Supporting Information for

Intramolecular Oxidative C(sp^3)-N Coupling Towards Pyrrolidine and Piperidine with Catalytic Amount of Iodoform

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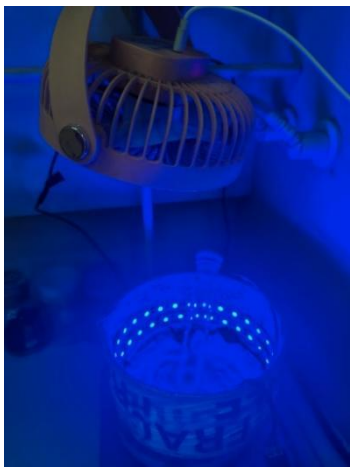
1. General information

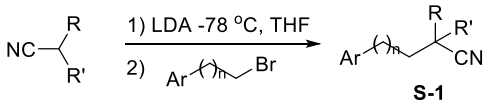
Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents used in reactions were p.A. grade and dried only if indicated. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063-0.2 mm). Melting points were measured on a Yanaco Micro Melting Point Apparatus. ^{1}H NMR and ^{13}C NMR were recorded on a Variance VNMR 400 or Bruker AV-600 spectrometer in $CDCl_3$. For ^{1}H NMR spectra, data are quoted in the following order: chemical shift (δ) in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$ at 7.26 ppm). Multiplicities are indicated s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), coupling constants (*J*) are in Hertz (Hz). For proton-decoupled ^{13}C NMR spectra, chemical shifts (*J*) are also quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm). High resolution mass spectra (HRMS) were obtained on AB 5800 MALDI-TOF/TOF and are recorded using electrospray ionization (ESI). X-ray crystallographic data were collected using D8 quest X-ray diffractometer.

2. Light Source, Material of the Irradiation Vessel and Set-up of Photograph

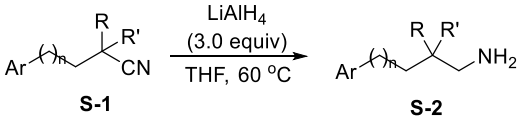


The light source used for photochemical experiments was a Blue LEDs (12V; 12W), purchased from Alibaba; https://m.tb.cn/h.UBe94wa?tk=LRG6dqDEVKN; Manufacturer: Huadeng. China;
Model: 12V-5050; Broadband source: λ = 450-465 nm;
Material of the irradiation vessel: borosilicate reaction tube.
Distance from the light source to the irradiation vessel: 7.5 cm (Use fans and not use any filters)

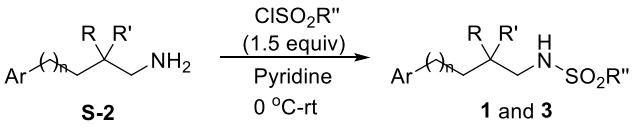
3. Preparation of starting materials[1]



Nitrile compound (1.0 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. A saturated solution of NH_4Cl was then added, and the resulting mixture was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulting crude product was used in the subsequent step without further purification.

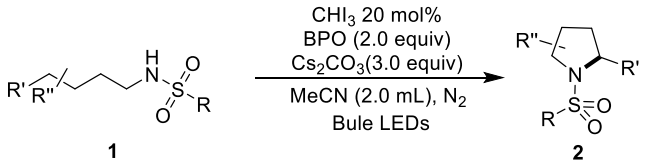


A two-neck flask equipped with a stirring bar and a reflux condenser was charged with $LiAlH_4$ (3.0 equiv). Subsequently, THF was added carefully, and the resulting suspension was cooled to 0 °C. The crude product **S-1** was dissolved in a small volume of Et_2O and added dropwise to the suspension. Then, the reaction mixture was refluxed for 2 hours, and 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 Na_2SO_4 and the solvent was removed under reduced pressure to yield the crude amine **S-2** in quantitative yields, and used for the next step without further purification.



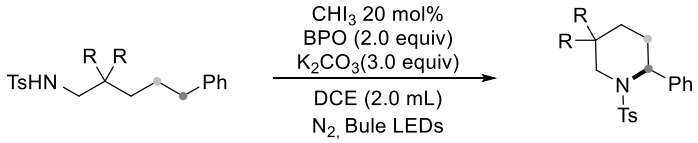
The crude amine **S-2** (1.0 equiv.) was dissolved in pyridine (0.4 M) and the resulting solution was cooled to 0 °C. Subsequently, the corresponding sulfonyl chloride was added in one portion, and the reaction mixture was stirred at room temperature for 12 hours. Then, the mixture was diluted with DCM and washed with 5% aqueous solution of HCl. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The resulting crude product was further purified by column chromatography on silica to give **1** and **3**, and the compound **1a**-**1r**, **4a**-**4e** were prepared according to the above procedures, and the characterization data for those compounds were consistent with the previous reports.[1-6]

4. General procedure for oxidative C-N coupling towards pyrrolidines



1 (0.1 mmol, 1.0 equiv), CHI_3 (7.8 mg, 20 mol%), BPO (48.4 mg, 0.2 mmol, 2.0 equiv) Cs_2CO_3 (97.5 mg, 0.3 mmol, 3.0 equiv) and a stir bar were added to a sealed tube under a nitrogen atmosphere and under a 12 W blue LEDs irradiation, acetonitrile (2.0 mL) as solvent was then added. The mixture was stirred for 12 hours at room-temperature. The crude mixture was directly purified by flash column chromatography on silica gel.

5. General procedure for oxidative C-N coupling towards pyrrolidines

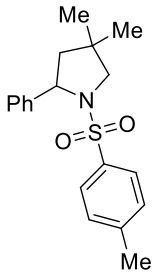


3 **4**

3 (0.1 mmol, 1.0 equiv), CHI_3 (7.8 mg, 20 mol%), BPO (48.4 mg, 0.2 mmol, 2.0 equiv) Cs_2CO_3 (97.5 mg, 0.3 mmol, 3.0 equiv) and a stir bar were added to a sealed tube under a nitrogen atmosphere and under a 12 W blue LEDs irradiation, DCE (2.0 mL) as solvent was then added. The mixture was stirred for 12 hours at room-temperature. The crude mixture was directly purified by flash column chromatography on silica gel

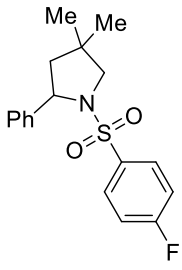
6. Characterization data of products

4,4-Dimethyl-2-phenyl-1-tosylpyrrolidine (2a)[1,3-5]



White solid (31.2 mg, 95% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.29–7.17 (m, 7H), 4.70 (dd, *J* = 9.4, 7.3 Hz, 1H), 3.47–3.30 (m, 2H), 2.38 (s, 3H), 2.01 (dd, *J* = 12.7, 7.3 Hz, 1H), 1.72 (dd, *J* = 12.8, 9.4 Hz, 1H), 1.04 (s, 3H), 0.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.8, 135.7, 129.2, 128.2, 127.3, 127.0, 126.4, 64.6, 62.6, 51.4, 39.2, 38.0, 26.0, 25.6, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{23}NNaO_2S^+$: 352.1342; found: 352.1343.

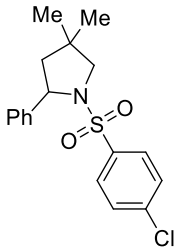
1-((4-fluorophenyl)sulfonyl)-4,4-dimethyl-2-phenylpyrrolidine (2b)



White solid (31.6mg, 95% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.52 (m, 2H), 7.28–7.15 (m, 5H), 7.04 (td, *J* = 8.7, 4.5 Hz, 2H), 4.80–4.72 (m, 1H), 3.59–3.30 (m, 2H), 2.15–2.00 (m, 1H), 1.80–1.70 (m, 1H), 1.09 (d, *J* = 4.1 Hz, 3H), 0.88 (d, *J* = 4.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (d, *J* = 257.6 Hz, 1C), 142.2, 135.4 (d, *J* = 2.0 Hz, 1C), 129.7 (d, *J* = 9.1 Hz,1C), 128.3, 126.6, 127.2, 115.7 (d, *J* = 22.2 Hz, 1C), 63.8, 61.7, 51.4, 38.1, 25.8, 25.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -106.19; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{20}FNNaO_2S^+$: 356.1091; found: 356.1081.

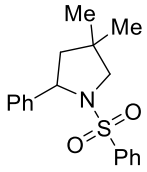
1-((4-chlorophenyl)sulfonyl)-4,4-dimethyl-2-phenylpyrrolidine (2c)[5]

White solid (32.1 mg, 92% yield) was obtained by the purification with flash column



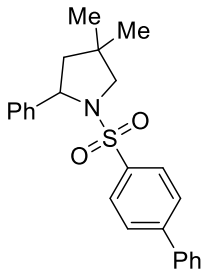
chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.21 (q, *J* = 8.0, 6.8 Hz, 4H), 4.76 (dd, *J* = 9.5, 7.3 Hz, 1H), 3.57–3.14 (m, 2H), 2.08 (dd, *J* = 12.6, 7.1 Hz, 1H), 1.75 (dd, *J* = 12.9, 9.6 Hz, 1H), 1.09 (s, 3H), 0.90 (s, 3H). 13C NMR (101 MHz, $CDCl_3$) δ 142.1, 138.5, 137.9, 128.8, 128.5, 128.3, 127.3, 126.7, 63.8, 61.7, 51.4, 38.2, 25.8, 25.6, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{20}ClNNaO_2S^+$: 372.0796; found: 372.0790.

4,4-dimethyl-2-phenyl-1-(phenylsulfonyl)pyrrolidine (2d)[6]



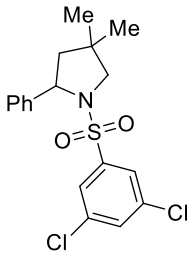
White solid (26.7 mg, 85% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.1 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.27–7.19 (m, 5H), 4.75 (dd, *J* = 9.5, 7.2 Hz, 1H), 3.53–3.30 (m, 2H), 2.04 (dd, *J* = 12.7, 7.2 Hz, 1H), 1.74 (dd, *J* = 12.8, 9.5 Hz, 1H), 1.07 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 138.8, 132.2, 128.6, 128.2, 127.13, 127.08, 126.5, 63.8, 61.8, 51.4, 38.1, 25.9, 25.5, 21.3 HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{21}NNaO_2S^+$: 338.1186; found: 338.1183.

1-([1,1'-biphenyl]-4-ylsulfonyl)-4,4-dimethyl-2-phenylpyrrolidine (2e)



White solid (34.8 mg, 89% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 4H), 7.52–7.40 (m, 3H), 7.31–7.16 (m, 5H), 4.81 (dd, *J* = 9.4, 7.3 Hz, 1H), 3.48 (dd, *J* = 70.4, 10.3 Hz, 2H), 2.08 (dd, *J* = 12.9, 7.3 Hz, 1H), 1.77 (dd, *J* = 12.8, 9.5 Hz, 1H), 1.10 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 142.5, 139.4, 137.6, 129.0, 128.3, 128.2,127.7, 127.18, 127.17, 127.1, 126.6, 63.8, 61.8, 51.4, 38.1, 25.9, 25.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{25}NNaO_2S^+$: 414.1499; found: 414.1500.

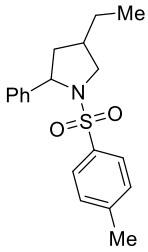
1-((3,5-dichlorophenyl)sulfonyl)-4,4-dimethyl-2-phenylpyrrolidine (2f)



White solid (29.1 mg, 76% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.35 (m, 1H), 7.26–7.18 (m, 5H), 7.14–7.10 (m, 2H), 4.82 (dd, *J* = 9.8, 7.2 Hz, 1H), 3.61 (d, *J* = 9.9 Hz, 1H), 3.27 (d, *J* = 9.9 Hz, 1H), 2.14 (dd, *J* = 12.9, 7.2 Hz, 1H), 1.78 (dd, *J* = 12.9, 9.9 Hz, 1H), 1.12 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 140.9, 135.3, 131.8, 128.3, 127.9, 127.1, 125.2, 63.9, 61.6, 51.1, 41.3, 38.3, 25.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}Cl_2NNaO_2S^+$: 406.0406; found: 406.0400.

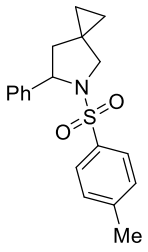
4-ethyl-2-phenyl-1-tosylpyrrolidine (2g)

White solid (22.4 mg, 67% yield, 1:1 dr) was obtained by the purification with flash column



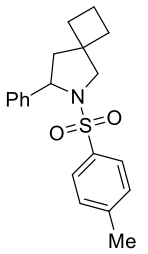
chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.59 (m, 2H), 7.31–7.20 (m, 7H), 4.86–4.60 (m, 1H), 3.88–3.73 (m, 1H), 3.14–2.88 (m, 1H), 2.41–2.37 (m, 3H), 2.28–1.87 (m, 1H), 1.60–1.42 (m, 1H), 1.35–1.19 (m, 2H), 0.84–0.77 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.20, 143.1 135.4, 129.4, 128.2, 127.4, 126.9, 126.2, 77.3, 77.0, 76.7, 64.4, 55.1, 43.2, 40.3, 25.4, 21.4, 12.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{23}NNaO_2S^+$: 352.1342; found: 352.1336.

6-phenyl-5-tosyl-5-azaspiro[2.4]heptane (2h)



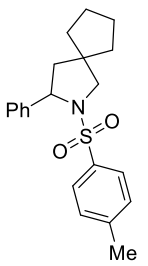
White solid (32.5 mg, 72% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 6.5 Hz, 2H), 7.34–7.18 (m, 5H), 4.88 (dd, J = 8.1, 4.4 Hz, 1H), 3.50–3.39 (m, 2H), 2.42 (s, 3H), 2.08 (dd, J = 12.4, 8.3 Hz, 1H), 1.70 (dd, J = 12.7, 4.3 Hz, 1H), 0.61–0.53 (m, 1H), 0.44–0.35 (m, 1H), 0.35–0.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 143.1, 135.0, 129.4, 128.1, 127.5, 126.9, 126.2, 64.1, 56.5, 44.1, 21.5, 20.6, 11.5, 8.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{21}NNaO_2S^+$: 350.1186; found: 350.1183.

7-phenyl-6-tosyl-6-azaspiro[3.4]octane (2i)



White solid (29.0 mg, 85% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.36–7.18 (m, 7H), 4.65 (t, J = 7.3 Hz, 1H), 3.63–3.45 (m, 2H), 2.41 (s, 3H), 2.18 (dd, J = 12.6, 7.6 Hz, 1H), 2.00–1.87 (m, 2H), 1.80–1.71 (m, 3H), 1.64–1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.9, 135.0, 129.4, 128.1, 127.5, 126.9, 126.2, 63.2, 60.3, 48.7, 44.4, 31.7, 30.4, 21.4, 15.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{23}NNaO_2S^+$: 364.1342; found: 364.1336.

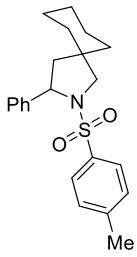
3-phenyl-2-tosyl-2-azaspiro[4.4]nonane (2j)[5]



White solid (28.4 mg, 80% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.36–7.18 (m, 7H), 4.66 (t, J = 7.9 Hz, 1H), 3.45 (d, J = 2.4 Hz, 2H), 2.40 (s, 3H), 2.08 (dd, J = 12.6, 7.3 Hz, 1H), 1.84 (dd, J = 12.6, 8.7 Hz, 1H), 1.57 (d, J = 12.8 Hz, 5H), 1.45–1.40 (m, 1H). 1.17 (d, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.8, 135.4, 129.3, 128.1, 127.3, 126.9, 126.4, 63.9, 60.3, 49.4, 49.1, 36.6, 35.9, 24.5, 24.4, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{27}NNaO_2S^+$: 392.1655; found: 392.1655.

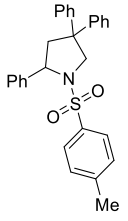
3-(4-chlorophenyl)-2-tosyl-2-azaspiro[4.5]decane (2k)[5]

White solid (31.0 mg, 84% yield) was obtained by the purification with flash column



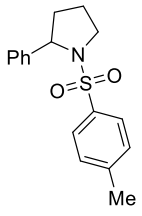
chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.32–7.19 (m, 7H), 4.61 (dd, *J* = 9.4, 7.3 Hz, 1H), 3.60 (s, 1H), 3.30 (d, *J* = 10.7 Hz, 1H), 2.40 (s, 3H), 2.11 (dd, *J* = 13.1, 7.2 Hz, 1H), 1.65 (dd, *J* = 12.9, 9.4 Hz, 1H), 1.42 (d, *J* = 8.1 Hz, 2H), 1.33–1.25 (m, 5H), 1.06–0.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 143.0, 135.4, 129.3, 128.2, 127.3, 127.0, 126.4, 63.0, 59.2, 49.5, 41.9, 36.3, 33.8, 29.6, 25.8, 23.7, 22.7, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{27}NNaO_2S^+$: 392.1655; found: 392.1651.

2,4,4-triphenyl-1-tosylpyrrolidine (2l)[3-5]



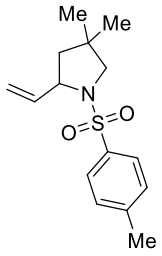
White solid (43.0 mg, 95% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 2H), 7.34–7.24 (m, 5H), 7.20 (dd, *J* = 8.7, 5.1 Hz, 9H), 7.05 (d, *J* = 7.9 Hz, 2H), 5.00–4.55 (m, 2H), 4.11 (d, *J* = 10.6 Hz, 1H), 3.30–3.00 (m, 1H), 2.69 (dd, *J* = 12.9, 9.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 144.1, 142.5, 141.1, 136.8, 129.0, 128.6, 128.5, 128.1, 127.3, 127.2, 126.7, 126.6, 126.51, 126.48, 126.4, 63.1, 58.8, 53.0, 49.0, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{27}NNaO_2S^+$: 476.1655; found: 376.1649.

2-phenyl-1-tosylpyrrolidine (2m)[3-5]

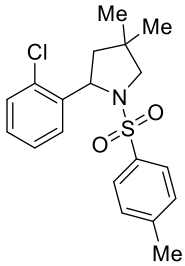


White solid (20.1 mg, 67% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.34–7.22 (m, 7H), 4.80 (dd, *J* = 7.9, 3.6 Hz, 1H), 3.72–3.55 (m, 1H), 3.52–3.38 (m, 1H), 2.44 (s, 3H), 2.08–1.94 (m, 1H), 1.92–1.77 (m, 2H), 1.73–1.61 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 143.0, 135.1, 129.5, 128.3, 128.2, 127.4, 127.0, 126.1, 63.2, 49.3, 35.7, 23.9, 21.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{29}NNaO_2S^+$: 324.1029; found: 324.1030.

4,4-dimethyl-1-tosyl-2-vinylpyrrolidine (2n)[5]



White solid (11.7 mg, 42% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.85 (dd, *J* = 16.1, 8.9 Hz, 1H), 5.12 (dd, *J* = 41.4, 13.5 Hz, 2H), 4.01 (d, *J* = 7.3 Hz, 1H), 3.18 (t, *J* = 10.6 Hz, 2H), 2.42 (s, 3H), 1.72 (d, *J* = 12.4 Hz, 1H), 1.66–1.53 (m, 1H), 1.05 (s, 3H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.8, 135.4, 129.4, 127.6, 115.1, 62.4, 61.4, 47.5, 37.5, 26.5, 26.0, 21.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{25}NNaO_2S^+$: 302.1186; found: 302.1182.

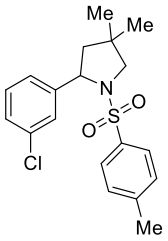


2-(2-chlorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2o)[3-5]

White solid (25.4 mg, 70% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 3H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.17–7.11 (m, 1H), 5.06 (t, *J* = 8.3 Hz,

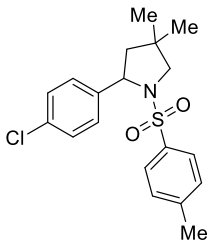
1H), 3.38 (dd, 2H), 2.41 (s, 3H), 2.13 (dd, J = 12.7, 7.8 Hz, 1H), 1.58 (dd, J = 12.8, 9.2 Hz, 1H), 1.02 (s, 3H), 0.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 140.7, 134.5, 131.6, 129.5, 129.2, 128.1, 128.0, 127.7, 127.0, 62.0, 60.8, 49.1, 38.1, 26.2, 25.7, 21.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}ClNNaO_2S^+$: 386.0952; found: 386.0944.

2-(3-chlorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2p)[3-5]



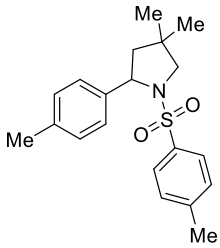
White solid (30.9 mg, 85% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.15 (dt, J = 5.8, 1.8 Hz, 4H), 4.66 (dd, J = 9.4, 7.3 Hz, 1H), 3.44 (d, J = 10.4 Hz, 1H), 3.31 (d, J = 10.4 Hz, 1H), 2.38 (s, 3H), 2.00 (dd, J = 12.8, 7.2 Hz, 1H), 1.65 (dd, J = 12.7, 9.5 Hz, 1H), 1.03 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 143.2, 135.5, 134.0, 129.5, 129.3, 127.2, 127.1, 126.4, 124.7, 63.2, 61.7, 51.3, 38.1, 25.9, 25.5, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}ClNNaO_2S^+$: 386.0952; found: 386.0942.

2-(4-chlorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2q)[3-5]



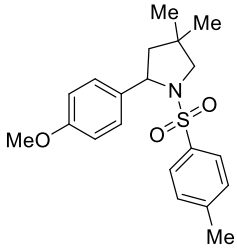
White solid (24.3 mg, 67% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 9.9 Hz, 6H), 4.65 (dd, J = 9.3, 7.3 Hz, 1H), 3.46–3.30 (m, 2H), 2.40 (s, 3H), 1.99 (dd, J = 13.9, 7.0 Hz, 1H), 1.66 (dd, J = 12.8, 9.4 Hz, 1H), 1.04 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.5, 135.3, 132.6, 129.4, 128.3, 127.8, 127.3, 63.1, 61.8, 51.3, 38.1, 26.0, 25.6, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}ClNNaO_2S^+$: 386.0952; found: 386.0950.

4,4-dimethyl-2-(p-tolyl)-1-tosylpyrrolidine (2r)[3-5]



White solid (31.2 mg, 91% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.20 (dd, J = 14.5, 7.9 Hz, 4H), 7.08 (d, J = 7.8 Hz, 2H), 4.66 (dd, J = 9.4, 7.2 Hz, 1H), 3.54–3.26 (m, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 2.05–1.96 (m, 1H), 1.05 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 139.8, 136.5, 135.6, 129.2, 128.9, 127.3, 126.3, 63.5, 61.8, 51.4, 37.9, 26.0, 25.6, 21.4, 21.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{25}NNaO_2S^+$: 366.1499; found: 366.1500.

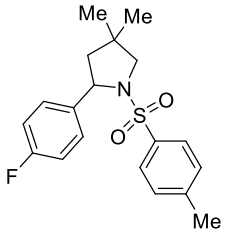
2-(4-methoxyphenyl)-4,4-dimethyl-1-tosylpyrrolidine (2s)[4,5]



White solid (25.8 mg, 72% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.8 Hz, 4H), 6.79 (d, J = 8.7 Hz, 2H), 4.90–4.36 (m, 1H), 3.78 (s, 1H), 3.51–3.18 (m, 2H), 2.39 (s, 4H), 1.98 (dd, J = 12.8, 7.2 Hz, 1H), 1.71 (dd, J = 12.8, 9.5 Hz, 1H), 1.05 (s, 3H), 0.76 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 142.8, 135.8,

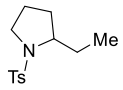
134.8, 129.2, 127.6, 127.2, 113.6, 63.2, 61.7, 55.2, 51.4, 37.8, 26.0, 25.6, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{25}NNaO_3S^+$: 382.1448; found: 382.1442.

2-(4-fluorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2t) [3,5]



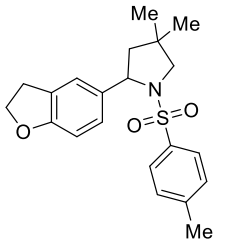
White solid (31.5 mg, 91% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 6.1 Hz, 2H), 7.22 (d, J = 5.4 Hz, 4H), 6.93 (t, J = 7.7 Hz, 2H), 4.67 (t, J = 8.5 Hz, 1H), 3.38 (q, 2H), 2.39 (s, 3H), 1.99 (dd, J = 12.8, 7.1 Hz, 1H), 1.74–1.63 (m, 1H), 1.05 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J = 246.4 Hz, 1C), 143.1, 138.6 (d, J = 3.0 Hz, 1C), 135.5, 129.3, 128.0 (d, J = 8.1 Hz, 1C), 127.2, 115.0 (d, J = 21.2 Hz, 1C), 63.1, 61.7, 51.4, 38.0, 26.0, 25.5, 21.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl^3$) δ -115.9 (s, 1F).HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}FNNaO_2S^+$: 370.1248; found: 370.1240.

2-ethyl-1-tosylpyrrolidine(2u)



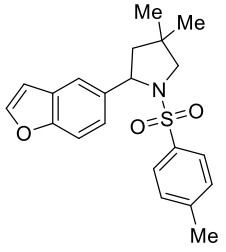
White solid (8.8 mg, 38% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 3.58–3.49 (m, 1H), 3.42 –3.34 (m, 1H), 3.24–3.14 (m, 1H), 2.42 (s, 3H), 1.92–1.71 (m, 2H), 1.60–1.42 (m, 4H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 134.9, 129.6, 127.5, 61.9, 49.0, 30.1, 29.2, 24.1, 21.0, 10.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{19}NNaO_2S^+$ 276.1029; found 276.1024.

2-(2,3-dihydrobenzofuran-5-yl)-4,4-dimethyl-1-tosylpyrrolidine (2v)



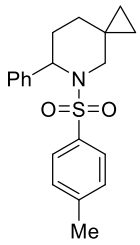
White solid (18.9 mg, 51% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.21 (s, 2H), 7.02 (d, J = 22.8 Hz, 2H), 6.66 (s, 1H), 4.59 (d, J = 49.2 Hz, 3H), 3.40 (d, J = 48.9 Hz, 2H), 3.21–2.99 (m, 2H), 2.40 (d, J = 5.1 Hz, 3H), 2.00 (s, 1H), 1.71 (s, 1H), 1.06 (s, 3H), 0.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 142.8, 136.1, 134.7, 129.2, 127.3, 127.0, 126.6, 123.2, 108.7, 71.3, 63.6, 61.8, 51.7, 37.9, 29.7, 26.1, 25.7, 21.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}NNaO_3S^+$: 394.1448; found: 394.1445.

2-(benzofuran-5-yl)-4,4-dimethyl-1-tosylpyrrolidine (2w)



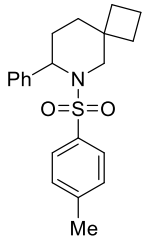
White solid (14.7 mg, 40% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.49 (d, J = 8.5 Hz, 3H), 7.36 (d, J = 8.3 Hz, 1H), 7.26 (s, 1H), 7.21–7.10 (m, 3H), 6.68 (s, 1H), 4.80 (d, J = 8.0 Hz, 1H), 3.41 (q, 2H), 2.36 (s, 3H), 2.05 (d, J = 13.3 Hz, 1H), 1.76 (d, J = 12.5 Hz, 1H), 1.07 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 145.3, 142.9, 137.4, 135.9, 129.2, 127.3, 123.0, 119.2, 111.1, 106.6, 63.9, 61.8, 52.0, 38.0, 29.7, 26.1, 25.7, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{23}NNaO_3S^+$: 392.1291; found: 392.1287.

6-phenyl-5-tosyl-5-azaspiro[2.5]octane(4a)



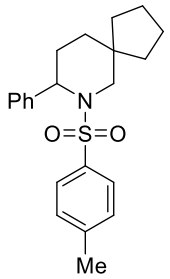
White solid (17.7 mg, 52% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.14 (m, 7H), 5.30 (s, 1H), 3.41 (d, *J* = 14.1 Hz, 1H), 2.99 (d, *J* = 14.1 Hz, 1H), 2.41 (s, 3H), 2.28 (d, *J* = 10.6 Hz, 1H), 2.00 (t, *J* = 13.5 Hz, 1H), 1.86 (d, *J* = 13.3 Hz, 1H), 0.73 (d, *J* = 12.9 Hz, 1H), 0.33 – 0.02 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 138.6, 138.5, 129.4, 128.5, 127.2, 126.9, 126.8, 55.1, 49.3, 28.4, 27.3, 21.4, 17.7, 13.1, 13.0, 9.9. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{23}NNaO_2S^+$: 364.1342; found: 364.1339.

7-phenyl-6-tosyl-6-azaspiro[3.5]nonane (4b)



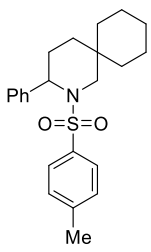
White solid (16.0 mg, 45% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.58 (m, 2H), 7.31–7.10 (m, 7H), 5.17 (s, 1H), 3.74 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.90 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.38 (s, 3H), 2.10 (d, *J* = 6.4 Hz, 1H), 1.95–1.83 (m, 1H), 1.80–1.70 (m, 2H), 1.65–1.46 (m, 5H), 1.34–1.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 138.8, 138.5, 129.4, 128.4, 127.0, 126.9, 126.6, 55.2, 50.9, 38.01, 37.99, 30.9, 30.52, 30.1, 25.7, 21.4, 14.71, 14.69. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}NNaO_2S^+$: 378.1499; found: 378.1496.

8-phenyl-7-tosyl-7-azaspiro[4.5]decane (4c)



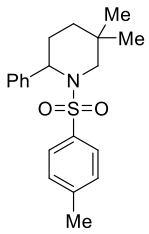
White solid (17.7 mg, 48% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.35–7.12 (m, 7H), 5.22 (d, *J* = 3.1 Hz, 1H), 3.47 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 13.4 Hz, 1H), 2.39 (s, 3H), 2.20–2.10 (m, 1H), 2.07–1.94 (m, 1H), 1.59–1.42 (m, 5H), 1.38–1.17 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 139.0, 138.5, 129.4, 128.3, 126.96, 126.92, 126.6, 55.5, 50.6, 42.5, 38.2, 34.4, 31.5, 27.3, 24.5, 23.9, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{27}NNaO_2S^+$: 392.1655; found: 392.1654.

3-phenyl-2-tosyl-2-azaspiro[5.5]undecane (4d)[1]



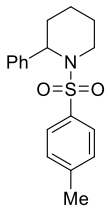
White solid (18.0 mg, 47% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.27–7.10 (m, 7H), 5.20 (s, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 2.77 (d, *J* = 13.6 Hz, 1H), 2.38 (s, 3H), 2.13–1.96 (m, 2H), 1.44–1.24 (m, 8H), 1.19–1.03 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 139.0, 138.5, 129.3, 128.3, 127.0, 126.9, 126.6, 55.9, 50.1, 37.8, 32.6, 31.8, 26.4, 24.9, 21.5, 21.4, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{29}NNaO_2S^+$: 406.1812; found: 406.1812.

5,5-dimethyl-2-phenyl-1-tosylpiperidine (4e)[3,4]



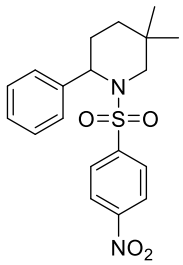
White solid (17.1 mg, 50% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.30–7.10 (m, 7H), 5.23 (s, 1H), 3.41 (d, *J* = 13.4 Hz, 1H), 2.84 (s, 1H), 2.40 (s, 3H), 2.10 (q, *J* = 4.6 Hz, 2H), 1.27 (d, *J* = 11.4 Hz, 2H), 0.80 (d, *J* = 4.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 138.9,138.5, 129.4, 128.4, 127.0, 126.9, 126.6, 55.3, 52.5, 32.5, 30.3, 28.6, 25.7, 24.1, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{25}NNaO_2S^+$: 366.1499; found: 366.1495.

2-phenyl-1-tosylpiperidine (4f)[4]



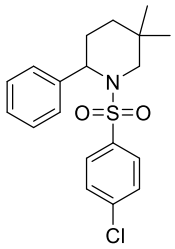
White solid (12.6 mg, 40% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.35–7.26 (m, 6H), 7.26–7.18 (m, 1H), 5.25 (d, *J* = 3.7 Hz, 1H), 3.82 (d, *J* = 14.3 Hz, 1H), 3.20–2.87 (m, 1H), 2.42 (s, 3H), 2.19 (d, *J* = 16.5 Hz, 1H), 1.71–1.58 (m, 1H), 1.53–1.43 (m, 1H), 1.41–1.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 138.8, 138.6, 129.6, 128.5, 126.94, 126.91, 126.7, 55.2, 41.8, 27.2, 24.2, 21.5, 18.9. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{21}NNaO_2S^+$: 338.1186; found: 338.1180.

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



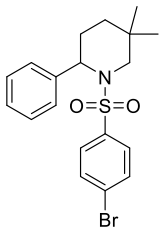
White solid (16.1 mg, 43% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15)^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.23 – 7.19 (m, 3H), 7.12–7.05 (m, 2H), 5.24 (t, *J* = 4.4 Hz, 1H), 3.47 (d, *J* = 13.3 Hz, 1H), 2.95 (d, *J* = 13.3 Hz, 1H), 2.15–2.07 (m, 2H), 1.35–1.29 (m, 2H), 0.86 (d, *J* = 2.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 138.4, 128.6, 128.0, 127.2, 126.8, 124.0, 56.1, 53.0, 32.3, 30.5, 29.7, 28.4, 26.1, 24.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}N_2NaO_4S^+$ 397.1193; found397.1188.

1-((4-chlorophenyl)sulfonyl)-5,5-dimethyl-2-phenylpiperidine(4h)



White solid (16.7 mg, 46% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15)^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.11 (d, *J* = 6.4 Hz, 2H), 5.20 (t, *J* = 4.3 Hz, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 2.88 (d, *J* = 13.3 Hz, 1H), 2.13–2.04 (m, 2H), 1.29–1.21 (m, 3H), 0.82 (d, *J* = 7.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 138.7, 138.4, 129.0, 128.5, 128.4, 126.9, 126.8, 55.6, 52.7, 32.4, 30.4, 28.5, 25.9, 24.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}ClNNaO_2S^+$ 386.0952; found386.0948.

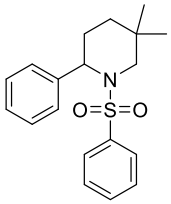
1-((4-bromophenyl)sulfonyl)-5,5-dimethyl-2-phenylpiperidine(4i)



White solid (17.1 mg, 42% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15)^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.50 (m, 4H), 7.26–7.18 (m, 3H), 7.10 (d, *J* = 6.0 Hz, 2H), 5.19 (t, *J* = 4.3 Hz, 1H), 3.40 (d, *J* = 13.3 Hz, 1H), 2.88 (d, *J* = 13.3 Hz, 1H), 2.08

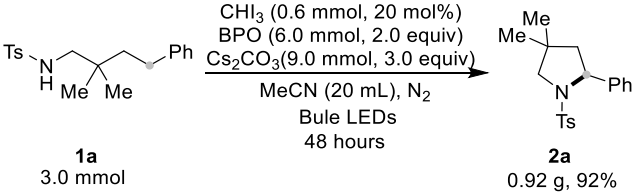
(dt, J = 8.1, 4.2 Hz, 2H), 1.27–1.22 (m, 2H), 0.82 (d, J = 8.1 Hz, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 140.4, 138.6, 132.3, 132.0, 128.5, 128.5, 126.9, 126.8, 55.7, 52.8, 32.4, 30.4, 28.5, 25.9, 24.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}NNaO_2S^+$ 430.0047; found430.0043.

5,5-dimethyl-2-phenyl-1-(phenylsulfonyl)piperidin(4j)



White solid (15.8 mg, 48% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:15)^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.72 (m, 2H), 7.53–7.46 (m, 1H), 7.44–7.36 (m, 2H), 7.29–7.15 (m, 3H), 7.13–7.07 (m, 2H), 5.24 (s, 1H), 3.42 (d, J = 13.0 Hz, 1H), 2.86 (d, J = 13.4 Hz, 1H), 2.20–1.99 (m, 2H), 0.78 (d, J = 1.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 138.7, 132.1, 128.8, 128.4, 126.9, 126.8, 126.7, 55.4, 52.5, 32.4, 30.3, 28.6, 25.7, 24.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{23}NNaO_2S^+$ 352.1342; found352.1335.

7. Gram-scale synthesis

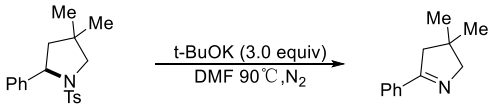


1a
3.0 mmol

2a
0.92 g, 92%

1a (993mg, 3.0 mmol, 1.0 equiv), CHI_3 (235.8 mg, 0.6 mmol, 20 mol%), BPO (1.45g, 6.0 mmol, 2.0 equiv) Cs_2CO_3 (2.9g, 9.0 mmol, 3.0 equiv) and a stir bar were added to a sealed tube under a nitrogen atmosphere and under a 12 W blue LEDs irradiation, acetonitrile (20.0 mL) as solvent was then added. The mixture was stirred for 12 hours at room-temperature. The crude mixture was directly purified by flash column chromatography on silica gel give 0.92 g of **2a**, in 92% yield.

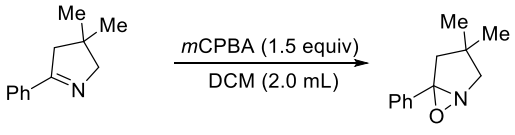
8. Synthetic transformation[7]



2a
0.1 mmol

5
85%

2a (32.9 mg, 0.1 mmol, 1.0 equiv), ^{t}BuOK (33.6mg, 0.3 mmol, 3.0 equiv) and a magnetic stir bar was added into a sealed tube under a nitrogen atmosphere, DMF (2.0 mL) as the solvent was added and stirred at 90 °C for 12 hours. The crude mixture was directly purified by flash column chromatography on silica gel to give **5** as a colorless liquid (14.7 mg, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.71 (m, 2H), 7.50–7.32 (m, 3H), 3.78 (q, J = 2.0 Hz, 2H), 2.76 (q, J = 2.0 Hz, 2H), 1.16 (d, J = 1.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 134.7, 130.2, 128.3, 127.3, 74.60, 49.7, 38.3, 28.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{25}NNa^+$ 196.1097; found 196.1092.

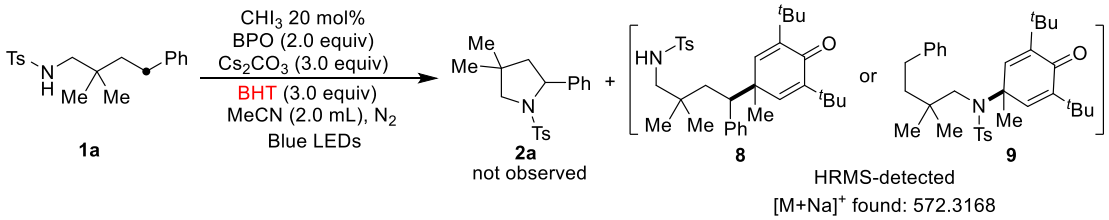


5
0.1 mmol

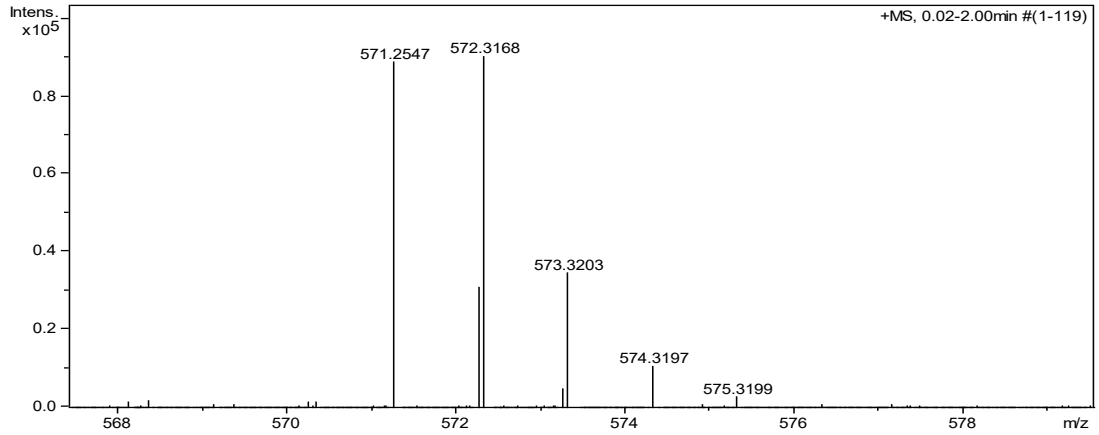
6
50%

5 (17.3mg, 0.1 mmol, 1.0 equiv), *m*CPBA (25.8mg, 1.5 mmol, 1.5 equiv) and a magnetic stir bar was added into a sealed tube under a nitrogen atmosphere, DCM (2.0 mL) as the solvent was added for 12 hours. The crude mixture was directly purified by flash column chromatography on silica gel to give **6** as a colorless liquid (9.5 mg, 50% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc:petroleum ether 1:1)^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (dd, *J* = 7.5, 2.5 Hz, 2H), 7.47–7.37 (m, 3H), 3.97 (s, 2H), 2.94 (s, 2H), 1.26 (s, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 140.8, 130.2, 129.3, 128.3, 127.3, 45.7, 31.9, 28.1, 28.0 HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{16}NO^+$; 190.1227 found 190.1226.

9. Radical inhibition experiments



1a (33.1 mg, 0.1 mmol, 1.0 equiv), CHI_3 (7.8 mg, 20 mol%), BPO (48.4 mg, 0.2 mmol, 2.0 equiv) Cs_2CO_3 (97.5 mg, 0.3 mmol, 3.0 equiv), BHT (butylated hydroxytoluene, 60.1 mg, 0.3 mmol, 3.0 equiv) and a stir bar were added to a sealed tube under a nitrogen atmosphere and under a 12 W blue LEDs irradiation, acetonitrile (2.0 mL) as solvent was then added. The mixture was stirred for 12 hours at room-temperature. The desired product **2a** was not observed, and the possible cross-coupling product **8** or **9** by BTH with nitrogen atom or benzyl radical was detected. The above reaction indicated that the present transformation underwent a radical reaction pathway, and the chlorine atom radical was generated under the present reaction conditions.



10. References

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[3] Herold, S.; Bafaluy, D.; Muñiz, K. *Green Chem* **2018**, *20*, 3191.

[4] Bafaluy, D.; Munoz-Molina, J. M.; Funes-Ardoiz, I.; Herold, S.; de Aguirre, A. J.; Zhang, H.; Maseras, F.; Belderrain, T. R.; Perez, P. J.; Muniz, K.,. *Angew Chem Int Ed.;* **2019**, *58*, 8912.

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[6] Nishiguchi, Y.; Moriyama, K. *Adv. Synth. Catal.* **2021,** *363*, 3354.

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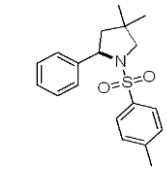
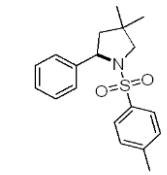
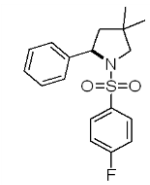
11. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of products



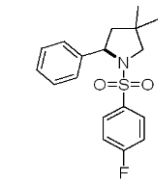
^{1}H NMR (400 MHz, $CDCl_3$)



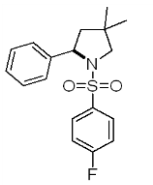
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



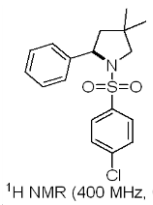
^{1}H NMR (400 MHz, $CDCl_3$)



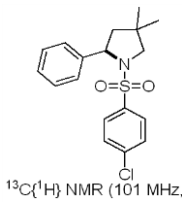
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



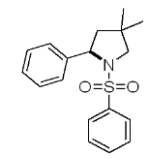
$^{19}F\{^{1}H\}$ NMR
(376MHz,$CDCl_3$)



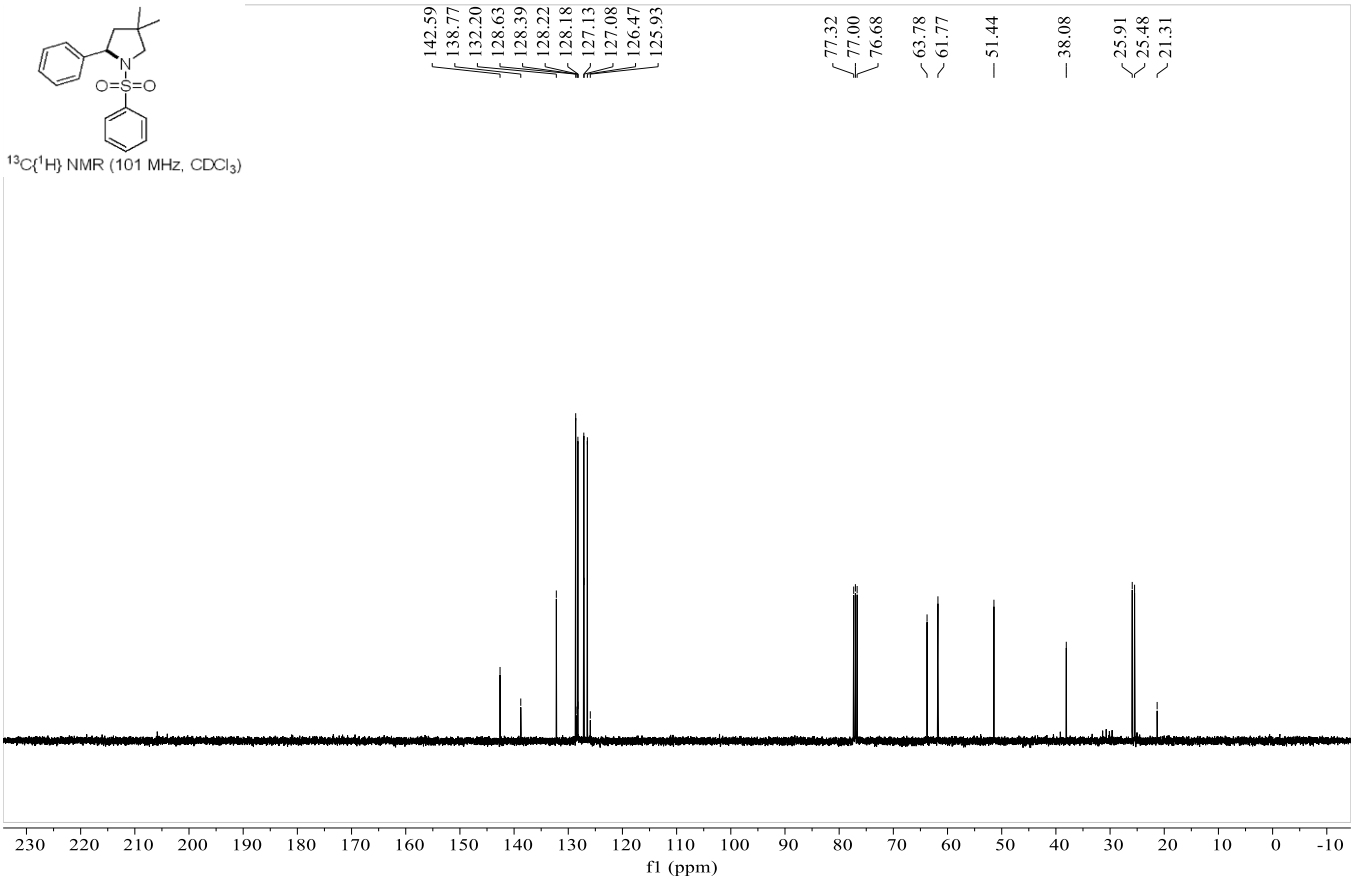
^{1}H NMR (400 MHz, $CDCl_3$)



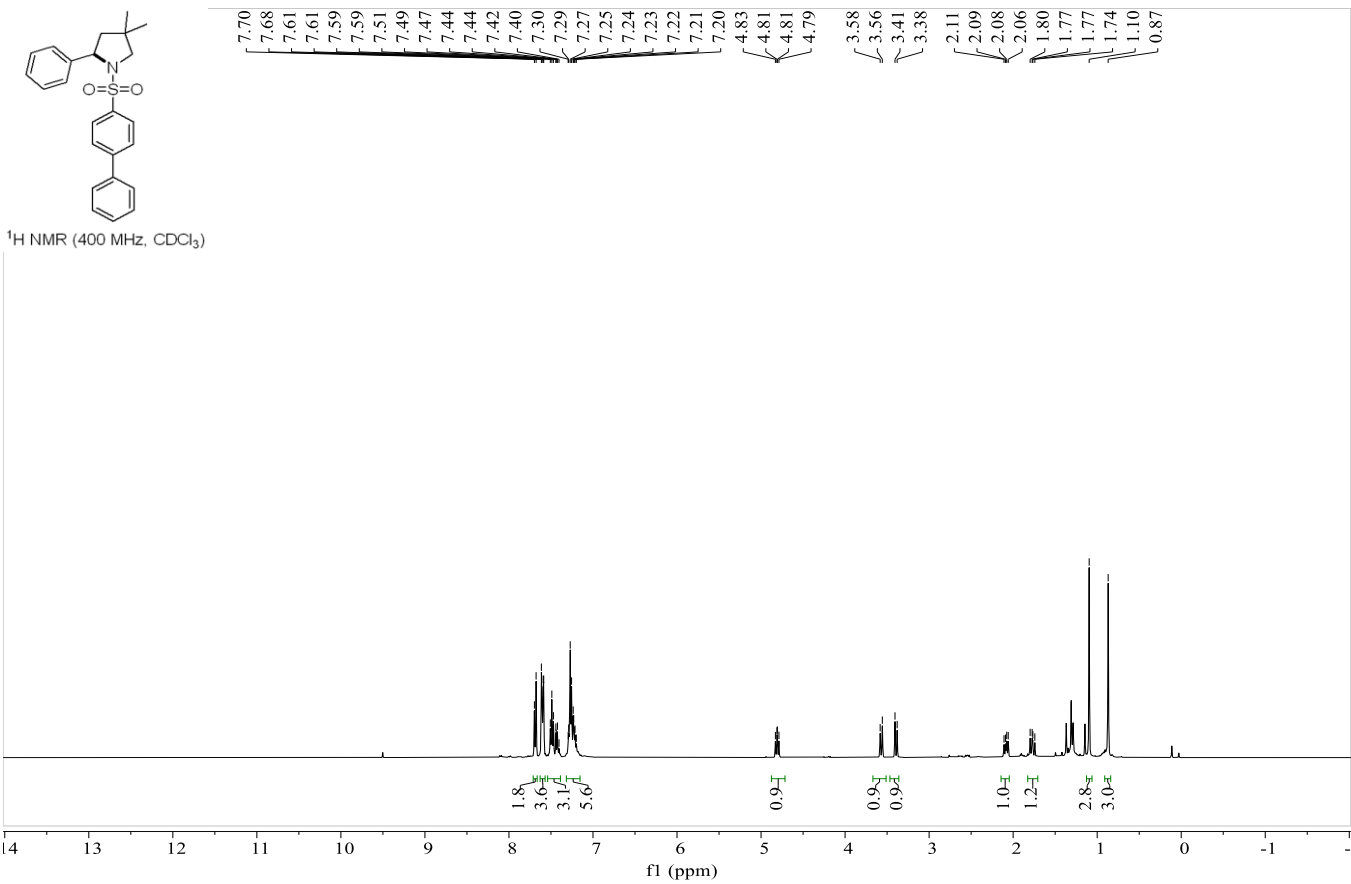
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



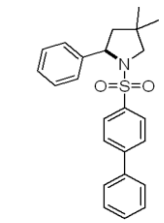
^{1}H NMR (400 MHz, $CDCl_3$)



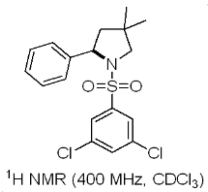
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



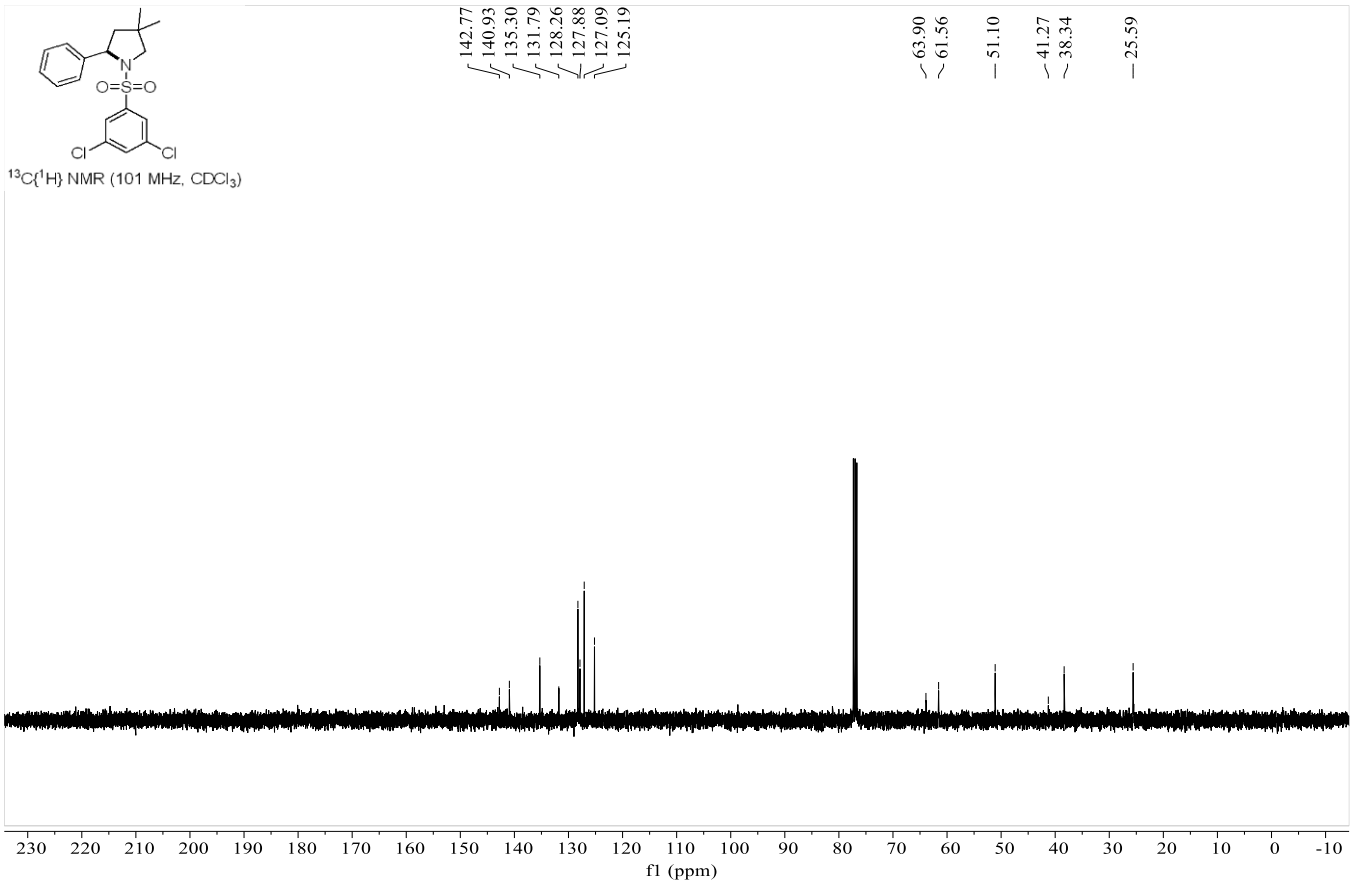
^{1}H NMR (400 MHz, $CDCl_3$)

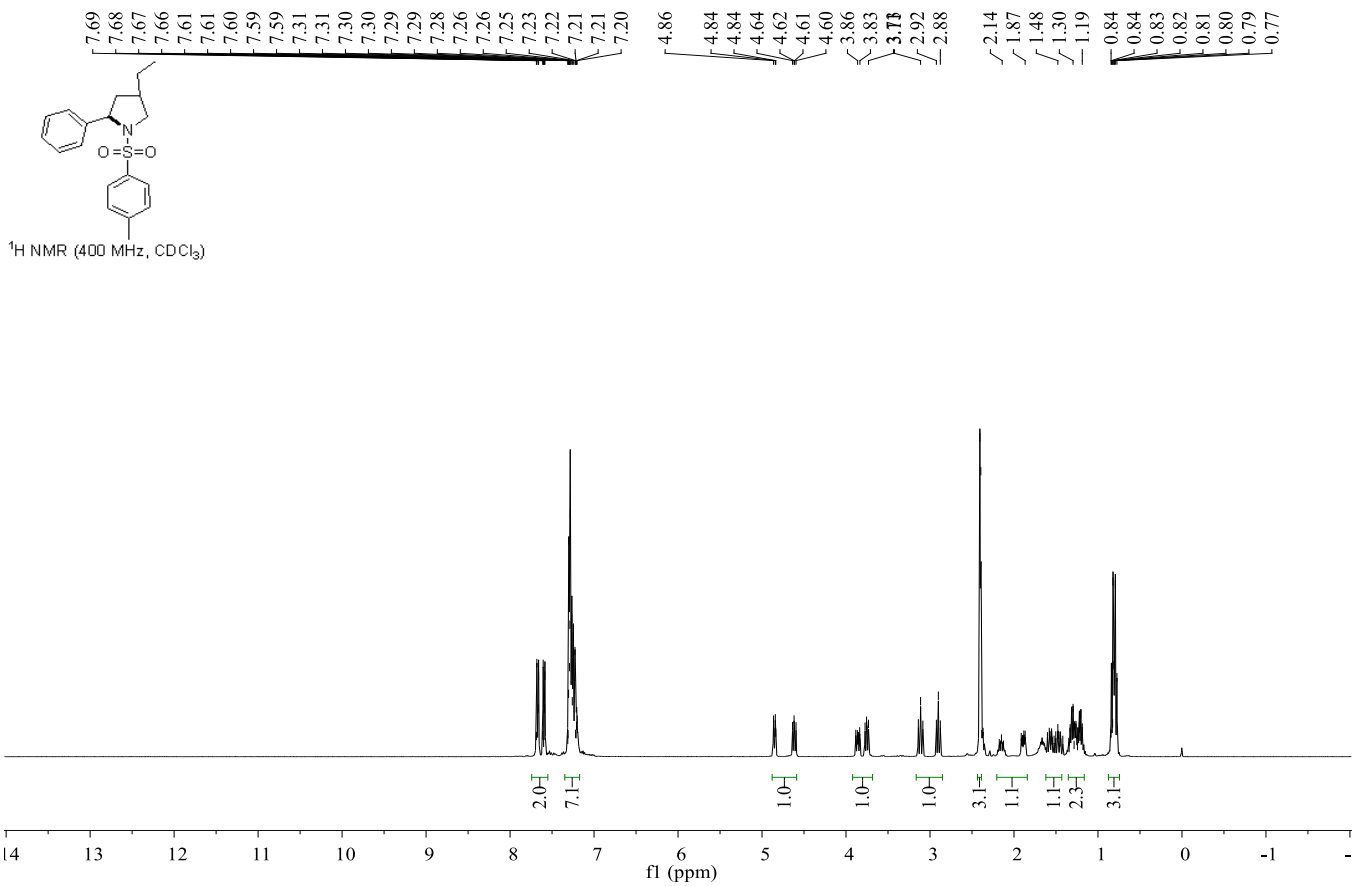


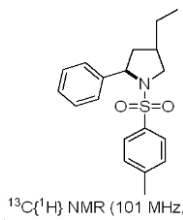
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



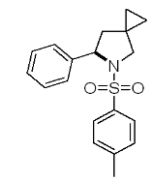
^1H NMR (400 MHz, $CDCl_3$)


142.77
140.93
135.30
131.79
128.26
127.88
127.09
125.19
63.90
61.56
51.10
41.27
38.34
25.59
O=S=O
Cl
Cl
13C{1H} NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

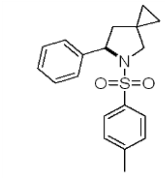

7.69
7.68
7.67
7.66
7.61
7.61
7.60
7.59
7.59
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.26
7.26
7.25
7.23
7.22
7.21
7.21
7.20
4.86
4.84
4.84
4.64
4.62
4.61
4.60
3.86
3.83
2.92
2.88
2.14
1.87
1.48
1.30
1.19
0.84
0.84
0.83
0.82
0.81
0.80
0.79
0.77
O=S=O
1H NMR (400 MHz, CDCl3)
2.0H
7.1H
1.0H
1.0H
1.0H
3.1H
1.1H
1.1H
2.3H
3.1H
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)



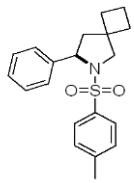
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



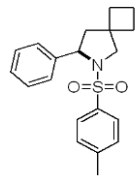
^1H NMR (400 MHz, $CDCl_3$)



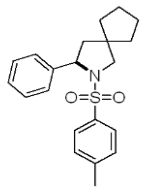
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



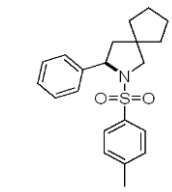
^{1}H NMR (400 MHz, $CDCl_3$)



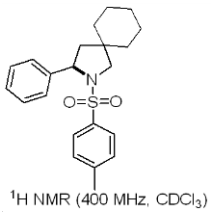
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



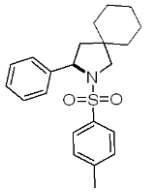
^{1}H NMR (400 MHz, $CDCl_3$)



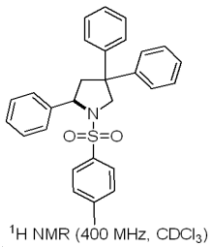
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



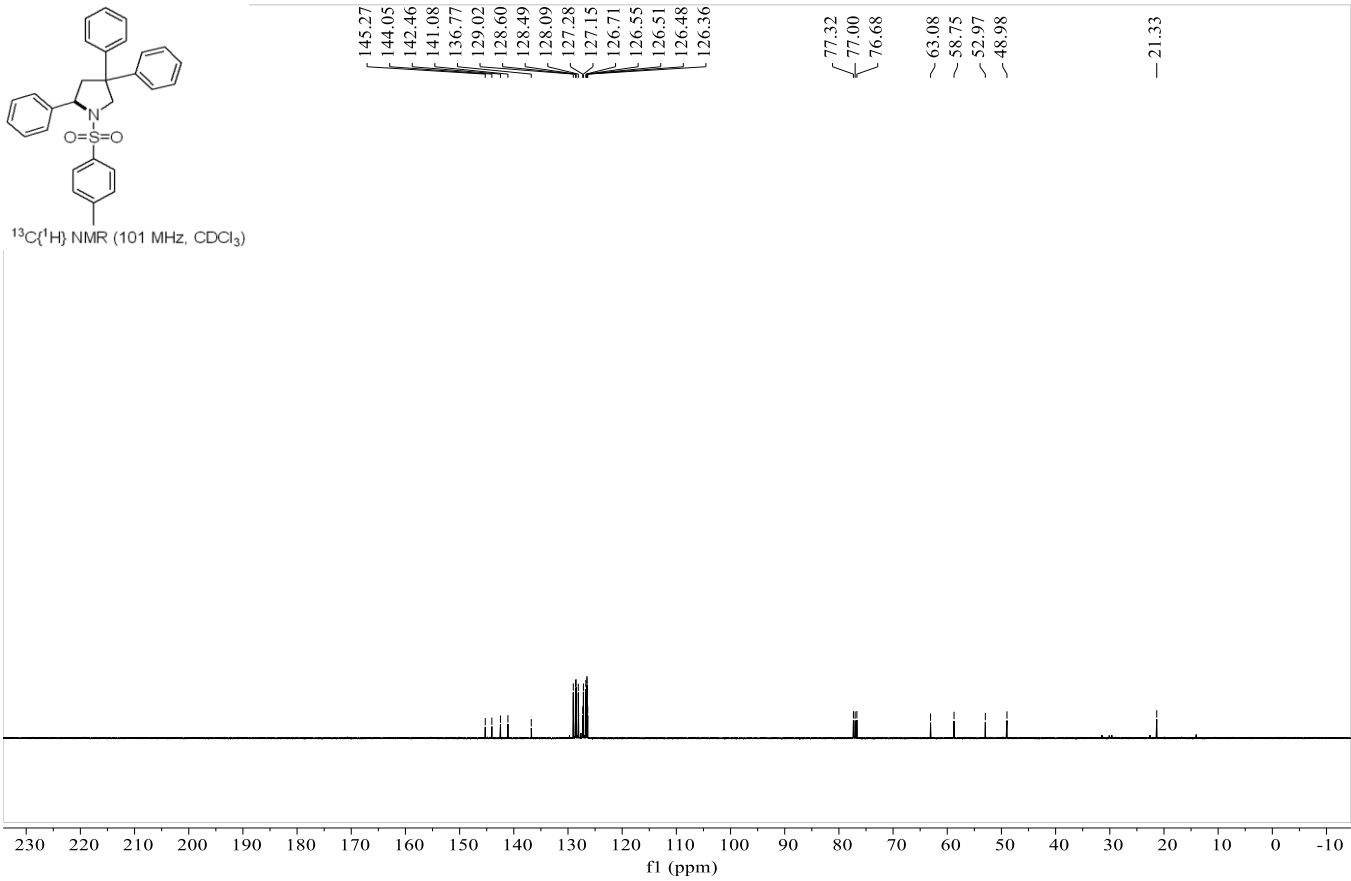
^{1}H NMR (400 MHz, $CDCl_3$)

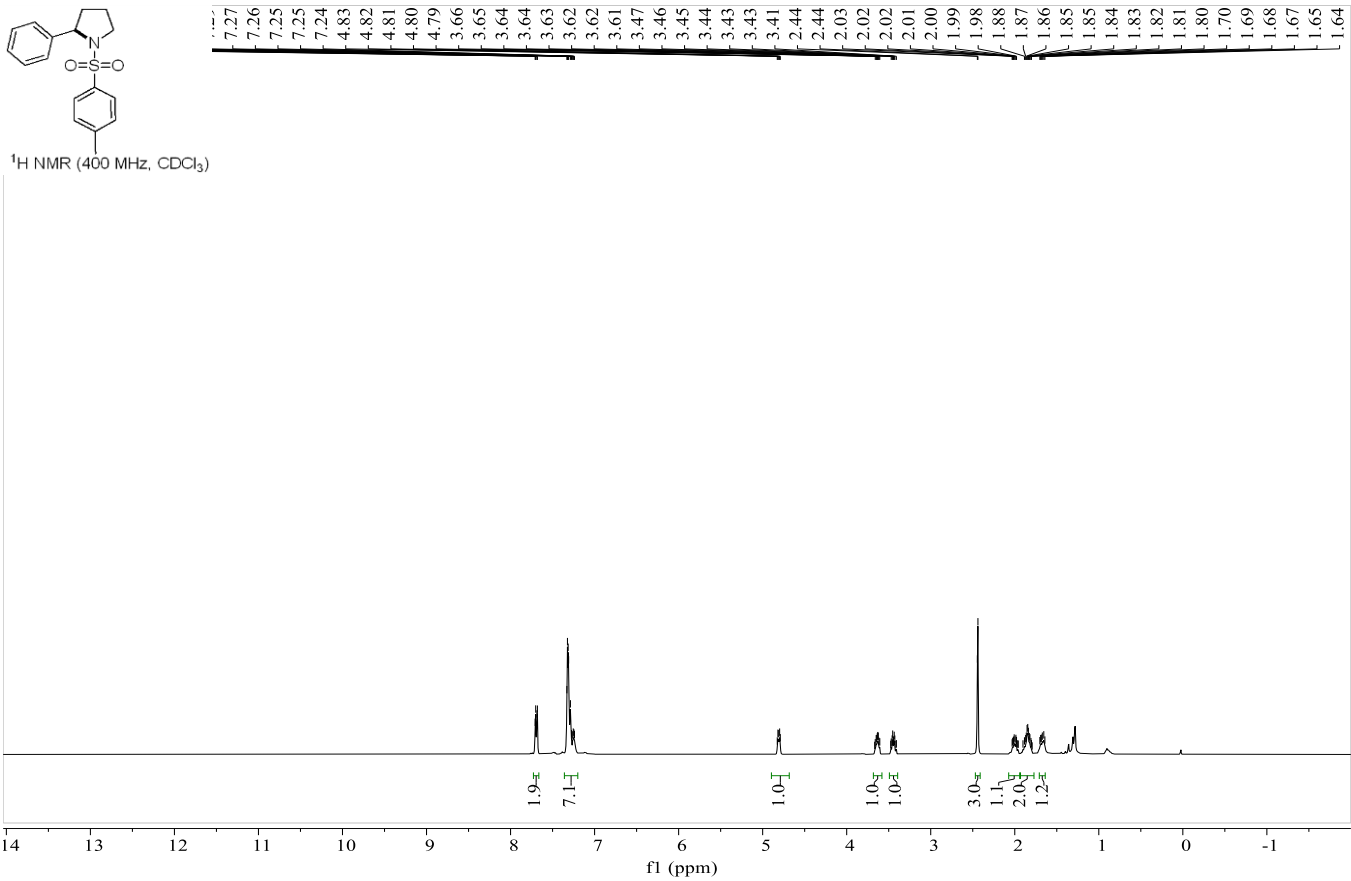


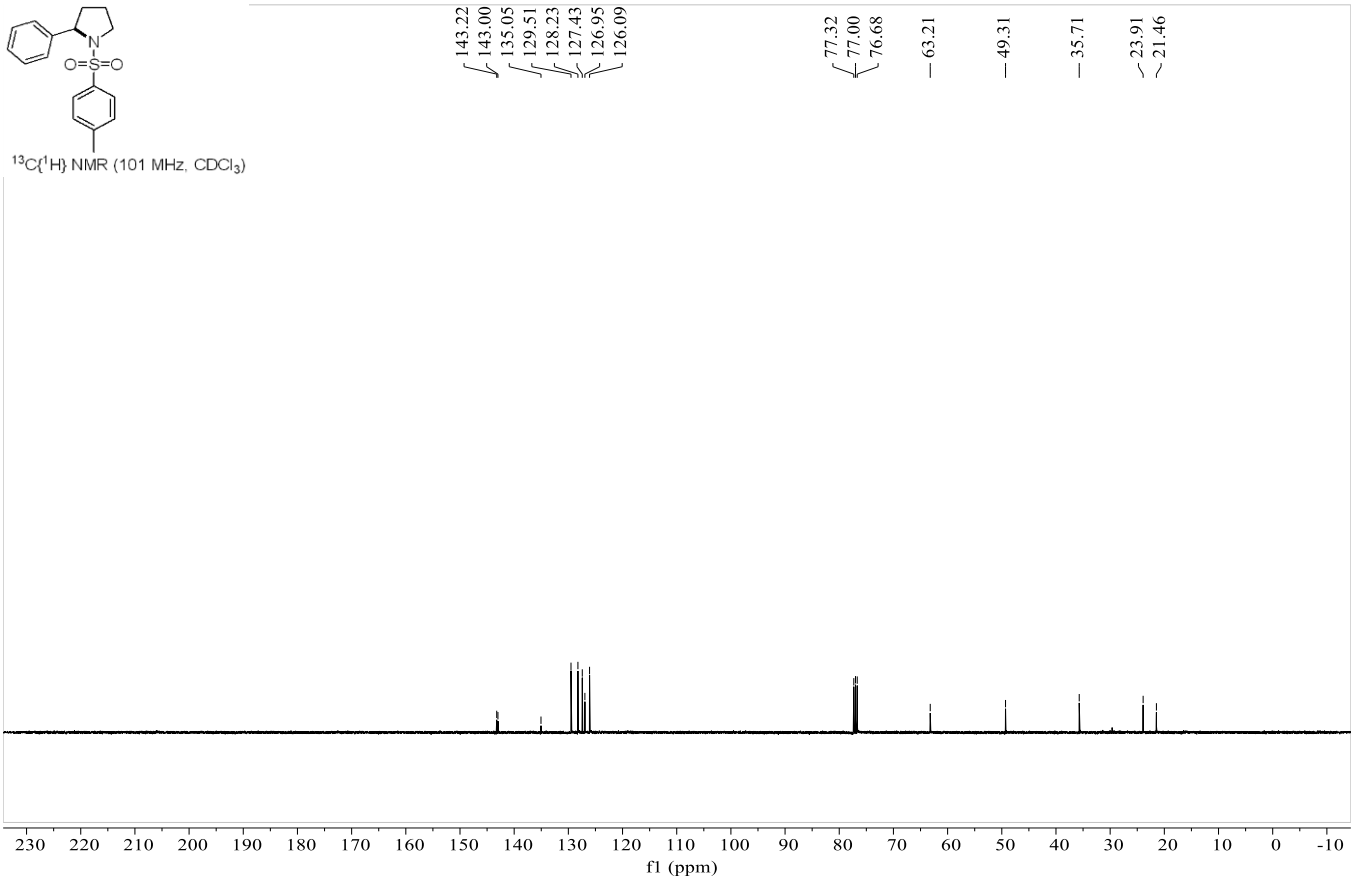
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

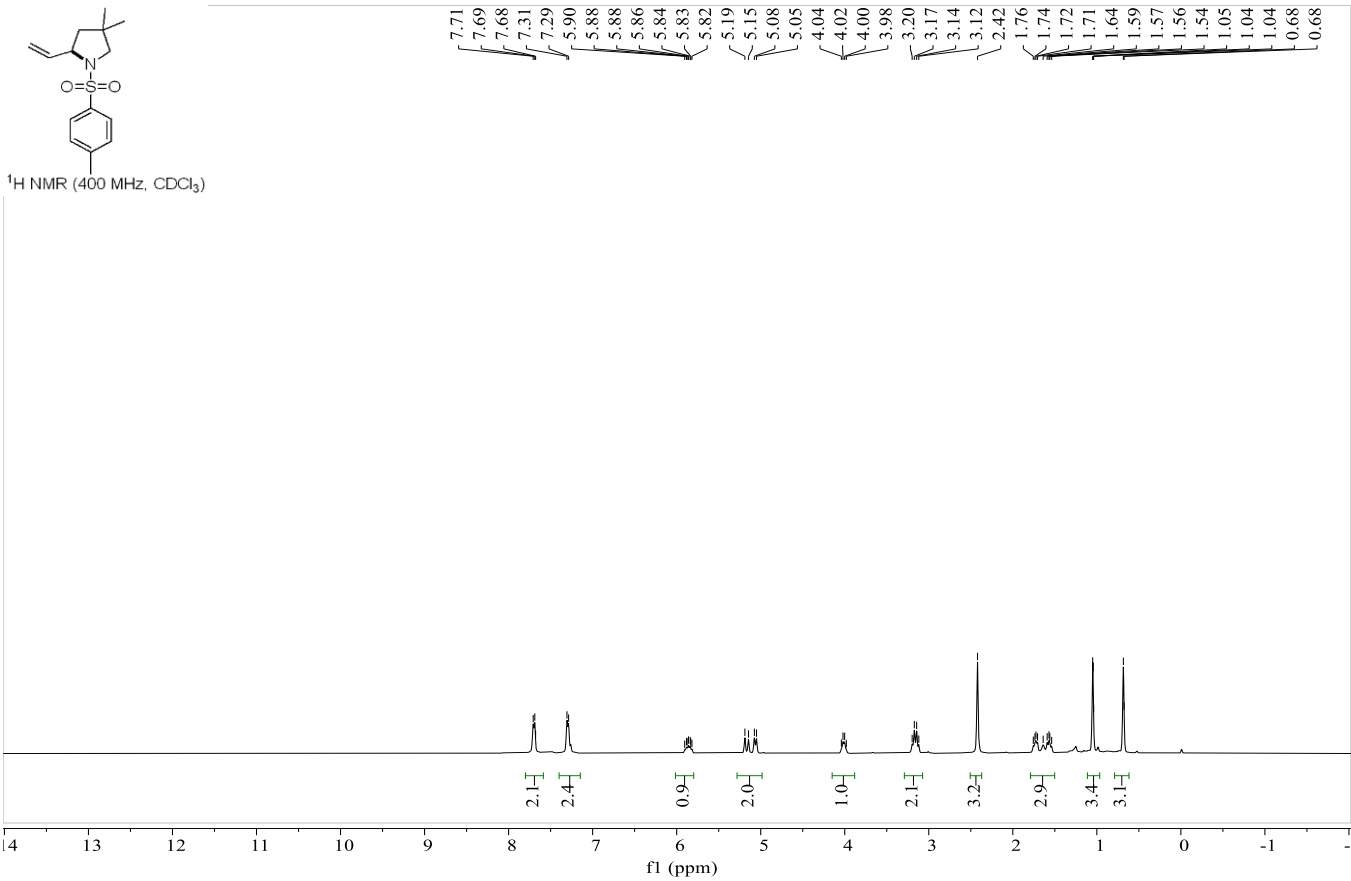


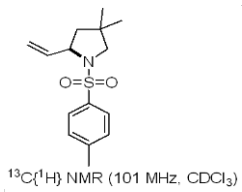
^1H NMR (400 MHz, $CDCl_3$)


145.27
144.05
142.46
141.08
136.77
129.02
128.60
128.49
128.09
127.28
127.15
126.71
126.55
126.51
126.48
126.36
77.32
77.00
76.68
63.08
58.75
52.97
48.98
21.33
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
f1 (ppm)

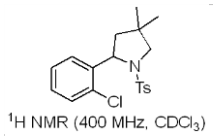

7.27
7.26
7.25
7.25
7.24
4.83
4.82
4.81
4.80
4.79
3.66
3.65
3.64
3.64
3.63
3.62
3.62
3.61
3.47
3.46
3.45
3.44
3.43
3.43
3.41
2.44
2.44
2.03
2.02
2.02
2.01
2.00
1.99
1.98
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.82
1.81
1.80
1.70
1.69
1.68
1.67
1.65
1.64
^{1}H NMR (400 MHz, $CDCl_3$)
1.9
7.1
1.0
1.0
1.0
3.0
1.1
2.0
1.2
f1 (ppm)


143.22
143.00
135.05
129.51
128.23
127.43
126.95
126.09
77.32
77.00
76.68
63.21
49.31
35.71
23.91
21.46
13C{1H} NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

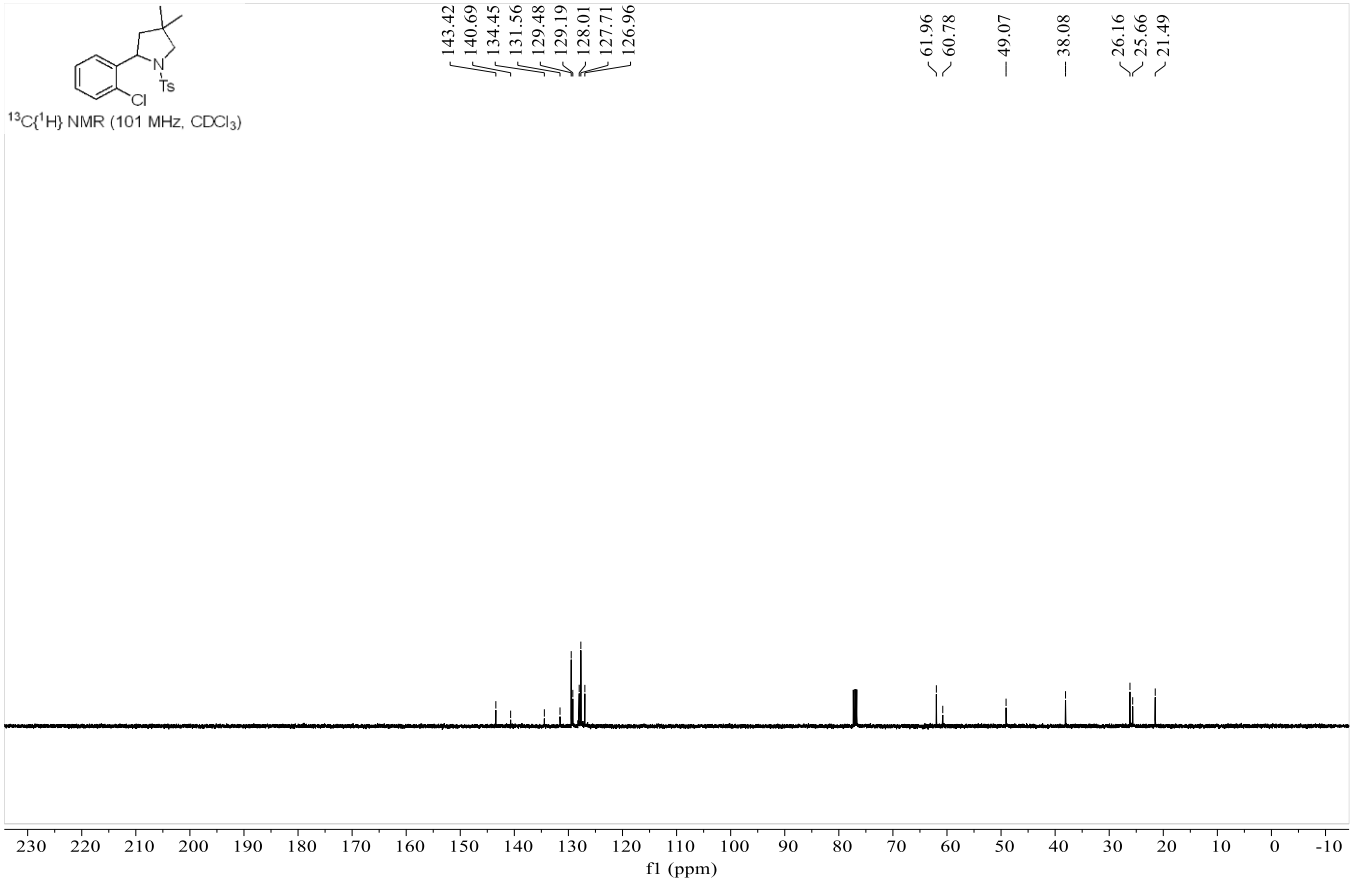

7.71
7.69
7.68
7.31
7.29
5.90
5.88
5.88
5.86
5.84
5.83
5.82
5.19
5.15
5.08
5.05
4.04
4.02
4.00
3.98
3.20
3.17
3.14
3.12
2.42
1.76
1.74
1.72
1.71
1.64
1.59
1.57
1.56
1.54
1.05
1.04
1.04
0.68
0.68
1H NMR (400 MHz, CDCl3)
2.1
2.4
0.9
2.0
1.0
2.1
3.2
2.9
3.4
3.1
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

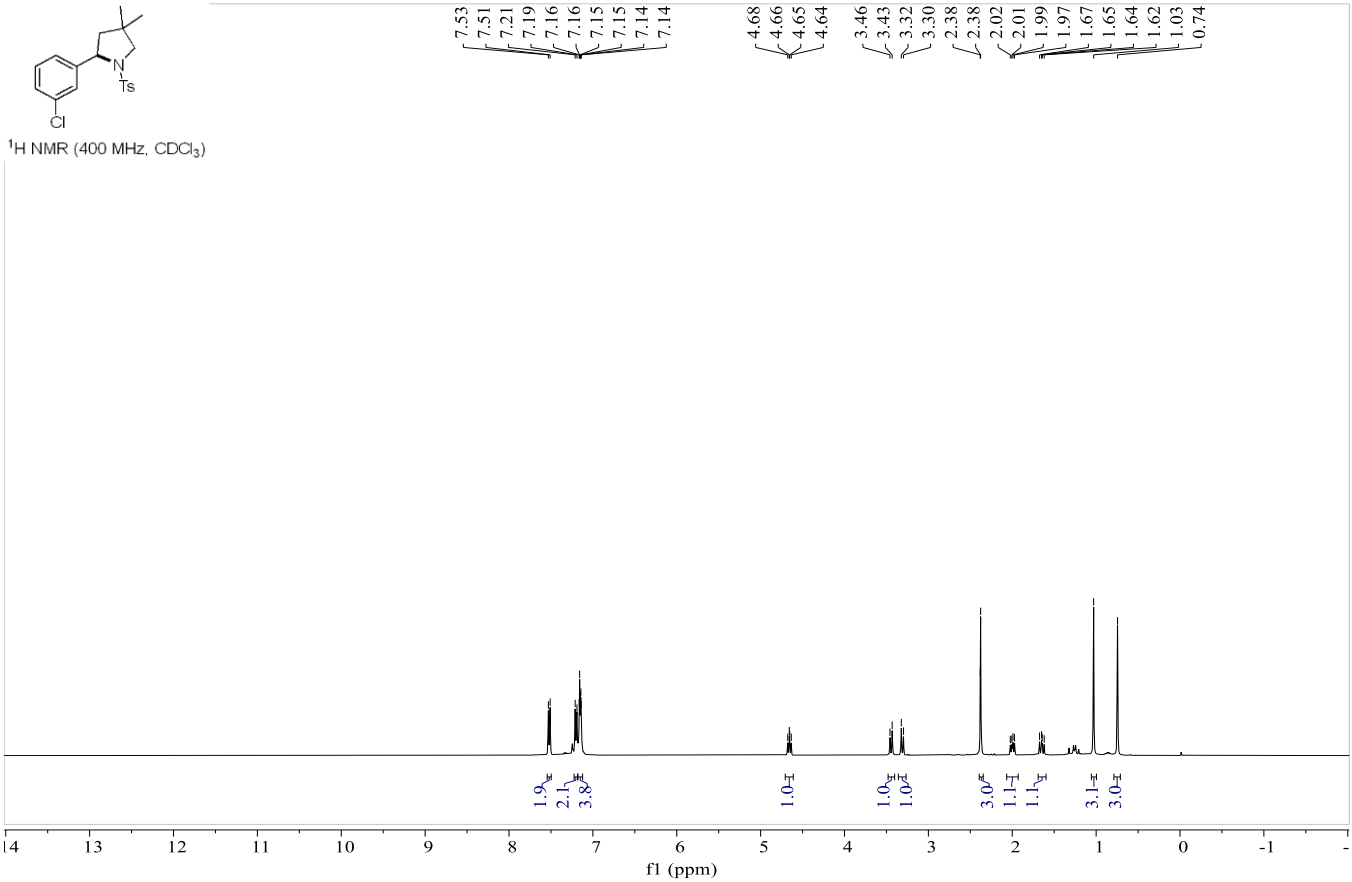


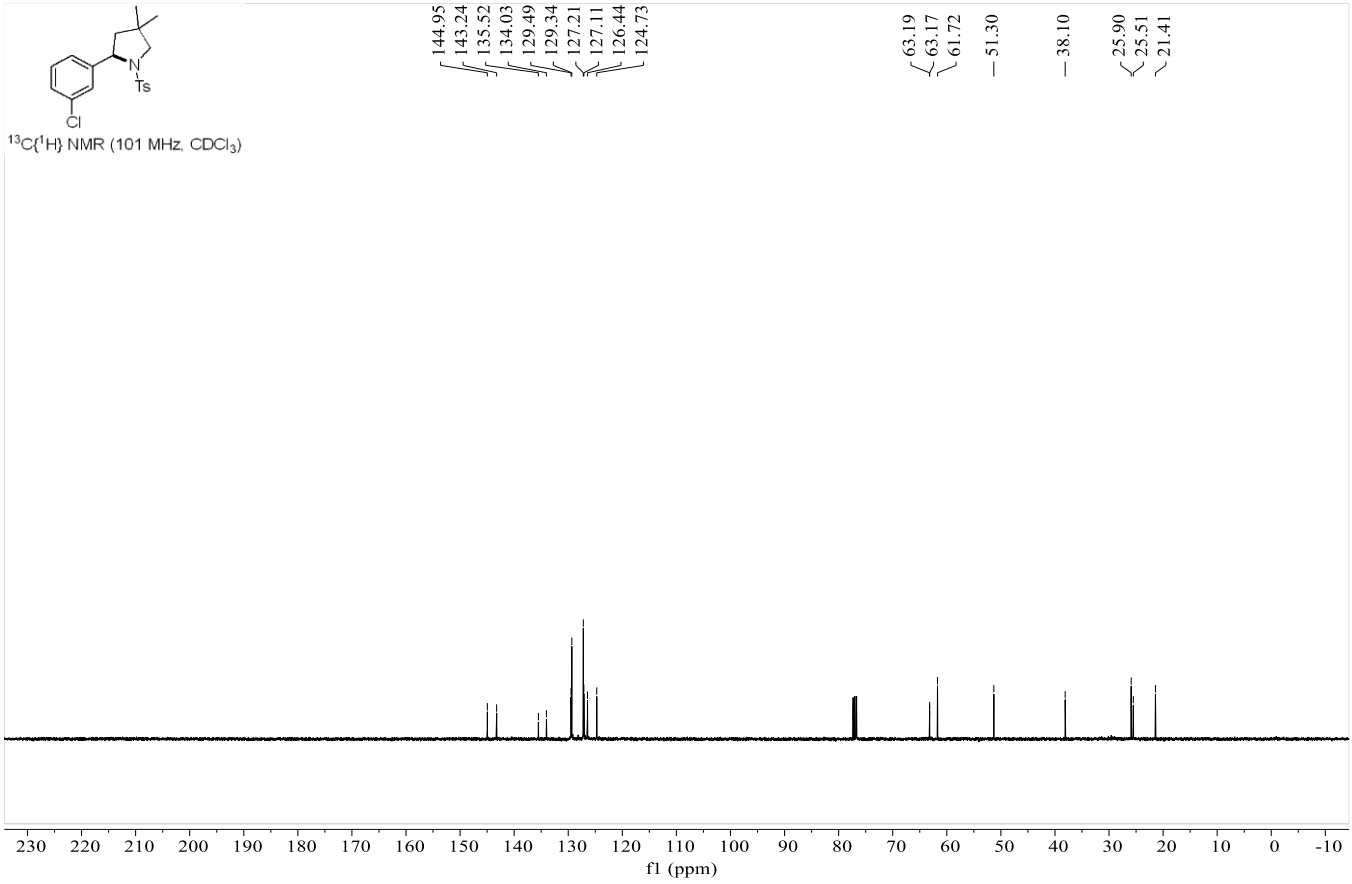
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

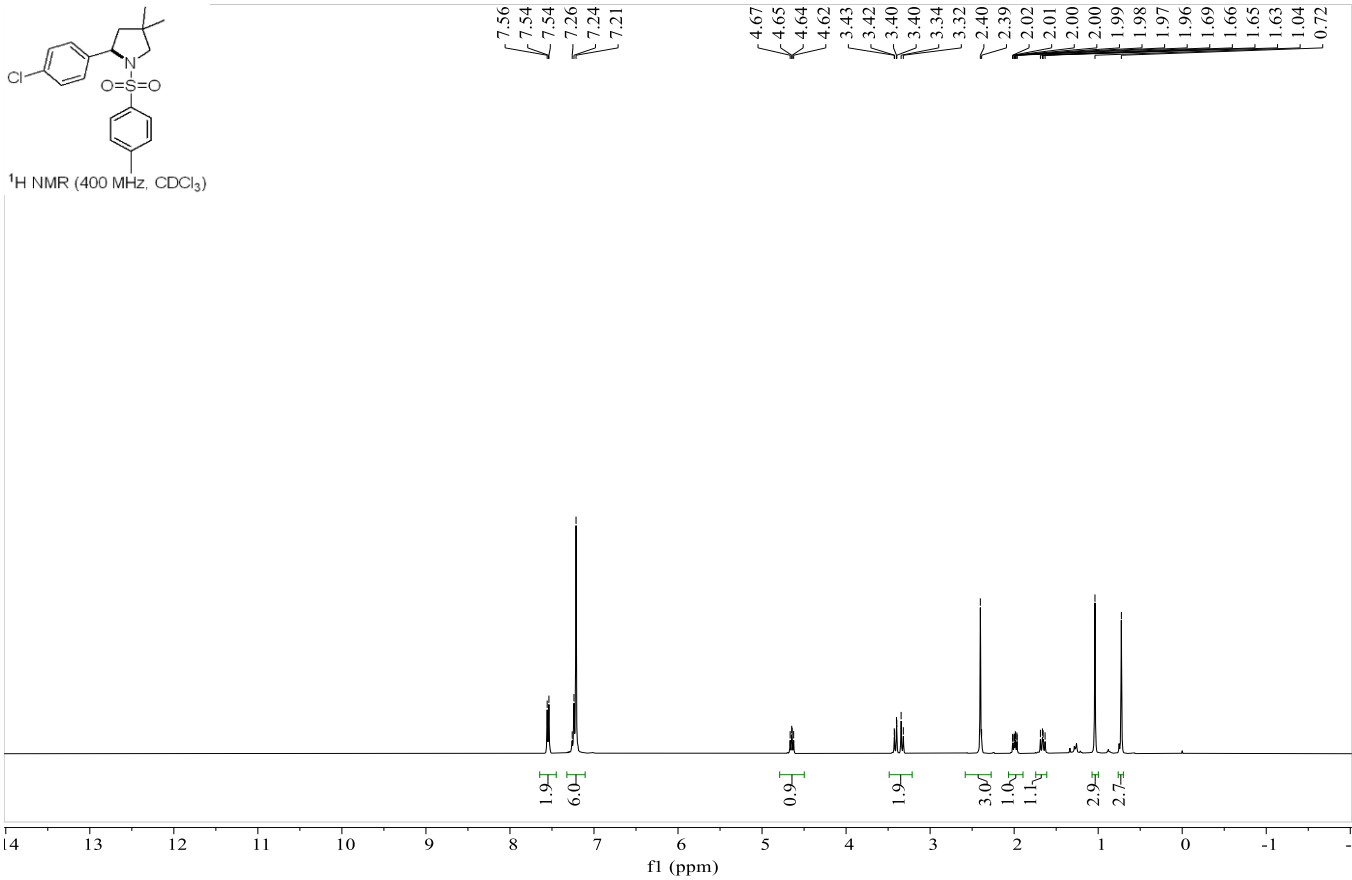


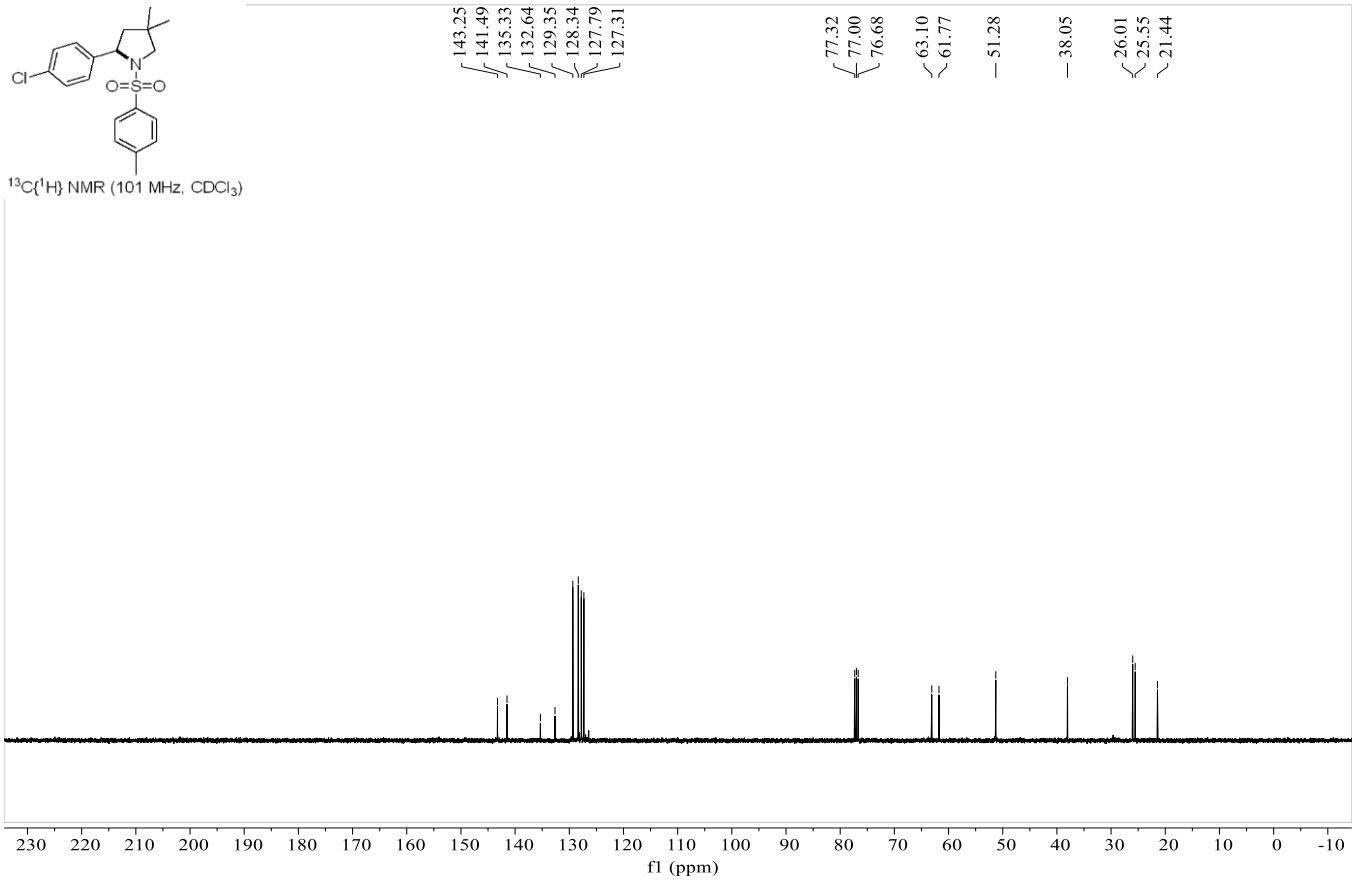
^{1}H NMR (400 MHz, $CDCl_3$)


Ts
Cl
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
143.42
140.69
134.45
131.56
129.48
129.19
128.01
127.71
126.96
61.96
60.78
49.07
38.08
26.16
25.66
21.49
f1 (ppm)

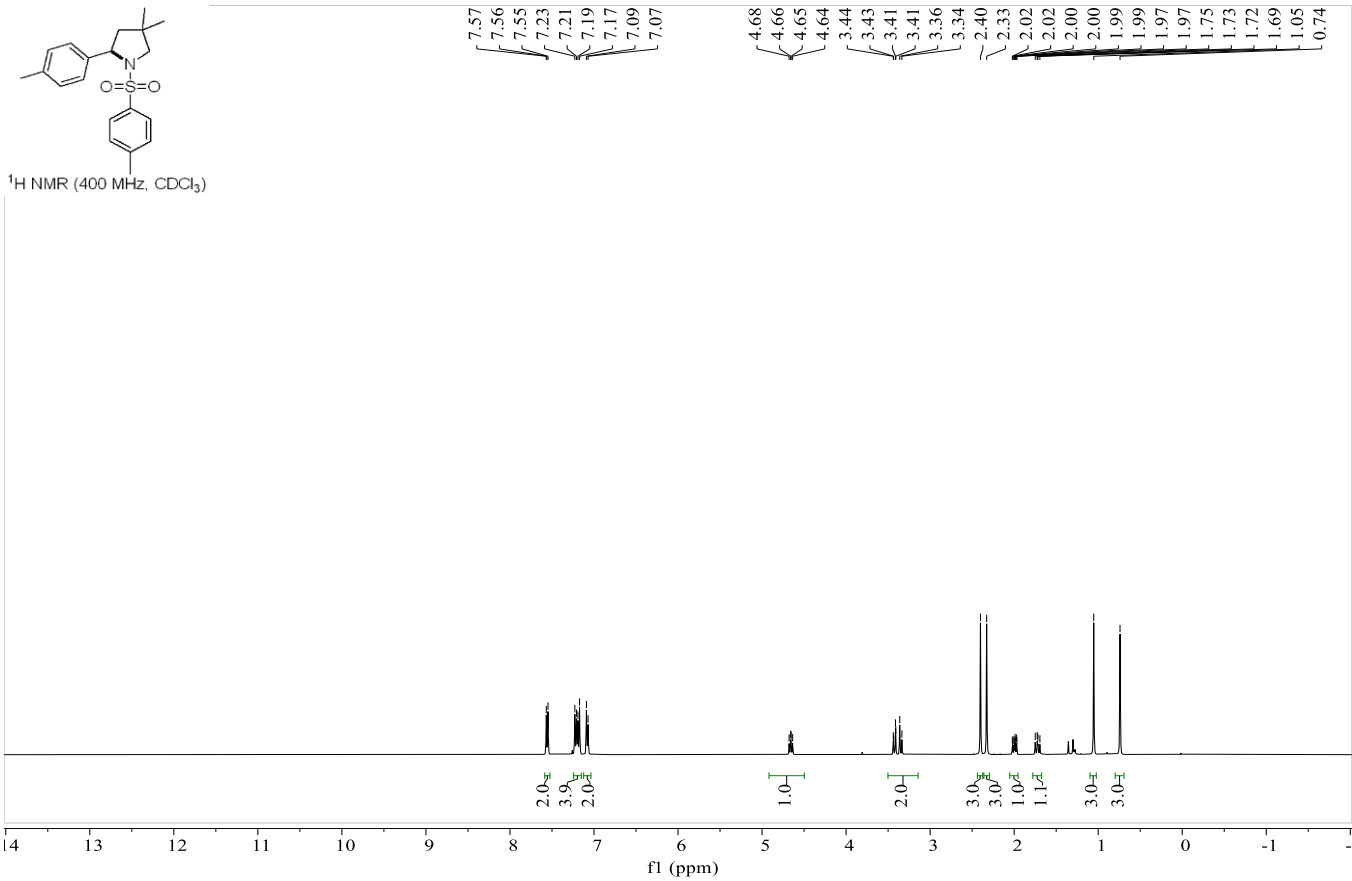

Ts
Cl
^{1}H NMR (400 MHz, $CDCl_3$)
7.53
7.51
7.21
7.19
7.16
7.16
7.15
7.15
7.14
7.14
4.68
4.66
4.65
4.64
3.46
3.43
3.32
3.30
2.38
2.38
2.02
2.01
1.99
1.97
1.67
1.65
1.64
1.62
1.03
0.74
1.9
2.1
3.8
1.0
1.0
1.0
3.0
1.1
1.1
3.1
3.0
f1 (ppm)


144.95
143.24
135.52
134.03
129.49
129.34
127.21
127.11
126.44
124.73
63.19
63.17
61.72
51.30
38.10
25.90
25.51
21.41
Cl
N
Ts
13C{1H} NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

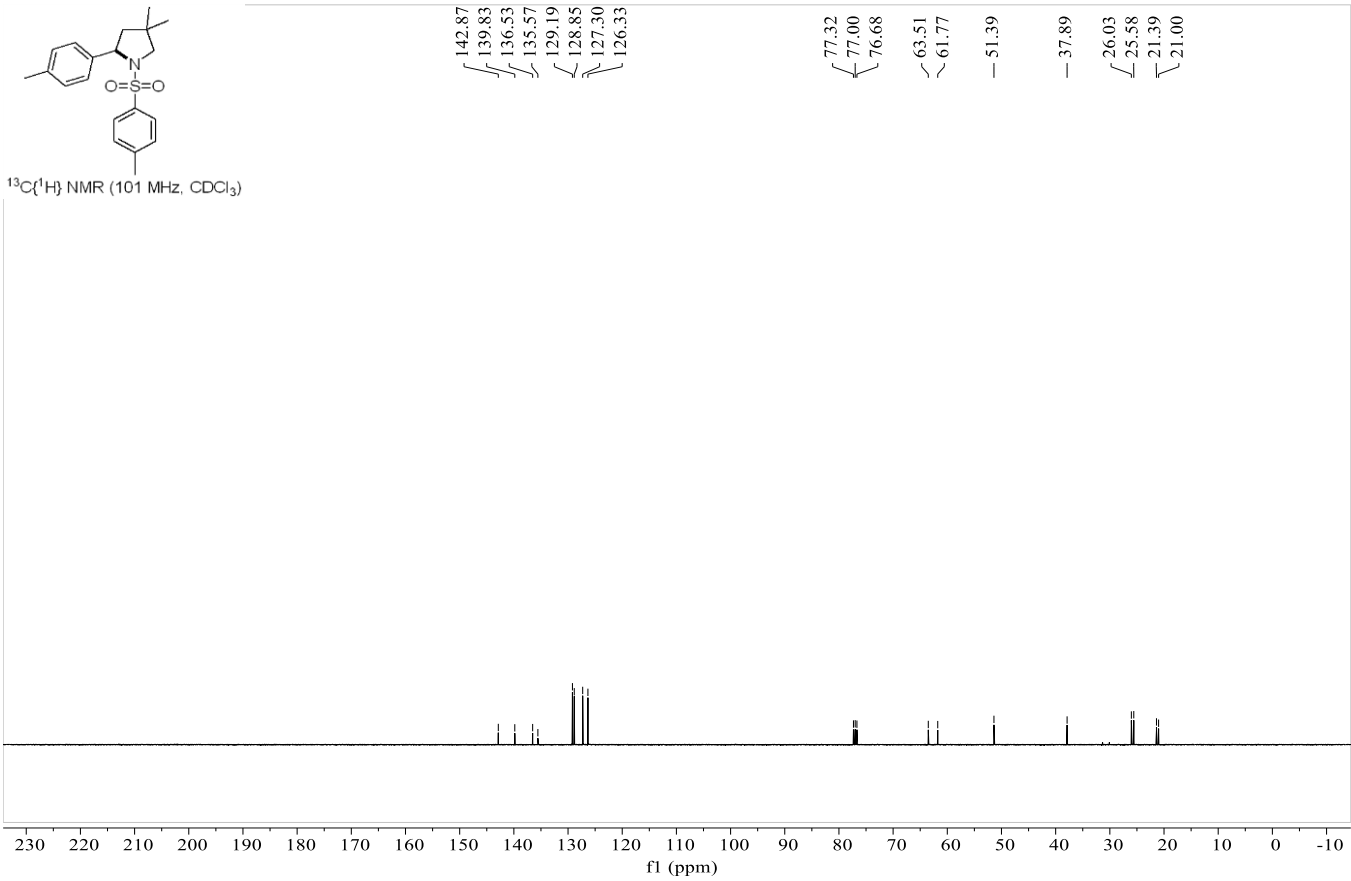

7.56
7.54
7.54
7.26
7.24
7.21
4.67
4.65
4.64
4.62
3.43
3.42
3.40
3.40
3.34
3.32
2.40
2.39
2.02
2.01
2.00
2.00
1.99
1.98
1.97
1.96
1.69
1.66
1.65
1.63
1.04
0.72
Cl
N
O=S=O
1H NMR (400 MHz, CDCl3)
1.9
6.0
0.9
1.9
3.0
1.0
1.1
2.9
2.7
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)



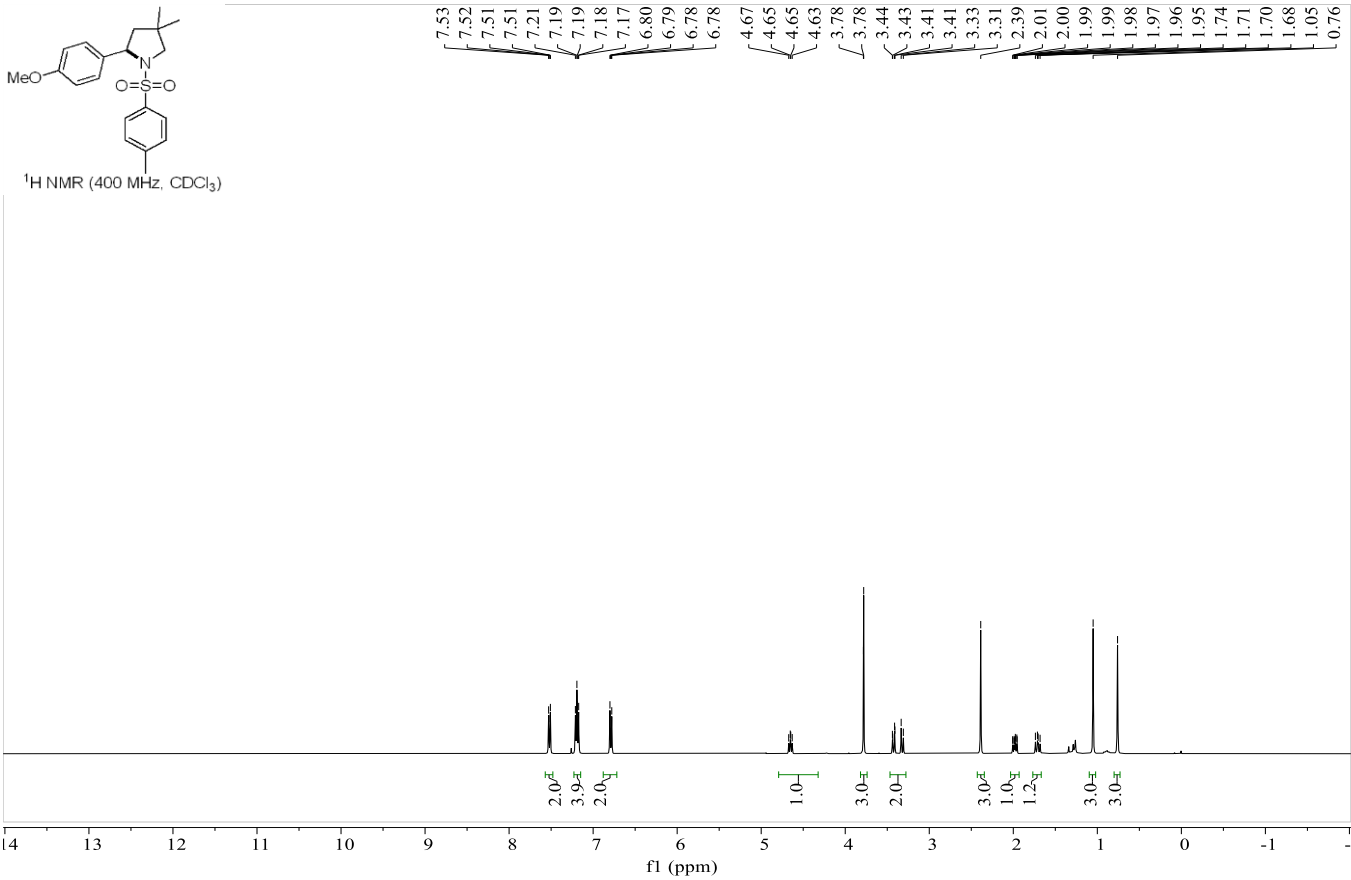
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



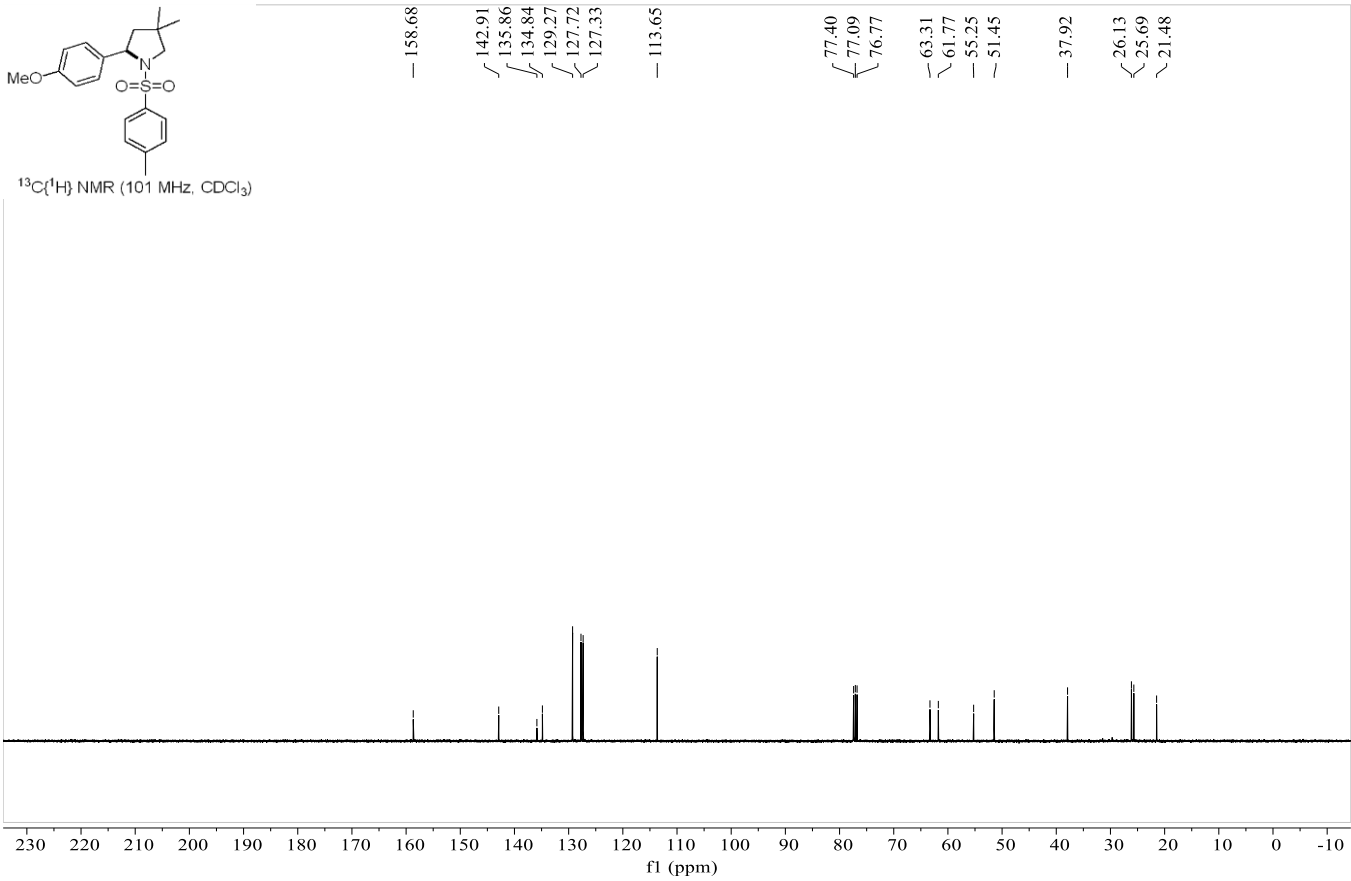
^{1}H NMR (400 MHz, $CDCl_3$)



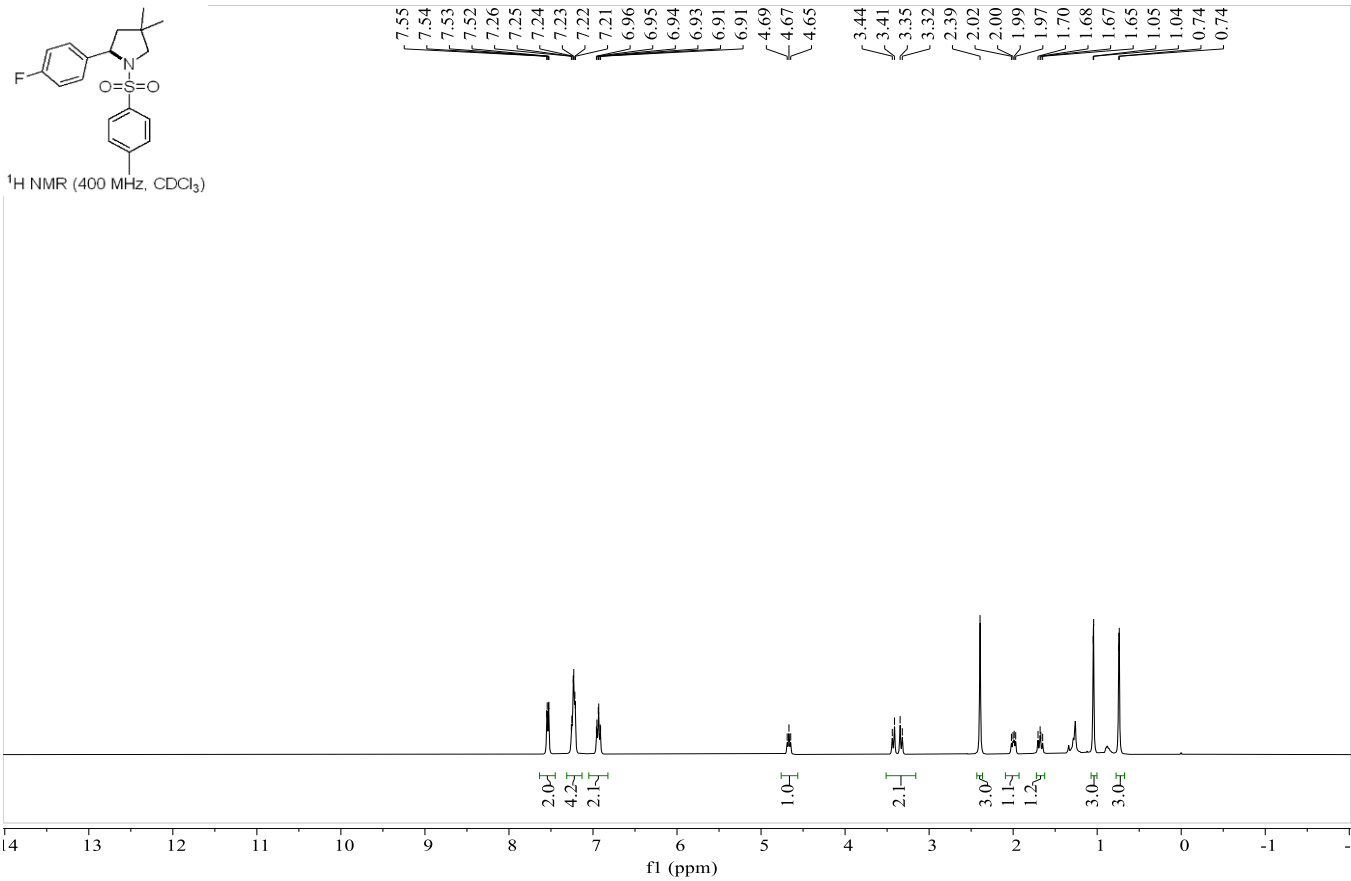
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



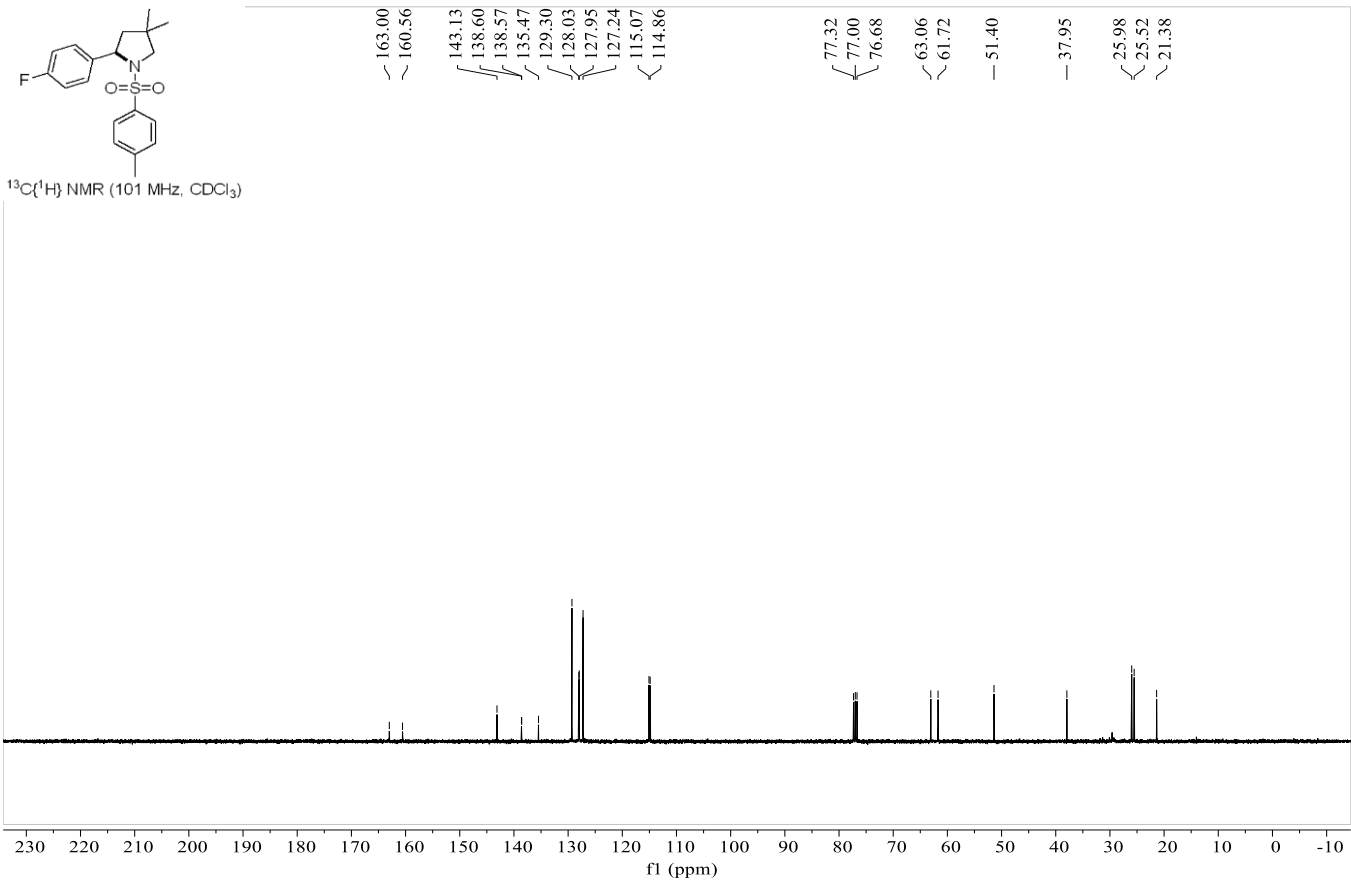
^{1}H NMR (400 MHz, $CDCl_3$)

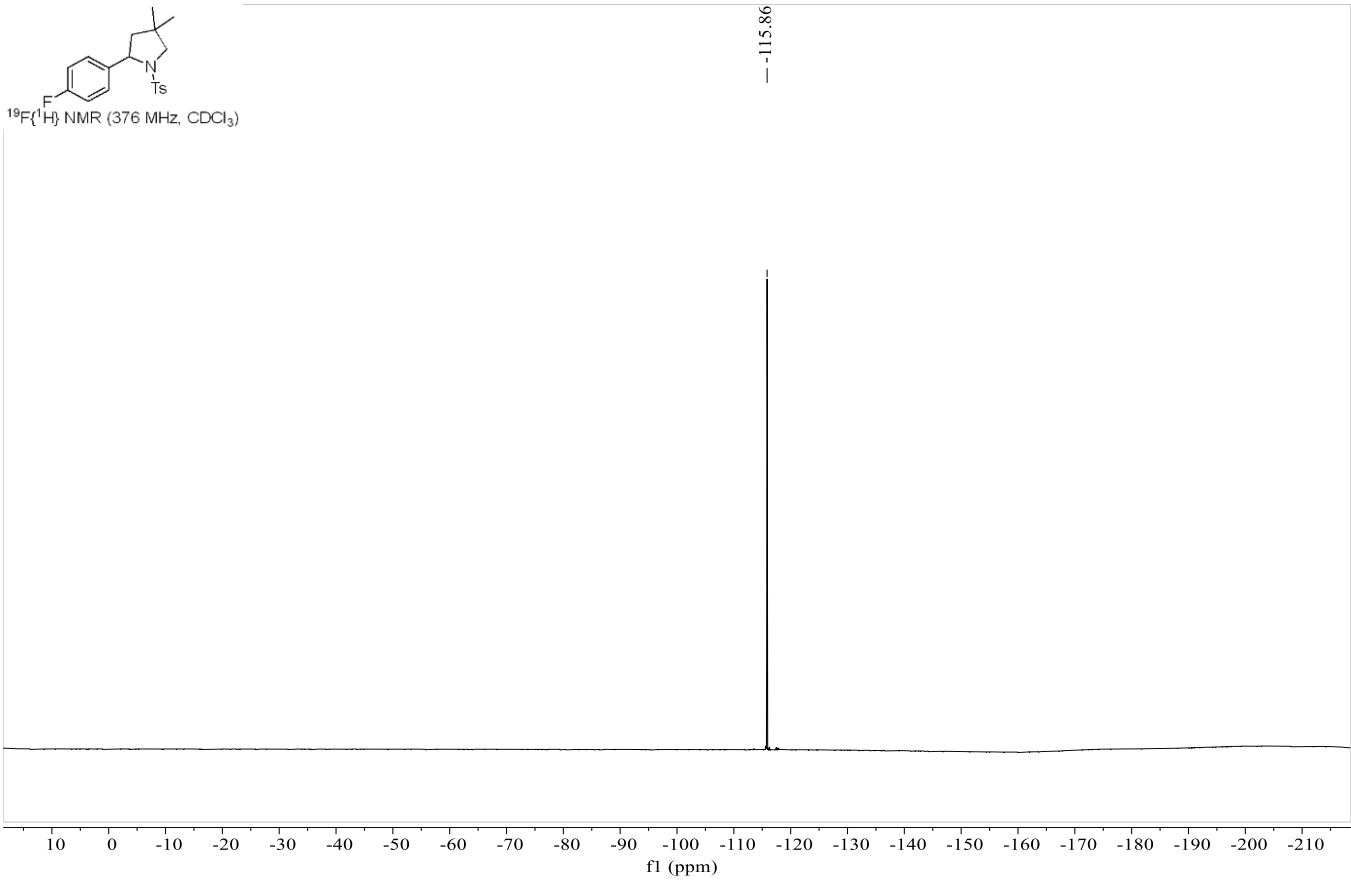


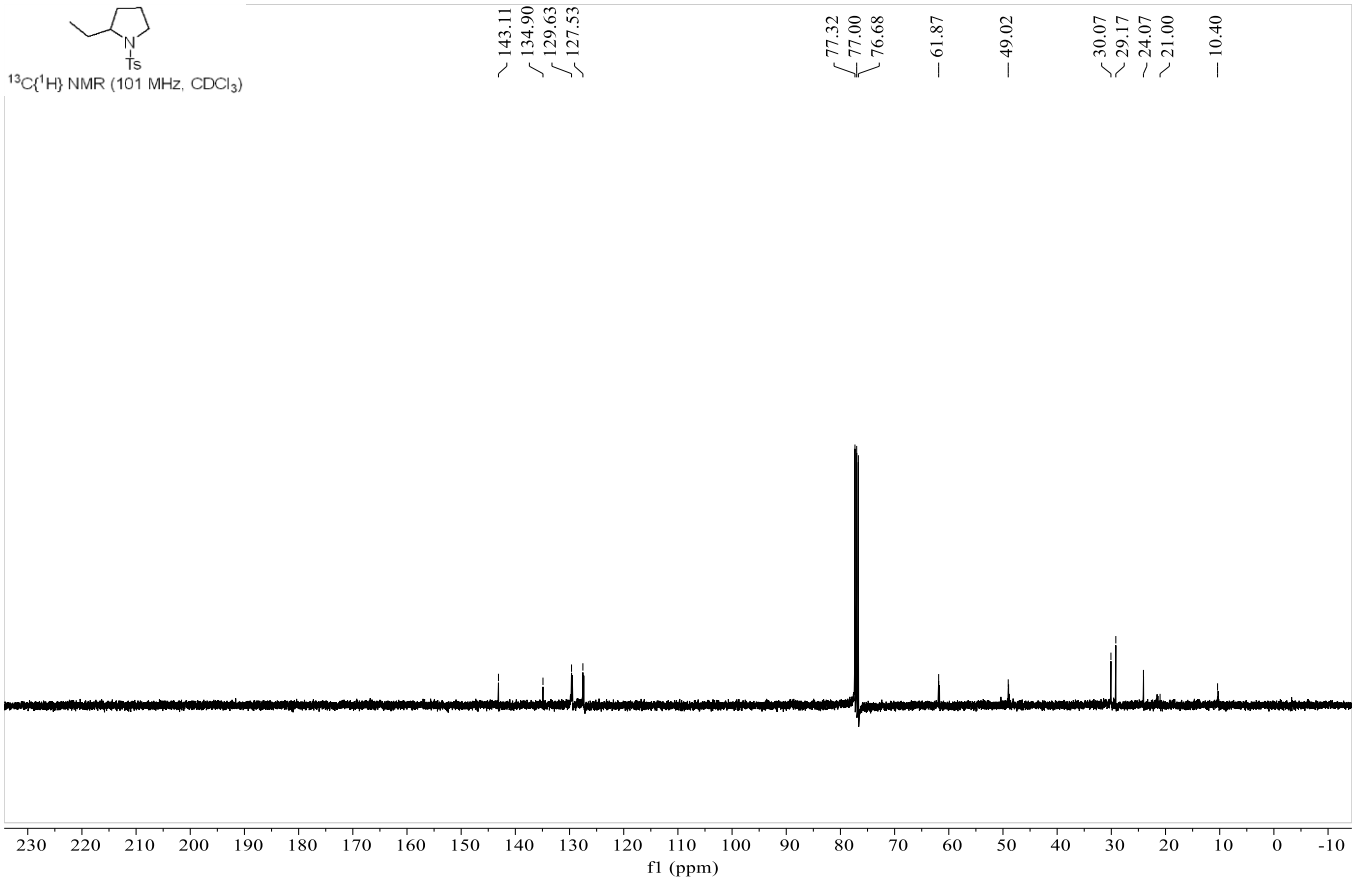
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

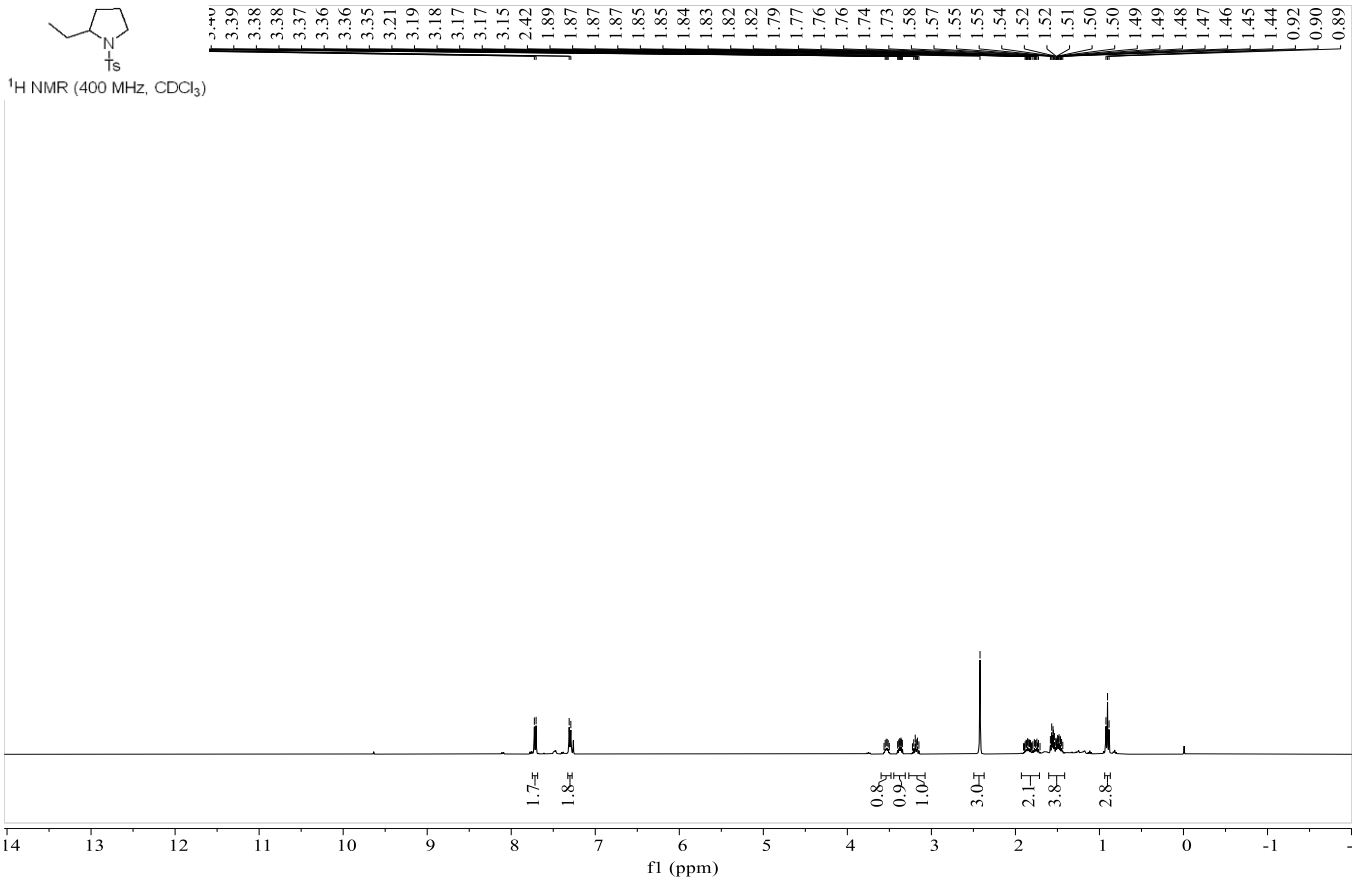


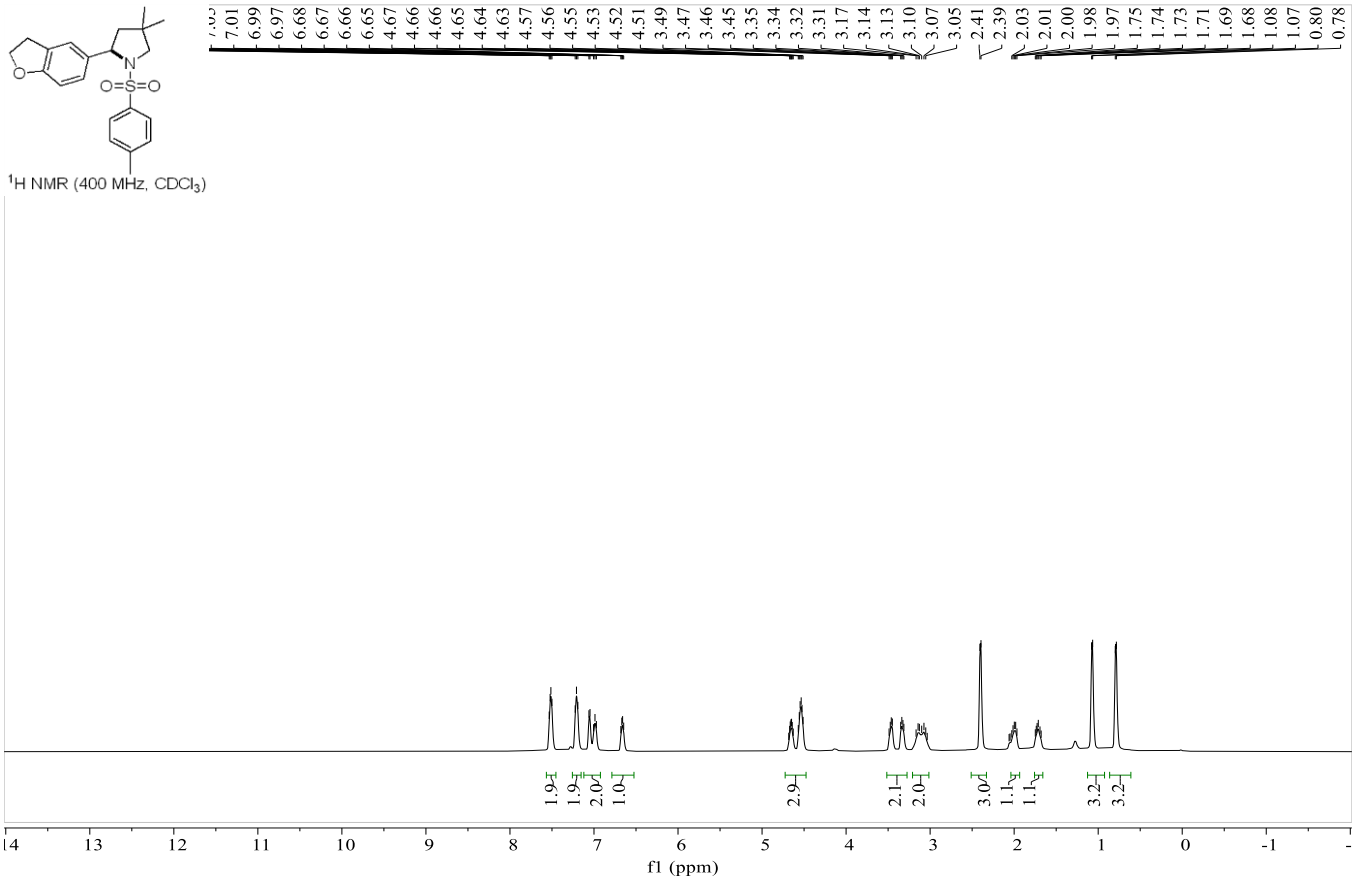
^{1}H NMR (400 MHz, $CDCl_3$)

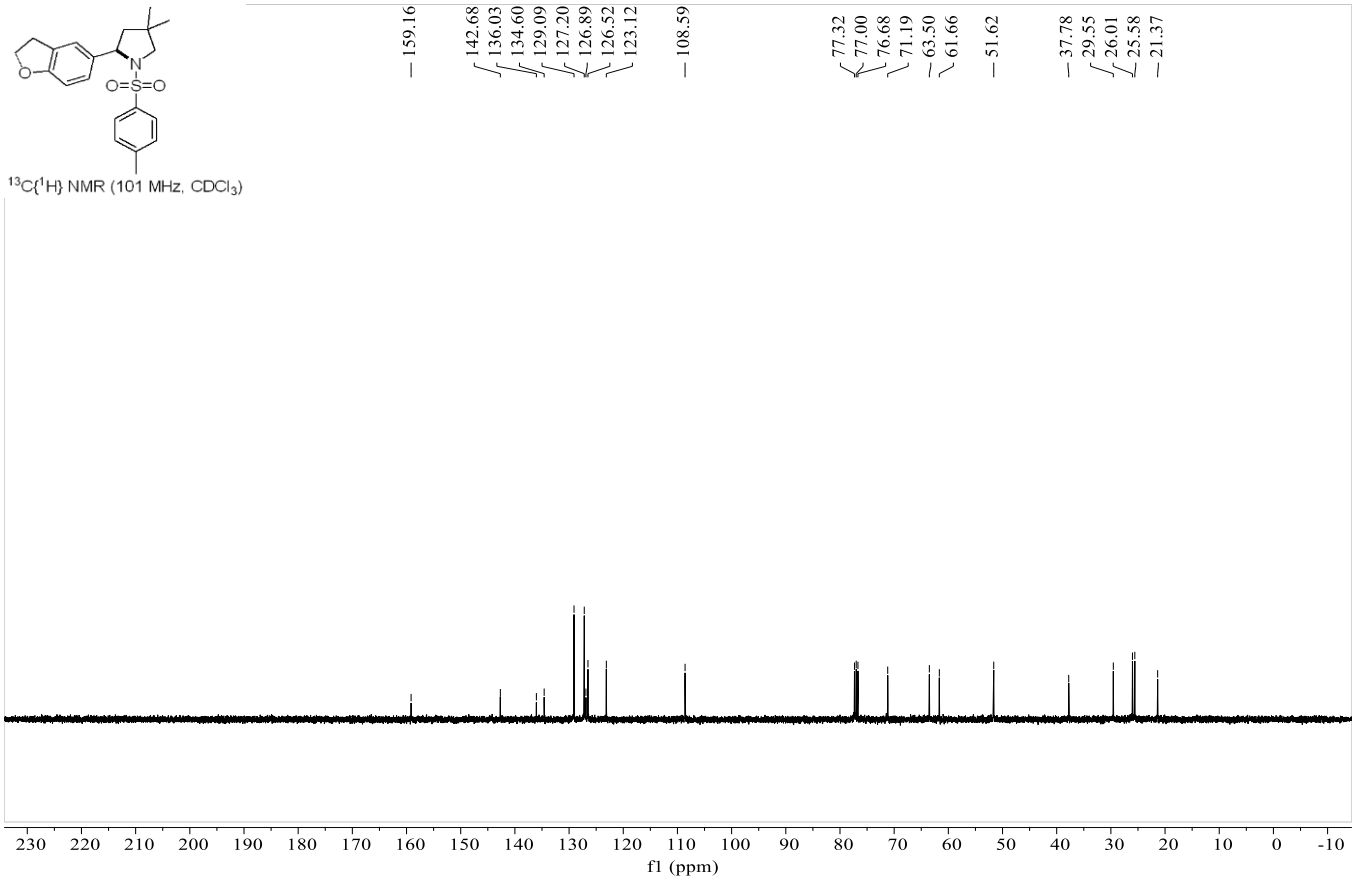

F
N
O=S=O
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
163.00
160.56
143.13
138.60
138.57
135.47
129.30
128.03
127.95
127.24
115.07
114.86
77.32
77.00
76.68
63.06
61.72
51.40
37.95
25.98
25.52
21.38
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

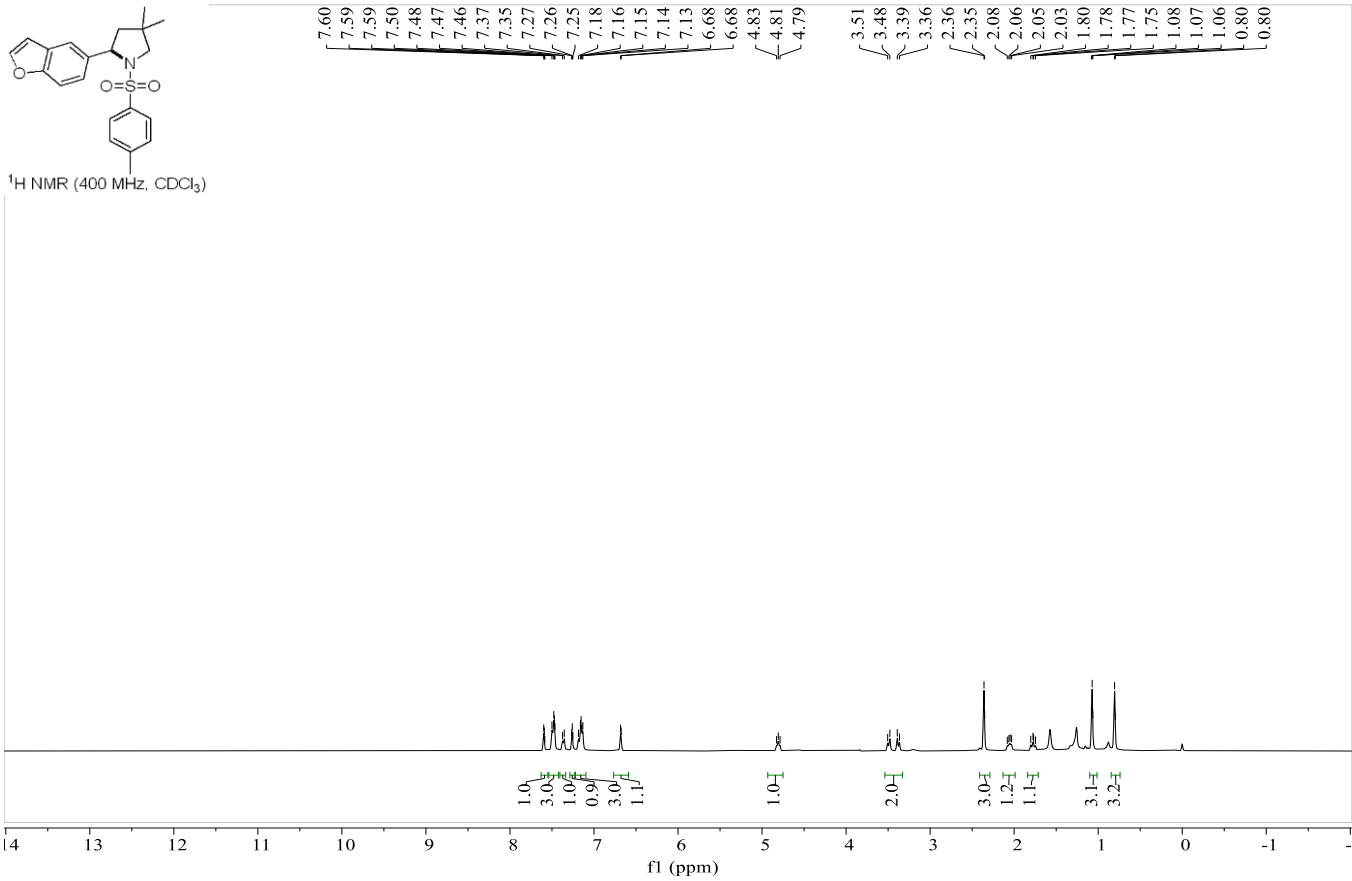

N
Ts
F
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)
-115.86
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

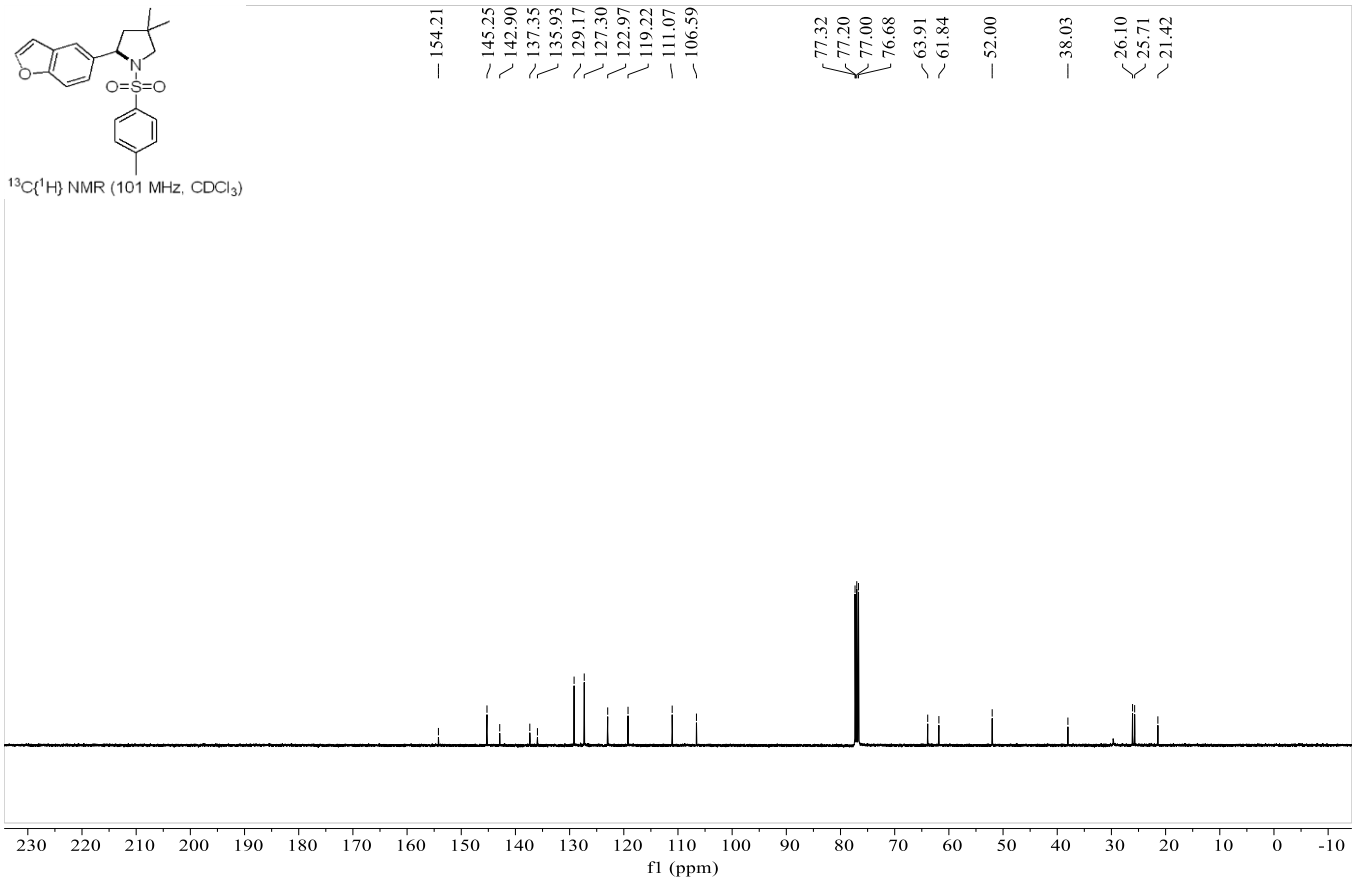

13C{1H} NMR (101 MHz, CDCl3)
143.11
134.90
129.63
127.53
77.32
77.00
76.68
61.87
49.02
30.07
29.17
24.07
21.00
10.40
f1 (ppm)

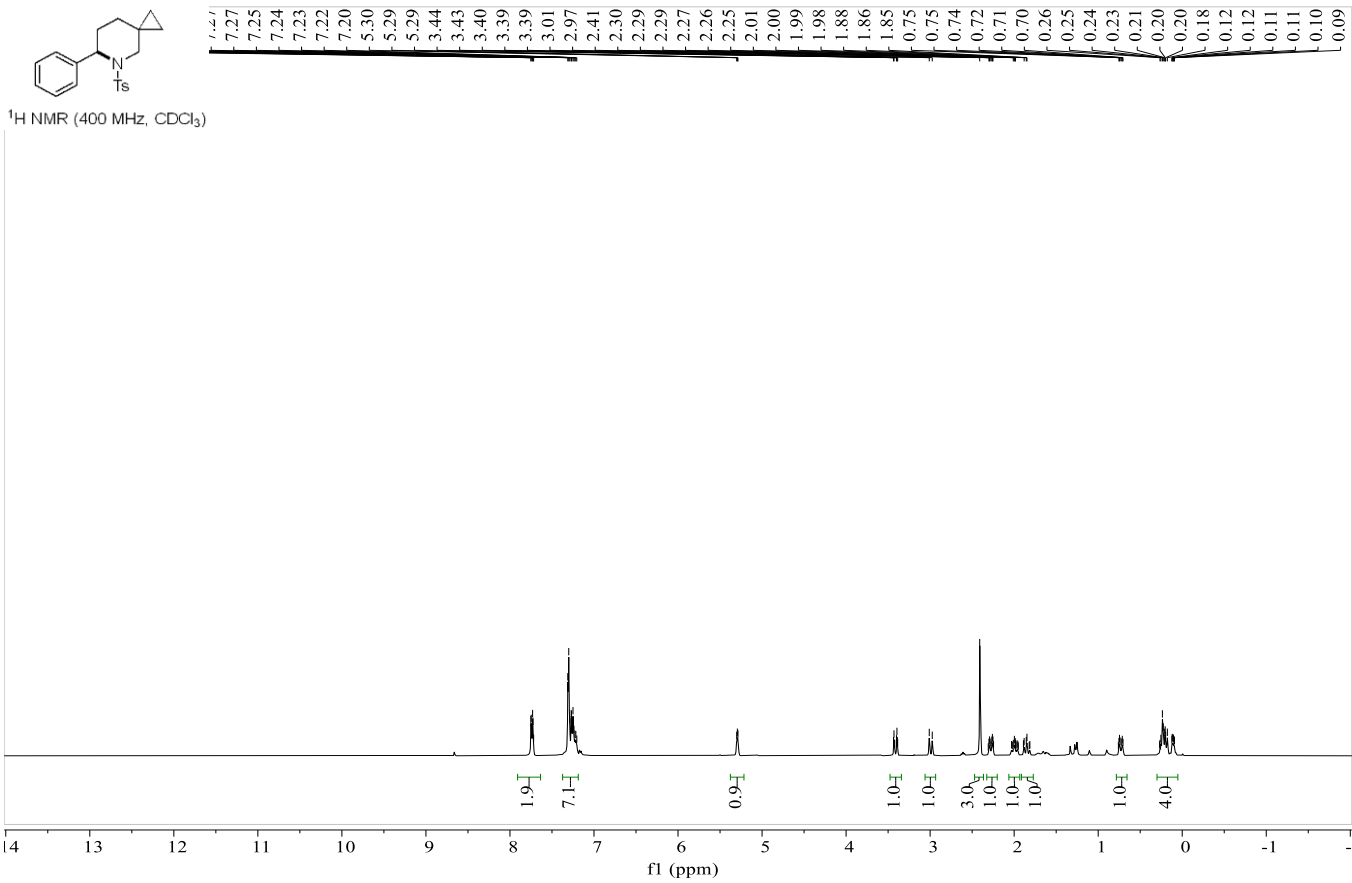

1H NMR (400 MHz, CDCl3)
f1 (ppm)


^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

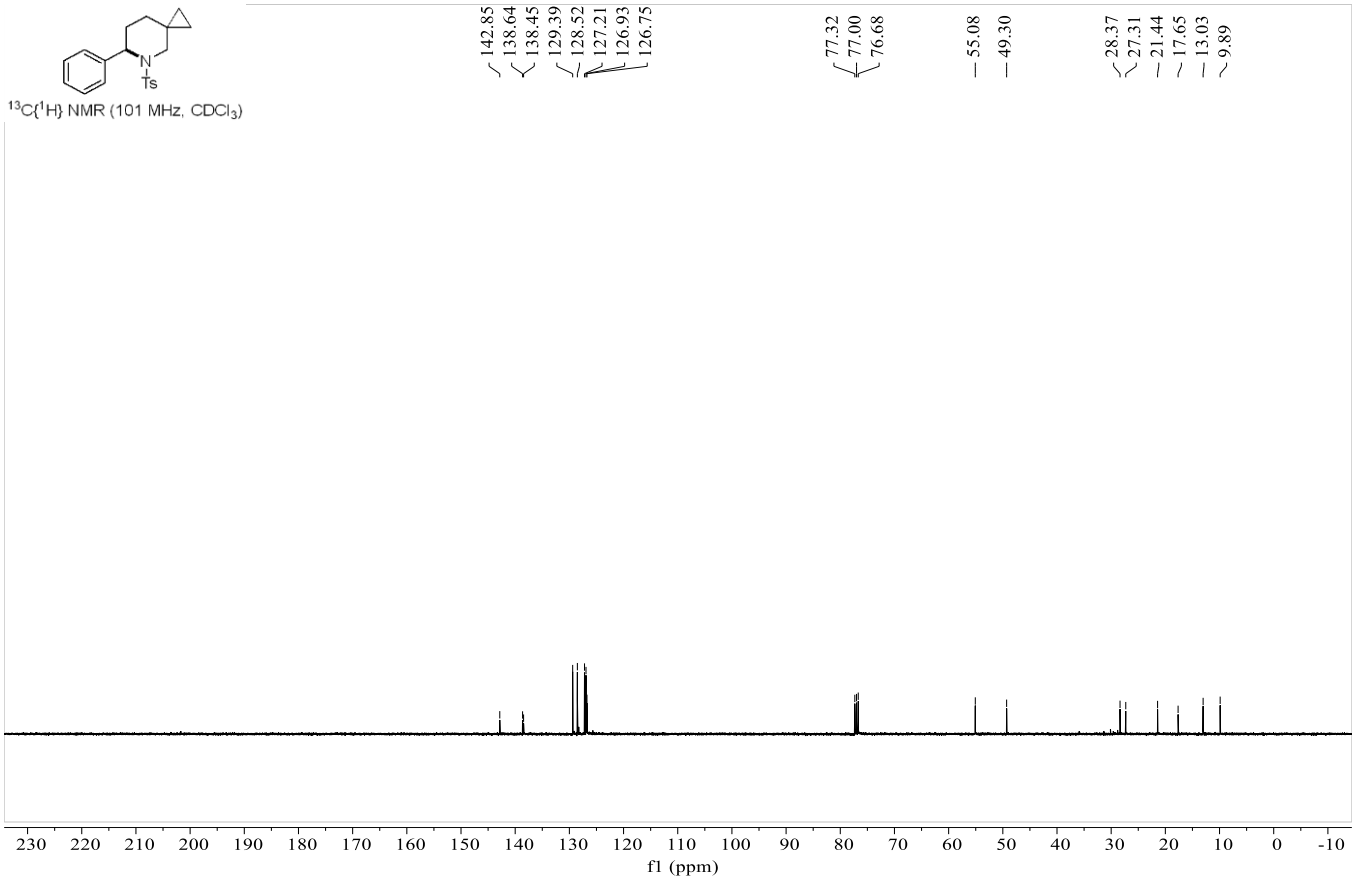

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)
f1 (ppm)


^{1}H NMR (400 MHz, $CDCl_3$)
7.60 7.59 7.59 7.50 7.48 7.47 7.46 7.37 7.35 7.27 7.26 7.25 7.18 7.16 7.15 7.14 7.13 6.68 6.68 4.83 4.81 4.79
3.51 3.48 3.39 3.36 2.36 2.35 2.08 2.06 2.05 2.03 1.80 1.78 1.77 1.75 1.08 1.07 1.06 0.80 0.80
1.0 3.0 1.0 0.9 3.0 1.1 1.0 2.0 3.0 1.2 1.1 3.1 3.2
f1 (ppm)

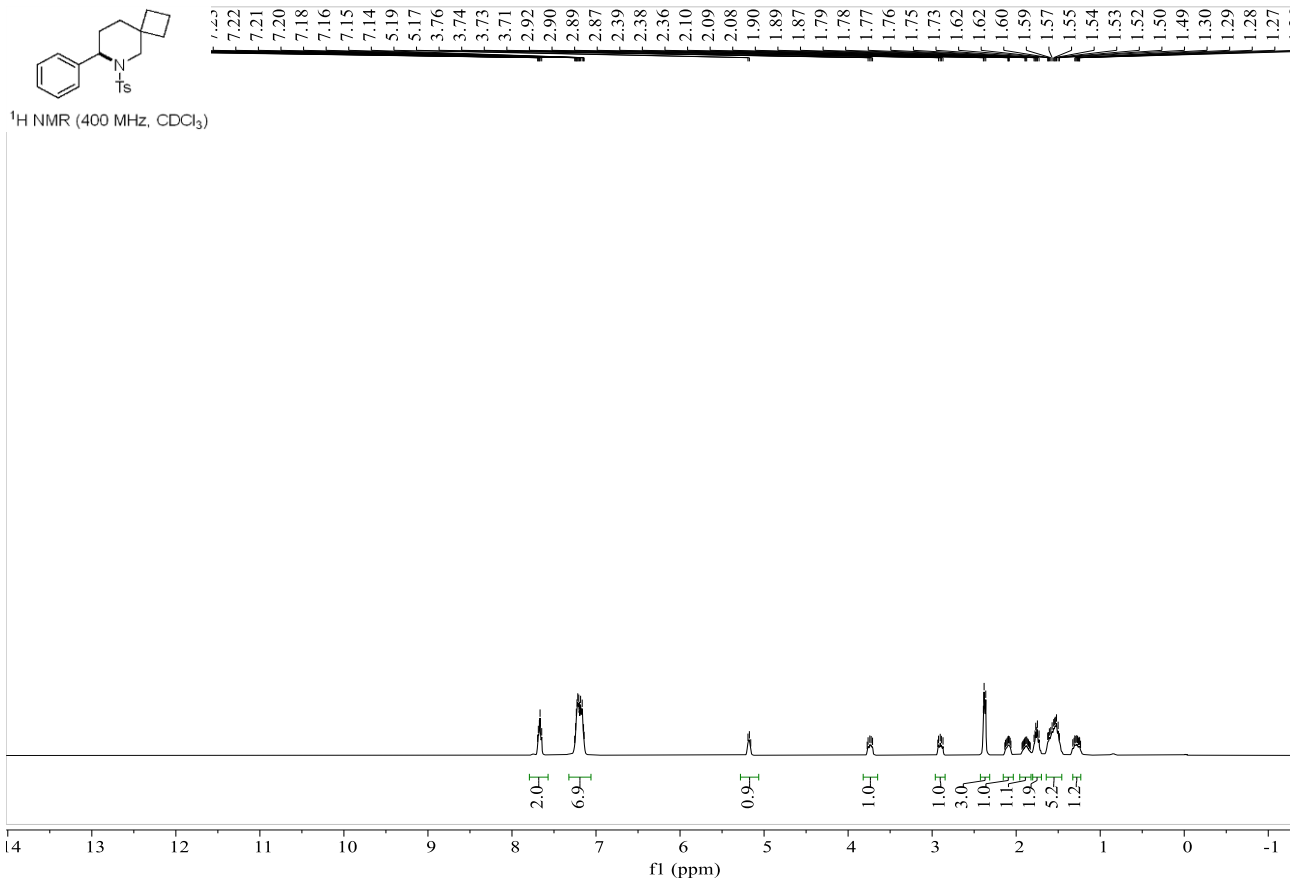

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)
154.21 145.25 142.90 137.35 135.93 129.17 127.30 122.97 119.22 111.07 106.59
77.32 77.20 77.00 76.68 63.91 61.84 52.00 38.03 26.10 25.71 21.42
f1 (ppm)



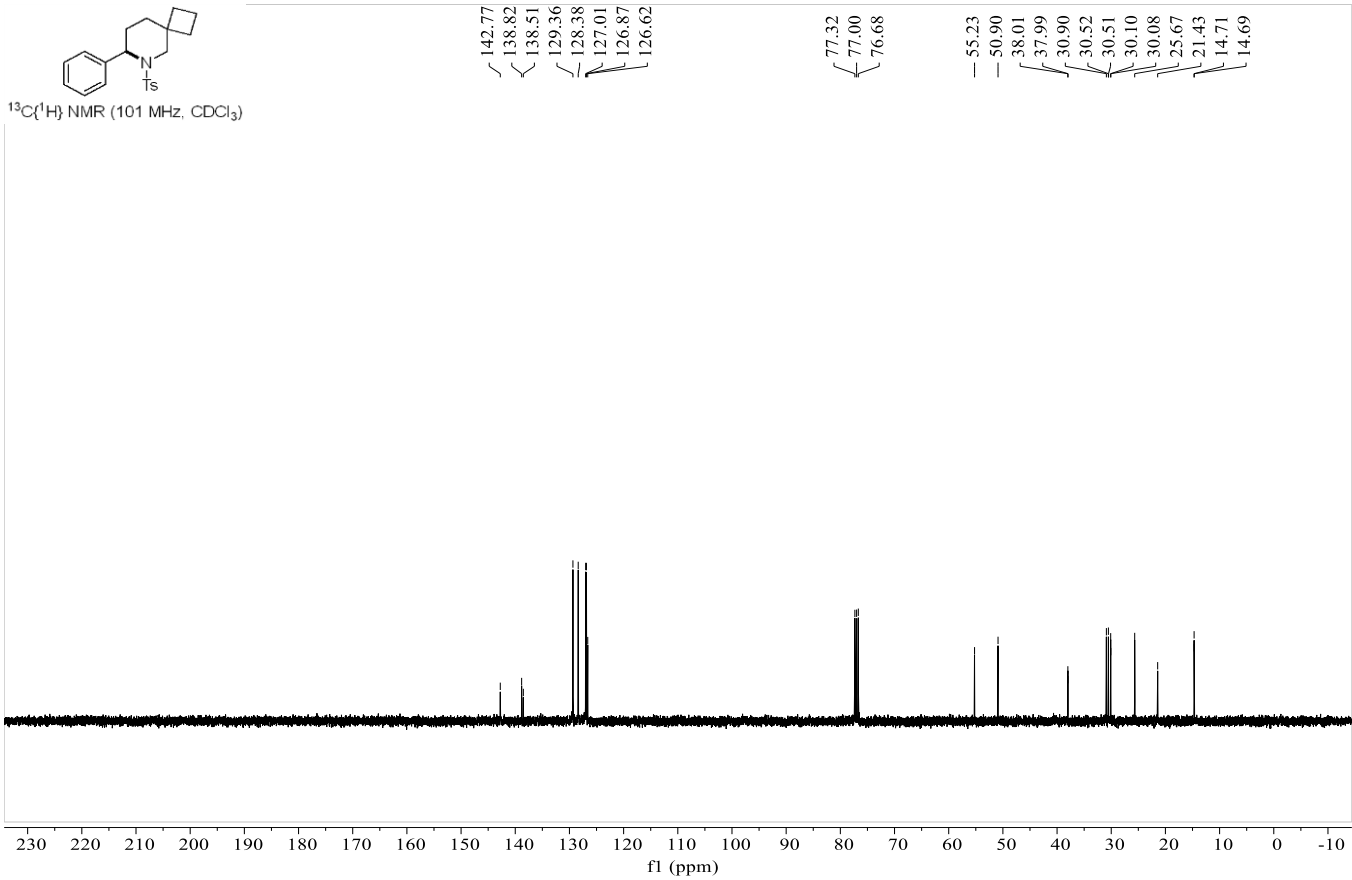
^{1}H NMR (400 MHz, $CDCl_3$)



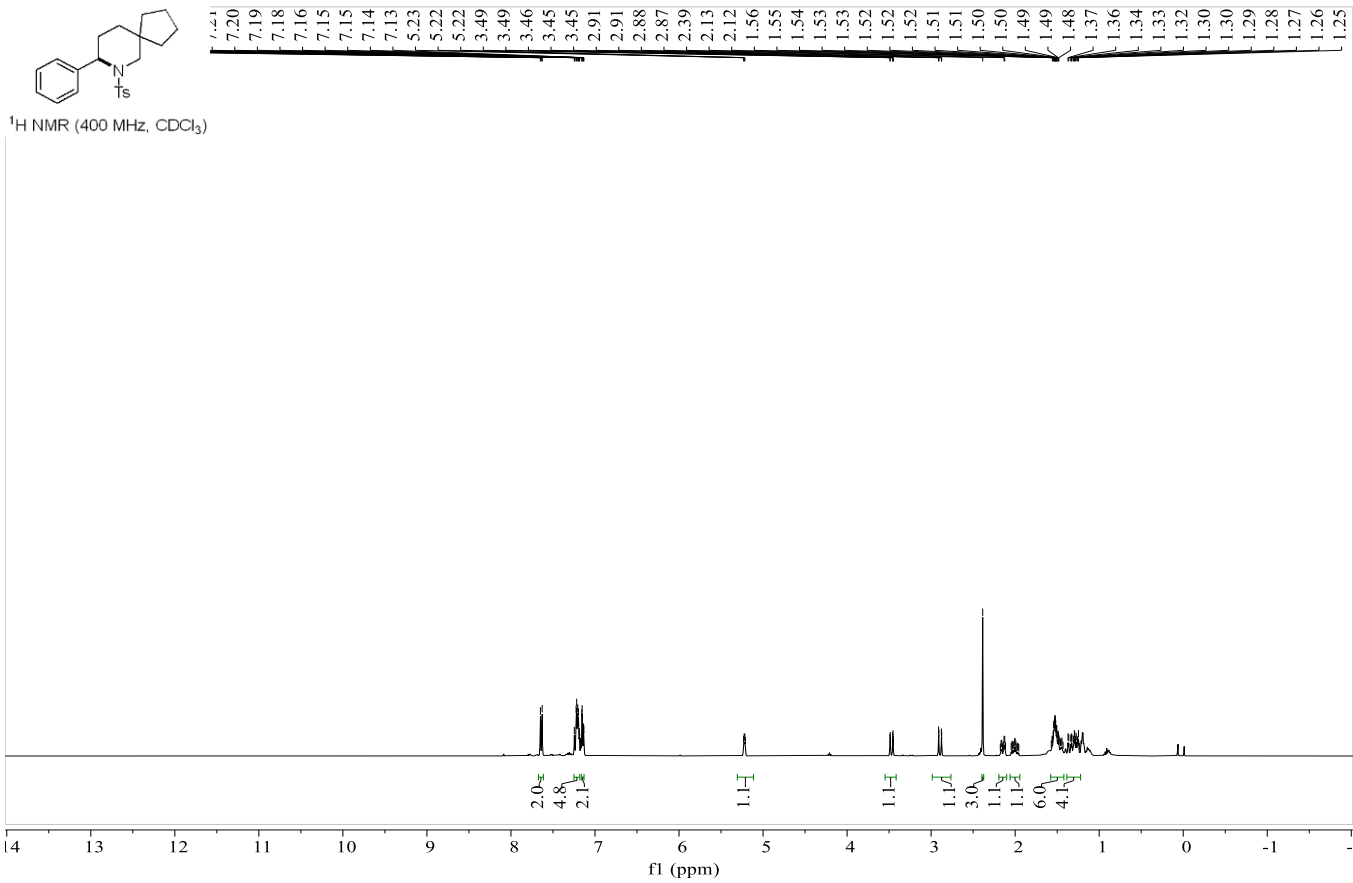
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



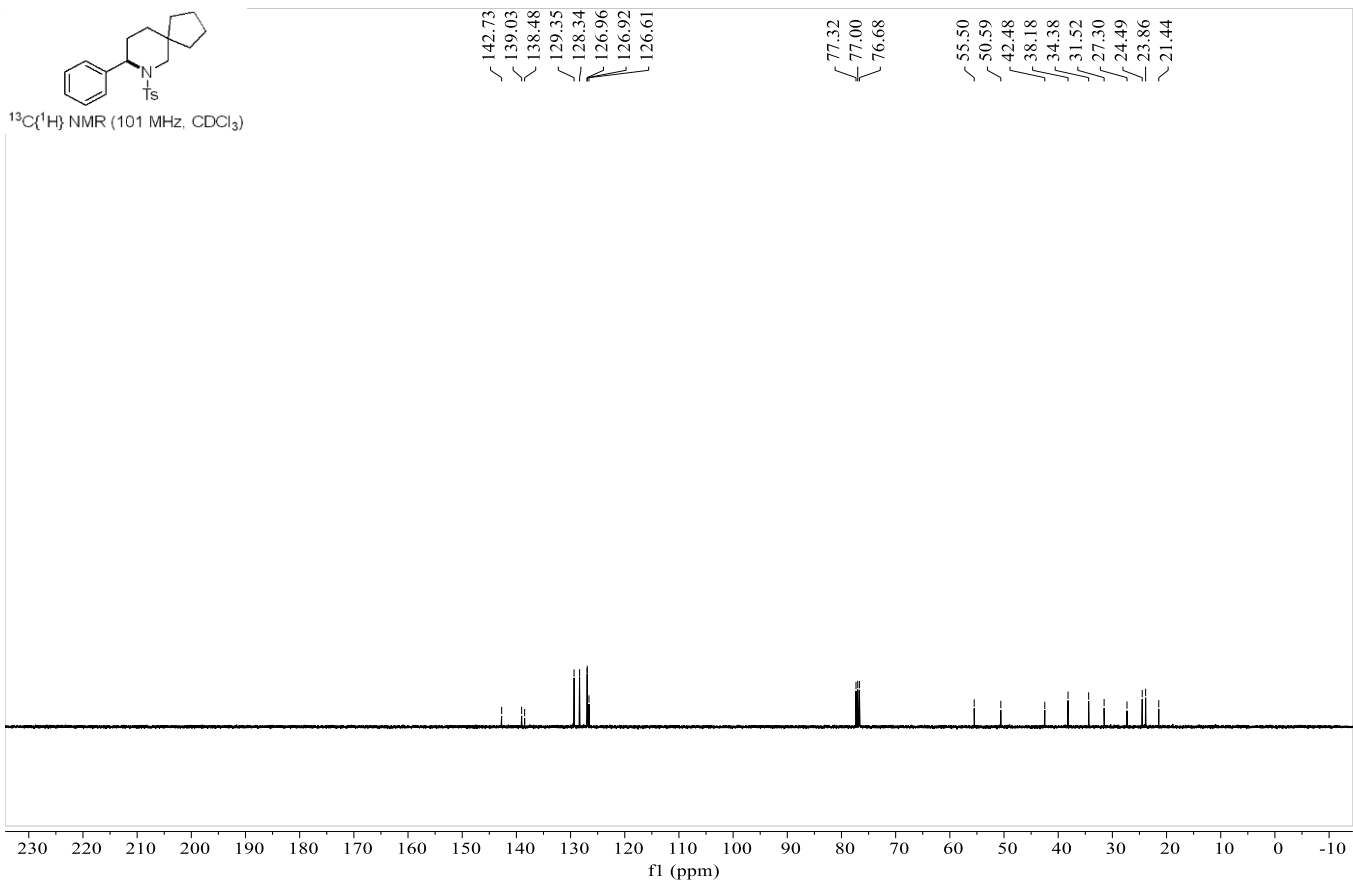
^{1}H NMR (400 MHz, $CDCl_3$)



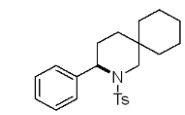
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



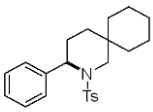
^{1}H NMR (400 MHz, $CDCl_3$)



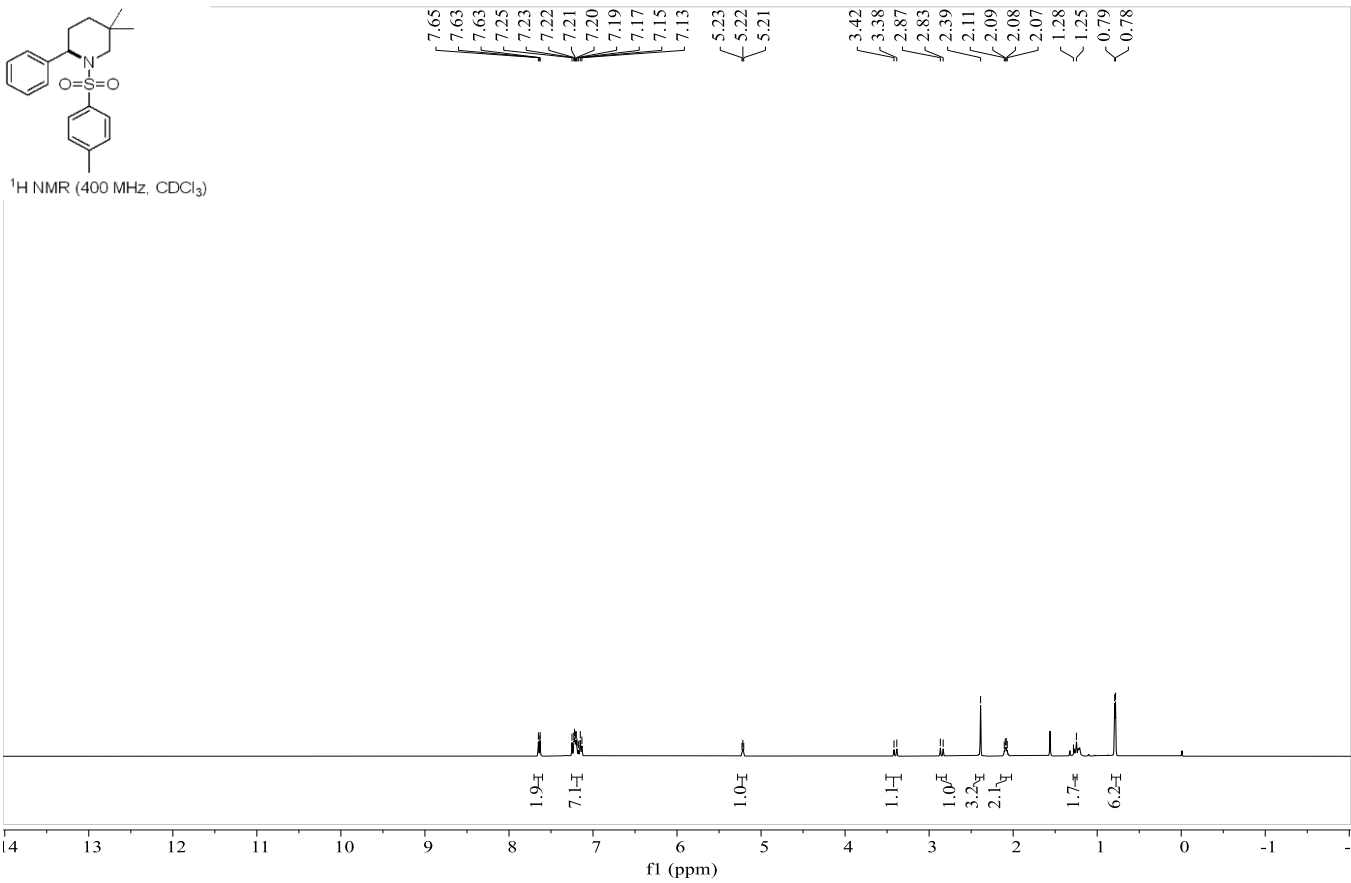
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



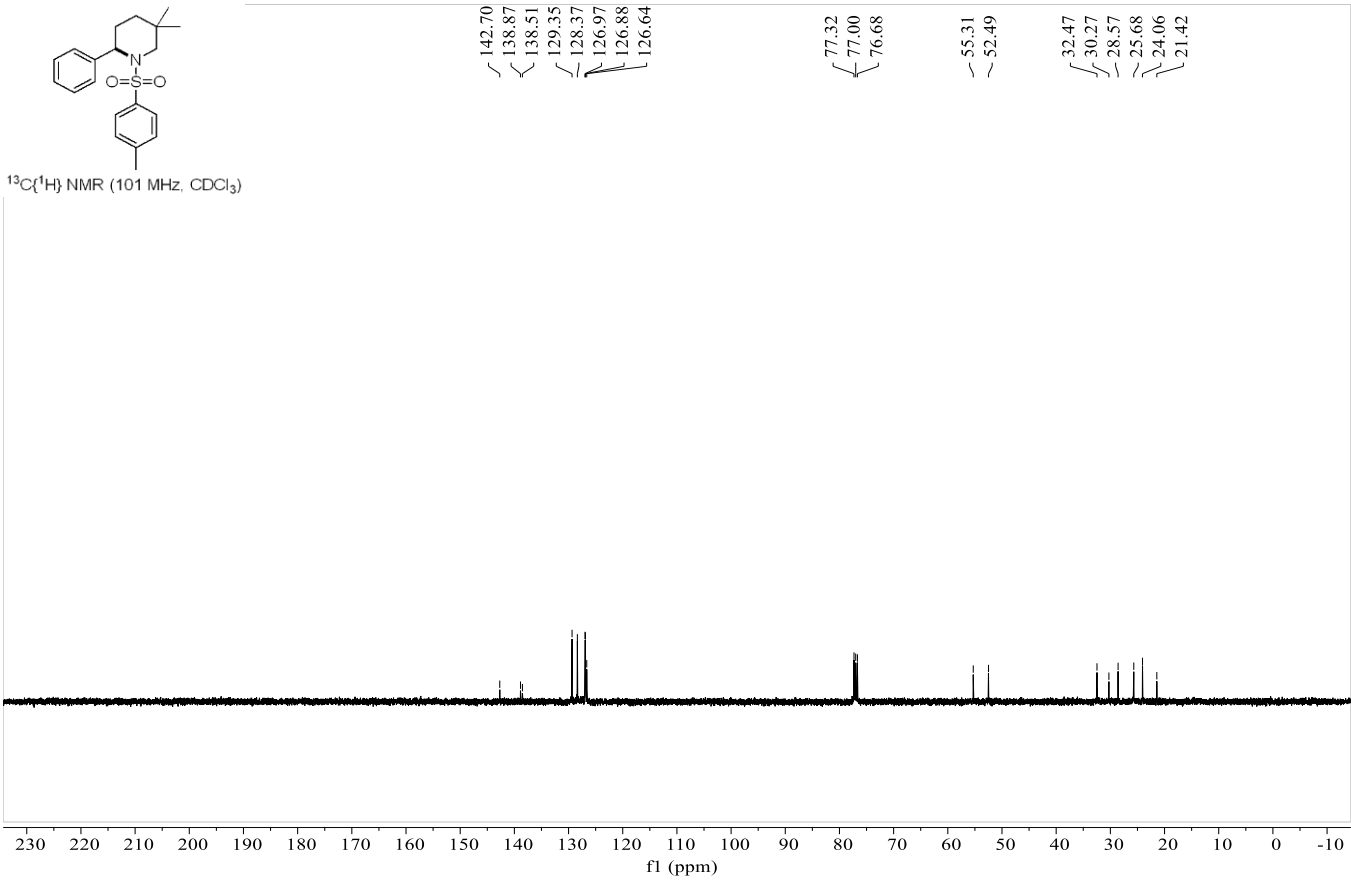
^{1}H NMR (400 MHz, $CDCl_3$)



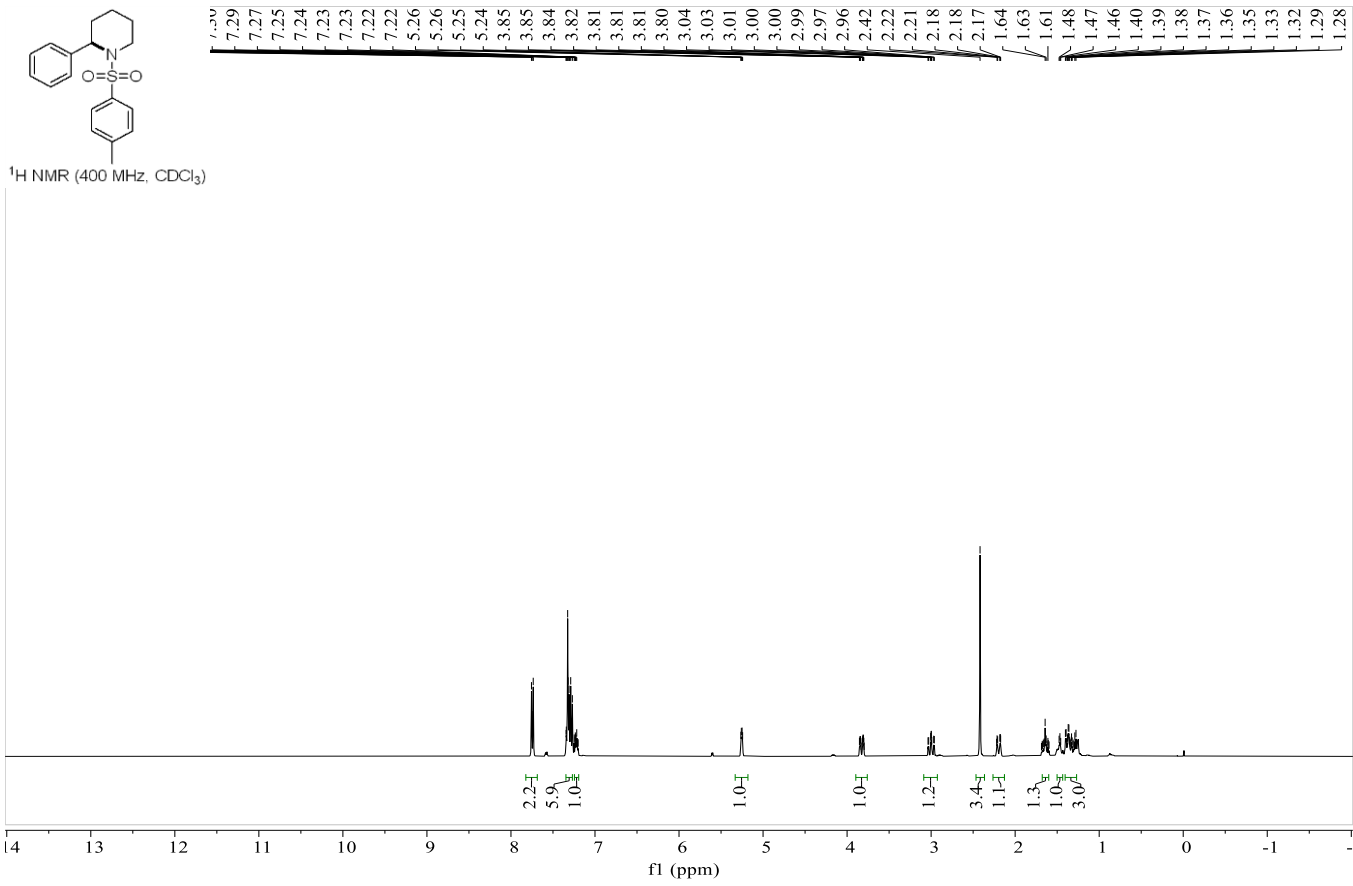
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



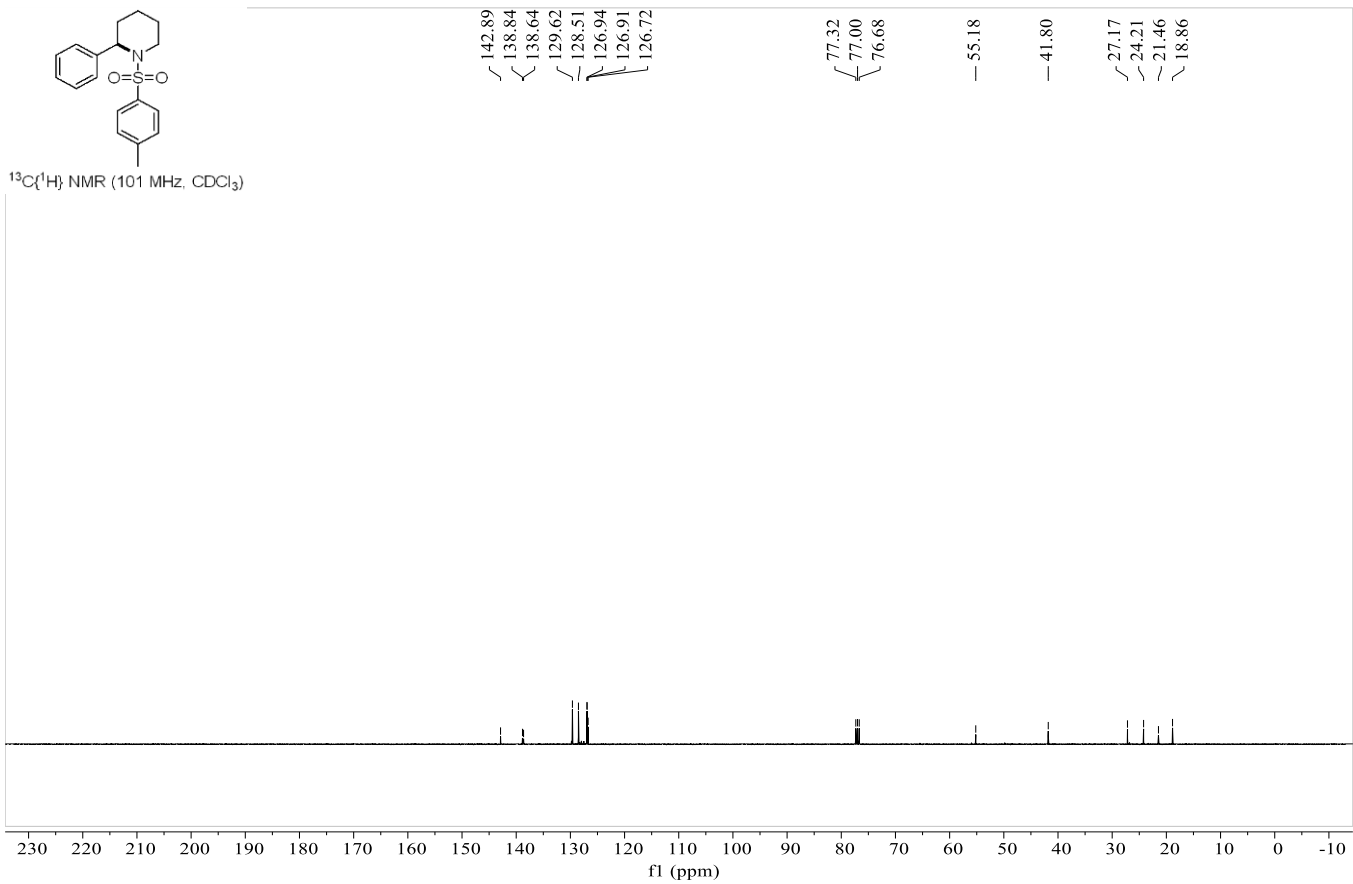
^{1}H NMR (400 MHz, $CDCl_3$)



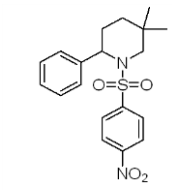
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



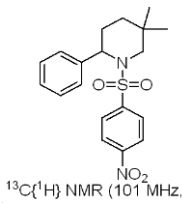
^{1}H NMR (400 MHz, $CDCl_3$)



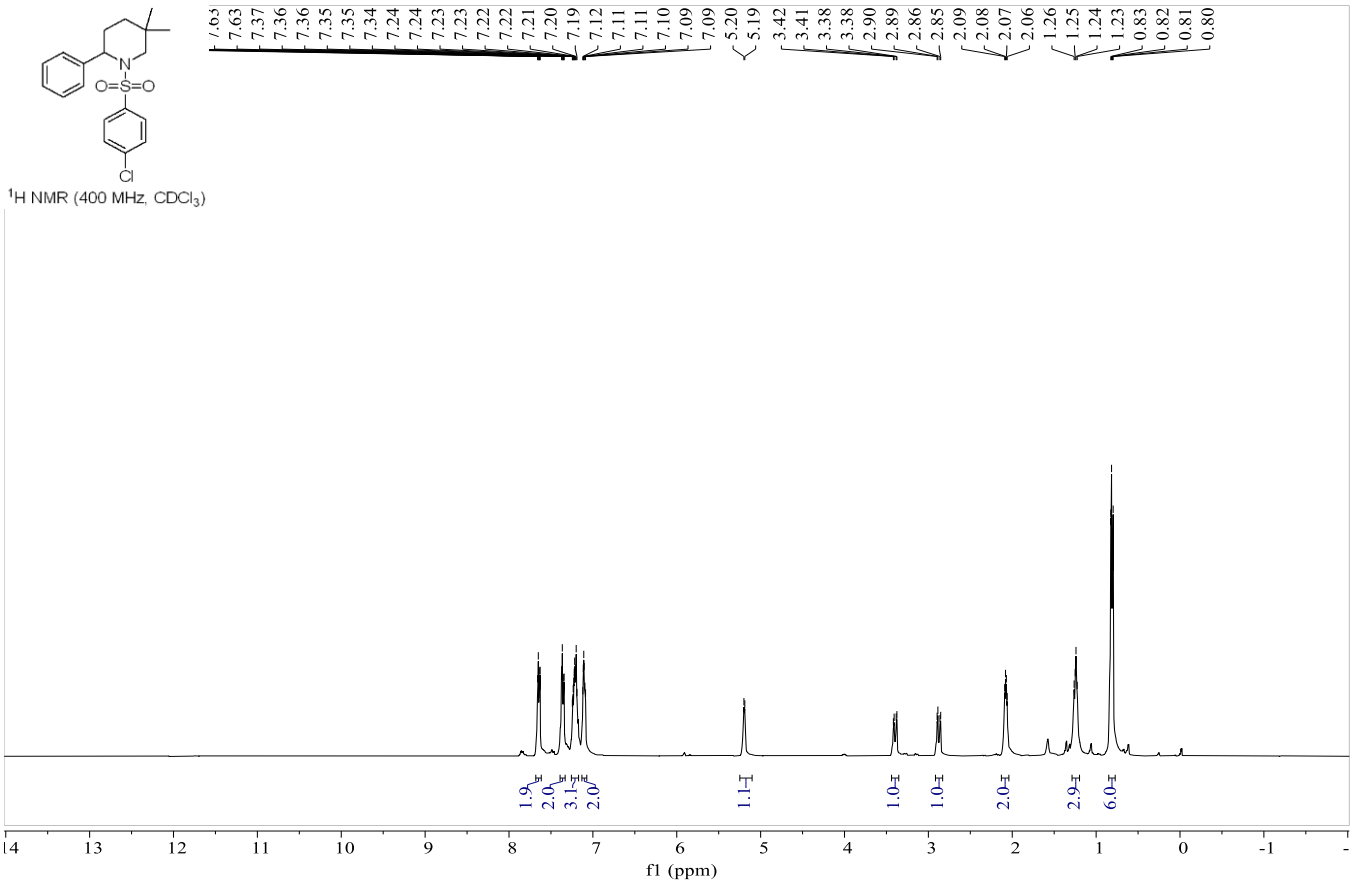
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



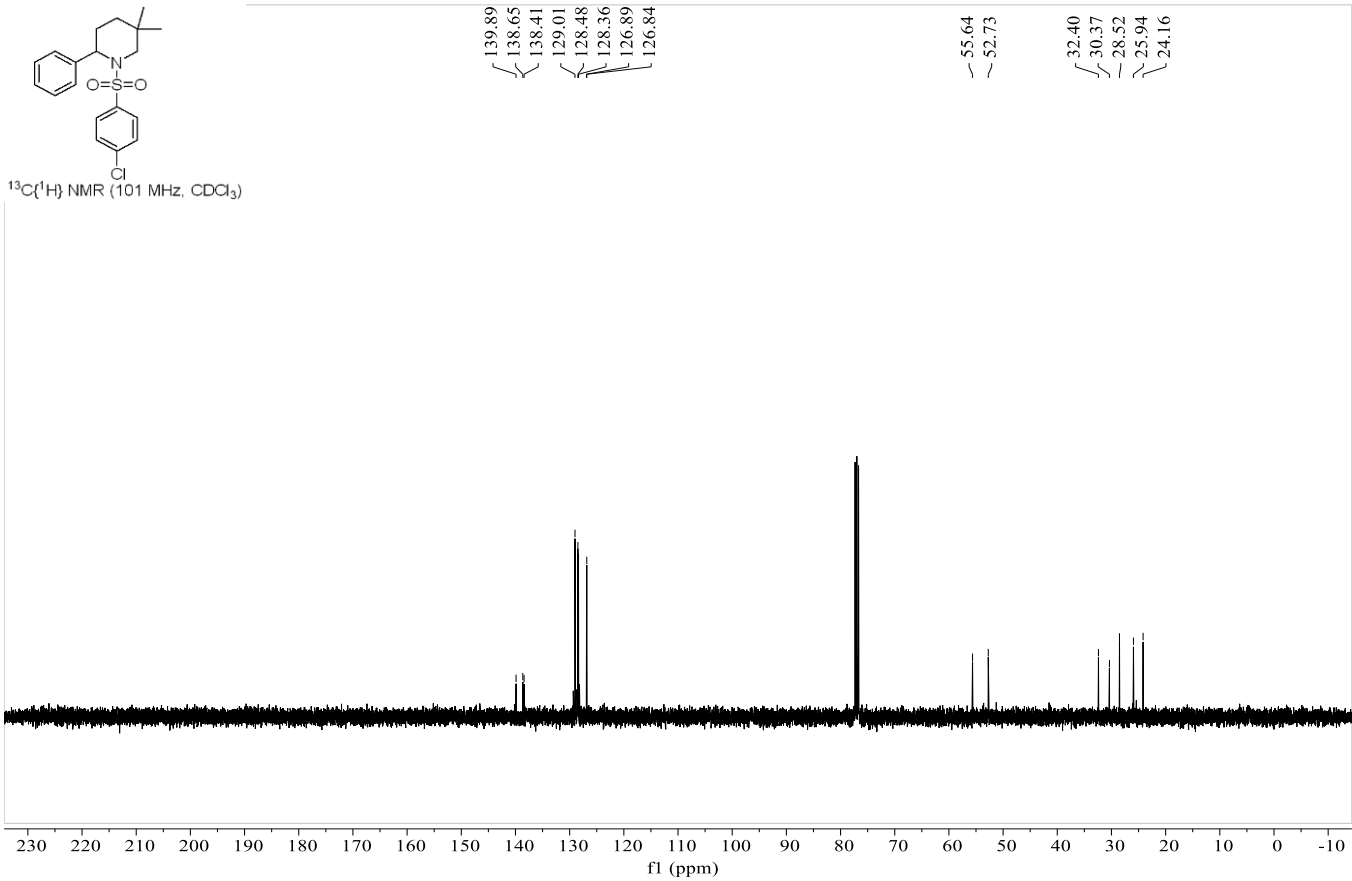
^{1}H NMR (400 MHz, $CDCl_3$)



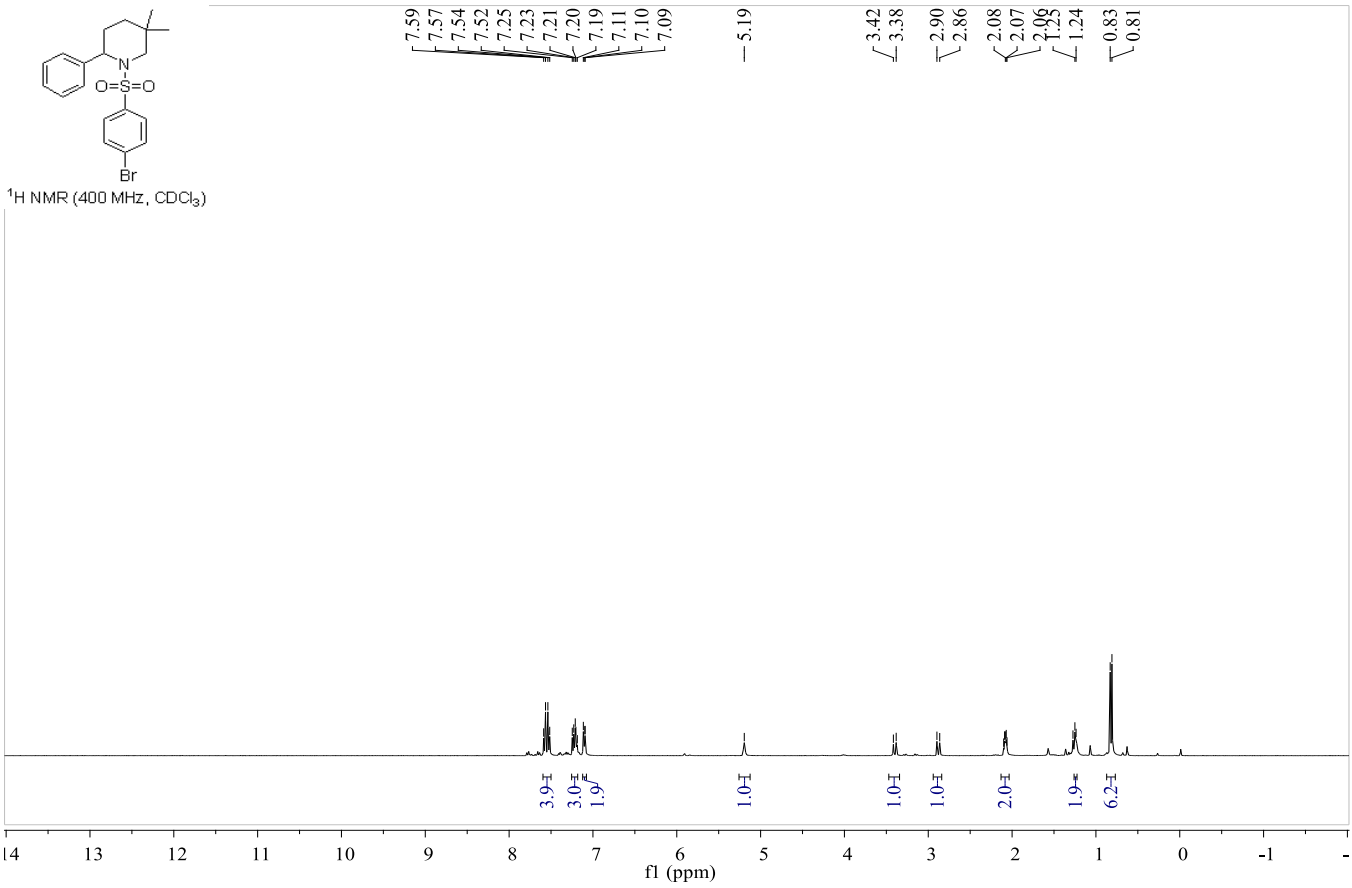
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



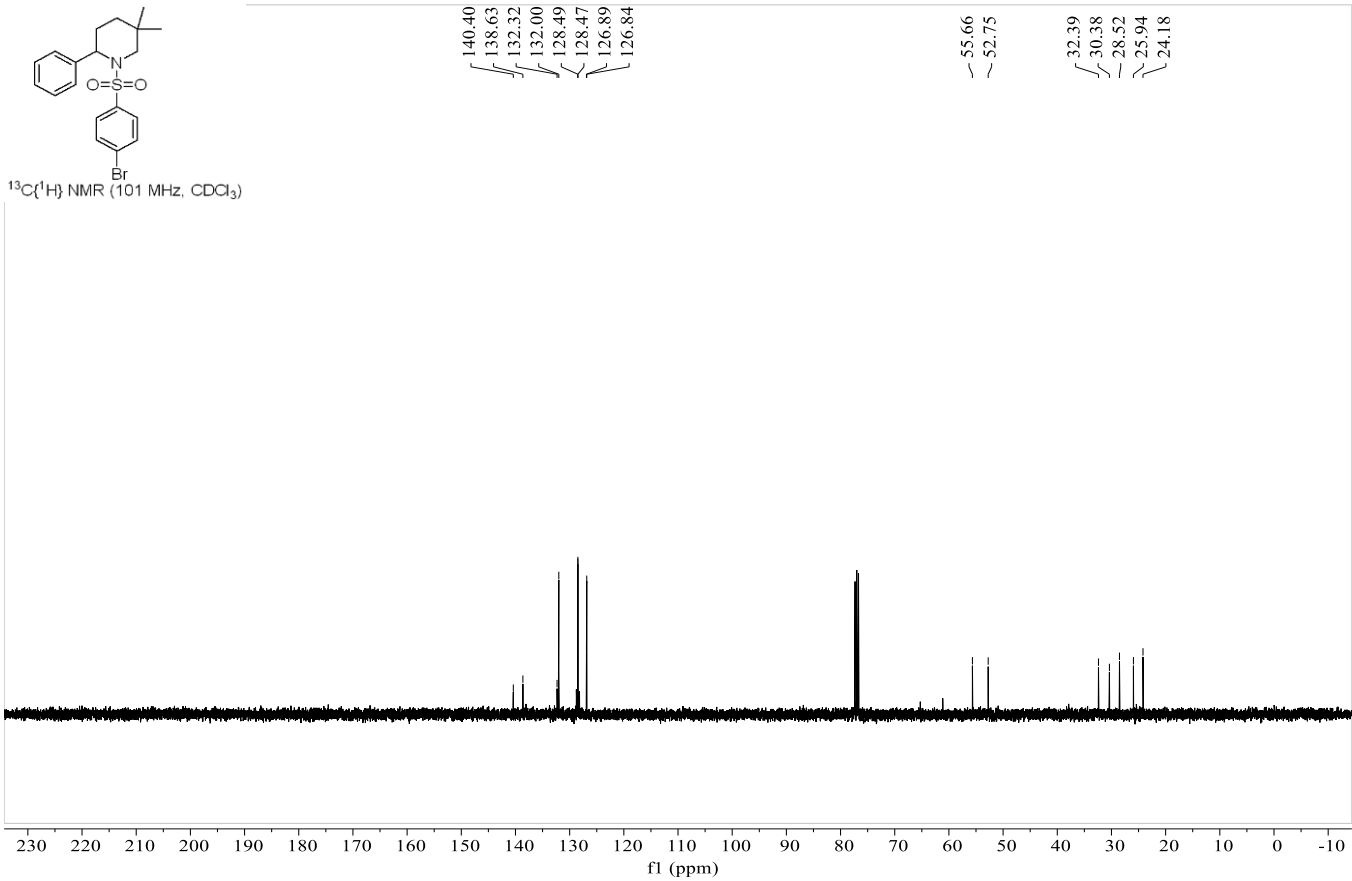
^{1}H NMR (400 MHz, $CDCl_3$)



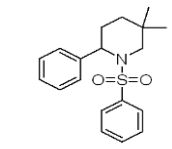
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



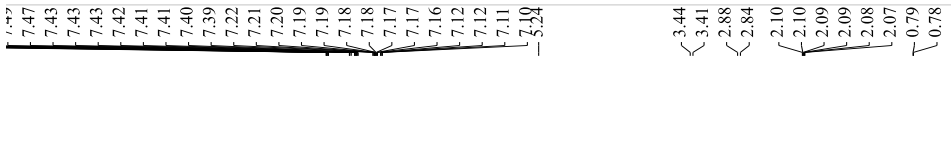
^{1}H NMR (400 MHz, $CDCl_3$)

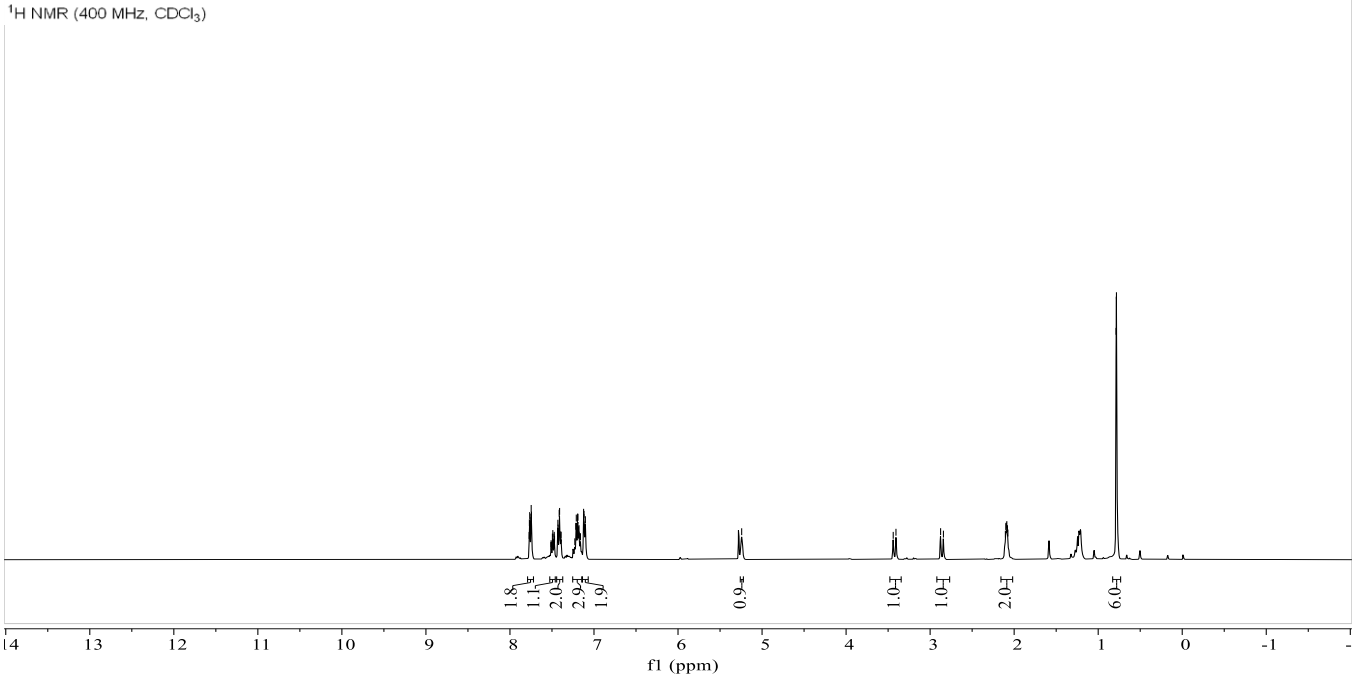


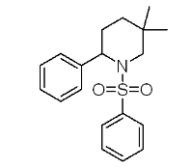
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



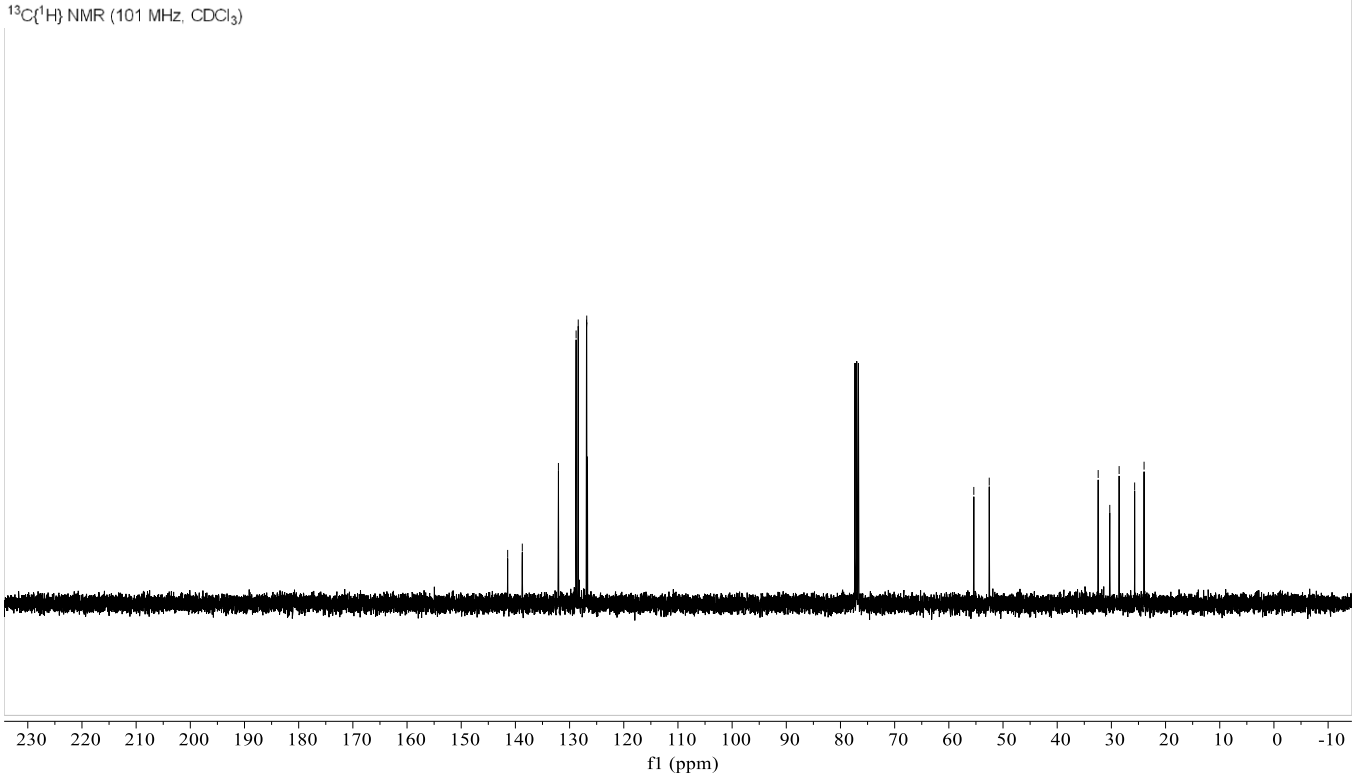
^{1}H NMR (400 MHz, $CDCl_3$)

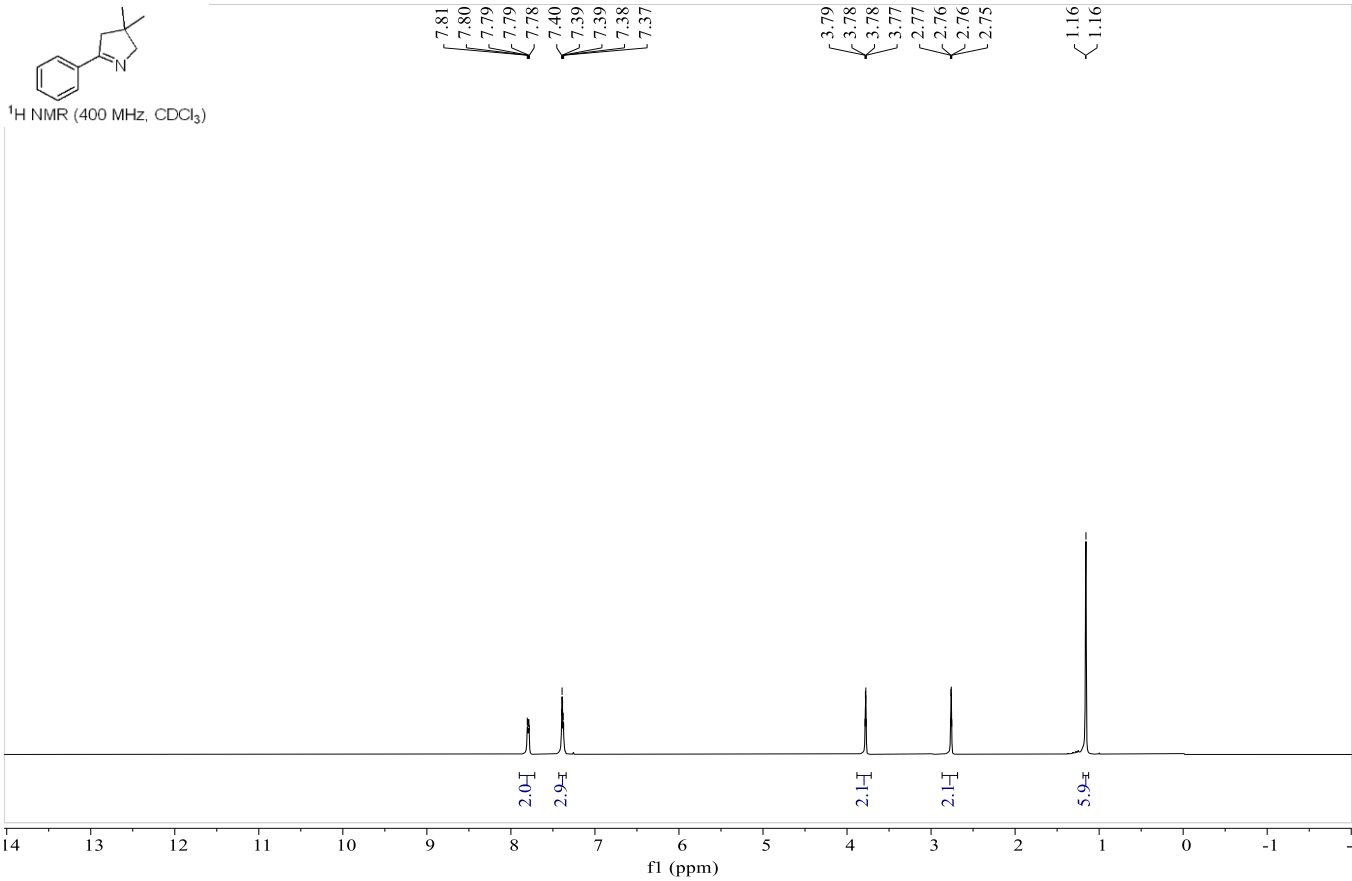


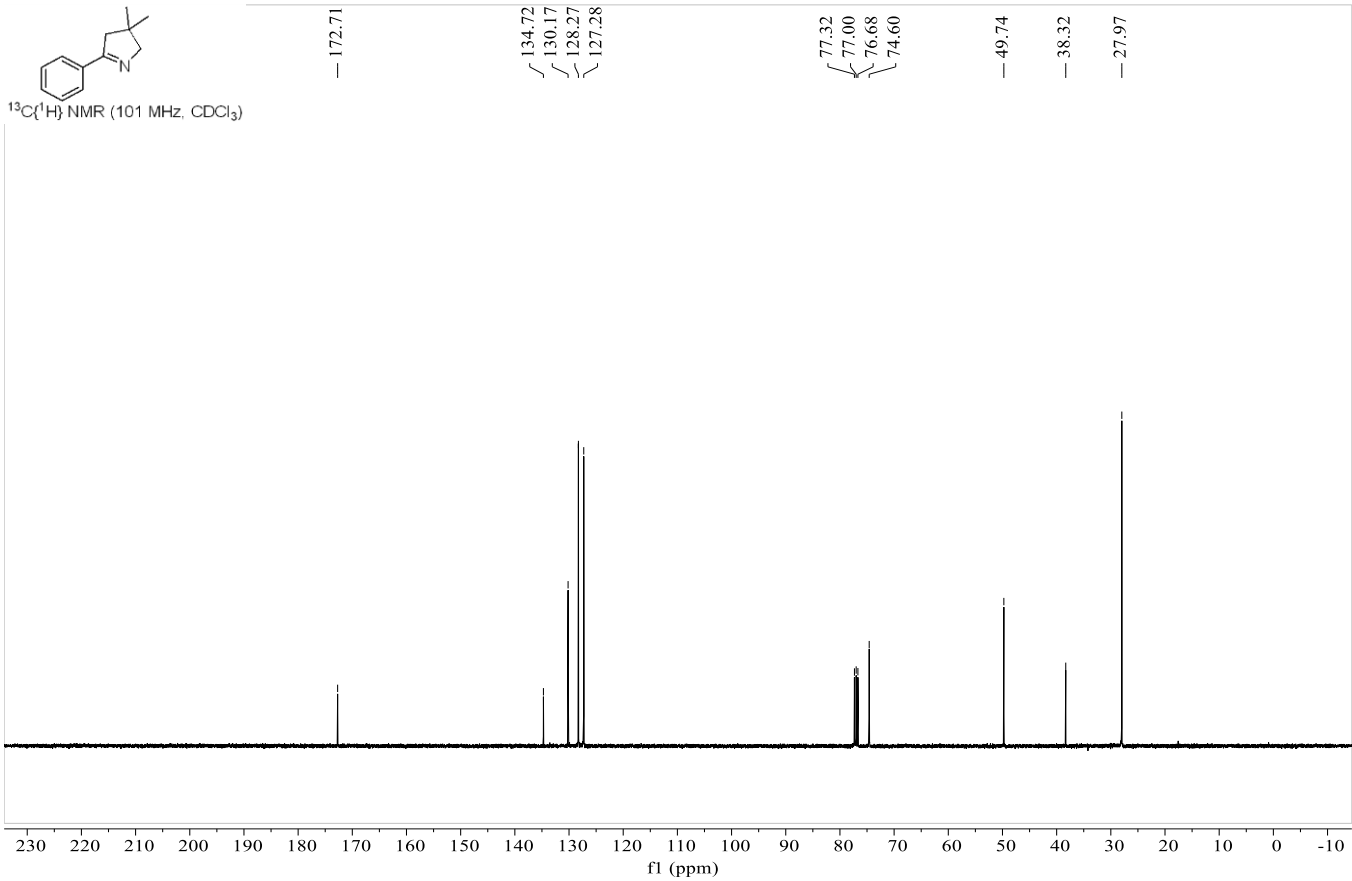


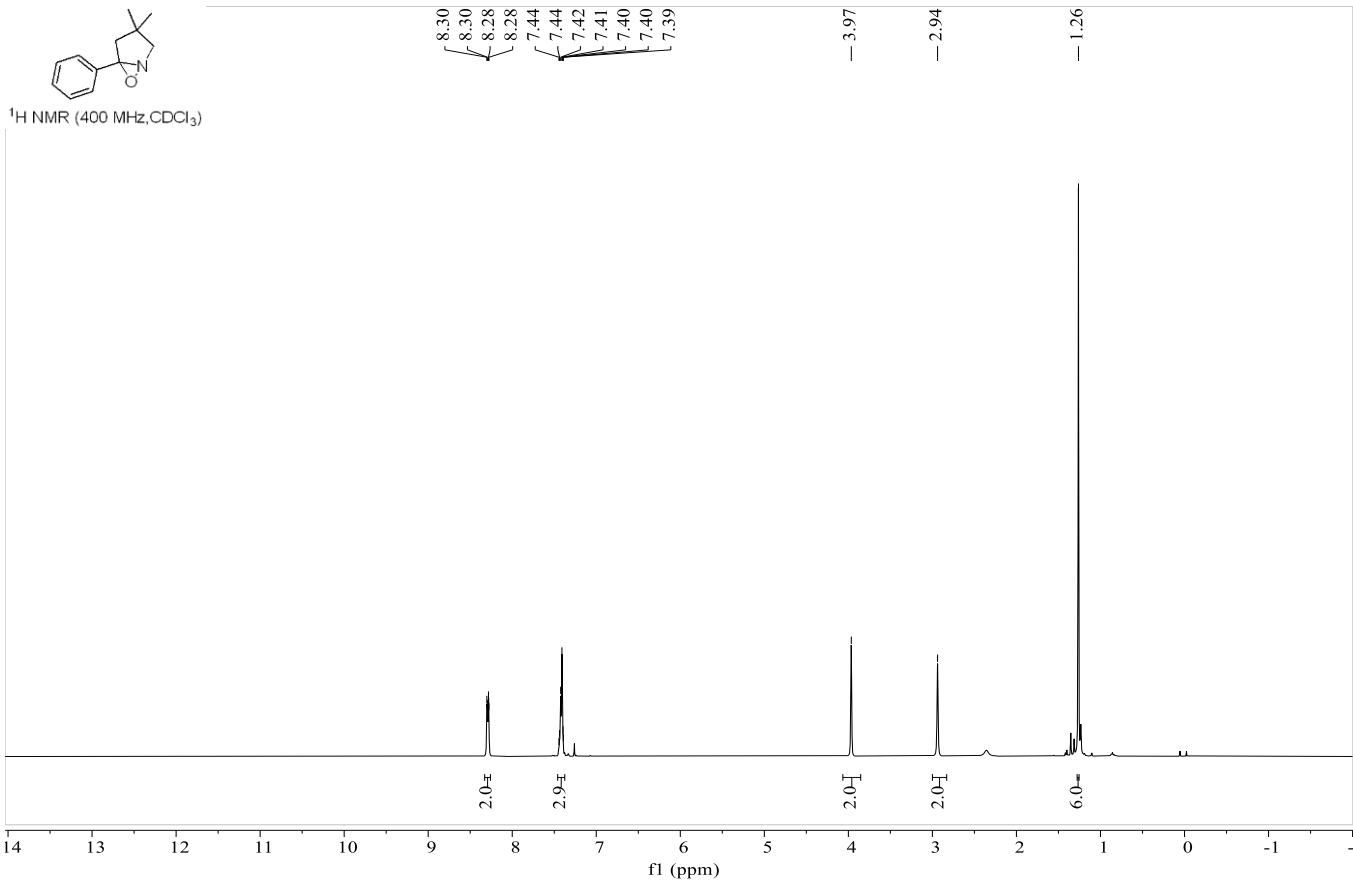


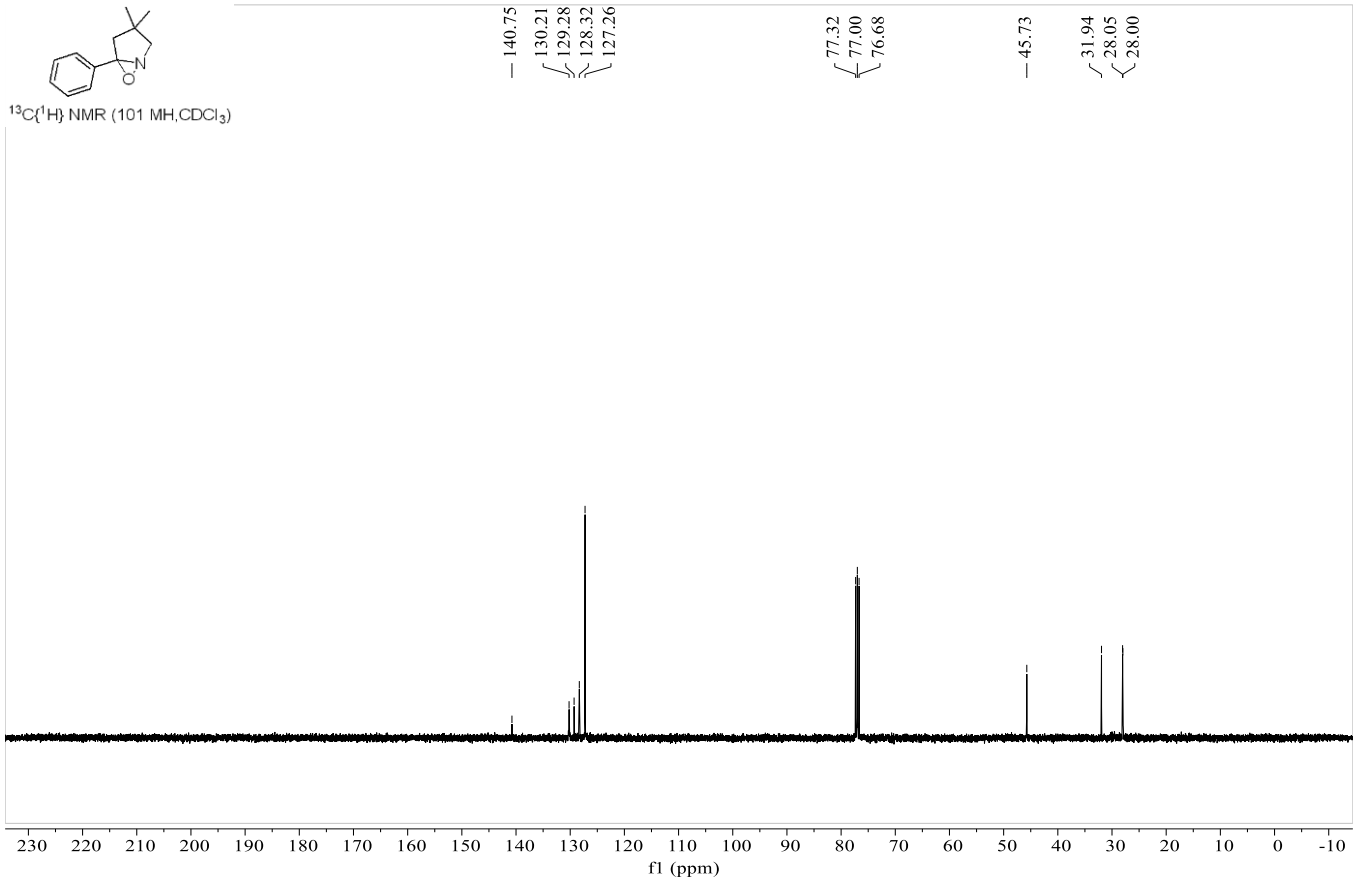
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)




^{1}H NMR (400 MHz, $CDCl_3$)
7.81
7.80
7.79
7.79
7.78
7.40
7.39
7.39
7.38
7.37
3.79
3.78
3.78
3.77
2.77
2.76
2.76
2.75
1.16
1.16
2.0
2.9
2.1
2.1
5.9
f1 (ppm)


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)
172.71
134.72
130.17
128.27
127.28
77.32
77.00
76.68
74.60
49.74
38.32
27.97
f1 (ppm)


^{1}H NMR (400 MHz,CDCl$_3$)
8.30
8.30
8.28
8.28
7.44
7.44
7.42
7.41
7.40
7.40
7.39
3.97
2.94
1.26
2.0
2.9
2.0
2.0
6.0
f1 (ppm)


^{13}C{^{1}H} NMR (101 MH,CDCl$_3$)
140.75
130.21
129.28
128.32
127.26
77.32
77.00
76.68
45.73
31.94
28.05
28.00
f1 (ppm)