Electronic Supporting Information (ESI)

Covalent Triazine Frameworks Supported Palladium as Ligand-free Catalysts for Selective Double Carbonylation of Aryl Iodides at Ambient Pressure of CO

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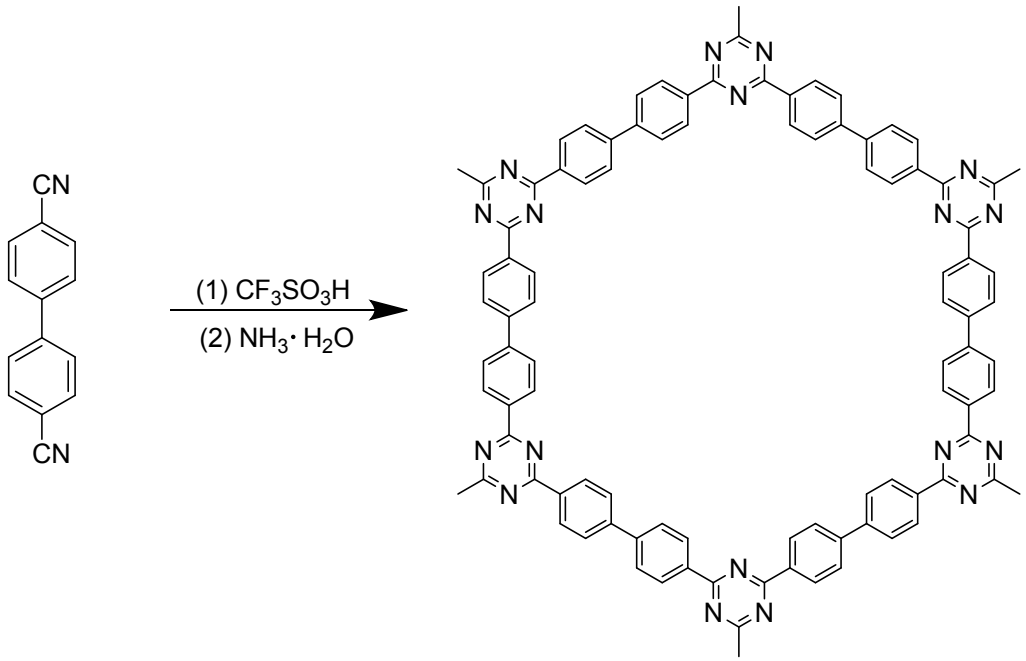
1. Experiment section

1.1 Reagents. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography.

1.2 Synthesis of covalent triazine frameworks (CTFs).

Covalent triazine frameworks was prepared according to the literature.[1] 5 mL of $CHCl_3$ was charged into a pre-dried 2-neck round bottom flask under N_2 atmosphere and then trifluoromethanesulfonic acid (1.2 g, 8 mmol) was added at 0℃. The [1,1'-biphenyl]-4,4'-dicarbonitrile (0.408g, 2 mmol) in 20 mL of $CHCl_3$ was added into the solution dropwise over 30 min. The mixture was stirred at 0 °C for another 2 h and then left overnight at room temperature. The solution turned red and solid precipitates were formed. Then, the mixture was poured into 40 mL of water containing 2 mL of ammonia solution and stirred for 2 h. The precipitates were filtered and washed with water, ethanol, acetone and chloroform successively. The CTFs was obtained as a light yellow solid.



1.3 Prepared of Pd/CTFs.

Pd/CTFs was prepared using the reported method.[2] Palladium chloride (8.4 mg) was dissolved in N,N-Dimethylformamide (35 mL) and then CTFs (100 mg) was added into the solution, and the mixture was stirred for 12 h at room temperature. After impregnation, the suspension was centrifuged to separate solid and washed with DMF. The solid was reduced by added dropwise into the solution of $NaBH_4$ in 10 mL DMF under vigorous stirring. The colour of mixture turned to

black immediately. After stirring about two hours, the solid was centrifuged and washed with DMF, water and ethanol and dried under vacuum at 60 ℃ and then kept for further use.

1.4 Prepared of Pd nanoparticle networks.

The Pd nanoparticle networks (Pd NNs) were prepared according to literature.[3] 3 ml of fresh 10 mM Na_2PdCl_4 was mixed with 40 ml H_2O in a beaker, followed by the addition of 12 mg trisodium citrate. The solution was stirred for 5 min, then 5 ml aqueous solution including 12 mg trisodium citrate and 6 mg $NaBH_4$ was injected into the beaker. The solution was kept stirred for about 30 min. The products were collected and washed with distilled water and ethanol for several times and then dried at 60 °C for 8 h.

2. Characterizations

NMR spectra was recorded on Varian Mercury Plus 400 instruments at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts were reported in parts per million (ppm) down field from internal tetramethylsilane. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in hertz (Hz). X-ray photoelectron spectroscopic (XPS) analyses were carried out on a Kratos Analytical Ltd. Axis Ultra DLD X-ray photoelectron spectrometer. The Pd content of each sample was analyzed by means of an inductively coupled plasma (ICP) spectrometer (USA, Agilent 7700x). Transmission electron microscopy (TEM), higher-magnification transmission electron microscopy (HRTEM), high angle annular dark field scanning transmission electron microscopy (HADDF-STEM), energy dispersive X-ray spectrometer (EDX) and EDX elemental mapping were characterized on a FEI Tecnai G2 F20 electron microscope. Scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopic (EDX) analysis were taken with a Hitachi S-4800 scanning electron microscope (SEM, 3 kV) equipped with the Thermo Scientific energy-dispersion X-ray fluorescence analyzer. The X-ray diffraction patterns (XRD) of the products were recorded with Bruker D8 Focus Diffraction System using a Cu Kαradiation. Fourier transform infrared spectra (FTIR) spectra was recorded on a MAGNA-IR 750 (Nicolet Instrument Co) FTIR spectrometer. The Brunauer-Emmett-Teller (BET) surface areas were screened by nitrogen adsorption and desorption at 77 K using a Quantachrome Automated Surface Area (NOVA2200e). The surface areas were calculated in the relative pressure (P/P_0) range from 0.01 to 0.05. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory (NL-DFT) pore model for pillared clay with cylindrical pore

geometry. Isotherm of carbon monoxide was measured at 298 K using a domestic apparatus.

3. General Experimental Procedure for mono and double carbonylation of Aryl Halides with Amines.

Pd/CTFs (30 mg), aryl halide (0.2 mmol), amines (0.8 mmol), K_2CO_3 (0.4 mmol), and 1mL CH_3CN were added into the pre-dried Schlenk tube under N_2 atmosphere. A CO (balloon) was introduced into the reaction mixture and the reactor was introduced into the oil bath at 70 ℃ or 100 ℃ and vigorously stirred (ca. 1000 rpm) when the reaction start. After 24 h, the reaction mixture was cooled to room temperature and then the solid residue was separated via centrifugation and washed with CH_2Cl_2 for three times. Combining all organic solvent was removed in vacuum and obtained mono or double carbonylation product by column chromatography (eluent: petroleum ether/ethyl acetate=10:1)

4. Procedure for the recycle of the catalyst.

The Pd/CTFs catalyst was recovered in the solid residue after centrifugation and separation from the organic layer (CH_3CN solution) containing the product. The solid residue was washed respectively with CH_2Cl_2, water and ethanol and then dried at 60 ℃. The solid residue containing recovered catalyst was directly used as catalyst in the subsequent runs.

5. Prepared of Pd/CTFs by $Pd(NO_3)_2$ as Pd precursor

In order to explore the effect of chloride anion to this reaction, we also chose $Pd(NO_3)_2$ as Pd precursors for preparing Pd/CTFs. The Pd/CTFs was prepared using the same methods as for Palladium chloride. We tested the catalytic activity of this catalyst using the model reaction under the optimized conditions. The yields of 3aa and 4aa are 85% and 11% respectively. The catalyst results was nearly same for Palladium chloride as Pd precursor. Thus, it is reasonable to think that chloride anion should not contributive to this reaction.

6. Hg (0) poisoning test.

Pd/CTFs (30 mg), 4-iodoanisole (0.2 mmol), morpholine (0.8 mmol), K_2CO_3 (0.4 mmol), and 1 mL CH_3CN with the addition of Elemental mercury (0.6mmol) were added into the pre-dried Schlenk tube under N_2 atmosphere. A CO (balloon) was introduced into the reaction mixture and the reactor was introduced into the oil bath at 70 ℃ for 24h, the desired product 3aa was formed in a trace amount, suggesting that the reaction is completely inhibited by the Hg (0).

7. The experiment of palladium leaching

The hot filtration test was performed to define directly the palladium leaching during this reaction. Pd/CTFs (30 mg), 4-iodoanisole (0.2 mmol), morpholine (0.8 mmol), K_2CO_3 (0.4 mmol)，and 1mL CH_3CN were charged into the pre-dried Schlenk tube under N_2 atmosphere. A CO (balloon) was introduced into the reaction mixture and the reactor was introduced into the oil bath at 70 ℃ and vigorously stirred (ca. 1000 rpm) for 2h. The yield of double carbonylation was measured in the mixture for 30%, and then the hot reaction mixture was drained into another Schlenk tube with inter filter membrane. The new K_2CO_3 (0.4mmol) was added into the hot reaction mixture without Pd/CTFs under N_2 atmosphere and then CO (balloon) was introduced into this reaction vessel to react for 12h. No more products were formed in the hot-filtration solution, suggesting that the carbonylation ceased in the absence of Pd/C. These results strongly suggests that the leaching out Pd species is negligible for such catalytic reactions, and Pd (0) naopartparticles are the active catalysts for the carbonylation of 4-iodoanisole.

8. **Supplementary Figures and Tables**

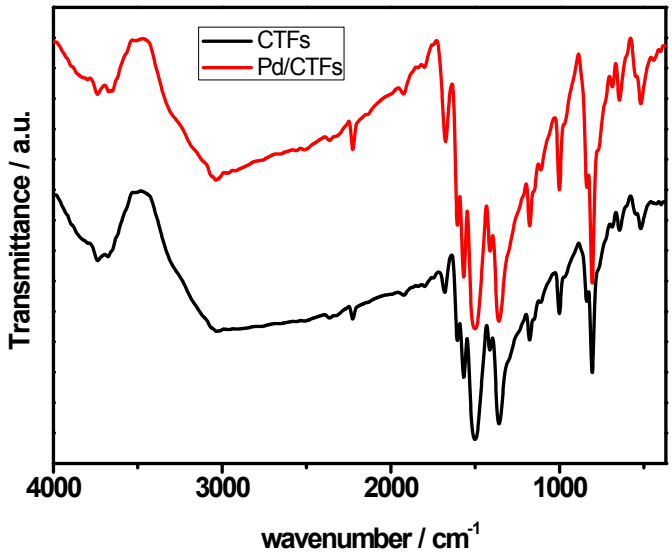


Fig. S1 IR spectra of CTFs and Pd/CTFs. The strong absorption bonds around 1500, 1360 and 800 cm^{-1} indicate the presence of triazine.

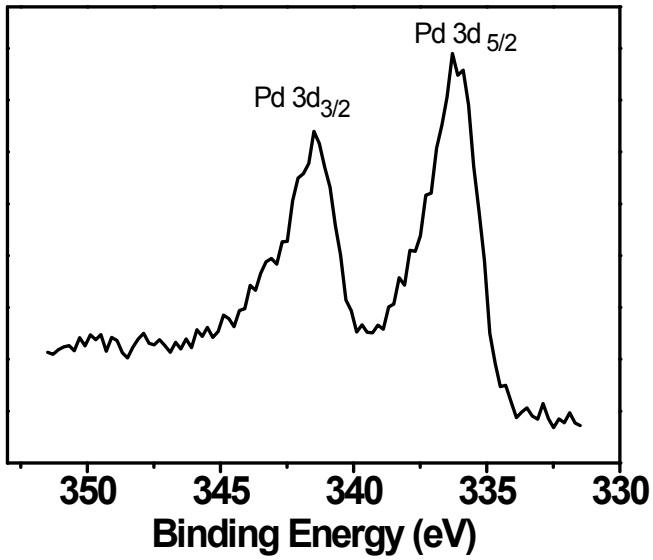


Fig. S2 The high-resolution Pd3d XPS spectra of Pd/CTFs. The banding energy peaks Pd $3d_{3/2}$ and $3d_{5/2}$ at 341.5eV and 336.3eV are indications of metallic Pd (0).

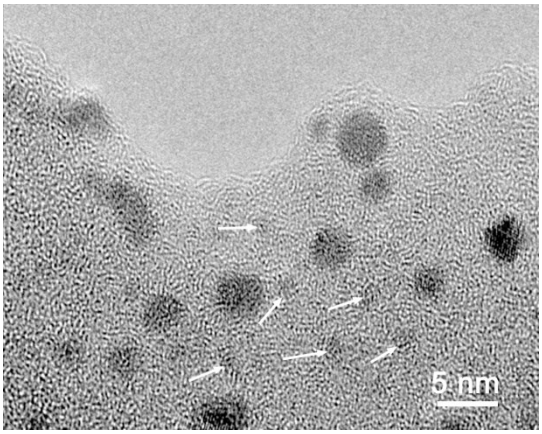


Fig. S3 HRTEM images of Pd/CTFs. The white arrows indicate the Pd NPs which are loaded into the interior of CTFs.

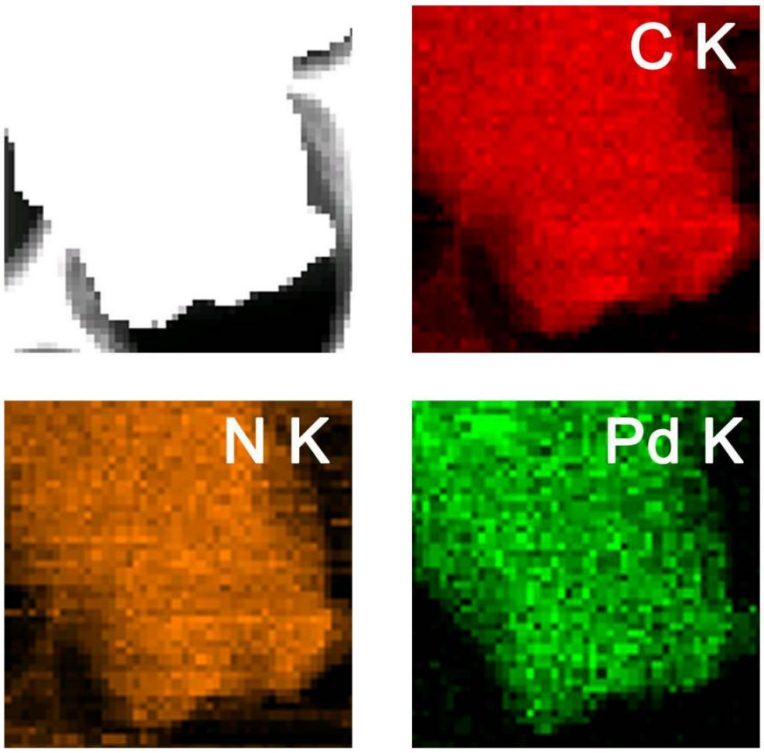


Fig. S4 HAADF-STEM and corresponding EDX mapping images of Pd/CTFs. We can find that Pd NPs distribute homogeneously throughout the CTFs by this images.

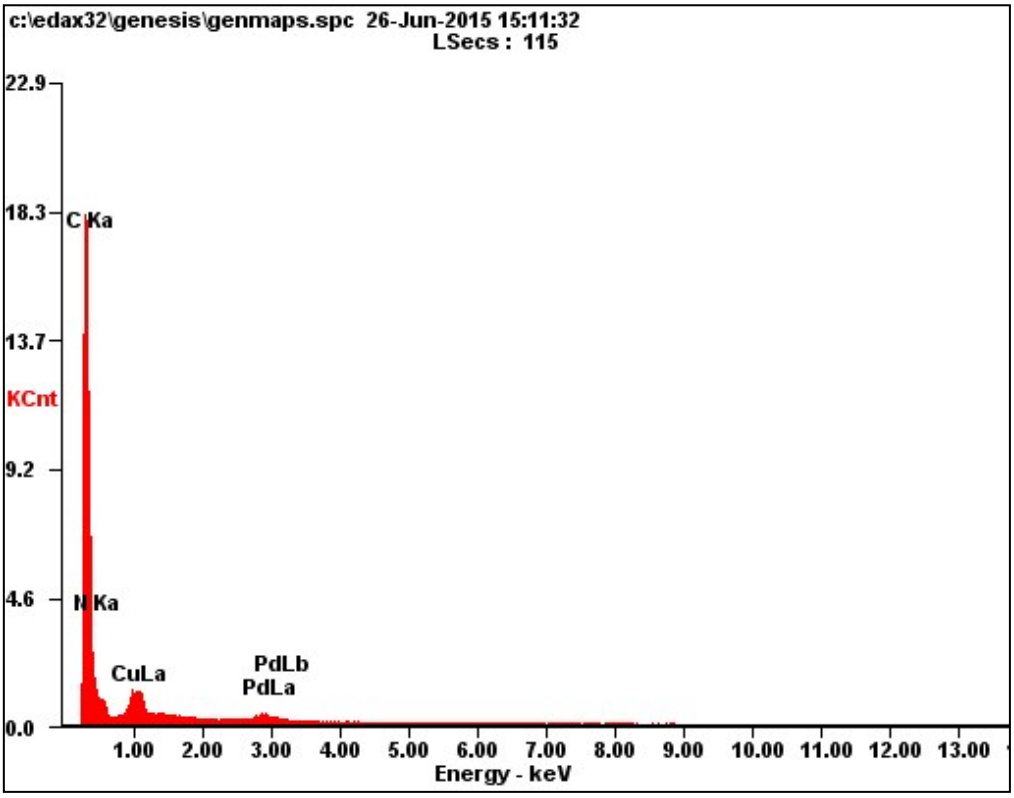


Fig. S5 EDX spectra of 2.05% Pd/CTFs. It shows the presence of Pd NPs.

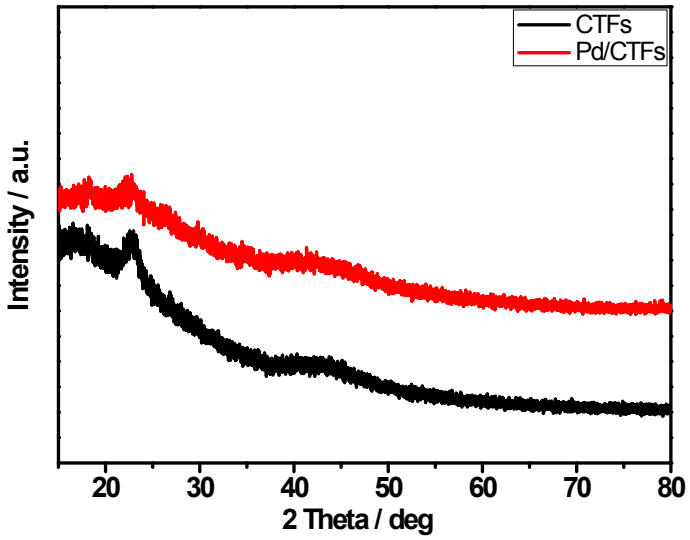


Fig. S6 Powder XRD patterns of CTFs and Pd/CTFs. No diffraction peaks of Pd species, indicating that the particles are highly dispersed on the support and the size of NPs is smaller than the detection limit.[4]

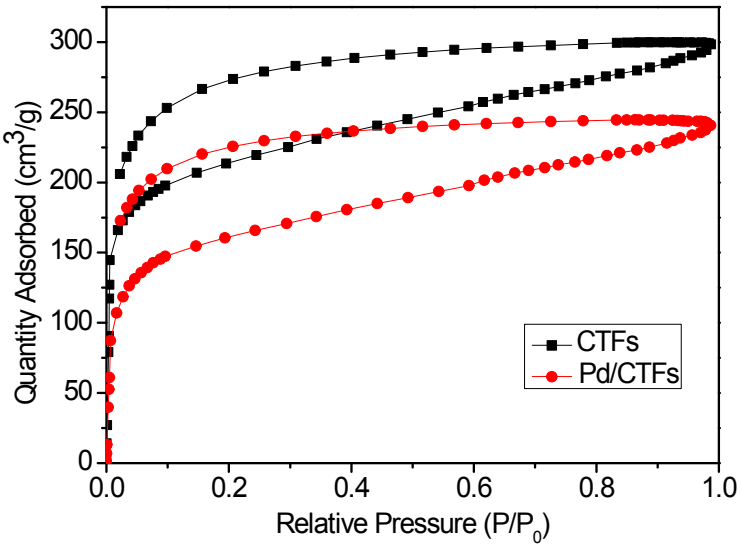


Fig. S7 N_2 adsorption and desorption isotherms of CTFs and Pd/CTFs. The BET surface area of pure CTFs and Pd/CTFs is 784 m^2/g and 607 m^2/g respectively.

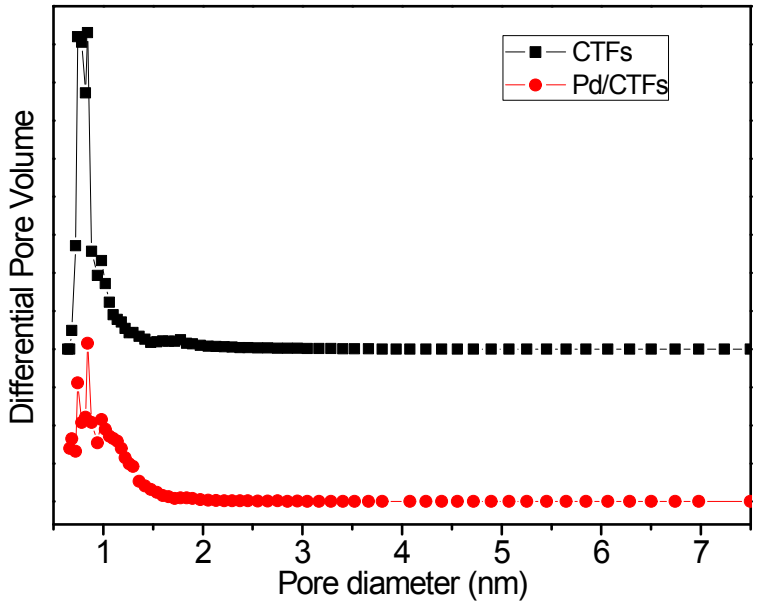


Fig. S8 The corresponding pore size distribution of CTFs and Pd/CTFs. The average pore diameter of CTFs is about 1.2 nm

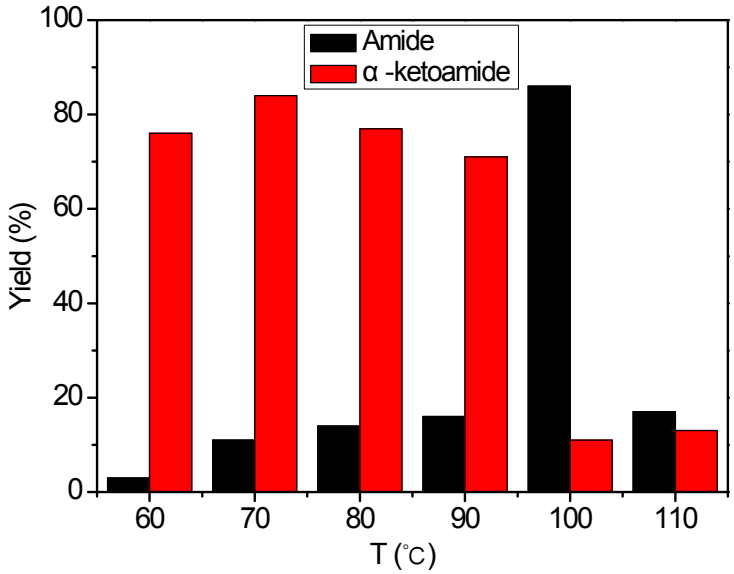


Fig. S9 Effect of temperature on double carbonylation of 4-iodoanisole with morpholine. With increasing of temperature, mono carbonylation products become gradualy main products. The optimized reaction tempreture of mono carbonylation is 100 ℃. Reaction conditions: 4-iodoanisole (0.2 mmol), K_2CO_3 (0.4 mmol), morpholine (0.8 mmol), Pd/CTFs (30 mg) in 1 mL CH_3CN for 24 h.

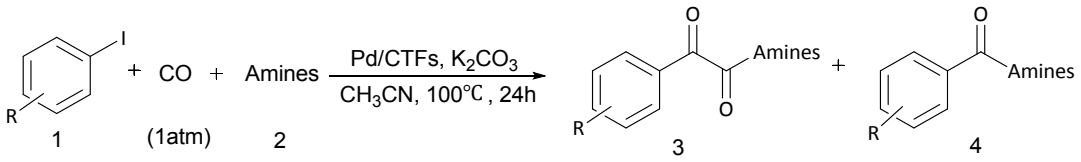
Table S1. Effect of different equivalent of amine on double carbonylation of 4-iodoanisole with morpholine.

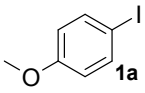
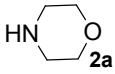
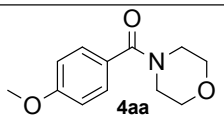
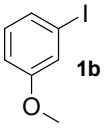
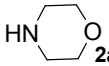
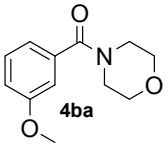
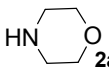
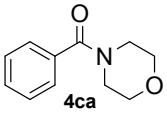
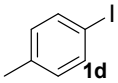
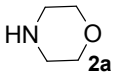
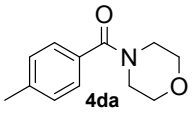
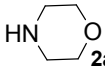
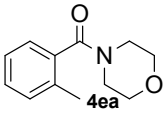
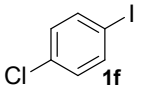
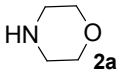
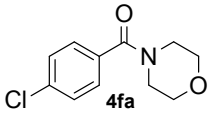
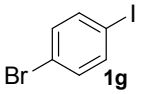
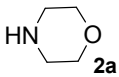
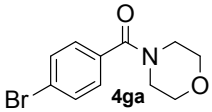
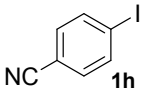
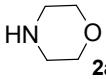
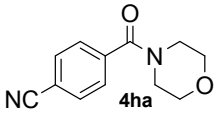
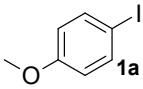
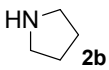
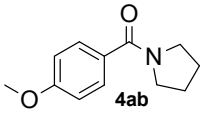
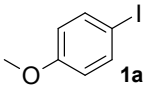
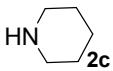
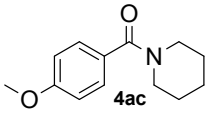
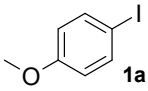
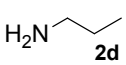
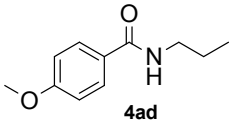
Entry	1a/2a	Cov. (%)	Yield(%)	
			3aa	4aa
1	1	55%	51%	4 %
2	2	58%	53%	5%
3	3	78%	72%	6%
4	4	95%	84%	11%
5	5	95%	83%	12%

Reaction conditions: 4-iodoanisole (0.2 mmol), K_2CO_3 (0.4 mmol), Pd/CTFs (30 mg) in 1 mL CH_3CN for 24 h. 1a/2a: morpholine /4-iodoanisole (mmol/mmol)

Increasing the amount of amine, the yields of 3aa rose obviously and 4aa rose slightly. The yield of 3aa was improved to 84% with conversion of 95% when a large excess of morpholine (4 equiv.) was used (Table S1, entry 4). The consequence of a further increase in the amount of morpholine however, was no significant change in conversion and selectivity for the double carbonylated product (Table S1, entry 5). So, we determined that four equivalent of amine was the optimal.

Table S2. Mono carbonylation reaction of aryl iodides with various amines[a]



Entry	1	3	4	Yield[%](4/3)[b]
1	 1a	 2a	 4aa	86(88/12)
2	 1b	 2a	 4ba	85
3	 1c	 2a	 4ca	92
4	 1d	 2a	 4da	88(93/7)
5	 1e	 2a	 4ea	90
6	 1f	 2a	 4fa	92
7	 1g	 2a	 4ga	90
8	 1h	 2a	 4ha	79
9	 1a	 2b	 4ab	97
10	 1a	 2c	 4ac	96
11	 1a	 2d	 4ad	91

[a]General conditions: 1 (0.2 mmol), 2 (0.8 mmol), CO (balloon pressure), Pd/CTFs (30 mg), K_2CO_3 (0.4 mmol) in CH_3CN (1.0 mL) at 100°C for 24 h. [b]Yield of isolated 4, the number in parenthesis

indicates 4/3 selectivity determined by flash column chromatography on silica gel.

The mono-carbonylation events are examined at 100°C to further estimate the efficiency of this strategy. To our amazement, under the selected conditions, the reactions display excellent yields and selectivity, and we nearly access the mono-carbonylated amides exclusively with respect to both diversified aryl iodides and amines (Table S2). These fascinating results further reveal that the mono- and di-carbonylation processes can be well controlled by the reaction temperature that lower temperature determines the di-carbonylation, while at higher temperature the mono-carbonylated products are almost delivered. The experiment of palladium leaching for mono-carbonylation used the same methods as for the double-carbonylation. The first yield of mono-carbonylation was measured as 15% for 4h. And then the further reaction result suggested that no more mono-carbonylation products were formed and mono-carbonylation ceased. The result also further illustrated that the palladium leaching was negligible for such catalytic reactions at 100℃.

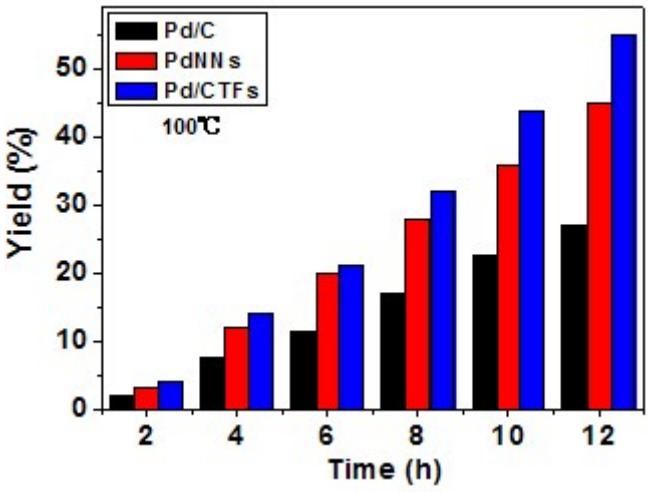


Fig. S10. Yields (%) as a function of time in mono carbonylation of aryl iodides with amines at 100 °C. In order to prove Pd/CTFs high catalyst activity, we draw the evolution of yield amides versus time with model reaction under the optimized conditions by comparing Pd/CTFs with 5wt% Pd/C and Pd NNs. With 12 h, Pd/CTFs exhibited higher activity than Pd NNs and Pd/C.

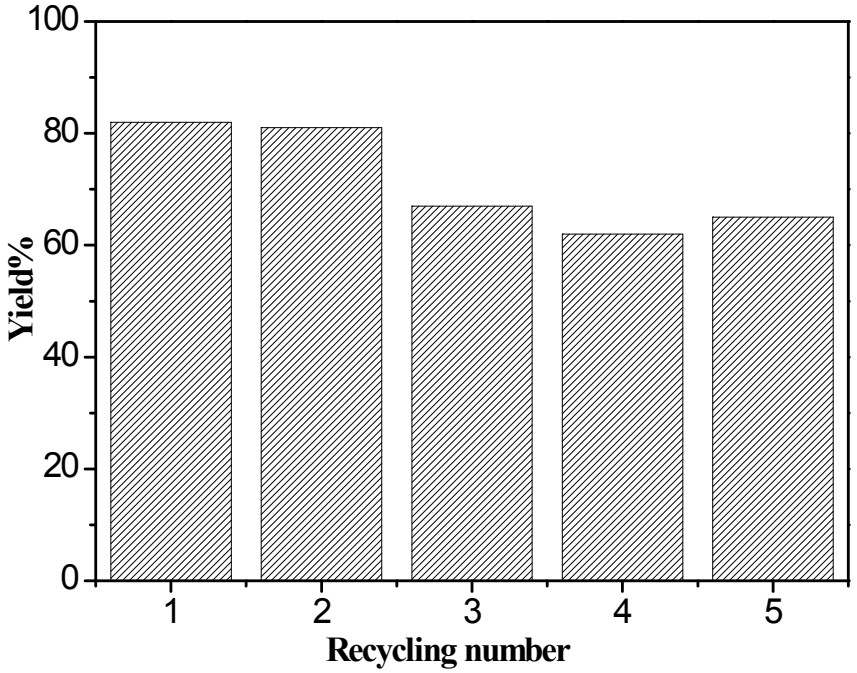


Fig. S11 Recycling tests with Pd/CTFs for double carbonylation of 4-iodoanisole with morpholine at 70 ℃. It shows that Pd/CTFs show good regeneration properties without obviously lowering activity and morphological change after five recycling tests.

Fig. S12 Pd leaching analysis by ICP-OES

Experiment	Pd leaching, ppm
Run 1	2.89
Run 2	1.46
Run 3	2.10
Run 4	2.15
Run 5	2.07

The Pd leaching is negligible (<3ppm) and no double carbonylation activity is detected using the supernatant liquid after the isolation of the solid catalyst.[5]

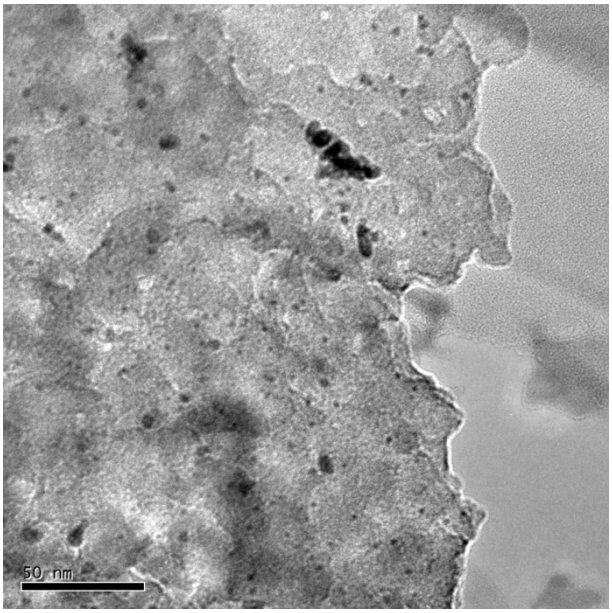


Fig. S13 TEM image after five recycle test of Pd/CTFs. It shows that Pd NPs aggregate weakly on the surface of CTFs which may lead to decrease activity of catalyst.

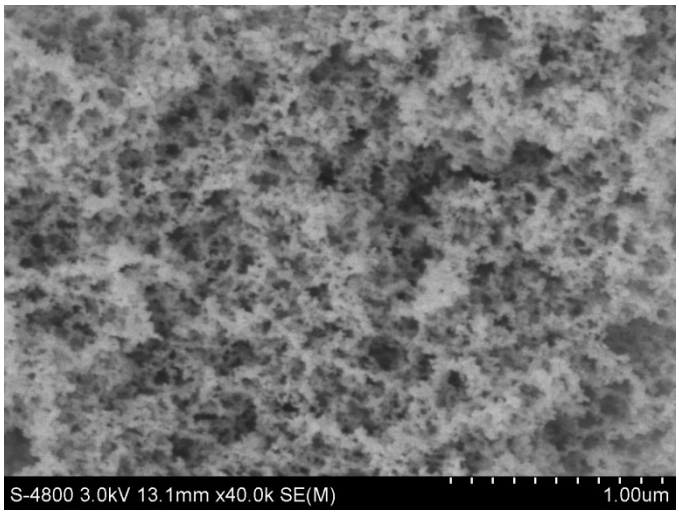


Fig. S14 The SEM image of palladium nanoparticle networks.[3]

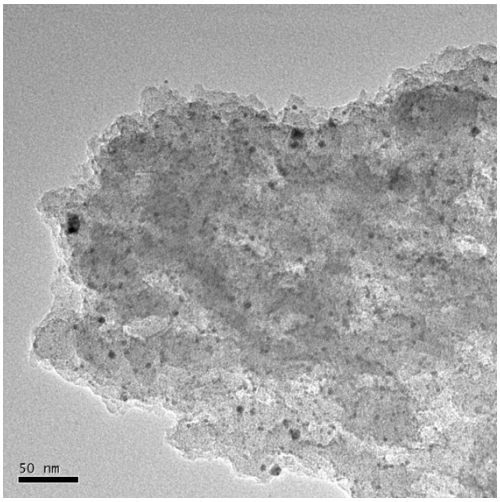
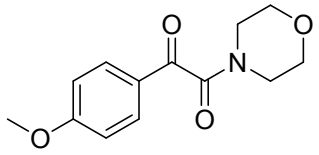


Fig. S15 The TEM image of 5wt% Pd/C. (HEOWNS)

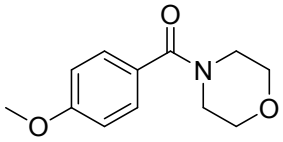
9. Spectra Data



1-(4-methoxyphenyl)-2-morpholinoethane-1,2-dione (3aa)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.0 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 2H), 3.89 (d, *J* = 1.8 Hz, 3H), 3.78 (s, 4H), 3.67 – 3.61 (m, 2H), 3.38 (d, *J* = 3.5 Hz, 2H).

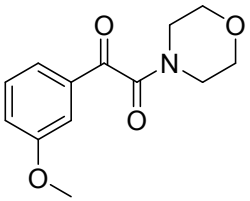
^{13}C NMR (100 MHz, $CDCl_3$): *δ* 189.83, 165.81, 165.04, 132.13, 126.15, 114.43, 66.77, 66.67, 55.67, 46.30, 41.56.



(4-methoxyphenyl)(morpholino)methanone (4aa)

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.41 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 3.68 (dd, *J* = 13.7, 8.6 Hz, 8H).

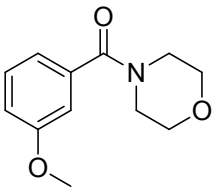
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.40, 160.91, 129.18, 127.34, 113.79, 66.90, 55.34, 48.01, 43.63.



1-(3-methoxyphenyl)-2-morpholinoethane-1,2-dione (3ba)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 4H), 3.70 – 3.65 (m, 2H), 3.43 – 3.35 (m, 2H).

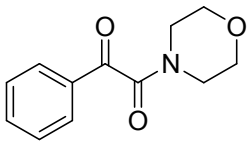
^{13}C NMR (100 MHz, $CDCl_3$): δ 191.09, 165.45, 160.18, 134.38, 130.16, 122.82, 121.82, 112.84, 66.72, 66.67, 55.56, 46.28, 41.64.



(3-methoxyphenyl)(morpholino)methanone (4ba)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 3H), 3.86 – 3.39 (m, 11H).

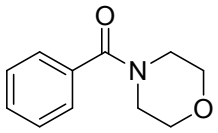
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.57, 166.09, 136.20, 134.53, 134.12, 130.94, 129.51, 128.82, 127.13, 125.77, 124.55, 123.95, 66.71, 46.43, 41.76.



1-morpholino-2-phenylethane-1,2-dione (3ca)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 3.81 (s, 4H), 3.72 – 3.64 (m, 2H), 3.45 – 3.35 (m, 2H).

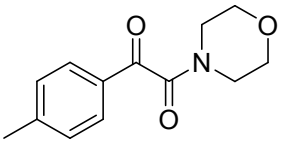
^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 165.5 , 133.1 , 1297 , 129.1 , 66.7,66.6, 46.3 , 41.6 .



morpholino(phenyl)methanone (4ca)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 5H), 3.83 – 3.40 (m, 8H).

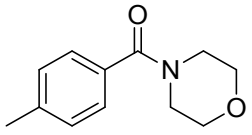
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.44, 135.33, 129.86, 128.55, 127.07, 66.87, 48.35, 42.60.



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

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.81 (s, 4H), 3.70 – 3.63 (m, 2H), 3.44 – 3.36 (m, 2H), 2.46 (s, 3H).

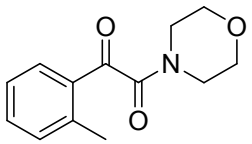
^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 165.7, 146.3, 130.7, 129.84,129.8, 66.7,66.6, 46.3, 41.6, 21.9.



morpholino(p-tolyl)methanone (4da)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 3.69 (s, 8H), 2.38 (s, 3H).

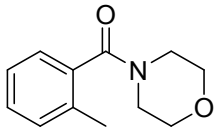
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.63, 140.06, 132.36, 129.13, 127.23, 66.90, 48.33, 42.94, 21.36.



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

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.2 Hz, 1H), 7.52 (td, *J* = 7.5, 1.1 Hz, 1H), 7.35 (dd, *J* = 10.2, 7.8 Hz, 2H), 3.85 – 3.77 (m, 4H), 3.73 – 3.66 (m, 2H), 3.46 – 3.39 (m, 2H), 2.69 (s, 3H).

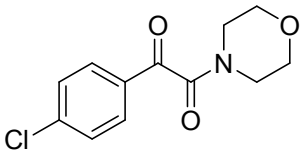
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.13, 166.22, 141.66, 133.91, 132.73, 131.53, 127.95, 126.24, 66.69, 66.67, 46.30, 41.65, 21.83.



morpholino(o-tolyl)methanone (4ea)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (ddd, *J* = 26.2, 19.9, 6.6 Hz, 4H), 3.84 (dd, *J* = 19.0, 4.5 Hz, 4H), 3.61 (s, 2H), 3.27 (d, *J* = 4.3 Hz, 2H), 2.35 (s, 3H).

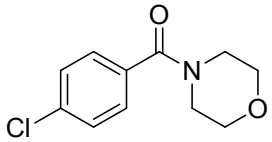
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.14, 135.68, 134.23, 130.53, 129.08, 126.03, 125.86, 67.03, 66.98, 47.29, 41.94, 19.04.



1-(4-chlorophenyl)-2-morpholinoethane-1,2-dione (3fa)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 3.79 (d, *J* = 7.4 Hz, 4H), 3.70 – 3.64 (m, 2H), 3.43 – 3.36 (m, 2H).

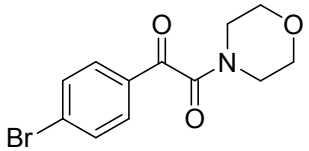
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 131.5, 131.0, 129.5, 66.7,66.6, 46.3, 41.7.



(4-chlorophenyl)(morpholino)methanone (4fa)

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.39 (q, *J* = 8.4 Hz, 4H), 3.59 (d, *J* = 90.4 Hz, 8H).

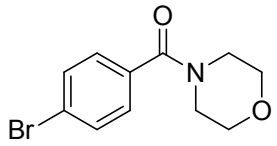
^{13}C NMR: (100 MHz, $CDCl_3$) δ 169.36, 136.02, 133.66, 128.87, 128.68, 66.82, 48.01, 42.45.



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

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 4H), 3.72 – 3.64 (m, 2H), 3.45 – 3.36 (m, 2H).

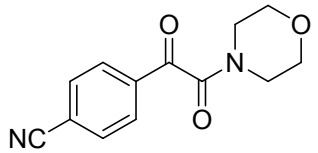
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.92, 164.88, 132.51, 131.90, 131.08, 130.51, 66.76, 66.66, 46.31, 41.74.



(4-bromophenyl)(morpholino)methanone (4ga)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 3.99 – 3.31 (m, 8H).

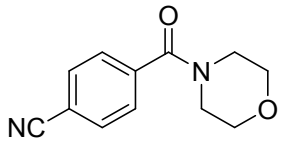
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.40, 134.10, 131.82, 128.84, 124.27, 66.81, 48.35, 42.32.



4-(2-morpholino-2-oxoacetyl)benzonitrile (3ha)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 10.5 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 3.87 – 3.56 (m, 8H).

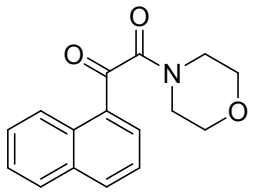
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.02, 164.14, 136.09, 132.82, 130.11, 117.95, 117.57, 66.76, 66.64, 46.36, 41.93.



4-(morpholine-4-carbonyl)benzonitrile (4ha)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 3.89 – 3.55 (m, 8H).

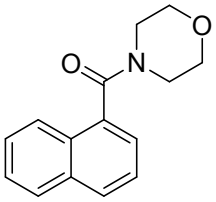
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.32, 139.66, 132.52, 127.83, 117.99, 113.71, 66.73, 48.03, 42.53.



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

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (d, *J* = 8.7 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.67 – 7.58 (m, 2H), 3.86 (s, 4H), 3.72 – 3.68 (m, 2H), 3.50 – 3.44 (m, 2H).

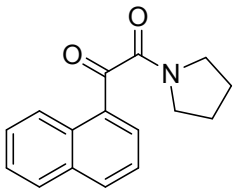
^{13}C NMR (100 MHz, $CDCl_3$): δ 193.60, 166.09, 136.20, 134.53, 134.12, 130.94, 129.51, 128.82, 127.13, 125.77, 124.55, 123.95, 66.71, 46.43, 41.76.



morpholino(naphthalen-1-yl)methanone (4ia)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (t, *J* = 10.0 Hz, 3H), 7.56 (ddd, *J* = 20.0, 13.7, 6.9 Hz, 3H), 7.46 (d, *J* = 6.9 Hz, 1H), 3.96 (ddd, *J* = 26.0, 10.7, 6.5 Hz, 4H), 3.55 (dd, *J* = 9.6, 6.9 Hz, 2H), 3.31 – 3.16 (m, 2H).

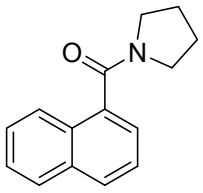
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.53, 133.71, 133.50, 129.58, 129.38, 128.54, 127.17, 126.56, 125.20, 124.64, 123.95, 67.12, 67.03, 47.65, 42.24.



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

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.64 – 7.53 (m, 2H), 3.72 (t, *J* = 6.7 Hz, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.03 – 1.94 (m, 4H).

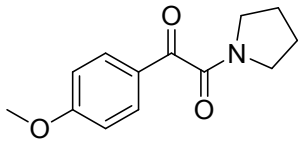
^{13}C NMR (100 MHz, $CDCl_3$): δ 194.14, 165.74, 135.61, 134.15, 134.09, 131.15, 129.15, 128.70, 128.57, 126.91, 125.82, 124.53, 46.74, 45.34, 25.95, 24.07.



naphthalen-1-yl(pyrrolidin-1-yl)methanone (4ib)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.83 (m, 3H), 7.56 – 7.44 (m, 4H), 3.81 (t, *J* = 7.0 Hz, 2H), 3.13 (t, *J* = 6.8 Hz, 2H), 2.06 – 1.96 (m, 2H), 1.83 (p, *J* = 6.7 Hz, 2H).

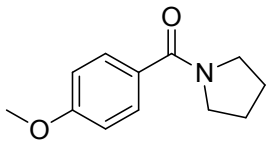
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.26, 135.86, 133.58, 129.23, 129.07, 128.40, 126.93, 126.27, 125.19, 124.91, 123.74, 48.58, 45.65, 26.01, 24.63.



1-(4-methoxyphenyl)-2-(pyrrolidin-1-yl)ethane-1,2-dione (3ab)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 3.66 (t, *J* = 5.7 Hz, 2H), 3.44 (d, *J* = 6.0 Hz, 2H), 1.96 (s, 4H).

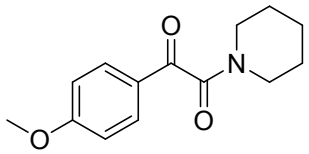
^{13}C NMR (100 MHz, $CDCl_3$): δ 190.31, 165.34, 164.79, 132.36, 126.02, 114.27, 55.63, 46.71, 45.20, 25.92, 24.05.



(4-methoxyphenyl)(pyrrolidin-1-yl)methanone (4ab)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.61 (d, *J* = 5.9 Hz, 2H), 3.46 (s, 2H), 1.89 (dd, *J* = 26.2, 5.8 Hz, 4H).

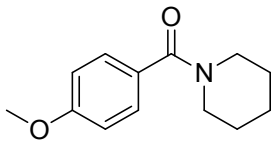
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.42, 160.79, 129.40, 129.12, 113.40, 55.29, 49.76, 46.30, 26.47, 24.42.



1-(4-methoxyphenyl)-2-(piperidin-1-yl)ethane-1,2-dione (3ac)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H), 3.70 (s, 2H), 3.34 – 3.26 (m, 2H), 1.70 (s, 4H), 1.55 (s, 2H).

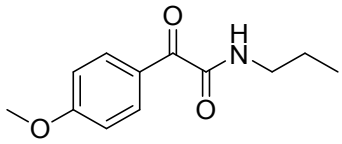
^{13}C NMR (100 MHz, $CDCl_3$): δ 190.69, 165.81, 164.80, 132.01, 126.40, 114.32, 55.63, 47.06, 42.09, 26.24, 25.48, 24.41.



(4-methoxyphenyl)(piperidin-1-yl)methanone (4ac)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.52 (s, 4H), 1.70 – 1.50 (m, 6H).

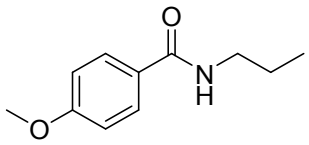
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.28, 160.52, 128.81, 128.61, 113.62, 55.29, 48.65, 43.25, 26.21, 25.98, 24.62.



2-(4-methoxyphenyl)-2-oxo-N-propylacetamide (3ad)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 8.6 Hz, 2H), 7.24 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.37 (dd, *J* = 13.6, 6.7 Hz, 2H), 1.65 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

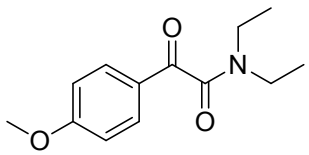
^{13}C NMR (100 MHz, $CDCl_3$): δ 185.93, 164.67, 162.39, 133.93, 126.47, 113.82, 55.55, 41.07, 29.71, 22.62, 11.40.



4-methoxy-N-propylbenzamide (4ad)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.19 (s, 1H), 3.85 (s, 3H), 3.41 (dd, *J* = 13.4, 6.7 Hz, 2H), 1.71 – 1.58 (m, 2H), 1.28 (d, *J* = 11.1 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

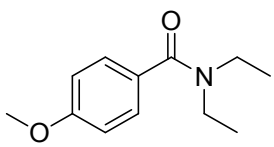
^{13}C NMR (100 MHz, $CDCl_3$): δ 167.09, 162.10, 128.60, 127.18, 113.70, 55.64, 55.38, 41.71, 22.98, 11.43.



N,N-diethyl-2-(4-methoxyphenyl)-2-oxoacetamide (3ae)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H), 3.58 (q, *J* = 7.1 Hz, 2H), 3.27 (q, *J* = 7.0 Hz, 2H), 1.32 (d, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.38, 167.09, 164.73, 132.07, 128.21, 114.28, 55.67, 42.14, 38.74, 14.14, 12.86.



N,N-diethyl-4-methoxybenzamide (4ae)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 3.42 (s, 4H), 1.43 – 1.25 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.26, 160.31, 129.57, 128.22, 113.67, 55.32, 29.70, 13.56.

10. References

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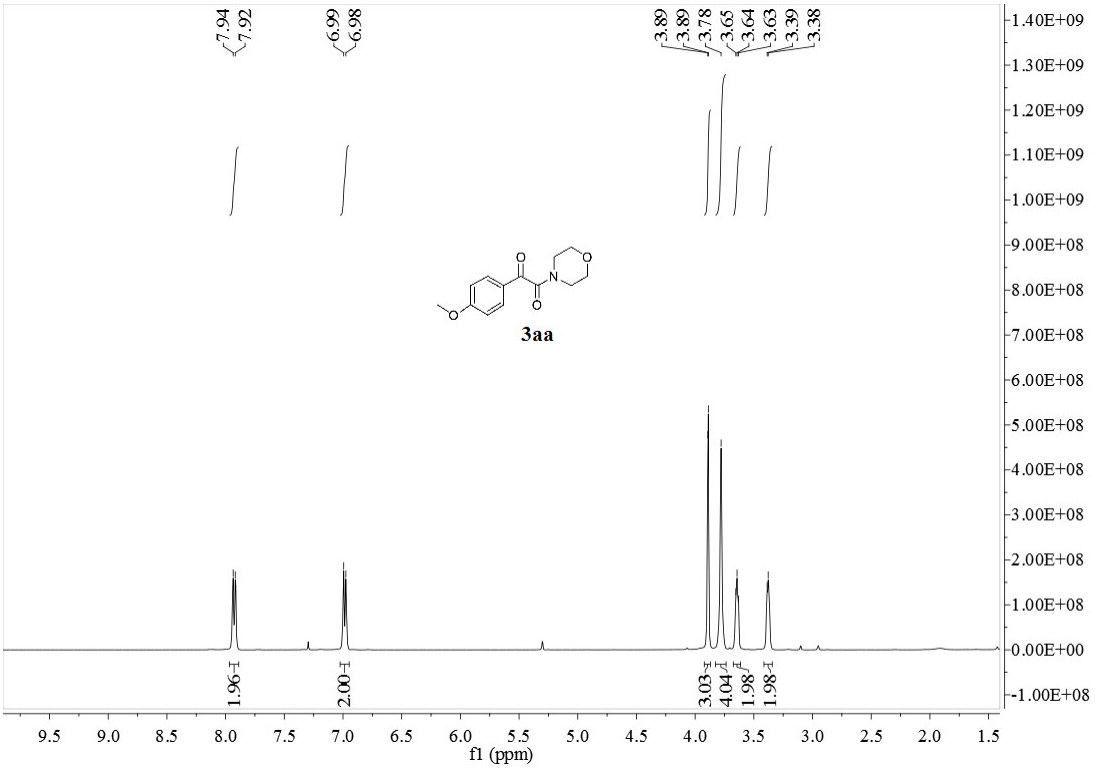
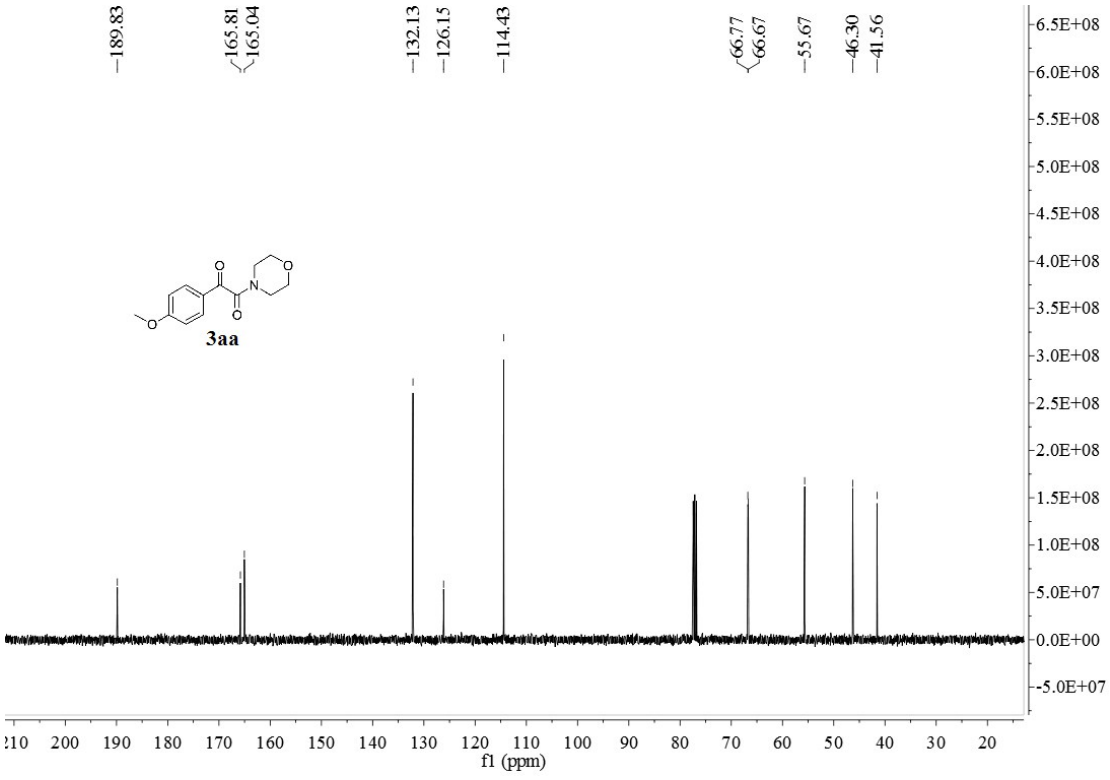
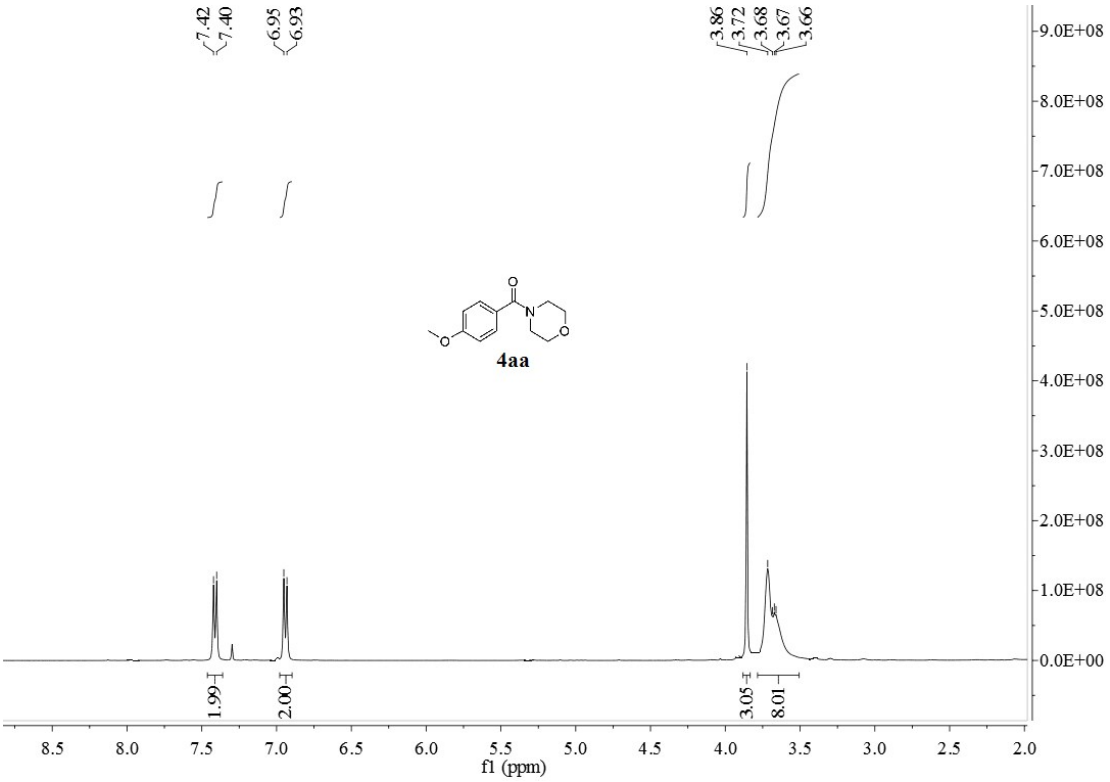
11. ^{1}H and ^{13}C Spectra

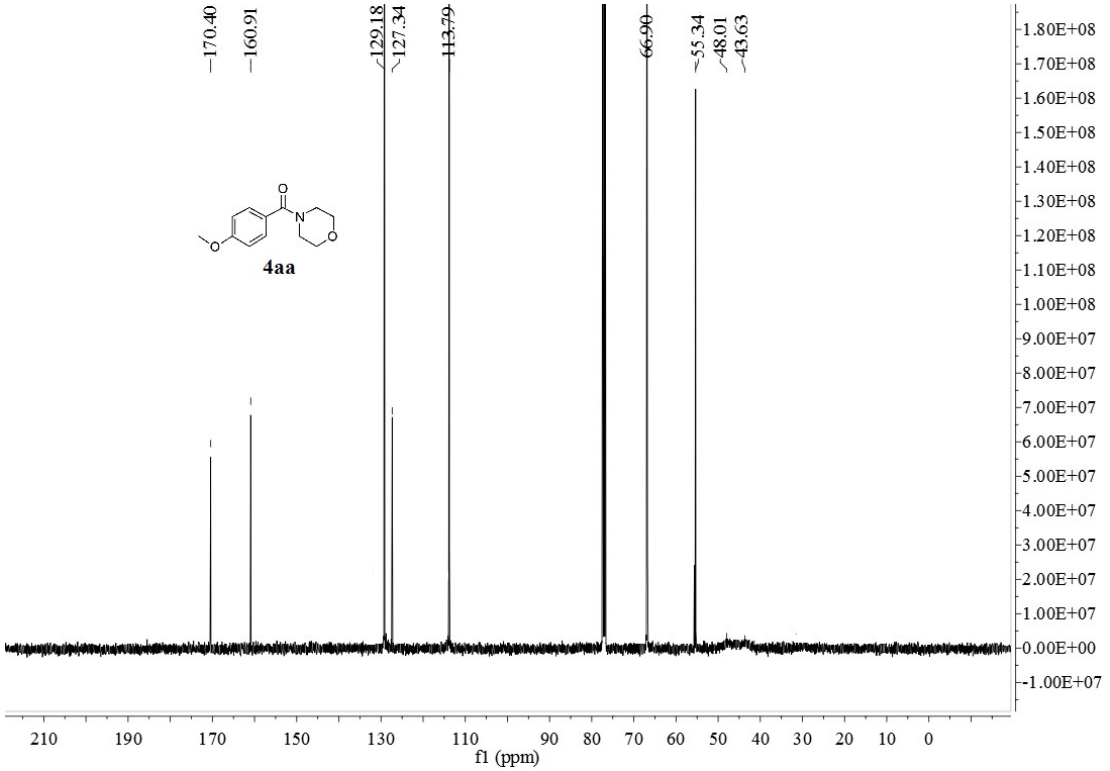
1-(4-methoxyphenyl)-2-morpholinoethane-1,2-dione (3aa)



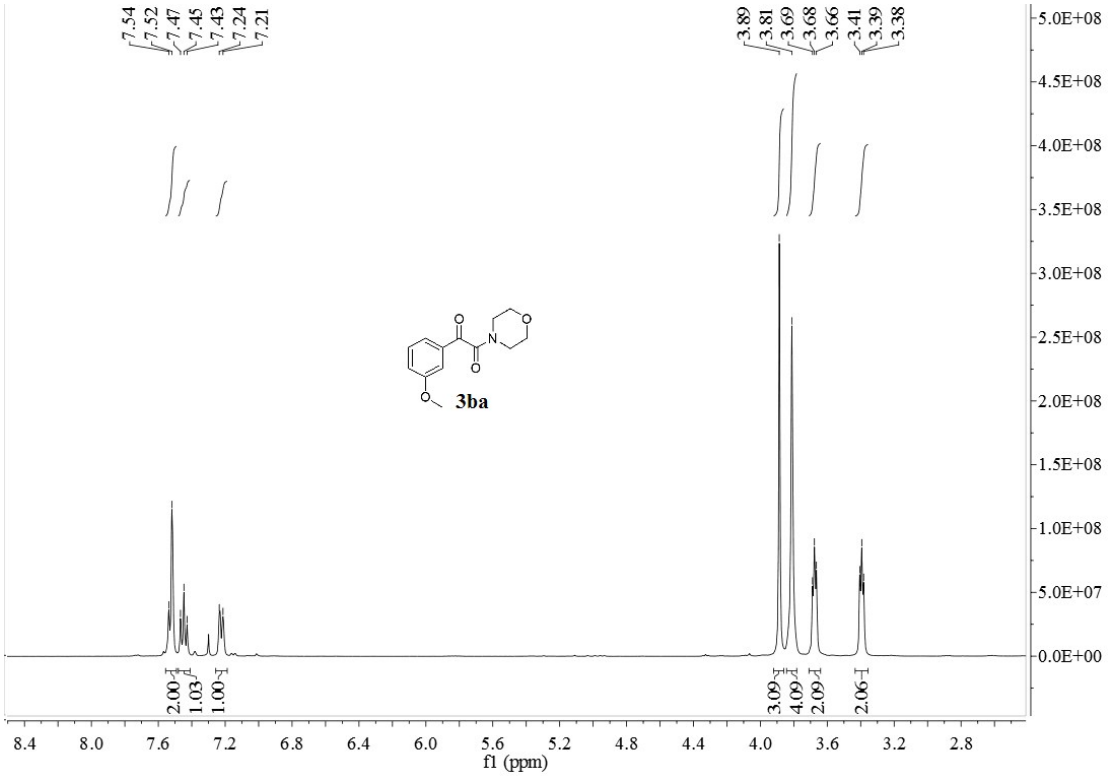


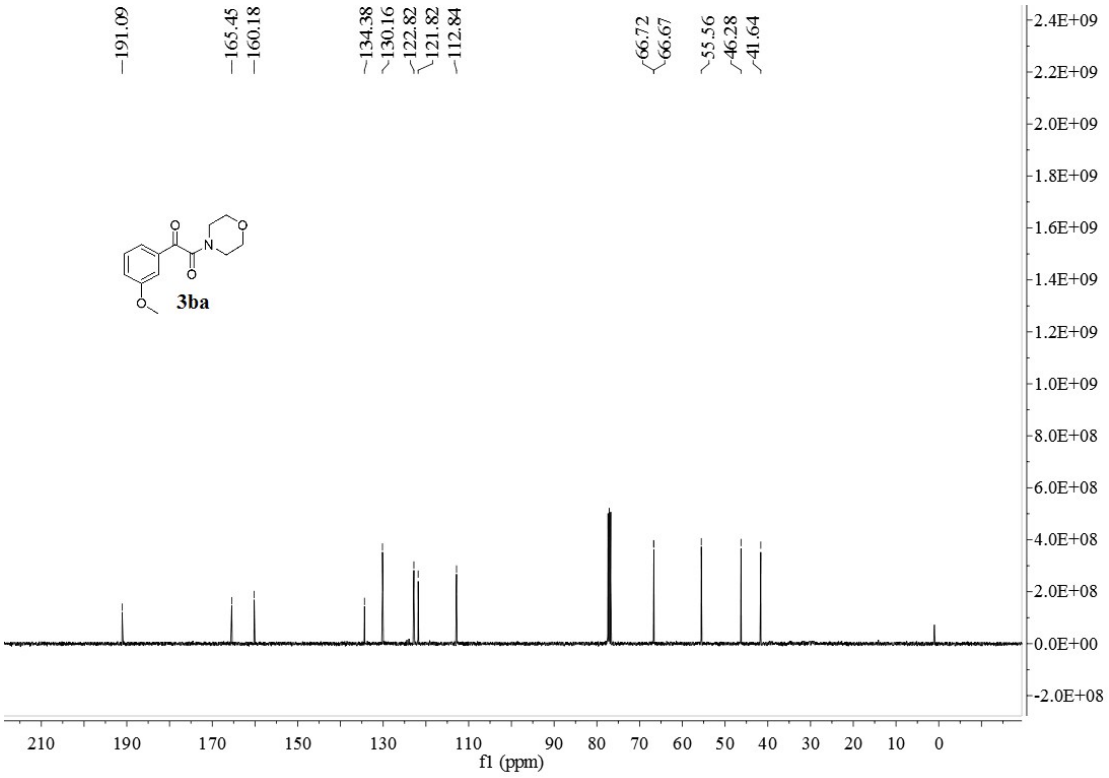
(4-methoxyphenyl)(morpholino)methanone (4aa)



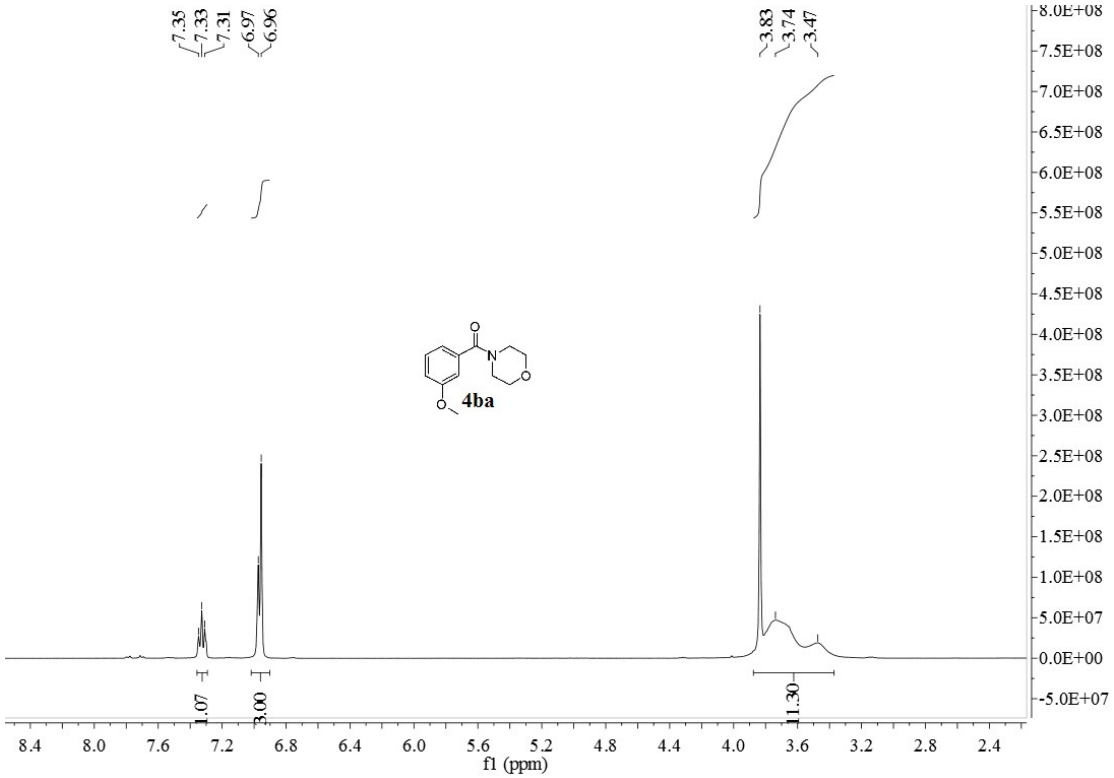


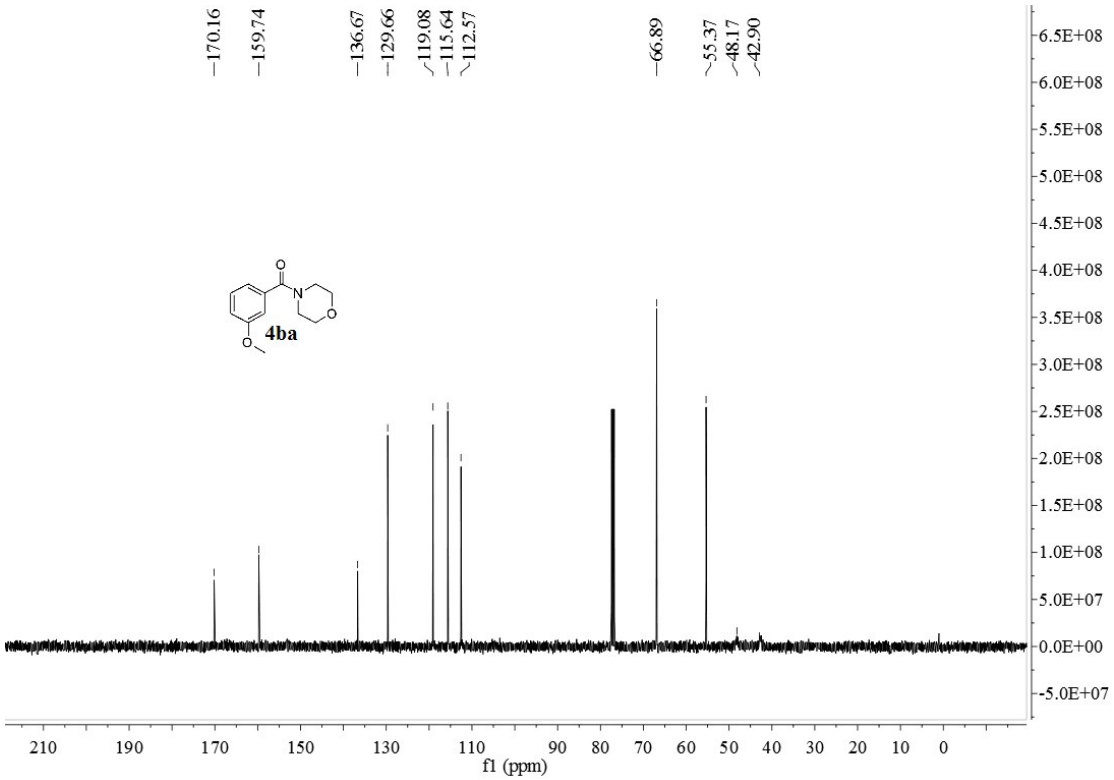
1-(3-methoxyphenyl)-2-morpholinoethane-1,2-dione (3ba)



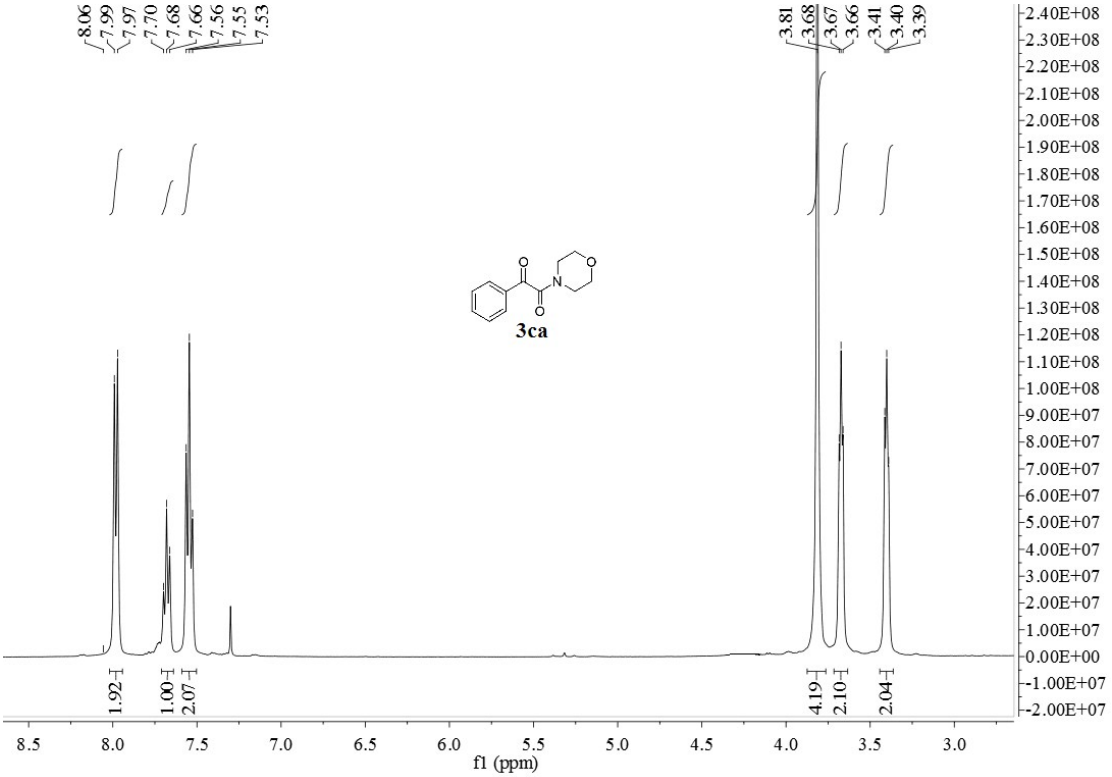


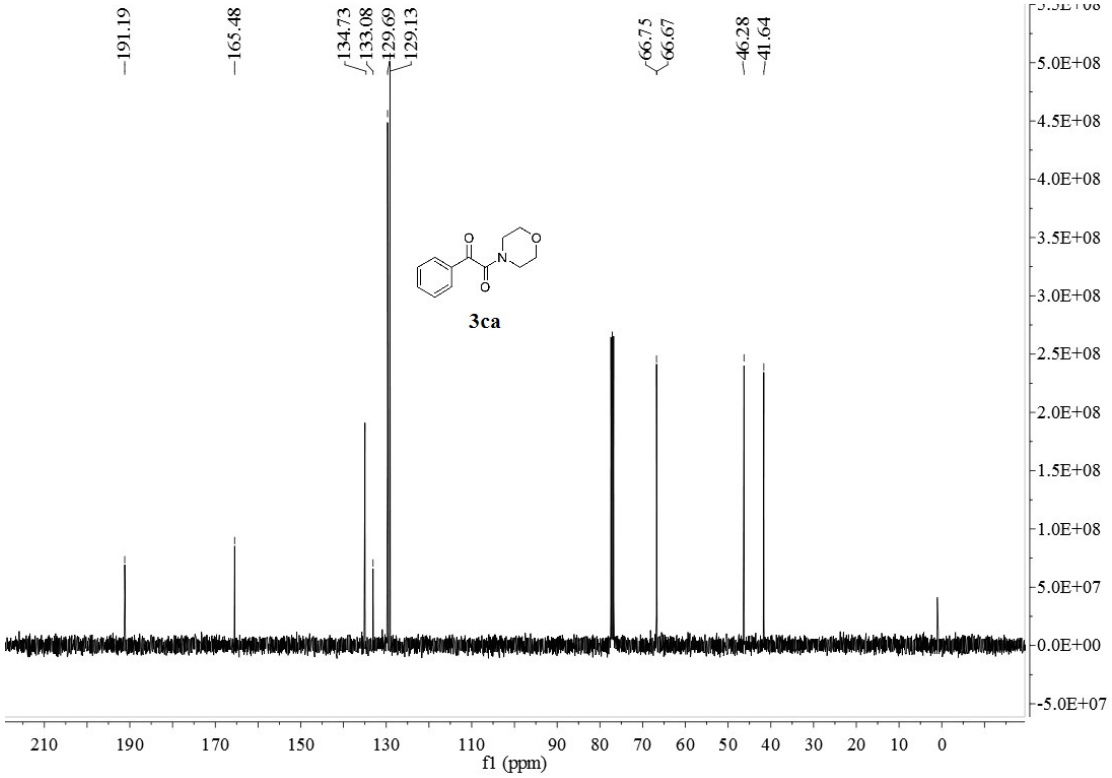
(3-methoxyphenyl)(morpholino)methanone (4ba)



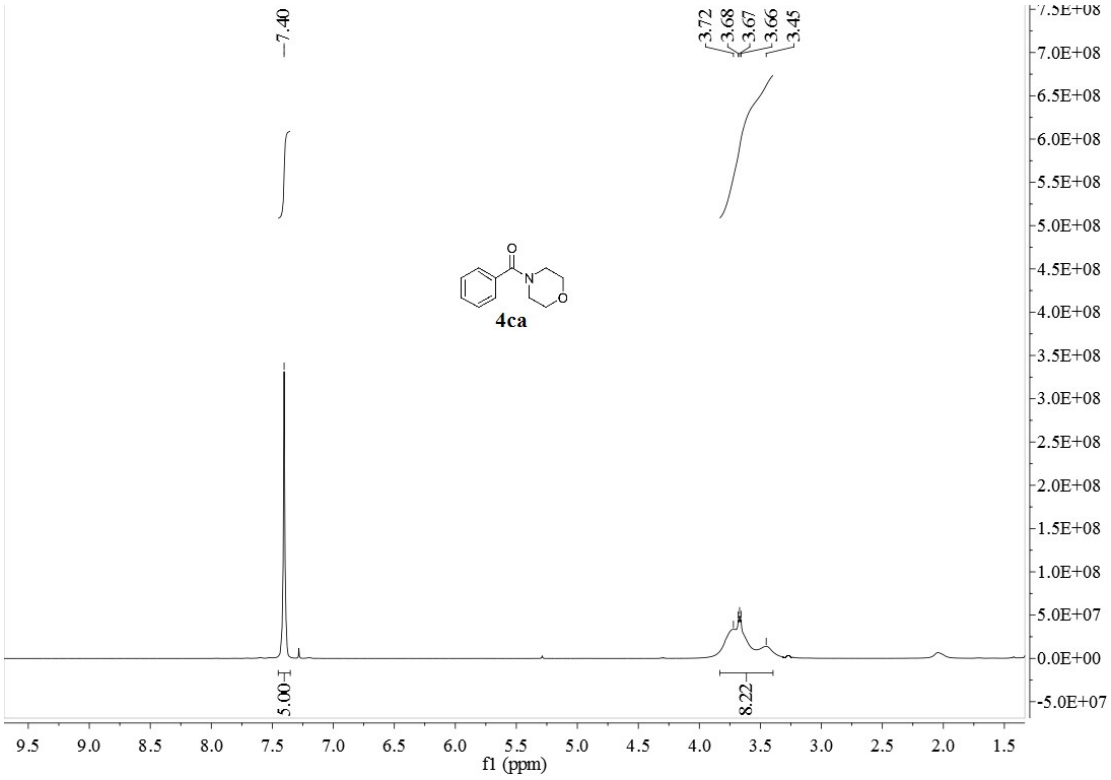


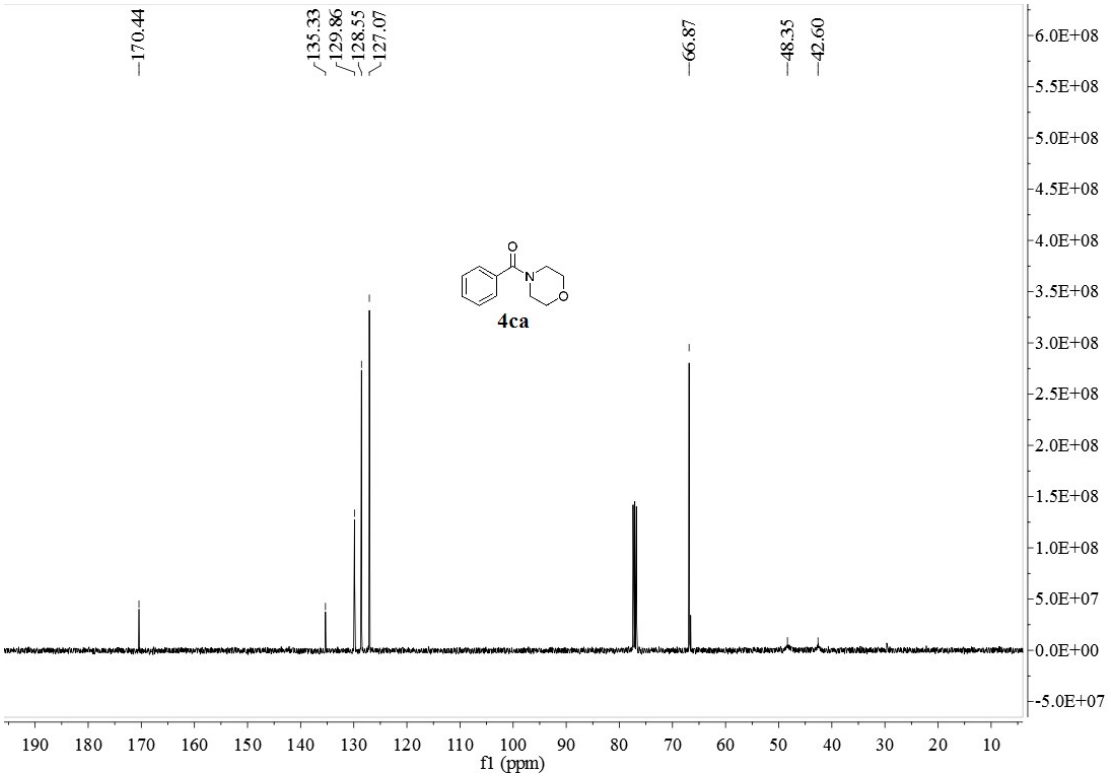
1-morpholino-2-phenylethane-1,2-dione (3ca)



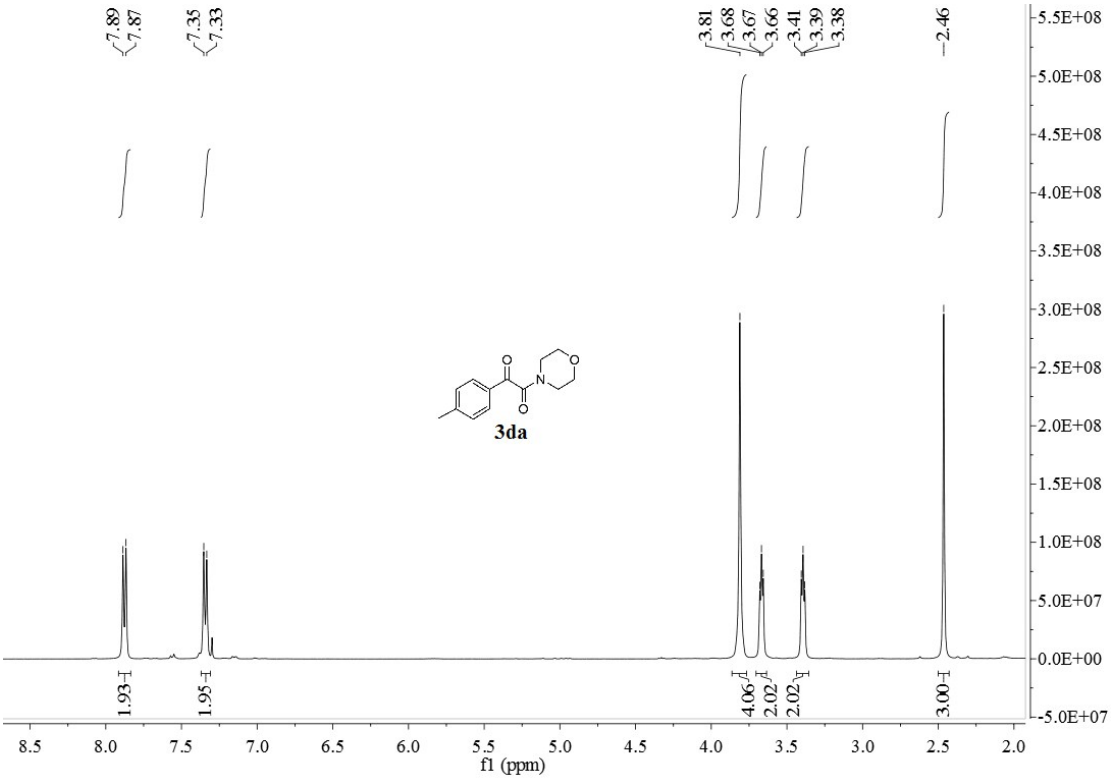


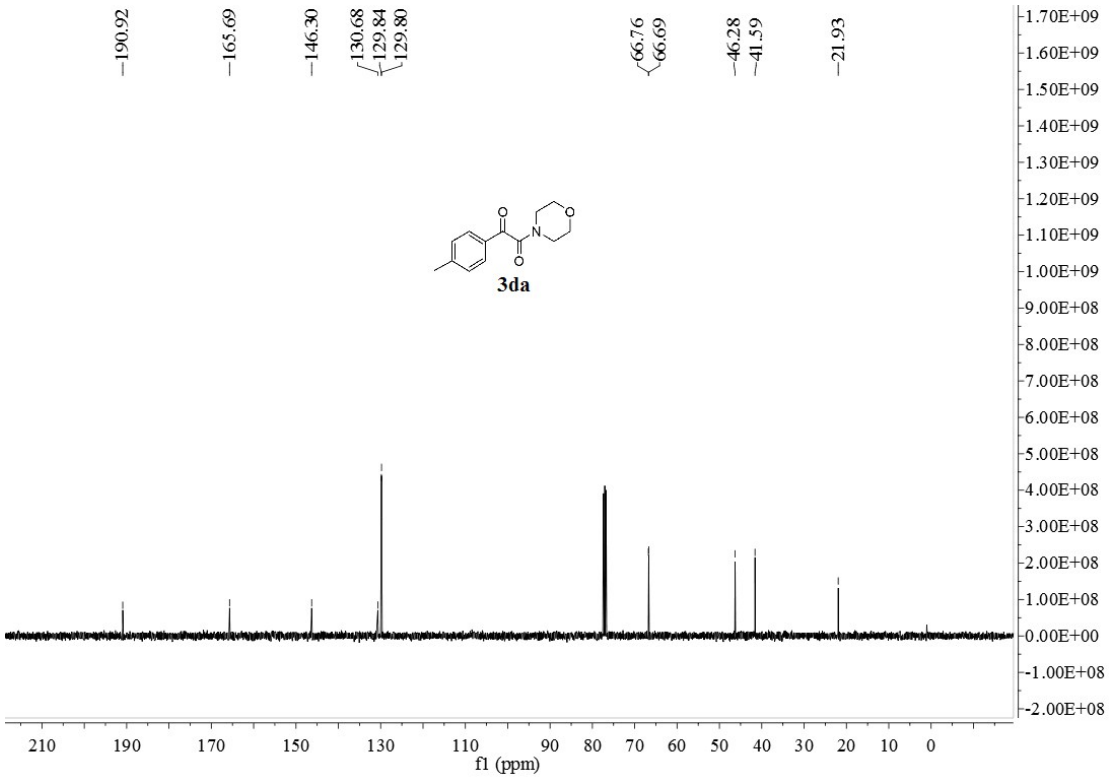
morpholino(phenyl)methanone (4ca)



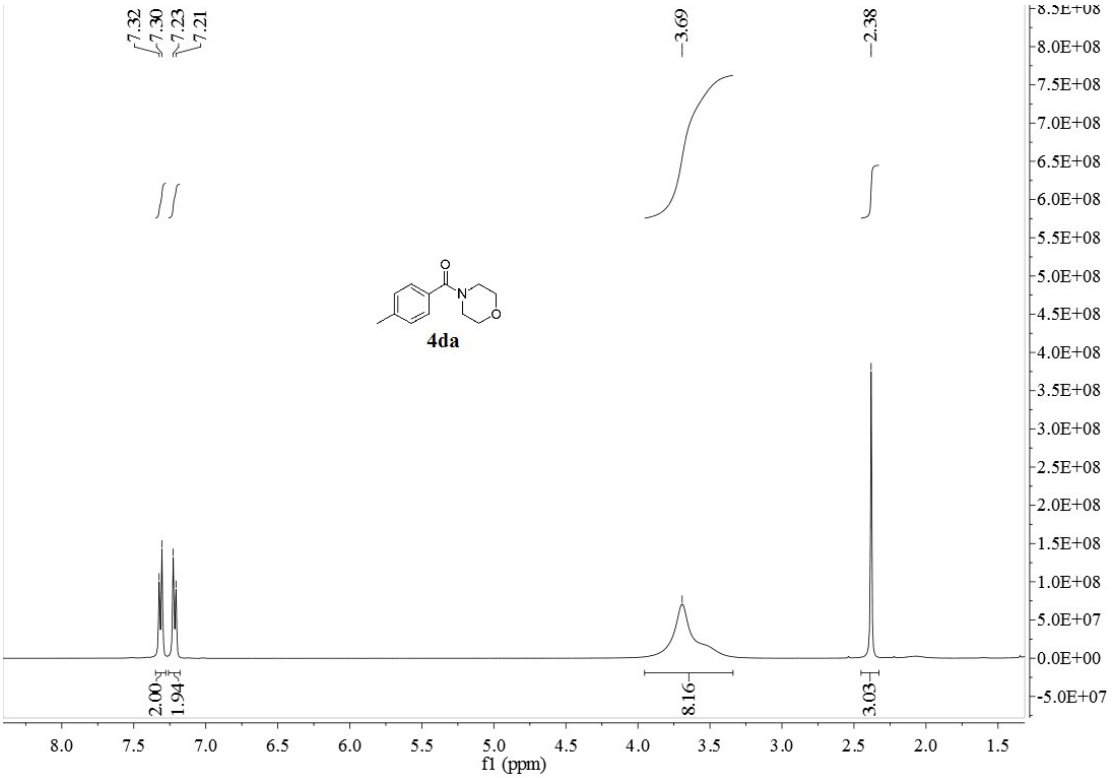


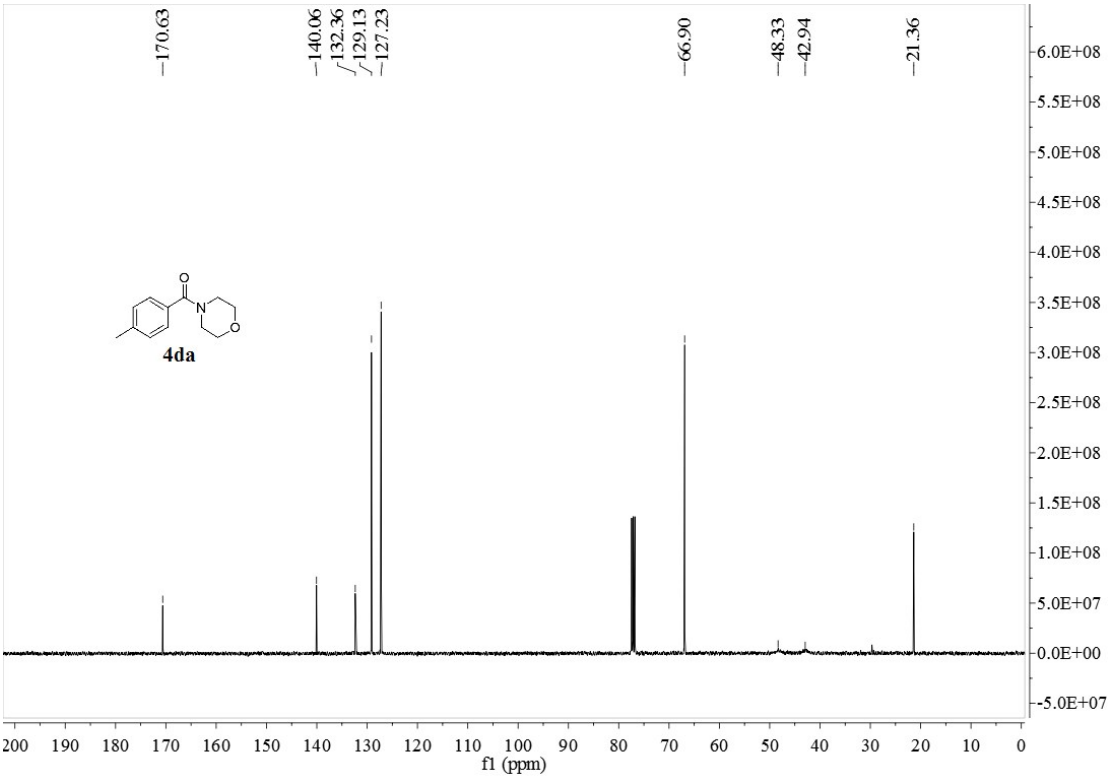
1-morpholino-2-(p-tolyl)ethane-1,2-dione (3da)



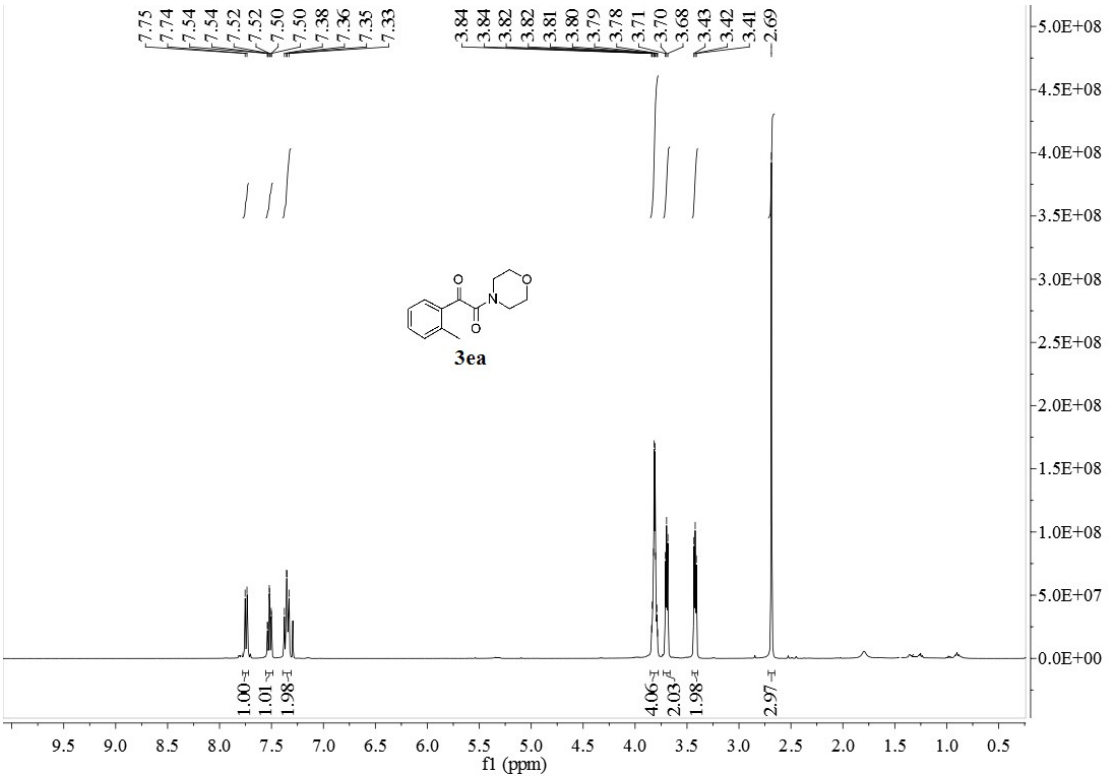


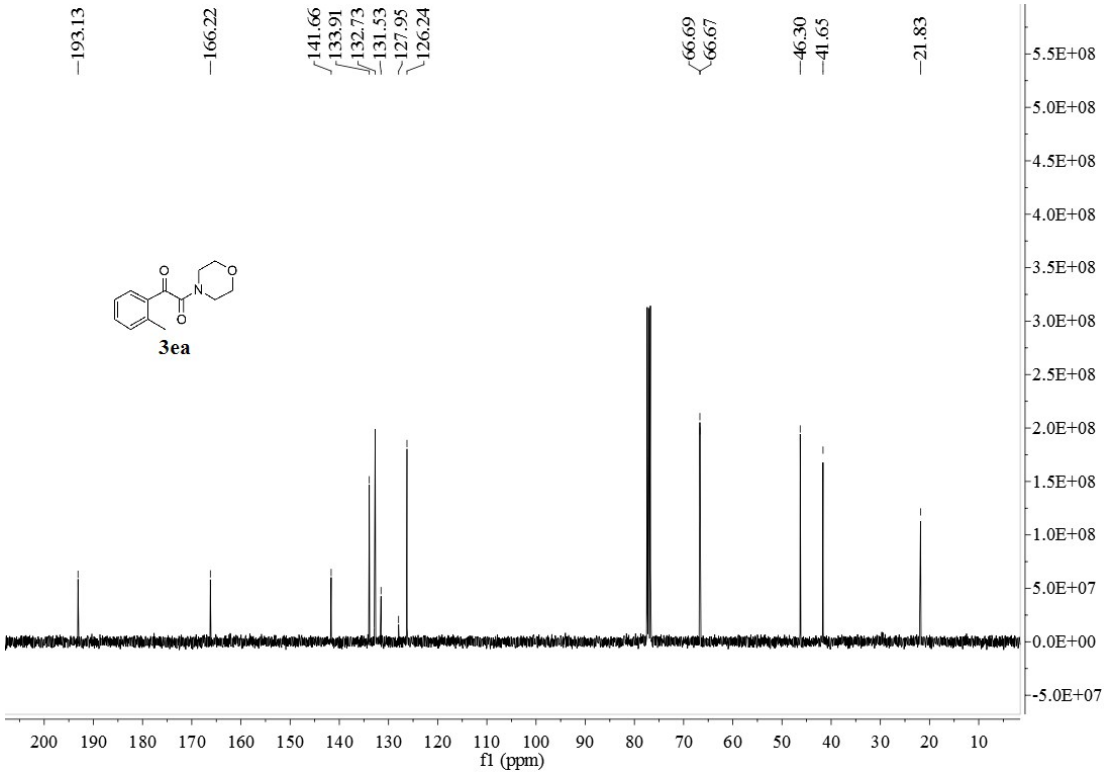
morpholino(p-tolyl)methanone (4da)



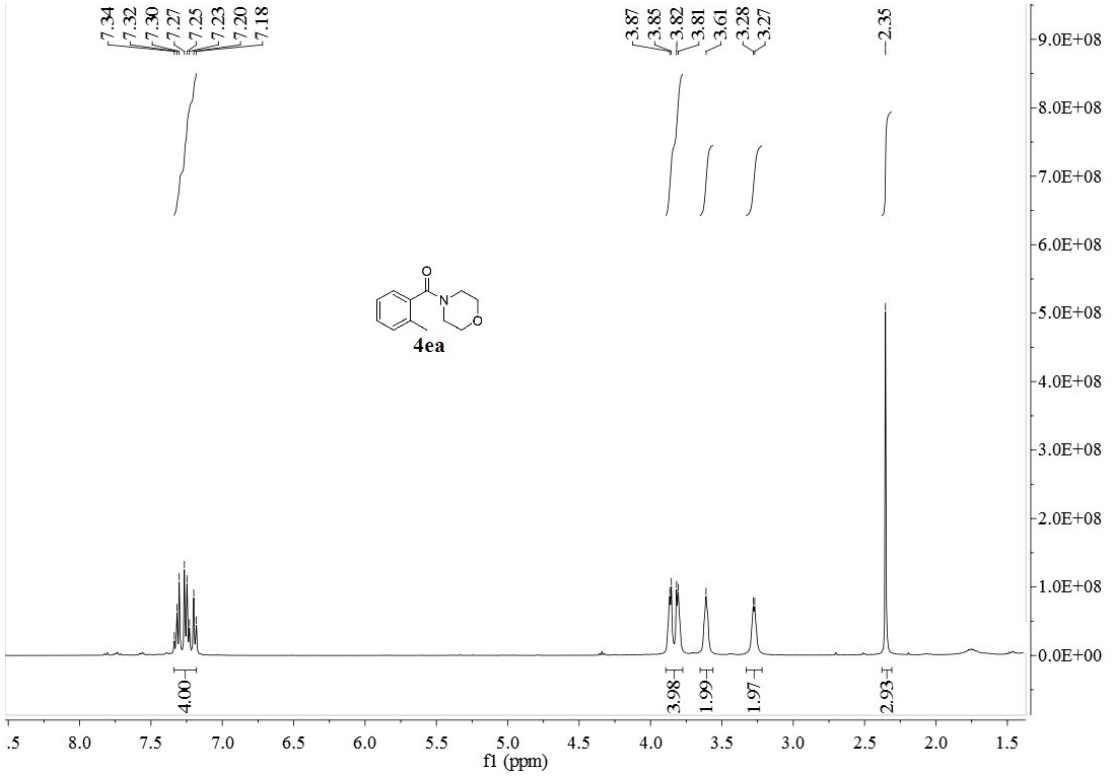


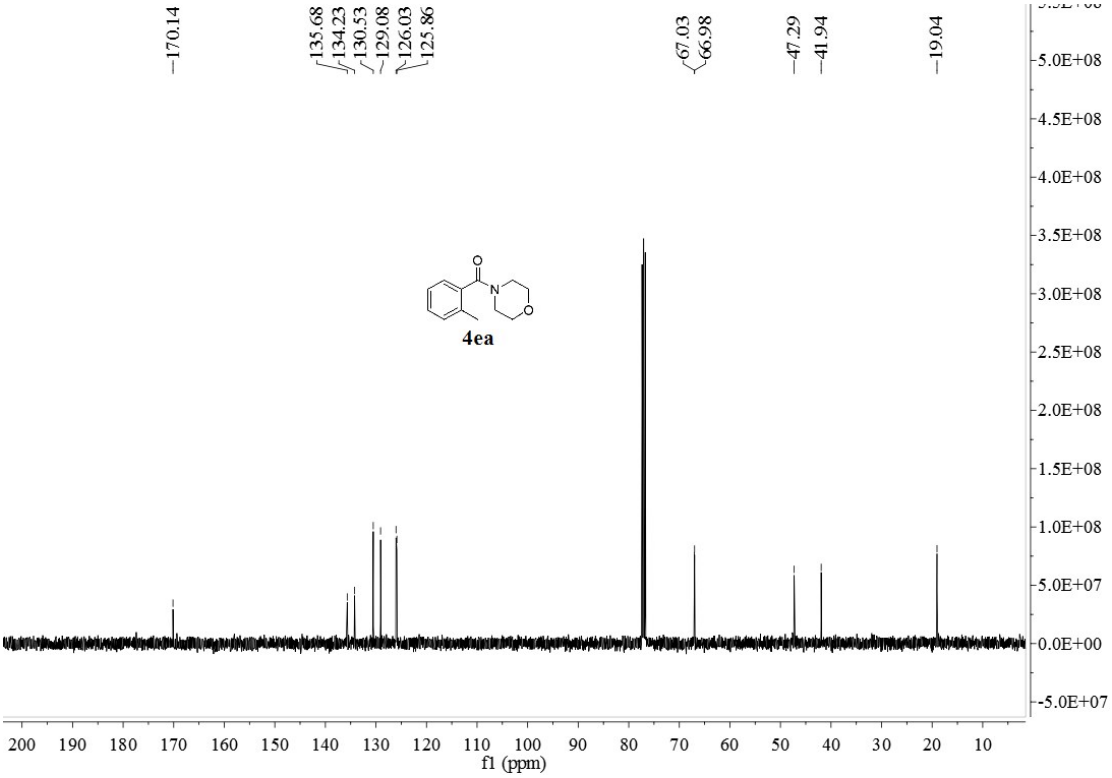
1-morpholino-2-(o-tolyl)ethane-1,2-dione (3ea)



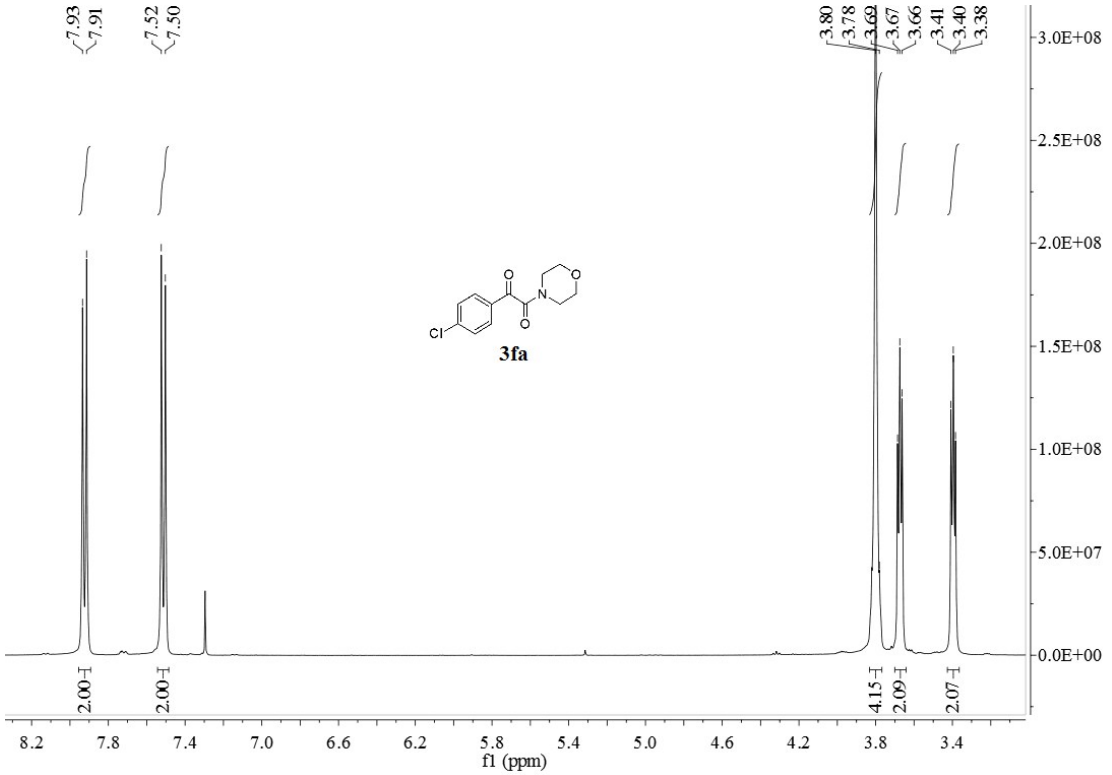


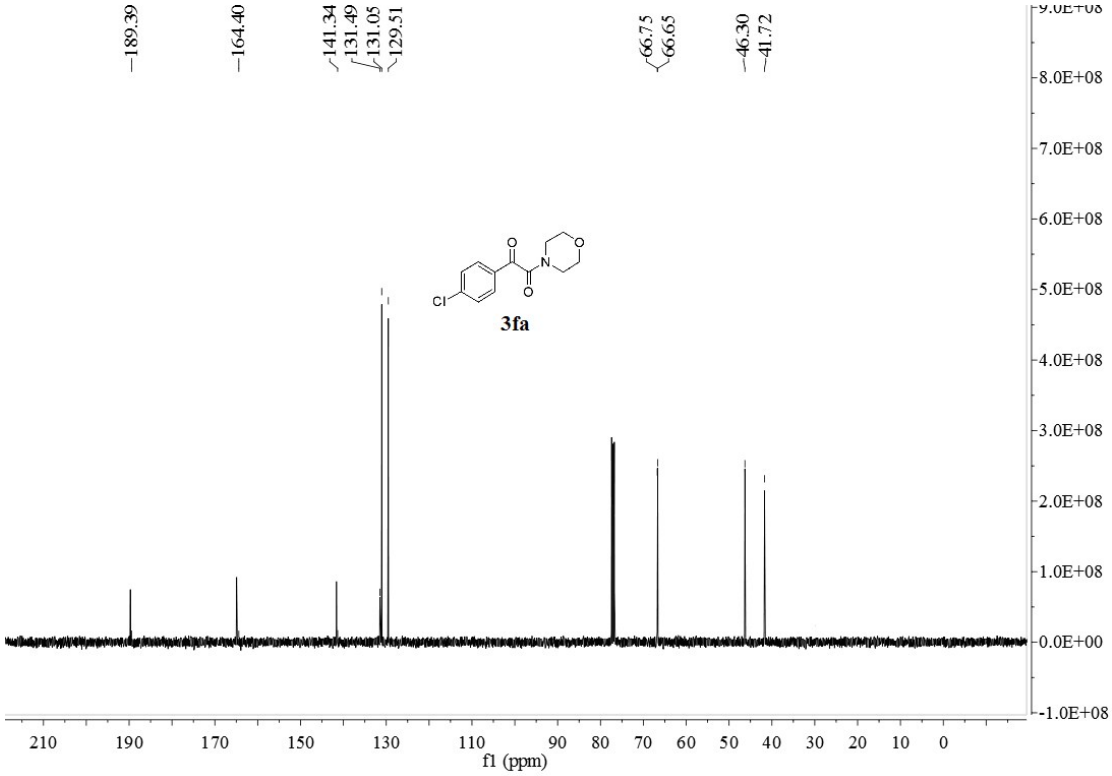
morpholino(o-tolyl)methanone (4ea)



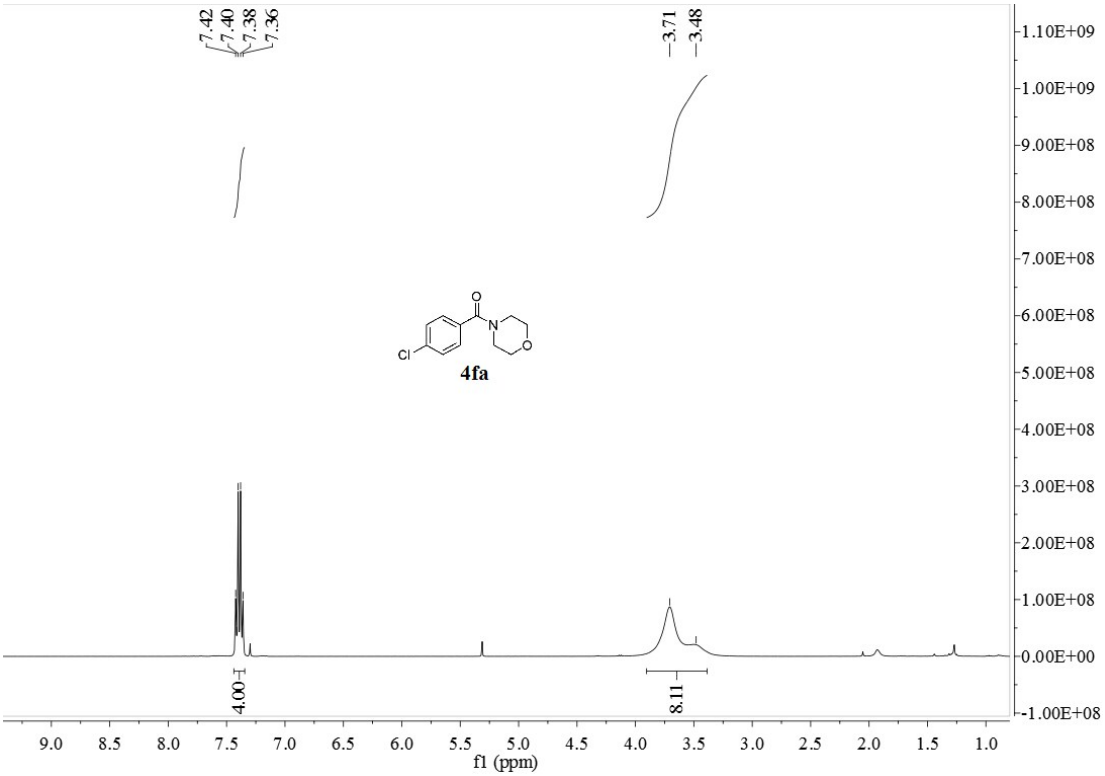


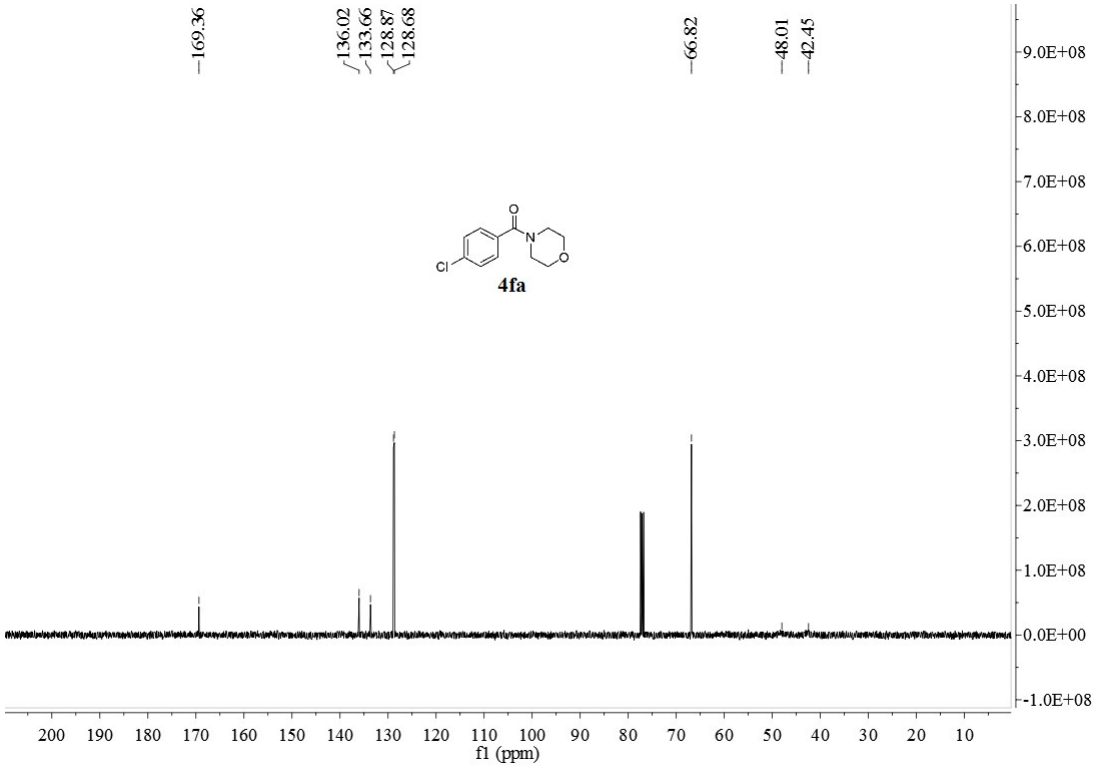
1-(4-chlorophenyl)-2-morpholinoethane-1,2-dione (3fa)



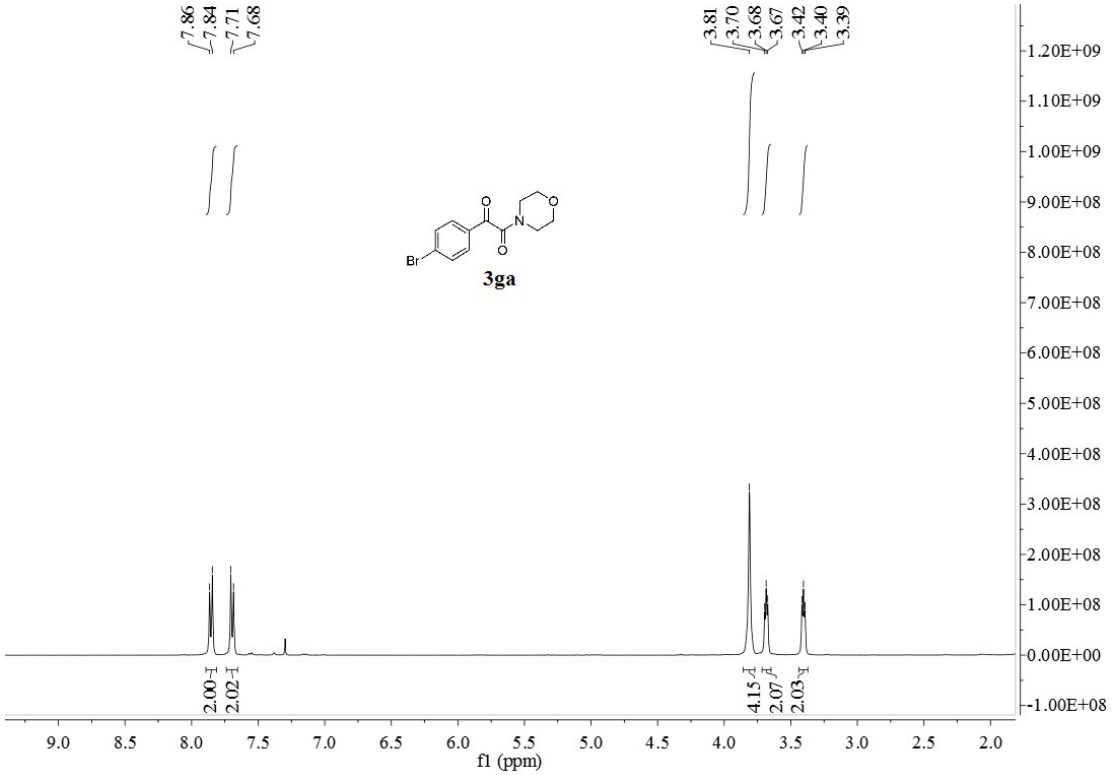


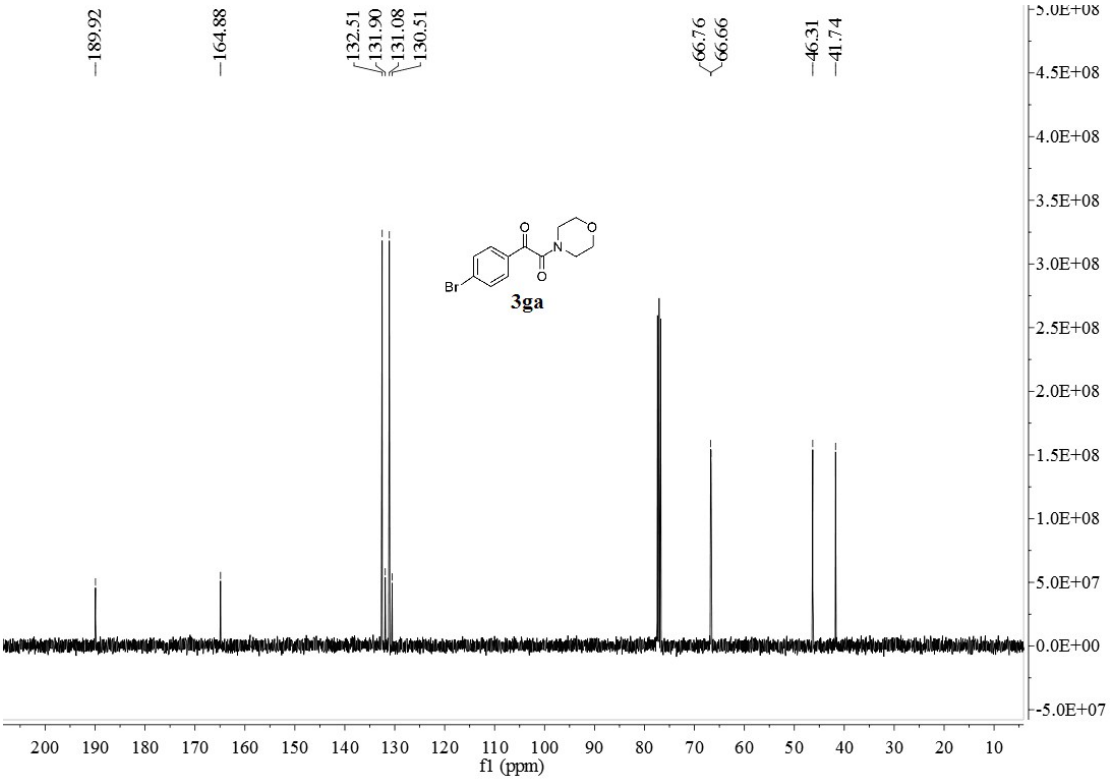
(4-chlorophenyl)(morpholino)methanone (4fa)



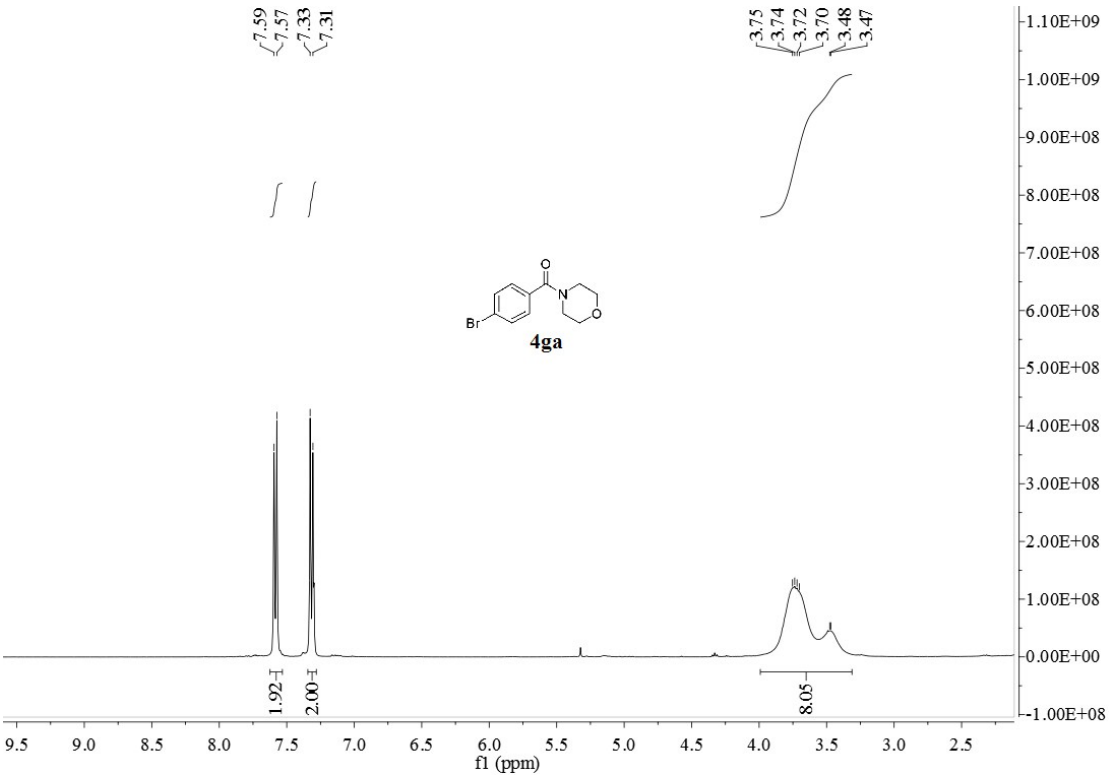


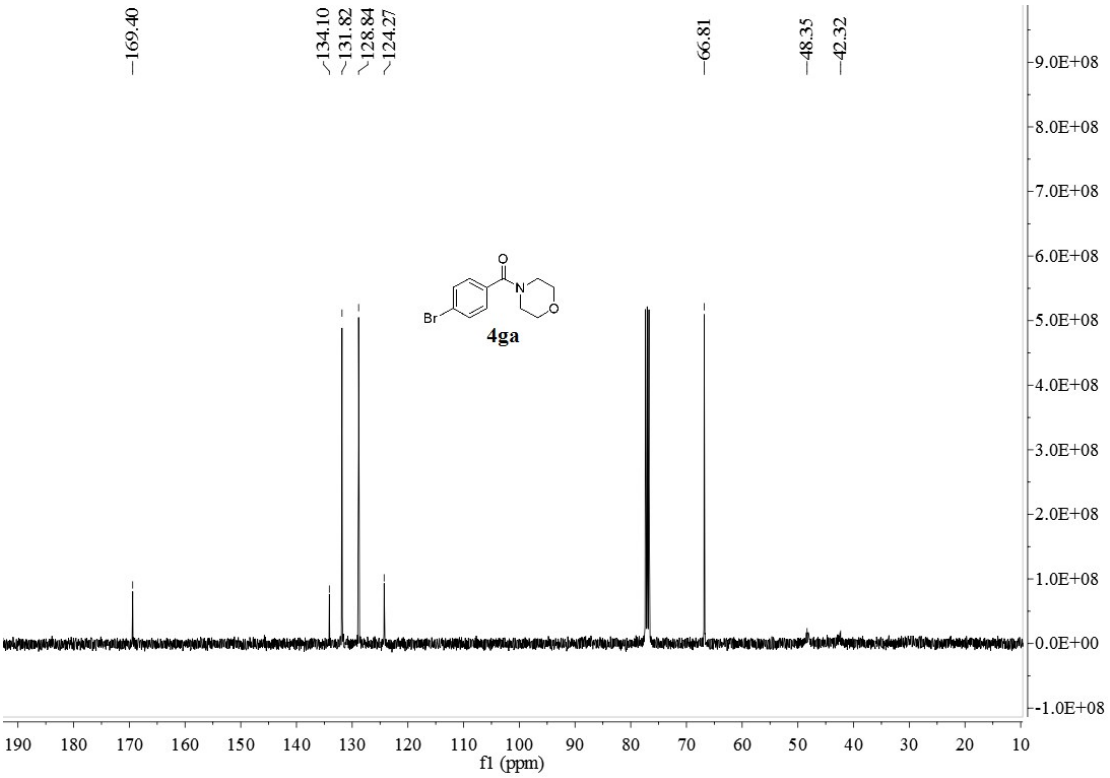
1-(4-bromophenyl)-2-morpholinoethane-1,2-dione (3ga)



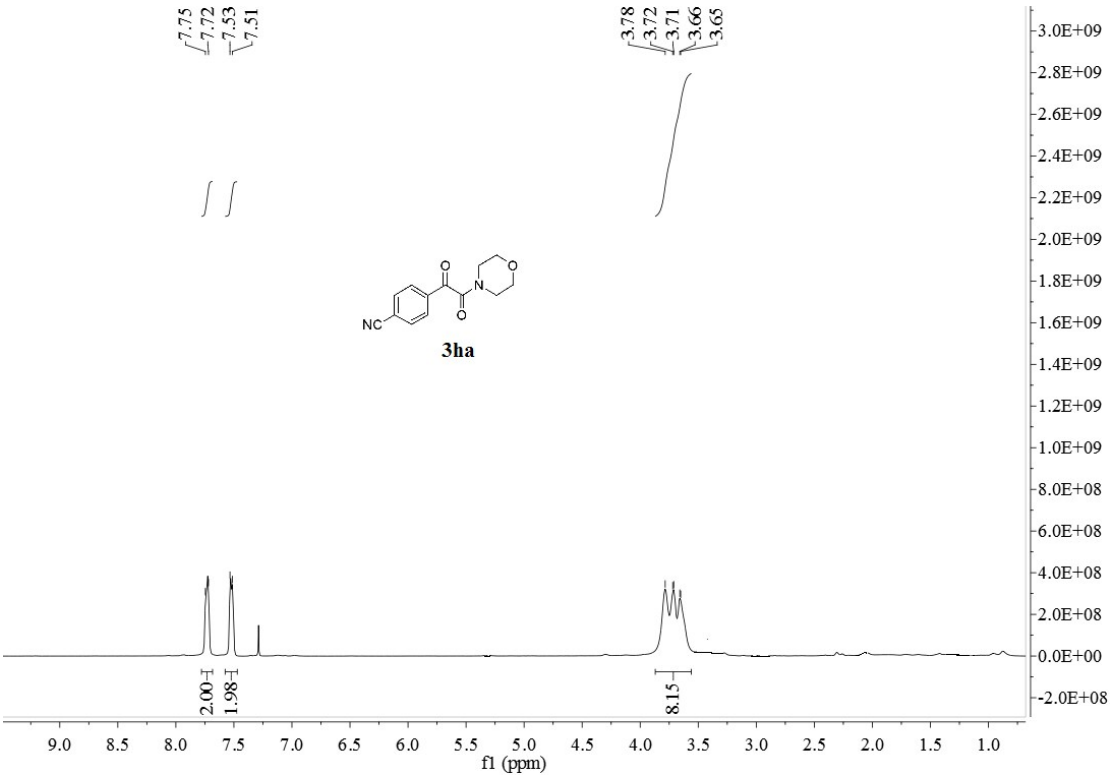


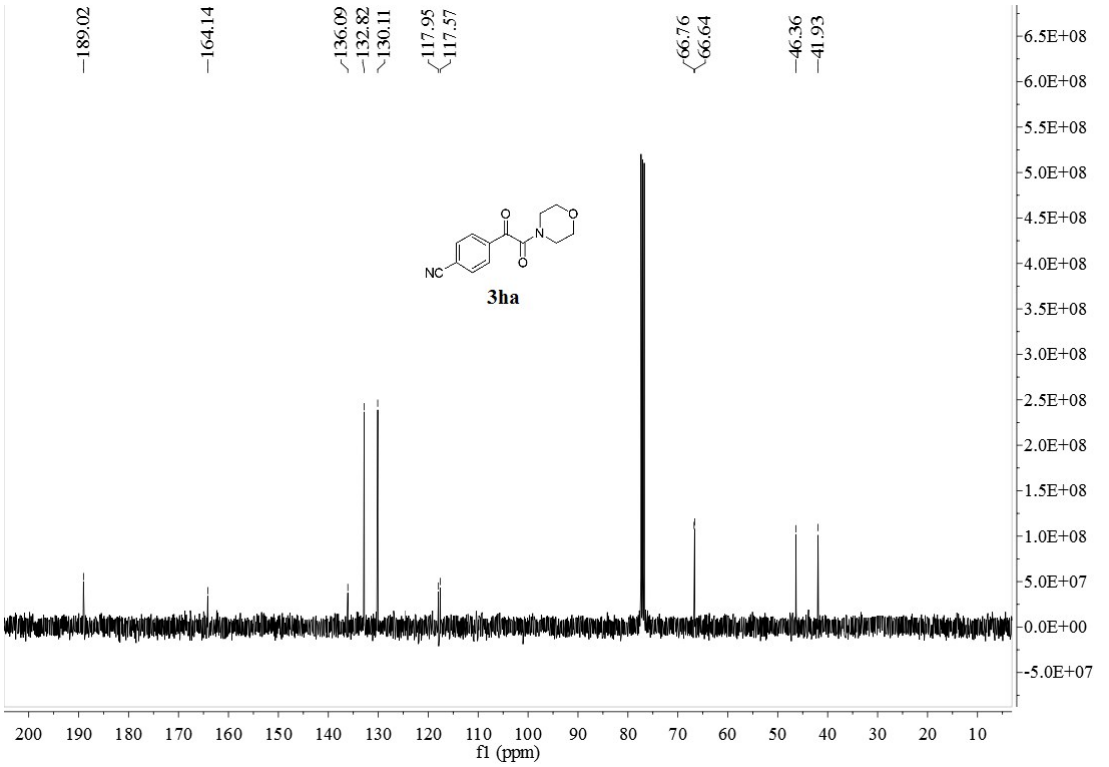
(4-bromophenyl)(morpholino)methanone (4ga)



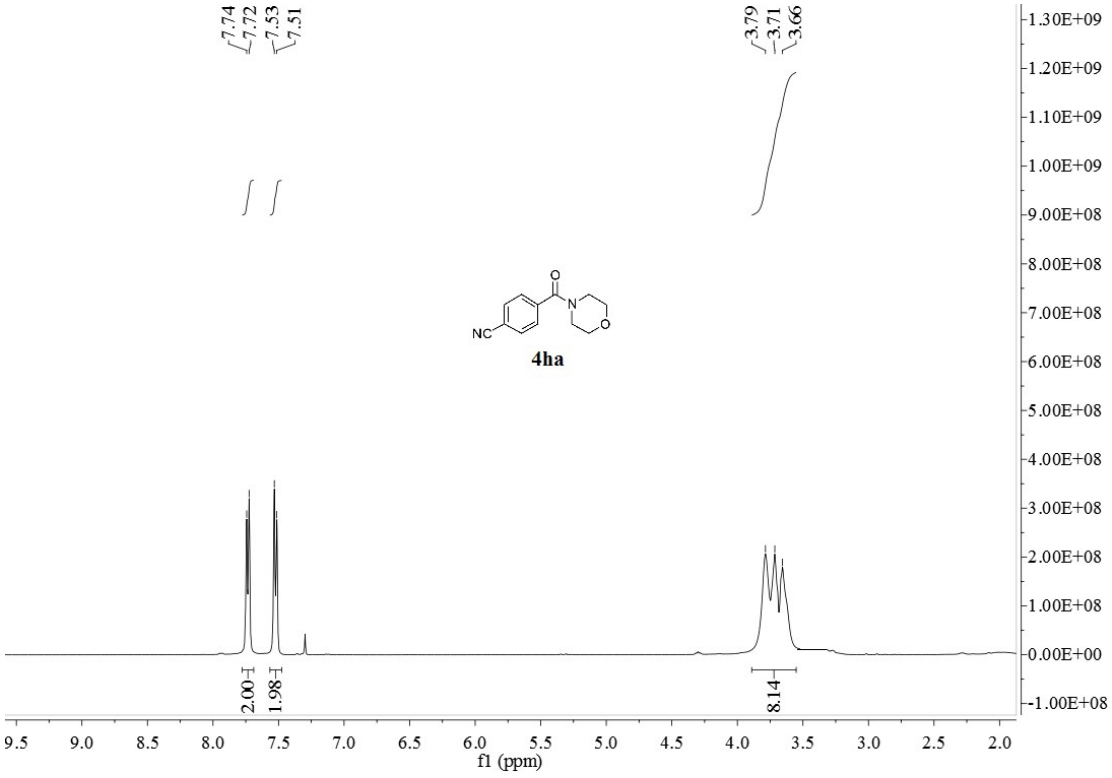


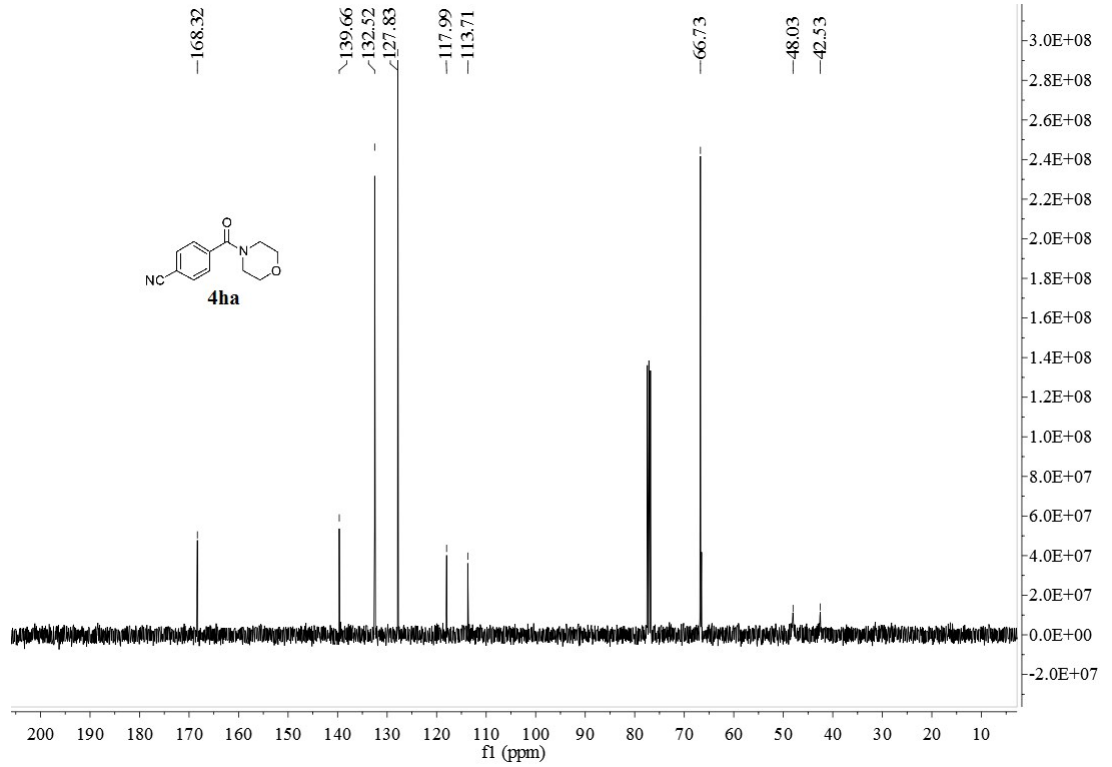
4-(2-morpholino-2-oxoacetyl)benzonitrile (3ha)



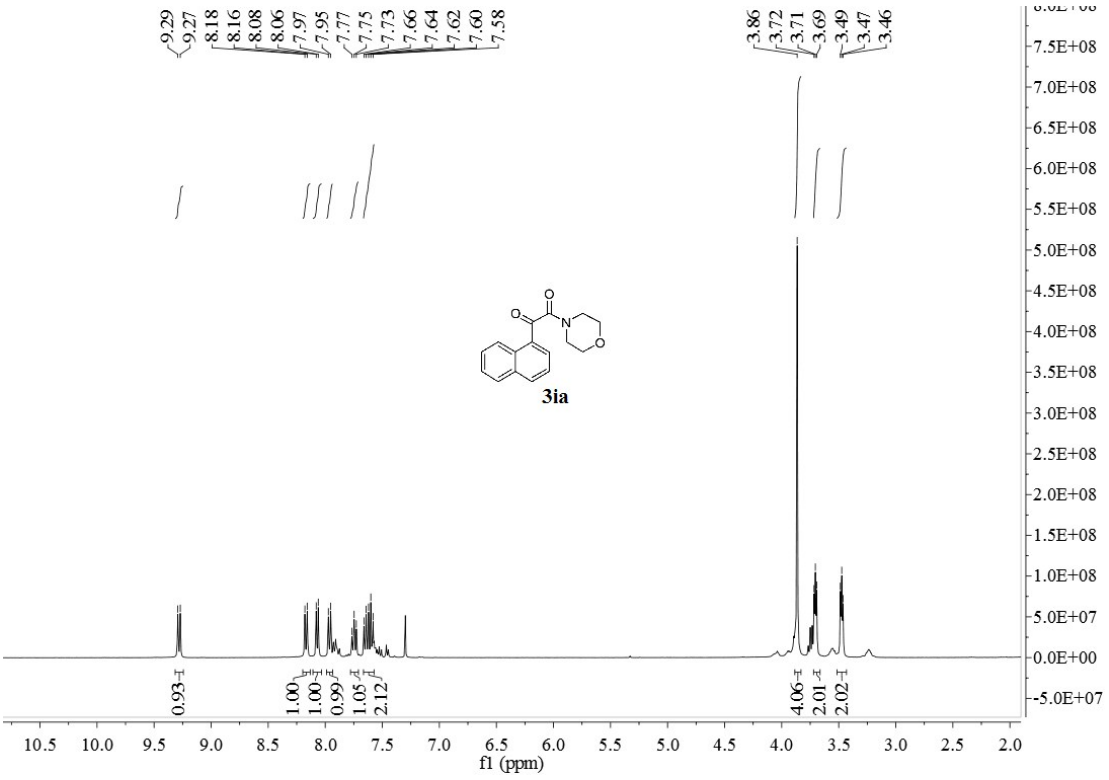


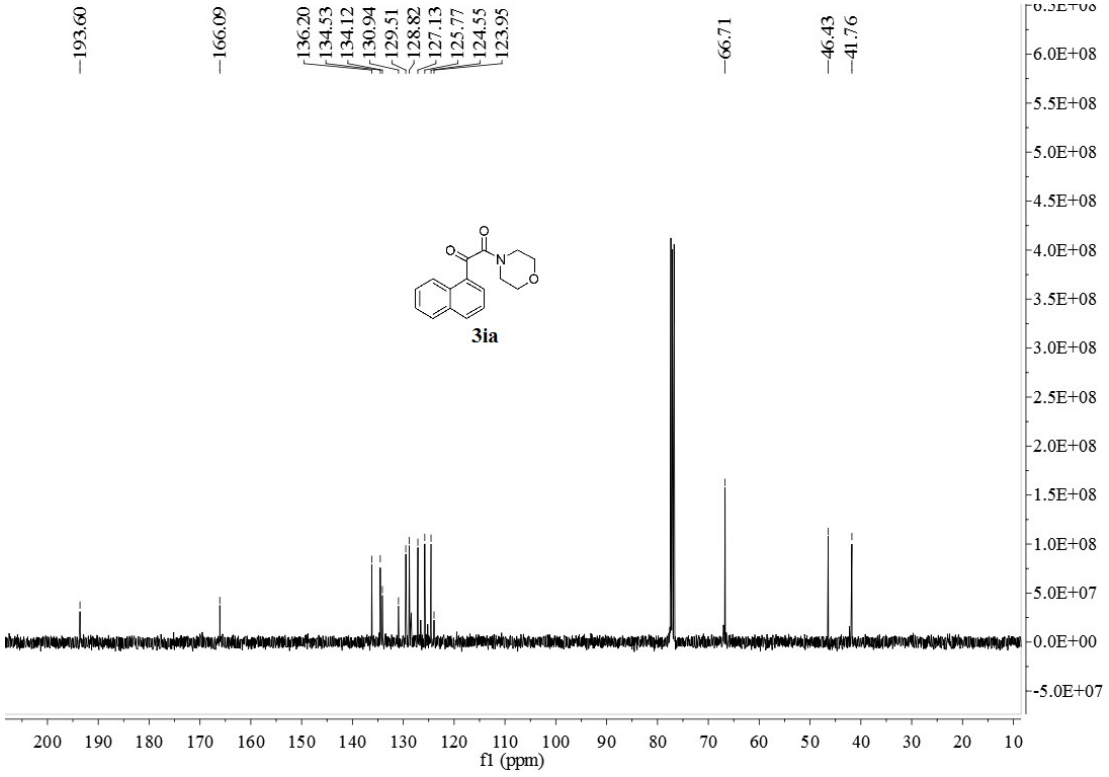
4-(morpholine-4-carbonyl)benzonitrile (4ha)



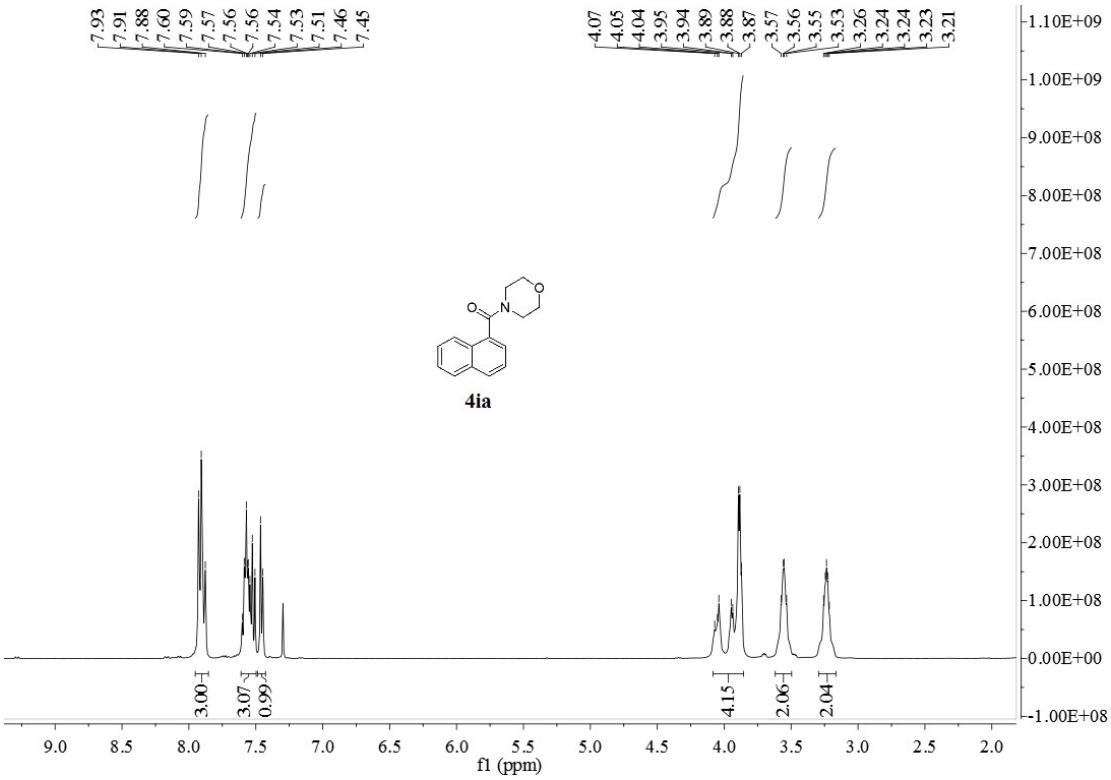


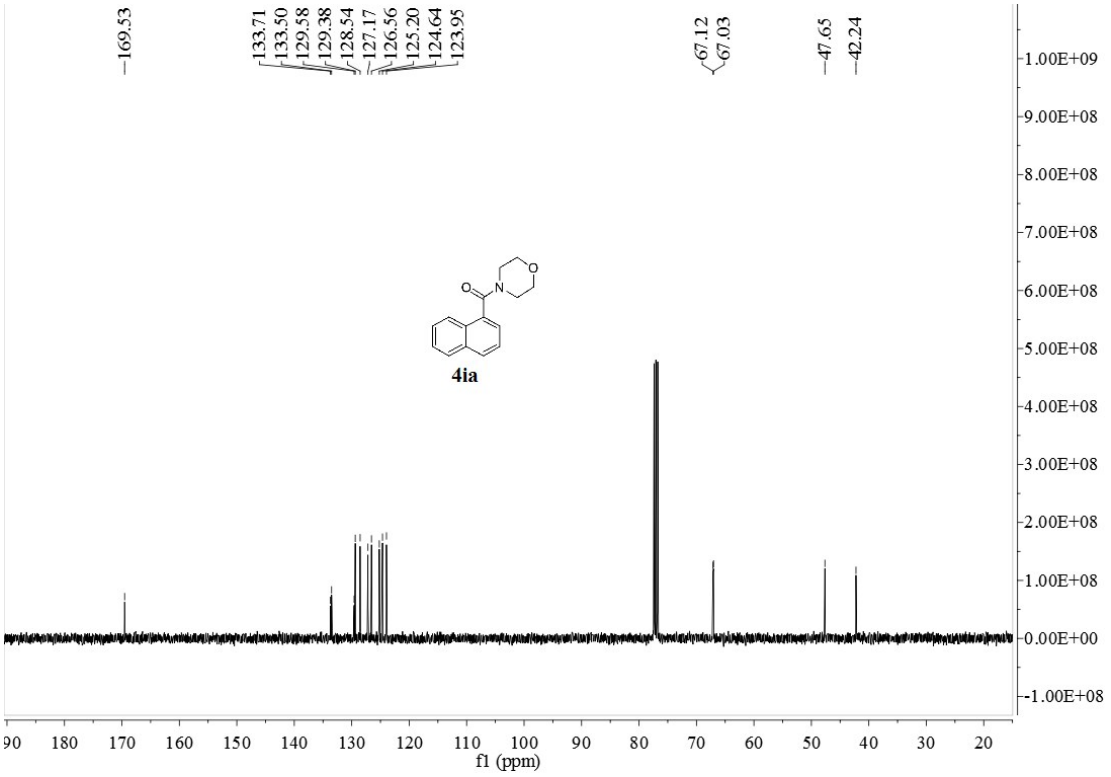
1-morpholino-2-(naphthalen-1-yl)ethane-1,2-dione (3ia)



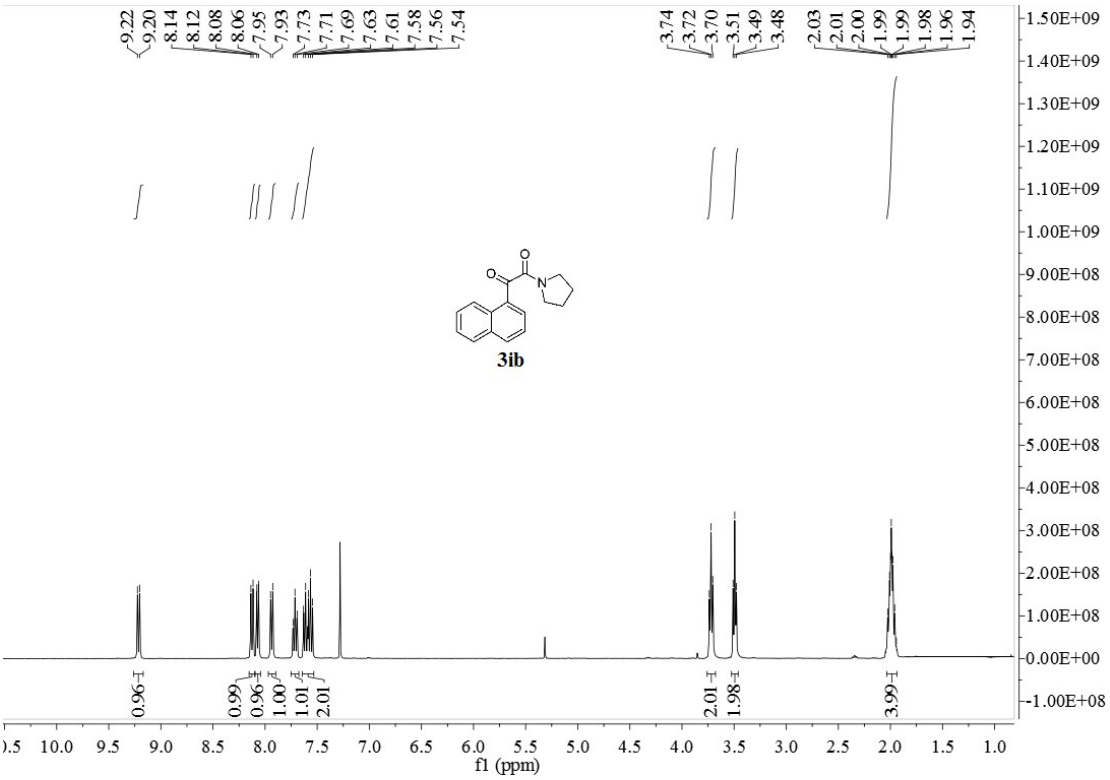


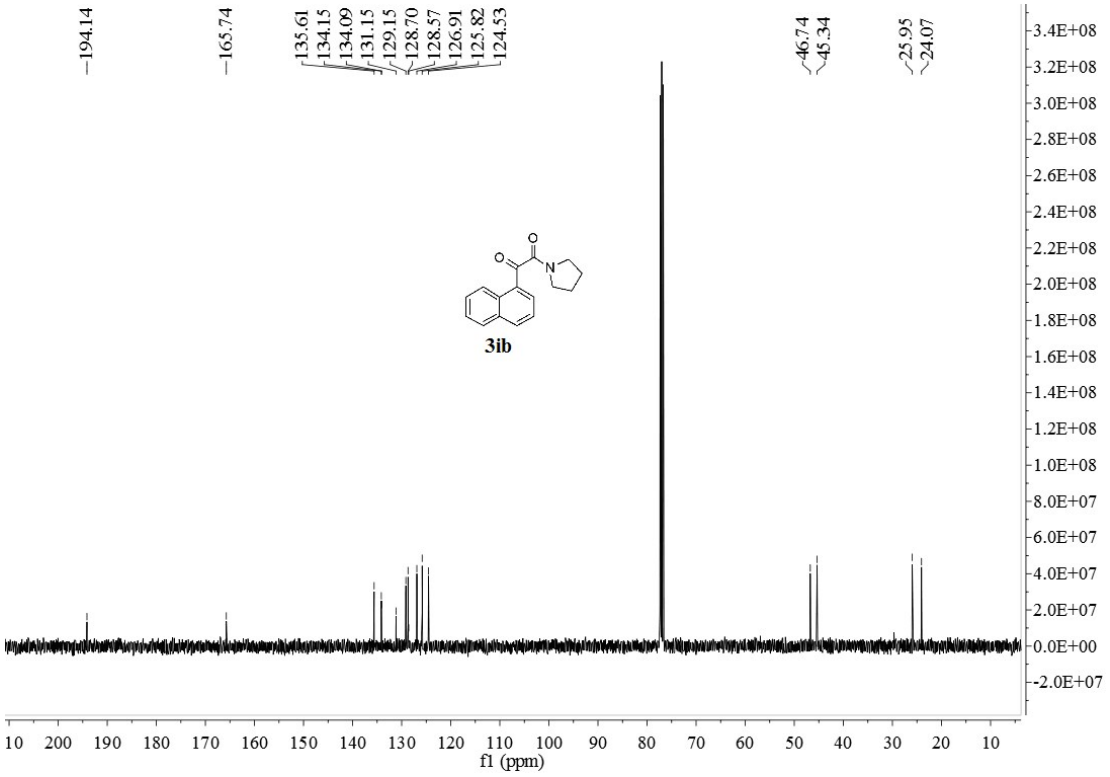
morpholino(naphthalen-1-yl)methanone (4ia)



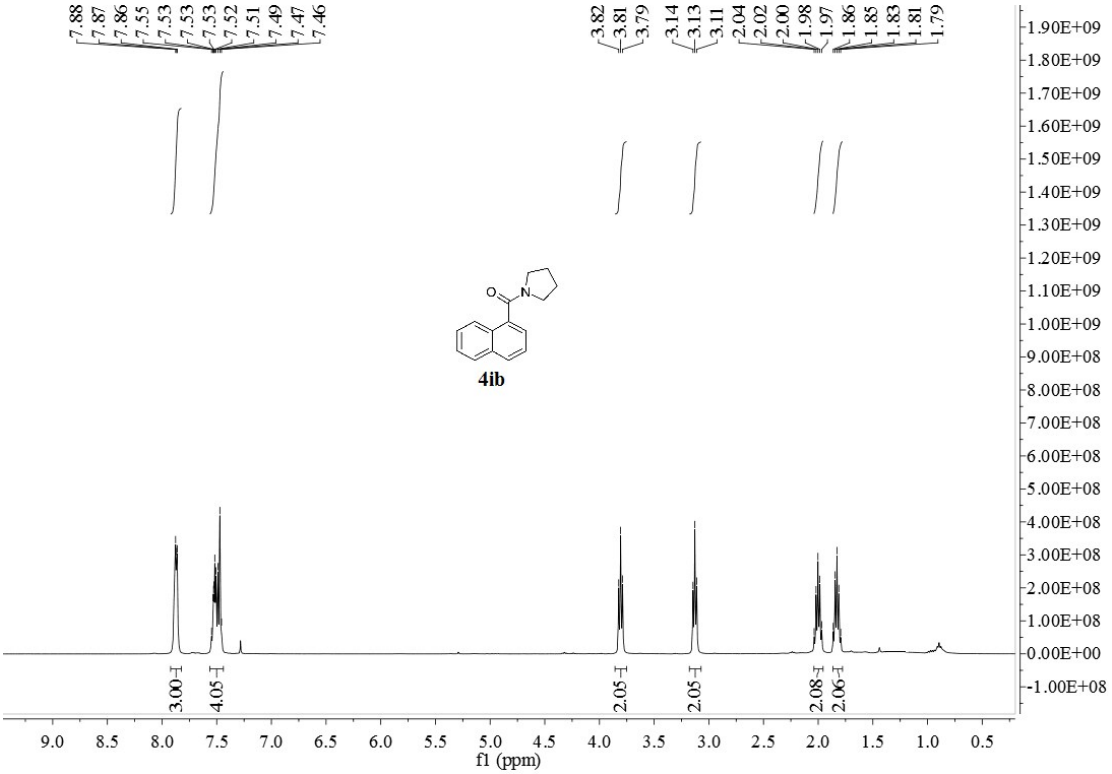


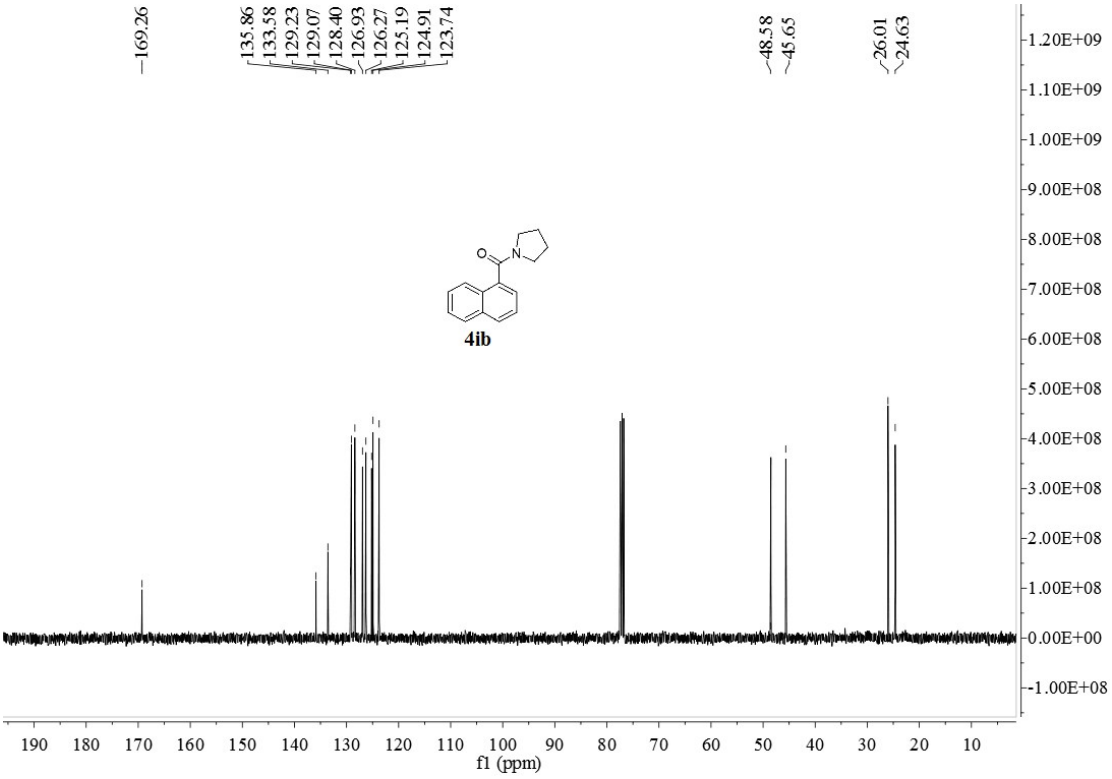
1-(naphthalen-1-yl)-2-(pyrrolidin-1-yl)ethane-1,2-dione (3ib)



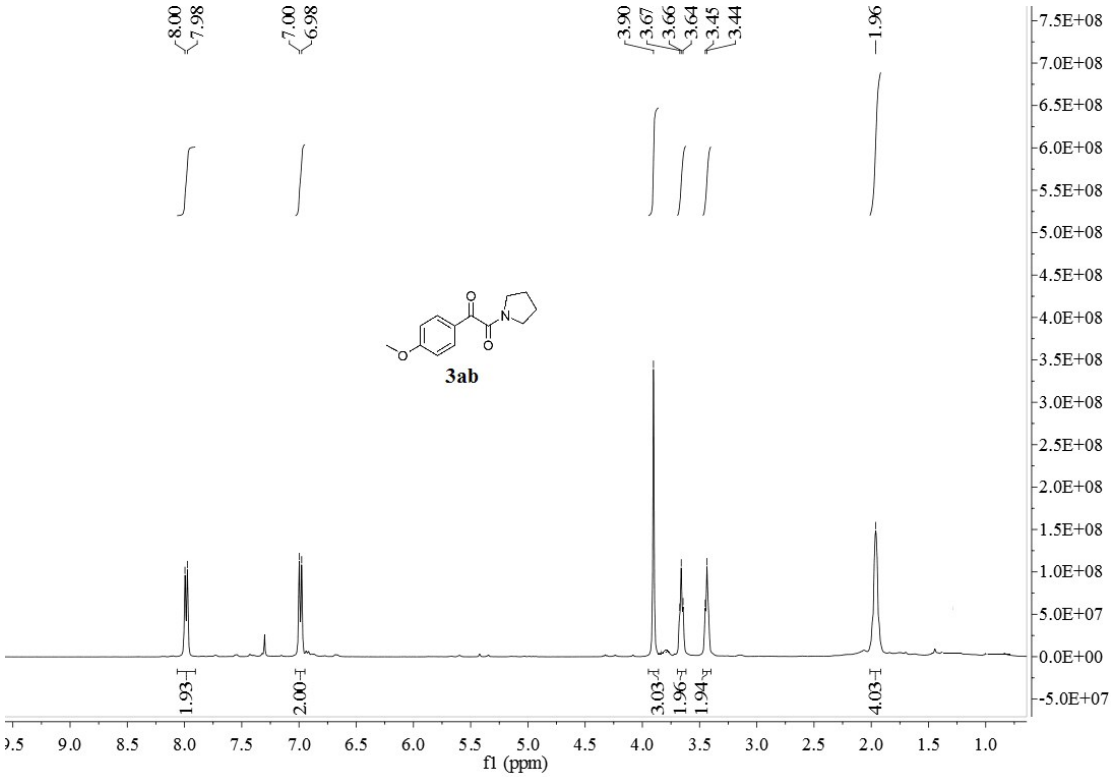


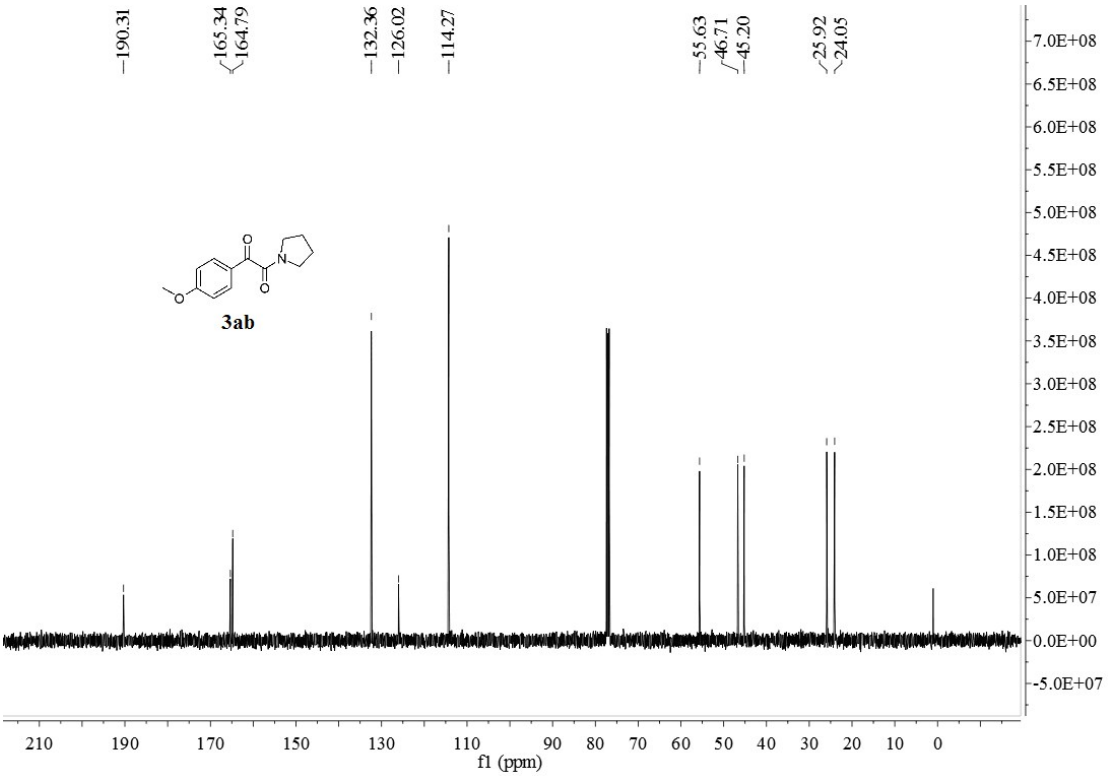
naphthalen-1-yl(pyrrolidin-1-yl)methanone (4ib)



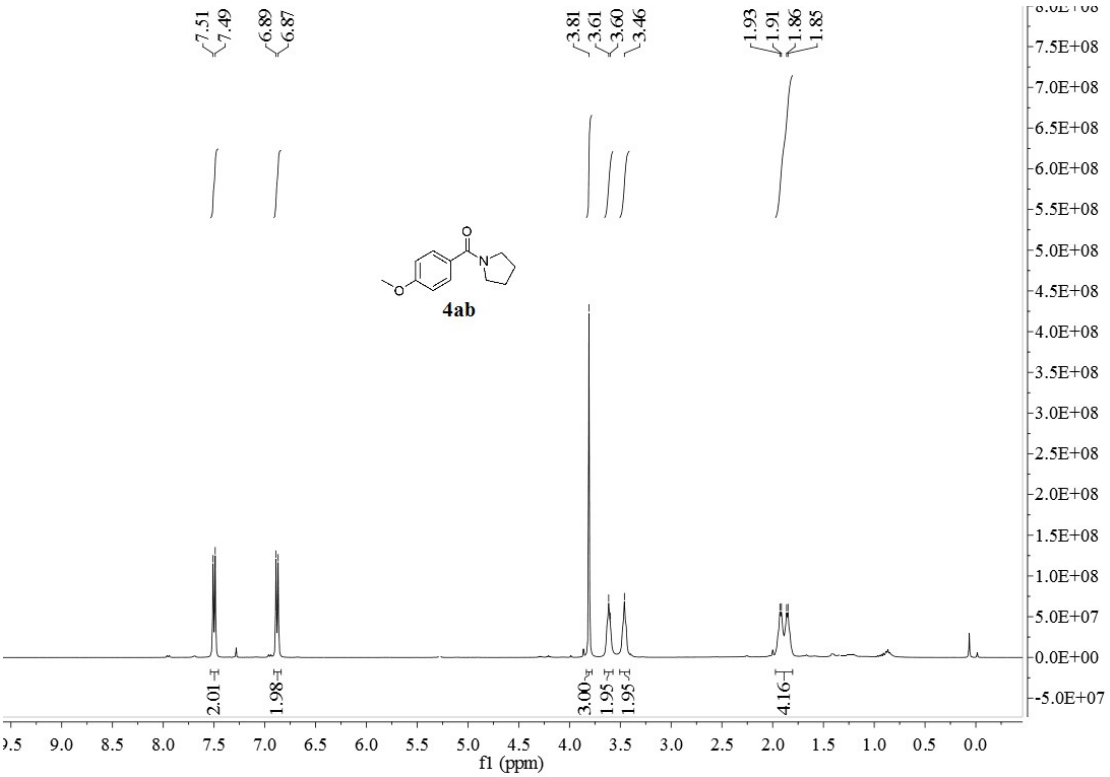


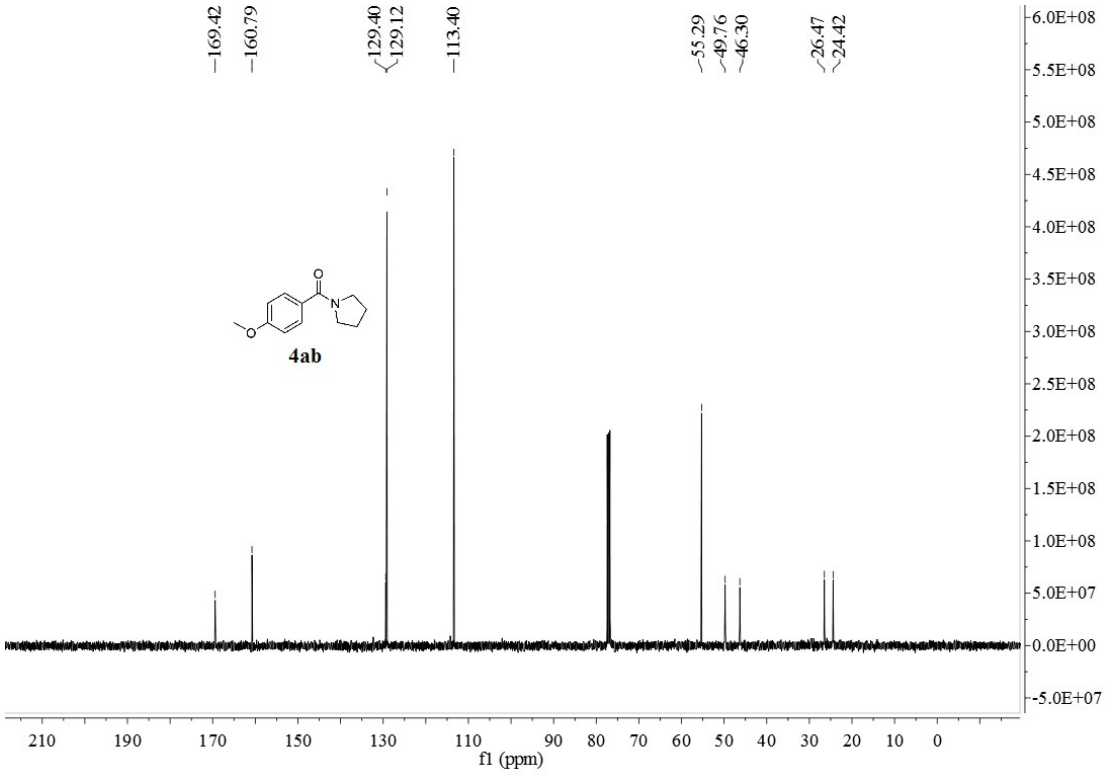
1-(4-methoxyphenyl)-2-(pyrrolidin-1-yl)ethane-1,2-dione (3ab)



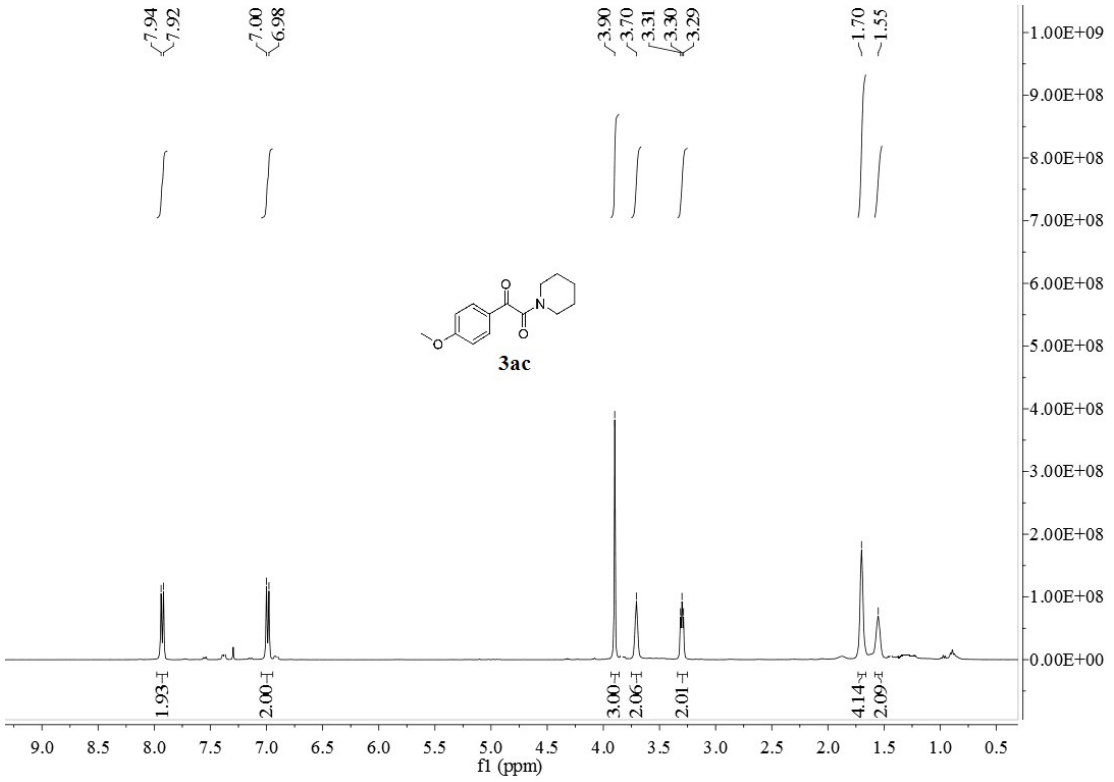


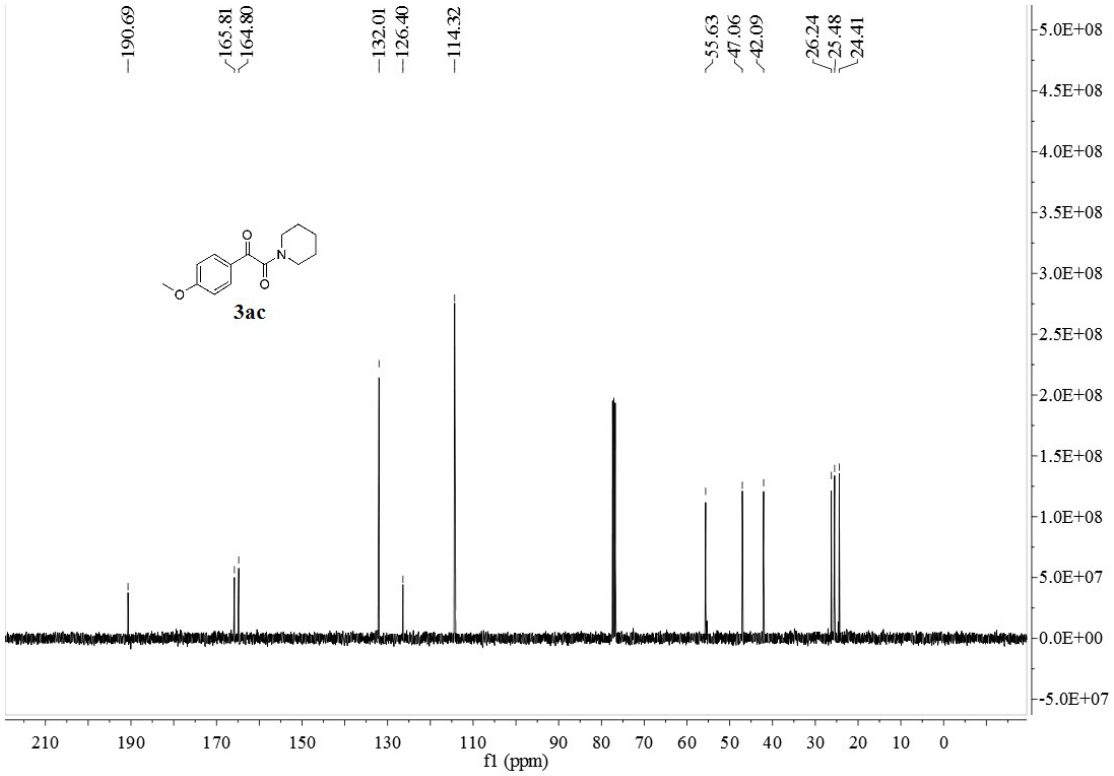
(4-methoxyphenyl)(pyrrolidin-1-yl)methanone (4ab)



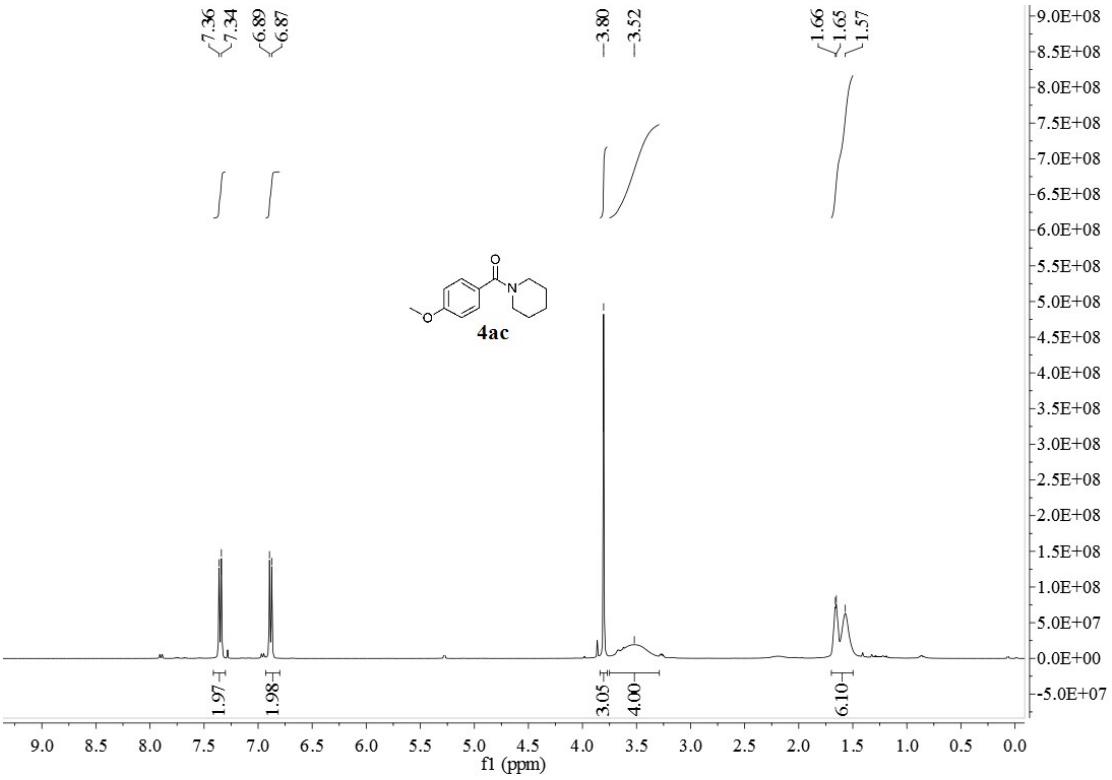


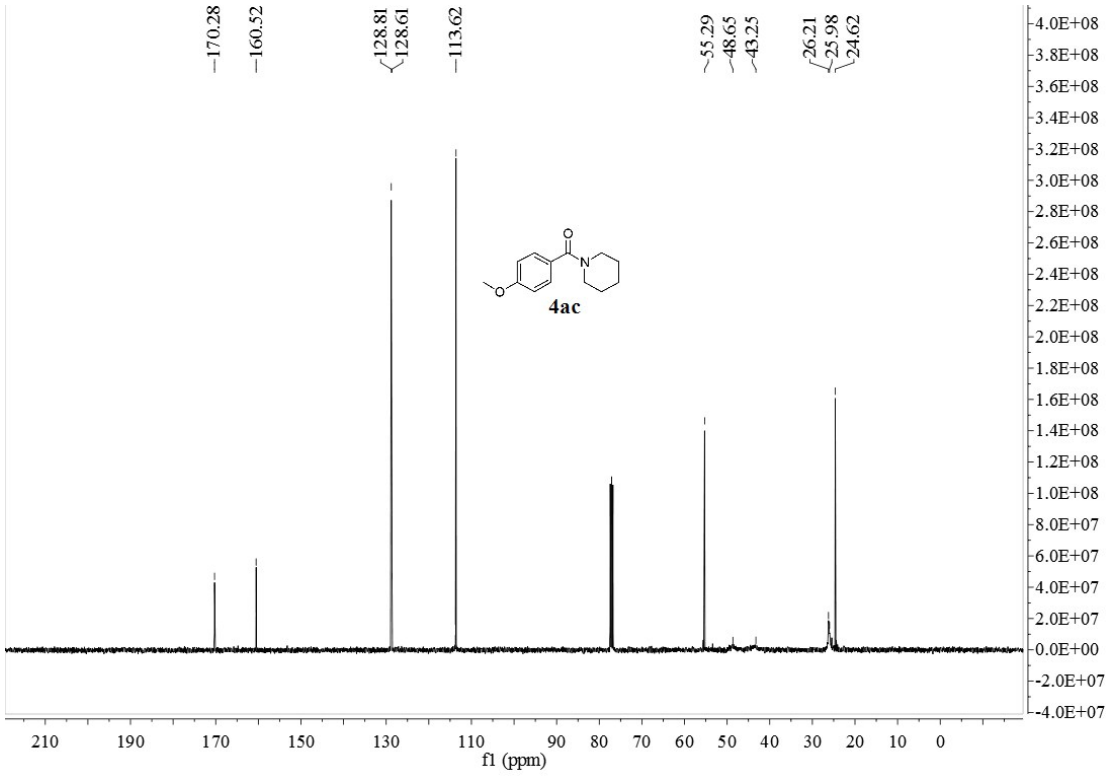
1-(4-methoxyphenyl)-2-(piperidin-1-yl)ethane-1,2-dione (3ac)



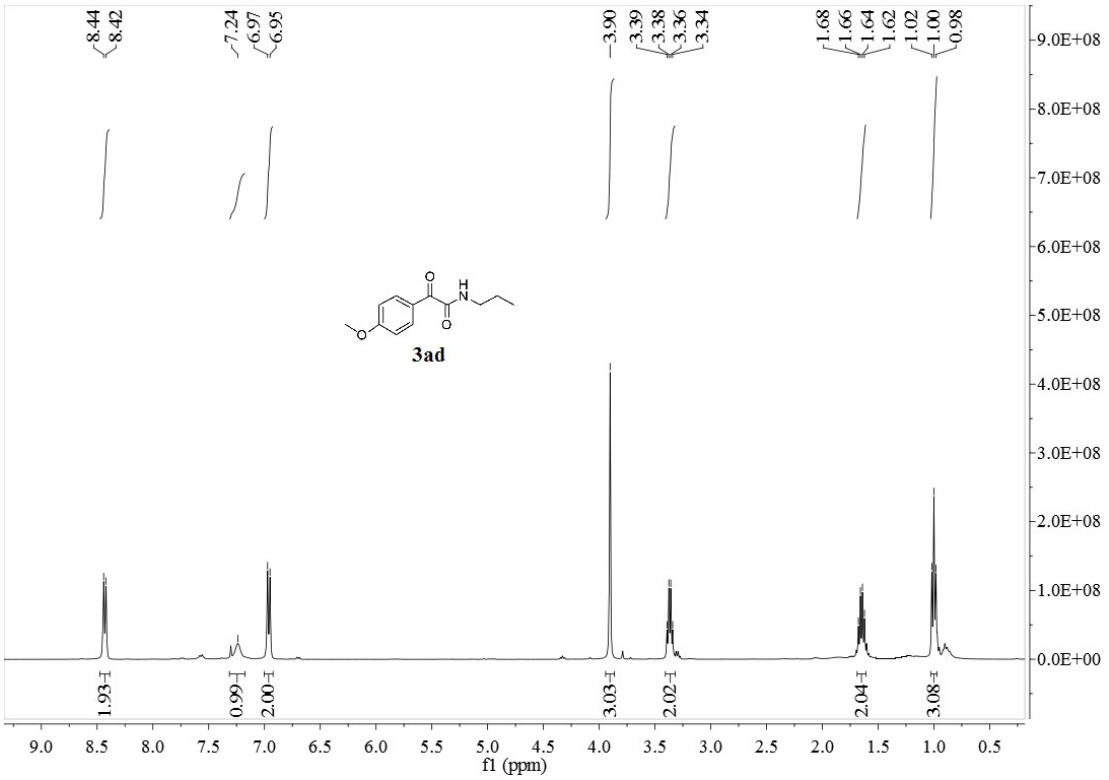


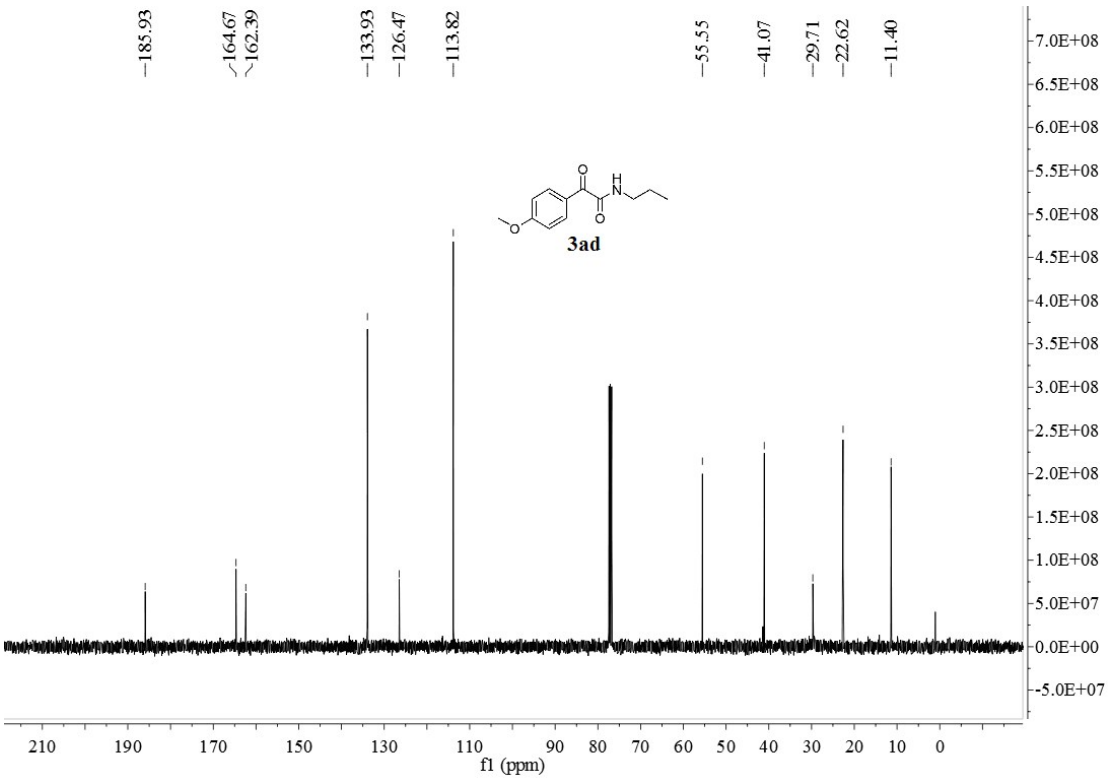
(4-methoxyphenyl)(piperidin-1-yl)methanone (4ac)



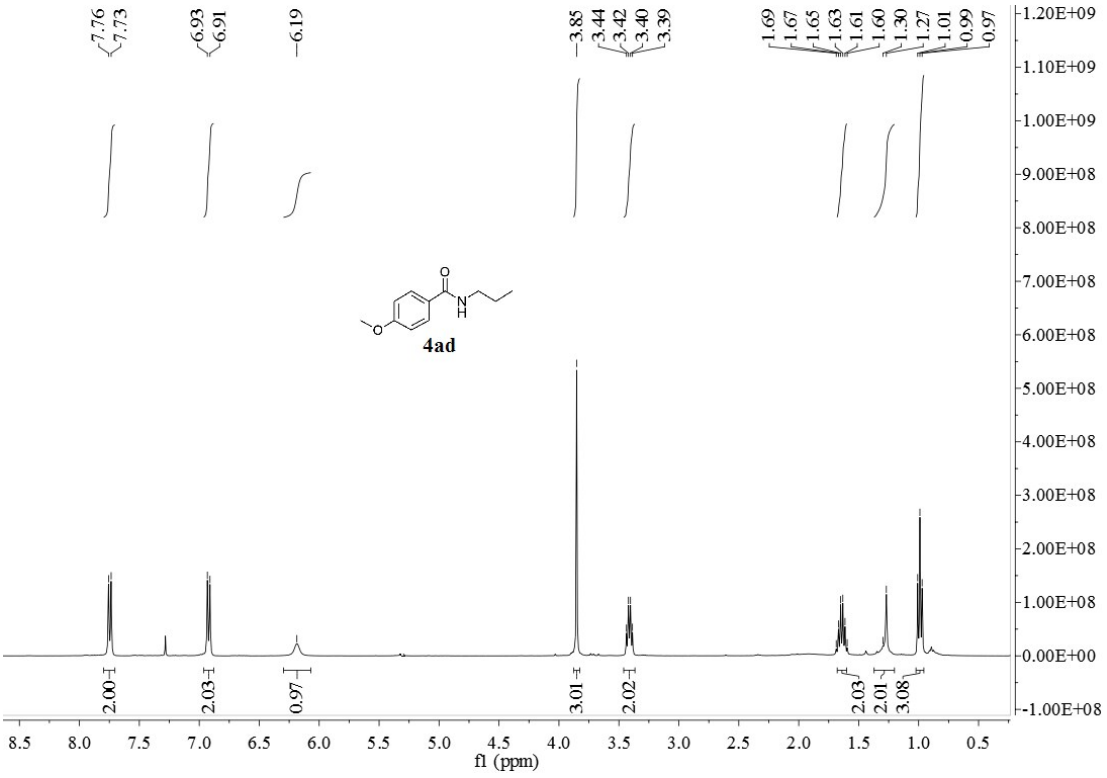


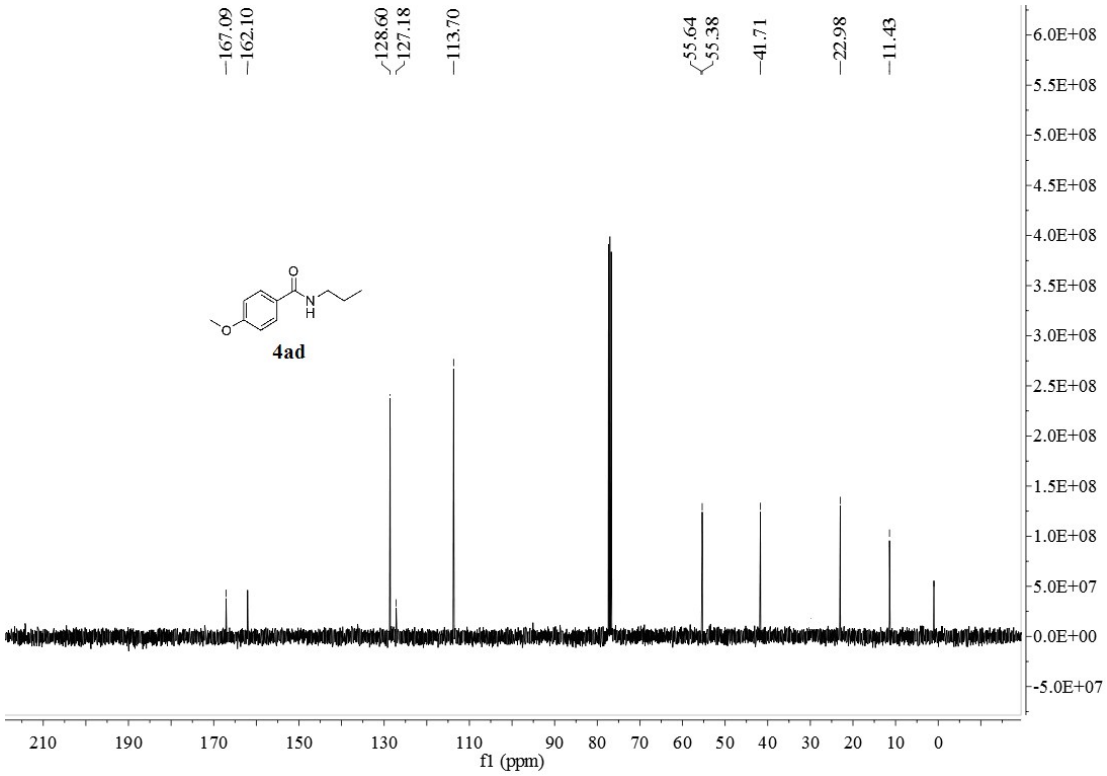
2-(4-methoxyphenyl)-2-oxo-N-propylacetamide (3ad)



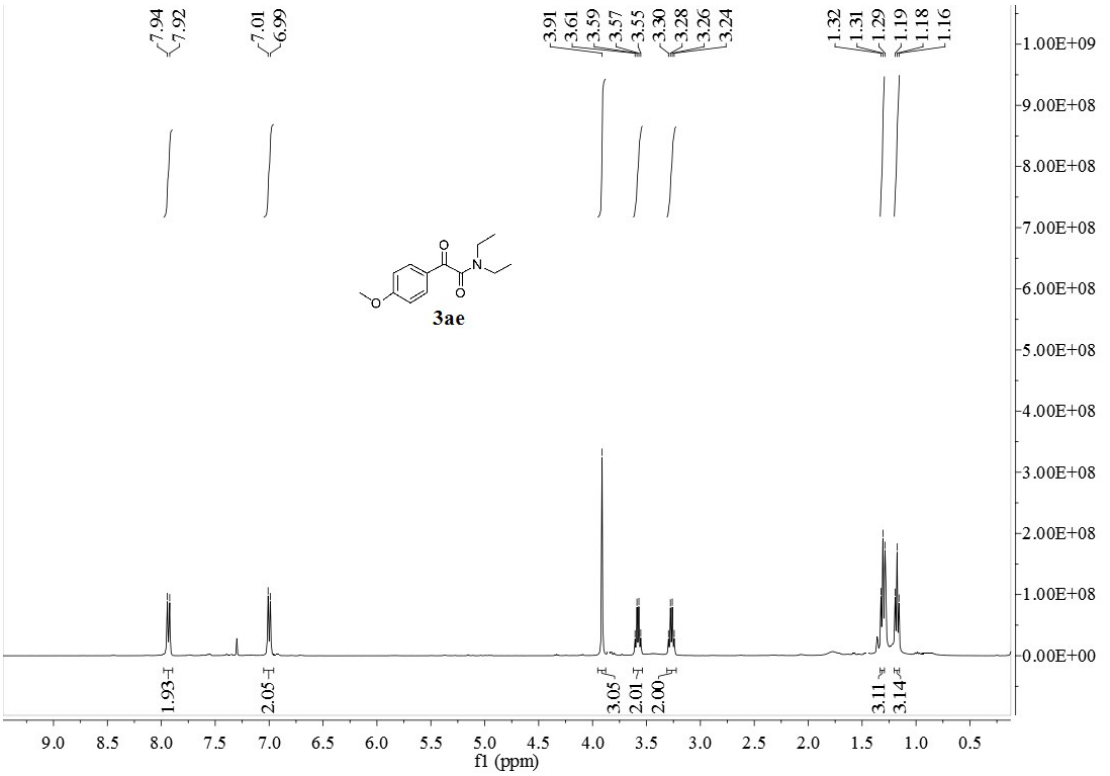


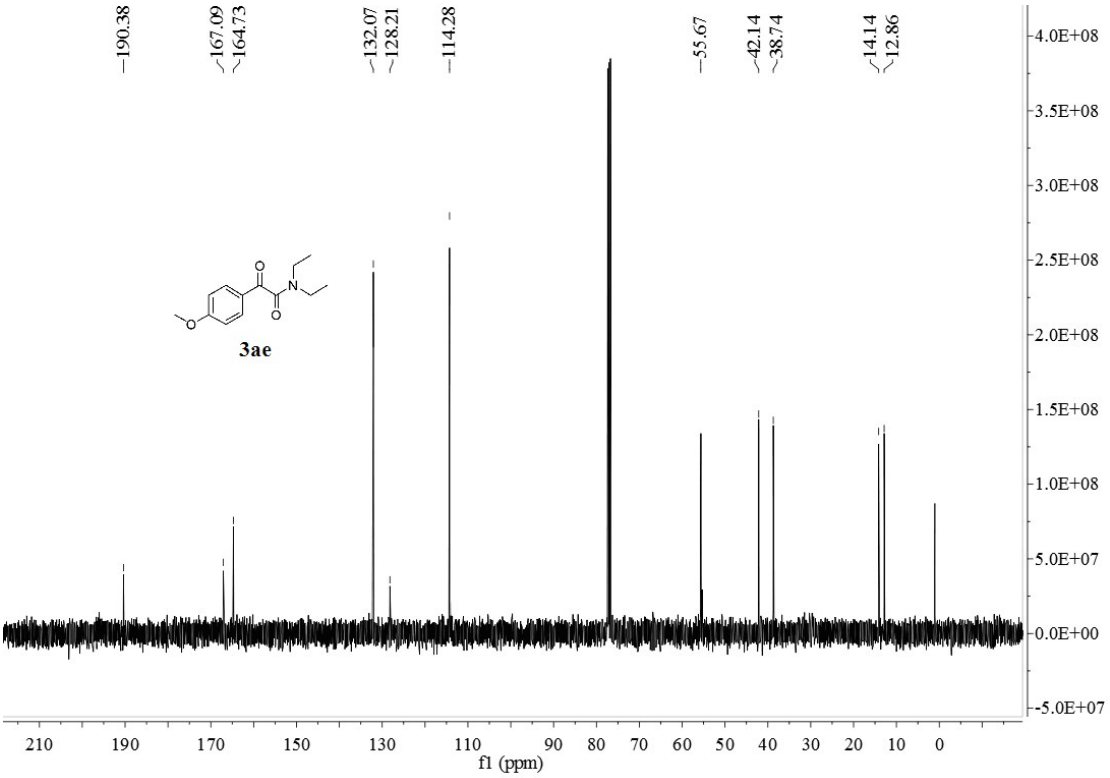
4-methoxy-N-propylbenzamide (4ad)





N,N-diethyl-2-(4-methoxyphenyl)-2-oxoacetamide (3ae)





N,N-diethyl-4-methoxybenzamide (4ae)