

Supporting Information

Palladium-Catalyzed Cascade *5-Exo-Trig* Radical Cyclization /Aromatic C–H Alkylation with Unactivated Alkyl Iodides

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1. General Information

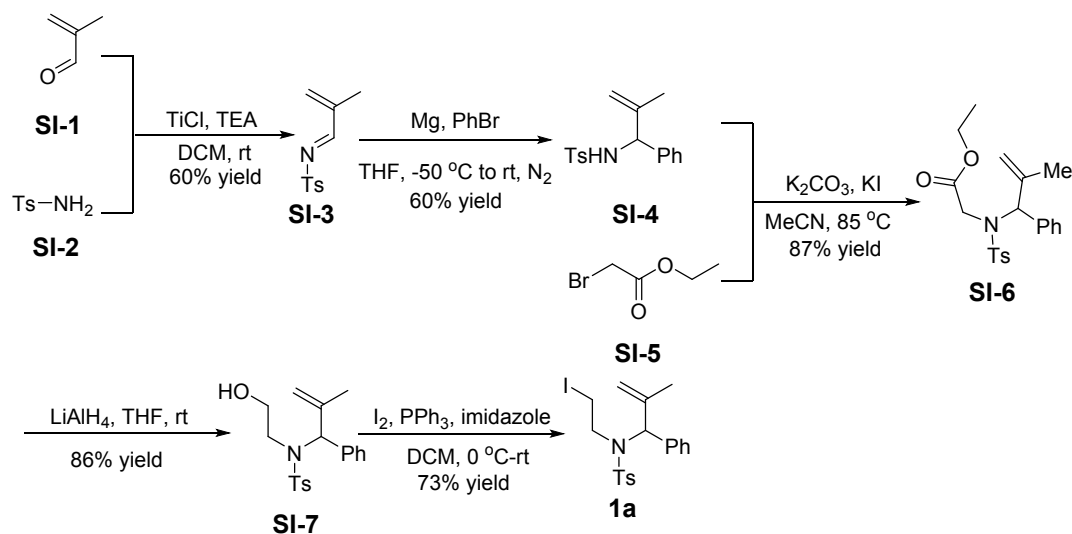
Organic solvents (Aldrich) were used without further purification. Purifications of reactions products were carried out by flash chromatography using Merck silica gel (40-63 μm). ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were obtained using an ESI/TOF Mariner Mass Spectrometer.

All commercially available reagents were bought from Macklin, Aladdin and used without further purification. Dry THF was steamed with metal sodium. Cesium carbonate was directly purchased from Macklin.

Reactions were conducted in dry solvents under Nitrogen atmosphere unless otherwise stated. The abbreviation "rt" refers to reactions carried out approximately at 23-27 $^{\circ}\text{C}$. Reaction mixtures were stirred using Teflon-coated Magnetic stirring rotor. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, flash chromatography was carried out on silica gel unless otherwise stated. Dryings were performed with anhydrous Na_2SO_4 or MgSO_4 . Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator, followed by residual solvent removal under high vacuum. The reactions were monitored by TLC or GC-MS.

2. Preparation of Starting Material.

General Procedure I:



Preparation of *N*-Tosyl-2-methylpropenimin **SI-3:** A solution of **SI-1** methacrolein (65 mmol, 5.36 mL), 4-methylbenzenesulfonamide **SI-2** (65 mmol, 11.13 g), and triethylamine (195 mmol, 27.1 mL) in dichloromethane (120 mL) was cooled to 0°C with stirring under nitrogen, a solution of titanium tetrachloride (45.5 mmol, 5.0 mL) in 20 mL of dichloromethane was added, and the mixture was stirred at 0°C for 90 min. The mixture was then filtered through Celite, and the solvents were evaporated to give a solid crystalline mass. The solids were broken up and refluxed with stirring for 10 min with 70 mL of ether. The ether solution was decanted off the residual solid, filtered through Celite, and then evaporated to give the imine **SI-3** (8.71 g, 39 mmol, 60% yield) as white solid.

Preparation of benzenesulfonamide **SI-4:** Imine **SI-3** (4.47 g, 20 mmol, 1.0 equiv.) was dissolved in THF under nitrogen and cooled to -50°C . Afterwards the Grignard compound (2.0 equiv.) was added dropwise and the reaction mixture was stirred for 2 h at -50°C , allowed to warm up to r.t. and then stirred for 2 h. The reaction was quenched by adding saturated aqueous NH_4Cl . Then the organic layer was extracted three times with AcOEt (40 mL). Drying over Na_2SO_4 and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography (PE:EA, 5:1) to give the benzenesulfonamide **SI-4** (3.62 g, 12 mmol, 60% yield) as white solid.

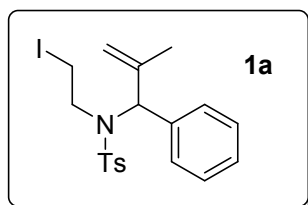
Preparation of ester **SI-6:** benzenesulfonamide **SI-4** (3.01 g, 10 mmol, 1.0 equiv.) in MeCN (80 mL) was added to a stirred mixture of **SI-5** ethyl bromoacetate (5.01 g, 30 mmol, 3.0 equiv.), K_2CO_3 (9.67 g, 70 mmol) and KI (0.83 g, 5 mmol). The mixture was heated to reflux

for 12 h. Then the reaction system was quenched with water, the organic layer was extracted three times with EtOAc (20 mL). Drying over Na₂SO₄ and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography (PE:EA, 5:1) to give the ester **SI-6** (3.37 g, 8.7 mmol, 87% yield) as a pale yellow oil.

Preparation of alcohol SI-7: LiAlH₄ (0.61 g, 16 mmol) was suspended in THF (10 mL) and a solution of ester **SI-6** (3.1 g, 8 mmol) in THF (60 mL) was then slowly added at 0 °C. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was slowly quenched with H₂O (5 mL), 10% aqueous NaOH (5 mL), H₂O (5 mL) at 0 °C, filtered through a small pad of celite. The filtrate was extracted with ethyl acetate (3 × 40 mL), washed with brine (40 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The alcohol **SI-7** (2.38 g, 6.88 mmol) was afforded as a colourless oil without further purification.

Preparation of alkyl iodide 1a: To a solution of **SI-7** (1.72 g, 5 mmol, 1.0 equiv) in 60 mL DCM was cooled to 0 °C. PPh₃ (3.93 g, 15 mmol, 3.0 equiv), imidazole (1.02 g, 15 mmol, 3.0 equiv), I₂ (3.81 g, 15 mmol, 3.0 equiv) was added successively. Then the reaction mixture was warmed to room temperature and stirred for 2 h. The precipitate was removed by filtration. After the concentration of the filtrate in vacuo, purification by column chromatography (PE:EA, 20:1) afforded the iodide **1a** (1.66 g, 3.65 mmol, 73% yield) as a white solid.

Analytical Data:



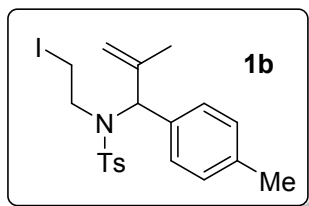
N-(2-iodoethyl)-4-methyl-*N*-(2-methyl-1-phenylallyl)benzenesulfonamide

C₁₉H₂₂INO₂S

The title compound was prepared according to **general procedure I**.

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.68 (d, *J* = 8.0 Hz, 2H), 7.32 (s, 1H), 7.31 (d, *J* = 1.6 Hz, 2H), 7.27 (d, *J* = 2.4 Hz, 2H), 7.17-7.15 (m, 2H), 5.6 (s, 1H), 4.96 (s, 1H), 4.47 (s, 1H), 3.62 (td, *J* = 15.2, 4.8 Hz, 1H), 3.40 (td, *J* = 12.8, 4.4 Hz, 1H), 3.1-3.04 (m, 1H), 2.42 (s, 3H), 2.15-2.08 (m, 1H), 1.64 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.5, 140.9, 137.1, 137.0, 129.5, 128.9, 128.8, 128.4, 127.4, 114.7, 66.0, 48.4, 21.6, 3.6.



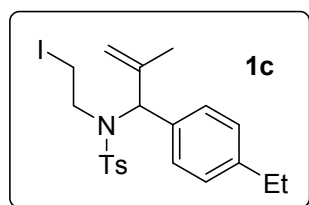
***N*-(2-iodoethyl)-4-methyl-*N*-(2-methyl-1-(*p*-tolyl)allyl)benzenesulfonamide**

$C_{20}H_{24}INO_2S$

The title compound was prepared according to **general procedure I**.

1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.61 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 7.6$ Hz, 2H), 5.48 (s, 1H), 4.86 (s, 1H), 4.39 (s, 1H), 3.53 (td, $J = 15.6, 4.8$ Hz, 1H), 3.31 (td, $J = 13.2, 4.4$ Hz, 1H), 3.02-2.96 (m, 1H), 2.34 (s, 3H), 2.26 (s, 3H), 2.08-2.02 (m, 1H), 1.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.4, 141.0, 138.2, 137.1, 134.0, 129.6, 129.5, 128.8, 127.4, 114.4, 65.8, 48.3, 21.6, 21.5, 21.2, 3.8.



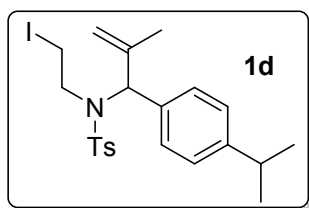
***N*-(1-(4-ethylphenyl)-2-methylallyl)-*N*-(2-iodoethyl)-4-methylbenzenesulfonamide**

$C_{21}H_{26}INO_2S$

The title compound was prepared according to **general procedure I**.

1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.60 (d, $J = 7.6$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 7.6$ Hz, 2H), 6.98 (d, $J = 7.6$ Hz, 2H), 5.48 (s, 1H), 4.86 (s, 1H), 4.40 (s, 1H), 3.54 (td, $J = 16, 4.0$ Hz, 1H), 3.30 (td, $J = 15.6, 3.6$ Hz, 1H), 3.00-2.94 (m, 1H), 2.55 (q, $J = 7.6$ Hz, 2H), 2.32 (s, 3H), 2.06-2.00 (m, 1H), 1.54 (s, 3H), 1.13 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.6, 143.4, 141.1, 137.1, 134.2, 129.5, 128.8, 128.4, 127.4, 114.5, 48.4, 28.5, 21.6, 15.6, 3.6.



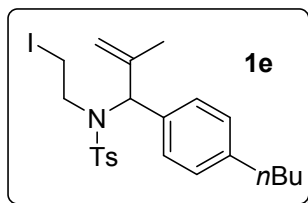
***N*-(2-iodoethyl)-*N*-(1-(4-isopropylphenyl)-2-methylallyl)-4-methylbenzenesulfonamide**

C₂₂H₂₈INO₂S

The title compound was prepared according to **general procedure I**.

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.60 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.08, (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 5.49 (s, 1H), 4.87 (s, 1H), 4.40 (s, 1H), 3.53 (td, *J* = 15.2, 4.8 Hz, 1H), 3.29 (td, *J* = 13.2, 4.0 Hz, 1H), 3.0-2.93 (m, 1H), 2.86-2.77 (m, 1H), 2.35 (s, 3H), 2.03-1.97 (m, 1H), 1.57 (s, 3H), 1.16 (dd, *J* = 6.8 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 149.3, 143.4, 141.4, 137.1, 134.3, 129.5, 128.8, 127.4, 126.9, 114.5, 65.9, 48.3, 33.8, 24.1, 23.9, 21.6, 3.5.

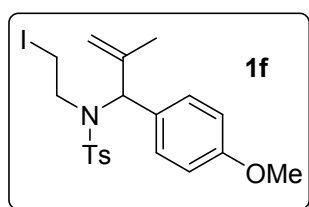


***N*-(1-(4-butylphenyl)-2-methylallyl)-*N*-(2-iodoethyl)-4-methylbenzenesulfonamide**

C₂₃H₃₀INO₂S

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.68 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 5.57 (s, 1H), 4.94 (s, 1H), 4.46 (s, 1H), 3.61 (td, *J* = 15.6, 4.8 Hz, 1H), 3.36 (td, *J* = 15.6, 4.4 Hz, 1H), 3.08-3.01 (m, 1H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.09-2.03 (m, 1H), 1.63 (s, 3H), 1.61-1.54 (m, 2H), 1.37-1.30 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.4, 143.3, 141.1, 137.1, 134.2, 129.5, 129.0, 128.7, 127.4, 114.4, 65.8, 48.3, 35.2, 33.5, 22.2, 21.6, 21.5, 14.0, 3.6.



***N*-(2-iodoethyl)-*N*-(1-(4-methoxyphenyl)-2-methylallyl)-4-methylbenzenesulfonamide**

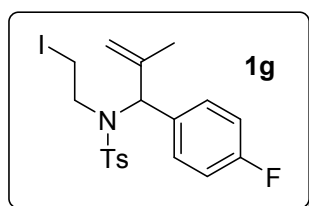
C₂₀H₂₄INO₃S

The title compound was prepared according to **general procedure I**.

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.69 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 5.55 (s, 1H), 4.92 (s, 1H), 4.45 (s, 1H), 3.81 (s, 3H), 3.61 (td, *J* = 15.6, 4.8 Hz, 1H), 3.36 (td, *J* = 15.6, 4.0 Hz, 1H), 3.11-3.05 (m, 1H), 2.42 (s, 3H), 2.15-2.09 (m, 1H), 1.60 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 159.5, 143.4, 141.1, 137.1, 130.1, 129.5, 128.9, 127.4, 114.3, 114.2, 65.5, 55.3, 48.3, 21.6, 21.5, 3.8.

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***N*-(1-(4-fluorophenyl)-2-methylallyl)-*N*-(2-iodoethyl)-4-methylbenzenesulfonamide**

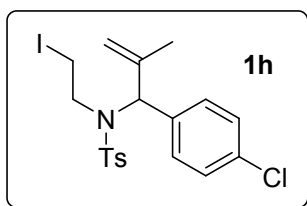
C₁₉H₂₁FINO₂S

The title compound was prepared according to **general procedure I**.

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.59 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 2H), 6.93 (t, *J* = 8.4 Hz, 2H), 5.50 (s, 1H), 4.89 (s, 1H), 4.39 (s, 1H), 3.54 (td, *J* = 15.6, 4.8 Hz, 1H), 3.31 (td, *J* = 13.2, 4.0 Hz, 1H), 3.07-3.01 (m, 1H), 2.35 (s, 3H), 2.18-2.12 (m, 1H), 1.55 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 162.4 (d, *J* = 246.6 Hz), 143.6, 140.9, 136.9, 130.5 (d, *J* = 8.1 Hz), 129.6, 128.5 (d, *J* = 12.3 Hz), 127.3, 115.9 (d, *J* = 21.4 Hz), 115.1, 65.3, 48.4, 21.6, 3.3.

¹⁹F NMR (376 MHz, CDCl₃, δ ppm): -133.1 (s, 1F).



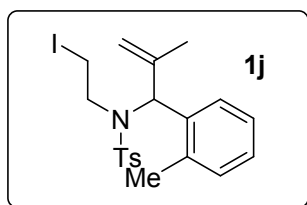
***N*-(1-(4-chlorophenyl)-2-methylallyl)-*N*-(2-iodoethyl)-4-methylbenzenesulfonamide**

C₁₉H₂₁ClINO₂S

The title compound was prepared according to **general procedure I**.

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.66 (d, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 4H), 7.07 (d, *J* = 7.6 Hz, 2H), 5.55 (s, 1H), 4.99 (s, 1H), 4.48 (s, 1H), 3.61 (td, *J* = 15.6, 4.0 Hz, 1H), 3.42 (td, *J* = 15.6, 4.0 Hz, 1H), 3.16-3.09 (m, 1H), 2.42 (s, 3H), 2.38-2.32 (m, 1H), 1.64 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.7, 140.9, 136.8, 135.8, 134.1, 130.0, 129.6, 129.0, 127.3, 115.6, 65.4, 48.4, 21.6, 3.3.



***N*-(2-iodoethyl)-4-methyl-*N*-(2-methyl-1-(*o*-tolyl)allyl)benzenesulfonamide**

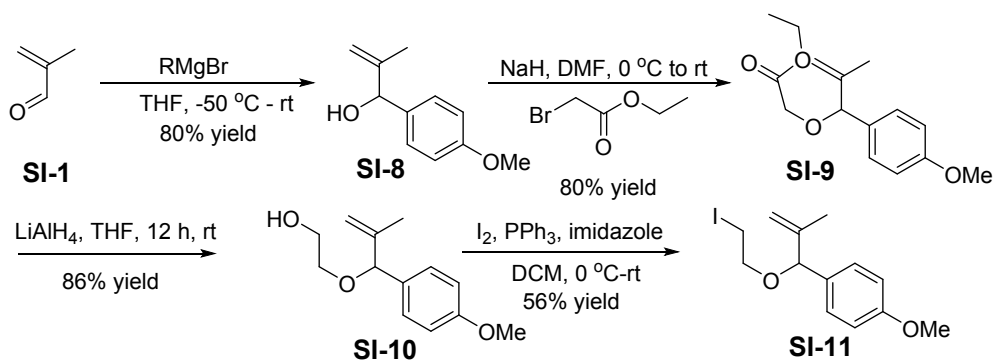
C₂₀H₂₄INO₂S

The title compound was prepared according to **general procedure I**.

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.66 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 3.6 Hz, 2H), 7.22 (d, *J* = 6 Hz, 2H), 7.11 (t, *J* = 6.8 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 5.81 (s, 1H), 4.89 (s, 1H), 4.22 (s, 1H), 3.55 (td, *J* = 15.6, 4.4 Hz, 1H), 3.35 (td, *J* = 15.6, 4.4 Hz, 1H), 3.09-3.03 (m, 1H), 2.48 (s, 3H), 2.42 (s, 3H), 1.99-1.93 (m, 1H), 1.62 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.5, 141.0, 138.2, 136.5, 134.9, 131.1, 129.3, 128.5, 127.8, 127.7, 126.3, 114.4, 63.1, 48.6, 21.6, 19.5, 3.3.

General Procedure II:



Preparation of alcohol SI-8: SI-1 methacrolein (30 mmol, 2.10 g, 1.0 equiv.) was dissolved in THF under nitrogen and cooled to $-50\text{ }^{\circ}\text{C}$. Afterwards the Grignard compound (2.0 equiv.) was added dropwise and the reaction mixture was stirred for 2 h at $-50\text{ }^{\circ}\text{C}$, allowed to warm up to r.t. and then stirred for 2 h. The reaction was quenched by adding saturated aqueous NH_4Cl . Then the organic layer was extracted three times with AcOEt (40 mL). Drying over Na_2SO_4 and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography (PE:EA, 5:1) to give the alcohol **SI-8** (4.28 g, 24 mmol, 80% yield) as a colorless oil.

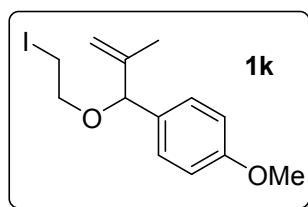
Preparation of ester SI-9: To a solution of **SI-8** (1.78 g, 10 mmol, 1.0 equiv.), was added NaH (0.36 g, 60% in mineral oil, 15 mmol, 1.5 equiv.) in portions in DMF (20 mL) at $0\text{ }^{\circ}\text{C}$. After stirring for 20 min, ethyl bromoacetate (5.01 g, 30 mmol, 3.33 mL, 3.0 equiv.) in DMF was added dropwise and the reaction mixture was stirred at room temperature overnight. The reaction was quenched with water. The residue was extracted with EtOAc twice, and the organic phase was washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated, and the residue was purified by column chromatography on silica gel (PE/EtOAc = 5: 1) to afford the ester **SI-9** as pale yellow oil (2.11 g, 80% yield).

Preparation of alcohol SI-10: LiAlH_4 (0.38 g, 10 mmol) was suspended in THF (10 mL) and a solution of ester **SI-9** (1.32 g, 5 mmol) in THF (40 mL) was then slowly added at $0\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was slowly quenched with H_2O (5 mL), 10% aqueous NaOH (5 mL), H_2O (5 mL) at $0\text{ }^{\circ}\text{C}$, filtered through a small pad of celite. The filtrate was extracted with ethyl acetate ($3 \times 40\text{ mL}$), washed with brine (40 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The alcohol **SI-10** (0.96 g, 4.3 mmol) was afforded as a colourless oil without further purification.

Preparation of alkyl iodide SI-11: To a solution of **SI-10** (0.45 g, 2.0 mmol, 1.0 equiv.) in 30 mL DCM was cooled to $0\text{ }^{\circ}\text{C}$. PPh_3 (1.57 g, 6 mmol, 3.0 equiv.), imidazole (0.408 g, 6 mmol, 3.0 equiv.), I_2 (1.52 g, 6 mmol, 3.0 equiv.) was added successively. Then the reaction

mixture was warmed to room temperature and stirred for 2 h. Then the precipitate was removed by filtration. After the concentration of the filtrate in *vacuo*, purification by column chromatography (PE:EA, 10:1) afforded the iodide **SI-11** (0.37 g, 1.12 mmol, 56% yield) as a colorless oil.

Analytical Data:



1-(1-(2-iodoethoxy)-2-methylallyl)-4-methoxybenzene

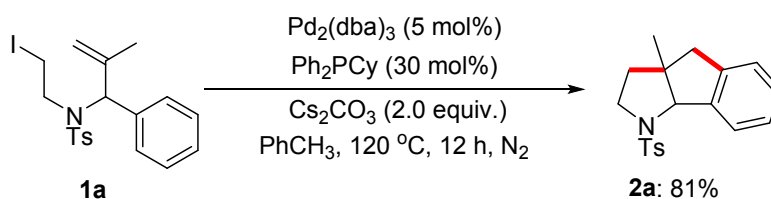


The title compound was prepared according to **general procedure II**.

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.19 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 1H), 4.88 (s, 1H), 4.64 (s, 1H), 3.71 (s, 3H), 3.64-3.50 (m, 2H), 3.20 (t, *J* = 6.8 Hz, 2H), 1.51 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 157.9, 143.9, 131.1, 126.8, 112.5, 111.9, 83.8, 68.0, 54.2, 16.9, 2.4.

3. Typical Procedure and Analytical Data for Palladium-Catalyzed Radical Cyclization Reaction.

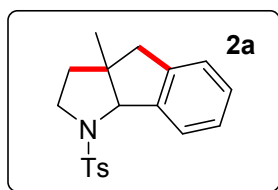


Typical Procedure:

Unactivated alkyl iodide **1a** (91.1 mg, 0.20 mmol, 1.0 equiv.), Pd₂(dba)₃ (9.2 mg, 0.01 mmol, 0.05 equiv.), Ph₂PCy (16.1 mg, 0.06 mmol, 0.3 equiv.) and Cs₂CO₃ (130.3 mg, 0.40 mmol, 2.0 equiv.) were added to a reaction tube and vacuum purged three times, backfilling with N₂. Then the toluene (2 mL) was added under nitrogen atmosphere. The resulting mixture was stirred at 120 °C for 12 h. After cooling the reaction mixture at rt, it was quenched with a saturated aqueous solution of NH₄Cl. The aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic phase was sequentially washed with saturated aqueous solution of NaCl and then concentrated *in vacuo*. The mixture was purified by silica gel column

chromatography (PE:EA, 20:1) to give the corresponding product **2a** (53.1 mg, 0.16 mmol, 81% yield).

Analytical Data:



3a-methyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

C₁₉H₂₁NO₂S MW: 327.44 g·mol⁻¹

White Solid

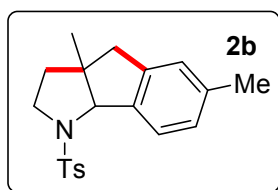
Isolated Amount: 53.0 mg **Yield:** 81%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (t, *J* = 8.0 Hz, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 4.67 (s, 1H), 3.49-3.44 (m, 1H), 3.31-3.24 (m, 1H), 2.84 (d, *J* = 16.0 Hz, 1H), 2.73 (d, *J* = 16.0 Hz, 1H), 2.45 (s, 3H), 1.85-1.77 (m, 1H), 1.60-1.55 (m, 1H), 0.73 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.5, 142.8, 140.7, 134.5, 129.6, 128.2, 127.7, 127.3, 126.8, 124.9, 74.5, 49.9, 48.5, 43.2, 37.3, 23.3, 21.6.

HRMS (ESI) calcd for C₁₉H₂₁NO₂SNa [M+Na]⁺ 350.1191, found 350.1193.

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3a,6-dimethyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

C₂₀H₂₃NO₂S MW: 341.47 g·mol⁻¹

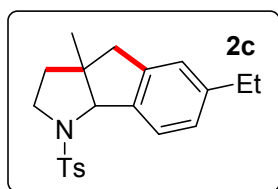
White Solid

Isolated Amount: 52.6 mg **Yield:** 77%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.8 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 4.63 (s, 1H), 3.47-3.42 (m, 1H), 3.30-3.23 (m, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.68 (d, *J* = 16.0 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H), 1.84-1.76 (m, 1H), 1.59-1.53 (m, 1H), 0.73 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 143.4, 140.9, 139.8, 138.0, 134.6, 129.6, 128.3, 127.7, 126.5, 125.5, 74.3, 50.1, 48.5, 43.2, 37.4, 23.4, 21.6, 21.4.

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 364.1347, found 364.1350.



6-ethyl-3a-methyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

$\text{C}_{21}\text{H}_{25}\text{NO}_2\text{S}$ **MW:** 355.50 $\text{g}\cdot\text{mol}^{-1}$

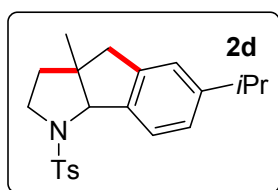
White Solid

Isolated Amount: 57.6 mg **Yield:** 81%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.80 (d, $J = 7.6$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.11 (d, $J = 7.6$ Hz, 1H), 6.95 (s, 1H), 4.63 (s, 1H), 3.47-3.43 (m, 1H), 3.30-3.23 (m, 1H), 2.81 (d, $J = 16.0$ Hz, 1H), 2.70 (d, $J = 16.0$ Hz, 1H), 2.70 (d, $J = 16.0$ Hz, 1H), 2.63 (q, $J = 7.6$ Hz, 2H), 2.45 (s, 3H), 1.85-1.78 (m, 1H), 1.57-1.54 (m, 1H), 1.22 (t, $J = 7.6$ Hz, 3H), 0.73 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 144.6, 143.4, 140.9, 140.1, 134.6, 129.6, 127.7, 127.2, 126.6, 124.2, 74.3, 50.1, 48.5, 43.2, 37.4, 28.8, 23.4, 21.6, 15.9.

HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 378.1504, found 378.1505.



6-isopropyl-3a-methyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

$\text{C}_{22}\text{H}_{27}\text{NO}_2\text{S}$ **MW:** 369.52 $\text{g}\cdot\text{mol}^{-1}$

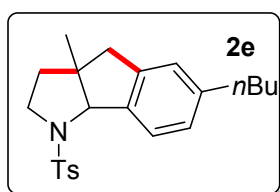
White Solid

Isolated Amount: 59.1 mg **Yield:** 80%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.79 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 4.63 (s, 1H), 3.48-3.43 (m, 1H), 3.30-3.24 (m, 1H), 2.92-2.87 (m, 1H), 2.82 (d, *J* = 16.0 Hz, 1H), 2.70 (d, *J* = 16.8 Hz, 1H), 2.45 (s, 3H), 1.86-1.79 (m, 1H), 1.59-1.54 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 6H), 0.73 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 149.3, 143.4, 140.9, 140.2, 134.6, 129.6, 127.7, 126.6, 125.8, 122.7, 74.3, 50.0, 48.5, 43.3, 37.4, 34.1, 24.2, 23.5, 21.6.

HRMS (ESI) calcd for C₂₂H₂₇NO₂SNa [M+Na]⁺ 392.1660, found 392.1664.



6-butyl-3a-methyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

C₂₃H₂₉NO₂S MW: 383.55 g·mol⁻¹

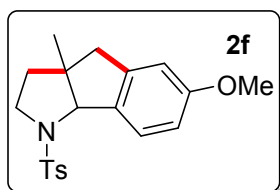
Yellow Oil

Isolated Amount: 62.9 mg **Yield:** 82%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 4.63 (s, 1H), 3.45 (t, *J* = 7.6 Hz, 1H), 3.30-3.23 (m, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.69 (d, *J* = 16.0 Hz, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 1.62-1.54 (m, 3H), 1.40-1.32 (m, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.73 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.4, 143.2, 140.8, 140.0, 134.6, 129.6, 127.7, 126.5, 124.8, 74.3, 60.4, 50.1, 48.5, 43.2, 37.4, 35.6, 33.9, 23.4, 22.4, 21.6, 14.0.

HRMS (ESI) calcd for C₂₃H₂₉NO₂SNa [M+Na]⁺ 406.1817, found 406.1818.



6-methoxy-3a-methyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

C₂₀H₂₃NO₃S MW: 357.47 g·mol⁻¹

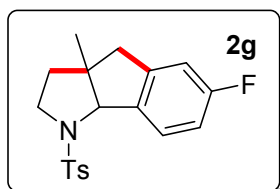
White Solid

Isolated Amount: 51.5 mg **Yield:** 72%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.65 (s, 1H), 4.61 (s, 1H), 3.79 (s, 3H), 3.48-3.43 (m, 1H), 3.30-3.23 (m, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.69 (d, *J* = 16.0 Hz, 1H), 2.45 (s, 3H), 1.85-1.77 (m, 1H), 1.57-1.53 (m, 1H), 0.74 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 160.1, 143.4, 142.4, 134.9, 134.7, 129.6, 127.7, 127.6, 113.4, 109.9, 74.0, 55.4, 50.4, 48.5, 43.4, 37.5, 23.5, 21.6.

HRMS (ESI) calcd for C₂₀H₂₃NO₃SNa [M+Na]⁺ 380.1296, found 380.1298.



6-fluoro-3a-methyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

C₁₉H₂₀FNO₂S **MW:** 345.43 g·mol⁻¹

White Solid

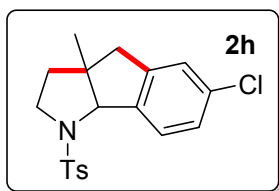
Isolated Amount: 25.6 mg **Yield:** 37%

¹H NMR (600 MHz, CDCl₃, δ ppm): 7.79 (d, *J* = 8.4 Hz, 2H), 7.72 (dd, *J* = 8.4, 5.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.94 (td, *J* = 9.0, 2.4 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 4.95 (s, 1H), 3.47-3.44 (m, 1H), 3.28-3.23 (m, 1H), 2.81 (d, *J* = 16.2 Hz, 1H), 2.70 (d, *J* = 16.2 Hz, 1H), 2.44 (s, 3H), 1.81-1.76 (m, 1H), 1.60-1.56 (m, 1H), 0.73 (s, H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 163.2 (d, *J* = 162.5 Hz), 143.6, 142.9 (d, *J* = 5.5 Hz), 138.3 (d, *J* = 1.6 Hz), 134.3, 129.6, 128.1 (d, *J* = 6.0 Hz), 127.6, 114.4 (d, *J* = 14.8 Hz), 111.5 (d, *J* = 14.5 Hz), 73.6, 50.5, 48.4, 43.1, 37.2, 23.2, 21.5.

¹⁹F NMR (376 MHz, CDCl₃, δ ppm): -114.9 (s, 1F).

HRMS (ESI) calcd for C₁₉H₂₀FNO₂SNa [M+Na]⁺ 368.1096, found 368.1110.



6-chloro-3a-methyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

C₁₉H₂₀ClNO₂S MW: 361.88 g·mol⁻¹

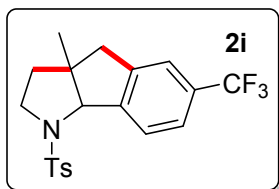
White Solid

Isolated Amount: 39.1 mg **Yield:** 54%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.10 (s, 1H), 4.60 (s, 1H), 3.49-3.44 (m, 1H), 3.29-3.22 (m, 1H), 2.81 (d, *J* = 16.4 Hz, 1H), 2.70 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H), 1.83-1.75 (m, 1H), 1.61-1.58 (m, 1H), 0.73 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.7, 142.6, 141.3, 134.3, 134.0, 129.7, 128.1, 127.7, 125.0, 73.8, 50.3, 48.4, 42.9, 37.3, 23.2, 21.6.

HRMS (ESI) calcd for C₁₉H₂₀ClNO₂SNa [M+Na]⁺ 384.0801 found 384.0802.



3a-methyl-1-tosyl-6-(trifluoromethyl)-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

C₂₀H₂₀F₃NO₂S MW: 395.44 g·mol⁻¹

Yellow Oil

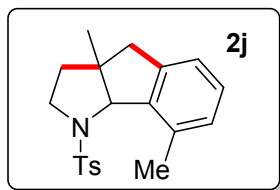
Isolated Amount: 31.6 mg **Yield:** 40%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.90 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 20.0, 8.0 Hz, 1H), 4.66 (s, 1H), 3.48 (t, *J* = 8.0 Hz, 1H), 3.27 (dd, *J* = 16.8, 10.0 Hz, 1H), 2.89 (d, *J* = 6.4 Hz, 1H), 2.77 (d, *J* = 16.4 Hz, 1H), 2.46 (s, 3H), 1.83-1.75 (m, 1H), 1.64-1.60 (m, 1H), 0.75 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 146.8, 143.8, 141.4, 134.1, 129.7 (d, *J* = 3.7 Hz), 128.9, 127.7, 127.3, 126.7, 124.5 (q, *J* = 3.7 Hz), 121.9 (q, *J* = 3.5 Hz), 73.9, 50.2, 48.5, 42.9, 37.1, 23.1, 21.6.

¹⁹F NMR (376 MHz, CDCl₃, δ ppm): -62.1 (s, 3F).

HRMS (ESI) calcd for $C_{20}H_{20}F_3NO_2SNa$ $[M+Na]^+$ 418.1065 found 418.1067.



3a,8-dimethyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole

$C_{20}H_{23}NO_2S$ MW: 341.47 $g \cdot mol^{-1}$

White Solid

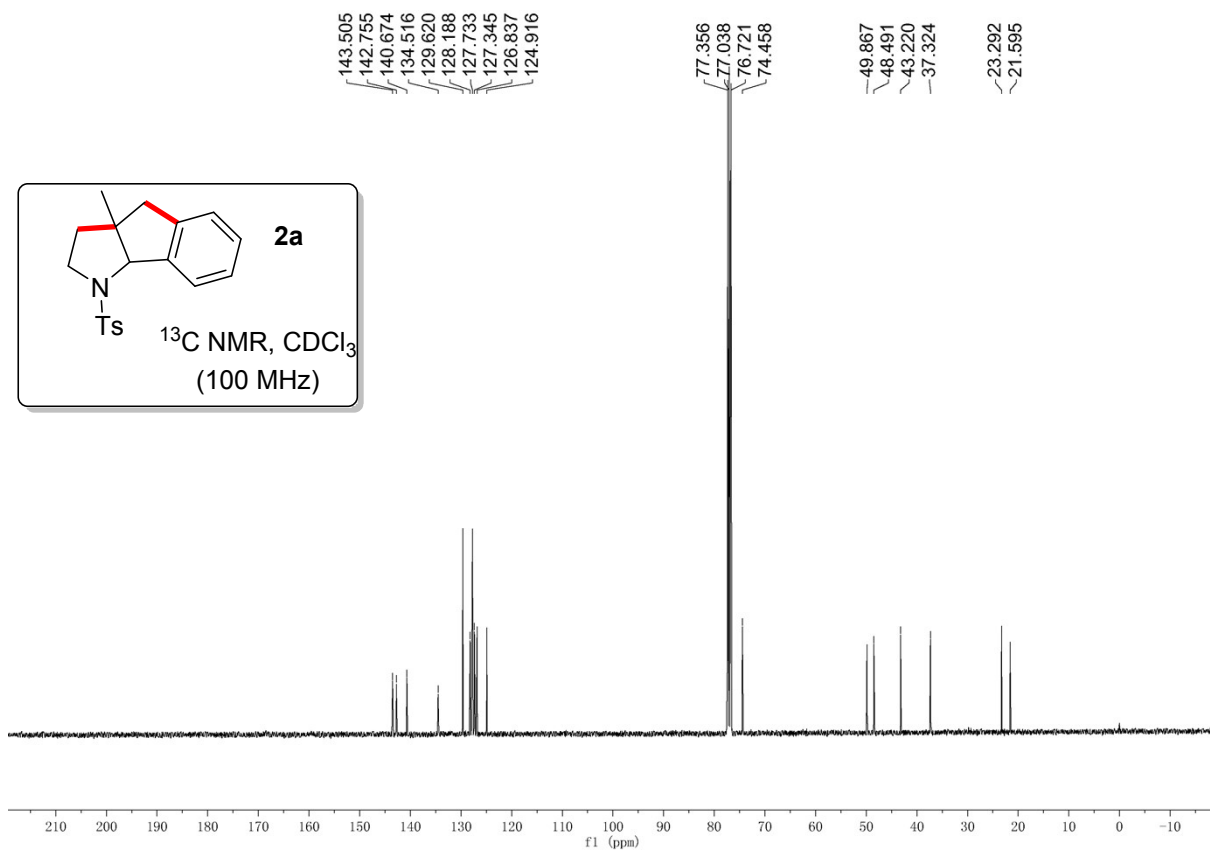
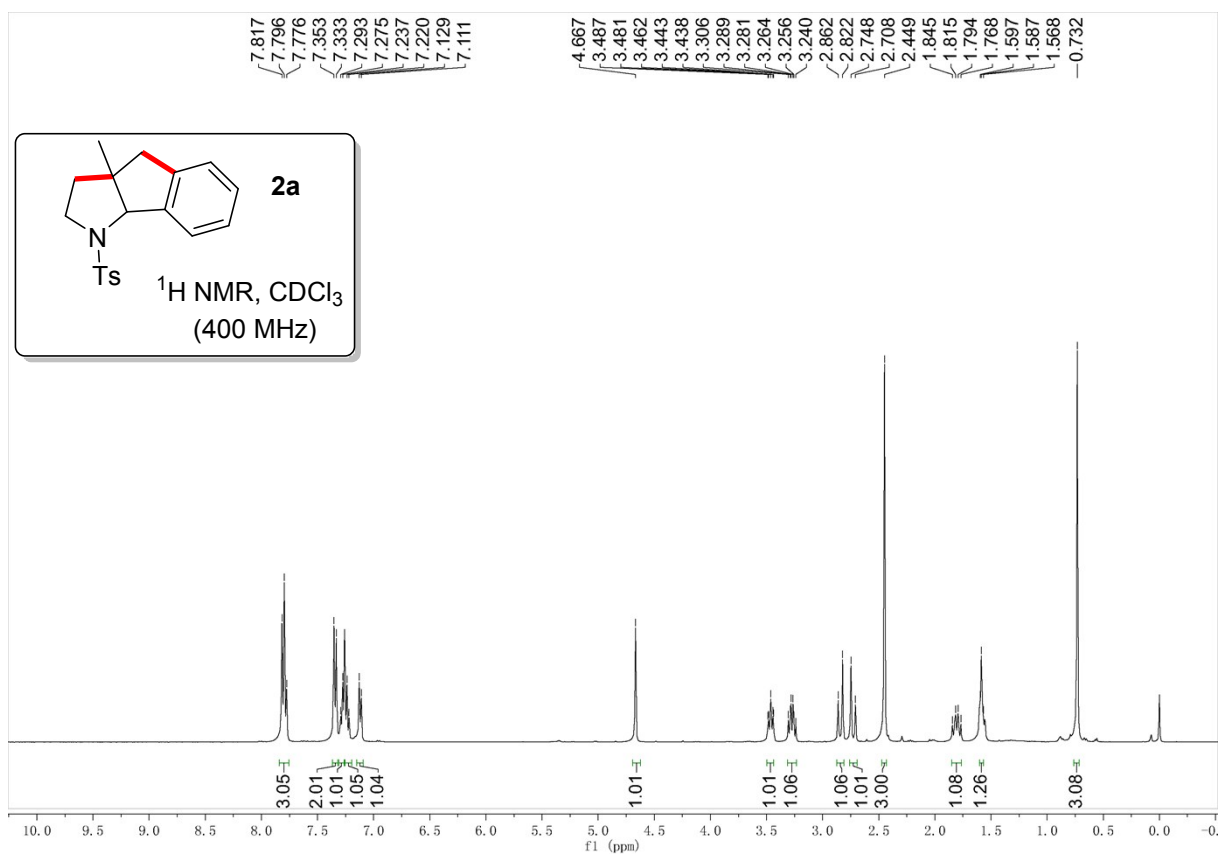
Isolated Amount: 45.1 mg **Yield:** 66%

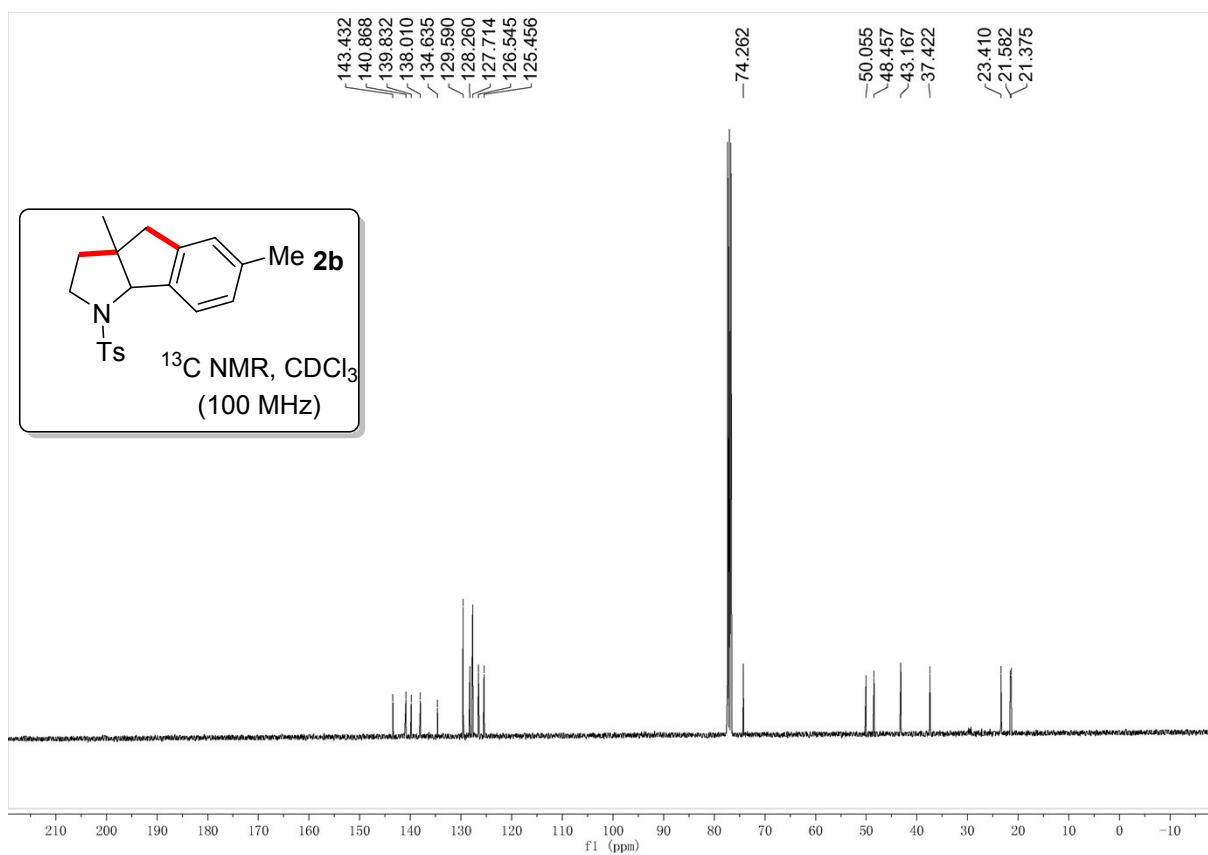
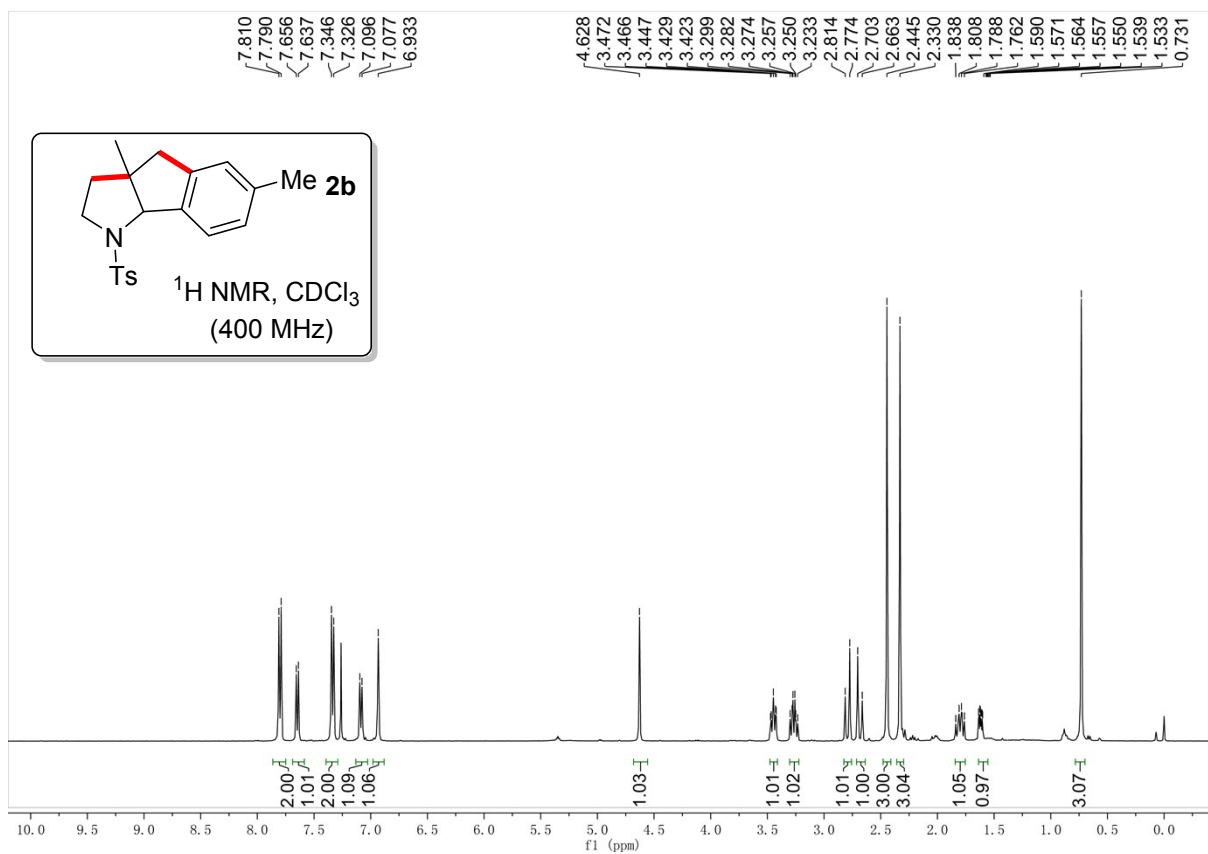
1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.79 (d, $J = 7.6$ Hz, 2H), 7.31(d, $J = 7.6$ Hz, 2H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 5.12 (s, 1H), 3.60-3.54 (m, 1H), 3.15-3.08 (m, 1H), 2.89 (d, $J = 16.4$ Hz, 1H), 2.76 (d, $J = 16.4$ Hz, 1H), 2.59 (s, 3H), 2.44 (s, 3H), 1.71-1.65 (m, 1H), 1.47-1.40 (m, 1H), 0.97 (s, 3H).

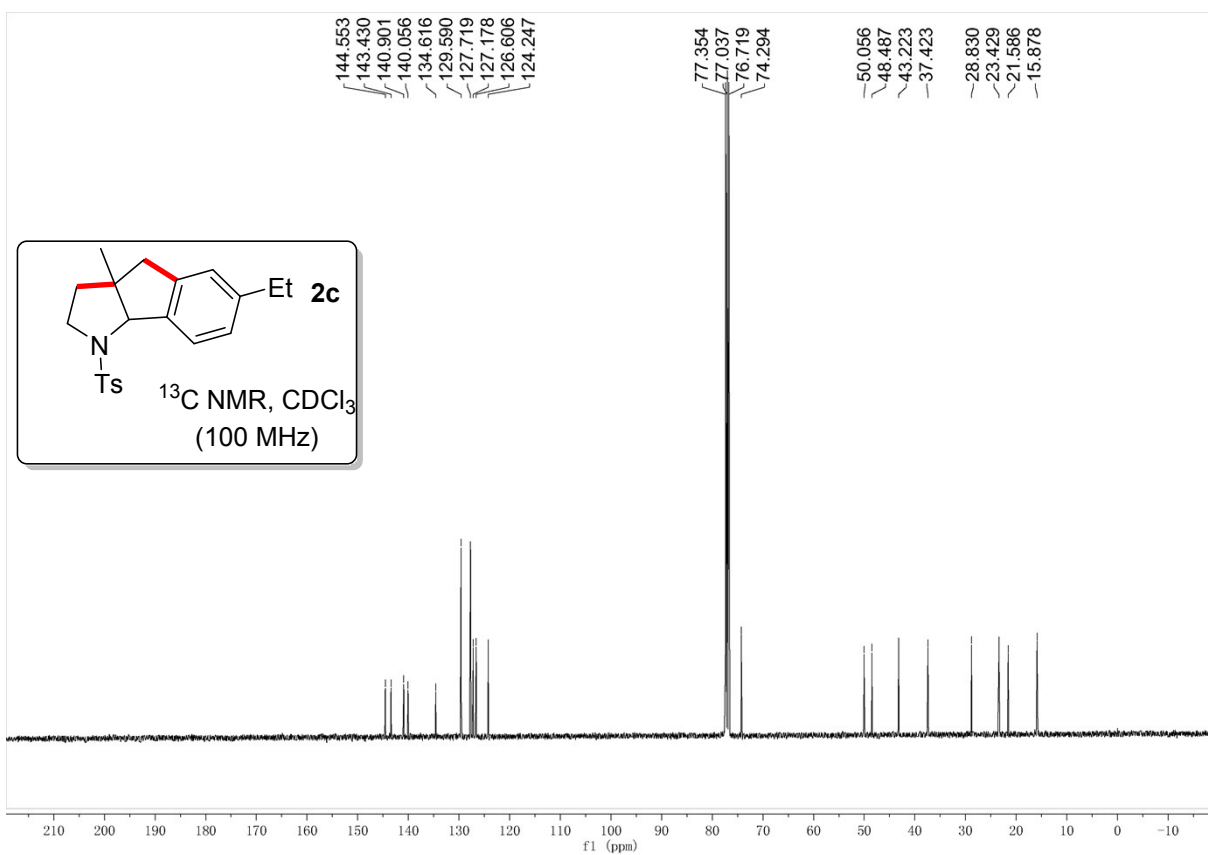
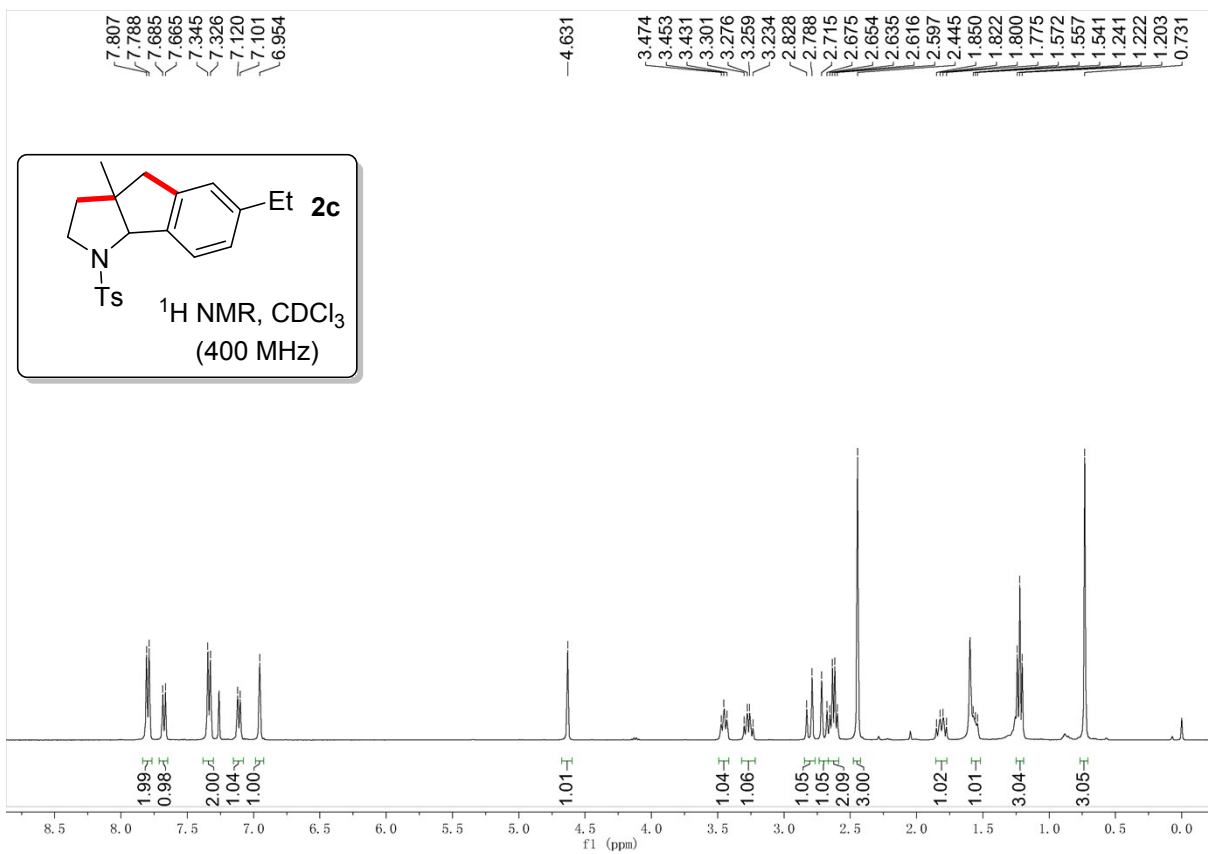
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.5, 142.6, 138.9, 137.6, 136.5, 129.6, 129.1, 128.6, 127.9, 122.1, 75.3, 49.9, 48.4, 45.1, 39.5, 25.4, 21.6, 19.7.

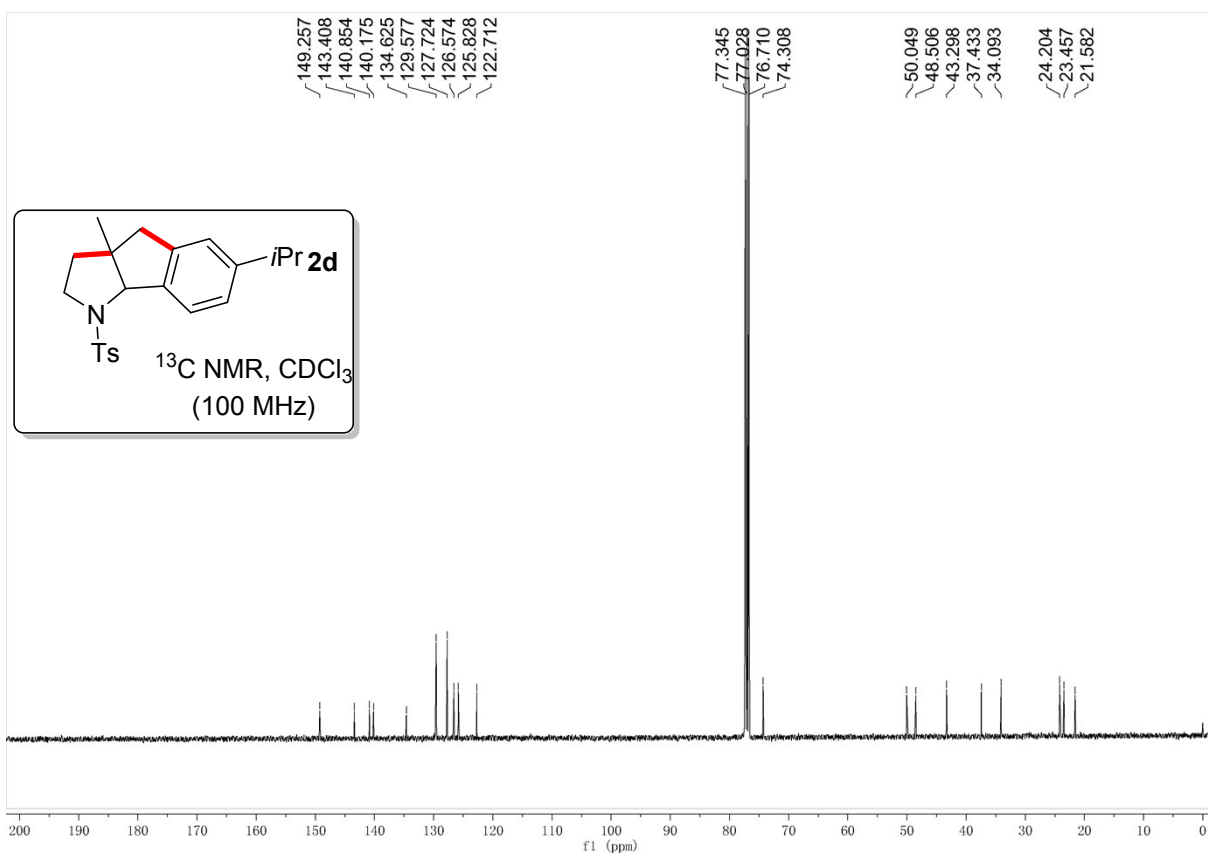
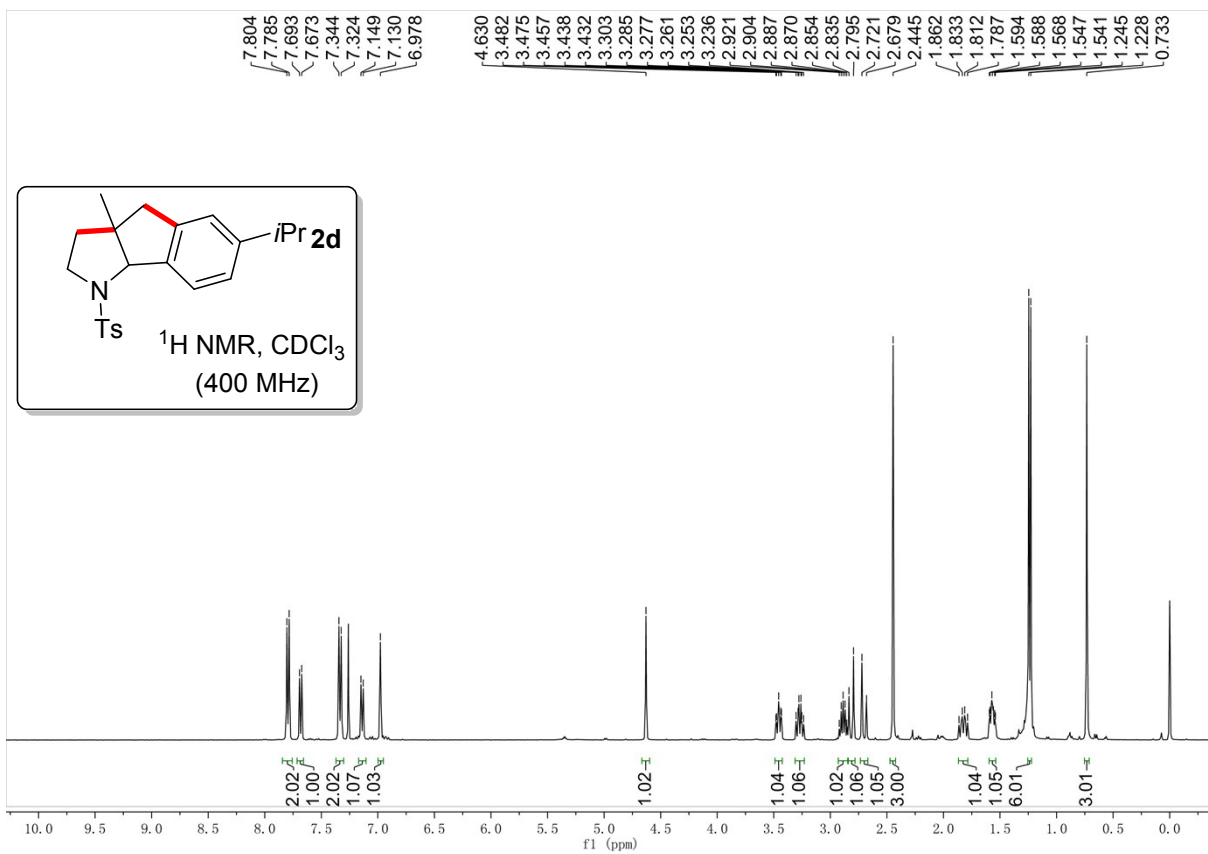
HRMS (ESI) calcd for $C_{20}H_{23}NO_2SNa$ $[M+Na]^+$ 364.1347 found 364.1350.

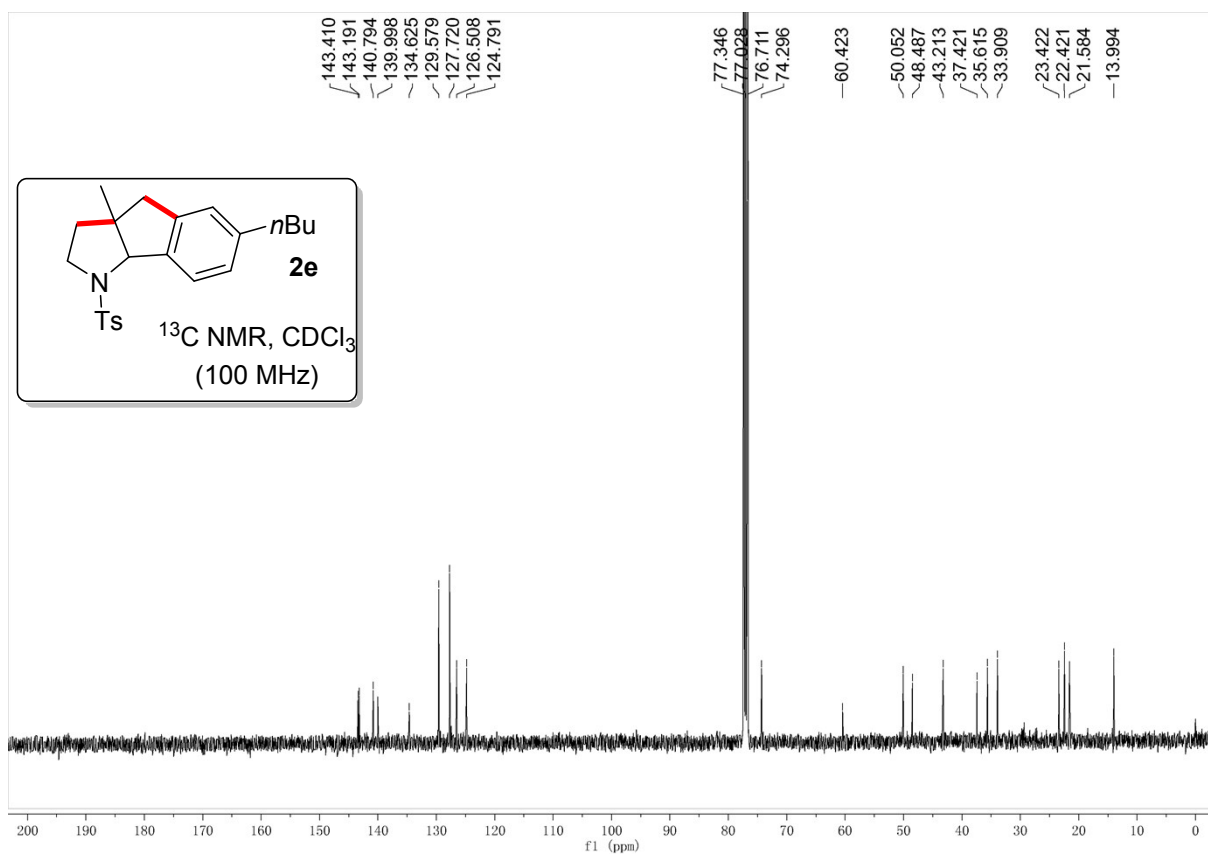
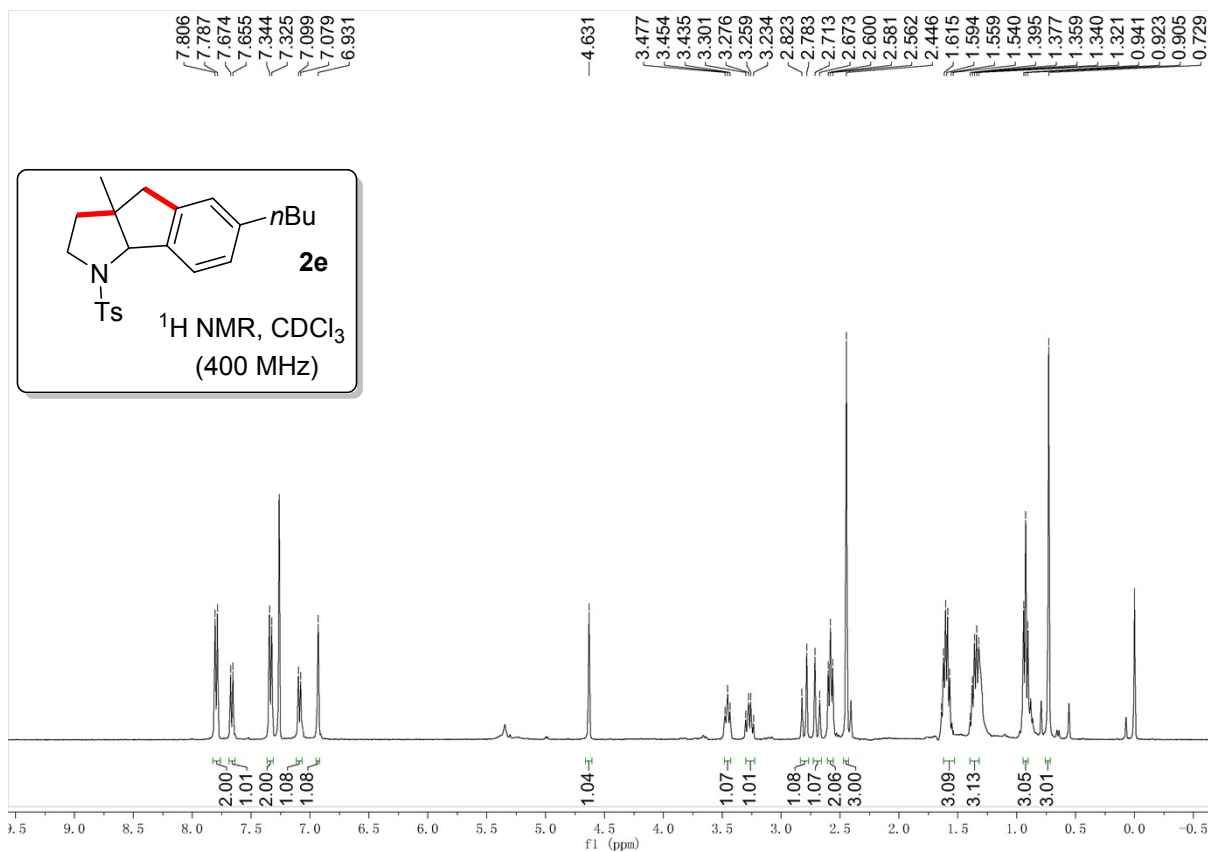
4. Copies of the ^1H NMR and ^{13}C NMR for Cyclization Products.

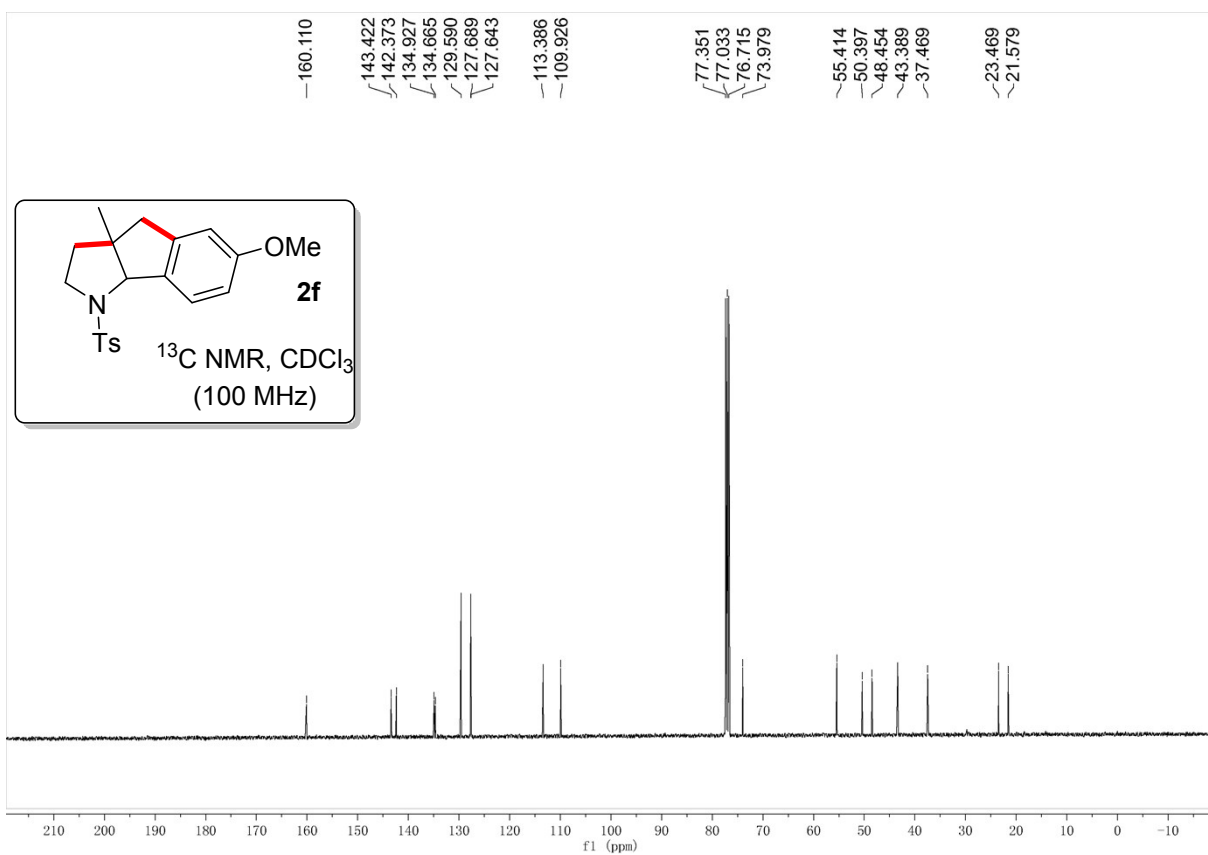
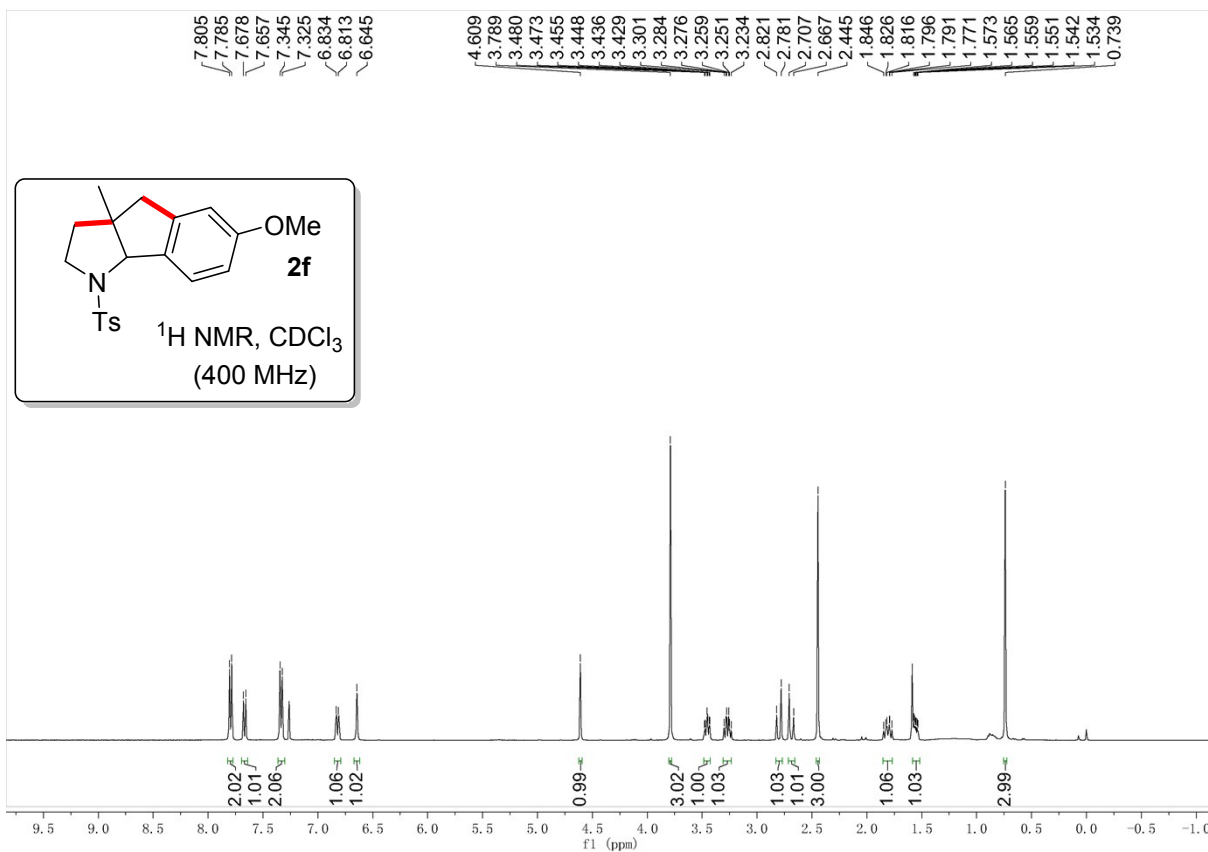


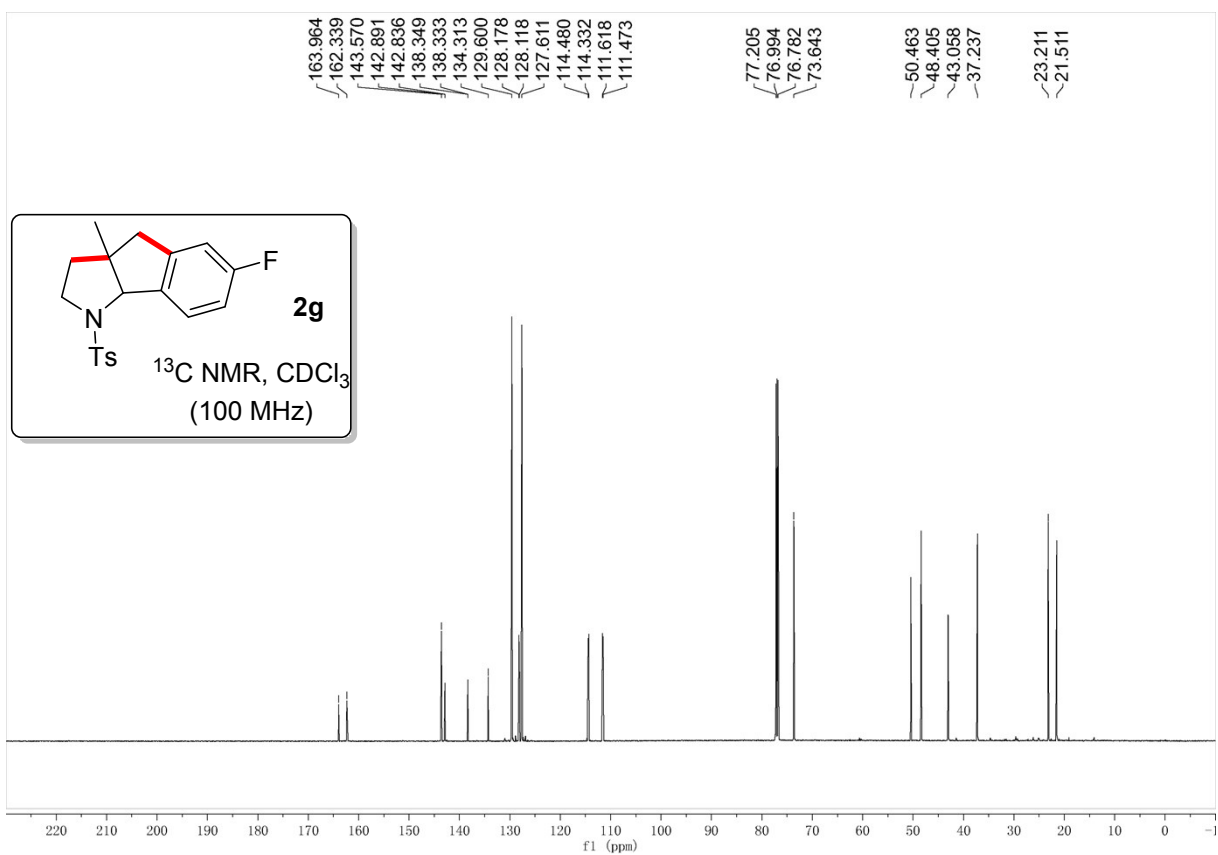
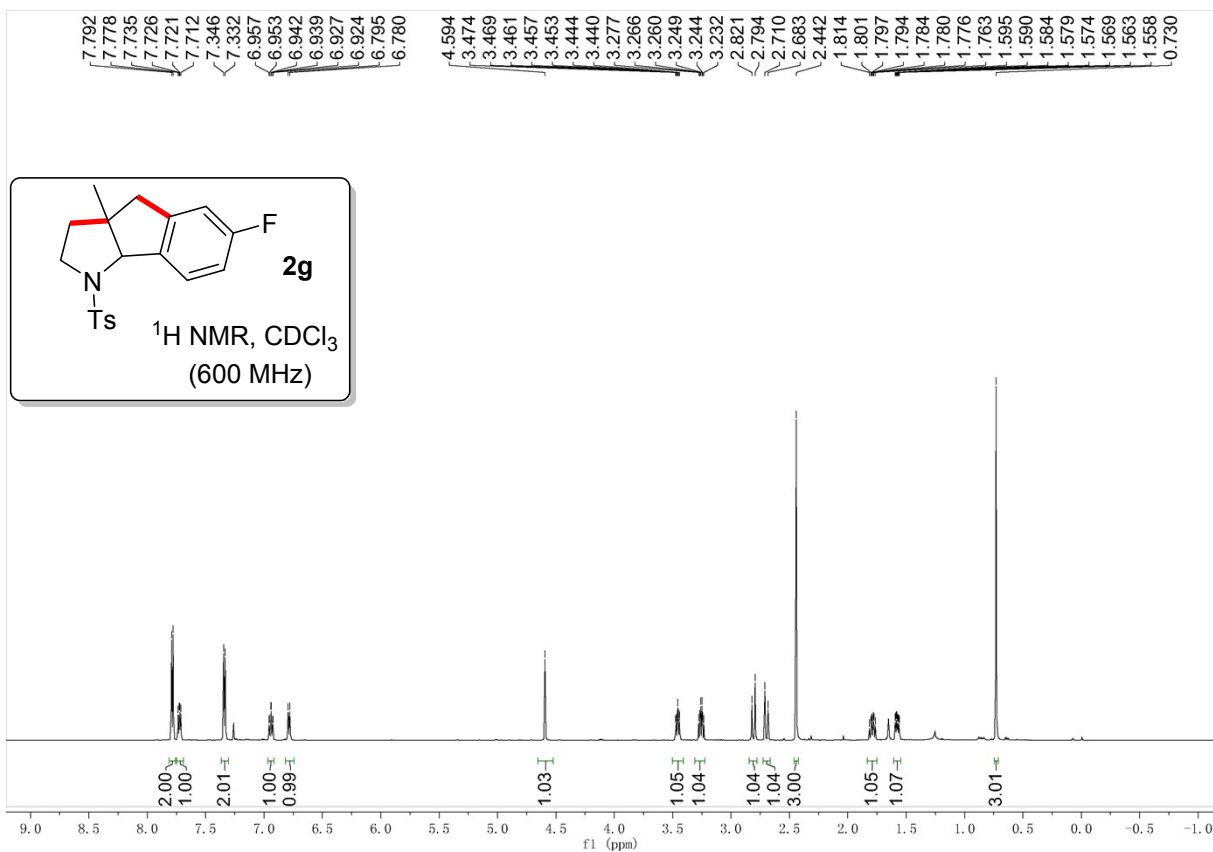


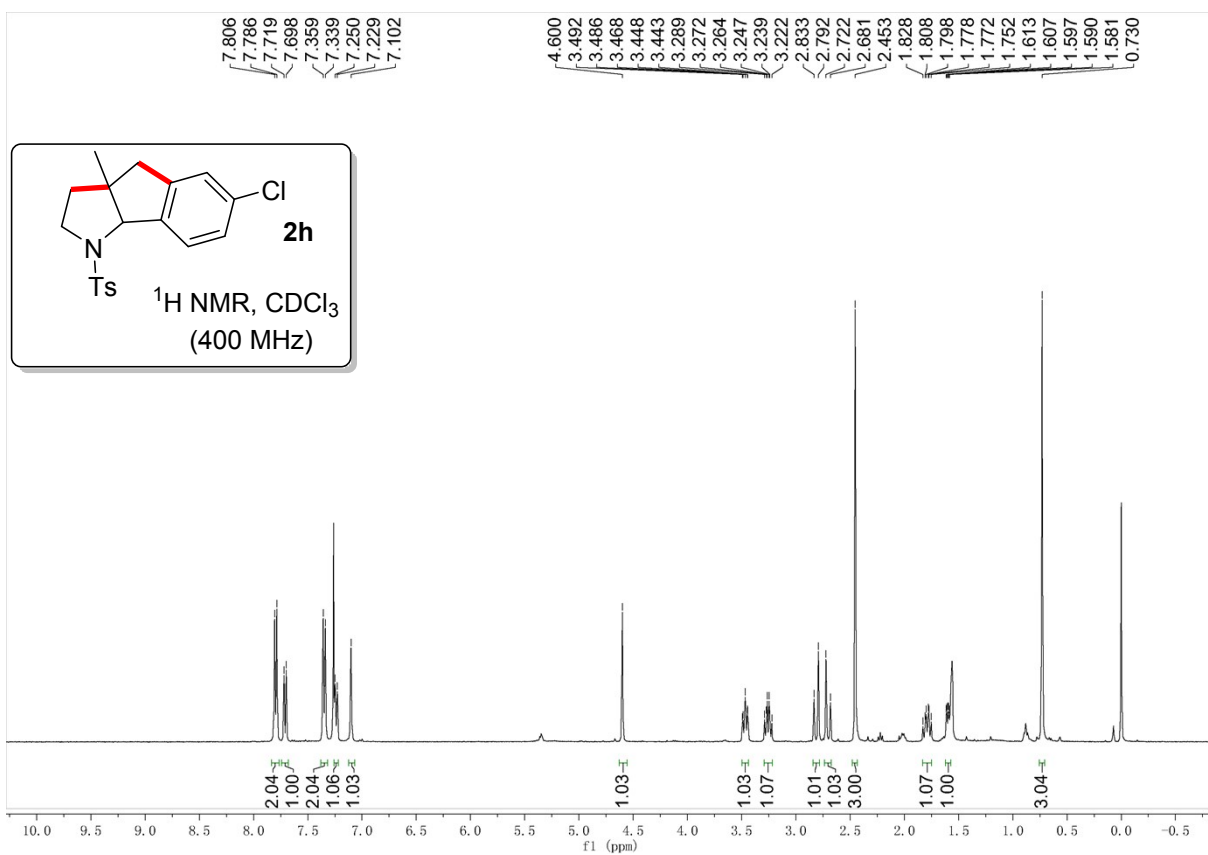
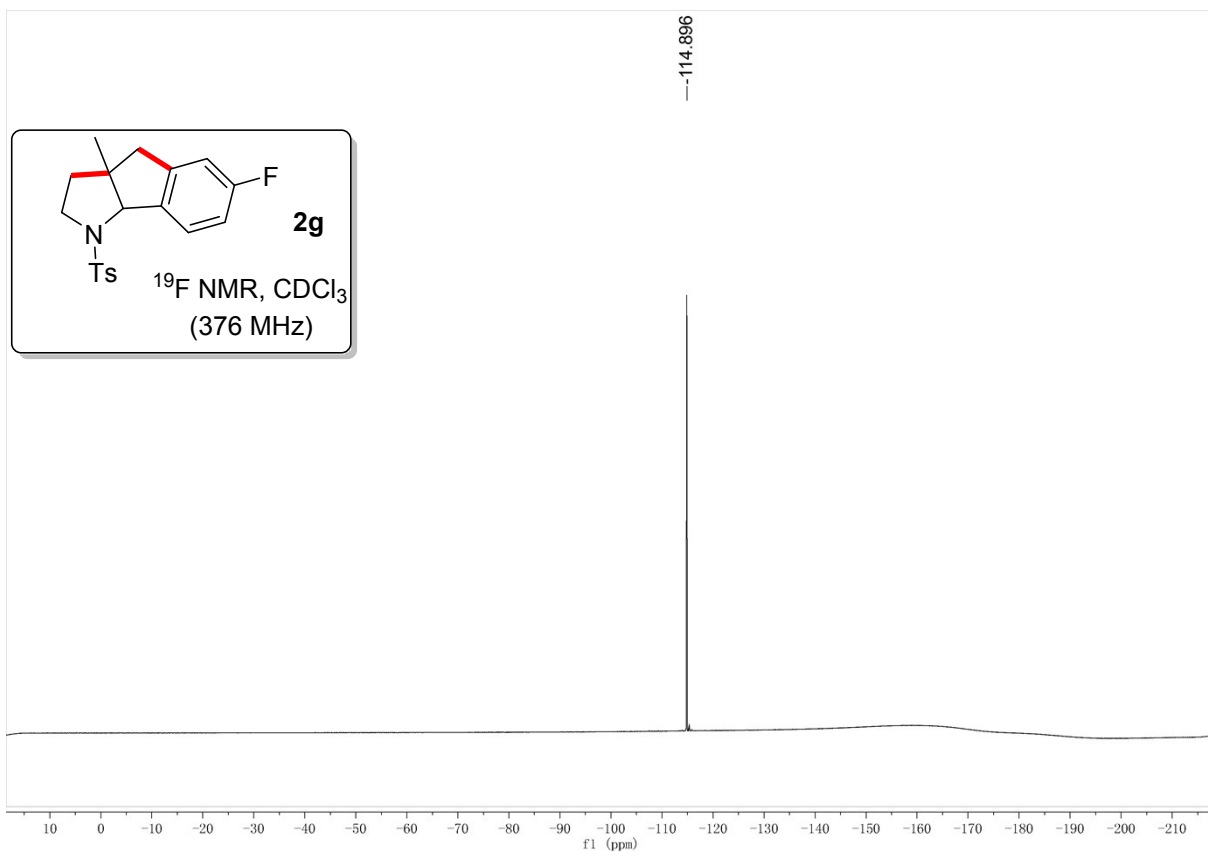


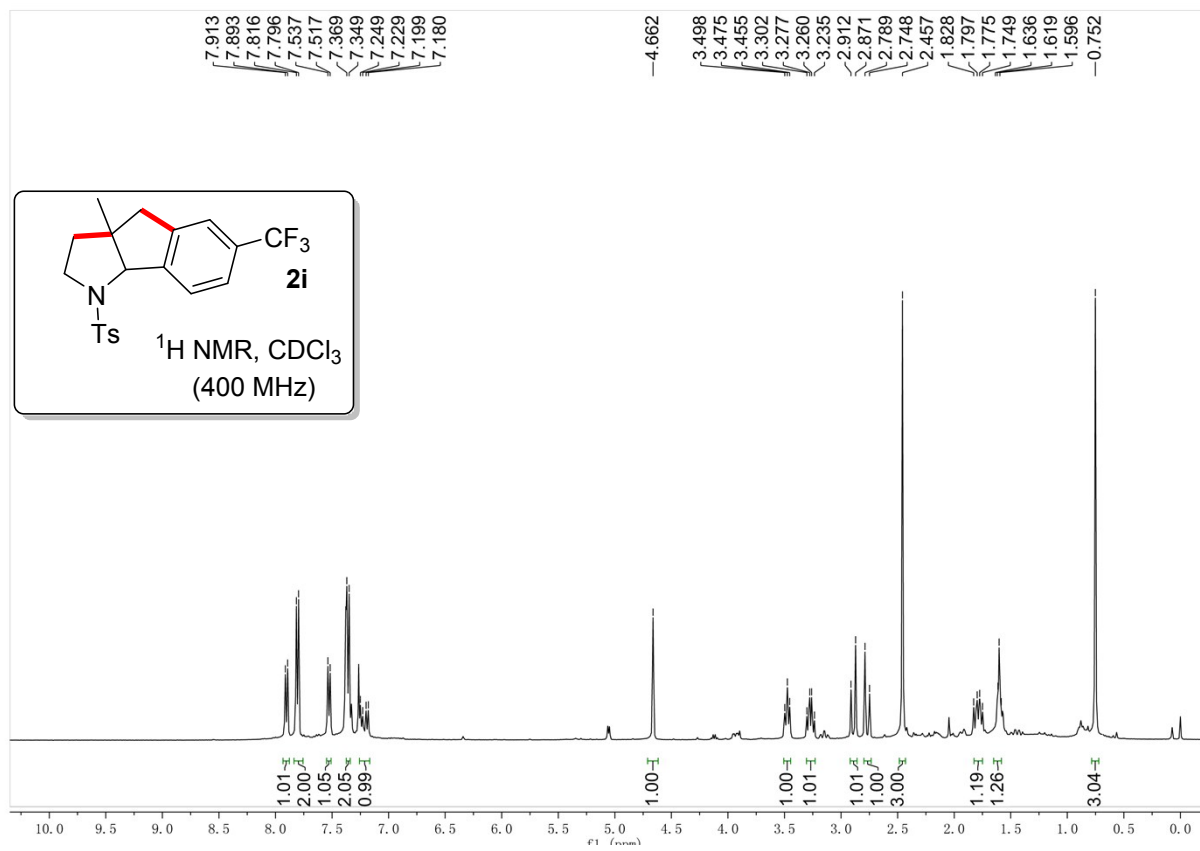
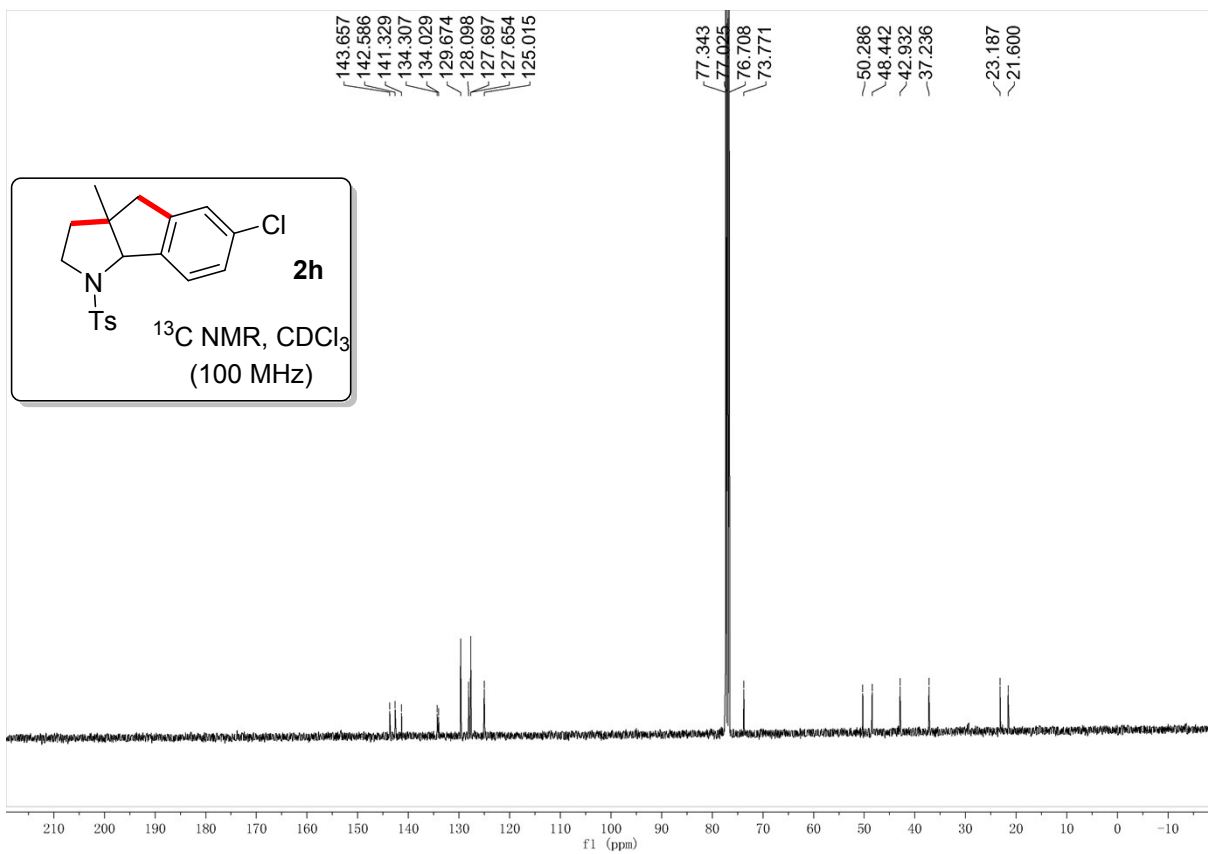


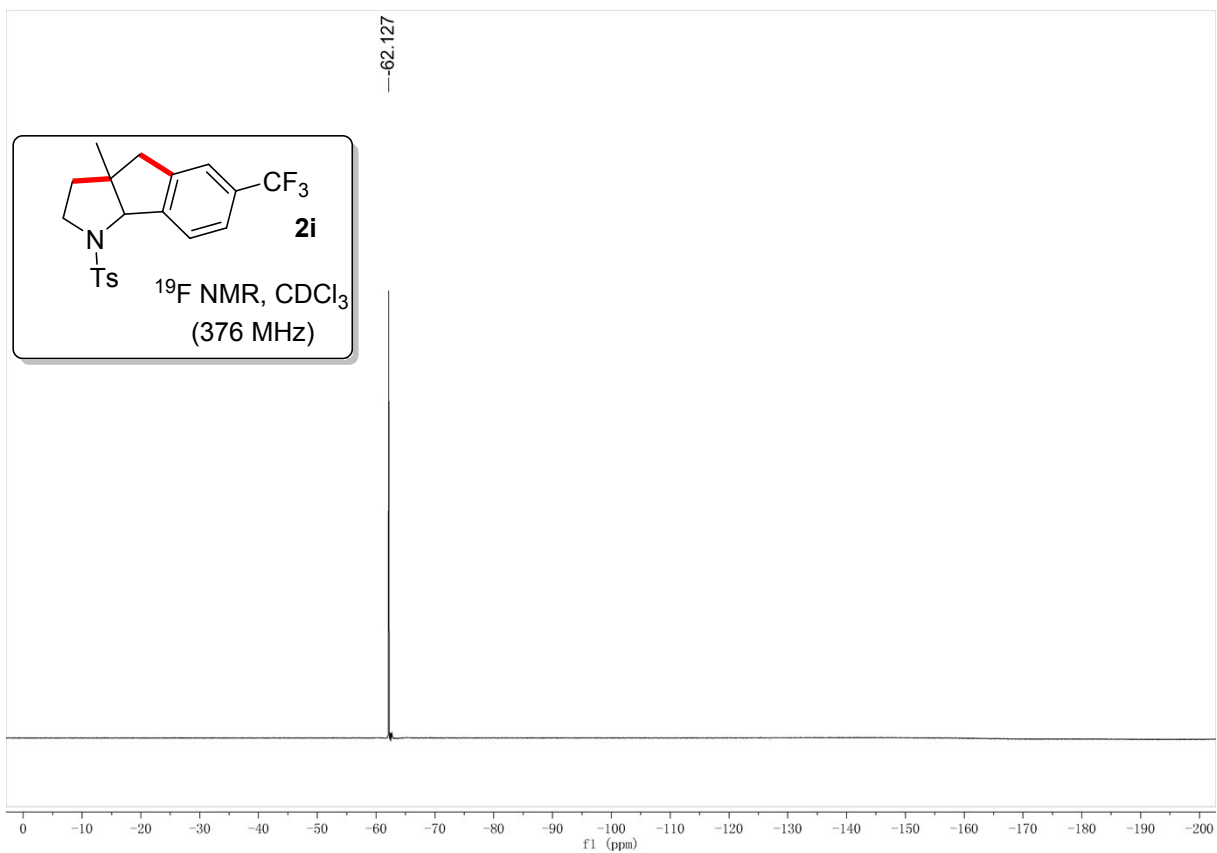
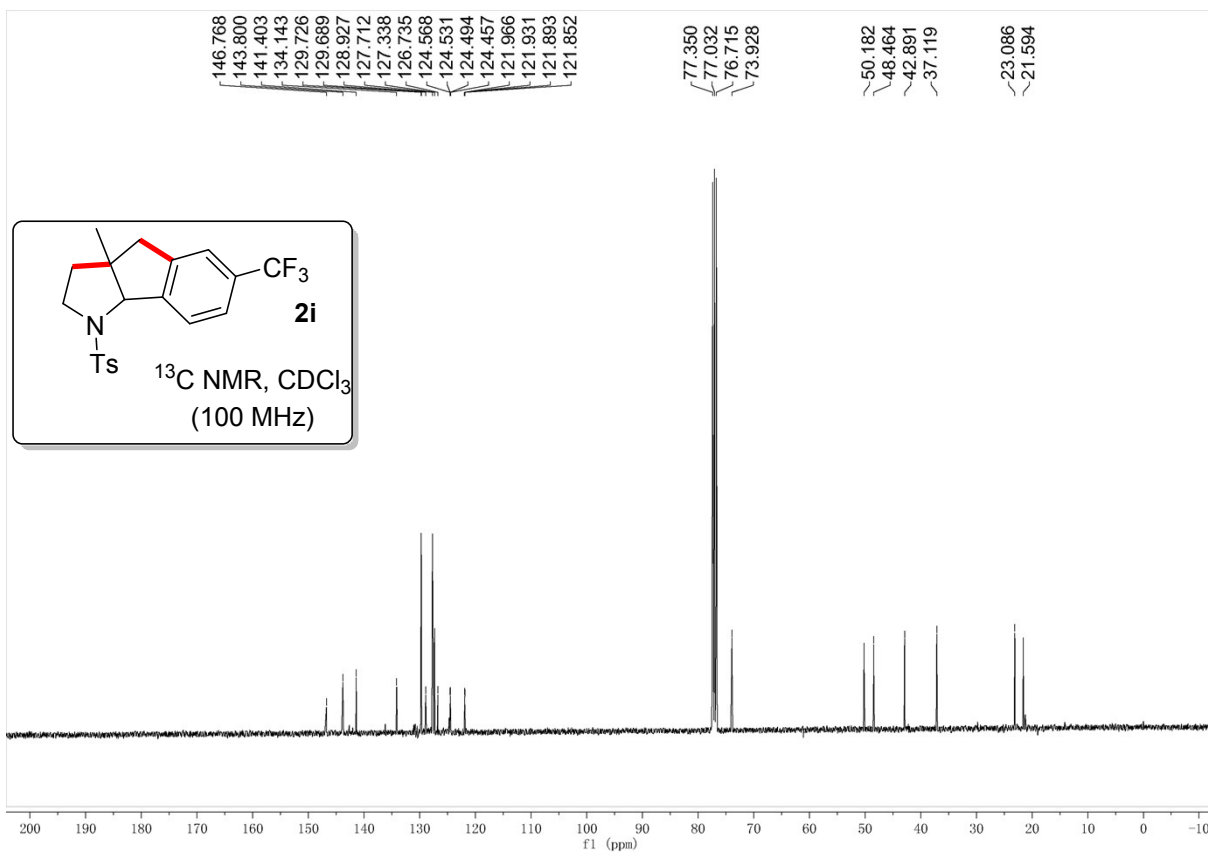


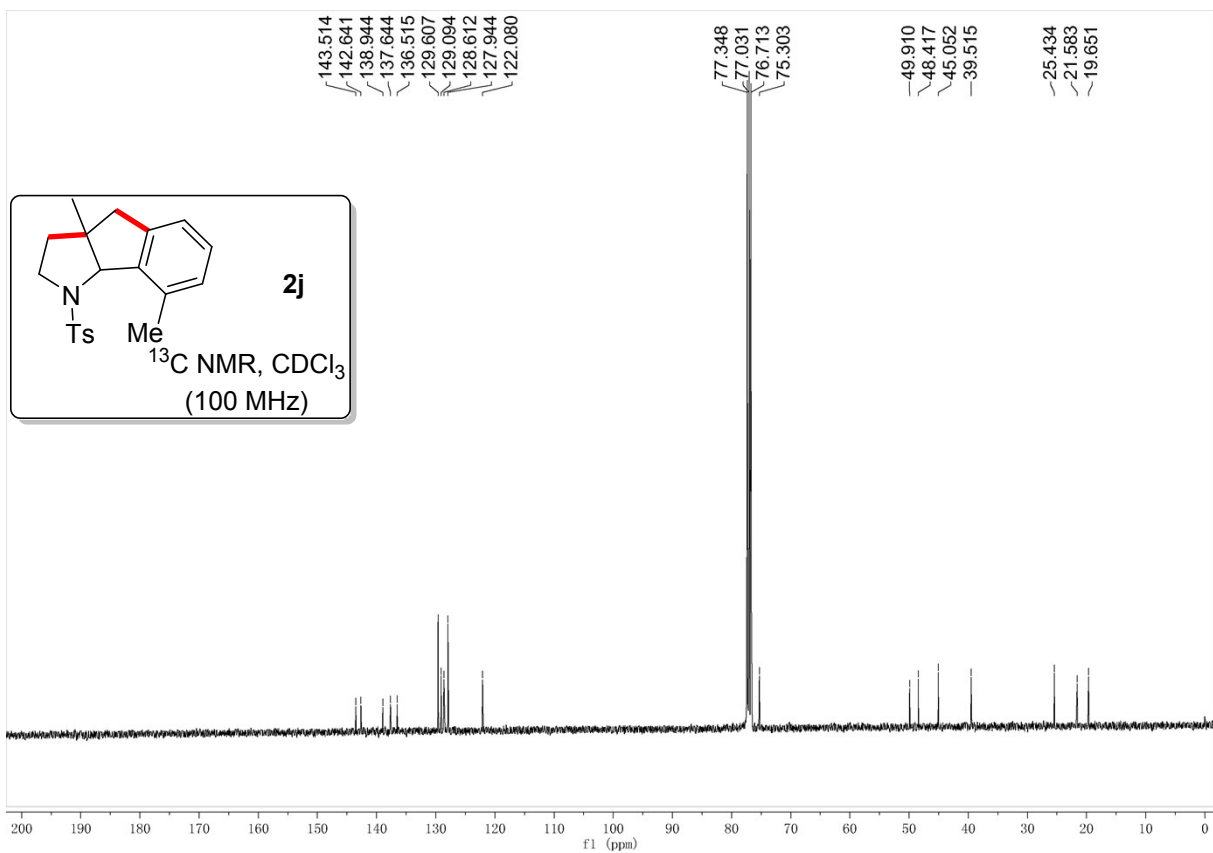
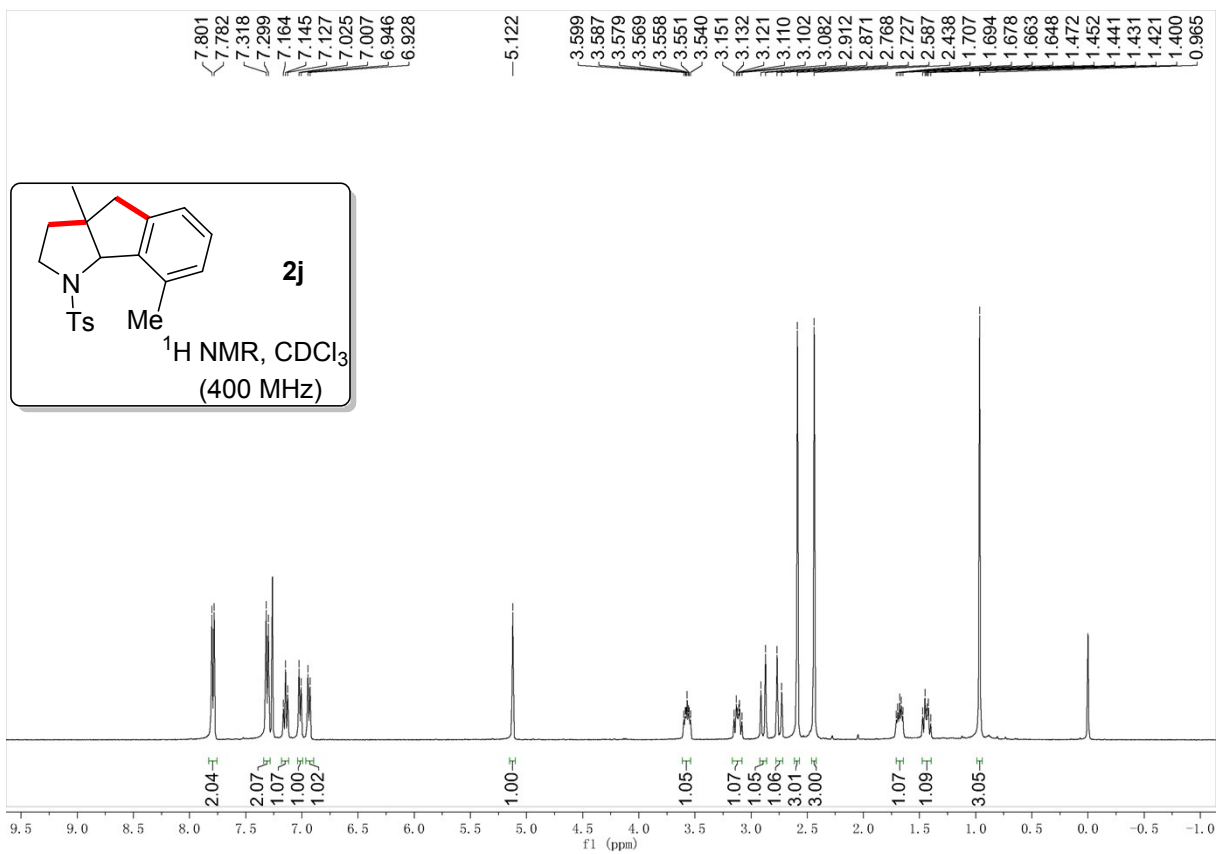












5. Copies of the ^1H NMR and ^{13}C NMR for Starting Material

