Supporting Information

Base-promoted [3+3] cyclization of cyclopropenones and cyclopropenethiones with amides for the synthesis of 6*H*-1,3-oxazin-6-ones and 6*H*-1,3-thiazin-6-ones

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Content 1

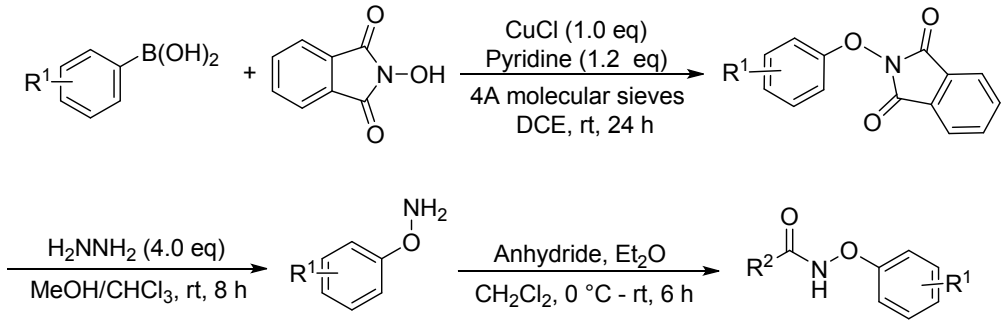
1. General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent DD2 400-MR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard; Chemical shifts (δ) are expressed in ppm and *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Infrared 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 **3a**, **5j** and **6ab** were assigned by X-ray crystal analysis.

2. General procedure for the preparation of *N*-(pivaloyloxy)amides

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

3. General procedure for the synthesis of *N*-aryloxyacetamides

The *N*-aryloxyacetamides were prepared according to the previously reported literature.[2]



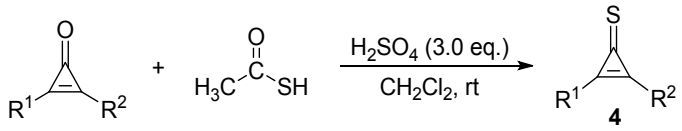
In a 100 mL round-bottom flask, *N*-hydroxyphthalimide (1.0 eq.), copper(I) chloride (1.0 eq.), freshly activated 4 Å molecular sieves (250 mg/mmol), and phenylboronic acid (2.0 eq.) were combined in 1,2-dichloroethane. The pyridine (1.2 eq.) was then added to the suspension. The reaction mixture was open to the atmosphere and stirred at room temperature over 24 h. Upon completion, the reaction mixture was filtered through a celite and the residue was concentrated under reduced pressure. Silica gel was added to the flask and the solvent was removed under vacuum. The desired *N*-aryloxyphthalimides were obtained by a flash column chromatography on silica gel.

Hydrazine monohydrate (4.0 eq.) was added to the solution of *N*-aryloxyphthalimide (1.0 eq.) in a mixed solvents of $CHCl_3$ and MeOH (V/V = 1/10). The reaction mixture was stirred for 8 h at room temperature. Upon completion, the reaction mixture was filtered off and washed with CH_2Cl_2.

The filtrate was concentrated under reduced pressure and the residue was purified by a flash silica gel column chromatography to give the corresponding *N*-aryloxyamines.

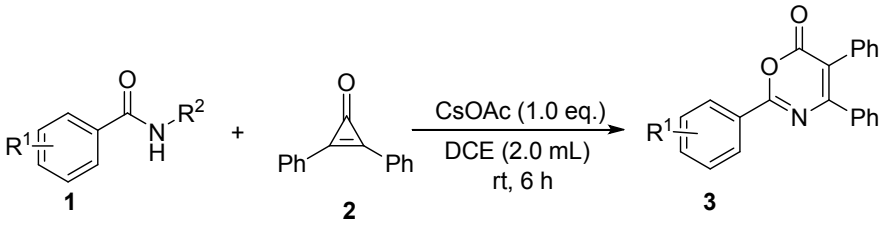
N-aryloxyamine (1.0 eq.) was dissolved in ether, and the flask was cooled in an ice bath, to which anhydride (2.0 eq.) was slowly added. The reaction mixture was allowed to be warmed to room temperature and the reaction mixture was stirred for 6 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by a flash silica gel column chromatography to give the corresponding *N*-aryloxyacetamides.

4. General procedure for the synthesis of starting materials 4.



A mixture of cyclopropenones, thioacetic acid (3.0 eq.) and sulfuric acid (1.8 eq.) in CH_2Cl_2 was stirred vigorously at room temperature until the starting materials was completely consumed. The mixture was poured into cooled water, and the organic layer was separated, dried over anhydrous sodium sulfate and purified by a flash silica gel column chromatography to give the corresponding compounds **4**.

5. General procedure for the synthesis of products 3.

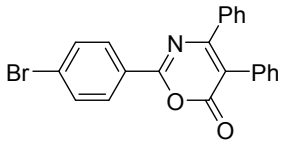


To a dried Schlenk tube was added benzamides **1** (0.2 mmol), cyclopropenones **2** (0.2 mmol) and CsOAc (1.0 eq.) in anhydrous DCE (2.0 mL) under argon. Then, the resulting solution was stired at room temperature for 6 h. The solvent was removed under reduced pressure and the mixture was purified by a flash column chromatography on silica gel (PE/EA = 10/1) directly to give the desired products **3**.

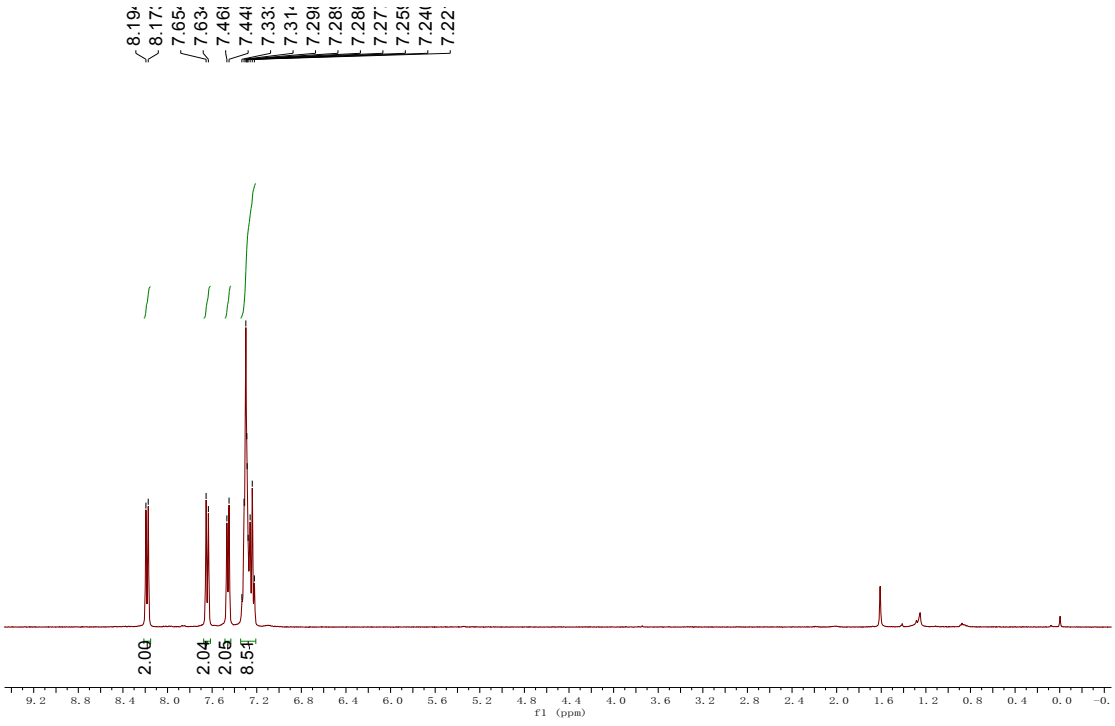
6. General procedure for the synthesis of products 5 and 6.

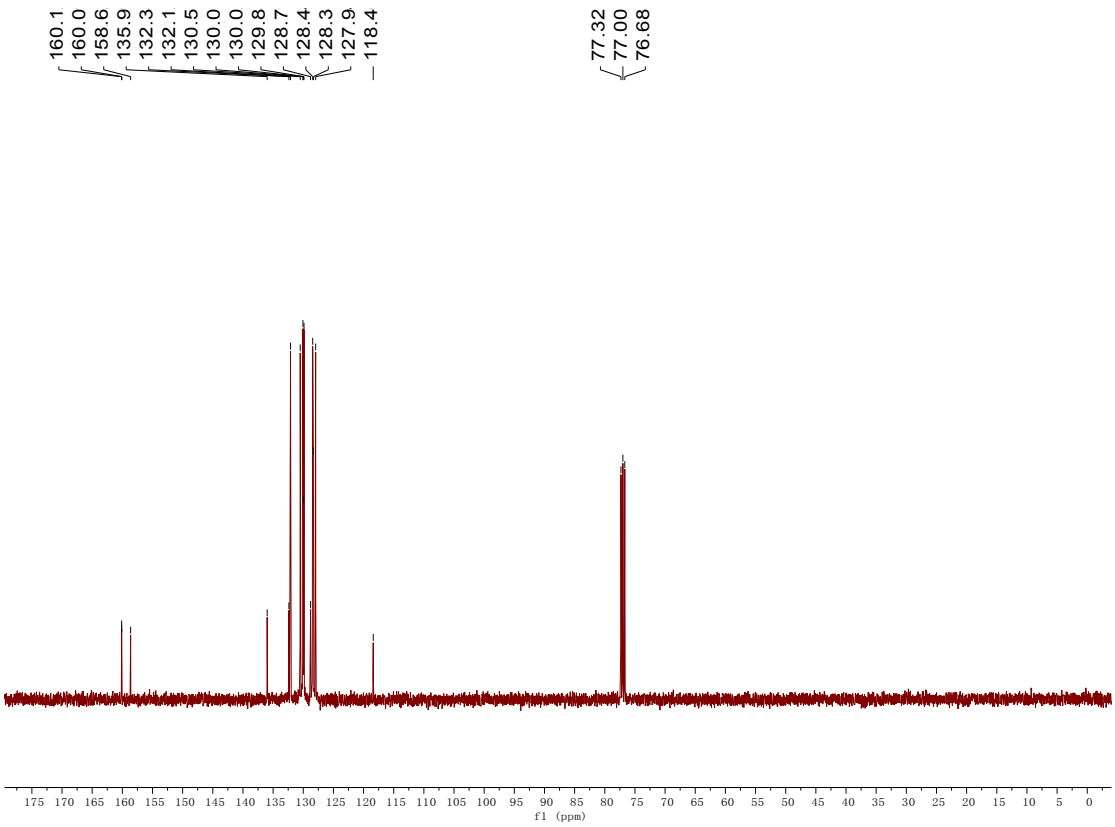
General procedure for the synthesis of products **5** and **6** was similar as that of products **3**.

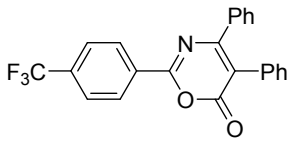
7. Spectroscopic data of the products.



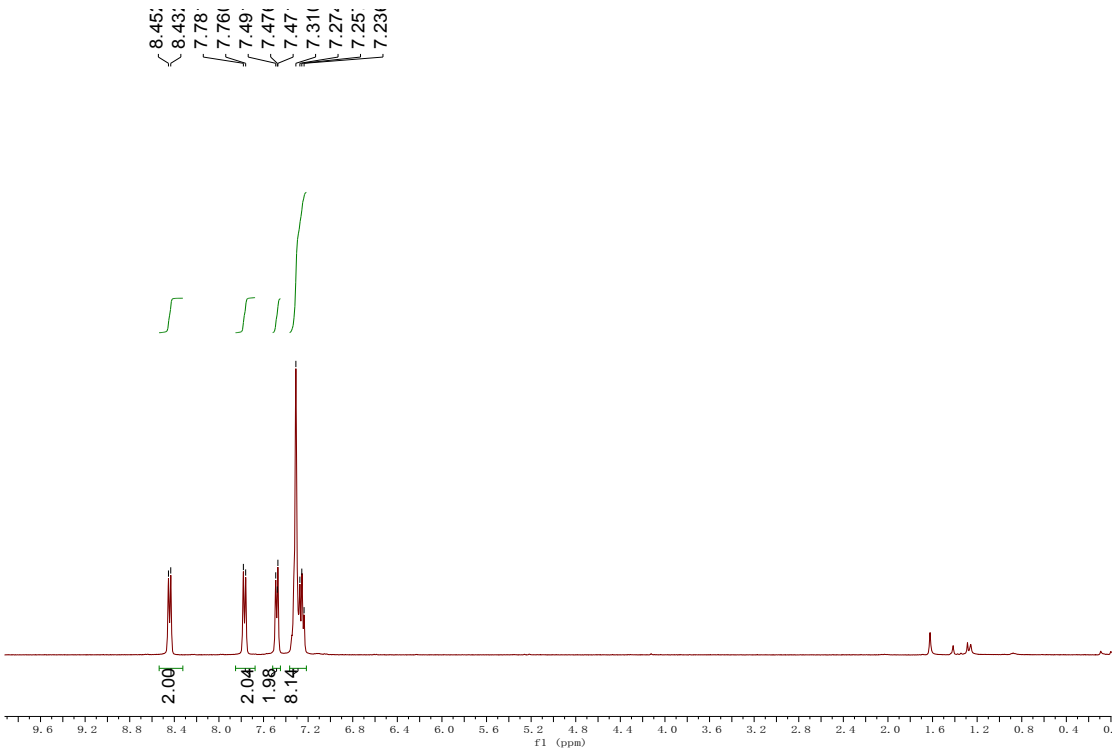
Compound 3a: Yield: 81 mg, 90%; A white solid; Mp: 193-194°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.34-7.21 (m, 8H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.12, 160.10, 158.6, 136.0, 132.4, 132.1, 130.5, 130.05, 130.02, 129.9, 128.8, 128.4, 128.3, 127.9, 118.4; IR (neat): ν 3062, 1741, 1608, 1577, 1540, 773, 755, 694 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{15}BrNO_2$ $[M+H]^+$: 404.0281, found: 404.0280.







Compound 3b: Yield: 57 mg, 75%; A white solid; Mp: 186-187 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 6.0 Hz, 2H), 7.37-7.22 (m, 8H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.9, 159.4,158.4,135.8,134.4 (q, *J* = 32.6 Hz), 133.1, 132.2, 130.5, 130.13 130.07, 128.8, 128.48, 128.46, 128.0, 125.7 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 271.1 Hz), 119.0; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -63.1; IR (neat): ν 2922, 2850, 1741, 1615, 1330, 1314, 1111, 1065, 695, 679 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{15}F_3NO_2$ $[M+H]^+$: 394.1049, found: 394.1042.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7.23
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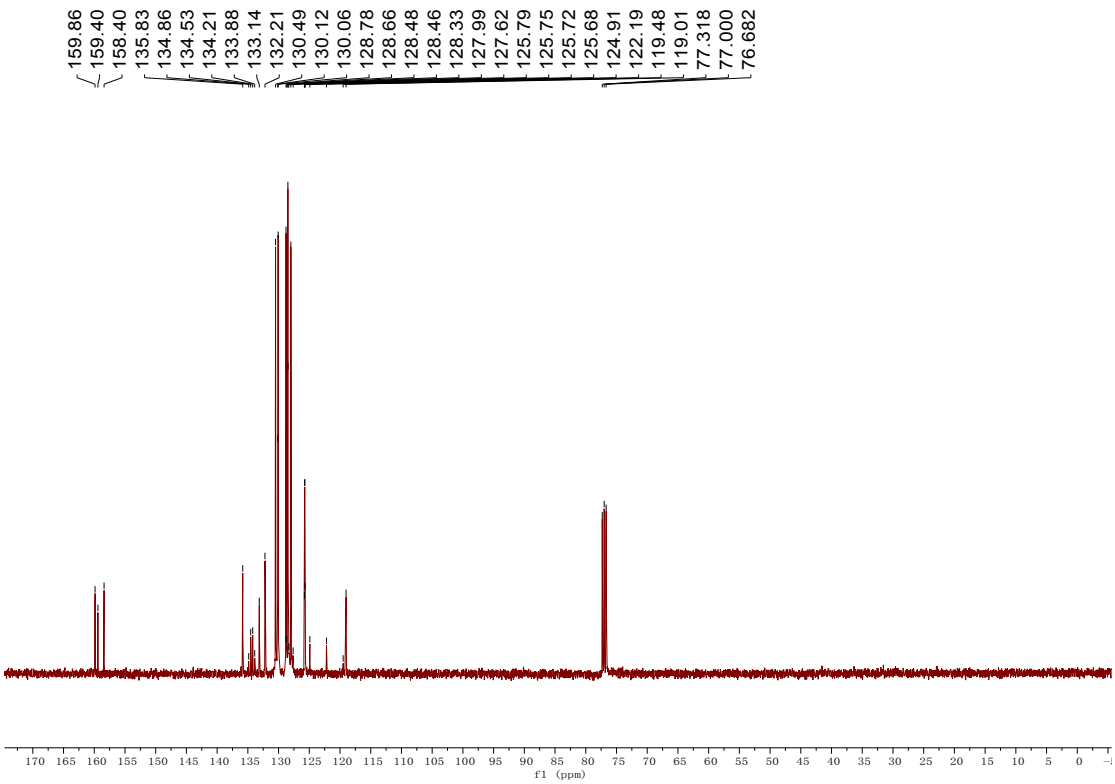
1.98
8.14
f1 (ppm)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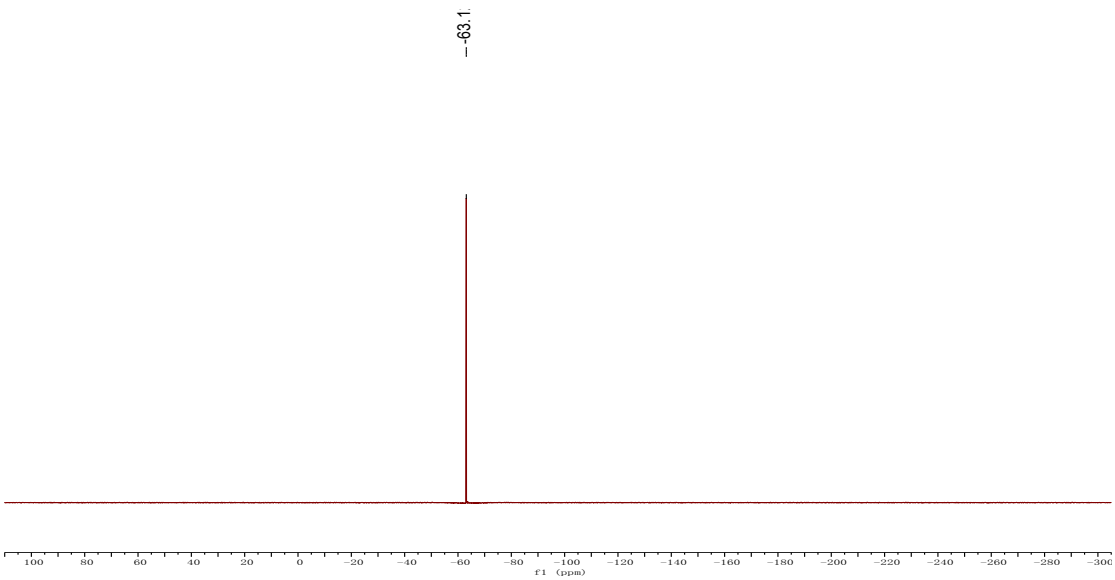
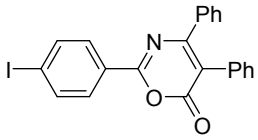
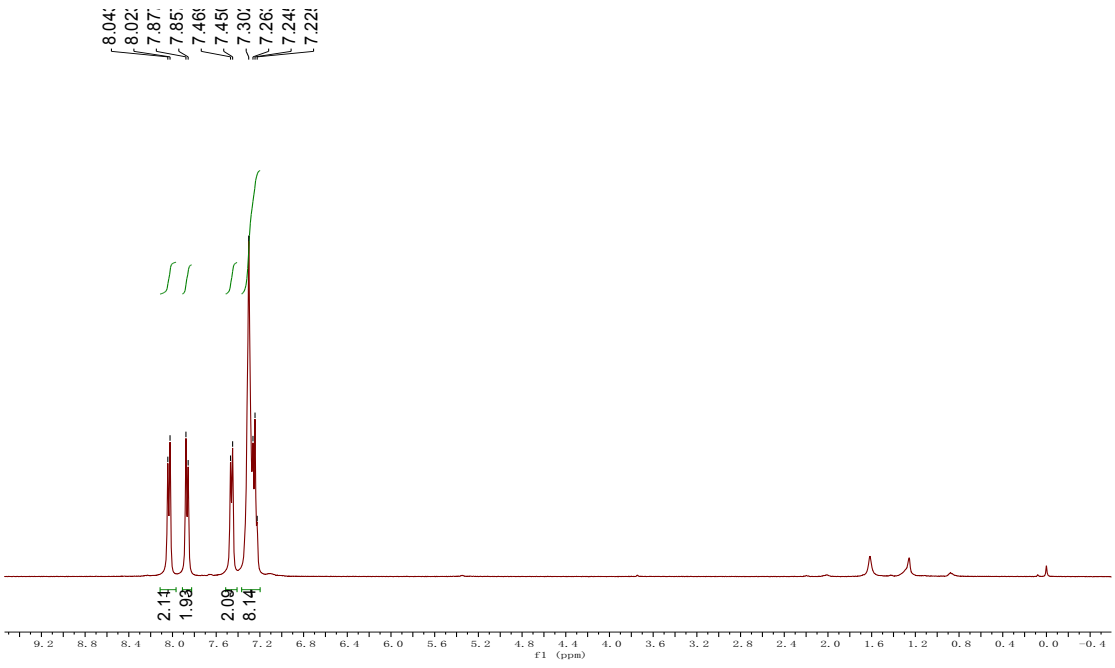
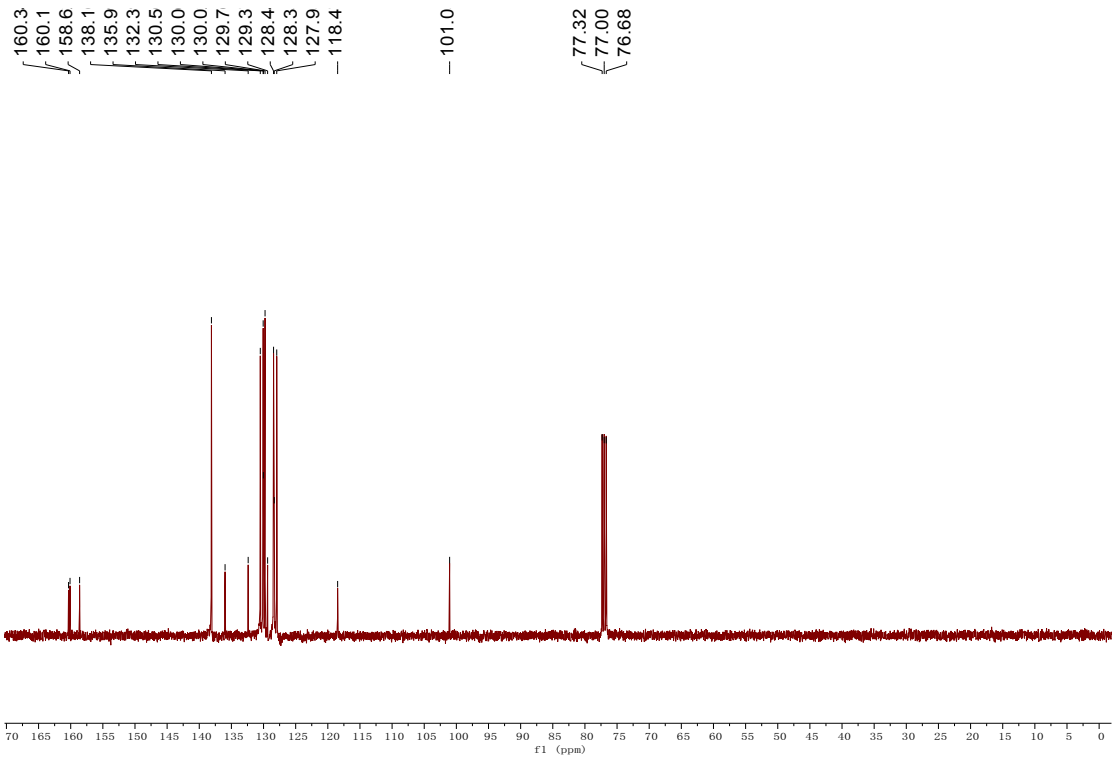
f1 (ppm)

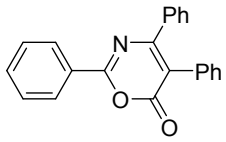




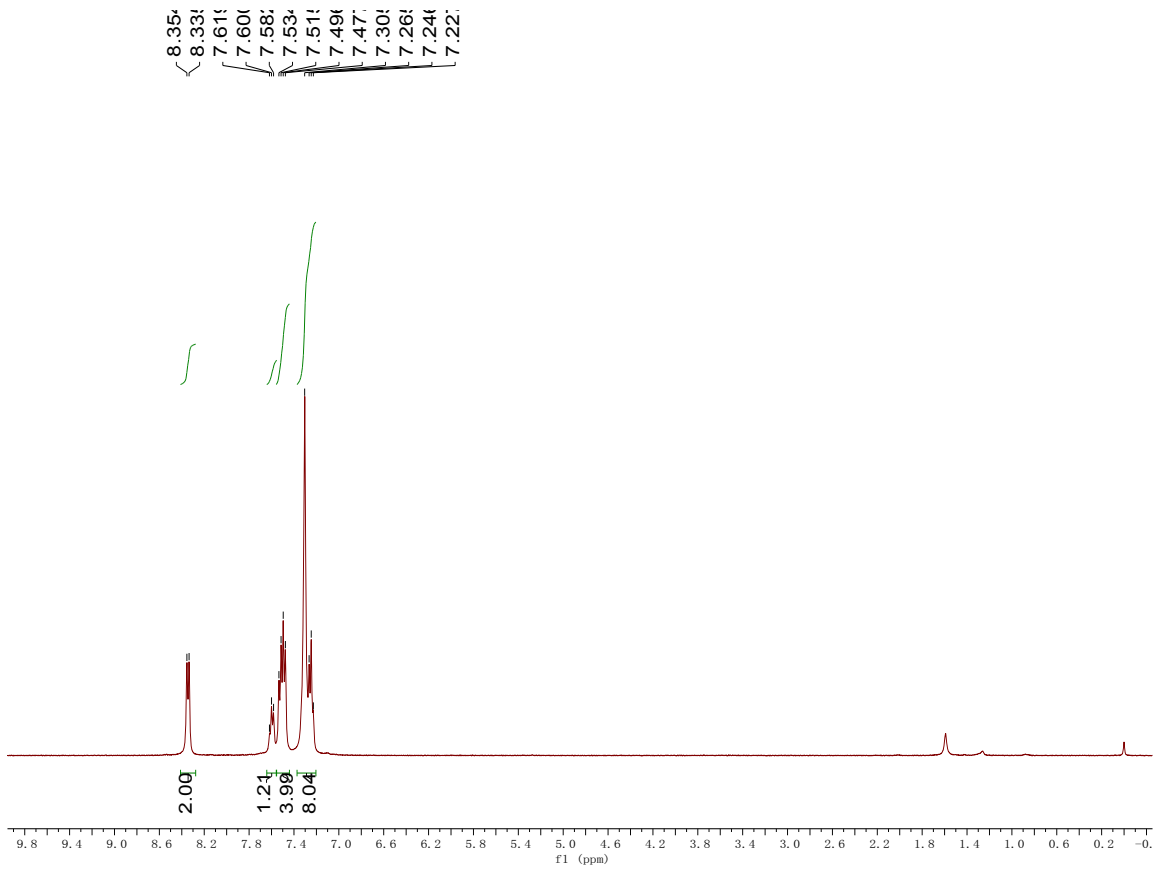
Compound 3c: Yield: 95 mg, 92%; A white solid; Mp: 219-221 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.37-7.20 (m, 8H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.3, 160.1, 158.6, 138.1, 136.0, 132.4, 130.5, 130.1, 130.0, 129.8, 129.4, 128.4, 128.3, 128.0, 118.5, 101.1; IR (neat): ν 2917, 2850, 1731, 1603, 1595, 1537, 773, 756, 697 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{15}INO_2$ $[M+H]^+$: 452.0142, found: 452.0138.







Compound 3d: Yield: 62 mg, 92%; A white solid; Mp: 216-217 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 7.6 Hz, 2H), 7.64-7.55 (m, 1H), 7.56-7.44 (m, 4H), 7.37-7.20 (m, 8H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.9, 160.4, 158.8, 136.2, 133.2, 132.6, 130.6, 130.1, 129.93, 129.89, 128.8, 128.5, 128.4, 128.2, 127.9, 118.2; IR (neat): ν 2920, 2850, 1731, 1598, 1608, 1547, 1449, 772, 698 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{16}NO_2$ $[M+H]^+$: 326.1176, found: 326.1171.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7.60
7.58
7.53
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7.30
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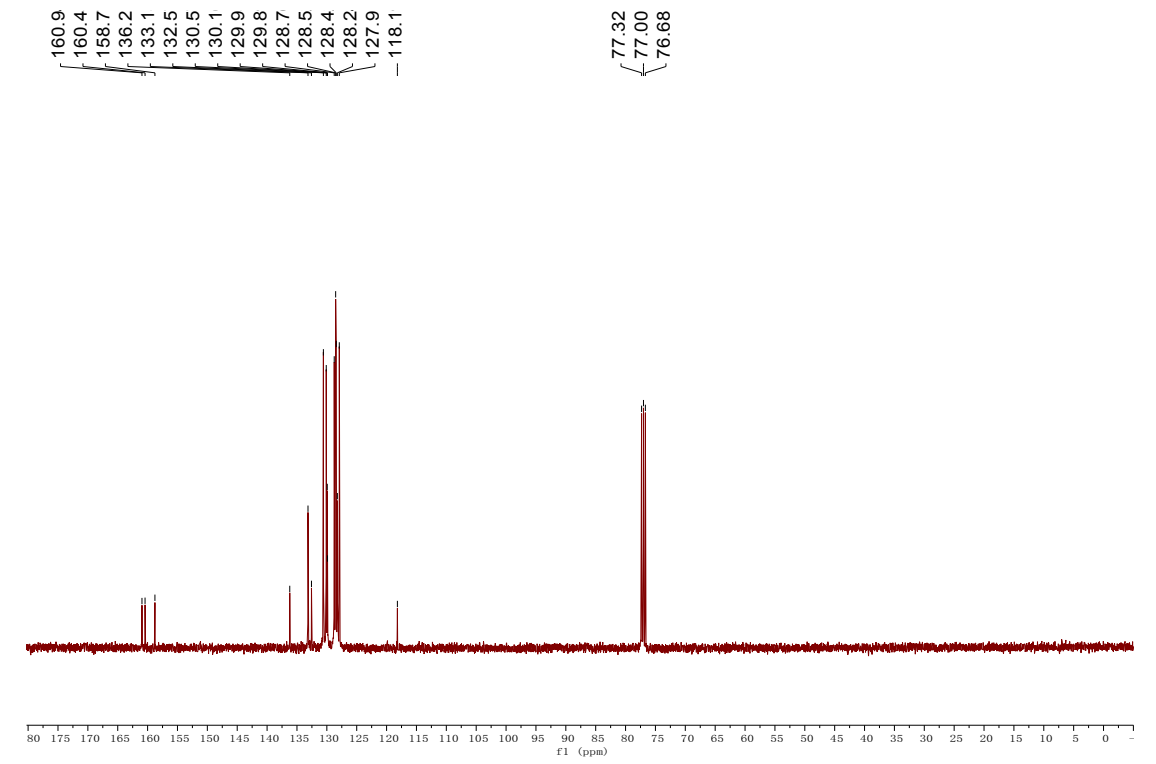
2.00
1.21
3.99
8.04
f1 (ppm)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133.1
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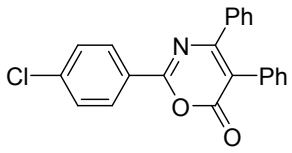
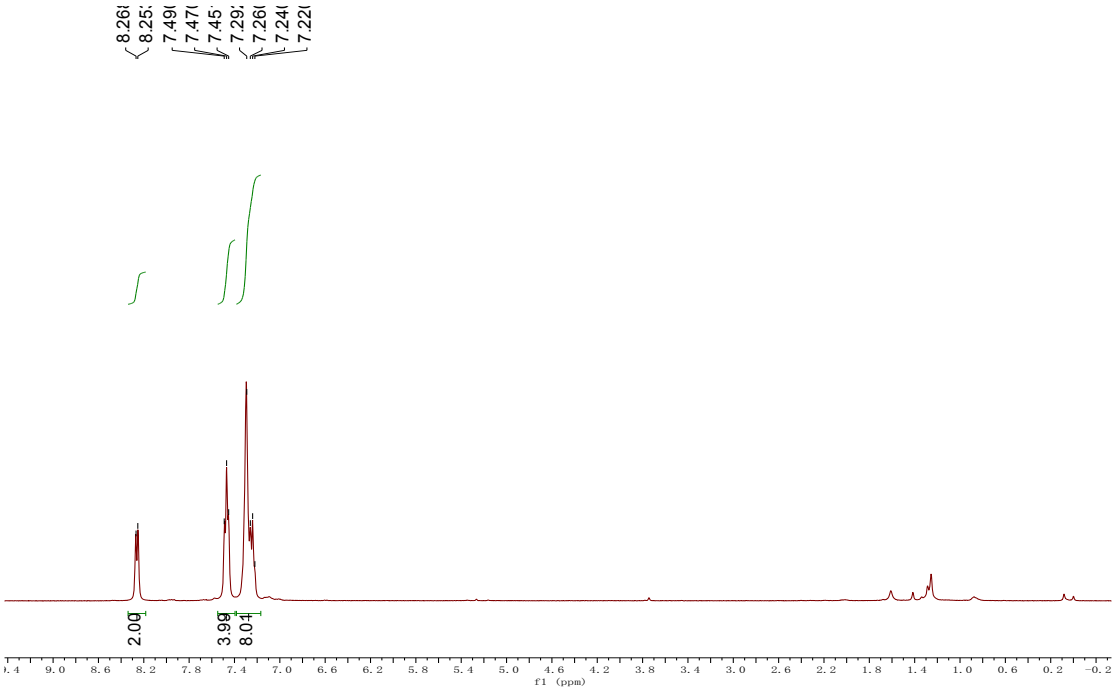
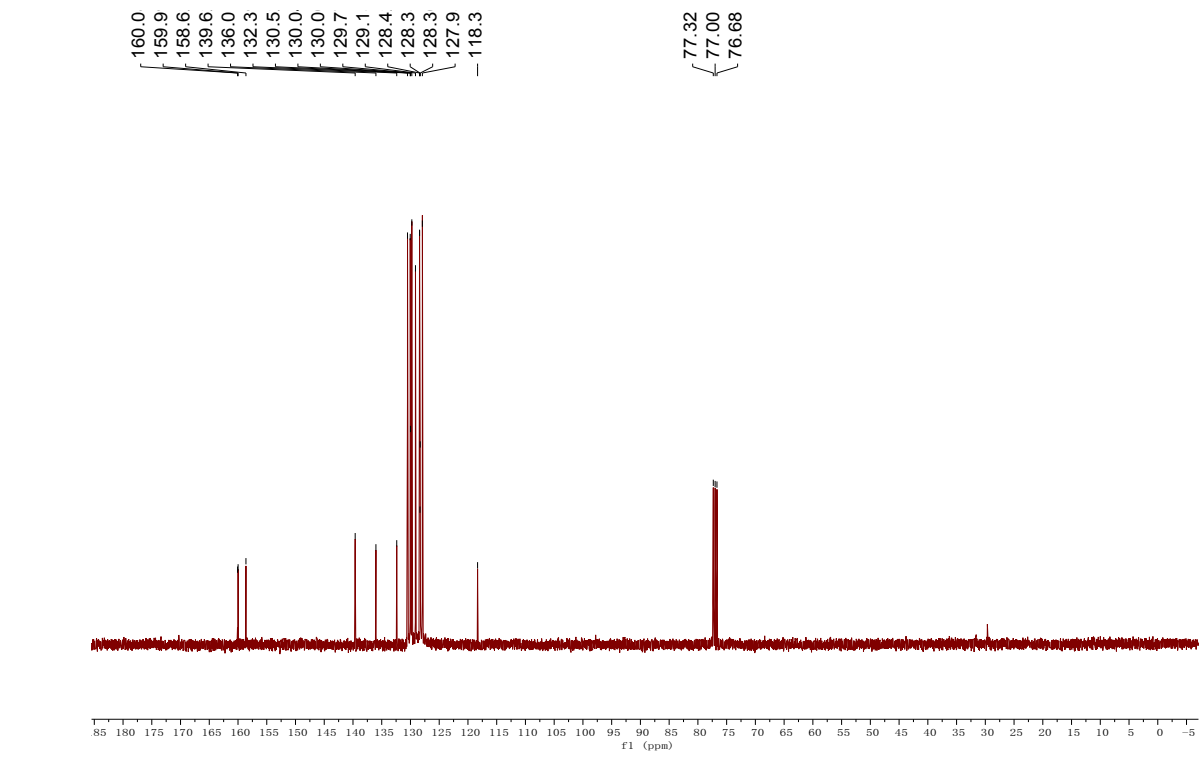
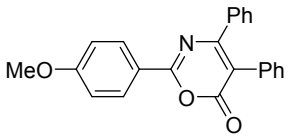
118.1
77.32
77.00
76.68
f1 (ppm)



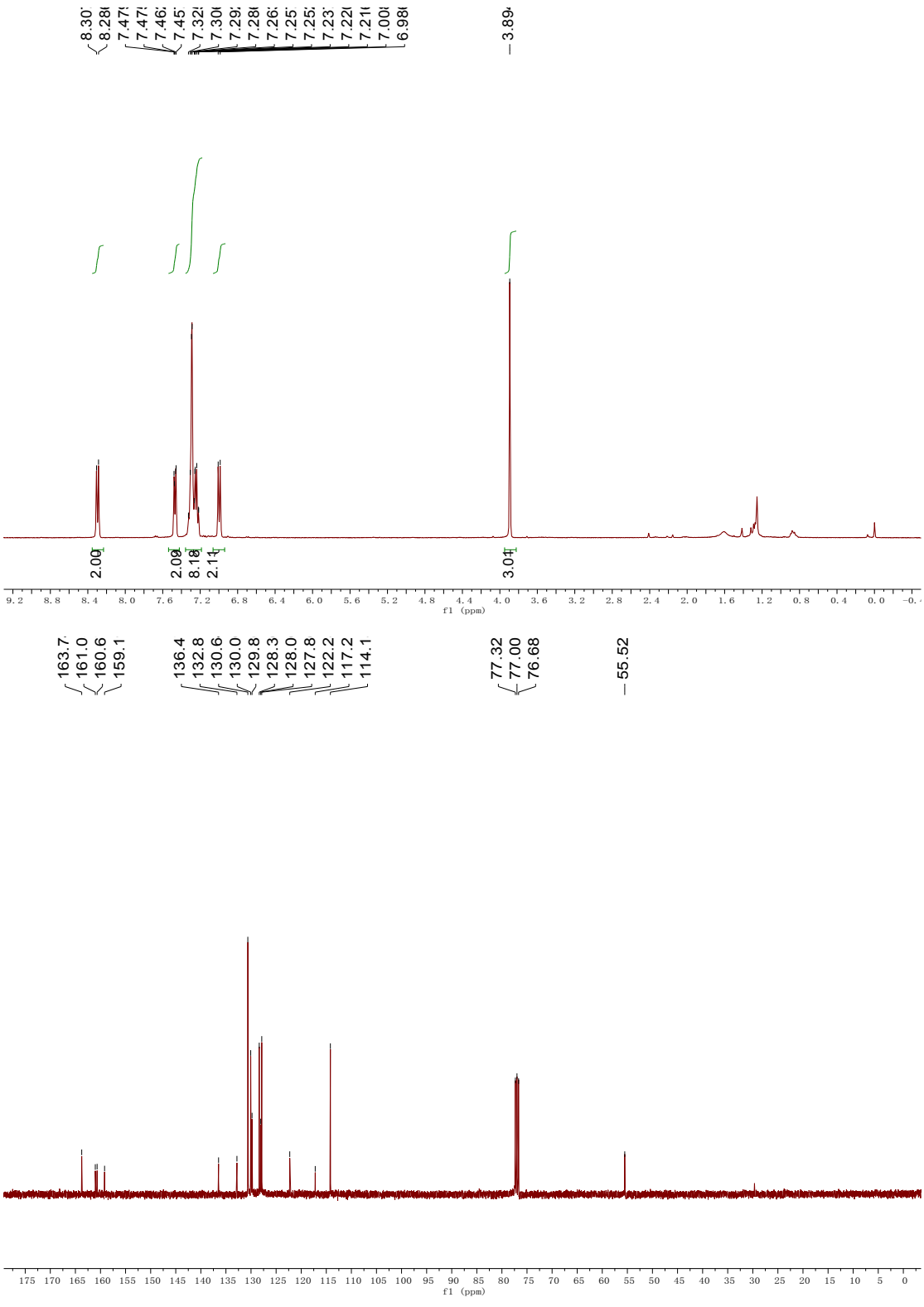
Compound 3e: Yield: 67 mg, 91%; A white solid; Mp: 189-190 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 6.0 Hz, 2H), 7.55-7.40 (m, 4H), 7.38-7.17 (m, 8H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.1, 160.0, 158.6, 139.6, 136.0, 132.4, 130.5, 130.04, 130.00, 129.8, 129.1, 128.42, 128.35, 128.3, 127.9, 118.3; IR (neat): ν 3067, 2915, 1740, 1608, 1598, 1540, 773, 692 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{15}ClNO_2[M+H]^+$: 360.0786, found: 360.0784.

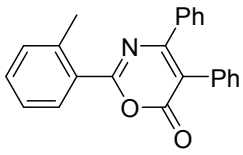






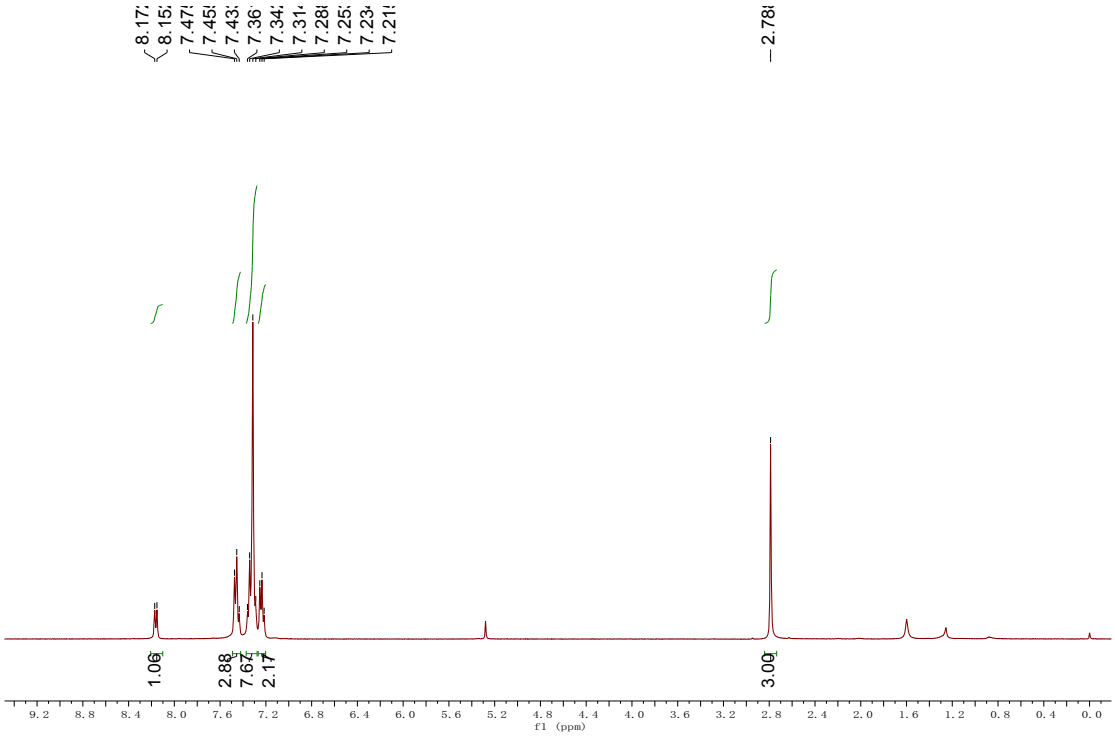
Compound 3f: Yield: 45 mg, 65%; A white solid; Mp: 211-212 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.36-7.19 (m, 8H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.7, 161.0, 160.7, 159.2, 136.5, 132.8, 130.6, 130.1, 129.8, 128.4, 128.1, 127.9, 122.3, 117.2, 114.2, 55.5; IR (neat): ν 3067, 1740, 1607, 1598, 1292, 773, 692 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{18}NO_3$ $[M+H]^+$: 356.1281, found: 356.1276.

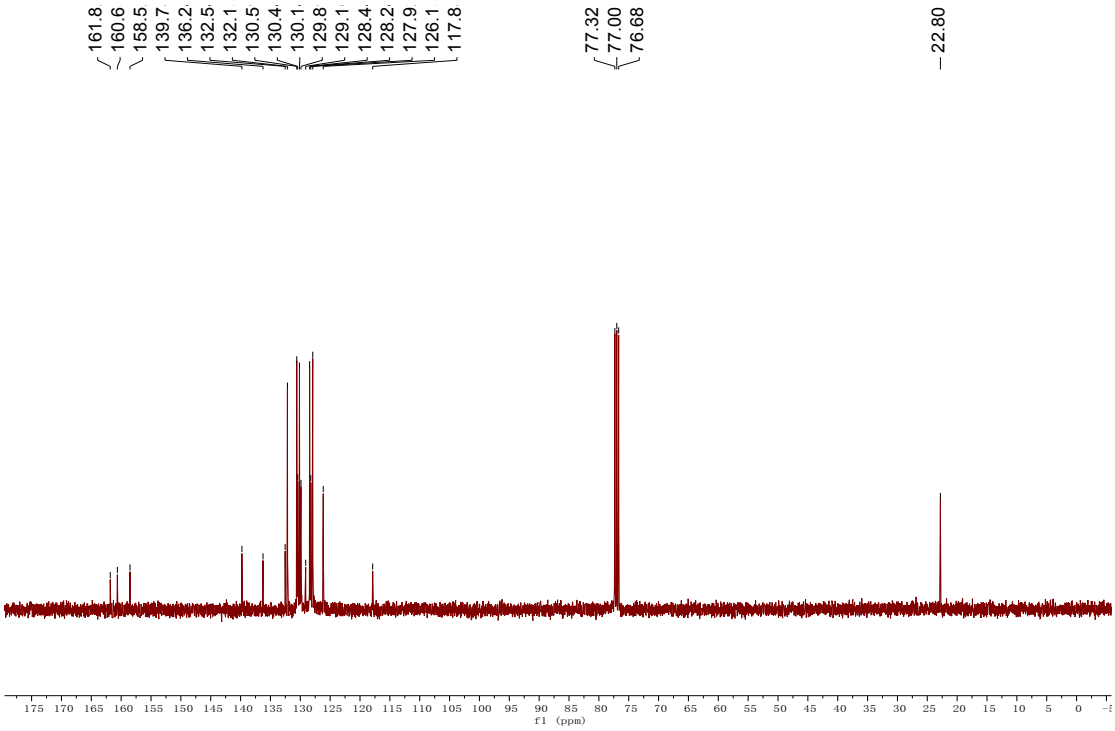


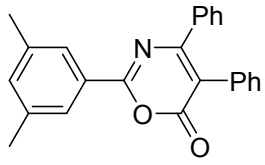


Compound 3g: Yield: 72 mg, 89%; A white solid; Mp: 173-175 ^{o}C;^{1}H NMR (400 MHz,

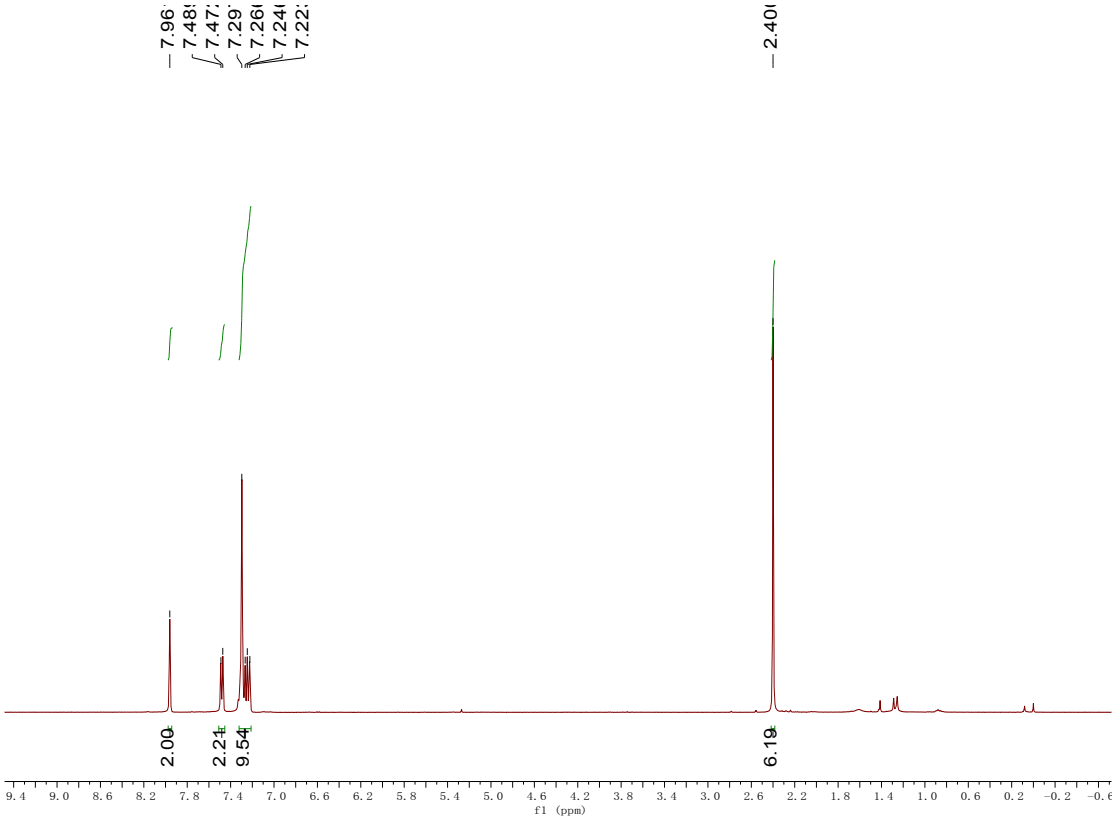
Chloroform-*d*) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.49-7.42 (m, 3H), 7.37-7.28 (m, 8H), 7.27-7.20 (m, 2H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.8, 160.6, 158.5, 139.8, 136.2, 132.5, 132.2, 130.6, 130.4, 130.1, 129.9, 129.1, 128.4, 128.2, 127.9, 126.2, 117.9, 22.8; IR (neat): ν 3057, 1740, 1607, 1598, 1298, 773, 690 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{18}NO_2$ $[M+H]^+$: 340.1332, found: 340.1326.

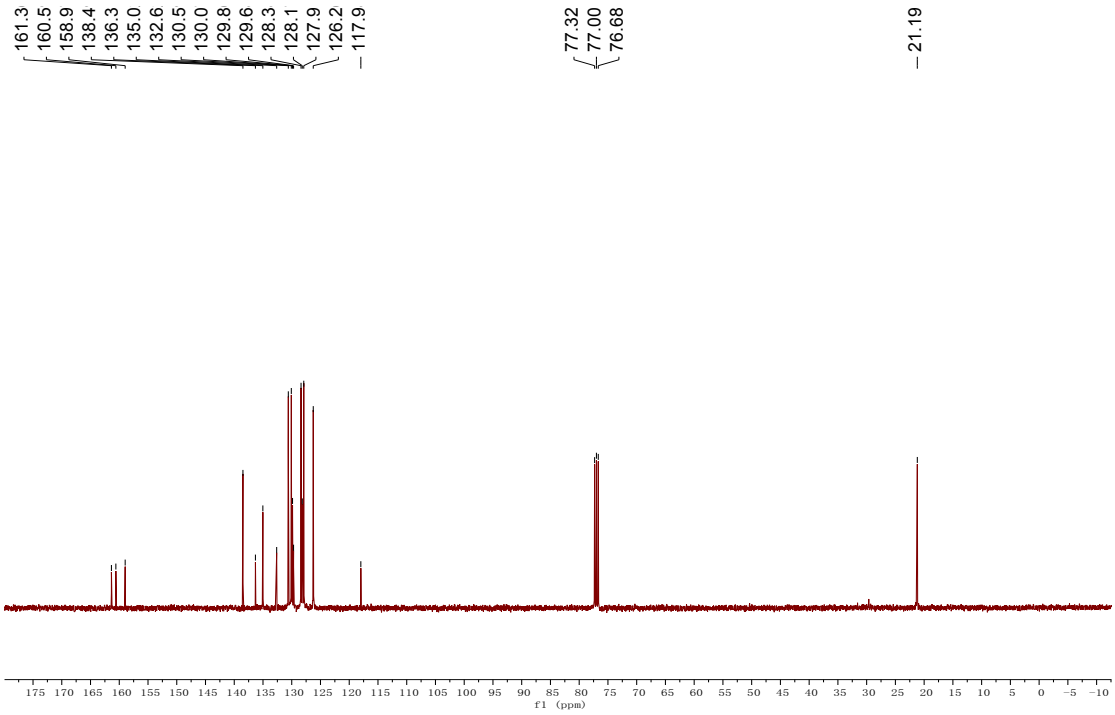


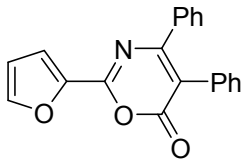




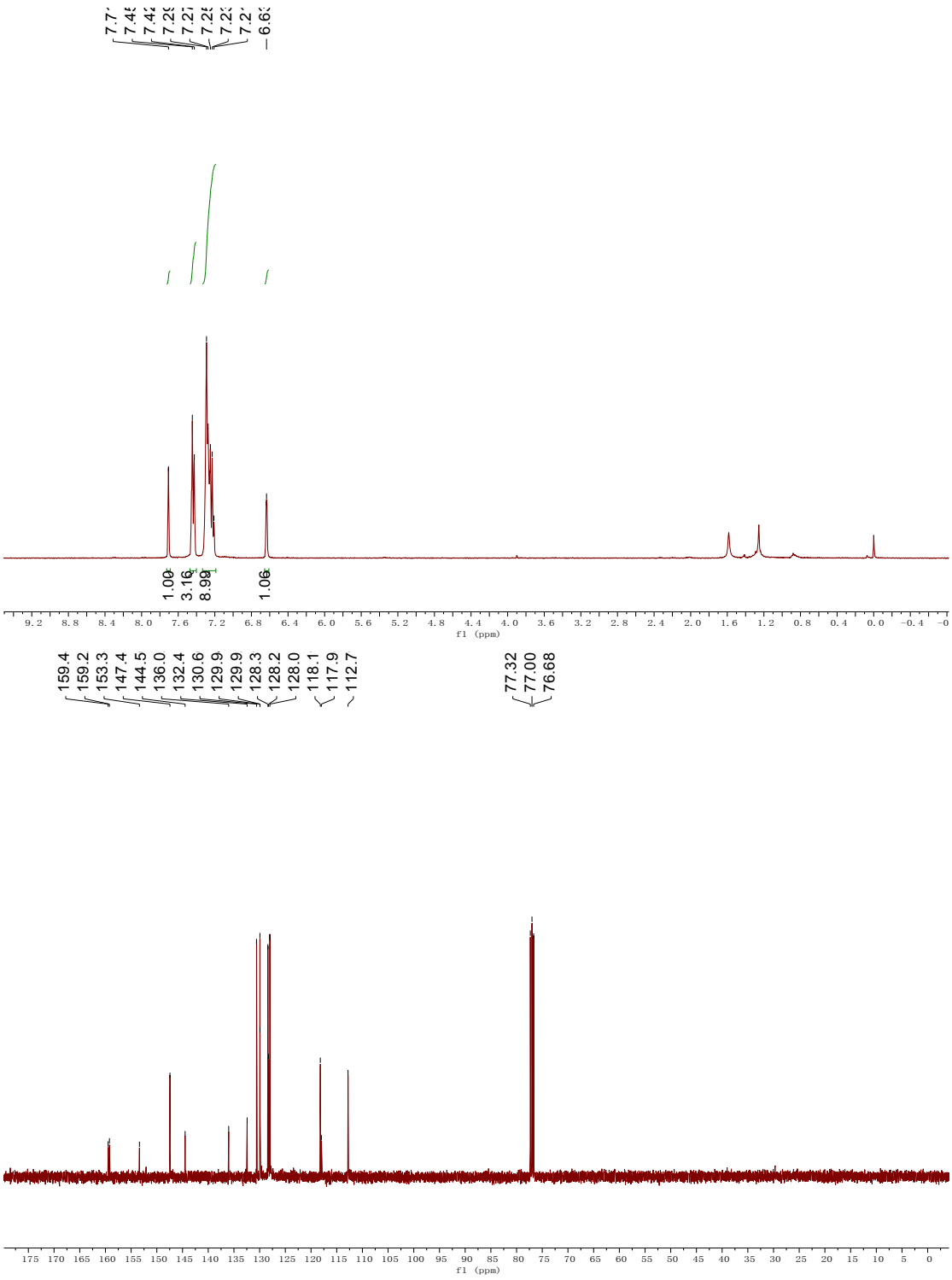
Compound 3h: Yield: 35 mg, 50%; A white solid; Mp: 216-218 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 2H), 7.51-7.46 (m, 2H), 7.34-7.21 (m, 9H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4, 160.6, 159.0, 138.5, 136.3, 135.0, 132.6, 130.6, 130.1, 129.9, 129.7, 128.4, 128.2, 127.9, 126.3, 118.0, 21.2; IR (neat): ν 2915, 1736, 1611, 1589, 1574, 1536, 798, 781, 770, 698 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{20}NO_2$ $[M+H]^+$: 354.1489, found: 354.1481.

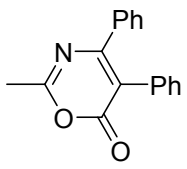






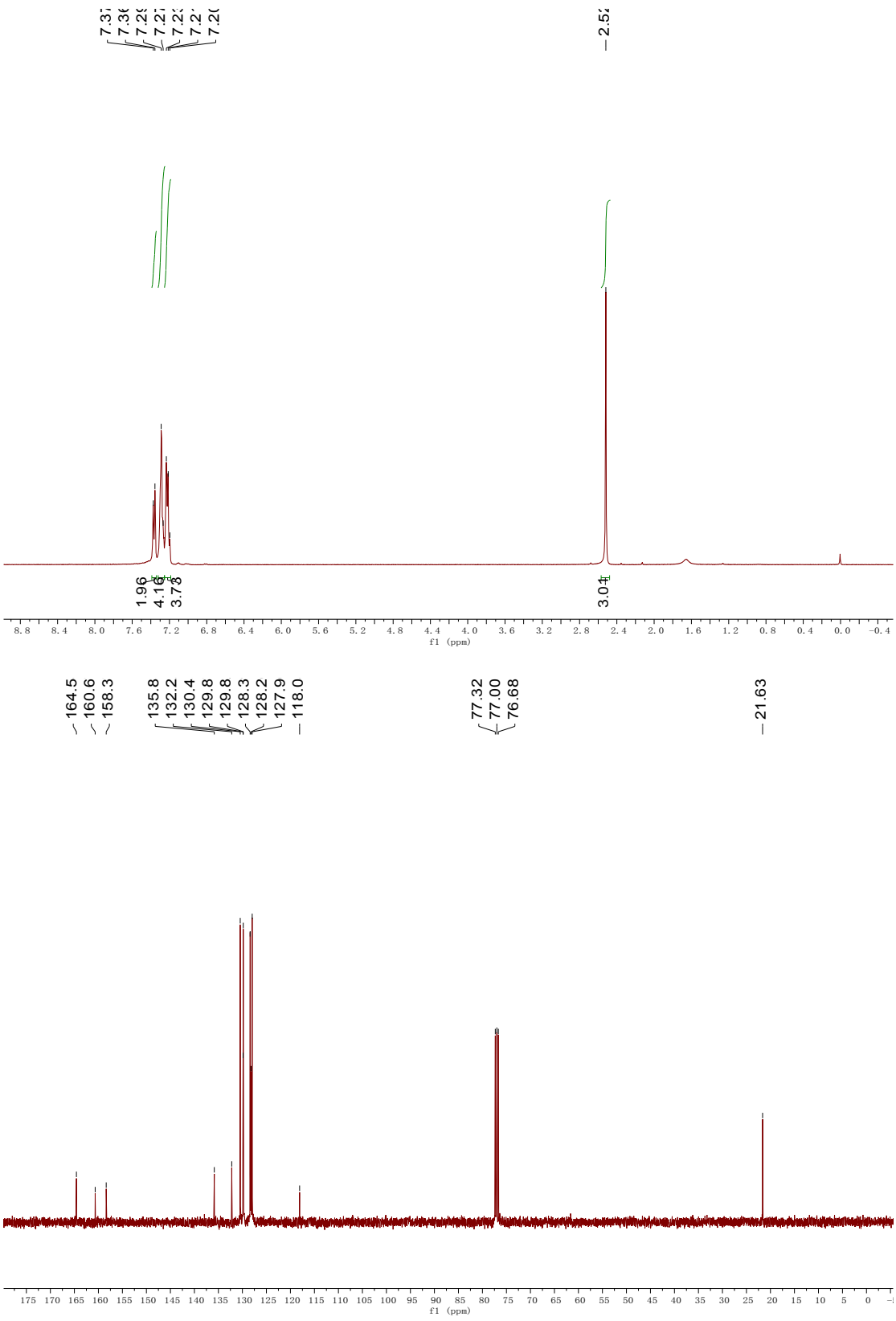
Compound 3i: Yield: 40 mg, 65%; A white solid; Mp: 192-194 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.47-7.40 (m, 3H), 7.33-7.18 (m, 8H), 6.67-6.60 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.5, 159.2, 153.4, 147.5, 144.5, 136.0, 132.4, 130.6, 129.94, 129.92, 128.4, 128.3, 128.0, 118.2, 118.0, 112.8; IR (neat): ν 1732, 1621, 1533, 766, 724 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{14}NO_3$ $[M+H]^+$: 316.0968, found: 316.0962.

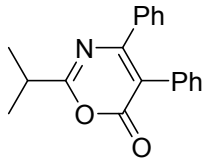




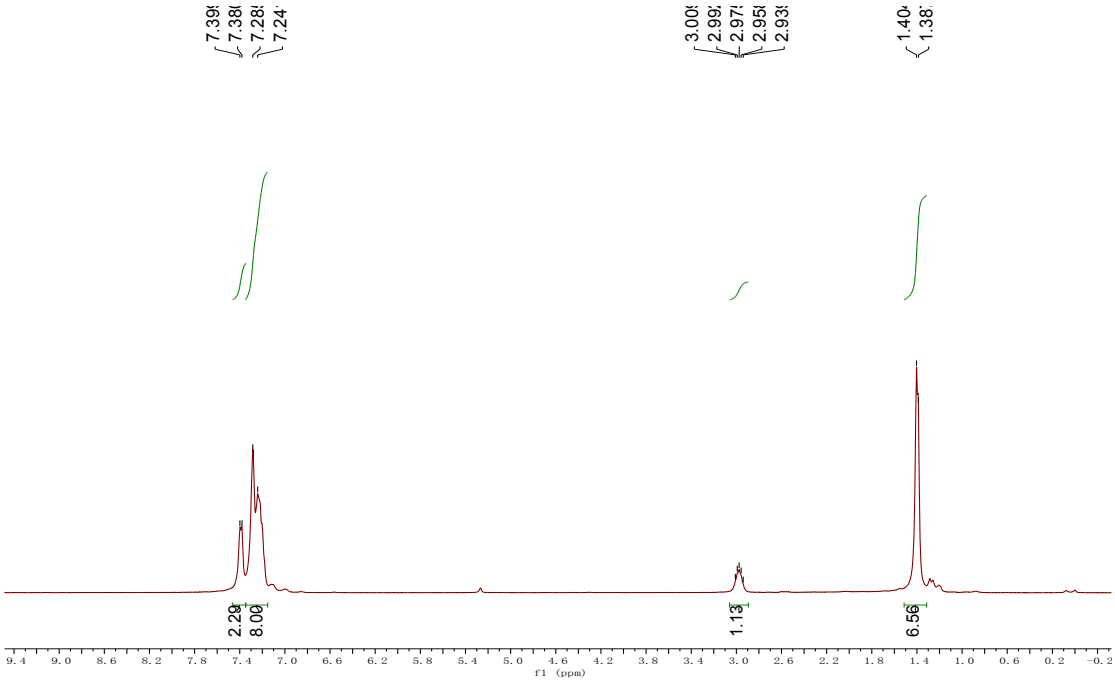
Compound 3j: Yield: 49 mg, 91%; A white solid; Mp: 184-186 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39-7.34 (m, 2H), 7.32-7.25 (m, 4H), 7.25-7.19 (m, 4H), 2.52 (s, 3H); ^{13}C NMR

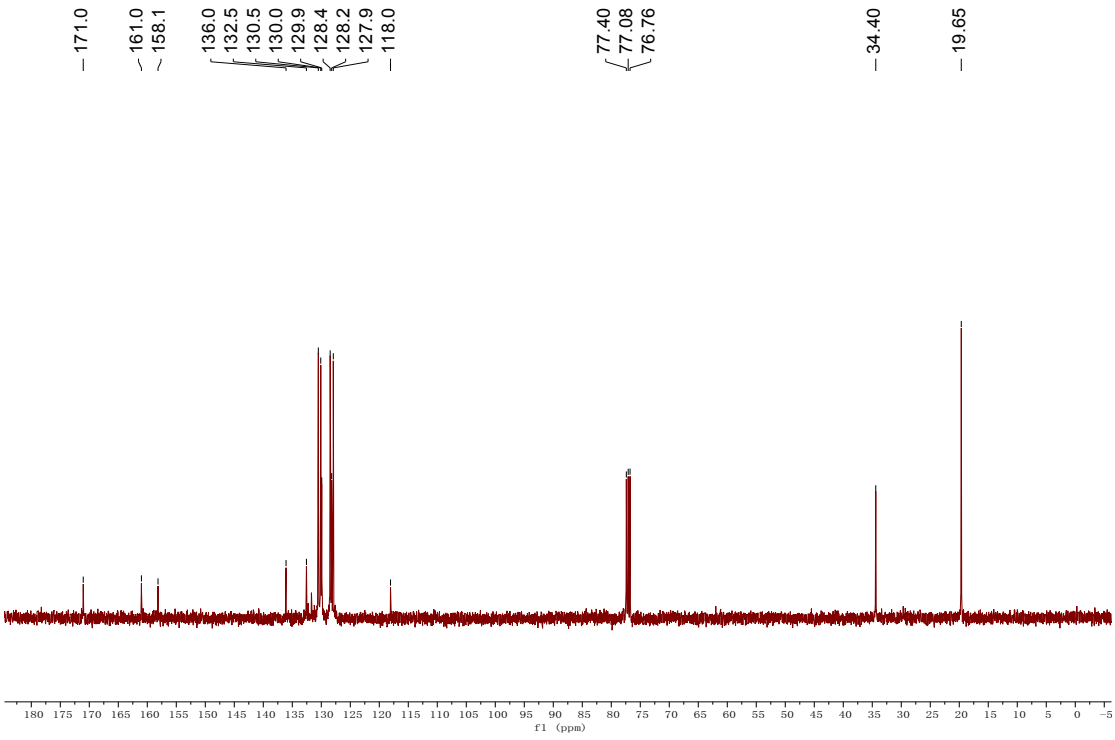
(100 MHz, Chloroform-*d*) δ 164.6, 160.7, 158.4, 135.9, 132.2, 130.5, 129.9, 129.8, 128.4, 128.2, 128.0, 118.1, 21.6; IR (neat): ν 2920, 2845, 1677, 1585, 1178, 1123, 705, 697, 683 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{14}NO_2$ $[M+H]^+$: 264.1019, found: 264.1016.

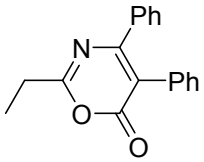




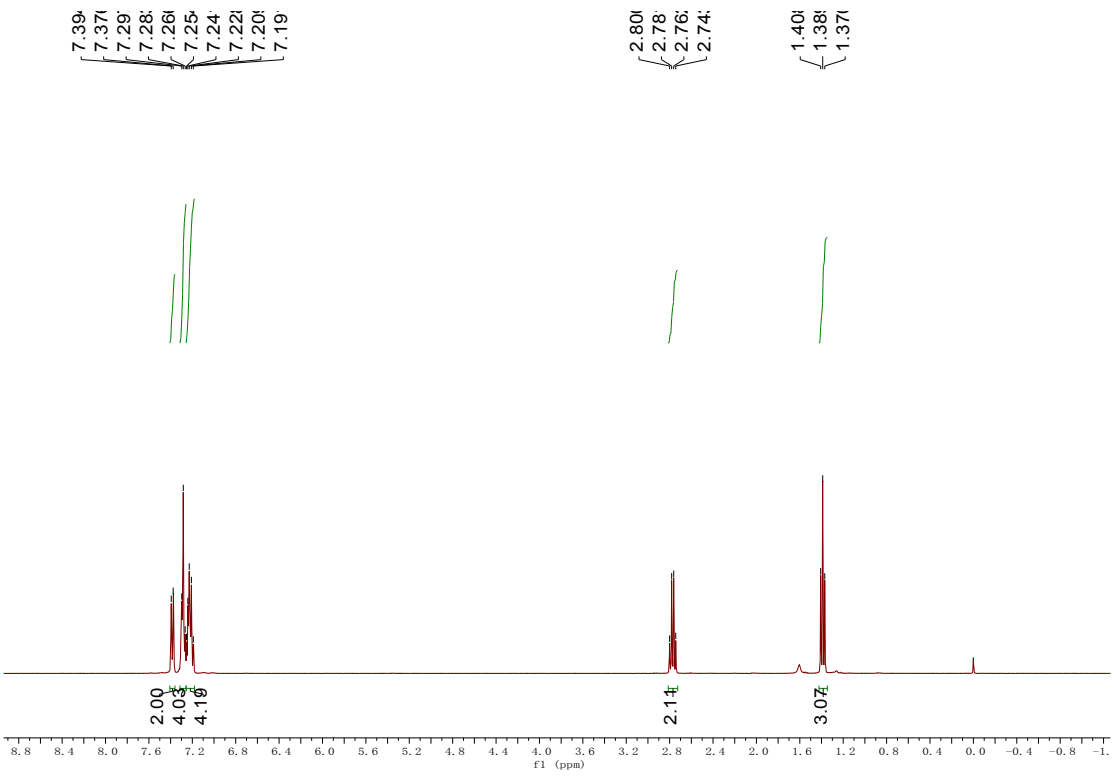
Compound 3k: Yield: 38 mg, 91%; A white solid; Mp: 151-153 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.35-7.15 (m, 8H), 3.06-2.89 (m, 1H), 1.40 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.0, 161.0, 158.2, 136.1, 132.6, 130.5, 130.1, 129.9, 128.5, 128.2, 127.9, 118.1, 34.4, 19.7; IR (neat): ν 2966, 1730, 1618, 1556, 774, 695 cm^{-1}; HRMS (ESI) Calcd. for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332, found:292.1328.

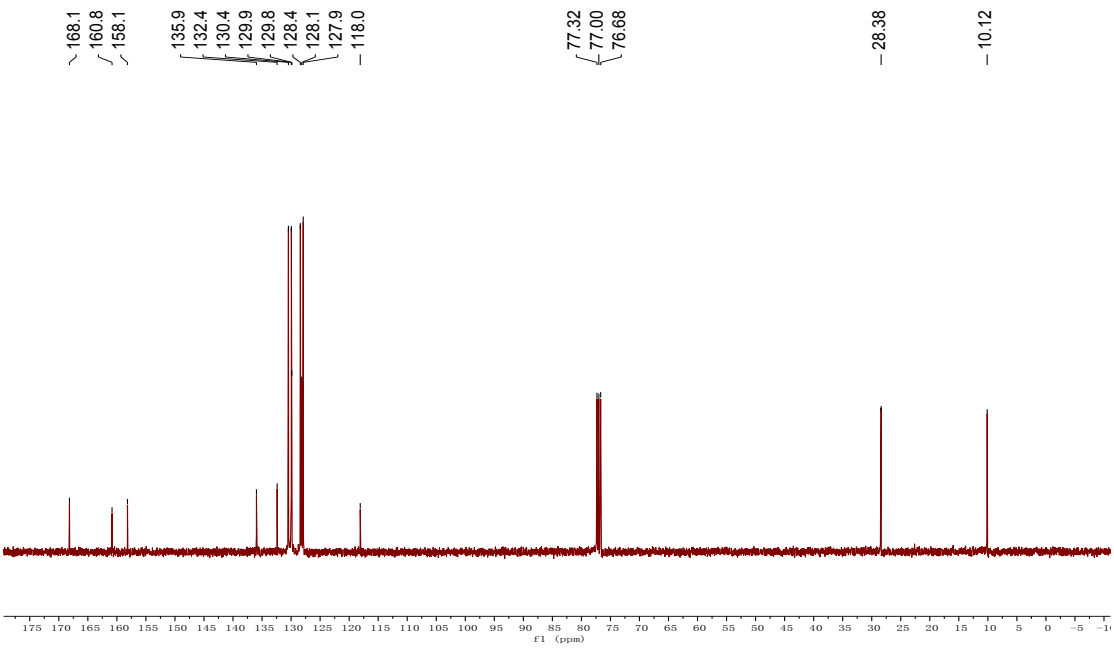


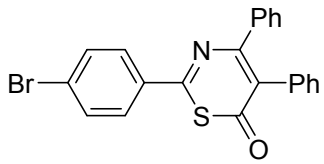




Compound 3l: Yield: 50 mg, 91%; A white solid; Mp: 148-151 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.36 (m, 2H), 7.31-7.26 (m, 4H), 7.26-7.18 (m, 4H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.39 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.2, 160.8, 158.2, 136.0, 132.4, 130.5, 129.95, 129.87, 128.4, 128.2, 127.9, 118.1 , 28.4, 10.1; IR (neat): ν 1678, 1591, 1503, 1218, 1121, 779, 692 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{16}NO_2$ $[M+H]^+$: 278.1176, found: 278.1171.

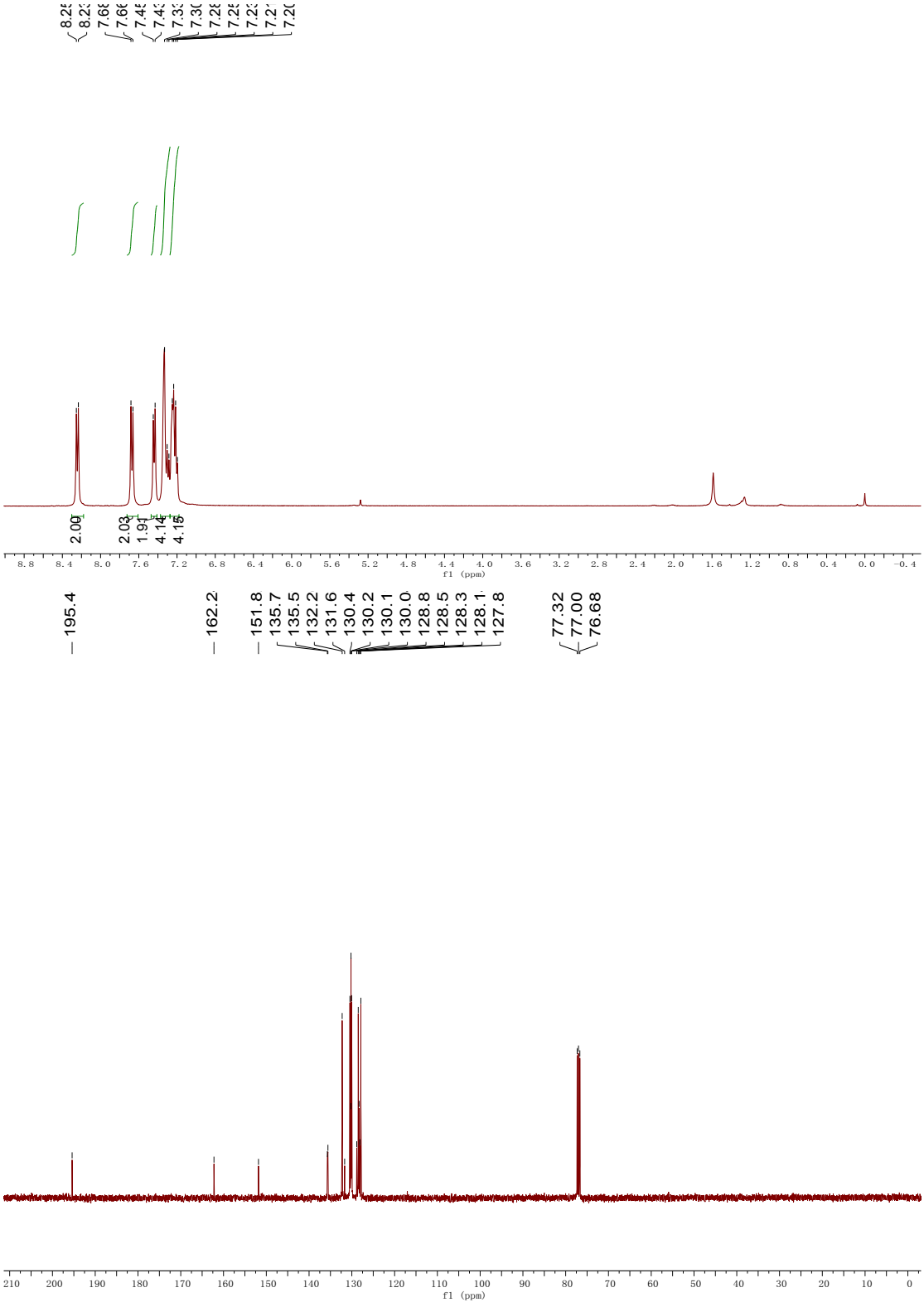


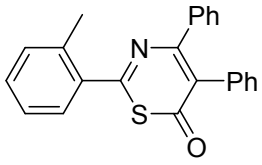




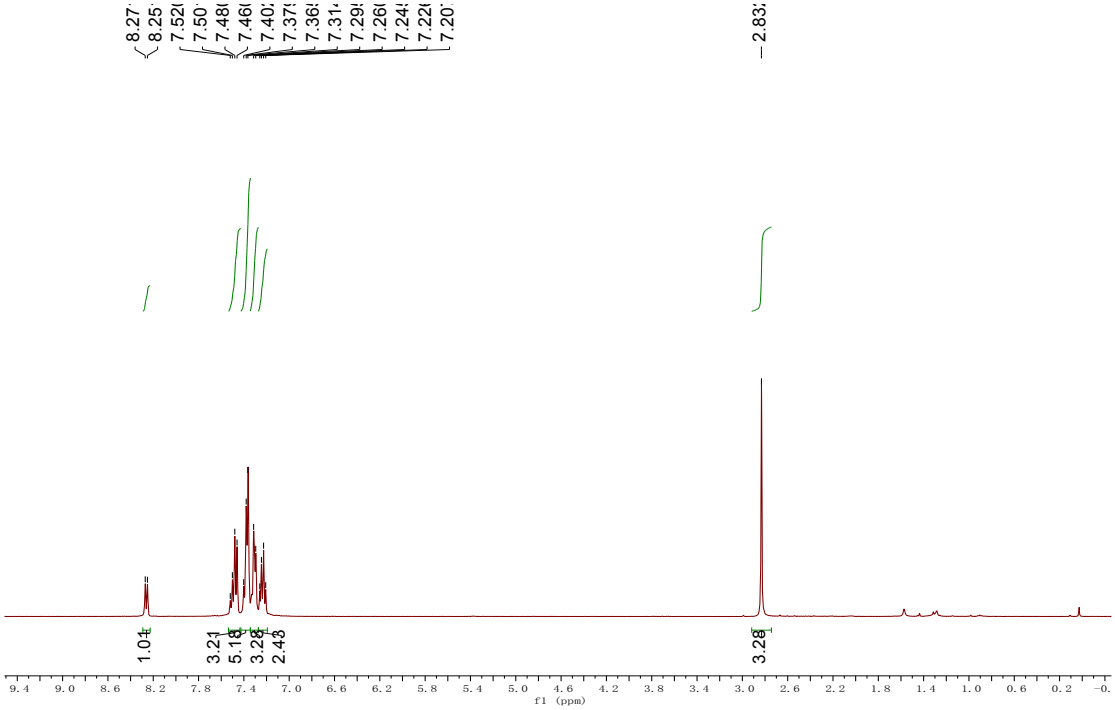
Compound 5a: Yield: 79 mg, 92%; A red solid; Mp: 179-181 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.37-7.27 (m, 4H), 7.27-7.18 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.4,162.2, 151.8, 135.7,

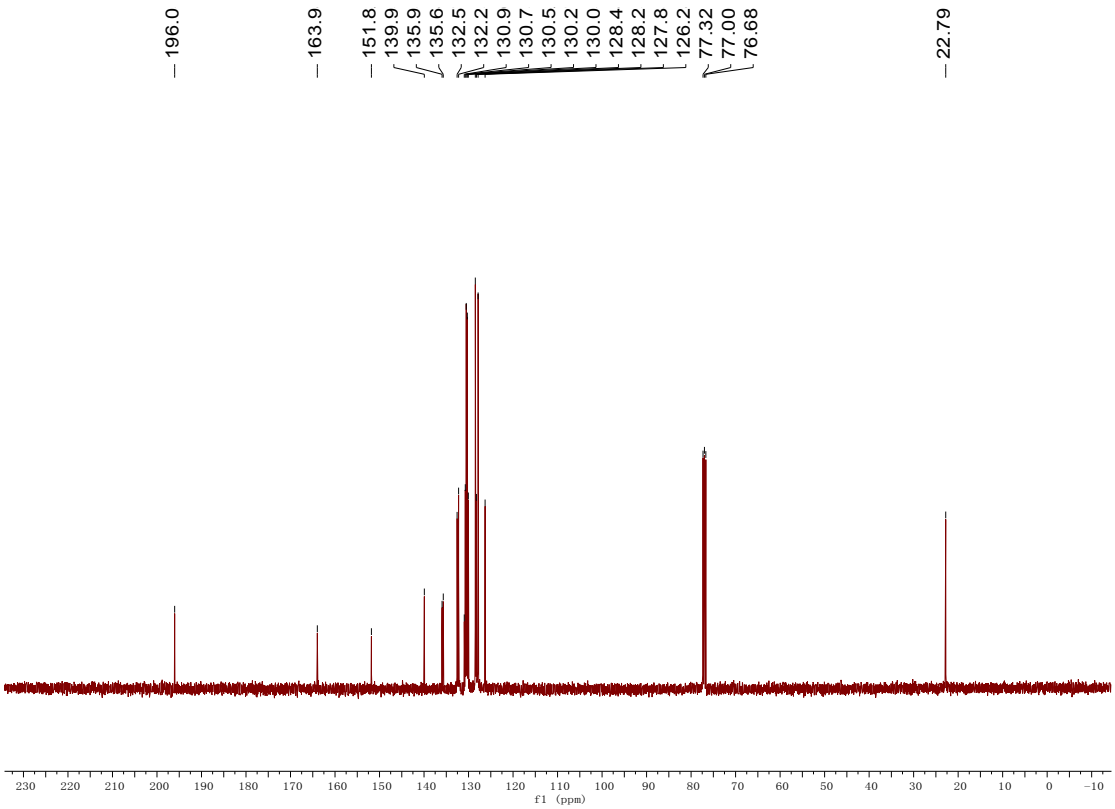
135.6, 132.3, 131.7, 130.5, 130.21, 130.19, 130.1, 128.9, 128.5, 128.3, 128.1, 127.9; IR (neat): ν 2920, 2848, 1592, 1473, 1291, 1275, 1123, 1104, 720, 695, 671 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{15}BrNOS$ $[M+H]^+$: 420.0052, found: 420.0053.

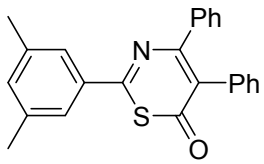




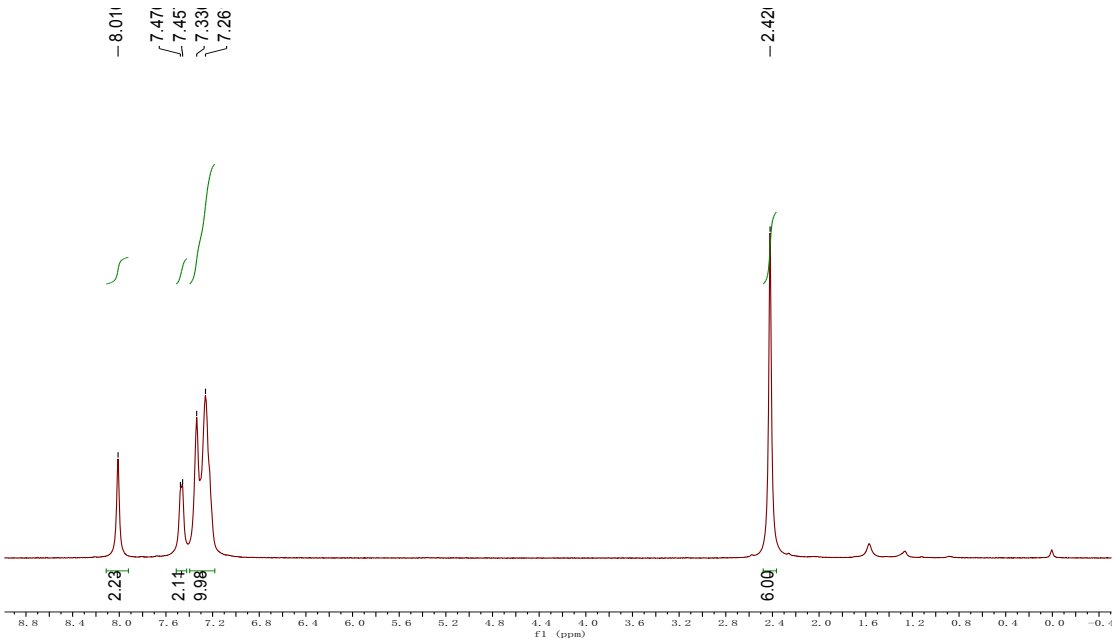
Compound 5b: Yield: 62 mg, 89%; A white solid; Mp: 183-184 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.54-7.44 (m, 3H), 7.43-7.34 (m, 5H), 7.34-7.27 (m, 3H), 7.27-7.19 (m, 2H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.0, 164.0, 151.8, 139.9, 136.0, 135.7, 132.6, 132.2, 131.0, 130.7, 130.5, 130.3, 130.1, 128.5, 128.2, 127.9, 126.3, 22.8; IR (neat): ν 2922, 1584, 1557, 1476, 1281, 1260, 760, 721, 741, 721, 694 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{18}NOS$ $[M+H]^{+}$: 356.1104, found: 356.1101.

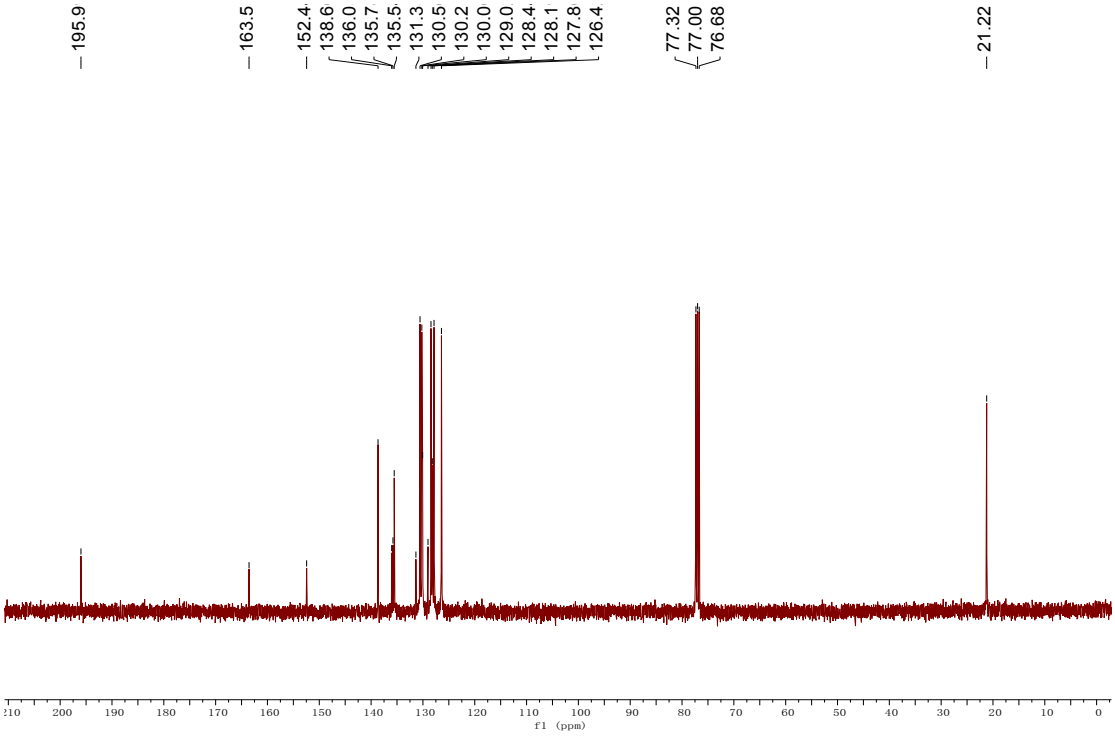


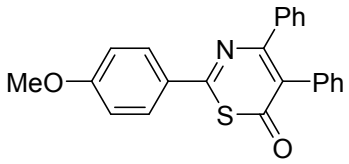




Compound 5c: Yield: 60 mg, 90%; A white solid; Mp: 150-151 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.40-7.18 (m, 9H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.1, 163.6, 152.4, 138.7, 136.1, 135.8, 135.6, 131.4, 130.6, 130.3, 130.1, 129.1, 128.5, 128.3, 127.9, 126.5, 21.3; IR (neat): ν 2912, 1609, 1586, 1573, 1474, 1281, 1270, 1115, 782, 768, 745, 703 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{20}NOS$ $[M+H]^{+}$: 370,1260, found: 370.1259.

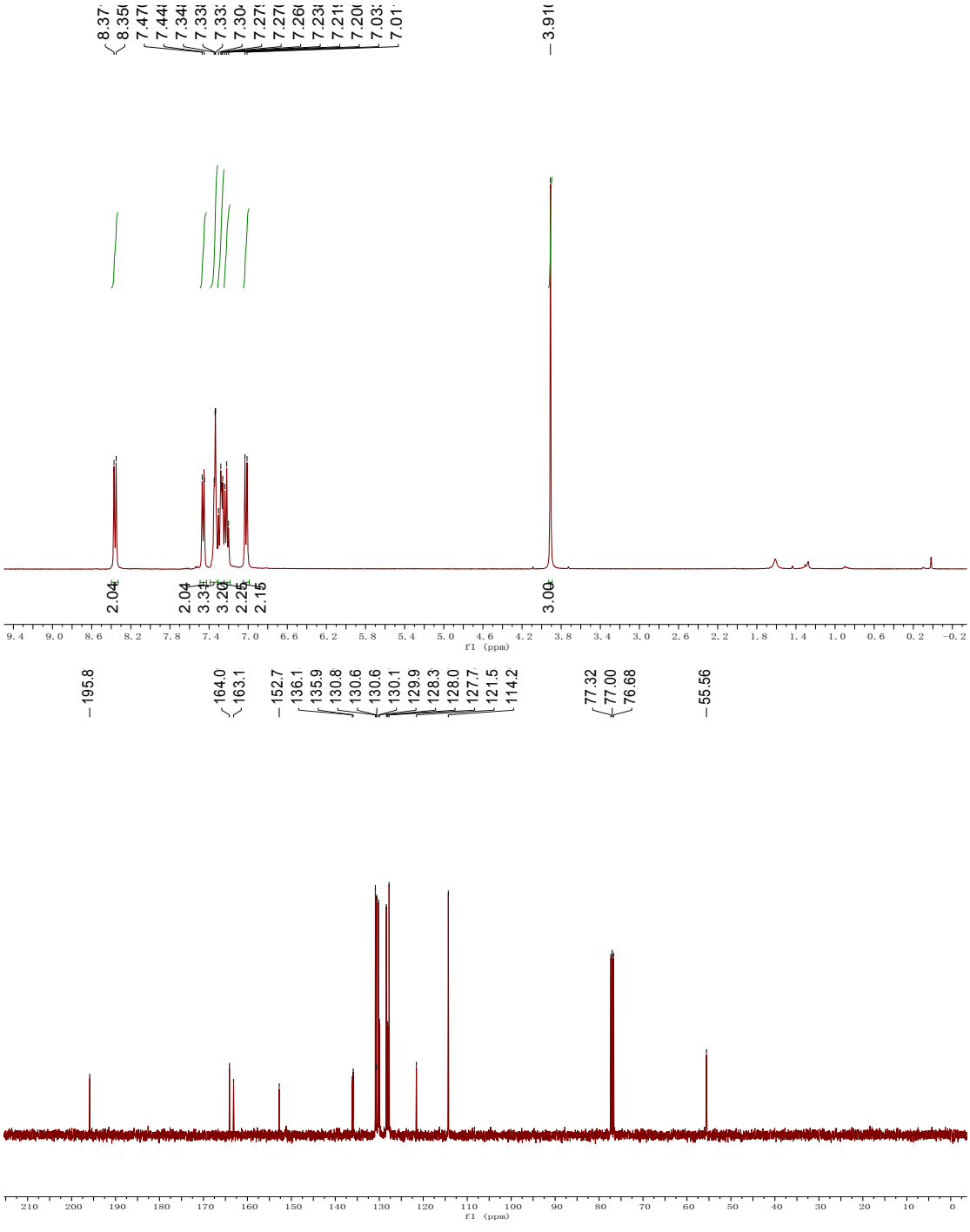


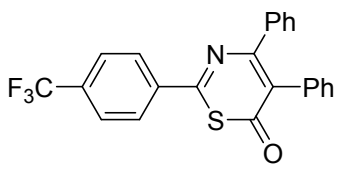




Compound 5d: Yield: 60 mg, 85%; A white solid; Mp: 156-158 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.39-7.31 (m, 3H), 7.31-7.25 (m, 3H), 7.25-7.19 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.9, 164.1, 163.2, 152.8, 136.2, 135.9, 130.9, 130.7, 130.6, 130.2, 130.0, 128.4,

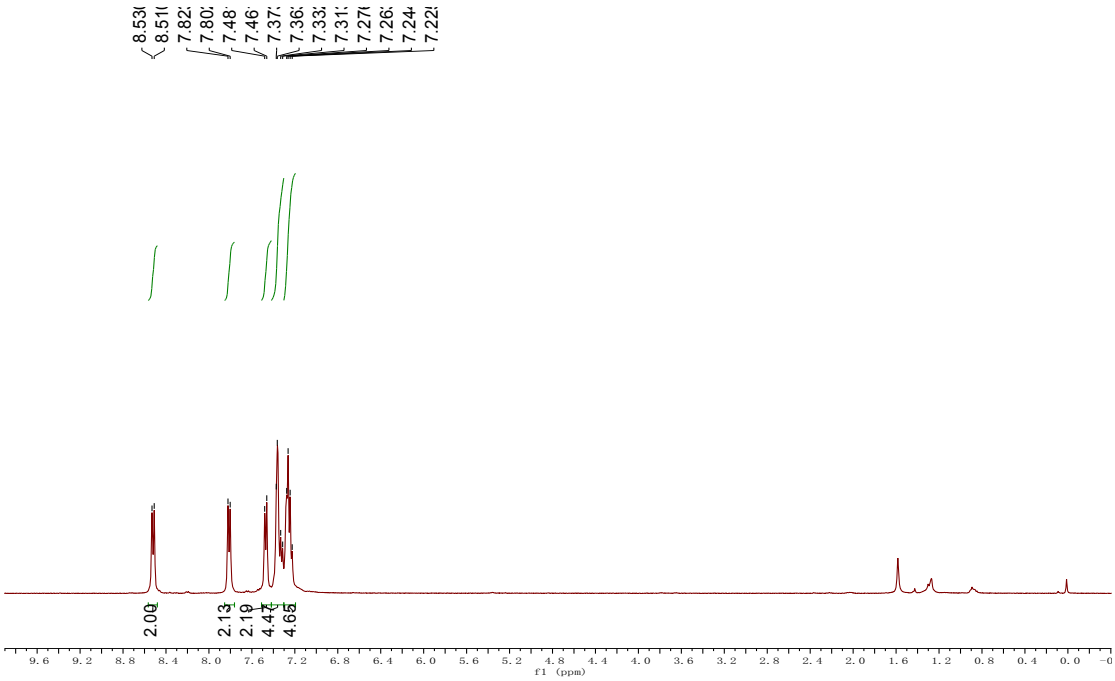
128.1, 127.8, 121.6, 114.3, 55.6; IR (neat): ν 2921, 2848, 1590, 1472, 1444, 1284, 1260, 1123, 1113, 730, 696 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{18}NO_2S$ $[M+H]^+$: 372.1053, found: 372.1049.

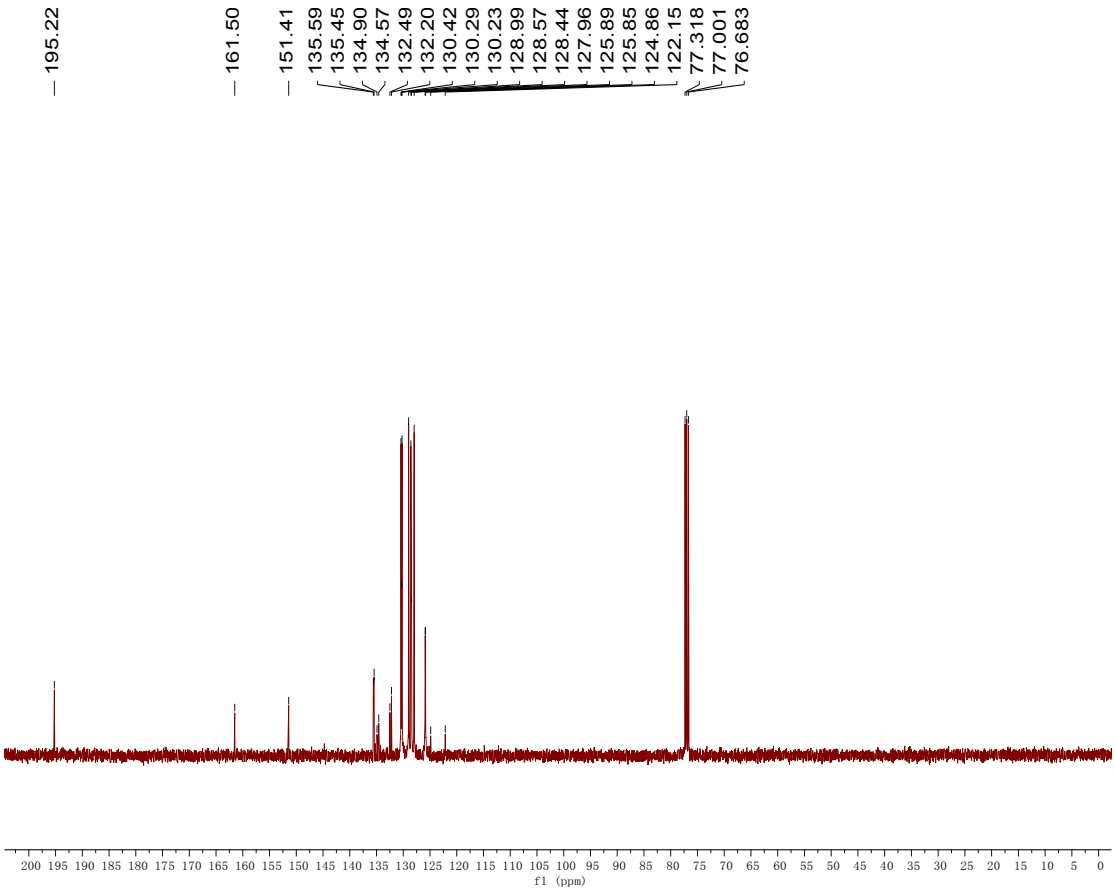


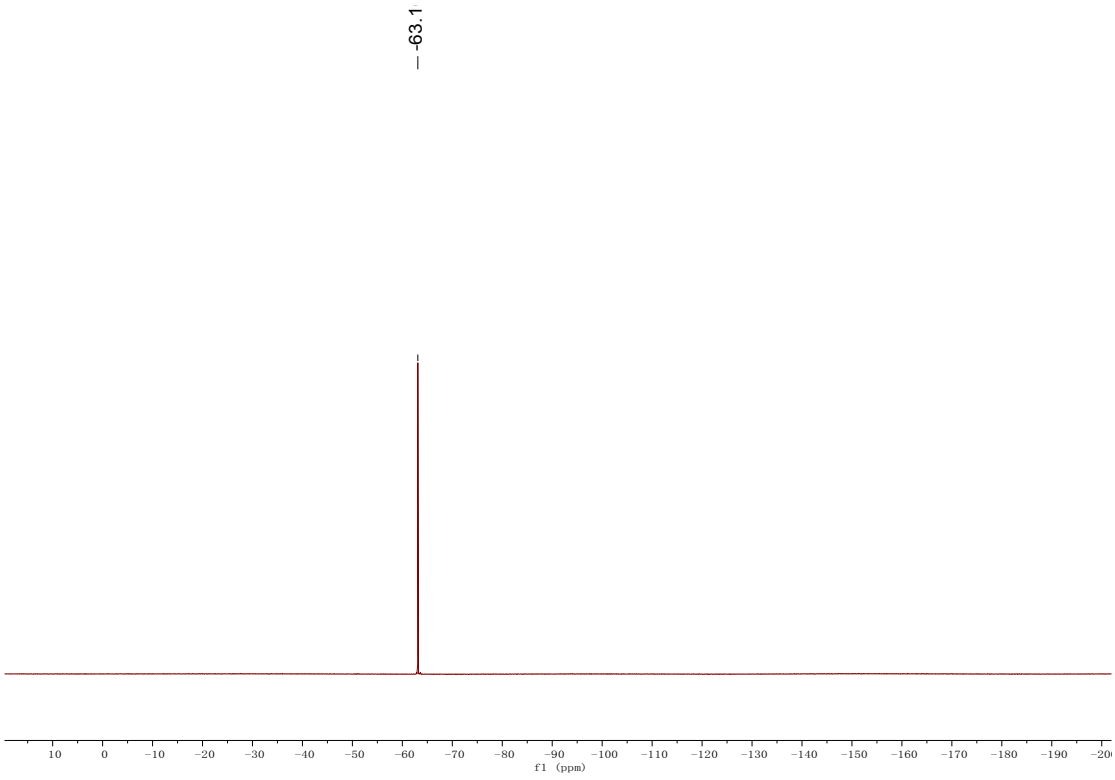


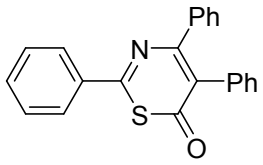
Compound 5e: Yield: 50 mg, 65%; A white solid; Mp: 127-129 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.42-

7.30 (m, 4H), 7.30-7.19 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.2, 161.5, 151.4, 135.6, 135.5, 134.7 (q, *J* = 32.5 Hz), 132.5, 132.2, 130.4, 130.3, 130.2, 129.0, 128.6, 128.4, 128.0, 125.9 (q, *J* = 3.8 Hz), 125.4 (q, *J* = 271.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -63.1; IR (neat): ν 2921, 2850, 1610, 1569, 1327, 1311, 1297, 1157, 1110, 739, 695, 679 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{15}F_3NOS$ $[M+H]^+$: 410.0821, found: 410.0820.

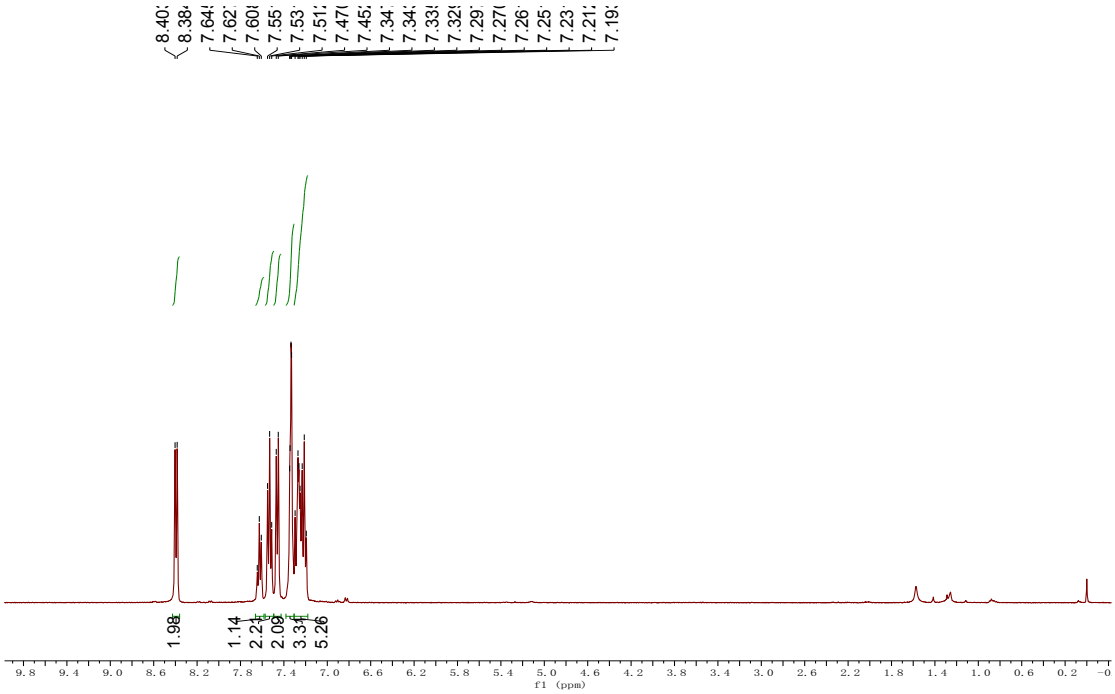


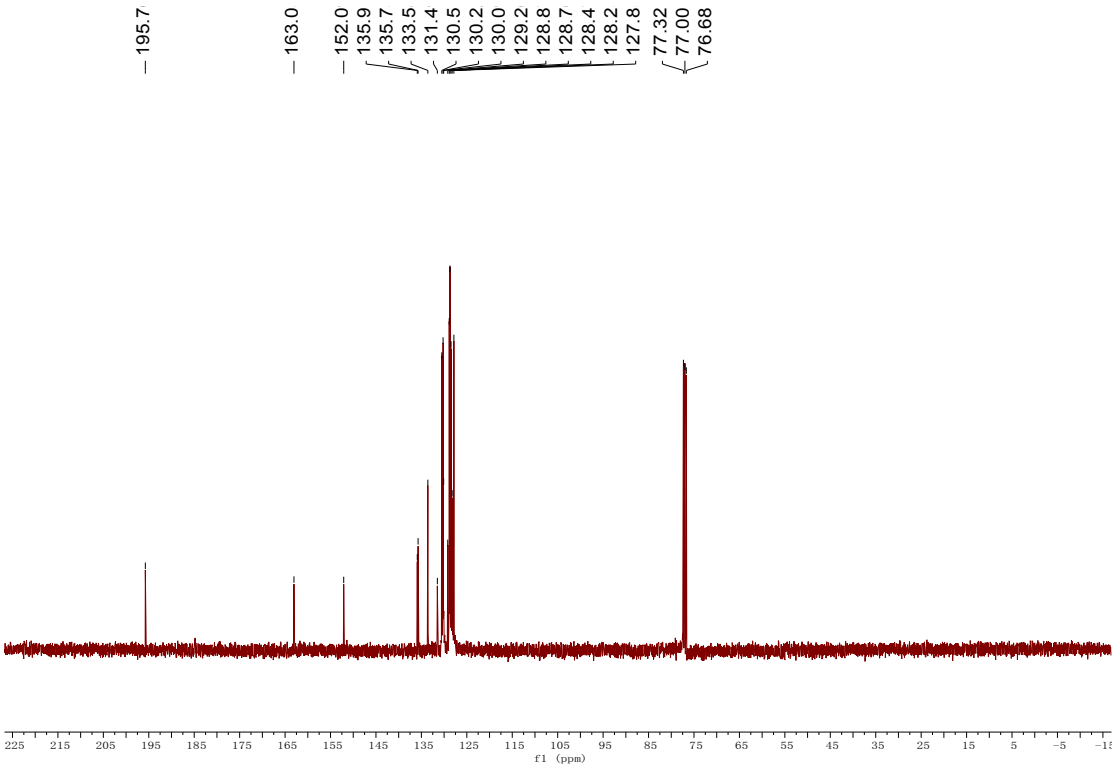

195.22
161.50
151.41
135.59
135.45
134.90
134.57
132.49
132.20
130.42
130.29
130.23
128.99
128.57
128.44
127.96
125.89
125.85
124.86
122.15
77.318
77.001
76.683
f1 (ppm)

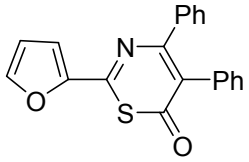

-63.1
f1 (ppm)



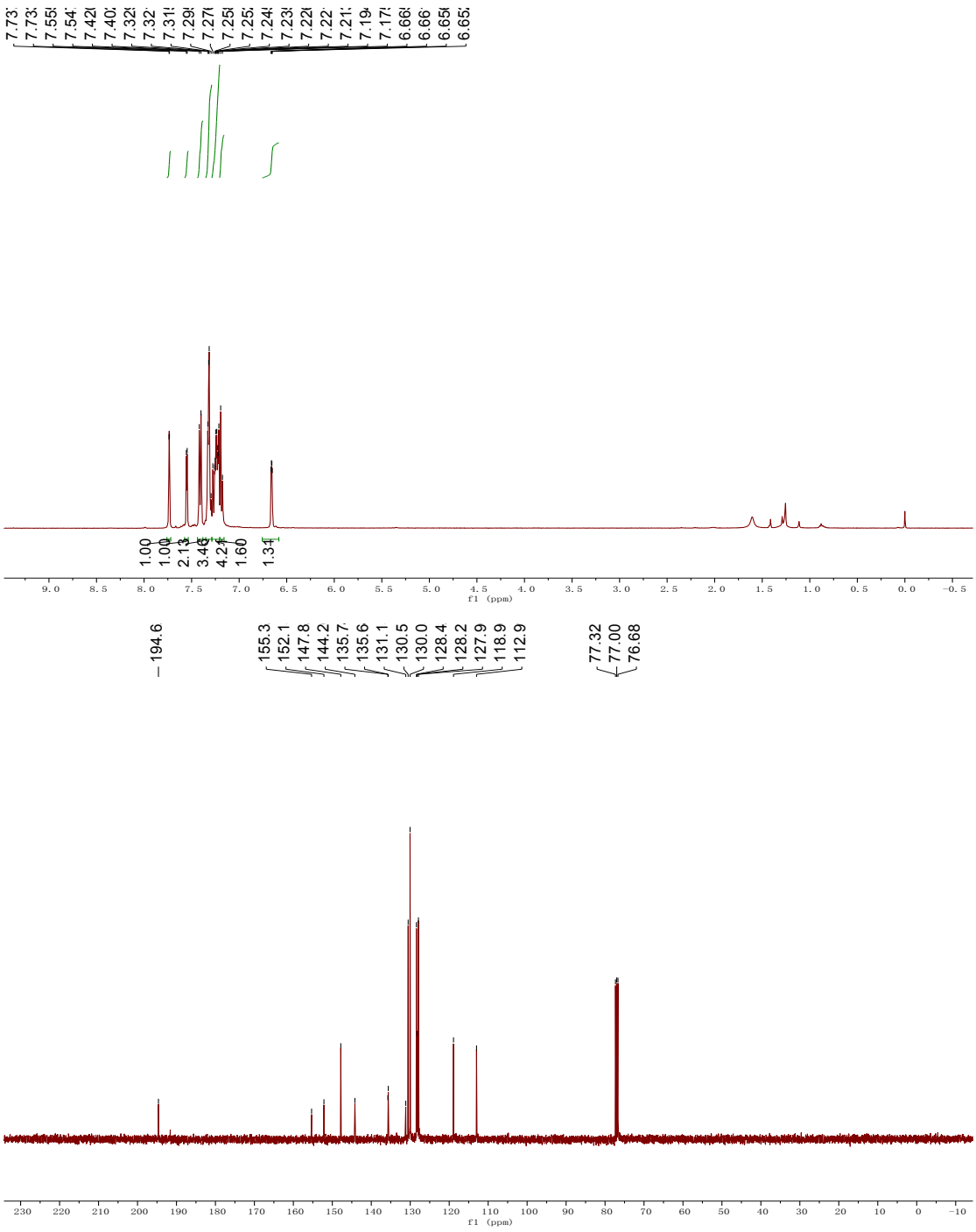
Compound 5f: Yield: 42 mg, 62%; a red solid; Mp: 120-122 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 7.6 Hz, 2H), 7.66-7.58 (m, 1H), 7.57-7.49 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.38-7.31 (m, 3H), 7.31-7.18 (m, 5H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.8, 163.1, 152.1, 135.9, 135.7, 133.6, 131.5, 130.5, 130.2, 130.1, 129.2, 128.9, 128.7, 128.5, 128.2, 127.9; IR (neat): ν 1629, 1584, 1560, 1443, 1251, 727, 698, 685 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{16}NOS$ $[M+H]^{+}$: 342.0947, found: 342.0943.

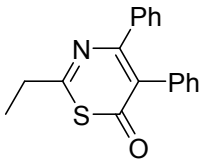






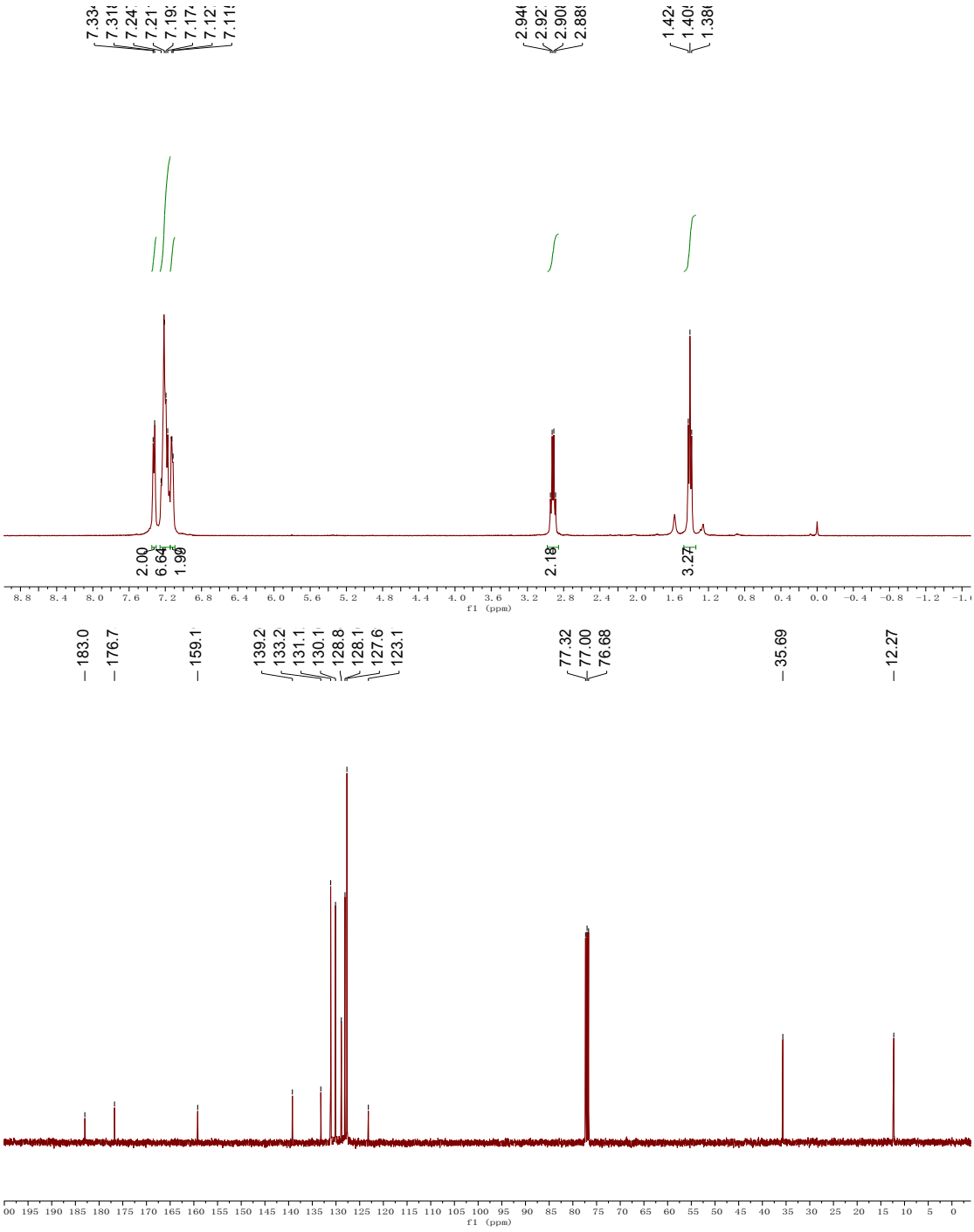
Compound 5g: Yield: 56 mg, 85%; a red solid; Mp: 129-131 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76-7.72 (m, 1H), 7.55 (d, *J* = 3.2 Hz, 1H), 7.44-7.38 (m, 2H), 7.35-7.29 (m, 3H), 7.29-7.20 (m, 3H), 7.20-7.16 (m, 2H), 6.76-6.58 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.6, 155.3, 152.2, 147.8, 144.2, 135.7, 135.6, 131.1, 130.5, 130.0, 128.4, 128.2, 127.9, 118.9, 113.0; IR (neat): ν 3101, 2922, 1669, 1598, 1472, 780, 757, 692 cm^{-1}; HRMS (ESI) Calcd. for $C_{20}H_{14}NO_2S$ $[M+H]^+$: 332.0740, found: 332.0737.

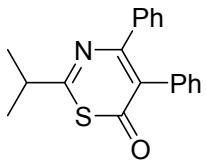




Compound 5h: Yield: 49 mg, 85%; a white solid; Mp: 120-122 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.30 (m, 2H), 7.26-7.15 (m, 6H), 7.15-7.09 (m, 2H), 2.92 (q, *J* = 7.6 Hz, 2H), 1.40 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.0, 176.8, 159.2, 139.2, 133.2, 131.2, 130.1, 128.9, 128.1, 127.7, 123.2, 35.7, 12.3; IR (neat): ν 3054, 2920, 2850, 1621, 1560,

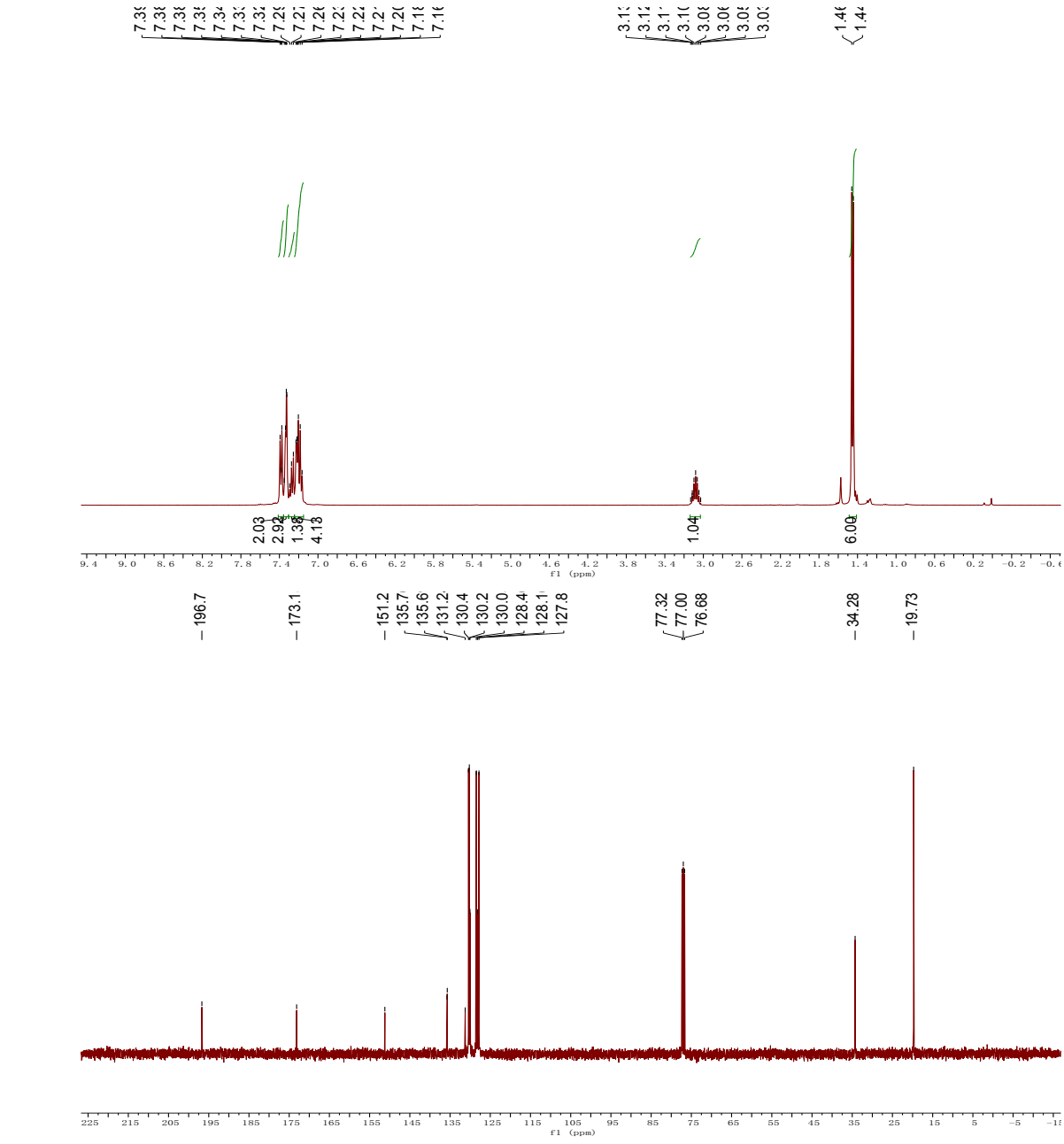
1519, 694 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{16}NOS$ $[M+H]^+$: 294.0947, found: 294.0943.





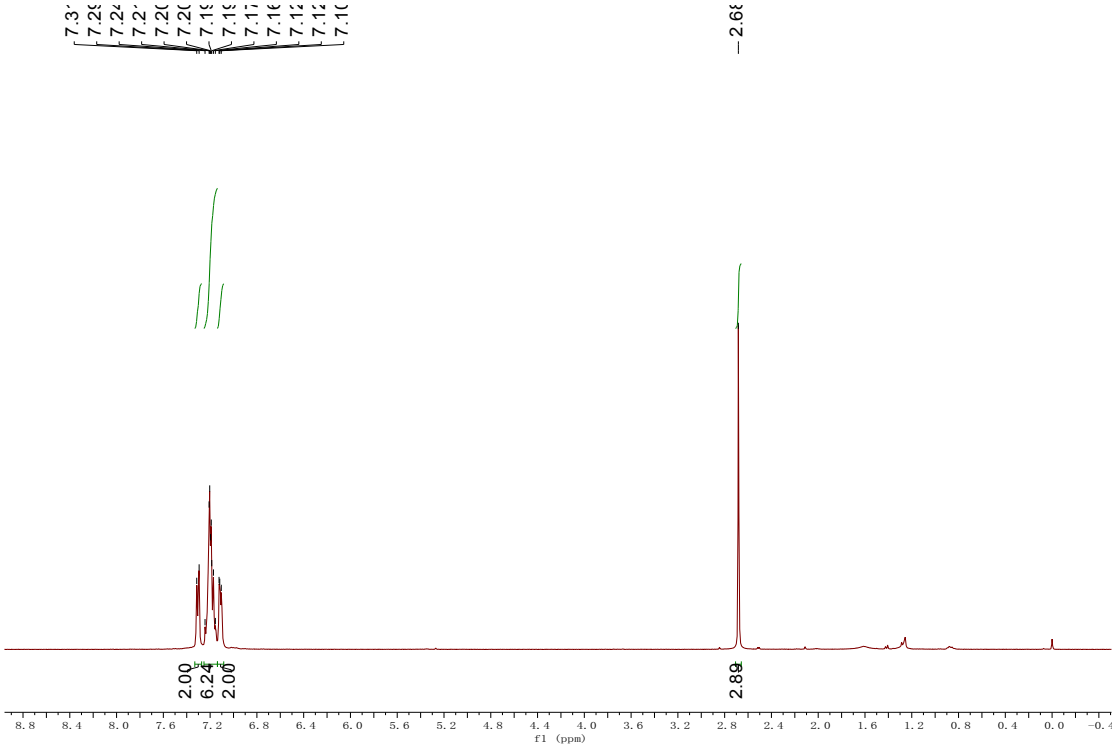
Compound 5i: Yield: 58 mg, 91%; a red solid; Mp: 137-138 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.36 (m, 2H), 7.36-7.31 (m, 3H), 7.30-7.24 (m, 1H), 7.24-7.15 (m, 4H), 3.14-3.03 (m, 1H), 1.46 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-d) δ 196.7, 173.2, 151.2, 135.8,

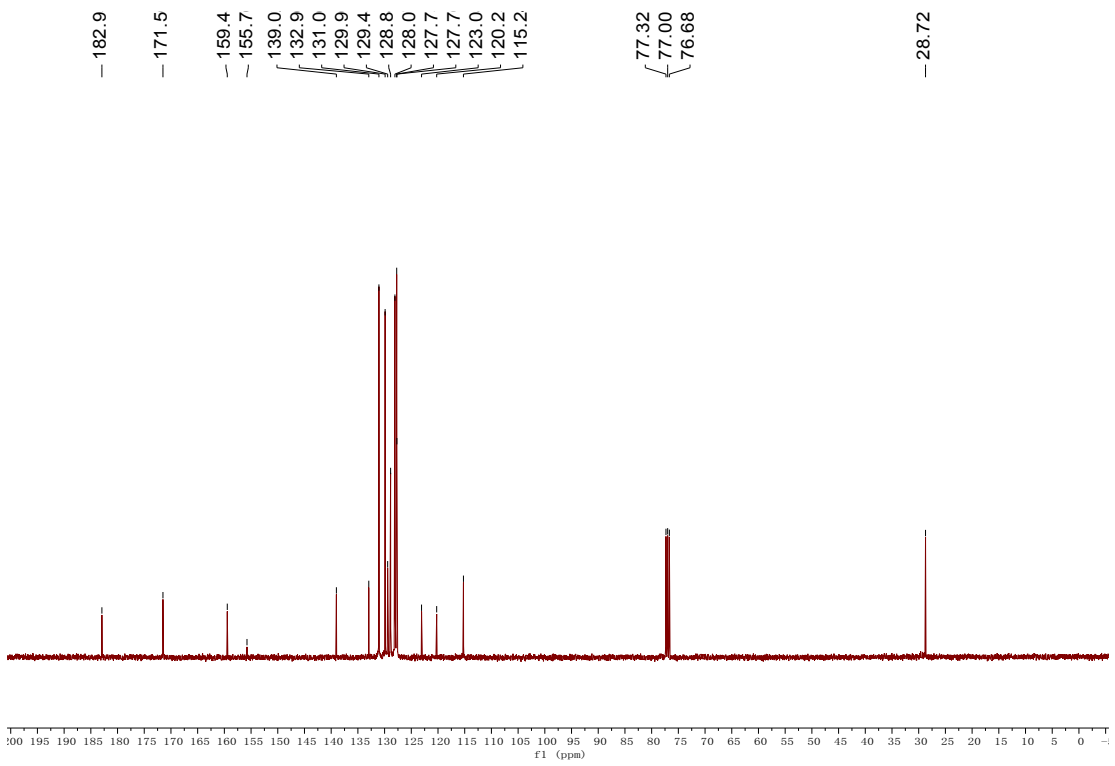
135.7, 131.2, 130.4, 130.2, 130.1, 128.5, 128.2, 127.8, 34.3, 19.7; IR (neat): ν 2920, 2845, 1615, 1524, 1479, 1284, 1095, 766, 691 cm^{-1}; HRMS (ESI) Calcd. for $C_{19}H_{18}NOS$ $[M+H]^+$: 308.1104, found: 308.1100.

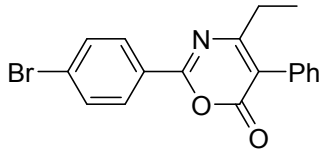


Compound 5j: Yield: 79 mg, 94%; A white solid; Mp: 179-181 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.27 (m, 2H), 7.25-7.14 (m, 6H), 7.14-7.08 (m, 2H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.9, 171.5, 159.5, 155.8, 139.0, 133.0, 131.1, 129.9, 129.4, 128.9,

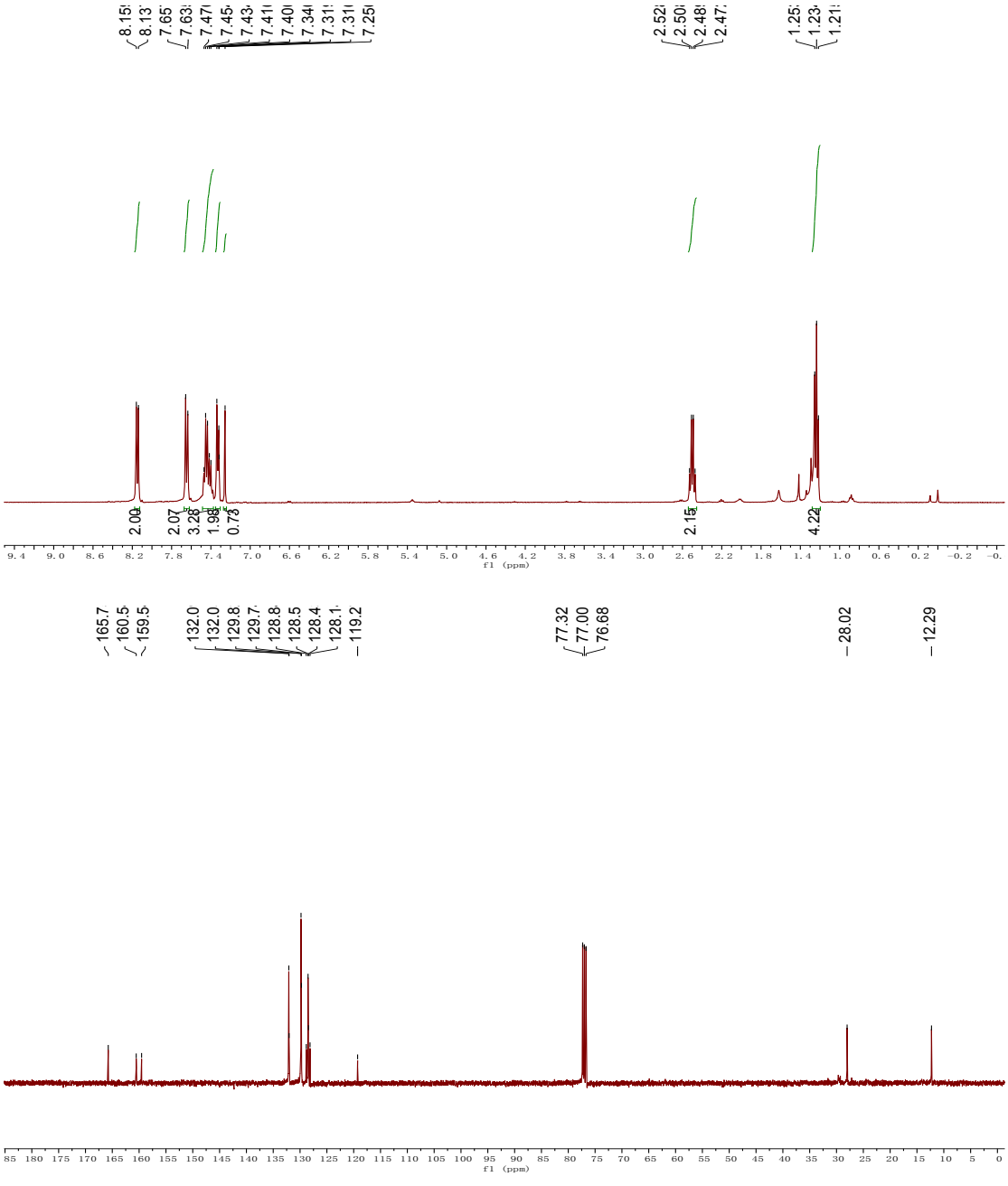
128.1, 127.73, 127.70, 123.1, 120.3, 115.2, 28.7; IR (neat): ν 3054, 1621, 1580, 1561, 1442, 724, 694 cm^{-1}; HRMS (ESI) Calcd. for: $C_{17}H_{14}NOS$ $[M+H]^+$: 280.0791, found: 280.0786.

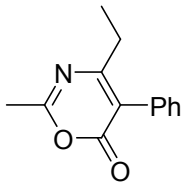




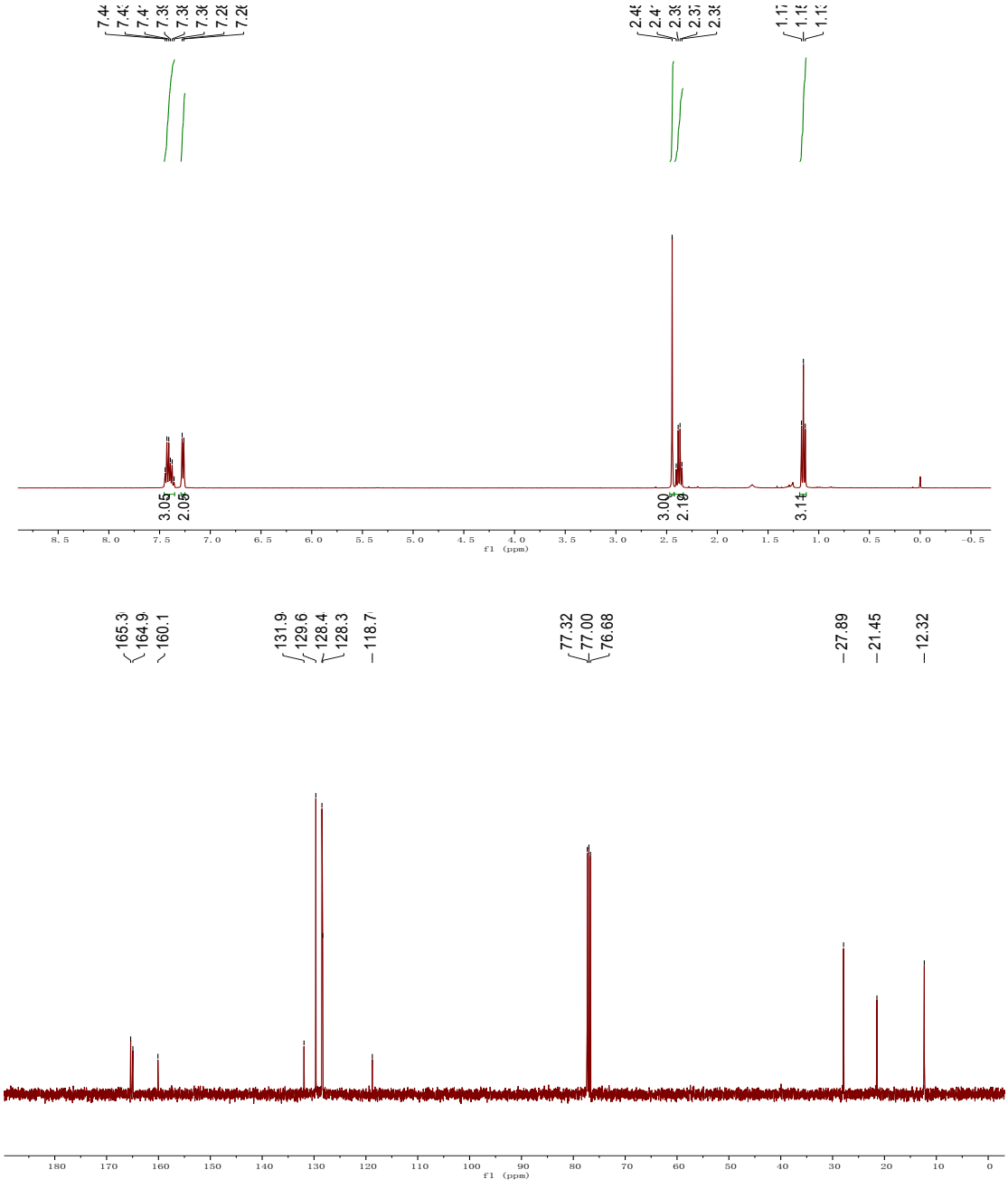


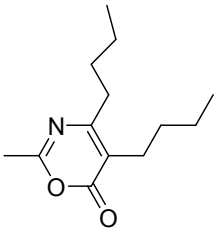
Compound 6ab: Yield: 50 mg, 71%; A white solid; Mp: 127-129 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.49-7.37 (m, 3H), 7.35-7.31 (m, 2H), 2.50 (q, *J* = 7.6Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.8, 160.5, 159.5, 132.09, 132.05, 129.8, 129.7, 128.8, 128.5, 128.4, 128.1, 119.3, 28.0, 12.3; IR (neat): ν 2919, 2848, 1741, 1617, 1599, 801, 787, 700 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{15}BrNO_2$ $[M+H]^+$: 356.0281, found: 356.0277.



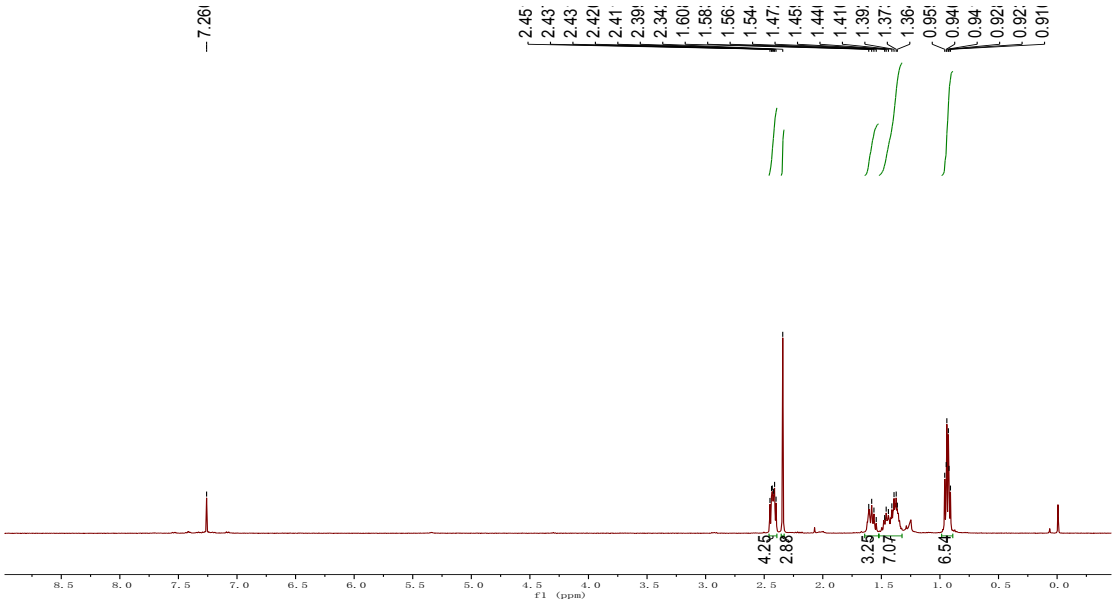


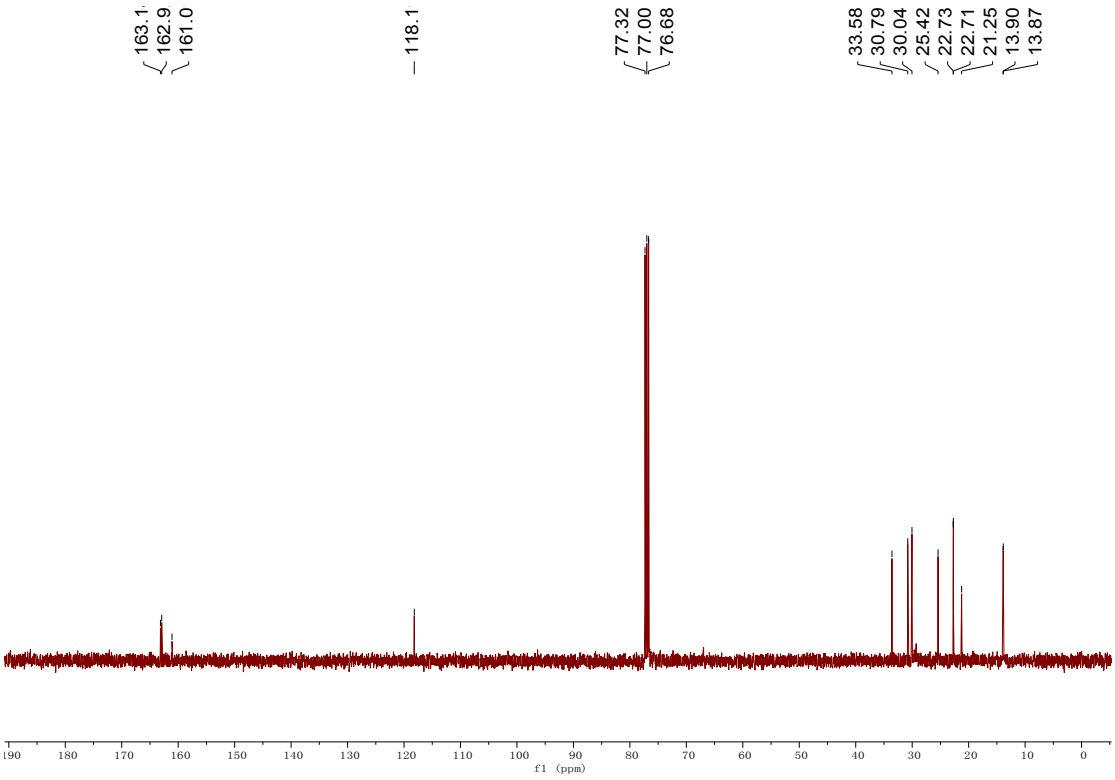
Compound 6jb: Yield: 32 mg, 75%; A colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45-7.35 (m, 3H), 7.29-7.25 (m, 2H), 2.45 (s, 3H), 2.38 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.4, 164.9, 160.1, 131.9, 129.7, 128.5, 128.3, 118.8, 27.9, 21.5, 12.3. IR (neat): ν 1596, 1474, 1198, 1172, 746,699, 677 cm^{-1}; HRMS (ESI) Calcd. for $C_{13}H_{14}NO_2$ $[M+H]^+$: 216.1019, found: 216.1022.



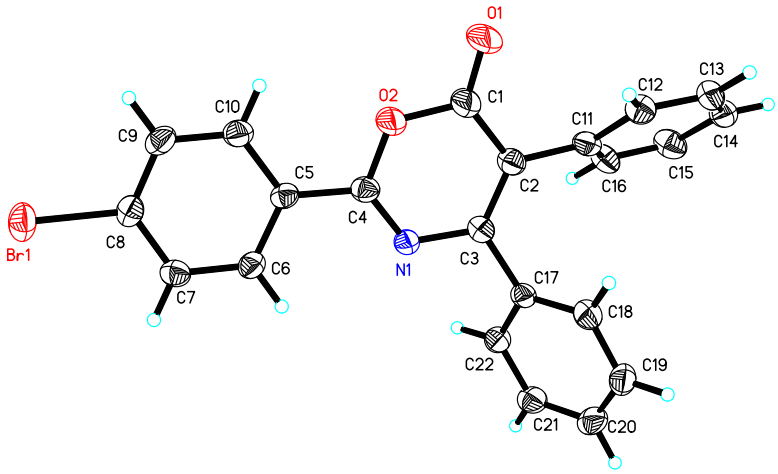


Compound 6jc: Yield: 25 mg, 51%; A colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.46-2.39 (m, 4H), 2.34 (s, 3H), 1.64-1.52 (m, 2H), 1.52-1.32 (m, 6H), 0.99-0.89 (m, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.1, 162.9, 161.1, 118.2, 33.6, 30.8, 30.0, 25.4, 22.73, 22.71, 21.3, 13.90, 13.87; IR (neat) ν □2956, 2928, 2853, 1738, 1633, 1028 cm^{-1}; HRMS (ESI) Calcd. for $C_{13}H_{22}NO_2$ $[M+H]^+$: 224.1645, found: 224.1643.



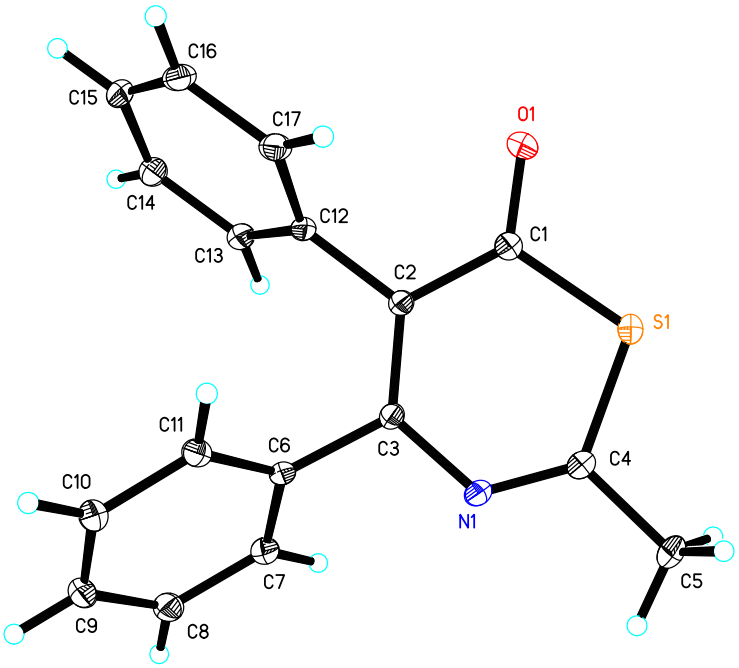

163.1
162.9
161.0
118.1
77.32
77.00
76.68
33.58
30.79
30.04
25.42
22.73
22.71
21.25
13.90
13.87
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8. X-ray crystal data of 3a.



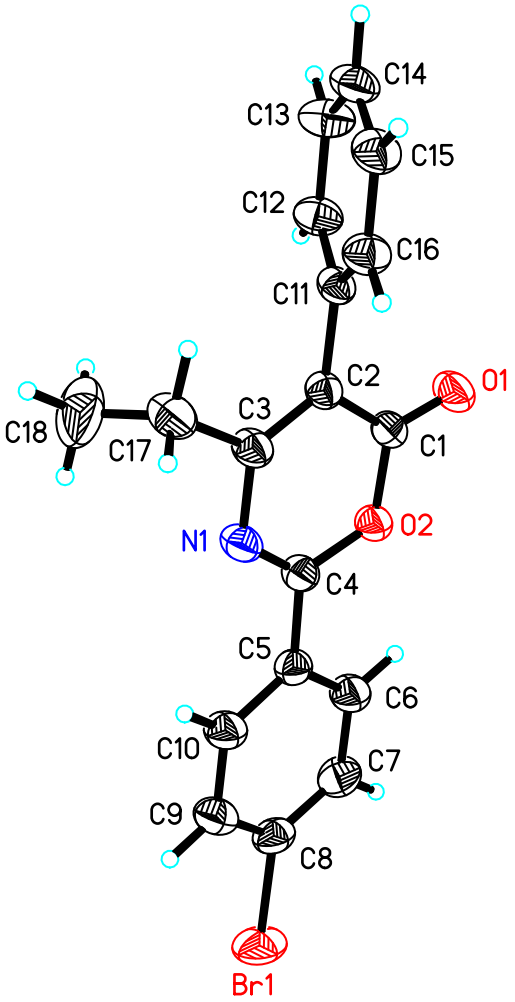
The crystal data of **3a** have been deposited in CCDC with number 1535814. Empirical Formula: $C_{22}H_{14}BrNO_2$; Formula Weight: 404.25; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.170 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 17.425(3)Å, b = 7.1016(12)Å, c = 29.618(5)Å, $\alpha = 90^o$, $\beta = 106.008(4)°$, $\gamma = 90^o$, V = 3523.0(10)$Å^3$; Space group: P 21/c; Z = 8; D_{calc}= 1.524 g/cm^3; F_{000} = 1632; Final R indices [I>2sigma(I)] R1 = 0.0418, wR2 = 0.0936.

X-ray crystal data of 5j



The crystal data of **5j** have been deposited in CCDC with number 1045751. Empirical Formula: $C_{17}H_{13}NOS$; Formula Weight: 279.34; Crystal Color, Habit: colorless; Crystal Dimensions: 0.25 x 0.2 x 0.15 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 6.9438(5)Å, b = 16.2467(11)Å, c = 24.2648(17)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2737.4(3)$Å^3$; Space group: P bca; Z = 8; D_{calc}= 1.356 g/cm^3; F_{000} = 1168; Final R indices [I>2sigma(I)] R1 = 0.0390, wR2 = 0.1042.

X-ray crystal data of 6ab



The crystal data of **6ab** have been deposited in CCDC with number 1576769. Empirical Formula: $C_{18}H_{14}BrNO_2$; Formula Weight: 356.21; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 15.2706(5)Å, b = 18.9516(6)Å, c = 11.5233(3)Å, α = 90°, β = 105.0310(10)°, γ = 90°, V = 3220.77(17)$Å^3$; Space group: P 21/c; Z = 8; D_{calc}= 1.469 g/cm^3; F_{000} = 1440; Final R indices [I>2sigma(I)] R1 = 0.0486, wR2 = 0.1042.

9. Reference:

[1] R. Zeng, C. Fu and S. Ma, *J. Am. Chem. Soc.*, 2012, **134**, 9597.

[2] H. M. Petrassi, K. B. Sharpless and J. W. Kelly, *Org. Lett*., 2001, **3**, 139.

[3] H. Yoshida, M. Nakajima and T. Ogata, *Synthesis*, 1981, 36.