrum (400 MHz, CDCl_3) of **2w**



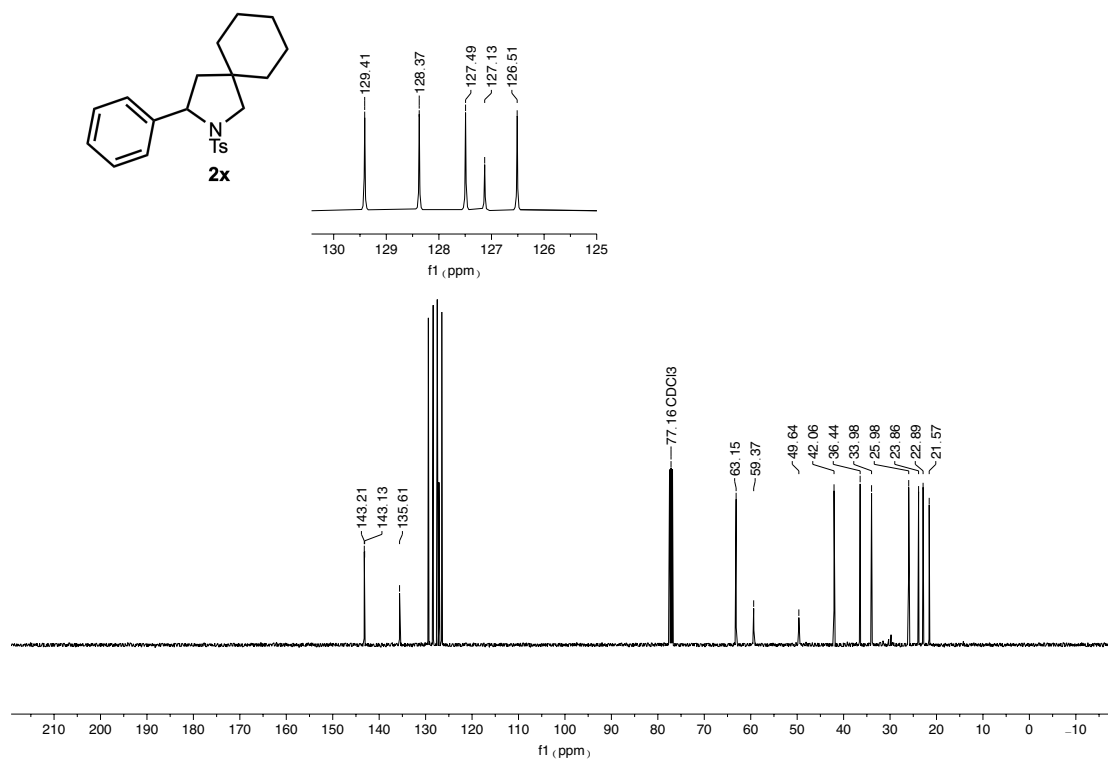
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2w**



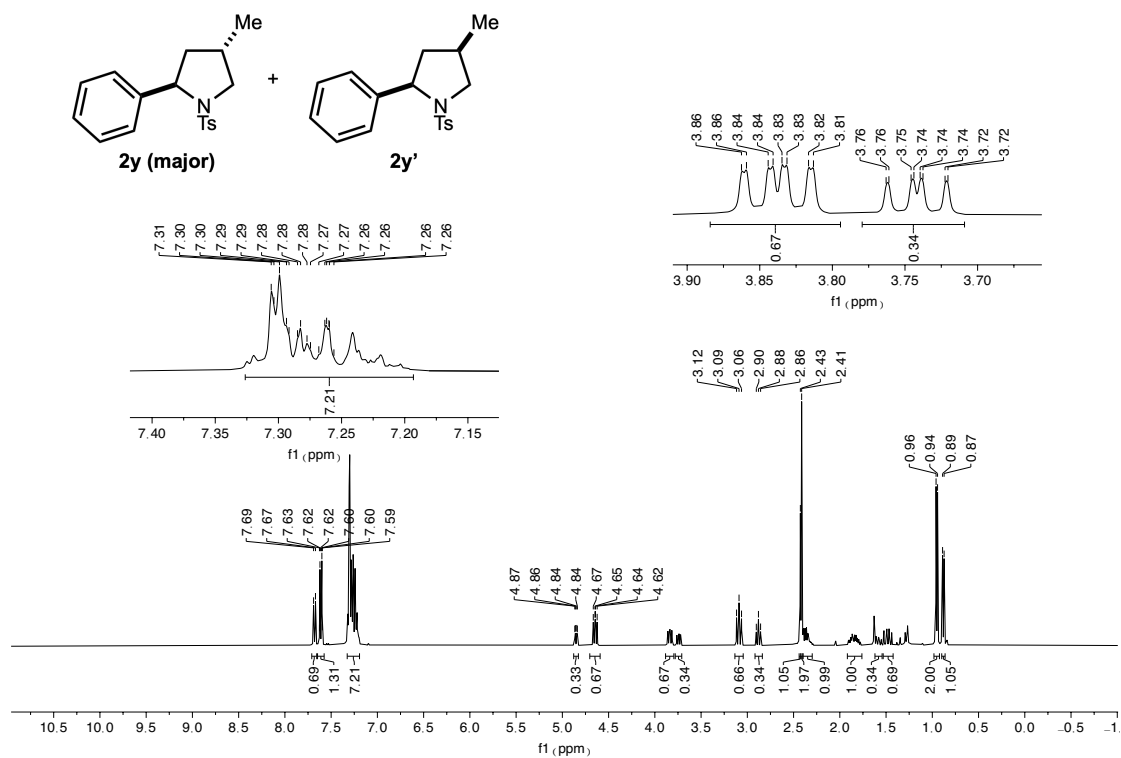
^1H NMR spectrum (400 MHz, CDCl_3) of **2x**

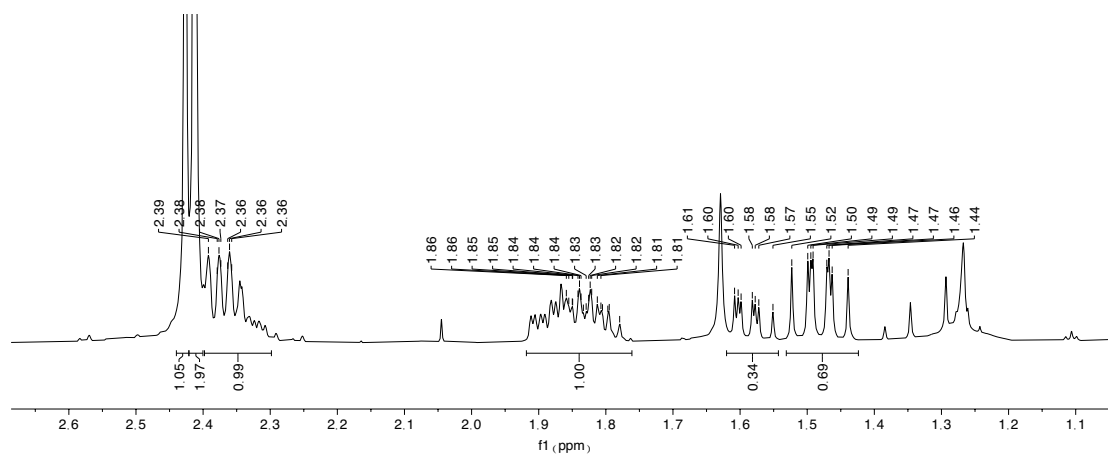


^{13}C NMR spectrum (100 MHz, CDCl_3) of **2x**

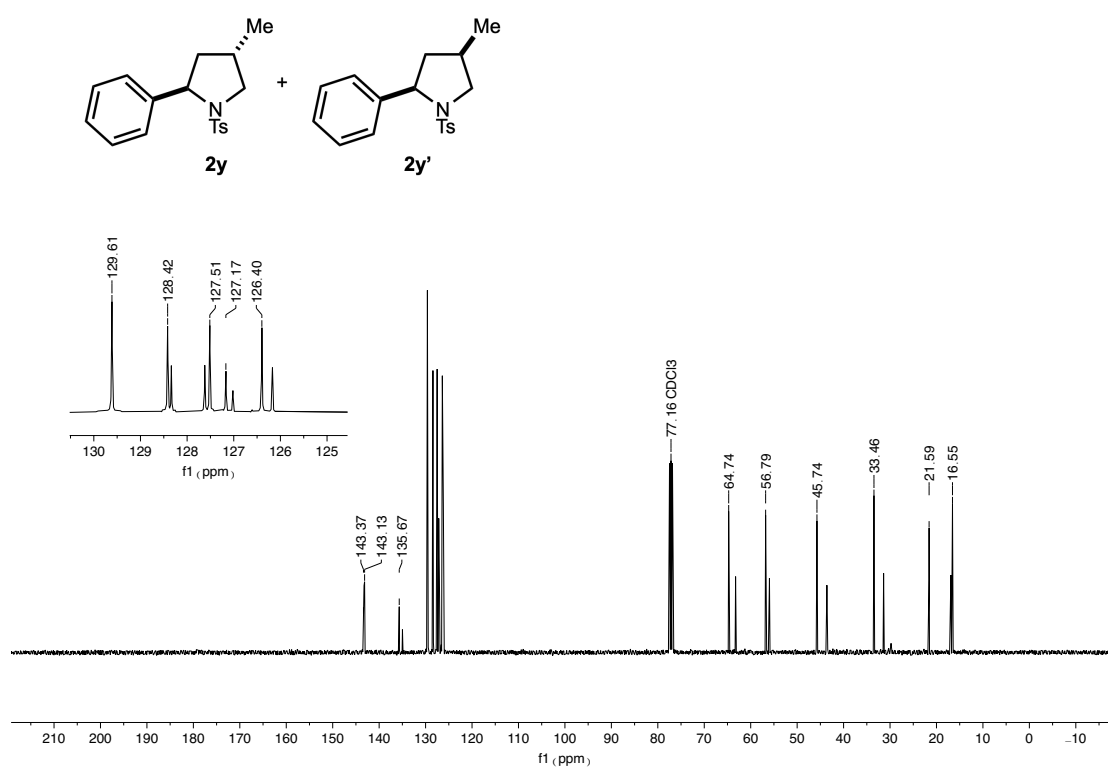


^1H NMR spectrum (400 MHz, CDCl_3) of **2y**

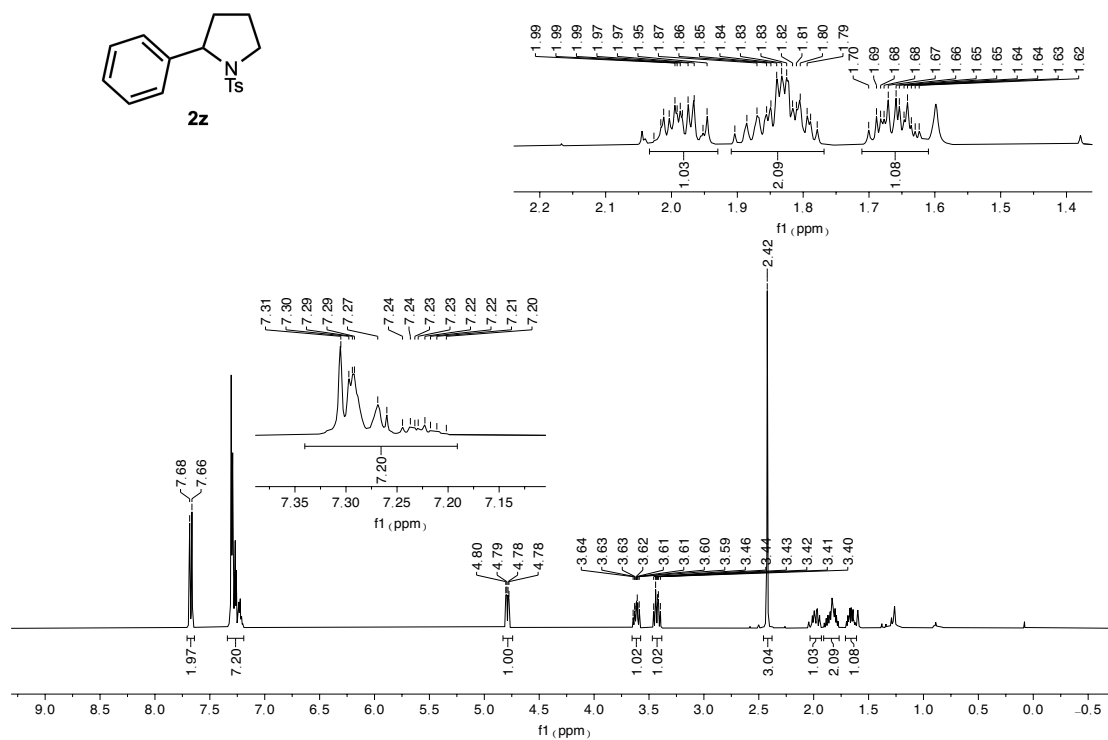




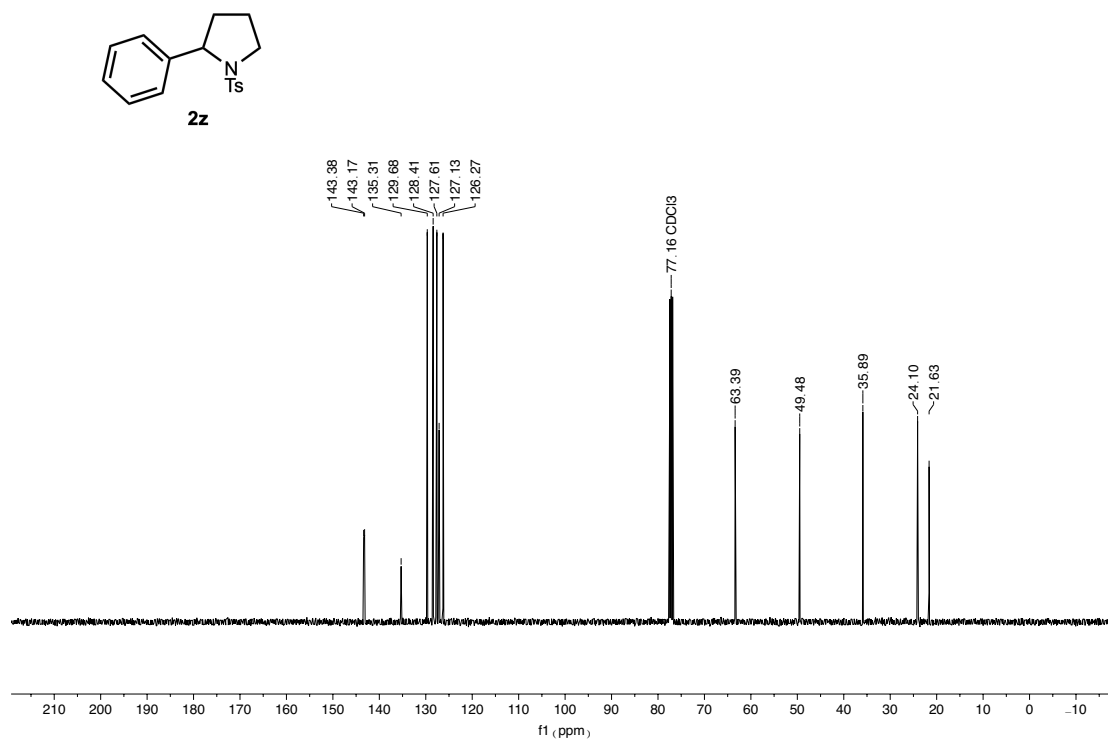
¹³C NMR spectrum (100 MHz, CDCl₃) of **2y**



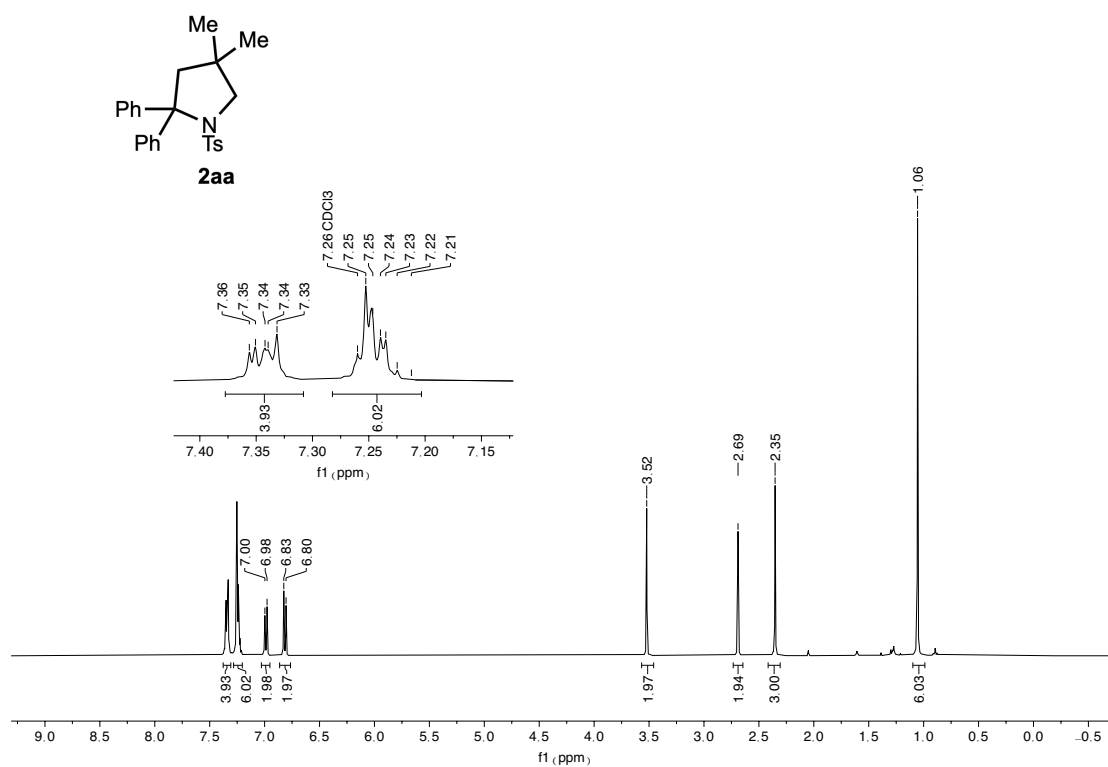
^1H NMR spectrum (400 MHz, CDCl_3) of **2z**



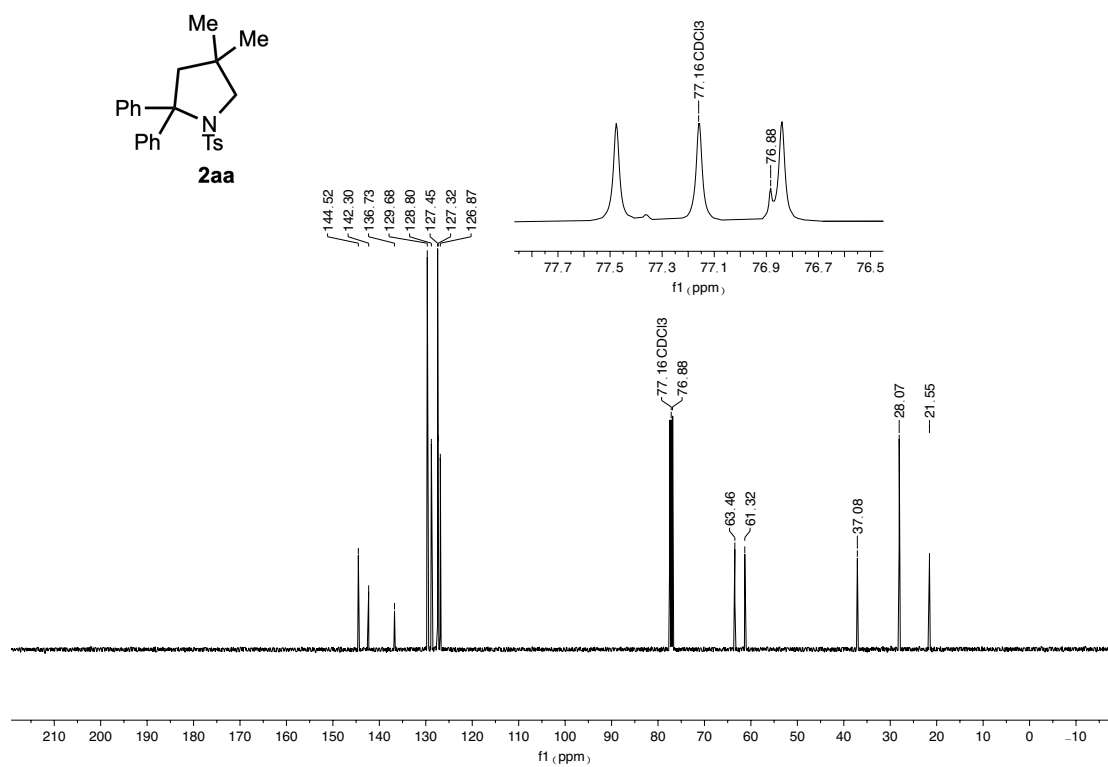
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2z**



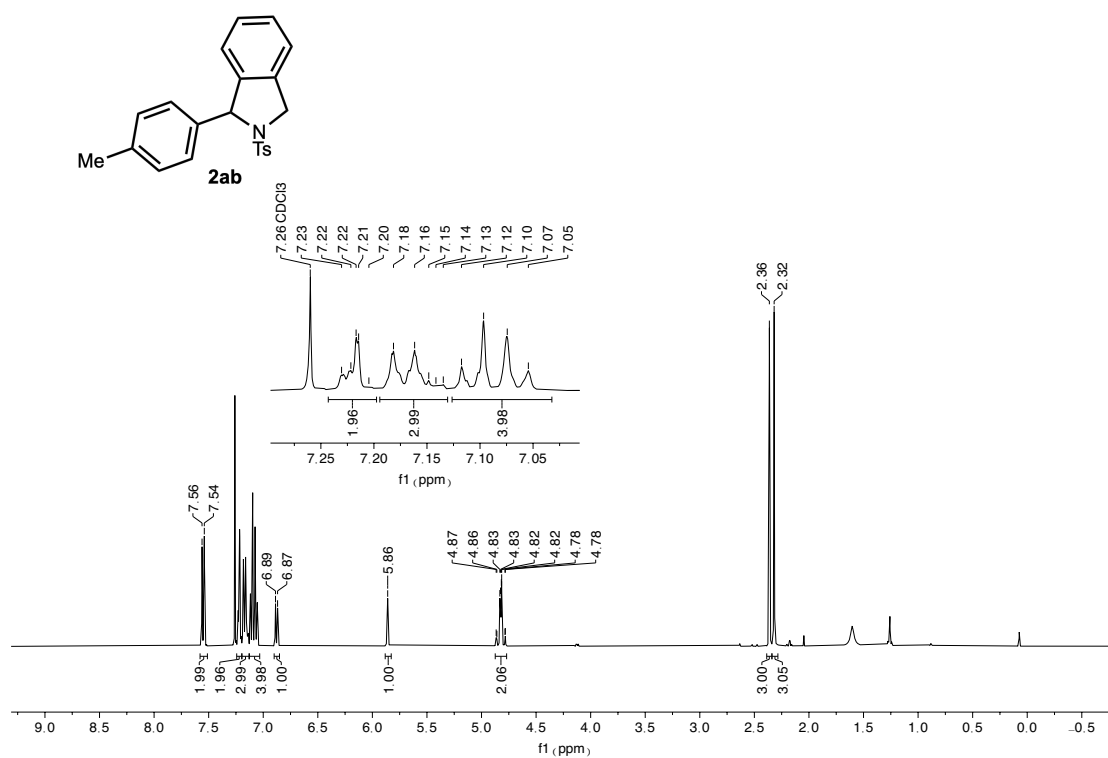
^1H NMR spectrum (400 MHz, CDCl_3) of **2aa**



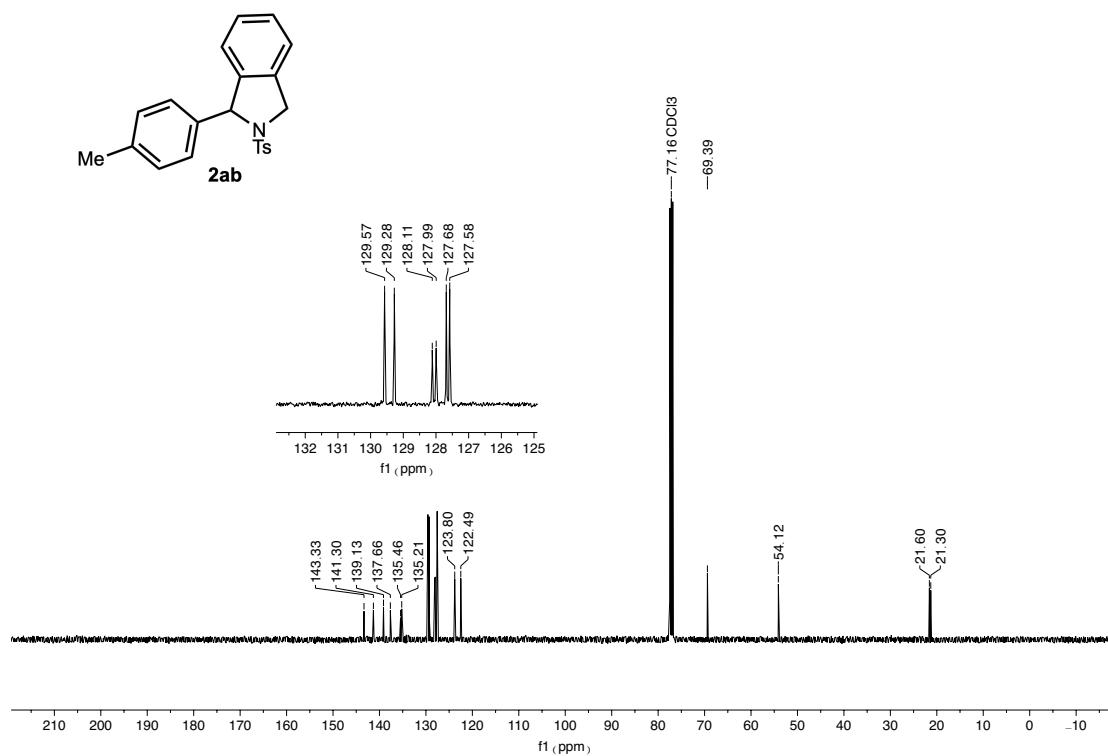
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2aa**



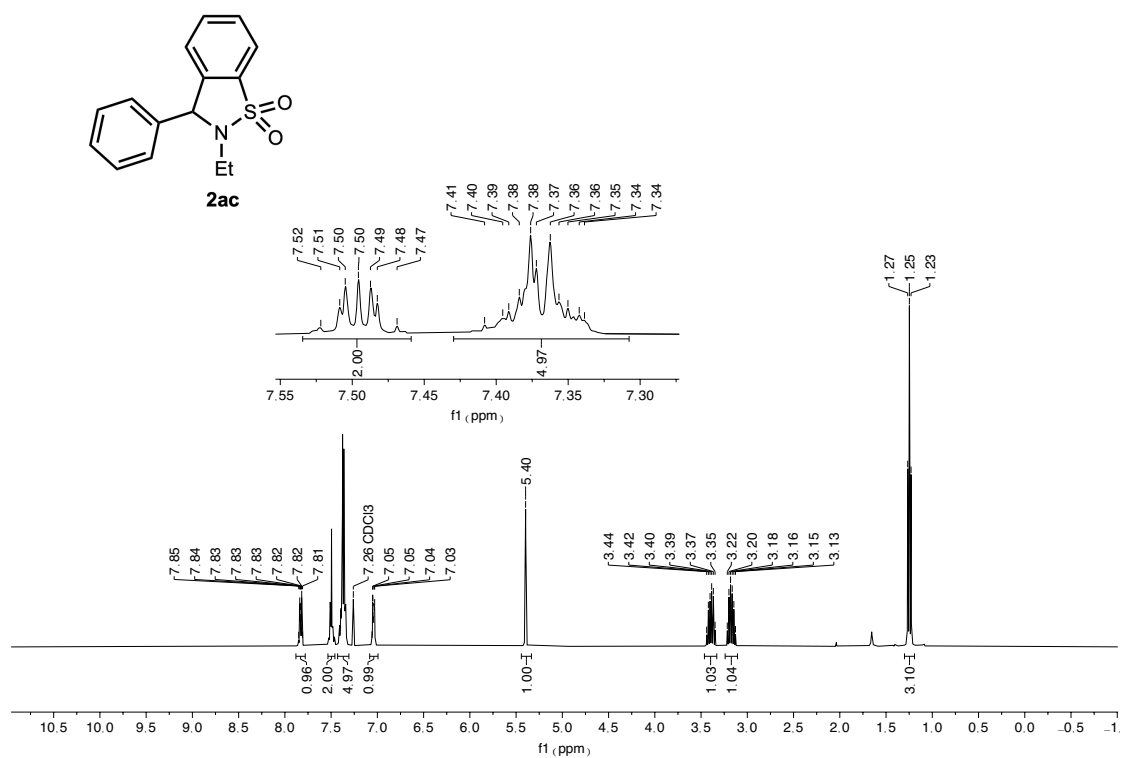
^1H NMR spectrum (400 MHz, CDCl_3) of **2ab**



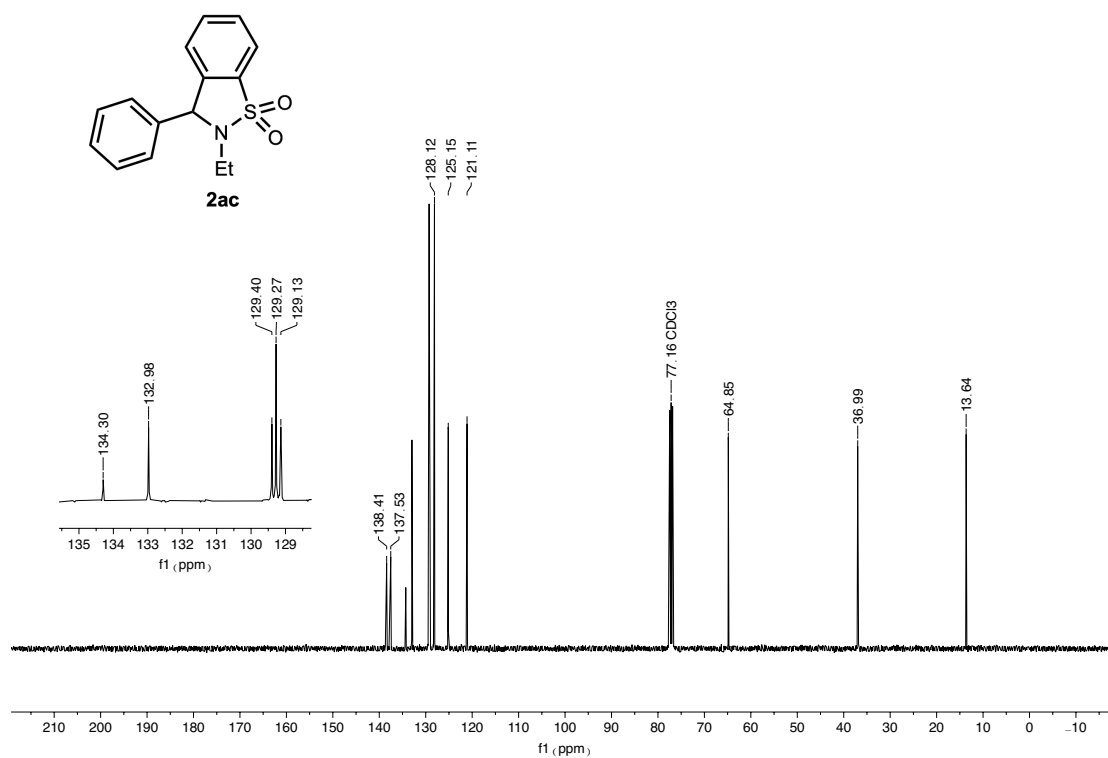
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ab**



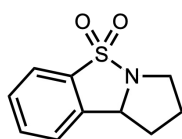
^1H NMR spectrum (400 MHz, CDCl_3) of **2ac**



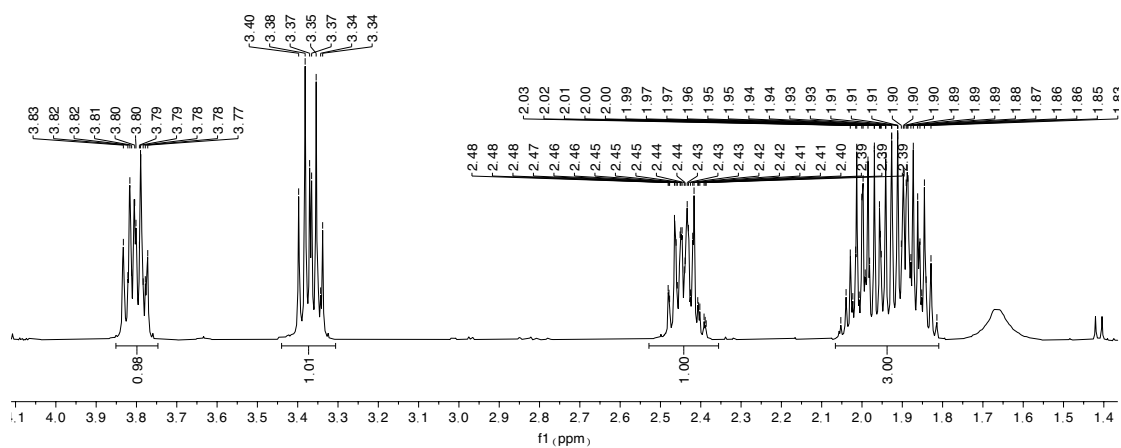
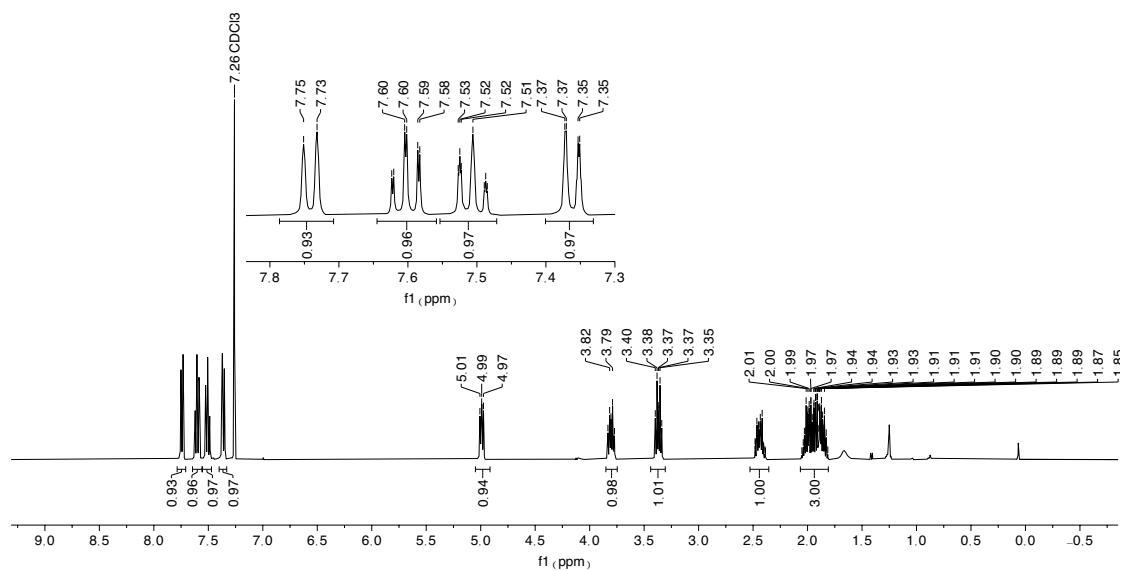
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ac**



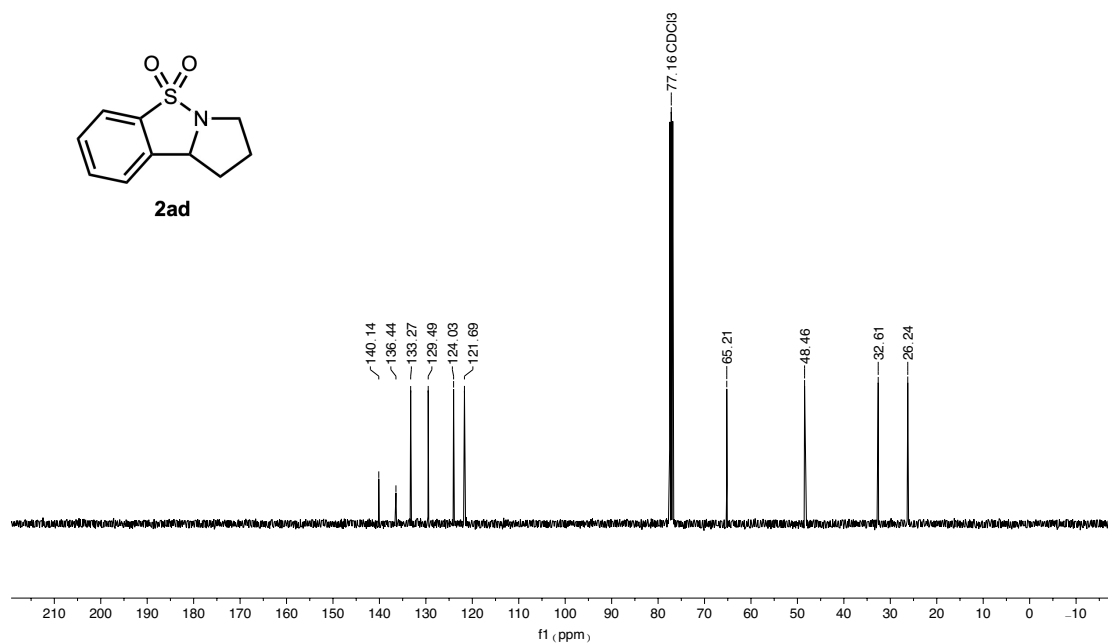
^1H NMR spectrum (400 MHz, CDCl_3) of **2ad**



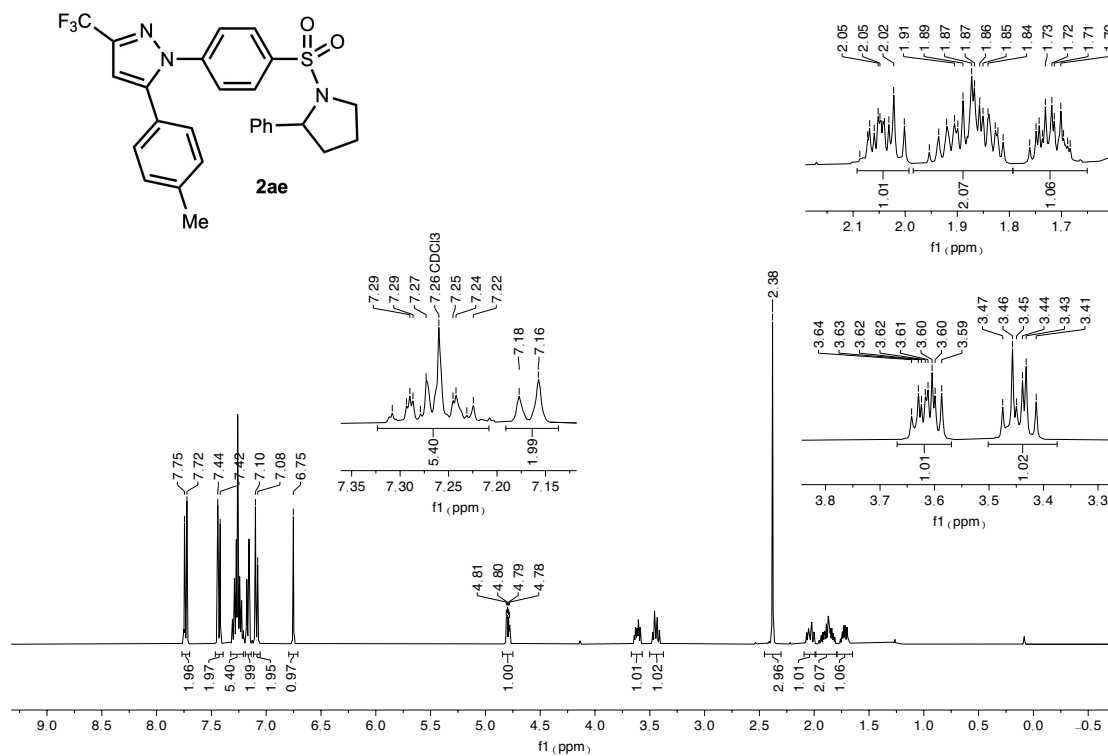
2ad



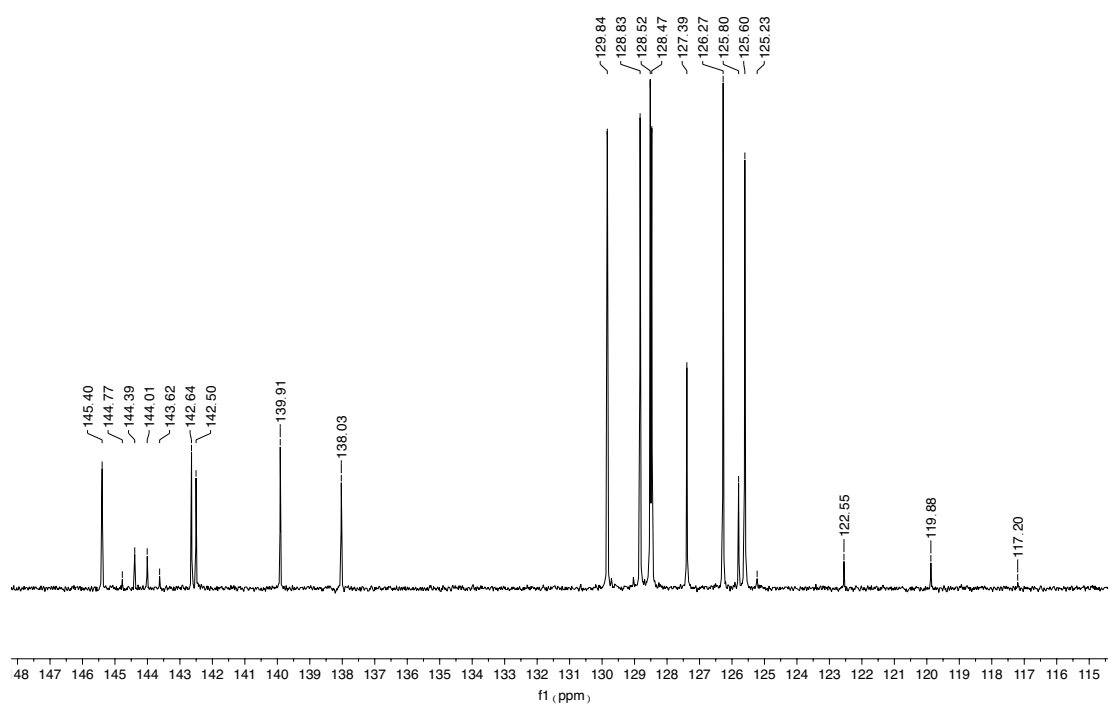
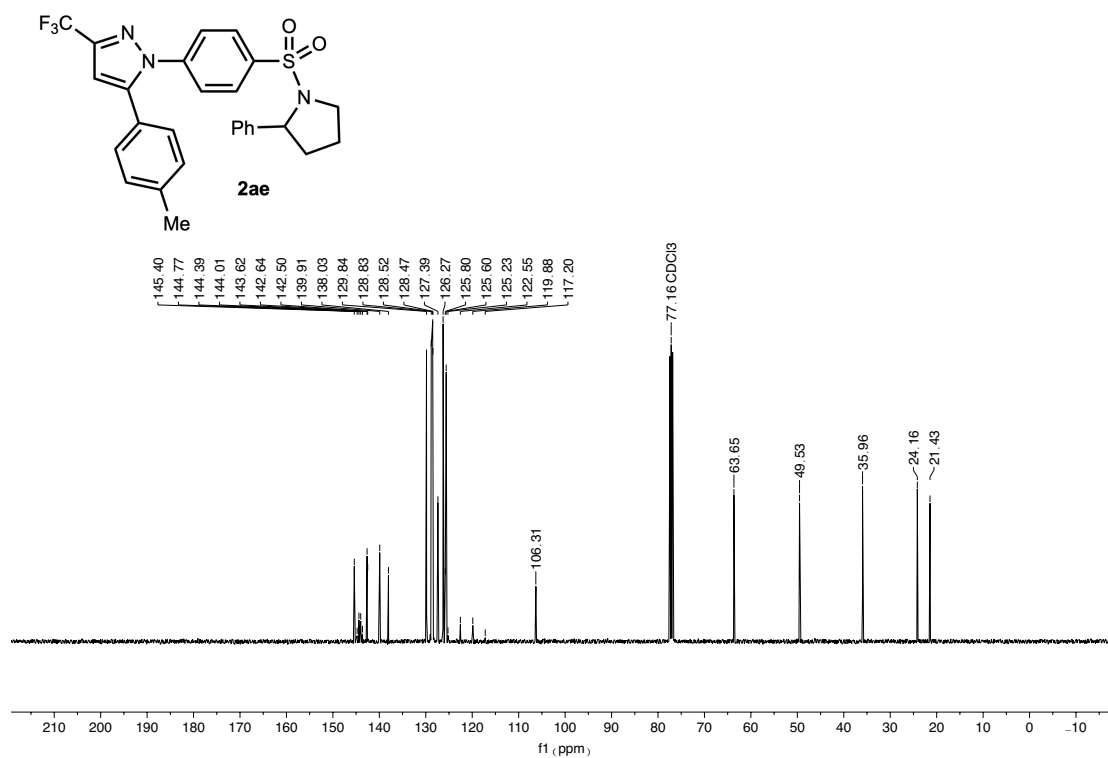
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ad**



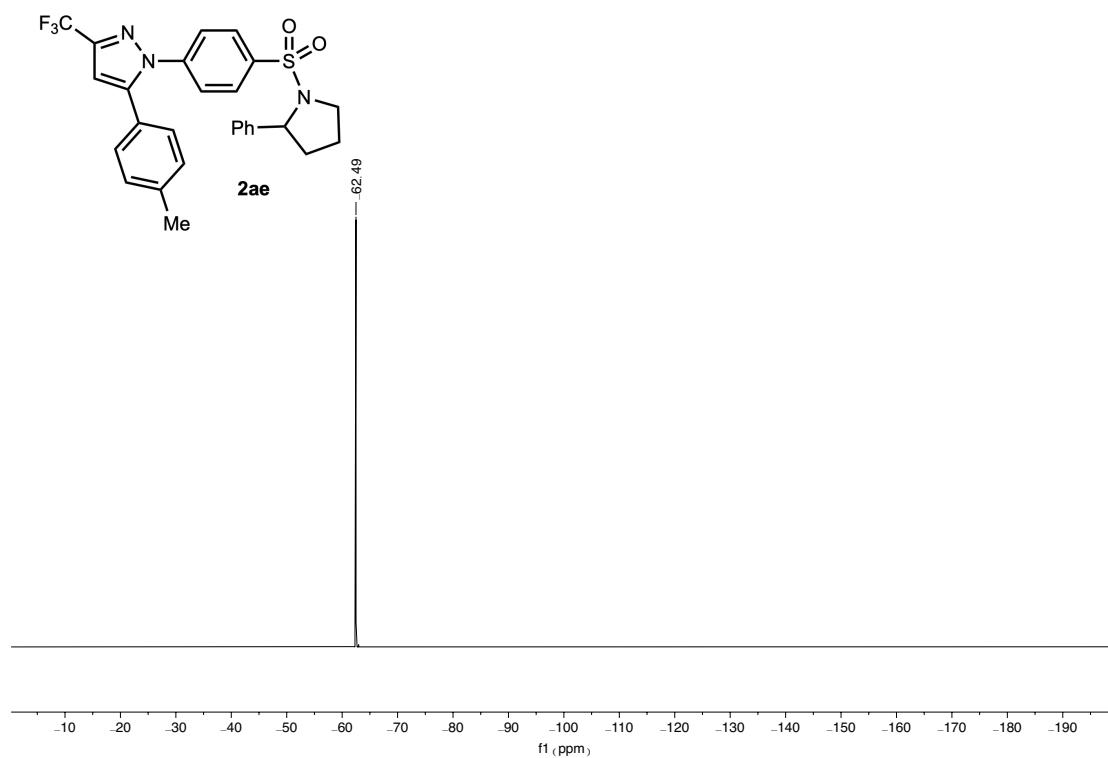
^1H NMR spectrum (400 MHz, CDCl_3) of **2ae**



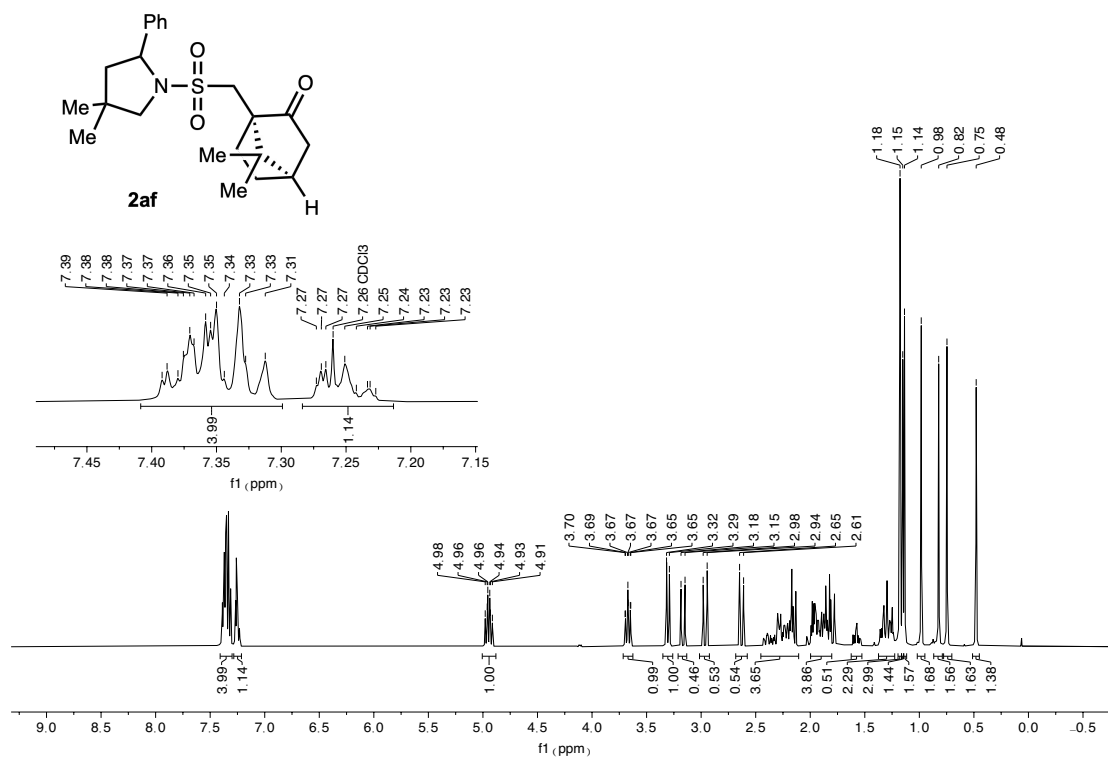
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ae**

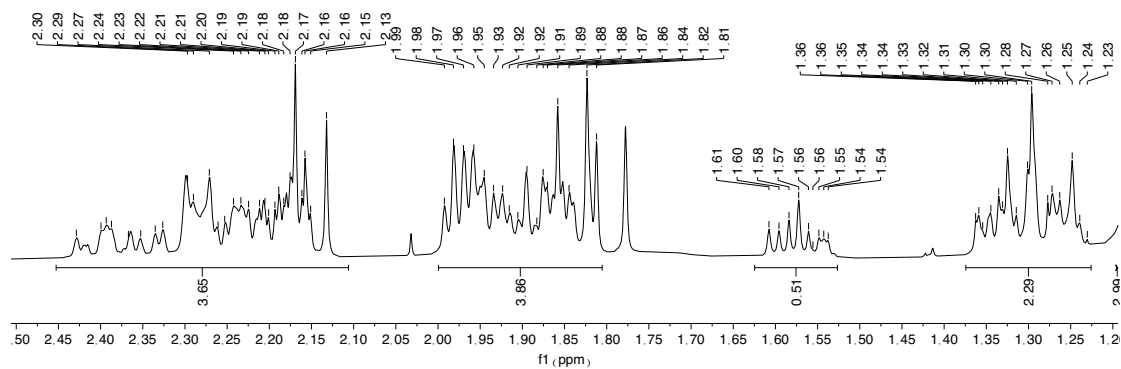


^{19}F NMR spectrum (375 MHz, CDCl_3) of **2ae**

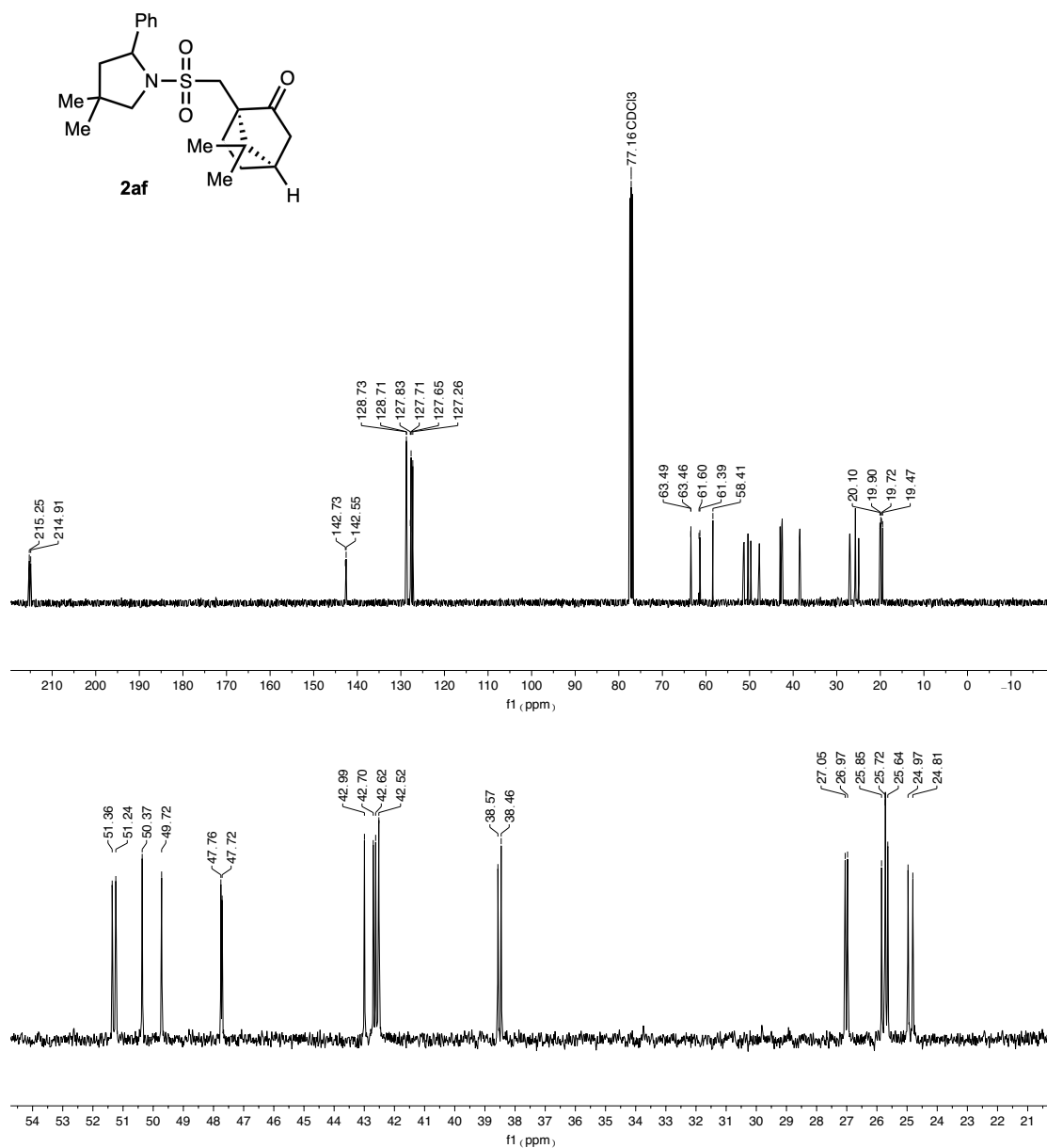


^1H NMR spectrum (400 MHz, CDCl_3) of **2af**

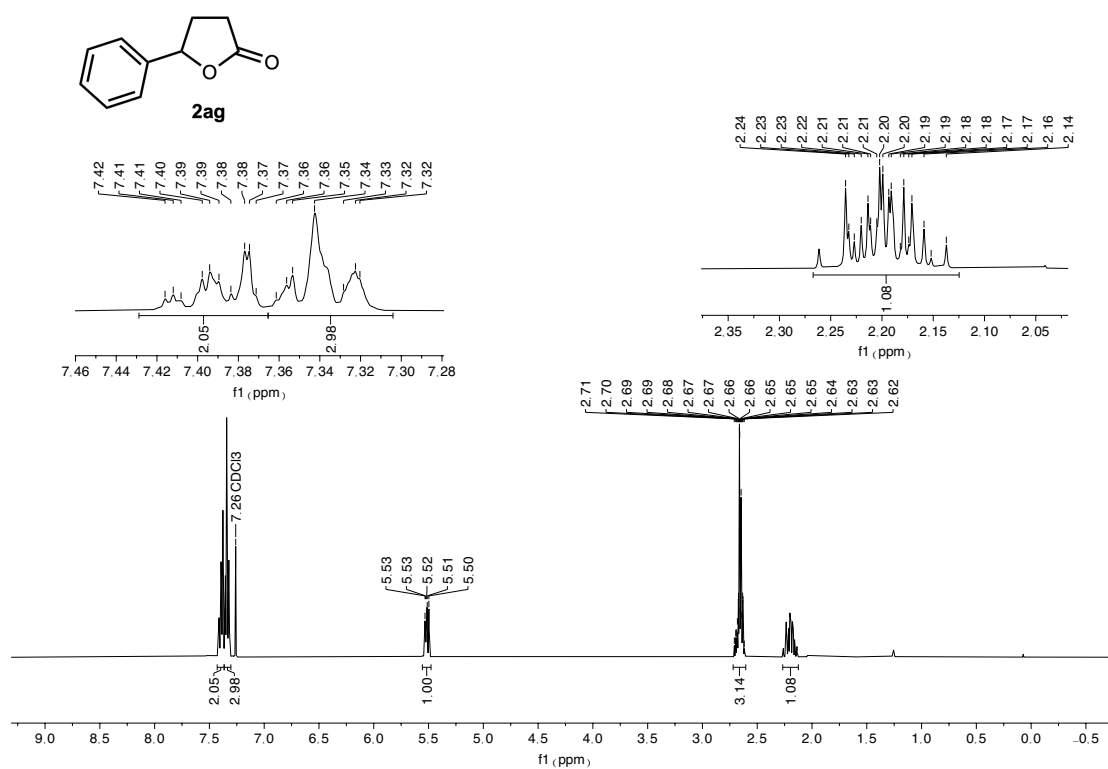




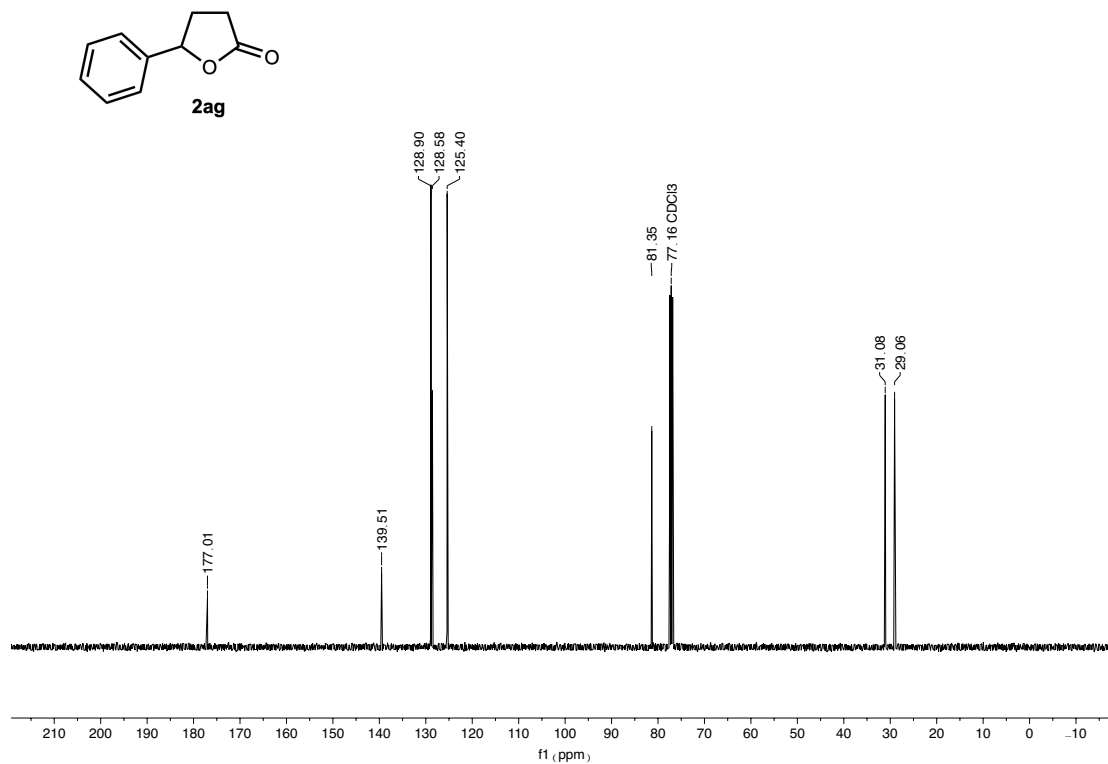
¹³C NMR spectrum (100 MHz, CDCl₃) of **2af**



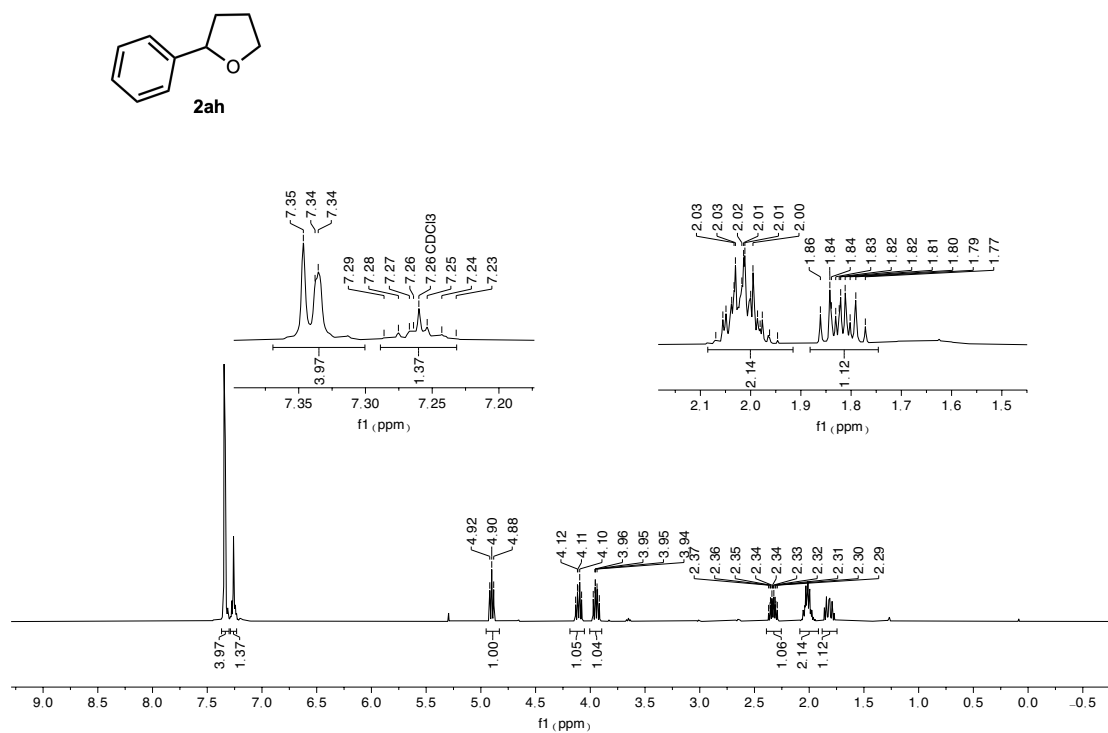
^1H NMR spectrum (400 MHz, CDCl_3) of **2ag**



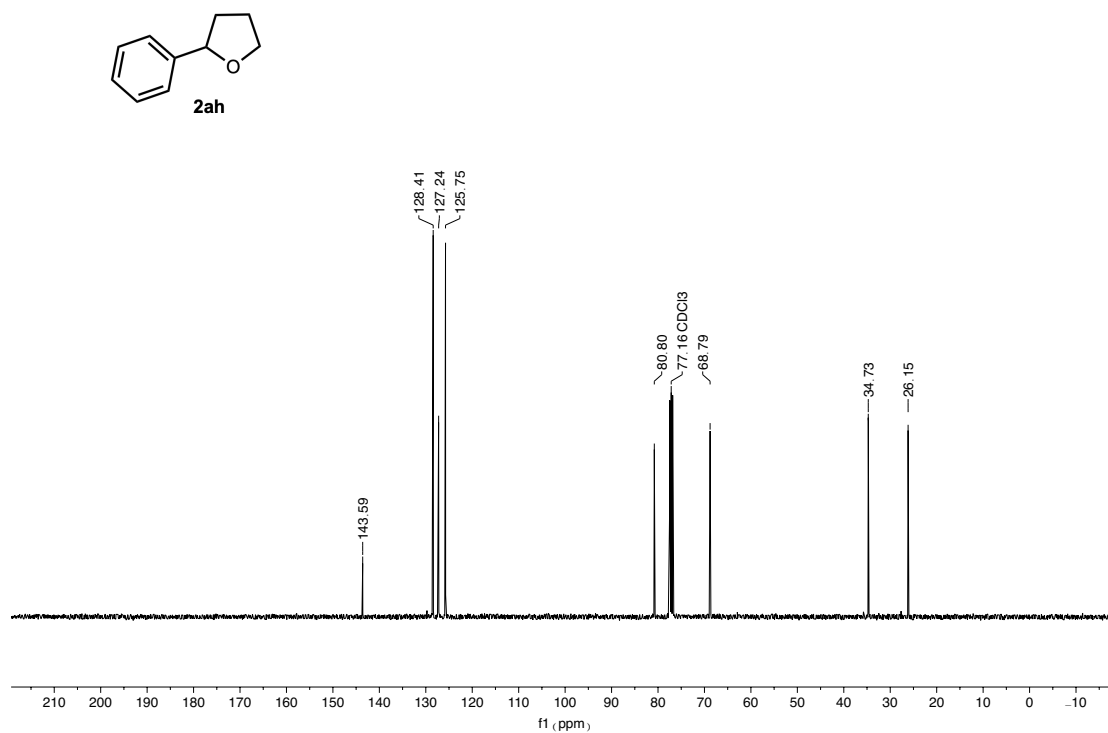
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ag**



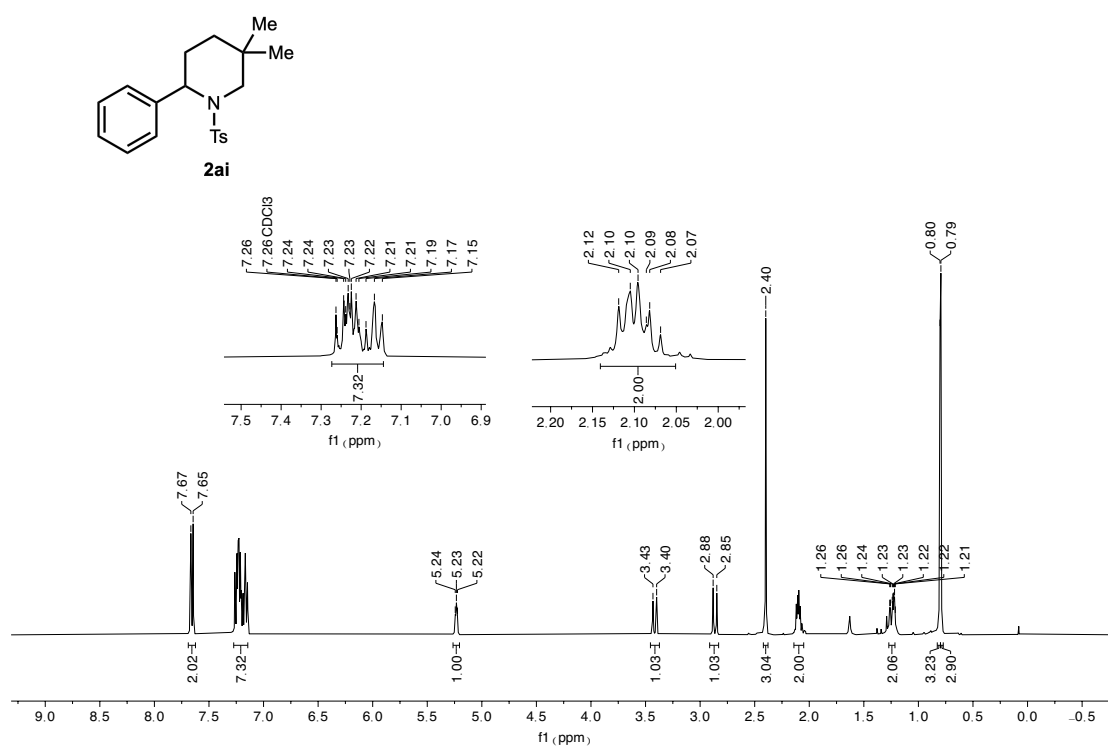
^1H NMR spectrum (400 MHz, CDCl_3) of **2ah**



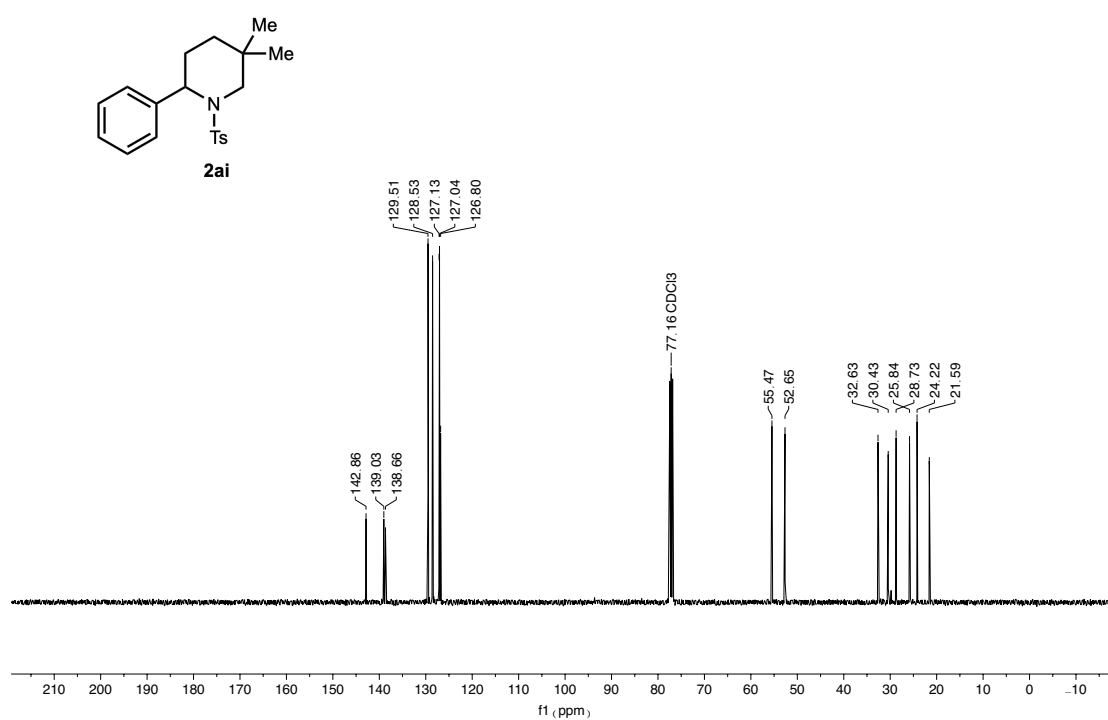
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ah**



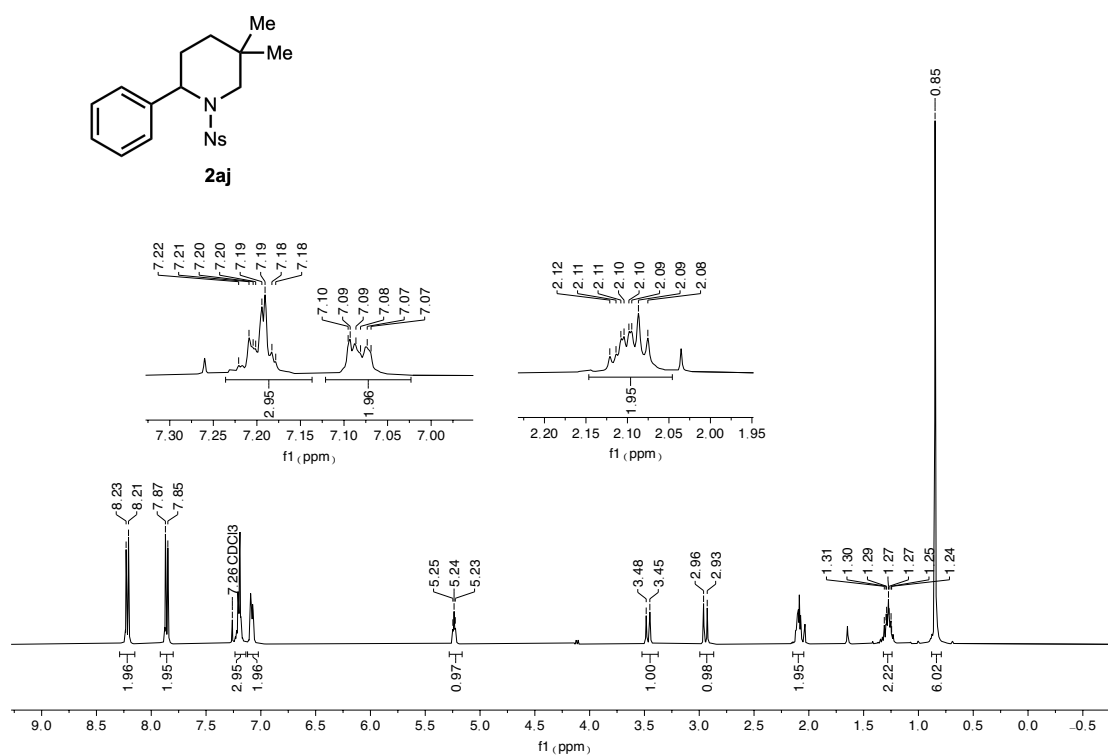
^1H NMR spectrum (400 MHz, CDCl_3) of **2ai**



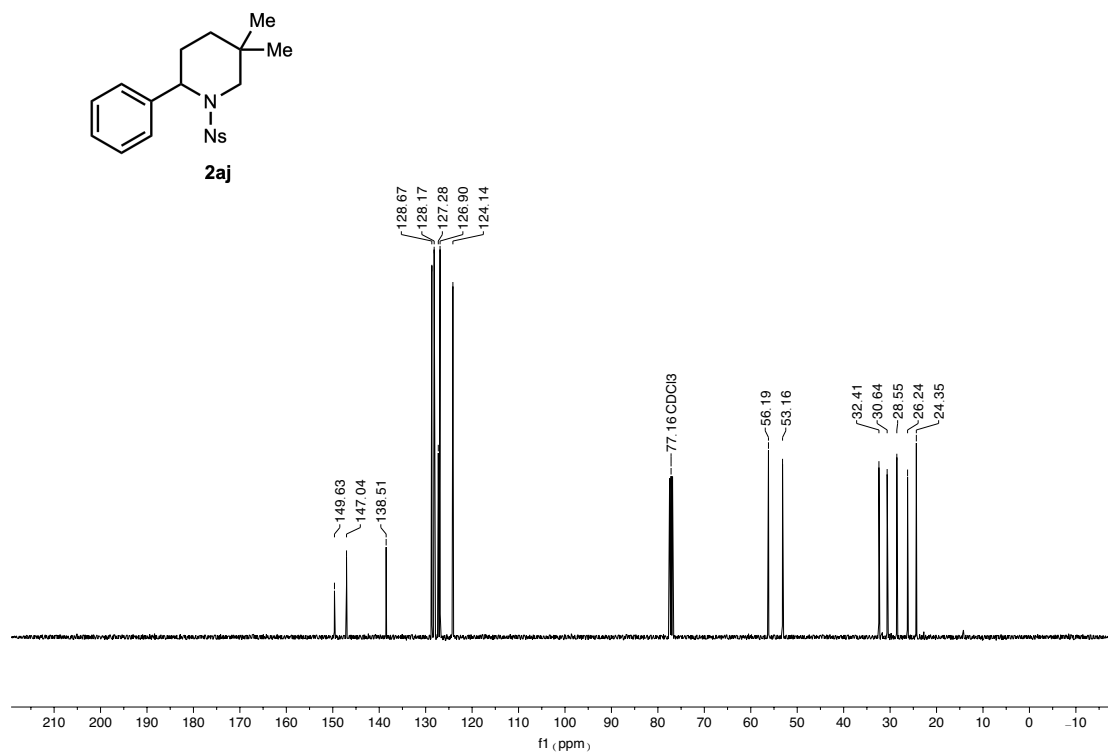
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ai**



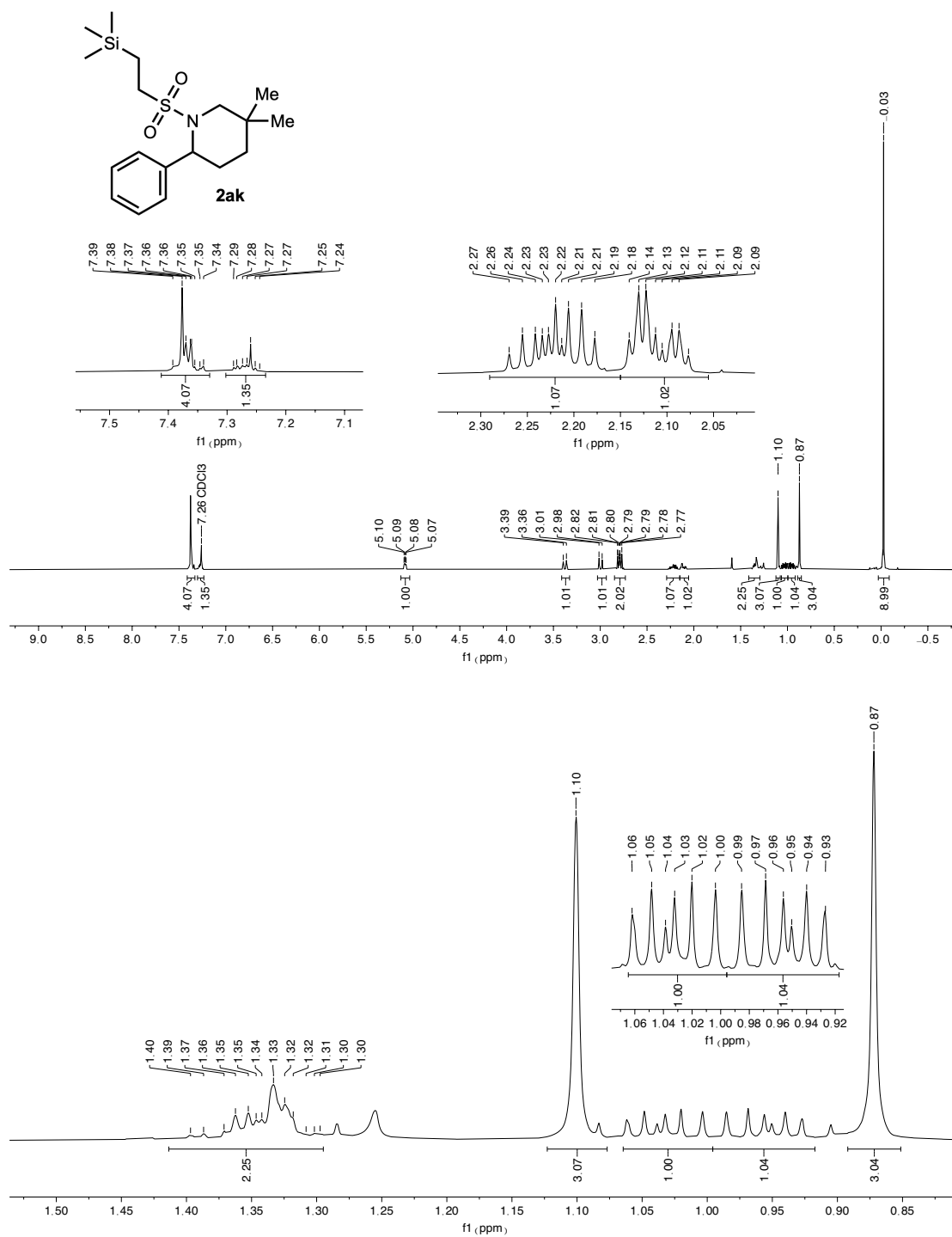
^1H NMR spectrum (400 MHz, CDCl_3) of **2aj**



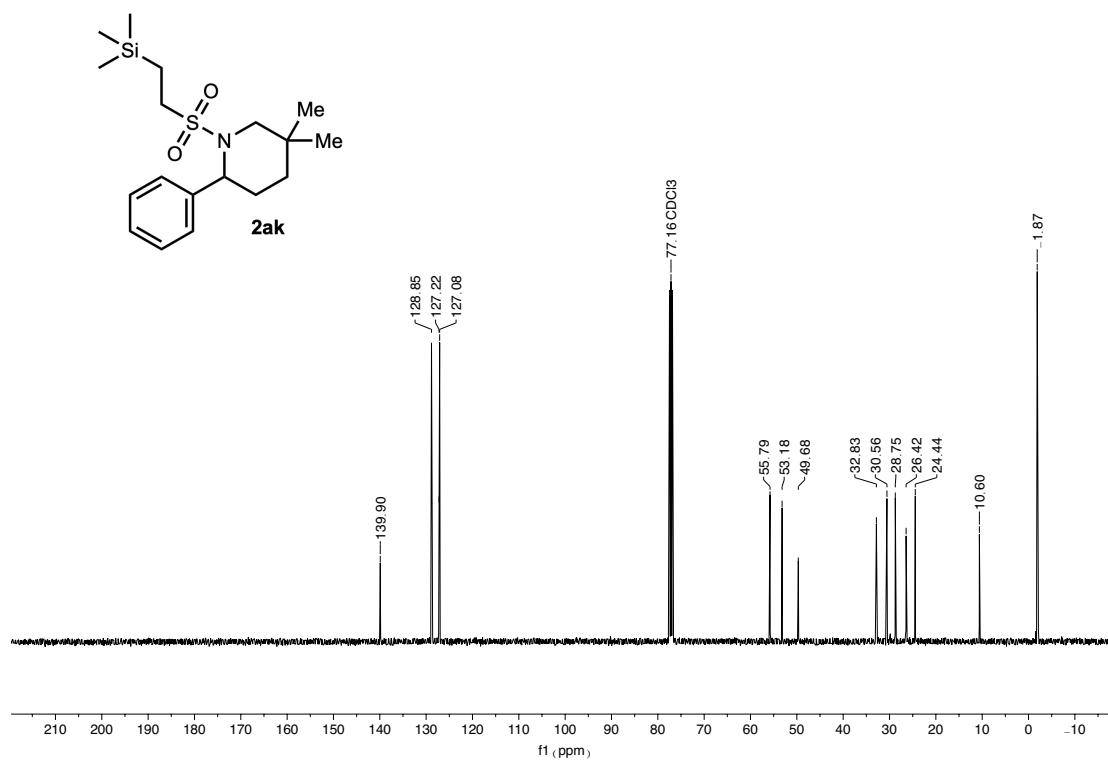
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2aj**



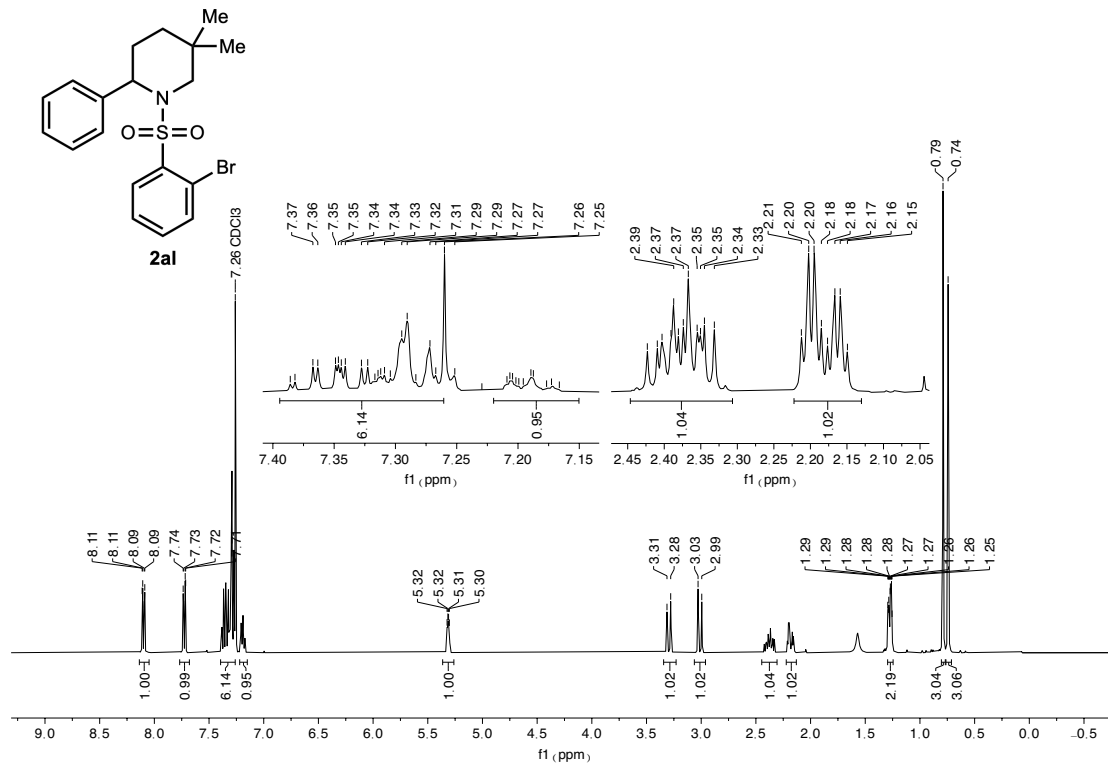
^1H NMR spectrum (400 MHz, CDCl_3) of **2ak**



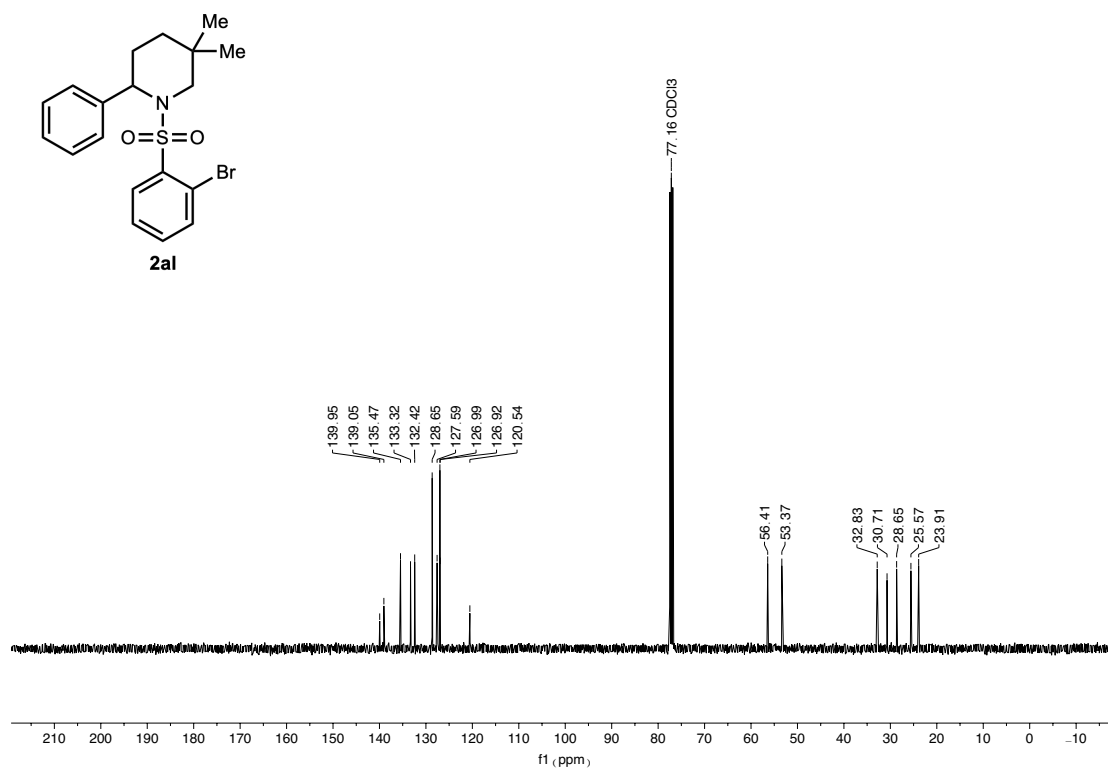
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ak**



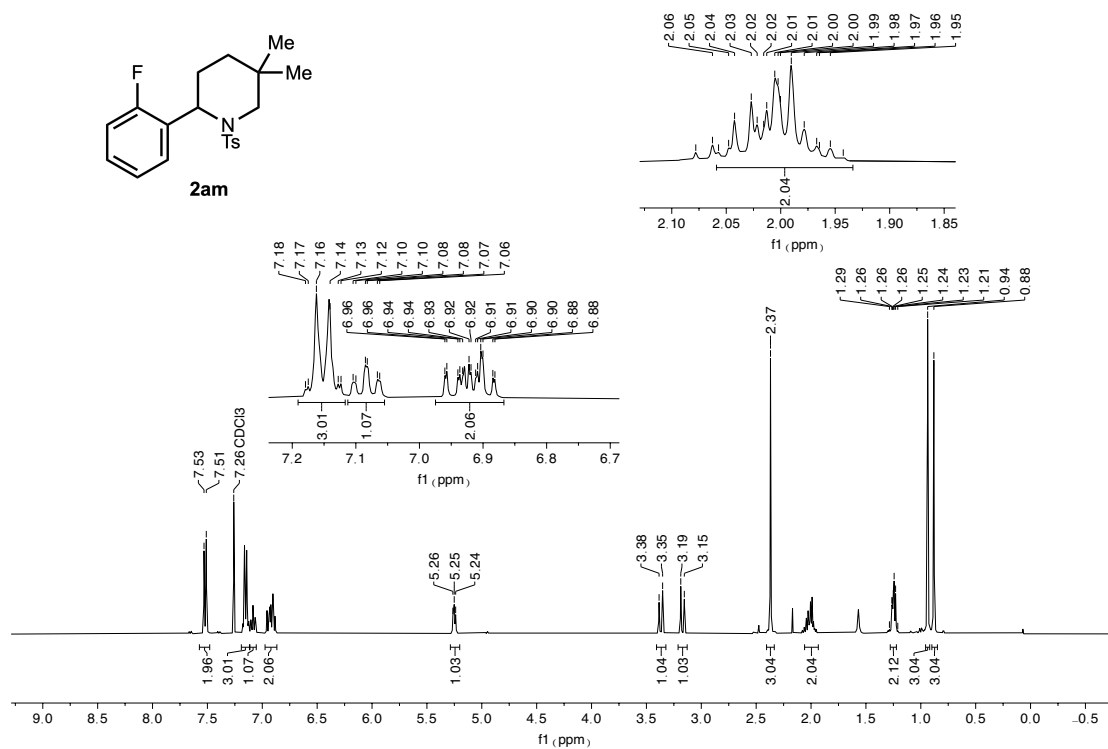
^1H NMR spectrum (400 MHz, CDCl_3) of **2al**



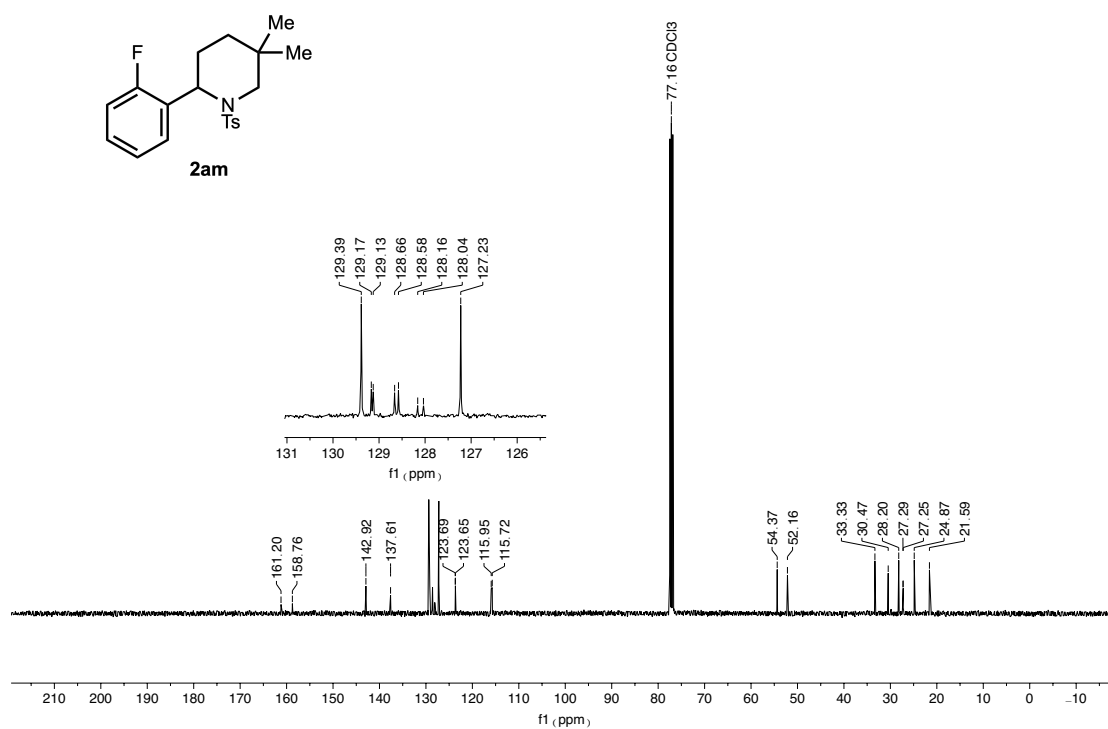
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2al**



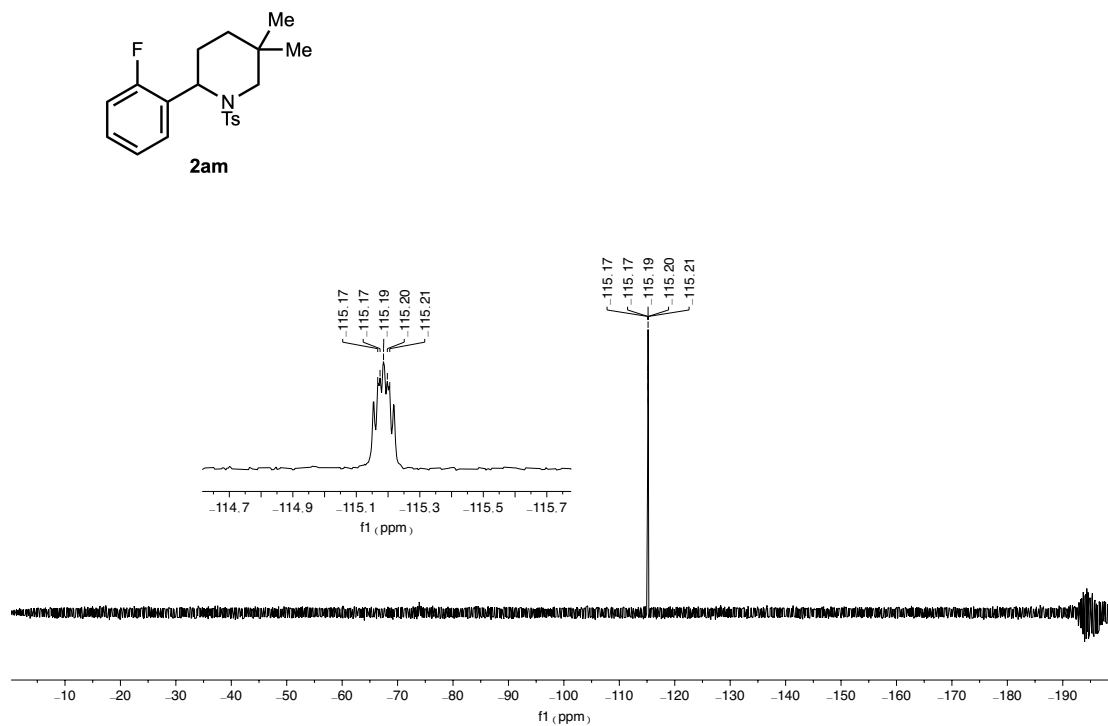
^1H NMR spectrum (400 MHz, CDCl_3) of **2am**



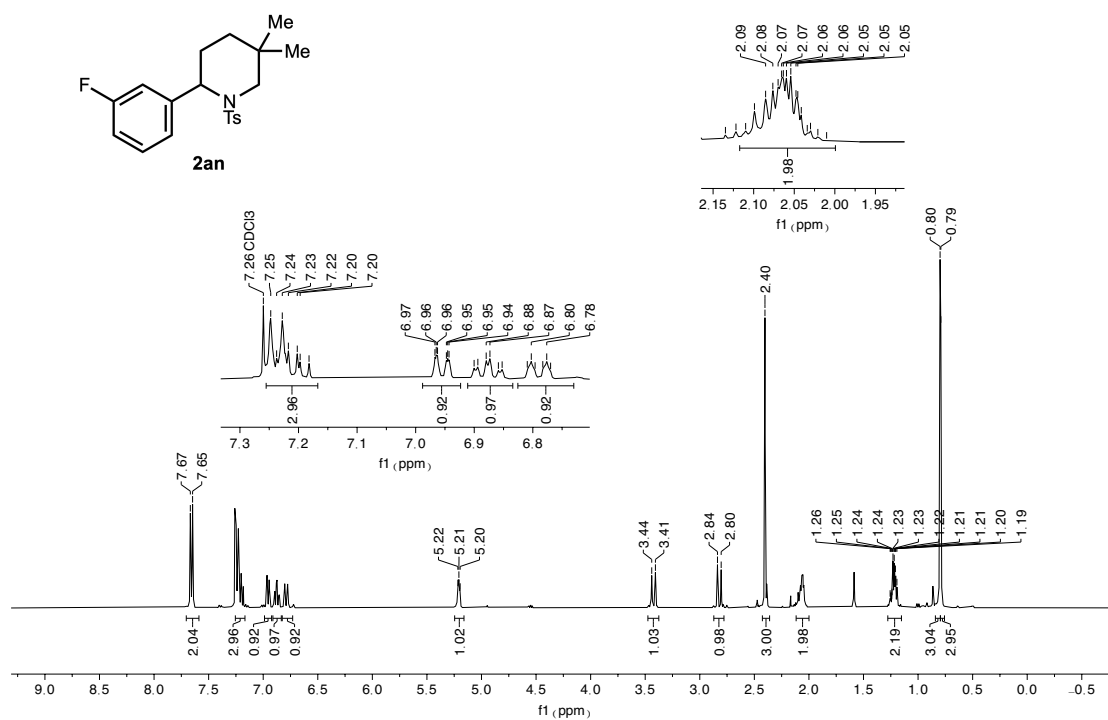
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2am**



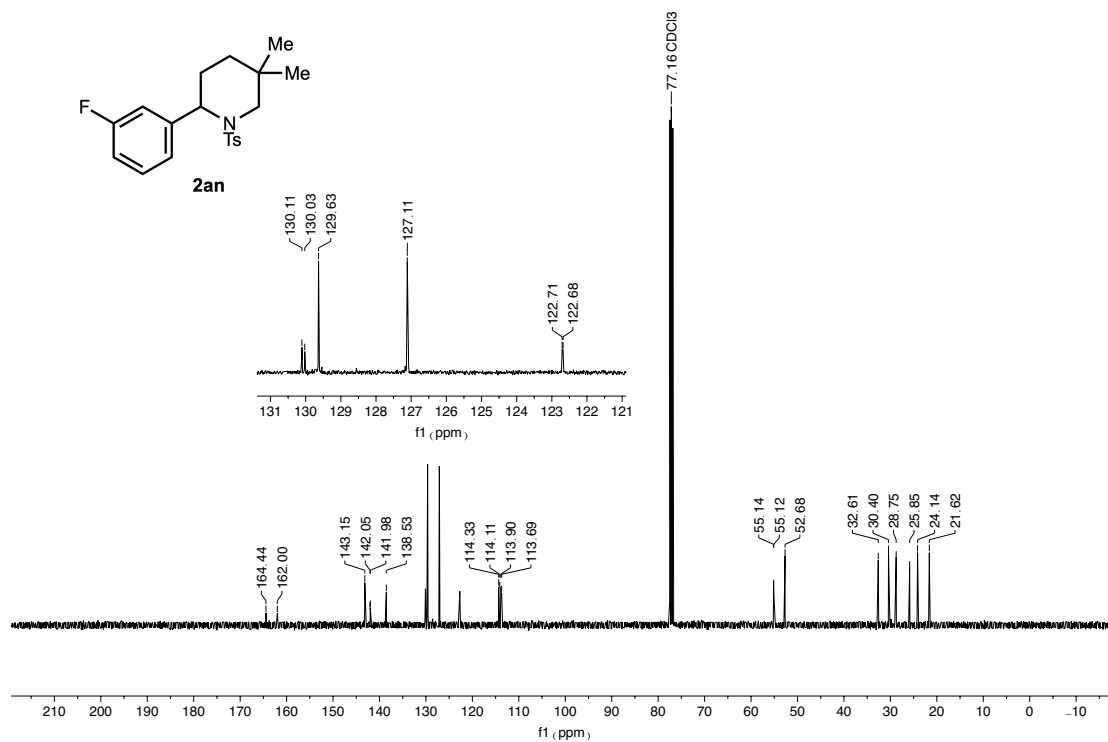
^{19}F NMR spectrum (375 MHz, CDCl_3) of **2am**



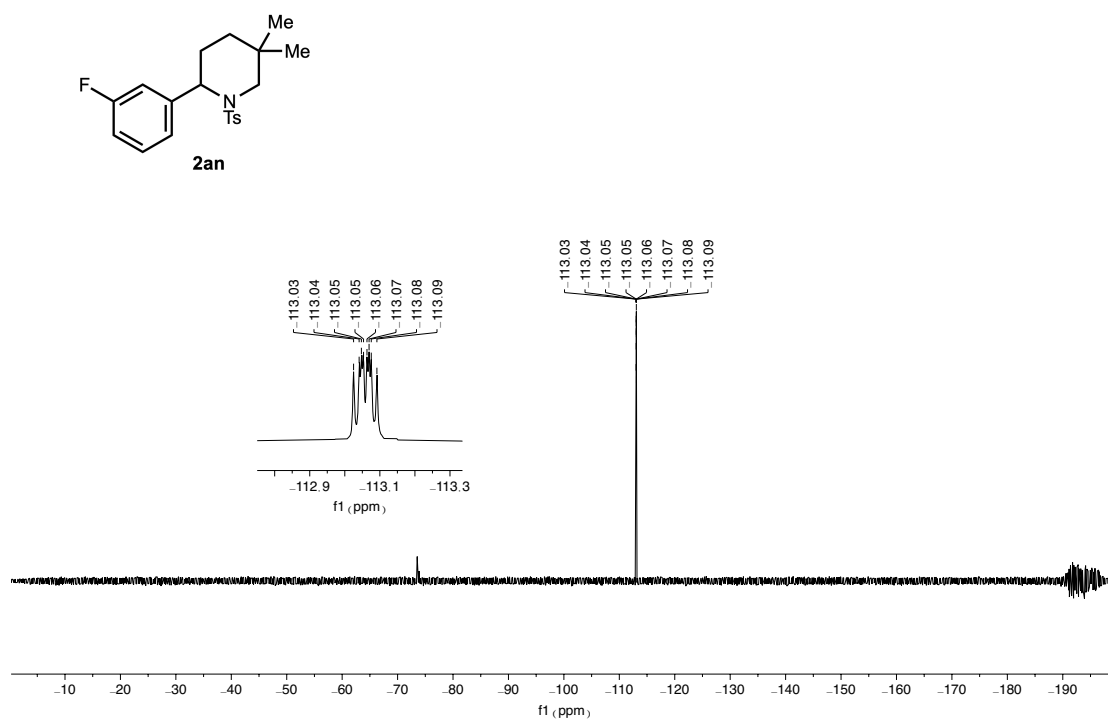
^1H NMR spectrum (400 MHz, CDCl_3) of **2an**



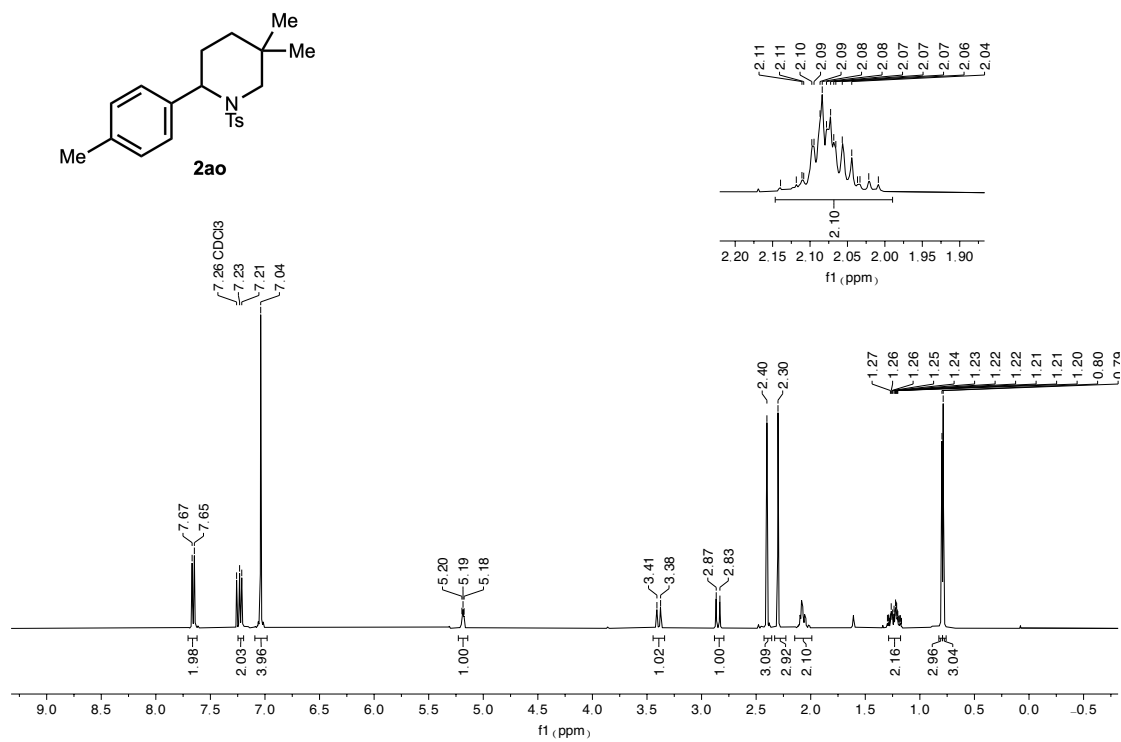
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2an**



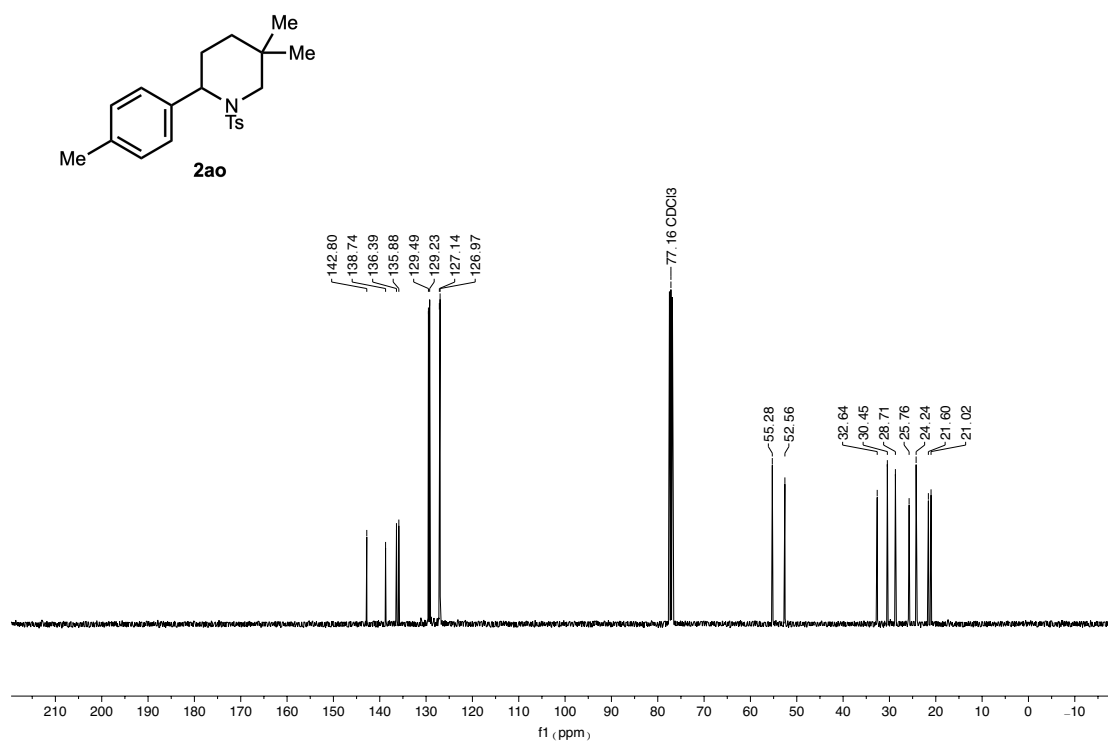
^{19}F NMR spectrum (375 MHz, CDCl_3) of **2an**



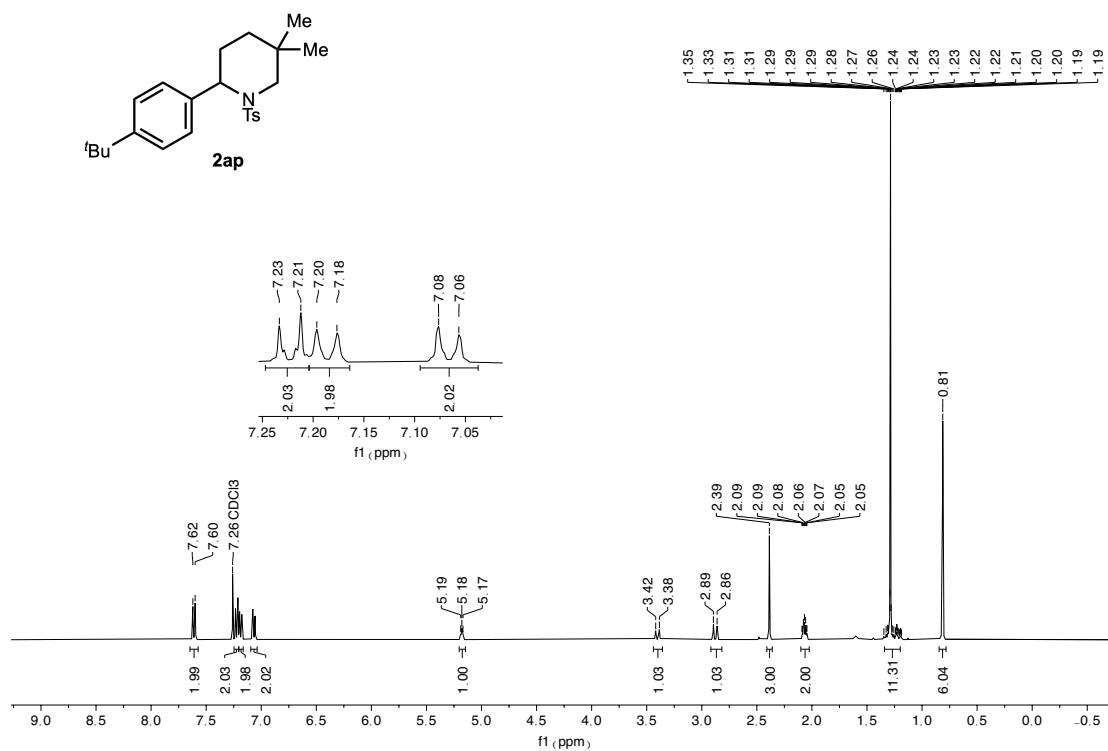
^1H NMR spectrum (400 MHz, CDCl_3) of **2ao**



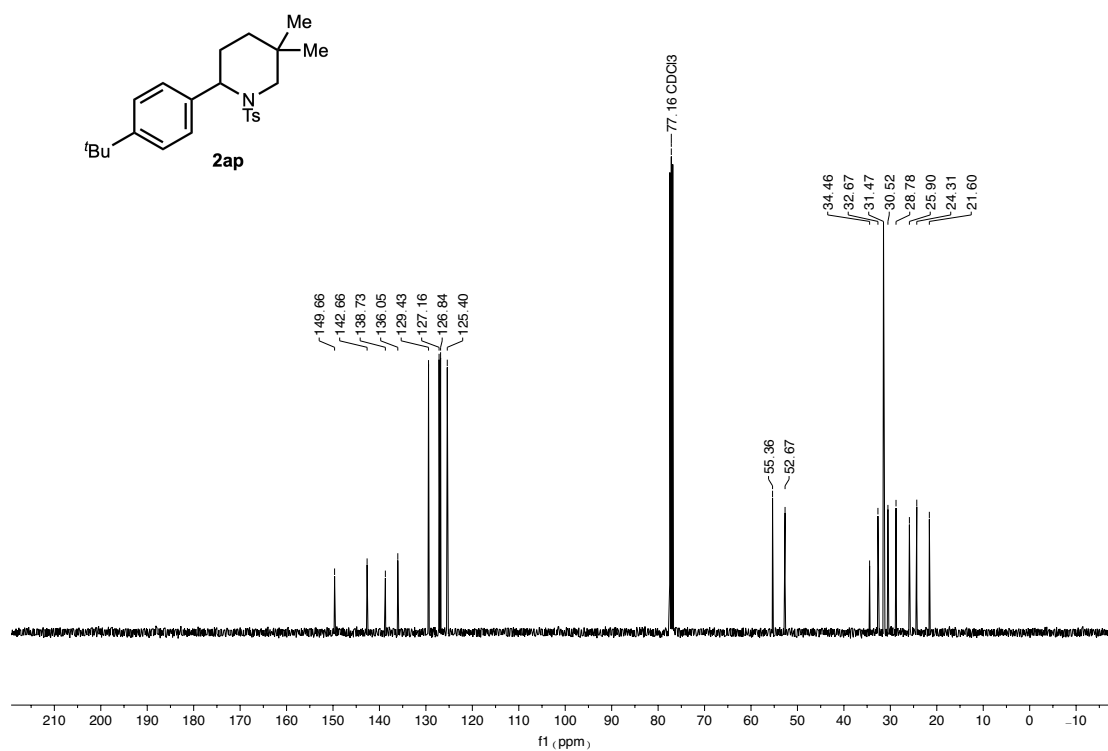
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ao**



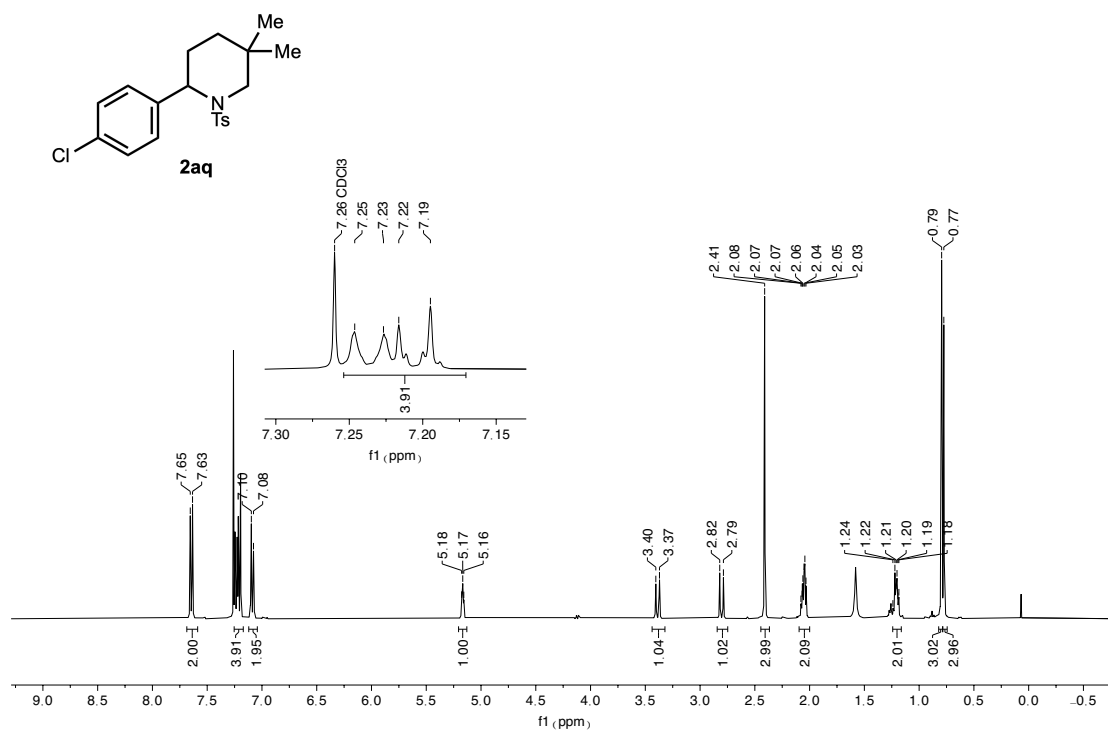
^1H NMR spectrum (400 MHz, CDCl_3) of **2ap**



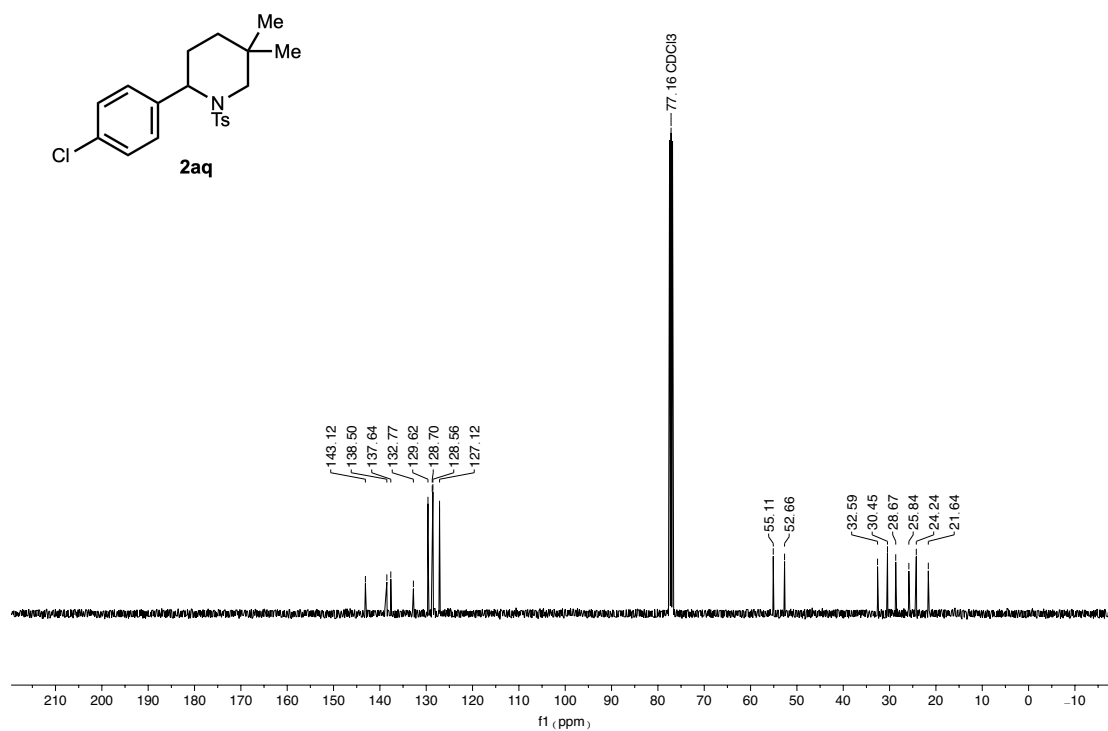
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ap**



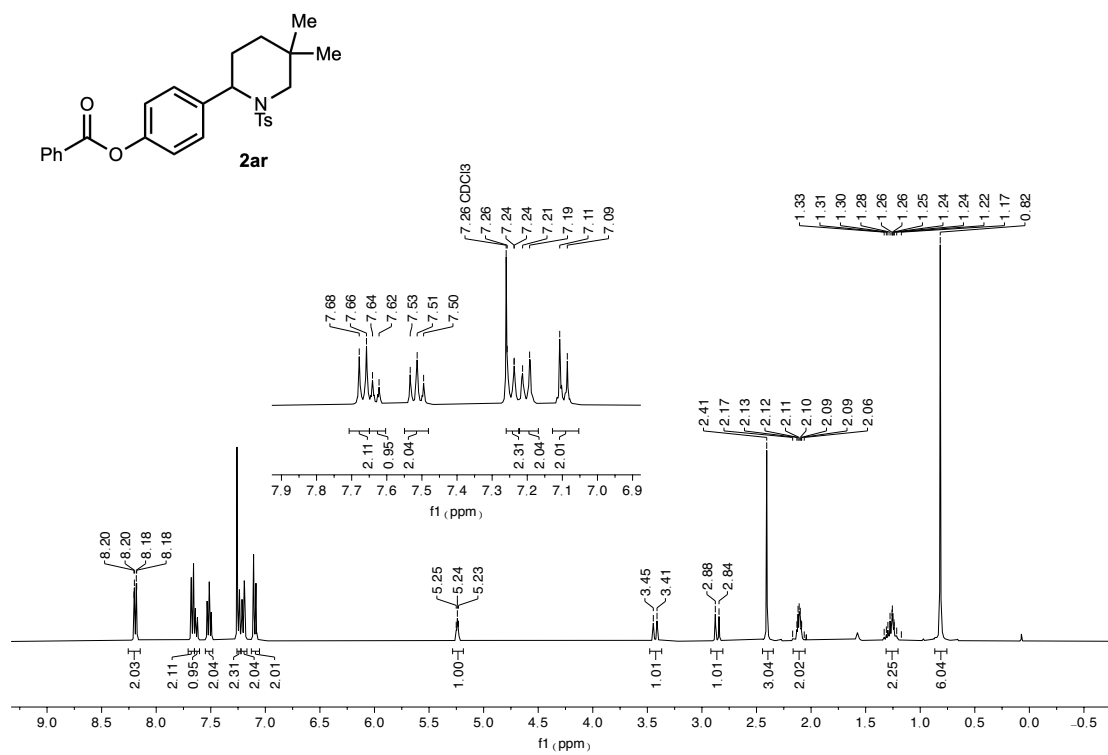
^1H NMR spectrum (400 MHz, CDCl_3) of **2aq**



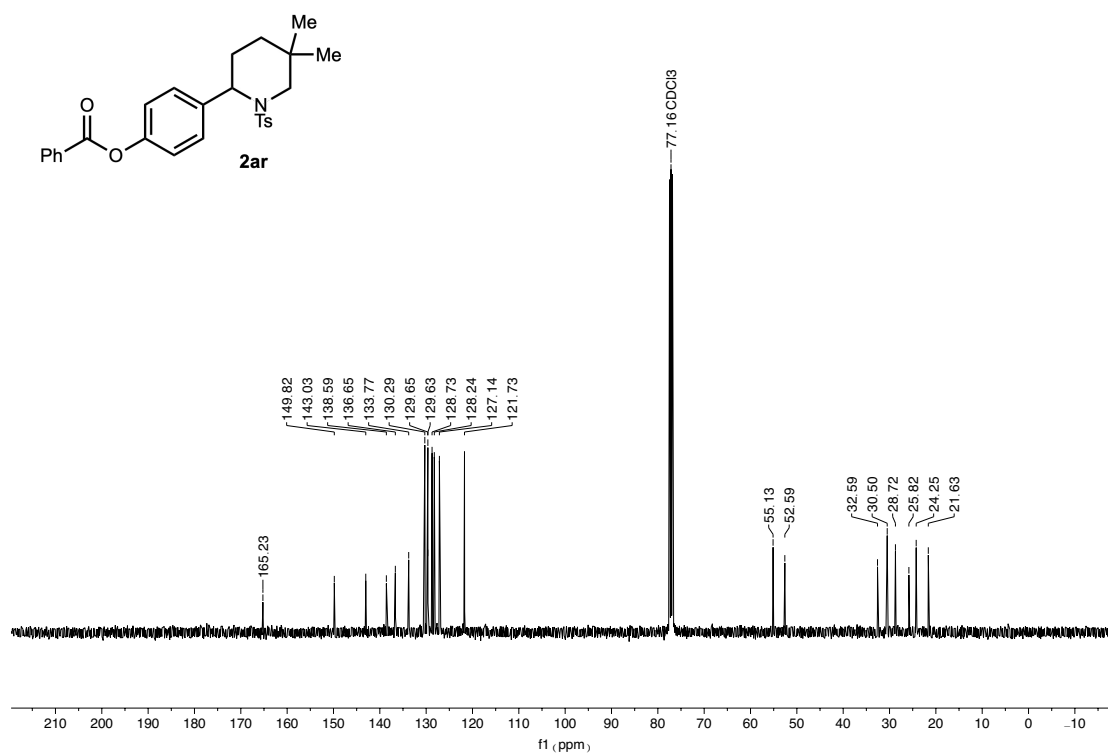
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2aq**



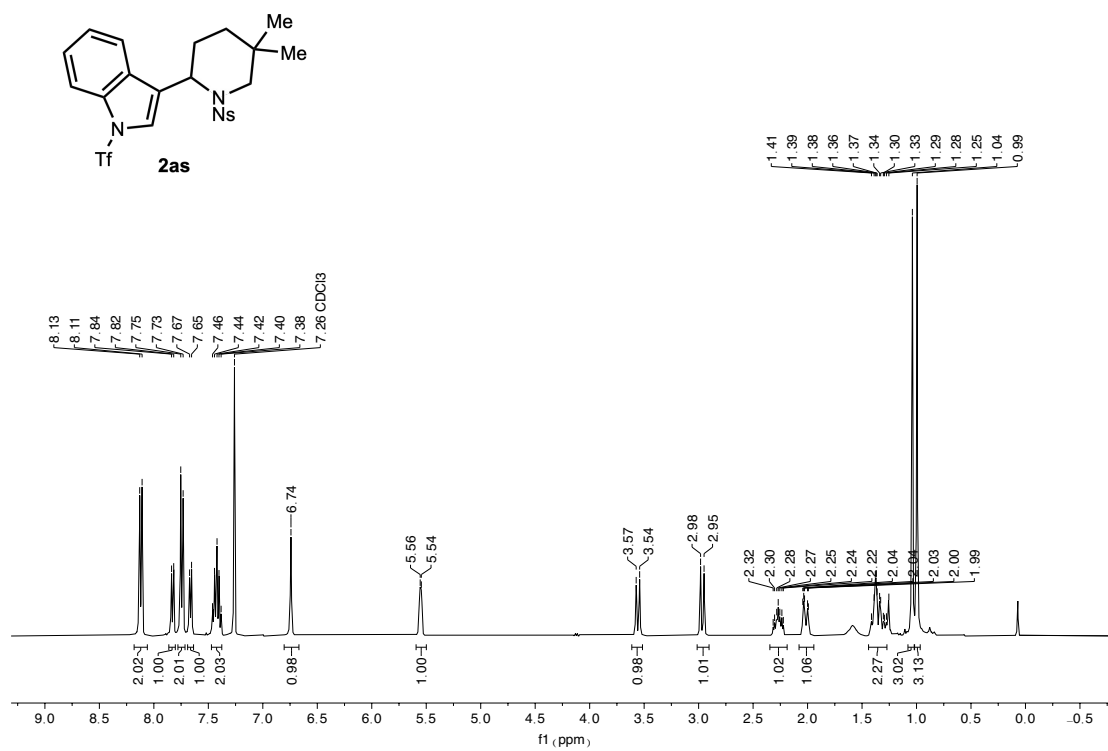
^1H NMR spectrum (400 MHz, CDCl_3) of **2ar**



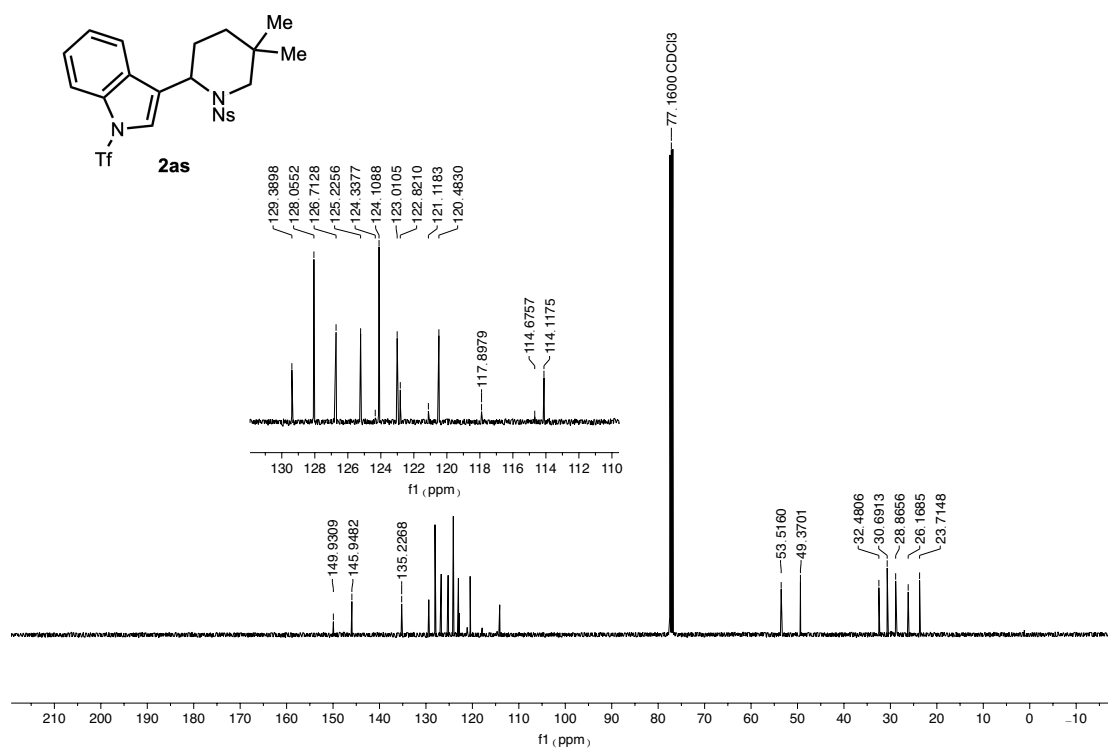
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2ar**



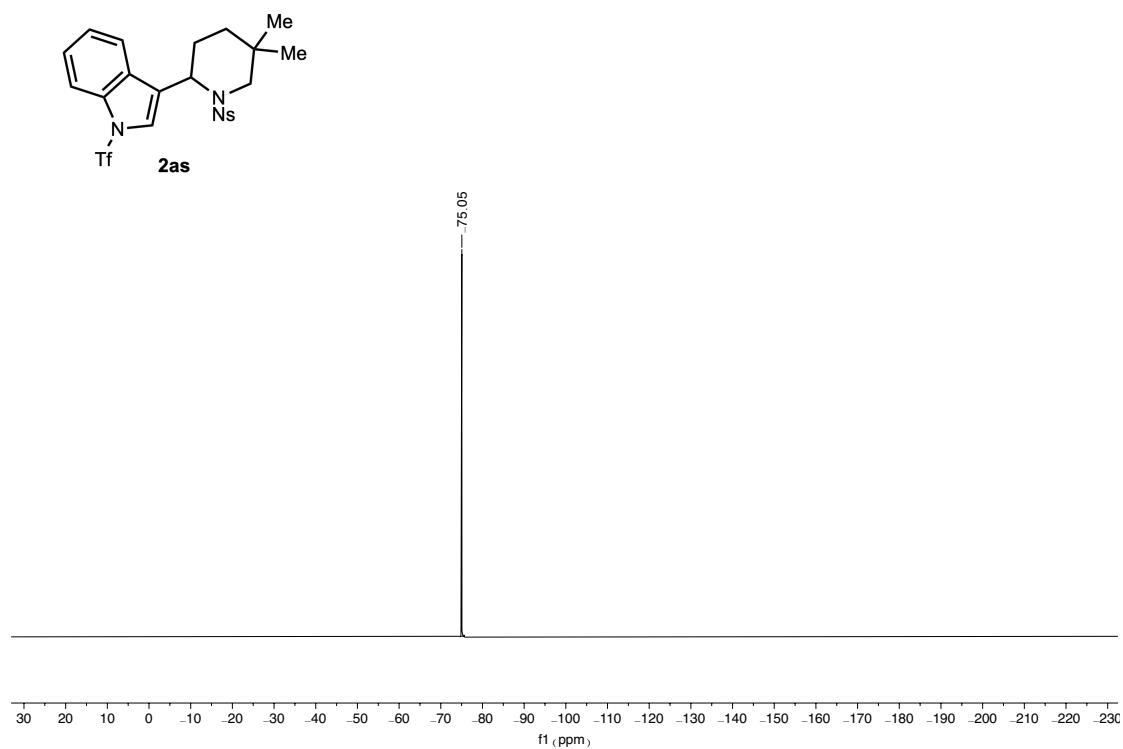
^1H NMR spectrum (400 MHz, CDCl_3) of **2as**



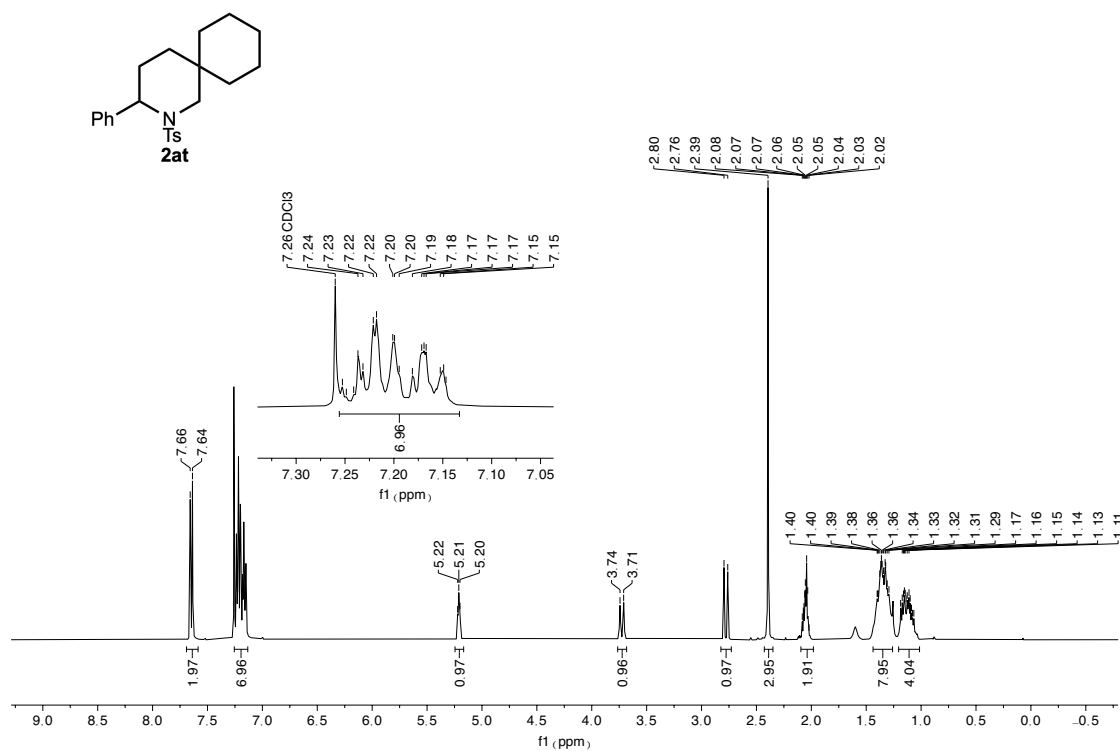
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2as**



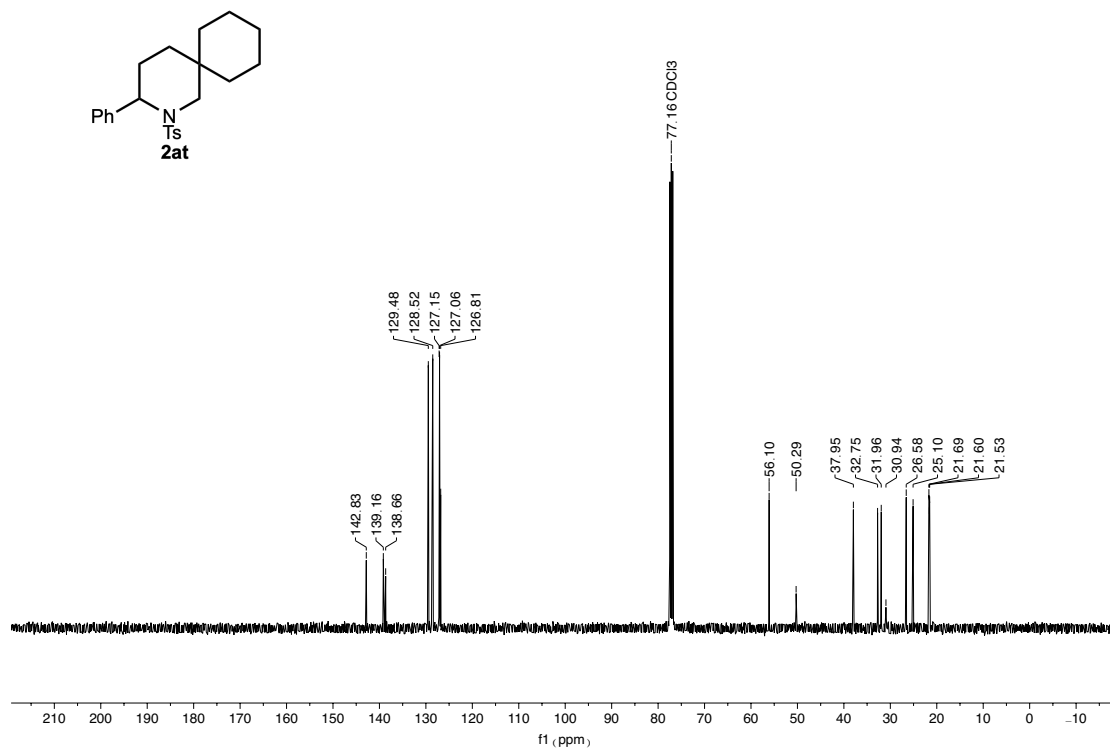
^{19}F NMR spectrum (375 MHz, CDCl_3) of **2as**



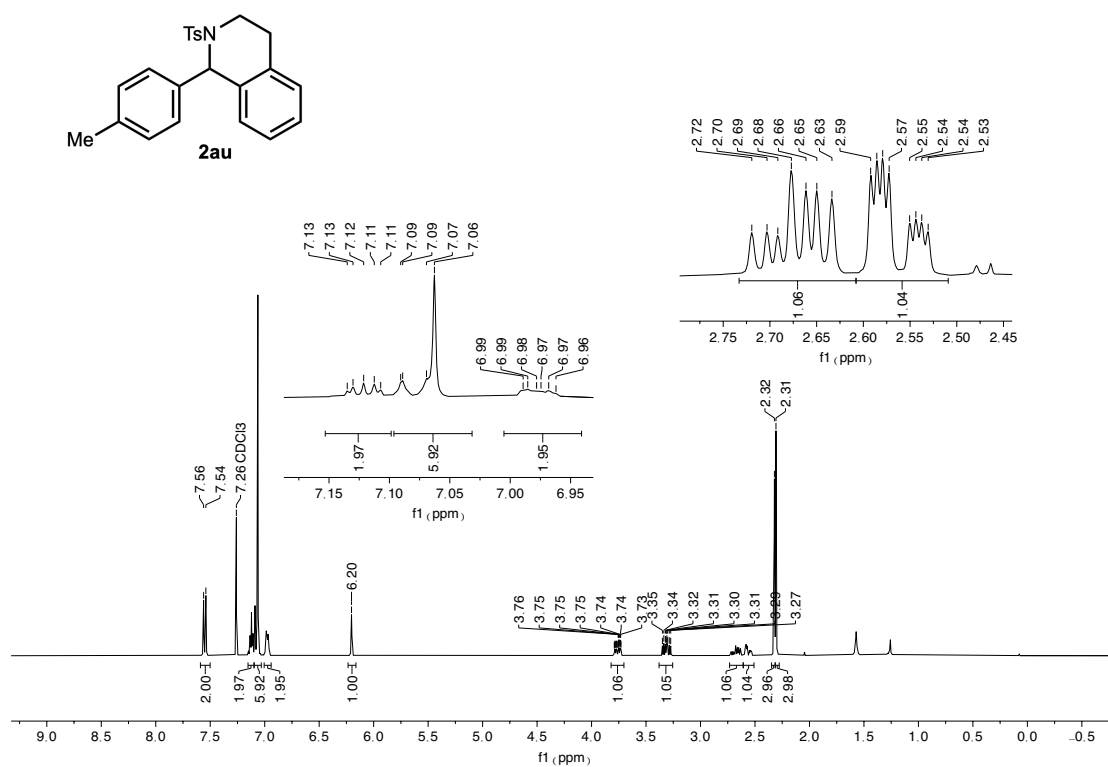
^1H NMR spectrum (400 MHz, CDCl_3) of **2at**



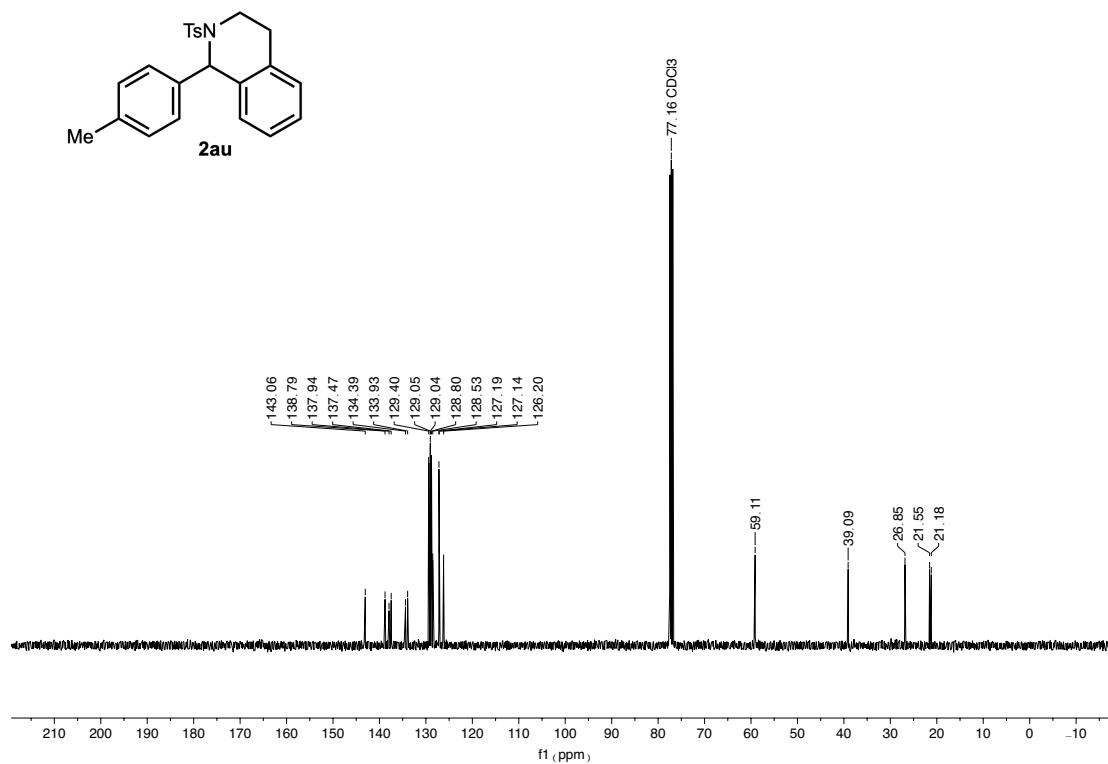
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2at**



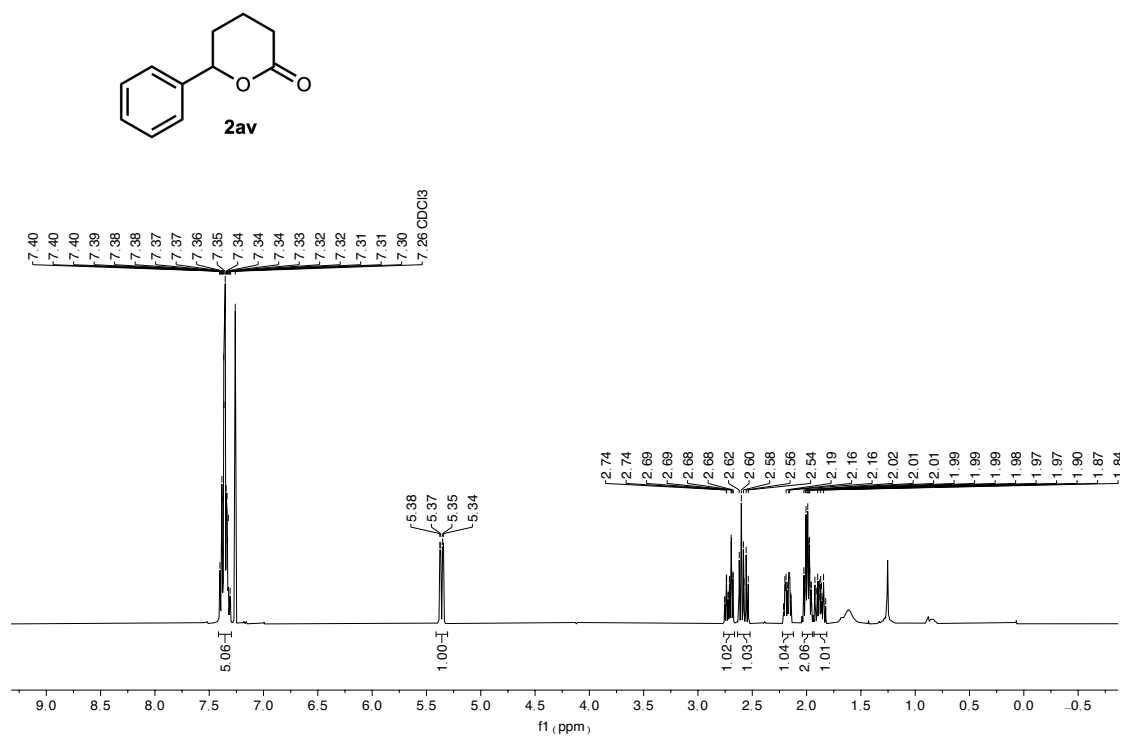
^1H NMR spectrum (400 MHz, CDCl_3) of **2au**



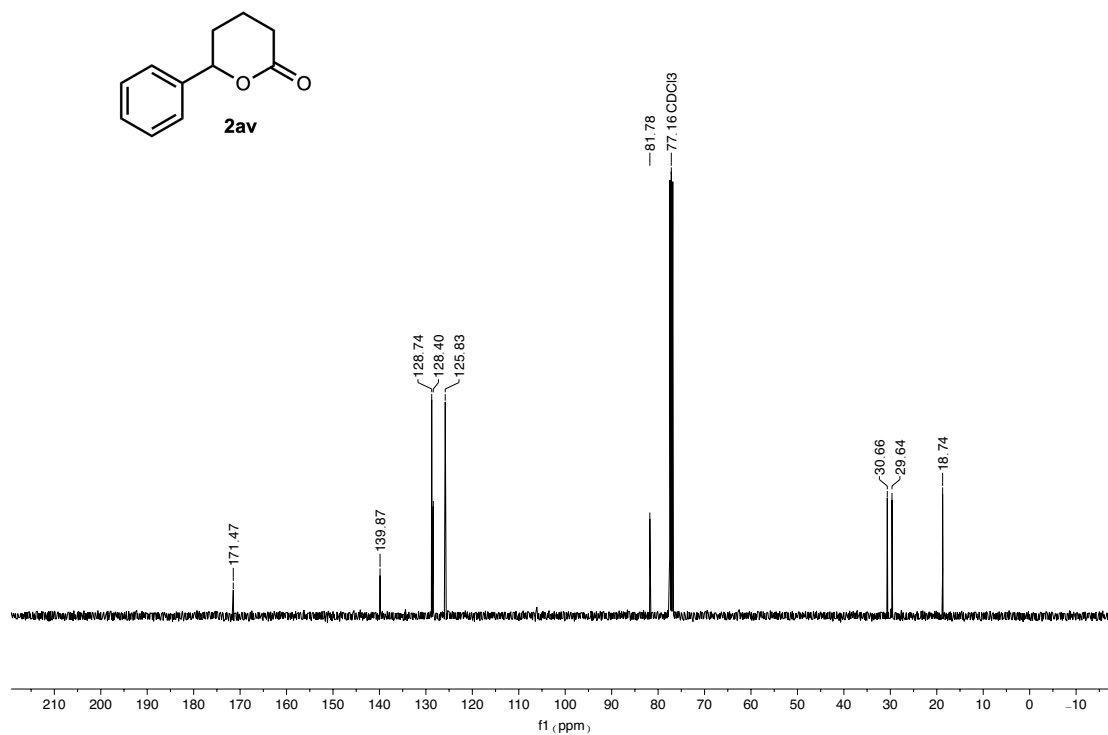
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2au**



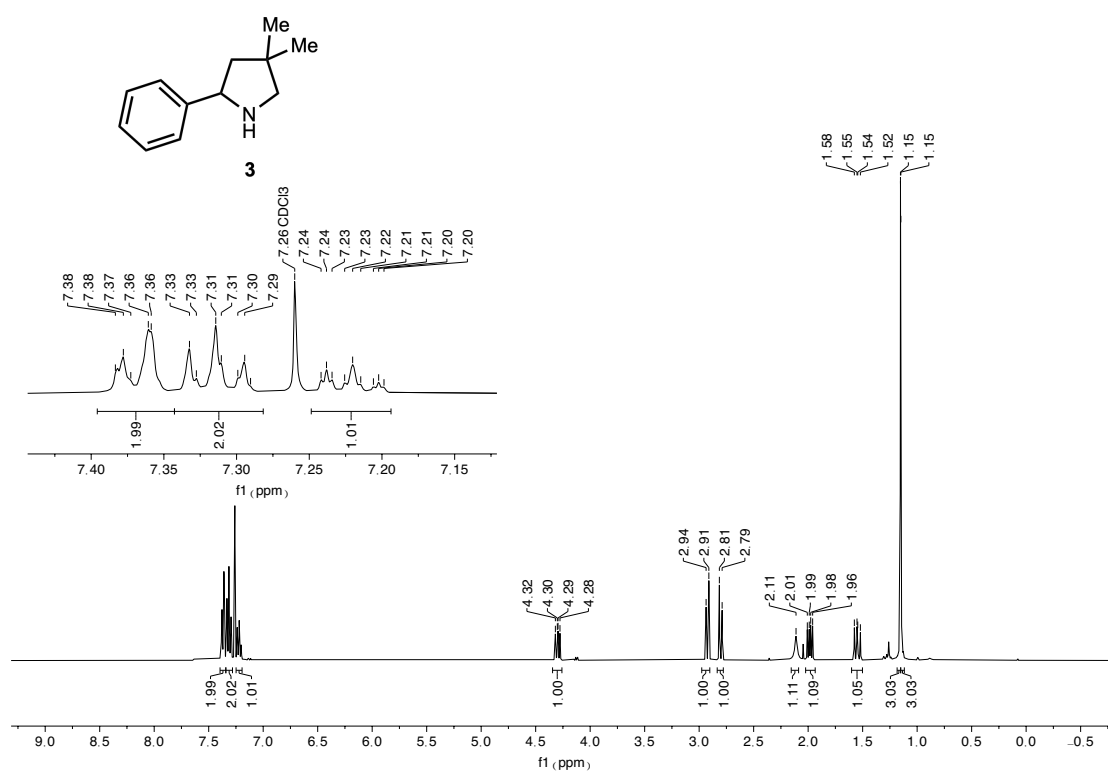
^1H NMR spectrum (400 MHz, CDCl_3) of **2av**



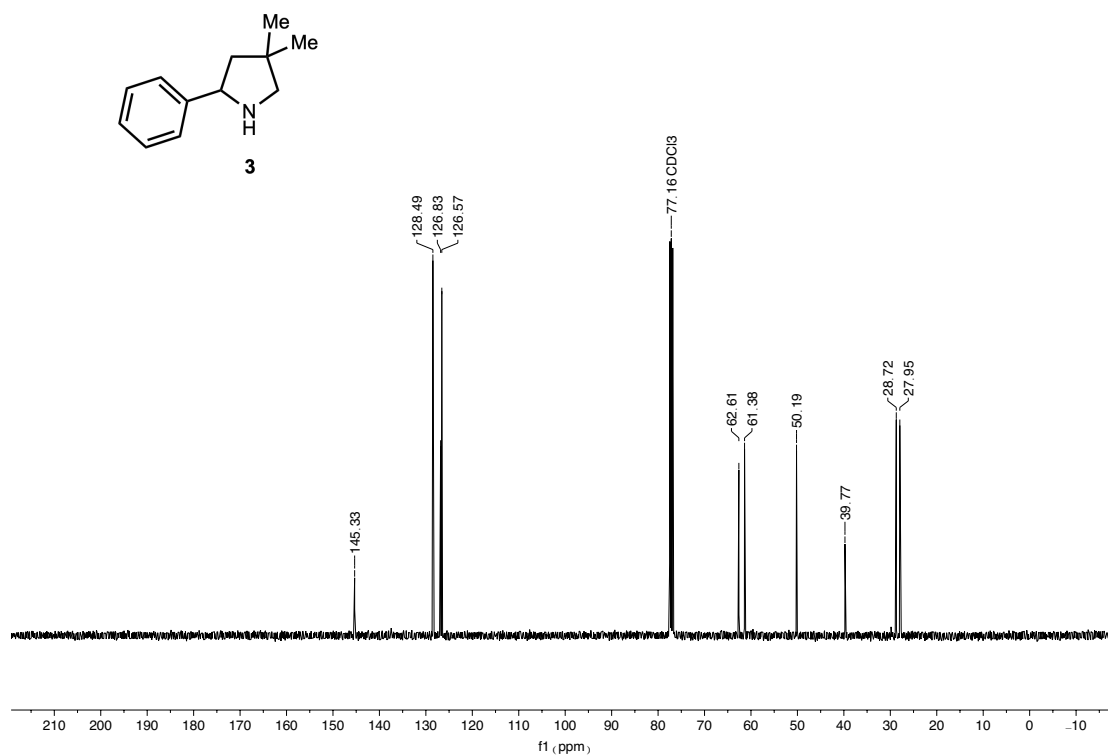
^{13}C NMR spectrum (100 MHz, CDCl_3) of **2av**



^1H NMR spectrum (400 MHz, CDCl_3) of **3**



^{13}C NMR spectrum (100 MHz, CDCl_3) of **3**



13. Cartesian coordinates of the optimized structures

1a					41	H	-4.6130	-0.6111	-1.6165
	Atom	X	Y	Z	42	H	-3.9889	0.7415	0.7168
1	C	-0.9106	-2.1049	1.4552	43	H	-1.9012	1.4696	1.8581
2	C	0.4630	-2.2462	1.2543	44	H	1.2964	0.1691	1.2371
3	C	1.0159	-2.3600	-0.0226	45	H	2.3660	1.5164	-1.1669
4	C	0.1378	-2.3088	-1.1126	46	H	1.4432	-0.0028	-1.1669
5	C	-1.2309	-2.1688	-0.9361	47	H	4.4442	-1.8873	0.3418
6	C	-1.7681	-2.0851	0.3529	48	H	3.1612	-1.2181	1.3311
7	O	-3.1181	-1.9990	0.4306	49	H	2.6991	-2.7947	-1.2699
8	C	-3.7017	-1.9491	1.7144	50	H	2.7746	-3.5014	0.3321
9	H	-4.7821	-1.8728	1.5586	51	H	1.1182	-2.2911	2.1271
10	H	-3.3594	-1.0732	2.2859	52	H	-1.2987	-2.0326	2.4688
11	H	-3.4838	-2.8601	2.2912	1j				
12	H	-1.9107	-2.1411	-1.7874		Atom	X	Y	Z
13	H	0.5402	-2.3885	-2.1244	1	C	3.6407	0.3536	-1.1419
14	C	2.4959	-2.5837	-0.2097	2	C	2.3561	0.5619	-0.6510
15	C	3.4245	-1.4720	0.2903	3	C	2.0738	1.6362	0.1982
16	C	3.5196	-0.1777	-0.5361	4	C	3.1112	2.5078	0.5353
17	C	4.5812	0.7148	0.1045	5	C	4.4002	2.3069	0.0441
18	H	4.3461	0.9311	1.1552	6	C	4.6702	1.2277	-0.7934
19	H	5.5669	0.2286	0.0702	7	H	5.6785	1.0672	-1.1732
20	H	4.6590	1.6751	-0.4270	8	H	5.1981	2.9951	0.3213
21	C	3.9345	-0.4833	-1.9745	9	H	2.9048	3.3516	1.1960
22	H	3.1540	-1.0256	-2.5273	10	C	0.6731	1.8446	0.7027
23	H	4.8489	-1.0942	-1.9939	11	C	-0.2532	2.3684	-0.3960
24	H	4.1400	0.4474	-2.5233	12	C	-1.7259	2.5627	-0.0082
25	C	2.1925	0.5846	-0.6115	13	C	-1.8587	3.4993	1.1919
26	N	1.6877	0.9583	0.7136	14	H	-2.9137	3.7497	1.3752
27	S	0.6557	2.2585	0.8260	15	H	-1.3171	4.4390	1.0098
28	O	0.3601	2.4076	2.2468	16	H	-1.4602	3.0520	2.1133
29	O	1.2702	3.3498	0.0778	17	C	-2.4601	3.1842	-1.1962
30	C	-0.8486	1.7955	0.0059	18	H	-2.0803	4.1969	-1.3933
31	C	-1.9539	1.4250	0.7717	19	H	-3.5396	3.2634	-0.9975
32	C	-3.1129	1.0174	0.1289	20	H	-2.3225	2.5990	-2.1169
33	C	-3.1759	0.9377	-1.2666	21	C	-2.3905	1.2379	0.3799
34	C	-2.0573	1.3202	-2.0116	22	N	-2.4113	0.2782	-0.7309
35	C	-0.8955	1.7601	-1.3862	23	S	-2.6378	-1.3325	-0.3522
36	H	-0.0394	2.0798	-1.9781	24	O	-3.3827	-1.4828	0.8966
37	H	-2.0988	1.2758	-3.0999	25	O	-3.1442	-1.9461	-1.5772
38	C	-4.4168	0.4252	-1.9277	26	C	-0.9826	-1.8994	-0.0632
39	H	-5.2974	1.0158	-1.6400	27	C	-0.2149	-2.3117	-1.1493
40	H	-4.3343	0.4442	-3.0208					

28	C	1.0895	-2.7381	-0.9300	21	C	-1.7535	2.2678	1.5696
29	C	1.6415	-2.7382	0.3550	22	C	-2.8302	2.1344	0.6843
30	C	0.8466	-2.3195	1.4283	23	C	-2.5640	1.8538	-0.6588
31	C	-0.4651	-1.9073	1.2311	24	C	-1.2610	1.6778	-1.1100
32	H	-1.0855	-1.6027	2.0723	25	H	-1.0559	1.4406	-2.1520
33	H	1.2650	-2.3218	2.4351	26	H	-3.3943	1.7525	-1.3588
34	C	3.0612	-3.1531	0.5874	27	H	-1.9485	2.4979	2.6171
35	H	3.1231	-3.9777	1.3105	28	H	0.3859	2.1808	1.8340
36	H	3.5454	-3.4756	-0.3420	29	C	3.0708	-0.0293	0.8824
37	H	3.6466	-2.3206	1.0032	30	C	3.6800	-1.3654	0.4482
38	H	1.6984	-3.0662	-1.7728	31	C	4.5039	-1.1739	-0.8226
39	H	-0.6374	-2.3066	-2.1526	32	H	4.8214	-2.1438	-1.2319
40	H	-3.0648	0.5211	-1.4781	33	H	3.9423	-0.6445	-1.6062
41	H	-3.4113	1.4335	0.7481	34	H	5.4071	-0.5842	-0.6101
42	H	-1.8382	0.7750	1.2098	35	C	4.5353	-1.9795	1.5432
43	H	0.1371	3.3377	-0.7514	36	H	5.3927	-1.3341	1.7839
44	H	-0.2025	1.6835	-1.2583	37	H	3.9549	-2.1318	2.4645
45	H	0.2875	0.8856	1.0864	38	H	4.9313	-2.9551	1.2265
46	H	0.6891	2.5442	1.5514	39	C	2.4157	-2.1847	0.1675
47	H	1.5500	-0.1239	-0.9202	40	H	2.6069	-3.0843	-0.4329
48	H	3.8396	-0.4972	-1.7946	41	H	1.9656	-2.5031	1.1214
2a					42	H	2.7947	-0.0487	1.9502
	Atom	X	Y	Z	43	H	3.7420	0.8210	0.7156
1	C	-1.9745	-1.6600	1.0001	44	H	1.7065	-1.1996	-1.6251
2	C	-0.6120	-1.4680	0.8656	45	H	-0.0115	-1.2452	1.7497
3	C	0.0014	-1.5096	-0.3936	46	H	-2.4623	-1.6012	1.9724
4	C	-0.7934	-1.7709	-1.5040	47	C	-4.2432	2.2367	1.1693
5	C	-2.1696	-1.9762	-1.3893	48	H	-4.6644	1.2336	1.3353
6	C	-2.7671	-1.9047	-0.1308	49	H	-4.3091	2.7819	2.1186
7	O	-4.0933	-2.0409	0.1015	50	H	-4.8869	2.7367	0.4345
8	C	-4.9459	-2.1698	-1.0164	PIFA				
9	H	-5.9651	-2.2189	-0.6233		Atom	X	Y	Z
10	H	-4.8591	-1.3024	-1.6882	1	I	-0.0002	-0.2479	-0.0024
11	H	-4.7360	-3.0876	-1.5848	2	O	-2.1559	0.0351	0.0067
12	H	-2.7597	-2.1649	-2.2831	3	C	-2.7642	-1.1075	0.0493
13	H	-0.3341	-1.7918	-2.4940	4	O	-2.2579	-2.2111	0.0704
14	C	1.4703	-1.2200	-0.5497	5	C	-4.2922	-0.9153	0.0653
15	N	1.8556	0.0812	0.0575	6	F	-4.9197	-2.0802	0.1364
16	S	1.4561	1.4809	-0.7291	7	F	-4.6565	-0.1735	1.1113
17	O	2.3135	2.5332	-0.1868	8	F	-4.6884	-0.2882	-1.0426
18	O	1.4246	1.2491	-2.1738	9	O	2.1557	0.0347	-0.0095
19	C	-0.2121	1.7913	-0.2043	10	C	2.7635	-1.1081	-0.0552
20	C	-0.4467	2.0951	1.1353	11	O	2.2566	-2.2113	-0.0812

12	C	4.2916	-0.9167	-0.0684	27	C	4.2971	-3.2877	-0.2797
13	F	4.6866	-0.2917	1.0411	28	C	2.9045	-3.1907	-0.1722
14	F	4.6579	-0.1735	-1.1128	29	C	2.1385	-3.1804	-1.3423
15	F	4.9185	-2.0819	-0.1404	30	C	2.7374	-3.2868	-2.5920
16	C	0.0002	1.8460	0.0021	31	H	2.1420	-3.2846	-3.5028
17	C	-0.4204	2.5062	1.1522	32	H	1.0543	-3.0911	-1.2698
18	C	-0.4202	3.8981	1.1414	33	C	2.2392	-3.1062	1.1666
19	C	0.0019	4.5904	0.0086	34	H	1.7360	-4.0526	1.4117
20	C	0.4231	3.9029	-1.1274	35	H	2.9615	-2.8974	1.9649
21	C	0.4218	2.5111	-1.1447	36	H	1.4684	-2.3238	1.1817
22	H	0.7425	1.9622	-2.0278	37	H	4.9043	-3.2708	0.6263
23	H	0.7500	4.4485	-2.0104	38	H	5.9968	-3.4678	-1.5961
24	H	0.0026	5.6789	0.0112	39	H	6.7034	-2.4609	-4.8691
25	H	-0.7464	4.4399	2.0270	40	H	5.1210	-0.8805	-5.7810
26	H	-0.7417	1.9536	2.0328	41	H	4.2121	-0.9724	-4.2687
Complex-1a					42	H	6.7458	1.0495	-2.3131
	Atom	X	Y	Z	43	H	6.6007	-0.7051	-2.3075
1	C	6.1790	0.1255	1.7059	44	H	4.0658	-0.4408	-2.1991
2	C	6.1082	0.2029	0.3117	45	H	4.2895	1.3014	-2.1080
3	C	4.8900	0.2420	-0.3618	46	H	7.0433	0.2366	-0.2457
4	C	3.7209	0.2110	0.4147	47	H	7.1532	0.0956	2.1883
5	C	3.7675	0.1468	1.7969	48	I	4.7346	3.6304	0.9091
6	C	5.0043	0.0926	2.4533	49	O	2.8881	3.5412	2.0551
7	H	2.8567	0.1373	2.3955	50	C	1.9360	3.1804	1.2552
8	H	2.7514	0.2510	-0.0866	51	O	2.0122	3.0188	0.0524
9	C	4.7709	0.3391	-1.8628	52	C	0.6235	2.9372	2.0214
10	C	6.0864	0.2198	-2.6156	53	F	-0.3626	2.6280	1.1924
11	C	6.0050	0.2400	-4.1482	54	F	0.7817	1.9299	2.8831
12	C	5.3023	1.5011	-4.6480	55	F	0.2731	4.0197	2.7139
13	H	5.3676	1.5738	-5.7436	56	O	6.7856	3.7251	0.1543
14	H	5.7699	2.3964	-4.2144	57	C	6.7373	3.5999	-1.1313
15	H	4.2369	1.5151	-4.3775	58	O	5.7389	3.5124	-1.8225
16	C	7.4305	0.2235	-4.7008	59	C	8.1425	3.5289	-1.7561
17	H	7.9647	1.1398	-4.4112	60	F	8.7326	2.3841	-1.3980
18	H	7.4297	0.1683	-5.8000	61	F	8.9088	4.5342	-1.3430
19	H	8.0105	-0.6272	-4.3151	62	F	8.0745	3.5640	-3.0810
20	C	5.2294	-0.9664	-4.6871	63	C	5.5920	4.1975	2.7375
21	N	5.8682	-2.2368	-4.3248	64	C	5.4706	3.3369	3.8237
22	S	4.9041	-3.5910	-4.2486	65	C	6.0346	3.7278	5.0351
23	O	3.8541	-3.5765	-5.2672	66	C	6.7115	4.9408	5.1354
24	O	5.8341	-4.7175	-4.2029	67	C	6.8210	5.7826	4.0309
25	C	4.1227	-3.3969	-2.6685	68	C	6.2495	5.4214	2.8140
26	C	4.9123	-3.3944	-1.5193	69	H	6.3183	6.0792	1.9498
					70	H	7.3451	6.7327	4.1138

71	H	7.1559	5.2348	6.0845	34	C	1.9823	-2.8531	0.8887	
72	H	5.9469	3.0718	5.8998	35	H	1.4647	-3.7965	1.1148	
73	H	4.9401	2.3894	3.7408	36	H	2.5838	-2.5860	1.7660	
74	O	4.9536	0.0341	3.8102	37	H	1.2053	-2.0886	0.7536	
75	C	6.1783	-0.0809	4.5055	38	H	4.6964	-3.0332	0.7357	
76	H	5.9269	-0.1131	5.5696	39	H	6.0904	-3.3172	-1.2995	
77	H	6.7099	-1.0036	4.2302	40	H	7.1762	-2.3360	-4.5438	
78	H	6.8367	0.7806	4.3166	41	H	5.6069	-0.9202	-5.7208	
Complex-1j					42	H	4.5435	-0.9951	-4.3121	
					43	H	6.7497	1.2757	-2.2205	
	Atom	X	Y	Z	44	H	6.6979	-0.4802	-2.1433	
	1	C	5.8021	0.3785	1.7739	45	H	4.1478	-0.3458	-2.2861
	2	C	5.8967	0.4219	0.3819	46	H	4.2832	1.4070	-2.2523
3	C	4.7482	0.4532	-0.4130	47	H	6.8827	0.4332	-0.0821	
4	C	3.5020	0.4639	0.2283	48	H	6.7117	0.3500	2.3739	
5	C	3.4020	0.4306	1.6139	49	I	4.6478	3.8733	0.9996	
6	C	4.5569	0.3763	2.3959	50	O	2.9991	3.8128	2.4109	
7	H	4.4830	0.3383	3.4826	51	C	1.8930	3.5209	1.8036	
8	H	2.4197	0.4477	2.0872	52	O	1.7203	3.3813	0.6100	
9	H	2.5957	0.5000	-0.3805	53	C	0.7461	3.3316	2.8135	
10	C	4.7813	0.4813	-1.9212	54	F	-0.4040	3.1061	2.1954	
11	C	6.1656	0.3988	-2.5407	55	F	1.0093	2.2900	3.6073	
12	C	6.2256	0.3463	-4.0736	56	F	0.6091	4.4099	3.5835	
13	C	5.4723	1.5189	-4.6997	57	O	6.6038	4.0104	0.0452	
14	H	5.6504	1.5600	-5.7843	58	C	6.4973	3.8571	-1.2338	
15	H	5.8058	2.4689	-4.2600	59	O	5.4790	3.6933	-1.8780	
16	H	4.3868	1.4416	-4.5447	60	C	7.8828	3.8762	-1.9085	
17	C	7.6940	0.4271	-4.4921	61	F	8.5718	2.7896	-1.5425	
18	H	8.1193	1.3985	-4.2012	62	F	8.5817	4.9481	-1.5454	
19	H	7.8032	0.3231	-5.5821	63	F	7.7750	3.8728	-3.2315	
20	H	8.3018	-0.3525	-4.0104	64	C	5.7261	4.4965	2.6851	
21	C	5.5985	-0.9407	-4.6184	65	C	5.9040	3.6024	3.7348	
22	N	6.2703	-2.1428	-4.1124	66	C	6.6155	4.0362	4.8497	
23	S	5.3851	-3.5523	-4.0712	67	C	7.1362	5.3276	4.8901	
24	O	4.4856	-3.6698	-5.2189	68	C	6.9472	6.2016	3.8219	
25	O	6.3629	-4.6097	-3.8236	69	C	6.2286	5.7936	2.7018	
26	C	4.3855	-3.3092	-2.6266	70	H	6.0669	6.4699	1.8646	
27	C	5.0060	-3.2471	-1.3797	71	H	7.3528	7.2108	3.8589	
28	C	4.2226	-3.0886	-0.2449	72	H	7.6946	5.6570	5.7645	
29	C	2.8288	-2.9938	-0.3383	73	H	6.7657	3.3560	5.6858	
30	C	2.2346	-3.0431	-1.6035	74	H	5.4973	2.5936	3.6861	
31	C	3.0030	-3.2060	-2.7502	PIFAanion					
32	H	2.5406	-3.2528	-3.7342						
33	H	1.1511	-2.9576	-1.6885	Atom	X	Y	Z		

1	I	-0.0104	-0.0902	0.0127	16	C	-2.5844	2.8560	-1.5995
2	O	-2.7622	0.2295	0.1235	17	H	-2.1407	3.7529	-2.0549
3	C	-3.0524	-0.9902	0.0900	18	H	-3.6386	3.0785	-1.3773
4	O	-2.3354	-1.9943	0.0237	19	H	-2.5545	2.0538	-2.3504
5	C	-4.5851	-1.2250	0.1548	20	C	-2.5527	1.3206	0.3766
6	F	-4.9249	-2.5117	0.0596	21	N	-2.6950	0.1384	-0.4798
7	F	-5.0854	-0.7659	1.3122	22	S	-2.6325	-1.3623	0.2362
8	F	-5.2161	-0.5732	-0.8324	23	O	-3.1927	-1.3497	1.5862
9	O	2.7247	0.2181	-0.0584	24	O	-3.1743	-2.2832	-0.7593
10	C	3.0352	-0.9979	-0.0854	25	C	-0.8822	-1.6188	0.3852
11	O	2.3359	-2.0150	-0.0652	26	C	-0.1266	-1.7422	-0.7806
12	C	4.5733	-1.1995	-0.1388	27	C	1.2381	-1.9621	-0.6772
13	F	5.1501	-0.7207	0.9743	28	C	1.8596	-2.0699	0.5765
14	F	5.1128	-0.5423	-1.1751	29	C	1.0810	-1.9233	1.7283
15	F	4.9327	-2.4794	-0.2514	30	C	-0.2907	-1.7046	1.6420
16	C	0.0048	2.0014	0.0024	31	H	-0.9003	-1.6029	2.5380
17	C	-0.6096	2.6944	1.0450	32	H	1.5556	-1.9947	2.7070
18	C	-0.6036	4.0863	1.0249	33	C	3.3198	-2.3796	0.6679
19	C	0.0152	4.7712	-0.0188	34	H	3.4890	-3.4637	0.5906
20	C	0.6288	4.0657	-1.0520	35	H	3.8811	-1.9173	-0.1567
21	C	0.6239	2.6739	-1.0509	36	H	3.7480	-2.0502	1.6229
22	H	1.1037	2.1169	-1.8535	37	H	1.8397	-2.0643	-1.5809
23	H	1.1133	4.5993	-1.8683	38	H	-0.6042	-1.6631	-1.7565
24	H	0.0189	5.8600	-0.0274	39	H	-3.4848	0.1689	-1.1266
25	H	-1.0844	4.6360	1.8326	40	H	-3.5405	1.6661	0.7213
26	H	-1.0947	2.1532	1.8550	41	H	-1.9983	1.0232	1.2783
A-1a					42	H	0.0316	2.9242	-1.2990
					43	H	-0.4441	1.2276	-1.4181
					44	H	0.1394	0.8981	1.0227
					45	H	0.5741	2.5749	1.1614
					46	H	1.7506	1.4749	-2.0714
					47	H	4.1385	0.9205	-2.4757
					48	O	5.8479	0.4626	-0.7063
					49	C	6.8254	0.1613	0.3043
					50	H	6.5023	-0.7076	0.8885
					51	H	7.7422	-0.0698	-0.2391
					52	H	6.9782	1.0306	0.9526
					A-1j				
					Atom	X	Y	Z	
1	C	3.7356	1.0039	-1.4688	1	C	3.7520	0.8353	-1.3377
2	C	2.4239	1.3064	-1.2346	2	C	2.4107	1.0635	-1.1236
3	C	1.9346	1.4027	0.0939	3	C	1.9063	1.2159	0.20328
4	C	2.8389	1.1720	1.1765	4	C	2.8027	1.0660	1.29895
5	C	4.1552	0.8751	0.9677					
6	C	4.6221	0.7753	-0.3720					
7	H	4.8262	0.7096	1.8060					
8	H	2.4537	1.2476	2.1929					
9	C	0.5308	1.7486	0.4297					
10	C	-0.3950	2.0838	-0.7266					
11	C	-1.8280	2.4717	-0.3290					
12	C	-1.8327	3.6641	0.6265					
13	H	-2.8583	4.0264	0.7859					
14	H	-1.2435	4.4955	0.2130					
15	H	-1.4182	3.4103	1.6125					

5	C	4.1386	0.8439	1.08217	OTFAanion				
6	C	4.6247	0.7304	-0.2424		Atom	X	Y	Z
7	H	5.6860	0.5571	-0.4113	1	O	-1.8145	1.7706	-0.3050
8	H	4.8296	0.7563	1.91729	2	C	-1.0337	2.7275	-0.1888
9	H	2.4077	1.1657	2.30945	3	O	-0.3910	3.1779	0.7754
10	C	0.4992	1.5679	0.50015	4	C	-0.7735	3.5399	-1.4934
11	C	-0.3851	1.9899	-0.6609	5	F	-1.0321	4.8535	-1.3284
12	C	-1.7961	2.4621	-0.2733	6	F	-1.4982	3.1459	-2.5534
13	C	-1.7365	3.6900	0.63447	7	F	0.5206	3.4580	-1.8708
14	H	-2.7446	4.0959	0.80052	IPhOTFAradical				
15	H	-1.1278	4.4817	0.17476		Atom	X	Y	Z
16	H	-1.3094	3.4622	1.62134	1	I	-0.1293	-0.0807	0.3217
17	C	-2.5359	2.8365	-1.5564	2	O	-2.7016	0.1203	-0.0637
18	H	-2.0340	3.6757	-2.059	3	C	-2.9993	-1.1064	0.0265
20	H	-2.5709	1.9983	-2.2668	4	O	-2.2874	-2.0835	0.2363
21	C	-2.5817	1.3808	0.47761	5	C	-4.5241	-1.3287	-0.1675
22	N	-2.7678	0.1604	-0.3132	6	F	-4.8533	-2.6134	-0.0956
23	S	-2.6155	-1.3242	0.40122	7	F	-5.2121	-0.6732	0.7710
24	O	-2.9620	-1.2862	1.81891	8	F	-4.9167	-0.8679	-1.3576
25	O	-3.2883	-2.2604	-0.4929	9	C	0.0399	1.9870	0.1789
26	C	-0.8583	-1.6009	0.30153	10	C	-0.0537	2.7591	1.3403
27	C	-0.2610	-1.6287	-0.9579	11	C	0.0667	4.1402	1.2377
28	C	1.1008	-1.8614	-1.0468	12	C	0.2730	4.7362	-0.0057
29	C	1.8751	-2.0921	0.1118	13	C	0.3599	3.9544	-1.1569
30	C	1.2455	-2.0457	1.368	14	C	0.2426	2.5717	-1.0746
31	C	-0.1150	-1.8078	1.46937	15	H	0.3072	1.9541	-1.9682
32	H	-0.6123	-1.7841	2.43678	16	H	0.5193	4.4228	-2.1264
33	H	1.8371	-2.2225	2.26586	17	H	0.3658	5.8183	-0.0783
34	C	3.3190	-2.4181	0.00092	18	H	-0.0016	4.7529	2.1348
35	H	3.5859	-3.2660	0.64562	19	H	-0.2168	2.2858	2.3066
36	H	3.6122	-2.6425	-1.0305	PhI				
37	H	3.9374	-1.5699	0.34821		Atom	X	Y	Z
38	H	1.5855	-1.9000	-2.0218	1	C	0.8644	-1.2145	0.0000
39	H	-0.8557	-1.4651	-1.8555	2	C	2.2571	-1.2130	0.0005
40	H	-3.5554	0.1609	-0.9616	3	C	2.9608	-0.0107	0.0000
41	H	-3.5623	1.7849	0.77354	4	C	2.2526	1.1896	-0.0010
42	H	-2.0697	1.1111	1.41191	5	C	0.8591	1.2029	-0.0015
43	H	0.1035	2.8139	-1.2064	6	C	0.1695	-0.0076	-0.0009
44	H	-0.4781	1.1569	-1.3753	7	H	0.3199	-2.1570	0.0004
45	H	0.0758	0.6808	1.02024	8	H	2.8066	-2.1529	0.0012
46	H	0.5171	2.3333	1.29528	9	H	4.0493	-0.0104	0.0004
47	H	1.7286	1.1588	-1.9658	10	H	0.3152	2.1456	-0.0022
48	H	4.1385	0.7376	-2.3492					

11	H	-0.9193	-0.0015	-0.0013	3	H	1.4291	0.7341	0.9995
12	I	3.3088	3.0185	-0.0016	4	C	1.8892	-2.3264	0.1214
OTFAradical					5	C	-0.1993	-0.8186	-0.0628
	Atom	X	Y	Z	6	F	-0.9329	-1.7176	0.6082
1	O	3.4837	0.4781	0.1163	7	F	-0.5143	-0.9531	-1.3522
2	C	4.5257	1.1233	-0.1104	8	F	-0.5809	0.4028	0.3319
3	O	5.4711	0.8579	0.6649	9	F	1.9020	-2.9377	1.3171
4	C	4.6277	2.1483	-1.2410	10	F	3.1584	-2.2454	-0.2813
5	F	3.7286	3.1034	-1.0480	11	F	1.2199	-3.1120	-0.7244
6	F	4.3751	1.5513	-2.3979	TFA				
7	F	5.8399	2.6745	-1.2657		Atom	X	Y	Z
CO₂					1	O	-1.9729	2.0202	-0.3330
	Atom	X	Y	Z	2	C	-0.7680	2.5685	-0.3916
1	O	-2.4831	1.0020	0.5123	3	O	0.1697	2.3349	0.3194
2	C	-2.4051	0.8413	-0.6386	4	C	-0.7301	3.5859	-1.5418
3	O	-2.3268	0.6806	-1.7895	5	F	-1.6484	4.5314	-1.3515
CF₃radical					6	F	-0.9898	2.9812	-2.6996
	Atom	X	Y	Z	7	F	0.4612	4.1555	-1.6147
1	C	-2.0986	0.1708	0.0296	8	H	-1.9828	1.3732	0.4029
2	F	-1.6422	0.8164	1.0805	A1-1a				
3	F	-1.6420	-1.0621	-0.0040		Atom	X	Y	Z
4	F	-3.4130	0.1904	-0.0039	1	C	3.1908	-0.2948	-2.6501
HFIP					2	C	1.9150	0.1156	-2.3815
	Atom	X	Y	Z	3	C	1.5288	0.4211	-1.0515
1	C	-2.3097	-0.8807	0.0284	4	C	2.4922	0.2843	0.0011
2	H	-1.9492	-0.4025	-0.8961	5	C	3.7751	-0.1132	-0.2527
3	O	-1.8695	-0.2591	1.1916	6	C	4.1409	-0.4171	-1.5890
4	H	-1.9165	0.7023	1.0661	7	H	4.4963	-0.2051	0.5553
5	C	-1.7374	-2.2886	0.0513	8	H	2.1507	0.5005	1.0200
6	C	-3.8330	-0.8661	-0.0247	9	C	0.1831	0.8882	-0.6673
7	F	-4.3771	-1.5597	0.9746	10	C	-0.8477	1.0871	-1.7611
8	F	-4.2950	-1.3602	-1.1730	11	C	-2.2077	1.6097	-1.2685
9	F	-4.2555	0.3980	0.0809	12	C	-2.0550	2.9572	-0.5623
10	F	-2.0319	-2.9272	1.1821	13	H	-3.0431	3.3742	-0.3170
11	F	-0.4101	-2.2391	-0.0532	14	H	-1.5434	3.6769	-1.2187
12	F	-2.2074	-3.0113	-0.9670	15	H	-1.4845	2.8825	0.3744
HFIPradical					16	C	-3.1193	1.7901	-2.4810
	Atom	X	Y	Z	17	H	-2.7156	2.5605	-3.1537
1	C	1.2590	-0.9849	0.1883	18	H	-4.1262	2.1095	-2.1725
2	O	1.9466	-0.0883	0.8998	19	H	-3.2180	0.8622	-3.0623
					20	C	-2.8572	0.6411	-0.2739
					21	N	-3.1570	-0.6616	-0.8792

22	S	-3.0772	-2.0165	0.0880	4	C	2.7504	0.86722	1.34733
23	O	-3.4168	-1.7123	1.4759	5	C	4.0545	0.49931	1.11589
24	O	-3.8304	-3.0407	-0.6326	6	C	4.5641	0.57962	-0.1962
25	C	-1.3492	-2.4115	0.0265	7	H	4.6763	0.14843	1.93555
26	C	-0.8313	-2.9513	-1.1534	8	H	2.3449	0.82898	2.3587
27	C	0.5189	-3.2520	-1.2169	9	C	0.5829	1.79283	0.64385
28	C	1.3622	-3.0222	-0.1175	10	C	-0.4212	2.13557	-0.4356
29	C	0.8208	-2.4578	1.0386	11	C	-1.8690	2.32177	0.04585
30	C	-0.5354	-2.1519	1.1224	12	C	-1.9648	3.29367	1.22107
31	H	-0.9405	-1.6839	2.0173	13	H	-3.0185	3.51472	1.44489
32	H	1.4672	-2.2358	1.8869	14	H	-1.4580	4.24138	0.99485
33	C	2.8100	-3.3912	-0.1964	15	H	-1.5153	2.88139	2.13586
34	H	2.9374	-4.4828	-0.1593	16	C	-2.6928	2.87302	-1.1167
35	H	3.2563	-3.0591	-1.1457	17	H	-2.3639	3.8909	-1.3701
36	H	3.3837	-2.9622	0.6344	18	H	-3.7606	2.92051	-0.8554
37	H	0.9385	-3.6737	-2.1309	19	H	-2.5886	2.25682	-2.021
38	H	-1.4829	-3.1311	-2.0075	20	C	-2.4578	0.98745	0.51355
39	H	-4.0254	-0.6908	-1.4156	21	N	-2.5509	0.01134	-0.5767
40	H	-3.7737	1.0949	0.1374	22	S	-2.4387	-1.6018	-0.1814
41	H	-2.1927	0.4736	0.5858	23	O	-3.0042	-1.8814	1.13753
42	H	-0.4629	1.8043	-2.5056	24	O	-2.9545	-2.3148	-1.3477
43	H	-1.0072	0.1376	-2.2981	25	C	-0.6843	-1.84	-0.0767
44	H	-0.1702	0.1718	0.1012	26	C	0.0735	-1.7553	-1.2456
45	H	0.3255	1.7996	-0.0518	27	C	1.4345	-2.0118	-1.1851
46	H	1.1931	0.2061	-3.1900	28	C	2.0499	-2.3586	0.02583
47	H	3.5193	-0.5406	-3.6577	29	C	1.2726	-2.406	1.1858
48	O	5.3282	-0.8374	-1.9567	30	C	-0.0956	-2.1554	1.14305
49	C	6.3524	-1.0519	-0.9739	31	H	-0.7045	-2.2108	2.04339
50	H	6.0277	-1.8100	-0.2518	32	H	1.7456	-2.6545	2.13606
51	H	7.2199	-1.4094	-1.5300	33	C	3.5075	-2.6983	0.06202
52	H	6.5916	-0.1125	-0.4637	34	H	3.6721	-3.7314	-0.2775
53	O	0.6547	0.3628	2.5626	35	H	4.0914	-2.0494	-0.6059
54	C	-0.0050	1.4192	2.5544	36	H	3.9156	-2.618	1.07724
55	O	0.2366	2.5322	2.0534	37	H	2.0364	-1.9552	-2.0926
56	C	-1.3554	1.3600	3.3194	38	H	-0.4022	-1.4971	-2.1911
57	F	-1.2472	1.9792	4.5103	39	H	-3.3510	0.14384	-1.1977
58	F	-1.7832	0.1149	3.5660	40	H	-3.4466	1.15618	0.96993
59	F	-2.3466	1.9800	2.6547	41	H	-1.8196	0.55743	1.2994
TSAB-1a					42	H	-0.1050	3.06314	-0.9431
					43	H	-0.4182	1.35197	-1.2131
					44	H	0.1775	1.27196	1.52445
					45	H	0.8666	2.86951	1.19509
					46	H	1.8290	1.78526	-1.822
					47	H	4.1710	1.09042	-2.251

48	O	5.8007	0.23418	-0.5446	30	C	-0.1230	-2.3366	0.9473	
49	C	6.6953	-0.2426	0.45697	31	H	-0.7172	-2.4843	1.8471	
50	H	6.3133	-1.1634	0.91611	32	H	1.7398	-2.8969	1.8644	
51	H	7.6350	-0.453	-0.0577	33	C	3.4766	-2.6973	-0.2230	
52	H	6.8595	0.51981	1.22869	34	H	3.6706	-3.6551	-0.7273	
53	O	0.8984	2.96119	3.70846	35	H	4.0418	-1.9297	-0.7696	
54	C	0.8924	3.99017	3.04738	36	H	3.8811	-2.7718	0.7940	
55	O	1.0476	4.16349	1.79346	37	H	1.9590	-1.7918	-2.2803	
56	C	0.5874	5.32928	3.75605	38	H	-0.4892	-1.3805	-2.3073	
57	F	1.4579	6.2868	3.42049	39	H	-3.4436	0.0730	-1.2143	
58	F	0.5997	5.21751	5.08251	40	H	-3.5744	1.0288	0.9656	
59	F	-0.6339	5.75409	3.39569	41	H	-1.9708	0.3879	1.3264	
B1-1a					42	H	-0.1289	2.9851	-0.6989	
					43	H	-0.5156	1.3685	-1.2490	
	Atom	X	Y	Z	44	H	0.0491	1.1385	1.6470	
	1	C	3.7810	1.2260	-1.0005	45	H	1.2917	3.2133	1.3471
	2	C	2.4371	1.4647	-0.8139	46	H	1.8420	1.8478	-1.6423
	3	C	1.8097	1.2007	0.4370	47	H	4.2583	1.4160	-1.9609
	4	C	2.6363	0.7022	1.4790	48	O	5.8710	0.5067	-0.2502
	5	C	3.9881	0.4697	1.2971	49	C	6.7040	-0.0281	0.7598
	6	C	4.5722	0.7225	0.0470	50	H	6.3510	-1.0157	1.0907
	7	H	4.5806	0.0832	2.1233	51	H	7.6971	-0.1329	0.3148
8	H	2.1817	0.4999	2.4503	52	H	6.7668	0.6434	1.6280	
9	C	0.4330	1.4306	0.6666	53	O	0.8042	3.2169	3.6561	
10	C	-0.5033	2.0046	-0.3445	54	C	1.0234	4.1636	2.9475	
11	C	-1.9484	2.1999	0.1367	55	O	1.3253	4.1516	1.6626	
12	C	-2.0006	3.1214	1.3546	56	C	0.9661	5.6160	3.4428	
13	H	-3.0420	3.3196	1.6463	57	F	2.1282	6.2305	3.2280	
14	H	-1.5294	4.0896	1.1276	58	F	0.6942	5.6593	4.7369	
15	H	-1.4910	2.6896	2.2277	59	F	0.0168	6.2812	2.7833	
16	C	-2.7571	2.8328	-0.9933	B-1a					
17	H	-2.3724	3.8361	-1.2262						
18	H	-3.8152	2.9364	-0.7101		Atom	X	Y	Z	
19	H	-2.7058	2.2367	-1.9154		1	C	3.7329	0.9392	-1.3775
20	C	-2.5731	0.8601	0.5374		2	C	2.4198	1.3233	-1.2036
21	N	-2.6468	-0.0718	-0.5925		3	C	1.8625	1.4864	0.0961
22	S	-2.4945	-1.7002	-0.2842		4	C	2.7273	1.2426	1.1940
23	O	-3.0266	-2.0569	1.0303		5	C	4.0494	0.8651	1.0245
24	O	-3.0253	-2.3593	-1.4755		6	C	4.5635	0.7033	-0.2696
25	C	-0.7352	-1.9193	-0.2291		7	H	4.6718	0.6872	1.8989
26	C	0.0039	-1.7170	-1.3959	8	H	2.3296	1.3559	2.2040	
27	C	1.3702	-1.9497	-1.3761	9	C	0.5208	1.8657	0.3111	
28	C	2.0101	-2.3945	-0.2105	10	C	-0.4388	2.2020	-0.7788	
29	C	1.2493	-2.5687	0.9477	11	C	-1.8705	2.5222	-0.3249	

12	C	-1.8865	3.7117	0.6337	2	F	-1.6669	0.7821	1.1283
13	H	-2.9194	3.9964	0.8818	3	F	-1.6669	-1.0866	0.0499
14	H	-1.3997	4.5830	0.1722	4	F	-3.4272	0.1593	0.0498
15	H	-1.3676	3.4968	1.5780	5	H	-1.7309	0.6915	-0.8722
16	C	-2.7071	2.8747	-1.5532					
17	H	-2.3296	3.7937	-2.0240	HFIPanion				
18	H	-3.7589	3.0463	-1.2788		Atom	X	Y	Z
19	H	-2.6760	2.0795	-2.3114	1	C	-2.2750	-0.8356	0.1193
20	C	-2.4891	1.3266	0.4042	2	H	-1.9852	-0.4227	-0.9108
21	N	-2.6238	0.1576	-0.4716	3	O	-1.8604	-0.2223	1.1885
22	S	-2.5241	-1.3507	0.2253	4	C	-1.7402	-2.2804	0.0270
23	O	-3.0410	-1.3532	1.5934	5	C	-3.8143	-0.8564	0.0144
24	O	-3.1025	-2.2624	-0.7595	6	F	-4.4040	-1.4365	1.0734
25	C	-0.7730	-1.6168	0.3104	7	F	-4.3034	-1.4812	-1.0815
26	C	-0.0586	-1.7609	-0.8798	8	F	-4.2806	0.4028	-0.0394
27	C	1.2967	-2.0459	-0.8207	9	F	-2.0979	-3.0403	1.0759
28	C	1.9488	-2.1994	0.4104	10	F	-0.3967	-2.2638	0.0085
29	C	1.2150	-2.0221	1.5856	11	F	-2.1181	-2.9599	-1.0804
30	C	-0.1461	-1.7351	1.5458					
31	H	-0.7212	-1.6131	2.4617	HFIPanion1				
32	H	1.7176	-2.1192	2.5483		Atom	X	Y	Z
33	C	3.3972	-2.5761	0.4564	1	C	-2.3799	-0.8616	0.0359
34	H	3.5237	-3.6508	0.2599	2	O	-1.9948	-0.2140	1.2666
35	H	3.9772	-2.0414	-0.3080	3	H	-1.4921	0.5666	1.0051
36	H	3.8364	-2.3677	1.4398	4	C	-1.7707	-2.1871	0.0291
37	H	1.8660	-2.1612	-1.7436	5	C	-3.8371	-0.8831	-0.0067
38	H	-0.5623	-1.6524	-1.8398	6	F	-4.4941	-1.4706	1.0610
39	H	-3.4352	0.1813	-1.0914	7	F	-4.3316	-1.5333	-1.0872
40	H	-3.4673	1.6091	0.8264	8	F	-4.3678	0.3669	-0.0343
41	H	-1.8497	1.0391	1.2511	9	F	-2.0773	-3.0339	1.0813
42	H	-0.0671	3.0720	-1.3553	10	F	-0.4152	-2.1257	0.0761
43	H	-0.4814	1.3757	-1.5125	11	F	-2.0826	-2.9159	-1.0697
44	H	0.1987	1.9562	1.3512					
45	H	1.7960	1.4953	-2.0805	C-1a				
46	H	4.1534	0.8076	-2.3739		Atom	X	Y	Z
47	O	5.8291	0.3142	-0.5524	1	C	3.7791	0.9860	-1.3371
48	C	6.7007	0.0634	0.5299	2	C	2.4624	1.3154	-1.2373
49	H	6.3306	-0.7520	1.1689	3	C	1.8343	1.4146	0.0481
50	H	7.6578	-0.2334	0.0921	4	C	2.6240	1.1503	1.2107
51	H	6.8502	0.9625	1.1454	5	C	3.9502	0.8259	1.1203
					6	C	4.5394	0.7334	-0.1614
HCF₃					7	H	4.5314	0.6310	2.0169
					8	H	2.1458	1.2177	2.1873
					9	C	0.5052	1.7348	0.2146
					10	C	-0.4668	2.0344	-0.8542
						Atom	X	Y	Z
1	C	-2.0947	0.1757	0.0209					

11	C	-1.8602	2.4785	-0.3893	2	C	-0.4330	-2.7190	1.4381
12	C	-1.7658	3.7492	0.4516	3	C	-0.3664	-2.3100	0.0820
13	H	-2.7679	4.0955	0.7407	4	C	-1.5501	-2.3731	-0.7045
14	H	-1.2824	4.5543	-0.1193	5	C	-2.7228	-2.8391	-0.1743
15	H	-1.1900	3.5971	1.3759	6	C	-2.7729	-3.2099	1.1861
16	C	-2.7060	2.7600	-1.6282	7	O	-3.9629	-3.5809	1.6346
17	H	-2.2750	3.5871	-2.2098	8	C	-4.1013	-3.9862	2.9962
18	H	-3.7287	3.0459	-1.3430	9	H	-3.5042	-4.8846	3.1951
19	H	-2.7658	1.8841	-2.2893	10	H	-5.1611	-4.2100	3.1330
20	C	-2.5213	1.3882	0.4590	11	H	-3.8036	-3.1794	3.6775
21	N	-2.6972	0.1406	-0.2891	12	H	-3.6371	-2.8965	-0.7609
22	S	-2.5060	-1.3056	0.5138	13	H	-1.5067	-2.0475	-1.7438
23	O	-2.8664	-1.1920	1.9256	14	C	0.8007	-1.8030	-0.5002
24	O	-3.1773	-2.2938	-0.3259	15	C	2.1790	-1.9308	0.0019
25	C	-0.7510	-1.5598	0.4290	16	C	3.1128	-0.7649	-0.4141
26	C	-0.1553	-1.7195	-0.8236	17	C	4.1462	-0.5657	0.6908
27	C	1.2013	-1.9951	-0.8937	18	H	4.8842	0.1935	0.3974
28	C	1.9710	-2.1319	0.2709	19	H	3.6729	-0.2380	1.6286
29	C	1.3511	-1.9573	1.5112	20	H	4.6829	-1.5030	0.8937
30	C	-0.0088	-1.6755	1.5999	21	C	3.8166	-1.0733	-1.7308
31	H	-0.4944	-1.5512	2.5658	22	H	3.0957	-1.3395	-2.5174
32	H	1.9433	-2.0489	2.4221	23	H	4.5192	-1.9094	-1.6106
33	C	3.4232	-2.4806	0.1788	24	H	4.3859	-0.1991	-2.0776
34	H	3.5547	-3.5670	0.0694	25	C	2.2782	0.5189	-0.5982
35	H	3.8941	-2.0158	-0.6982	26	N	1.0698	0.4205	0.2310
36	H	3.9713	-2.1763	1.0799	27	S	-0.1205	1.5984	-0.0555
37	H	1.6794	-2.1177	-1.8659	28	O	0.3780	2.9090	0.3519
38	H	-0.7507	-1.6265	-1.7314	29	O	-0.5579	1.3951	-1.4311
39	H	-3.5409	0.0965	-0.8618	30	C	-1.3715	1.0638	1.0698
40	H	-3.4890	1.7533	0.8366	31	C	-1.1638	1.2122	2.4427
41	H	-1.9086	1.1715	1.3463	32	C	-2.1456	0.7727	3.3172
42	H	-0.0380	2.8013	-1.5230	33	C	-3.3367	0.2069	2.8411
43	H	-0.5577	1.1327	-1.4880	34	C	-3.5197	0.0850	1.4615
44	H	0.1544	1.7627	1.2511	35	C	-2.5429	0.5086	0.5675
45	H	1.8804	1.5046	-2.1373	36	H	-2.6863	0.4100	-0.5067
46	H	4.2806	0.8998	-2.2982	37	H	-4.4412	-0.3570	1.0812
47	O	5.7952	0.4079	-0.3702	38	C	-4.3998	-0.2383	3.7960
48	C	6.6495	0.1047	0.7396	39	H	-4.9983	0.6183	4.1383
49	H	6.2638	-0.7591	1.2938	40	H	-5.0885	-0.9519	3.3264
50	H	7.6203	-0.1365	0.3040	41	H	-3.9668	-0.7028	4.6912
51	H	6.7420	0.9731	1.4015	42	H	-1.9939	0.8736	4.3918
TSCD-1a					43	H	-0.2488	1.6661	2.8228
	Atom	X	Y	Z	44	H	1.2892	0.3890	1.2341
1	C	-1.6122	-3.1571	1.9887	45	H	2.8765	1.4090	-0.3524

46	H	1.9377	0.6143	-1.6381	36	H	-2.8551	0.2563	-0.3136
47	H	2.5766	-2.8683	-0.4283	37	H	-4.5297	-0.3047	1.4292
48	H	2.1853	-2.0755	1.0909	38	C	-4.3160	0.0490	4.1241
49	H	0.6966	-1.4487	-1.5316	39	H	-4.6518	0.9570	4.6436
50	H	0.4537	-2.6588	2.0666	40	H	-5.1968	-0.4489	3.7031
51	H	-1.6477	-3.4423	3.0363	41	H	-3.8763	-0.6073	4.8874
D-1a					42	H	-1.8753	1.1551	4.4811
					43	H	-0.1894	1.7333	2.7592
					44	H	1.1010	-0.1029	1.2044
	Atom	X	Y	Z	45	H	2.8234	1.2009	0.3161
1	C	-1.6795	-2.9961	1.8669	46	H	2.2076	0.8953	-1.3369
2	C	-0.5403	-2.3768	1.3662	47	H	2.2185	-2.7471	-1.1108
3	C	-0.4552	-1.9905	0.0275	48	H	2.1374	-2.4704	0.6350
4	C	-1.5284	-2.2784	-0.8226	49	H	0.5929	-1.0027	-1.5603
5	C	-2.6593	-2.9185	-0.3462	50	H	0.2891	-2.1759	2.0490
6	C	-2.7508	-3.2652	1.0071	51	H	-1.7240	-3.2624	2.9199
7	O	-3.9063	-3.8432	1.3891	D1-1a				
8	C	-4.0681	-4.1666	2.7567					
9	H	-3.3256	-4.9066	3.0874		Atom	X	Y	Z
10	H	-5.0696	-4.5936	2.8543	1	C	-1.6169	-2.4089	2.3690
11	H	-3.9940	-3.2706	3.3902	2	C	-0.6441	-1.6726	1.6995
12	H	-3.5001	-3.1424	-1.0002	3	C	-0.4850	-1.7666	0.3166
13	H	-1.4755	-1.9852	-1.8716	4	C	-1.3181	-2.6437	-0.3848
14	C	0.7494	-1.2862	-0.5098	5	C	-2.2844	-3.3942	0.2668
15	C	2.0978	-1.9722	-0.3440	6	C	-2.4479	-3.2742	1.6508
16	C	3.1774	-0.8677	-0.4398	7	O	-3.4308	-4.0220	2.2010
17	C	4.1565	-0.9757	0.7231	8	C	-3.6433	-3.9104	3.5932
18	H	4.9350	-0.2032	0.6549	9	H	-2.7584	-4.2266	4.1645
19	H	3.6434	-0.8598	1.6894	10	H	-4.4791	-4.5740	3.8312
20	H	4.6485	-1.9580	0.7192	11	H	-3.9071	-2.8816	3.8799
21	C	3.9184	-0.9217	-1.7696	12	H	-2.9381	-4.0721	-0.2799
22	H	3.2157	-0.9132	-2.6152	13	H	-1.2103	-2.7312	-1.4670
23	H	4.5208	-1.8380	-1.8332	14	C	0.5819	-1.0159	-0.4301
24	H	4.5947	-0.0622	-1.8790	15	C	1.9984	-1.5101	-0.1590
25	C	2.3823	0.4525	-0.3475	16	C	2.9234	-0.4067	-0.6966
26	N	1.0334	0.0527	0.1839	17	C	4.1731	-0.2520	0.1624
27	S	-0.2277	1.3944	-0.0723	18	H	4.8245	0.5421	-0.2311
28	O	0.5166	2.5821	0.2933	19	H	3.9144	0.0024	1.1994
29	O	-0.6993	1.1620	-1.4211	20	H	4.7510	-1.1874	0.1711
30	C	-1.4342	1.0111	1.1334	21	C	3.3207	-0.7023	-2.1402
31	C	-1.1381	1.2811	2.4737	22	H	2.4387	-0.8721	-2.7750
32	C	-2.0838	0.9576	3.4301	23	H	3.9536	-1.5998	-2.1897
33	C	-3.3126	0.3848	3.0684	24	H	3.8864	0.1363	-2.5713
34	C	-3.5777	0.1408	1.7172	25	C	2.0415	0.8642	-0.6457
35	C	-2.6454	0.4491	0.7358					

26	N	0.7292	0.4291	-0.0616	5	C	2.4561	-2.2221	1.8712
27	S	-0.5049	1.4909	-0.5941	6	C	1.2195	-2.8104	2.1772
28	O	-0.0194	2.8207	-0.2336	7	C	0.0776	-2.4450	1.4901
29	O	-0.8255	1.1957	-1.9898	8	H	-0.8708	-2.9064	1.7659
30	C	-1.9130	1.1105	0.4019	9	H	1.1822	-3.5512	2.9748
31	C	-1.9673	1.5867	1.7096	10	O	3.5102	-2.6317	2.6126
32	C	-3.0688	1.2753	2.4934	11	C	4.7586	-2.0142	2.3756
33	C	-4.1241	0.5123	1.9806	12	H	4.7071	-0.9265	2.5371
34	C	-4.0532	0.0692	0.6553	13	H	5.1193	-2.2091	1.3551
35	C	-2.9533	0.3603	-0.1399	14	H	5.4594	-2.4508	3.0925
36	H	-2.8954	0.0036	-1.1663	15	H	3.4719	-0.7967	0.5894
37	H	-4.8686	-0.5278	0.2467	16	H	1.4355	-0.1463	-0.6104
38	C	-5.3136	0.1868	2.8284	17	N	-1.6968	0.5177	0.9981
39	H	-5.0430	0.1168	3.8893	18	S	-1.5815	2.4991	1.4617
40	H	-6.0825	0.9680	2.7403	19	O	-1.6543	2.9544	2.8728
41	H	-5.7758	-0.7597	2.5213	20	O	-2.4241	3.1769	0.4591
42	H	-3.1120	1.6278	3.5240	21	C	0.1216	2.6253	0.9456
43	H	-1.1615	2.1964	2.1126	22	C	1.1286	2.4006	1.8782
44	H	1.3136	0.5362	1.6602	23	C	2.4503	2.3501	1.4463
45	H	2.4629	1.6576	-0.0188	24	C	2.7745	2.5173	0.0975
46	H	1.8950	1.2713	-1.6577	25	C	1.7392	2.7368	-0.8207
47	H	2.1769	-2.4831	-0.6359	26	C	0.4140	2.7800	-0.4081
48	H	2.1318	-1.6433	0.9257	27	H	-0.3915	2.9369	-1.1246
49	H	0.3743	-1.0781	-1.5129	28	H	1.9815	2.8652	-1.8764
50	H	-0.0202	-0.9953	2.2843	29	C	4.1967	2.4453	-0.3686
51	H	-1.7241	-2.2901	3.4448	30	H	4.2998	1.7592	-1.2205
52	C	1.6996	1.8322	3.0586	31	H	4.5562	3.4278	-0.7059
53	H	1.0969	2.5251	2.4470	32	H	4.8644	2.1008	0.4307
54	O	1.8336	0.5703	2.5006	33	H	3.2471	2.1670	2.1682
55	C	0.9969	1.6973	4.4031	34	H	0.8818	2.2646	2.9304
56	C	3.0870	2.4506	3.1713	35	C	-3.1035	0.0848	1.1699
57	F	3.9466	1.6385	3.7846	36	C	-3.5113	-0.6864	-0.0877
58	F	3.0614	3.6074	3.8351	37	C	-4.8330	-1.4047	0.1361
59	F	3.5686	2.6903	1.9470	38	H	-4.7712	-2.1022	0.9843
60	F	1.7130	0.9806	5.2703	39	H	-5.6409	-0.6877	0.3438
61	F	-0.1733	1.0747	4.2354	40	H	-5.1197	-1.9807	-0.7556
62	F	0.7516	2.8878	4.9519	41	C	-3.6383	0.2639	-1.2752

TABE-1a

	Atom	X	Y	Z
1	C	-1.0559	-0.9681	-0.2096
2	C	0.1208	-1.4813	0.4580
3	C	1.3727	-0.9085	0.1693
4	C	2.5272	-1.2679	0.8524

E-1a	49	H	-3.2146	-0.5569	2.0576	39	H	-5.6230	-1.7327	-0.3542
	50	H	-0.8260	-0.3256	-1.0628	40	H	-4.8537	-2.8369	-1.5110
	51	H	-1.1505	0.1831	1.8004	41	C	-3.8996	-0.3124	-1.9687
						42	H	-4.8455	0.2135	-1.7732
						43	H	-4.0169	-0.8807	-2.9029
		Atom	X	Y	Z	44	H	-3.1277	0.4517	-2.1378
	1	C	-1.1738	-0.8345	-0.6871	45	C	-2.1983	-1.9233	-1.0294
	2	C	0.1584	-1.3410	-0.2036	46	H	-2.0669	-2.3190	-2.0462
	3	C	1.2644	-1.3282	-1.0493	47	H	-2.0890	-2.7608	-0.3204
	4	C	2.5101	-1.8025	-0.6390	48	H	-3.9392	0.4171	0.5856
5	C	2.6635	-2.2895	0.6600	49	H	-3.3677	-1.0881	1.3509	
6	C	1.5597	-2.3124	1.5224	50	H	-0.9833	-0.2263	-1.5921	
7	C	0.3267	-1.8528	1.0901	51	H	-1.3810	0.1122	1.1771	
8	H	-0.5232	-1.8891	1.7752	Cplx1					
9	H	1.6956	-2.7024	2.5301			Atom	X	Y	Z
10	O	3.8251	-2.7568	1.1739		1	C	-0.6507	-1.4612	4.0368
11	C	4.9477	-2.8180	0.3197		2	F	0.1733	-0.8477	4.8527
12	H	5.2503	-1.8197	-0.0292		3	F	-0.8439	-2.7086	4.4046
13	H	4.7556	-3.4593	-0.5531		4	F	-1.7961	-0.8139	3.9441
14	H	5.7606	-3.2500	0.9101		5	H	-0.7666	0.5286	1.9256
15	H	3.3483	-1.7746	-1.3318		6	O	0.1501	0.2156	1.8436
16	H	1.1565	-0.9316	-2.0603		7	C	0.1589	-0.9267	1.0490
17	N	-1.8794	0.0073	0.2974		8	C	-0.1113	-0.5573	-0.4052
18	S	-1.7700	2.5611	-0.4356	9	F	-0.2328	-1.6371	-1.1745	
19	O	-2.2826	3.1232	0.8386	10	F	0.8481	0.2128	-0.9152	
20	O	-2.0060	3.3162	-1.6990	11	F	-1.2590	0.1261	-0.4673	
21	C	0.0125	2.3967	-0.2691	12	C	1.5215	-1.5725	1.2423	
22	C	0.5504	2.1013	0.9811	13	F	2.5129	-0.7159	1.0121	
23	C	1.9099	1.8367	1.0846	14	F	1.6707	-2.6135	0.4235	
24	C	2.7356	1.8541	-0.0451	15	F	1.6483	-2.0119	2.4964	
25	C	2.1668	2.1498	-1.2884	16	H	-0.5982	-1.6766	1.3383	
26	C	0.8067	2.4117	-1.4114	TS12					
27	H	0.3630	2.6251	-2.3826			Atom	X	Y	Z
28	H	2.8001	2.1599	-2.1762		1	C	-0.9226	-1.6761	3.3841
29	C	4.2002	1.5661	0.0779		2	F	-0.4733	-0.8486	4.3132
30	H	4.5963	1.1032	-0.8353		3	F	-0.5188	-2.9068	3.6420
31	H	4.7715	2.4907	0.2464		4	F	-2.2406	-1.6314	3.3365
32	H	4.4061	0.8992	0.9252		5	H	-0.0528	1.2009	1.6646
33	H	2.3408	1.5965	2.0571		6	O	0.7415	0.6376	1.6943
34	H	-0.0885	2.0839	1.8632		7	C	0.4251	-0.6279	1.2889
35	C	-3.2602	-0.4427	0.4610		8	C	-0.3377	-0.6822	-0.0175
36	C	-3.5557	-1.2456	-0.8095	9	F	-0.8698	-1.8832	-0.2210	
37	C	-4.6811	-2.2449	-0.6005						
38	H	-4.4492	-2.9415	0.2181						

10	F	0.4346	-0.3867	-1.0657	4	F	-2.1725	-2.3222	4.2990
11	F	-1.3279	0.2167	0.0230	5	H	0.2208	1.4793	1.3779
12	C	1.6828	-1.4659	1.3294	6	O	0.9058	0.8359	1.6437
13	F	2.6682	-0.9377	0.6064	7	C	0.6329	-0.3685	1.1366
14	F	1.4398	-2.6943	0.8748	8	C	-0.2578	-0.4928	-0.0545
15	F	2.1080	-1.5622	2.5910	9	F	-1.1221	-1.5053	0.0544
16	H	-0.3313	-1.2118	2.1631	10	F	0.4309	-0.6976	-1.1855
Cplx2					11	F	-0.9595	0.6374	-0.2004
	Atom	X	Y	Z	12	C	1.7038	-1.3723	1.3797
1	C	-1.1681	-2.0226	3.4784	13	F	2.8149	-1.1050	0.6753
2	F	-0.7796	-0.7727	3.7407	14	F	1.2889	-2.5911	1.0268
3	F	-0.1489	-2.8354	3.7540	15	F	2.0554	-1.3922	2.6642
					16	H	-1.4715	-2.1214	2.4311