Supplementary Information

Metal-Free Synthesis of 2-Aminonaphthalenes by Intramolecular Transannulation of 1-Sulfonyl-4-(2-alkenylphenyl)-1,2,3-triazoles

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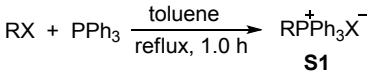
1. General

Analytical thin layer chromatography (TLC) was performed using Silica Gel $HSGF_{254}$ pre-coated plates. Flash column chromatography was performed using 200 - 300 Mesh Silica Gel. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded using Brucker Avance II DMX 400 MHz spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or $CDCl_3$ (7.26 ppm). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded using a Brucker Avance II DMX 400 spectrometer at 100 MHz. Chemical shift is reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm). High resolution mass spectra (HRMS) were obtained by Center for Instrumental Analysis of Zhejiang Sci-Tech University and a Waters TOFMS GCT Premier instrument for HRMS. The results are reported as m/e (relative ratio). All the substituted 2-bromobenzaldehyde were commercially purchased, triazole **1** was prepared according to the reported methods in the literature. [1-8]

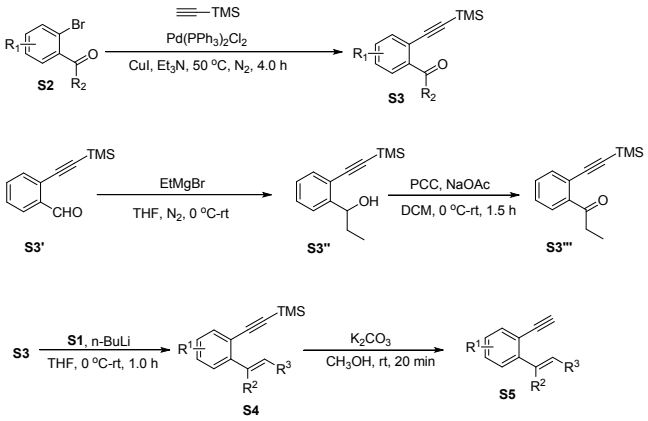
2. Synthetic procedures and spectra data of 1-sulfonyl-1,2,3-triazole.

2.1 General procedure for formation of phosphonium salt (S1) [1] :



Triphenylphosphine (6.57 g, 25.0 mmol) was dissolved in toluene (20 mL) in a round bottom flask charged with a stir bar and a condenser. The solution of halide RX (30.0 mmol) in toluene (10 mL) was added dropwise at rt. The mixture was then warmed up to reflux and a solid precipitated. The mixture was stirred for an additional 30 mins. The solid was filtered out after the mixture was cooled to rt. The obtained solid was washed with PE (15 mL × 3), giving the desired **S1** as a white solid.

2.2 General procedure for formation of 1-ethynyl-2-vinylbenzene (S5):



2.2.1 Synthesis of 2-((trimethylsilyl)ethynyl)benzaldehyde (S3) [2]:

Under a nitrogen atmosphere, to a triethylamine solution (40 mL) of $Pd(PPh_3)_2Cl_2$ (0.84 g, 1.2 mmol) and CuI (0.76 g, 4.0 mmol) was added 2-bromobenzaldehyde (5.0 g, 40.0 mmol) and stirred for 10 mins, then added trimethylsilylacetylene (4.7 g, 48.0 mmol) dropwise over 30 mins. The resulting suspension was allowed to be stirred for 4.0 hours at 50 °C. After completion of the reaction, the mixture was filtered through a short celite bed and concentrated under reduced pressure. The residue was eluted through a silica column (PE) to afford compound **S3** (R^1 = H, R^2 = H, 7.9 g, 98 %) as a pale yellow oil.

2.2.2 Synthesis of 1-(2-((trimethylsilyl)ethynyl)phenyl)propan-1-ol (S3'') [3]:

Under a nitrogen atmosphere, a solution of bromoethane (6.0 mmol) in dry THF (5.0 mL) was added via syringe to reaction flask charged with active Magnesium (576 mg, 24.0 mmol) being stirred at rt to initiate the reaction. After the reaction was initiated, the mixture was cooled to 0 °C in ice-bath and the remained solution of bromoethane (12.0 mmol) in dry THF (10 mL) was added to the resulting mixture at 0 °C dropwise over 30 mins. After the bromoethane addition was complete, the mixture was allowed to be stirred for 1.0 hour at rt. Then a solution of **S3'** (2.42 g, 12.0 mmol) in dry THF (10 mL) was added to the resulting mixture at 0 °C dropwise over 1.0 hour. The mixture was allowed to be stirred for 2.0 hours at room temperature, until TLC analysis showed that **S3'** was completely consumed. The reaction was diluted with saturated aqueous NH_4Cl and extracted by EtOAc (20 mL × 2). The combined organics were washed with water, saturated brine, dried (Na_2SO_4) and filtered through celite. The eluent was concentrated in vacuo. The obtained crude product was purified by a silica column (PE: EA = 30:1) to give the desired product **S3''** (2.36 g, 85.0 %) as a colorless oil.

2.2.3 Synthesis of 1-(2-((trimethylsilyl)ethynyl)phenyl)propan-1-one (S3''') [4]:

To the mixture of PCC (3.88 g, 18.0 mmol) and sodium acetate (0.145 g, 1.8 mmol) in dry DCM (15 mL) was added **S3''** (12.0 mmol) at 0 °C. Stirred at rt constantly until the reaction was complete, the mixture was filtered through a short celite bed and concentrated under reduced pressure. The residue was eluted through a silica column (PE: EA = 40:1) to afford compound **S3'''**(2.18 g, 79 %) as a pale yellow oil.

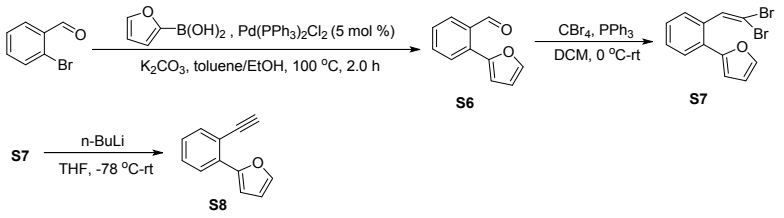
2.2.4 Synthesis of trimethyl((2-vinylphenyl)ethynyl)silane (S4) [2]:

A THF solution (20 mL) of methyltriphenylphosphineiodide (6.1 g, 15.0 mmol) was cooled to 0 °C before addition of *n*-BuLi (4.8 mL, 2.5 M in hexane, 12.0 mm. The reaction was kept at 0 °C for 30 mins, and a THF solution of (5 mL) compound **S3** (2-((trimethylsilyl)ethynyl) benzaldehyde) (2.02 g, 10.0 mmol) was added to this mixture and continued to stir for 30 mins at rt. The resulting mixture was quenched with water and extracted with PE (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was eluted through a short pad of silica column to afford **S4** (1.48 g, 74 %) as a colorless oil.

2.2.5 Synthesis of 2-ethynylbenzaldehyde (S5) [2]:

K_2CO_3 (1.2 equiv) were added to the solution of **S4** (1.0 equiv) in 10 mL of MeOH and the mixture was stirred at rt until TLC analysis showed that **S4** was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography with PE as eluent to give the corresponding product **S5** (94 %) as a colorless oil.

2.3 General procedure for formation of 2-(2-ethynylphenyl)furan (S8)



2.3.1 Synthesis of 2-(furan-2-yl)benzaldehyde (S6) [5]:

A mixture of furan-2-ylboronic acid (738 mg, 6.6 mmol) and $Pd(PPh_3)_2Cl_2$ (210 mg, 0.3 mmol) was added to a reaction flask, then toluene (15.0 mL), ethanol (10.0 mL), saturated aqueous solution of K_2CO_3 (5.0 mL) and 2-bromobenzaldehyde (0.69 mL, 6.0 mmol) were added respectively and heated at 100 °C with magnetic stirring under nitrogen atmosphere. When TLC analysis showed that 2-bromobenzaldehyde was completely consumed, the reaction mixture was cooled to rt and filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography with PE/EtOAc (40:1) as eluent to give product **S6** (987.4 mg, 96 %) as a colorless oil.

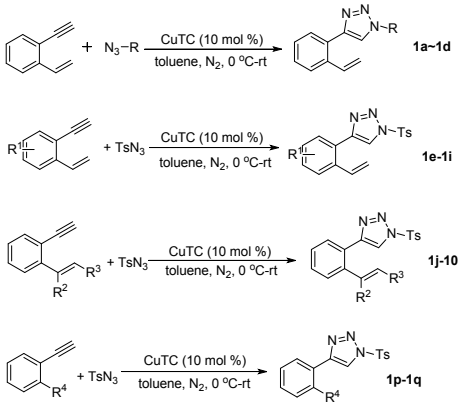
2.3.2 Synthesis of 2-(2-(2,2-dibromovinyl)phenyl)furan (S7) [6]:

To a solution of **S6** (887.0 mg, 5.1 mmol) and CBr_4 (3.38 g, 10.2 mmol) in CH_2Cl_2 (10 mL) was added the solution of PPh_3 (5.35 g, 20.4 mmol) in CH_2Cl_2 (10 mL) via syringe at 0 °C. After stirring for 30 mins, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford **S7** (1.33 g, 80 %) as a pale yellow solid.

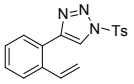
2.3.3 Synthesis of 2-(2-ethynylphenyl)furan (S8) [6]:

To a solution of **S7** (1.33 g, 4.1 mmol) in THF (10 mL) was added *n*-BuLi (8.2 mmol, 3.28 mL, 2.5 M in hexane) dropwise at –78 °C. After stirring for 4.0 hours, MeOH (8 mL) was added and the mixture was stirred for an additional 1.0 hour, then the reaction was quenched with saturated aqueous NH_4Cl at 0 °C, and the aqueous phase was extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford **S8** (581.4 mg, 84 %) as a pale yellow oil.

2.4 General procedures for formation of 1-sulfonyl-1,2,3-triazoles (1a~1q) [7]:

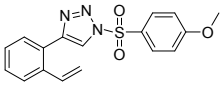


Under a nitrogen atmosphere, dry toluene (15 mL) was added to a reaction flask charged with copper (I) thiophene-2-carboxylate (CuTC, 0.095 g, 0.5 mmol,) and the alkyne (5.0 mmol). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (6.0 mmol, 1.2 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture was allowed to warm to rt and stirred until TLC analysis showed that alkyne was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography with PE/EtOAc (10:1) as eluent to give the corresponding product **1**.



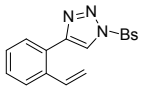
1a

1-tosyl-4-(2-vinylphenyl)-1H-1,2,3-triazole (1a): white solid, m.p.: 106 ~ 108 °C, 1.48 g, yield: 91 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.20 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.31-7.35 (m, 2H), 6.92 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.72 (d, *J* = 17.4 Hz, 1H), 5.36 (d, *J* = 10.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.45, 145.88, 136.70, 135.28, 133.01, 130.52, 129.26, 129.23, 128.74, 128.01, 127.05, 126.90, 121.90, 117.25, 21.87. HRMS (ESI) calcd for $C_{17}H_{16}N_3O_2S^+$ 326.0963, found 326.0967.



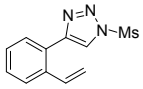
1b

1-((4-methoxyphenyl)sulfonyl)-4-(2-vinylphenyl)-1H-1,2,3-triazole (1b): white solid, m.p.: 113 ~ 115 °C, 0.99 g, yield: 80 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (s, 1H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.46 – 7.32 (m, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.95 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.74 (d, *J* = 17.4 Hz, 1H), 5.39 (d, *J* = 11.0 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 165.45, 145.78, 136.68, 135.28, 131.28, 129.26, 129.20, 128.01, 127.13, 126.88, 121.77, 117.21, 115.16, 55.99. HRMS (ESI) calcd for $C_{17}H_{16}N_3O_3S^+$ 342.0912, found 342.0916.



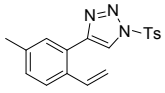
1c

1-((4-bromophenyl)sulfonyl)-4-(2-vinylphenyl)-1H-1,2,3-triazole (1c): white solid, m.p.: 114 ~ 116 °C, 1.49 g, yield: 75 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.22 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.76 (dd, *J* = 12.7, 8.5 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.46 – 7.33 (m, 2H), 6.94 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.75 (d, *J* = 17.4 Hz, 1H), 5.40 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.09, 136.75, 135.20, 134.96, 133.30, 131.64, 130.07, 129.39, 129.28, 128.07, 126.98, 126.76, 121.90, 117.44. HRMS (ESI) calcd for $C_{16}H_{13}BrN_3O_2S^+$ 389.9912, found 389.9913.



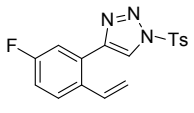
1d

1-(methylsulfonyl)-4-(2-vinylphenyl)-1H-1,2,3-triazole (1d): white solid, m.p.: 99 ~ 101 °C, 1.02 g, yield: 82 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.33 (m, 2H), 6.97 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.77 (d, *J* = 17.4 Hz, 1H), 5.41 (d, *J* = 11.0 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.02, 136.83, 135.16, 129.45, 129.33, 128.11, 127.00, 126.79, 121.78, 117.51, 42.69. HRMS (ESI) calcd for $C_{11}H_{12}N_3O_2S^+$ 250.0650, found 250.0648.



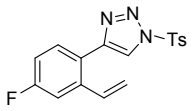
1e

4-(5-methyl-2-vinylphenyl)-1-tosyl-1H-1,2,3-triazole (1e): white solid, m.p.: 116 ~ 118 °C, 1.27 g, yield: 75 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.18 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.54 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 6.87 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.68 (d, *J* = 17.4 Hz, 1H), 5.31 (d, *J* = 10.9 Hz, 1H), 2.45 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100MHz, Chloroform-d) δ 147.38, 145.97, 137.91, 135.04, 133.90, 133.07, 130.49, 130.07, 129.75, 128.72, 126.82, 126.79, 121.84, 116.37, 21.86, 21.05. HRMS (ESI) calcd for $C_{18}H_{18}N_3O_2S^+$ 340.1120, found 340.1122.



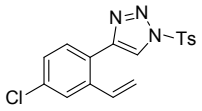
1f

4-(5-fluoro-2-vinylphenyl)-1-tosyl-1H-1,2,3-triazole (1f): white solid, m.p.: 136 ~ 138 °C, 1.37 g, yield: 80 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.19 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.70 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.28 (dd, *J* = 9.8, 2.7 Hz, 1H), 7.06 (td, *J* = 8.3, 2.6 Hz, 1H), 6.88 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.75 (d, *J* = 17.3 Hz, 1H), 5.44 (d, *J* = 11.0 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100MHz, Chloroform-d), δ 163.15 (d, *J* = 248.7 Hz), 147.55, 145.06, 138.91 (d, *J* = 8.0 Hz), 134.29, 132.89, 131.34 (d, *J* = 8.7 Hz), 130.54, 128.78, 123.29, 121.74, 118.33, 115.18 (d, *J* = 21.5 Hz), 113.38 (d, *J* = 21.9 Hz), 21.89. HRMS (ESI) calcd for $C_{17}H_{15}FN_3O_2S^+$ 344.0869, found 344.0869.



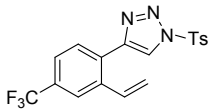
1g

4-(4-fluoro-2-vinylphenyl)-1-tosyl-1H-1,2,3-triazole (1g): white solid, m.p.: 125 ~ 127 °C, 1.34 g, yield: 78 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.25 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.52 (ddd, *J* = 12.6, 9.1, 4.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.09 (td, *J* = 8.3, 2.6 Hz, 1H), 6.86 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.69 (d, *J* = 17.3 Hz, 1H), 5.39 (d, *J* = 11.0 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 162.21 (d, *J* = 247.3 Hz), 147.63, 144.77, 134.37, 132.88, 132.85, 132.81, 130.57, 128.99 (d, *J* = 8.2 Hz), 128.80, 128.72, 122.13 (d, *J* = 2.7 Hz), 117.41, 116.30 (d, *J* = 21.4 Hz), 21.90. HRMS (ESI) calcd for $C_{17}H_{15}FN_3O_2S^+$ 344.0869, found 344.0868.



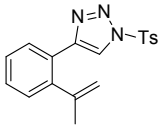
1h

4-(4-chloro-2-vinylphenyl)-1-tosyl-1H-1,2,3-triazole (1h): white solid, m.p.: 118 ~ 120 °C, 1.38 g, yield: 77 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.88 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.76 (d, *J* = 17.3 Hz, 1H), 5.49 – 5.40 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.58, 144.89, 138.22, 135.16, 134.22, 132.85, 130.56, 128.79, 128.07, 126.90, 125.57, 121.92, 118.53, 21.89. HRMS (ESI) calcd for $C_{17}H_{15}ClN_3O_2S^+$ 360.0574, found 360.0574.



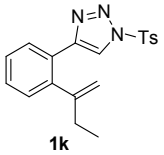
1i

1-tosyl-4-(4-(trifluoromethyl)-2-vinylphenyl)-1H-1,2,3-triazole (1i): white solid, m.p.: 103 ~ 105 °C, 1.61 g, yield: 82 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.30 (s, 1H), 8.07 (d, *J* = 8.3 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.82 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 6.96 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.82 (d, *J* = 17.4 Hz, 1H), 5.52 (d, *J* = 11.0 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.70, 144.55, 137.30, 134.33, 132.76, 130.58, 130.34, 129.69, 128.85, 124.50 (q, *J* = 3.6 Hz), 124.02 (q, *J* = 3.7 Hz). 122.50, 122.44, 119.09, 21.88 . HRMS (ESI) calcd for $C_{18}H_{15}F_3N_3O_2S^+$ 394.0837, found 394.0836.



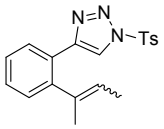
1j

4-(2-(prop-1-en-2-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (1j): white solid, m.p.: 102 ~ 104 °C, 1.44 g, yield: 85 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.36 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.94 (dd, *J* = 5.8, 3.3 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.37-7.32 (m, 2H), 7.23 (dd, *J* = 5.8, 3.3 Hz, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 2.45 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.36, 146.13, 145.94, 142.72, 133.17, 130.49, 129.16, 128.93, 128.74, 128.56, 127.52, 126.06, 121.24, 116.71, 23.80, 21.85 . HRMS (ESI) calcd for $C_{18}H_{18}N_3O_2S^+$ 340.1120, found 340.1120.



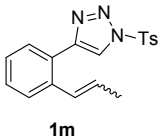
1k

4-(2-(but-1-en-2-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (1k): white solid, m.p.: 108 ~ 110 °C, 1.59 g, yield: 90 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.33 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.98 – 7.91 (m, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.28 (s, 1H), 7.19 (dd, *J* = 6.9, 2.0 Hz, 1H), 5.26 (s, 1H), 5.06 (s, 1H), 2.45 (s, 3H), 2.08 (q, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100MHz, Chloroform-d) δ 152.07, 147.35, 146.02, 142.27, 133.21, 130.48, 129.75, 128.72, 128.62, 128.51, 127.48, 126.23, 121.18, 114.42, 29.80, 21.81, 12.41. HRMS (ESI) calcd for $C_{19}H_{20}N_3O_2S^+$ 354.1276, found 354.1280.



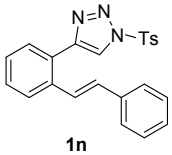
1l

(*E/Z*)-4-(2-(but-2-en-2-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (1l): white solid, m.p.: 98 ~ 100 °C, 1.27 g, yield: 72%; ^{1}H NMR (400 MHz, Chloroform-d) *ratio* = 2.82 : 1, for the mixyure: δ 8.46 – 7.78 (m, 4H), 7.57 – 6.91 (m, 5H), 5.55 (m, 1H), 2.44 (s, 3H), 2.04 – 1.06 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.33, 146.29, 145.73, 144.57, 140.34, 138.26, 136.74, 133.23, 130.48, 130.15, 129.49, 129.39, 129.06, 128.86, 128.64, 128.60, 128.52, 128.42, 127.22, 127.07, 126.42, 126.15, 125.39, 123.77, 121.21, 120.59, 24.75, 21.84, 17.85, 17.58, 14.57, 13.94. HRMS (ESI) calcd for $C_{19}H_{20}N_3O_2S^+$ 354.1276, found 354.1281.



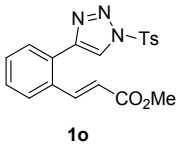
1m

(*E/Z*)-4-(2-(prop-1-en-1-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (1m): white solid, m.p.: 93 ~ 95 °C, 1.20 g, yield: 71 %; ^{1}H NMR (400 MHz, Chloroform-d) *E:Z* = 1.31 : 1, for *E*: δ 8.15 (s, 1H, *E*), 8.03–7.99 (m, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.40–7.24 (m, 4H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.16 (dt, *J* = 15.7, 6.7 Hz, 1H), 2.44 (s, 3H), 1.87 (d, *J* = 6.6 Hz, 3H); for *Z*: 8.27 (s, 1H, *E*), 8.03–7.99 (m, 2H), 7.40–7.24 (m, 6H), 6.43 (d, *J* = 11.5 Hz, 1H), 6.16 (dt, *J* = 11.5, 7.0 Hz, 1H), 2.43 (s, 3H), 1.72 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.40, 147.32, 146.24, 145.78, 136.91, 135.29, 133.14, 133.11, 130.50, 130.46, 130.27, 129.29, 129.17, 129.14, 129.12, 129.03, 128.71, 128.69, 128.66, 128.52, 128.42, 127.60, 127.28, 127.09, 126.96, 126.51, 21.86, 21.84, 18.75, 14.35. HRMS (ESI) calcd for $C_{18}H_{18}N_3O_2S^+$ 340.1120, found 340.1121.



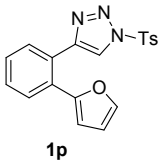
1n

(*E*)-4-(2-styrylphenyl)-1-tosyl-1H-1,2,3-triazole (1n): white solid, m.p.: 112 ~ 114 °C, 1.36 g, yield: 58 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.19 (s, 1H), 8.04 – 8.06 (m, 2H), 7.73 (t, *J* = 7.0 Hz, 2H), 7.53 – 7.29 (m, 10H), 7.05 – 7.09 (m, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.45, 146.40, 137.07, 136.32, 133.08, 131.61, 130.55, 129.60, 129.35, 128.79, 128.71, 128.00, 127.83, 127.41, 126.74, 126.70, 126.59, 121.99, 21.91. HRMS (ESI) calcd for $C_{23}H_{20}N_3O_2S^+$ 402.1276, found 402.1278.



1o

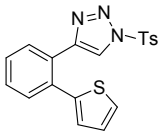
(*E*)-methyl 3-(2-(1-tosyl-1H-1,2,3-triazol-4-yl)phenyl)acrylate (1o): white solid, m.p.: 112 ~ 114 °C, 1.40 g, yield: 63 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (s, 1H), 8.11 – 8.03 (m, 2H), 7.90 – 7.94 (m, 1H), 7.78 – 7.71 (m, 1H), 7.68 – 7.63 (m, 1H), 7.44 (m, 4H), 6.48 – 6.39 (m, 1H), 3.82 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 166.89, 147.54, 145.39, 142.66, 133.22, 132.91, 130.60, 130.10, 129.81, 129.42, 128.83, 128.81, 127.37, 122.23, 120.79, 51.84, 21.89. HRMS (ESI) calcd for $C_{19}H_{18}N_3O_4S^+$ 384.1018, found 384.1015.



1p

4-(2-(furan-2-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (1p) [8] : white solid, 1.34 g, yield: 76 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.92 – 7.89 (m, 1H), 7.57 – 7.38 (m, 6H), 6.63 – 6.38 (m, 1H), 6.24 (d, *J* = 3.3 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ

152.64, 147.27, 146.05, 142.02, 133.24, 130.42, 129.83, 129.73, 129.56, 129.05, 128.70, 128.59, 127.53, 121.51, 111.62, 108.88, 21.85.

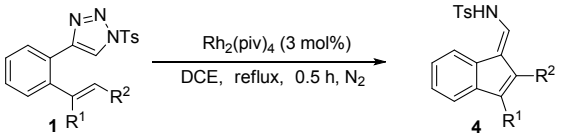


1q

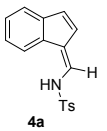
4-(2-(thiophen-2-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (1q) [8] : white solid, 1.37 g, yield: 72 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.05 – 8.03 (m, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.37 (m, 6H), 7.27 (s, 1H), 7.12 – 7.03 (m, 1H), 6.86 (d, *J* = 3.4 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.20, 145.67, 141.75, 133.21, 133.06, 131.44, 130.37, 129.17, 128.77, 128.74, 128.54, 127.43, 127.01, 126.33, 121.60, 21.86.

3. Procedure and structure determination of **4**

Procedure for the preparation of 4

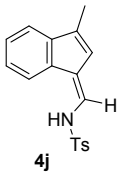


General procedure: Under a nitrogen atmosphere, dry DCE (2.0 mL) was added to a reaction flask charged with $Rh_2(piv)_4$ (3 mol%) and 1-sulfonyl-1,2,3-triazole **1** (0.2 mmol) at rt. Then the reaction mixture was stirred at reflux for the specified time (as depicted in Table 1) until **1** disappeared by TLC monitoring. The mixture was cooled to rt and filtered through a short plug of neutral silica gel, concentrated and purified by flash chromatography of neutral silica gel with PE/EtOAc (8:1) as eluent to give the corresponding product **4**.



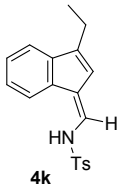
4a

N-((1H-inden-1-ylidene)methyl)-4-methylbenzenesulfonamide (4a): pale yellow solid, m.p.: 117 ~ 119 °C, 42.2 mg, yield: 71 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.49 (m, 1H), 7.38 – 7.29 (m, 4H), 7.24 – 7.17 (m, 2H), 6.85 (d, *J* = 5.5 Hz, 1H), 6.76 – 6.66 (m, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.66, 141.54, 136.63, 136.30, 131.09, 130.19, 126.74, 126.28, 124.79, 122.84, 122.33, 121.57, 121.24, 118.25, 21.61. HRMS (ESI) calcd for $C_{17}H_{16}NO_2S^+$ 298.0902, found 298.0902.



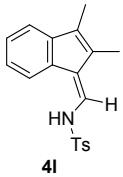
4j

4-methyl-N-((3-methyl-1H-inden-1-ylidene)methyl)benzenesulfonamide (4j): pale yellow solid, m.p.: 106 ~ 108 °C, 60.5 mg, yield: 93 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.10 (m, 4H), 6.38 (s, 1H), 2.36 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100MHz, Chloroform-d) δ 144.47, 142.44, 141.16, 136.88, 136.79, 130.13, 126.71, 126.19, 124.92, 122.71, 119.66, 119.03, 118.05, 117.97, 21.58, 13.25. HRMS (ESI) calcd for $C_{18}H_{18}NO_2S^+$ 312.1058, found 312.1052.



4k

N-((3-ethyl-1H-inden-1-ylidene)methyl)-4-methylbenzenesulfonamide (4k): pale yellow solid, m.p.: 103 ~ 105 °C, 48.8 mg, yield: 75 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.79 (br, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.27 – 7.15 (m, 3H), 6.41 (s, 1H), 2.61 (q, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 1.27 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.46, 144.48, 141.83, 137.04, 136.78, 130.13, 126.74, 126.13, 124.95, 122.56, 119.71, 119.05, 118.16, 115.80, 21.59, 20.89, 12.32. HRMS (ESI) calcd for $C_{19}H_{20}NO_2S^+$ 326.1215, found 326.1213.

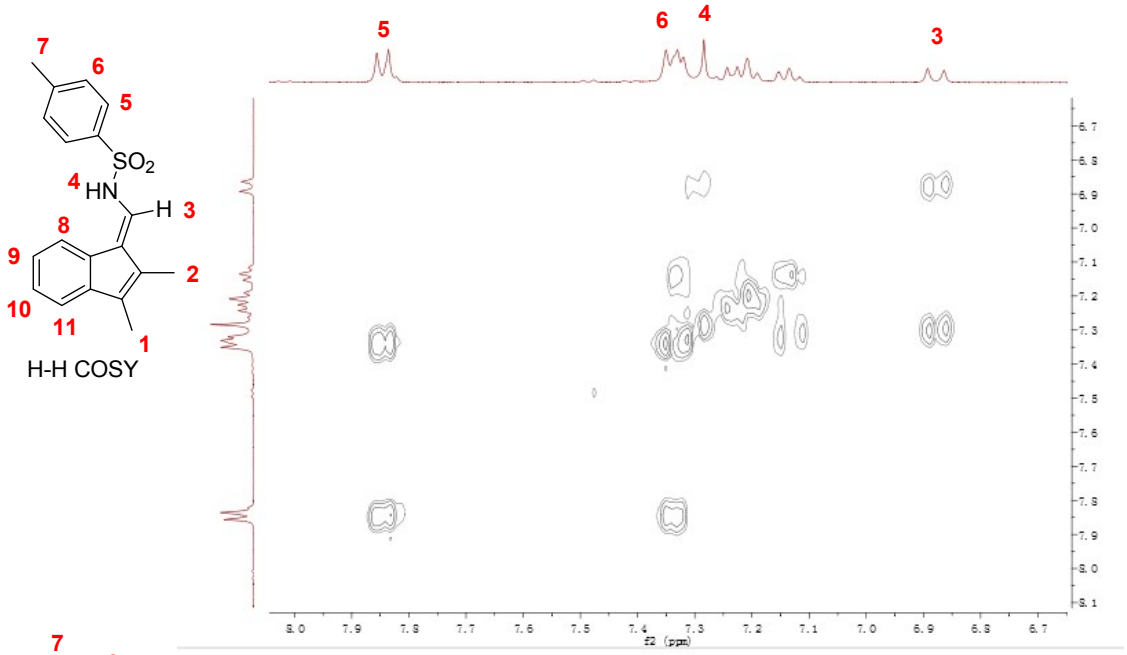


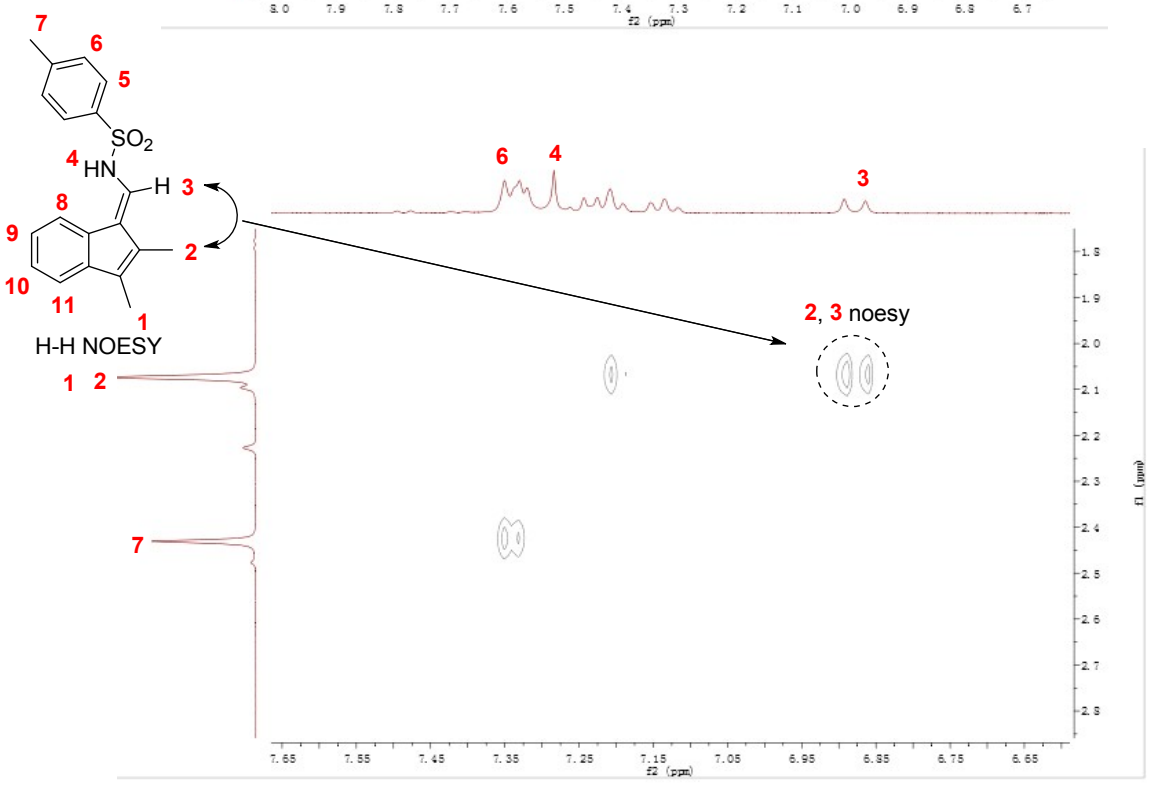
4l

N-((2,3-dimethyl-1H-inden-1-ylidene)methyl)-4-methylbenzenesulfonamide (4l): pale yellow solid, m.p.: 99 ~ 101 °C, 48.1 mg, yield: 74 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.23 – 7.14 (m, 2H), 7.13 – 7.07 (m, 1H), 6.85 (br, 1H), 2.39 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.67, 144.49, 136.84, 132.57, 132.30, 131.71, 130.11, 126.98, 126.74, 124.13, 123.84, 121.89, 120.78, 118.35, 21.58, 10.29, 9.96. HRMS (ESI) calcd for $C_{19}H_{20}NO_2S^+$ 326.1215, found 326.1211.

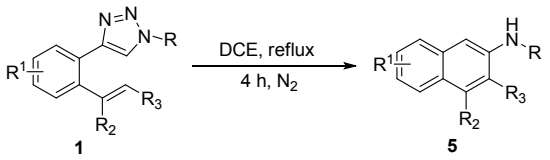
Determination of the configuration of 4

H-H COSY and H-H NOESY of **4l** were utilized to confirm the configuration the C=C double bond. A strong noesy signal between the vinyl hydrogen and the 2-methyl was detected as shown below, indicating the *Z* -configuration of **4l**; and the configurations of **4a**, **4j** and **4k** was then inferred to be *Z* as well.

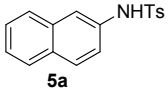




4. Procedure for the preparation of **5**

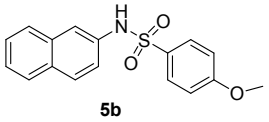


General procedure: Under nitrogen atmosphere, newly distilled dry DCE (2.0 mL) was added to reaction flask charged with 1-sulfonyl-1,2,3-triazole **1** (0.2 mmol) and a stir bar at rt. Then the reaction mixture was stirred at reflux for the specified time (as depicted in Scheme 3). The reaction mixture was then cooled to rt and filtered through a short plug of silica gel. The filtrate was concentrated and then the residue was purified by flash chromatography on silica gel with PE/EtOAc (8:1) as eluent to give the corresponding product **5**.



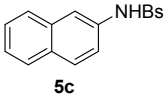
5a

4-methyl-N-(naphthalen-2-yl)benzenesulfonamide (5a) [9] **:** pale yellow solid, 51.7 mg, yield: 87 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.70 (m, 5H), 7.61 (s, 1H), 7.44 (dt, *J* = 15.6, 6.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.94, 136.01, 134.21, 133.66, 131.00, 129.71, 129.34, 127.62, 127.52, 127.31, 126.63, 125.42, 120.92, 118.14, 21.50.



5b

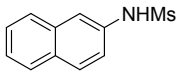
4-methoxy-N-(naphthalen-2-yl)benzenesulfonamide (5b): yellow solid, m.p.: 160 ~ 162 °C, 47.0 mg, yield: 75 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.74 (dd, *J* = 13.5, 8.3 Hz, 3H), 7.68 – 7.58 (m, 2H), 7.49 – 7.36 (m, 2H), 7.30 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 163.13, 134.37, 133.67, 130.96, 130.42, 129.48, 129.34, 127.63, 127.52, 126.63, 125.39, 120.94, 118.05, 114.26, 55.51. HRMS (ESI) calcd for $C_{17}H_{16}NO_3S^+$ 314.0851, found 314.0847.



5c

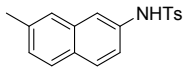
4-bromo-N-(naphthalen-2-yl)benzenesulfonamide (5c): yellow solid, m.p.: 166 ~ 168 °C, 61.4 mg, yield: 85 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.69 (m, 5H), 7.65 – 7.58 (m, 1H), 7.58 – 7.51 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 8.7, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 137.86, 133.59, 132.42, 131.23, 129.60, 128.78, 128.26, 127.70, 127.58, 126.86,

125.78, 121.06, 118.85. HRMS (ESI) calcd for $C_{16}H_{13}BrNO_2S^+$ 361.9850, found 361.9846.



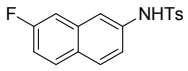
5d

N-(naphthalen-2-yl)methanesulfonamide (5d) [9]: white solid, 31.0 mg, yield: 70 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.90 – 7.80 (m, 3H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.57 – 7.44 (m, 2H), 7.37 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.99 (br, 1H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 134.18, 133.78, 131.10, 129.88, 127.75, 127.51, 127.04, 125.72, 120.38, 117.34, 39.30. HRMS (ESI) calcd for $C_{11}H_{12}NO_2S^+$ 222.0589, found 222.0593.



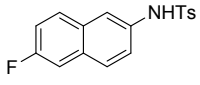
5e

4-methyl-N-(7-methylnaphthalen-2-yl)benzenesulfonamide (5e): yellow solid, m.p.: 158 ~ 160 °C, 51.0 mg, yield: 82 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.56 (m, 3H), 7.47 (s, 1H), 7.44(s, 1H), 7.22 – 7.16 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.88, 136.38, 136.02, 134.30, 133.91, 129.70, 129.27, 129.02, 127.71, 127.41, 127.33, 126.51, 120.04, 117.56, 21.69, 21.49. HRMS (ESI) calcd for $C_{18}H_{18}NO_2S^+$ 312.1058, found 312.1048.



5f

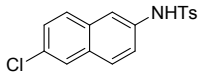
N-(7-fluoronaphthalen-2-yl)-4-methylbenzenesulfonamide (5f): yellow solid, m.p.: 163 ~ 165 °C, 44.1 mg, yield: 70 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.79 (m, 3H), 7.75 – 7.65 (m, 2H), 7.53 (s, 1H), 7.34 – 7.24 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.16 (td, *J* = 8.7, 2.4 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 161.15 (d, *J* = 246.7 Hz), 144.17, 135.83, 135.35, 134.58 (d, *J* = 9.7 Hz), 130.06 (d, *J* = 9.4 Hz), 129.81, 129.38, 127.81, 127.31, 119.73 (d, *J* = 2.5 Hz), 116.66 (d, *J* = 5.4 Hz), 115.66 (d, *J* = 25.5 Hz), 110.59 (d, *J* = 21.0 Hz), 21.53. HRMS (ESI) calcd for $C_{17}H_{15}FNO_2S^+$ 316.0808, found 316.0806.



5g

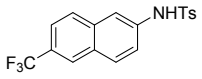
N-(6-fluoronaphthalen-2-yl)-4-methylbenzenesulfonamide (5g): yellow solid, m.p.: 167 ~ 169 °C, 45.4 mg, yield: 72 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.95 (br, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.73 – 7.61 (m, 3H), 7.44 – 7.31 (m, 2H), 7.27 – 7.15 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 160.27 (d, *J* = 245.9 Hz), 144.09, 135.81, 133.66, 131.60 (d, *J* = 9.2 Hz), 130.57,

129.90, 129.78, 128.60 (d, J = 5.4 Hz), 127.32, 122.09, 118.39, 117.01 (d, J = 25.3 Hz), 110.74 (d, J = 20.6 Hz), 21.52. HRMS (ESI) calcd for $C_{17}H_{15}FNO_2S^+$ 316.0808, found 316.0809.



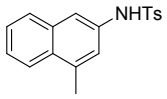
5h

N-(6-chloronaphthalen-2-yl)-4-methylbenzenesulfonamide (5h): yellow solid, m.p.: 166 ~ 168 °C, 34.4 mg, yield: 52 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77 (d, J = 8.1 Hz, 2H), 7.72 (s, 1H), 7.69 – 7.60 (m, 3H), 7.57 (s, 1H), 7.38 (d, J = 8.7 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.21 (d, J = 8.1 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.16, 135.81, 134.50, 131.87, 131.45, 131.09, 129.79, 129.04, 128.51, 127.56, 127.29, 126.35, 121.81, 117.81, 21.53. HRMS (ESI) calcd for $C_{17}H_{15}ClNO_2S^+$ 332.0512, found 332.0506.



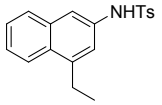
5i

4-methyl-N-(6-(trifluoromethyl)naphthalen-2-yl)benzenesulfonamide (5i): yellow solid, m.p.: 163 ~ 165 °C, 31.4 mg, yield: 43 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (s, 1H), 7.81 (t, J = 9.1 Hz, 4H), 7.71 – 7.54 (m, 2H), 7.40 (dd, J = 8.8, 2.1 Hz, 1H), 7.23 (d, J = 8.2 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.34, 136.40, 135.75, 134.98, 130.32, 129.86, 129.40, 128.45, 127.29, 125.36 (q, J = 4.5 Hz), 122.28 (q, J = 3.2 Hz), 121.45, 116.70, 21.51. HRMS (ESI) calcd for $C_{18}H_{15}F_3NO_2S^+$ 366.0776, found 366.0774.



5j

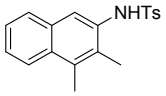
4-methyl-N-(4-methylnaphthalen-2-yl)benzenesulfonamide (5j): pale yellow solid, m.p.:146 ~ 148 °C, 23.6 mg, yield: 38 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 10.43 (br, 1H), 8.52 (s, 1H), 8.09 (s, 1H), 7.77 (dd, J = 13.4, 8.4 Hz, 4H), 7.57 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.20 – 7.18 (m, 3H), 3.94 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.89, 136.32, 136.08, 133.85, 133.72, 130.30, 129.69, 128.16, 127.30, 126.37, 125.23, 123.95, 121.40, 116.12, 21.51, 19.30. HRMS (ESI) calcd for $C_{18}H_{18}NO_2S^+$ 312.1058, found 312.1054.



5k

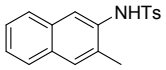
N-(4-ethylnaphthalen-2-yl)-4-methylbenzenesulfonamide (5k): yellow solid, m.p.: 150 ~ 152 °C, 22.1 mg, yield: 34 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 – 7.93 (m, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.75 – 7.69 (m, 1H), 7.46 – 7.42 (m, 3H), 7.21 (d, J = 8.1 Hz, 2H), 7.11 (s, 1H), 3.03 (q, J =

7.5 Hz, 2H), 2.35 (s, 3H), 1.31 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.87, 142.30, 136.11, 134.18, 133.85, 129.65, 129.49, 128.39, 127.34, 126.24, 125.23, 123.58, 119.84, 116.40, 25.69, 21.49, 14.76. HRMS (ESI) calcd for $C_{19}H_{20}NO_2S^+$ 326.1215, found 326.1199.



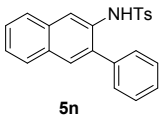
5l

N-(3,4-dimethylnaphthalen-2-yl)-4-methylbenzenesulfonamide (5l): pale yellow solid, m.p.: 137 ~ 139 °C, 31.2 mg, yield: 48 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.56 (m, 4H), 7.51 – 7.34 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 1H), 2.53 (s, 3H), 2.36 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.74, 136.71, 133.18, 132.58, 131.96, 131.20, 129.59, 128.64, 128.39, 127.30, 125.85, 125.37, 123.84, 121.21, 21.55, 15.38, 14.75. HRMS (ESI) calcd for $C_{19}H_{20}NO_2S^+$ 326.1215, found 326.1213.



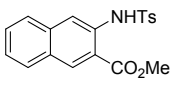
5m

4-methyl-N-(3-methylnaphthalen-2-yl)benzenesulfonamide (5m): pale yellow solid, m.p.: 140 ~ 142 °C, 43.0 mg, yield: 69 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 (s, 1H), 7.75 – 7.71 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 3H), 7.51 (s, 1H), 7.43 – 7.34 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.89, 136.67, 133.05, 132.46, 131.53, 129.66, 129.62, 129.10, 127.56, 127.20, 126.83, 125.79, 125.77, 121.19, 21.53, 18.15. HRMS (ESI) calcd for $C_{18}H_{18}NO_2S^+$ 312.1058, found 312.1050.



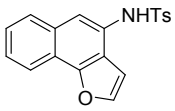
5n

4-methyl-N-(3-phenylnaphthalen-2-yl)benzenesulfonamide (5n): pale yellow solid, m.p.: 166 ~ 168 °C, 53.0 mg, yield: 71 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.18 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.60 (s, 1H), 7.57 – 7.37 (m, 7H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.71 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.96, 137.04, 136.08, 133.33, 133.22, 131.72, 130.53, 129.61, 129.47, 129.16, 128.33, 127.66, 127.53, 127.23, 126.75, 125.82, 118.16, 21.57. HRMS (ESI) calcd for $C_{23}H_{20}NO_2S^+$ 374.1215, found 374.1211.



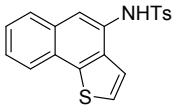
5o

methyl 3-(4-methylphenylsulfonamido)-2-naphthoate (5o) [10] **:** white solid, 20.6 mg, yield: 29 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 10.43 (s, 1H), 8.52 (s, 1H), 8.09 (s, 1H), 7.77 (dd, *J* = 13.4, 8.4 Hz, 4H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 168.18 , 143.76 , 136.34 , 136.02 , 135.19 , 133.60 , 133.48 , 129.51 , 128.94 , 128.76 , 127.38 , 127.30 , 125.82 , 116.96 , 116.49 , 52.66 , 21.48 .



5p

4-methyl-N-(naphtho[1,2-b]furan-4-yl)benzenesulfonamide (5p): yellow solid, m.p.: 181 ~ 183 °C, 31.0 mg, yield: 46 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.77 (m, 4H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.61 (s, 1H), 7.51 (dt, *J* = 21.1, 7.4 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 1.9 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 151.16, 144.23, 144.10, 135.89, 131.50, 129.72, 128.15, 127.81, 127.35, 125.89, 125.81, 119.91, 119.58, 118.74, 114.16, 104.93, 21.52. HRMS (ESI) calcd for $C_{19}H_{16}NO_3S^+$ 338.0851, found 338.0848.



5q

4-methyl-N-(naphtho[1,2-b]thiophen-4-yl)benzenesulfonamide (5q): yellow solid, m.p.: 187 ~ 189 °C, 31.8 mg, yield: 45 %; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.09 – 8.02 (m, 1H), 7.92 – 7.82 (m, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.70 (s, 1H), 7.58 (s, 1H), 7.56 – 7.47 (m, 2H), 7.47 (q, *J* = 5.4 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.02, 138.90, 136.07, 132.78, 131.00, 129.68, 129.09, 128.74, 127.34, 126.39, 126.21, 125.60, 123.35, 121.18, 117.77, 21.52. HRMS (ESI) calcd for $C_{19}H_{16}NO_2S_2^+$ 354.0622, found 354.0623.

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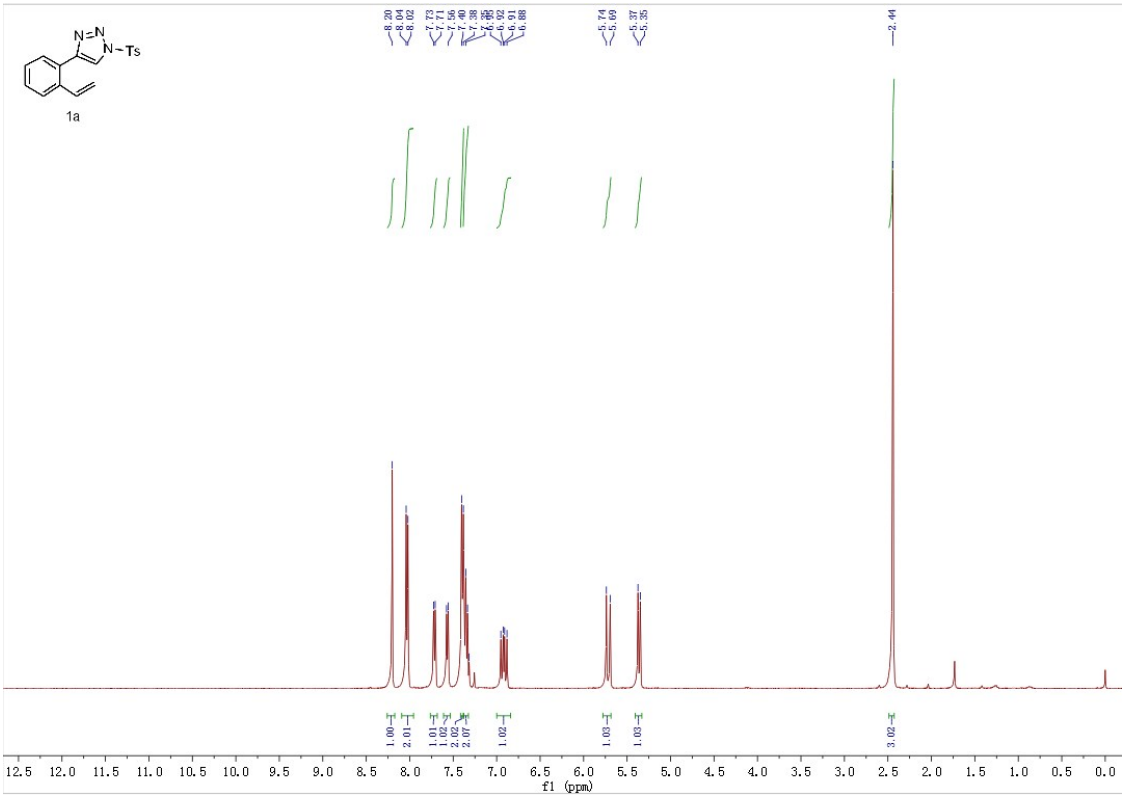
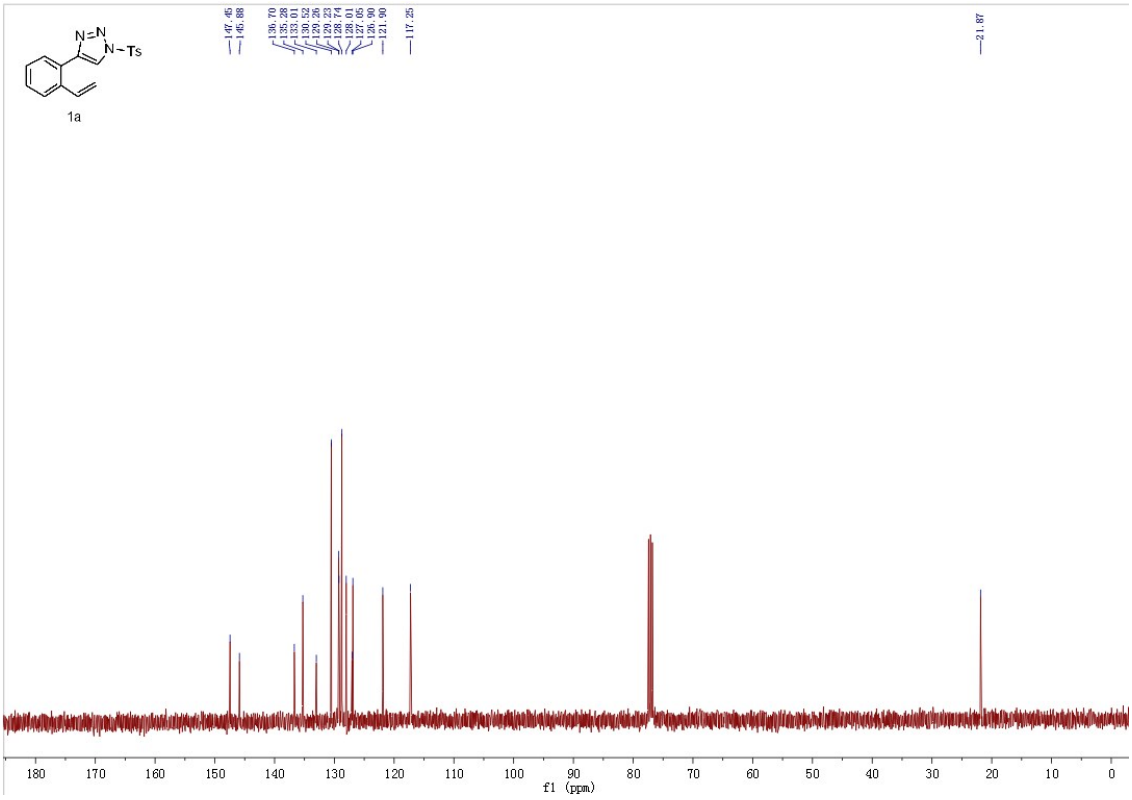
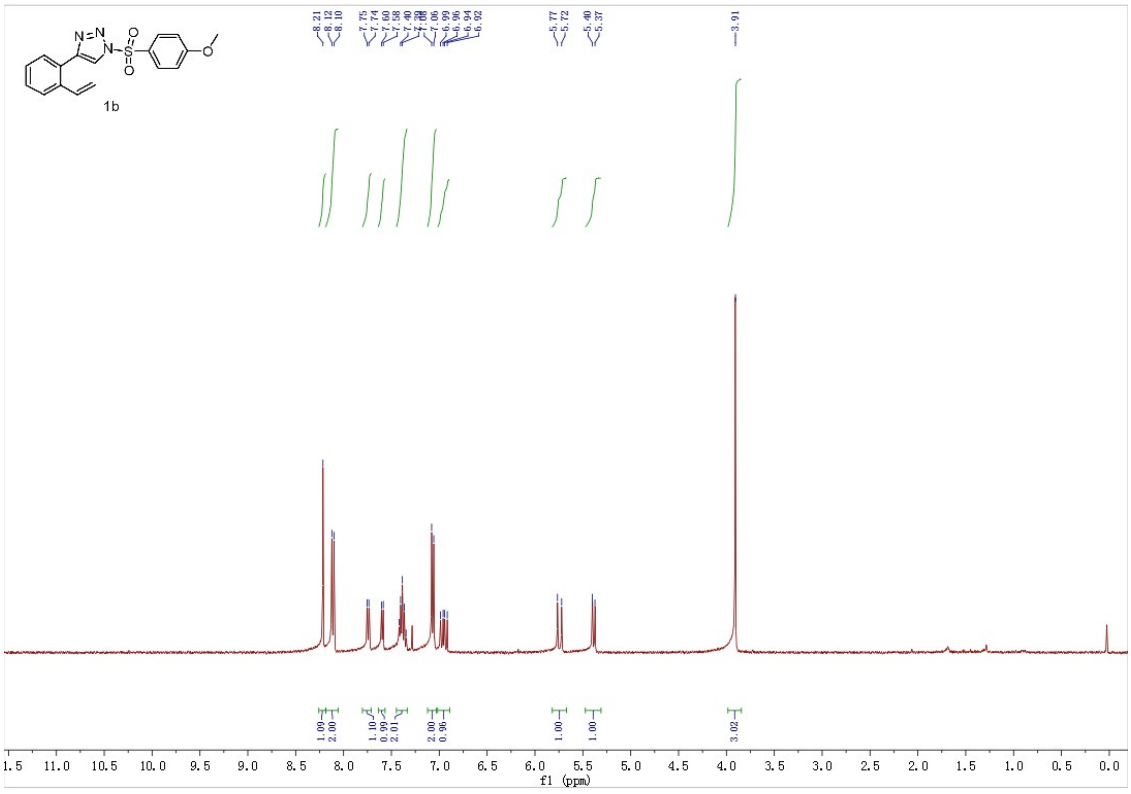
6. ^{1}H and ^{13}C NMR spectra for new compounds



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7.06
6.99
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6.94
6.92
5.77
5.72
5.40
5.37
3.91
1.09
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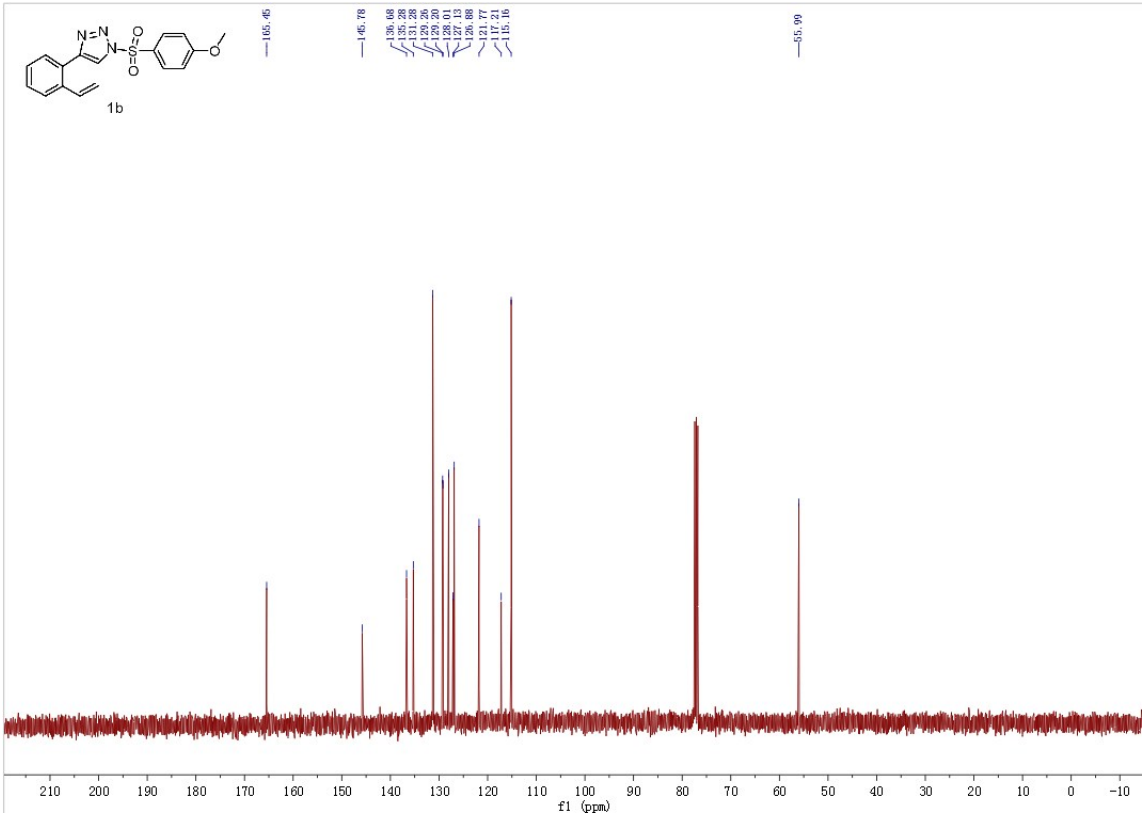
1.10
0.99
2.01
2.00
0.96
1.00
1.00
3.02
f1 (ppm)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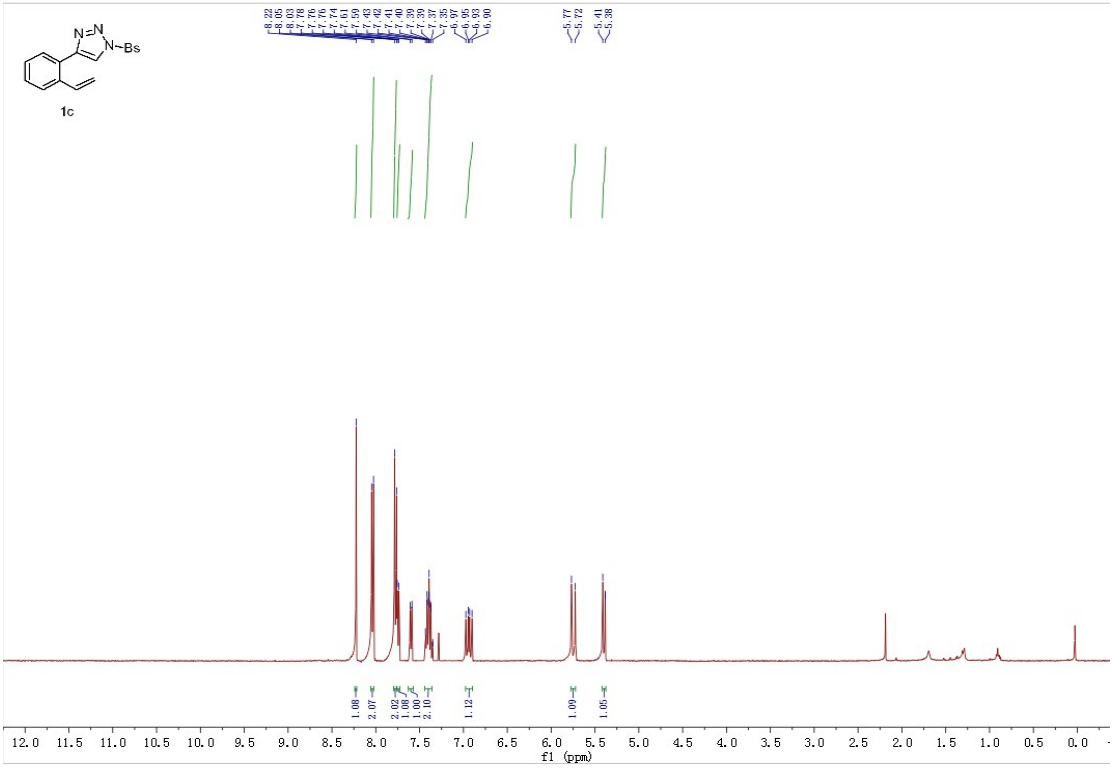
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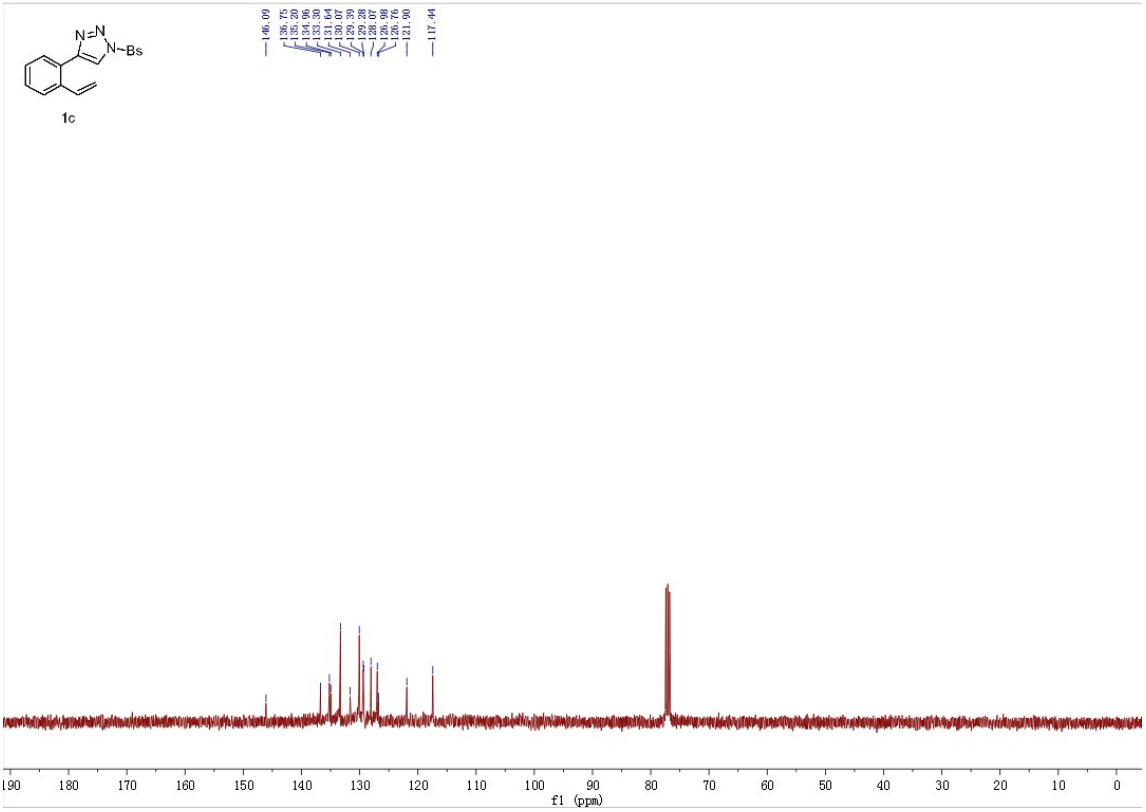
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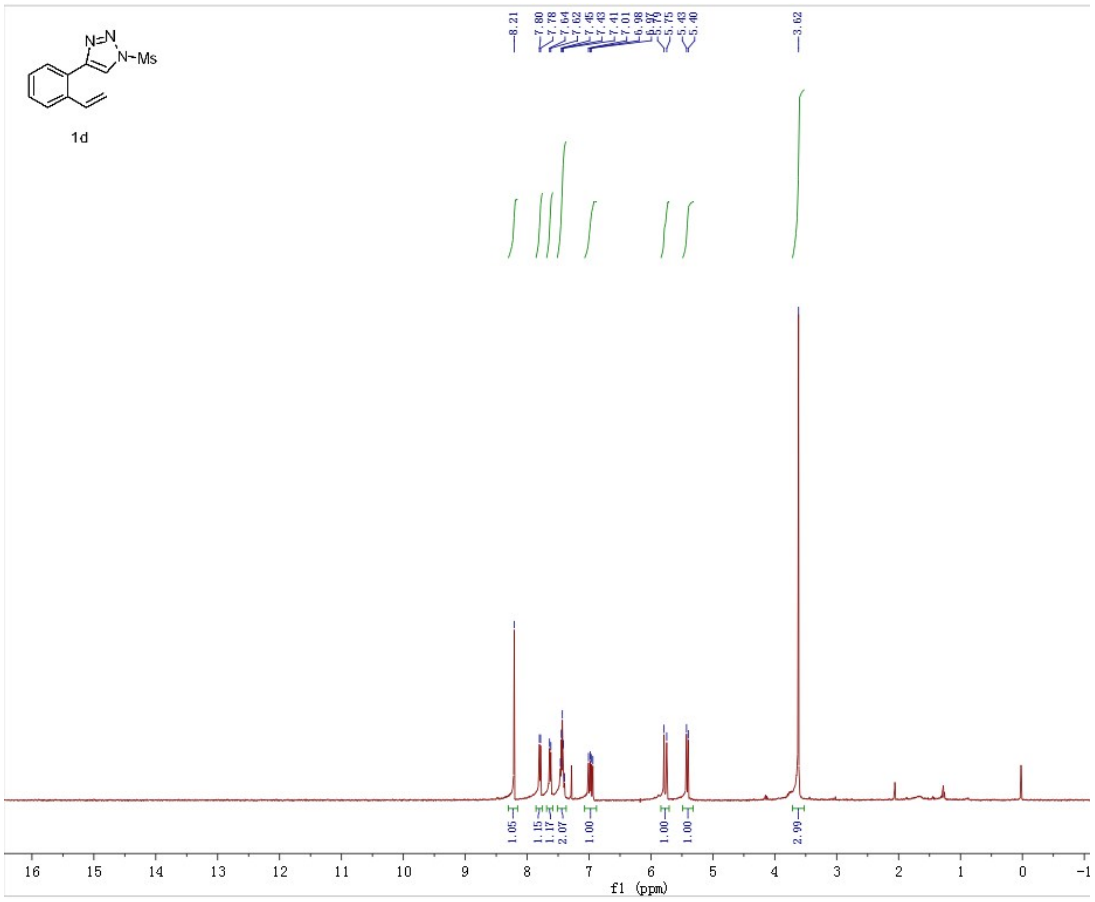
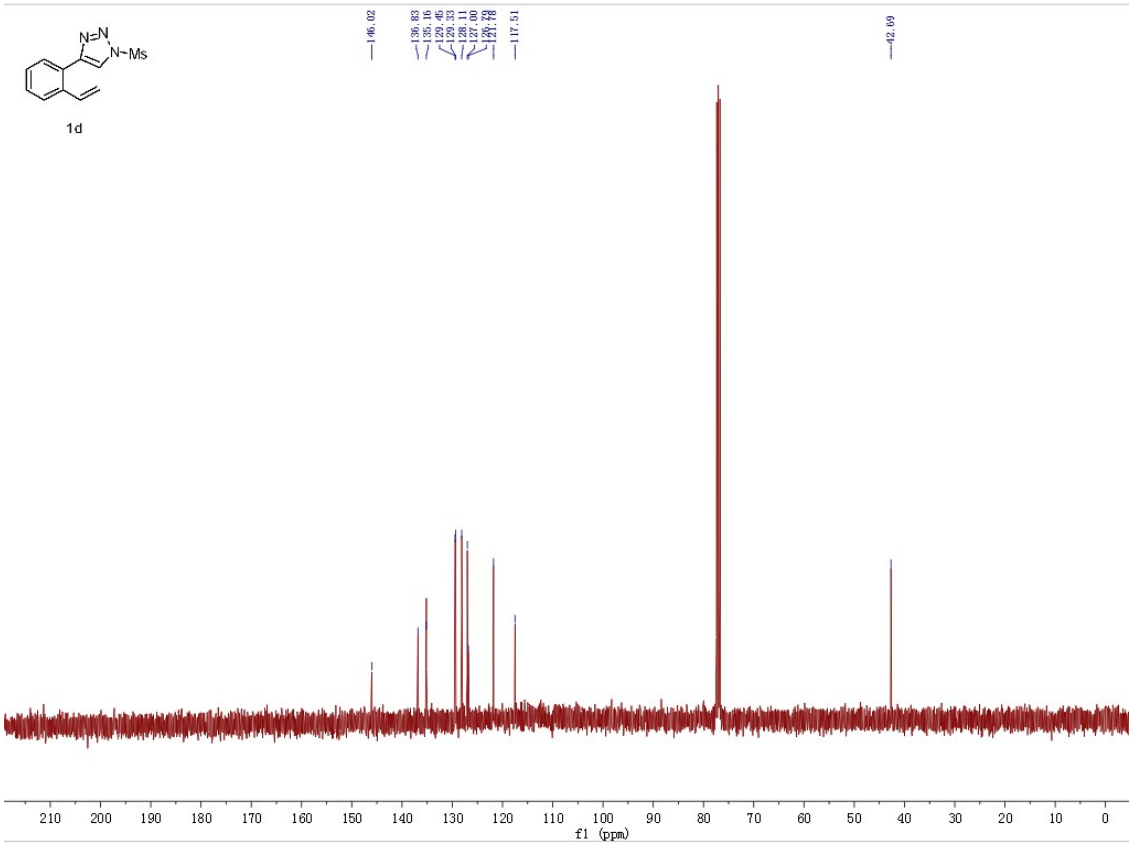

1d
8.21
7.80
7.78
7.64
7.62
7.45
7.43
7.41
7.01
6.98
5.75
5.43
5.40
3.62
1.05
1.15
1.17
2.07
1.00
1.00
1.00
2.99
f1 (ppm)


1d
146.02
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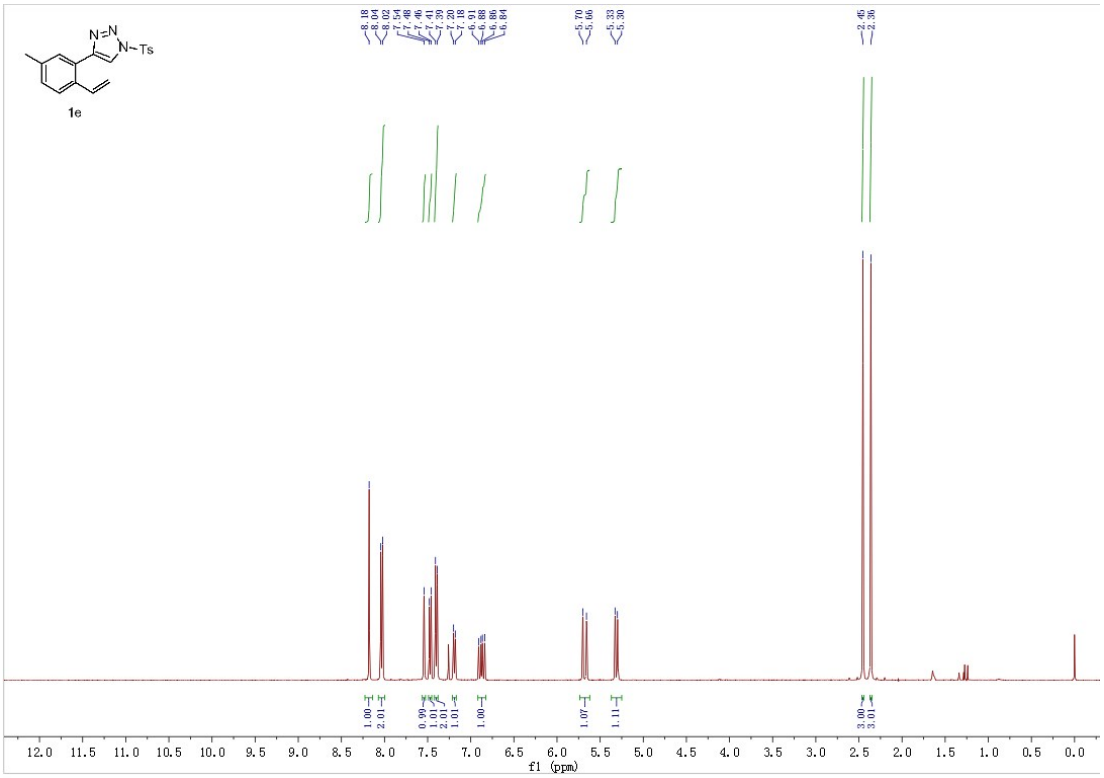
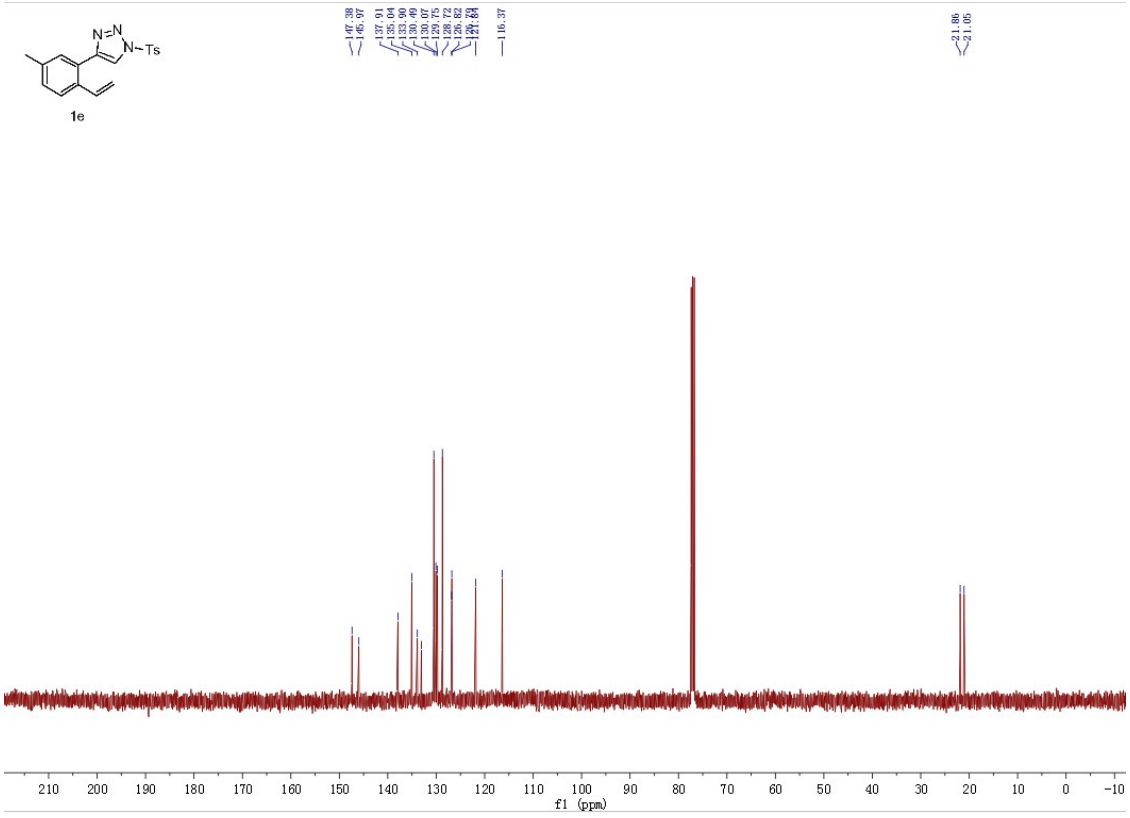
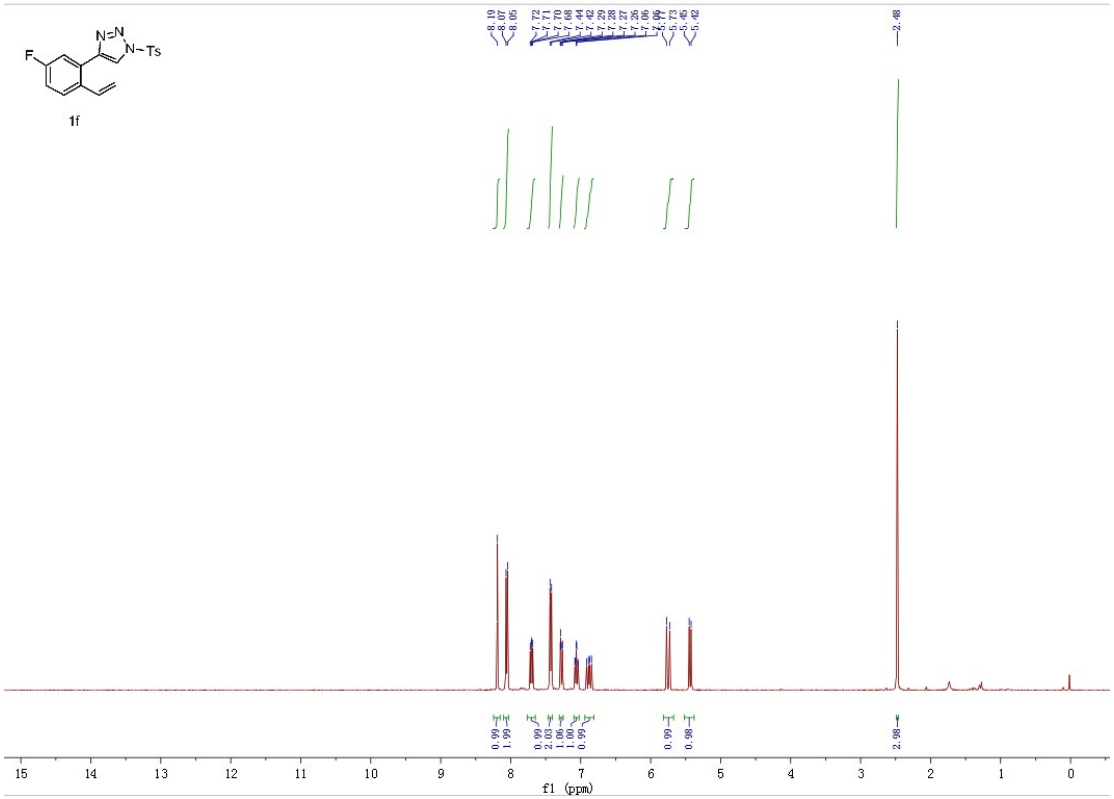
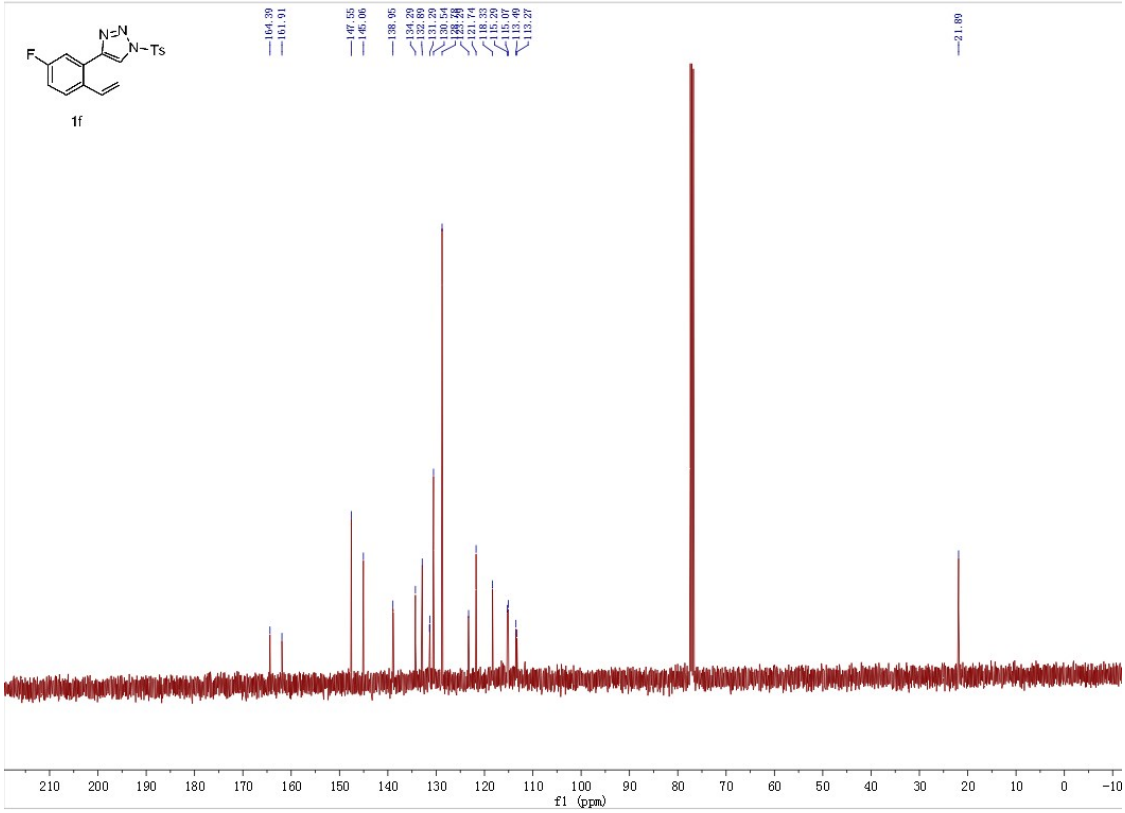
135.16
129.45
129.33
128.11
127.00
121.78
117.51
42.69
f1 (ppm)


1e
8.18
8.04
8.02
7.54
7.48
7.46
7.41
7.39
7.23
7.18
6.91
6.88
6.86
6.84
5.70
5.66
5.33
5.30
2.45
2.36
1.00
2.01
0.99
2.01
2.01
1.01
1.00
1.07
1.11
3.00
3.01
f1 (ppm)


1e
147.38
145.97
137.91
135.04
133.90
130.49
130.07
129.75
128.72
126.82
116.37
21.86
21.05
f1 (ppm)


1f
8.19
8.07
8.05
7.72
7.71
7.70
7.68
7.44
7.42
7.29
7.28
7.27
7.26
7.06
5.47
5.43
5.42
2.48
0.99
1.99
0.99
2.02
1.06
1.00
0.99
0.99
0.98
2.98
f1 (ppm)


1f
164.39
161.91
147.55
145.06
138.95
134.29
132.89
131.29
130.54
121.74
118.33
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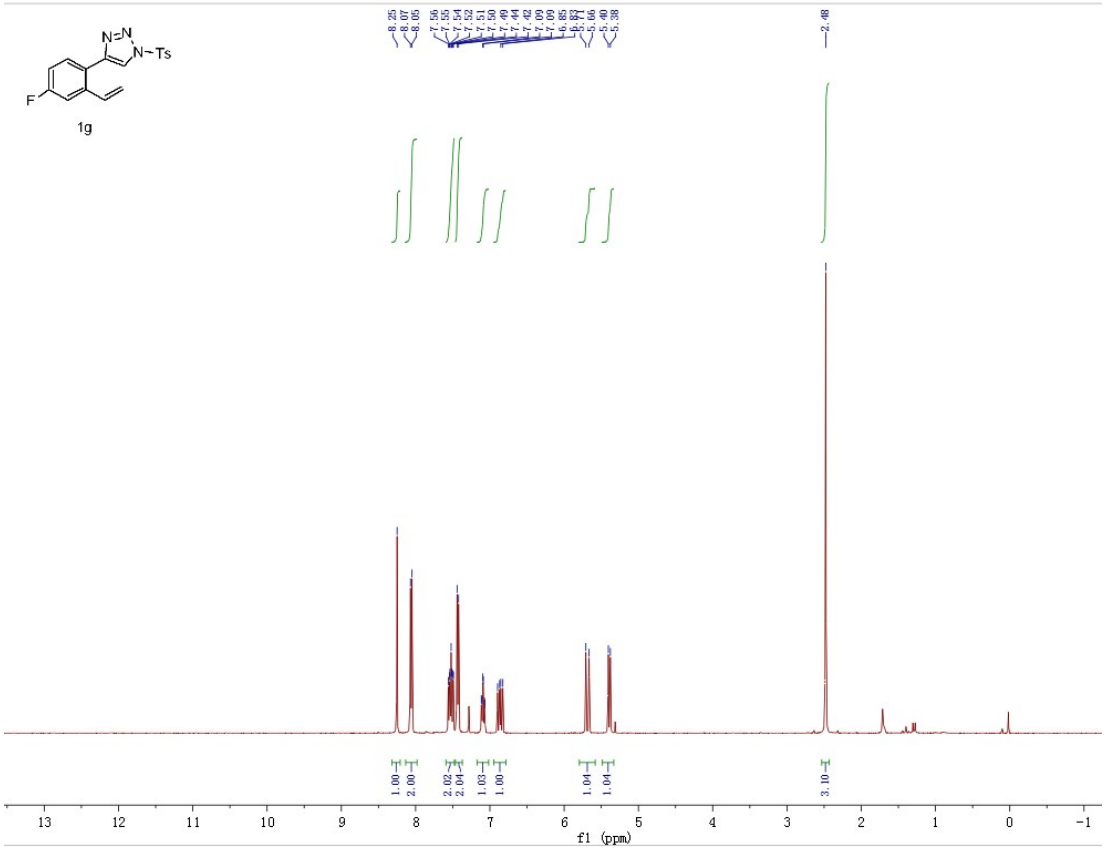
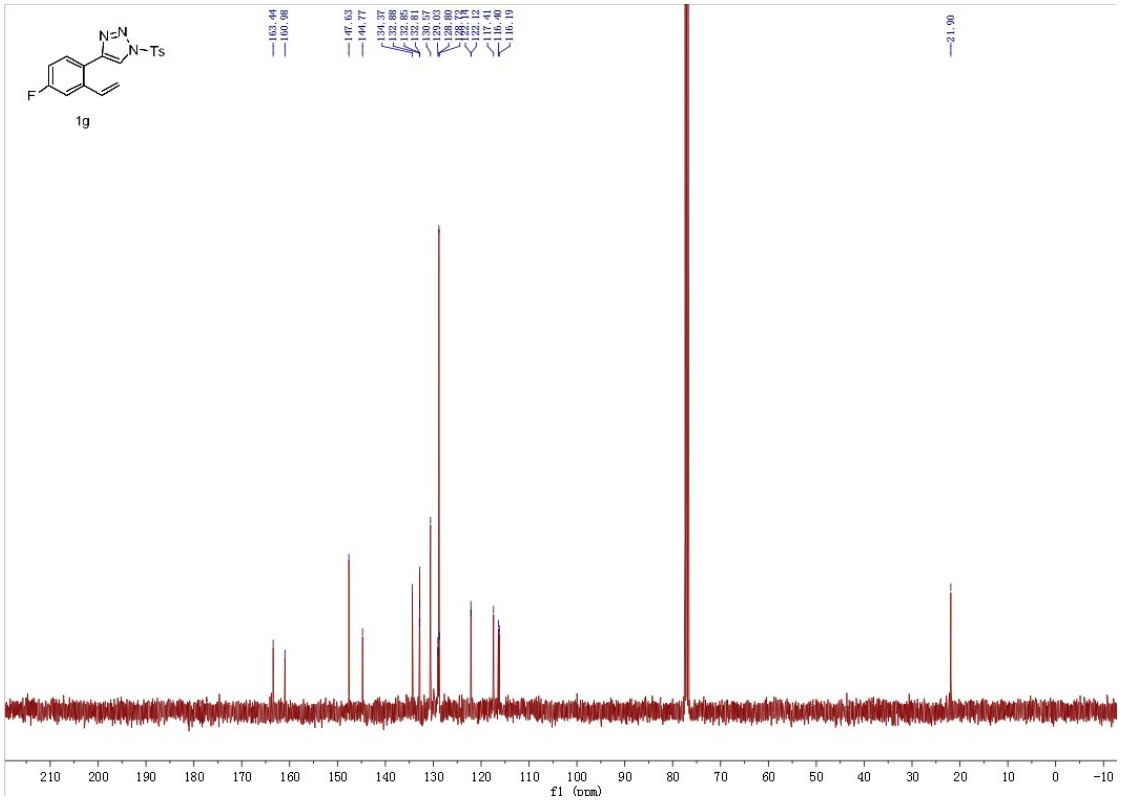
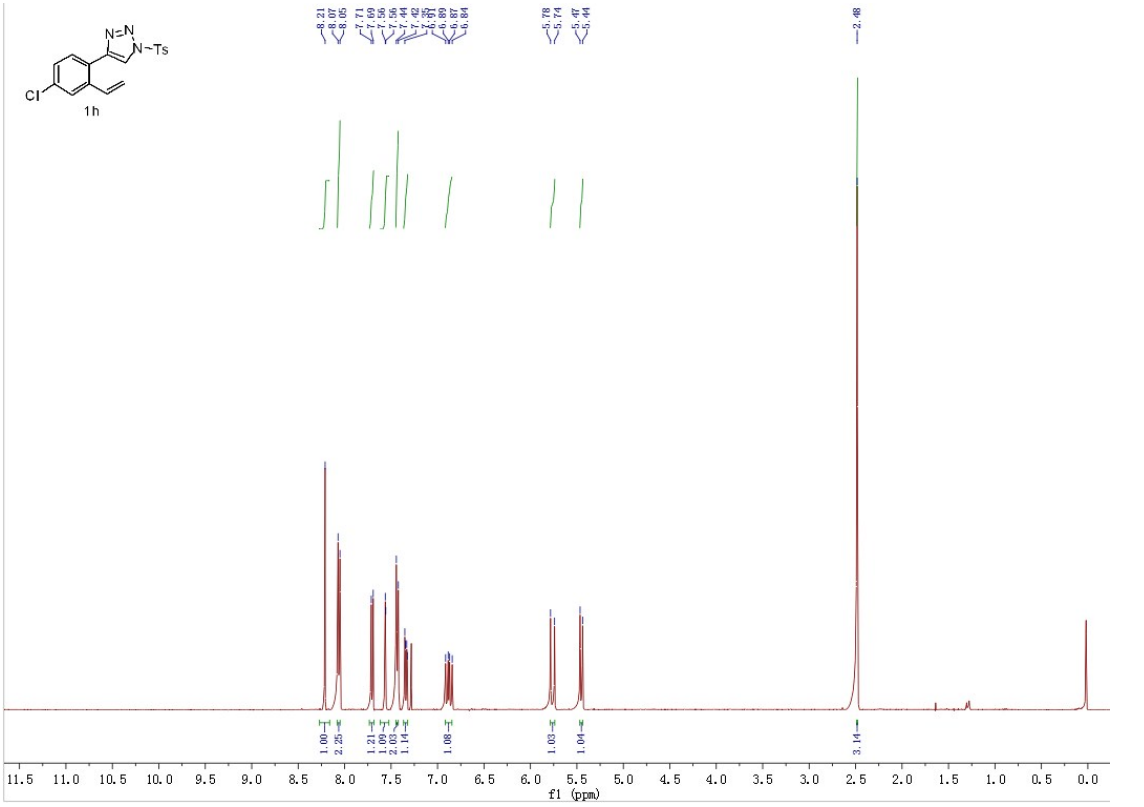
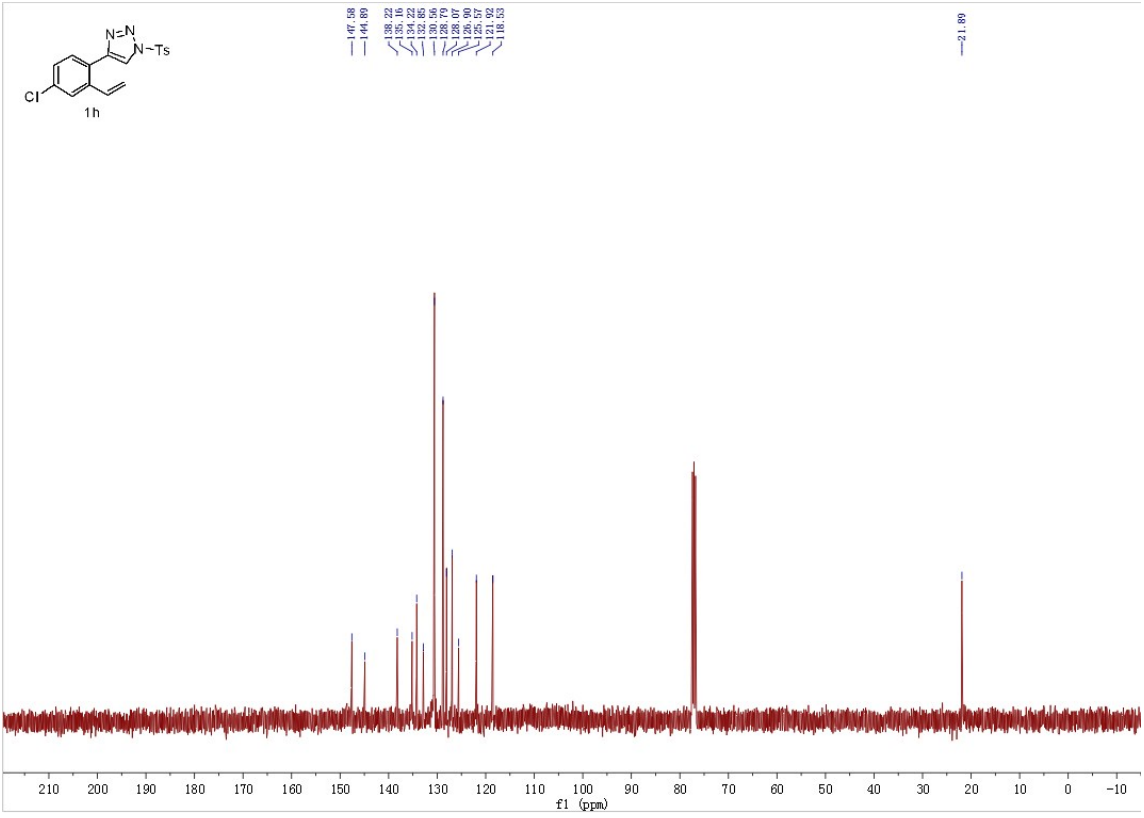
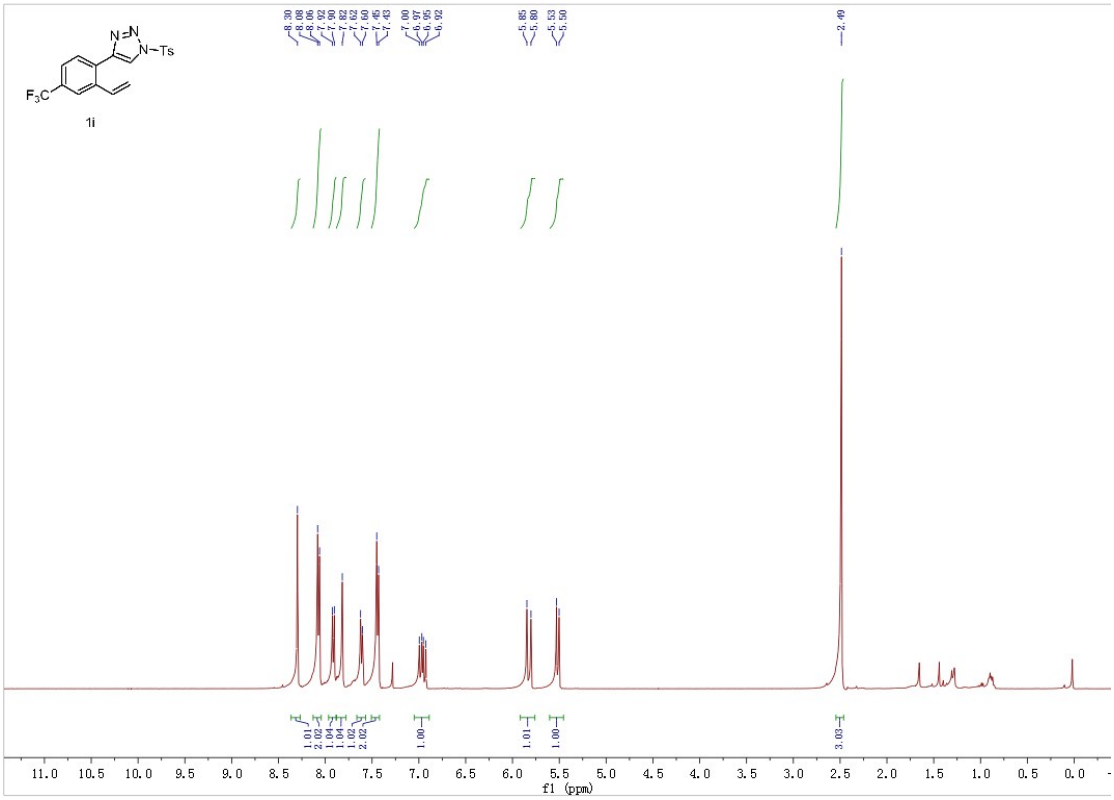
115.07
113.49
113.27
21.89
f1 (ppm)

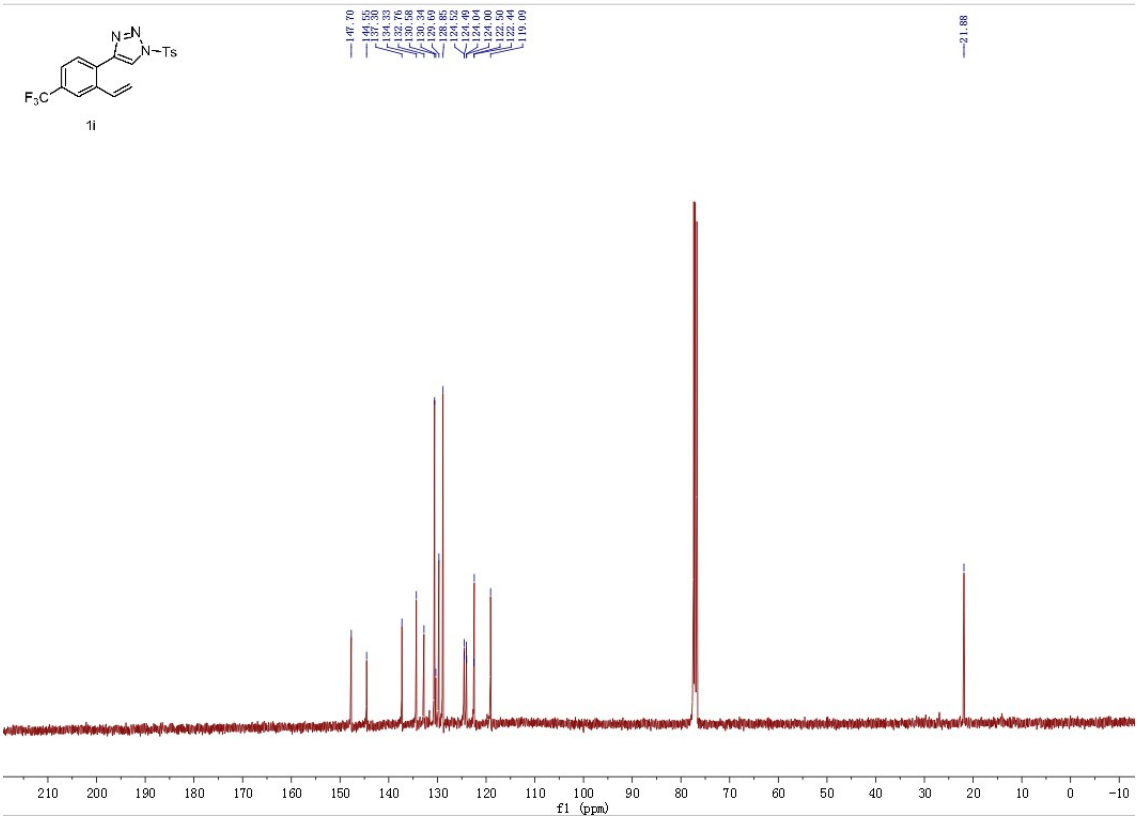

1g
f1 (ppm)

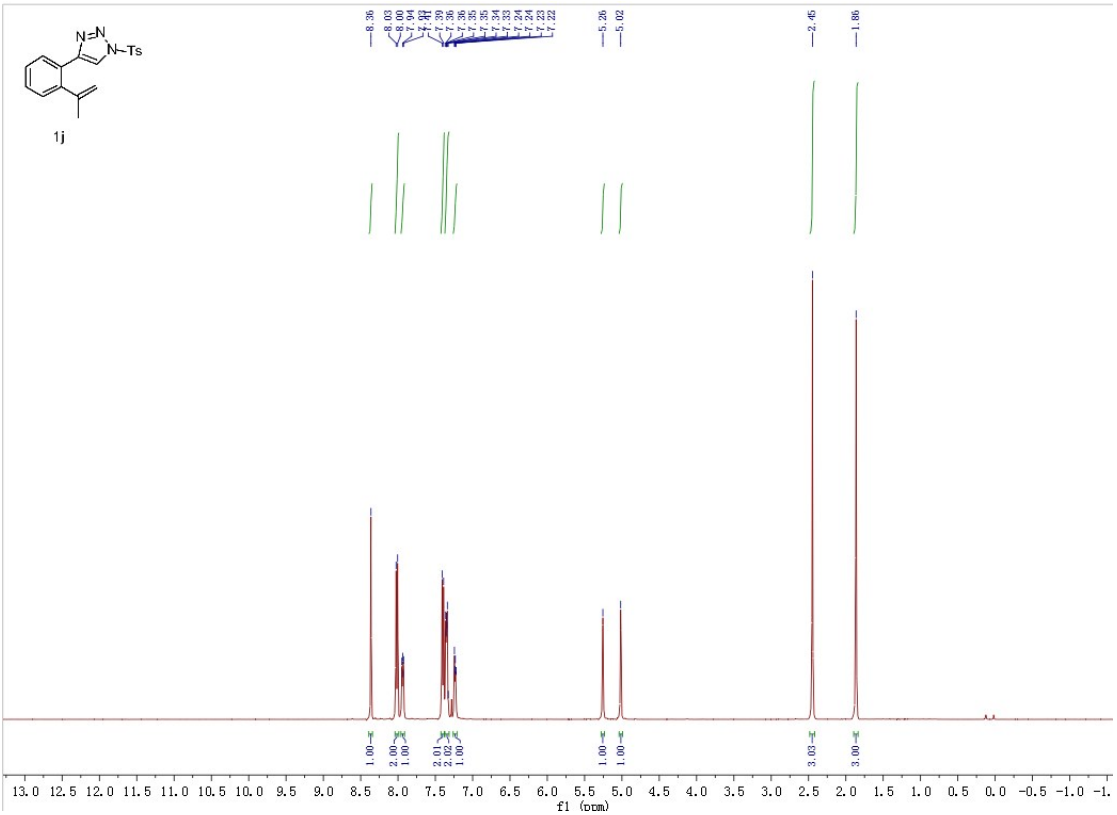

1g
f1 (ppm)

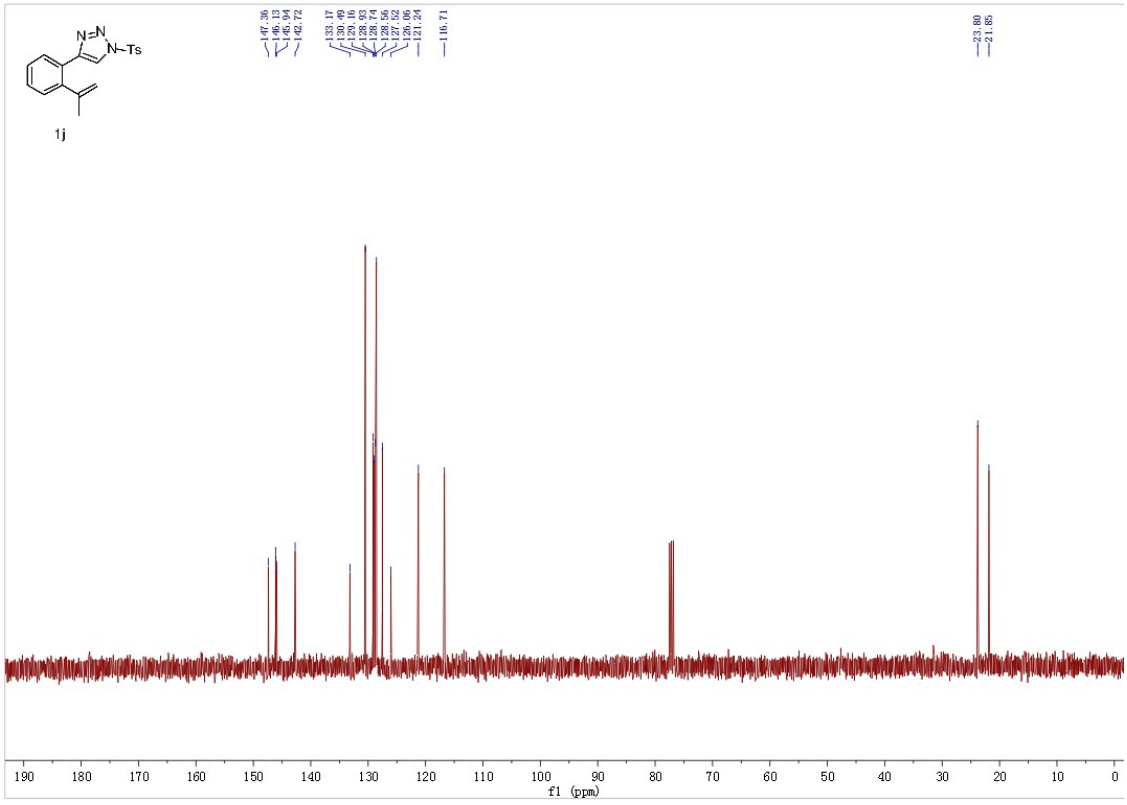

1h
8.21
8.07
8.05
7.71
7.69
7.56
7.54
7.44
7.42
6.89
6.87
6.84
5.78
5.74
5.47
5.44
2.48
1.00
2.25
1.21
1.09
2.03
1.14
1.08
1.03
1.04
3.14
f1 (ppm)

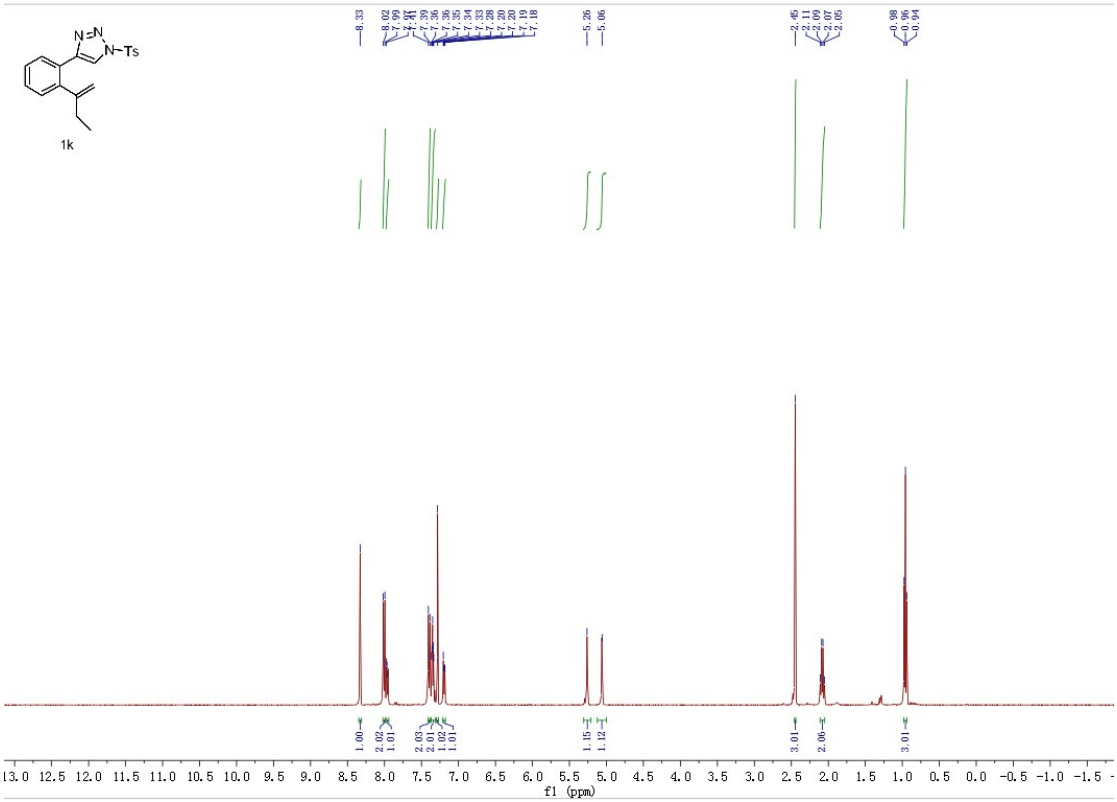

1h
147.58
144.89
138.22
135.16
134.22
132.65
130.56
128.79
128.07
126.90
125.57
121.32
118.53
21.89
f1 (ppm)

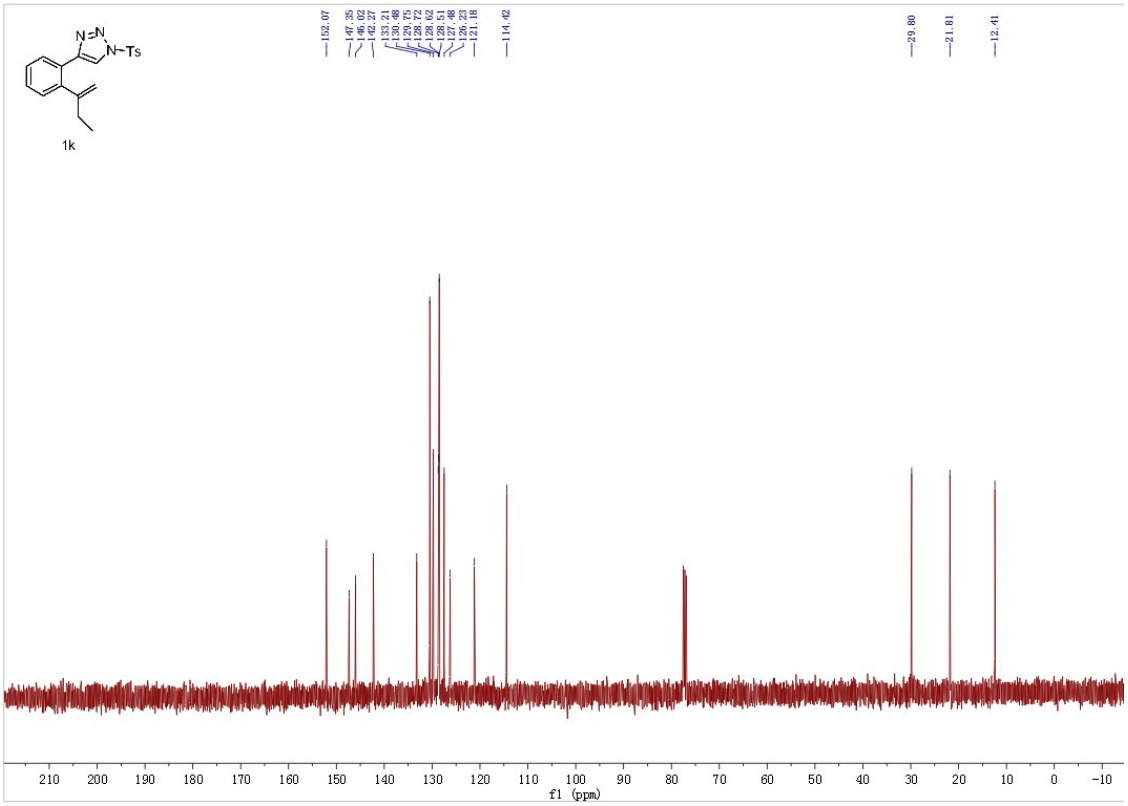

1i
8.30
8.08
8.06
7.93
7.90
7.82
7.62
7.60
7.45
7.43
7.00
6.97
6.95
6.92
5.85
5.80
5.53
5.50
2.49
1.01
2.02
1.04
1.04
1.02
2.02
1.00
1.01
1.00
3.03
f1 (ppm)

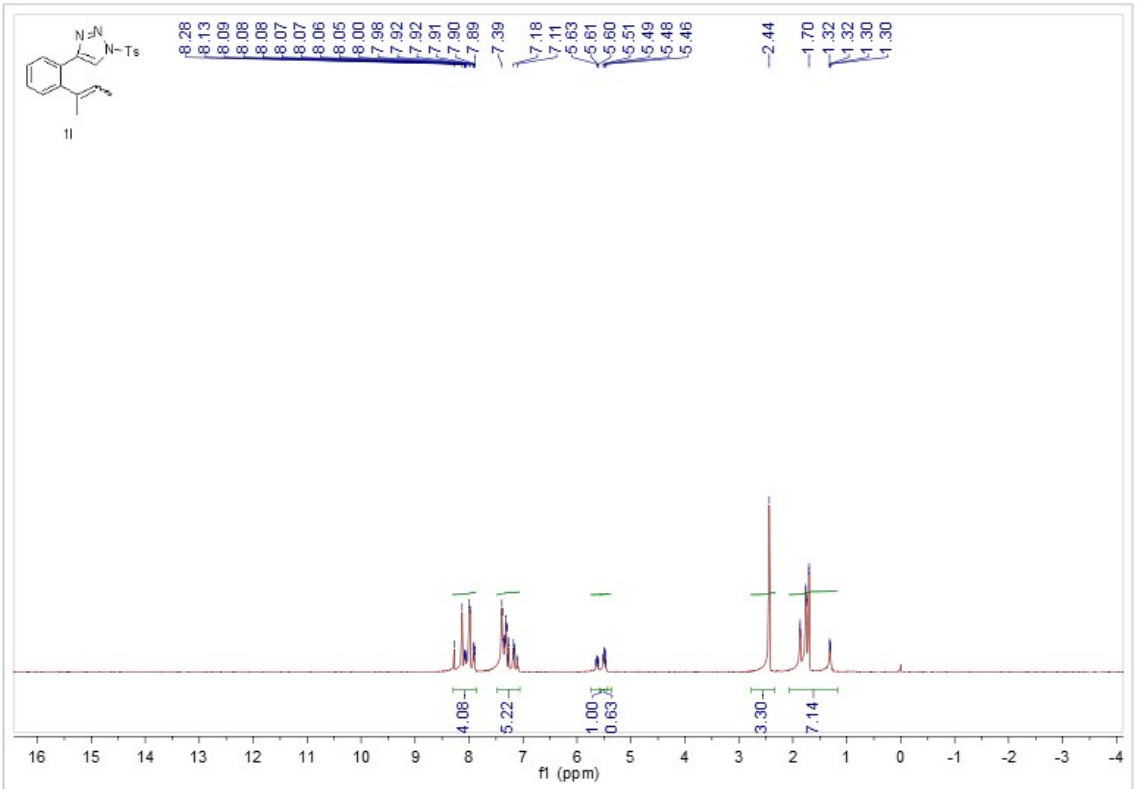

1i
147.70
144.55
137.38
134.33
132.76
130.98
130.74
129.69
128.85
124.52
124.49
124.44
124.00
122.50
122.44
119.09
21.88
f1 (ppm)

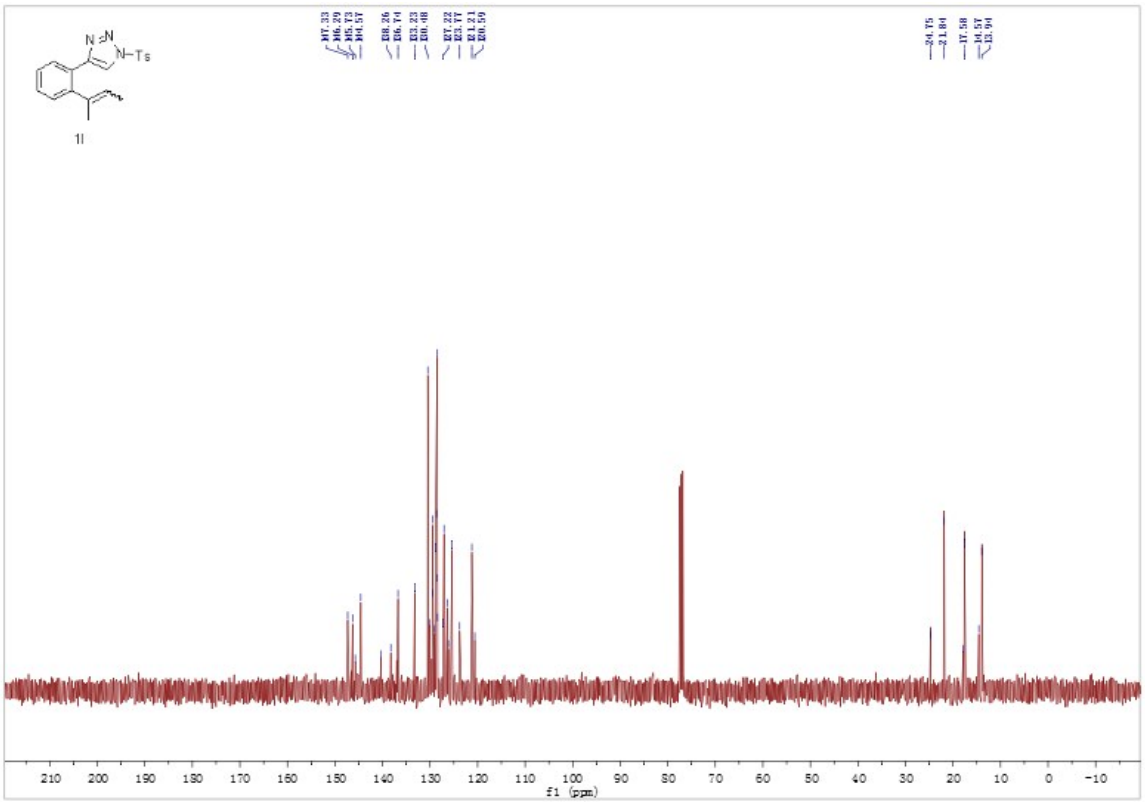

1j
8.36
8.03
8.00
7.94
7.41
7.39
7.36
7.35
7.34
7.33
7.24
7.23
7.22
5.26
5.02
2.45
1.86
1.00
2.00
1.00
2.01
2.02
1.00
1.00
1.00
3.03
3.00
f1 (ppm)

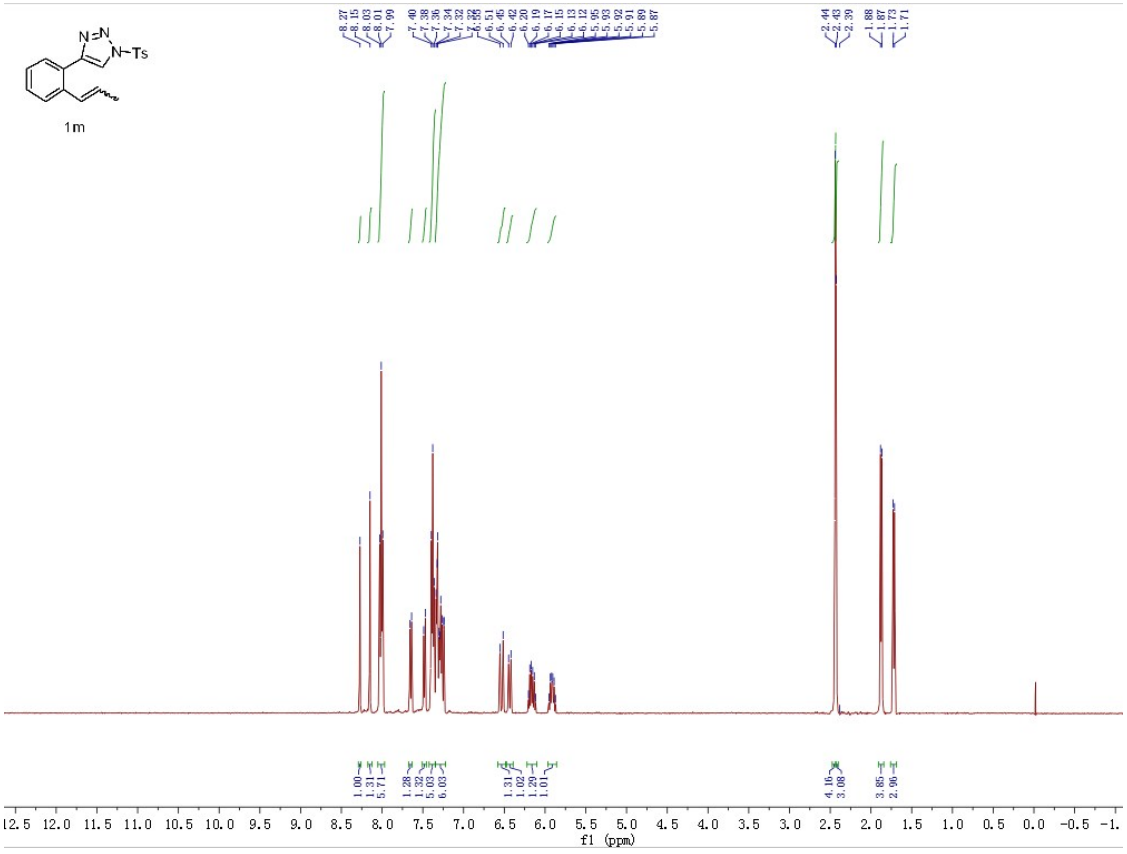

1j
147.36
146.13
145.94
142.72
133.17
130.49
129.16
128.97
128.74
128.56
127.52
126.06
121.24
116.71
23.80
21.85
f1 (ppm)

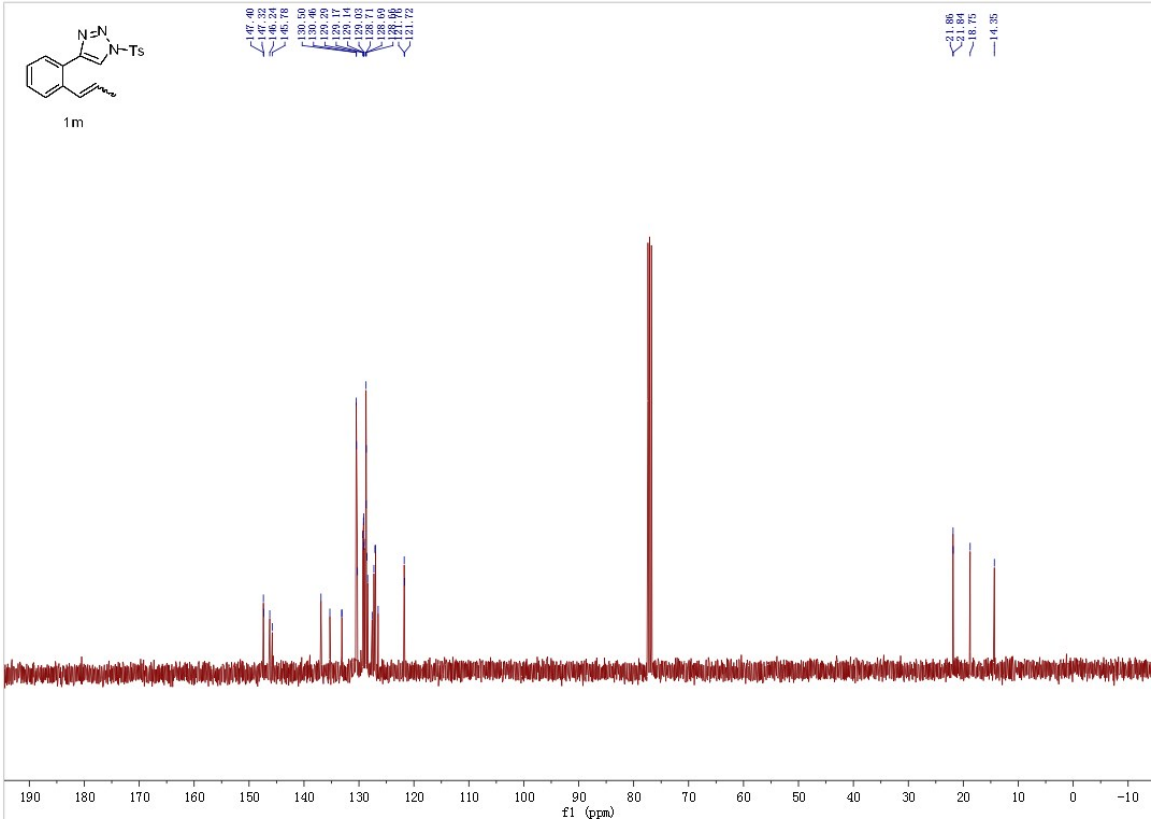

1k
8.33
8.02
7.99
7.41
7.39
7.38
7.36
7.35
7.34
7.33
7.20
7.19
7.18
5.26
5.06
2.45
2.11
2.09
2.07
2.05
0.98
0.96
0.94
1.00
2.02
1.01
2.03
2.01
1.02
1.01
1.15
1.12
3.01
2.06
3.01
f1 (ppm)

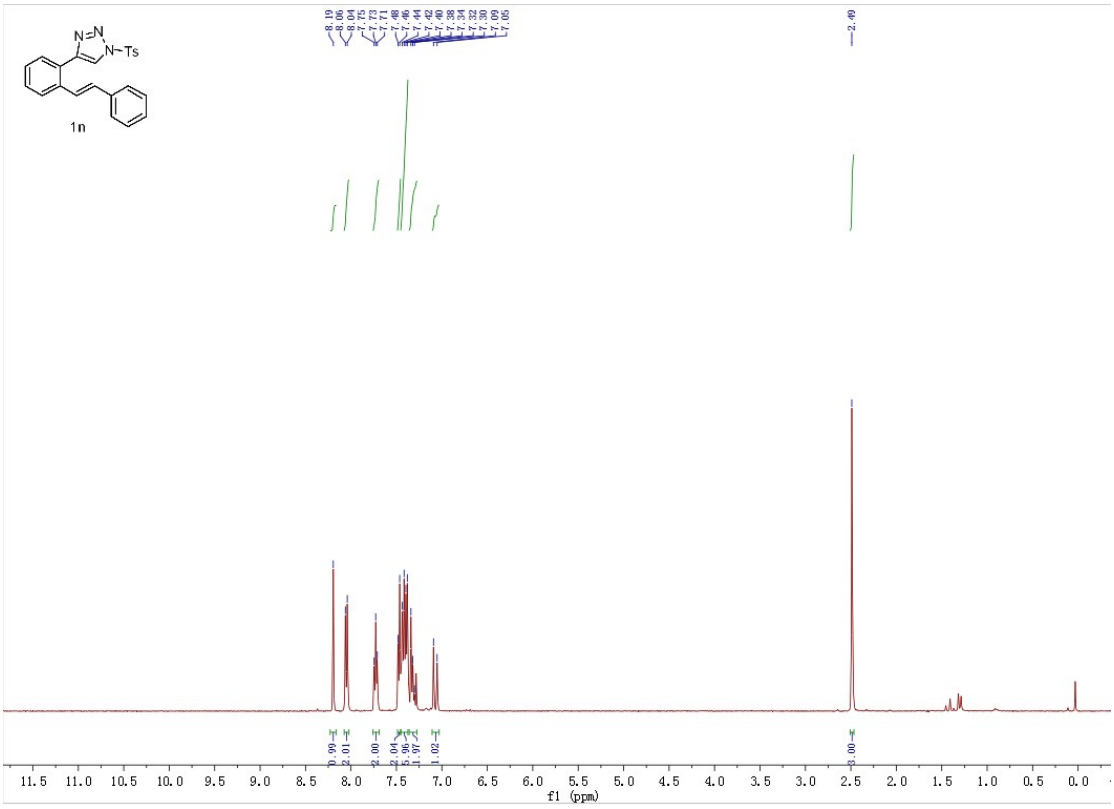

1k
152.07
147.35
146.02
142.27
133.21
130.48
129.75
129.72
128.62
128.51
127.48
120.23
121.18
114.42
29.80
21.81
12.41
f1 (ppm)

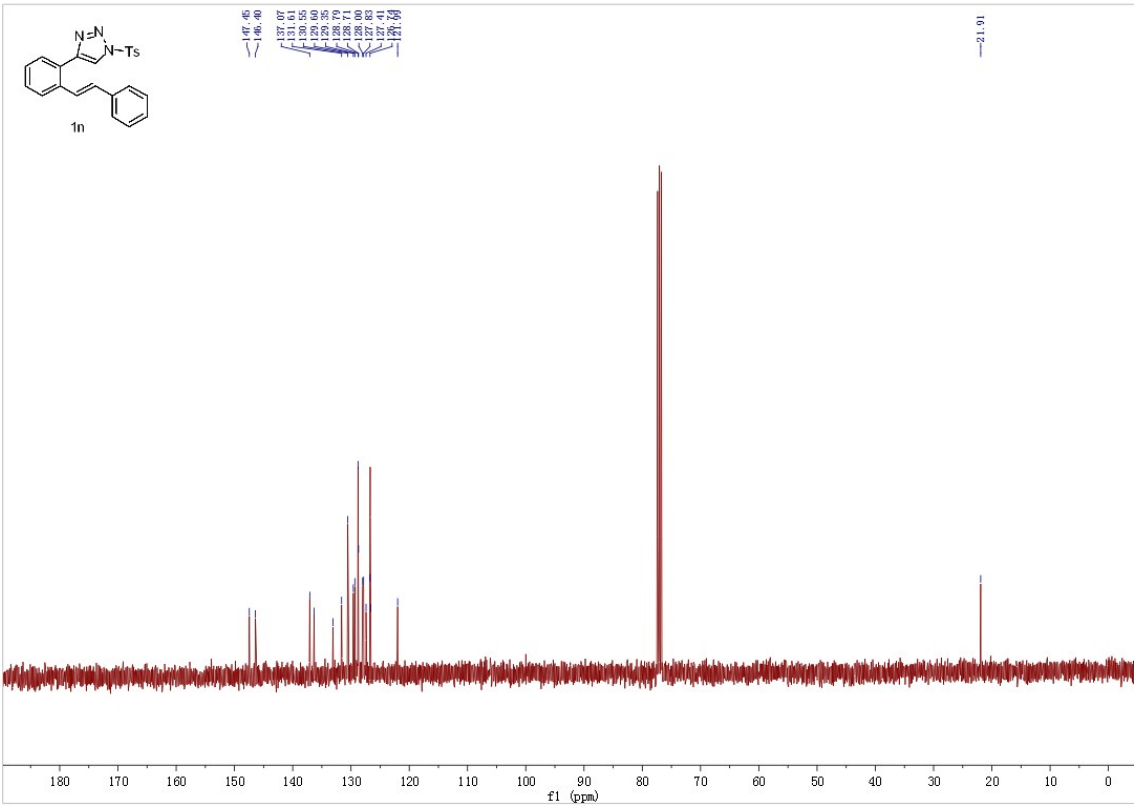

1l
8.28
8.13
8.09
8.08
8.08
8.07
8.07
8.06
8.05
8.00
7.98
7.92
7.92
7.91
7.90
7.89
7.39
7.18
7.11
5.63
5.61
5.60
5.51
5.49
5.48
5.46
2.44
1.70
1.32
1.30
1.30
4.08
5.22
1.00
0.63
3.30
7.14
f1 (ppm)

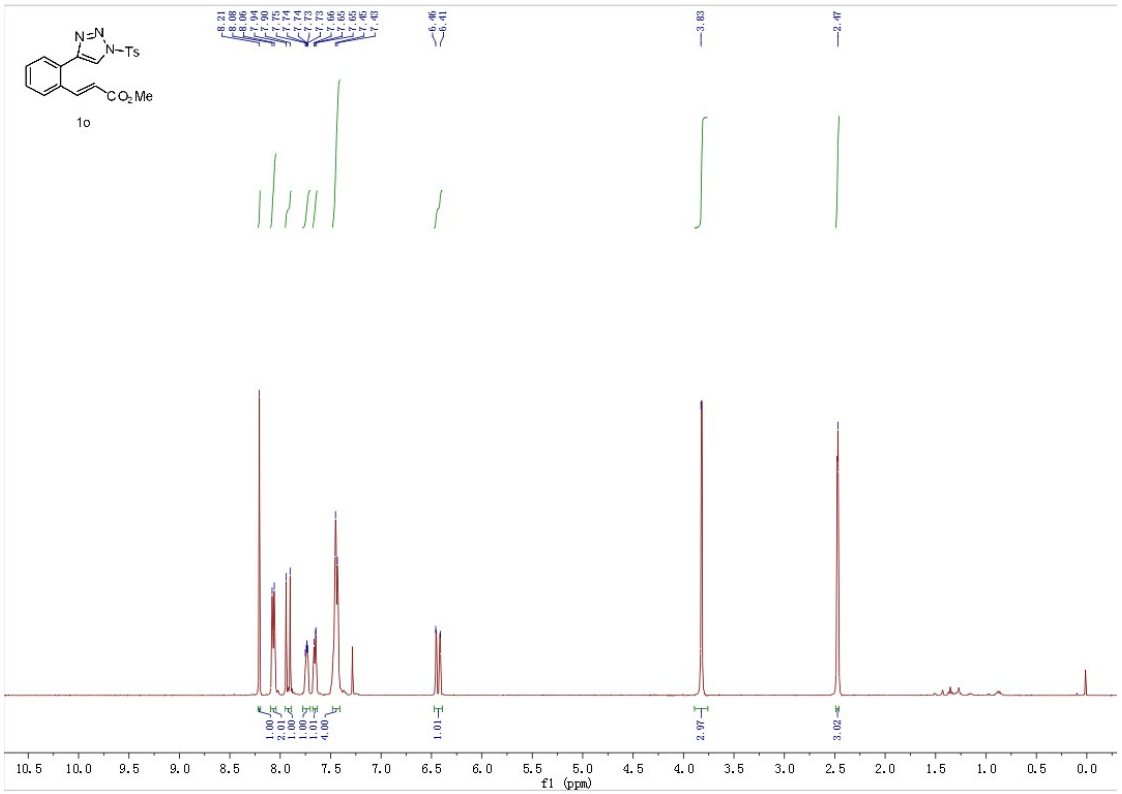

1l
f1 (ppm)

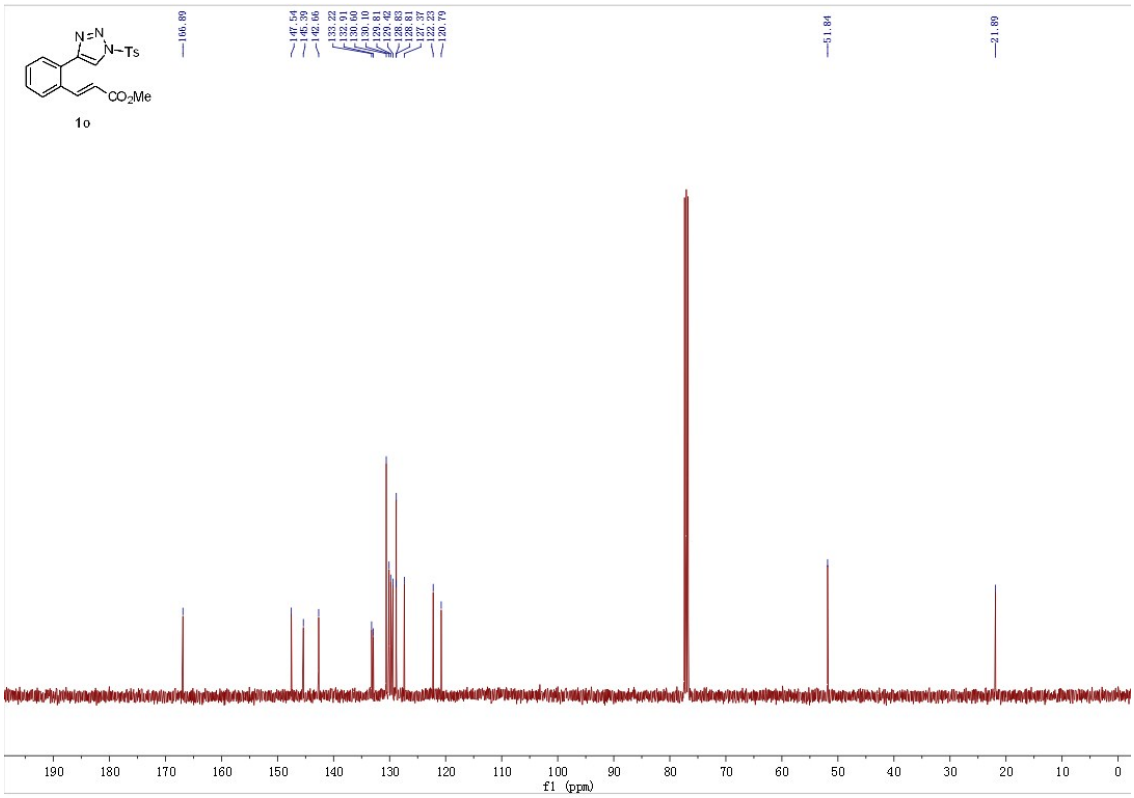

1m
f1 (ppm)

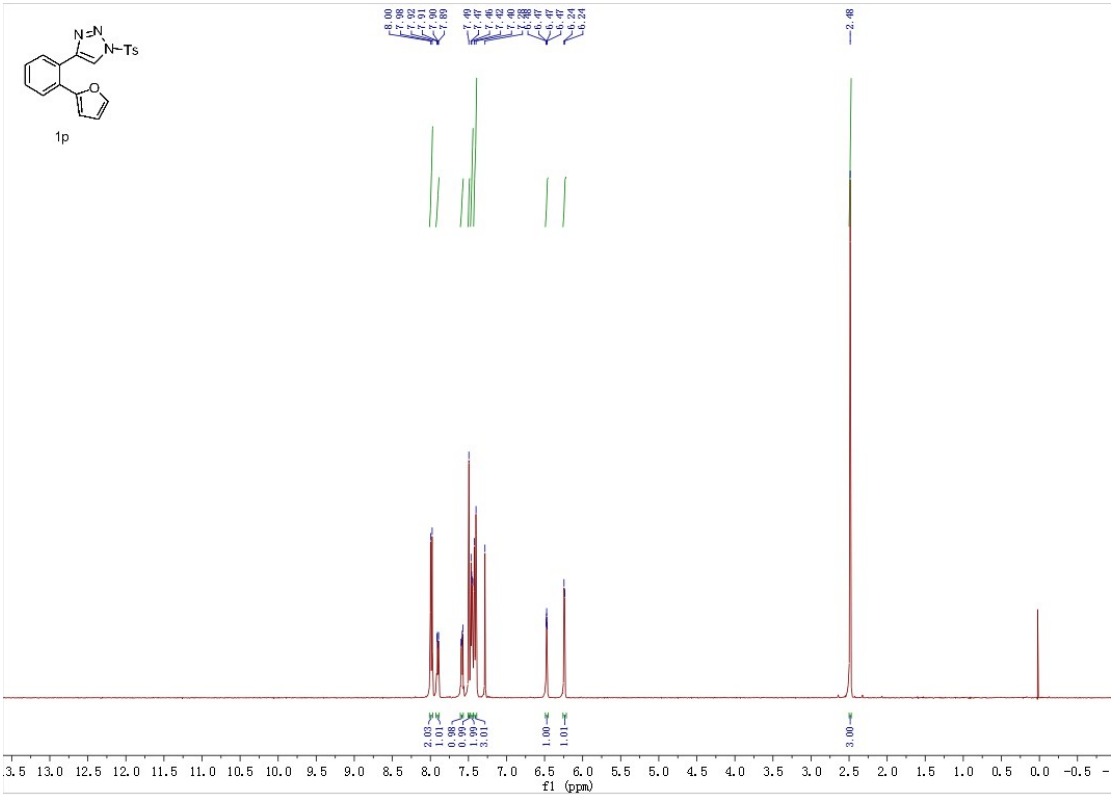

1m
f1 (ppm)

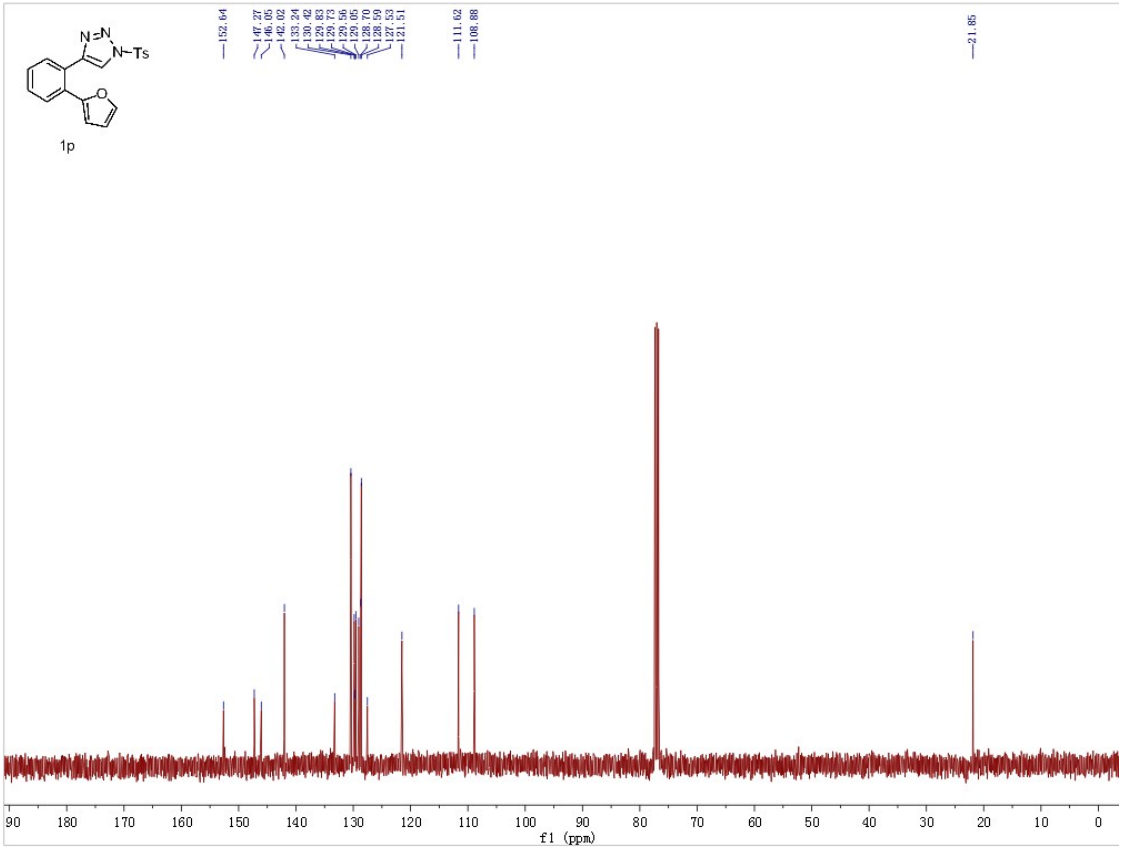

1n
8.19
8.06
8.04
7.75
7.73
7.71
7.48
7.46
7.44
7.42
7.40
7.38
7.34
7.32
7.30
7.09
7.05
2.49
0.99
2.01
2.00
2.04
1.97
1.02
3.00
f1 (ppm)

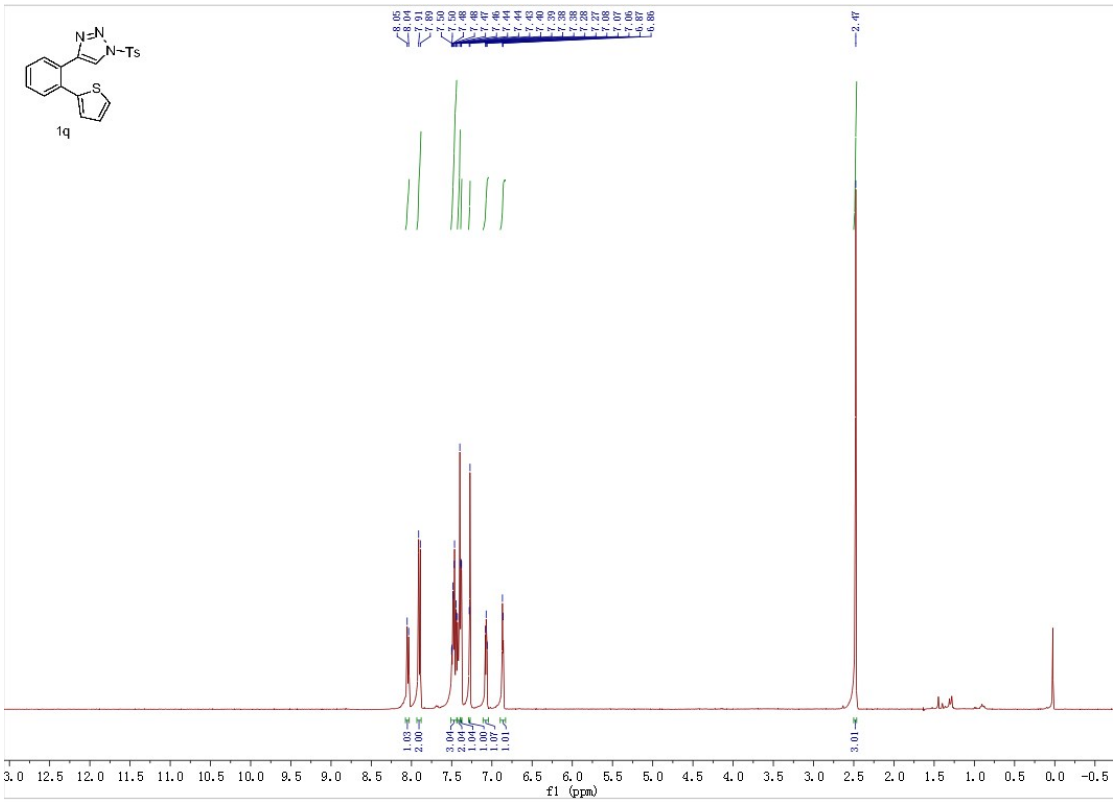

1n
147.45
146.40
137.07
134.61
131.61
130.55
129.60
129.35
128.79
128.71
128.00
127.83
127.41
121.99
21.91
f1 (ppm)

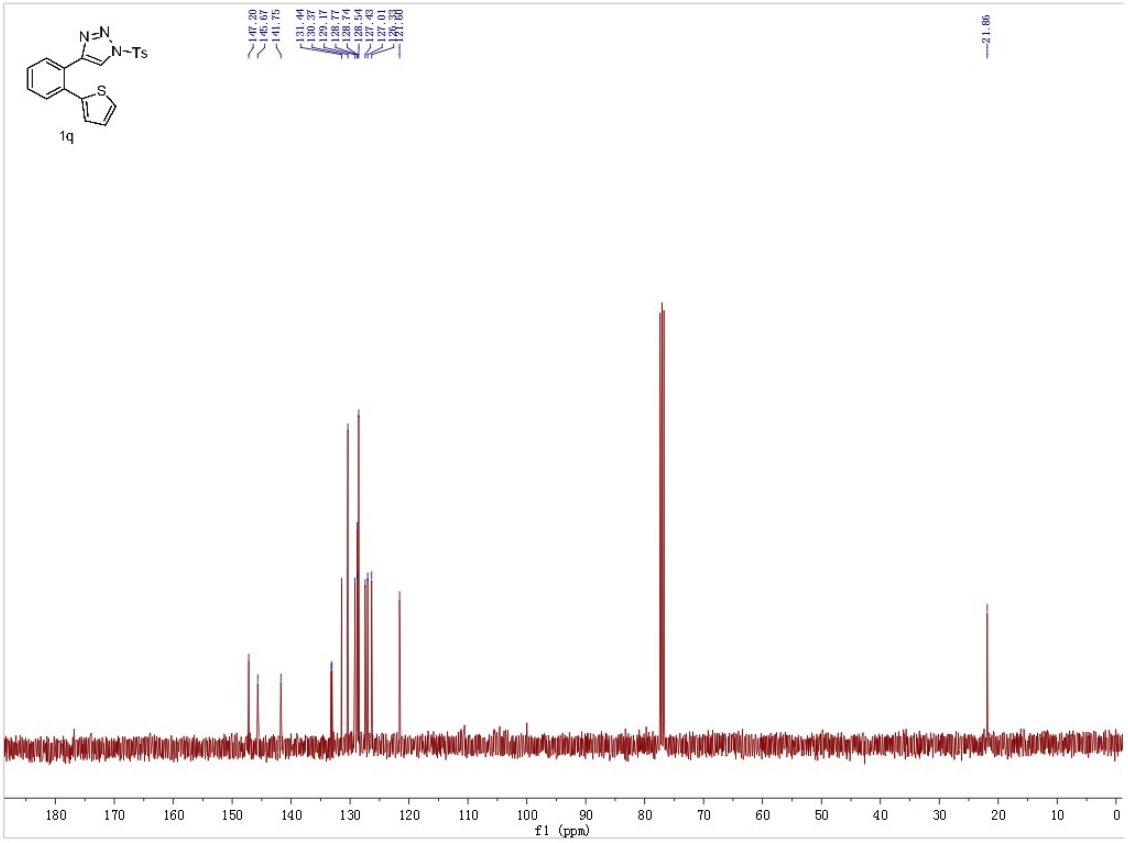

1o
8.21
8.08
8.06
7.94
7.90
7.75
7.74
7.74
7.73
7.73
7.66
7.65
7.47
7.46
7.43
6.46
6.41
3.83
2.47
1.00
2.01
1.00
1.00
1.01
4.08
1.01
2.97
3.02
f1 (ppm)

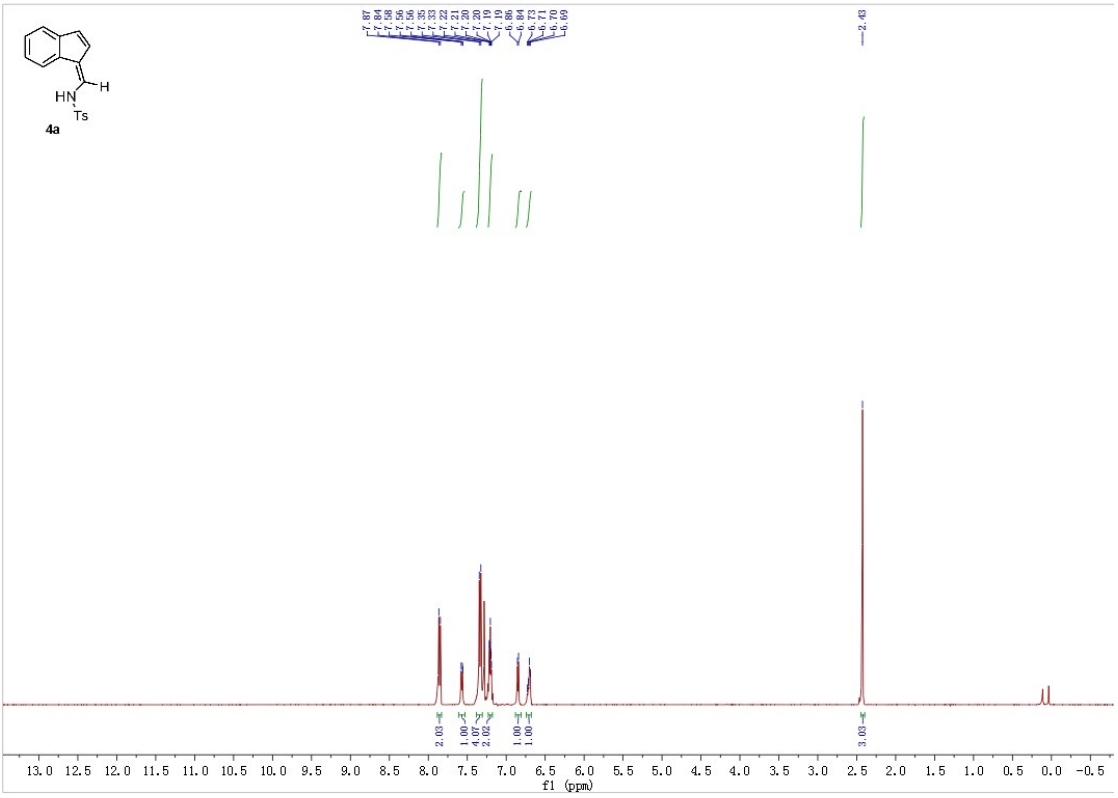

1o
166.89
147.54
145.39
142.66
133.22
132.91
130.60
130.10
129.81
129.42
128.83
128.81
127.37
122.23
120.79
51.84
21.89
f1 (ppm)

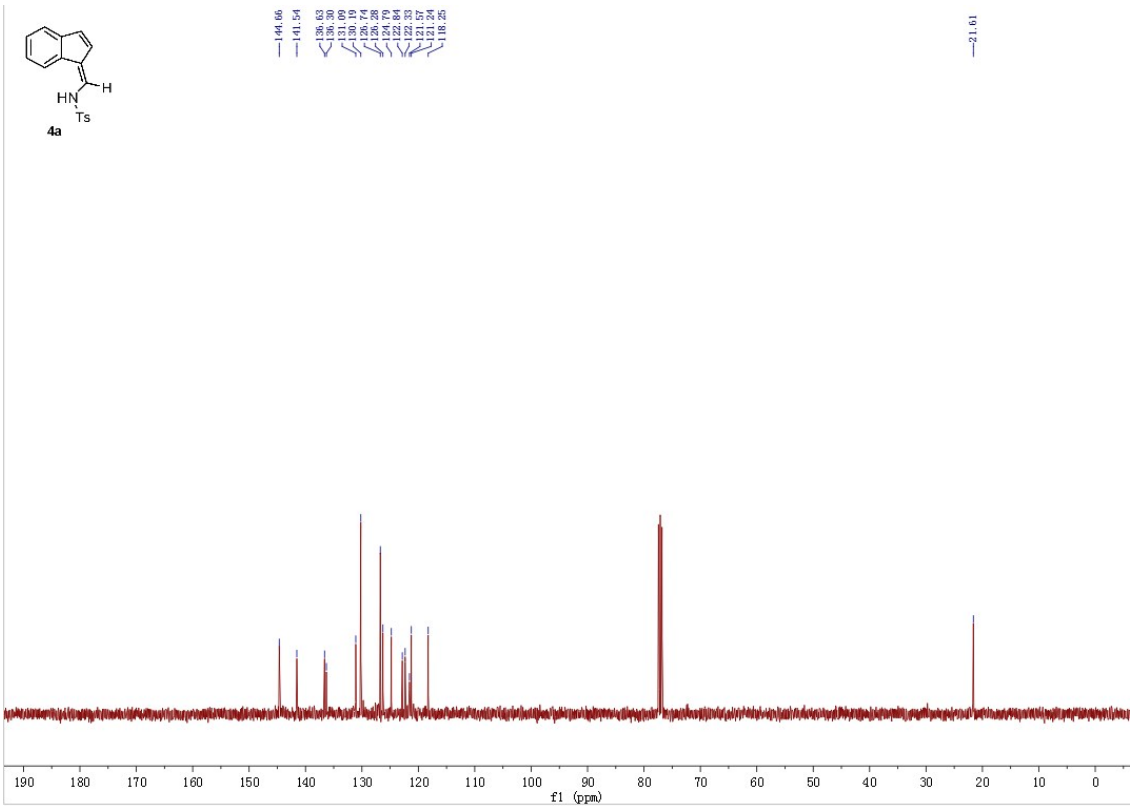

1p
8.00
7.98
7.92
7.91
7.90
7.89
7.49
7.47
7.46
7.42
7.40
6.47
6.47
6.24
6.24
2.48
2.03
1.01
0.98
0.96
1.99
3.01
1.00
1.01
3.00
f1 (ppm)

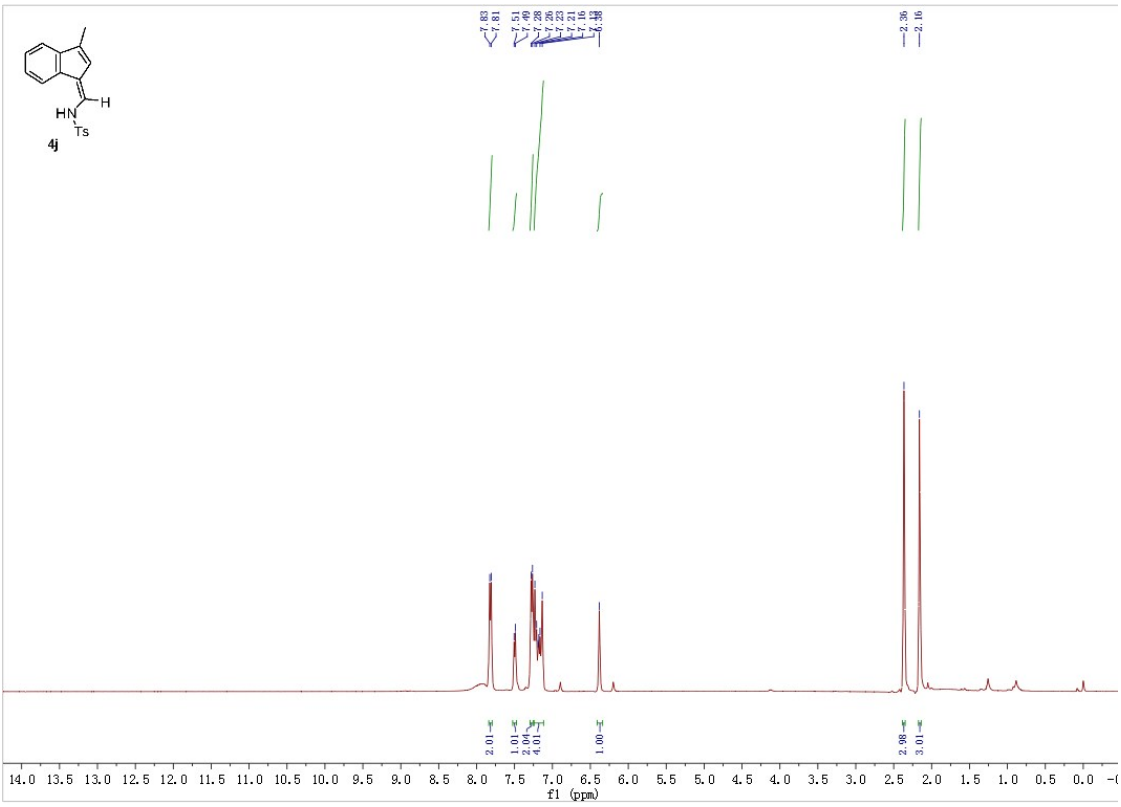

1p
152.64
147.27
146.05
142.02
133.24
130.62
129.83
129.73
129.56
129.05
128.70
128.59
127.53
121.51
111.62
108.88
21.85
f1 (ppm)

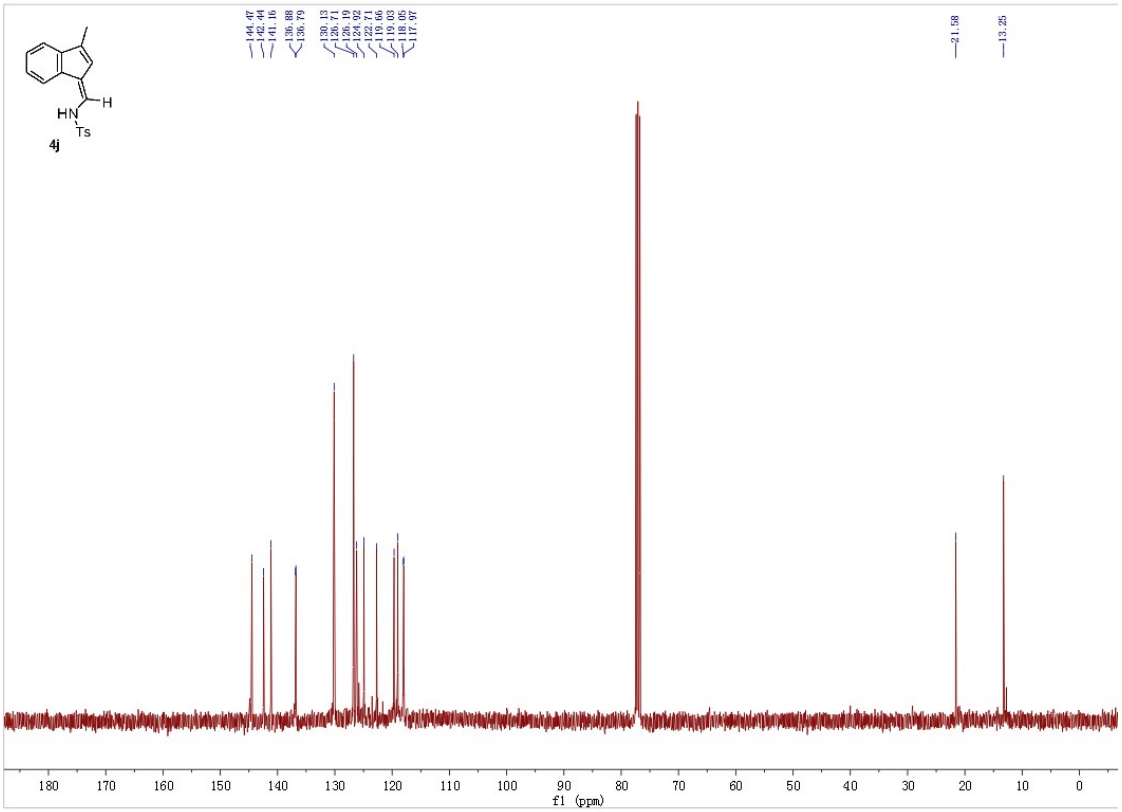

1q
f1 (ppm)


1q
f1 (ppm)


4a
7.87
7.84
7.58
7.56
7.35
7.33
7.22
7.21
7.20
7.20
7.19
7.19
6.86
6.84
6.73
6.71
6.70
6.69
2.43
2.03
1.00
4.07
2.02
1.00
1.00
3.03
f1 (ppm)


4a
144.66
141.54
136.63
136.30
131.09
130.19
129.74
126.28
124.79
122.84
122.33
121.57
121.24
118.25
21.61
f1 (ppm)


4j
7.83
7.81
7.51
7.49
7.28
7.26
7.23
7.21
7.16
2.36
2.16
2.01
1.01
2.04
4.01
1.00
2.98
3.01
f1 (ppm)


4j
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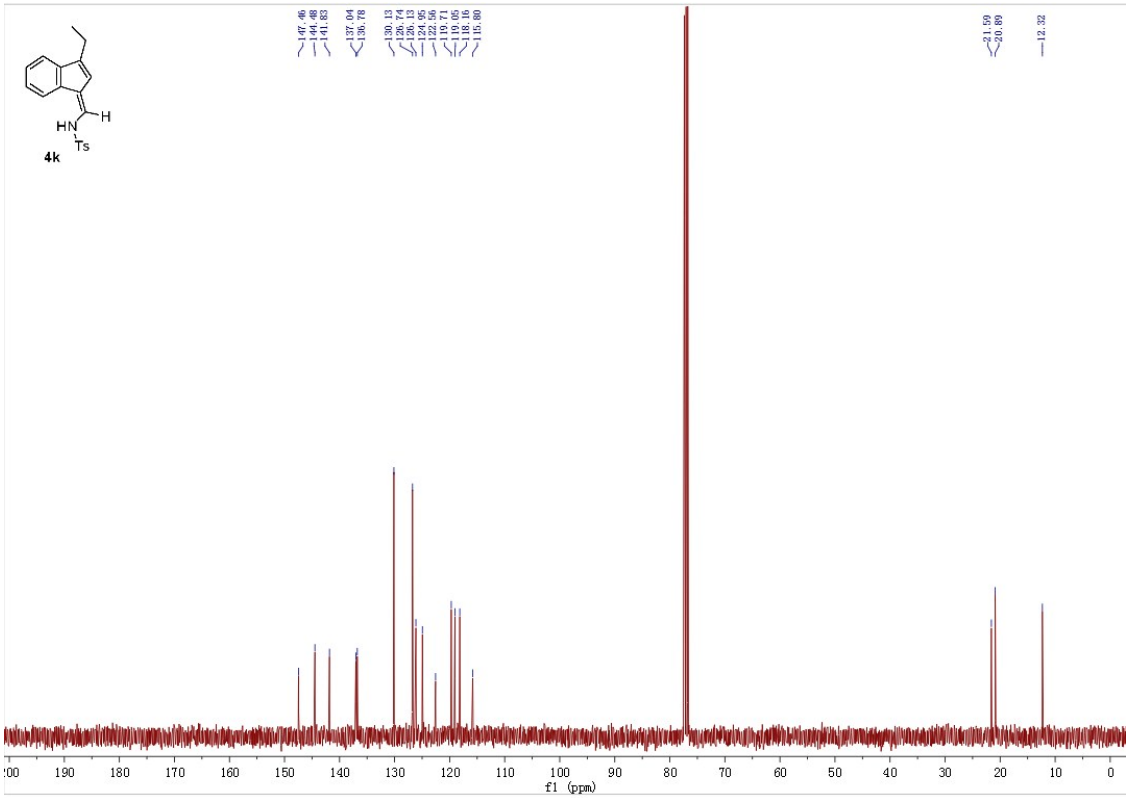
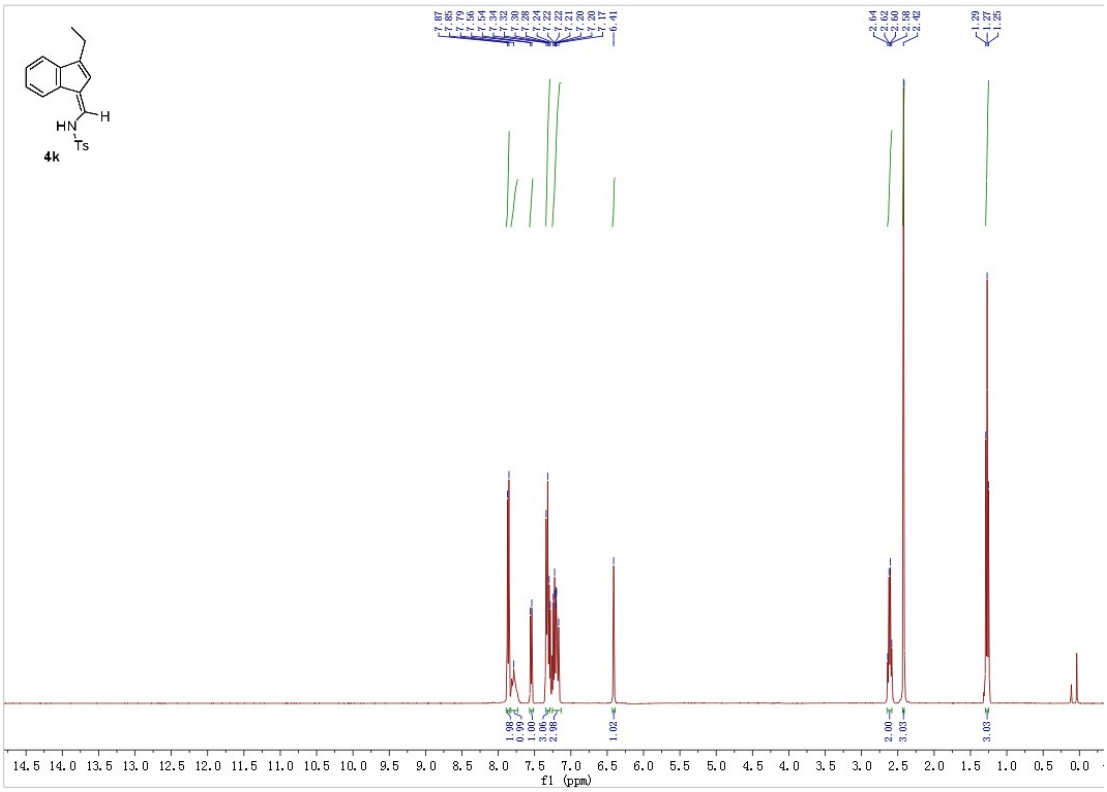
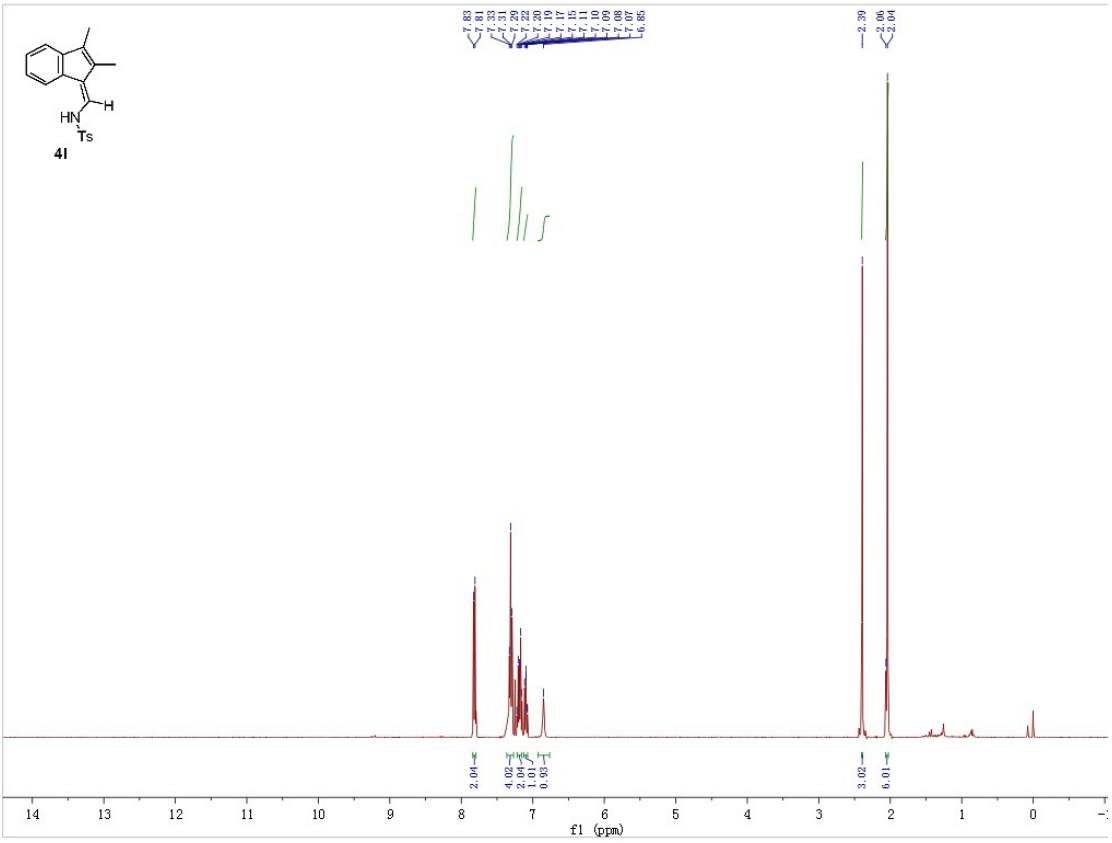
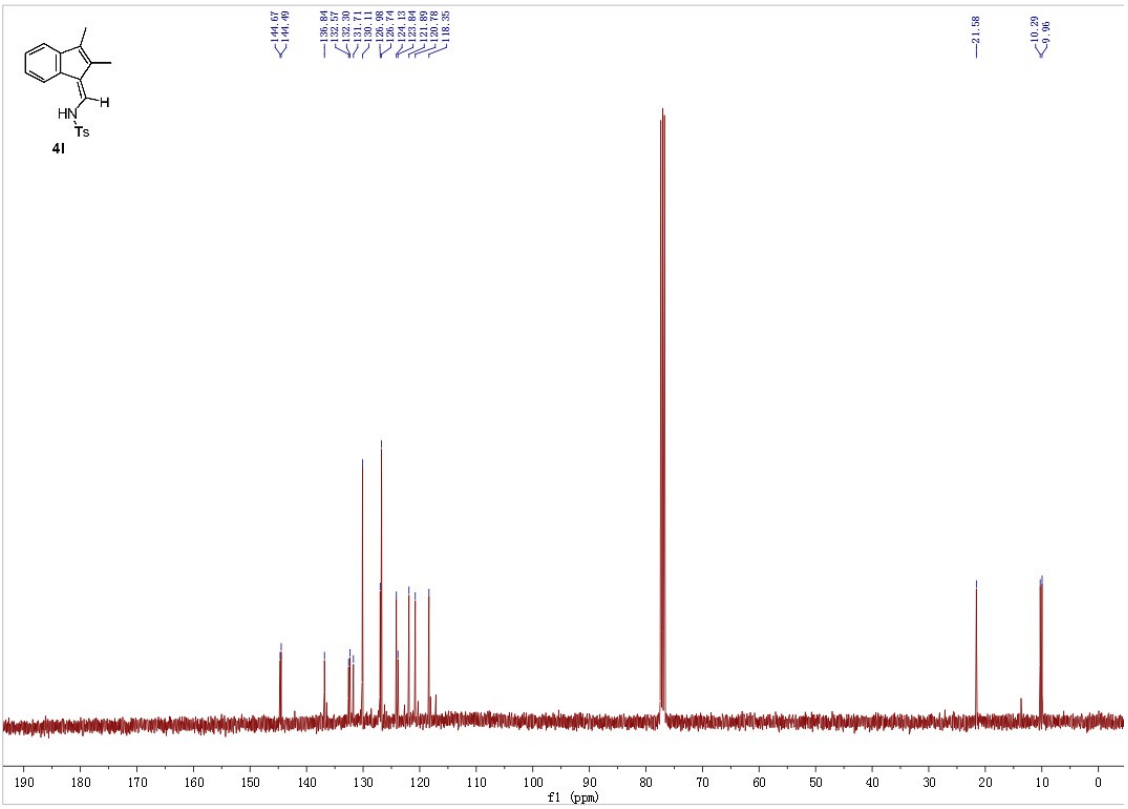
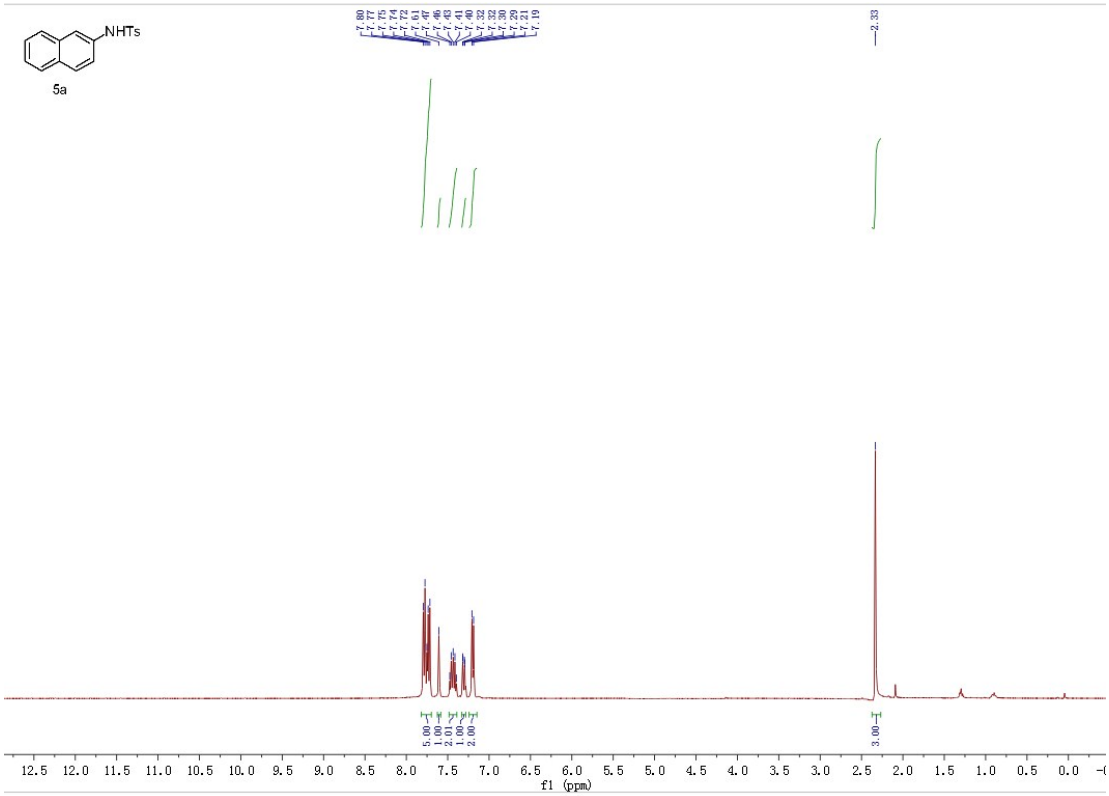
141.16
136.88
136.79
130.13
126.71
126.19
124.92
122.71
119.66
119.03
118.05
117.97
21.58
13.25
f1 (ppm)

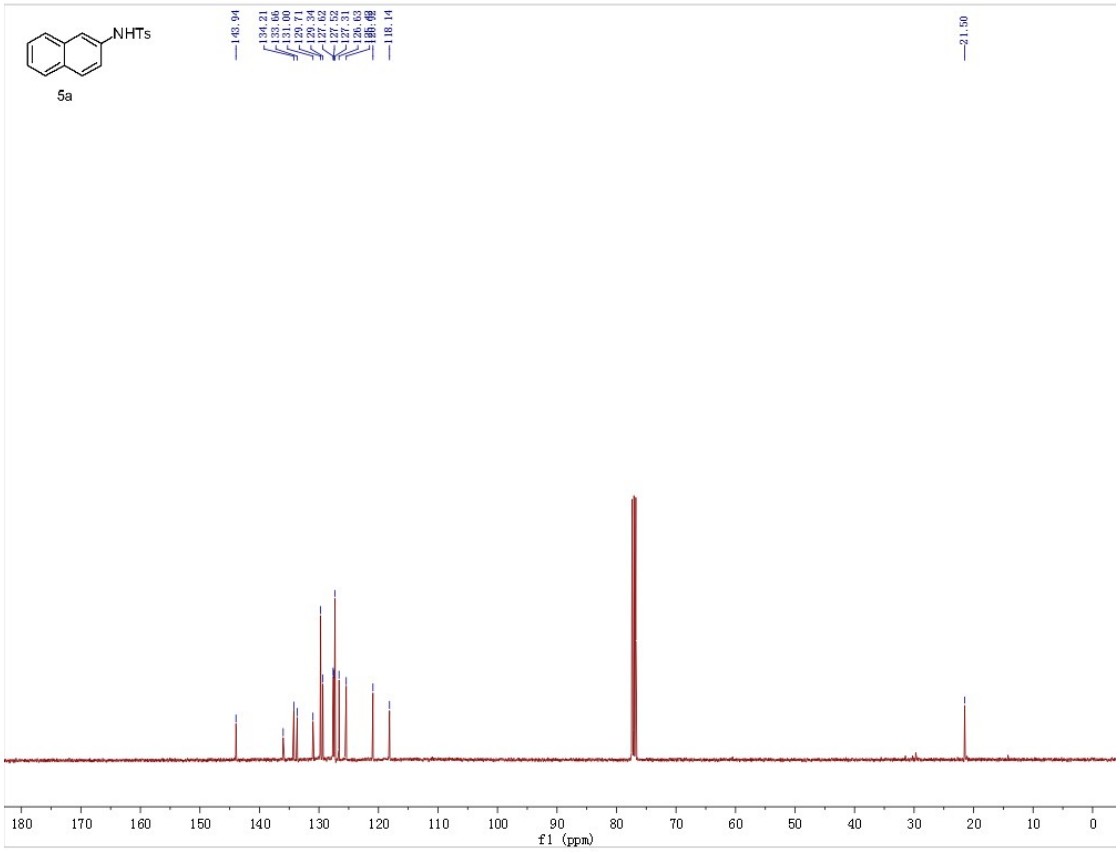

4k
f1 (ppm)

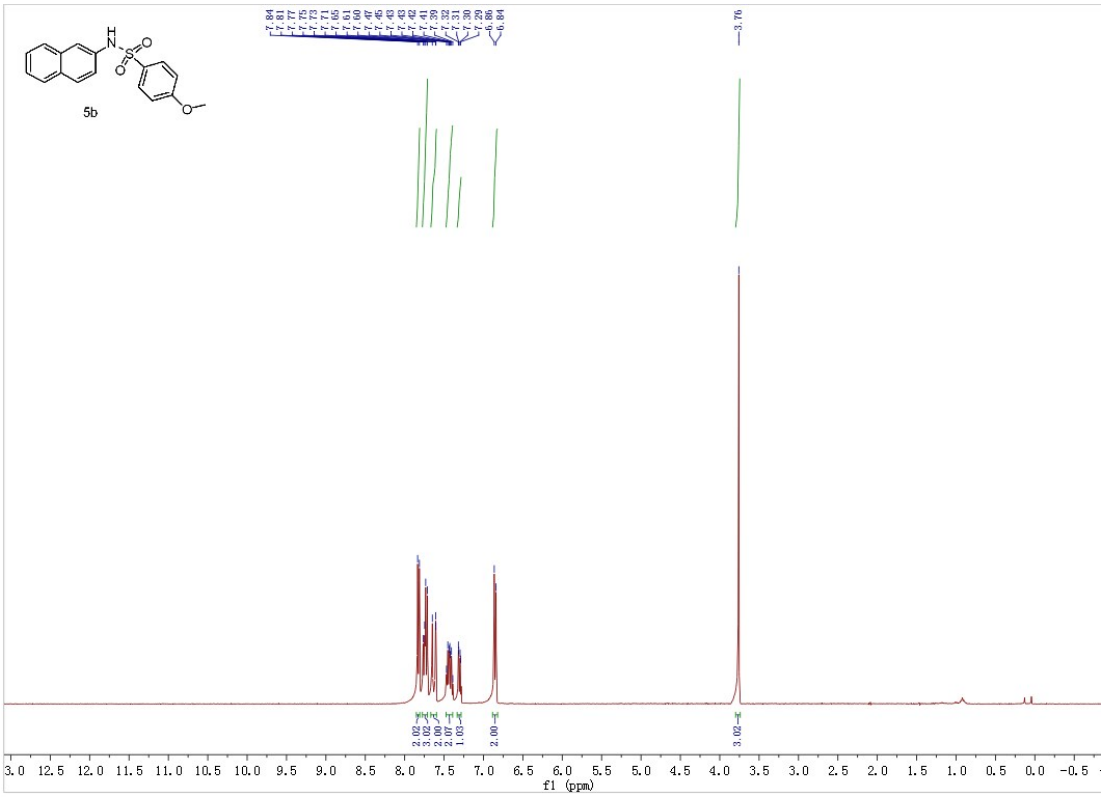

4k
f1 (ppm)

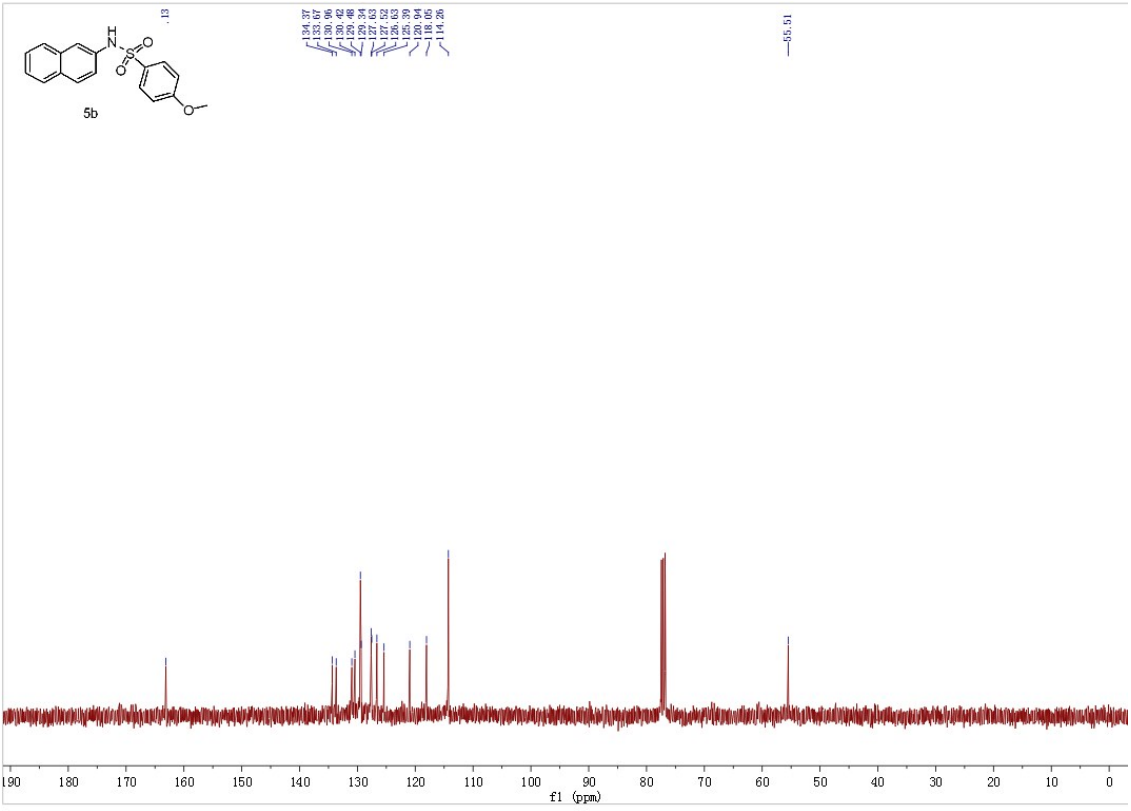

HN
Ts
4l
f1 (ppm)

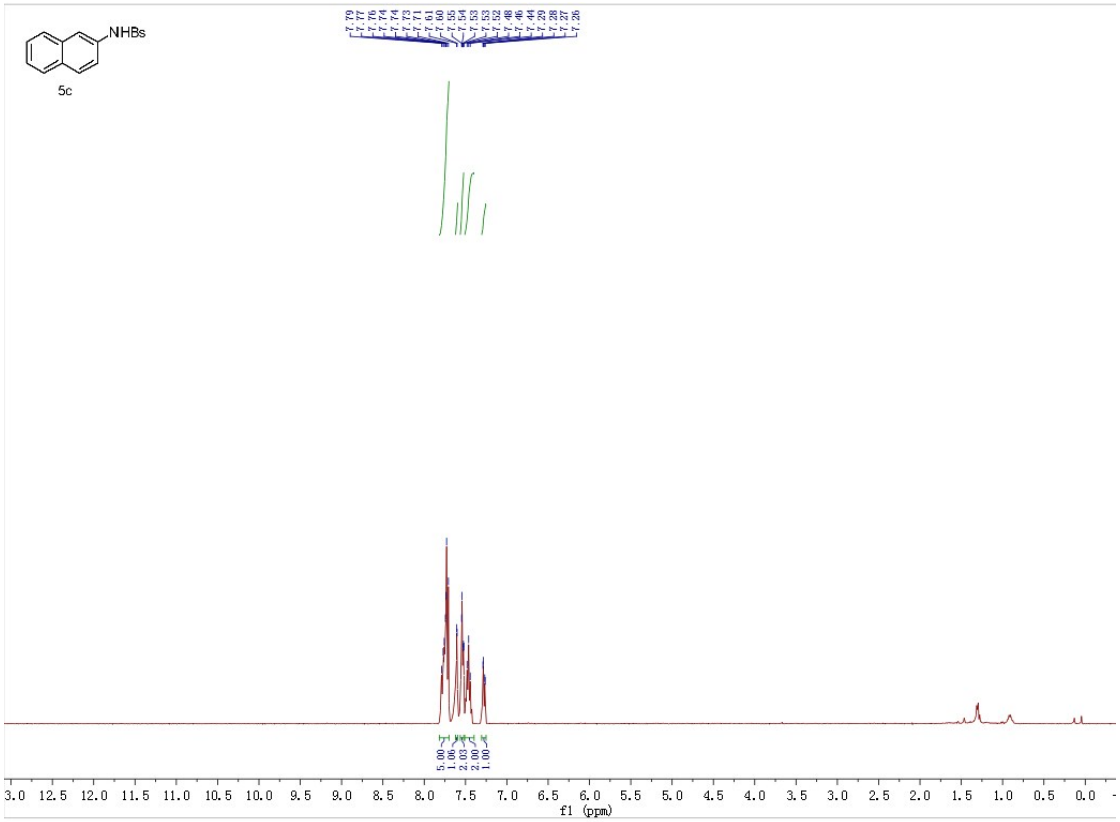

HN
Ts
4l
f1 (ppm)

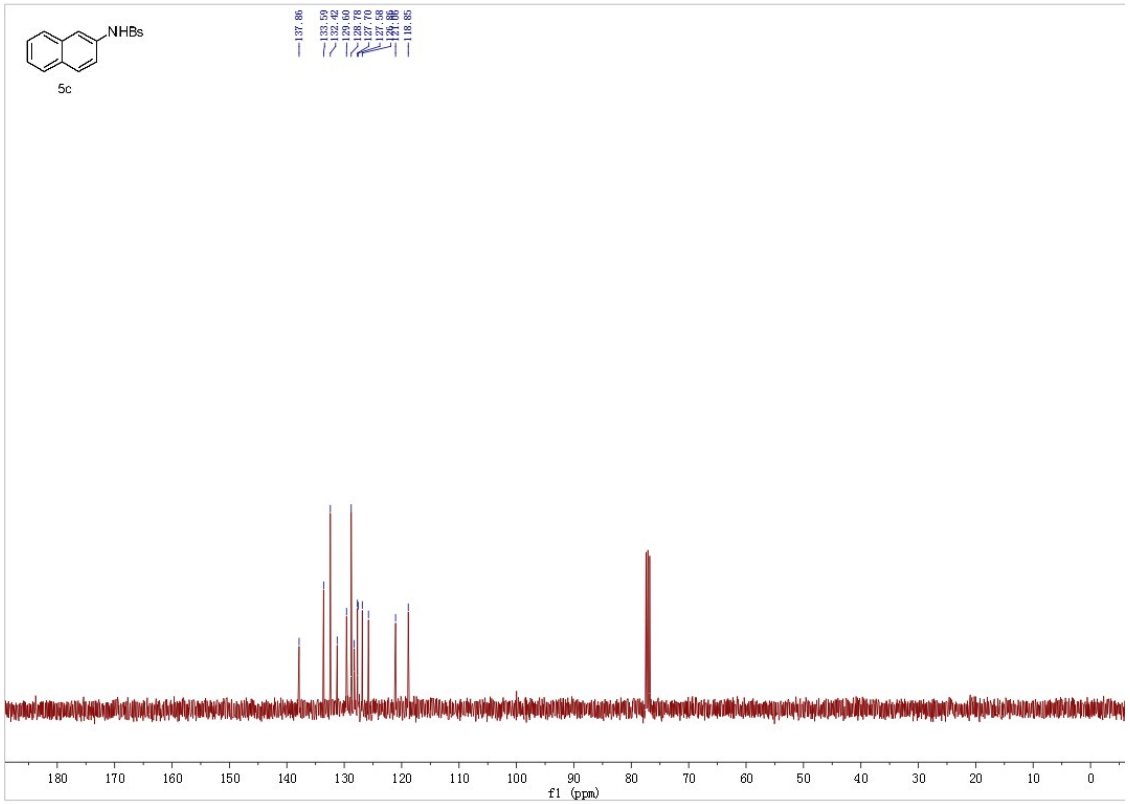

NHTs
5a
7.80
7.77
7.75
7.74
7.72
7.61
7.47
7.46
7.45
7.41
7.40
7.32
7.32
7.30
7.29
7.21
7.19
2.33
5.00
1.01
1.00
2.00
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

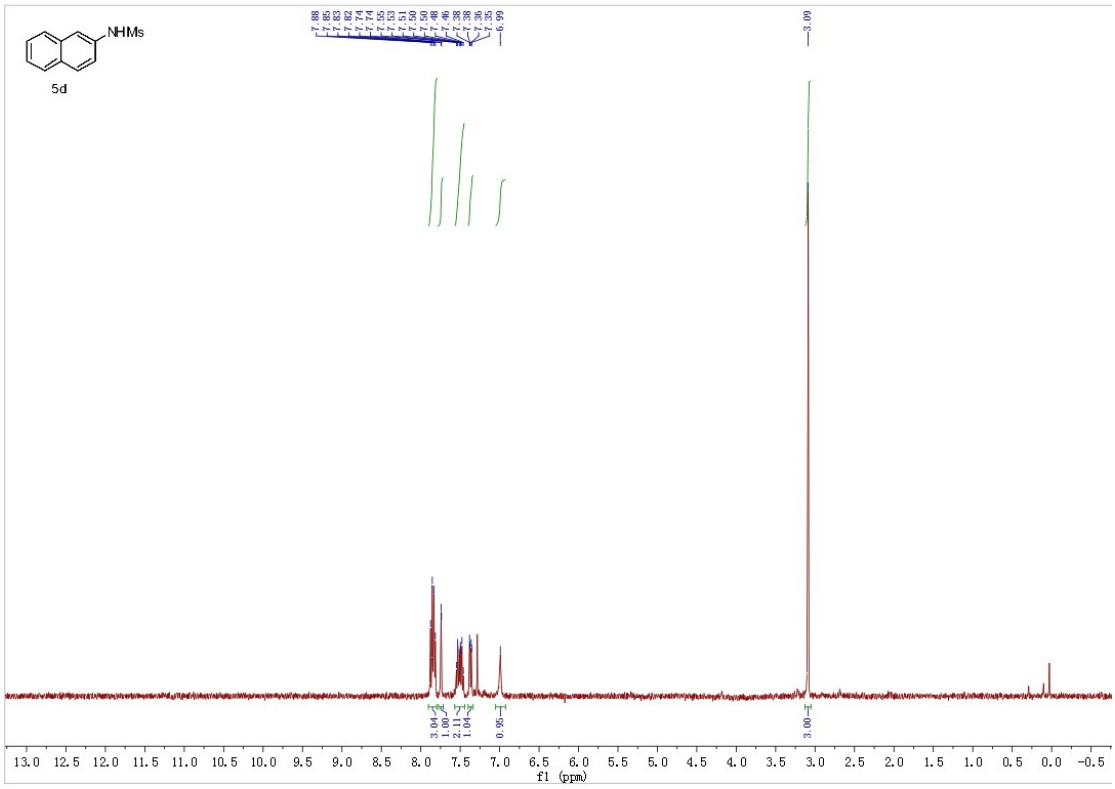

NHTs
5a
143.94
134.21
133.06
131.00
129.71
129.34
127.62
127.52
127.31
126.63
118.14
21.50
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

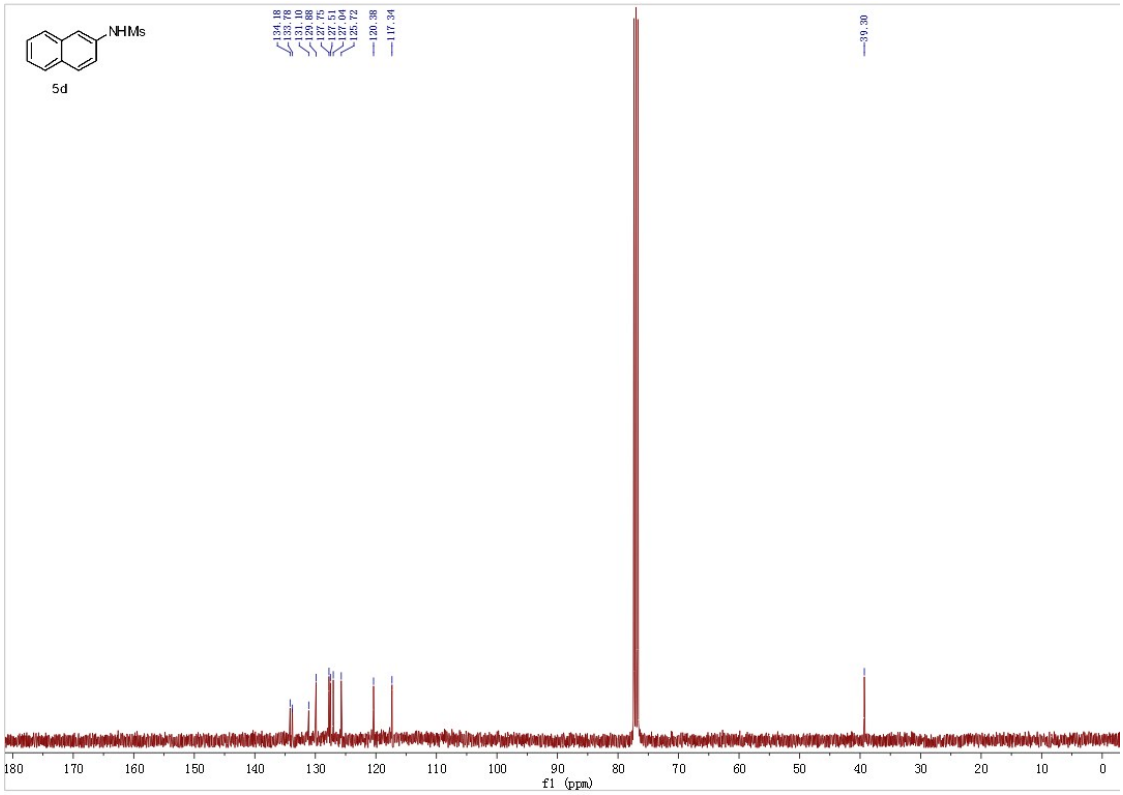

5b
7.84
7.81
7.77
7.75
7.73
7.71
7.65
7.61
7.60
7.47
7.45
7.43
7.42
7.41
7.39
7.33
7.31
7.30
7.29
6.86
6.84
3.76
2.02
3.02
2.00
2.07
1.03
2.00
3.02
f1 (ppm)

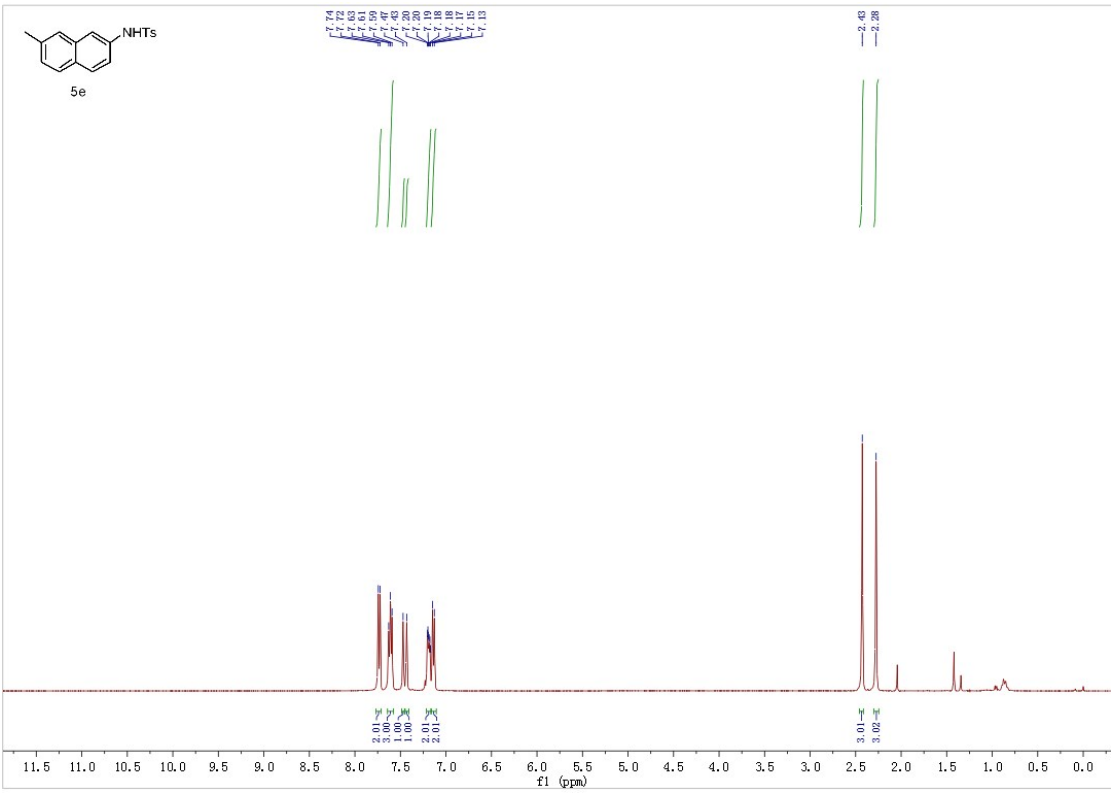

5b
134.37
133.67
130.96
130.42
129.48
129.34
127.63
127.52
126.63
125.39
120.94
118.05
114.26
55.51
f1 (ppm)

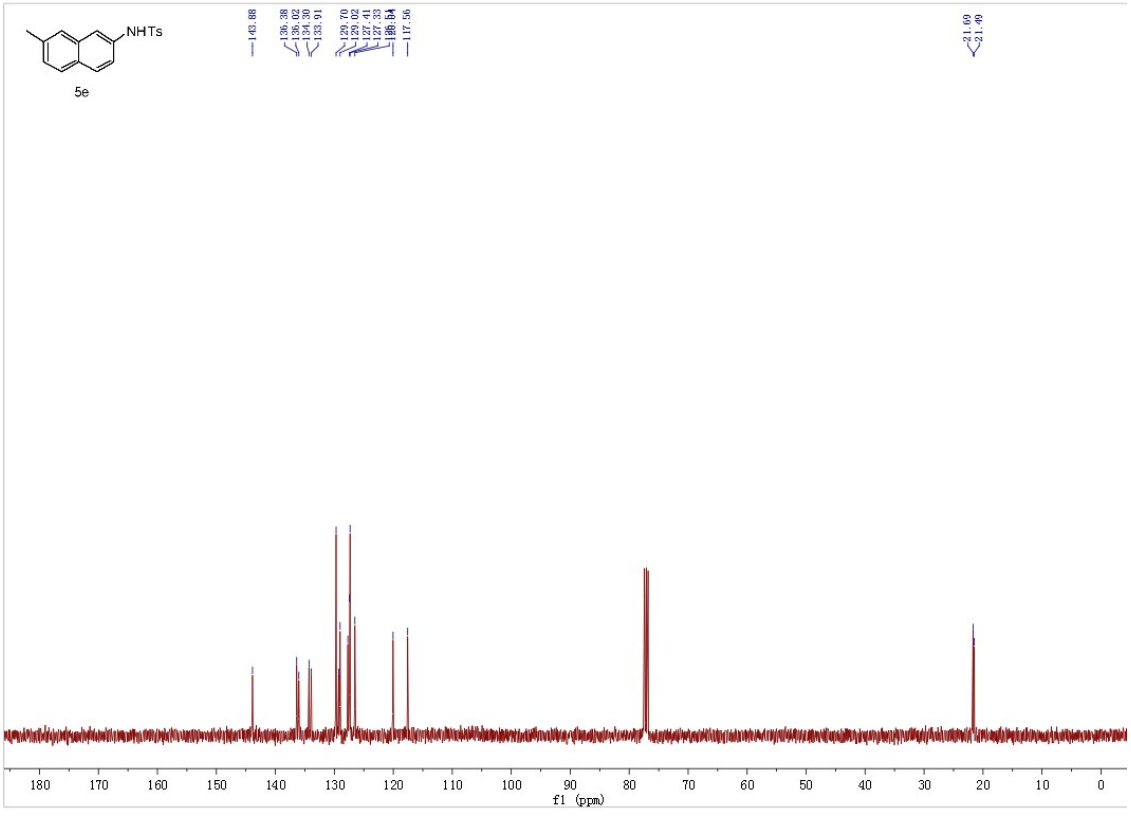

NHBs
5c
7.79
7.77
7.76
7.74
7.74
7.73
7.71
7.61
7.60
7.55
7.54
7.53
7.52
7.48
7.46
7.44
7.29
7.28
7.27
7.25
5.00
1.06
2.03
2.00
1.00
f1 (ppm)

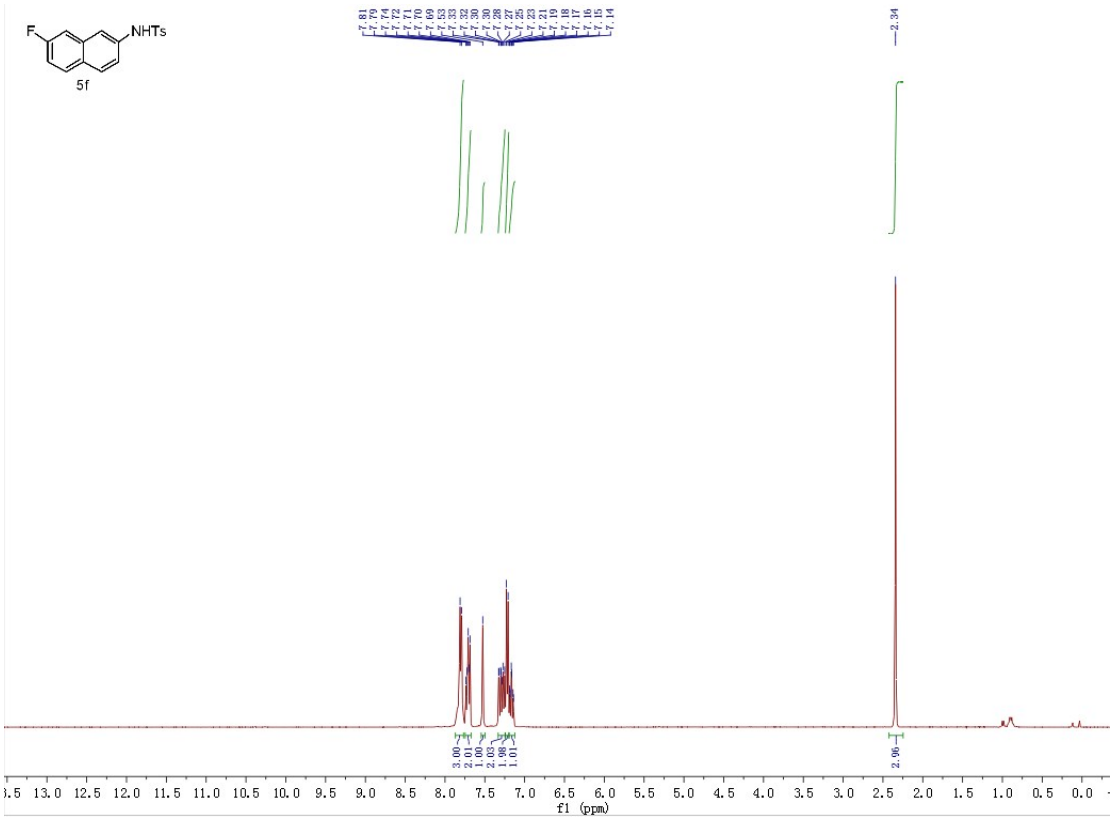

NHBs
5c
137.86
133.59
132.42
129.60
128.78
127.70
127.58
126.88
121.06
116.85
f1 (ppm)

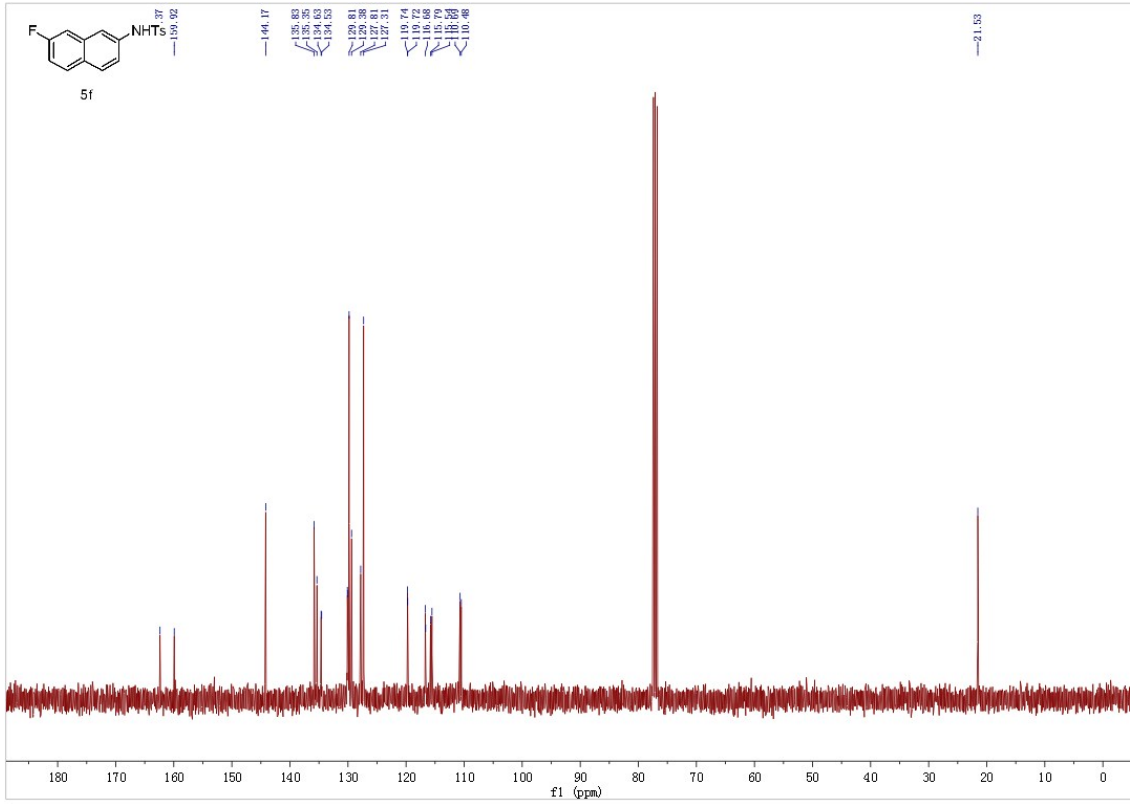

NHMs
5d
7.88
7.85
7.83
7.82
7.74
7.55
7.53
7.51
7.50
7.48
7.46
7.38
7.36
7.35
6.99
3.09
3.04
1.00
2.11
1.04
0.95
3.00
f1 (ppm)

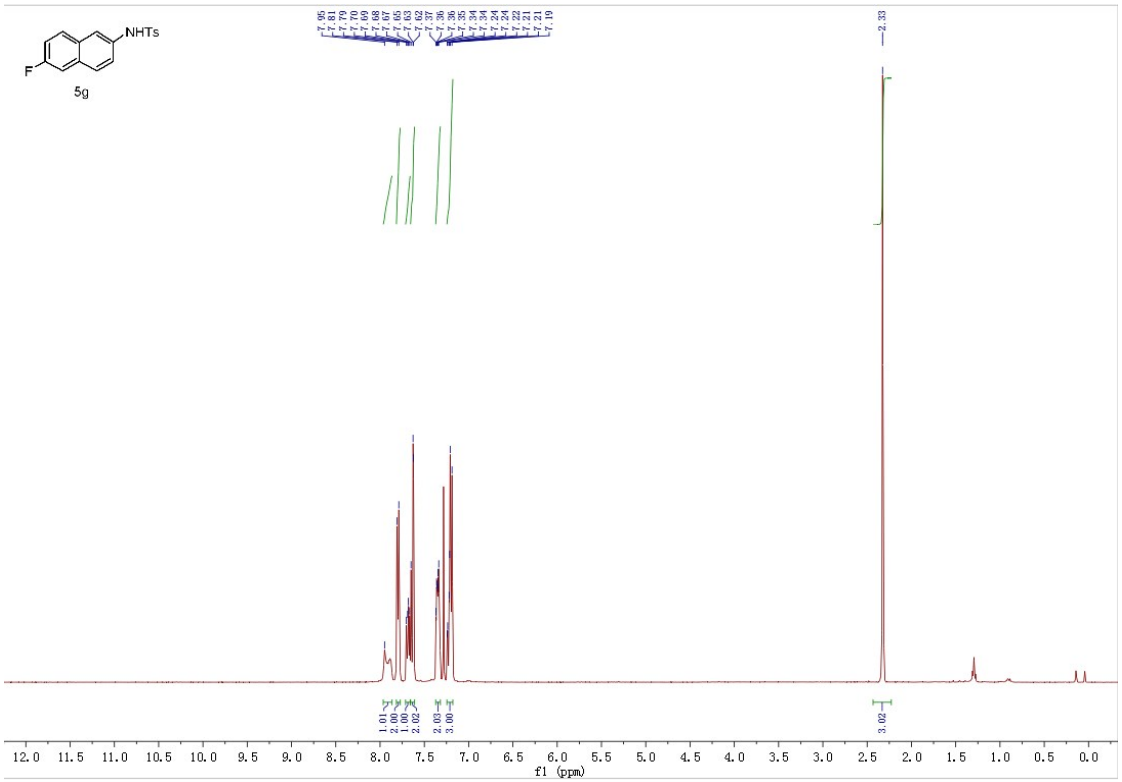

NHMs
5d
134.18
133.78
131.10
130.88
127.75
127.51
127.04
125.72
120.38
117.34
39.30
f1 (ppm)

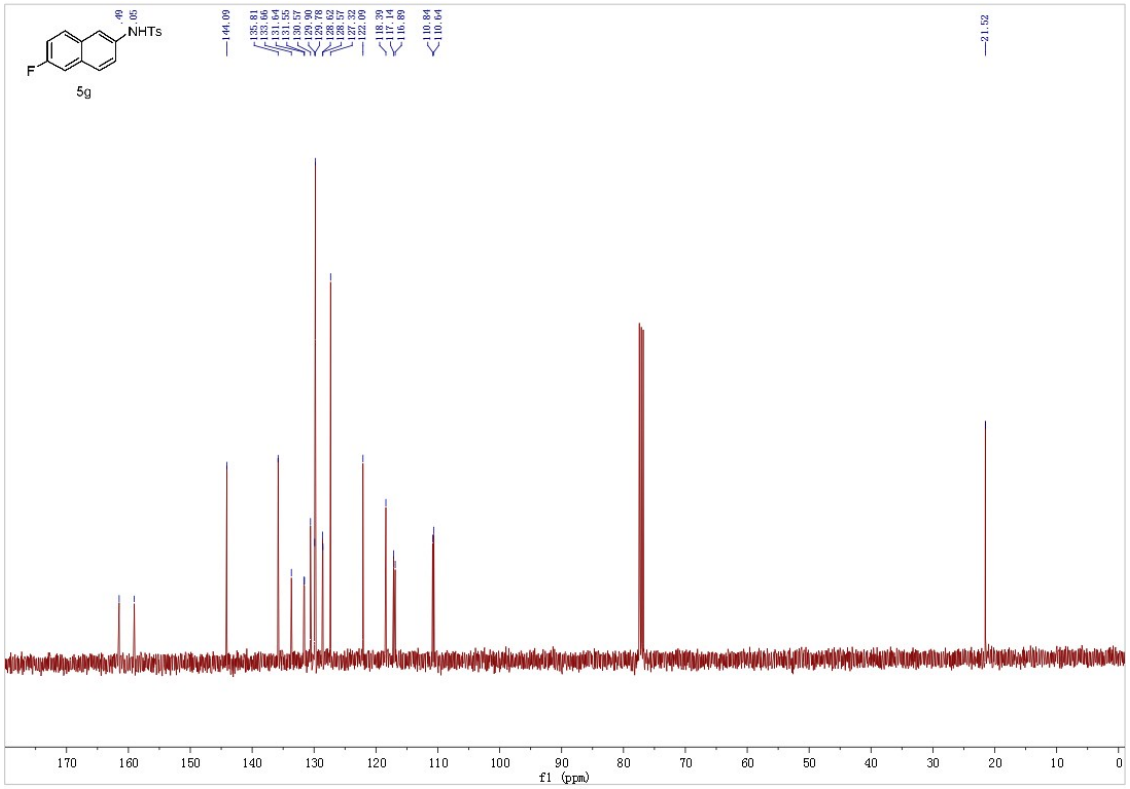

NHTs
5e
7.74
7.72
7.63
7.61
7.59
7.47
7.43
7.20
7.19
7.18
7.17
7.15
7.13
2.43
2.28
2.01
3.00
1.00
1.00
2.01
2.01
3.01
3.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

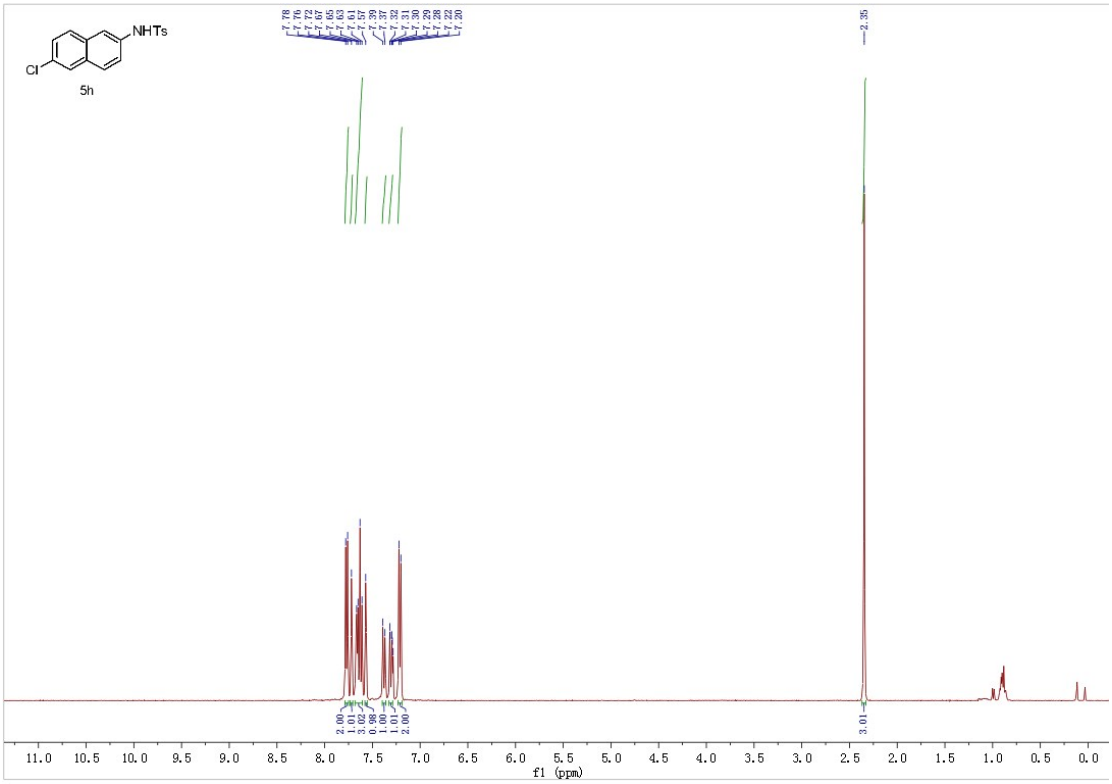

NHTs
5e
143.88
136.38
136.02
134.30
133.91
129.70
129.02
127.41
127.33
126.54
126.14
117.56
21.60
21.49
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

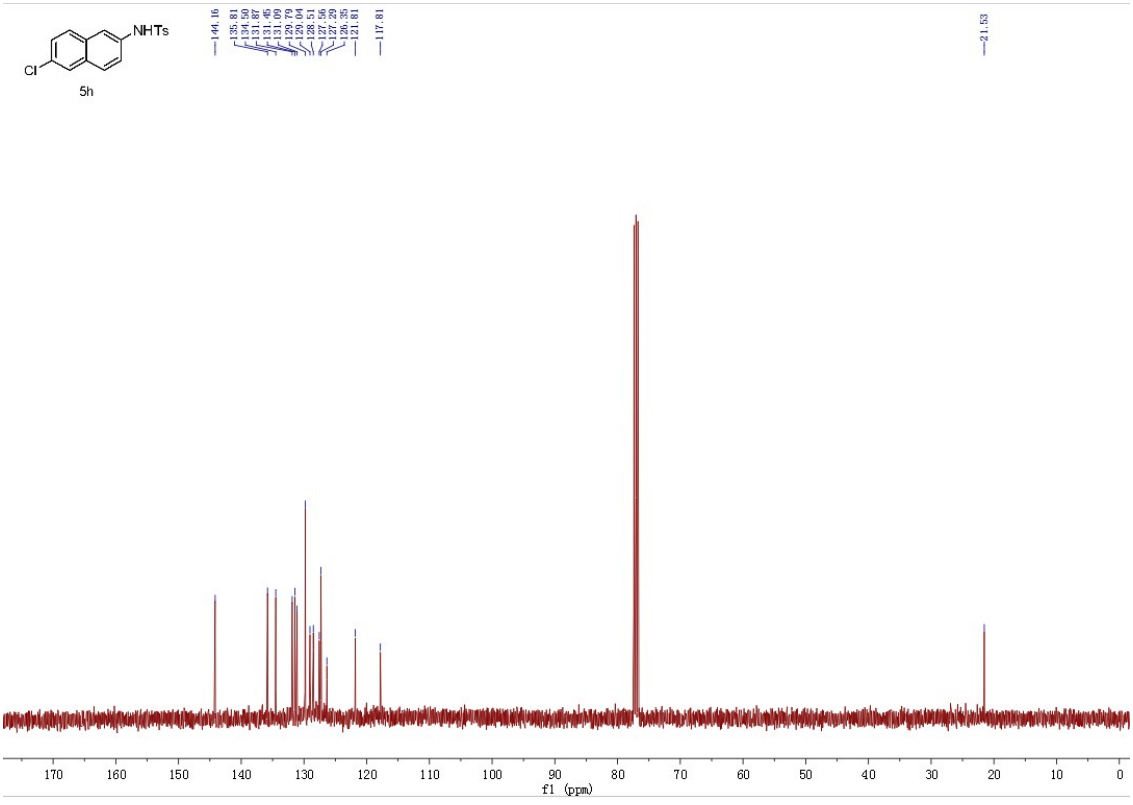

F
NHTs
5f
7.81
7.79
7.74
7.72
7.71
7.70
7.69
7.53
7.32
7.30
7.28
7.27
7.25
7.23
7.21
7.19
7.18
7.17
7.16
7.15
7.14
2.34
3.00
2.01
1.00
2.05
1.98
1.01
2.06
f1 (ppm)

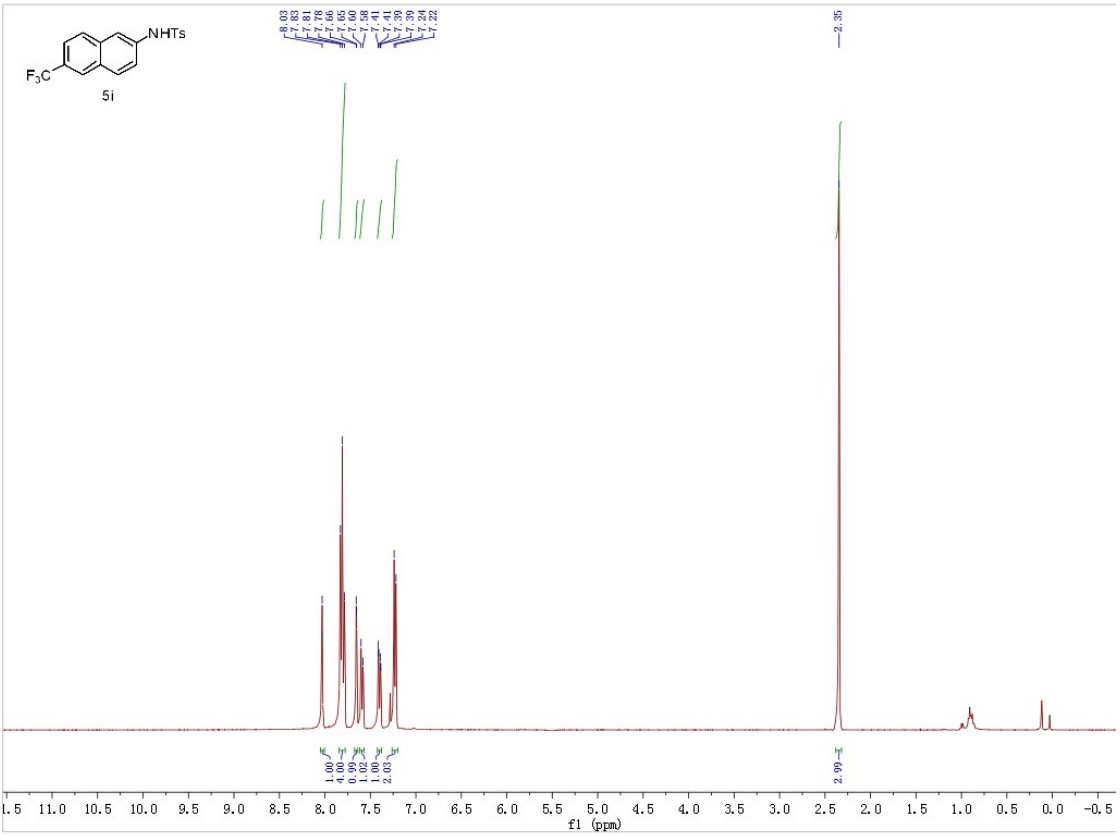

F
NHTs
5f
159.92
144.17
135.83
135.35
134.63
134.53
129.81
129.38
127.81
127.31
119.74
119.72
116.68
115.79
110.66
110.48
21.53
f1 (ppm)

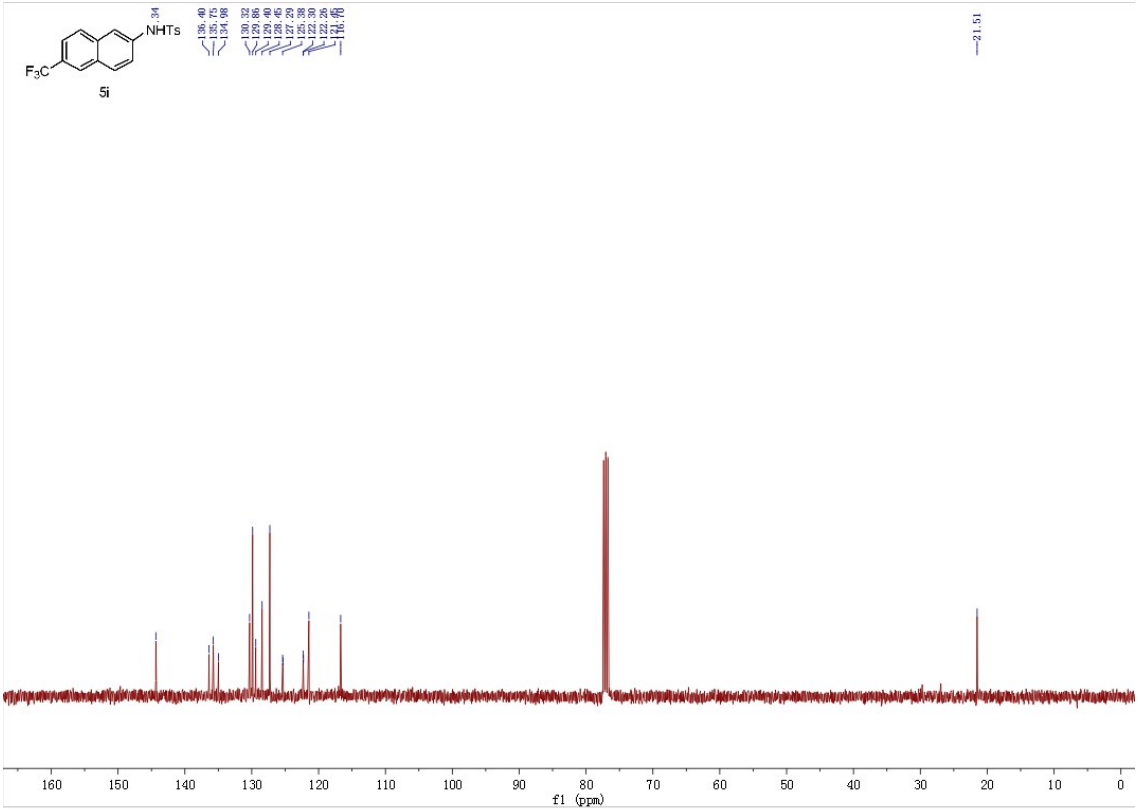

NHTs
F
5g
f1 (ppm)

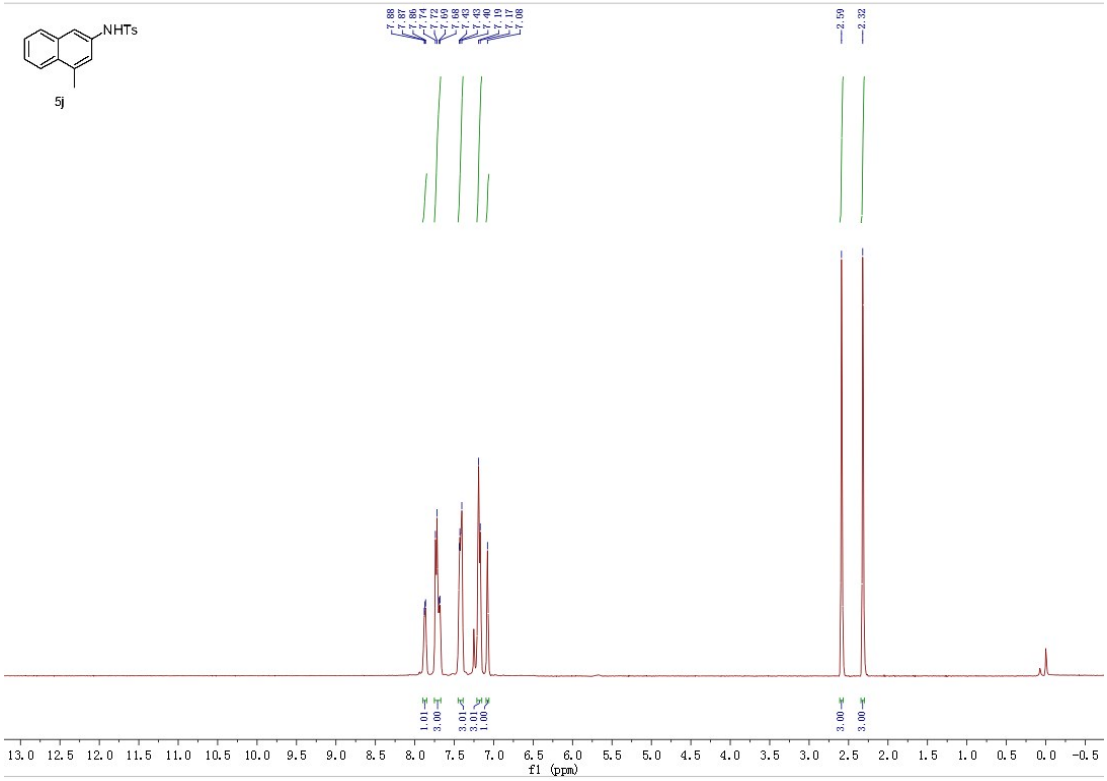

NHTs
F
5g
f1 (ppm)

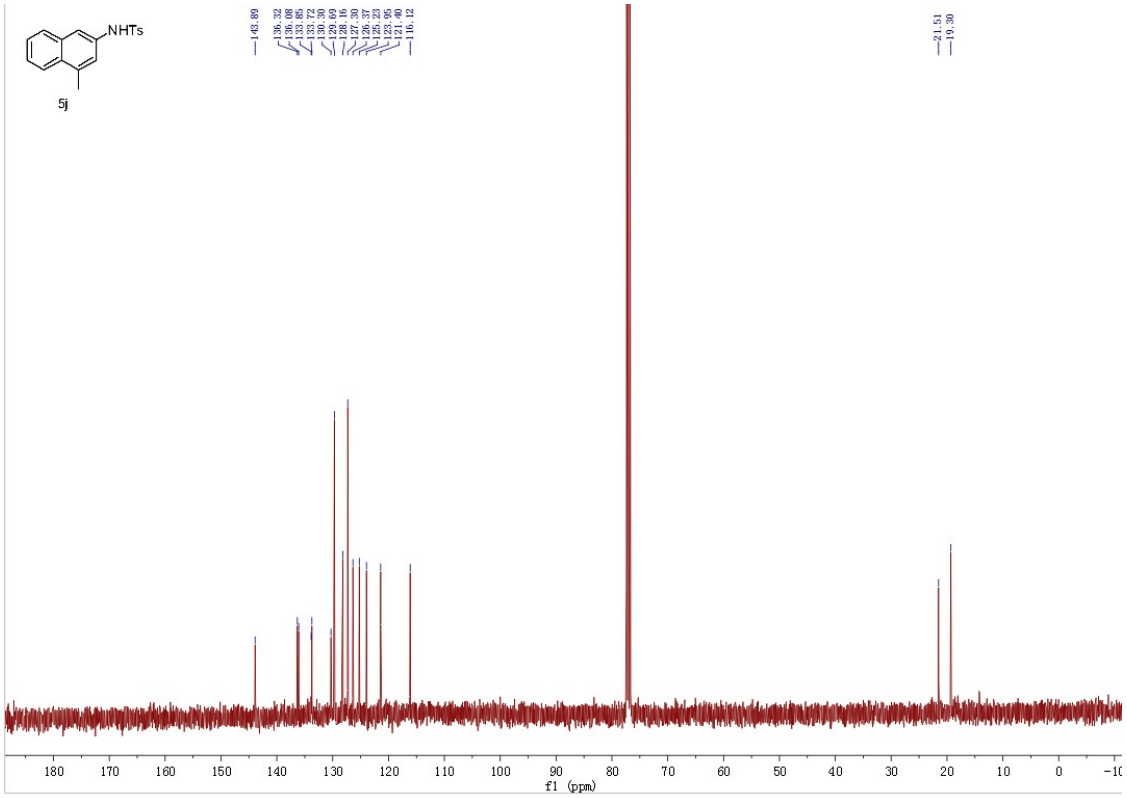

NHTs
Cl
5h
f1 (ppm)

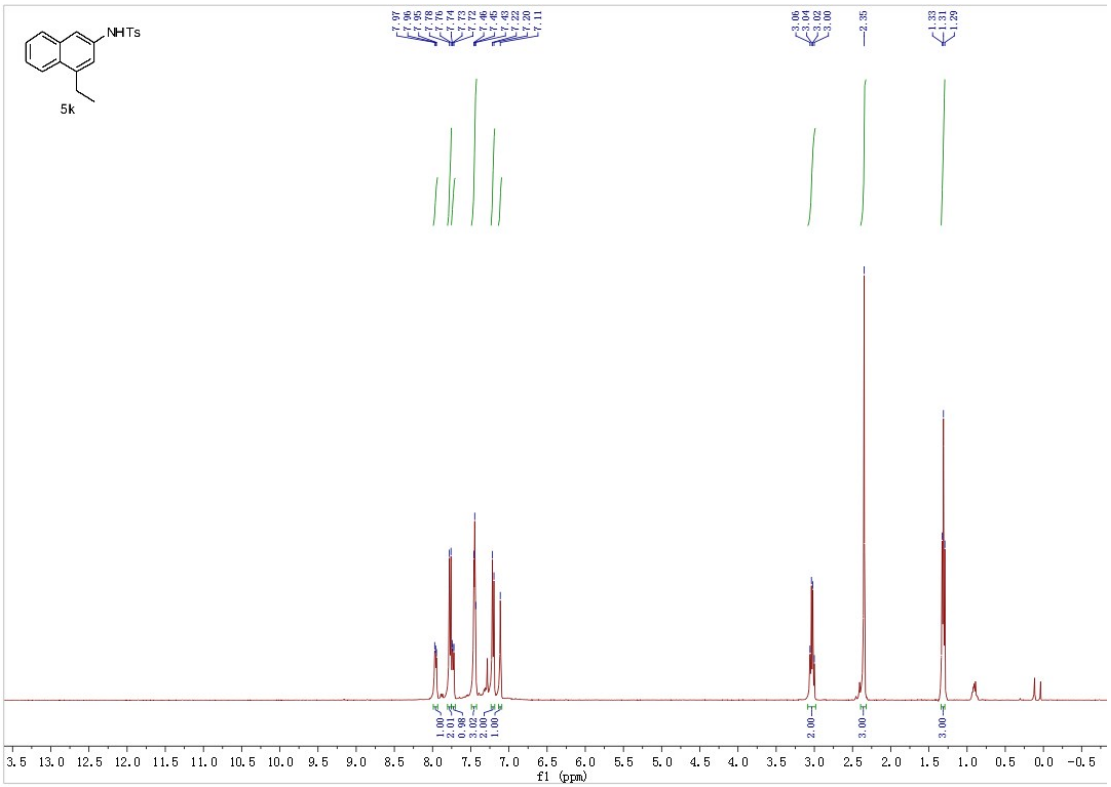

NHTs
Cl
5h
f1 (ppm)

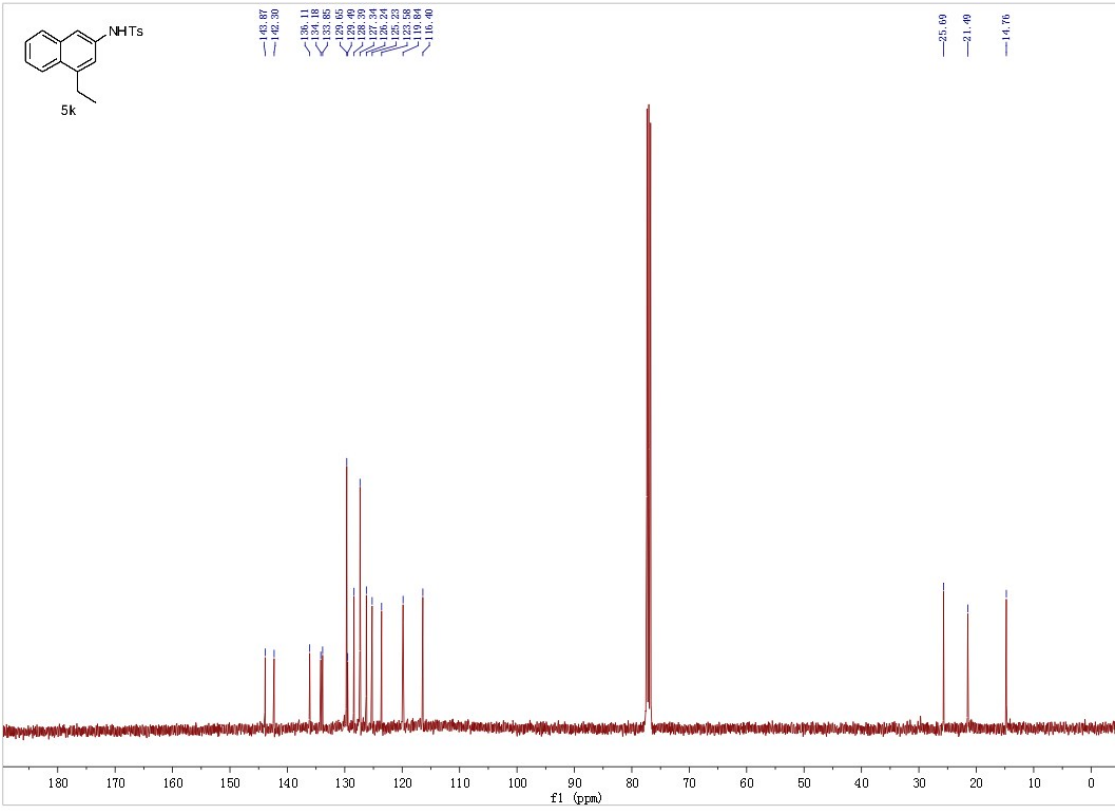

NHTs
F3C
5i
8.03
7.83
7.81
7.78
7.66
7.65
7.60
7.58
7.41
7.39
7.39
7.24
7.22
2.35
1.00
4.00
0.99
1.02
1.00
2.03
2.99
f1 (ppm)

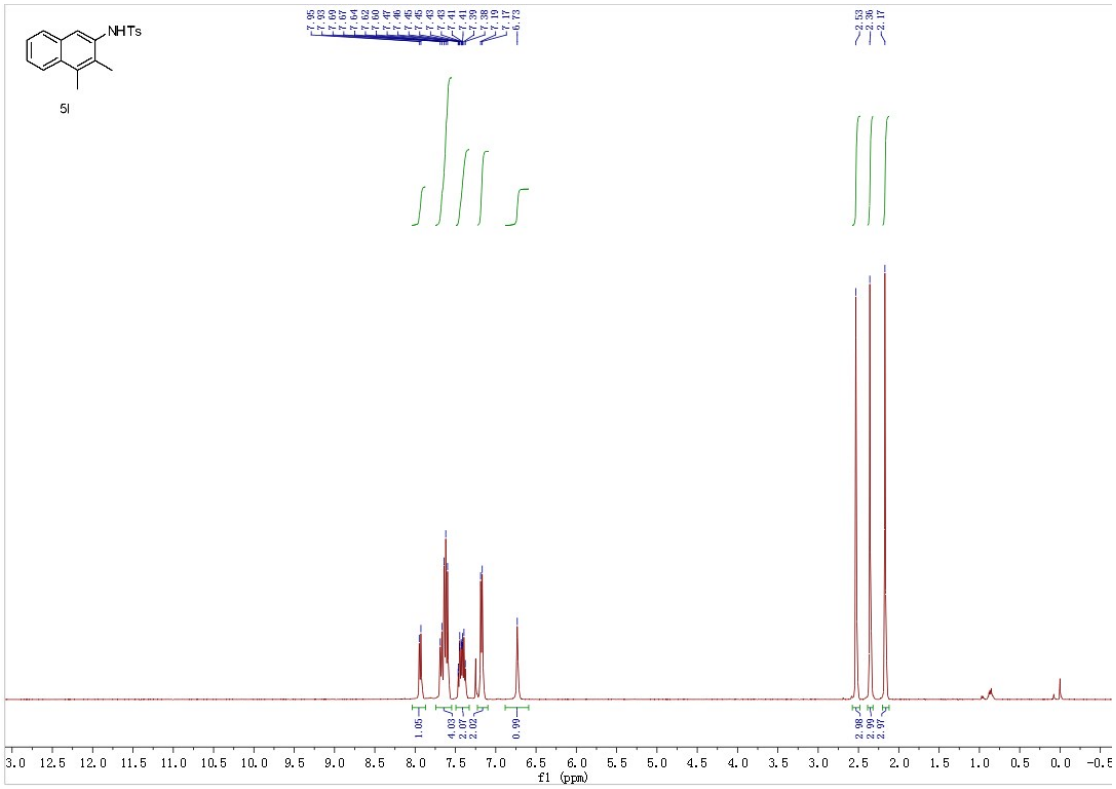

NHTs
F3C
5i
136.40
135.75
134.98
130.32
129.86
129.49
128.45
127.29
125.38
122.30
122.25
116.76
21.51
f1 (ppm)

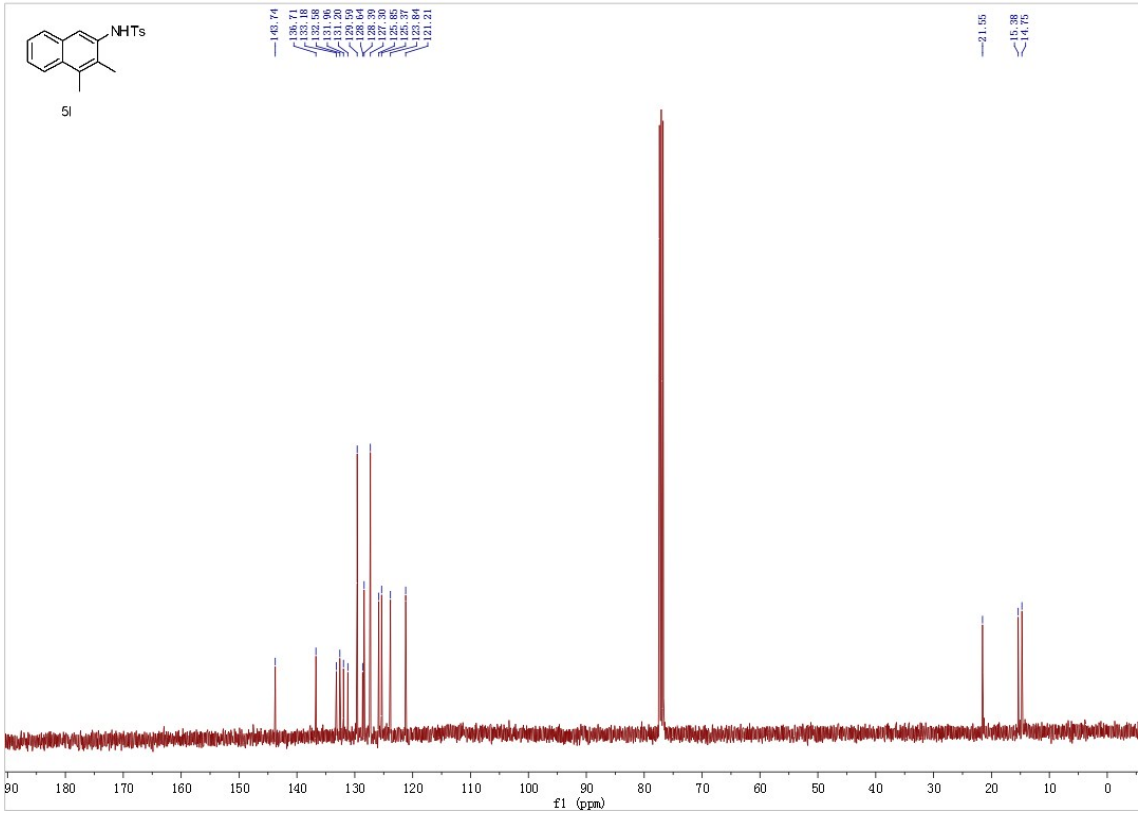

NHTs
5j
7.88
7.87
7.86
7.74
7.72
7.69
7.68
7.43
7.42
7.40
7.19
7.17
7.06
2.59
2.32
1.01
3.00
3.01
3.01
1.00
3.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

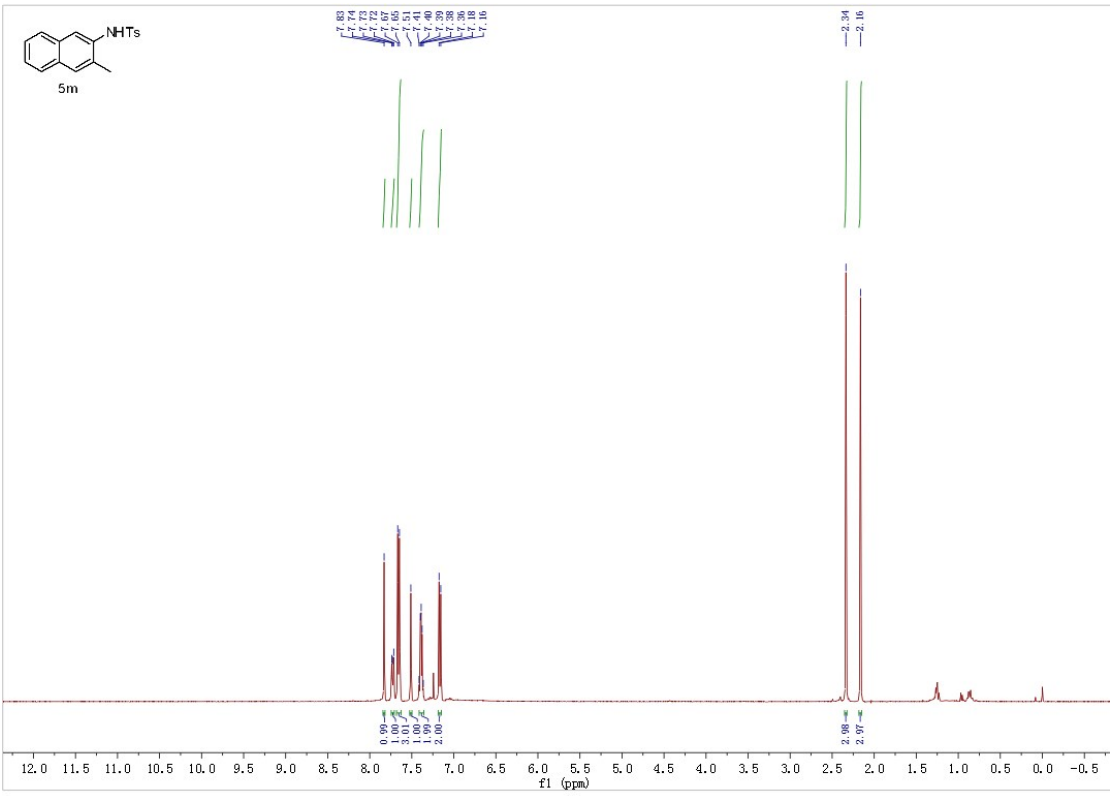

NHTs
5j
143.89
136.32
136.08
133.85
132.72
130.38
129.69
128.16
127.30
126.37
126.23
123.95
121.40
116.12
21.51
19.30
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

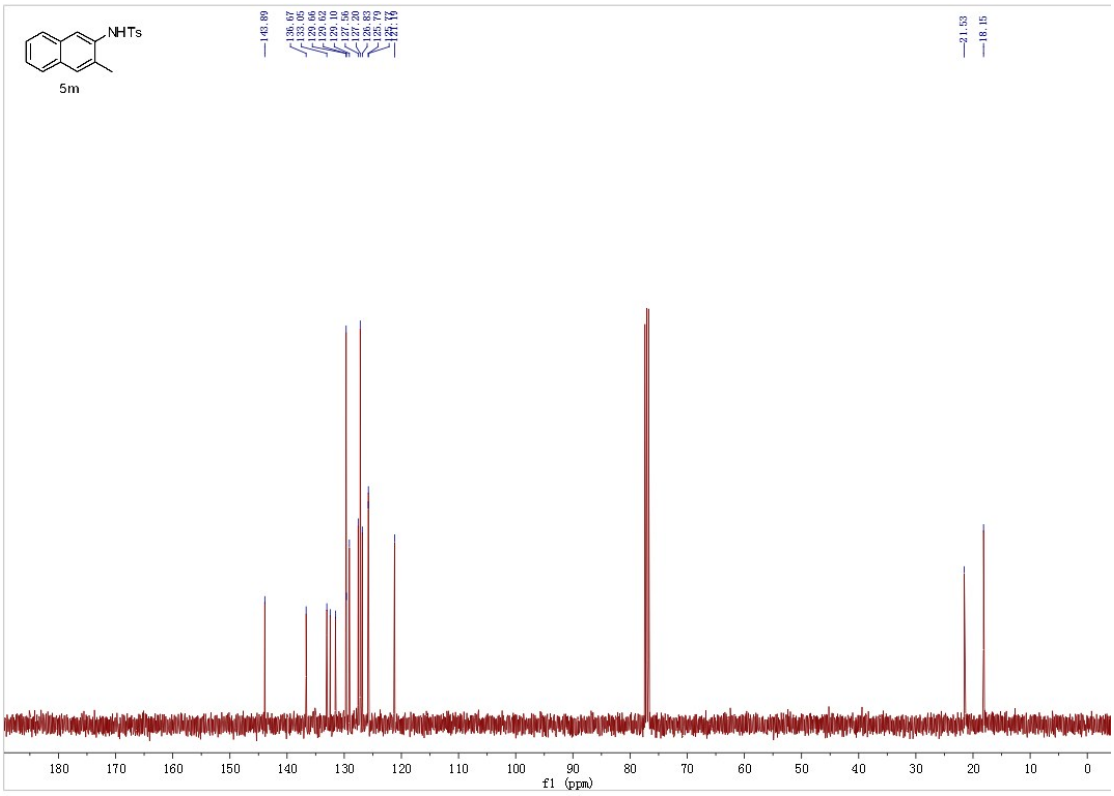

NHTs
5k
7.97
7.96
7.95
7.78
7.76
7.74
7.73
7.72
7.46
7.45
7.22
7.20
7.11
3.06
3.04
3.02
3.00
2.35
1.33
1.31
1.29
1.00
2.01
0.98
3.05
2.00
1.00
2.00
3.00
3.00
f1 (ppm)

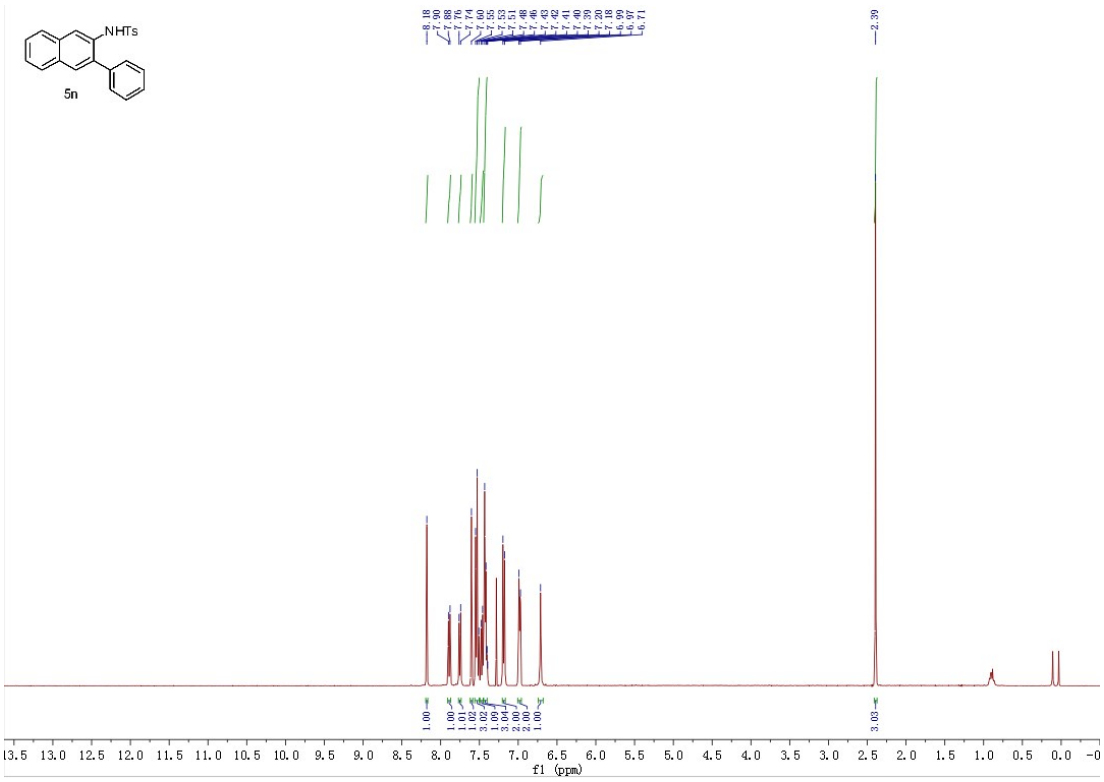

NHTs
5k
143.87
142.30
136.11
134.18
133.85
129.65
129.49
128.93
127.34
126.24
125.23
123.38
119.84
116.40
25.69
21.49
14.76
f1 (ppm)

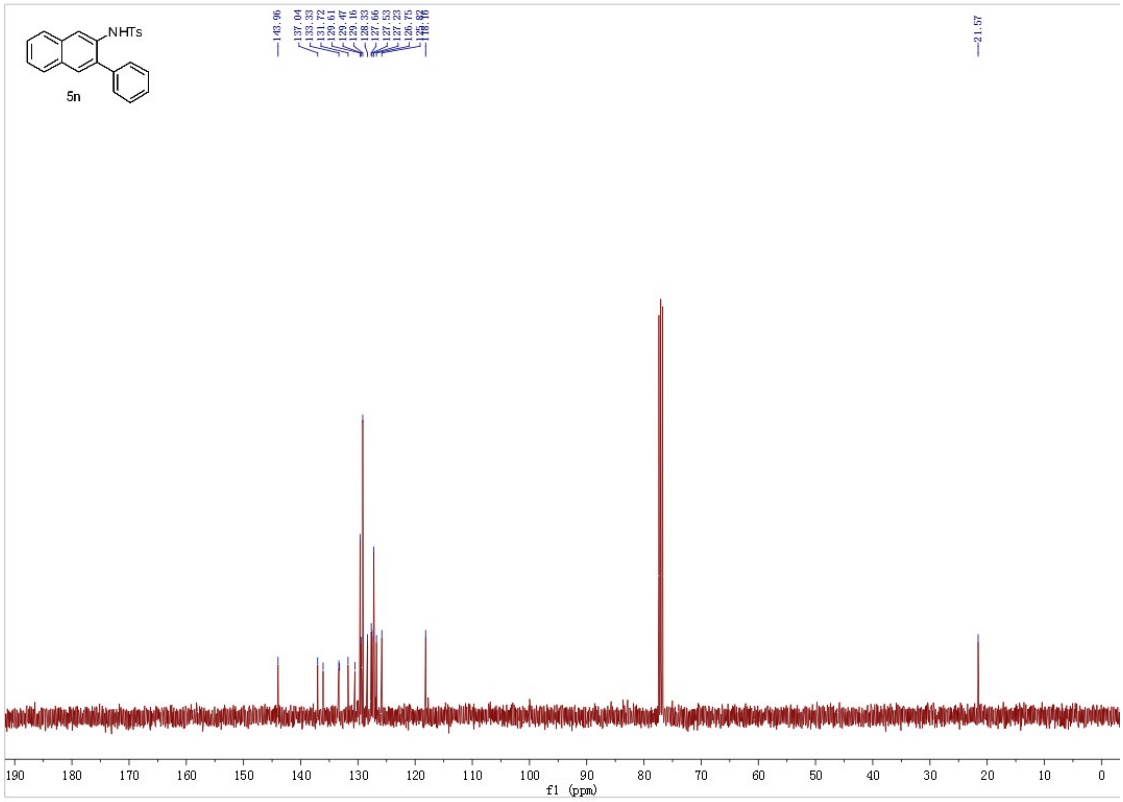

NHTs
5l
7.95
7.93
7.69
7.67
7.64
7.62
7.49
7.47
7.46
7.45
7.45
7.43
7.41
7.41
7.39
7.38
7.19
7.17
6.73
2.53
2.36
2.17
1.05
4.03
2.07
2.02
0.99
2.98
2.99
2.97
f1 (ppm)

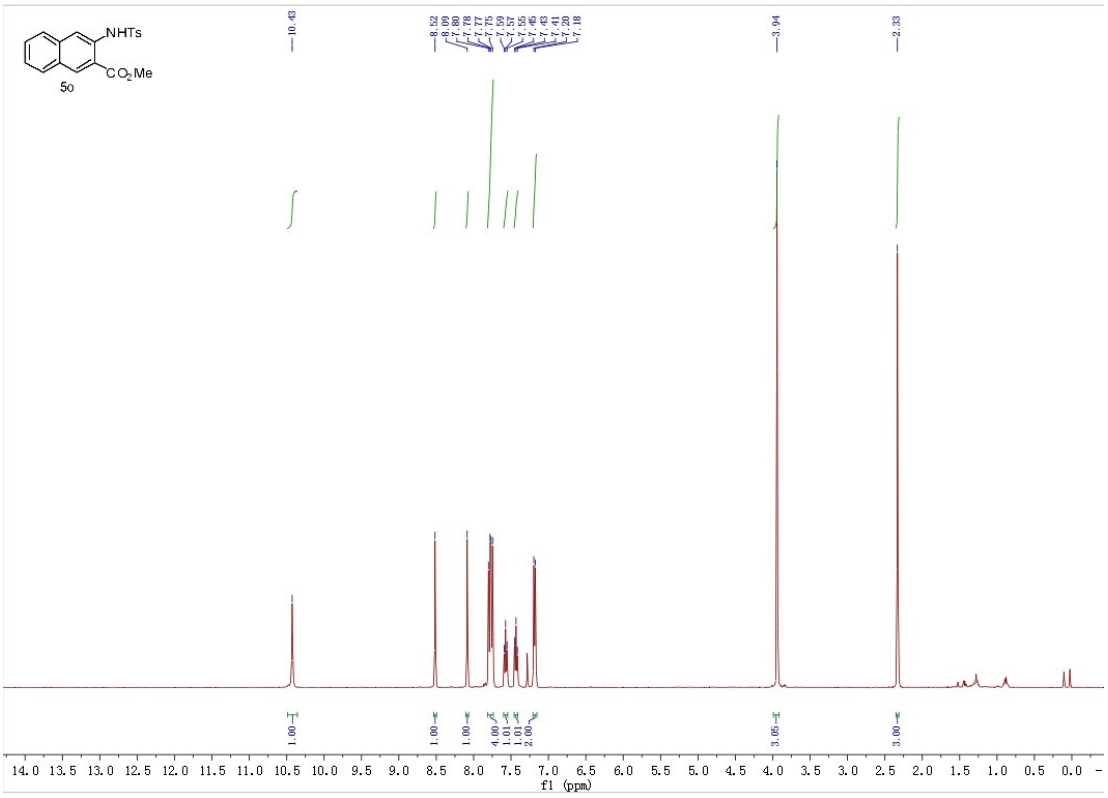

NHTs
5l
143.74
136.71
133.18
132.58
131.96
131.20
129.59
128.64
128.39
127.30
125.85
125.37
123.84
121.21
21.55
15.38
14.75
f1 (ppm)

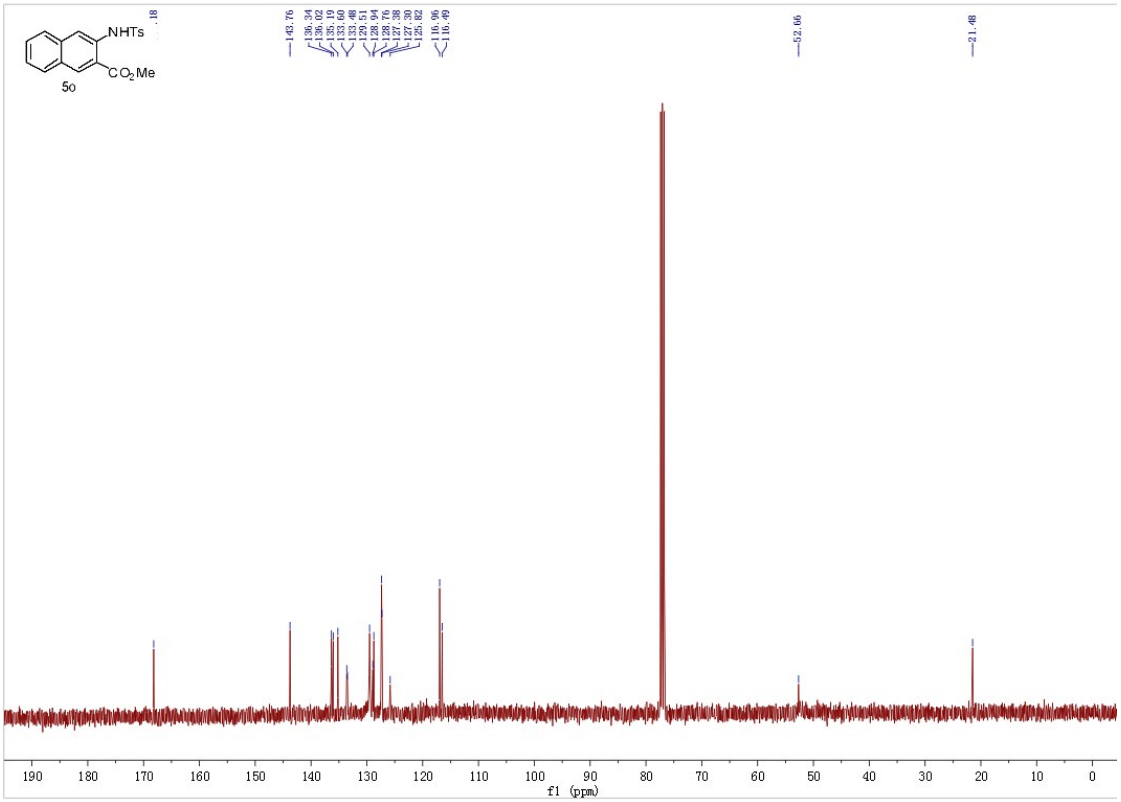

NHTs
5m
7.83
7.74
7.73
7.72
7.67
7.65
7.51
7.41
7.40
7.39
7.38
7.36
7.18
7.16
2.34
2.16
0.99
1.00
3.01
1.00
1.99
2.00
2.98
2.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

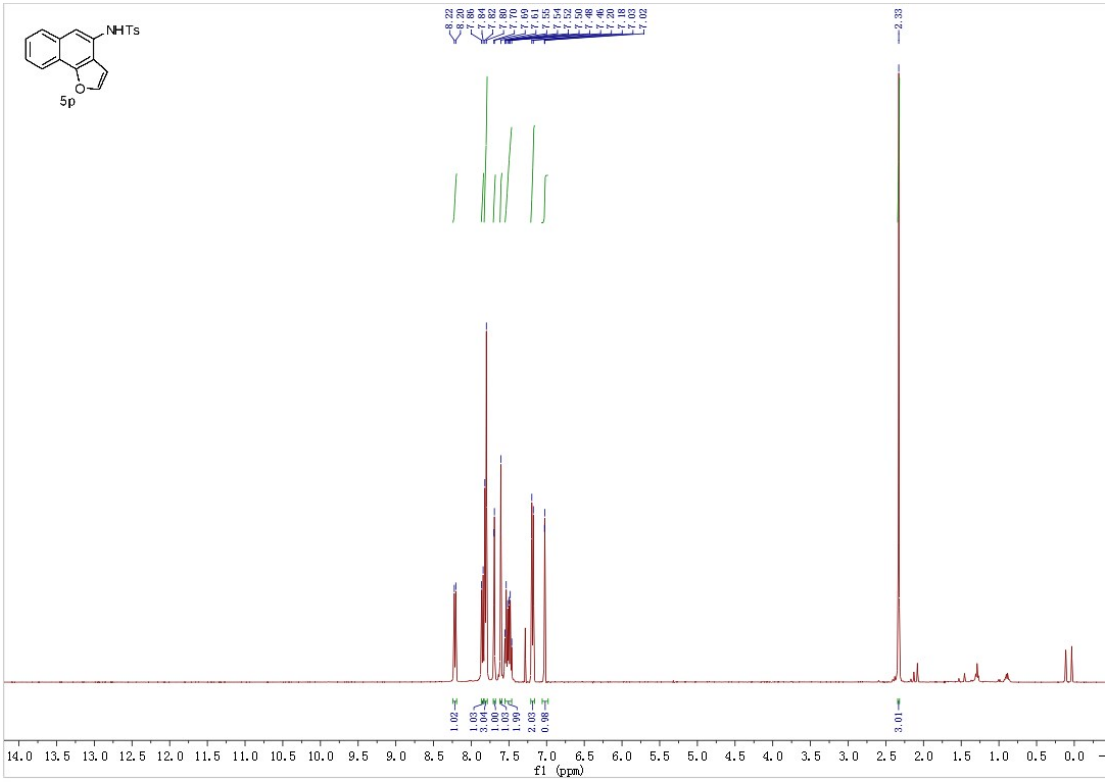

NHTs
5m
143.89
136.67
133.05
129.66
129.62
129.10
127.56
127.20
126.83
125.79
121.19
21.53
18.15
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

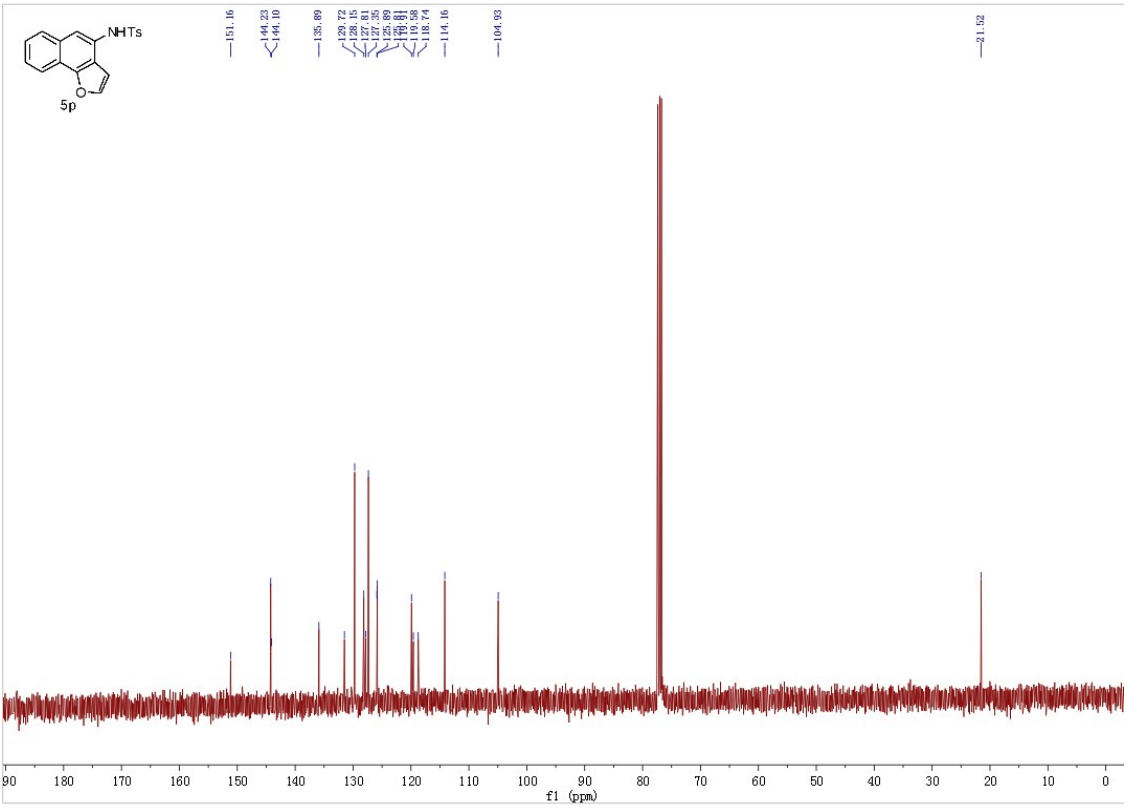

NHTs
5n
f1 (ppm)

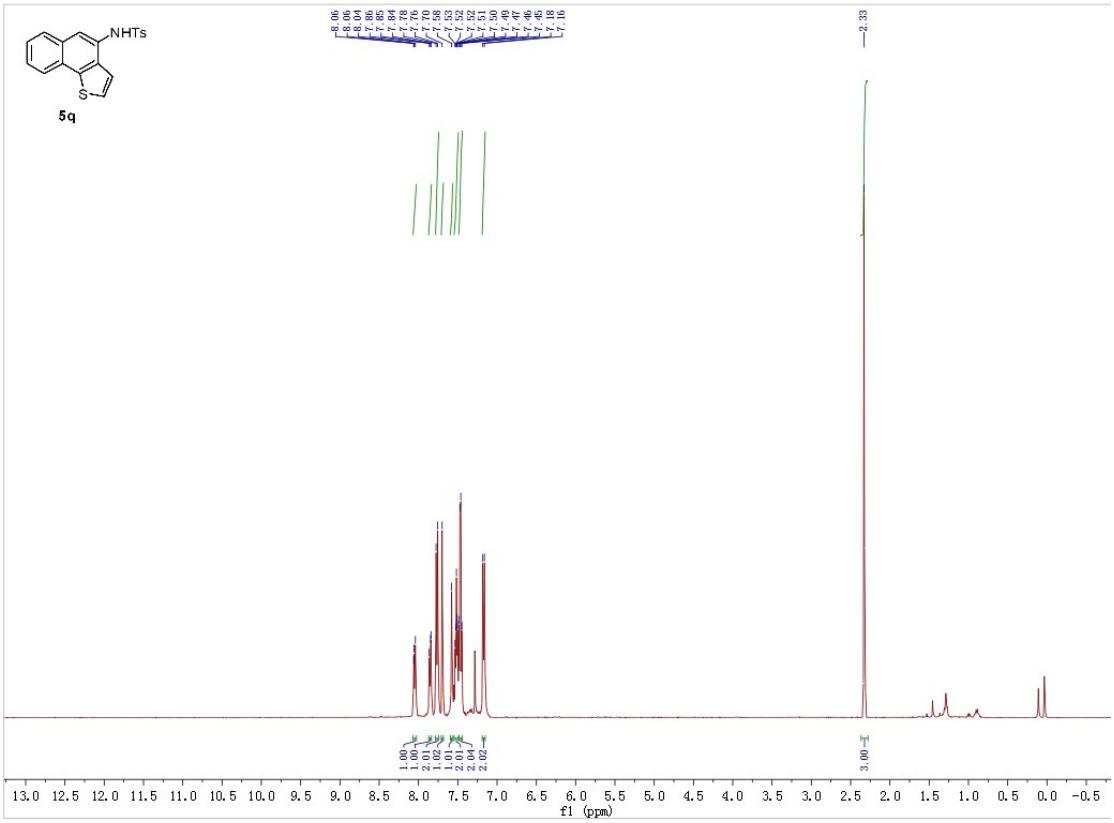

NHTs
5n
f1 (ppm)

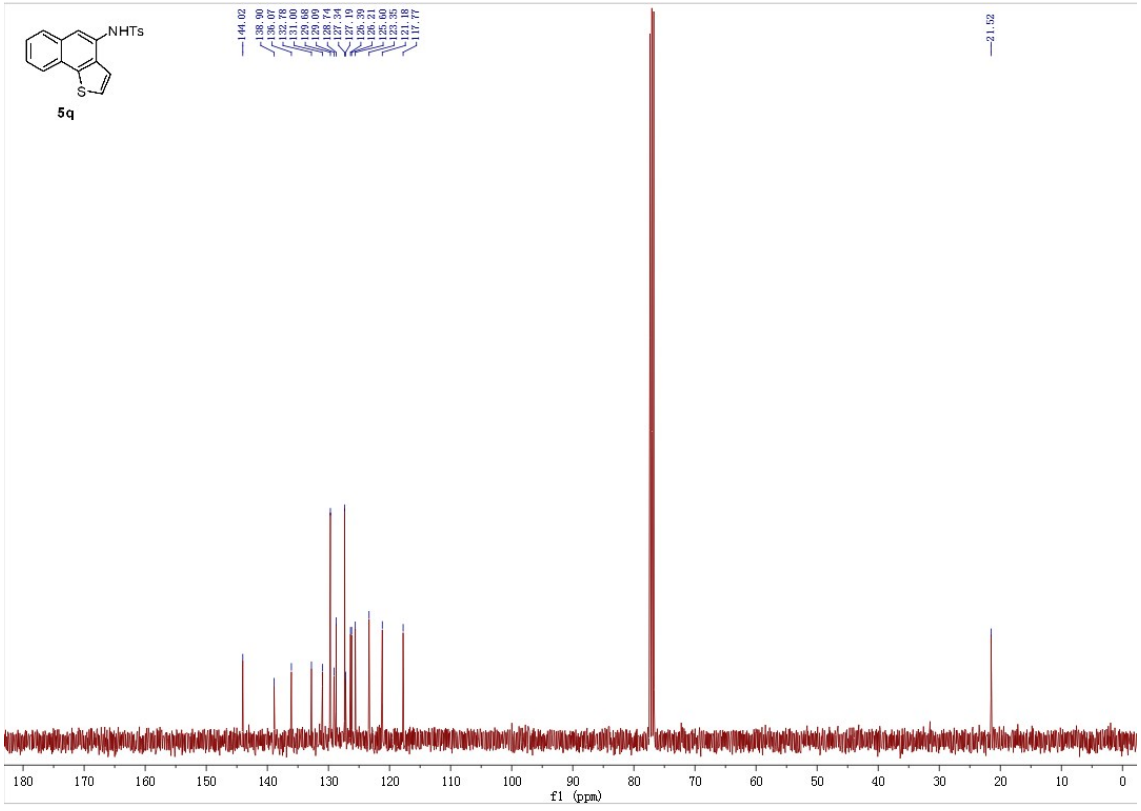

NHTs
CO2Me
5o
10.43
8.52
8.09
7.80
7.78
7.77
7.75
7.59
7.57
7.55
7.45
7.43
7.41
7.20
7.18
3.94
2.33
1.00
1.00
1.00
4.00
1.01
1.04
2.00
3.05
3.00
f1 (ppm)


NHTs
CO2Me
5o
143.76
136.34
136.02
135.19
133.60
132.48
129.51
128.94
128.76
127.38
127.30
125.82
116.96
110.49
52.66
21.48
f1 (ppm)


NHTs
5p
f1 (ppm)


NHTs
5p
f1 (ppm)


NHTs
S
5q
8.06
8.06
8.04
7.86
7.85
7.84
7.78
7.76
7.70
7.58
7.53
7.52
7.52
7.51
7.50
7.49
7.47
7.46
7.45
7.18
7.16
2.33
1.00
1.00
2.01
1.02
1.01
1.01
2.04
2.02
3.00
13.0 12.5 12.0 11.5 11.0 10.5 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 -0.5
f1 (ppm)


NHTs
S
5q
144.02
138.90
136.07
132.78
131.08
129.68
129.09
128.74
127.34
127.19
126.39
126.21
125.60
125.35
121.18
117.77
21.52
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)