Copper Iodide-Catalyzed Coupling Reaction of Benzofuran-3(2*H*)-ones with Amines: an Approach to α-Ketoamides

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Supporting Information

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1. General information

All manipulations were carried out under air atmosphere. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) data were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as solvent at room temperature unless specified otherwise. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. HRMS were performed on Agilent ESI-quadrupole.

2. General procedures for reactions

A solution of aryl ketones **1** or **4** (0.3 mmol), secondary amine **2** (4.0 equiv, 1.2 mmol), cuprous iodide (20 mol%, 0.06 mmol), *tert*-butyl hydroperoxide (5.0 equiv, 1.5 mmol, 70% in water) and 1,4-dioxane (2 mL) was stirred in a 10 mL sealed tube at 70 °C for 12 h. After completion of the reaction, the reaction solution was then quenched with saturated Na_2SO_3 solution and extracted with ethyl acetate (10 mL × 3). The combined organic layer was combined and dried with anhydrous Na_2SO_4. Removal of the organic solvent followed by flash column chromatographic purification afforded the desired products using petroleum and ethyl acetate.

3. Isotope labelled experiment

A solution of benzofuran-3(2*H*)-one **1a** (0.3 mmol), morpholine **2a** (4.0 equiv, 1.2 mmol), cuprous iodide (20 mol%, 0.06 mmol), *tert*-butyl hydroperoxide (5.0 equiv, 1.5 mmol, 70% in water) $H_2{}^{18}O$ (2.0 equiv, 0.6 mmol) and 1,4-dioxane (2 mL) was stirred in a 10 mL sealed tube at 70 °C for 12 h. After completion of the reaction, the reaction solution was then quenched with saturated Na_2SO_3 solution and extracted with ethyl acetate (10 mL × 3). The combined organic layer was combined and dried with anhydrous Na_2SO_4. Removal of the organic solvent followed by flash column chromatographic purification afforded **3a** (60 mg, 86% yield) using petroleum and ethyl acetate (3:1). **3a** and **3a**-^{18}O were detected by LC-MS and the ratio was approximately 2.3 : 1.

Display Report

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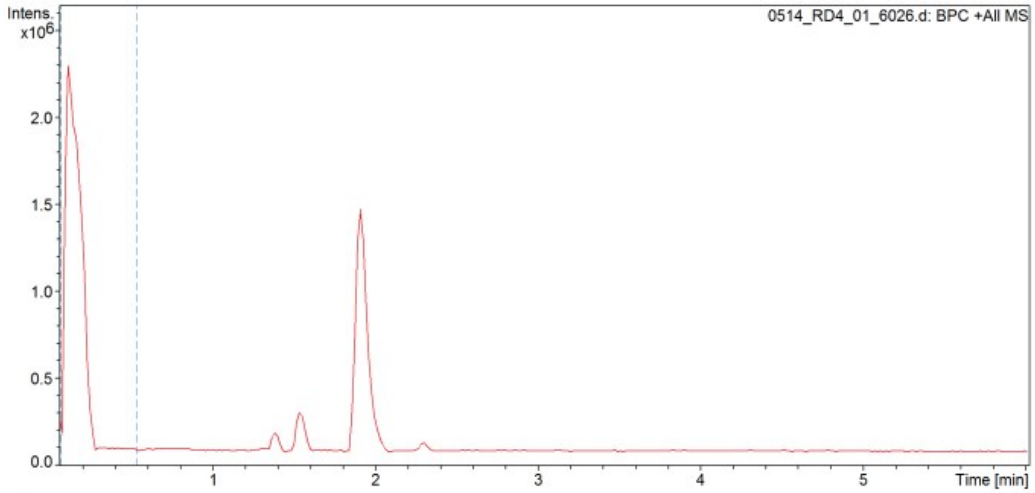

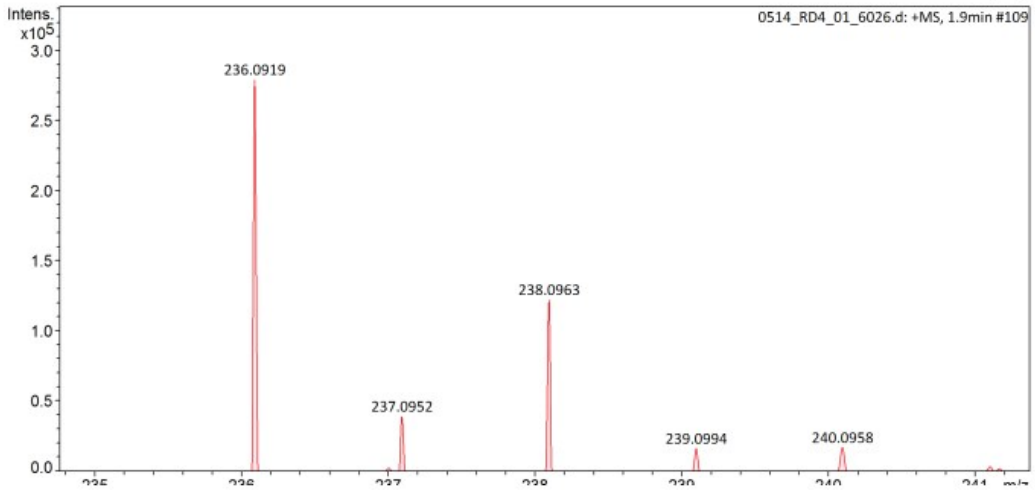

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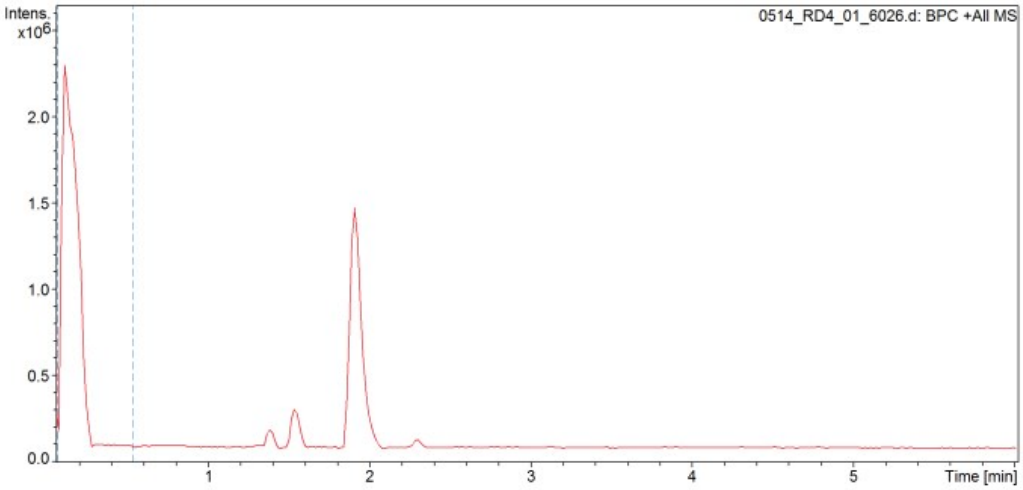
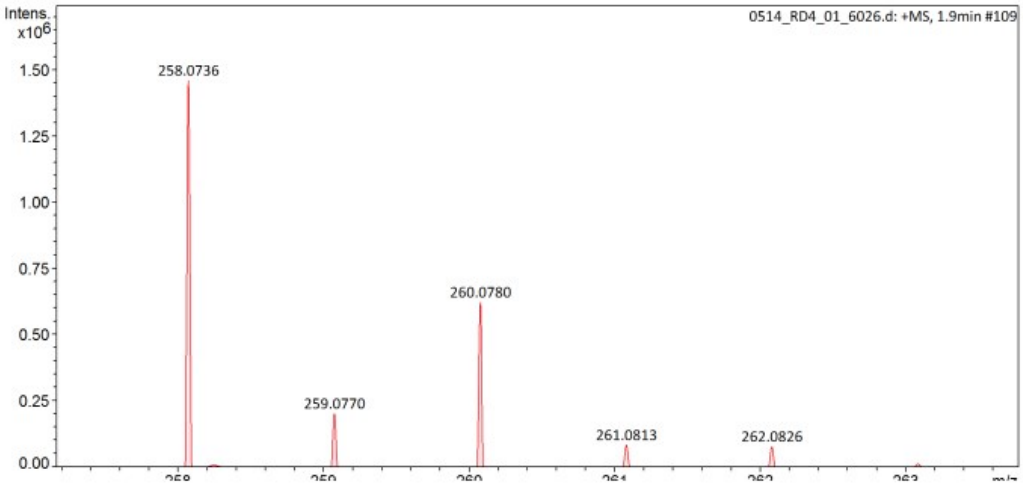
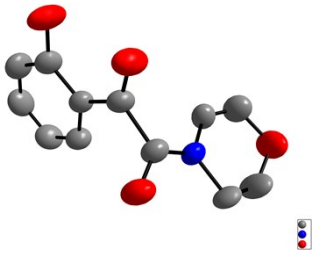
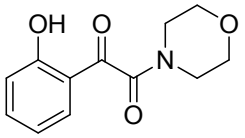




3. X-ray crystal structure of 3a





3a (CCDC 2068416)

Table S1. Crystal data and structure refinement for **3a**.

Empirical formula	$C_{12}H_{13}NO_4$
Formula weight	235.08
Temperature	296(2) K
Wavelength	71.073 pm
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 12.5895(17) pm α= 90°
	b = 5.0682(7) pm β= 92.174(2)°
	c = 18.033(2) pm γ = 90°
Volume	1149.8(3) nm^3
Z	4
Density (calculated)	1.356 Mg/m^3
Absorption coefficient	0.103 mm^{-1}
F(000)	494
Crystal size	0.260 x 0.250 x 0.230 mm^3
Theta range for data collection	3.239 to 24.996°
Index ranges	-14<=h<=14, -5<=k<=6, -21<=l<=15
Reflections collected	5511
Independent reflections	2009 [R(int) = 0.0196]
Completeness to theta = 24.996°	99.7 %
Data / restraints / parameters	2009 / 15 / 211
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.1156

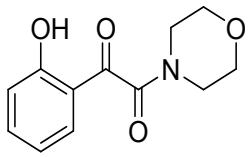
R indices (all data)	R1 = 0.0603, wR2 = 0.1240
Extinction coefficient	0.031(4)
Largest diff. peak and hole	0.242 and -0.229 e.Å^{-3}

Table S2. Bond lengths [pm] and angles [°] for **3a**.

C(1)-C(2)	1.363(2)	C(10A)-H(10A)	0.9700
C(1)-C(6)	1.398(2)	C(10A)-H(10B)	0.9700
C(1)-H(1A)	0.9300	C(11A)-O(4A)	1.394(17)
C(2)-C(3)	1.380(3)	C(11A)-C(12A)	1.482(10)
C(2)-H(2)	0.9300	C(11A)-H(11C)	0.9700
C(3)-C(4)	1.368(3)	C(11A)-H(11D)	0.9700
C(3)-H(3)	0.9300	C(12A)-N(1A)	1.458(8)
C(4)-C(5)	1.382(2)	C(12A)-H(12C)	0.9700
C(4)-H(4)	0.9300	C(12A)-H(12D)	0.9700
C(5)-O(1)	1.349(2)	O(1)-H(1)	0.8200
C(5)-C(6)	1.410(2)	C(2)-C(1)-C(6)	121.47(17)
C(6)-C(7)	1.452(2)	C(2)-C(1)-H(1A)	119.3
C(7)-O(2)	1.2305(19)	C(6)-C(1)-H(1A)	119.3
C(7)-C(8)	1.534(2)	C(1)-C(2)-C(3)	118.99(18)
C(8)-O(3)	1.2193(19)	C(1)-C(2)-H(2)	120.5
C(8)-N(1A)	1.346(6)	C(3)-C(2)-H(2)	120.5
C(8)-N(1)	1.353(4)	C(4)-C(3)-C(2)	121.49(18)
C(9)-N(1)	1.477(6)	C(4)-C(3)-H(3)	119.3
C(9)-C(10)	1.511(7)	C(2)-C(3)-H(3)	119.3
C(9)-H(9A)	0.9700	C(3)-C(4)-C(5)	120.18(17)
C(9)-H(9B)	0.9700	C(3)-C(4)-H(4)	119.9
C(10)-O(4)	1.432(12)	C(5)-C(4)-H(4)	119.9
C(10)-H(10)	0.9300	O(1)-C(5)-C(4)	118.11(15)
C(11)-O(4)	1.411(13)	O(1)-C(5)-C(6)	122.51(15)
C(11)-C(12)	1.496(6)	C(4)-C(5)-C(6)	119.38(16)
C(11)-H(11A)	0.9700	C(1)-C(6)-C(5)	118.48(15)
C(11)-H(11B)	0.9700	C(1)-C(6)-C(7)	120.64(14)
C(12)-N(1)	1.448(5)	C(5)-C(6)-C(7)	120.86(14)
C(12)-H(12A)	0.9700	O(2)-C(7)-C(6)	123.76(14)
C(12)-H(12B)	0.9700	O(2)-C(7)-C(8)	117.87(15)
C(9A)-N(1A)	1.465(7)	C(6)-C(7)-C(8)	118.26(14)
C(9A)-C(10A)	1.491(10)	O(3)-C(8)-N(1A)	125.1(3)
C(9A)-H(9AA)	0.9700	O(3)-C(8)-N(1)	121.6(2)
C(9A)-H(9AB)	0.9700	O(3)-C(8)-C(7)	117.53(15)
C(10A)-O(4A)	1.449(17)	N(1A)-C(8)-C(7)	113.9(3)

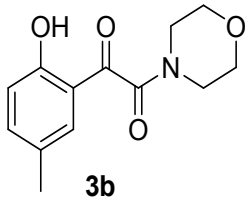
N(1)-C(8)-C(7)	119.9(2)	O(4A)-C(10A)-C(9A)	111.5(7)
N(1)-C(9)-C(10)	108.7(3)	O(4A)-C(10A)-H(10A)	109.3
N(1)-C(9)-H(9A)	110.0	C(9A)-C(10A)-H(10A)	109.3
C(10)-C(9)-H(9A)	110.0	O(4A)-C(10A)-H(10B)	109.3
N(1)-C(9)-H(9B)	110.0	C(9A)-C(10A)-H(10B)	109.3
C(10)-C(9)-H(9B)	110.0	H(10A)-C(10A)-H(10B)	108.0
H(9A)-C(9)-H(9B)	108.3	O(4A)-C(11A)-C(12A)	114.3(8)
O(4)-C(10)-C(9)	111.3(4)	O(4A)-C(11A)-H(11C)	108.7
O(4)-C(10)-H(10)	124.3	C(12A)-C(11A)-H(11C)	108.7
C(9)-C(10)-H(10)	124.3	O(4A)-C(11A)-H(11D)	108.7
O(4)-C(11)-C(12)	112.6(6)	C(12A)-C(11A)-H(11D)	108.7
O(4)-C(11)-H(11A)	109.1	H(11C)-C(11A)-H(11D)	107.6
C(12)-C(11)-H(11A)	109.1	N(1A)-C(12A)-C(11A)	109.2(6)
O(4)-C(11)-H(11B)	109.1	N(1A)-C(12A)-H(12C)	109.8
C(12)-C(11)-H(11B)	109.1	C(11A)-C(12A)-H(12C)	109.8
H(11A)-C(11)-H(11B)	107.8	N(1A)-C(12A)-H(12D)	109.8
N(1)-C(12)-C(11)	110.0(3)	C(11A)-C(12A)-H(12D)	109.8
N(1)-C(12)-H(12A)	109.7	H(12C)-C(12A)-H(12D)	108.3
C(11)-C(12)-H(12A)	109.7	C(8)-N(1)-C(12)	123.7(3)
N(1)-C(12)-H(12B)	109.7	C(8)-N(1)-C(9)	122.5(4)
C(11)-C(12)-H(12B)	109.7	C(12)-N(1)-C(9)	113.7(4)
H(12A)-C(12)-H(12B)	108.2	C(8)-N(1A)-C(12A)	119.6(5)
N(1A)-C(9A)-C(10A)	109.8(5)	C(8)-N(1A)-C(9A)	126.5(5)
N(1A)-C(9A)-H(9AA)	109.7	C(12A)-N(1A)-C(9A)	113.5(5)
C(10A)-C(9A)-H(9AA)	109.7	C(5)-O(1)-H(1)	109.5
N(1A)-C(9A)-H(9AB)	109.7	C(11)-O(4)-C(10)	110.2(6)
C(10A)-C(9A)-H(9AB)	109.7	C(11A)-O(4A)-C(10A)	110.5(8)
H(9AA)-C(9A)-H(9AB)	108.2		

4. Compound characterizations



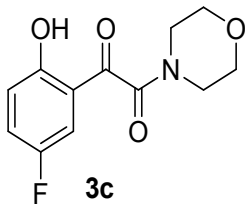
3a

1-(2-hydroxyphenyl)-2-morpholinoethane-1,2-dione (3a).[1] Light yellow solid (88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 3.78 (d, *J* = 9.1 Hz, 4H), 3.69 – 3.64 (m, 2H), 3.43 – 3.37 (m, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 163.4, 163.2, 138.0, 131.9, 119.8 118.6, 116.7, 66.6, 66.5, 46.3, 41.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{13}NO_4$: 258.0737, Found: 258.0737 ($M+Na^+$).



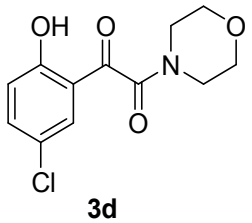
3b

1-(2-hydroxy-5-methylphenyl)-2-morpholinoethane-1,2-dione (3b). Yellow solid (70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.33 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 3.81 (d, *J* = 7.3 Hz, 4H), 3.69 – 3.66 (m, 2H), 3.43 – 3.38 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 163.6, 161.4, 139.4, 131.3, 129.2, 118.4, 116.4, 66.7, 66.6, 46.4, 41.6, 20.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{15}NO_4$: 250.1074, Found: 250.1064 ($M+H^+$).



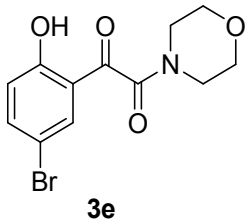
3c

1-(5-fluoro-2-hydroxyphenyl)-2-morpholinoethane-1,2-dione (3c). White solid (55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 7.27 – 7.18 (m, 2H), 6.95 (dd, *J* = 9.1, 4.3 Hz, 1H), 3.73 (q, *J* = 7.2 Hz, 4H), 3.64 – 3.60 (m, 2H), 3.36 – 3.32 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.63; ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 162.9, 159.7, 155.2 (d, *J* = 241.4 Hz), 126.0 (d, *J* = 23.2 Hz), 120.2 (d, *J* = 7.1 Hz), 116.5 (d, *J* = 23.2 Hz), 116.2(d, *J* = 7.1 Hz), 66.64, 66.55, 46.4, 41.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{12}FNO_4$: 254.0823, Found: 254.0819 ($M+H^+$).



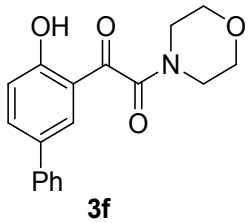
3d

1-(5-chloro-2-hydroxyphenyl)-2-morpholinoethane-1,2-dione (3d). Light yellow solid (37% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 7.55 (s, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.26 (s, 2H), 7.01 (d, *J* = 8.9 Hz, 1H), 3.81 (d, *J* = 3.1 Hz, 4H), 3.72 – 3.68 (m, 2H), 3.44 – 3.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 162.9, 161.9, 138.1, 130.9, 124.7, 120.4, 117.4, 66.7, 66.6, 46.4, 41.9; HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{12}ClNO_4$: 270.0528, Found: 270.0529 (M+ H^+).



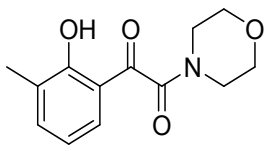
3e

1-(5-bromo-2-hydroxyphenyl)-2-morpholinoethane-1,2-dione (3e). Light yellow solid (71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.20 (s, 1H), 7.69 (d, *J* = 2.3 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 1H), 3.81 (q, *J* = 7.3 Hz, 4H), 3.71 – 3.67 (m, 2H), 3.43 – 3.39 (m, 2H); ^{113}C NMR (101 MHz, $CDCl_3$) δ 194.7, 162.8, 162.2, 140.8, 133.8, 120.7, 118.0, 111.4, 66.6, 66.5, 46.4, 41.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{12}BrNO_4$: 314.0022, Found: 314.0016 (M+H^+).



3f

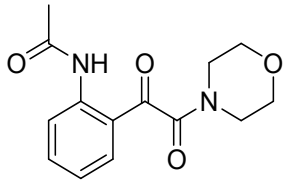
1-(4-hydroxy-[1,1'-biphenyl]-3-yl)-2-morpholinoethane-1,2-dione (3f). Yellow solid (47% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.85 – 7.72 (m, 2H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 1H), 3.80 (s, 4H), 3.71 – 3.65 (m, 2H), 3.45 – 3.38 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 163.4, 162.7, 139.2, 137.1, 133.38, 130.0, 129.0, 127.5, 126.7, 119.1, 116.8, 66.7, 66.6, 46.4, 41.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{17}NO_4$: 334.1050, Found: 334.1049 (M+Na^+).



3g

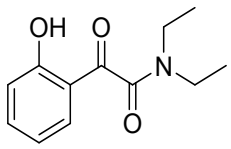
1-(2-hydroxy-3-methylphenyl)-2-morpholinoethane-1,2-dione (3g). Light yellow solid (71%

yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (s, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 6.87 (t, *J* = 7.7 Hz, 1H), 3.82 – 3.76 (m, 4H), 3.68 – 3.64 (m, 2H), 3.41 – 3.36 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 163.7, 161.8, 138.8, 129.5, 127.9, 119.3, 116.0, 66.65, 66.59, 46.3, 41.6, 15.2; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{15}NO_4$: 250.1074, Found: 250.1069 ($M+H^+$).



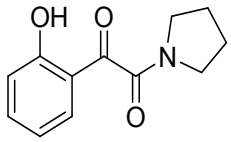
3h

N-(2-(2-morpholino-2-oxoacetyl)phenyl)acetamide (3h).[2] Brown solid (47% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.80 (d, *J* = 8.5 Hz, 1H), 7.74 – 7.58 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 3.83 – 3.75 (m, 4H), 3.70 – 3.63 (m, 2H), 3.40 – 3.33 (m, 2H), 2.27 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 169.4, 164.4, 142.4, 137.1, 133.4, 122.7, 120.7, 117.6, 66.5, 46.3, 41.6, 25.5.; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{16}N_2O_4$: 299.1002, Found: 299.1003 ($M+Na^+$).



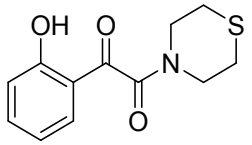
3i

***N,N*-diethyl-2-(2-hydroxyphenyl)-2-oxoacetamide (3i)**. Yellow liquid (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 7.49 – 7.39 (m, 2H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 3.48 (q, *J* = 7.2 Hz, 2H), 3.18 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 164.7, 163.1, 137.6, 131.9, 119.6, 118.4, 116.7, 42.2, 38.7, 13.9, 12.6; HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{15}NO_3$: 244.0944, Found: 244.0953 ($M+Na^+$).



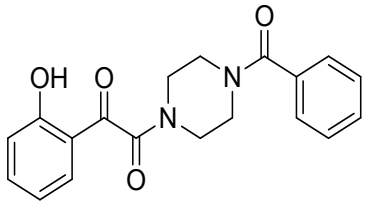
3j

1-(2-hydroxyphenyl)-2-(pyrrolidin-1-yl)ethane-1,2-dione (3j). Yellow liquid (52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 7.59 – 7.53 (m, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 3.59 (t, *J* = 6.7 Hz, 2H), 3.37 (t, *J* = 6.4 Hz, 2H), 1.94 – 1.85 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 163.5, 163.2, 137.8, 132.3, 119.7, 118.4, 116.5, 46.7, 45.3, 25.8, 24.0; HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{13}NO_3$: 242.0788, Found: 242.0791 ($M+Na^+$).



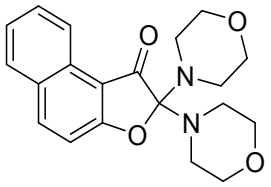
3k

1-(2-hydroxyphenyl)-2-thiomorpholinoethane-1,2-dione (3k). Yellow solid (69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H), 7.55 (dd, *J* = 17.8, 8.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 4.08 – 3.96 (m, 2H), 3.69 – 3.58 (m, 2H), 2.80 – 2.71 (m, 2H), 2.67 – 2.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 163.7, 163.3, 138.1, 131.9, 119.8, 118.6, 116.6, 48.8, 43.7, 27.8, 27.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{13}NO_3S$: 252.0689, Found: 252.0692 ($M+H^+$).



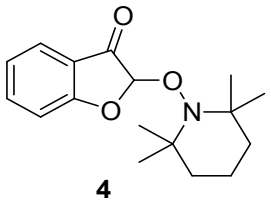
3l

1-(4-benzoylpiperazin-1-yl)-2-(2-hydroxyphenyl)ethane-1,2-dione (3l). Yellow solid (86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.57 (t, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 11.3 Hz, 5H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 3.74 (d, *J* = 40.5 Hz, 6H), 3.42 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 170.7, 163.6, 163.3, 138.2, 134.7, 131.9, 130.3, 128.7, 127.0, 119.9, 118.7, 116.7, 46.06, 46.02, 41.43, 41.40; HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{18}N_2O_4$: 361.1159, Found: 361.1165 ($M+Na^+$).



3p′

2,2-dimorpholinonaphtho[2,1-b]furan-1(2*H*)-one (3p′).[3] Yellow solid (28% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 9.0 Hz, 1H), 3.69 (t, *J* = 4.6 Hz, 8H), 3.03 – 2.94 (m, 4H), 2.80 – 2.73 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 173.3, 141.4, 130.3, 129.0, 128.6, 128.5, 125.4, 123.0, 113.2, 113.1, 110.5, 66.9, 45.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{22}N_2O_4$: 377.1472, Found: 377.1478 ($M+Na^+$).



4

2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzofuran-3(2*H*)-one (4).[4] White solid (20% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 13.5, 7.7 Hz, 2H), 7.04 (dd, *J* = 8.0, 5.6 Hz, 2H), 5.73 (s, 1H), 1.54 (d, *J* = 6.6 Hz, 5H), 1.46 (s, 3H), 1.35 (s, 4H), 1.23 (s, 3H), 1.12 – 1.03 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 171.1, 138.7, 124.7, 121.8, 119.8, 113.3, 106.3, 61.7, 59.6, 40.4, 40.2, 33.8, 32.2, 20.4, 20.1, 17.0; HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{23}NO_3$: 290.1751, Found: 290.1758 ($M+H^+$).

5.Reference

[1] L. Dutta and P. J. Bhuyan, *Tetrahedron*, 2018, **74**, 5770.

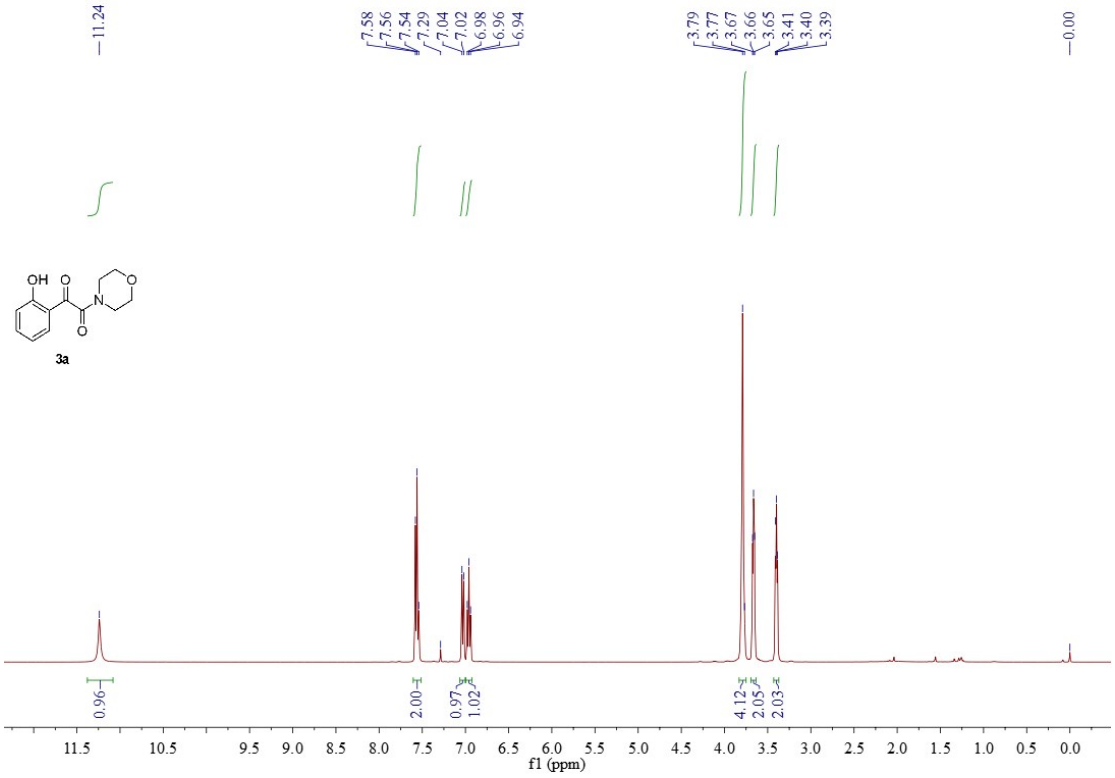
[2] B. T. Gonçalves, P. M. Esteves, A. C. Pinto, C. R. Kaiser, F. L. da Silva, E. Miguez and J. F. M. da Silva, *Magn. Reson. Chem.* 2008, **46**, 418.

[3] H. Yu, W. Huang and F. Zhang, *Eur. J. Org. Chem.* 2014, **2014**, 3156.

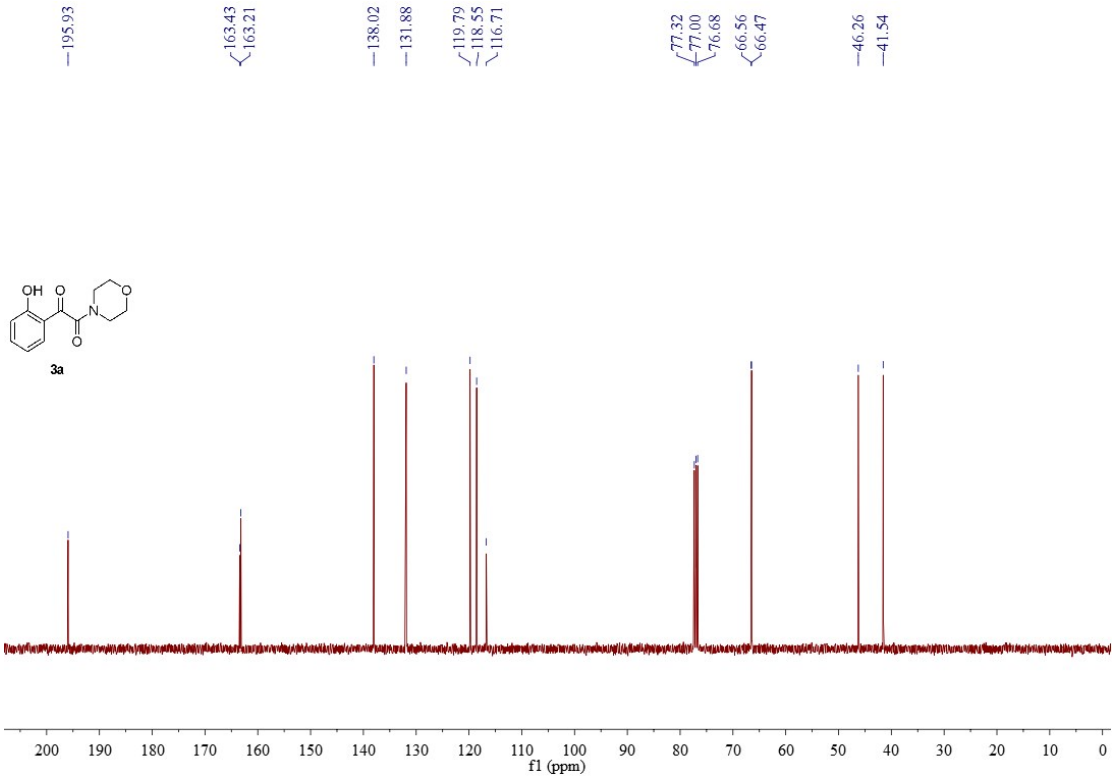
[4] Y.-X. Xie, R.-J. Song, Y. Liu, Y.-Y. Liu, J.-N. Xiang and J.-H. Li, *Adv. Synth. Catal.* 2013, **355**, 3387.

6. Spectroscopic data for products

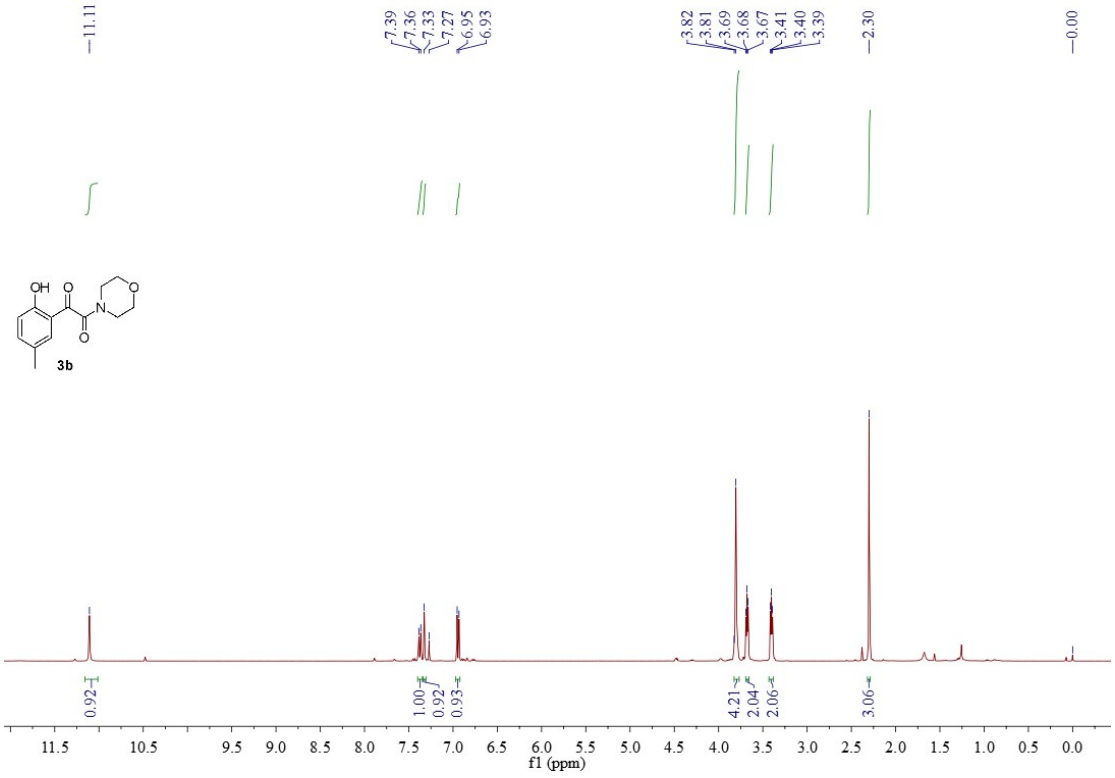
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3a**



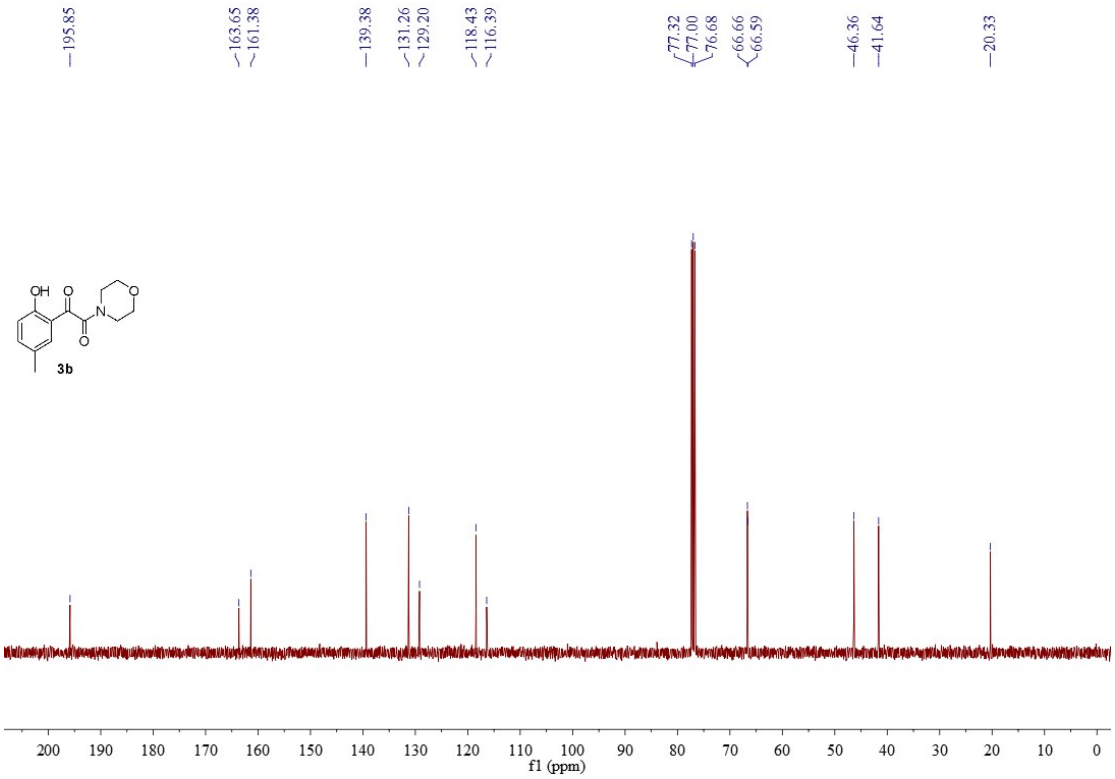
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3a**



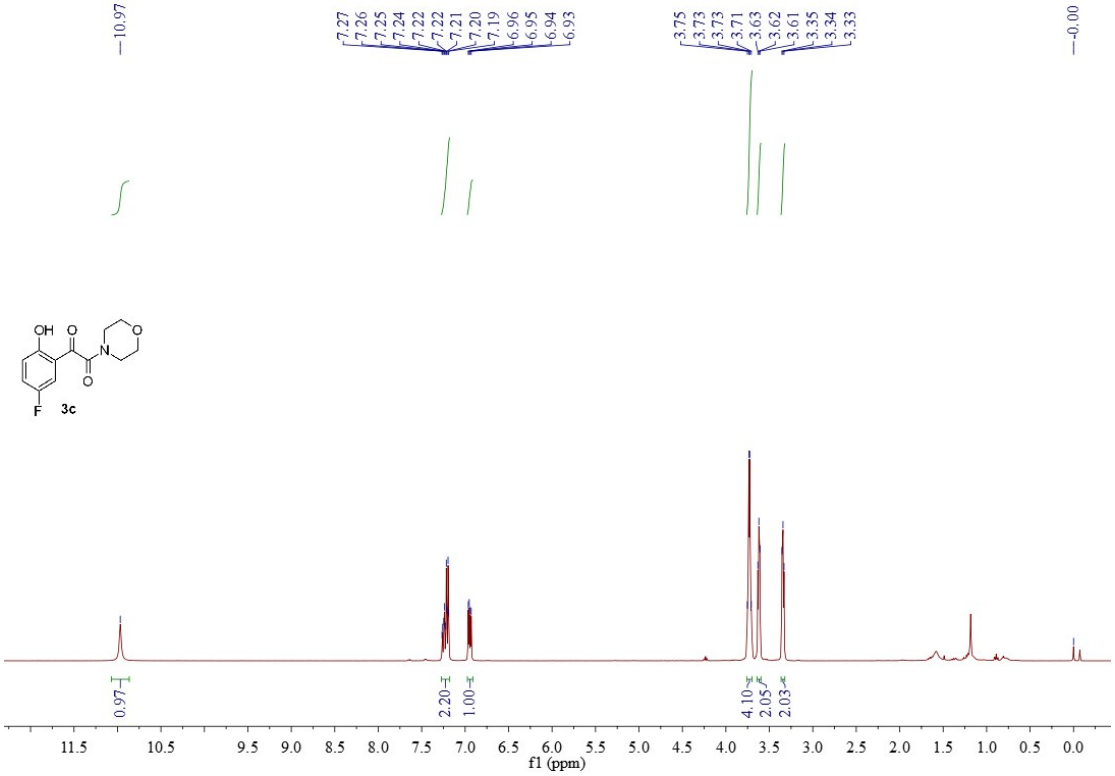
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3b**



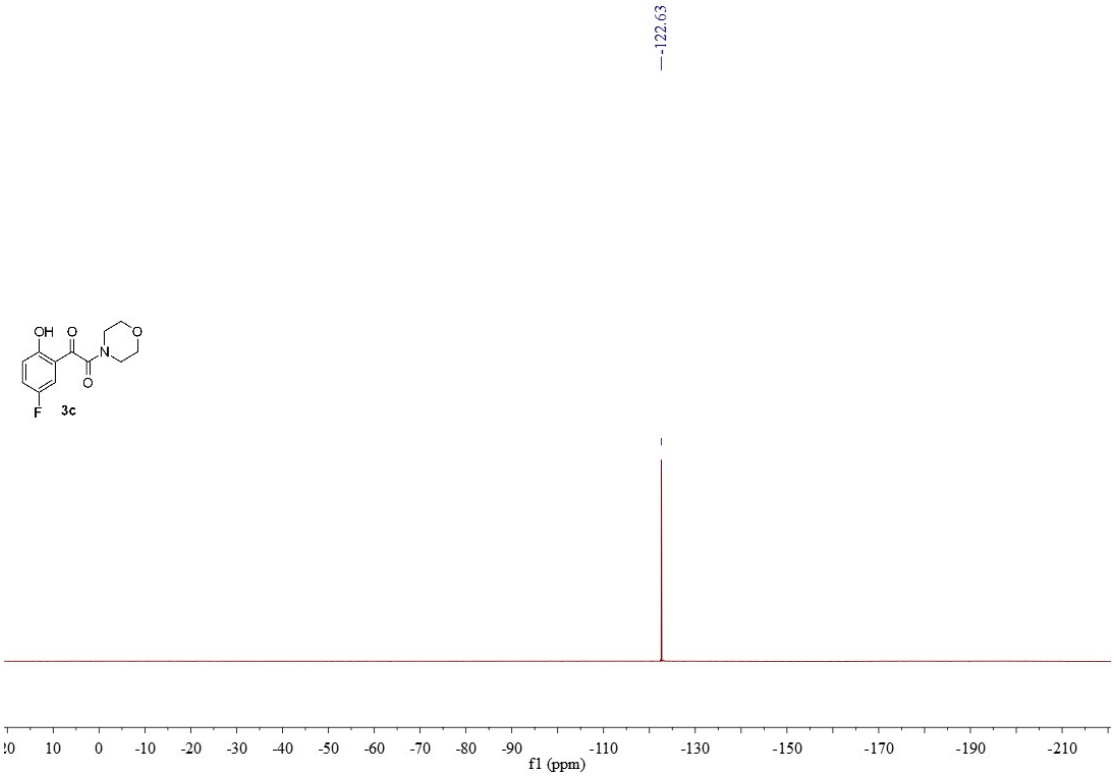
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3b**



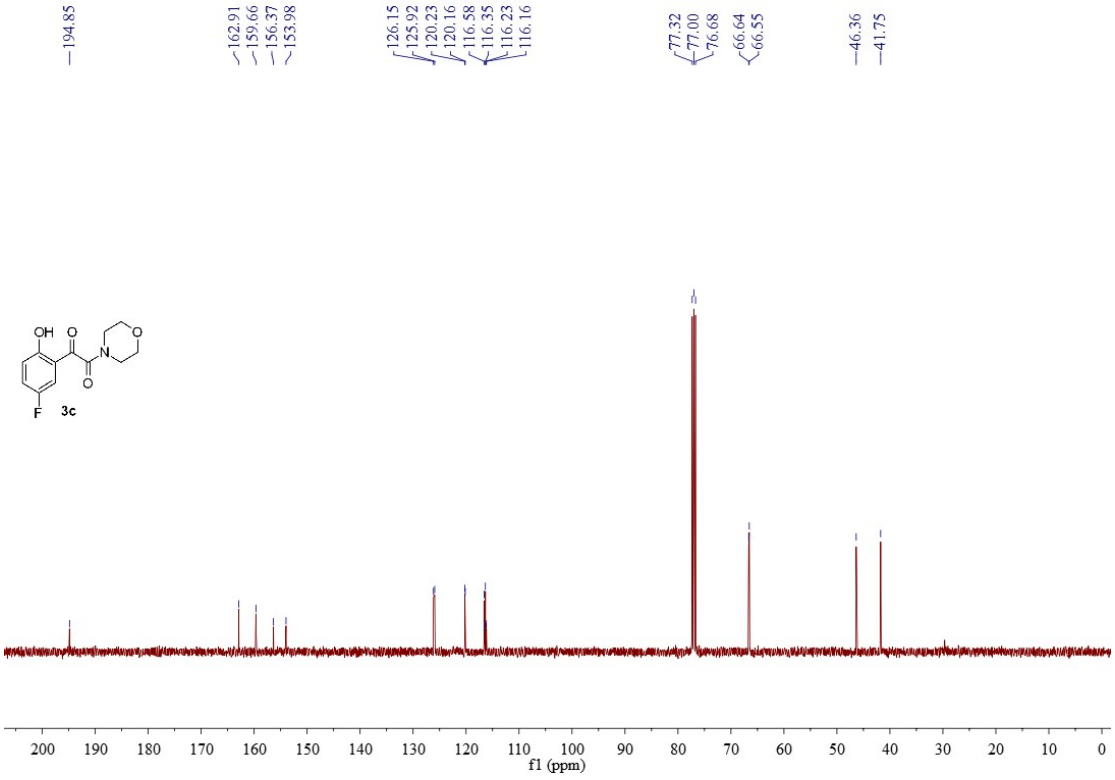
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3c**



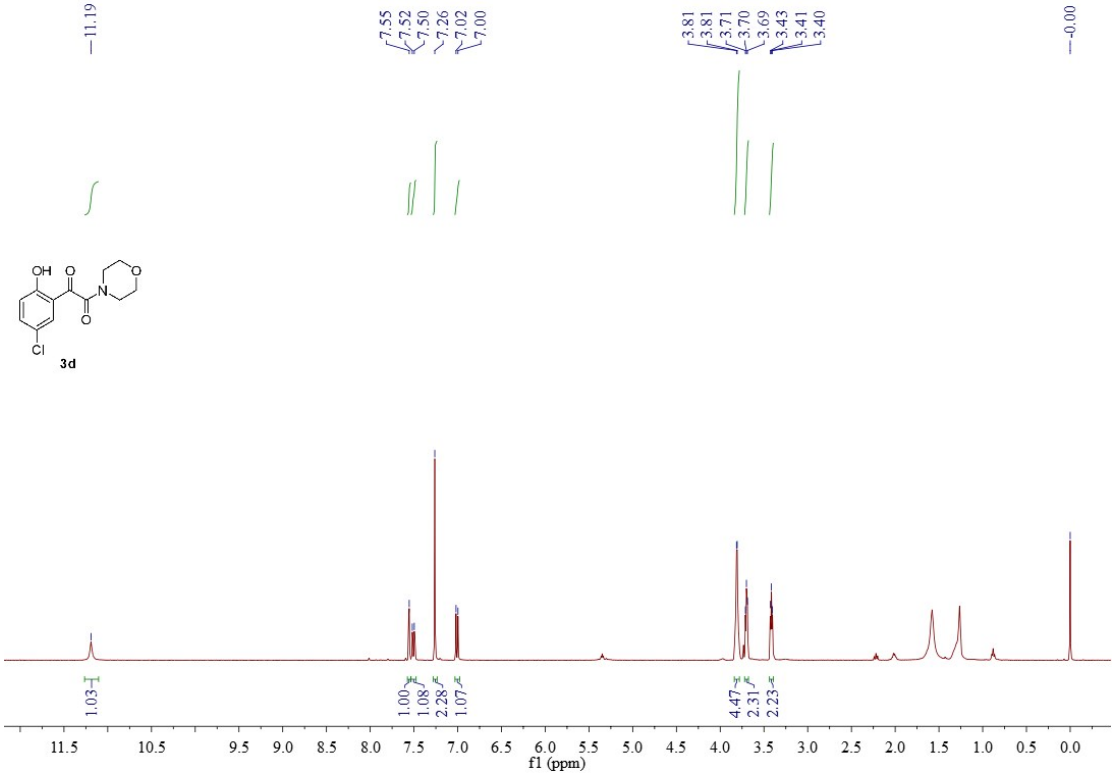
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3c**



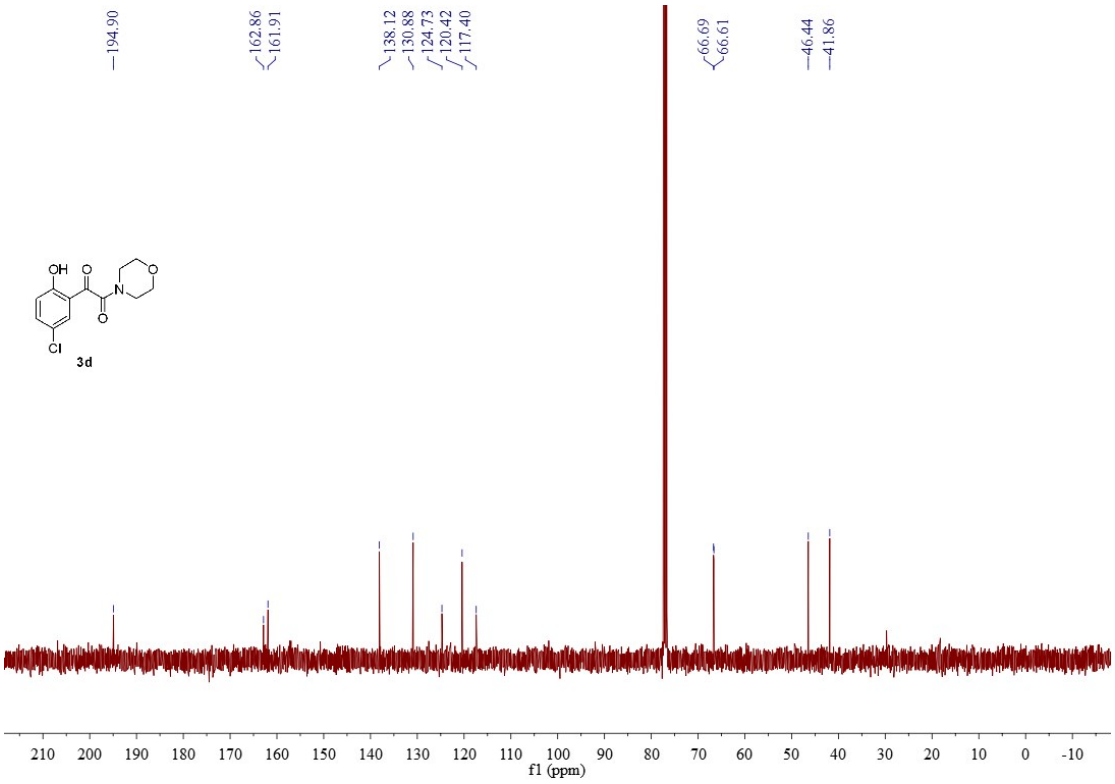
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3c**



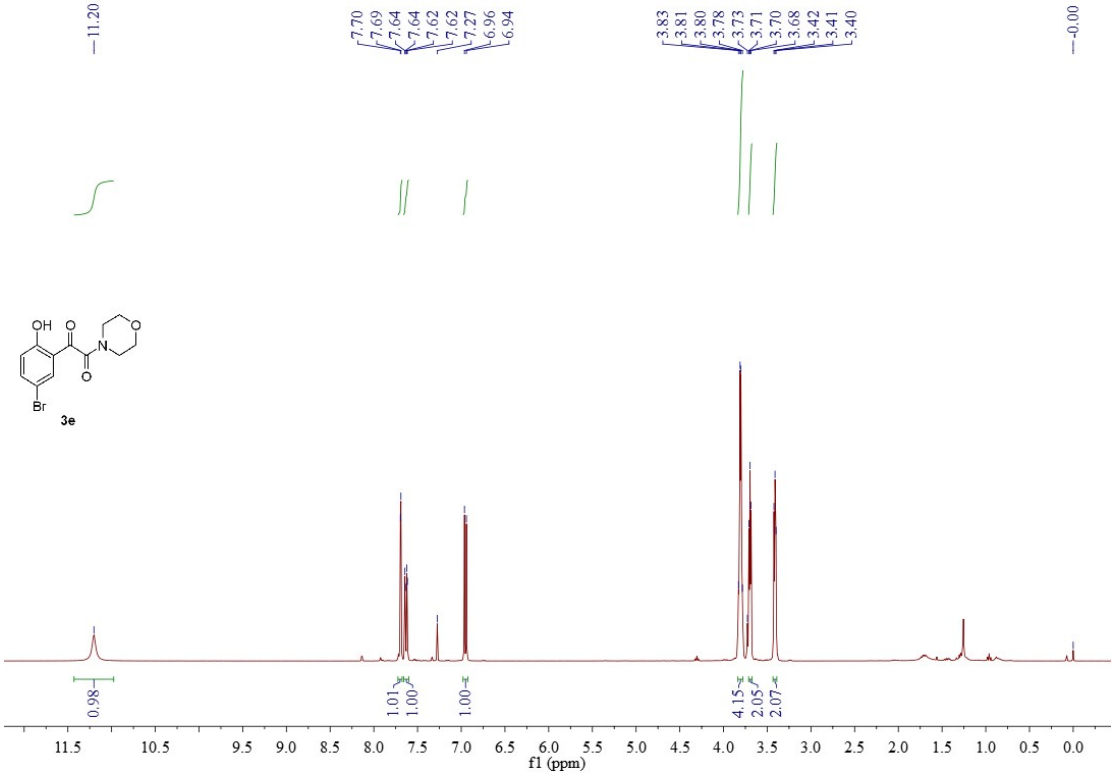
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3d**



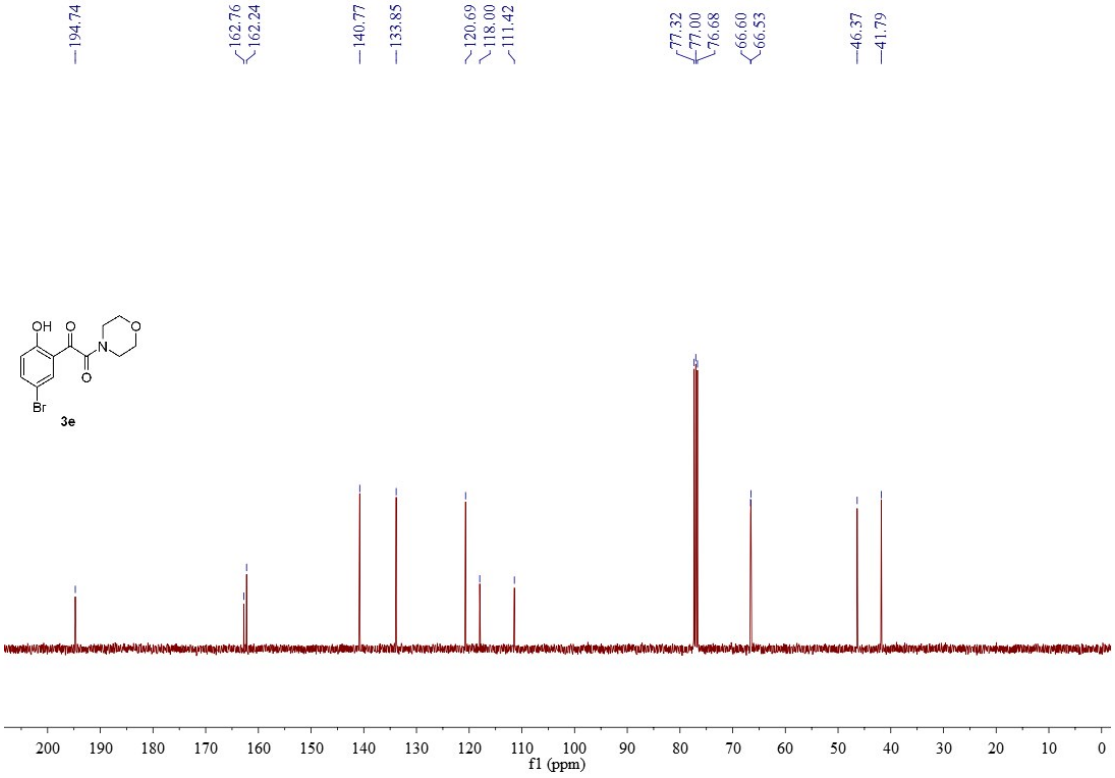
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3d**



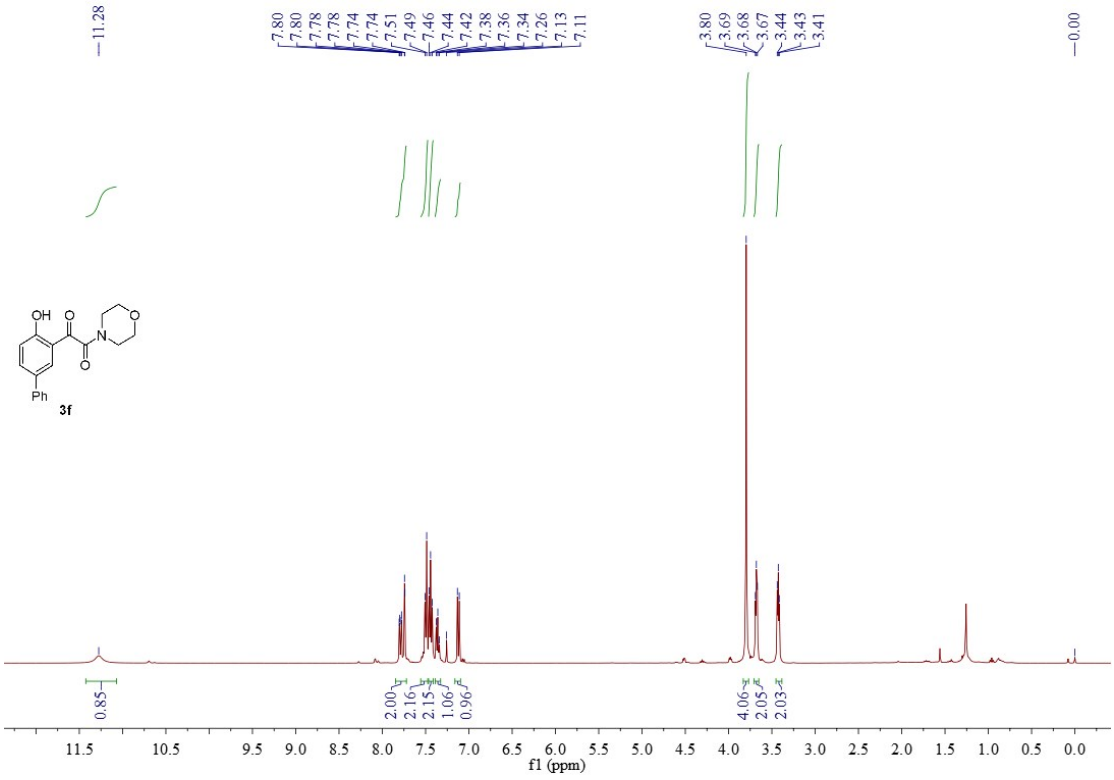
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3e**



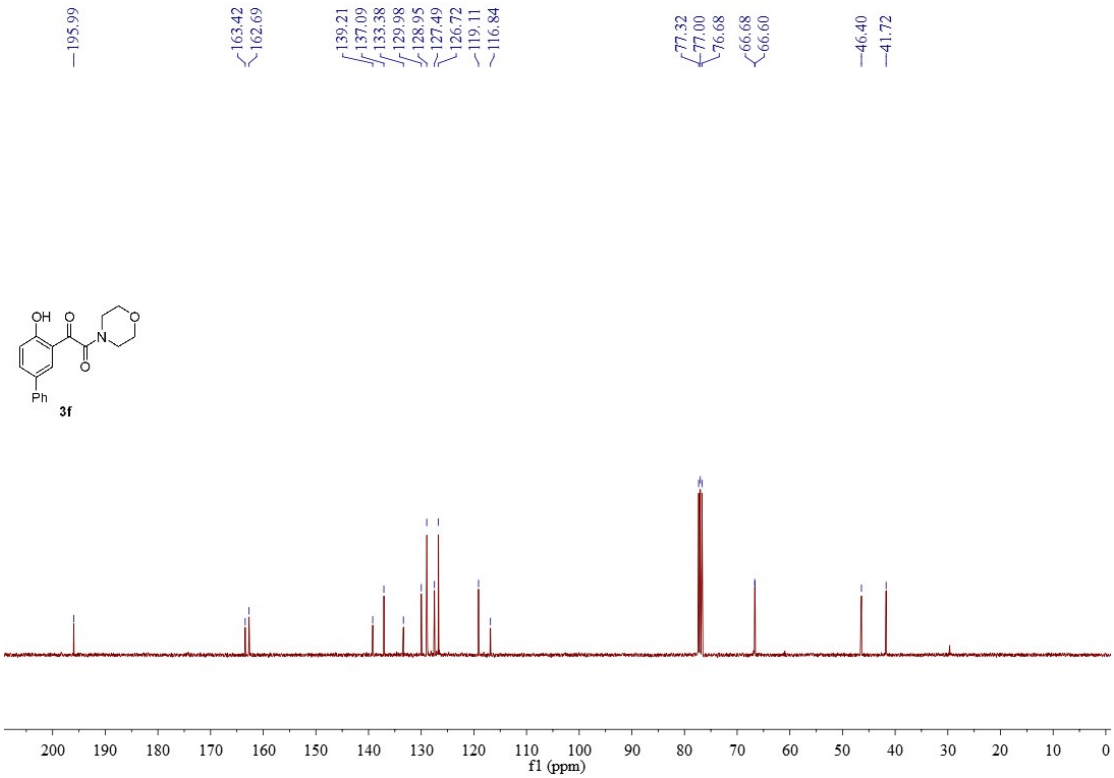
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3e**



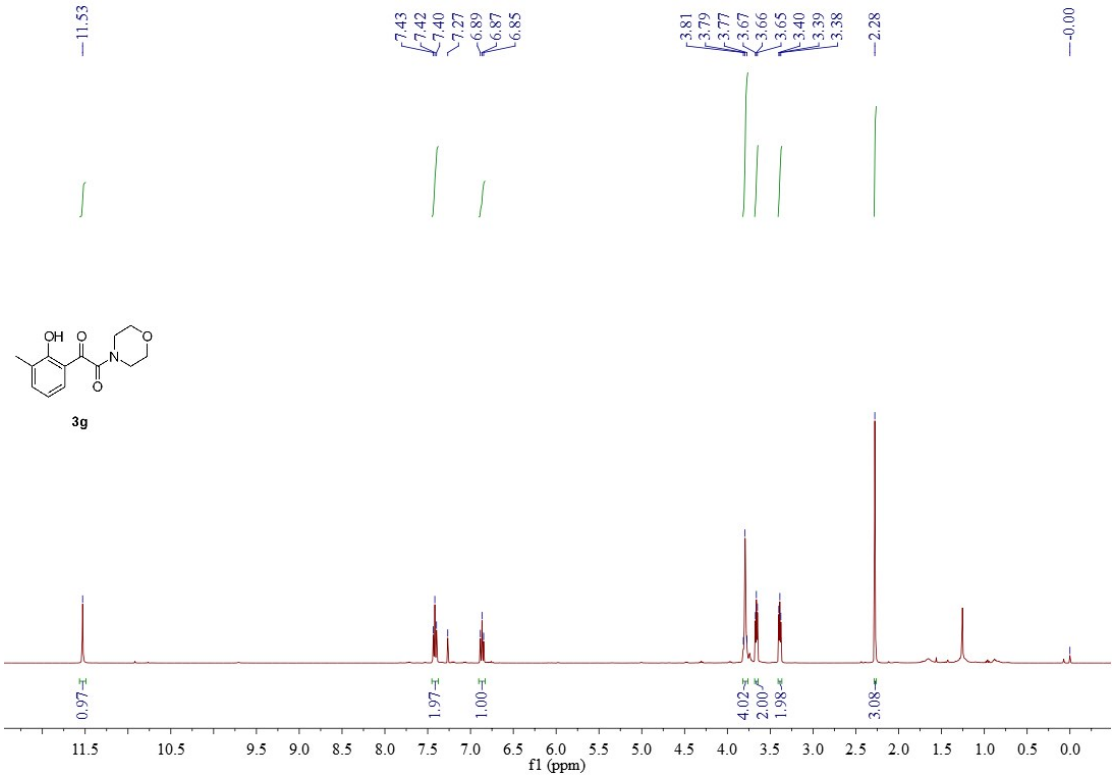
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3f**



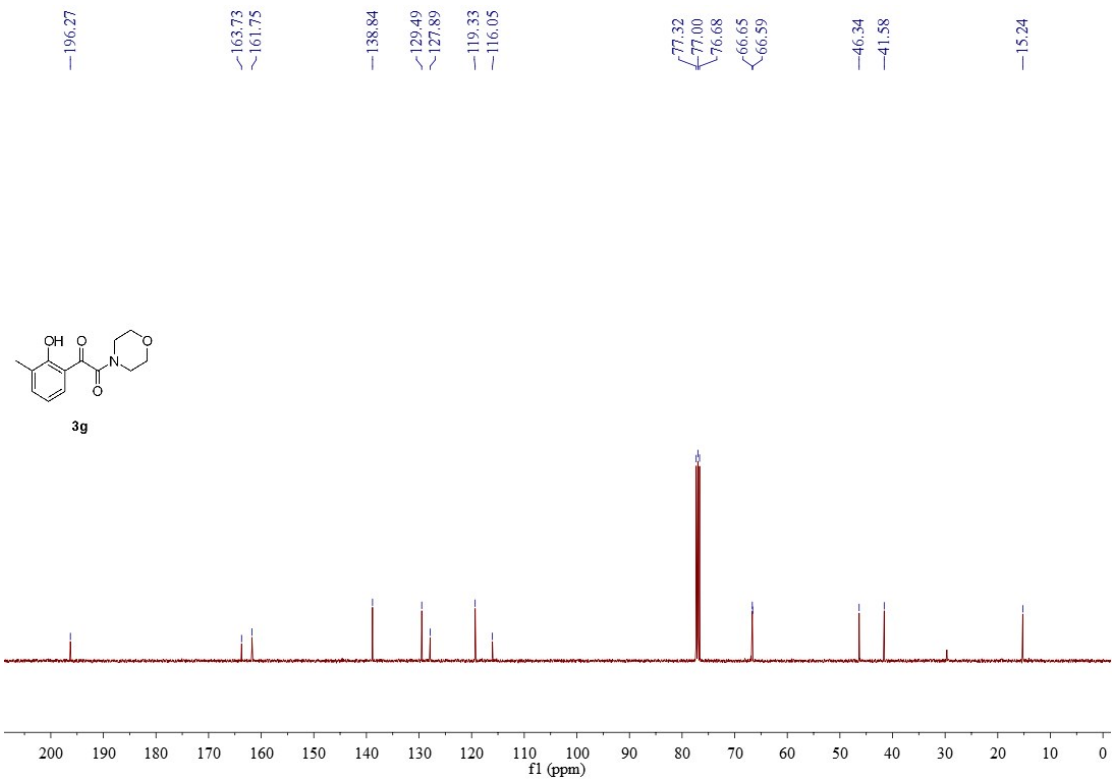
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3f**



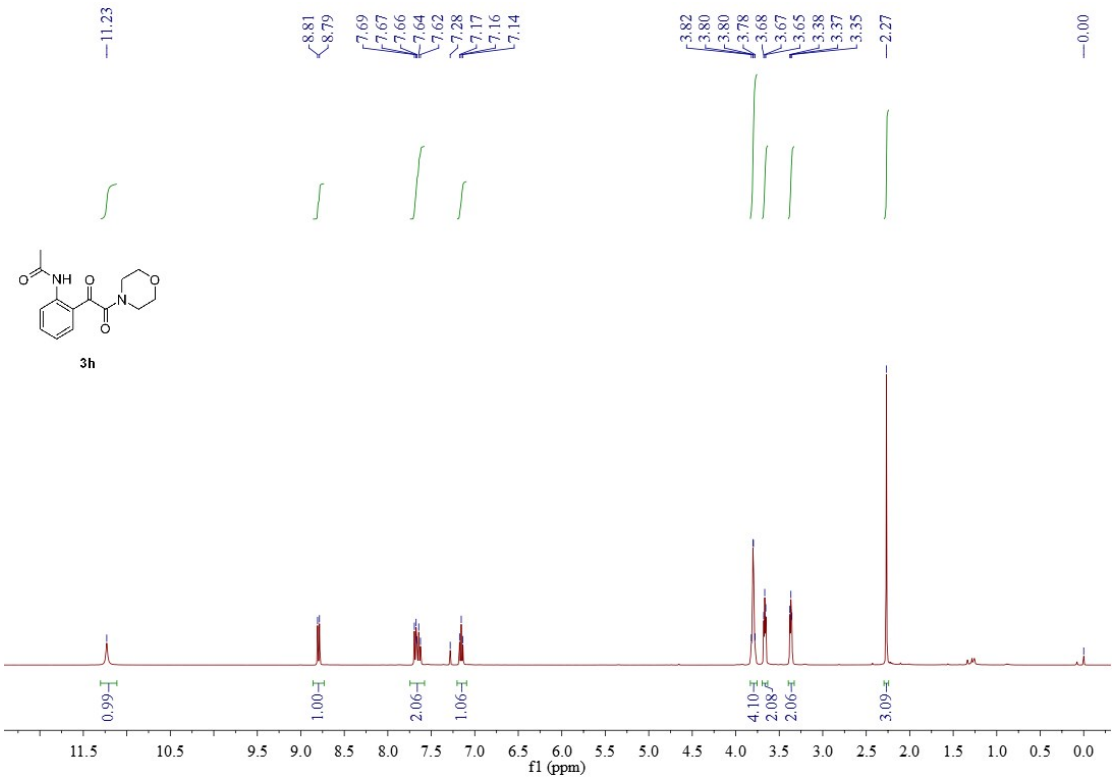
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3g**



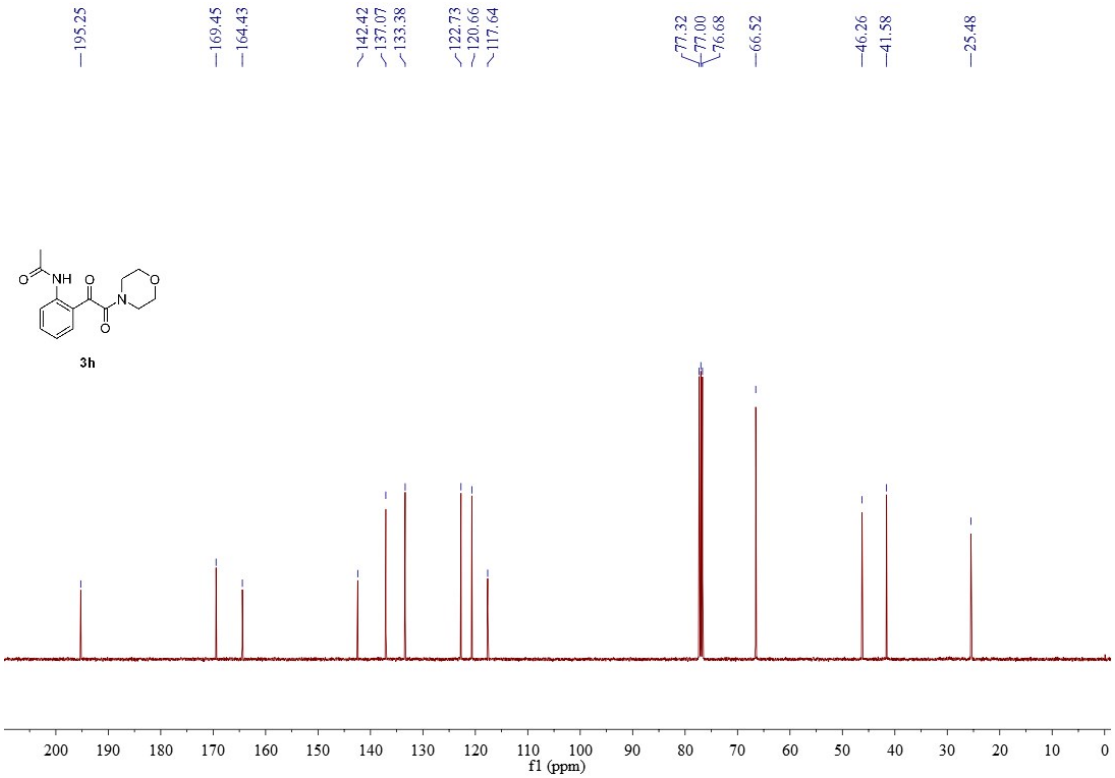
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3g**



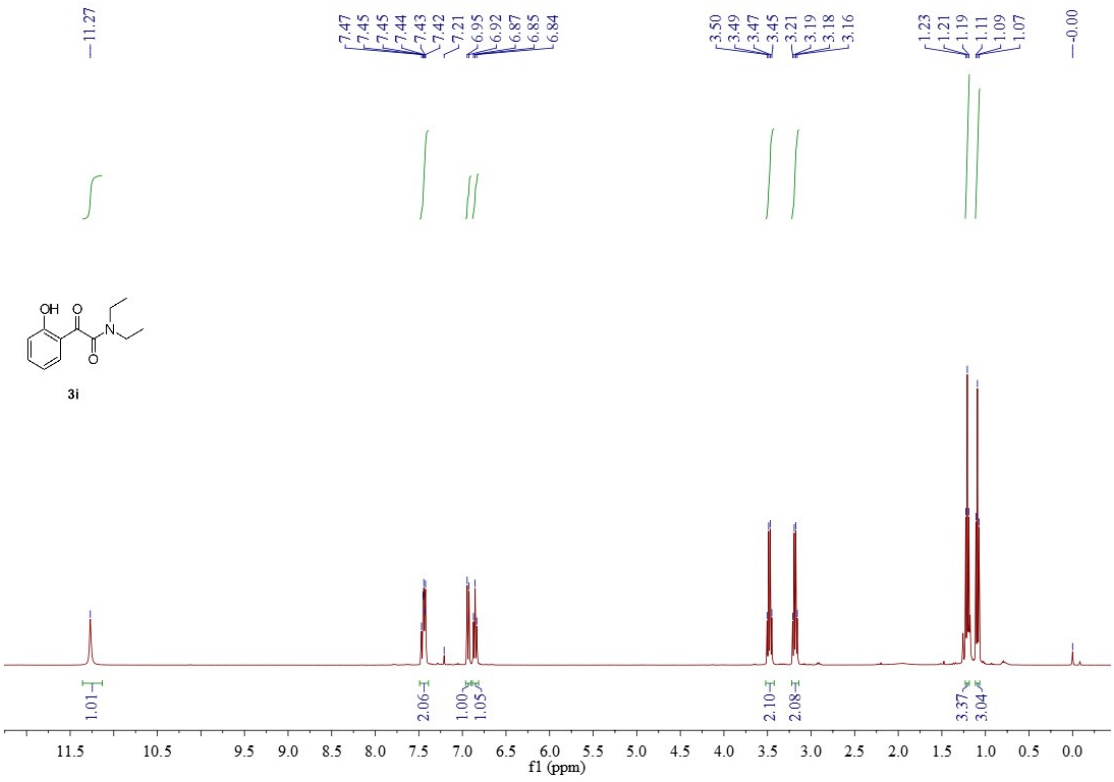
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3h**



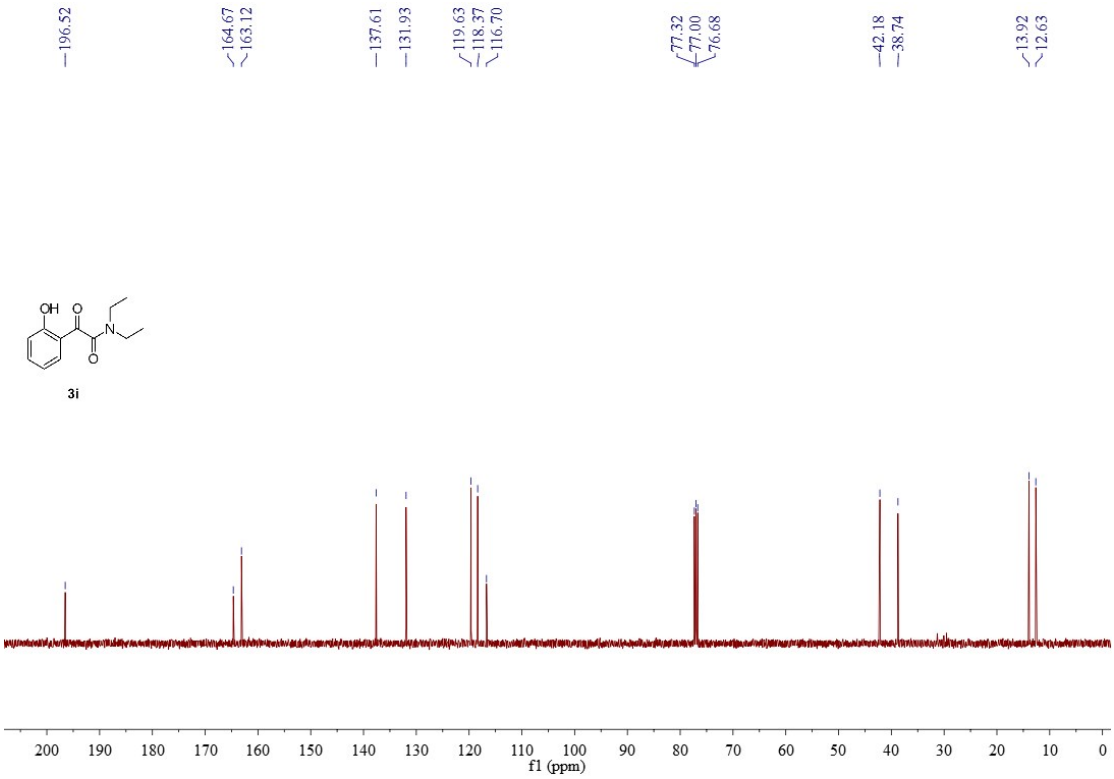
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3h**



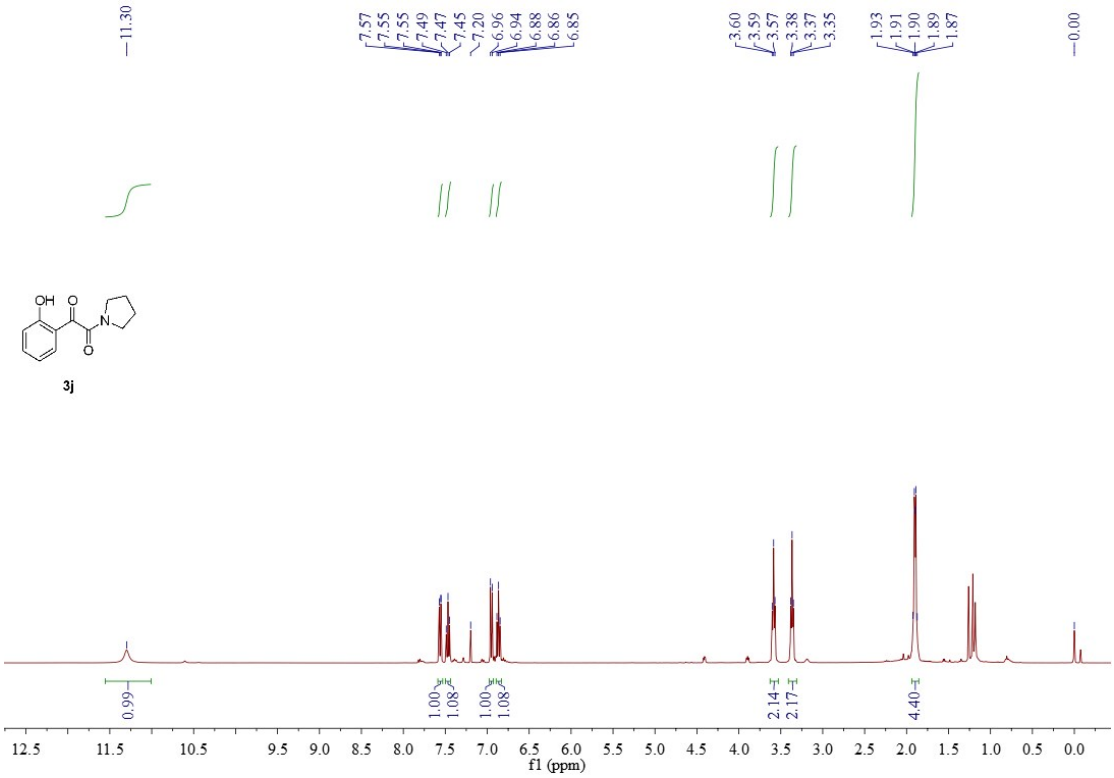
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3i**



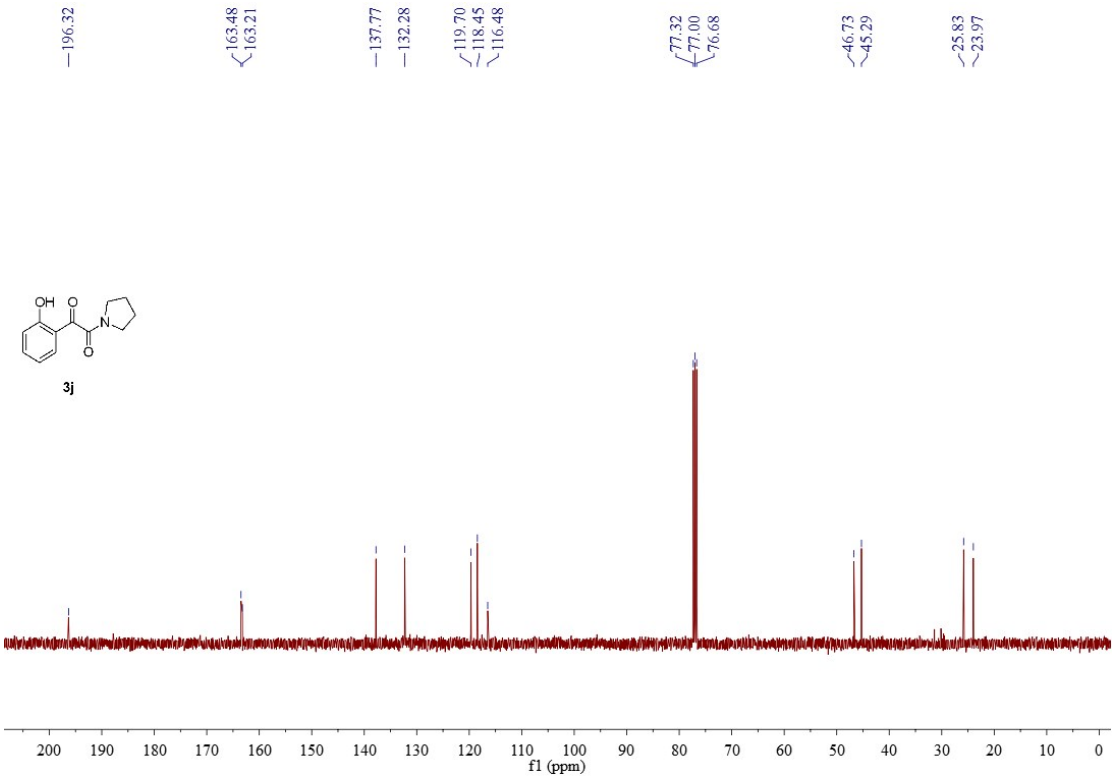
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3i**



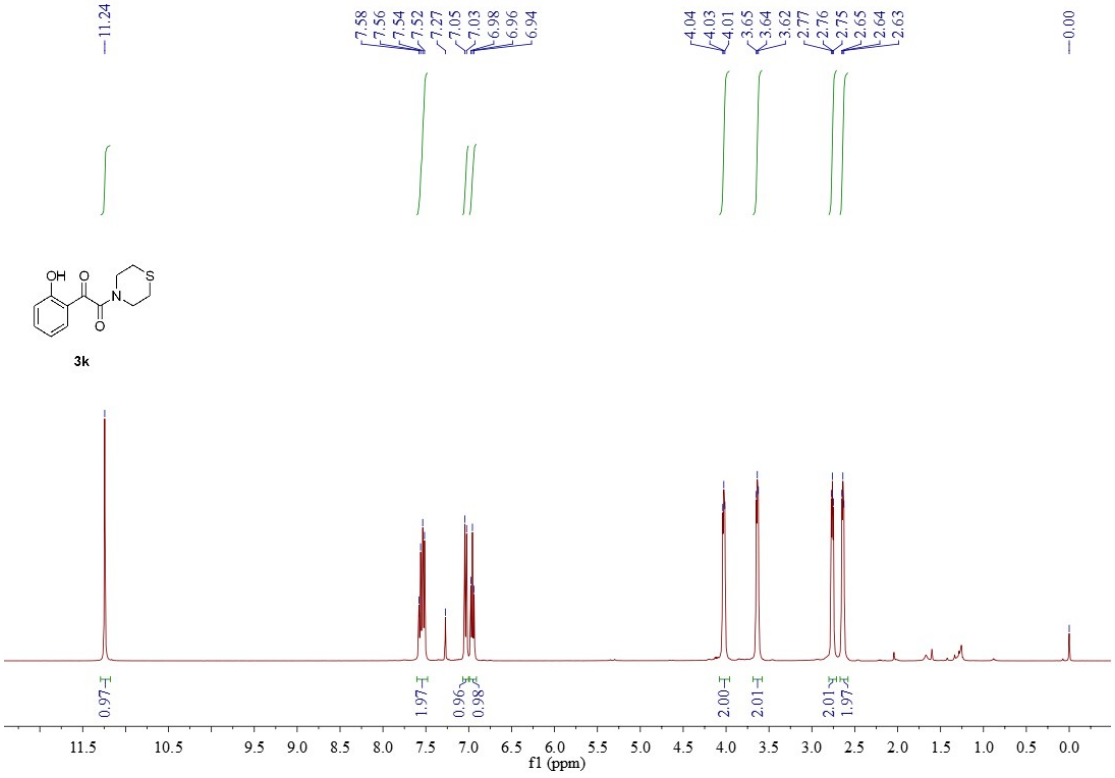
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3j**



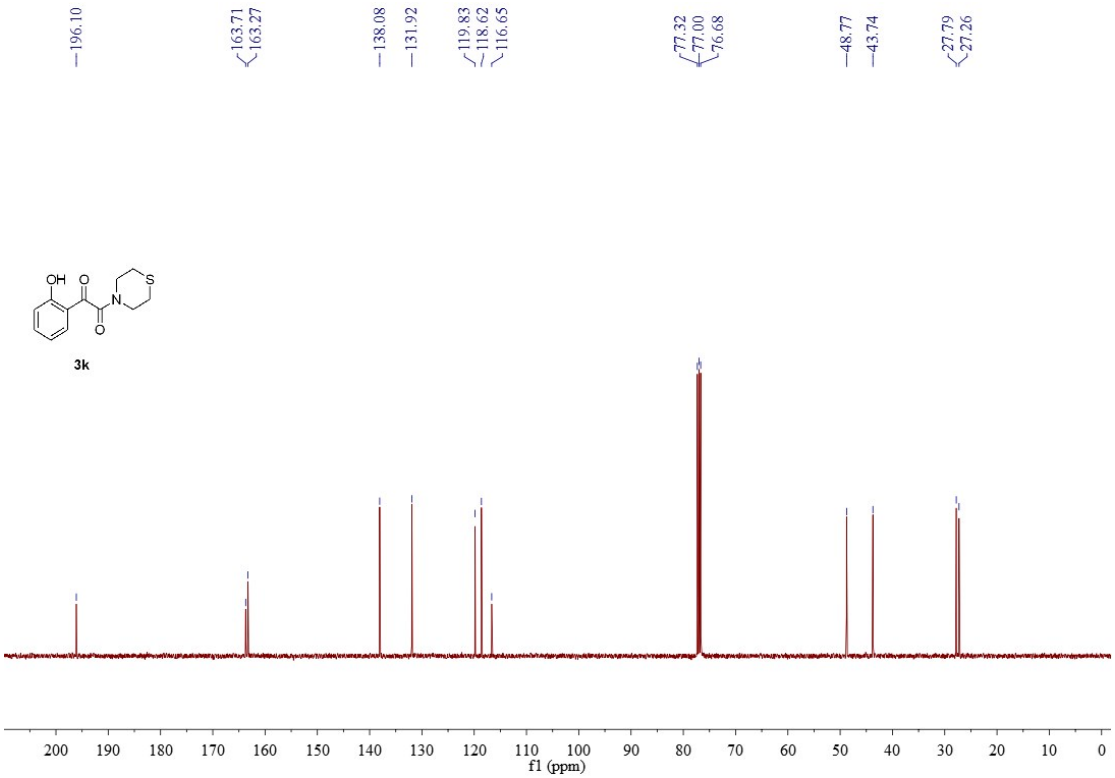
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3j**



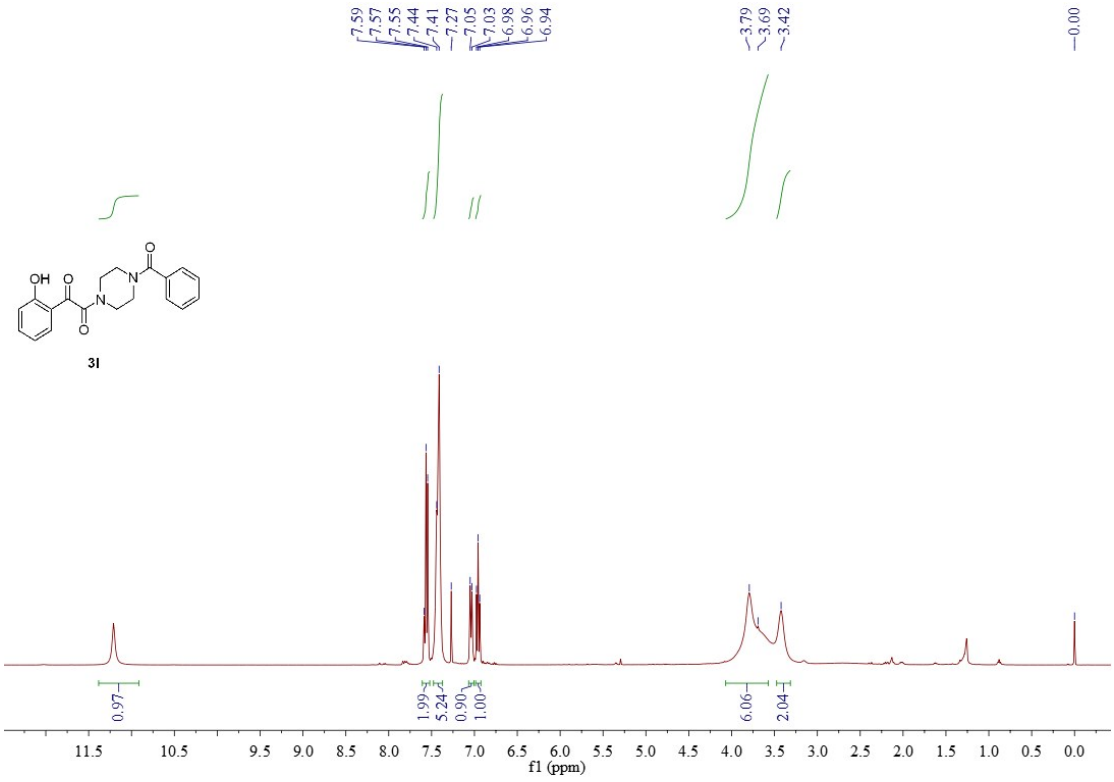
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3k**



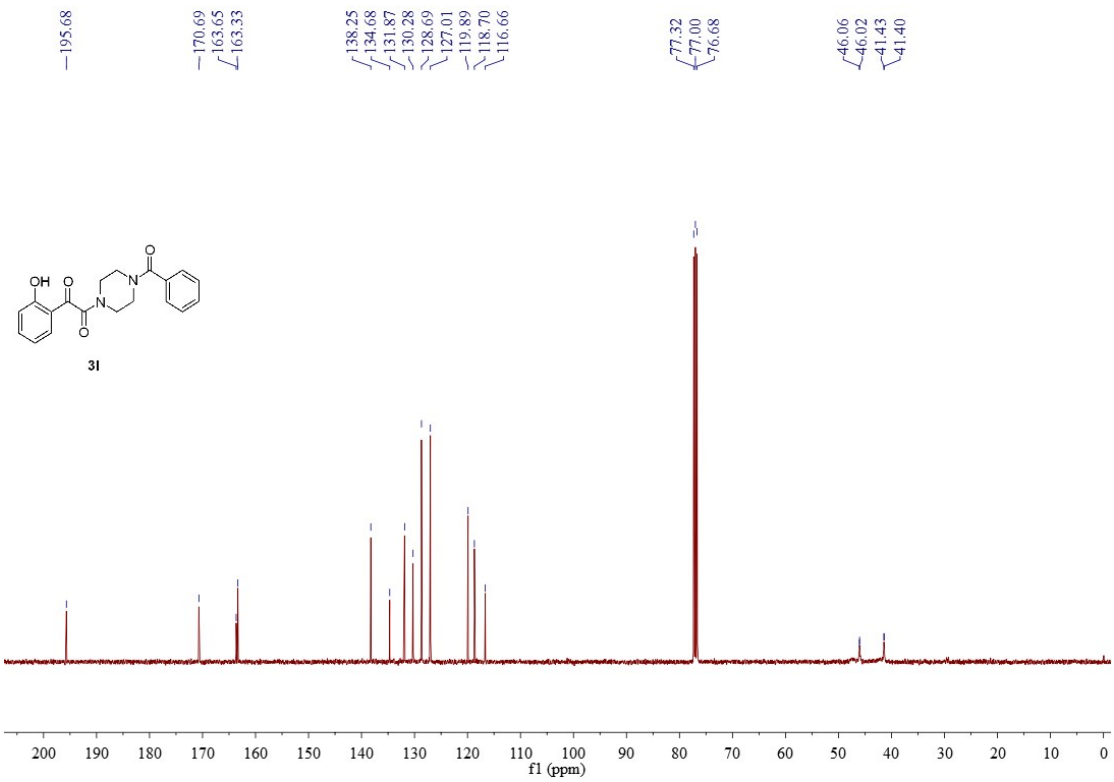
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3k**



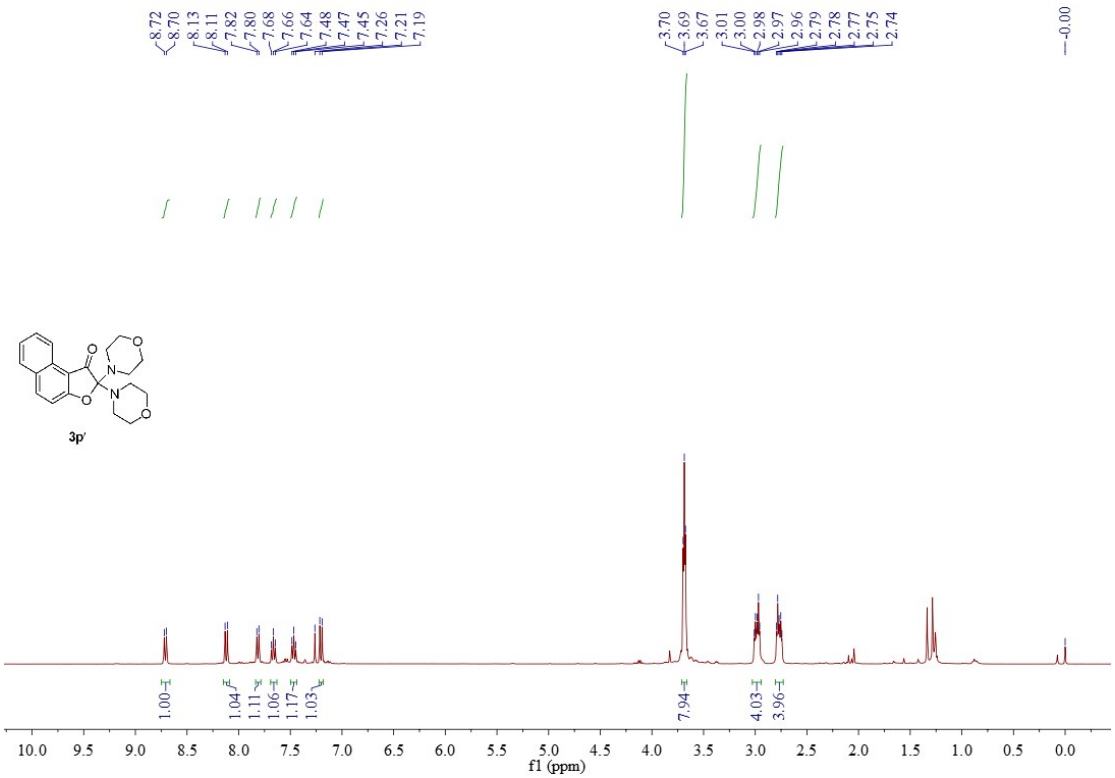
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3l**



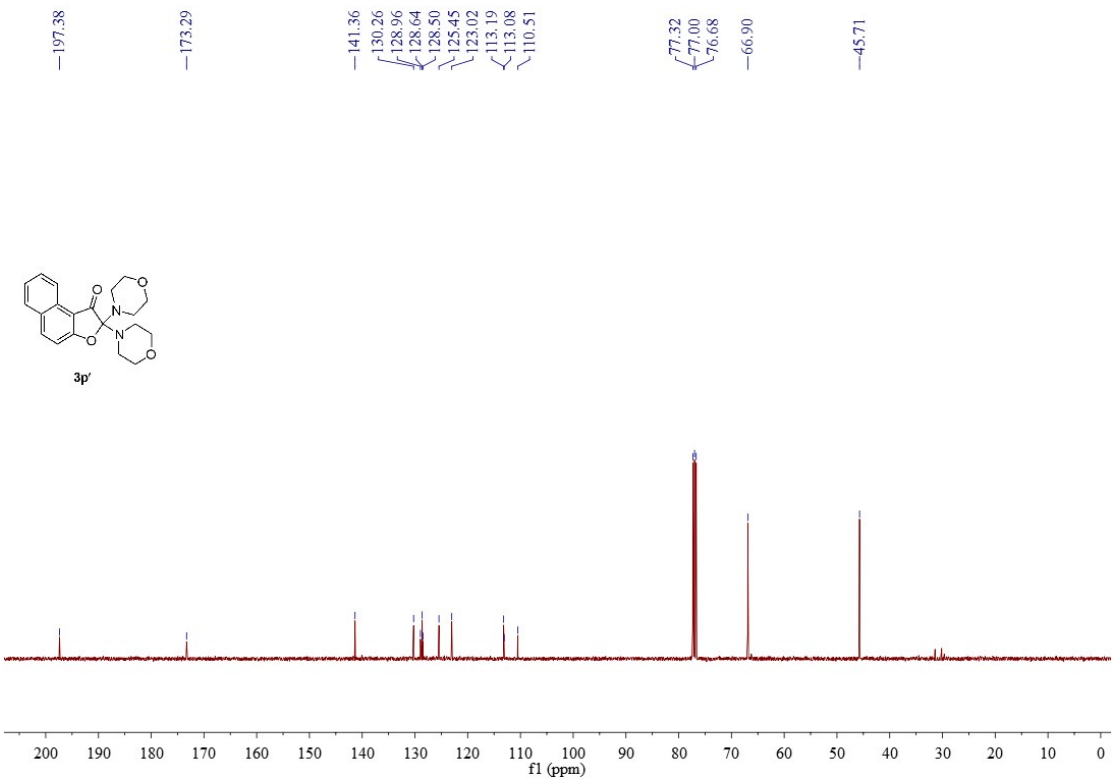
^{13}C NMR (101MHz, $CDCl_3$) spectra of **3l**



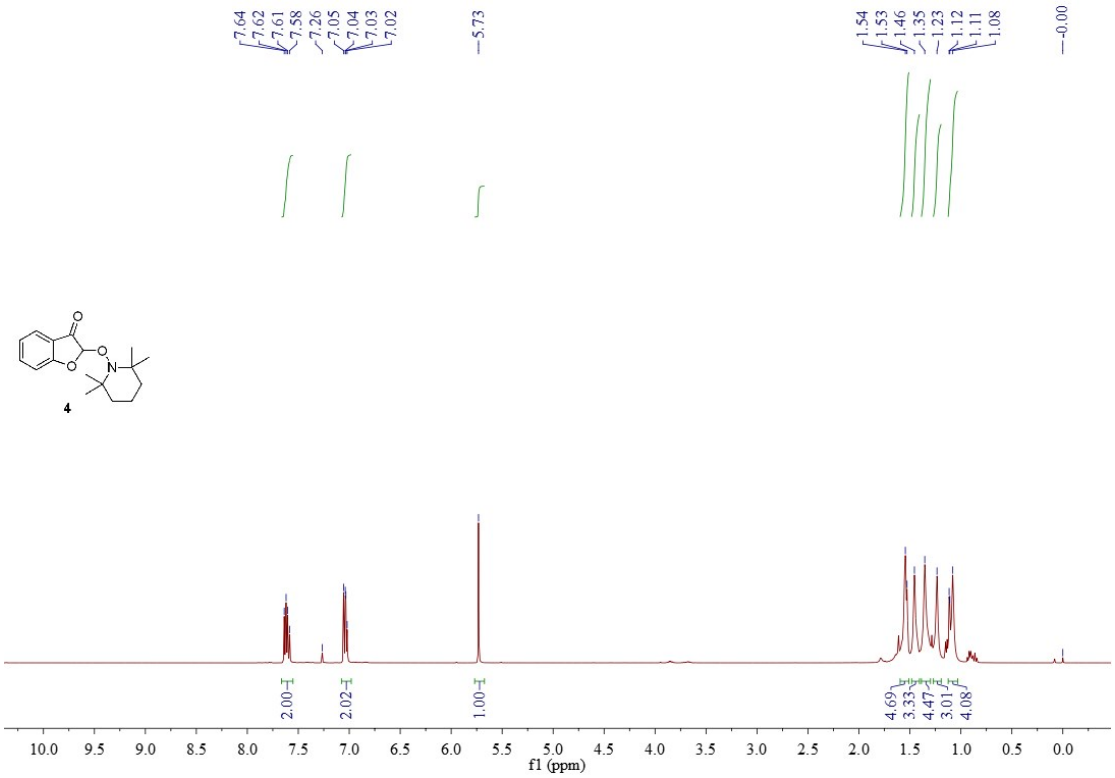
^{1}H NMR (400MHz, $CDCl_3$) spectra of **3p′**



^{13}C NMR (101MHz, $CDCl_3$) spectra of **3p′**



^{1}H NMR (400MHz, $CDCl_3$) spectra of **4**



^{13}C NMR (101MHz, $CDCl_3$) spectra of **4**