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Supporting Information

Mitsunobu-initiated cascade cyclization of *p*-quinamines and 2-furanylmethanols: highly regio- and diastereoelective synthesis of functionalized hydrobenzo[*c*,*d*]indoles

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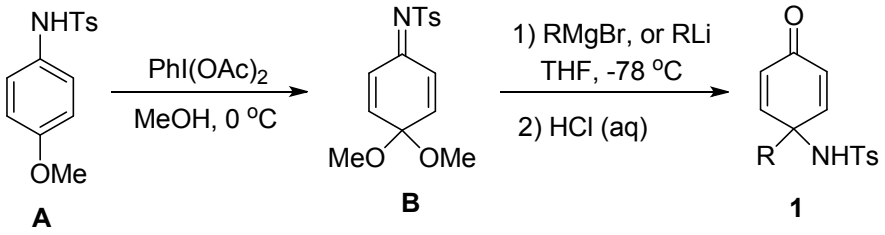
CONTENTS

1. General remarks.

Melting point (MP) was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Infrared spectra were measured on a spectrometer. ^{1}H NMR spectra were recorded on a Agilent DD2 400-MR spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. ^{13}C NMR spectra were recorded at 100 MHz. ^{19}F NMR spectra were recorded at 376 MHz. Data for ^{1}H, ^{13}C, ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). 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.

Compounds **1a**, **1b**, **1d**, and **1i-1o** were prepared according to the previously reported procedures.[1]

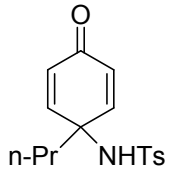
2. General procedure for synthesis of 1.



To a solution of **A** (10.0 mmol, 1.0 equiv), in MeOH (50 mL), $PhI(OAc)_2$ (10.0 mmol, 1.0 equiv) was added dropwise at 0 °C under Ar. The resulting mixture was stirred for 3 hours at 0 °C. Then, an aqueous solution of saturated $NaHCO_3$ was carefully added to quench the reaction. Next, the solution was extracted by DCM for 3 times, dried over anhydrous Na_2SO_4, and concentrated in vacuum. Finally, the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 8 / 1~4 / 1) to give intermediate **B** as a white solid.

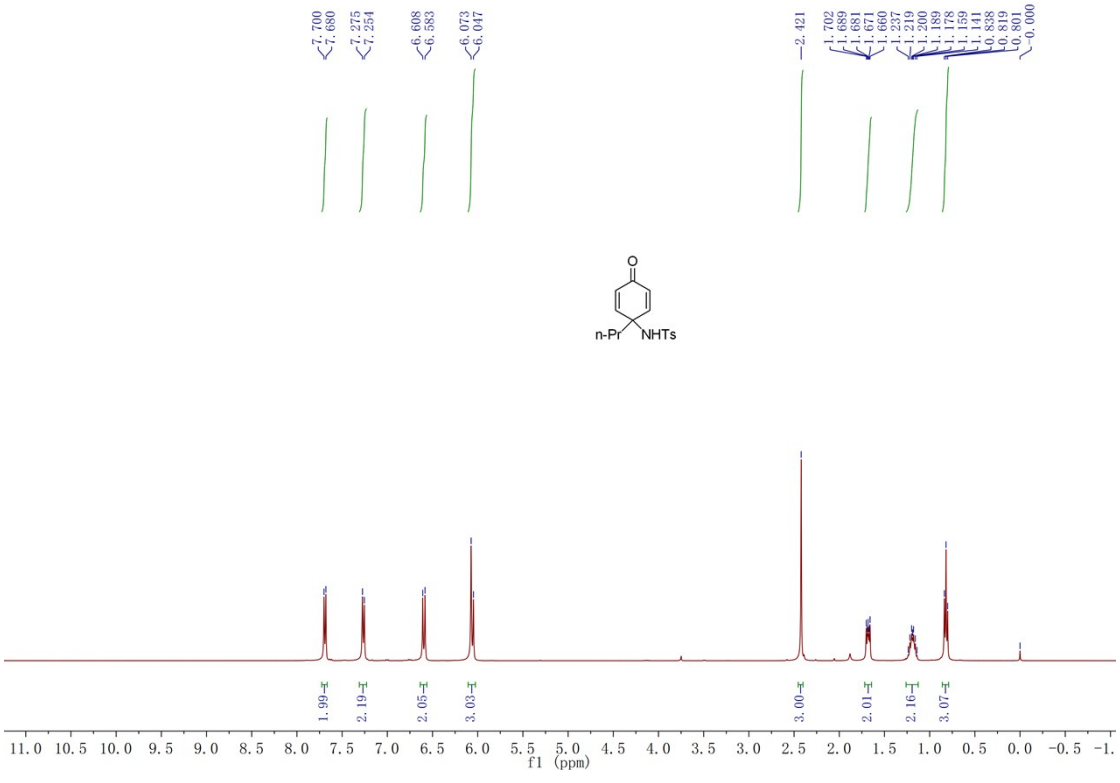
To a solution of **B** (8.0 mmol, 1.0 equiv) in anhydrous THF (25 mL), RMgBr or RLi (13.0 mmol, 1.3 equiv) was carefully added dropwise at -78 °C under argon atmosphere. After the reaction completed, the reaction was quenched by HCl (2.0 M aq). The reaction mixture was extracted by EA for 3 times and the combined organic layers were washed with brine and dried over sodium sulfate. Then, the solution was concentrated in vacuo to yield the crude product, which was purified by a flash chromatography on silica gel (eluent: PE/EtOAc = 8/1 ~ 6/1) to furnish the desired product **1**.

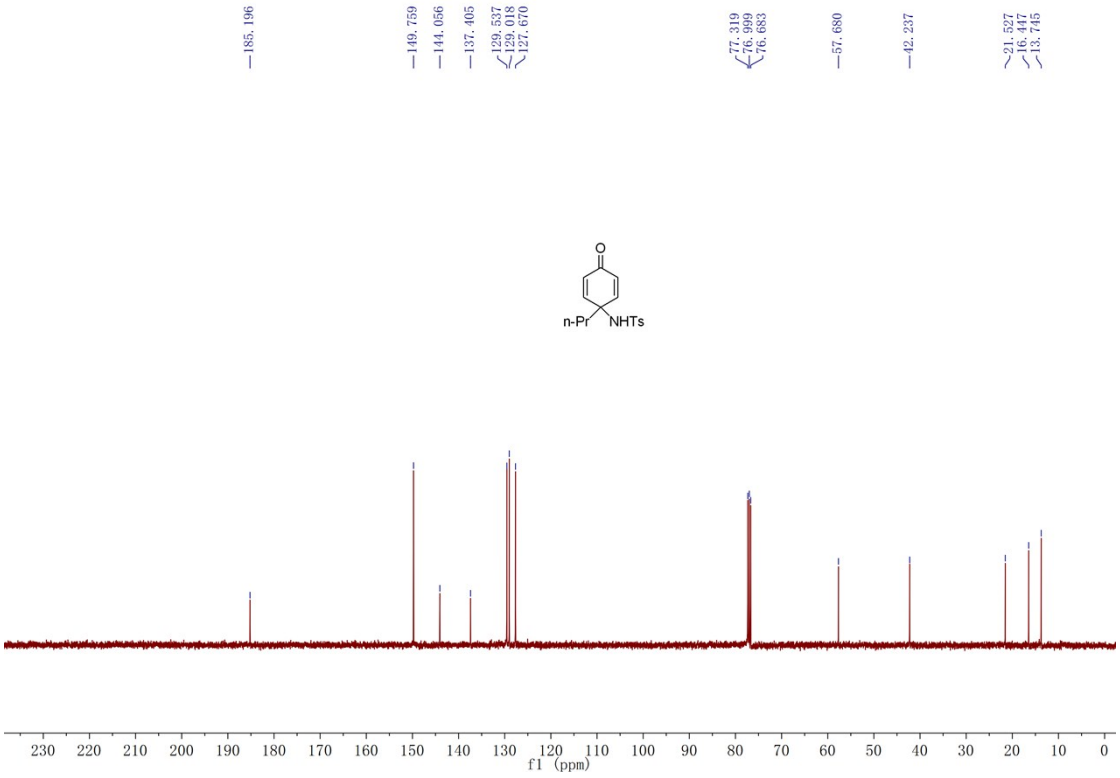
3. Characterization and spectra charts for 1.

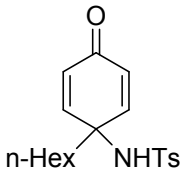


Compound 1c:

8.0 mmol scale, a white solid, 28% yield (678.7 mg). M.p.: 165-168 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.82 (t, *J* = 7.6 Hz, 3H), 1.14-1.24 (m, 2H), 1.66-1.71 (m, 2H), 2.42 (s, 3H), 6.06 (d, *J* = 10.0 Hz, 2H), 6.07 (s, 1H), 6.60 (d, *J* = 10.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.7, 16.4, 21.5, 42.2, 57.7, 127.7, 129.0, 129.5, 137.4, 144.1, 149.8, 185.2. IR (neat) ν 3246, 3125, 3044, 2964, 2932, 2898, 2875, 1663, 1614, 1494, 1455, 1382, 1340, 1178, 1157, 1128, 1093, 1024, 980, 941, 924, 855, 813, 776, 735, 723, 706, 672 cm^{-1}. HRMS (ESI) Calcd. for $C_{16}H_{19}NO_3SNa^{+1}$(M+Na)$^{+}$ requires: 328.0978, Found: 328.0976.

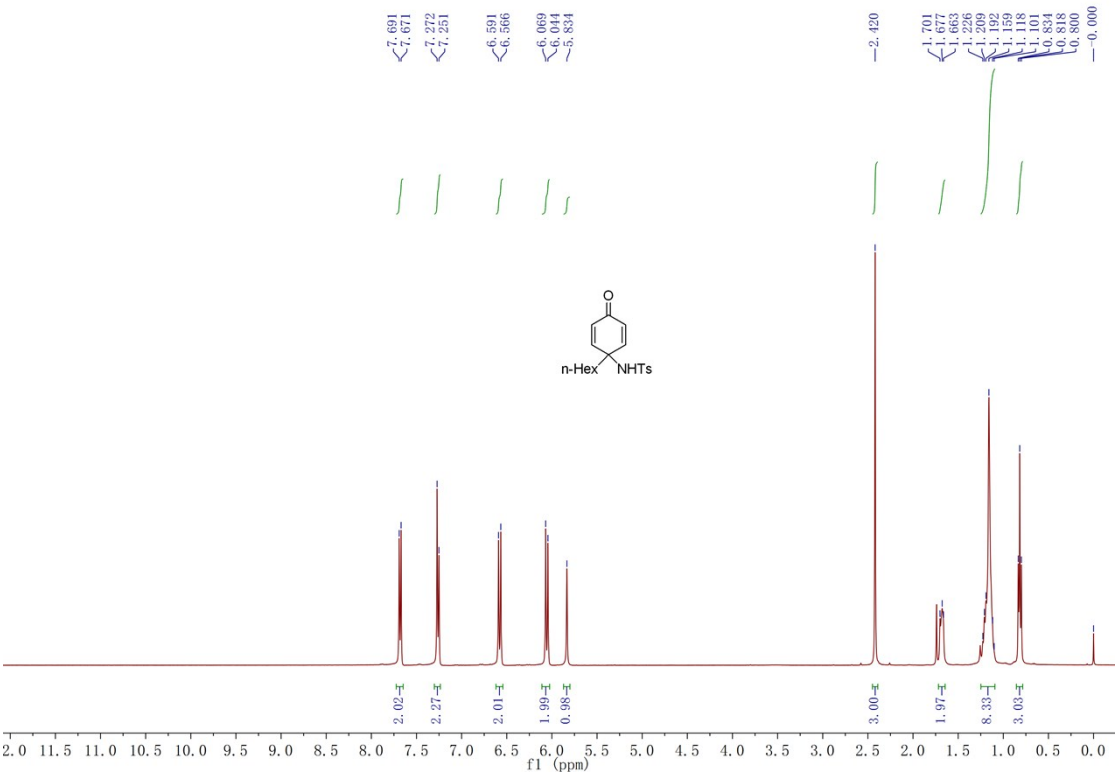






Compound 1e:

8.0 mmol scale, a light yellow solid, 50% yield (1.3961 g). M.p.: 88-90 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.10-1.23 (m, 8H), 1.66-1.71 (m, 2H), 2.42 (s, 3H), 5.83 (s, 1H), 6.06 (d, *J* = 10.0 Hz, 2H), 6.58 (d, *J* = 10.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.9, 21.5, 22.4, 23.0, 28.9, 31.4, 40.3, 57.7, 127.7, 129.1, 129.6, 137.4, 144.1, 149.7, 185.1. IR (neat) ν 3247, 3063, 3044, 2950, 2927, 2858, 1663, 1621, 1598, 1509, 1495, 1455, 1397, 1381, 1336, 1304, 1157, 1091, 1021, 938, 907, 858, 814, 734, 705, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{29}N_2O_3S^{+1}(M+NH_4)^+$ requires: 365.1893, Found: 365.1888.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1.226
1.209
1.192
1.159
1.118
1.101
0.834
0.818
0.800
0.000
n-Hex
NHTs
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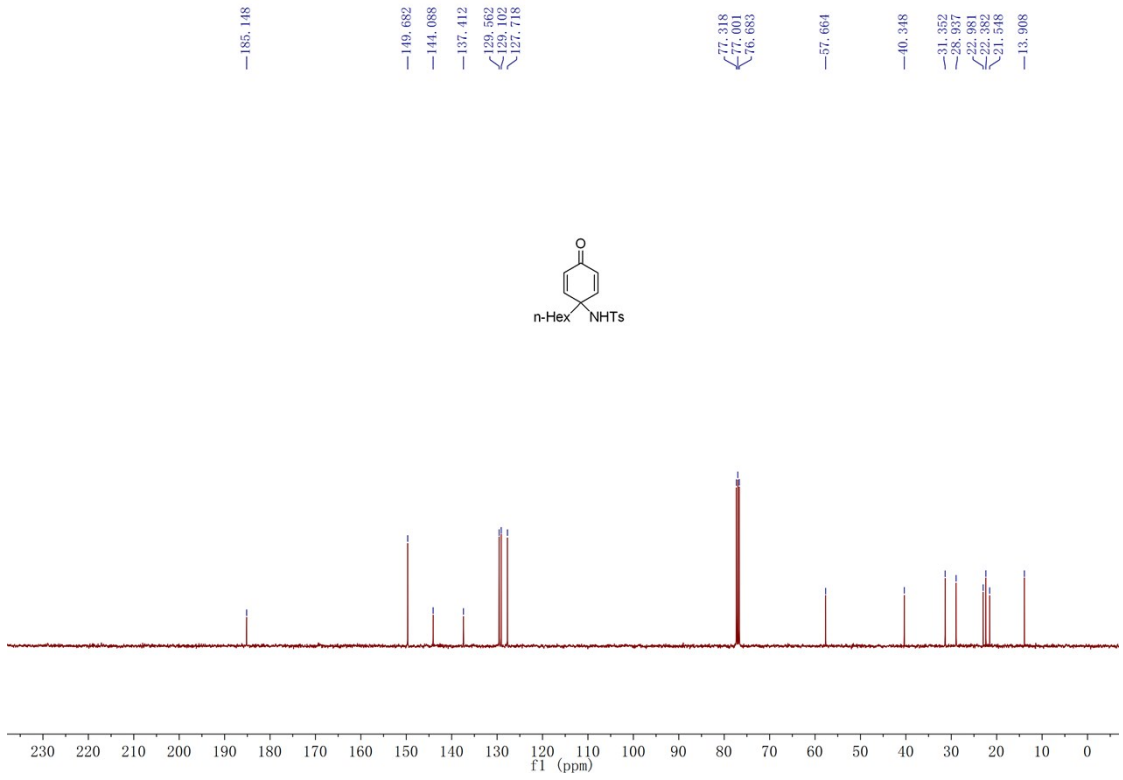
1.99
0.98
3.00
1.97
8.33
3.03
f1 (ppm)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77.001
76.683
57.664
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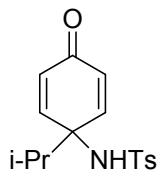
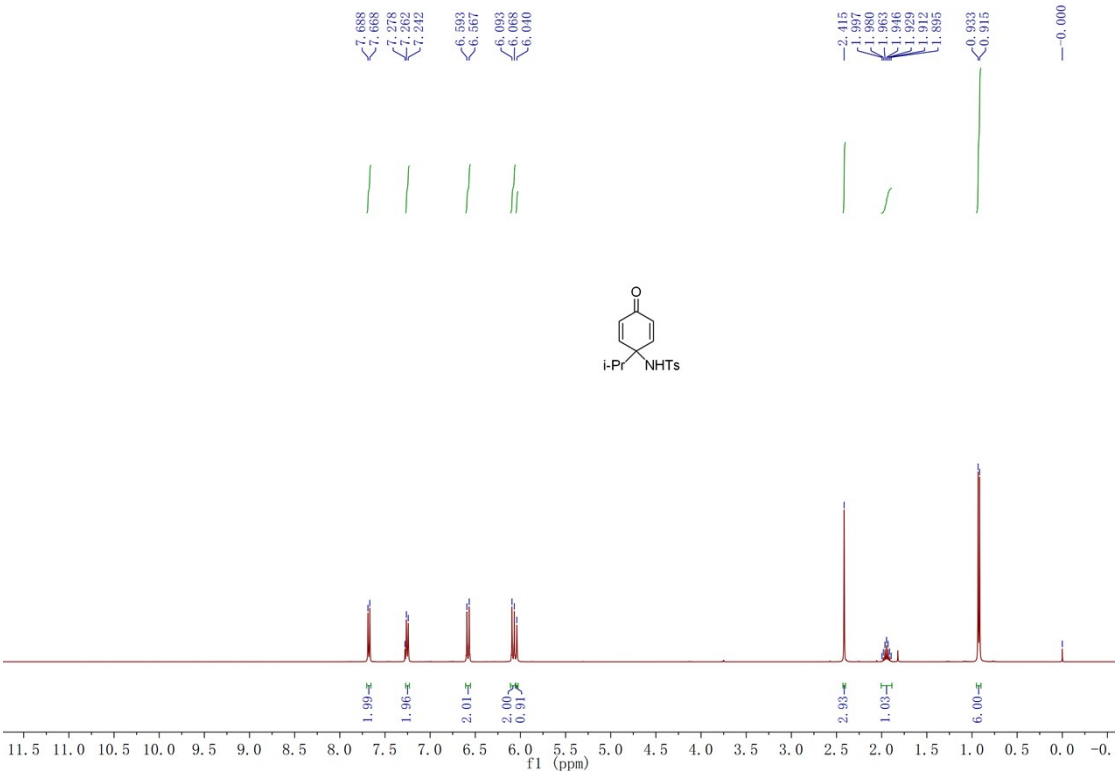
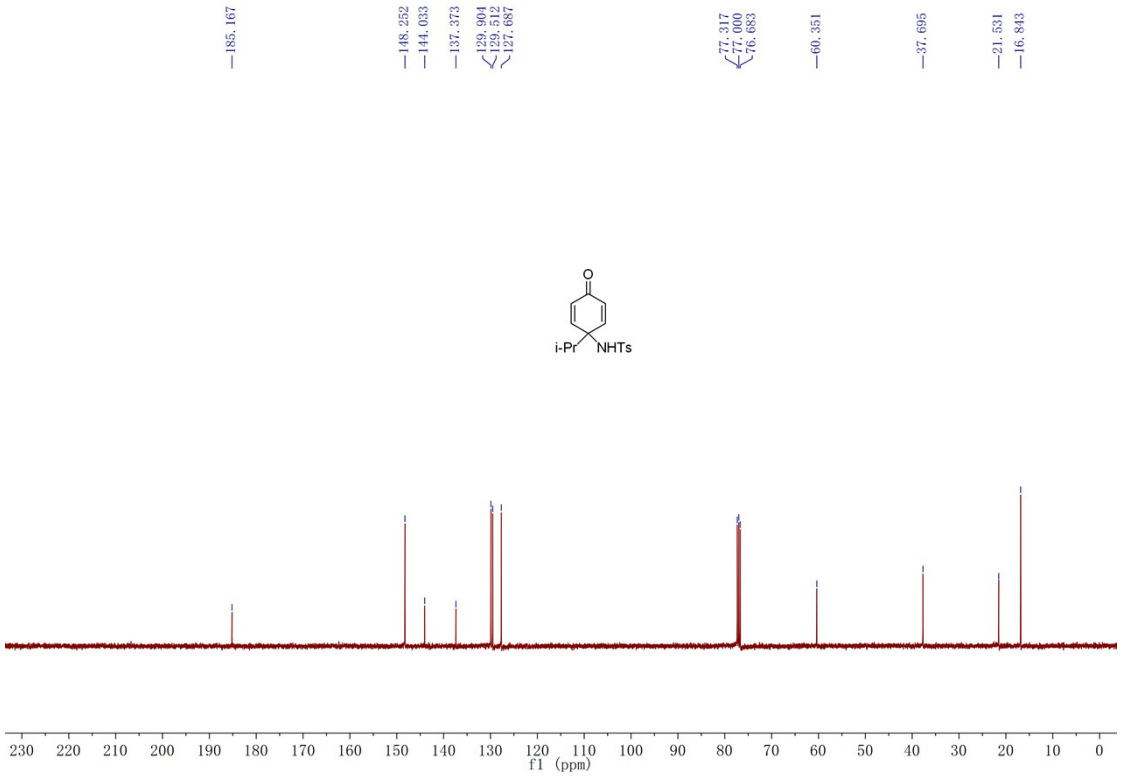
22.382
21.548
13.908
n-Hex
NHTs
f1 (ppm)

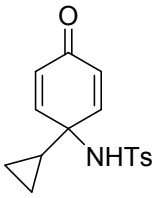

i-Pr
NHTs

Compound 1f:

8.0 mmol scale, a white solid, 38% yield (926.2 mg). M.p.: 180-183 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.92 (d, *J* = 7.2 Hz, 6H), 1.89-2.00 (m, 1H), 2.42 (s, 3H), 6.04 (s, 1H), 6.08 (q, *J* = 10.0 Hz, 2H), 6.58 (d, *J* = 10.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 16.8, 21.5, 37.7, 60.4, 127.7, 129.5, 129.9, 137.4, 144.0, 148.3, 185.2. IR (neat) ν 3249, 3099, 2972, 2934, 2911, 2874, 2783, 1663, 1616, 1463, 1386, 1341, 1323, 1230, 1183, 1159, 1140, 1117, 1092, 1063, 1042, 997, 975, 936, 906, 848, 815, 707, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{16}H_{19}NO_3SNa^{+1}$(M+Na)$^+$ requires: 328.0978, Found: 328.0977.

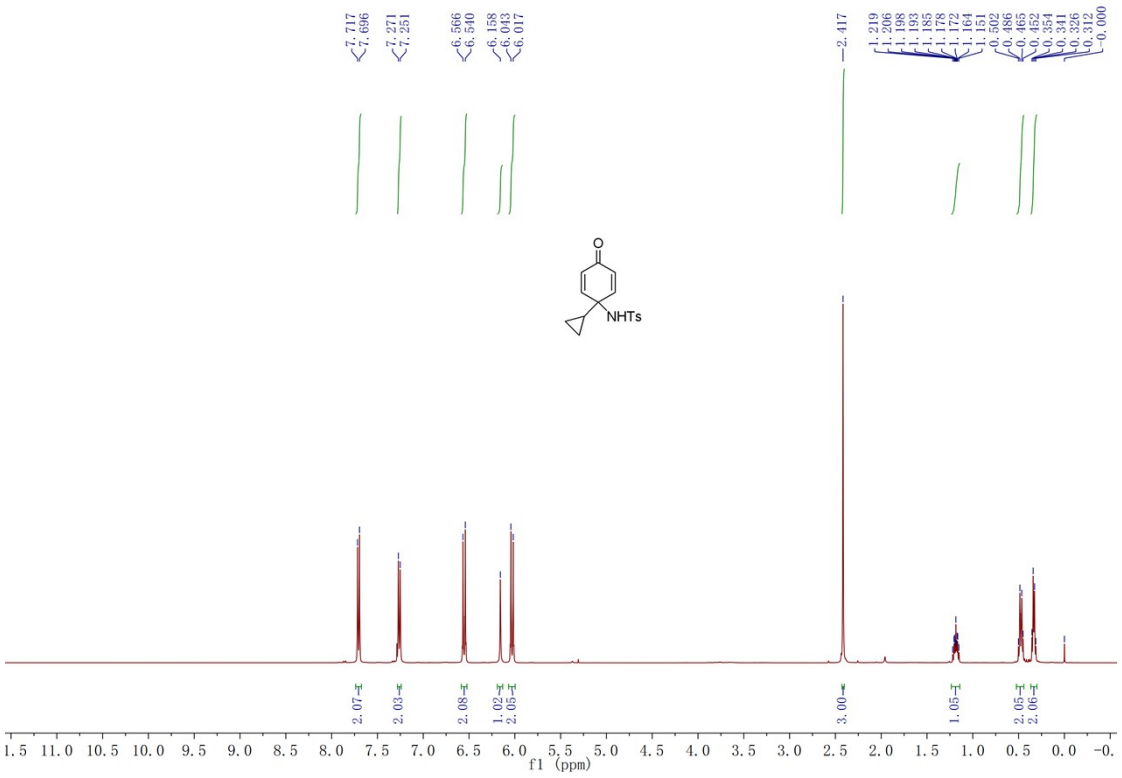






Compound 1g:

8.0 mmol scale, a yellow solid, 71% yield (1.7095 g). M.p.: 160-162 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.31-0.36 (m, 2H), 0.45-0.51 (m, 2H), 1.15-1.22 (m, 1H), 2.42 (s, 3H), 6.03 (d, J = 10.4 Hz, 2H), 6.16 (s, 1H), 6.55 (d, J = 10.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.6, 20.8, 21.5, 56.9, 127.6, 128.8, 129.5, 137.5, 144.0, 148.1, 184.9. IR (neat) ν 3244, 3060, 3008, 2921, 2864, 1663, 1621, 1494, 1431, 1383, 1327, 1239, 1181, 1157, 1090, 1038, 1001, 945, 894, 842, 814, 734, 705, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{16}H_{17}NO_3SNa^{+1}$(M+Na)$^{+}$ requires: 326.0821, Found: 326.0821.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1.198
1.193
1.185
1.178
1.172
1.164
1.151
0.502
0.486
0.465
0.452
0.354
0.341
0.326
0.312
0.000
NHTs
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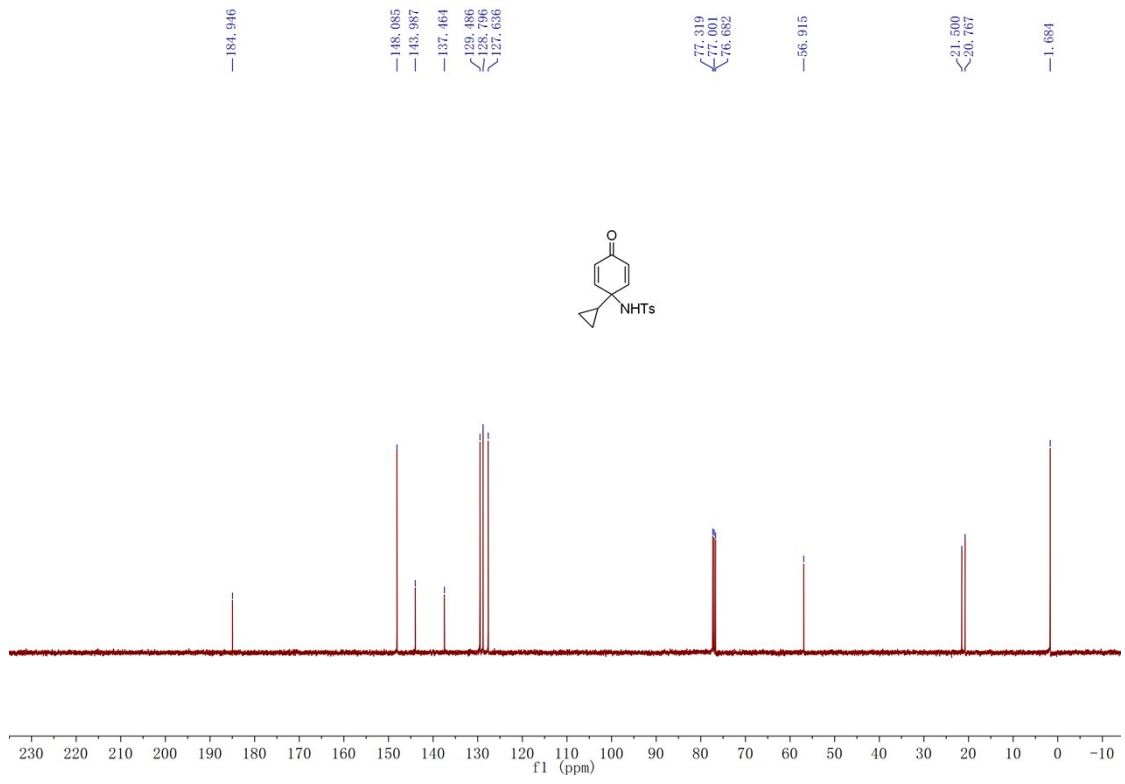
2.03
2.08
1.02
2.05
3.00
1.05
2.05
2.06
f1 (ppm)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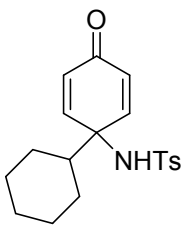
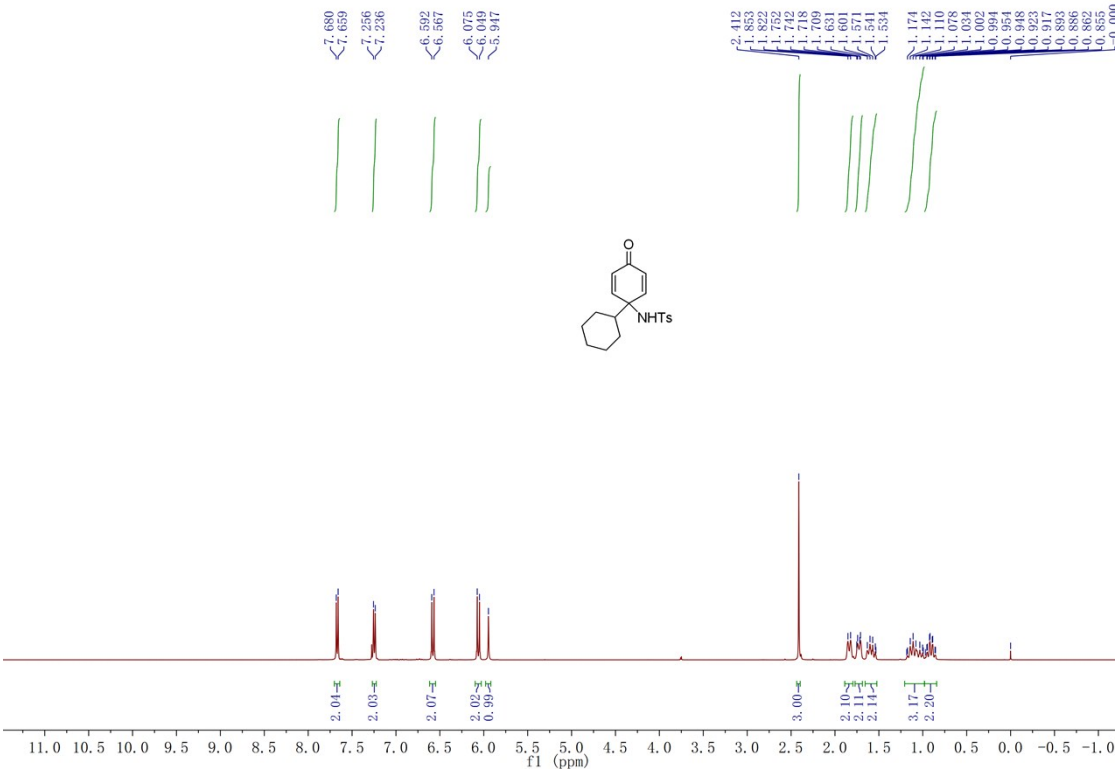
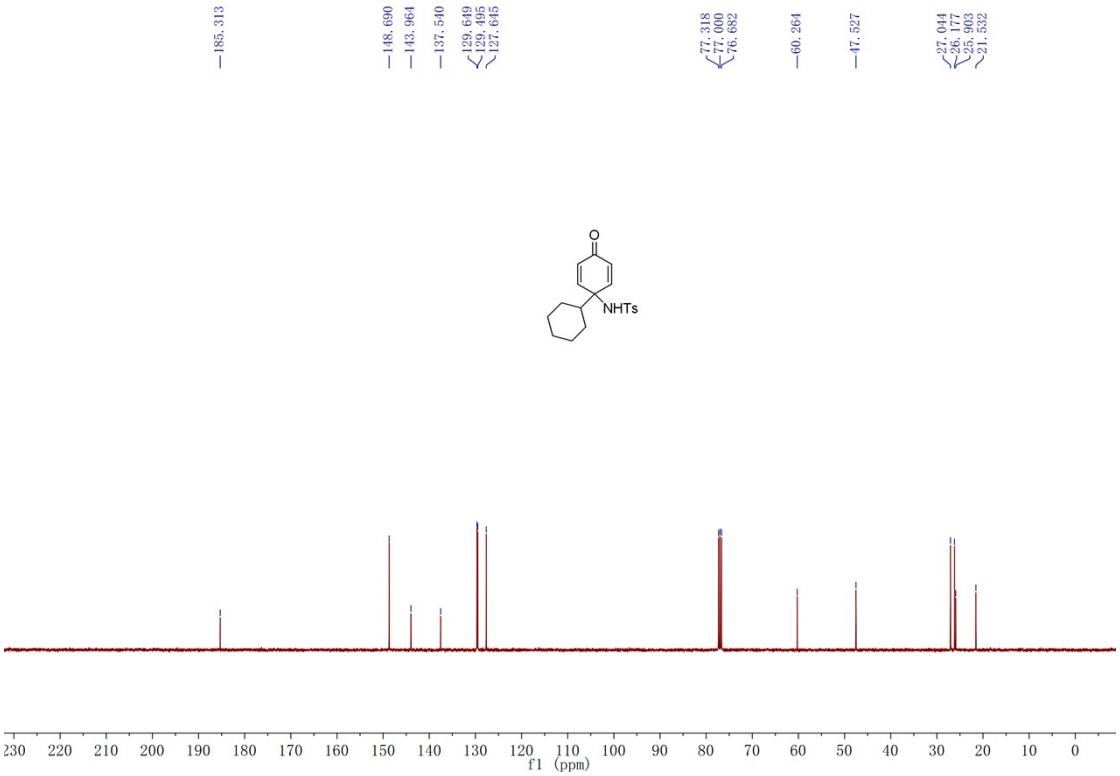
NHTs
f1 (ppm)

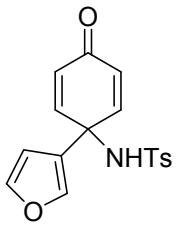

O
NHTs

Compound 1h:

8.0 mmol scale, a white solid, 28% yield (766.7 mg). M.p.: 190-193 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.85-0.97 (m, 2H), 0.99-1.19 (m, 3H), 1.53-1.64 (m, 2H), 1.71-1.76 (m, 2H), 1.82-1.86 (m, 2H), 2.41 (s, 3H), 5.95 (s, 1H), 6.06 (d, *J* = 10.0 Hz, 2H), 6.58 (d, *J* = 10.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 25.9, 26.2, 27.0, 47.5, 60.3, 127.6, 129.5, 129.6, 137.5, 144.0, 148.7, 185.3. IR (neat) ν 3241, 3069, 2930, 2908, 2851, 1775, 1663, 1620, 1455, 1405, 1390, 1364, 1337, 1216, 1179, 1155, 1090, 1064, 1045, 1028, 979, 937, 893, 865, 845, 811, 713, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{27}N_2O_3S^{+1}(M+NH_4)^+$ requires: 363.1737, Found: 363.1733.

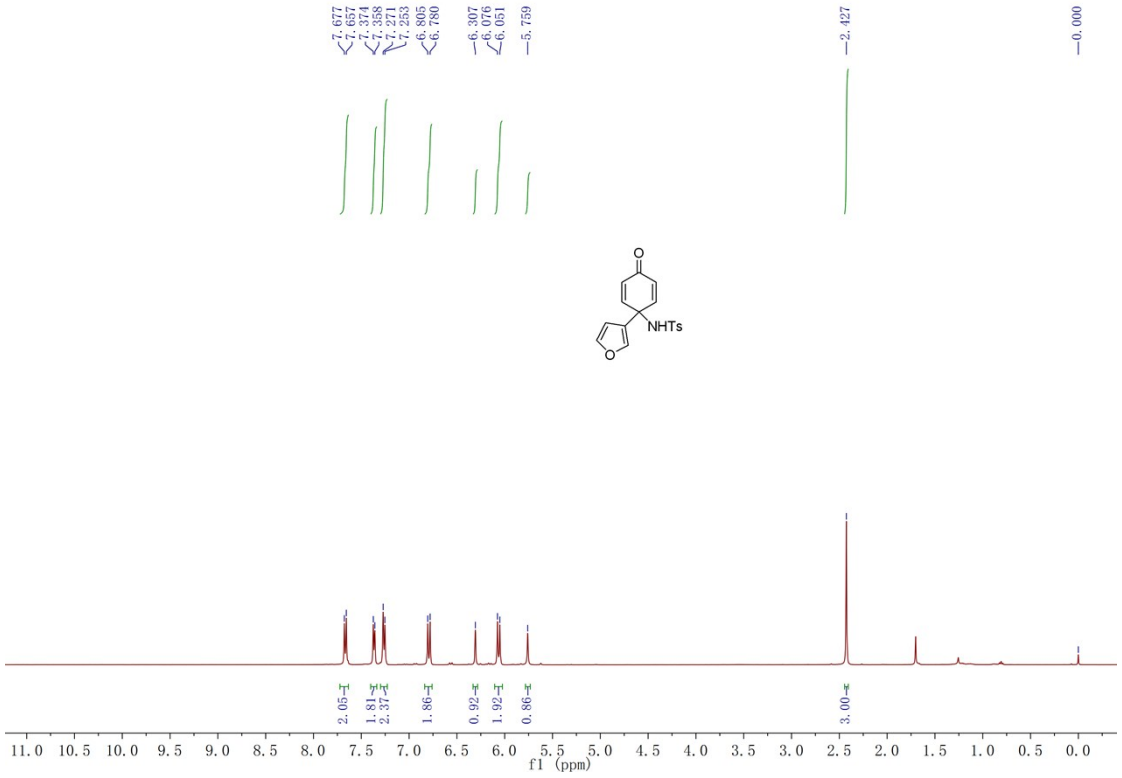






Compound 1p:

10.0 mmol scale, a brown solid, 79% yield (2.5991 g). M.p.: 165-168 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H), 5.76 (s, 1H), 6.06 (d, J = 10.0 Hz, 2H), 6.31 (s, 1H), 6.79 (d, J = 10.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 6.4 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.6, 54.7, 108.2, 124.1, 127.8, 127.9, 129.6, 137.2, 139.6, 144.25, 144.33, 147.9, 184.5. IR (neat) ν 3237, 3144, 3063, 2961, 1924, 2866, 1667, 1625, 1598, 1497, 1396, 1380, 1331, 1159, 1089, 1027, 1005, 938, 913, 873, 836, 814, 774, 734, 705, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}NO_4SNa^{+1}(M+Na)^{+}$ requires: 352.0614, Found: 352.0612.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NHTs
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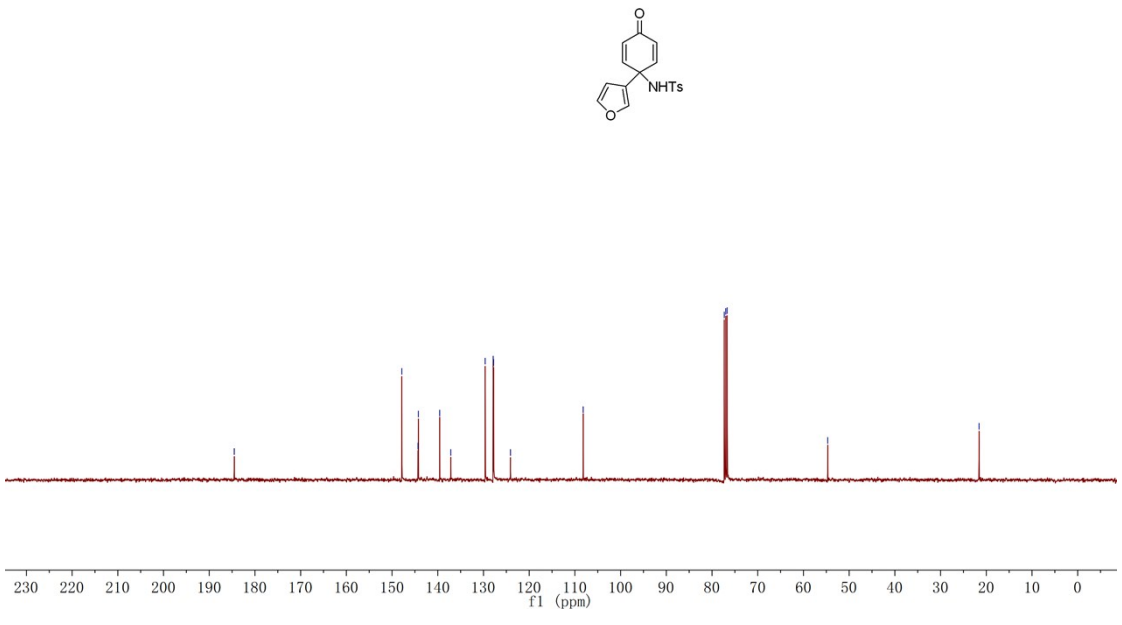
0.92
1.92
0.86
3.00
f1 (ppm)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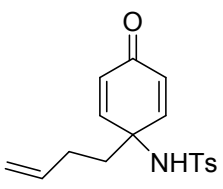
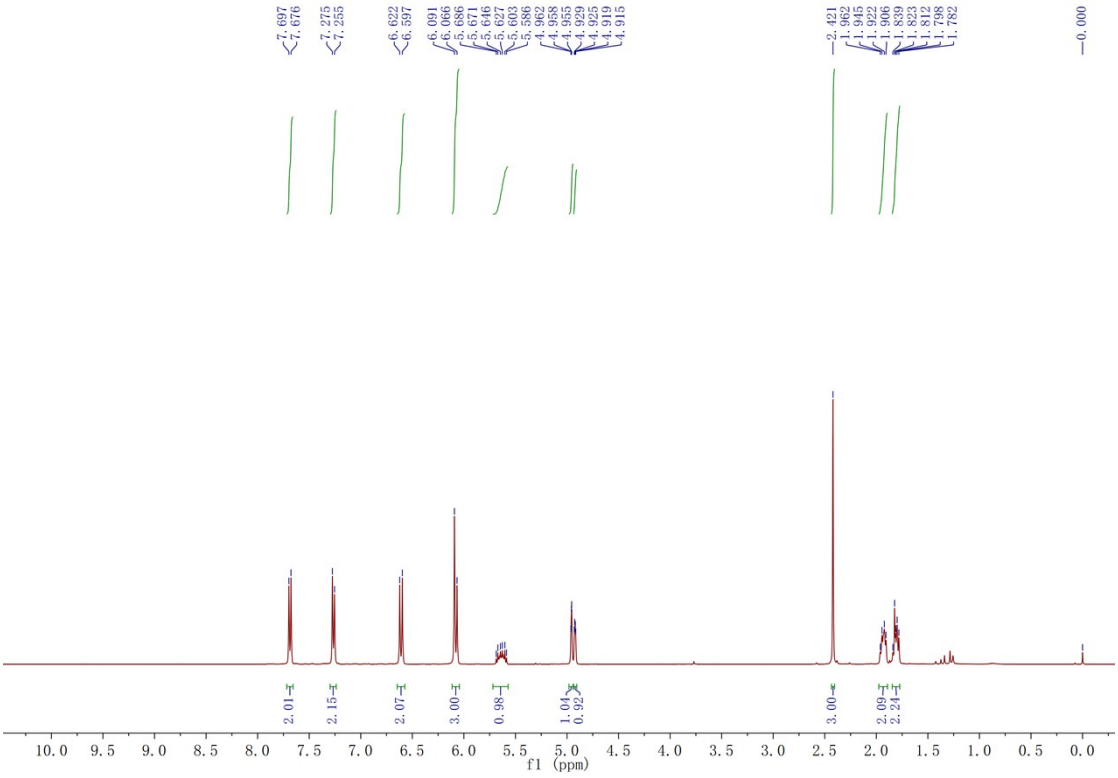
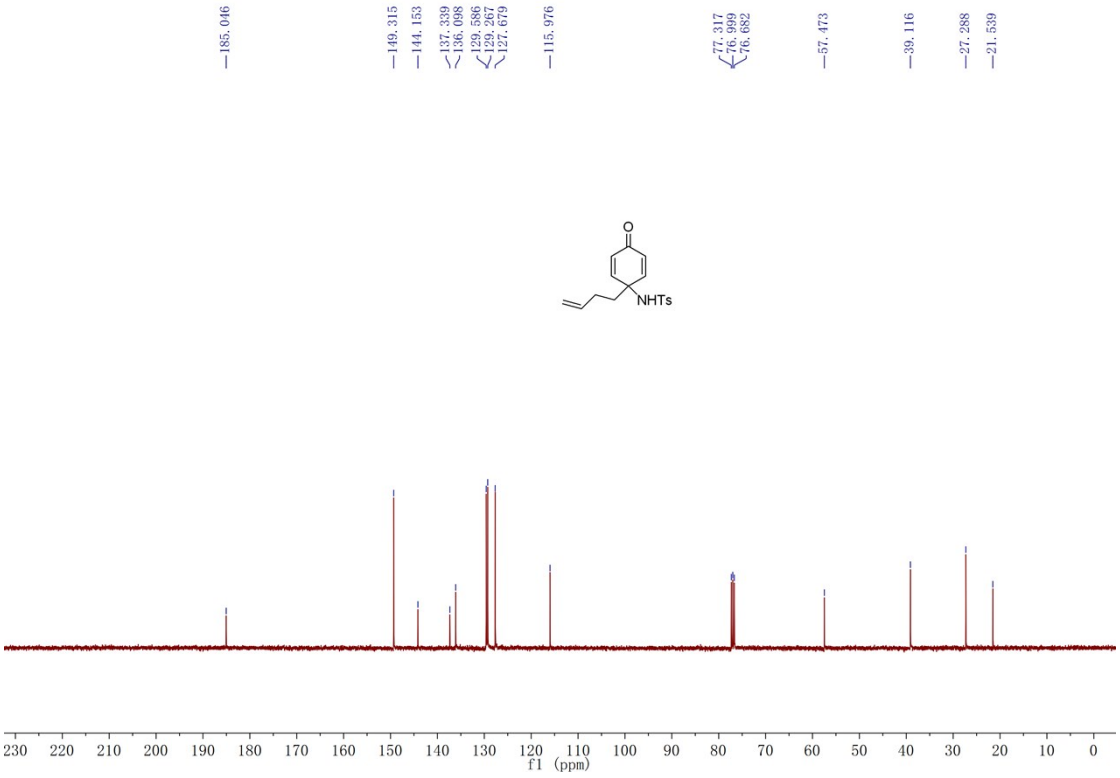
NHTs
f1 (ppm)

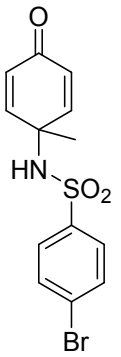

O
NHTs

Compound 1q:

8.0 mmol scale, a white solid, 36% yield (904.6 mg). M.p.: 148-150 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.78-1.84 (m, 2H), 1.90-1.97 (m, 2H), 2.42 (s, 3H), 4.91-4.93 (m, 1H), 4.95-4.97 (m, 1H), 5.58-5.69 (m, 1H), 6.08 (d, *J* = 10.0 Hz, 2H), 6.09 (s, 1H), 6.61 (d, *J* = 10.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 27.3, 39.1, 57.5, 116.0, 127.7, 129.3, 129.6, 136.1, 137.3, 144.2, 149.3, 185.0. IR (neat) ν 3105, 3073, 3002, 2981, 2902, 2919, 2853, 1660, 1614, 1493, 1472, 1444, 1402, 1388, 1341, 1310, 1295, 1253, 1180, 1157, 1123, 1090, 1045, 1022, 999, 966, 921, 869, 843, 811, 711, 652 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{19}NO_3SNa^{+1}(M+Na)^+$ requires: 340.0978, Found: 340.0977.

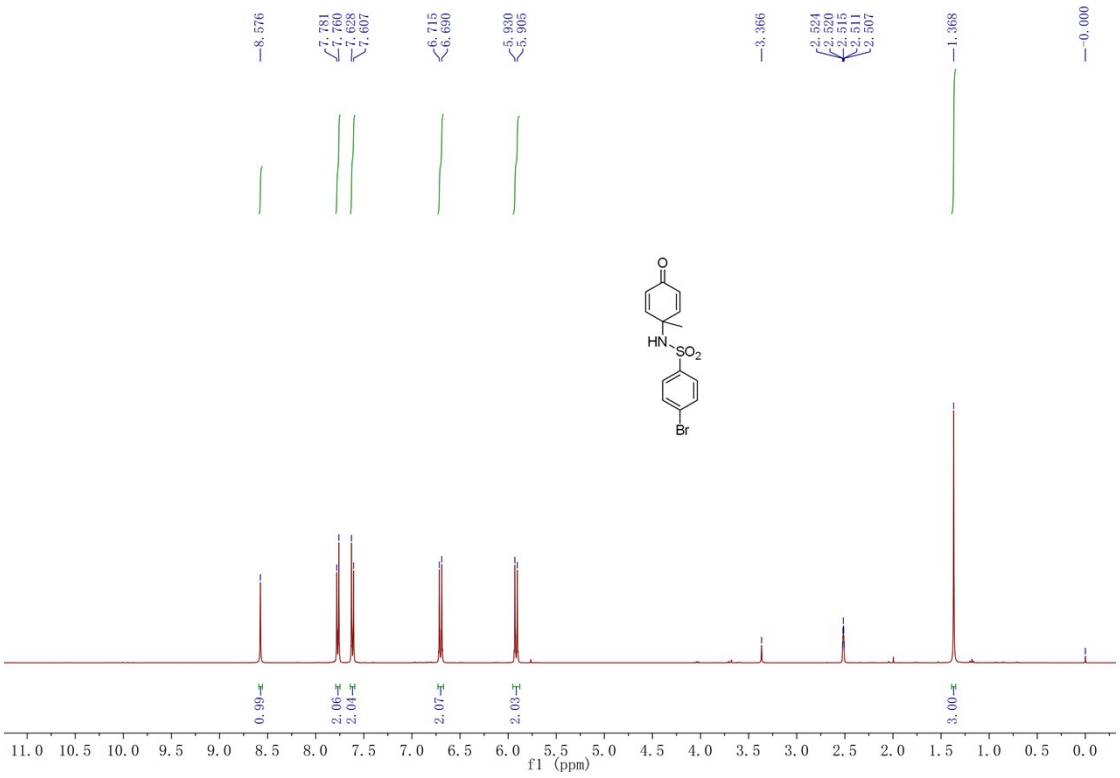






Compound 1r:

8.0 mmol scale, a white solid, 39% yield (1.0710 g). M.p.: 189-191 °C. ^{1}H NMR (*d*^{6}-DMSO, TMS, 400 MHz) δ 1.37 (s, 3H), 5.92 (d, *J* = 10.0 Hz, 2H), 6.70 (d, *J* = 10.0 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 8.58 (s, 1H). ^{13}C NMR (*d*^{6}-DMSO, TMS, 100 MHz) δ 27.5, 54.4, 127.0, 127.3, 129.5, 132.5, 140.9, 152.2, 184.7. IR (neat) ν 3228, 3140, 2945, 2882, 2851, 2764, 2715, 1661, 1616, 1574, 1468, 1427, 1404, 1387, 1365, 1339, 1289, 1249, 1187, 1170, 1157, 1141, 1099, 1088, 1069, 1043, 1008, 998, 987, 966, 941, 882, 864, 829, 813, 779, 738, 702, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{13}H_{13}BrNO_3S^{+1}(M+H)^+$ requires: 341.9794, Found: 341.9790.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7.628
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6.690
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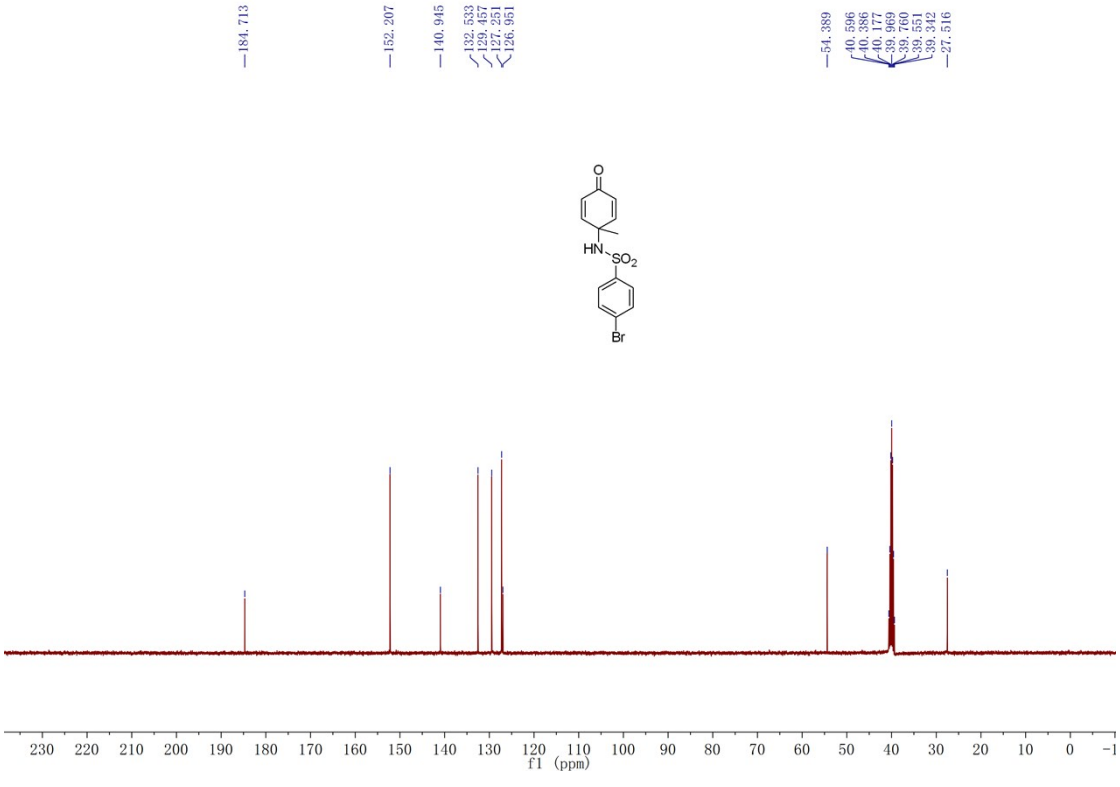
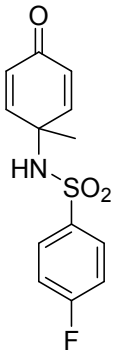
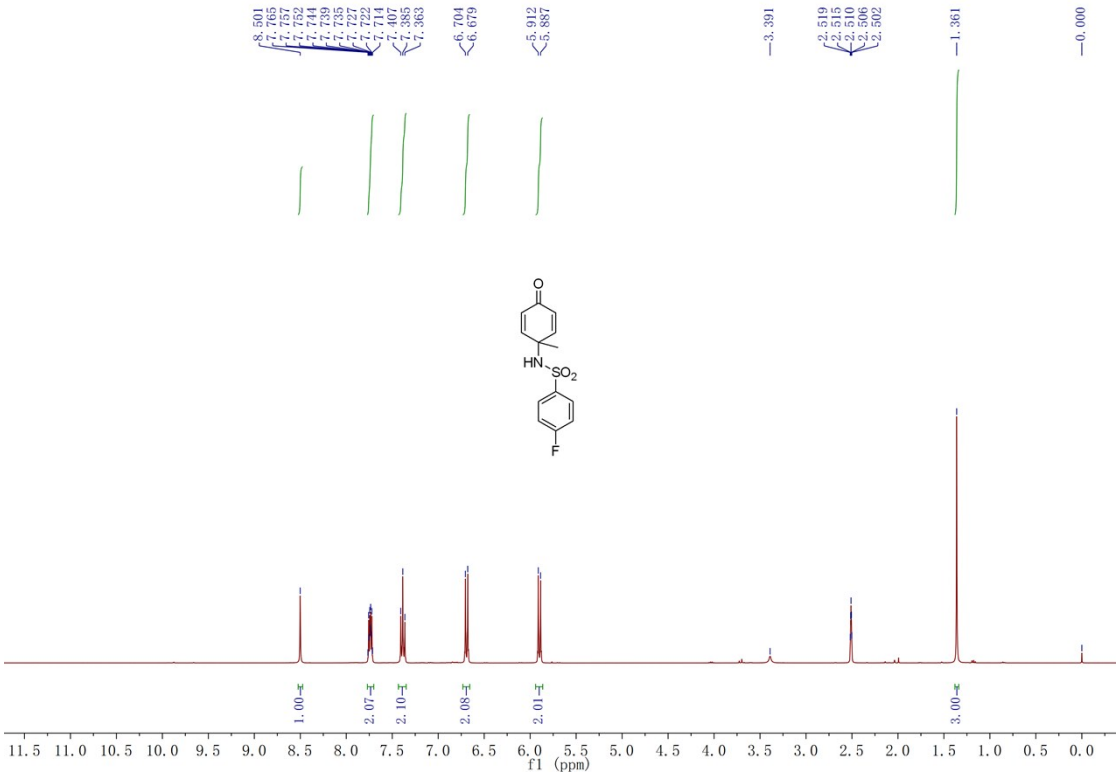
2.515
2.511
2.507
1.368
0.000
O
HN
SO2
Br
0.99
2.06
2.04
2.07
2.03
3.00
f1 (ppm)

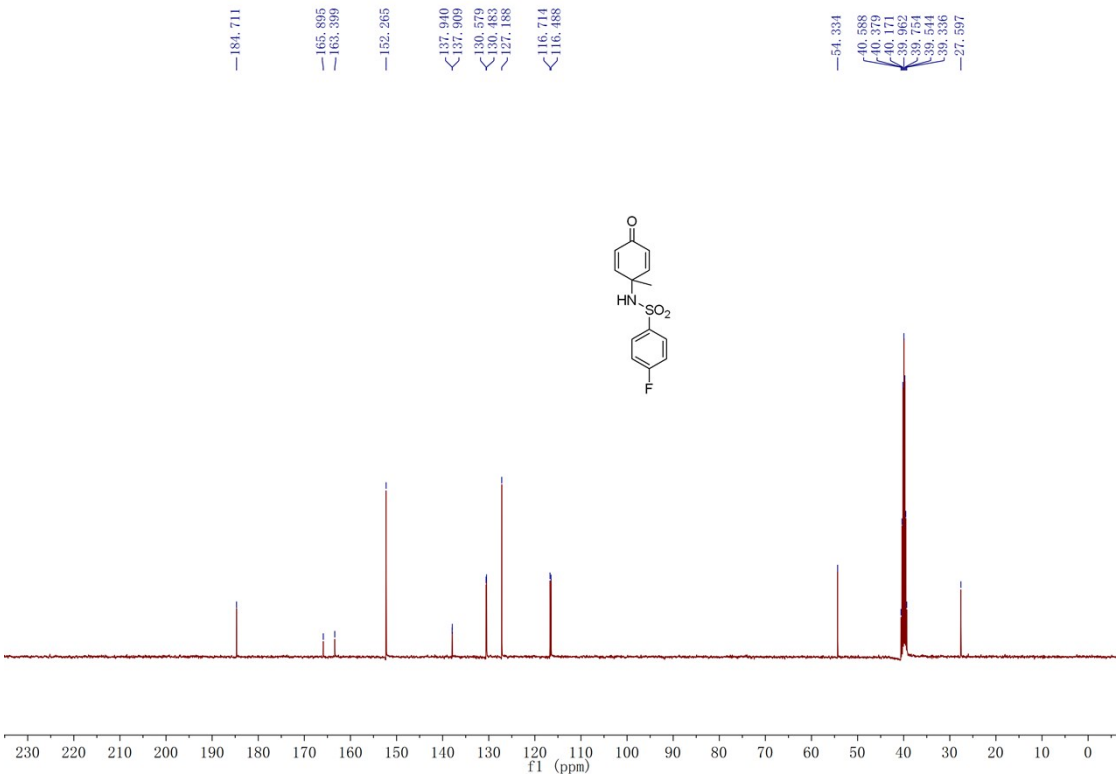

184.713
152.207
140.945
132.533
129.457
127.251
126.951
54.389
40.596
40.386
40.177
39.969
39.760
39.551
39.342
27.516
O
HN
SO2
Br
f1 (ppm)

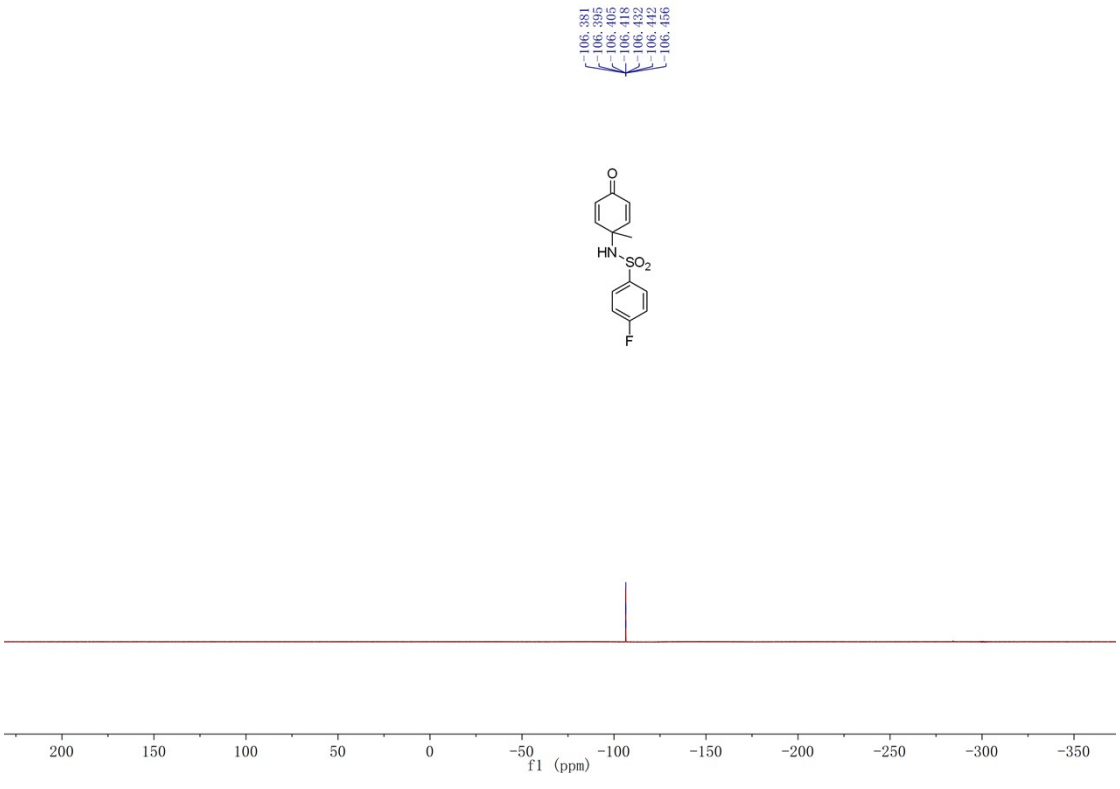


Compound 1s:

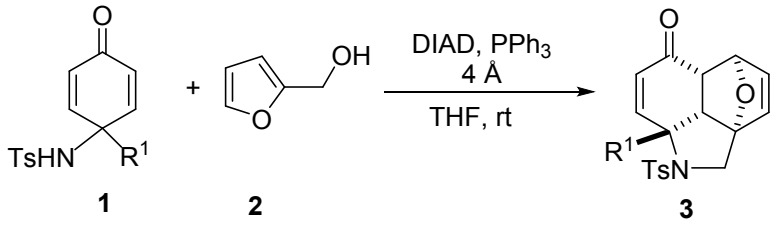
8.0 mmol scale, a yellow solid, 66% yield (1.4845 g). M.p.: 175-178 ^{o}C. ^{1}H NMR (d^{6}-DMSO, TMS, 400 MHz) δ 1.36 (s, 3H), 5.90 (d, J = 10.0 Hz, 2H), 6.69 (d, J = 10.0 Hz, 2H), 7.36-7.41 (m, 2H), 7.71-7.77 (m, 2H), 8.50 (s, 1H). ^{13}C NMR (d^{6}-DMSO, TMS, 100 MHz) δ 27.6, 54.3, 116.6 (d, J = 22.6 Hz), 127.2, 130.5 (d, J = 9.6 Hz), 137.9 (d, J = 3.1 Hz), 152.3, 164.6 (d, J = 249.6 Hz), 184.7. ^{19}F NMR (d^{6}-DMSO, $CFCl_3$, 376 MHz) δ -106.46- -106.38 (m). IR (neat) ν 3222, 3109, 3084, 3065, 3008, 2976, 2932, 2873, 2832, 2817, 2775, 1715, 1665, 1621, 1601, 1589, 1492, 1455, 1441, 1399, 1382, 1337, 1295, 1247, 1223, 1187, 1166, 1154, 1143, 1101, 1091, 1048, 1014, 1002, 988, 940, 861, 842, 822, 747, 709, 674 cm^{-1}. HRMS (ESI) Calcd. for $C_{13}H_{13}FNO_3S^{+1}(M+H)^{+}$ requires: 282.0595, Found: 282.0597.




184.711
165.895
163.399
152.265
137.940
137.909
130.579
130.483
127.188
116.714
116.488
54.334
40.588
40.379
40.171
39.962
39.754
39.544
39.336
27.597
O
HN
SO2
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

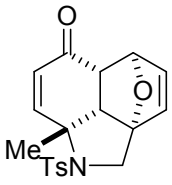

106.381
106.395
106.405
106.418
106.432
106.442
106.456
O
HN
SO2
F
200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)

4. General procedure for the Mitsunobu-initiated cascade polycyclization.



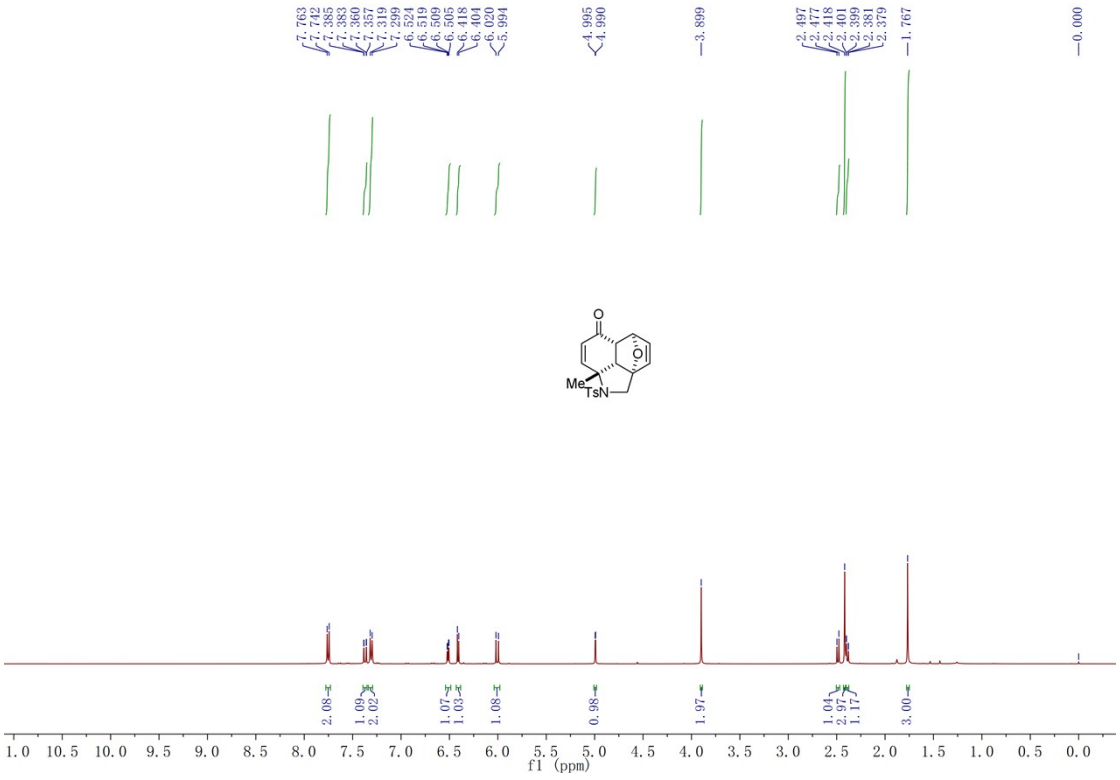
To a solution of **1** (0.3 mmol, 1.0 equiv.), 2-furanylmethanol **2** (39 μL, 0.45 mmol, 1.5 equiv.), triphenylphosphane (94.3 mg, 0.36 mmol, 1.2 equiv.) and 4 Å molecular sieves (200 mg) in THF (3.0 mL), (65 μL, 0.33 mmol, 1.1 equiv.), DIAD was added dropwise at 0 ^{o}C. The resulting mixture was allowed 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 the desired product **3** as a white solid.

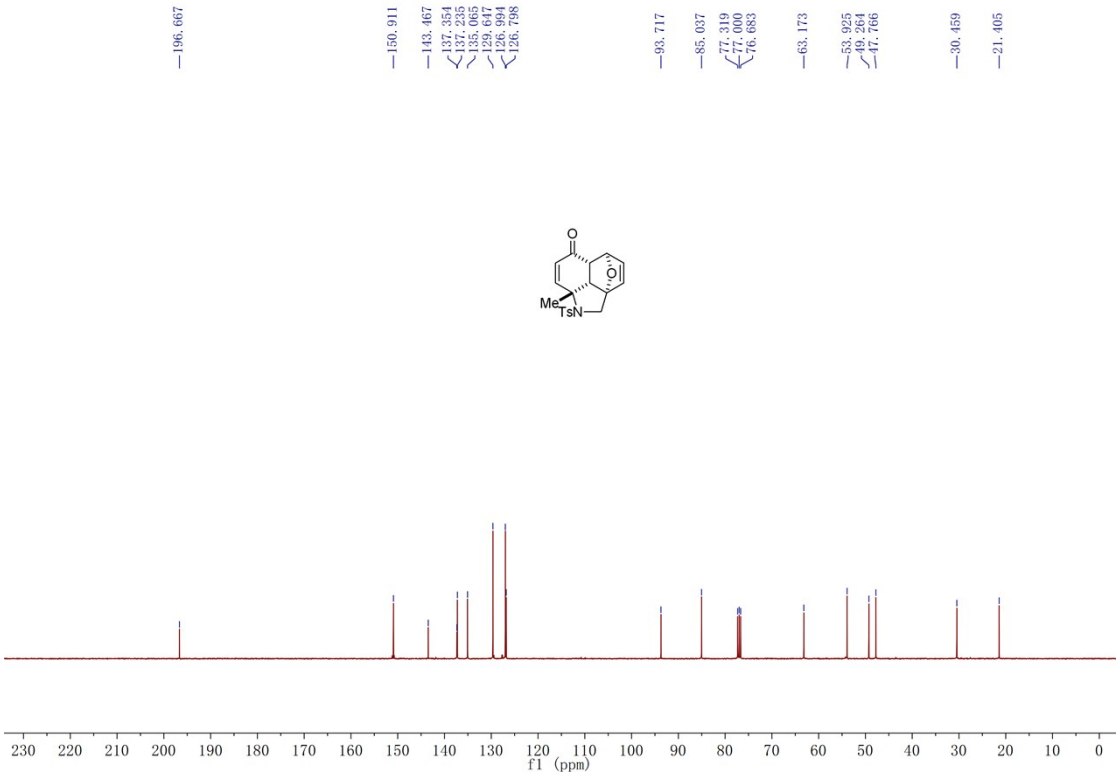
5. Characterization and spectra charts for 3.

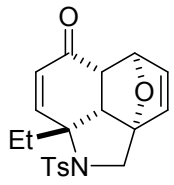


Compound 3a:

0.30 mmol scale, a light yellow solid, 78% yield (83.5 mg). M.p.: 150-153 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.77 (s, 3H), 2.39 (dd, *J* = 0.8 Hz, 8.0 Hz, 1H), 2.42 (s, 3H), 2.49 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 2H), 4.99 (d, *J* = 2.0 Hz, 1H), 6.01 (d, *J* = 10.4 Hz, 1H), 6.41 (d, *J* = 5.6 Hz, 1H), 6.51 (dd, *J* = 2.0 Hz, 5.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.37 (dd, *J* = 0.8 Hz, 10.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 30.5, 47.8, 49.3, 53.9, 63.2, 85.0, 93.7, 126.8, 127.0, 129.6, 135.1, 137.2, 137.4, 143.5, 150.9, 196.7. IR (neat) ν 3073, 3052, 3031, 3004, 2974, 2916, 2906, 2848, 1671, 1620, 1595, 1495, 1474, 1391, 1375, 1335, 1313, 1273, 1233, 1200, 1155, 1143, 1121, 1104, 1090, 1065, 1055, 1017, 987, 925, 910, 877, 858, 841, 818, 768, 725, 712, 689, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{23}N_2O_4S^{+1}(M+NH_4)^+$ requires: 375.1373, found: 375.1373.

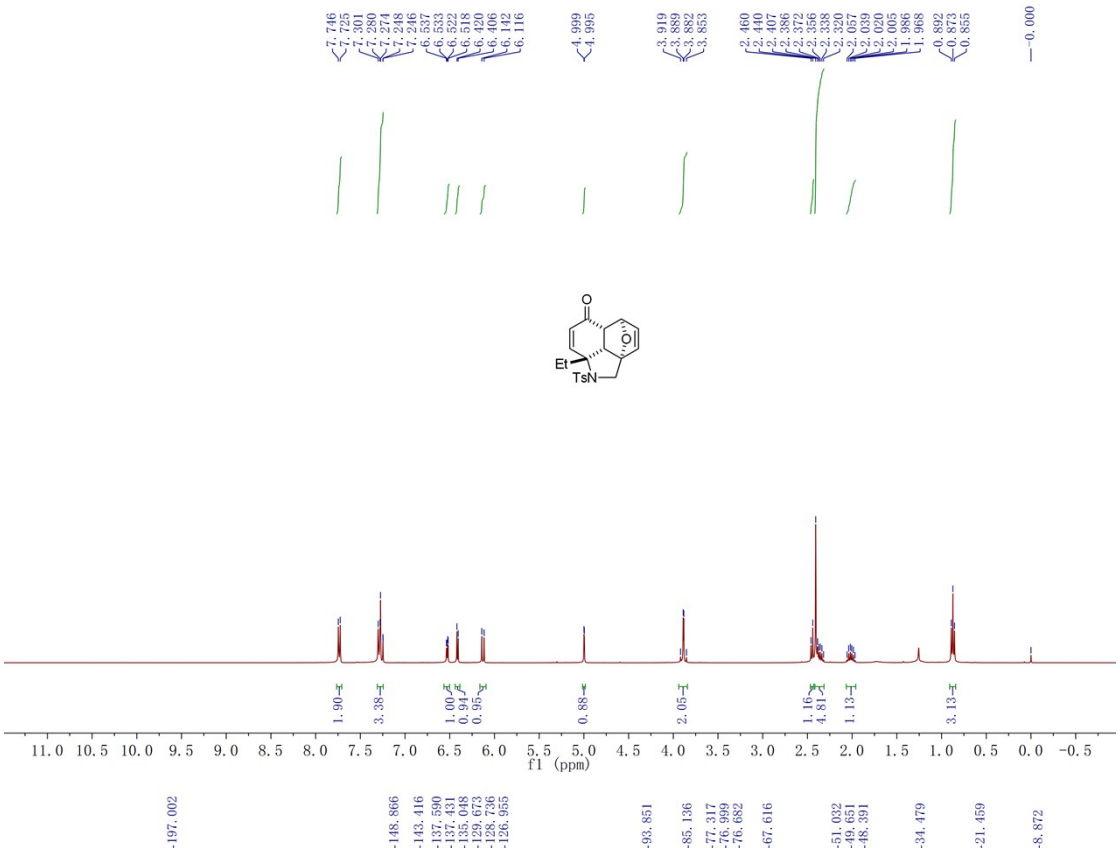


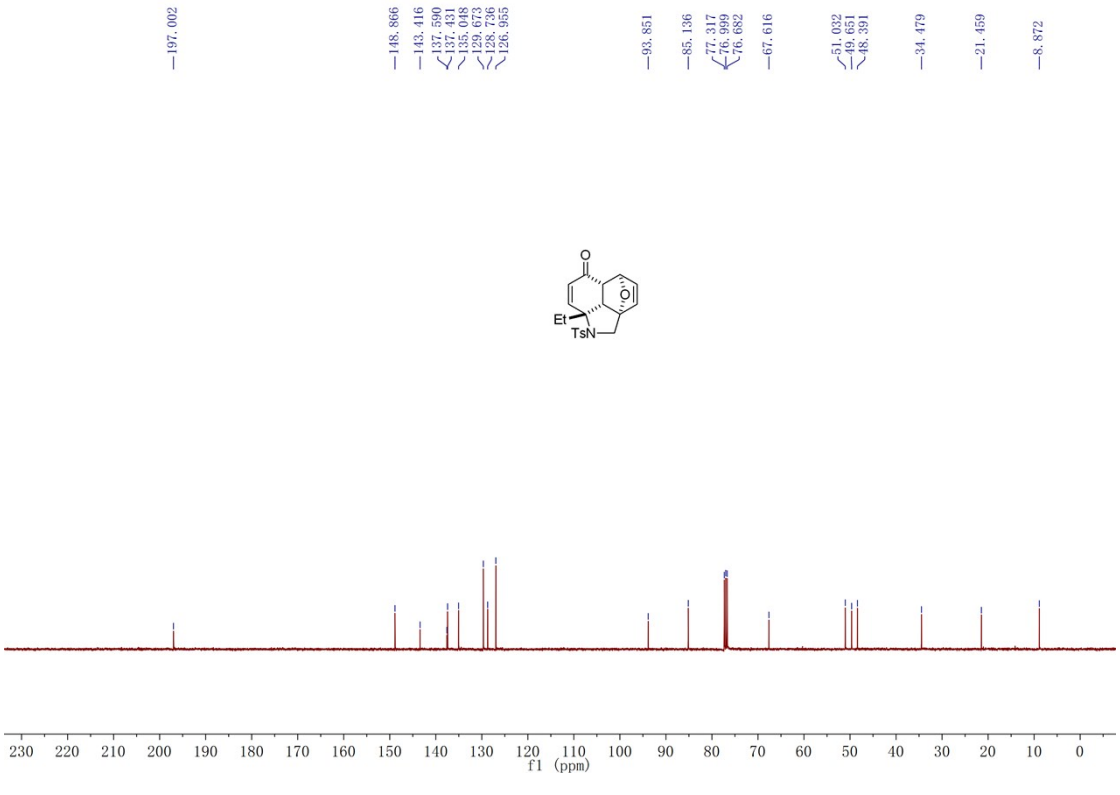


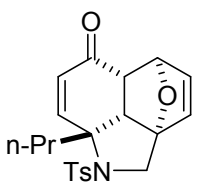


Compound 3b:

0.30 mmol scale, a white solid, 77% yield (85.2 mg). M.p.: 128-130 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.96-2.06 (m, 1H), 2.32-2.41 (m, 5H), 2.45 (d, *J* = 8.0 Hz, 1H), 3.87 (d, *J* = 12.0 Hz, 1H), 3.90 (d, *J* = 12.0 Hz, 1H), 5.00 (d, *J* = 1.6 Hz, 1H), 6.13 (d, *J* = 10.4 Hz, 1H), 6.41 (d, *J* = 5.6 Hz, 1H), 6.53 (dd, *J* = 1.6 Hz, 5.6 Hz, 1H), 7.24-7.31 (m, 3H), 7.74 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 8.9, 21.5, 34.5, 48.4, 49.7, 51.0, 67.6, 85.1, 93.9, 127.0, 128.7, 129.7, 135.0, 137.4, 137.6, 143.4, 148.9, 197.0. IR (neat) ν 3057, 2971, 2937, 2927, 2877, 2848, 1667, 1597, 1494, 1460, 1391, 1321, 1262, 1155, 1100, 1063, 991, 951, 925, 888, 866, 841, 813, 777, 733, 722, 706, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{25}N_2O_4S^{+1}(M+NH_4)^+$ requires: 389.1530, found: 389.1528.

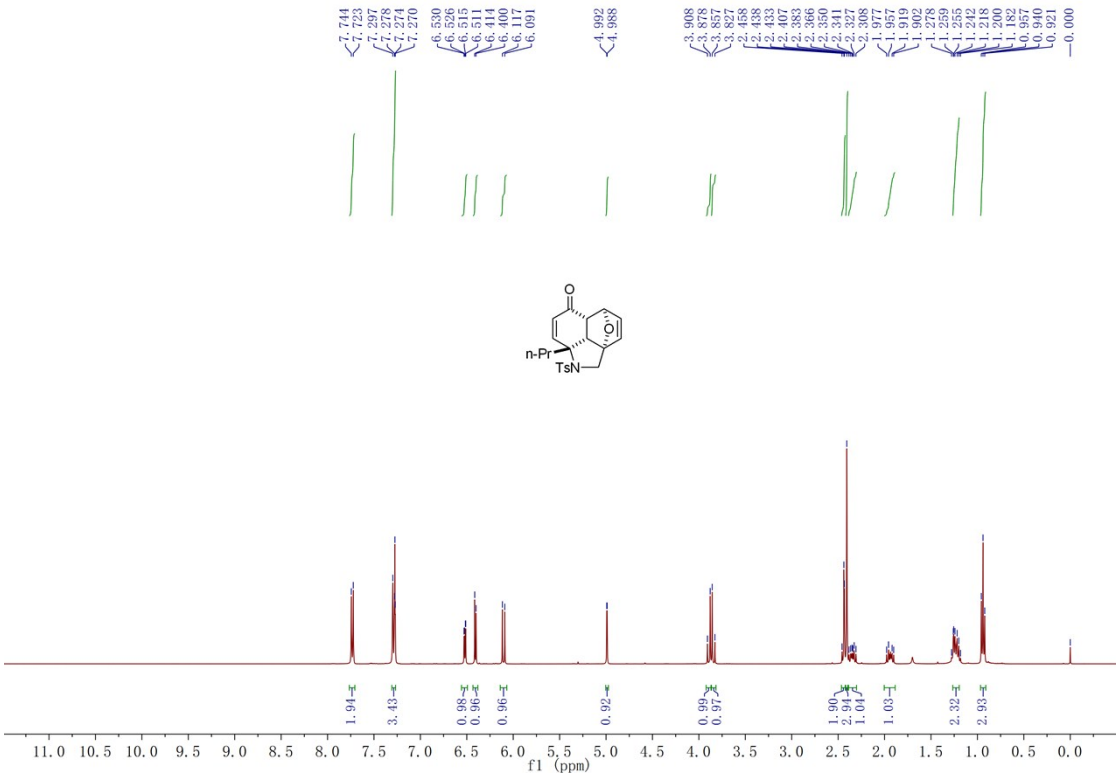

7.746
7.725
7.301
7.280
7.274
7.248
7.246
6.537
6.533
6.522
6.518
6.420
6.406
6.142
6.116
4.999
4.995
3.919
3.889
3.882
3.853
2.460
2.440
2.407
2.386
2.372
2.356
2.338
2.320
2.057
2.039
2.020
2.005
1.986
1.968
0.892
0.873
0.855
-0.000
O
Et
TsN
1.90
3.38
1.00
0.94
0.95
0.88
2.05
1.16
4.81
1.13
3.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

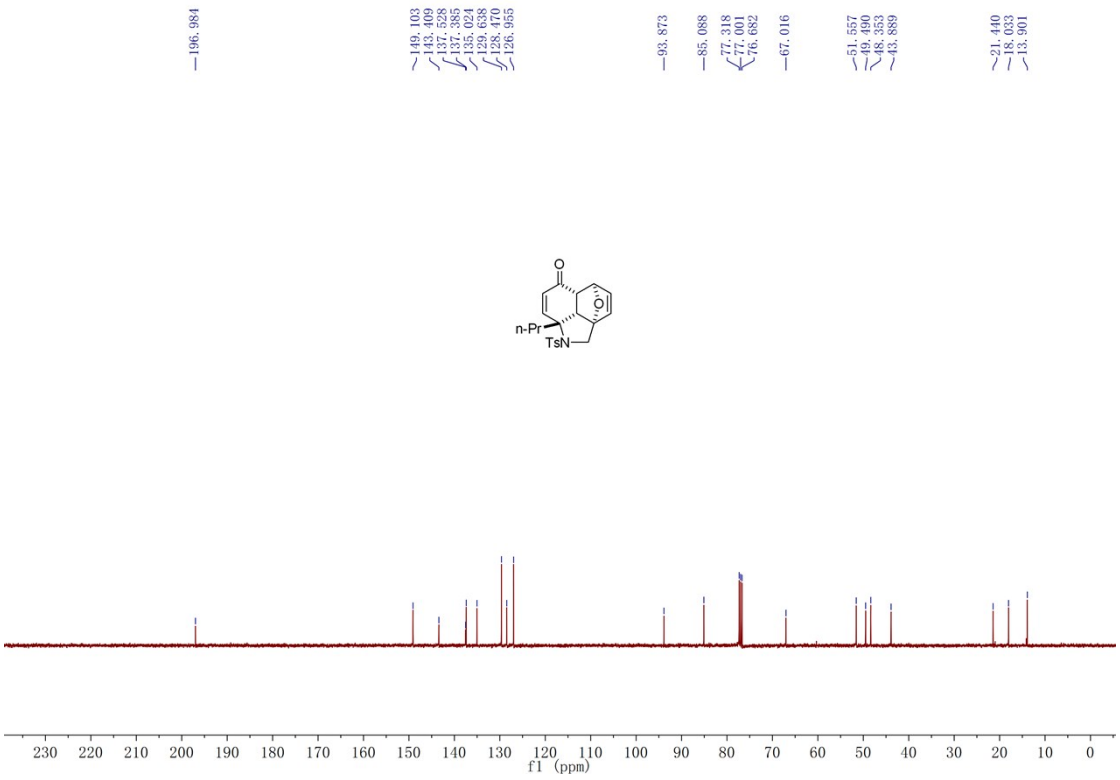

197.002
148.866
143.416
137.590
137.431
135.048
129.673
128.736
126.955
93.851
85.136
77.317
76.999
76.682
67.616
51.032
49.651
48.391
34.479
21.459
8.872
O
Et
TsN
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

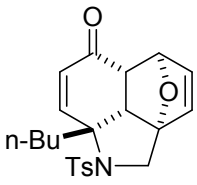

O
n-Pr
TsN

Compound 3c:

0.30 mmol scale, a white solid, 73% yield (84.4 mg). M.p.: 148-150 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.18-1.28 (m, 2H), 1.90-1.98 (m, 1H), 2.30-2.39 (m, 1H), 2.41 (s, 3H), 2.43-2.46 (m, 2H), 3.84 (d, *J* = 12.0 Hz, 1H), 3.89 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 1.6 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 6.41 (d, *J* = 5.6 Hz, 1H), 6.52 (dd, *J* = 1.6 Hz, 5.6 Hz, 1H), 7.27-7.30 (m, 3H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.9, 18.0, 21.4, 43.9, 48.4, 49.5, 51.6, 67.0, 85.1, 93.9, 127.0, 128.5, 129.6, 135.0, 137.4, 137.5, 143.4, 149.1, 197.0. IR (neat) ν 3052, 2960, 2927, 2873, 1667, 1597, 1494, 1458, 1390, 1338, 1319, 1231, 1155, 1142, 1103, 1087, 1070, 992, 926, 874, 845, 814, 780, 734, 706, 673 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{27}N_2O_4S^{+1}(M+NH_4)^+$ requires: 403.1686, found: 403.1684.

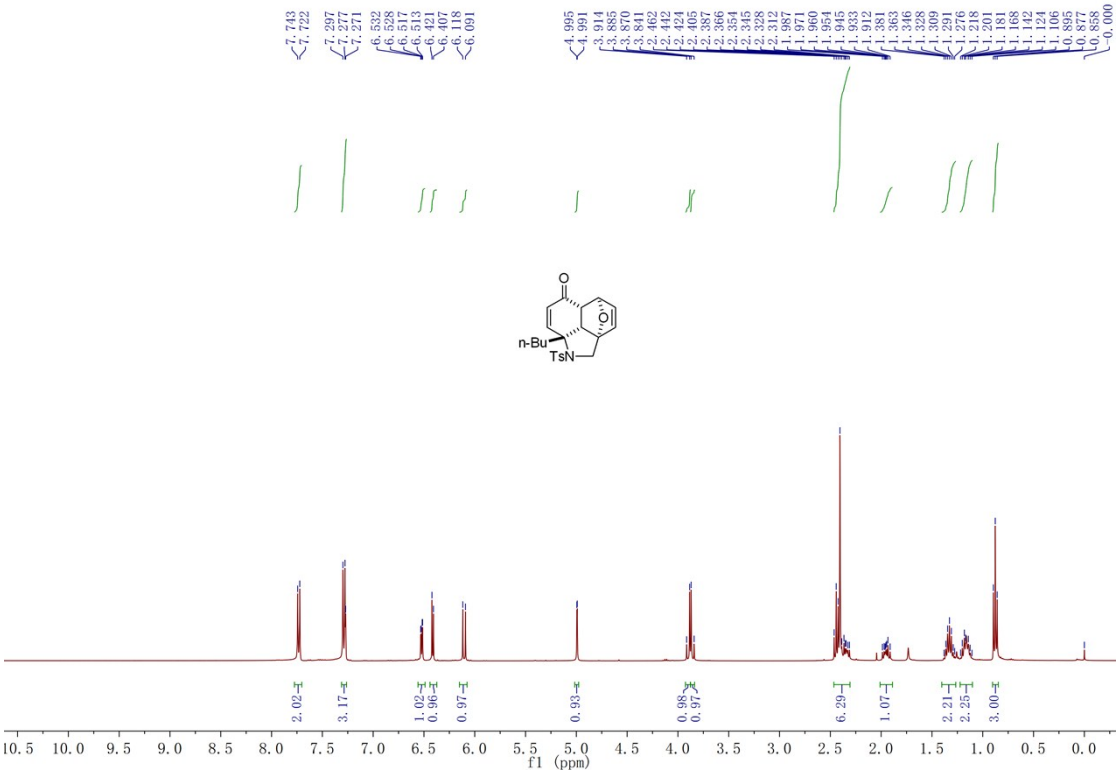






Compound 3d:

0.30 mmol scale, a white solid, 84% yield (100.3 mg). M.p.: 102-103 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.10-1.22 (m, 2H), 1.27-1.39 (m, 2H), 1.91-1.99 (m, 1H), 2.31-2.47 (m, 6H), 3.86 (d, *J* = 11.6 Hz, 1H), 3.90 (d, *J* = 11.6 Hz, 1H), 4.99 (d, *J* = 1.6 Hz, 1H), 6.10 (d, *J* = 10.8 Hz, 1H), 6.41 (d, *J* = 5.6 Hz, 1H), 6.52 (dd, *J* = 1.6 Hz, 5.6 Hz, 1H), 7.27-7.30 (m, 3H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.9, 21.4, 22.6, 26.7, 41.5, 48.4, 49.5, 51.5, 57.0, 85.1, 93.9, 127.0, 128.5, 129.6, 135.0, 137.4, 137.6, 143.4, 149.2, 197.0. IR (neat) ν 3055, 2957, 2929, 2870, 1668, 1597, 1494, 1461, 1390, 1320, 1265, 1155, 1104, 1088, 1070, 993, 925, 866, 844, 814, 779, 733, 706, 673 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{29}N_2O_4S^{+1}(M+NH_4)^+$ requires: 417.1843, found: 417.1842.


7.743
7.722
7.297
7.277
7.271
6.532
6.528
6.517
6.513
6.421
6.407
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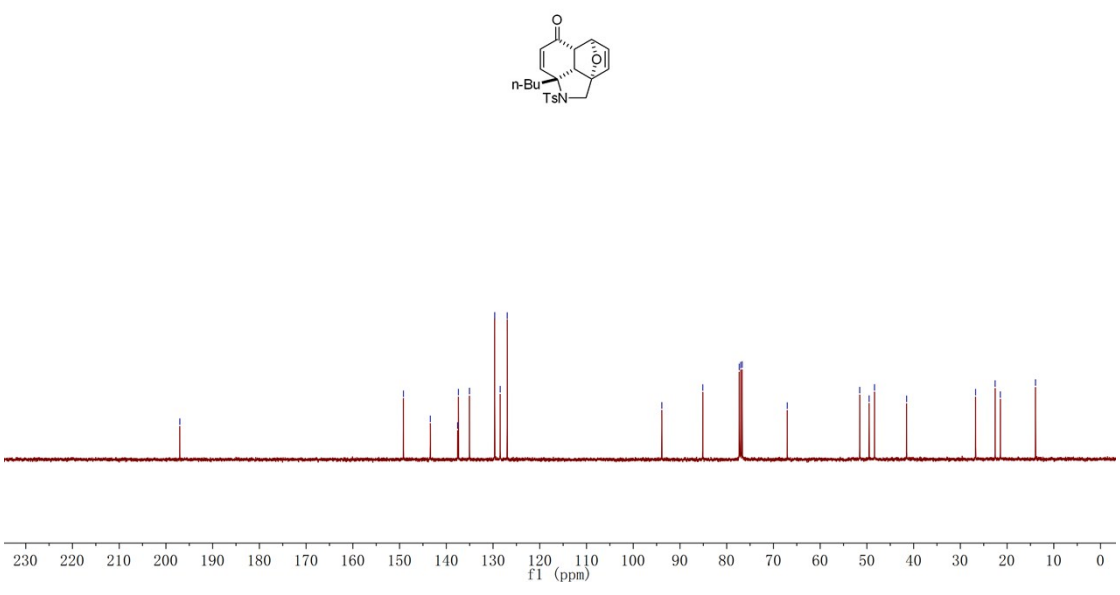
6.091
4.995
4.991
3.914
3.885
3.870
3.841
2.462
2.442
2.424
2.405
2.387
2.366
2.354
2.345
2.328
2.312
1.987
1.971
1.960
1.954
1.945
1.933
1.912
1.381
1.363
1.346
1.328
1.309
1.291
1.276
1.218
1.201
1.181
1.168
1.142
1.124
1.106
0.895
0.877
0.858
0.000
n-Bu
TsN
2.02
3.17
1.02
0.96
0.97
0.93
0.98
0.97
6.29
1.07
2.21
2.25
3.00
f1 (ppm)


197.025
149.174
143.414
137.587
137.404
135.040
129.643
128.467
126.965
93.882
85.117
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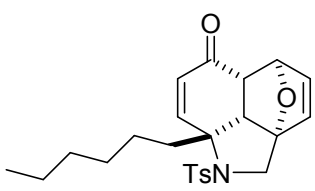
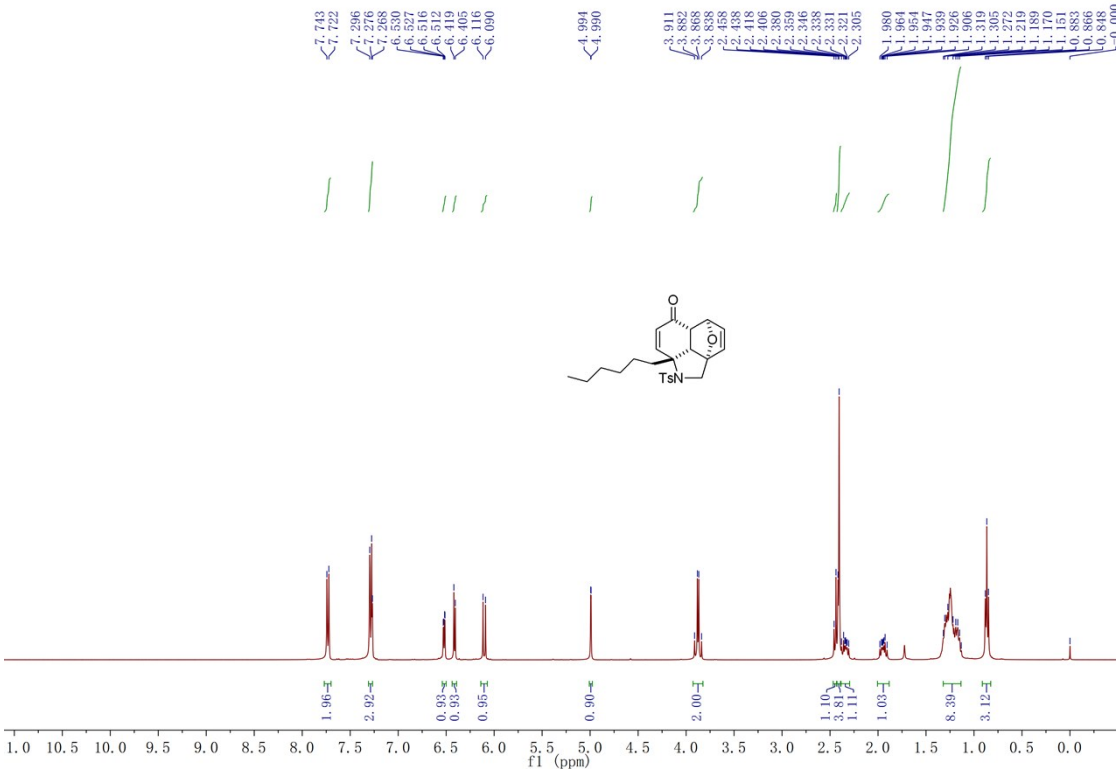
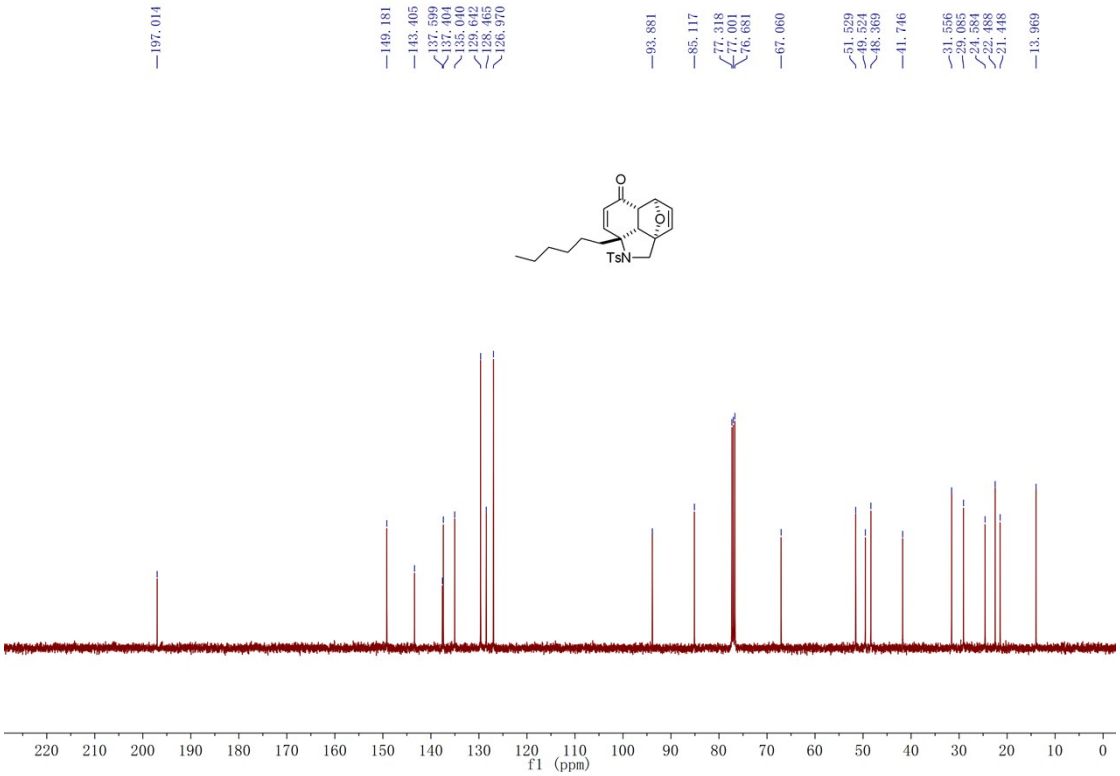
77.000
76.681
67.036
51.538
49.524
48.371
41.502
26.734
22.564
21.448
13.917
n-Bu
TsN
f1 (ppm)

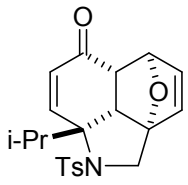

O
O
TsN

Compound 3e:

0.30 mmol scale, a white solid, 64% yield (81.8 mg). M.p.: 92-93 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.13-1.32 (m, 8H), 1.90-1.98 (m, 1H), 2.30-2.36 (m, 1H), 2.38-2.42 (m, 4H), 2.45 (d, *J* = 8.0 Hz, 1H), 3.85 (d, *J* = 12.0 Hz, 1H), 3.89 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 1.2 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 6.41 (d, *J* = 5.6 Hz, 1H), 6.52 (dd, *J* = 1.6 Hz, 5.6 Hz, 1H), 7.26-7.30 (m, 3H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 14.0, 21.4, 22.5, 24.6, 29.1, 31.6, 41.7, 48.4, 49.5, 51.5, 67.1, 85.1, 93.9, 127.0, 128.5, 129.6, 135.0, 137.4, 137.6, 143.4, 149.2, 197.0. IR (neat) ν 3055, 2953, 2926, 2857, 1669, 1597, 1494, 1461, 1390, 1320, 1259, 1155, 1106, 1093, 1068, 988, 925, 870, 845, 814, 780, 724, 706, 673 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{33}N_2O_4S^{+1}(M+NH_4)^+$ requires: 445.2156, found: 445.2154.

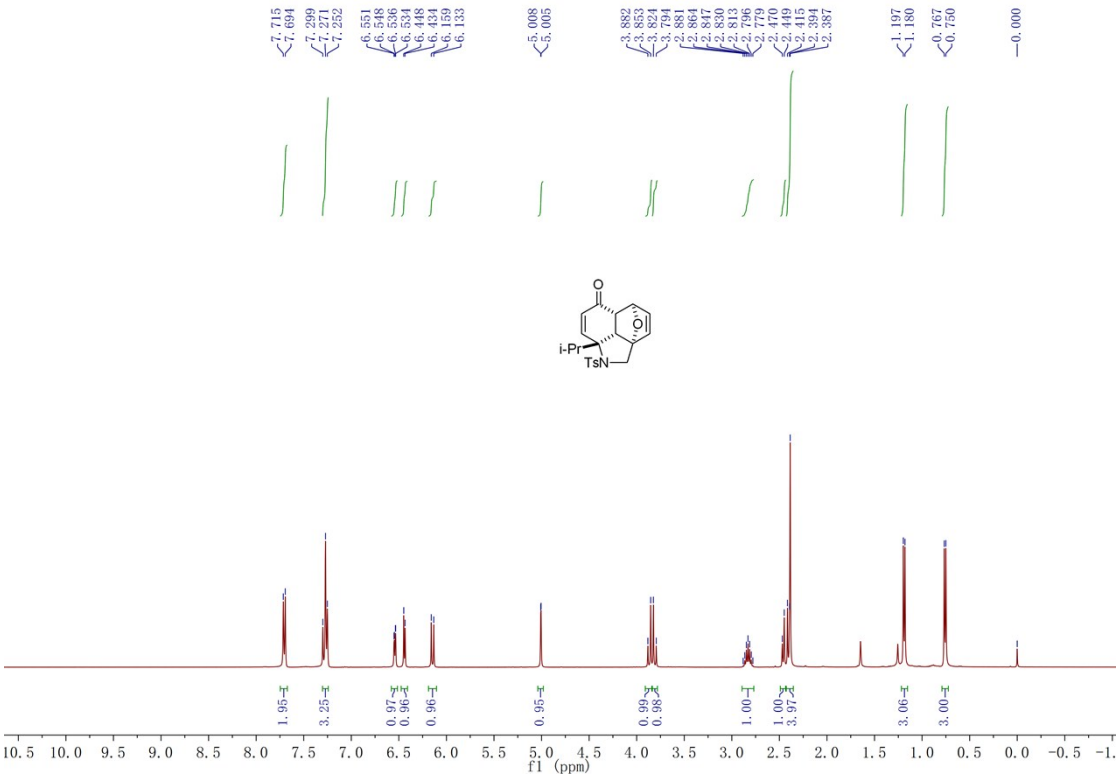






Compound 3f:

0.30 mmol scale, a light yellow solid, 53% yield (61.6 mg). M.p.: 57-60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.76 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 2.39 (s, 3H), 2.40 (d, *J* = 8.4 Hz, 1H), 2.46 (d, *J* = 8.4 Hz, 1H), 2.77-2.89 (m, 1H), 3.81 (d, *J* = 12.0 Hz, 1H), 3.87 (d, *J* = 12.0 Hz, 1H), 5.01 (d, *J* = 1.2 Hz, 1H), 6.15 (d, *J* = 10.4 Hz, 1H), 6.44 (d, *J* = 5.6 Hz, 1H), 6.54 (dd, *J* = 1.2 Hz, 5.6 Hz, 1H), 7.25-7.30 (m, 3H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 16.1, 17.9, 21.5, 36.3, 45.7, 48.4, 50.4, 70.8, 85.2, 94.0, 126.8, 129.0, 129.7, 135.0, 137.6, 137.7, 143.3, 148.9, 197.2. IR (neat) ν 3060,2963, 2924, 2877, 2851, 1667, 1597, 1494, 1460, 1391, 1331, 1315, 1265, 1155, 1105, 1086, 1062, 994, 962, 924, 900, 863, 839, 813, 734, 720, 707, 672 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{27}N_2O_4S^{+1}(M+NH_4)^+$ requires: 403.1686, found: 403.1680.


7.715
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7.252
6.551
6.548
6.536
6.534
6.448
6.434
6.159
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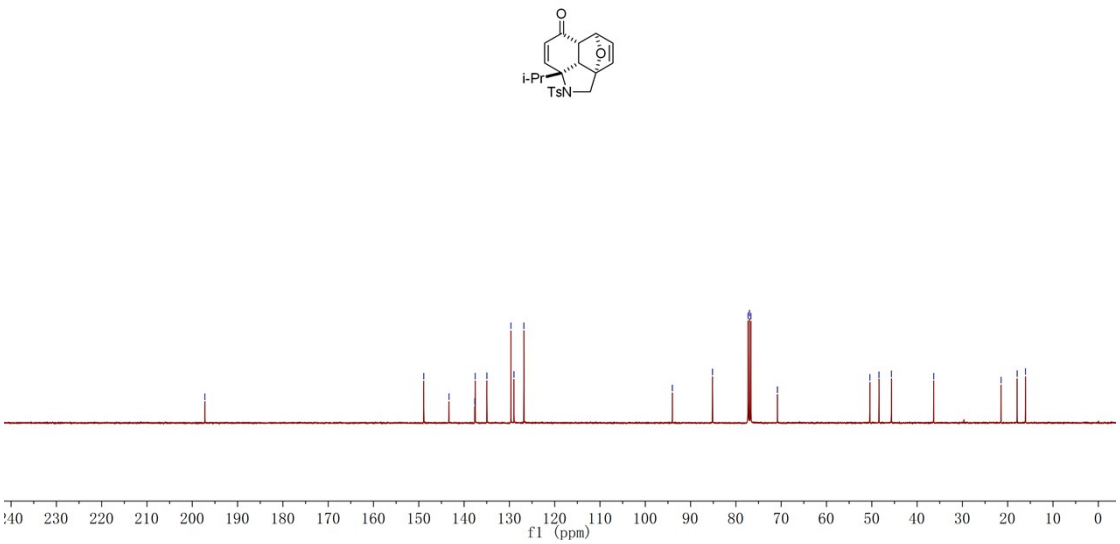
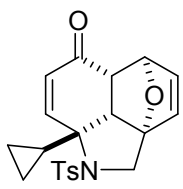
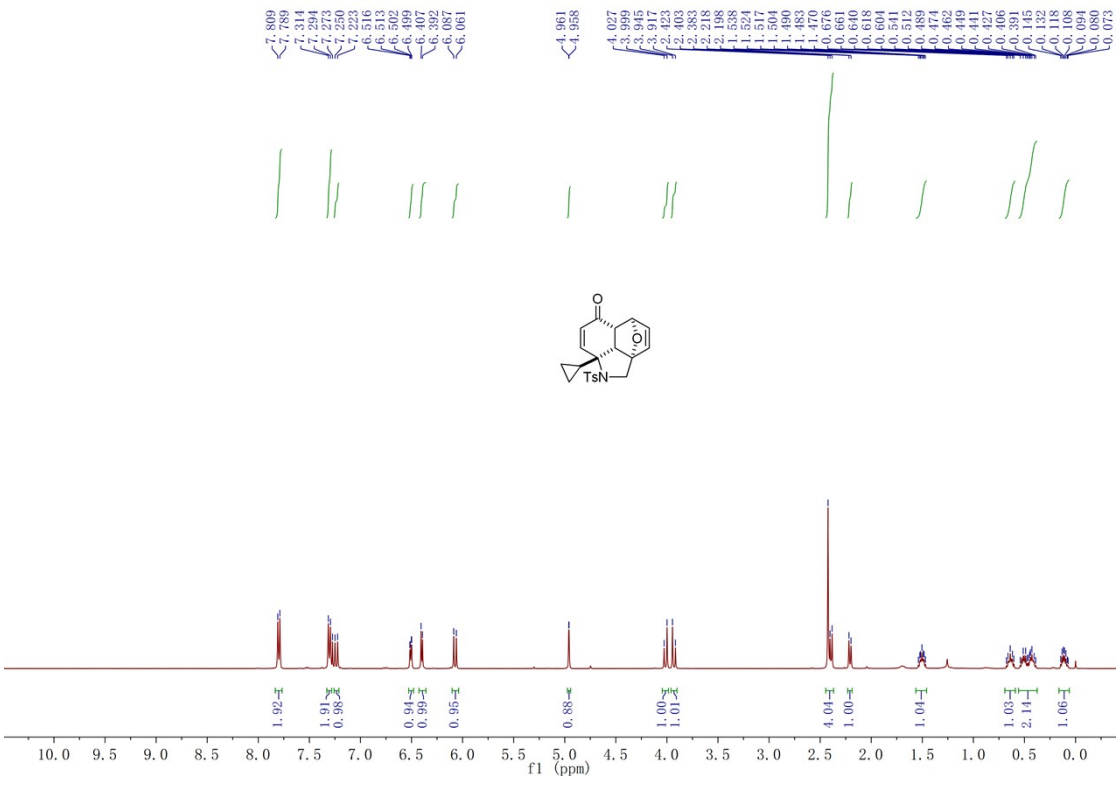
5.008
5.005
3.882
3.853
3.824
3.794
2.881
2.864
2.847
2.830
2.813
2.796
2.779
2.470
2.449
2.415
2.394
2.387
1.197
1.180
0.767
0.750
0.000
i-Pr
TsN
1.95
3.25
0.97
0.96
0.96
0.95
0.99
0.98
1.00
1.00
3.97
3.06
3.00
f1 (ppm)

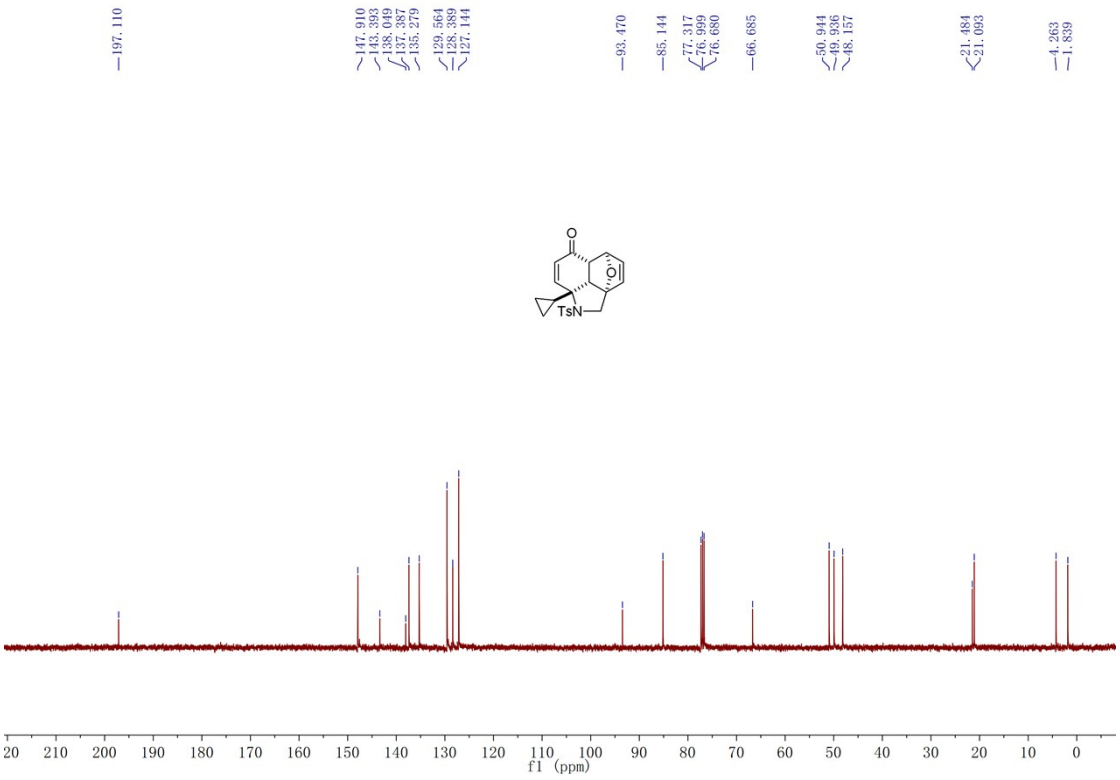

197.226
148.902
143.333
137.636
137.552
134.966
129.655
128.987
126.798
94.028
85.162
77.317
77.000
76.683
70.823
50.426
48.417
45.665
36.326
21.463
17.907
16.077
i-Pr
TsN
f1 (ppm)

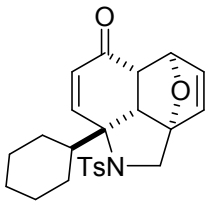

TsN

Compound 3g:

0.30 mmol scale, a white solid, 70% yield (80.2 mg). M.p.: 128-129 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.07-0.15 (m, 1H), 0.39-0.55 (m, 2H), 0.60-0.68 (m, 1H), 1.47-1.54 (m, 1H), 2.21 (d, *J* = 8.0 Hz, 1H), 2.39 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H), 3.93 (d, *J* = 11.2 Hz, 1H), 4.01 (d, *J* = 11.2 Hz, 1H), 4.96 (d, *J* = 1.2 Hz, 1H), 6.07 (d, *J* = 10.4 Hz, 1H), 6.40 (d, *J* = 6.0 Hz, 1H), 6.51 (dd, *J* = 1.2 Hz, 6.0 Hz, 1H), 7.24 (d, *J* = 10.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 1.8, 4.3, 21.1, 21.5, 48.2, 49.9, 50.9, 66.7, 85.1, 93.5, 127.1, 128.4, 129.6, 135.3, 137.4, 138.0, 143.4, 147.9, 197.1. IR (neat) ν 3084, 3060, 3006, 2953, 2924, 2869, 1667, 1597, 1494, 1461, 1390, 1335, 1265, 1154, 1133, 1095, 1065, 1019, 989, 924, 879, 864, 839, 814, 777, 733, 721, 707, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{22}NO_4S^{+1}(M+H)^+$ requires: 384.1264, found: 384.1272.

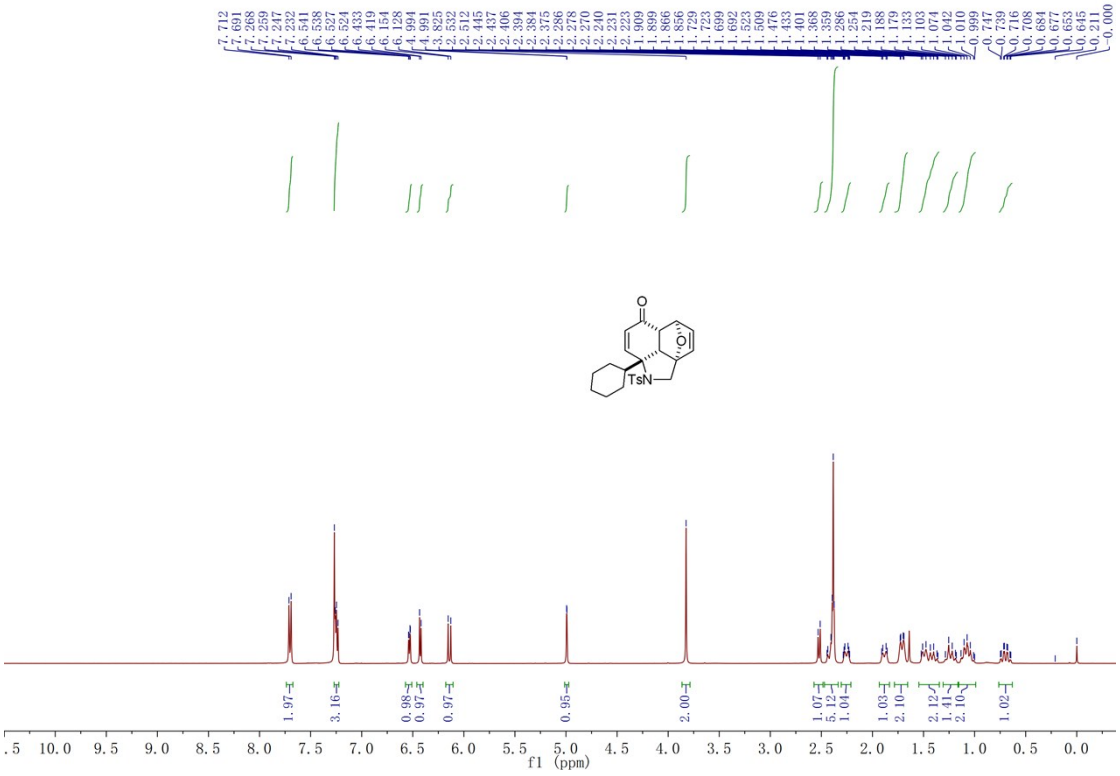






Compound 3h:

0.30 mmol scale, a white solid, 79% yield (100.3 mg). M.p.: 80-83 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.64-0.75 (m, 1H), 0.99-1.14 (m, 2H), 1.17-1.29 (m, 1H), 1.35-1.53 (m, 2H), 1.69-1.73 (m, 2H), 1.85-1.91 (m, 1H), 2.22-2.29 (m, 1H), 2.37-2.45 (m, 5H), 2.52 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 2H), 4.99 (d, *J* = 1.2 Hz, 1H), 6.14 (d, *J* = 10.4 Hz, 1H), 6.43 (d, *J* = 5.6 Hz, 1H), 6.53 (dd, *J* = 1.2 Hz, 5.6 Hz, 1H), 7.23-7.27 (m, 3H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 25.7, 25.8, 26.2, 28.1, 46.2, 46.9, 48.3, 50.4, 70.6, 85.1, 94.0, 126.7, 129.1, 129.6, 134.9, 137.5, 137.8, 143.3, 148.8, 197.3. IR (neat) ν 3057, 2927, 2853, 1666, 1597, 1494, 1450, 1392, 1329, 1317, 1305, 1267, 1232, 1185, 1154, 1114, 1097, 1070, 1047, 993, 962, 924, 906, 892, 869, 852, 841, 829, 814, 780, 734, 709, 666 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{31}N_2O_4S^{+1}(M+NH_4)^+$ requires: 443.1999, found: 443.1993.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7.691
7.268
7.259
7.247
7.232
6.541
6.538
6.527
6.524
6.433
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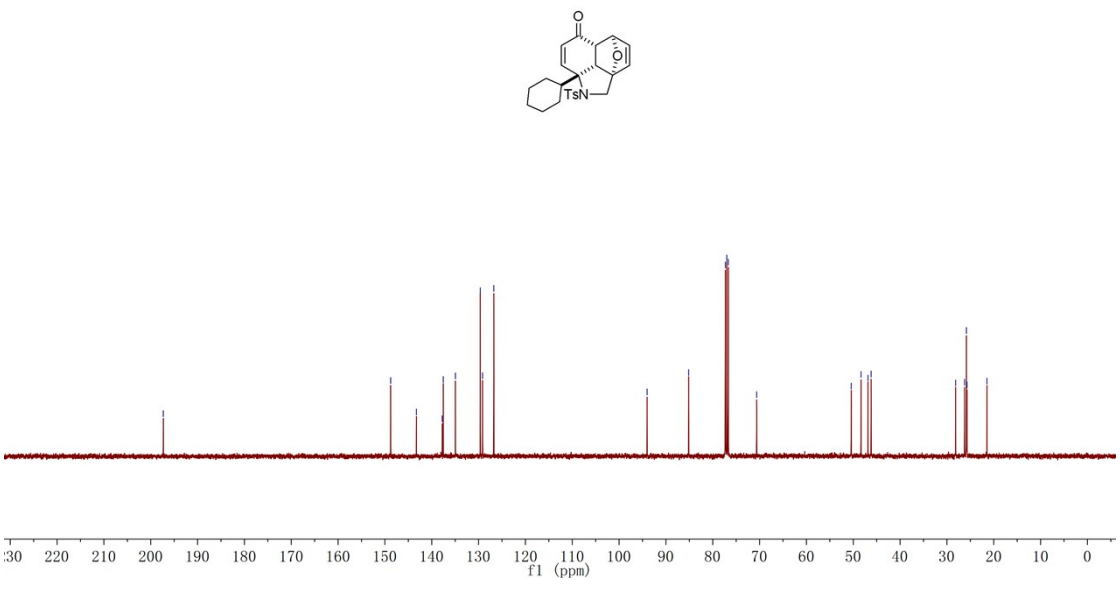
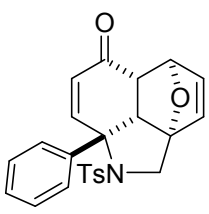
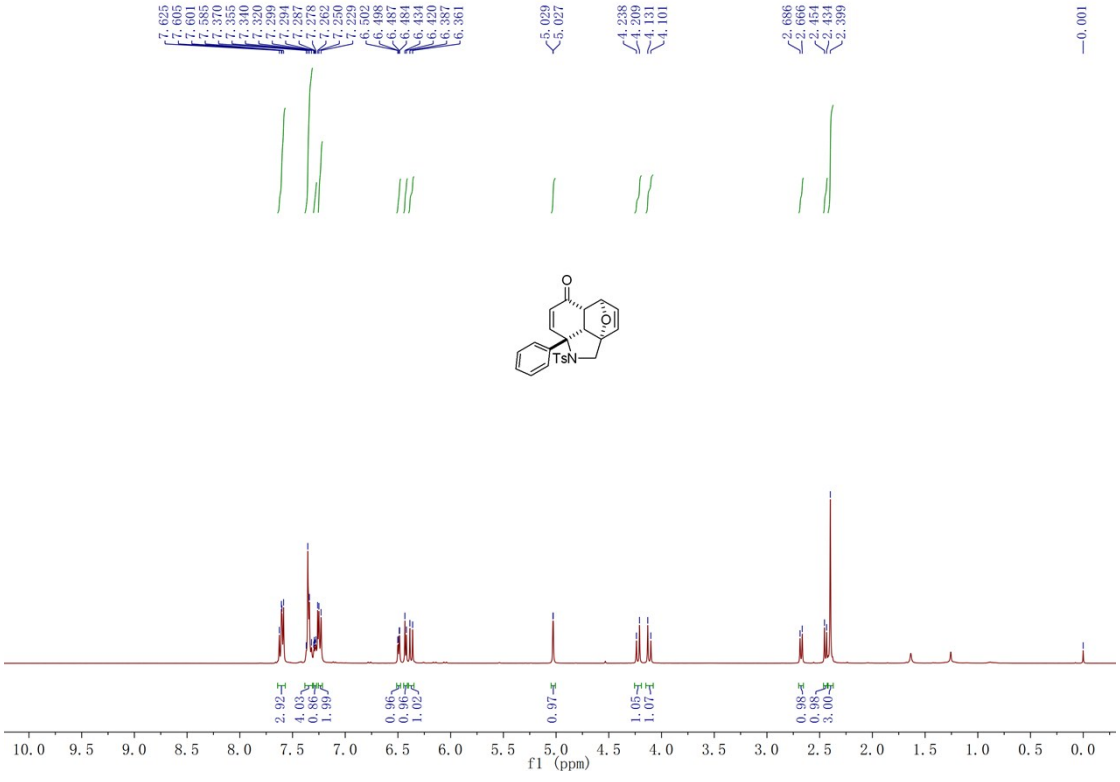
6.154
6.128
4.994
4.991
3.825
2.532
2.512
2.445
2.437
2.406
2.394
2.384
2.375
2.286
2.278
2.270
2.240
2.231
2.223
1.909
1.899
1.866
1.856
1.729
1.723
1.699
1.692
1.523
1.509
1.476
1.433
1.401
1.368
1.359
1.286
1.254
1.219
1.188
1.179
1.133
1.103
1.074
1.042
1.010
0.999
0.747
0.739
0.716
0.708
0.684
0.677
0.653
0.645
0.211
0.000
O
O
TsN
1.97
3.16
0.98
0.97
0.97
0.95
2.00
1.07
5.12
1.04
1.03
2.10
2.12
1.41
2.10
1.02
f1 (ppm)

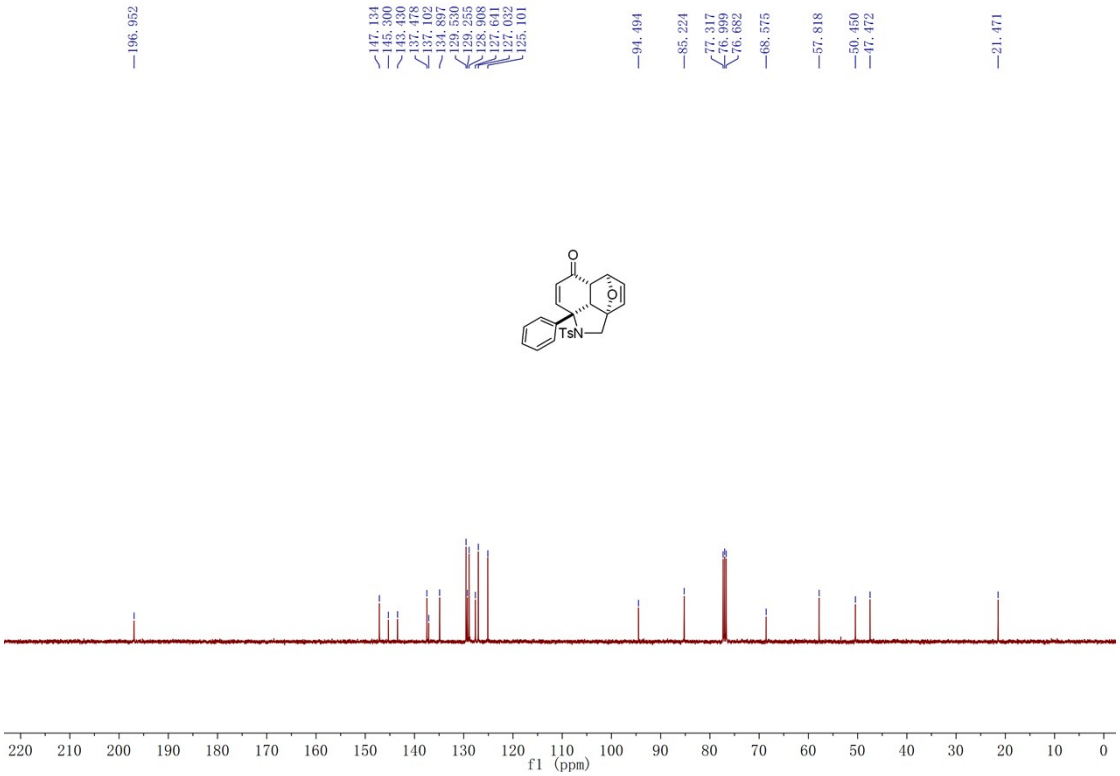

197.322
148.766
143.274
137.774
137.539
134.946
129.634
129.145
126.749
94.014
85.147
77.319
77.001
76.683
70.622
50.435
48.340
46.854
46.187
28.142
26.218
25.839
25.709
21.455
O
O
TsN
f1 (ppm)

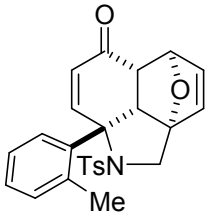

O
O
TsN

Compound 3i:

0.30 mmol scale, a white solid, 65% yield (81.6 mg). M.p.: 187-189 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.44 (d, *J* = 8.0 Hz, 1H), 2.80 (d, *J* = 8.0 Hz, 1H), 4.12 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 5.03 (d, *J* = 1.2 Hz, 1H), 6.38 (d, *J* = 10.4 Hz, 1H), 6.43 (d, *J* = 5.6 Hz, 1H), 6.49 (dd, *J* = 1.2 Hz, 5.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.27-7.30 (m, 1H), 7.32-7.37 (m, 4H), 7.58-7.63 (m, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 47.5, 50.5, 57.8, 68.6, 85.2, 94.5, 125.1, 127.0, 127.6, 128.9, 129.3, 129.5, 134.9, 137.1, 137.5, 143.4, 145.3, 147.1, 197.0. IR (neat) ν 3058, 3029, 2958, 2919, 2872, 2843, 1668, 1597, 1492, 1447, 1388, 1334, 1292, 1263, 1185, 1155, 1137, 1097, 1065, 996, 963, 942, 922, 886, 842, 813, 781, 733, 721, 697, 672 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{25}N_2O_4S^{+1}(M+NH_4)^+$ requires: 437.1530, found: 437.1529.

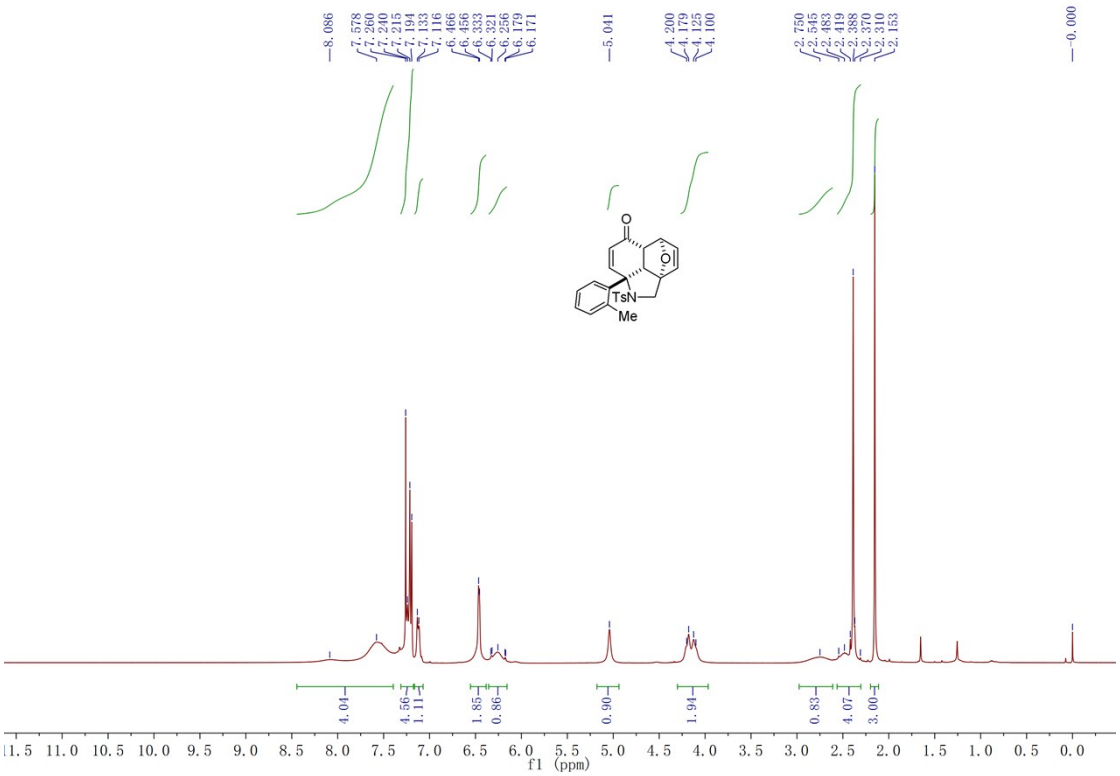


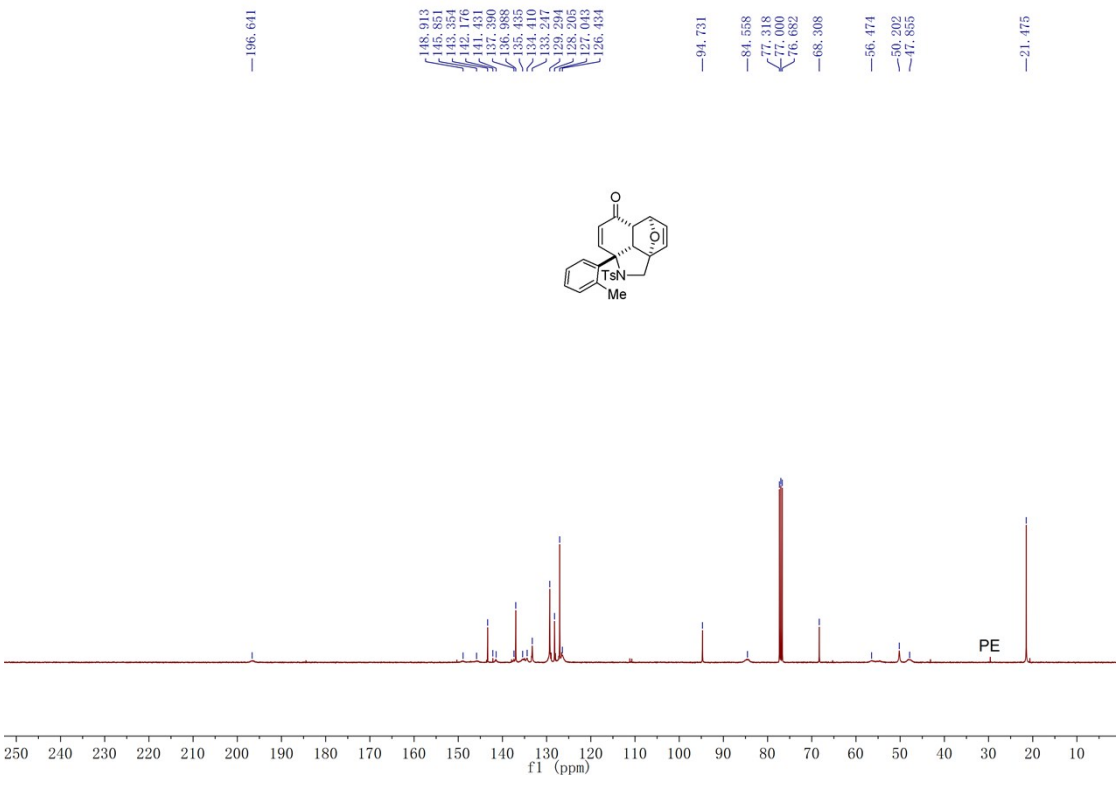


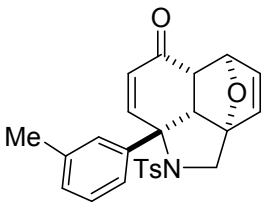


Compound 3j:

0.30 mmol scale, a light yellow solid, 65% yield (84.3 mg). M.p.: 72-75 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.15 (s, 3H), 2.31-2.55 (m, 4H), 2.75 (br, 1H), 4.10-4.20 (m, 2H), 5.04 (br, 1H), 6.17-6.34 (m, 1H), 6.46 (d, *J* = 4.0 Hz, 2H), 7.12 (d, *J* = 6.8 Hz, 1H), 7.19-7.26 (m, 4H), 7.57-8.09 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 47.9 (br), 50.2, 56.5 (br), 68.3, 84.6 (br), 94.7, 126.4 (br), 127.0, 128.2, 129.3, 133.2, 134.4 (br), 135.4 (br), 137.0, 137.4, 141.4 (br), 142.2, 143.4, 145.9 (br), 148.9 (br), 196.6 (br). IR (neat) ν 3055, 3013, 2963, 2923, 2872, 1668, 1597, 1476, 1387, 1336, 1290, 1262, 1155, 1135, 1094, 1065, 990, 964, 940, 920, 871, 841, 813, 780, 758, 733, 718, 703, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{27}N_2O_4S^{+1}(M+NH_4)^+$ requires: 451.1686, found: 451.1689.

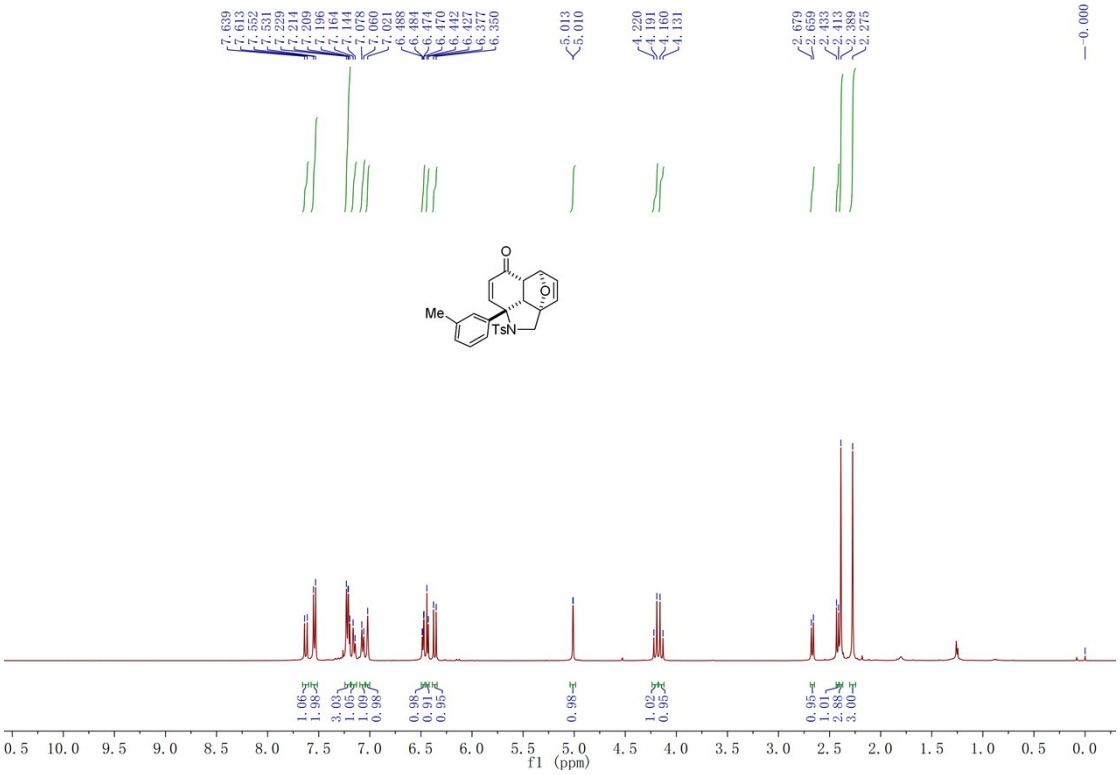

8.086
7.578
7.260
7.240
7.215
7.194
7.133
7.116
6.466
6.456
6.333
6.321
6.256
6.179
6.171
5.041
4.200
4.179
4.125
4.100
2.750
2.545
2.483
2.419
2.388
2.370
2.310
2.153
0.000
O
O
TsN
Me
4.04
4.56
1.11
1.85
0.86
0.90
1.94
0.83
4.07
3.00
f1 (ppm)

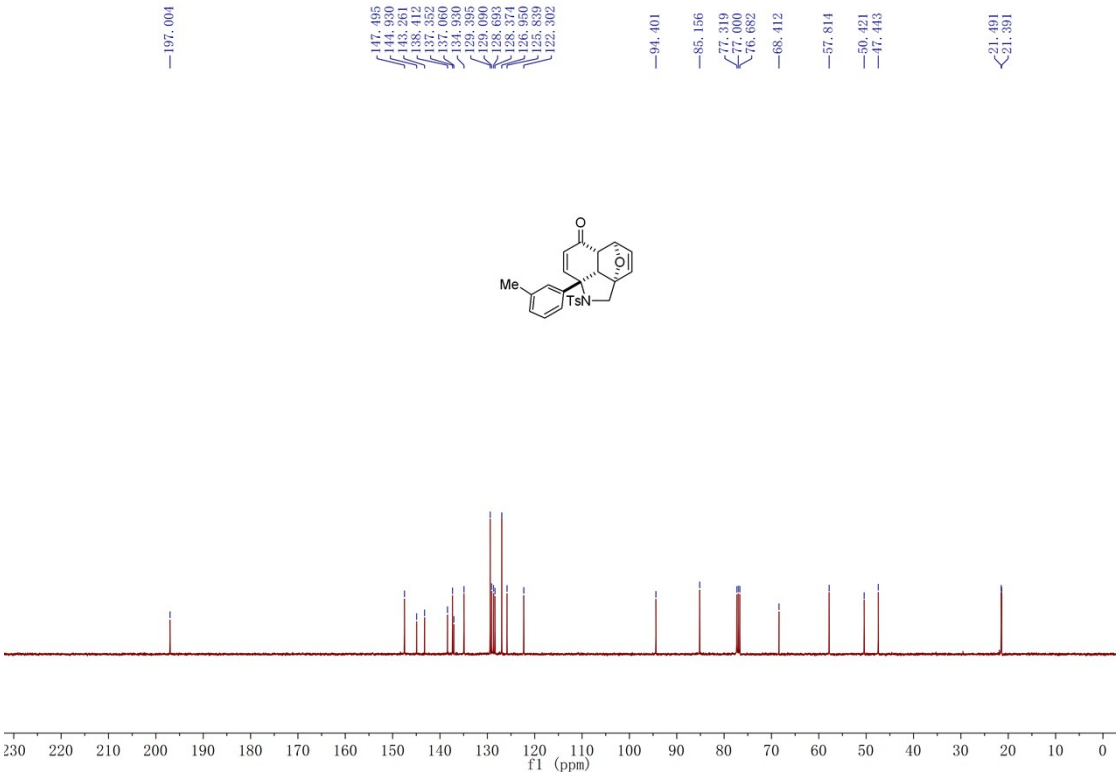

196.641
148.913
145.851
143.354
142.176
141.431
137.390
136.988
135.435
134.410
133.247
129.294
128.205
127.043
126.434
94.731
84.558
77.318
77.000
76.682
68.308
56.474
50.202
47.855
21.475
O
O
TsN
Me
PE
f1 (ppm)

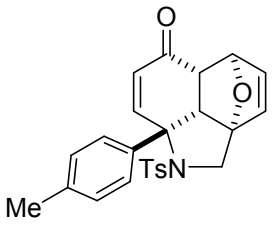

O
O
Me
TsN

Compound 3k:

0.30 mmol scale, a white solid, 65% yield (84.4 mg). M.p.: 171-173 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.28 (s, 3H), 2.39 (s, 3H), 2.42 (d, J = 8.0 Hz, 1H), 2.67 (d, J = 8.0 Hz, 1H), 4.15 (d, J = 11.6 Hz, 1H), 4.21 (d, J = 11.6 Hz, 1H), 5.01 (d, J = 1.2 Hz, 1H), 6.37 (d, J = 10.8 Hz, 1H), 6.43 (d, J = 6.0 Hz, 1H), 6.48 (dd, J = 1.2 Hz, 6.0 Hz, 1H), 7.02 (s, 1H), 7.07 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.19-7.23 (m, 3H), 7.54 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 10.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 21.5, 47.4, 50.4, 57.8, 68.4, 85.2, 94.4, 122.3, 125.8, 127.0, 128.4, 128.7, 129.1, 129.4, 134.9, 137.1, 137.4, 138.4, 143.3, 144.9, 147.5, 197.0. IR (neat) ν 3052, 2979, 2955, 2923, 2874, 2858, 1668, 1598, 1489, 1461, 1387, 1336, 1292, 1264, 1156, 1135, 1097, 1066, 994, 961, 923, 894, 867, 837, 814, 787, 733, 718, 697, 672 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{27}N_2O_4S^{+1}(M+NH_4)^+$ requires: 451.1686, found: 451.1687.

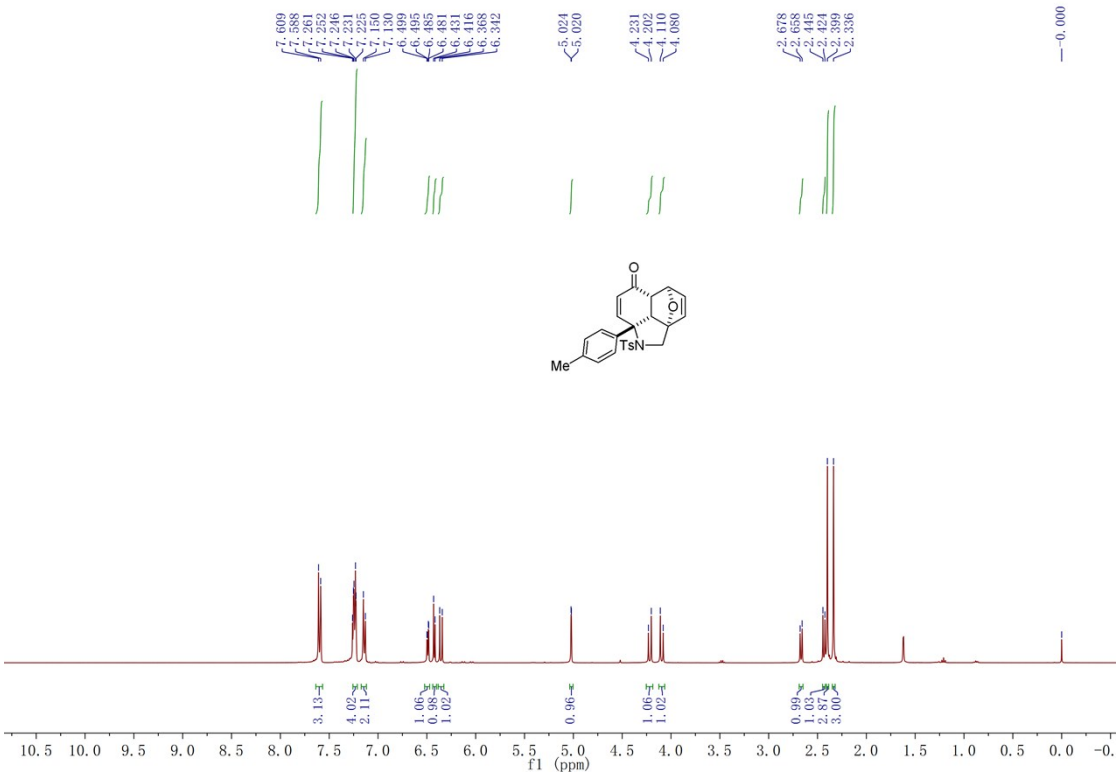






Compound 3l:

0.30 mmol scale, a light yellow solid, 86% yield (112.2 mg). M.p.: 165-166 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H), 2.40 (s, 3H), 2.43 (d, J = 8.0 Hz, 1H), 2.67 (d, J = 8.0 Hz, 1H), 4.10 (d, J = 12.0 Hz, 1H), 4.22 (d, J = 12.0 Hz, 1H), 5.02 (d, J = 1.6 Hz, 1H), 6.36 (d, J = 10.4 Hz, 1H), 6.42 (d, J = 6.0 Hz, 1H), 6.49 (dd, J = 1.6 Hz, 6.0 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.22-7.27 (m, 4H), 7.60 (d, J = 8.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.0, 21.5, 47.5, 50.5, 57.9, 68.4, 85.2, 94.5, 125.0, 127.1, 129.1, 129.5, 129.6, 134.9, 137.2, 137.5, 142.5, 143.4, 147.4, 197.0. IR (neat) ν 3055, 3026, 2953, 2921, 2869, 1667, 1597, 1510, 1494, 1456, 1387, 1334, 1292, 1263, 1184, 1155, 1137, 1113, 1097, 1066, 996, 962, 942, 922, 901, 886, 866, 845, 812, 733, 718, 702, 670 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{27}N_2O_4S^{+1}(M+NH_4)^+$ requires: 451.1686, found: 451.1684.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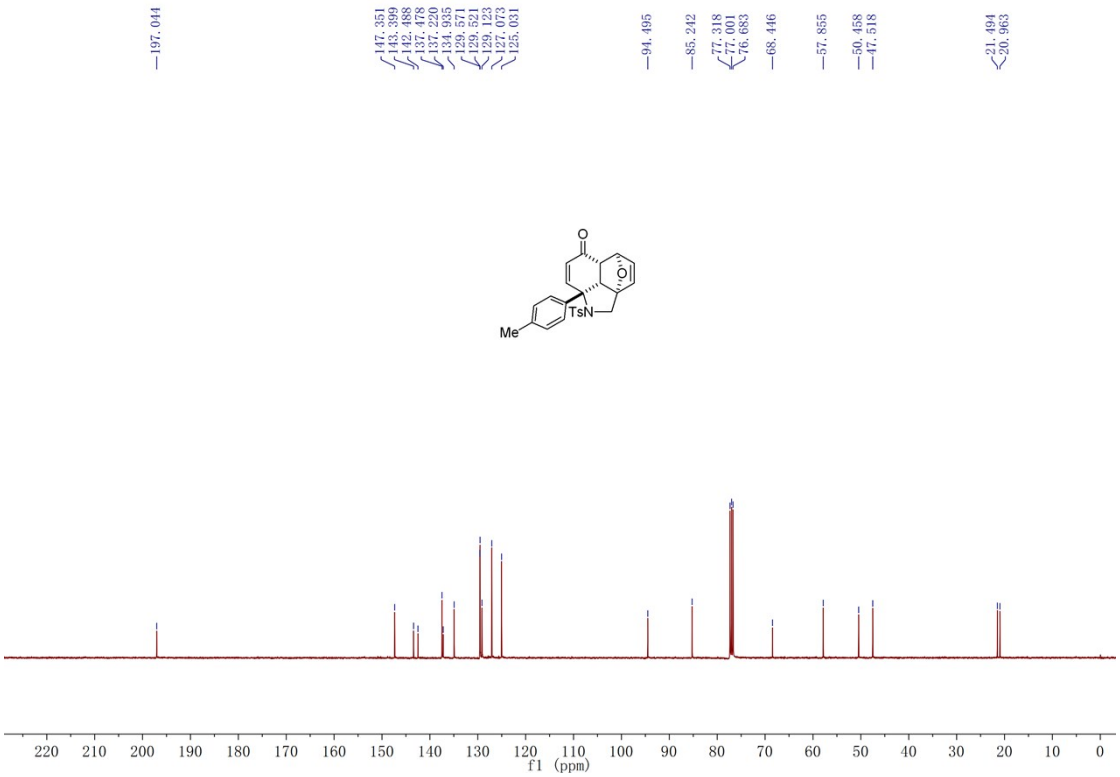
7.351
7.252
7.246
7.231
7.225
7.150
7.130
6.499
6.495
6.485
6.481
6.431
6.416
6.368
6.342
5.024
5.020
4.231
4.202
4.110
4.080
2.678
2.658
2.445
2.424
2.399
2.336
-0.000
O
O
TsN
Me
3.13
4.02
2.11
1.06
0.98
1.02
0.96
1.06
1.02
0.99
1.03
2.87
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


197.044
147.351
143.399
142.488
137.578
137.220
134.935
129.571
129.521
129.123
127.073
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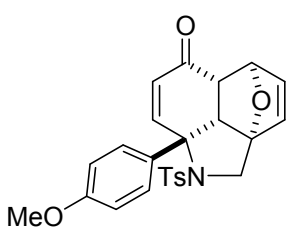
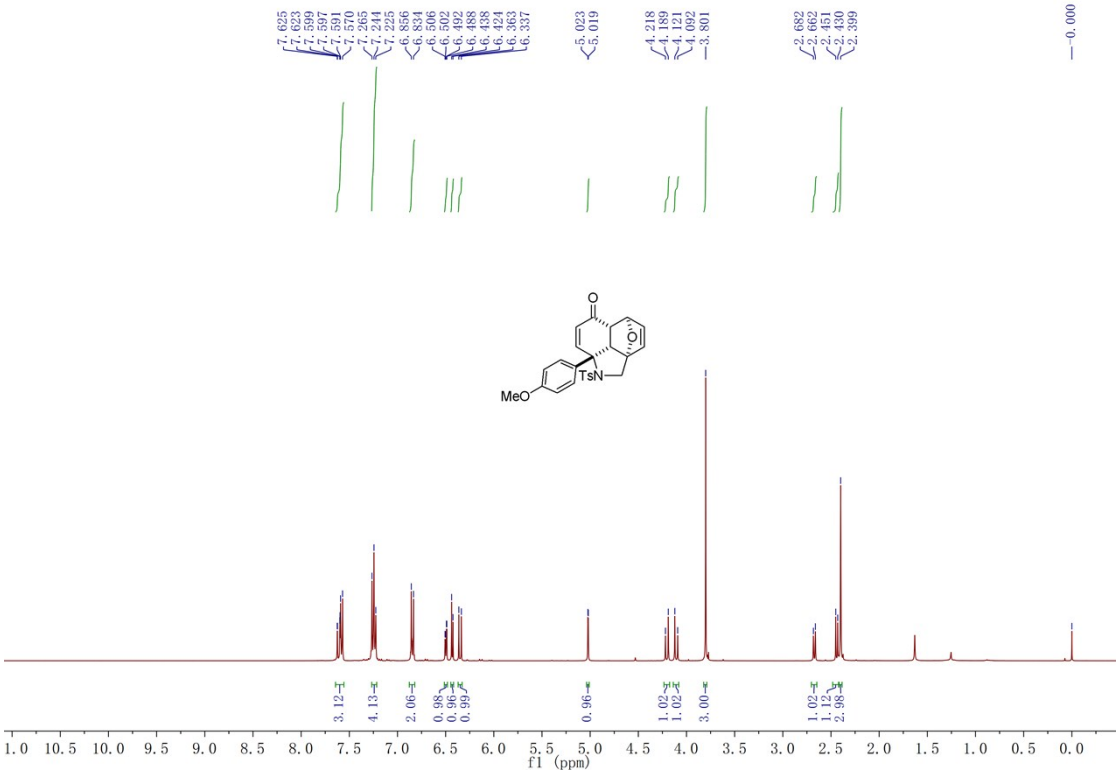
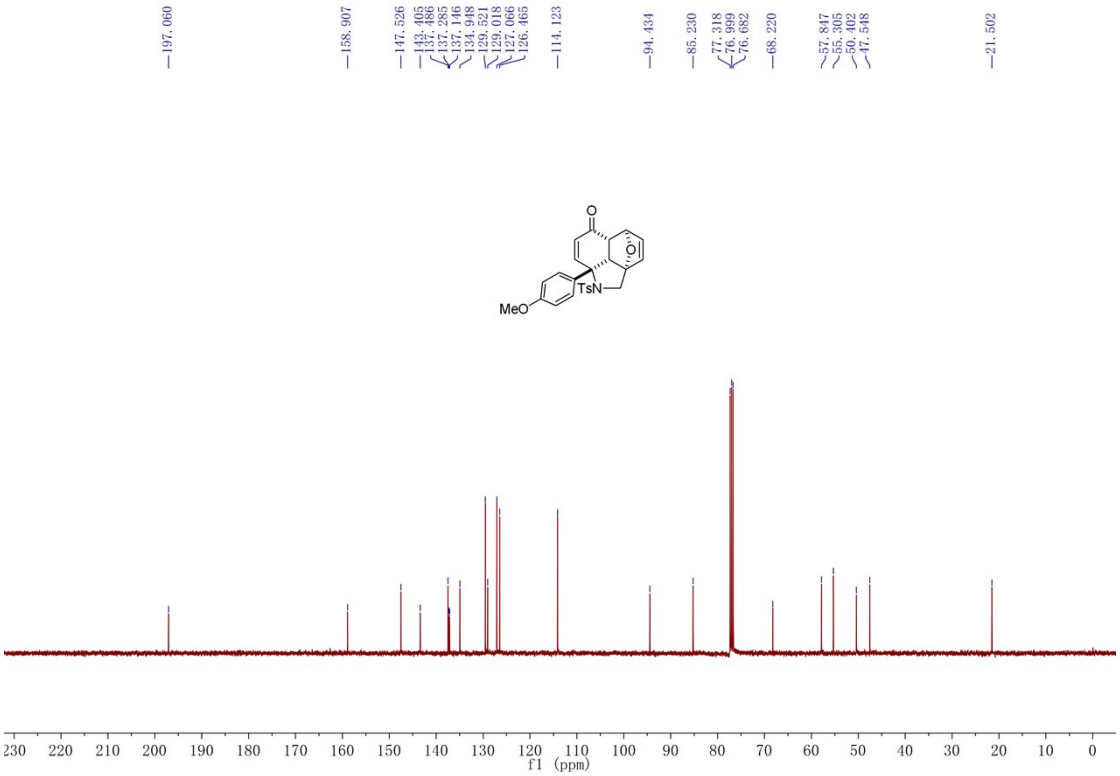
94.495
85.242
77.318
77.001
76.683
68.446
57.855
50.458
47.518
21.494
20.963
O
O
TsN
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

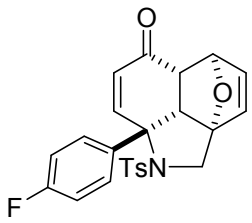

O
O
TsN
MeO

Compound 3m:

0.30 mmol scale, a white solid, 75% yield (100.4 mg). M.p.: 170-172 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.44 (d, *J* = 8.0 Hz, 1H), 2.67 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 4.11 (d, *J* = 11.6 Hz, 1H), 4.20 (d, *J* = 11.6 Hz, 1H), 5.02 (d, *J* = 1.6 Hz, 1H), 6.35 (d, *J* = 10.4 Hz, 1H), 6.43 (d, *J* = 5.6 Hz, 1H), 6.50 (dd, *J* = 1.6 Hz, 5.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.22-7.27 (m, 4H), 7.57-7.63 (m, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 47.5, 50.4, 55.3, 57.8, 68.2, 85.2, 94.4, 114.1, 126.5, 127.1, 129.0, 129.5, 134.9, 137.1, 137.3, 137.5, 143.4, 147.5, 158.9, 197.1. IR (neat) ν 3057, 3008, 2961, 2932, 2877, 2835, 1667, 1607, 1509, 1462, 1388, 1335, 1251, 1179, 1155, 1136, 1113, 1096, 1066, 1034, 994, 963, 942, 922, 900, 866, 845, 813, 731, 718, 703, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{24}NO_5S^{+1}(M+H)^+$ requires: 450.1370, found: 450.1371.

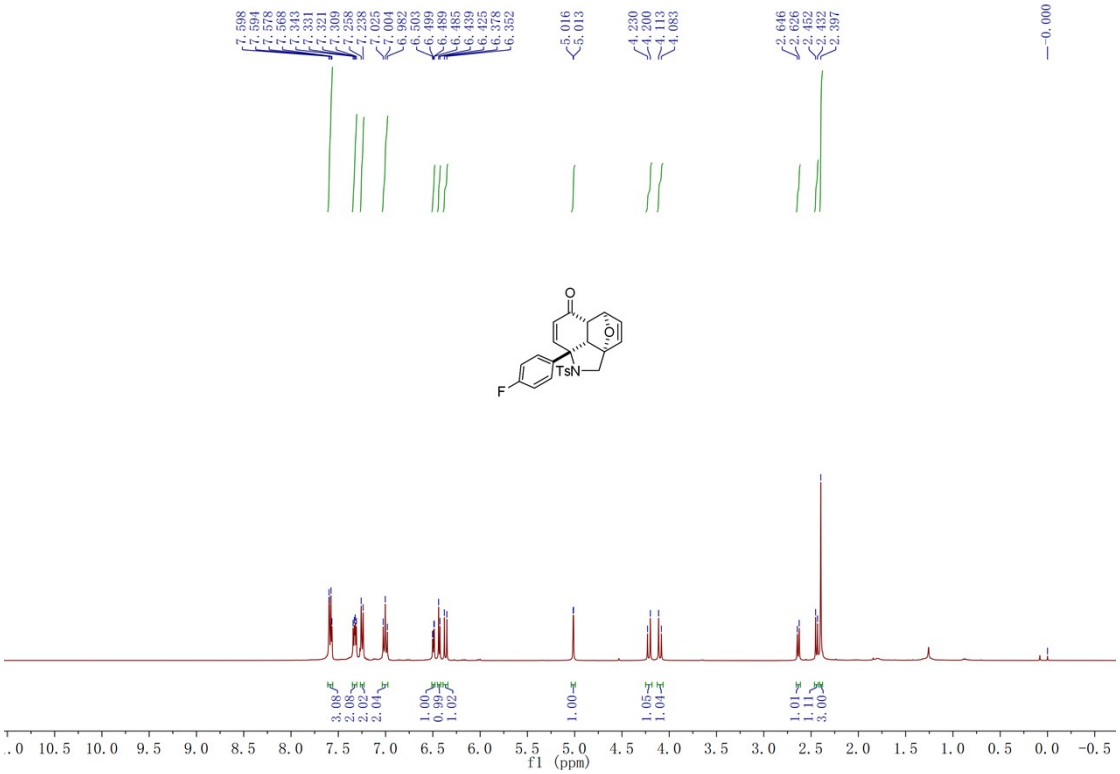


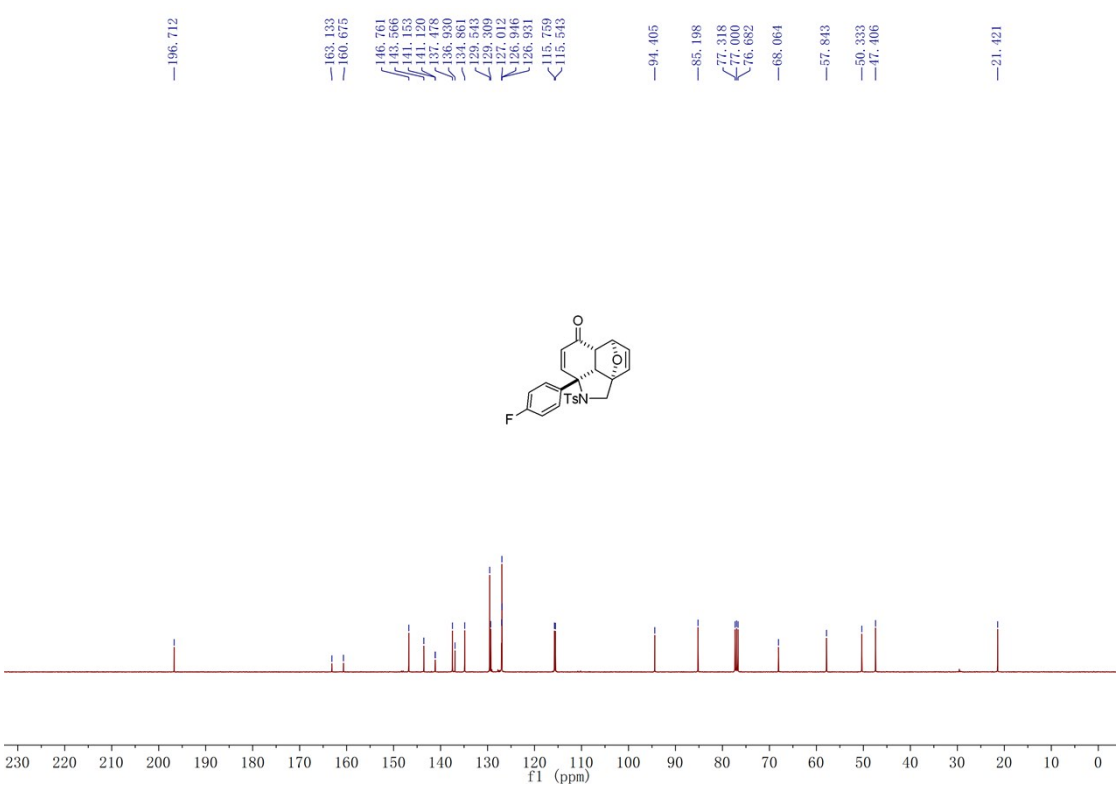




Compound 3n:

0.30 mmol scale, a white solid, 66% yield (86.0 mg). M.p.: 91-93 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.44 (d, *J* = 8.0 Hz, 1H), 2.64 (d, *J* = 8.0 Hz, 1H), 4.10 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 5.01 (d, *J* = 1.2 Hz, 1H), 6.37 (d, *J* = 10.4 Hz, 1H), 6.43 (d, *J* = 5.6 Hz, 1H), 6.50 (dd, *J* = 1.2 Hz, 5.6 Hz, 1H), 7.00 (dd, *J* = 8.4 Hz, 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.30-7.35 (m, 2H), 7.56-7.60 (m, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 47.4, 50.3, 57.8, 68.1, 85.2, 94.4, 115.7 (d, *J* = 21.6 Hz), 126.9, 127.0 (d, *J* = 8.1 Hz), 129.3, 129.5, 134.9, 136.9, 137.5, 141.1 (d, *J* = 3.3 Hz), 143.6, 146.8, 161.9 (d, *J* = 245.8 Hz), 196.7. ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -114.67- -114.60 (m). IR (neat) ν 3063, 3005, 2981, 2953, 2925, 2874, 2845, 1669, 1599, 1506, 1462, 1386, 1335, 1264, 1229, 1186, 1155, 1136, 1096, 1066, 996, 963, 943, 922, 901, 867, 847, 814, 733, 718, 702, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{24}N_2O_4SF^{+1}(M+NH_4)^+$ requires: 455.1435, found: 455.1435.


7.598
7.594
7.578
7.568
7.343
7.331
7.311
7.309
7.258
7.238
7.025
7.004
6.982
6.503
6.499
6.489
6.485
6.439
6.425
6.378
6.352
5.016
5.013
4.230
4.200
4.113
4.083
2.646
2.626
2.452
2.432
2.397
-0.000
O
O
TsN
F
3.08
2.06
2.02
2.04
1.00
0.99
1.02
1.00
1.05
1.04
1.01
1.11
3.00
f1 (ppm)


196.712
163.133
160.675
146.761
143.566
141.153
141.120
137.478
136.930
136.861
129.543
129.309
127.012
126.946
126.931
115.759
115.543
94.405
85.198
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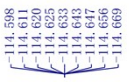
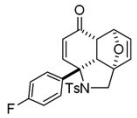
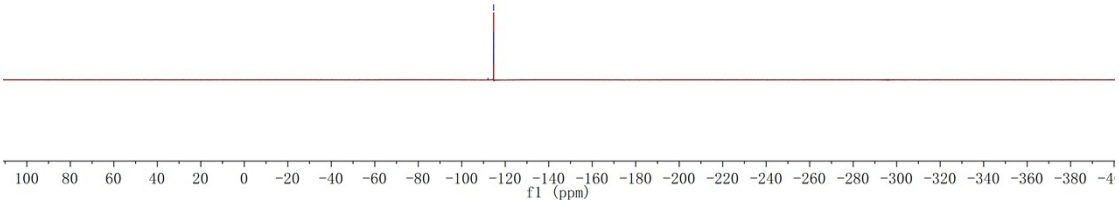
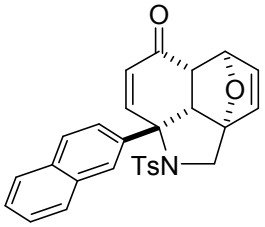
77.000
76.682
68.064
57.843
50.333
47.406
21.421
O
O
TsN
F
f1 (ppm)



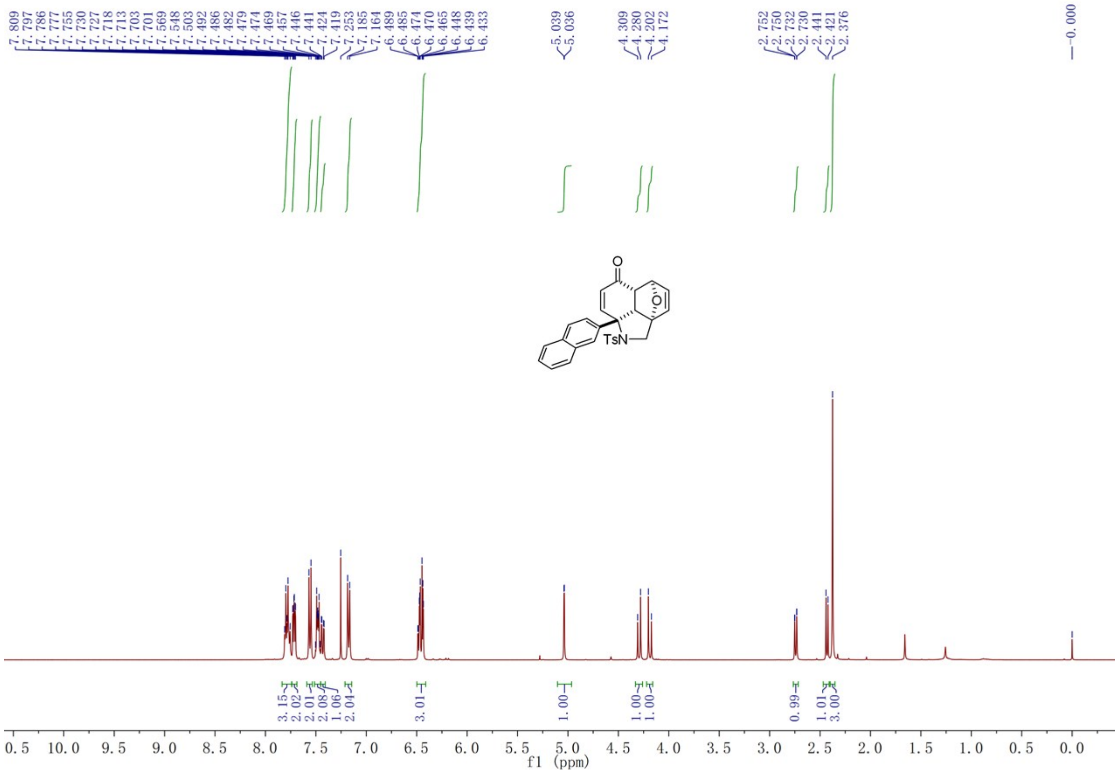


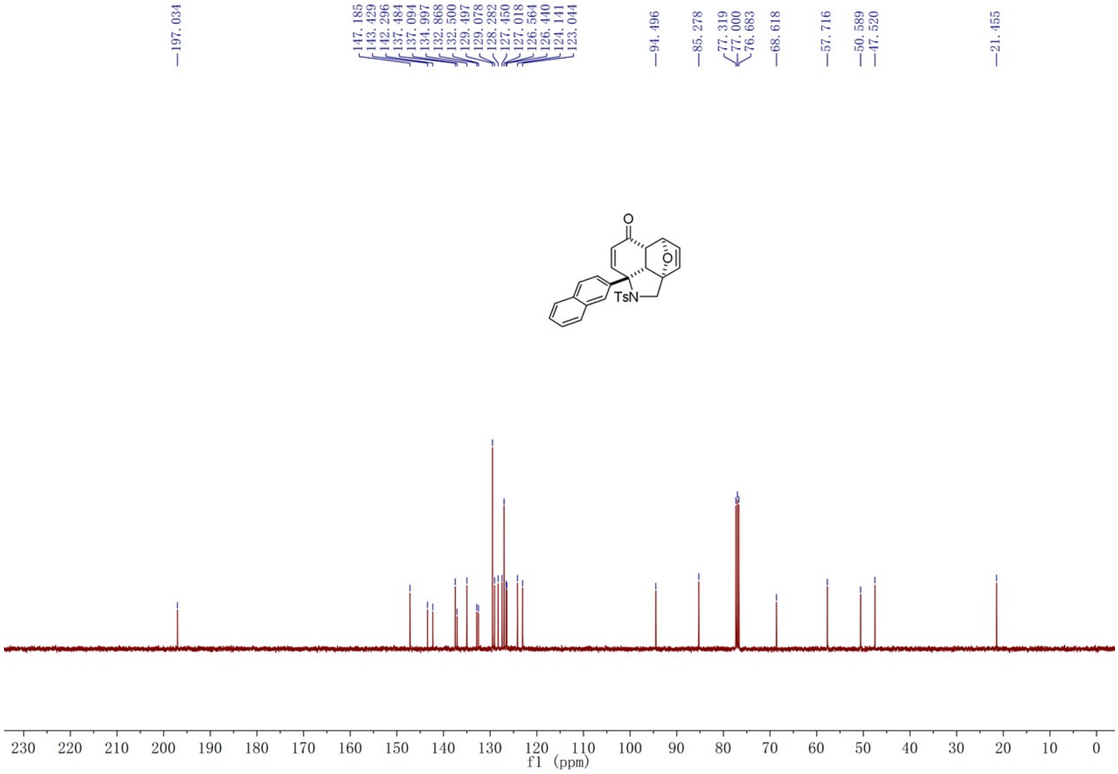


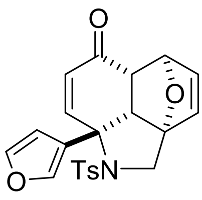


Compound 3o:

0.30 mmol scale, a white solid, 62% yield (87.5 mg). M.p.: 107-109 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.43 (d, *J* = 8.0 Hz, 1H), 2.74 (dd, *J* = 0.8 Hz, 8.0 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 5.04 (d, *J* = 1.2 Hz, 1H), 6.43-6.49 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.43 (dd, *J* = 6.0 Hz, 8.8 Hz, 1H), 7.45-7.51 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.70-7.73 (m, 2H), 7.75-7.81 (m, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 47.5, 50.6, 57.7, 68.6, 85.3, 94.5, 123.0, 124.1, 126.4, 126.6, 127.0, 127.5, 128.3, 129.1, 129.5, 132.5, 132.9, 135.0, 137.1, 137.5, 142.3, 143.4, 147.2, 197.0. IR (neat) ν 3055, 3010, 2981, 2958, 2924, 2874, 1668, 1597, 1506, 1461, 1389, 1334, 1292, 1264, 1155, 1136, 1121, 1096, 1066, 995, 962, 932, 922, 908, 869, 857, 838, 814, 732, 717, 705, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{27}N_2O_4S^{+1}(M+NH_4)^+$ requires: 487.1686, found: 487.1679.

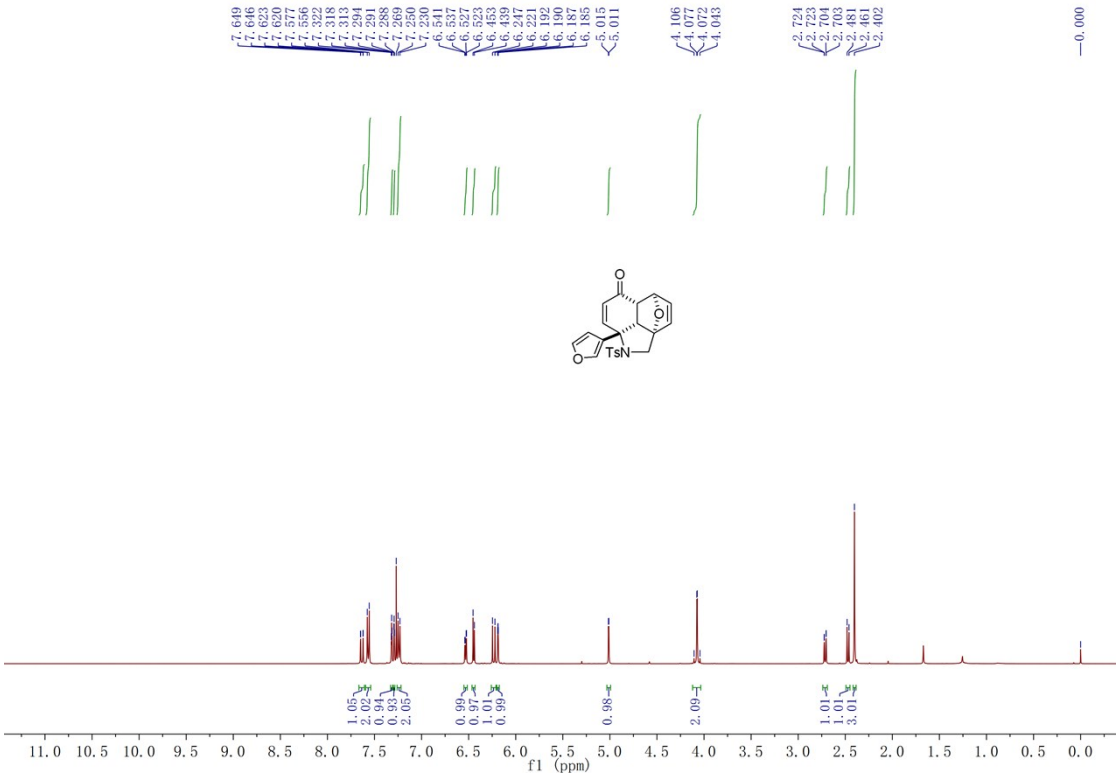

7.809 7.797 7.786 7.777 7.755 7.730 7.727 7.718 7.713 7.703 7.701 7.569 7.548 7.503 7.492 7.486 7.482 7.479 7.474 7.469 7.457 7.446 7.441 7.424 7.419 7.253 7.185 7.164 6.489 6.485 6.474 6.470 6.465 6.448 6.439 6.433
5.039 5.036
4.309 4.280 4.202 4.172
2.752 2.750 2.732 2.730 2.441 2.421 2.376
0.000
TsN
O
3.15 2.02 2.01 2.08 1.06 2.04
3.01
1.00
1.00 1.00
0.99
1.01 3.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

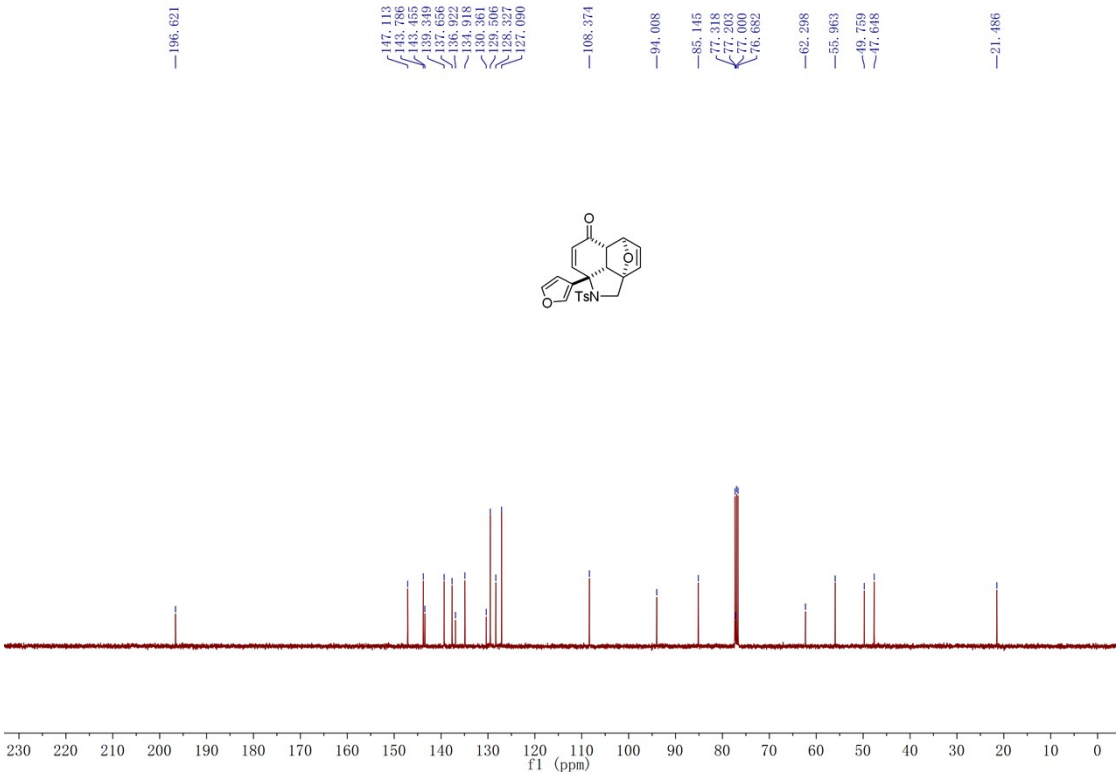

197.034
147.185 143.429 142.296 137.484 137.094 134.997 132.868 132.500 129.497 129.078 128.282 127.450 127.018 126.564 126.440 124.141 123.044
94.496
85.278
77.319 77.000 76.683
68.618
57.716
50.589 47.520
21.455
TsN
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

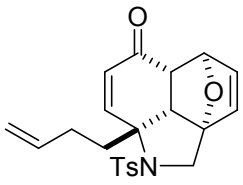

O
TsN
O
O

Compound 3p:

0.30 mmol scale, a white solid, 50% yield (61.6 mg). M.p.: 74-76 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 2.47 (d, *J* = 8.0 Hz, 1H), 2.71 (dd, *J* = 0.4 Hz, 8.0 Hz, 1H), 4.06 (d, *J* = 11.6 Hz, 1H), 4.09 (d, *J* = 11.6 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 6.19 (dd, *J* = 0.8 Hz, 2.0 Hz, 1H), 6.23 (d, *J* = 10.4 Hz, 1H), 6.45 (d, *J* = 5.6 Hz, 1H), 6.53 (dd, *J* = 1.6 Hz, 5.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.28-7.30 (m, 1H), 7.32 (dd, *J* = 1.2 Hz, 2.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.64 (dd, *J* = 1.2 Hz, 10.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 47.6, 49.8, 56.0, 62.3, 85.1, 94.0, 108.4, 127.1, 128.3, 129.5, 130.4, 134.9, 136.9, 137.7, 139.3, 143.5, 143.8, 147.1, 196.6. IR (neat) ν 3144, 3128, 3060, 2987, 2955, 2924, 2866, 1668, 1597, 1495, 1462, 1390, 1336, 1292, 1266, 1156, 1134, 1116, 1096, 1066, 1036, 993, 924, 905, 883, 872, 840, 814, 793, 732, 716, 705, 670 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{23}N_2O_5S^{+1}(M+NH_4)^+$ requires: 427.1322, found: 427.1320.

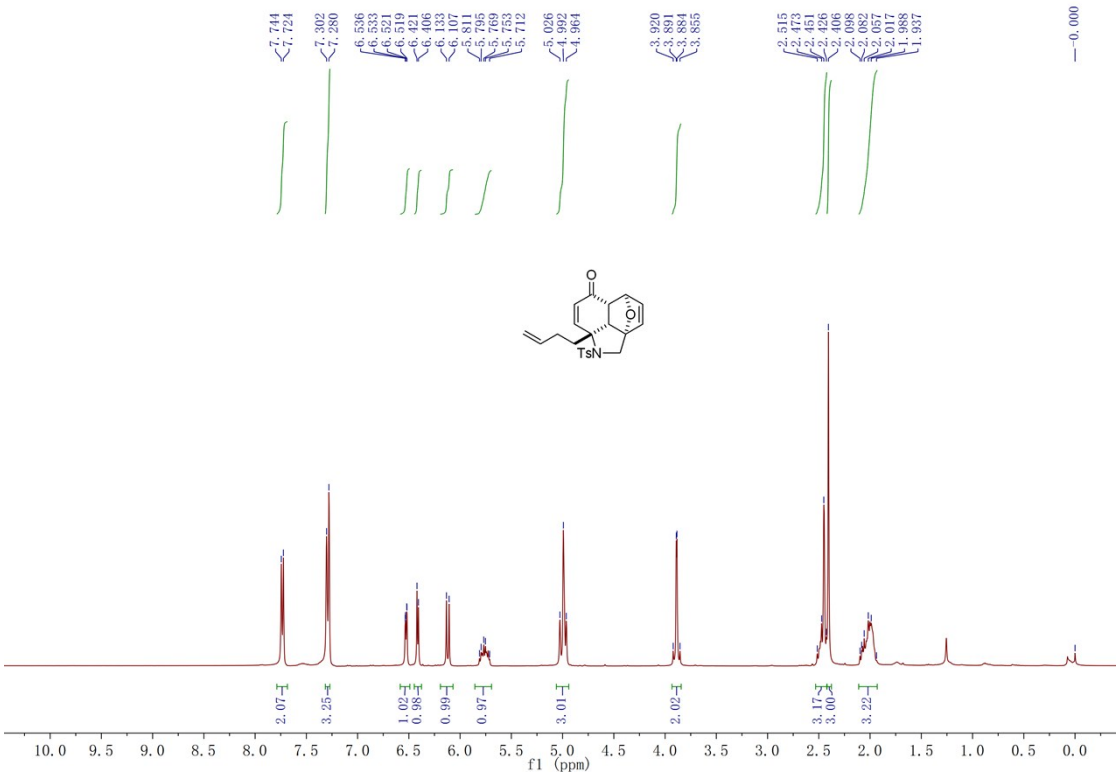


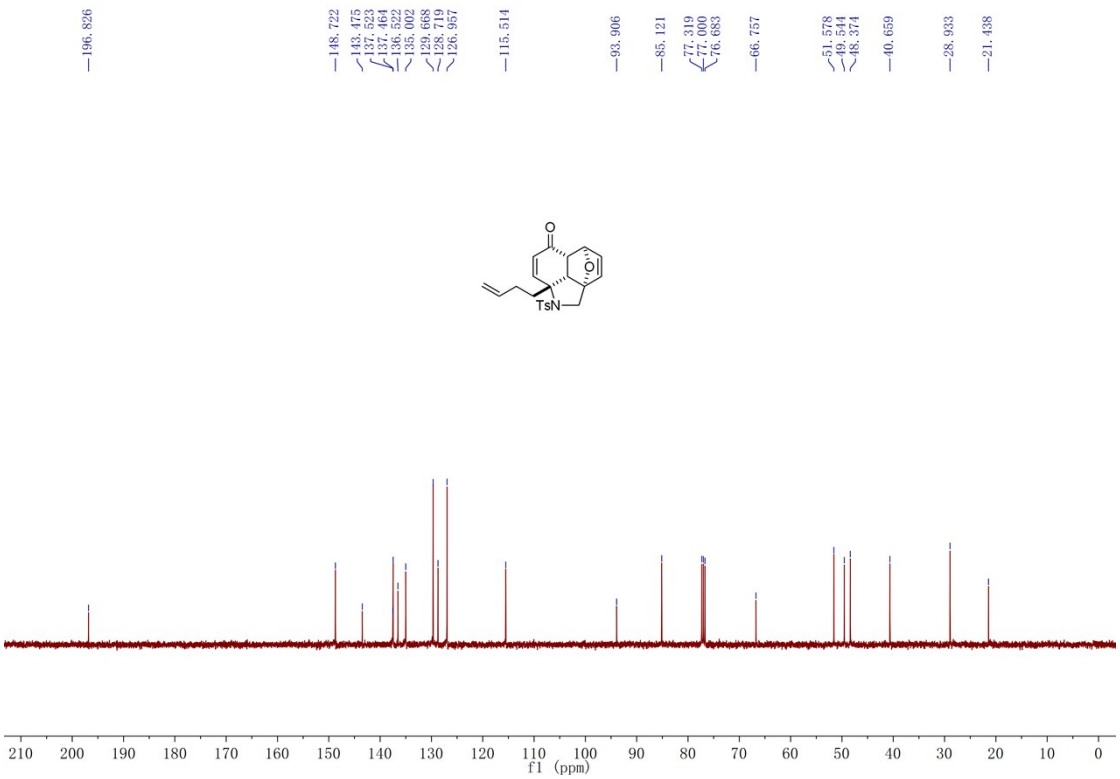




Compound 3q:

0.30 mmol scale, a white solid, 72% yield (85.3 mg). M.p.: 92-94 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.93-2.10 (m, 3H), 2.41 (s, 3H), 2.42-2.52 (m, 3H), 3.87 (d, J = 11.6 Hz, 1H), 3.91 (d, J = 11.6 Hz, 1H), 4.96-5.03 (m, 3H), 5.71-5.82 (m, 1H), 6.12 (d, J = 10.4 Hz, 2H), 6.41 (d, J = 6.0 Hz, 1H), 6.53 (dd, J = 1.2 Hz, 6.0 Hz, 1H), 7.28-7.31 (m, 3H), 7.73 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 28.9, 40.7, 48.4, 49.5, 51.6, 66.8, 85.1, 93.9, 115.5, 127.0, 128.7, 129.7, 135.0, 136.5, 137.46, 137.52, 143.5, 148.7, 196.8. IR (neat) ν 3063, 3005, 2979, 2958, 2925, 2872, 2845, 1668, 1597, 1494, 1459, 1390, 1338, 1319, 1264, 1155, 1098, 1067, 988, 923, 888, 868, 844, 814, 779, 734, 706, 669 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{27}N_2O_4S^{+1}(M+NH_4)^+$ requires: 415.1686, found: 415.1685.


7.744
7.724
7.302
7.280
6.536
6.533
6.521
6.519
6.421
6.406
6.133
6.107
5.811
5.795
5.769
5.753
5.712
5.026
4.992
4.964
3.920
3.891
3.884
3.855
2.515
2.473
2.451
2.426
2.406
2.098
2.082
2.057
2.017
1.988
1.937
0.000
O
O
TsN
2.07
3.25
1.02
0.98
0.99
0.97
3.01
2.02
3.17
3.00
3.22
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)


196.826
148.722
143.475
137.523
137.464
136.522
135.002
129.668
128.719
126.957
115.514
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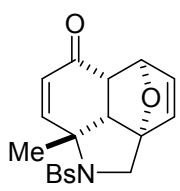
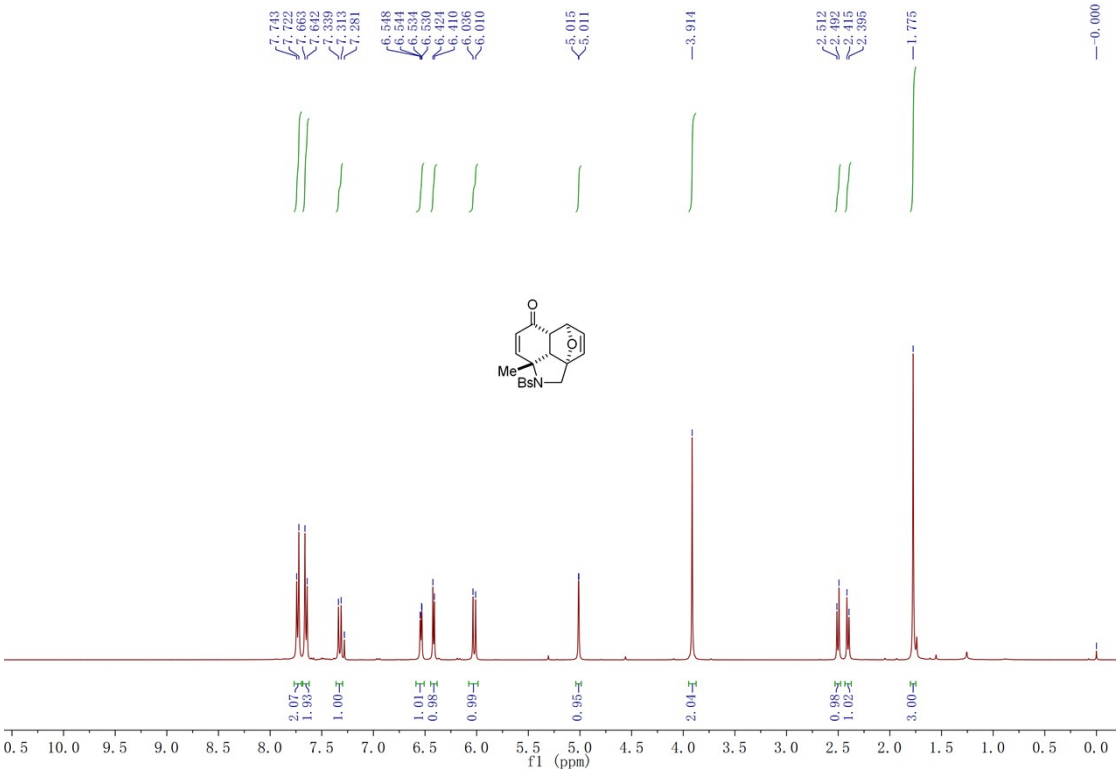
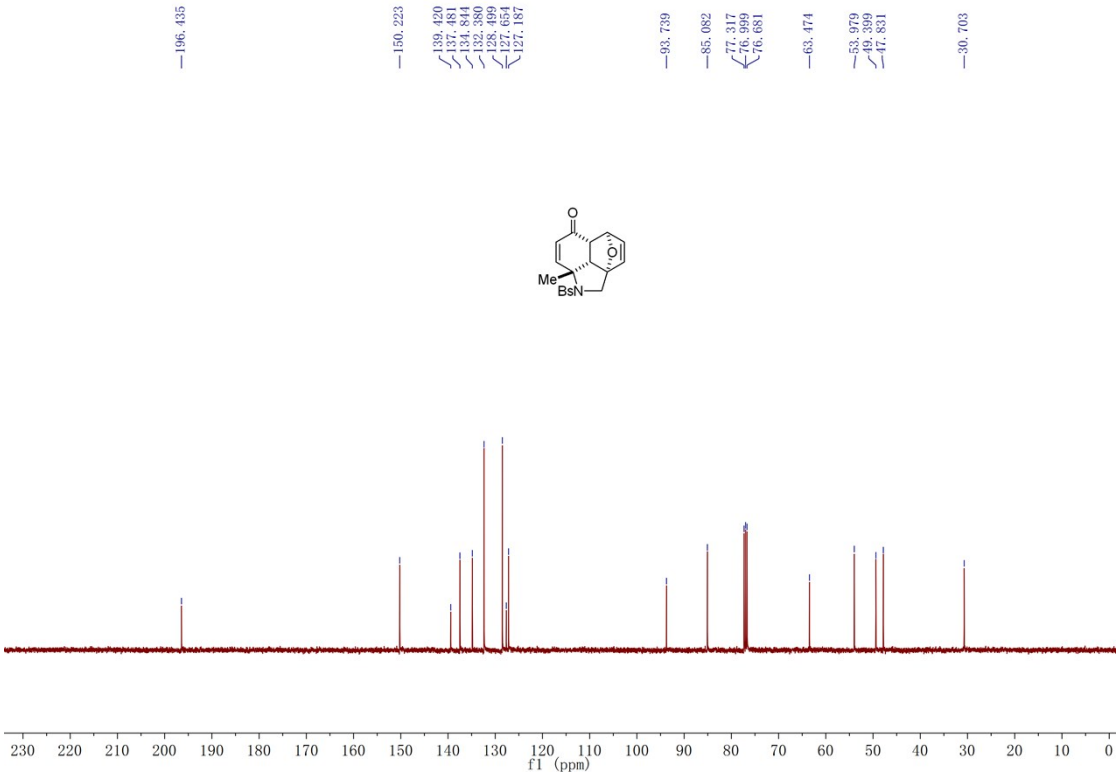
85.121
77.319
77.000
76.683
66.757
51.578
49.544
48.374
40.659
28.933
21.438
O
O
TsN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

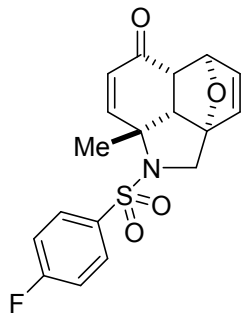

O
O
Me
BsN

Compound 3r:

0.30 mmol scale, a white solid, 75% yield (95.2 mg). M.p.: 148-150 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.78 (s, 3H), 2.41 (d, *J* = 8.0 Hz, 1H), 2.50 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 2H), 5.01 (d, *J* = 1.6 Hz, 1H), 6.02 (d, *J* = 10.4 Hz, 1H), 6.42 (d, *J* = 5.6 Hz, 1H), 6.54 (dd, *J* = 1.6 Hz, 5.6 Hz, 1H), 7.33 (d, *J* = 10.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.7, 47.8, 49.4, 54.0, 63.5, 85.1, 93.7, 127.2, 127.7, 128.5, 132.4, 134.8, 137.5, 139.4, 150.2, 196.4. IR (neat) ν 3088, 3057, 2997, 2974, 2927, 2872, 2848, 1670, 1573, 1464, 1388, 1341, 1295, 1265, 1218, 1202, 1157, 1128, 1100, 1083, 1067, 1009, 995, 973, 924, 893, 880, 858, 820, 773, 737, 703, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}NO_4SBr^{+1}(M+H)^+$ requires: 422.0056, found: 422.0053.

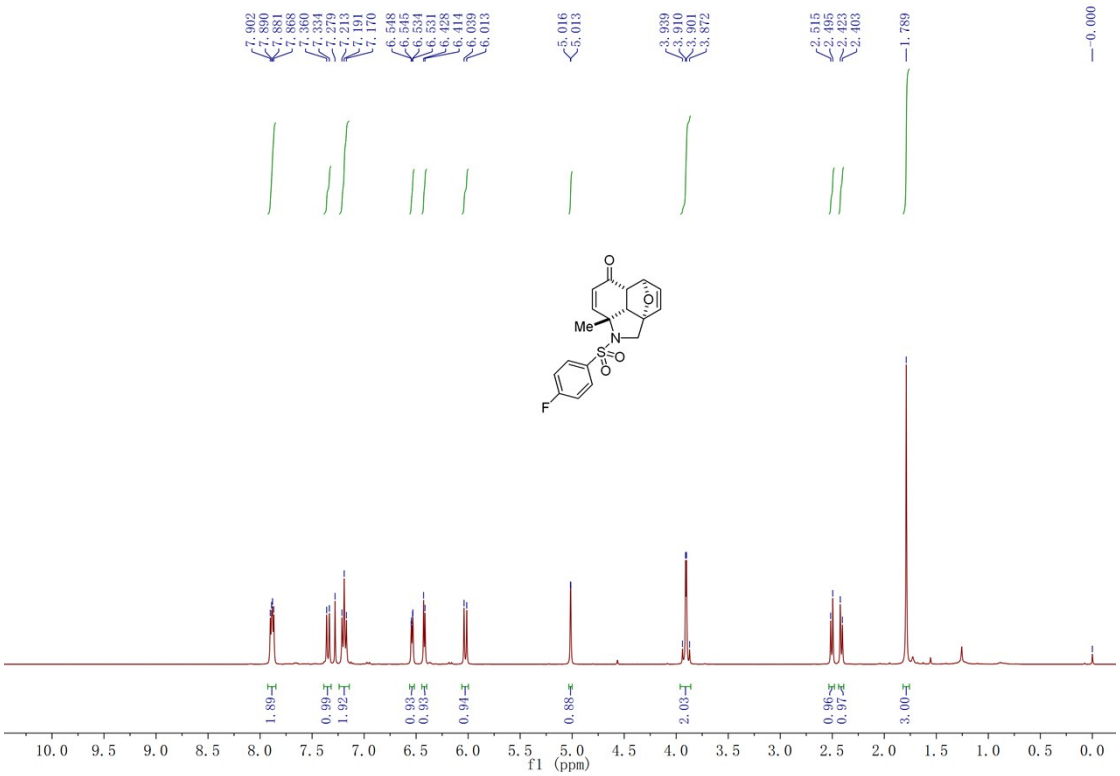






Compound 3s:

0.30 mmol scale, a light yellow solid, 73% yield (79.1 mg). M.p.: 158-189 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.79 (s, 3H), 2.41 (d, J = 8.0 Hz, 1H), 2.51 (d, J = 8.0 Hz, 1H), 3.89 (d, J = 11.6 Hz, 1H), 3.92 (d, J = 11.6 Hz, 1H), 5.01 (d, J = 1.2 Hz, 1H), 6.03 (d, J = 10.4 Hz, 1H), 6.42 (d, J = 5.6 Hz, 1H), 6.54 (dd, J = 1.2 Hz, 5.6 Hz, 1H), 7.17-7.22 (m, 2H), 7.35 (d, J = 10.4 Hz, 1H), 7.86-7.91 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.7, 47.8, 49.4, 54.0, 63.4, 85.1, 93.8, 116.3 (d, J = 22.5 Hz), 127.2, 129.7 (d, J = 9.2 Hz), 134.9, 136.5 (d, J = 3.3 Hz), 137.5, 150.3, 164.9 (d, J = 253.5 Hz), 196.5. ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -104.98- -104.90 (m). IR (neat) ν 3104, 3070, 3044, 3002, 2955, 2928, 2866, 1669, 1590, 1493, 1461, 1393, 1371, 1339, 1292, 1274, 1231, 1164, 1153, 1097, 1068, 980, 925, 877, 855, 838, 818, 775, 762, 735, 723, 711, 676 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{20}N_2O_4SF^{+1}(M+NH_4)^+$ requires: 379.1122, found: 379.1123.


7.902
7.890
7.881
7.868
7.360
7.334
7.279
7.213
7.191
7.170
6.548
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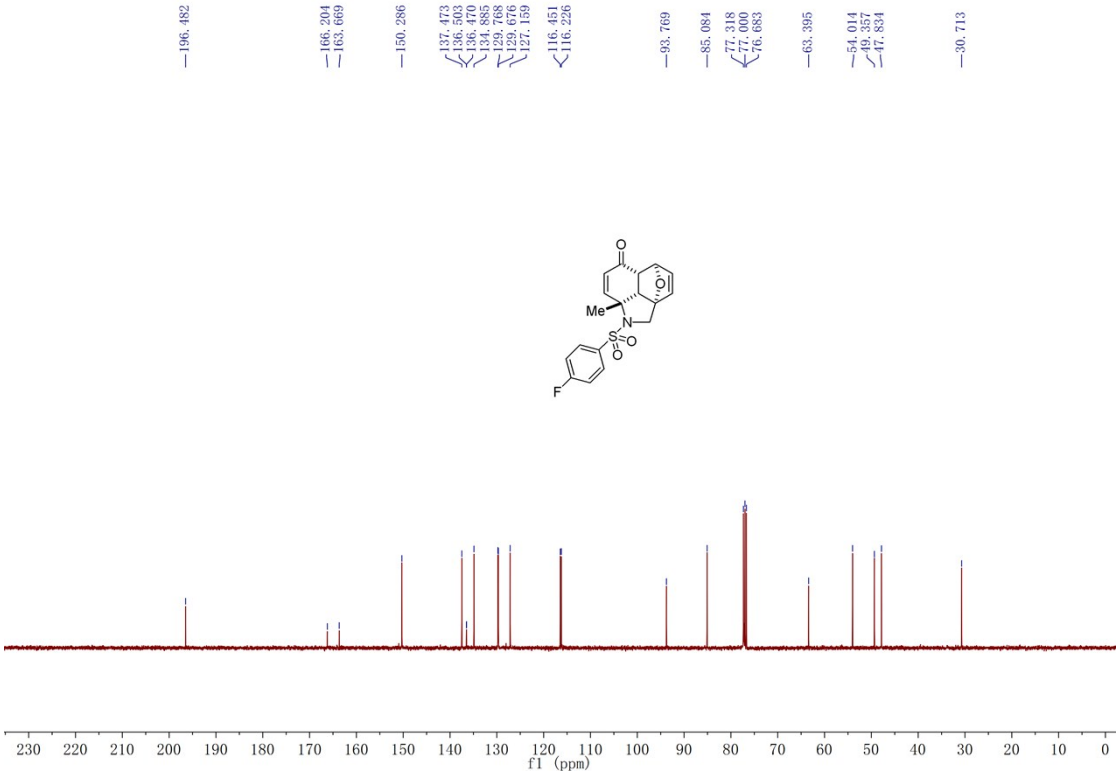
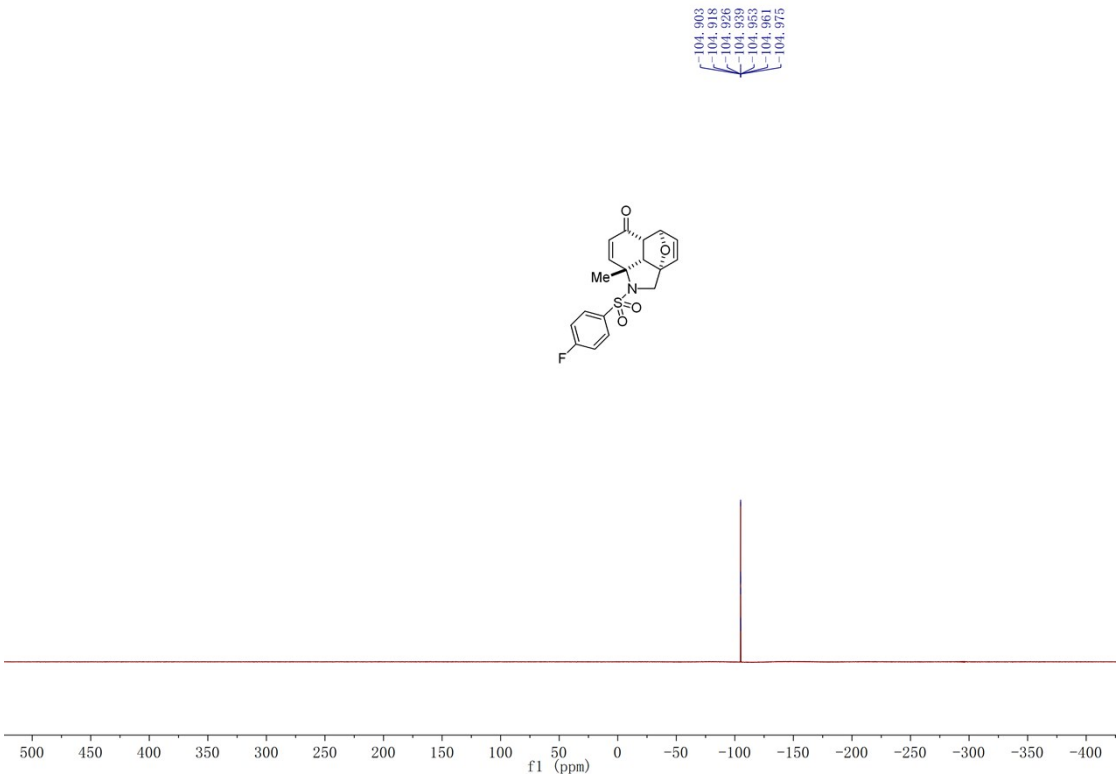
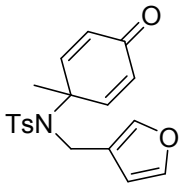
6.531
6.428
6.414
6.039
6.013
5.016
5.013
3.939
3.910
3.901
3.872
2.515
2.495
2.423
2.403
1.789
0.000
Me
N
S
O
F
1.89
0.99
1.92
0.93
0.93
0.94
0.88
2.03
0.96
0.97
3.00
f1 (ppm)

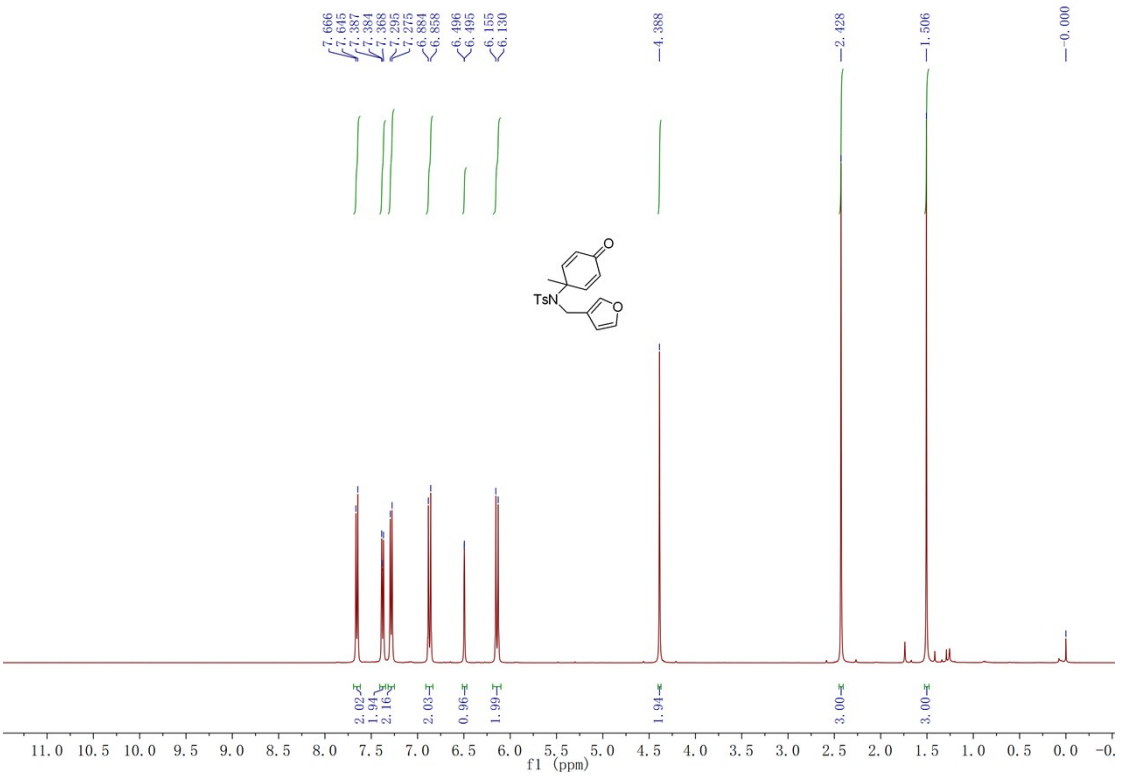

196.482
166.204
163.669
150.286
137.473
136.503
136.470
134.885
129.768
129.676
127.159
116.451
116.226
93.769
85.084
77.318
77.000
76.683
63.395
54.014
49.357
47.834
30.713
Me
N
S
O
F
f1 (ppm)

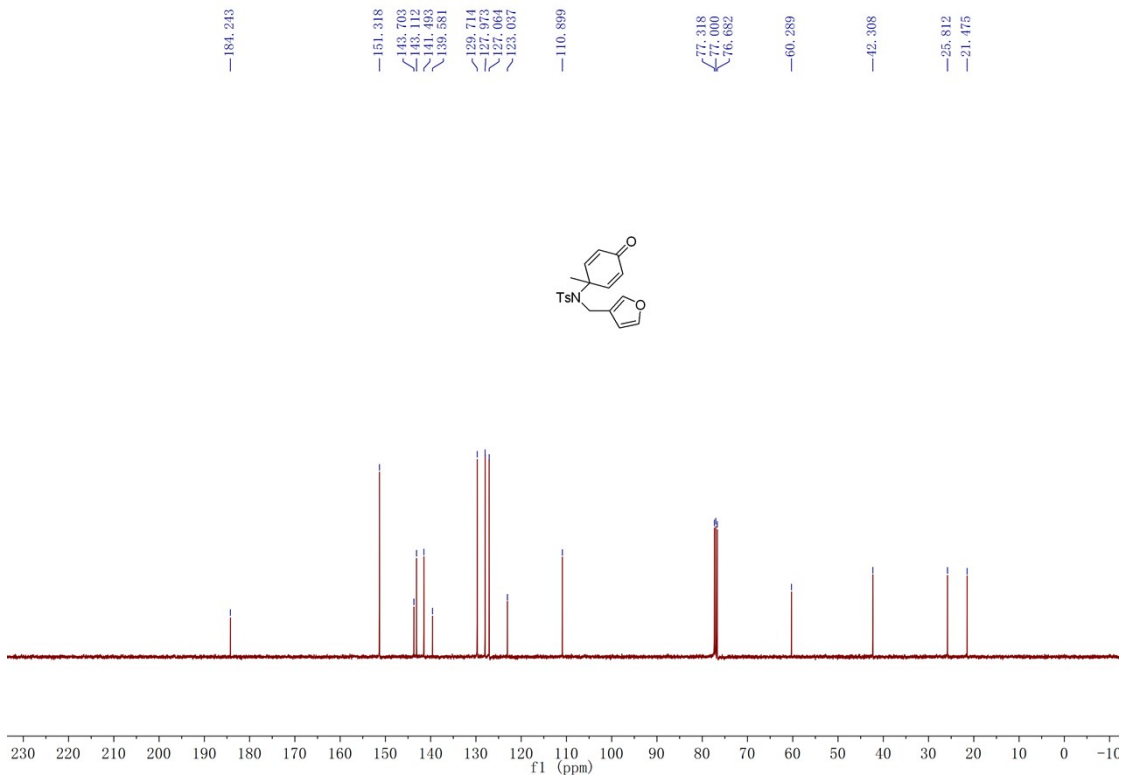


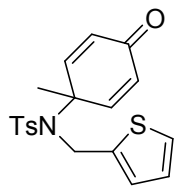


Compound 3ae′:

0.3 mmol scale, a white solid, 73% yield (78.3 mg). M.p.: 117-119 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.51 (s, 3H), 2.43 (s, 3H), 4.39 (s, 2H), 6.14 (d, J = 10.0 Hz, 2H), 6.50 (d, J = 0.4 Hz, 1H), 6.87 (d, J = 10.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.36-7.39 (m, 2H), 7.66 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.5, 25.8, 42.3, 60.3, 110.9, 123.0, 127.1, 128.0, 129.7, 139.6, 141.5, 143.1, 143.7, 151.3, 184.2. IR (neat) 3146.8, 3125, 3063, 3036, 3002, 2988, 2955, 2919, 2869, 1667, 1628, 1598, 1496, 1448, 1391, 1325, 1305, 1275, 1260, 1181, 1154, 1088, 1068, 1021, 965, 885, 874, 862, 807, 764, 749, 706, 685, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{20}NO_4S^{+1}(M+H)^+$ requires: 358.1108, Found: 358.1104.

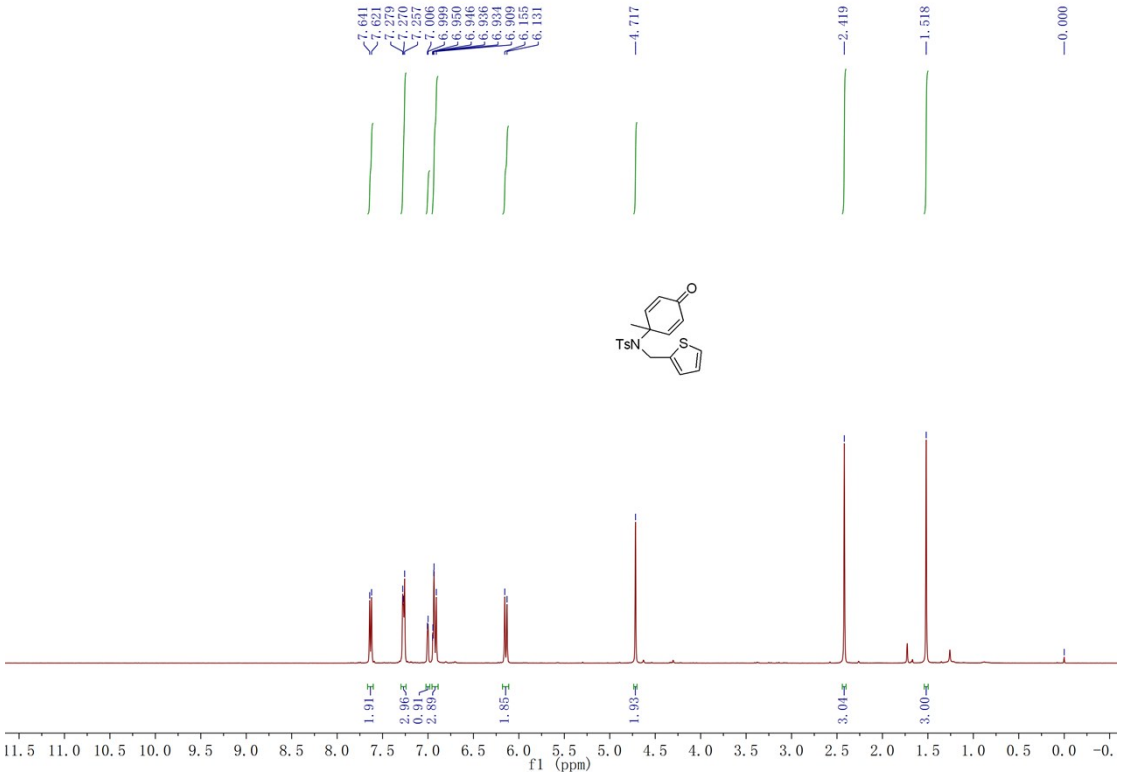


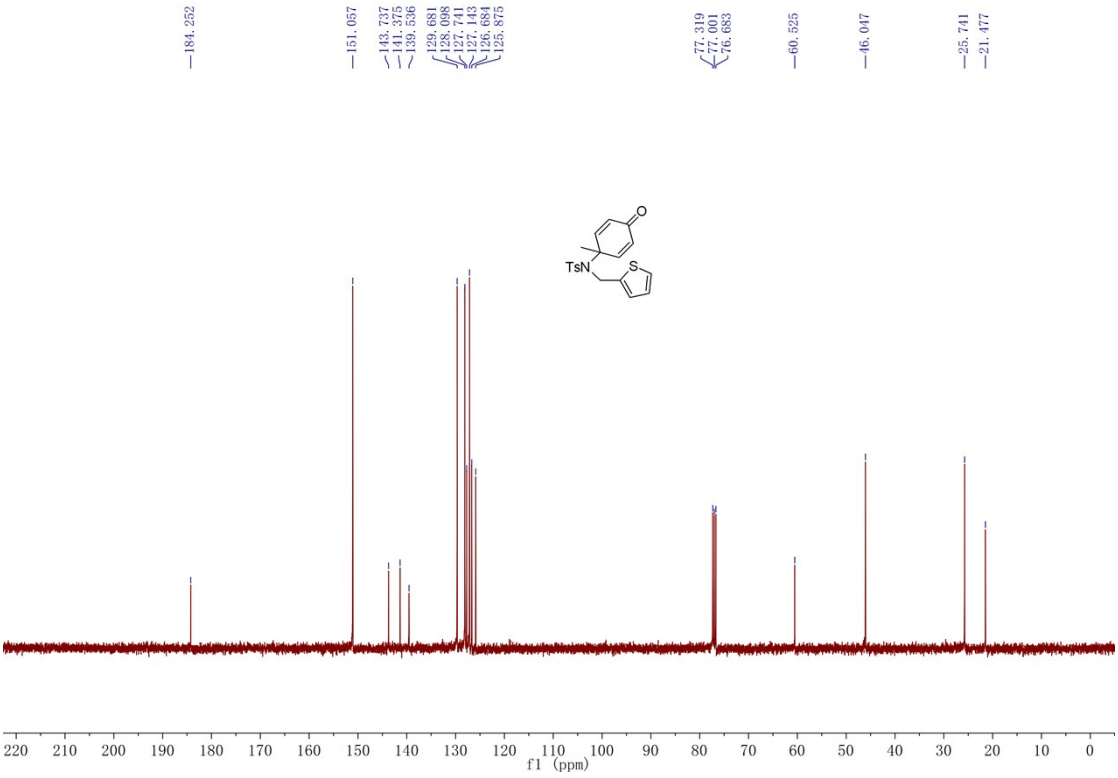




Compound 1af′:

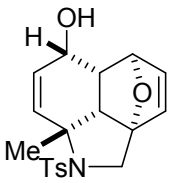
0.3 mmol scale, a light yellow solid, 87% yield (97.5 mg). M.p.: 185-188 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.52 (s, 3H), 2.42 (s, 3H), 4.72 (s, 2H), 6.14 (d, *J* = 9.6 Hz, 2H), 6.90-6.95 (m, 3H), 7.00 (d, *J* = 2.8 Hz, 1H), 7.25-7.28 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) 21.5, 25.7, 46.0, 60.5, 125.9, 126.7, 127.1, 127.7, 128.1, 129.7, 139.5, 141.4, 143.7, 151.1, 184.3. IR (neat) 3105, 3063, 3047, 2985, 2924, 2846, 1704, 1666, 1628, 1597, 1494, 1453, 1436, 1390, 1343, 1325, 1305, 1266, 1246, 1228, 1182, 1153, 1087, 1063, 1041, 955, 885, 861, 811, 766, 733, 703, 662 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{23}N_2O_3S_2^{+1}$(M+$NH_4$)$^+$ requires: 391.1145, Found: 391.1154.




184.252
151.057
143.737
141.375
139.536
129.681
128.098
127.741
127.143
126.684
125.875
77.319
77.001
76.683
60.525
46.047
25.741
21.477
O
TsN
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

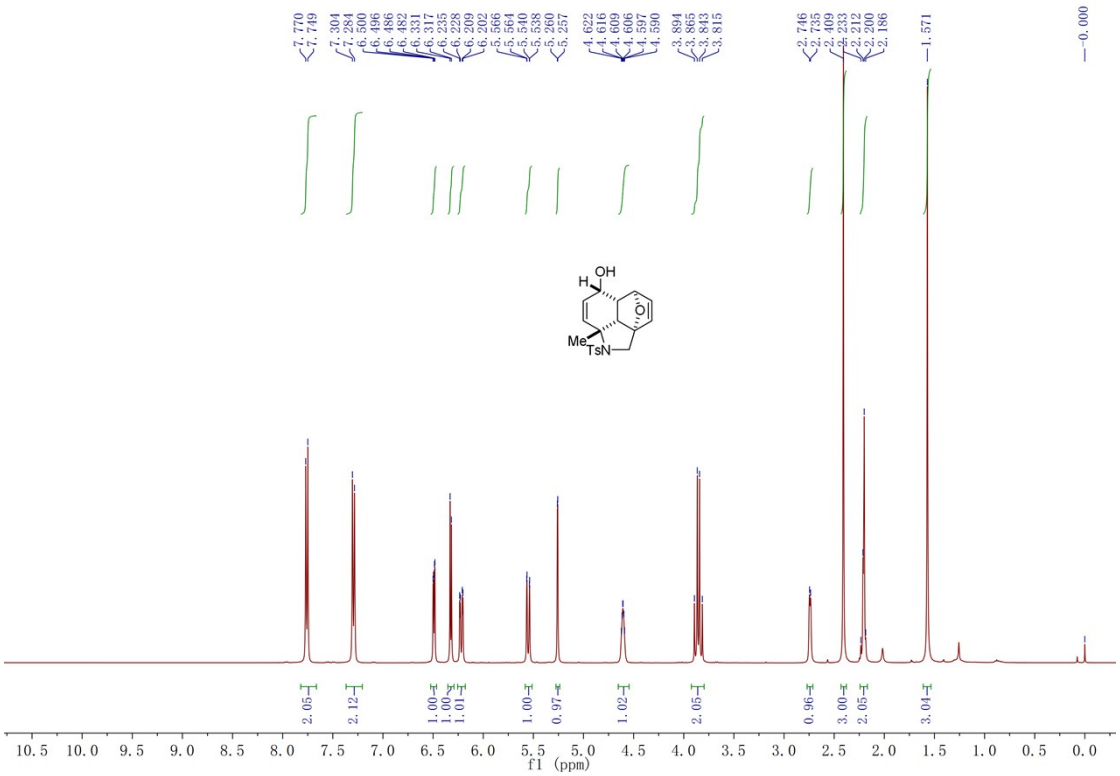
6. General procedure for the synthesis of 4, 5 and their characterization and spectra charts.

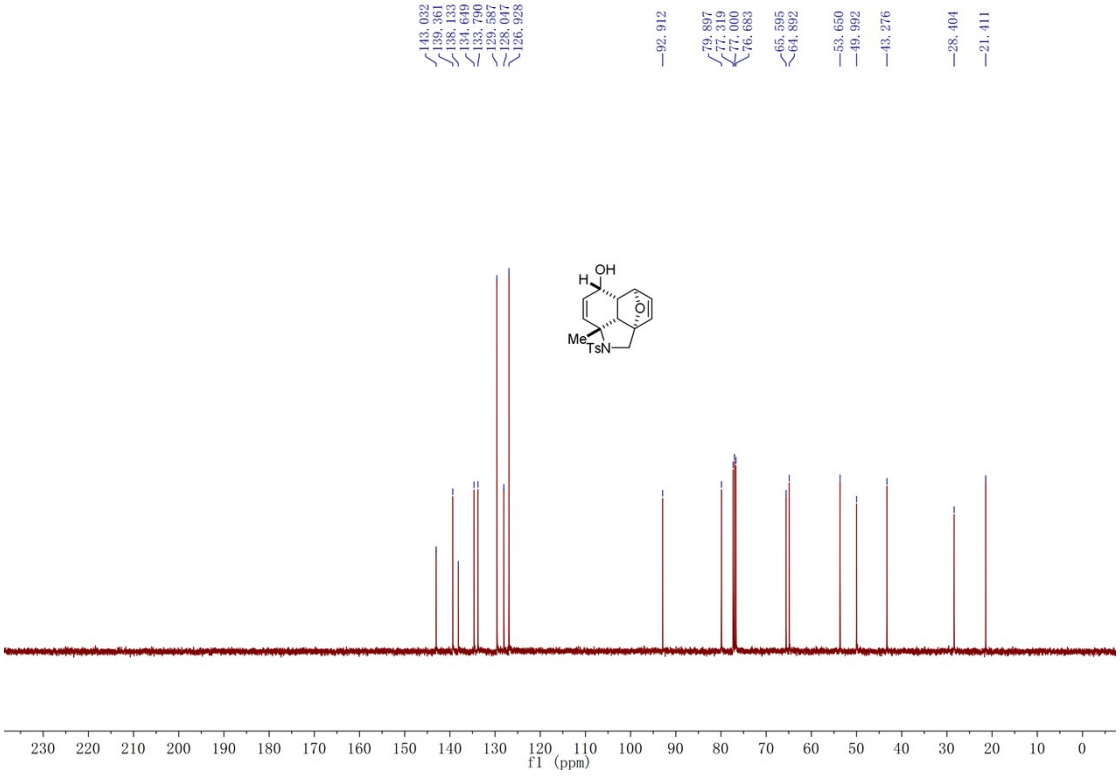
To a solution of **1a** (0.3 mmol, 1.0 equiv.) and $CeCl_3 \cdot 7H_2O$ (0.36 mmol, 1.2 equiv.) in MeOH (30.0 mL), $NaBH_4$ (0.33 mmol, 1.1 equiv.) was carefull added in portion at 0 °C. Then, the resulting mixture was allowed to warm to room temperature and was stirred for 5 hours. Next, the reaction was quenched by water (0.2 mL). After the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE/EA = 2/1) to give the desired product **4** as a white solid.

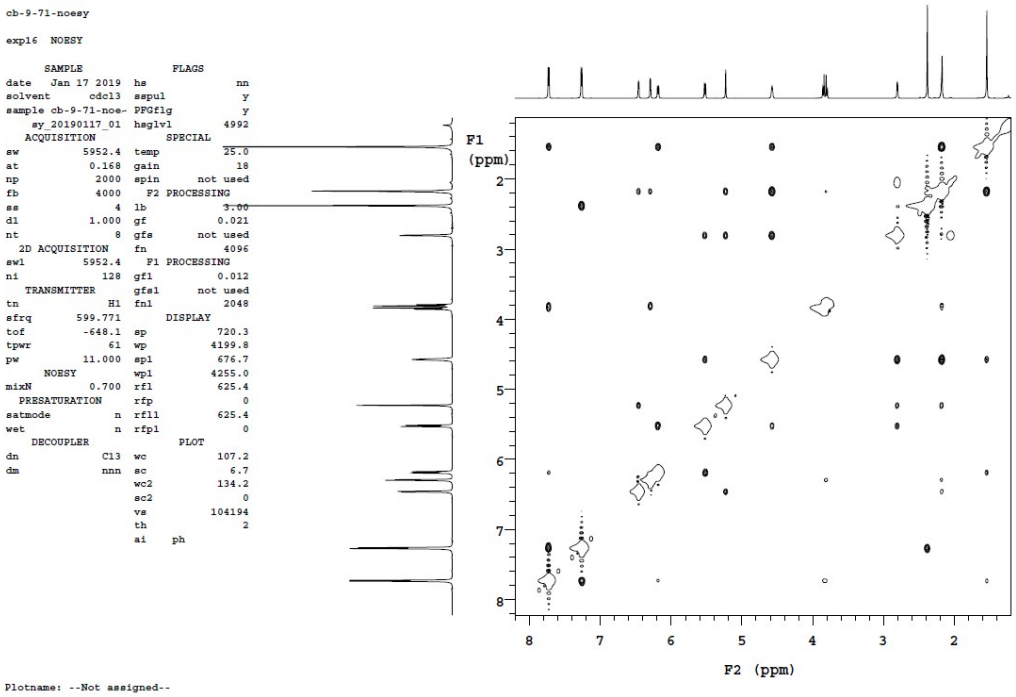


Compound 4:

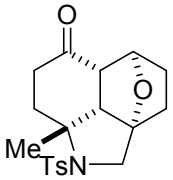
0.30 mmol scale, a white solid, 83% yield (89.5 mg). M.p.: 170-172 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.57 (s, 3H), 2.18-2.24 (m, 2H), 2.41 (s, 3H), 2.74 (d, *J* = 4.4 Hz, 1H), 3.83 (d, *J* = 11.2 Hz, 1H), 3.88 (d, *J* = 11.2 Hz, 1H), 4.59-4.63 (m, 1H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.55 (dd, *J* = 0.8 Hz, 10.4 Hz, 1H), 6.22 (dd, *J* = 2.8 Hz, 10.4 Hz, 1H), 6.32 (d, *J* = 5.6 Hz, 1H), 6.49 (dd, *J* = 1.6 Hz, 5.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.4, 28.4, 43.3, 50.0, 53.7, 64.9, 65.6, 79.9, 92.9, 126.9, 128.0, 129.6, 133.8, 134.6, 138.1, 139.4, 143.0. IR (neat) ν 3382, 3332, 3078, 3050, 3029, 3005, 2966, 2928, 2887, 2866, 2851, 2819, 1597, 1495, 1461, 1388, 1367, 1317, 1301, 1278, 1262, 1215, 1180, 1149, 1122, 1101, 1073, 1060, 1018, 990, 960, 900, 880, 862, 845, 809, 758, 735, 717, 707, 688, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{25}N_2O_4S^{+1}(M+NH_4)^+$ requires: 377.1530, found: 377.1526.


7.770
7.749
7.304
7.284
6.500
6.496
6.486
6.482
6.331
6.317
6.235
6.228
6.209
6.202
5.566
5.564
5.540
5.538
5.260
5.257
4.622
4.616
4.609
4.606
4.597
4.590
3.894
3.865
3.843
3.815
2.746
2.735
2.409
2.233
2.212
2.200
2.186
1.571
0.000
OH
H
Me
TsN
2.05
2.12
1.00
1.00
1.01
1.00
0.97
1.02
2.05
0.96
3.00
2.05
3.04
f1 (ppm)


143.032
139.361
138.133
134.649
133.790
129.587
128.047
126.928
92.912
79.897
77.319
77.000
76.683
65.595
64.892
53.650
49.992
43.276
28.404
21.411
OH
H
Me
TsN
f1 (ppm)

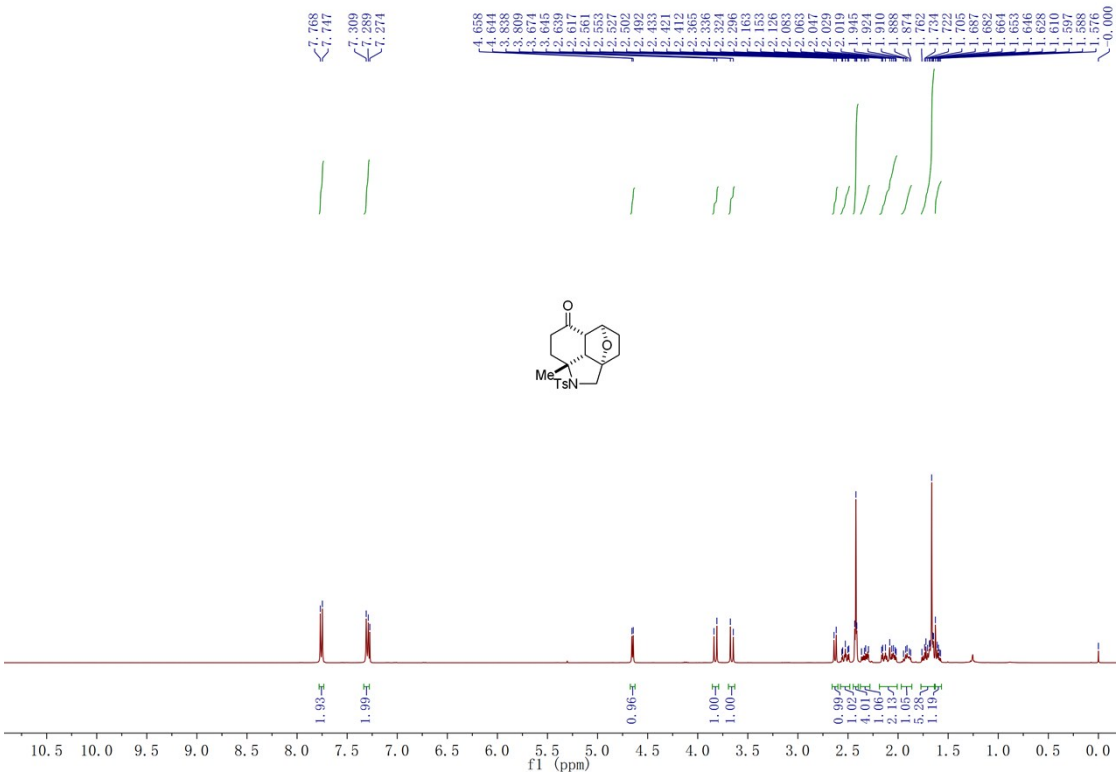


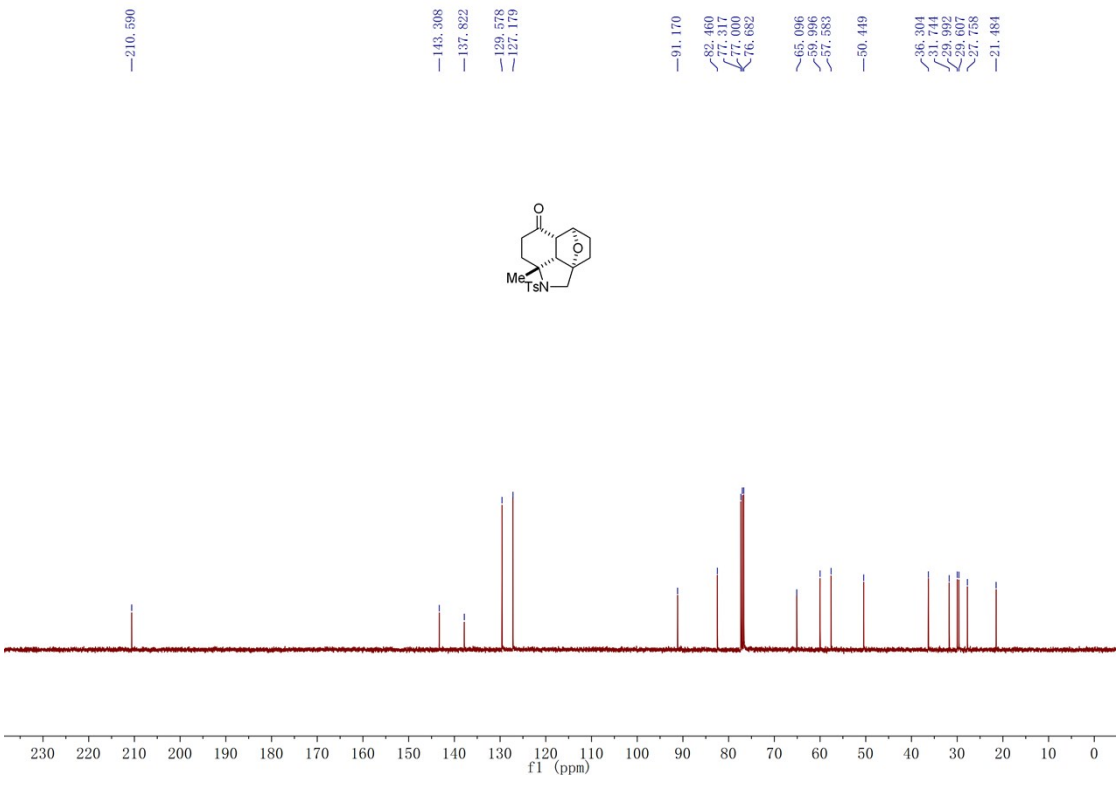
To a Schlenk tube was added **1a** (0.3 mmol) and Pd/C (0.03 mmol) and MeOH (3.0 mL), then, the resulting solution was evacuated and backfilled with H_2 for 3 times and stirred at 25 ^oC for 24 h under H_2. The solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE/EA = 3/1) to give the desired product **5** as a white solid.



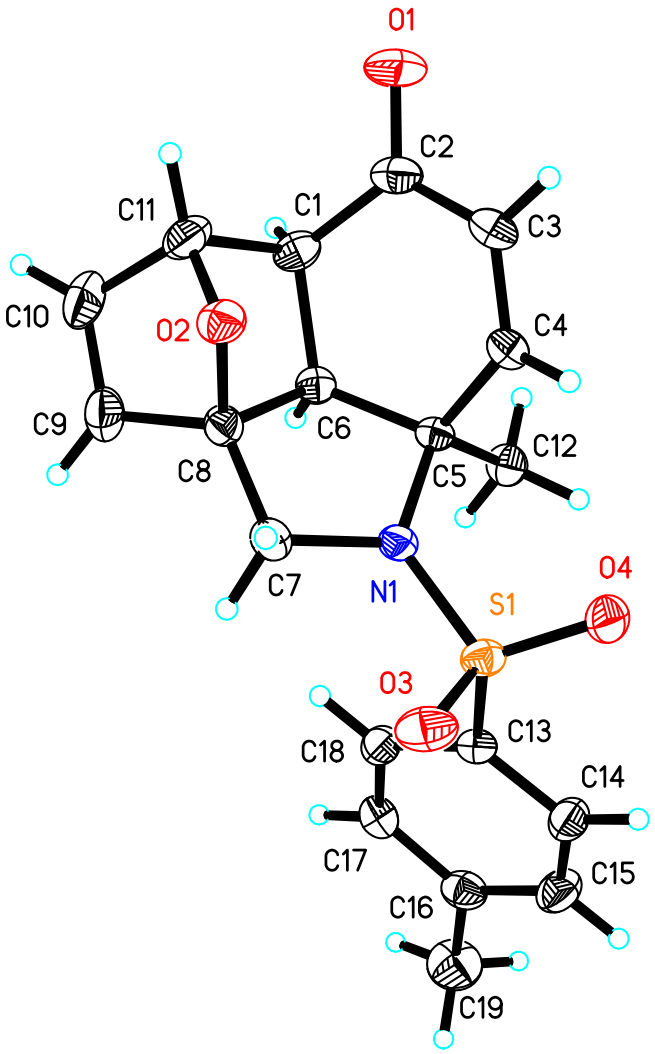
Compound 5:

0.30 mmol scale, a white solid, 60% yield (64.9 mg). M.p.: 158-159 ^oC. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.57-1.63 (m, 1H), 1.64-1.77 (m, 5H), 1.87-1.95 (m, 1H), 2.01-2.17 (m, 2H), 2.29-2.37 (m, 1H), 2.41-2.44 (m, 4H), 2.49-2.57 (m, 1H), 2.63 (d, J = 8.8 Hz, 1H), 3.66 (d, J = 11.6 Hz, 1H), 3.82 (d, J = 11.6 Hz, 1H), 4.65 (d, J = 5.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 27.8, 29.6, 30.0, 31.7, 36.3, 50.4, 57.6, 60.0, 65.1, 82.5, 91.2, 127.2, 129.6, 137.8, 143.3, 210.6. IR (neat) ν 3060, 3029, 2951, 2874, 1705, 1598, 1494, 1463, 1381, 1333, 1303, 1197, 1152, 1121, 1086, 1042, 1013, 975, 880, 831, 815, 733, 708, 680 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{24}NO_4S^{+1}(M+H)^+$ requires: 362.1421, found: 362.1421.


7.768
7.747
7.309
7.289
7.274
4.658
4.644
4.638
3.809
3.674
3.645
2.639
2.617
2.561
2.553
2.527
2.502
2.492
2.433
2.421
2.412
2.365
2.336
2.324
2.296
2.163
2.153
2.126
2.083
2.063
2.047
2.029
2.019
1.945
1.924
1.910
1.888
1.874
1.762
1.734
1.722
1.705
1.687
1.682
1.664
1.653
1.646
1.628
1.610
1.597
1.588
1.576
0.000
Me
TsN
1.93
1.99
0.96
1.00
1.00
0.99
1.02
4.01
1.06
2.13
1.05
5.28
1.19
f1 (ppm)


210.590
143.308
137.822
129.578
127.179
91.170
82.460
77.317
77.000
76.682
65.096
59.996
57.583
50.449
36.304
31.744
29.992
29.607
27.758
21.484
Me
TsN
f1 (ppm)

7. X-ray crystallographic information of product 3a.



The crystal data of **3a** have been deposited in CCDC with number 1873972. Empirical Formula: $C_{19}H_{19}NO_4S$; Formula Weight: 357.41; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.110 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 16.3542(10)Å, b = 6.0255(4)Å, c = 17.1246(12)Å, α = 90°, β = 98.854(2)°, γ = 90°, V = 1667.39(19)$Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1.424 g/cm^3; F_{000} = 752; Final R indices [I>2sigma(I)] R1 = 0.0433, wR2 = 0.1060.

8. **References.**

[1] (a) S. C. Banfield, M. A. Kerr, *Can. J. Chem.* **2004**, *82*, 131; (b) P. Jia, Q. Zhang, Jin, H. Y. Huang, *Org. Lett.* **2017**, *19*, 412; (c) B. Cao, Y. Wei, M. Shi, *Chem. Commun.*, **2018**, *54*, 14085.