

Supporting Information

Copper(I)-Catalyzed 5-*exo-trig* Radical Cyclization/Borylation of Alkyl Halides: Access to Functionalized Pyrrolidine Derivates

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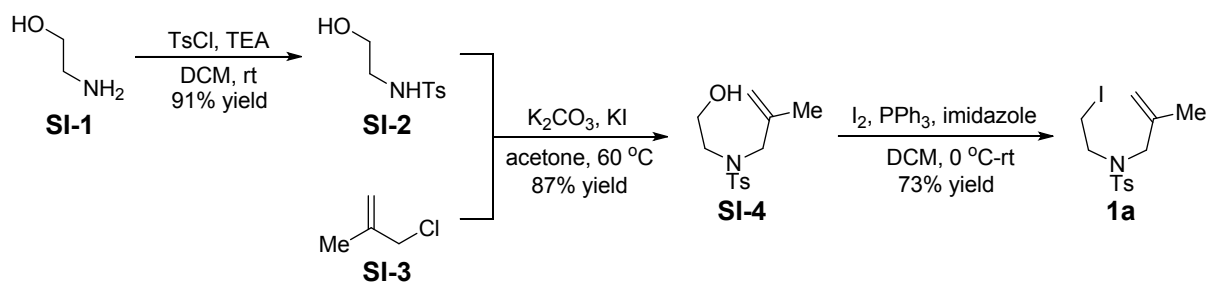
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1. General Information

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. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

2. Preparation of Starting Material.

General Procedure I:

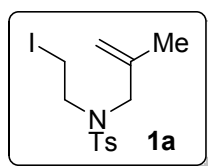


Preparation of alcohol SI-2: To a solution of 2-Aminoethanol **SI-1** (12.2 g, 200 mmol, 1.0 equiv) in DCM (150 mL) at room temperature was added TsCl (38.0 g, 200 mmol, 1.0 equiv). Then a solution of triethylamine (22.2 g, 220 mmol, 1.1 equiv) in 50 mL DCM was added dropwise by constant pressure funnel under vigorous stirring. The mixture was stirred at room temperature over night and then washed with water (50 mL × 3). The organic layer was dried over Na₂SO₄ and concentrated to afford the crude alcohol **SI-2** (39.3 g, 183 mmol, 91% yield) as a white solid, which was used without further purification.

Preparation of alcohol SI-4: The **SI-2** (2.15 g, 10 mmol, 1.0 equiv) was dissolved in 40 mL acetone, and **SI-3** (1.2 mL, 12 mmol, 1.2 equiv), K₂CO₃ (1.66 g, 12 mmol, 1.2 equiv), KI (0.33 g, 2 mmol, 0.2 equiv) was added successively. The mixture was stirred and refluxed at 60 °C over night. Then the reaction system was quenched with water, the organic layer was exacted 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, 2:1) to give the alcohol **SI-4** (2.33 g, 8.65 mmol, 87% yield) as light yellow solid.

Preparation of alkyl iodide 1a: To a solution of **SI-4** (1.66 g, 5 mmol, 1.0 equiv) in 40 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 6 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** (1.39 g, 3.67 mmol, 73% yield) as a white solid.

Analytical Data:



***N*-(2-iodoethyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide**

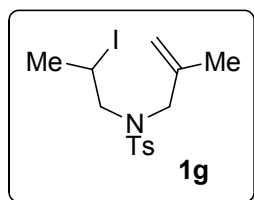
C₁₃H₁₈INO₂S

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

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.69 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.93 (s, 1H), 4.88 (s, 1H), 3.67 (s, 2H), 3.39 (t, *J* = 8.4 Hz, 2H), 3.19 (t, *J* = 8.4 Hz, 2H), 2.43 (s, 3H), 1.73 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.6, 140.5, 136.2, 129.8, 127.1, 115.3, 55.5, 50.8, 21.5, 19.7, 1.7.

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***N*-(2-iodopropyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide**

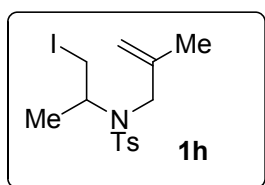
C₁₄H₂₀INO₂S

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

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.69 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.91 (s, 1H), 4.85 (s, 1H), 4.31-4.26 (m, 1H), 3.78 (d, *J* = 14.8 Hz, 1H), 3.55-3.47 (m, 2H), 3.36 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.43 (s, 3H), 1.90 (d, *J* = 6.8 Hz, 3H), 1.68 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.6, 140.5, 136.0, 129.7, 127.3, 115.6, 58.3, 56.5, 25.4, 24.0, 21.5, 19.9.

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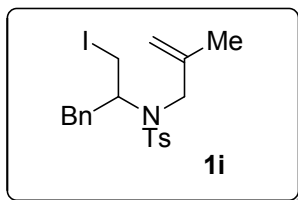
***N*-(1-iodopropan-2-yl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide**

C₁₄H₂₀INO₂S

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

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.69 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.94 (s, 1H), 4.91 (s, 1H), 4.09-4.00 (m, 1H), 3.85 (d, *J* = 15.6 Hz, 1H), 3.64 (d, *J* = 15.6 Hz, 1H), 3.34-3.30 (m, 1H), 3.14 (t, *J* = 9.6 Hz, 1H), 2.42 (s, 3H), 1.78 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 143.4, 142.6, 137.5, 129.7, 127.1, 114.3, 56.1, 50.5, 21.5, 19.9, 17.0, 8.5.



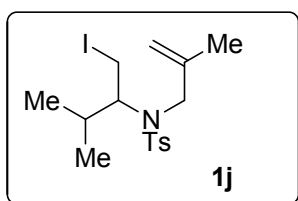
***N*-(1-iodo-3-phenylpropan-2-yl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide**

$\text{C}_{20}\text{H}_{24}\text{INO}_2\text{S}$

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

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.69 (d, $J = 8.0$ Hz, 2H), 7.56 (s, 2H), 7.24 (s, 3H), 7.14-7.12 (m, 2H), 5.02 (d, $J = 12.4$ Hz, 2H), 4.12 (t, $J = 6.80$ Hz, 1H), 3.86 (d, $J = 9.20$ Hz, 2H), 3.50-3.45 (m, 1H), 3.34-3.30 (m, 1H), 3.12-3.10 (m, 2H), 2.43 (s, 3H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 143.2, 142.4, 137.6, 137.2, 128.8, 128.5, 127.4, 126.5, 115.3, 62.4, 51.7, 38.9, 21.4, 20.0, 6.2.



***N*-(1-iodo-3-methylbutan-2-yl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide**

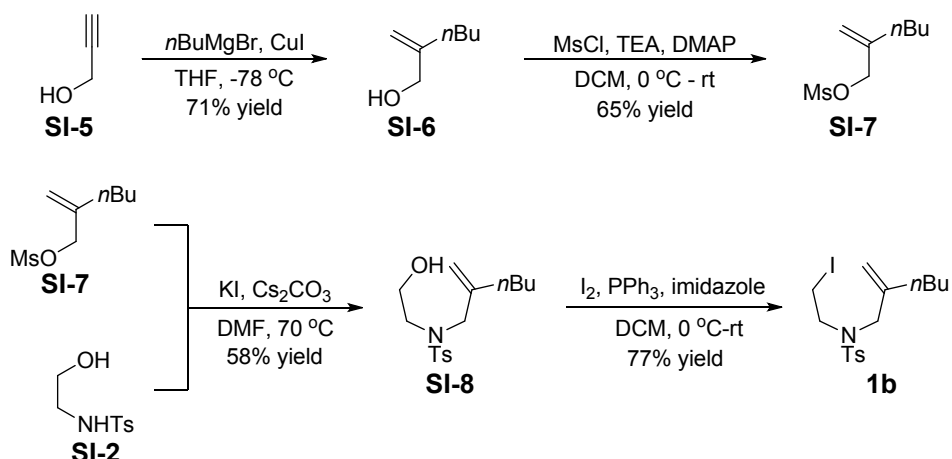
$\text{C}_{16}\text{H}_{24}\text{INO}_2\text{S}$

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

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.77 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 4.97 (s, 1H), 4.90 (s, 1H), 3.81 (d, $J = 16.0$ Hz, 1H), 3.74-3.68 (m, 2H), 3.33 (dd, $J = 11.2, 4.8$ Hz, 1H), 3.21 (dd, $J = 10.8, 6.8$ Hz, 1H), 2.42 (s, 3H), 2.06-1.97 (m, 1H), 1.71 (s, 3H), 1.02 (d, $J = 6.4$ Hz, 3H), 0.90 (d, $J = 6.8$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 142.1, 137.7, 129.4, 127.9, 115.2, 66.2, 51.3, 32.3, 21.5, 20.8, 20.6, 20.5, 5.2.

General Procedure II:



Preparation of alcohol **SI-6**:

All of the following operations were carried out under a nitrogen atmosphere.

(1) In a 250 mL oven-dried three-necked round bottom flask, Mg (2.19 g, 90 mmol, 2.5 equiv) and dry THF (5 mL) was added under a nitrogen atmosphere. Then 0.3 mL of $n\text{BuBr}$ was added by a syringe. The mixture was heated at $70\text{ }^\circ\text{C}$ until the colorless solution turned to light taupe, then the hot plate was removed. A solution of $n\text{BuBr}$ (9.6 mL, 90 mmol, 2.5 equiv) in dry THF (90 mL) was added dropwise. The resulting mixture was stirred at room temperature for 2 h, until the Mg was completely consumed, to give the solution of $n\text{BuMgBr}$ (90 mmol, 2.5 equiv).

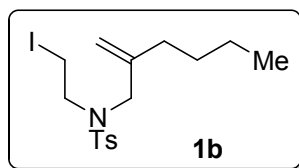
(2) In another 250 mL oven-dried three-necked round bottom flask, propargyl alcohol **SI-5** (2.1 mL, 36 mmol, 1.0 equiv) was dissolved in dry THF (40 mL). Then CuI (0.343g, 1.8 mmol, 0.1 equiv) was added under stirring. The suspension was cooled to $-78\text{ }^\circ\text{C}$. Then a solution of $n\text{BuMgBr}$ (90 mmol, 2.5 equiv) in THF (95 mL) was added dropwise by constant pressure funnel under vigorous stirring. The resulting mixture held at $-78\text{ }^\circ\text{C}$ for 1 h. Then it was warmed to room temperature and stirred for 18 h. The mixture was cooled to $-78\text{ }^\circ\text{C}$ again and quenched slowly with H_2O (10 mL). After the suspension was warmed to room temperature, dilute HCl solution (1 N, 150 mL) was added and the aqueous layer was extracted with EtOAc ($70\text{ mL} \times 3$). The combined organic layers were washed brine (50 mL), dried with Na_2SO_4 , and concentrated *in vacuo*. Purification by column chromatography (PE:EA, 3:1) afforded the **SI-6** (2.90 g, 25.4 mmol, 71%) as a light yellow liquid.

Preparation of alkene SI-7: In a 50 mL oven-dried round bottom flask **SI-6** (571.0 mg, 5.0 mmol, 1.0 equiv) was dissolved in DCM (12 mL). TEA (1.4 mL, 10.0 mmol, 2.0 equiv), DMAP (61.1 mg, 0.5 mmol, 0.1 equiv) was added successively to this solution. Then a solution of MsCl (0.43 mL, 5.5 mmol, 1.1 equiv) in 3 mL DCM was added dropwise at 0 °C. The resulting mixture was stirred at room temperature for 1.5 h and quenched with aq. NH₄Cl. Then dilute HCl solution (1 N, 15 mL) was added and the aqueous layer was extracted with DCM (10 mL × 3). The combined organic layers were washed brine (10 mL), dried with Na₂SO₄, and concentrated *in vacuo*. Purification by column chromatography (PE:EA, 3:1) afforded the **SI-7** (630.6 mg, 3.3 mmol, 65%) as a colorless oil.

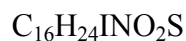
Preparation of alcohol SI-8: In a 50 mL oven-dried round bottom flask **SI-7** (630.6 mg, 3.3 mmol, 1.0 equiv) was dissolved in *N,N*-dimethylformamide (20 mL), and then **SI-2** (861.1 mg, 4.0 mmol, 1.2 equiv), Cs₂CO₃ (2.69 g, 8.3 mmol, 2.5 equiv), KI (116.2 mg, 0.7 mmol, 0.2 equiv) was added successively. The mixture was stirred and refluxed at 70 °C for 5 h. Then the reaction system was quenched with water, the organic layer was exacted with 80 mL AcOEt. The organic extracts were washed with water (25 mL × 3). Drying over Na₂SO₄ and concentration *in vacuo*, the crude material was purified by silica gel column chromatography (PE:EA, 3:1) to give the alcohol **SI-8** (601.1 mg, 1.9 mmol, 58% yield) as colorless oil.

Preparation of alkyl iodide 1b: To a solution of **SI-8** (601.1 mg, 1.9 mmol, 1.0 equiv) in 20 mL DCM was cooled to 0 °C. PPh₃ (1.50 g, 5.7 mmol, 3.0 equiv), imidazole (388.1 mg, 5.7 mmol, 3.0 equiv), I₂ (1.45 g, 5.7 mmol, 3.0 equiv) was added successively. Then the reaction mixture was warmed to room temperature and stirred for 6 h. Then 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 **1b** (616.4 mg, 1.5 mmol, 77% yield) as a white solid.

Analytical Data:



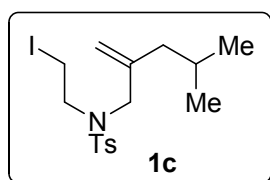
N-(2-iodoethyl)-4-methyl-*N*-(2-methylenehexyl)benzenesulfonamide



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

1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.69 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 4.93 (s, 1H), 4.90 (s, 1H), 3.68 (s, 2H), 3.40-3.63 (m, 2H), 3.20-3.16 (m, 2H), 2.43 (s, 3H), 2.00 (t, $J = 7.6$ Hz, 2H), 1.42-1.35 (m, 2H), 1.33-1.24 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.6, 143.6, 136.3, 129.8, 127.2, 114.2, 54.2, 50.7, 32.5, 29.6, 22.4, 21.5, 13.9, 1.7.



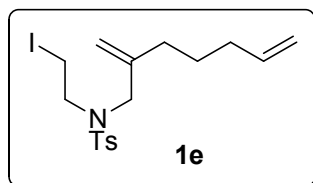
N-(2-iodoethyl)-4-methyl-*N*-(4-methyl-2-methylenepentyl)benzenesulfonamide



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

1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.69 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 4.94 (s, 1H), 4.91 (s, 1H), 3.65 (s, 2H), 3.41-3.37 (m, 2H), 3.21-3.17 (m, 2H), 2.43 (s, 3H), 1.89 (d, $J = 7.2$ Hz, 2H), 1.79-1.69 (m, 1H), 0.85 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 143.2, 136.2, 129.8, 127.2, 115.7, 53.9, 50.7, 42.4, 27.8, 25.9, 22.3, 21.5, 1.6.



N-(2-iodoethyl)-4-methyl-*N*-(2-methylenehept-6-en-1-yl)benzenesulfonamide

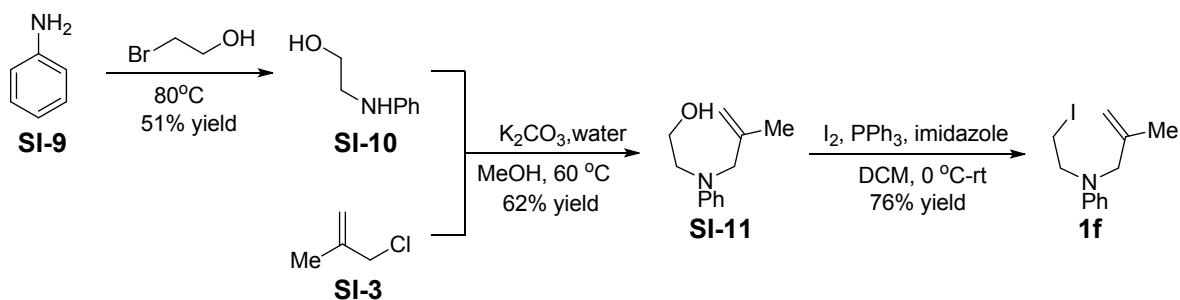
C₁₇H₂₄INO₂S

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

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.63 (d, *J* = 12.00 Hz, 2H), 7.25 (d, *J* = 8.00 Hz, 2H), 5.77-5.67 (m, 1H), 4.96-4.91 (m, 2H), 4.87 (d, *J* = 8.00 Hz, 2H), 3.61 (s, 2H), 3.32 (t, *J* = 8.00 Hz, 2H), 3.11 (t, *J* = 8.00 Hz, 2H), 2.36 (s, 3H), 1.97-1.96 (m, 2H), 1.96-1.94 (m, 2H), 1.49-1.43 (m, 2H).

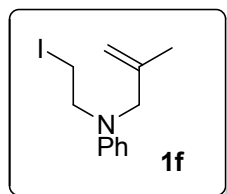
¹³C NMR (100 MHz, CDCl₃, δ ppm): 142.7, 142.0, 136.7, 134.6, 128.2, 125.5, 113.2, 112.9, 52.5, 49.1, 31.6, 30.6, 25.0, 19.9, 0.0.

General Procedure III:



Preparation of alcohol SI-10: Aniline (1.23 g, 13.2 mmol, 1.1 equiv) and 2-bromoethanol (1.50 g, 12.0 mmol, 1.0 equiv) were charged in a reaction bottle. The mixture was heated at 80°C for 1 h, and the reaction monitored by TLC. The reaction mixture was allowed to come to room temperature and basified with a saturated solution of sodium bicarbonate. The mixture was extracted with EtOAc (30 mL \times 2). The combined organic layer was dried over Na_2SO_4 and concentrated to afford the crude material, which was then purified by silica gel column chromatography (PE:EA, 2:1) to give the alcohol **SI-10** (0.84 g, 6.12 mmol, 51% yield) as light yellow oil. The other compound was prepared according to **general procedure I**.

Analytical Data:



N-(2-iodoethyl)-*N*-(2-methylallyl)aniline

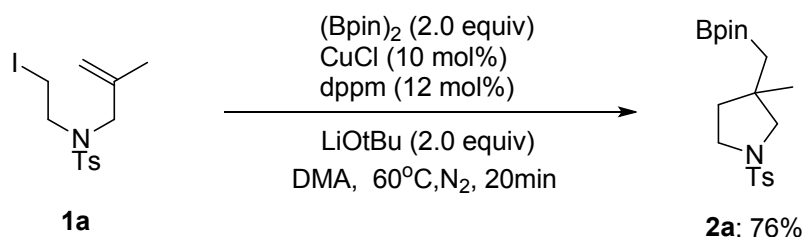
$C_{12}H_{16}IN$

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

1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.18-7.12 (m, 2H), 6.66-6.63 (m, 1H), 6.56 (d, $J = 8.0$ Hz, 2H), 4.79-4.78 (m, 1H), 4.70 (s, 1), 3.76 (s, 2H), 3.65 (t, $J = 8.0$ Hz, 2H), 3.19-3.14 (m, 2H), 1.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 145.2, 138.5, 127.4, 115.0, 109.9, 109.0, 54.6, 52.0, 18.0, 0.0.

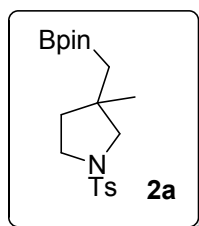
3. Typical Procedure and Analytical Data for Copper(I)-Catalyzed 5-exo-trig Cyclization/Borylation Reaction.



Typical Procedure:

Unactivated alkyl iodide **1a** (75.9 mg, 0.20 mmol, 1.0 equiv), (Bpin)₂ (101.6 mg, 0.40 mmol, 2.0 equiv), CuCl (2.0 mg, 0.02 mmol, 0.1 equiv), dppm (9.23 mg, 0.024 mmol, 0.12 equiv) and LiOtBu (32.0 mg, 0.40 mmol, 2.0 equiv) were added to a reaction tube and vacuum purged three times, backfilling with N₂. Then the N,N-Dimethylaniline (2 mL) was added under nitrogen atmosphere. The resulting mixture was stirred at 60 °C for 20 min. After cooling the reaction mixture at room temperature, it was quenched by H₂O and extracted with EtOAc three times. The combined organic phase was dried over MgSO₄ and then concentrated *in vacuo*. The mixture was purified by silica gel column chromatography (PE:EA, 20:1) to give the reductive product **2a** (57.6 mg, 0.15 mmol, 76% yield).

Analytical Data:



3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

$C_{19}H_{30}BNO_4S$

MW: 379.32 g·mol⁻¹

White Solid

Melting Point: 77.3°C

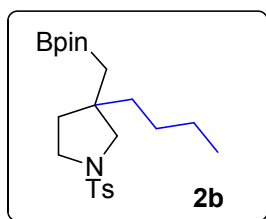
Isolated Amount: 57.6 mg

Yield: 76%

¹H NMR (600 MHz, CDCl₃, δ ppm): 7.65 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.25-3.21 (m, 2H), 2.99 (dd, *J* = 22.4, 9.6 Hz, 2H), 2.35 (s, 3H), 1.57-1.53 (m, 2H), 1.13 (d, *J* = 2.4 Hz, 12H), 0.86 (s, 3H), 0.72 (s, 2H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.0, 134.4, 129.5, 127.5, 83.1, 60.6, 46.8, 40.0, 39.5, 25.6, 24.8, 21.5.

MS (EI) *m/z* 379 (M⁺); **HRMS (ESI)** Calcd for C₁₉H₃₀BNO₄S+H 380.2067, Found 380.2069.



3-butyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

$C_{22}H_{36}BNO_4S$

MW: 421.40 g·mol⁻¹

White Solid

Melting Point: 76.8°C

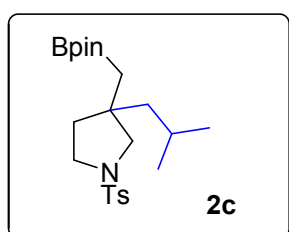
Isolated Amount: 65.7 mg

Yield: 78%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.72 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.30-3.25 (m, 2H), 3.08 (s, 2H), 2.42 (s, 3H), 1.68-1.64 (m, 2H), 1.27 (d, *J* = 15.6 Hz, 3H), 1.19 (d, *J* = 2.8 Hz, 15H), 0.85-0.81 (m, 3H), 0.74 (s, 2H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.0, 137.4, 129.5, 127.5, 83.0, 59.3, 58.0, 46.8, 43.4, 37.9, 29.2, 27.0, 24.8, 23.3, 21.1, 14.0.

MS (EI) *m/z* 421 (M⁺); **HRMS (ESI)** Calcd for C₂₂H₃₆BNO₄S+H 422.2536, Found 422.2537.



3-isobutyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

$C_{22}H_{36}BNO_4S$

MW: 421.40 $g \cdot mol^{-1}$

White Solid

Melting Point: 76.2°C

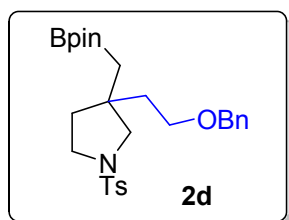
Isolated Amount: 48.0 mg

Yield: 57%

1H NMR (400 MHz, DMSO, δ ppm): 7.65 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 3.24-3.18 (m, 2H), 3.12 (d, $J = 9.6$ Hz, 1H), 2.93 (d, $J = 9.6$ Hz, 1H), 2.35 (s, 3H), 1.71-1.65 (m, 1H), 1.57-1.53 (m, 2H), 1.18-1.16 (m, 2H), 1.12 (d, $J = 4.0$ Hz, 12H), 0.76 (d, $J = 6.4$ Hz, 6H), 0.68 (s, 2H).

^{13}C NMR (100 MHz, DMSO, δ ppm): 143.0, 134.4, 129.5, 127.5, 83.0, 60.2, 47.5, 46.5, 43.6, 38.8, 25.0, 24.8, 24.8, 24.5, 24.3, 21.5.

MS (EI) m/z 421 (M⁺); HRMS (ESI) Calcd for $C_{22}H_{36}BNO_4S+H$ 422.2536, Found 422.2535.



3-(2-(benzyloxy)ethyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

$C_{27}H_{38}BNO_5S$

MW: 499.47 $g \cdot mol^{-1}$

Colorless Oil

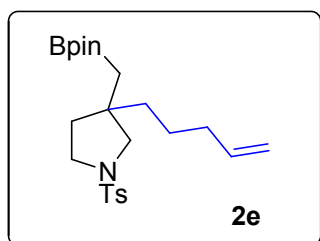
Isolated Amount: 50.0 mg

Yield: 46%

1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.63 (d, $J = 8.4$ Hz, 2H), 7.26-7.19 (m, 7H), 4.35 (s, 2H), 3.38-3.36 (m, 2H), 3.24-3.18 (m, 2H), 3.05 (s, 2H), 2.33 (s, 3H), 1.65-1.57 (m, 4H), 1.10 (d, $J = 2.4$ Hz, 12H), 0.71 (d, $J = 1.6$ Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.1, 138.4, 134.2, 130.9, 129.5, 128.3, 127.5, 83.1, 73.0, 67.3, 59.8, 46.6, 42.3, 38.3, 37.9, 24.8, 21.2, 18.9.

MS (EI) m/z 499 (M⁺); HRMS (ESI) Calcd for $C_{27}H_{38}BNO_5S+H$ 500.2642, Found 500.2640.



3-(pent-4-en-1-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

$C_{23}H_{36}BNO_4S$ MW: 433.41 g·mol⁻¹

Yellow Oil

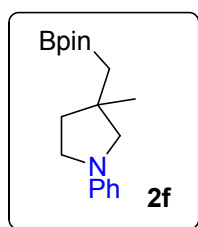
Isolated Amount: 52.0 mg **Yield:** 60%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.65 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.68-5.61 (m, 1H), 4.90-4.83 (m, 2H), 3.23-3.18 (m, 2H), 3.0 (s, 2H), 1.83 (d, *J* = 6.4 Hz, 2H), 1.61-1.56 (m, 2H), 1.17-1.15 (m, 4H), 1.12 (d, *J* = 2.8 Hz, 12H), 0.68 (s, 2H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.1, 138.5, 134.2, 129.5, 127.5, 114.6, 83.1, 59.2, 46.7, 43.3, 38.1, 37.9, 34.2, 24.8, 24.1, 21.5.

MS (EI) *m/z* 433 (M⁺); **HRMS (ESI)** Calcd for C₂₃H₃₆BNO₄S+H 434.2536, Found 434.2539.

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3-methyl-1-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidine

$C_{18}H_{28}BNO_2$ MW: 301.23 g·mol⁻¹

White Solid **Melting Point:** 77.4°C

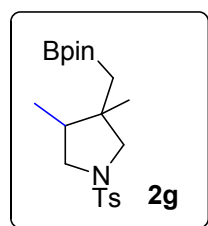
Isolated Amount: 36.8 mg **Yield:** 61%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.17-7.11 (m, 2H), 6.55 (t, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 2H), 3.29-3.25 (m, 2H), 3.03 (dd, *J* = 24.0, 8.8 Hz, 2H), 1.83-1.72 (m, 2H), 1.17 (s, 12H), 1.08 (s, 3H), 0.96 (s, 2H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 148.1, 129.1, 115.0, 111.3, 100.0, 83.0, 61.0, 46.8, 39.7, 39.6, 26.4, 24.9, 24.8.

MS (EI) *m/z* 301 (M⁺); **HRMS (ESI)** Calcd for C₁₈H₂₈BNO₂+H 302.2291, Found 302.2294.

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3,4-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

$C_{20}H_{32}BNO_4S$ MW: 393.35 g·mol⁻¹

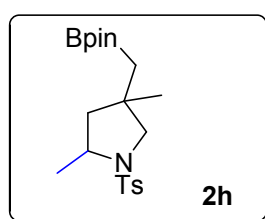
Yellow Oil.

Isolated Amount: 63.7 mg **Yield:** 81%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.66 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.43-3.36 (m, 2H), 2.93 (d, *J* = 10.0 Hz, 1H), 2.77 (d, *J* = 9.6 Hz, 1H), 2.34 (s, 3H), 1.72-1.67 (m, 1H), 1.15 (d, *J* = 6.8 Hz, 12H), 0.86 (s, 3H), 0.66 (d, *J* = 6.8 Hz, 3H), 0.43 (dd, *J* = 72.0, 15.2 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 142.9, 134.6, 129.5, 127.5, 83.1, 59.5, 43.5, 41.9, 24.9, 24.7, 24.5, 21.5, 12.3.

MS (EI) *m/z* 393 (M⁺); **HRMS (ESI)** Calcd for C₂₀H₃₂BNO₄S+H 394.2223, Found 394.2225.



2,4-dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

C₂₀H₃₂BNO₄S MW: 393.35 g·mol⁻¹

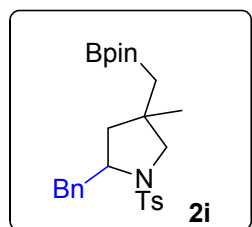
Yellow Oil.

Isolated Amount: 65.3 mg **Yield:** 83%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.65 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.61-3.56 (m, 1H), 3.14 (s, 0.85H), 3.12 (s, 0.15H), 2.34 (s, 3H), 1.78-1.73 (m, 1H), 1.42-1.37 (m, 1H), 1.31 (d, *J* = 6.0 Hz, 3H), 1.14 (s, 12H), 0.80 (s, 2H), 0.46 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 142.9, 135.9, 129.4, 127.4, 83.1, 61.8, 55.8, 49.3, 38.6, 25.2, 24.8, 22.6, 21.5.

MS (EI) *m/z* 393 (M⁺); **HRMS (ESI)** Calcd for C₂₀H₃₂BNO₄S+H 394.2223, Found 394.2222.



2-benzyl-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

C₂₆H₃₆BNO₄S MW: 469.44 g·mol⁻¹

white solid

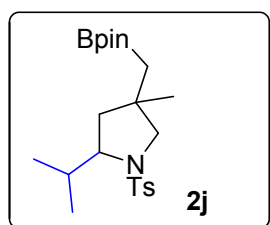
Melting Point: 77.8 °C

Isolated Amount: 76.1 mg **Yield:** 81%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.71 (d, *J* = 8.0 Hz, 2H), 7.25-7.13 (m, 7H), 3.73-3.66 (m, 1H), 3.47 (dd, *J* = 13.2, 3.2 Hz, 1H), 3.14 (dd, *J* = 26.8, 10.4 Hz, 2H), 2.73-2.68 (m, 1H), 2.35 (s, 3H), 1.52-1.46 (m, 2H), 1.12 (s, 12H), 0.78 (d, *J* = 18.0 Hz, 2H), 0.38 (s, 2.61H), 0.35 (s, 0.39H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.2, 138.6, 135.7, 129.6, 129.5, 128.3, 127.8, 127.5, 126.3, 83.1, 61.9, 61.4, 46.2, 42.8, 38.7, 25.3, 24.8, 24.7, 21.5.

MS (EI) m/z 469 (M⁺); **HRMS (ESI) Calcd** for C₂₆H₃₆BNO₄S+H 470.2536, Found 470.2533.



2-isopropyl-4-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

C₂₂H₃₆BNO₄S MW: 421.40 g·mol⁻¹

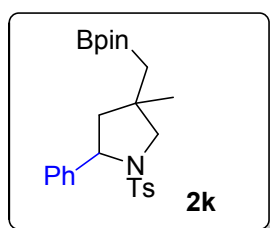
Yellow Oil.

Isolated Amount: 56.5 mg **Yield:** 67%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.65 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.62-3.57 (m, 1H), 3.30 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.00 (d, *J* = 11.2 Hz, 1H), 2.45-2.41 (m, 1H), 2.34 (s, 3H), 1.54-1.42 (m, 2H), 1.15 (s, 11.16H), 1.12 (s, 0.72H), 0.78-0.73 (m, 8H), 0.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 142.8, 136.7, 129.4, 127.4, 127.2, 83.1, 64.7, 62.0, 39.4, 38.6, 30.4, 25.4, 24.9, 24.8, 21.5, 19.2, 14.5.

MS (EI) m/z 421 (M⁺); **HRMS (ESI) Calcd** for C₂₂H₃₆BNO₄S+H 422.2536, Found 422.2538.



4-methyl-2-phenyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine

C₂₅H₃₄BNO₄S MW: 455.42 g·mol⁻¹

Yellow Oil.

Isolated Amount: 49.2 mg **Yield:** 54%

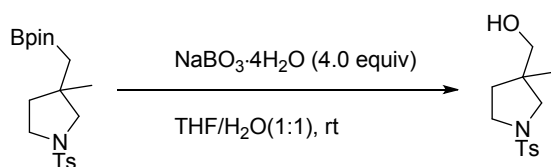
¹H NMR (400 MHz, CDCl₃, δ ppm): 7.43 (d, *J* = 8.0 Hz, 2H), 7.19-7.09 (m, 7H), 4.63-4.59 (m, 1H), 3.50 (d, *J* = 10.4 Hz, 1H), 3.33 (d, *J* = 10.8 Hz, 1H), 2.31 (s, 3H), 2.09-2.04 (m, 1H), 1.76-1.71 (m, 1H), 1.15 (s, 9.6 H), 1.13 (s, 2.4H), 0.85 (s, 2H), 0.71 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.1, 142.8, 136.3, 129.2, 128.2, 127.3, 126.7, 83.2, 63.7, 62.3, 51.8, 39.5, 25.1, 24.8, 21.5, 19.2.

MS (EI) m/z 455 (M⁺); **HRMS (ESI)** Calcd for C₂₅H₃₄BNO₄S+H 456.2380, Found 456.2382.

4. Derivatization of Borylation Products.

Experimental Procedure for the NaBO₃ Oxidation of 2a.

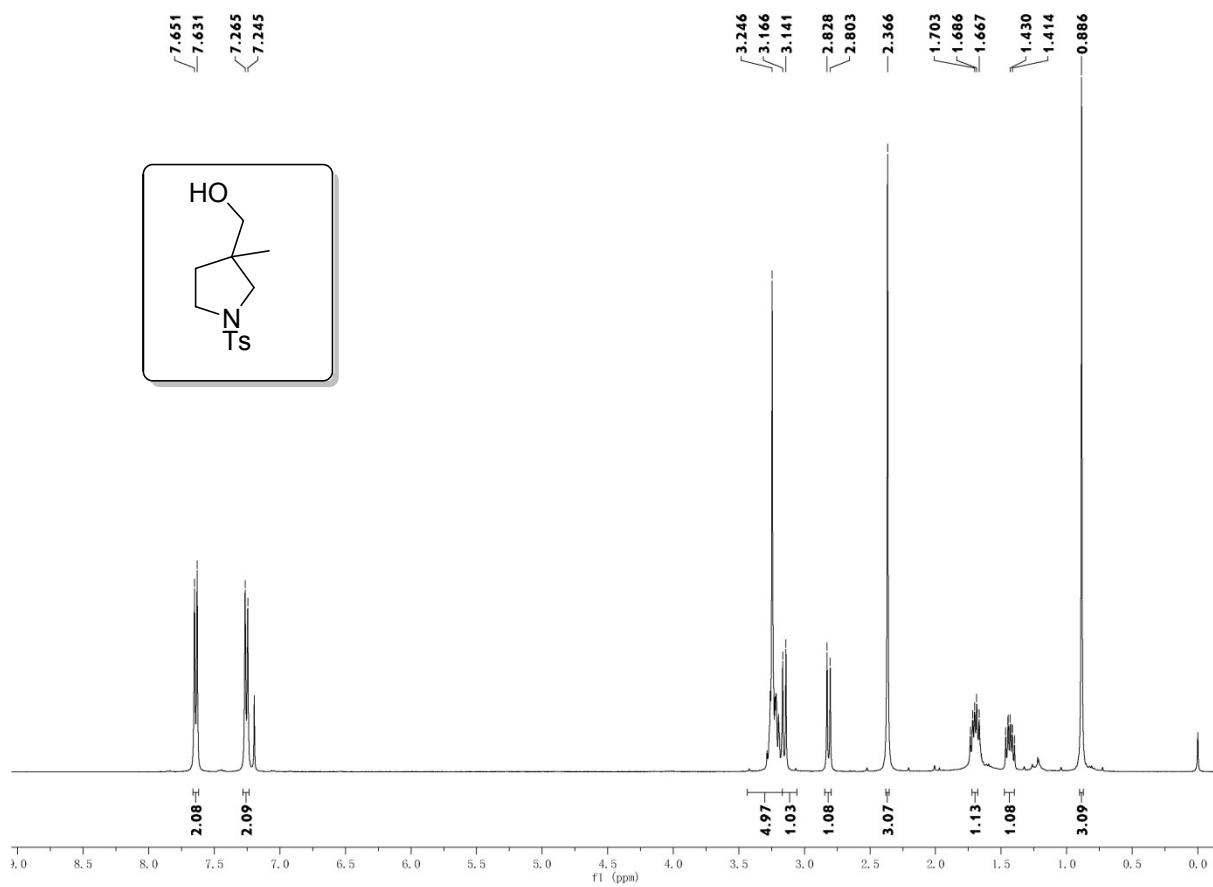


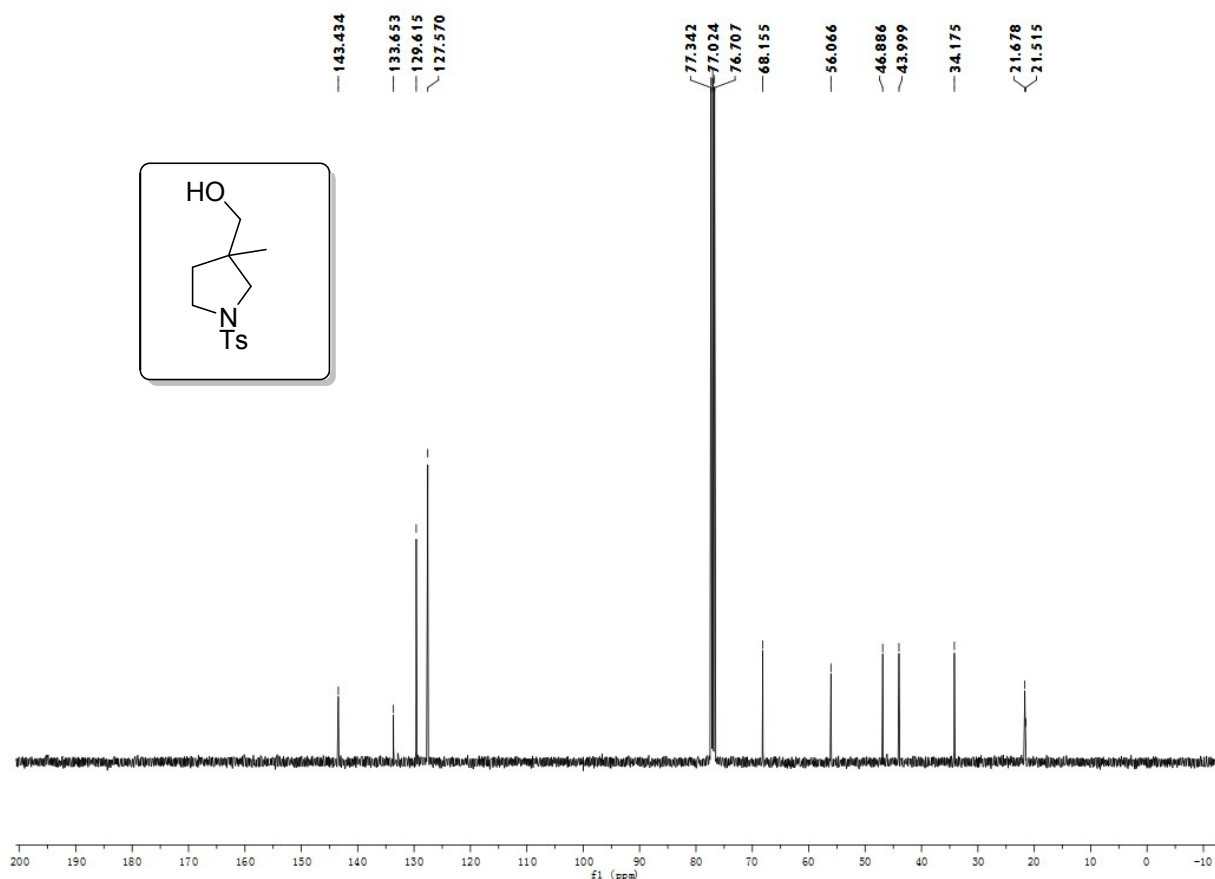
The oxidation was performed according to the literature procedure.

In a reaction vial, NaBO₃·4H₂O (123.1 mg, 0.8 mmol) was dissolved in THF/H₂O (1:1, 2 mL). **2a** (75.9 mg, 0.2 mmol) was then added at room temperature. After stirred for 5.5 h, the reaction mixture was extracted three times with EtOAc, dried over NaSO₄, and filtered. The crude material was purified by flash column chromatography to obtain the corresponding alcohol (46.3 mg, 0.17 mmol, 86%) as a white solid.

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.64 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.26-3.20 (m, 5H), 2.99 (dd, *J* = 135.2, 10.0 Hz, 2H), 2.37 (s, 3H), 1.74-1.67 (m, 1H), 1.47-1.40 (m, 1H), 0.89 (s, 3H).

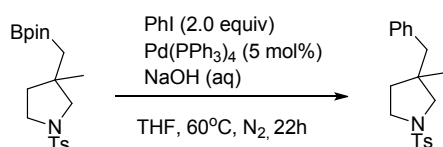
¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.4, 133.7, 129.6, 127.6, 68.2, 56.1, 46.9, 44.0, 34.2, 21.7, 21.5.



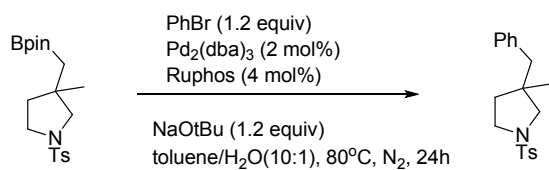


Experimental Procedure for the Suzuki cross-coupling of Borylation Product **2a**.

Suzuki cross-coupling reaction was performed according to the literature procedure. In these reactions, the low yields were obtained. It was only detected by the GCMS in the reaction system, not isolated.

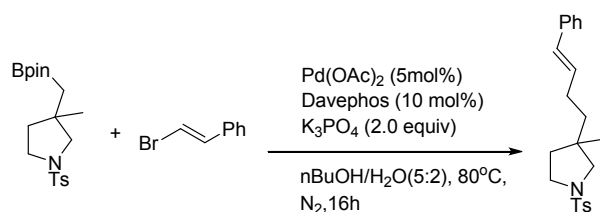


A mixture of Pd(PPh₃)₄ (5.8 mg, 0.005 mmol), PhI (40.8 mg, 0.2 mmol), NaOH (0.008 mL, 3.0 M aq.), and **2a** (37.9 mg, 0.1 mmol) was stirred in THF (1 mL) at 60°C for 22 h under a nitrogen atmosphere. After full consumption of starting material **2a** as monitored by TLC. Then the corresponding coupling product was traced by GCMS in the reaction system. However, the content was very little in the system.

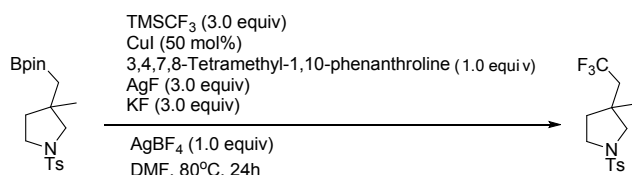


Pd₂(dba)₃ (3.7 mg, 0.004 mmol), NaOtBu (23.1 mg, 0.24 mmol), Ruphos (3.7 mg, 0.008 mmol), and bromobenzene (37.7 mg, 0.24 mmol) were added in an oven-dried reaction vial. Then toluene (0.5 mL) and H₂O (0.05 mL) and **2a** (75.9 mg, 0.2 mmol) were added in the vial

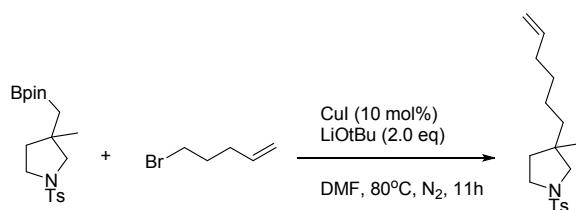
under a nitrogen atmosphere. The mixture was stirred at 80°C for 24 h. Upon completion, as judged by TLC analysis. And we detected the coupling product through GCMS in the reaction system, but the content was very little.



Pd(OAc)₂ (2.3 mg, 0.01 mmol.), Davephos (7.9 mg, 0.02 mmol), and K₃PO₄ (84.9 mg, 0.4 mmol) were added to a reaction tube. The tube was purged with N₂. And **2a** (75.9 mg, 0.2 mmol) in n-BuOH (2 mL) was added followed by water (0.8 mL) and (E)-2-bromovinylbenzene (36.6 mg, 0.2 mmol). The mixture was heated to 80°C for 16 h. The tube was purged with N₂. Upon completion, as judged by TLC analysis. The product is very light. In the reaction system, the product was only detected by GCMS.

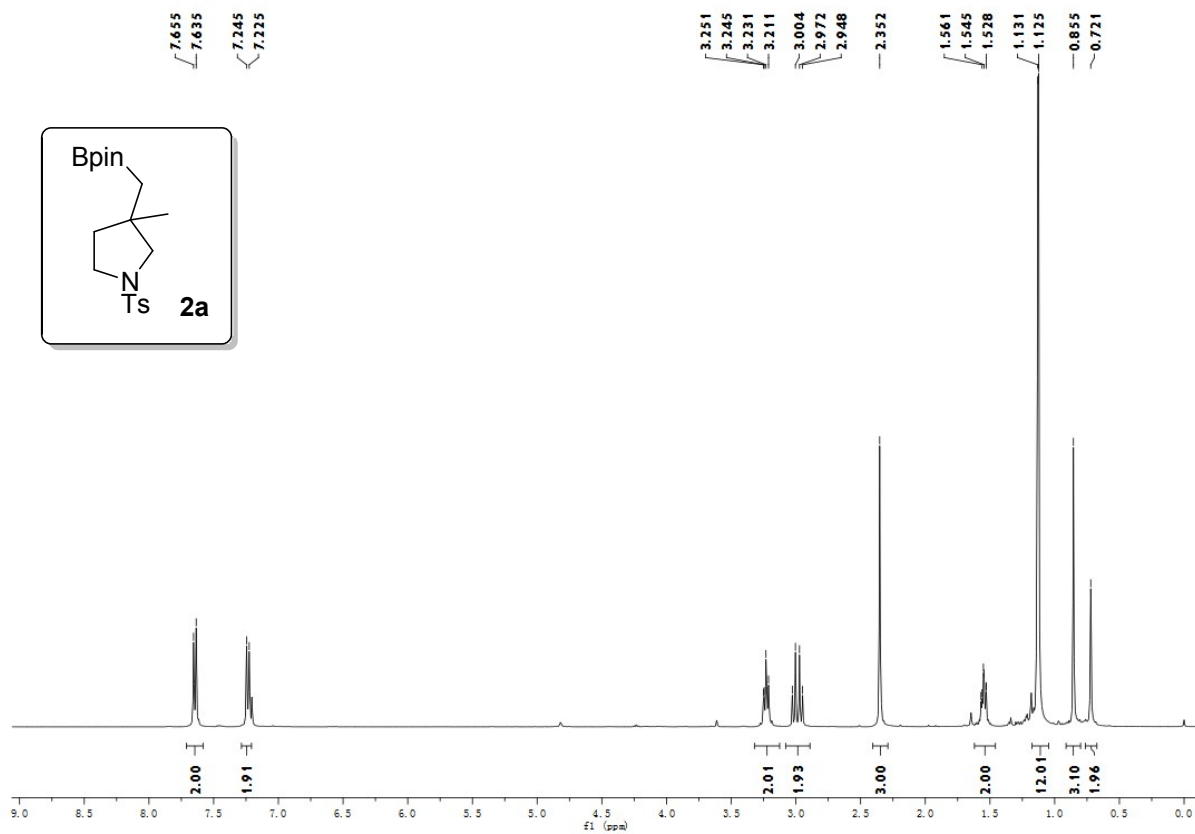


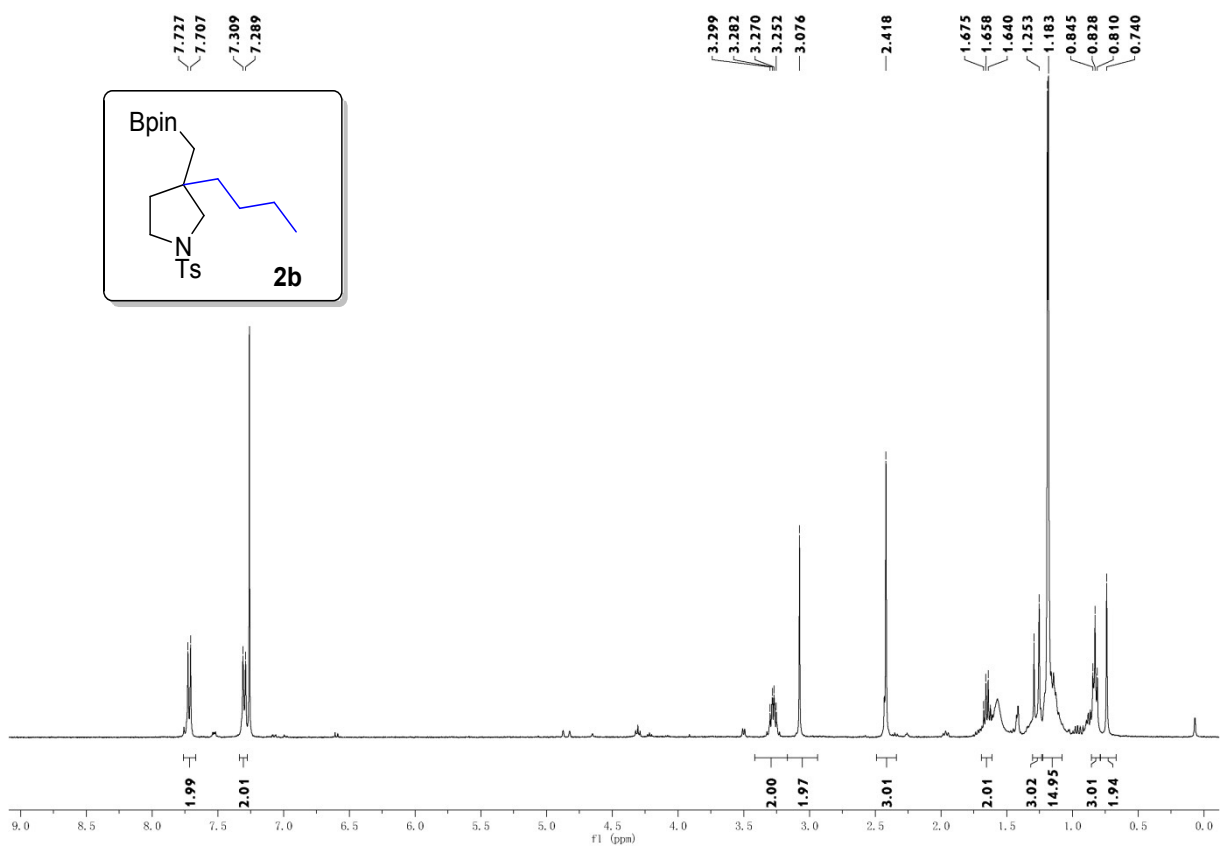
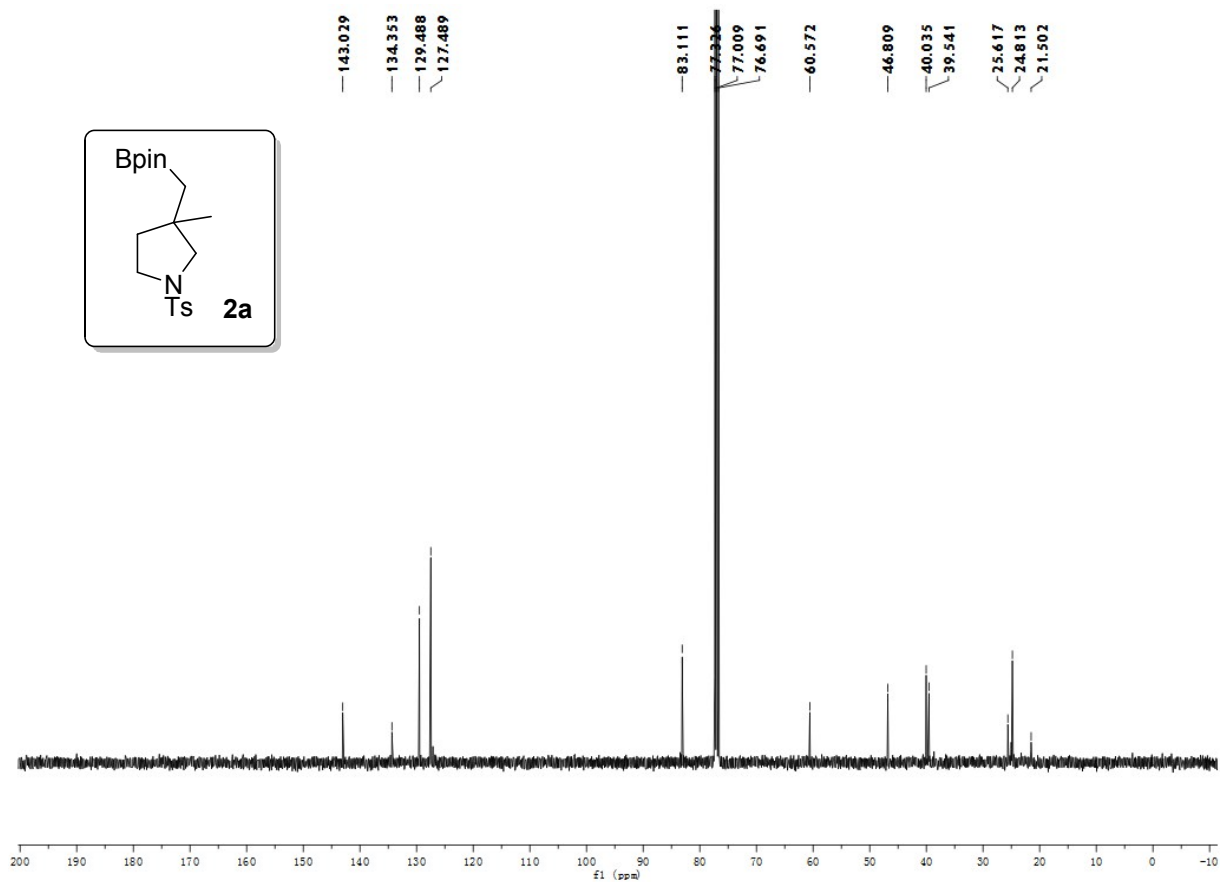
CuI (19.0 mg, 0.1 mmol), 3,4,7,8-Tetramethyl-1,10-phenanthroline (47.3 mg, 0.2 mmol), AgF (76.1 mg, 0.6 mmol), KF (34.9 mg, 0.6 mmol) and AgBF₄ (38.9 mg, 0.2 mmol) were added in an oven-dried reaction vial. Then **2a** (75.9 mg, 0.2 mmol) in DMF (1.5 mL) was added in the vial. Followed by TMSCF₃ (85.3 mg, 0.6 mmol) was added. The mixture was stirred at 80°C for 24 h under a nitrogen atmosphere. Upon completion, the desired product was not detected by GCMS in the reaction system, only the material.

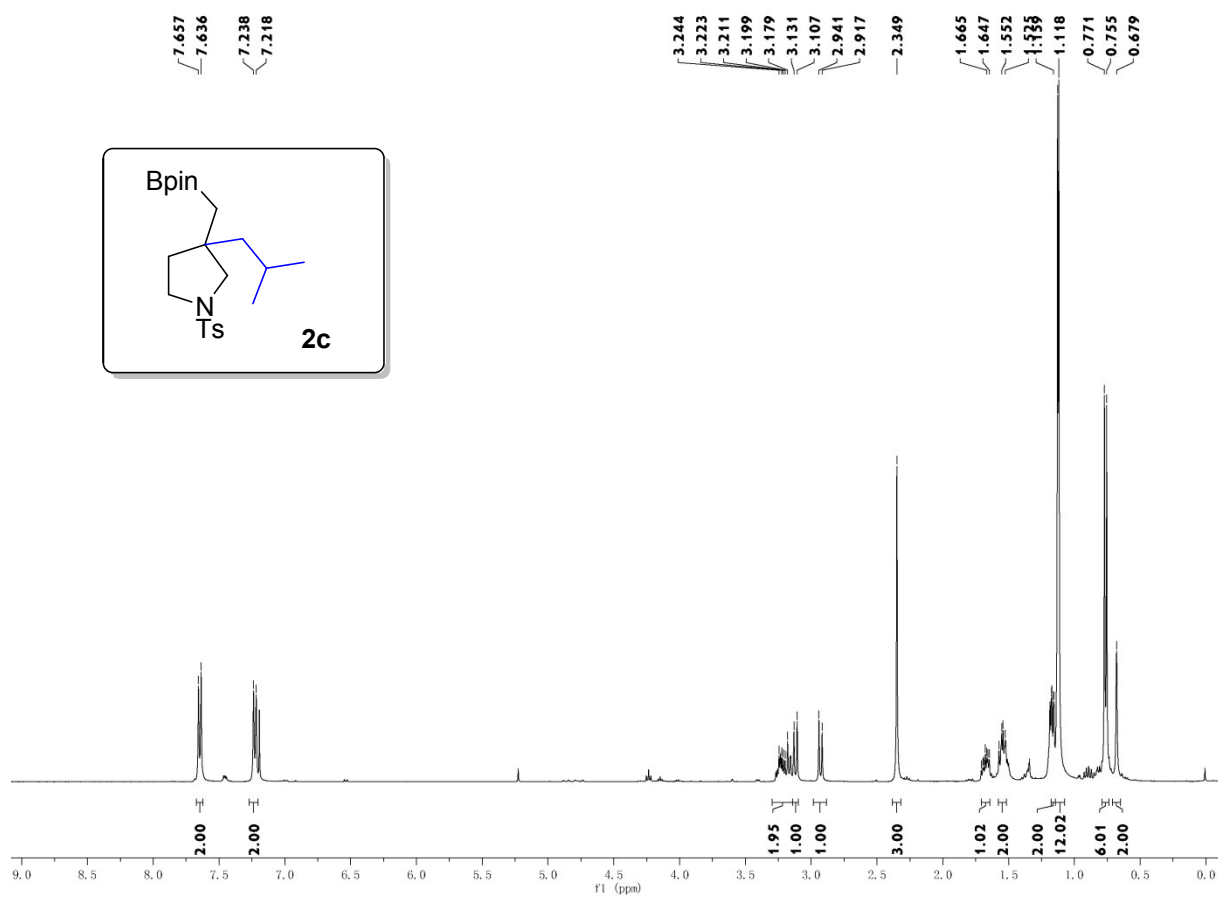
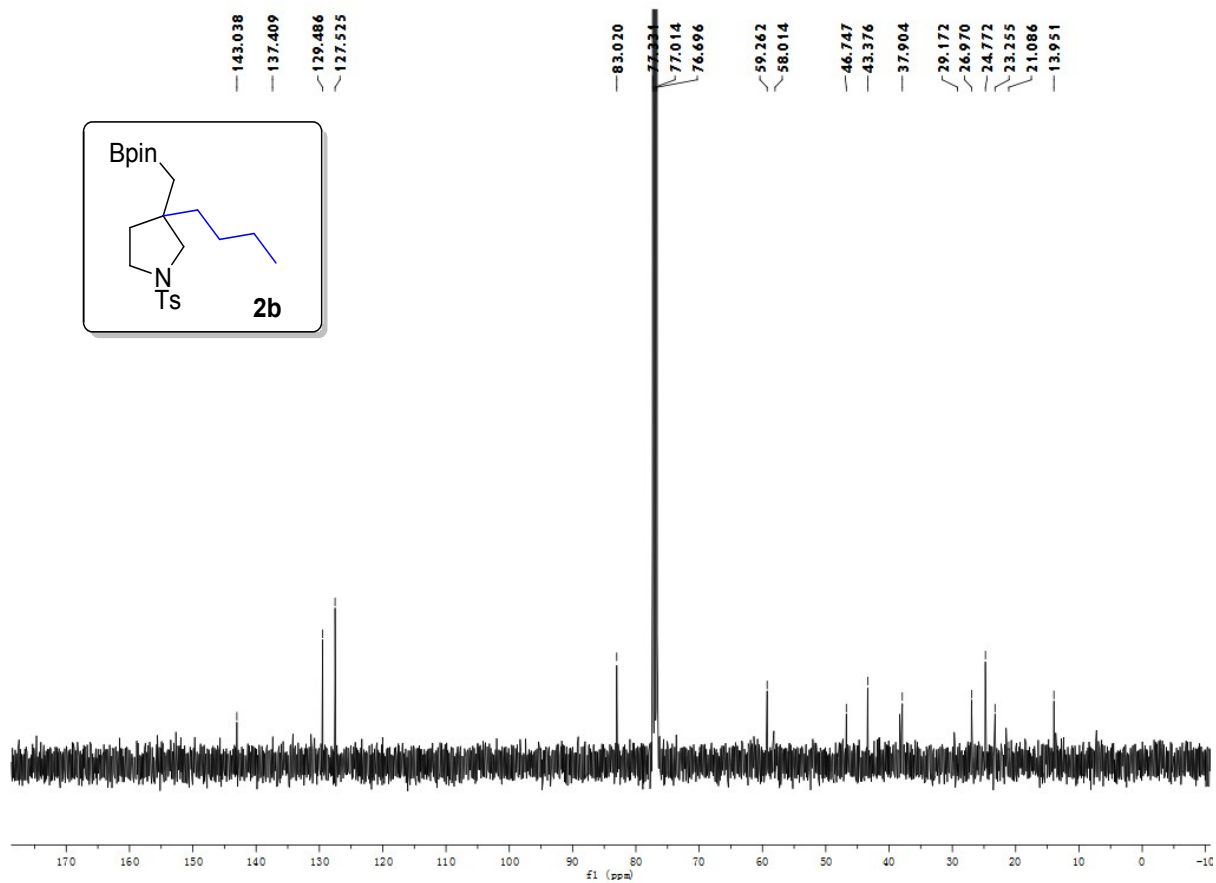


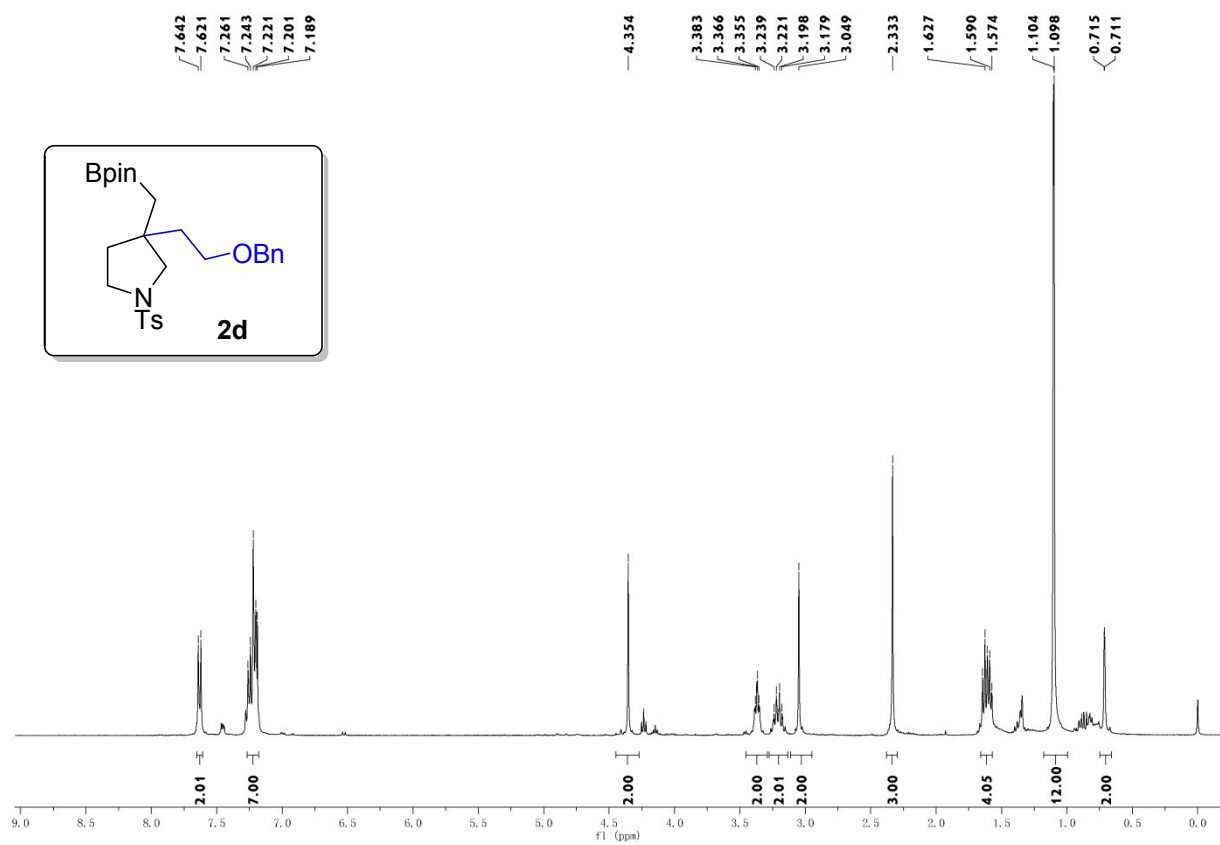
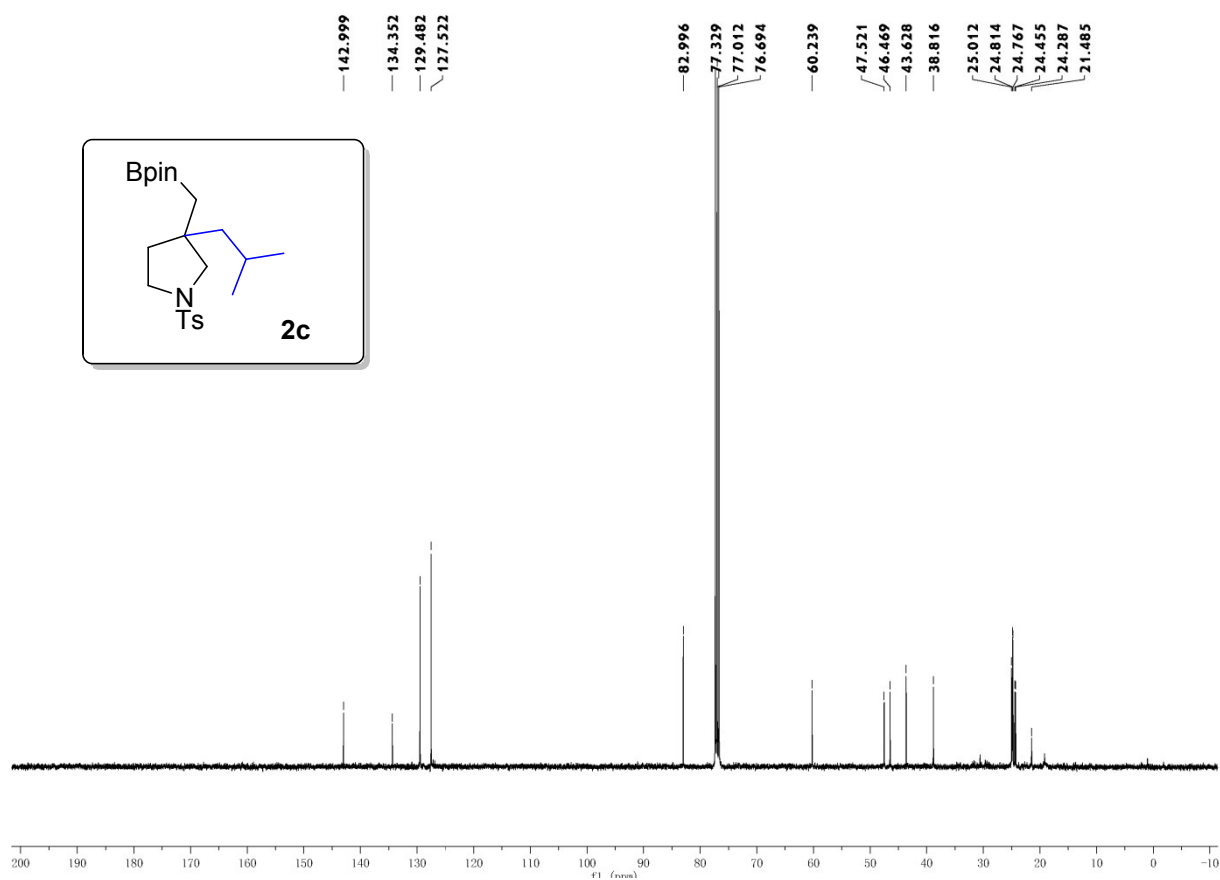
In a reaction vial, CuI (3.8 mg, 0.02 mmol) and LiOtBu (32.0 mg, 0.4 mmol) were added in a reaction vial. Then **2a** (75.9 mg, 0.2 mmol) in DMF (0.5 mL) was added in the vial. Followed by 5-bromo-1-pentene (44.7 mg, 0.3 mmol) was added. The vial was purged with N₂. The mixture was stirred at 80°C for 11 h. In the reaction system, the corresponding coupling product was traced by GCMS. However, as seen from the diagram, the content was very little.

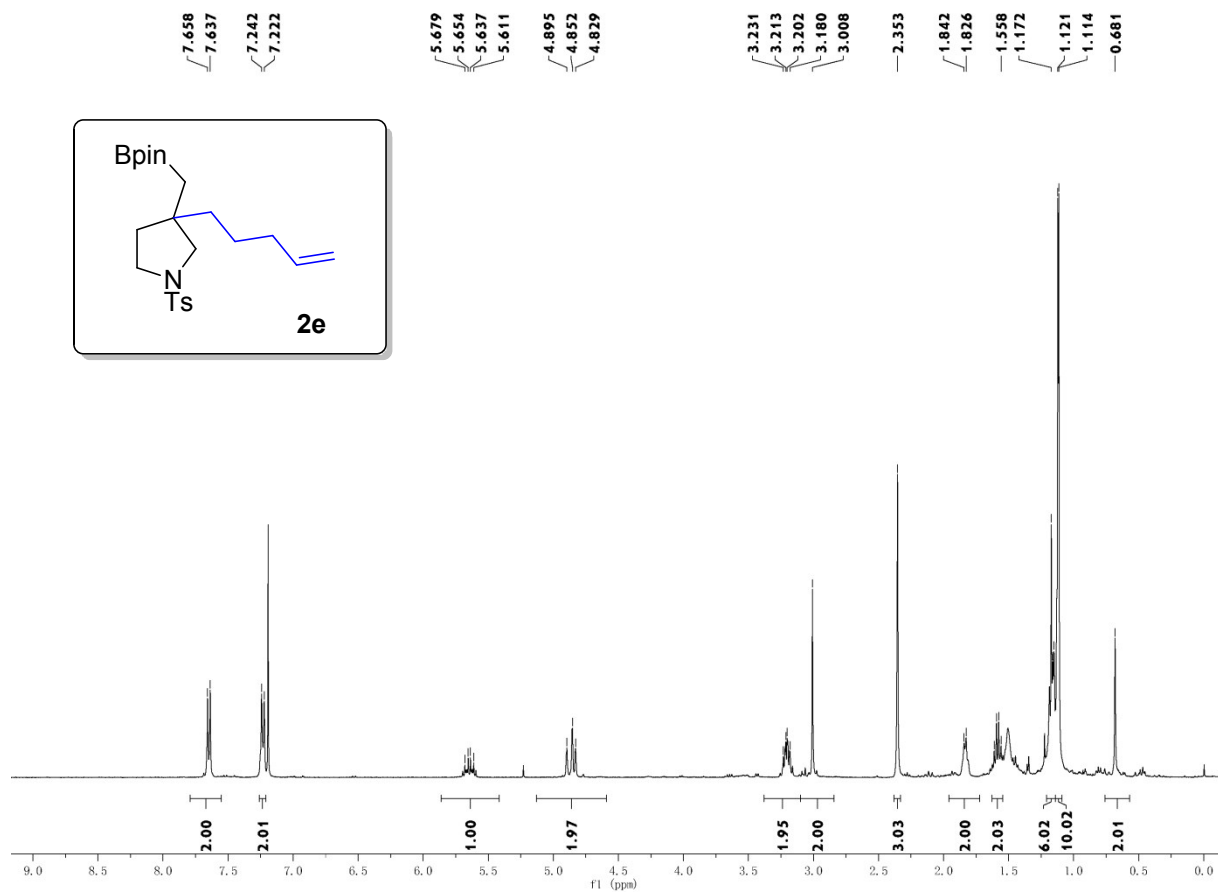
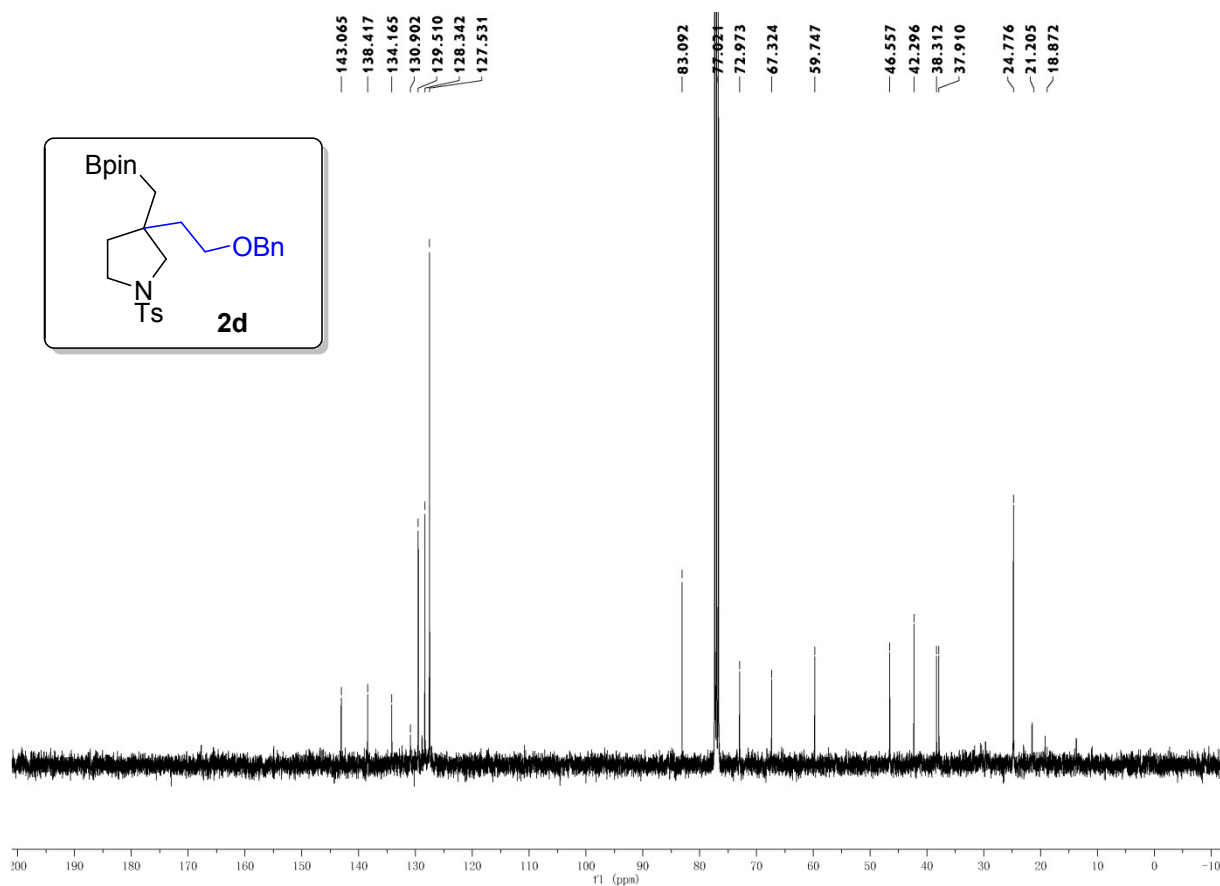
5. Copies of the ^1H NMR and ^{13}C NMR for Borylation Product.

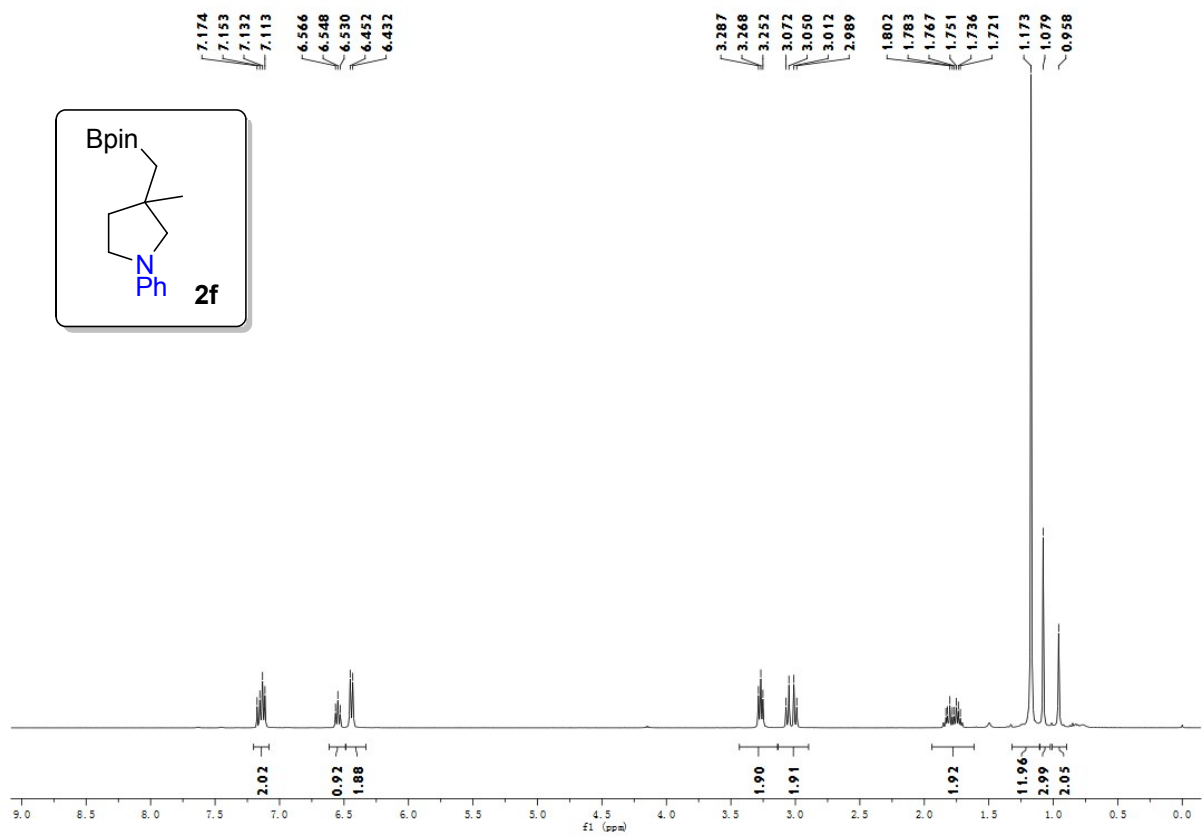
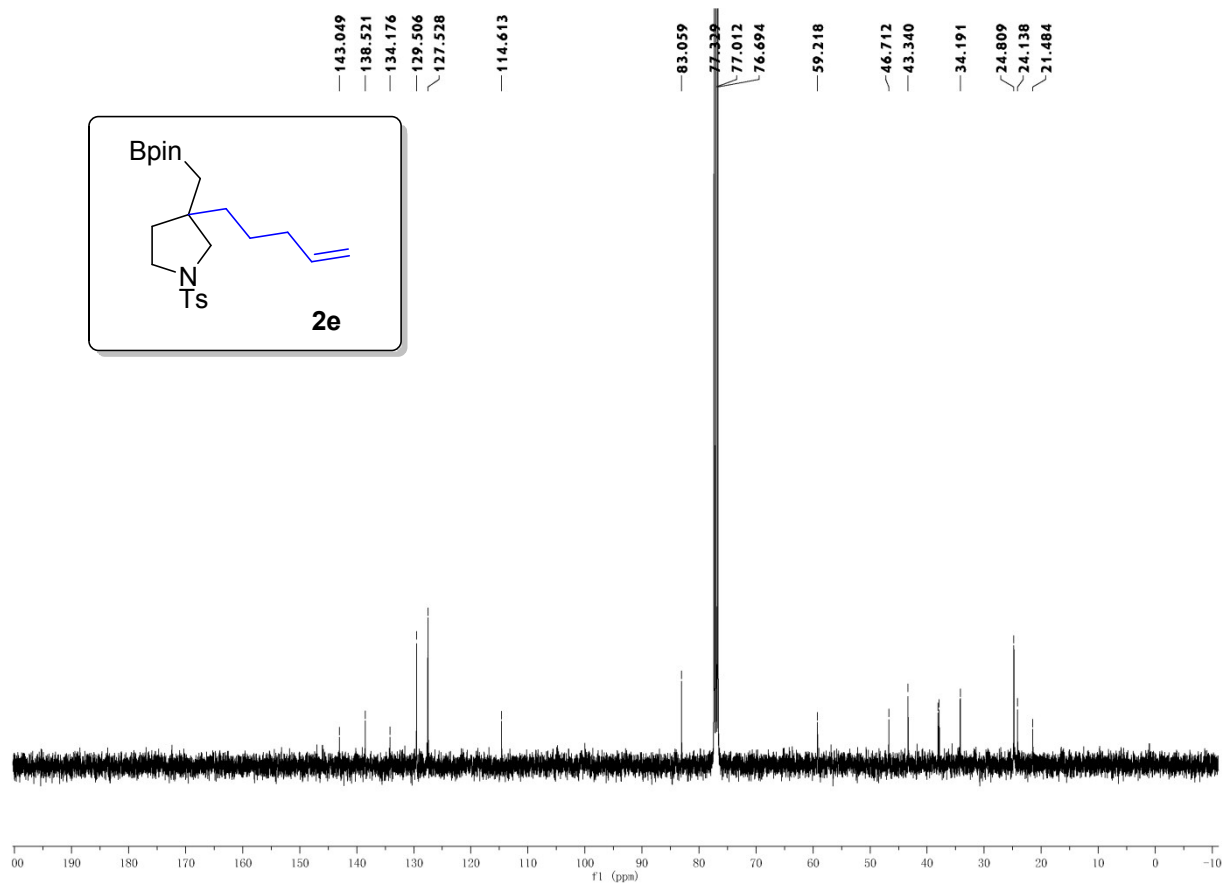


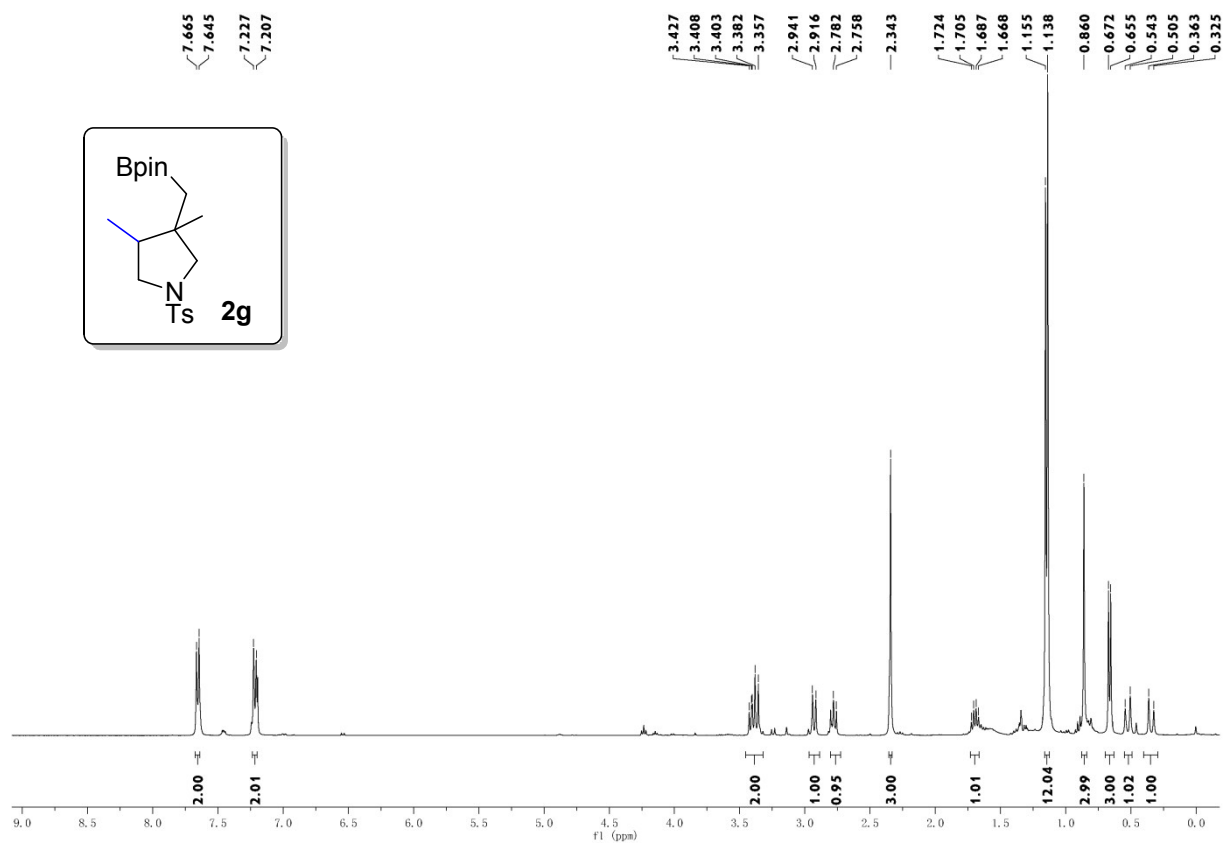
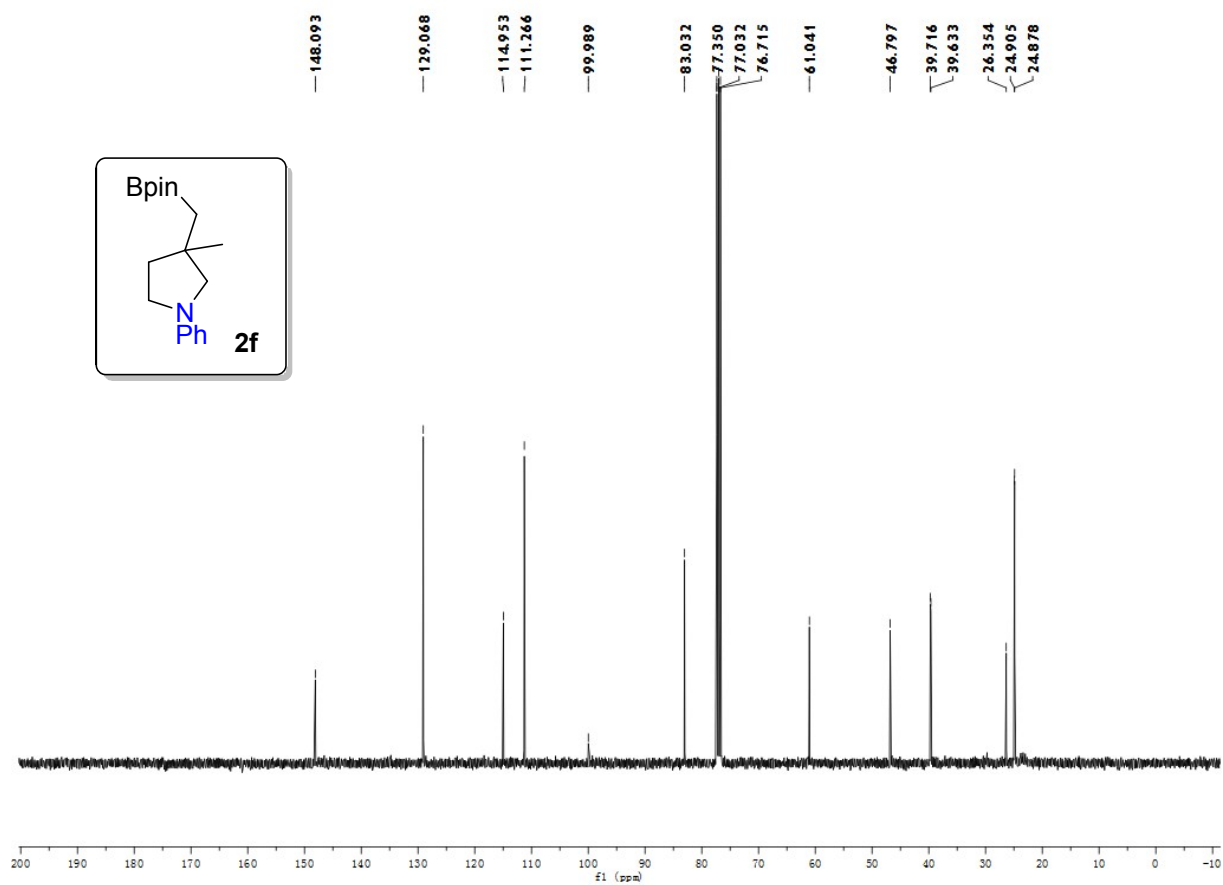


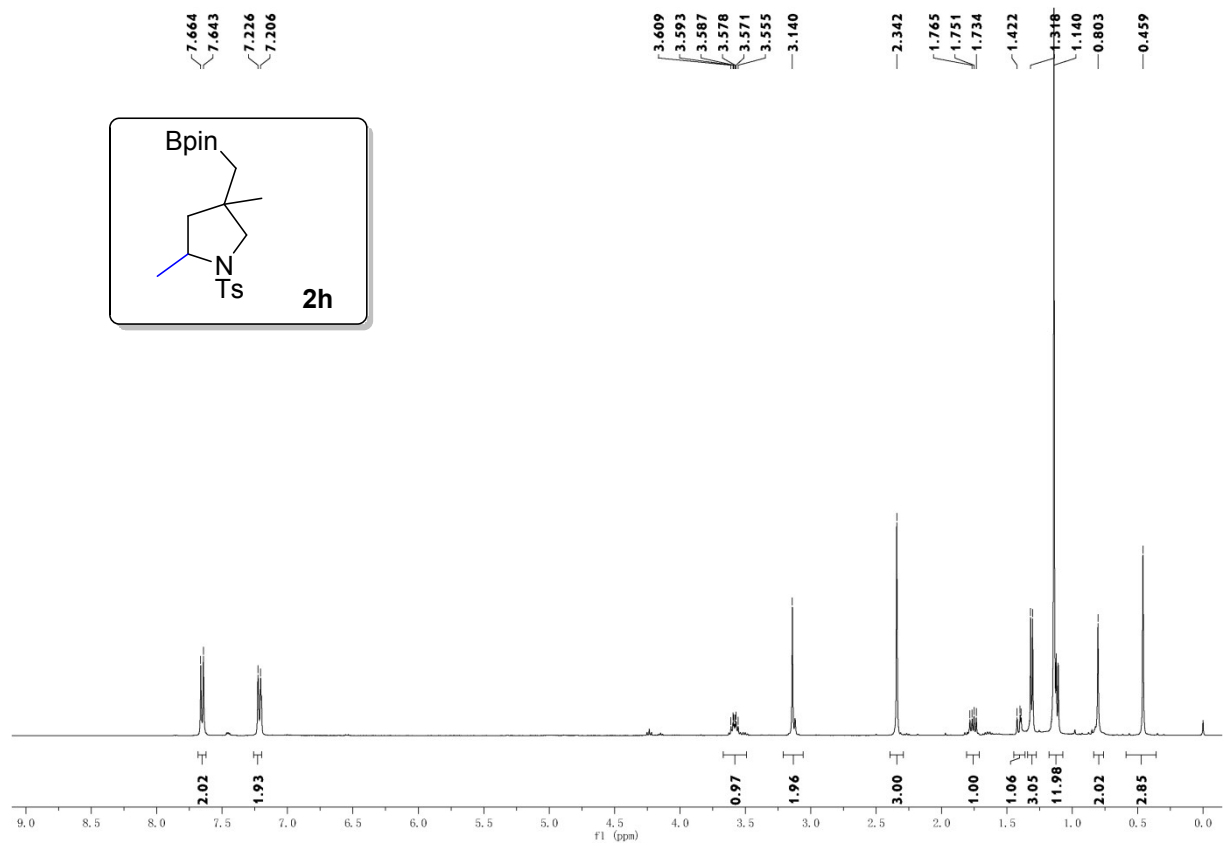
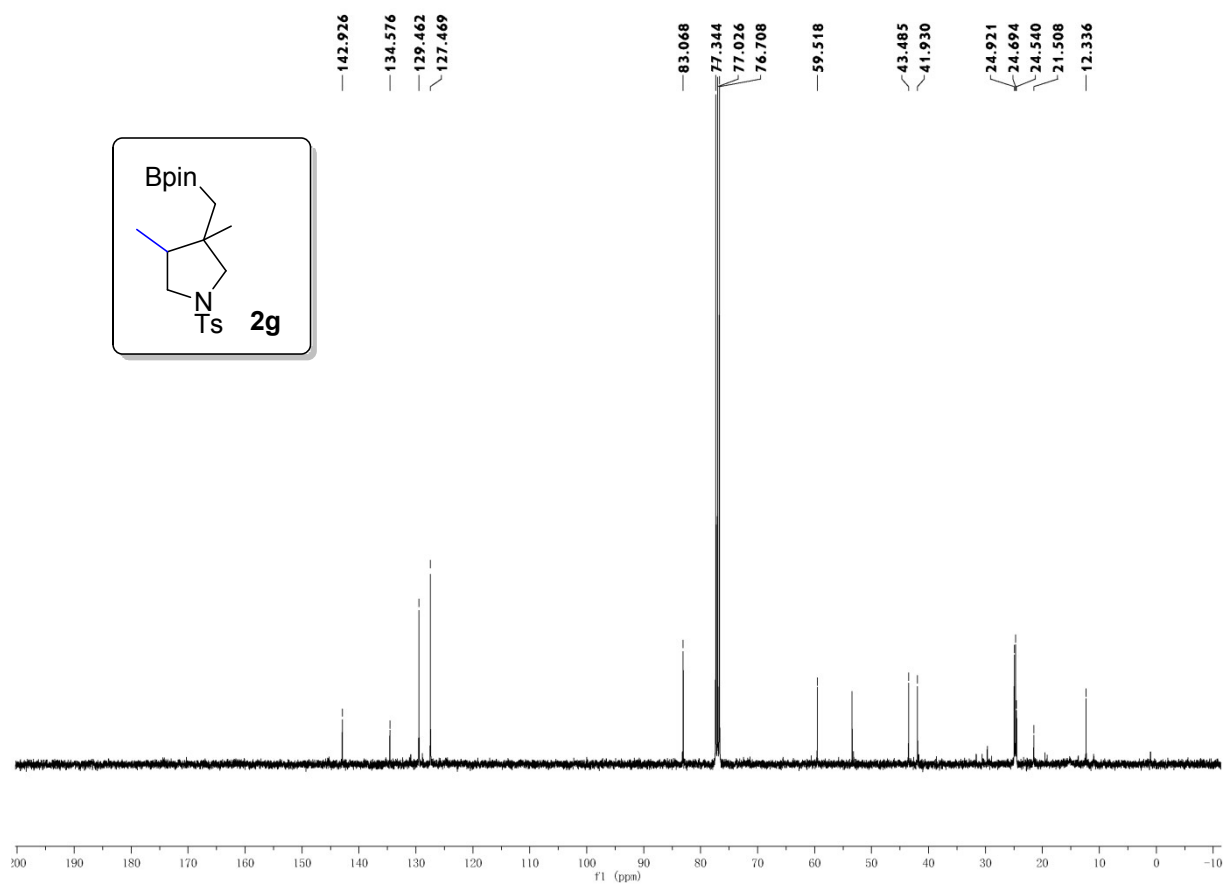


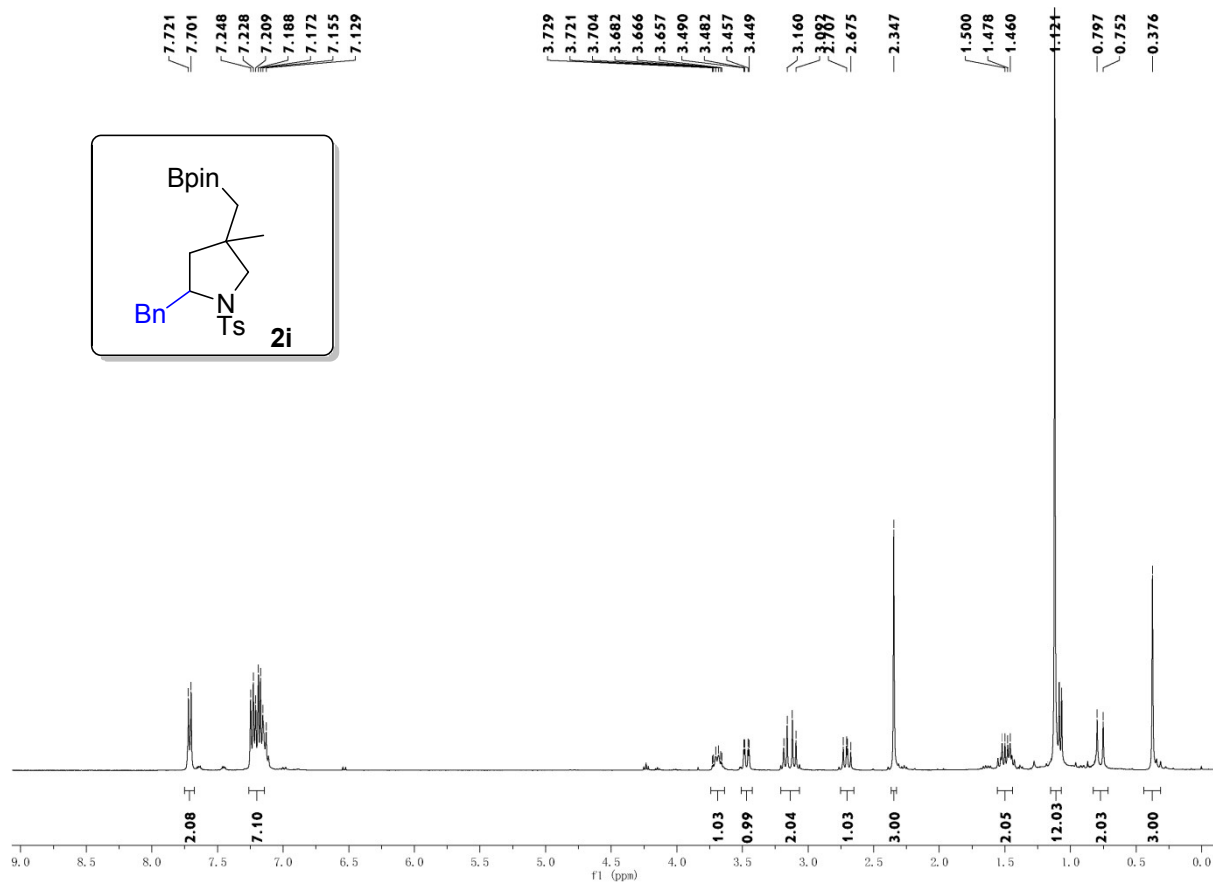
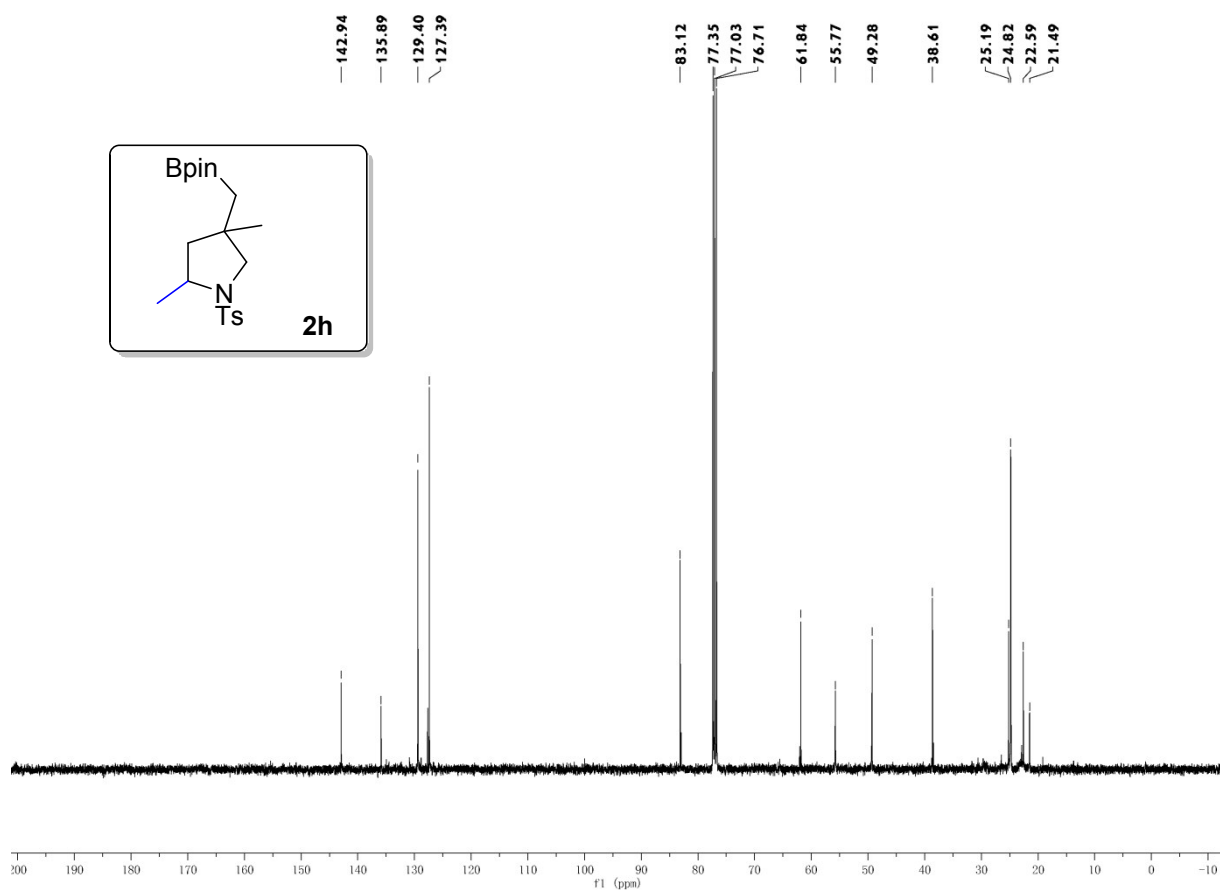


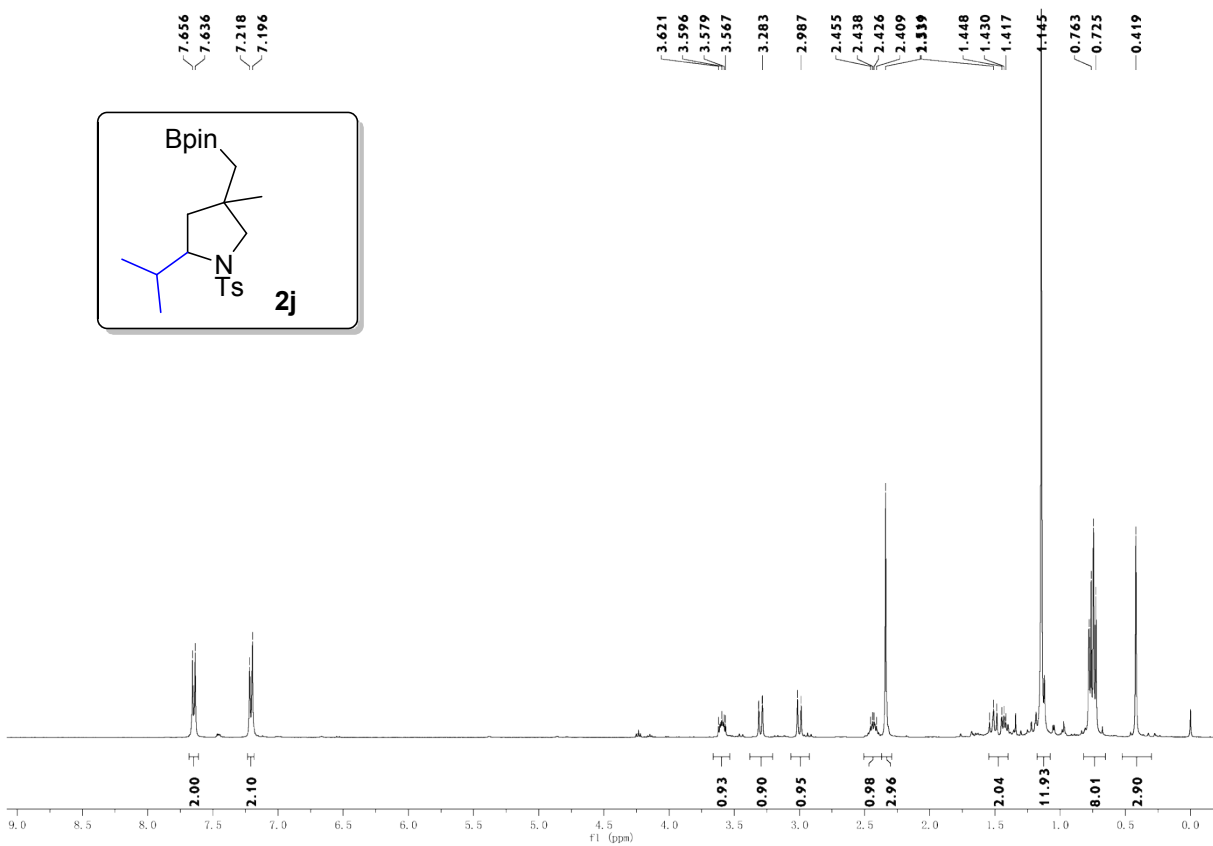
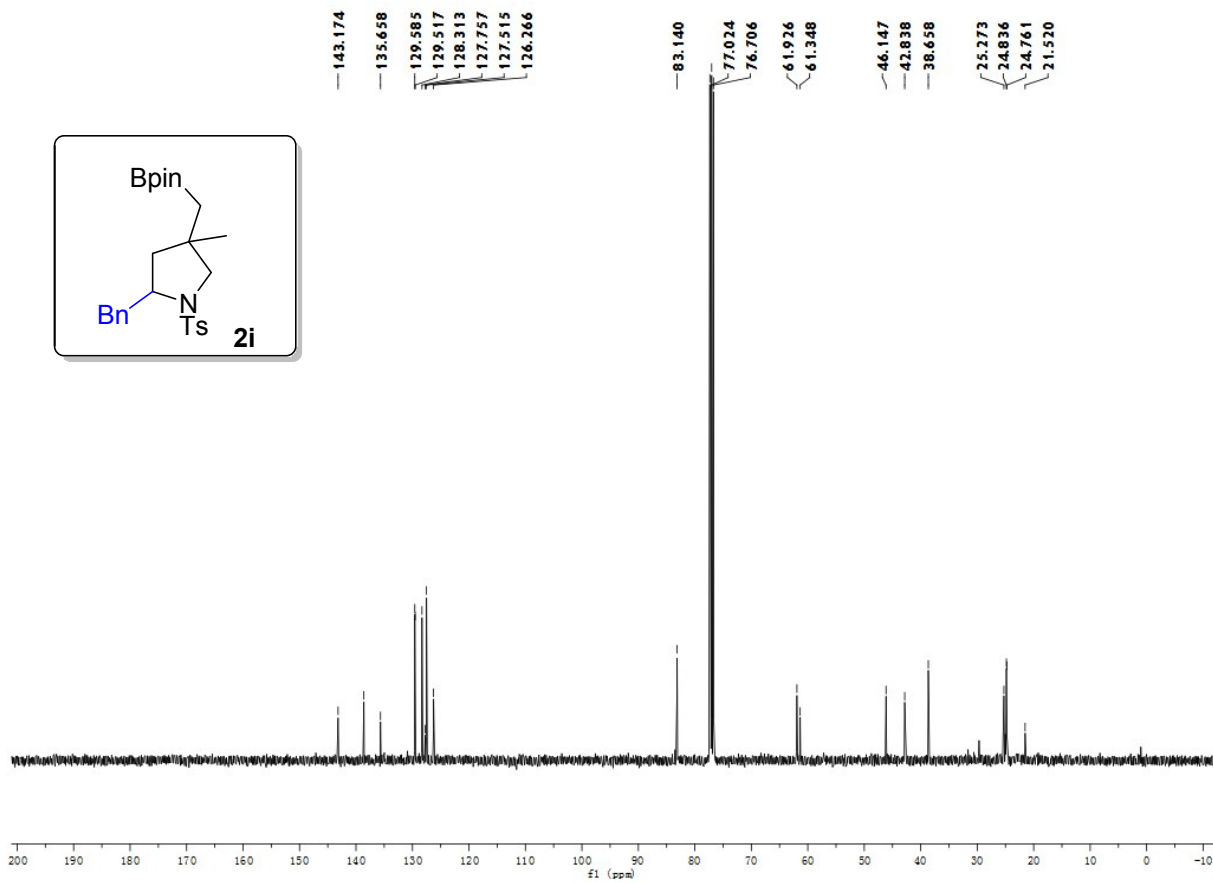


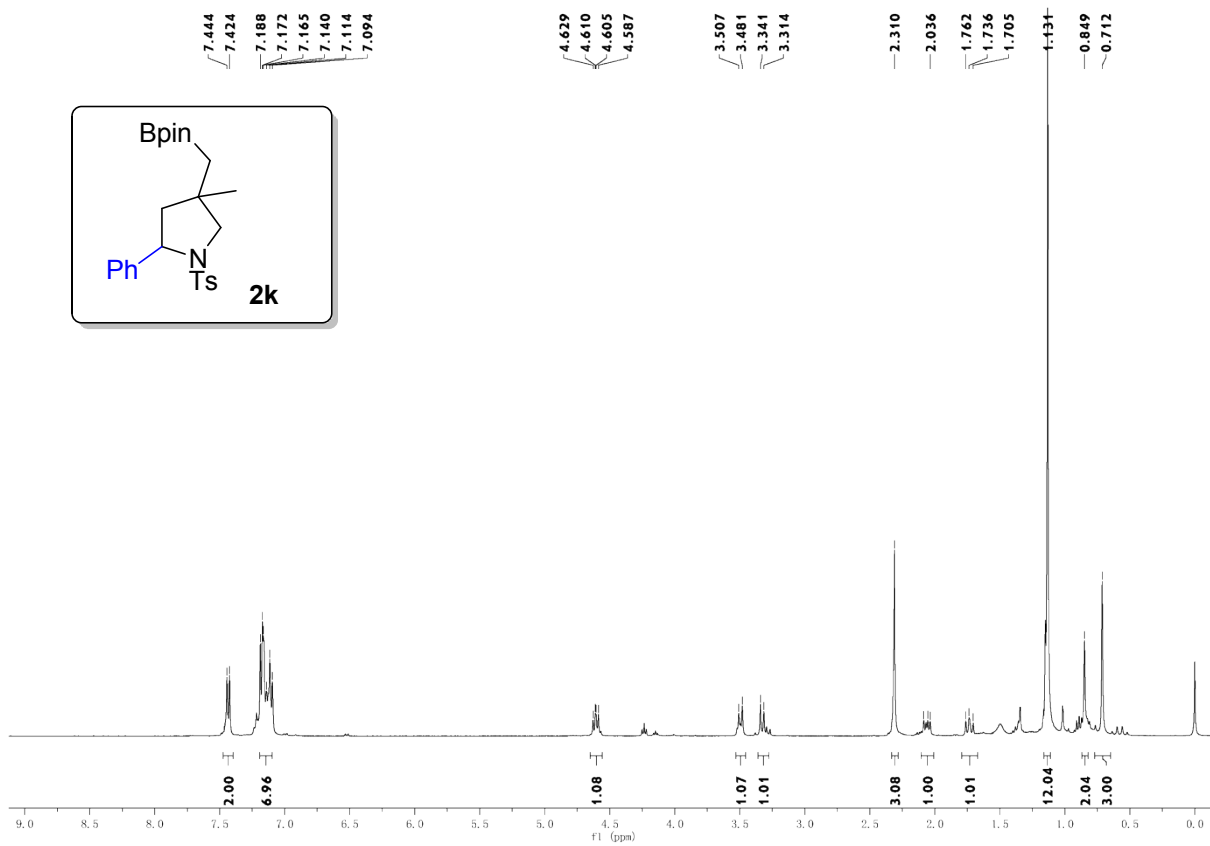
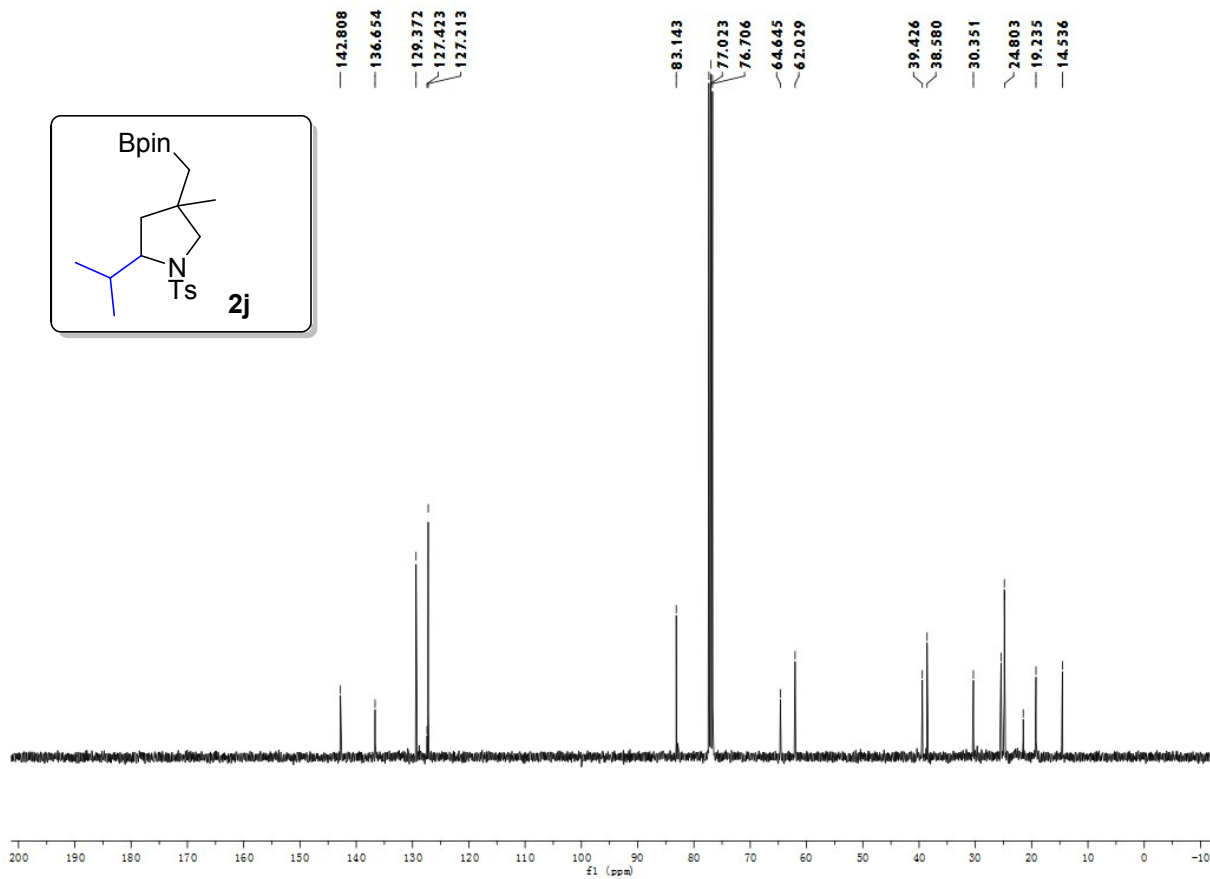


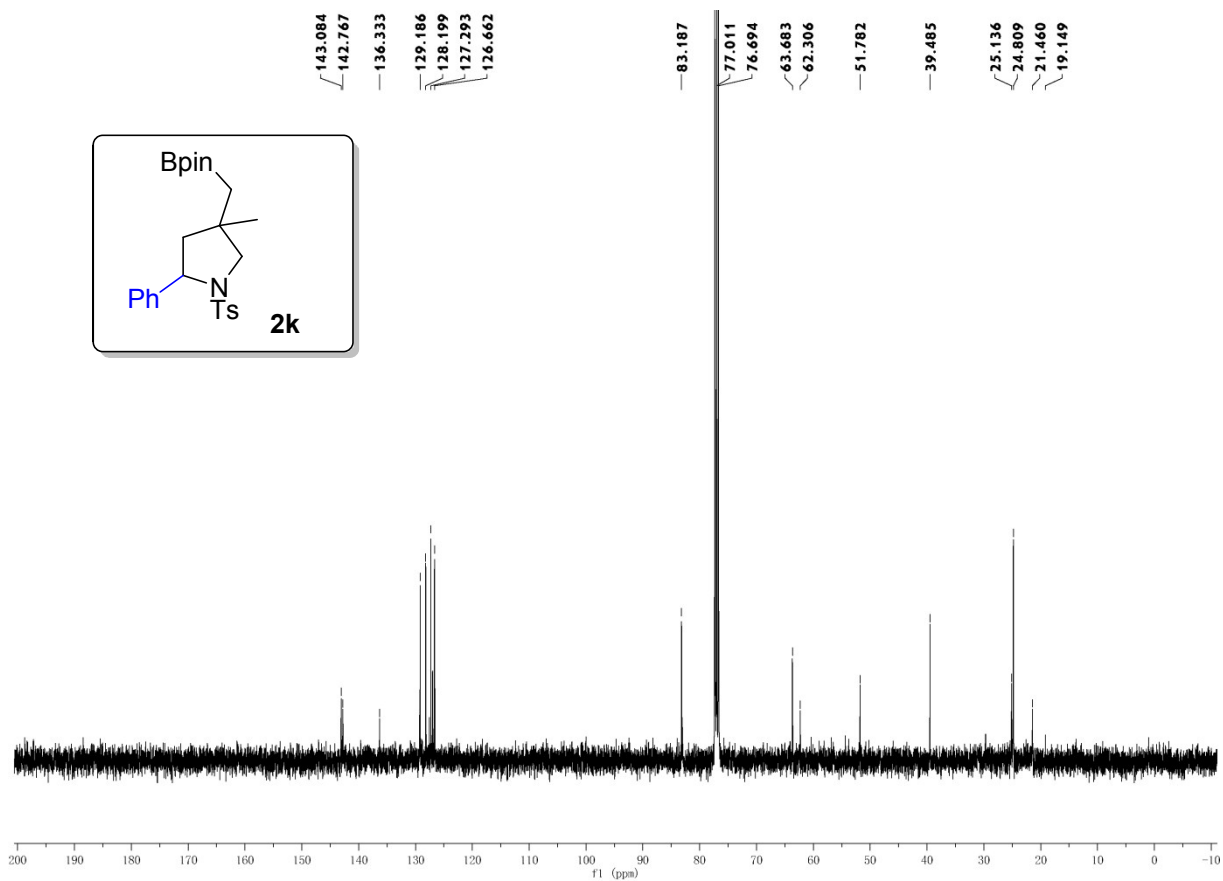




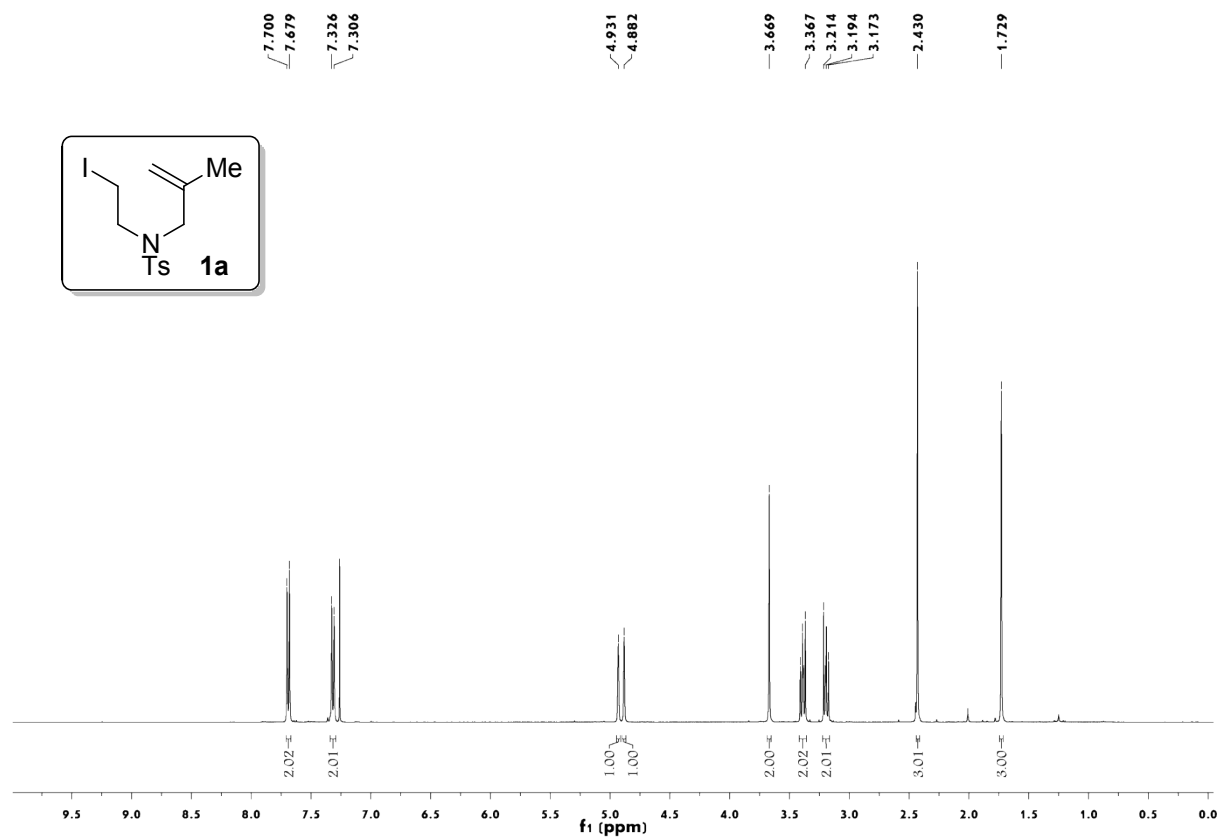


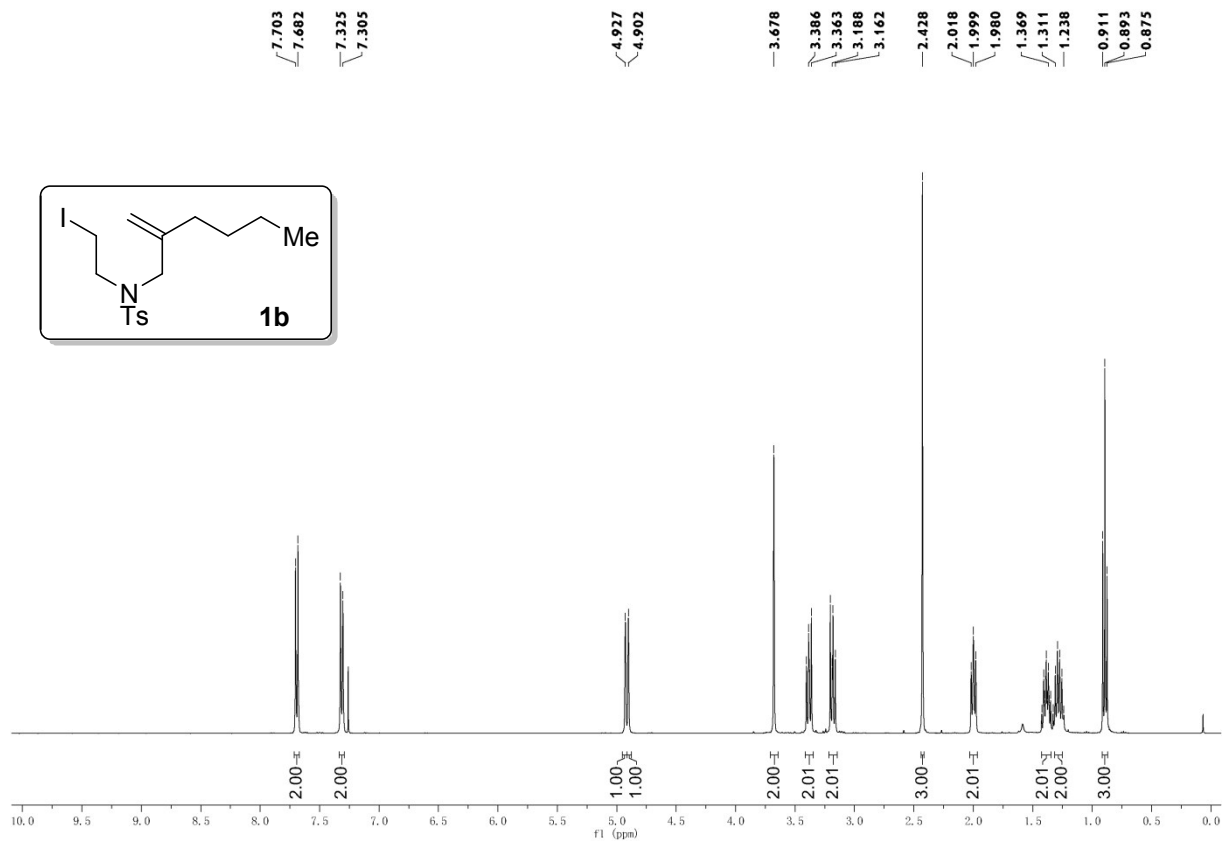
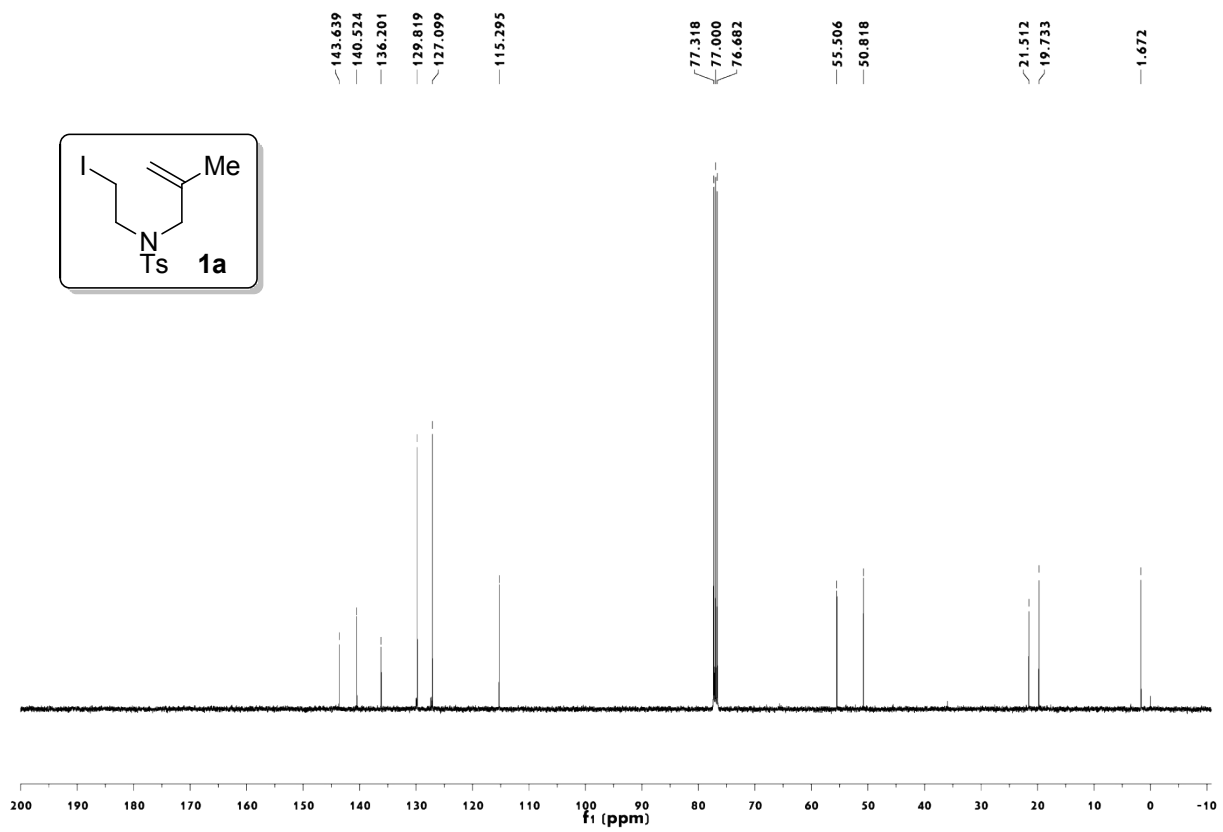


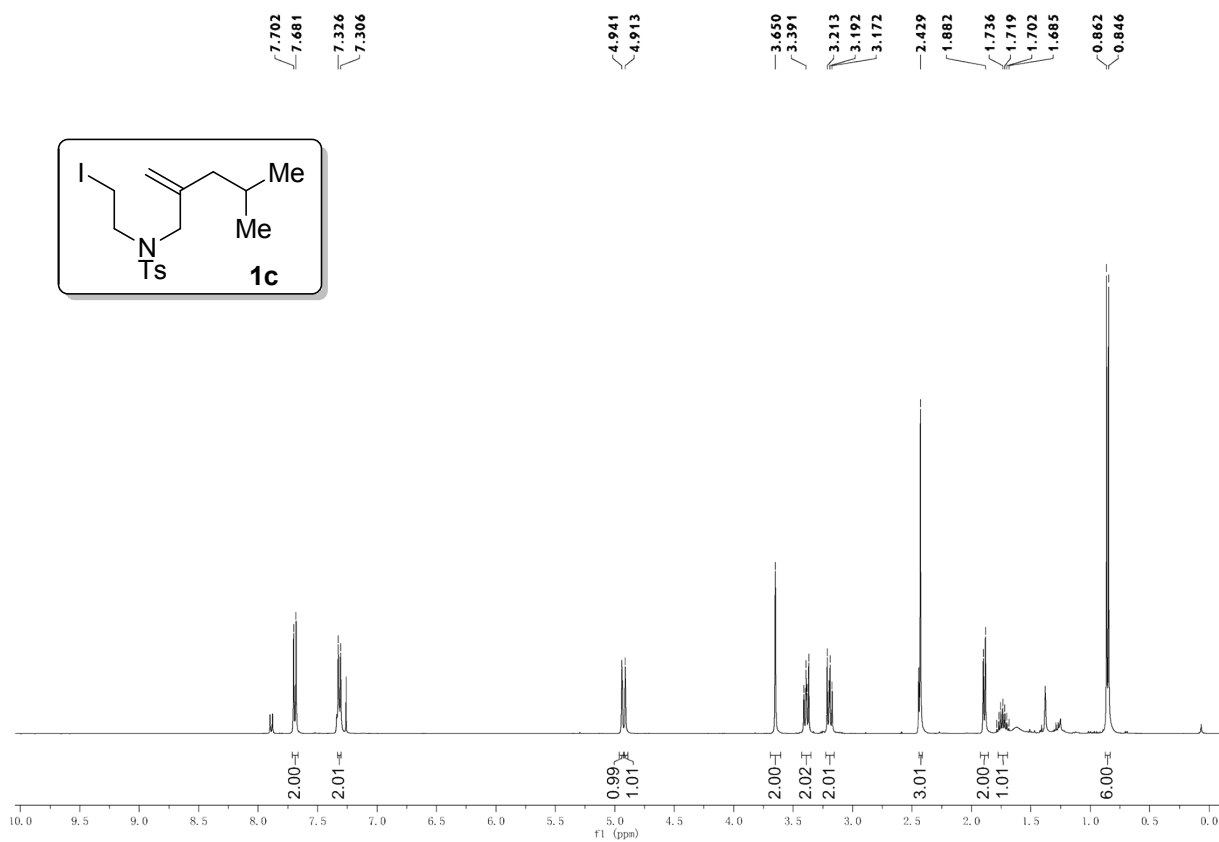
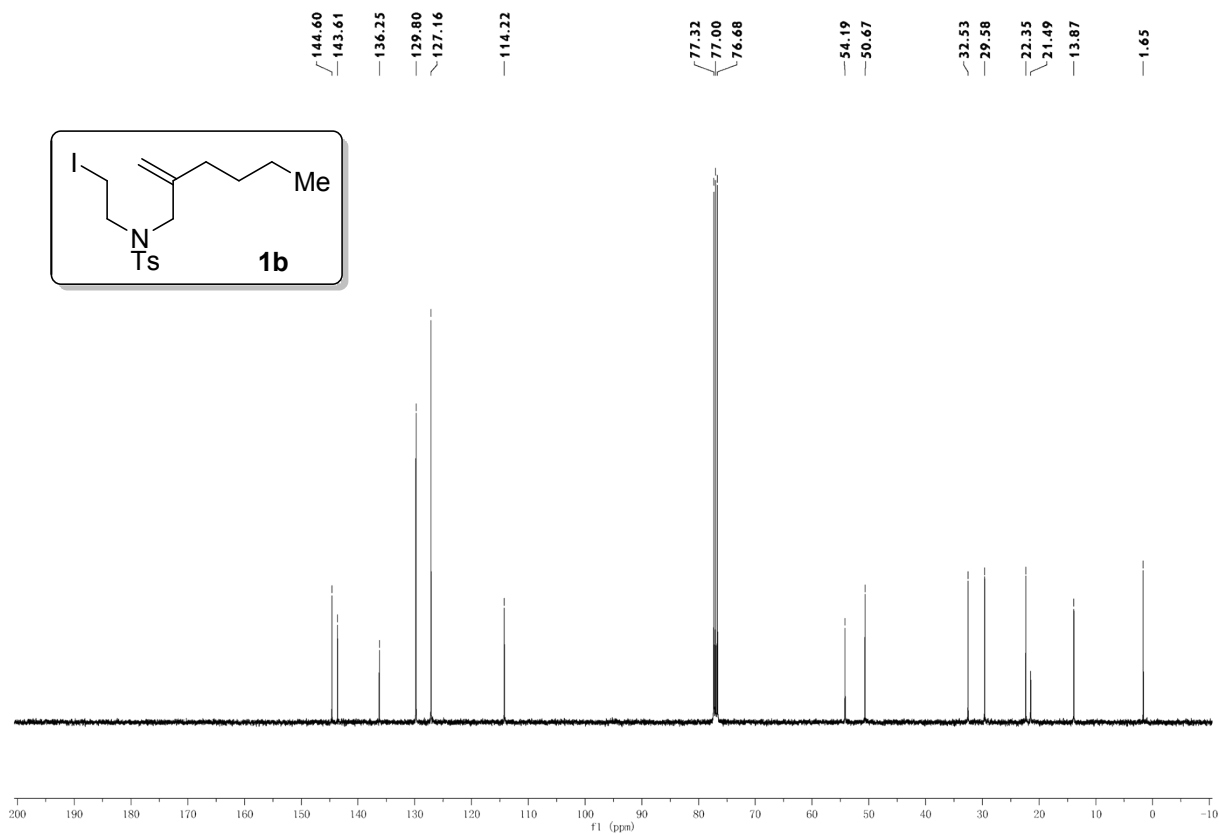


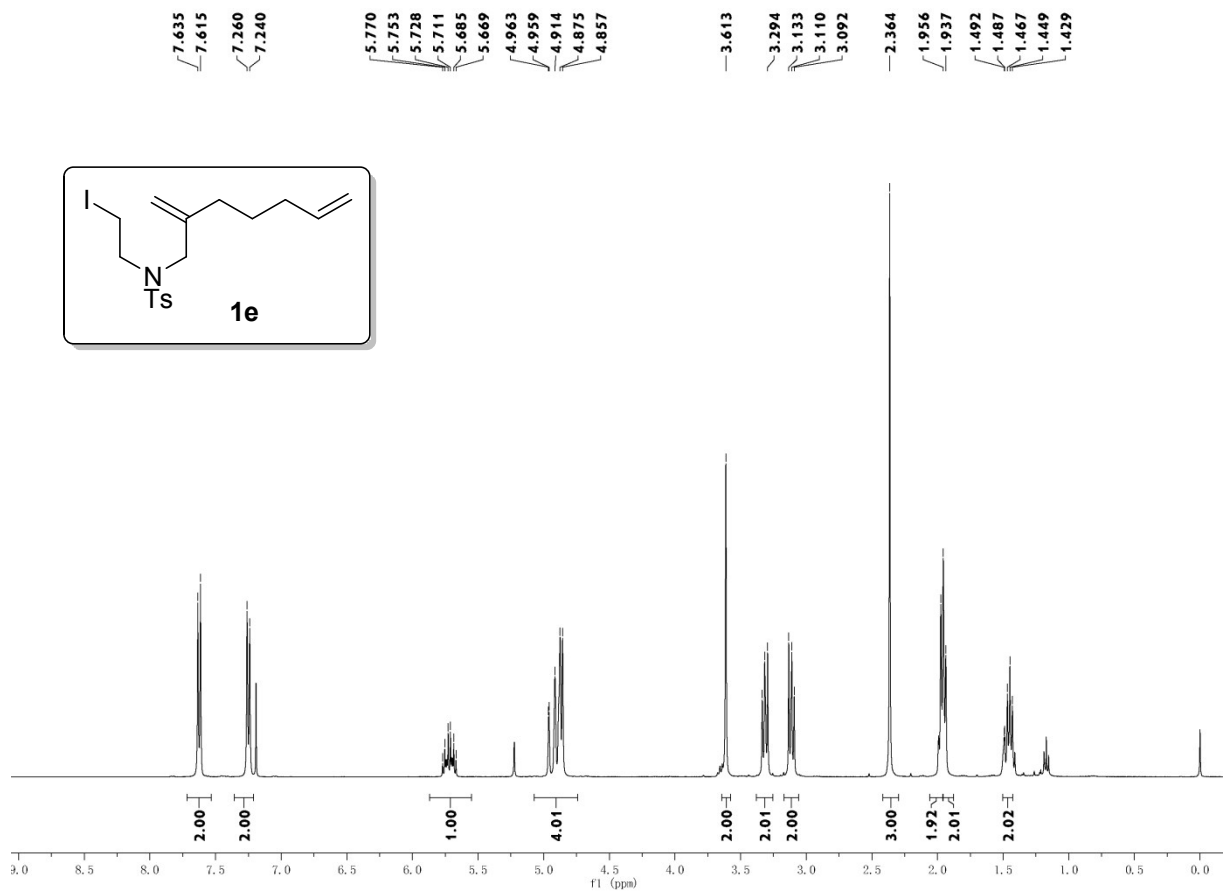
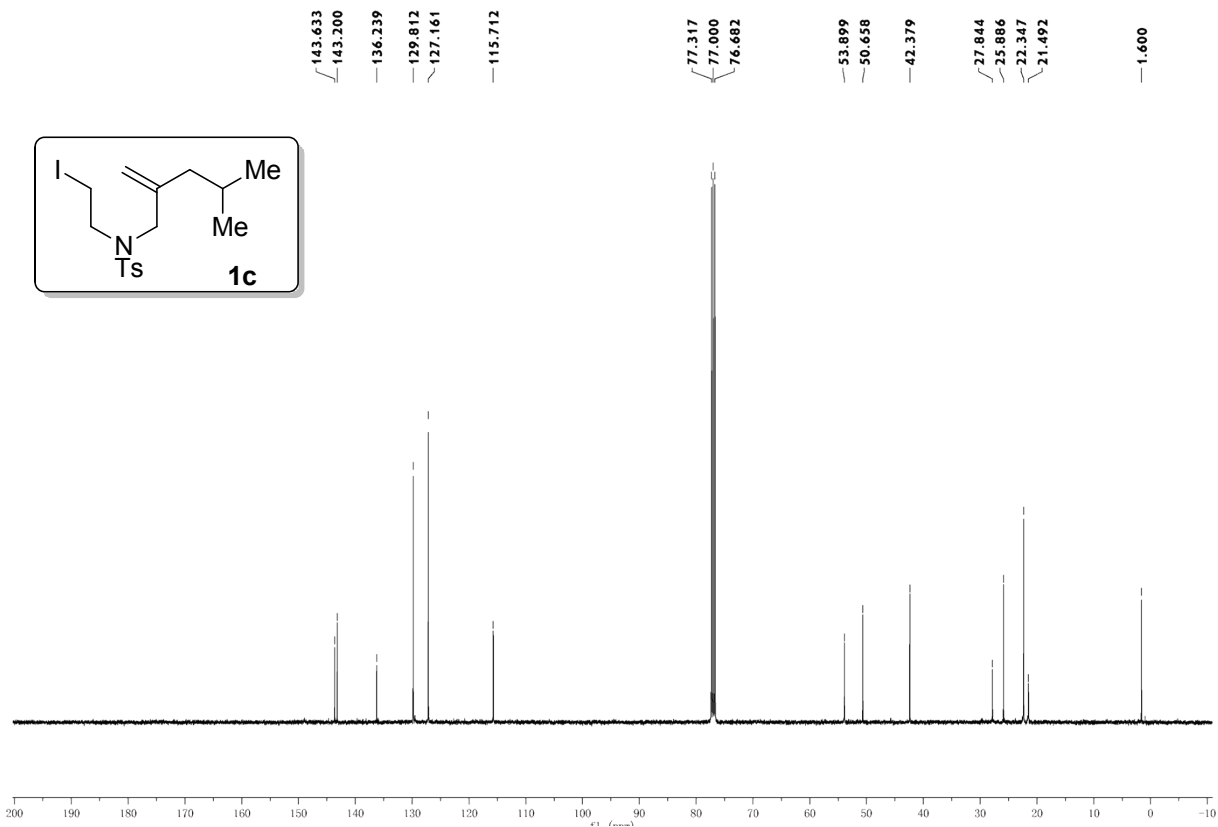


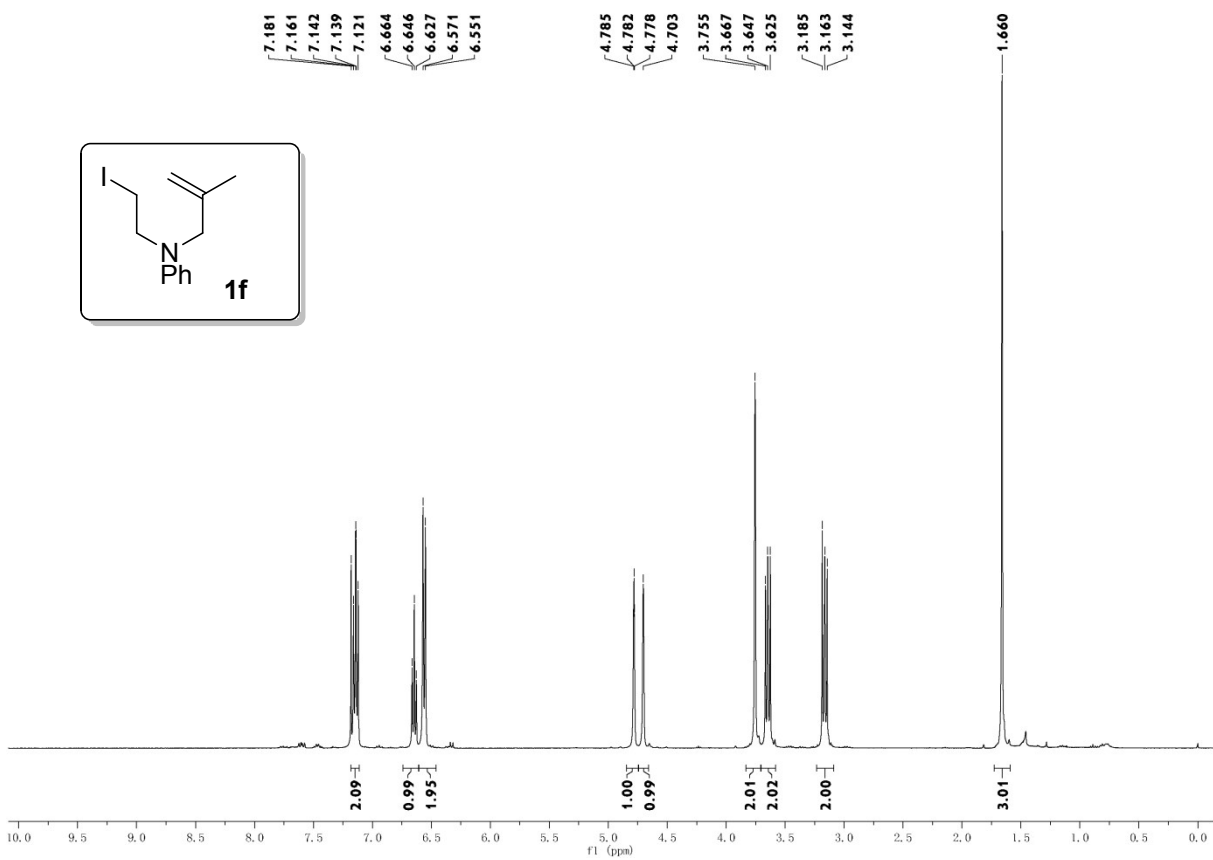
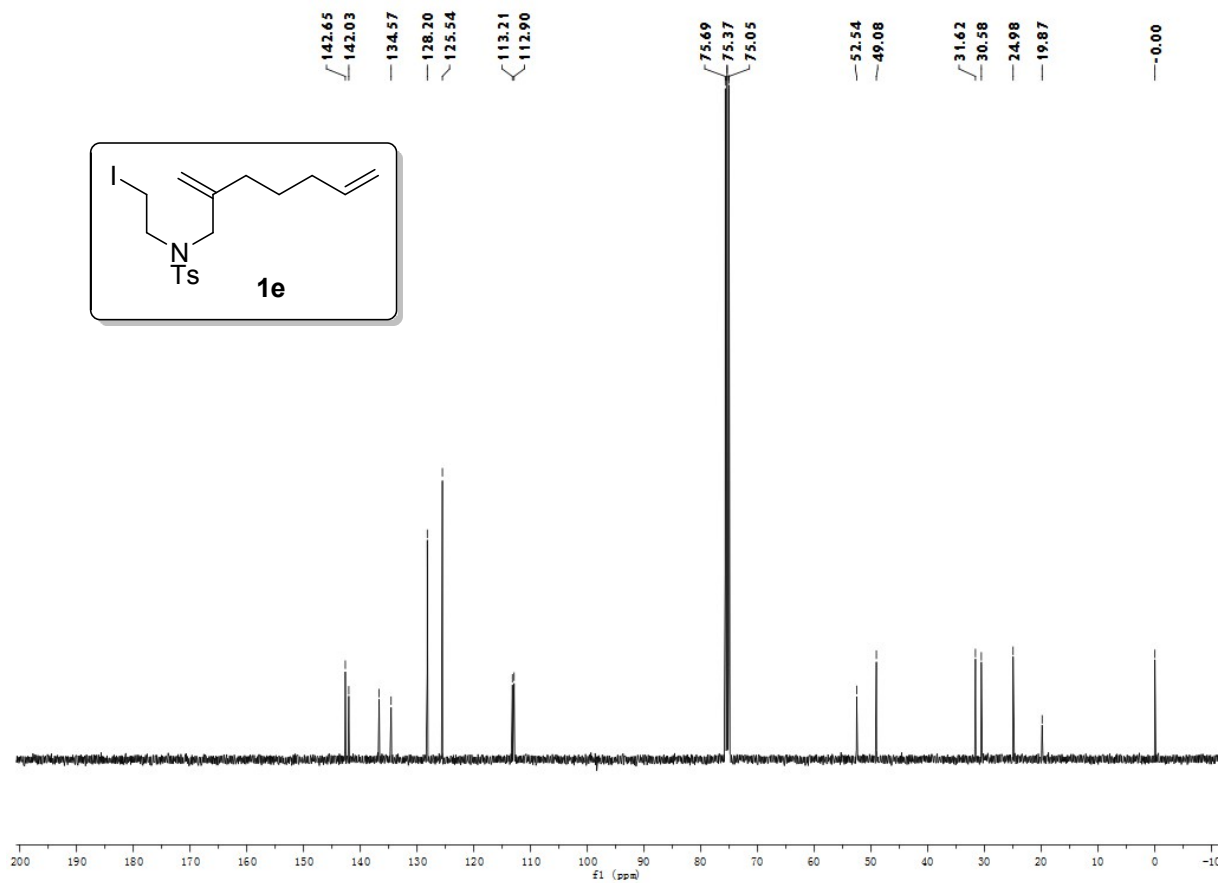
6. Copies of the ^1H NMR and ^{13}C NMR for Material

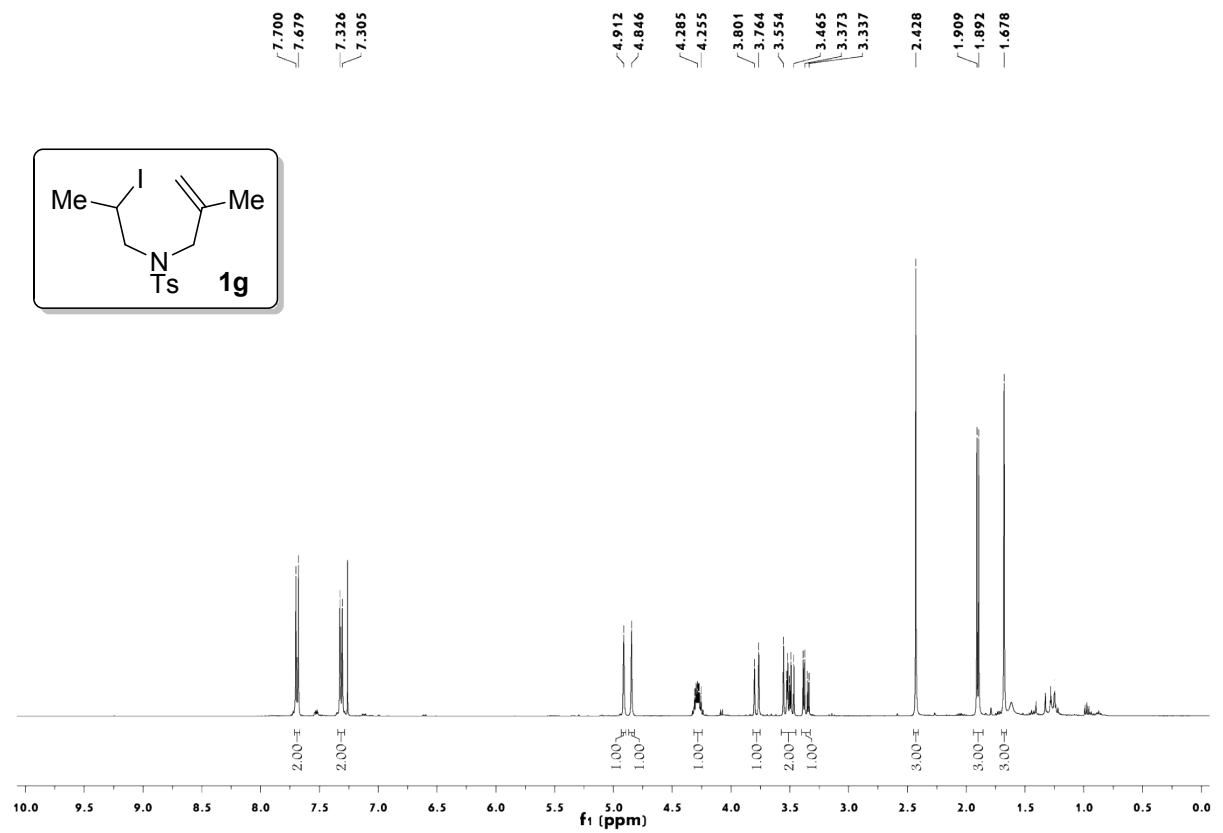
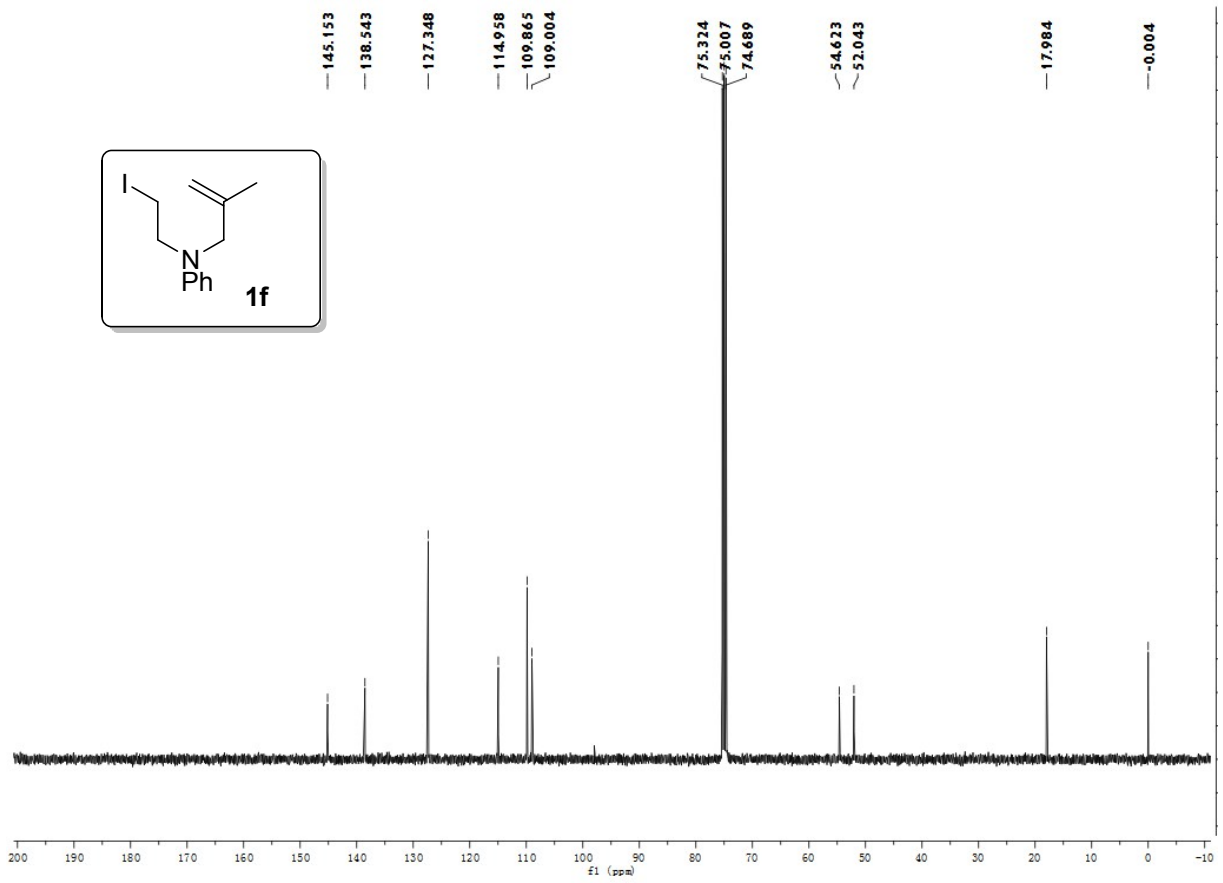


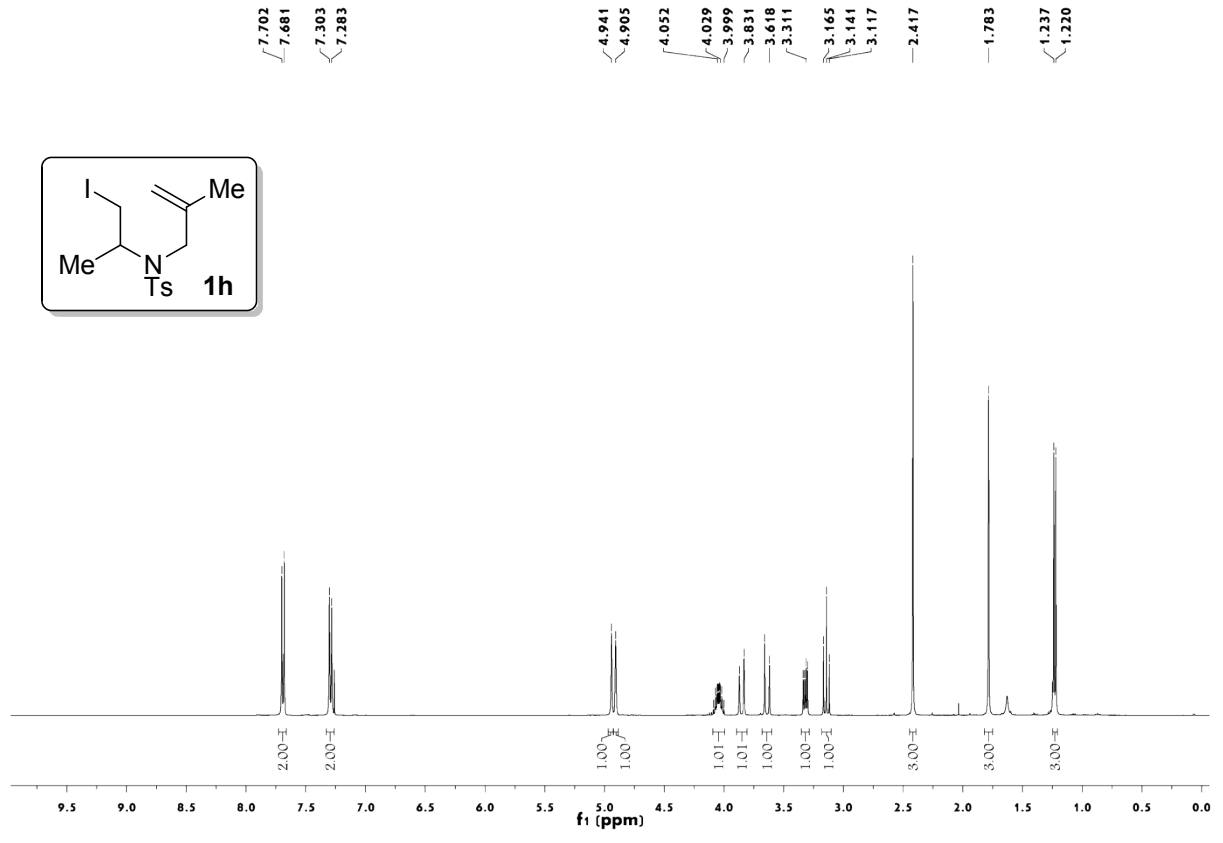
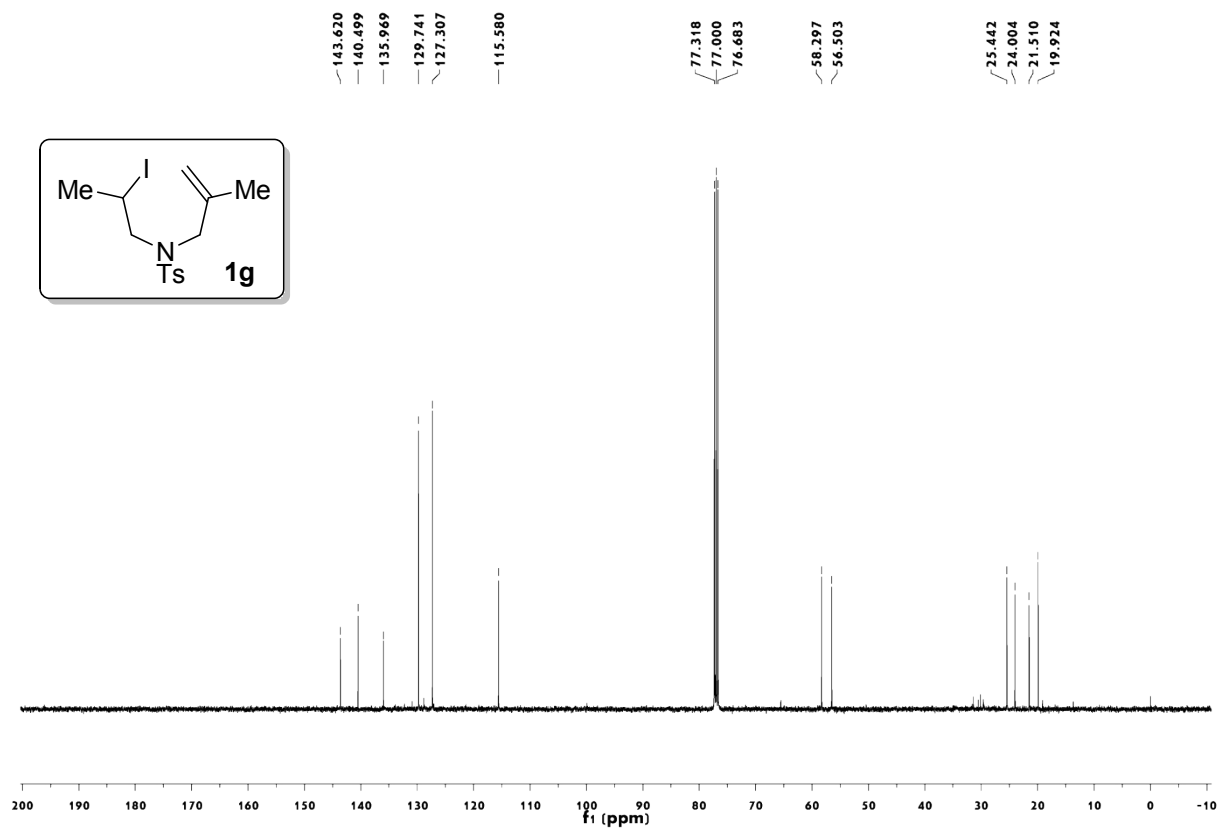


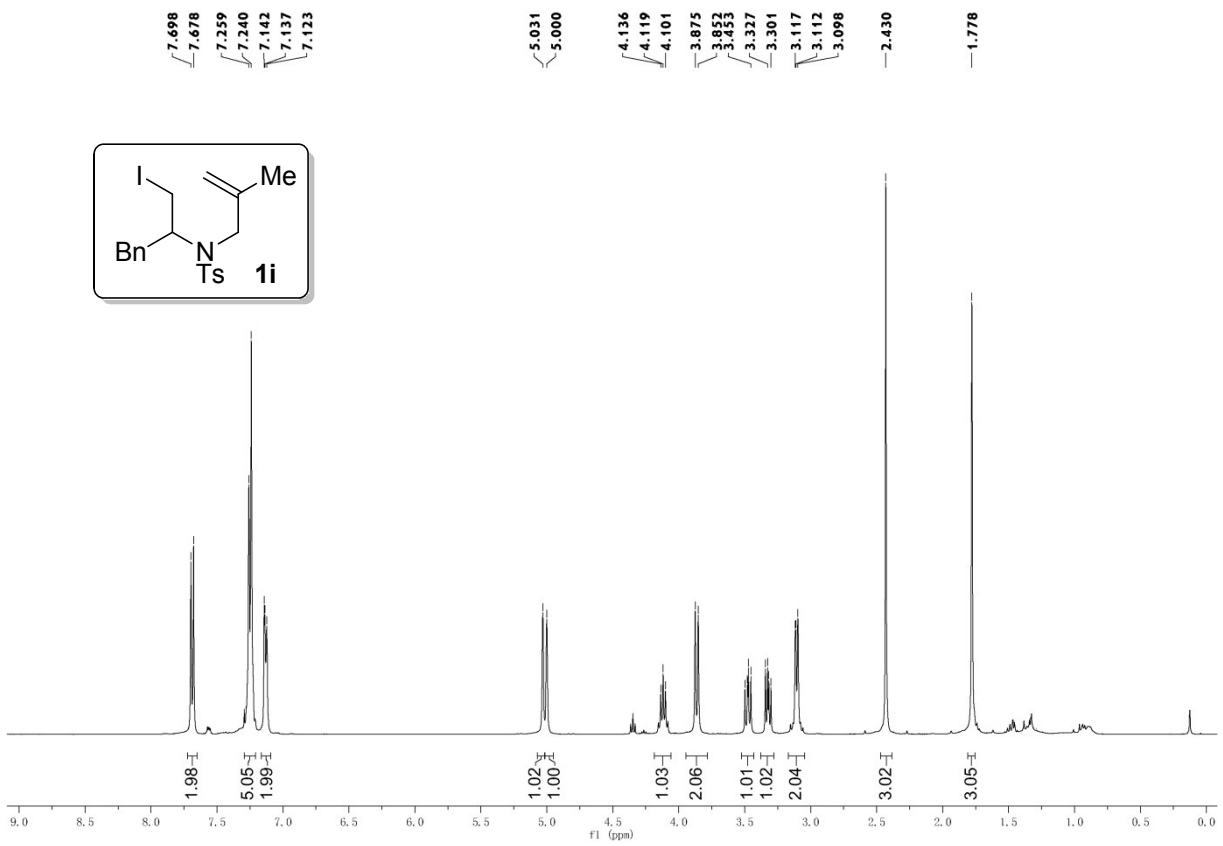
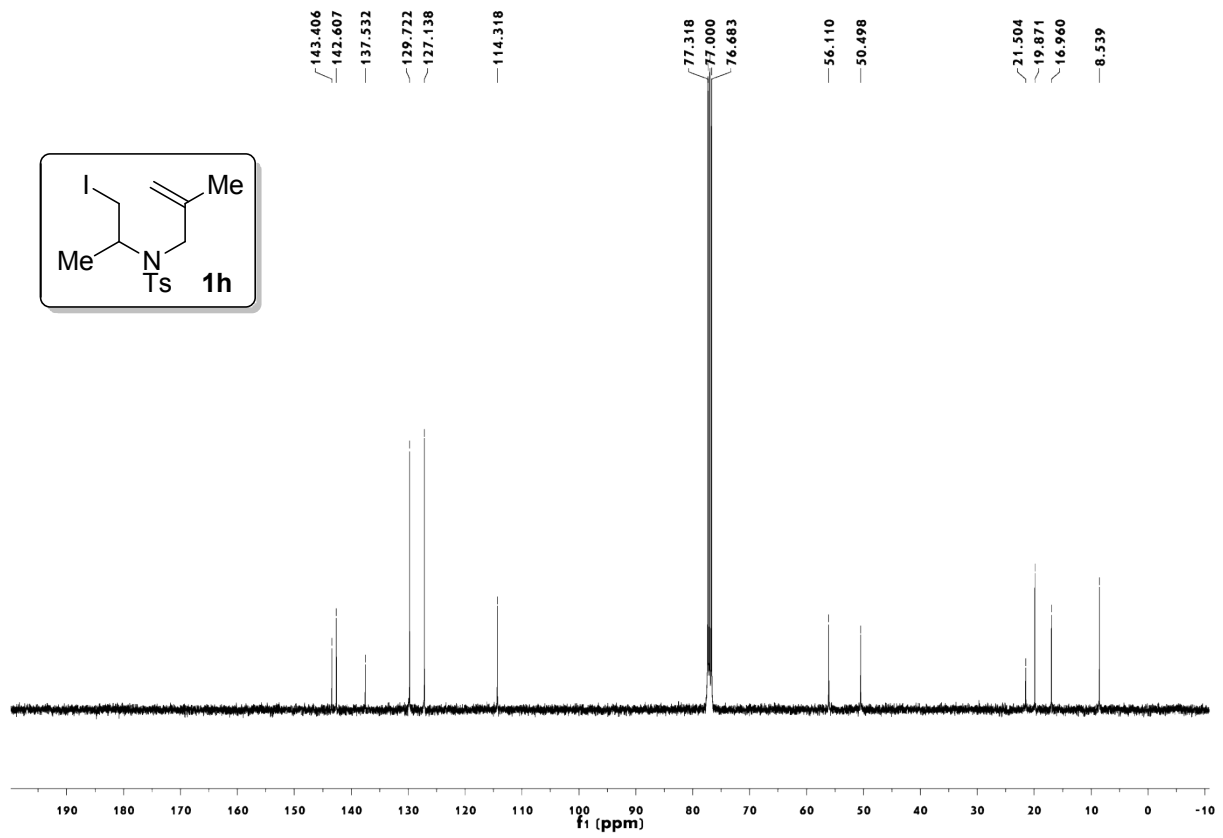


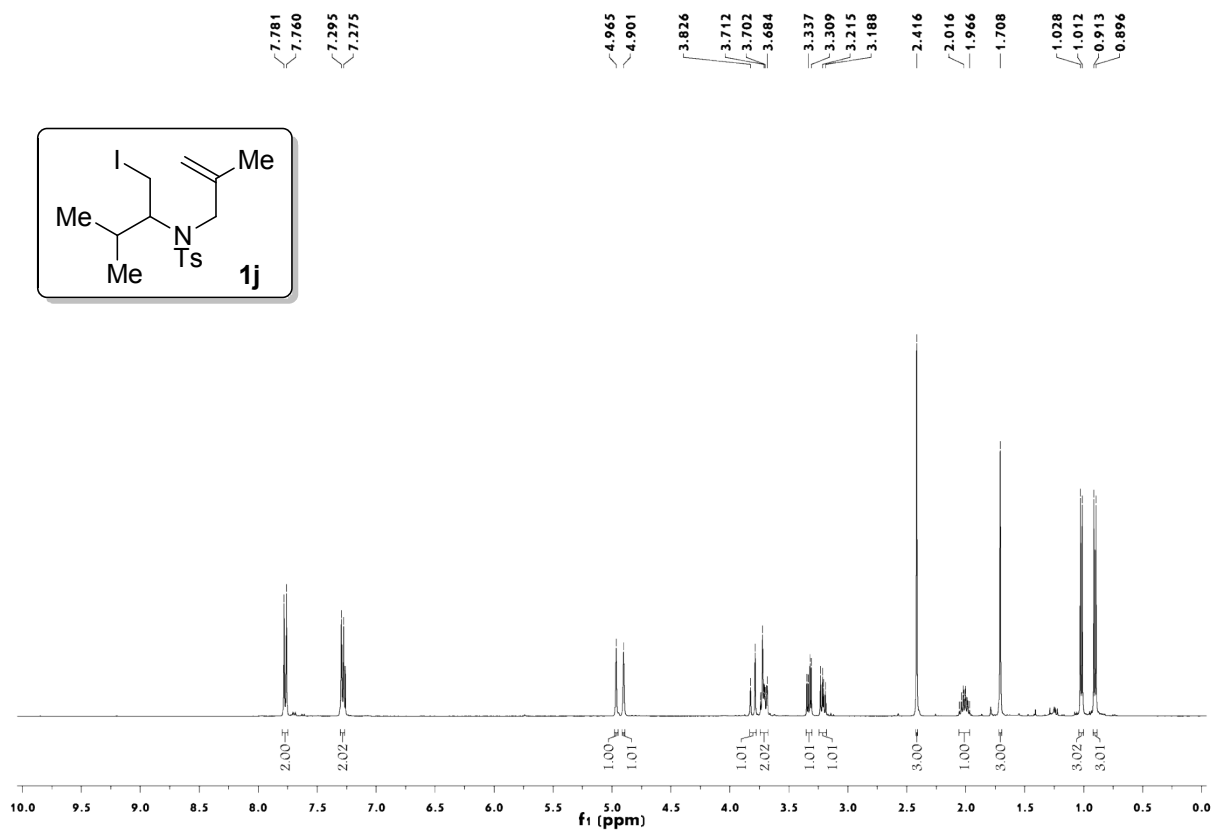
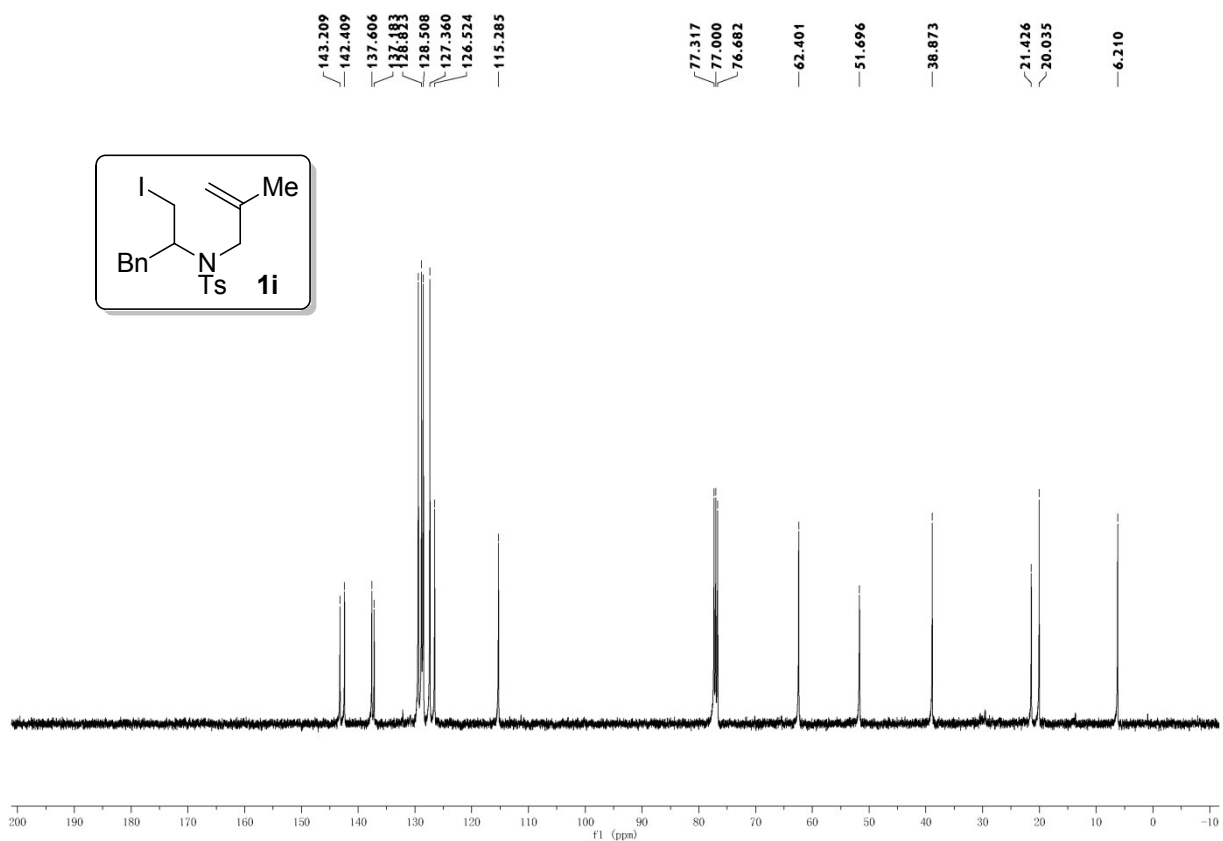


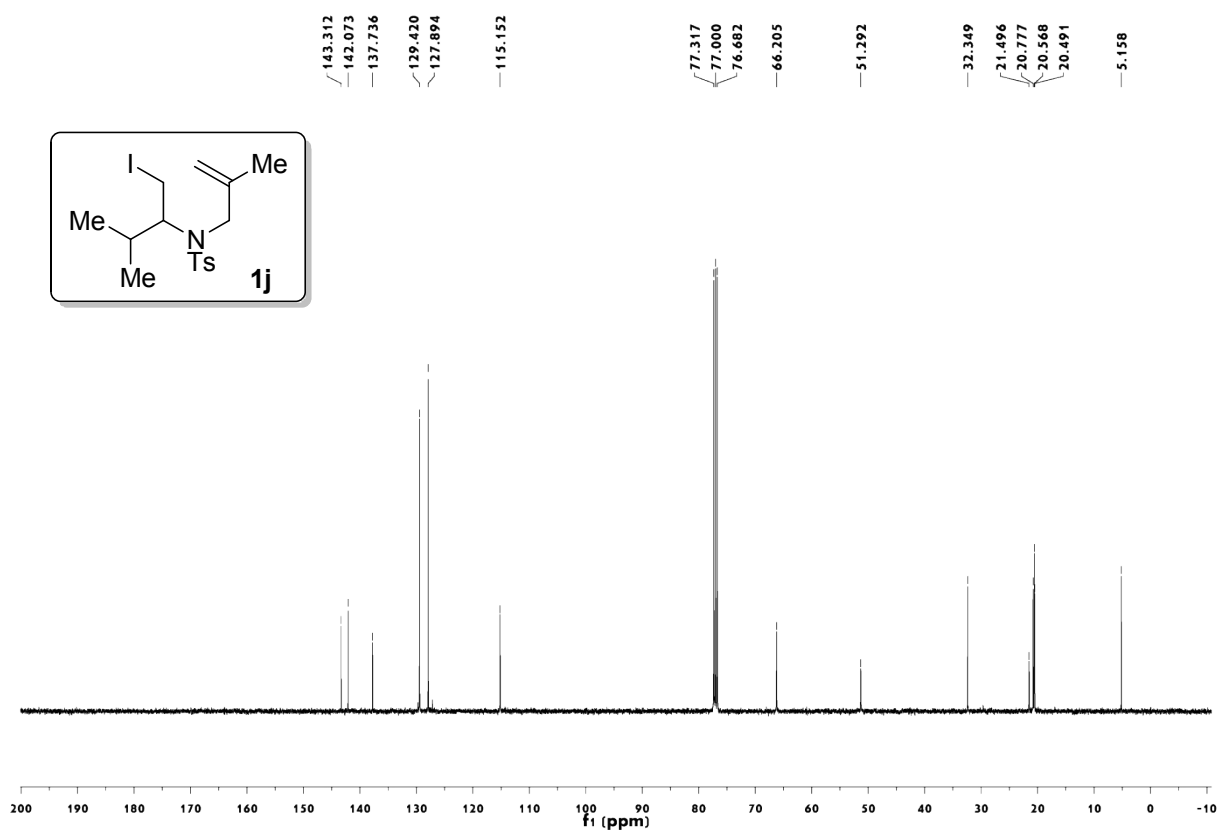




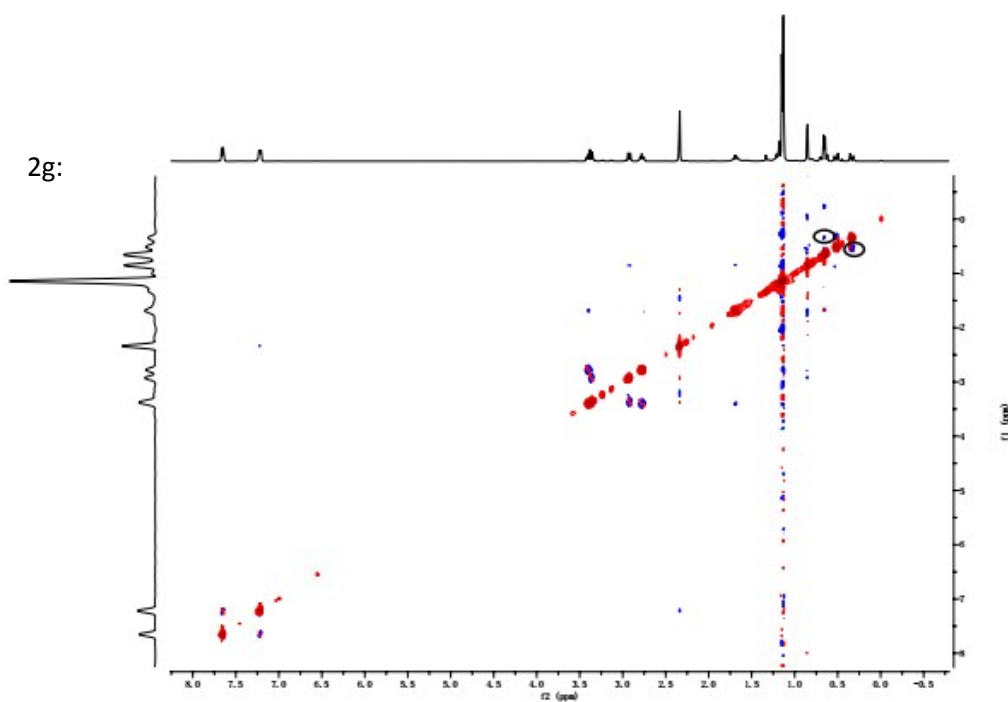






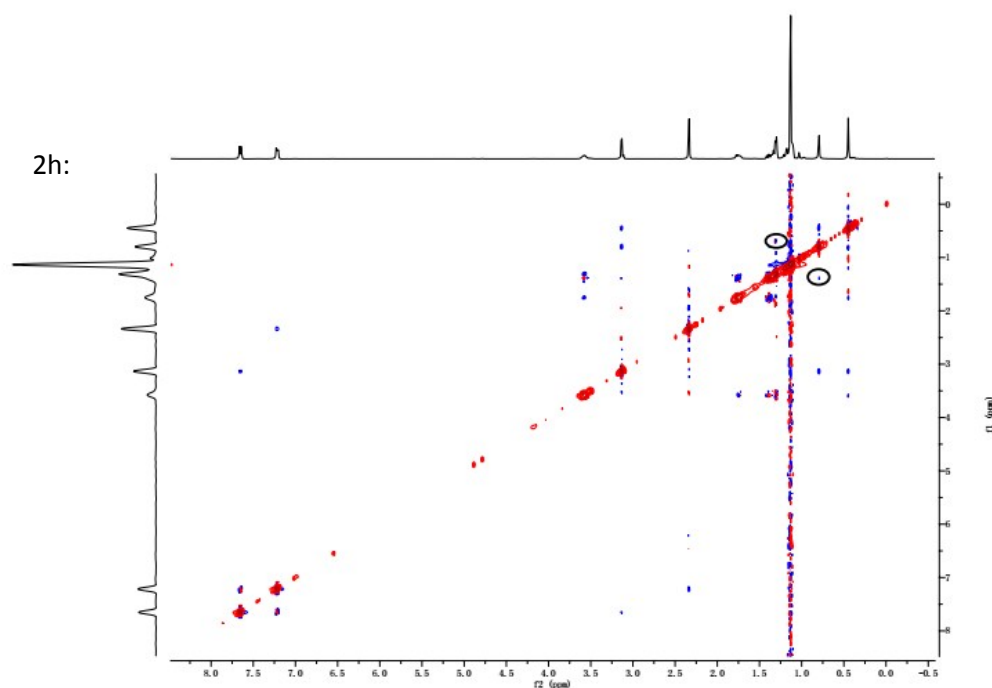
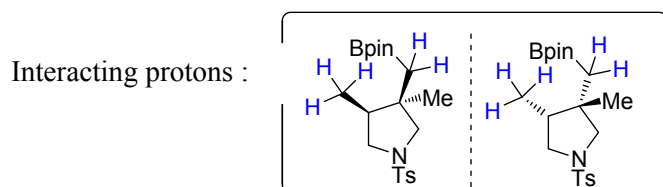
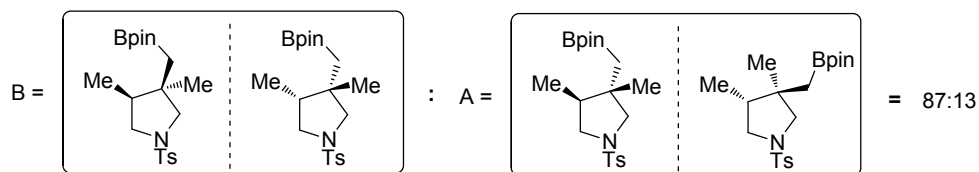


7. Copies of the NOESY for Borylation Product

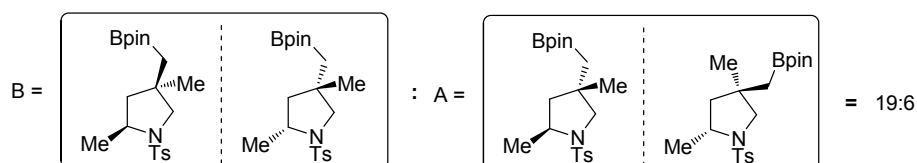


From the view of the spectrum **2g**, there was no signal between protons of methyl group on the left and the right of **2g** showed below. This showed that the two methyl groups were located on the opposite side. In addition, between the methyl on the left and methylene group

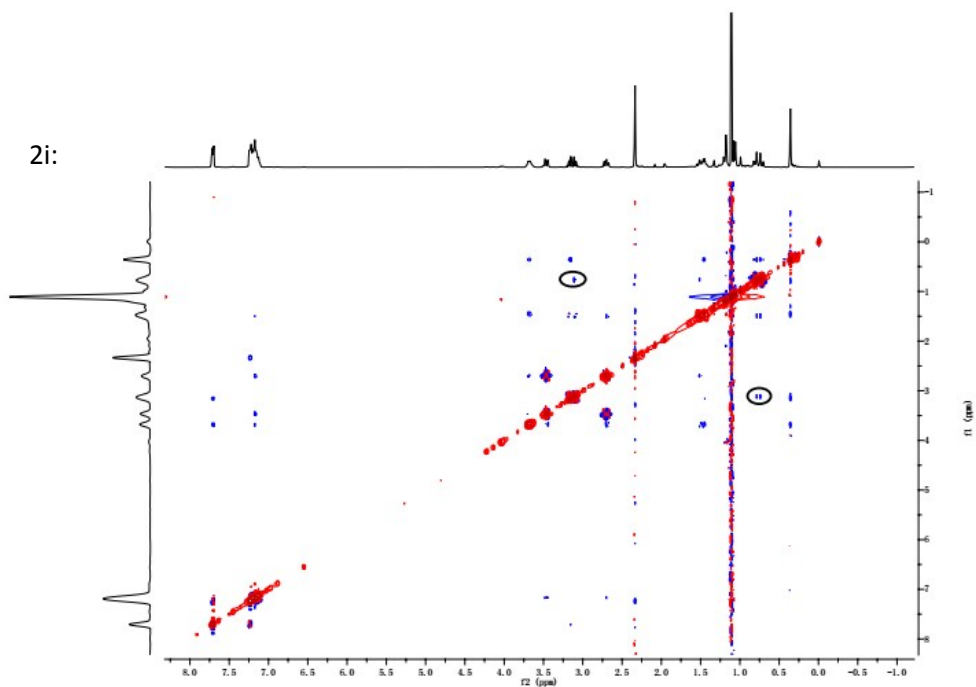
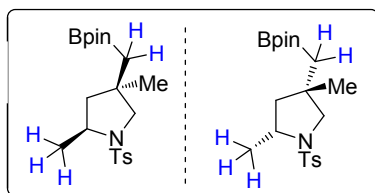
with the boron group showed a signal at 0.6/0.5 ppm. This showed that the two groups were located on the same side. So the ratio was B:A = 87:13.



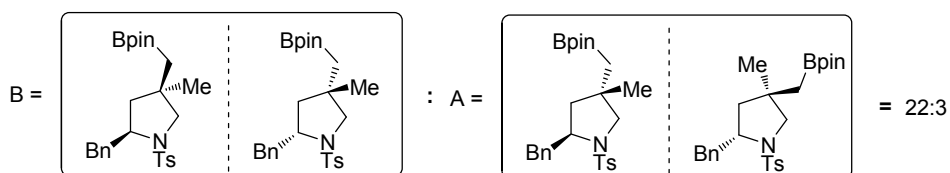
From the view of the spectrum **2h**, protons of methyl group on the left and protons of methylene group with the boron group showed a signal at 1.3/0.8 ppm. This indicated that the two groups were located on the same side. Besides, there was no signal between protons of methyl group on the left and the right of **2h**. This showed that the two methyl groups were located on the opposite side. So the ratio was B:A = 19:6.



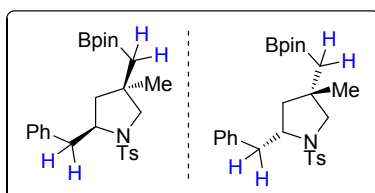
Interacting protons :



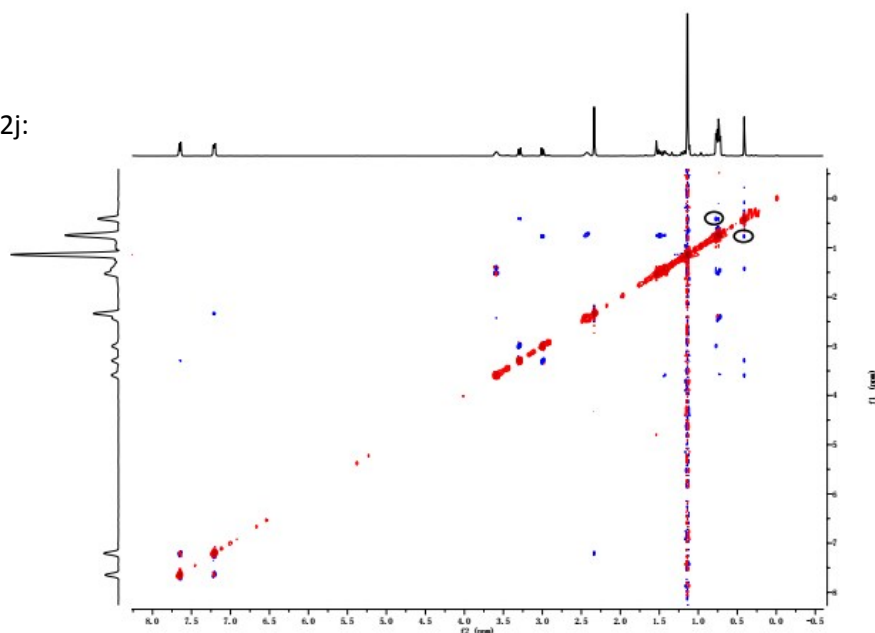
In the above spectrum **2i**, there was no signal between protons of benzyl group and methyl group on the right. This showed that the two groups were located on the opposite side. In addition, between protons of benzyl group and protons of methylene group with the boron group had a weak signal around 0.8/3.1 ppm. This indicated that the two groups were located on the same side. So the ratio was B:A = 22:3.



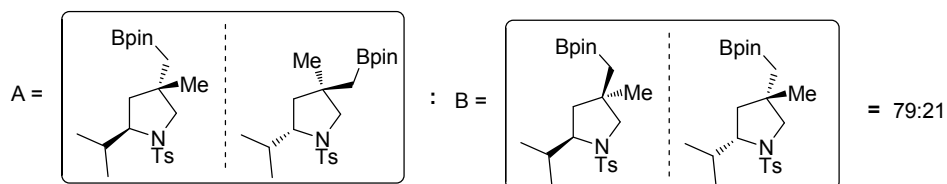
Interacting protons :



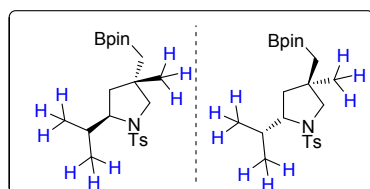
2j:

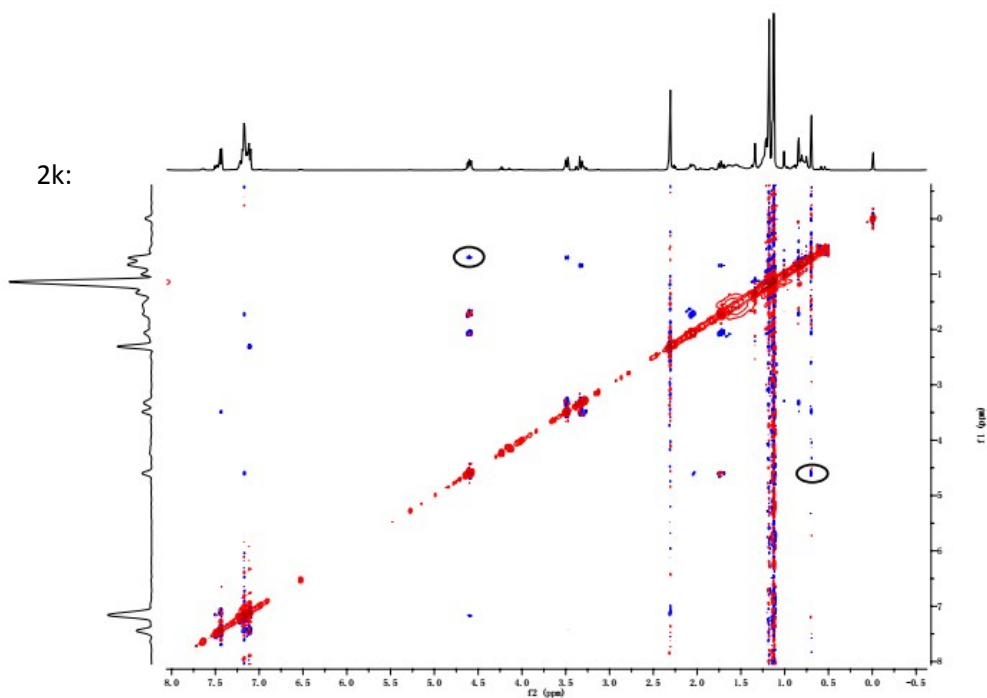


In the above spectrum **2j**, protons of isopropyl group and protons of methyl group on the right had a signal at 0.4/0.78 ppm, indicating that the two groups were located on the same side. But there was no signal between protons of isopropyl group and methylene group with the boron group. So the ratio was B:A = 79:21.

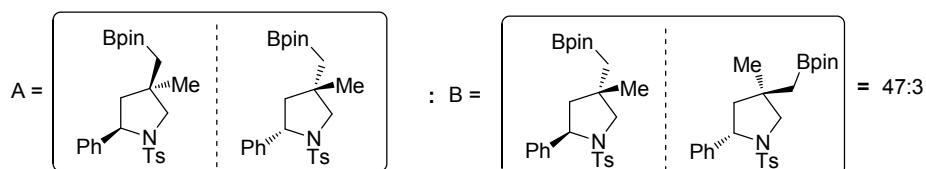


Interacting protons :

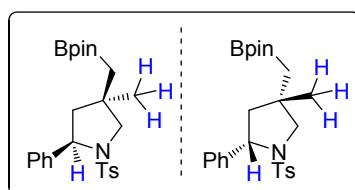




From the view of the spectrum **2k**, there was no signal between protons of phenyl group and methylene group with the boron group. This indicated that the two groups were located on the opposite side. In addition, protons of carbon atoms which linked to phenyl group and protons of methyl group on the right had a signal at 4.6/0.7 ppm. This showed that the two groups were located on the same side.

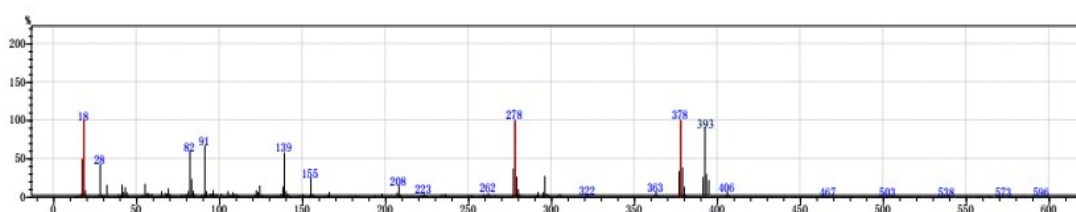
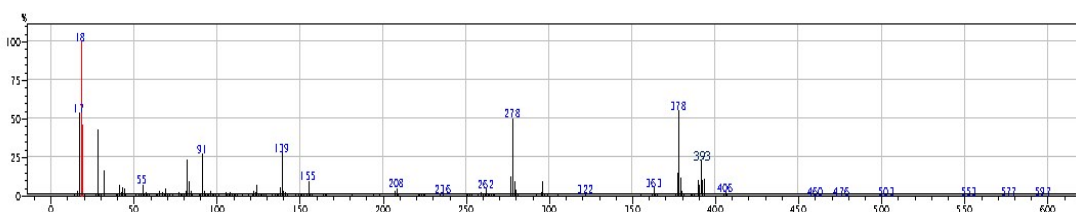
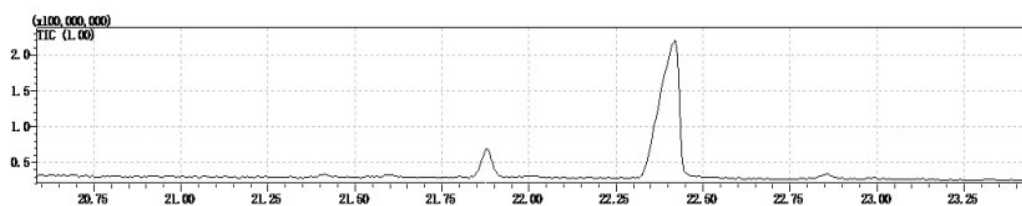


Interacting protons:



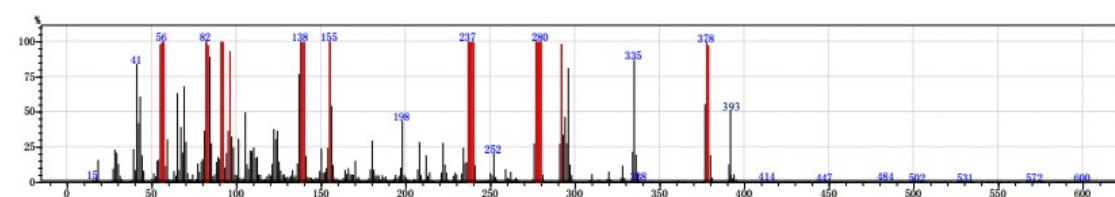
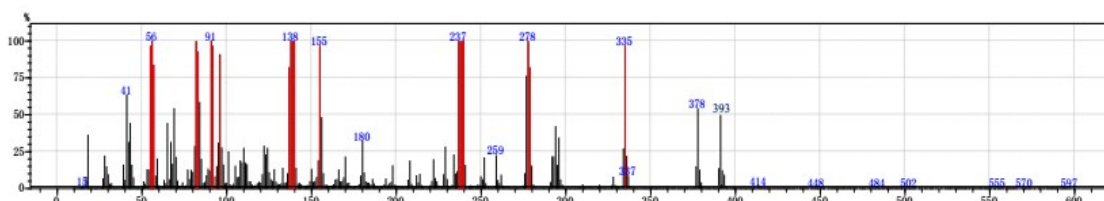
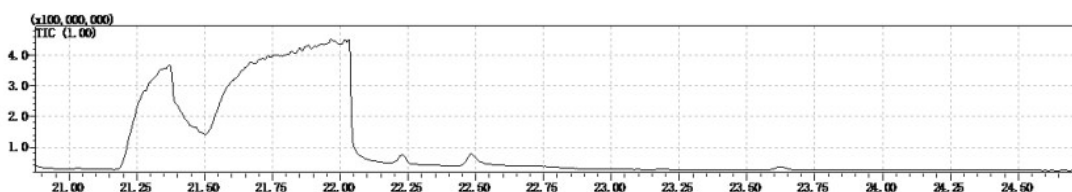
8. Copies of the GC-MS for Borylation Product

2g :



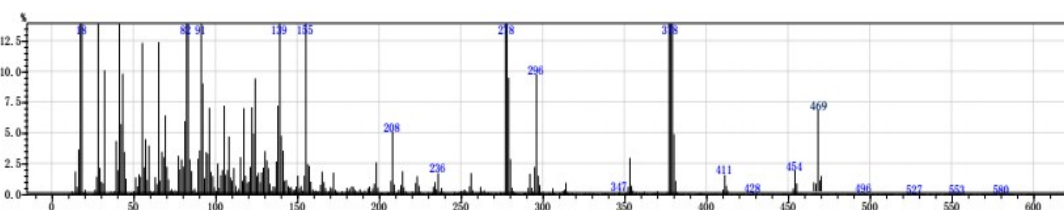
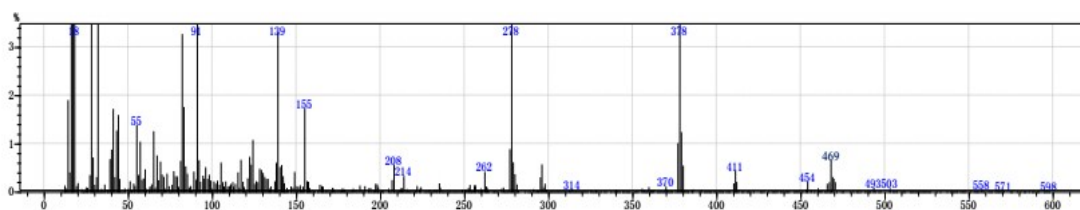
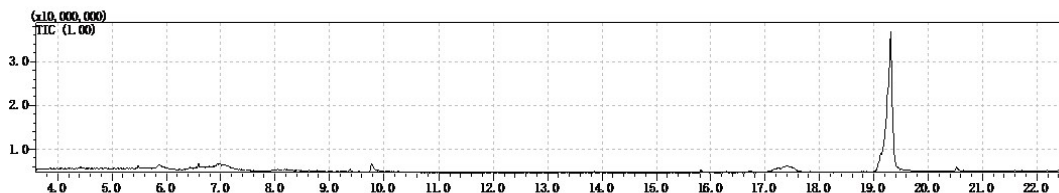
In the above chart, the two peaks corresponded to the same molecular weight, i.e. 393 g/mol, which was consistent with the molecular weight of the target product **2g**. The ratio of big peak to small peak is 87 to 13.

2h :



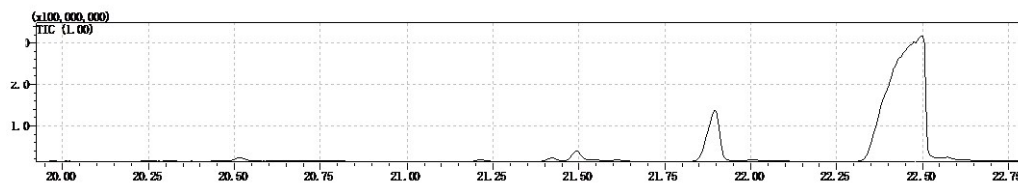
From the view of the chart, the two peaks had the same molecular weight, i.e. 393 g/mol. This was the molecular weight of the product **2h**. The ratio of big peak to small peak is 19 to 6.

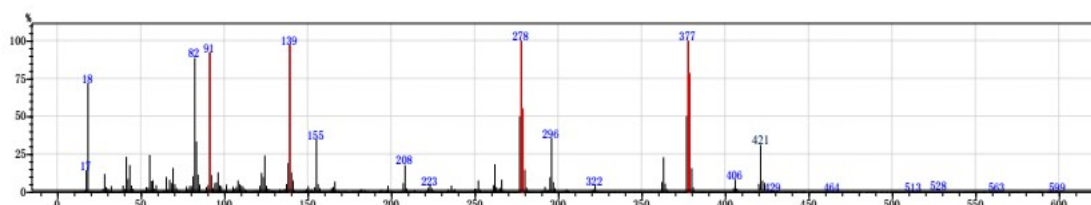
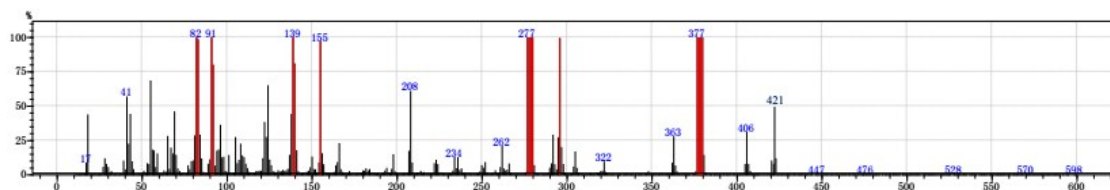
2i :



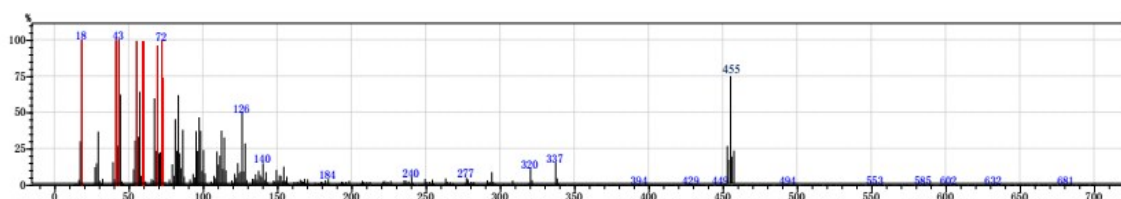
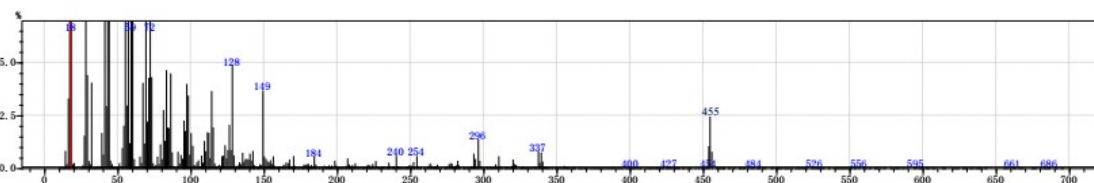
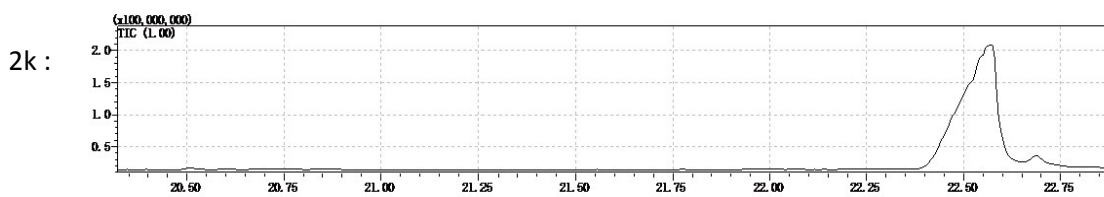
By GCMS test, this substance was divided into two peaks of the same molecular weight, i.e. 469 g/mol. This was the molecular weight of the product **2i**. The ratio of big peak to small peak is 22 to 3.

2j :





In the above chart, the two peaks corresponded to the same molecular weight, i.e. 421 g/mol. This was the molecular weight of the product **2j**. The ratio of big peak to small peak is 79 to 21.



By GCMS, this substance was divided into two peaks of the same molecular weight, i.e. 455 g/mol, which was consistent with the molecular weight of the target product **2k**. The ratio of big peak to small peak is 47 to 3.