Supporting Information

Indium(III)-Catalyzed Intramolecular Dearomative Cycloaddition of *N*-Sulfonylaziridines to Indoles: Facile Synthesis of Tetraycyclic Pyrroloindoline Skeletons

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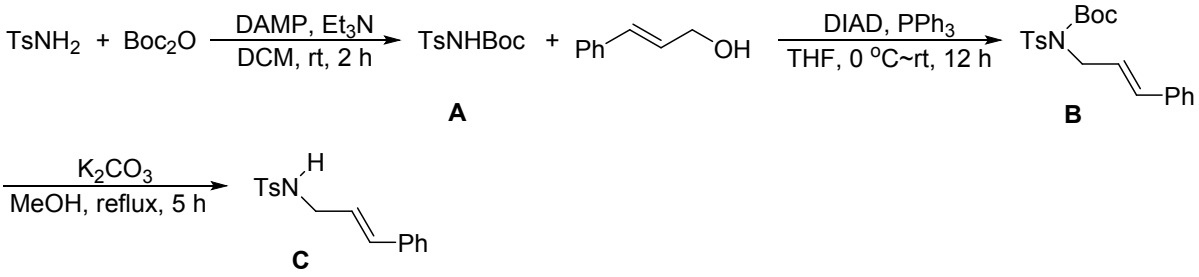
CONTENTS

1. General remarks.

MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Infra-red spectra were measured on a spectrometer. ^{1}H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; ^{19}F NMR spectra were recorded for a solution in $CDCl_3$ with $CFCl_3$ as the external reference. *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques.

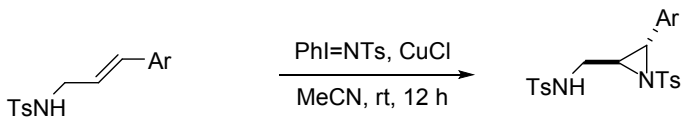
2. General procedure for synthesis of aziridines D



Under argon atmosphere 4-methylbenzenesulfonamide (8.6 g, 50 mmol, 1.0 equiv.) and *N*,*N*-dimethyl-4-aminopyridine (0.6 g, 5 mmol, 10.0 mol %) were dissolved in 100 mL dry dichloromethane. Dry triethylamine (7.7 mL, 55 mmol, 1.1 equiv.) as well as di-*tert*-butyl dicarbonate (12.6 mL, 55 mmol, 1.1 equiv.) were added. After 2 h the solution was concentrated and the crude product was dissolved in EtOAc. It was washed with HCl (1 M), water as well as brine. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give a white powder. The product was recrystallized from a mixture of DCM and petroleum ether. The crystals were washed with petrol ether and dried in vacuum to give white crystals **A** (11.3 g, 86%).

To a solution of **A** (2.7 g, 10.0 mmol, 1.0 equiv.), cinnamyl alcohol (1.5 mL, 11.0 mmol, 1.1 equiv.), and triphenylphosphane (3.1 g, 12.0 mmol, 1.2 equiv.) in THF (50 mL), (2.4 mL, 12.0 mmol, 1.2 equiv.) DIAD was added dropwise at 0 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 12 hours. Then, the resulting solution was concentrated in vacuum and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 8 / 1) to give white solid **B** (3.0 g, 78%).

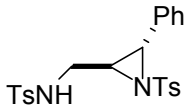
Under argon atmosphere, a solution of **B** (2.9 g, 7.5 mmol, 1.0 equiv.) and K_2CO_3 (2.1 g, 15.0 mmol, 2.0 equiv.) in MeOH (30 mL) was stirred at 80 °C. After 5 h the solution was concentrated and the crude product was dissolved in EtOAc (30 mL). It was washed with water as well as brine. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give a white powder. The product was recrystallized from a mixture of DCM and petroleum ether. The crystals were washed with petrol ether and dried in vacuum to give white solid **C** (2.0 g, 90%).



C **D**

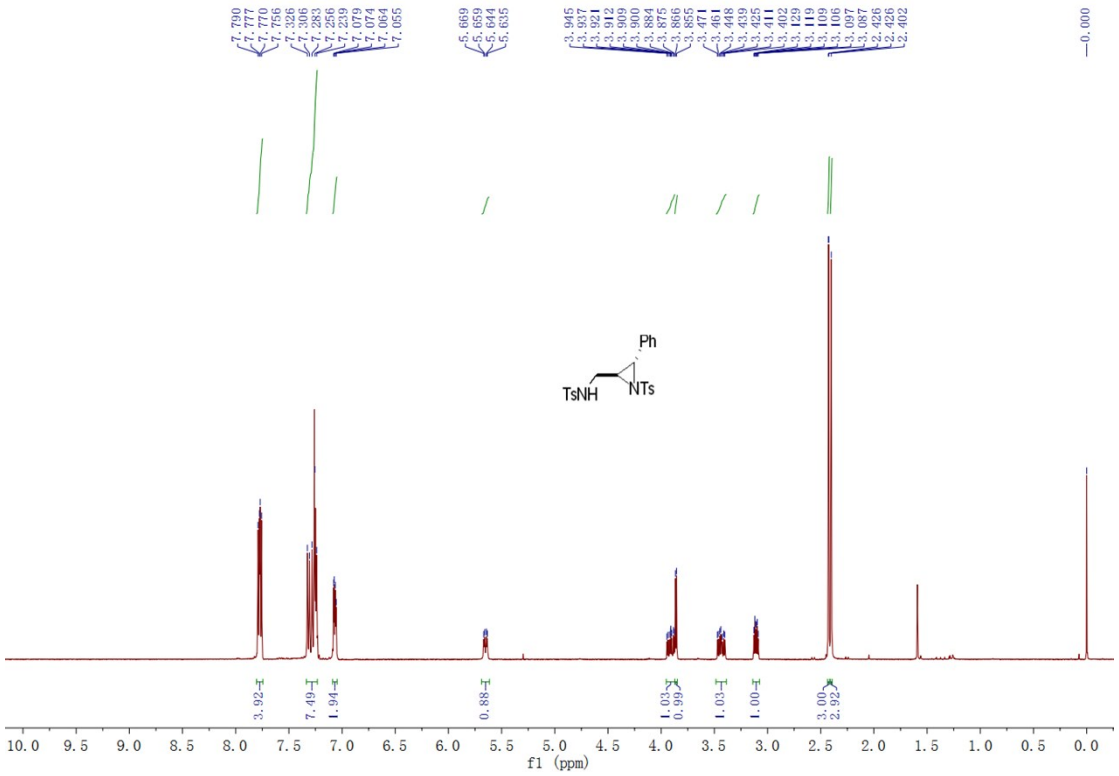
Under argon atmosphere, CuCl (10 mol %) was added to a suspension of the N-cinnamyl-4-methylbenzenesulfonamide **C** (1.0 equiv) and PhI=NTs (1.1 equiv) in MeCN at room temperature. The reaction system was stirred for 12h. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 6/1) to give **D**[1] as a white solid in 41% yield.

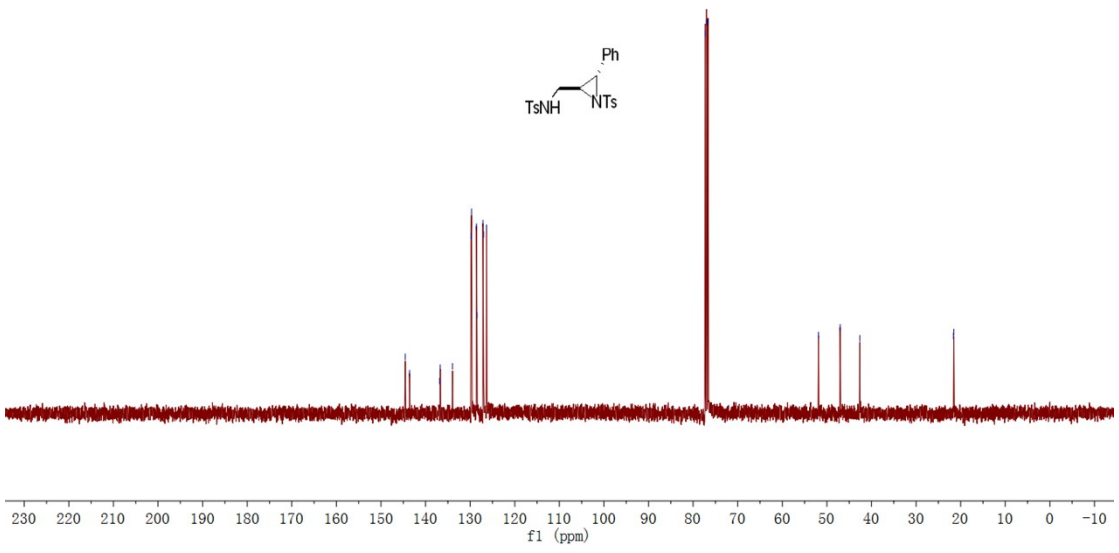
3. Characterization and spectra charts for D

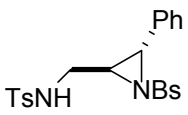


Compound D1:

5.2 mmol scale, a white solid, 41% yield (1.324g). M.p.: 125-127 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.43 (s, 3H), 3.08-3.13 (m, 1H), 3.40-3.48 (m, 1H), 3.86 (d, J = 4.4 Hz, 1H), 3.87-3.95 (m, 1H), 5.65 (dd, J = 4.0 Hz, 10.0 Hz, 1H), 7.05-7.08 (m, 2H), 7.23-7.33 (m, 7H), 7.75-7.79 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.5, 21.6, 42.6, 47.0, 51.9, 126.3, 127.0, 127.1, 128.5, 128.6, 129.7, 129.8, 134.0, 136.7, 136.8, 143.6, 144.6. IR (neat) 3281, 3245, 3064, 3031, 2920, 2878, 1596, 1494, 1446, 1425, 1340, 1304, 1290, 1185, 1153, 1121, 1085, 1018, 987, 909, 876, 816, 760, 696, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{24}N_2O_4NaS_2^{+1}$$(M+Na)^+$ requires 479.1070, Found: 479.1069.

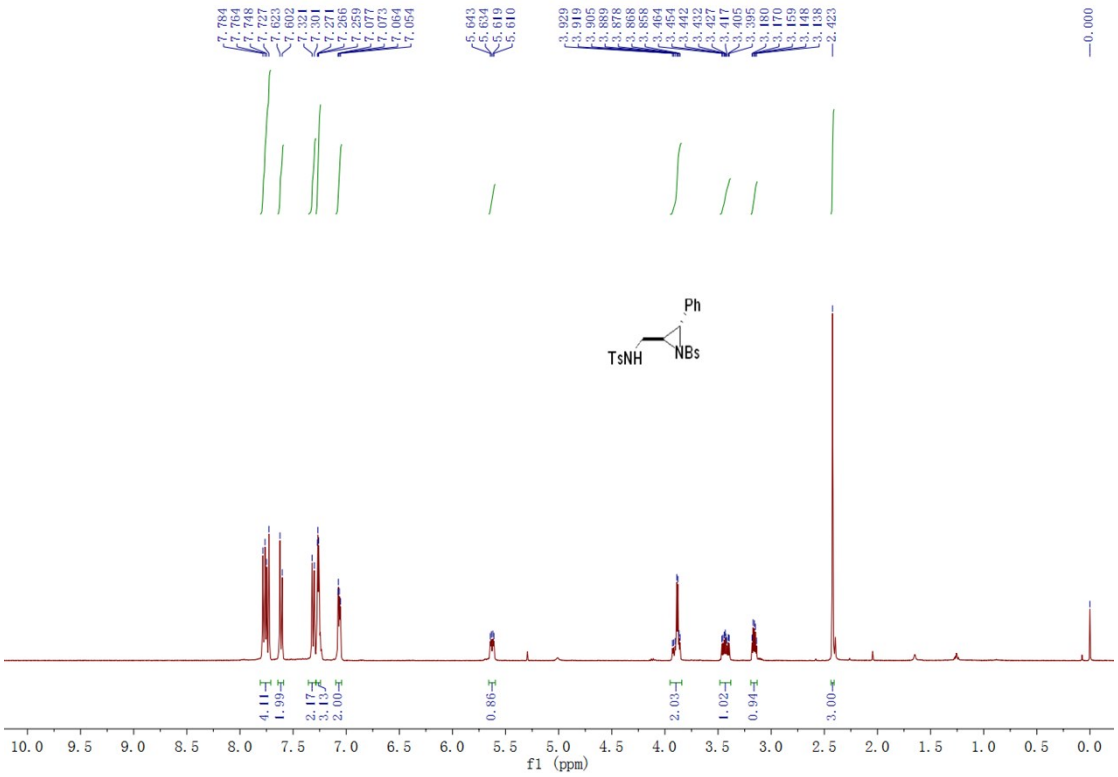


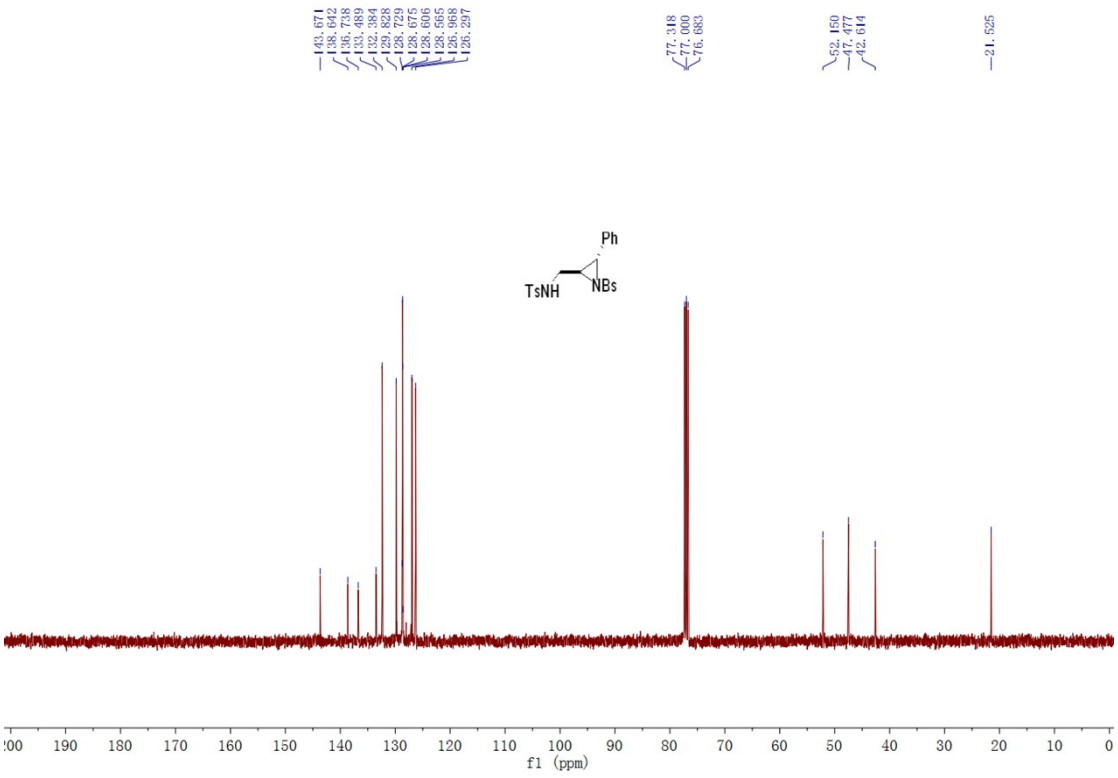


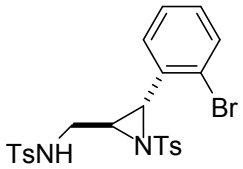


Compound D2:

4.0 mmol scale, a white solid, 37% yield (778.8 mg). M.p.: 54-57 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.42 (s, 3H), 3.13-3.18 (m, 1H), 3.39-3.47 (m, 1H), 3.85-3.93 (m, 1H), 3.88 (d, J = 4.4 Hz, 1H), 5.63 (dd, J = 3.6 Hz, 9.6 Hz, 1H), 7.05-7.08 (m, 2H), 7.25-7.28 (m, 3H), 7.31 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.5, 42.6, 47.5, 52.2, 126.3, 127.0, 128.57, 128.61, 128.68, 128.73, 129.8, 132.4, 133.5, 136.7, 138.6, 143.7. IR (neat) 3293, 3090, 3062, 3031, 2922, 2866, 1597, 1574, 1495, 1424, 1390, 1321, 1154, 1085, 1068, 1010, 984, 908, 813, 748, 696 cm^{-1}. HRMS (APCI) Calcd. for $C_{22}H_{22}BrN_2O_4S_2^{+1}$(M+H)$^+$ requires 521.0199, Found: 521.0188.

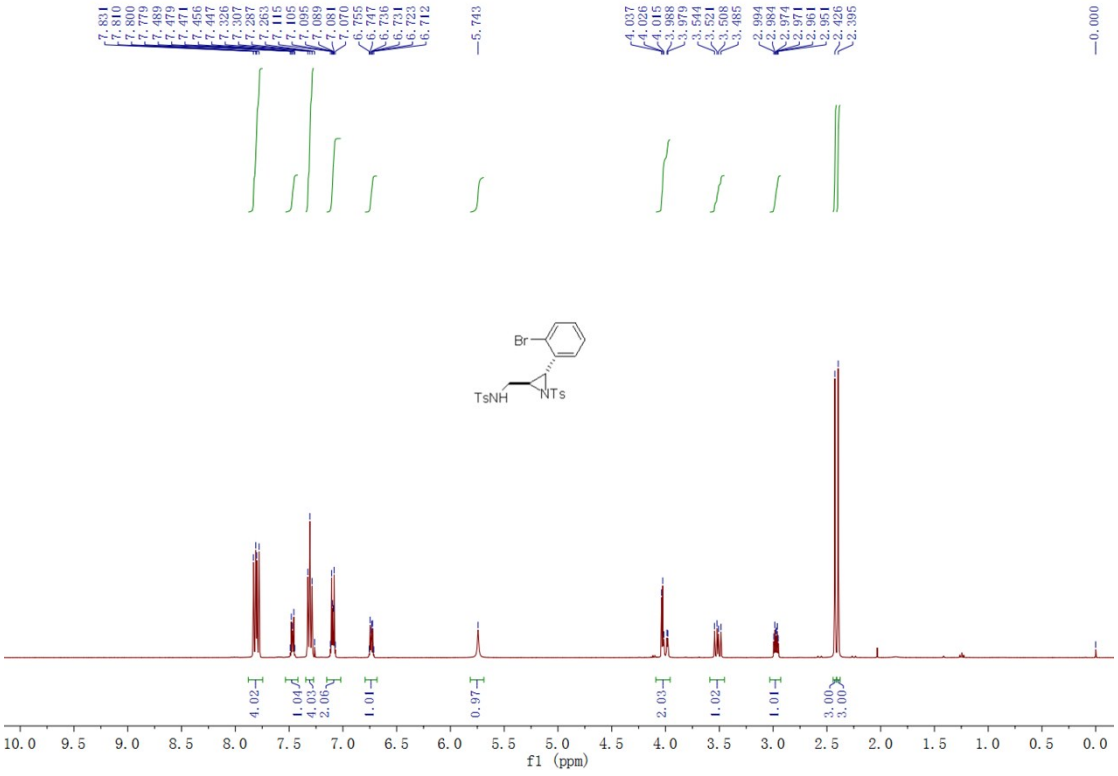






Compound D3:

2.7 mmol scale, a light yellow gem, 69% yield (994.5 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.43 (s, 3H), 2.95-3.00 (m, 1H), 3.51 (dd, *J* = 9.2 Hz, 14.4 Hz, 1H), 4.00 (dd, *J* = 4.0 Hz, 14.4 Hz, 1H), 4.03 (d, *J* = 4.0 Hz, 1H), 5.74 (s, 1H), 6.71-6.76 (m, 1H), 7.07-7.12 (m, 2H), 7.26-7.33 (m, 4H), 7.44-7.49 (m, 1H), 7.77-7.84 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.4, 21.6, 42.7, 47.3, 51.2, 122.9, 126.8, 127.16, 127.24, 127.5, 129.7, 132.2, 133.6, 136.2, 136.6, 143.5, 144.8. HRMS (ESI) Calcd. for $C_{23}H_{24}BrN_2O_4S_2^{+1}(M+H)^+$ requires 535.0355, Found: 535.0352.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7.115
7.105
7.095
7.089
7.081
7.070
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6.747
6.736
6.731
6.723
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5.743
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3.521
3.508
3.485
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2.984
2.974
2.971
2.961
2.951
2.426
2.395
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Br
TsNH
NTs
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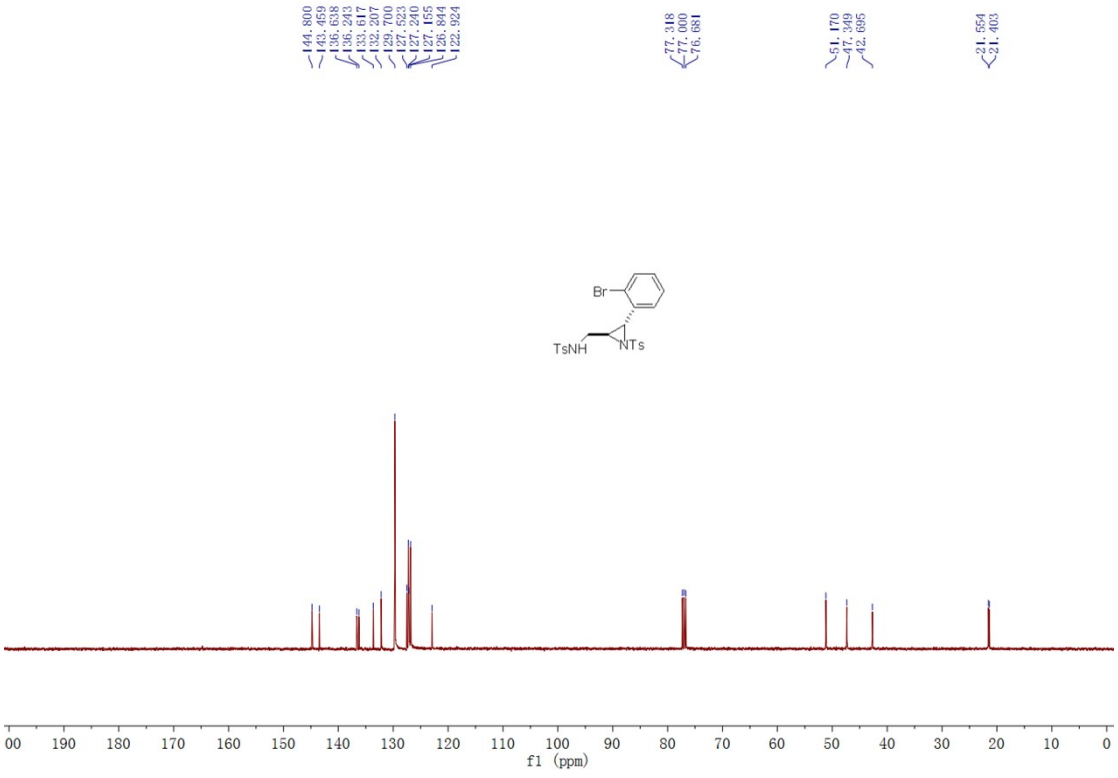
1.04
4.03
2.06
1.01
0.97
2.03
1.02
1.01
3.00
3.00
f1 (ppm)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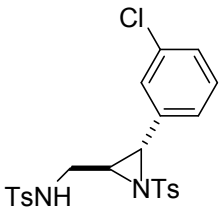
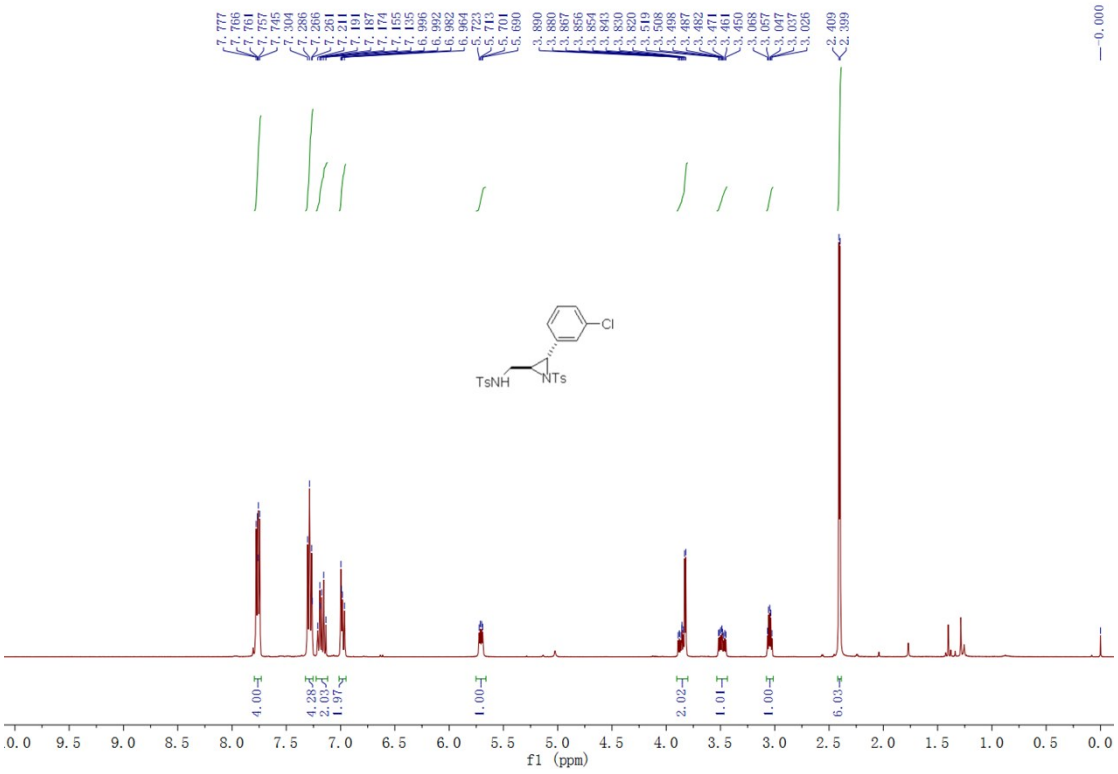
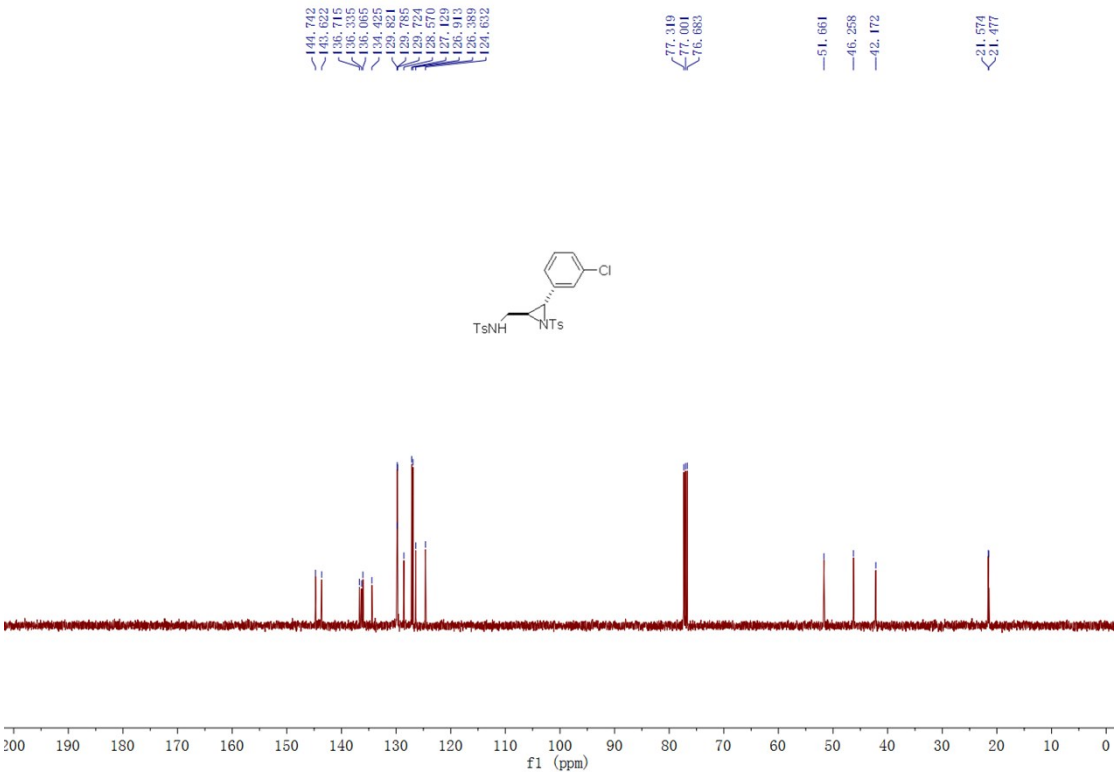
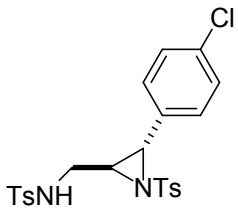


Compound D4:

4.0 mmol scale, a white solid, 63% yield (1.2350 g). M.p.: 49-50 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.41 (s, 3H), 3.02-3.07 (m, 1H), 3.45-3.52 (m, 1H), 3.82-3.89 (m, 2H), 5.71 (dd, J = 4.0 Hz, 8.8 Hz, 1H), 6.96-7.00 (m, 2H), 7.13-7.22 (m, 2H), 7.26-7.31 (m, 4H), 7.74-7.78 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.5, 21.6, 42.2, 46.3, 51.7, 124.6, 126.4, 126.9, 127.1, 128.6, 129.72, 129.79, 129.82, 134.4, 136.1, 136.3, 136.7, 143.6, 144.7. IR (neat) 3284, 3064, 3026, 2956, 2923, 2858, 1597, 1574, 1494, 1440, 1398, 1321, 1304, 1287, 1185, 1154, 1119, 1085, 1039, 1018, 989, 920, 812, 783, 687, 662, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{24}ClN_2O_4S_2^{+1}$(M+H)$^{+}$ requires 491.0861, Found: 491.0859.

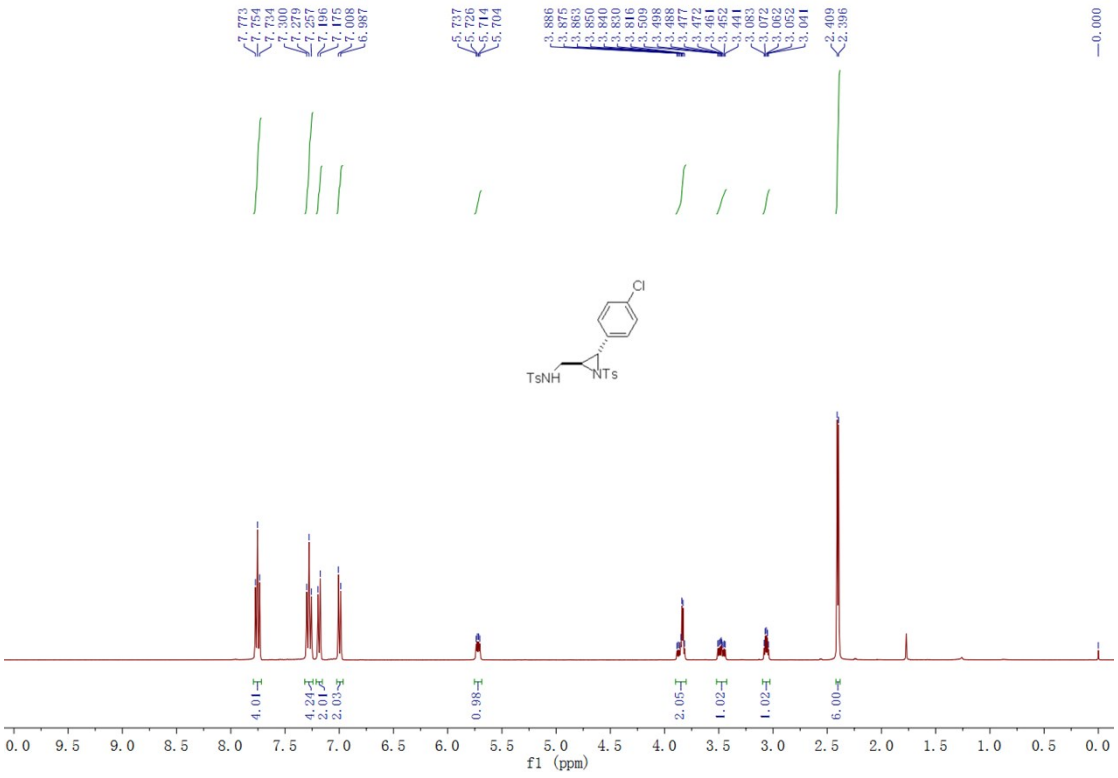






Compound D5:

4.0 mmol scale, a white solid, 63% yield (1.1566 g). M.p.: 58-60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.41 (s, 3H), 3.04-3.09 (m, 1H), 3.44-3.51 (m, 1H), 3.81-3.89 (m, 2H), 5.72 (dd, J = 4.0 Hz, 8.8 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.25-7.30 (m, 4H), 7.34-7.78 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.5, 21.6, 42.2, 46.5, 51.7, 126.9, 127.1, 127.7, 128.7, 129.7, 129.8, 132.5, 134.2, 136.5, 136.7, 143.6, 144.7. IR (neat) 3284, 3064, 3028, 2922, 2865, 1596, 1494, 1437, 1398, 1320, 1304, 1290, 1185, 1154, 1119, 1085, 1015, 986, 911, 812, 722, 705, 687, 661 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{24}ClN_2O_4S_2^{+1}(M+H)^+$ requires 491.0861, Found: 491.0861.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3.062
3.052
3.041
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Cl
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NTs
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2.03
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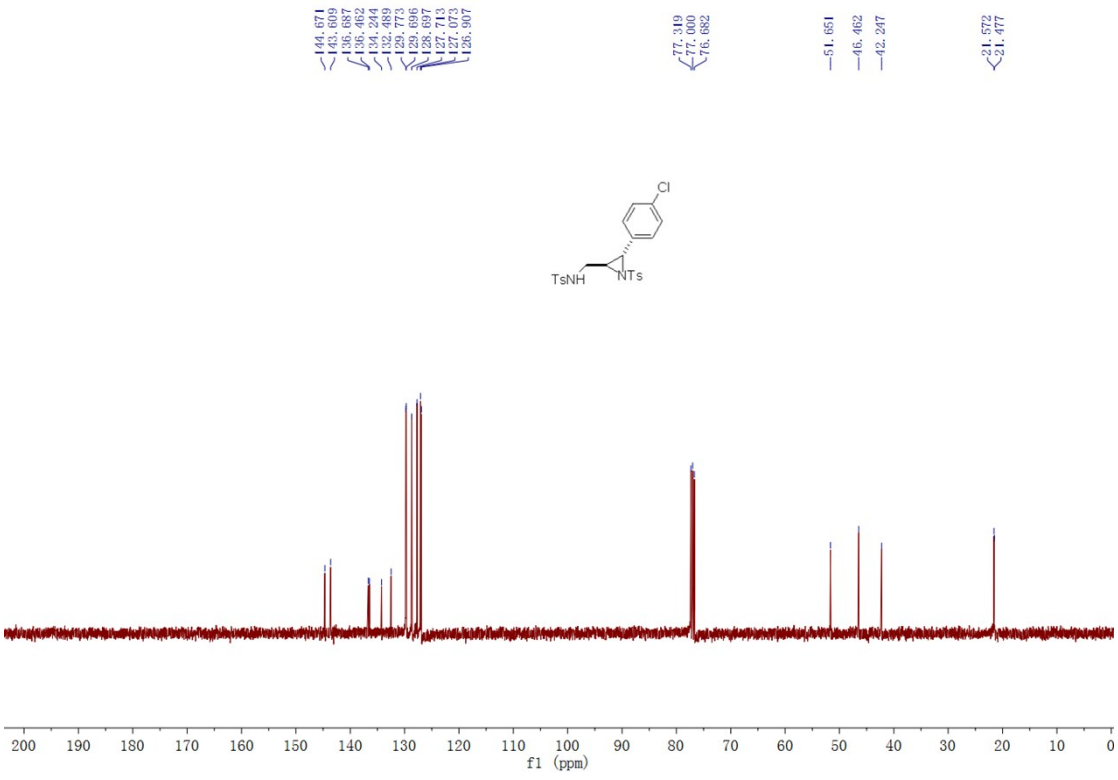
1.02
1.02
6.00
f1 (ppm)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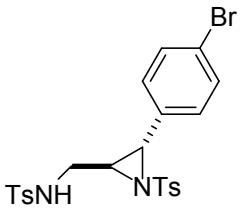
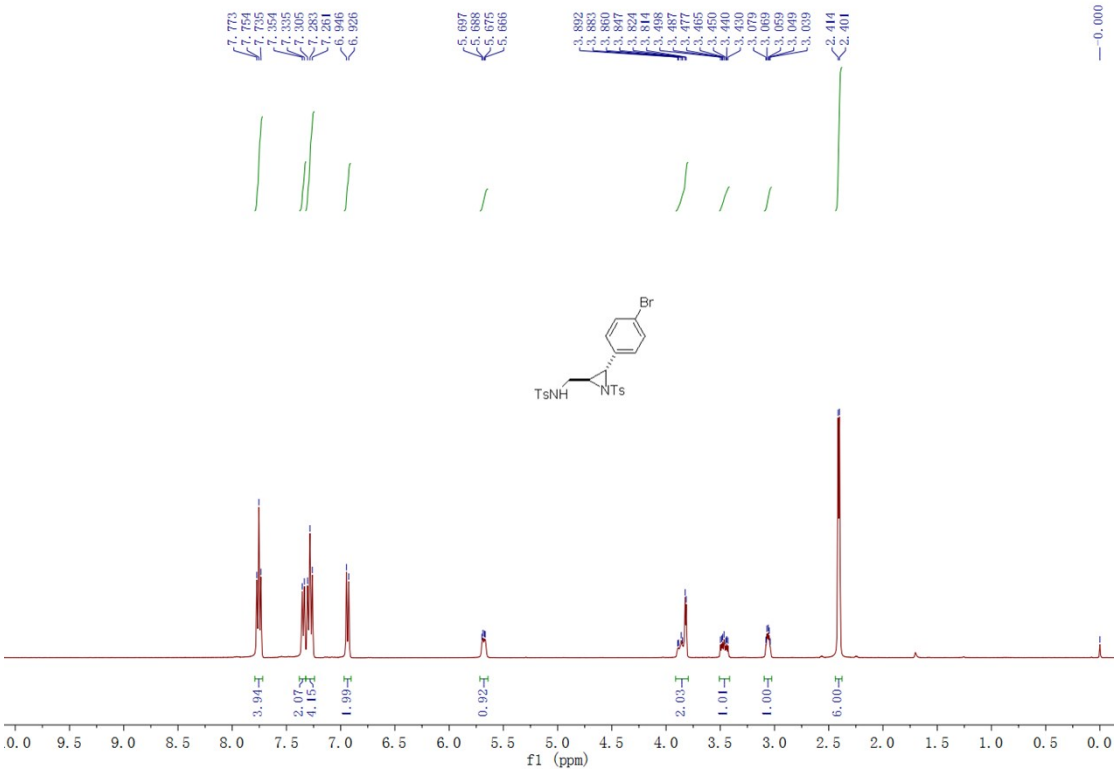
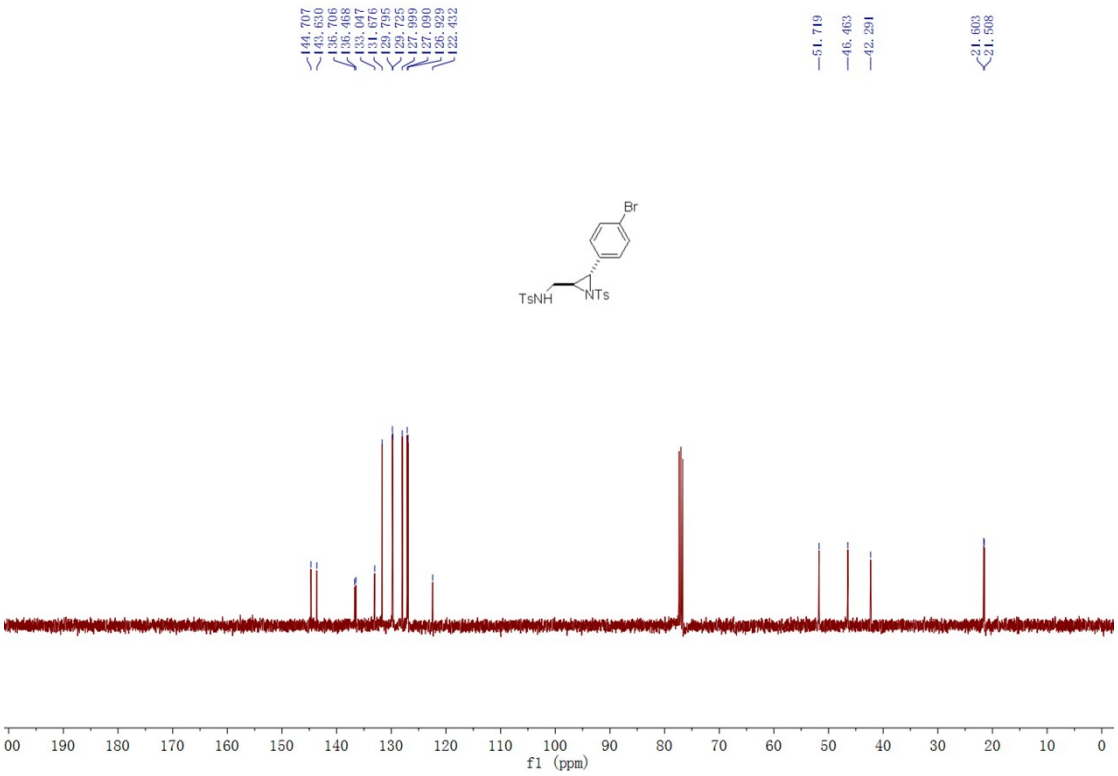
f1 (ppm)

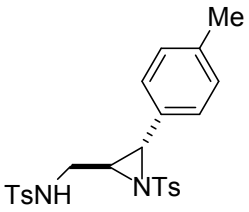


Compound D6:

4.0 mmol scale, a white solid, 72% yield (1.5379 g). M.p.: 69-71 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.41 (s, 3H), 3.03-3.08 (m, 1H), 3.43-3.50 (m, 1H), 3.81-3.90 (m, 2H), 5.68 (dd, J = 3.6 Hz, 8.8 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 7.26-7.31 (m, 4H), 7.34 (d, J = 7.6 Hz, 2H), 7.73-7.78 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.5, 21.6, 42.3, 46.5, 51.7, 122.4, 126.9, 127.1, 128.0, 129.7, 129.8, 131.7, 133.0, 136.5, 136.7, 143.6, 144.7. IR (neat) 3282, 3064, 2922, 1596, 1491, 1436, 13936, 1320, 1304, 1184, 1154, 1085, 1071, 1011, 986, 910, 871, 812, 719, 705, 687, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{24}BrN_2O_4S_2^{+1}$(M+H)$^{+}$ requires 535.0355, Found: 535.0356.

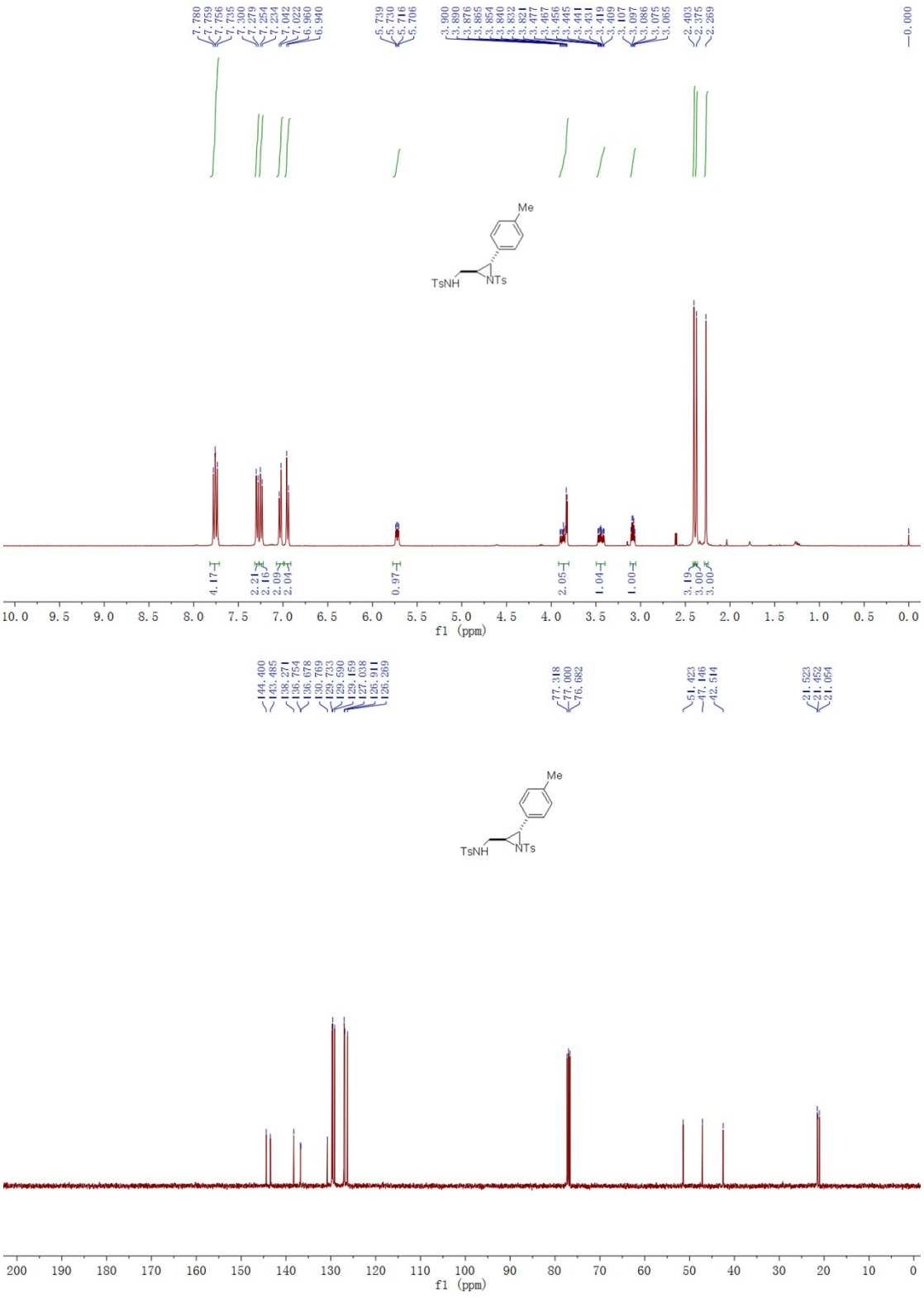




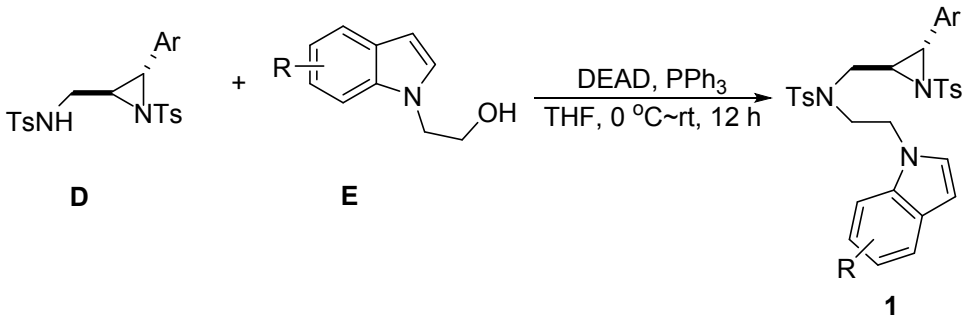


Compound D7:

4.0 mmol scale, a white solid, 72% yield (827.3 mg). M.p.: 55-58 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.27 (s, 3H), 2.38 (s, 3H), 2.40 (s, 3H), 3.06-3.11 (m, 1H), 3.41-3.48 (m, 1H), 3.82-3.90 (m, 2H), 5.72 (dd, J = 4.0 Hz, 9.2 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.1, 21.45, 21.52, 42.5, 47.1, 51.4, 126.3, 126.9, 127.0, 129.2, 129.6, 129.7, 130.8, 136.7, 136.8, 138.3, 143.5, 144.4. IR (neat) 3294, 3064, 3031, 2974, 2923, 2868, 1597, 1518, 1494, 1444, 1401, 1323, 1303, 1290, 1185, 1157, 1086, 1041, 1018, 990, 915, 813, 759, 706, 689, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{27}N_2O_4S_2^{+1}(M+H)^+$ requires 471.1407, Found: 471.1405.

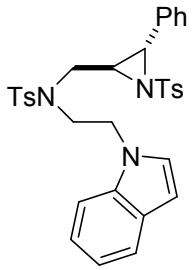


4. General procedure for synthesis of 1



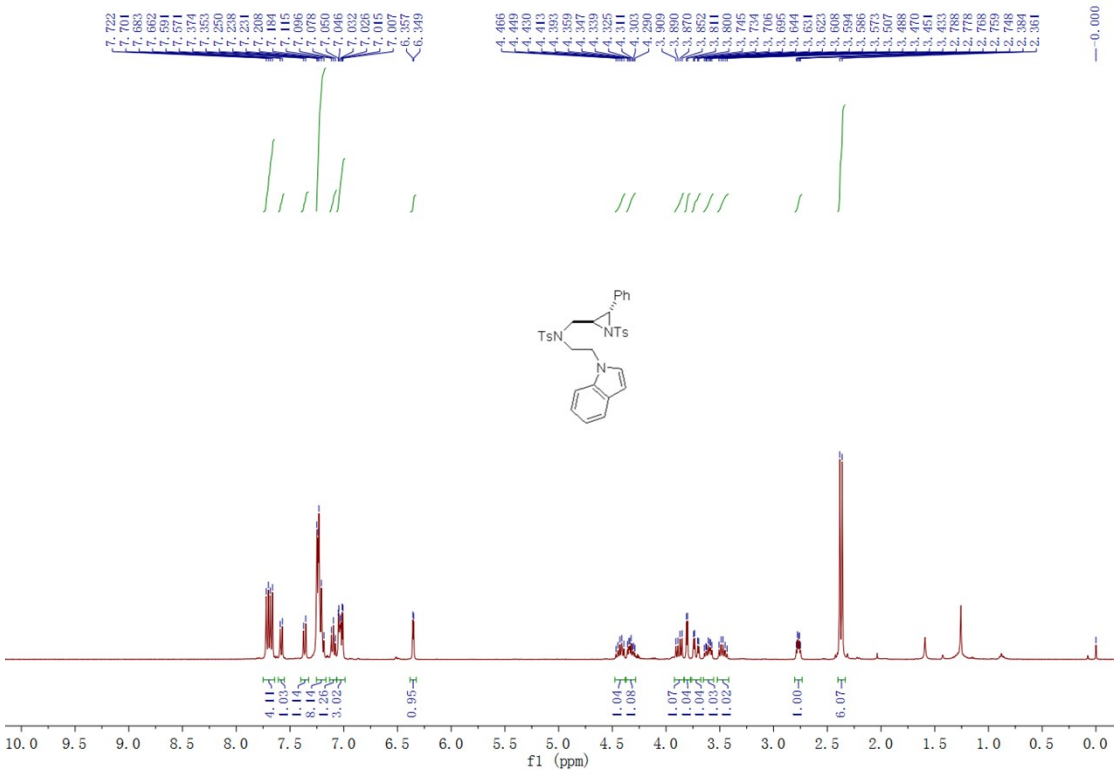
To a solution of **D** (0.6 mmol, 1.0 equiv.), **E**[2] (0.72 mmol, 1.2 equiv.), and triphenylphosphane (0.72 mmol, 1.2 equiv.) in THF (20 mL), (0.72 mmol, 1.2 equiv.) DEAD was added dropwise at 0 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 12 hours. Then, the resulting solution was concentrated in vacuum and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 6 / 1) to give white solid **1** in moderate yield.

5. Characterization and spectra charts for 1



Compound 1a:

1.6 mmol scale, a white solid, 25% yield (238.0 mg). M.p.: 70-73°C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H), 2.38 (s, 3H), 2.74-2.79 (m, 1H), 3.43-3.51 (m, 1H), 3.57-3.65 (m, 1H), 3.72 (dd, *J* = 4.4 Hz, 15.6 Hz, 1H), 3.81 (d, *J* = 4.4 Hz, 1H), 3.88 (dd, *J* = 7.2 Hz, 15.6 Hz, 1H), 4.29-4.36 (m, 1H), 4.39-4.47 (m, 1H), 6.35 (d, *J* = 3.2 Hz, 1H), 7.00-7.05 (m, 3H), 7.10 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.18-7.25 (m, 8H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 45.9, 48.4, 48.5, 49.5, 49.8, 101.9, 109.1, 119.6, 121.0, 121.9, 126.8, 127.2, 127.3, 127.9, 128.4, 128.5, 128.6, 129.6, 130.0, 133.6, 135.3, 135.6, 136.6, 144.0, 144.4. IR (neat) 3057, 3039, 3005, 2974, 2943, 2922, 1595, 1462, 1336, 1320, 1305, 1259, 1155, 1120, 1085, 1034, 1017, 994, 968, 924, 910, 895, 813, 761, 732, 693 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{34}N_3O_4S_2^{+1}$(M+H)$^+$ requires 600.1985, Found: 600.1986.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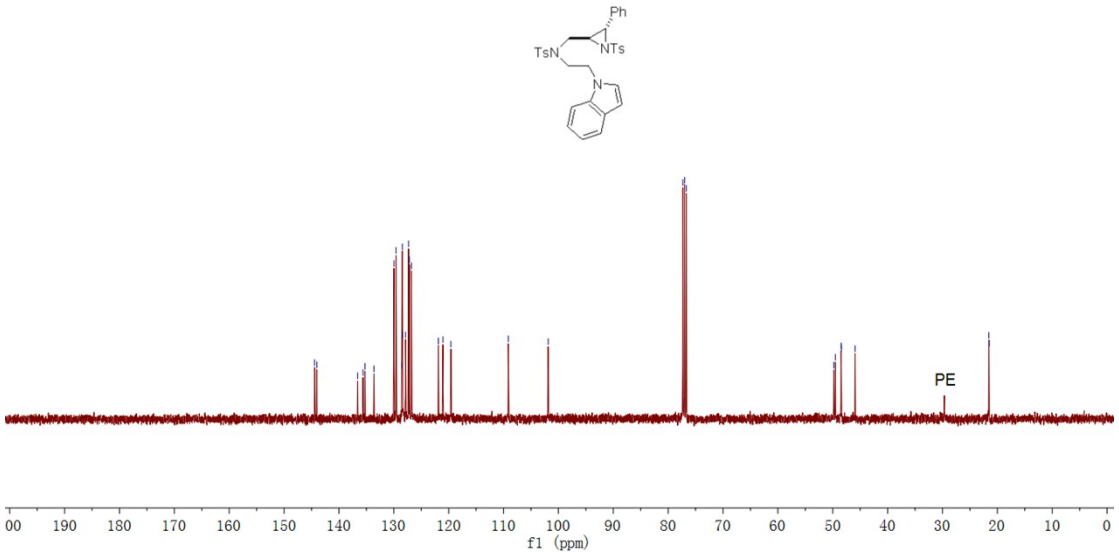
NTs
N
f1 (ppm)


Ph
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NTs
N
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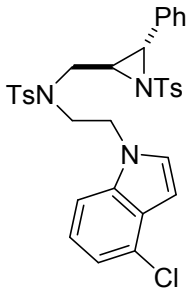
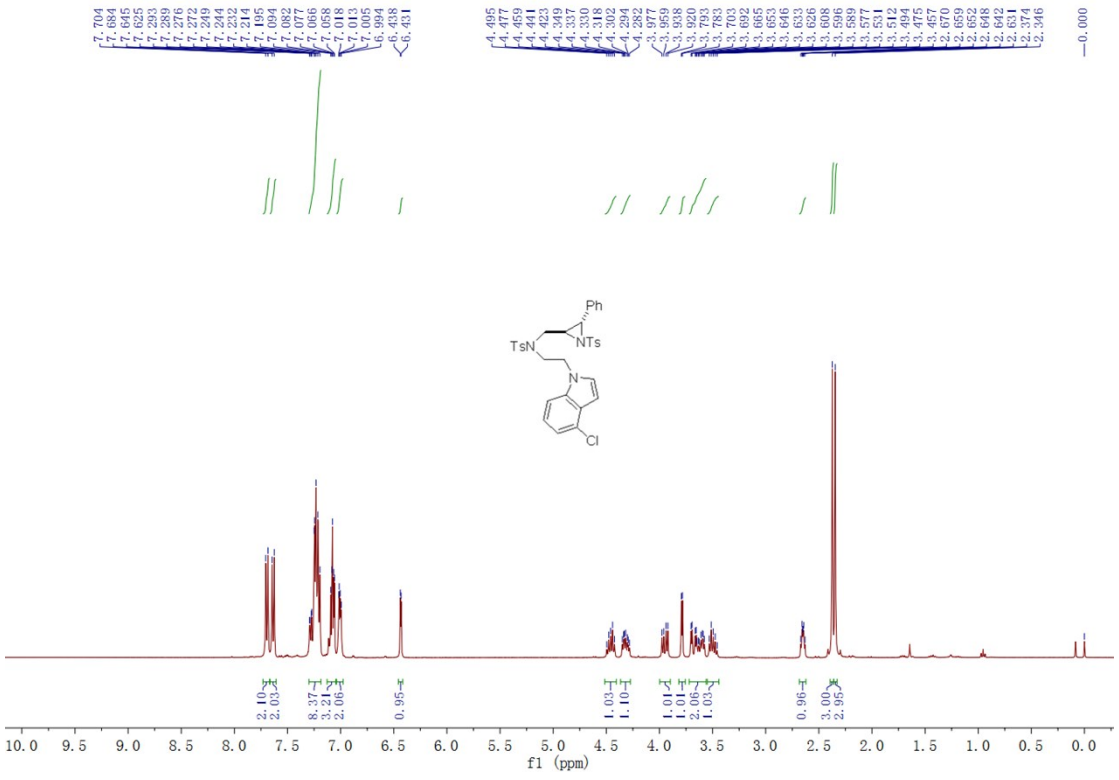
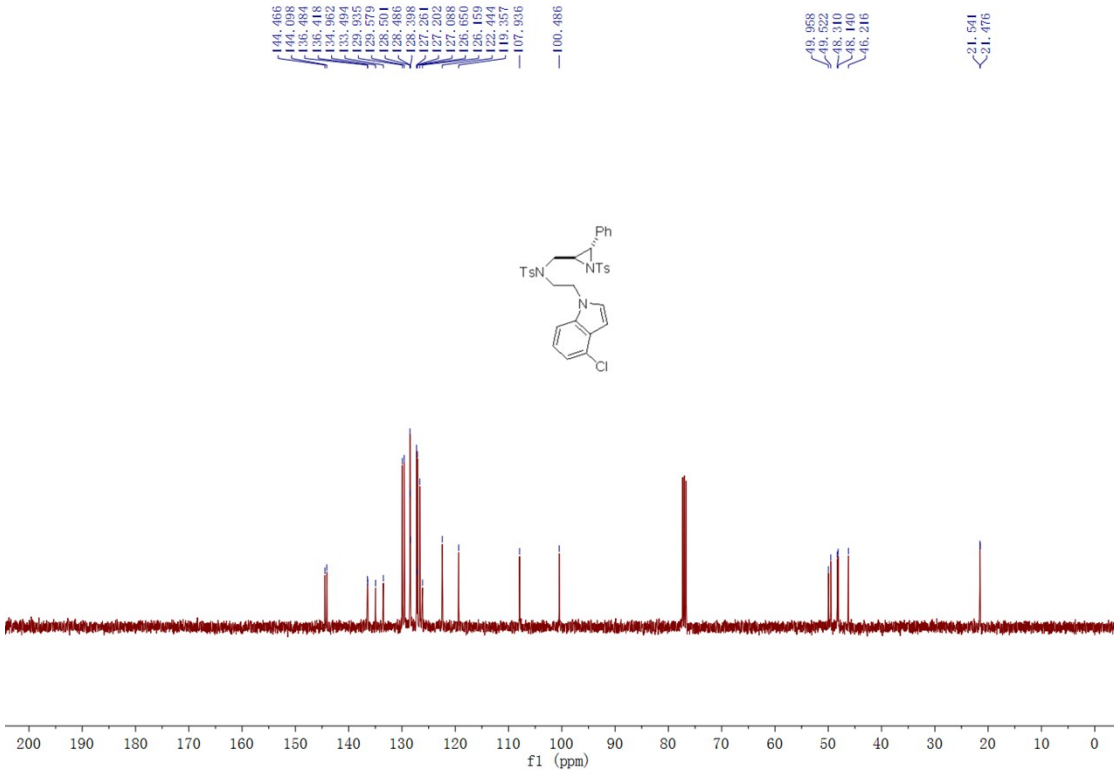
f1 (ppm)

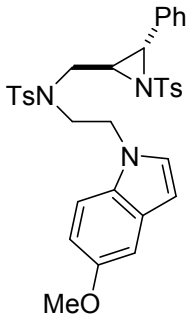


Compound 1b:

0.6 mmol scale, a white solid, 68% yield (258.8 mg). M.p.: 75-78 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H), 2.37 (s, 3H), 2.63-2.67 (m, 1H), 3.45-3.54 (m, 1H), 3.57-3.71 (m, 2H), 3.79 (d, J = 4.0 Hz, 1H), 3.95 (dd, J = 7.2 Hz, 15.6 Hz, 1H), 4.28-4.35 (m, 1H), 4.42-4.50 (m, 1H), 6.43 (d, J = 2.8 Hz, 1H), 6.99-7.02 (m, 2H), 7.05-7.10 (m, 3H), 7.19-7.30 (m, 8H), 7.64 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.48, 21.54, 46.2, 48.1, 48.3, 49.5, 50.0, 100.5, 107.9, 119.4, 122.4, 126.2, 126.7, 127.1, 127.2, 127.3, 128.40, 128.49, 128.50, 129.6, 129.9, 133.5, 135.0, 136.4, 136.5, 144.1, 144.5. IR (neat) 3000, 2975, 2942, 1621, 1598, 1488, 1450, 1335, 1318, 1306, 1241, 1154, 1088, 1036, 909, 811, 750, 731, 694, 652 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+H)$^{+}$ requires 634.1596, Found: 634.1582.

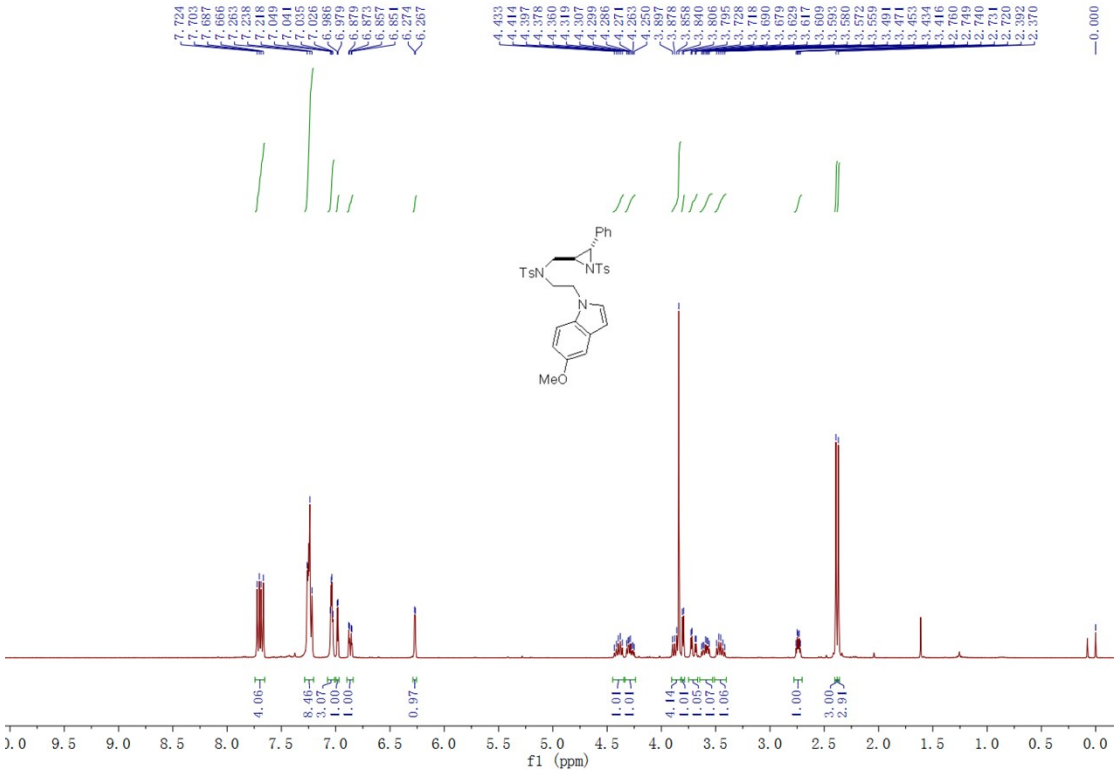






Compound 1c:

0.6 mmol scale, a white solid, 38% yield (157.0 mg). M.p.: 82-85 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 2.39 (s, 3H), 2.72-2.76 (m, 1H), 3.41-3.50 (m, 1H), 3.55-3.63 (m, 1H), 3.70 (dd, *J* = 4.4 Hz, 15.6 Hz, 1H), 3.80 (d, *J* = 4.4 Hz, 1H), 3.84-3.90 (m, 4H), 4.25-4.32 (m, 1H), 4.36-4.44 (m, 1H), 6.27 (d, *J* = 2.8 Hz, 1H), 6.87 (dd, *J* = 2.4 Hz, 8.8 Hz, 1H), 6.98 (d, *J* = 2.8 Hz, 1H), 7.02-7.05 (m, 3H), 7.21-7.27 (m, 8H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 46.2, 48.45, 48.47, 49.7, 49.8, 55.8, 101.4, 102.6, 109.9, 112.1, 126.8, 127.2, 127.3, 128.39, 128.40, 128.44, 128.9, 129.6, 130.0, 130.9, 133.6, 135.2, 136.5, 144.0, 144.4, 154.1. IR (neat) 3061, 3045, 3025, 2989, 2948, 2925, 2828, 1621, 1596, 1571, 1486, 1449, 1338, 1320, 1304, 1238, 1155, 1120, 1087, 1030, 940, 905, 812, 753, 710, 689, 652 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{36}N_3O_5S_2^{+1}$(M+H)$^+$ requires 630.2091, Found: 630.2091.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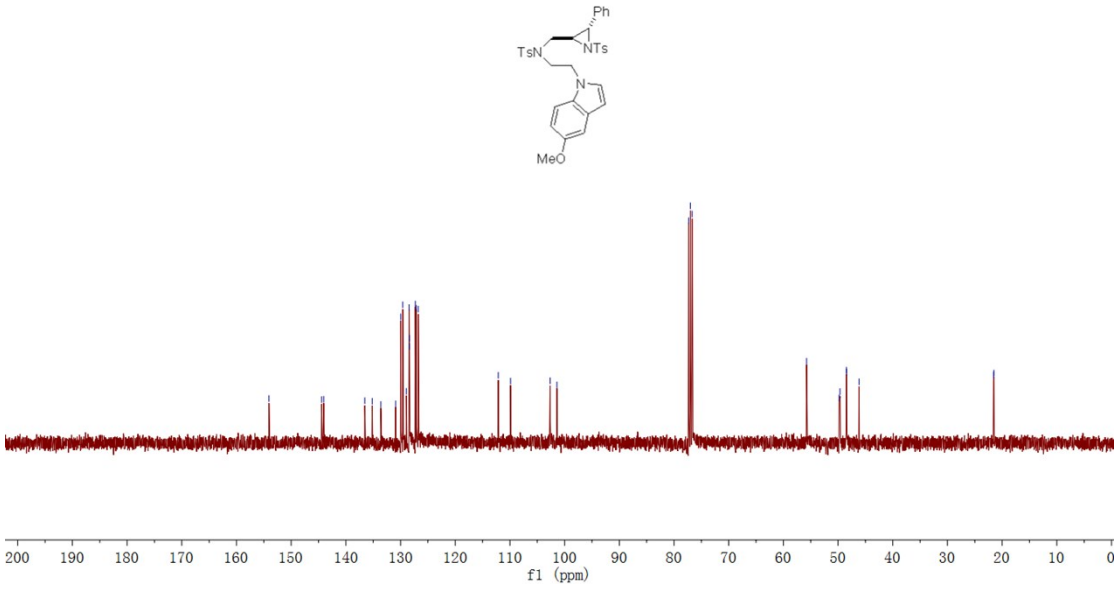
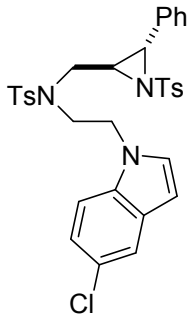
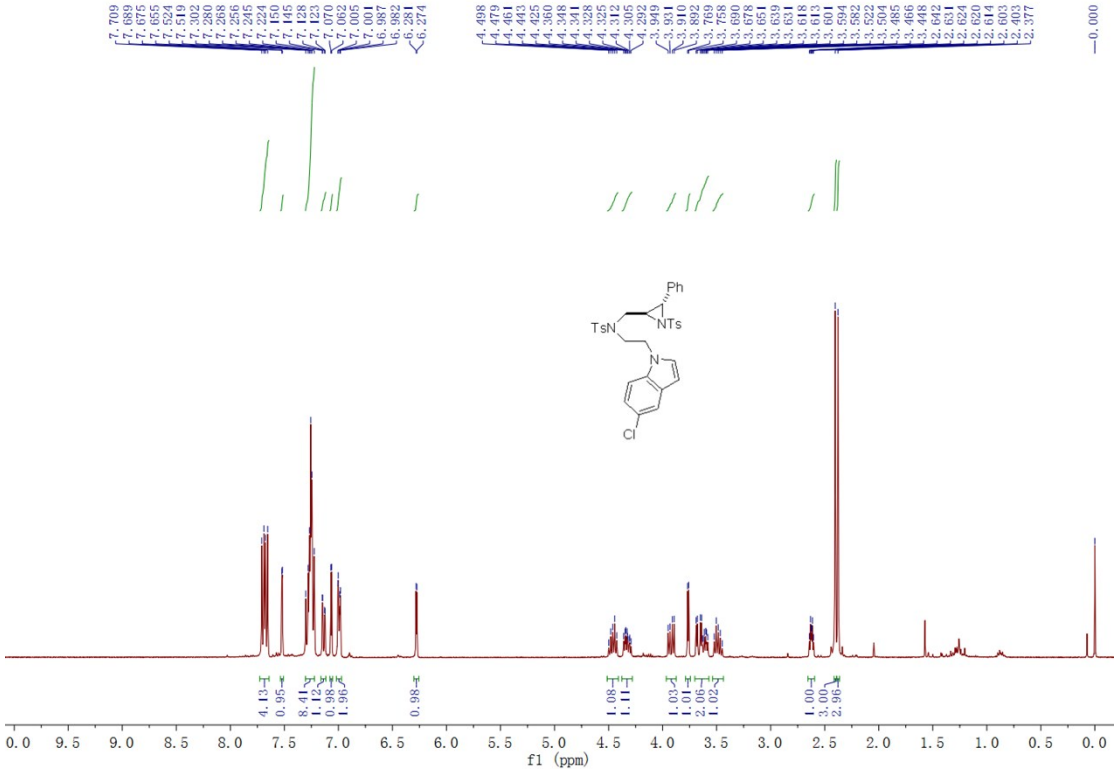
TsN
N
MeO
f1 (ppm)

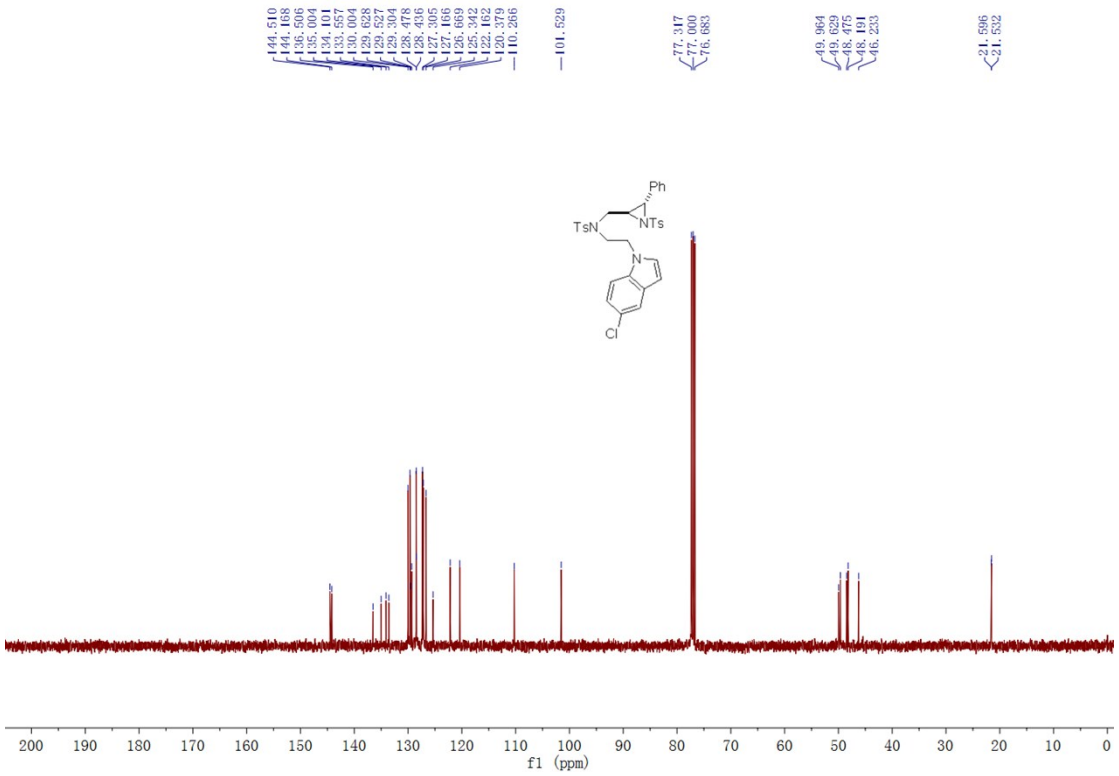

Ph
NTs
TsN
N
MeO
f1 (ppm)

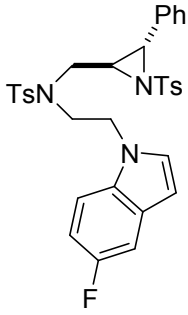


Compound 1d:

0.6 mmol scale, a white solid, 72% yield (275.5 mg). M.p.: 70-73 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.40 (s, 3H), 2.60-2.65 (m, 1H), 3.44-3.53 (m, 1H), 3.58-3.64 (m, 1H), 3.66 (dd, *J* = 4.8 Hz, 15.6 Hz, 1H), 3.76 (d, *J* = 4.4 Hz, 1H), 3.92 (dd, *J* = 7.2 Hz, 15.6 Hz, 1H), 4.29-4.36 (m, 1H), 4.42-4.50 (m, 1H), 6.28 (d, *J* = 2.8 Hz, 1H), 6.98-7.01 (m, 2H), 7.07 (d, *J* = 2.8 Hz, 1H), 7.14 (dd, *J* = 2.0 Hz, 8.8 Hz, 1H), 7.22-7.31 (m, 8H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 46.2, 48.2, 48.5, 49.6, 50.0, 101.5, 110.3, 120.4, 122.2, 125.3, 126.7, 127.2, 127.3, 128.4, 128.5, 129.3, 129.5, 129.6, 130.0, 133.6, 134.1, 135.0, 136.5, 144.2, 144.5. IR (neat) 3042, 2998, 2942, 2917, 2837, 1621, 1596, 1486, 1449, 1337, 1318, 1305, 1238, 1154, 1120, 1086, 1031, 995, 948, 909, 846, 812, 800, 752, 710, 691 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{32}ClN_3O_4S_2Na^{+1}$(M+Na)$^{+}$ requires 656.1415, Found: 656.1413.



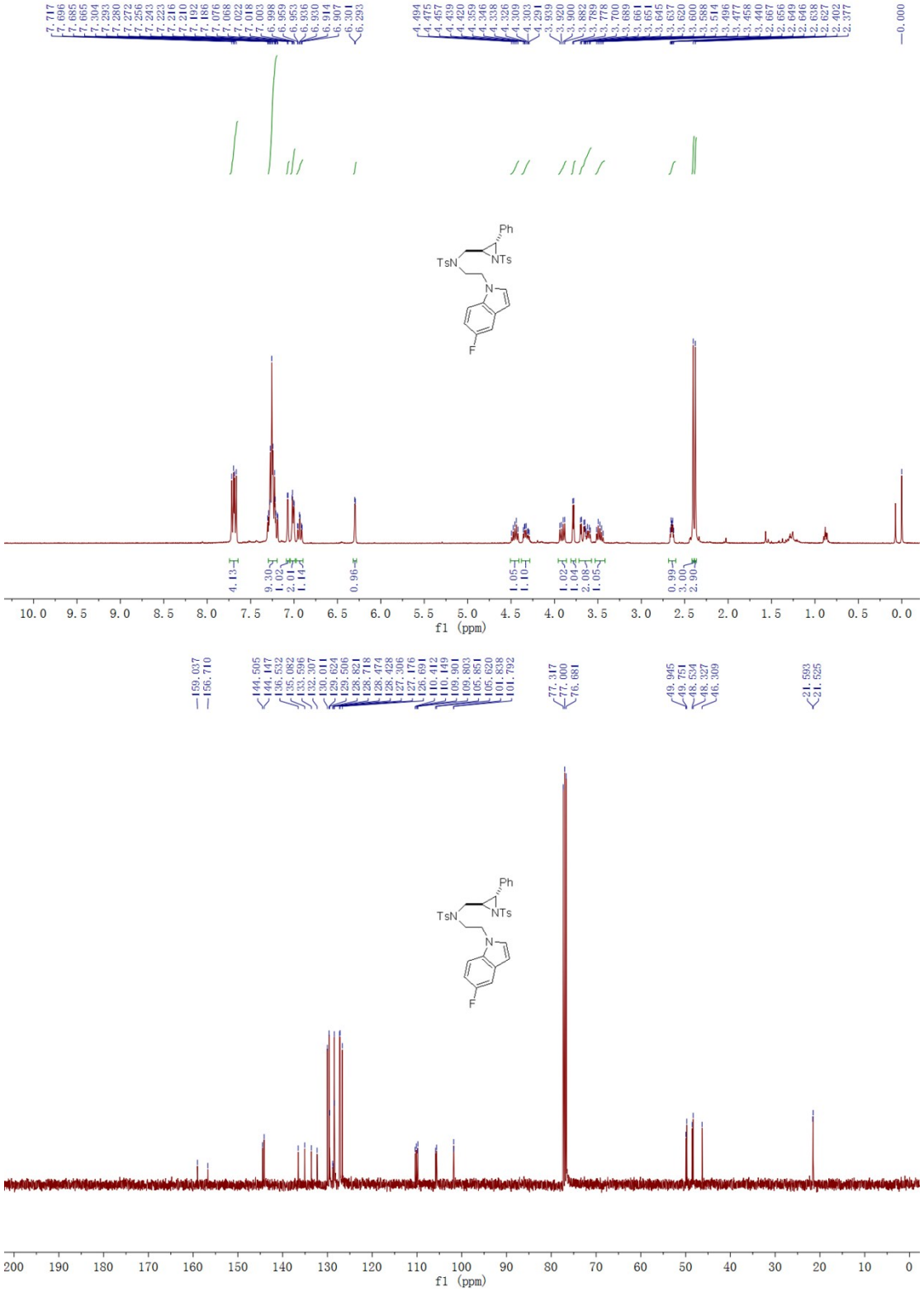


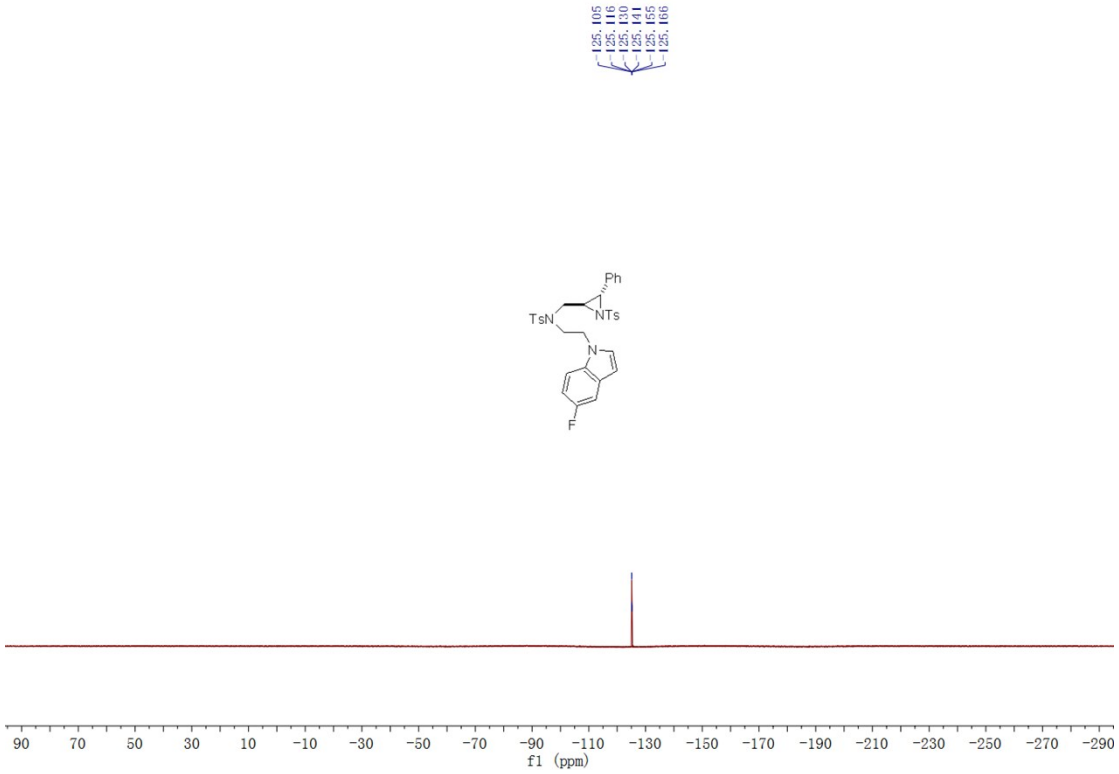


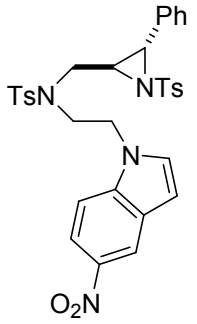
Compound 1e:

0.6 mmol scale, a white solid, 75% yield (279.1 mg). M.p.: 161-162 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.40 (s, 3H), 2.62-2.67 (m, 1H), 3.44-3.52 (m, 1H), 3.58-3.70 (m, 2H), 3.78 (d, J = 4.4 Hz, 1H), 3.91 (dd, J = 7.2 Hz, 15.6 Hz, 1H), 4.29-4.36 (m, 1H), 4.42-4.50 (m, 1H), 6.30 (d, J = 3.2 Hz, 1H), 6.90-6.96 (m, 1H), 6.99-7.03 (m, 2H), 7.07 (d, J = 3.2 Hz, 1H), 7.18-7.31 (m, 9H), 7.68 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 46.3, 48.3, 48.5, 49.8, 49.9, 101.8 (d, J = 4.6 Hz), 105.7 (d, J = 23.1 Hz), 109.9 (d, J = 9.8 Hz), 110.3 (d, J = 26.3 Hz), 126.7, 127.2, 127.3, 128.4, 128.5, 128.8 (d, J = 10.3 Hz), 129.5, 129.6, 130.0, 132.3, 133.6, 135.1, 136.5, 144.1, 144.5, 157.9 (d, J = 232.7 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -125.11- -125.17 (m). IR (neat) 3067, 3034, 2992, 2942, 2917, 1595, 1486, 1448, 1338, 1318, 1305, 1231, 1156, 1120, 1086, 1033, 995, 969, 948, 910, 846, 813, 799, 752,

733, 718, 693, 679 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{33}FN_3O_4S_2^{+1}(M+H)^+$ requires 618.1891, Found: 618.1891.

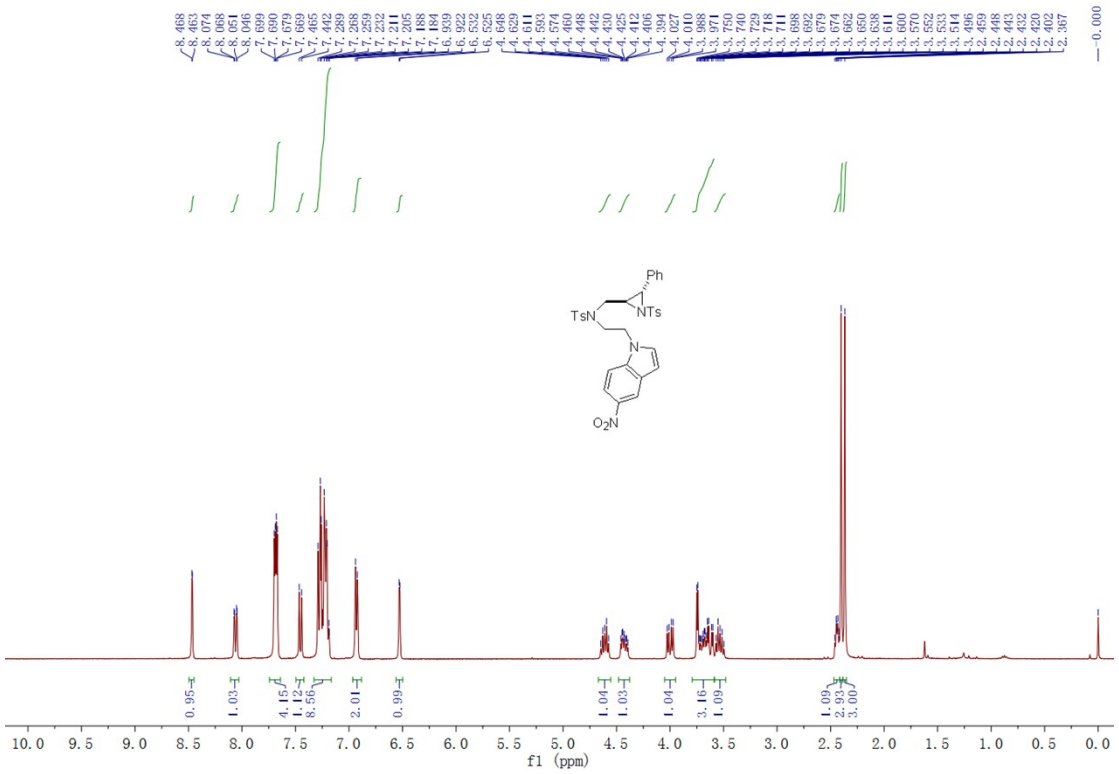


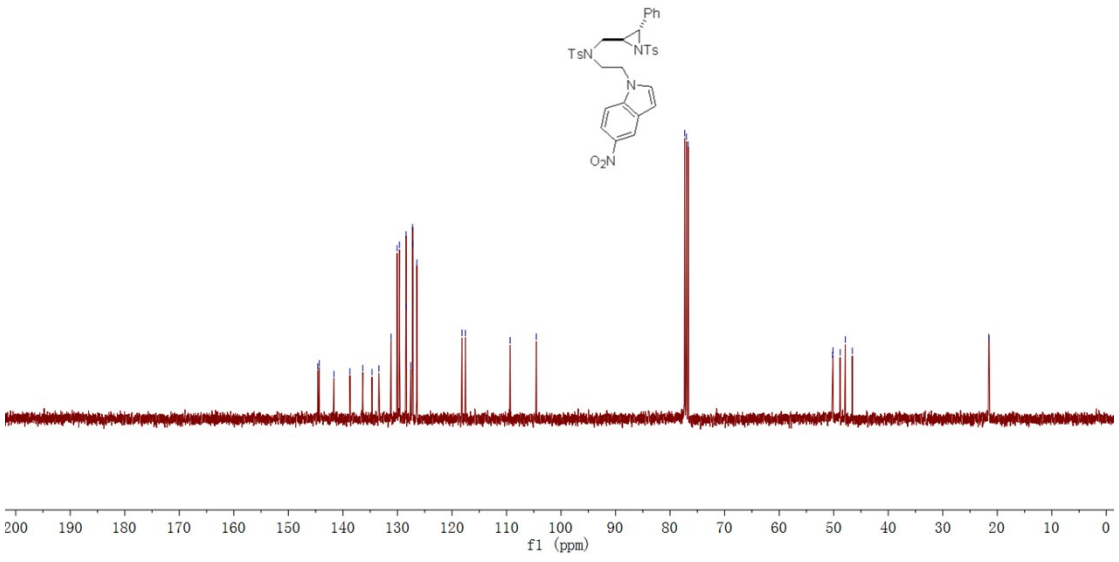


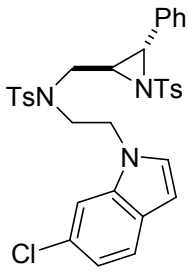


Compound 1f:

0.6 mmol scale, a yellow solid, 47% yield (177.6 mg). M.p.: 88-90 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 2.40 (s, 3H), 2.42-2.46 (m, 1H), 3.49-3.57 (m, 1H), 3.60-3.75 (m, 3H), 4.00 (dd, *J* = 6.8 Hz, 15.6 Hz, 1H), 4.39-4.46 (m, 1H), 4.57-4.65 (m, 1H), 6.53 (d, *J* = 2.8 Hz, 1H), 6.93 (d, *J* = 6.8 Hz, 2H), 7.18-7.24 (m, 8H), 7.45 (d, *J* = 9.2 Hz, 1H), 7.66-7.70 (m, 4H), 8.06 (dd, *J* = 3.2 Hz, 9.2 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 46.6, 47.9, 48.8, 50.1, 50.2, 104.5, 109.3, 117.5, 118.2, 126.4, 127.18, 127.22, 127.6, 128.42, 128.44, 129.6, 130.1, 131.2, 133.4, 134.7, 136.4, 138.7, 141.6, 144.3, 144.6. IR (neat) 3050, 3025, 3003, 2942, 2909, 2839, 1624, 1590, 1576, 1486, 1449, 1338, 1319, 1305, 1238, 1155, 1120, 1086, 1030, 952, 905, 813, 802, 713, 689 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{36}N_5O_6S_2^{+1}$(M+ NH_4)$^+$ requires 662.2102, Found: 662.2098.

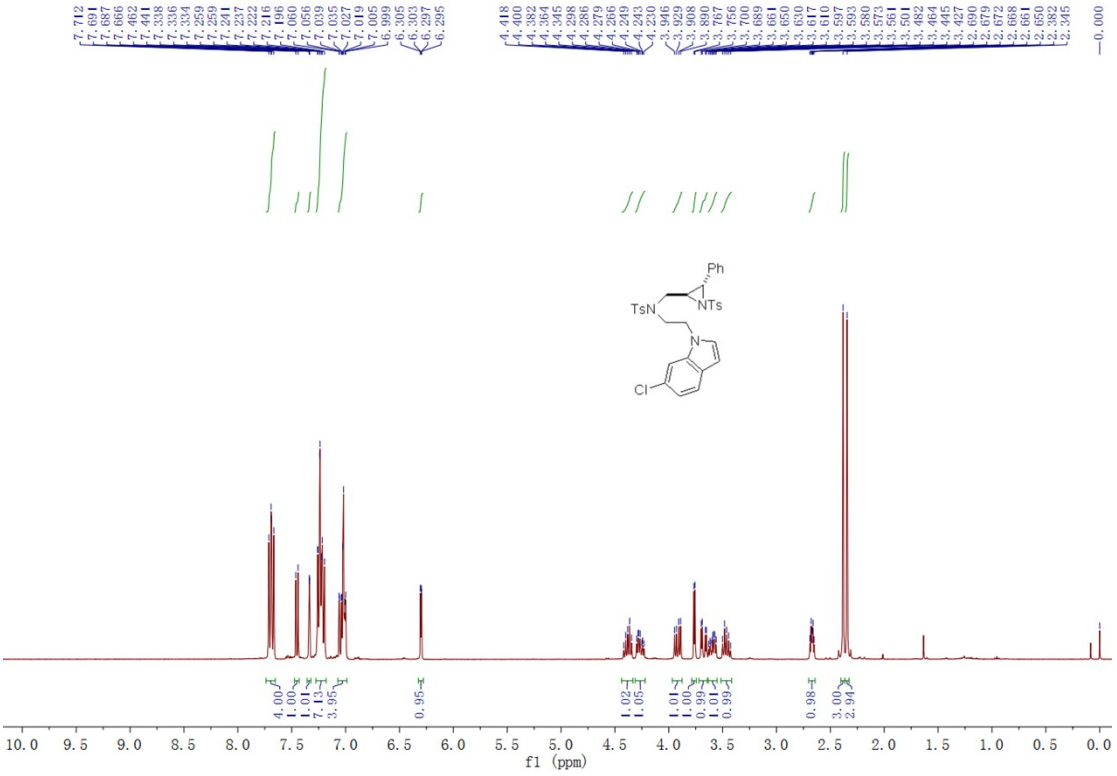

Ph
TsN
NTs
N
O2N
f1 (ppm)

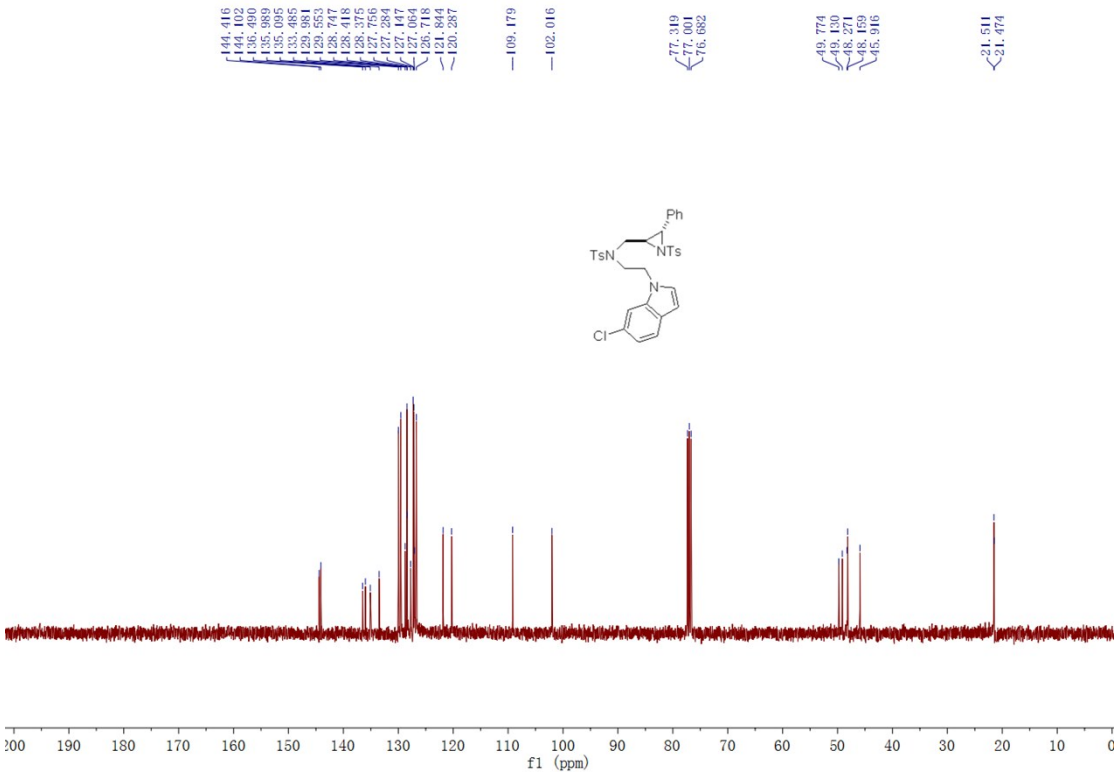

Ph
TsN
NTs
N
O2N
f1 (ppm)

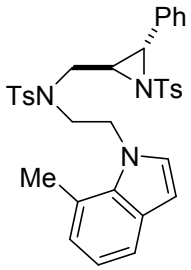


Compound 1g:

0.6 mmol scale, a white solid, 76% yield (289.9 mg). M.p.: 75-78 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H), 2.38 (s, 3H), 2.65-2.69 (m, 1H), 3.42-3.50 (m, 1H), 3.56-3.63 (m, 1H), 3.68 (dd, *J* = 4.4 Hz, 15.6 Hz, 1H), 3.76 (d, *J* = 4.4 Hz, 1H), 3.92 (dd, *J* = 7.2 Hz, 15.6 Hz, 1H), 4.23-4.30 (m, 1H), 4.35-4.42 (m, 1H), 6.30 (dd, *J* = 0.8 Hz, 3.2 Hz, 1H), 6.99-7.06 (m, 4H), 7.19-7.26 (m, 7H), 7.34 (dd, *J* = 0.8 Hz, 0.8 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.47, 21.51, 45.9, 48.2, 48.3, 49.1, 49.8, 102.0, 109.2, 120.3, 121.8, 126.7, 127.06, 127.15, 127.3, 127.8, 128.38, 128.42, 128.7, 129.6, 130.0, 133.5, 135.1, 136.0, 136.5, 144.1, 144.4. IR (neat) 3039, 3028, 3017, 2945, 2920, 2831, 1621, 1595, 1486, 1448, 1337, 1318, 1305, 1238, 1153, 1119, 1086, 1032,995, 968, 948, 908, 845, 812, 799, 753, 733, 711, 691 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+ H)$^{+}$ requires 634.1596, Found: 634.1601.

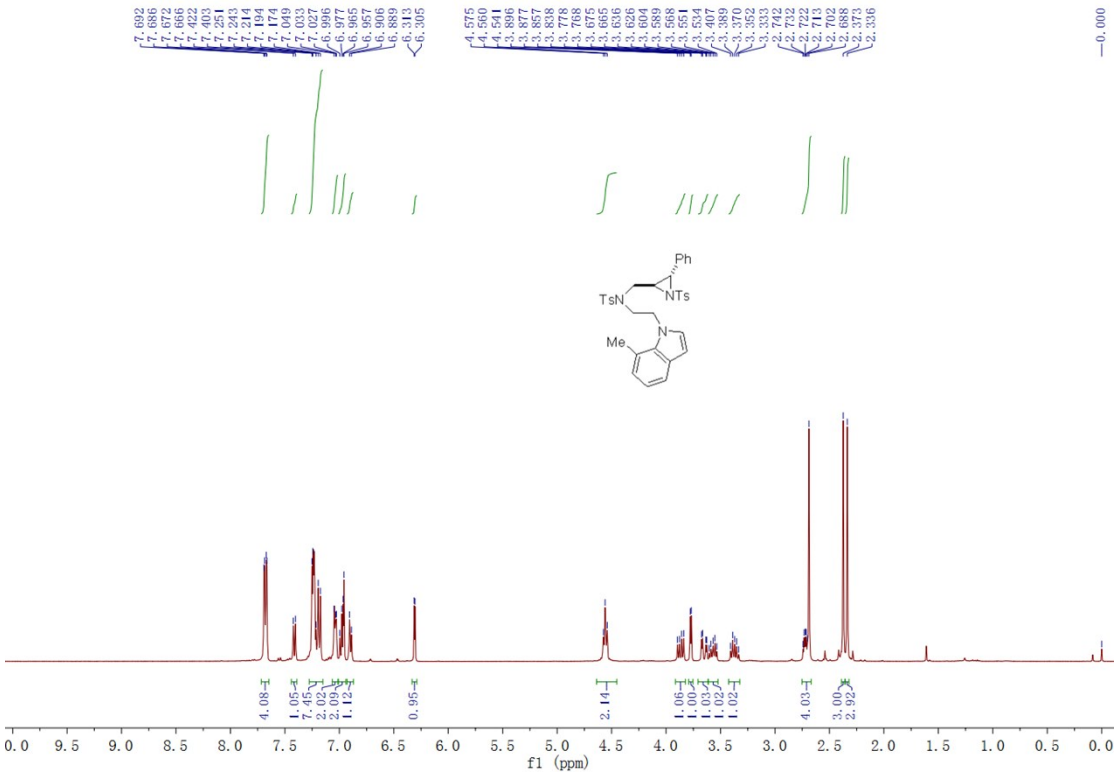






Compound 1h:

0.6 mmol scale, a white solid, 59% yield (216.4 mg). M.p.: 119-121 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H), 2.37 (s, 3H), 2.68-2.75 (m, 4H), 3.33-3.41 (m, 1H), 3.53-3.61 (m, 1H), 3.65 (dd, *J* = 4.0 Hz, 15.6 Hz, 1H), 3.77 (d, *J* = 4.0 Hz, 1H), 3.87 (dd, *J* = 7.6 Hz, 15.6 Hz, 1H), 4.54-4.58 (m, 2H), 6.31 (d, *J* = 3.2 Hz, 1H), 6.90 (d, *J* = 6.8 Hz, 1H), 6.95-7.00 (m, 2H), 7.02-7.05 (m, 2H), 7.17-7.26 (m, 7H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.66-7.70 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.8, 21.4, 21.5, 48.0, 48.5, 48.6, 49.4, 51.5, 102.5, 119.2, 119.8, 120.4, 124.9, 126.8, 127.1, 127.3, 128.3, 128.4, 129.46, 129.53, 129.7, 129.9, 133.5, 134.2, 135.2, 136.5, 144.0, 144.4. IR (neat) 3070, 3031, 2942, 2914, 2828, 1621, 1596, 1486, 1448, 1401, 1337, 1318, 1305, 1238, 1185, 1155, 1120, 1086, 1033, 995, 967, 940, 908, 888, 846, 812, 799, 753, 733, 710, 692 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{36}N_3O_4S_2^{+1}$(M+ H)$^+$ requires 614.2142, Found: 614.2140.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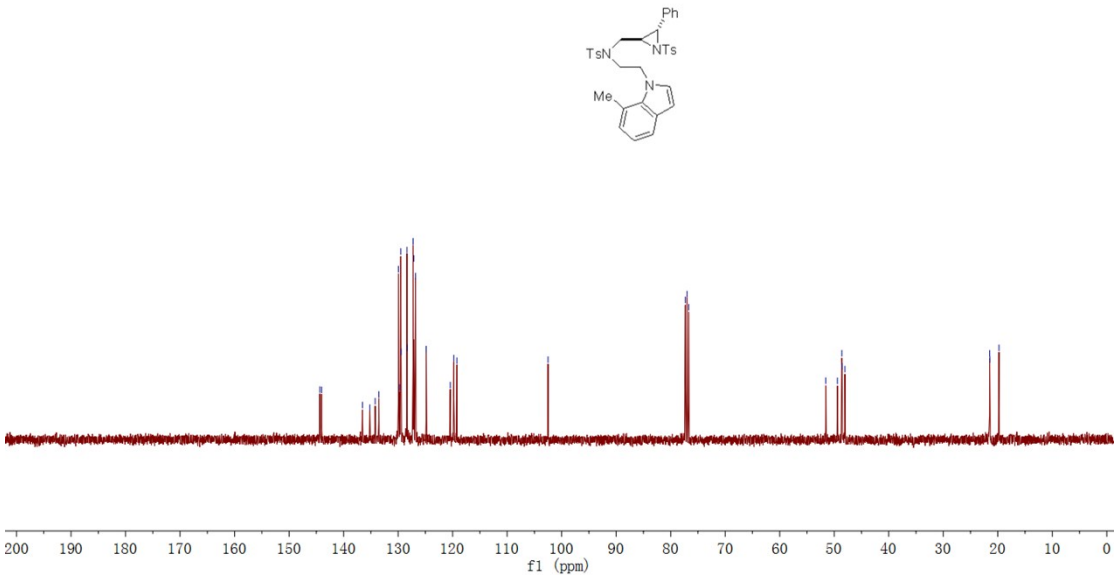
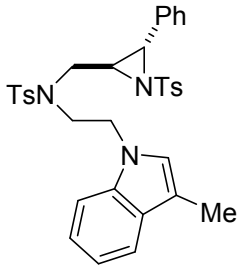
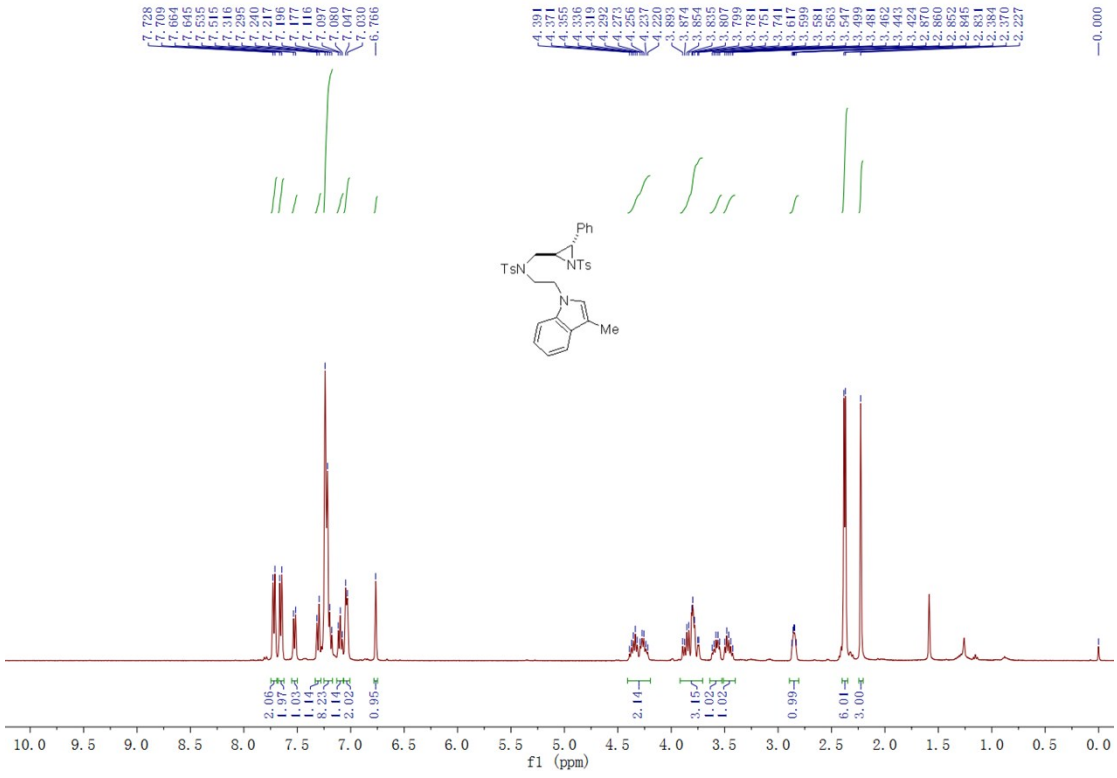
TsN
N
Me
f1 (ppm)

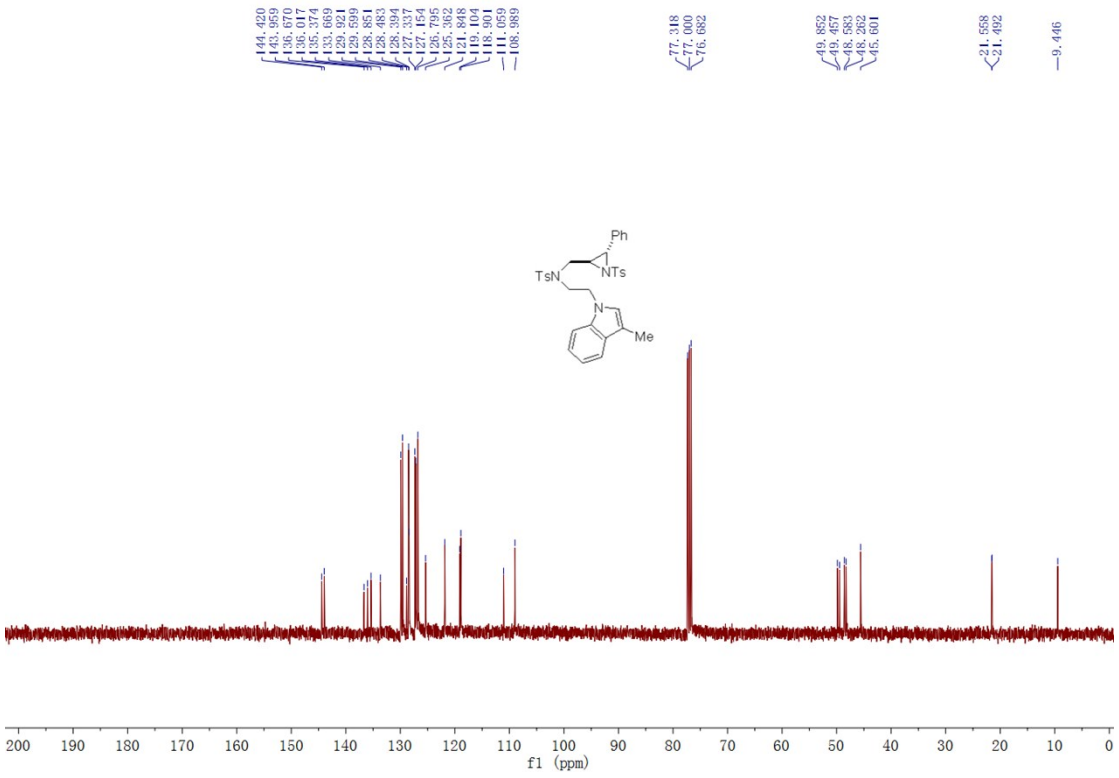

Ph
NTs
TsN
N
Me
f1 (ppm)

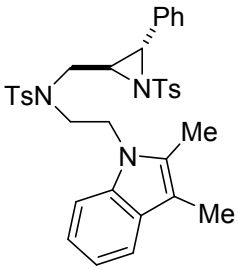


Compound 1i:

0.7 mmol scale, a white solid, 36% yield (154.8 mg). M.p.: 57-59 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.23 (s, 3H), 2.37 (s, 3H), 2.38 (s, 3H), 2.83-2.87 (m, 1H), 3.42-3.50 (m, 1H), 3.54-3.62 (m, 1H), 3.74-3.90 (m, 3H), 4.22-4.30 (m, 1H), 4.32-4.40 (m, 1H), 6.77 (s, 1H), 7.03-7.05 (m, 2H), 7.10 (dd, J = 7.2 Hz, 7.2 Hz, 1H), 7.17-7.24 (m, 8H), 7.31 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 9.4, 21.5, 21.6, 45.6, 48.3, 48.6, 49.5, 49.9, 109.0, 111.1, 118.9, 119.1, 121.8, 125.4, 126.8, 127.2, 127.3, 128.4, 128.5, 128.9, 129.6, 129.9, 133.7, 135.4, 136.0, 136.7, 144.0, 144.4. IR (neat) 3067, 3031, 2967, 2925, 2884, 2853, 1612, 1597, 1485, 1465, 1455, 1327, 1304, 1288, 1155, 1087, 1043, 969, 944, 906, 813, 741, 692, 674 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{36}N_3O_4S_2^{+1}$(M+ H)$^{+}$ requires 614.2142, Found: 614.2132.

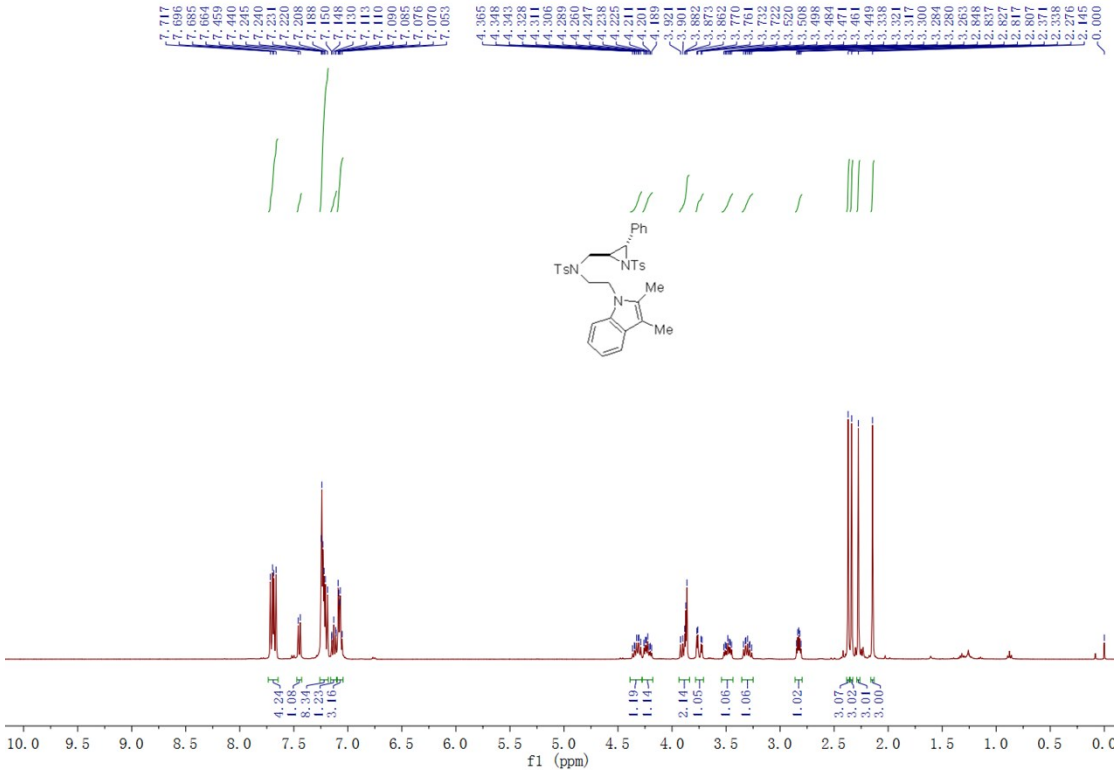






Compound 1j:

0.6 mmol scale, a white solid, 53% yield (200.5 mg). M.p.: 77-80 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.15 (s, 3H), 2.28 (s, 3H), 2.34 (s, 3H), 2.37 (s, 3H), 2.80-2.85 (m, 1H), 3.26-3.34 (m, 1H), 3.44-3.52 (m, 1H), 3.75 (dd, *J* = 4.0 Hz, 15.6 Hz, 1H), 3.86-3.93 (m, 2H), 4.18-4.26 (m, 1H), 4.28-4.37 (m, 1H), 7.05-7.09 (m, 3H), 7.11-7.15 (m, 1H), 7.18-7.25 (m, 8H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 8.7, 10.0, 21.45, 21.49, 42.9, 48.7, 48.8, 49.4, 49.5, 107.1, 108.3, 118.1, 119.0, 121.0, 126.8, 127.1, 127.3, 128.35, 128.43, 128.7, 129.5, 129.9, 131.8, 133.6, 135.3, 135.5, 136.6, 144.0, 144.4. IR (neat) 3064, 3025, 2981, 2948, 2925, 1624, 1596, 1486, 1449, 1401, 1338, 1319, 1305, 1285, 1238, 1185, 1155, 1119, 1086, 1032, 995, 969, 908, 846, 813, 796, 753, 734, 712, 691 cm^{-1}. HRMS (ESI) Calcd. for $C_{35}H_{38}N_3O_4S_2^{+1}$(M+ H)$^+$ requires 628.2298, Found: 628.2297.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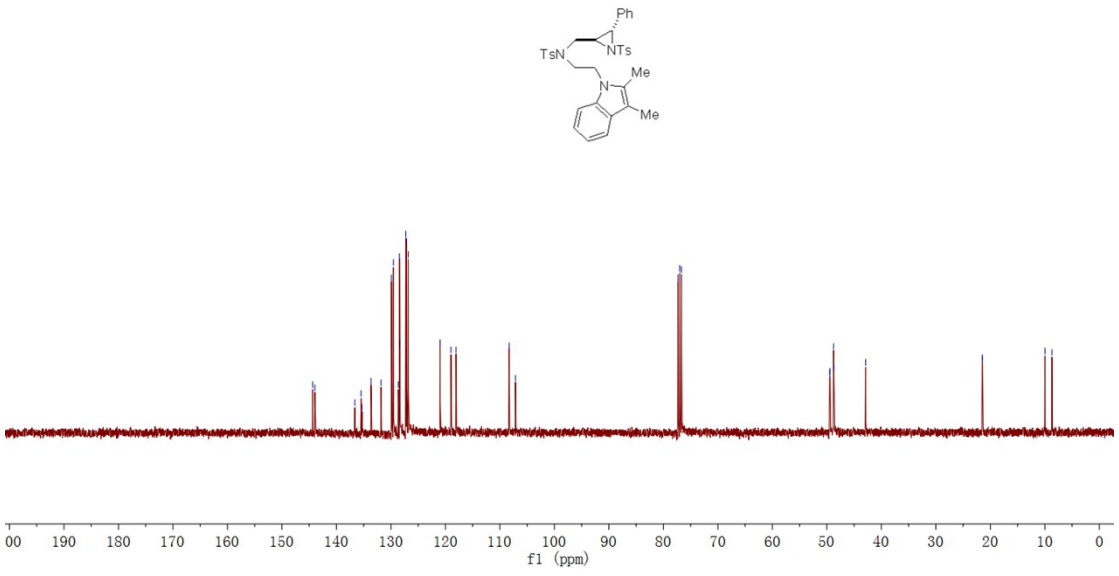
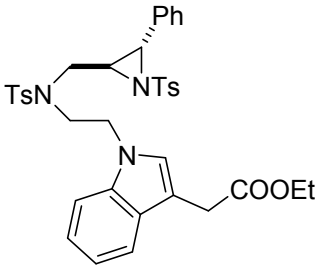
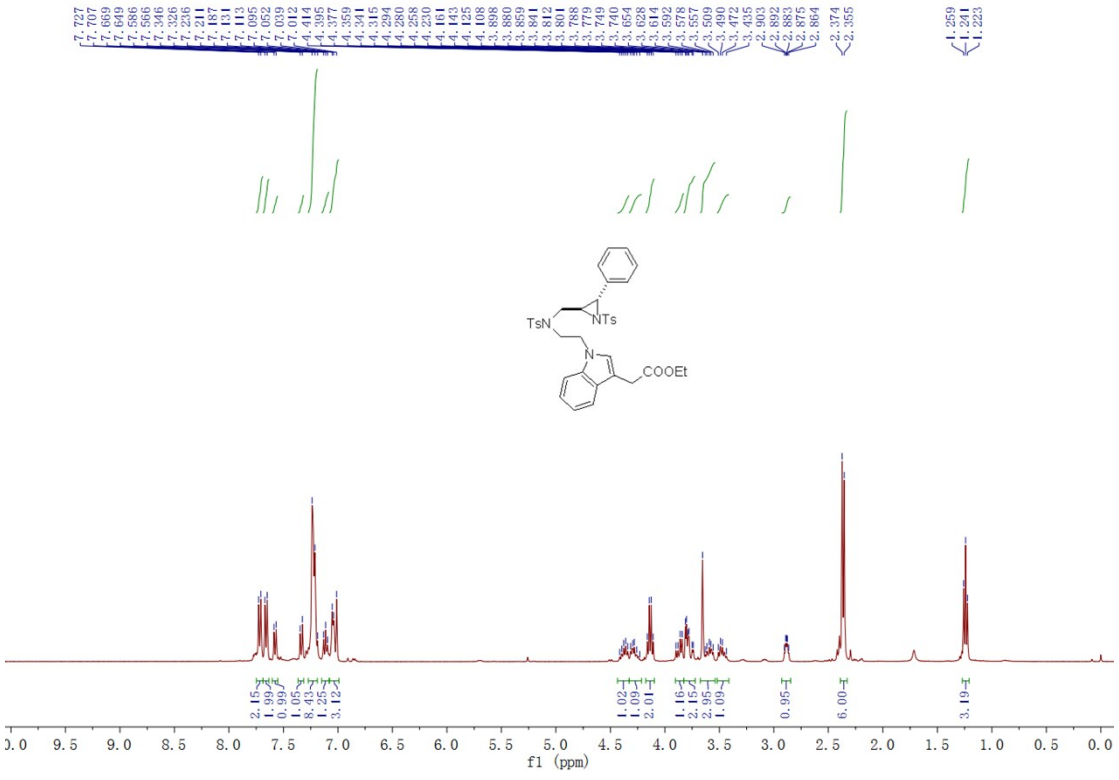
NTs
TsN
N
Me
Me
f1 (ppm)

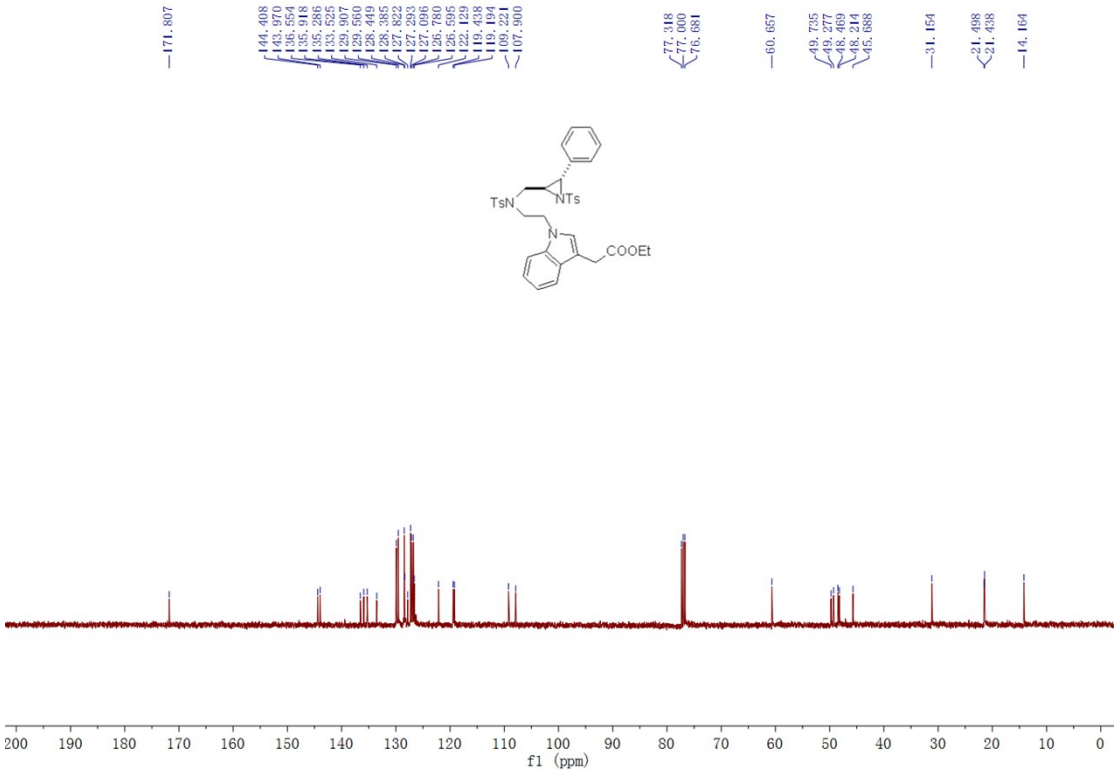

Ph
NTs
TsN
N
Me
Me
f1 (ppm)

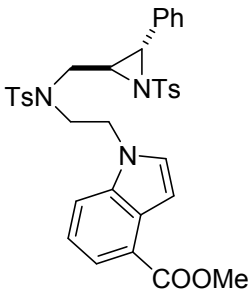


Compound 1k:

1.0 mmol scale, a yellow gem, 59% yield (405.3 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24 (t, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 2.37 (s, 3H), 2.86-2.91 (m, 1H), 3.43-3.51 (m, 1H), 3.55-3.66 (m, 3H), 3.70-3.82 (m, 2H), 3.87 (dd, *J* = 7.2 Hz, 15.6 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.23-4.32 (m, 1H), 4.34-4.42 (m, 1H), 7.01-7.06 (m, 3H), 7.11 (dd, *J* = 7.2 Hz, 7.2 Hz, 1H), 7.18-7.24 (m, 8H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 14.2, 21.4, 21.5, 31.2, 45.7, 48.2, 48.5, 49.3, 49.7, 60.7, 107.9, 109.2, 119.2, 119.4, 122.1, 126.6, 126.8, 127.1, 127.3, 127.8, 128.39, 128.45, 129.6, 129.9, 133.5, 135.3, 135.9, 136.6, 144.0,144.4, 171.8. IR (neat) 3065, 3036, 2982, 2922, 1729, 1596, 1491, 1466, 1450, 1331, 1319, 1305, 1293, 1154, 1087, 1017, 934, 903, 812, 739, 688, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{37}H_{43}N_4O_6S_2^{+1}$(M+ NH_4)$^+$ requires 703.2619, Found: 703.2613.

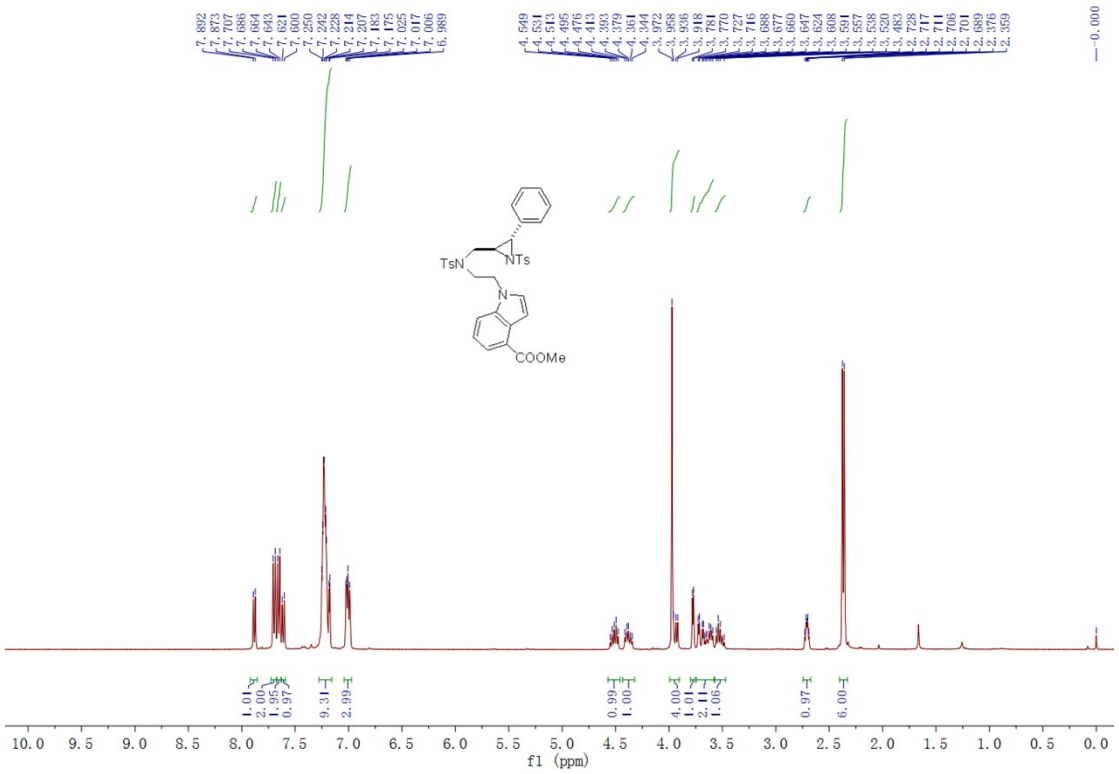






Compound 1l:

0.8 mmol scale, a white solid, 32% yield (170.0 mg). M.p.: 74-77 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H), 2.38 (s, 3H), 2.68-2.73 (m, 1H), 3.48-3.56 (m, 1H), 3.59-3.66 (m, 1H), 3.70 (dd, *J* = 4.4 Hz, 15.6 Hz, 1H), 3.78 (d, *J* = 4.4 Hz, 1H), 3.91-3.98 (m, 4H), 4.34-4.42 (m, 1H), 4.47-4.55 (m, 1H), 6.98-7.03 (m, 3H), 7.17-7.25 (m, 9H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.45, 21.53, 46.1, 48.1, 48.4, 49.6, 49.9, 51.7, 103.2, 114.1, 121.1, 121.7, 123.3, 126.7, 127.1, 127.3, 128.0, 128.40, 128.45, 129.6, 130.0, 133.4, 135.1, 136.5, 144.1, 144.5, 167.9. IR (neat) 3111, 3065, 3036, 2992, 2946, 2842, 1708, 1604, 1574, 1507, 1471, 1439, 1371, 1343, 1270, 1194, 1152, 1132, 1111, 1088, 1067, 1001, 904, 814, 753, 732, 710, 696, 655 cm^{-1}. HRMS (ESI) Calcd. for $C_{35}H_{36}N_3O_6S_2^{+1}$(M+H)$^+$ requires 658.2040, Found: 658.2039.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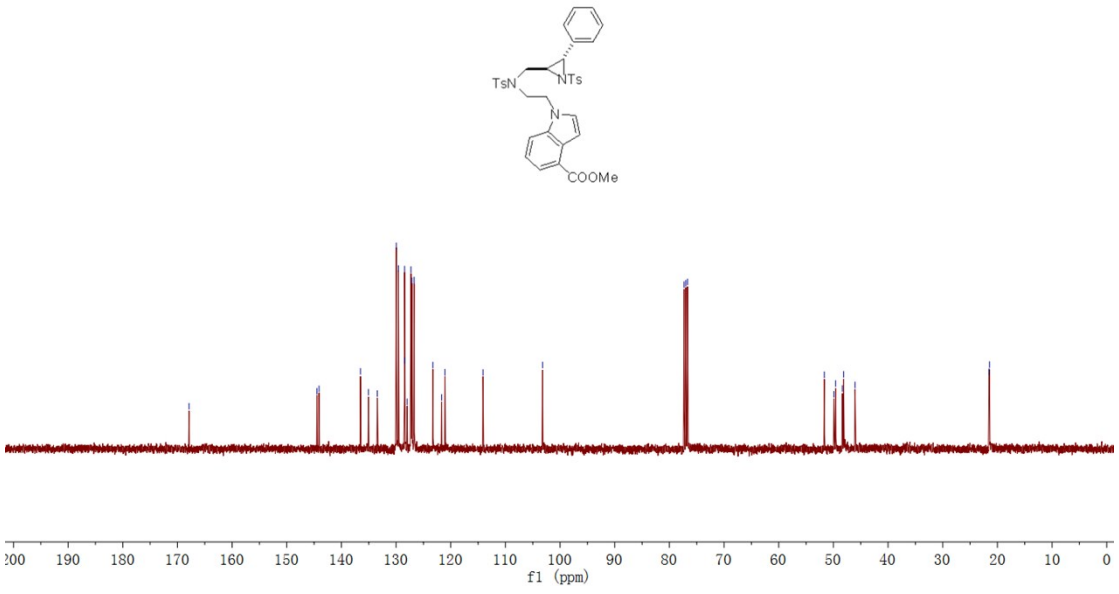
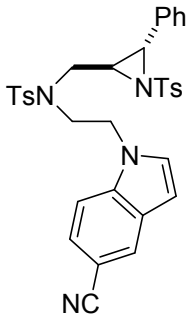
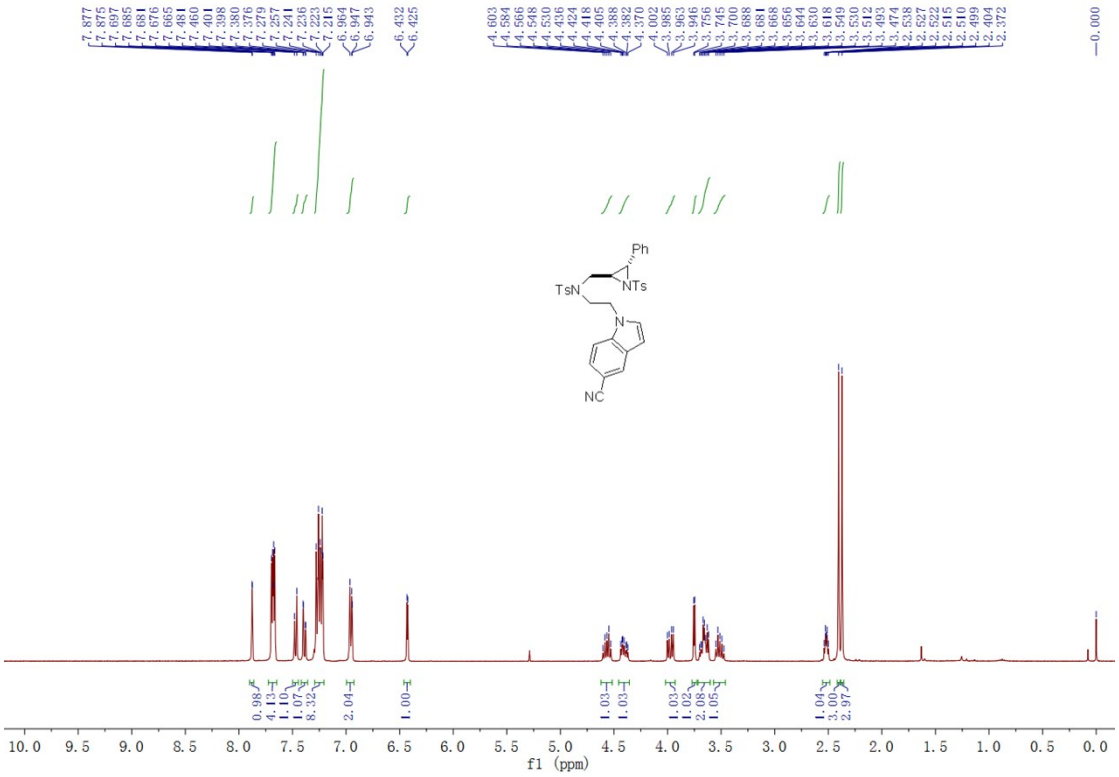
NTs
N
COOMe
f1 (ppm)

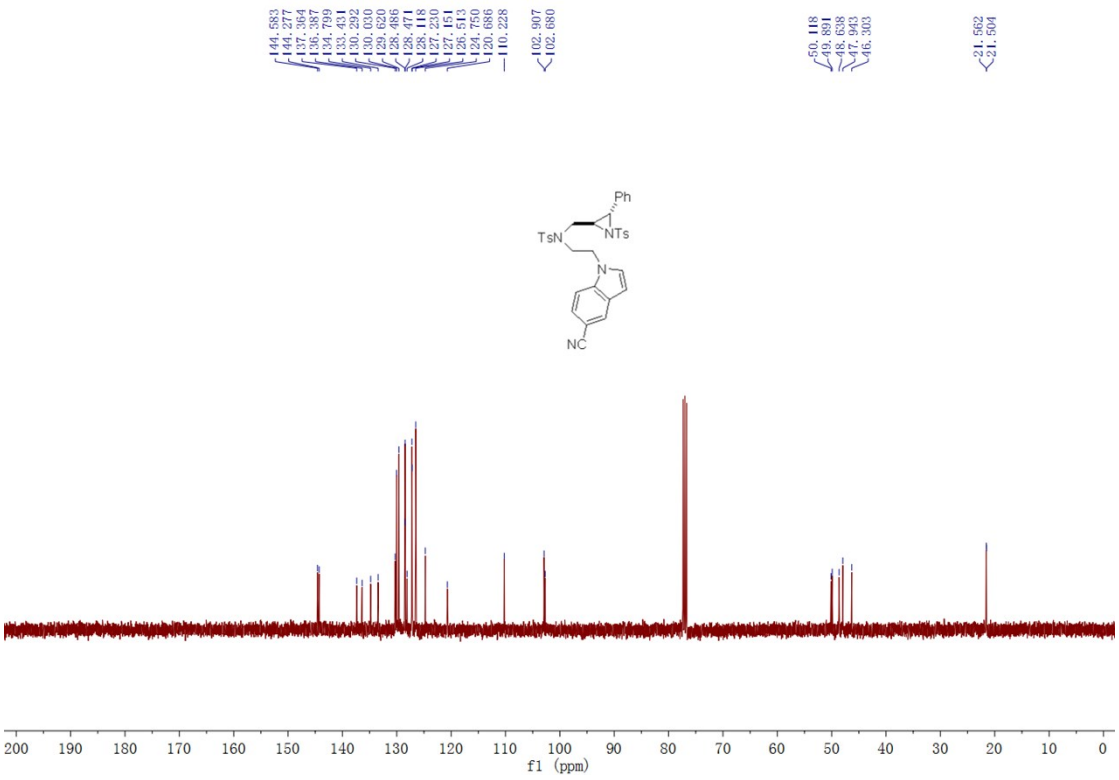

TsN
NTs
N
COOMe
f1 (ppm)

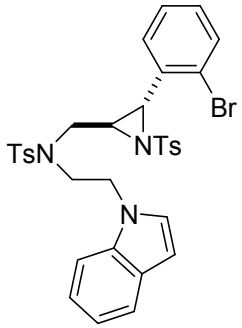


Compound 1m:

0.6 mmol scale, a white solid, 51% yield (190.0 mg). M.p.: 92-93 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 2.40 (s, 3H), 2.49-2.54 (m, 1H), 3.47-3.55 (m, 1H), 3.61-3.70 (m, 2H), 3.75 (d, *J* = 4.4 Hz, 1H), 3.97 (dd, *J* = 7.6 Hz, 15.6 Hz, 1H), 4.37-4.44 (m, 1H), 4.53-4.61 (m, 1H), 6.43 (d, *J* = 2.8 Hz, 1H), 6.94-6.97 (m, 2H), 7.21-7.28 (m, 8H), 7.39 (dd, *J* = 1.2 Hz, 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.66-7.70 (m, 4H), 7.88 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 46.3, 47.9, 48.6, 49.9, 50.1, 102.7, 102.9, 110.2, 120.7, 124.8, 126.5, 127.15, 127.23, 128.1, 128.47, 128.49, 129.6, 130.0, 130.3, 133.4, 134.8, 136.4, 137.4, 144.3, 144.6. IR (neat) 3061, 3031, 2967, 2939, 2920, 2831, 1618, 1596, 1486, 1449, 1337, 1318, 1305, 1238, 1154, 1119, 1086, 1030, 994, 940, 845, 812, 799, 752, 710, 688, 677 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{32}N_4O_4S_2Na^{+1}$(M+ Na)$^{+}$ requires 647.1757, Found: 647.1754.

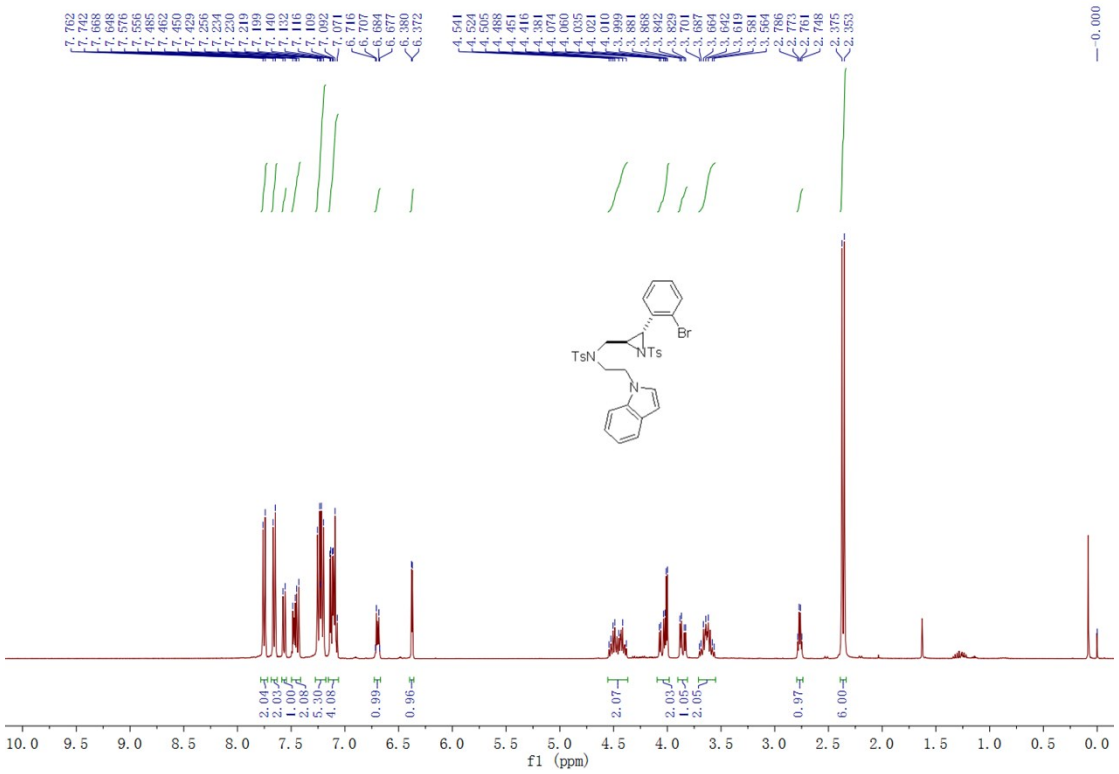






Compound 1n:

1.0 mmol scale, a white solid, 64% yield (479.2 mg). M.p.: 78-80 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H), 2.38 (s, 3H), 2.74-2.79 (m, 1H), 3.56-3.71 (m, 2H), 3.86 (dd, *J* = 5.2 Hz, 15.6 Hz, 1H), 4.00 (d, *J* = 4.4 Hz, 1H), 4.05 (dd, *J* = 5.6 Hz, 15.6 Hz, 1H), 4.38-4.55 (m, 2H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.67-6.72 (m, 1H), 7.07-7.14 (m, 4H), 7.19-7.26 (m, 5H), 7.42-7.49 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 21.6, 45.7, 47.3, 47.7, 48.9, 50.3, 101.6, 109.2, 119.4, 120.9, 121.8, 123.9, 127.1, 127.3, 127.49, 127.52, 128.0, 128.5, 129.6, 129.7, 129.9, 132.4, 133.2, 135.3, 135.7, 136.2, 143.9, 144.7. IR (neat) 3101, 3054, 3028, 2972, 2920, 2866, 1597, 1574, 1512, 1463, 1399, 1331, 1317, 1303, 1287, 1205, 1184, 1156, 1118, 1086, 1045, 1017, 914, 813, 784, 763, 739, 715, 685, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{33}BrN_3O_4S_2^{+1}$(M+ H)$^{+}$ requires 678.1090, Found: 678.1086.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7.556
7.485
7.462
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7.429
7.256
7.234
7.230
7.219
7.199
7.140
7.132
7.116
7.109
7.092
7.071
6.716
6.707
6.694
6.577
6.380
6.372
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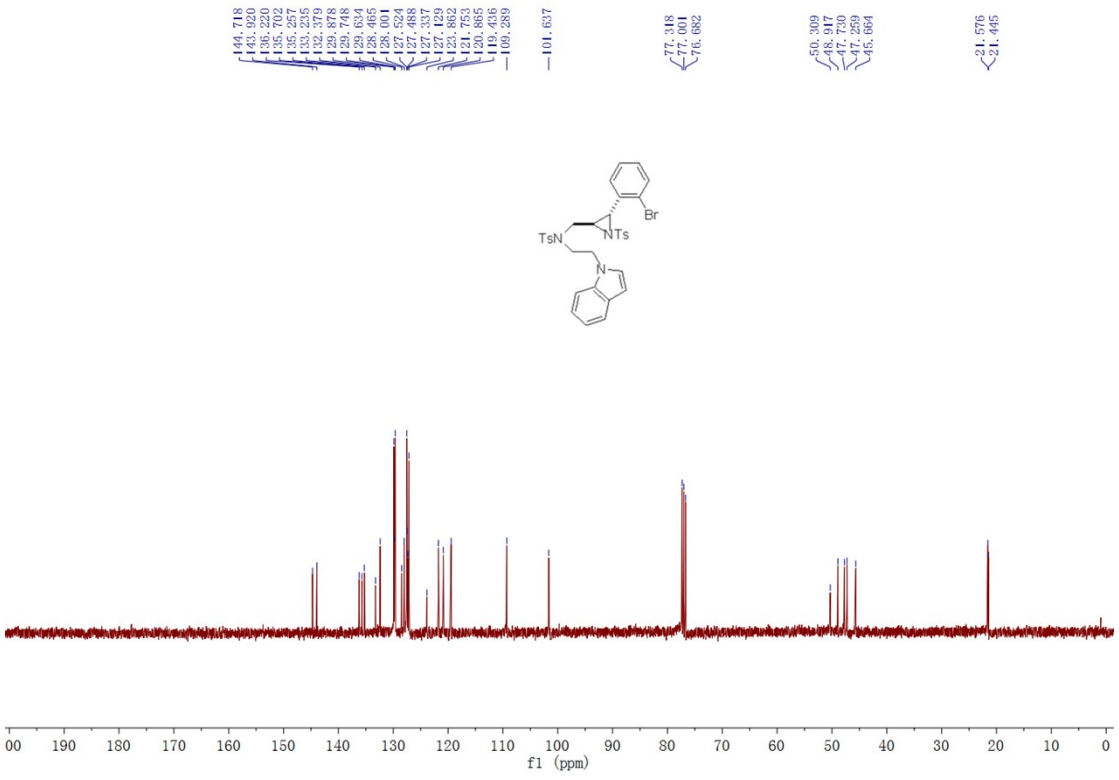
2.375
2.353
0.000
Br
TsN
NTs
N
2.04
2.03
1.00
2.08
5.30
4.08
0.99
0.96
2.07
2.03
1.05
2.05
0.97
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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47.730
47.259
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NTs
N
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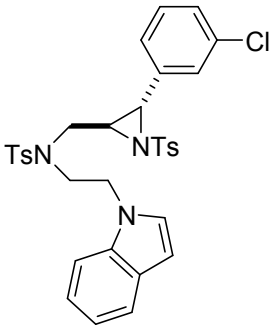
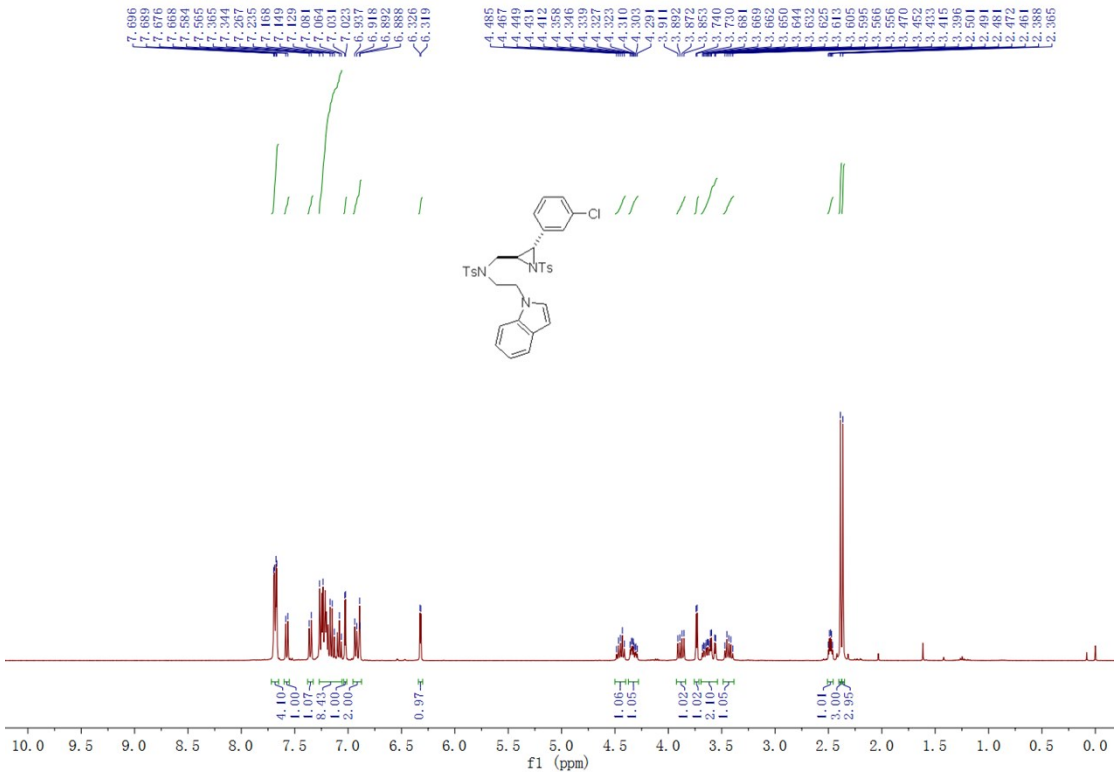
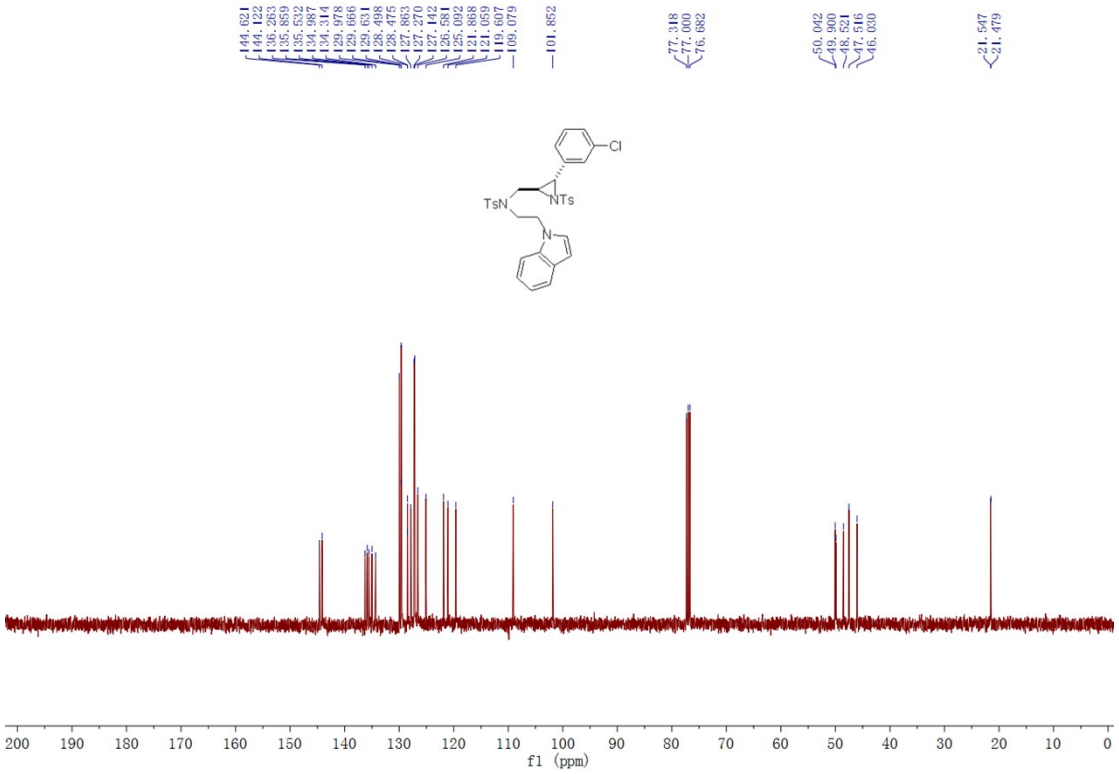
f1 (ppm)

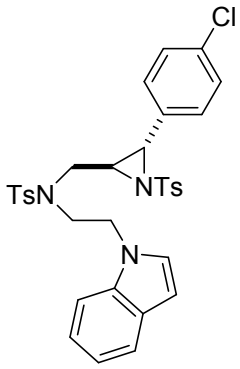


Compound 1o:

0.93 mmol scale, a white solid, 51% yield (302.4 mg). M.p.: 68-70 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 2.39 (s, 3H), 2.46-2.51 (m, 1H), 3.39-3.47 (m, 1H), 3.55-3.69 (m, 2H), 3.74 (d, *J* = 4.0 Hz, 1H), 3.88 (dd, *J* = 7.6 Hz, 15.6 Hz, 1H), 4.29-4.36 (m, 1H), 4.41-4.49 (m, 1H), 6.32 (d, *J* = 2.8 Hz, 1H), 6.88-6.94 (m, 2H), 7.03 (d, *J* = 3.2 Hz, 1H), 7.06-7.27 (m, 8H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.66-7.70 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.48, 21.55, 46.0, 47.5, 48.5, 49.9, 50.0, 101.9, 109.1, 119.6, 121.1, 121.9, 125.1, 126.6, 127.1, 127.3, 127.9, 128.48, 128.50, 129.6, 129.7, 130.0, 134.3, 135.0, 135.5, 135.9, 136.3, 144.1, 144.6. IR (neat) 3103, 3059, 3026, 2951, 2920, 2866, 1597, 1574, 1513, 1481, 1463, 1400, 1318, 1205, 1185, 1156, 1118, 1087, 1040, 1017, 914, 813, 785, 763, 738, 715, 685, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+H)$^+$ requires 634.1596, Found: 634.1595.



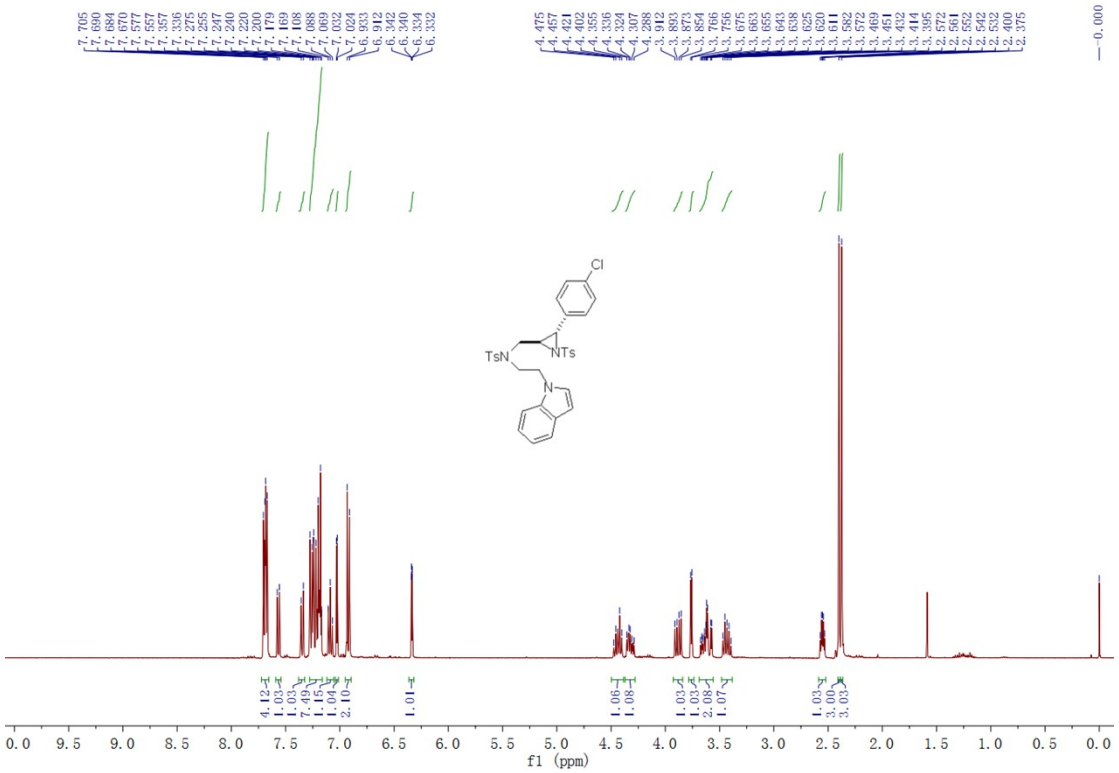


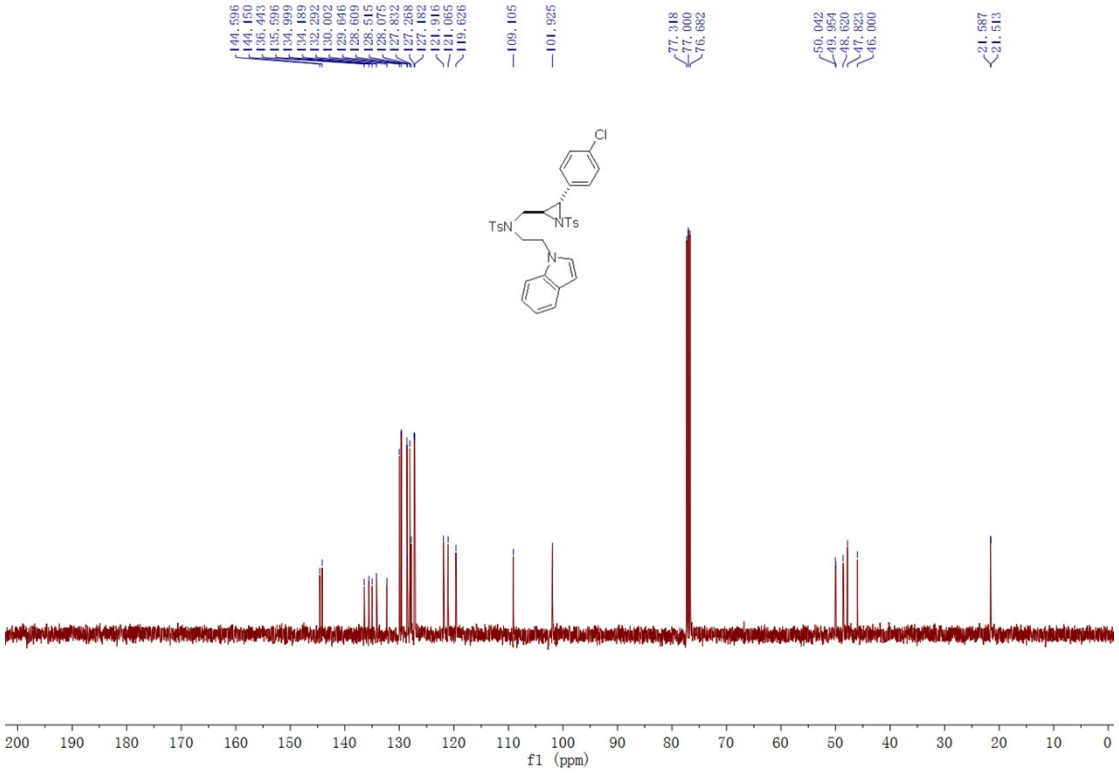


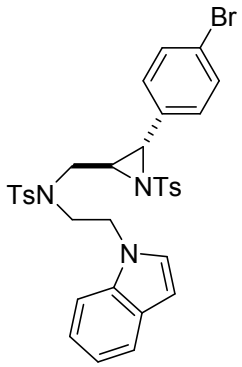
Compound 1p:

1.0 mmol scale, a white solid, 77% yield (491.6 mg). M.p.: 70-73 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.40 (s, 3H), 2.53-2.58 (m, 1H), 3.39-3.47 (m, 1H), 3.57-3.68 (m, 2H), 3.76 (d, J = 4.0 Hz, 1H), 3.88 (dd, J = 7.6 Hz, 15.6 Hz, 1H), 4.28-4.36 (m, 1H), 4.40-4.48 (m, 1H), 6.34 (dd, J = 0.8 Hz, 3.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 3.2 Hz, 1H), 7.07-7.11 (m, 1H), 7.16-7.28 (m, 7H), 7.35 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.67-7.71 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 46.0, 47.8, 48.6, 49.95, 50.04, 101.9, 109.1, 119.6, 121.1, 121.9, 127.2, 127.3, 127.8, 128.1, 128.5, 128.6, 129.6, 130.0, 132.3, 134.2, 135.0, 135.6, 136.4, 144.2, 144.6. IR (neat) 3062, 3026, 2974, 2946, 2922, 2873, 1596, 1491, 1462, 1440, 1336, 1320, 1300, 1290, 1259, 1185, 1155, 1119, 1086, 1017, 993, 969, 910, 812, 732, 691 cm^{-1}. HRMS (ESI)

Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}(M+H)^+$ requires 634.1596, Found: 634.1593.

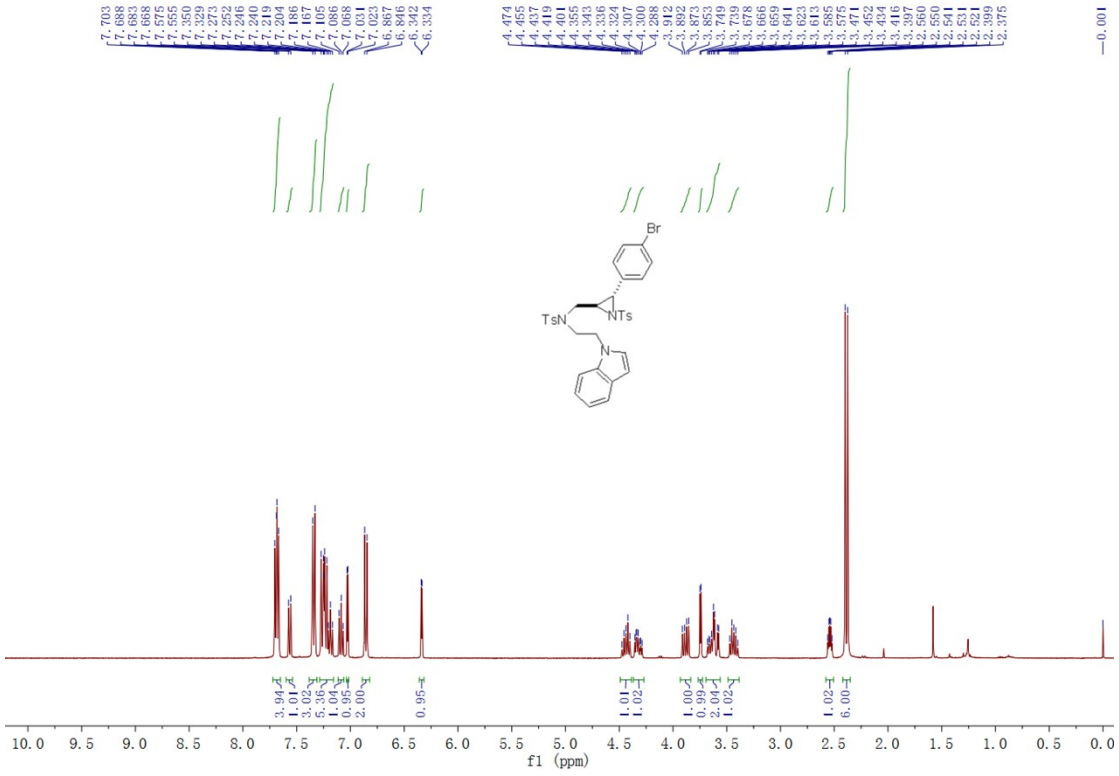






Compound 1q:

1.0 mmol scale, a white solid, 71% yield (484.9 mg). M.p.: 72-75 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.40 (s, 3H), 2.52-2.56 (m, 1H), 3.39-3.48 (m, 1H), 3.57-3.68 (m, 2H), 3.74 (d, *J* = 4.0 Hz, 1H), 3.88 (dd, *J* = 8.0 Hz, 15.6 Hz, 1H), 4.28-4.36 (m, 1H), 4.40-4.48 (m, 1H), 6.34 (d, *J* = 3.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 3.2 Hz, 1H), 7.09 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.16-7.28 (m, 5H), 7.32-7.35 (m, 3H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.66-7.71 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 46.0, 47.9, 48.6, 49.9, 50.1, 101.9, 109.1, 119.6, 121.1, 121.9, 122.4, 127.2, 127.3, 127.8, 128.4, 128.5, 129.7, 130.0, 131.6, 132.9, 135.0, 135.6, 136.5, 144.1, 144.6. IR (neat) 3052, 3023, 2972, 2922, 2871, 1596, 1513, 1489, 1463, 1399, 1336, 1316, 1300, 1287, 1214, 1184, 1155, 1118, 1086, 1045, 1011, 941, 900, 812, 763, 740, 723, 705, 687, 653 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}BrN_3O_4S_2^{+1}$(M+ H)$^{+}$ requires 678.1090, Found: 678.1102.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7.668
7.575
7.555
7.350
7.329
7.273
7.252
7.246
7.240
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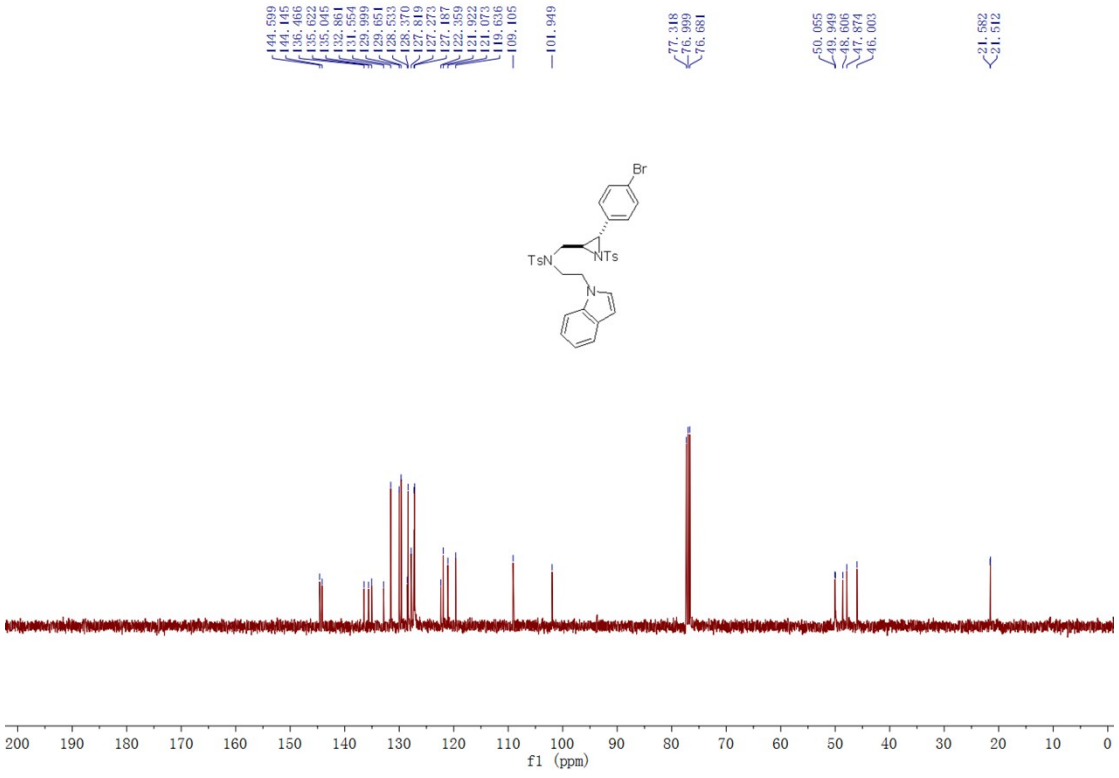
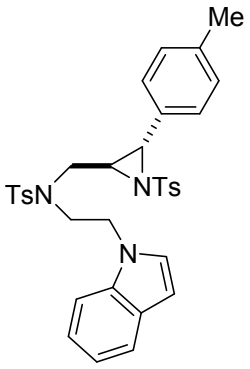
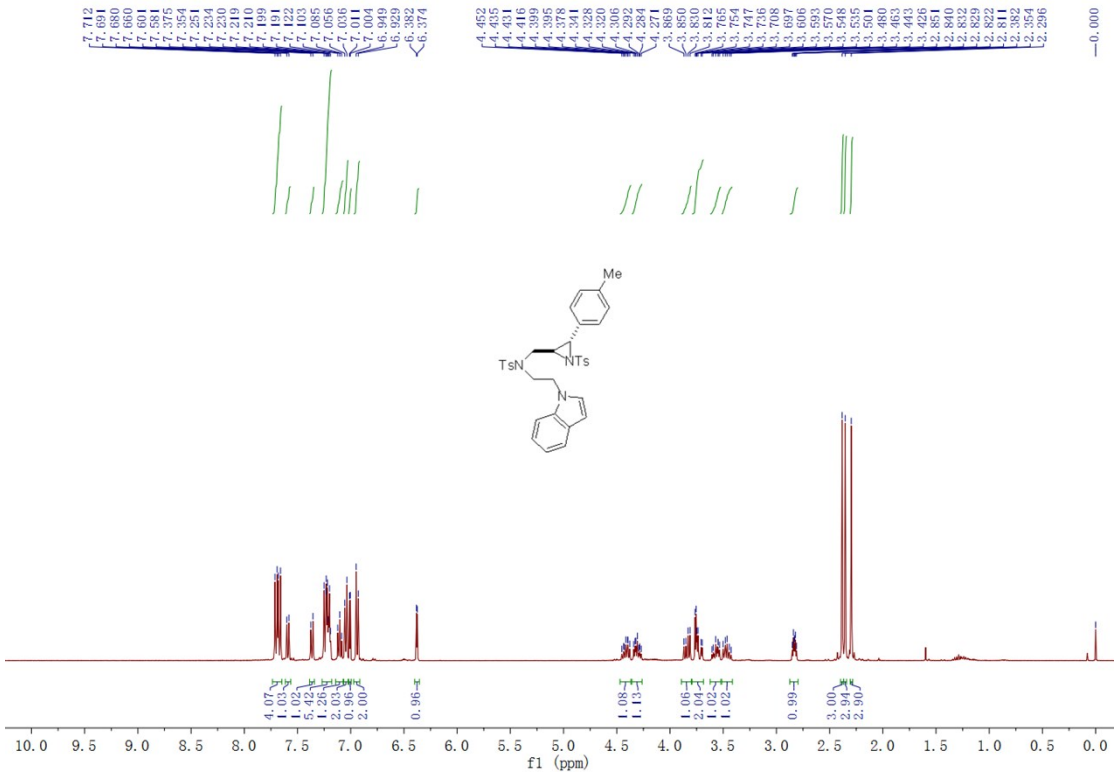
7.204
7.186
7.157
7.105
7.086
7.068
7.031
7.023
6.867
6.846
6.342
6.334
4.474
4.455
4.437
4.419
4.401
4.355
4.343
4.326
4.324
4.307
4.300
4.288
3.912
3.892
3.873
3.853
3.749
3.739
3.678
3.666
3.659
3.641
3.623
3.613
3.585
3.575
3.471
3.452
3.434
3.416
3.397
2.560
2.550
2.541
2.531
2.521
2.399
2.375
0.001
Br
TsN
NTs
N
3.94
1.01
1.02
3.35
1.04
0.95
2.00
0.95
1.01
1.02
1.00
0.99
2.04
1.02
1.02
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

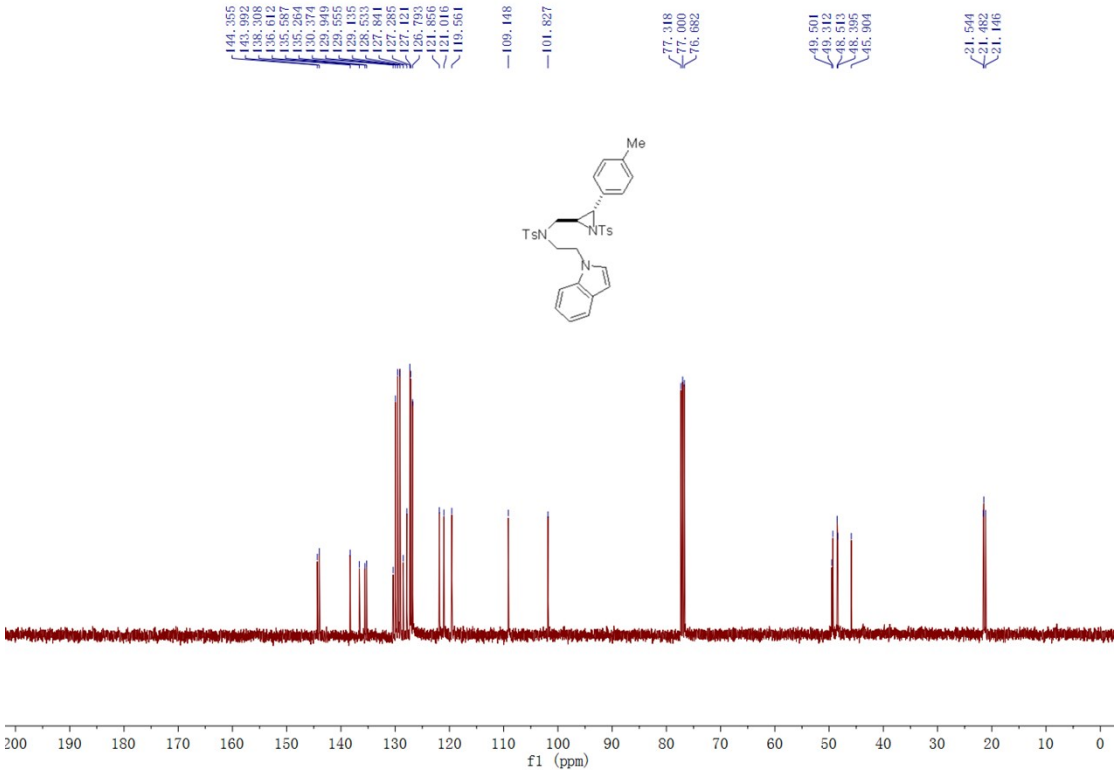

144.599
144.145
136.466
135.622
135.045
132.861
131.554
129.999
129.651
128.533
128.370
128.349
127.273
127.187
122.359
121.922
121.073
119.636
109.105
101.949
77.318
76.999
76.681
50.055
49.949
48.606
47.874
46.003
21.582
21.512
Br
TsN
NTs
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

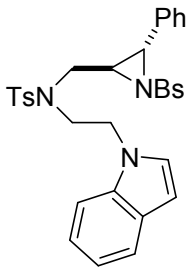


Compound 1r:

1.0 mmol scale, a white solid, 68% yield (417.0 mg). M.p.: 70-73 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.30 (s, 3H), 2.35 (s, 3H), 2.38 (s, 3H), 2.81-2.86 (m, 1H), 3.42-3.51 (m, 1H), 3.54-3.61 (m, 1H), 3.72 (dd, *J* = 4.4 Hz, 15.6 Hz, 1H), 3.76 (d, *J* = 4.4 Hz, 1H), 3.84 (dd, *J* = 7.6 Hz, 15.6 Hz, 1H), 4.27-4.35 (m, 1H), 4.37-4.46 (m, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 3.2 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.08-7.13 (m, 1H), 7.19-7.25 (m, 5H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.66-7.72 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.1, 21.48, 21.54, 45.9, 48.4, 48.5, 49.3, 49.5, 101.8, 109.1, 119.6, 121.0, 121.9, 126.8, 127.1, 127.3, 127.8, 128.5, 129.1, 129.6, 129.9, 130.4, 135.3, 135.6, 136.6, 138.3, 144.0, 144.4. IR (neat) 3103, 3054, 3026, 2979, 2953, 2923, 2863, 1725, 1597, 1513, 1463, 1400, 1331, 1316, 1300, 1287, 1258, 1214, 1184, 1155, 1118, 1087,1038, 1017, 941, 906, 812, 762, 740, 706, 688, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{36}N_3O_4S_2^{+1}$(M+ H)$^{+}$ requires 614.2142, Found: 614.2142.

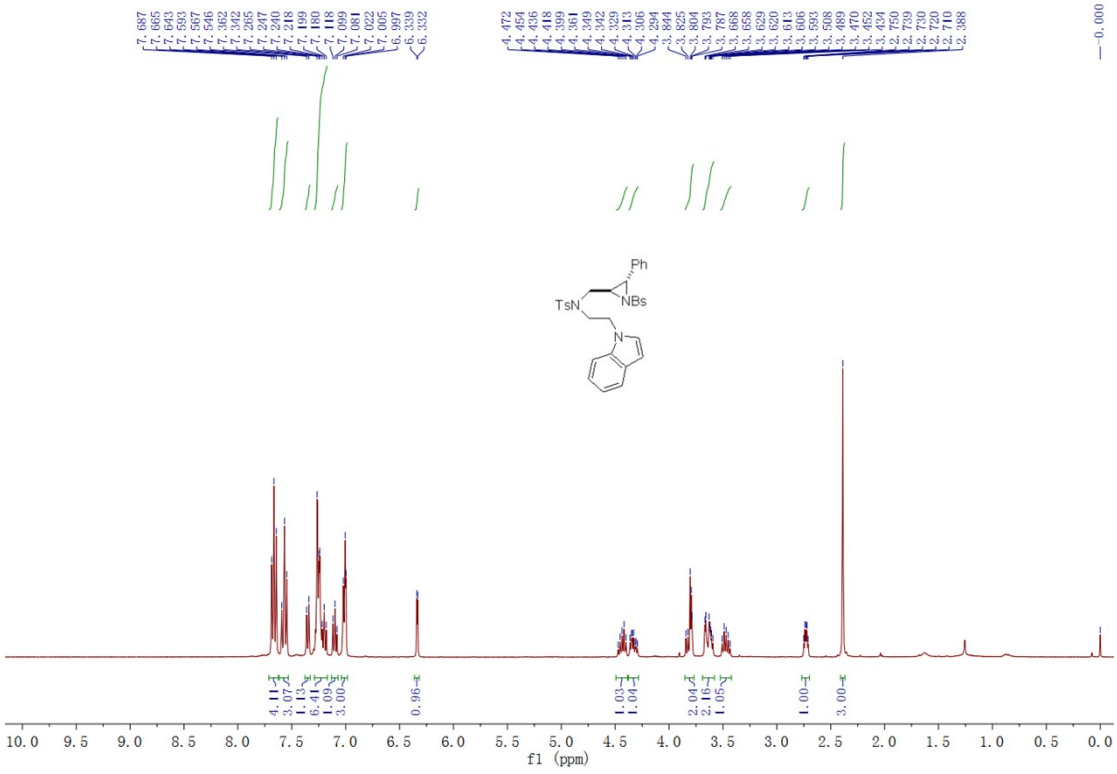

Me
TsN
NTs
N
f1 (ppm)

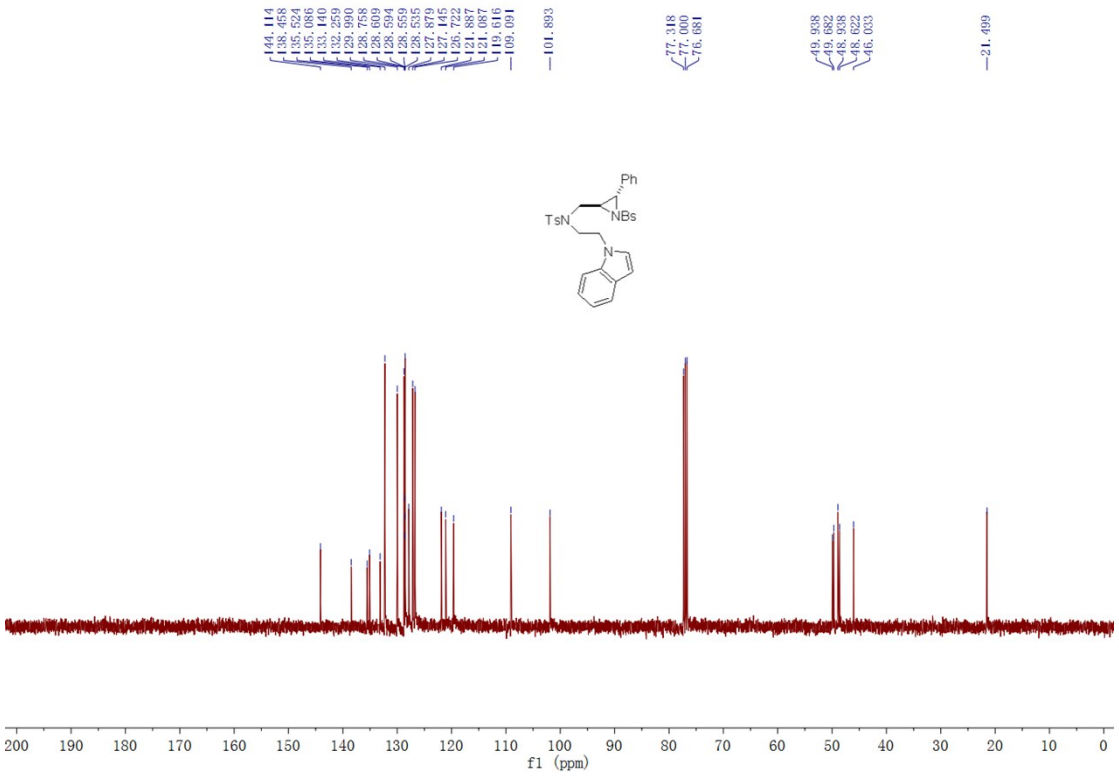

Me
TsN
NTs
N
f1 (ppm)

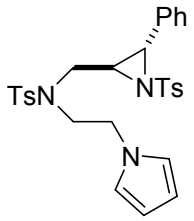


Compound 1s:

0.6 mmol scale, a white solid, 47% yield (207.5 mg). M.p.: 76-78 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.71-2.75 (m, 1H), 3.43-3.51 (m, 1H), 3.59-3.67 (m, 2H), 3.78-3.85 (m, 2H), 4.29-4.37 (m, 1H), 4.39-4.48 (m, 1H), 6.34 (d, *J* = 2.8 Hz, 1H), 6.99-7.03 (m, 3H), 7.10 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.18-7.27 (m, 6H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.54-7.60 (m, 3H), 7.64-7.69 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 46.0, 48.6, 48.9, 49.7, 49.9, 101.9, 109.1, 119.6, 121.1, 121.9, 126.7, 127.1, 127.9, 128.54, 128.56, 128.59, 128.61, 128.8, 130.0, 132.3, 133.1, 135.1, 135.5, 138.5, 144.1. IR (neat) 3095, 3053, 2914, 1593, 1571, 1510, 1460, 1388, 1338, 1160, 1082, 1007, 941, 905, 816, 741, 658 cm^{-1}. HRMS (ESI) Calcd. for $C_{32}H_{31}BrN_3O_4S_2^{+1}$(M+ H)$^+$ requires 664.0934, Found: 664.0932.

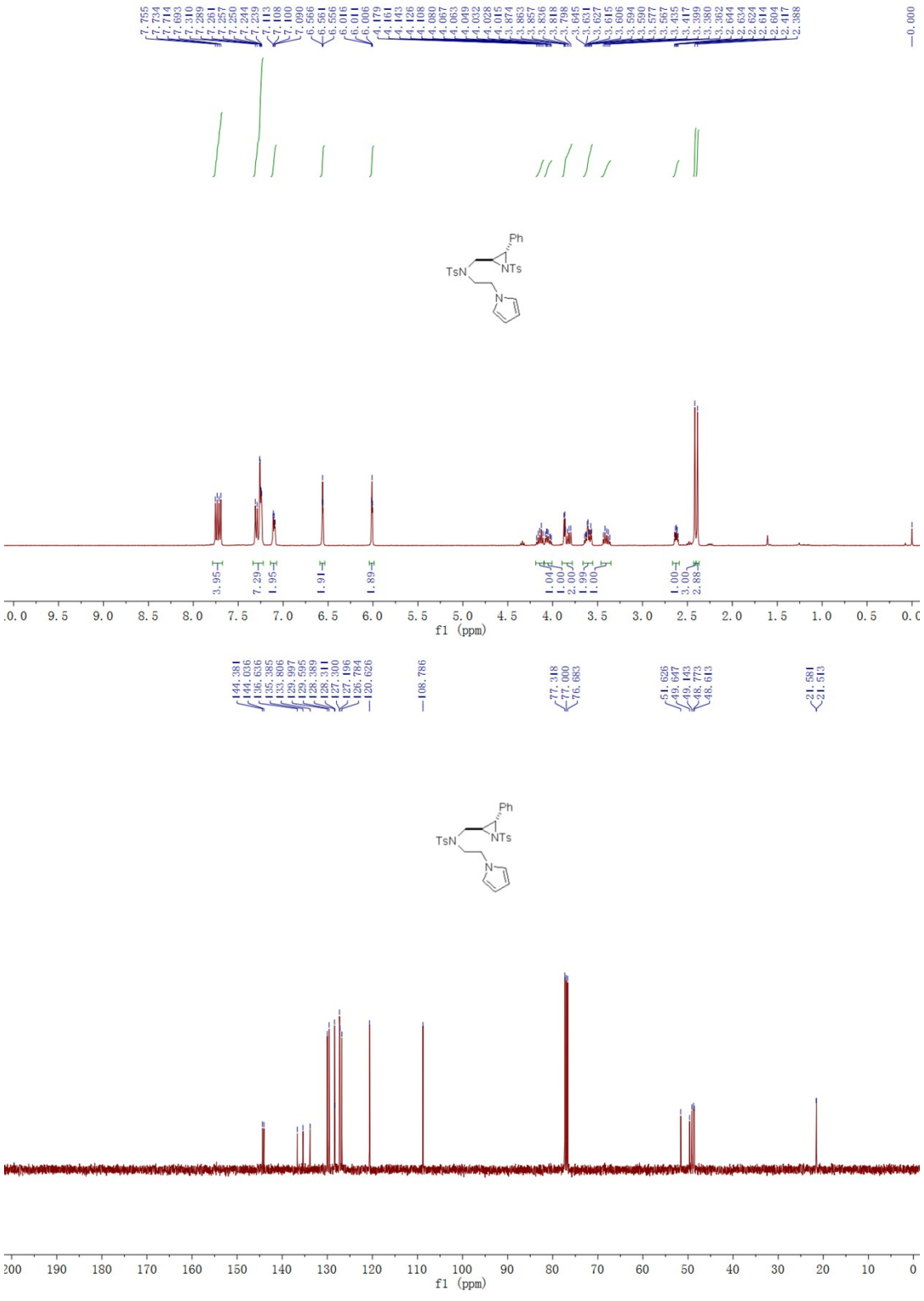






Compound 1t:

0.6 mmol scale, a light yellow solid, 42% yield (138.9 mg). M.p.: 129-132 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.42 (s, 3H), 2.60-2.65 (m, 1H), 3.36-3.44 (m, 1H), 3.56-3.65 (m, 2H), 3.79-3.88 (m, 2H), 4.01-4.08 (m, 1H), 4.10-4.18 (m, 1H), 6.00-6.02 (m, 2H), 6.55-6.57 (m, 2H), 7.09-7.12 (m, 2H), 7.23-7.31 (m, 7H), 7.70 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 48.6, 48.8, 49.1, 49.6, 51.6, 108.8, 120.6, 126.8, 127.2, 127.3, 128.3, 128.4, 129.6, 130.0, 133.8, 135.4, 136.6, 144.0, 144.4. IR (neat) 3052, 3026, 2966, 2922, 2871, 1729, 1596, 1513, 1463, 1399, 1334, 1316, 1303, 1290, 1256, 1214, 1184, 1154, 1118, 1086, 1043, 1017, 941, 902, 811, 761, 740, 722, 706, 687, 652 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{32}N_3O_4S_2^{+1}$(M+ H)$^+$ requires 550.1829, Found: 550.1829.


7.755
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7.693
7.310
7.289
7.261
7.257
7.250
7.244
7.239
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7.108
7.100
7.090
6.566
6.561
6.556
6.016
6.011
6.006
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4.126
4.108
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3.435
3.417
3.399
3.380
3.362
2.644
2.634
2.624
2.614
2.604
2.447
2.388
0.000
Ph
TsN
NTs
N
3.95
7.29
1.95
1.91
1.89
1.04
1.00
2.00
1.99
1.00
1.00
3.00
2.88
f1 (ppm)
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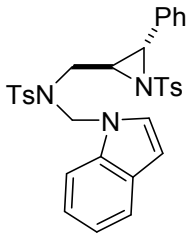
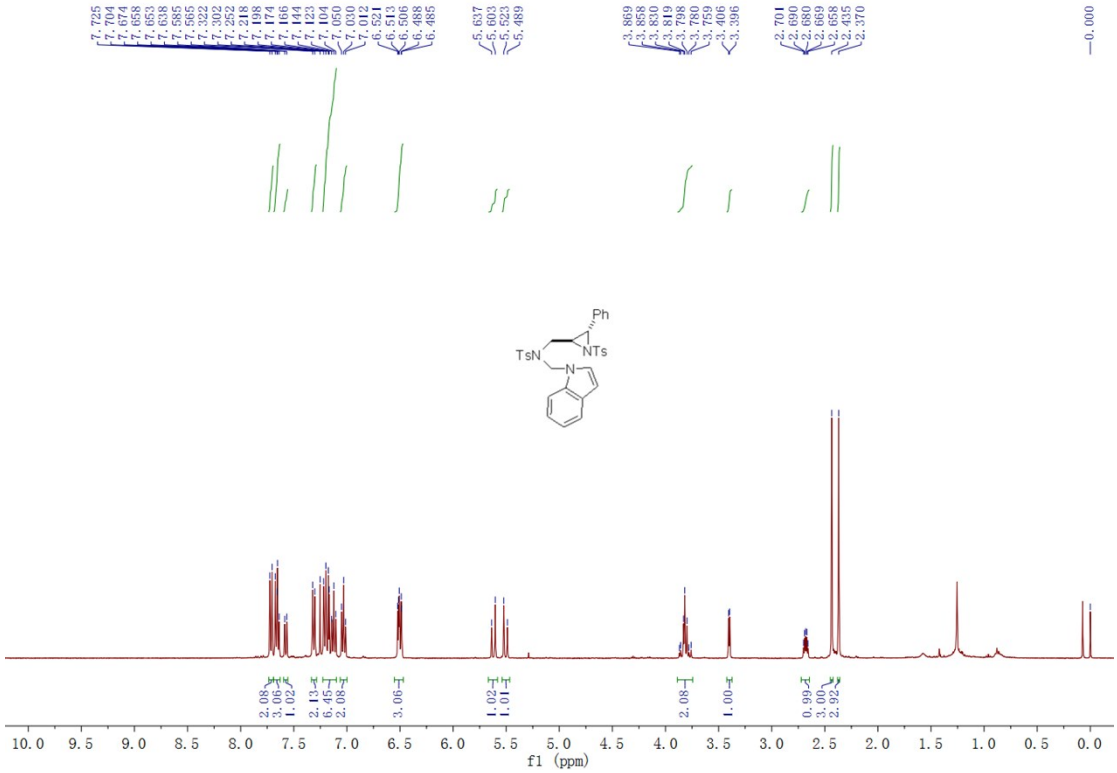
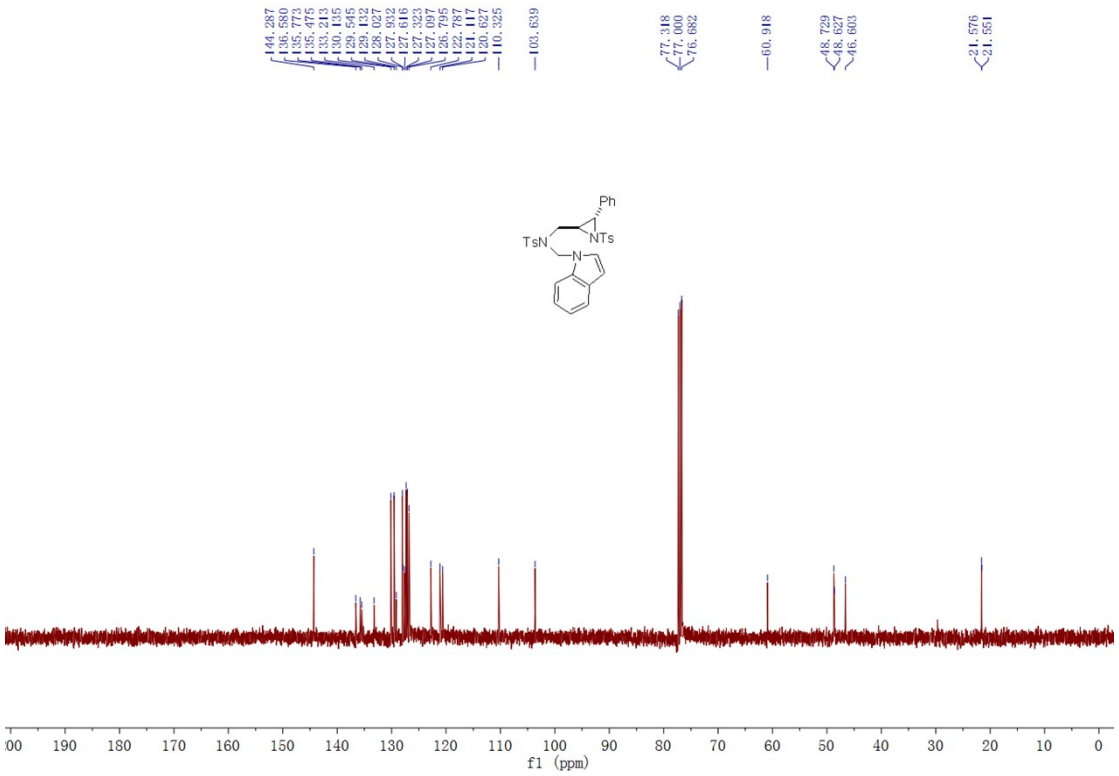
77.318
77.000
76.683
51.626
49.647
49.143
48.773
48.613
21.581
21.513
Ph
TsN
NTs
N
f1 (ppm)

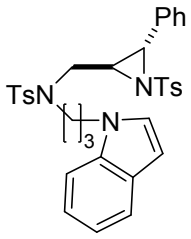


Compound 1u:

0.8 mmol scale, a white solid, 19% yield (88.1mg). M.p.: 198-200 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 2.44 (s, 3H), 2.65-2.71 (m, 1H), 3.40 (d, *J* = 4.0 Hz, 1H), 3.75-3.87 (m, 2H), 5.51 (d, *J* = 13.6 Hz, 1H), 5.62 (d, *J* = 13.6 Hz, 1H), 6.48-6.53 (m, 3H), 7.01-7.05 (m, 2H), 7.10-7.22 (m, 6H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.63-7.68 (m, 3H), 7.71 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.55, 21.58, 46.6, 48.6, 48.7, 60.9, 103.6, 110.3, 120.6, 121.1, 122.8, 126.8, 127.1, 127.3, 127.6, 127.9, 128.0, 129.1, 129.5, 130.1, 133.2, 135.5, 135.8, 136.6, 144.3. IR (neat) 3064, 3044, 3031, 2958, 2922, 2850, 1734, 1597, 1515, 1491, 1460, 1339, 1316, 1300, 1158, 1089, 1016, 926, 895, 810, 744, 694, 670, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{32}H_{32}N_3O_4S_2^{+1}$(M+ H)$^+$ requires 586.1829, Found: 586.1826.

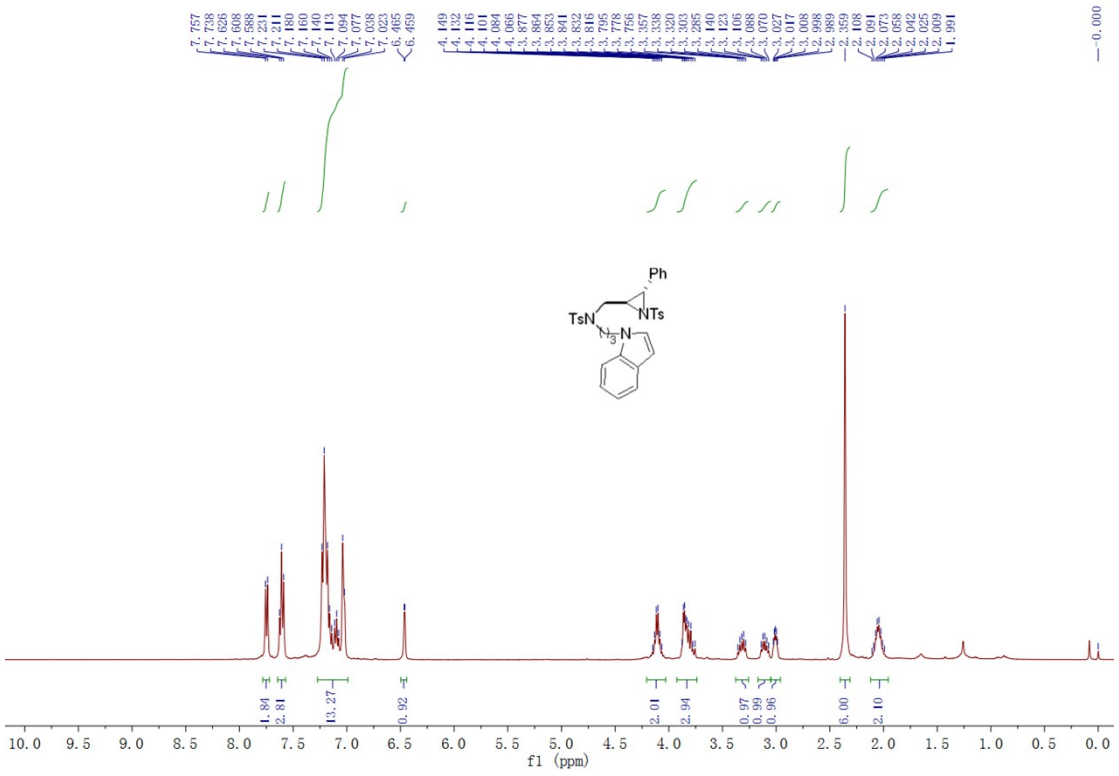


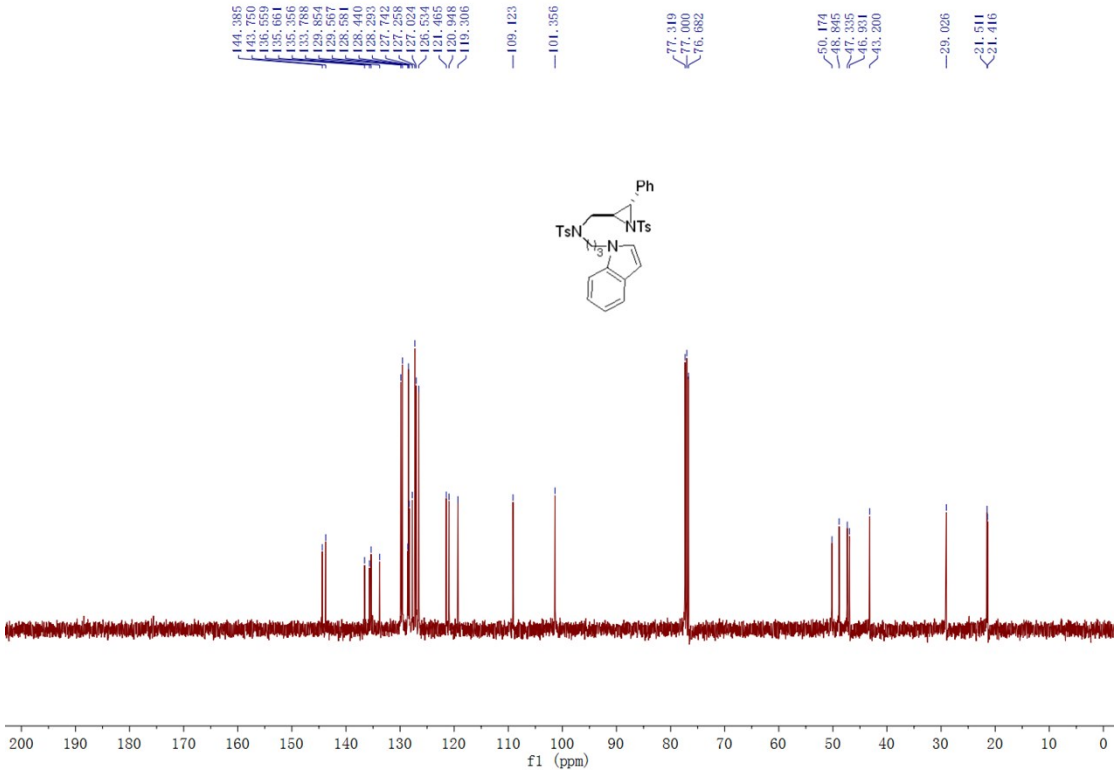




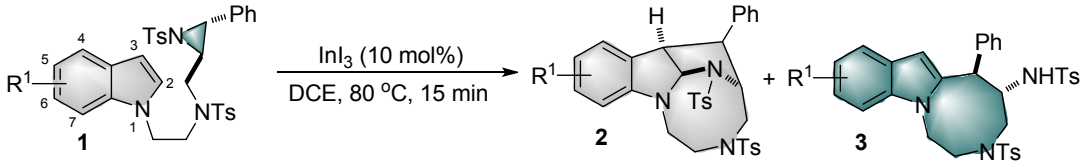
Compound 1v:

1.0 mmol scale, a white solid, 18% yield (119.1 mg). M.p.: 60-62 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.99-2.11 (m, 2H), 2.36 (s, 6H), 2.98-3.03 (m, 1H), 3.07-3.14 (m, 1H), 3.28-3.36 (m, 1H), 3.75-3.88 (m, 3H), 4.06-4.15 (m, 2H), 6.46 (d, J = 2.4 Hz, 1H), 7.02-7.24 (m, 13H), 7.58-7.63 (m, 3H), 7.75 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 21.5, 29.0, 43.2, 46.9, 47.3, 48.8, 50.2, 101.4, 109.1, 119.3, 120.9, 121.5, 126.5, 127.0, 127.3, 127.7, 128.3, 128.4, 128.6, 129.6, 129.9, 133.8, 135.4, 135.7, 136.6, 143.8, 144.4. IR (neat) 3061, 3025, 2925, 2870, 1723, 1596, 1511, 1493, 1462, 1400, 1317, 1302, 1290, 1242, 1185, 1156, 1118, 1087, 1017, 940, 899, 844, 813, 740, 710, 691, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{36}N_3O_4S_2^{+1}$(M+ H)$^{+}$ requires 614.2142, Found: 614.2140.


Ph
TsN
NTs
N
f1 (ppm)


Ph
TsN
NTs
N
f1 (ppm)

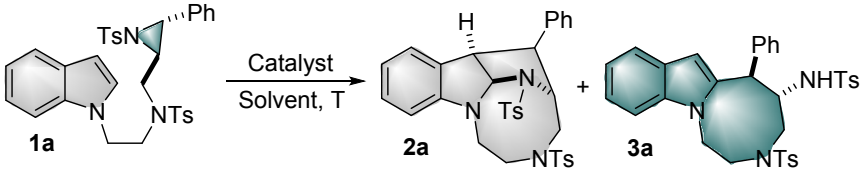
6. General procedure for indium-catalyzed intramolecular dearomative cycloaddition of *N*-Sulfonylaziridines to Indoles



A solution of InI_3 (0.01 mmol, 10 mol %) and **1** (0.15 mmol) in DCE (1.5 mL) was stirred at 80 ^oC under argon atmosphere for 15 minutes. The mixture was concentrated in vacuo to yield the crude product, which was purified by a flash chromatography on silica gel (eluent: PE/EtOAc = 4/1 ~ 6/1) to furnish the desired product **2** and **3**.

7. Screening of conditions for the intramolecular dearomative cyclization of 1a

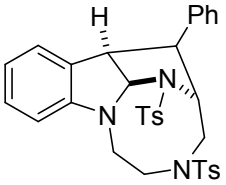
Table SI-1. Screening of Catalysts for the Intramolecular Dearomative Cyclization of **1a**.



Entry[a]	Catalyst	Solvent	T (°C)	yield (%)[b]	
				2a	**3a**
1	$[(CH_3CN)_4Cu]PF_6$	DCM	25	20	41
2	$[(CH_3CN)_4Cu]BF_4$	DCM	25	27	39
3	$[(CH_3CN)_4Cu]BF_4$	HFIP	25	40	26
4	$Cu(OTf)_2$	toluene	25	25	42
5	$Fe(OTf)_2$	toluene	25	10	23
6	$Fe(OTf)_3$	xylene	25	18	36
7	$Yb(OTf)_3$	toluene	25	30	45
8	$Sc(OTf)_3$	toluene	25	28	48
9	$Bi(OTf)_3$	MeCN	25	23	40
10	$Eu(OTf)_3$	MeCN	25	23	25
11	IPrAuOTf	DCE	25	10	23
12	$In(OTf)_3$	DCE	25	28	53
13	$InCl_3$	DCE	25	44	27
14	$InBr_3$	DCE	25	38	27
15	InI_3	DCE	25	58	21
16	$CeCl_3$	DCE	25	6	5
17	$CrCl_2$	DCE	25	13	11
18	$AuCl_3$	DCE	25	trace	trace
19	$ZnCl_2$	MeCN	25	23	15
20	$ZnBr_2$	DCE	25	42	30
21	CuBr	MeCN	70	0	0
22	$CuBr_2$	DCE	80	trace	trace
23	$NiBr_2$	DCE	80	0	0
24	ZnI_2	DCE	25	29	32
25	KI	DCE	70	0	0
26	CuI	DCE	70	0	0
27	PtI_2	DCE	70	0	0
28	PdI_2	DCE	70	0	0
29	$AgNTf_2$	DCE	25	31	32
30	$BF_3 \cdot Et_2O$	DCE	25	7	18
31	$Ti(i\text{-}PrO)_4$	DCE	25	0	0
32	$Pd(OAc)_2$	toluene	70	0	0
33	$[Rh(cod)_2]BF_4$	toluene	70	21	28

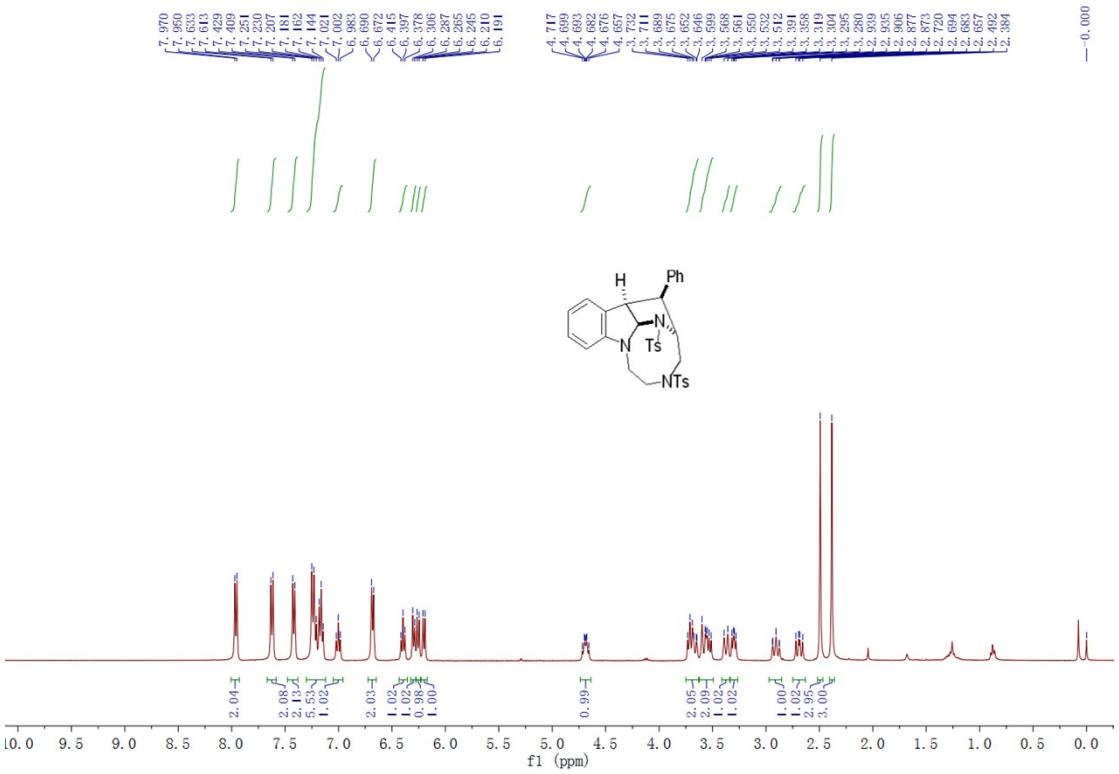
[a] Unless otherwise specified, all reactions were performed with **1a** (0.1 mmol) and cat. (0.01 mmol) in solvent (1 mL) in 12 h. [b] Yields are determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

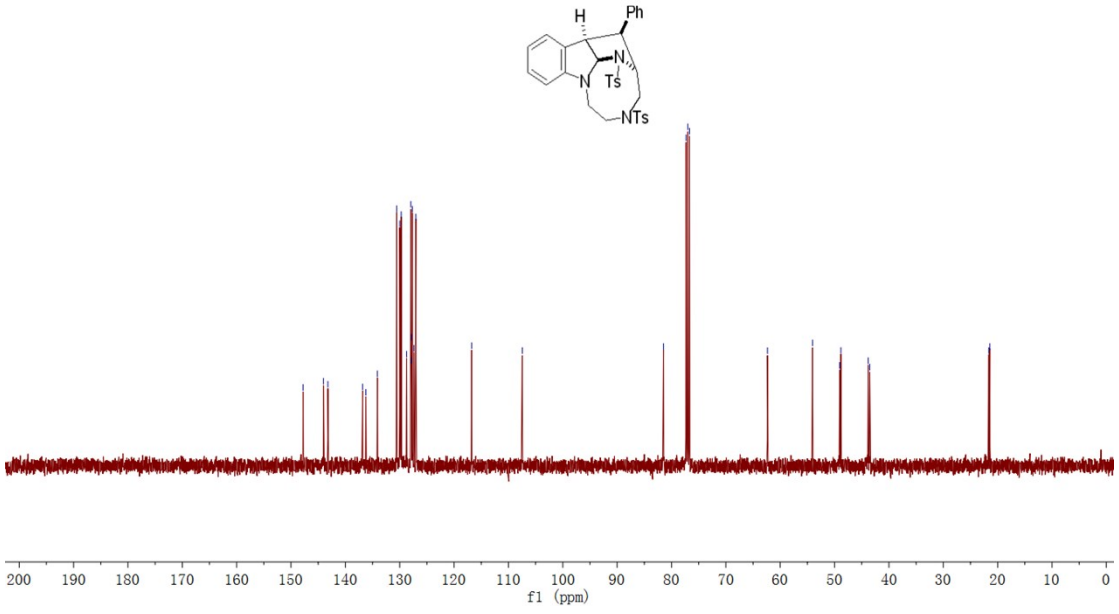
8. Characterization and spectra charts for 2

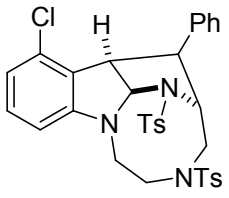


Compound 2a:

0.15 mmol scale, a white solid, 68% yield (61.2g). M.p.: 230-232 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.49 (s, 3H), 2.69 (dd, *J* = 10.4 Hz, 14.8 Hz, 1H), 2.87-2.94 (m, 1H), 3.30 (dd, *J* = 6.0 Hz, 9.6 Hz, 1H), 3.35-3.40 (m, 1H), 3.51-3.60 (m, 2H), 3.64-3.74 (m, 2H), 4.65-4.72 (m, 1H), 6.20 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 6.30 (d, *J* = 7.6 Hz, 1H), 6.44 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.68 (d, *J* = 7.2 Hz, 2H), 7.00 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.14-7.26 (m, 5H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 21.6, 43.5, 43.8, 48.8, 49.1, 54.1, 62.3, 81.5, 107.5, 116.8, 127.0, 127.4, 127.7, 127.85, 127.89, 127.95, 128.7, 129.7, 130.0, 130.6, 134.1, 136.2, 136.8, 143.2, 144.0, 147.8. IR (neat) 3093, 3054, 3026, 2982, 2946, 2921, 2853, 1601, 1486, 1465, 1453, 1367, 1346, 1305, 1289, 1264, 1245, 1219, 1185, 1156, 1092, 1062, 1040, 971, 890, 853, 839, 815, 774, 738, 713, 676, 658 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{37}N_4O_4S_2^{+1}(M+NH_4)^+$ requires: 617.2251, found: 617.2251.

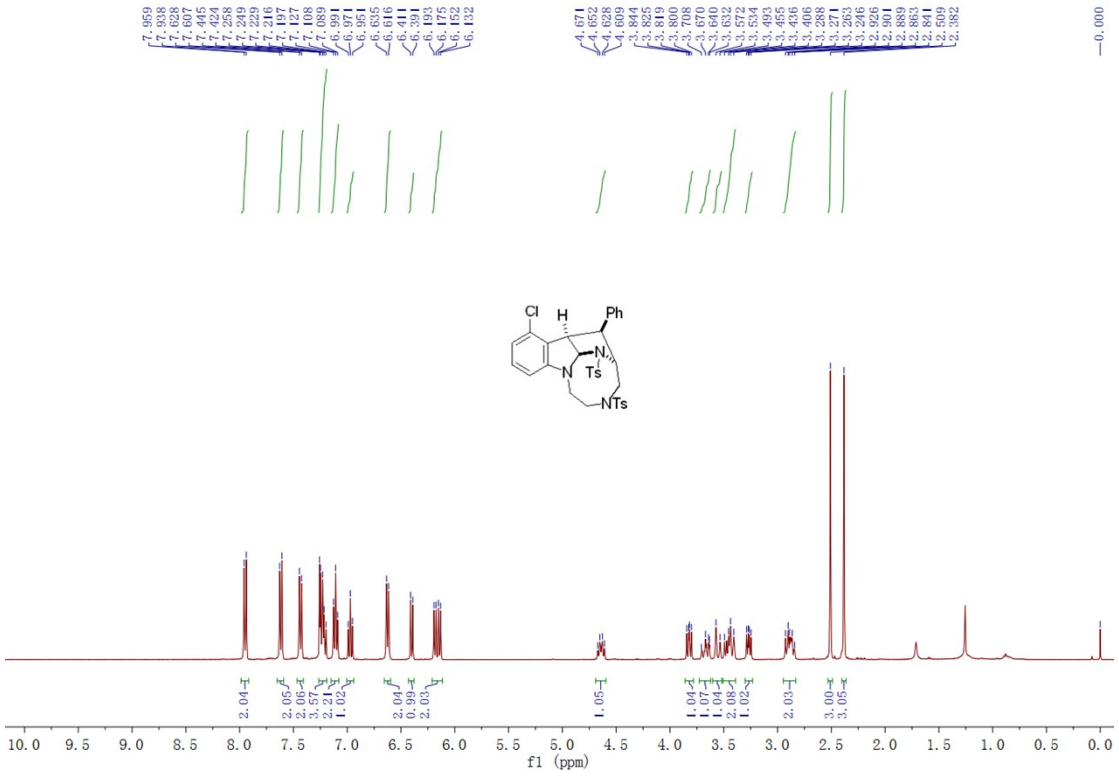

H
Ph
N
N
Ts
NTs
f1 (ppm)

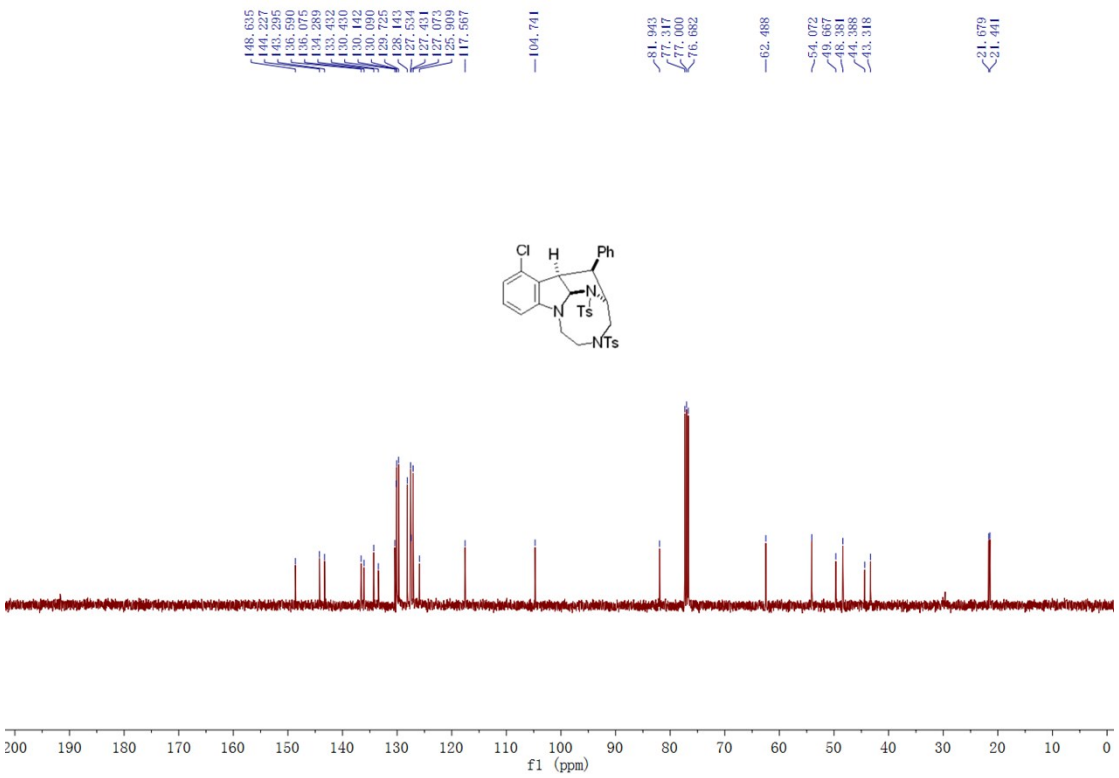

H
Ph
N
N
Ts
NTs
f1 (ppm)

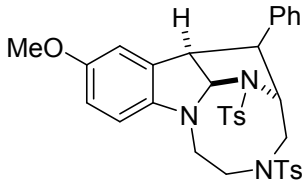

Cl
H
Ph
N
N
Ts
NTs

Compound 2b:

0.15 mmol scale, a white solid, 55% yield (52.2 mg). M.p.: 284-285 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.51 (s, 3H), 2.84-2.93 (m, 2H), 3.27 (dd, *J* = 6.8 Hz, 10.0 Hz, 1H), 3.40-3.54 (m, 2H), 3.53-3.58 (m, 1H), 3.63-3.71 (m, 1H), 3.82 (dd, *J* = 7.6 Hz, 10.0 Hz, 1H), 4.60-4.68 (m, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 6.18 (d, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 2H), 6.97 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 7.08-7.13 (m, 2H), 7.19-7.26 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 21.8, 43.3, 44.4, 48.4, 49.7, 54.1, 62.5, 81.9, 104.7, 117.6, 125.9, 127.1, 127.4, 127.5, 128.1, 129.7, 130.09, 130.14, 130.4, 133.4, 134.3, 136.1, 136.6, 143.3, 144.2, 148.6. IR (neat) 3090, 3059, 3028, 2979, 2956, 2920, 2855, 1598, 1493, 1465, 1372, 1345, 1304, 1265, 1247, 1222, 1184, 1156, 1129, 1094, 1065, 1042, 1014, 971, 895, 856, 815, 777, 757, 731, 712, 703, 676, 659 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+$NH_4$)$^+$ requires: 634.1596, found: 634.1609.

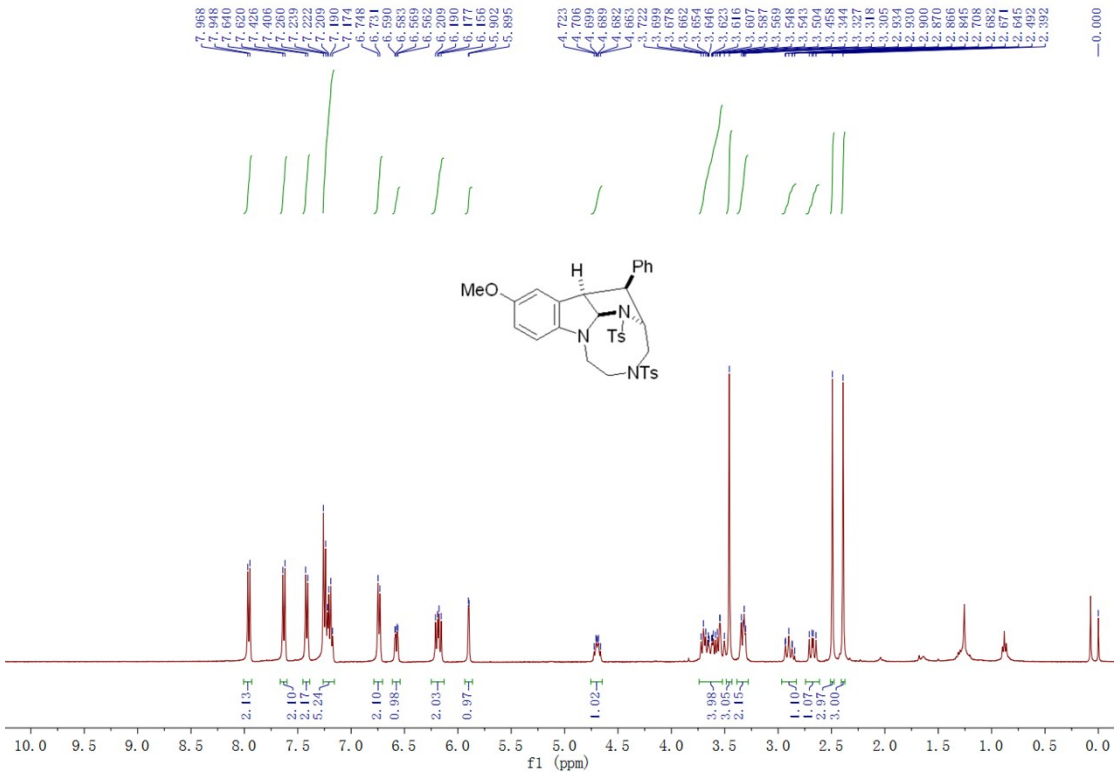


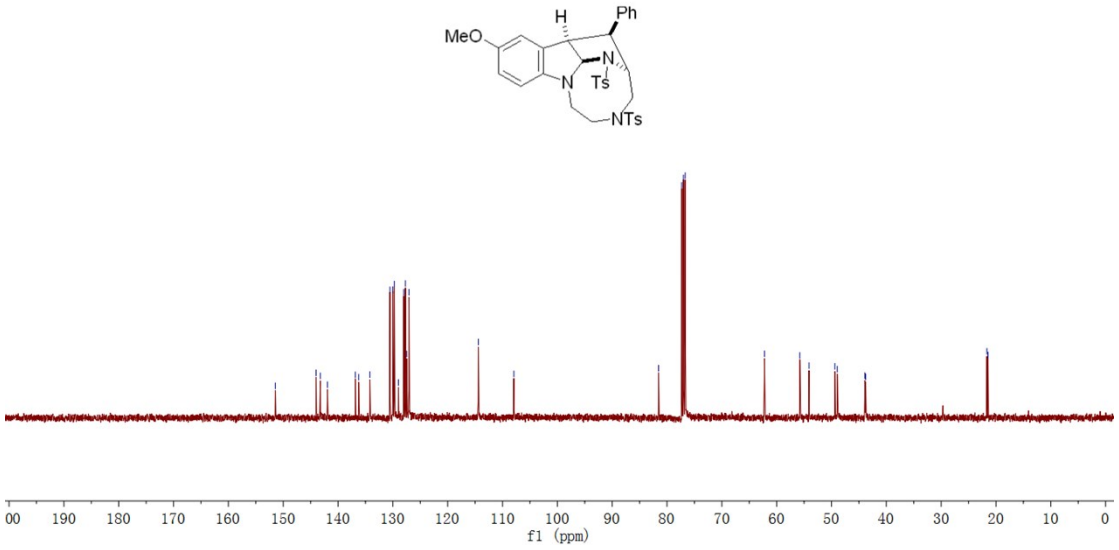


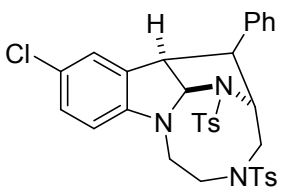


Compound 2c:

0.15 mmol scale, a light yellow solid, 62% yield (58.5 mg). M.p.: 144-147 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.49 (s, 3H), 2.68 (dd, *J* = 10.4 Hz, 14.8 Hz, 1H), 2.84-2.94 (m, 1H), 3.30-3.35 (m, 2H), 3.46 (s, 3H), 3.50-3.73 (m, 4H), 4.66-4.73 (m, 1H), 5.90 (d, *J* = 2.8 Hz, 1H), 6.15-6.21 (m, 2H), 6.58 (dd, *J* = 2.8 Hz, 8.4 Hz, 1H), 6.73-6.75 (m, 2H), 7.17-7.26 (m, 5H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.7, 43.8, 43.9, 48.9, 49.4, 54.1, 55.8, 62.2, 81.5, 107.9, 114.4, 127.1, 127.5, 127.7, 128.0, 129.0, 129.7, 130.0, 130.5, 134.2, 136.2, 136.8, 141.9, 143.2, 144.0, 151.4. IR (neat) 3096, 3062, 3028, 2953, 2923, 2904, 2853, 2827, 1596, 1492, 1453, 1346, 1304, 1261, 1237, 1158, 1093, 1063, 1033, 1014, 975, 897, 849, 813, 778, 757, 737, 719, 706, 689, 672, 658 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{35}N_3O_5S_2Na^{+1}$(M+Na)$^{+}$ requires: 652.1910, found: 652.1910.

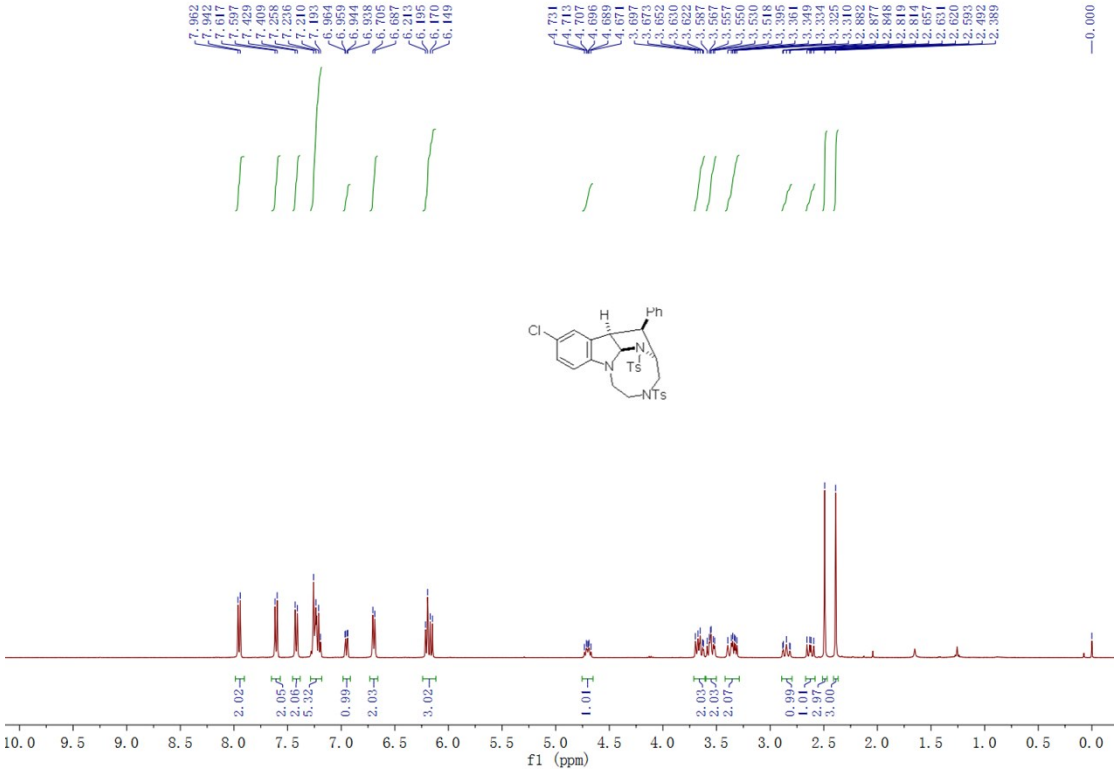

MeO
H
Ph
N
Ts
N
NTs
f1 (ppm)

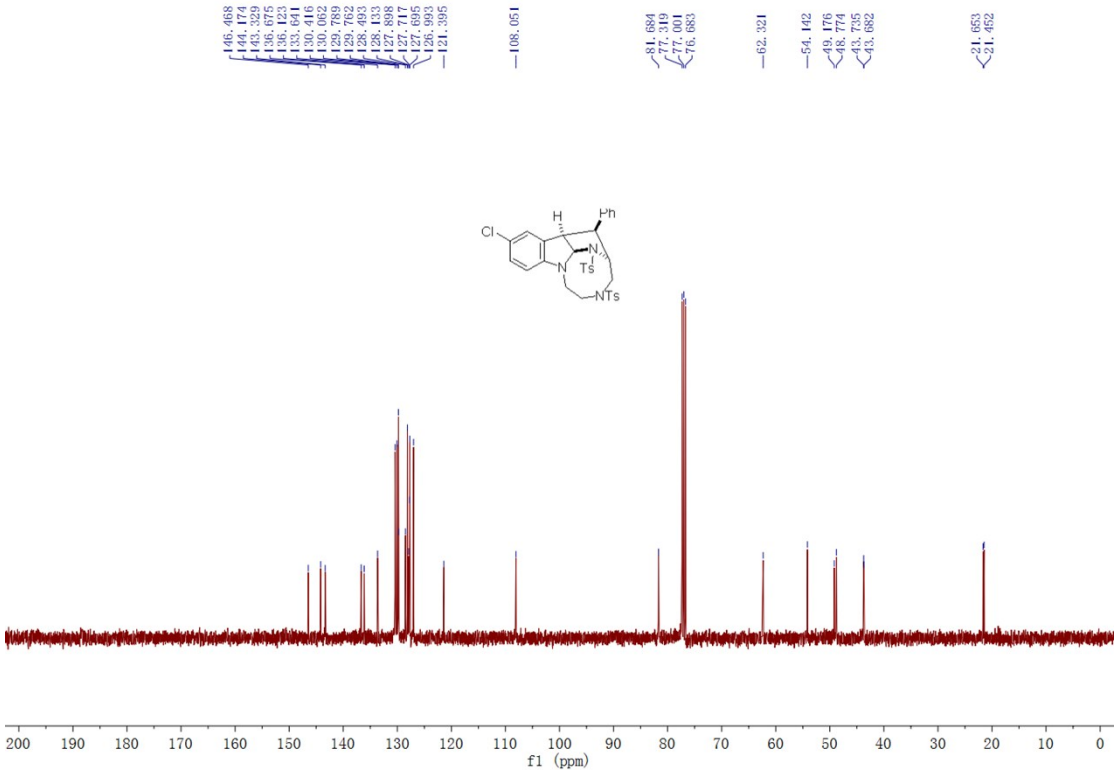

MeO
H
Ph
N
Ts
N
NTs
f1 (ppm)

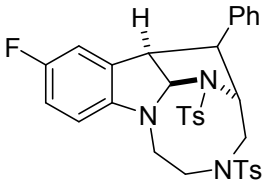

Cl
H
Ph
N
Ts
N
NTs

Compound 2d:

0.15 mmol scale, a white solid, 82% yield (77.3 mg). M.p.: 279-281 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.49 (s, 3H), 2.63 (dd, *J* = 10.4 Hz, 15.2 Hz, 1H), 2.81-2.89 (m, 1H), 3.31-3.40 (m, 2H), 3.51-3.59 (m, 2H), 3.62-3.70 (m, 2H), 4.67-4.74 (m, 1H), 6.14-6.22 (m, 3H), 6.68-6.71 (m, 2H), 6.95 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 7.19-7.26 (m, 5H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.7, 43.68, 43.74, 48.8, 49.2, 54.1, 62.3, 81.7, 108.1, 121.4, 127.0, 127.70, 127.72, 127.9, 128.1, 128.5, 129.76, 129.79, 130.1, 130.4, 133.6, 136.1, 136.7, 143.3, 144.2, 146.5. IR (neat) 3098, 3065, 3031, 2956, 2917, 2889, 2863, 1596, 1482, 1451, 1373, 1343, 1325, 1305, 1296, 1244, 1219, 1186, 1152, 1087, 1067, 1026, 1006, 974, 959, 925, 885, 847, 815, 789, 774, 746, 734, 714, 707, 691, 677, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+H)$^{+}$ requires: 634.1596, found: 634.1581.

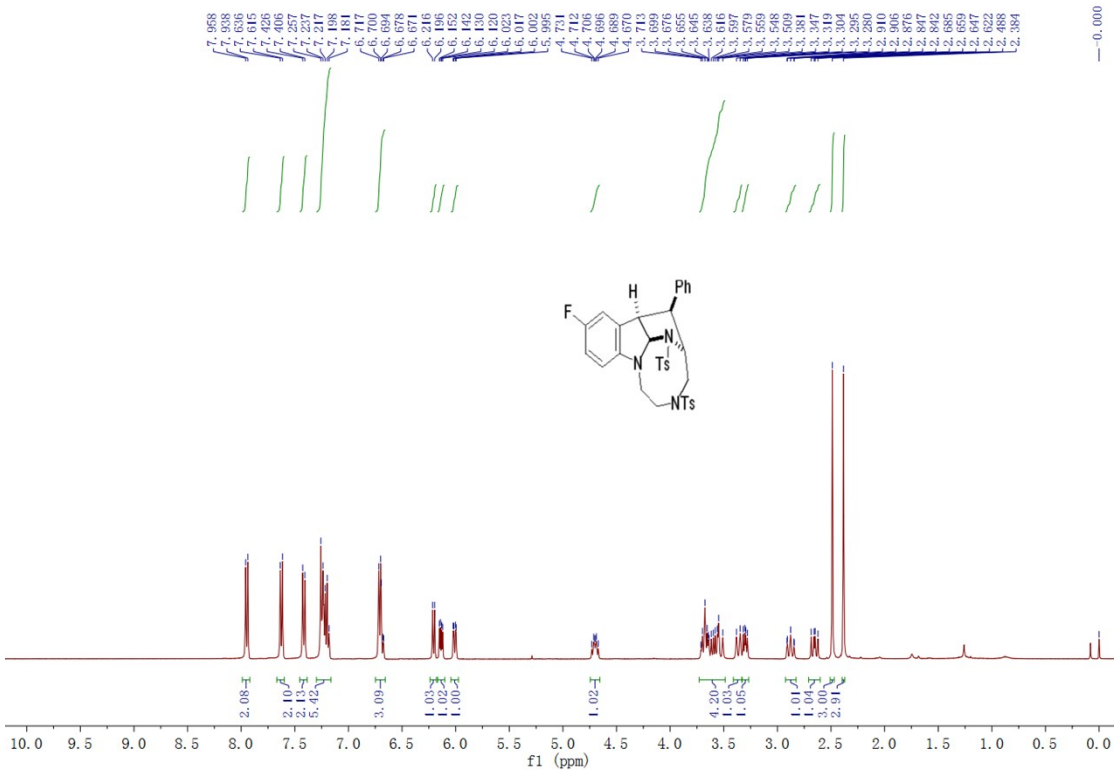






Compound 2e:

0.15 mmol scale, a light red solid, 73% yield (67.6 mg). M.p.: 267-269 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.49 (s, 3H), 2.65 (dd, *J* = 10.0 Hz, 14.8 Hz, 1H), 2.84-2.91 (m, 1H), 3.30 (dd, *J* = 6.0 Hz, 10.0 Hz, 1H), 3.34-3.39 (m, 1H), 3.50-3.72 (m, 4H), 4.67-4.74 (m, 1H), 6.01 (dd, *J* = 2.8 Hz, 8.8 Hz, 1H), 6.14 (dd, *J* = 4.0 Hz, 8.8 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 6.67-6.72 (m, 3H), 7.18-7.26 (m, 5H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.4, 21.6, 43.7, 43.8, 48.9, 49.0, 54.1, 62.2, 81.7, 107.3 (d, *J* = 8.0 Hz), 114.7 (d, *J* = 23.1 Hz), 115.3 (d, *J* = 24.6 Hz), 127.0, 127.6, 128.1, 129.3 (d, *J* = 8.0 Hz), 129.7, 130.0, 130.3, 133.7, 136.1, 136.7, 143.3, 144.0 (d, *J* = 0.9 Hz), 144.1, 155.1 (d, *J* = 234.3 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -127.33- -127.39 (m). IR (neat) 3096, 3062, 3026, 2974, 2951, 2920, 2904, 2858, 1597, 1489, 1453, 1370, 1346, 1305, 1233, 1157, 1092, 1062, 1040, 1014, 976, 961, 941, 901, 879, 850, 810, 779, 761, 736, 705, 689, 682, 658 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{36}FN_4O_4S_2^{+1}(M+NH_4)^+$ requires 635.2157, found: 635.2156.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2.847
2.842
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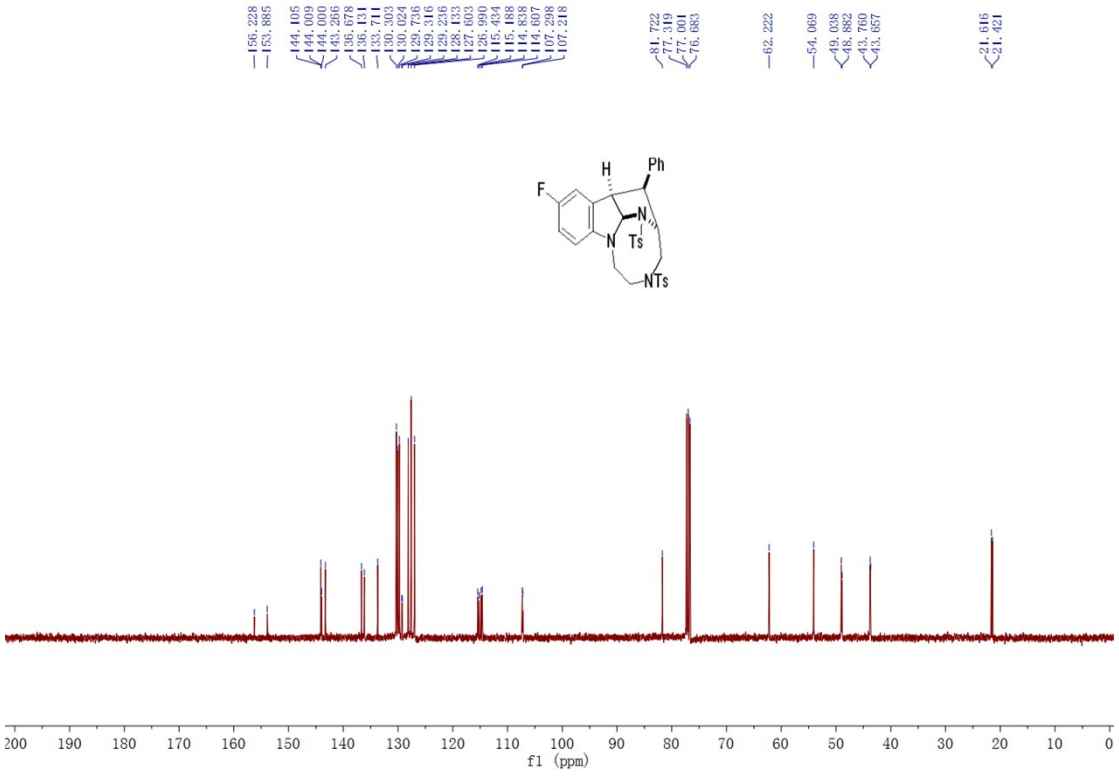
2.647
2.622
2.488
2.384
0.000
H
Ph
F
N
Ts
N
NTs
2.08
2.10
2.13
5.42
3.09
1.03
1.02
1.00
1.02
4.20
1.03
1.05
1.01
1.04
3.00
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.236
128.133
127.603
126.990
115.434
115.188
114.838
114.607
107.298
107.218
81.722
77.319
77.001
76.683
62.222
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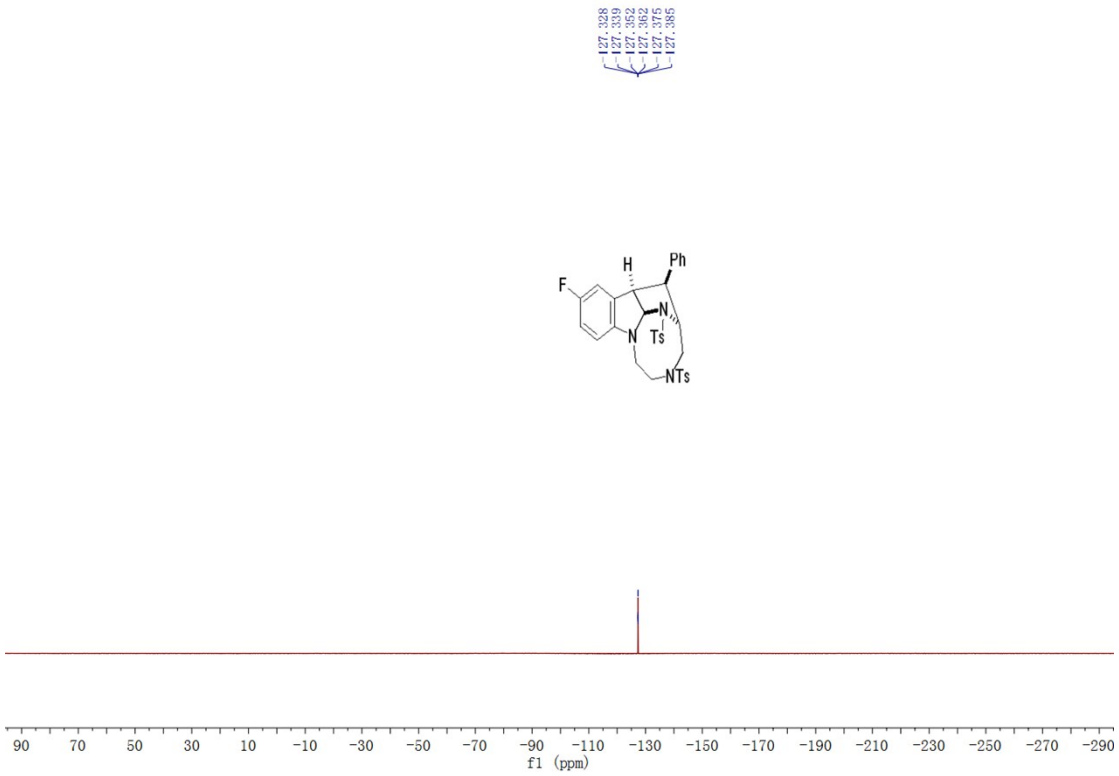
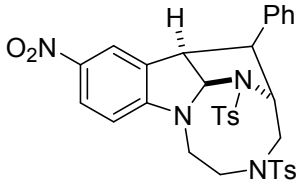
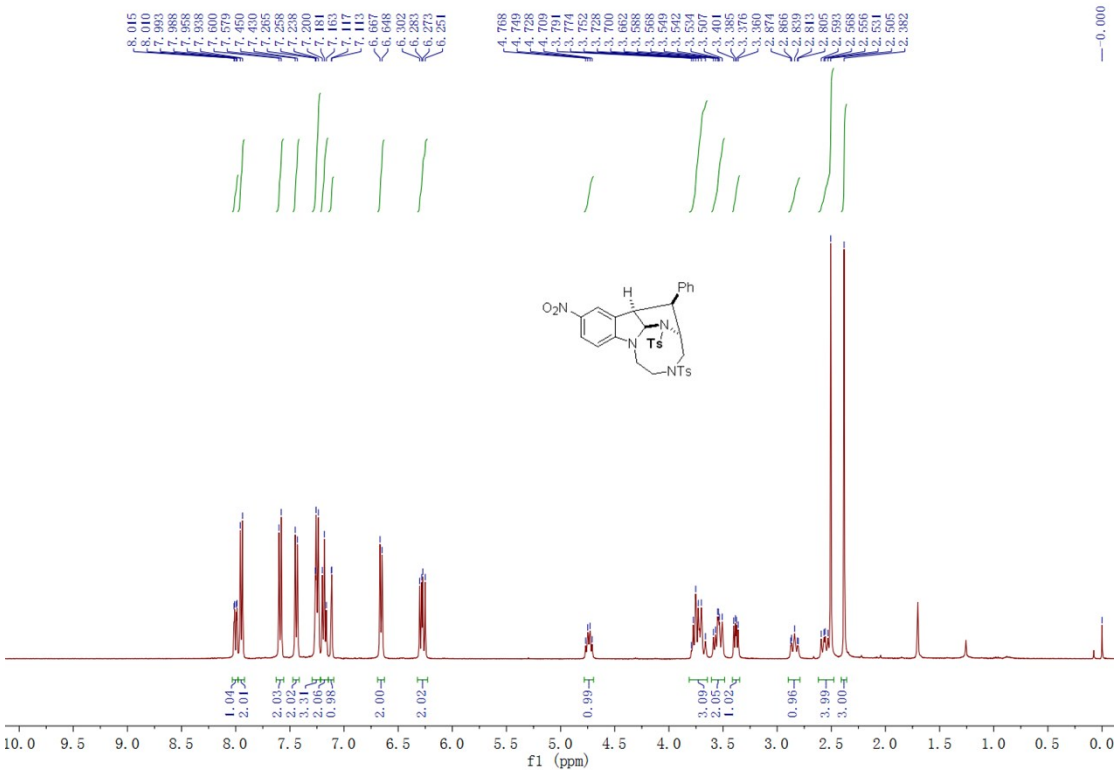
48.882
43.760
43.657
21.616
21.421
H
Ph
F
N
Ts
N
NTs
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)





Compound 2f:

0.15 mmol scale, a yellow solid, 75% yield (72.9 mg). M.p.: 169-172 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.51 (s, 3H), 2.56 (dd, *J* = 10.0 Hz, 14.8 Hz, 1H), 2.80-2.88 (m, 1H), 3.38 (dd, *J* = 6.4 Hz, 10.0 Hz, 1H), 3.50-3.59 (m, 2H), 3.66-3.80 (m, 3H), 4.70-4.77 (m, 1H), 6.26 (d, *J* = 8.8 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 1.6 Hz, 1H), 7.16-7.20 (m, 2H), 7.23-7.27 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.00 (dd, *J* = 1.6 Hz, 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.7, 43.8, 44.5, 47.8, 49.5, 54.2, 62.5, 82.6, 105.7, 123.8, 126.9, 127.1, 127.6, 128.1, 128.4, 128.6, 129.9, 130.20, 130.21, 132.8, 135.8, 136.2, 138.3, 143.6, 144.6, 153.4. IR (neat) 3093, 3062, 3028, 2982, 2951, 2921, 2855, 1606, 1496, 1453, 1347, 1315, 1282, 1246, 1219, 1185, 1158, 1092, 1063, 1040, 1007, 974, 903, 851, 815, 782, 752, 736, 713, 677, 660 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}N_4O_6S_2^{+1}(M+H)^+$ requires: 645.1836, found: 645.1847.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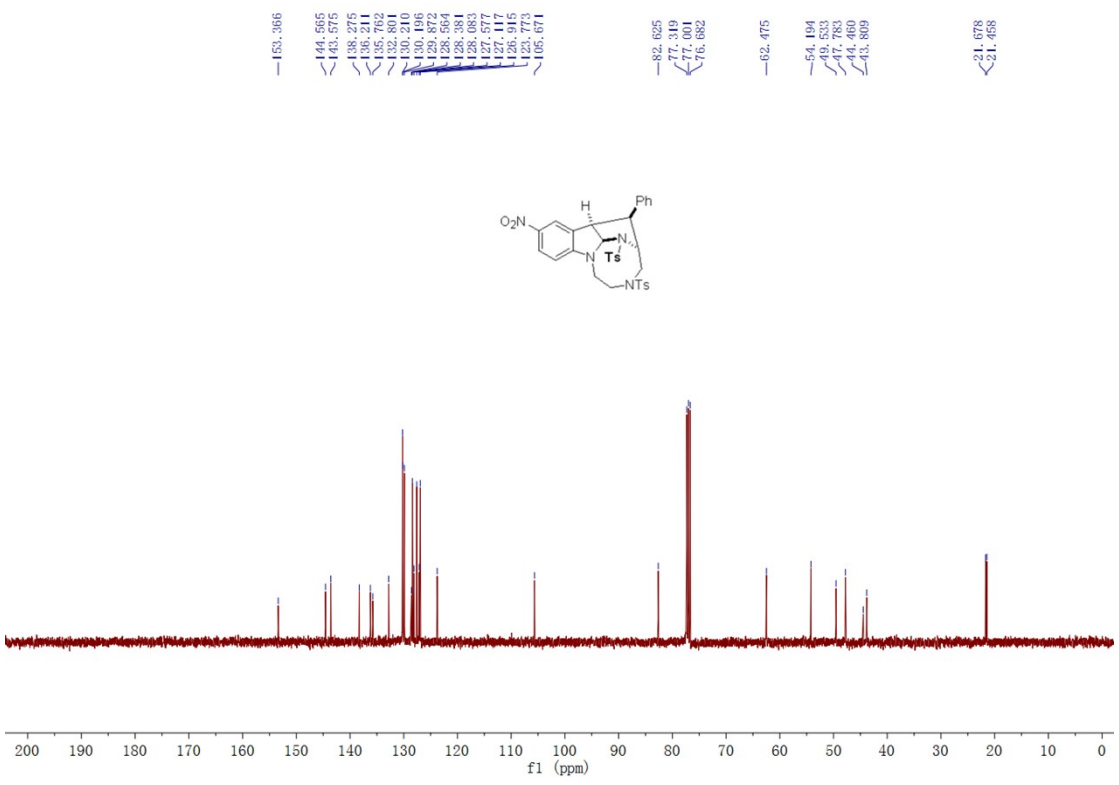
7.238
7.200
7.181
7.163
7.117
7.113
6.667
6.648
6.302
6.283
6.273
6.251
4.768
4.749
4.728
4.709
3.791
3.774
3.752
3.728
3.700
3.662
3.588
3.568
3.549
3.542
3.534
3.507
3.401
3.385
3.376
3.360
2.874
2.866
2.829
2.813
2.805
2.593
2.568
2.556
2.531
2.505
2.382
-0.000
O2N
H
Ph
N
Ts
N
NTs
1.04
2.01
2.03
2.02
3.31
2.06
0.98
2.00
2.02
0.99
3.09
2.05
1.02
0.96
3.99
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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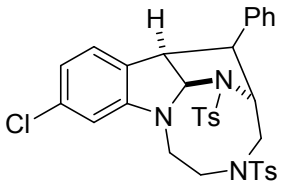
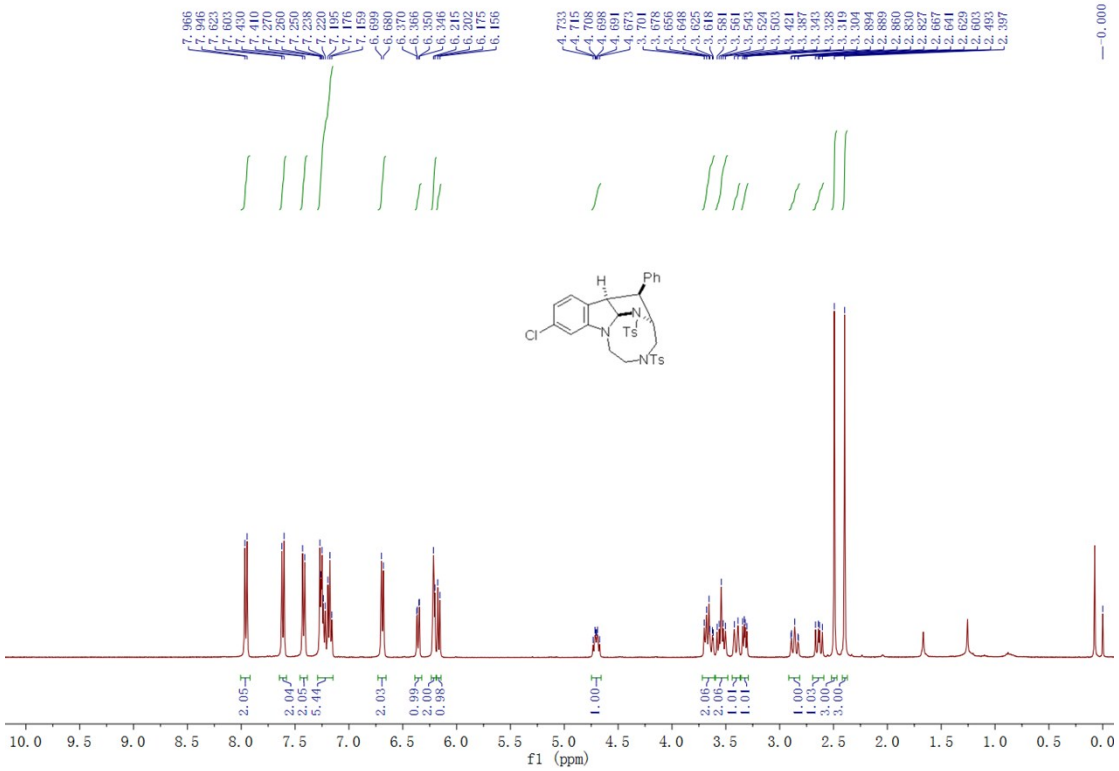
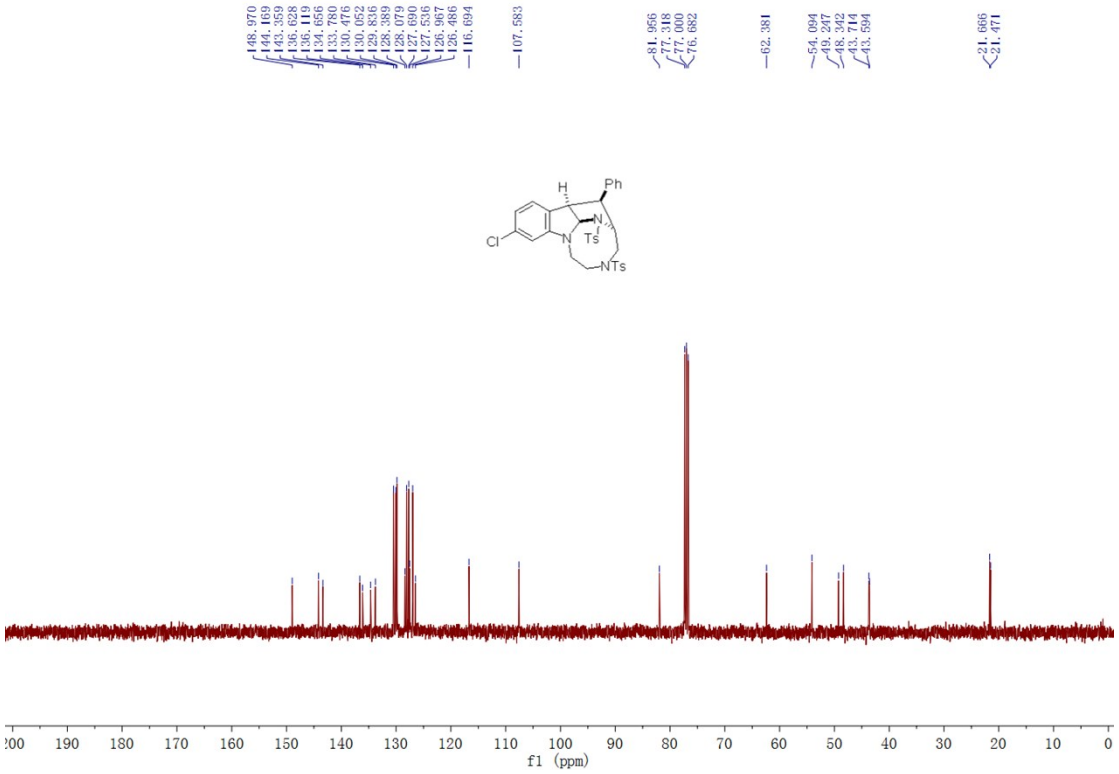
127.577
127.117
126.915
123.773
105.671
82.625
77.319
77.001
76.682
62.475
54.194
49.523
47.783
44.460
43.809
21.678
21.458
O2N
H
Ph
N
Ts
N
NTs
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

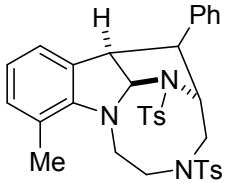

H
Ph
N
Cl
N
Ts
NTs

Compound 2g:

0.15 mmol scale, a white solid, 66% yield (62.8 mg). M.p.: 300-303 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.49 (s, 3H), 2.64 (dd, *J* = 10.4 Hz, 15.2 Hz, 1H), 2.82-2.90 (m, 1H), 3.32 (dd, *J* = 6.0 Hz, 9.6 Hz, 1H), 3.38-3.43 (m, 1H), 3.50-3.59 (m, 2H), 3.61-3.71 (m, 2H), 4.67-4.74 (m, 1H), 6.17 (d, *J* = 7.6 Hz, 1H), 6.20-6.22 (m, 2H), 6.36 (dd, *J* = 1.6 Hz, 8.0 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 2H), 7.15-7.27 (m, 5H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.7, 43.6, 43.7, 48.3, 49.2, 54.1, 62.4, 82.0, 107.6, 116.7, 126.5, 127.0, 127.5, 127.7, 128.1, 128.4, 129.8, 130.1, 130.5, 133.8, 134.7, 136.1, 136.6, 143.4, 144.2, 149.0. IR (neat) 3088, 3065, 3028, 2961, 2951, 2917, 2860, 1602, 1488, 1453, 1348, 1305, 1219, 1185, 1159, 1094, 1067, 1041, 1014, 973, 893, 857, 812, 772, 740, 716, 706, 677, 660 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+H)$^{+}$ requires: 634.1596, found: 634.1619.

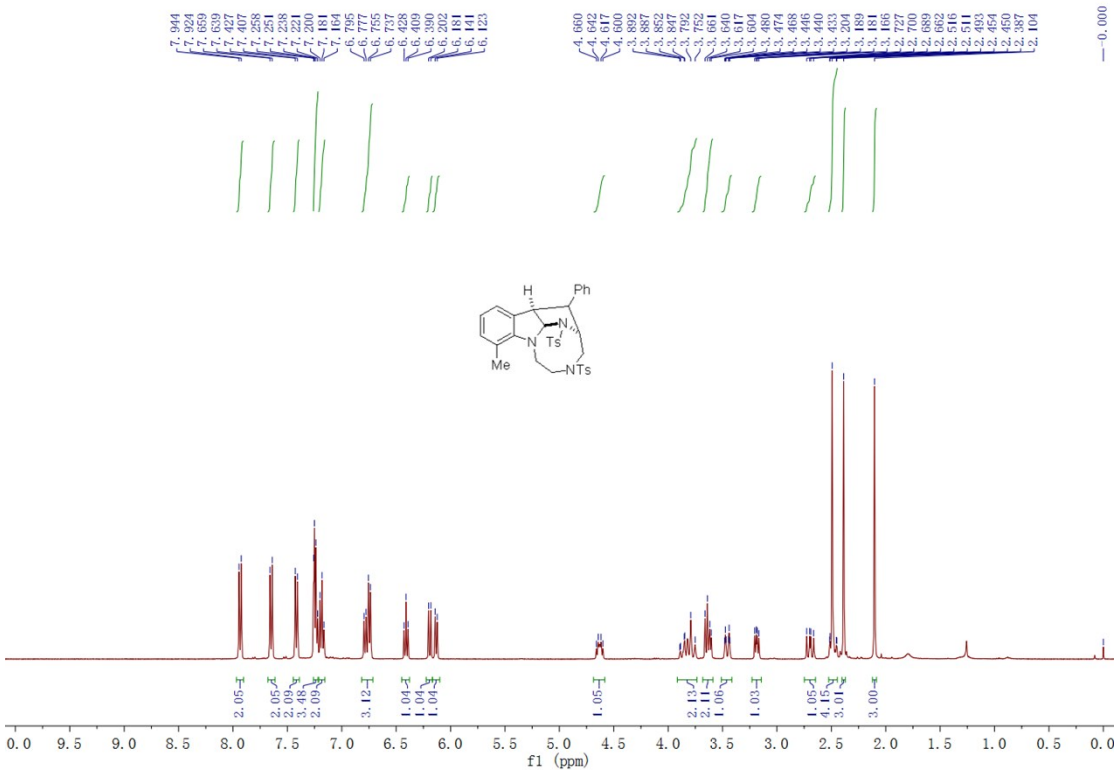


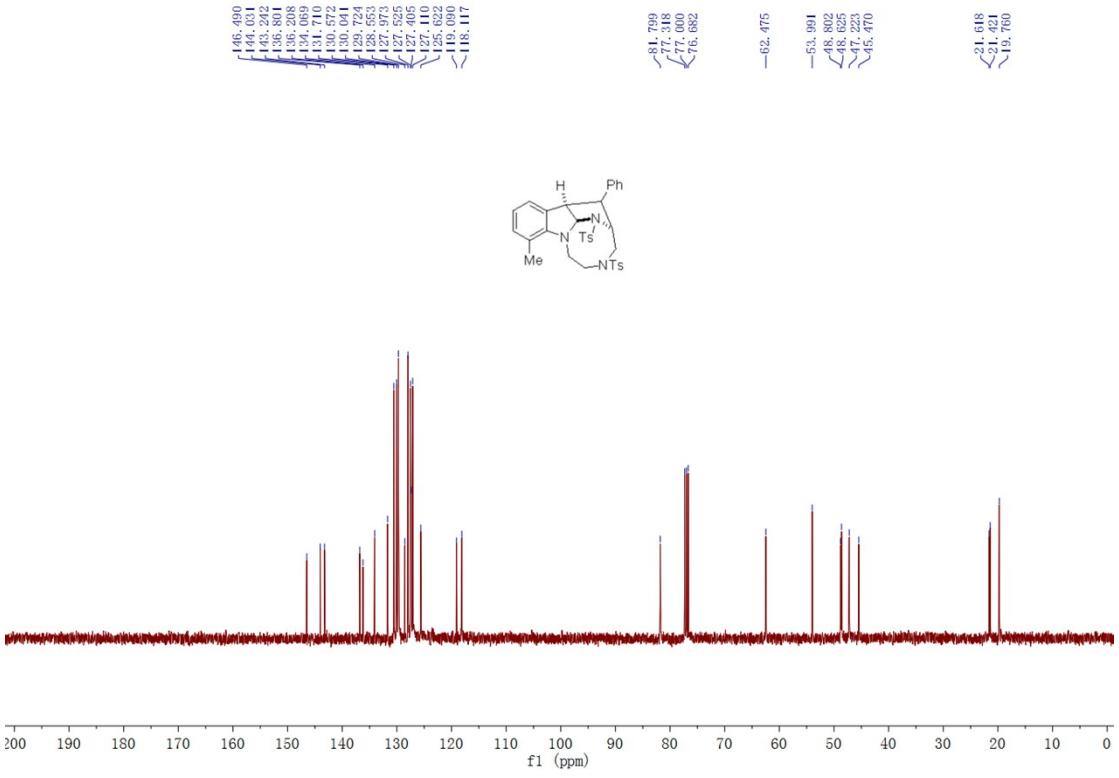


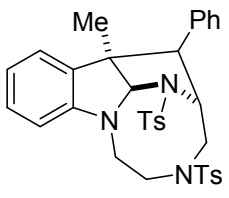


Compound 2h:

0.15 mmol scale, a white solid, 61% yield (55.9 mg). M.p.: 125-128 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.10 (s, 3H), 2.39 (s, 3H), 2.45-2.52 (m, 4H), 2.69 (dd, *J* = 10.8 Hz, 15.2 Hz, 1H), 3.19 (dd, *J* = 6.0 Hz, 9.2 Hz, 1H), 3.43-3.48 (m, 1H), 3.60-3.67 (m, 2H), 3.75-3.89 (m, 2H), 4.60-4.65 (m, 1H), 6.13 (d, *J* = 7.2 Hz, 1H), 6.19 (d, *J* = 8.4 Hz, 1H), 6.41 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.73-6.80 (m, 3H), 7.16-7.20 (m, 2H), 7.22-7.26 (m, 3H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.8, 21.4, 21.6, 45.5, 47.2, 48.6, 48.8, 54.0, 62.5, 81.8, 118.1, 119.1, 125.6, 127.1, 127.4, 127.5, 128.0, 128.6, 129.7, 130.0, 130.6, 131.7, 134.1, 136.2, 136.8, 143.2, 144.0, 146.5. IR (neat) 3090, 3059, 3046, 3023, 2947, 2907, 2866, 1597, 1494, 1455, 1420, 1367, 1347, 1305, 1250, 1214, 1158, 1092, 1055, 1043, 1014, 976, 944, 899, 881, 852, 816, 764, 742, 718, 706, 683, 662 cm^{-1}. HRMS (APCI) Calcd. for $C_{34}H_{36}ClN_3O_4S_2^{+1}$(M+H)$^{+}$ requires: 614.2142, found: 614.2153.

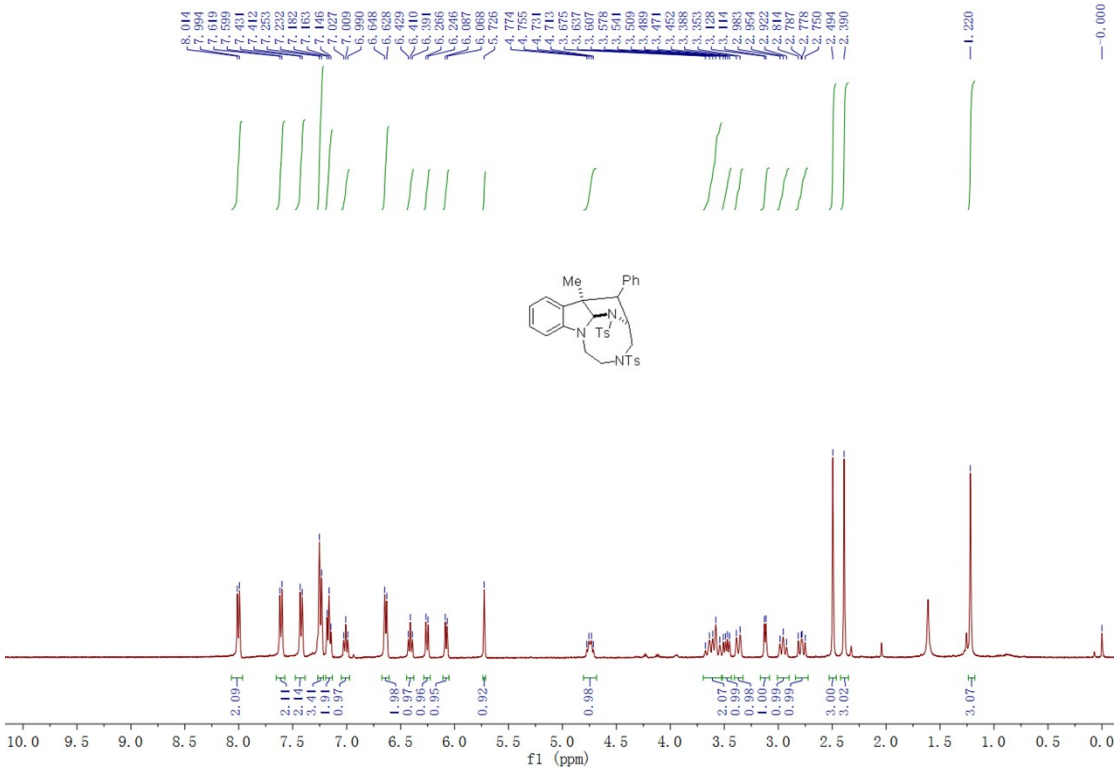

H
Ph
N
N
Ts
Me
NTs
f1 (ppm)

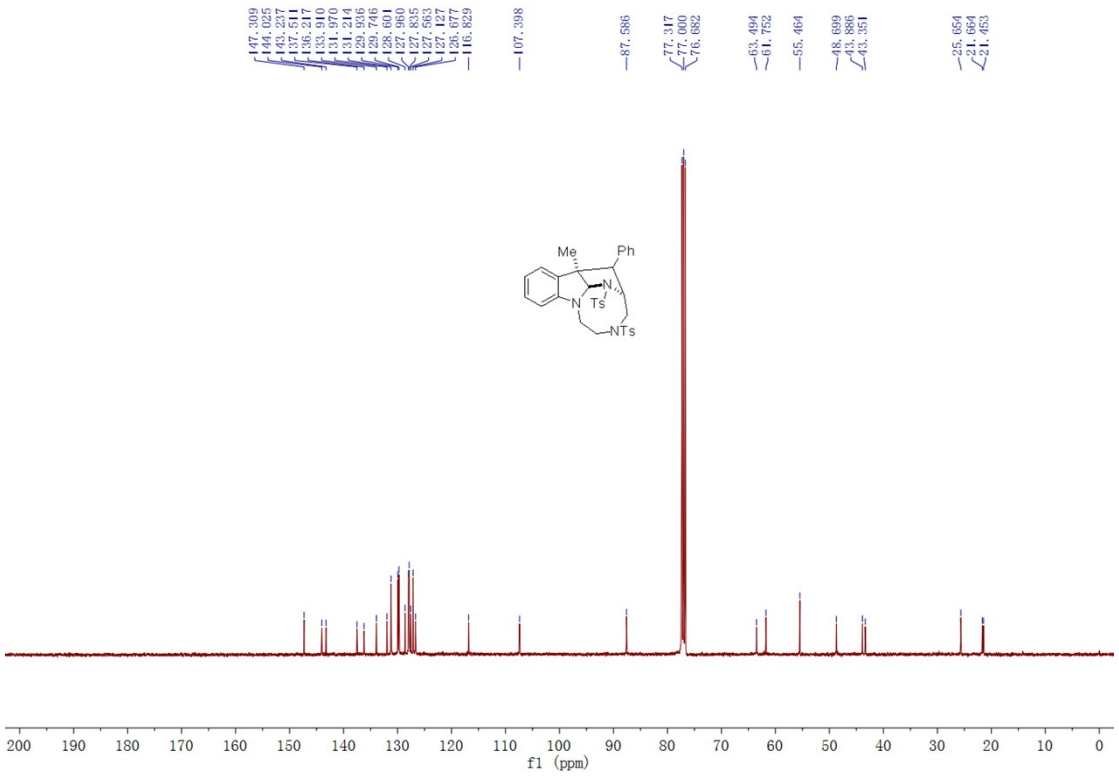

H
Ph
N
N
Ts
Me
NTs
f1 (ppm)

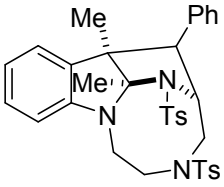

Me
Ph
N
N
Ts
NTs

Compound 2i:

0.15 mmol scale, a white solid, 43% yield (39.6 mg). M.p.: 149-152 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.22 (s, 3H), 2.39 (s, 3H), 2.49 (s, 3H), 2.78 (dd, *J* = 10.8 Hz, 14.8 Hz, 1H), 2.92-2.99 (m, 1H), 3.12 (d, *J* = 5.6 Hz, 1H), 3.35-3.39 (m, 1H), 3.48 (dd, *J* = 8.0 Hz, 14.8 Hz, 1H), 3.54-3.68 (m, 2H), 4.71-4.78 (m, 1H), 5.73 (s, 1H), 6.08 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 6.41 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 7.01 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.14-7.19 (m, 2H), 7.23-7.26 (m, 3H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.7, 25.7, 43.4, 43.9, 48.7, 55.5, 61.8, 63.5, 87.6, 107.4, 116.8, 126.7, 127.1, 127.6, 127.8, 128.0, 128.6, 129.7, 129.9, 131.2, 132.0, 133.9, 136.2, 137.5, 143.2, 144.0, 147.3. IR (neat) 3062, 3028, 2956, 2923, 2866, 2853, 1600, 1487, 1466, 1452, 1346, 1312, 1288, 1161, 1118, 1091, 1065, 1049, 1023, 968, 816, 779, 742, 723, 702, 678, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{39}N_4O_4S_2^{+1}$(M+$NH_4$)$^+$ requires: 631.2407, found: 631.2407.

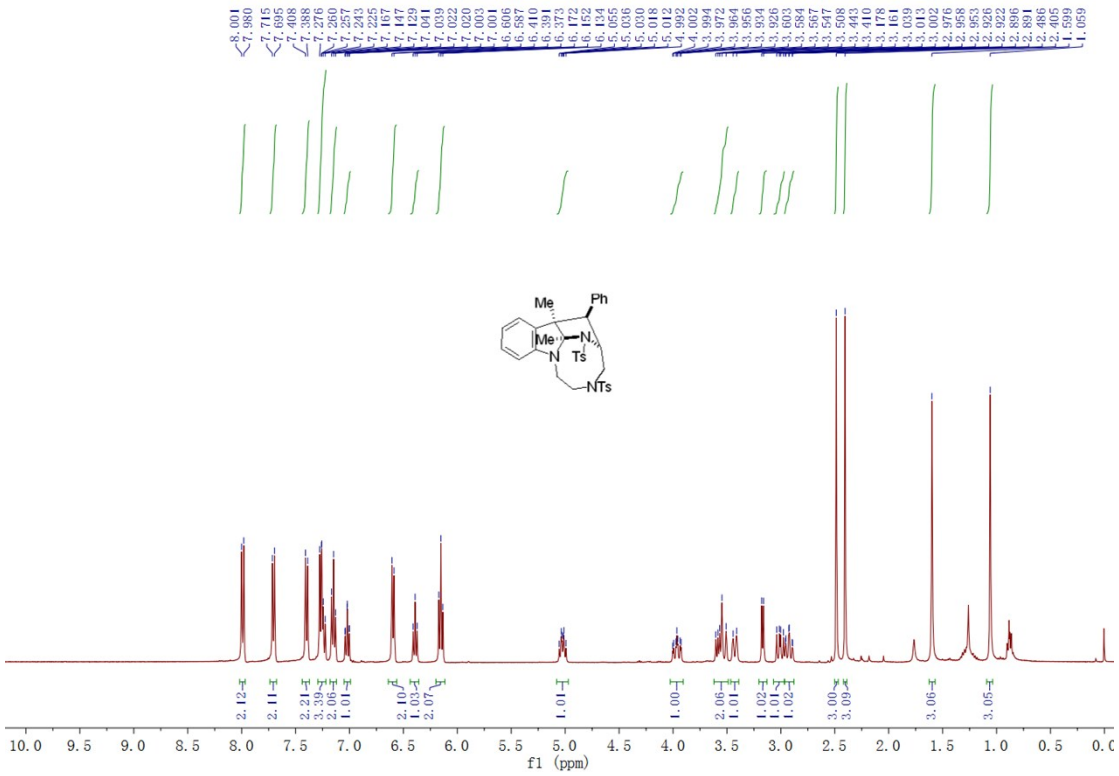


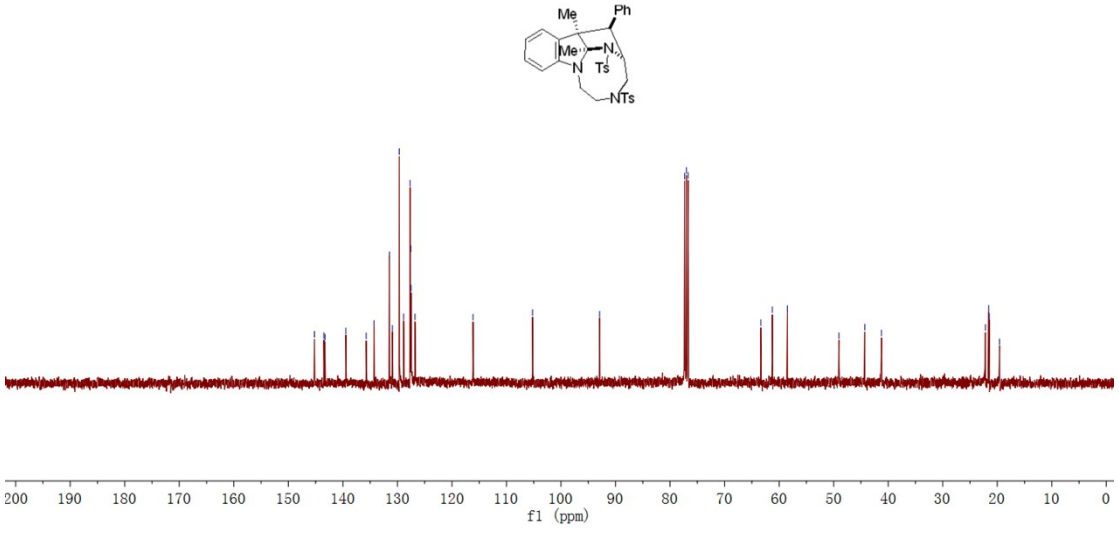


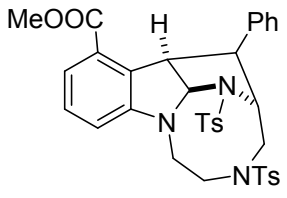


Compound 2j:

0.15 mmol scale, a white solid, 54% yield (50.9 mg). M.p.: 260-262 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.06 (s, 3H), 1.60 (s, 3H), 2.41 (s, 3H), 2.49 (s, 3H), 2.89-2.96 (m, 1H), 3.01 (dd, J = 10.4 Hz, 14.8 Hz, 1H), 3.17 (d, J = 6.8 Hz, 1H), 3.41-3.45 (m, 1H), 3.50-3.61 (m, 2H), 3.92-4.01 (m, 1H), 4.99-5.06 (m, 1H), 6.13-6.18 (m, 2H), 6.39 (d, J = 7.6 Hz, 1H), 6.60 (d, J = 7.6 Hz, 2H), 7.00-7.05 (m, 1H), 7.12-7.17 (m, 2H), 7.22-7.28 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.6, 21.5, 21.6, 22.2, 41.2, 44.3, 49.0, 58.5, 61.3, 63.4, 92.9, 105.2, 116.1, 126.8, 127.50, 127.53, 127.7, 128.9, 129.7, 130.9, 131.5, 134.3, 135.7, 139.5, 143.3, 143.5, 145.2. IR (neat) 3062, 3028, 2979, 2953, 2923, 2897, 2868, 2853, 1604, 1491, 1453, 1386, 1344, 1315, 1288, 1224, 1159, 1092, 1068, 1041, 1020, 1005, 972, 926, 903, 883, 816, 778, 736, 703, 688, 665 cm^{-1}. HRMS (APCI) Calcd. for $C_{35}H_{38}N_3O_4S_2^{+1}$(M+H)$^+$ requires: 628.2298, found: 628.2314.

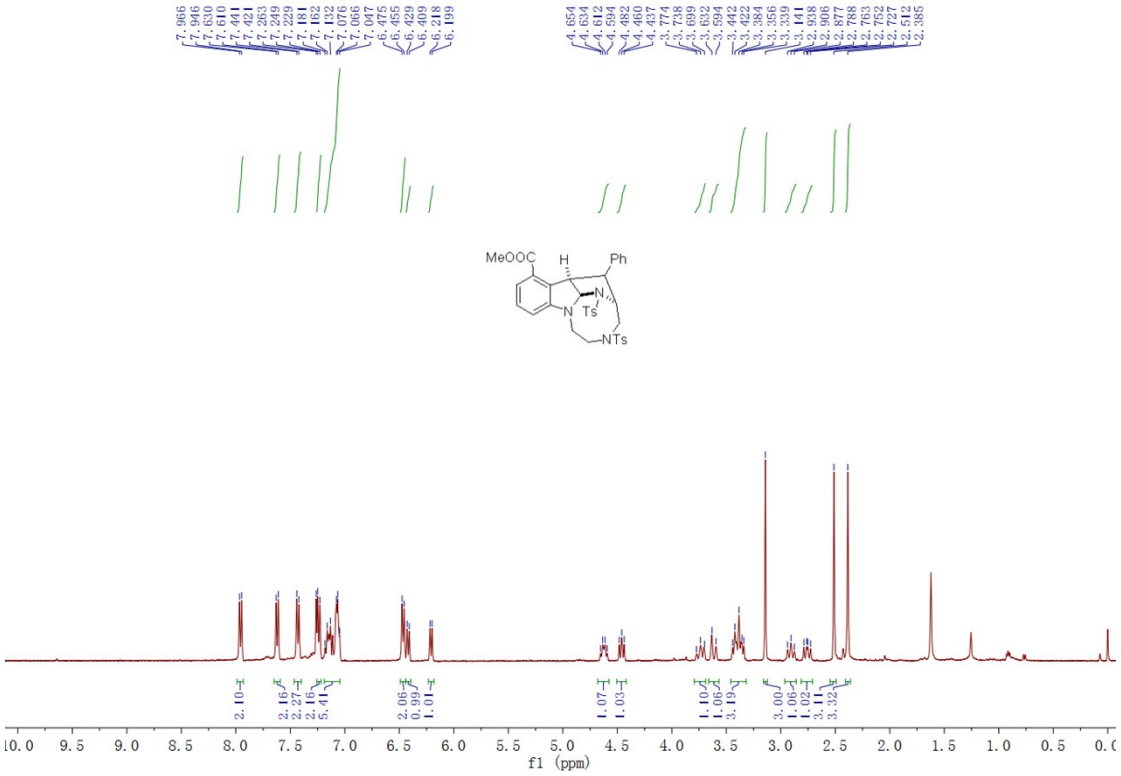

Me
Ph
Me
N
Ts
NTs
f1 (ppm)

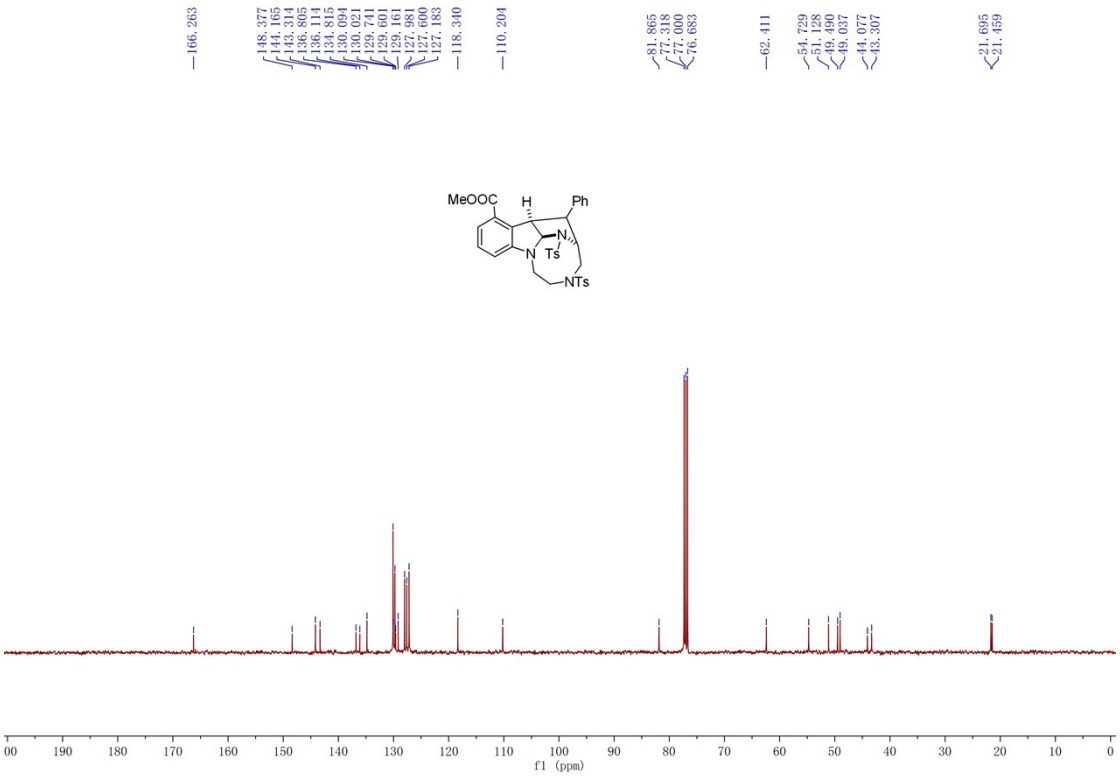

Me
Ph
Me
N
Ts
NTs
f1 (ppm)

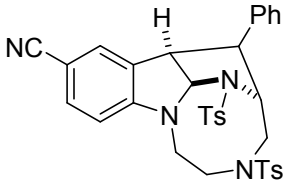

MeOOC
H
Ph
N
N
Ts
NTs

Compound 2l:

0.15 mmol scale, a yellow solid, 48% yield (47.7 mg). M.p.: 130-133 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.51 (s, 3H), 2.76 (dd, *J* = 10.0 Hz, 14.4 Hz, 1H), 2.87-2.94 (m, 1H), 3.14 (s, 3H), 3.33-3.45 (m, 3H), 3.59-3.64 (m, 1H), 3.69-3.78 (m, 1H), 4.43-4.49 (m, 1H), 4.59-4.66 (m, 1H), 6.21 (d, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 2H), 7.04-7.19 (m, 5H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.7, 43.3, 44.1, 49.0, 49.5, 51.1, 54.7, 62.4, 81.9, 110.2, 118.3, 127.2, 127.6, 128.0, 129.2, 129.6, 129.7, 130.0, 130.1, 134.8, 136.1, 136.8, 143.3, 144.2, 148.4, 166.2. IR (neat) 3057, 3028, 2948, 2821, 1850, 1716, 1596, 1493, 1469, 1454, 1434, 1373, 1345, 1305, 1268, 1223, 1208, 1156, 1132, 1091, 1043, 1015, 970, 897, 865, 840, 813, 779, 732, 713, 703, 677, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{35}H_{39}N_4O_6S_2^{+1}$(M+$NH_4$)$^+$ requires: 675.2306, found: 675.2305.

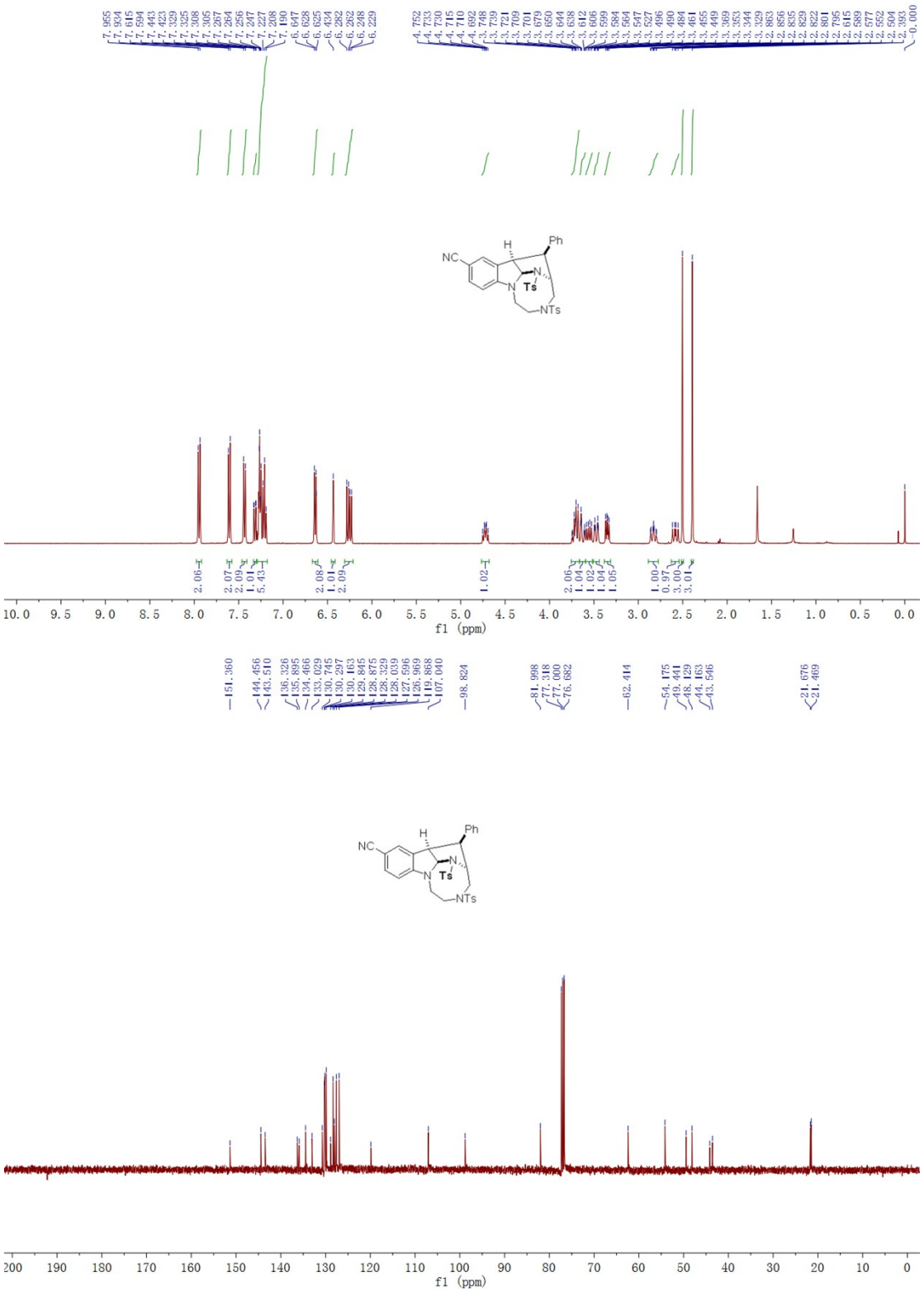


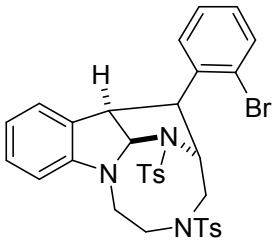




Compound 2m:

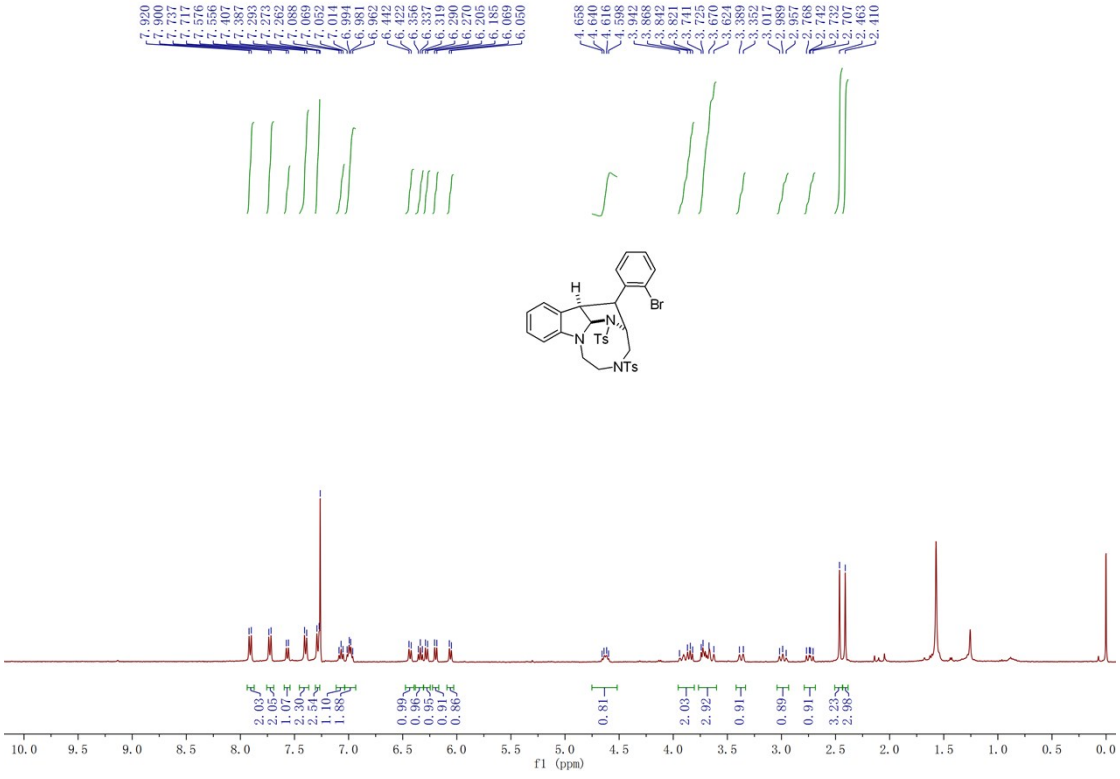
0.15 mmol scale, a white solid, 63% yield (59.0 mg). M.p.: 288-291 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.50 (s, 3H), 2.58 (dd, *J* = 10.0 Hz, 14.8 Hz, 1H), 2.80-2.87 (m, 1H), 3.35 (dd, *J* = 6.0 Hz, 10.0 Hz, 1H), 3.44-3.50 (m, 1H), 3.56 (dd, *J* = 8.0 Hz, 14.8 Hz, 1H), 3.59-3.60 (m, 1H), 3.67-3.75 (m, 2H), 4.69-4.76 (m, 1H), 6.24 (d, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 6.43 (s, 1H), 6.62-6.65 (m, 2H), 7.19-7.27 (m, 5H), 7.32 (dd, *J* = 1.2 Hz, 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.7, 43.5, 44.2, 48.1, 49.4, 54.2, 62.4, 82.0, 98.8, 107.0, 119.9, 127.0, 127.6, 128.0, 128.3, 128.9, 129.8, 130.2, 130.3, 130.7, 133.0, 134.5, 135.9, 136.3, 143.5, 144.5, 151.4. IR (neat) 3088, 3059, 3028, 2979, 2959, 2920, 2868, 2855, 2214, 1610, 1497, 1452, 1371, 1347, 1305, 1248, 1220, 1159, 1115, 1093, 1062, 1040, 1014, 975, 900, 850, 815, 780, 754, 741, 721, 706, 684, 667 cm^{-1}. HRMS (APCI) Calcd. for $C_{34}H_{33}N_4O_4S_2^{+1}(M+H)^+$ requires: 625.1938, found: 625.1952.

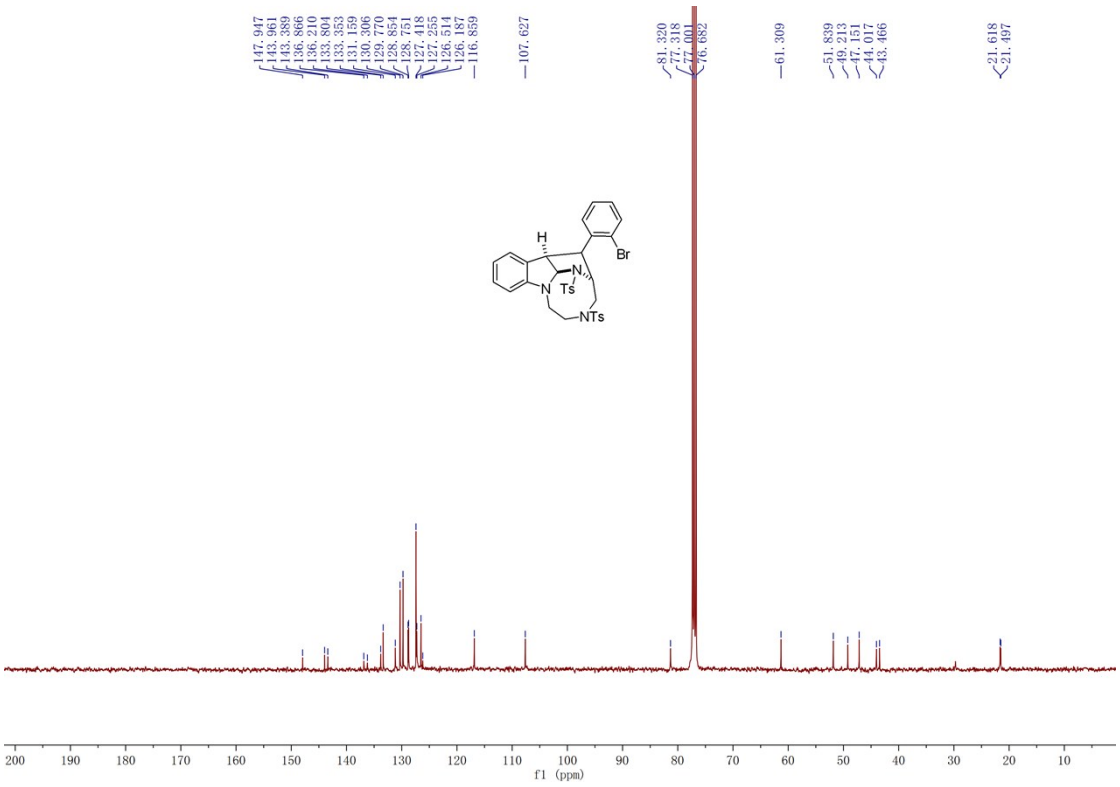

7.955 7.934 7.615 7.594 7.443 7.423 7.329 7.325 7.308 7.305 7.267 7.264 7.256 7.247 7.227 7.208 7.190 6.647 6.628 6.625 6.434 6.282 6.262 6.248 6.229
4.752 4.733 4.730 4.715 4.710 4.692 3.748 3.739 3.721 3.709 3.701 3.679 3.650 3.644 3.638 3.612 3.606 3.599 3.584 3.564 3.547 3.527 3.496 3.490 3.484 3.461 3.455 3.449 3.369 3.353 3.344 3.329 2.883 2.856 2.835 2.829 2.822 2.801 2.795 2.645 2.589 2.577 2.552 2.504 2.393 0.000
NC
H
Ph
N
Ts
N
NTs
2.06 2.07 2.09 1.01 5.43 2.08 1.01 2.09 1.02 2.06 1.04 1.02 1.04 1.05 1.00 0.97 3.00 3.01
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)
151.360 144.456 143.510 136.326 135.895 134.466 133.029 130.745 130.297 130.163 129.845 128.875 128.329 128.039 127.596 126.969 119.868 107.040 98.824 81.998 77.318 77.000 76.682 62.414 54.175 49.441 48.129 44.163 43.546 21.676 21.469
NC
H
Ph
N
Ts
N
NTs
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

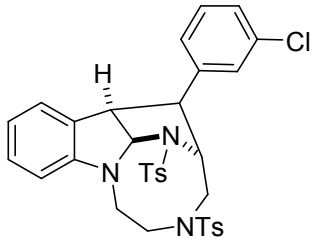


Compound 2n:

0.15 mmol scale, a white solid, 40% yield (40.6 mg). M.p.: 155-156 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.41 (s, 3H), 2.46 (s, 3H), 2.74 (dd, *J* = 10.0 Hz, 14.4 Hz, 1H), 2.95-3.02 (m, 1H), 3.35-3.39 (m, 1H), 3.62-3.75 (m, 3H), 3.82-3.95 (m, 2H), 4.59-4.66 (m, 1H), 6.06 (d, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 6.34 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 6.96-7.02 (m, 2H), 7.07 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 43.5, 44.0, 47.2, 49.2, 51.8, 61.3, 81.3, 107.6, 116.9, 126.2, 126.5, 127.3, 127.4, 128.8, 128.9, 129.8, 130.3, 131.2, 133.4, 133.8, 136.2, 136.9, 143.4, 144.0, 147.9. IR (neat) 3054, 3028, 2956, 2921, 2853, 1724, 1599, 1486, 1465, 1437, 1370, 1347, 1305, 1290, 1243, 1221, 1186, 1157, 1091, 1063, 1041, 1019, 973, 890, 855, 814, 774, 747, 713, 671, 655 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{36}BrN_4O_4S_2^{+1}$(M+$NH_4$)$^+$ requires: 695.1356, found: 695.1355.



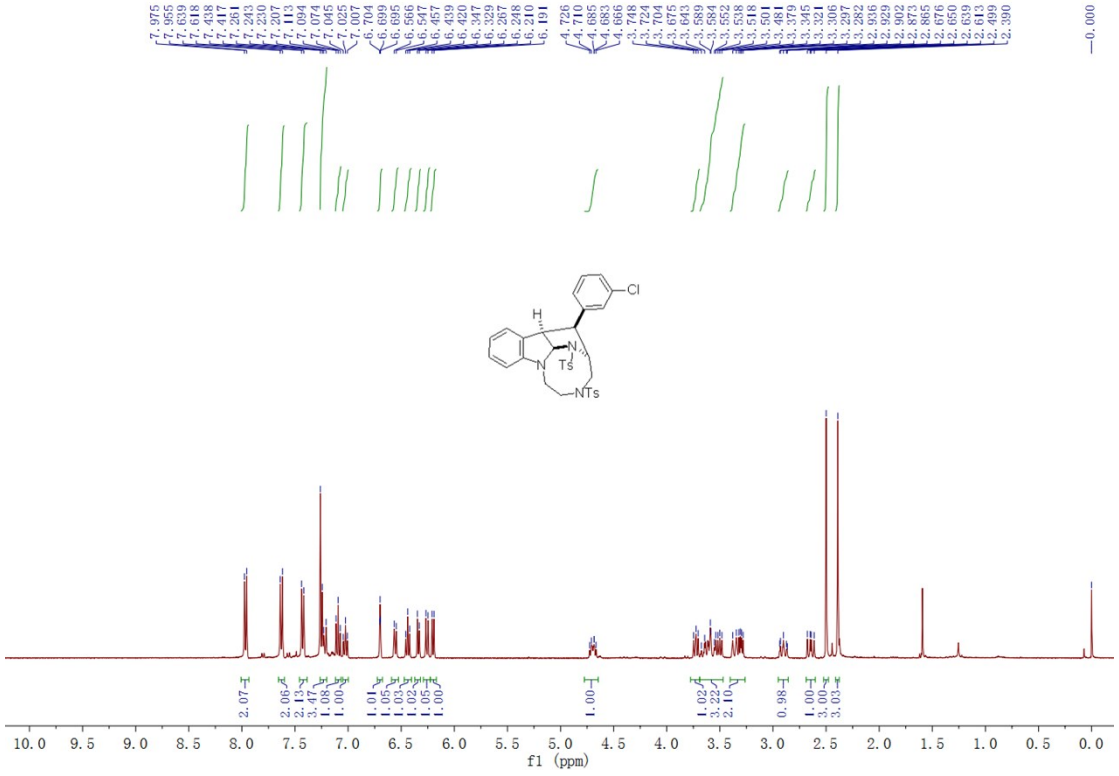


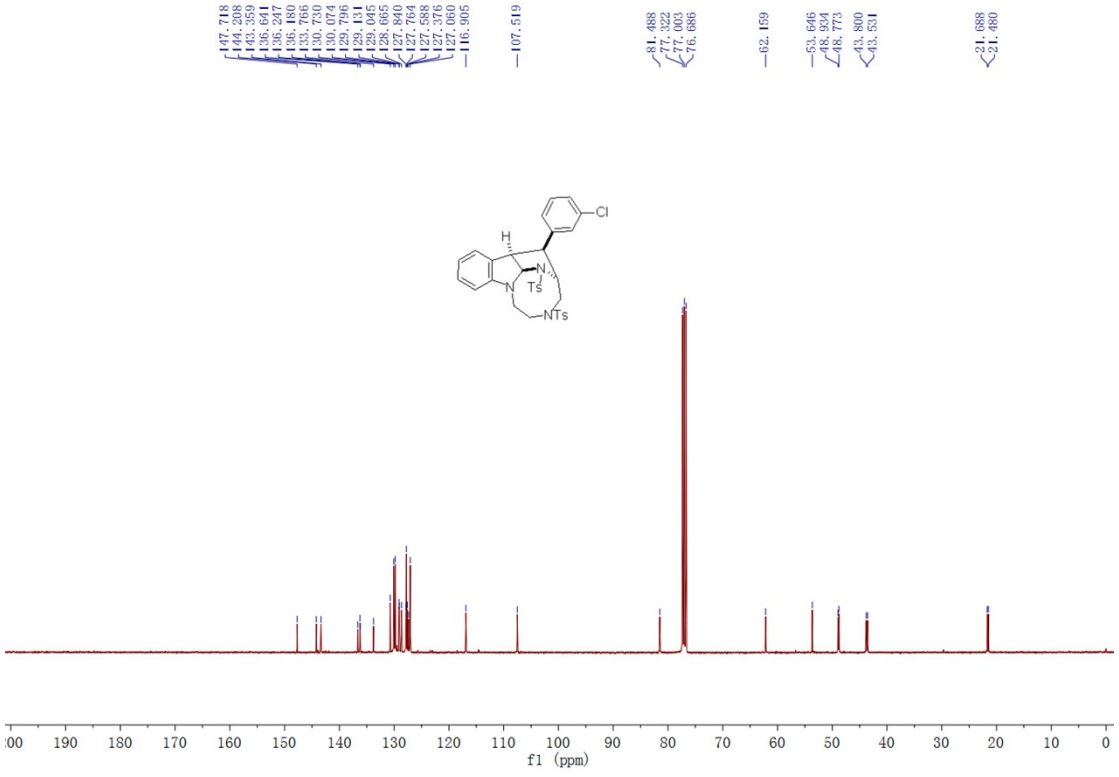


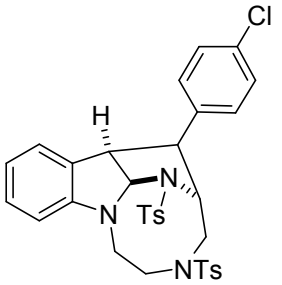
Compound 2o:

0.15 mmol scale, a light yellow solid, 56% yield (53.5g). M.p.: 230-233 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.50 (s, 3H), 2.64 (dd, *J* = 10.4 Hz, 14.8 Hz, 1H), 2.86-2.94 (m, 1H), 3.30 (dd, *J* = 6.0 Hz, 9.6 Hz, 1H), 3.34-3.38 (m, 1H), 3.48-3.68 (m, 3H), 3.70-3.75 (m, 1H), 4.66-4.73 (m, 1H), 6.20 (d, *J* = 7.6 Hz, 1H), 6.25 (d, *J* = 7.6 Hz, 1H), 6.34 (d, *J* = 7.2 Hz, 1H), 6.44 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.70 (dd, *J* = 1.6 Hz, 1.6 Hz, 1H), 7.01-7.05 (m, 1H), 7.09 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.20-7.27 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.7, 43.5, 43.8, 48.8, 48.9, 53.6, 62.2, 81.5, 107.5, 116.9, 127.1, 127.4, 127.6, 127.76, 127.84, 128.7, 129.0, 129.1, 129.8, 130.1, 130.7, 133.8, 136.18, 136.25, 136.6, 143.4, 144.2, 147.7. IR (neat) 3065, 3031, 2984, 2951, 2920, 2894, 2853, 1596, 1485, 1372, 1343, 1305, 1289, 1264, 1244, 1219, 1185, 1155, 1091, 1065, 1036, 1015, 973, 957, 887, 839, 814, 779, 734, 712, 673, 657 cm^{-1}.

HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}(M+H)^+$ requires: 634.1596, found: 634.1617.

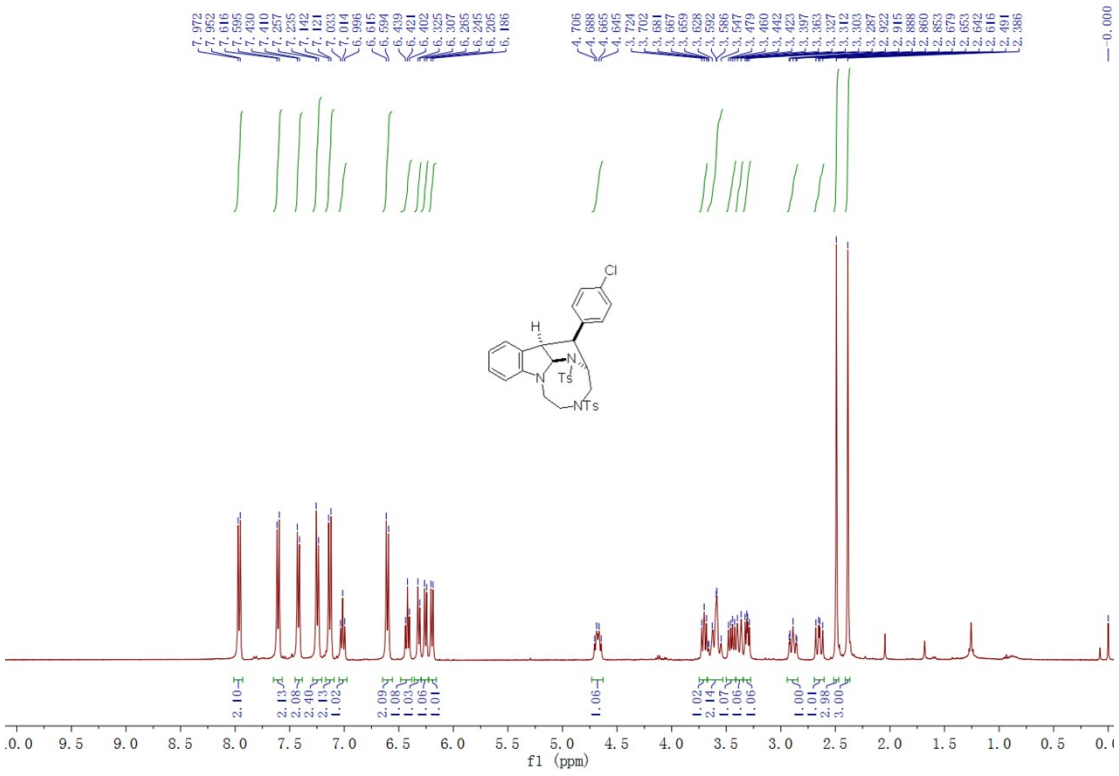






Compound 2p:

0.15 mmol scale, a light yellow solid, 74% yield (70.5 mg). M.p.: 140-143 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.49 (s, 3H), 2.65 (dd, *J* = 10.4 Hz, 14.8 Hz, 1H), 2.85-2.93 (m, 1H), 3.31 (dd, *J* = 6.4 Hz, 10.0 Hz, 1H), 3.36-3.40 (m, 1H), 3.45 (dd, *J* = 7.6 Hz, 14.8 Hz, 1H), 3.54-3.67 (m, 2H), 3.68-3.73 (m, 1H), 4.64-4.71 (m, 1H), 6.20 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 6.32 (d, *J* = 7.2 Hz, 1H), 6.42 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 7.01 (dd, *J* = 7.2 Hz, 7.2 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 21.7, 43.5, 43.9, 48.7, 49.0, 53.4, 62.2, 81.5, 107.4, 116.8, 127.0, 127.5, 127.7, 127.8, 128.1, 128.9, 129.8, 130.0, 131.9, 132.6, 133.4, 136.1, 136.7, 143.3, 144.1, 147.7. IR (neat) 3049, 3028, 2977, 2951, 2921, 2897, 2853, 1598, 1486, 1464, 1372, 1344, 1305, 1289, 1265, 1245, 1220, 1185, 1156, 1092, 1062, 1040, 1013, 972, 890, 854, 815, 772, 748, 737, 713, 694, 674, 654 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{36}ClN_4O_4S_2^{+1}(M+NH_4)^+$ requires: 651.1861, found: 651.1860.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7.616
7.595
7.490
7.410
7.257
7.235
7.142
7.121
7.033
7.014
6.996
6.615
6.594
6.439
6.421
6.402
6.325
6.307
6.265
6.245
6.205
6.186
4.706
4.688
4.665
4.645
3.724
3.702
3.694
3.687
3.659
3.628
3.592
3.586
3.547
3.479
3.460
3.442
3.423
3.397
3.363
3.327
3.312
3.303
3.287
2.922
2.915
2.888
2.860
2.853
2.679
2.675
2.642
2.616
2.491
2.386
0.000
Cl
H
N
Ts
NTs
2.10
2.13
2.08
2.40
2.13
1.02
2.09
1.08
1.03
1.06
1.01
1.06
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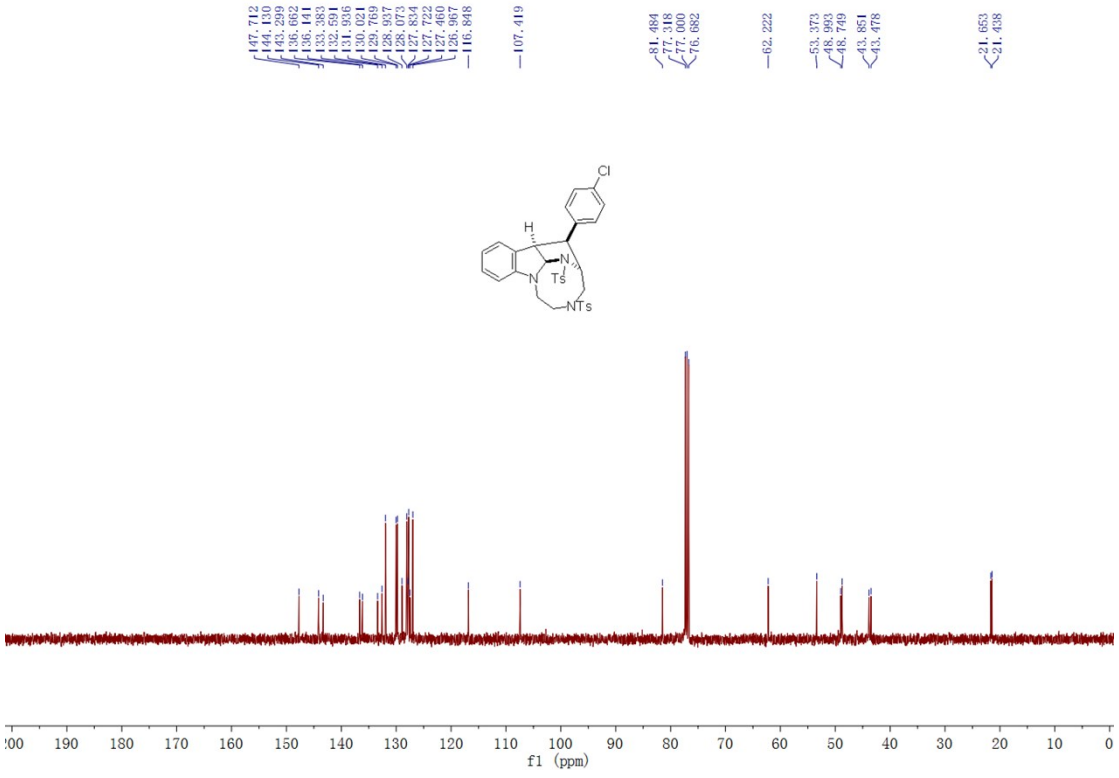
1.00
1.01
2.98
3.00
f1 (ppm)


147.712
144.150
143.299
136.622
135.141
133.383
132.591
131.936
130.021
129.769
128.937
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127.722
127.460
126.967
116.848
107.419
81.484
77.318
77.000
76.682
62.222
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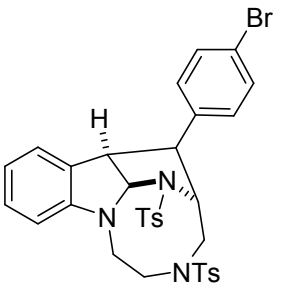
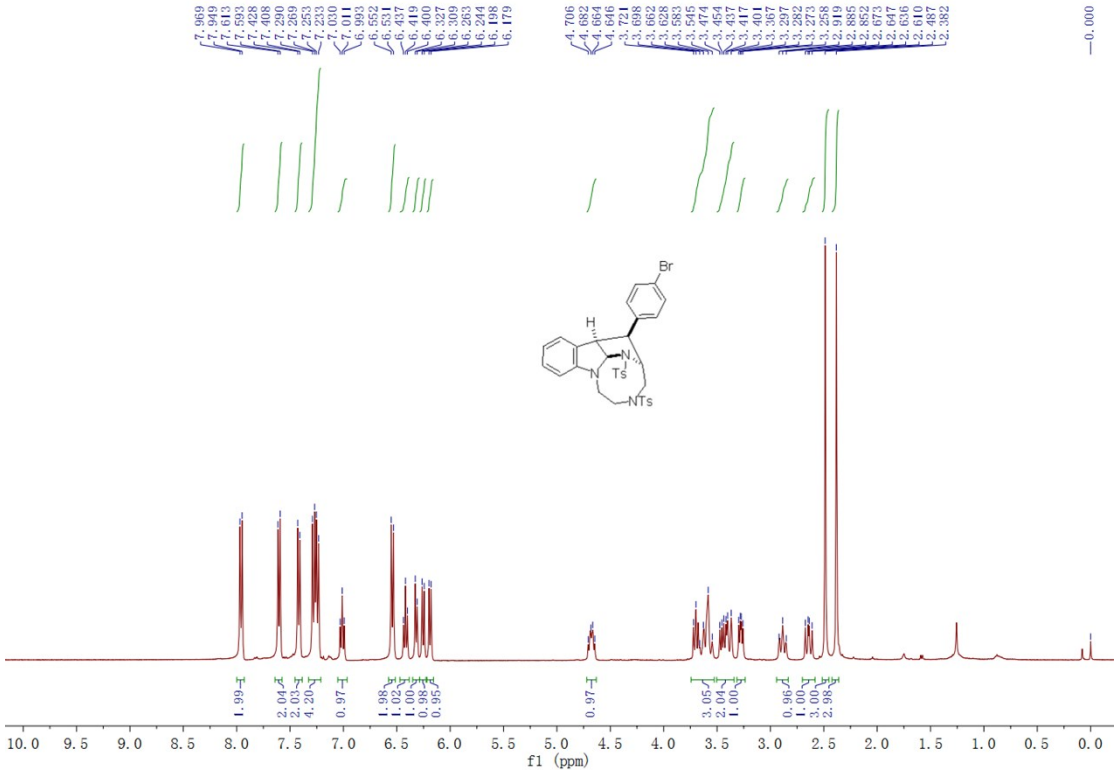
21.438
Cl
H
N
Ts
NTs
f1 (ppm)



Compound 2q:

0.15 mmol scale, a light yellow solid, 75% yield (76.3 mg). M.p.: 145-148 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.49 (s, 3H), 2.64 (dd, *J* = 10.4 Hz, 14.8 Hz, 1H), 2.85-2.92 (m, 1H), 3.28 (dd, *J* = 6.0 Hz, 9.6 Hz, 1H), 3.36-3.48 (m, 2H), 3.54-3.73 (m, 3H), 4.64-4.71 (m, 1H), 6.19 (d, *J* = 7.6 Hz, 1H), 6.25 (d, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 7.2 Hz, 1H), 6.42 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 7.01 (dd, *J* = 7.2 Hz, 7.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 21.6, 43.4, 43.8, 48.7, 49.0, 53.4, 62.1, 81.5, 107.4, 116.8, 121.5, 126.9, 127.4, 127.7, 127.8, 128.9, 129.7, 130.0, 131.0, 132.2, 133.1, 136.1, 136.6, 143.3, 144.1, 147.7. IR (neat) 3054, 3028, 2956, 2921, 2855, 1602, 1486, 1464, 1372, 1345, 1305, 1289, 1245, 1220, 1185, 1157, 1092, 1062, 1040, 1009, 972, 890, 854, 816, 771, 748, 713, 671, 653 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}BrN_3O_4S_2^{+1}(M+H)^+$ requires: 678.1090, found: 678.1100.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7.949
7.613
7.593
7.428
7.408
7.290
7.269
7.253
7.233
7.030
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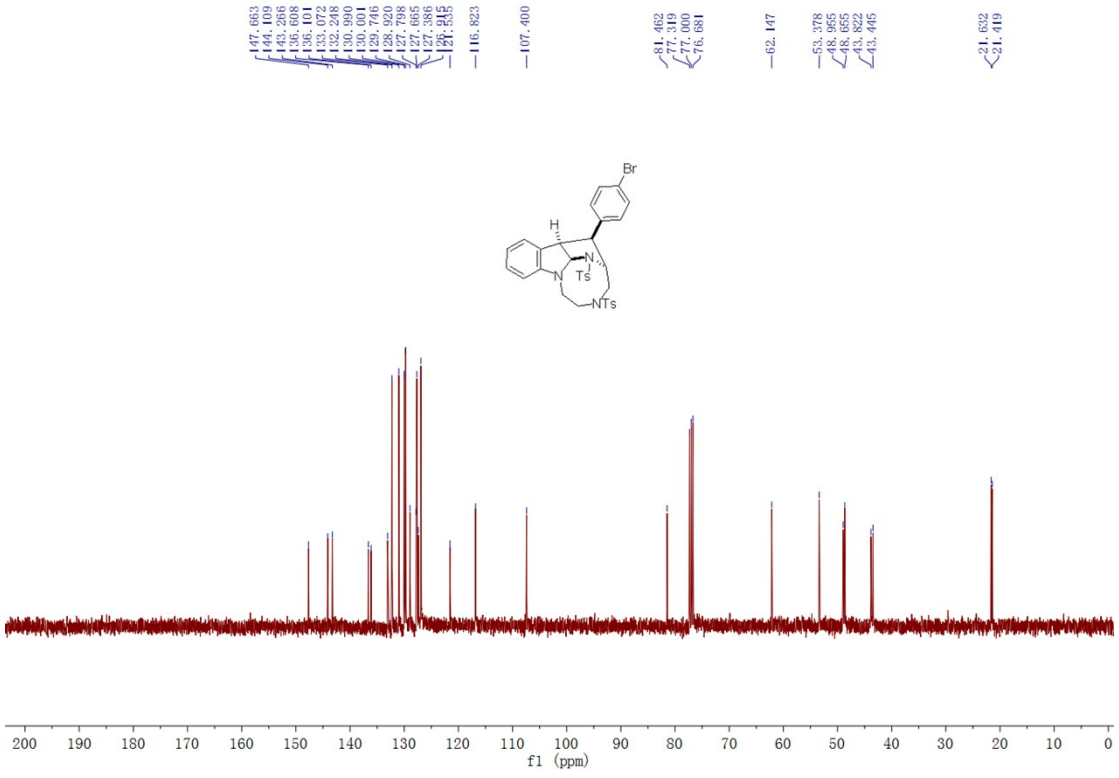
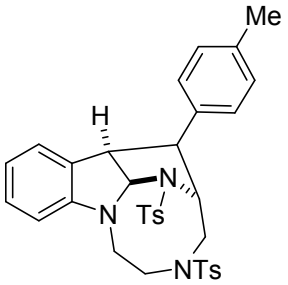
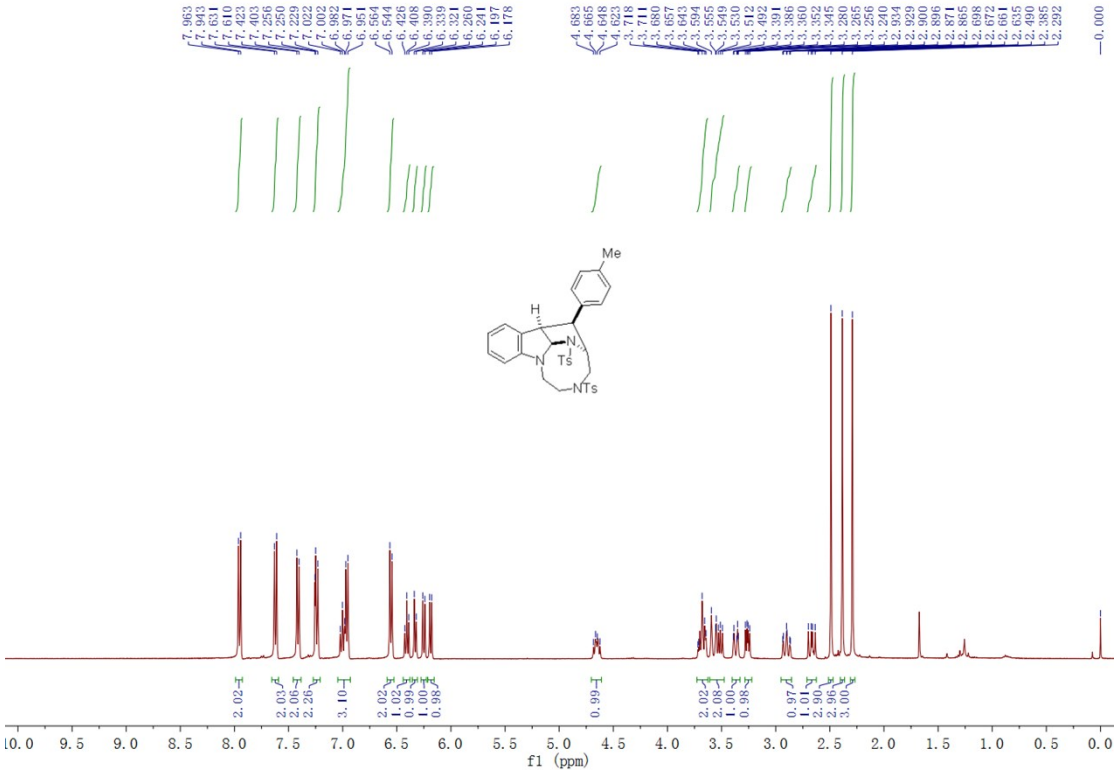
6.993
6.552
6.531
6.437
6.419
6.400
6.327
6.309
6.263
6.244
6.198
6.179
4.706
4.682
4.664
4.646
3.721
3.698
3.662
3.628
3.583
3.545
3.474
3.454
3.437
3.417
3.401
3.367
3.297
3.282
3.273
3.258
2.919
2.885
2.852
2.673
2.647
2.636
2.610
2.487
2.382
0.000
Br
H
N
Ts
N
NTs
1.99
2.04
2.03
4.20
0.97
1.98
1.02
1.00
0.98
0.95
0.97
3.05
2.04
1.00
0.96
1.00
3.00
2.98
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)

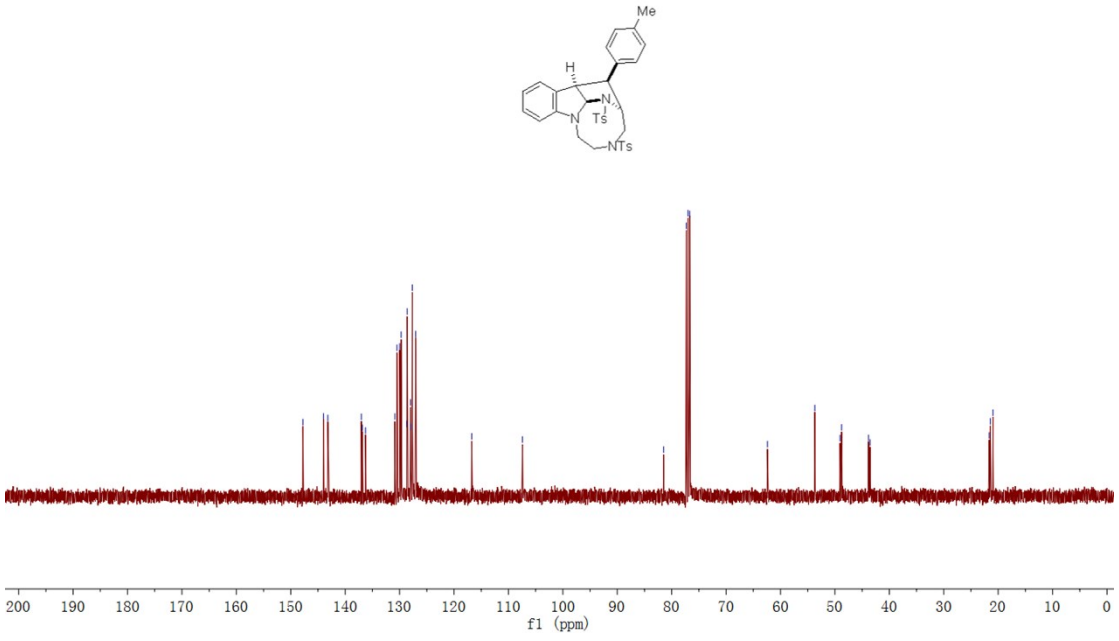

147.663
144.109
143.266
136.608
136.171
135.072
133.278
132.990
130.001
129.746
128.920
127.798
127.665
127.386
121.535
116.823
107.400
81.462
77.319
77.000
76.681
62.147
53.378
48.955
48.655
43.822
43.445
21.632
21.419
Br
H
N
Ts
N
NTs
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

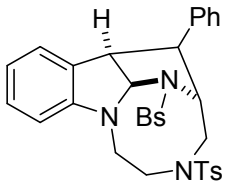


Compound 2r:

0.15 mmol scale, a light yellow solid, 47% yield (43.3 mg). M.p.: 134-136 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.29 (s, 3H), 2.39 (s, 3H), 2.49 (s, 3H), 2.67 (dd, *J* = 10.4 Hz, 14.8 Hz, 1H), 2.86-2.94 (m, 1H), 3.26 (dd, *J* = 6.4 Hz, 10.0 Hz, 1H), 3.34-3.40 (m, 1H), 3.49-3.60 (m, 2H), 3.64-3.72 (m, 2H), 4.62-4.68 (m, 1H), 6.19 (d, *J* = 7.6 Hz, 1H), 6.25 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 7.2 Hz, 1H), 6.41 (dd, *J* = 7.2 Hz, 7.2 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 6.95-7.03 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.0, 21.4, 21.6, 43.5, 43.8, 48.8, 49.1, 53.7, 62.4, 81.5, 107.4, 116.7, 127.0, 127.7, 127.96, 127.98, 128.6, 128.7, 129.7, 130.0, 130.5, 130.9, 136.3, 136.9, 137.0, 143.2, 144.0, 147.8. IR (neat) 3054, 3028, 2984, 2951, 2920, 2891, 2858, 1599, 1514, 1485, 1464, 1371, 1344, 1305, 1289, 1265, 1244, 1218, 1185, 1156, 1119, 1091, 1063, 1039, 1020, 971, 924, 890, 854, 841, 814, 772, 711, 676, 656 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{39}N_4O_4S_2^{+1}(M+NH_4)^+$ requires: 631.2407, found: 631.2406.

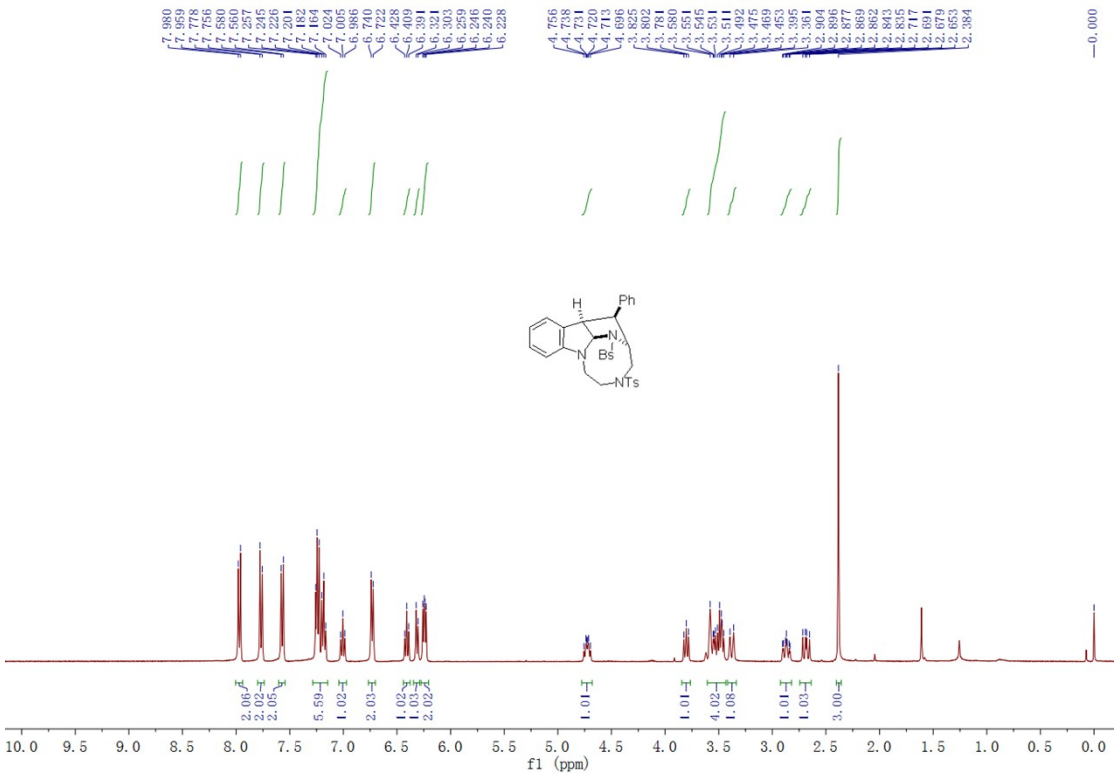

Me
H
N
Ts
NTs
f1 (ppm)

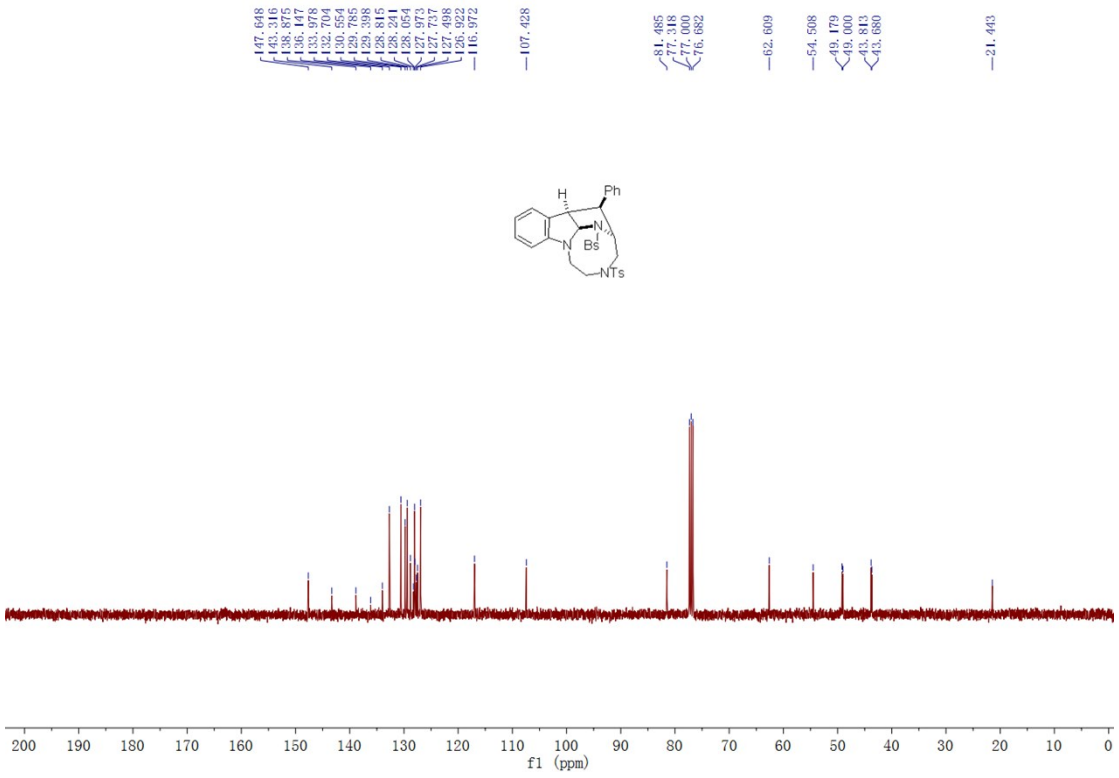

Me
H
N
Ts
NTs
f1 (ppm)


H
Ph
N
N
Bs
NTs

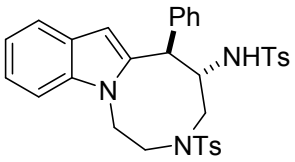
Compound 2s:

0.15 mmol scale, a light yellow solid, 68% yield (67.7 mg). M.p.: 308-310 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.69 (dd, *J* = 10.4 Hz, 15.2 Hz, 1H), 2.83-2.91 (m, 1H), 3.36-3.40 (m, 1H), 3.45-3.58 (m, 4H), 3.78-3.83 (m, 1H), 4.69-4.76 (m, 1H), 6.24 (d, *J* = 7.2 Hz, 1H), 6.25 (d, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 7.2 Hz, 1H), 6.41 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.73 (d, *J* = 7.2 Hz, 2H), 7.01 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.16-7.26 (m, 5H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 43.7, 43.8, 49.0, 49.2, 54.5, 62.6, 81.5, 107.4, 117.0, 126.9, 127.5, 127.7, 128.0, 128.1, 128.2, 128.8, 129.4, 129.8, 130.6, 132.7, 134.0, 136.1, 138.9, 143.3, 147.7. IR (neat) 3088, 3057, 3026, 2953, 2922, 2855, 1064, 1574, 1486, 1466, 1453, 1345, 1306, 1289, 1245, 1220, 1157, 1091, 1067, 1040, 1008, 971, 890, 853, 839, 816, 780, 743, 713, 702, 670 cm^{-1}. HRMS (APCI) Calcd. for $C_{32}H_{31}BrN_3O_4S_2^{+1}$(M+H)$^+$ requires: 664.0934, found: 664.0930.



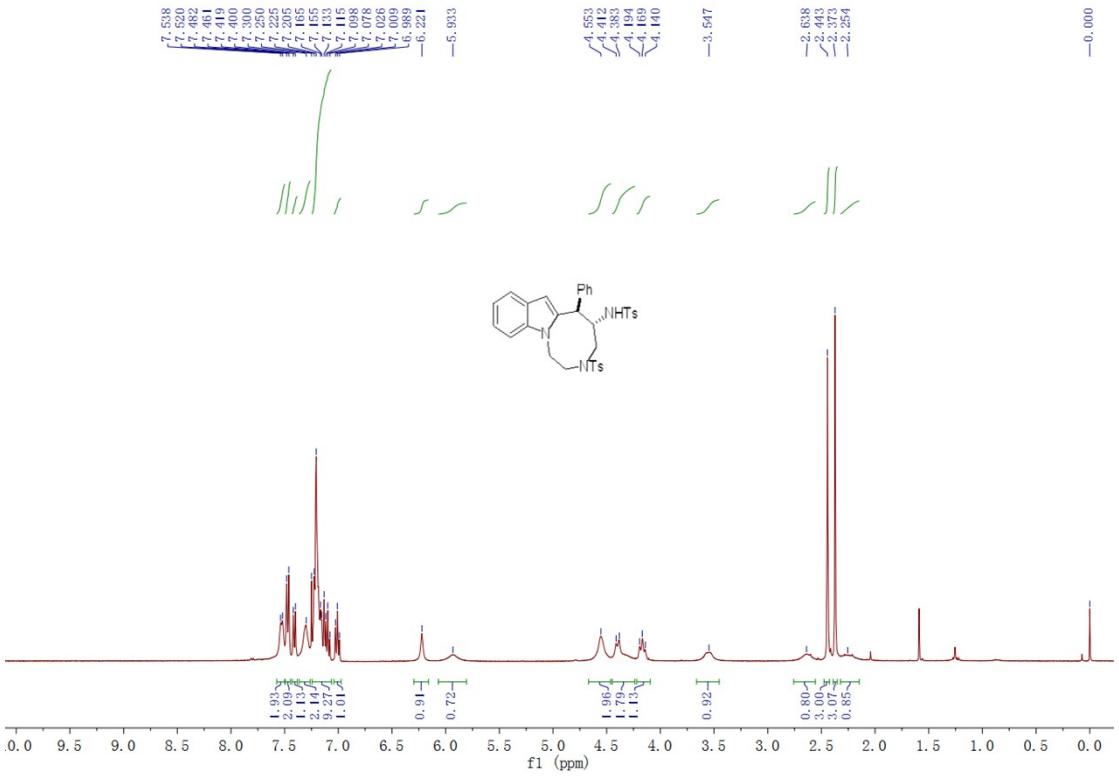


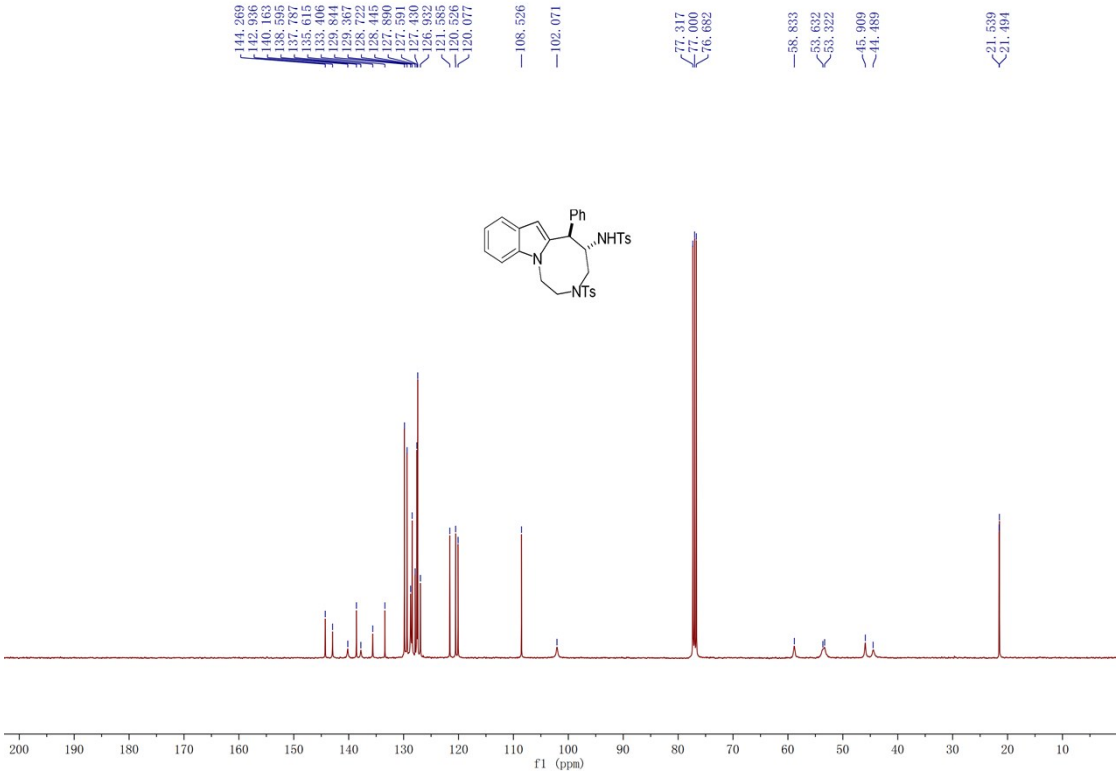
9. Characterization and spectra charts for 3.

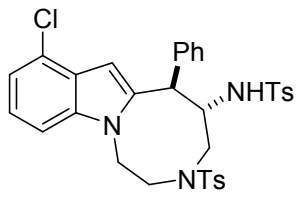


Compound 3a:

0.15 mmol scale, a light yellow solid, 19% yield (17.0 mg). M.p.: 153-156 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.25 (br, 1H), 2.38 (s, 3H), 2.44 (s, 3H), 2.64 (br, 1H), 3.55 (br, 1H), 4.14-4.20 (m, 1H), 4.38-4.42 (m, 2H), 4.55 (br, 2H), 5.93 (br, 1H), 6.22 (s, 1H), 6.98-7.03 (m, 1H), 7.07-7.23 (m, 9H), 7.30 (br, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.49, 21.54, 44.4 (br), 45.9 (br), 53.3 (br), 53.6 (br), 58.8 (br), 102.1 (br), 108.5, 120.1, 120.5, 121.6, 126.9, 127.4, 127.6, 127.9, 128.4, 128.7 (br), 129.4, 129.8, 133.4, 135.6, 137.8 (br), 138.6, 140.2 (br), 142.9, 144.3. IR (neat) 3290, 3058, 3031, 2982, 2953, 2920, 2858, 1597, 1533, 1494, 1459, 1445, 1413, 1364, 1332, 1289, 1265, 1184, 1156, 1117, 1088, 1063, 1025, 987, 969, 914, 875, 811, 775, 749, 732, 719, 701, 661 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{34}N_3O_4S_2^{+1}(M+H)^+$ requires: 600.1985, found: 600.1985.

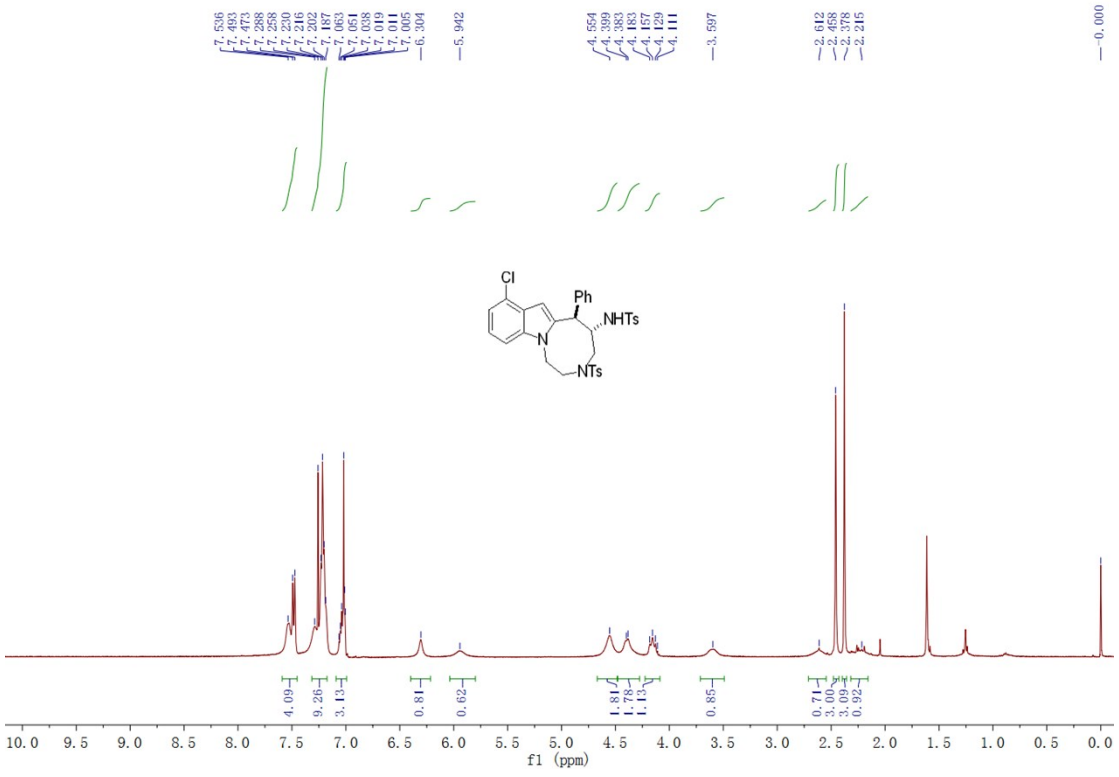

Ph
NHTs
NTs
f1 (ppm)

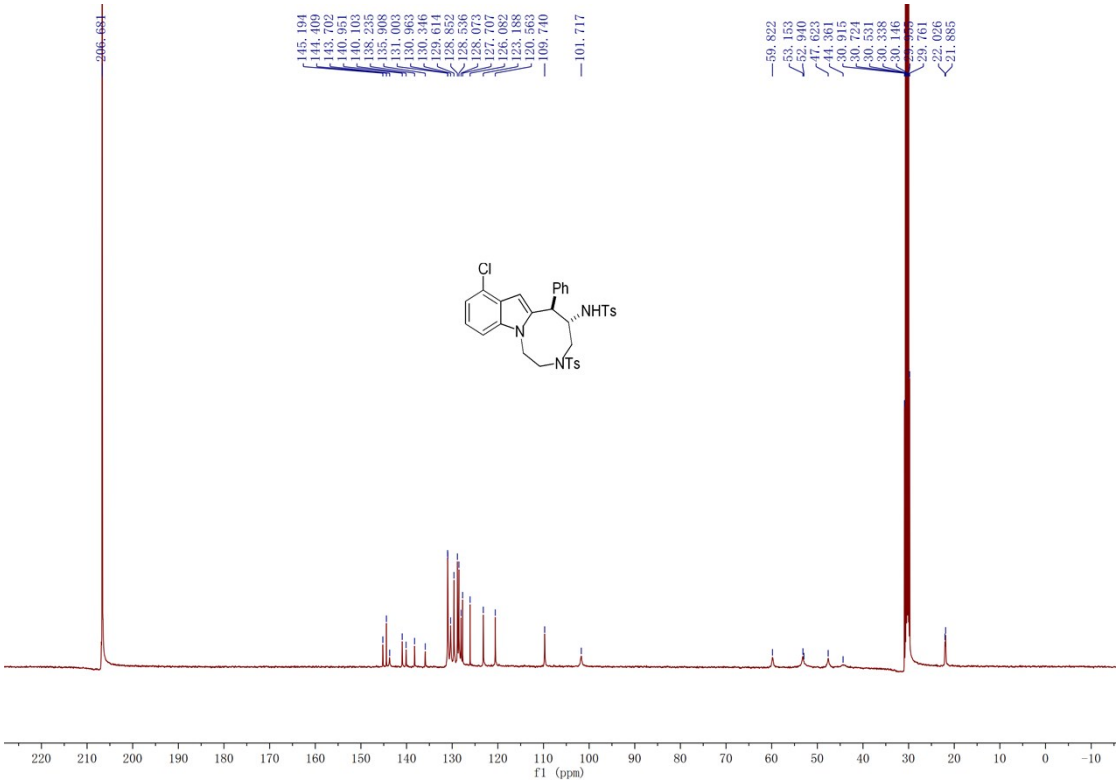

Ph
NHTs
NTs
f1 (ppm)

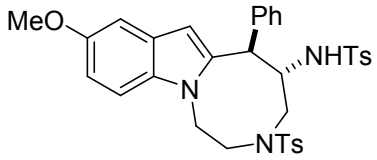

Cl
Ph
NHTs
N
NTs

Compound 3b:

0.15 mmol scale, a white solid, 29% yield (28.4 mg). M.p.: 158-160 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.22 (br, 1H), 2.38 (s, 3H), 2.46 (s, 3H), 2.61 (br, 1H), 3.60 (br, 1H), 4.11-4.19 (m, 1H), 4.38-4.40 (m, 2H), 4.55 (br, 2H), 5.94 (br, 1H), 6.30 (s, 1H), 7.00-7.07 (m, 3H), 7.18-7.29 (m, 9H), 7.47-7.54 (m, 4H). ^{13}C NMR (d^6-Acetone, TMS, 100 MHz) δ 21.9, 22.0, 44.4 (br), 47.6 (br), 53.0 (br), 53.2 (br), 59.8 (br), 101.7 (br), 109.7, 120.6, 123.2, 126.1, 127.7, 128.1, 128.5, 128.9, 129.6, 130.3, 130.96, 131.00, 135.9, 138.2, 140.1, 141.0, 143.7 (br), 144.4, 145.2. IR (neat) 3297, 3067, 3031, 2956, 2923, 2848, 1597, 1528, 1494, 1478, 1438, 1335, 1305, 1264, 1156, 1115, 1088, 1066, 1026, 969, 931, 875, 811, 765, 720, 701, 665 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+H)$^+$ requires: 634.1596, found: 634.1612.

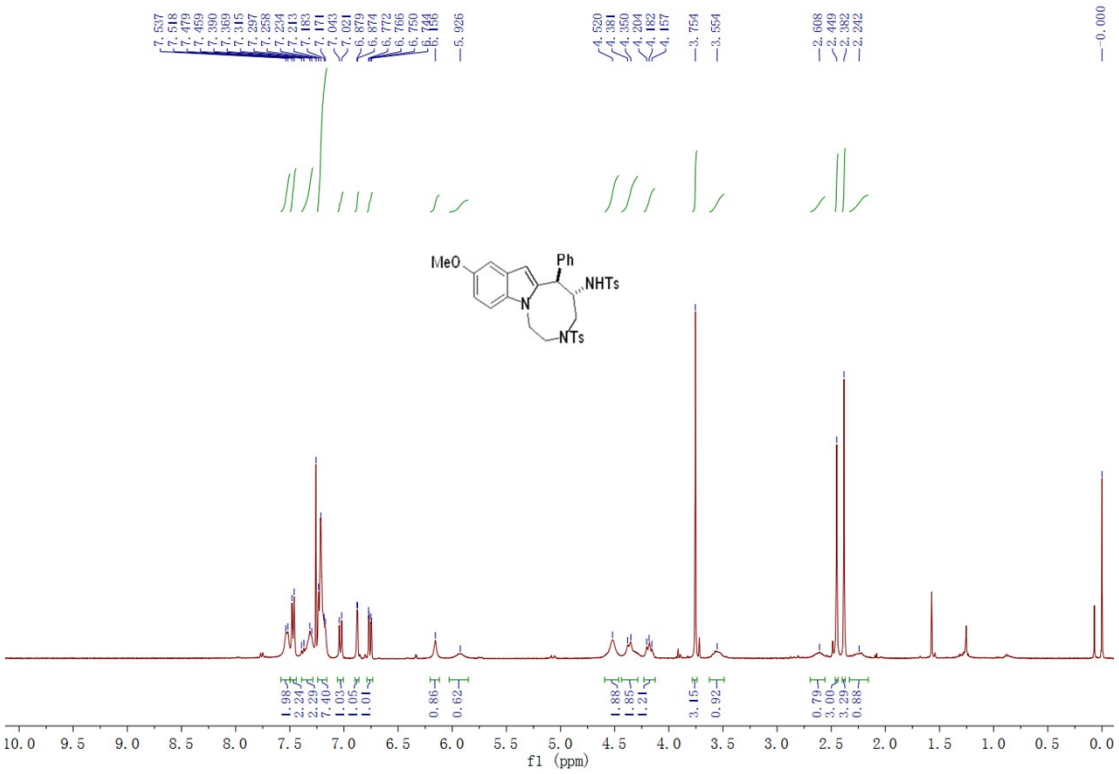


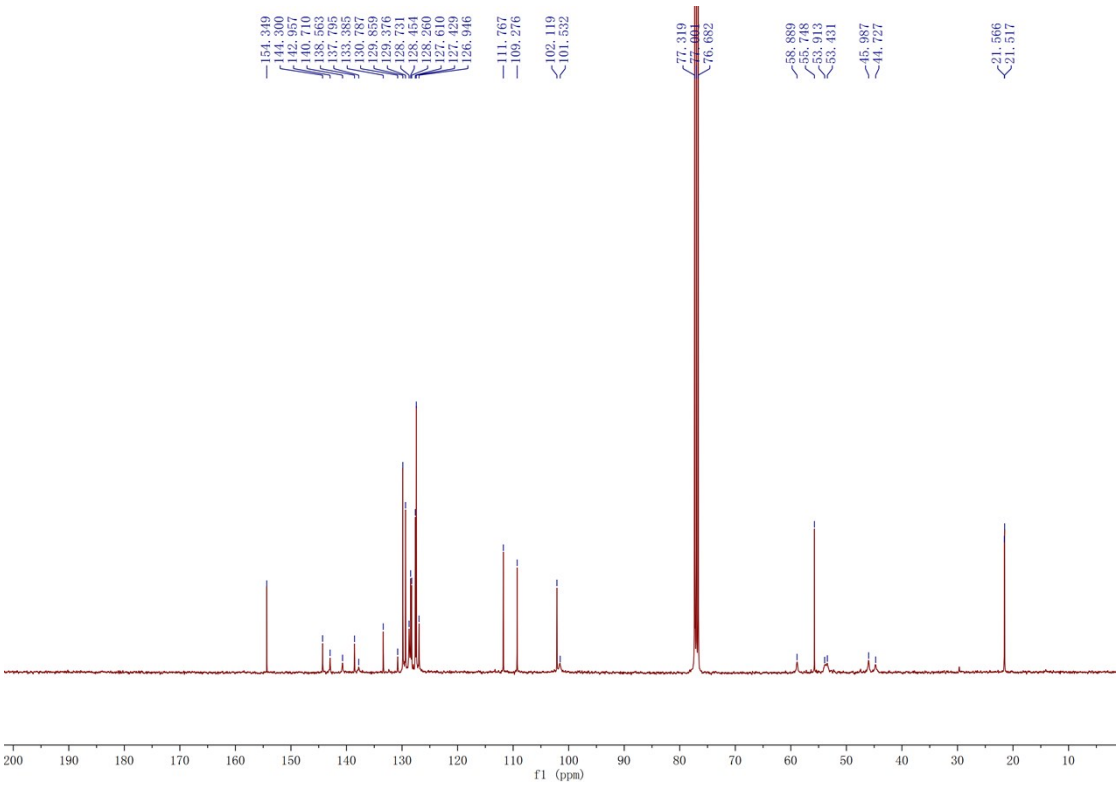


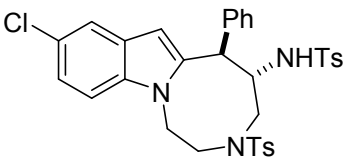


Compound 3c:

0.15 mmol scale, a light red solid, 10% yield (9.4 mg). M.p.: 159-162 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.24 (br, 1H), 2.38 (s, 3H), 2.45 (s, 3H), 2.61 (br, 1H), 3.55 (br, 1H), 3.75 (s, 3H), 4.15-4.21 (m, 1H), 4.35-4.39 (m, 2H), 4.52 (br, 2H), 5.93 (br, 1H), 6.16 (s, 1H), 6.76 (dd, *J* = 2.4 Hz, 8.8 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.17-7.24 (m, 7H), 7.29-7.39 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.51-7.54 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 44.7 (br), 46.0 (br), 53.4 (br), 53.9 (br), 55.7, 58.9 (br), 101.5 (br), 102.1, 109.3, 111.8, 126.9, 127.4, 127.6, 128.3, 128.5, 128.7, 129.4, 129.9, 130.8, 133.4, 137.8 (br), 138.6, 140.7 (br), 143.0, 144.3, 154.3. IR (neat) 3291, 3062, 3031, 2956, 2923, 2853, 2827, 1618, 1597, 1478, 1450, 1364, 1334, 1293, 1265, 1212, 1156, 1120, 1088, 1063, 1028, 987, 969, 889, 870, 839, 812, 784, 732, 719, 701, 656 cm^{-1}. HRMS (APCI) Calcd. for $C_{34}H_{36}N_3O_5S_2^{+1}$(M+H)$^{+}$ requires: 630.2091, found: 630.2072.

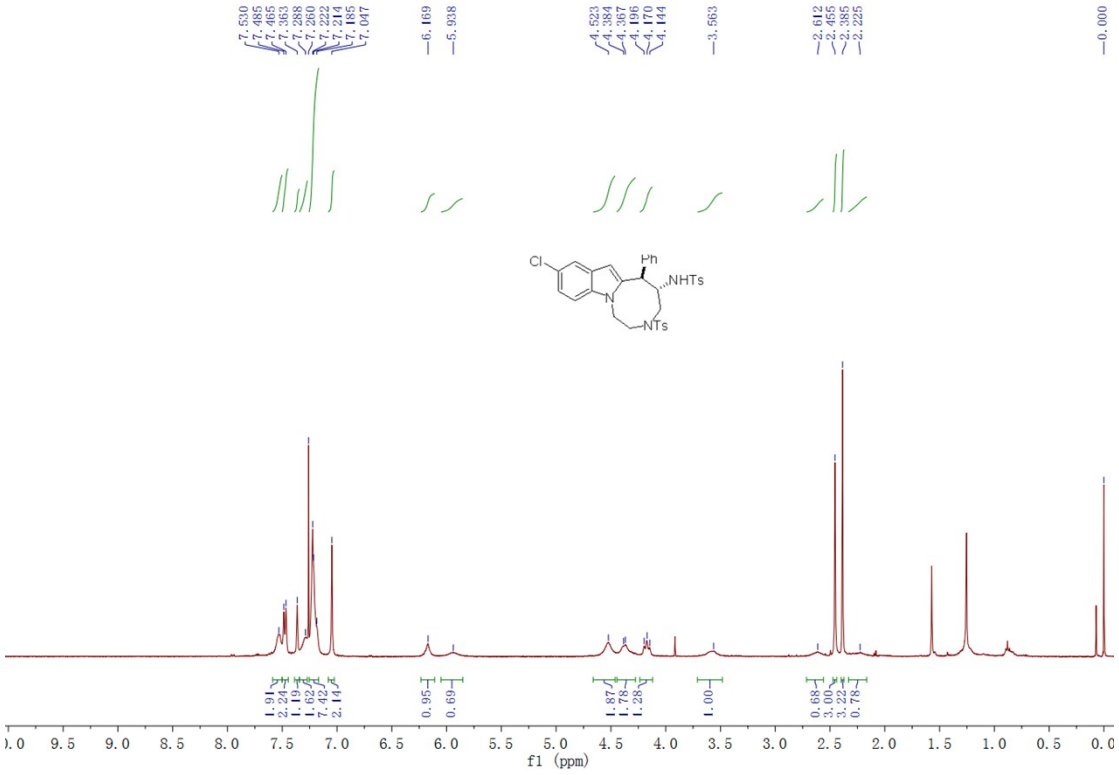


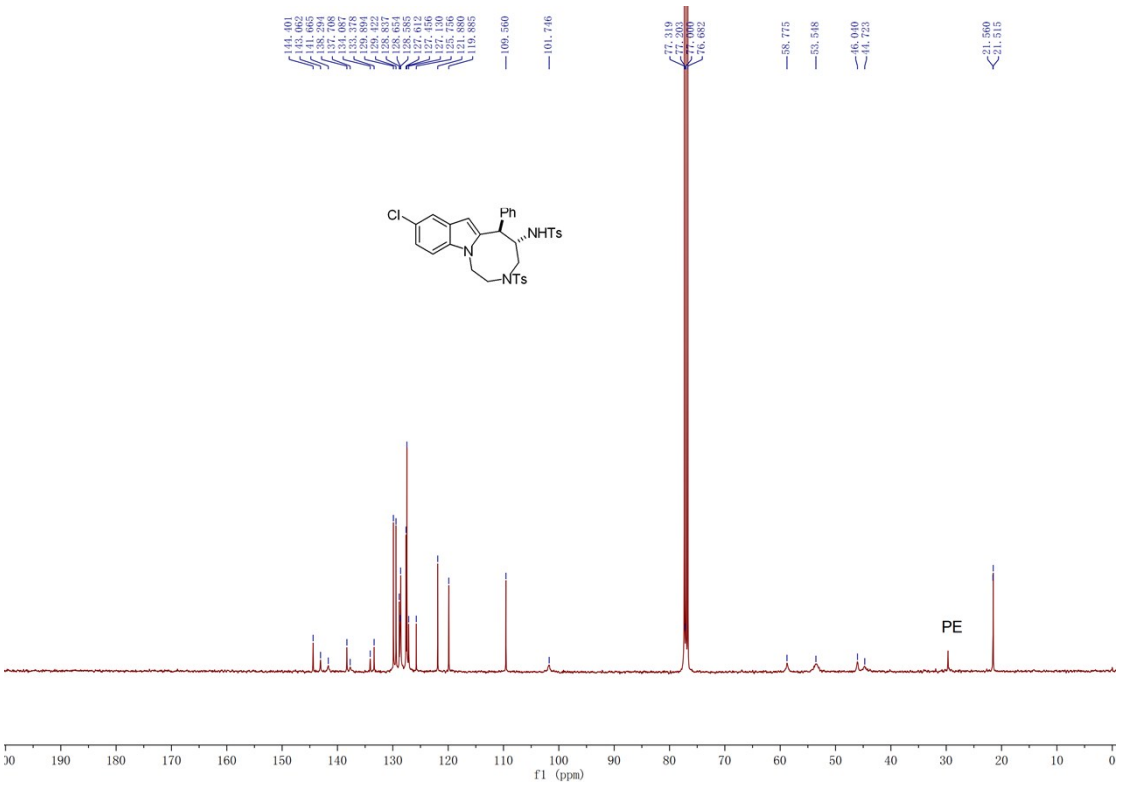


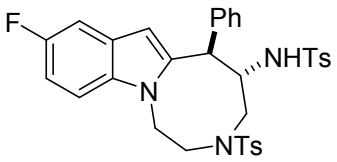


Compound 3d:

0.15 mmol scale, a white solid, 16% yield (15.2 mg). M.p.: 161-164 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.23 (br, 1H), 2.39 (s, 3H), 2.46 (s, 3H), 2.61 (br, 1H), 3.56 (br, 1H), 4.14-4.20 (m, 1H), 4.36-4.39 (m, 2H), 4.52 (br, 2H), 5.94 (br, 1H), 6.17 (s, 1H), 7.05 (s, 2H), 7.18-7.23 (m, 7H), 7.29 (br, 2H), 7.36 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.53 (br, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 44.7 (br), 46.0 (br), 53.5 (br), 58.8 (br), 101.7 (br), 109.6, 119.9, 121.9, 125.8, 127.1, 127.5, 127.6, 128.6, 128.7, 128.8, 129.4, 129.9, 133.4, 134.1, 137.7 (br), 138.3, 141.7 (br), 143.1, 144.4. IR (neat) 3287, 3065, 3028, 2953, 2923, 2853, 1597, 1494, 1452, 1412, 1334, 1305, 1290, 1184, 1157, 1112, 1089, 1068, 1026, 969, 919, 888, 868, 812, 777, 739, 719, 701, 665 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$ $(M+H)^+$ requires: 634.1596, found: 634.1581.

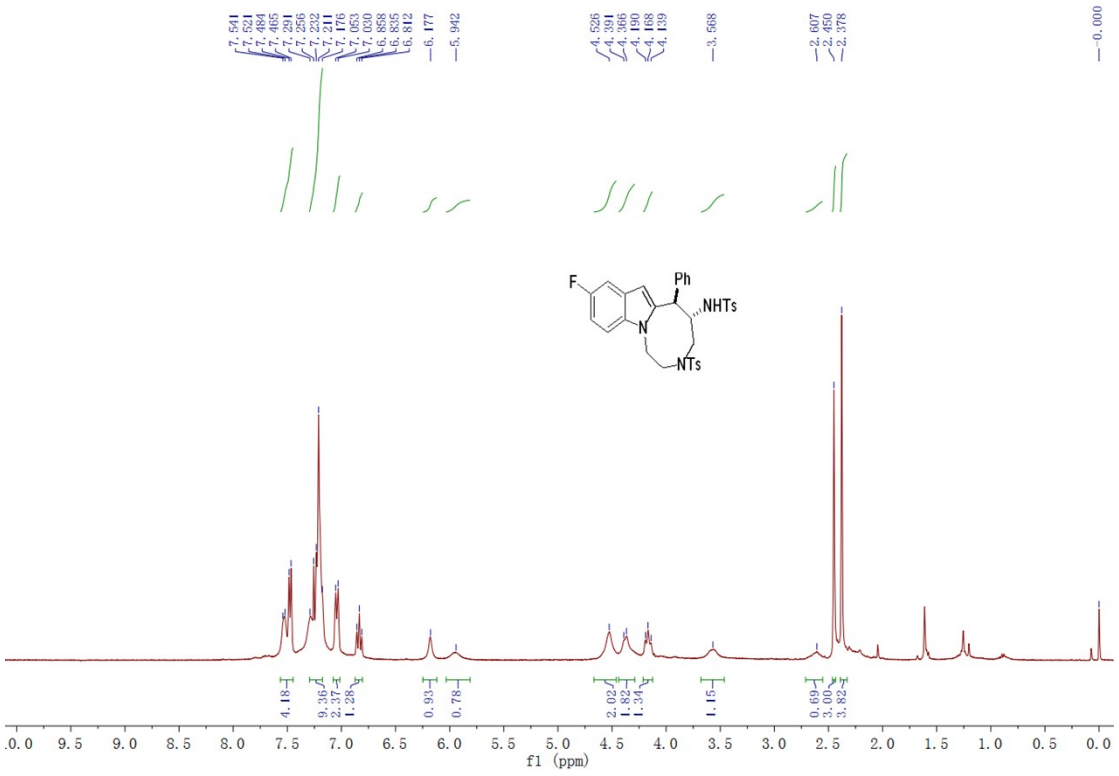


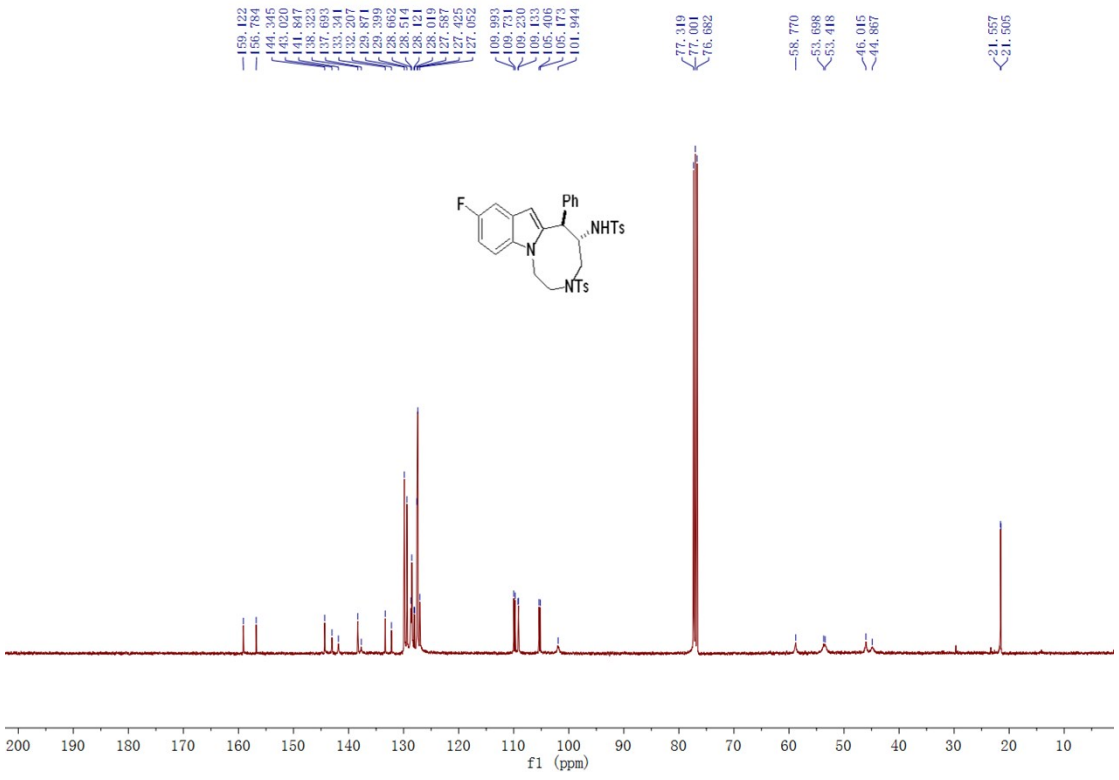


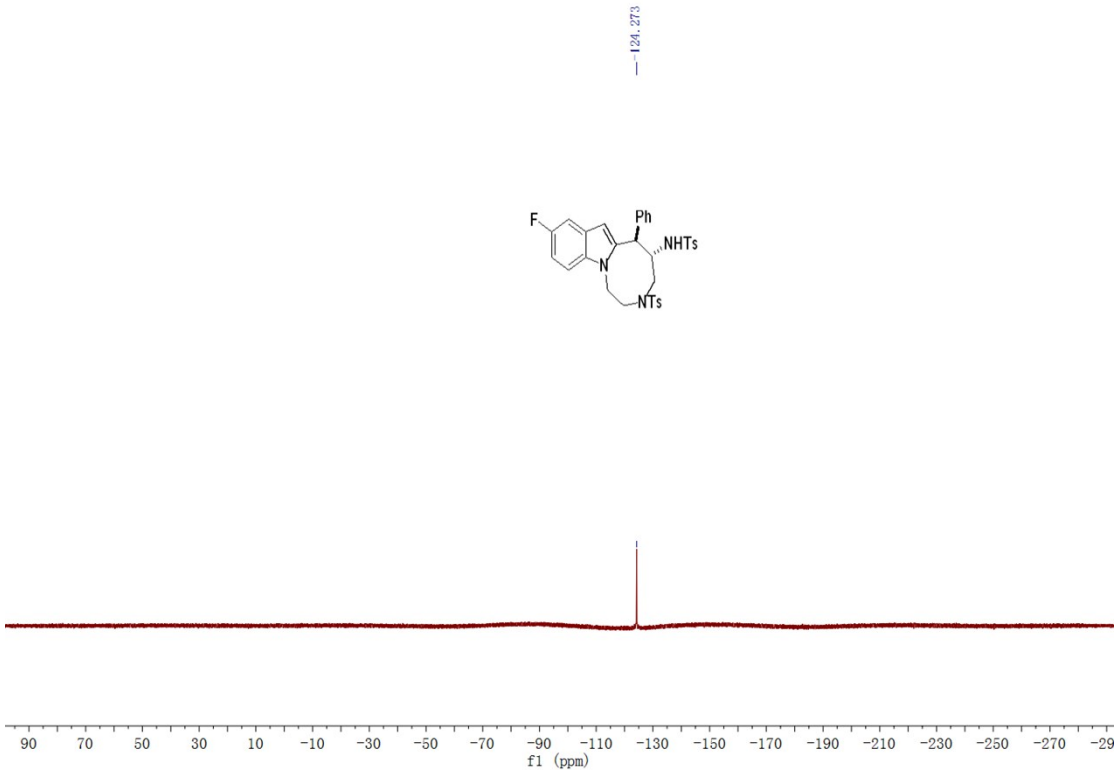


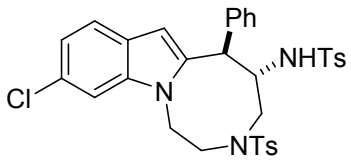
Compound 3e:

0.15 mmol scale, a light yellow solid, 16% yield (14.8 mg). M.p.: 157-160 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.29-2.38 (m, 4H), 2.45 (s, 3H), 2.61 (br, 1H), 3.57 (br, 1H), 4.13-4.19 (m, 1H), 4.36-4.40 (m, 2H), 4.53 (br, 2H), 5.94 (br, 1H), 6.18 (s, 1H), 6.81-6.86 (m, 1H), 7.03-7.06 (m, 2H), 7.17-7.30 (m, 9H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.52-7.55 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 44.9 (br), 46.0 (br), 53.4 (br), 53.7 (br), 58.8 (br), 101.9 (br), 105.3 (d, *J* = 23.3 Hz), 109.2 (d, *J* = 9.7 Hz), 109.9 (d, *J* = 26.2 Hz), 127.1, 127.4, 127.6, 128.1 (d, *J* = 10.2 Hz), 128.5, 128.7 (br), 129.4, 129.9, 132.2, 133.3, 137.7 (br), 138.3, 141.8 (br), 143.0 (br), 144.3, 158.0 (d, *J* = 233.8 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -124.27 (br). IR (neat) 3278, 3062, 3036, 2979, 2953, 2928, 2855, 1730, 1622, 1596, 1477, 1448, 1416, 1366, 1335, 1307, 1290, 1265, 1185, 1157, 1118, 1088, 1061, 1026, 989, 973, 954, 907, 892, 875, 849, 813, 786, 732, 718, 701, 670, 655 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}FN_3O_4S_2^{+1}$(M+H)$^+$ requires: 618.1891, found: 618.1865.


7.541
7.521
7.494
7.485
7.291
7.256
7.232
7.211
7.176
7.053
7.030
6.858
6.835
6.812
6.177
5.942
4.526
4.391
4.366
4.190
4.168
4.139
3.568
2.607
2.450
2.378
0.000
F
Ph
NHTs
N
NTs
4.18
9.36
2.37
1.28
0.93
0.78
2.02
1.82
1.34
1.15
0.69
3.00
3.82
f1 (ppm)

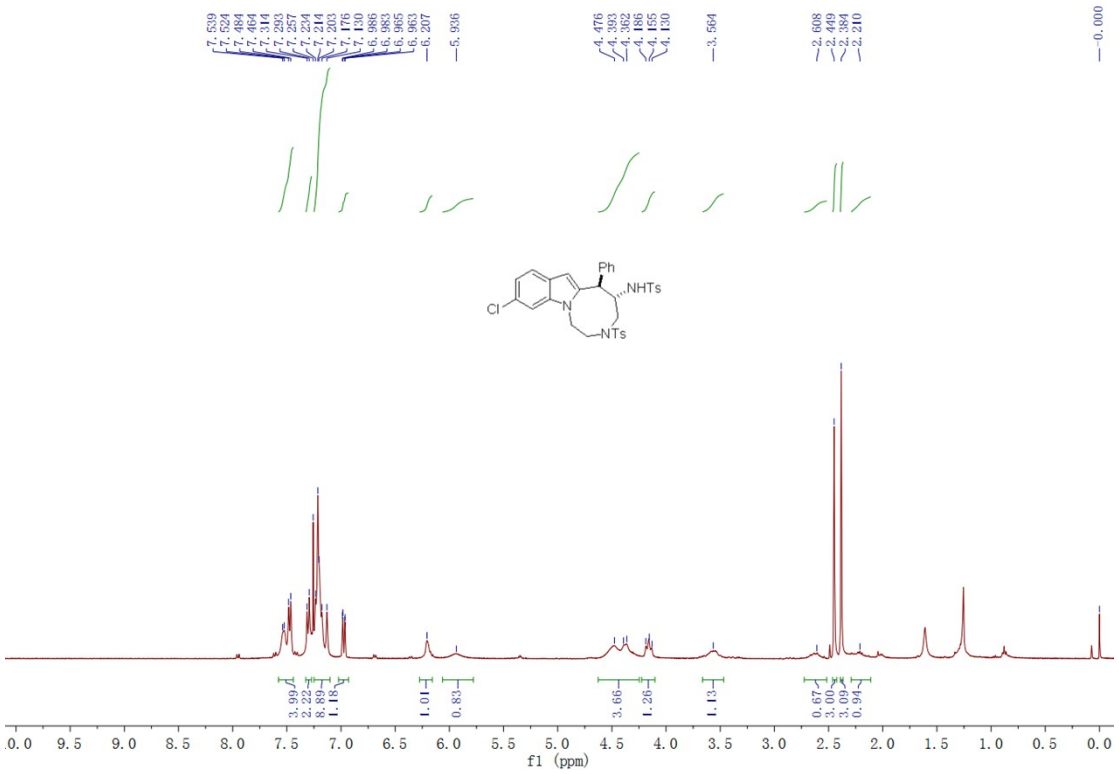

159.122
156.784
144.345
143.020
141.847
138.323
137.693
133.341
132.207
129.871
129.399
128.692
128.514
128.121
128.019
127.587
127.425
127.052
109.993
109.731
109.230
109.133
105.406
105.173
101.944
77.319
77.001
76.682
58.770
53.698
53.418
46.015
44.867
21.557
21.505
F
Ph
NHTs
N
NTs
f1 (ppm)

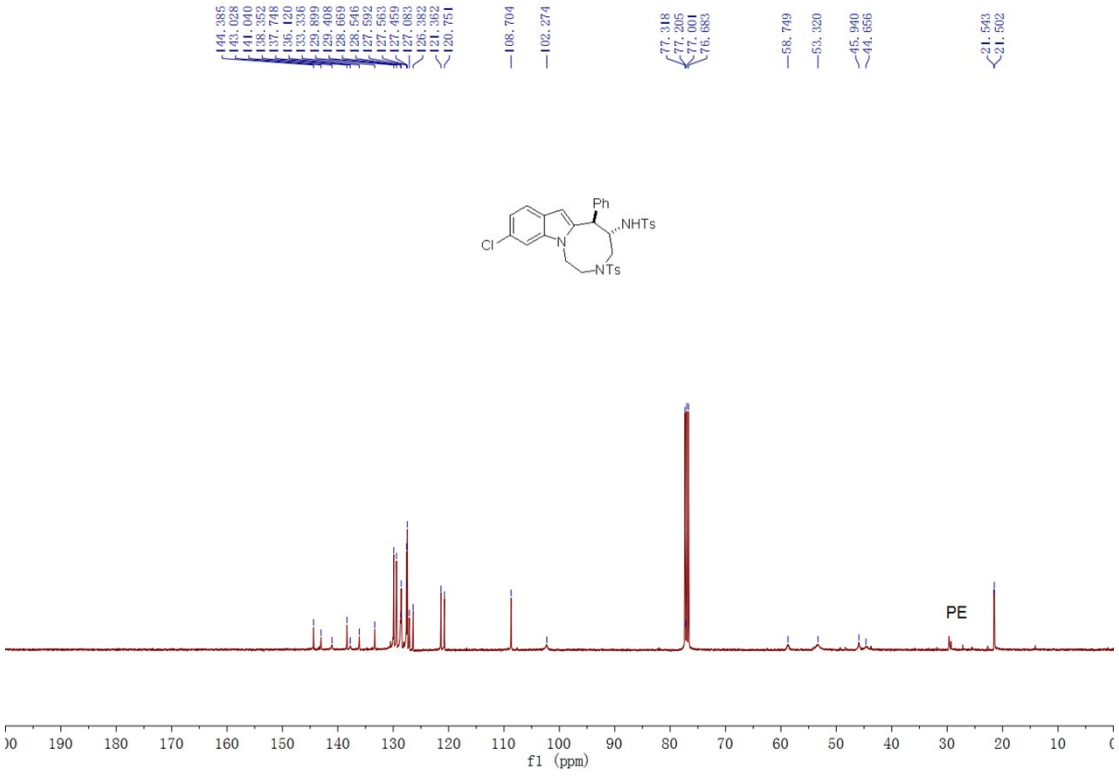


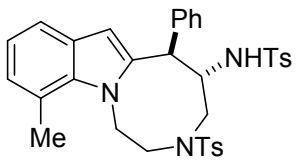


Compound 3g:

0.15 mmol scale, a white solid, 20% yield (19.1 mg). M.p.: 125-127 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.21 (br, 1H), 2.38 (s, 3H), 2.45 (s, 3H), 2.61 (br, 1H), 3.56 (br, 1H), 4.13-4.19 (m, 1H), 4.36-4.48 (m, 4H), 5.94 (br, 1H), 6.21 (s, 1H), 6.97 (dd, *J* = 0.8 Hz, 8.0 Hz, 1H), 7.13-7.24 (m, 9H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.52-7.54 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.50, 21.54, 44.7 (br), 45.9 (br), 53.3 (br), 58.7 (br), 102.3 (br), 108.7, 120.8, 121.4, 126.4, 127.1, 127.5, 127.56, 127.59, 128.5, 128.7, 129.4, 129.9, 133.3, 136.1, 137.7 (br), 138.4, 141.0 (br), 143.0, 144.4. IR (neat) 3297, 3062, 3028, 2951, 2923, 2850, 1597, 1529, 1494, 1465, 1454, 1407, 1333, 1306, 1283, 1265, 1184, 1156, 1115, 1089, 1062, 1025, 992, 969, 923, 899, 811, 791, 736, 719, 702, 663 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{34}ClN_3O_4S_2^{+1}(M+H)^+$ requires: 634.1596, found: 634.1606.

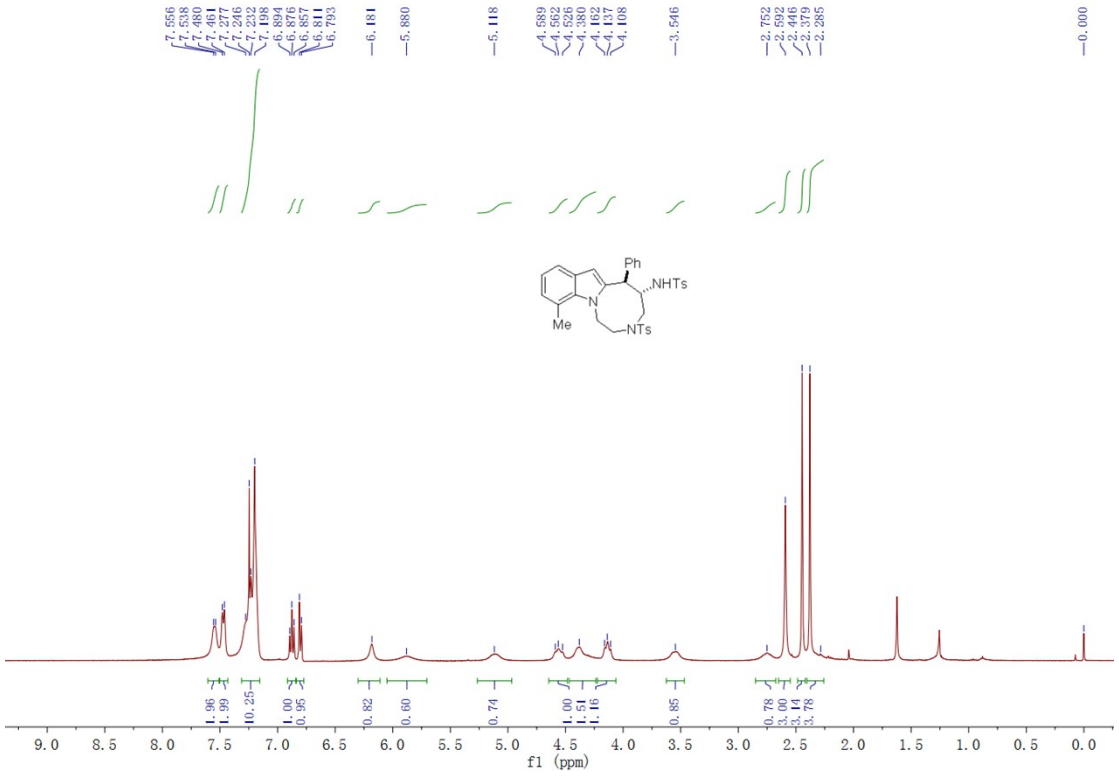


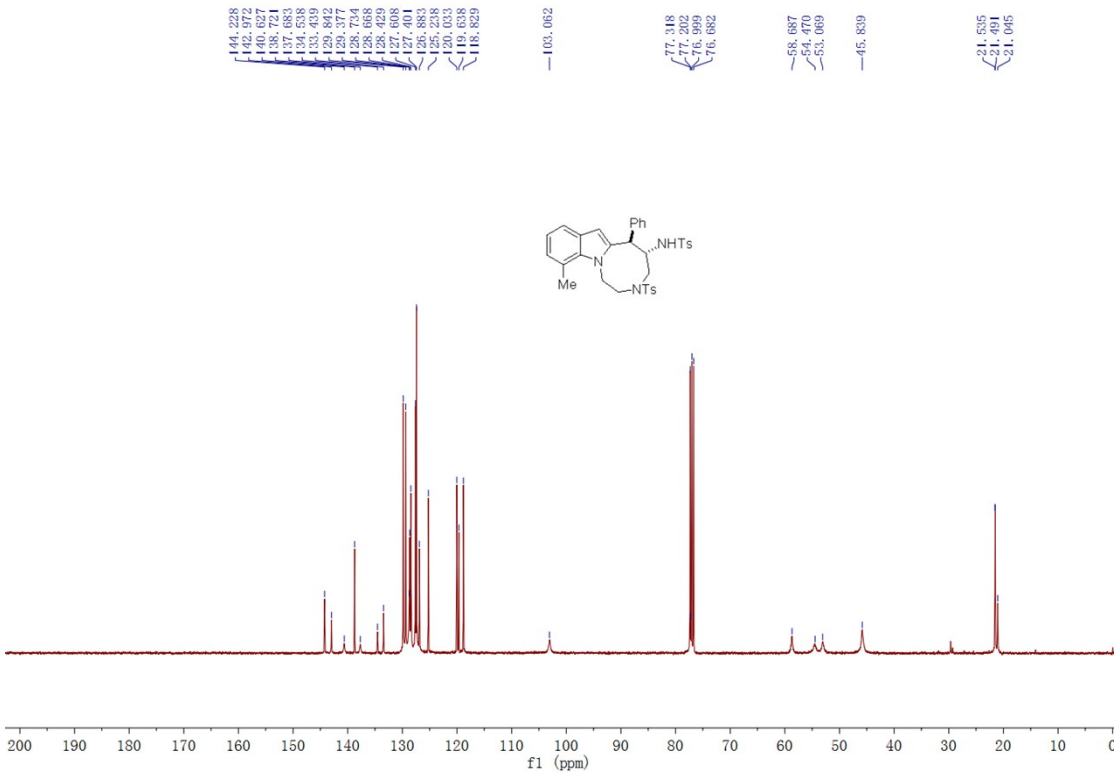


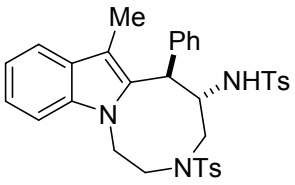


Compound 3h:

0.15 mmol scale, a white solid, 22% yield (19.1 mg). M.p.: 150-153 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.29 (br, 1H), 2.38 (s, 3H), 2.45 (s, 3H), 2.59 (s, 3H), 2.75 (br, 1H), 3.55 (br, 1H), 4.10-4.16 (m, 1H), 4.38 (br, 2H), 4.52-4.59 (m, 1H), 5.12 (br, 1H), 5.88 (br, 1H), 6.18 (s, 1H), 6.80 (d, J = 7.2 Hz, 1H), 6.88 (dd, J = 7.2 Hz, 7.2 Hz, 1H), 7.19-7.28 (m, 10H), 7.47 (d, J = 7.6 Hz, 2H), 7.53-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.0, 21.49, 21.54, 45.8 (br), 53.1 (br), 54.5 (br), 58.7 (br), 103.1 (br), 118.8, 119.6, 120.0, 125.2, 126.9, 127.4, 127.6, 128.4, 128.67, 128.73 (br), 129.4, 129.8, 133.4, 134.5, 137.7 (br), 138.7, 140.6 (br), 143.0, 144.2. IR (neat) 3291, 3065, 3046, 3021, 2959, 2922, 2853, 1597, 1540, 1493, 1450, 1413, 1329, 1287, 1265, 1184, 1156, 1112, 1088, 1058, 1024, 969, 888, 870, 798, 733, 720, 701, 662 cm^{-1}. HRMS (APCI) Calcd. for $C_{34}H_{36}N_3O_4S_2^{+1}$(M+H)$^+$ requires: 614.2142, found: 614.2157.

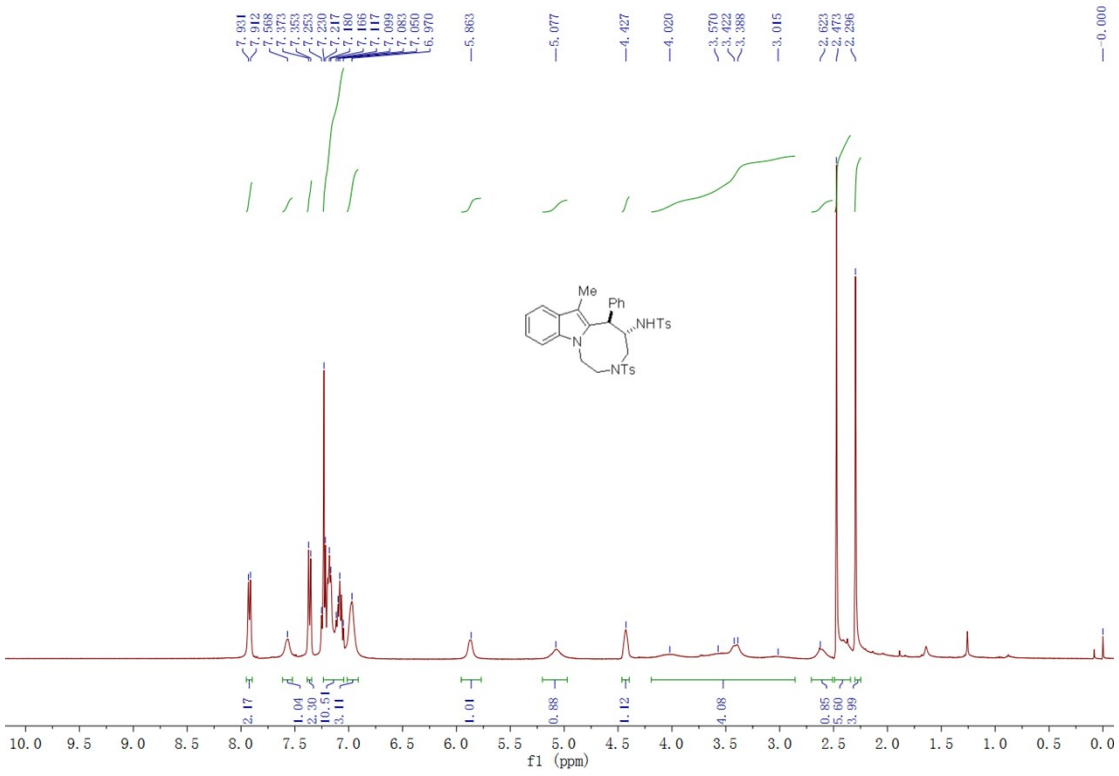


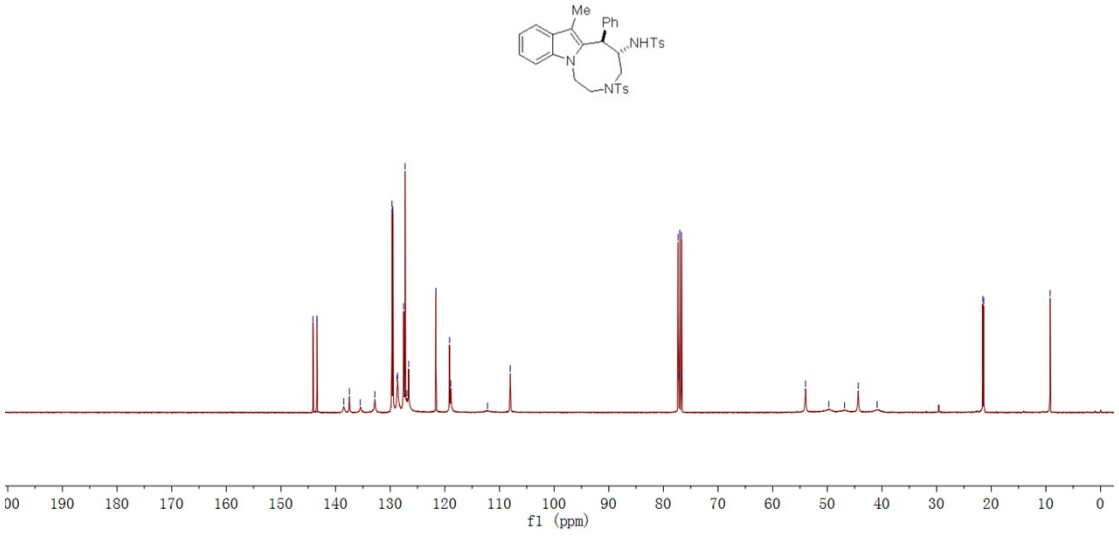


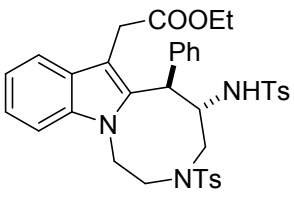


Compound 3i:

0.15 mmol scale, a light yellow solid, 47% yield (43.2 mg). M.p.: 140-143 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.29 (br, 4H), 2.47 (s, 6H), 2.62 (br, 1H), 3.01-4.02 (m, 4H), 4.43 (br, 1H), 5.08 (br, 1H), 5.86 (br, 1H), 6.97 (br, 3H), 7.05-7.26 (m, 10H), 7.36 (d, J = 8.0 Hz, 2H), 7.57 (br, 1H), 7.92 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 9.23, 21.4, 21.6, 40.9 (br), 44.4, 46.9 (br), 49.7 (br), 54.0, 108.0, 112.2 (br), 118.9, 119.1, 121.6, 126.6, 126.9, 127.3, 127.5, 128.6 (br), 128.7, 129.5, 129.7, 132.8, 135.5 (br), 137.5, 138.5 (br), 143.4, 144.1. IR (neat) 3277, 3055, 3028, 2951, 2920, 2855, 1597, 1495, 1467, 1446, 1330, 1305, 1290, 1265, 1220, 1185, 1154, 1120, 1087, 1032, 1003, 978, 936, 863, 786, 764, 735, 719, 701, 686, 662 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{36}N_3O_4S_2^{+1}(M+H)^+$ requires: 614.2142, found: 614.2143.

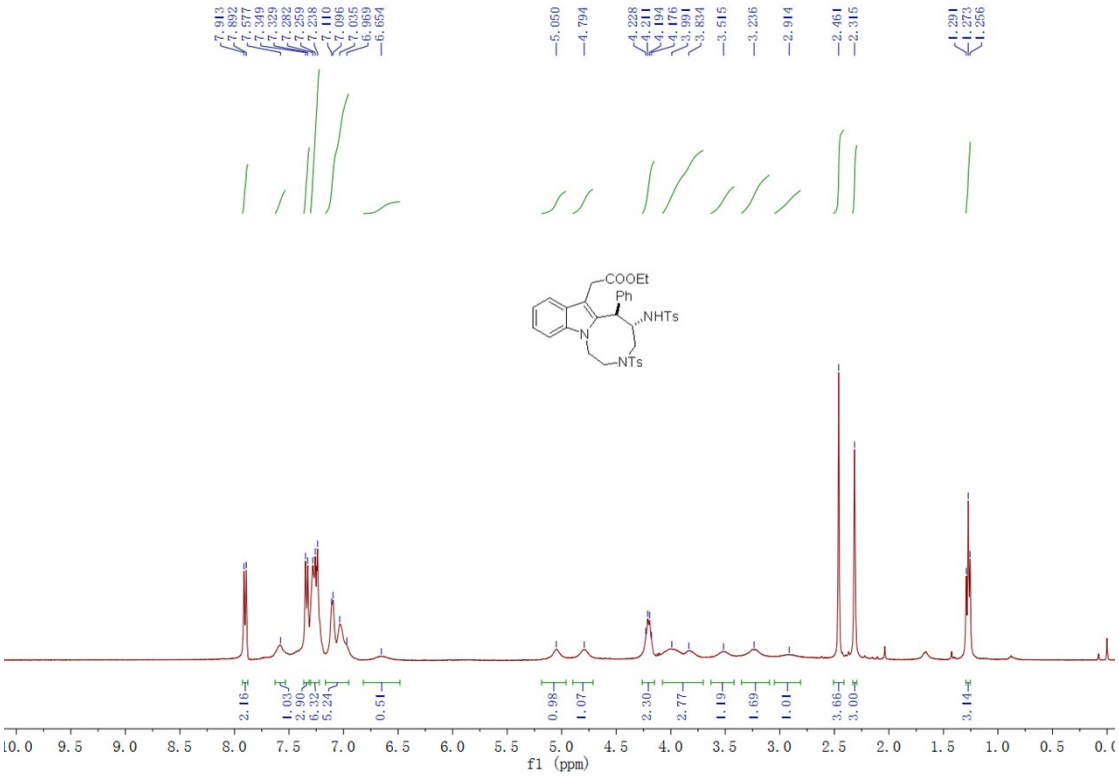

Me
Ph
NHTs
N
NTs
f1 (ppm)

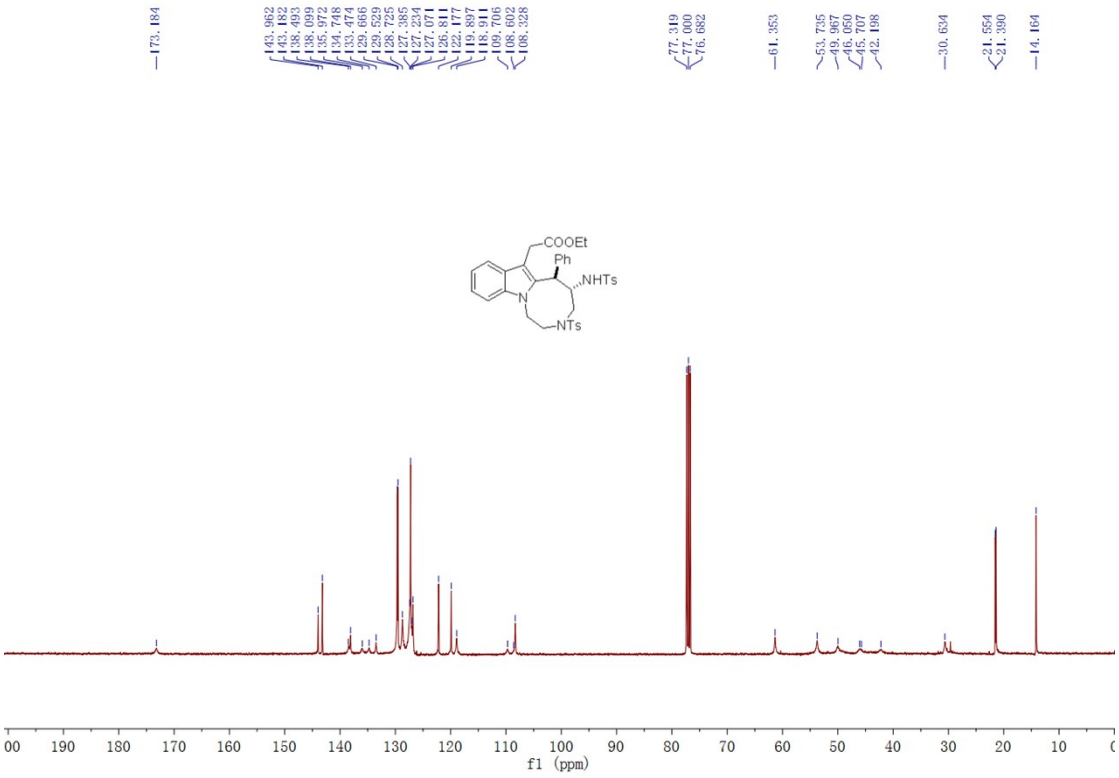

Me
Ph
NHTs
N
NTs
f1 (ppm)

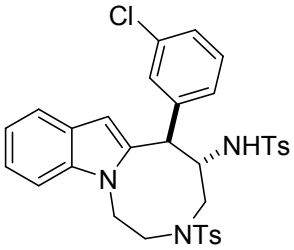

COOEt
Ph
NHTs
N
NTs

Compound 3k:

0.15 mmol scale, a yellow solid, 54% yield (55.9 mg). M.p.: 127-128 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.27 (t, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 2.46 (br, 4H), 2.91 (br, 1H), 3.24 (br, 2H), 3.52 (br, 1H), 3.83-4.00 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.80 (br, 1H), 5.05 (br, 1H), 6.65 (br, 1H), 6.96-7.12 (m, 5H), 7.23-7.29 (m, 6H), 7.32-7.35 (m, 3H), 7.58 (br, 1H), 7.90 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 14.2, 21.4, 21.6, 30.6 (br), 42.2 (br), 45.7 (br), 46.1 (br), 50.0 (br), 53.7 (br), 61.4 (br), 108.3, 108.6 (br), 109.7 (br), 118.9 (br), 119.9, 122.2, 126.8, 127.1 (br), 127.2, 127.4 (br), 128.7 (br), 129.5, 129.7, 133.5 (br), 134.7 (br), 136.0 (br), 138.1, 138.5 (br), 143.2, 144.0, 173.2 (br). IR (neat) 3272, 3057, 3026, 2979, 2925, 2866, 1726, 1597, 1495, 1466, 1446, 1365, 1330, 1305, 1265, 1155, 1088, 1020, 971, 935, 869, 814, 733, 701, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{37}H_{43}N_4O_6S_2^{+1}$(M+$NH_4$)$^+$ requires: 703.2619, found: 703.2612.



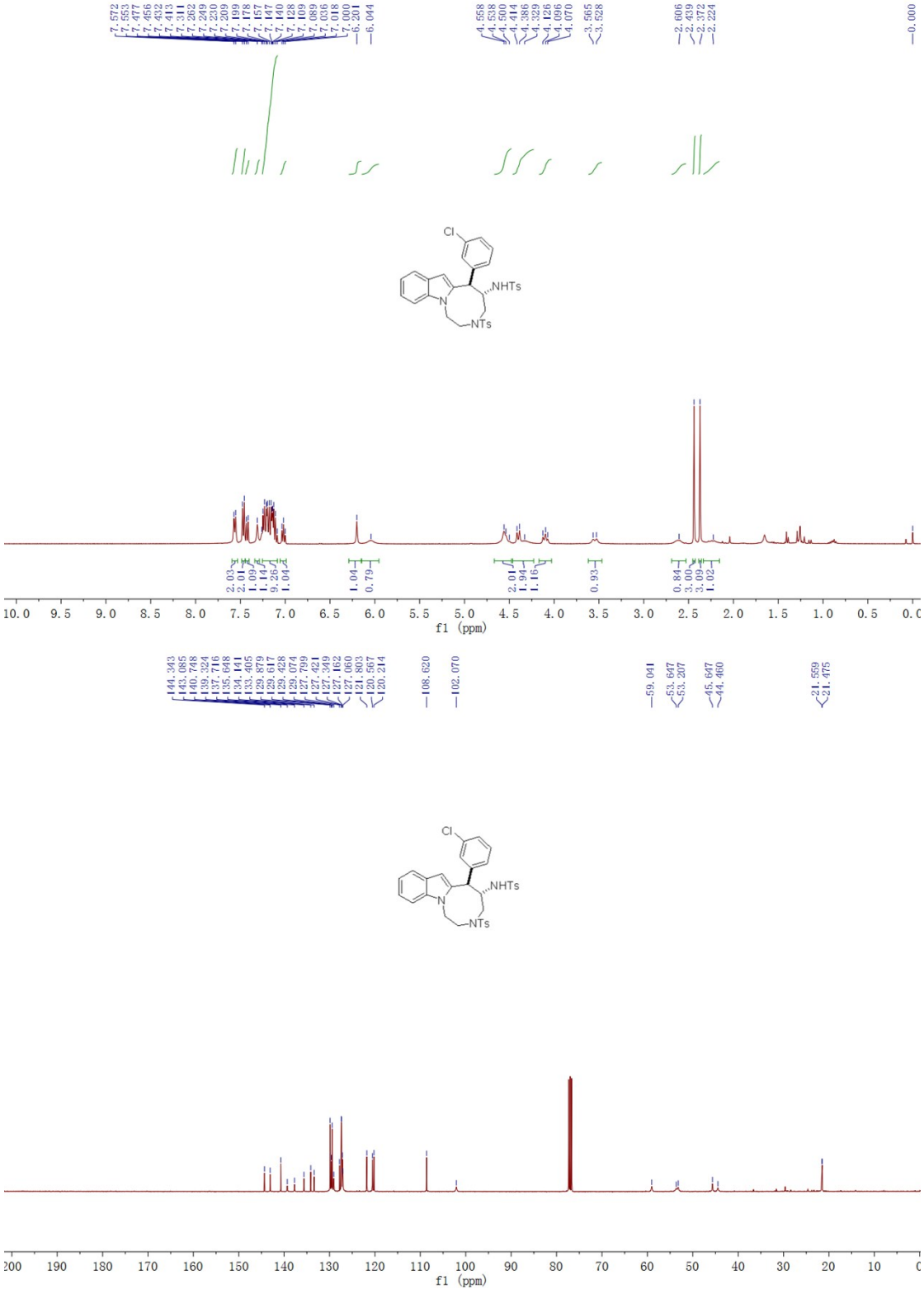


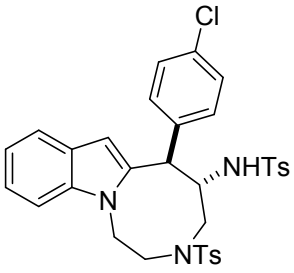


Compound 3o:

0.15 mmol scale, a yellow solid, 32% yield (30.5 mg). M.p.: 145-148 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.22 (br, 1H), 2.37 (s, 3H), 2.44 (s, 3H), 2.61 (br, 1H), 3.55 (d, J = 14.8 Hz, 1H), 4.07-4.13 (m, 1H), 4.33 (br, 1H), 4.40 (d, J = 8.4 Hz, 1H), 4.50-4.56 (m, 2H), 6.04 (br, 1H), 6.20 (s, 1H), 7.02 (dd, J = 7.2 Hz, 7.2 Hz, 1H), 7.08-7.27 (m, 9H), 7.31 (s, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 44.5 (br), 45.6 (br), 53.2 (br), 53.6 (br), 59.0 (br), 102.1 (br), 108.6, 120.2, 120.6, 121.8, 127.1 (br), 127.2, 127.3, 127.4, 127.8, 129.1 (br), 129.4, 129.6, 129.9, 133.4, 134.1, 135.6, 137.7 (br), 139.3 (br), 140.7, 143.1, 144.3. IR (neat) 3289, 3057, 3028, 2953, 2923, 2858, 1664, 1596, 1574, 1533, 1493, 1460, 1448, 1432, 1364, 1334, 1290, 1185, 1158, 1089, 1064, 1027, 990, 971, 883, 813, 786, 749, 730, 714, 661 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+H)$^{+}$ requires: 634.1596,

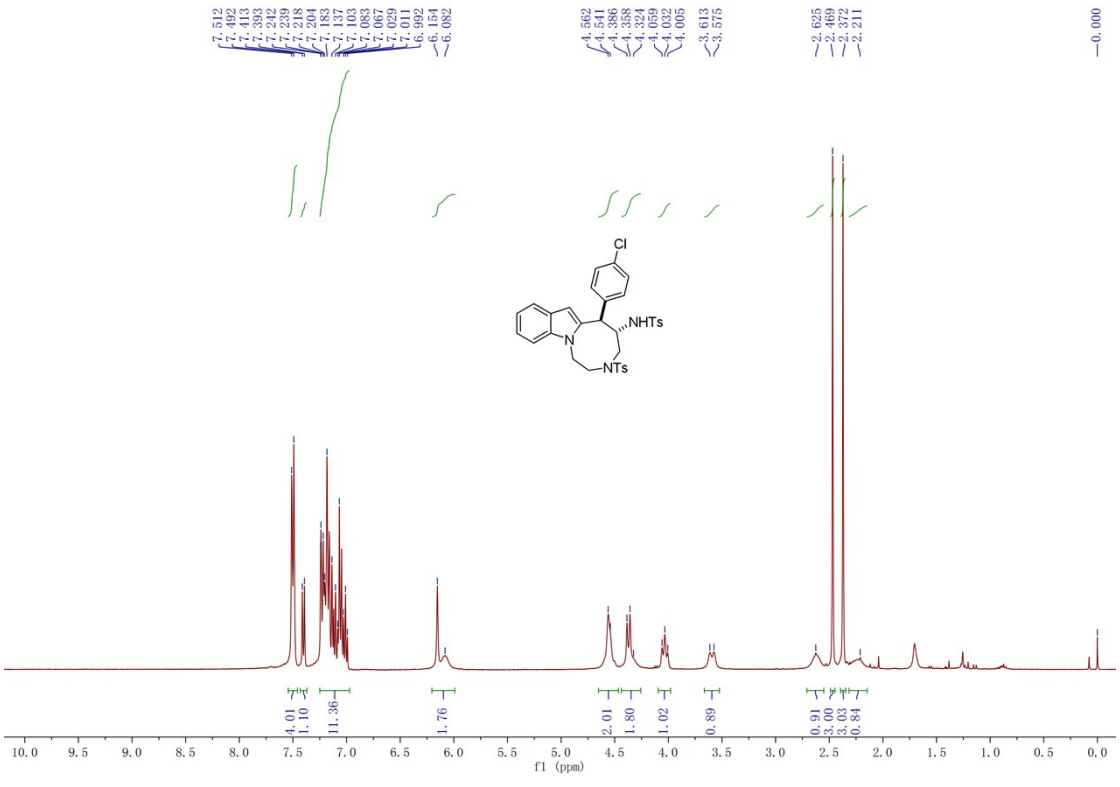
found: 634.1612.

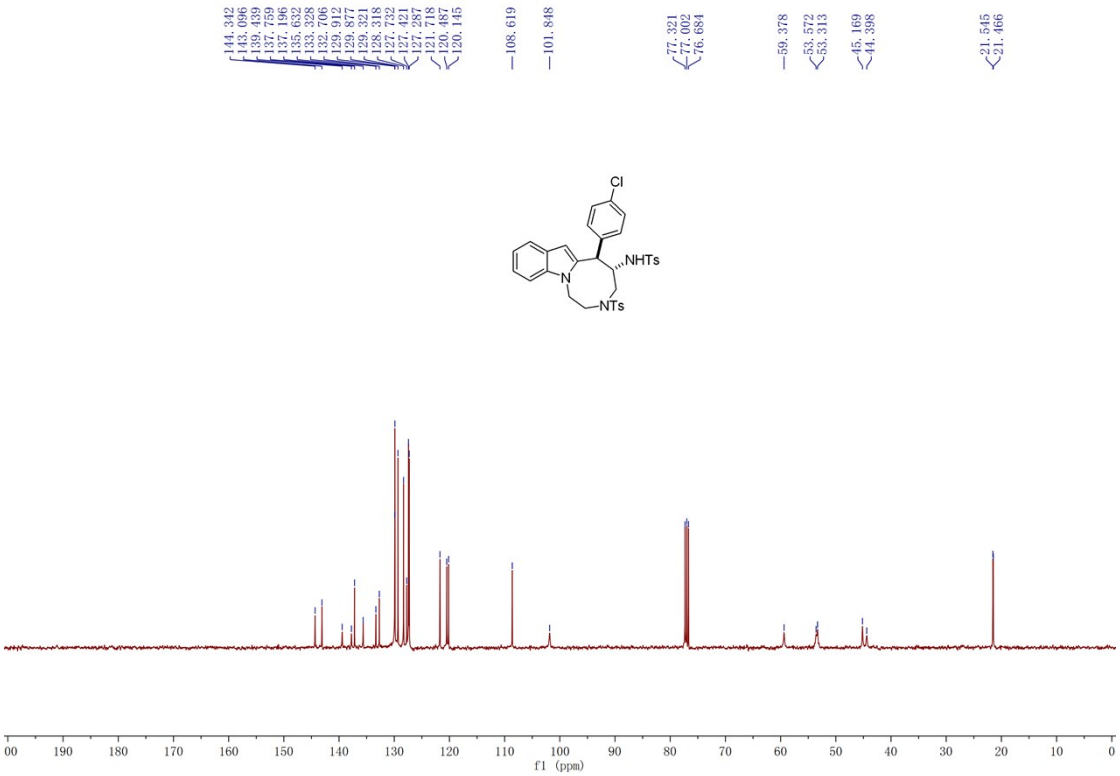


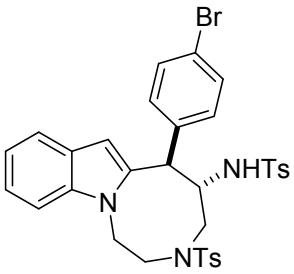


Compound 3p:

0.15 mmol scale, a yellow solid, 25% yield (23.6 mg). M.p.: 139-142 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.21 (br, 1H), 2.37 (s, 3H), 2.47 (s, 3H), 2.63 (br, 1H), 3.59 (d, J = 15.2 Hz, 1H), 4.00-4.06 (m, 1H), 4.32-4.39 (m, 2H), 4.54-4.57 (m, 2H), 6.08 (br, 1H), 6.15 (s, 1H), 6.99-7.25 (m, 11H), 7.40 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 44.4 (br), 45.2 (br), 53.3 (br), 53.6 (br), 59.4 (br), 101.8 (br), 108.6, 120.1, 120.5, 121.7, 127.3, 127.4, 127.7, 128.3, 129.3, 129.88, 129.91, 132.7, 133.3, 135.6 (br), 137.2, 137.8 (br), 139.4 (br), 143.1, 144.3. IR (neat) 3293, 3052, 3031, 2946, 2923, 2868, 2850, 1597, 1493, 1460, 1445, 1417, 1364, 1330, 1290, 1184, 1158, 1089, 1064, 1027, 1014, 970, 878, 813, 785, 748, 724, 712, 658 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}ClN_3O_4S_2^{+1}$(M+H)$^+$ requires: 634.1596, found: 634.1621.

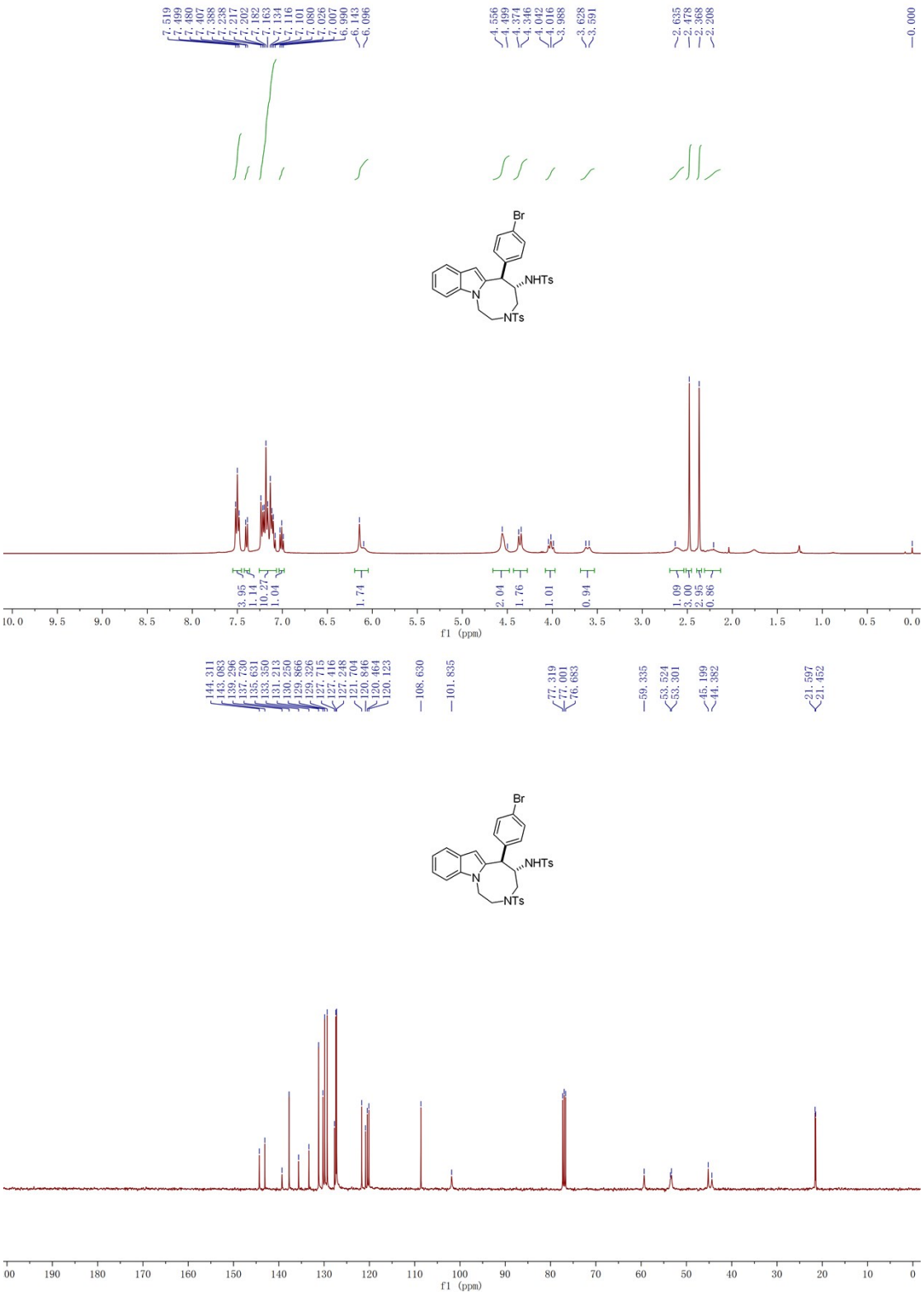






Compound 3q:

0.15 mmol scale, a yellow solid, 20% yield (20.5 mg). M.p.: 155-158 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.21 (br, 1H), 2.37 (s, 3H), 2.48 (s, 3H), 2.64 (br, 1H), 3.61 (d, *J* = 14.8 Hz, 1H), 3.98-4.05 (m, 1H), 4.34-4.38 (m, 2H), 4.49-4.56 (m, 2H), 6.10 (br, 1H), 6.14 (s, 1H), 6.99-7.03 (m, 1H), 7.08-7.24 (m, 10H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 21.6, 44.4 (br), 45.2 (br), 53.3 (br), 53.5 (br), 59.3 (br), 101.8 (br), 108.6, 120.1, 120.5, 120.8, 121.7, 127.2, 127.4, 127.7, 129.3, 129.9, 130.3, 131.2, 133.4, 135.6 (br), 137.7, 139.3 (br), 143.1, 144.3. IR (neat) 3287, 3052, 3028, 2948, 2917, 1855, 1597, 1490, 1460, 1417, 1364, 1329, 1305, 1290, 1184, 1157, 1107, 1089, 1064, 1027, 1010, 970, 879, 813, 785, 748, 721, 656 cm^{-1}. HRMS (APCI) Calcd. for $C_{33}H_{33}BrN_3O_4S_2^{+1}(M+H)^+$ requires: 678.1090, found: 678.1099.


7.519
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7.480
7.407
7.388
7.238
7.217
7.202
7.182
7.163
7.134
7.116
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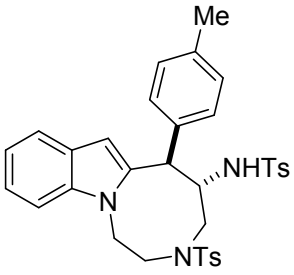
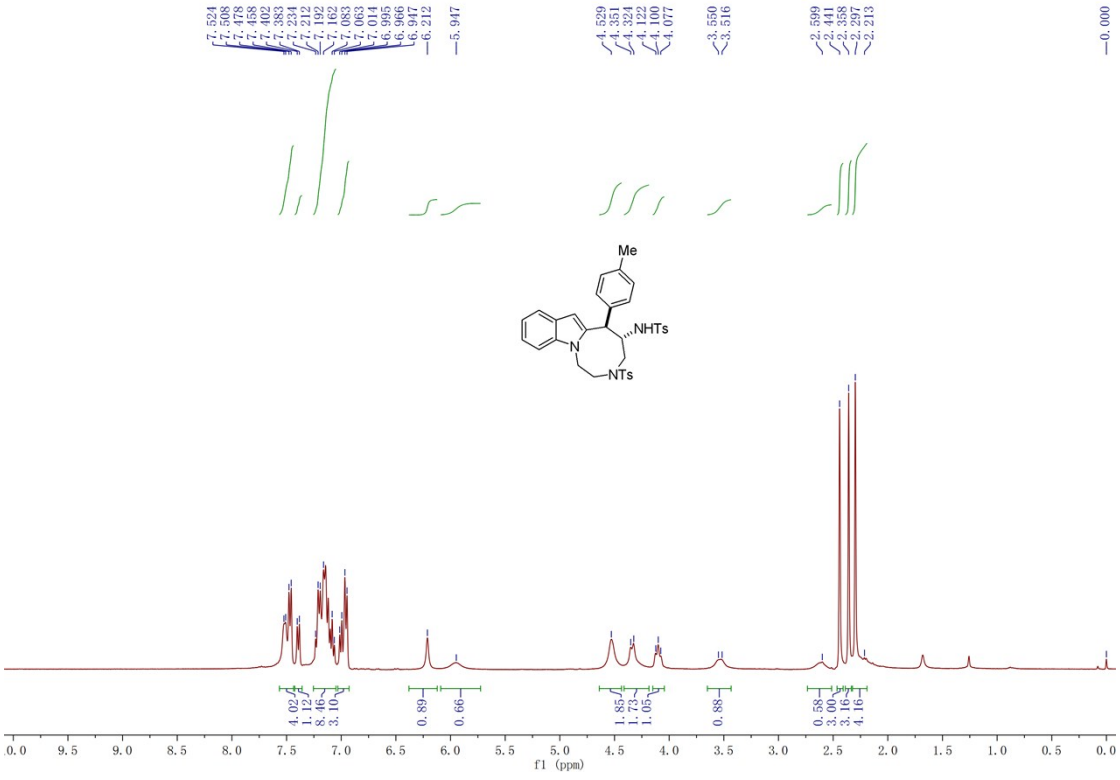
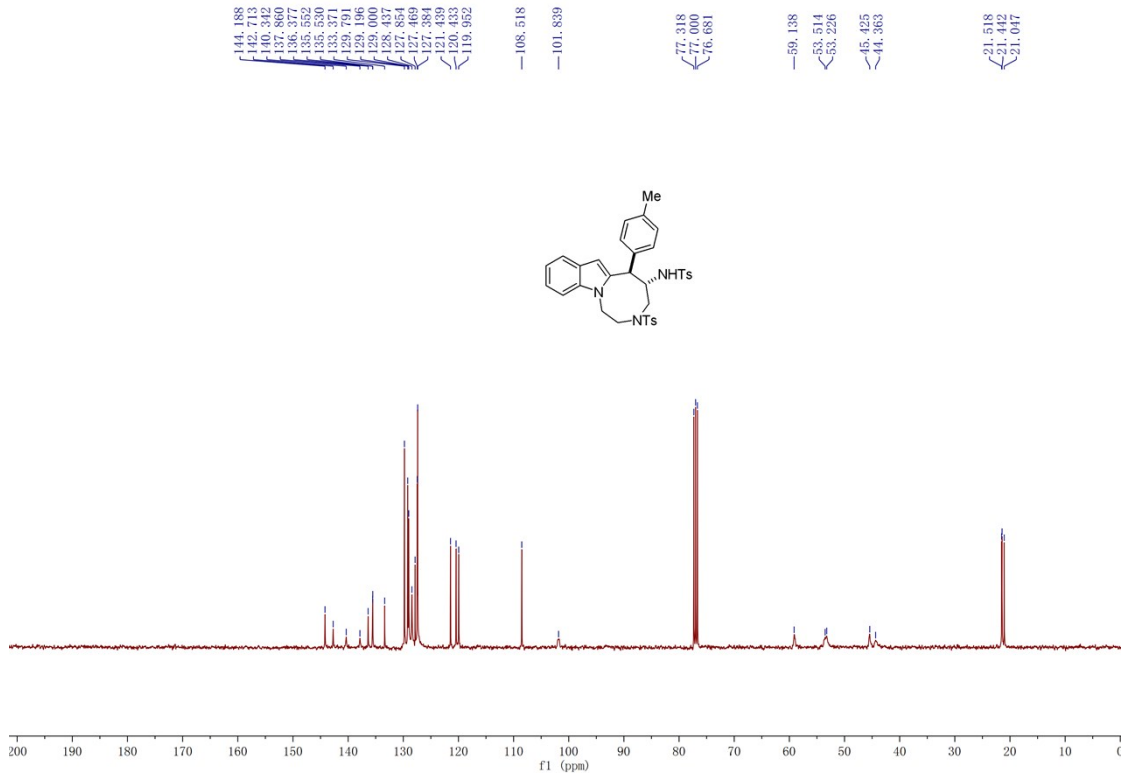
7.080
7.026
7.007
6.990
6.143
6.096
4.556
4.499
4.374
4.346
4.042
4.016
3.988
3.628
3.591
2.635
2.478
2.368
2.208
0.000
Br
NHTs
NTs
3.95
1.14
10.27
1.04
1.74
2.04
1.76
1.01
0.94
1.09
3.00
2.95
0.86
f1 (ppm)
144.311
143.083
139.296
137.730
135.671
133.350
131.213
130.250
129.866
129.326
127.715
127.416
127.248
121.704
120.846
120.464
120.123
108.630
101.835
77.319
77.001
76.683
59.335
53.524
53.301
45.199
44.382
21.597
21.452
f1 (ppm)

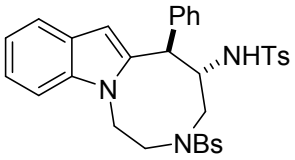


Compound 3r:

0.15 mmol scale, a yellow solid, 44% yield (40.8 mg). M.p.: 148-150 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.21 (br, 1H), 2.30 (s, 3H), 2.36 (s, 3H), 2.44 (s, 3H), 2.60 (br, 1H), 3.53 (d, J = 13.6 Hz, 1H), 4.07-4.13 (m, 1H), 4.32-4.36 (m, 2H), 4.53 (br, 2H), 5.95 (br, 1H), 6.21 (s, 1H), 6.94-7.02 (m, 3H), 7.06-7.24 (m, 8H), 7.39 (d, J = 7.6 Hz, 1H), 7.45-7.53 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.0, 21.4, 21.5, 44.4 (br), 45.4 (br), 53.2 (br), 53.5 (br), 59.1 (br), 101.8 (br), 108.5, 120.0, 120.4, 121.4, 127.4, 127.5, 127.9, 128.4, 129.0, 129.2, 129.8, 133.4, 135.5, 135.6, 136.4, 137.9 (br), 140.3 (br), 142.7, 144.2. IR (neat) 3293, 3054, 3031, 2984, 2948, 2922, 2860, 1597, 1515, 1493, 1459, 1364, 1332, 1289, 1185, 1157, 1108, 1089, 1063, 1027, 990, 970, 879, 813, 787, 748, 733, 718, 703, 658 cm^{-1}. HRMS (ESI) Calcd. for $C_{34}H_{36}N_3O_4S_2^{+1}(M+H)^+$ requires: 614.2142, found: 614.2142.

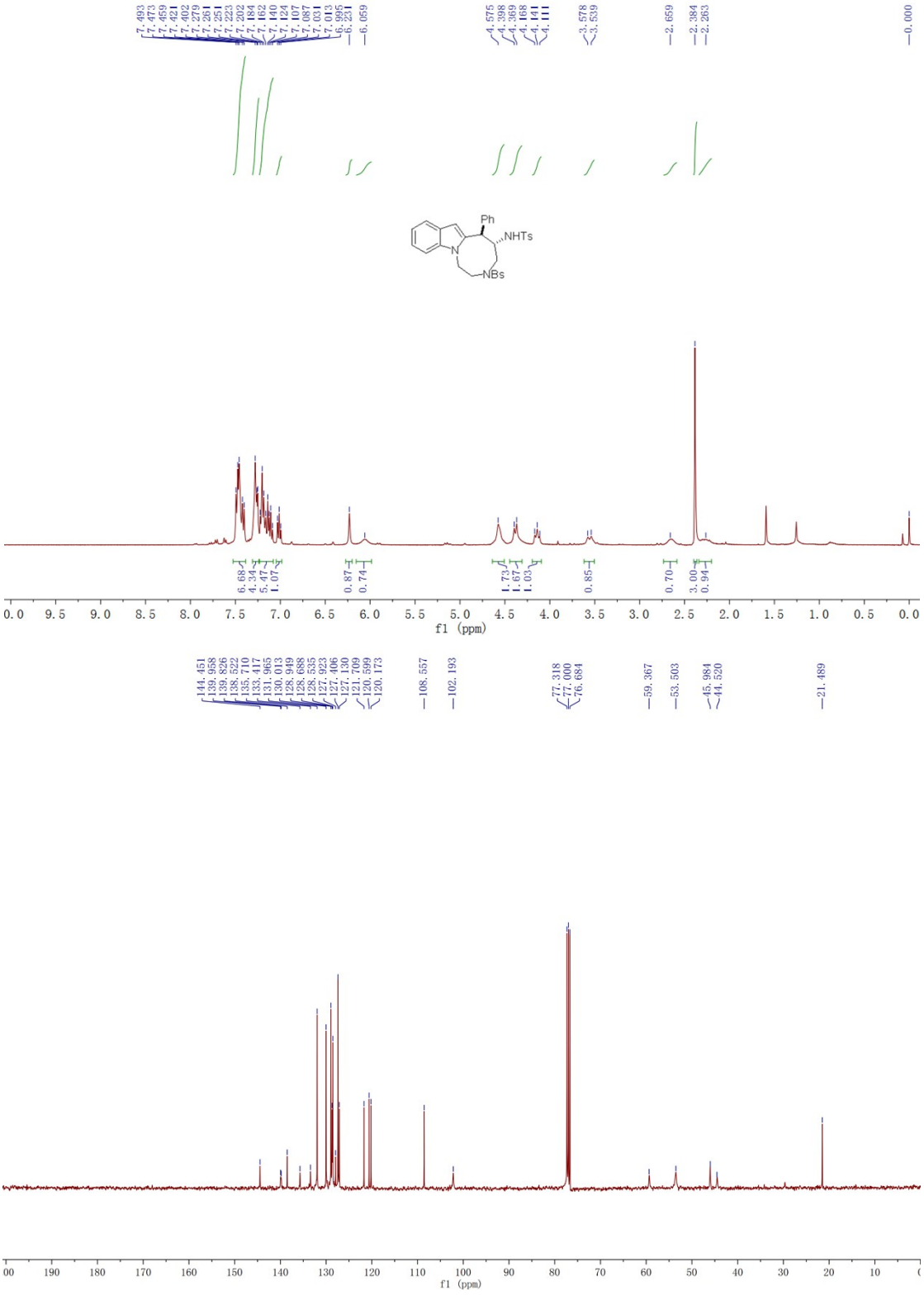






Compound 3s:

0.15 mmol scale, a white solid, 19% yield (19.3 mg). M.p.: 156-159 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.26 (br, 1H), 2.38 (s, 3H), 2.66 (br, 1H), 3.53-3.58 (m, 1H), 4.11-4.17 (m, 1H), 4.36-4.40 (m, 2H), 4.58 (br, 2H), 6.06 (br, 1H), 6.23 (s, 1H), 7.01 (dd, *J* = 7.2 Hz, 7.2 Hz, 1H), 7.08-7.23 (m, 5H), 7.25-7.28 (m, 4H), 7.40-7.50 (m, 7H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 44.5 (br), 46.0 (br), 53.5 (br), 59.4 (br), 102.2 (br), 108.6, 120.2, 120.6, 121.7, 127.1, 127.4, 127.9, 128.5, 128.7, 128.9, 130.0, 132.0, 133.4, 135.7, 138.5, 139.8 (br), 140.0 (br), 144.5. IR (neat) 3300, 3088, 3059, 3031, 2953, 2924, 2850, 1597, 1574, 1495, 1459, 1388, 1332, 1290, 1265, 1157, 1108, 1088, 1026, 1011, 989, 970, 916, 891, 811, 775, 735, 718, 701, 670 cm^{-1}. HRMS (APCI) Calcd. for $C_{32}H_{31}BrN_3O_4S_2^{+1}$(M+H)$^+$ requires: 664.0934, found: 664.0938.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7.421
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7.379
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7.251
7.223
7.202
7.184
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7.107
7.087
7.031
7.013
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6.059
4.575
4.398
4.369
4.168
4.141
4.111
3.578
3.539
2.659
2.384
2.263
0.000
Ph
NHTs
N
NBs
6.68
4.34
5.47
1.07
0.87
0.74
1.73
1.67
1.03
0.85
0.70
3.00
0.94
f1 (ppm)
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139.958
139.826
138.522
135.710
133.417
131.965
130.013
128.949
128.688
128.535
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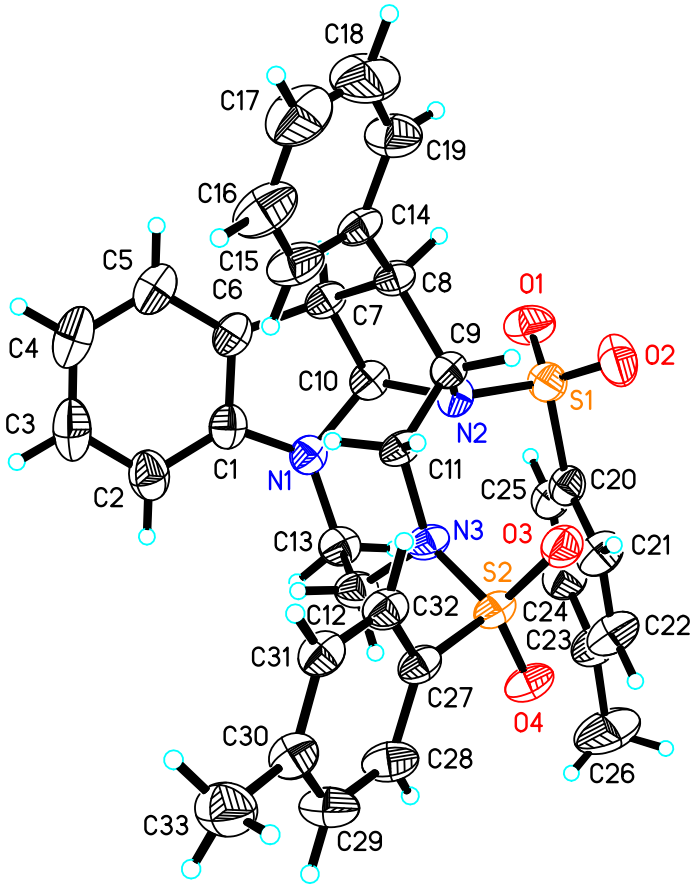
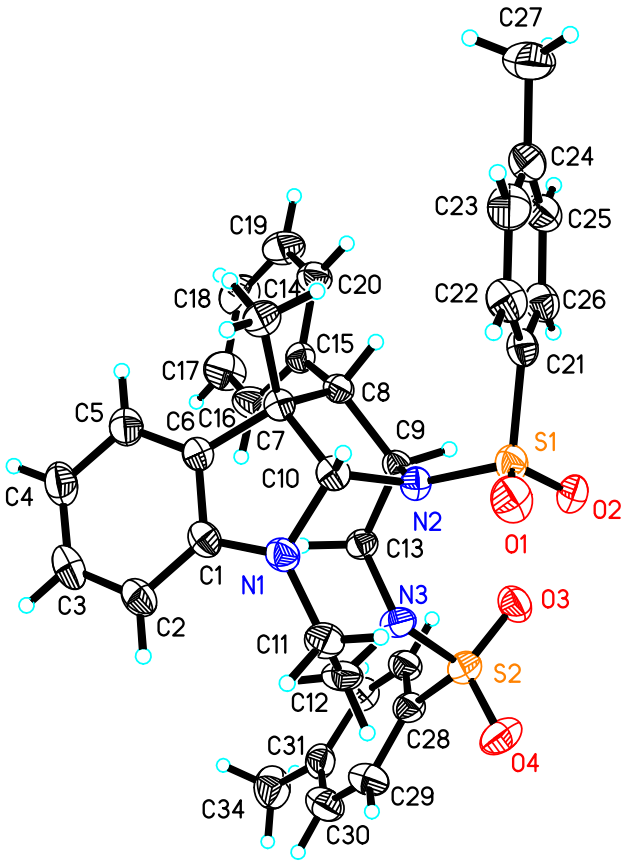
127.496
127.130
121.709
120.599
120.173
108.557
102.193
77.318
77.000
76.684
59.367
53.503
45.984
44.520
21.489
f1 (ppm)

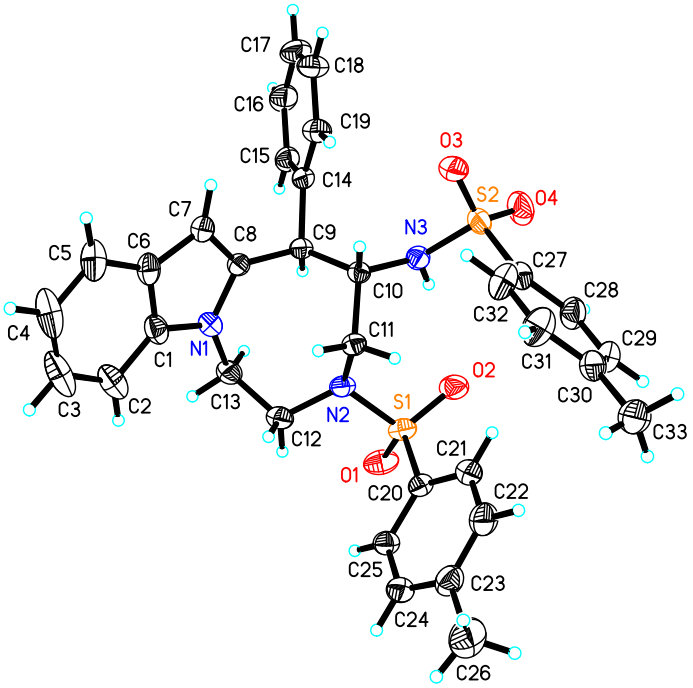
10. X-ray crystallographic information of product 2a, 2i, 3a and $Cu(CH_3CN)ClO_4$



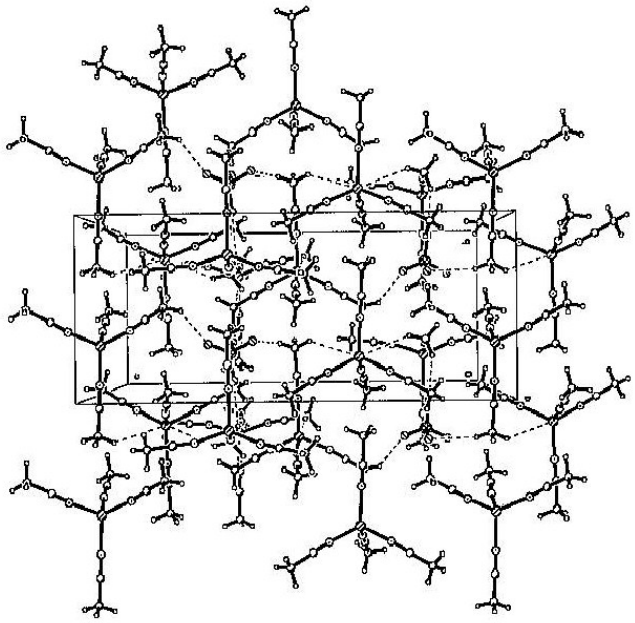
The crystal data of **2a** have been deposited in CCDC with number 1444005. Empirical Formula: $C_{33}H_{33}N_3O_4S_2$; Formula Weight: 599.74; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.180 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 33.342(3)Å, b = 14.1163(13)Å, c = 13.8882(14)Å, α = 90°, β = 113.533(2)°, γ = 90°, V = 5993.1(10)$Å^3$; Space group: C 2/c; Z = 8; D_{calc}= 1.329 g/cm^3; F_{000} = 2528; Final R indices [I>2sigma(I)] R1 = 0.0524, wR2 = 0.1319.



The crystal data of **2i** have been deposited in CCDC with number 1428608. Empirical Formula: $C_{35}H_{37}Cl_2N_3O_4S_2$; Formula Weight: 698.69; Crystal Color, Habit: colorless, Crystal Dimensions: 0.180 x 0.140 x 0.100 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 8.616(4)Å, b = 21.777(9)Å, c = 18.552(8)Å, $\alpha = 90^o$, $\beta = 100.259(9)^o$, $\gamma = 90^o$, V = 3426(3)$Å^3$; Space group: P 21/n; Z = 4; D_{calc}= 1.355 g/cm^3; F_{000} = 1464; Final R indices [I>2sigma(I)] R1 = 0.0540, wR2 = 0.1211.



The crystal data of **3a** have been deposited in CCDC with number 1437967. Empirical Formula: $C_{33}H_{33}N_3O_4S_2$; Formula Weight: 599.74; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.170 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 20.618(2)Å, b = 12.7286(14)Å, c = 11.5829(13)Å, $\alpha = 90^o$, $\beta = 96.577(2)^o$, $\gamma = 90^o$, V = 3019.7(6)$Å^3$; Space group: P 21/c; Z = 4; D_{calc}= 1.319 g/cm^3; F_{000} = 1264; Final R indices [I>2sigma(I)] R1 = 0.0436, wR2 = 0.1133.



The crystal data of $Cu(MeCN)_4ClO_4$ have been deposited in CCDC with number 994520. Empirical Formula: $C_{24}H_{36}N_{12}O_{12}Cl_3Cu_3$; Formula Weight: 981.62; Crystal Color, Habit: colorless; Crystal Dimensions: 0.606 x 0.356 x 0.289 mm; Crystal System: Orthorhombic; Lattice Parameters: a = 24.106(3)Å, b = 8.4201(10)Å, c = 20.584(2)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 4178.1(8)Å^3; Space group: Pna2(1); Z = 4; D_{calc} = 1.561 g/cm^3; F_{000} = 1992; Final R indices [I>2sigma(I)] R1 = 0.0743, wR2 = 0.1769.

11. **References**

[1] (a) Z. Zhang, M. Shi, *Eur. J. Org. Chem.* **2011**, 2610; (b) Z. Zhang, M. Shi, *Tetrahedron Lett.* **2011**, *52*, 6541; (c) J.-M. Yang, Z. Zhang, Y. Wei, M. Shi, *Tetrahedron Lett.* **2012**, *53*, 6173.

[2] (a) J. A. Schiffner, T. H. Wöste, M. Oestreich, *Eur. J. Org. Chem.* **2010**, 174-18; (b) J.-M. Yang, C.-Z. Zhu, X.-Y. Tang, M. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 5142.