Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Catalyst-Controlled Synthesis of 4-Amino-isoquinolin-1(2*H*)-one and Oxazole Derivatives

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Content

1. General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent DD2 400-MR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard; Chemical shifts (□) are expressed in ppm and *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Dichloroethane were distilled from CaH_2 under argon (Ar) atmosphere. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. The structures of **3aa** and **5aa** were assigned by X-ray analysis.

2. Preparation of the starting materials

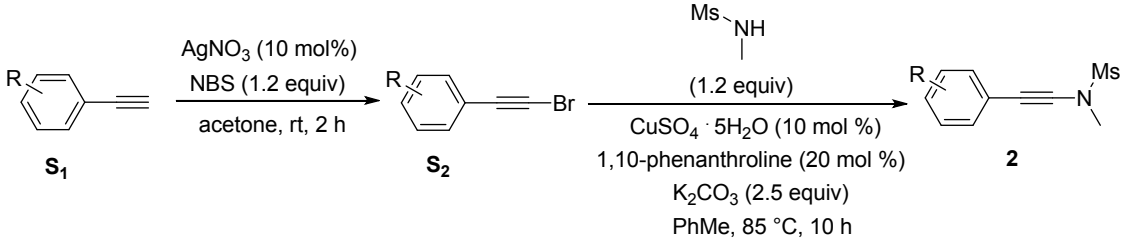
2.1 Preparation of substrates 1

The *N*-(pivaloyloxy)amides were prepared according to previously described methods.[1]

2.2 Preparation of substrates 2

The ynamides **2** were prepared according to previously described methods.[2]

2.3. General procedure A:



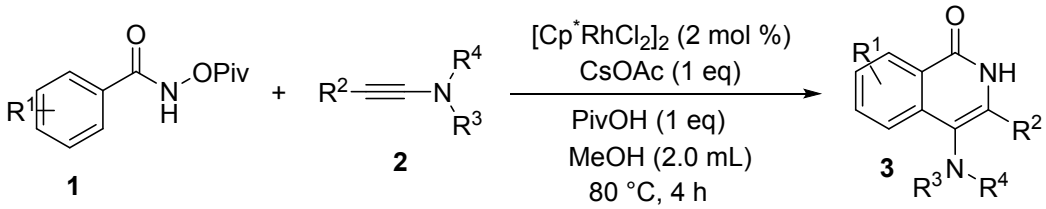
To a solution of substituted phenylacetylenes $\mathbf{S_1}$ (10.0 mmol, 1.0 equiv) in acetone (50 mL) was added NBS (2.14 g, 12.0 mmol, 1.2 equiv) and $AgNO_3$ (169.9 mg, 1.0 mmol, 10 mol%), and the resulting mixture was stirred under Ar at room temperature for 2 hours. After removing excess acetone, the reaction was quenched with saturated NH_4Cl solution. The organic layer was extracted with petroleum ether (40 mL x 2), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford bromoalkynes $\mathbf{S_2}$.

To a dried flask was added *N*-methymethanesulphonamide (1.31 g, 12.0 mmol, 1.2 equiv), $CuSO_4 \cdot 5H_2O$ (250.0 mg, 1.0 mmol, 10 mol %), 1,10-phenanthroline (360.4 mg, 2.0 mmol, 20 mol%) and K_2CO_3 (3.46 g, 25.0 mmol, 2.5 equiv). The resulting mixture was subsequently used to

react with bromoalkynes **S$_2$** in anhydrous toluene, and the resulting mixture was stirred at 85 °C for overnight under Ar atmosphere. After completion of the reaction monitored by TLC, the crude mixtures were cooled to room temperature, filtered through a Celite, and concentrated in vacuo. The residue was purified by a flash column chromatography on silica gel, giving the pure ynamides **2**.

3. General procedure for the synthesis of compounds 3.

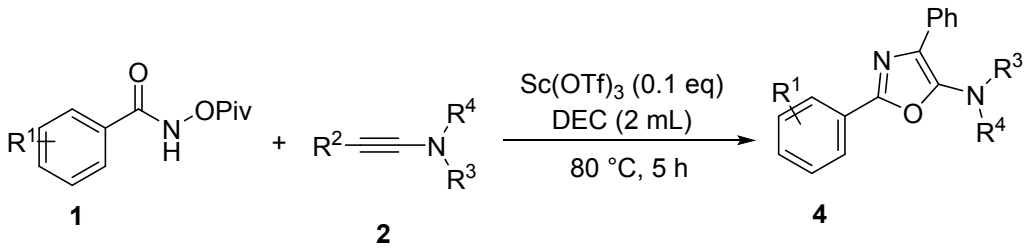
General procedure B:



A sealable tube with a magnetic stir bar was charged with [RhCp*Cl$_2$]$_2$ (3 mg, 4 μmol, 2 mol%), CsOAc (38 mg, 0.2 mmol, 1.0 equiv), *N*-(pivaloyloxy)amide **1** (0.2 mmol), ynamides **2** (0.2 mmol, 1.0 equiv), and MeOH (2.0 mL) under an N_2 atmosphere. The reaction mixture was stirred at 80°C for 4 h. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a Celite pad, and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by a column chromatography on silica gel to provide the desired product.

4. General procedure for the synthesis of compounds 4.

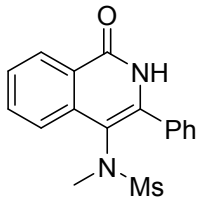
General procedure C:



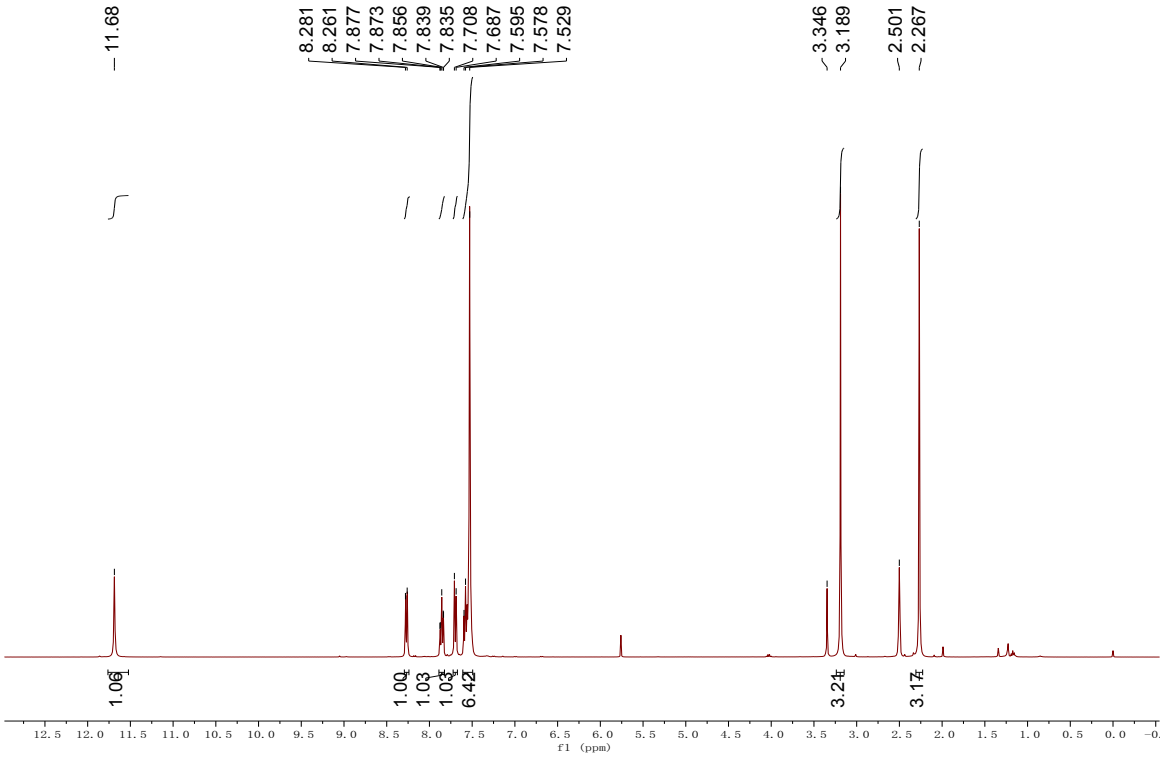
N-(Pivaloyloxy)amide **1** (0.2 mmol, 1.0 equiv), Sc(OTf)$_3$ (10 mg, 10 mol%), DCE (2.0 mL) and ynamide **2** (0.26 mmol, 1.3 equiv) were added to a Schlenk tube. The resulting mixture was stirred at 80 °C for 4 h under Ar atmosphere, then the reaction mixture was diluted with EtOAc (10 mL).

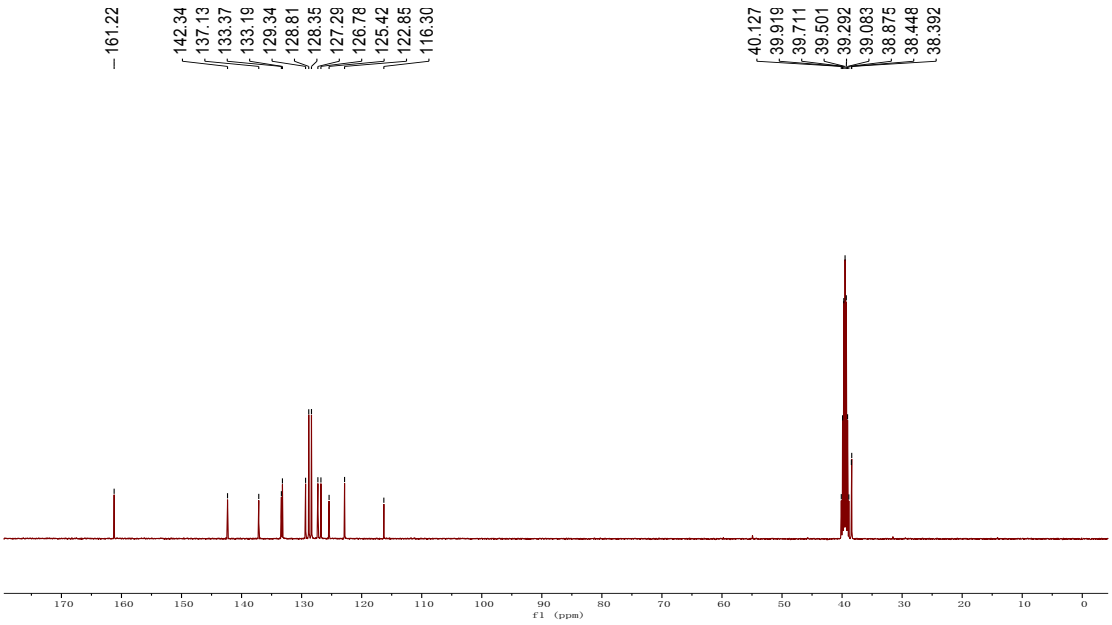
The solvent was removed under reduced pressure and the residue was purified by a column chromatography on silica gel to afford the desired products 4.

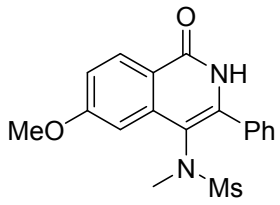
5. Spectroscopic data of the products.



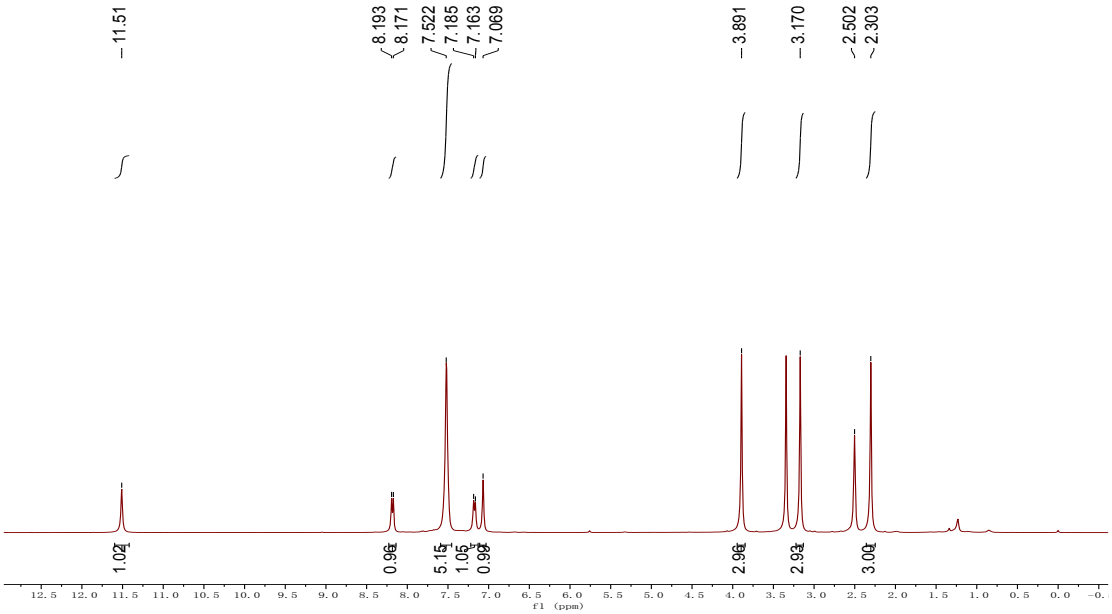
Compound 3aa: Yield: 62 mg, 87%; A white solid; Mp: 240-242 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.69 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.86 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.61-7.53 (m, 6H), 3.19 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.2, 142.3, 137.1, 133.4, 133.2, 129.3, 128.8, 128.4, 127.3, 126.8, 125.4, 122.9, 116.3, 38.5, 38.4; IR (neat): ν 2974, 2930, 1493, 1363, 1338, 1152, 783, 764, 702 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{17}N_2O_3S$ $[M+H]^+$: 329.0954, found: 329.0955.

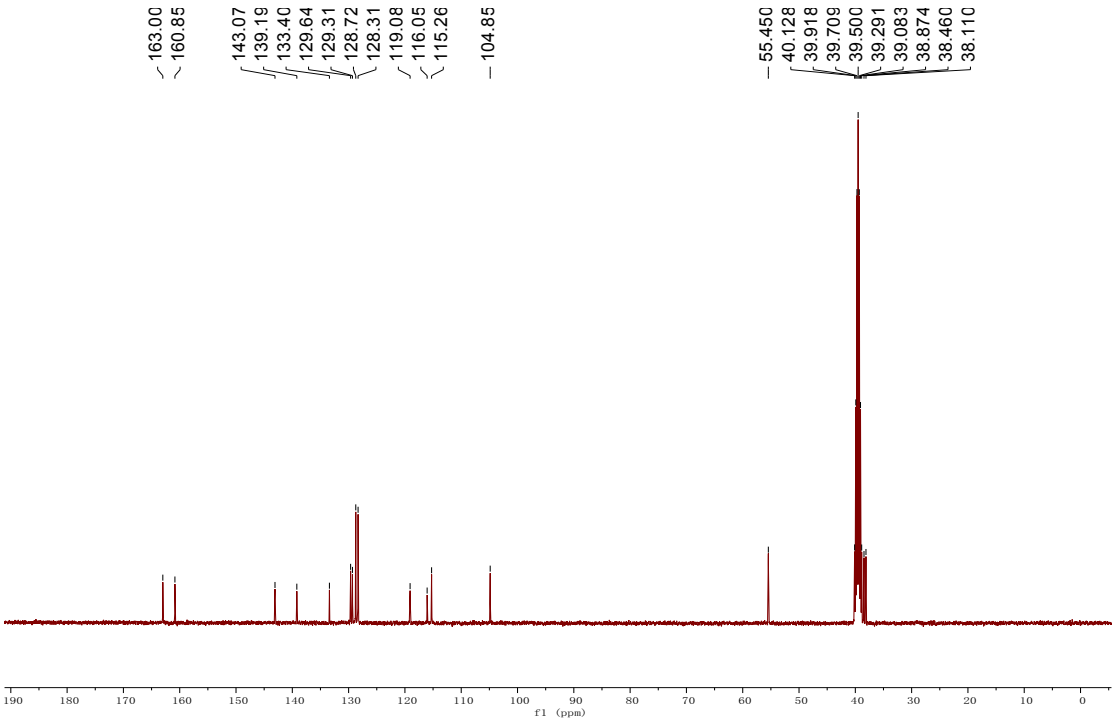


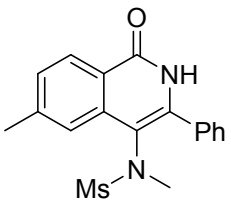




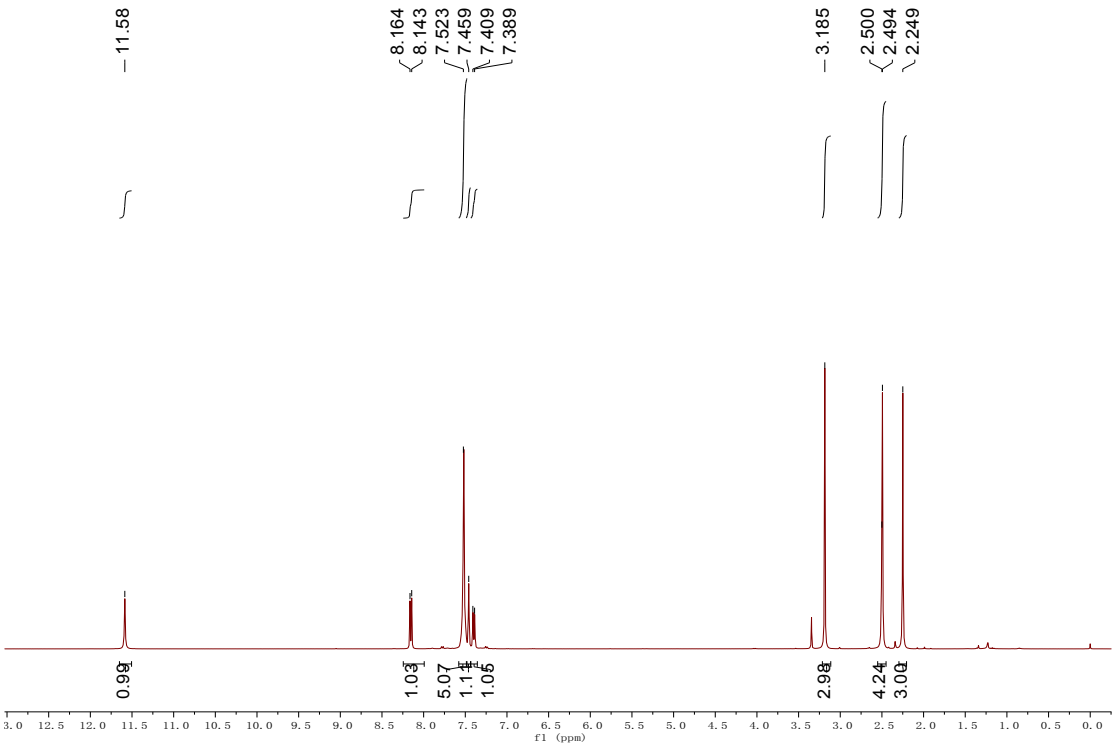
Compound 3ba: Yield: 45 mg, 71%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.51 (s, 1H), 8.18 (d, J = 8.8 Hz, 1H), 7.52 (brs, 5H), 7.17 (d, J = 8.8 Hz, 1H), 7.07 (s, 1H), 3.89 (s, 3H), 3.17 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 163.0, 160.9, 143.1, 139.2, 133.4, 129.7, 129.3, 128.7, 128.3, 119.1, 116.1, 115.3, 104.9, 55.5, 38.5, 38.1; IR (neat): ν 3003, 2897, 1648, 1609, 1640, 1325, 1143, 1027, 779, 699 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{19}N_2O_4S$ $[M+H]^+$: 359.1060, found: 359.1056.







Compound 3ca: Yield: 58 mg, 85%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.59 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.52 (brs, 5H), 7.46 (s, 1H), 7.40 (d, J = 8.4 Hz, 1H), 3.19 (s, 3H), 2.50 (d, J = 2.5 Hz, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.1, 143.3, 142.4, 137.2, 133.5, 129.3, 128.8, 128.4, 128.2, 127.4, 123.3, 122.4, 116.1, 38.4, 21.9; IR (neat): ν 2915, 2842, 2222, 1731, 1610, 11538, 742, 694, 664 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{19}N_2O_3S$ $[M+H]^+$: 343.1111, found: 343.1108.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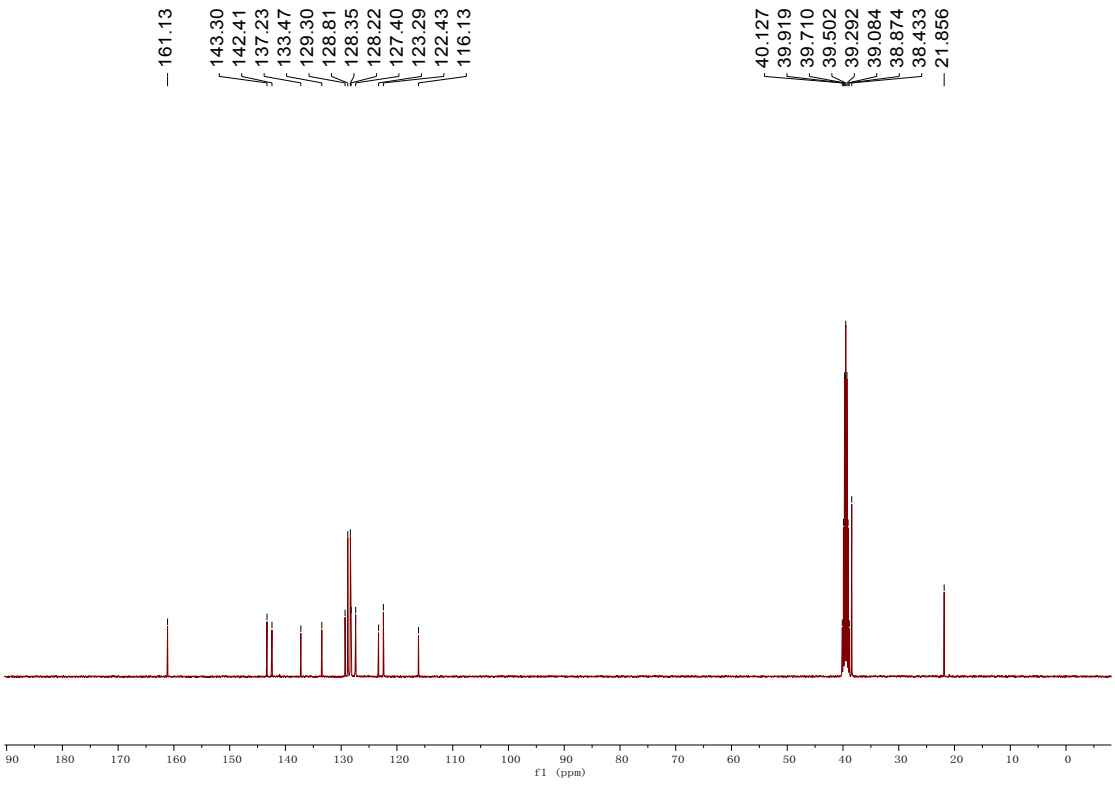
8.164
8.143
7.523
7.459
7.409
7.389
3.185
2.500
2.494
2.249
0.99
1.03
5.07
1.14
1.05
2.98
4.24
3.00
f1 (ppm)


161.13
143.30
142.41
137.23
133.47
129.30
128.81
128.35
128.22
127.40
123.29
122.43
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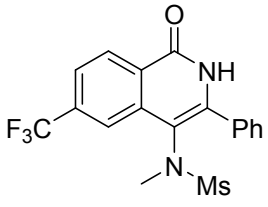
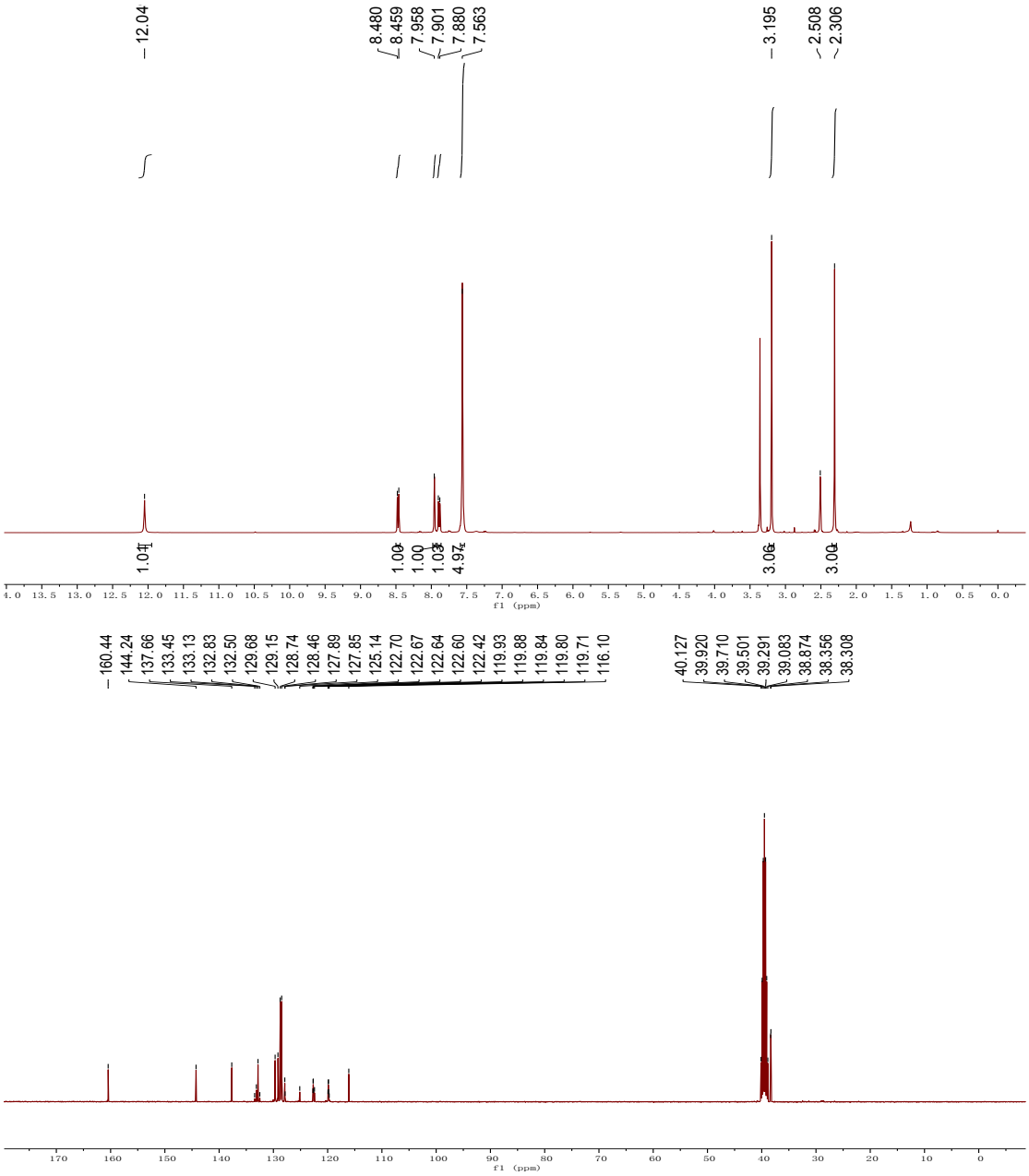
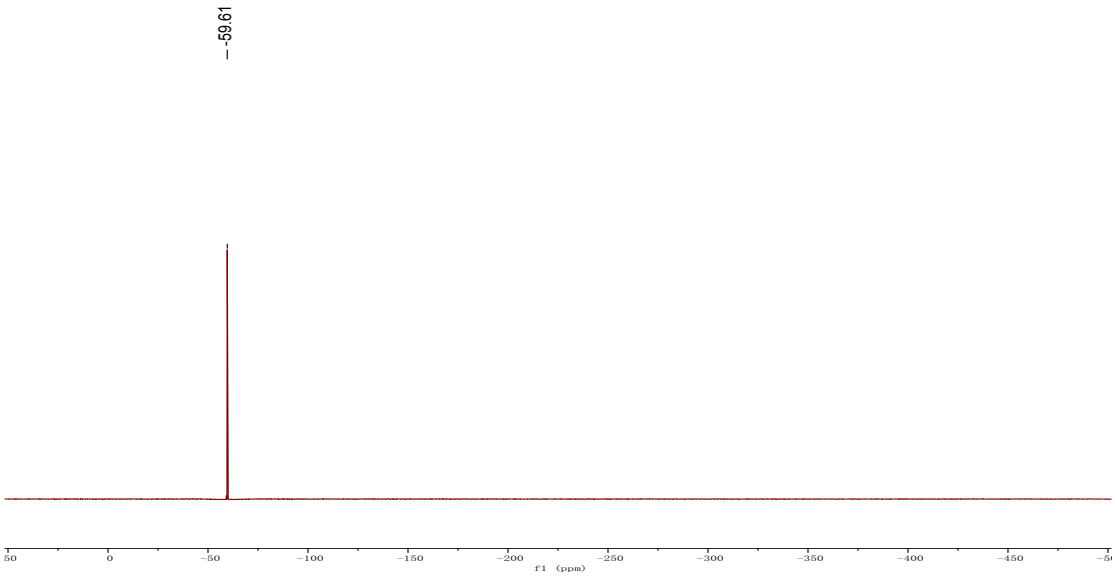
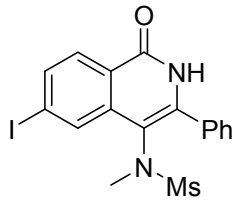
39.084
38.874
38.433
21.856
f1 (ppm)


O
NH
F3C
Ph
N
Ms

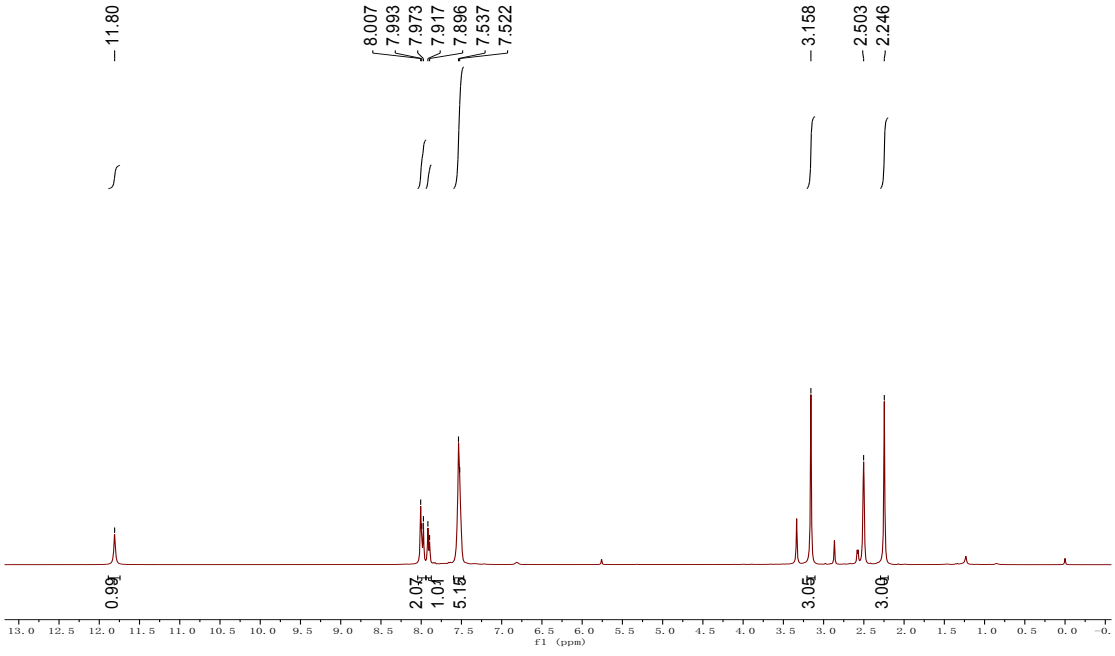
Compound 3da: Yield: 65 mg, 61%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.05 (s, 1H), 8.47 (d, J = 8.4 Hz, 1H), 7.96 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.56 (brs, 5H), 3.20 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.5, 144.3, 137.7, 133.0 (q, J = 30.3 Hz), 132.8, 129.7, 129.2, 128.8, 128.5, 128.0, 123.8 (q, J = 271.5 Hz), 122.64 (q, J = 3.4 Hz), 119.87 (q, J = 4.4 Hz), 116.1, 38.4, 38.3; ^{19}F NMR (376 MHz, D_2O) δ -59.6; IR (neat): ν 3173, 3046, 2922, 1654, 1360, 1305, 1131, 1067, 792, 722 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{16}F_3N_2O_3S$ $[M+H]^+$: 397.0828, found: 397.0825.

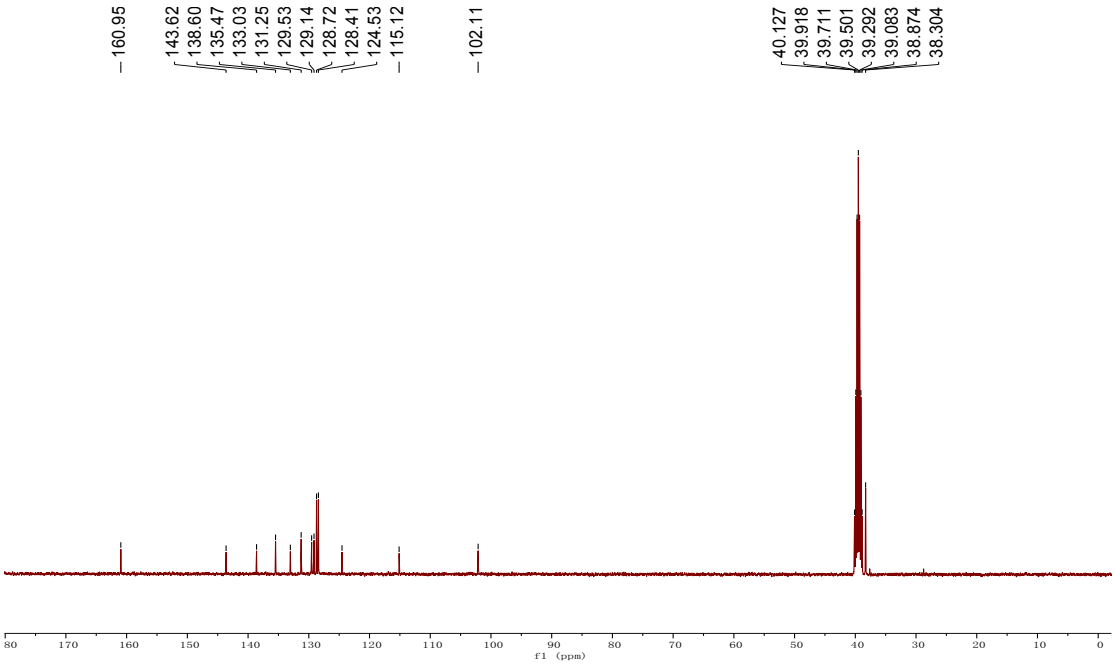


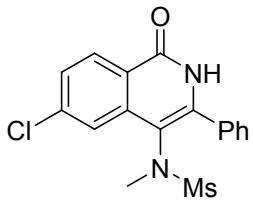




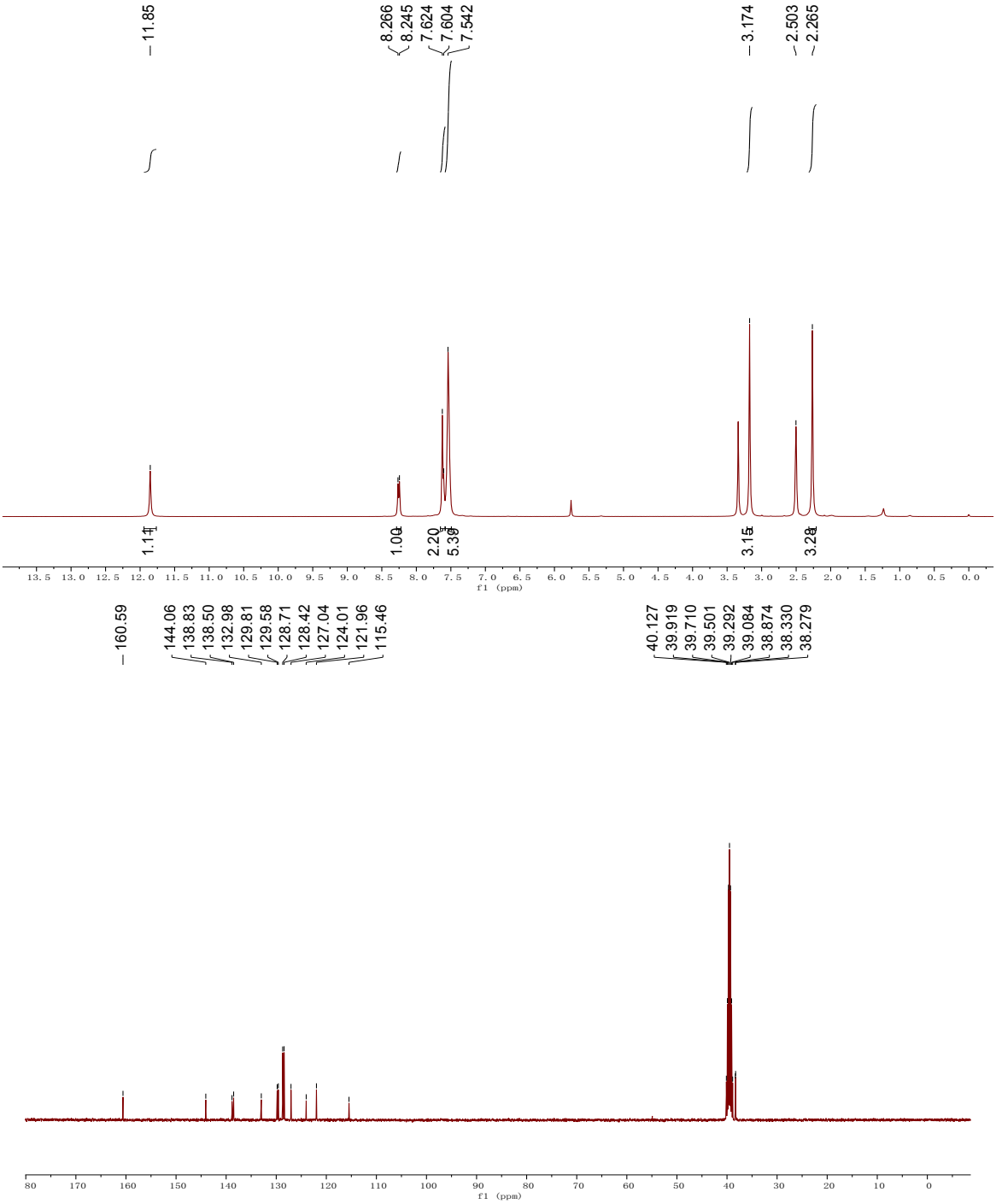
Compound 3ea: Yield: 51 mg, 81%; A white solid; Mp: >250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 8.01 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.54-7.52 (m, 5H), 3.16 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.0, 143.6, 138.6, 135.5, 133.0, 131.3, 129.5, 129.1, 128.7, 128.4, 124.5, 115.1, 102.1, 38.3; IR (neat): ν 3178, 3070, 2910, 1652, 1617, 1585, 1142, 962, 786, 697 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{16}IN_2O_3S$ $[M+H]^+$: 454.9921, found: 454.9917.

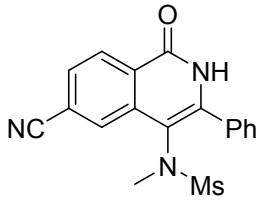






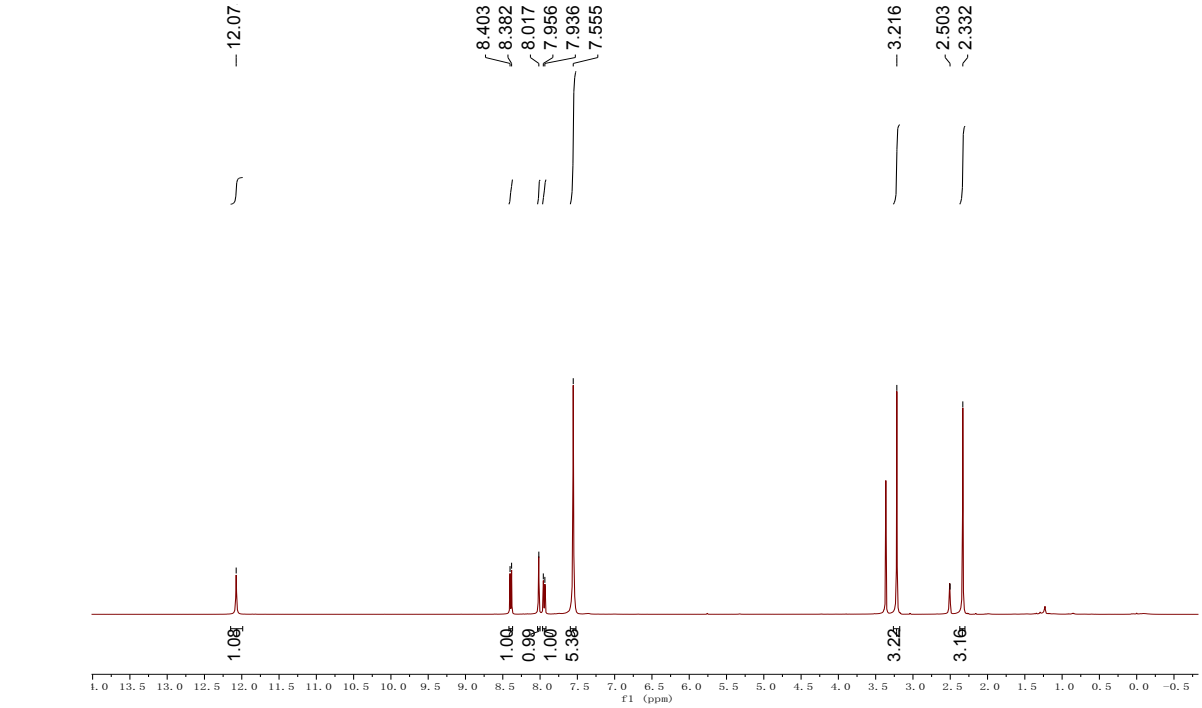
Compound 3fa: Yield: 57 mg, 80%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.85 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.54 (brs, 5H), 3.17 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.6, 144.1, 138.8, 138.5, 133.0, 129.8, 129.6, 128.7, 128.4, 127.1, 124.0, 122.0, 115.5, 38.3, 38.28; IR (neat): ν 2925, 1484, 1335, 1323, 1092, 1004, 850,839, 761, 737 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{16}ClN_2O_3S$ $[M+H]^+$: 363.0565, found: 363.0562.

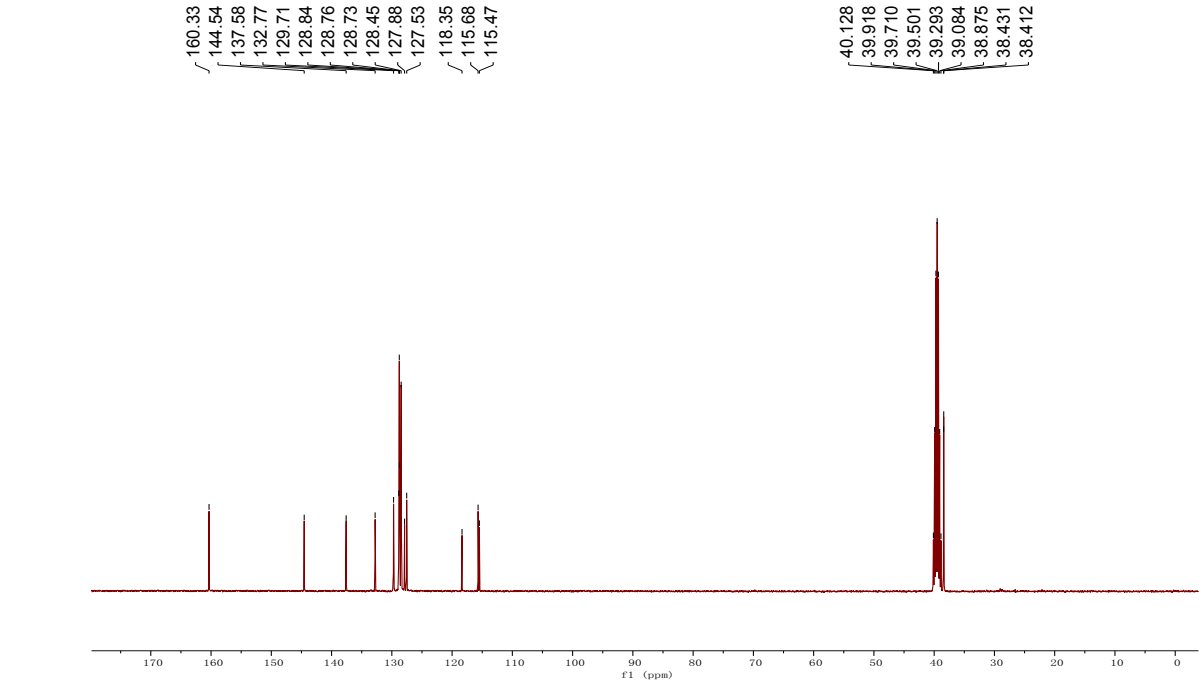


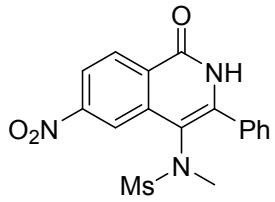


Compound 3ga: Yield: 55 mg, 78%; A white solid; Mp: >250°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.07 (s, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.02 (s, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.56 (brs, 5H), 3.22 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100MHz, DMSO) δ 160.3, 144.5, 137.6, 132.8, 129.7, 128.9,

128.8, 128.7, 128.5, 127.9, 127.5, 118.4, 115.7, 115.5, 38.43, 38.41; IR (neat): ν 2915, 2842, 2222, 1731, 1610, 11538, 742, 694, 664 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{16}N_3O_3S$ $[M+H]^+$: 354.0907, found: 354.0905.

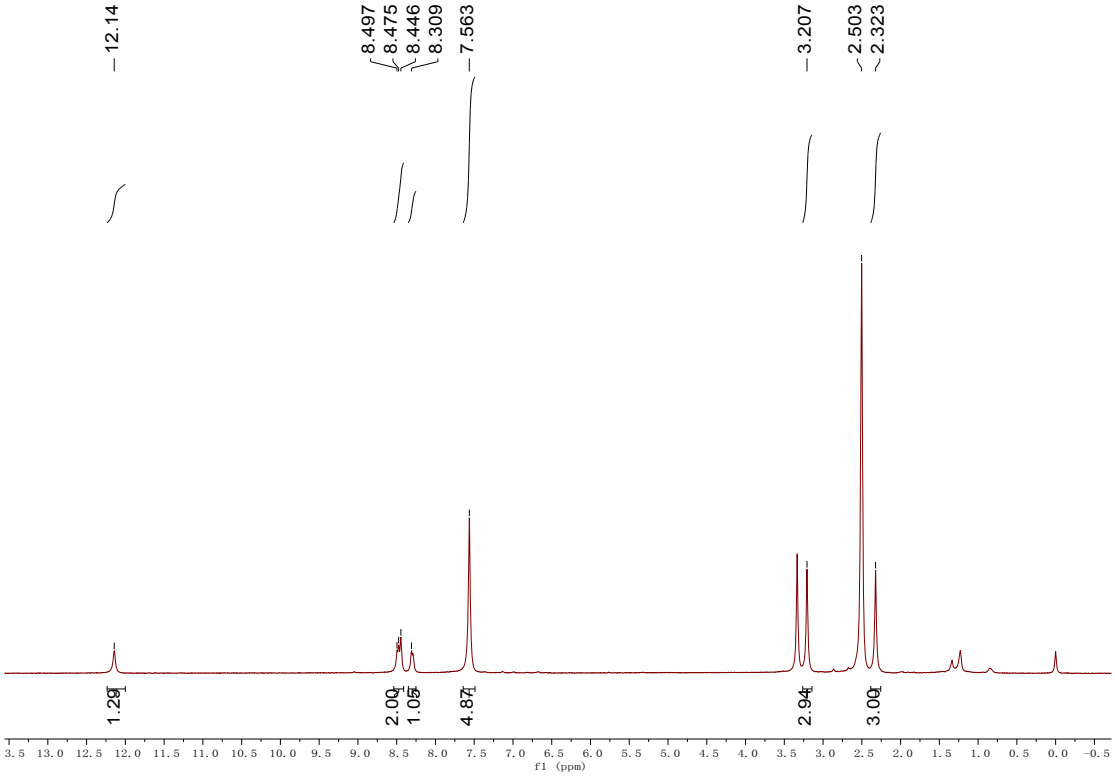


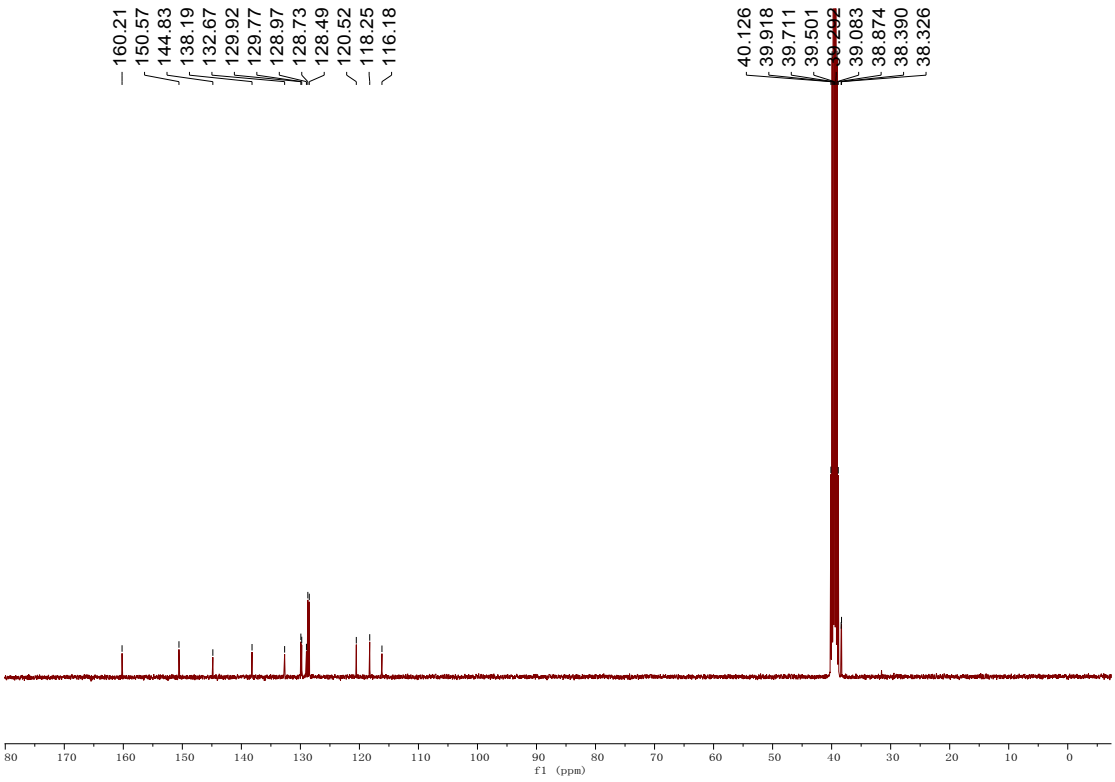


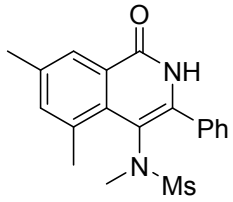


Compound 3ha: Poor solubility in DMSO-*d*6. Yield: 61 mg, 88%; A yellow solid; Mp: > 250 °C;

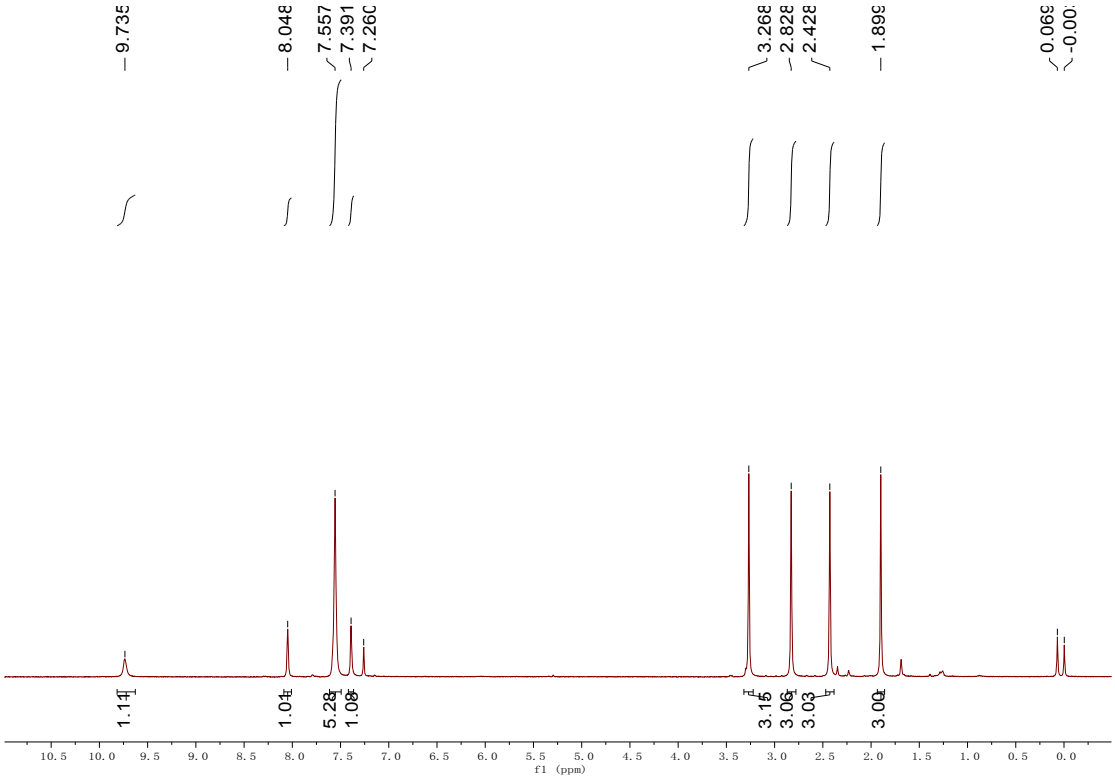
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.14 (s, 1H), 8.54-8.41 (m, 2H), 8.30 (d, J = 7.2 Hz, 1H), 7.56 (brs, 5H), 3.21 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 160.2, 150.6, 144.8, 138.2, 132.7, 129.9, 129.8, 129.0, 128.7, 128.5, 120.5, 118.3, 116.2, 38.4, 38.3; IR (neat): ν 3354, 3028, 2889, 1663, 1617, 1528, 1324, 1145, 892, 750 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{16}N_3O_5S$ $[M+H]^+$: 374.0804, found: 374.0803.

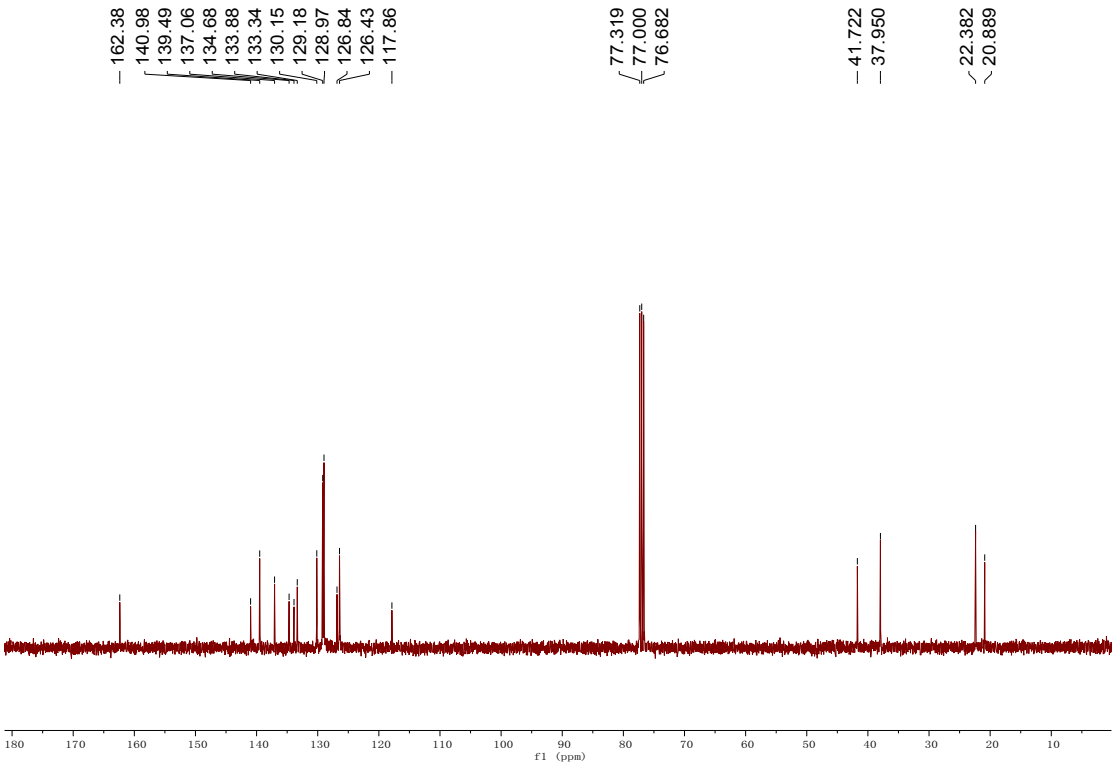


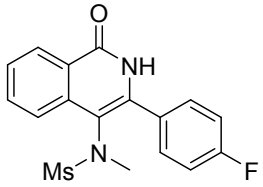




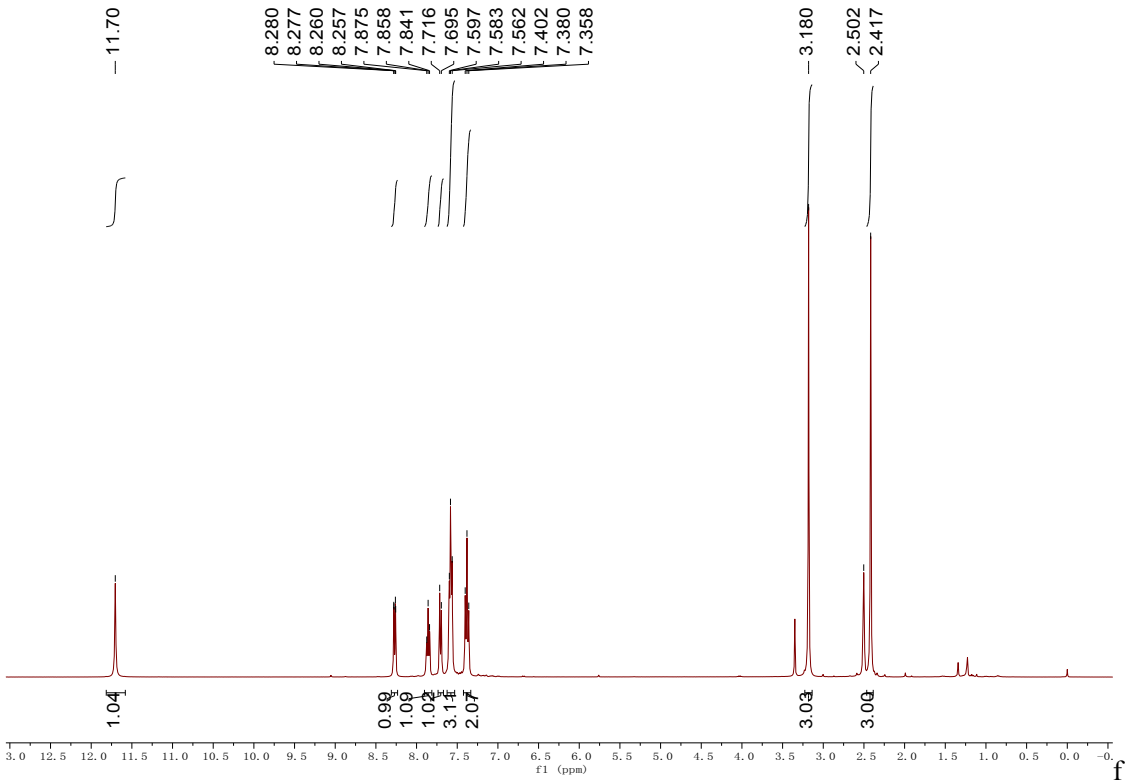
Compound 3ia: Yield: 51 mg, 71%; A yellow solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.74 (s, 1H), 8.05 (s, 1H), 7.56 (brs, 5H), 7.39 (s, 1H), 3.27 (s, 3H), 2.83 (s, 3H), 2.43 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 141.0, 139.5, 137.1, 134.7, 133.9, 133.4, 130.2, 129.2, 129.0, 126.9, 126.4, 117.9, 41.7, 38.0, 22.4, 20.9; IR (neat): ν 3354, 3298, 2889, 1687, 1617, 1528, 1342, 1145, 892, 705 cm^{-1}; HRMS (ESI) Calcd. for $C_{19}H_{21}N_2O_3S$ $[M+H]^+$: 357.1267, found: 357.1263.







Compound 3ab: Yield: 49 mg, 70%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H), 8.27 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.85 (td, J_1 = 7.6, J_2 = 1.6, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.56-7.59 (m, 3H), 7.38 (t, J = 8.8 Hz, 2H), 3.18 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 162.5 (d, J = 244.1 Hz), 161.2, 141.5, 137.0, 133.2, 131.3 (d, J = 8.5 Hz), 129.7 (d, J = 3.2 Hz), 127.3, 126.9, 125.5, 122.9, 116.4, 115.4 (d, J = 21.6 Hz), 38.7, 38.3; ^{19}F NMR (376 MHz, D_2O) δ -109.6; IR (neat): ν 3026, 1651, 1604, 1509, 1334, 1323, 1141, 895, 837, 764 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{16}FN_2O_3S$ $[M+H]^+$: 347.0860, found: 347.0857.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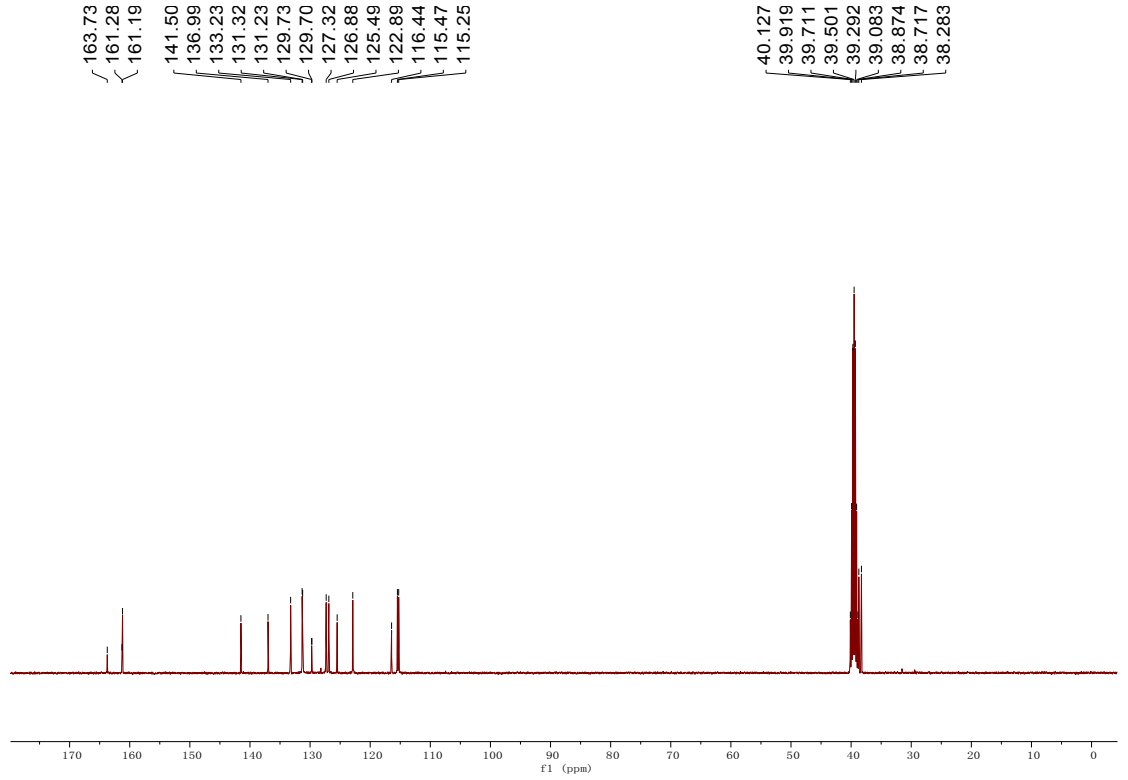
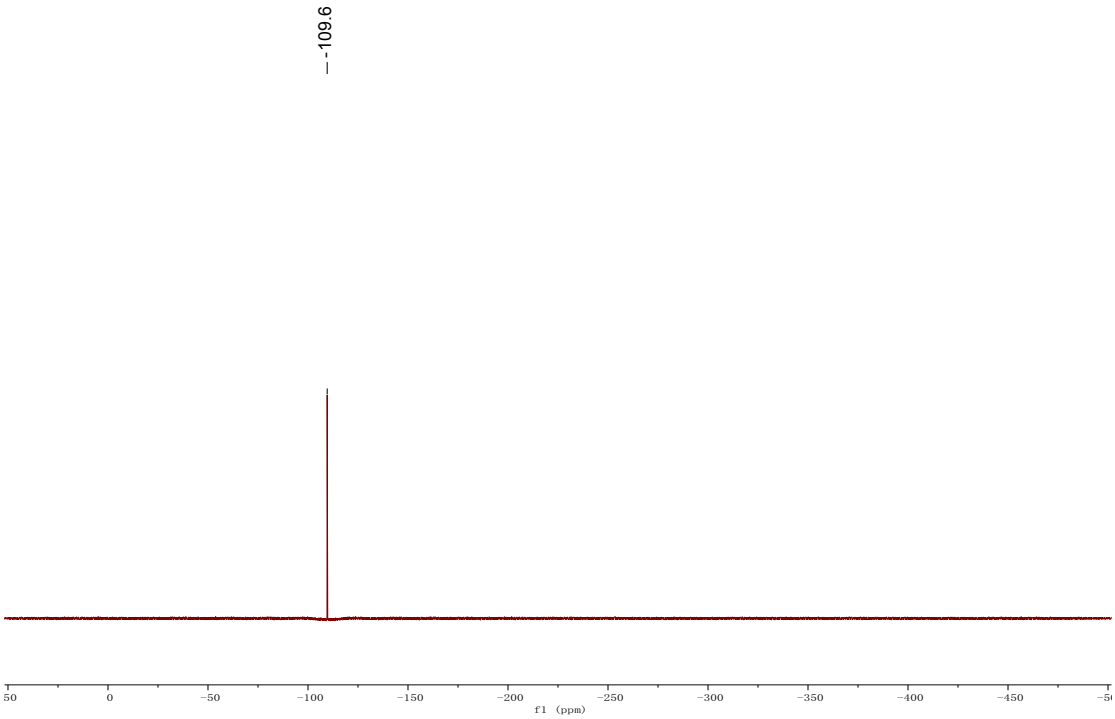
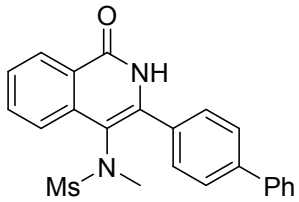
8.277
8.260
8.257
7.875
7.858
7.841
7.716
7.695
7.597
7.583
7.562
7.402
7.380
7.358
3.180
2.502
2.417
1.04
0.99
1.09
1.02
3.14
2.07
3.03
3.00
f1 (ppm)

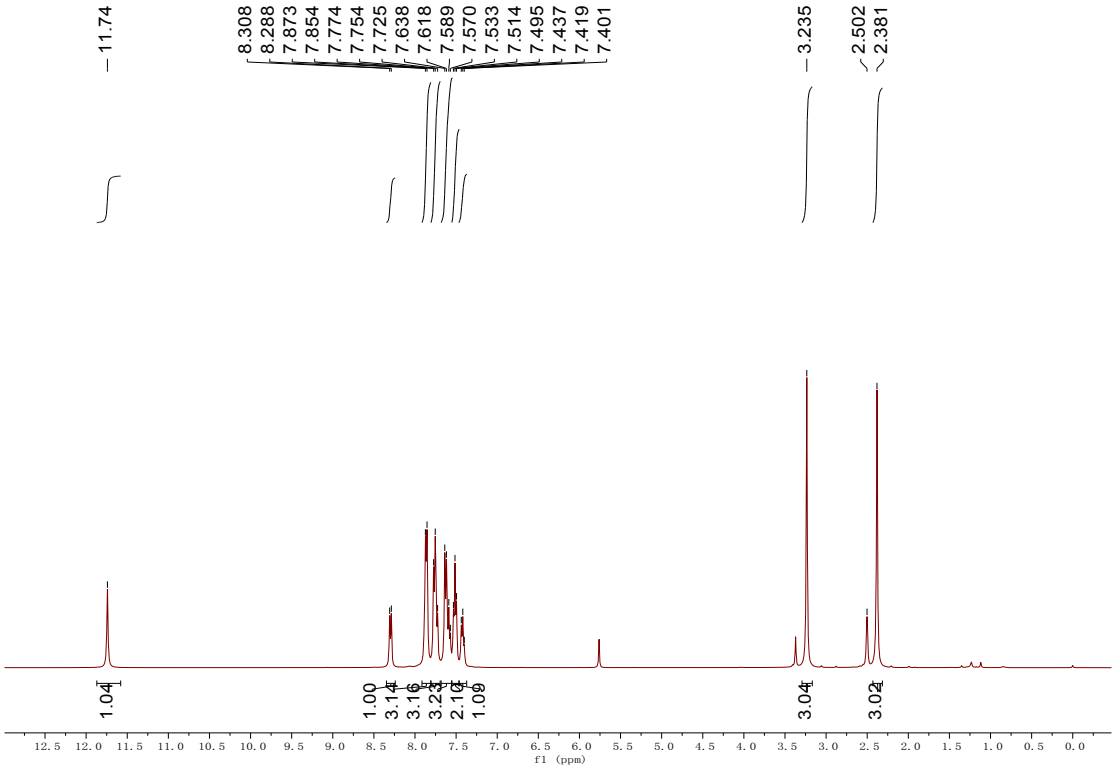
f

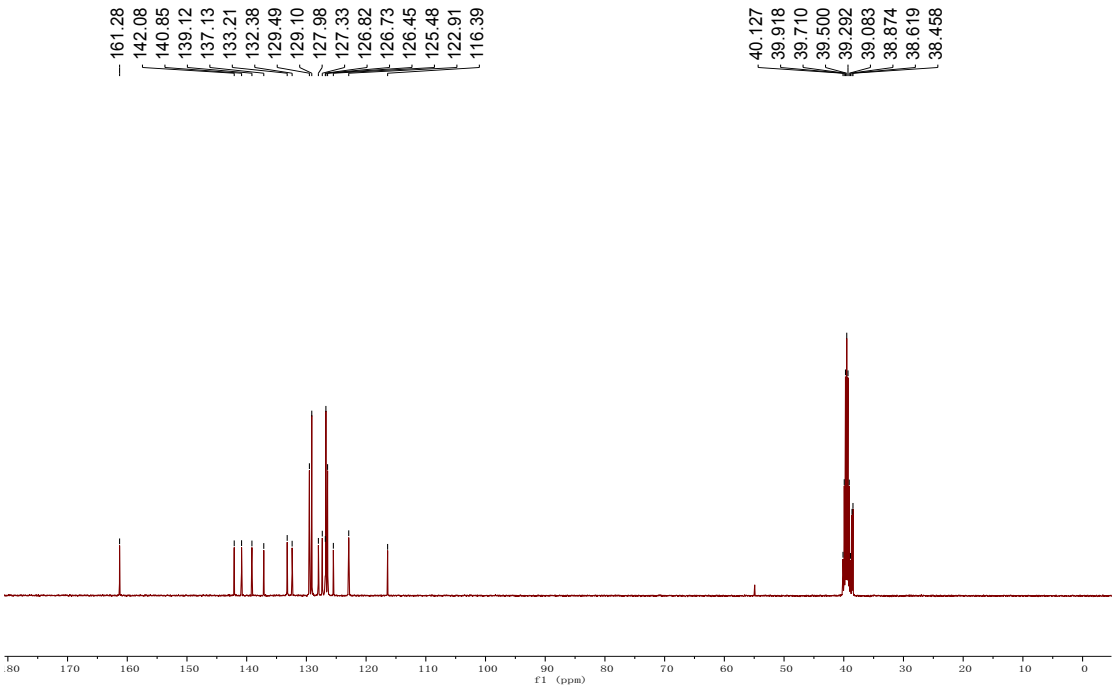

163.73
161.28
161.19
141.50
136.99
133.23
131.32
131.23
129.73
129.70
127.32
126.88
125.49
122.89
116.44
115.47
115.25
40.127
39.919
39.711
39.501
39.292
39.083
38.874
38.717
38.283
f1 (ppm)

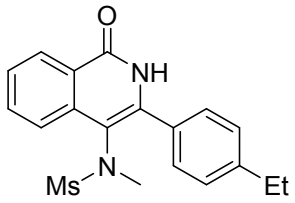




Compound 3ac: Yield: 49 mg, 73%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.74 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.2 Hz, 3H), 7.77-7.73 (m, 3H), 7.64-7.57 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H), 7.44-7.40 (m, 1H), 3.23 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.3, 142.1, 140.9, 139.1, 137.1, 133.2, 132.4, 129.5, 129.1, 128.0, 127.3, 126.8, 126.7, 126.5, 125.5, 122.9, 116.4, 38.6, 38.5; IR (neat): ν 3168, 2917, 2842, 1641, 1618, 1332, 1325, 1144, 778, 762 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1267, found: 405.1276.

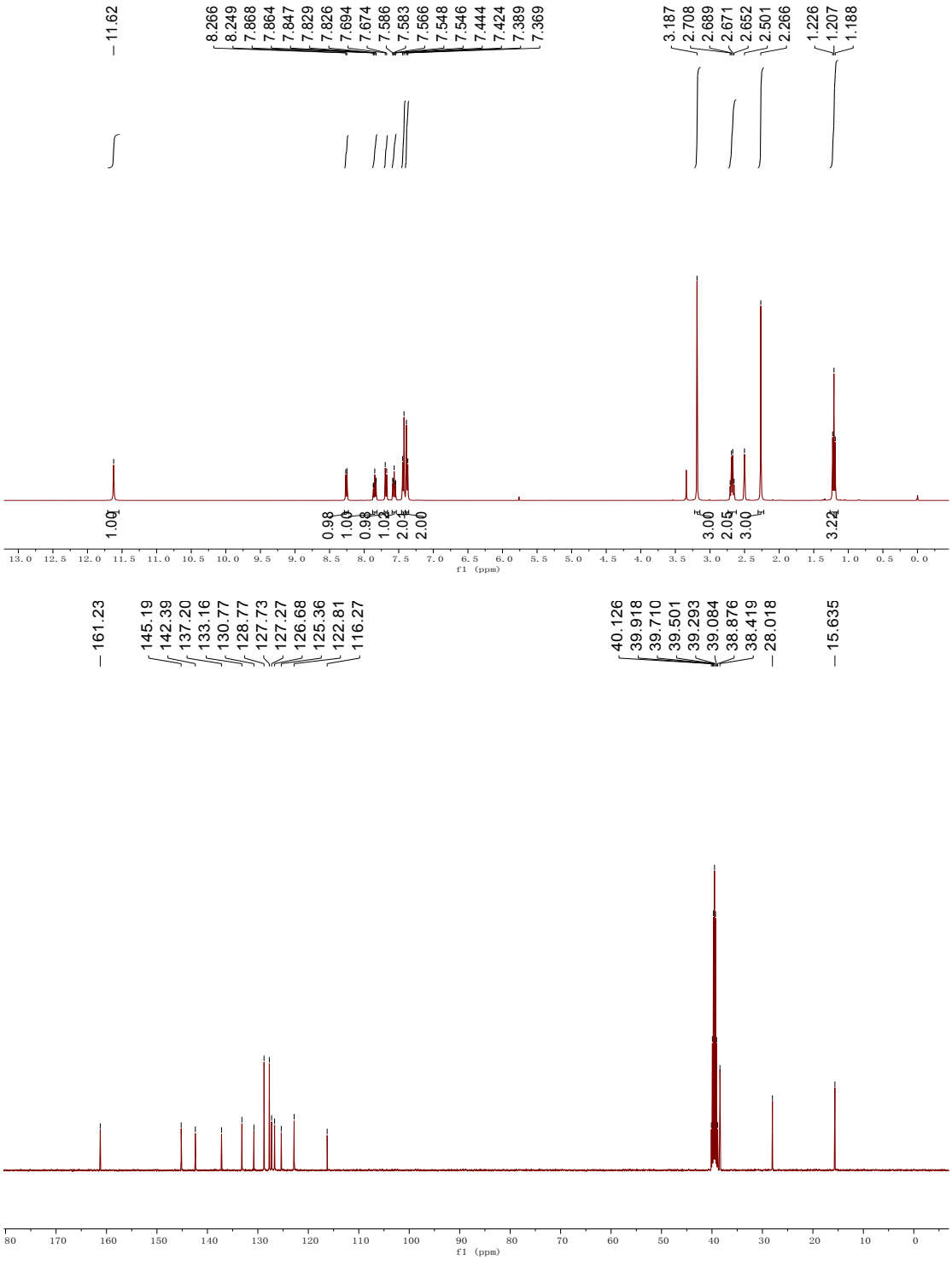


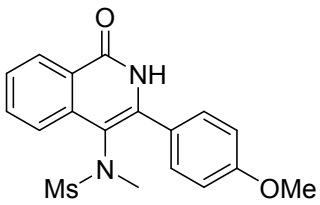




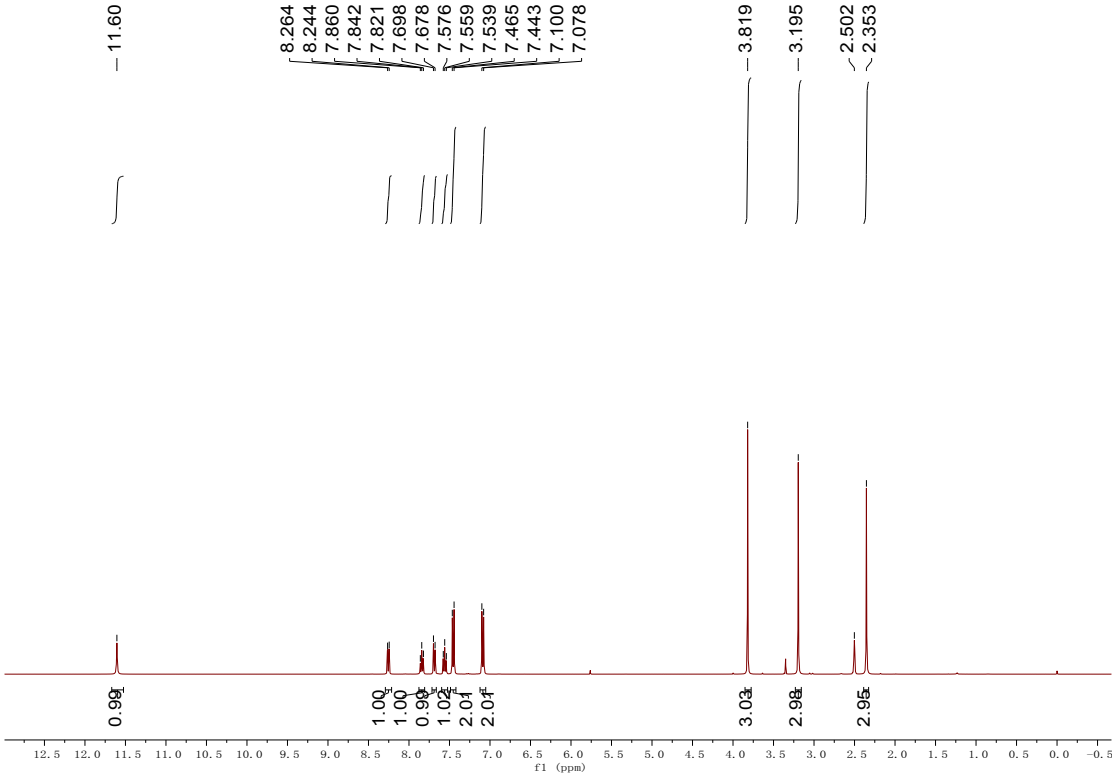
Compound 3ad: Yield: 42 mg, 61%; A white solid; Mp: >250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.62 (s, 1H), 8.26 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.84 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.68

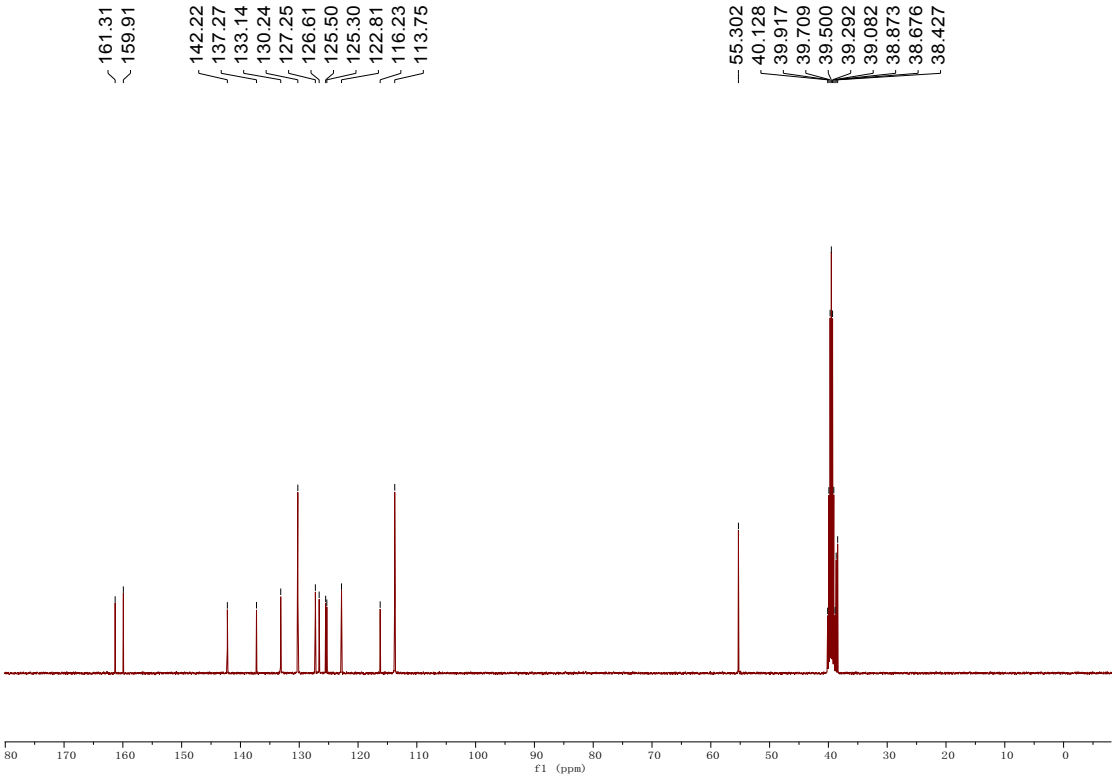
(d, J = 8.0 Hz, 1H), 7.57 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 3.19 (s, 3H), 2.68 (q, J = 7.6 Hz, 2H), 2.27 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.2, 145.2, 142.4, 137.2, 133.2, 130.8, 128.8, 127.7, 127.3, 126.7, 125.4, 122.8, 116.3, 38.4, 28.0, 15.6; IR (neat): ν 3158, 2956, 1643, 1603, 1319, 1143, 1325, 891, 777 cm^{-1}; HRMS (ESI) Calcd. for $C_{19}H_{21}N_2O_3S$ $[M+H]^+$: 357.1267, found: 357.1264.

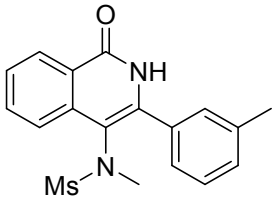




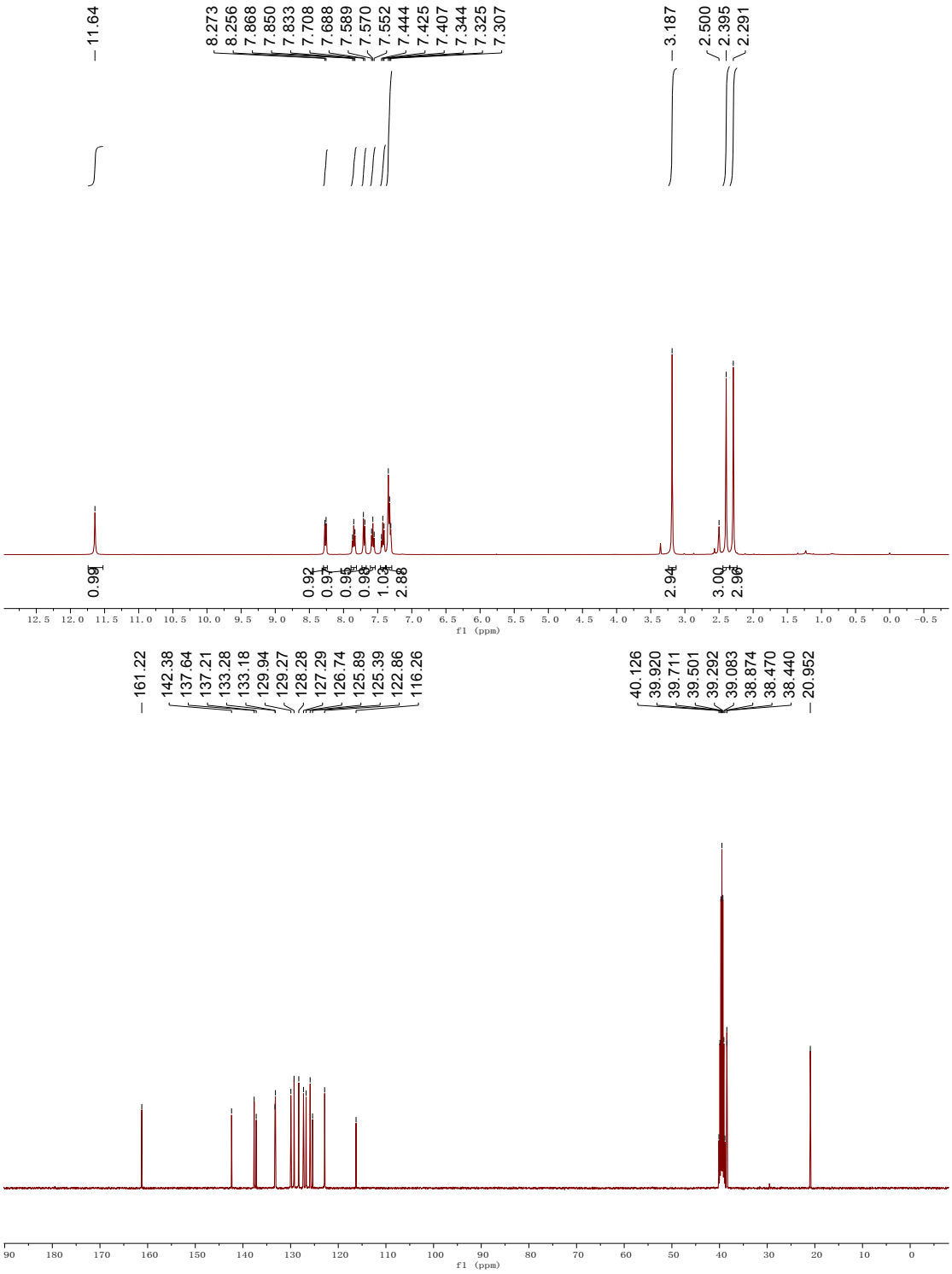
Compound 3ae: Yield: 51 mg, 85%; A white solid; Mp: >250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.61 (s, 1H), 8.26 (d, J_1 = 8.0 Hz, 1H), 7.84 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.56 (td, J_1 = 7.4 Hz, J_2 = 1.2 Hz,1H), 7.45 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 3.19 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.3, 159.9, 142.2, 137.3, 133.2, 130.2, 127.3, 126.6, 125.5, 125.3, 122.8, 116.2, 113.8, 55.3, 38.7, 38.4; IR (neat): ν 2920, 2854, 1509, 1343, 1331, 1187, 1174, 830, 693 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{19}N_2O_4S$ $[M+H]^+$: 359.1060, found: 359.1056.

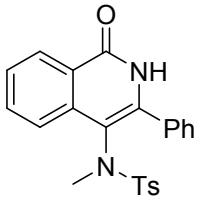






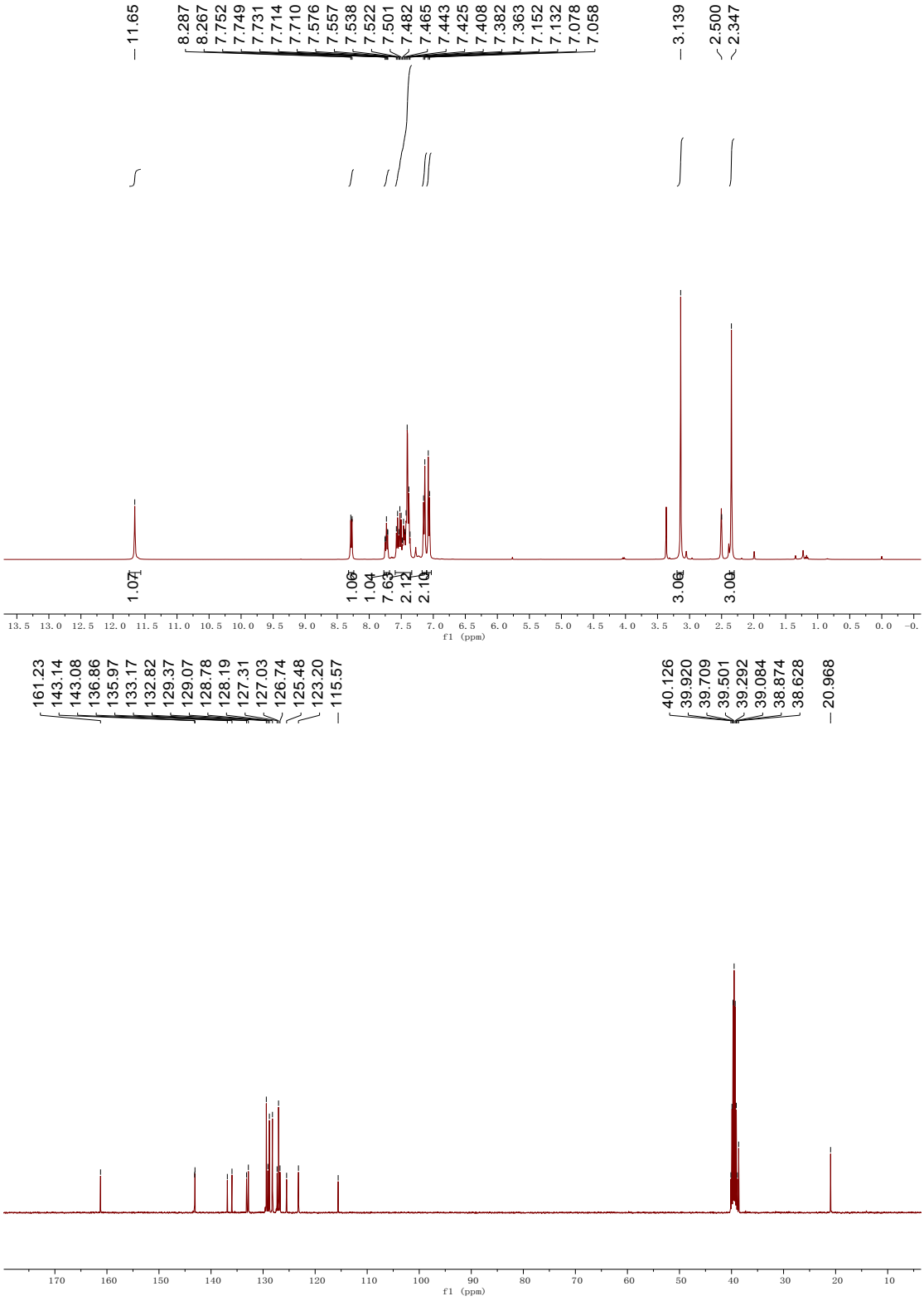
Compound 3af: Yield: 47 mg, 77%; A white solid; Mp: > 250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.64 (s, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.83 (t, J_1 = 7.2Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.34-7.31 (m, 3H), 3.19 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.2, 142.4, 137.6, 137.2, 133.3, 133.2, 129.9, 129.3, 128.3, 127.3, 126.8, 125.9, 125.4, 122.9, 116.3, 38.5, 38.4, 21.0; IR (neat): ν 2920, 2854, 1509, 1343, 1331, 1187, 1174, 830, 693 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{19}N_2O_3S$ $[M+H]^+$: 343.1111, found: 343.1108.

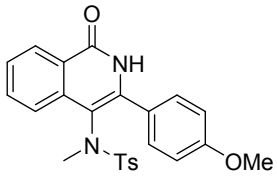




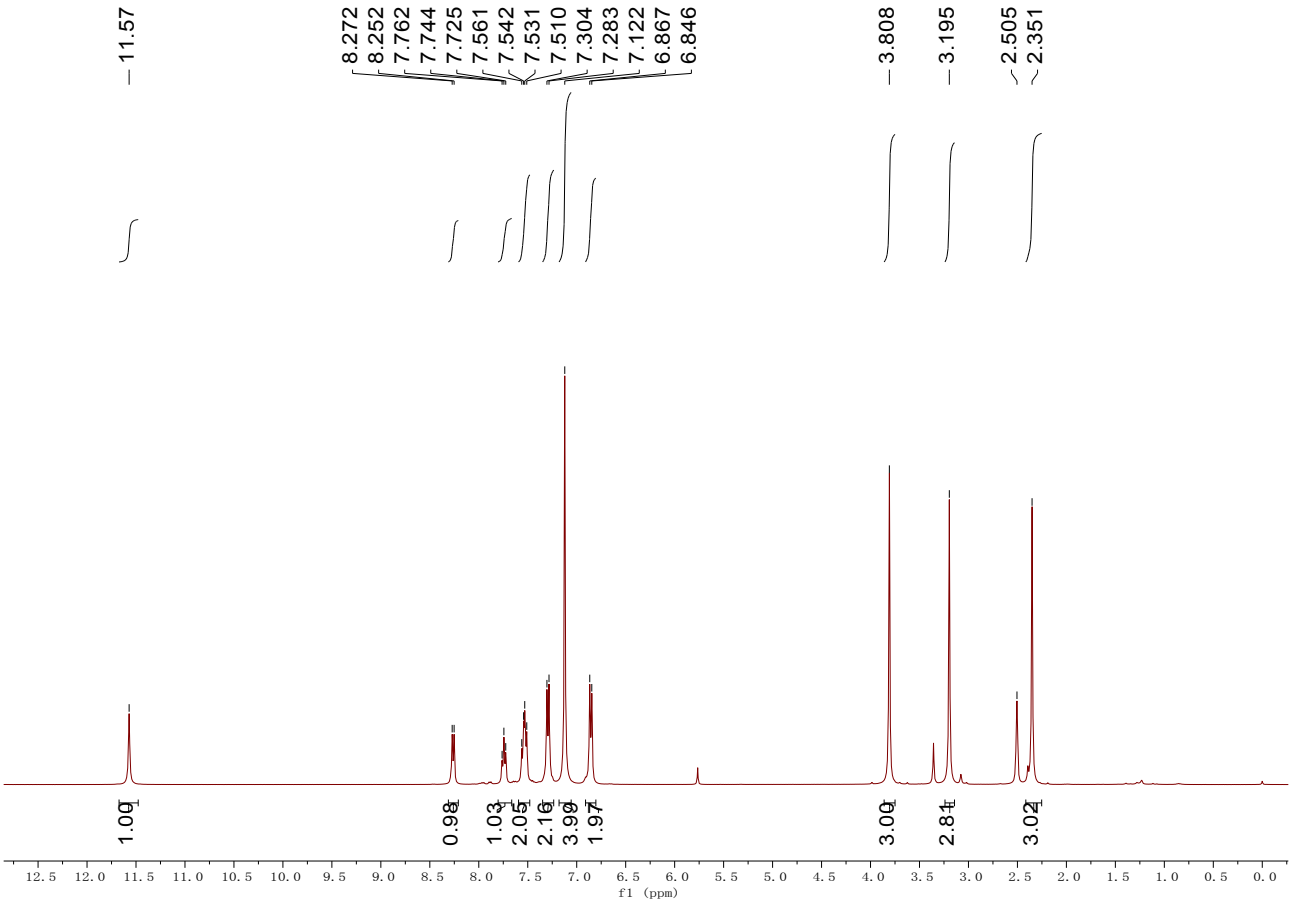
Compound 3ag: This is a known compound.[3] Yield: 56 mg, 70%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.66 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.731 (td, J_1 = 8.0 Hz, J_2 =

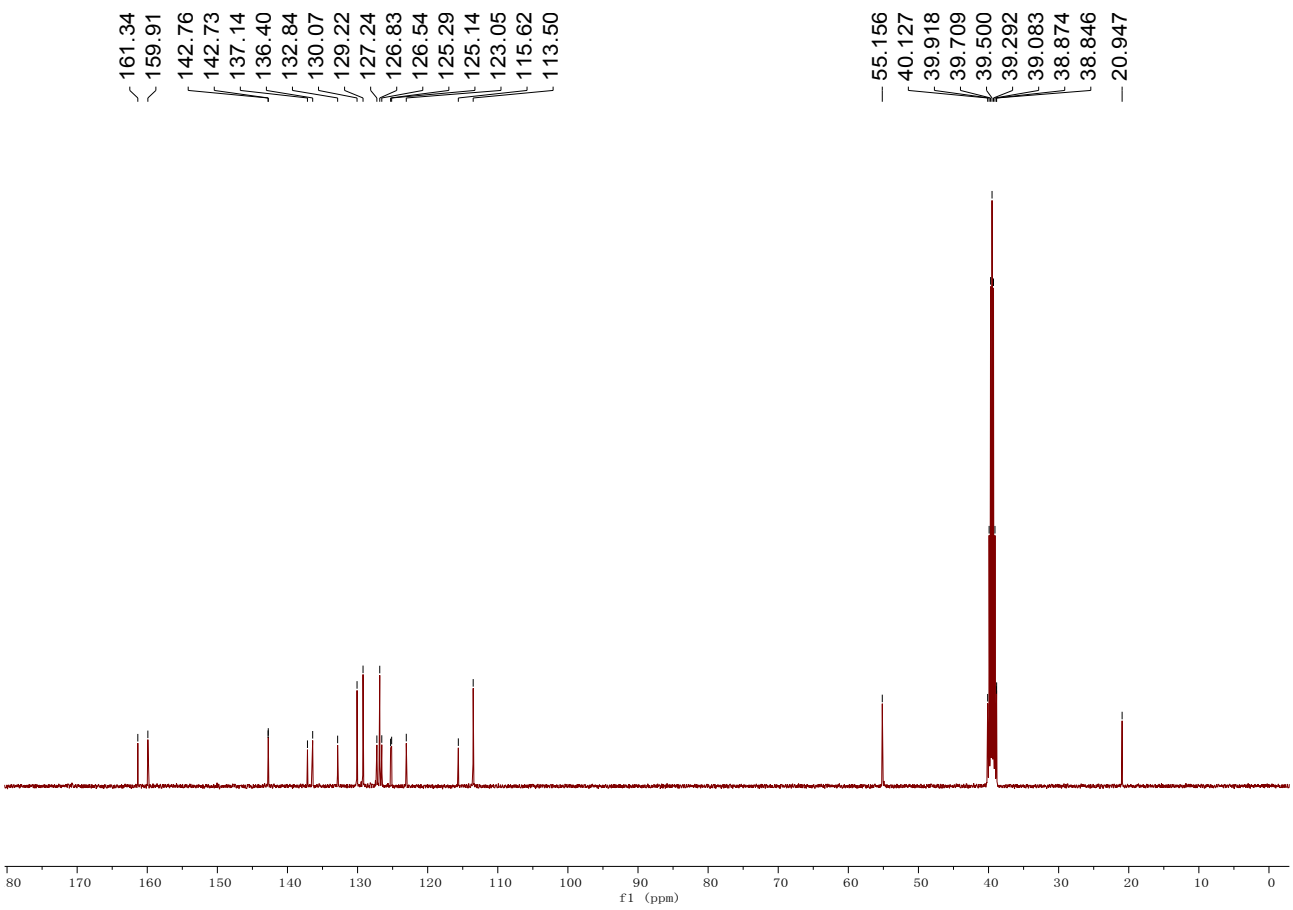
1.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.49-7.44 (m, 1H), 7.44-7.35 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.14 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.2, 143.2, 143.1, 136.9, 136.0, 133.2, 132.9, 129.4, 129.1, 128.8, 128.2, 127.3, 127.0, 126.8, 125.5, 123.2, 115.6, 38.6, 21.0; IR (neat): ν 3003, 2889, 1639, 1606, 1329, 1149, 769, 708, 708 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1267, found: 405.1260.

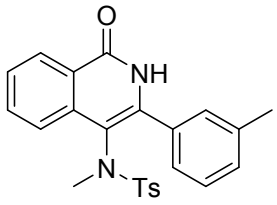




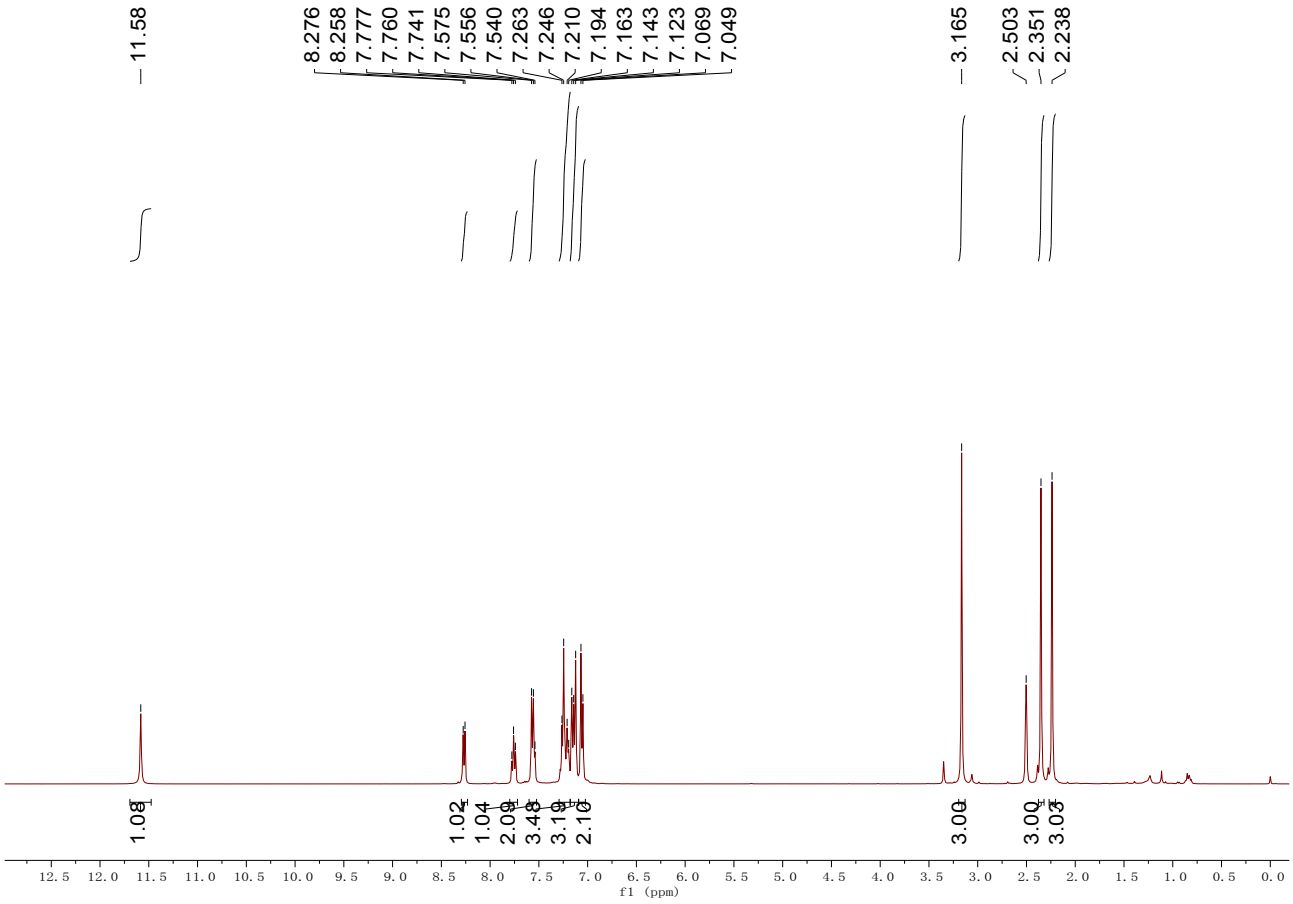
Compound 3ah: Yield: 70 mg, 80%; A white solid; Mp: >250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.57 (s, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.78-7.70 (m, 1H), 7.59-7.48 (m, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.12 (s, 4H), 6.86 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 3.20 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.3, 159.9, 142.8, 142.7, 137.1, 136.4, 132.8, 130.1, 129.2, 127.2, 126.8, 126.5, 125.3, 125.1, 123.1, 115.6, 113.5, 55.2, 38.8, 20.9; IR (neat): ν 3149, 3003, 2888, 1640, 1151, 892, 777 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$: 435.1373, found: 435.1376.







Compound 3ai: Yield: 65 mg, 77%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d6) δ 11.58 (s, 1H), 8.27 (d, *J* = 7.2 Hz, 1H), 7.80-7.72 (m, 1H), 7.60-7.52 (m, 2H), 7.29-7.18 (m, 3H), 7.18-7.09 (m, 3H), 7.09-7.02 (m, 2H), 3.16 (s, 3H), 2.35 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.2, 143.0, 142.9, 137.4, 137.0, 136.1, 133.0, 132.9, 129.7, 129.3, 129.2, 128.1, 127.3, 126.8, 126.7, 125.9, 125.4, 123.2, 115.6, 38.8, 21.0; IR (neat): ν 3170, 3021, 2833, 1644, 1605, 1332, 1150, 1088, 695 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$: 419.1424, found: 419.1428.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7.210
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7.163
7.143
7.123
7.069
7.049
3.165
2.503
2.351
2.238
1.08
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1.04
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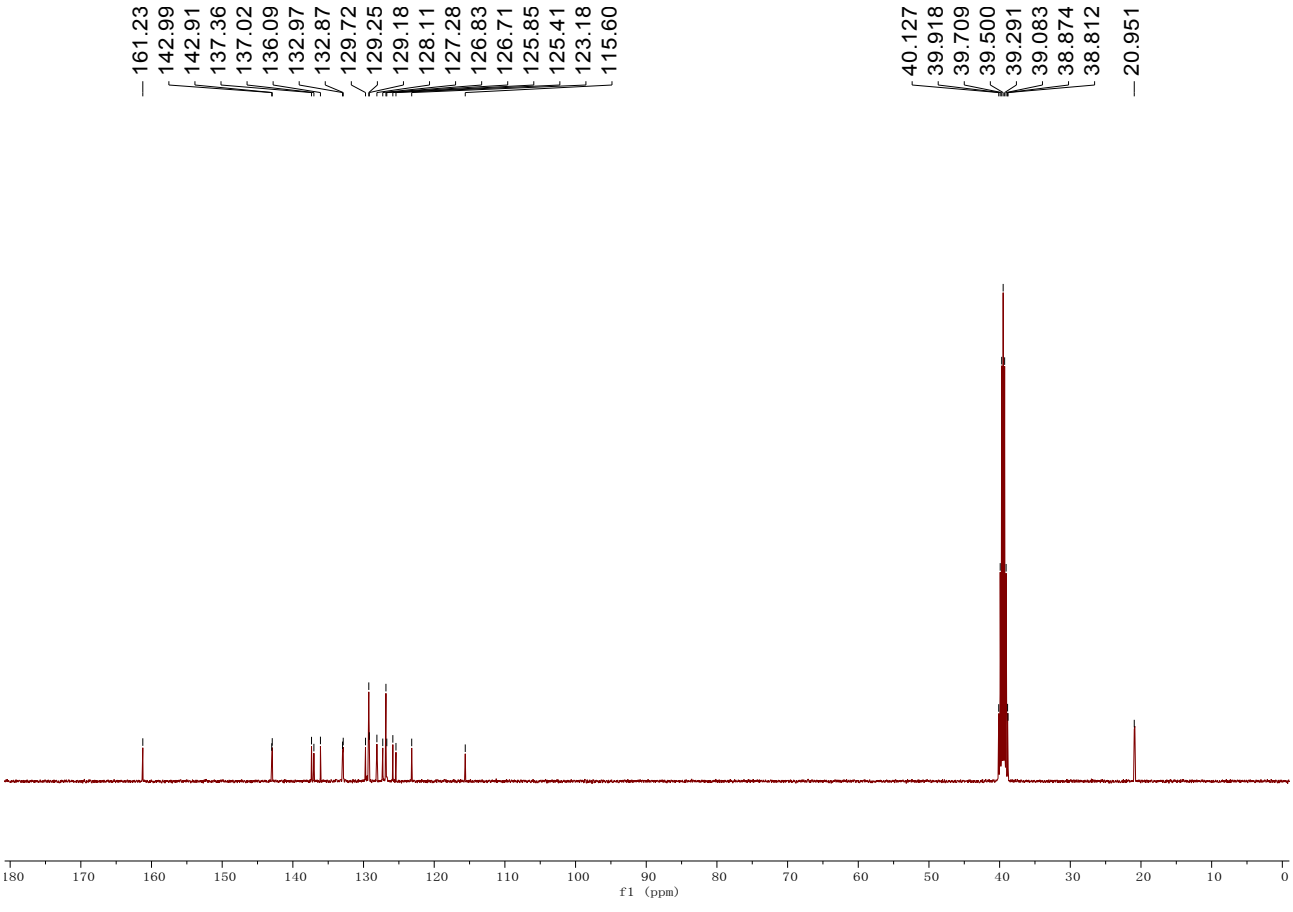
3.48
3.19
2.10
3.00
3.00
3.03
f1 (ppm)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132.97
132.87
129.72
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126.71
125.85
125.41
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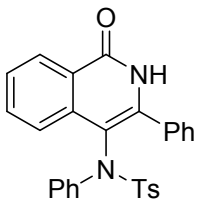
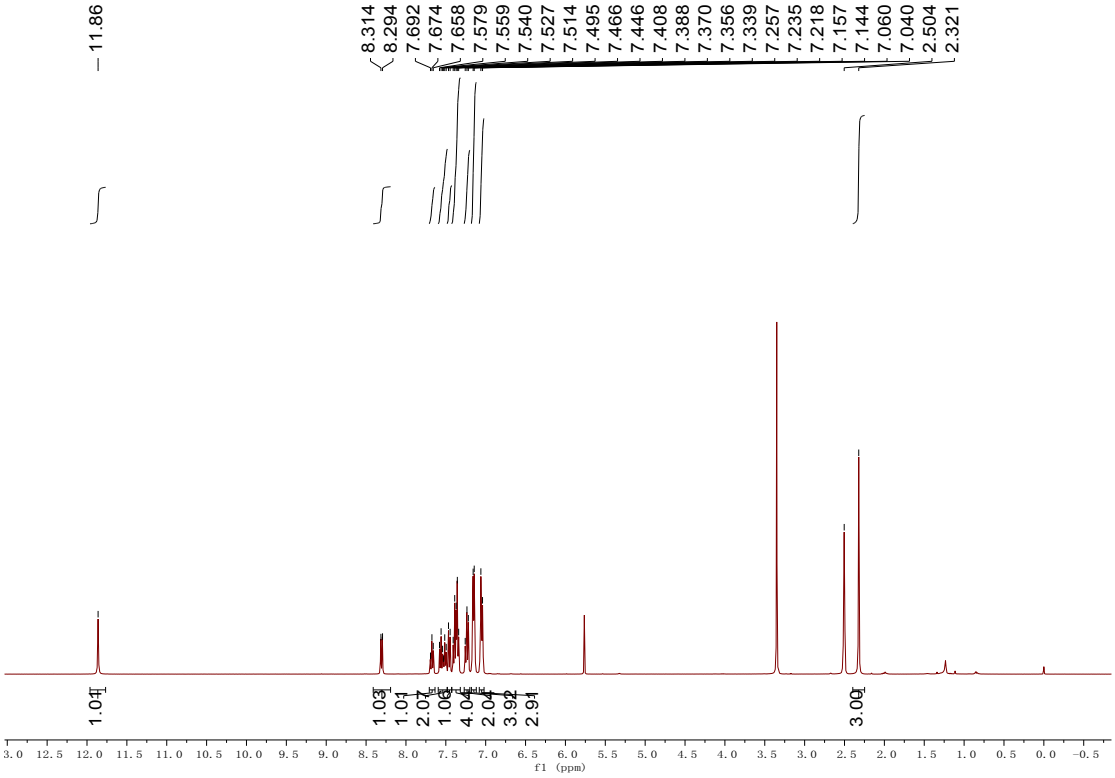
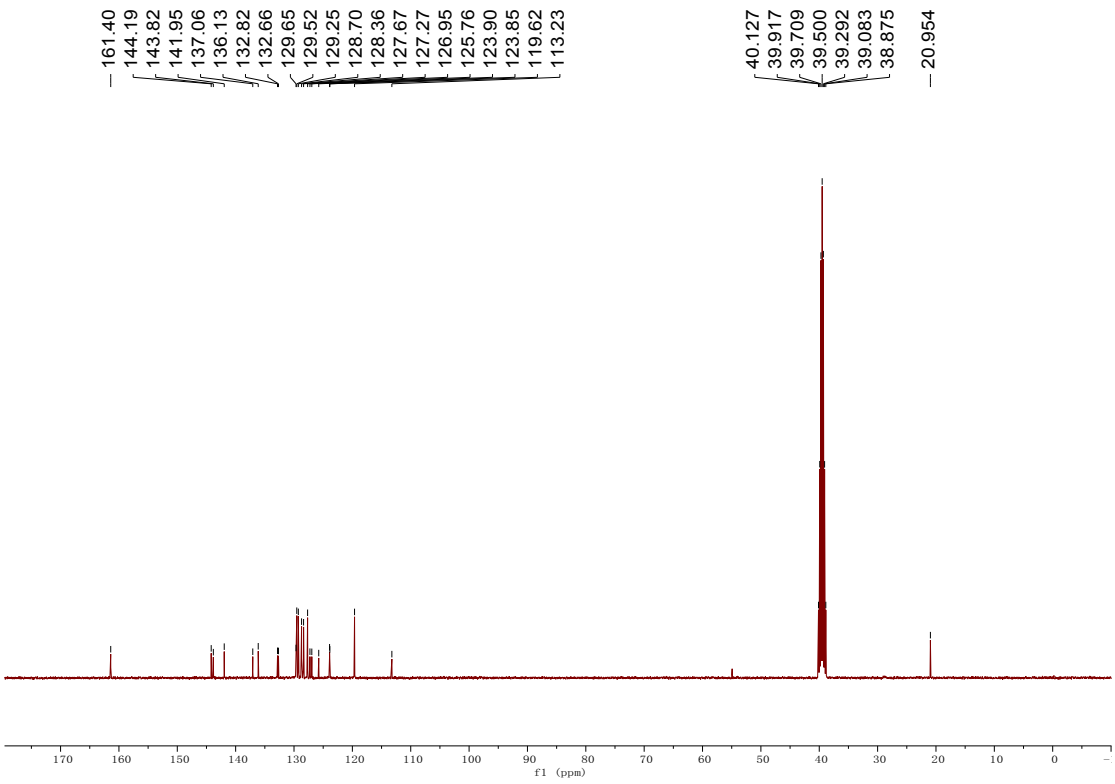
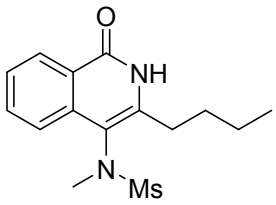
38.874
38.812
20.951
f1 (ppm)



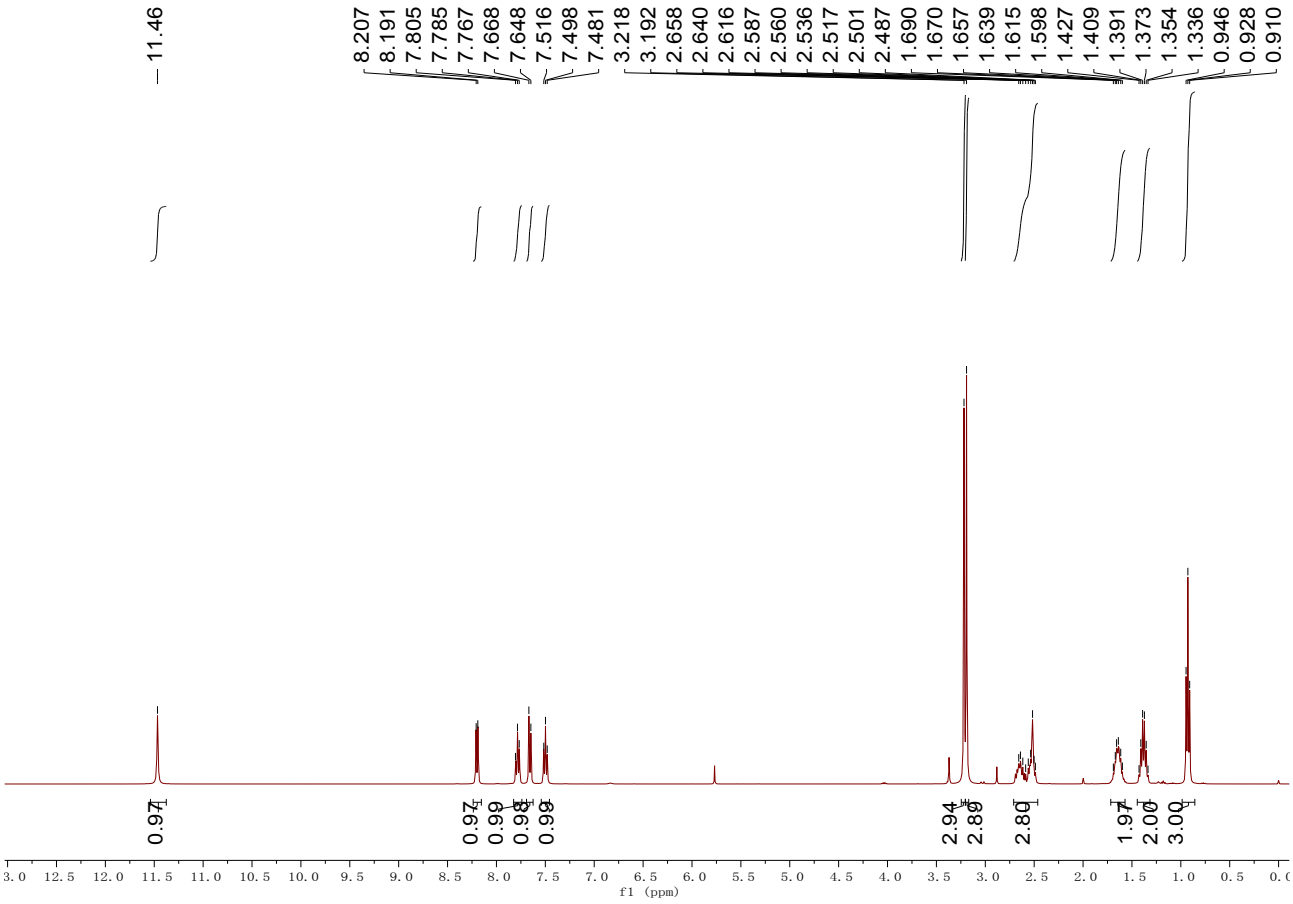
Compound 3aj: Yield: 74 mg, 85%; A white solid; Mp: >250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.68 (td, J_1 = 7.6, J_2 = 1.6, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.43-7.32 (m, 4H), 7.27-7.20 (m, 2H), 7.15 (dd, J_1 = 9.2, J_2 = 3.2, 4H), 7.04-7.07 (m,3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.4, 144.2, 143.8, 142.0, 137.1, 136.1, 132.8, 132.7, 129.7, 129.5, 129.3, 128.7, 128.4, 127.7, 127.3, 127.0, 125.8, 123.91, 123.86, 119.6, 113.2, 21.0; IR (neat): ν 2995, 2899, 1642, 1606, 1346, 1184, 1166, 770, 706 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{23}N_2O_3S$ $[M+H]^+$: 467.1424, found: 467.1419.







Compound 3ak: Yield: 51 mg, 82%; A white solid; Mp: 231-232°C; ^{1}H NMR (400 MHz, DMSO-d6) δ 11.47 (s, 1H), 8.20 (d, *J* = 6.4 Hz, 1H), 7.82-7.74 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.54-7.46 (m, 1H), 3.22 (s, 3H), 3.19 (s, 3H), 2.71-2.46 (m, 3H), 1.72-1.57 (m, 2H), 1.45-1.32 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.5, 144.6, 136.9, 133.0, 127.2, 126.0, 124.7, 122.4, 114.8, 39.6, 37.7, 30.4, 29.0, 22.3, 13.7; IR (neat): ν 3029, 2961, 2852, 1667, 1334, 1319, 1134, 778, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{15}H_{21}N_2O_3S$ $[M+H]^+$: 309.1267, found: 309.1264.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7.648
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7.498
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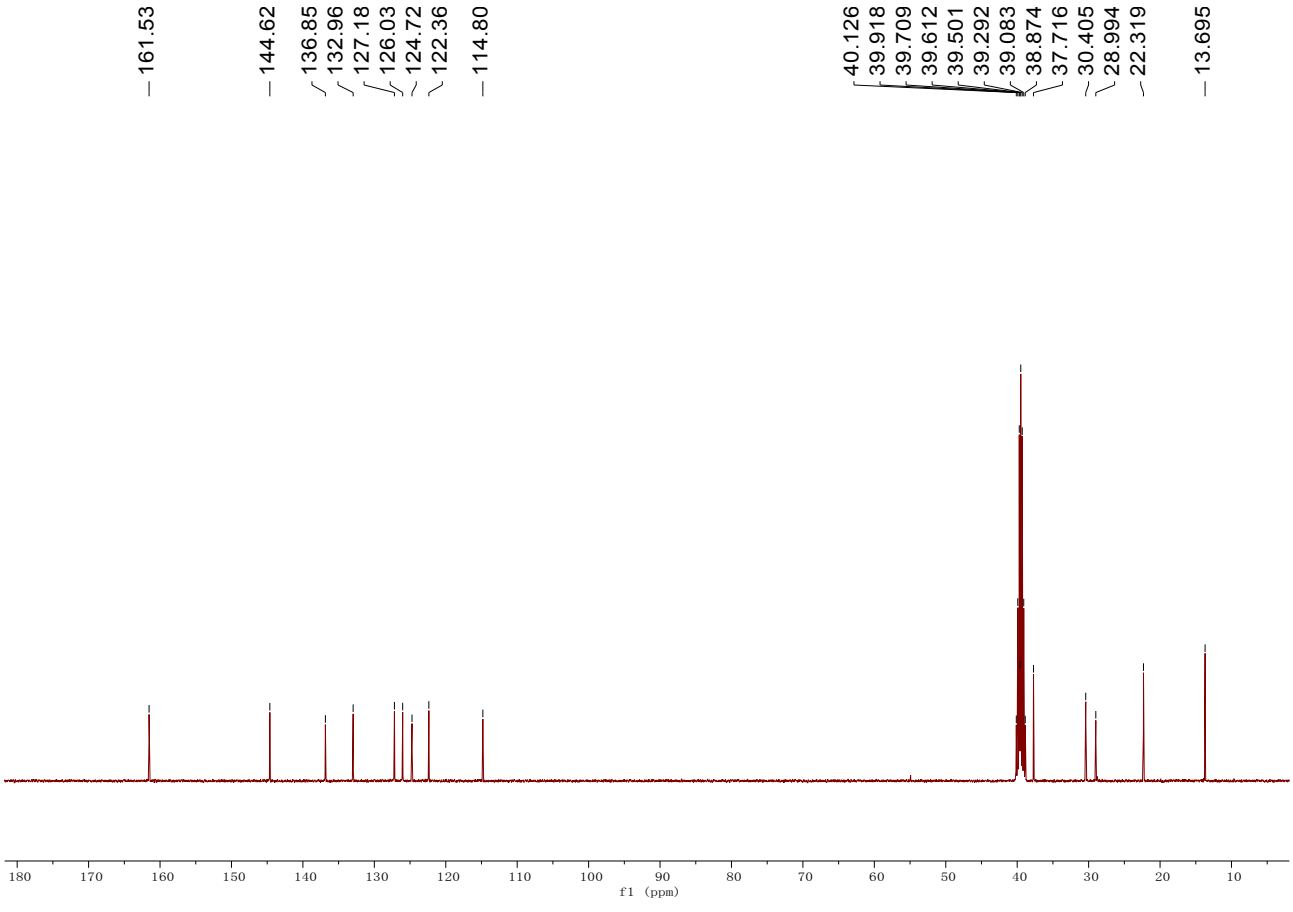
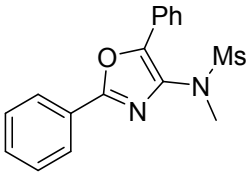
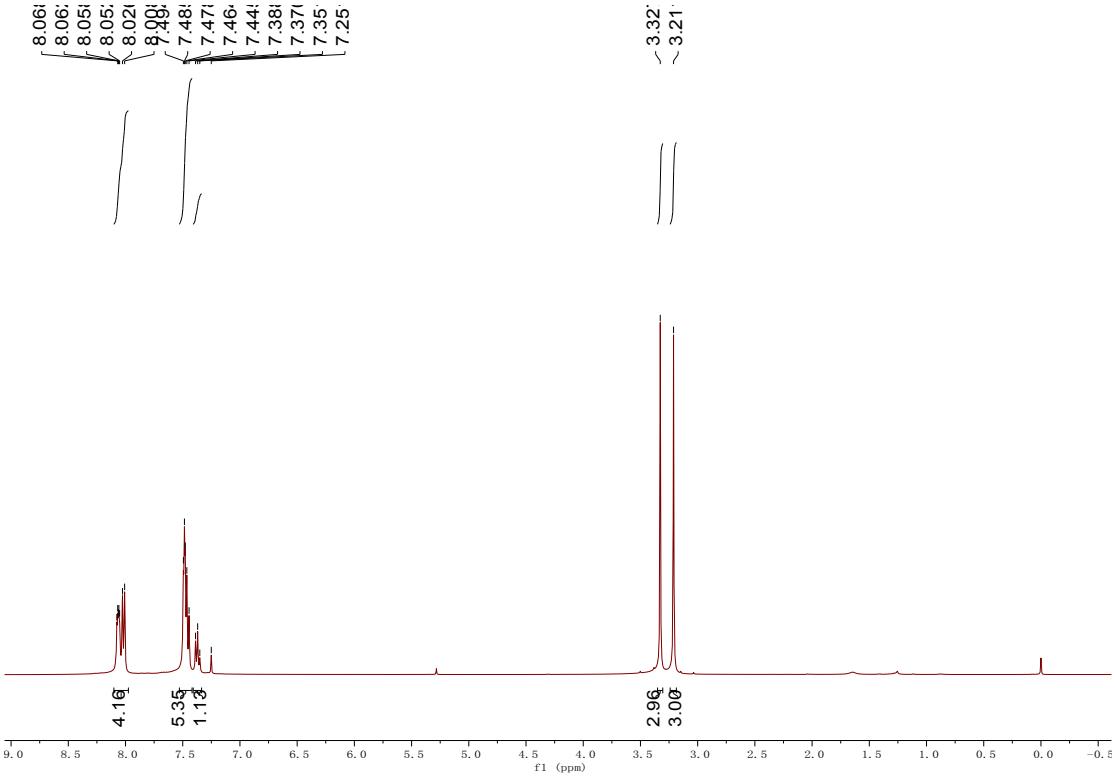
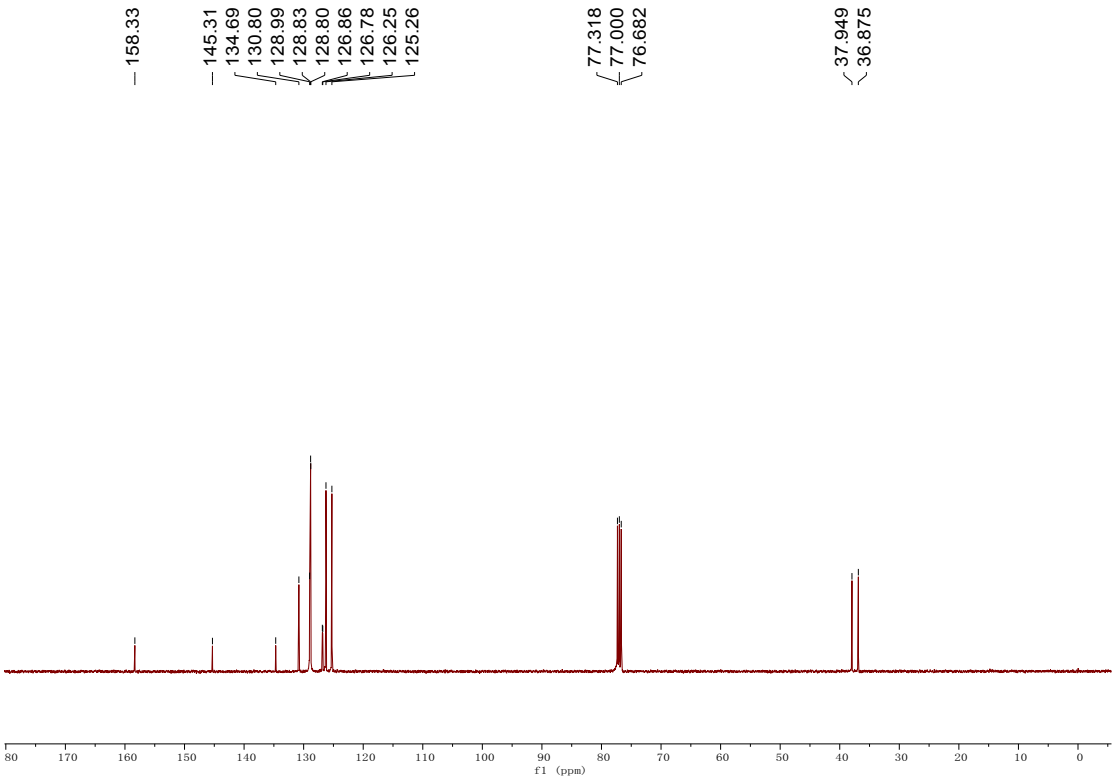
1.598
1.427
1.409
1.391
1.373
1.354
1.336
0.946
0.928
0.910
0.97
0.97
0.99
0.98
0.99
2.94
2.89
2.80
1.97
2.00
3.00
f1 (ppm)

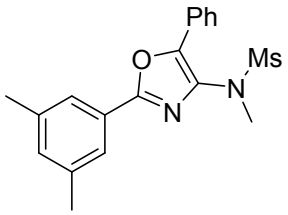

161.53
144.62
136.85
132.96
127.18
126.03
124.72
122.36
114.80
40.126
39.918
39.709
39.612
39.501
39.292
39.083
38.874
37.716
30.405
28.994
22.319
13.695
f1 (ppm)



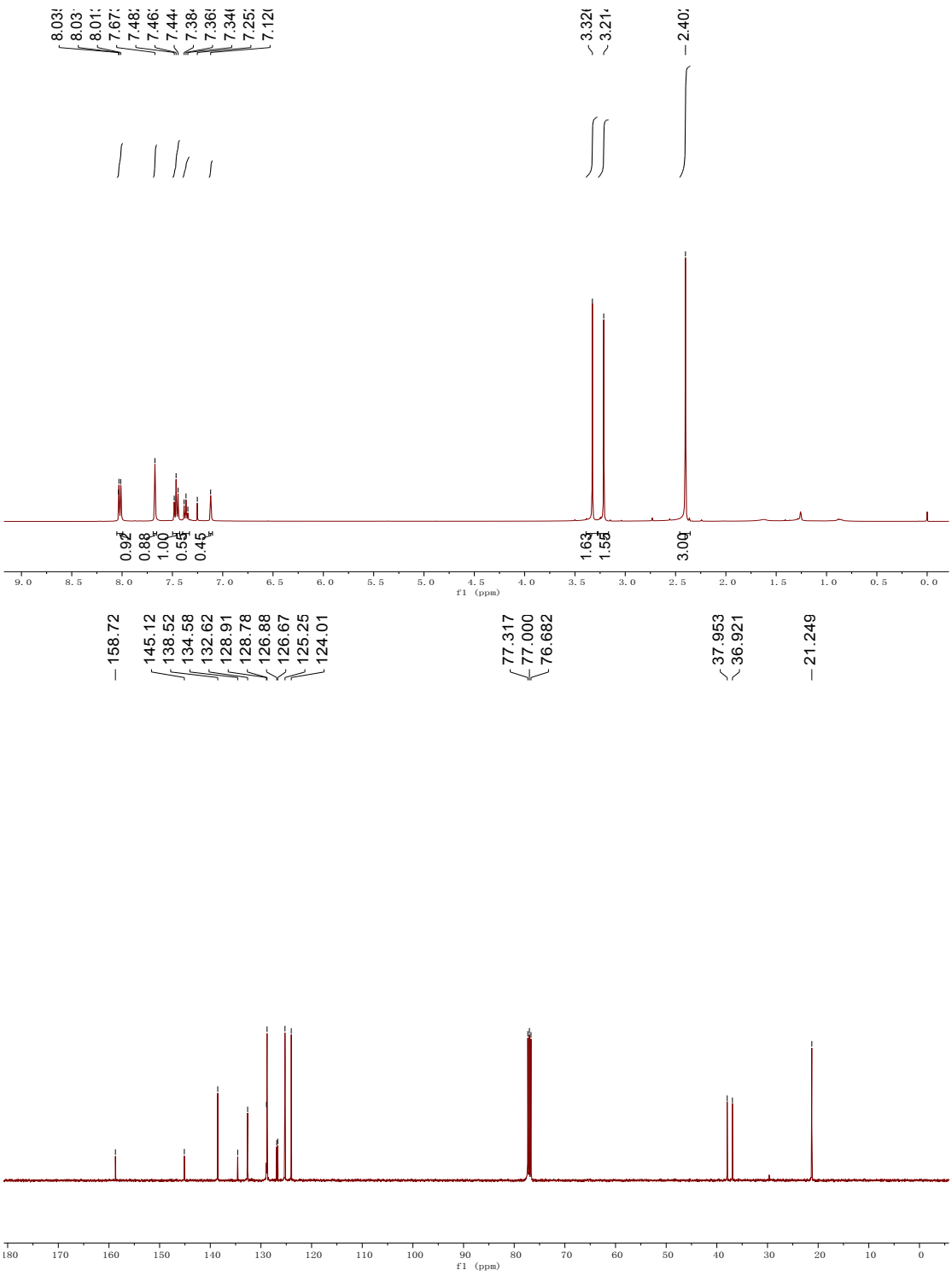
Compound 4aa: Yield: 48 mg, 80%; A white solid; Mp: 189-191°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10-8.04 (m, 2H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.53-7.42 (m, 5H), 7.37 (t, *J* = 3.6 Hz, 1H), 3.33 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 145.3, 134.7, 130.8, 129.0, 128.83, 128.80, 126.9, 126.8, 126.3, 125.3, 38.0, 36.9; IR (neat): ν 2917, 2842, 1364, 1349, 1337, 1152, 778, 697, 685 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{17}N_2O_3S$ $[M+H]^+$: 329.0954, found: 329.0950.

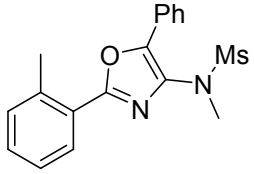






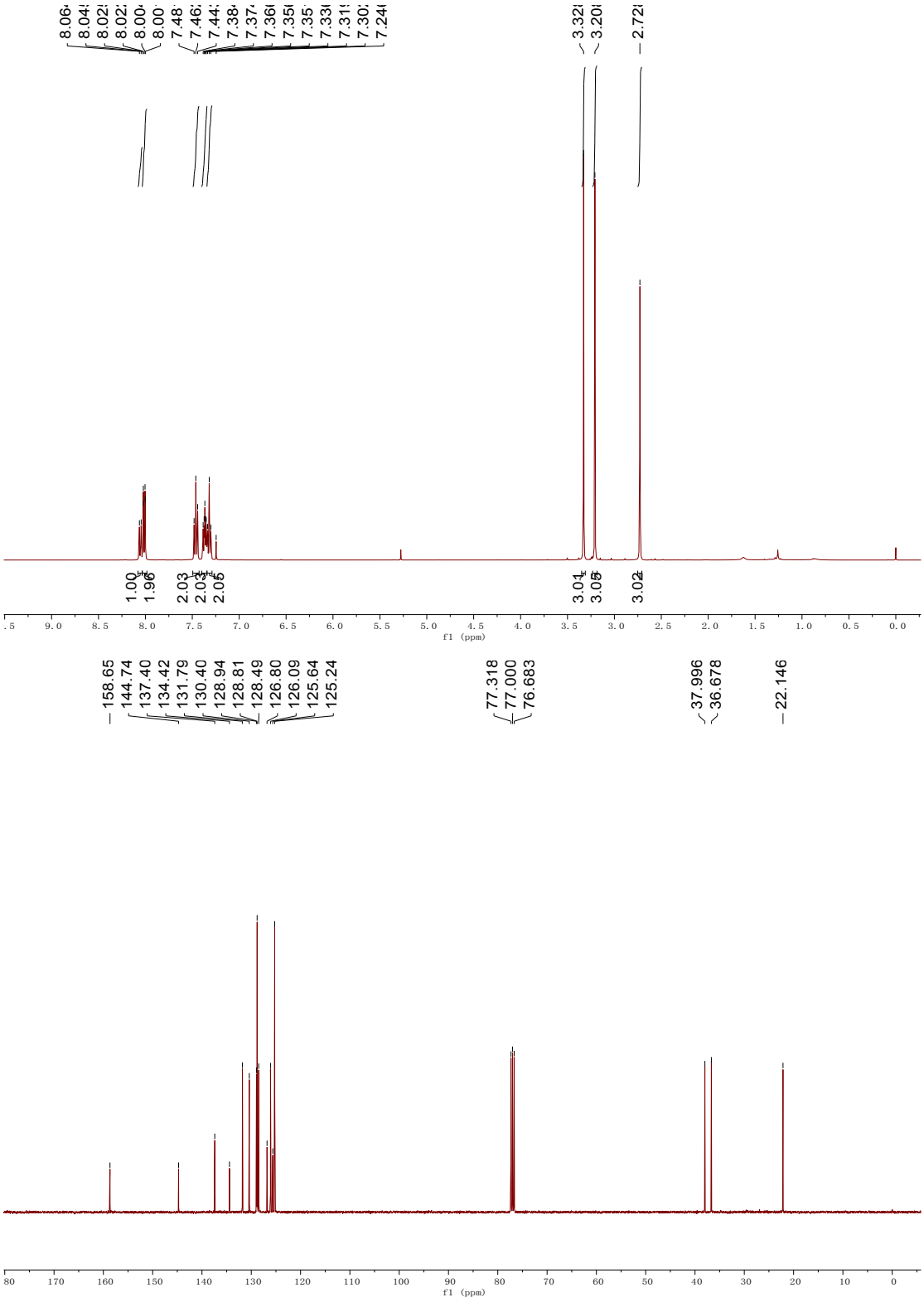
Compound 4ba: Yield: 42 mg, 65%; A white solid; Mp: 198-199 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05-7.99 (m, 2H), 7.67 (s, 2H), 7.50-7.43 (m, 2H), 7.40-7.33 (m, 1H), 7.12 (s, 1H), 3.33 (s, 3H), 3.21 (s, 3H), 2.40 (s, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 145.1, 138.5, 134.6, 132.6, 128.9, 128.8, 126.9, 126.7, 125.3, 124.0, 38.0, 36.9, 21.3; IR (neat): ν 2953, 2918, 2849, 1361, 1345, 1157, 769, 710 cm^{-1}; HRMS (ESI) Calcd. for $C_{19}H_{21}N_2O_3S$ $[M+H]^+$: 357.1267, found: 357.1263.

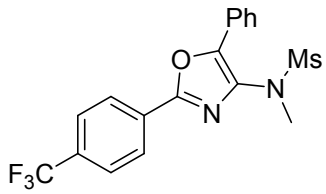




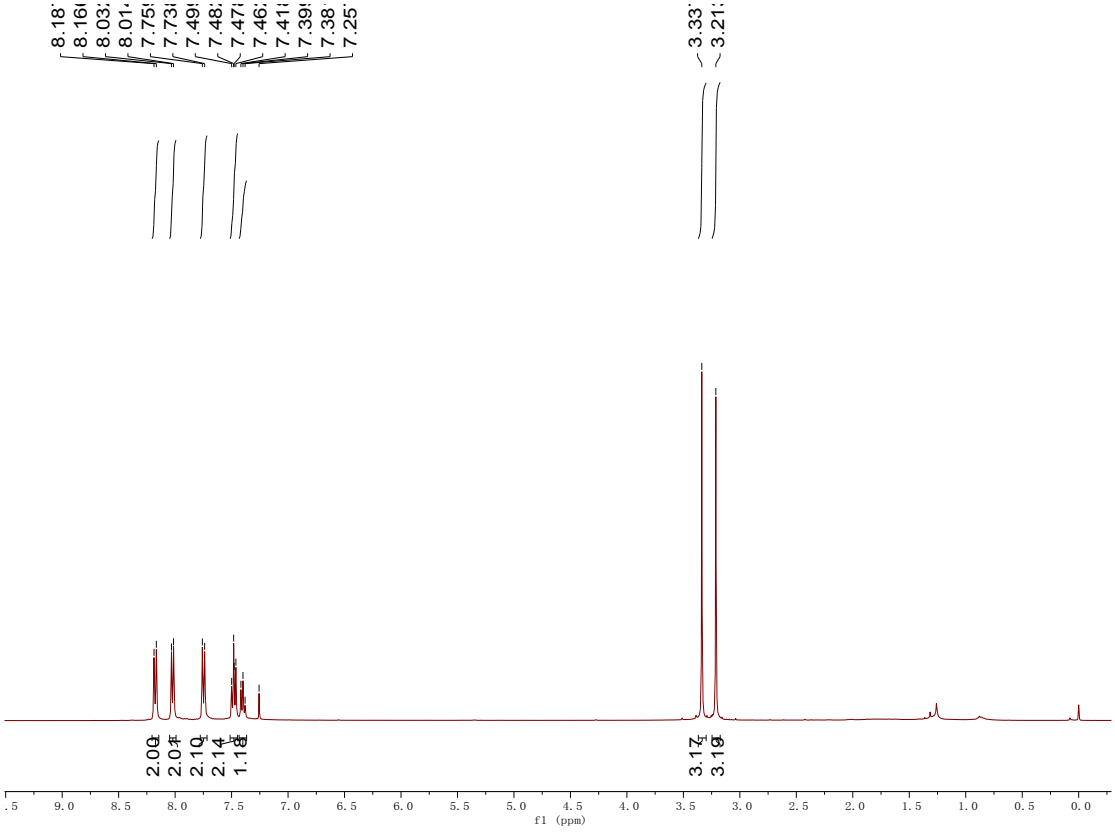
Compound 4ca: Yield: 51 mg, 75%; A white solid; Mp: 165-167 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08-8.03 (m, 1H), 8.03-7.98 (m, 2H), 7.49-7.43 (m, 2H), 7.40-7.34 (m, 2H), 7.34-

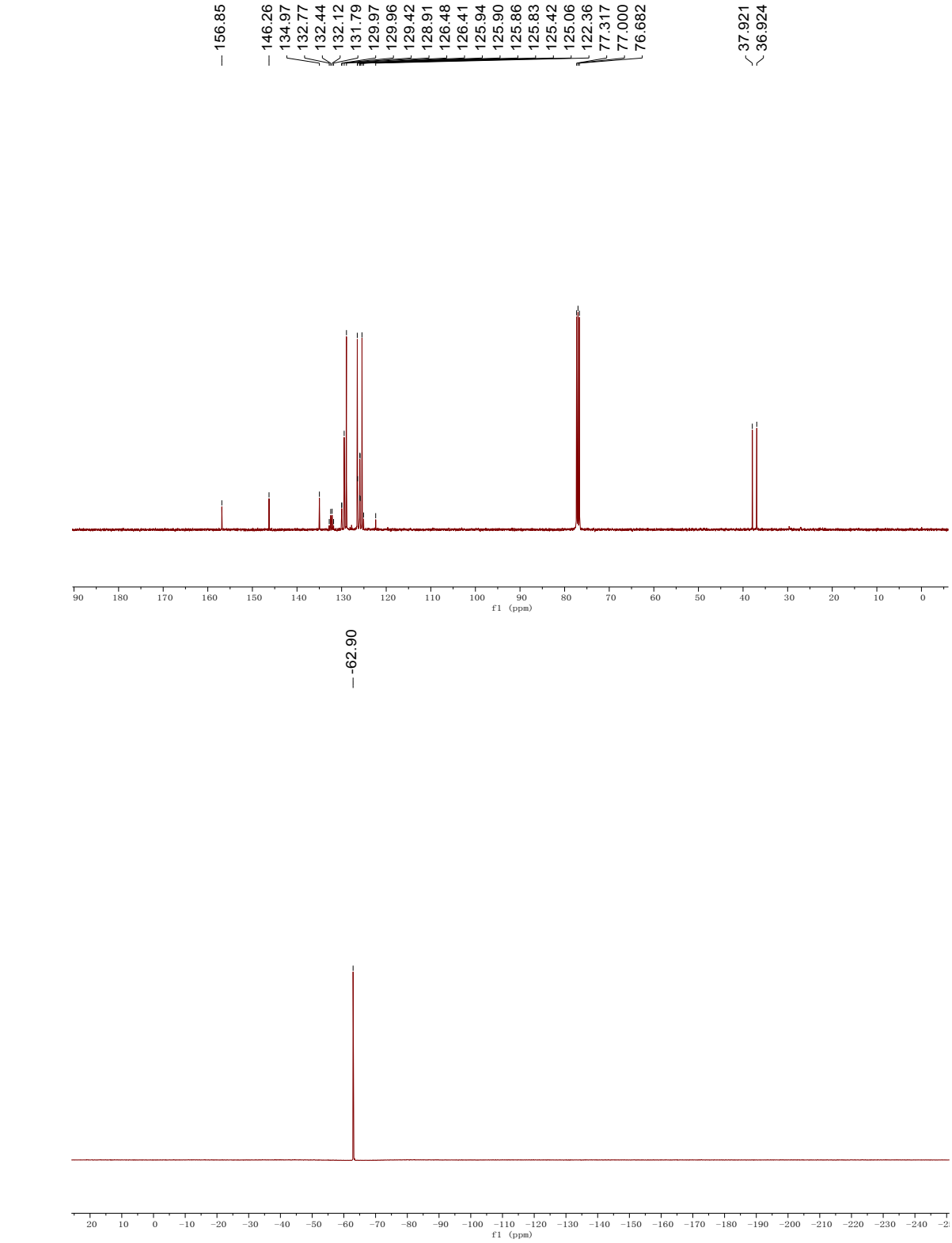
7.29 (m, 2H), 3.33 (s, 3H), 3.21 (s, 3H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 144.7, 137.4, 134.4, 131.8, 130.4, 129.0, 128.8, 128.5, 126.8, 126.1, 125.6, 125.3, 38.0, 36.7, 22.2; IR (neat): ν 2920, 2848, 1362, 1342, 1155, 780, 773, 733 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{19}N_2O_3S$ $[M+H]^+$: 343.1111, found: 343.1105.

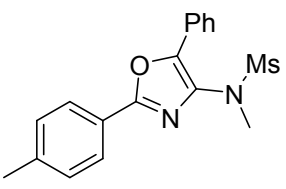




Compound 4da: Yield: 51 mg, 55%; A white solid; Mp: 193-195 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 3.34 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 146.3, 135.0, 132.3 (q, *J* = 32.6 Hz), 130.0, 129.4, 128.9, 126.5, 126.4, 125. 9 (q, *J* = 3.7 Hz), 125.4, 123.7 (q, *J* = 270.8 Hz), 37.9, 36.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9; IR (neat): ν 2917, 2845, 1613, 1346, 1321, 1154, 1113, 1092, 1059, 700, 689 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{16}F_3N_2O_3S$ $[M+H]^+$: 397.0828, found: 397.0822.

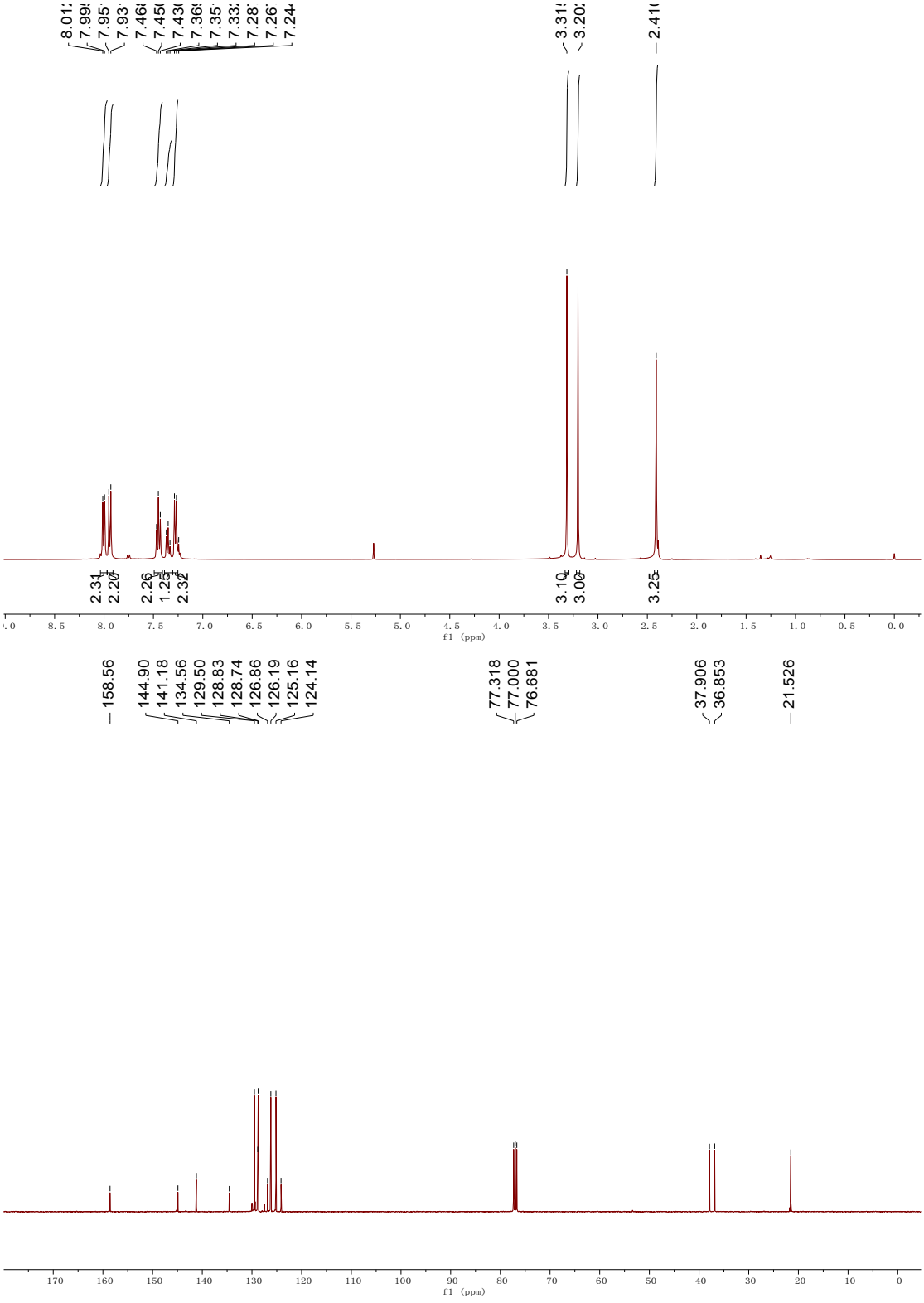


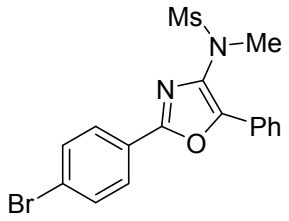




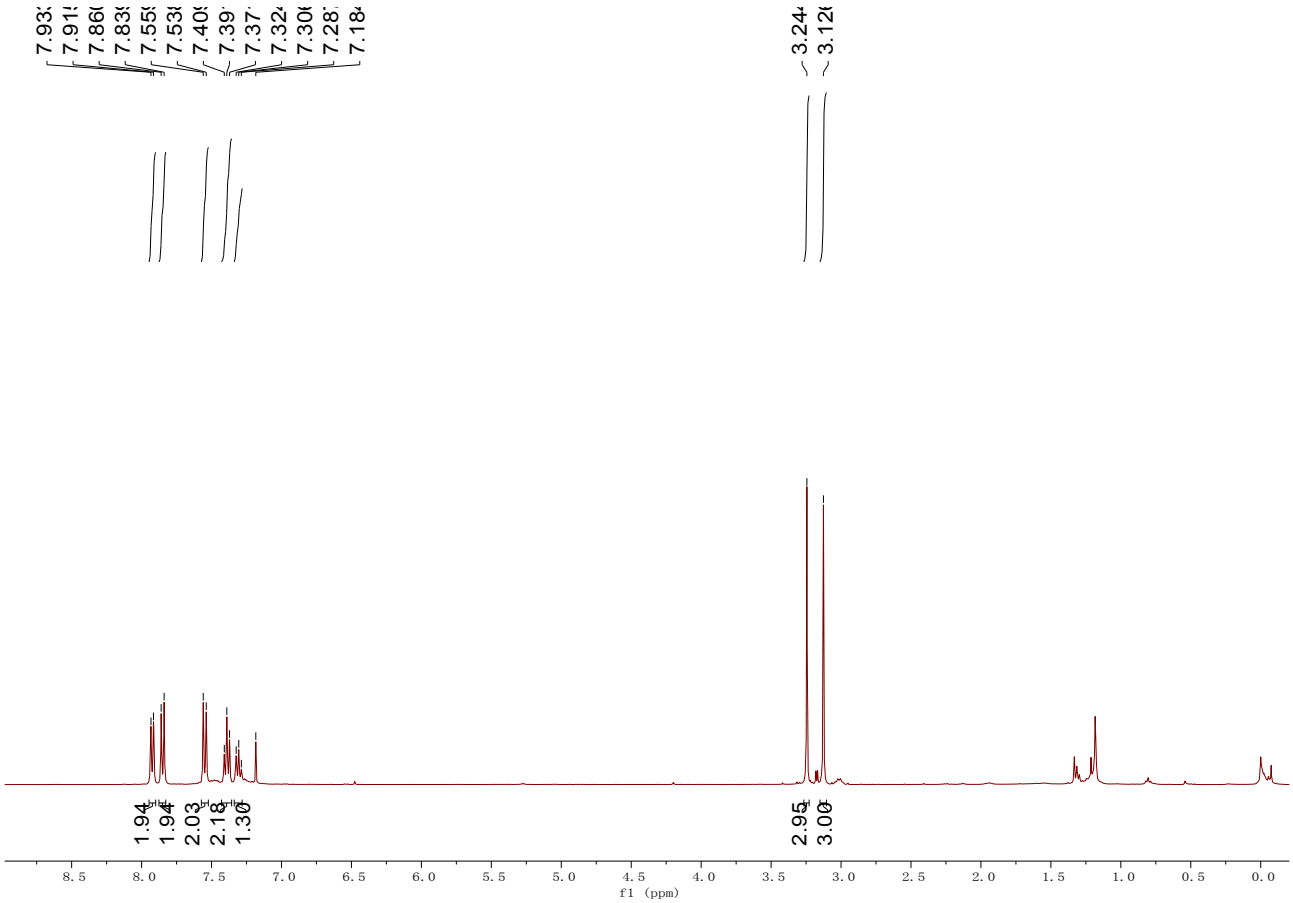
Compound 4ea: Yield: 41 mg, 71%; A white solid; Mp: 203-205 ^{o}C; ^{1}H NMR (400 MHz,

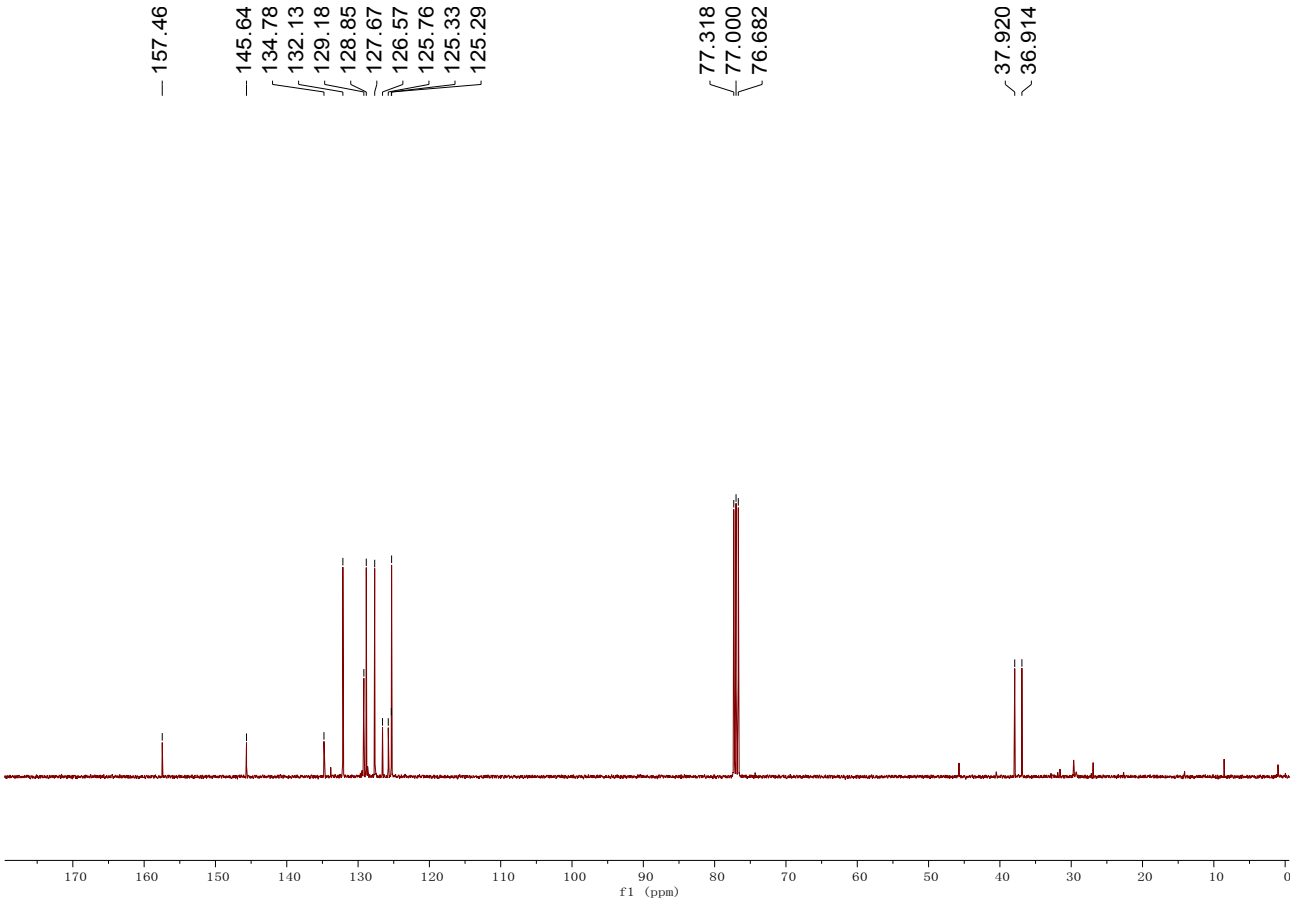
Chloroform-*d*) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.31 (s, 3H), 3.20 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 144.9, 141.2, 134.6, 129.5, 128.8, 128.7, 126.9, 126.2, 125.2, 124.2, 37.9, 36.9, 21.5; IR (neat): ν 2920, 1496, 1364, 1346, 1321, 1164, 1138, 1059, 768, 757, 685 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{19}N_2O_3S$ $[M+H]^+$: 343.1111, found: 343.1105.

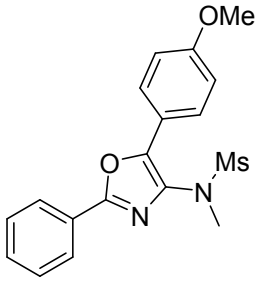




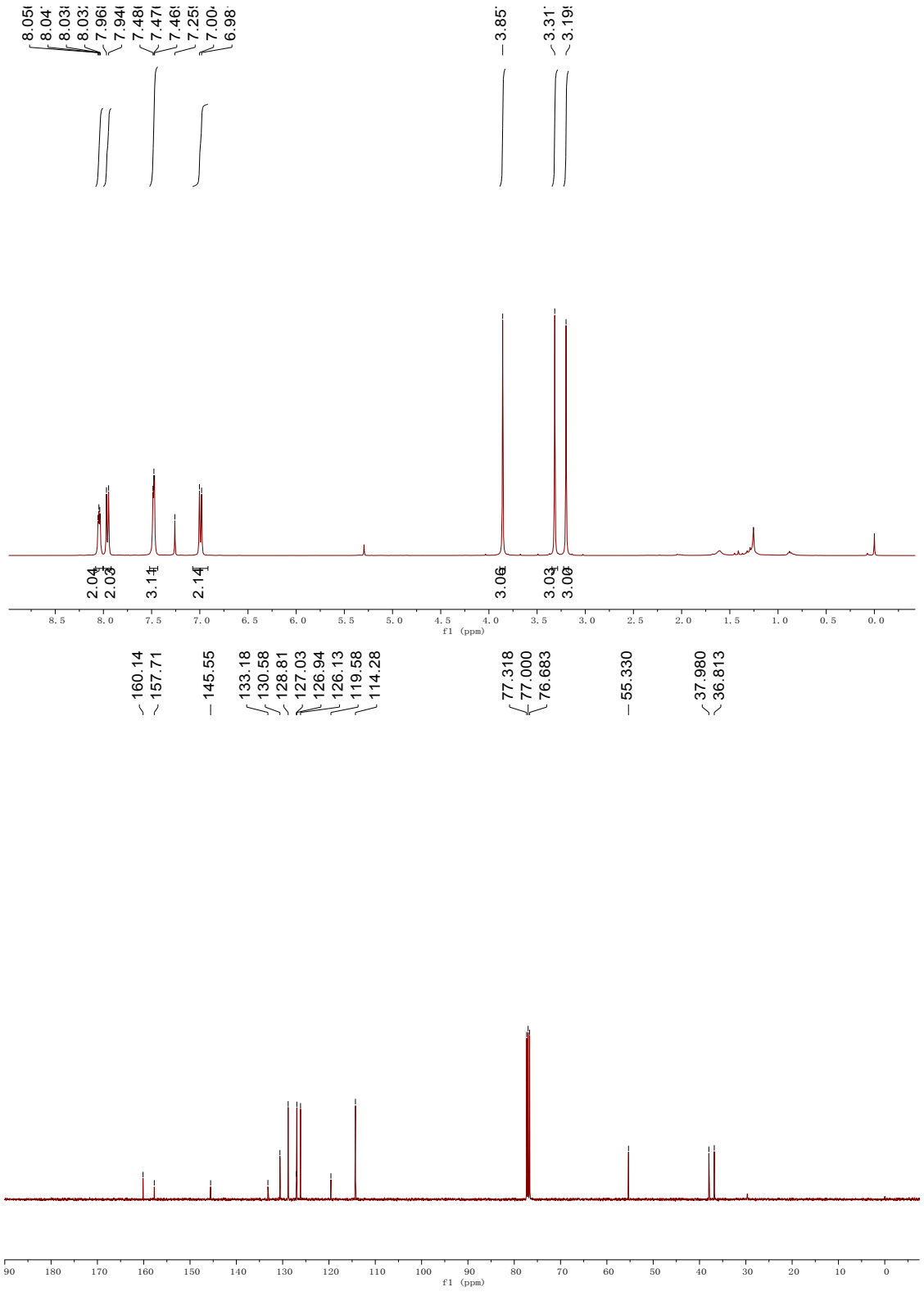
Compound 4fa: Yield: 46 mg, 70%; A white solid; Mp: 214-215 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.43-7.36 (m, 2H), 7.34-7.28 (m, 1H), 3.24 (s, 3H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 157.5, 145.6, 134.8, 132.1, 129.2, 128.9, 127.7, 126.6, 125.8, 125.33, 125.30, 37.9, 36.9; IR (neat): ν 2921, 1479, 1367, 1346, 1331, 1154, 1049, 757, 651cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{16}BrN_2O_3S$ $[M+H]^+$: 407.0060, found: 407.0057.

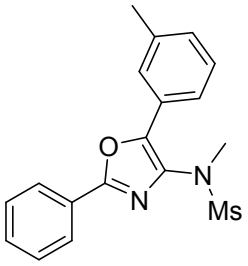




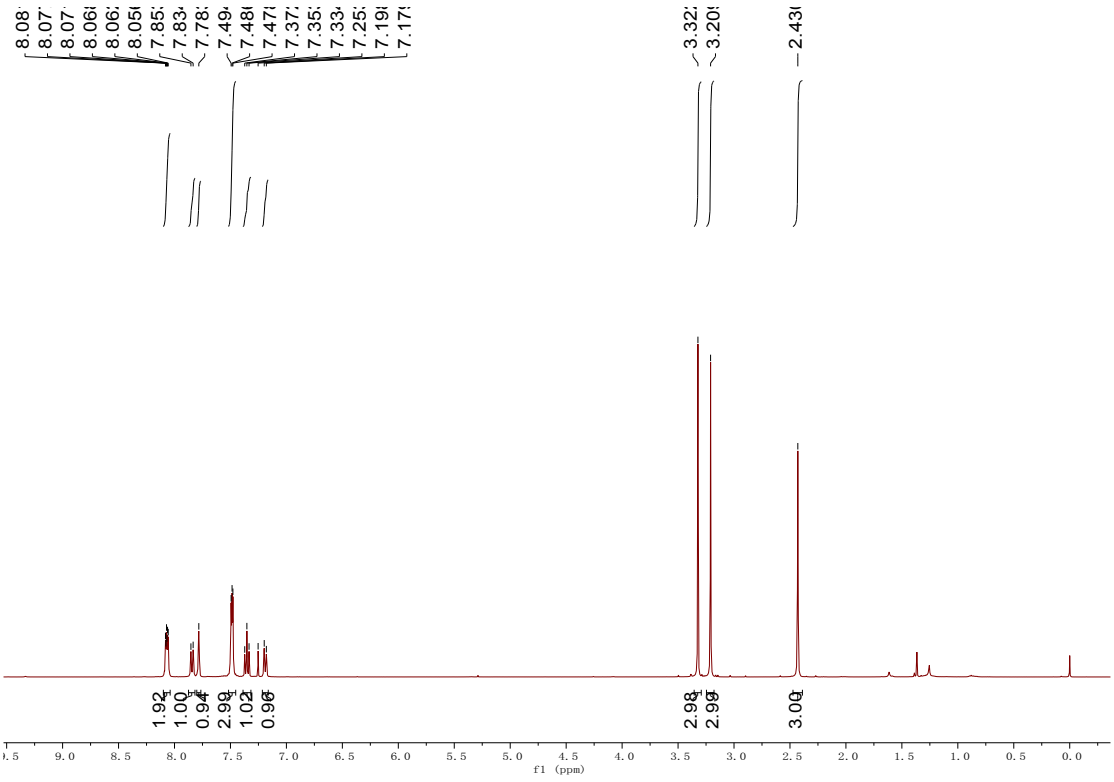


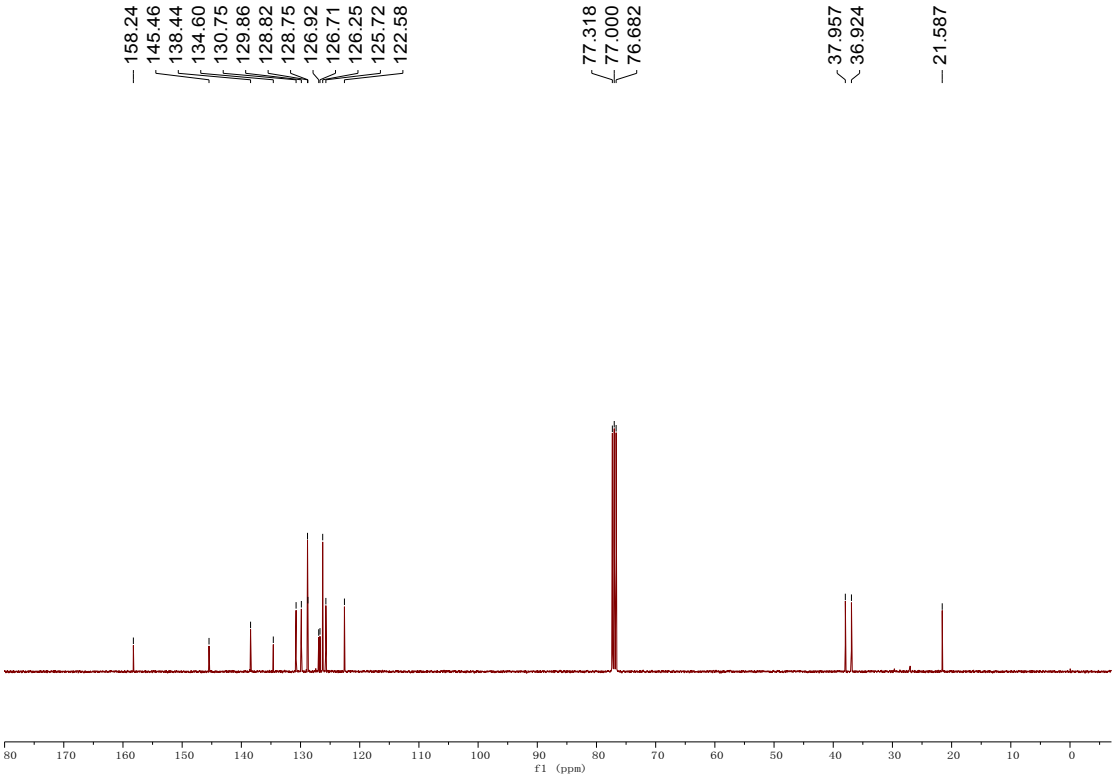
Compound 4ab: Yield: 52 mg, 66%; A white solid; Mp: 224-225 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08-8.01 (m, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.52-7.44 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.32 (s, 3H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 157.7, 145.6, 133.2, 130.6, 128.8, 127.0, 126.9, 126.1, 119.6, 114.3, 55.3, 38.0, 36.8; IR (neat): ν 2920, 1489, 1364, 1346, 1321, 1164, 1138, 1049, 768, 757, 675 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{19}N_2O_4S$ $[M+H]^+$: 359.1060, found: 359.1054.

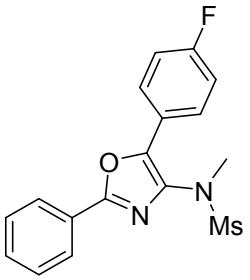

8.05
8.04
8.03
8.03
7.96
7.94
7.48
7.47
7.46
7.25
7.00
6.98
3.85
3.31
3.19
2.04
2.03
3.14
2.14
3.06
3.03
3.00
f1 (ppm)
160.14
157.71
145.55
133.18
130.58
128.81
127.03
126.94
126.13
119.58
114.28
77.318
77.000
76.683
55.330
37.980
36.813
f1 (ppm)



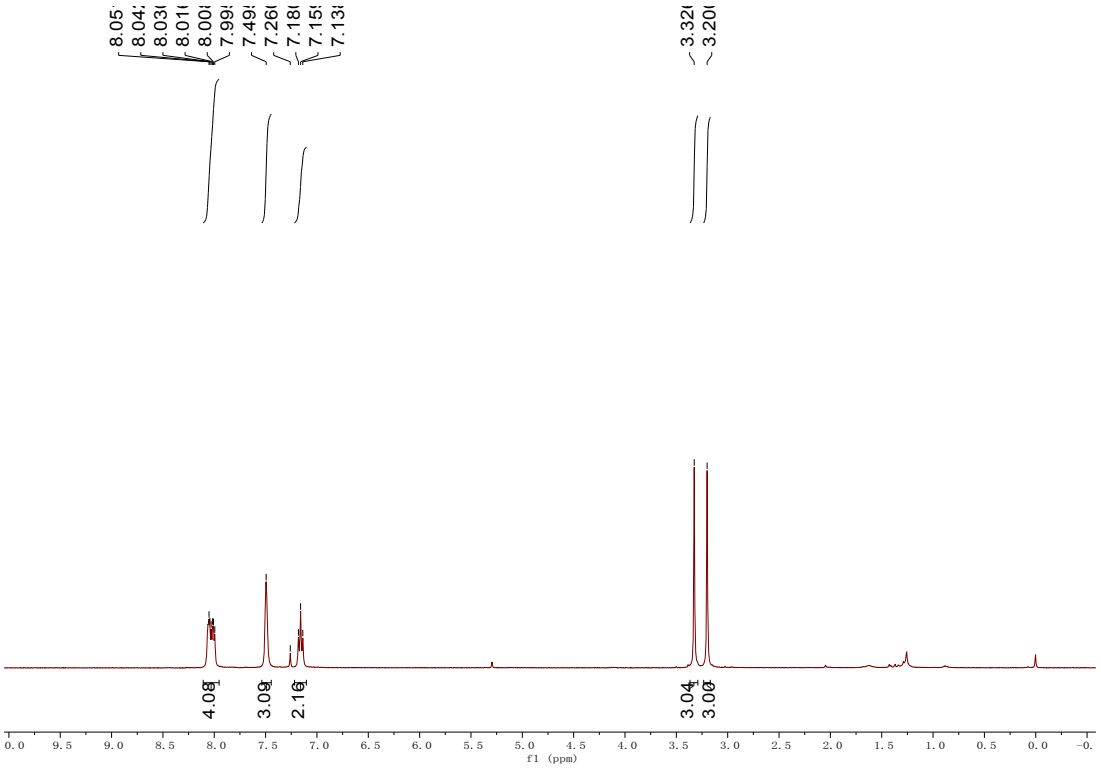
Compound 4ac: Yield: 51 mg, 74%; A white solid; Mp: 177-178 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10-8.04 (m, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.78 (s, 1H), 7.52-7.45 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 3.32 (s, 3H), 3.21 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 145.5, 138.4, 134.6, 130.8, 129.9, 128.82, 128.76, 126.9, 126.7, 126.3, 125.7, 122.9, 38.0, 36.9, 21.6; IR (neat): ν 2925, 1484, 1335, 1323, 1155, 1139, 1092, 1004, 993, 850, 761 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{19}N_2O_3S$ $[M+H]^+$: 343.1111, found: 343.1105.

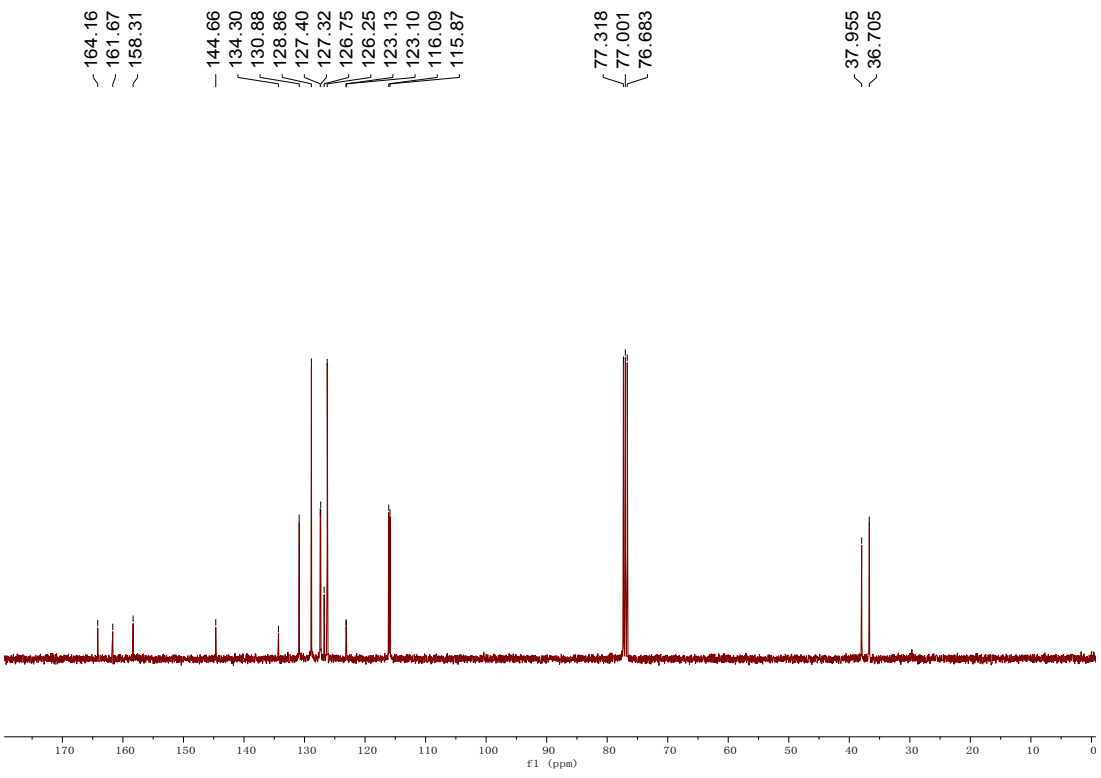






Compound 4ad: Yield: 49 mg, 80%; A white solid; Mp: 185-186 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11-7.95 (m, 4H), 7.49 (brs, 3H), 7.16 (t, *J* = 8.0 Hz, 2H), 3.33 (s, 3H), 3.20 (s, 3H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 162.9 (d. *J* = 248.7 Hz), 158.3, 144.7, 134.3, 130.9, 128.9, 127.4 (d, *J* = 8.3 Hz), 126.8, 126.3, 123.1 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 21.9 Hz), 38.0, 36.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.0; IR (neat): ν 2935, 1484, 1365, 1323, 1155, 1100, 1092, 993, 850, 761 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{16}FN_2O_3S$ $[M+H]^+$: 347.0860, found: 347.0854.


8.05
8.04
8.03
8.01
8.00
7.99
7.49
7.26
7.18
7.15
7.13
3.32
3.20
4.08
3.09
2.16
3.04
3.00
f1 (ppm)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128.86
127.40
127.32
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126.25
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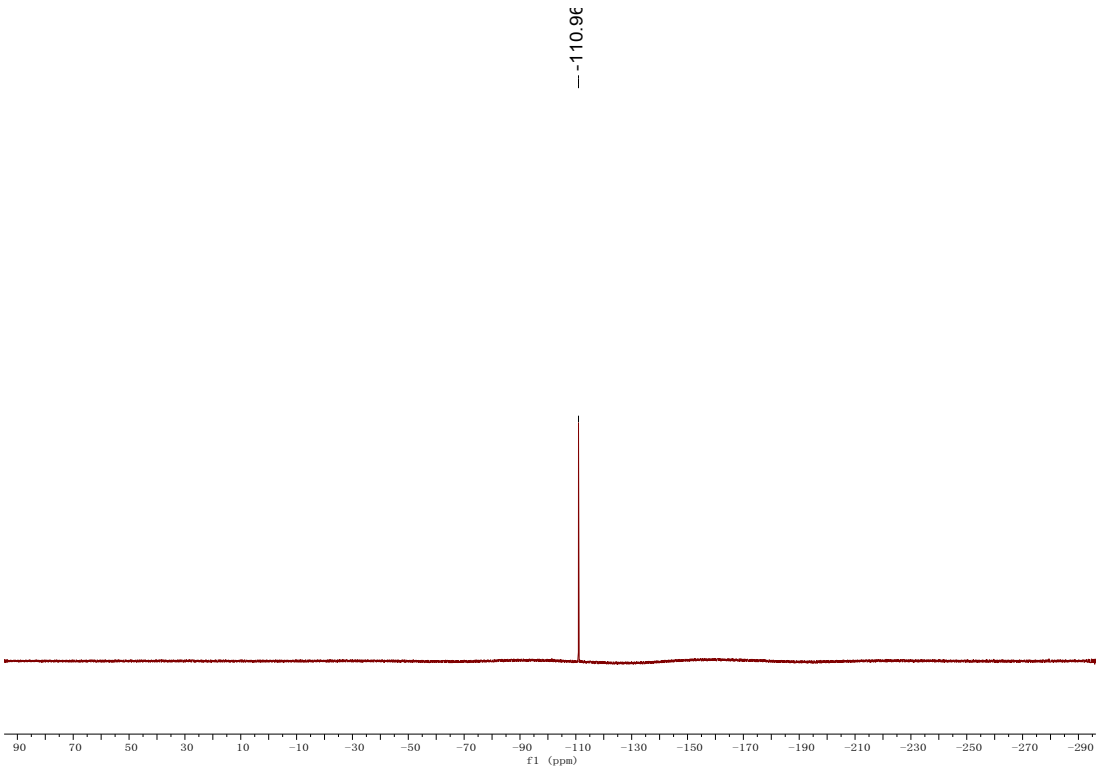
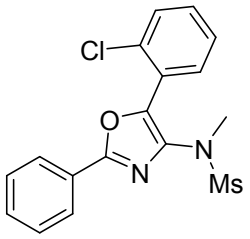
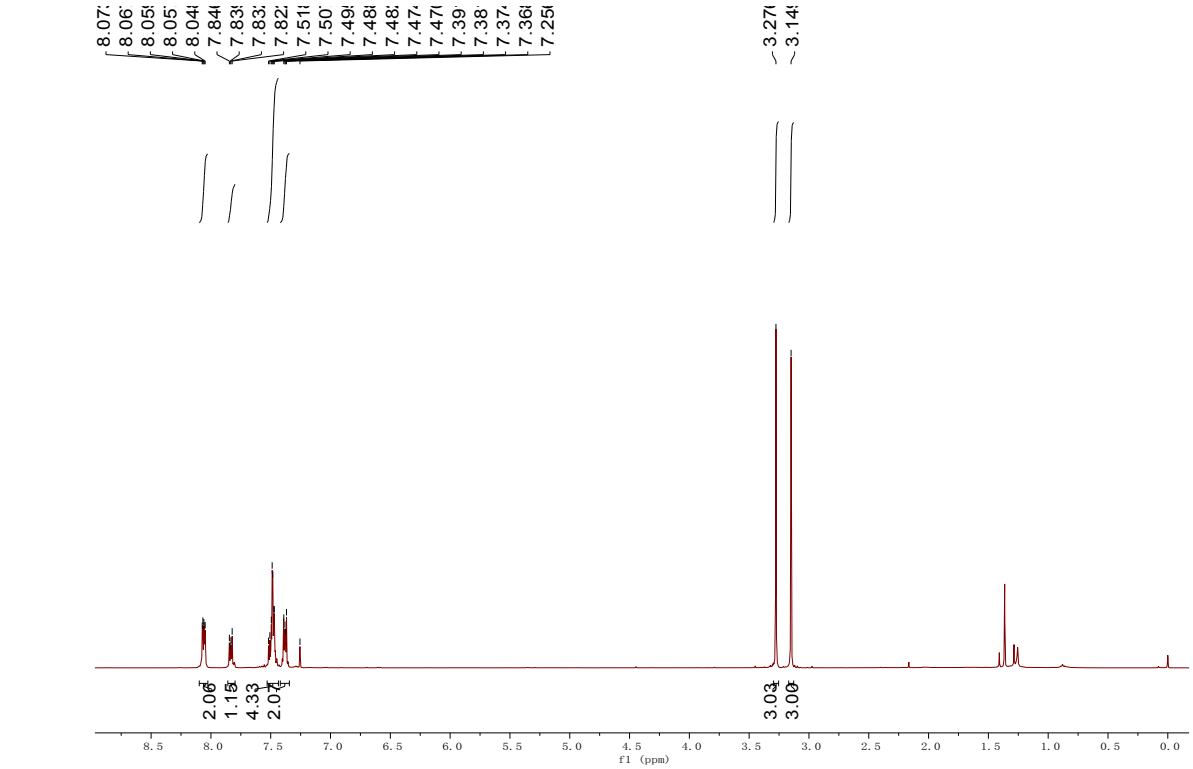
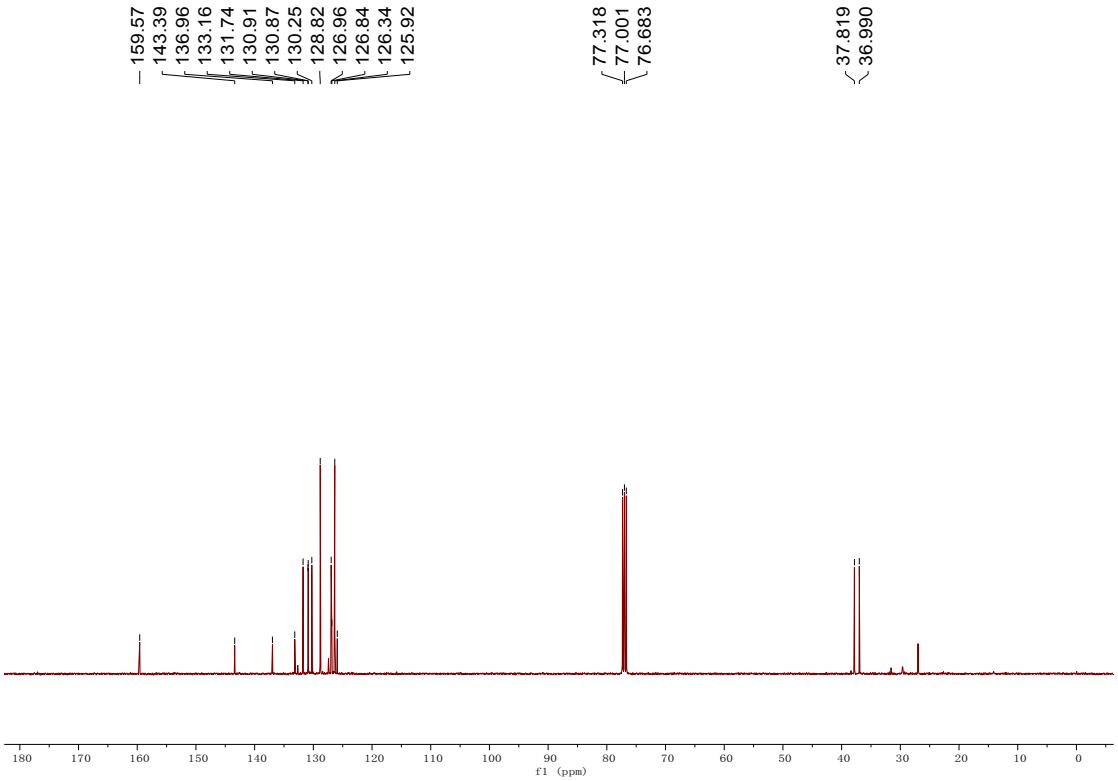
77.001
76.683
37.955
36.705
f1 (ppm)

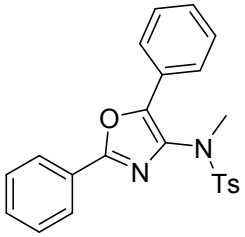




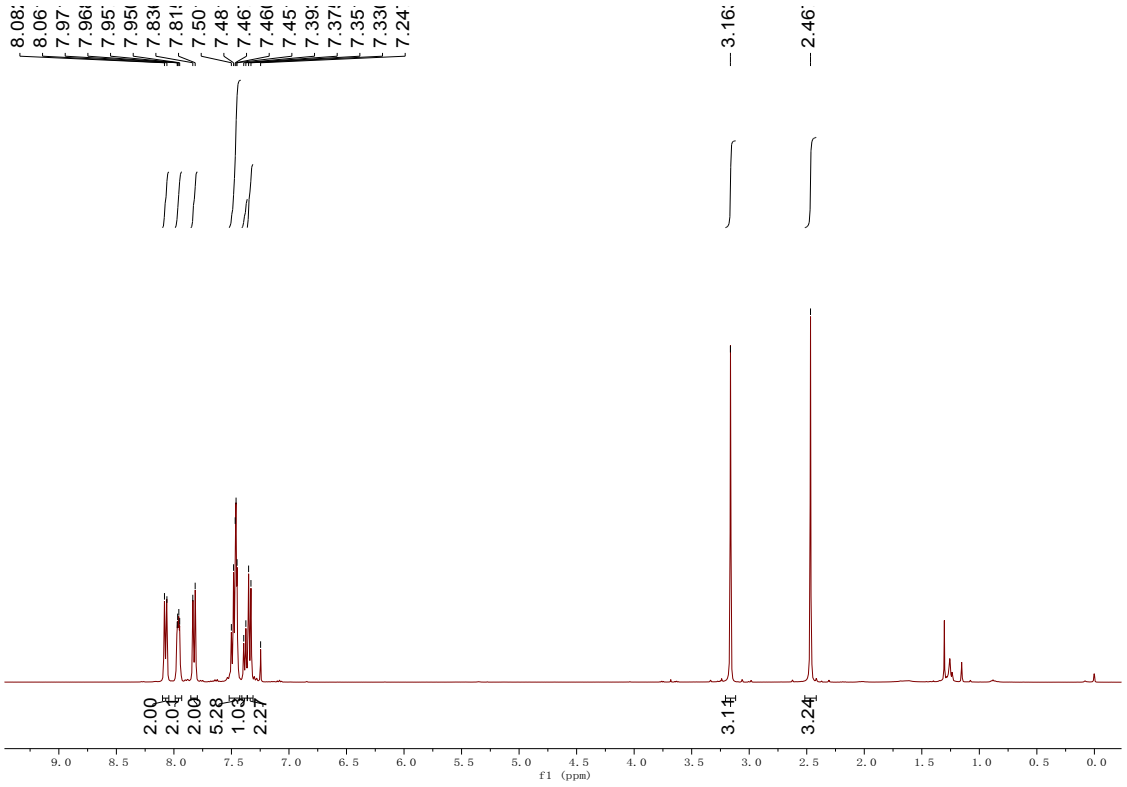
Compound 4ae: Yield: 48 mg, 75%; A white solid; Mp: 175-176 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11-8.03 (m, 2H), 7.87-7.79 (m, 1H), 7.54-7.45 (m, 4H), 7.42-7.35 (m, 2H), 3.28 (s, 3H), 3.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 143.4, 137.0, 133.2, 131.8, 130.91, 130.88, 130.3, 128.8, 127.0, 126.9, 126.4, 125.9, 37.8, 37.0; IR (neat): ν 2925, 1484, 1335, 1323, 1155, 1139, 1092, 1004, 993, 850, 761 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{16}ClN_2O_3S$ $[M+H]^+$: 363.0565, found: 363.0562.

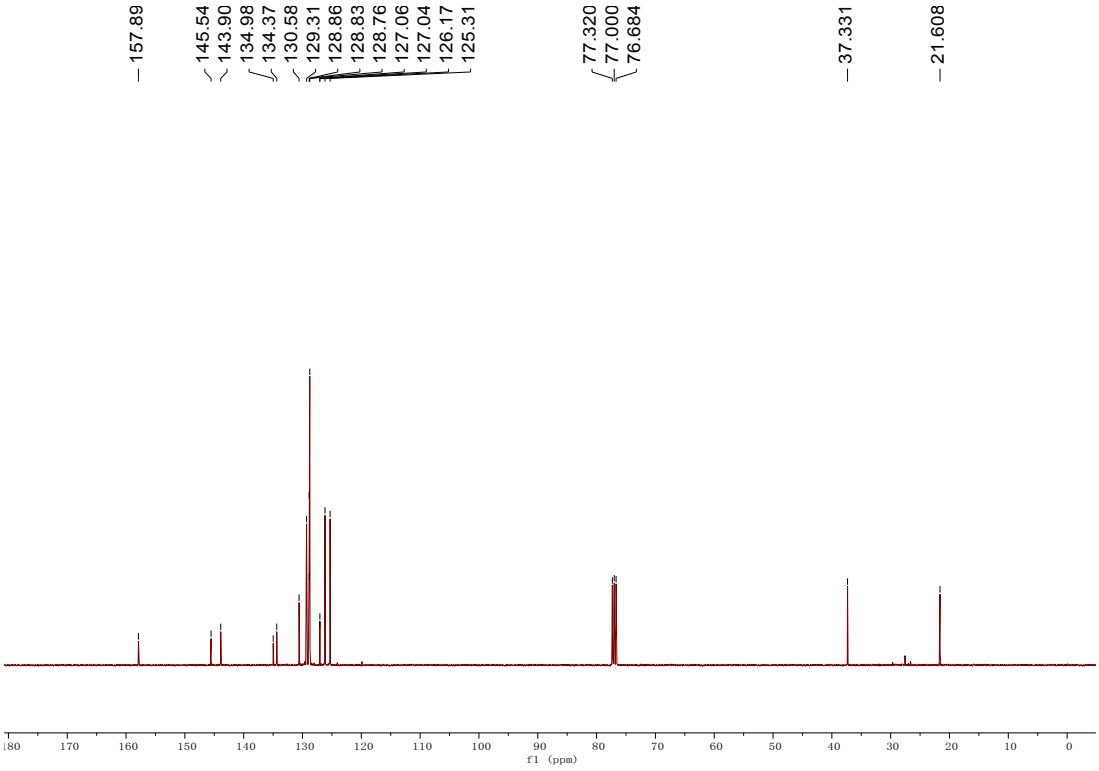


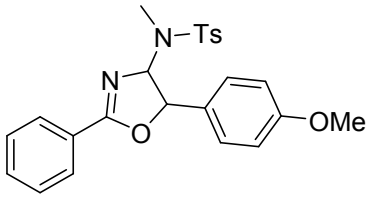



O
N
N
Ts

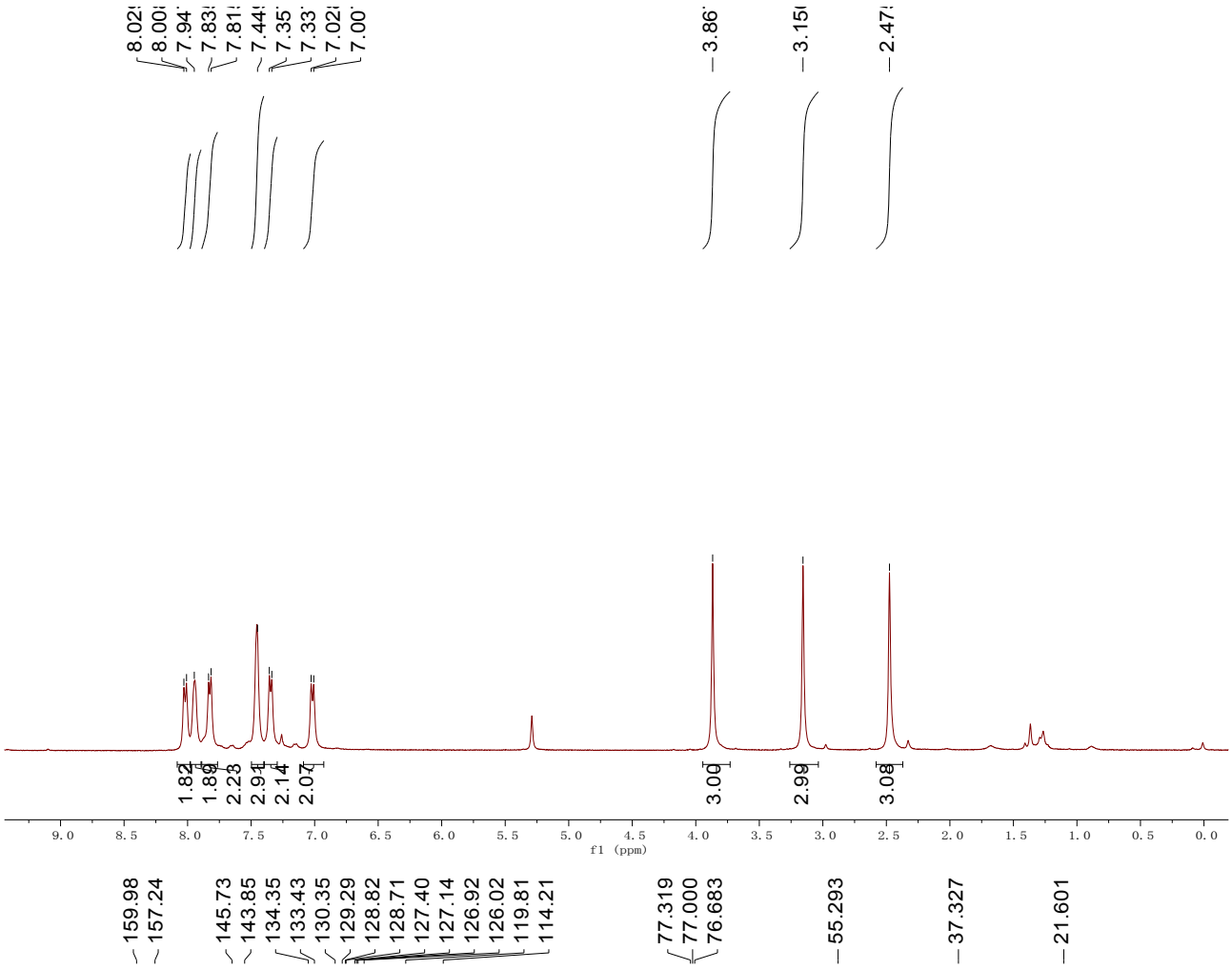
Compound 4af: Yield: 70 mg, 80%; A white solid; Mp: 185-186 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.99-7.93 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.52-7.43 (m, 5H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 3.16 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 145.6, 143.9, 135.0, 134.4, 130.6, 129.3, 128.9, 128.83, 128.76, 127.1, 127.0, 126.2, 125.3, 37.3, 21.6; IR (neat): ν 2930, 2907, 1349, 1163, 1087, 858, 813, 775, 712, 701, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1267, found: 405.1261.

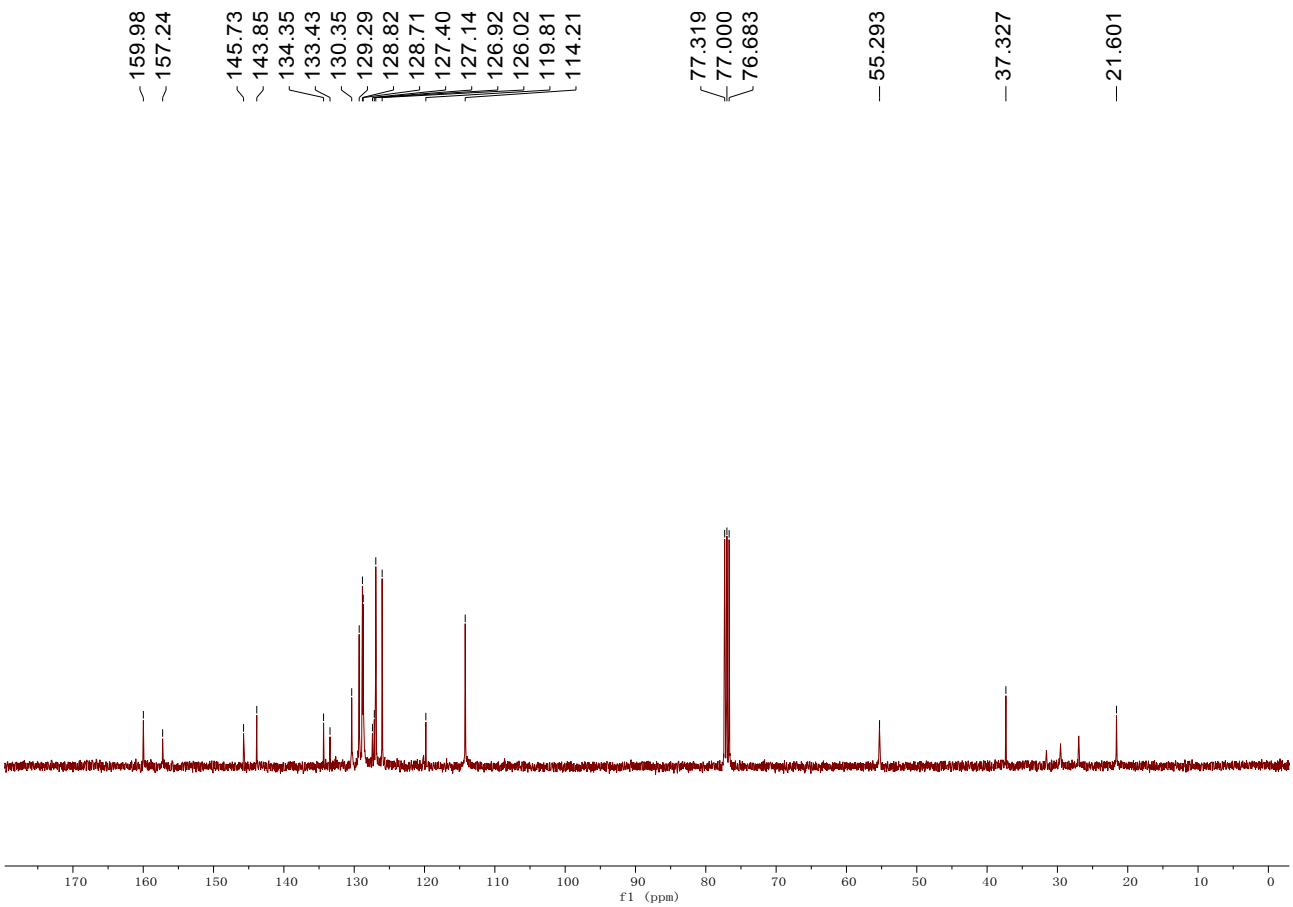


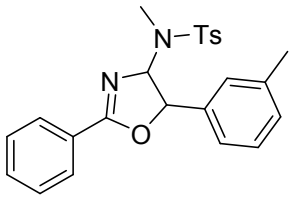




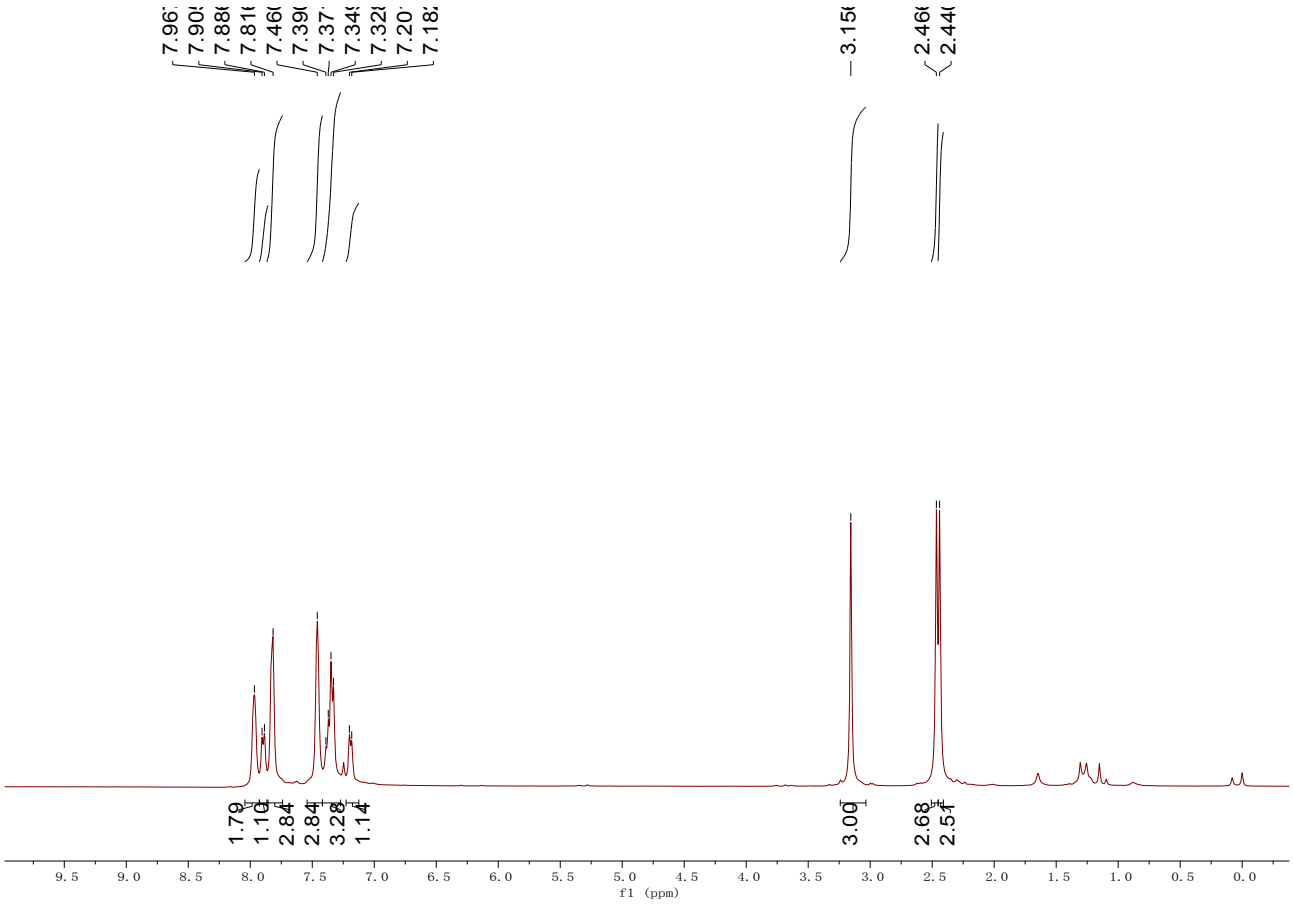
Compound 4ag: Yield: 62 mg, 74%; A white solid; Mp: 183-184 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.95 (brs, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.45 (brs, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.16 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 157.2, 145.7, 143.9, 134.4, 133.4, 130.4, 129.3, 128.8, 128.7, 127.4, 127.1, 126.9, 126.0, 119.8, 114.2, 55.3, 37.3, 21.6; IR (neat): ν 2985, 2935, 2825, 1508, 1343, 1174, 1086, 719, 704, 666 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$: 435.1373, found: 435.1379.

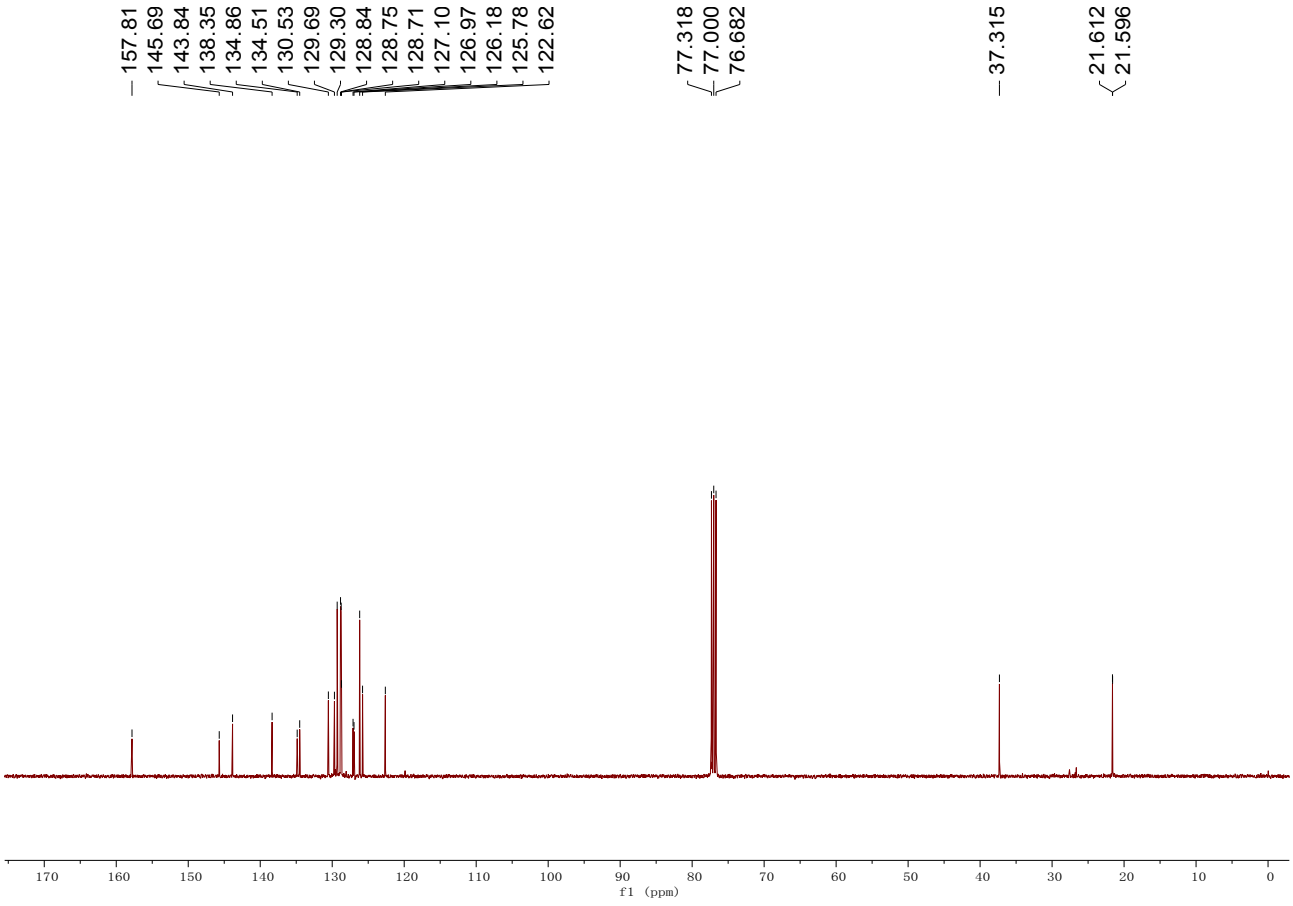

8.02
8.00
7.94
7.83
7.81
7.44
7.35
7.33
7.02
7.00
3.86
3.15
2.47
1.82
1.89
2.23
2.91
2.14
2.07
3.00
2.99
3.08
f1 (ppm)


159.98
157.24
145.73
143.85
134.35
133.43
130.35
129.29
128.82
128.71
127.40
127.14
126.92
126.02
119.81
114.21
77.319
77.000
76.683
55.293
37.327
21.601
f1 (ppm)

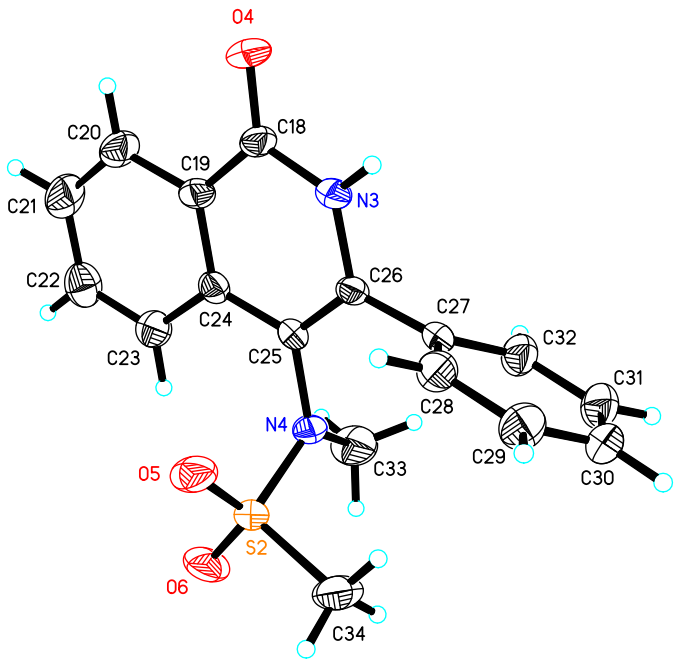


Compound 4ah: Yield: 54 mg, 62%; A white solid; Mp: 167-168 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 (s, 2H), 7.93-7.86 (m, 1H), 7.82 (s, 3H), 7.46 (s, 3H), 7.42-7.27 (m, 3H), 7.23 -7.12 (m, 1H), 3.16 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 145.7, 143.8, 138.4, 134.9, 134.5, 130.5, 129.7, 129.3, 128.84, 128.75, 128.7, 127.1, 127.0, 126.2, 125.8, 122.6, 37.3, 21.61, 21.59; IR (neat): ν 3037, 2925, 2841, 1350, 1164, 1155, 1086, 1018, 807, 781, 687 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$: 419.1424, found: 419.1423.



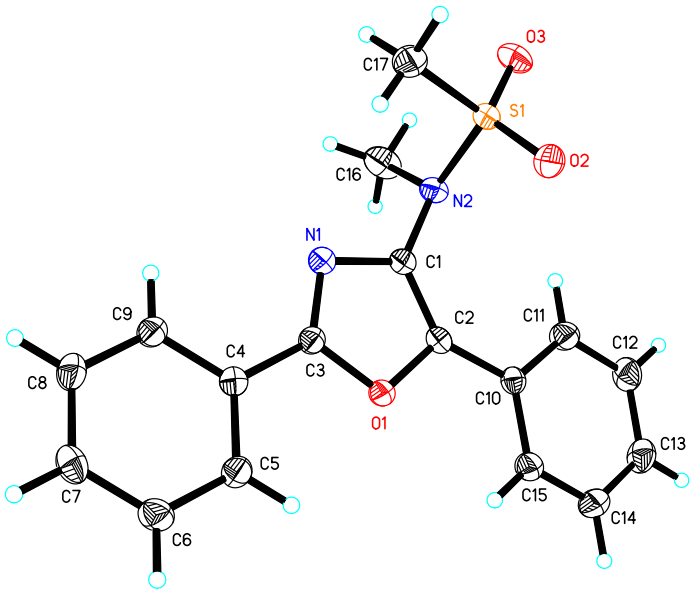

157.81
145.69
143.84
138.35
134.86
134.51
130.53
129.69
129.30
128.84
128.75
128.71
127.10
126.97
126.18
125.78
122.62
77.318
77.000
76.682
37.315
21.612
21.596
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6. X-ray crystal data of 3aa.



The crystal data of **3aa** have been deposited in CCDC with number 1545434. Empirical formula: $C_{17}H_{16}N_2O_3S$, Formula weight: 328.38, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 10.862(2) Å, α = 78.329(5)°; b = 10.941(2) Å, β = 70.263(5)°; c = 15.640(3) Å, γ = 67.246(5)°. Volume: 1607.8(6) $Å^3$, Z = 4, Density (calculated): 1.357 Mg/m^3, F(000) = 688, Crystal size: 0.150 x 0.110 x 0.040 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0785, wR2 = 0.1613.

X-ray crystal data of 4aa.



The crystal data of **4aa** have been deposited in CCDC with number 1545423. Empirical formula: C17H16N2O3S, Formula weight: 328.38, Crystal system: Monoclinic, Space group: P 21/n, Unit cell dimensions: a = 8.4348(10) Å, α = 90°; b = 10.6163(13) Å, β = 94.274(2)°; c = 17.427(2) Å, γ = 90°. Volume: 1556.1(3) Å3, Z = 4, Density (calculated): 1.402 Mg/m3, F(000) = 688, Crystal size: 0.200 x 0.160 x 0.120 mm3, Final R indices [I>2sigma(I)]: R1 = 0.0370, wR2 = 0.0968.

7. References

[1] (a) H. G. Wang and F. Glorius, *Angew. Chem. Int. Ed*. 2012, **51**, 7318. (b) Ch. Feng and T. -P. Loh, *Angew. Chem. Int. Ed*. 2014, **53**, 2722.

[2] N. Guimond, S. I. Gorelsky and K. Fagnou, *J. Am. Chem. Soc.* 2011, **133**, 6449.

[3] G. Y. Tan, X. L. Huang, Q. Wu, L. -Q. Zhang and J. You, *RSC Adv*., 2014, **4**, 49186.