Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Ag-Catalyzed cycloisomerization of 1,6-enynamide: an intramolecular Type II Alder-ene Reaction

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Supporting Information

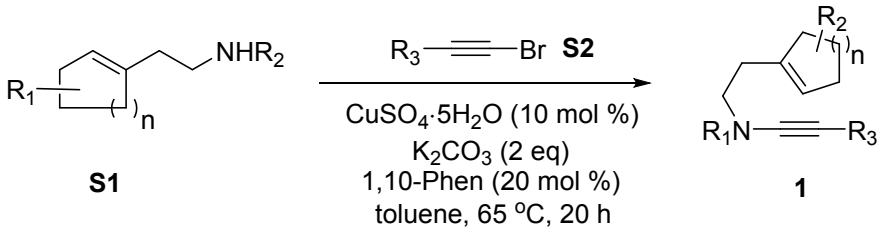
Contents

I. General information and material

NMR spectra were recorded using Bruker AV-300 / AV-400 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, t d = triplet of doublets), coupling constants (Hz) and integration. High resolution mass spectra were acquired on an agilent 6230 spectrometer and were obtained by peak matching. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 60Å (40 – 60 μm) mesh silica gel (SiO2). All reactions were carried out under nitrogen or argon with anhydrous solvents in oven-dried glassware, unless otherwise noted. All reagents were commercially obtained and, where appropriate, purified prior to use.

II. Preparation and characterization of substrates

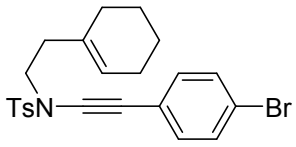
General procedure for the synthesis of enynamide compounds



S1 were obtained following literature protocols.[1-4]

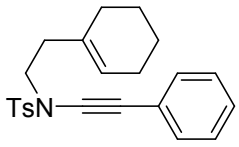
S2 were obtained following the method reported by Feng and co-workers.[5]

A 25 mL round-bottom flask were charged with S**1** (3.0 mmol), S**2** (3.9 mmol), K_2CO_3 (6.0 mmol), $CuSO_4·5H_2O$ (0.3 mmol) and 1,10-Phen (0.6 mmol) and PhMe (10.0 ml). The mixture was heated at 65 °C under N_2 for 20 h. The reaction was monitored by TLC. Upon disappearance of the starting material, the resulting reaction solution was concentrated under reduced pressure. Purification via column chromatography on silica gel afforded enynamides **1**.



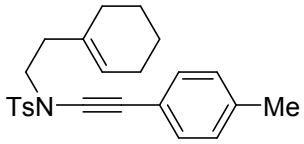
1a

1a: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.45 (s, 1H), 3.47 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 2.29 (t, *J* = 7.4 Hz, 2H), 2.00 – 1.89 (m, 4H), 1.64 – 1.57 (m, 2H), 1.56 – 1.48 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 134.9, 133.4, 132.8, 131.6, 129.9, 127.8, 124.4, 122.1, 121.9, 83.7, 70.1, 50.4, 36.5, 28.3, 25.4, 22.9, 22.3, 21.8. HRMS (ESI) *m/z* Calculated for $C_{23}H_{25}BrNO_2S^+$ $[M + H]^+$ 458.0784, found 458.0777.



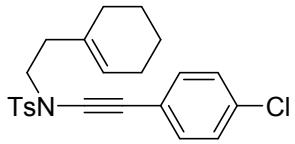
1b

1b: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.32 – 7.27 (m, 3H), 5.46 (s, 1H), 3.47 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.00 – 1.90 (m, 4H), 1.64 – 1.59 (m, 2H), 1.56 – 1.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.66, 134.85, 133.42, 131.42, 129.85, 128.36, 127.81, 127.76, 124.32, 123.07, 82.53, 70.09, 50.40, 36.44, 28.27, 25.34, 22.89, 22.29, 21.76. HRMS (ESI) *m/z* Calculated for $C_{23}H_{25}NNaO_2S^+$ $[M + Na]^+$ 402.1498, found 402.1495.



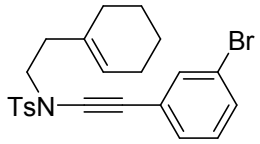
1c

1c: oil. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.40 (s, 1H), 3.44 (t, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 2.29 (s, 3H), 2.22 (t, *J* = 6.9 Hz, 2H), 1.95 – 1.83 (m, 4H), 1.57 – 1.39 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d6) δ 144.9, 137.8, 133.9, 133.2, 131.0, 130.1, 129.3, 127.4, 123.5, 119.0, 81.8, 70.2, 49.8, 35.8, 27.4, 24.7, 22.3, 21.8, 21.1, 21.0. HRMS (ESI) *m/z* Calculated for $C_{24}H_{28}NO_2S^+$ $[M + H]^+$ 394.1835, found 394.1836.



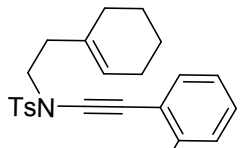
1d

1d: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.24 (m, 4H), 5.47 (s, 1H), 3.48 (t, *J* = 7.5 Hz, 2H), 2.46 (s, 3H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.01 – 1.89 (m, 4H), 1.65 – 1.50 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 134.9, 133.8, 133.4, 132.6, 129.9, 128.7, 127.8, 124.4, 121.6, 83.5, 70.0, 50.4 , 36.5, 28.3, 25.4, 22.9, 22.3, 21.8. HRMS (ESI) *m/z* Calculated for $C_{23}H_{25}ClNO_2S^+$ $[M + H]^+$ 414.1289, found 414.1283.



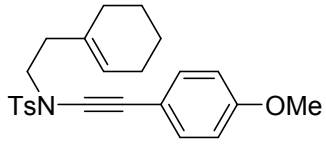
1e

1e: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 1.6 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.30 – 7.26 (m, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 5.45 (s, 1H), 3.47 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 2.29 (t, *J* = 7.4 Hz, 2H), 2.00 – 1.89 (m, 4H), 1.64 – 1.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 134.8, 133.8, 133.2, 130.8, 129.9, 129.8, 129.7, 127.7, 125.1, 124.4, 122.1, 83.9, 69.8, 50.3, 36.4, 28.2, 25.3, 22.9, 22.2, 21.7. HRMS (ESI) *m/z* Calculated for $C_{23}H_{25}BrNO_2S^+$ $[M + H]^+$ 458.0784, found 458.0780.



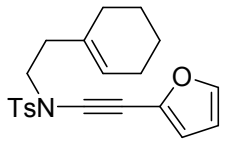
1f

1f: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.54 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.11 (td, *J* = 7.8, 1.6 Hz, 1H), 5.48 (s, 1H), 3.51 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.99 – 1.90 (m, 4H), 1.64 – 1.58 (m, 2H), 1.56 – 1.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 134.9, 133.4, 132.6, 132.4, 129.9, 128.6, 127.8, 127.1, 125.5, 124.7, 124.5, 87.1, 70.3, 50.6, 36.3, 28.3, 25.4, 22.9, 22.3, 21.8. HRMS (ESI) *m/z* Calculated for $C_{23}H_{25}BrNO_2S^+$ $[M + H]^+$ 458.0784, found 458.0777.



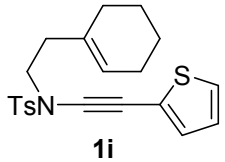
1g

1g: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H) 6.82 (d, *J* = 8.8 Hz, 2H), 5.45 (s, 1H), 3.80 (s, 3H), 3.45 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.98 – 1.89 (m, 4H), 1.63 – 1.58 (m, 2H), 1.55 – 1.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.55, 144.54, 134.90, 133.54, 133.50, 129.80, 127.79, 124.22, 115.00, 114.00, 81.01, 70.46, 55.42, 50.48, 36.42, 28.30, 25.36, 22.91, 22.31, 21.77. HRMS (ESI) *m/z* Calculated for $C_{24}H_{28}NO_3S^+$ $[M + H]^+$ 410.1784, found 410.1783.



1h

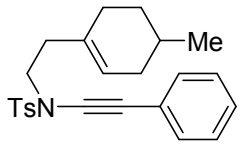
1h: oil. ^{1}H NMR (300 MHz, DMSO-d6) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.73 (dd, *J* = 1.8, 0.6 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 6.80 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.55 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.38 (s, 1H), 3.49 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.18 (t, *J* = 6.9 Hz, 2H), 1.96 – 1.81 (m, 4H), 1.56 – 1.40 (m, 4H). ^{13}C NMR (75 MHz, DMSO) δ 145.3, 145.2, 135.6, 134.0, 133.1, 130.3, 127.3, 123.8, 117.7, 111.6, 86.5, 61.1, 49.9, 35.9, 27.3, 24.8, 22.3, 21.8, 21.2. HRMS (ESI) *m/z* Calculated for $C_{21}H_{24}NO_3S^+$ $[M + H]^+$ 370.1471, found 370.1468.



1i

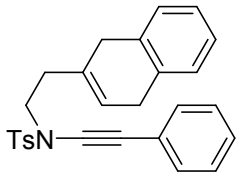
1i: oil. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 5.0 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 3.3 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.8 Hz, 1H), 5.38 (s, 1H), 3.47 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.19 (t, *J* = 6.8 Hz, 2H), 1.96 – 1.81 (m, 4H), 1.57 – 1.41 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d6) δ 145.1, 133.9, 133.4, 133.1, 130.2, 129.2, 127.7, 127.3, 123.7, 121.7, 86.0, 63.5, 49.9, 36.0, 27.3,

24.8, 22.3, 21.8, 21.2. HRMS (ESI) *m/z* Calculated for $C_{21}H_{24}NO_2S_2^+$ $[M + H]^+$ 386.1243， found 386.1243.



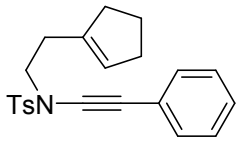
1j

1j: oil. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.35 (s, 5H), 5.37 (s, 1H), 3.46 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 2.24 (t, *J* = 6.7 Hz, 2H), 2.04 – 1.87 (m, 4H), 1.65 – 1.58 (m, 1H), 1.54 – 1.49 (m, 1H), 1.14 – 1.07 (m, 1H), 0.86 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 145.0, 133.9, 132.8, 130.9, 130.1, 128.7, 128.0, 127.4, 123.1, 122.1, 82.5, 70.3, 49.8, 35.4, 33.3, 30.5, 27.6, 27.4, 21.5, 21.1. HRMS (ESI) *m/z* Calculated for $C_{24}H_{27}NNaO_2S^+$ $[M + Na]^+$ 416.1655, found 416.1654.



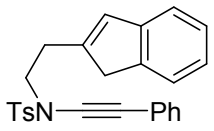
1k

1k: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.28 (m, 5H), 7.17 – 7.09 (m, 3H), 6.99 – 6.93 (m, 1H), 6.24 (s, 1H), 3.63 (t, *J* = 7.3 Hz, 2H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.26 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 136.9, 134.7, 134.5, 134.4, 131.6, 129.9, 128.4, 128.0, 127.8, 127.3, 126.7, 126.5, 125.8, 125.2, 122.9, 82.3, 71.2, 50.1, 36.0, 28.0, 27.2, 21.8. HRMS (ESI) *m/z* Calculated for $C_{27}H_{26}NO_2S^+$ $[M + H]^+$ 428.1679, found 428.1681.



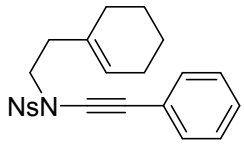
1l

1l: oil. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.35 (s, 5H), 5.41 (s, 1H), 3.51 (t, *J* = 7.1 Hz, 2H), 2.43 – 2.37 (m, 5H), 2.20 (t, *J* = 7.4 Hz, 4H), 1.82 – 1.68 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.0, 139.8, 133.7, 130.9, 130.1, 128.6, 128.1, 127.4, 125.8, 122.1, 82.4, 70.3, 49.7, 34.3, 32.1, 29.1, 22.7, 21.1. HRMS (ESI) *m/z* Calculated for $C_{22}H_{24}NO_2S^+$ $[M + H]^+$ 366.1522, found 366.1527.



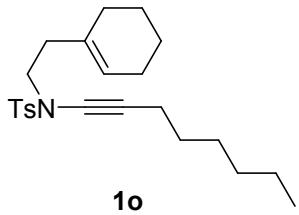
1m

1m: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.28 (m, 7H), 7.26 – 7.21 (m, 3H), 7.13 (td, *J* = 7.1, 1.7 Hz, 1H), 6.56 (s, 1H), 3.70 (t, *J* = 7.2 Hz, 2H), 3.32 (s, 2H), 2.90 (t, *J* = 7.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.14, 145.05, 144.79, 143.21, 134.60, 131.58, 129.87, 129.02, 128.41, 128.00, 127.73, 126.44, 124.26, 123.61, 122.85, 120.45, 82.04, 71.42, 50.94, 41.10, 29.82, 21.79. HRMS (ESI) *m/z* Calculated for $C_{26}H_{23}NNaO_2S^+$ $[M + Na]^+$ 436.1342, found 436.1344.



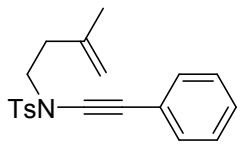
1n

1n: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 2H), 8.14 (d, *J* = 8.6 Hz, 2H), 7.42 – 7.28 (m, 5H), 5.48 (s, 1H), 3.54 (t, *J* = 7.4 Hz, 2H), 2.33 (t, *J* = 7.3 Hz, 2H), 2.02 – 1.85 (m, 4H), 1.65 – 1.57 (m, 2H), 1.56 – 1.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.66, 143.21, 132.98, 131.70, 128.96, 128.54, 128.47, 124.88, 124.53, 122.23, 81.08, 71.55, 50.91, 36.51, 28.24, 25.37, 22.86, 22.25. HRMS (ESI) *m/z* Calculated for $C_{22}H_{22}KN_2O_4S^+$ $[M + K]^+$ 449.0932, found 449.0931.



1o

1o: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.42 (s, 1H), 3.32(t, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 2.28 – 2.18 (m, 4H), 1.97 – 1.87 (m, 4H), 1.62 – 1.55 (m, 2H), 1.54 – 1.42 (m, 4H), 1.38 – 1.24 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 134.9, 133.7, 129.7, 127.7, 124.0, 73.1, 70.5, 50.3, 36.3, 31.5, 29.0, 28.6, 28.3, 25.3, 22.9, 22.7, 22.3, 21.7, 18.6, 14.2.

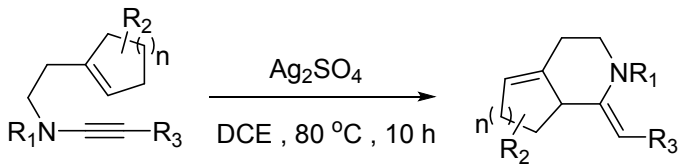


1p

1p: oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.34 (m, 4H),

7.33 – 7.26 (m, 3H), 4.84 – 4.79 (m, 1H), 4.75 (s, 1H), 3.53 (t, *J* = 7.5 Hz, 2H), 2.46 (s, 3H), 2.41 (t, *J* = 7.3 Hz, 2H), 1.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.3, 134.6, 131.4, 129.9, 128.4, 127.9, 127.8, 122.9, 113.0, 82.3, 71.0, 50.1, 36.0, 22.4, 21.8.

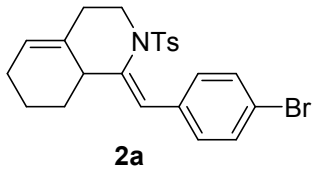
III. Alder-Ene reaction



1 **2**

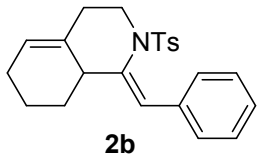
General procedure

To a 10 mL sealed tube equipped with a stir bar were added **1** (0.2 mmol), Ag_2SO_4 (0.04 mmol) and anhydrous DCE (2.0 ml). The mixture was heated at 80 °C (the temperature of oil bath) under N_2 for 10 h. When completed as indicated by TLC, the resulting reaction solution was concentrated under reduced pressure. Purification via column chromatography on silica gel afforded **2** in 40 ~ 70% yields.



2a

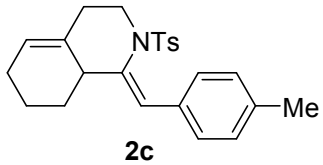
2a: half solid. Yield 55%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.07 – 6.98 (m, 4H), 6.23 (d, *J* = 2.0 Hz, 1H), 5.54 – 5.44 (m, 1H), 4.20 – 4.05 (m, 1H), 3.23 – 3.01 (m, 2H), 2.61 – 2.46 (m, 1H), 2.37 (s, 3H), 2.21 – 2.12 (m, 1H), 2.06 – 1.94 (m, 3H), 1.84 – 1.73 (m, 1H), 1.73 – 1.52 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 140.5, 137.7, 135.5, 134.9, 131.1, 130.4, 129.3, 127.4, 123.8, 122.7, 120.9, 49.1, 42.4, 34.0, 26.7, 25.4, 21.7, 21.3. HRMS (ESI) *m/z* Calculated for $C_{23}H_{25}BrNO_2S^+$ $[M + H]^+$ 458.0784, found 458.0786.



2b

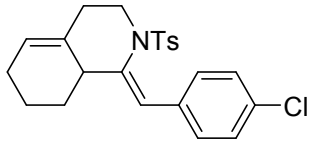
2b: oil. Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.23 – 7.11 (m, 5H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.33 (s, 1H), 5.48 (s, 1H), 4.08 (dd, *J* = 13.6, 4.6 Hz, 1H), 3.23 – 3.03 (m, 2H), 2.53 (t, *J* = 14.2 Hz, 1H), 2.32 (s, 3H), 2.14 (d, *J* = 14.1 Hz, 1H), 2.06 – 1.94(m, 3H), 1.84 – 1.67 (m, 2H), 1.57 – 1.50 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 139.3, 137.4, 136.1, 135.9, 129.2, 128.9, 128.1, 127.7,

127.0, 125.2, 122.5, 48.8, 42.2, 33.8, 26.7, 25.5, 21.6, 21.3. HRMS (ESI) *m/z* Calculated for $C_{23}H_{25}NNaO_2S^+$ $[M + Na]^+$ 402.1498, found 402.1496.



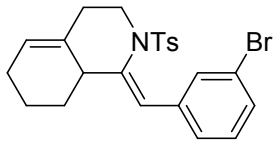
2c

2c: solid, mp 129~133 °C. Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.30 (s, 1H), 5.46 (s, 1H), 4.10 (dd, *J* = 13.2, 4.2 Hz, 1H), 3.26 – 3.10 (m, 1H), 3.09 – 3.00 (m, 1H), 2.55 – 2.45 (m, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 2.16 – 2.10 (m, 1H), 2.05 – 1.95 (m, 3H), 1.83 – 1.76 (m, 1H), 1.74 – 1.67 (m, 1H), 1.58 – 1.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.91, 138.54, 137.79, 136.70, 135.88, 133.05, 129.11, 128.72, 128.67, 127.60, 124.97, 122.34, 48.80, 42.12, 33.77, 26.63, 25.43, 21.54, 21.32, 21.27. HRMS (ESI) *m/z* Calculated for $C_{24}H_{27}NNaO_2S^+$ $[M + Na]^+$ 416.1655, found 416.1653.



2d

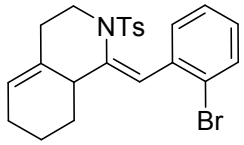
2d: solid, mp 122~124 °C. Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.07 – 7.01 (m, 4H), 6.25 (d, *J* = 1.9 Hz, 1H), 5.48 (s, 1H), 4.13 (dd, *J* = 13.3, 4.3 Hz, 1H), 3.24 – 3.03 (m, 2H), 2.58 – 2.46 (m, 1H), 2.35 (s, 3H), 2.19 – 2.12 (m, 1H), 2.06 – 1.95 (m, 3H), 1.84 – 1.76 (m, 1H), 1.74 – 1.64 (m, 1H), 1.58 – 1.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.3, 137.8, 135.6, 134.5, 132.7, 130.0, 129.3, 128.2, 127.4, 123.7, 122.7, 49.1, 42.4, 34.0, 26.7, 25.4, 21.6, 21.3. HRMS (ESI) *m/z* Calculated for $C_{23}H_{24}ClNNaO_2S^+$ $[M + Na]^+$ 436.1108, found 436.1107.



2e

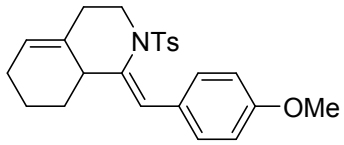
2e: oil. Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.05 – 6.97 (m, 3H), 6.22 (d, *J* = 1.8 Hz, 1H), 5.49 (s, 1H), 4.13 (dd, *J* = 13.5, 4.3 Hz, 1H), 3.21 – 3.05 (m, 2H), 2.67 – 2.51 (m, 1H), 2.33 (s, 3H), 2.20 – 2.13 (m, 1H), 2.06 – 1.95 (m, 3H), 1.83 – 1.76(m, 1H), 1.72 – 1.65 (m, 1H), 1.59 – 1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 141.0, 138.1, 137.1, 135.5, 131.6, 129.8, 129.5, 129.3, 127.5, 127.4, 123.6, 122.8, 122.2, 49.0, 42.3, 34.0, 26.7, 25.4, 21.6, 21.3. HRMS (ESI) *m/z* Calculated for $C_{23}H_{24}BrNNaO_2S^+$ [M +

Na]$^+$ 480.0603, found 480.0593.



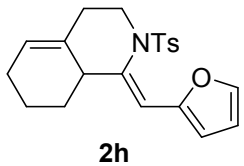
2f

2f: solid, mp 145~149 ^{o}C. Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 3H), 7.21 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.07 – 7.01 (m, 1H), 7.00 – 6.93 (m, 3H), 6.40 (d, *J* = 1.9 Hz, 1H), 5.50 (s, 1H), 4.17 – 4.09 (m, 1H), 3.21 – 3.11 (m, 2H), 2.66 – 2.53 (m, 1H), 2.30 (s, 3H), 2.22 – 2.16 (m, 1H), 2.12 – 2.05 (m, 1H), 2.03 – 1.96 (m, 2H), 1.85 – 1.78 (m, 1H), 1.75 – 1.68 (m, 1H), 1.61 – 1.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 140.8, 136.7, 136.3, 135.6, 132.2, 130.3, 129.2, 128.3, 127.5, 126.9, 124.7, 124.4, 122.7, 49.1, 42.1, 34.0, 26.7, 25.4, 21.6, 21.3. HRMS (ESI) *m/z* Calculated for $C_{23}H_{24}BrNNaO_2S^+$ [M + Na]$^+$ 480.0603, found 480.0605.



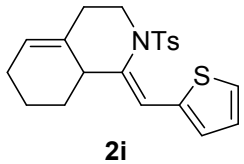
2g

2g: half solid. Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.25 (d, *J* = 0.92 Hz, 1H), 5.45 (s, 1H), 4.12 (dd, *J* = 13.2, 4.2 Hz, 1H), 3.77 (s, 3H), 3.16 (t, *J* = 12.3 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.33 (s, 3H), 2.15 – 2.08 (m, 1H), 2.03 – 1.94 (m, 3H), 1.82 – 1.75 (m, 1H), 1.73 – 1.65(m, 1H), 1.55 – 1.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 143.0, 137.8, 137.6, 135.9, 130.0, 129.1, 128.4, 127.6, 124.5, 122.3, 113.4, 55.2, 48.7, 41.9, 33.7, 26.6, 25.4, 21.5, 21.2. HRMS (ESI) *m/z* Calculated for $C_{24}H_{28}NO_3S^+$ [M+H]$^+$ 410.1784, found 410.1790.



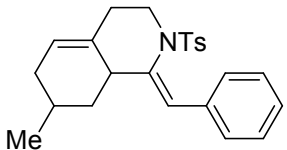
2h

2h: half solid. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.22 (m, 3H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.35 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.32 (d, *J* = 1.8 Hz, 1H), 5.36 (s, 1H), 4.11 – 4.02 (m, 1H), 3.17 (td, *J* = 13.1, 2.6 Hz, 1H), 2.88 – 2.79 (m, 1H), 2.40 (s, 3H), 2.10 – 1.99 (m, 1H), 1.97 – 1.87 (m, 4H), 1.81 – 1.72 (m, 1H), 1.69 – 1.62 (m, 1H), 1.51 – 1.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 143.5, 141.3, 138.5, 137.1, 135.4, 129.7, 127.8, 122.4, 115.4, 111.6, 110.4, 48.2, 41.1, 32.5, 26.4, 25.3, 21.7, 21.1. HRMS (ESI) *m/z* Calculated for $C_{21}H_{24}NO_3S^+$ [M + H]$^+$ 370.1471, found 370.1468.



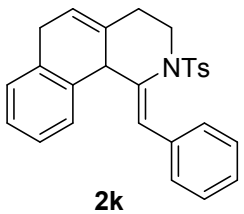
2i

2i: solid, mp 125~128 °C. Yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 3H), 7.03 (d, *J* = 3.4 Hz, 1H), 6.89 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.60 (d, *J* = 1.8 Hz, 1H), 5.36 (s, 1H), 4.17 (dd, *J* = 13.9, 4.8 Hz, 1H), 3.21 (td, *J* = 13.4, 3.0 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.40 (s, 3H), 2.23 – 2.11 (m, 1H), 2.00 – 1.88 (m, 4H), 1.80 – 1.73 (m, 1H), 1.71 – 1.64 (m, 1H), 1.51 – 1.41 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 138.3, 138.2, 136.9, 135.6, 129.7, 128.8, 128.1, 126.6, 125.8, 122.3, 120.2, 48.4, 40.7, 32.4, 26.3, 25.3, 21.7, 21.1. HRMS (ESI) *m/z* Calculated for $C_{21}H_{23}NNaO_2S^+$ $[M + Na]^+$ 408.1062, found 408.1059.



2j

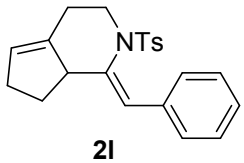
2j: oil. Yield: 53%. Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.25 – 7.12 (m, 5H), 7.04 – 6.97 (m, 2H), 6.29 (s, 1H), 5.44 (s, 1H), 4.19 – 4.11 (m, 1H), 3.23 – 3.00 (m, 2H), 2.47 – 2.38 (m, 1H), 2.32 (s, 3H), 2.19 – 1.90 (m, 4H), 1.69 – 1.56 (m, 2H), 0.97 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.06, 139.21, 137.32, 135.94, 135.83, 129.14, 128.75, 128.01, 127.58, 126.89, 124.11, 120.90, 49.53, 41.12, 34.07, 33.29, 28.47, 24.98, 21.46, 20.71. Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.25 – 7.12 (m, 5H), 7.04 – 6.97 (m, 2H), 6.33 (s, 1H), 5.44 (s, 1H), 4.11 – 4.02 (m, 1H), 3.23 – 3.00 (m, 2H), 2.47 – 2.38 (m, 1H), 2.31 (s, 3H), 2.19 – 1.90 (m, 4H), 1.69 – 1.56 (m, 2H), 1.03 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.99, 139.16, 137.18, 135.74, 135.18, 129.09, 128.70, 127.96, 127.58, 126.81, 124.11, 120.90, 48.33, 41.12, 34.15, 32.82, 28.47, 24.98, 22.27, 21.46. HRMS (ESI) *m/z* Calculated for $C_{24}H_{27}NNaO_2S^+$ $[M + Na]^+$ 416.1655, found 416.1651.



2k

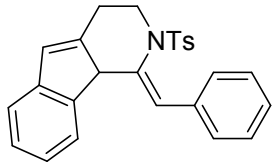
2k: solid, mp 132~135 °C. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.26 (m, 3H), 7.24 – 7.10 (m, 8H), 5.87 (s, 1H), 5.63 (s, 1H), 4.39 (dd, *J* = 13.5, 5.1 Hz, 1H), 4.23 – 4.16 (m, 1H), 3.51 – 3.39 (m, 1H), 3.38 – 3.27 (m, 2H), 2.57 – 2.47 (m, 1H), 2.34 (s, 3H), 2.29 (dd, *J* = 13.2, 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.4, 137.7, 135.2, 135.1, 134.4, 132.2, 130.5, 129.5, 128.9,

128.6, 128.0, 127.7, 127.3, 127.1, 126.7, 126.4, 117.8, 50.5, 48.1, 34.5, 29.6, 21.6. HRMS (ESI) *m/z* Calculated for $C_{27}H_{25}NNaO_2S^+$ $[M + Na]^+$ 450.1498, found 450.1495.



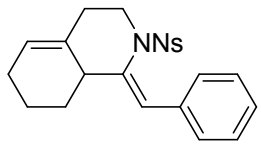
2l

2l: half solid. Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.18 (m, 2H), 7.15 – 7.10 (m, 3H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.23 (d, *J* = 2.4 Hz, 1H), 5.45 – 5.37 (m, 1H), 4.18 (ddd, *J* = 13.8, 5.4, 1.5 Hz, 1H), 3.52 – 3.44 (m, 1H), 3.07 (ddd, *J* = 13.7, 12.5, 4.2 Hz, 1H), 2.49 – 2.34 (m, 3H), 2.31 (s, 3H), 2.28 – 2.06 (m, 2H), 1.93 – 1.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 141.1, 140.2, 137.6, 135.9, 129.3, 128.7, 128.1, 127.7, 126.9, 124.9, 123.1, 49.4, 48.1, 30.7, 27.9, 27.6, 21.6. HRMS (ESI) *m/z* Calculated for $C_{22}H_{23}NNaO_2S^+$ $[M + Na]^+$ 388.1342, found 388.1344.



2m

2m: oil. Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.21 – 7.16 (m, 2H), 7.14 – 7.10 (m, 3H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.53 – 6.42 (m, 2H), 4.44 (dd, *J* = 13.6, 5.8 Hz, 1H), 4.20 (s, 1H), 3.21 (td, *J* = 13.0, 3.6 Hz, 1H), 2.89 (td, *J* = 13.0, 5.8 Hz, 1H), 2.73 (dd, *J* = 13.8, 3.2 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 144.7, 143.5, 141.9, 137.3, 136.2, 134.8, 129.4, 128.9, 128.0, 127.7, 127.5, 127.4, 125.7, 125.4, 124.4, 123.8, 121.4, 55.1, 50.3, 28.8, 21.6. HRMS (ESI) *m/z* Calculated for $C_{26}H_{23}NNaO_2S^+$ $[M + Na]^+$ 436.1342, found 436.1348.



2n

2n: solid, mp 122~125 °C. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.08 – 6.92 (m, 5H), 6.32 (s, 1H), 5.55 (s, 1H), 4.23 (dd, *J* = 12.2, 3.3 Hz, 1H), 3.31 – 3.09 (m, 2H), 2.78 – 2.60 (m, 1H), 2.29 (d, *J* = 14.1 Hz, 1H), 2.13 – 1.98 (m, 3H), 1.85 – 1.77 (m, 1H), 1.77 – 1.67 (m, 1H), 1.63 – 1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 146.0, 139.6, 135.6, 135.1, 128.6, 128.5, 128.2, 127.2, 125.1, 123.6, 123.4, 49.9, 42.9, 34.9, 26.7, 25.5, 21.3. HRMS (ESI) *m/z* Calculated for $C_{22}H_{23}N_2O_4S^+$ $[M + H]^+$ 411.1373, found 411.1388.

IV. References

1. Dobbs, Adrian P.; Guesne, Sebastien J. J.; *Org. Biomol. Chem.* **2010**, *8*, 1064.
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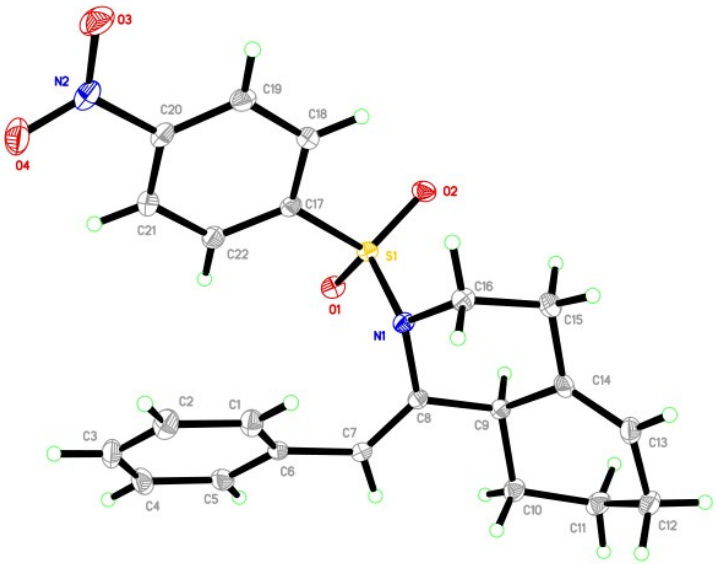
3. Ellingboe, J. W.; Alessi, T. R. *J. Med. Chem.* **1992**, *35*, 1176.
4. Maria, C. M.; Valerio, C. *Synthesis.* **2006**, *16*, 2760.
5. Xu, H. J.; Feng, Y. S. *Org. Lett*. **2013**, *7*, 1472.

V. Crystal data and structure refinement for 2n (CCDC 1951227)



Bond precision: C-C = 0.0025 A Wavelength=0.71073

Cell: a=7.3192(14) b=11.674(2) c=23.041(4)

alpha=90 beta=95.345(6) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1960.2(6)	1960.2(7)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C22 H22 N2 O4 S	?
Sum formula	C22 H22 N2 O4 S	C22 H22 N2 O4 S
Mr	410.48	410.47
Dx,g cm-3	1.391	1.391
Z	4	4
Mu (mm-1)	0.198	0.198
F000	864.0	864.0
F000'	864.88	
h,k,lmax	8,13,27	8,13,27
Nref	3463	3456
Tmin, Tmax	0.950, 0.957	
Tmin'	0.950	

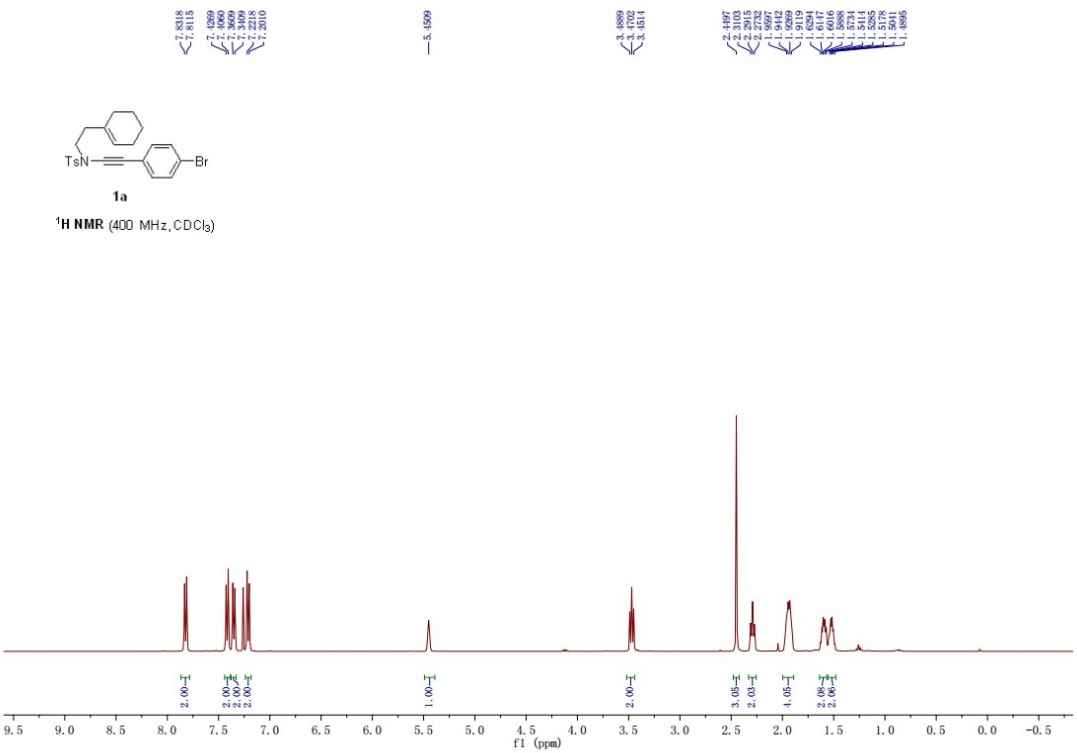
Correction method= Not given

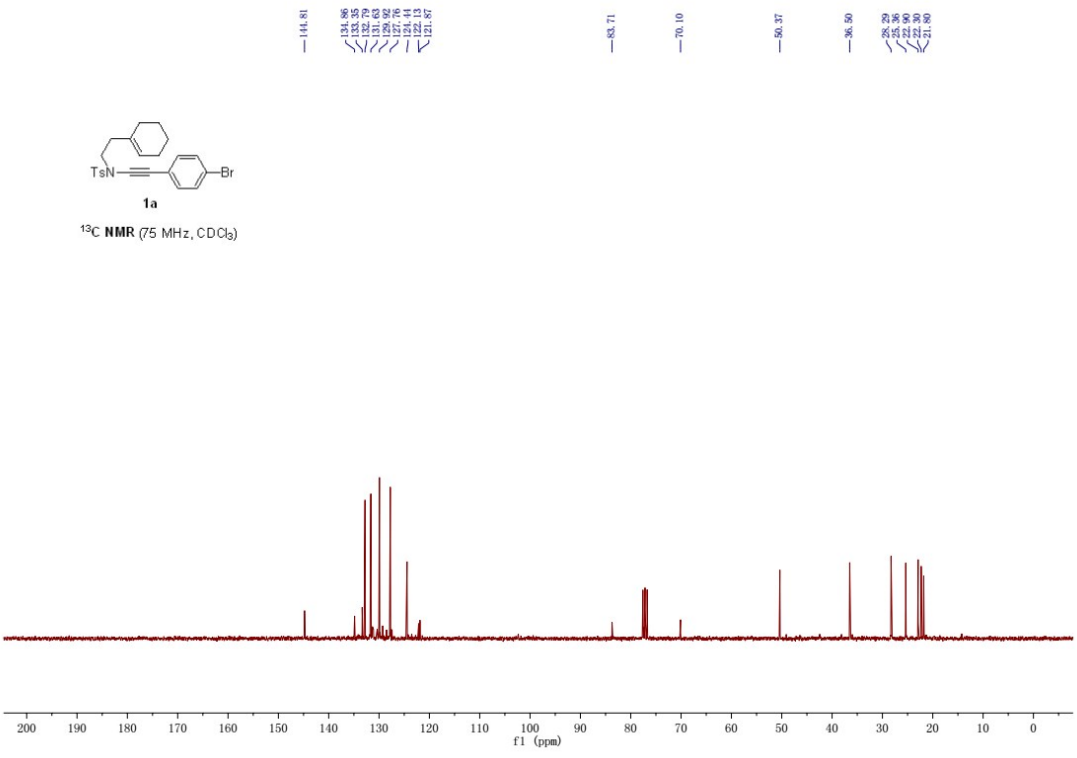
Data completeness= 0.998 Theta(max)= 25.009

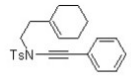
R(reflections)= 0.0368(2982) wR2(reflections)= 0.0942(3456)

S = 1.017 Npar= 262

VI. ^{1}H and ^{13}C NMR Spectra of Compounds

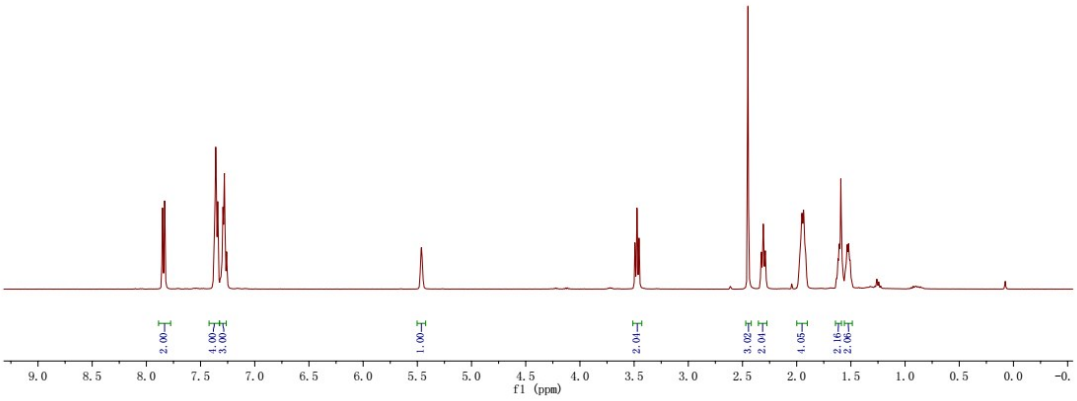


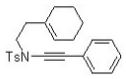




1b

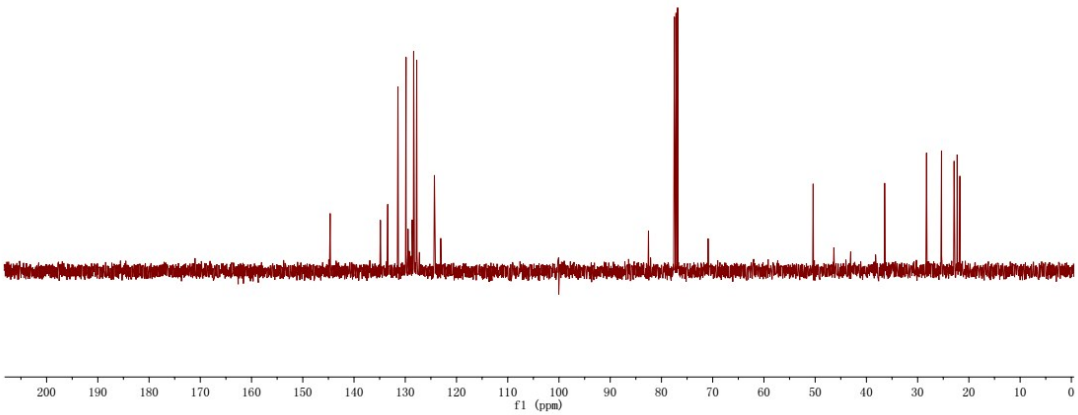
^{1}**H NMR** (400 MHz, $CDCl_3$)

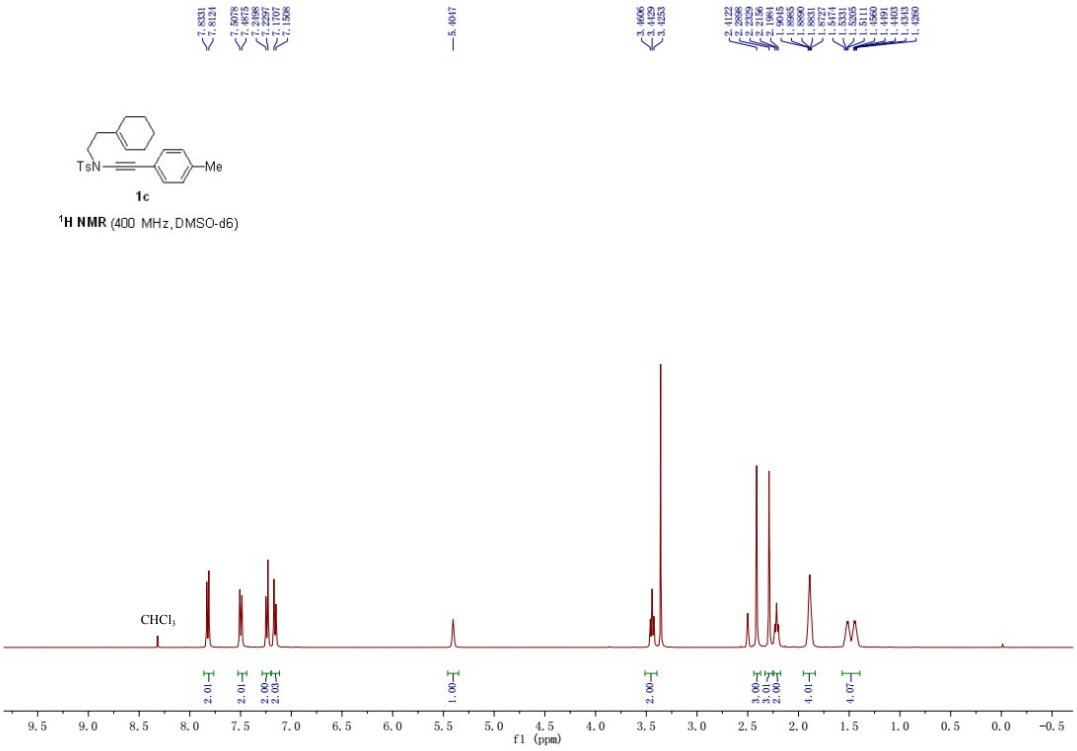


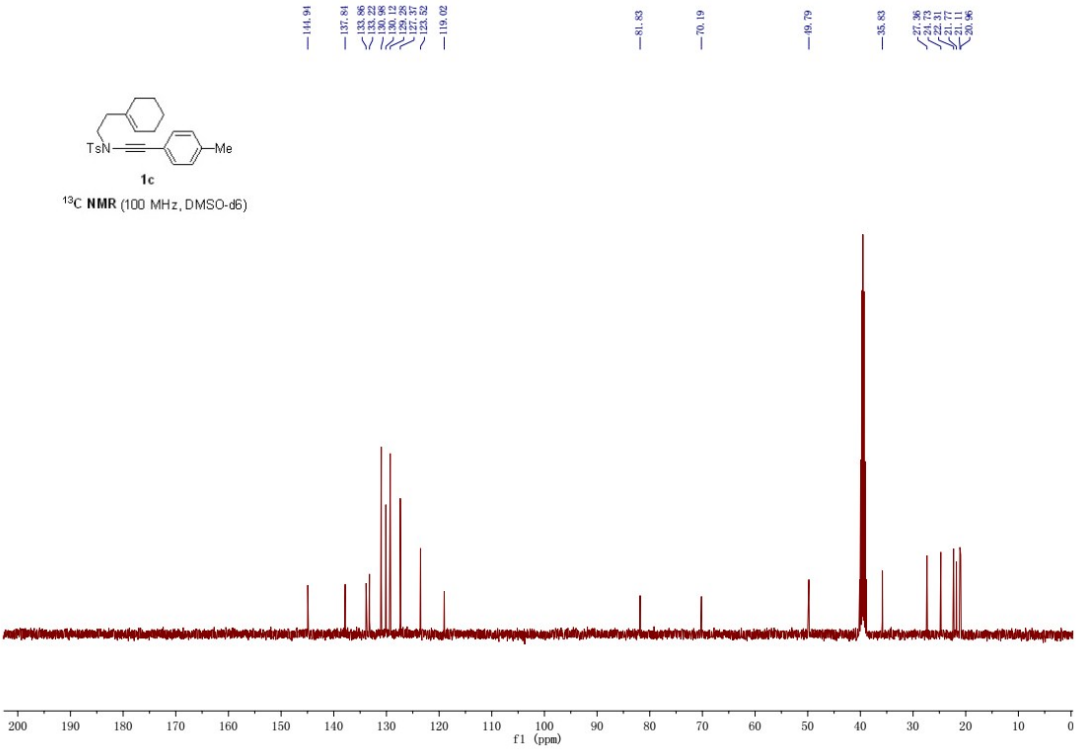


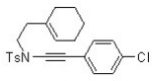
1b

^{13}**C NMR** (100 MHz, $CDCl_3$)



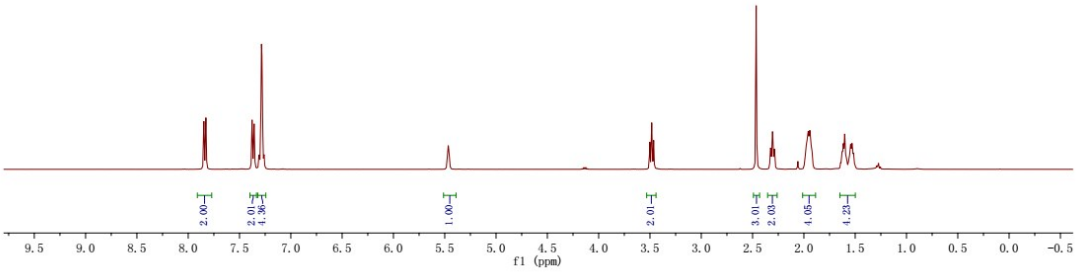

TsN
Me
1c
1H NMR (400 MHz, DMSO-d6)
CHCl3
f1 (ppm)

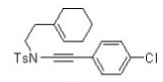

TsN
Me
1c
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)



1d

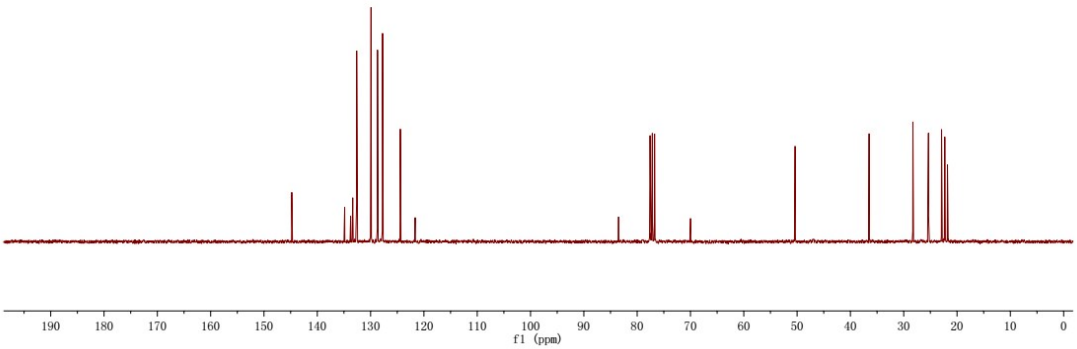
^{1}**H NMR** (400 MHz, $CDCl_3$)

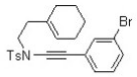




1d

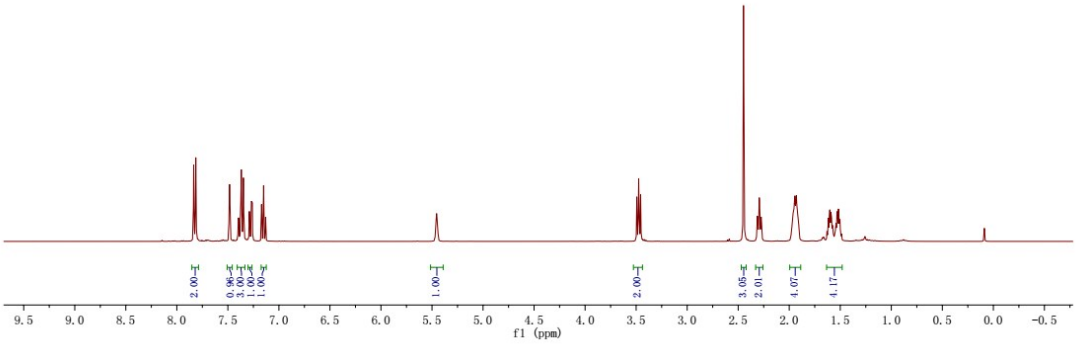
^{13}**C NMR** (75 MHz, $CDCl_3$)

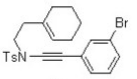




1e

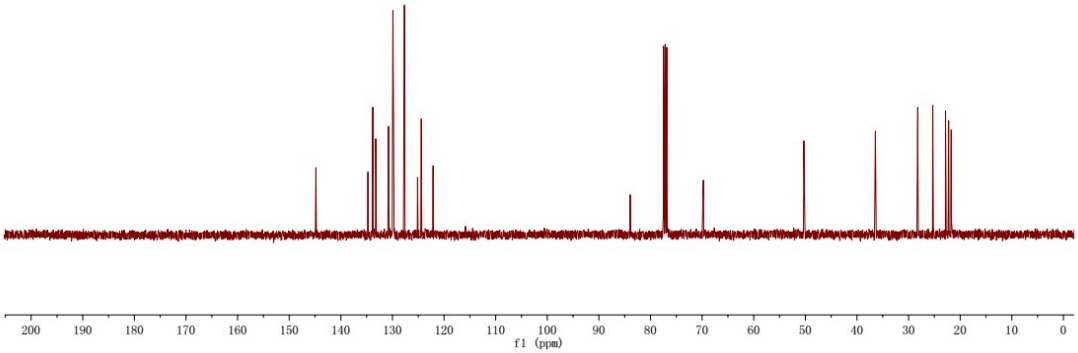
^{1}**H NMR** (400 MHz, $CDCl_3$)

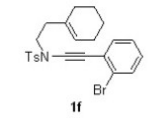




1e

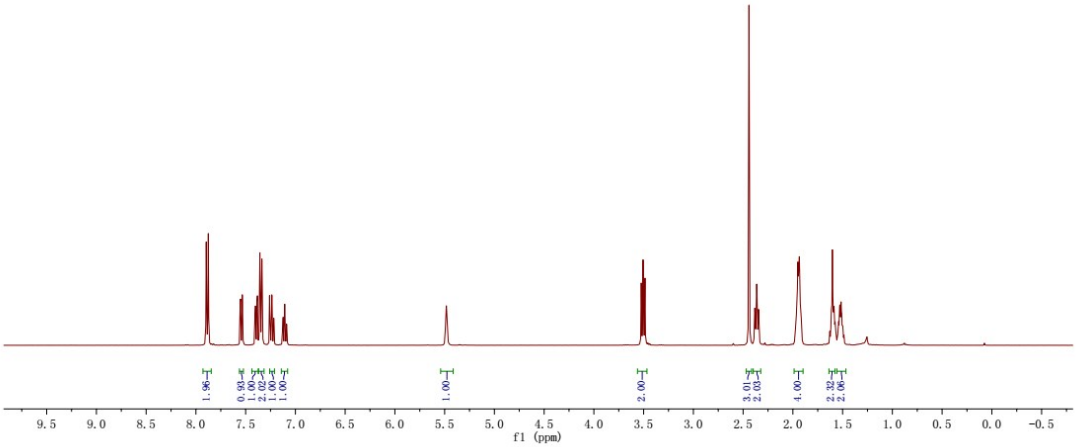
^{13}**C NMR** (100 MHz, $CDCl_3$)

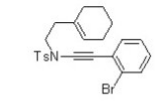




1f

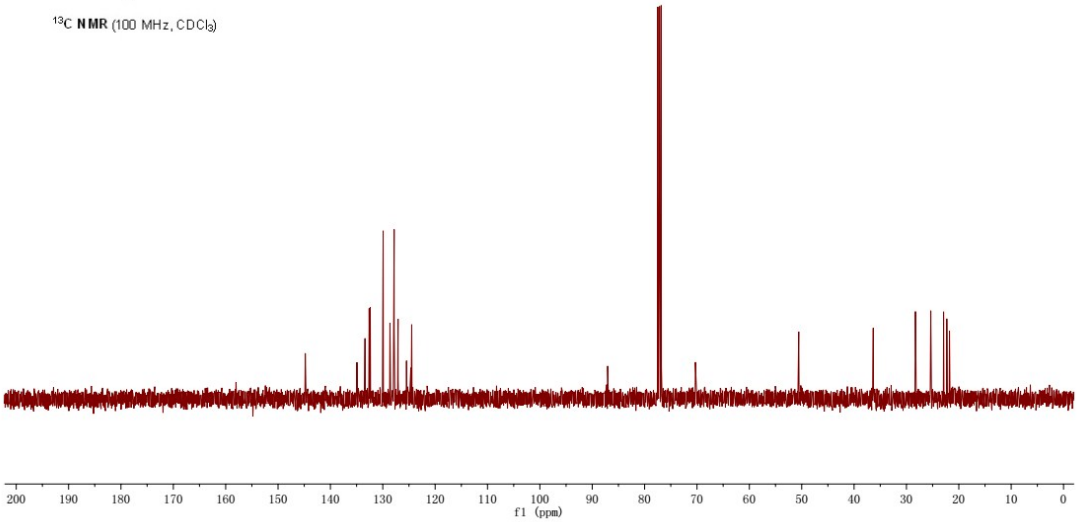
^{1}H NMR (400 MHz, $CDCl_3$)

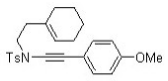




1f

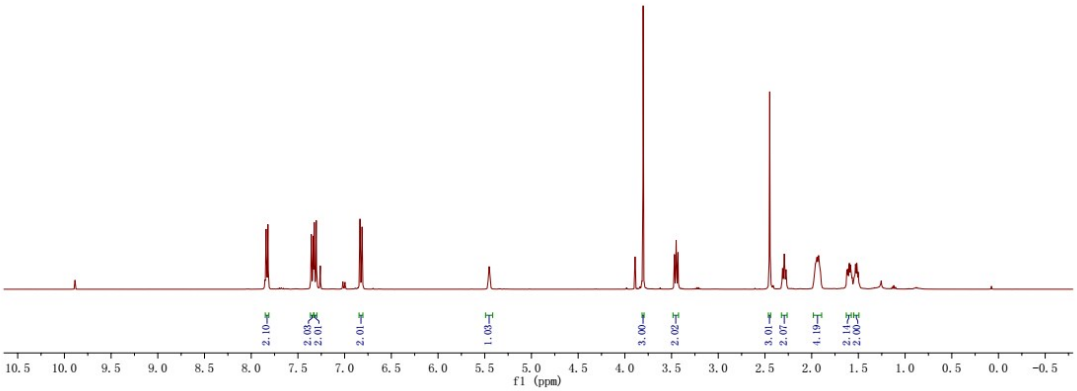
^{13}C NMR (100 MHz, $CDCl_3$)

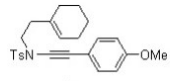




1g

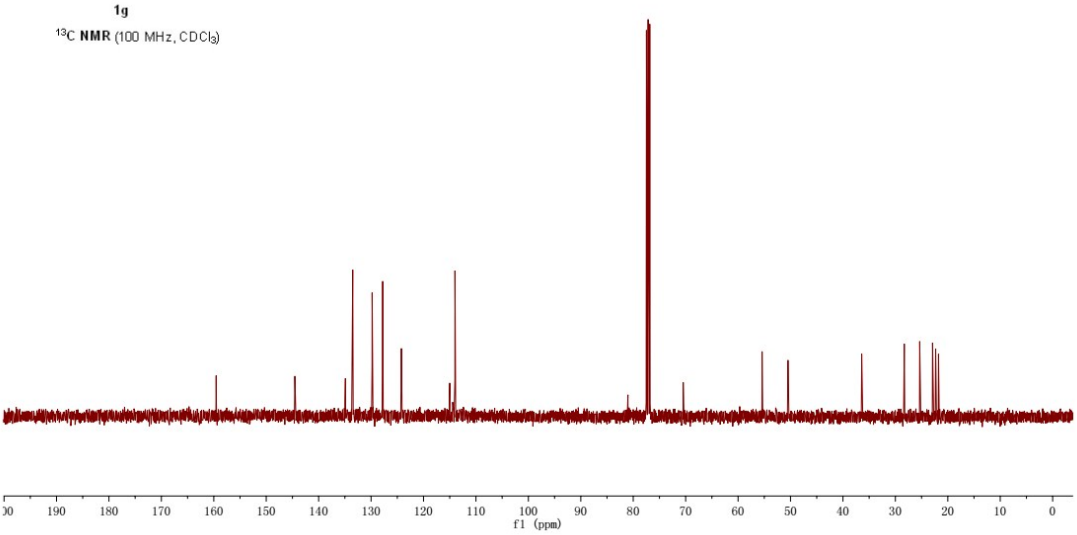
^{1}H NMR (400 MHz, $CDCl_3$)

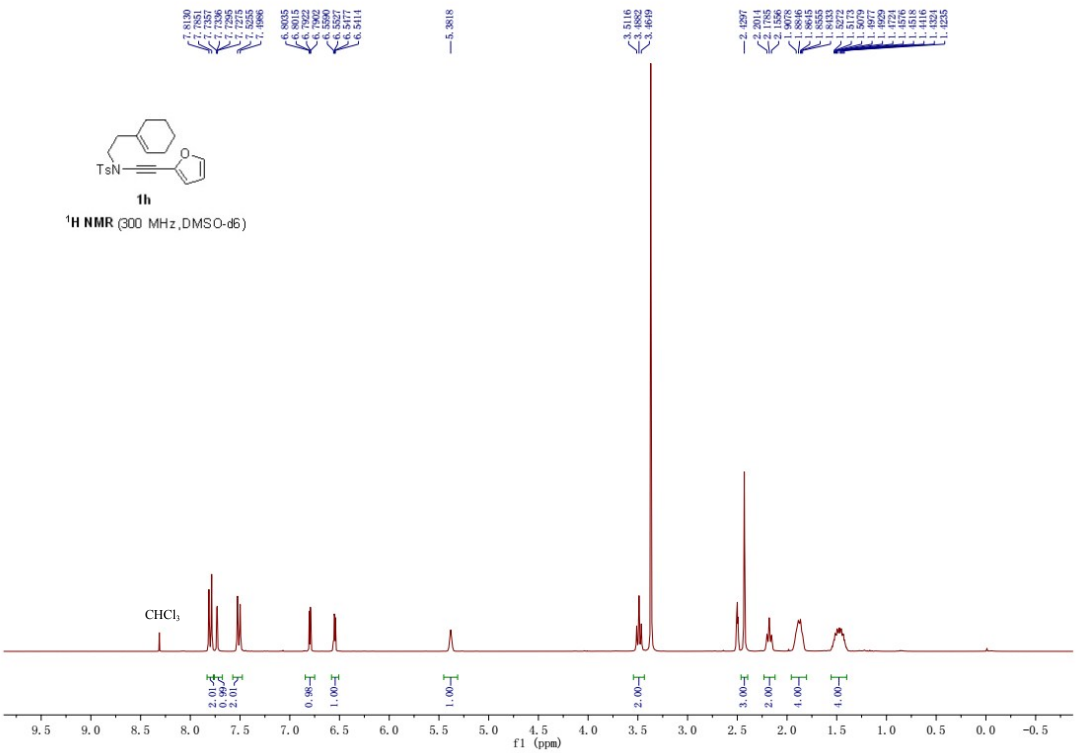


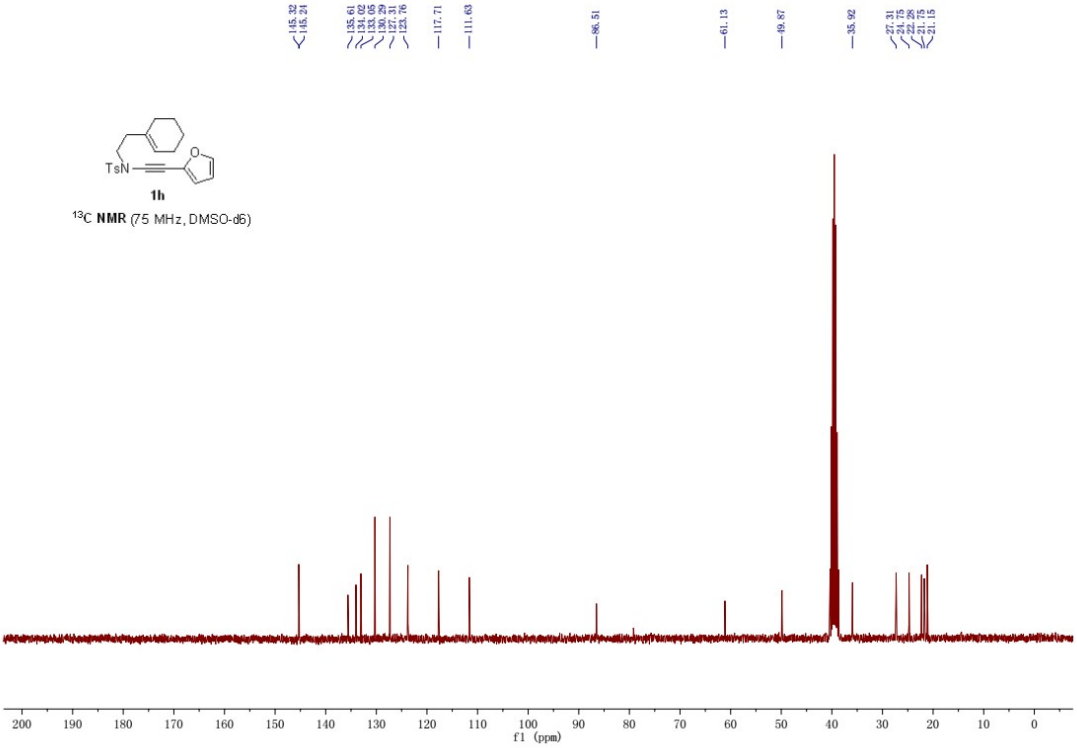


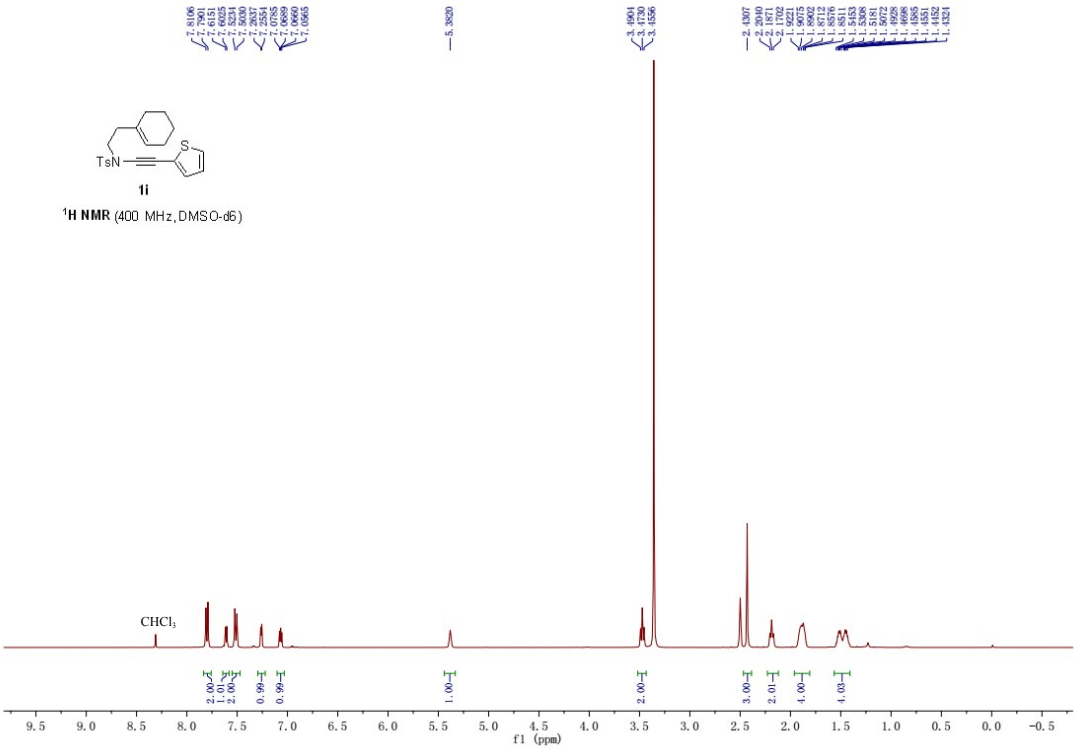
1g

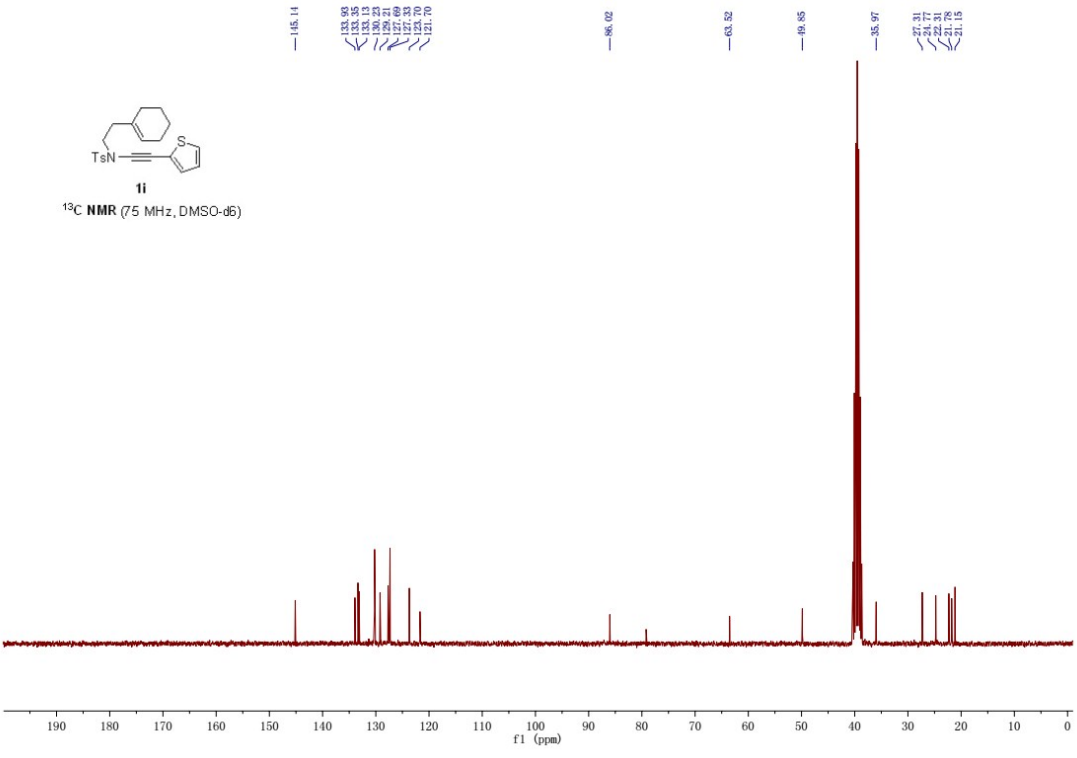
^{13}C NMR (100 MHz, $CDCl_3$)

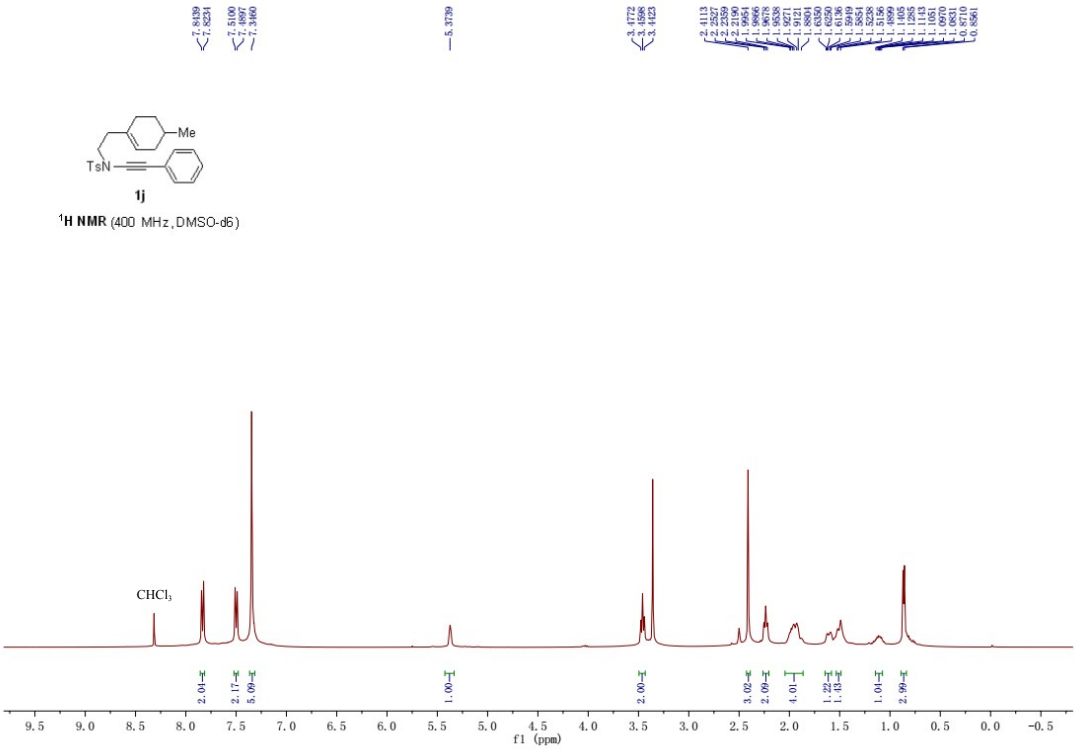


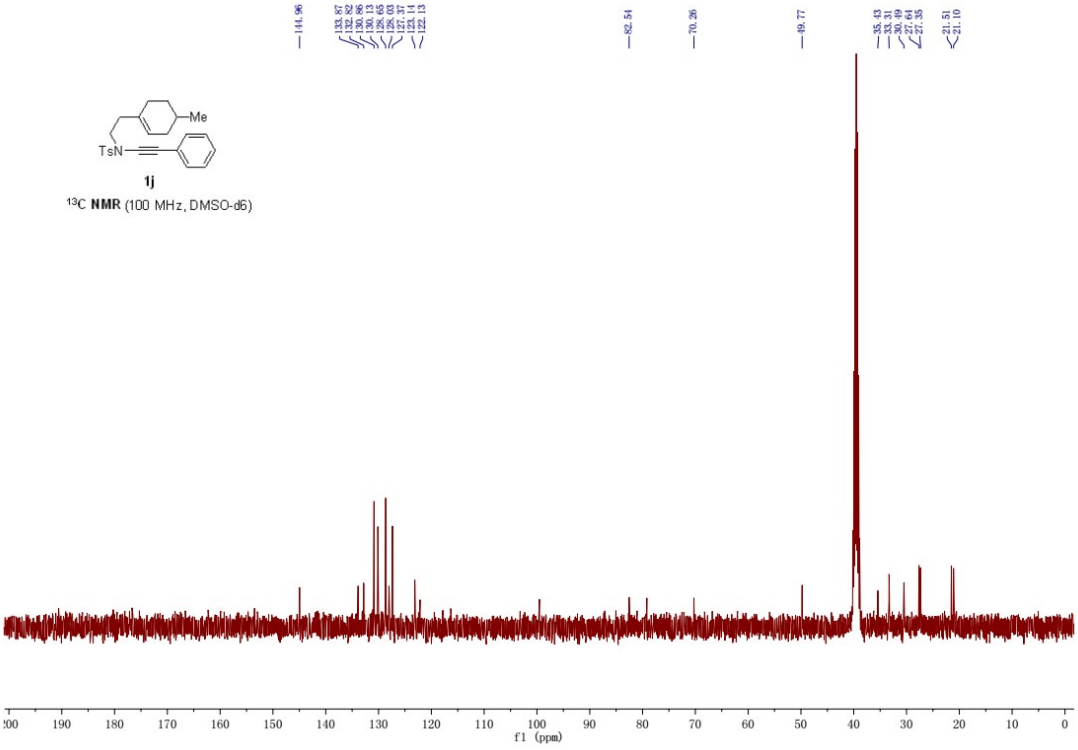

TsN
O
1h
^{1}H NMR (300 MHz, DMSO-d6)
CHCl3
f1 (ppm)

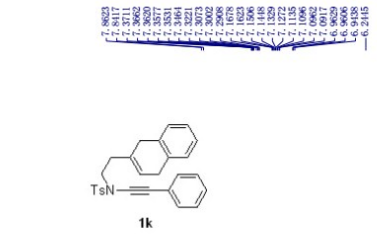

TsN
O
1h
^{13}C NMR (75 MHz, DMSO-d6)
f1 (ppm)


TsN
S
1i
^{1}H NMR (400 MHz, DMSO-d6)
CHCl3
f1 (ppm)


TsN
S
1i
^{13}C NMR (75 MHz, DMSO-d6)
f1 (ppm)

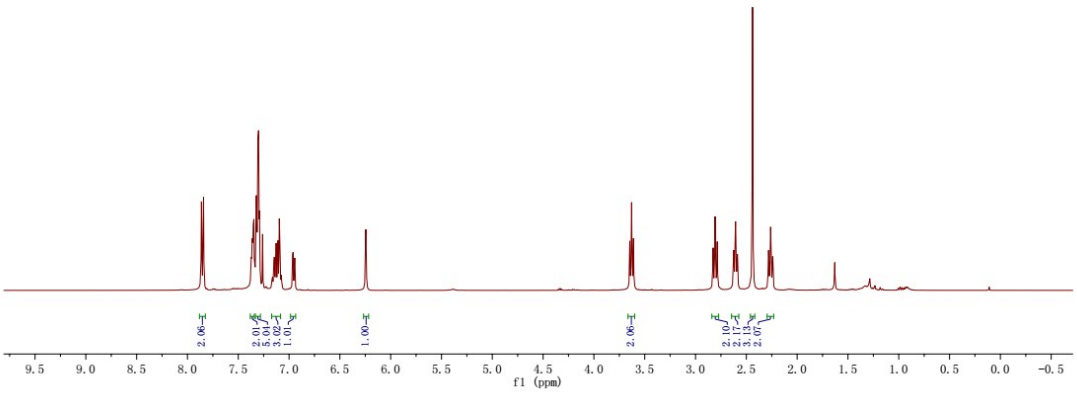

Me
TsN
1j
^{1}H NMR (400 MHz, DMSO-d6)
CHCl$_3$
f1 (ppm)

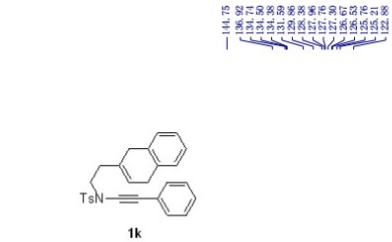

Me
TsN
1j
^{13}C NMR (100 MHz, DMSO-d6)
f1 (ppm)



1k

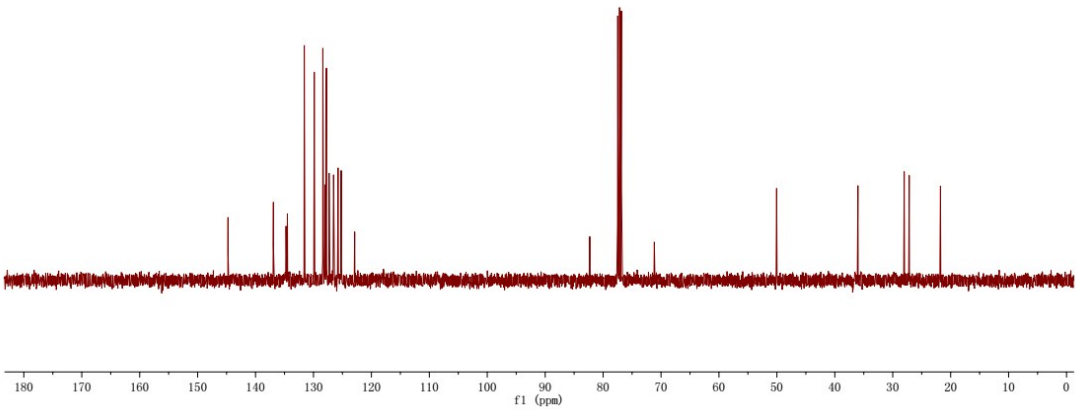
^{1}H NMR (400 MHz, $CDCl_3$)

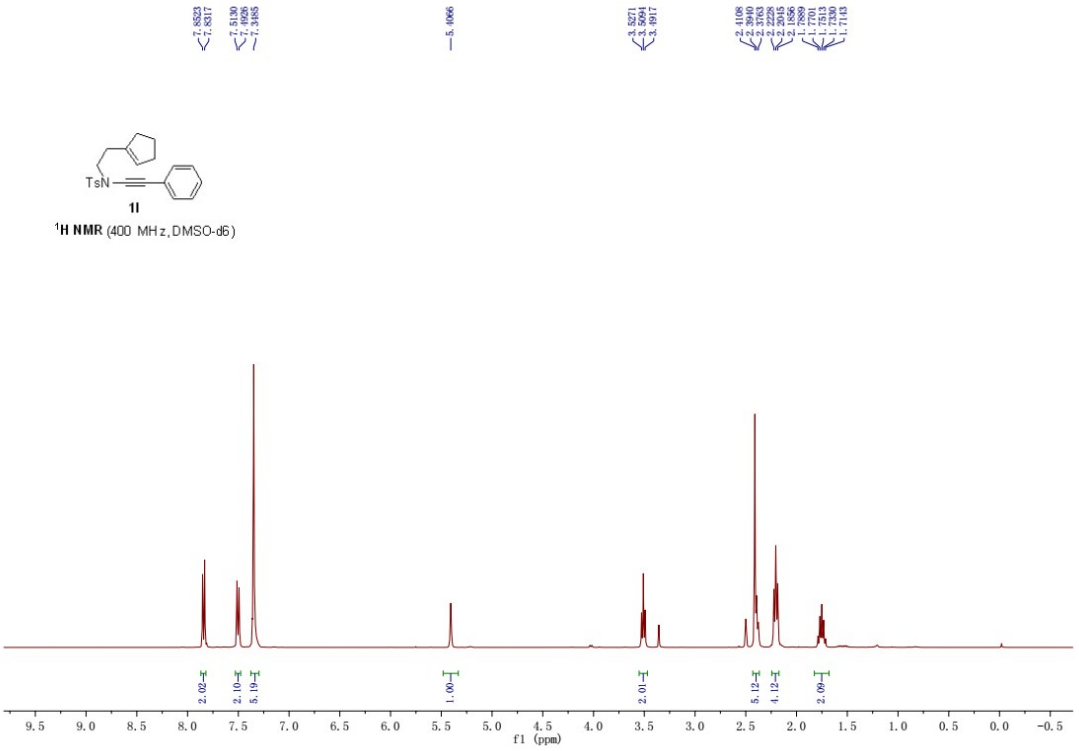


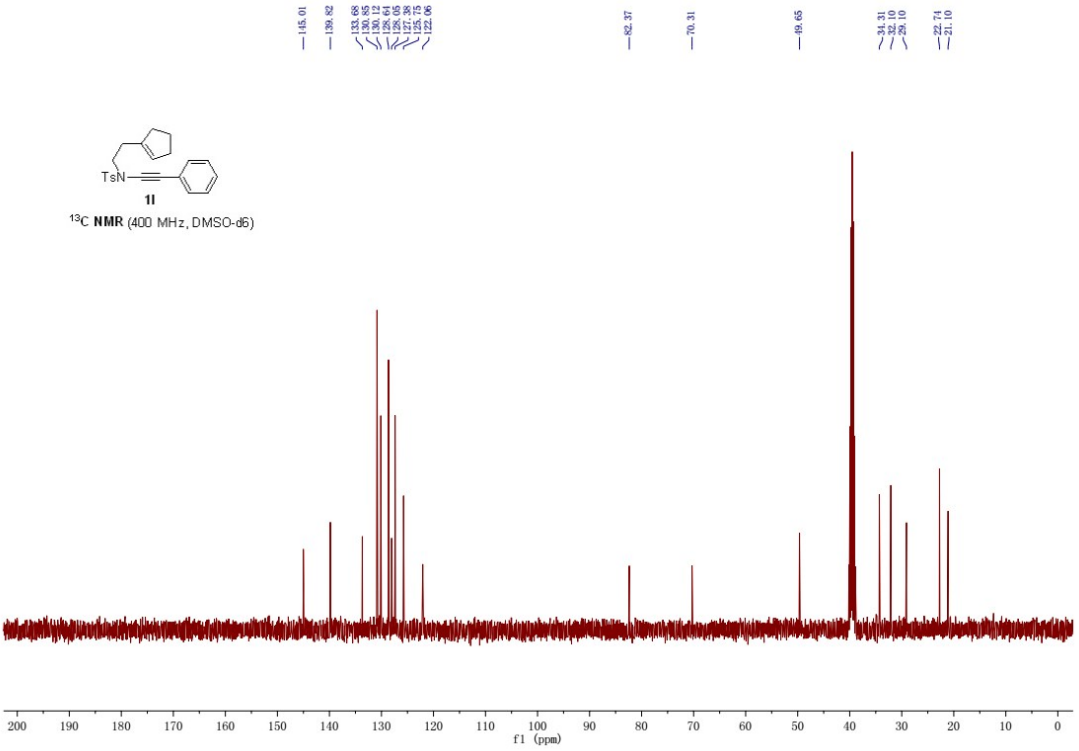


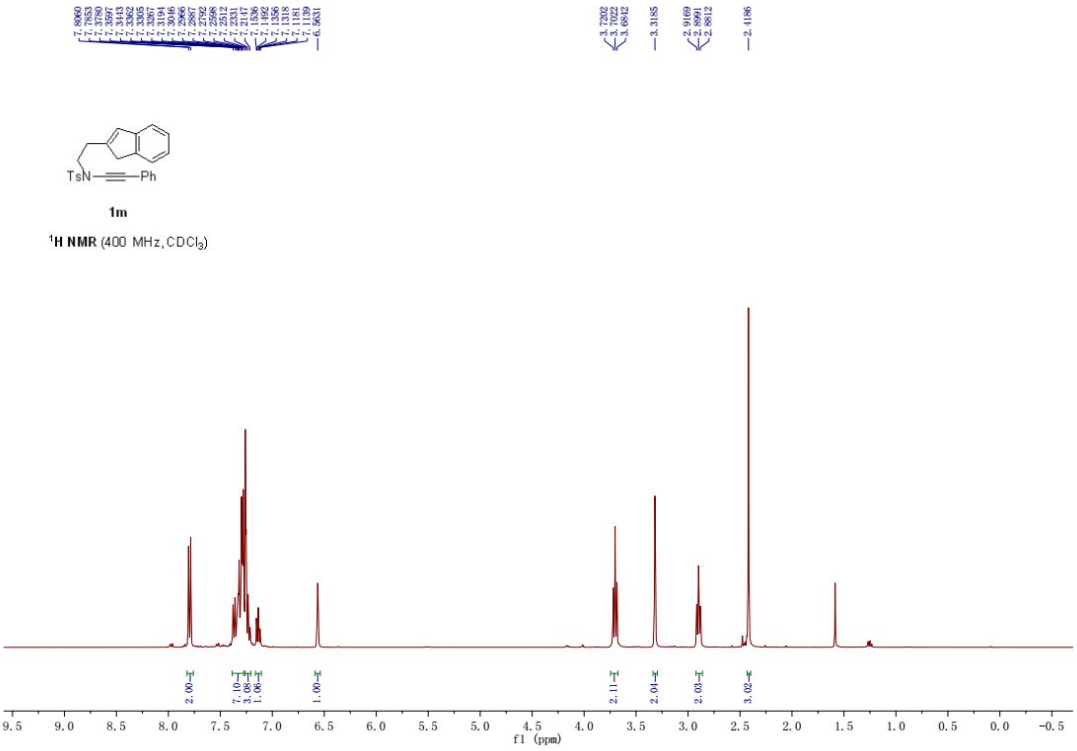
1k

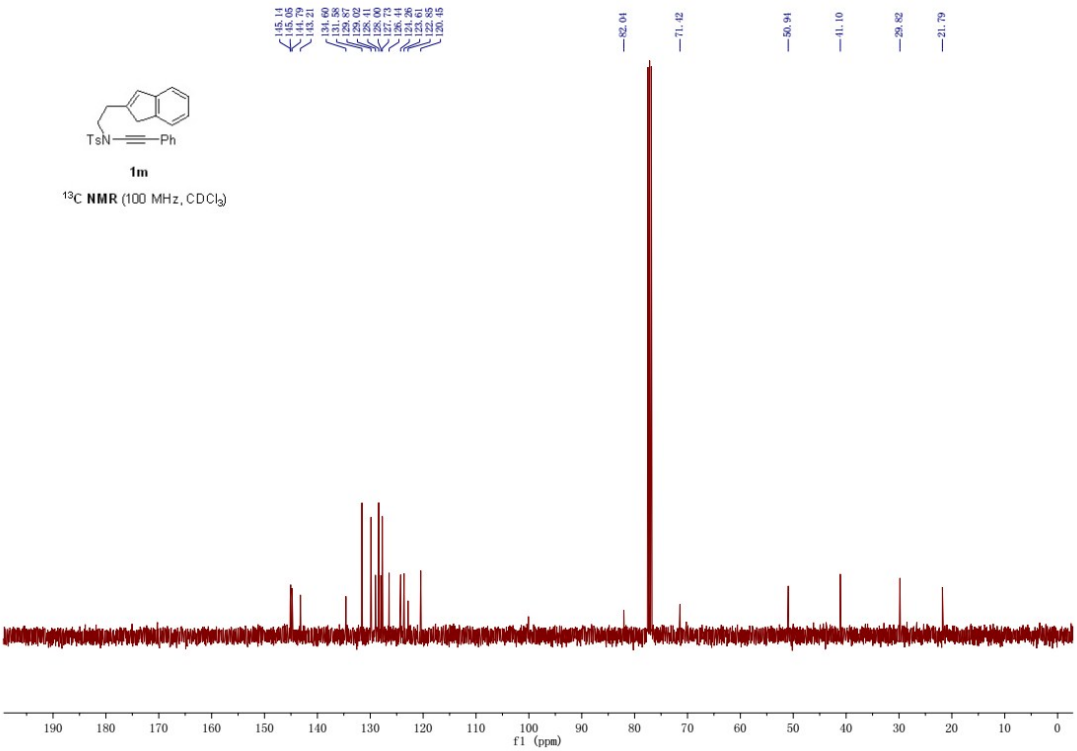
^{13}C NMR (100 MHz, $CDCl_3$)

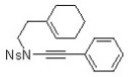



7.8323
7.8317
7.5130
7.4926
7.3485
5.4066
3.5271
3.5094
3.4917
2.4108
2.3940
2.3763
2.2228
2.0915
2.0856
1.7889
1.7701
1.7513
1.7330
1.7143
TsN
1l
1H NMR (400 MHz, DMSO-d6)
2.02
2.10
5.19
1.00
2.01
5.12
4.12
2.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


145.01
139.82
133.68
130.85
130.12
128.64
128.05
127.38
125.15
122.06
82.37
70.31
69.65
34.31
32.10
29.10
22.74
21.10
TsN
1l
13C NMR (400 MHz, DMSO-d6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

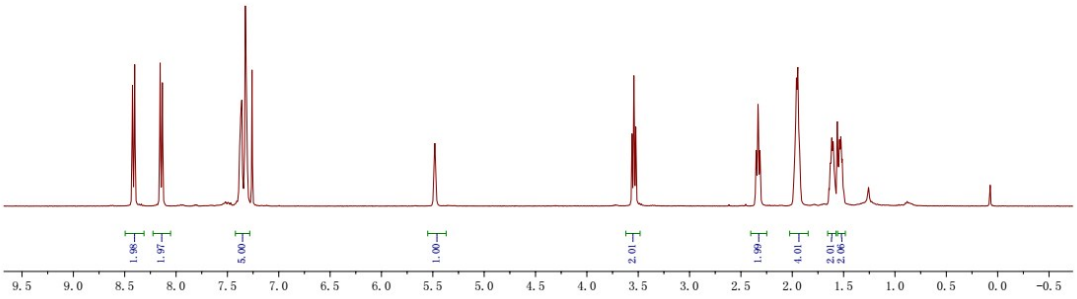

7.8060
7.7853
7.3790
7.3597
7.3443
7.3362
7.3305
7.3257
7.3191
7.3046
7.2966
7.2857
7.2792
7.2598
7.2512
7.2331
7.2147
7.1536
7.1492
7.1358
7.1318
7.1181
7.1139
6.8831
3.7202
3.7022
3.6842
3.3185
2.9169
2.8991
2.8812
2.4186
TsN
Ph
1m
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
7.10
3.06
1.06
1.00
2.11
2.04
2.03
3.02
f1 (ppm)

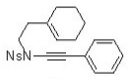

145.14
145.05
144.79
143.21
134.60
131.58
129.57
129.02
128.41
128.00
127.73
127.17
126.44
124.26
123.61
122.85
120.45
82.04
71.42
50.94
41.10
29.82
21.79
TsN
Ph
1m
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



1n

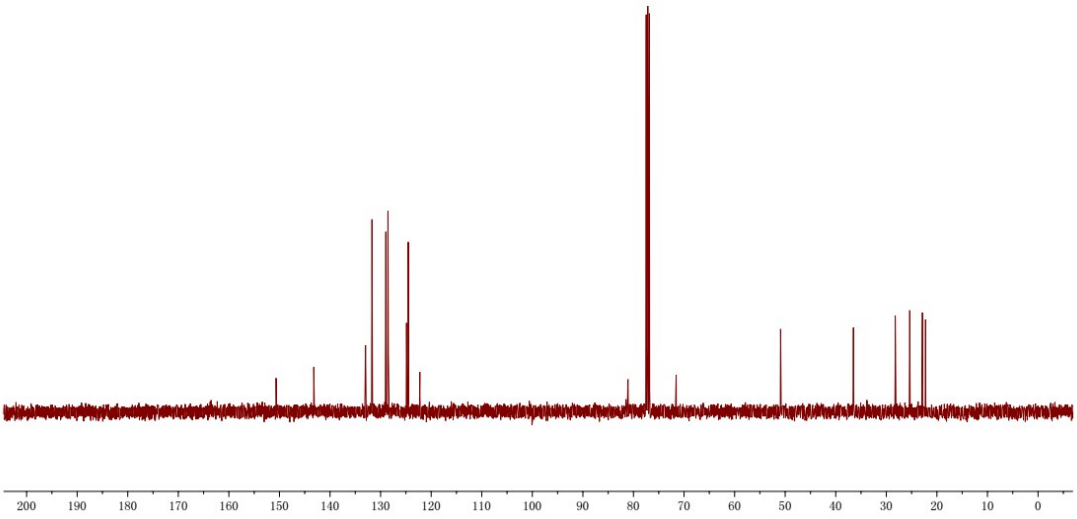
^{1}H NMR (400 MHz, $CDCl_3$)

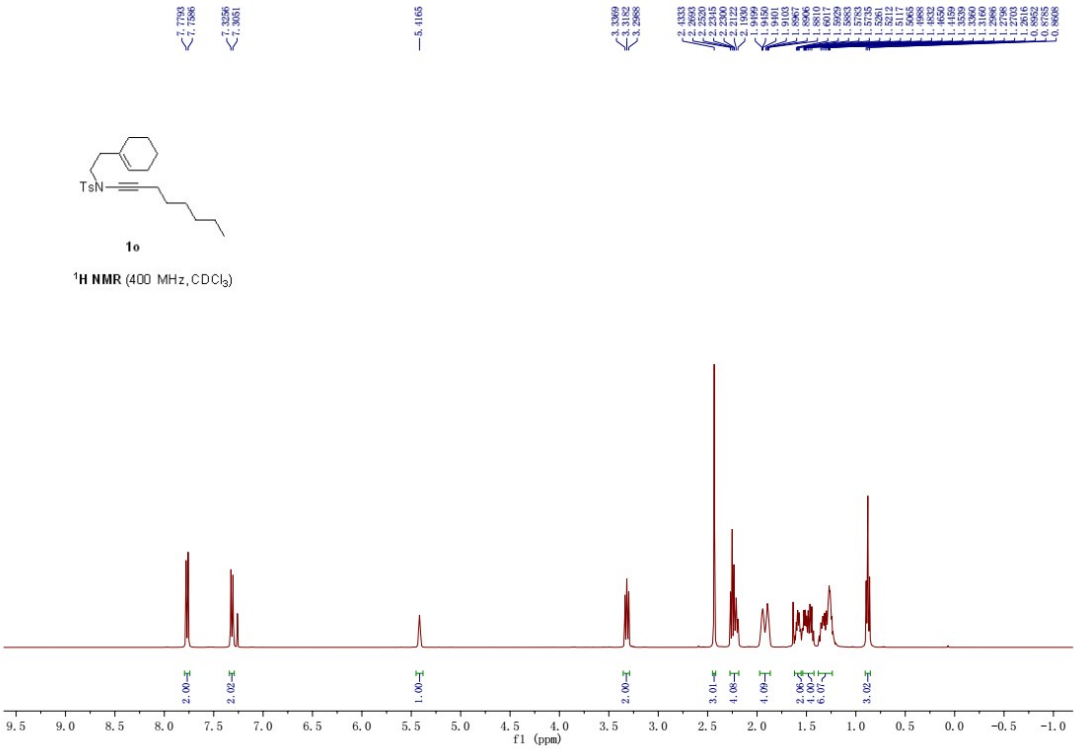


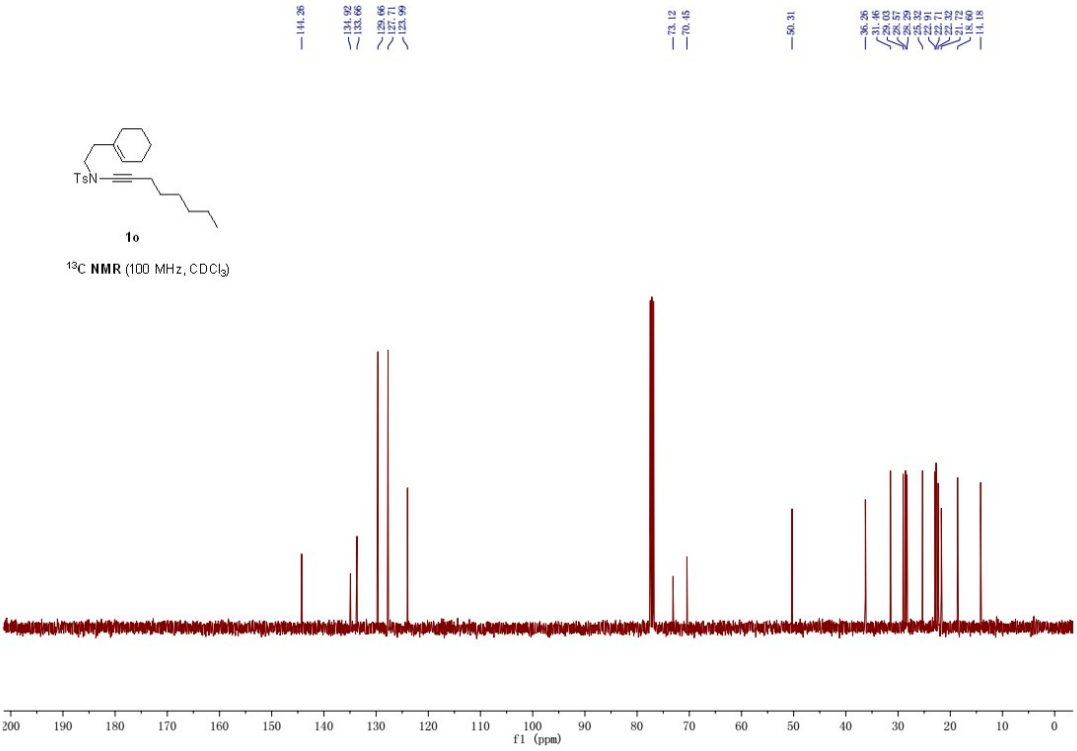


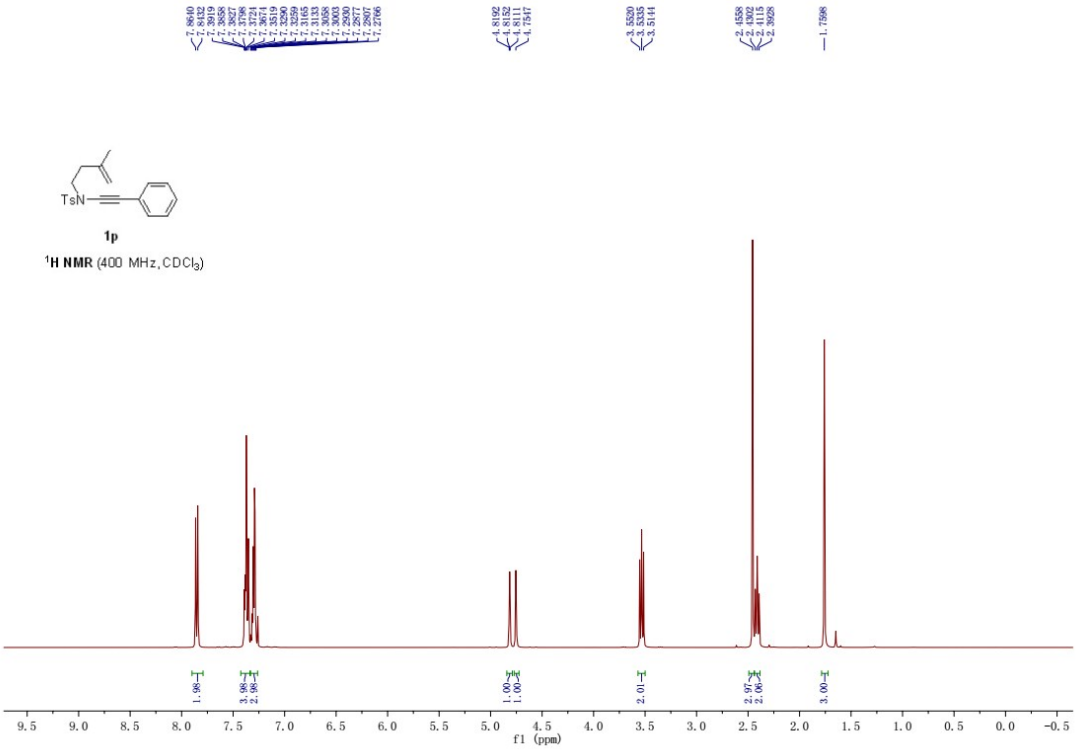
1n

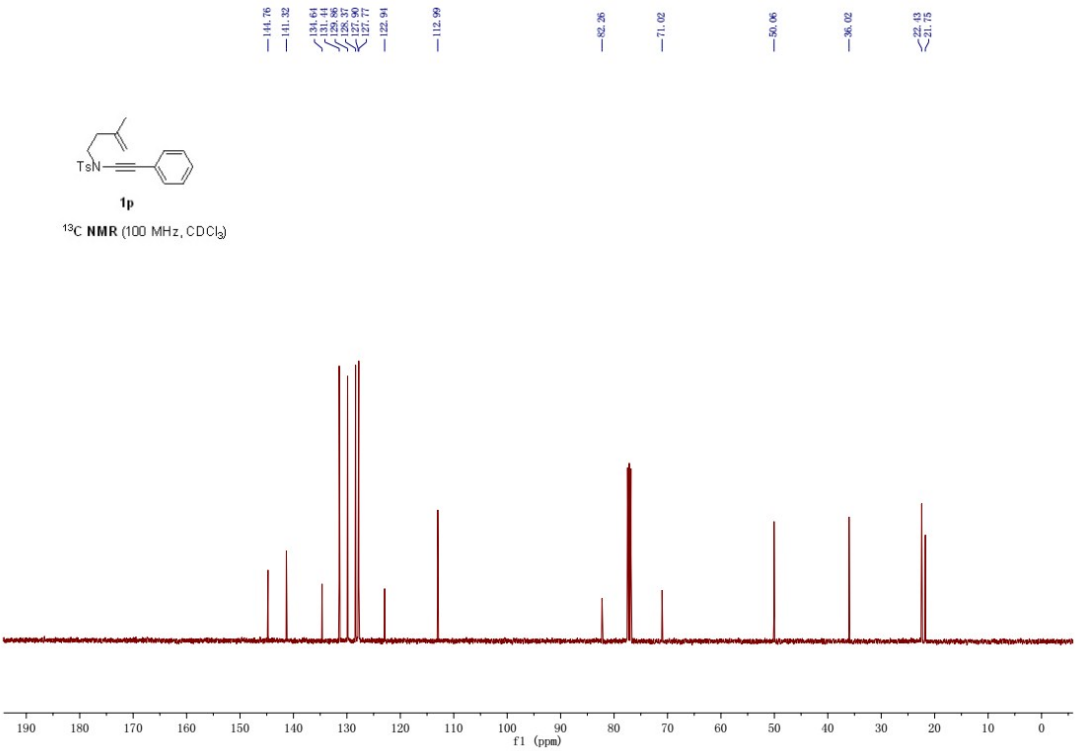
^{13}C NMR (100 MHz, $CDCl_3$)

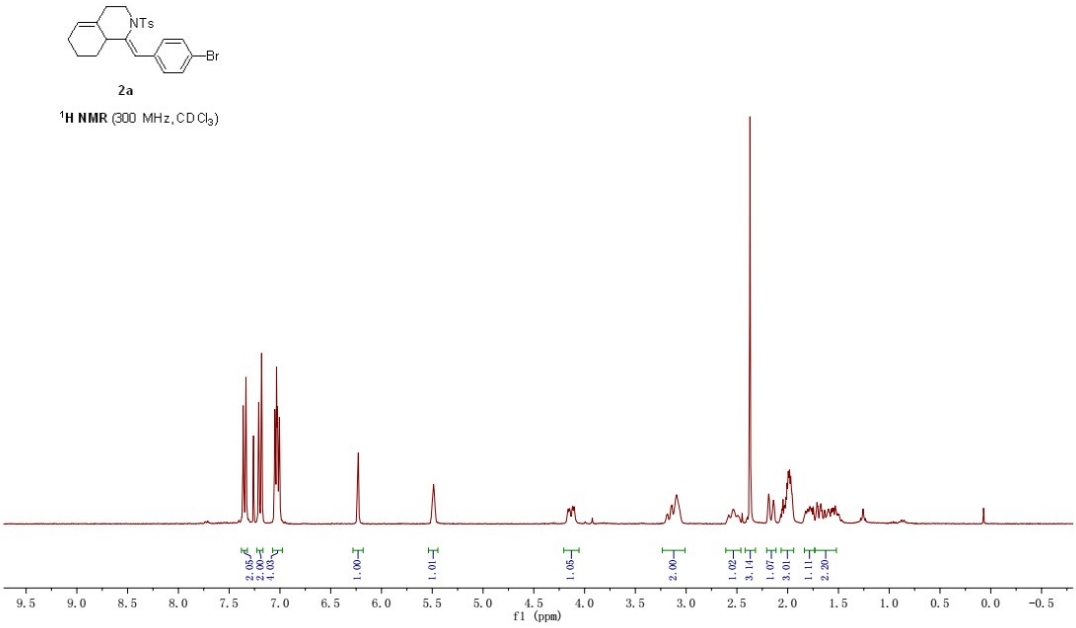


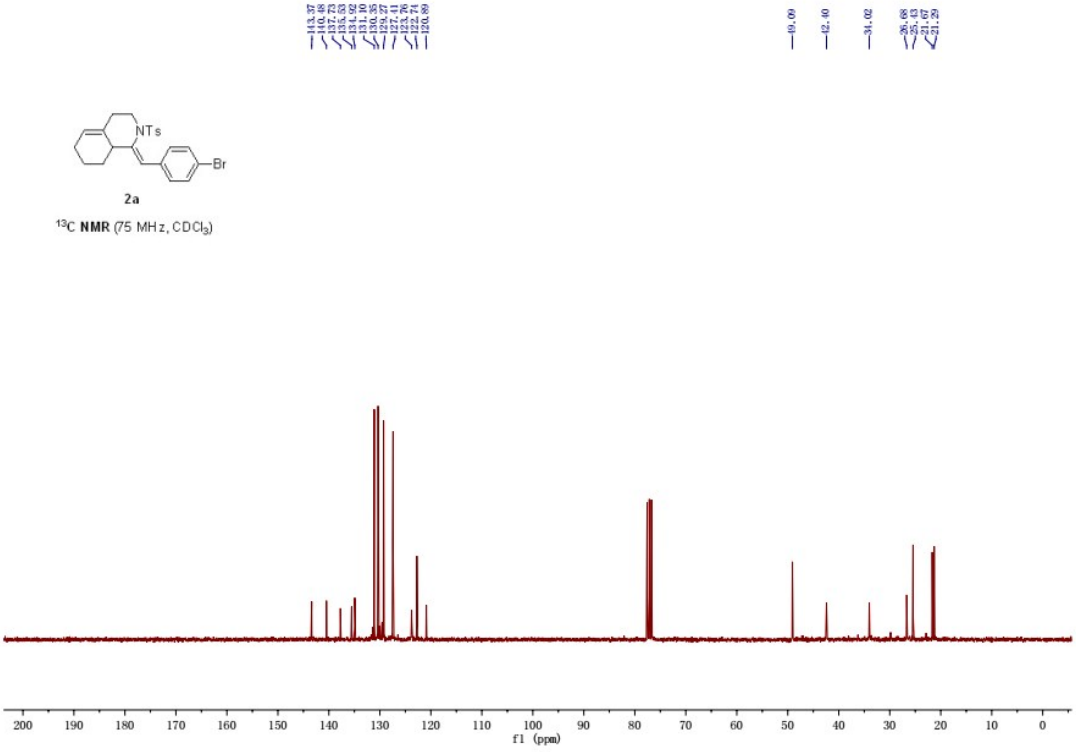

7.7793
7.7386
7.3256
7.3051
5.4165
3.3069
3.2837
3.2686
2.4333
2.3693
2.2520
2.2345
2.2150
2.2122
2.1930
2.1499
2.1459
2.1401
2.1103
2.0957
2.0866
2.0810
2.0617
2.0503
2.0083
1.9783
1.9735
1.9581
1.9211
1.9117
1.9065
1.8966
1.8832
1.8650
1.8459
1.8359
1.3360
1.3160
1.2996
1.2736
1.2703
1.2616
0.9582
0.9505
0.8808
TsN
1o
1H NMR (400 MHz, CDCl3)
2.00
2.02
1.00
2.00
3.01
4.08
4.09
2.06
4.00
6.07
3.02
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 −1.0
f1 (ppm)

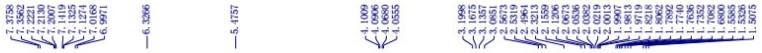

144.26
134.92
133.66
129.66
127.71
123.99
73.12
70.45
50.31
36.36
31.46
29.03
28.57
28.39
25.35
22.91
22.71
22.32
21.72
18.60
14.18
TsN
1o
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

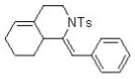

7.8640
7.8432
7.3919
7.3856
7.3827
7.3796
7.3724
7.3671
7.3519
7.3290
7.3259
7.3165
7.3133
7.3068
7.3003
7.2930
7.2877
7.2766
4.8192
4.8152
4.8111
4.7947
3.5320
3.5235
3.5144
2.4558
2.4302
2.4115
2.3928
1.7998
TsN
1p
1H NMR (400 MHz, CDCl3)
1.98
3.98
2.98
1.00
1.00
2.01
2.97
2.06
3.00
f1 (ppm)


144.76
141.32
134.64
131.44
129.95
128.35
127.90
127.77
122.94
112.99
82.26
71.02
50.06
36.02
22.43
21.75
TsN
1p
13C NMR (100 MHz, CDCl3)
f1 (ppm)


NTs
Br
2a
1H NMR (300 MHz, CDCl3)
f1 (ppm)

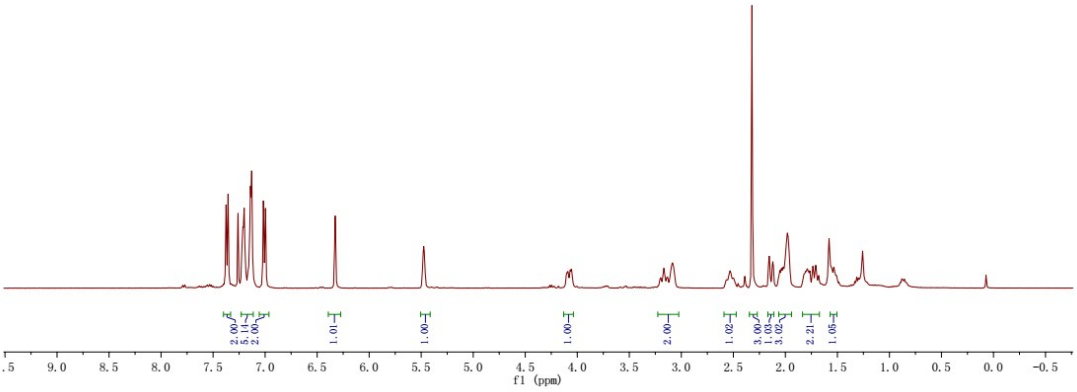

NTs
Br
2a
13C NMR (75 MHz, CDCl3)
f1 (ppm)

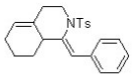




2b

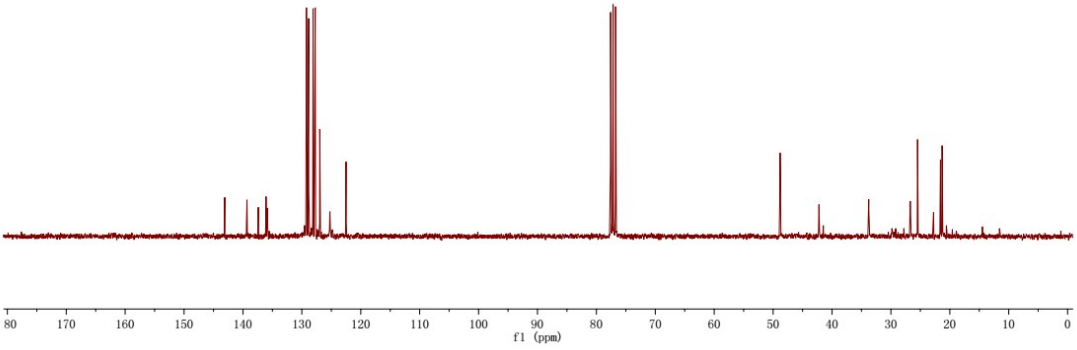
^{1}**H NMR** (400 MHz, $CDCl_3$)

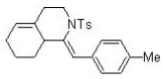




2b

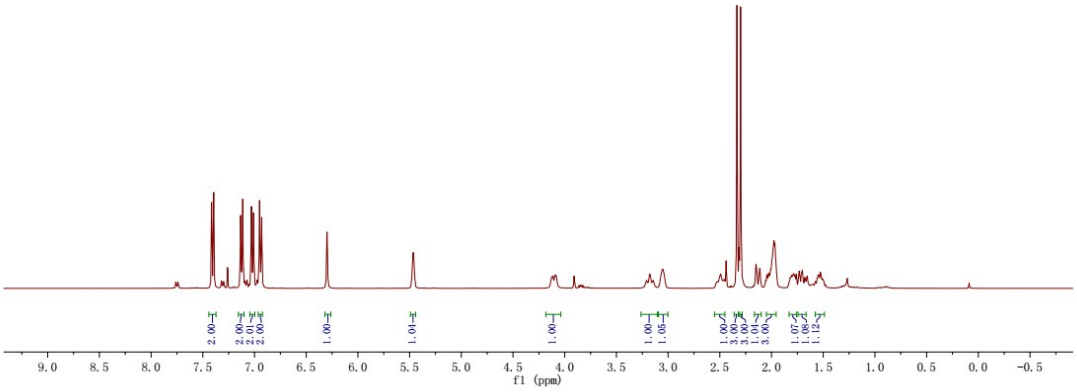
^{13}**C NMR** (75 MHz, $CDCl_3$)

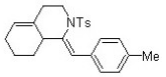




2c

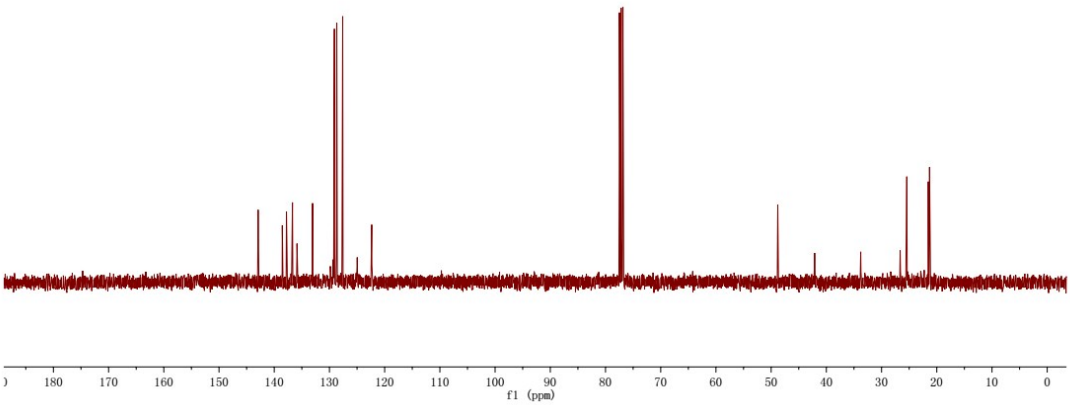
^{1}H **NMR** (400 MHz, $CDCl_3$)

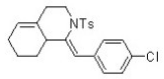




2c

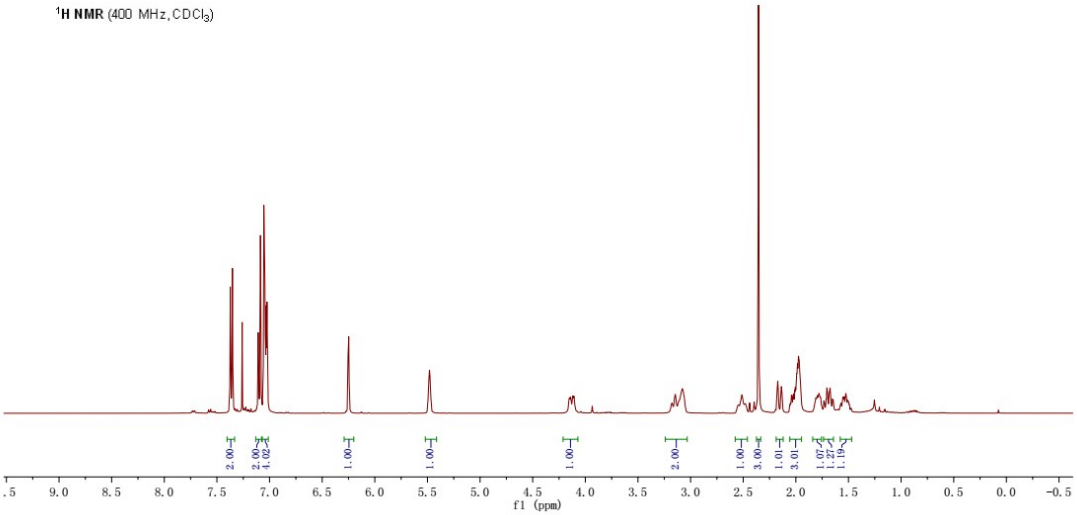
^{13}C **NMR** (100 MHz, $CDCl_3$)

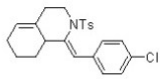




2d

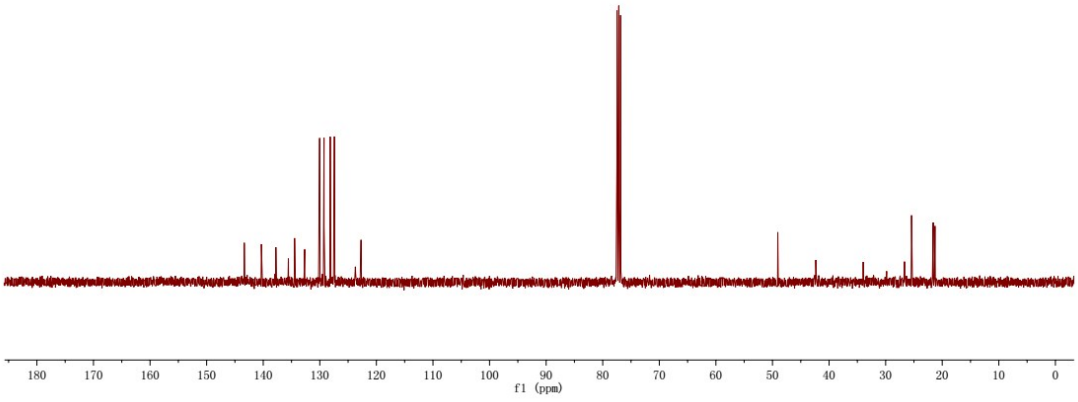
^{1}H NMR (400 MHz, $CDCl_3$)

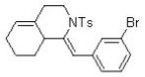




2d

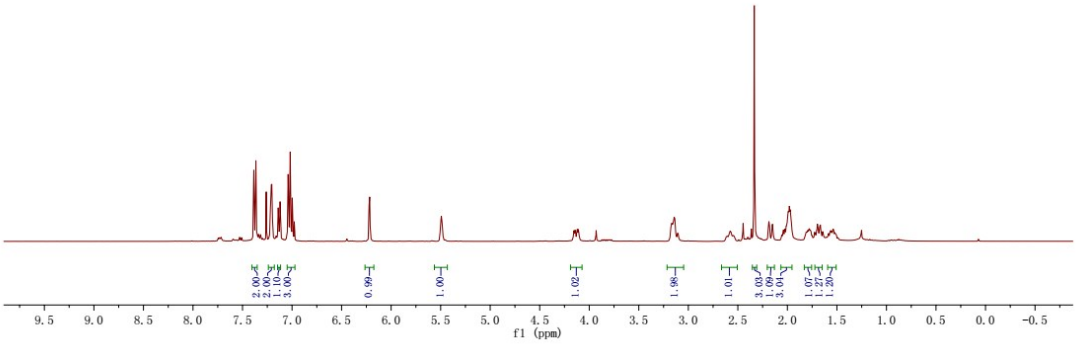
^{13}C NMR (100 MHz, $CDCl_3$)

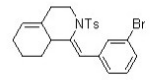




2e

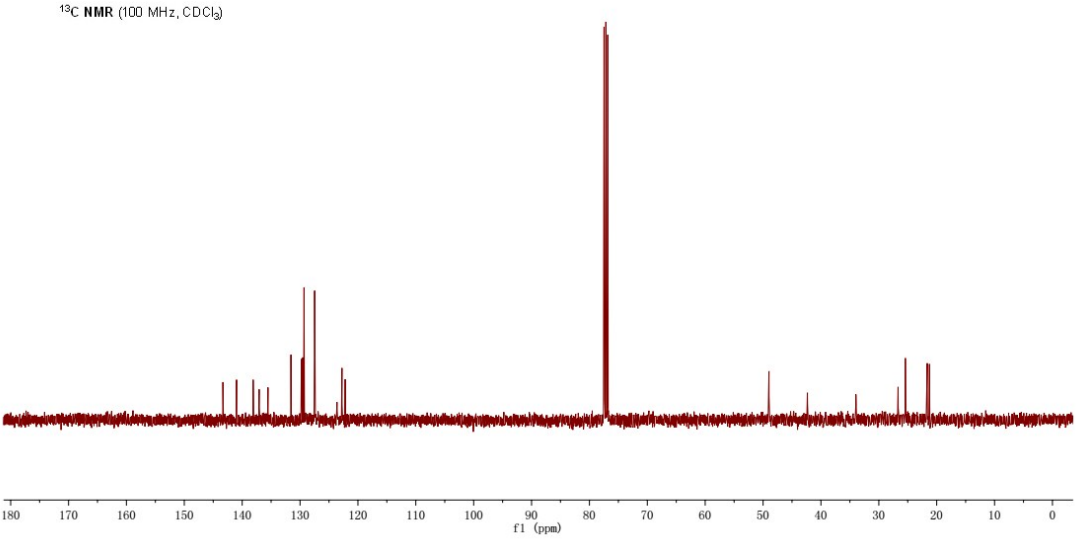
^{1}H NMR (400 MHz, $CDCl_3$)

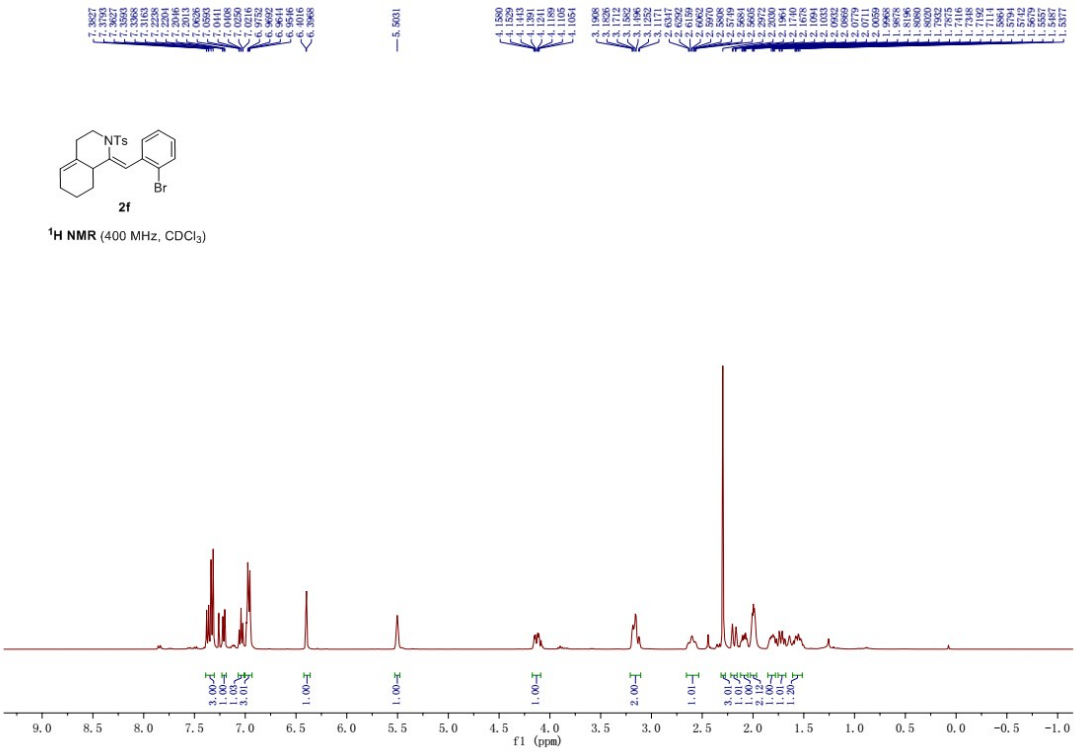


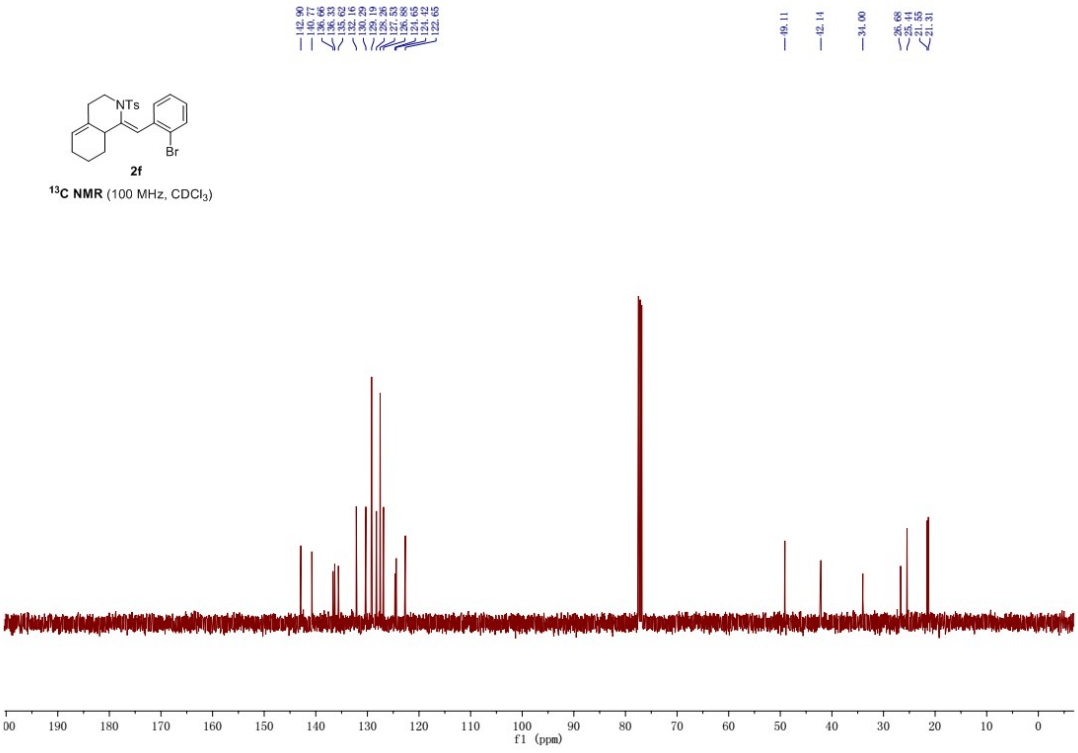


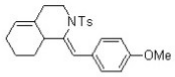
2e

^{13}C NMR (100 MHz, $CDCl_3$)



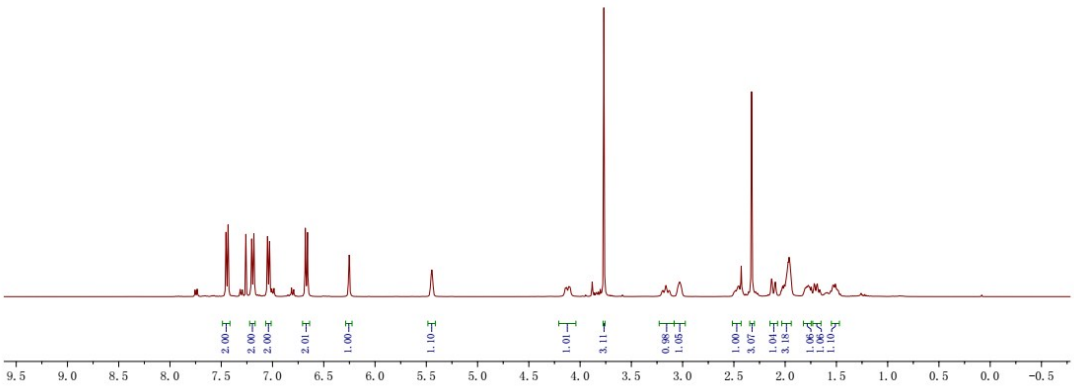

NTs
Br
2f
1H NMR (400 MHz, CDCl3)
f1 (ppm)

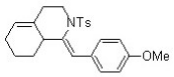

NTs
Br
2f
13C NMR (100 MHz, CDCl3)
f1 (ppm)



2g

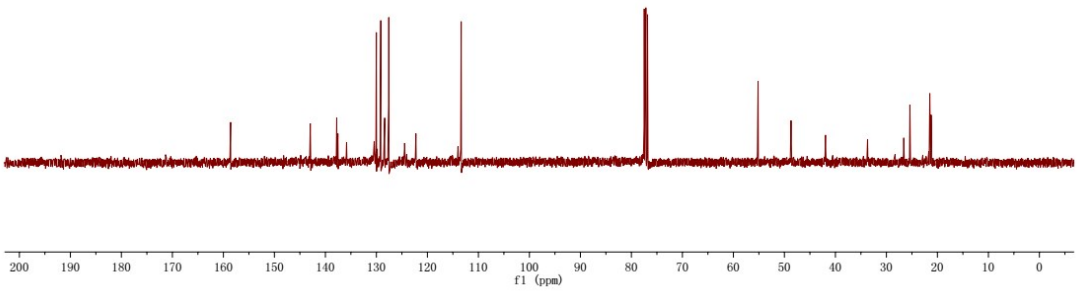
^{1}H NMR (400 MHz, $CDCl_3$)

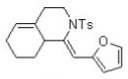




2g

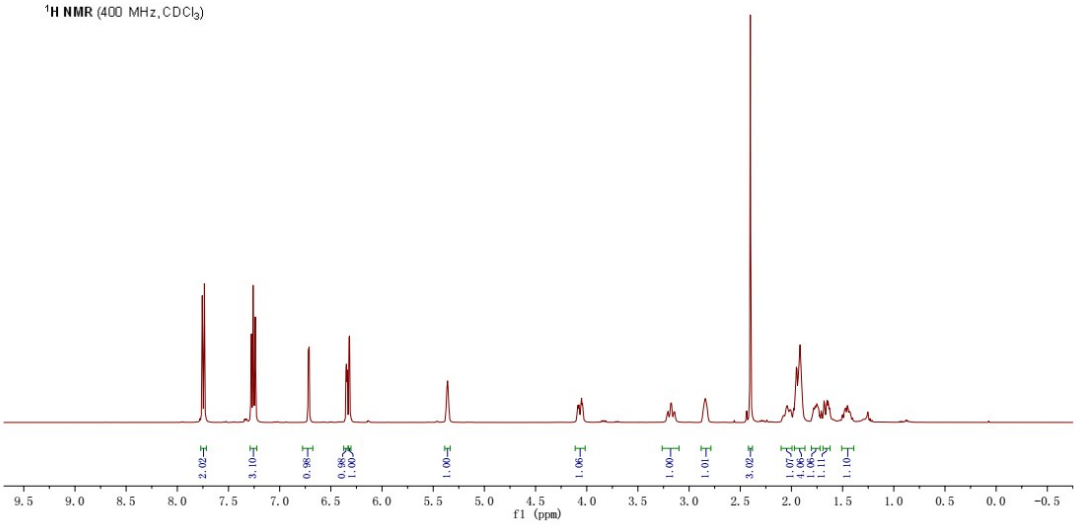
^{13}C NMR (100 MHz, $CDCl_3$)

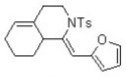




2h

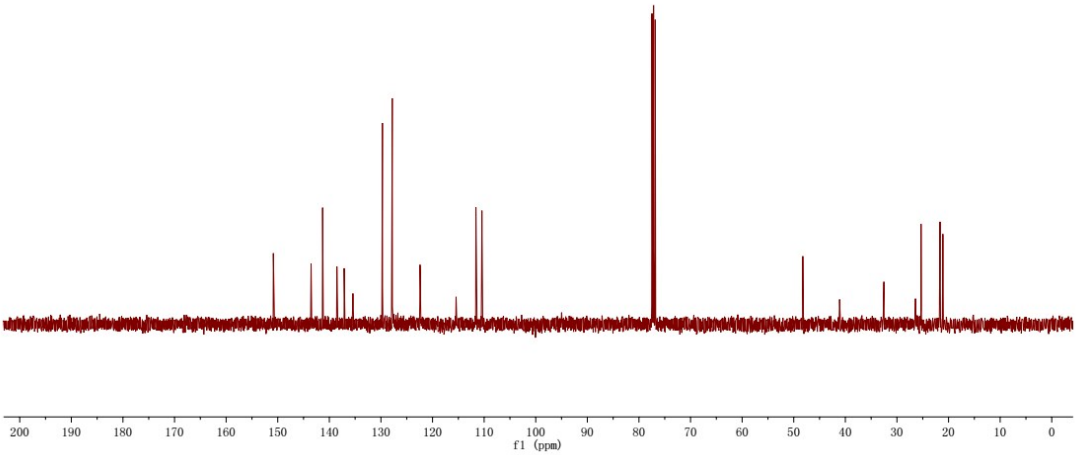
^{1}H NMR (400 MHz, $CDCl_3$)

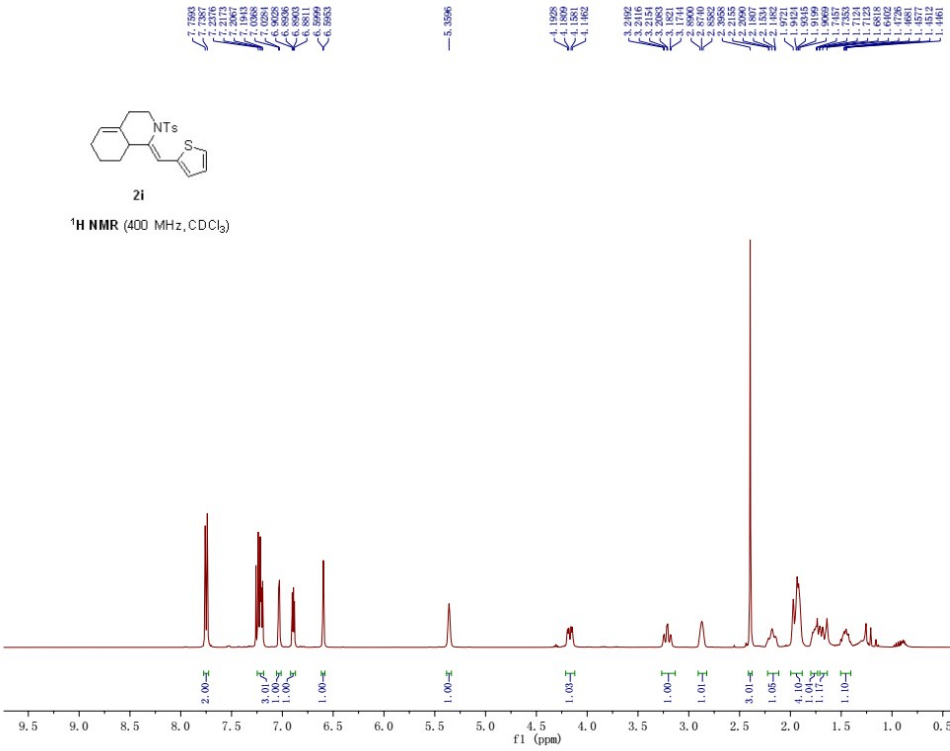


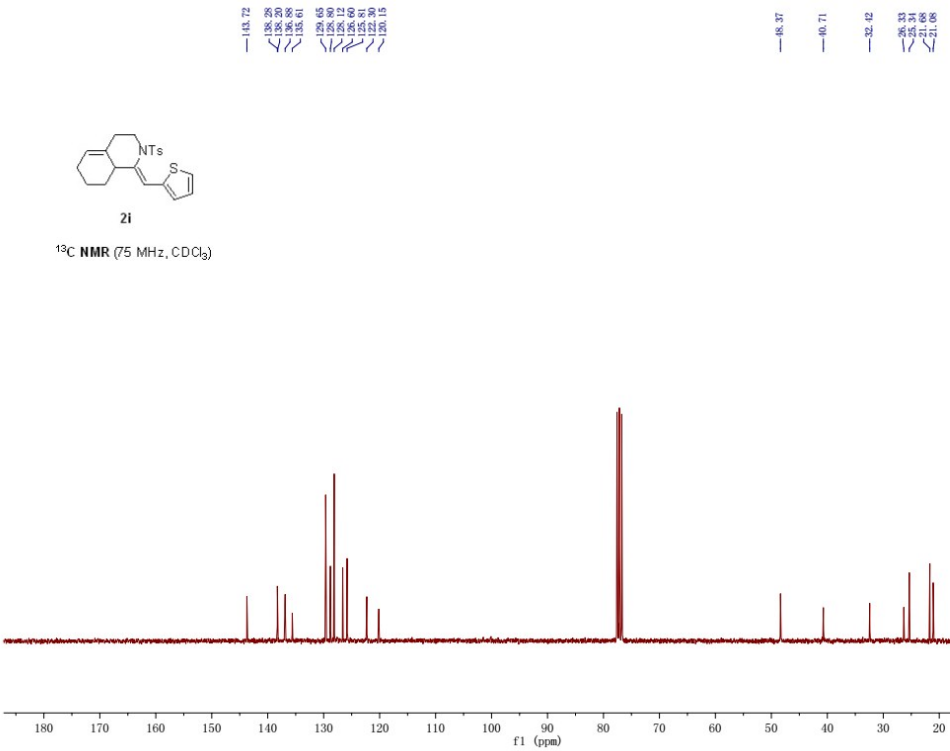


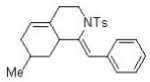
2h

^{13}C NMR (100 MHz, $CDCl_3$)



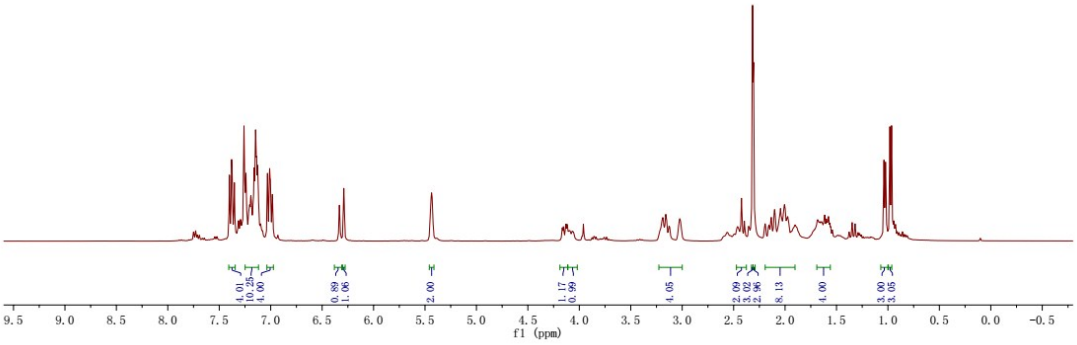

NTs
S
2i
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

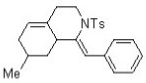

NTs
S
2i
^{13}C NMR (75 MHz, CDCl$_3$)
f1 (ppm)



2j

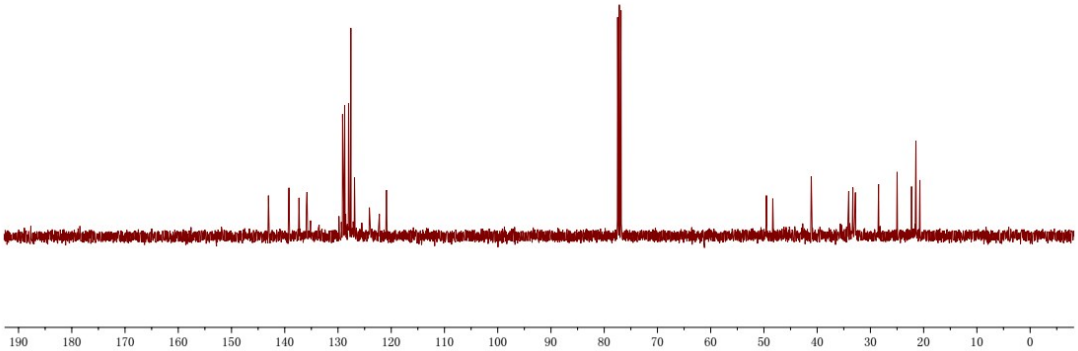
^{1}**H NMR** (400 MHz, $CDCl_3$)

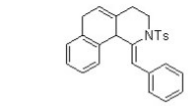




2j

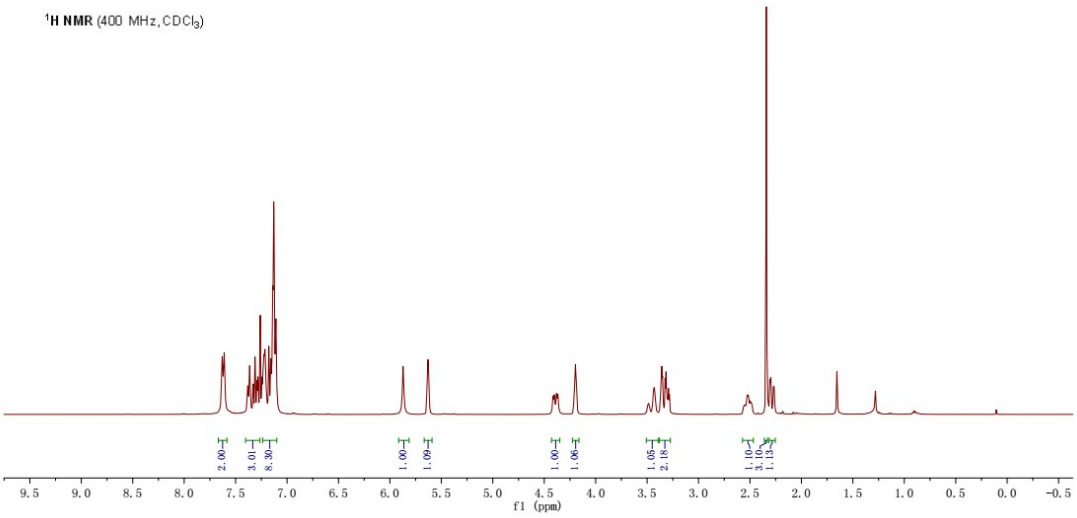
^{13}**C NMR** (100 MHz, $CDCl_3$)

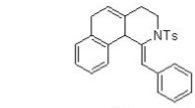




2k

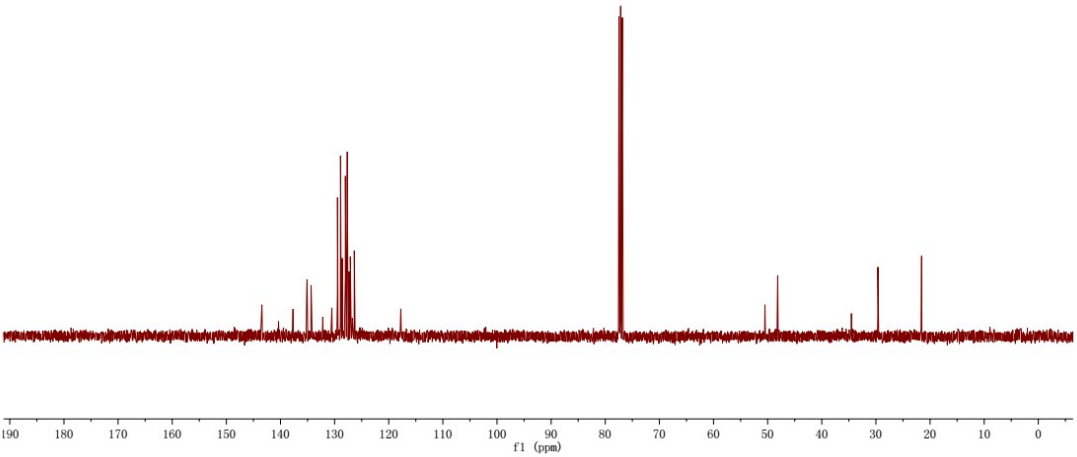
^{1}H NMR (400 MHz, $CDCl_3$)

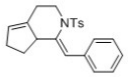




2k

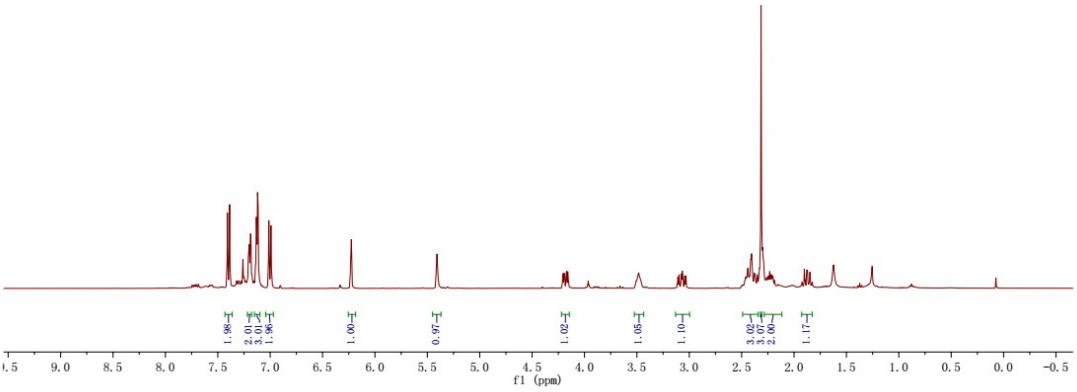
^{13}C NMR (100 MHz, $CDCl_3$)

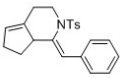




2l

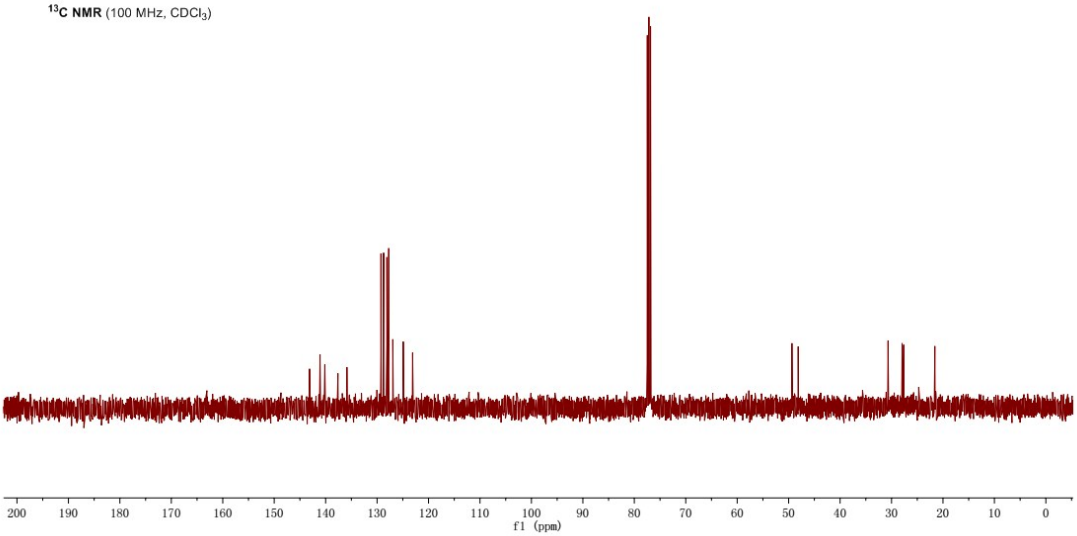
^{1}H NMR (400 MHz, $CDCl_3$)

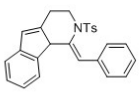




2l

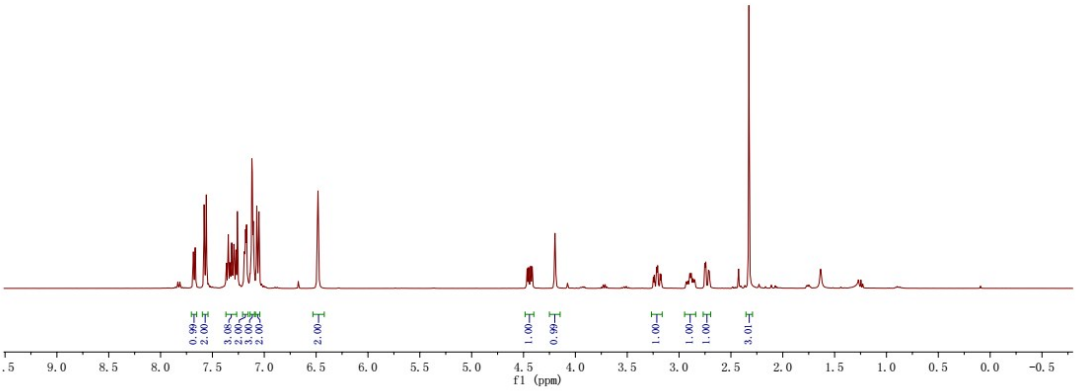
^{13}C NMR (100 MHz, $CDCl_3$)

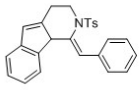




2m

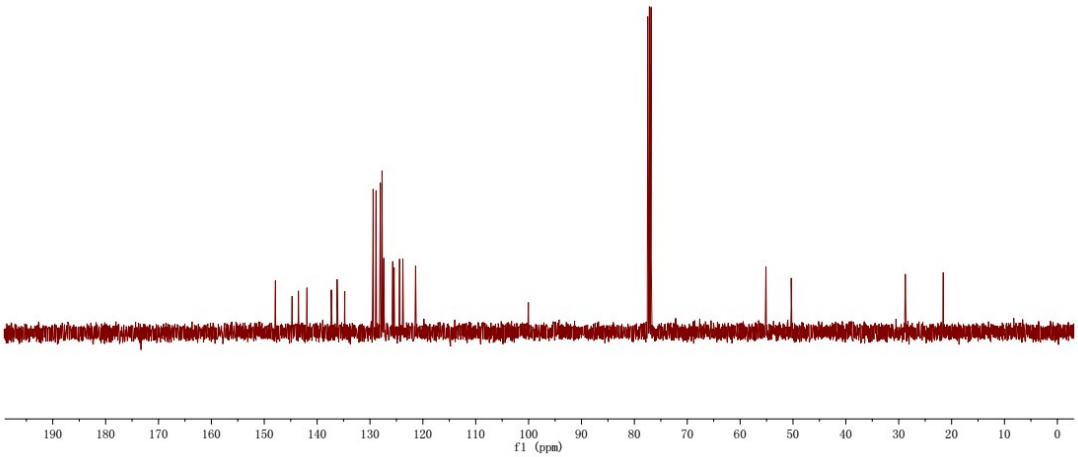
^{1}H NMR (400 MHz, $CDCl_3$)

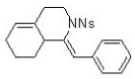




2m

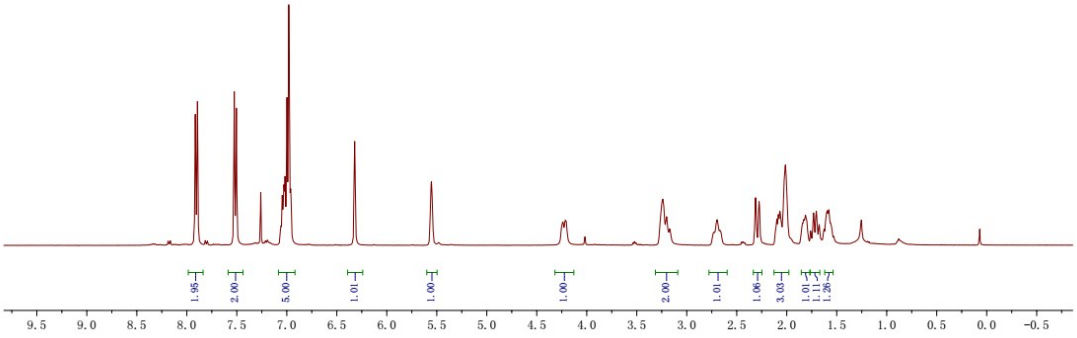
^{13}C NMR (100 MHz, $CDCl_3$)

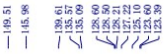


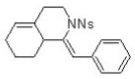


2n

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







2n

^{13}C NMR (100 MHz, $CDCl_3$)