Supporting information

Intramolecular Hydrogen-bonding-assisted Phosphine-catalysed [3+2] Cyclisation of Ynones with o-Hydroxy/amino Benzaldehydes

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1. General Information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. ^{31}P NMR spectra were recorded at 162 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh).

2. General procedures for the reaction of ynones and 1

Salicylaldehyde **1** (0.30 mmol) and Ph_3P (0.06 mmol) were well mixed, and then 4-phenylbut-3-yn-2-one (0.60 mmol) in CH_2Cl_2/MeOH (1:1, 1mL/1mL) was added to it and the resulting mixture was stirred at room temperature for 12 h. Subsequently, another portion of PPh_3 (0.09 mmol) was added and stirred at room temperature for additional 24 h. Following, the solvent was concentrated under reduced pressure and the residue was purified by flash chromatography using silica gel (EtOAc/PE = 1:9-1:1) to give the corresponding products.

3. General procedures for the reaction of ynones and 4

2-Sulfamoylbenzaldehyde **4** (0.30 mmol) and Ph_3P (0.06 mmol) were well mixed, and then 4-phenylbut-3-yn-2-one (0.60 mmol) in THF/EtOH (1:1, 1mL/1mL) was added to it and the resulting

mixture was stirred at room temperature for 12 h. Subsequently, another portion of PPh_3 (0.09 mmol) was added and stirred at room temperature for additional 24 h. The solvent was concentrated under reduced pressure and the residue was then purified by flash chromatography using silica gel (EtOAc/PE = 1:9-1:1) to give the corresponding products.

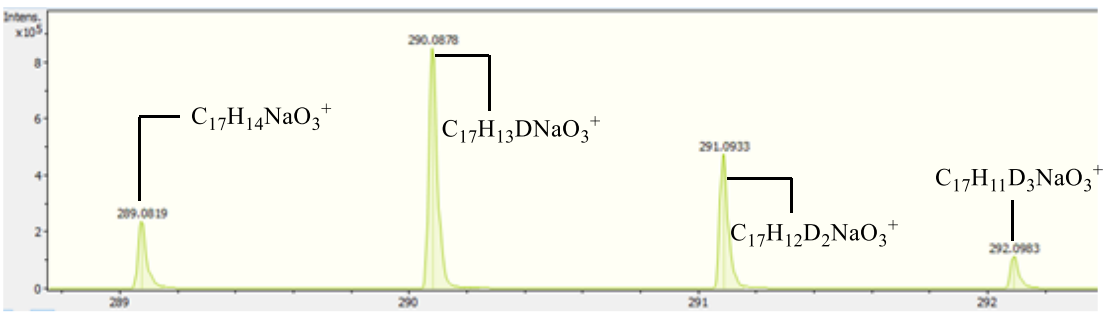
4. Mechanistic studies

^{31}P NMR studies

4 standard reactions were set up parallel on a 0.30 mmol scale according to the general procedure and stopped over time intervals of 6 h, 12 h, 24 h, 36 h. The solvent was concentrated under reduced pressure and the residue was analyzed by ^{31}P NMR in $CDCl_3$.

Labelling experiments

Salicylaldehyde **1a** (0.30 mmol) and Ph_3P (0.06 mmol) were well mixed, and then 4-phenylbut-3-yn-2-one (0.60 mmol) in CH_2Cl_2/CD_3OD (1:1, 1mL/1mL) was added to it and the resulting mixture was stirred at room temperature for 12 h. Subsequently, another portion of PPh_3 (0.09 mmol) was added and stirred at room temperature for additional 24 h. Following, the solvent was concentrated under reduced pressure and the residue was purified by flash chromatography using silica gel (EtOAc/PE = 1:9-1:1) to give the corresponding product **3a′** (52% yield).



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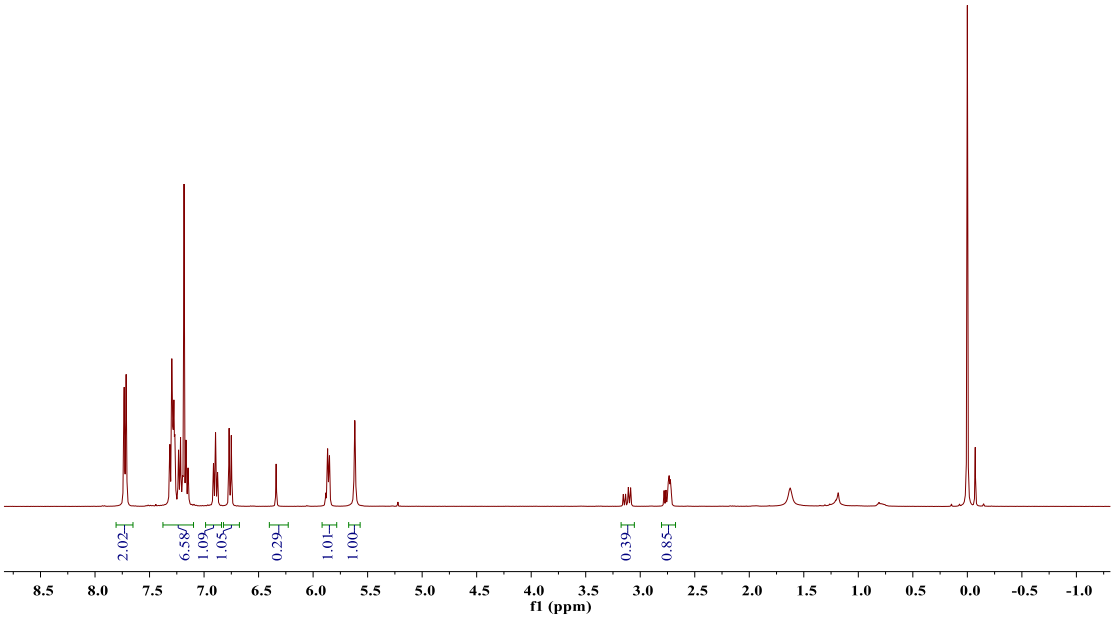
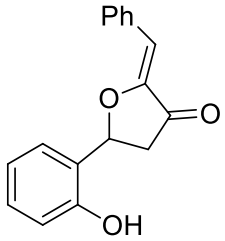
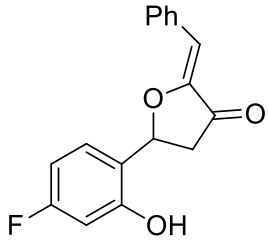


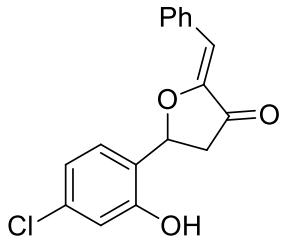
5. Characterization data of 3a-3p, 5a-5o, 6a-6l and 7



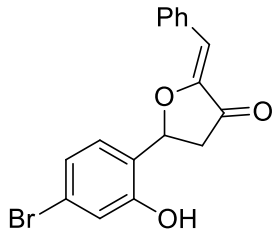
β-alkoxyenone **3a**: white solid (54 mg, yield 68%); m.p. 157-159 ℃; IR (KBr) 2922, 2514, 2135, 1793, 1454, 1262, 1172, 846, 681 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, J = 7.2 Hz, 2H), 7.34-7.39 (m, 3H), 7.30 (d, J = 7.2 Hz, 1H), 7.21-7.25 (m, 1H), 6.96 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.41 (s, 1H), 5.94 (t, J = 7.2 Hz, 1H), 3.19 (dd, J = 18.8, 7.6 Hz, 1H), 2.82 (dd, J = 18.4, 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.6, 153.1, 147.2, 133.7, 130.2, 129.7, 128.7, 128.3, 126.9, 126.6, 121.0, 116.0, 105.2, 77.2, 41.5; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{14}NaO_3^+$ 289.0835, found 289.0827.



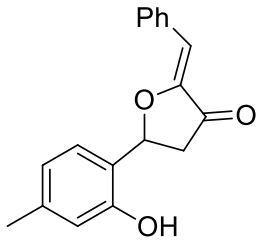
β-alkoxyenone **3b**: yellow solid (35 mg, yield 41%); m.p. 154-156 ℃; IR (KBr) 3182, 2922, 2514, 2130, 1793, 1614, 1449, 1095, 686 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 10.43 (s, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.32-7.39 (m, 3H), 7.27 (t, J = 7.2 Hz, 1H), 6.61-6.69 (m, 2H), 6.21 (s, 1H), 5.92 (dd, J = 8.4, 5.6 Hz, 1H), 3.21 (dd, J = 18.4, 8.8 Hz, 1H), 2.78 (dd, J = 18.4, 6.0 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.9, 163.1 (d, $^{1}J_{C-F}$ = 243.9 Hz), 157.1 (d, $^{3}J_{C-F}$ = 11.2 Hz), 148.4, 134.3, 130.0, 129.7 (d, $^{3}J_{C-F}$ = 10.4 Hz), 129.1, 128.2, 123.5 (d, $^{4}J_{C-F}$ = 2.9 Hz), 105.9 (d, $^{2}J_{C-F}$ = 21.4 Hz), 103.3 (d, $^{2}J_{C-F}$ = 24.0 Hz), 102.0, 77.2, 40.6; HRMS (TOF-ESI) m/z $[M+K]^+$ calcd for $C_{17}H_{13}FKO_3^+$ 323.0480, found 323.0455.



β-alkoxyenone **3c**: white solid (54 mg, yield 60%); m.p. 154-156 ℃; IR (KBr) 2930, 2509, 2147, 1796, 1504, 1317, 1115, 759, 686 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 10.44 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H), 6.90 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.89 (d, *J* = 6.0 Hz, 1H), 6.22 (s, 1H), 5.93 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.23 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.76 (dd, *J* = 18.8, 5.6 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.8, 156.5, 148.3, 134.3, 133.8, 130.0, 129.5, 129.1, 128.3, 126.3, 119.4, 115.8, 102.2, 77.0, 40.6; HRMS (TOF-ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{14}ClO_3^+$ 301.0626, found 301.0607.

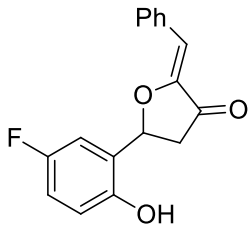


β-alkoxyenone **3d**: white solid (61 mg, yield 59%); m.p. 160-162 ℃; IR (KBr) 3174, 2930, 2509, 1798, 1703, 1589, 1260, 1020, 689 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) *δ* 10.44 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 6.0 Hz, 2H), 7.02-7.05 (m, *2*H), 6.23 (s, 1H), 5.92 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.23 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.76 (dd, *J* = 18.8, 6.0 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) *δ* 199.7, 156.6, 148.3, 134.3, 130.0, 129.8, 129.1, 128.3, 126.7, 122.3, 122.2, 118.7, 102.2, 77.1; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{13}BrNaO_3^+$ 366.9940, found 366.9925.

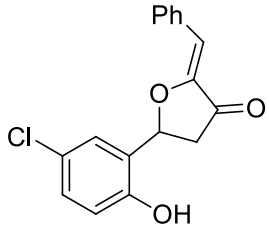


β-alkoxyenone **3e**: white solid (38 mg, yield 45%); m.p. 159-161 ℃; IR (KBr) 3219, 2918, 2511, 1796, 1711, 1374, 1018, 945, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 7.78 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.65 (s, 1H), 6.40 (s, 1H), 5.89 (t, *J* = 7.2 Hz, 1H), 5.49 (s, 1H), 3.15 (dd, *J* = 18.4, 8.4 Hz, 1H), 2.83

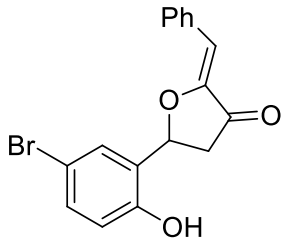
(dd, *J* = 18.8, 7.2 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.5, 153.1, 147.2, 140.1, 133.7, 130.2, 128.6, 128.3, 127.0, 123.4, 121.7, 116.8, 105.2, 77.2, 41.5, 21.1; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{16}NaO_3^+$ 303.0992, found 303.0966.



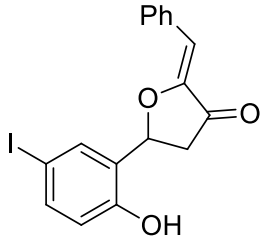
β-alkoxyenone **3g**: white solid (59 mg, yield 69%); m.p. 163-165 ℃; IR (KBr) 3080, 2935, 2512, 1798, 1704, 1502, 1101, 991, 644 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 9.91 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.15 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.01-7.06 (m, 1H), 6.85 (dd, *J* = 8.8, 4.8 Hz, 1H), 6.24 (s, 1H), 5.93 (dd, *J* = 8.0, 6.4 Hz, 1H), 3.23 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.77 (dd, *J* = 18.4, 6.0 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.6, 155.7 (d, $^1J_{C\text{-}F}$ = 243.9 Hz), 151.6 (d, $^4J_{C\text{-}F}$ = 1.6 Hz), 148.2, 134.2, 130.1, 129.1, 128.39 (d, $^3J_{C\text{-}F}$ = 6.7 Hz), 128.31, 116.9 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 116.0 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 114.2 (d, $^2J_{C\text{-}F}$ = 23.8 Hz), 102.4, 76.8, 40.8; HRMS (TOF-ESI) m/z $[M+K]^+$ calcd for $C_{17}H_{13}FKO_3^+$ 323.0480, found 323.0454.



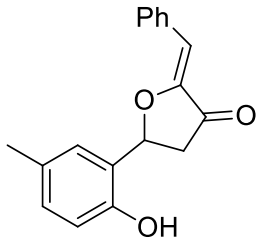
β-alkoxyenone **3h**: white solid (62 mg, yield 69%); m.p. 169-171 ℃; IR (KBr) 3222, 2962, 2511, 1796, 1596, 1373, 1120, 996, 687 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 10.22 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.24 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.23 (s, 1H), 5.92 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.22 (dd, *J* = 18.8, 8.8 Hz, 1H), 2.78 (dd, *J* = 18.8, 6.0 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.6, 154.2, 148.2, 134.2, 130.0, 129.6, 129.1, 129.0, 128.3, 127.6, 122.9, 117.7, 102.3, 76.9; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{13}ClNaO_3^+$ 323.0445, found 323.0437.



β-alkoxyenone **3i**: white solid (73 mg, yield 70%); m.p. 175-177 ℃; IR (KBr) 3222, 2961, 2514, 1794, 1589, 1347, 1172, 978, 681 cm^{-1}; ^1H NMR (DMSO-*d6*, 400 MHz) δ 10.25 (s, 1H), 7.77 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 2.4 Hz, 1H), 7.34-7.40 (m, 3H), 7.28 (t, J = 7.2 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.23 (s, 1H), 5.91 (dd, J = 8.4, 6.0 Hz, 1H), 3.22 (dd, J = 18.4, 8.4 Hz, 1H), 2.78 (dd, J = 18.4, 6.0 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 200.1, 155.5, 148.8, 134.8, 133.1, 131.0, 130.6, 130.1, 129.7, 128.8, 118.8, 111.0, 102.8, 77.5, 41.1; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{13}BrNaO_3^+$ 366.9940, found 366.9912.

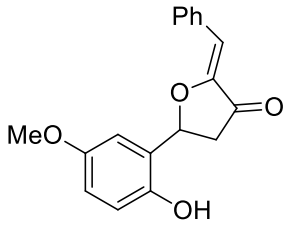


β-alkoxyenone **3j**: white solid (60 mg, yield 51%); m.p. 164-166 ℃; IR (KBr) 3414, 2925, 2512, 1796, 1592, 1367, 1175, 976, 667 cm^{-1}; ^1H NMR (DMSO-*d6*, 400 MHz) δ 10.22 (s, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 1.6 Hz, 1H), 7.50 (dd, J = 8.4, 2.0 Hz, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 6.21 (s, 1H), 5.88 (dd, J = 8.8, 6.4 Hz, 1H), 3.20 (dd, J = 18.8, 8.8 Hz, 1H), 2.78 (dd, J = 18.4, 6.0 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.7, 155.6, 148.3, 138.4, 136.4, 134.3, 130.0, 129.9, 129.1, 128.3, 118.8, 102.1, 81.3, 77.0, 40.5; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{13}INaO_3^+$ 414.9802, found 414.9775.

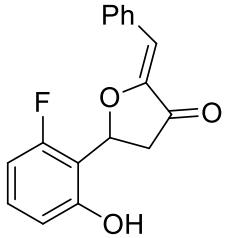


β-alkoxyenone **3k**: white solid (46 mg, yield 55%); m.p. 158-160 ℃; IR (KBr) 3270, 2916, 2509, 1794, 1559, 1350, 1158, 966, 687 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.26-7.30 (m, 1H), 7.13 (s, 1H), 7.03 (dd, J = 8.0, 1.2 Hz, 1H), 6.73 (d, J

= 8.4 Hz, 1H), 6.40 (s, 1H), 5.88 (t, *J* = 7.6 Hz, 1H), 5.60 (s, 1H), 3.16 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.82 (dd, *J* = 18.4, 6.8 Hz, 1H), 2.3 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.8, 151.0, 147.3, 133.7, 130.30, 130.25, 130.1, 128.7, 128.3, 127.5, 126.2, 116.0, 105.2, 77.2, 41.5, 20.6; HRMS (TOF-ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{17}O_3^+$ 281.1172, found 281.1191.

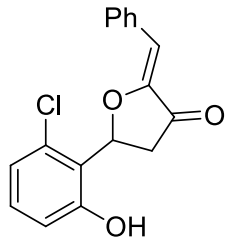


β-alkoxyenone **3l**: white solid (44 mg, yield 50%); m.p.167-169 ℃; IR (KBr) 3227, 2966, 2509, 1791, 1506, 1367, 1140, 986, 664 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 9.39 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 3.2 Hz, 1H), 6.88 (s, 1H), 6.77 (s, 2H), 6.21 (s, 1H), 5.90 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.65 (s, 3H), 3.21 (dd, *J* = 18.4, 8.4 Hz, 1H), 2.77 (dd, *J* = 18.4, 5.6 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 200.0, 154.5, 149.1, 148.4, 134.4, 130.0, 129.1, 128.2, 127.7, 116.7, 114.8, 113.6, 102.0, 77.5, 55.8, 40.9; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{16}NaO_4^+$ 319.0941, found 319.0934.

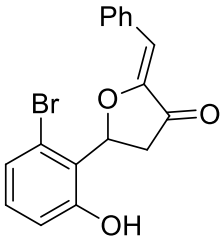


β-alkoxyenone **3n**: white solid (66 mg, yield 77%); m.p.178-180 ℃; IR (KBr) 3202, 2965, 2511, 1796, 1586, 1379, 1075, 950, 687 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 10.45 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.19-7.25 (m, 2H), 6.66-6.71 (m, 2H), 6.24 (dd, *J* = 9.6, 5.2 Hz, 1H), 6.17 (s, 1H), 3.24 (dd, *J* = 18.4, 9.6 MHz, 1H), 2.89 (dd, *J* = 18.8, 4.8 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.9, 161.8 (d, $^1J_{C\text{-}F}$ = 244.9 Hz), 157.8 (d, $^3J_{C\text{-}F}$ = 7.3 Hz), 148.5, 134.4, 131.2 (d, $^3J_{C\text{-}F}$ = 11.3 Hz), 129.9, 129.0, 128.0, 114.3 (d, $^2J_{C\text{-}F}$ = 14.3 Hz), 112.5 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 106.5 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 101.3, 71.4 (d, $^3J_{C\text{-}F}$ = 5.4 Hz), 39.2; HRMS (TOF-ESI) m/z $[M+K]^+$ calcd for

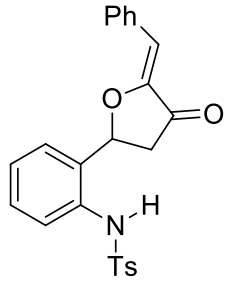
$C_{17}H_{13}FKO_3^+$ 323.0480, found 323.0458.



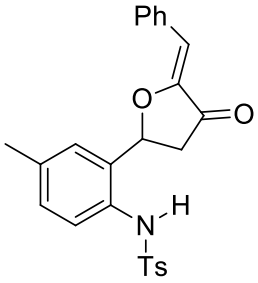
β-alkoxyenone **3o**: white solid (87 mg, yield 96%); m.p.174-176 ℃; IR (KBr) 3164, 2923, 2514, 1794, 1484, 1380, 1081, 948, 687 cm^{-1}; ^1H NMR (DMSO-*d6*, 400 MHz) *δ* 10.48 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H),6.95 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.40 (dd, *J* = 10.0, 5.2 Hz, 1H), 6.15 (s, 1H), 3.21 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.91 (dd, *J* = 18.8, 5.6 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) *δ* 199.9, 158.2, 148.9, 134.5, 133.9, 131.2, 129.8, 129.0, 127.9, 123.8, 120.6, 115.6, 101.0, 75.2, 38.8; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{13}ClNaO_3^+$ 323.0445, found 323.0428.



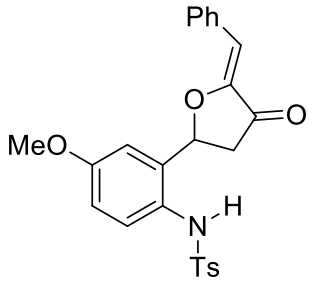
β-alkoxyenone **3p**: yellow solid (94 mg, yield 91%); m.p.175-177 ℃; IR (KBr) 3165, 2923, 2514, 1784, 1489, 1377, 1118, 951, 692 cm^{-1}; ^1H NMR (DMSO-*d6*, 400 MHz) *δ* 10.48 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.12-7.16 (m, 2H), 6.82 (dd, *J* = 6.0, 2.8 Hz, 1H), 6.36 (dd, *J* = 10.0, 5.2 Hz, 1H), 6.14 (s, 1H), 3.20 (dd, *J* = 18.8, 10.0Hz, 1H), 2.89 (dd, *J* = 18.4, 4.8 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) *δ* 200.0, 158.2, 148.9, 134.5, 131.7, 129.8, 129.0, 127.9, 125.2, 124.3, 123.9, 116.3, 100.9, 78.2, 38.8; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{13}BrNaO_3^+$ 366.9940, found 366.9936;



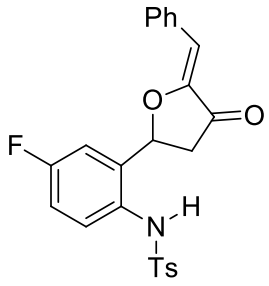
β-alkoxyenone **5a**: white solid (58 mg, yield 69%); m.p.185-187 ℃; IR (KBr) 3299, 2922, 2509, 2137, 1728, 1314, 1142, 1020, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.30 (t, J = 8.0 Hz, 3H), 7.19-7.24 (m, 3H), 7.17-7.14 (m, 2H), 6.94 (dd, J = 7.6, 1.2 Hz, 1H), 6.80 (*br* s, 1H), 6.35 (s, 1H), 5.91 (t, J = 8.0 Hz, 1H), 3.07 (dd, J = 18.8, 8.0 Hz, 1H), 2.49 (dd, J = 18.8, 8.0 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.4, 145.6, 143.3, 135.09, 135.06, 132.6, 132.3, 129.2, 128.8, 128.3, 127.7, 127.5, 126.7, 126.3, 125.8, 125.3, 104.9, 75.3, 40.8, 20.6; HRMS (TOF-ESI) m/z $[M+K]^+$ calcd for $C_{24}H_{21}KNO_4S^+$ 458.0823, found 458.0800.



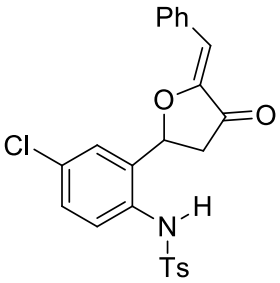
β-alkoxyenone **5b**: white solid (49 mg, yield 57%); m.p.198-200 ℃; IR (KBr) 3222, 2922, 2516, 2137, 1793, 1496, 1152, 1095, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.18-7.24 (m, 3H), 7.11 (s, 1H), 6.95 (dd, J = 8.0, 1.2 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.50 (*br* s, 1H), 6.34 (s, 1H), 5.91 (t, J = 8.0 Hz, 1H), 3.05 (dd, J = 18.8, 8.0 Hz, 1H), 2.52 (dd, J = 18.8, 8.0 Hz, 1H), 2.34 (s, 3H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.6, 145.8, 143.1, 137.1, 135.6, 135.2, 132.4, 129.7, 129.2, 128.9, 128.7, 127.7, 127.4, 126.4, 126.3, 125.9, 104.6, 75.1, 41.0, 20.6, 20.2; HRMS (TOF-ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{24}NO_4S^+$ 434.1421, found 434.1403.



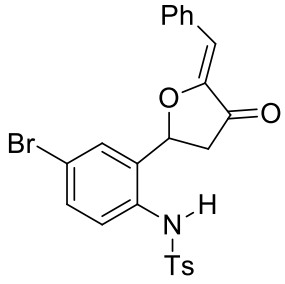
β-alkoxyenone **5c**: white solid (51 mg, yield 58%); m.p.194-196 ℃; IR (KBr) 3214, 2913, 2511, 2140, 1791, 1606, 1424, 1020, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 7.2 Hz, 2H), 7.18-7.22 (m, 3H), 6.87 (d, J = 2.4 Hz, 1H), 6.60-6.66 (m, 2H), 6.42 (*br* s, 1H), 6.32 (s, 1H), 5.98 (t, J = 7.6 Hz, 1H), 3.64 (s, 3H), 3.11 (dd, J = 18.4, 8.0 Hz, 1H), 2.49 (dd, J = 18.4, 7.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7, 159.5, 147.0, 144.2, 140.6, 136.1, 133.5, 130.2, 129.8, 129.6, 128.6, 128.4, 127.5, 125.3, 114.1, 111.7, 105.5, 75.8, 55.5, 42.4, 21.6; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{25}H_{23}NNaO_5S^+$ 472.1189, found 472.1185.



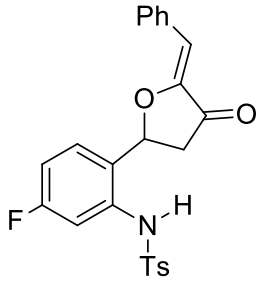
β-alkoxyenone **5d**: yellow solid (53 mg, yield 61%); m.p.196-198 ℃; IR (KBr) 3272, 2922, 2514, 2137, 1793, 1434, 1150, 876, 669 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 9.85 (s, 1H), 7.73 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.38-7.42 (m, 4H), 7.29-7.32 (m, 2H), 7.12-7.17 (m, 1H), 6.83 (dd, J = 8.8, 1.2 Hz, 1H), 6.27 (s, 1H), 5.94 (t, J = 7.6 Hz, 1H), 3.09 (dd, J = 18.4, 7.6 Hz, 1H), 2.65 (dd, J = 18.4, 7.6 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.0, 161.5 (d, $^{1}J_{C\text{-}F}$ = 245.1 Hz), 147.8, 143.9, 141.6 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 137.0, 133.9, 130.35, 130.28, 130.23, 130.22, 129.2, 128.6, 127.4, 116.4 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 113.9 (d, $^{2}J_{C\text{-}F}$ = 24.1 Hz), 103.4, 75.4, 42.5, 21.4; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{20}FNNaO_4S^+$ 460.0989, found 460.0994.



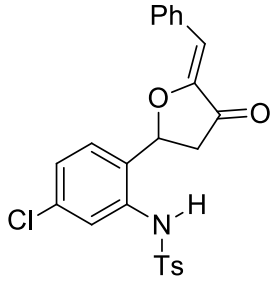
β-alkoxyenone **5e**: white solid (54 mg, yield 59%); m.p.165-167 ℃; IR (KBr) 3262, 2920, 2511, 2132, 1793, 1641, 1327, 1155, 980, 689 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 9.98 (*br* s, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.38-7.42 (m, 5H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.27 (s, 1H), 5.92 (t, *J* = 7.6 Hz, 1H), 3.08 (dd, *J* = 18.4, 7.6 Hz, 1H), 2.56 (dd, *J* = 18.4, 8.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 198.9, 147.8, 144.0, 140.6, 136.9, 133.9, 133.2, 132.5, 130.3, 130.2, 129.5, 129.4, 129.2, 128.6, 127.3, 127.1, 103.4, 75.3, 42.5, 21.4; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{20}ClNNaO_4S^+$ 476.0694, found 476.0719.



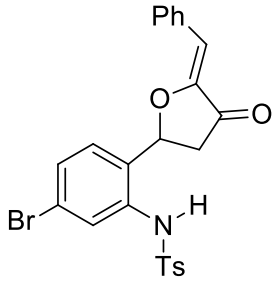
β-alkoxyenone **5f**: white solid (61 mg, yield 61%); m.p.199-201 ℃; IR (KBr) 3262, 2922, 2514, 1731, 1417, 1245, 1155, 818, 686 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 9.95 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.38-7.42 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.27 (s, 1H), 5.91 (t, *J* = 7.6 Hz, 1H), 3.07 (dd, *J* = 18.4, 7.6 Hz, 1H), 2.66 (dd, *J* = 18.4, 8.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 198.9, 147.8, 144.0, 140.7, 136.9, 133.9, 133.6, 132.4, 130.3, 130.2, 130.0, 129.7, 129.2, 128.6, 127.3, 120.9, 103.4, 75.2, 42.5, 21.4; HRMS (TOF-ESI) m/z $[M+K]^+$ calcd for $C_{24}H_{20}BrKNO_4S^+$ 535.9928, found 535.9900.



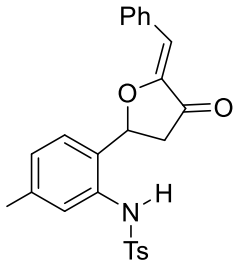
β-alkoxyenone **5g**: white solid (37 mg, yield 42%); m.p.177-179 ℃; IR (KBr) 3267, 2915, 2511, 2132, 1793, 1556, 1327, 1018, 873cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.19-7.26 (m, 4H), 7.10 (*br* s, 1H), 6.84-6.90 (m, 2H), 6.37 (s, 1H), 5.73 (t, J = 8.0 Hz, 1H), 2.98 (dd, J = 18.4, 7.6 Hz, 1H), 2.52 (dd, J = 18.4, 7.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.6, 161.7 (d, $^{1}J_{C-F}$ = 249.6 Hz), 145.1, 143.6, 135.0, 134.9 (d, $^{3}J_{C-F}$ = 10.3 Hz), 132.1, 129.2, 129.0, 128.4 (d, $^{4}J_{C-F}$ = 3.5 Hz), 127.4 (d, $^{3}J_{C-F}$ = 9.5 Hz), 127.3, 126.2, 112.7 (d, $^{2}J_{C-F}$ = 21.5 Hz), 111.1 (d, $^{2}J_{C-F}$ = 24.7 Hz), 105.6, 75.4, 40.3, 20.6; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{20}FNNaO_4S^+$ 460.0989, found 460.0967.



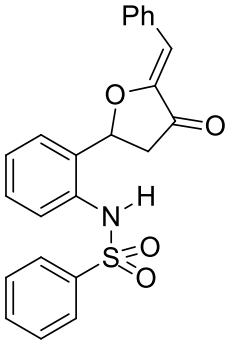
β-alkoxyenone **5h**: white solid (35 mg, yield 39%); m.p.170-172 ℃; IR (KBr) 3261, 2921, 2509, 2122, 1719, 1676, 1161, 960, 575 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 10.08 (s, 1H), 7.71 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 1H), 7.37-7.41 (m, 5H), 7.30 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 2.0 Hz, 1H), 6.26 (s, 1H), 5.90 (t, J = 7.6 Hz, 1H), 3.08 (dd, J = 18.0, 7.2 Hz, 1H), 2.56 (dd, J = 18.8, 7.2 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.0, 147.8, 144.1, 137.2, 136.8, 135.5, 133.9, 133.1, 130.3, 130.2, 129.1, 128.9, 128.6, 128.1, 127.3, 126.9, 103.4, 75.0, 42.5, 21.4; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{20}ClNNaO_4S^+$ 476.0694, found 476.0667.



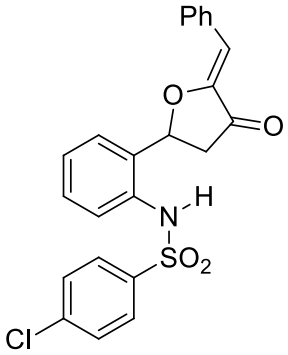
β-alkoxyenone **5i**: white solid (41 mg, yield 41%); m.p.176-178 ℃; IR (KBr) 3259, 2918, 2514, 2137, 1796, 1491, 1155, 978, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.29-7.32 (m, 3H), 7.21-7.26 (m, 3H), 7.14-7.17 (m, 2H), 6.83 (*br* s, 1H), 6.36 (s, 1H), 5.78 (t, J = 8.0 Hz, 1H), 3.02 (dd, J = 18.4, 8.0 Hz, 1H), 2.49 (dd, J = 18.4, 8.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.6, 145.2, 143.7, 134.9, 133.1, 132.1, 129.4, 129.3, 129.0, 127.8, 127.2, 126.3, 121.7, 105.5, 75.2, 40.5, 20.6; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{20}BrNNaO_4S^+$ 520.0189, found 520.0217.



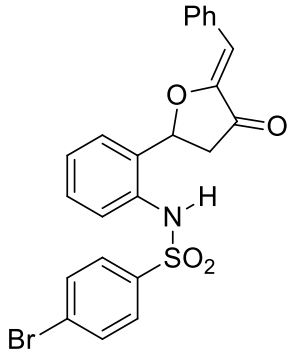
β-alkoxyenone **5j**: white solid (53 mg, yield 41%); m.p.146-148 ℃; IR (KBr) 3385, 2922, 1627, 1447, 1255, 1086, 815, 697, 555 cm^{-1}; ^{1}H NMR (CDCl3, 400 MHz) δ 7.65 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.15-7.23 (m, 5H), 7.00 (d, J = 8.0 Hz, 1H), 6.81 (s, 1H), 6.33 (s, 1H), 5.78 (t, J = 8.0 Hz, 1H), 2.98 (dd, J = 18.4, 8.0 Hz, 1H), 2.51 (dd, J = 18.8, 8.0 Hz, 1H), 2.32 (s, 3H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.5, 145.6, 143.2, 138.6, 135.2, 132.5, 132.3, 131.5, 129.2, 128.7, 127.7, 127.5, 127.3, 126.3, 125.8, 125.6, 104.8, 75.3, 40.7, 20.5, 20.0; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{25}H_{23}NNaO_4S^+$ 456.1240, found 456.1244.



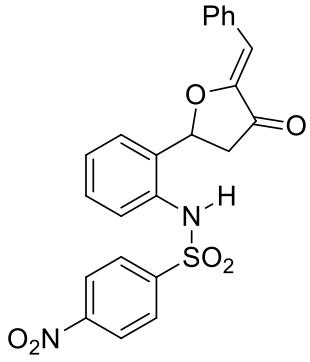
β-alkoxyenone **5k**: yellow solid (48 mg, yield 59%); m.p.184-186 ℃; IR (KBr) 3257, 3065, 2509, 2132, 1798, 1327, 1155, 980, 631 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (dd, J = 7.2, 2.0 Hz, 4H), 7.52 (d, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 3H), 7.21-7.25 (m, 2H), 7.15-7.17 (m, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.84 (*br* s, 1H), 6.36 (s, 1H), 5.89 (t, J = 8.0 Hz, 1H), 3.05 (dd, J = 18.4, 8.0 Hz, 1H), 2.52 (dd, J = 18.4, 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.3, 146.5, 139.1, 136.1, 133.5, 133.4, 133.3, 130.3, 129.4, 129.3, 128.7, 128.6, 127.8, 127.3, 126.9, 126.4, 106.0, 76.3, 41.8; HRMS (TOF-ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{20}NO_4S^+$ 406.1108, found 406.1083.



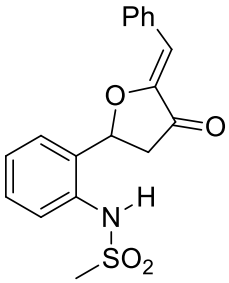
β-alkoxyenone **5l**: white solid (50 mg, yield 57%); m.p.191-193 ℃; IR (KBr) 3272, 2927, 2511, 2137, 1793, 1561, 1295, 1088, 754 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 10.05 (s, 1H), 7.66-7.74 (m, 6H), 7.45 (dd, J = 8.0, 1.6 Hz, 1H), 7.25-7.40 (m, 5H), 6.83 (dd, J = 7.6, 1.2 Hz, 1H), 6.28 (s, 1H), 6.07 (t, J = 7.6 Hz, 1H), 3.18 (dd, J = 18.8, 8.0 Hz, 1H), 2.62 (dd, J = 18.4, 6.8 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.3, 147.9, 139.0, 138.9, 138.4, 134.0, 133.7, 130.2, 129.9, 129.4, 129.3, 129.1, 128.6, 128.5, 127.8, 127.1, 103.2, 75.5, 42.8; HRMS (TOF-ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{19}ClNO_4S^+$ 440.0718, found 440.0407.



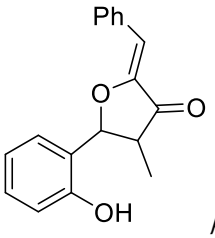
β-alkoxyenone **5m**: yellow solid (60 mg, yield 62%); m.p.195-197 ℃; IR (KBr) 3269, 2922, 2514, 2137, 1796, 1452, 1155, 978, 746 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 10.04 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.45 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.40-7.25 (m, 5H), 6.82 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.28 (s, 1H), 6.07 (t, *J* = 7.6 Hz, 1H), 3.18 (dd, *J* = 18.8, 8.0 Hz, 1H), 2.62 (dd, *J* = 18.4, 7.2 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.3, 147.9, 139.3, 139.0, 134.0, 133.6, 132.9, 130.2, 129.4, 129.3, 129.2, 128.6, 128.5, 127.7, 127.4, 127.1, 103.2, 75.5, 42.8; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{23}H_{18}BrNNaO_4S^+$ 506.0032, found 506.0037.



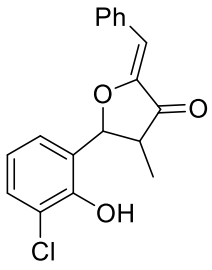
β-alkoxyenone **5n**: white solid (43mg, yield 48%);m.p.191-193℃; IR (KBr) 3272, 2905, 2511, 2140, 1796, 1509, 1160, 878, 691 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ 10.36 (s, 1H), 8.42 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 3H), 7.30-7.25 (m, 2H), 6.82 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.26 (s, 1H), 6.03 (t, *J* = 7.6 Hz, 1H), 3.20 (dd, *J* = 18.4, 8.0 Hz, 1H), 2.65 (dd, *J* = 18.4, 7.2 Hz, 1H); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ 199.3, 150.3, 147.9, 145.5, 139.1, 133.9, 133.3, 130.1, 129.6, 129.1, 129.0, 128.8, 128.5, 127.9, 127.2, 125.2, 103.2, 75.5, 42.8; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{23}H_{18}N_2NaO_6S^+$ 473.0778, found 473.0807.



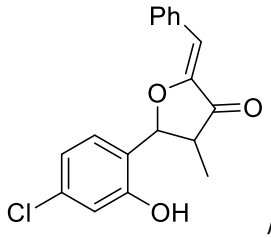
β-alkoxyenone **5o**: white solid (38 mg, yield 55%); m.p.162-164℃; IR (KBr)3260, 2913, 2510, 2128, 1722, 1583, 1303, 1160, 576 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, J = 7.2 Hz, 2H), 7.35-7.42 (m, 3H), 7.30-7.33 (m, 1H), 7.19-7.27 (m, 3H), 6.80 (*br* s, 1H), 6.37 (s, 1H), 6.06 (t, J = 8.0 Hz, 1H), 3.01 (dd, J = 18.4, 7.6 Hz, 1H), 3.01 (s, 3H), 2.49 (dd, J = 18.8, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.2, 145.5, 134.5, 132.9, 132.3, 129.2, 128.8, 127.7, 127.6, 126.7, 126.3, 124.1, 105.1, 75.3, 40.6, 39.0; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{17}NNaO_4S^+$ 366.0770, found 366.0757.



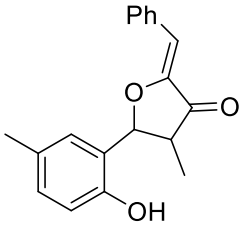
β-alkoxyenone **6a**: yellow oil (82 mg, yield 98%, 9:1 dr); IR (KBr) 3371, 1715, 1626, 1454, 1254, 1176, 964, 738, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.78 (d, J = 7.2 Hz, 2H), 7.28-7.37 (m, 4H), 7.24 (s, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.47 (s, 1H), 6.34 (*br* s, 1H), 5.42 (d, J = 8.4 Hz, 1H), 2.80-2.87 (m, 1H), 1.34 (*d*, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 202.1, 154.0, 147.0, 133.5, 130.4, 130.0, 128.7, 128.5, 127.5, 124.9, 120.9, 116.5, 106.5, 84.9, 47.2, 12.6; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{16}NaO_3^+$ 303.0992, found 303.0989.



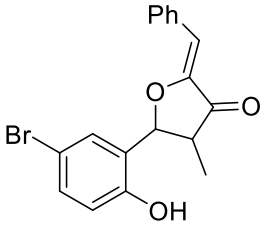
β-alkoxyenone **6b**: yellow oil (81 mg, yield 86%, 3:1 dr); IR (KBr) 3372, 1717, 1625, 1453, 1244, 964, 855, 734, 688 cm^{-1}; ^{1}H NMR (CDCl3, 400 MHz, major diastereomer) δ 7.72 (d, J = 8.0 Hz, 2H), 7.17-7.32 (m, 5H), 6.85 (t, J = 7.6 Hz, 1H), 6.35 (s, 1H), 5.87 (s, 1H), 5.47 (d, J = 7.6 Hz, 1H), 2.61-2.68 (m, 1H), 1.31 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) δ 200.7, 147.8, 146.1, 132.7, 129.3, 127.9, 127.6, 127.3, 126.5, 124.7, 120.4, 119.4, 104.6, 81.9, 46.5, 12.3; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{15}ClNaO_3^+$ 337.0602, found 337.0611.



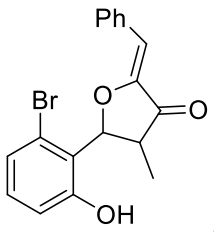
β-alkoxyenone **6c**: yellow oil (81 mg, yield 86%, 9:1 dr); IR (KBr) 3370, 1703, 1361, 1236, 1174, 956, 740, 691, 543 cm^{-1}; ^{1}H NMR (CDCl3, 400 MHz, major diastereomer) δ 7.70 (d, J = 7.2 Hz, 2H), 7.15-7.30 (m, 4H), 6.86-6.89 (m, 2H), 6.54 (br s, 1H), 6.40 (s, 1H), 5.30 (d, J = 8.4 Hz, 1H), 2.67-2.75 (m, 1H), 1.26 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) δ 201.8, 154.7, 146.7, 135.1, 133.3, 130.4, 128.8, 128.7, 128.4, 123.7, 121.1, 116.9, 106.9, 84.3, 47.1, 12.6; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C18H15ClNaO3^+$ 337.0602, found 337.0604.



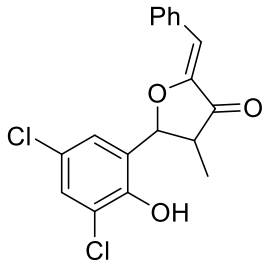
β-alkoxyenone **6d**: yellow oil (81 mg, yield 92%, 5:1 dr); IR (KBr) 3373, 1718, 1625, 1452, 1247, 1175, 965, 746, 546 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.1 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.45 (s, 1H), 6.16 (br s, 1H), 5.37 (d, *J* = 8.4 Hz, 1H), 2.79-2.87 (m, 1H), 2.29 (s, 3H), 1.32 (d, *J* =7.2 Hz, 3H); ^{13}C NMR($CDCl_3$, 100 MHz, *major diastereomer*) δ 202.3, 151.8, 147.1, 133.6, 130.43, 130.40, 130.2, 128.7, 128.5, 128.0, 124.5, 116.5, 106.3, 84.9, 47.1, 20.6, 12.4; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{19}H_{18}NaO_3^+$ 317.1148, found 317.1143.



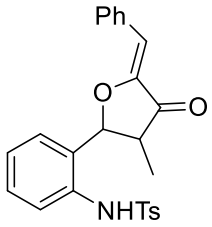
β-alkoxyenone **6e**: yellow oil (89 mg, yield 83%, 5:1 dr); IR (KBr) 3370, 1717, 1626, 1489, 1361, 1261, 1179, 971, 611 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.44 (s, *J* = 2.0 Hz, 1H), 7.28-7.40 (m, 4H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.52 (*br* s, 1H), 6.47 (s, 1H), 5.37 (d, *J* = 8.4 Hz, 1H), 2.74-2.81 (m, 1H), 1.34 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 201.9, 153.1, 146.8, 133.3, 132.6, 130.4, 130.2, 128.74, 128.70, 127.3, 118.2, 112.9, 106.9, 83.9, 47.3, 12.6; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{28}H_{15}BrNaO_3^+$ 381.0097, found 381.0093.



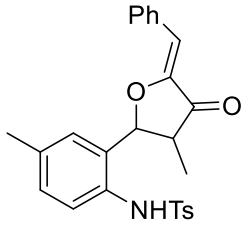
β-alkoxyenone **6f**: yellow oil (96 mg, yield 89%, 6:1 dr); IR (KBr) 3375, 1718, 1626, 1452, 1248, 1176, 966, 741, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.70 (d, J = 7.6 Hz, 2H), 7.31-7.35 (m, 3H), 7.28-7.29 (m, 1H), 7.20-7.22 (m, 1H), 7.11 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.46 (s, 1H), 5.90 (d, J = 8.8 Hz, 1H), 3.00-3.07 (m, 1H), 1.32 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 201.6, 156.5, 146.6, 133.2, 131.0, 130.4, 128.7, 125.5, 124.0, 123.2, 117.1, 107.2, 86.2, 45.4, 12.7; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{28}H_{15}BrNaO_3^+$ 381.0097, found 381.0089.



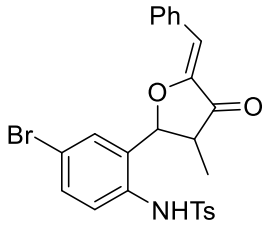
β-alkoxyenone **6g**: yellow oil (71 mg, yield 68%, 3:1 dr); IR (KBr) 3373, 1718, 1625, 1451, 1249, 1175, 966, 744, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.78 (d, J = 7.6 Hz, 2H), 7.39-7.42 (m, 5H), 6.45 (s, 1H), 5.93 (*br* s, 1H), 5.50 (d, J = 7.6 Hz, 1H), 2.64-2.74 (m, 1H), 1.39 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 201.1, 147.7, 146.8, 133.5, 130.4, 128.7, 128.51, 128.48, 126.0, 125.8, 121.0, 106.2, 82.3, 47.7, 13.2; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{14}Cl_2NaO_3^+$ 371.0212, found 371.0219.



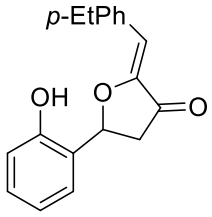
β-alkoxyenone **6h**: yellow oil (120 mg, yield 92%, 5:1 dr); IR (KBr) 3371, 1718, 1626, 1452, 1247, 1175, 966, 746, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.72 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.21-7.43 (m, 10 H), 6.48 (s, 1H), 5.09 (d, J = 9.2 Hz, 1H), 2.44-2.51 (m, 1H), 2.36 (s, 3H), 1.15 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 200.1, 146.0, 144.3, 136.6, 135.3, 133.1, 130.6, 130.4, 129.94, 129.89, 128.85, 128.81, 127.4, 127.1, 126.4, 124.9, 107.3, 85.0, 45.9, 21.5, 11.9; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{25}H_{23}NNaO_4S^+$ 456.1240, found 456.1236.



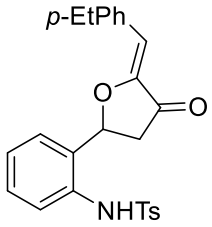
β-alkoxyenone **6i**: yellow oil (123 mg, yield 92%, 6:1 dr); IR (KBr) 3374, 1719, 1625, 1453, 1248, 1177, 966, 747, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.64 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.98-7.31 (m, 9H), 6.37 (s, 1H), 5.00 (d, J = 9.2 Hz, 1H), 2.35-2.41 (m, 1H), 2.27(s, 3H), 2.24 (s, 3H), 1.06 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 200.5, 146.2, 144.1, 136.9, 136.7, 133.2, 132.3, 131.8, 130.5, 130.4, 129.8, 128.8, 128.7, 127.9, 127.1, 125.9, 106.9, 84.6, 46.2, 21.5, 21.1, 12.0; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{26}H_{25}NNaO_4S^+$ 470.1397, found 470.1425.



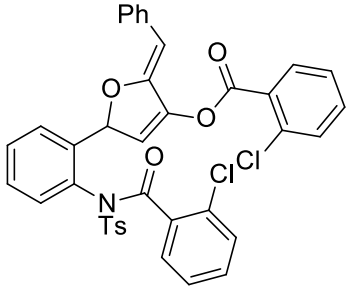
β-alkoxyenone **6j**: white solid (143 mg, yield 93%, 7:1 dr); IR (KBr) 3370, 1718, 1625, 1451, 1248, 1175, 966, 745, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.71 (d, J = 7.2 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.4 (dd, J = 8.6, 2.1 Hz, 1H), 7.23-7.39 (m, 8H), 6.48 (s, 1H), 5.02 (d, J = 9.2 Hz, 1H), 2.39-2.42 (m, 1H), 2.37(s, 3H), 1.14(d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 199.4, 145.6, 144.5, 136.3, 134.3, 132.9, 130.4, 130.0, 129.0, 128.8, 127.1, 126.7, 119.8, 107.8, 84.3, 46.0, 21.6, 11.9; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{25}H_{22}BrNNaO_4S^+$ 534.0345, found 534.0367.



β-alkoxyenone **6k**: yellow solid (18 mg, yield 32%); m.p.145-147 ℃; IR (KBr) 3226, 2920, 2852, 1707, 1626, 1448, 1255, 1017, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 7.2 Hz, 1H), 7.12-7.16 (m, 3H), 6.89 (t, J = 7.2 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.34 (s, 1H), 5.85 (t, J = 8.0 Hz, 1H), 5.59 (*br* s, 1H), 3.10 (dd, J = 18.4, 10.0 Hz, 1H), 2.73 (dd, J = 18.8, 11.6 Hz, 1H), 2.58 (q, J = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.2, 152.1, 145.6, 143.9, 130.0, 129.3, 128.6, 127.2, 125.8, 125.6, 120.0, 115.1, 104.7, 76.2, 40.6, 27.8, 14.3; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{19}H_{18}NaO_3^+$ 317.1148, found 317.1151.



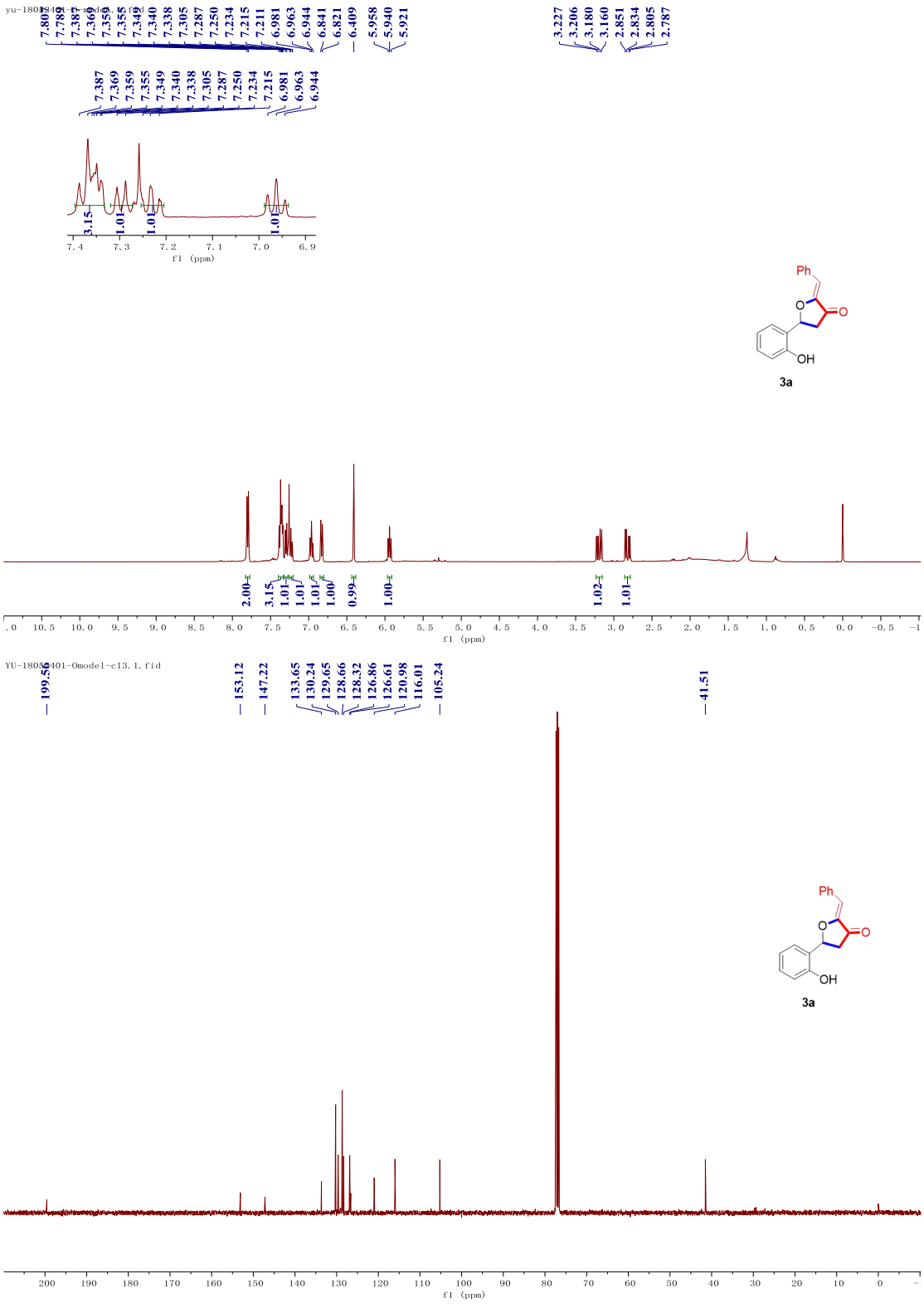
β-alkoxyenone **6l**: yellow solid (53 mg, yield 52%); m.p.154-156 ℃; IR (KBr) 3288, 2922, 1710, 1627, 1446, 1250, 1159, 1018, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, J = 8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.27-7.30 (m, 1H), 7.11-7.20 (m, 7H), 6.98-7.00 (m, 1H), 6.34 (s, 1H), 5.85 (t, J = 8.0 Hz, 1H), 3.02 (dd, J = 18.4, 8.0 Hz, 1H), 2.49-2.60 (m, 3H), 2.31 (s, 3H), 1.15 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.2, 145.1, 144.2, 143.2, 135.3, 134.8, 132.7, 129.7, 129.3, 128.8, 128.3, 127.3, 126.5, 126.3, 125.7, 125.2, 105.2, 75.3, 40.8, 27.8, 20.5, 14.3; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{26}H_{25}NNaO_4S^+$ 470.1397, found 470.1380.



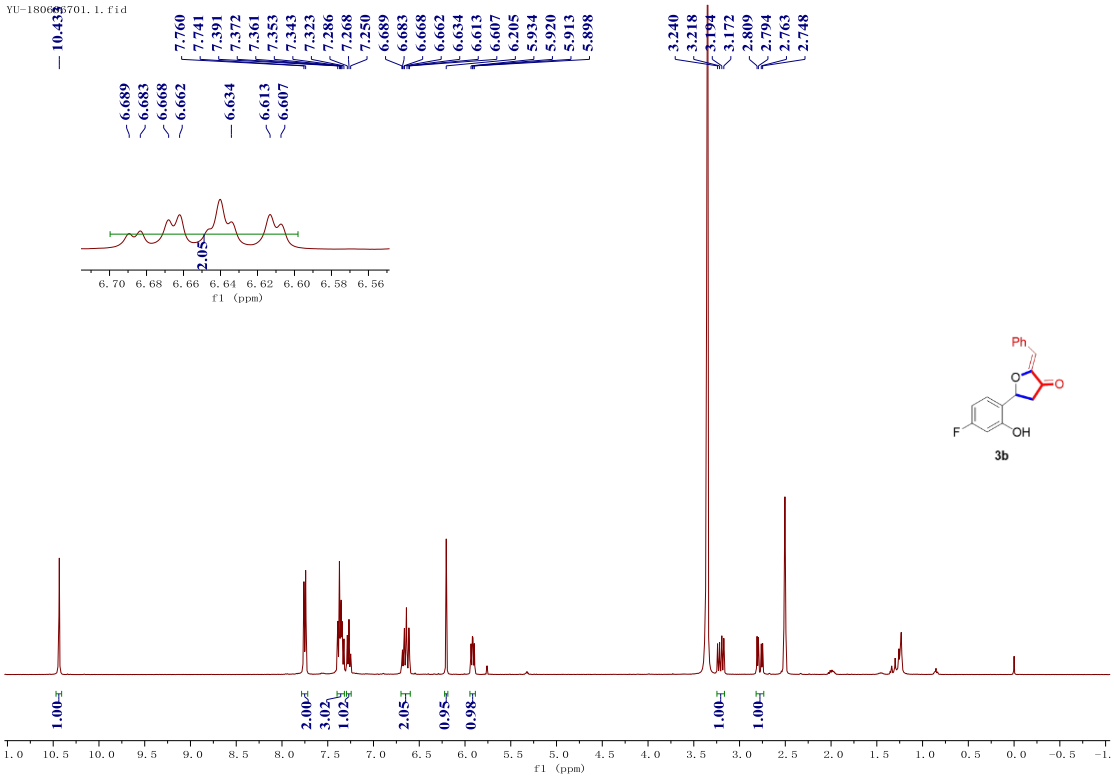
Dispirooxindole-piperazine **7**: compound **5a** (0.1mmol, 42 mg) and 2-chlorobenzoyl chloride (0.25 mmol, 44 mg) was mixed. Then Et_3N (0.5 mmol, 0.5 g) was added for additional 2h. Then the solvent was concentrated under reduced pressure and the residue was then purified by flash chromatography using silica gel (EtOAc/PE = 1:9-1:1) to give the corresponding product 6. white solid (38 mg, yield 55%); m.p.162-164℃; IR (KBr)2920, 1700, 1360, 1272, 1171, 1109, 957, 740, 547 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.03 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.50-7.55 (m, 4H), 7.05-7.39 (m, 14H), 6.89-6.92 (m, 2H), 6.62 (s, 1H), 5.68 (s, 1H), 2.42 (dd, J = 18.8, 8.0 Hz, 1H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 166.8, 161.6, 152.6, 146.3, 139.5, 135.7, 134.9, 134.7, 134.5, 134.4, 134.0, 132.3, 131.7, 131.2, 130.9, 130.8, 129.9, 129.73, 129.65, 129.02, 128.99, 128.97, 128.4, 128.1, 127.2, 127.0, 126.6, 126.0, 118.2, 107.5, 96.1, 82.5, 21.7; HRMS (TOF-ESI) m/z $[M+Na]^+$ calcd for $C_{38}H_{27}Cl_2NNaO_6S^+$ 718.0828,

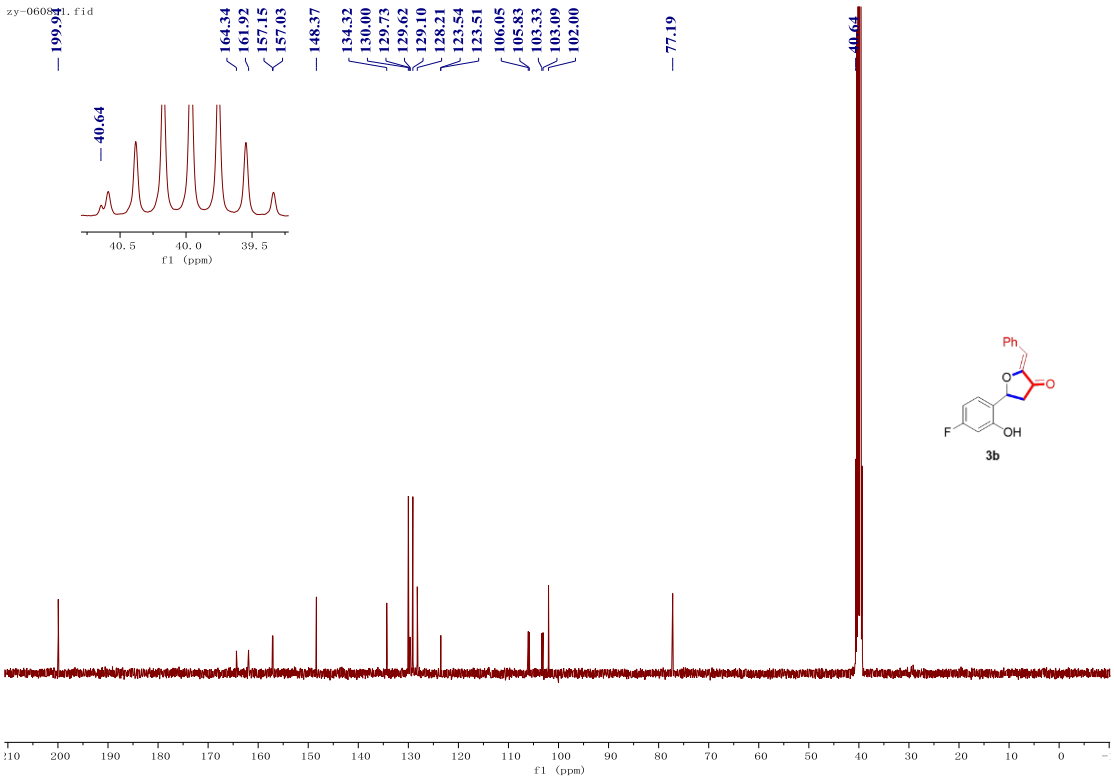
found 718.00847.

Product **3a**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

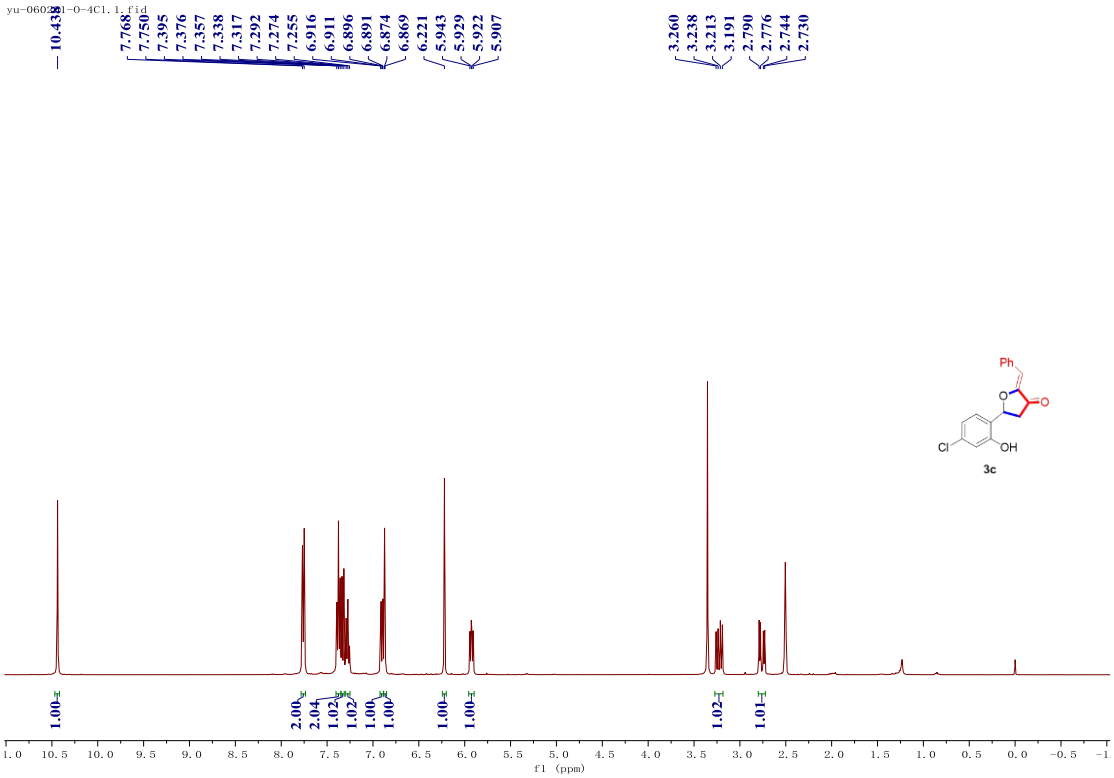


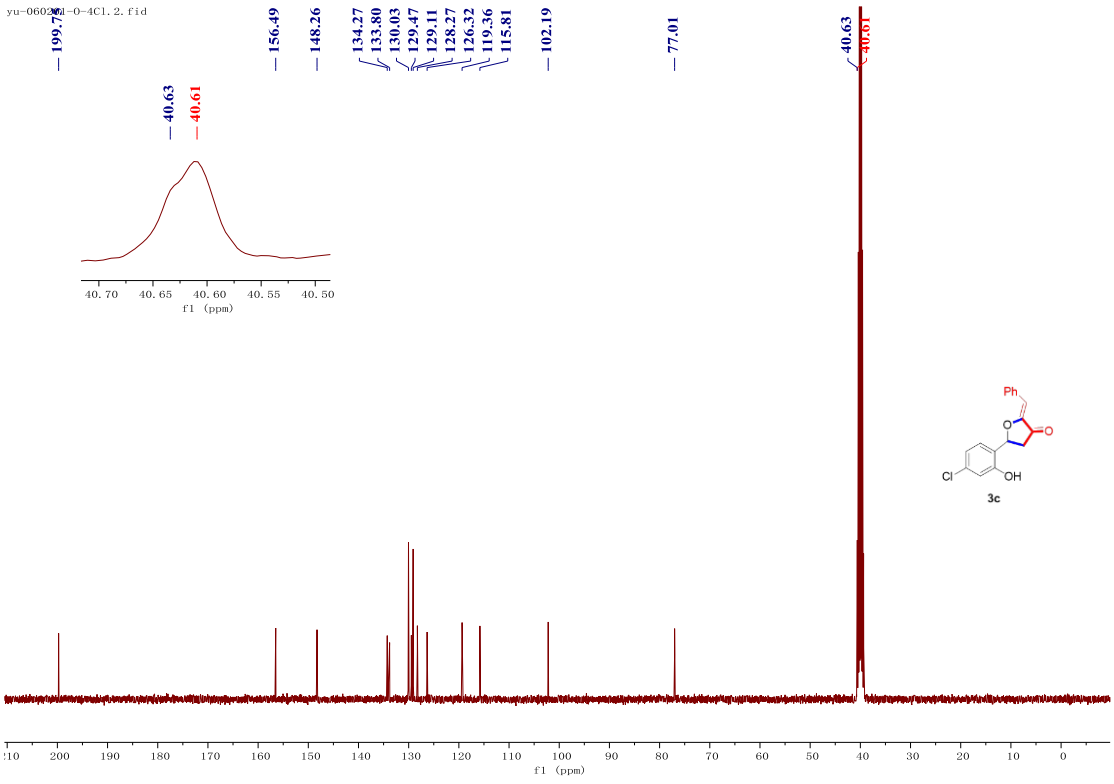
Product **3b**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



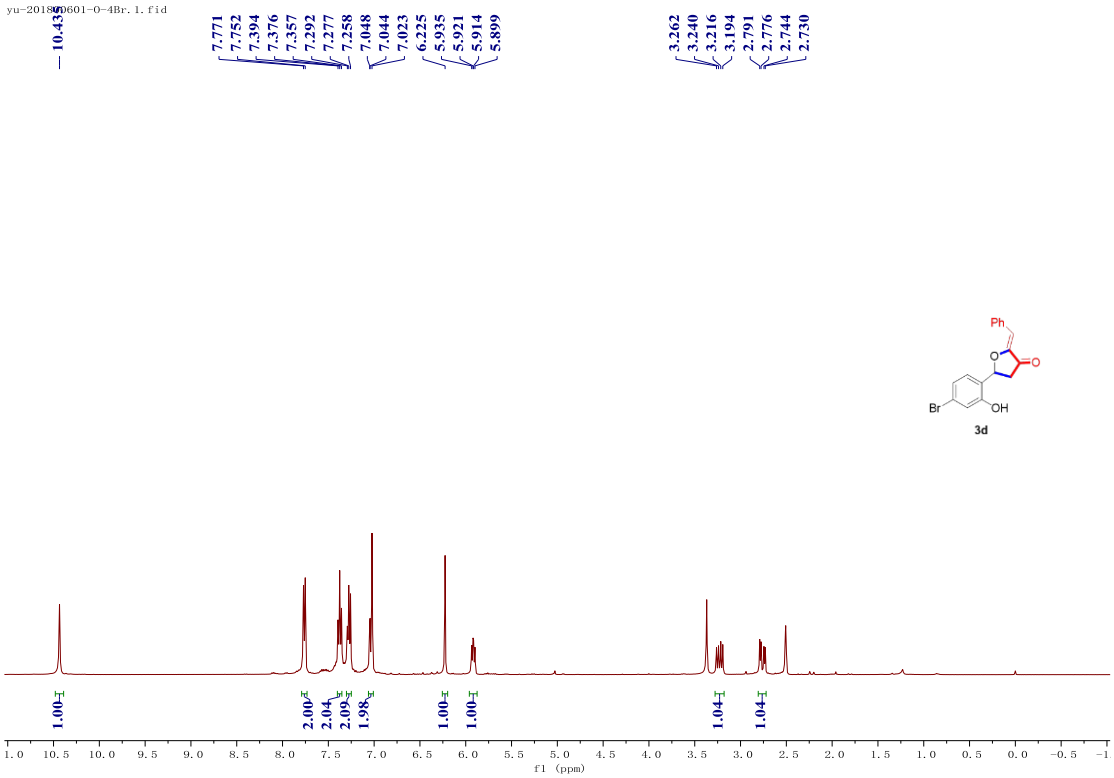


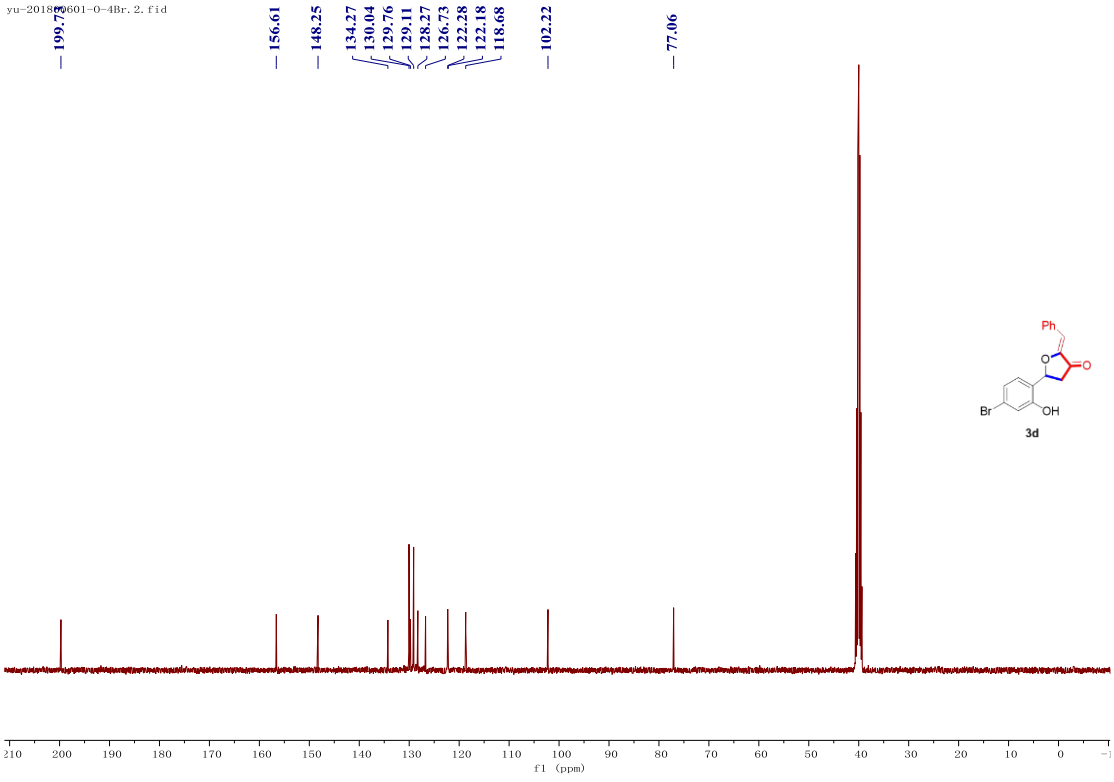
Product **3c**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



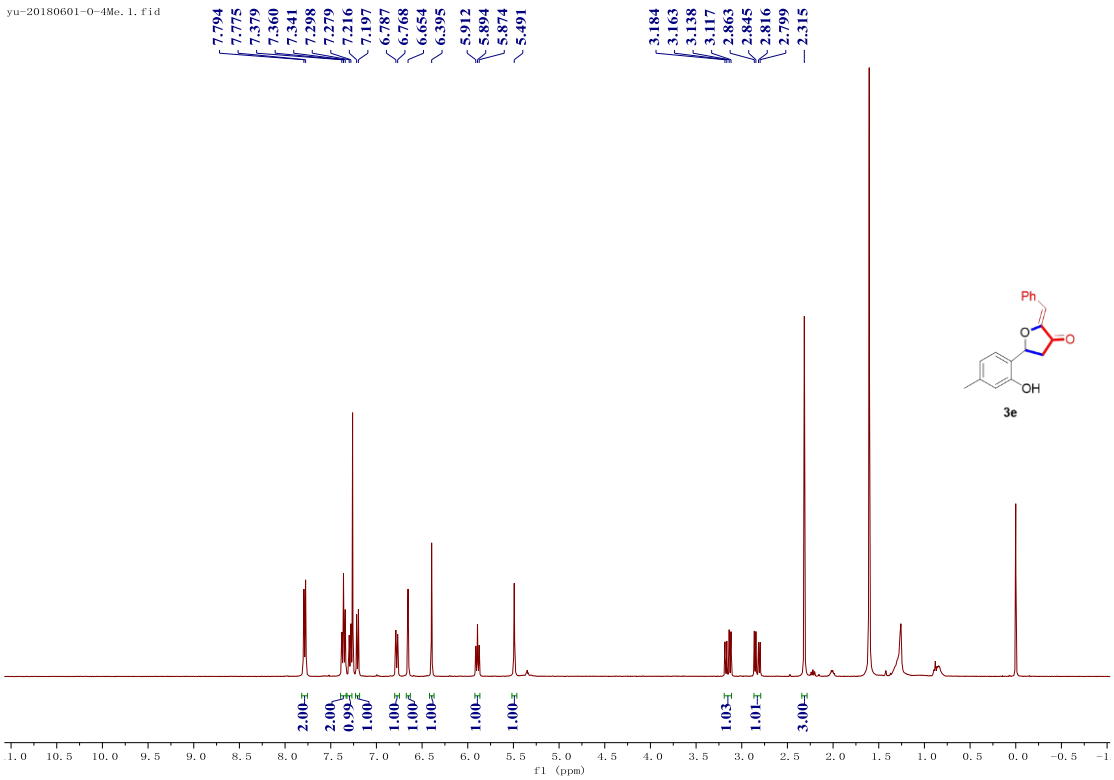


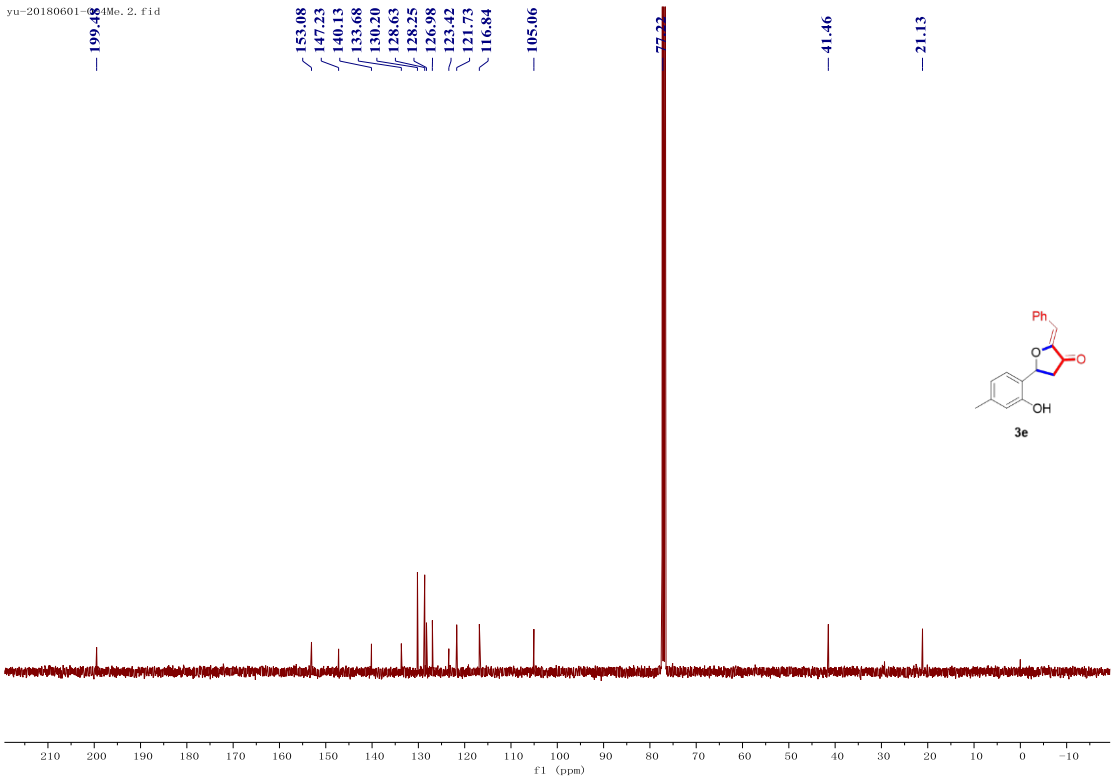
Product **3d**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



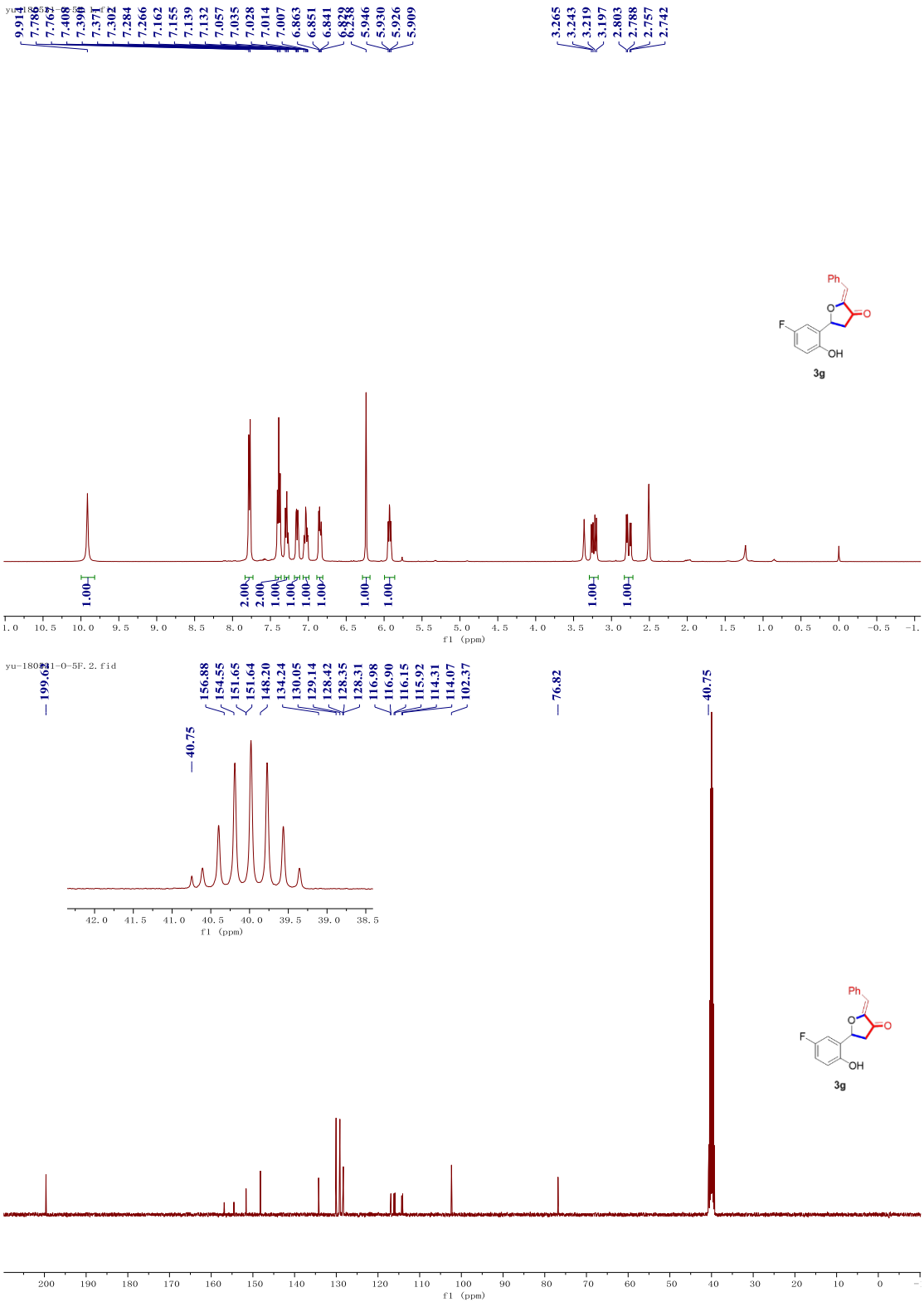


Product **3e**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

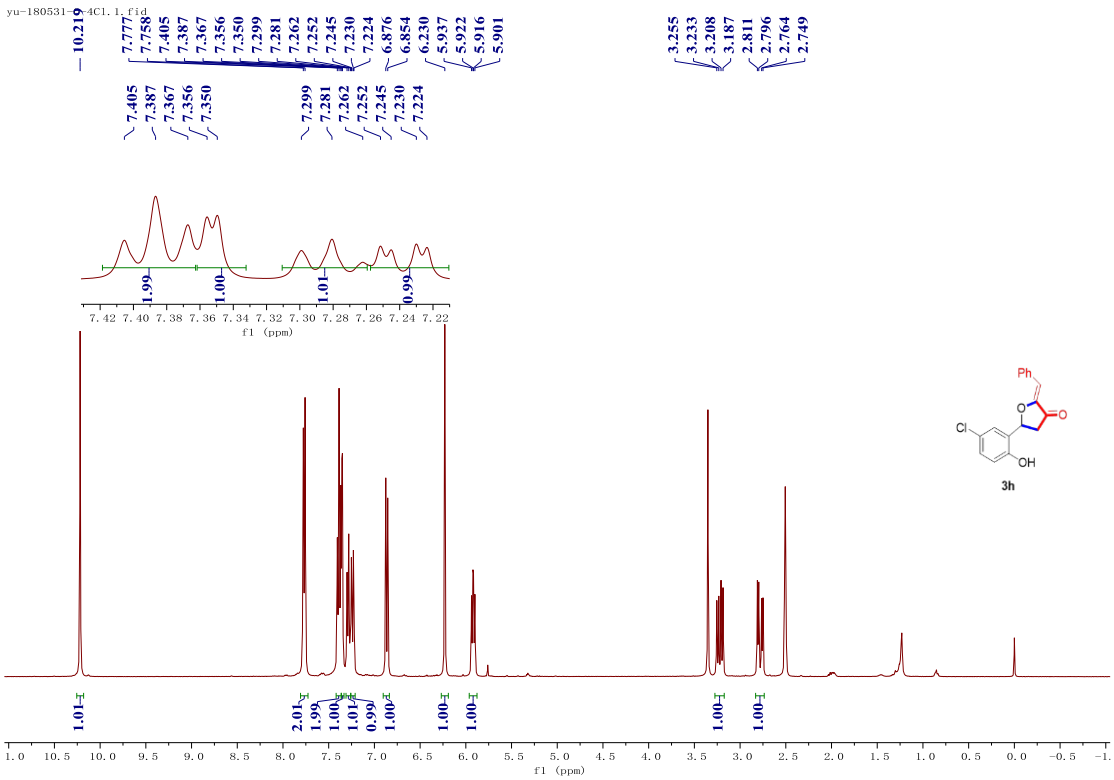


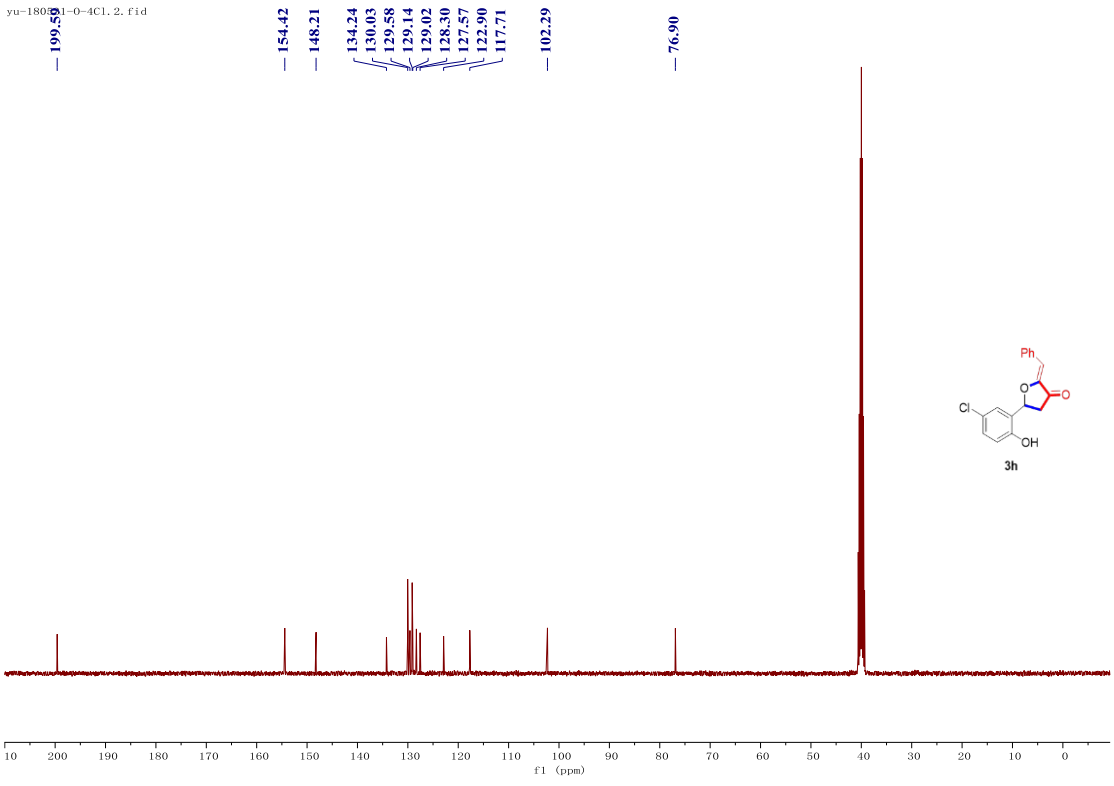


Product **3g**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)

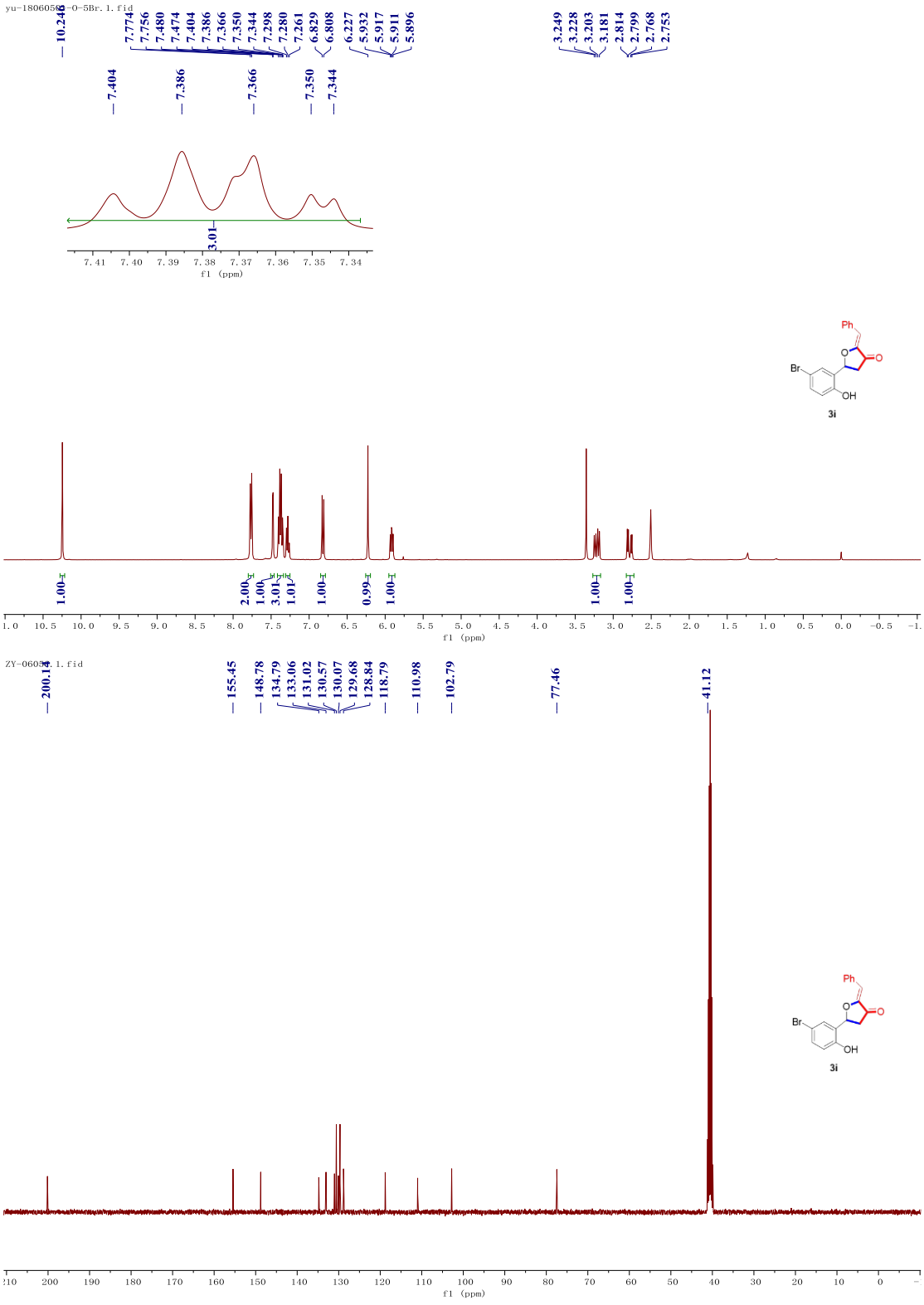


Product **3h**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)

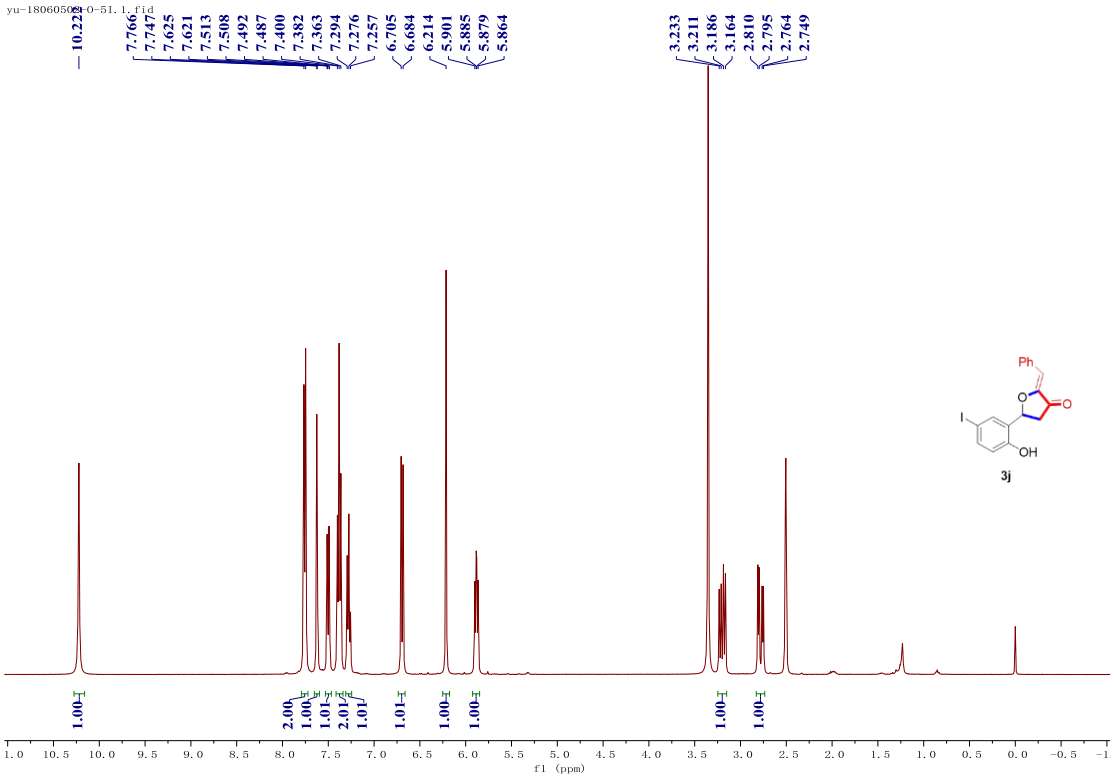


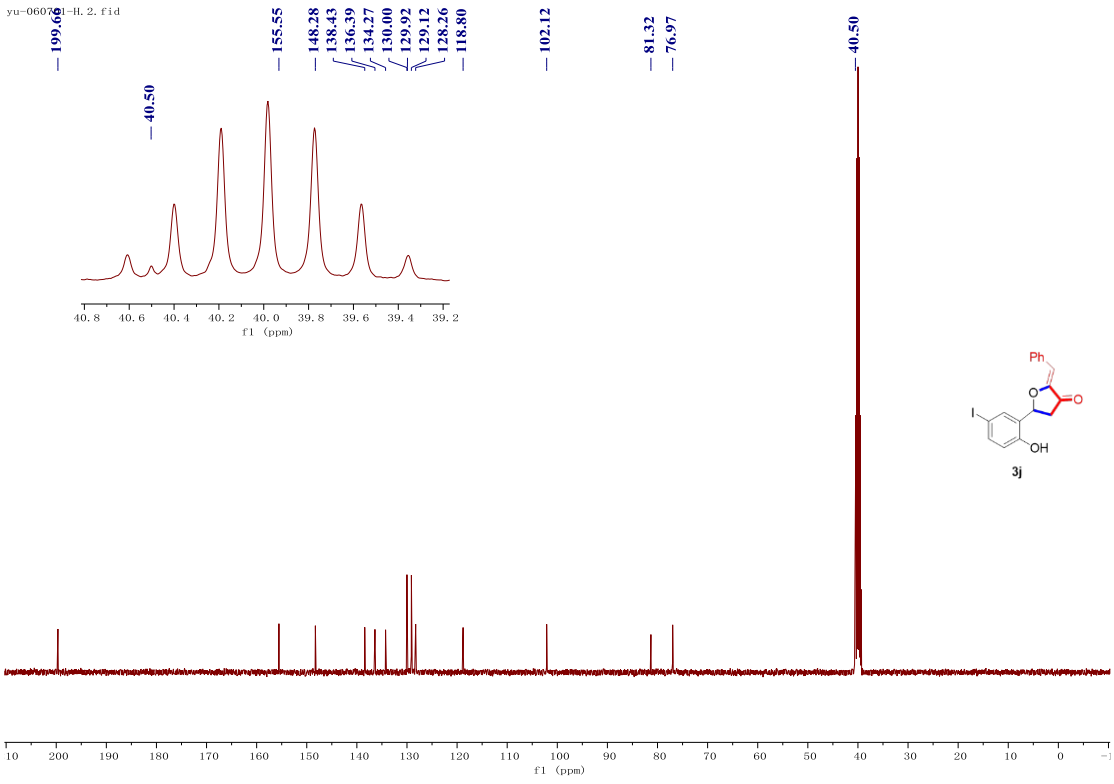


Product **3i**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)

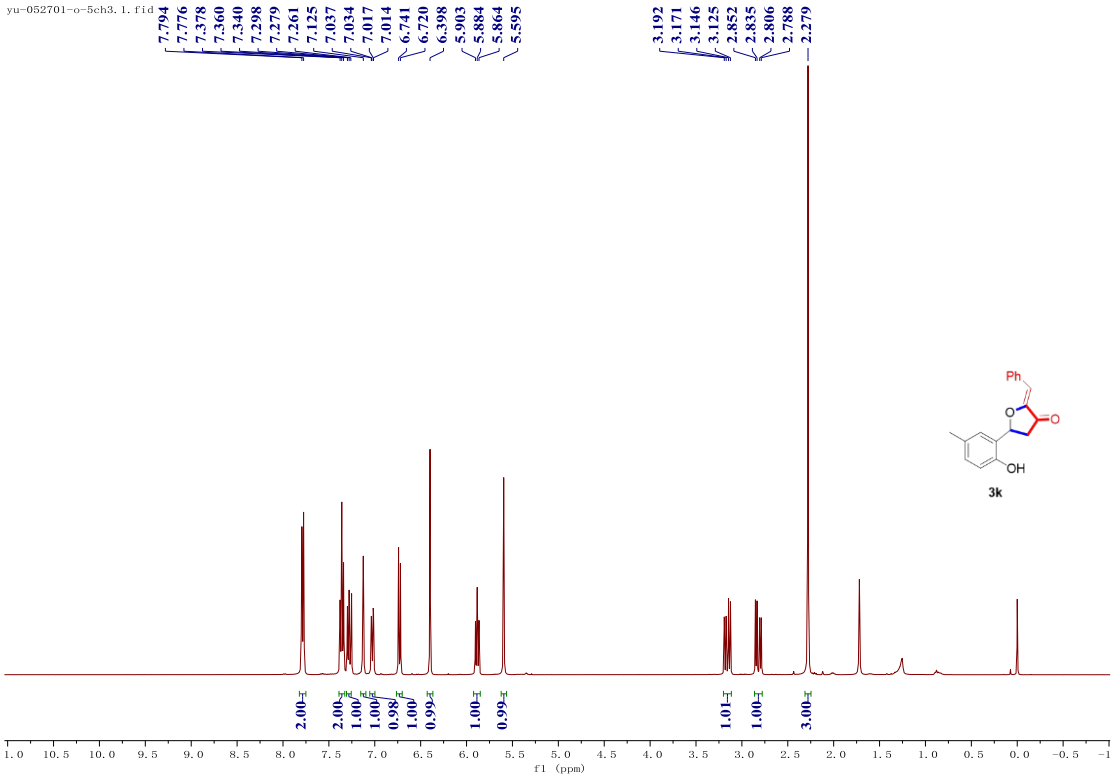


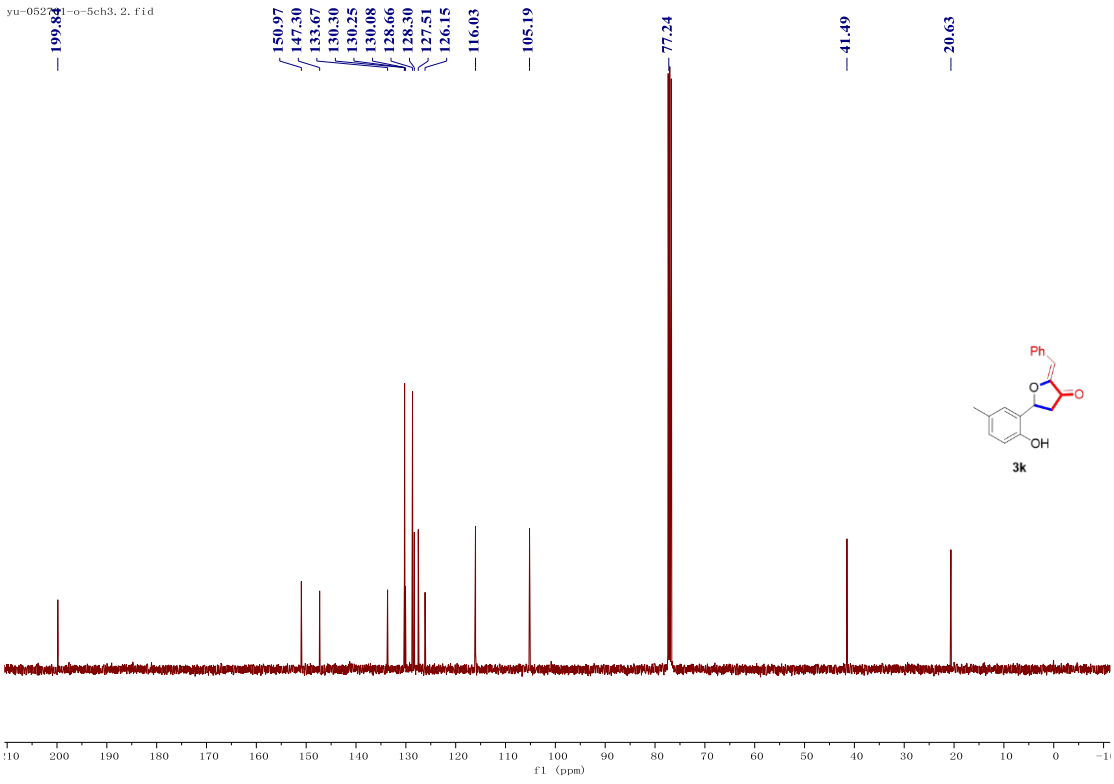
Product **3j**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



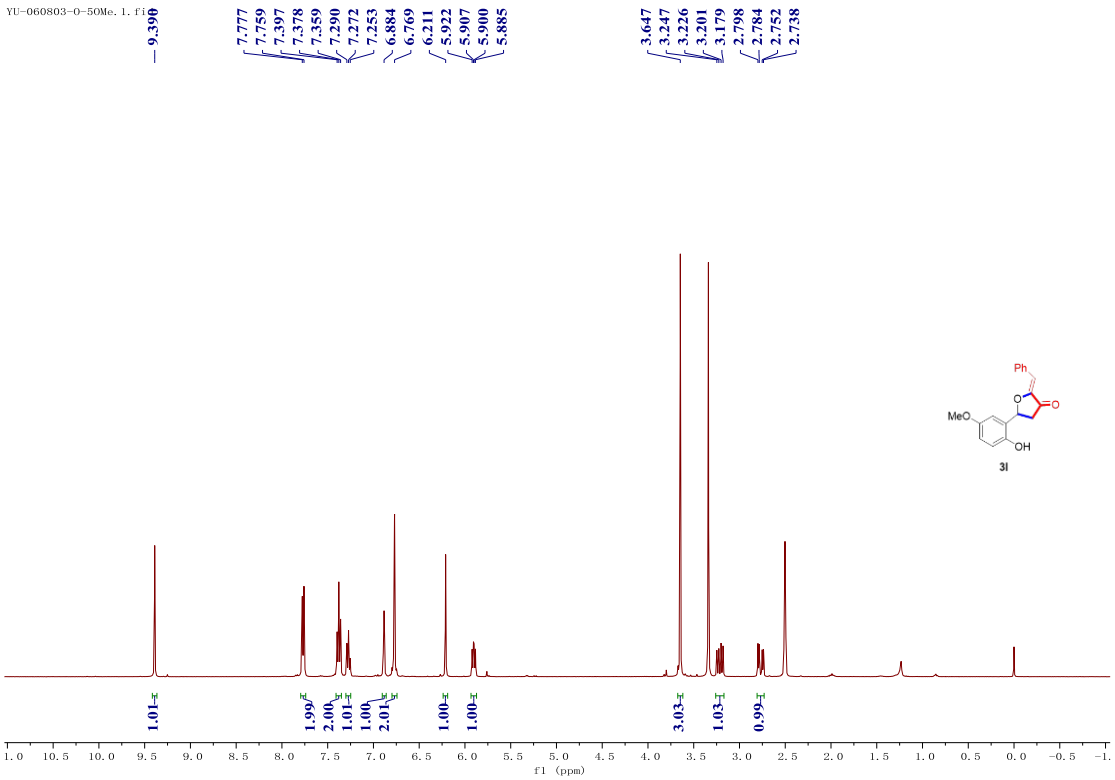


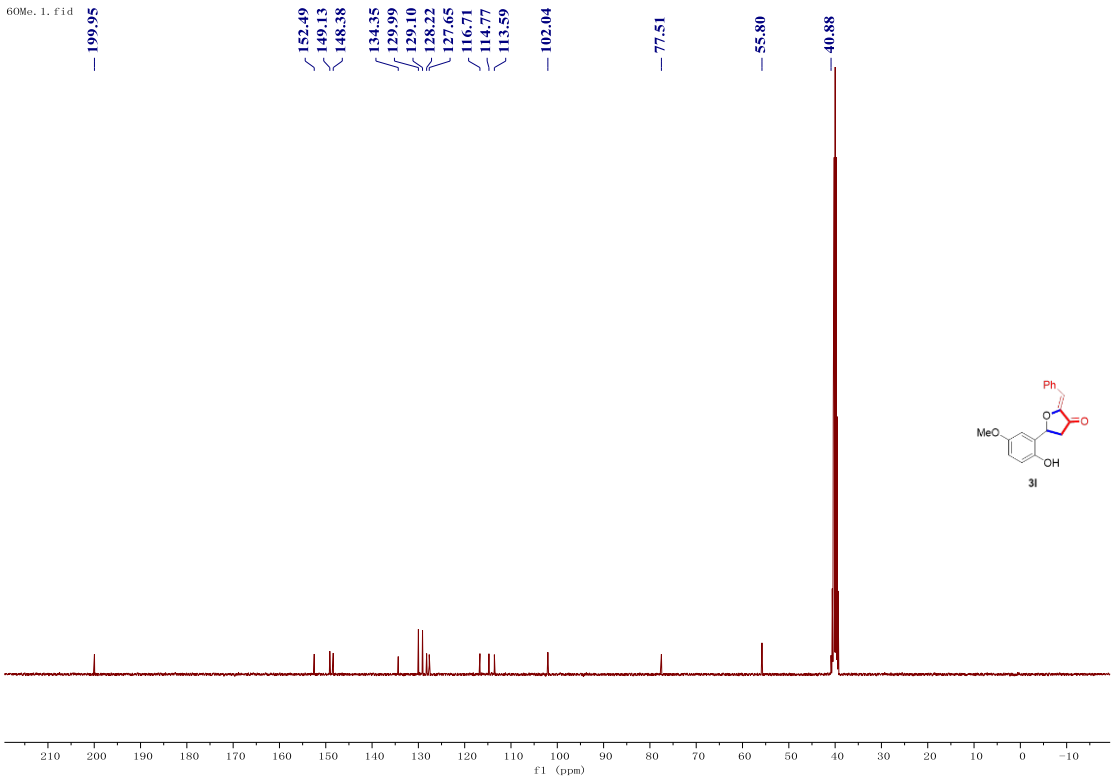
Product **3k**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)



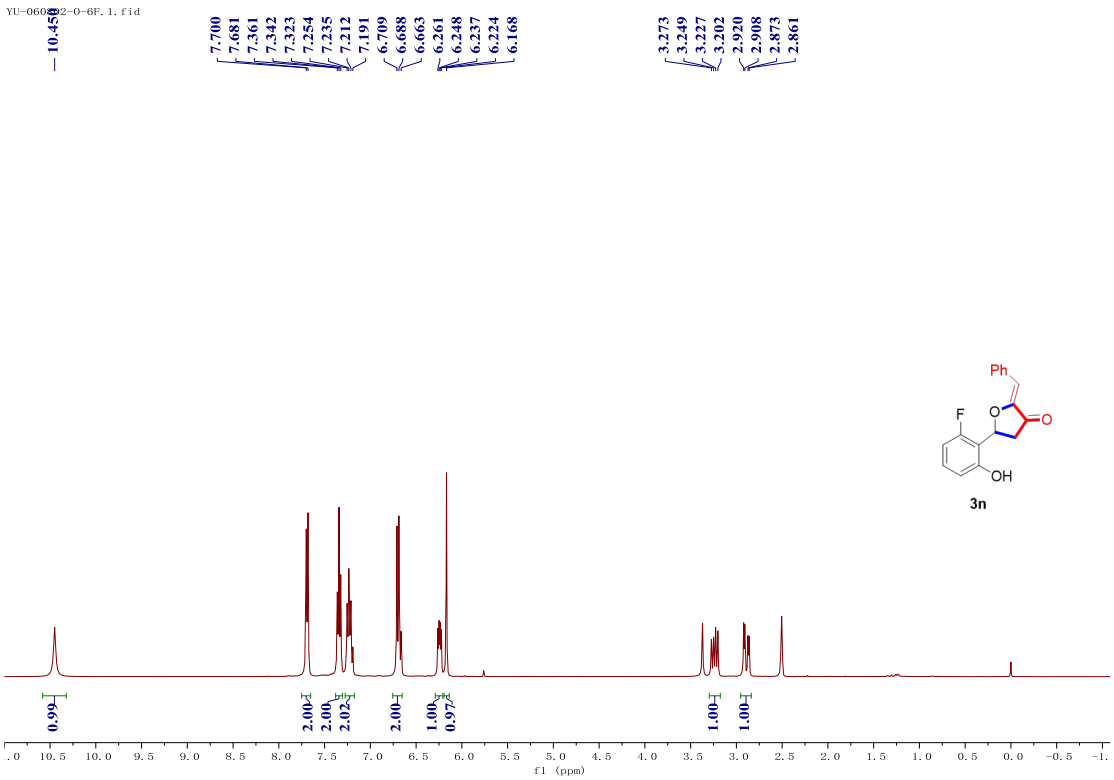


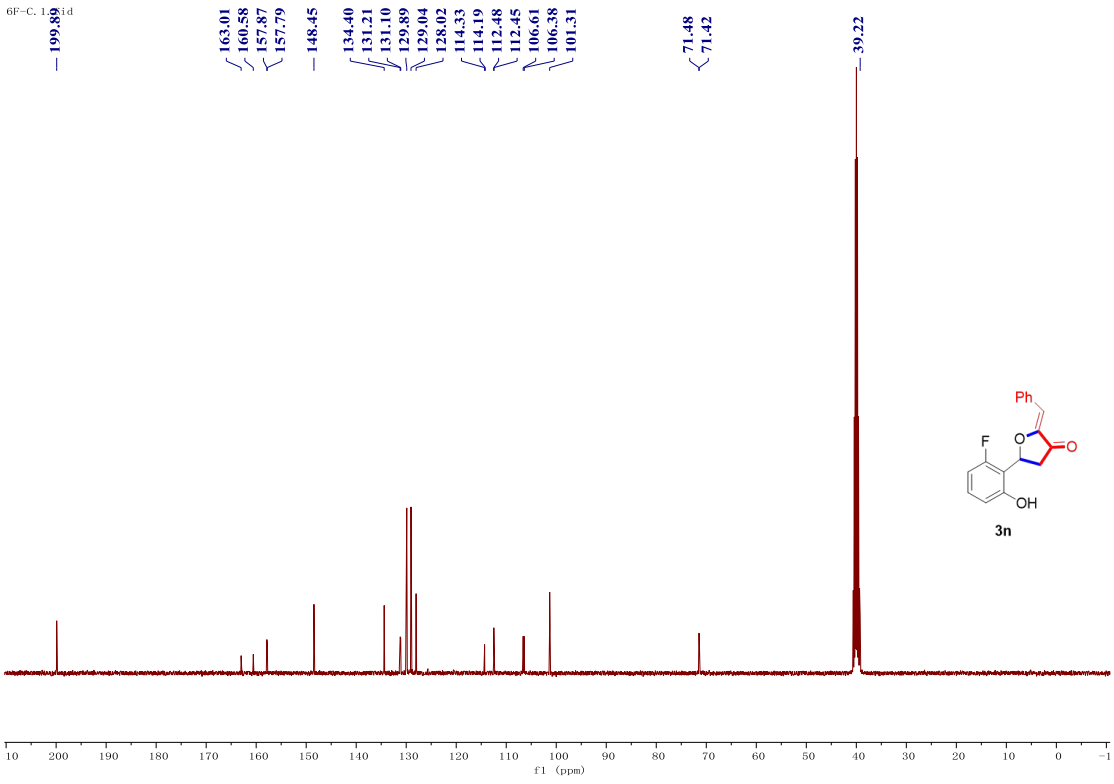
Product **3l**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



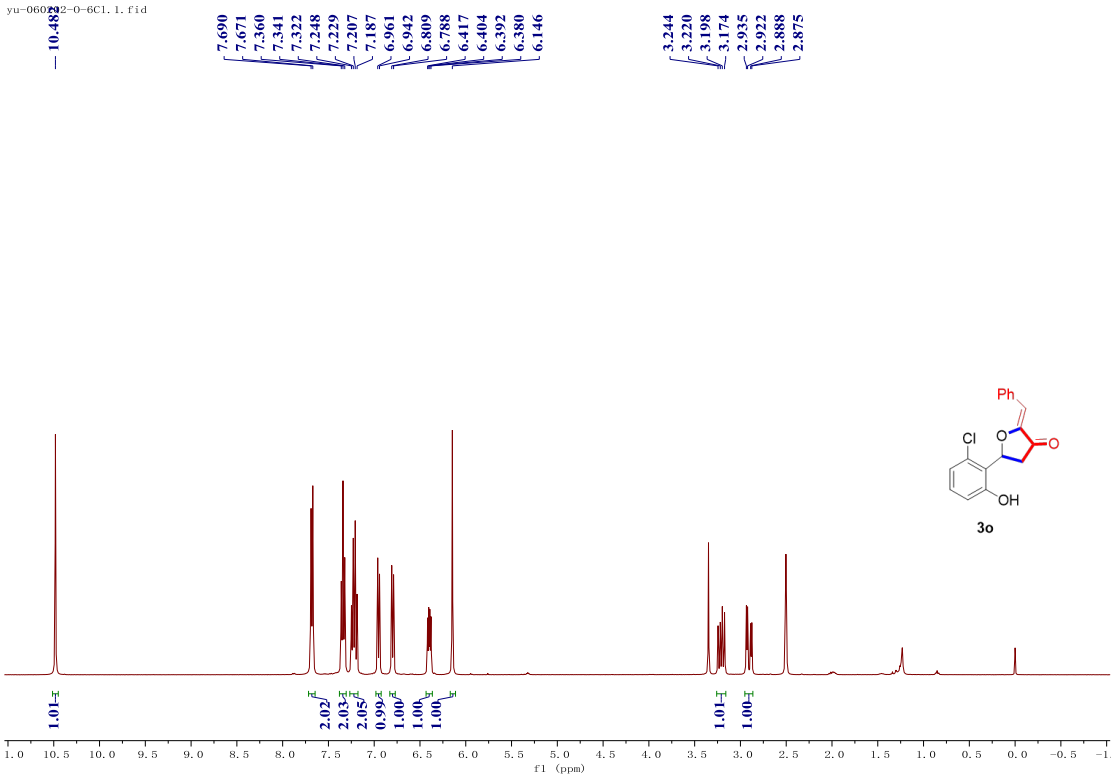


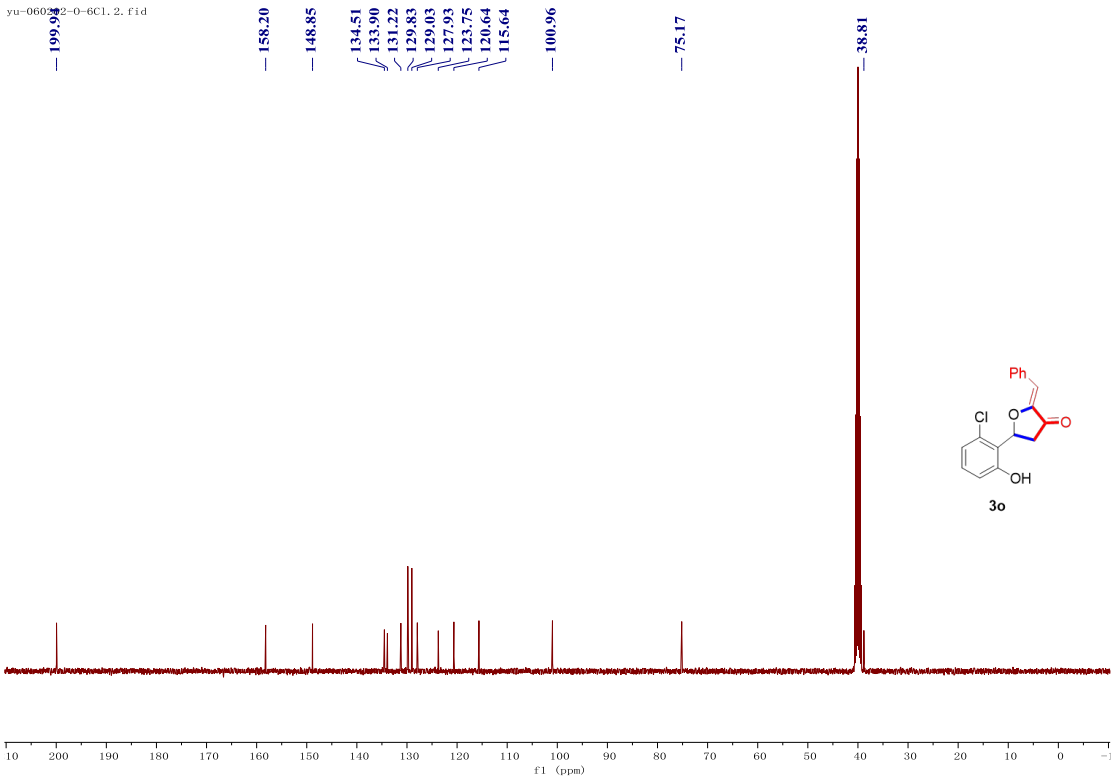
Product **3n**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



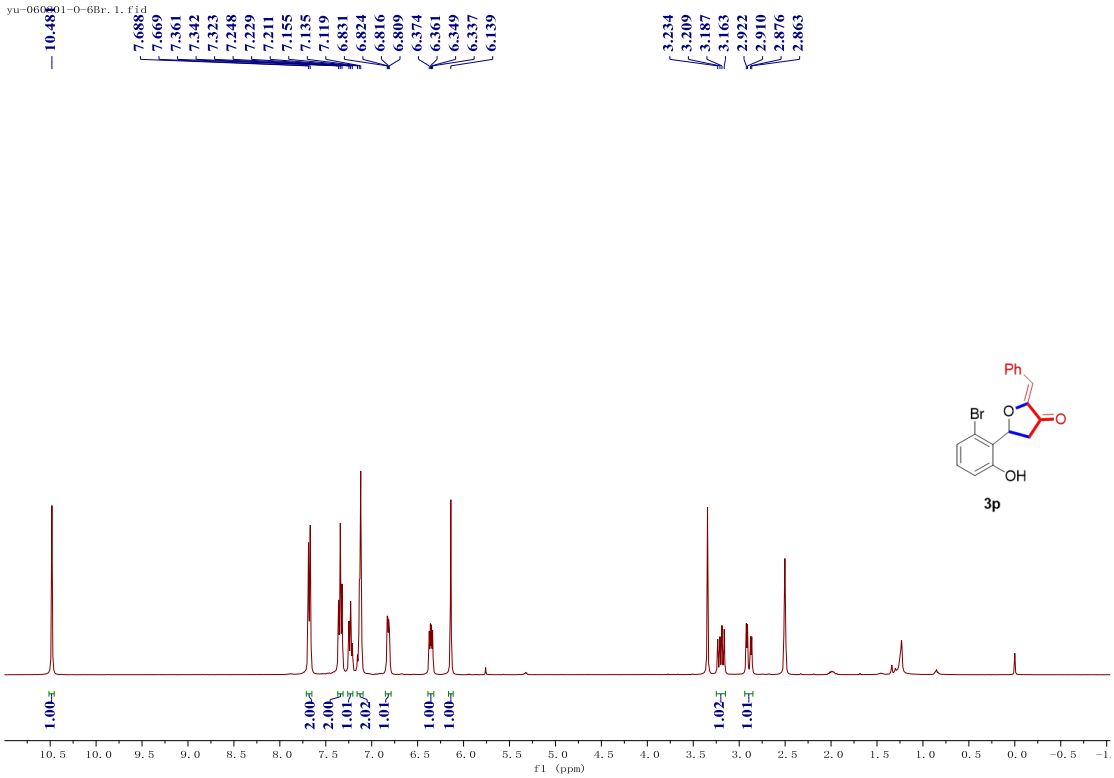


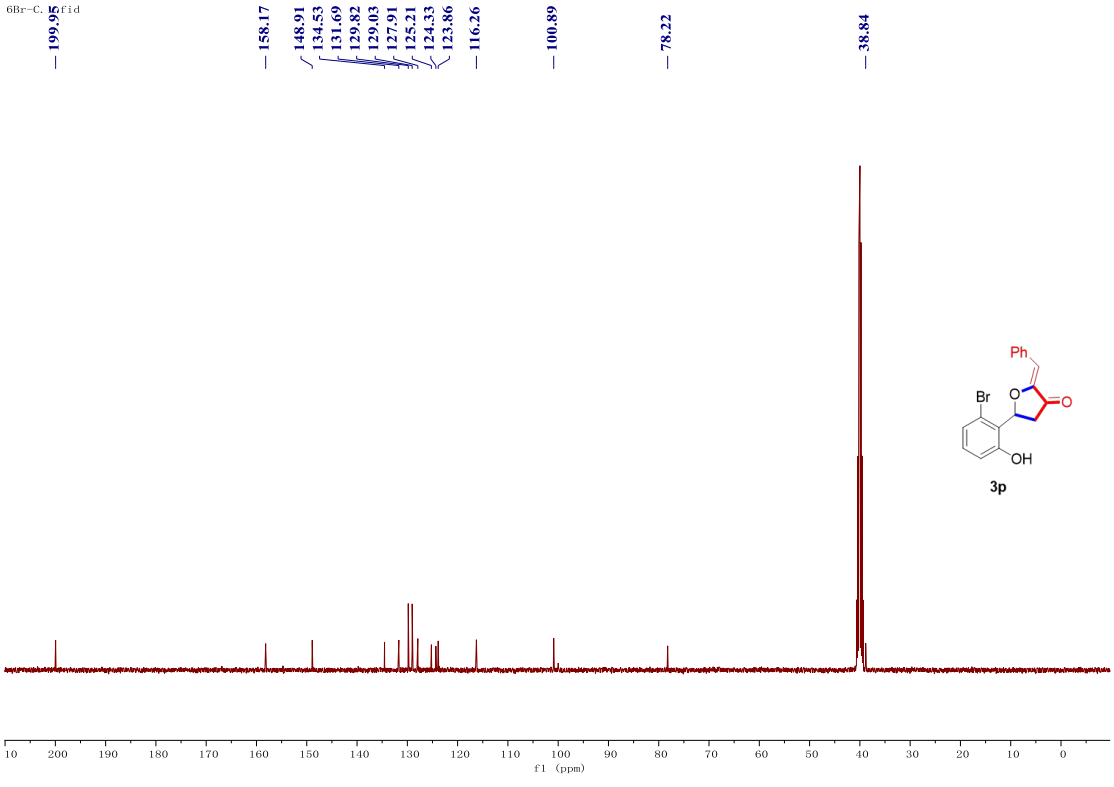
Product **3o**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



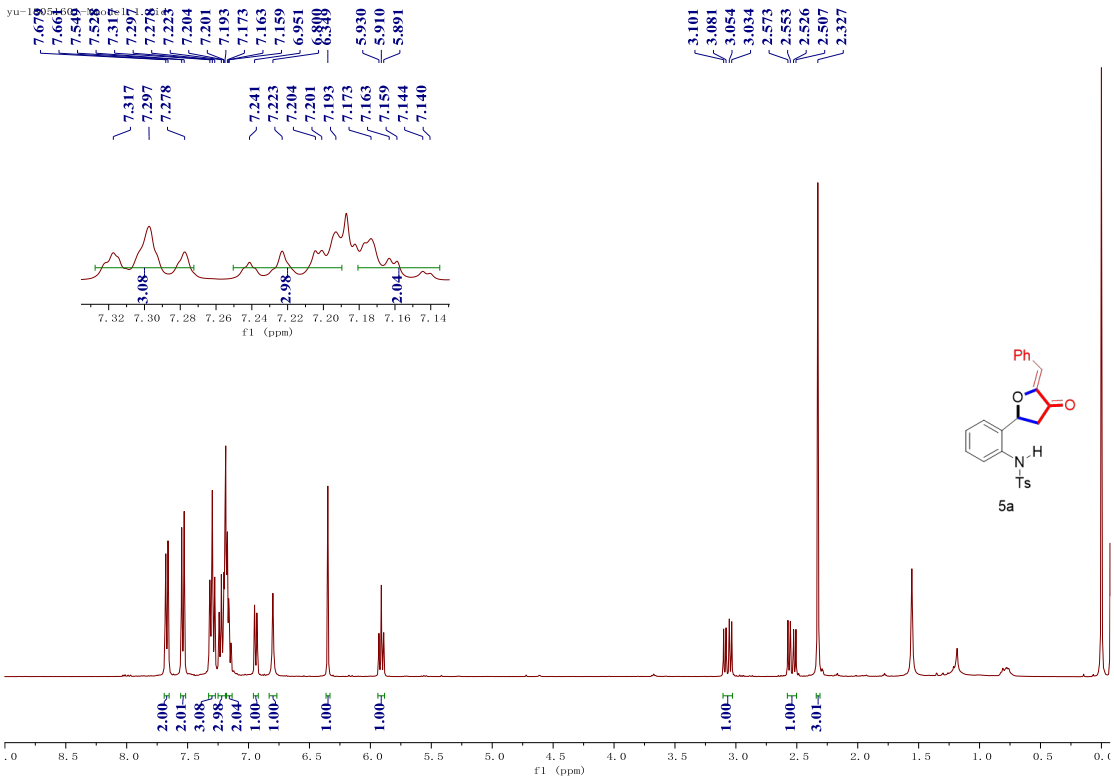


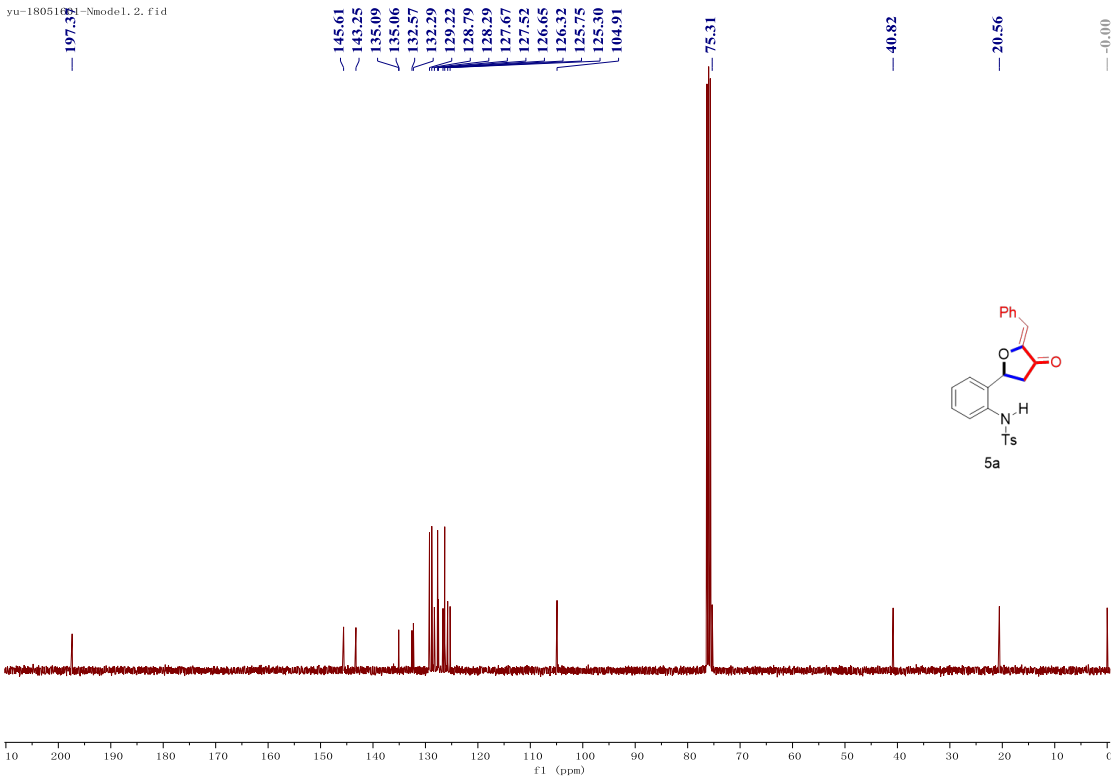
Product **3p**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



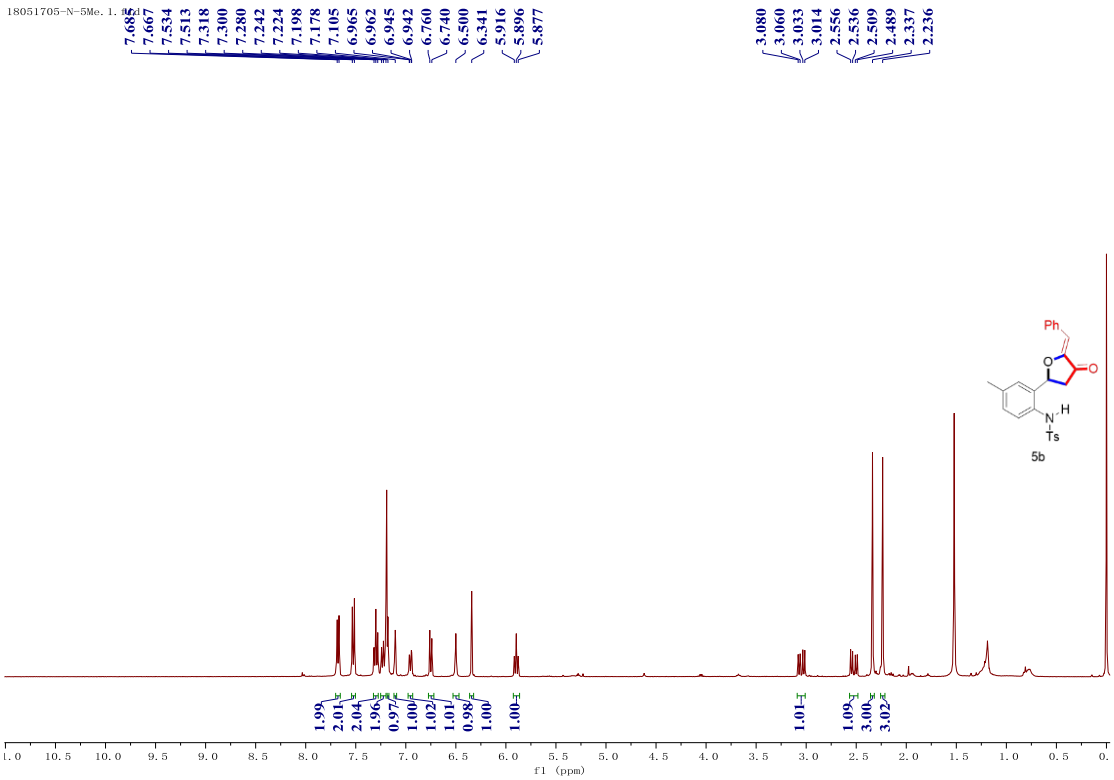


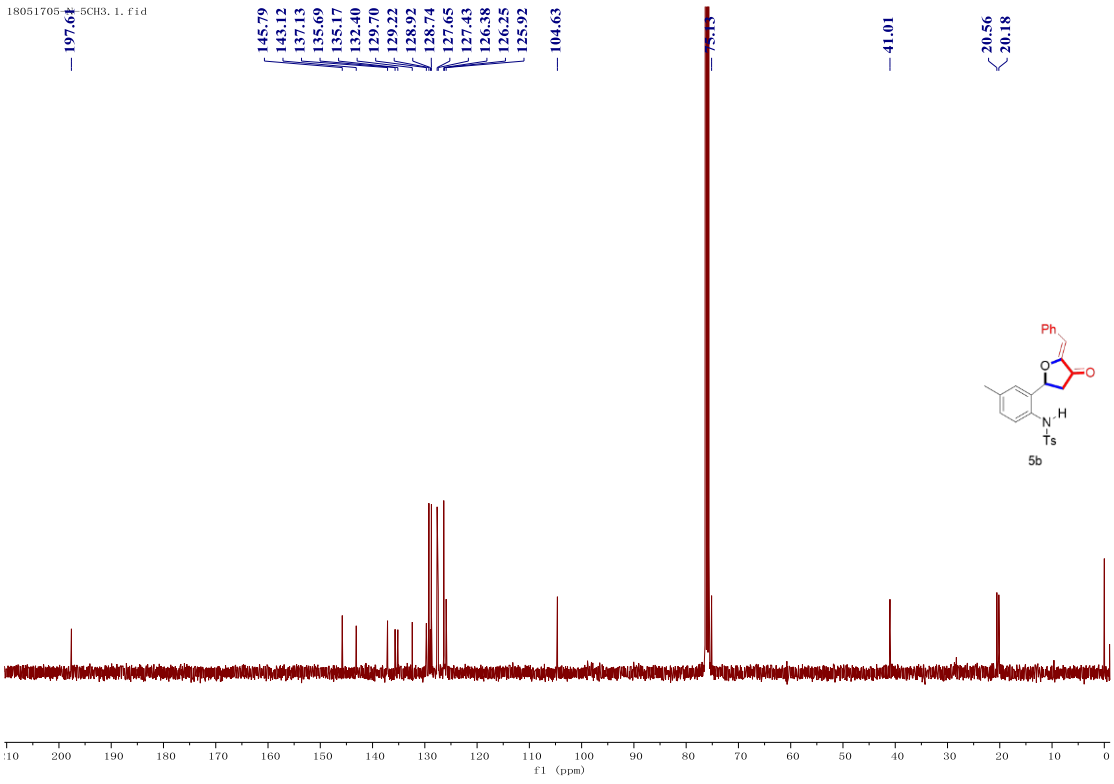
Product **5a**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)



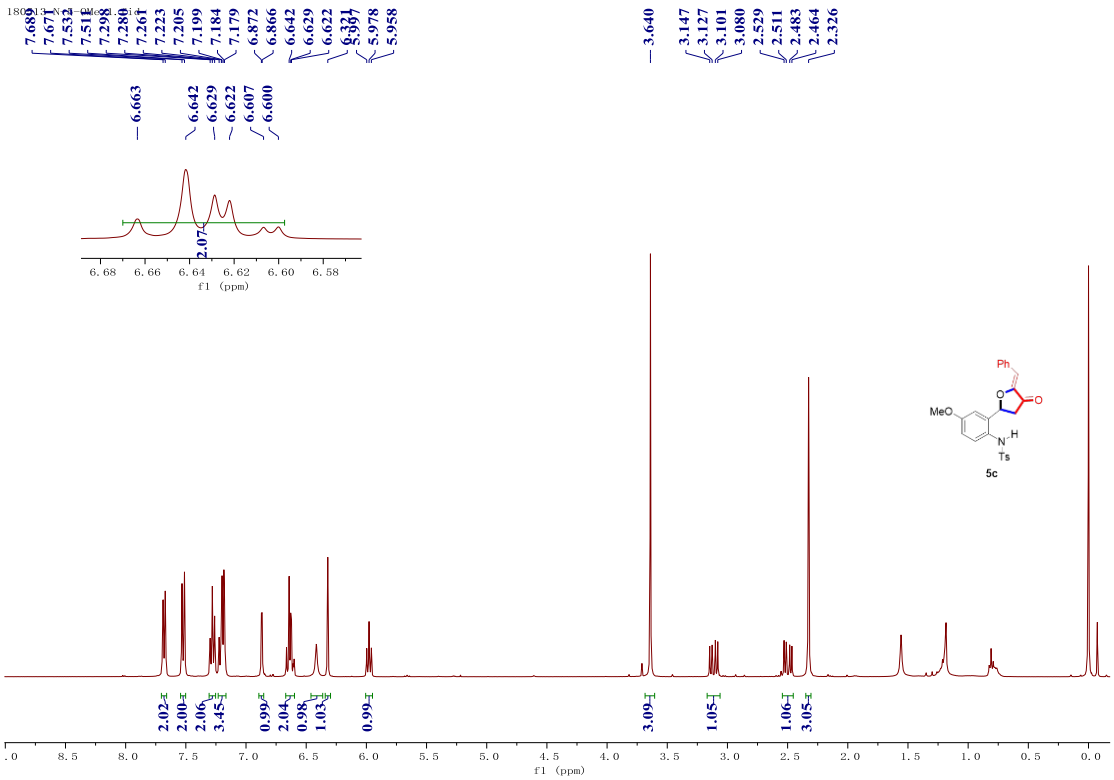


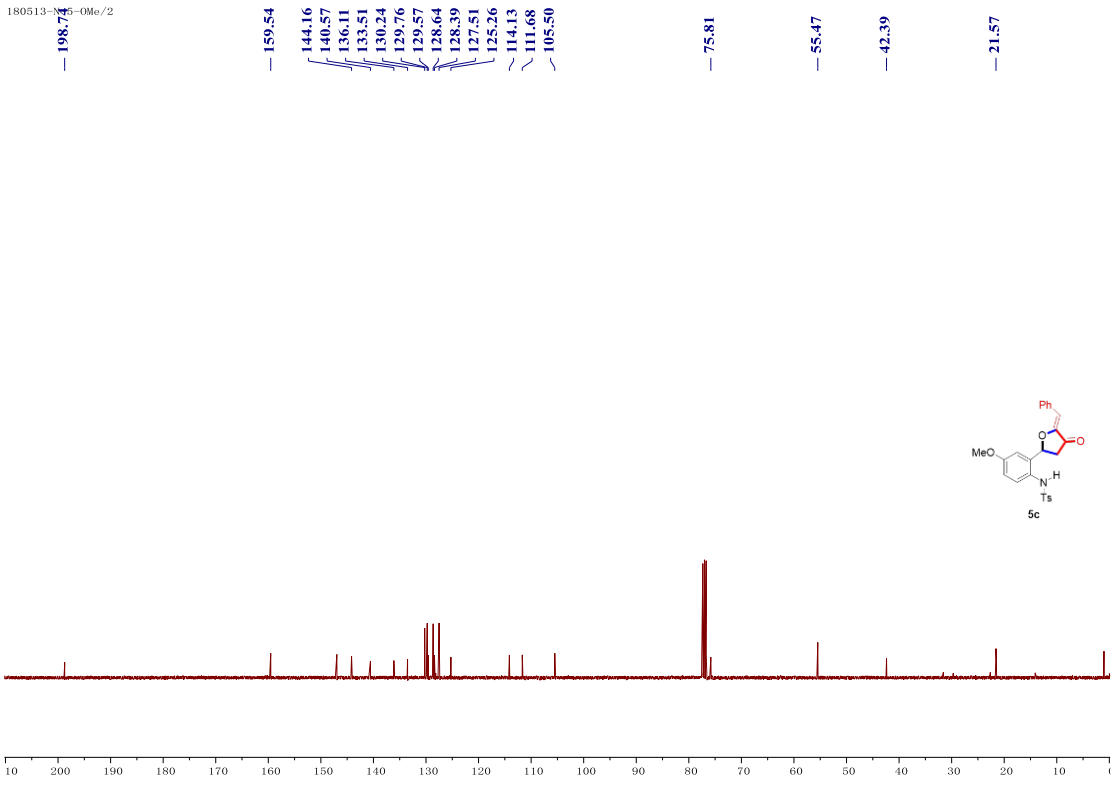
Product **5b**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)



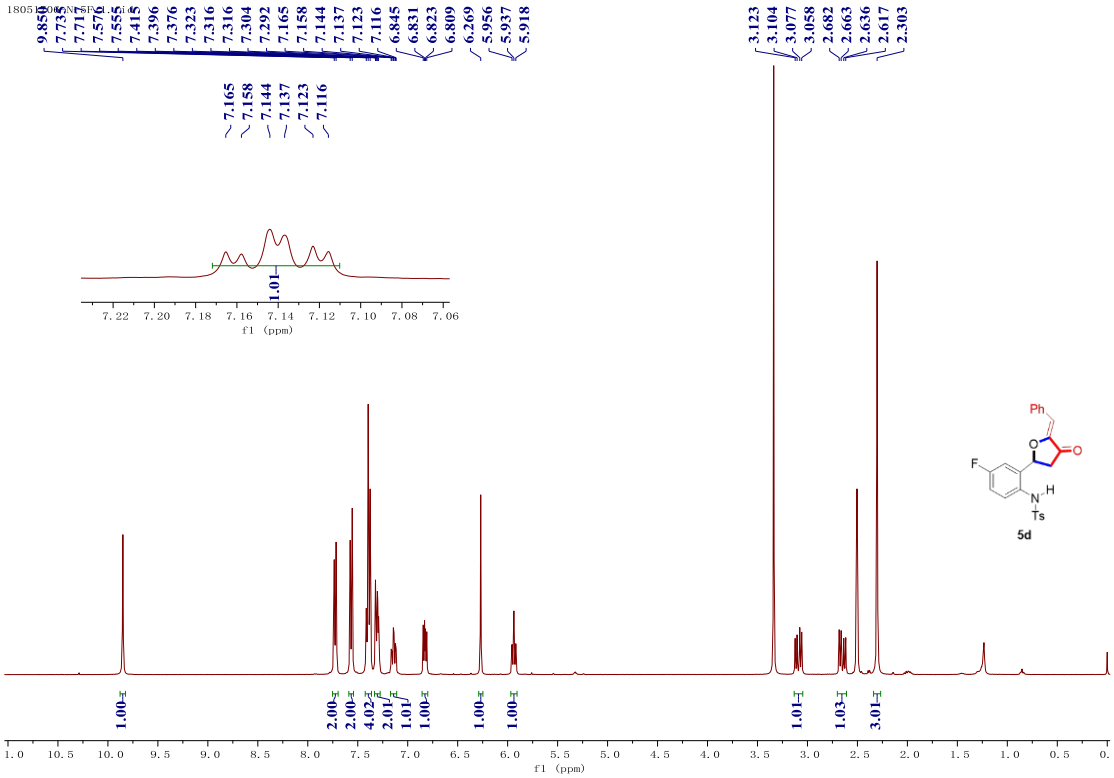


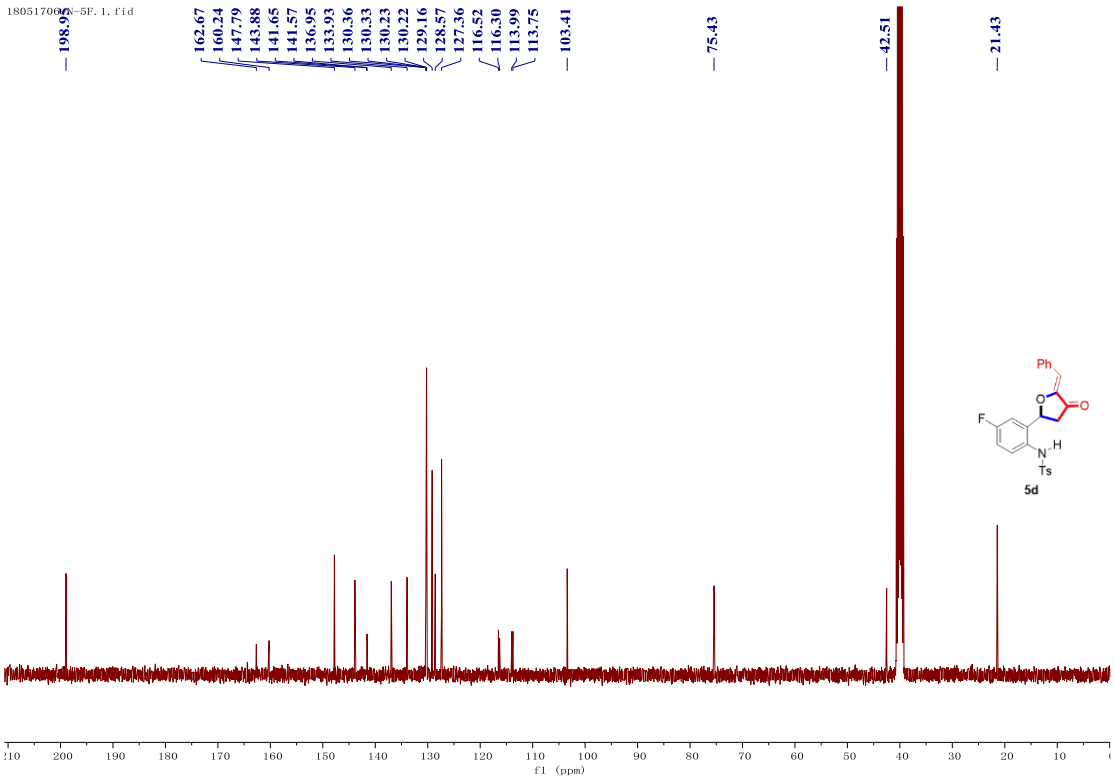
Product **5c**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)



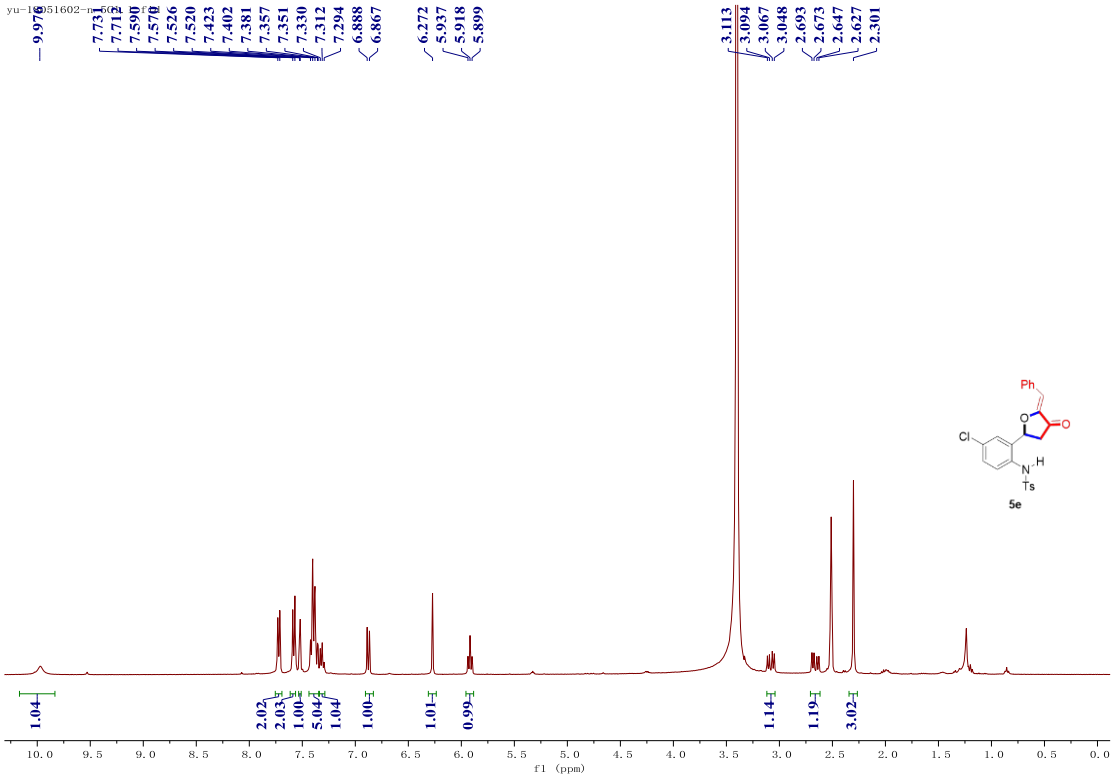


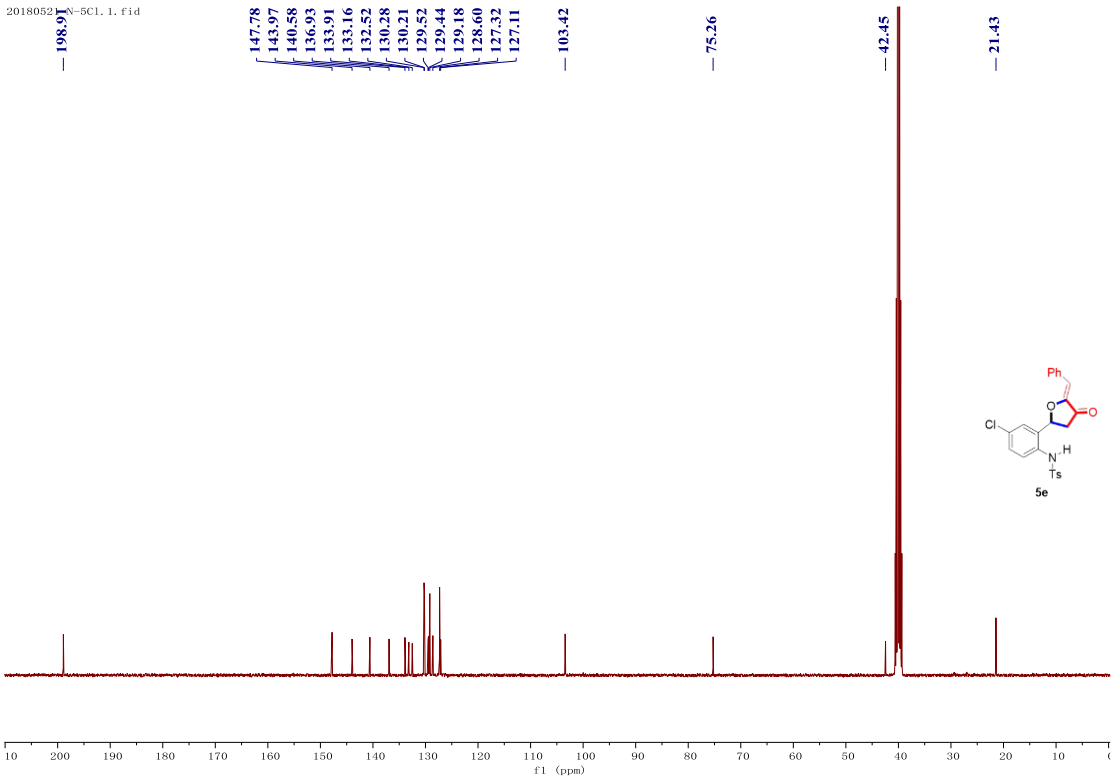
Product **5d**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



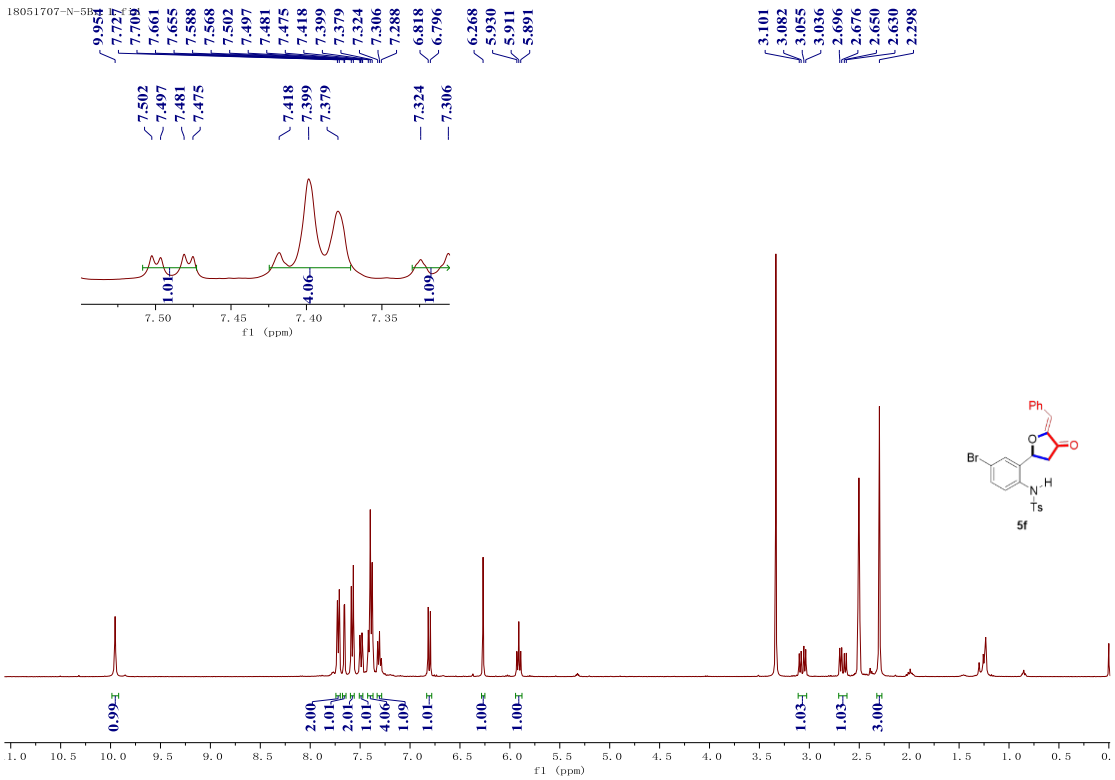


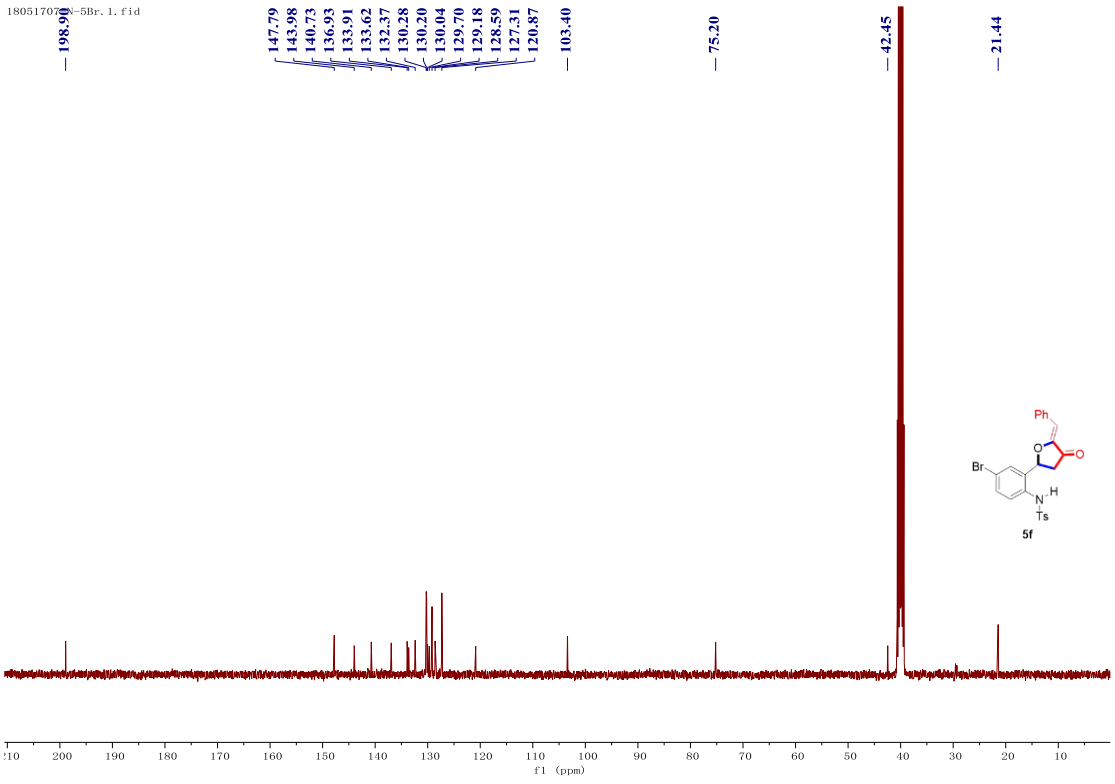
Product **5e**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



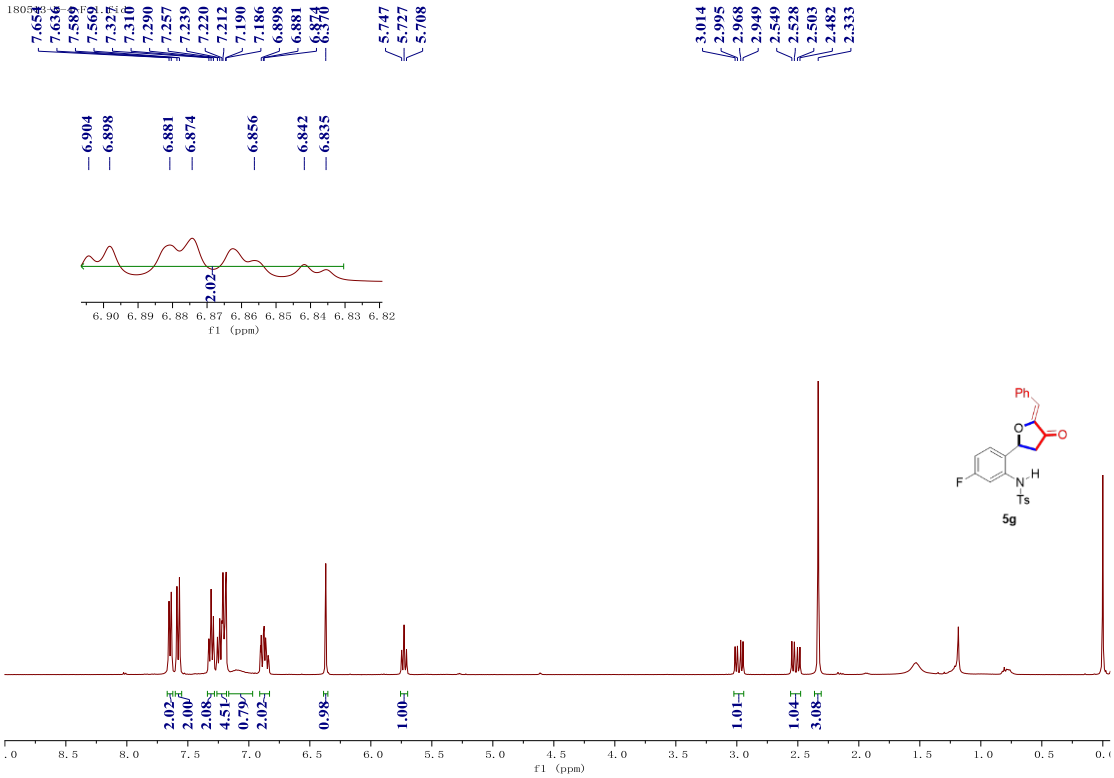


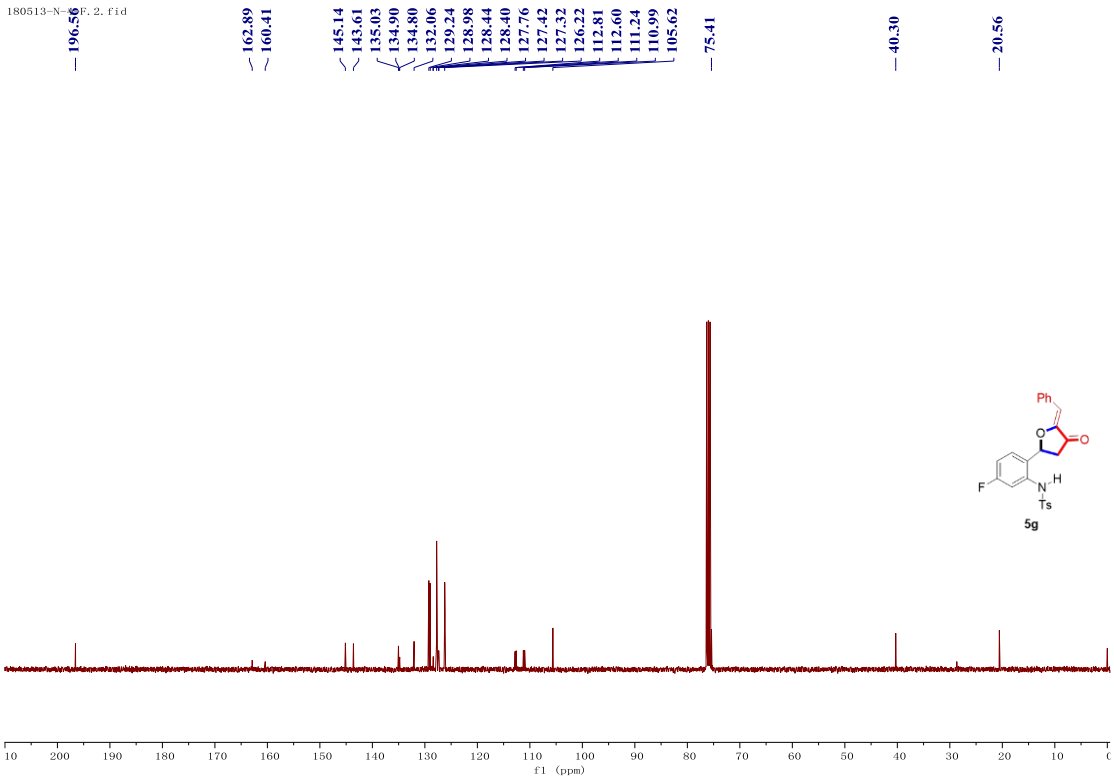
Product **5f**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



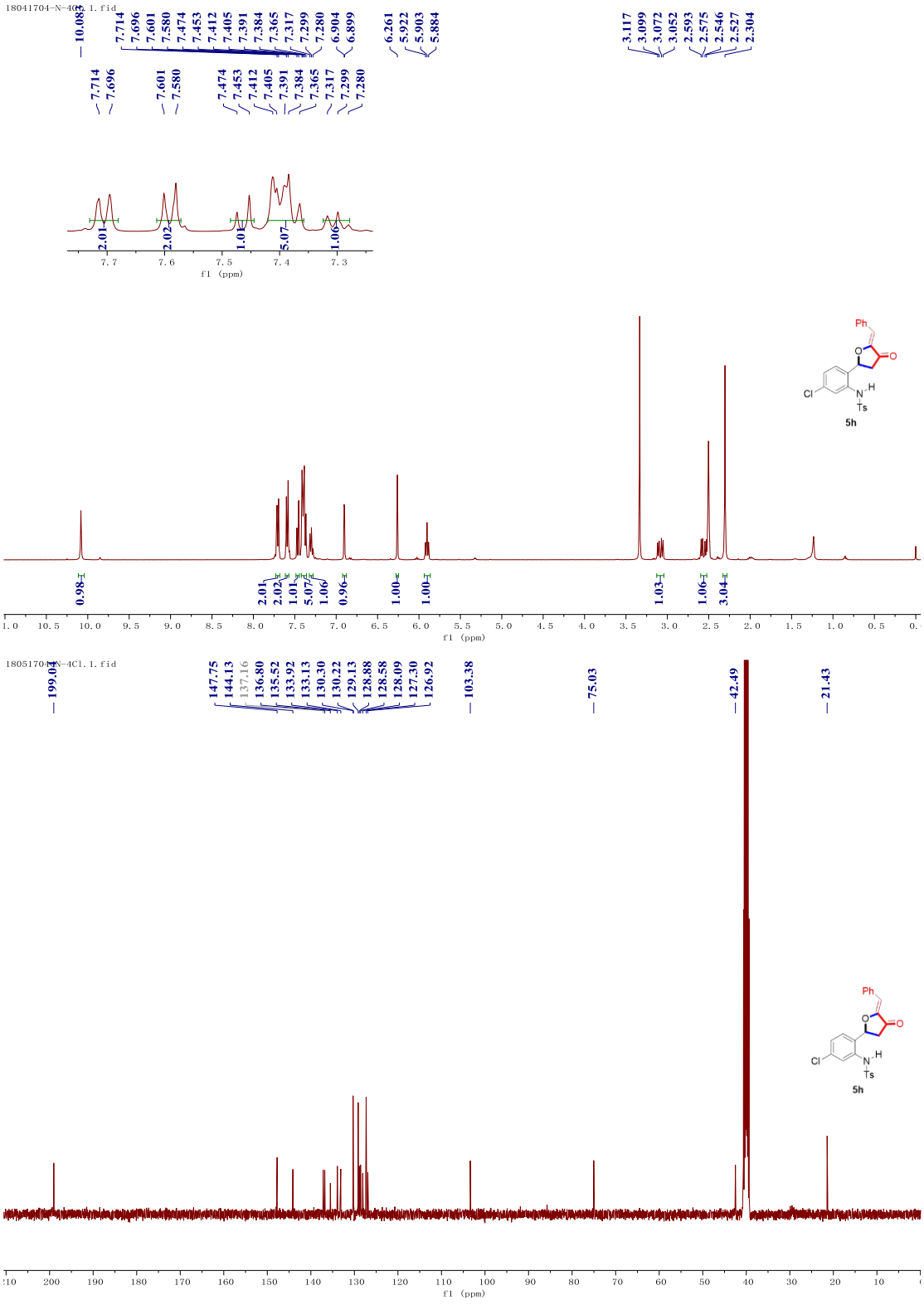


Product **5g**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

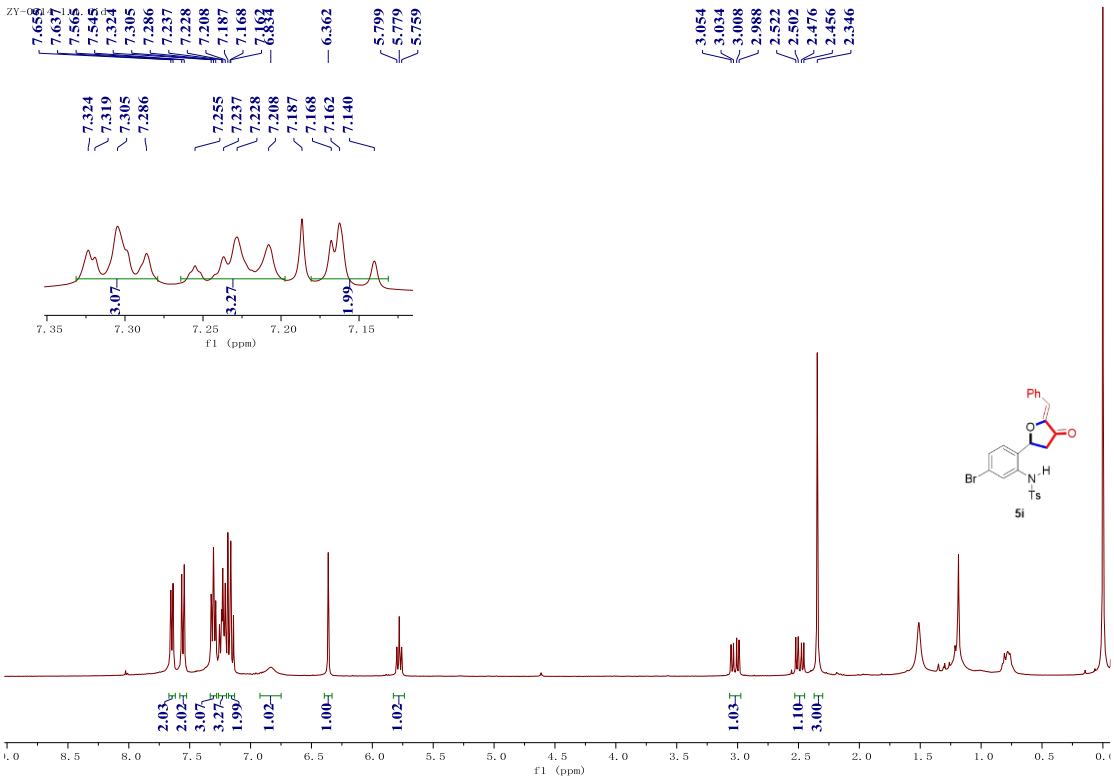


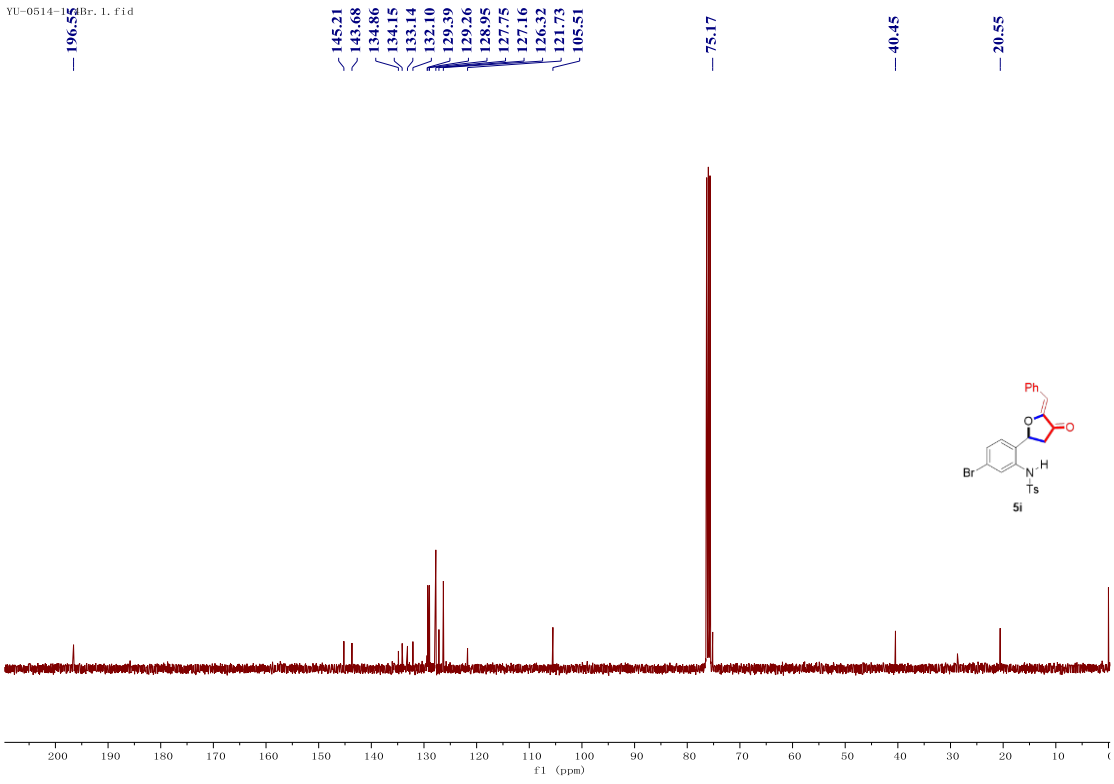


Product **5h**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)

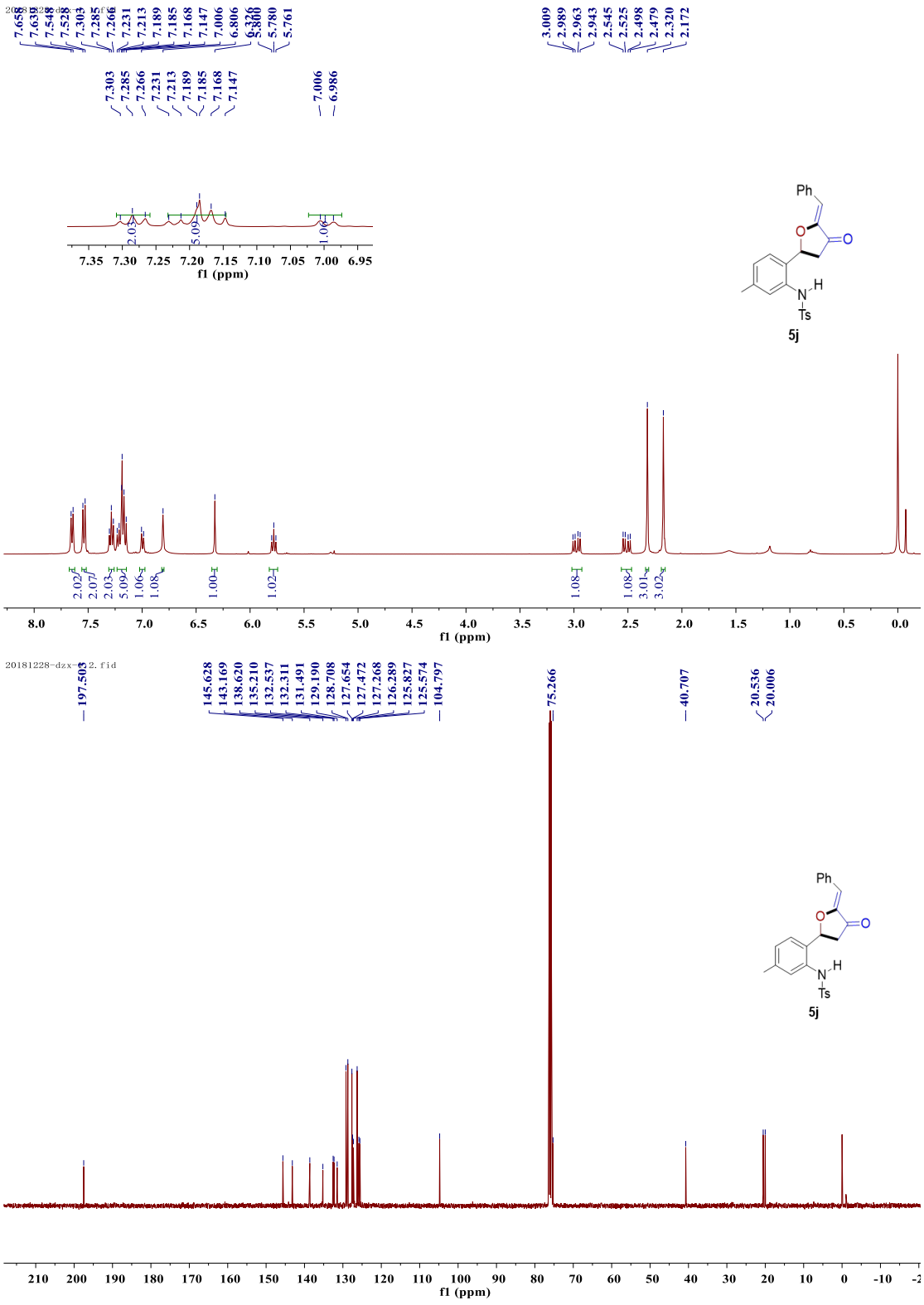


Product **5i**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

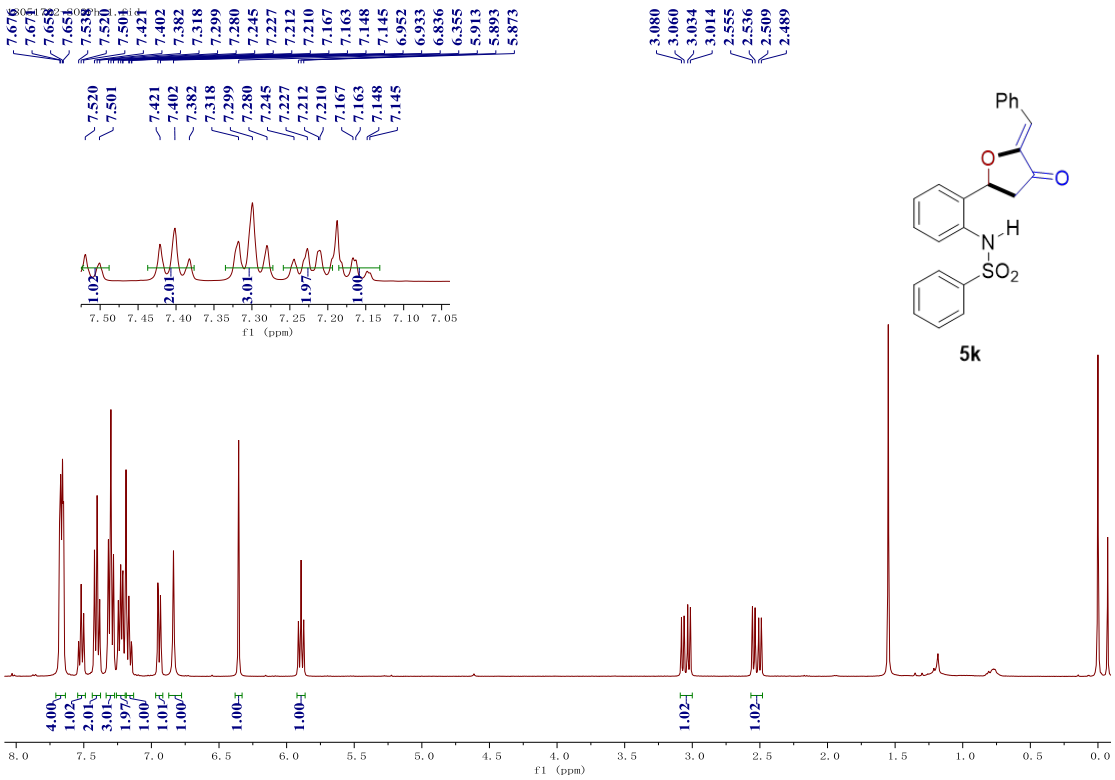


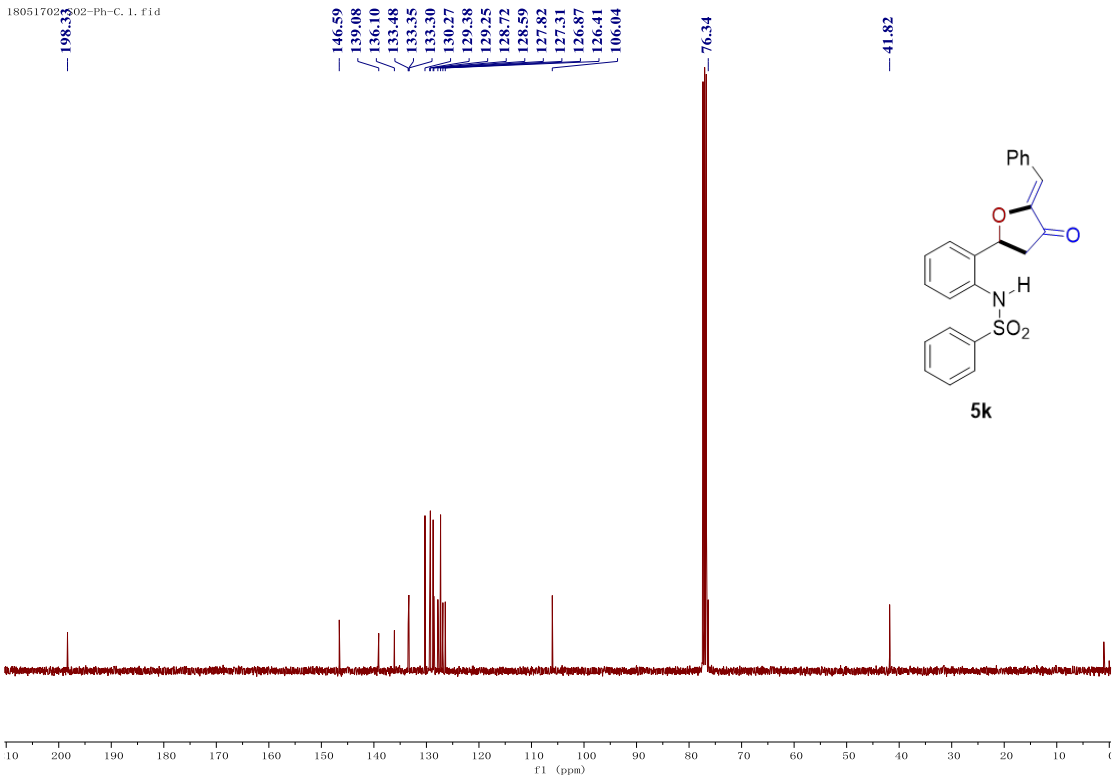


Product **5j**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

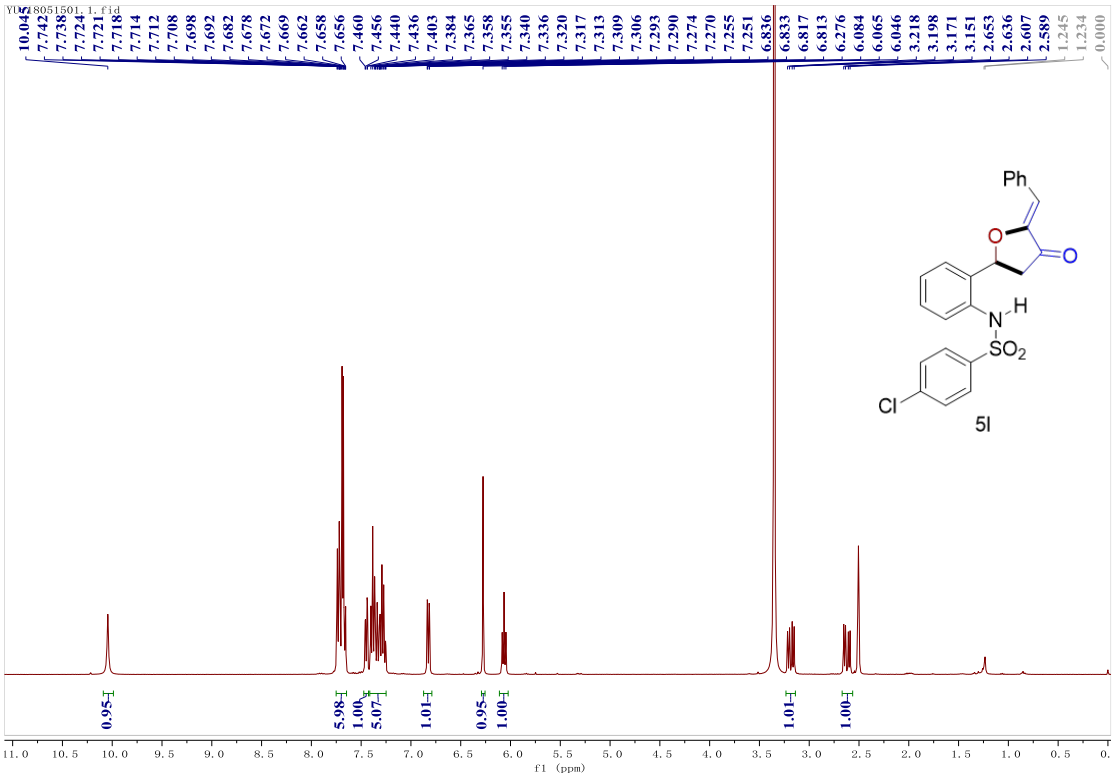


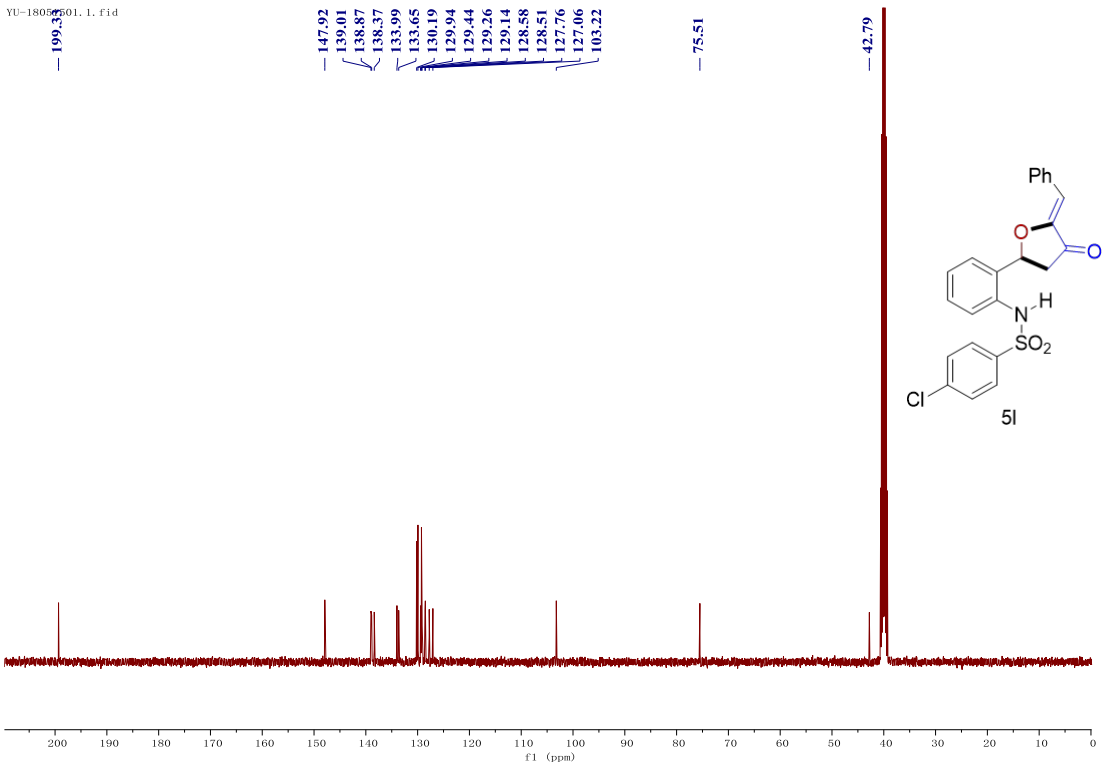
Product **5k**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)



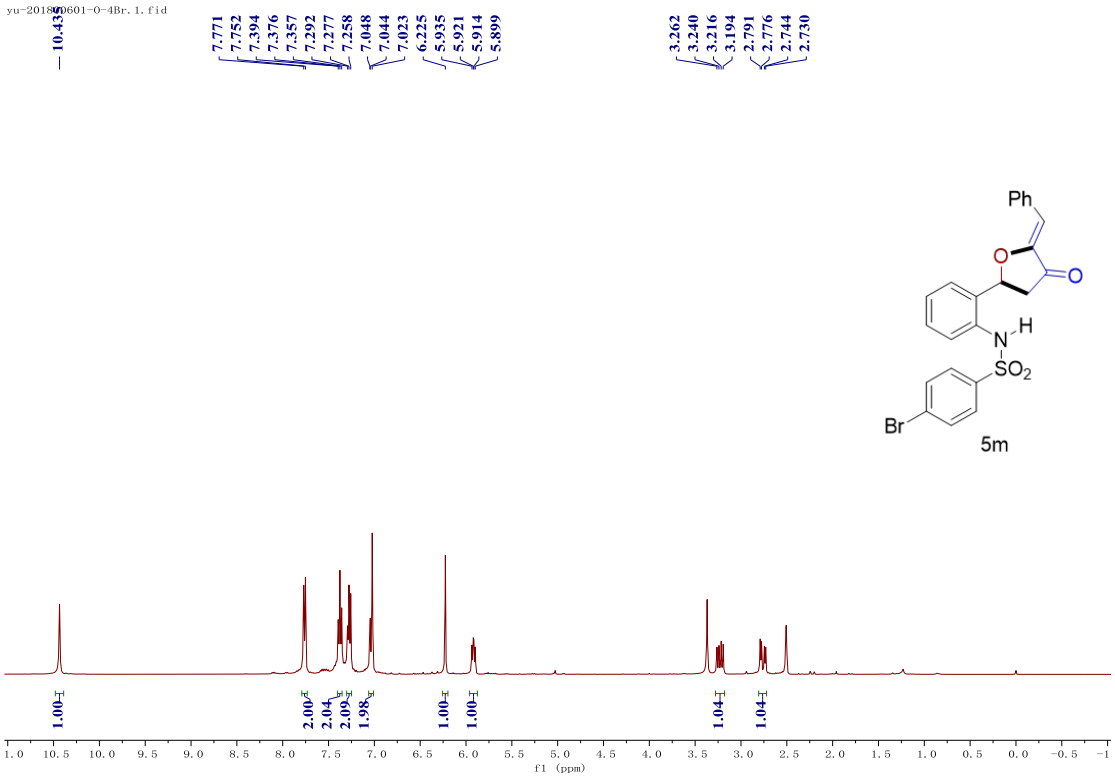


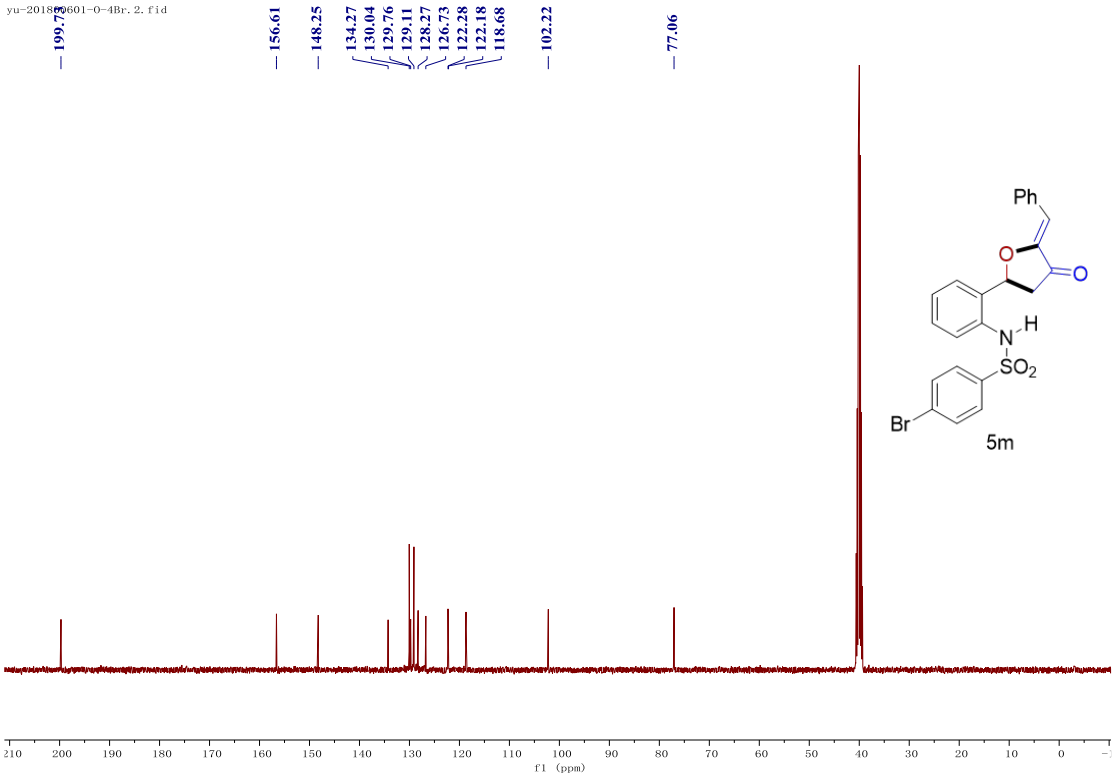
Product **5l**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



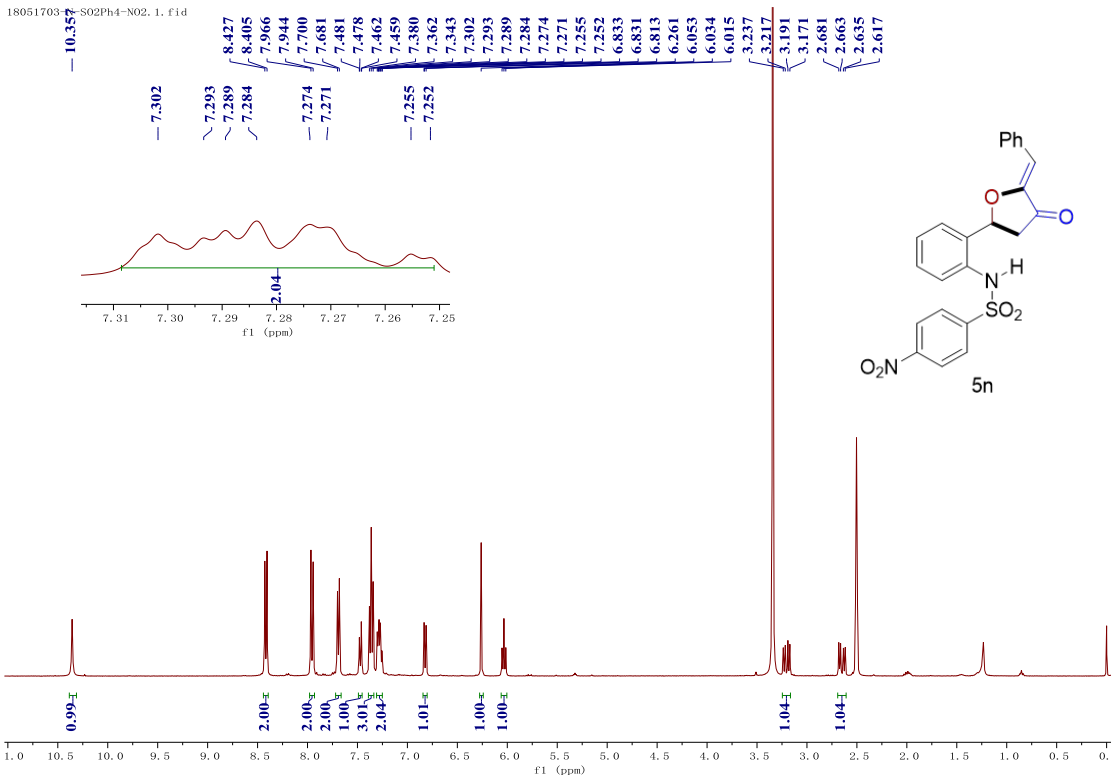


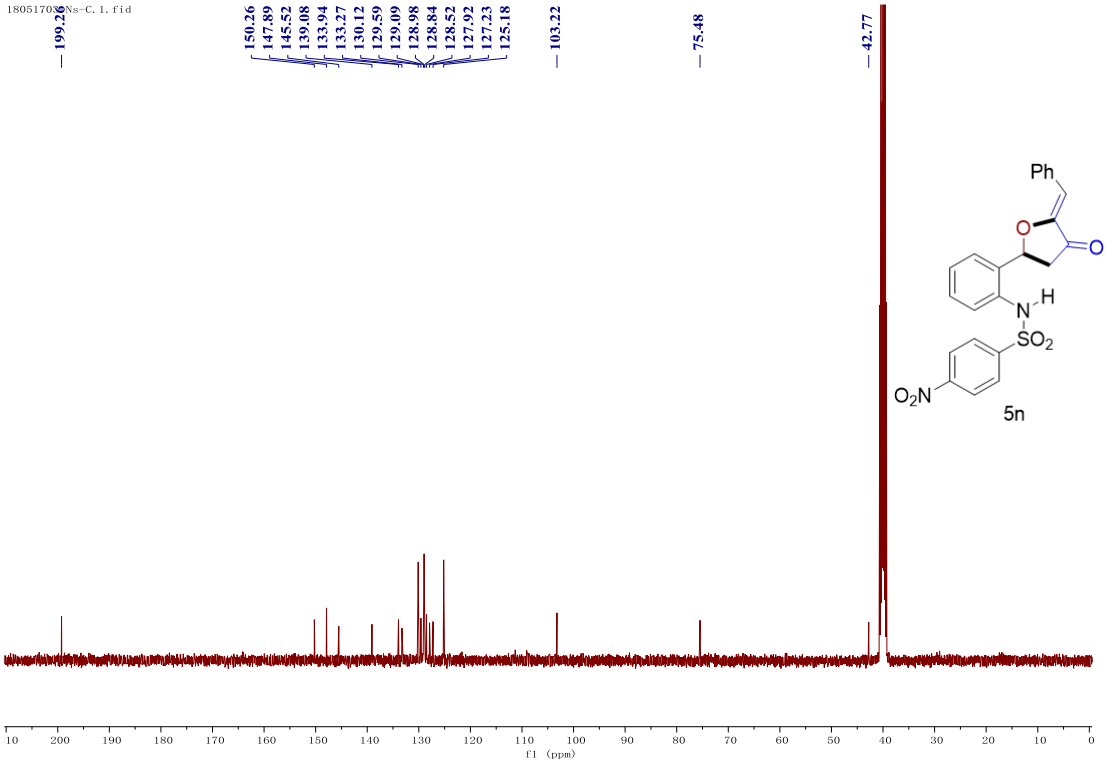
Product **5m**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



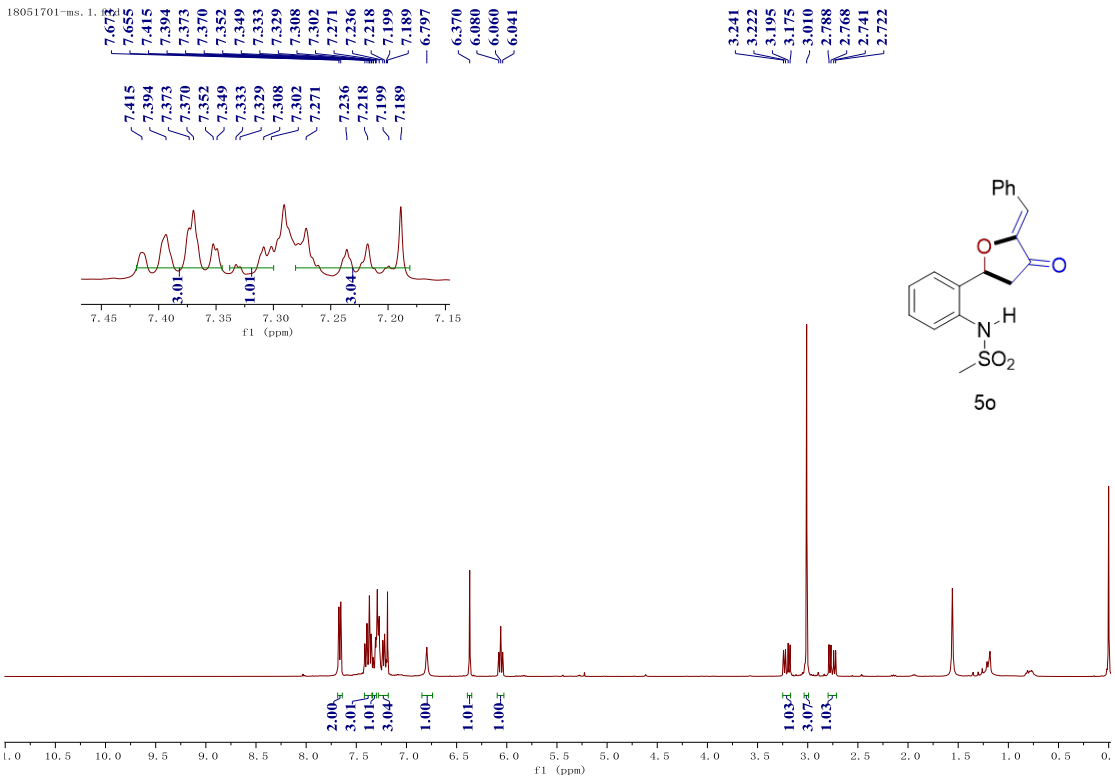


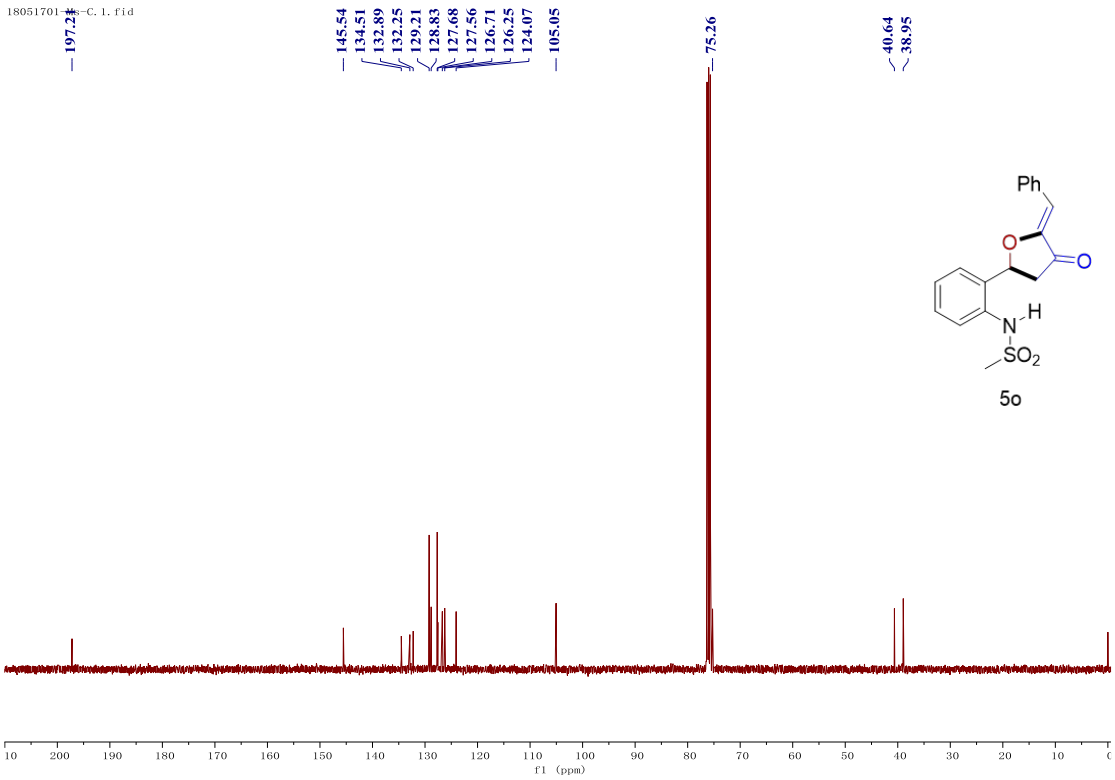
Product **5n**: ^{1}H NMR (DMSO-*d6*, 400 MHz), ^{13}C NMR (DMSO-*d6*, 100 MHz)



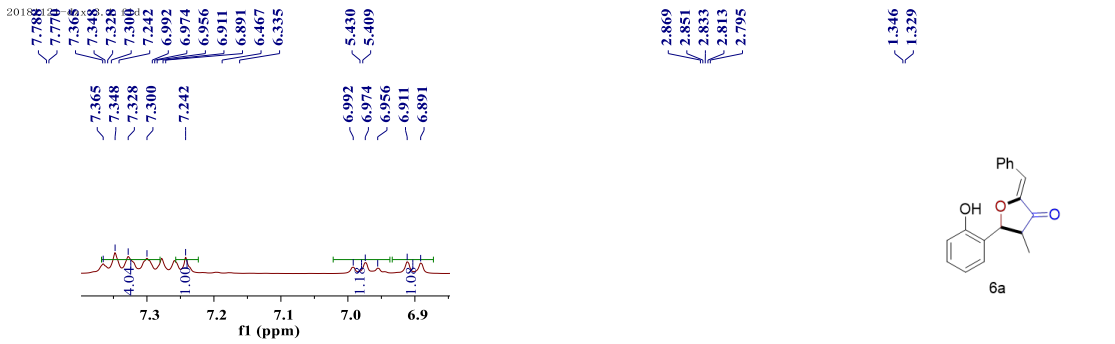


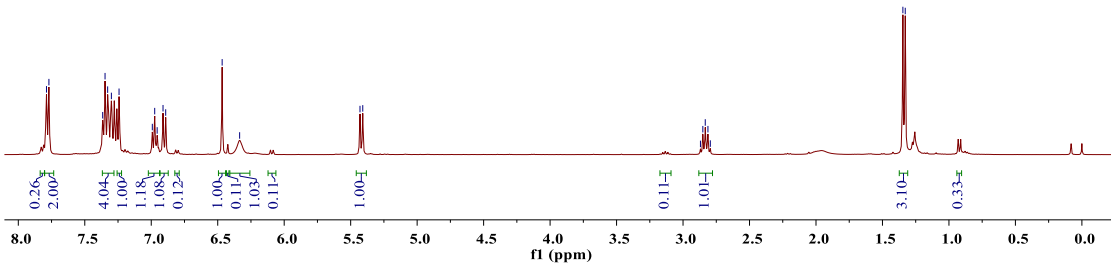
Product **5o**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

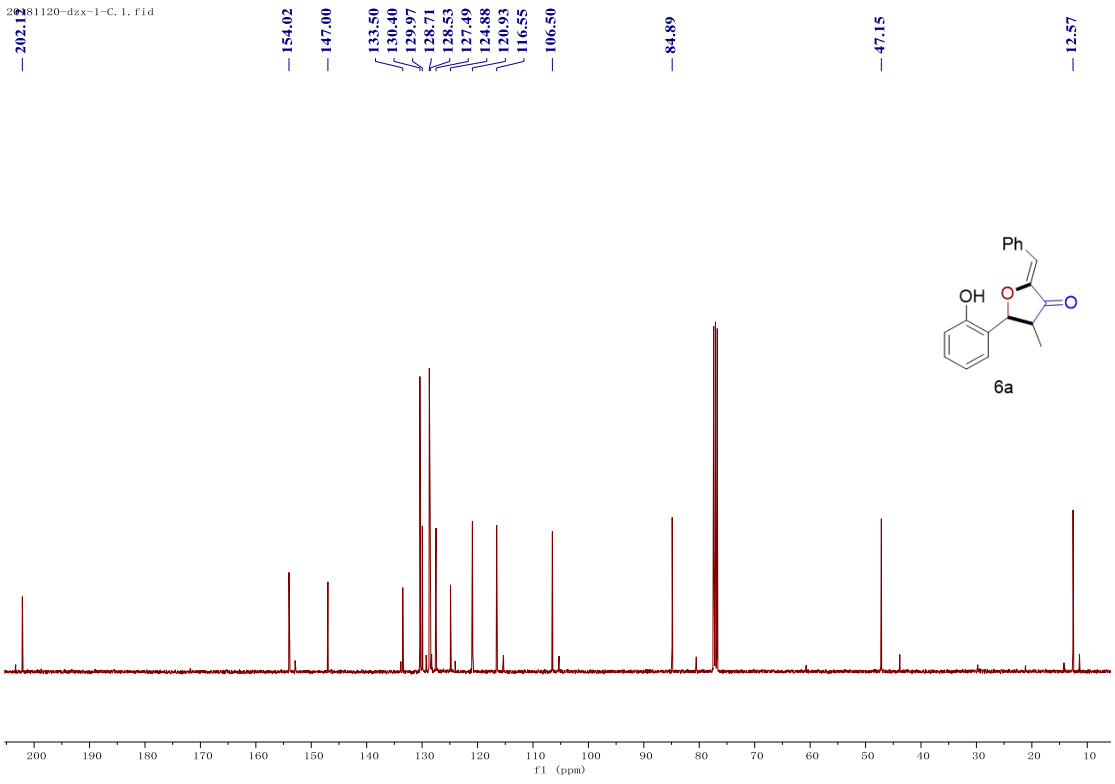




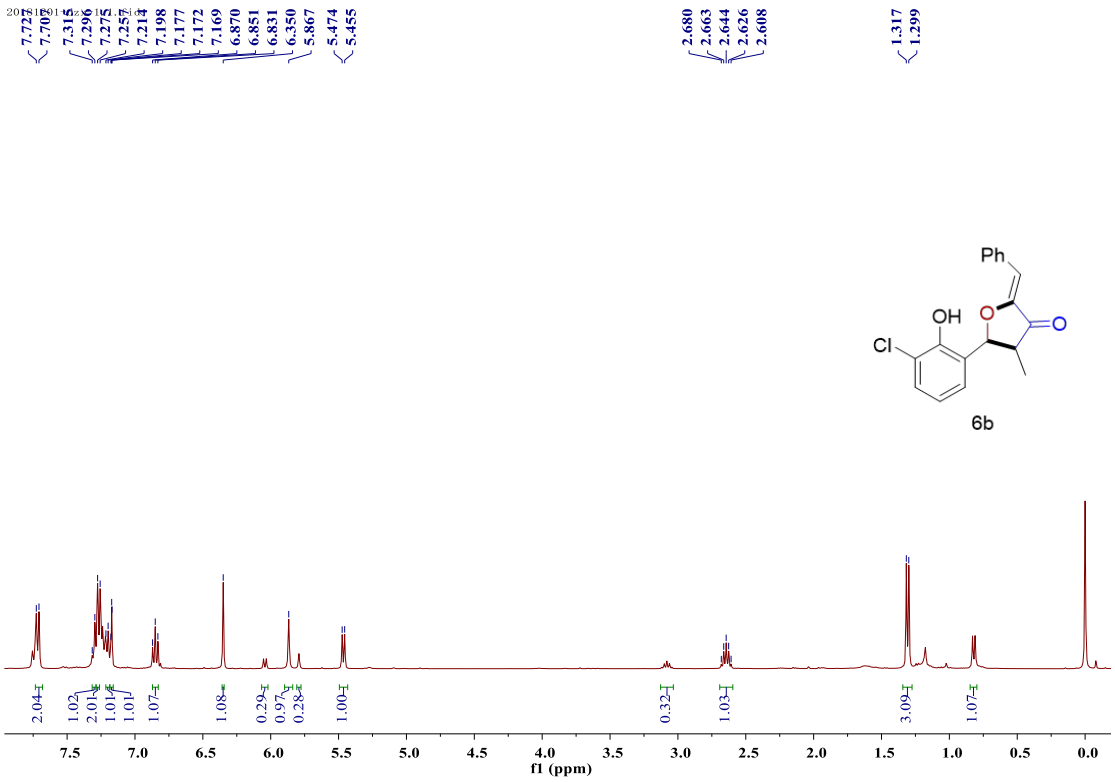
Product **6a**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

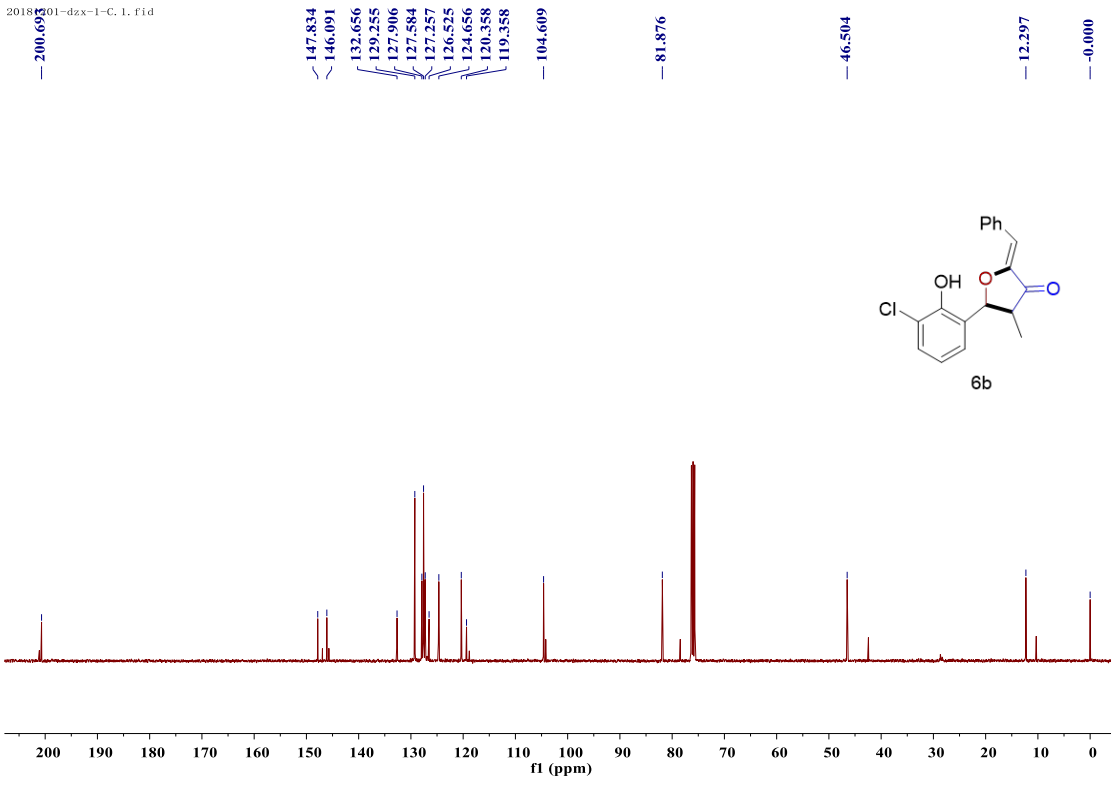




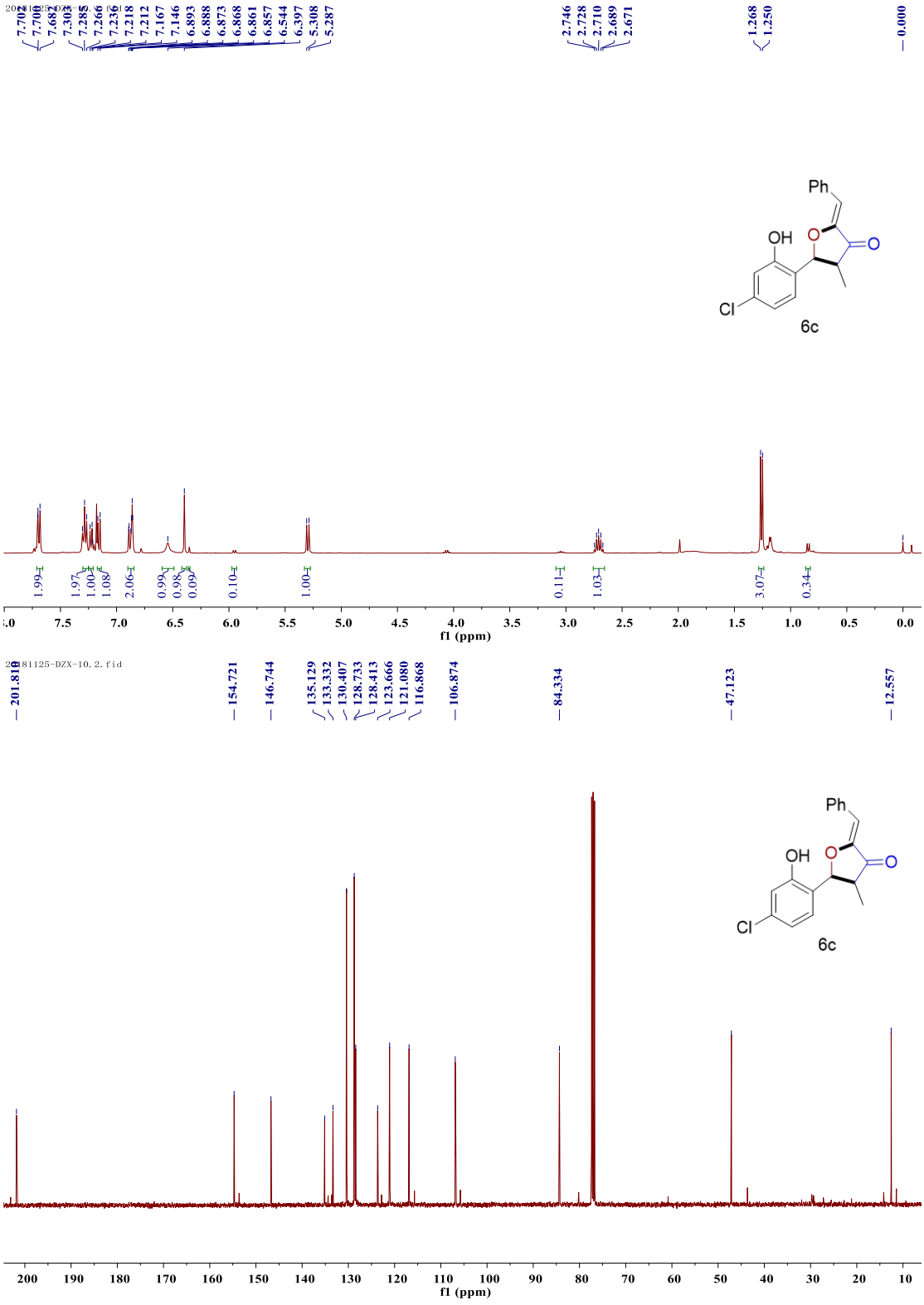


Product **6b**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

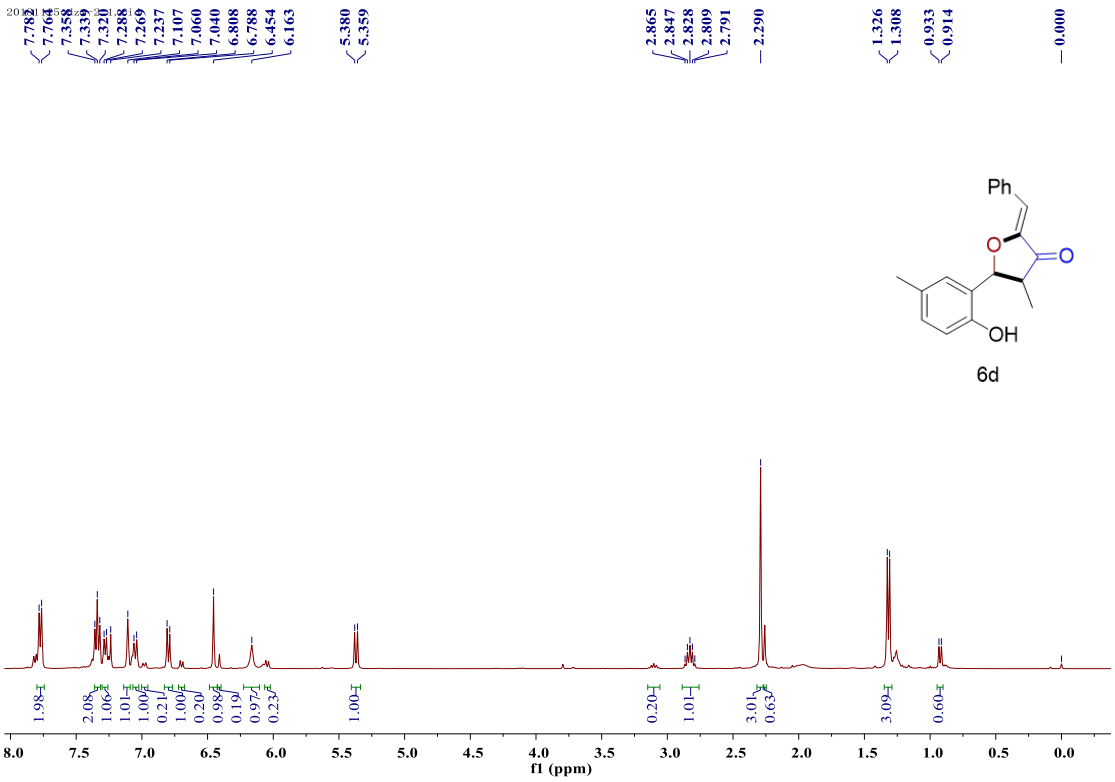


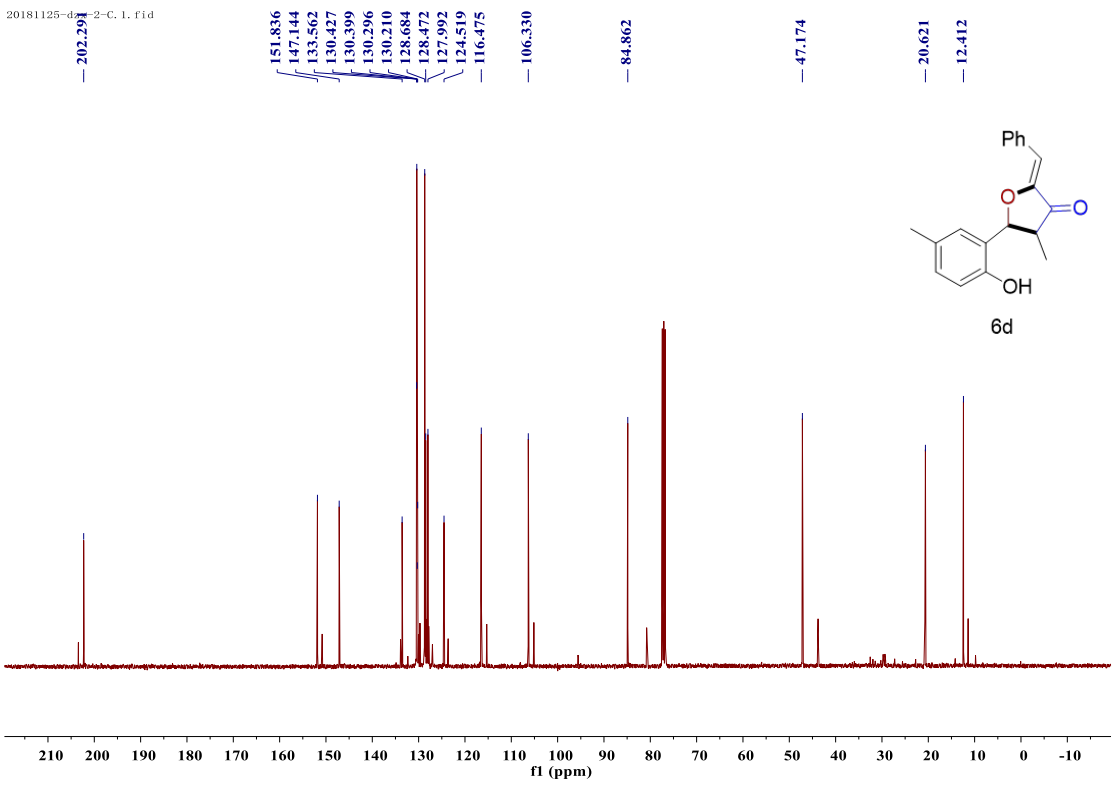


Product **6c**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

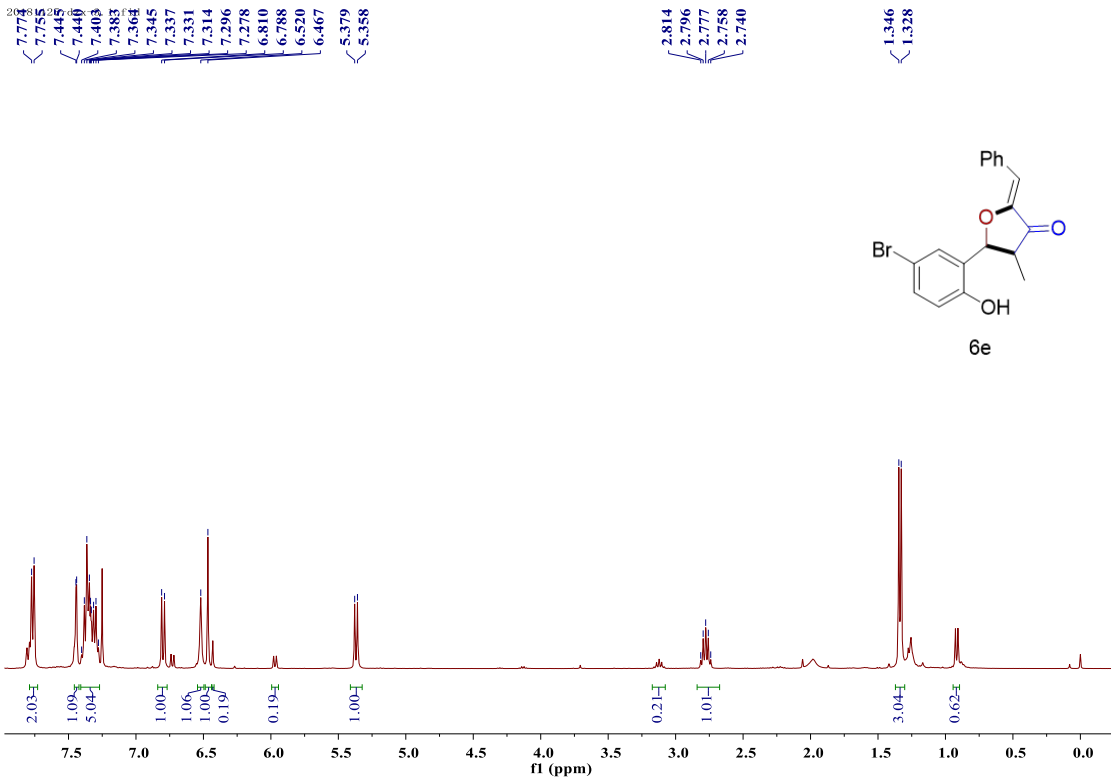


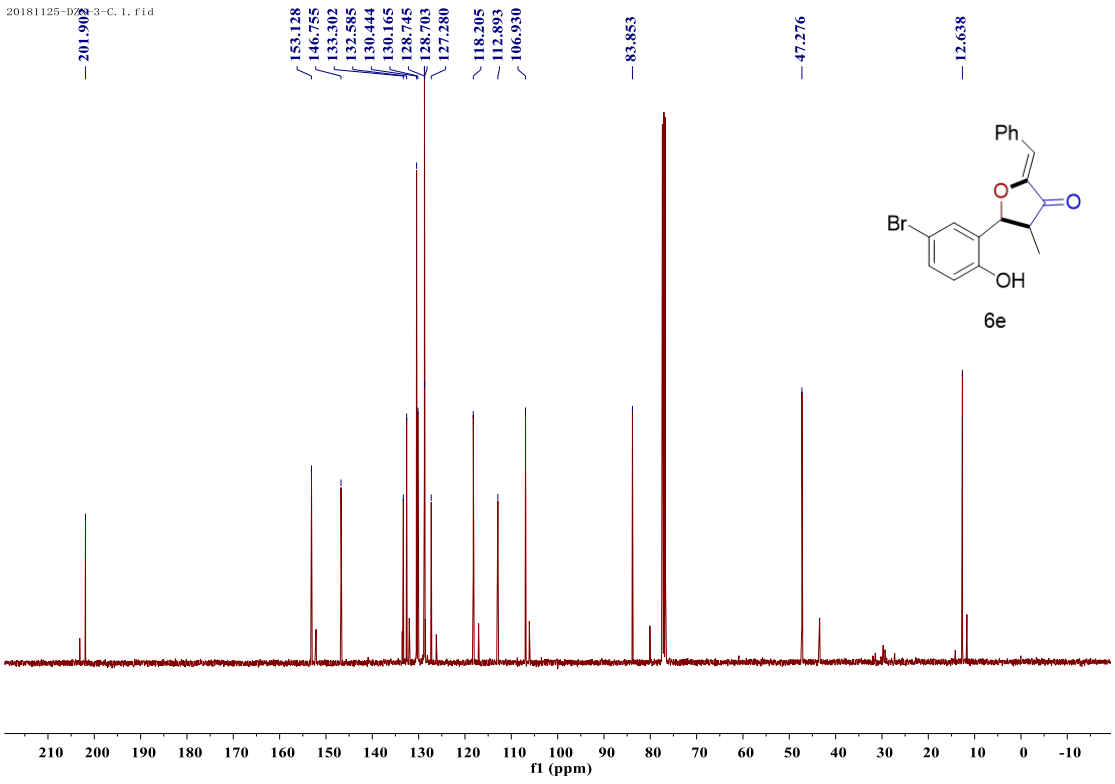
Product **6d**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)



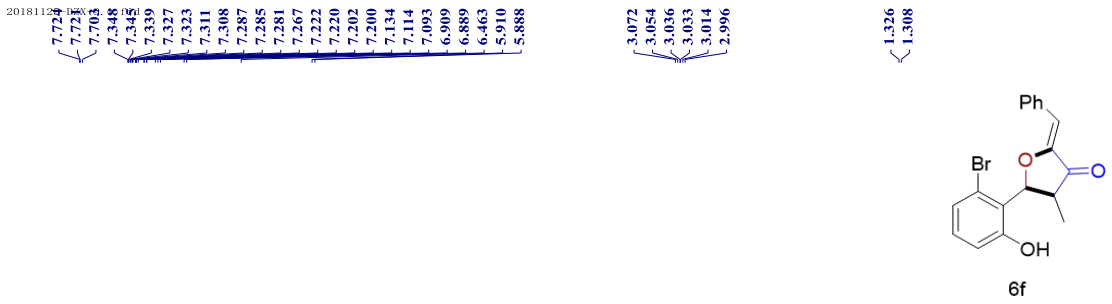


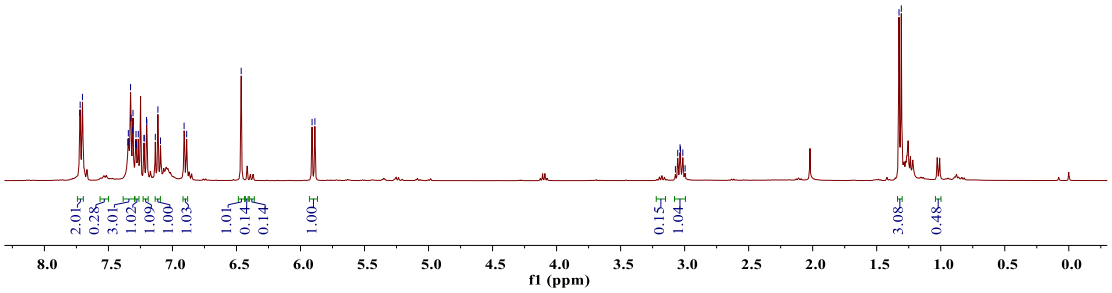
Product **6e**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

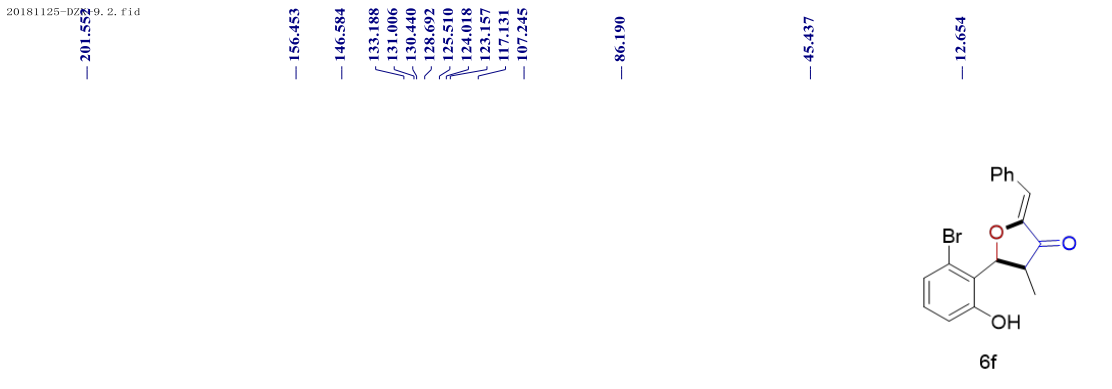




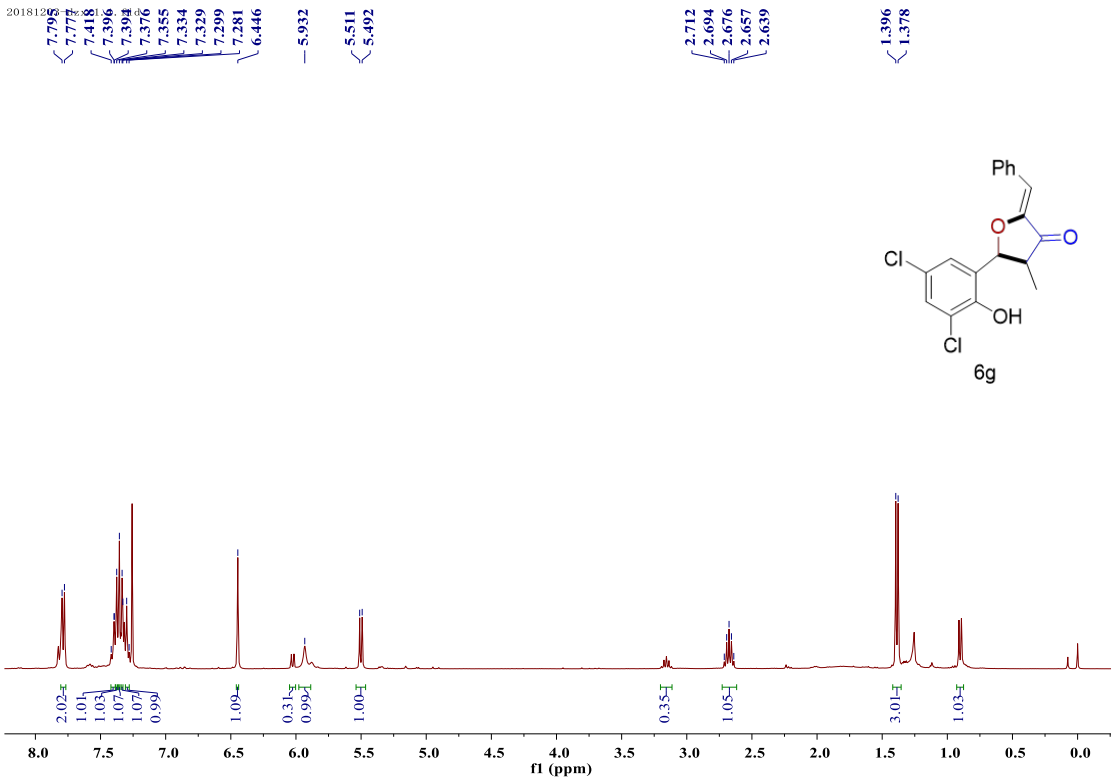
Product **6f**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

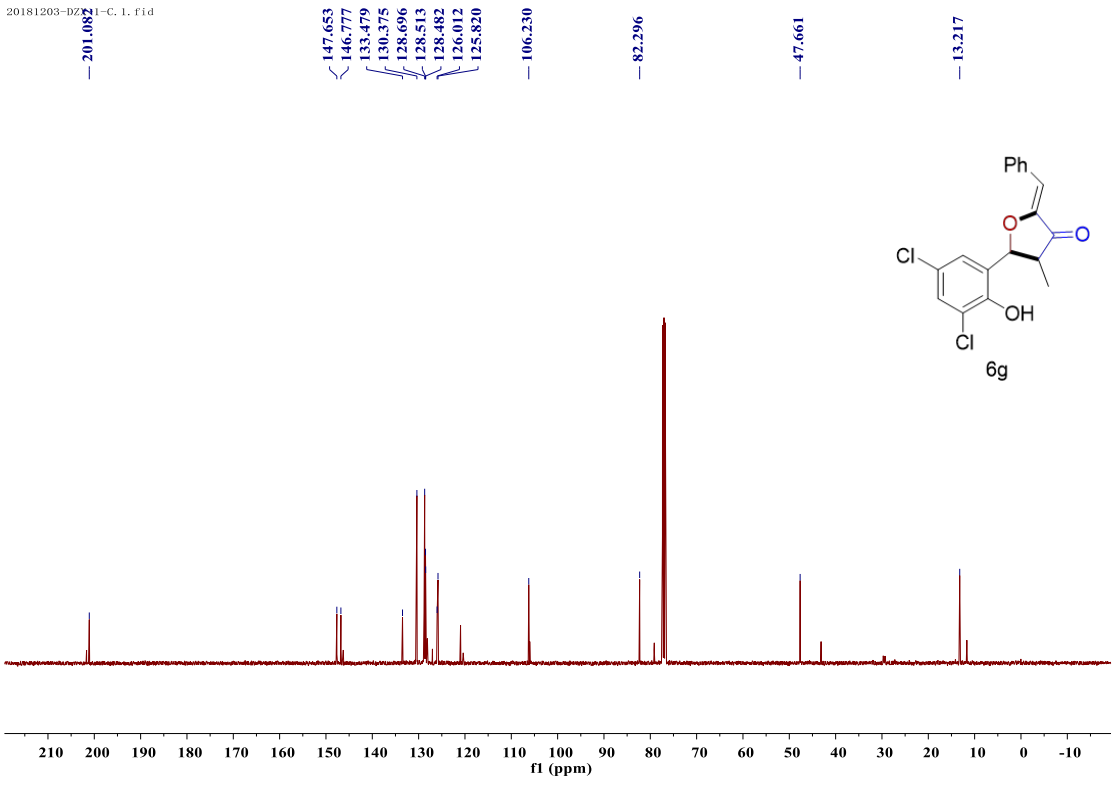




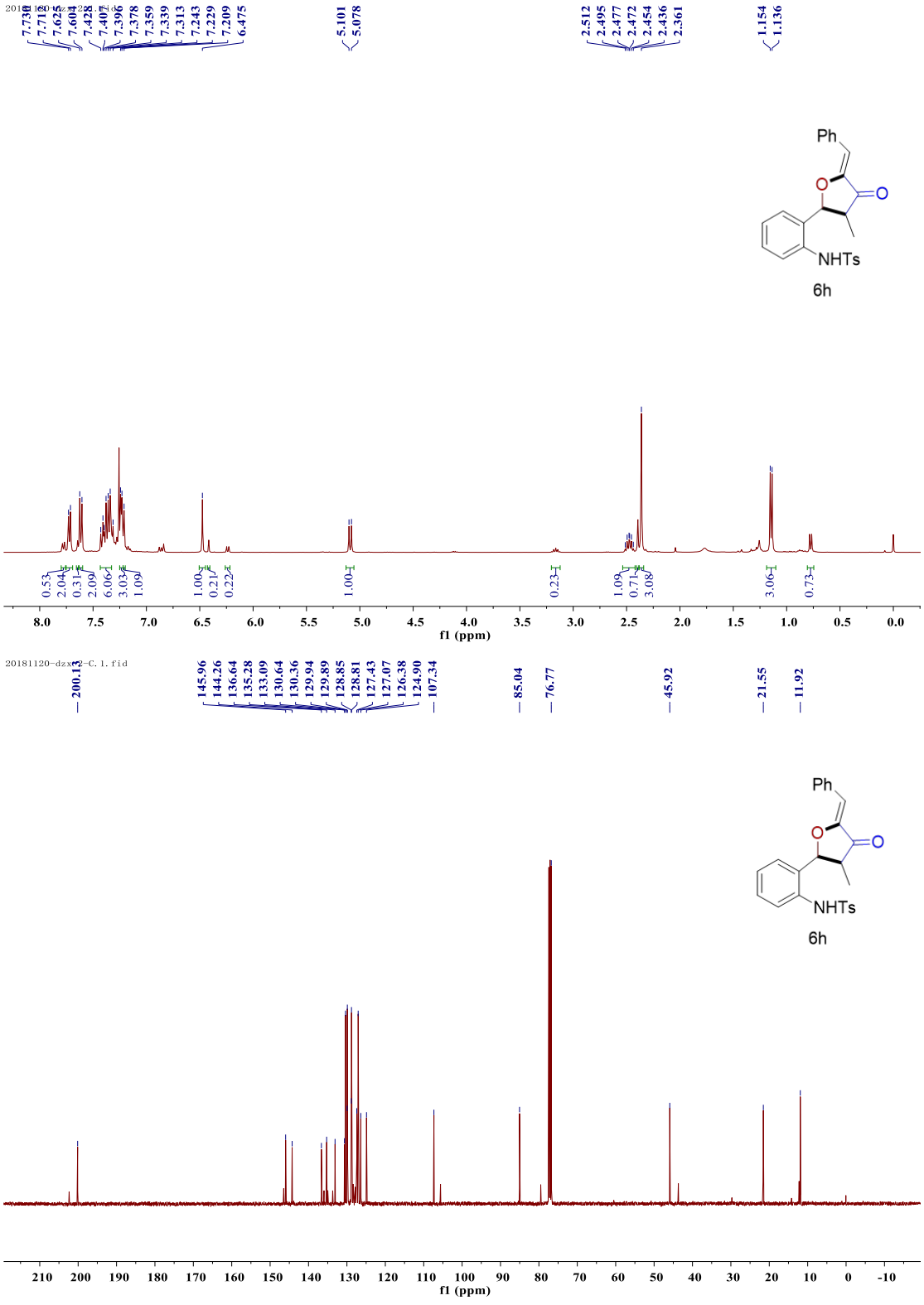


Product **6g**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

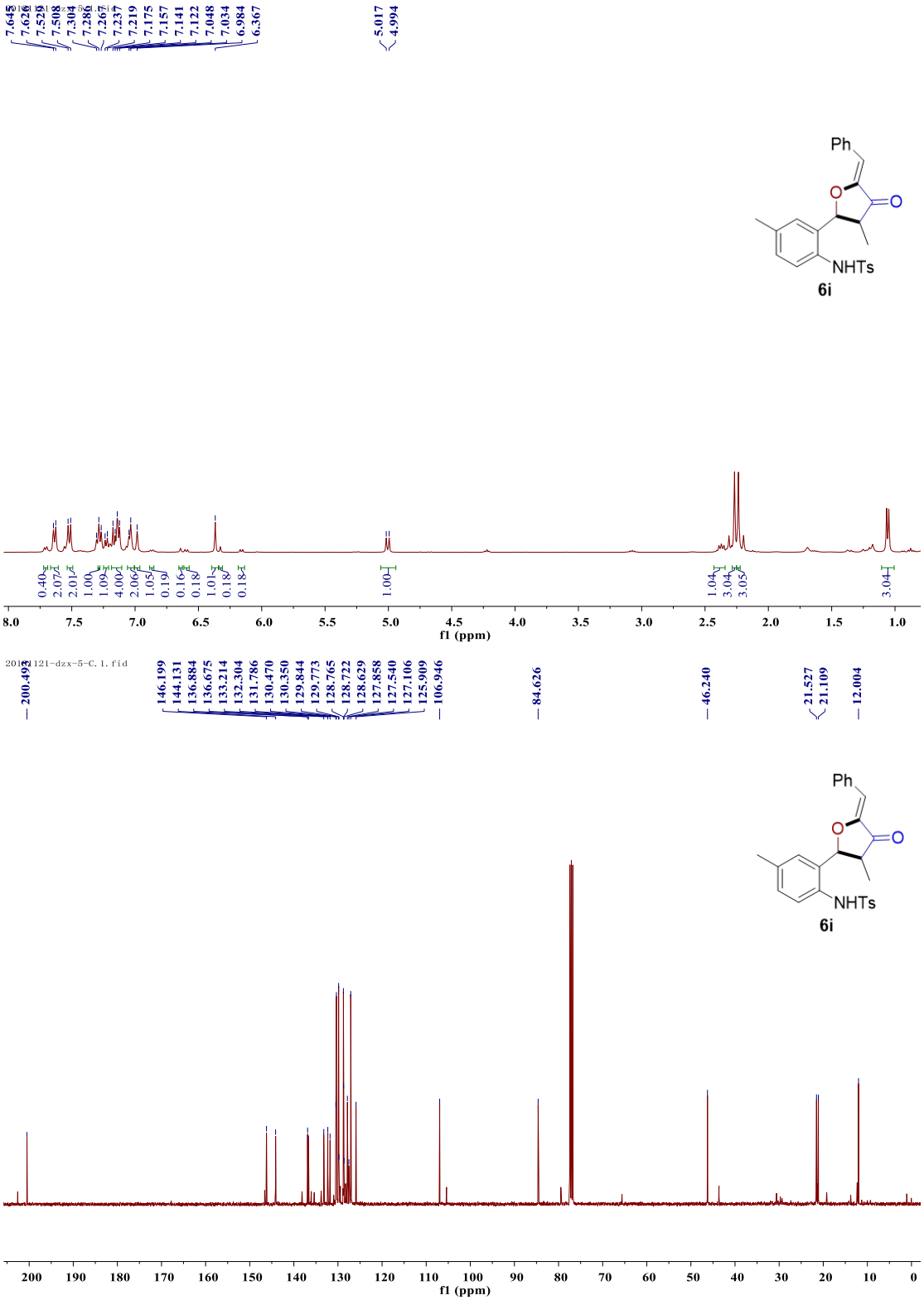




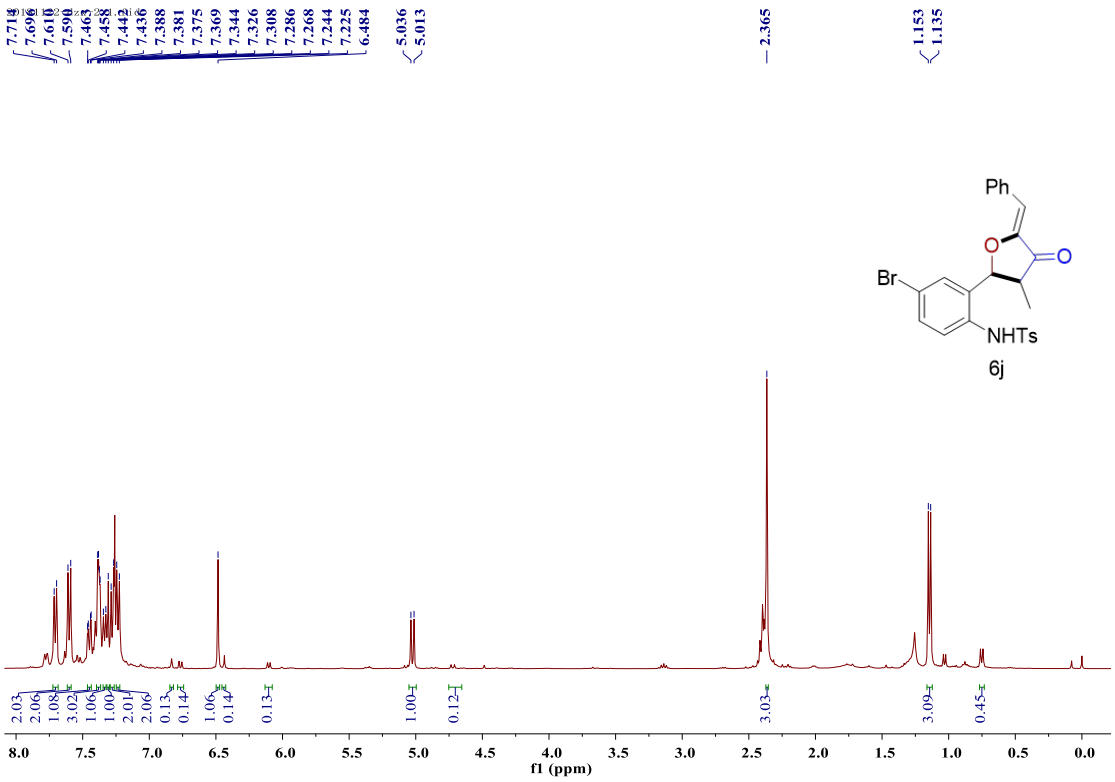
Product **6h**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

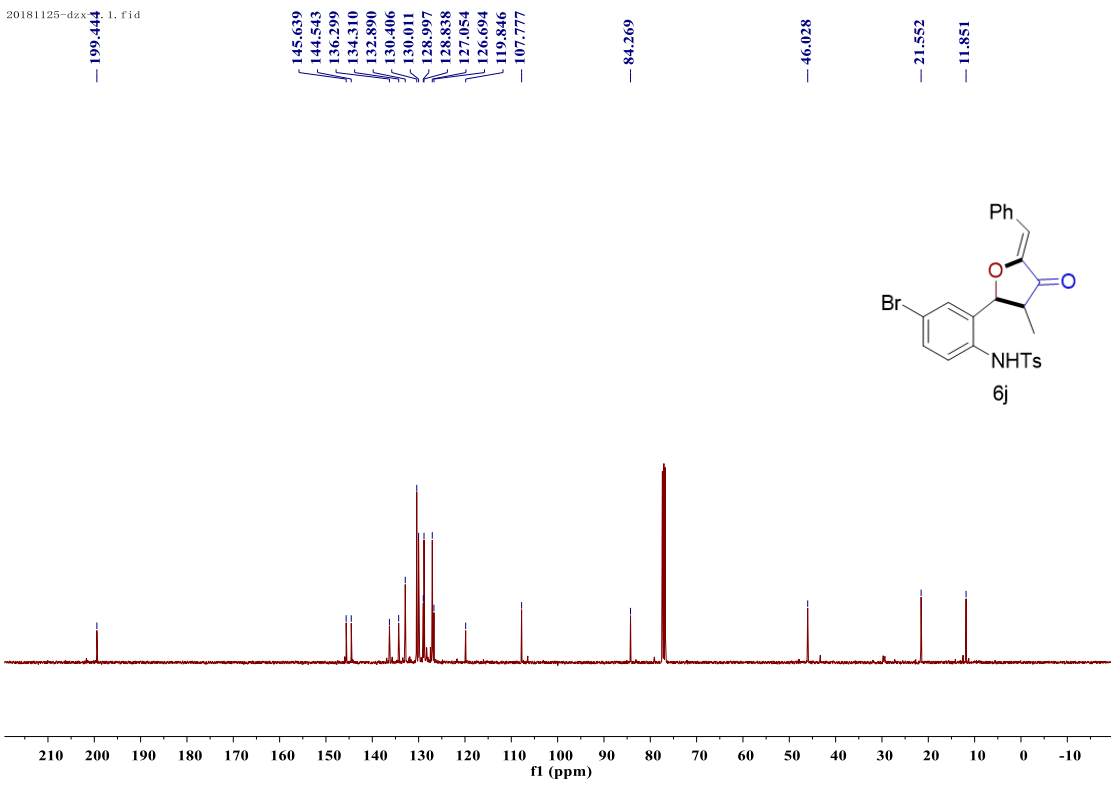


Product **6i**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

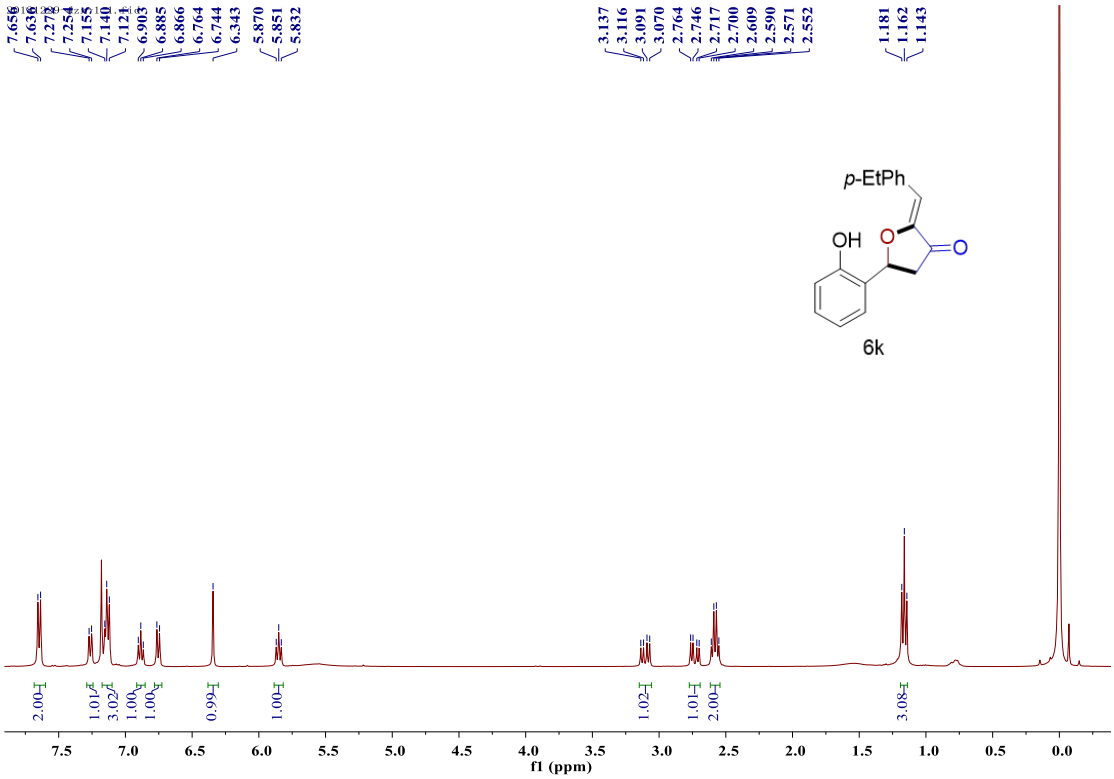


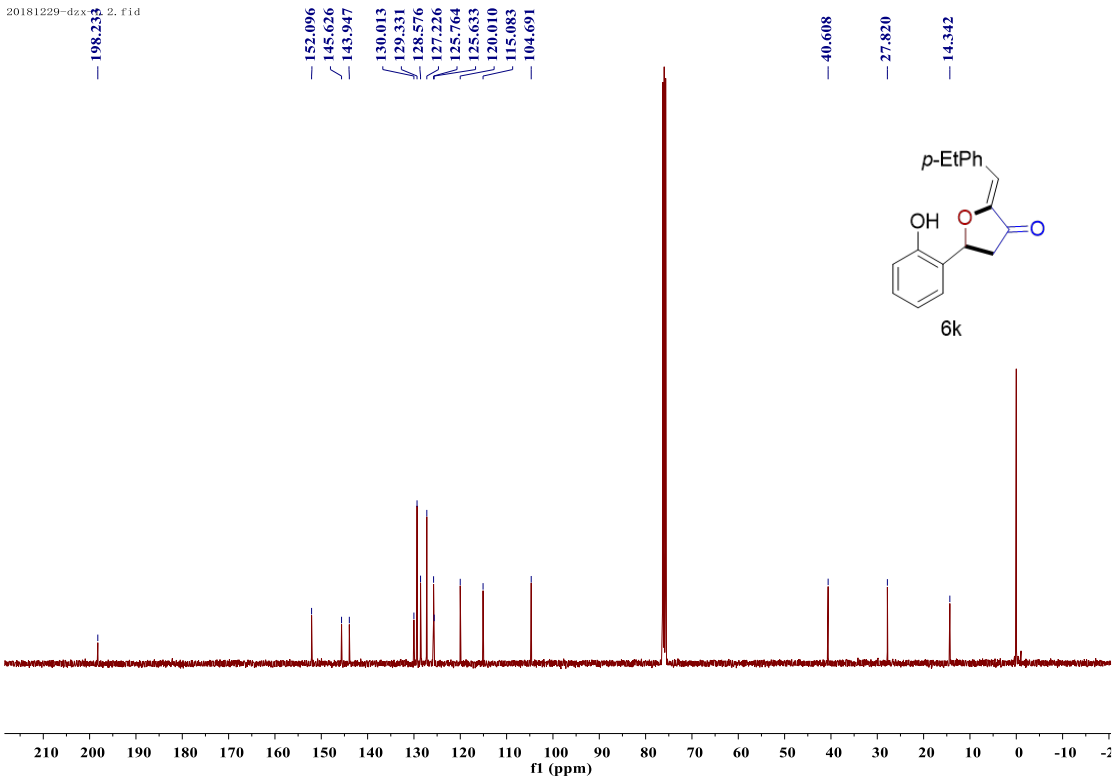
Product **6j**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)



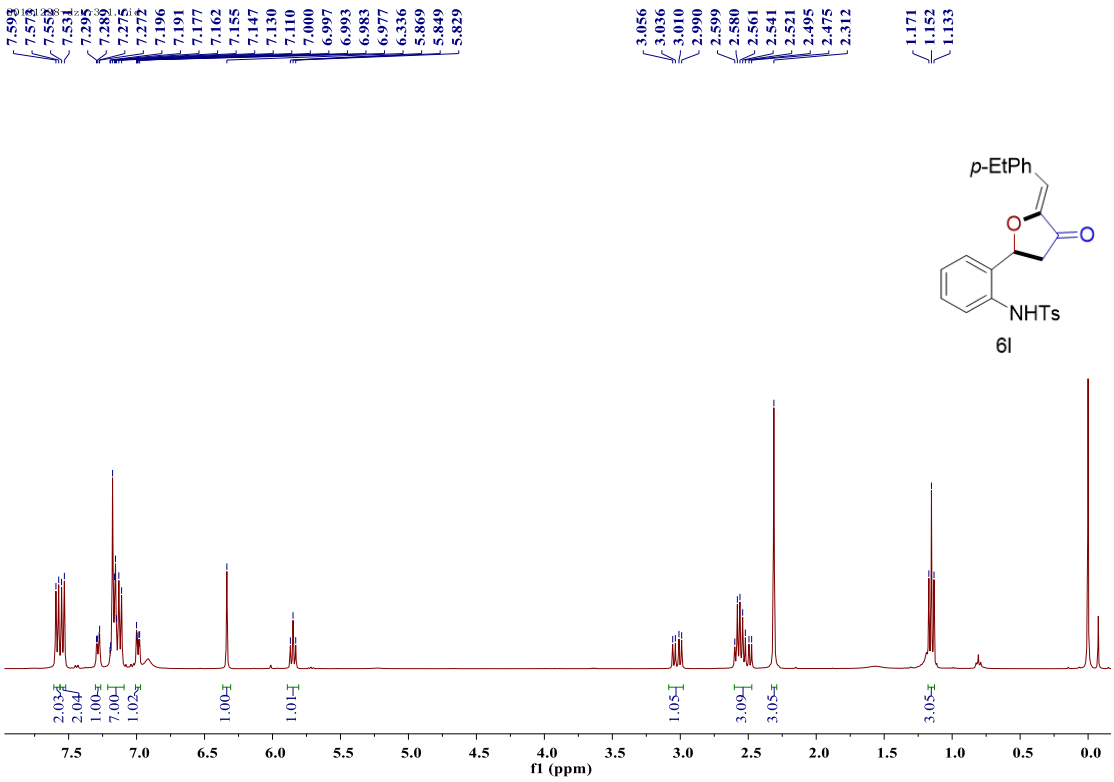


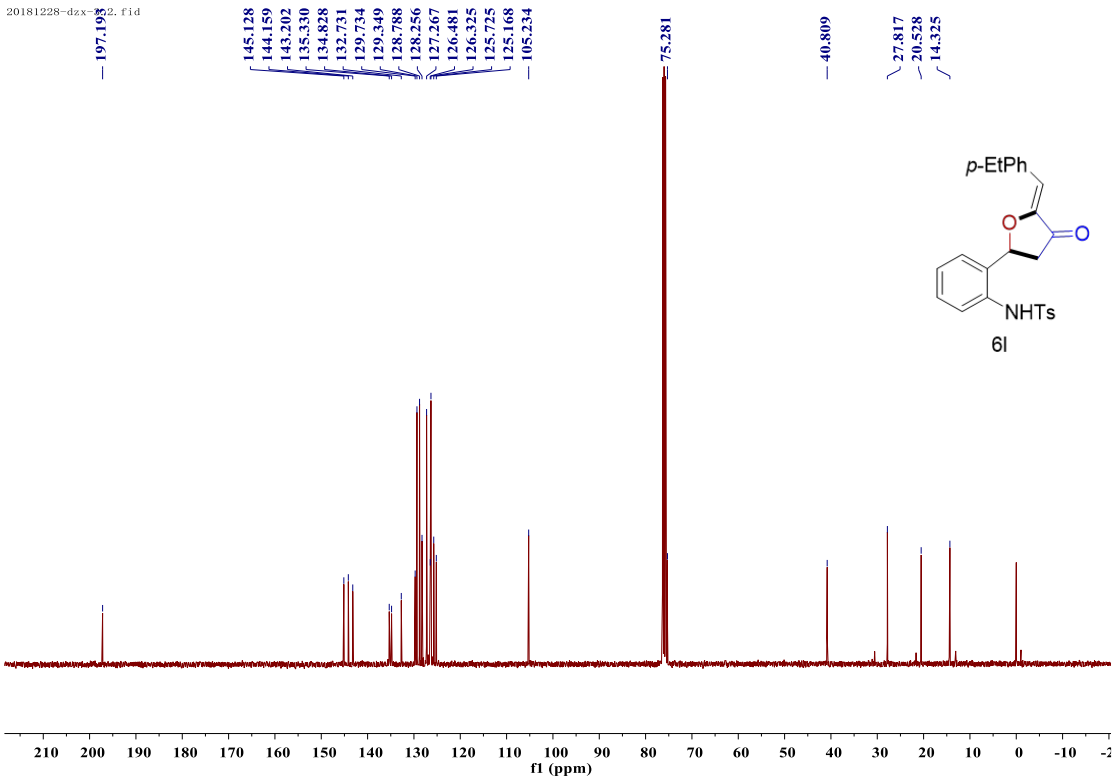
Product **6k**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)



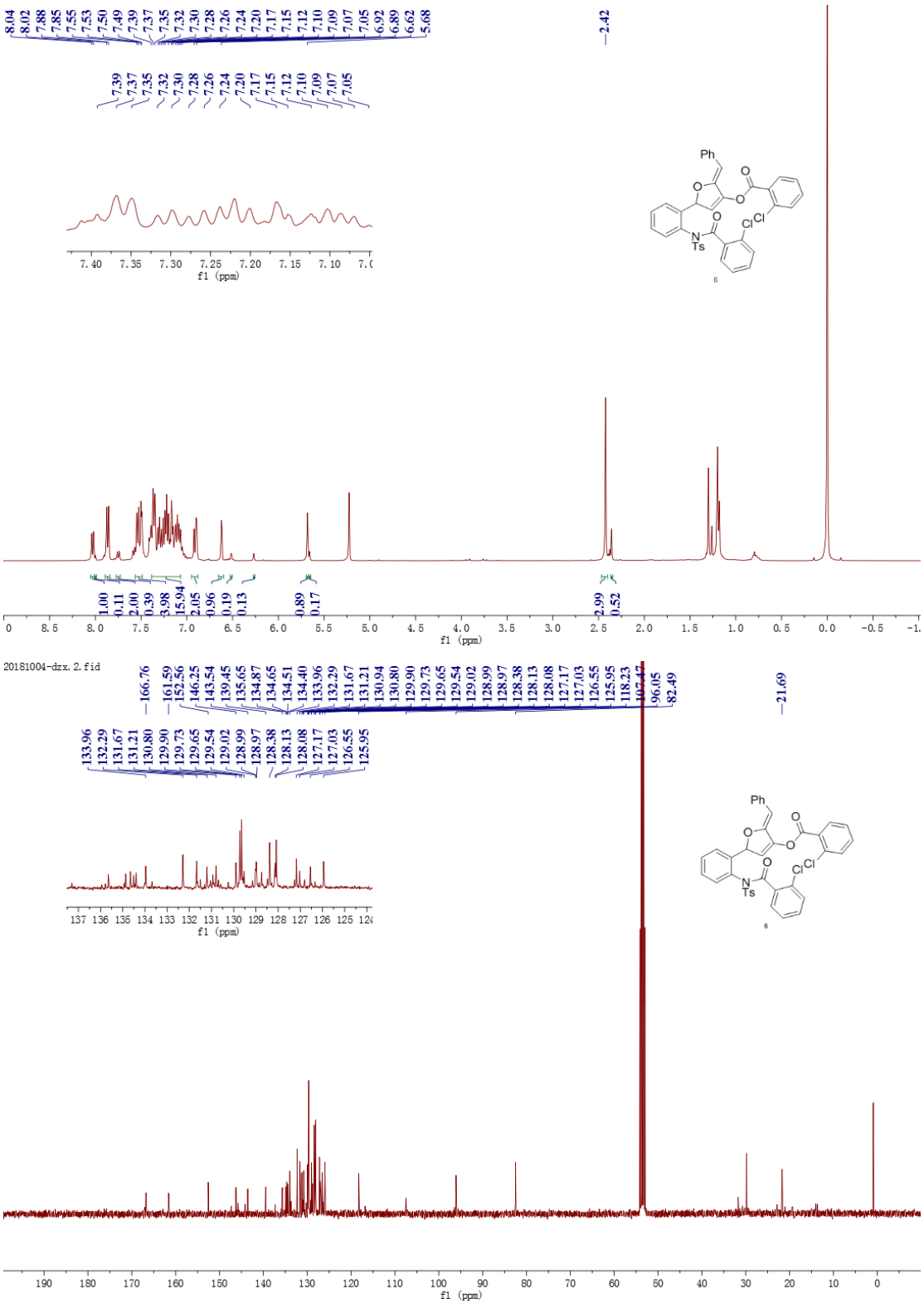


Product **6l**: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz)

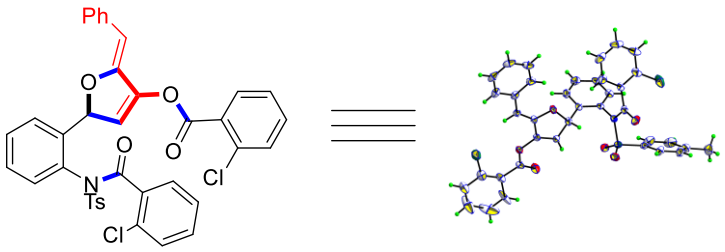




Product **7**: ^{1}H NMR (CD_2Cl_2, 400 MHz), ^{13}C NMR (CD_2Cl_2, 100 MHz)



6. X-Ray crystallographic analysis of dispirooxindole-piperazine **7** (CCDC 1871902)



Bond precision: C-C = 0.0105 A Wavelength=0.71073

Cell: a=11.8316(3) b=18.9651(5) c=15.2168(4)
alpha=90 beta=101.139(1) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	3350.14(15)	3350.14(15)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C38 H27 Cl2 N O6 S	?
Sum formula	C38 H27 Cl2 N O6 S	C4.75 H3.38 Cl0.25 N0.13 O0.75 S0.13
Mr	696.57	87.07
Dx,g cm-3	1.381	1.381
Z	4	32
Mu (mm-1)	0.305	0.305
F000	1440.0	1440.0
F000'	1442.31	
h,k,lmax	14,22,18	14,22,18
Nref	6127	6123
Tmin,Tmax	0.929,0.941	
Tmin'	0.913	

Correction method= Not given

Data completeness= 0.999 Theta(max)= 25.340

R(reflections)= 0.0999(3782) wR2(reflections)= 0.3436(6123)

S = 1.089 Npar= 397