

supporting information for

**Synthesis of α -ketoamides via oxidative amidation of Diazo Compounds with *O*-
benzoyl hydroxylamines as Nitrogen Source and Oxidant**

Wenwen Chen,^{* a} Xinyin Zhang,^a Xinyu Wang,^a EnXuan Zhang,^c Zuli Wang,^{*b} and Jianfeng Jia^{*}

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1. General information

Unless otherwise stated, all commercial reagents were used without additional purification. Column chromatography was undertaken on silica gel (200-300 mesh) using a proper eluent system. ^1H NMR, and ^{13}C NMR spectra were recorded on a spectrometer at 600 MHz, with deuterated chloroform as solvent. The chemical shifts δ are reported in ppm relative to tetramethylsilane ($\delta = 0$ ppm) or residual CHCl_3 ($\delta = 77.00$ ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), Coupling constants *J* are reported in Hertz (Hz). High-resolution mass spectrometry (HRMS) was performed on a Bruker Impact II spectrometer using electrospray ionization (ESI).

2. Effect of solvent on the reaction

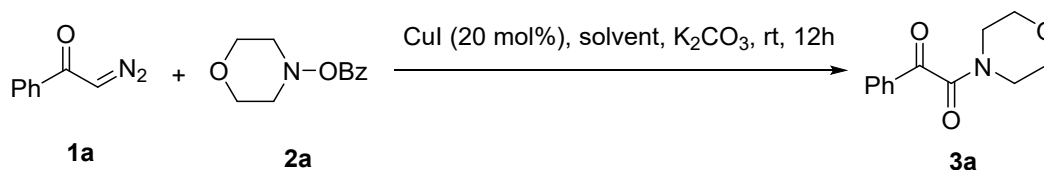


Table S1 Influence of solvent on reaction ^a

Entry	Solvent	Base	Temp (°C)	Time(h)	Yield (%) ^c
1	EtOH	K ₂ CO ₃	rt	12	NR
2	DMF	K ₂ CO ₃	rt	12	5
3	NMP	K ₂ CO ₃	rt	12	Trace
4	DCM	K ₂ CO ₃	rt	12	NR
5	Toluene	K ₂ CO ₃	rt	12	Trace
6	MeCN	K ₂ CO ₃	rt	12	31
7	H ₂ O	K ₂ CO ₃	rt	12	7.2
8	THF	K ₂ CO ₃	rt	12	26.2
9	DCE	K ₂ CO ₃	rt	12	9.6
10	EtOAc	K ₂ CO ₃	rt	12	Trace
11	4-Bromoanisole	K ₂ CO ₃	rt	12	trace
12 ^b	MeCN	K ₂ CO ₃	rt	12	32
13 ^c	MeCN	K ₂ CO ₃	rt	12	39
14 ^d	MeCN	K ₂ CO ₃	rt	12	20

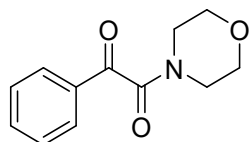
^a Reactions run using 0.5 mmol of α-Carbonyl 2-diazo-1-phenylethan-1-one, 0.6 mmol of morpholino benzoate, 1.0 mmol base, 20 mol % of CuI, solvent 1 mL at room temperature for 12 h;

^b solvent 1.5 ml; ^c solvent 2 ml; ^d solvent 2.5 ml; ^e Isolated yields.

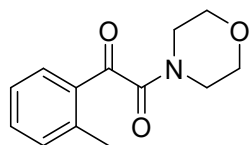
3. General procedure for 1-morpholino-2-phenylethane-1,2-dione

The experimental procedure involved the synthesis of α -ketoamides through the reaction of 2-diazo-1-phenylethan-1-one with morpholino-4-benzoate. Specifically, 2-diazo-1-phenylethan-1-one (72 mg, 0.5 mmol), morpholino-4-benzoate (207mg, 1mmol), K_2CO_3 (138mg, 1mmol) and CuI (20 mg) were added to a 10 mL Schlenk tube. The system was subjected to three pumping-charging cycles for N_2 atmosphere. Then MeCN (2 mL) were injected and the resulting mixture was stirred under 40 °C (oil bath) for 12 hours. At the end of the reaction, the reaction mixture was directly purified by a silica gel column chromatography (PE:EtOAc=5:1) without any treatment to give the products. Furthermore, the structure of the product were determined by 1H NMR spectra and ^{13}C NMR data. The ^{18}O content in the product is determined by performing HRMS on the isolated product by a silica gel column chromatography.

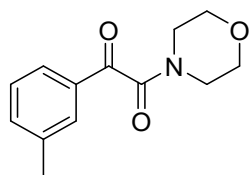
4. Characterization of the products



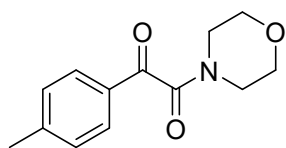
3a 1-morpholino-2-phenylethane-1,2-dione : Yellow oil (105.4 mg, 96% yield), 1H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 7.1 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 3.80 (s, 4H), 3.67 – 3.65 (t, J = 4.8 Hz, 2H), 3.40 – 3.37 (t, J = 4.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.18, 165.47, 134.97, 133.06, 129.69, 129.12, 66.75, 66.68, 46.28, 41.64.



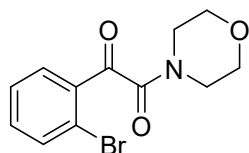
3b 1-morpholino-2-(o-tolyl)ethane-1,2-dione : Yellow oil (83.8mg, 72% yield), 1H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.71 (d, J = 6Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.33 (dd, J = 14.1, 7.5 Hz, 2H), 3.79 (d, J = 6.5 Hz, 4H), 3.69 – 3.66 (t, J = 6Hz, 2H), 3.41 – 3.39 (t, J = 12Hz, 2H), 2.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.12, 166.21, 141.67, 133.90, 132.74, 132.71, 131.52, 126.24, 66.70, 66.67, 46.30, 41.65, 21.86, 21.84.



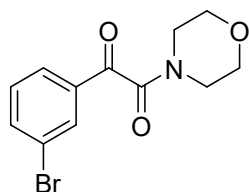
3c 1-morpholino-2-(m-tolyl)ethane-1,2-dione : Yellow oil (90.5 mg, 78% yield), ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, $J = 9.2$ Hz, 2H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 3.80 (d, $J = 1.4$ Hz, 4H), 3.67 – 3.64 (t, $J = 6$ Hz, 2H), 3.39 – 3.37 (t, $J = 12$ Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 191.41, 165.61, 139.10, 135.81, 133.09, 129.96, 129.00, 127.01, 66.75, 66.69, 46.28, 41.62, 21.29.



3d 1-morpholino-2-(p-tolyl)ethane-1,2-dione : Yellow solid (103.5 mg, 89% yield), m.p. = 47-49°C^[1]. ^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 3.81 – 3.78 (d, $J = 6$ Hz, 4H), 3.66 – 3.64 (t, $J = 12$ Hz, 2H), 3.39 – 3.36 (t, $J = 6$ Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 190.91, 165.68, 146.28, 130.69, 129.83, 129.81, 66.77, 66.70, 46.28, 41.59, 21.93.

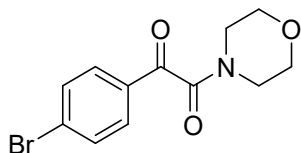


3e 1-(2-bromophenyl)-2-morpholinoethane-1,2-dione : Yellow solid (53.9 mg, 36% yield), m.p. = 122-126°C^[2]. ^1H NMR (600 MHz, CDCl_3) δ 7.81 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.64 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.44 (dtd, $J = 17.1, 7.4, 1.5$ Hz, 2H), 3.82 – 3.80 (t, $J = 12$ Hz, 2H), 3.79 – 3.77 (t, $J = 12$ Hz, 2H), 3.75 – 3.72 (t, $J = 12$ Hz, 2H), 3.59 – 3.56 (t, $J = 6$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 190.43, 164.84, 135.51, 134.26, 134.05, 132.68, 127.87, 121.48, 66.31, 66.26, 46.31, 42.06.

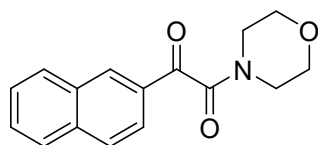


3f 1-(3-bromophenyl)-2-morpholinoethane-1,2-dione : Yellow solid (119.4 mg, 80% yield), m.p. = 90 -93°C^[2]. ^1H NMR (600 MHz, CDCl_3) δ 8.10 (s, 1H), 7.89 (d, $J = 7.8$

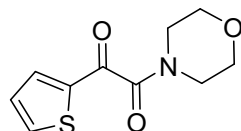
Hz, 1H), 7.78 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 3.80 (d, $J = 4.0$ Hz, 4H), 3.69 – 3.66 (t, $J = 6$ Hz, 2H), 3.40 – 3.38 (t, $J = 12$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 189.49, 164.64, 137.75, 134.87, 132.41, 131.57, 130.65, 128.33, 123.38, 66.74, 66.66, 46.31, 41.78.



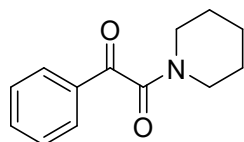
3g 1-(4-bromophenyl)-2-morpholinoethane-1,2-dione : Yellow solid (128.3 mg, 86% yield), m.p. = 121-124°C^[3]. ^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 8.6$ Hz, 2H), 7.67 (d, $J = 8.6$ Hz, 2H), 3.79 (d, $J = 3.7$ Hz, 4H), 3.68 – 3.65 (t, $J = 6$ Hz, 2H), 3.40 – 3.37 (t, $J = 6$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 189.91, 164.87, 132.51, 131.90, 131.07, 130.51, 66.76, 66.66, 46.31, 41.74.



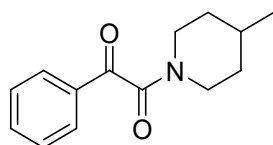
3h 1-morpholino-2-(naphthalen-2-yl)ethane-1,2-dione : Yellow solid (108.5 mg, 80% yield), m.p. = 116-119°C^[4]. ^1H NMR (600 MHz, CDCl_3) δ 8.47 (s, 1H), 8.03 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.95 (d, $J = 8.6$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.67 – 7.64 (t, $J = 18$ Hz, 1H), 7.60 – 7.57 (m, $J = 18$ Hz, 1H), 3.85 (s, 4H), 3.68 – 3.66 (t, $J = 12$ Hz, 2H), 3.44 – 3.41 (t, $J = 6$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 191.25, 165.62, 136.46, 133.08, 132.45, 130.45, 129.94, 129.58, 129.22, 128.00, 127.26, 123.60, 66.79, 66.73, 46.39, 41.75.



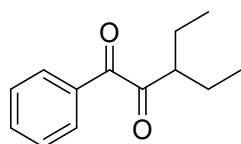
3i 1-morpholino-2-(thiophen-2-yl)ethane-1,2-dione : Yellow oil (70.7mg, 63% yield), ^1H NMR (600 MHz, CDCl_3) δ 7.85 (dd, $J = 3.8, 1.1$ Hz, 1H), 7.82 (dd, $J = 4.9, 1.1$ Hz, 1H), 7.20 (t, $J = 12$ Hz, 1H), 3.80 – 3.78 (m, 2H), 3.77 – 3.75 (m, 2H), 3.69 – 3.67 (t, $J = 6, 2$ H), 3.51 – 3.49 (t, $J = 6, 2$ H). ^{13}C NMR (151 MHz, CDCl_3) δ 182.82, 164.34, 140.32, 136.78, 136.29, 128.74, 66.83, 66.65, 46.47, 41.98.



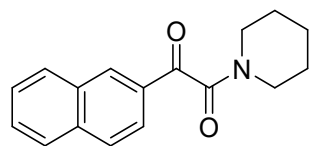
3j 1-phenyl-2-(piperidin-1-yl)ethane-1,2-dione : Yellow solid (75 mg, 69% yield), m.p. = 104-105°C^[5]. ¹H NMR (600 MHz, CDCl₃) δ 7.95 (d, *J* = 7.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 3.71 (s, 2H), 3.31 – 3.28 (t, *J* = 12 Hz, 2H), 1.72 – 1.68 (t, *J* = 6 Hz, 4H), 1.55 (s, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 191.96, 165.46, 134.64, 133.31, 129.59, 129.00, 47.05, 42.17, 26.22, 25.47, 24.41.



3k 1-(4-methylpiperidin-1-yl)-2-phenylethane-1,2-dione : Yellow oil (72.4 mg, 63% yield), ¹H NMR (600 MHz, CDCl₃) δ 7.95 (d, *J* = 7.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 4.63 (d, *J* = 13.2 Hz, 1H), 3.53 (d, *J* = 13.6 Hz, 1H), 3.09 – 3.03 (td, *J* = 18, 6 Hz, 1H), 2.80 (td, *J* = 12.8, 3.1 Hz, 1H), 1.80 (d, *J* = 13.7 Hz, 1H), 1.71 – 1.66 (m, 1H), 1.62 (d, *J* = 13.3 Hz, 1H), 1.27 – 1.24 (m, 1H), 1.18 – 1.11 (m, 1H), 0.98 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 191.95, 165.45, 134.64, 133.29, 129.58, 129.00, 46.34, 41.53, 34.30, 33.60, 31.06, 21.62.

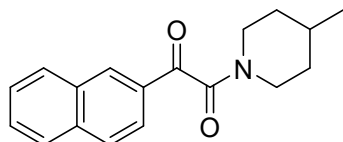


3l N,N-diethyl-2-oxo-2-phenylacetamide : Yellow oil (23.6 mg, 23% yield), ¹H NMR (600 MHz, CDCl₃) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 3.57 (q, *J* = 7.2 Hz, 2H), 3.24 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 191.60, 166.75, 134.56, 133.30, 129.63, 128.96, 42.12, 38.81, 14.12, 12.85.

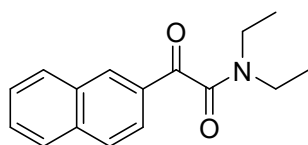


3m 1-(naphthalen-2-yl)-2-(piperidin-1-yl)ethane-1,2-dione : Yellow solid (101.4 mg, 89% yield), m.p. = 32.1-37.6°C^[4]. ¹H NMR (600 MHz, CDCl₃) δ 8.45 (s, 1H), 8.03 (d,

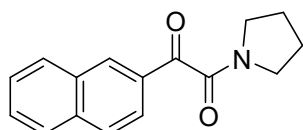
$J = 8.6$ Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.95 (d, $J = 8.6$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.65 (dd, $J = 8.0, 7.1$ Hz, 1H), 7.58 (t, $J = 7.5$ Hz, 1H), 3.77 (t, $J = 5.0$ Hz, 2H), 3.34 – 3.32 (t, $J = 12$ Hz, 2H), 1.73 (s, 4H), 1.56 (s, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 191.04, 164.56, 135.32, 131.78, 131.46, 129.64, 128.85, 128.31, 128.04, 126.93, 126.08, 122.65, 46.13, 41.24, 25.22, 24.50, 23.40.



3n 1-(4-methylpiperidin-1-yl)-2-(naphthalen-2-yl)ethane-1,2-dione : Yellow oil (87.2 mg, 62% yield), ^1H NMR (600 MHz, CDCl_3) δ 8.44 (s, 1H), 8.02 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.94 (d, $J = 8.6$ Hz, 1H), 7.89 (d, $J = 8.2$ Hz, 1H), 7.66 – 7.62 (td, $J = 6, 1.7$ Hz, 1H), 7.59 – 7.56 (t, $J = 18$ Hz, 1H), 4.72 – 4.67 (dt, $J = 12, 1.7$ Hz, 1H), 3.60 – 3.56 (dt, $J = 12, 1.7$ Hz, 1H), 3.11 – 3.06 (td, $J = 12, 6$ Hz, 1H), 2.85 (td, $J = 12.8, 3.1$ Hz, 1H), 1.83 (d, $J = 13.5$ Hz, 1H), 1.71 – 1.66 (m, 1H), 1.61 (d, $J = 13.3$ Hz, 1H), 1.30 (dd, $J = 12.9, 4.0$ Hz, 1H), 1.17 (ddd, $J = 24.6, 12.5, 4.3$ Hz, 1H), 0.98 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 191.02, 164.55, 135.33, 131.78, 131.46, 129.62, 128.85, 128.31, 128.04, 126.93, 126.09, 122.65, 45.42, 40.61, 33.29, 32.63, 30.05, 20.62.



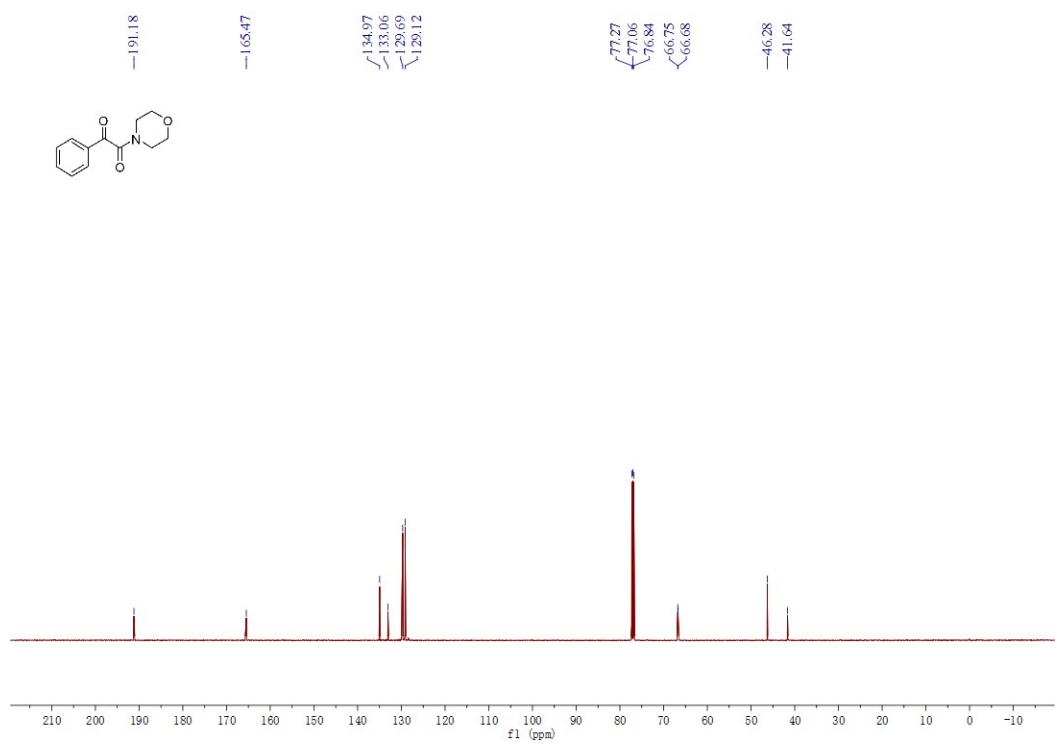
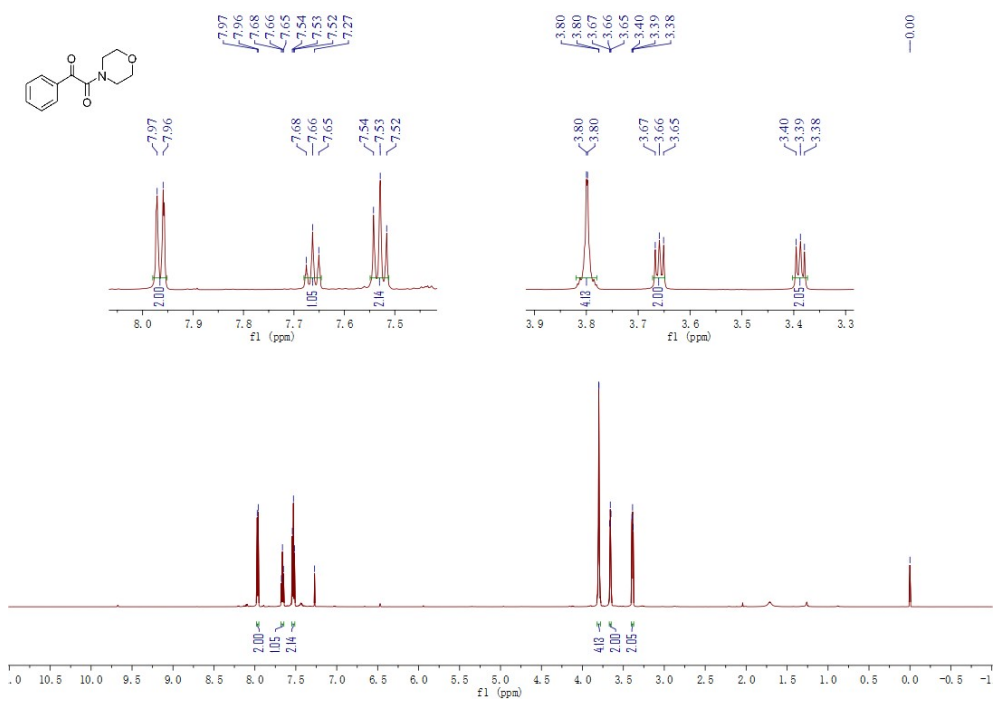
3o N,N-diethyl-2-(naphthalen-2-yl)-2-oxoacetamide : Yellow oil (28.4mg, 22% yield), ^1H NMR (600 MHz, CDCl_3) δ 8.43 (s, 1H), 8.02 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.95 (d, $J = 8.6$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.65 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.59 – 7.56 (td, $J = 6, 1.2$ Hz, 1H), 3.63 (q, $J = 7.2$ Hz, 2H), 3.29 (q, $J = 7.1$ Hz, 2H), 1.34 (t, $J = 7.2$ Hz, 3H), 1.17 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 190.67, 165.84, 135.29, 131.77, 131.43, 129.63, 128.87, 128.27, 127.98, 126.92, 126.05, 122.77, 41.18, 37.86, 13.15, 11.88.



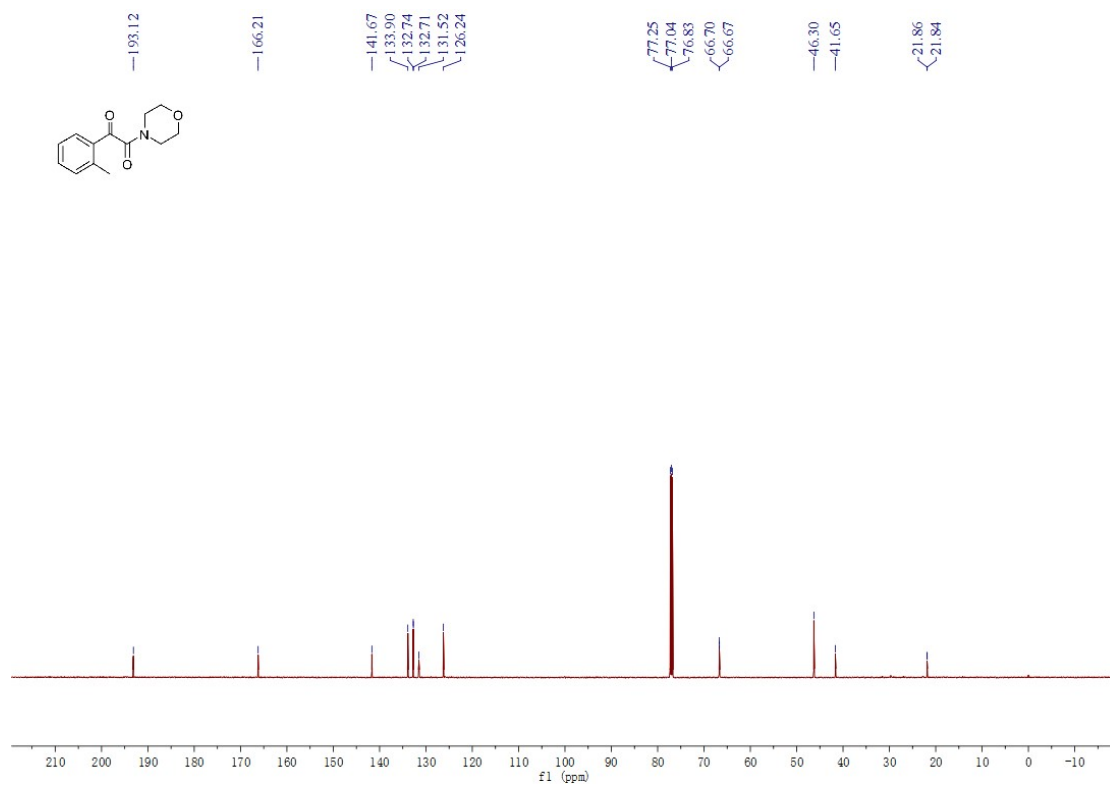
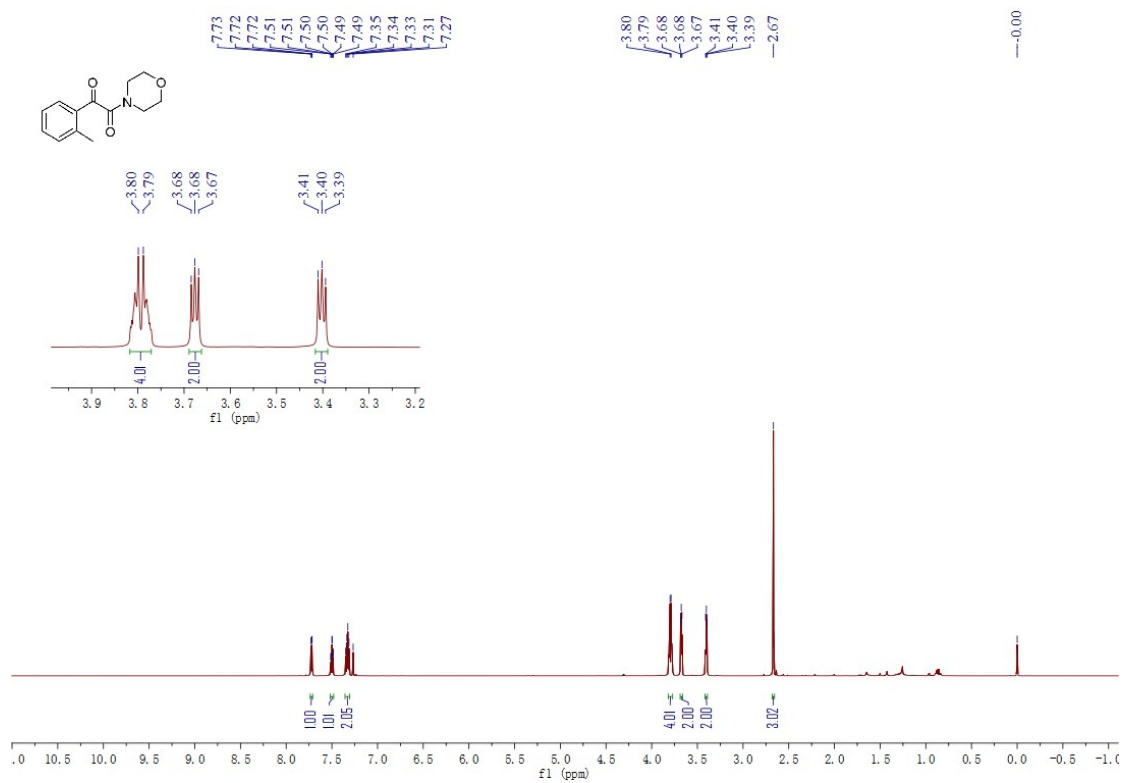
3p 1-(naphthalen-2-yl)-2-(pyrrolidin-1-yl)ethane-1,2-dione : Yellow oil (41.4mg, 33% yield), ^1H NMR (600 MHz, CDCl_3) δ 8.52 (s, 1H), 8.06 (dd, $J = 8.6, 1.5$ Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.94 (d, $J = 8.6$ Hz, 1H), 7.89 (d, $J = 8.2$ Hz, 1H), 7.64 (dd, $J = 11.1, 4.0$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 3.72 (t, $J = 6.9$ Hz, 2H), 3.47 (t, $J = 6.6$ Hz, 2H), 2.01 – 1.94 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 191.66 , 165.06 , 136.34 , 133.27 , 132.48 , 130.34 , 129.94 , 129.32 , 128.98 , 127.94 , 127.05 , 123.94 , 46.79, 45.35, 25.96, 24.08.

5.Copies of ^1H and ^{13}C NMR spectra

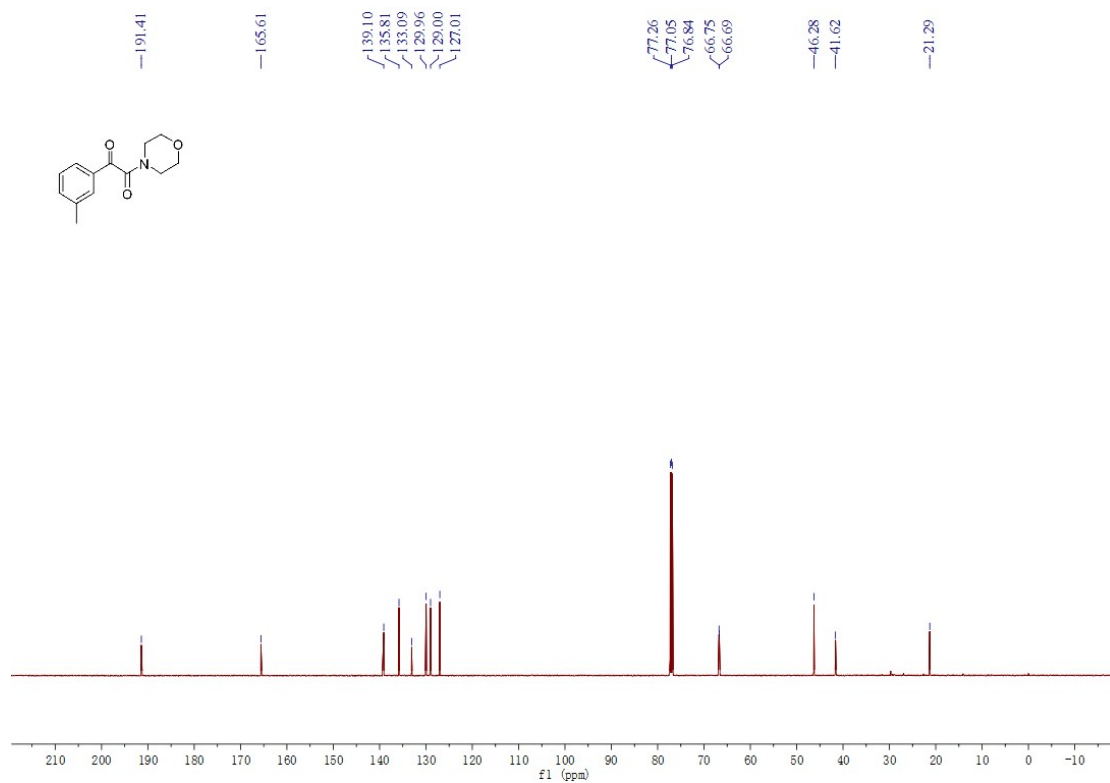
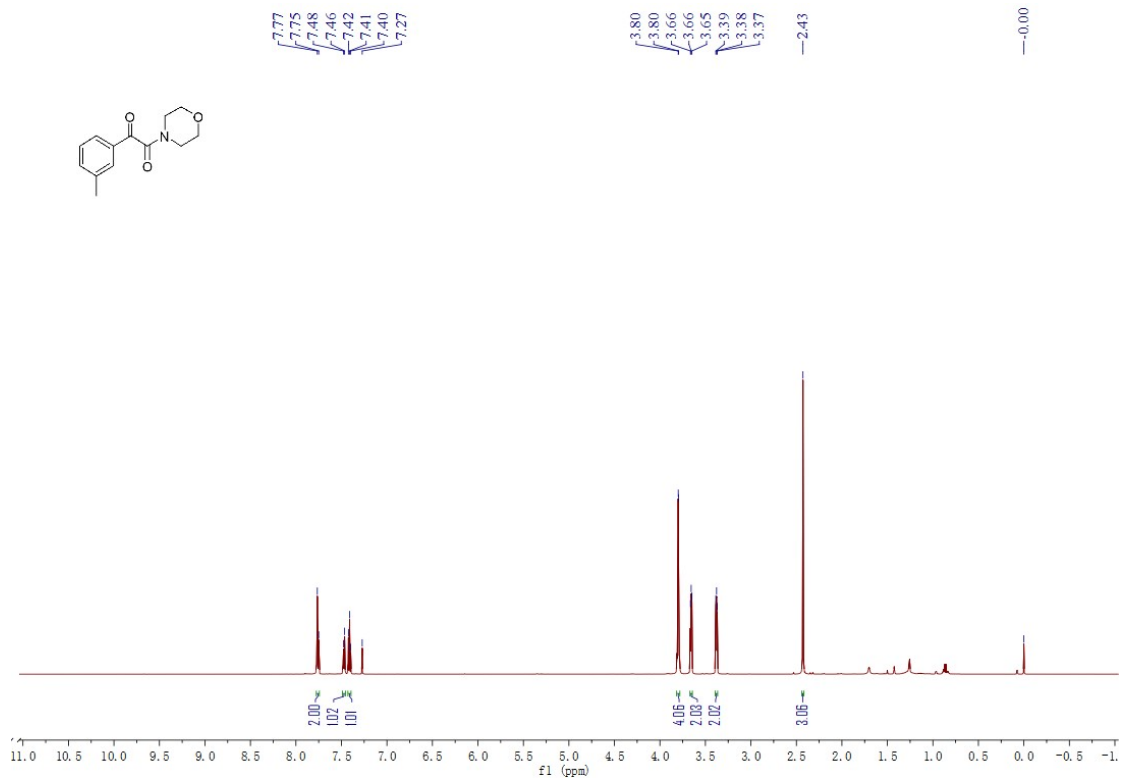
3a 1-morpholino-2-phenylethane-1,2-dione



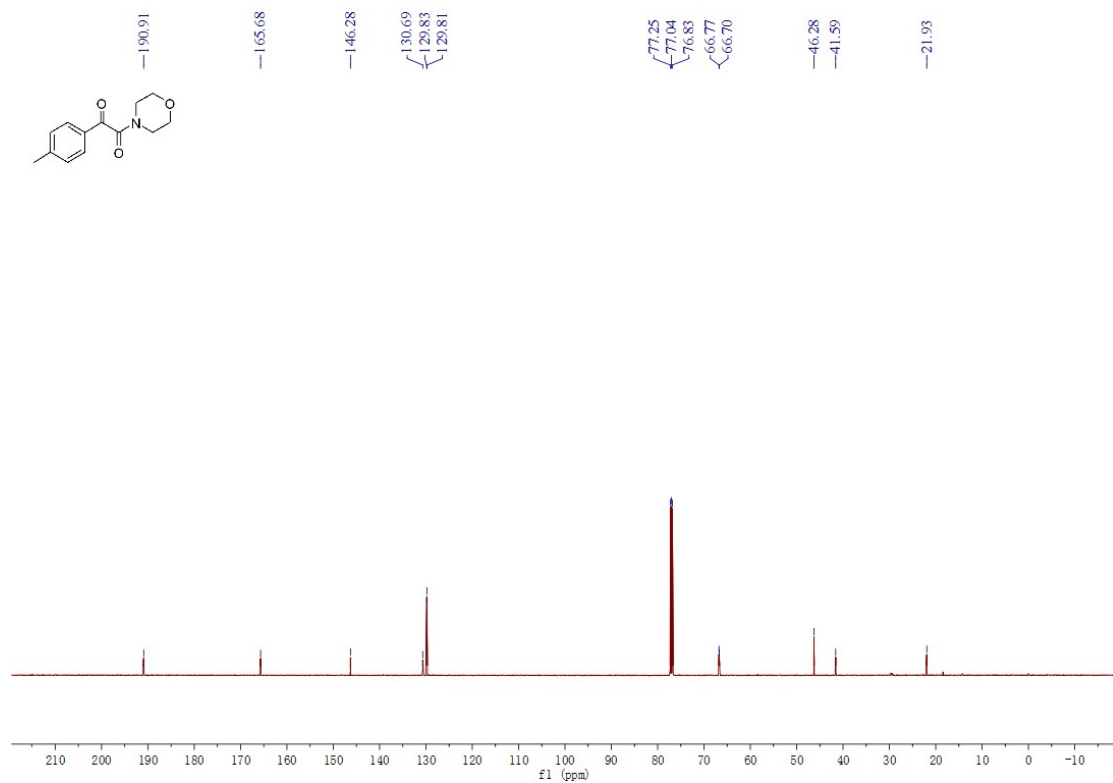
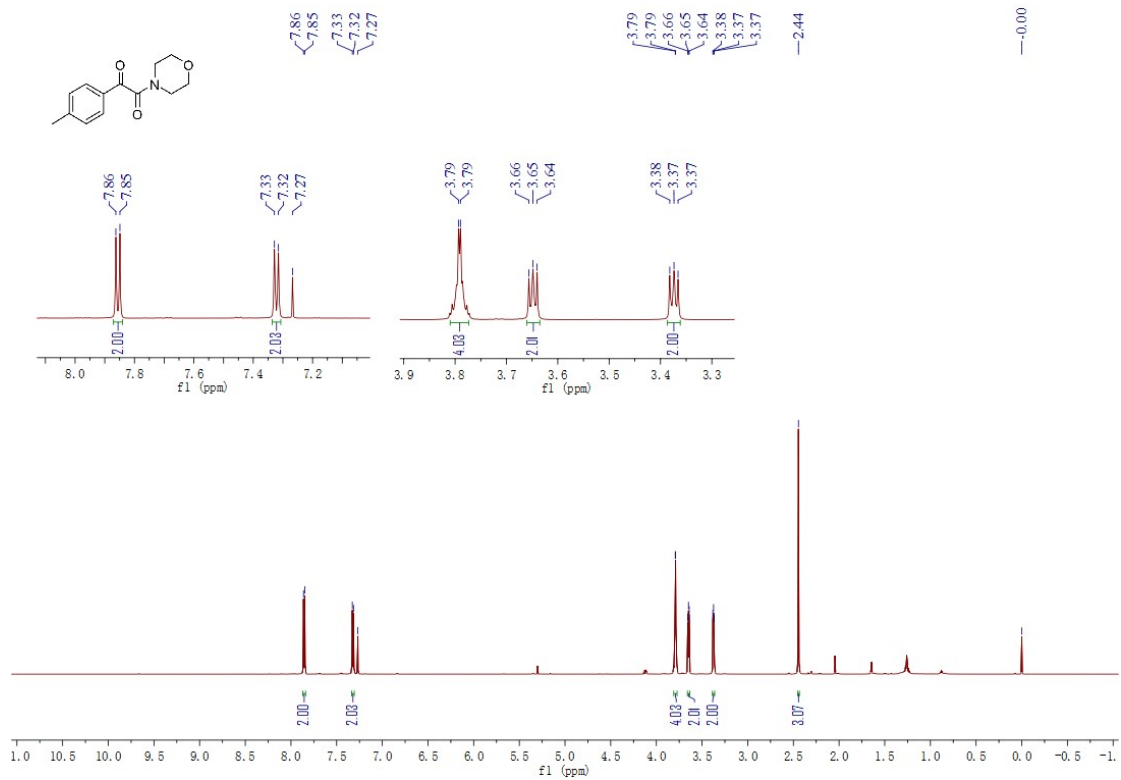
3b 1-morpholino-2-(o-tolyl)ethane-1,2-dione



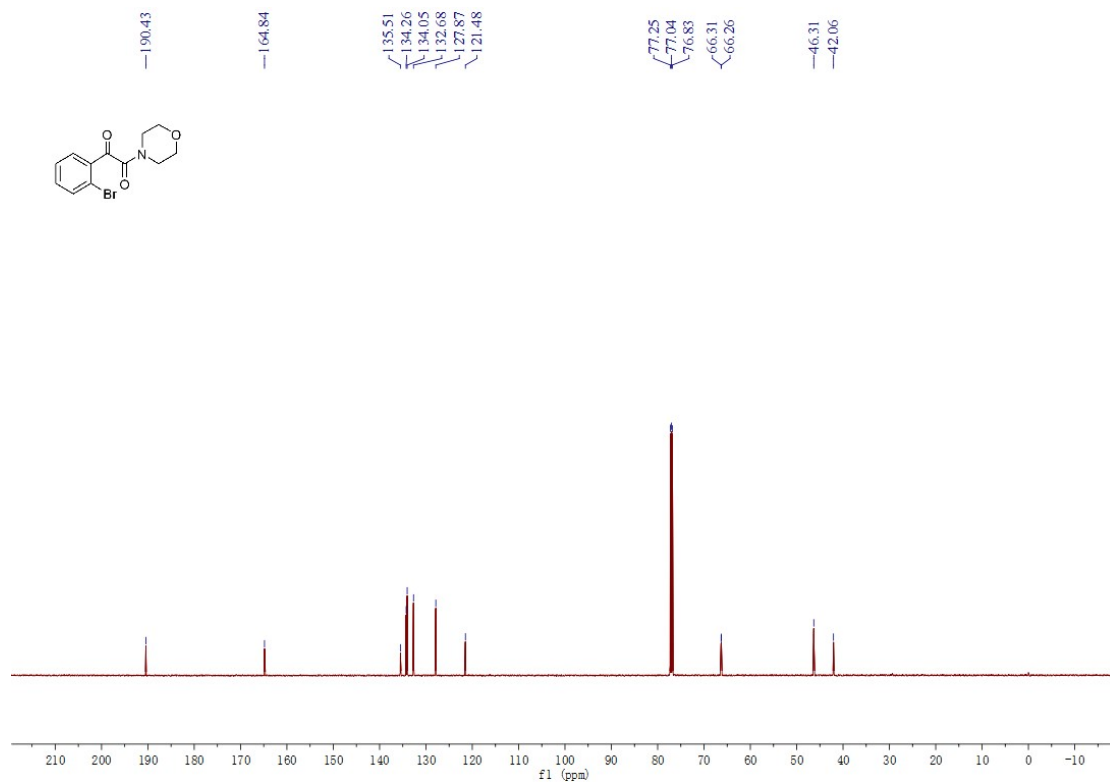
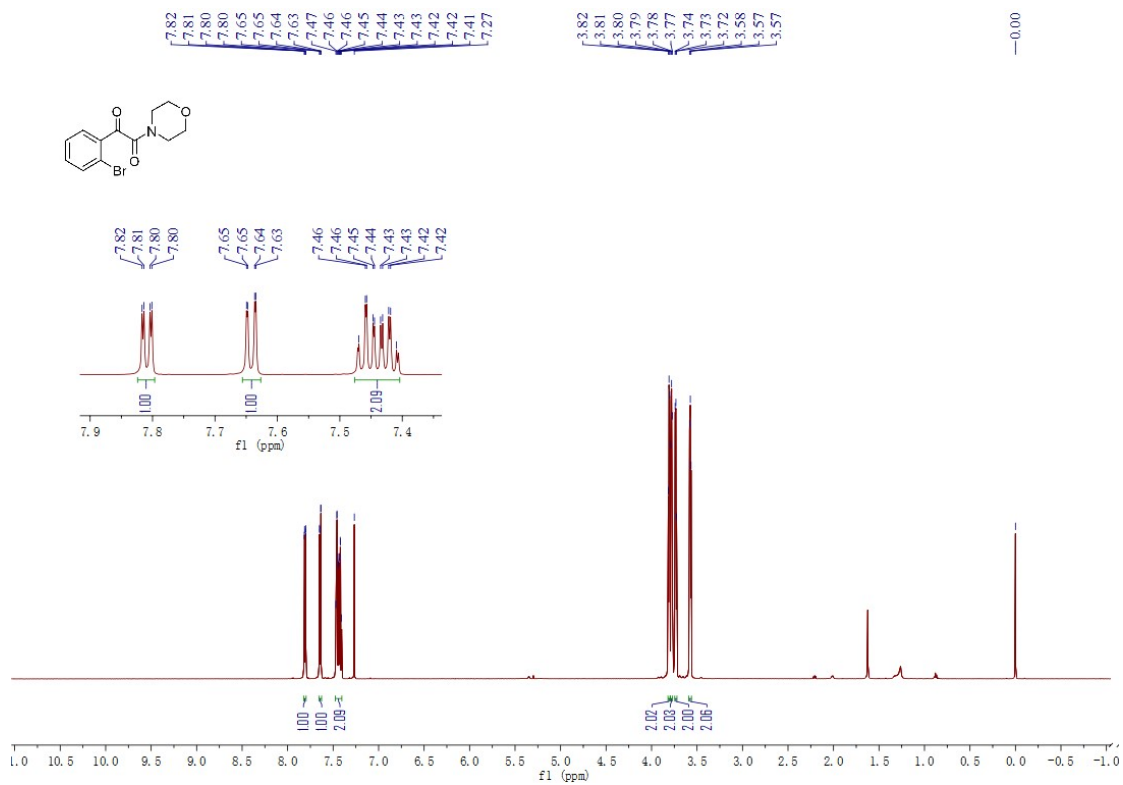
3c 1-morpholino-2-(m-tolyl)ethane-1,2-dione



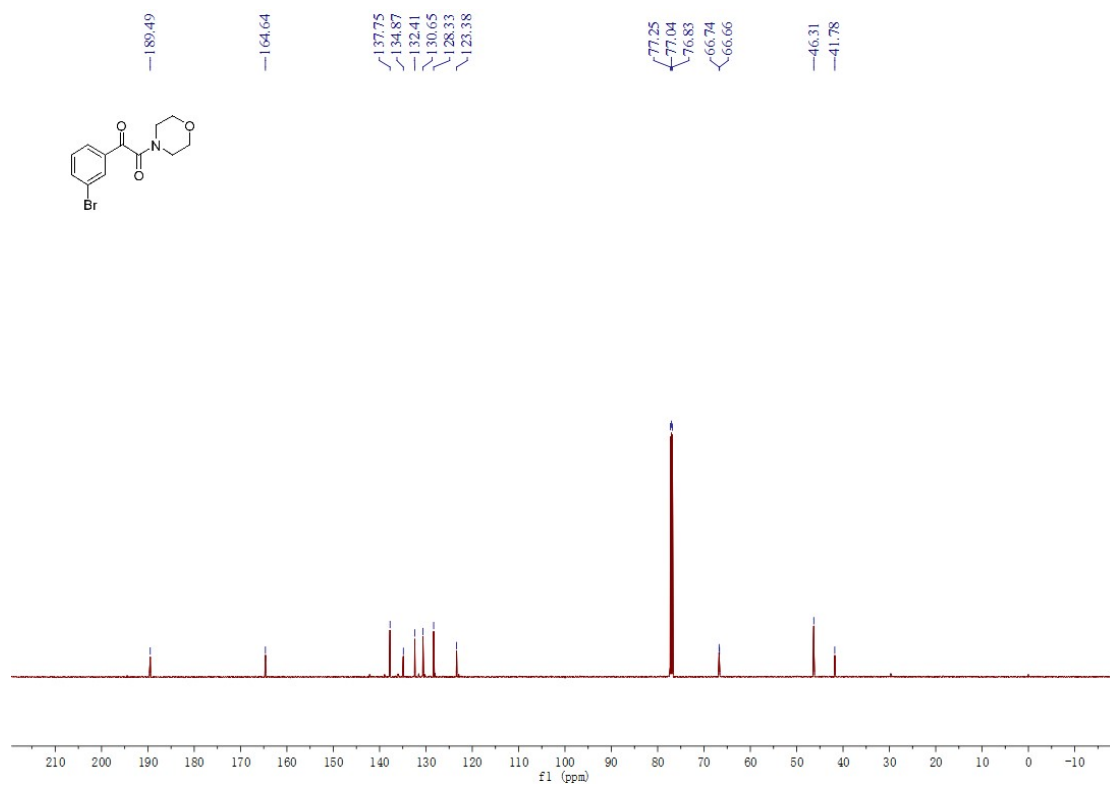
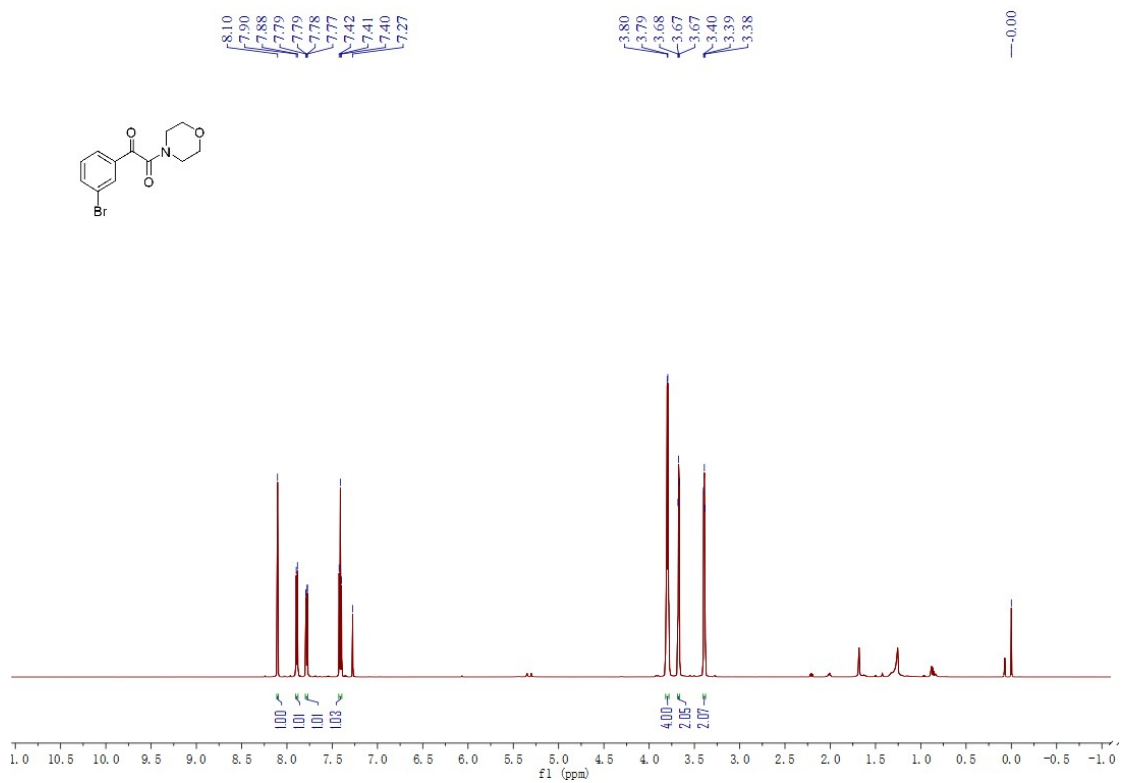
3d 1-morpholino-2-(p-tolyl)ethane-1,2-dione



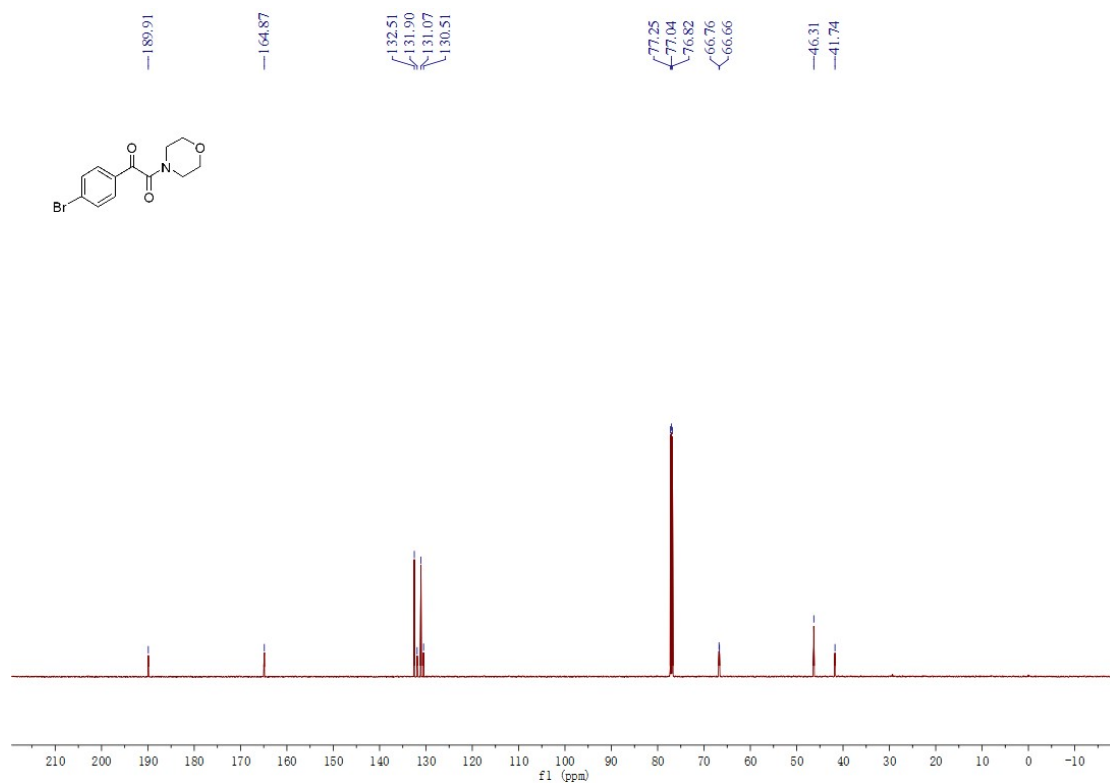
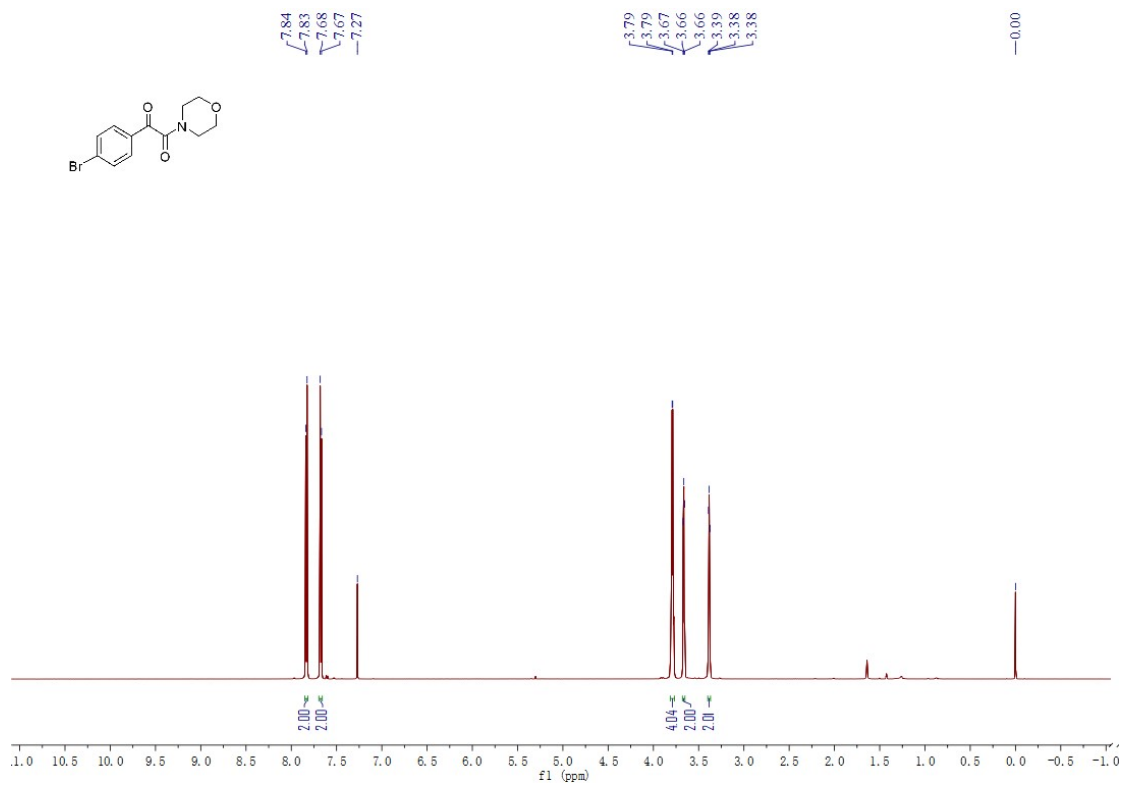
3e 1-(2-bromophenyl)-2-morpholinoethane-1,2-dione



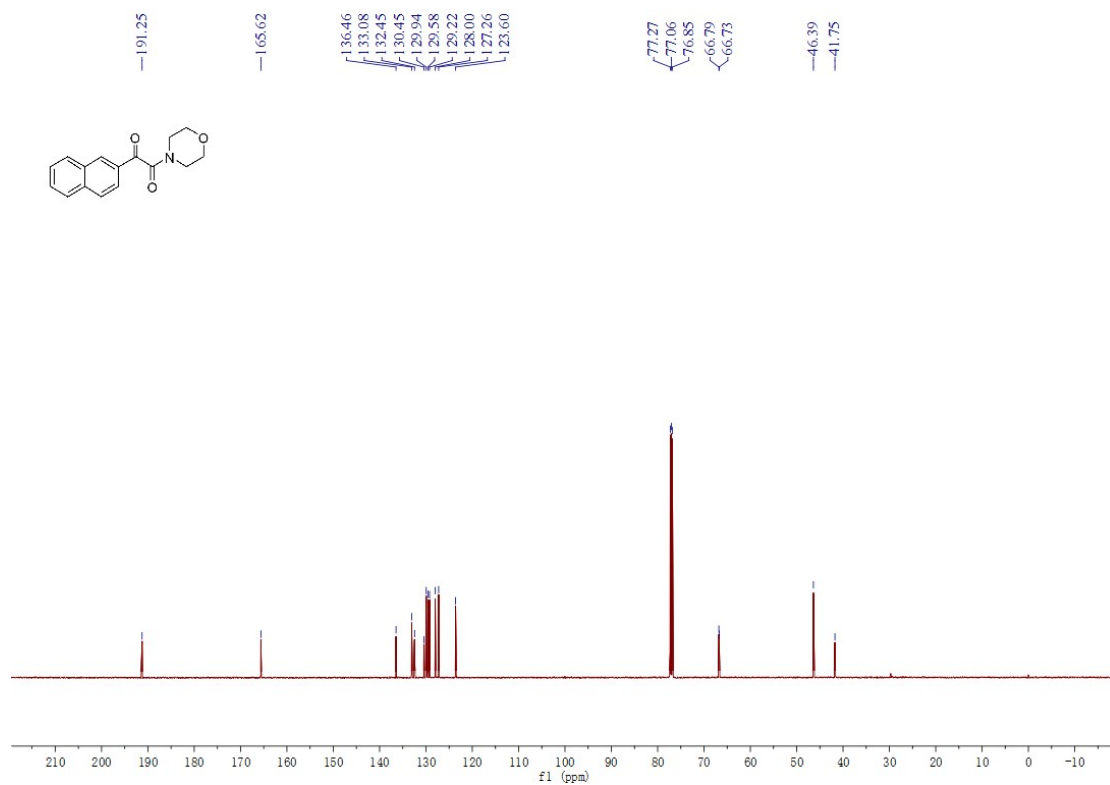
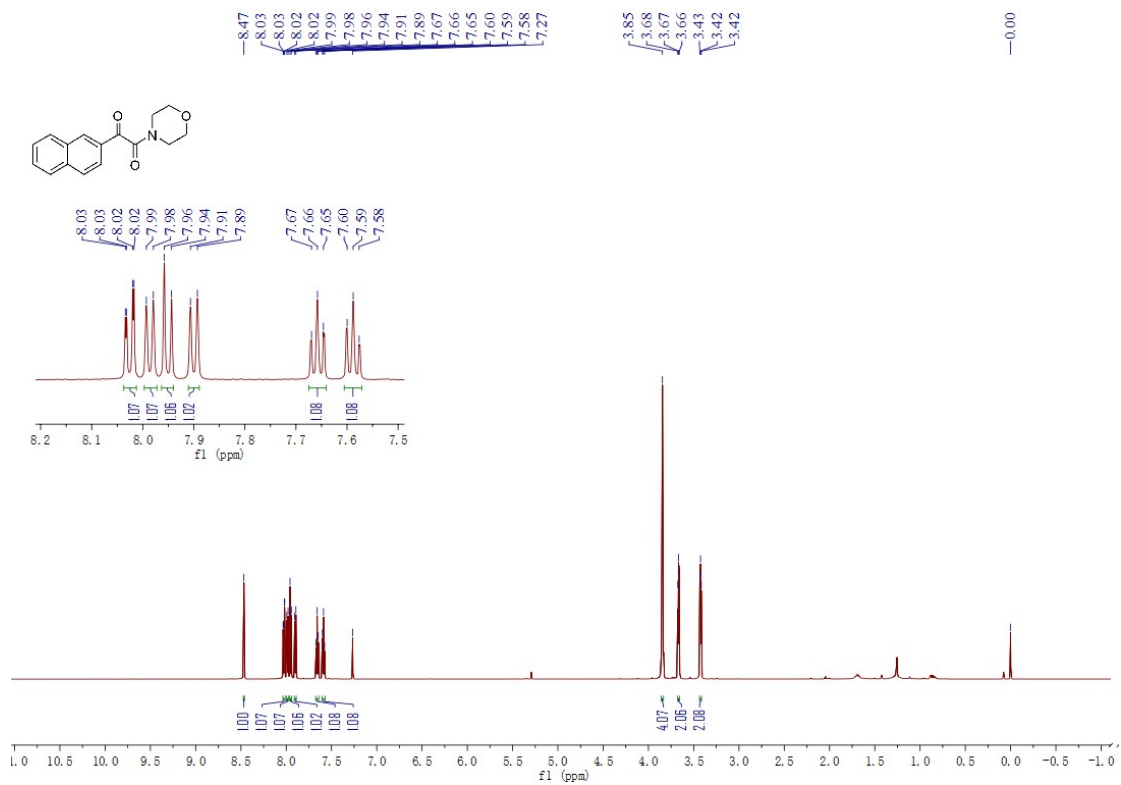
3f 1-(3-bromophenyl)-2-morpholinoethane-1,2-dione



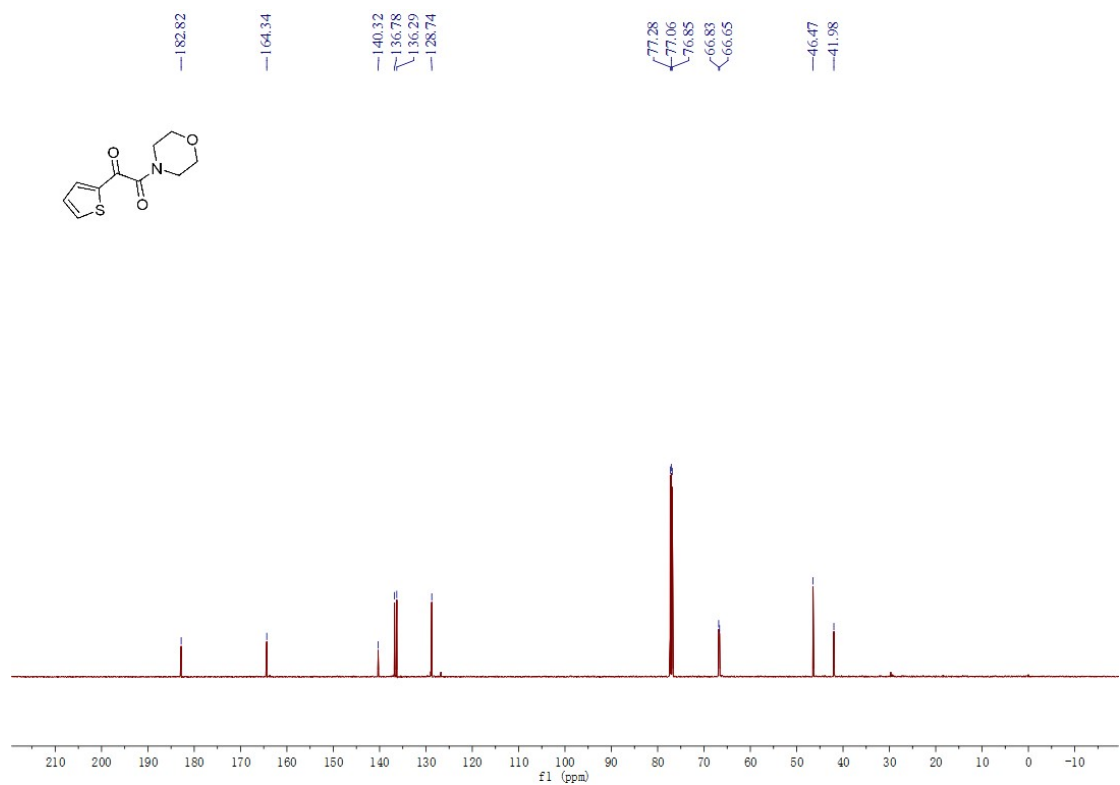
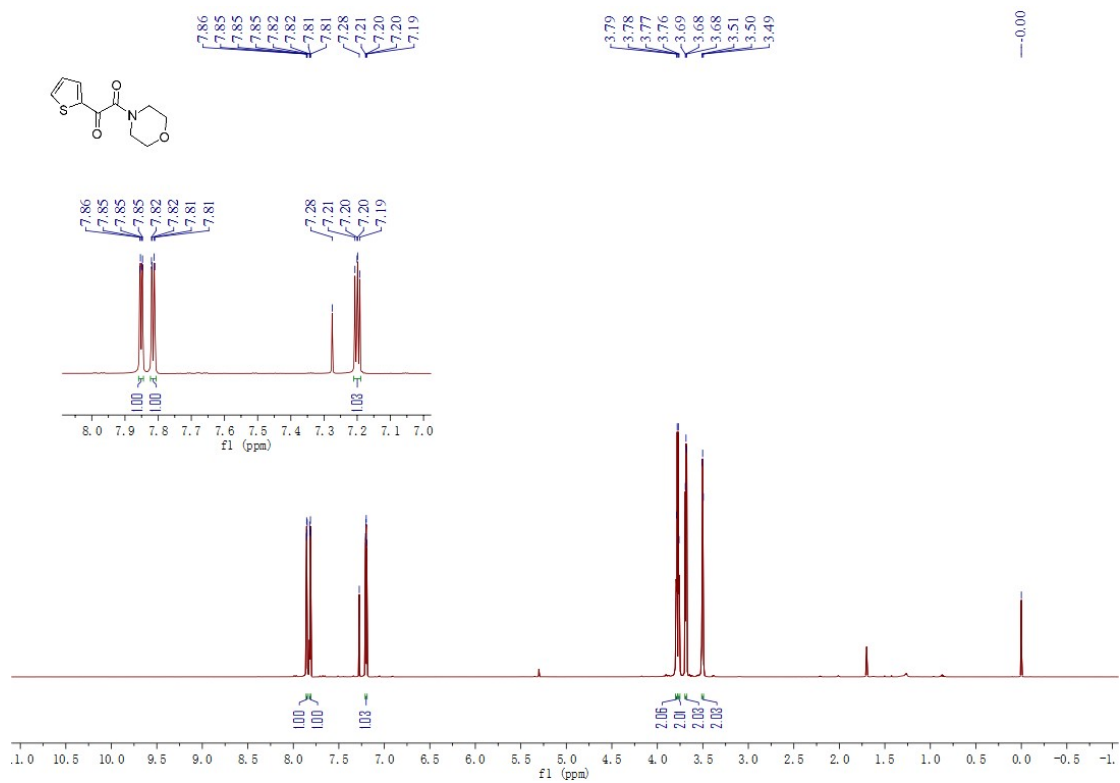
3g 1-(4-bromophenyl)-2-morpholinoethane-1,2-dione



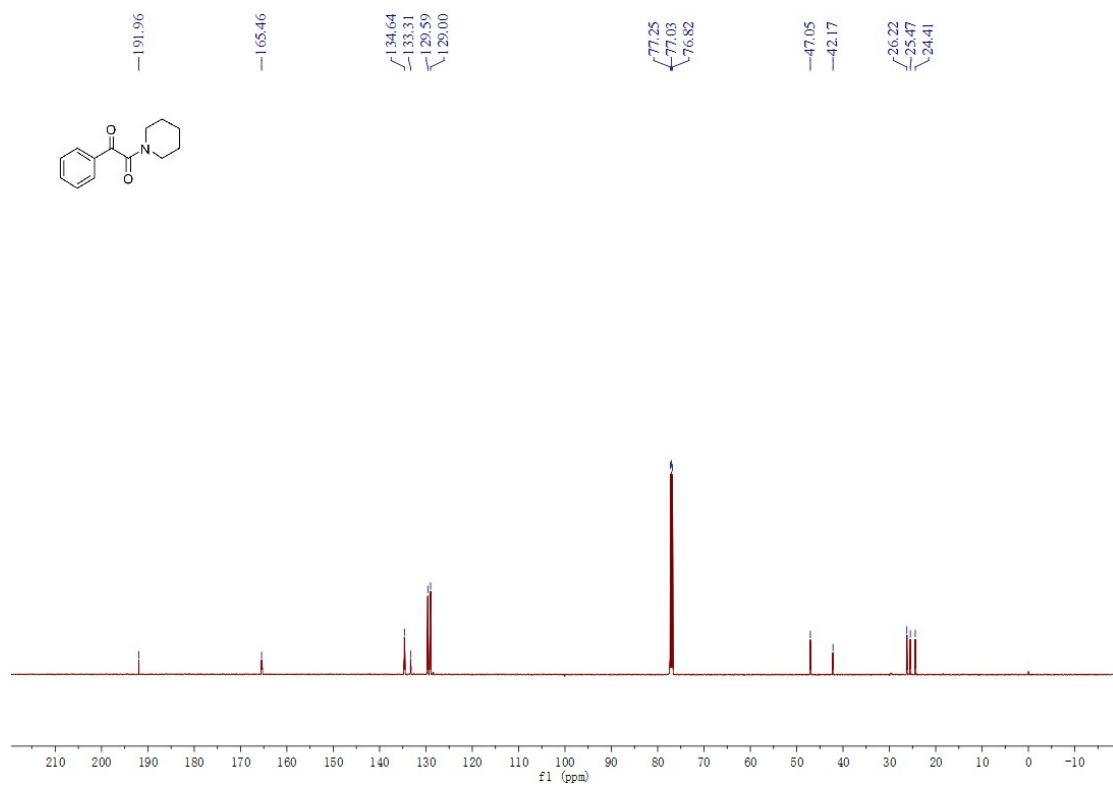
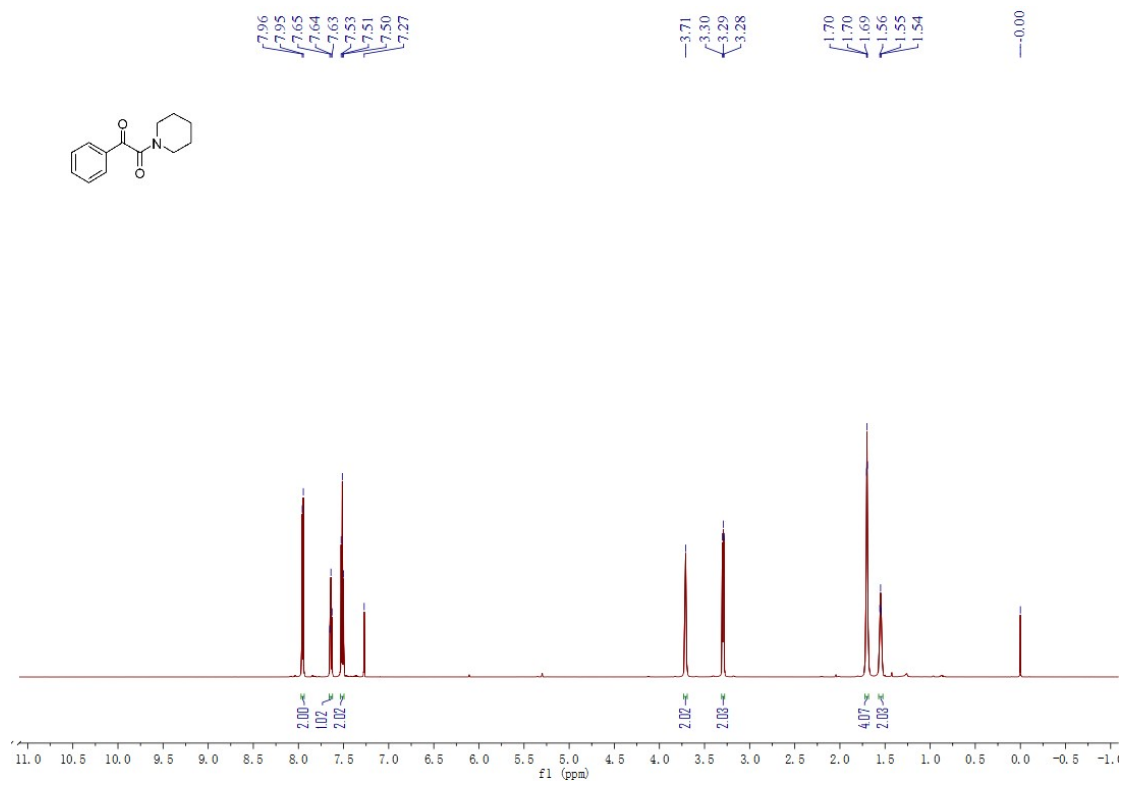
3h 1-morpholino-2-(naphthalen-2-yl)ethane-1,2-dione



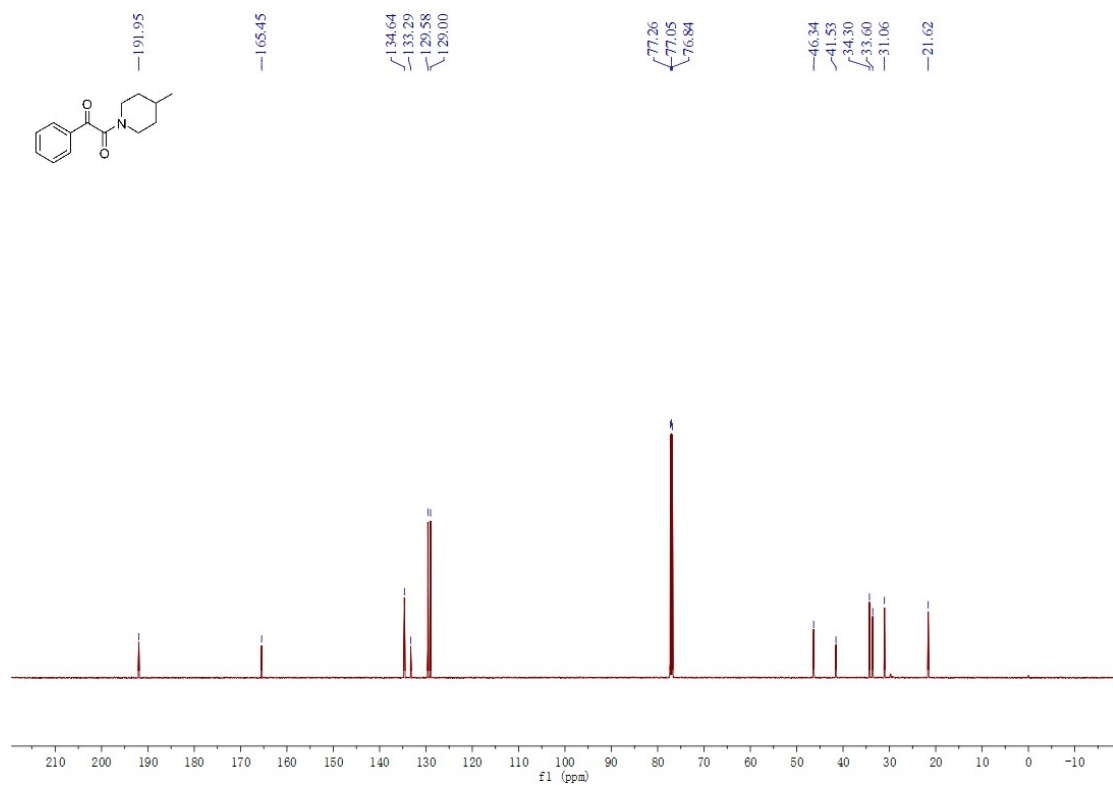
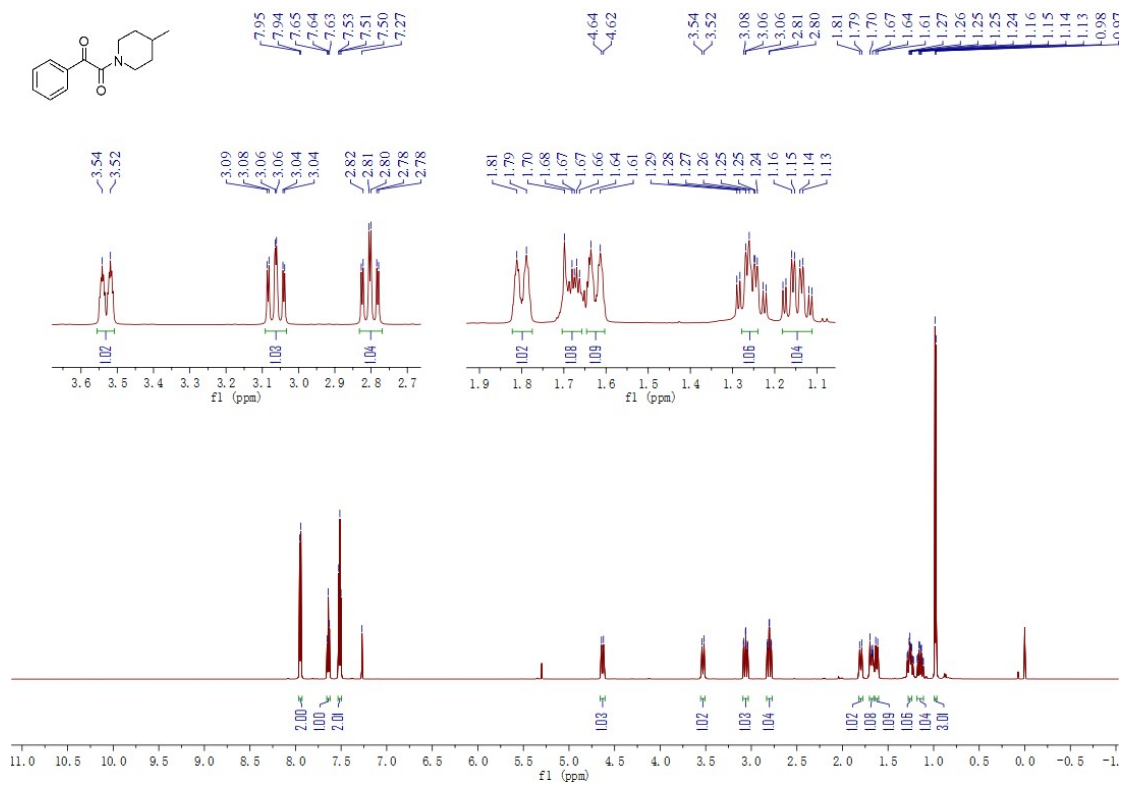
3i 1-morpholino-2-(thiophen-2-yl)ethane-1,2-dione



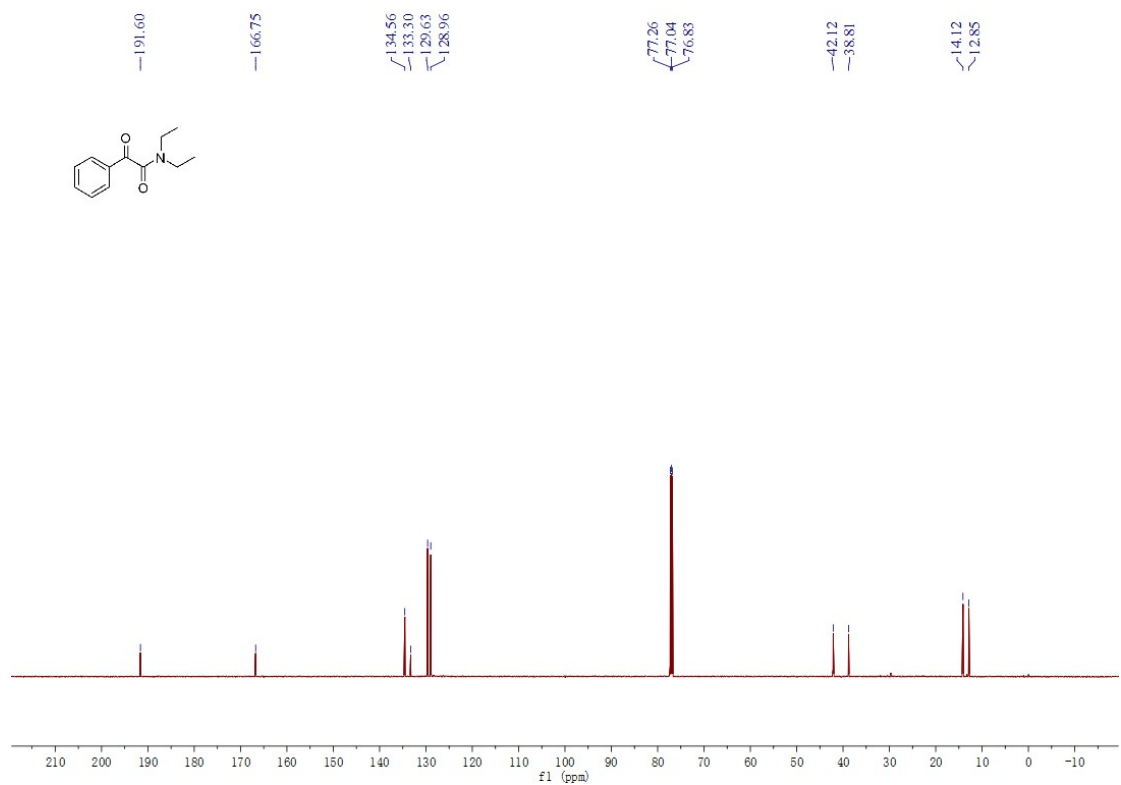
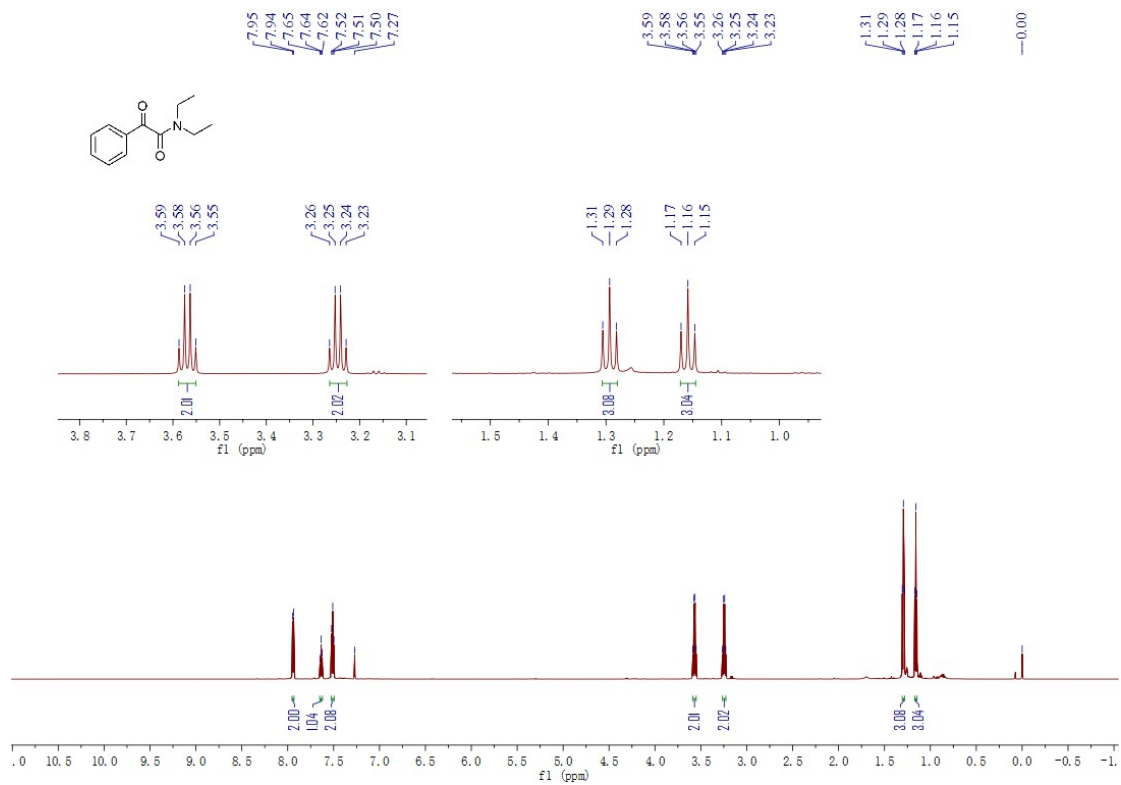
3j 1-phenyl-2-(piperidin-1-yl)ethane-1,2-dione



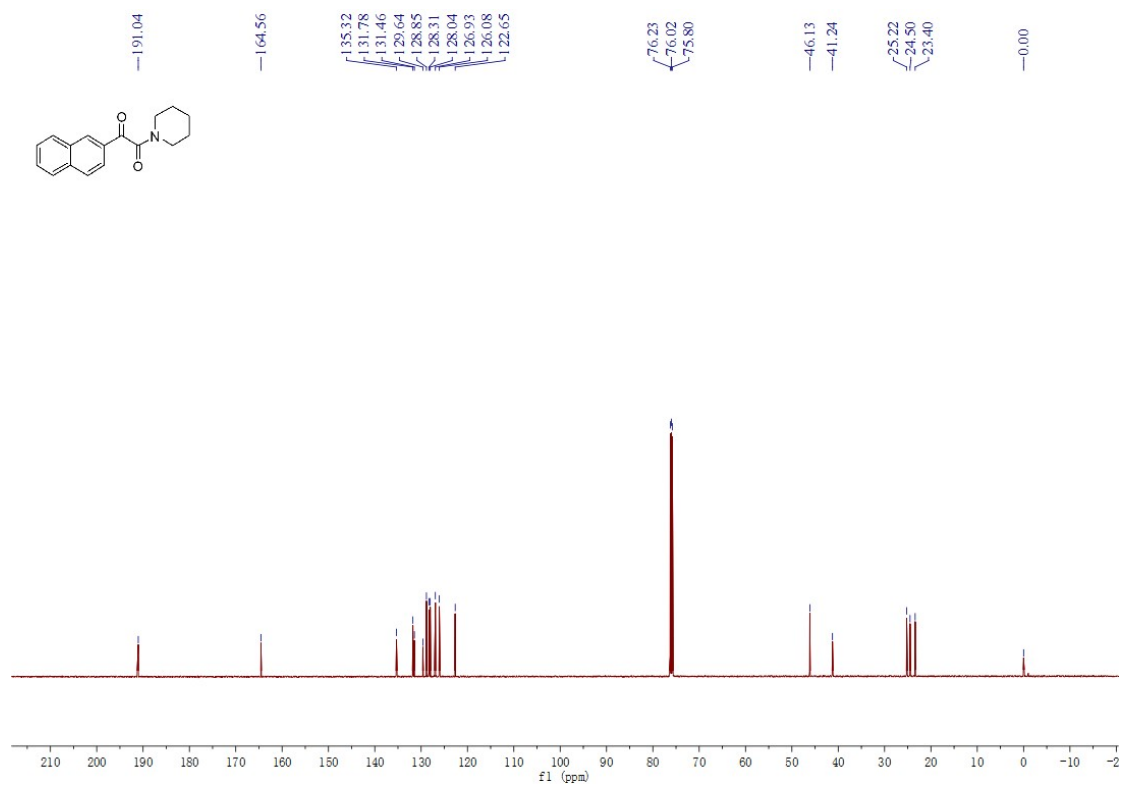
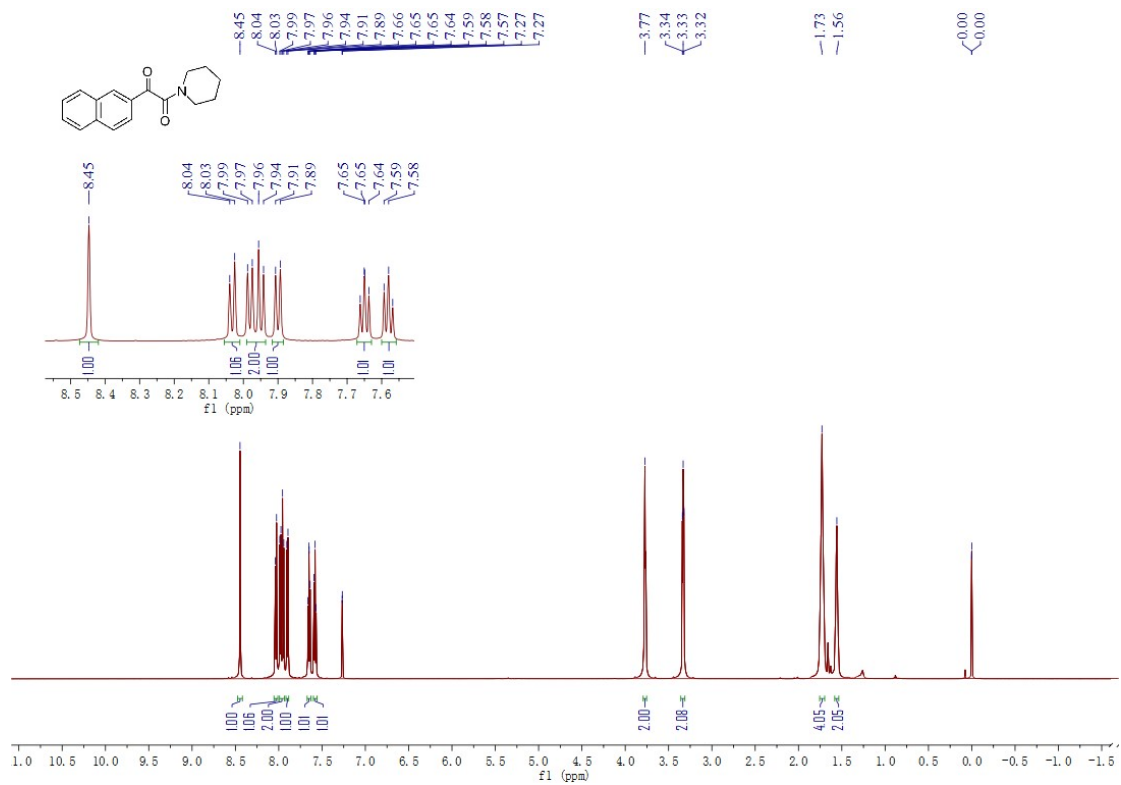
3k 1-(4-methylpiperidin-1-yl)-2-phenylethane-1,2-dione



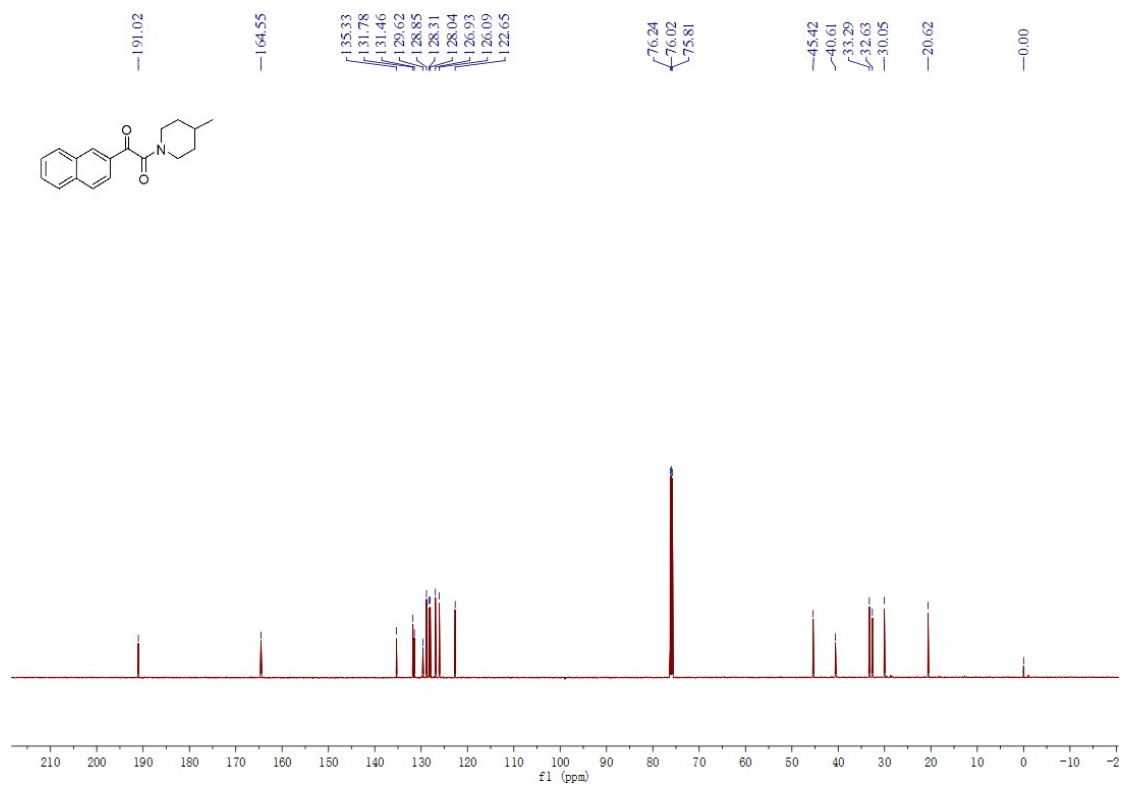
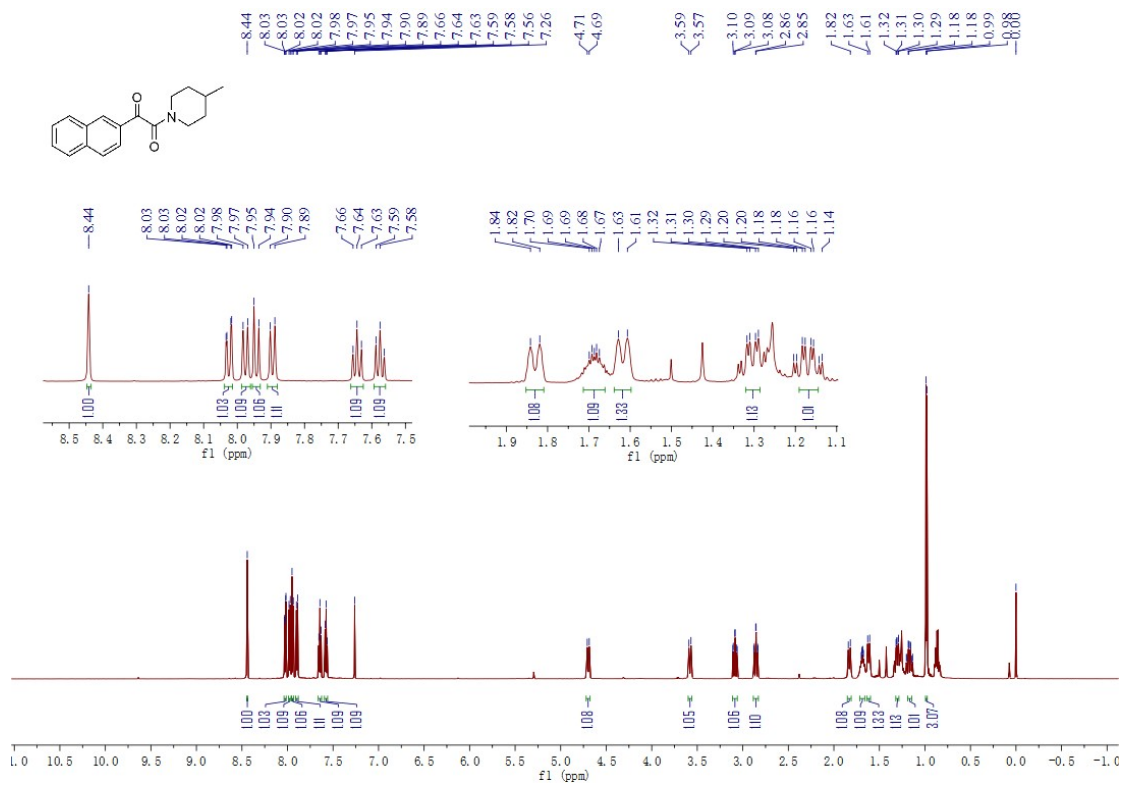
31 N,N-diethyl-2-oxo-2-phenylacetamide



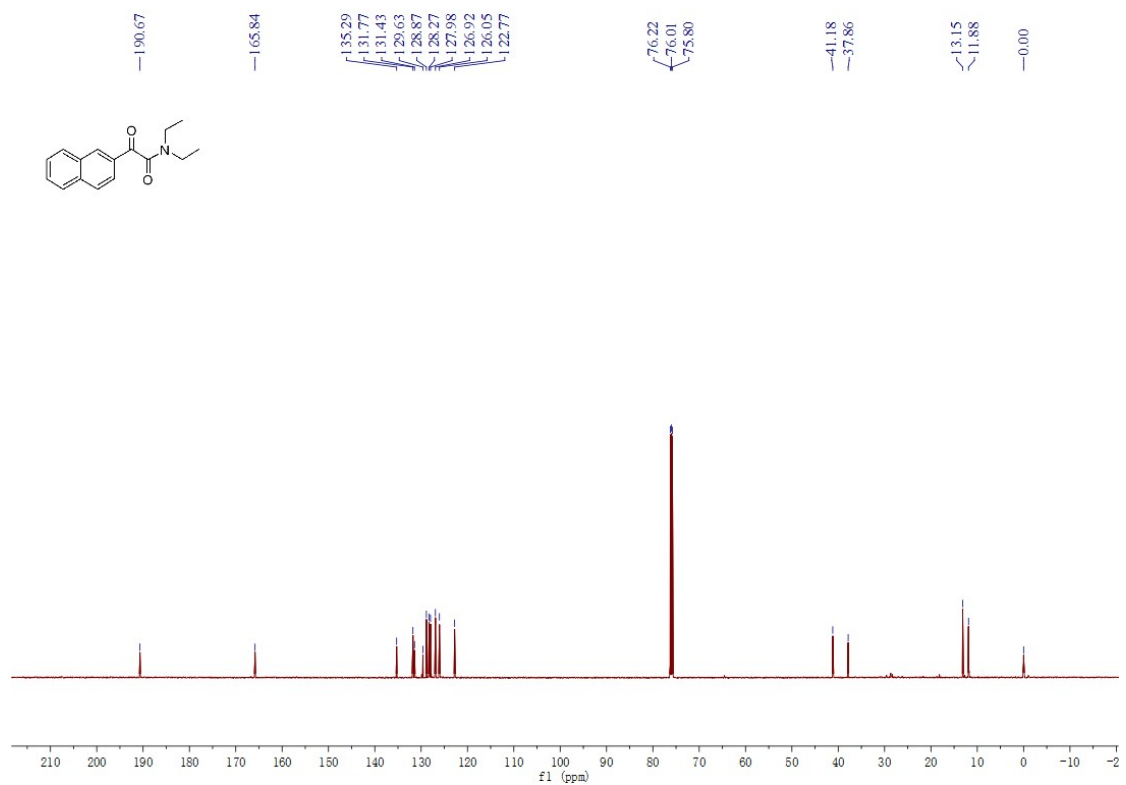
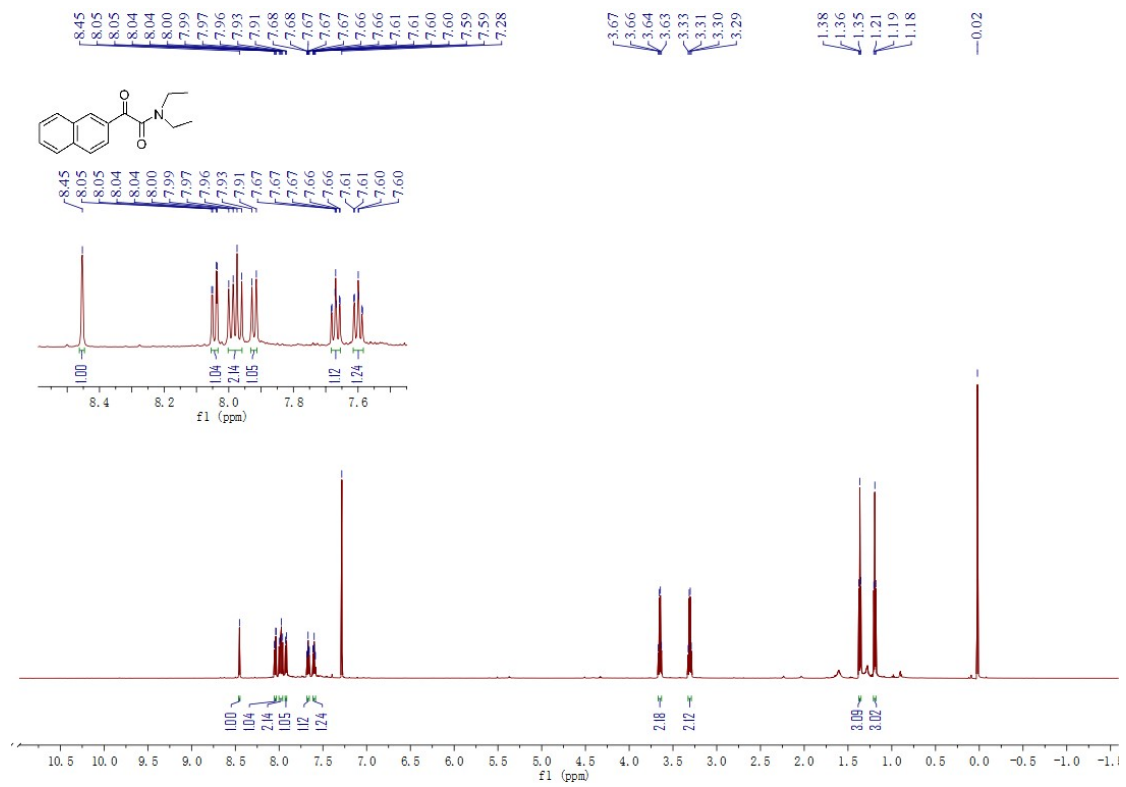
3m 1-(naphthalen-2-yl)-2-(piperidin-1-yl)ethane-1,2-dione



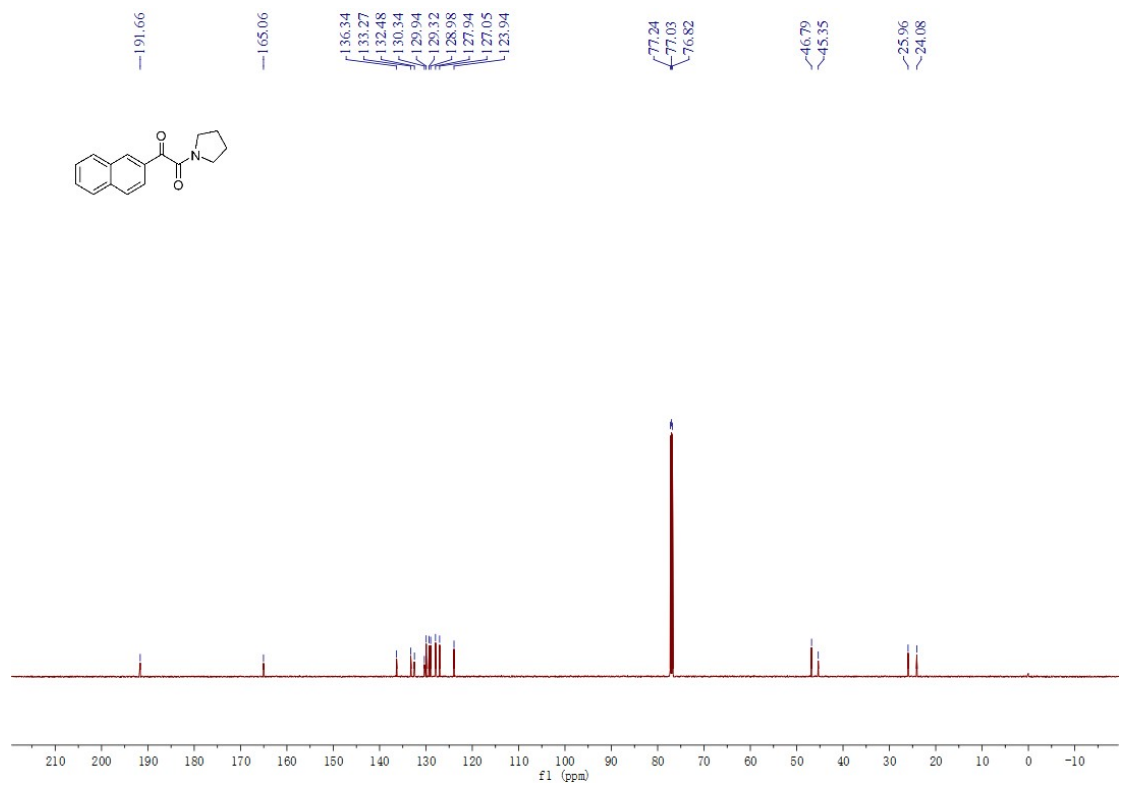
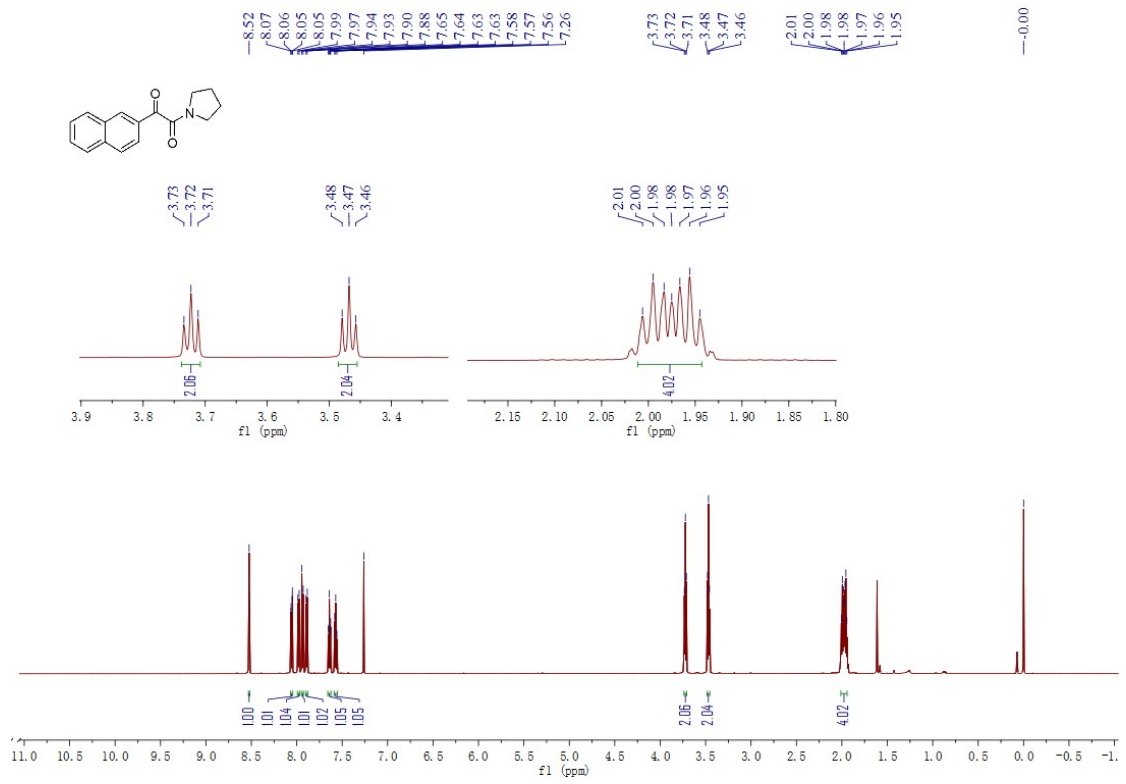
3n 1-(4-methylpiperidin-1-yl)-2-(naphthalen-2-yl)ethane-1,2-dione



30 N,N-diethyl-2-(naphthalen-2-yl)-2-oxoacetamide



3p 1-(naphthalen-2-yl)-2-(pyrrolidin-1-yl)ethane-1,2-dione



6. References

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