Supporting Information

Palladium-Catalyzed 6-Endo Selective Alkyl-Heck Reactions: Access to 5-Phenyl-1,2,3,6-Tetrahydropyridine Derivatives

Xu Dong,[†] Ying Han,[†] Fachao Yan,[†] Qing Liu,[*,†] Ping Wang,[†] Kexun Chen,[†] Yueyun Li,[†] Zengdian Zhao,[†] Yunhui Dong[†] and Hui Liu[*,†,‡]

[†] School of Chemical Engineering, Shandong University of Technology, 266 West Xincun Road, Zibo 255049, P. R. China

[‡] College of Materials Science and Engineering, Hunan University, Changsha, Hunan 410082, China

*E-mail: huiliu1030@sdut.edu.cn.

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I. 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). ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Brucker 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.

II. Representative Bioactive Molecules Built on 5-Phenyl-1,2,3,6-Tetrahydropyridine Core Scaffold

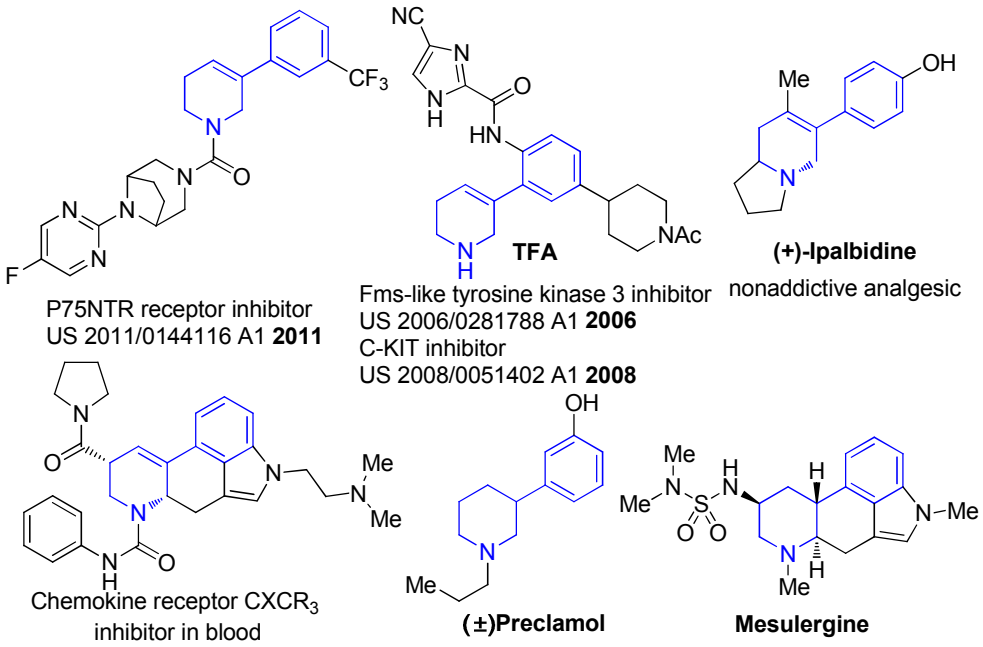
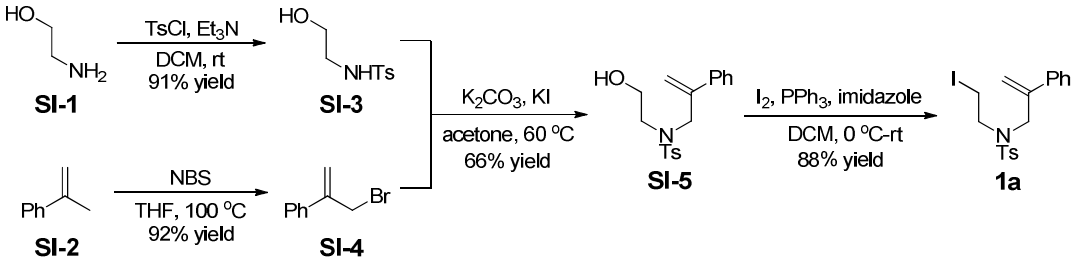


Figure S1. Representative Bioactive Molecules Built on 5-Phenyl-1,2,3,6-Tetrahydropyridine Core Scaffold

The 5-phenyl-1,2,3,6-tetrahydropyridine derivatives exist in numerous bioactivity molecules, such as P75NTR receptor inhibitor, Fms-like tyrosine kinase 3 inhibitor, C-KIT inhibitor, Chemokine receptor $CXCR_3$ inhibitor, and (+)-Ipalbidine. The reductive structure 3-arylpiperidines are also important classes of synthetic block, such as existing in (±)-Preclamol (the first autoreceptor-selective agonist) and Mesulergine (for the treatment of hyperprolactinemia, acromegaly and Parkinson's disease). Thus we envision this strategy may become a useful tool for bio- and medicinal chemistry.

III. The General Synthetic Procedure and Analytical Data for Unactivated Alkyl Iodides



General Procedure:

Preparation of alcohol SI-3: 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 x 3). The organic layer was dried over Na_2SO_4 and concentrated to afford the crude alcohol **SI-3** (39.3 g, 183 mmol, 91% yield) as a white solid, which was used without further purification.

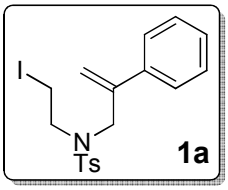
Preparation of bromide SI-4: To a solution of alpha-methylstyrene (4.6 g, 39 mmol, 1.0 equiv) in 6 mL $CHCl_3$ was added NBS (8.0 g, 45 mmol, 1.15 equiv). The mixture was stirred and heated to 60 ^oC under reflux for 4 h. Then the reaction liquid was concentrated and petroleum ether was added. The precipitate that had formed was filtered off and then the organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (PE only) to give the bromide **SI-4** (7.1 g, 36 mmol, 92% yield) as a light yellow liquid.

Preparation of alcohol SI-5: The **SI-3** (2.15 g, 10 mmol, 1.0 equiv) was dissolved in 40 mL acetone, and **SI-4** (2.36 g, 12 mmol, 1.2 equiv), K_2CO_3 (1.66 g, 12 mmol, 1.2 equiv), KI (0.33 g, 2 mmol, 0.2 equiv) was added successively. Then the mixture was stirred and refluxed at 60 ^oC over night. After successive filtration and purification by column chromatography (PE:EA, 2:1), alcohol **SI-5** (2.19 g, 6.6 mmol, 66% yield) was given as colorless oil.

Preparation of unactivated alkyl iodide 1a: To a solution of **SI-5** (1.66 g, 5 mmol, 1.0 equiv) in 40 mL DCM was cooled to 0 ^oC. PPh_3 (3.93 g, 15 mmol, 3.0 equiv), imidazole (1.02 g, 15 mmol, 3.0 equiv), I_2 (3.81 g, 15 mmol, 3.0 equiv) was added successively. Then the mixture was warmed to room temperature and stirred for 2 h. The precipitate was removed by

filtration. Purification by column chromatography (PE:EA, 10:1) afforded the iodide **1a** (1.94 g, 4.4 mmol, 88% yield) as a white solid.

Analytical Data:



$C_{18}H_{20}INO_2S$

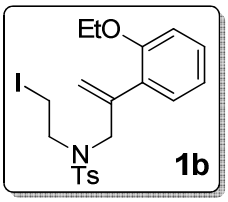
MW: 441.33 g·mol^{-1}

White solid

Yield: 88%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.61 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.30-7.26 (m, 3H), 7.26-7.24 (m, 2H), 5.47 (s, 1H), 5.16 (s, 1H), 4.12 (s, 2H), 3.27 (t, *J* = 8.8 Hz, 2H), 2.92 (t, *J* = 8.8 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.7, 142.5, 137.4, 135.3, 129.8, 128.5, 128.2, 127.1, 126.2, 117.1, 52.9, 50.2, 21.4, 1.8.



$C_{20}H_{24}INO_3S$

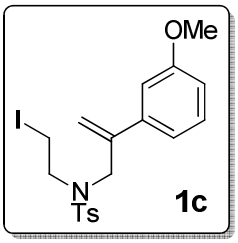
MW: 485.38 g·mol^{-1}

Off-White solid

Yield: 79%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.58 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.07 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.92-6.85 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.34 (s, 1H), 5.23 (s, 1H), 4.22 (s, 2H), 4.00 (q, *J* = 6.8 Hz, 2H), 3.45 (t, *J* = 8.4 Hz, 2H), 3.19 (t, *J* = 8.4 Hz, 2H), 2.41 (s, 3H), 1.42 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 155.9, 143.5, 143.3, 136.2, 130.3, 129.6, 129.2, 127.4, 127.1, 120.5, 117.9, 111.3, 63.5, 52.7, 50.9, 21.4, 14.9, 2.0.



$C_{19}H_{22}INO_3S$

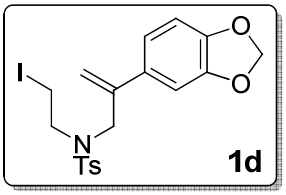
MW: 471.35 g·mol^{-1}

Off-White solid

Yield: 71%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.70 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30-7.28 (m, 1H), 7.09-7.07 (m, 2H), 6.91-6.88 (m, 1H), 5.58 (s, 1H), 5.26 (s, 1H), 4.20 (s, 2H), 3.86 (s, 3H), 3.37 (t, *J* = 8.8 Hz, 2H), 3.02 (t, *J* = 8.4 Hz, 2H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.7, 143.8, 142.6, 138.9, 135.5, 129.9, 129.6, 127.3, 118.7, 117.3, 114.2, 111.8, 55.3, 53.2, 50.5, 21.5, 1.9.



$C_{19}H_{20}INO_4S$

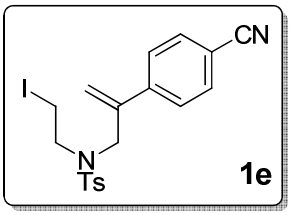
MW: 485.34 g·mol^{-1}

White solid

Yield: 55%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.59 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.80-6.74 (m, 3H), 6.53 (s, 1H), 5.98 (s, 2H), 5.97 (s, 1H), 4.41 (s, 2H), 3.31 (t, *J* = 8.4 Hz, 2H), 3.07 (t, *J* = 8.4 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 147.8, 147.7, 144.3, 143.9, 134.8, 133.8, 129.8, 127.4, 121.4, 119.9, 108.2, 106.5, 101.2, 53.5, 21.6, 17.2, 1.0.



$C_{19}H_{19}IN_2O_2S$

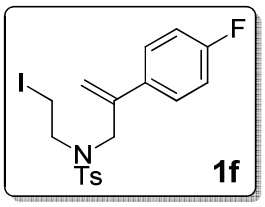
MW: 466.34 g·mol^{-1}

Off-White solid

Yield: 60%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.67 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.65 (s, 1H), 5.39 (s, 1H), 4.18 (s, 2H), 3.32 (t, *J* = 8.4 Hz, 2H), 2.94 (t, *J* = 8.4 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.1, 141.8, 141.4, 135.1, 132.3, 129.9, 127.2, 127.0, 120.1, 118.5, 111.9, 52.8, 50.5, 21.5, 1.1.



$C_{18}H_{19}FINO_2S$

MW: 459.32 g·mol^{-1}

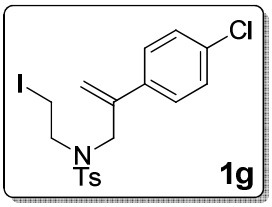
Off-White solid

Yield: 69%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.67 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 5.49 (s, 1H), 5.21 (s, 1H), 4.15 (s, 2H), 3.31 (t, *J* = 8.4 Hz, 2H), 2.96 (t, *J* = 8.4 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.0, 143.9, 141.7, 135.3, 133.4, 129.9, 128.1 (d, *J* = 8.0 Hz), 127.3, 117.2, 115.5 (d, *J* = 21.4 Hz), 53.3, 50.4, 21.6, 1.6.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, δ ppm): –113.4.



$C_{18}H_{19}ClINO_2S$

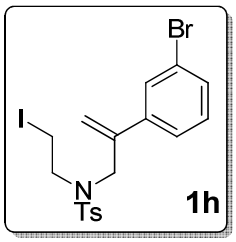
MW: 475.77 g·mol^{-1}

Off-White solid

Yield: 89%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.66 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 5.53 (s, 1H), 5.24 (s, 1H), 4.15 (s, 2H), 3.32 (t, *J* = 8.4 Hz, 2H), 2.97 (t, *J* = 8.4 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.9, 141.6, 135.8, 135.3, 134.2, 129.9, 128.7, 127.7, 127.2, 117.7, 53.0, 50.1, 21.5, 1.5.



$C_{18}H_{19}BrINO_2S$

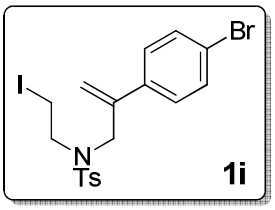
MW: 520.22 g·mol^{-1}

Off-White solid

Yield: 80%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.66 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 1.6 Hz, 2H), 7.44-7.38 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 5.53 (s, 1H), 5.28 (s, 1H), 4.15 (s, 2H), 3.36 (t, *J* = 8.4 Hz, 2H), 3.02 (t, *J* = 8.4 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.8, 141.4, 139.6, 135.3, 131.2, 130.0, 129.8, 129.2, 127.2, 125.0, 122.6, 118.2, 52.6, 50.3, 21.5, 1.4.



$C_{18}H_{19}BrINO_2S$

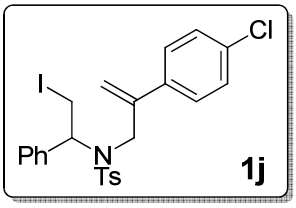
MW: 520.22 g·mol^{-1}

Off-White solid

Yield: 93%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.66 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.53 (s, 1H), 5.25 (s, 1H), 4.15 (s, 2H), 3.32 (t, *J* = 8.4 Hz, 2H), 2.97 (t, *J* = 8.4 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.9, 141.7, 136.2, 135.2, 131.6, 129.9, 128.0, 127.2, 122.4, 117.8, 52.9, 50.3, 21.5, 1.5.



$C_{24}H_{23}ClINO_2S$

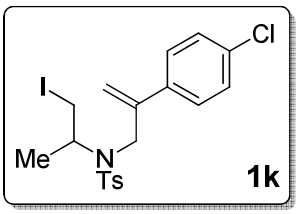
MW: 551.87 g·mol^{-1}

Off-White solid

Yield: 52%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.58 (d, *J* = 8.4 Hz, 2H), 7.31-7.27 (m, 2H), 7.26-7.20 (m, 5H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 5.34 (s, 1H), 5.19 (s, 1H), 5.04 (dd, *J* = 11.6, 4.0 Hz, 1H), 4.30 (d, *J* = 16.4 Hz, 1H), 3.80 (d, *J* = 16.4 Hz, 1H), 3.66 (t, *J* = 10.8 Hz, 1H), 3.40 (dd, *J* = 10.0, 4.0 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.7, 143.6, 136.9, 136.8, 134.0, 133.9, 129.7, 129.1, 128.6, 128.5, 128.4, 127.8, 127.3, 117.1, 62.7, 49.1, 21.6, 4.4.



$C_{19}H_{21}ClINO_2S$

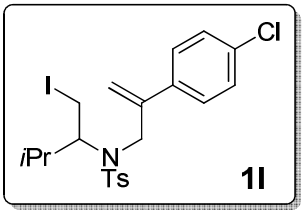
MW: 489.80 g·mol^{-1}

Off-White solid

Yield: 70%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.68 (d, *J* = 8.4 Hz, 2H), 7.37-7.30 (m, 6H), 5.46 (s, 1H), 5.36 (s, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 4.06 (d, *J* = 16.0 Hz, 1H), 3.98 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.04 (d, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 1.18 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.8, 143.7, 136.9, 136.5, 134.0, 129.8, 128.7, 127.9, 127.2, 117.0, 56.1, 48.4, 21.5, 16.5, 8.7.



$C_{21}H_{25}ClINO_2S$

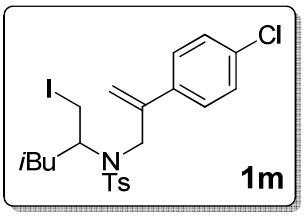
MW: 517.85 g·mol^{-1}

Off-White solid

Yield: 68%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.73 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 3.6 Hz, 4H), 5.42 (s, 1H), 5.40 (s, 1H), 4.25 (s, 2H), 3.68-3.61 (m, 1H), 3.31 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.13 (dd, *J* = 10.8, 6.4 Hz, 1H), 2.43 (s, 3H), 1.97-1.90 (m, 1H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.67 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 143.3, 137.4, 137.4, 133.8, 129.6, 128.5, 127.9, 127.9, 117.9, 65.9, 32.5, 21.6, 20.7, 20.5, 5.2.



$C_{22}H_{27}ClINO_2S$

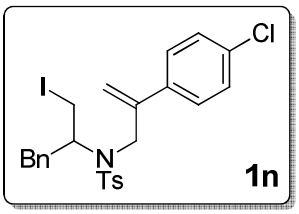
MW: 531.88 g·mol^{-1}

Off-White solid

Yield: 68%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.69 (d, *J* = 8.0 Hz, 2H), 7.36-7.28 (d, *J* = 8.0 Hz, 6H), 5.46 (s, 1H), 5.39 (s, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 3.90-3.83 (m, 1H), 3.04 (t, *J* = 9.2 Hz, 1H), 2.93 (dd, *J* = 9.6, 4.4 Hz, 1H), 2.44 (s, 3H), 1.56-1.43 (m, 2H), 1.33-1.27 (m, 1H), 0.73 (d, *J* = 6.4 Hz, 3H), 0.71 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.8, 143.7, 137.1, 136.8, 134.0, 129.8, 128.6, 128.0, 127.4, 117.3, 58.9, 48.6, 40.1, 24.6, 22.8, 21.5, 21.4, 7.8.



$C_{25}H_{25}ClINO_2S$

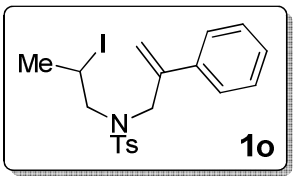
MW: 565.89 g·mol^{-1}

Off-White solid

Yield: 47%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.66 (d, *J* = 8.4 Hz, 2H), 7.26-7.19 (m, 9H), 7.05-7.00 (m, 2H), 5.46 (s, 1H), 5.31 (s, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.18 (d, *J* = 15.6 Hz, 1H), 4.01-3.94 (m, 1H), 3.28-3.19 (m, 2H), 3.04 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.93 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.7, 143.4, 137.8, 137.0, 136.7, 134.0, 129.6, 129.0, 128.6, 128.6, 127.9, 127.7, 126.7, 118.1, 62.6, 50.2, 39.1, 21.6, 6.6.



$C_{19}H_{22}INO_2S$

MW: 455.35 g·mol^{-1}

Off-White solid

Yield: 52%

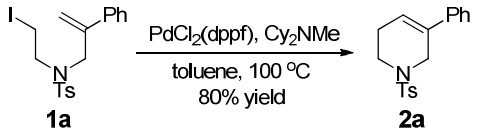
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.68 (d, *J* = 8.4 Hz, 2H), 7.47 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.36-7.30 (m, 5H), 5.53 (s, 1H), 5.18 (s, 1H), 4.36 (d, *J* = 14.4 Hz, 1H), 4.20-4.13 (m, 1H), 3.94 (d, *J* = 14.4 Hz, 1H), 3.51 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.28 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.45 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.8, 142.7, 137.4, 135.1, 129.8, 128.6, 128.3, 127.5, 126.4, 117.1, 58.2, 54.4, 25.1, 24.4, 21.5.

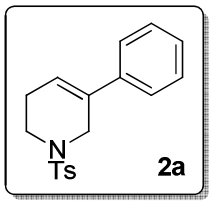
IV. The General Synthetic Procedure and Analytical Data for 5-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine

General Synthetic Procedure:

Unactivated alkyl iodide **1a** (88.2 mg, 0.2 mmol, 1.0 equiv) and $PdCl_2$(dppf) (14.6 mg, 0.02 mmol, 0.1 equiv) were added to a reaction vessel and vacuum purged three times, backfilling with N_2. Toluene (2 mL) and *N,N*-dicyclohexylmethylamine (85.8 μL, 0.4 mmol, 2.0 equiv) was added successively and the reaction was heated at 110 °C for 16 h. The reaction was cooled to room temperature and quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc. The combined organic layers were concentrated in vacuo. Purification by column chromatography (PE:EA, 10:1) afforded the desired 5-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine **2a** (51 mg, 0.016 mmol, 80% yield).



Analytical Data:



$C_{18}H_{19}NO_2S$

MW: 313.41 g·mol^{-1}

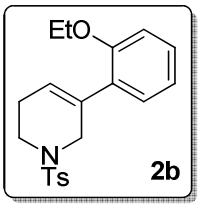
White solid

Isolated Amount: 50.3 mg **Yield:** 80%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.72 (d, *J* = 8.0 Hz, 2H), 7.33-7.27 (m, 7H), 6.08-6.06 (m, 1H), 3.96-3.91 (m, 2H), 3.24 (t, *J* = 5.6 Hz, 2H), 2.43 (s, 3H), 2.43-2.37 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 138.7, 133.3, 129.7, 128.5, 127.7, 125.2, 122.1, 46.4, 42.3, 25.6, 21.5.

MS (EI) m/z 313 (M+); **HRMS (ESI)** Calcd for $C_{18}H_{19}NO_2S$+H 314.1215, Found 314.1217.



$C_{20}H_{23}NO_3S$

MW: 357.47 g·mol^{-1}

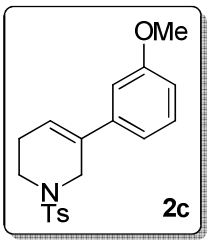
Off-white solid

Isolated Amount: 36.6 mg **Yield:** 51%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.71 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (td, *J* = 8.4, 2.0 Hz, 1H), 7.07 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.90-6.82 (m, 2H), 5.77-5.74 (m, 1H), 4.02-3.98 (m, 4H), 3.26 (t, *J* = 5.6 Hz, 2H), 2.42 (s, 3H), 2.35-2.30 (m, 2H), 1.38-1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 156.1, 143.3, 134.4, 133.9, 130.0, 129.5, 129.3, 128.9, 127.7, 123.5, 120.6, 111.6, 63.7, 47.2, 42.5, 25.4, 21.5, 14.7.

MS (EI) m/z 357 (M+); **HRMS (ESI)** Calcd for $C_{20}H_{23}NO_3S$+H 358.1477, Found 358.1476.



$C_{19}H_{21}NO_3S$

MW: 343.44 g·mol^{-1}

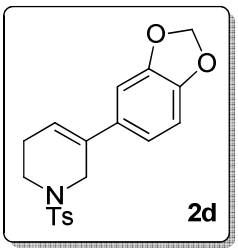
Off-white solid

Isolated Amount: 49.4 mg **Yield**: 72%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.71 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24-7.20 (m, 1H), 6.88-6.81 (m, 3H), 6.09-6.05 (m, 1H), 3.93-3.89 (m, 2H), 3.81 (s, 3H), 3.23 (t, *J* = 5.6 Hz, 2H), 2.43 (s, 3H), 2.40-2.36 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.7, 143.6, 133.4, 129.7, 129.5, 127.7, 122.4, 117.7, 112.8, 111.3, 55.3, 46.4, 42.3, 25.6, 21.5.

MS (EI) m/z 343 (M+); **HRMS (ESI)** Calcd for $C_{19}H_{21}NO_3S$+H 344.1320, Found 344.1322.



$C_{19}H_{19}NO_4S$

MW: 357.42 g·mol^{-1}

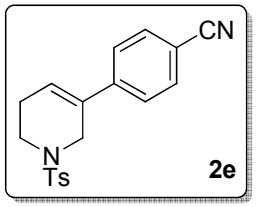
Off-white solid

Isolated Amount: 63.4 mg **Yield:** 89%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.74 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.81-6.72 (m, 3H), 5.95 (s, 2H), 5.47-5.41 (m, 1H), 4.45-4.01 (m, 2H), 3.08-3.03 (m, 2H), 2.42 (s, 3H), 2.38-2.33 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 147.6, 146.6, 143.5, 137.8, 137.5, 136.8, 129.7, 127.1, 122.0, 119.1, 107.9, 106.2, 101.0, 42.8, 28.9, 21.5, 16.3.

MS (EI) m/z 357 (M+); **HRMS (ESI)** Calcd for $C_{19}H_{19}NO_4S$+H 358.1113, Found 358.1110.



$C_{19}H_{18}N_2O_2S$

MW: 338.42 g·mol^{-1}

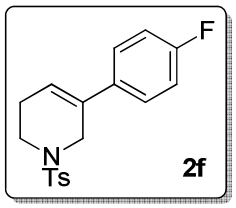
Off-white solid

Isolated Amount: 53.2 mg **Yield**: 79%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.71 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.26-6.20 (m, 1H), 3.92 (d, *J* = 2.0 Hz, 2H), 3.54 (t, *J* =5.6 Hz, 1H), 3.29 (t, *J* = 6.0 Hz, 1H), 3.25-3.23 (m, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.8, 142.9, 136.8, 133.2, 132.4, 132.1, 129.8, 127.6, 125.6, 118.6, 111.2, 45.9, 42.1, 25.8, 21.5.

MS (EI) m/z 338 (M+); **HRMS (ESI)** Calcd for $C_{19}H_{18}N_2O_2S$+H 339.1167, Found 339.1169.



$C_{18}H_{18}FNO_2S$

MW: 331.40 g·mol^{-1}

Off-white solid

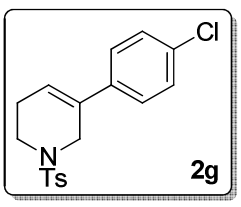
Isolated Amount: 49.2 mg **Yield**: 74%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.71 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25-7.22 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.02-6.00 (m, 1H), 3.89 (dd, *J* = 4.4, 2.4 Hz, 2H), 3.22 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 2.41-2.36 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.7, 134.8, 133.3, 132.5, 129.7, 127.7, 126.9 (d, *J* = 7.8 Hz), 122.2, 115.4 (d, *J* = 21.3 Hz), 46.5, 42.3, 25.6, 21.6.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, δ ppm): –114.5.

MS (EI) m/z 331 (M+); **HRMS (ESI)** Calcd for $C_{18}H_{18}FNO_2S$+H 332.1121, Found 332.1120.



$C_{18}H_{18}ClNO_2S$

MW: 347.86 g·mol^{-1}

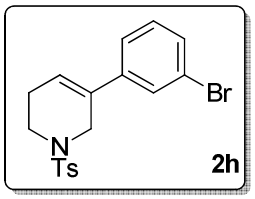
White solid

Isolated Amount: 47.2 mg **Yield:** 68%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.71 (d, *J* = 5.6 Hz, 2H), 7.33 (d, *J* = 5.6 Hz, 2H), 7.28 (d, *J* = 5.6 Hz, 2H), 7.21 (d, *J* = 5.6 Hz, 2H), 6.07-6.06 (m, 1H), 3.90 (d, *J* = 1.2 Hz, 2H), 3.23 (t, *J* = 4.0 Hz, 2H), 2.43 (s, 3H), 2.40-2.36 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.7, 137.1, 133.4, 133.2, 132.4, 129.7, 128.6, 127.6, 126.4, 122.8, 46.2, 42.2, 25.6, 21.5.

MS (EI) m/z 347 (M+); **HRMS (ESI)** Calcd for $C_{18}H_{18}ClNO_2S$+H 348.0825, Found 348.0828.



$C_{18}H_{18}BrNO_2S$

MW: 392.31 g·mol^{-1}

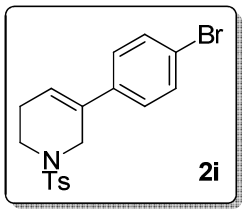
Off-white solid

Isolated Amount: 46.1 mg **Yield:** 59%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.72 (d, *J* = 8.4 Hz, 2H), 7.33-7.29 (m, 6H), 6.10-6.04 (m, 1H), 3.96-3.92 (m, 2H), 3.24 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 2.41-2.37 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 138.7, 133.5, 133.4, 129.7, 128.5, 127.7, 125.2, 122.2, 46.4, 42.4, 25.7, 21.5.

MS (EI) m/z 391 (M+); **HRMS (ESI)** Calcd for $C_{18}H_{18}BrNO_2S$+H 392.0320, Found 392.0319.



$C_{18}H_{18}BrNO_2S$

MW: 392.31 g·mol^{-1}

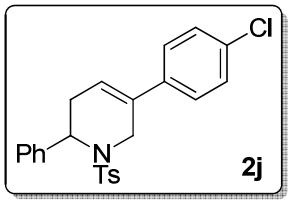
Off-white solid

Isolated Amount: 48.0 mg **Yield:** 61%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.72 (d, *J* = 8.0 Hz, 2H), 7.33-7.29 (m, 6H), 6.09-6.06 (m, 1H), 3.94-3.93 (m, 2H), 3.23 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 2.41-2.37 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 138.7, 133.4, 133.2, 129.7, 128.5, 127.7, 125.2, 122.2, 46.4, 42.3, 25.6, 21.5.

MS (EI) m/z 391 (M+); **HRMS (ESI)** Calcd for $C_{18}H_{18}BrNO_2S$+H 392.0320, Found 392.0317.



$C_{24}H_{22}ClNO_2S$

MW: 423.95 g·mol^{-1}

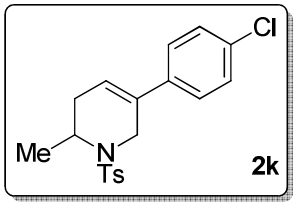
Off-white solid

Isolated Amount: 68.6 mg **Yield:** 81%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.68 (d, *J* = 8.0 Hz, 2H), 7.34-7.28 (m, 4H), 7.24-7.14 (m, 7H), 6.12-6.06 (m, 1H), 5.34 (d, *J* = 6.4 Hz, 1H), 4.47 (d, *J* = 17.6 Hz, 1H), 3.68-3.60 (m, 1H), 2.63-2.46 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.7, 143.6, 133.4, 129.7, 129.5, 127.7, 122.4, 117.7, 112.8, 111.3, 55.3, 42.3, 25.6, 21.5.

MS (EI) m/z 423 (M+); **HRMS (ESI)** Calcd for $C_{24}H_{22}ClNO_2S$+H 424.1138, Found 424.1141.



$C_{19}H_{20}ClNO_2S$

MW: 361.89 g·mol^{-1}

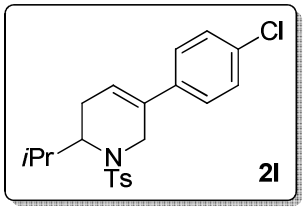
Off-white solid

Isolated Amount: 56.5 mg **Yield:** 78%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.71 (d, *J* = 8.4 Hz, 2H), 7.31-7.27 (m, 4H),7.25-7.22 (m, 2H), 5.99-5.97 (m, 1H), 4.49 (d, *J* = 17.2 Hz, 1H), 4.37-4.30 (m, 1H), 3.86-3.80 (m, 1H), 2.51-2.44 (m, 1H), 2.41 (s, 3H), 1.97-1.91 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.3, 137.1, 136.9, 133.4, 131.3, 129.7, 128.7, 127.1, 126.2, 121.1, 45.7, 41.2, 31.1, 21.5, 16.7.

MS (EI) m/z 361 (M+); **HRMS (ESI)** Calcd for $C_{19}H_{20}ClNO_2S$+H 362.0982, Found 362.0984.



$C_{21}H_{24}ClNO_2S$

MW: 389.94 g·mol^{-1}

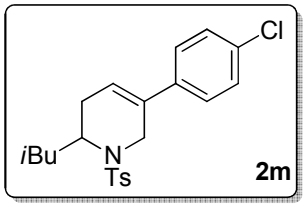
Off-white solid

Isolated Amount: 50.5 mg **Yield:** 65%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.66 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.91-5.86 (m, 1H), 4.58-4.50 (m, 1H), 3.95-3.86 (m, 1H), 3.65 (dd, *J* = 10.4, 6.4 Hz, 1H), 2.39 (s, 3H), 2.22-2.15 (m, 1H), 2.06-1.99 (m, 1H), 1.83-1.77 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.0, 138.1, 136.8, 133.4, 131.6, 129.5, 128.7, 126.8, 126.0, 121.4, 56.5, 41.9, 28.2, 25.2, 21.5, 20.2, 20.1.

MS (EI) m/z 389 (M+); **HRMS (ESI)** Calcd for $C_{21}H_{24}ClNO_2S$+H 390.1295, Found 390.1295.



$C_{22}H_{26}ClNO_2S$

MW: 403.97 g·mol^{-1}

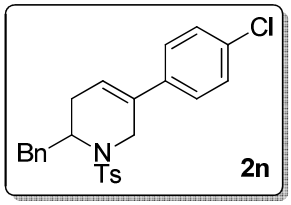
Off-white solid

Isolated Amount: 49.8 mg **Yield**: 62%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.61 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 5.85-5.80 (m, 1H), 4.45 (d, *J* = 17.6 Hz, 1H), 3.79 (d, *J* = 17.2 Hz, 1H), 3.00-2.83 (m, 1H), 2.32 (s, 3H), 2.20-2.13 (m, 1H), 1.86-1.80 (m, 1H), 1.62-1.54 (m, 2H), 1.47-1.41 (m, 1H), 0.85 (d, *J* = 6.0 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.1, 137.7, 137.0, 133.4, 131.4, 129.5, 128.7, 127.0, 126.1, 121.5, 48.1, 41.4, 40.5, 28.4, 24.7, 22.9, 22.2, 21.5.

MS (EI) m/z 403 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{26}ClNO_2S$+H 404.1451, Found 404.1453.



$C_{25}H_{24}ClNO_2S$

MW: 437.98 g·mol^{-1}

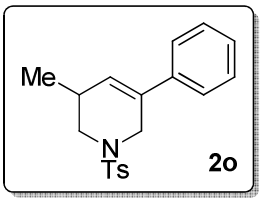
Off-white solid

Isolated Amount: 61.1 mg **Yield**: 70%

^{1}H NMR (400 MHz, DMSO, δ ppm): 7.65 (d, *J* = 8.0 Hz, 2H), 7.34-7.29 (m, 5H), 7.24-7.13 (m, 6H), 6.06-6.01 (m, 1H), 4.53 (d, *J* = 17.6 Hz, 1H), 4.44-4.38 (m, 1H), 3.99-3.94 (m, 1H), 2.76-2.65 (m, 2H), 2.39 (s, 3H), 2.29-2.23 (m, 1H), 2.07-2.01 (m, 1H).

^{13}C NMR (100 MHz, DMSO, δ ppm): 143.3, 138.0, 137.2, 136.8, 133.5, 131.7, 129.7, 129.2, 128.7, 128.6, 127.0, 126.6, 126.2, 121.1, 51.5, 41.8, 37.1, 27.1, 21.5.

MS (EI) m/z 437 (M+); **HRMS (ESI)** Calcd for $C_{25}H_{24}ClNO_2S$+H 438.1295, Found 438.1292.



$C_{19}H_{21}NO_2S$

MW: 327.44 g·mol^{-1}

White solid

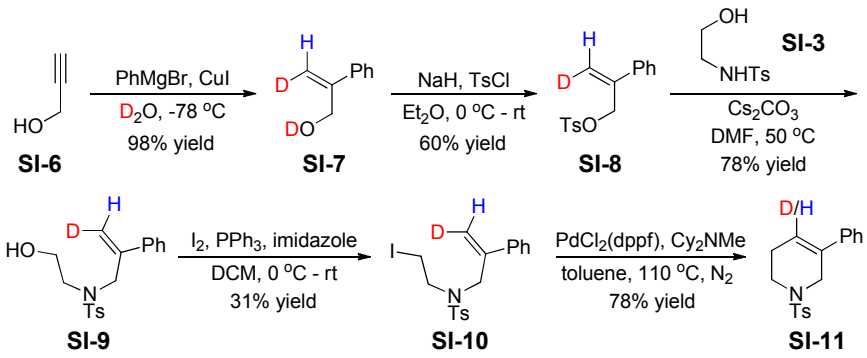
Isolated Amount: 37.9 mg **Yield:** 58%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.72 (d, *J* = 5.2 Hz, 2H), 7.34-7.28 (m, 7H), 5.96-5.92 (m, 1H), 4.08 (d, *J* = 10.4 Hz, 1H), 3.71 (d, *J* = 10.8 Hz, 1H), 3.52 (dd, *J* = 7.2, 2.8 Hz, 1H), 2.66-2.59 (m, 1H), 2.59-2.54 (m, 1H), 2.43 (s, 3H), 1.09 (d, *J* = 4.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 140.9, 138.5, 132.6, 129.7, 128.6, 128.5, 127.7, 127.7, 125.3, 49.1, 46.3, 30.6, 21.5, 18.4.

MS (EI) m/z 327 (M+); **HRMS (ESI)** Calcd for $C_{19}H_{21}NO_2S$+H 328.1371, Found 328.1369.

V. The Synthetic Procedure and Analytical Data for Deuterium- Substrate.



General Procedure:

Preparation of SI-7: To a solution of propargyl alcohol **SI-6** (1.0 g, 18 mmol, 1.0 equiv) in dry THF (40 mL) was vacuum purged three times, backfilling with N_2. CuI (0.343 g, 1.8 mmol, 0.1 equiv) was added under stirring and N_2 atmosphere. The suspension was cooled to –78 °C. Then a solution of PhMgBr (8.2 g, 45 mmol, 2.5 equiv) in 60 mL THF was added dropwise by constant pressure funnel under vigorous stirring. The resulting mixture held at –78 °C for 1 h. Then it was warmed to room temperature and stirred for 18 h. The mixture was cooled to –78 °C again and quenched slowly with D_2O (3.6 g, 180 mmol, 10.0 equiv). 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 (50 mL x 3). The combined organic layers were washed brine (30 mL), dried with Na_2SO_4, and concentrated in vacuo. Purification by column chromatography (PE:EA, 5:1) afforded the **SI-7** as a yellow liquid (2.4 g, 17.6 mmol, 98% yield). **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 7.46 (d, *J* = 8.4 Hz, 2H), 7.39-7.30 (m, 3H), 5.46 (s, 1H), 5.34 (s, 0.10H), 4.54 (s, 2H).

Preparation of SI-8: To a suspension of NaH (Purity is 60%) (0.178 g, 4.4 mmol, 1.5 equiv) in 10 mL Et_2O was added **SI-7** (0.406 g, 3.0 mmol, 1.0 equiv) under N_2 atmosphere. The mixture was stirred for 30 min at room temperature and then cooled to 0 °C. A solution of TsCl (0.564 g, 3.0 mmol, 1.0 equiv) in 10 mL Et_2O was added dropwise. The resulting mixture was warmed to room temperature and stirred for 1 h. Then the solution was quenched with a saturated aqueous solution of NH_4Cl (30 mL). The aqueous layer was extracted with Et_2O (10 mL x 3). The combined organic layers were washed with brine (25 mL), dried with Na_2SO_4, and concentrated in vacuo to afford the crude product **SI-8** as a yellow solid (0.521 g, 1.8 mmol, 60% yield), which was used without further purification. **^{1}H NMR (400 MHz,**

$CDCl_3$, δ ppm): 7.76 (d, *J* = 8.4 Hz, 2H), 7.36-7.27 (m, 7H), 5.52 (s, 1H), 5.35 (s, 0.10H), 4.92 (s, 2H), 2.45 (s, 3H).

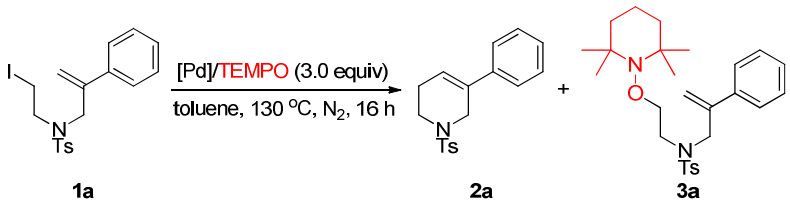
Preparation of SI-9: To a solution of **SI-8** (0.490 g, 1.7 mmol, 1.0 equiv) in 10 mL DMF was added **SI-3** (0.732 g, 3.4 mmol, 2.0 equiv) and Cs_2CO_3 (1.662 g, 5.1 mmol, 3.0 equiv). The mixture was heated to 50 ^oC and stirred for 5 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl (30 mL), the aqueous layer was extracted with EtOAc (20 mL). The combined organic layers were washed with brine (30 mL x 3), dried with Na_2SO_4, and evaporated. The crude product was purified by column chromatography (PE:EA, 2:1) to give the **SI-9** (0.443g, 1.3 mmol, 78% yield) as a yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 7.67 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.35-7.30 (m, 5H), 5.49 (s, 1H), 5.23 (s, 0.10H), 4.24 (s, 2H), 3.60-3.52 (m, 2H), 3.16 (t, *J* = 5.2 Hz, 2H), 2.44 (s, 3H).

Preparation of SI-10: To a solution of **SI-9** (0.443 g, 1.3 mmol, 1.0 equiv) in 10 mL DCM was cooled to 0 ^oC. PPh_3 (1.047 g, 4.0 mmol, 3.0 equiv), imidazole (0.272 g, 4.0 mmol, 3.0 equiv), I_2 (1.013 g, 4.0 mmol, 3.0 equiv) was added successively. Then the mixture was warmed to room temperature and stirred for 2 h. The precipitate was removed by filtration. Purification by column chromatography (PE:EA, 10:1) afforded the iodide **SI-10** (0.182 g, 0.4 mmol, 31% yield) as a light yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 7.67 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.35-7.31 (m, 5H), 5.52 (s, 1H), 5.23 (s, 0.10H), 4.18 (s, 2H), 3.33 (t, *J* = 8.4 Hz, 2H), 2.97 (t, *J* = 8.4 Hz, 2H), 2.45 (s, 3H).

Preparation of SI-11: SI-10 (55.1 mg, 0.12 mmol, 1.0 equiv) and $PdCl_2$(dppf) (8.8 mg, 0.012 mmol, 0.1 equiv) were added to a reaction vessel and vacuum purged three times, backfilling with N_2. Toluene (2 mL) and *N,N*-dicyclohexylmethylamine (51.4 μL, 0.24 mmol, 2.0 equiv) was added successively and the reaction was heated at 110 ^oC for 16 h. The reaction was cooled to room temperature and quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc. The combined organic layers were concentrated in vacuo. Purification by column chromatography (PE:EA, 10:1) afforded the desired **SI-11** (29.4 mg, 0.09 mmol, 78% yield). **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 7.72 (d, *J* = 8.4 Hz, 2H), 7.34-7.27 (m, 7H), 6.09-6.06 (m, 0.44H), 3.96-3.91 (m, 2H), 3.24 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 2.40-2.36 (m, 2H).

VI. The Optimization, Synthetic Procedure and Analytical Data for TEMPO Adduct.

Table S1. Optimization of the TEMPO Testing Experiment[a]

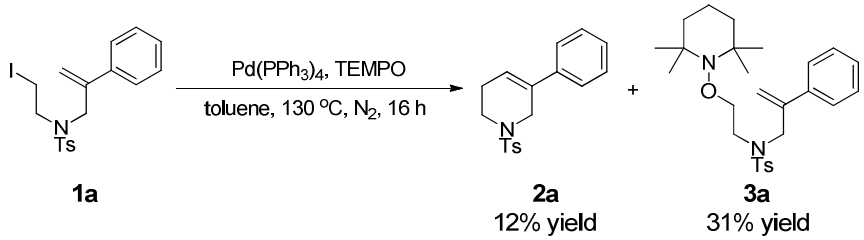


1a **2a** **3a**

Entry	Catalyst	Recovered **1a**[b]	**2a**[b]	**3a**[b]
1	$PdCl_2(dppf)$ (10 mol %)	79%[c](75%)[d]	trace	trace
2	$PdCl_2(dppf)$ (100 mol %)	70%	trace	trace
3	$Pd(PPh_3)_4$ (10 mol %)	72%	trace	9%
4	$Pd(PPh_3)_4$ (50 mol %)	35%	trace	16%
5	$Pd(PPh_3)_4$ (100 mol %)	none	12%	31%

[a]Reaction Conditions: 1a (0.2 mmol), toluene (2.0 mL), 130 °C, N_2, 16 h. [b]Isolated yields. [c]Without base. [d]With 2.0 equiv Cy_2NMe.

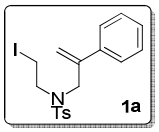
Synthetic Procedure and Analytical Data:

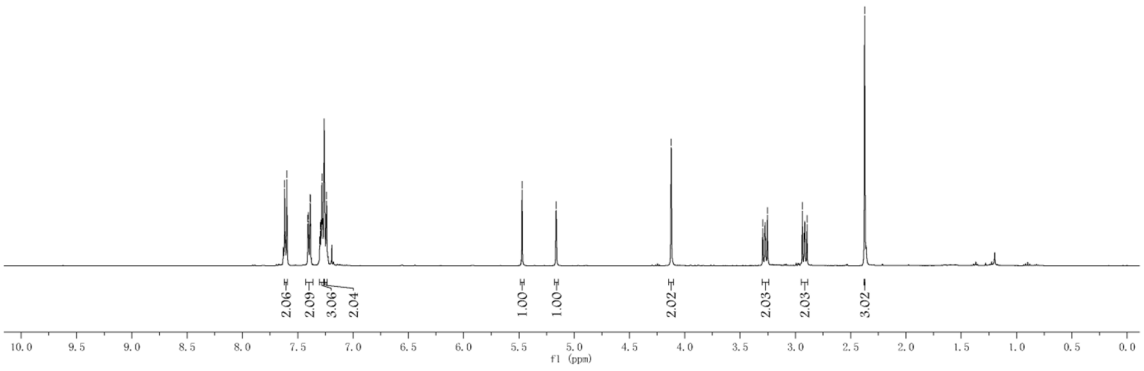


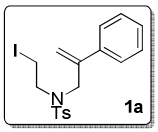
1a **2a** 12% yield **3a** 31% yield

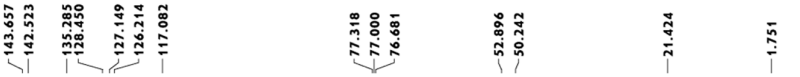
1a (44.1 mg, 0.1 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol, 1.0 equiv) and TEMPO (31.3 mg, 0.2 mmol, 2.0 equiv) were added to a reaction vessel and vacuum purged three times, backfilling with N_2. Toluene (2 mL) was added and the reaction was heated at 130 °C for 16 h. The reaction was cooled to room temperature and quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc. The combined organic layers were concentrated in vacuo. Purification by column chromatography (PE:EA, 10:1) afforded the desired **2a** (3.7 mg, 0.012 mmol, 12% yield) and **3a** (14.6 mg, 0.031 mmol, 31% yield) respectively. Analytical data for **3a**: **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 7.65 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.35-7.31 (m, 5H), 5.46 (s, 1H), 5.28 (s, 1H), 4.37 (s, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 3.29 (t, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 1.52-1.46 (m, 2H), 1.43-1.38 (m, 4H), 0.99 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):** 142.9, 138.6, 137.2, 135.1, 129.6, 128.3, 127.9, 127.2, 126.5, 116.2, 75.1, 59.6, 52.3, 45.2, 39.5, 32.8, 21.5, 21.4, 17.0.

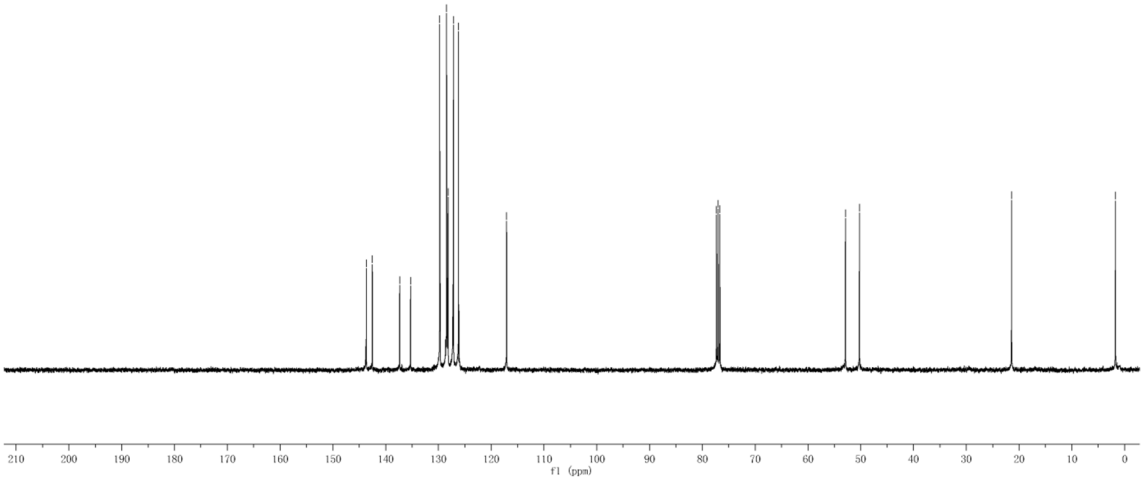
VII. Copies of the ^{1}H NMR, ^{13}C NMR, ^{19}F NMR

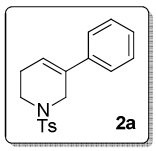








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Ts
2a

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6.080
6.070
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6.040
3.964
3.952
3.946
3.941
3.934
3.914
3.255
3.240
3.226
2.424
2.406
2.391
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7.00
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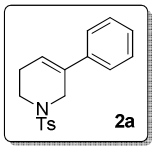
2.02
3.00
2.02
f1 (ppm)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Ts
2a

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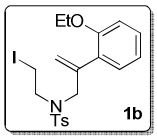
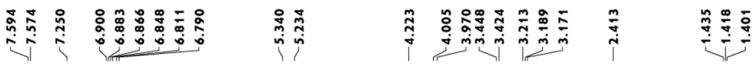
f1 (ppm)


EtO
I
N
Ts
1b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6.866
6.848
6.811
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5.340
5.234
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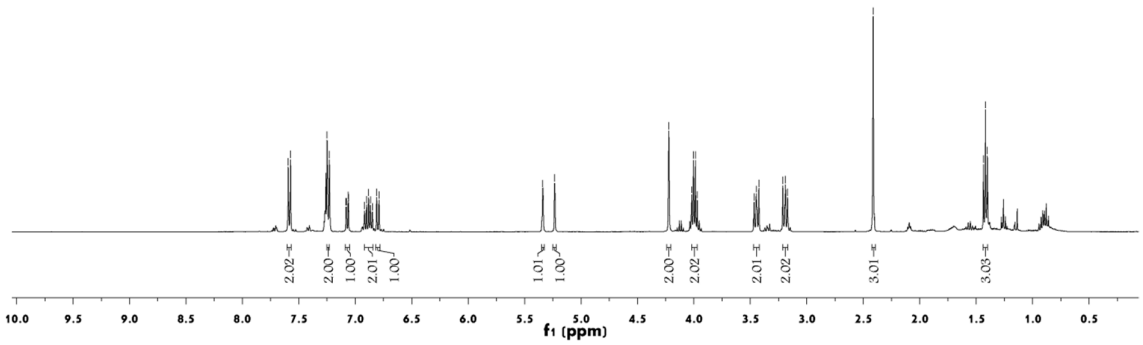
3.448
3.424
3.213
3.189
3.171
2.413
1.435
1.418
1.401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1.01
1.00
2.00
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2.02
3.01
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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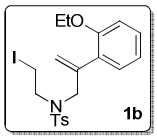
2.0
1.5
1.0
0.5
f1 (ppm)


EtO
I
N
Ts
1b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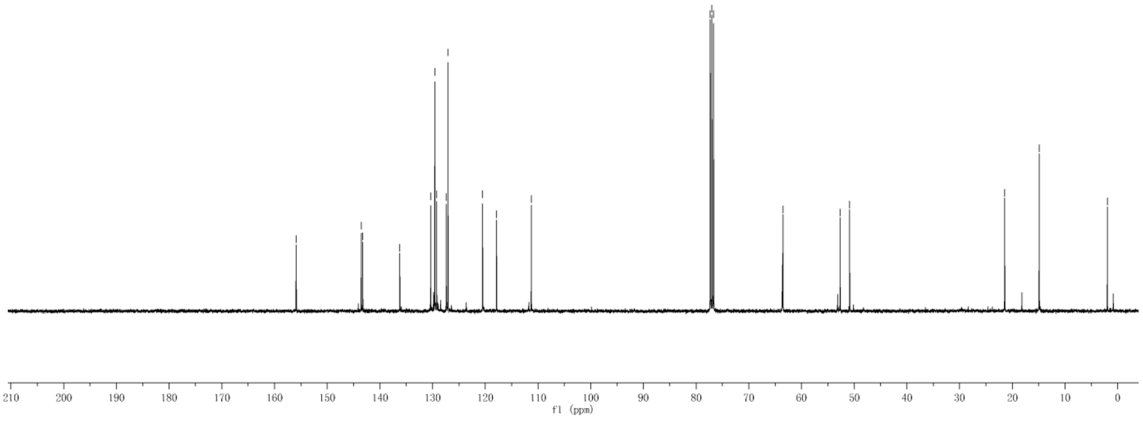
14.916
1.974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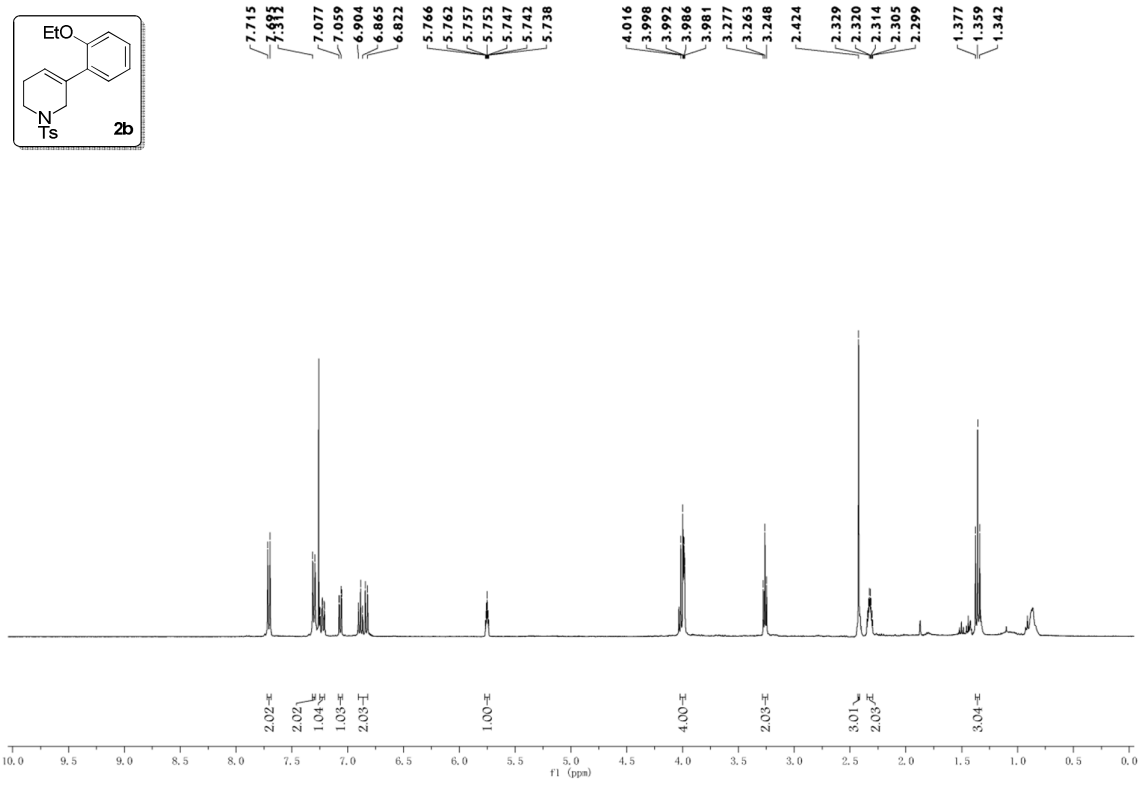
f1 (ppm)


EtO
N
Ts
2b
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7.059
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6.865
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5.762
5.757
5.752
5.747
5.742
5.738
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3.998
3.992
3.986
3.981
3.277
3.263
3.248
2.424
2.329
2.320
2.314
2.305
2.299
1.377
1.359
1.342
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1.03
2.05
1.00
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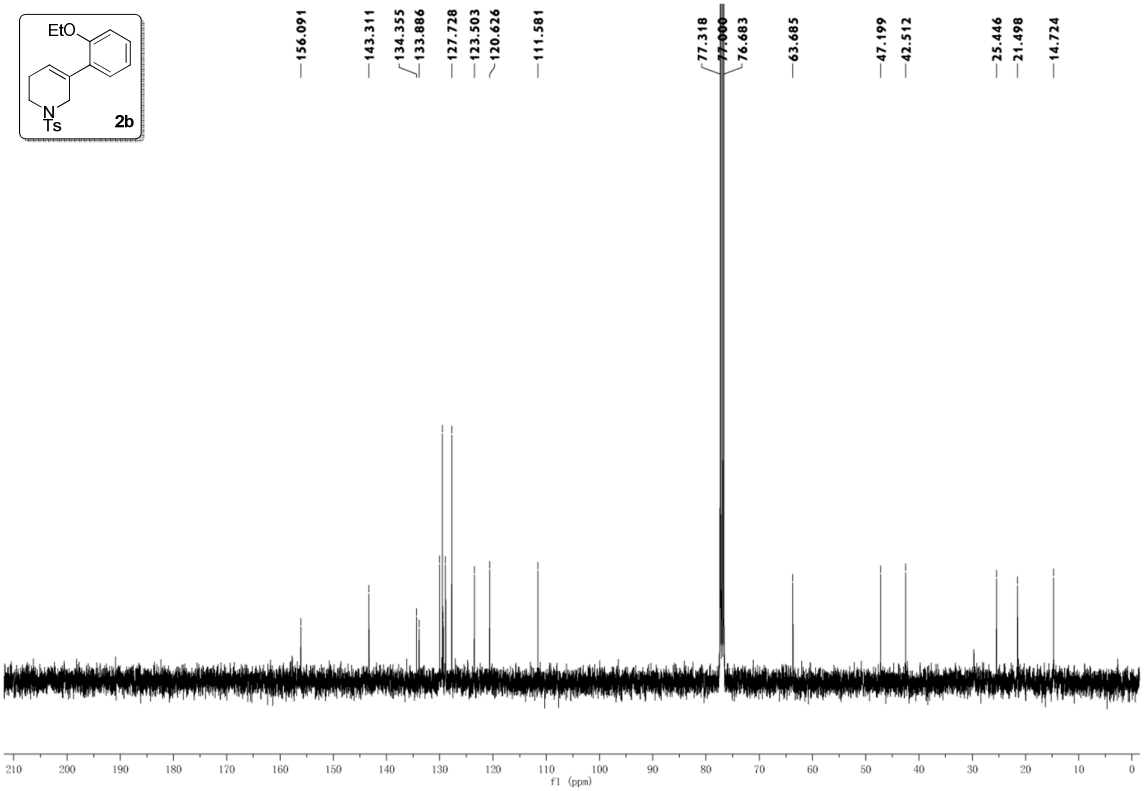
2.03
3.01
2.03
3.04
f1 (ppm)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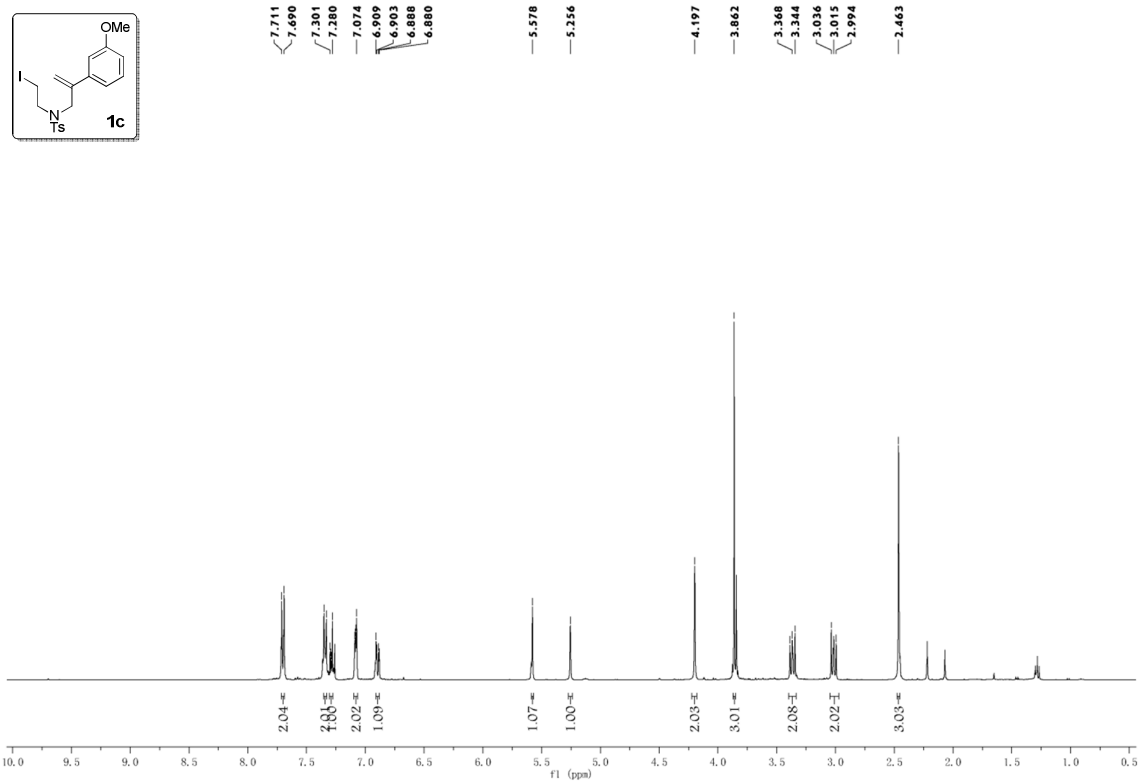
f1 (ppm)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6.903
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5.578
5.256
4.197
3.862
3.368
3.344
3.036
3.015
2.994
2.463
2.04
2.01
1.00
2.02
1.09
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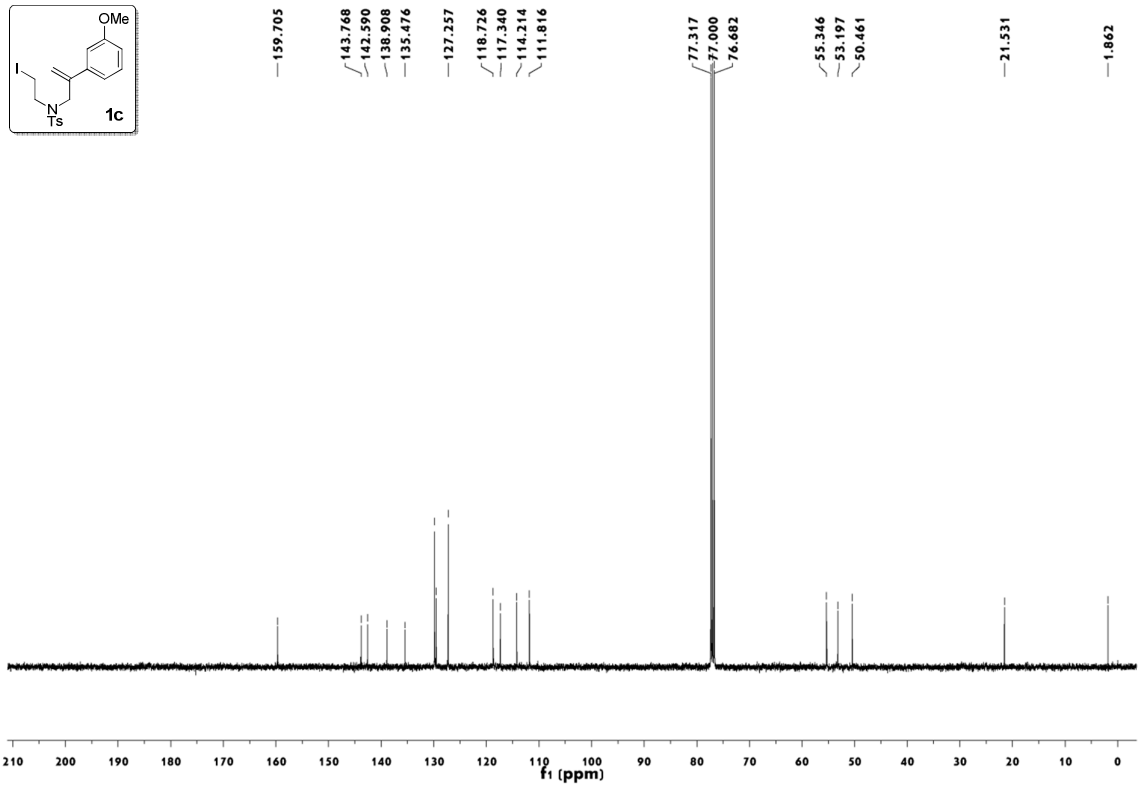
1.00
2.03
3.01
2.08
2.02
3.03
f1 (ppm)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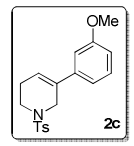
f1 (ppm)


OMe
N
Ts
2c

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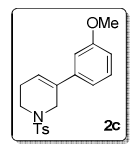
3.01
2.02
f1 (ppm)


OMe
N
Ts
2c

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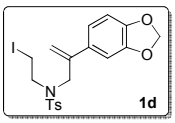
I
O
O
N
Ts
1d

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4.405
3.326
3.304
3.284
3.094
3.052
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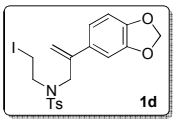
2.00
2.02
2.02
3.08
f1 (ppm)


I
O
O
N
Ts
1d

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77.000
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21.555
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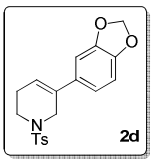
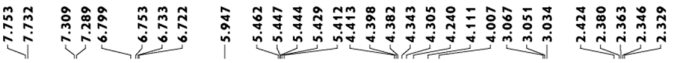
f1 (ppm)


O
O
N
Ts
2d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6.753
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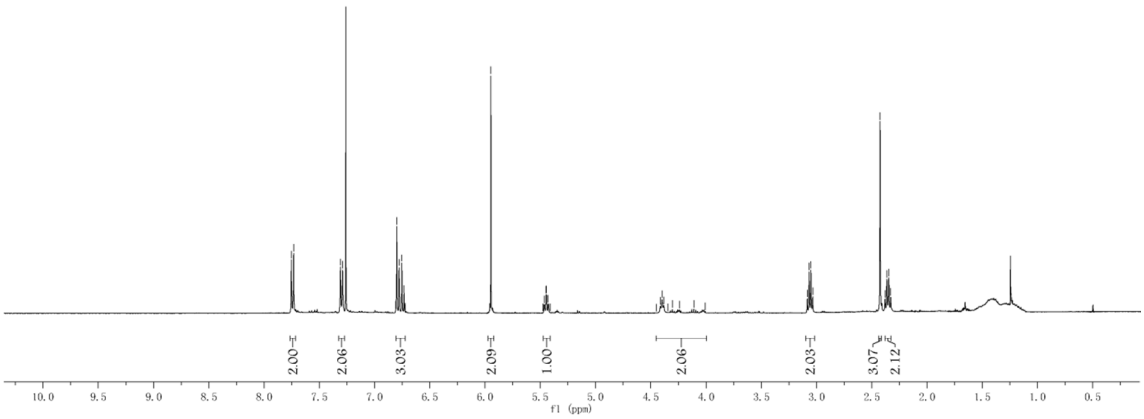
5.412
4.413
4.398
4.382
4.343
4.305
4.240
4.111
4.007
3.067
3.051
3.034
2.424
2.380
2.363
2.346
2.329


2.00
2.06
3.03
2.09
1.00
2.06
2.03
3.07
2.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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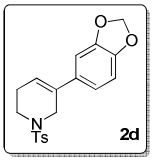
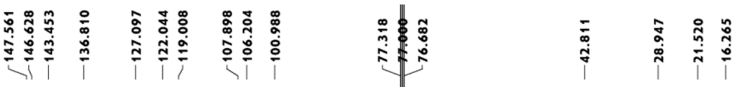
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
O
N
Ts
2d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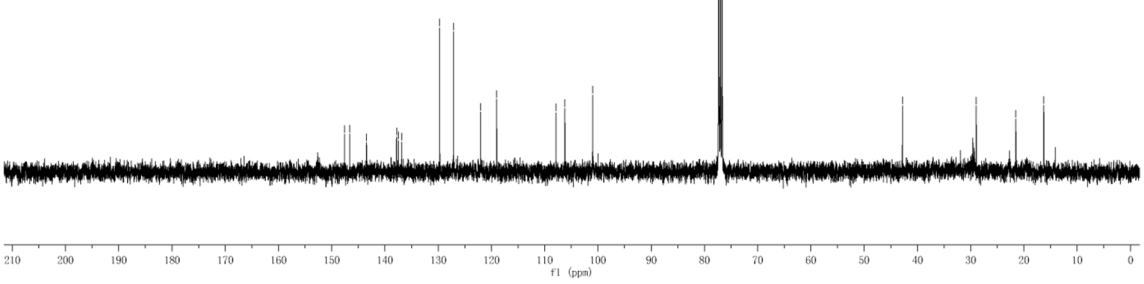
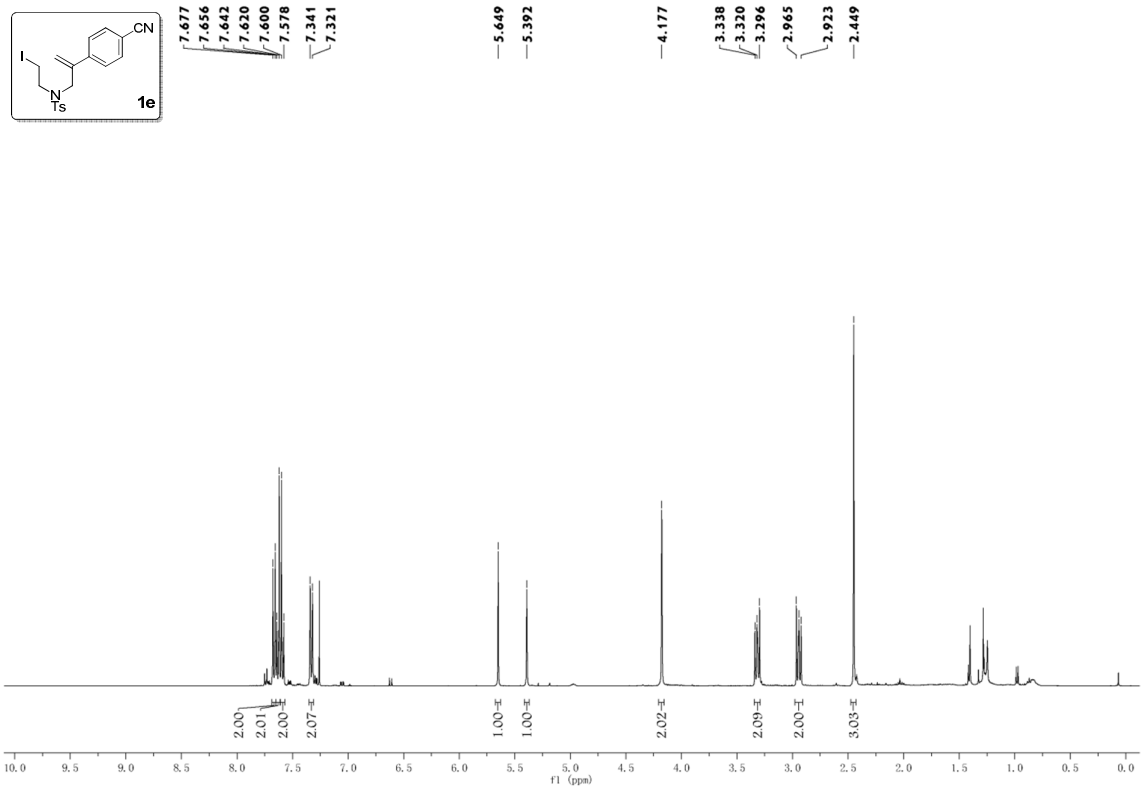
146.628
143.453
136.810
127.097
122.044
119.008
107.898
106.204
100.988
77.318
77.000
76.682
42.811
28.947
21.520
16.265


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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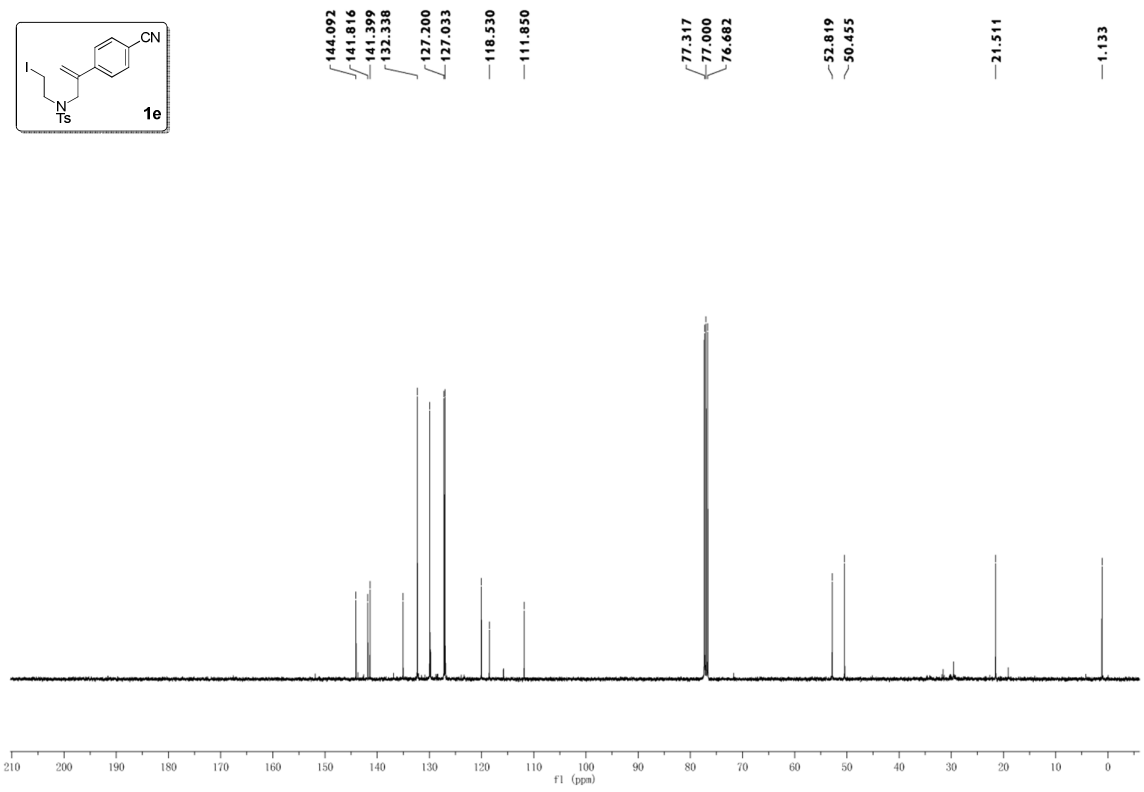
7.642
7.620
7.600
7.578
7.341
7.321
5.649
5.392
4.177
3.338
3.320
3.296
2.965
2.923
2.449
1e
2.00
2.01
2.00
2.07
1.00
1.00
2.02
2.09
2.00
3.03
f1 (ppm)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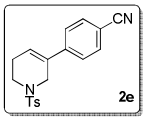
141.399
132.338
127.200
127.033
118.530
111.850
77.317
77.000
76.682
52.819
50.455
21.511
1.133
1e
f1 (ppm)


CN
N
Ts
2e

7.720
7.700
7.611
7.590
7.383
7.345
7.325
6.259
6.237
6.227
6.217
6.195
3.919
3.914
3.541
3.526
3.293
3.254
3.225
2.425
2.02
2.05
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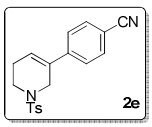
1.00
2.00
1.04
1.05
2.03
3.06


CN
N
Ts
2e

143.849
142.928
132.355
129.785
125.613
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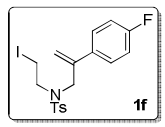
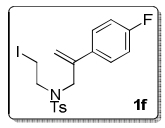
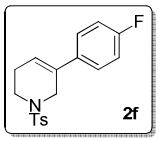
111.182
77.254
77.000
76.746
45.852
42.107
25.777
21.511
f1 (ppm)


F
I
N
Ts
1f

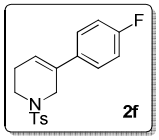
7.683
7.662
7.453
7.320
7.058
7.036
7.014
5.494
5.207
4.146
3.333
3.314
3.290
2.979
2.958
2.936
2.451
2.01
1.04
1.01
2.02
1.00
1.00
1.00
1.01
2.03
2.04
2.05
3.00
f1 (ppm)


F
I
N
Ts
1f

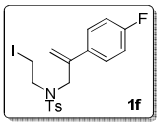
163.985
143.904
141.671
129.911
128.169
128.089
127.282
117.173
115.634
115.420
77.317
77.000
76.682
53.255
50.353
21.554
1.644
f1 (ppm)


F
N
Ts
2f

7.722
7.701
7.339
7.218
7.026
7.004
6.983
6.021
6.016
6.011
6.006
6.001
3.897
3.891
3.886
3.880
3.238
3.223
3.209
2.427
2.407
2.400
2.386
2.377
2.371
2.362
2.356
2.15
2.19
1.96
0.99
1.03
1.00
1.96
2.03
3.08
2.16
f1 (ppm)

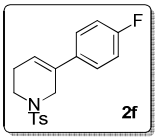

F
N
Ts
2f

143.665
129.711
127.684
126.883
126.805
122.191
115.481
115.268
77.317
77.000
76.682
46.400
42.280
25.586
21.519
f1 (ppm)


F
I
N
Ts

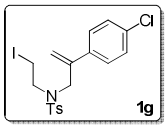
1f

-113.379
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

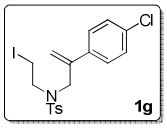

F
N
Ts

2f

-114.480
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


Cl
I
N
Ts
1g

7.672
7.651
7.413
7.391
7.331
7.315
7.310
7.293
5.527
5.243
4.147
3.342
3.321
3.300
2.990
2.970
2.948
2.448
2.00
2.01
2.02
2.06
1.01
1.00
2.01
2.01
2.02
3.00
f1 (ppm)


Cl
I
N
Ts
1g

143.887
141.624
134.189
128.707
127.664
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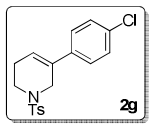
77.318
77.000
76.682
53.019
50.315
21.509
1.547
f1 (ppm)



7.717
7.703
7.320
7.289
7.275
7.212
7.198
6.072
6.068
6.065
6.062
6.058
3.897
3.894
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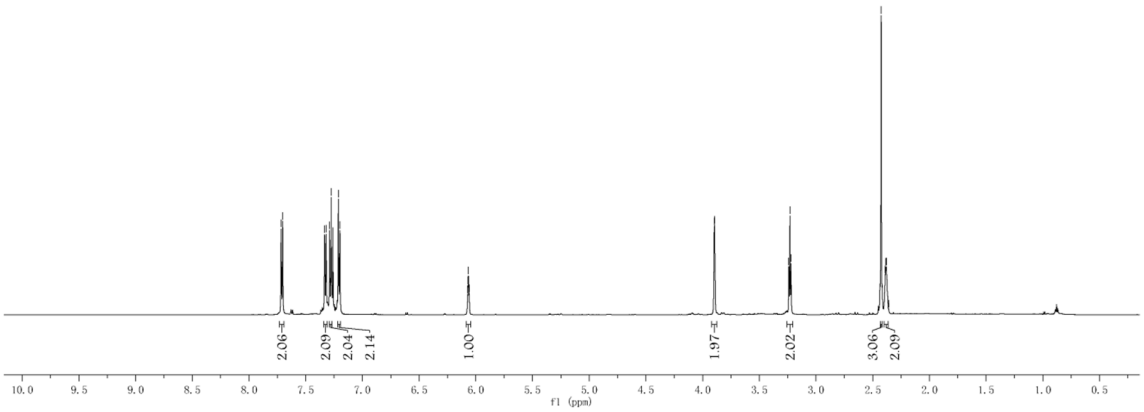
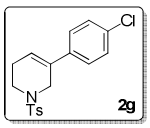
3.230
3.220
2.425
2.389
2.385
2.379
2.358





143.689
137.062
133.445
133.206
132.374
129.708
128.621
127.645
126.405
122.783
77.318
77.000
76.683
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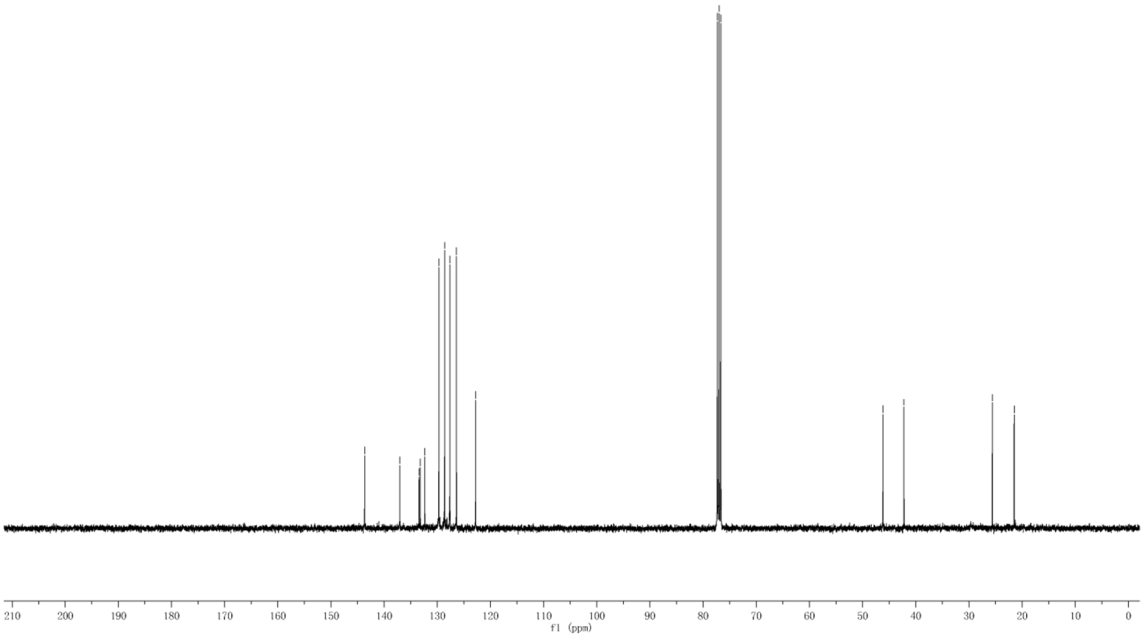
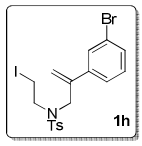
42.224
25.593
21.493





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7.545
7.541
7.443
7.425
7.402
7.382
7.323
7.303
7.229
7.209
7.189
5.526
5.275
4.152
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3.359
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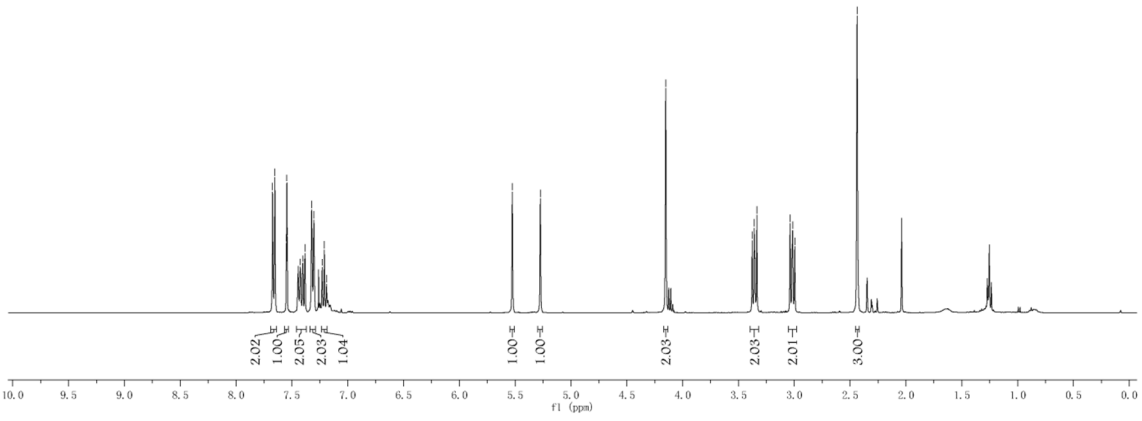
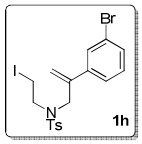
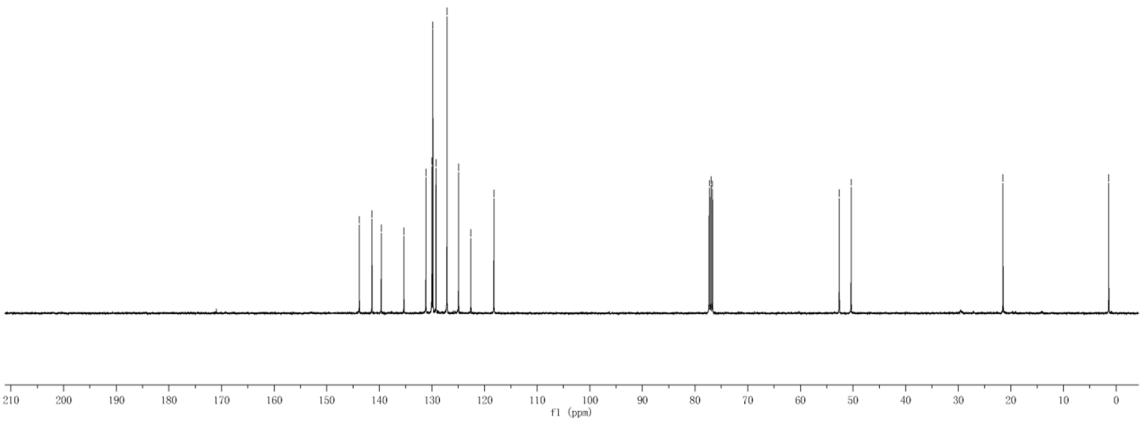
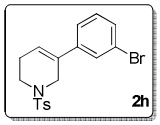
2.996
2.438





143.815
141.406
139.641
135.340
129.829
127.154
122.617
118.237
77.318
77.000
76.682
52.602
50.344
21.484
1.388





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7.313
7.306
7.289
6.085
6.080
6.075
6.070
6.065
6.059
6.055
6.041
3.958
3.948
3.942
3.936
3.930
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3.252
3.237
3.223
2.425
2.407
2.399
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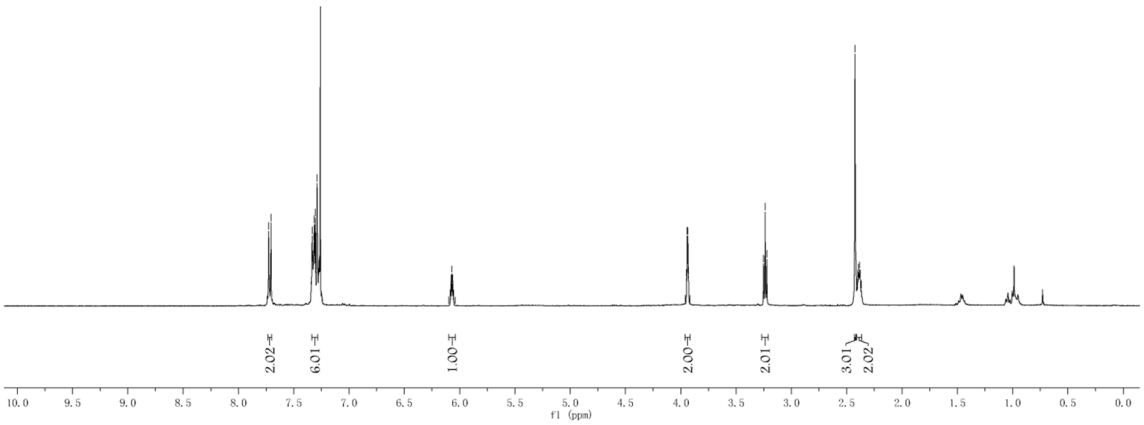
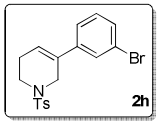
2.368





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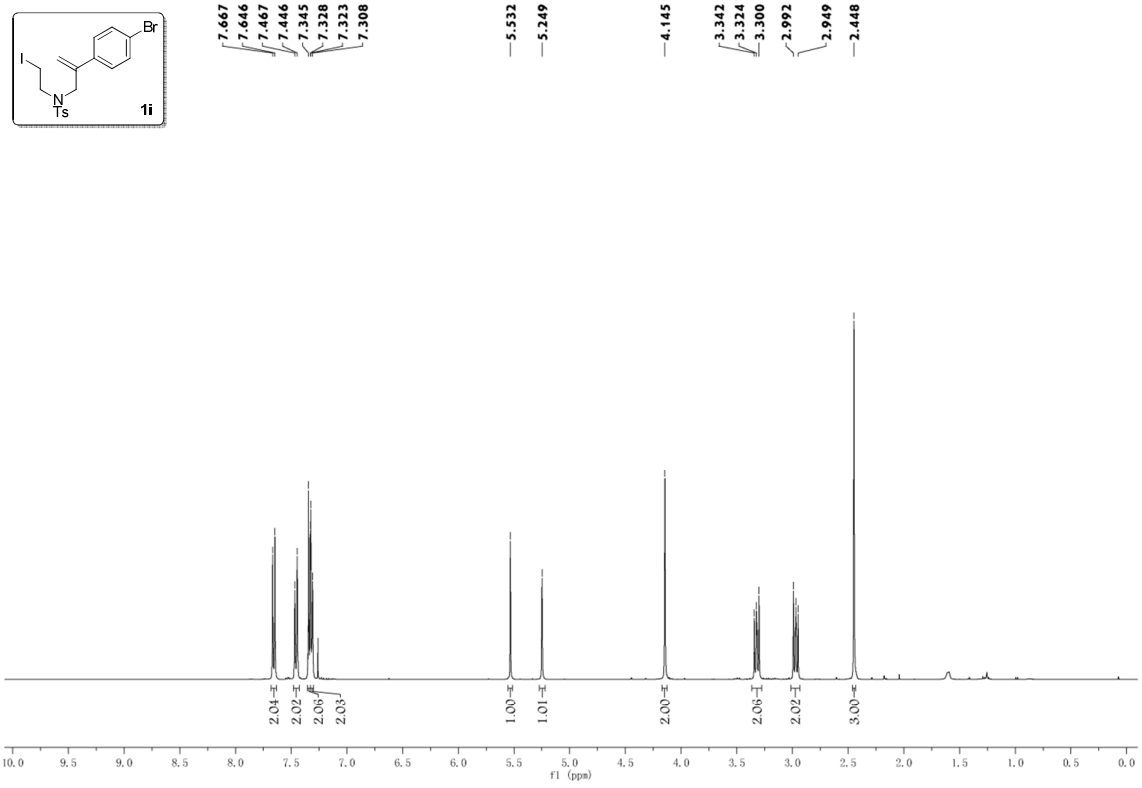
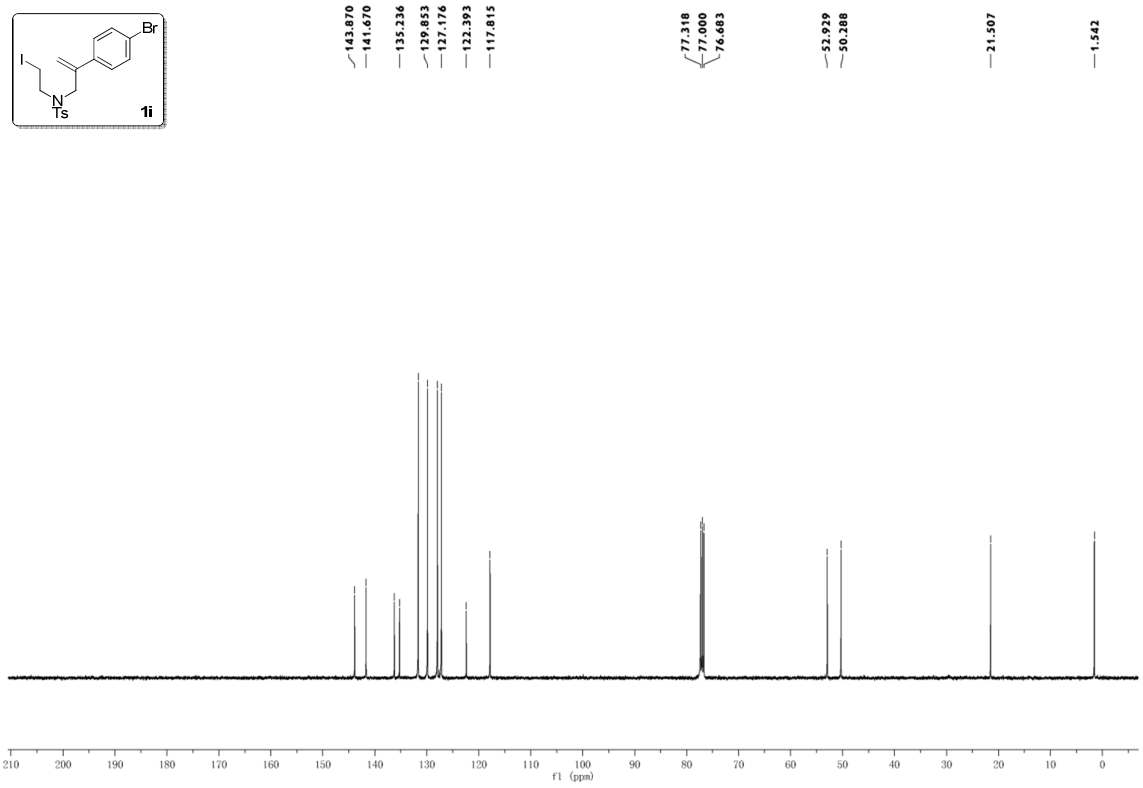
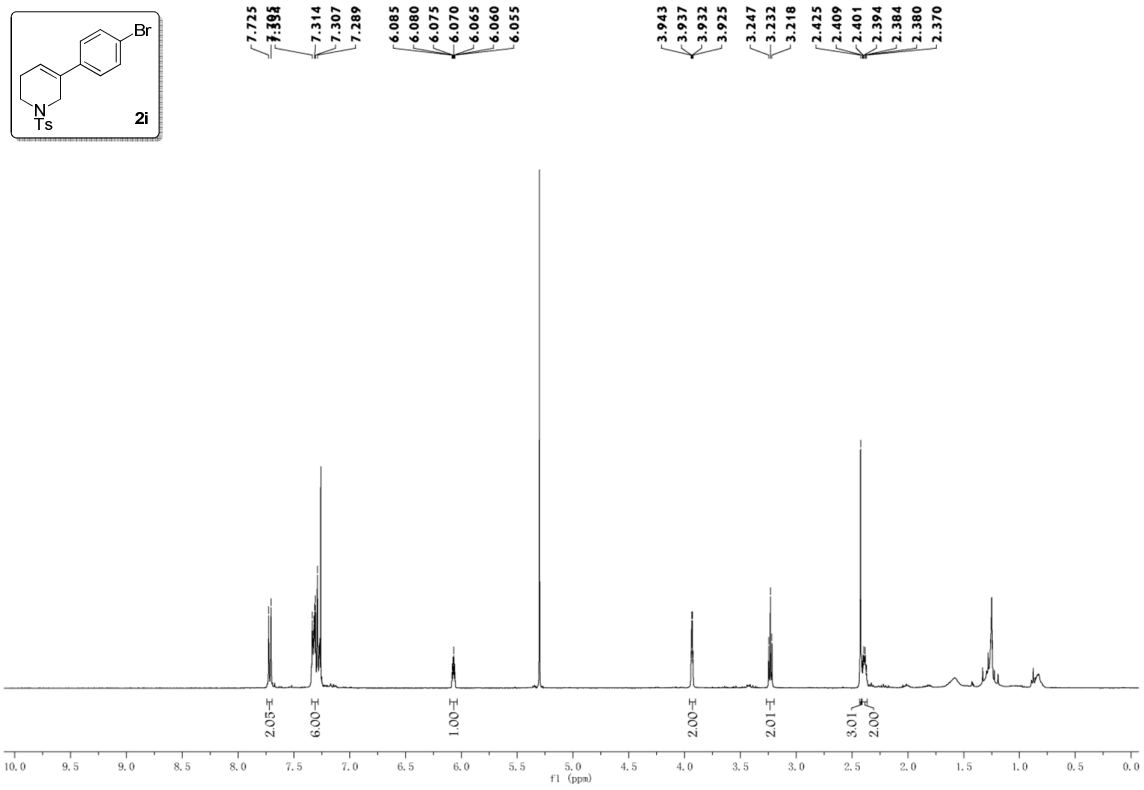
138.712
133.446
133.324
129.683
128.513
127.698
125.206
122.164
77.317
77.000
76.682
46.380
42.338
25.621
21.516


1i
7.667
7.646
7.467
7.446
7.345
7.328
7.323
7.308
5.532
5.249
4.145
3.342
3.324
3.300
2.992
2.949
2.448
2.04
2.02
2.06
2.03
1.00
1.01
2.00
2.06
2.02
3.00
f1 (ppm)


1i
143.870
141.670
135.236
129.853
127.176
122.393
117.815
77.318
77.000
76.683
52.929
50.288
21.507
1.542
f1 (ppm)


Br
N
Ts
2i
7.725
7.314
7.307
7.289
6.085
6.080
6.075
6.070
6.065
6.060
6.055
3.943
3.937
3.932
3.925
3.247
3.232
3.218
2.425
2.409
2.401
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2.384
2.380
2.370
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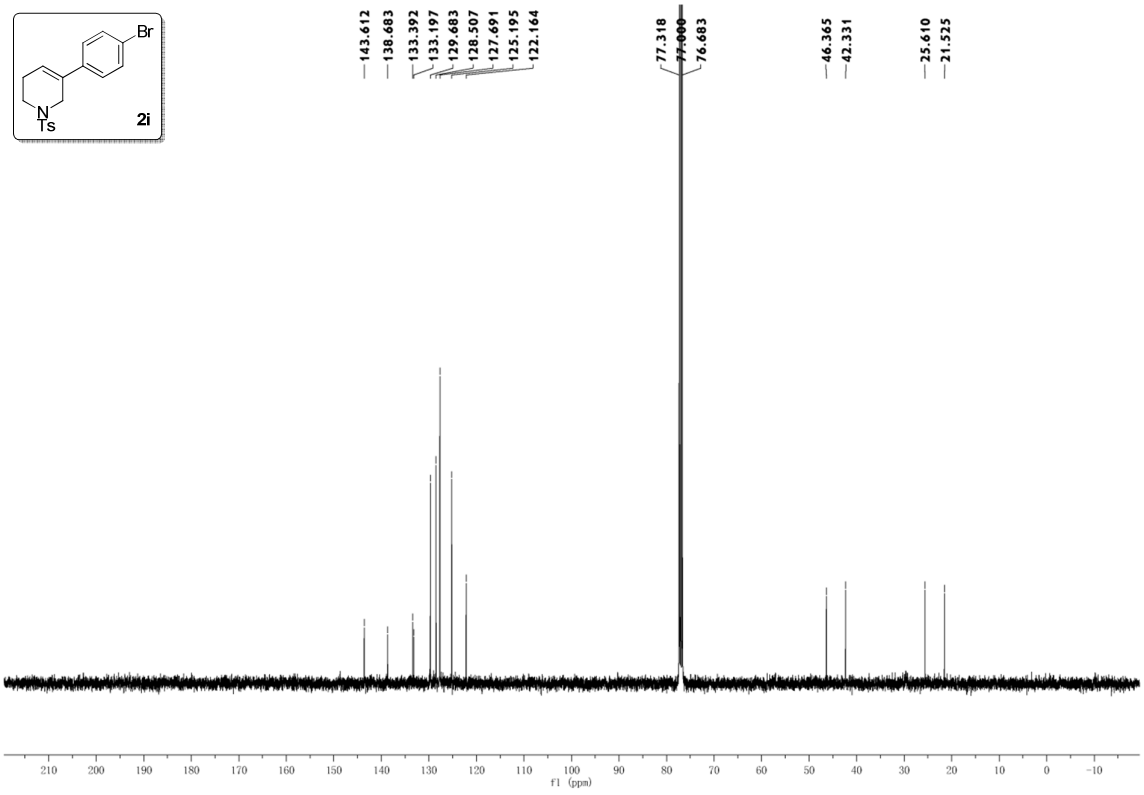
2.00
2.01
3.01
2.00
f1 (ppm)


Br
N
Ts
2i
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138.683
133.392
133.197
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122.164
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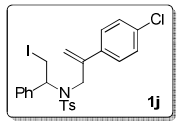
46.365
42.331
25.610
21.525
f1 (ppm)


Cl
I
Ph
N
Ts
1j

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7.571
7.230
7.127
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6.931
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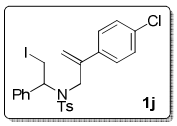
5.190
5.055
5.045
5.026
5.016
4.324
4.283
3.819
3.665
3.636
3.407
3.392
3.382
2.451
2.03
2.02
1.00
0.99
1.01
1.05
1.05
1.09
1.00
3.00
f1 (ppm)


Cl
I
Ph
N
Ts
1j

143.735
143.594
133.879
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117.089
77.317
77.000
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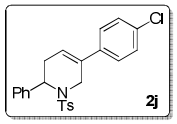
62.729
49.121
21.566
4.351
f1 (ppm)



7.690
7.670
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7.215
7.137
6.124
6.113
6.095
6.084
6.070
6.056
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5.331
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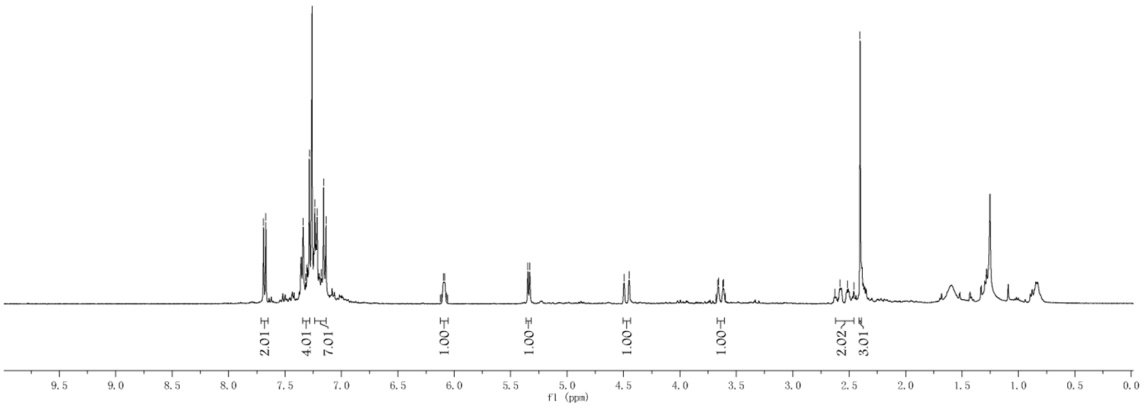
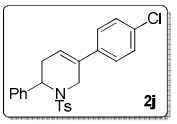
2.403





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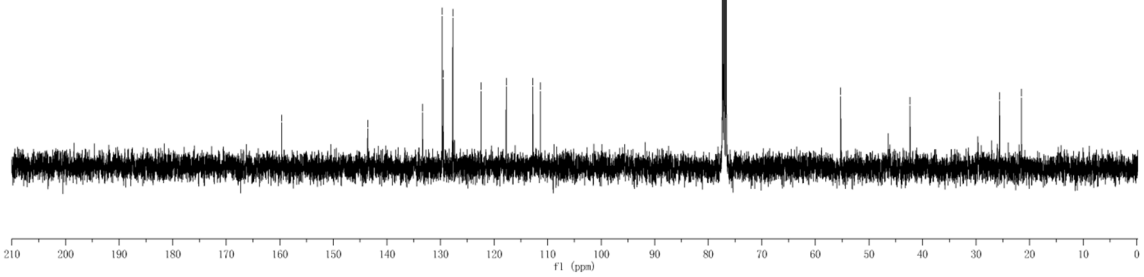
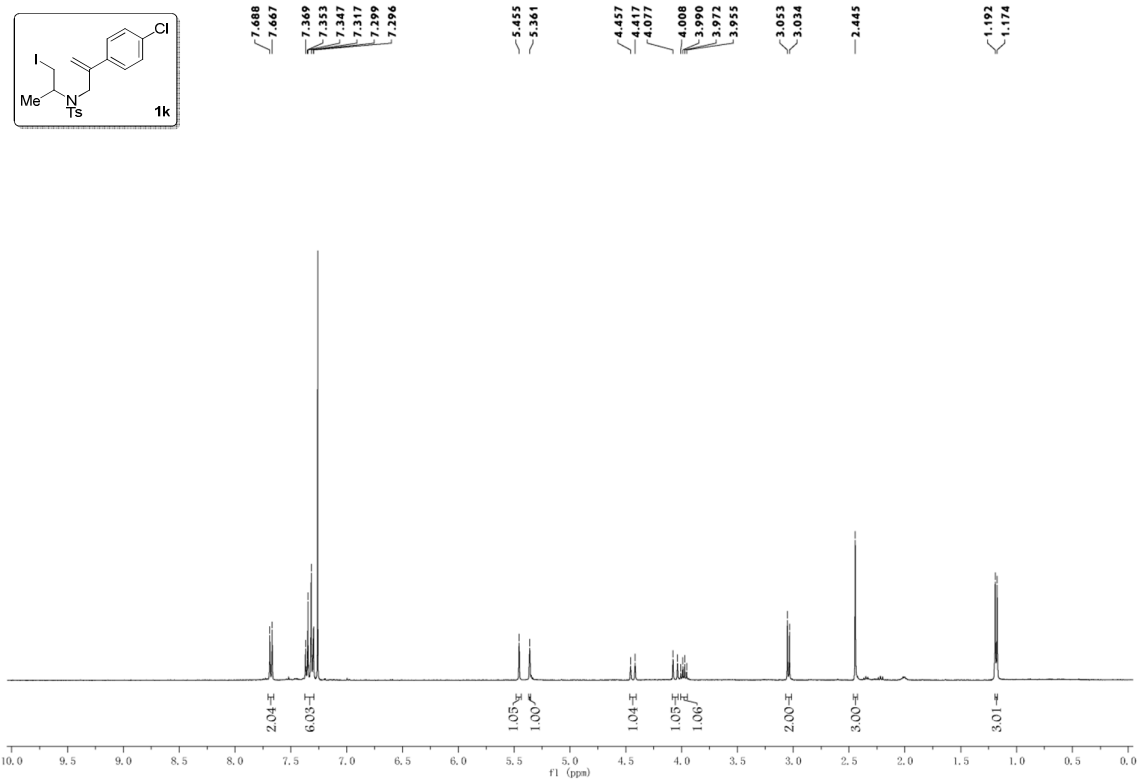
143.605
129.687
129.491
127.701
122.430
117.725
112.757
111.341
77.317
77.000
76.682
55.271
42.333
25.606
21.519

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7.317
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7.296
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5.361
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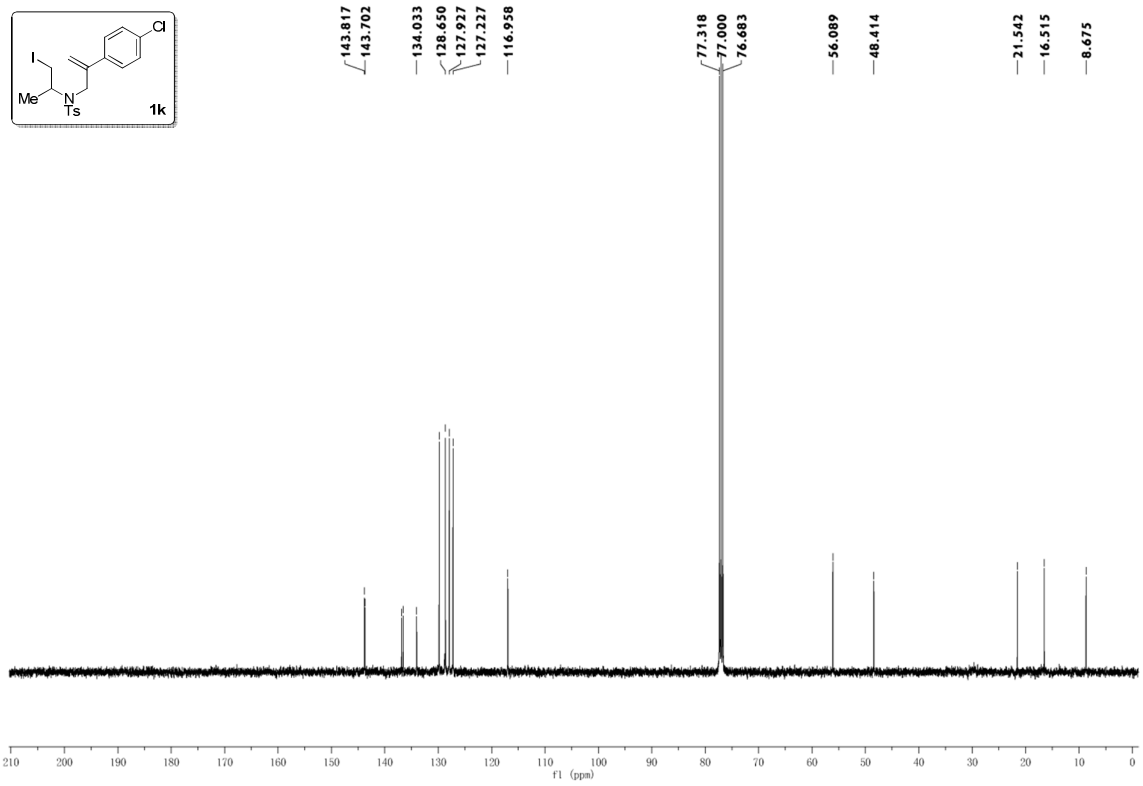
4.417
4.077
4.008
3.990
3.972
3.955
3.053
3.034
2.445
1.192
1.174
Cl
I
Me
N
Ts
1k
2.04
6.03
1.05
1.00
1.04
1.05
1.06
2.00
3.00
3.01
f1 (ppm)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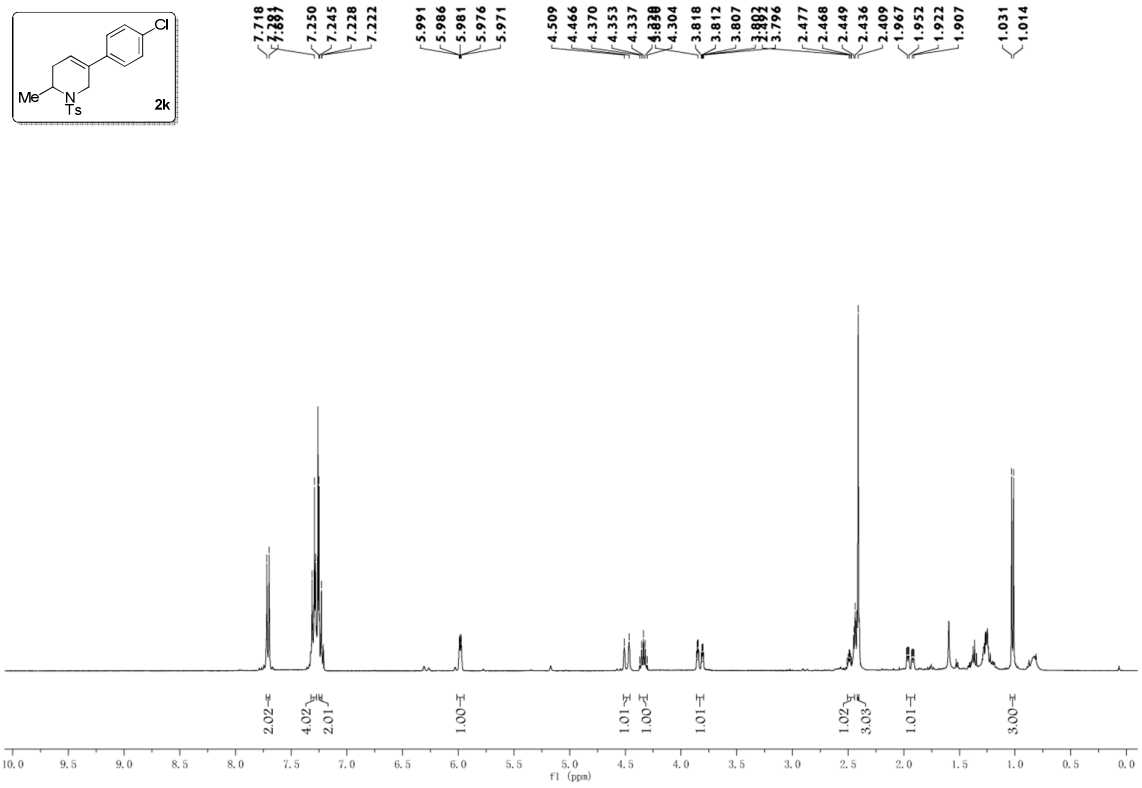
143.702
134.033
128.650
127.927
127.227
116.958
77.318
77.000
76.683
56.089
48.414
21.542
16.515
8.675
Cl
I
Me
N
Ts
1k
f1 (ppm)


Cl
Me
N
Ts
2k
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7.245
7.228
7.222
5.991
5.986
5.981
5.976
5.971
4.509
4.466
4.370
4.353
4.337
4.304
3.818
3.812
3.807
2.477
2.468
2.449
2.436
2.409
1.967
1.952
1.922
1.907
1.031
1.014
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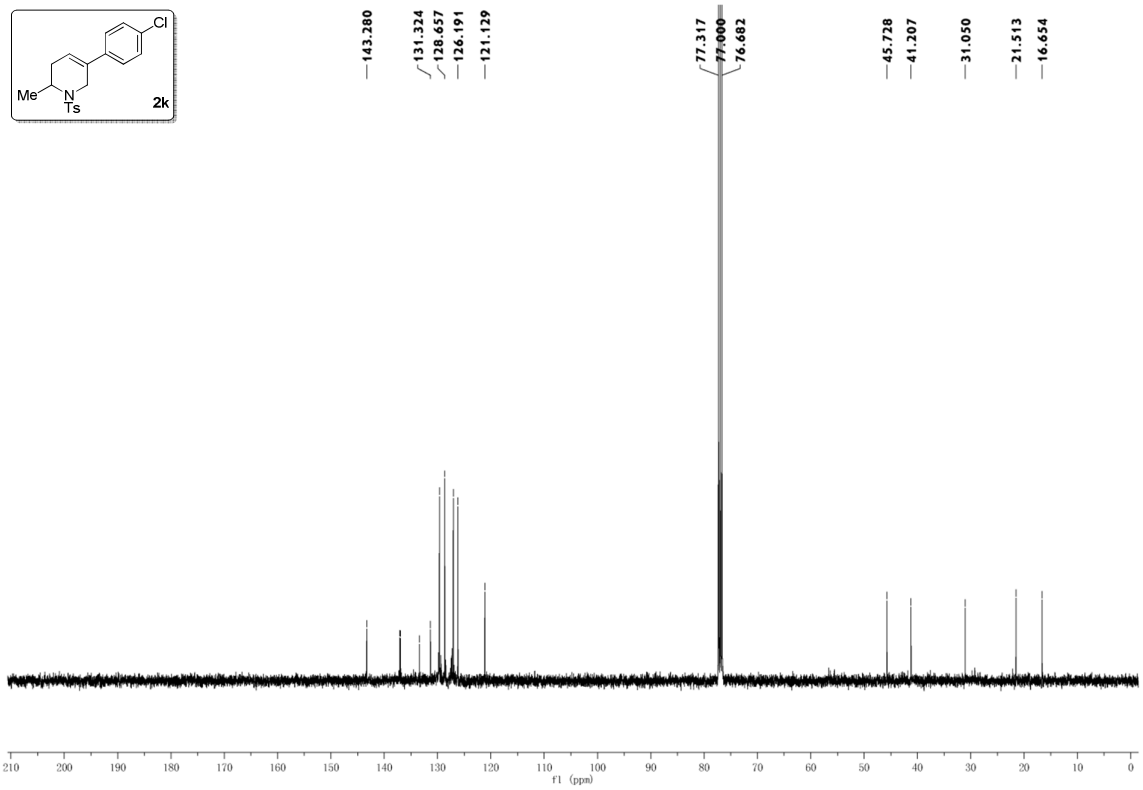
1.02
3.03
1.01
3.00
f1 (ppm)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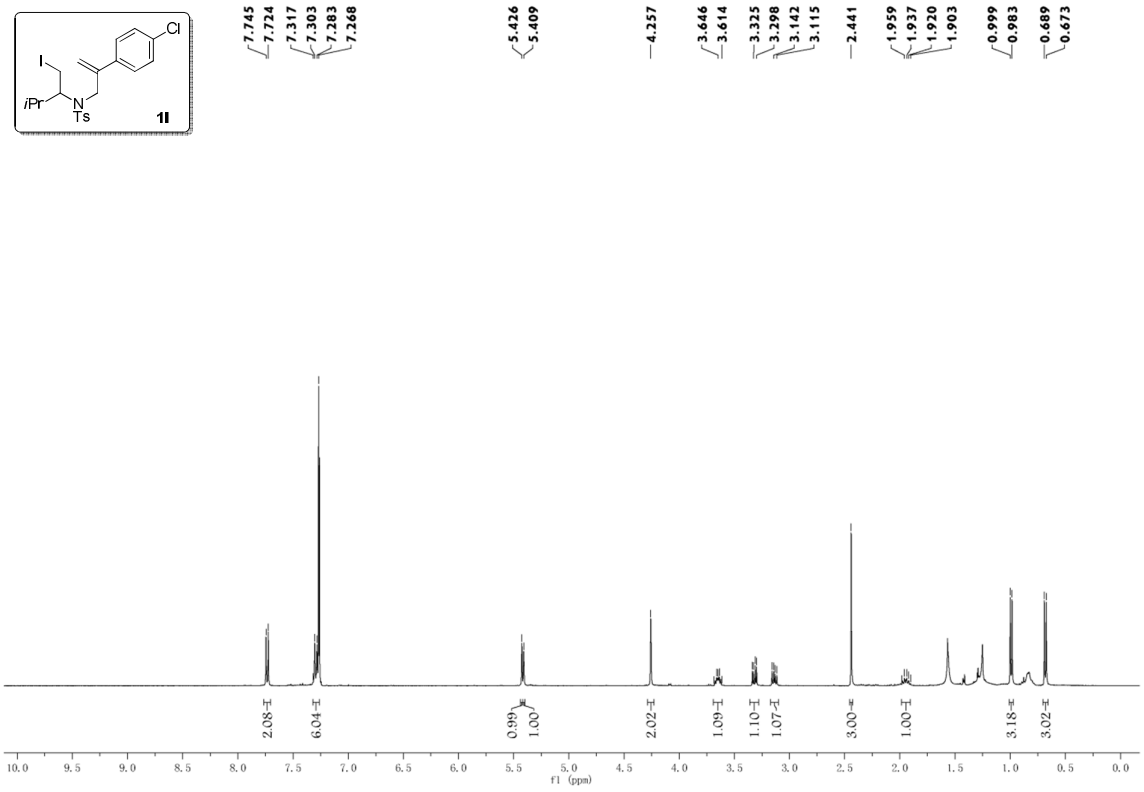
Me
N
Ts
2k
143.280
131.324
128.657
126.191
121.129
77.317
77.000
76.682
45.728
41.207
31.050
21.513
16.654
f1 (ppm)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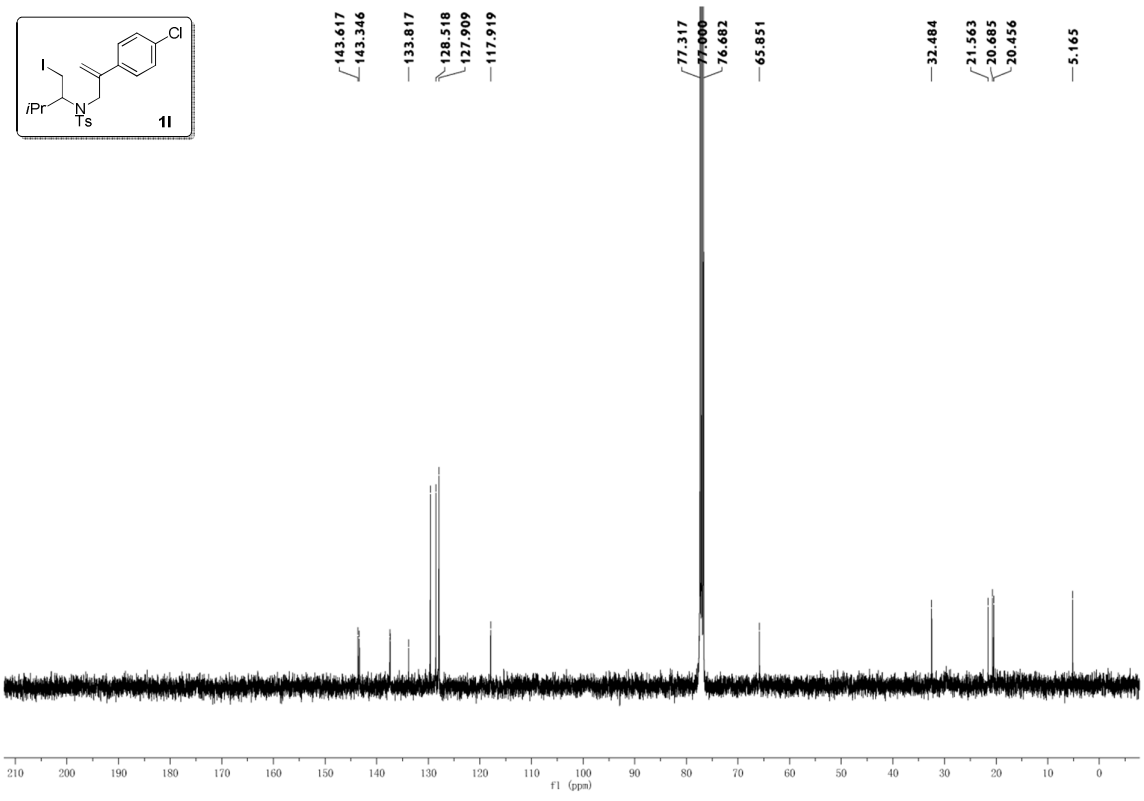
7.724
7.317
7.303
7.283
7.268
5.426
5.409
4.257
3.646
3.614
3.325
3.298
3.142
3.115
2.441
1.959
1.937
1.920
1.903
0.999
0.983
0.689
0.673
Cl
I
iPr
N
Ts
1l
2.08
6.04
0.99
1.00
2.02
1.09
1.10
1.07
3.00
1.00
3.18
3.02
f1 (ppm)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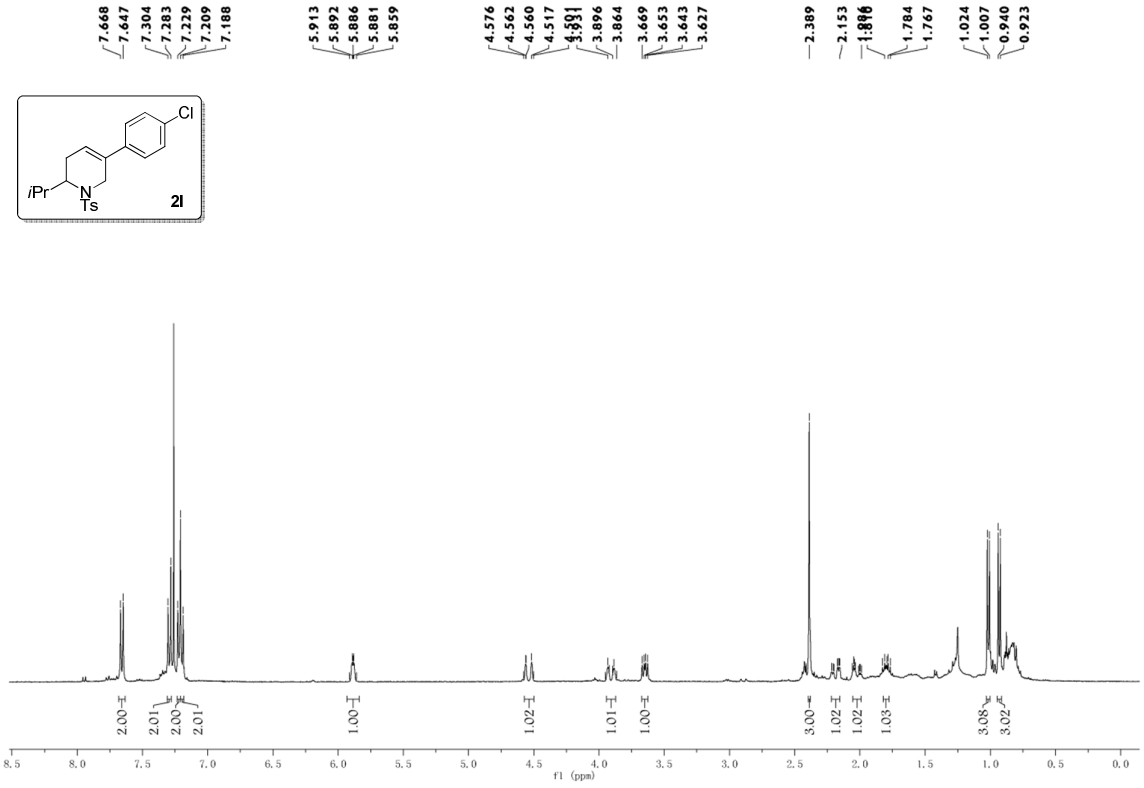
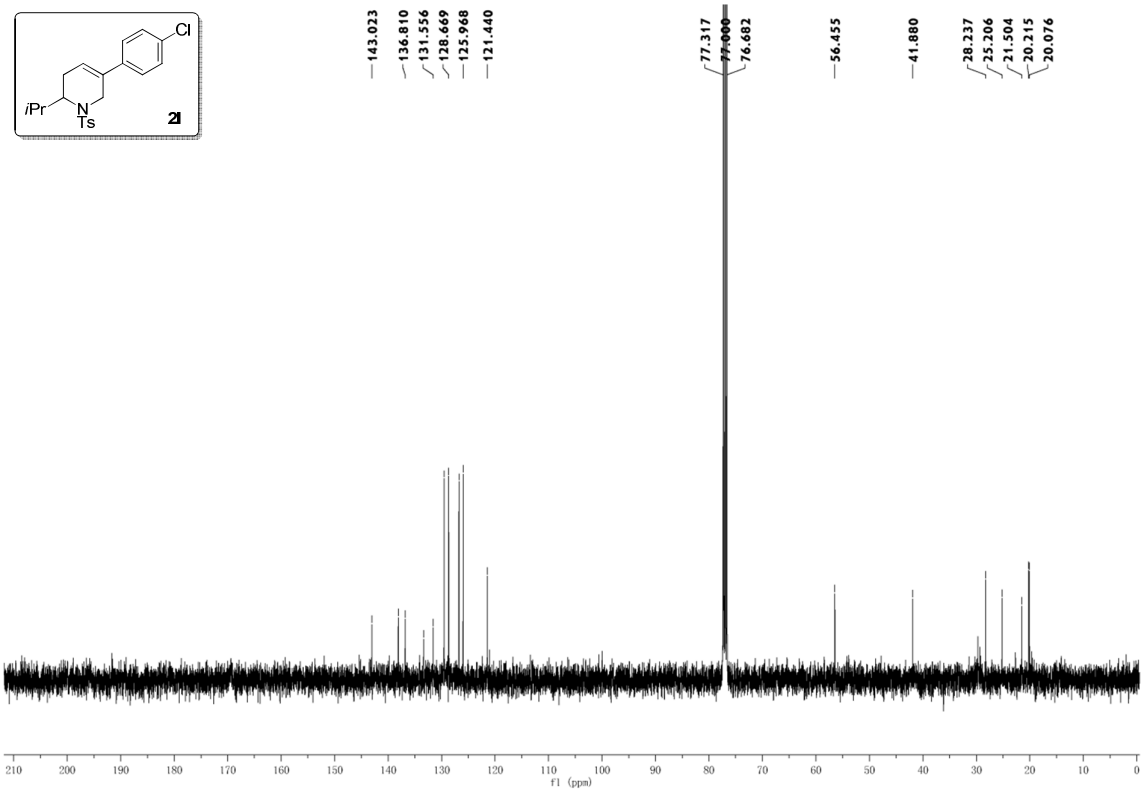
143.346
133.817
128.518
127.909
117.919
77.317
77.000
76.682
65.851
32.484
21.563
20.685
20.456
5.165
Cl
I
iPr
N
Ts
1l
f1 (ppm)


7.668
7.647
7.304
7.283
7.229
7.209
7.188
5.913
5.892
5.886
5.881
5.859
4.576
4.562
4.560
4.517
3.896
3.864
3.669
3.653
3.643
3.627
2.389
2.153
1.784
1.767
1.024
1.007
0.940
0.923
Cl
iPr
N
Ts
2l
2.00
2.01
2.00
2.01
1.00
1.02
1.01
1.00
3.00
1.02
1.02
1.03
3.08
3.02
f1 (ppm)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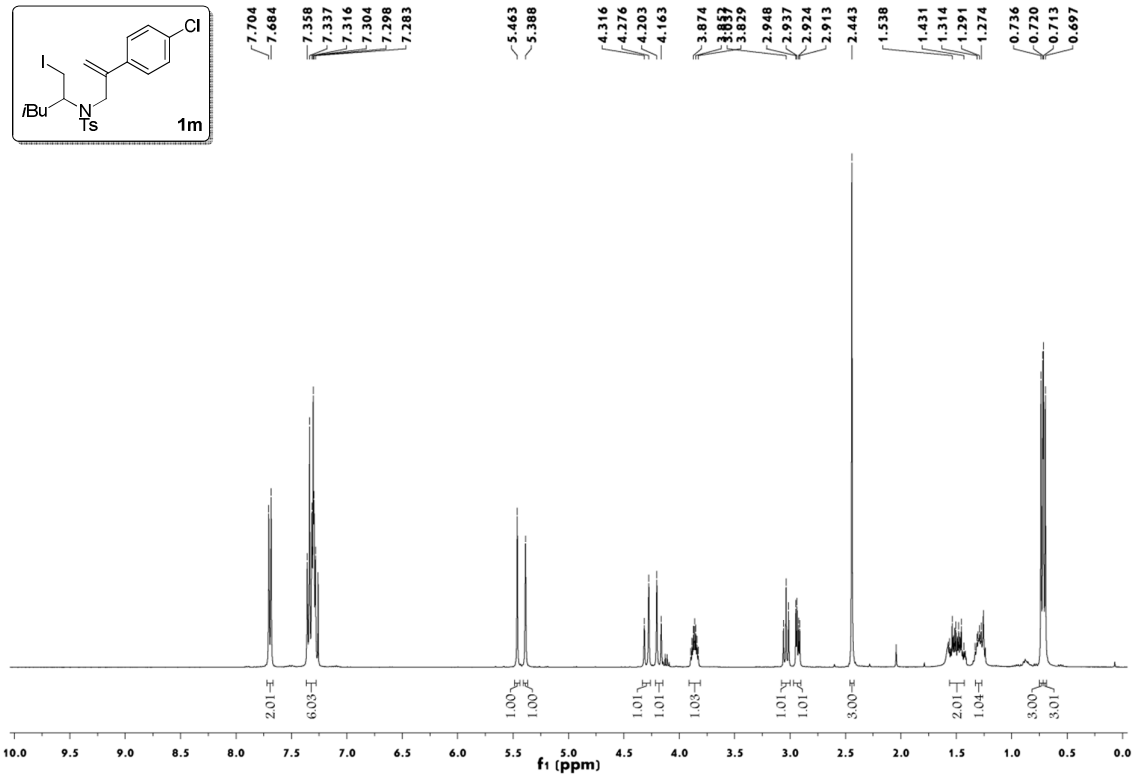
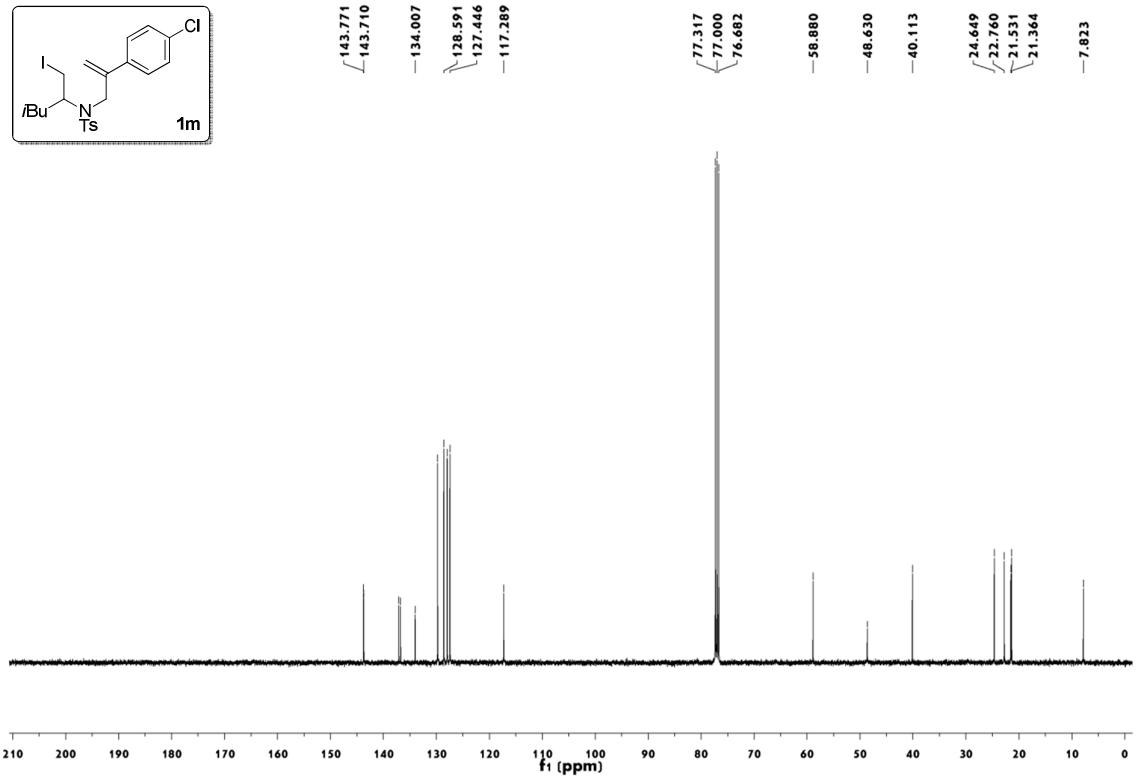
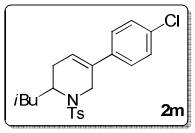
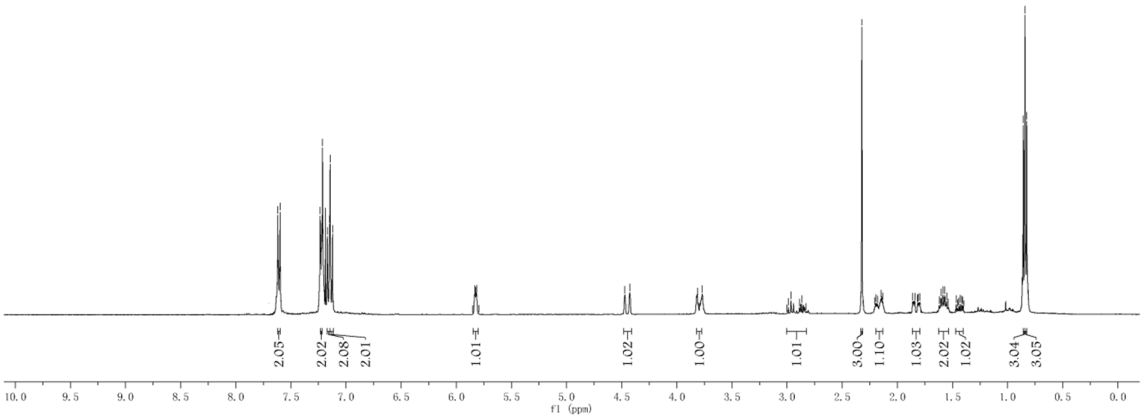
136.810
131.556
128.669
125.968
121.440
77.317
77.000
76.682
56.455
41.880
28.237
25.206
21.504
20.215
20.076
Cl
iPr
N
Ts
2l
f1 (ppm)

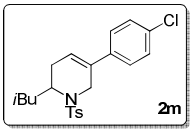

Cl
I
iBu
N
Ts
1m
7.704
7.684
7.358
7.337
7.316
7.304
7.298
7.283
5.463
5.388
4.316
4.276
4.203
4.163
3.874
3.857
3.829
2.948
2.937
2.924
2.913
2.443
1.538
1.431
1.314
1.291
1.274
0.736
0.720
0.713
0.697
2.01
6.03
1.00
1.00
1.01
1.01
1.03
1.01
1.01
3.00
2.01
1.04
3.00
3.01
f1 (ppm)


Cl
I
iBu
N
Ts
1m
143.771
143.710
134.007
128.591
127.446
117.289
77.317
77.000
76.682
58.880
48.630
40.113
24.649
22.760
21.531
21.364
7.823
f1 (ppm)



7.619
7.598
7.213
7.149
7.145
7.123
5.852
5.834
5.825
5.815
5.796
4.471
4.427
3.813
3.770
2.989
2.964
2.888
2.864
2.178
2.132
1.862
1.569
1.454
1.407
0.858
0.843
0.827





143.147
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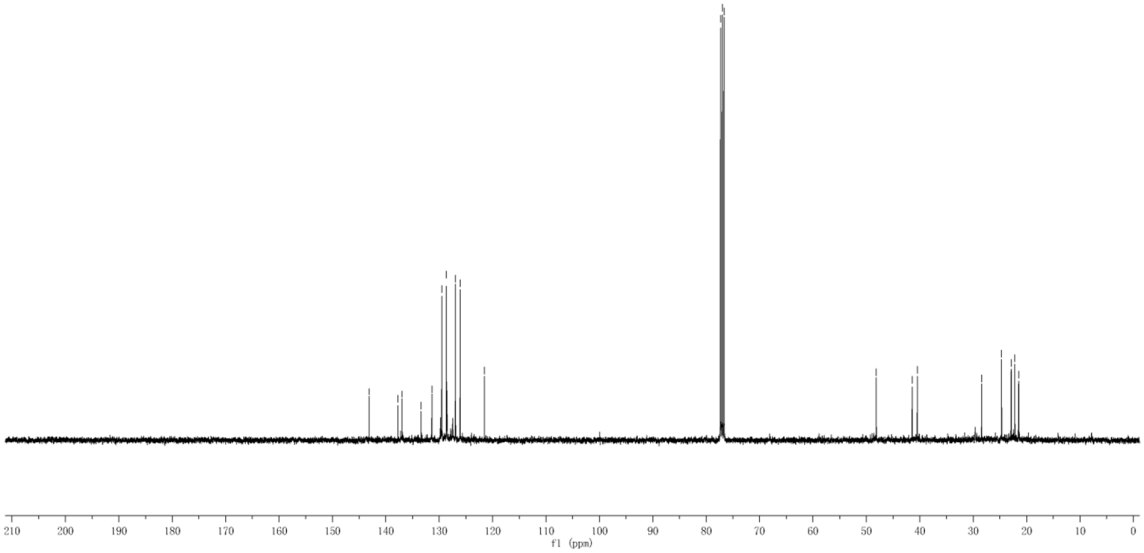
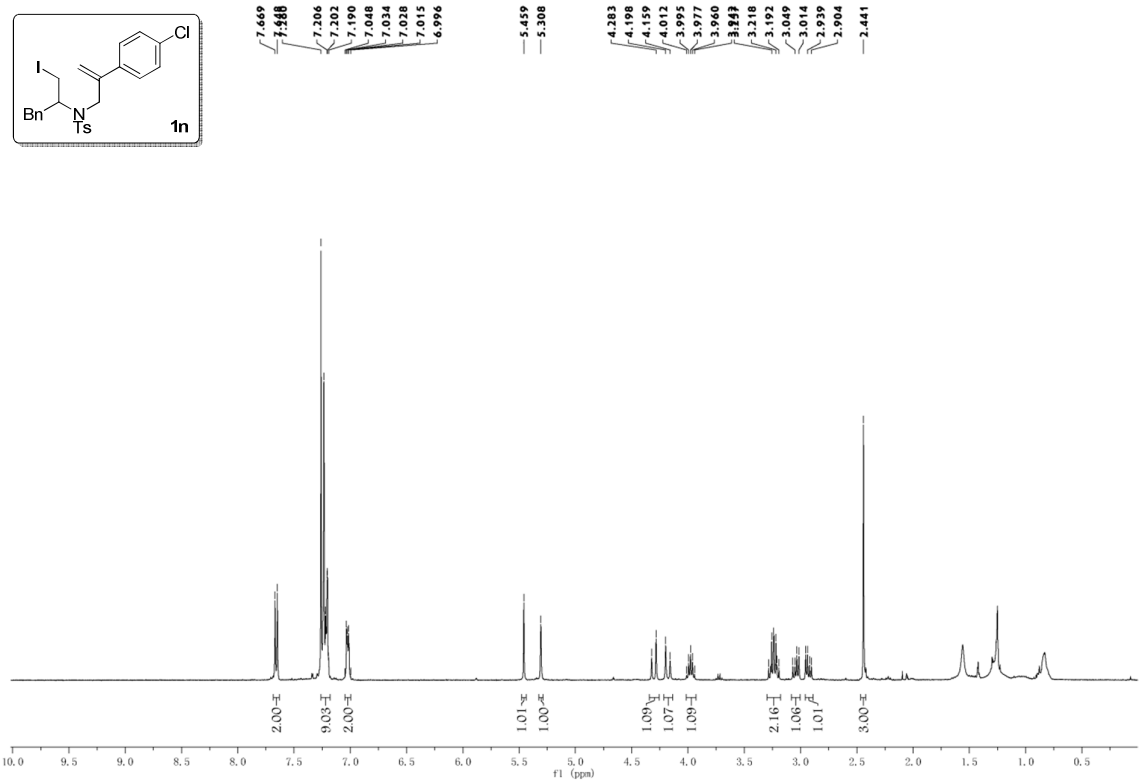
128.661
126.077
121.536
77.318
77.000
76.683
48.148
41.423
40.461
28.399
24.677
22.878
22.198
21.474




Cl
I
Bn
N
Ts
1n
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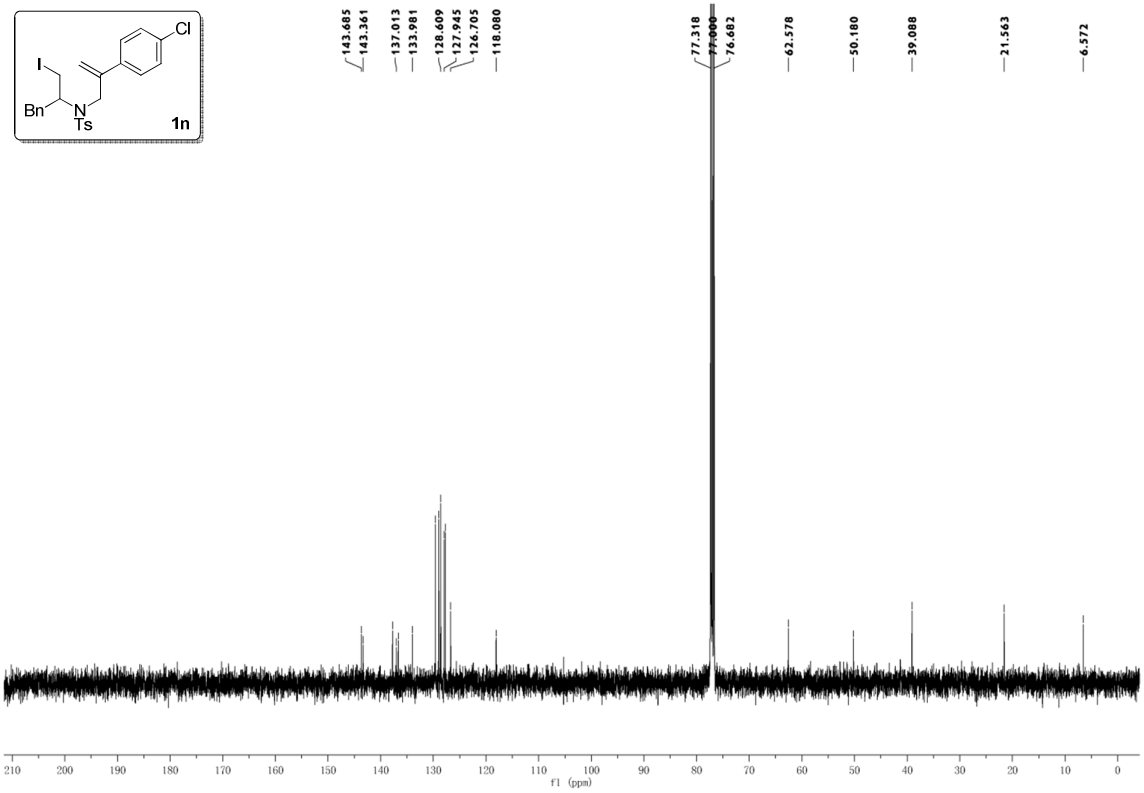
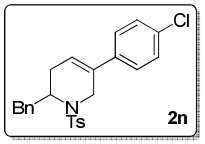
7.206
7.202
7.190
7.048
7.034
7.028
7.015
6.996
5.459
5.308
4.283
4.198
4.159
4.012
3.995
3.977
3.960
3.218
3.192
3.049
3.014
2.939
2.904
2.441
2.00
9.03
2.00
1.01
1.00
1.09
1.07
1.09
2.16
1.06
1.01
3.00
f1 (ppm)


Cl
I
Bn
N
Ts
1n
143.685
143.361
137.013
133.981
128.609
127.945
126.705
118.080
77.318
77.000
76.682
62.578
50.180
39.088
21.563
6.572
f1 (ppm)


Cl
Bn
N
Ts
2n


7.660
7.640
7.321
7.225
7.170
7.129
6.064
6.045
6.042
6.031
6.008
4.509
4.420
4.412
4.397
4.382
3.993
3.988
3.959
3.949
3.945
2.722
2.708
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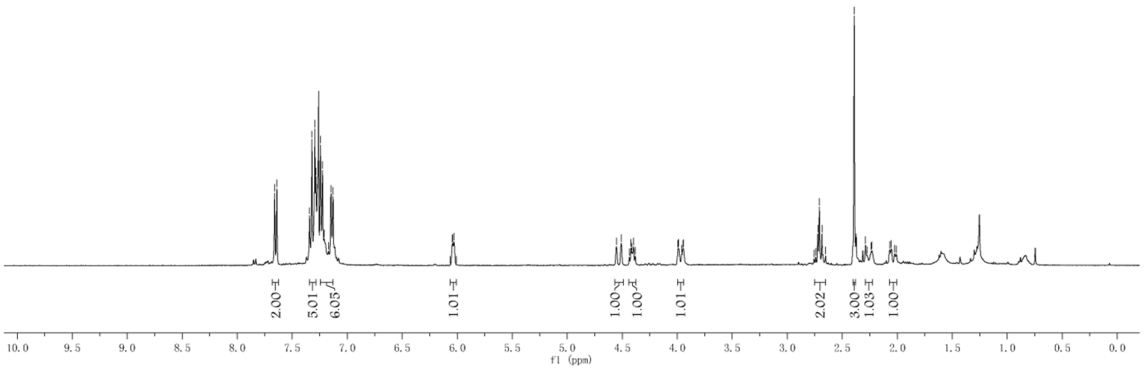
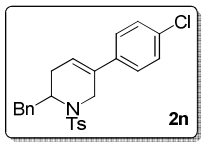
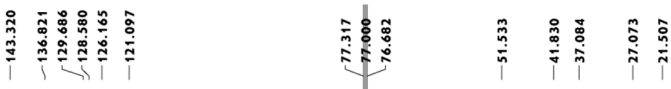
2.651
2.391
2.288
2.274
2.236
2.230
2.068
2.055
2.022
2.008


2.00
5.01
6.05
1.01
1.00
1.00
1.01
2.02
3.00
1.03
1.00
f1 (ppm)


Cl
Bn
N
Ts
2n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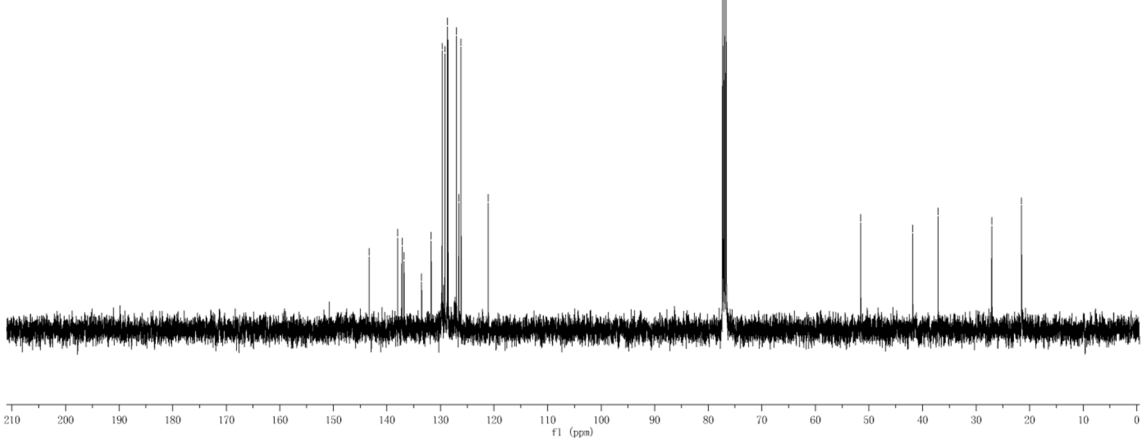
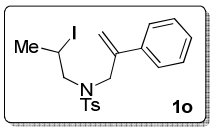
128.580
126.165
121.097
77.317
77.000
76.682
51.533
41.830
37.084
27.073
21.507


f1 (ppm)


Me
I
N
Ts
1o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7.674
7.464
7.361
7.354
7.339
7.320
7.298
5.528
5.183
4.341
4.165
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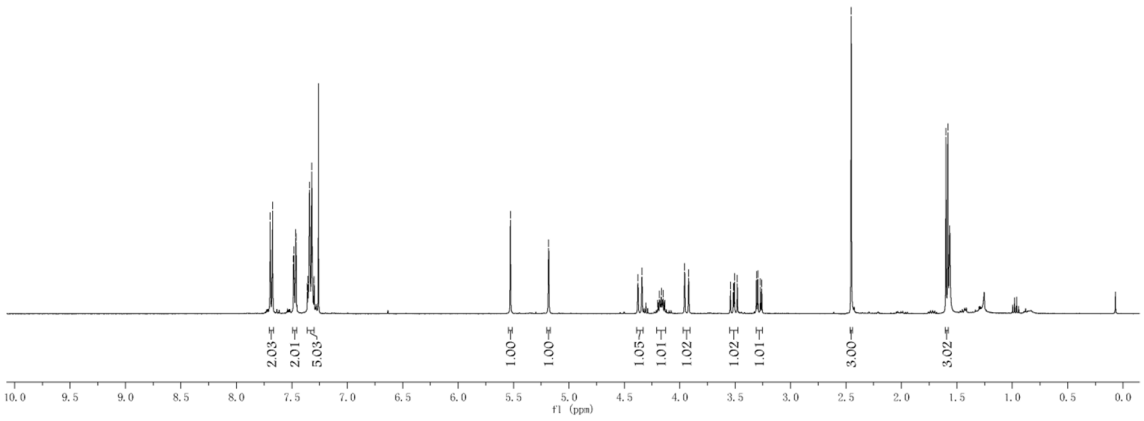
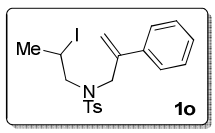
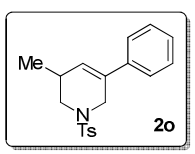
4.134
3.956
3.308
3.296
3.272
3.260
2.453
1.598
1.581

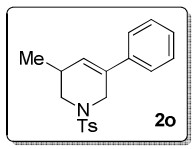

2.03
2.01
5.03
1.00
1.00
1.05
1.01
1.02
1.02
1.01
3.00
3.02
f1 (ppm)


Me
I
N
Ts
1o

143.795
142.656
135.063
128.570
127.527
126.407
117.124
77.318
77.000
76.682
58.193
54.388
25.087
24.400
21.547
f1 (ppm)


Me
N
Ts
2o

7.723
7.710
7.335
7.318
7.305
7.294
7.280
5.960
5.940
5.923
4.093
4.067
3.700
3.529
3.510
2.659
2.623
2.592
2.578
2.560
2.547
2.537
2.427
1.094
1.083
2.02
7.03
1.00
1.02
1.02
1.01
1.00
1.01
3.03
3.01
f1 (ppm)


Me
N
Ts
2o

143.563
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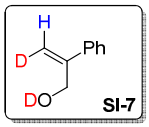
138.522
132.560
129.697
128.573
128.507
127.733
127.686
125.280
77.317
77.000
76.682
49.120
46.329
30.636
21.517
18.431
f1 (ppm)


H
D
Ph
DO
SI-7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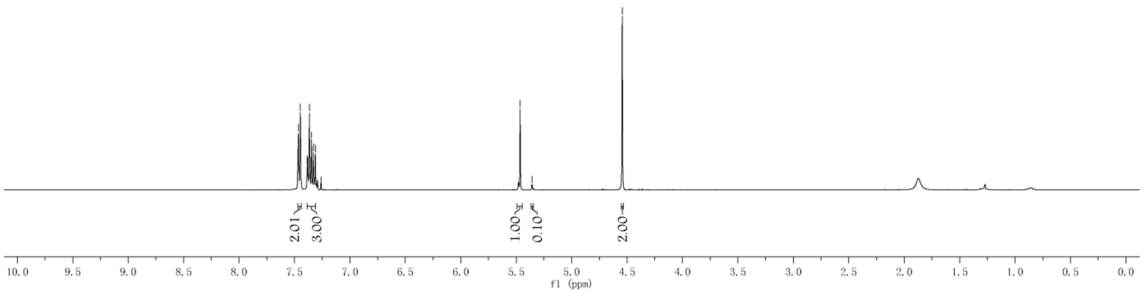
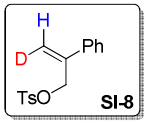
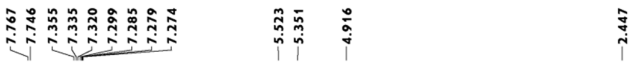
7.328
7.311
5.464
5.356
4.544


2.01
3.00
1.00
0.10
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H
D
Ph
TsO
SI-8


7.767
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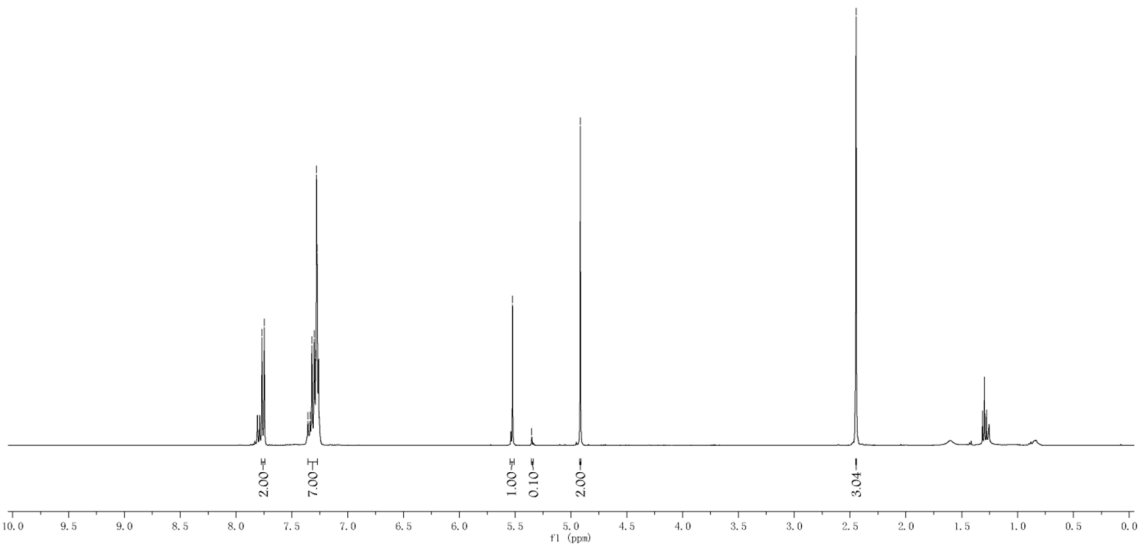
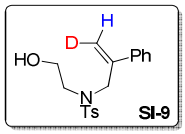
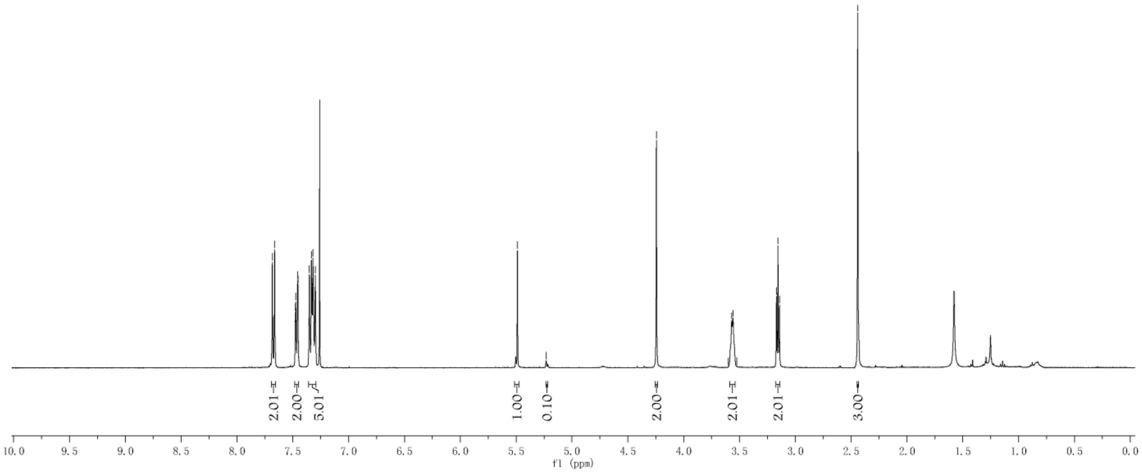
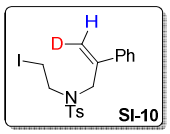
7.320
7.299
7.285
7.279
7.274
5.523
5.351
4.916
2.447


2.00
7.00
1.00
0.10
2.00
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H
D
HO
Ph
N
Ts
SI-9


7.683
7.663
7.352
7.333
7.329
7.325
7.320
7.299
5.489
5.231
4.244
3.570
3.558
3.524
3.169
3.156
3.142
2.441


2.01
2.00
5.01
1.00
0.10
2.00
2.01
2.01
3.00
f1 (ppm)


H
D
I
Ph
N
Ts
SI-10


7.684
7.663
7.467
7.452
7.448
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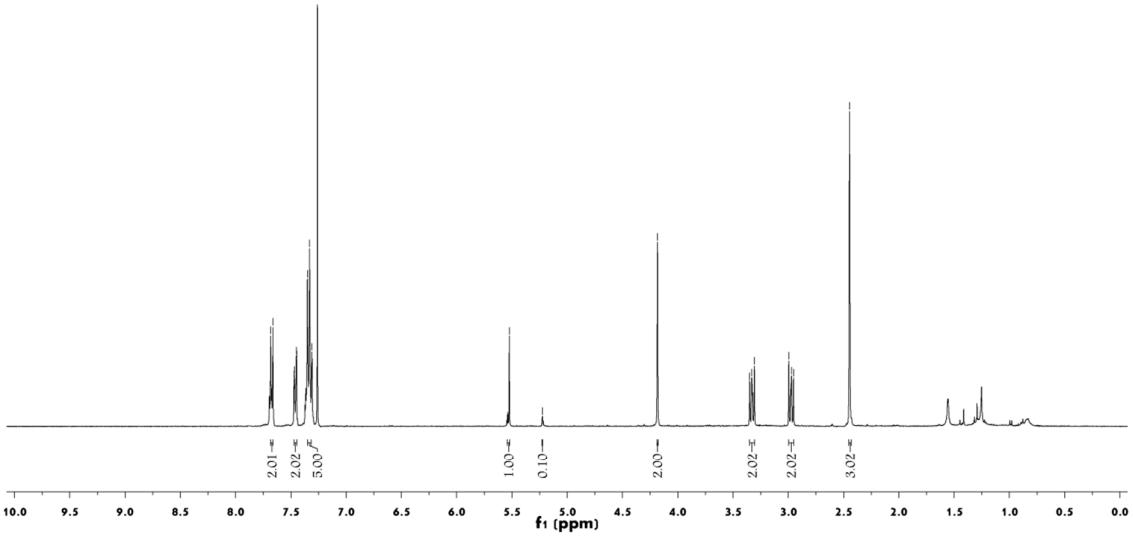
7.331
7.310
5.524
5.225
4.184
3.350
3.331
3.307
2.996
2.953
2.447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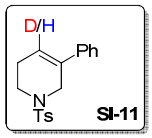
2.02
5.00
1.00
0.10
2.00
2.02
2.02
3.02
f1 (ppm)


D/H
Ph
N
Ts
SI-11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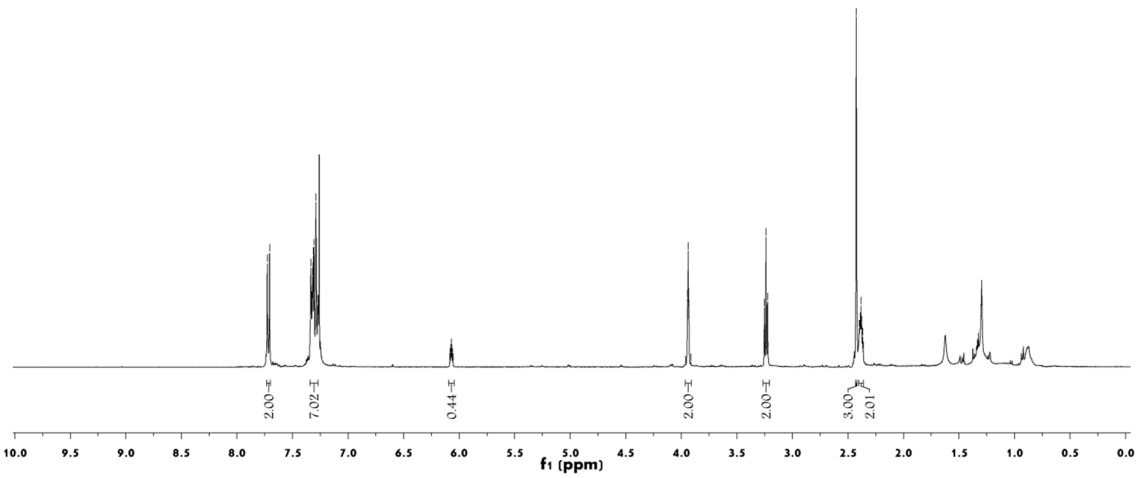
7.707
7.334
7.319
7.306
7.272
6.085
6.080
6.075
6.070
6.065
6.060
6.055
3.961
3.942
3.938
3.931
3.914
3.252
3.237
3.223
2.425
2.397
2.390
2.383
2.376
2.368
2.362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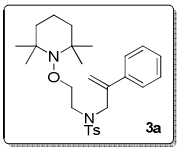
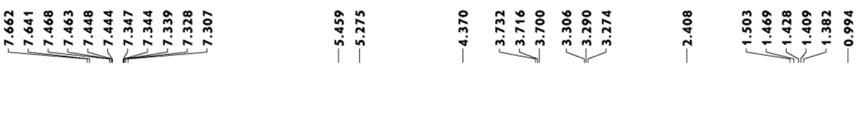
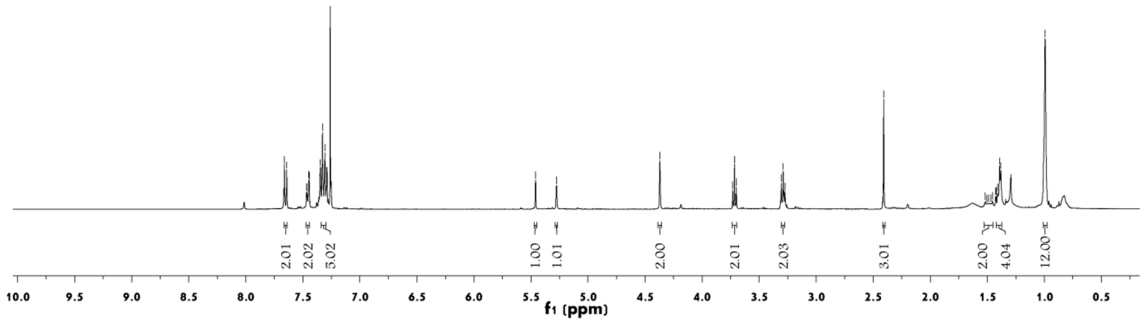
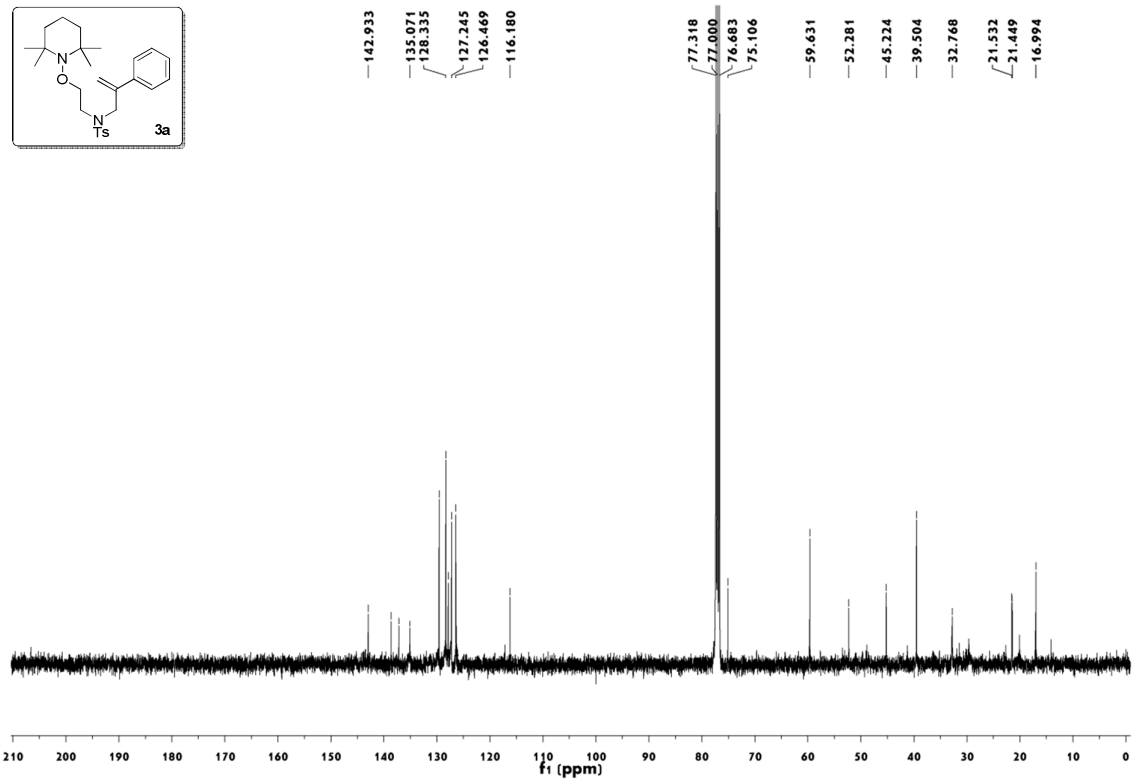
2.00
2.00
3.00
2.01
f1 (ppm)


N
O
N
Ts
3a


7.662
7.641
7.468
7.463
7.448
7.444
7.347
7.344
7.339
7.328
7.307
5.459
5.275
4.370
3.732
3.716
3.700
3.306
3.290
3.274
2.408
1.503
1.469
1.428
1.409
1.382
0.994


2.01
2.02
5.02
1.00
1.01
2.00
2.01
2.03
3.01
2.00
4.04
12.00
f1 (ppm)


3a
142.933
135.071
128.335
127.245
126.469
116.180
77.318
77.000
76.683
75.106
59.631
52.281
45.224
39.504
32.768
21.532
21.449
16.994
f1 (ppm)