Supporting Information

Cu(II)-mediated Keto C(sp^3)-H Bond α-Acyloxylation of *N,N*-dialkylamides with Aromatic Carboxylic Acid

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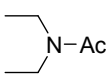
1. General remarks

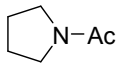
All reagents and starting materials were purchased from commercial sources and used as supplied, unless otherwise illustrated. All solvents were purified according to the established procedures. With the exception of *N,N*-dimethylacetamide (DMAc), all acetamides were prepared according to the literature procedure[1] (see Synthesis of acetamides **2b-f**). Column chromatography was performed with silica gel (Merck, 300-400 mesh). ^{1}H NMR spectra were recorded on Bruker Avance 400 MHz spectrometers. Chemical shifts were reported in ppm referenced to 7.26 ppm of chloroform-*d*. ^{13}C NMR spectra were recorded on Bruker Avance 101 MHz spectrometers, and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of chloroform-*d*. HRMS was recorded on a commercial apparatus (ESI Source, TOF). Melting points were obtained by XT4A micro Melting-point Measurement Instruments. Electron paramagnetic resonance (EPR) experiment was recorded by A300.

2. Synthesis of acetamides

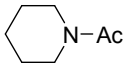
Synthetic procedure A: To an oven-dried round bottom flask, ammonium chloride (2.60 g, 50 mmol), amine (50 mmol) and EtOH (50 mL) were added. The solution was heated to reflux for two hours followed by dropping in trimethyl orthoacetate (14.3 mL, 75 mmol). The reactions were monitored by Thin-Layer Chromatography (TLC) on Iodine cylinder. Upon completion, the reaction mixture was cooled to room temperature. After the solvent was removed under the reduced pressure, the product was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE:EA=1:1) as eluent to afford the acetamides.[1]



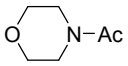
N,N-Diethylacetamide (**2b**). Following the synthetic procedure A. A canary yellow liquid in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.34 – 3.18 (m, 4H), 2.00 (s, 3H), 1.15 – 1.08 (m, 6H).



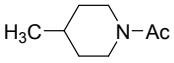
N-Acetylpyrrolidine (**2c**). Following the synthetic procedure A. A yellow liquid in 70 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.43 – 3.32 (m, 4H), 1.98 (s, 3H), 1.93 – 1.75 (m, 4H).



N-Acetylpiperidine (**2d**). Following the synthetic procedure A. A yellow liquid in 65 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.53 – 3.45 (m, 2H), 3.38 – 3.31 (m, 2H), 2.03 (s, 3H), 1.63 – 1.44 (m, 6H).



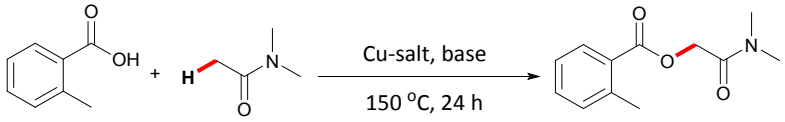
N-Acetylmorpholine (**2e**). Following the synthetic procedure A. A canary yellow liquid in 68 % yield . ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.67 – 3.53 (m, 6H), 3.45 – 3.39 (m, 2H), 2.05 (d, J = 3.3 Hz, 3H).



4-Methyl-*N*-Acetylpiperidine (**2f**). Following the synthetic procedure A. A yellow liquid in 62 % yield . ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.42 – 4.35 (m, 1H), 3.67 – 3.58 (m, 1H), 2.92 – 2.80 (m, 1H), 1.57 – 1.43 (m, 1H), 1.91 (s, 3H), 1.58 – 1.40 (m, 3H), 0.99 – 0.86 (m, 2H), 0.79 (d, J = 6.5 Hz, 3H).

3. Optimization of the reaction conditions

Table 1 Optimization of reaction conditions for *o*-methylbenzoic acid[a]



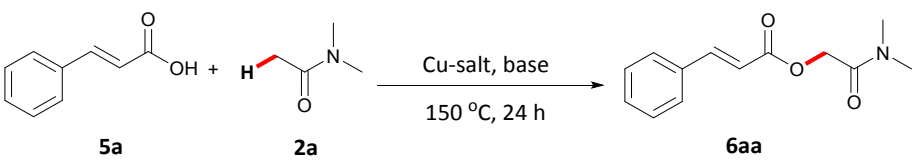
1a **2a** **3aa**

Entry	Cu-salt	Oxidant	Base (equiv)	Yield of **3aa** [%][b]
1	$CuCl_2$ (10)	$K_2S_2O_8$	KOAc (2.0)	trace[d]
2	$CuCl_2$ (30)	$K_2S_2O_8$	KOAc (2.0)	trace
3	$CuCl_2$ (50)	$K_2S_2O_8$	KOAc (2.0)	trace
4	$CuCl_2$ (50)	$Cu(OAc)_2$	KOAc (2.0)	trace
5	$CuCl_2$ (50)	Ag_2CO_3	KOAc (2.0)	trace
6	$CuCl_2$ (50)	AgOAc	KOAc (2.0)	trace
7	$CuCl_2$ (50)	Ag_2O	KOAc (2.0)	trace

8	$CuCl_2$ (50)	H_2O_2	KOAc (2.0)	trace
9	$CuCl_2$ (30)	TBHP	KOAc (2.0)	trace
10	CuI (1.0)	–	NaOAc (1.0)	32
11	$CuCl_2$ (1.0)	–	NaOAc (1.0)	33
12	CuCl (1.0)	–	NaOAc (1.0)	25
13	$CuBr_2$ (1.0)	–	NaOAc (1.0)	33
14	Cu_2O (1.0)	–	NaOAc (1.0)	5
15	$Cu(OAc)_2$ (1.0)	–	NaOAc (1.0)	trace
16	$CuSO_4$ (1.0)	–	NaOAc (1.0)	trace
17	CuBr (1.0)	–	NaOAc (1.0)	10
18	$CuCl_2$ (1.0)	–	K_2CO_3 (1.0)	6
19	$CuCl_2$ (1.0)	–	CsOAc (1.0)	14
20	$CuCl_2$ (1.0)	–	LiOAc (1.0)	21
21	$CuCl_2$ (1.0)	–	K_3PO_4 (1.0)	21
22	$CuCl_2$ (1.0)	–	Cs_2CO_3 (1.0)	5
23	$CuCl_2$ (1.0)	–	KOAc (1.0)	33
24	$CuCl_2$ (2.0)	–	KOAc (1.0)	41
25	$CuCl_2$ (2.5)	–	KOAc (1.0)	44
26	$CuCl_2$ (3.0)	–	KOAc (1.0)	50
27	$CuCl_2$ (4.0)	–	KOAc (1.0)	43
28	$CuCl_2$ (3.0)	–	KOAc (2.0)	62
29	$CuCl_2$ (3.0)	–	KOAc (3.0)	75
30	$CuCl_2$ (3.0)	–	KOAc (4.0)	42
31	$CuCl_2$ (3.0)	–	KOAc (3.0)	87[c]

[a]Reaction conditions: *o*-methylbenzoic acid **1a** (0.25 mmol, 34.0 mg), $CuCl_2$ (10-50 mmol%, 1.0 -3.0 equiv), Oxidant (0.5 mmol) and DMAc (1.0 mL) at 150 °C for 24 h under N_2. [b]Isolated yields. [c]Under N_2 balloon. [d] Determined by TLC.

Table 2 Optimization of reaction conditions for cinnamic acid[a]

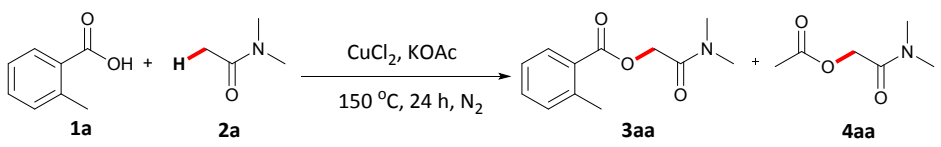


5a **2a** **6aa**

Entry	Cu-salt (equiv)	Addition (equiv)	Temp (°C)	Yield **6aa**[%][b,c]
1	CuBr (1.0)	KOAc (1.0)	150	16
2	$CuCl_2$ (1.0)	KOAc (1.0)	150	55
3	CuCl (1.0)	KOAc (1.0)	150	19
4	$CuSO_4$ (1.0)	KOAc (1.0)	150	trace
5	$Cu(OAc)_2$ (1.0)	KOAc (1.0)	150	trace
6	$CuCl_2$ (1.0)	$LiCO_3$ (1.0)	150	51
7	$CuCl_2$ (1.0)	K_2CO_3 (1.0)	150	19
8	$CuCl_2$ (1.0)	NaOH (1.0)	150	48
9	$CuCl_2$ (1.0)	Cs_2CO_3 (1.0)	150	37
10	$CuCl_2$ (1.0)	$KHCO_3$ (1.0)	150	20
11	$CuCl_2$ (1.0)	LiOAc (1.0)	150	trace
12	$CuCl_2$ (1.0)	K_3PO_4 (1.0)	150	22
13	$CuCl_2$ (1.0)	NaO^tBu (1.0)	150	32
14	$CuCl_2$ (1.0)	KO^tBu (1.0)	150	32
15	$CuCl_2$ (1.0)	CsOAc (1.0)	150	20
16	$CuCl_2$ (1.0)	KOAc (1.0)	120	50
17	$CuCl_2$ (1.0)	KOAc (1.0)	130	37
18	$CuCl_2$ (1.0)	KOAc (1.0)	140	28
19	$CuCl_2$ (2.0)	KOAc (2.0)	150	58
20	$CuCl_2$ (2.0)	$K_2S_2O_8$ (2.0)	150	17 (53[d])
21	$CuCl_2$(2.0)	AgOAc (2.0)	150	12 (43[d])
22	$CuCl_2$ (2.0)	$AgCO_3$ (2.0)	150	trace (23[d])

[a] Reaction conditions: cinnamic acid **5a** (0.25 mmol, 37.0 mg) and DMAc (1.0 mL) at X °C for 24 h under N_2. [b]Isolated yields. [c]Around 5-30% ^1H NMR yield of transamidation by-product was detected. [d]The transamidation by-product was reported in an isolated yield.

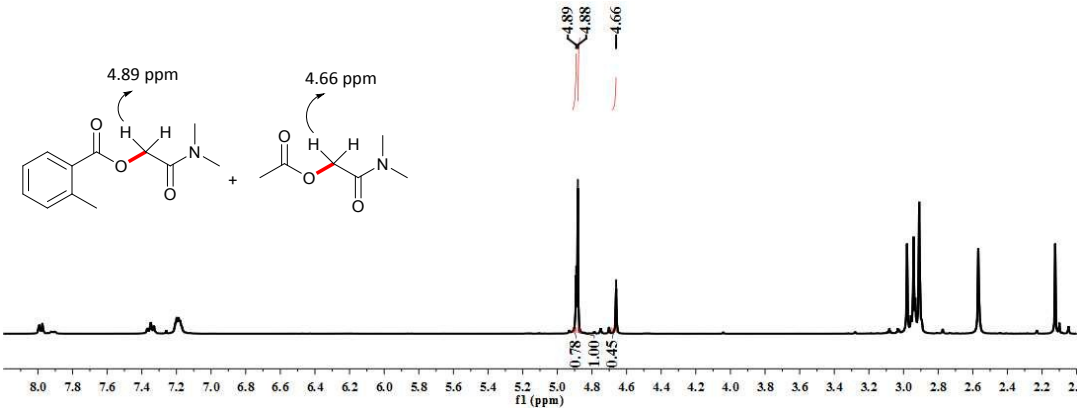
Table 3 Influence of the ratio of KOAc/$CuCl_2$ on the reaction outcome.



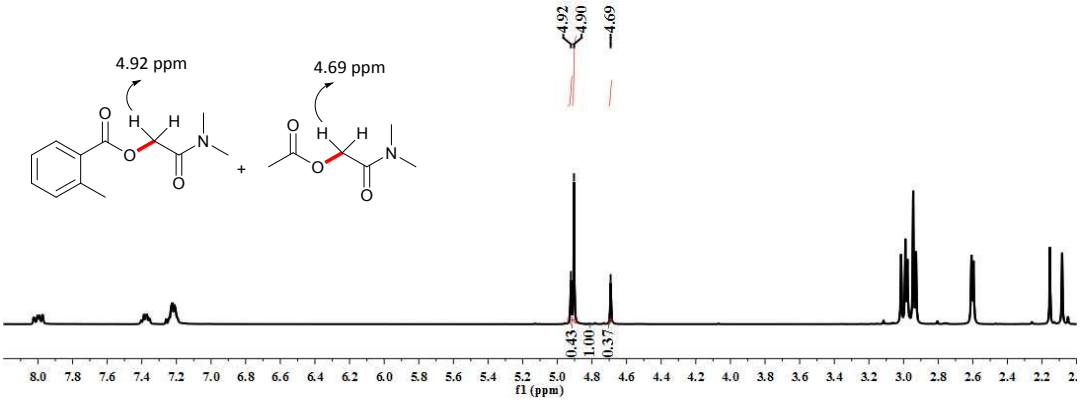
Entry	**1a**/$CuCl_2$/KOAc	Yield of **3aa** [%][b]	Yield of **4aa** [%][b]	**[4aa]/[3aa]**
1	1/3/3	78	45	0.58
2	1/3/4	43	37	0.86
3	1/3/5	30	27	0.90

[a]Reaction conditions: *o*-methylbenzoic acid **1a** (0.25 mmol, 34.0 mg), $CuCl_2$ (0.75 mmol, 108.6 mg) and DMAc (1.0 mL) at 150 °C for 24 h under N_2. [b]Crude ^1H NMR yield (CH_2Br_2).

***o*-methylbenzoic acid 1a/$CuCl_2$/KOAc=1/3/3: ^1H NMR ($CDCl_3$, 400 MHz)**



***o*-methylbenzoic acid 1a/$CuCl_2$/KOAc=1/3/4: ^1H NMR ($CDCl_3$, 400 MHz)**



***o*-methylbenzoic acid 1a/$CuCl_2$/KOAc=1/3/5: ^1H NMR ($CDCl_3$, 400 MHz)**

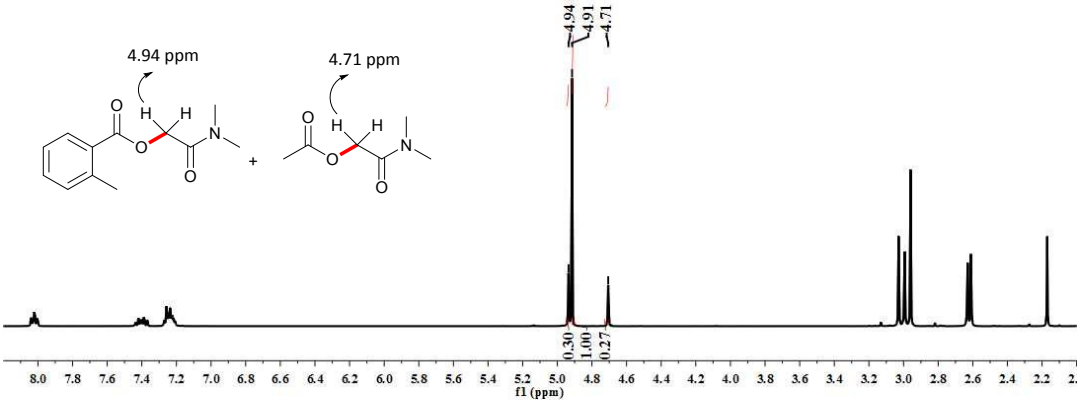
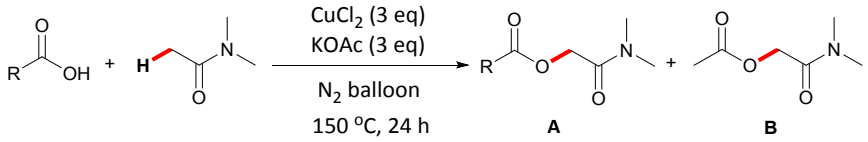


Table 4 The reactivity for aliphatic acid with DMAc[a]

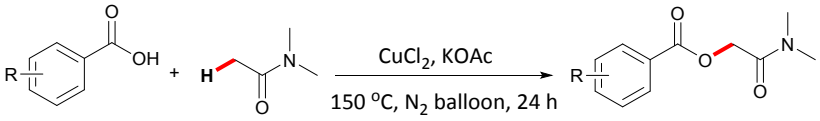


Entry	R	Yield of **A** [%][b]	Yield of **B** [%][b]
1	CH_3-	NR	10
2	CH_3CH_2-	NR	12
3	$C(CH_3)_3$-	NR	24
4	CN-	NR	30
5	NO_2-	NR	21
6	CF_3-	NR	18

[a]Reaction conditions: aliphatic acid (0.25 mmol), $CuCl_2$ (0.75 mmol, 108.6 mg), KOAc (0.75 mmol, 73.6 mg) and DMAc (1 mL) at 150 °C for 24 h under N_2 balloon. [b]^{1}H NMR yield.

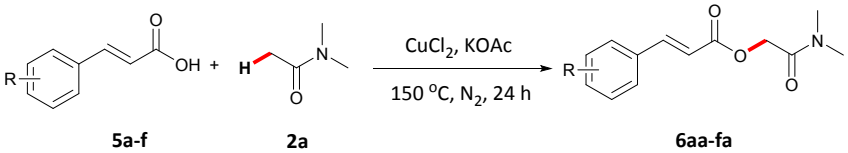
4. General procedures

General procedure A: Synthesis of 3aa-ya



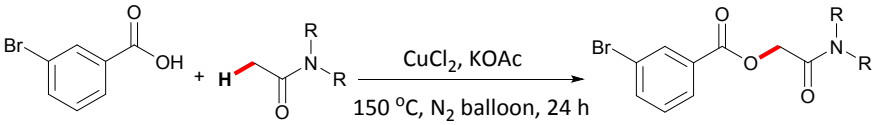
An oven-dried Schlenk tube was sequentially charged with benzoic acid **1a-y** (0.25 mmol), cupric chloride (0.75 mmol, 108.6 mg), potassium acetate (0.75 mmol, 73.6 mg) and DMAc (1.0 mL). The reaction mixture was stirred at 150 °C for 24 h under nitrogen balloon. Then, the reaction mixture was filtered and the resulting filtrate was concentrated in vacuo. The product was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE:EA=2:1) as eluent to afford the desired products.

General procedure B: Synthesis of 6aa-fa



An oven-dried Schlenk tube was sequentially charged with cinnamic acid **5a-f** (0.25 mmol), cupric chloride (0.5 mmol, 72.4 mg), potassium acetate (0.5 mmol, 49.1 mg) and DMAc (1.0 mL). The reaction mixture was stirred at 150 °C for 24 h under nitrogen atmosphere. Then, the reaction mixture was extracted by ethyl acetate. Organic extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo. The product was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE:EA=1:1) as eluent to afford the desired products.

General procedure C: Synthesis of 4kb-ki

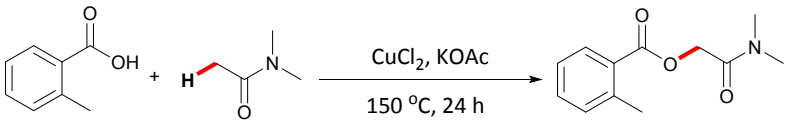


1k **2b-i** **4kb-ki**

An oven-dried Schlenk tube was sequentially charged with *m*-bromobenzoic acid **1k** (0.25 mmol, 50.3 mg), cupric chloride (0.75 mmol, 108.6 mg), potassium acetate (0.75 mmol, 73.6 mg) and *N,N*-disubstituted acetamides **2b-i** (1.0 mL). The reaction mixture was stirred at 150 °C for 24 h under nitrogen balloon. Then, the reaction mixture was extracted by ethyl acetate. Organic extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo. The product was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE:EA=5:1) as eluent to afford the desired products.

5. Control experiment

Table 5 Influence of reaction atmosphere[a]

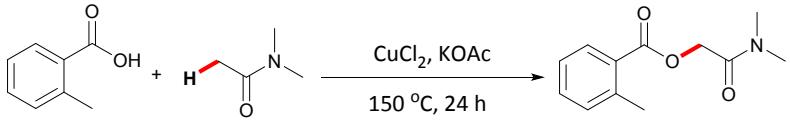


1a **2a** **3aa**

Entry	Cu-salt	Base	Atmopshere	Yield **3aa**[%][b]
1	$CuCl_2$	KOAc	N_2 balloon	87
2	$CuCl_2$	KOAc	O_2 balloon	63
3	$CuCl_2$	KOAc	Air balloon	69

[a]Reaction conditions: *o*-methylbenzoic acid **1a** (0.25 mmol, 34.0 mg), $CuCl_2$ (0.75 mmol, 108.6 mg), KOAc (0.75mmol, 73.6 mg) and DMAc (1 mL) at 150 °C for 24 h. [b]Isolated yields.

Table 6 Influence of radical scavenger[a]

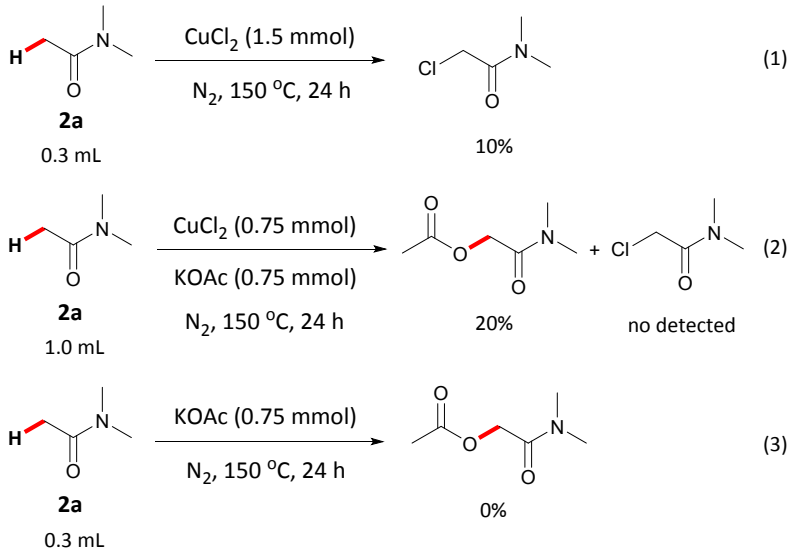


1a **2a** **3aa**

Entry	Radical Scavenger	Equivalent	Yield **3aa**[%][b]
1	TEMPO	1.0	26
2	TEMPO	2.0	trace

[a]Reaction conditions: *o*-methylbenzoic acid **1a** (0.25 mmol, 34.0 mg), $CuCl_2$ (0.75 mmol, 108.6 mg), KOAc (0.75mmol, 73.6 mg) and DMAc (1 mL) at 150 °C for 24 h under nitrogen balloon. [b]Isolated yields. TEMPO: 2, 2, 6, 6-tetramethyl-piperidine-N-oxyl.

Table 7 Control experiments for the reaction in the absence of benzoic acid



6. Electron paramagnetic resonance (EPR) experiment[2]

(1) EPR experiment on reaction system

An oven-dried Schlenk tube was sequentially charged with *o*-methylbenzoic acid **1a** (0.2 mmol, 27.2 mg), cupric chloride (0.1 mmol, 36.2 mg), potassium acetate (0.2 mmol, 49.1 mg) and DMAc (1.0 mL). The reaction mixture was stirred at 150 °C for 24 h under nitrogen atmosphere, followed by the addition of 8.0 mg DPMO. Then,

this reaction solution was taken out by capillary and was analyzed by EPR at room temperature. EPR spectrometer parameters were: Microwave Frequency 9.43 GHz, Sweep Width 80 G; Center Field 3360 G; Time Constant 40.96 ms; Modulation Amplitude 1.00 G; Modulation Frequency 100.00 kHz; Receiver Gain $1.00*10^3$; Microwave Power 121.25 mW. Finally, test data was processed by Biomolecular EPR Spectroscopy Software hyperfine spectrum (Fig. 1). An EPR signal consisted of six peaks with calculated hyperfine splittings ($g_0 = 2.0061$, $\alpha_N = 14.3$ G, $\alpha_H = 20.3$ G).

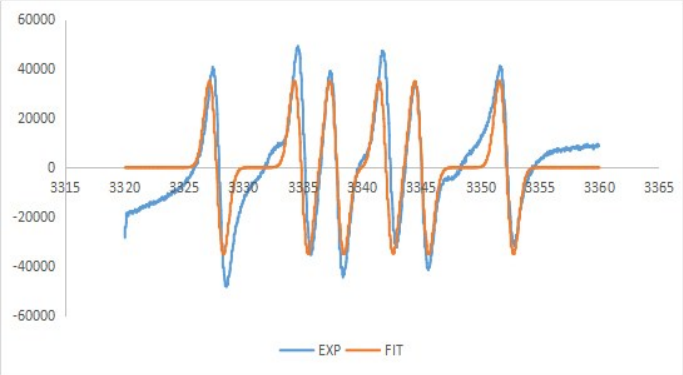


Fig. 1 The electron paramagnetic resonance (EPR) spectrum (X band, 9.4 GHz, room temperature) of conditions: *o*-methylbenzoic acid **1a** (0.2 mmol, 27.2 mg), $CuCl_2$ (0.1 mmol, 36.2 mg), KOAc (0.2 mmol, 49.1 mg) in DMAc (1.0 mL) heated 2 h at 150 °C under N_2 balloon, followed by the addition of 8.0 mg DPMO (5,5-dimethyl-1-pyrroline *N*-oxide).

(2) EPR studies on Cu (II) species

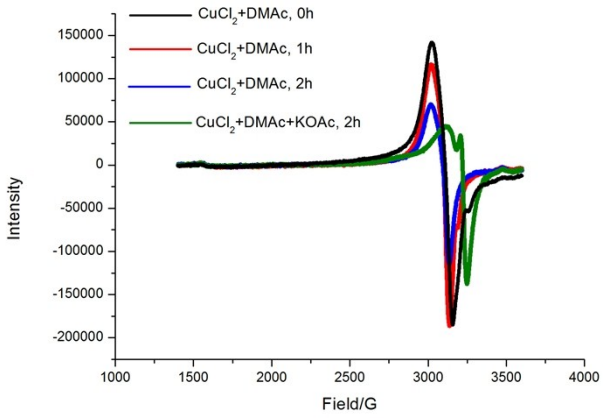
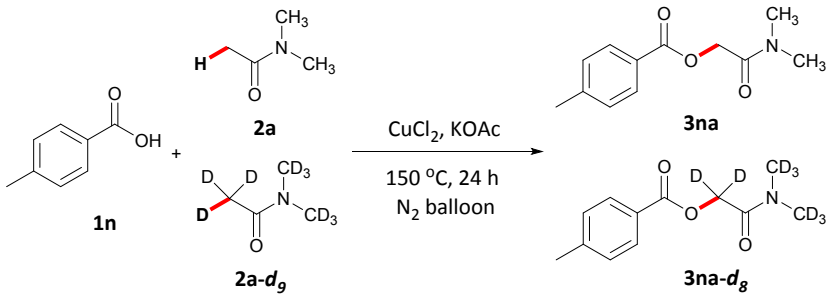


Fig. 2 The electron paramagnetic resonance (EPR) spectra (X band, 9.4 GHz, room temperature) of conditions: (a) $CuCl_2$ (0.1 mmol, 36.2 mg) in DMAc (1.0 mL) heated at 150 °C for 0 h, 1 h, 2 h

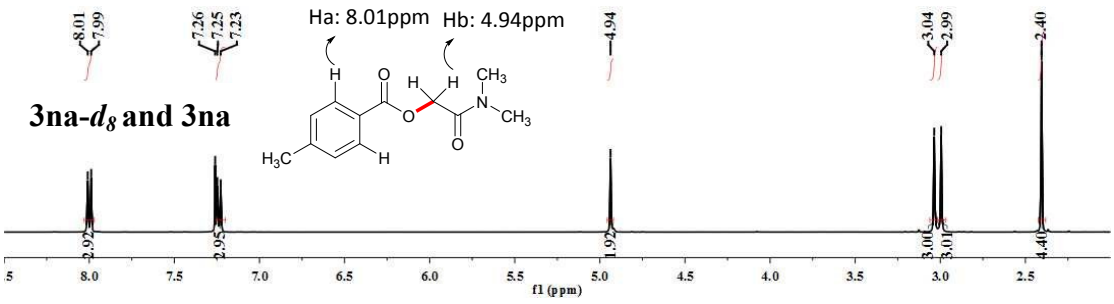
under N_2 balloon, followed by the addition of 8.0 mg DPMO; (b) $CuCl_2$ (0.1 mmol, 36.2 mg), KOAc (0.2 mmol, 49.1 mg) in DMAc (1.0 mL) heated at 150 °C for 2 h under N_2 balloon, followed by the addition of 8.0 mg DPMO.

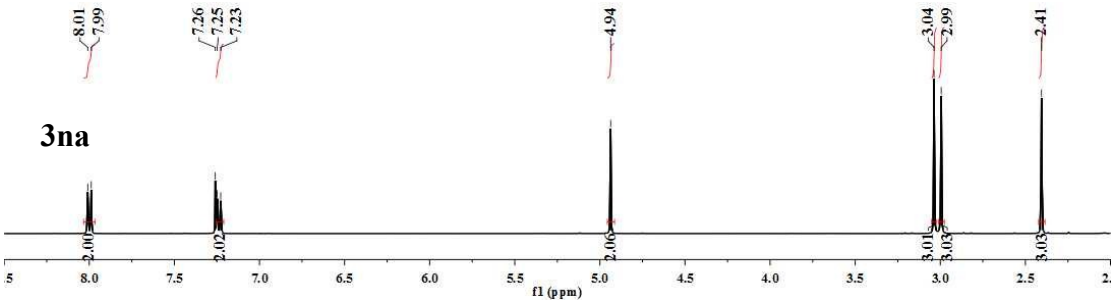
7. Procedure for Kinetic Isotope Experiments



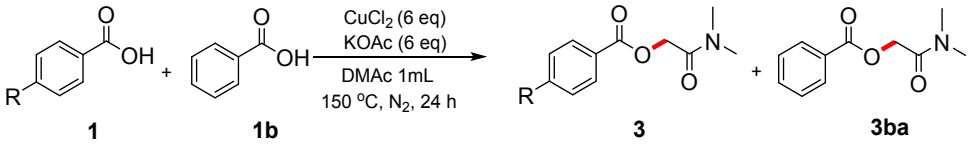
An oven-dried Schlenk tube was sequentially charged with 4-methylbenzoic acid **1n** (0.125 mmol, 17.0 mg), cupric chloride (0.375 mmol, 54.3 mg), potassium acetate (0.375 mmol, 36.8 mg) and DMAc (**2a**, 0.25 mL), deuterated DMAc (**2a-*d*$_9$**, 0.25 mL). The reaction mixture was stirred at 150 °C for 24 h under nitrogen balloon. Then, the reaction mixture was filtered and the resulting filtrate was concentrated in vacuo. The crude product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE:EA=2:1) as eluent. The deuterated and non-deuterated product was determined by ^{1}H NMR analysis (Fig. 5) and the KIE value (K_H/K_D = 2.0) was calculated by the relative integration value of the Hb (4.94 ppm) based on the integral difference between Ha (8.01 ppm) and Hb (4.94 ppm).

Fig. 3 ^{1}H NMR spectra of the KIE value (K_H/K_D = 2.0)





8. Hammett Competition Experiments[3]



An oven-dried Schlenk tube was sequentially charged with *para*-substituted benzoic acids **1** (0.125 mmol), benzoic acid **1b** (0.125 mmol, 16.5mg), cupric chloride (0.750 mmol, 108.6 mg), potassium acetate (0.750 mmol, 73.6 mg) and DMAc (1.0 mL). The reaction mixture was stirred at 150 °C for 24 h under nitrogen atmosphere. Upon completion, the reaction mixture was filtered and the resulting filtrate was concentrated in vacuo. Organic extracts was recorded by using ^{1}H NMR spectroscopy with CH_2Br_2 as the internal standard, which provided the information about the ratios of products **3** to **3ba**.

Table 8 Hammett competition experiment.

Entry	**[3]**	**[3ba]**	Log([**3**]/[**3ba**])	R	σ_p	σ^+
1	0.33	0.51	-0.19	OMe	-0.26	-0.78
2	0.33	0.43	-0.12	CH_3	-0.17	-0.31
3	0	0	0	H	0	0
4	0.51	0.38	0.13	CN	1.00	0.66
5	0.79	0.45	0.24	NO_2	1.27	0.79

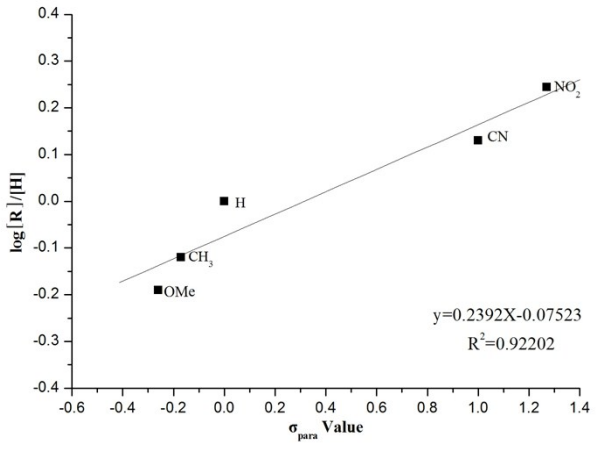


Fig. 4 Hammett correlation with σ_p values.

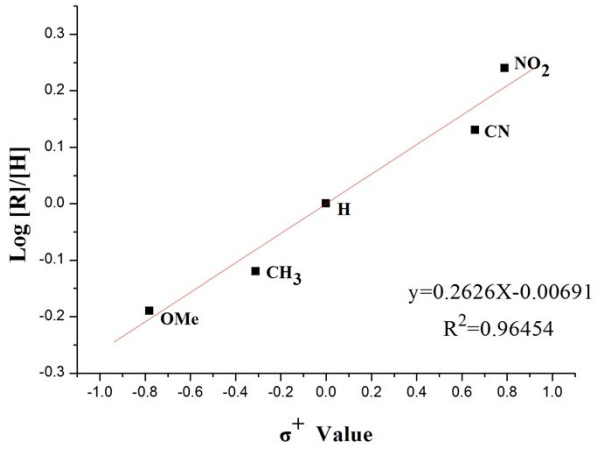
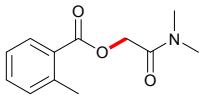


Fig. 5 Hammett correlation with σ^+ values.

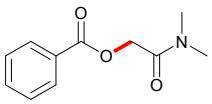
9. Characterization data of products

2-(Dimethylamino)-2-oxoethyl 2-methylbenzoate (3aa).



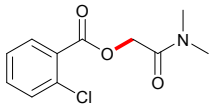
Prepared according to procedure A. A white solid (48.1 mg, 87%). M.p. 85 °C − 86 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (dd, J = 8.1, 1.3 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.26 – 7.20 (m, 2H), 4.92 (s, 2H), 3.01 (s, 3H), 2.98 (s, 3H), 2.61 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 167.3, 166.6, 140.7, 132.4, 131.7, 131.2, 129.0, 125.9, 61.71, 36.0, 35.8, 21.8. HRMS (ESI) calcd for $C_{12}H_{15}NO_3$ ($M + H^+$) 222.1125, found 222.1101.

2-(Dimethylamino)-2-oxoethyl benzoate (3ba).



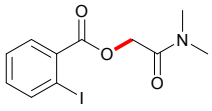
Prepared according to procedure A. A white solid (32.6 mg, 63%). M.p. 105 °C − 107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 − 8.08 (m, 2H), 7.58 − 7.53 (m, 1H), 7.43 (dd, *J* = 10.6, 4.7 Hz, 2H), 4.94 (s, 2H), 3.02 (s, 3H), 2.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ166.4, 166.3, 133.3, 130.0, 129.6, 128.4, 61.9, 36.0, 35.6. HRMS (ESI) calcd for $C_{11}H_{13}NO_3$ (M + H^+) 208.0968, found 208.0948.

2-(Dimethylamino)-2-oxoethyl 2-chlorobenzoate (3ca).



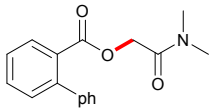
Prepared according to procedure A. A white solid (35.3 mg, 58%). M.p. 130 °C − 132 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 − 7.98 (m, 1H), 7.45 − 7.38 (m, 2H), 7.32 − 7.26 (m, 1H), 4.94 (s, 2H), 3.00 (s, 3H), 2.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.1, 165.2, 134.0, 133.0, 132.2, 131.1, 129.5, 126.7, 62.0, 36.0, 35.7. HRMS (ESI) calcd for $C_{11}H_{12}ClNO_3$ (M + H^+) 242.0578, found 242.0565.

2-(Dimethylamino)-2-oxoethyl 2-iodobenzoate (3da).



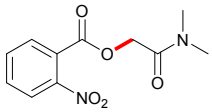
Prepared according to procedure A. A white solid (52.2 mg, 63%). M.p. 128 °C − 130 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47 − 7.40 (m, 2H), 7.35 − 7.30 (m, 1H), 4.96 (s, 2H), 3.03 (s, 3H), 3.00 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.2, 165.2, 134.1, 133.0, 132.2, 131.1, 129.5, 126.8, 62.1, 36.0, 35.8. HRMS (ESI) calcd for $C_{11}H_{12}INO_3$ (M + H^+) 355.9754, found 355.9764.

2-(Dimethylamino)-2-oxoethyl 2-phenylbenzoate (3ea).



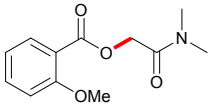
Prepared according to procedure A. A white gummy solid (57.0 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.56 − 7.51 (m, 1H), 7.48 − 7.28 (m, 8H), 4.73 (s, 2H), 2.91 (s, 3H), 2.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 167.7, 166.2, 143.0, 141.2, 131.7, 130.9, 130.6, 129.9, 128.7, 128.0, 127.3 (d, *J* = 1.4 Hz), 61.9, 35.9, 35.6. HRMS (ESI) calcd for $C_{17}H_{17}NO_3$ (M + H^+) 284.1281, found 284.1266.

2-(Dimethylamino)-2-oxoethyl 2-nitrobenzoate (3fa).



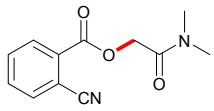
Prepared according to procedure A. A yellow solid (39.6 mg, 63%). M.p. 140 °C − 142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 − 7.92 (m, 2H), 7.73 − 7.69 (m, 1H), 7.64 (dd, *J* = 7.9, 1.6 Hz, 1H), 4.97 (s, 2H), 3.02 (s, 3H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 165.8, 165.4, 147.7, 133.4, 131.9, 130.6, 127.8, 124.1, 62.8, 36.0, 35.8. HRMS (ESI) calcd for $C_{11}H_{12}N_2O_5$ (M + H^+) 253.0819, found 253.0804.

2-(Dimethylamino)-2-oxoethyl 2-methoxybenzoate (3ga).



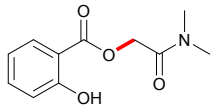
Prepared according to procedure A. A canary yellow solid (39.6 mg, 67%). M.p. 91 °C − 93 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 – 7.93 (m, 1H), 7.50 – 7.44 (m, 1H), 6.97 (t, *J* = 7.9 Hz, 2H), 4.91 (s, 2H), 3.88 (s, 3H), 3.02 (s, 3H), 2.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.7, 165.6, 159.6, 134.0, 132.3, 120.3, 119.3, 112.1, 61.7, 56.1, 36.1, 35.7. HRMS (ESI) calcd for $C_{12}H_{15}NO_4$ (M + H^+) 238.1074, found 238.1057.

2-(Dimethylamino)-2-oxoethyl 2-cyanobenzoate (3ha).



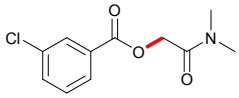
Prepared according to procedure A. A canary yellow solid (25.4 mg, 44%). M.p. 142 °C − 144 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 − 8.23 (m, 1H), 7.82 − 7.78 (m, 1H), 7.70 − 7.64 (m, 2H), 5.02 (s, 2H), 3.02 (s, 3H), 2.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 101MHz): δ 165.6, 163.8, 134.9, 133.1, 132.6, 131.8, 117.5, 113.2, 62.4, 35.9, 35.7; HRMS (ESI) calcd for $C_{12}H_{12}N_2O_3$ (M + H^+) 233.0921, found 233.0902.

2-(Dimethylamino)-2-oxoethyl 2-hydroxybenzoate (3ia).



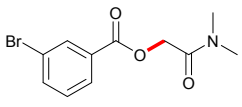
Prepared according to procedure A. A canary yellow solid (27 mg, 24%). M.p. 61 °C − 63 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.46 (s, 1H), 7.95 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.51 − 7.43 (m, 1H), 7.02 − 6.95 (m, 1H), 6.94 − 6.86 (m, 1H), 4.99 (s, 2H), 3.04 (s, 3H), 3.01 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 169.6, 166.0, 161.7, 136.2, 130.5, 119.5, 117.8, 112.3, 62.0, 36.0, 35.8. HRMS (ESI) calcd for $C_{11}H_{13}NO_4$ (M + H^+) 224.0917, found 224.0917.

2-(Dimethylamino)-2-oxoethyl 3-chlorobenzoate (3ja).



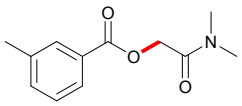
Prepared according to procedure A. A canary yellow solid (47.9 mg, 79%). M.p. 93 °C − 95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (t, J=1.7 Hz, 1H), 8.00 − 7.97 (m, 1H), 7.55 − 7.50 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 4.95 (s, 2H), 3.02 (s, 3H), 2.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.1, 165.2, 134.6, 133.4, 131.4, 130.1, 129.8, 128.2, 62.1, 35.9, 35.7. HRMS (ESI) calcd for $C_{11}H_{12}ClNO_3$ (M + H^+) 242.0578, found 242.0552.

2-(Dimethylamino)-2-oxoethyl 3-bromobenzoate (3ka).



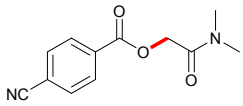
Prepared according to procedure A. A canary yellow solid (67.3 mg, 94%). M.p. 90 °C − 92 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (t, *J* = 1.8 Hz, 1H), 8.00 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.54 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 4.97 (s, 2H), 3.04 (s, 3H), 3.00 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.1, 165.3, 134.7, 133.4, 131.4, 130.2, 129.9, 128.3, 62.2, 36.0, 35.8. HRMS (ESI) calcd for $C_{11}H_{12}BrNO_3$(M + H^+) 286.0073, found 286.0063.

2-(Dimethylamino)-2-oxoethyl 3-methylbenzoate (3la).



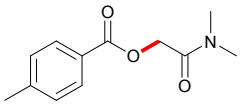
Prepared according to procedure A. A canary yellow solid (45.6 mg, 82%). M.p. 59 °C − 60 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 − 7.88 (m, 2H), 7.38 − 7.28 (m, 2H), 4.94 (s, 2H), 3.02 (s, 3H), 2.98 (s, 3H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.5, 138.3, 134.1, 130.6, 129.5, 128.4, 127.2, 61.9, 36.1, 35.7, 21.4. HRMS (ESI) calcd for $C_{12}H_{15}NO_3$ (M + H^+) 222.1125, found 222.1101.

2-(Dimethylamino)-4-oxoethyl 4-cyanobenzoate (3ma).



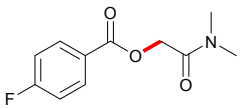
Prepared according to procedure A. A white solid (36.1 mg, 62%). M.p. 110 °C − 112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 – 8.17 (m, 2H), 7.77 – 7.72 (m, 2H), 4.99 (s, 2H), 3.03 (s, 3H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.8, 166.1, 163.7, 132.2, 122.0, 113.7, 61.8, 55.6, 36.1, 35.7. HRMS (ESI) calcd for $C_{12}H_{12}N_2O_3$ (M + H^+) 233.0921, found 233.0912.

2-(Dimethylamino)-2-oxoethyl 4-methylbenzoate (3na).



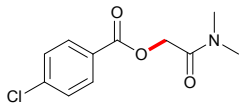
Prepared according to procedure A. A white solid (46.2 mg, 84%). M.p. 82 °C − 84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.94 (s, 2H), 3.04 (s, 3H), 2.99 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.7, 166.4, 144.1, 130.1, 129.2, 126.9, 61.9, 36.1, 35.7, 21.8. HRMS (ESI) calcd for $C_{12}H_{15}NO_3$ (M + H^+) 222.1125, found 222.1101.

2-(Dimethylamino)-2-oxoethyl 4-fluorobenzoate (3oa).



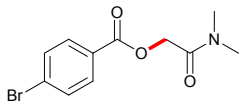
Prepared according to procedure A. A canary yellow solid (45.6 mg, 81%). M.p. 61 °C − 63 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16 − 8.09 (m, 2H), 7.13 − 7.07 (m, 2H), 4.94 (s, 2H), 3.03 (s, 3H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.3, 166.1, 165.4, 132.7, 125.9, 115.8, 62.0, 36.0, 35.7. HRMS (ESI) calcd for $C_{11}H_{12}FNO_3$ (M + H^+) 226.0874, found 226.0852.

2-(Dimethylamino)-2-oxoethyl 4-chlorobenzoate (3pa).



Prepared according to procedure A. A white solid (45.1 mg, 75%). M.p. 102 °C − 104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 − 8.02 (m, 2H), 7.44 − 7.38 (m, 2H), 4.95 (s, 2H), 3.03 (s, 3H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.2, 165.6, 139.9, 131.5, 128.9, 128.1, 62.0, 36.0, 35.7. HRMS (ESI) calcd for $C_{11}H_{12}ClNO_3$ (M + H^+) 242.0578, found 242.0560.

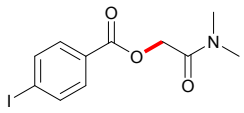
2-(Dimethylamino)-2-oxoethyl 4-bromobenzoate (3qa).



Prepared according to procedure A. A white solid (61.9 mg, 80%). M.p.118 °C − 120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 − 8.01 (m, 2H), 7.45 − 7.39 (m, 2H), 4.95 (s, 2H), 3.03 (s, 3H), 2.99 (s, 3H). ^{13}C

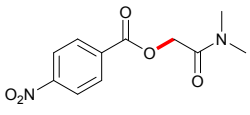
NMR ($CDCl_3$, 101MHz): δ 166.3, 165.6, 139.9, 131.5, 128.9, 128.1, 62.0, 36.0, 35.7. HRMS (ESI) calcd for $C_{11}H_{12}BrNO_3$ (M + H^+) 286.0073, found 286.0072.

2-(Dimethylamino)-2-oxoethyl 4-iodobenzoate (3ra).



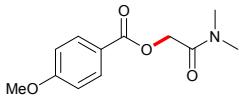
Prepared according to procedure A. A white solid (58.6 mg, 70%). M.p. 105 °C − 107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 − 8.02 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 4.95 (s, 2H), 3.03 (s, 3H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.3, 165.6, 131.5, 128.9, 128.1, 100.1, 62.1, 36.0, 35.7. HRMS (ESI) calcd for $C_{11}H_{12}INO_3$ (M + H^+) 333.9935, found 333.9901.

2-(Dimethylamino)-2-oxoethyl 4-nitrobenzoate (3sa).



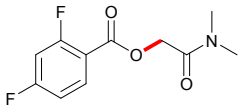
Prepared according to procedure A. A canary yellow solid (44.2 mg, 70%). M.p. 132 °C − 134 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (s, 4H), 5.00 (s, 2H), 3.03 (s, 3H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 165.7, 164.6, 150.8, 135.1, 131.2, 123.6, 62.4, 35.9, 35.7. HRMS (ESI) calcd for $C_{11}H_{12}N_2O_5$ (M + H^+) 253.0819, found 253.0799.

2-(Dimethylamino)-4-oxoethyl 4-methoxybenzoate (3ta).



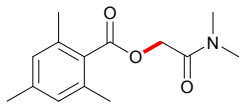
Prepared according to procedure A. A canary yellow solid (40.1 mg, 68%). M.p. 87 °C − 89 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.93 (s, 2H), 3.85 (s, 3H), 3.01 (d, *J* = 16.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.8, 166.1, 163.7, 132.2, 122.0, 113.7, 61.8, 55.6, 36.1, 35.7. HRMS (ESI) calcd for $C_{12}H_{15}NO_4$ (M + H^+) 238.1074, found 238.1066.

2-(Dimethylamino)-2-oxoethyl 2, 4-difluorobenzoate (3ua).



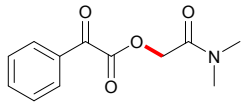
Prepared according to procedure A. A canary yellow solid (43.8 mg, 72%). M.p. 59 °C − 61 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (td, *J* = 8.5, 6.6 Hz, 1H), 6.95 − 6.82 (m, 2H), 4.94 (s, 2H), 3.00 (s, 3H), 2.96 (s, 3H). ^{13}C NMR($CDCl_3$, 101MHz): δ 166.0, 164.6, 163.0, 134.4, 114.7, 111.8, 105.3, 62.0, 35.9, 35.6. HRMS (ESI) calcd for $C_{11}H_{11}F_2NO_3$(M + H^+) 244.0780, found 244.0757.

2-(Dimethylamino)-2-oxoethyl 2, 4, 6-Trimethylbenzoate (3va).



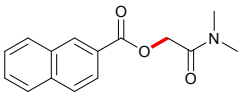
Prepared according to procedure A. A canary yellow solid (54.3 mg, 87%). M.p. 106 °C − 108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.85 (s, 2H), 4.92 (s, 2H), 3.01 (s, 3H), 2.99 (s, 3H), 2.38 (s, 6H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 169.6, 166.3, 139.6, 136.0, 130.0, 128.5, 61.6, 36.0, 35.7, 21.2, 20.0. HRMS (ESI) calcd for $C_{14}H_{19}NO_3$ (M + Na^+) 272.1257, found 272.1238.

2-(Dimethylamino)-2-oxoethyl 2-oxo-2-phenylacetate (3wa).



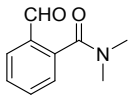
Prepared according to procedure A. A white solid (32.0 mg, 54%). M.p. 59 °C − 62 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14 − 8.09 (m, 2H), 7.59 − 7.54 (m, 1H), 7.44 (dd, *J* = 10.6, 4.7 Hz, 2H), 4.96 (s, 2H), 3.04 (s, 3H), 3.00 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.5, 166.4, 133.4, 130.1, 129.6, 128.5, 62.0, 36.1, 35.7. HRMS (ESI) calcd for $C_{12}H_{13}NO_4$ (M + Na^+) 258.0737, found 258.0793.

2-(Dimethylamino)-2-oxoethyl 2-naphthoate (3xa).



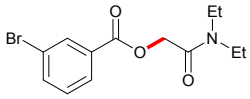
Prepared according to procedure A. A white solid (42.2 mg, 66%). M.p. 110 °C − 112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.71 (s, 1H), 8.12 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 − 7.94 (m, 1H), 7.88 (dd, *J* = 8.4, 4.9 Hz, 2H), 7.61 − 7.51 (m, 2H), 5.02 (s, 2H), 3.05 (s, 3H), 3.01 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.5, 135.8, 132.6, 131.7, 129.6, 128.5, 128.4, 127.9, 126.8, 126.7, 125.5, 62.0, 36.1, 35.7. HRMS (ESI) calcd for $C_{15}H_{15}NO_3$ (M + H^+) 258.1125, found 258.1109.

2-Formyl-*N,N*-dimethylbenzamide[4]



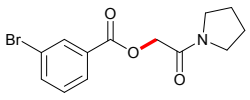
Prepared according to procedure A. A white gummy solid (10.2 mg, 23%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.04 (s, 1H), 7.93 (dd, J = 7.7, 0.9 Hz, 1H), 7.68 − 7.62 (m, 1H), 7.59 − 7.53 (m, 1H), 7.37 (d, J = 7.5 Hz, 1H), 3.18 (s, 3H), 2.81 (s, 3H). HRMS (ESI) calcd for $C_{10}H_{12}NO_2$ (M + H^+) 178.0863.

2-(Diethylamino)-2-oxoethyl 3-bromobenzoate (4kb).



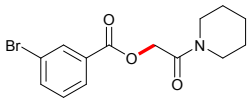
Prepared according to procedure C. A white gummy solid (60.8 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (t, *J* = 1.8 Hz, 1H), 8.01 − 7.98 (m, 1H), 7.53 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 4.95 (s, 2H), 3.44 − 3.38 (m, 2H), 3.33 − 3.27 (m, 2H), 1.27 − 1.23 (m, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 165.3, 134.6, 133.4, 131.4, 130.1, 129.8, 128.2, 62.1, 41.1, 40.6, 14.3, 13.0. HRMS (ESI) calcd for $C_{13}H_{16}BrNO_3$ (M + H^+) 314.0386, found 314.0362.

2-Oxo-2-(pyrrolidin-1-yl) ethyl 3-bromobenzoate (4kc).



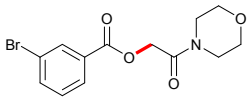
Prepared according to procedure C. A white solid (48.0 mg, 58%). M.p. 101 °C − 103 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (t, *J* = 1.8 Hz, 1H), 8.00 − 7.97 (m, 1H), 7.53 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 4.86 (s, 2H), 3.51 (t, *J* = 6.9 Hz, 2H), 3.44 (t, *J* = 6.8 Hz, 2H), 2.03 − 1.97 (m, 2H), 1.90 − 1.82 (m, 2H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 165.2, 164.7, 134.6, 133.4, 131.3, 130.1, 129.8, 128.2, 62.7, 46.1, 45.4, 26.3, 24.0. HRMS (ESI) calcd for $C_{13}H_{14}BrNO_3$ (M + H^+) 312.0230, found 312.0224.

2-oxo-2-(piperidin-1-yl)ethyl 3-bromobenzoate (4kd).



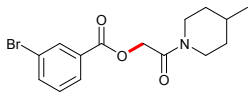
Prepared according to procedure C. A white gummy solid (57.0 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (t, J = 1.8 Hz, 1H), 8.01 − 7.97 (m, 1H), 7.53 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 4.96 (s, 2H), 3.61 − 3.54 (m, 2H), 3.40 − 3.34 (m, 2H), 1.71 − 1.57 (m, 6H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 165.2, 164.3, 134.6, 133.3, 131.4, 130.1, 129.8, 128.2, 62.3, 45.7, 43.2, 26.4, 25.4, 24.5. HRMS (ESI) calcd for $C_{14}H_{16}BrNO_3$ (M + H^+) 326.0386, found 326.0397.

2-Morpholino-2-oxoethyl 3-bromobenzoate (4ke).



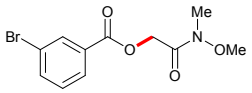
Prepared according to procedure C. A white solid (57.3 mg, 70%). M.p. 63 °C − 65 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (t, J = 1.8 Hz, 1H), 8.01 − 7.97 (m, 1H), 7.56 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 4.97 (s, 2H), 3.72 (s, 4H), 3.65 (s, 2H), 3.47 (d, J = 4.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 165.2, 165.0, 134.8, 133.6, 131.2, 130.2, 129.9, 128.2, 66.9, 66.5, 62.0, 45.2, 42.3; HRMS (ESI) calcd for $C_{13}H_{14}BrNO_4$ (M + H^+) 328.0179, found 328.0158.

2-(4-Methylpiperidin-1-yl)-2-oxoethyl 3-bromobenzoate (4kf).



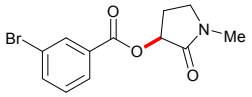
Prepared according to procedure C. A white gummy solid (59.5 mg, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (t, J = 1.8 Hz, 1H), 7.98 − 7.95 (m, 1H), 7.51 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 4.94 (s, 2H), 4.50 (d, J = 13.3 Hz, 1H), 3.64 (d, J = 13.5 Hz, 1H), 3.08 − 3.00 (m, 1H), 2.64 − 2.56 (m, 1H), 1.76 − 1.58 (m, 3H), 1.26 − 1.04 (m, 3H), 0.93 (d, J = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 165.1, 164.3, 134.5, 133.3, 131.4, 130.0, 129.7, 128.1, 62.2, 44.9, 42.5, 34.4, 33.5, 31.0, 21.7. HRMS (ESI) calcd for $C_{15}H_{18}BrNO_3$ (M + H^+) 340.0543, found 340.0535.

2-(methoxy(methyl)amino)-2-oxoethyl 3-bromobenzoate (4kg).



Prepared according to procedure C. A white gummy solid (60.1 mg, 51%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 5.07 (s, 2H), 3.78 (s, 3H), 3.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 167.8, 165.3, 134.6, 133.4, 131.3, 130.1, 129.8, 128.2, 61.9, 61.7, 32.4. HRMS (ESI) calcd for $C_{11}H_{12}BrNO_4$ (M + H^+) 302.0022, found 302.0037.

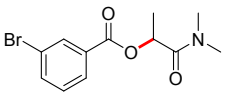
1-methyl 2-oxopyrrolidin 3-yl 3-bromobenzoate (4kh).



Prepared according to procedure C. A yellow gummy solid (17.6 mg, 22%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (s, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.54 (dd, J = 8.0, 0.8 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 5.51 (t, J = 8.0 Hz, 1H), 3.52 − 3.40 (m, 2H), 2.96 (s, 3H), 2.73 − 2.65 (m, 1H), 2.16 − 2.06 (m, 1H).

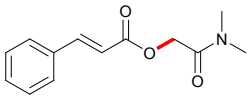
^{13}C NMR ($CDCl_3$, 101MHz): δ 169.9, 165.0, 134.7, 133.5, 131.3, 130.1, 129.8, 128.2, 72.0, 46.1, 30.4, 26.1. HRMS (ESI) calcd for $C_{12}H_{12}BrNO_3$ (M + Na^+) 319.9893, found 319.9751.

1-(dimethylamino)-1-oxopropan-2-yl 3-bromobenzoate (4ki).



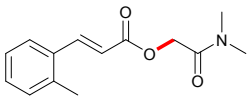
Prepared according to procedure C. A white gummy solid (15.0 mg, 20%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (t, *J* = 1.8 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.55 – 7.50 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 5.61 (q, *J* = 6.7 Hz, 1H), 3.10 (s, 3H), 2.99 (s, 3H), 1.56 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 167.0, 165.1, 134.6, 133.4, 131.4, 130.0, 129.8, 128.1, 68.0, 36.9, 36.1, 16.8. HRMS (ESI) calcd for $C_{12}H_{14}BrNO_3$ (M + H^+) 300.0230, found 300.0221.

2-(Dimethylamino)-2-oxoethyl cinnamate (6aa).



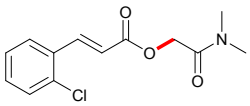
Prepared according to procedure B. A canary yellow solid (34.0 mg, 58%). M.p. 90 °C − 92 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.56 − 7.51 (m, 2H), 7.41 − 7.36 (m, 3H), 6.57 (d, *J* = 16.0 Hz, 1H), 4.85 (s, 2H), 3.02 (s, 3H), 3.00 (s, 3H). ^{13}C NMR ($CDCl_3$,101MHz): δ 166.7, 146.1, 134.4, 130.6, 129.0, 128.4, 117.3, 61.6, 36.1, 35.8. HRMS (ESI) calcd for $C_{13}H_{15}NO_3$ (M + H^+) 234.1125, found 234.1113.

2-(Dimethylamino)-2-oxoethyl (*E*)-3-(o-tolyl)acrylate (6ba).



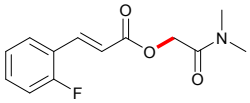
Prepared according to procedure B. A canary yellow solid (41.1 mg, 67%). M.p. 118 °C − 120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 15.9 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 4.85 (s, 2H), 3.02 (s, 3H), 3.00 (s, 3H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.7 (d, *J* = 10.6 Hz), 143.8, 138.0, 133.4, 130.9, 130.3, 126.6 (d, *J* = 17.7 Hz), 118.2, 61.6, 36.1, 35.8, 19.9. HRMS (ESI) calcd for $C_{14}H_{17}NO_3$ (M + H^+) 248.1281, found 248.1269.

2-(Dimethylamino)-2-oxoethyl (*E*)-3-(2-chlorophenyl)acrylate (6ca).



Prepared according to procedure B. A yellow solid (40.0 mg, 60%). M.p. 99 °C − 101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (d, *J* = 16.0 Hz, 1H), 7.63 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.42 − 7.38 (m, 1H), 7.32 − 7.24 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 4.85 (s, 2H), 3.01 (s, 3H), 2.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.4, 166.1, 141.7, 135.2, 132.6, 131.3, 130.3, 127.8, 127.2, 119.9, 61.6, 36.0, 35.7. HRMS (ESI) calcd for $C_{13}H_{14}ClNO_3$ (M + H^+) 268.0735, found 268.0736.

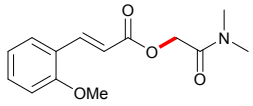
2-(Dimethylamino)-2-oxoethyl (*E*)-3-(2-fluorophenyl)acrylate (6da).



Prepared according to procedure B. A canary yellow solid (34.8 mg, 55%). M.p. 100 °C − 102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, *J*

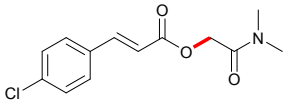
= 16.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.38 − 7.32(m, 1H), 7.17 − 7.06 (m, 2H), 6.66 (d, *J* = 16.2 Hz, 1H), 4.85 (s, 2H), 3.01 (s, 3H), 2.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.45 (d, *J* = 3.4 Hz), 161.5, 138.6, 132.0, 129.3, 124.6, 122.6, 119.9, 116.4, 61.6, 36.0, 35.7. HRMS (ESI) calcd for $C_{13}H_{14}FNO_3$ (M + H^+) 252.1030, found 252.1026.

2-(Dimethylamino)-2-oxoethyl (*E*)-3-(2-methoxyphenyl)acrylate (6ea).



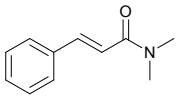
Prepared according to procedure B. A canary yellow solid (38.8 mg, 59%). M.p. 88 °C − 90 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, *J* = 16.2 Hz, 1H), 7.51 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.36 − 7.32 (m, 1H), 6.97 − 6.88 (m, 2H), 6.66 (d, *J* = 16.2 Hz, 1H), 4.84 (s, 2H), 3.87 (s, 3H), 3.01 (s, 3H), 2.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 167.1, 166.8, 158.6, 141.6, 131.8, 129.3, 123.4, 120.8, 117.7, 111.2, 61.5, 55.6, 36.1, 35.7. HRMS (ESI) calcd for $C_{14}H_{17}NO_4$ (M + H^+) 264.1230, found 264.1236.

2-(Dimethylamino)-2-oxoethyl (*E*)-3-(4-chlorophenyl)acrylate (6fa).



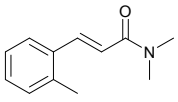
Prepared according to procedure B. A yellow solid (43.5 mg, 65%). M.p. 137 °C − 139 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.83 (s, 2H), 2.99 (s, 3H), 2.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.3, 144.5, 136.4, 132.9, 129.4, 129.3 (d, *J* = 18.8 Hz), 117.9, 61.5, 35.9, 35.7. HRMS (ESI) calcd for $C_{13}H_{14}ClNO_3$ (M + H^+) 268.0735, found 268.0738.

***N,N*-dimethylcinnamamide (7aa)**.



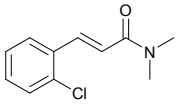
Prepared according to procedure B. A canary yellow solid (15.8 mg, 36%). M.p. 87 °C − 89 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 15.5 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.40 − 7.32 (m, 3H), 6.89 (d, *J* = 15.5 Hz, 1H), 3.18 (s, 3H), 3.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.8, 142.5, 135.5, 129.6, 128.9, 127.9, 117.5, 37.5, 36.1. HRMS (ESI) calcd for $C_{11}H_{13}NO$ (M + H^+) 176.1070, found 176.1068.

(*E*)-*N,N*-dimethyl-3-(o-tolyl)acrylamide (7ba).



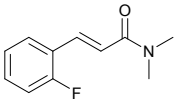
Prepared according to procedure B. A canary yellow solid (12.3 mg, 26%). M.p. 66 °C − 68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 15.3 Hz, 1H), 7.55 − 7.50 (m, 1H), 7.26 − 7.16 (m, 3H), 6.79 (d, *J* = 15.3 Hz, 1H), 3.23 − 3.13 (m, 3H), 3.10 (s, 3H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 167.0, 140.4, 137.6, 134.7, 130.8, 129.4, 126.3 (d, *J* = 2.1 Hz), 118.9, 37.6, 36.6, 20.0. HRMS (ESI) calcd for $C_{12}H_{15}NO$ (M + H^+) 190.1226, found 190.1223.

(*E*)-3-(2-chlorophenyl)-*N,N*-dimethylacrylamide (7ca).



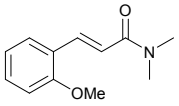
Prepared according to procedure B. A yellow solid (18.3 mg, 35%). M.p. 81 °C − 83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, *J* = 15.5 Hz, 1H), 7.62 − 7.55 (m, 1H), 7.43 − 7.37 (m, 1H), 7.29 − 7.23 (m, 2H), 6.87 (d, *J* = 15.5 Hz, 1H), 3.13 (d, *J* = 17.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.5, 138.4, 134.8, 134.0, 130.3 (d, *J* = 11.7 Hz), 127.8, 127.0, 120.8, 37.7, 36.1. HRMS (ESI) calcd for $C_{11}H_{12}ClNO$ ($M + H^+$) 210.0680, found 210.0673.

(*E*)-3-(2-fluorophenyl)-*N*,*N*-dimethylacrylamide (7da).



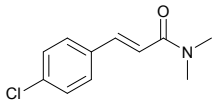
Prepared according to procedure B. A yellow solid (19.3 mg, 40%). M.p. 55 °C − 57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, *J* = 15.7 Hz, 1H), 7.53 − 7.48 (m, 1H), 7.34 − 7.27 (m, 1H), 7.17 − 7.05 (m, 2H), 7.03 (d, *J* = 15.7 Hz, 1H), 3.16 (s, 3H), 3.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.8, 161.4, 135.5, 130.9, 130.0, 124.5, 123.5, 120.7, 116.4, 37.5, 36.1. HRMS (ESI) calcd for $C_{11}H_{12}FNO$ ($M + H^+$) 194.0976, found 194.0979.

(*E*)-3-(2-methoxyphenyl)-*N*,*N*-dimethylacrylamide (7ea).



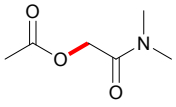
Prepared according to procedure B. A yellow solid (16.9 mg, 33%). M.p. 59 °C − 60 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 15.6 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.34 − 7.28 (m, 1H), 7.03 − 6.90 (m, 3H), 3.88 (s, 3H), 3.11 (s, 6H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 167.5, 158.3, 138.0, 130.7, 129.1, 124.6, 120.7, 118.6, 111.2, 55.6, 37.6, 36.0. HRMS (ESI) calcd for $C_{12}H_{15}NO_2$ ($M + H^+$) 206.1176, found 206.1165.

(*E*)-3-(4-chlorophenyl)-*N*,*N*-dimethylacrylamide (7fa).



Prepared according to procedure B. A yellow solid (15.6 mg, 30%). M.p. 120 °C − 122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, *J* = 15.2 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 15.4 Hz, 1H), 3.17 (s, 3H), 3.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 166.6, 141.1, 135.5, 134.0, 129.2, 129.1, 118.1, 37.6, 36.1. HRMS (ESI) calcd for $C_{11}H_{12}ClNO$ ($M + H^+$) 210.0680, found 210.0674.

2-(dimethylamino)-2-oxoethyl acetate.



Prepared according to procedure A. A canary yellow gummy solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.69 (s, 2H), 2.95 (d, J = 3.8 Hz, 6H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 170.8, 166.5, 61.4, 35.9, 35.7, 20.7. HRMS (ESI) calcd for $C_6H_{12}NO_3$ ($M + H^+$) 146.0812.

10. References

1. M. J. D. Grandi, C. Bennett, K. Cagino, A. Muccini, C. Suraci and S. Saba, *Synth. Commun.,* 2015, **45**, 2601-2607.

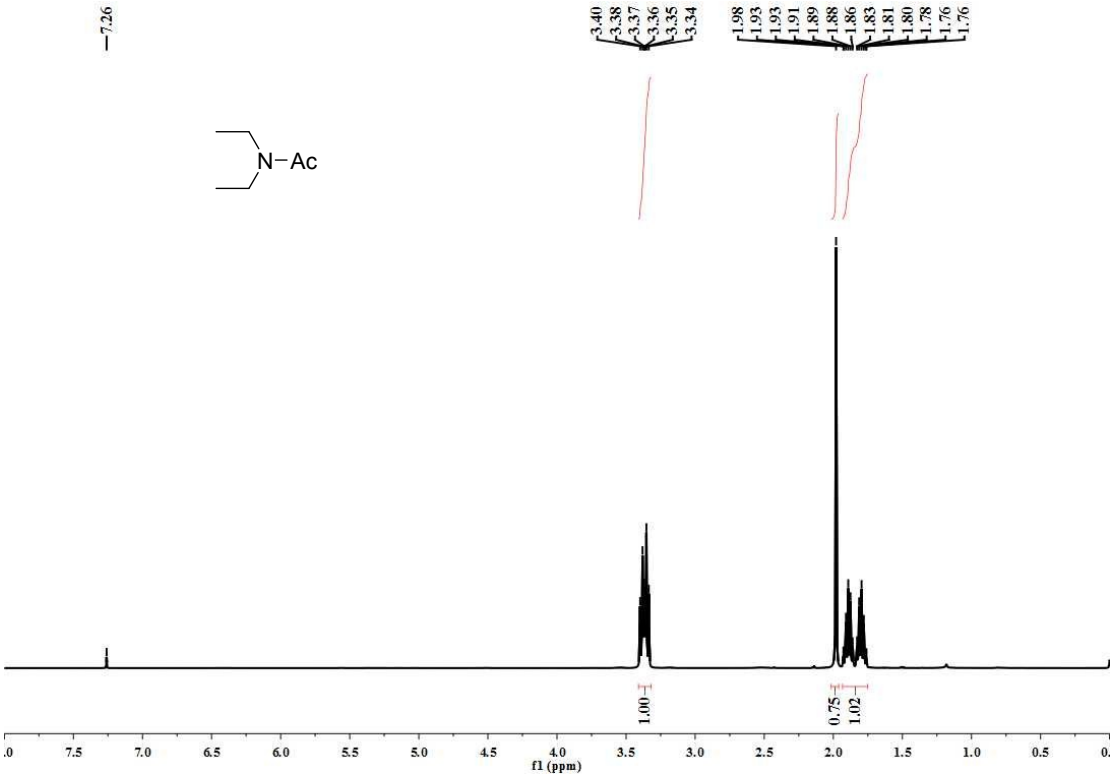
2. (a) J. Liu, X. Zhang, H. Yi, C. Liu, R. Liu, H. Zhang, K. Zhuo and A. Lei, *Angew. Chem., Int. Ed.*, 2015, 54, 1261-1265; (b) Q. Wu, Y. Luo, A. Lei and J. You, *J. Am. Chem. Soc.*, 2016, **138**, 2885-2888.

3. K. Yang, F. Zhou, Z. Kuang, G. Gao, T. G. Driver and Q. Song, *Org. Lett.*, 2016, **18**, 4088-4091.

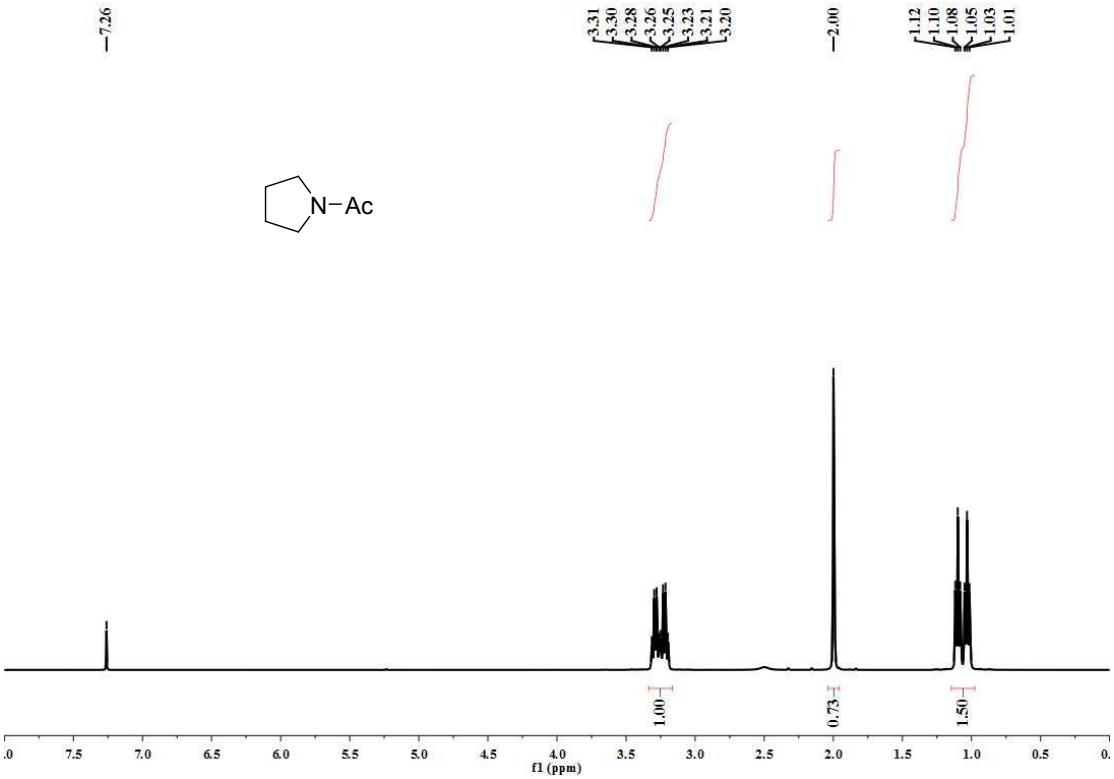
4. S. Priyadarshini, P. J. A. Joseph and M. L. Kantam, *RSC Adv*., 2013, **3**, 18283-18287.

11. NMR spectra

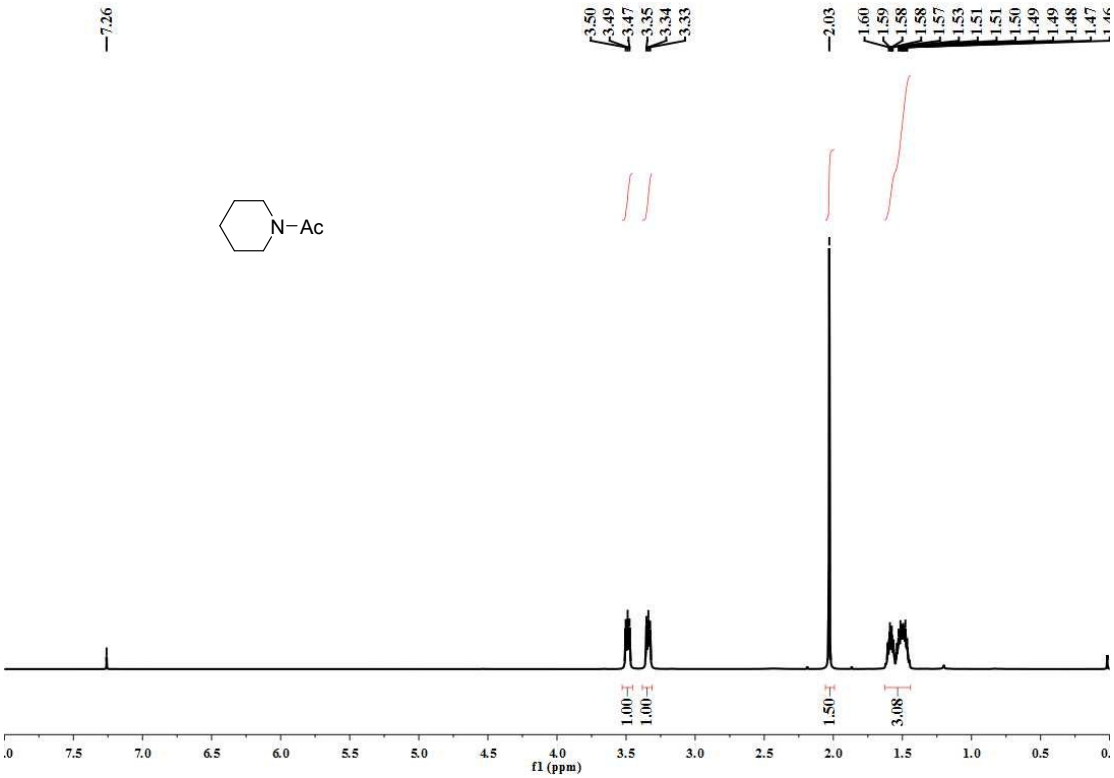
***N,N*-Diethylacetamide (2b): ^{1}H NMR ($CDCl_3$, 400 MHz)**



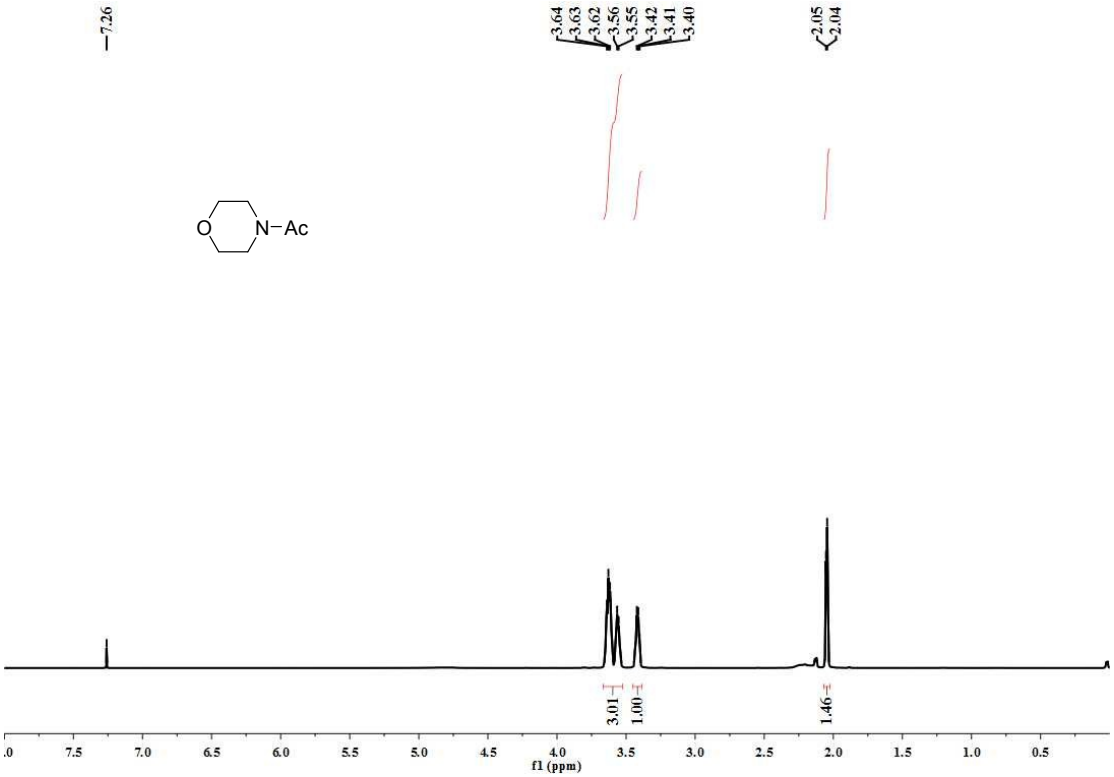
***N*-Acetylpyrrolidine (2c): ^{1}H NMR ($CDCl_3$, 400 MHz)**



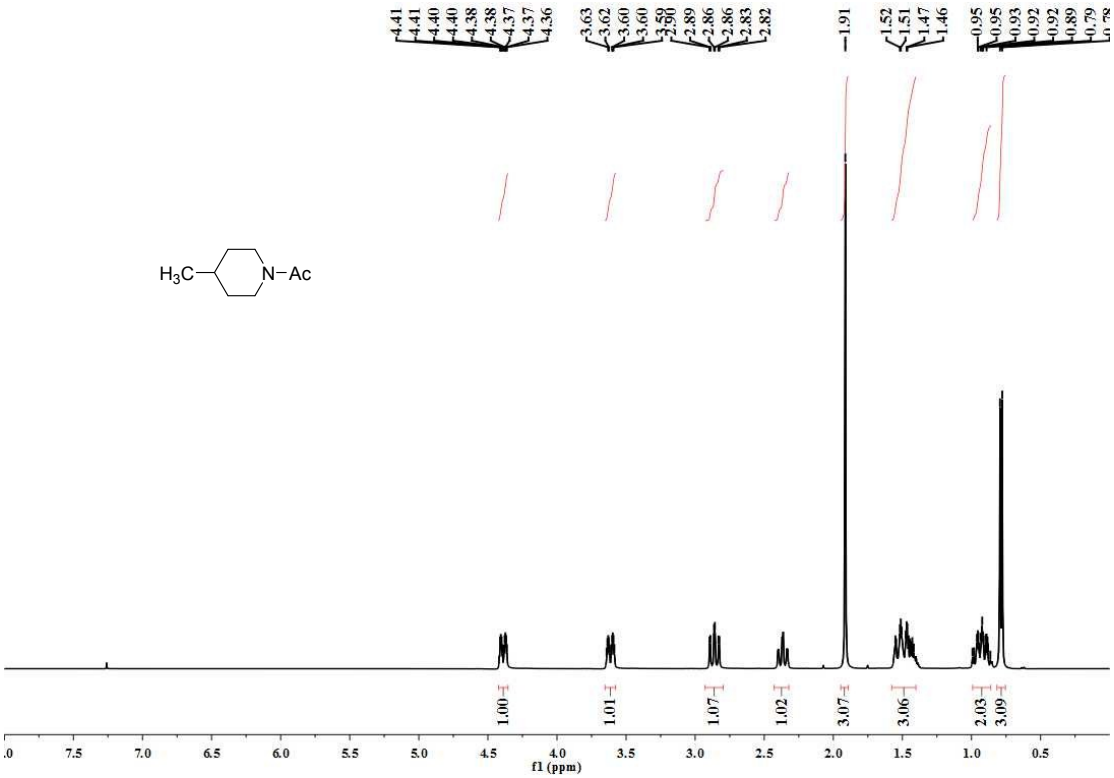
***N*-Acetylpiperidine (2d): ^{1}H NMR ($CDCl_3$, 400 MHz)**



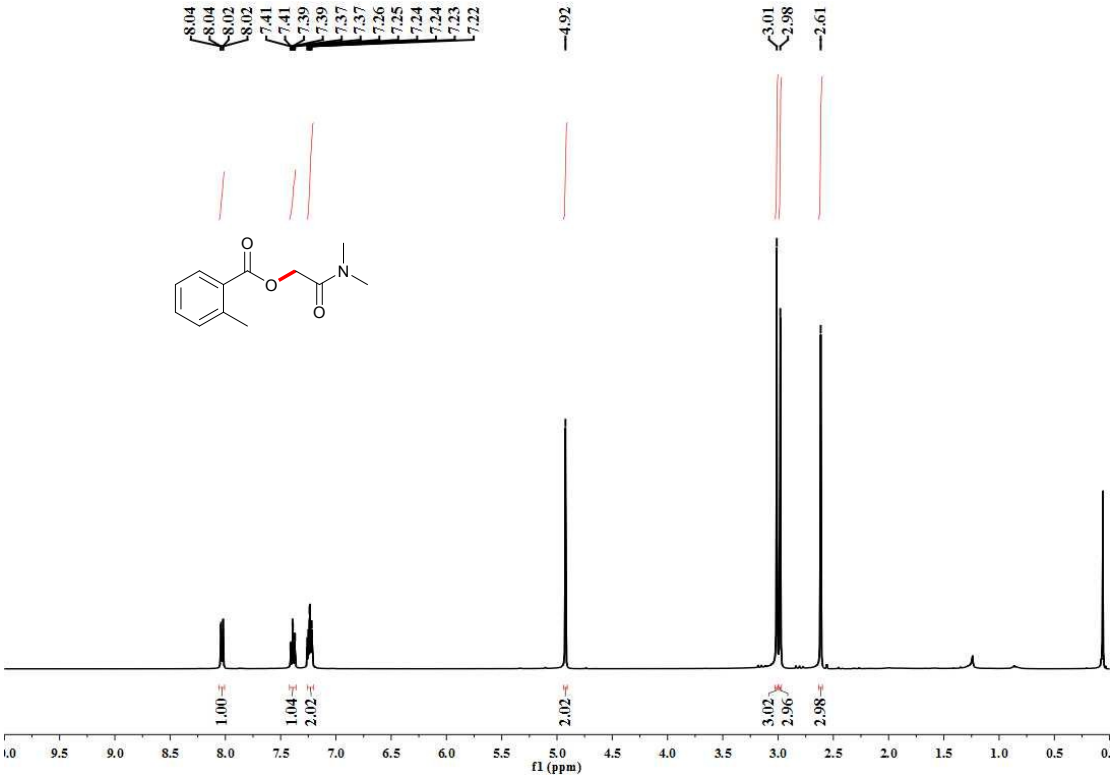
***N*-Acetylmorpholine (2e): ^{1}H NMR ($CDCl_3$, 400 MHz)**



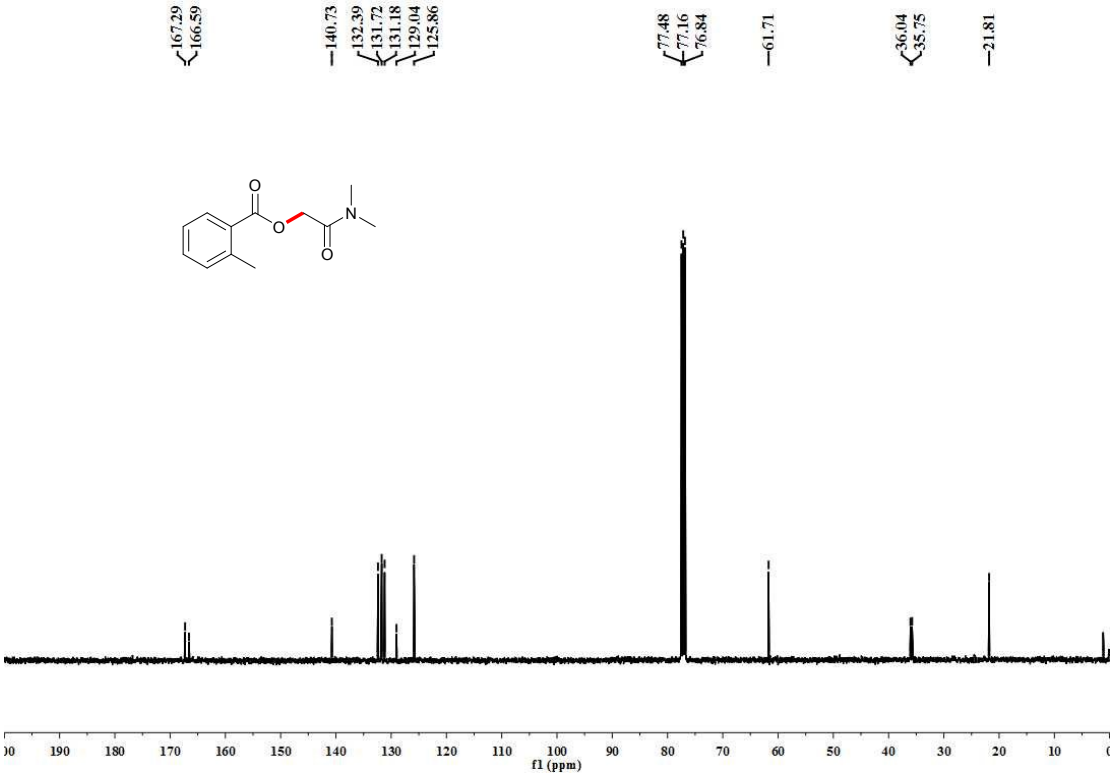
4-Methylpiperidine (2f): ^{1}H NMR ($CDCl_3$, 400 MHz)



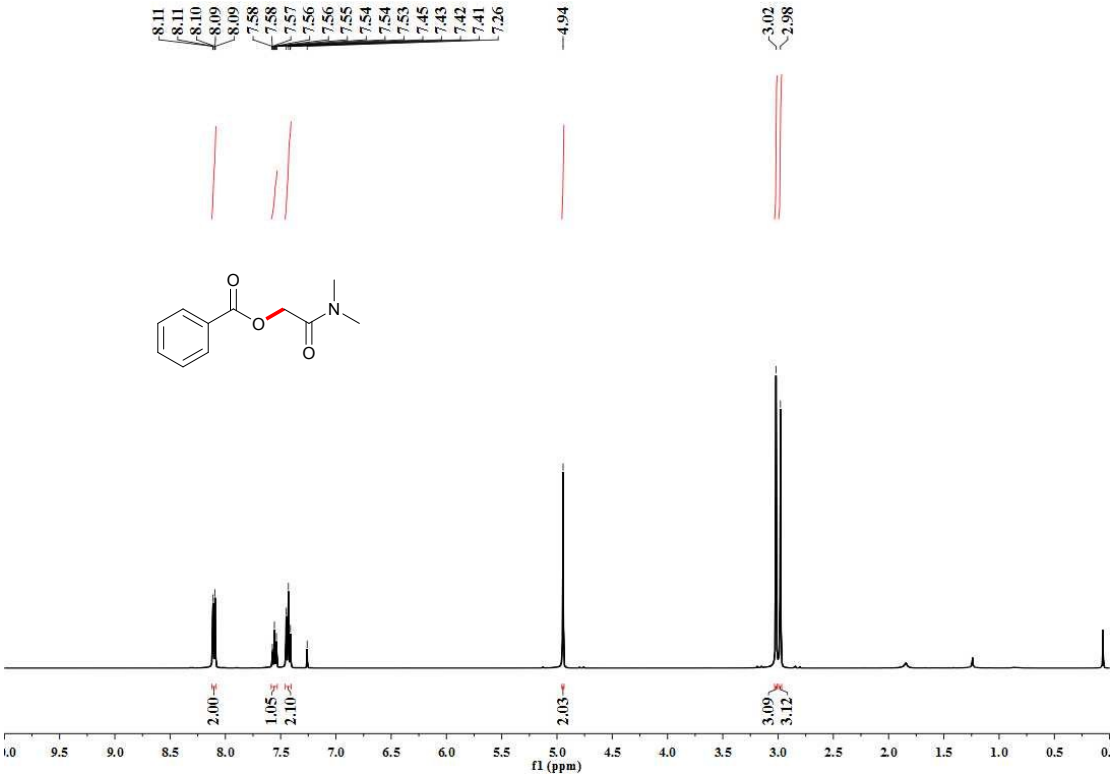
2-(Dimethylamino)-2-oxoethyl 2-methylbenzoate (3aa): ^{1}H NMR ($CDCl_3$, 400 MHz)



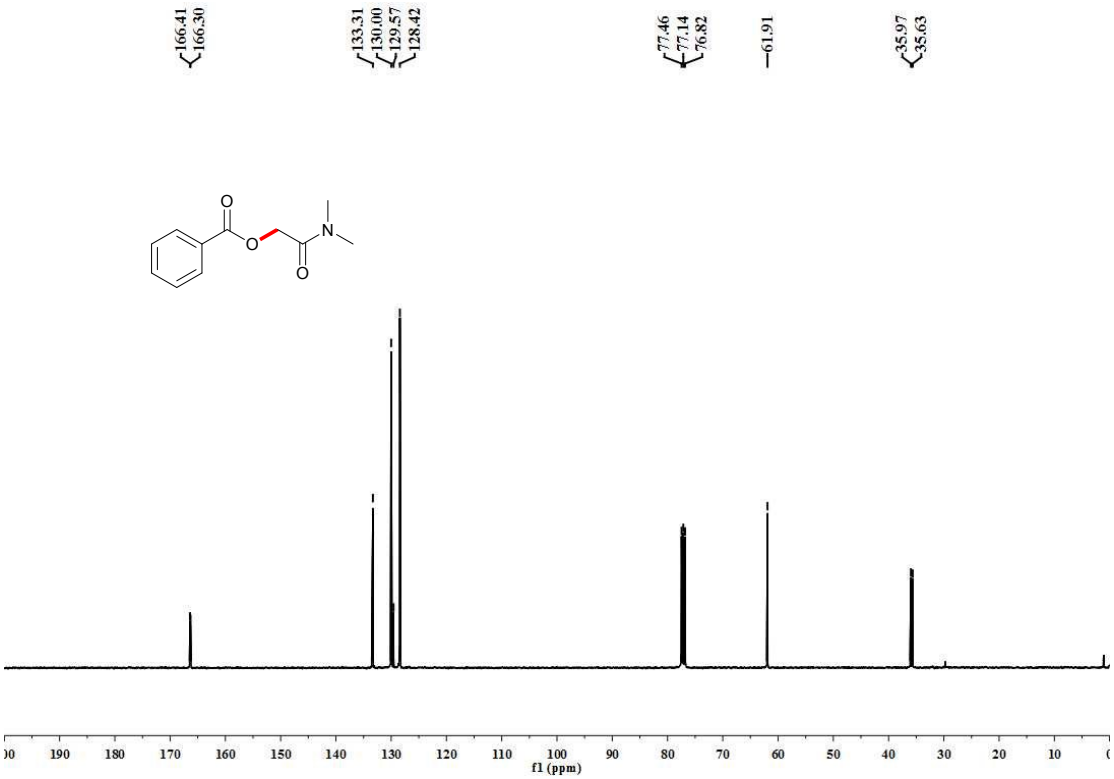
2-(Dimethylamino)-2-oxoethyl 2-methylbenzoate (3aa): ^{13}C NMR ($CDCl_3$, 101 MHz)



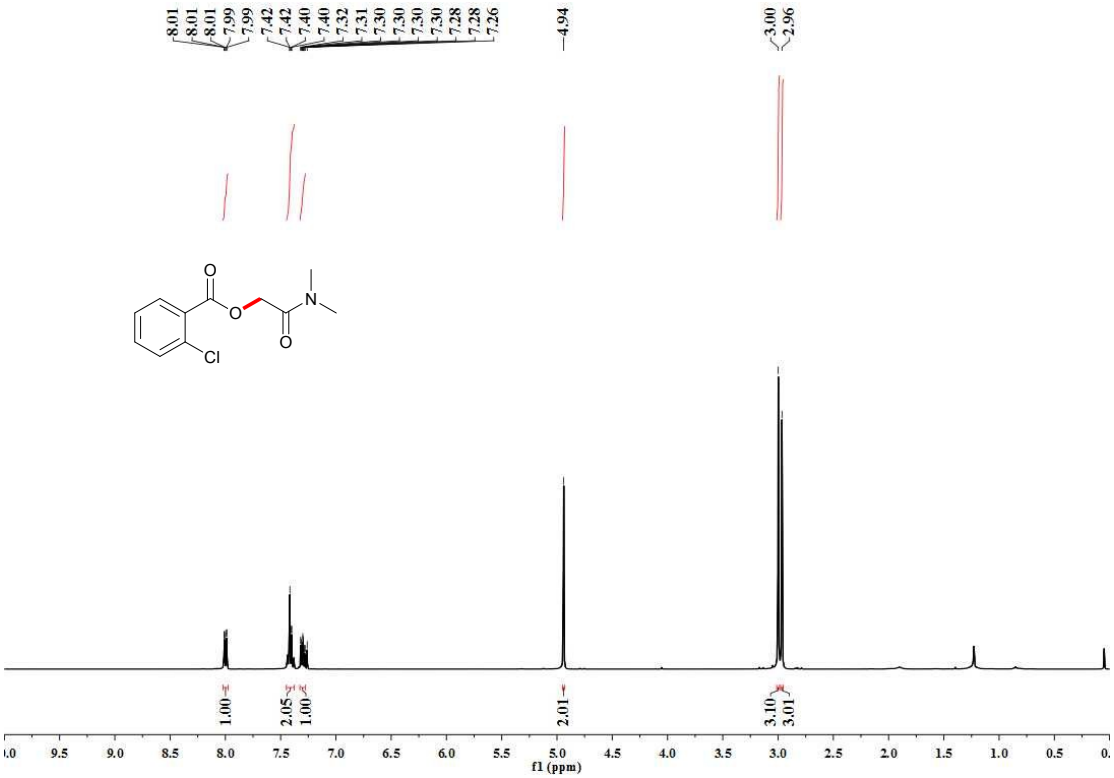
2-(Dimethylamino)-2-oxoethyl benzoate (3ba): ^{1}H NMR ($CDCl_3$, 400 MHz)



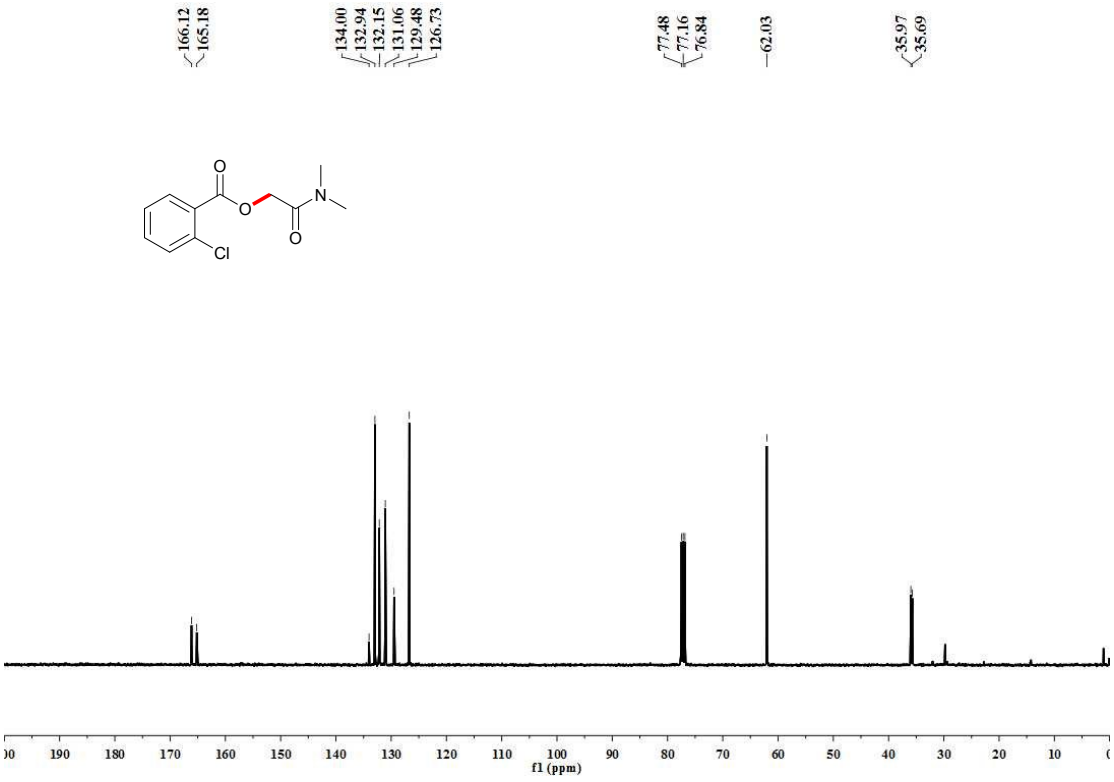
2-(Dimethylamino)-2-oxoethyl benzoate (3ba): ^{13}C NMR ($CDCl_3$, 101MHz)



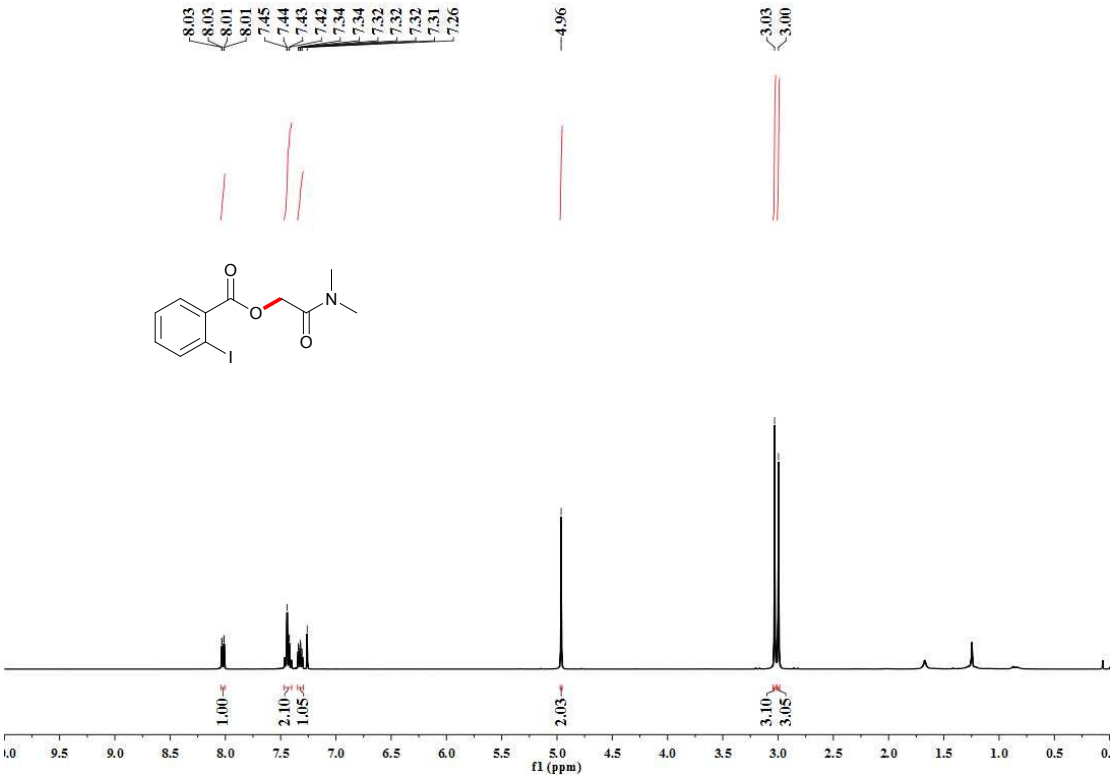
2-(Dimethylamino)-2-oxoethyl 2-chlorobenzoate (3ca): ^{1}H NMR ($CDCl_3$, 400 MHz)



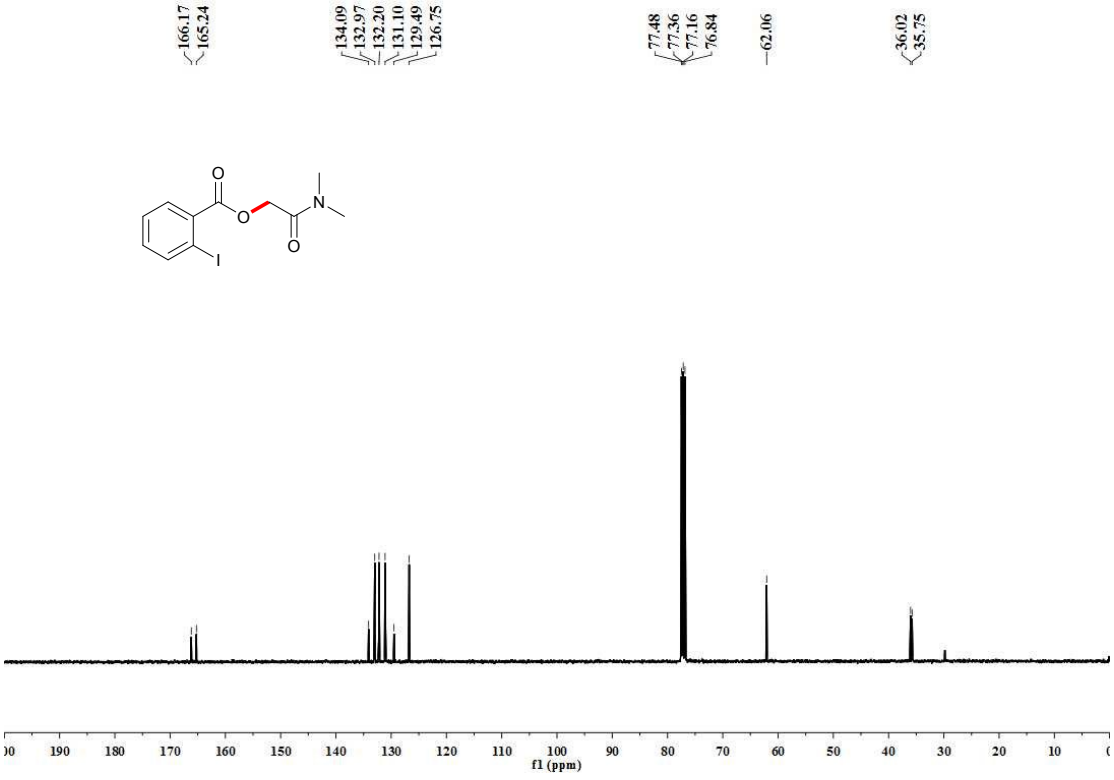
2-(Dimethylamino)-2-oxoethyl 2-chlorobenzoate (3ca): ^{13}C NMR ($CDCl_3$, 101 MHz)



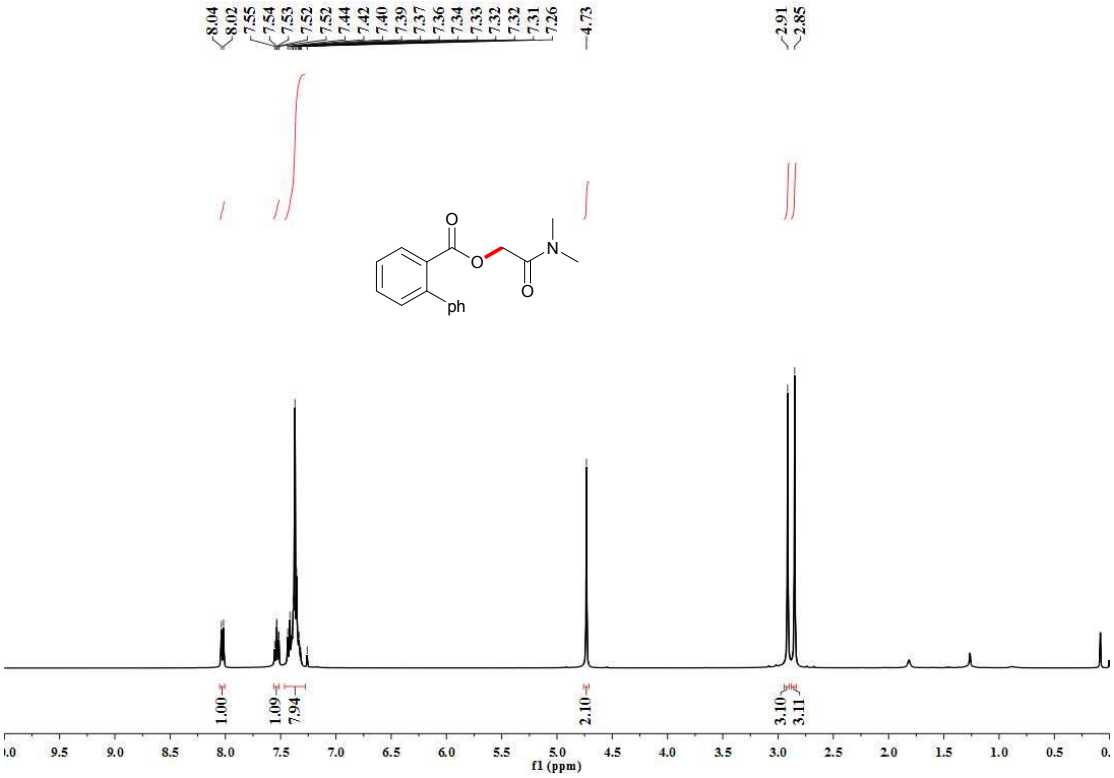
2-(Dimethylamino)-2-oxoethyl 2-iodobenzoate (3da): ^{1}H NMR ($CDCl_3$, 400 MHz)



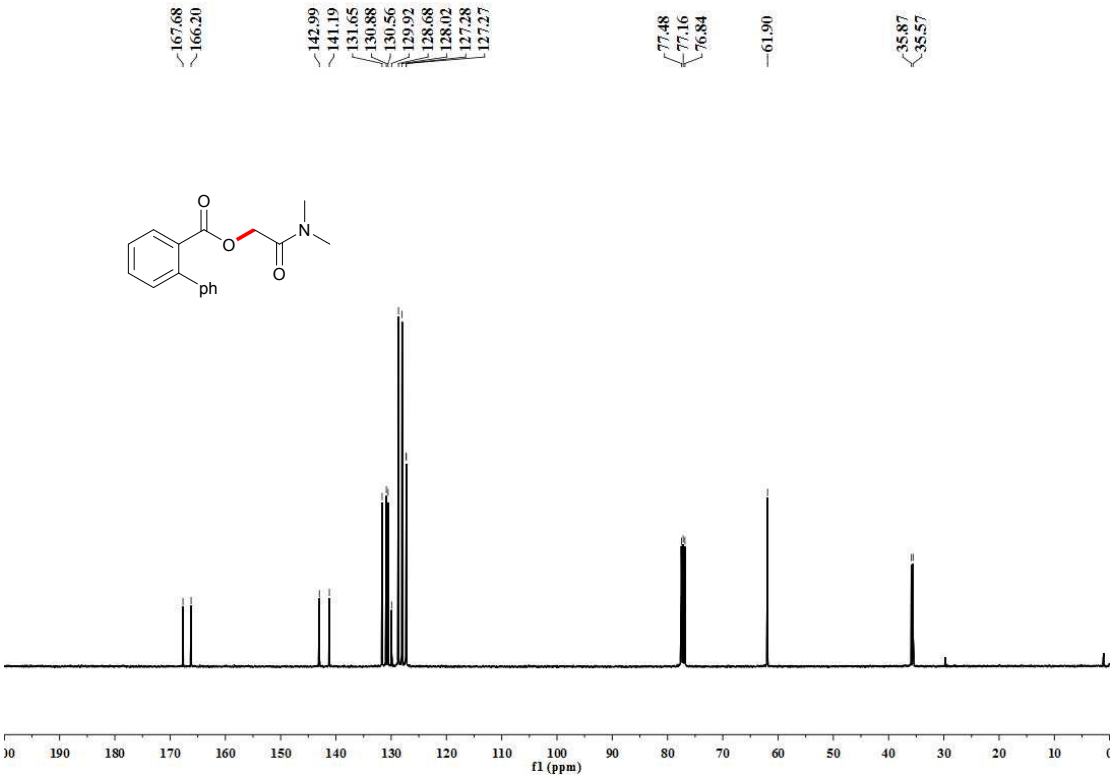
2-(Dimethylamino)-2-oxoethyl 2-iodobenzoate (3da): ^{13}C NMR ($CDCl_3$, 101 MHz)



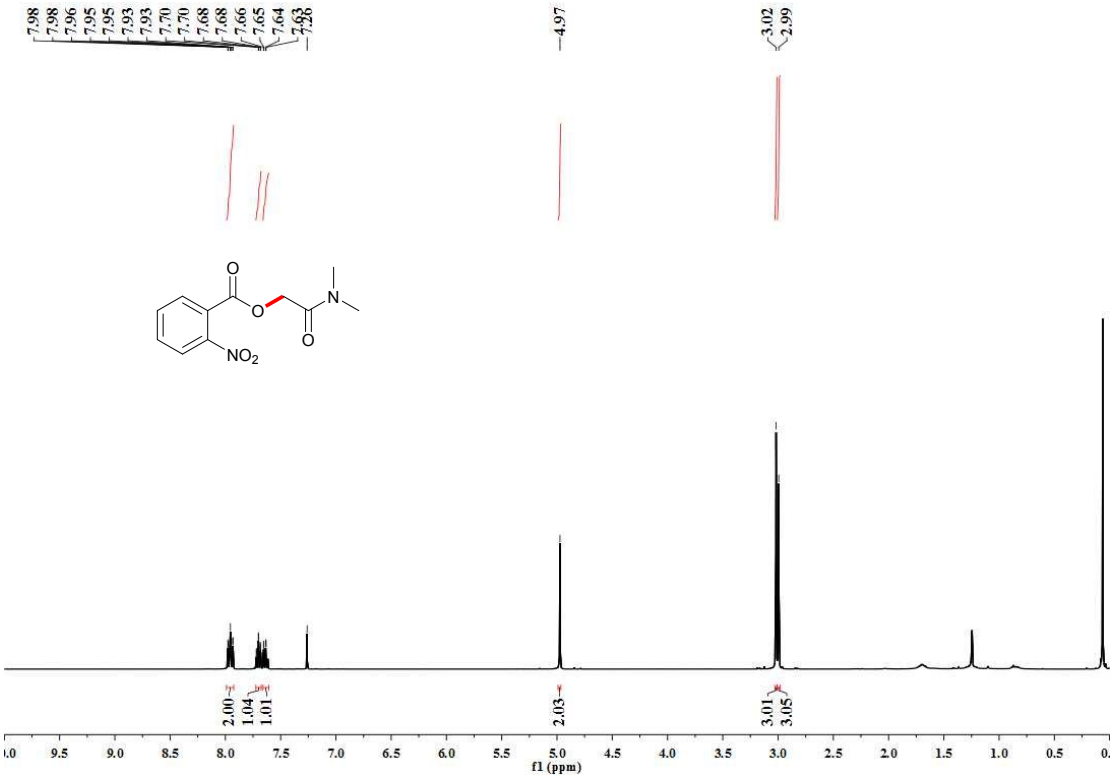
2-(Dimethylamino)-2-oxoethyl 2-phenylbenzoate (3ea): ^{1}H NMR ($CDCl_3$, 400 MHz)



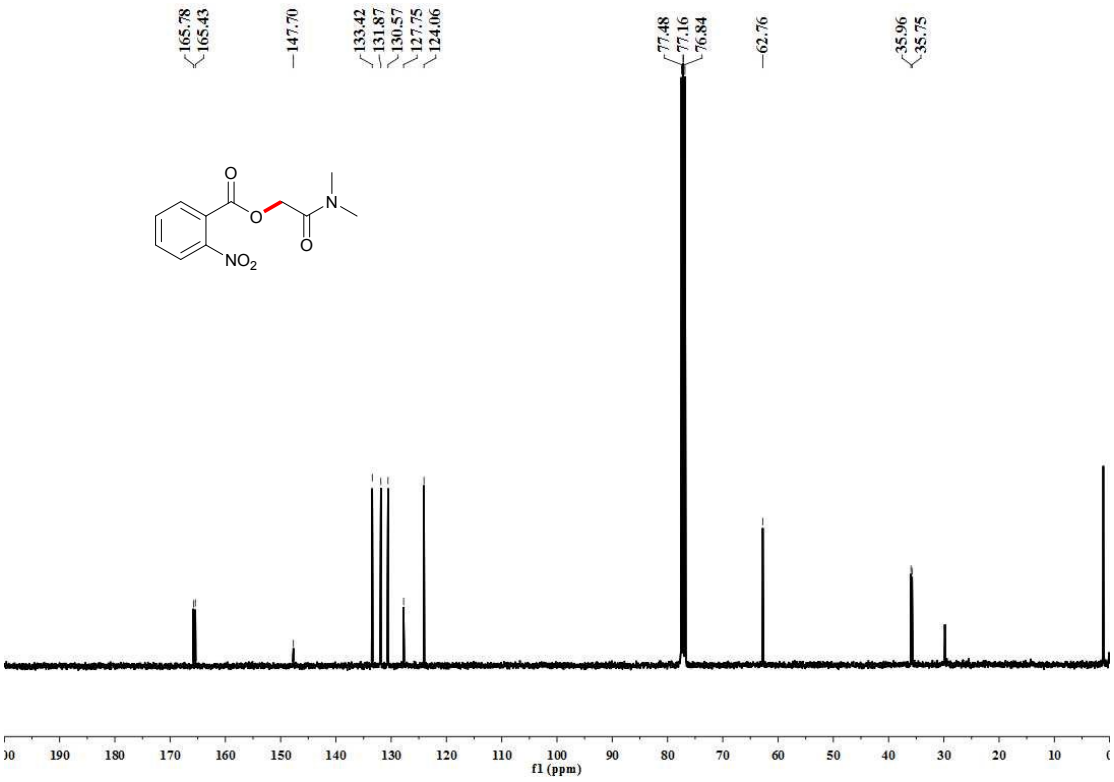
2-(Dimethylamino)-2-oxoethyl 2-phenylbenzoate (3ea): ^{13}C NMR ($CDCl_3$, 101 MHz)



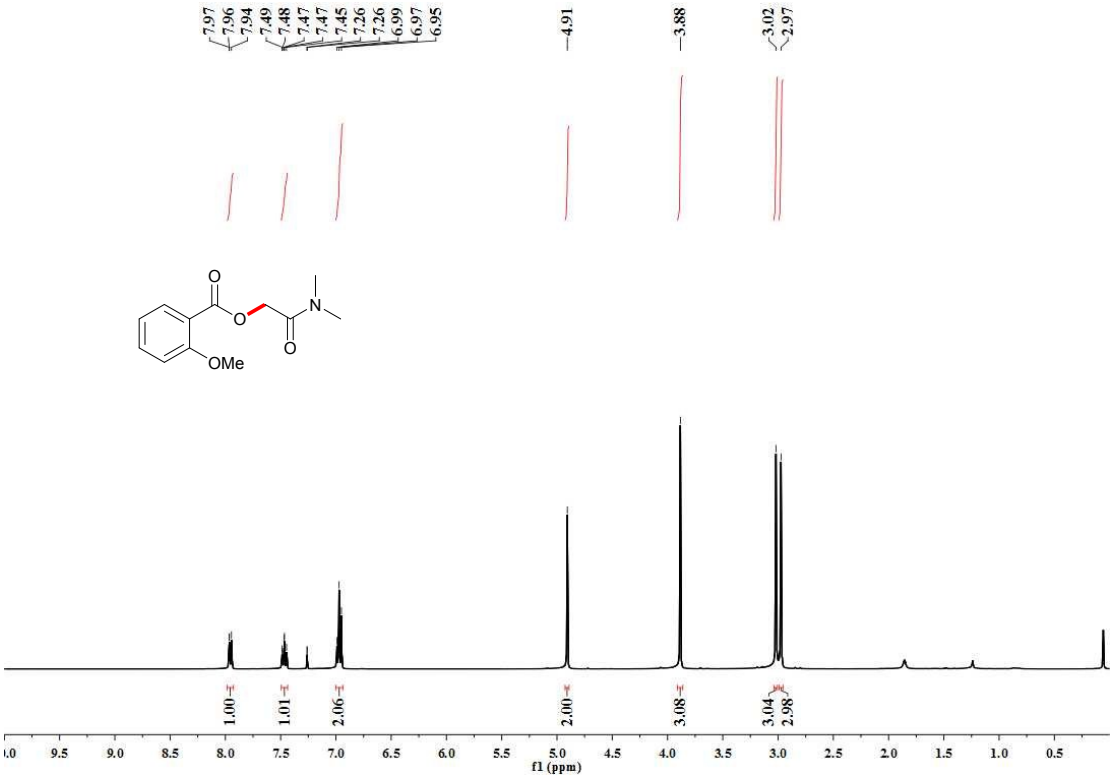
2-(Dimethylamino)-2-oxoethyl 2-nitrobenzoate (3fa): ^{1}H NMR ($CDCl_3$, 400 MHz)



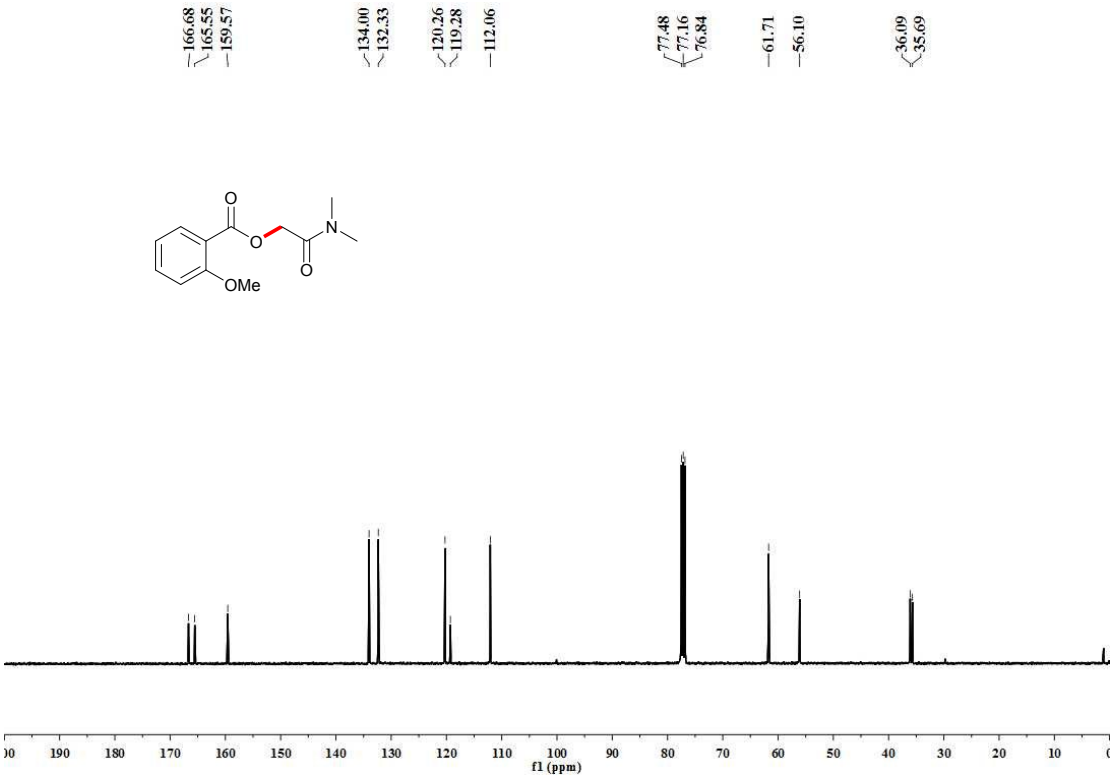
2-(Dimethylamino)-2-oxoethyl 2-nitrobenzoate (3fa): ^{13}C NMR ($CDCl_3$, 101 MHz)



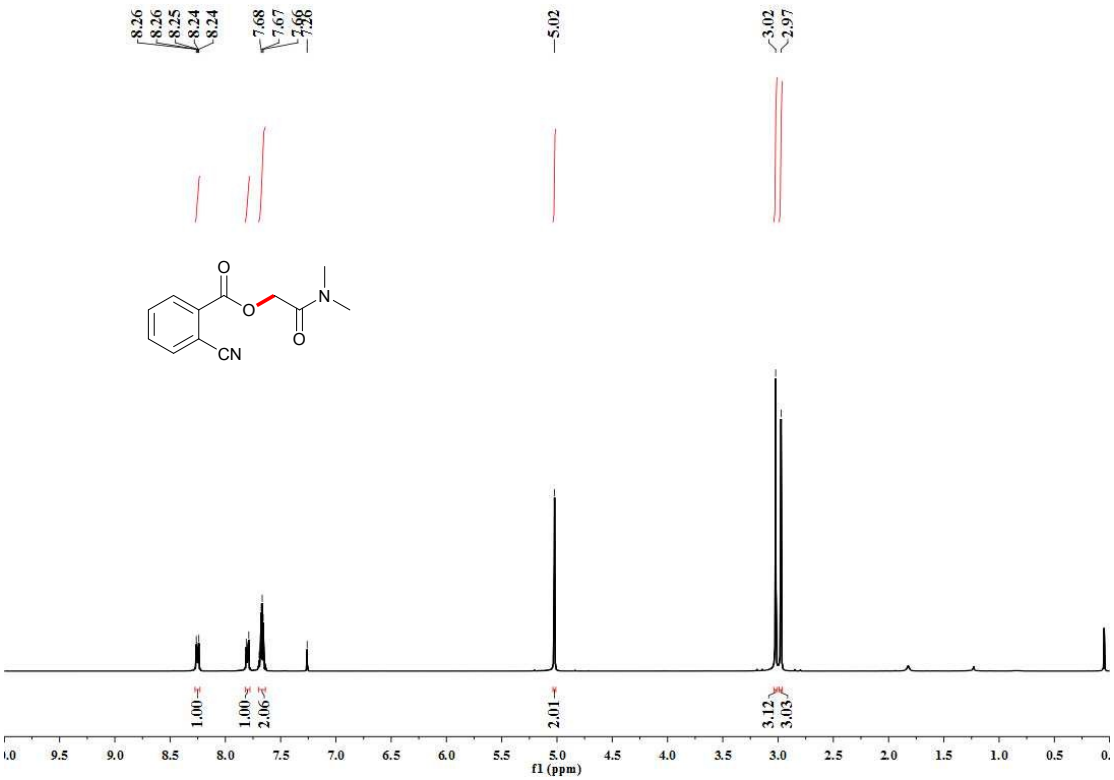
2-(Dimethylamino)-2-oxoethyl 2-methoxybenzoate (3ga): ^{1}H NMR ($CDCl_3$, 400 MHz)



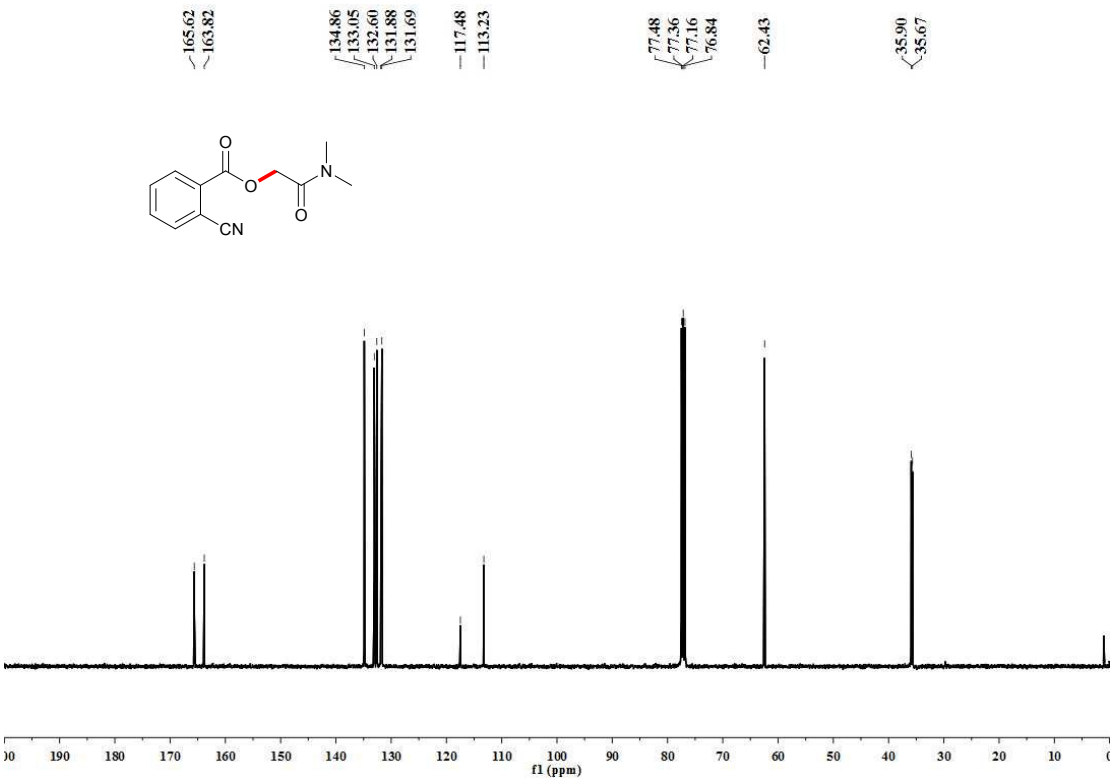
2-(Dimethylamino)-2-oxoethyl 2-methoxybenzoate (3ga): ^{13}C NMR ($CDCl_3$, 101 MHz)



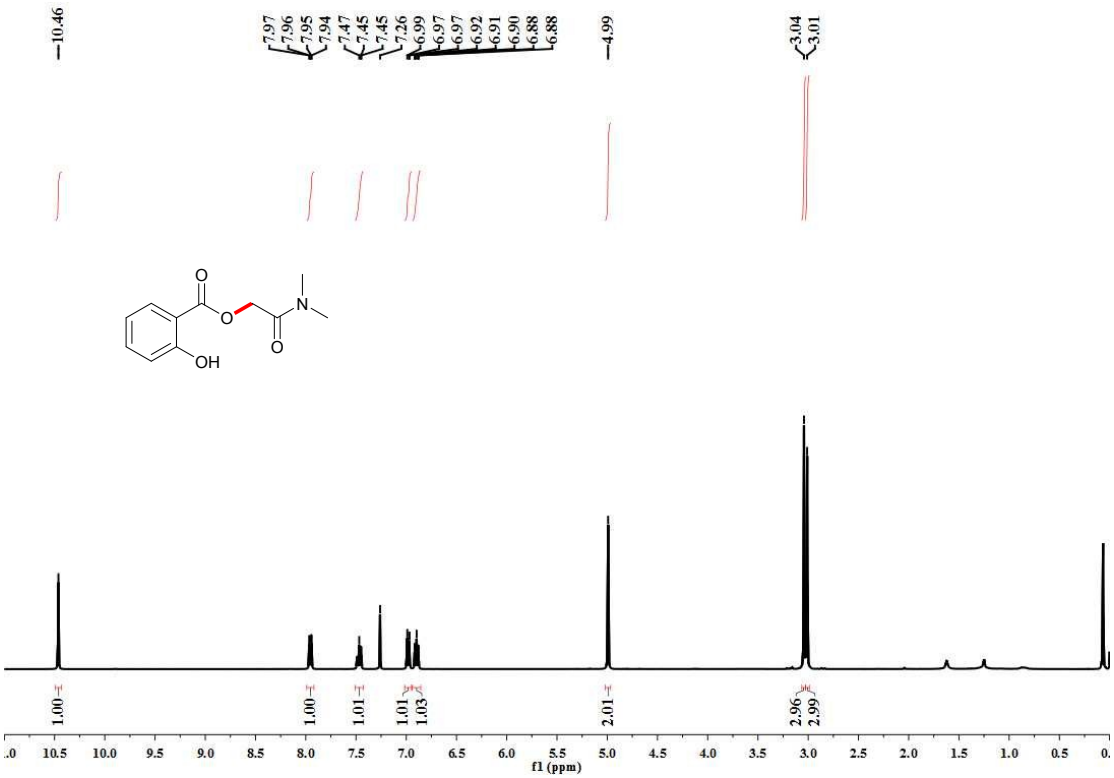
2-(Dimethylamino)-2-oxoethyl 2-cyanobenzoate (3ha): ^{1}H NMR ($CDCl_3$, 400 MHz)



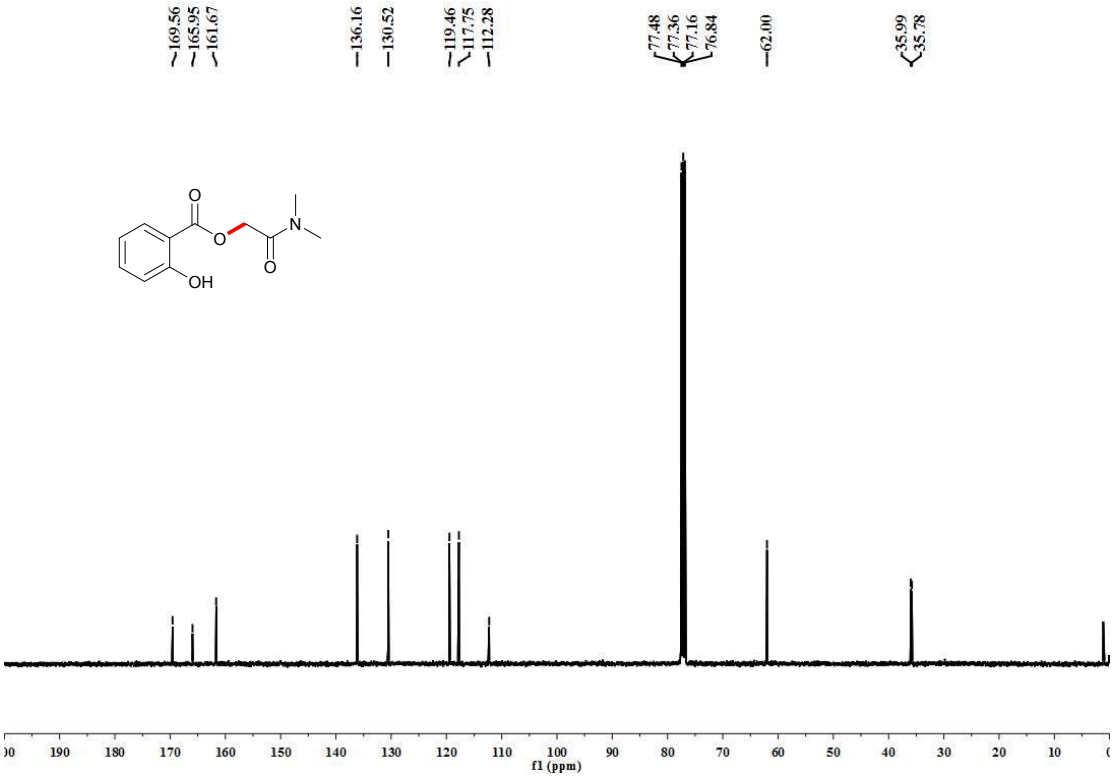
2-(Dimethylamino)-2-oxoethyl 2-cyanobenzoate (3ha): ^{13}C NMR ($CDCl_3$, 101 MHz)



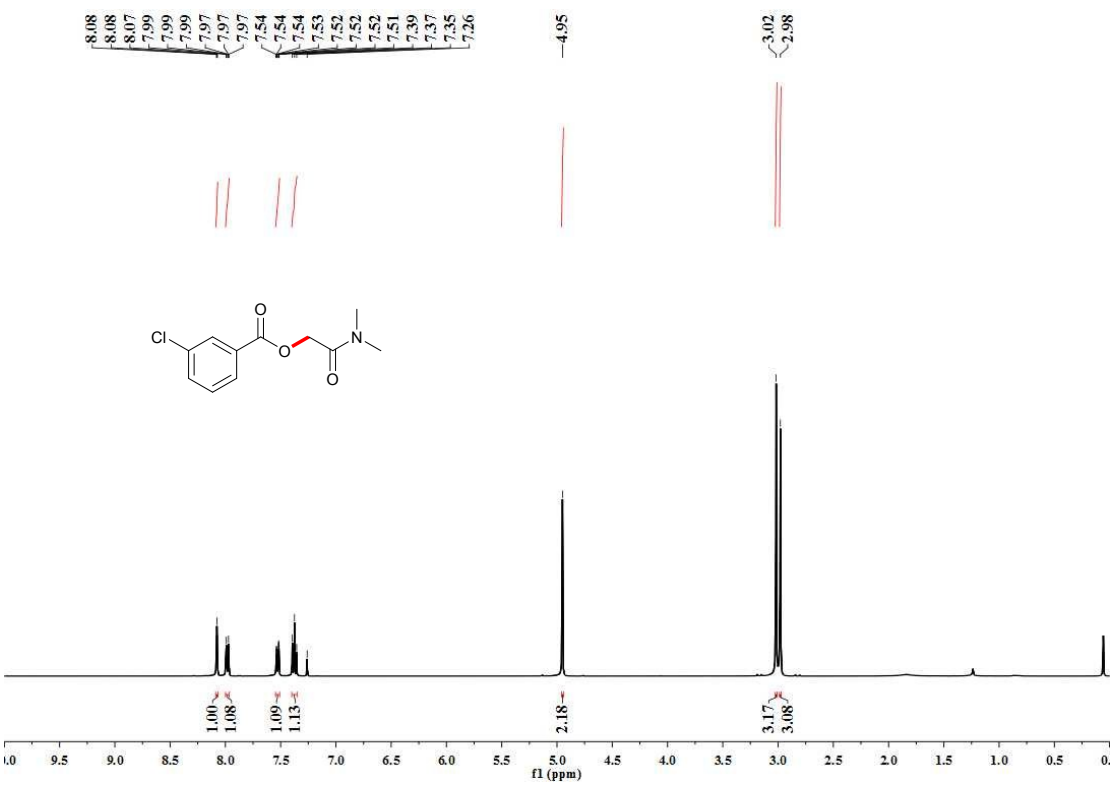
2-(Dimethylamino)-2-oxoethyl 2-hydroxylbenzoate (3ia): ^{1}H NMR ($CDCl_3$, 400 MHz)



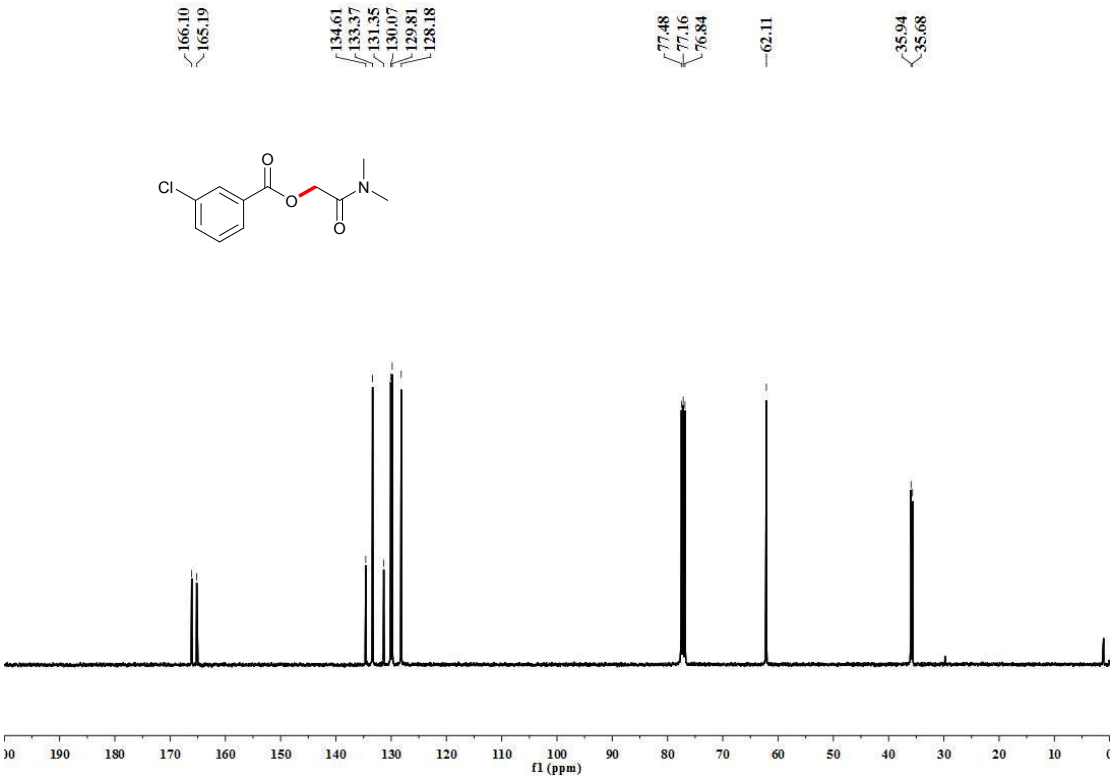
2-(Dimethylamino)-2-oxoethyl 2-hydroxylbenzoate (3ia): ^{13}C NMR ($CDCl_3$, 101 MHz)



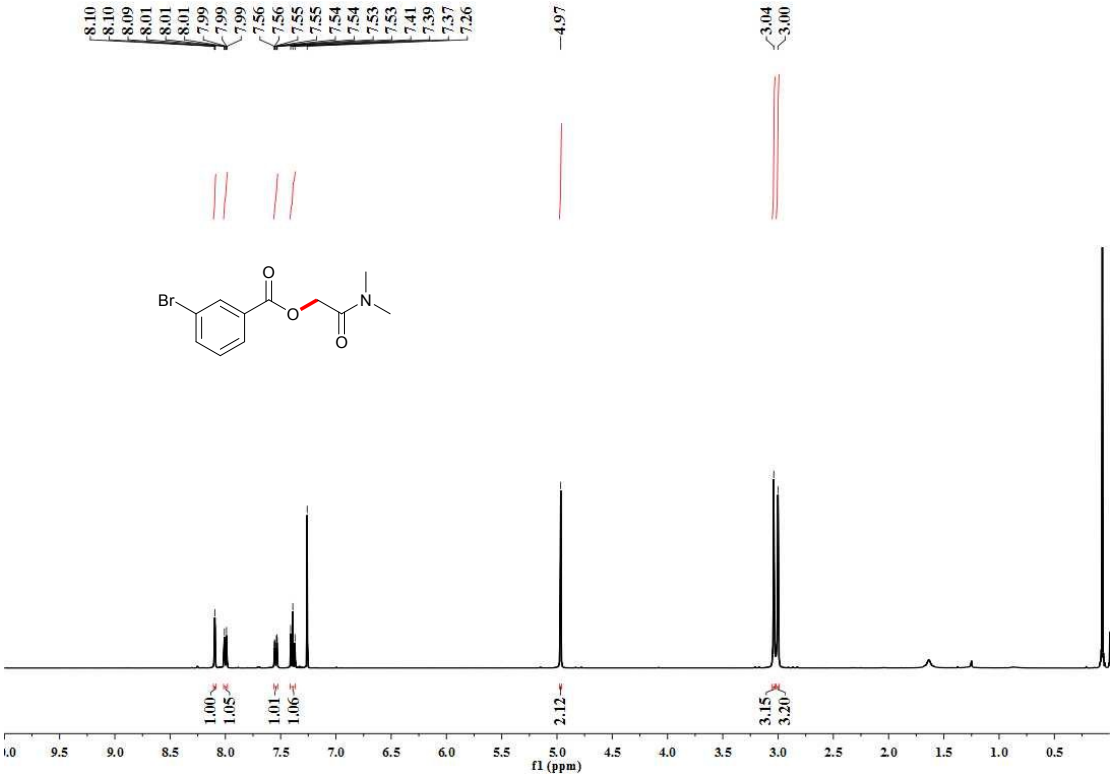
2-(Dimethylamino)-2-oxoethyl 3-chlorobenzoate (3ja): ^{1}H NMR ($CDCl_3$, 400 MHz)



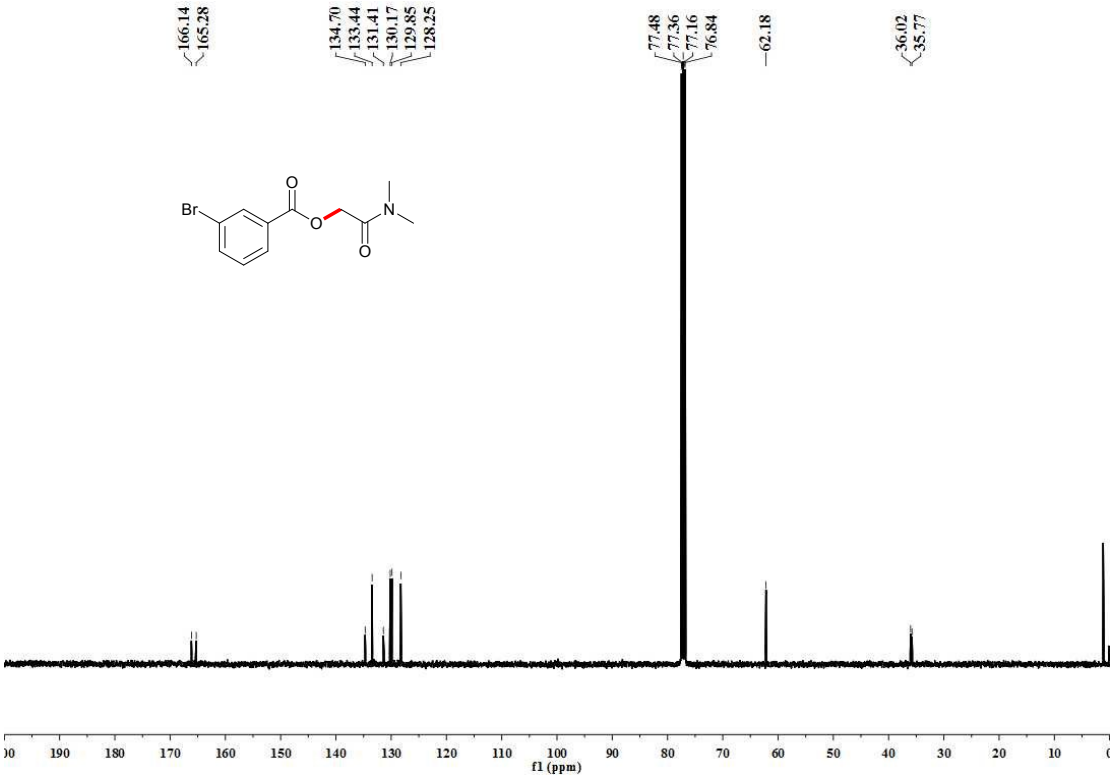
2-(Dimethylamino)-2-oxoethyl 3-chlorobenzoate (3ja): ^{13}C NMR ($CDCl_3$, 101 MHz)



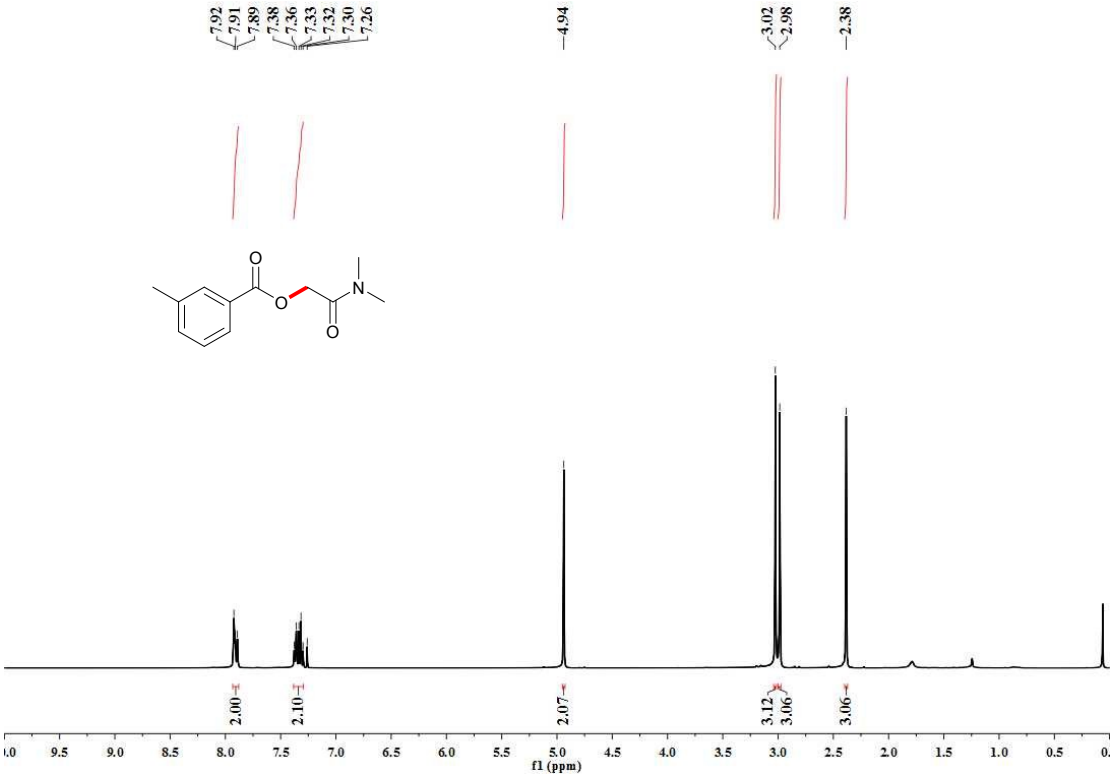
2-(Dimethylamino)-2-oxoethyl 3-bromobenzoate (3ka): ^{1}H NMR ($CDCl_3$, 400 MHz)



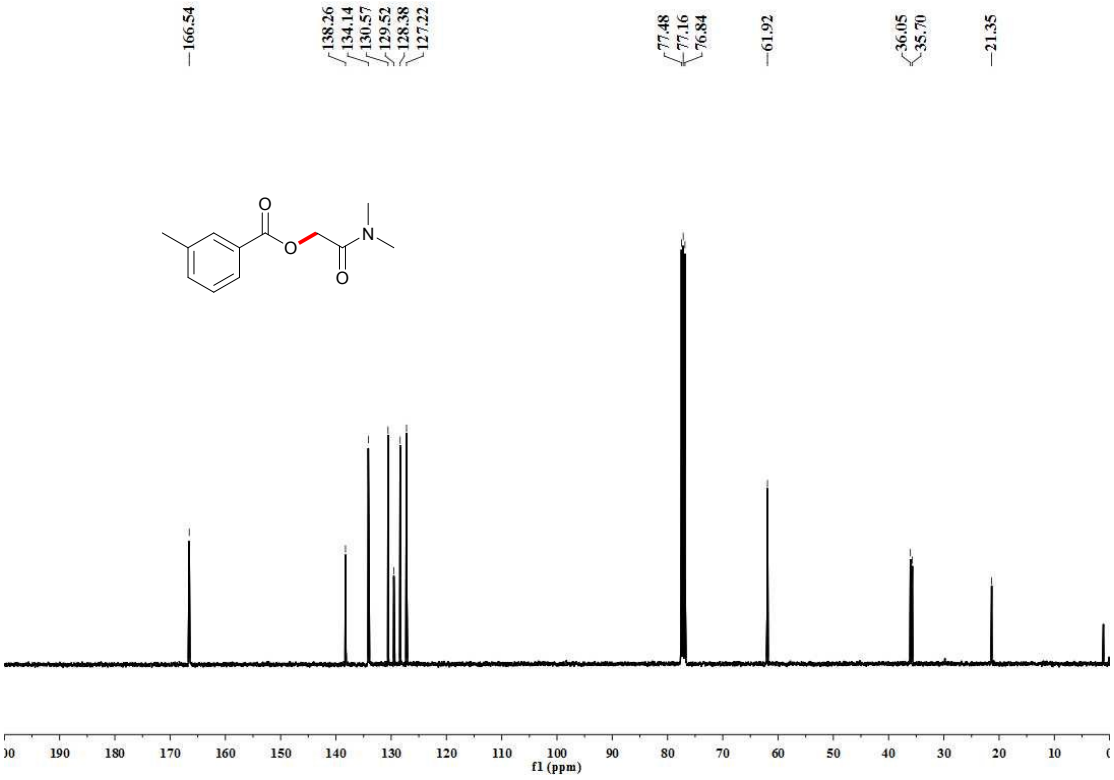
2-(Dimethylamino)-2-oxoethyl 3-bromobenzoate (3ka): ^{13}C NMR ($CDCl_3$, 101 MHz)



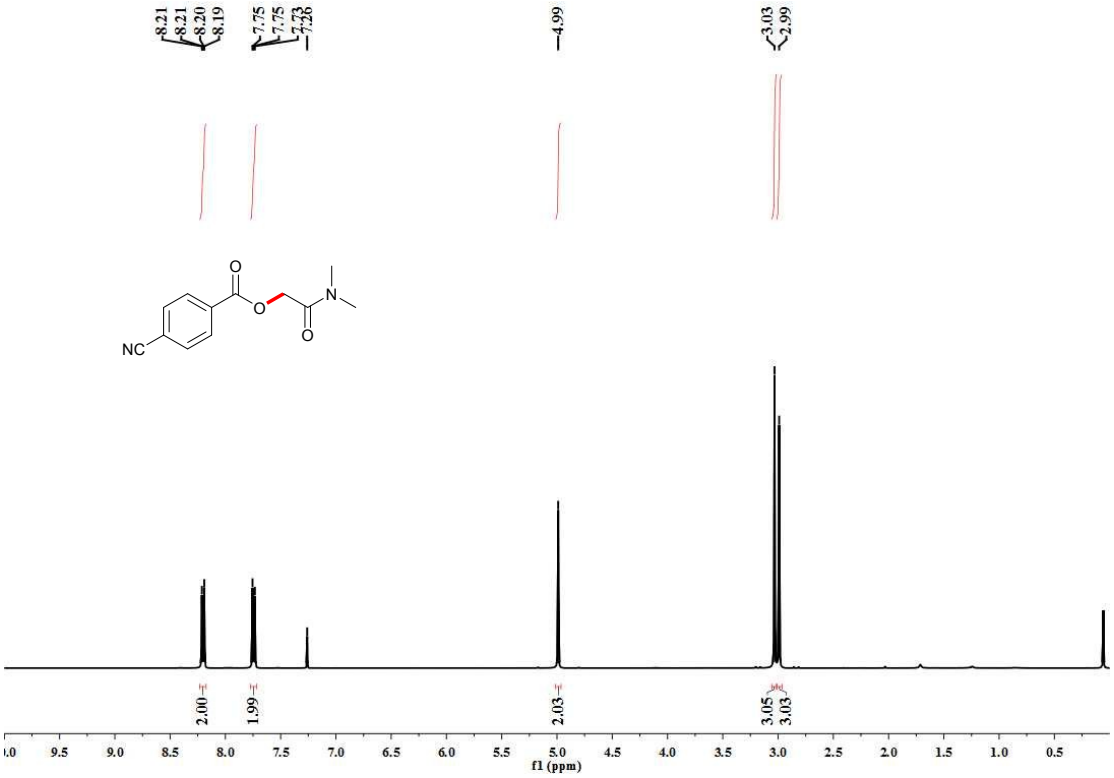
2-(Dimethylamino)-2-oxoethyl 3-methylbenzoate (3la): ^{1}H NMR ($CDCl_3$, 400 MHz)



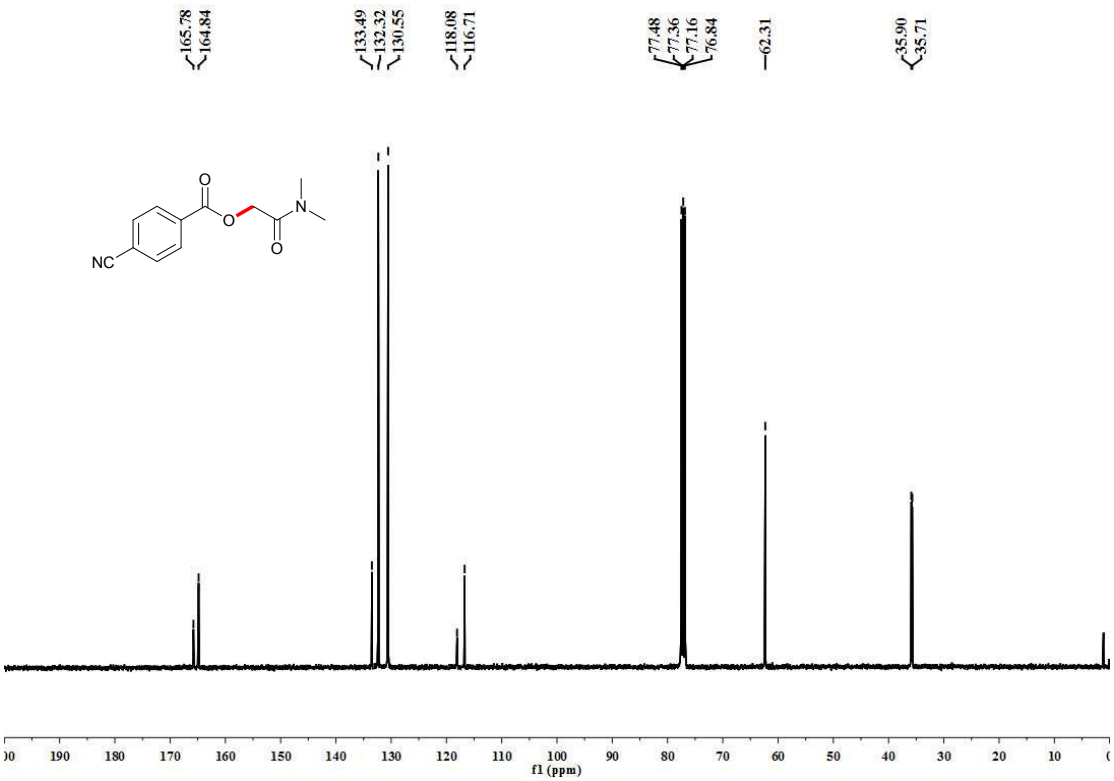
2-(Dimethylamino)-2-oxoethyl 3-methylbenzoate (3la): ^{13}C NMR ($CDCl_3$, 101 MHz)



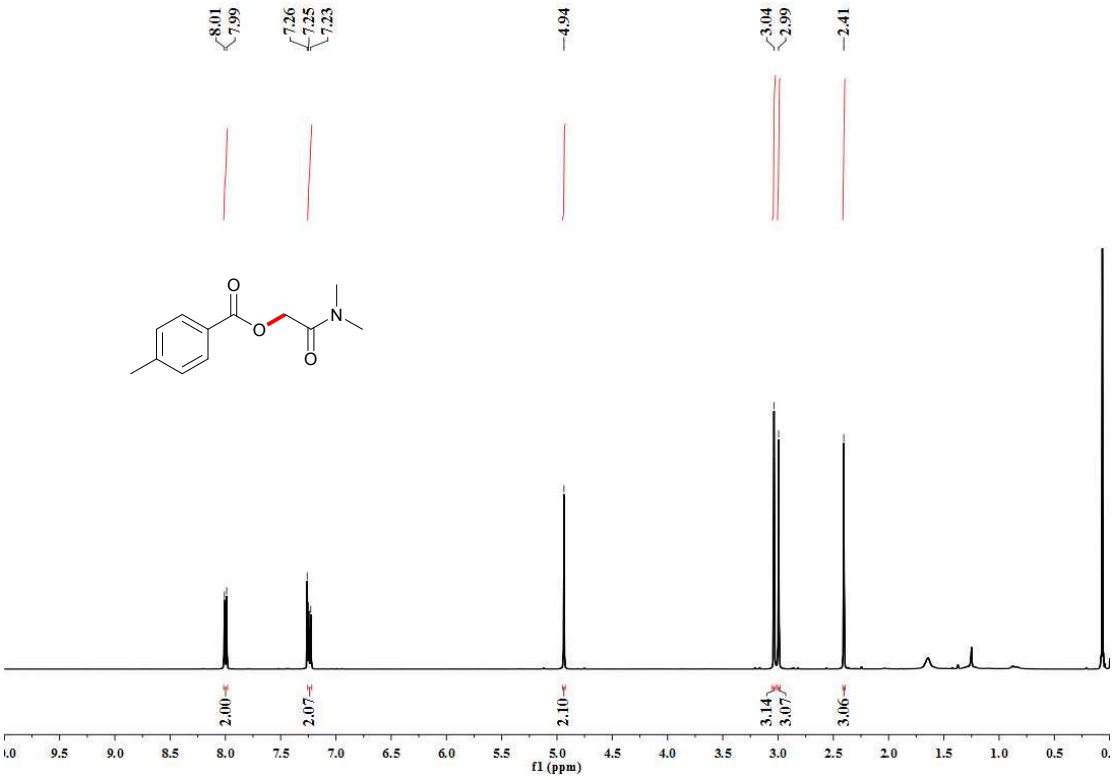
2-(Dimethylamino)-2-oxoethyl 4-cyanobenzoate (3ma): ^{1}H NMR ($CDCl_3$, 400 MHz)



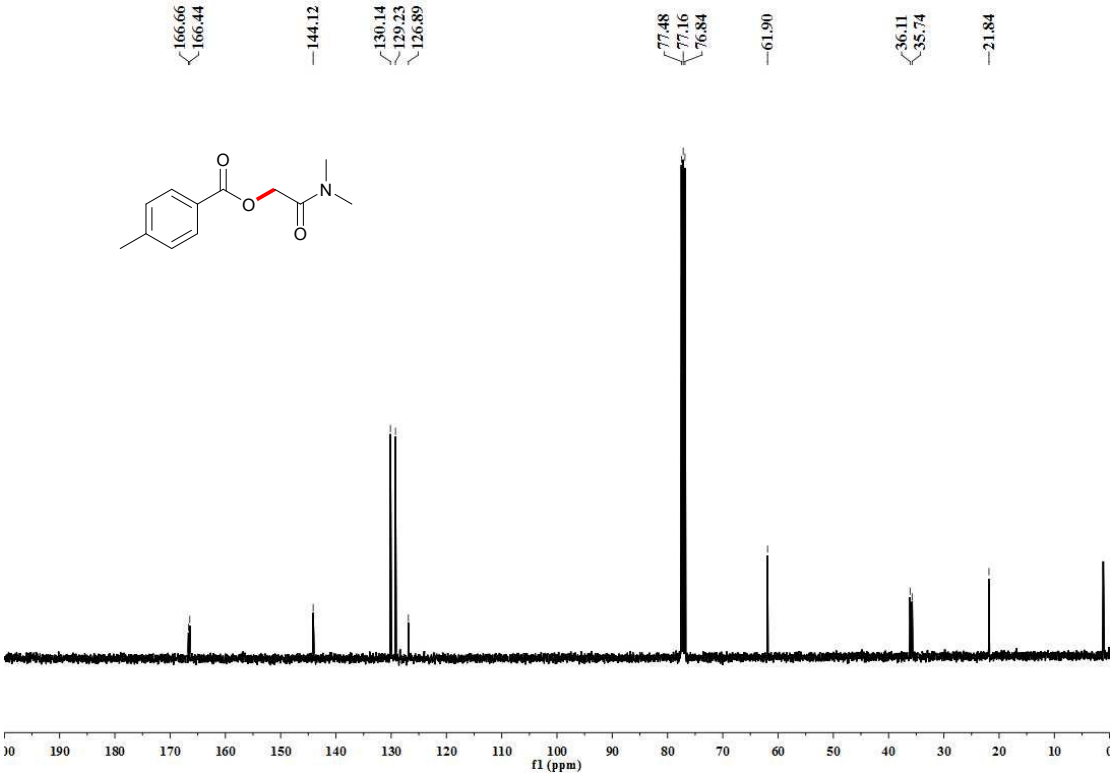
2-(Dimethylamino)-2-oxoethyl 4-cyanobenzoate (3ma): ^{13}C NMR ($CDCl_3$, 101 MHz)



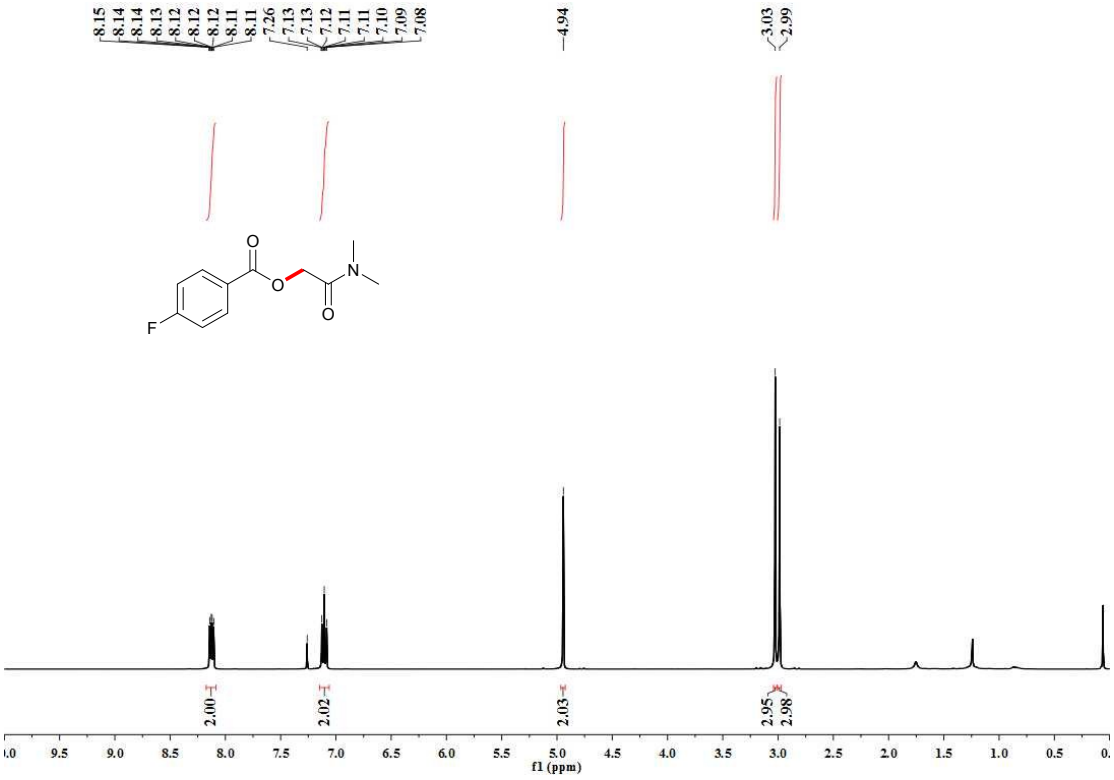
2-(Dimethylamino)-2-oxoethyl 4-methylbenzoate (3na): ^{1}H NMR ($CDCl_3$, 400 MHz)



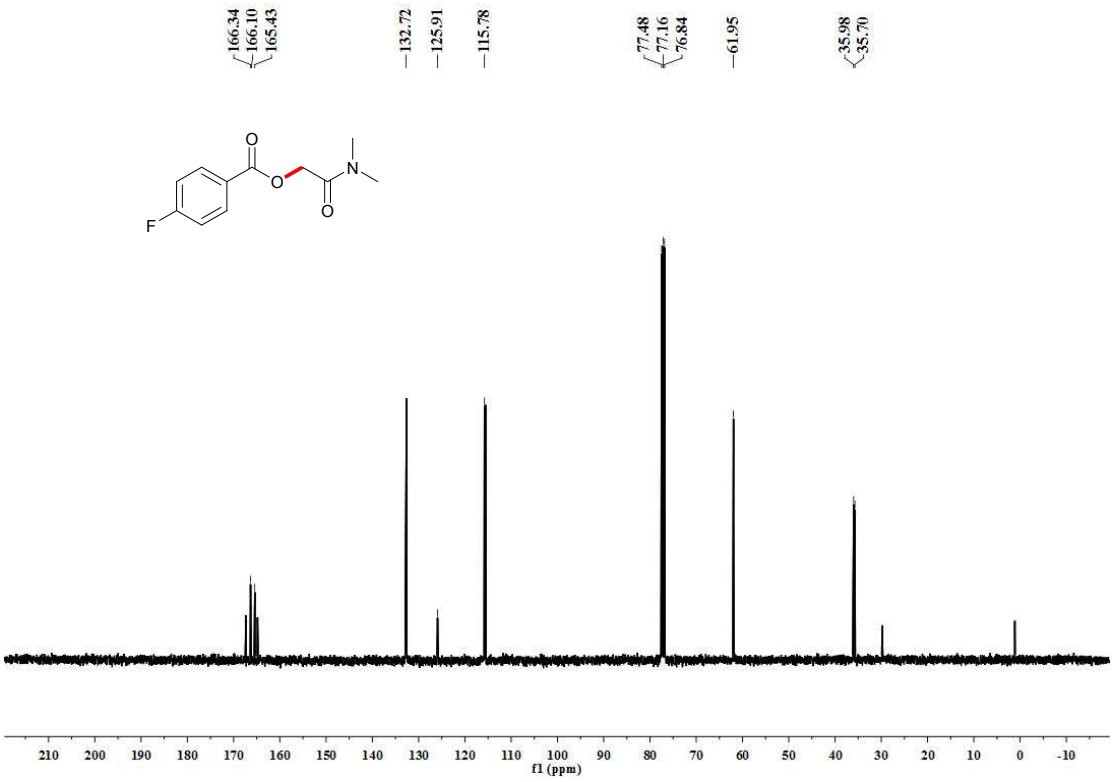
2-(Dimethylamino)-2-oxoethyl 4-methylbenzoate (3na): ^{13}C NMR ($CDCl_3$, 101 MHz)



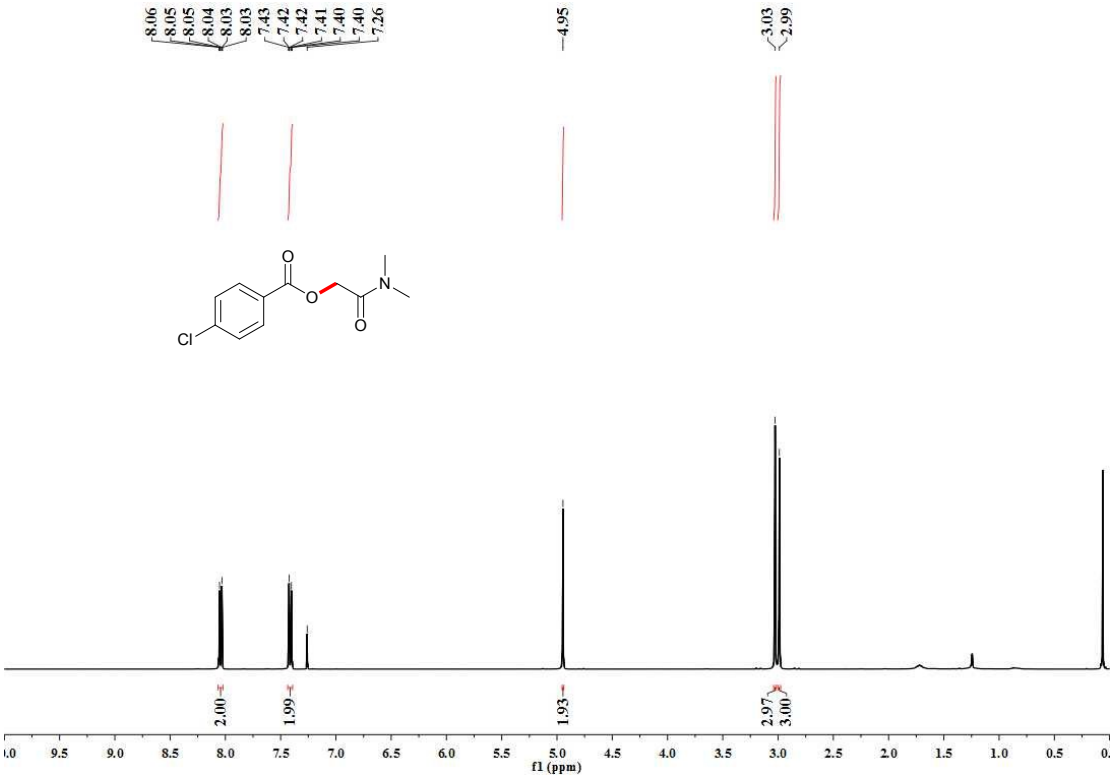
2-(Dimethylamino)-2-oxoethyl 4-fluorobenzoate (3oa): ^{1}H NMR ($CDCl_3$, 400 MHz)



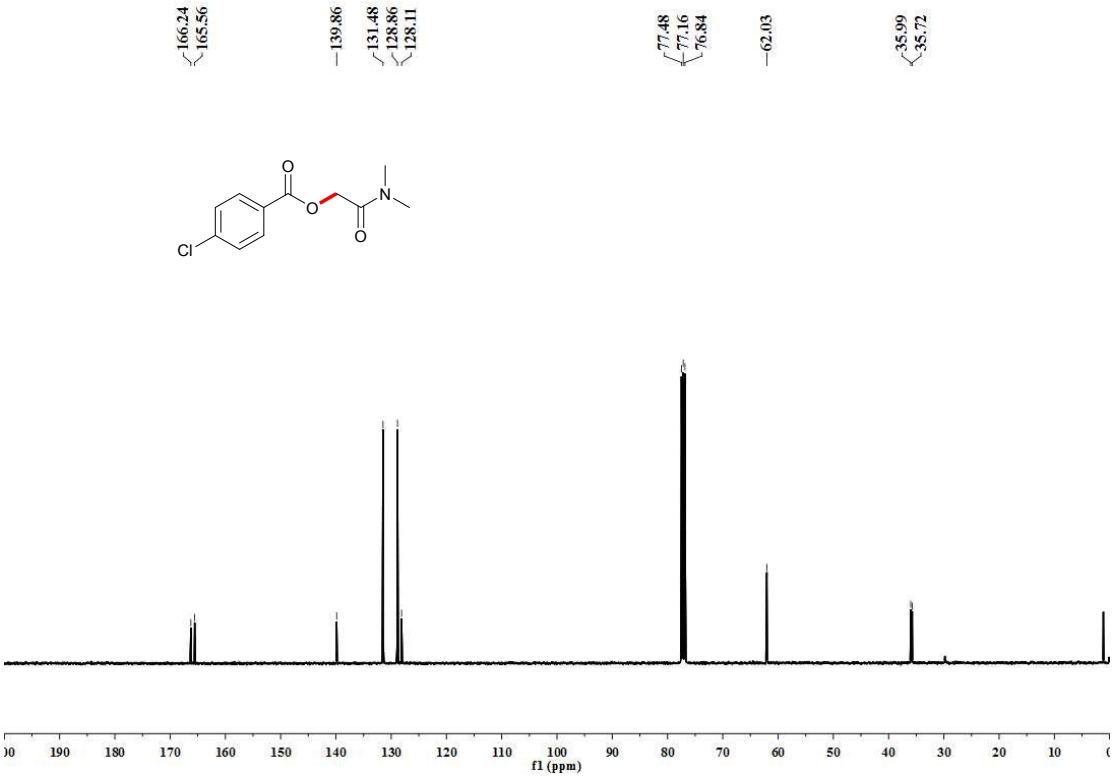
2-(Dimethylamino)-2-oxoethyl 4-fluorobenzoate (3oa): ^{13}C NMR ($CDCl_3$, 101 MHz)



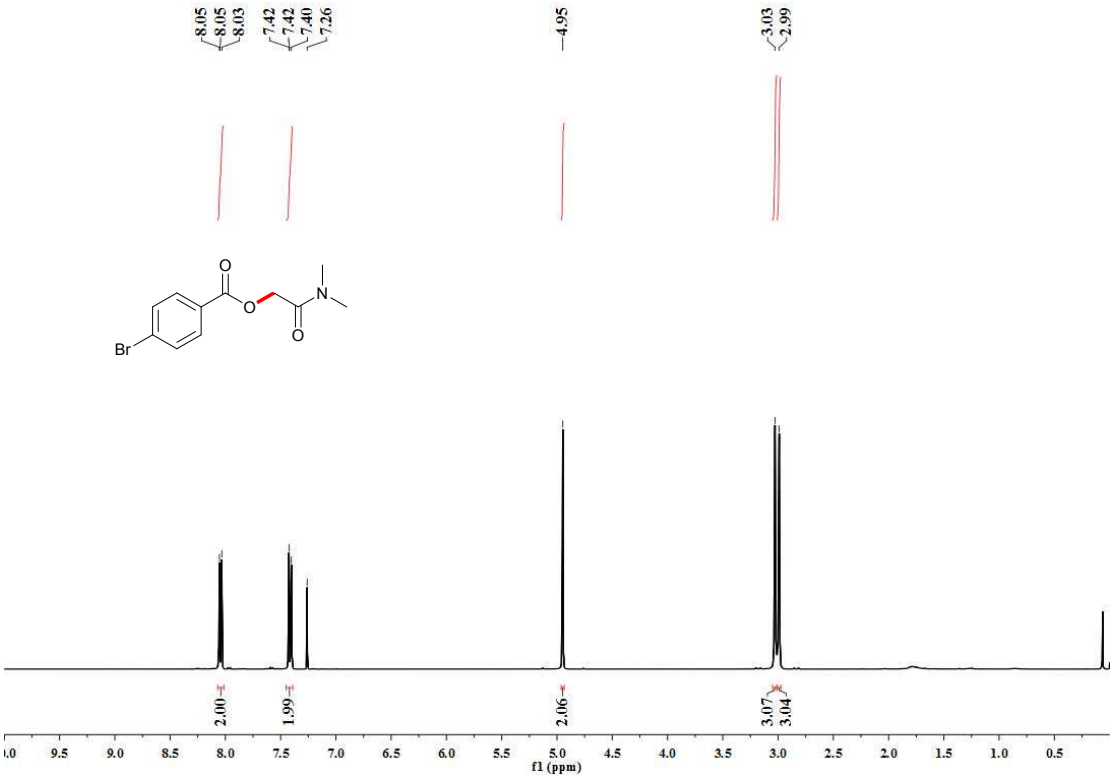
2-(Dimethylamino)-2-oxoethyl 4-chlorobenzoate (3pa): ^{1}H NMR ($CDCl_3$, 400 MHz)



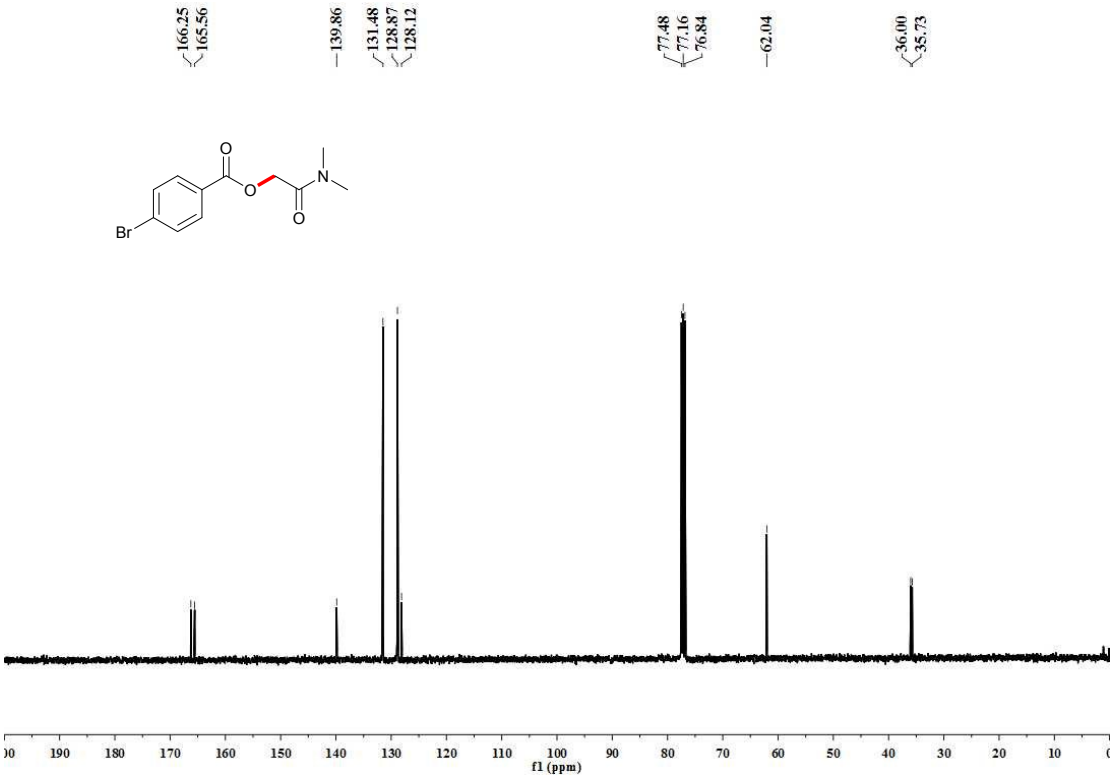
2-(Dimethylamino)-2-oxoethyl 4-chlorobenzoate (3pa): ^{13}C NMR ($CDCl_3$, 101 MHz)



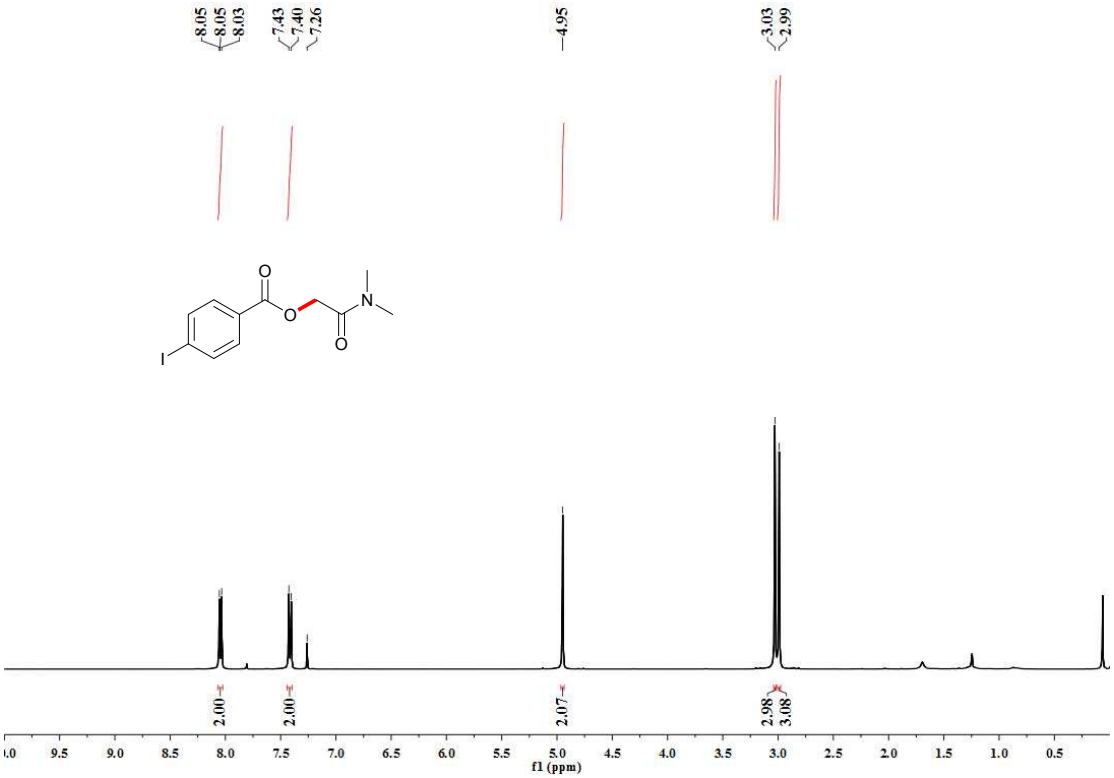
2-(Dimethylamino)-2-oxoethyl 4-bromobenzoate (3qa): ^{1}H NMR ($CDCl_3$, 400 MHz)



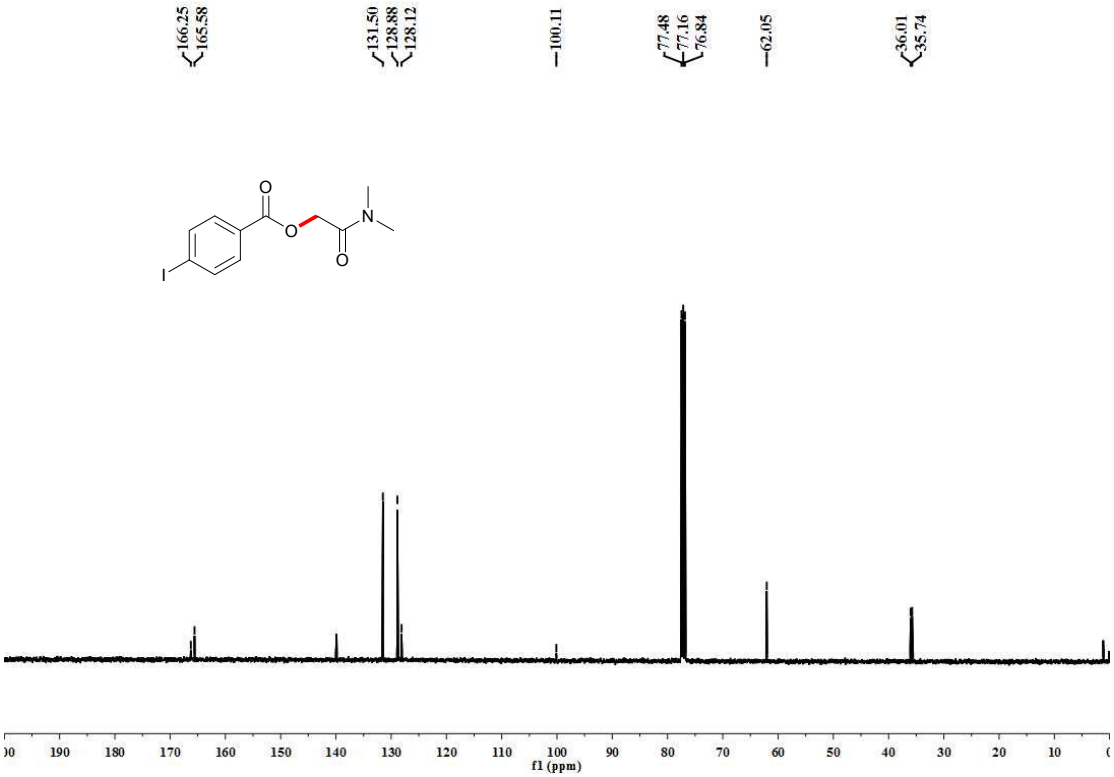
2-(Dimethylamino)-2-oxoethyl 4-bromobenzoate (3qa): ^{13}C NMR ($CDCl_3$, 101 MHz)



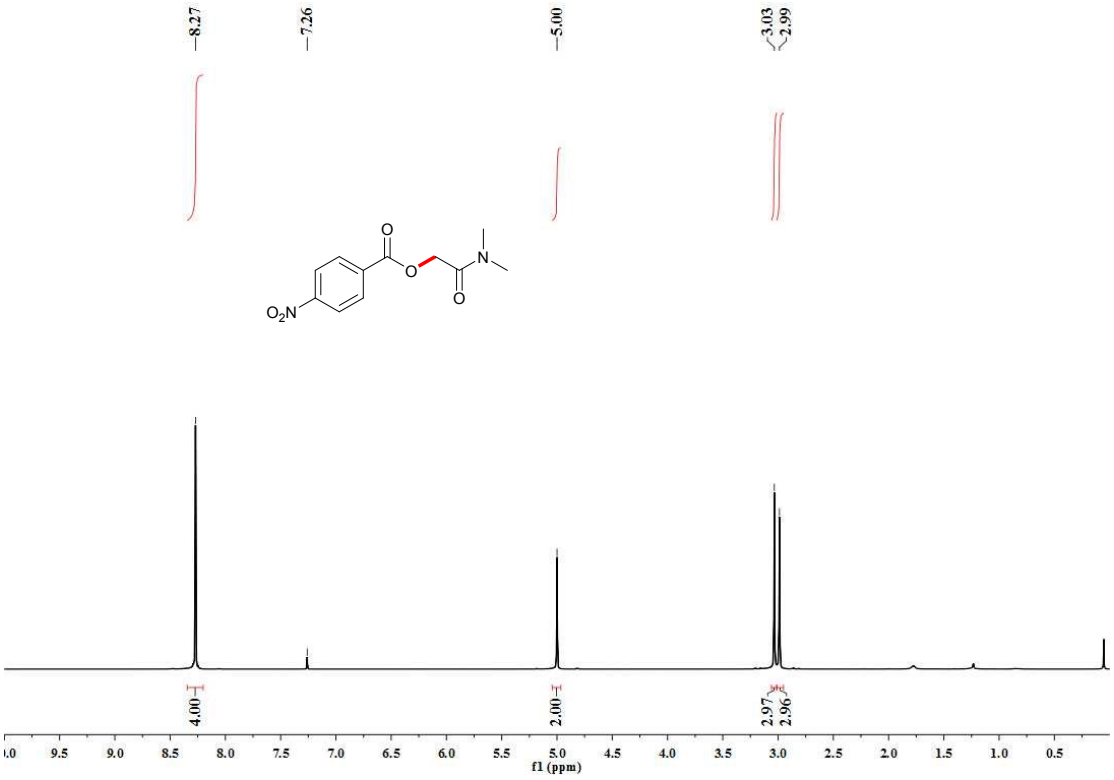
2-(Dimethylamino)-2-oxoethyl 4-iodobenzoate (3ra): ^{1}H NMR ($CDCl_3$, 400 MHz)



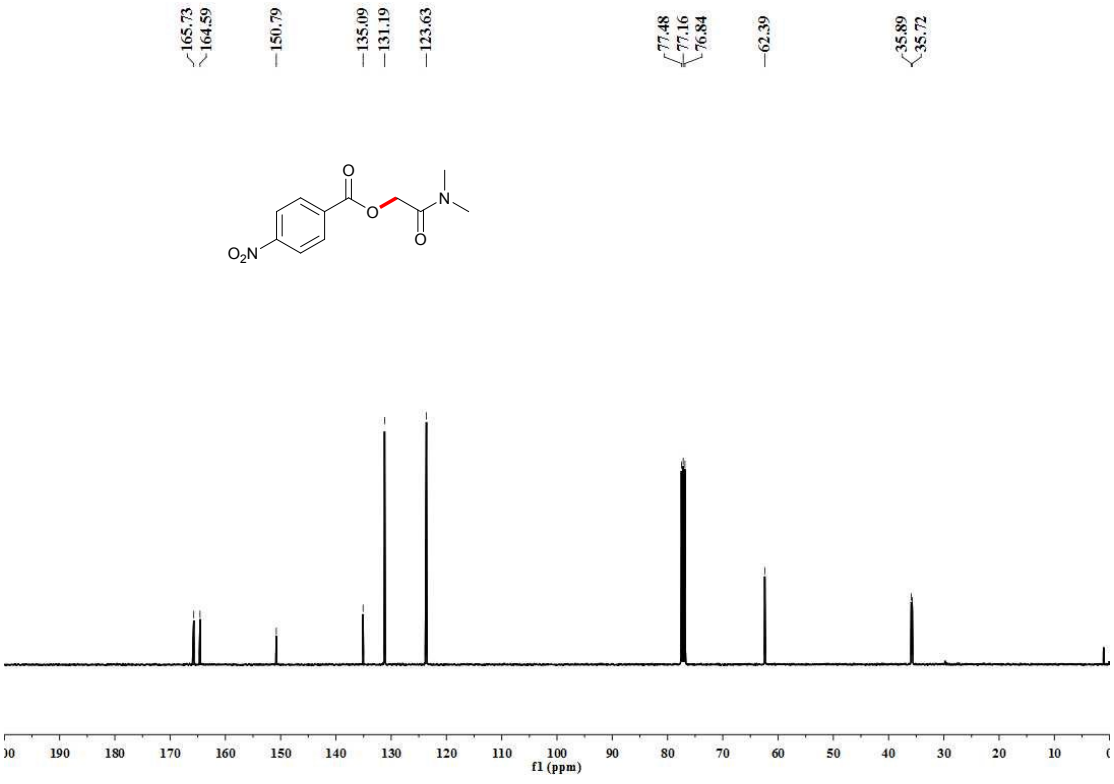
2-(Dimethylamino)-2-oxoethyl 4-iodobenzoate (3ra): ^{13}C NMR ($CDCl_3$, 101 MHz)



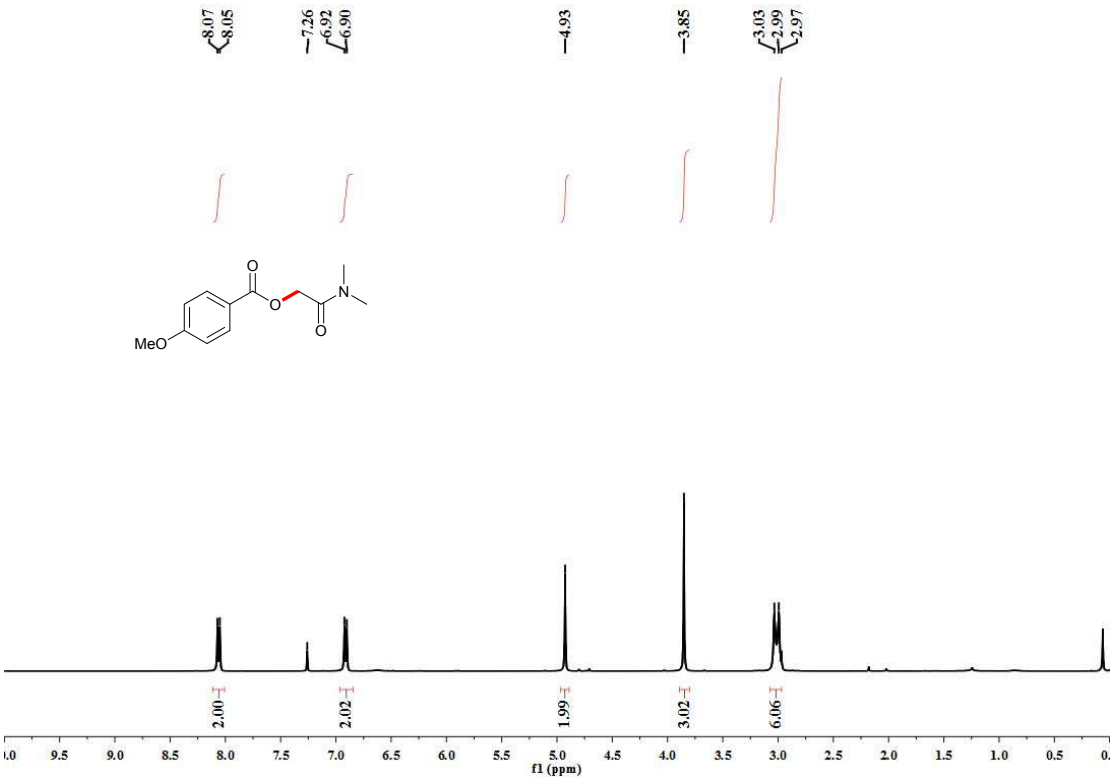
2-(Dimethylamino)-2-oxoethyl 4-nitrobenzoate (3sa): ^{1}H NMR ($CDCl_3$, 400 MHz)



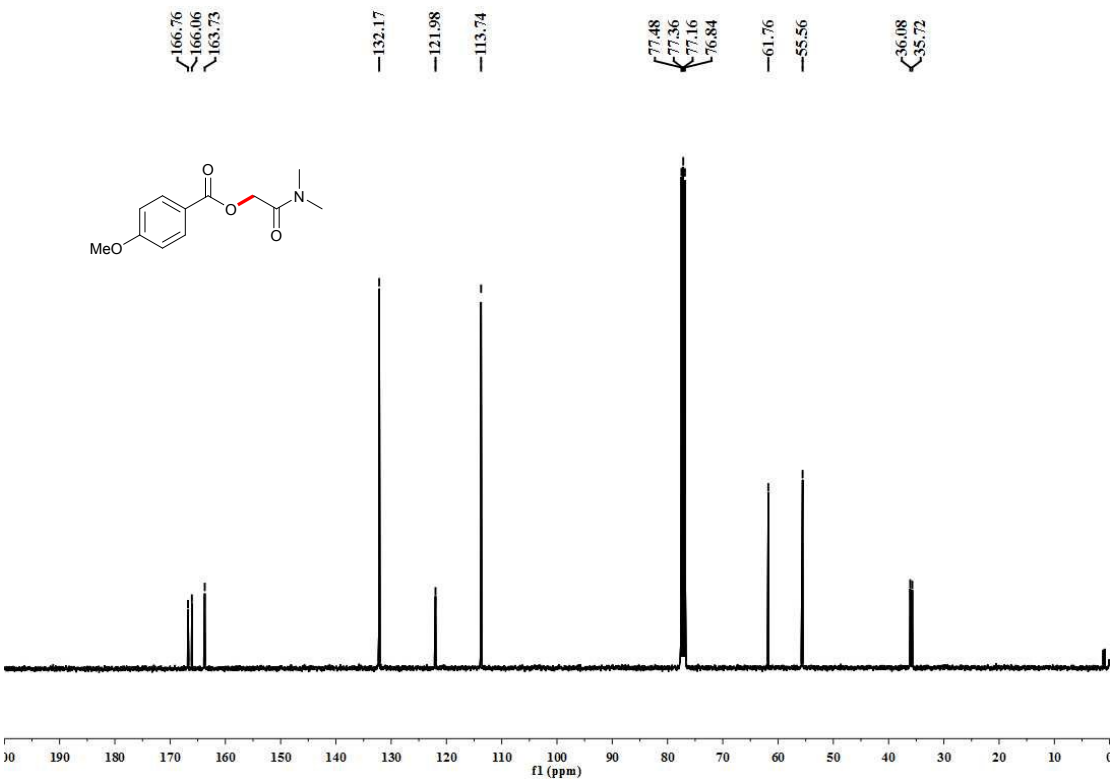
2-(Dimethylamino)-2-oxoethyl 4-nitrobenzoate (3sa): ^{13}C NMR ($CDCl_3$, 101 MHz)



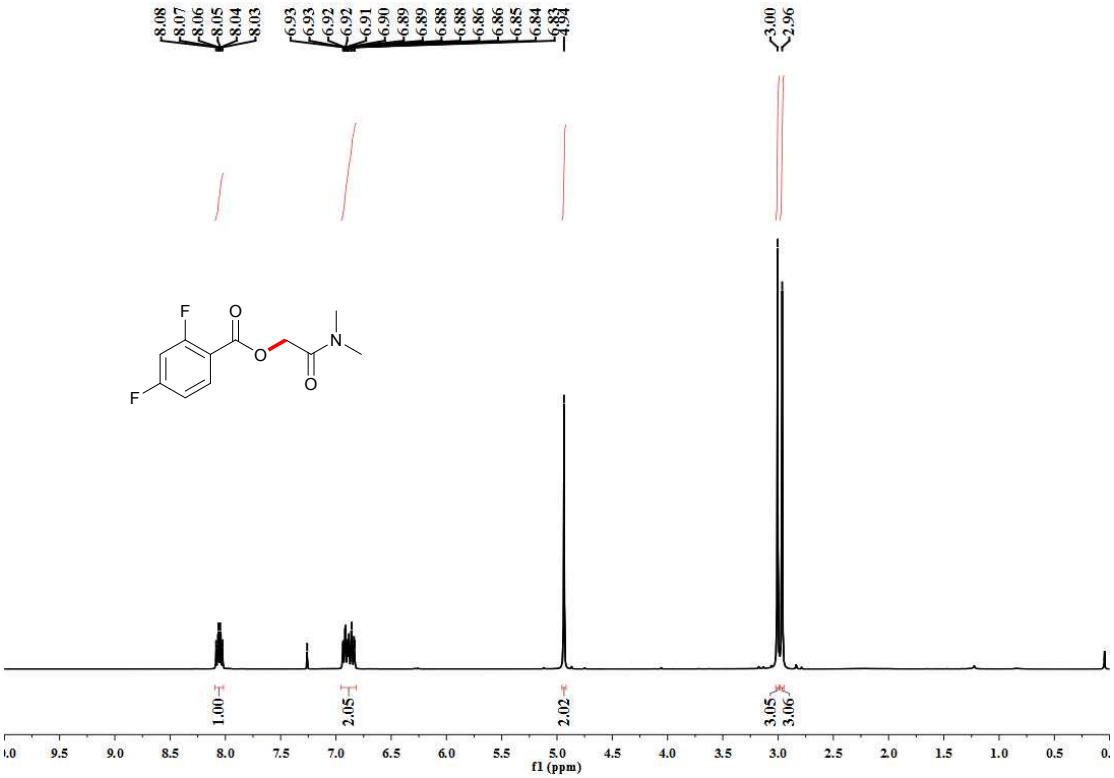
2-(Dimethylamino)-2-oxoethyl 4-methoxybenzoate (3ta): ^{1}H NMR ($CDCl_3$, 400 MHz)



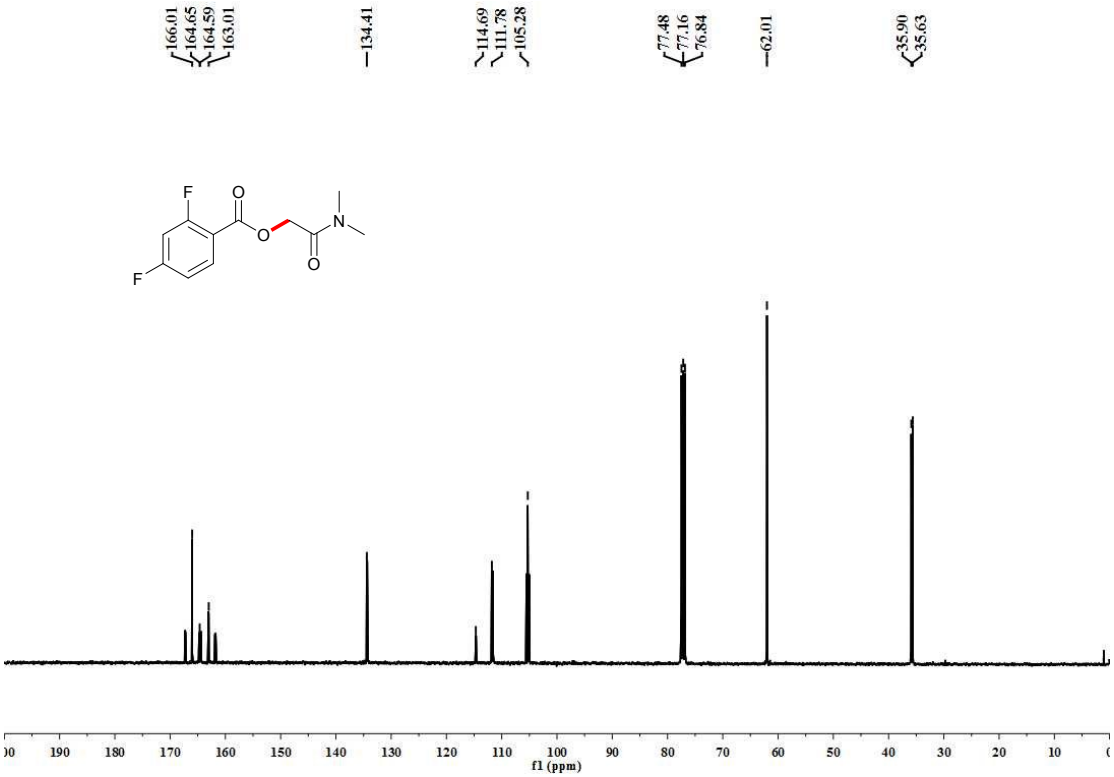
2-(Dimethylamino)-2-oxoethyl 4-methoxybenzoate (3ta): ^{13}C NMR ($CDCl_3$, 101 MHz)



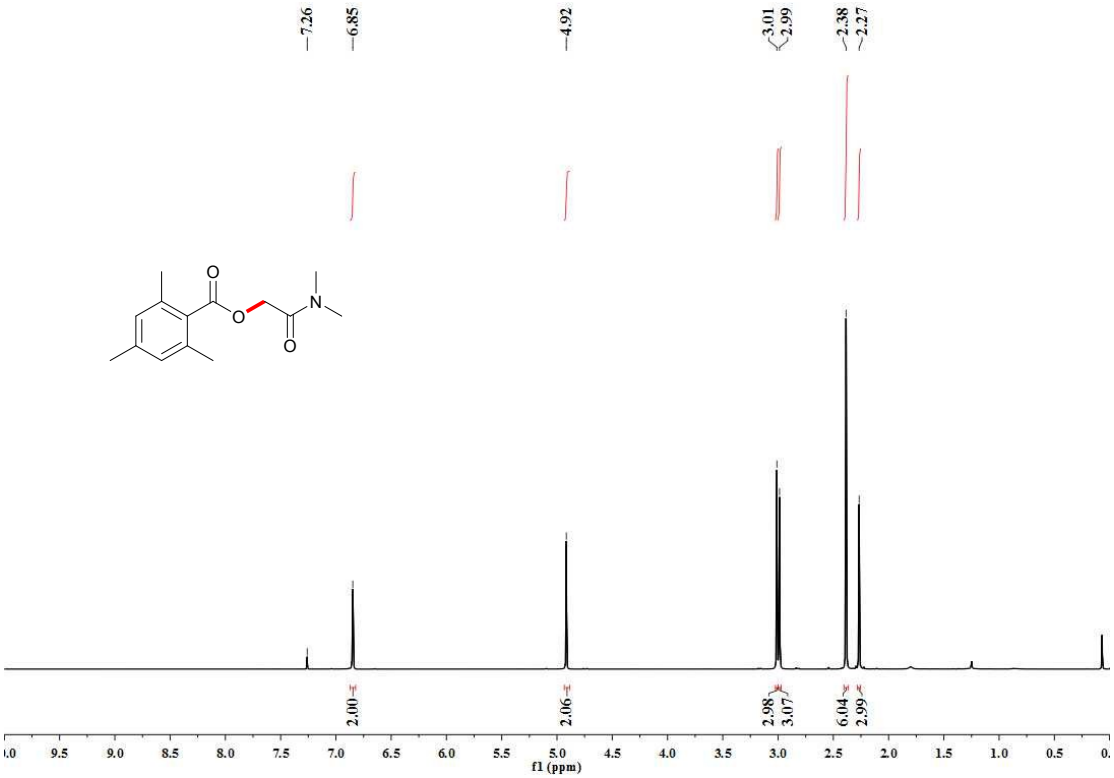
2-(Dimethylamino)-2-oxoethyl 2, 4-difluorobenzoate (3ua): ^{1}H NMR ($CDCl_3$, 400 MHz)



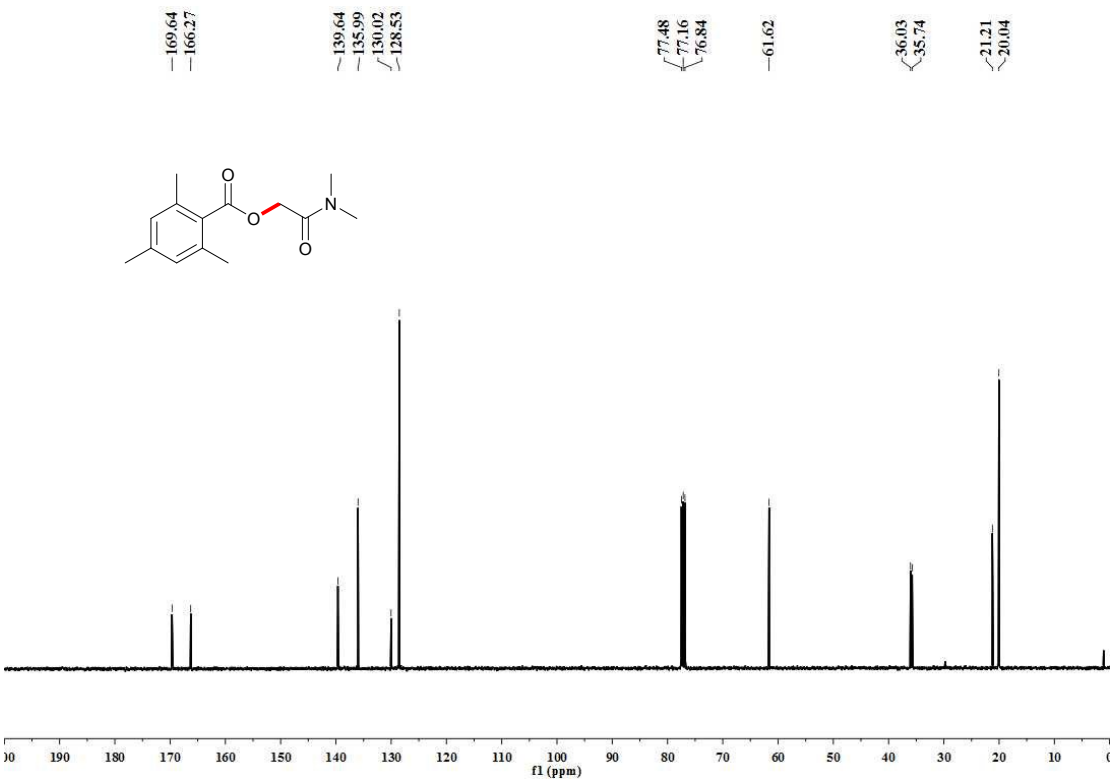
2-(Dimethylamino)-2-oxoethyl 2, 4-difluorobenzoate (3ua): ^{13}C NMR ($CDCl_3$, 101 MHz)



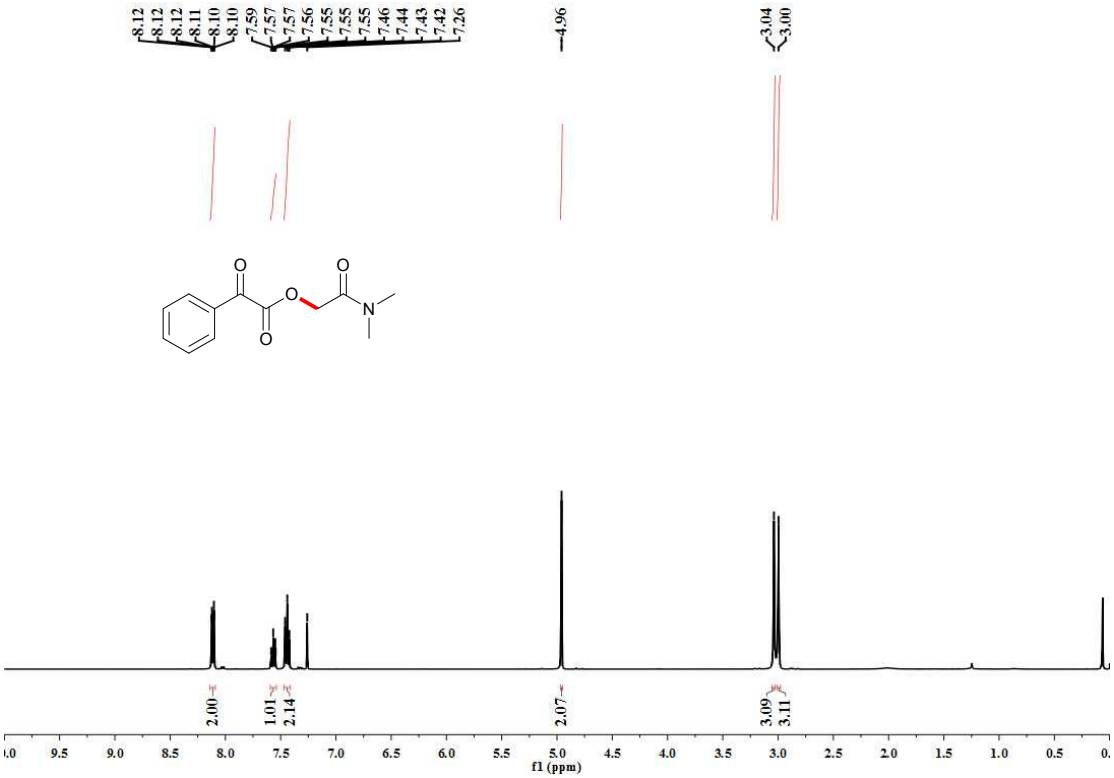
2-(Dimethylamino)-2-oxoethyl 2, 4, 6-Trimethylbenzoate (3va): ^{1}H NMR ($CDCl_3$, 400 MHz)



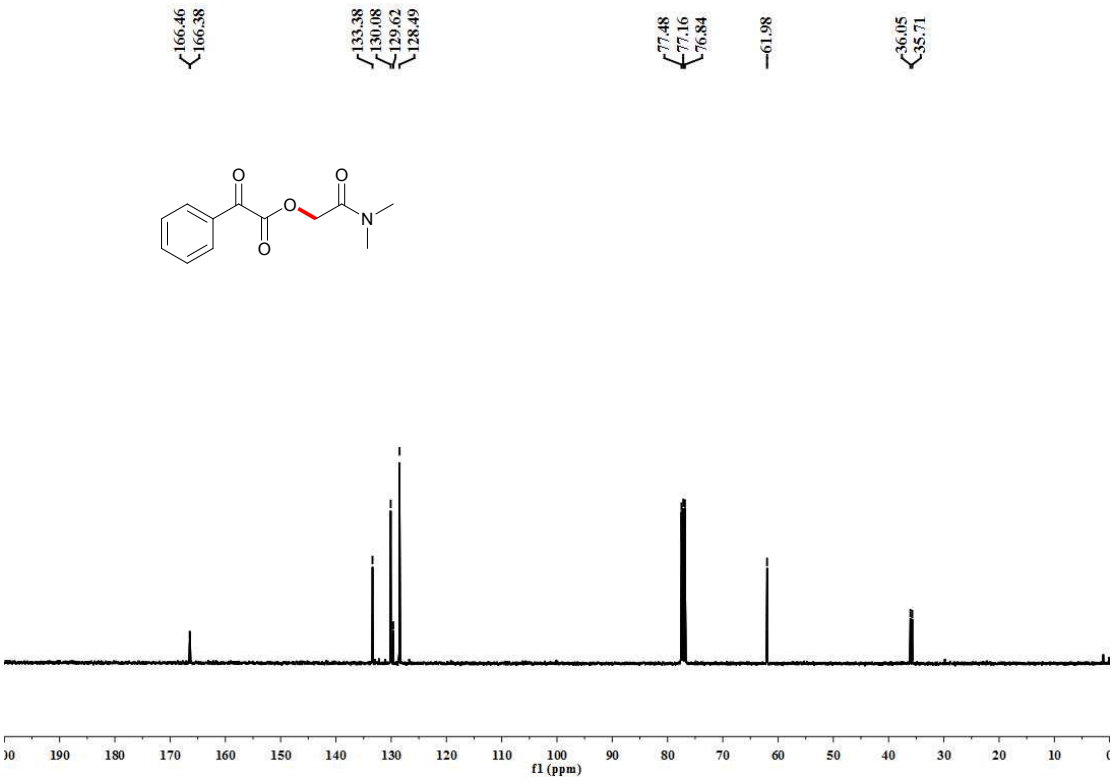
2-(Dimethylamino)-2-oxoethyl 2, 4, 6-Trimethylbenzoate (3va): ^{13}C NMR ($CDCl_3$, 101 MHz)



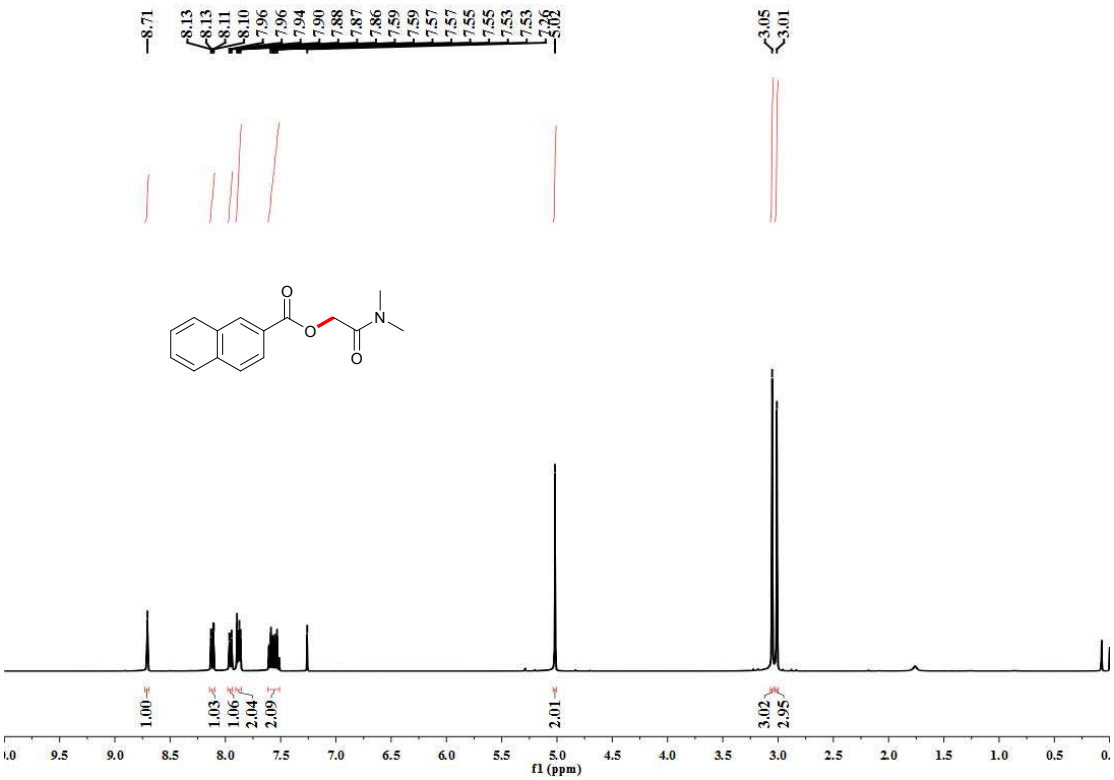
2-(Dimethylamino)-2-oxoethyl 2-oxo-2-phenylacetate (3wa): ^{1}H NMR ($CDCl_3$, 400 MHz)



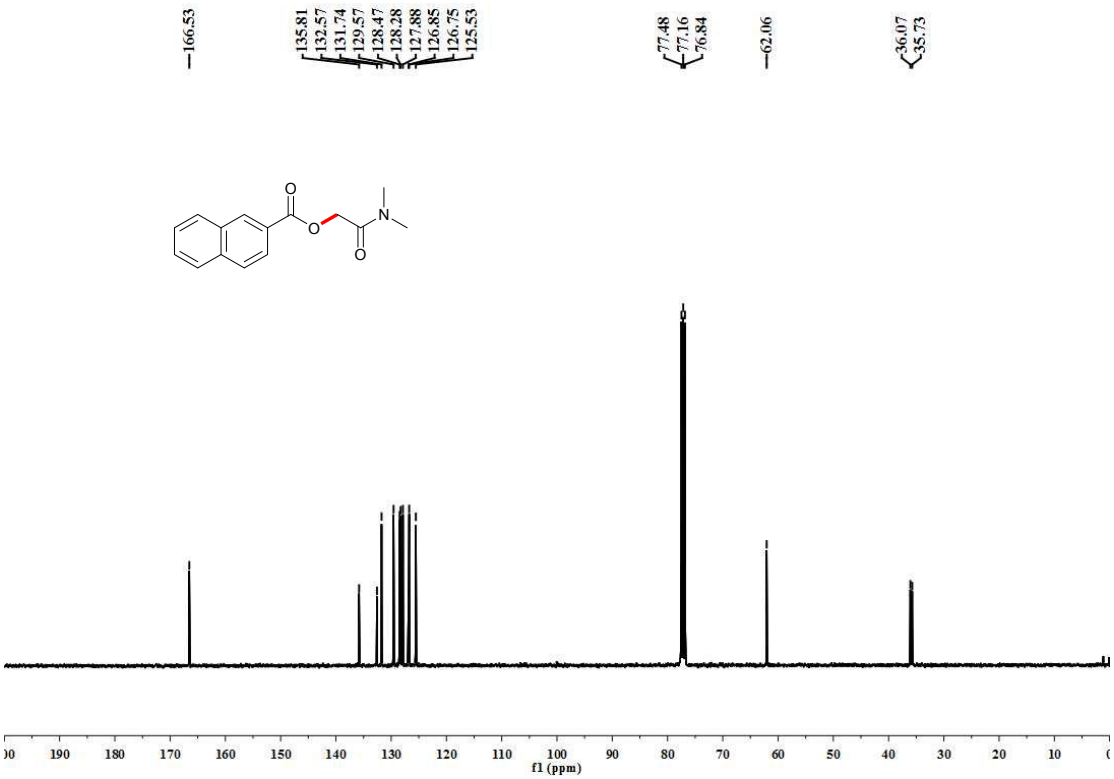
2-(Dimethylamino)-2-oxoethyl 2-oxo-2-phenylacetate (3wa): ^{13}C NMR ($CDCl_3$, 101 MHz)



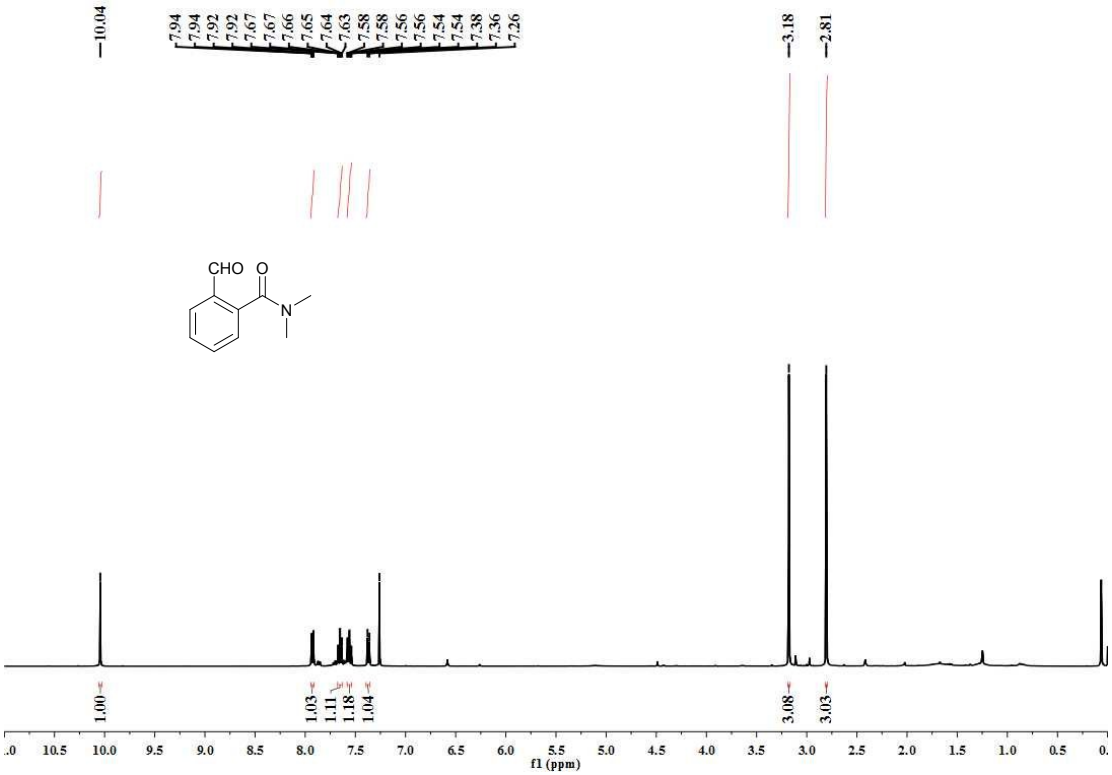
2-(Dimethylamino)-2-oxoethyl 2-naphthoate (3xa): ^{1}H NMR ($CDCl_3$, 400 MHz)



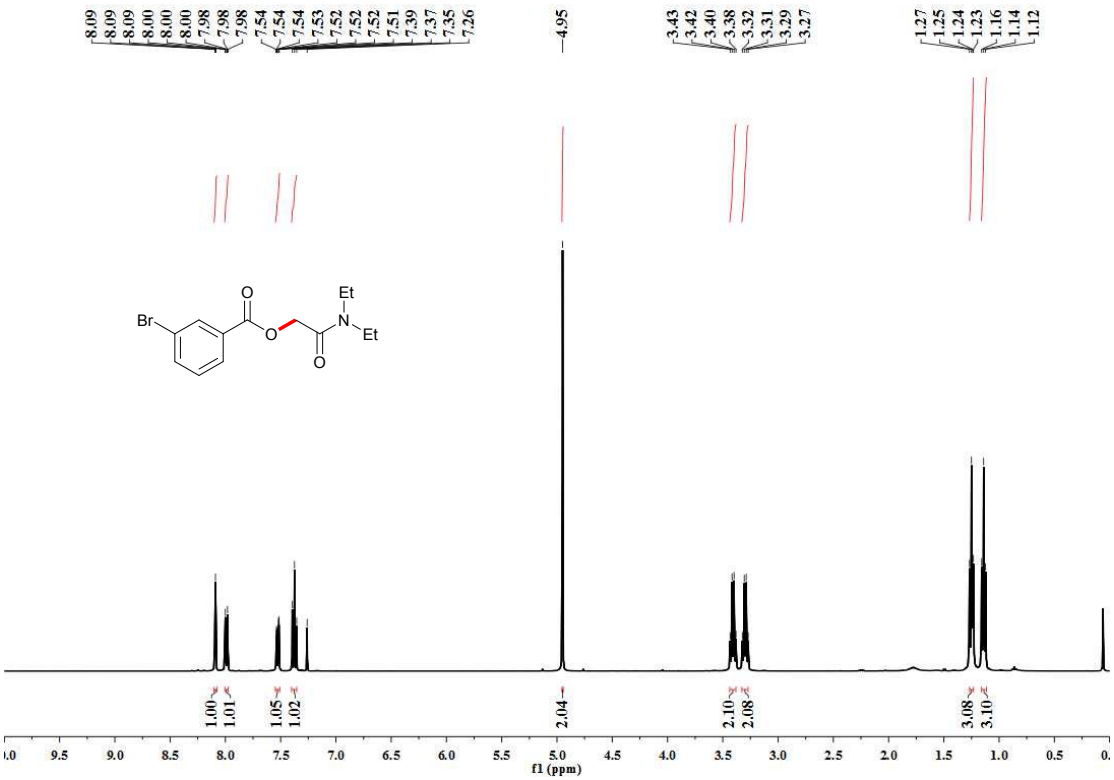
2-(Dimethylamino)-2-oxoethyl 2-naphthoate (3xa): ^{13}C NMR ($CDCl_3$, 101 MHz)



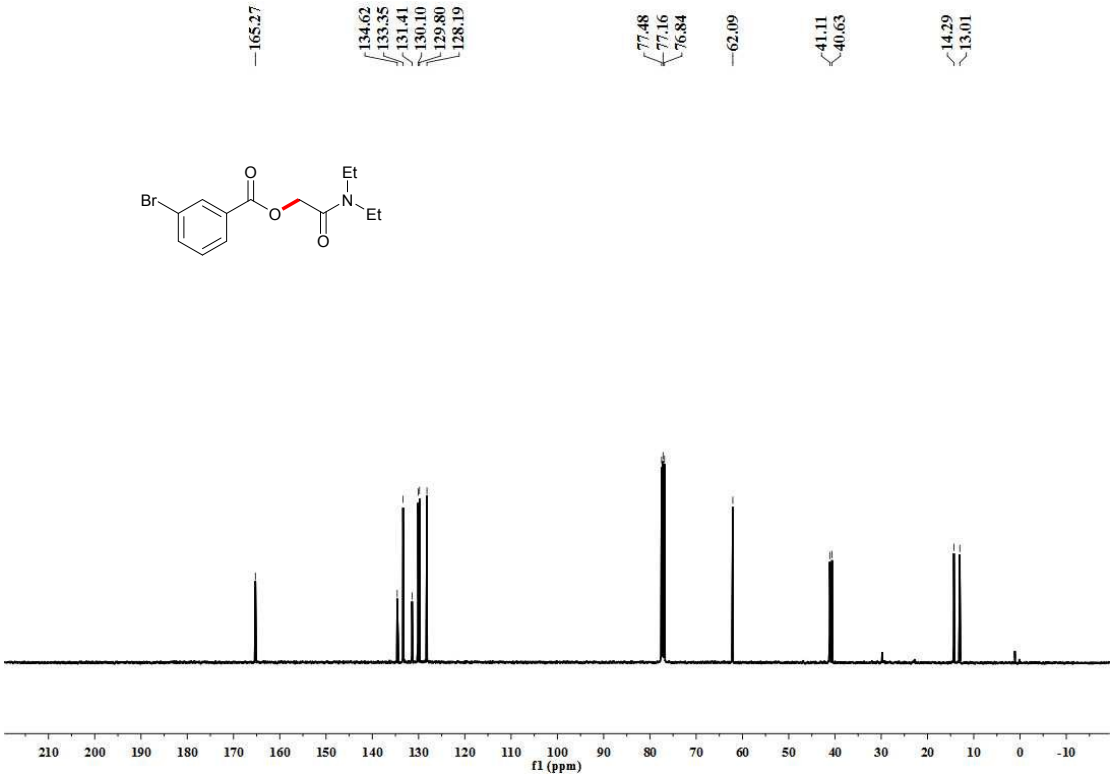
2-Formyl-*N*,*N*-dimethylbenzamide: ^{1}H NMR ($CDCl_3$, 400 MHz)



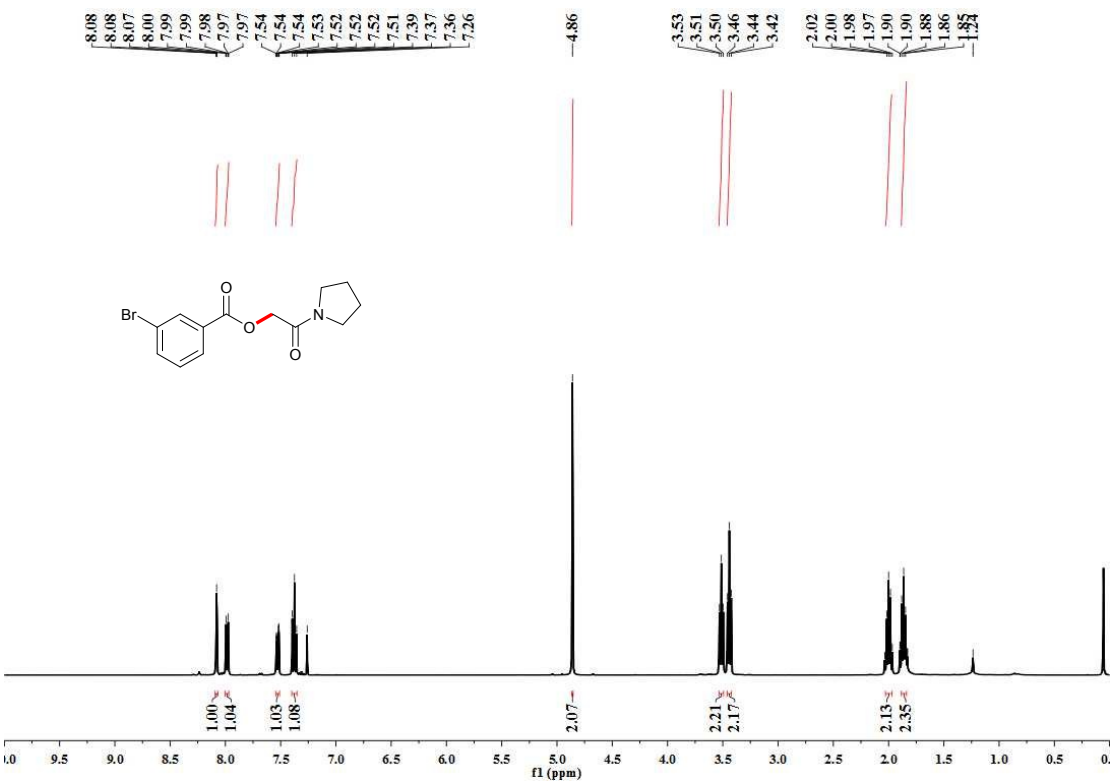
2-(Diethylamino)-2-oxoethyl 3-bromobenzoate (4kb): ^{1}H NMR ($CDCl_3$, 400 MHz)



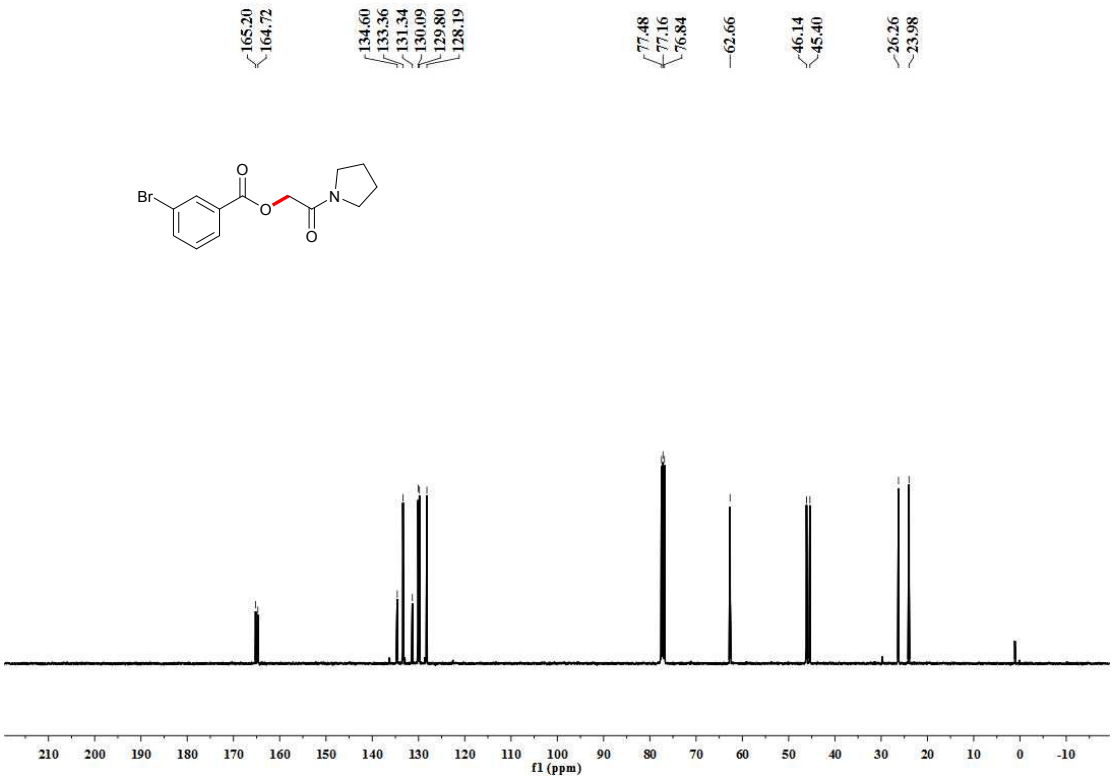
2-(Diethylamino)-2-oxoethyl 3-bromobenzoate (4kb): ^{13}C NMR ($CDCl_3$, 101 MHz)



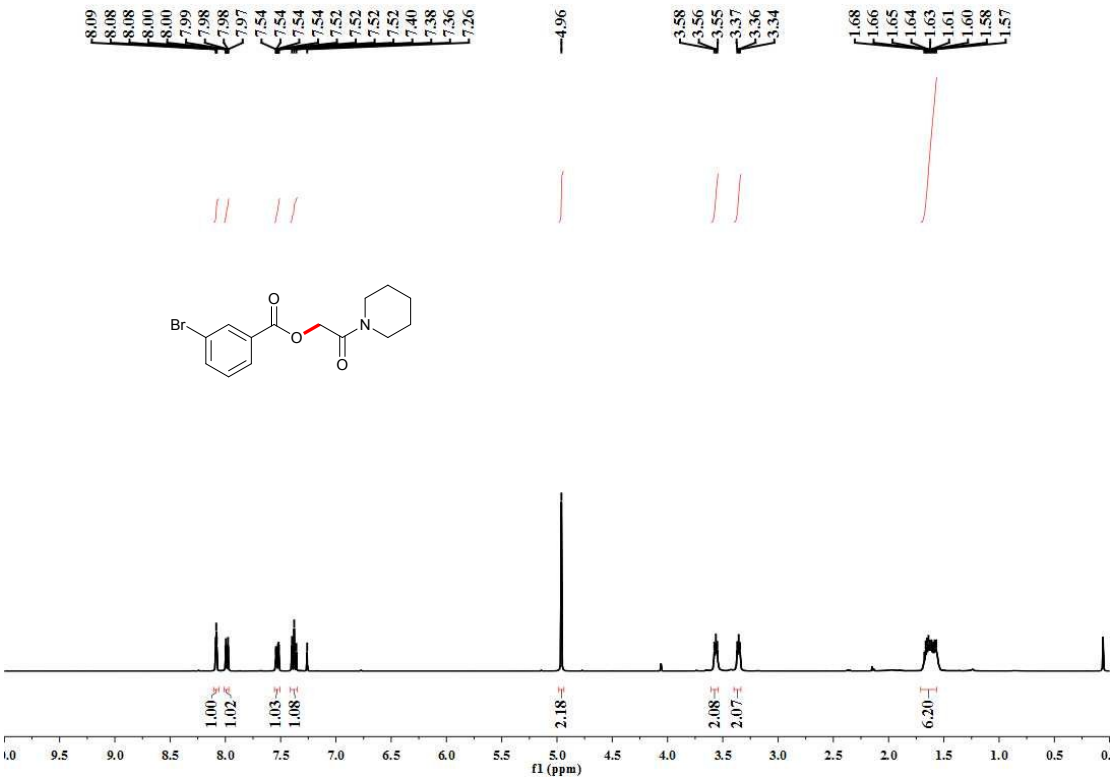
2-Oxo-2-(pyrrolidin-1-yl)ethyl 3-bromobenzoate (4kc): ^{1}H NMR ($CDCl_3$, 400 MHz)



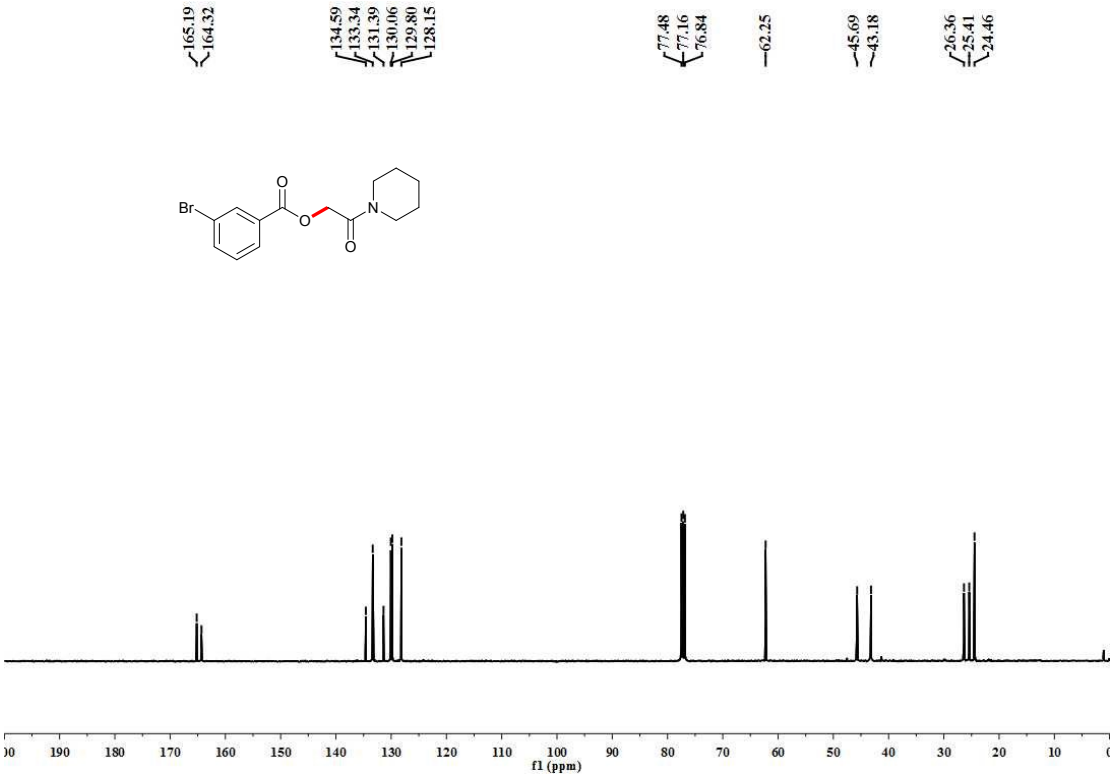
2-Oxo-2-(pyrrolidin-1-yl)ethyl 3-bromobenzoate (4kc): ^{13}C NMR ($CDCl_3$, 101 MHz)



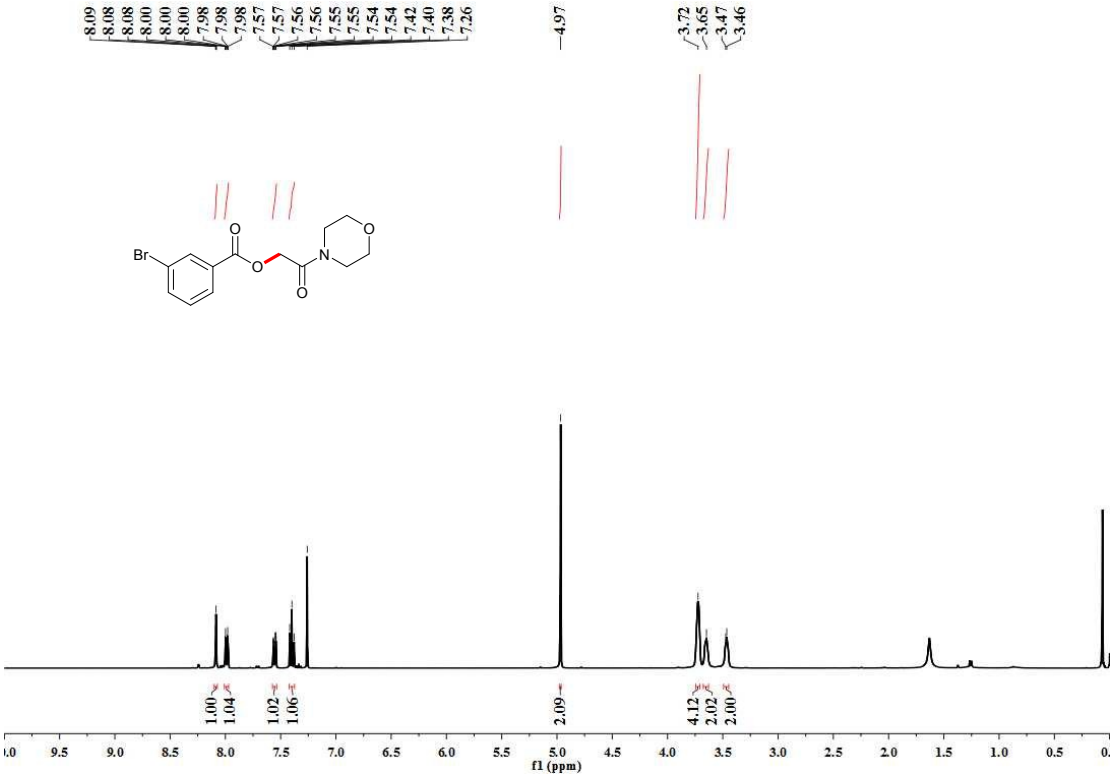
2-Oxo-2-(piperidin-1-yl)ethyl 3-bromobenzoate (4kd): ^{1}H NMR ($CDCl_3$, 400 MHz)



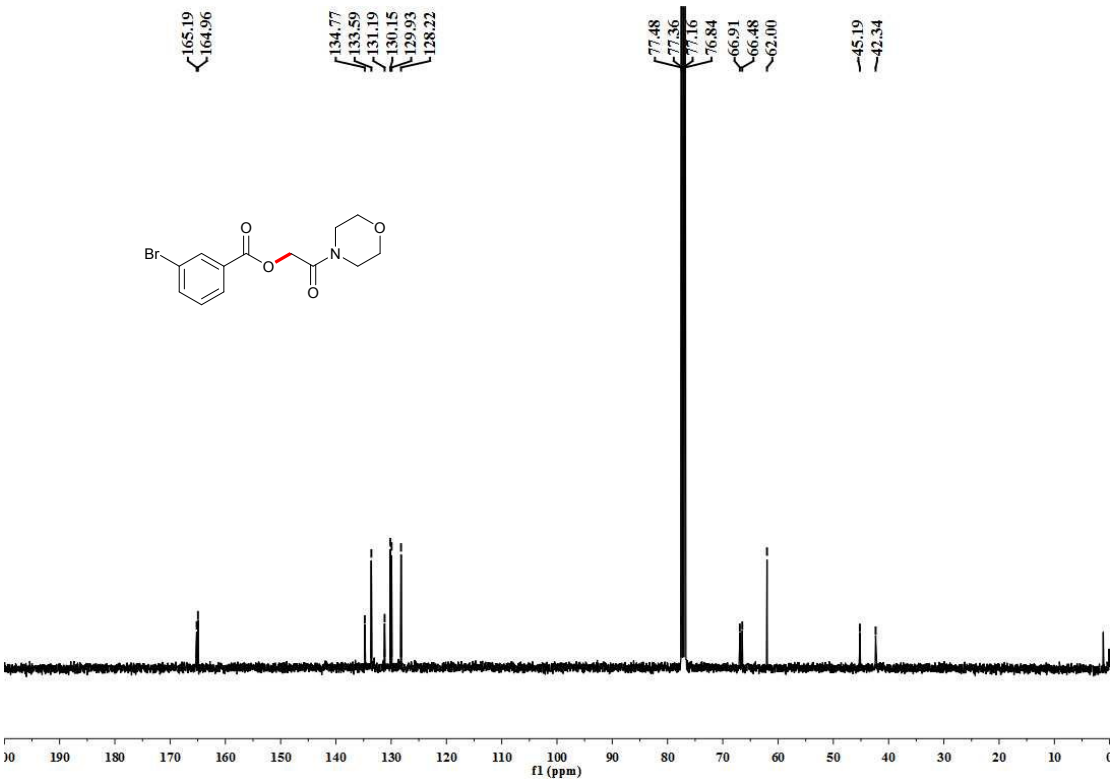
2-Oxo-2-(piperidin-1-yl)ethyl 3-bromobenzoate (4kd): ^{13}C NMR ($CDCl_3$, 101 MHz)



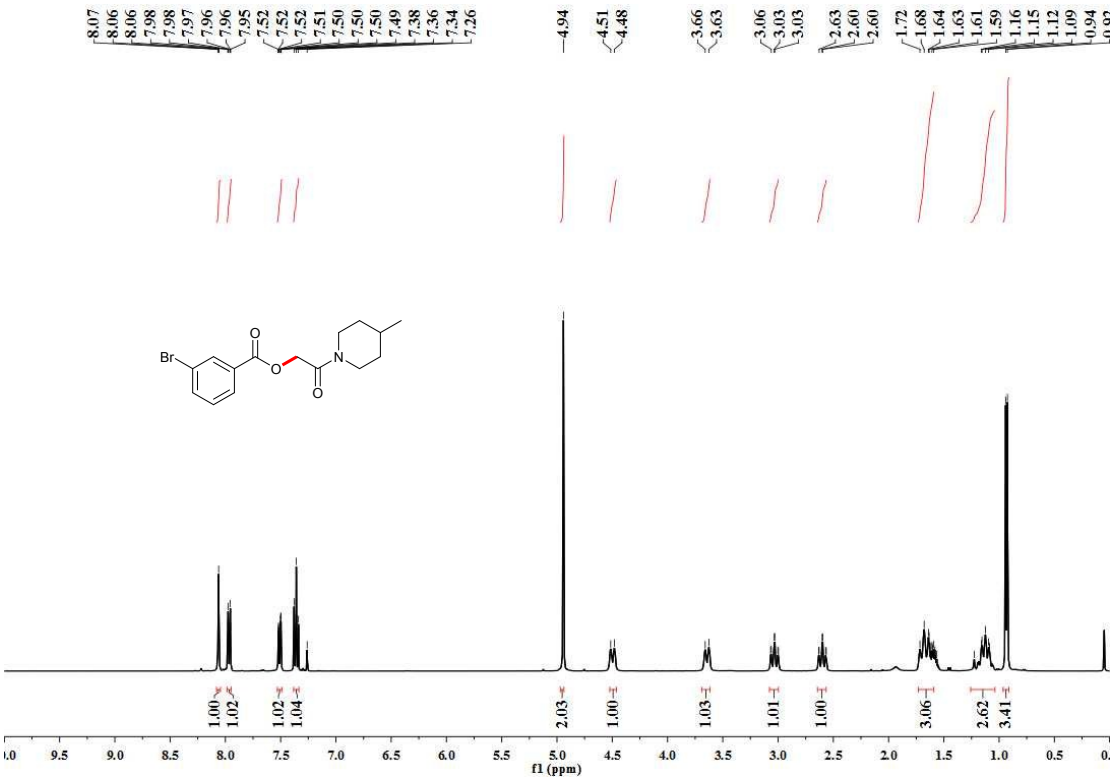
2-Morpholino-2-oxoethyl 3-bromobenzoate (4ke): ^{1}H NMR ($CDCl_3$, 400 MHz)



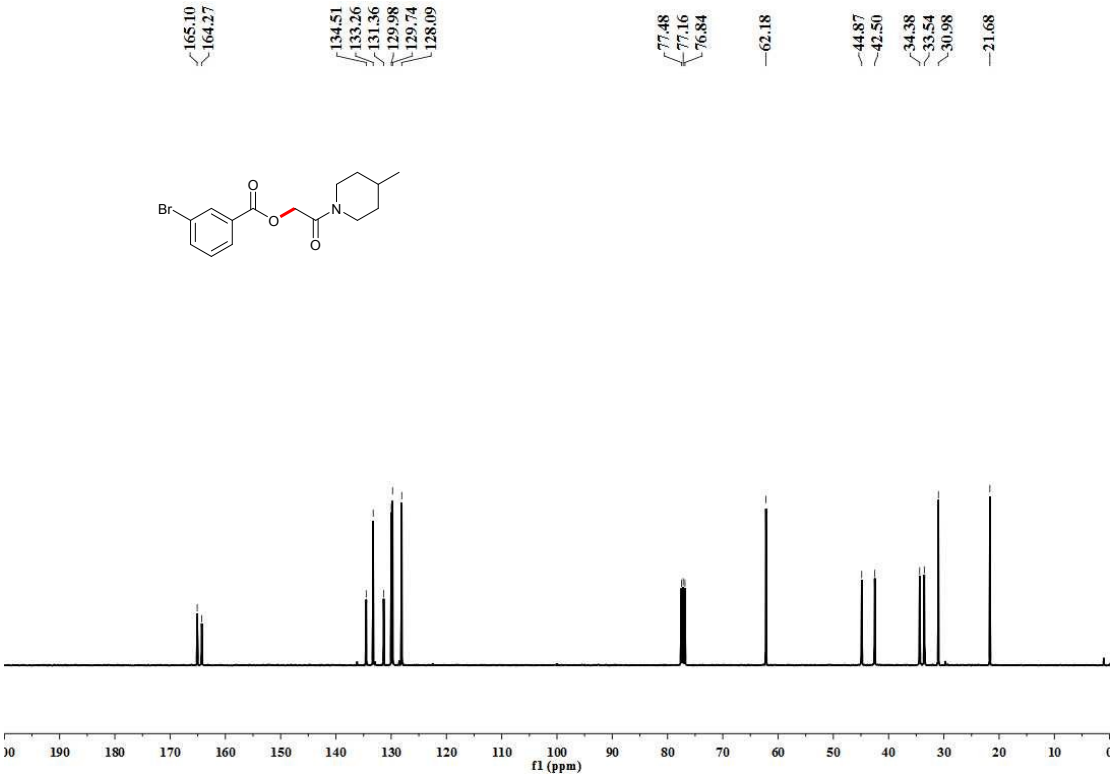
2-Morpholino-2-oxoethyl 3-bromobenzoate (4ke): ^{13}C NMR ($CDCl_3$, 101MHz)



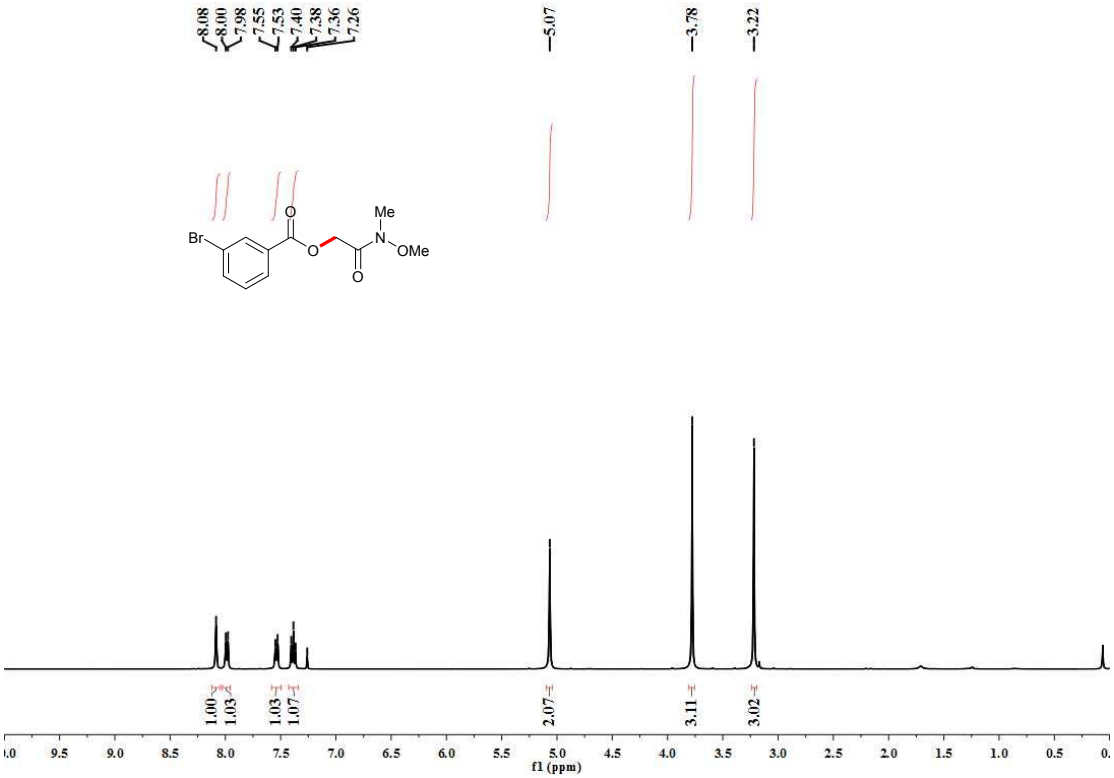
2-(4-Methylpiperidin-1-yl)-2-oxoethyl 3-bromobenzoate (4kf): ^{1}H NMR ($CDCl_3$, 400 MHz)



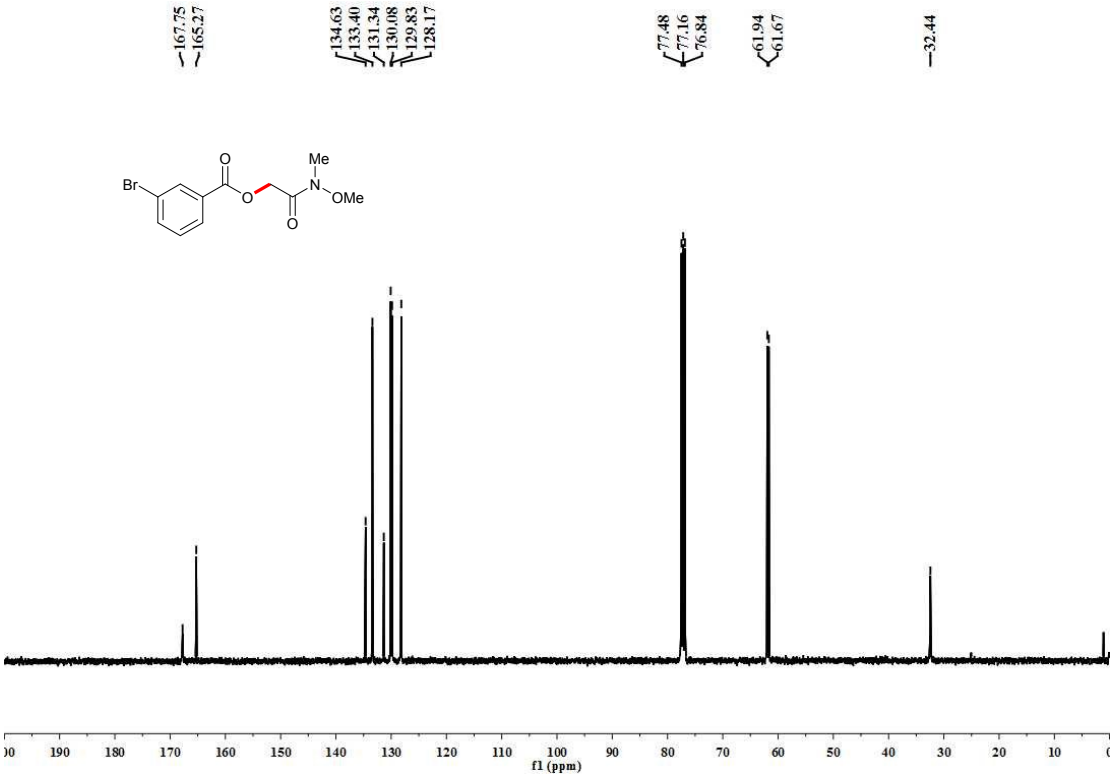
2-(4-Methylpiperidin-1-yl)-2-oxoethyl 3-bromobenzoate (4kf): ^{13}C NMR ($CDCl_3$, 101 MHz)



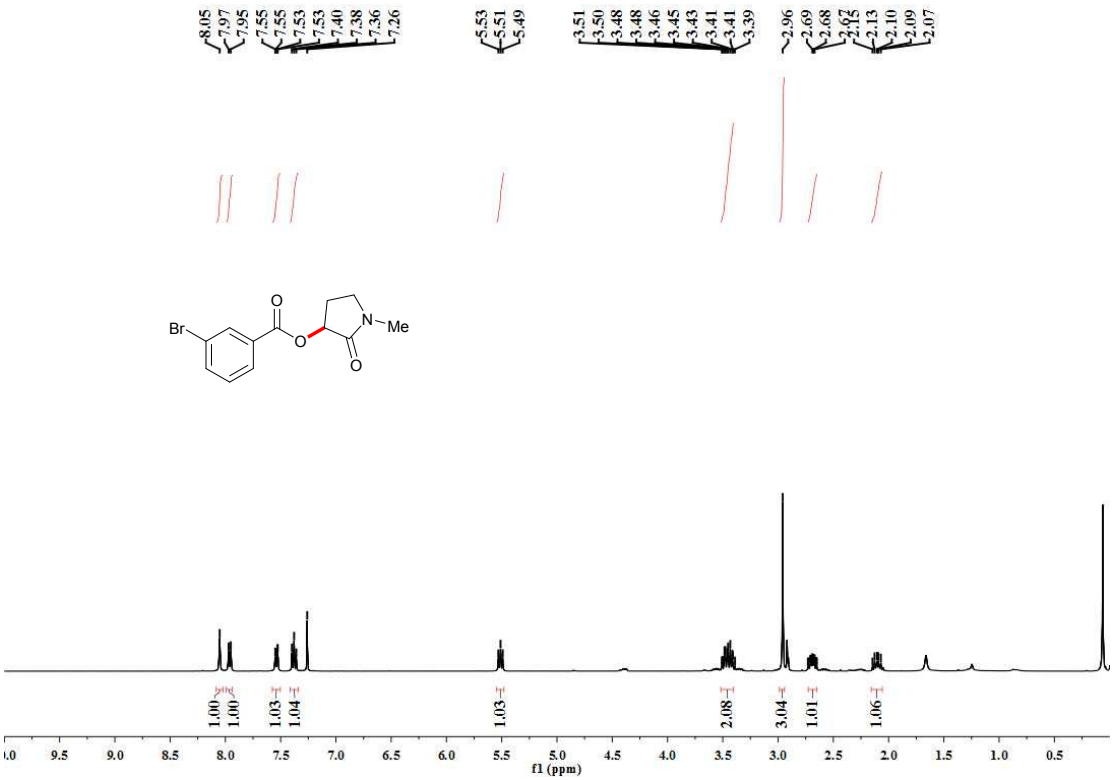
2-(methoxy(methyl)amino)-2-oxoethyl 3-bromobenzoate (4kg): ^{1}H NMR ($CDCl_3$, 400 MHz)



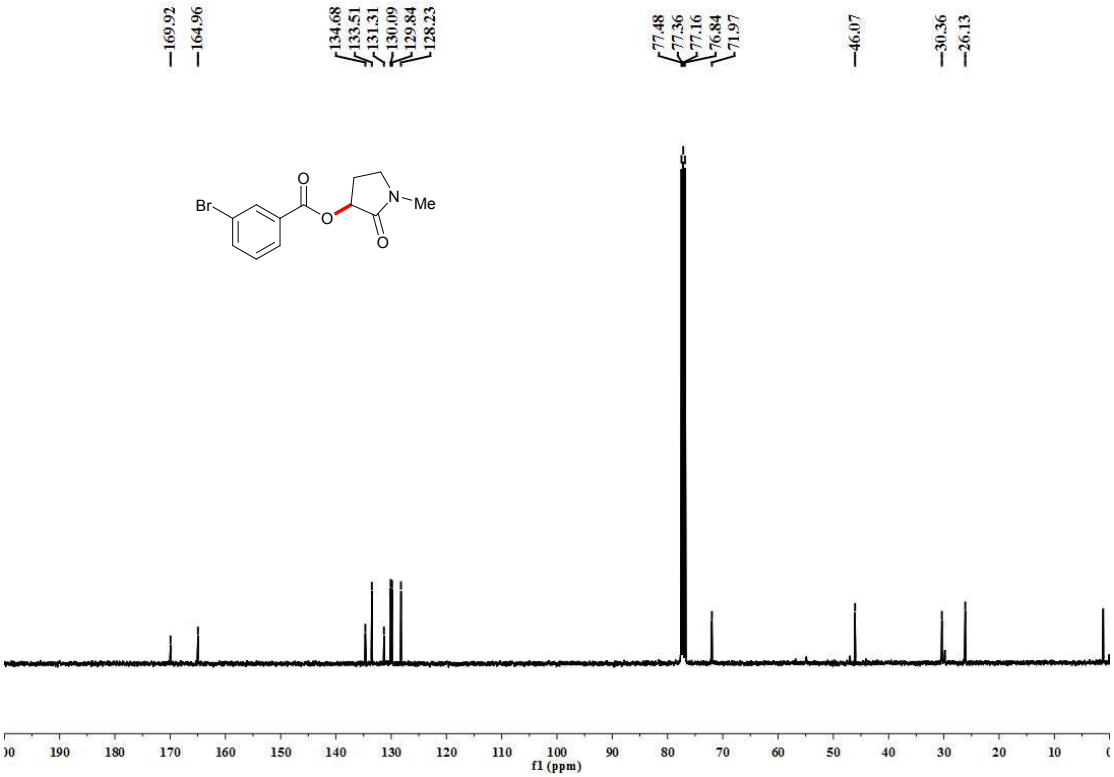
2-(methoxy(methyl)amino)-2-oxoethyl 3-bromobenzoate (4kg): ^{13}C NMR ($CDCl_3$, 101 MHz)



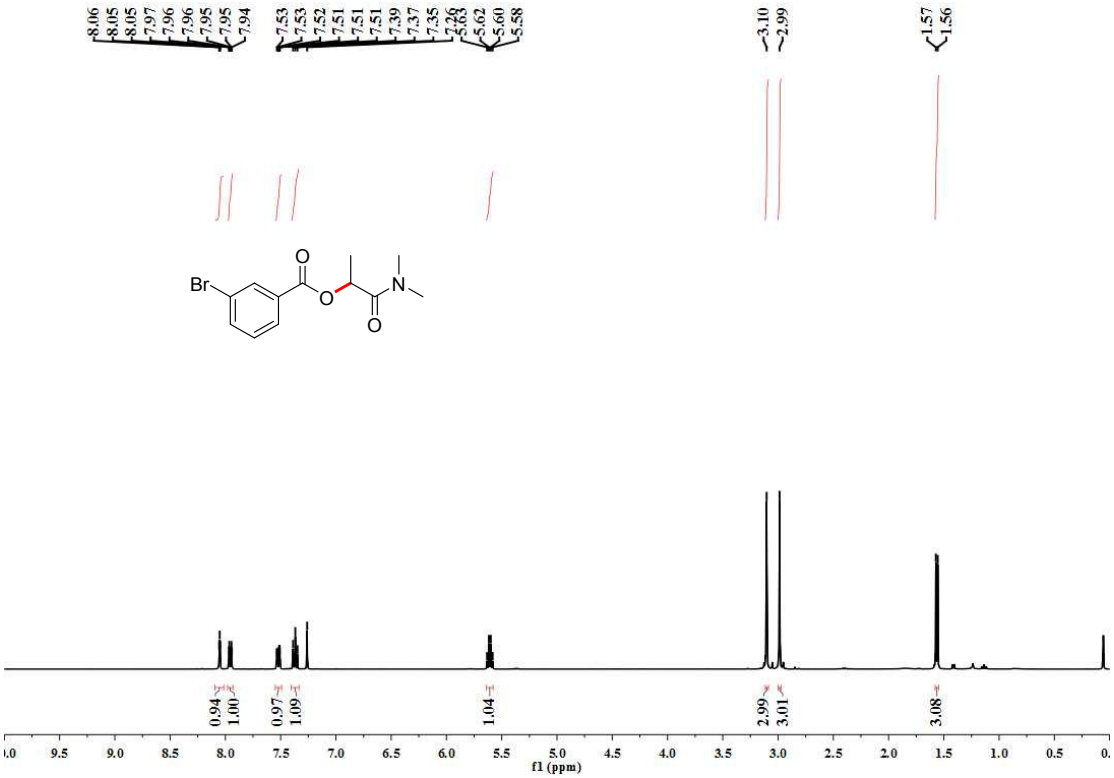
1-methyl-2-oxopyrrolidin-3-yl 3-bromobenzoate (4kh): ^{1}H NMR ($CDCl_3$, 400 MHz)



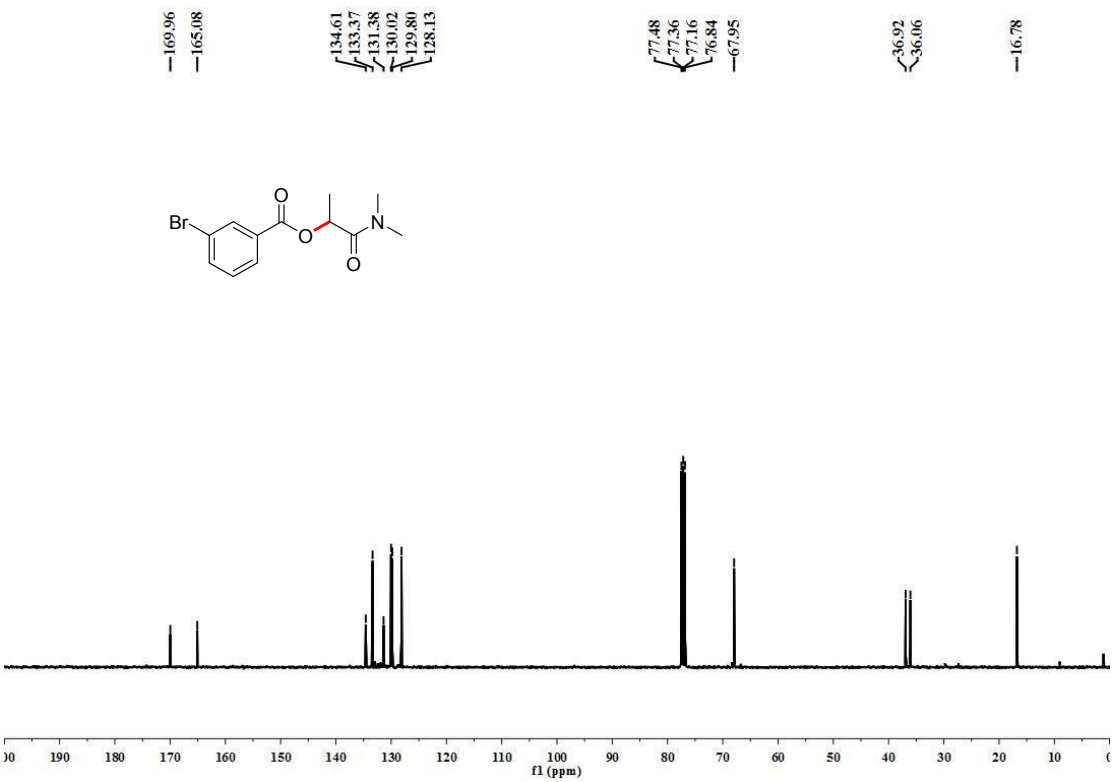
1-methyl-2-oxopyrrolidin-3-yl 3-bromobenzoate (4kh): ^{13}C NMR ($CDCl_3$, 101MHz)



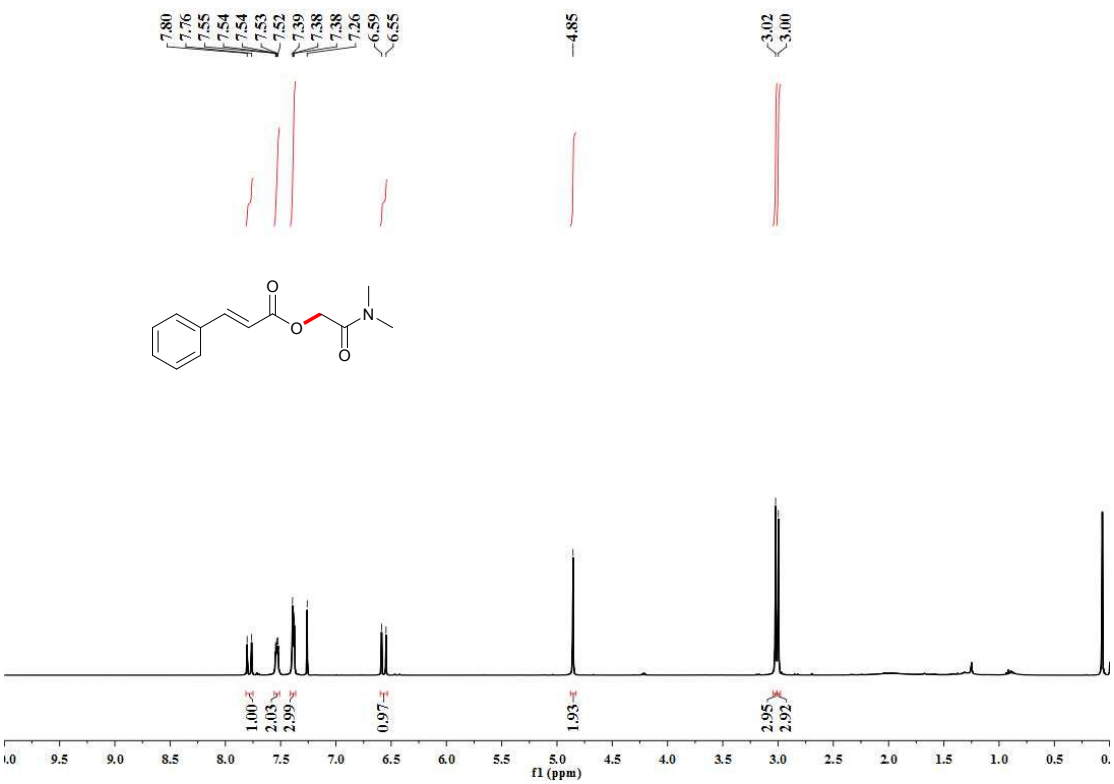
1-(dimethylamino)-1-oxopropan-2-yl 3-bromobenzoate (4ki): ^{1}H NMR ($CDCl_3$, 400 MHz)



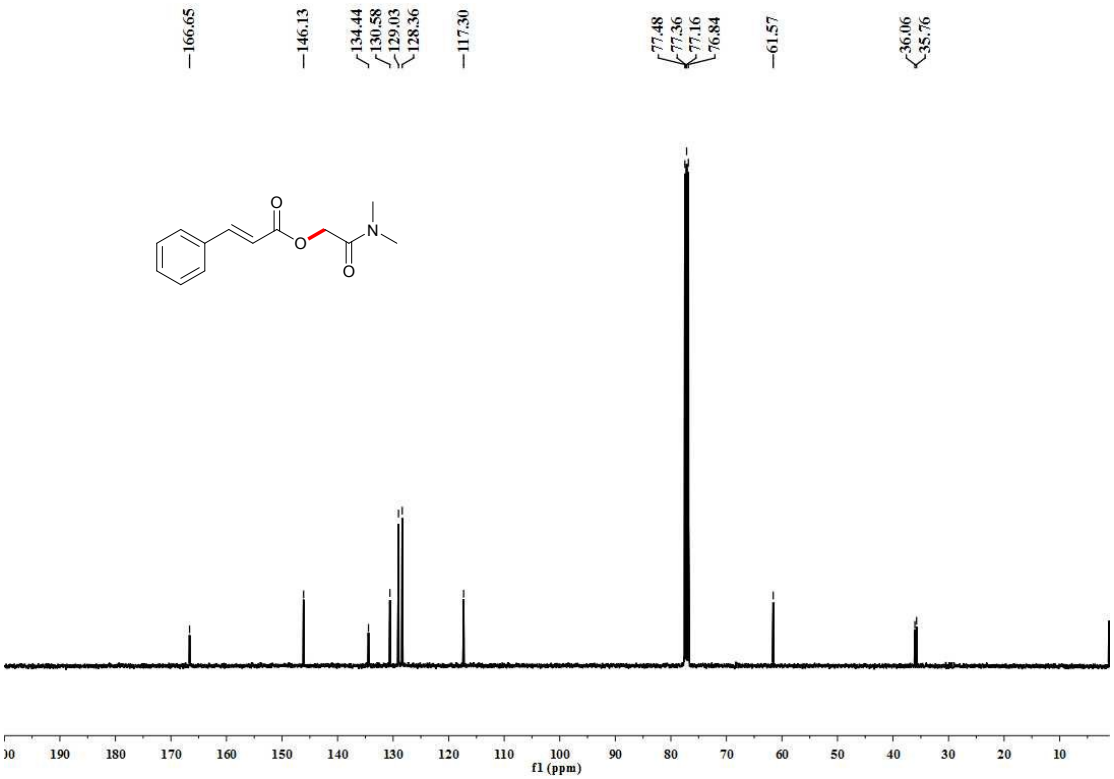
1-(dimethylamino)-1-oxopropan-2-yl 3-bromobenzoate (4ki): ^{13}C NMR ($CDCl_3$, 101 MHz)



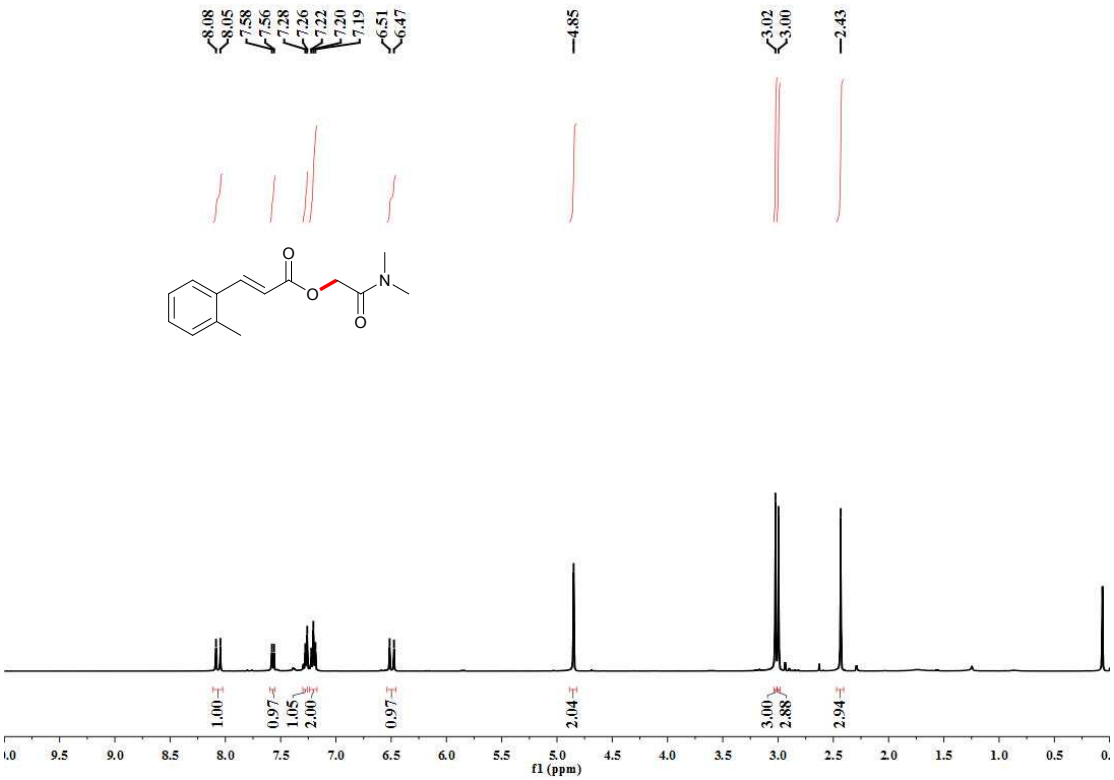
2-(Dimethylamino)-2-oxoethyl cinnamate (6aa): ^{1}H NMR ($CDCl_3$, 400 MHz)



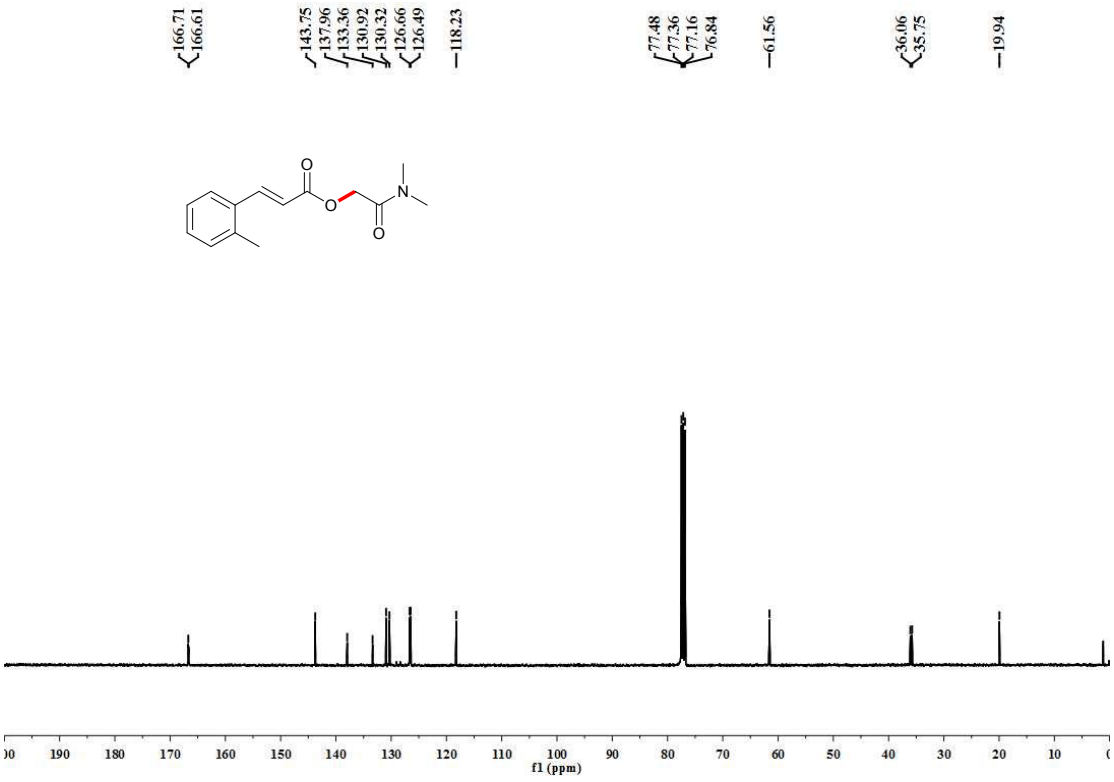
2-(Dimethylamino)-2-oxoethyl cinnamate (6aa): ^{13}C NMR ($CDCl_3$, 101 MHz)



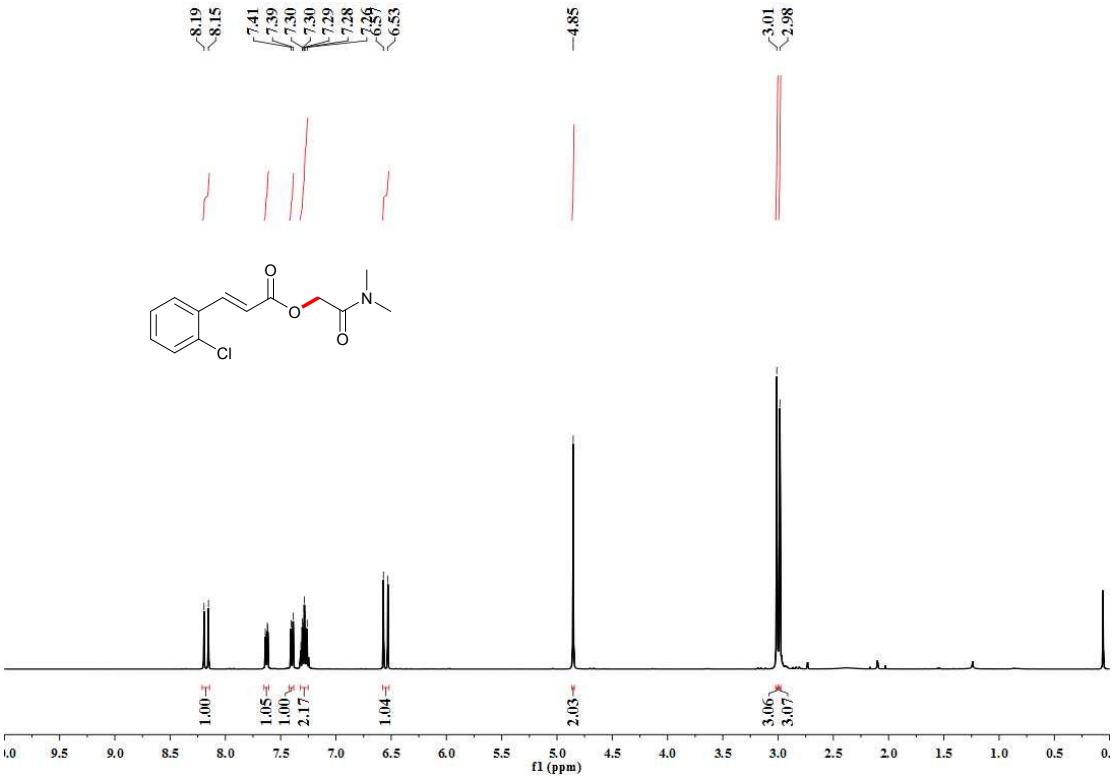
2-(Dimethylamino)-2-oxoethyl (*E*)-3-(o-tolyl)acrylate (6ba): ^{1}H NMR ($CDCl_3$, 400 MHz)



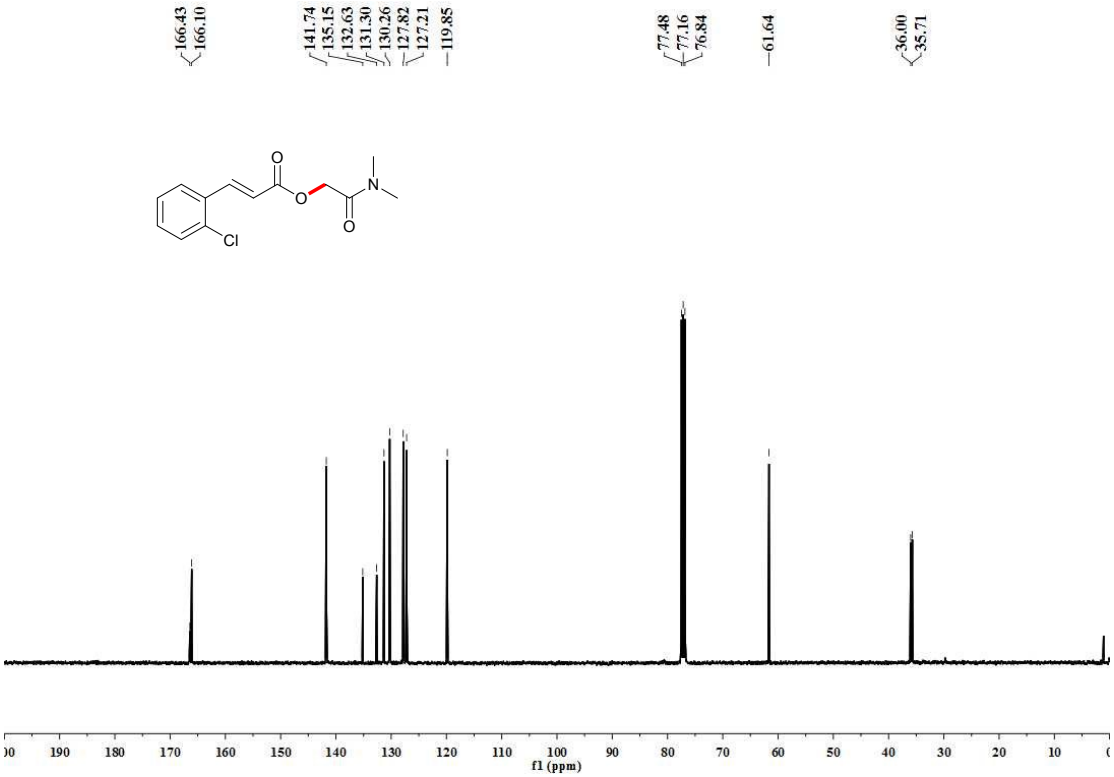
2-(Dimethylamino)-2-oxoethyl (*E*)-3-(o-tolyl)acrylate (6ba): ^{13}C NMR ($CDCl_3$, 101 MHz)



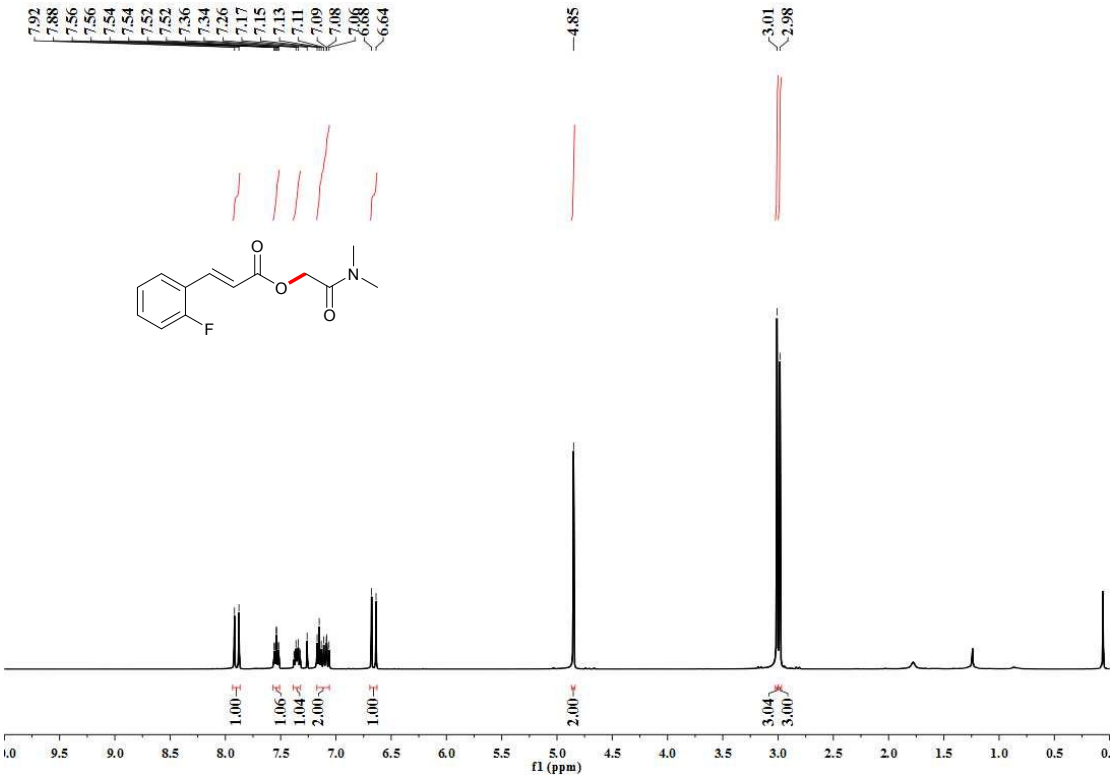
2-(dimethylamino)-2-oxoethyl (*E*)-3-(2-chlorophenyl)acrylate (6ca): ^{1}H NMR ($CDCl_3$, 400 MHz)



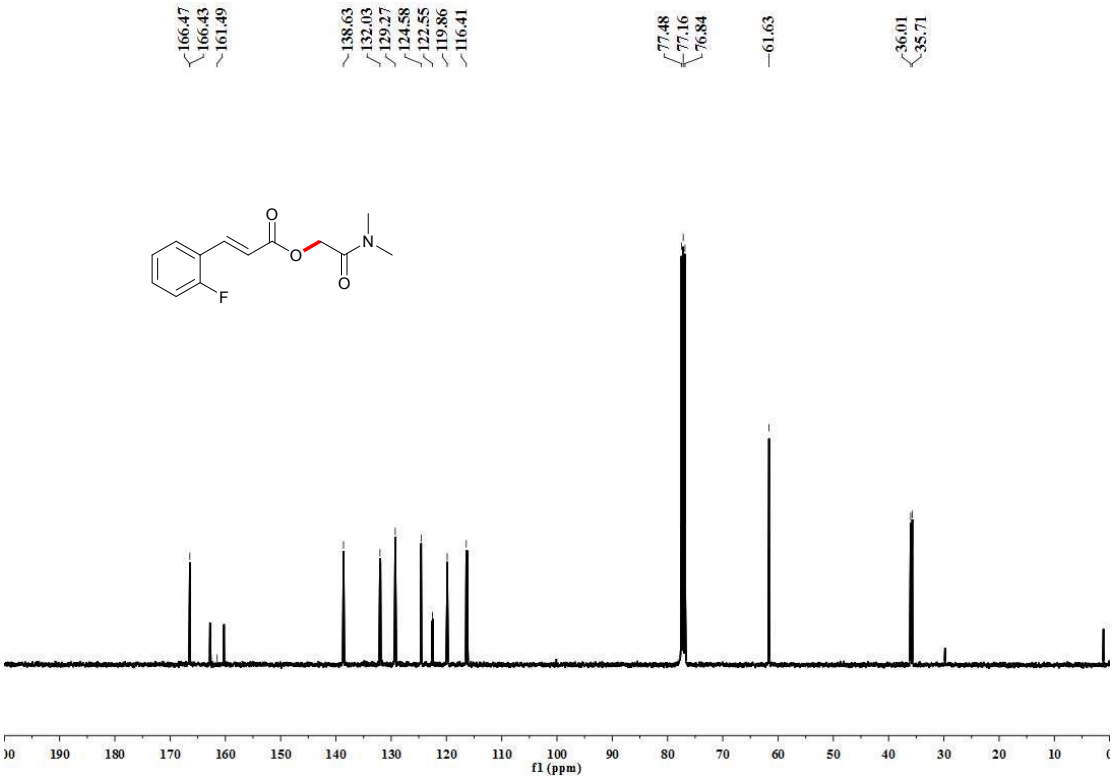
2-(dimethylamino)-2-oxoethyl (*E*)-3-(2-chlorophenyl)acrylate (6ca): ^{13}C NMR ($CDCl_3$, 101 MHz)



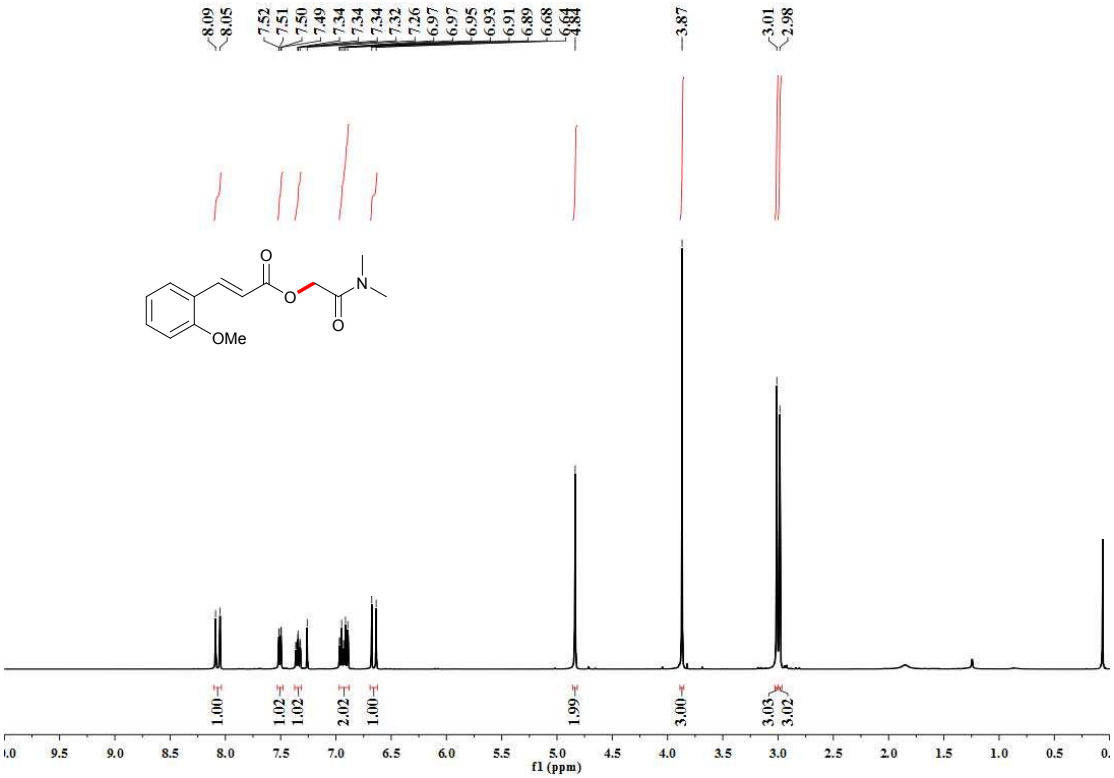
2-(Dimethylamino)-2-oxoethyl (*E*)-3-(2-fluorophenyl)acrylate (6da): ^{1}H NMR ($CDCl_3$, 400 MHz)



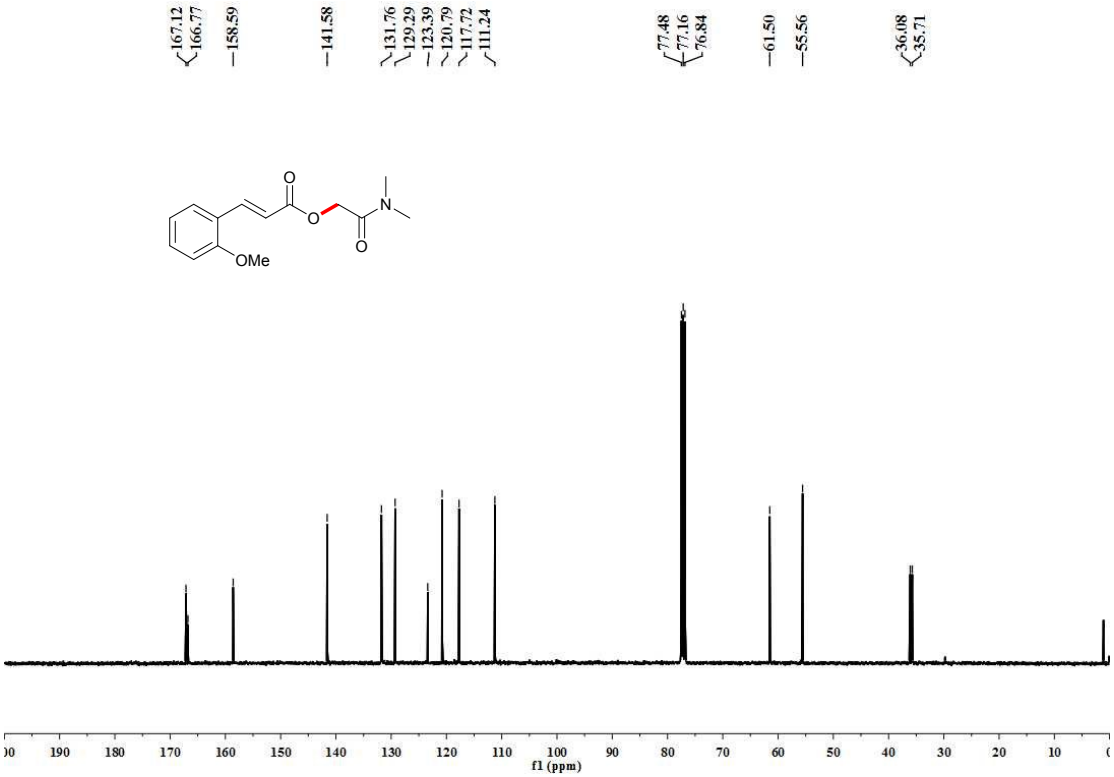
2-(dimethylamino)-2-oxoethyl (*E*)-3-(2-fluorophenyl)acrylate (6da): ^{13}C NMR ($CDCl_3$, 101 MHz)



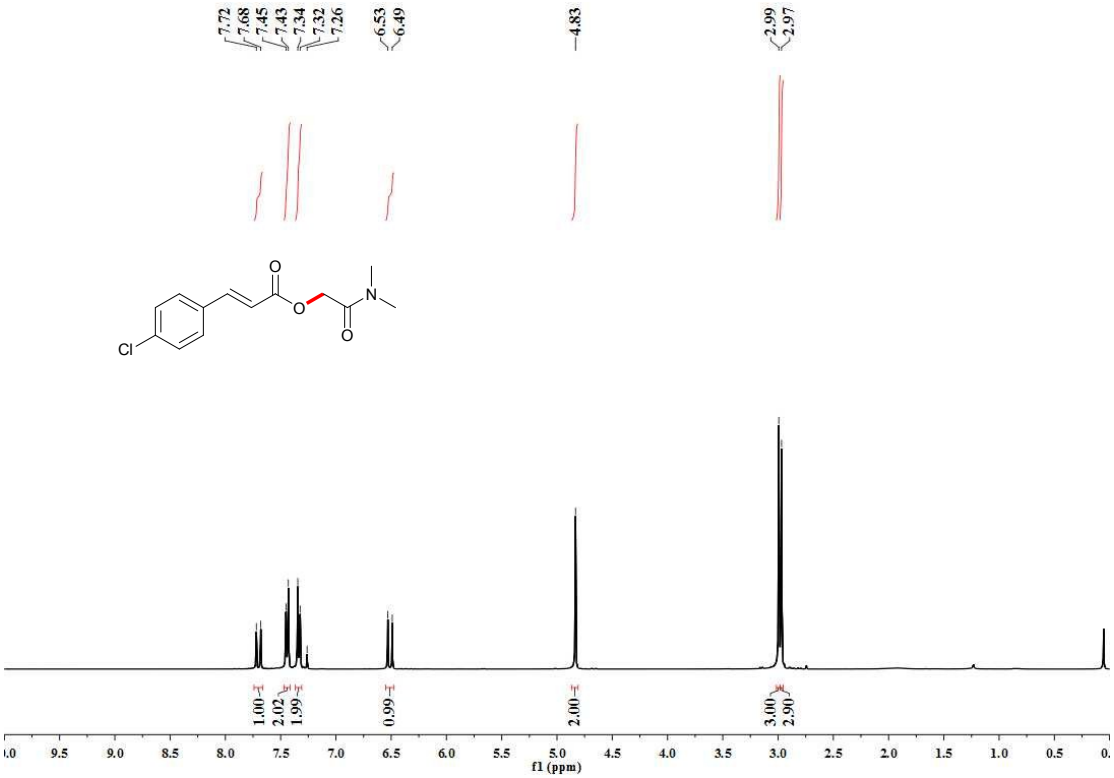
2-(Dimethylamino)-2-oxoethyl (*E*)-3-(2-methoxyphenyl)acrylate (6ea): ^{1}H NMR ($CDCl_3$, 400 MHz)



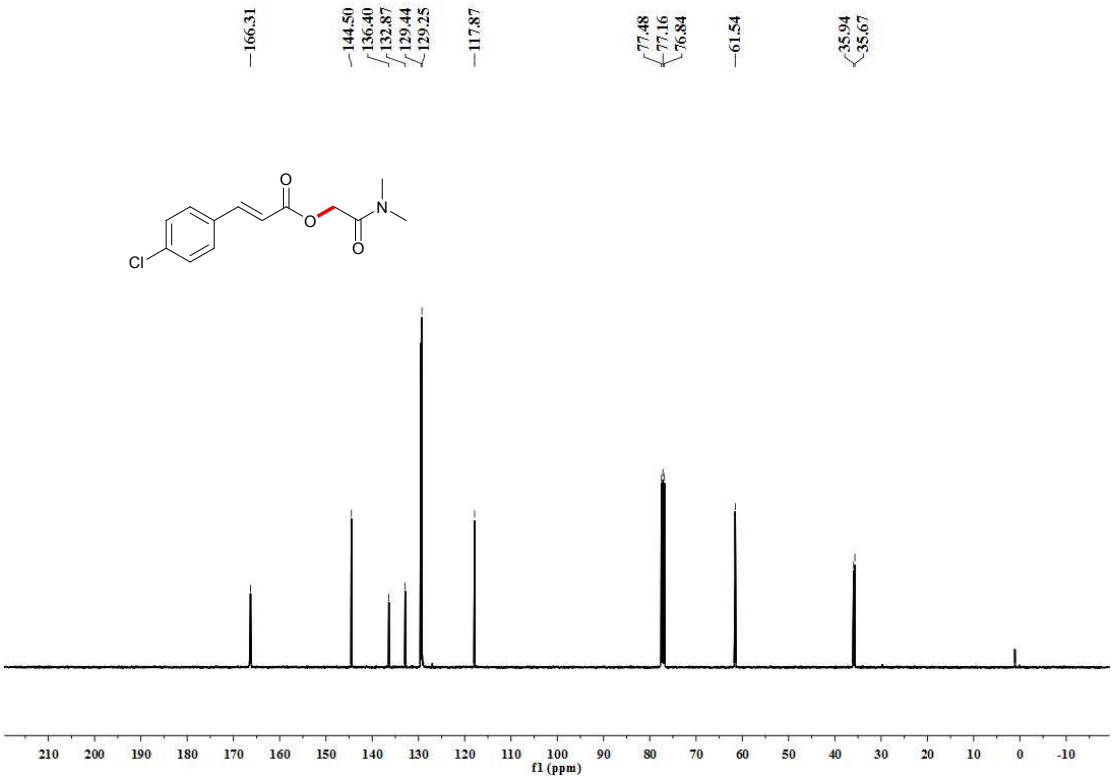
2-(Dimethylamino)-2-oxoethyl (*E*)-3-(2-methoxyphenyl)acrylate (6ea): ^{13}C NMR ($CDCl_3$, 101 MHz)



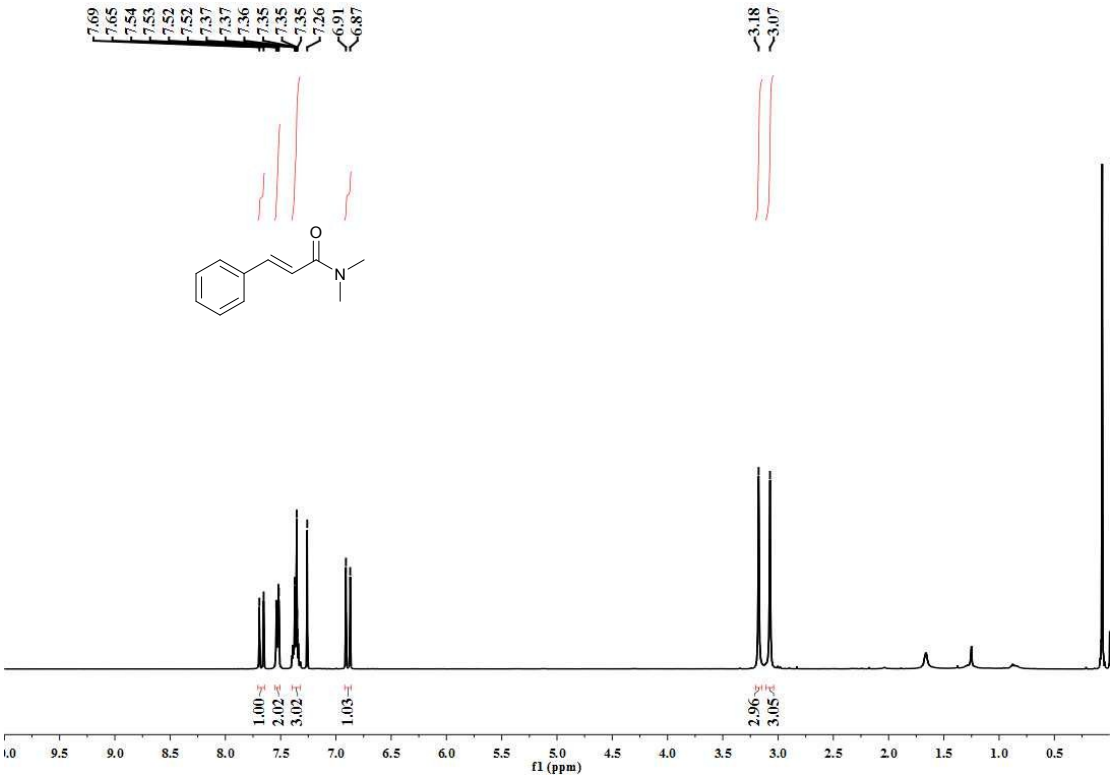
2-(dimethylamino)-2-oxoethyl (*E*)-3-(4-chlorophenyl)acrylate (6fa): ^{1}H NMR ($CDCl_3$, 400 MHz)



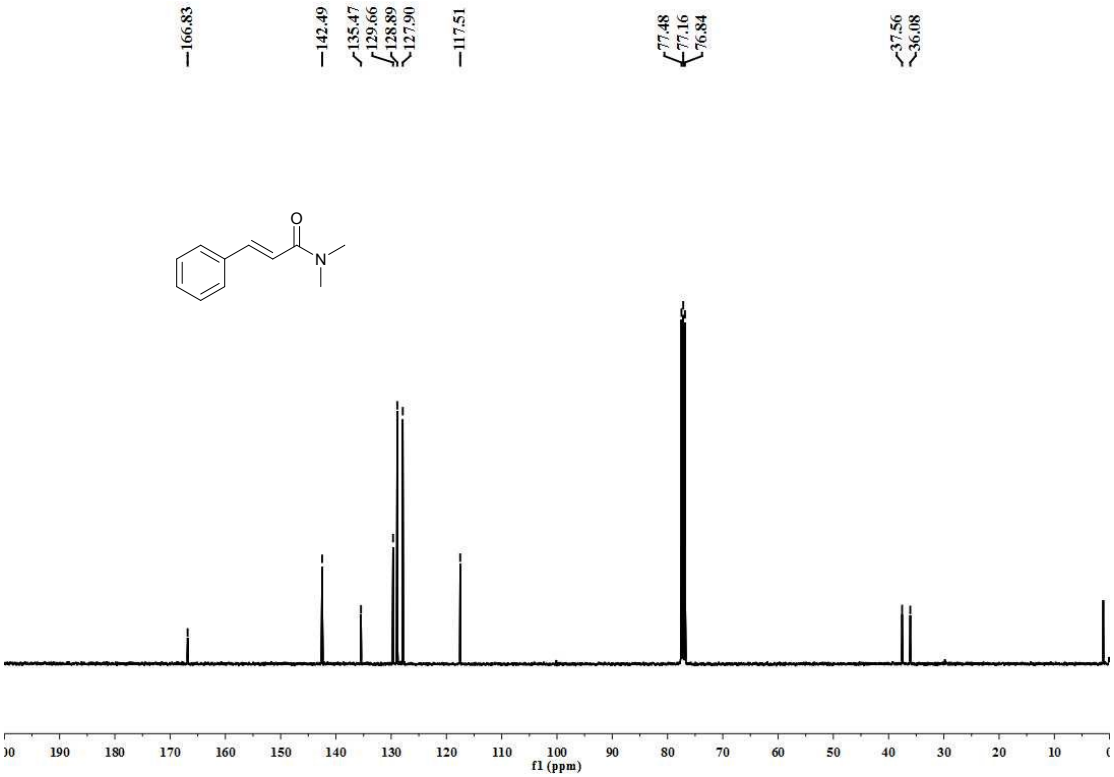
2-(dimethylamino)-2-oxoethyl (*E*)-3-(4-chlorophenyl)acrylate (6fa): ^{13}C NMR ($CDCl_3$, 101 MHz)



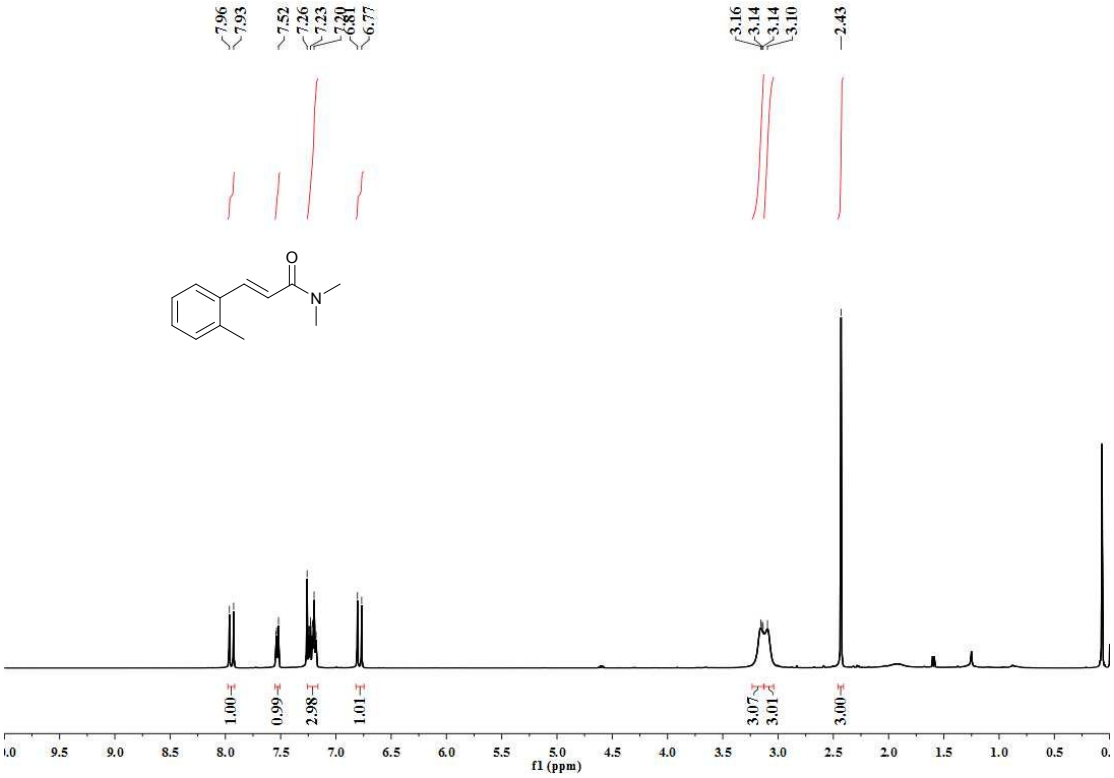
***N,N*-dimethylcinnamamide (7aa): ^{1}H NMR ($CDCl_3$, 400 MHz)**



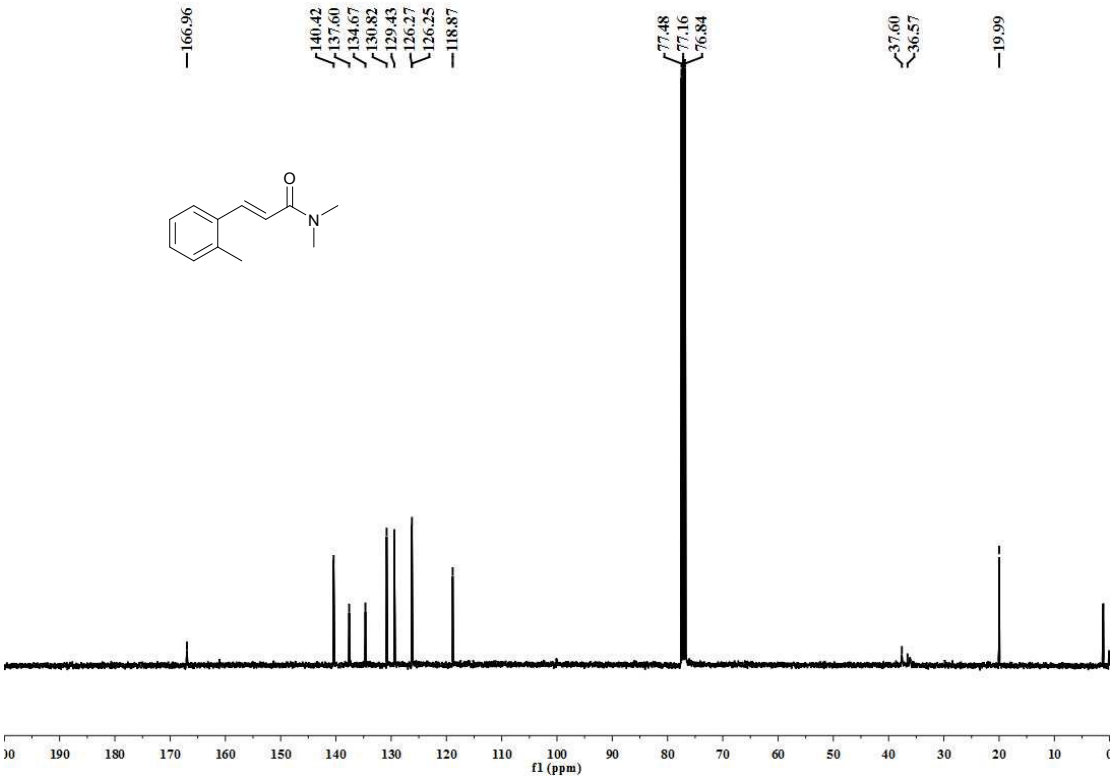
***N,N*-dimethylcinnamamide (7aa): ^{13}C NMR ($CDCl_3$, 101 MHz)**



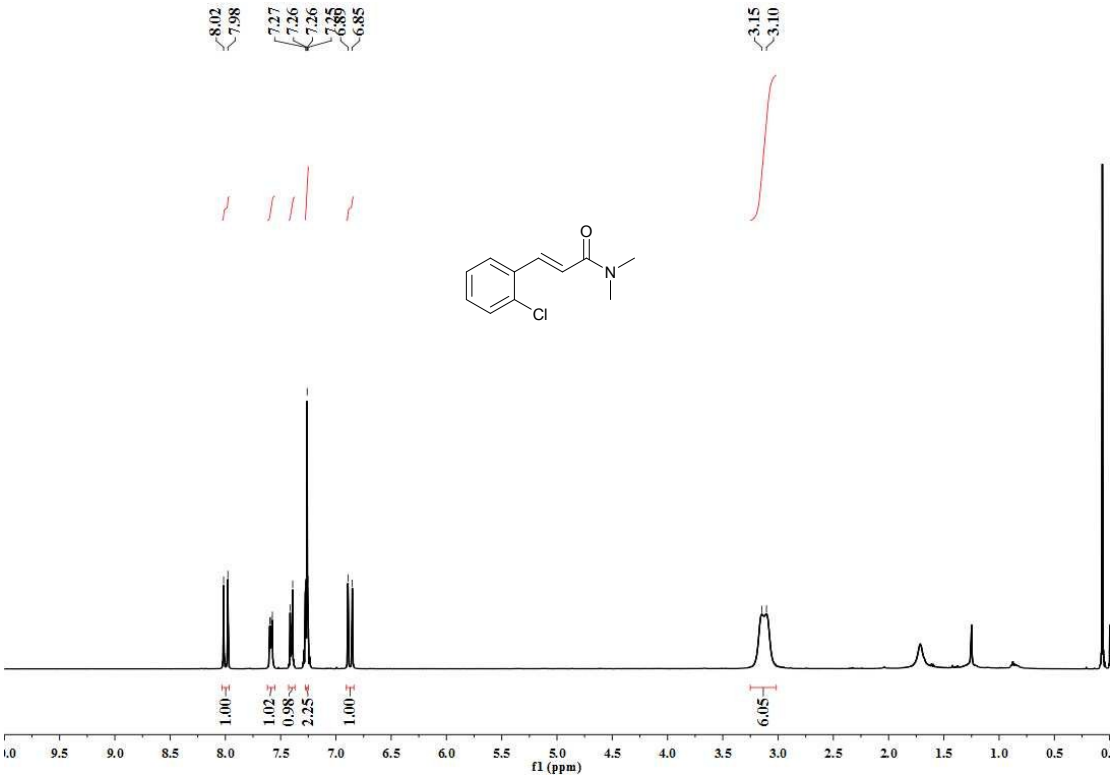
(*E*)-*N*,*N*-dimethyl-3-(o-tolyl)acrylamide (7ba): ^{1}H NMR ($CDCl_3$, 400 MHz)



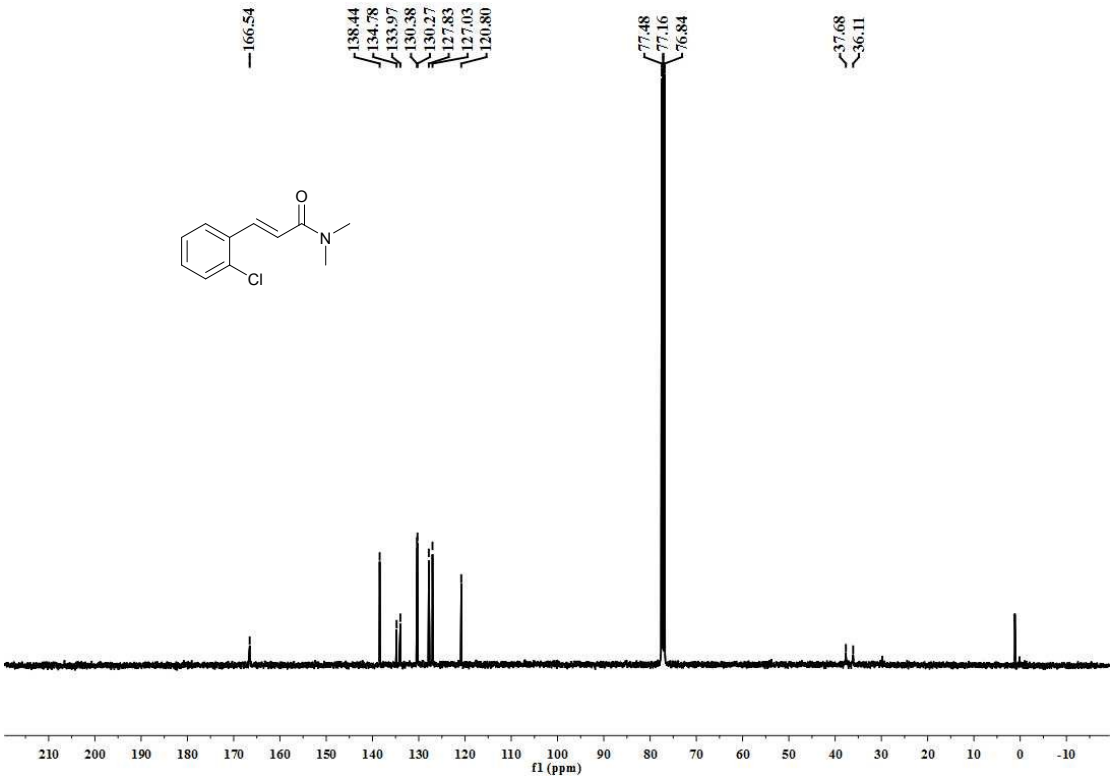
(*E*)-*N*,*N*-dimethyl-3-(o-tolyl)acrylamide (7ba): ^{13}C NMR ($CDCl_3$, 101 MHz)



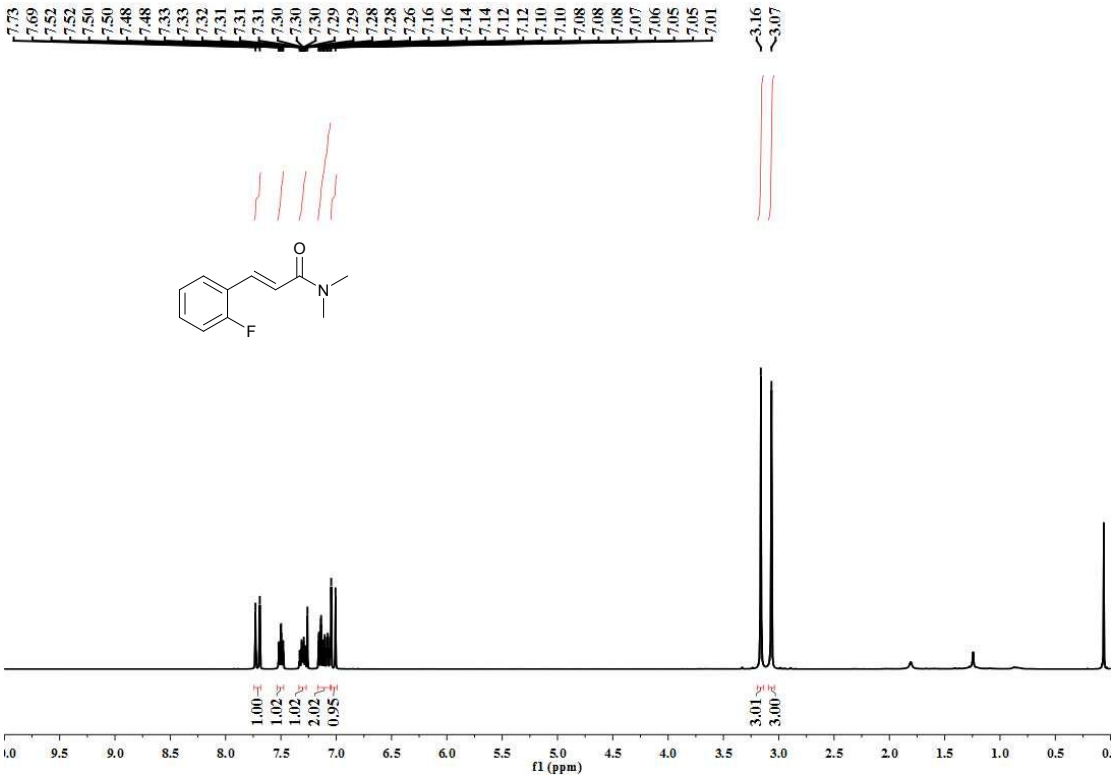
(*E*)-3-(2-chlorophenyl)-*N*,*N*-dimethylacrylamide (7ca): **^{1}H NMR ($CDCl_3$, 400 MHz)**



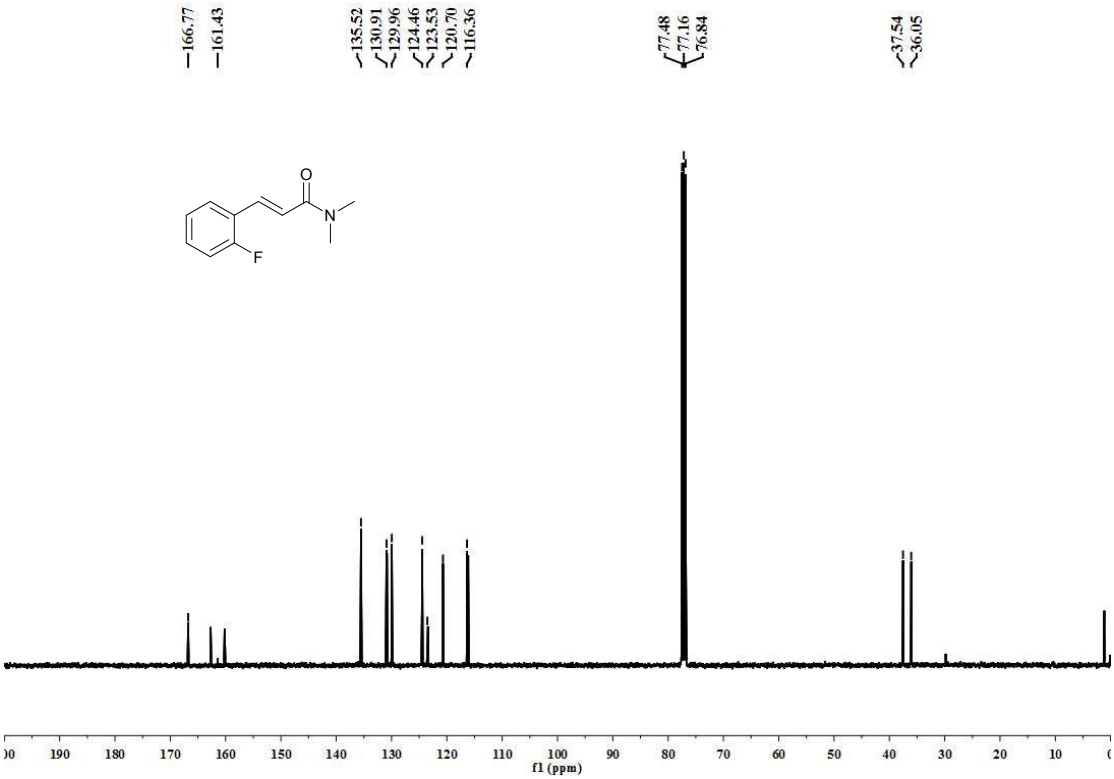
***(E)*-3-(2-chlorophenyl)-*N*,*N*-dimethylacrylamide (7ca)**: **^{13}C NMR ($CDCl_3$, 101 MHz)**



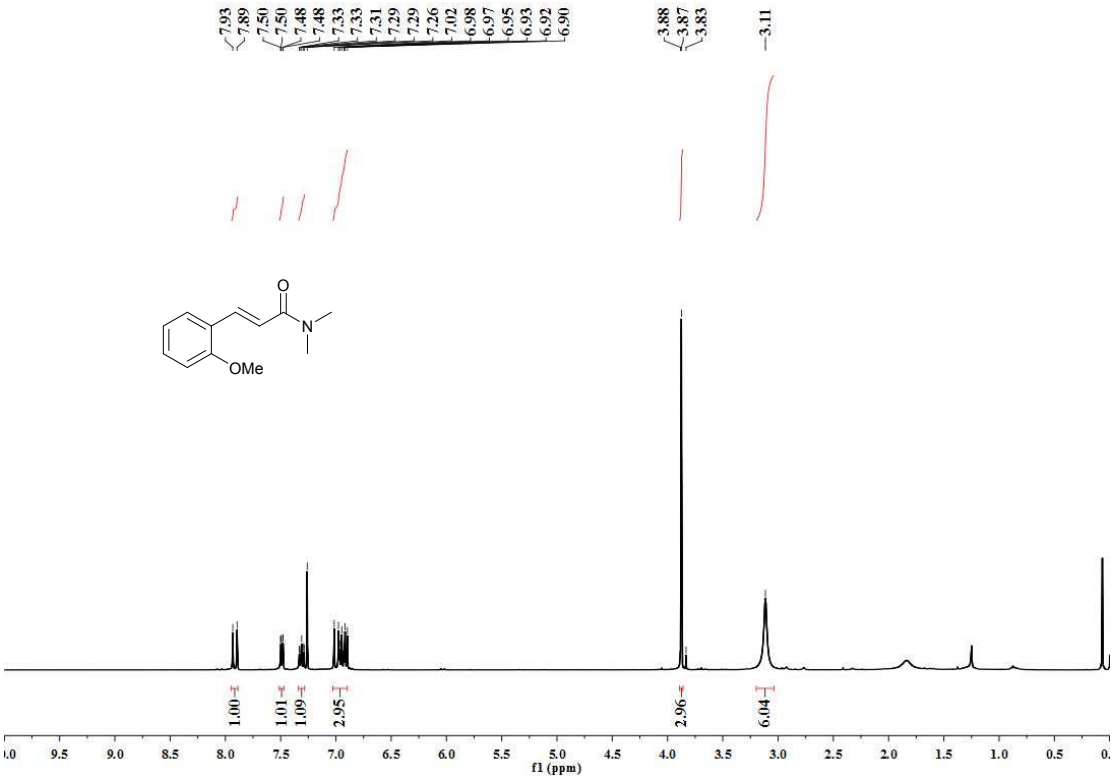
(*E*)-3-(2-fluorophenyl)-*N*,*N*-dimethylacrylamide (7da): **^{1}H NMR ($CDCl_3$, 400 MHz)**



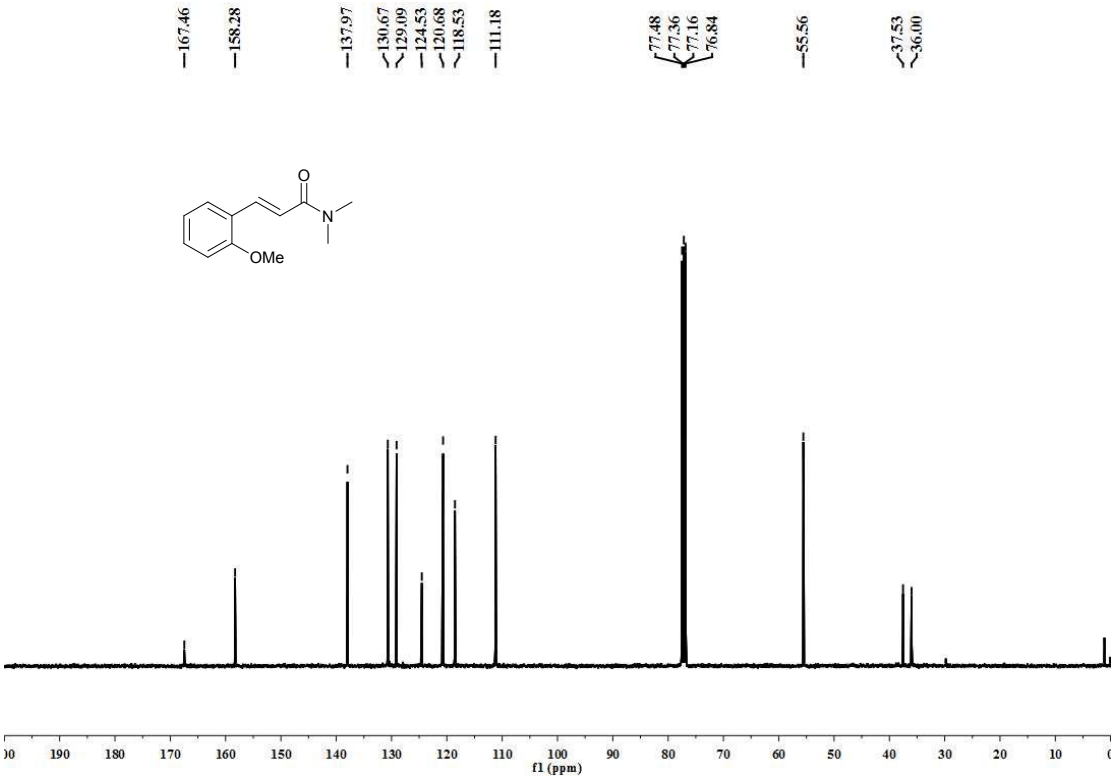
(*E*)-3-(2-fluorophenyl)-*N*,*N*-dimethylacrylamide (7da): ^{13}C NMR ($CDCl_3$, 101 MHz)



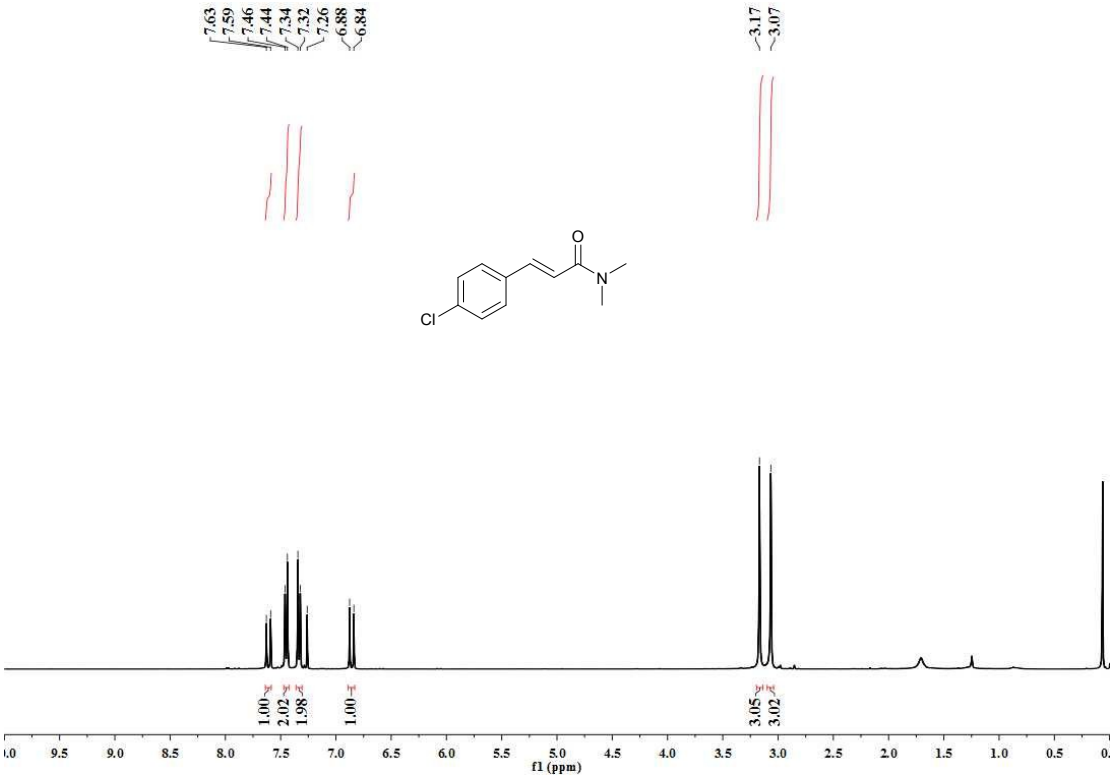
(*E*)-3-(2-methoxyphenyl)-*N*,*N*-dimethylacrylamide (7ea): ^{1}H NMR ($CDCl_3$, 400 MHz)



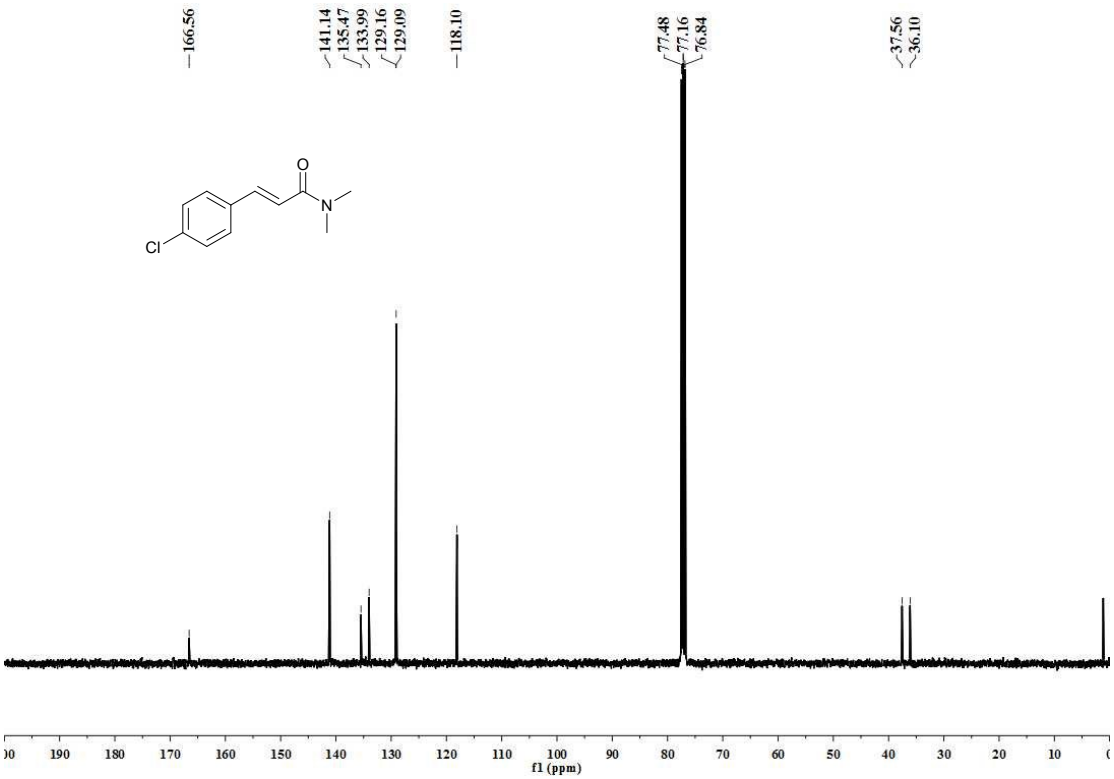
(*E*)-3-(2-methoxyphenyl)-*N*,*N*-dimethylacrylamide (7ea): ^{13}C NMR ($CDCl_3$, 101 MHz)



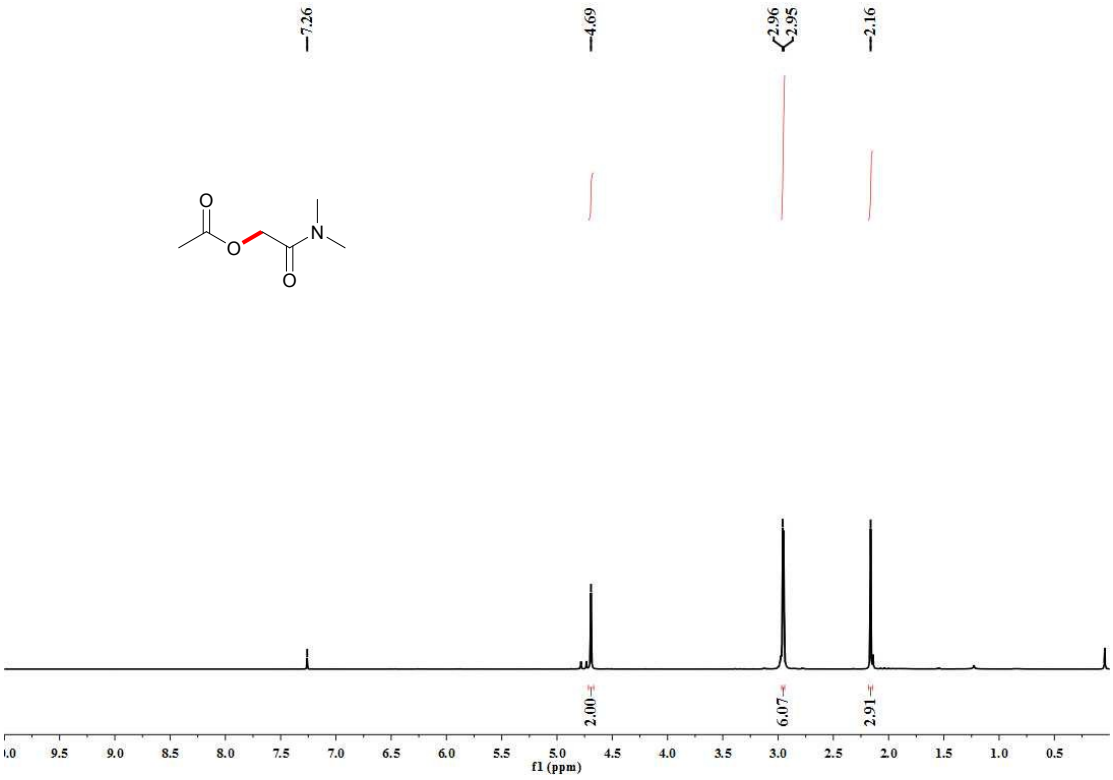
(*E*)-3-(4-chlorophenyl)-*N*,*N*-dimethylacrylamide (7fa): ^{1}H NMR ($CDCl_3$, 400 MHz)



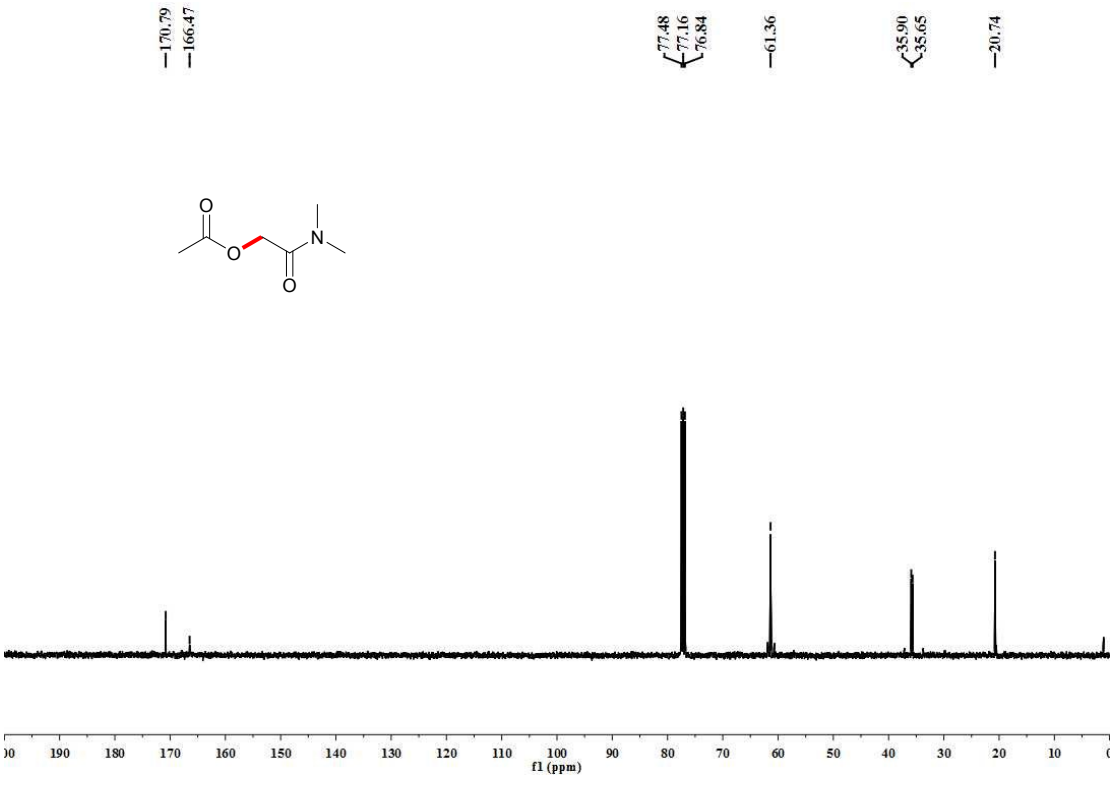
(*E*)-3-(4-chlorophenyl)-*N*,*N*-dimethylacrylamide (7fa): ^{13}C NMR ($CDCl_3$, 101 MHz)



2-(dimethylamino)-2-oxoethyl acetate : ^{1}H NMR ($CDCl_3$, 400 MHz)



2-(dimethylamino)-2-oxoethyl acetate : ^{13}C NMR ($CDCl_3$, 101 MHz)



2-chloro-*N*,*N*-dimethylacetamide: ^{1}H NMR ($CDCl_3$, 400 MHz)