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Supporting Information

Visible-light-mediated radical difunctionalization of alkenes with aromatic aldehydes

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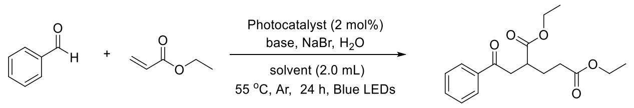
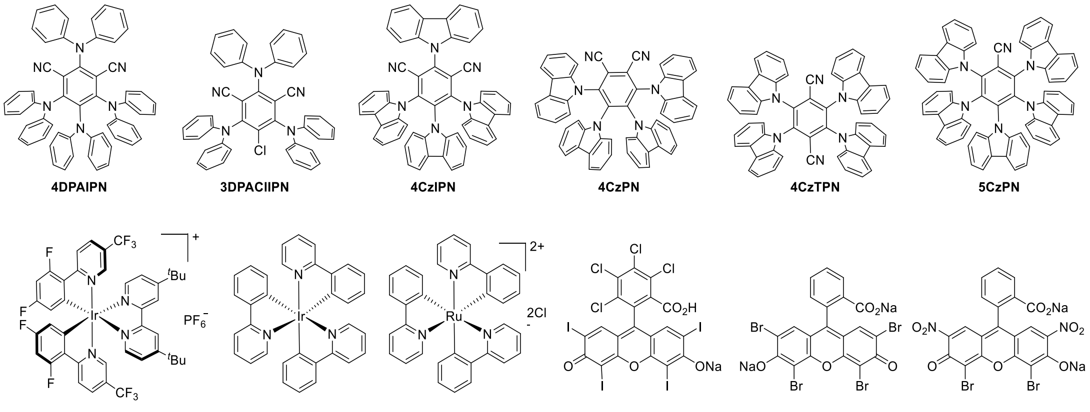
1. General Information

The reactions via general procedure were carried out under an atmosphere of argon unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AVANCE-III-HD (400 and 100 MHz, respectively) and processed using either MestReNova. ^{1}H NMR chemical shifts are given in ppm with respect to the residual $CDCl_3$ peak (δ 7.26 ppm), or an internal TMS standard (δ 0.00 ppm), ^{13}C NMR shifts are given in ppm with respect to $CDCl_3$ (δ 77.00 ppm). Mass spectra were measured on Agilent 5977 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those in literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Fluorescence quenching experiments were recorded with PTI-QM40 spectrophotometer. A commercially available blue LED (35W, HIPAR30, luminous flux is not less than 3200 lm) was purchased from Shenzhen Jing Feng Times Lighting Technology Co., Ltd as the reaction light source. All irradiation reactions were carried out in borosilicate glass vessel. The distance from the light source to the irradiation vessel is around 4-5 cm. Unless otherwise noted, all other reagents were obtained from commercial suppliers and used without further purification.

2. Table S1 Optimization of the reaction conditions[a]



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



4DPAIPN **3DPACIIPN** **4CzIPN** **4CzPN** **4CzTPN** **5CzPN**

[Ir]PF$_6$ = [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$ ***fac*-Ir(ppy)$_3$** **Ru(bpy)$_3$Cl$_2$** **Rose Bengal** **Eosin Y** **Eosin B**

entry	PC	base (equiv)	NaBr (equiv)	H_2O (equiv)	solvent	yield (%)[b]
1	**4CzIPN**	HE(1.0)	NaBr	10	DCM	36
2	**4CzIPN**	HE(1.5)	NaBr	10	DCM	54
3	**4CzIPN**	HE(2.0)	NaBr	10	DCM	18
4	**4CzIPN**	HE(2.5)	NaBr	10	DCM	40
5	**4CzIPN**	HE(3.0)	NaBr	10	DCM	48
6	**4DPAIPN**	HE(1.5)	NaBr	10	DCM	trace
7	**3DPACIIPN**	HE(1.5)	NaBr	10	DCM	trace
8	**4CzIPN**	HE(1.5)	NaBr	10	DCM	54
9	**4CzPN**	HE(1.5)	NaBr	10	DCM	58
10	**4CzTPN**	HE(1.5)	NaBr	10	DCM	54
11	**5CzBN**	HE(1.5)	NaBr	10	DCM	trace
12	***fac*-Ir(ppy)$_3$**	HE(1.5)	NaBr	10	DCM	38
13	**[Ir]PF$_6$**	HE(1.5)	NaBr	10	DCM	33
14	**Ru(bpy)$_3$Cl$_2$**	HE(1.5)	NaBr	10	DCM	n.d.
15	**Rose bengal**	HE(1.5)	NaBr	10	DCM	trace
16	**Eosin Y**	HE(1.5)	NaBr	10	DCM	trace
17	**Eosin B**	HE(1.5)	NaBr	10	DCM	trace
18	-	HE(1.5)	NaBr	10	DCM	n.d.
19	**4CzPN**	DIPEA(1.5)	NaBr	10	DCM	trace
20	**4CzPN**	DABCO(1.5)	NaBr	10	DCM	n.d.
21	**4CzPN**	TMEDA(1.5)	NaBr	10	DCM	trace
22	**4CzPN**	Et_3N(1.5)	NaBr	10	DCM	trace
23	**4CzPN**	CH_3ONa(1.5)	NaBr	10	DCM	trace
24	**4CzPN**	HE(1.5)	NaBr	10	CyH	trace
25	**4CzPN**	HE(1.5)	NaBr	10	hexane	60
26	**4CzPN**	HE(1.5)	NaBr	10	PE	64
27	**4CzPN**	HE(1.5)	NaBr	10	toluene	58
28	**4CzPN**	HE(1.5)	NaBr	20	PE	54
29	**4CzPN**	HE(1.5)	NaBr	30	PE	68

30	**4CzPN**	HE(1.5)	NaBr	40	PE	78(60[c])
31	**4CzPN**	HE(1.5)	NaBr	50	PE	48
32	**4CzPN**	HE(1.5)	NaBr	-	PE	28[d]
33	**4CzPN**	HE(1.5)	$NiCl_2•6H_2O$	40	PE	74
34	**4CzPN**	HE(1.5)	$NiCl_2•xH_2O$	40	PE	58
35	**4CzPN**	HE(1.5)	KCl	40	PE	32
36	**4CzPN**	HE(1.5)	KBr	40	PE	56
37	**4CzPN**	HE(1.5)	KI	40	PE	trace
38	**4CzPN**	HE(1.5)	$BiBr_3$	40	PE	52
39	**4CzPN**	HE(1.5)	$CoCl_3$	40	PE	38
40	**4CzPN**	HE(1.5)	-	40	PE	20[d]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.52 mmol, 2.6 equiv), HE (1.5 equiv), H_2O (40 equiv), NaBr (1.0 equiv) and photocatalyst (**PC**, 0.004 mmol, 2 mol%) in solvent (2 mL) at 55 °C under Ar atmosphere and 35 W blue LEDs irradiation for 24 h. [b] NMR yield. [c] Isolated yield. [d] GC-MS yield.

3. General Procedure for the Reaction of arylacrylamide and alkenyl esters

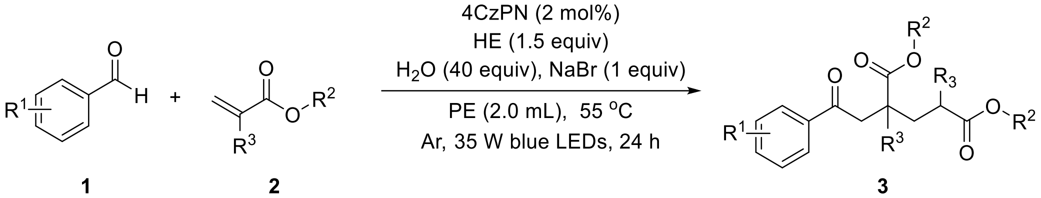


Figure S1

General Procedure: A 20 mL reaction vessel was charged with 4CzPN (3.2 mg, 0.004 mmol, 2 mol%), aromatic aldehydes (**1**, 0.2 mmol, 1.0 equiv), alkenyl esters (**2**, 0.52 mmol, 2.6 equiv), HE (76.0 mg, 1.5 equiv), NaBr (21.0 mg, 1.0 equiv) and H_2O (144.0 μL, 40 equiv) in 2.0 mL PE under Ar atmosphere. The resulting mixture was stirred for 24 h under irradiation with a 35 W blue LEDs at 55-60 ºC. The reaction was monitored by TLC. The crude reaction mixture was dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **3**.

Scale-up experiment

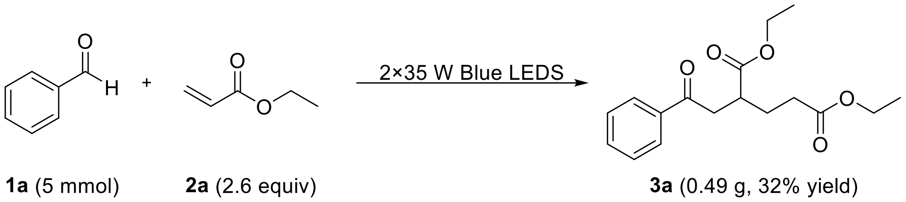


Figure S2

5 mmol scale reaction: A 100 mL oven-dried reaction vessel was charged with 4CzPN (20.0 mg, 0.036 mmol, 0.5 mol%), aromatic aldehydes (508.0 μL, 5 mmol, 1.0 equiv), alkenyl esters (1413.0 μL, 13 mmol, 2.6 equiv), HE (1.9 g, 7.5 mmol,1.5 equiv), NaBr (525.0 mg, 5 mmol,1.0 equiv) and H_2O (3.6 mL, 200 mmol, 40 equiv) in 50.0 mL PE under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with 2 × 35 W blue LEDs at 55 ºC. The reaction was monitored by TLC. The crude reaction mixture was dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) to give the product **3a** (0.49 g, 32% yield).

4. Mechanistic studies

4.1 Radical trapping experiments

(i) The following reaction was carried out under standard conditions: A 20 mL reaction vessel was charged with 4CzPN (3.2 mg, 0.004 mmol, 2 mol%), aromatic aldehydes **1a** (21.0 µL, 0.2 mmol, 1.0 equiv), alkenyl esters **2a** (57.0 µL, 0.52 mmol, 2.6 equiv), HE (76.0 mg, 1.5 equiv), NaBr (21.0 mg, 1.0 equiv), and H_2O (144 µL, 40 equiv) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (78.1 mg, 0.5 mmol, 2.5 equiv) in 2.0 mL PE under Ar atmosphere. The resulting mixture was stirred for 24 h under irradiation with a 35 W Blue LEDs at 55 ºC. After completion, the crude residues were analyzed by GC-MS. Yield of **3a** was reduced to trace and TEMPO-trapped product was not detected by GC-MS.

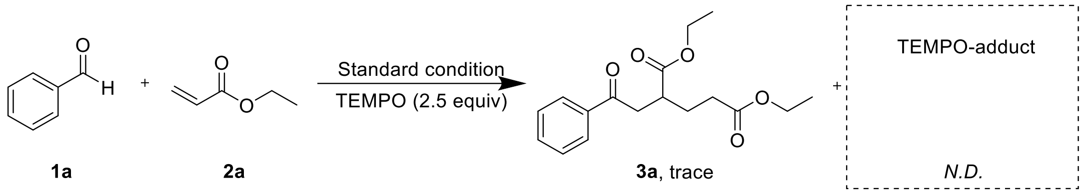


Figure S3

(ii) The following reaction was carried out under standard conditions: A 20 mL reaction vessel was charged with 4CzPN (3.2 mg, 0.004 mmol, 2 mol%), aromatic aldehydes **1a** (21.0 µL, 0.2 mmol, 1.0 equiv), alkenyl esters **2a** (57.0 µL, 0.52 mmol, 2.6 equiv), HE (76.0 mg, 1.5 equiv), NaBr (21.0 mg, 1.0 equiv), and H_2O (144.0 µL, 40 equiv) and 1,1-diphenylethene (DPE) (88.3 uL, 0.5 mmol, 2.5 equiv) in 2.0 mL PE under Ar atmosphere. The resulting mixture was stirred for 24 h under irradiation with a 35 W Blue LEDs at 55 ºC. After completion, the crude residues were analyzed by GC-MS. Yield of **3a** was reduced to trace and DPE-trapped product was not detected by GC-MS.

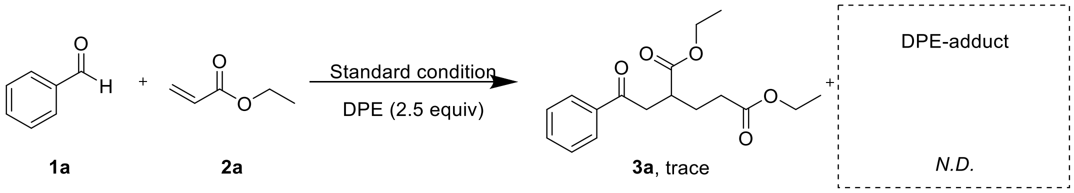


Figure S4

(iii) The following reaction was carried out under standard conditions: A 20 mL reaction vessel was charged with 4CzPN (3.2 mg, 0.004 mmol, 2 mol%), aromatic aldehydes **1a** (21.0 µL, 0.2 mmol, 1.0 equiv), alkenyl esters **2a** (57.0 µL, 0.52 mmol, 2.6 equiv), HE (76.0 mg, 1.5 equiv), NaBr (21.0 mg, 1.0 equiv), and H_2O (144.0 µL, 40 equiv) and and butylated hydroxytoluene (BHT) (110.2 mg, 0.5 mmol, 2.5 equiv) in 2.0 mL PE under Ar atmosphere. The resulting mixture was stirred for 24 h under irradiation with a 35 W Blue LEDs at 55 ºC. After completion, the crude residues were analyzed by GC-MS. Yield of **3a** was 25% and BHT-trapped product was not detected by GC-MS.

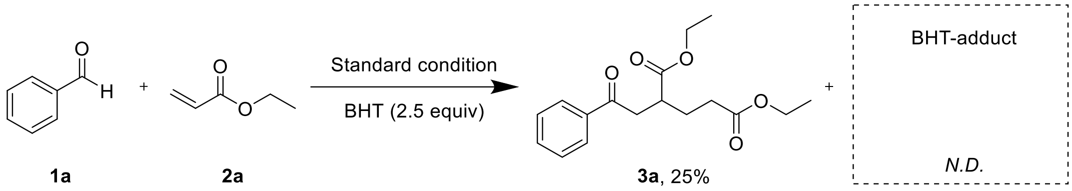


Figure S5

4.2 Stern-Volmer quenching

Formulation solution: Benzaldehyde (**1a**, 51.0 μL) was dissolved in acetone in a 25.0 mL volumetric flask to set the concentration to be 0.02 M. Ethyl acrylate (**2a**, 54.4 μL) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.02 M. Photocatalyst 4CzPN (2.0 mg) was dissolved in acetone (25.0 mL) to set the concentration to be 0.1 mM.

Experimental procedure: The resulting 0.1 mM solution (200 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding THF to prepare a 10 μM solution. The resulting mixture was sparged with argon for 3 minutes and then irradiated at 400 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 10.0 μL of an aromatic aldehydes solution was successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 3 minutes and irradiated at 400 nm. Fluorescence emission spectra of 0 μL, 10.0 μL, 20.0 μL, 30.0 μL, 40.0 μL 50.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn. The results were shown in the following figures.

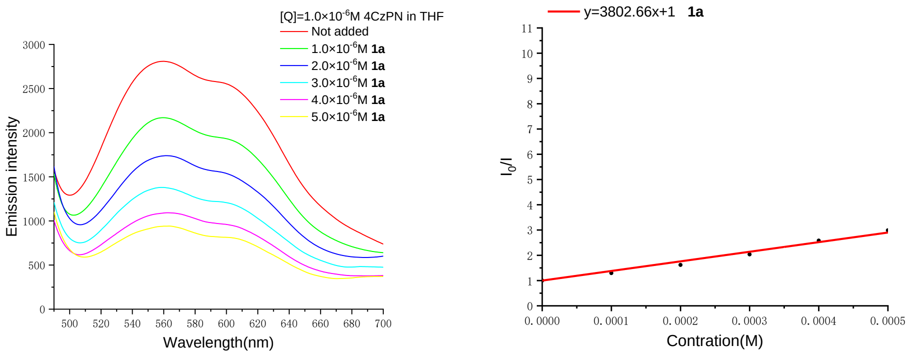


Figure S6. Emission quenching of 4CzPN with benzaldehyde (**1a**) in THF

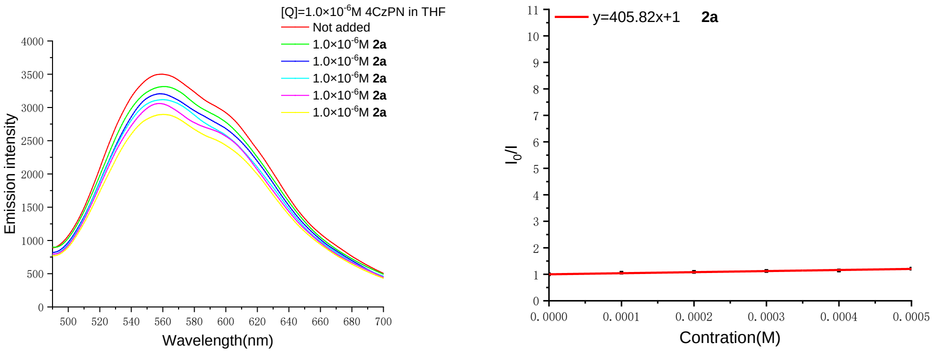


Figure S7. Emission quenching of 4CzPN with ethyl acrylate (**2a**) in THF

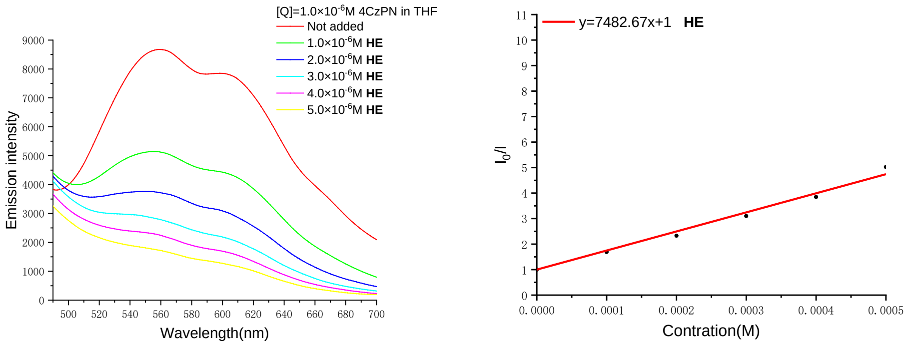


Figure S8. Emission quenching of 4CzPN with HE in THF

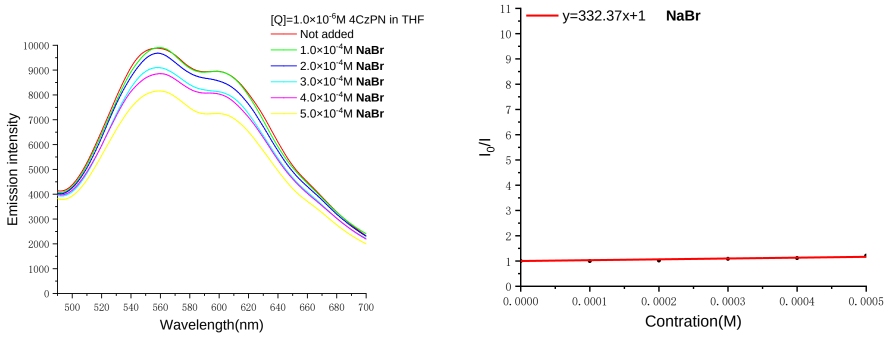


Figure S9. Emission quenching of 4CzPN with NaBr in THF

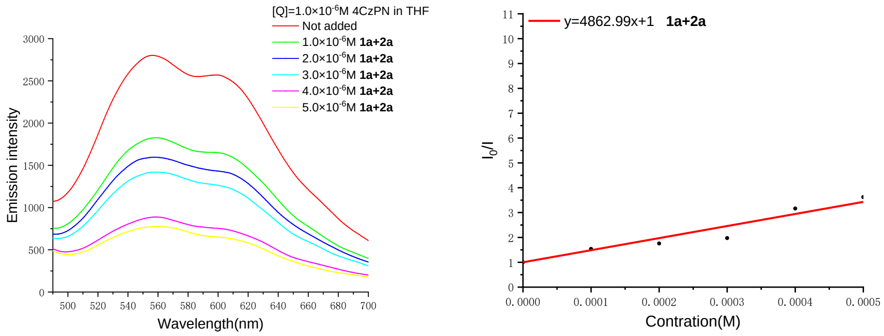


Figure S10. Emission quenching of 4CzPN with benzaldehyde (**1a**) + ethyl acrylate (**2a**) in THF

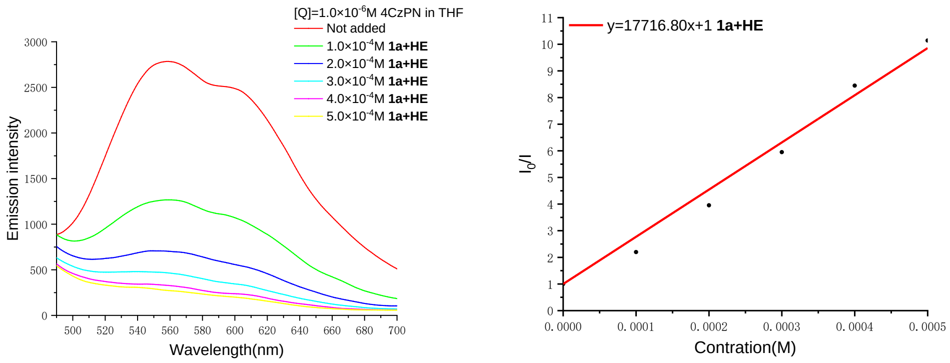


Figure S11. Emission quenching of 4CzPN with benzaldehyde (**1a**) + HE in THF

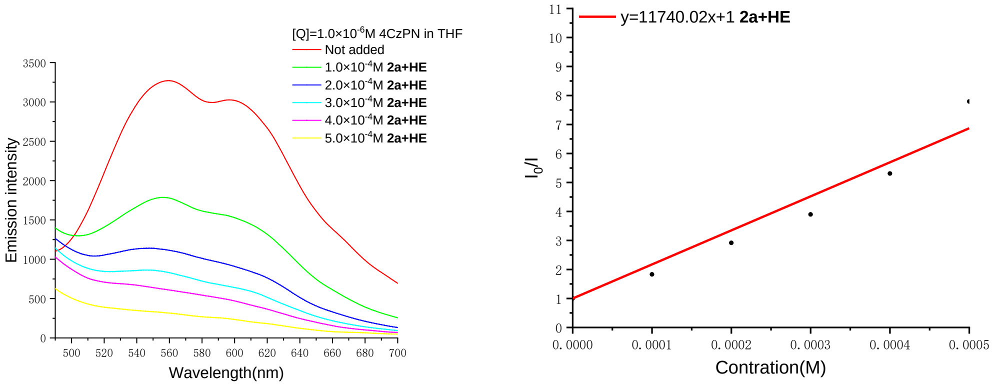


Figure S12. Emission quenching of 4CzPN with ethyl acrylate (**2a**) + HE in THF

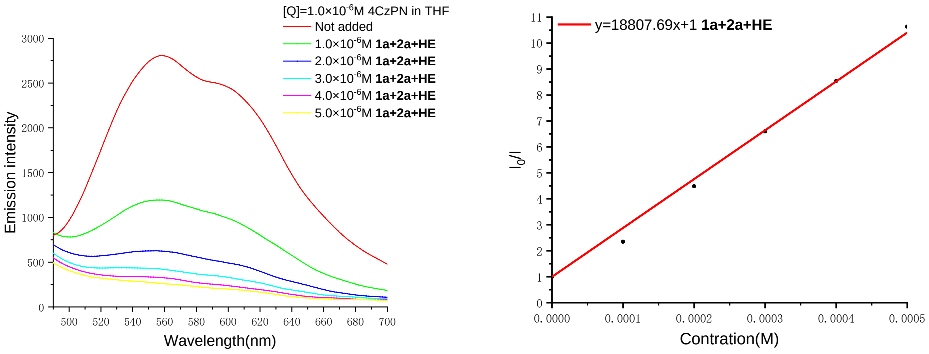


Figure S13. Emission quenching of 4CzPN with benzaldehyde (**1a**) + ethyl acrylate (**2a**) + HE in THF

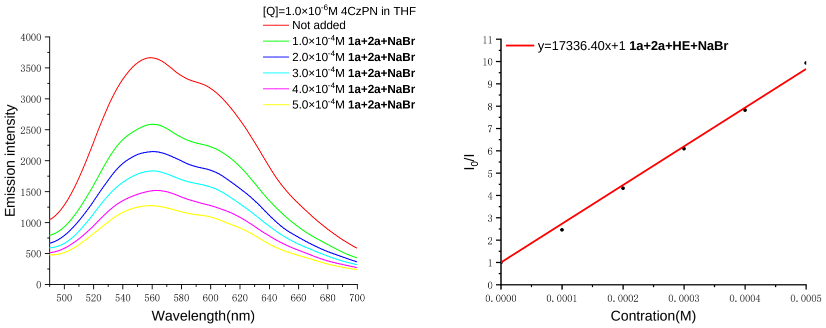


Figure S14. Emission quenching of 4CzPN with benzaldehyde (**1a**) + ethyl acrylate (**2a**) + HE + NaBr in THF

4.3 Switch light experiments

Conducted the relationship of products with light on-off under standard conditions. Subsequent samples (each 100 μL) taken at regular time intervals and determined by GC-MS with dodecane as the internal standard. The corresponding experimental results were constructed in **Figure S15**.

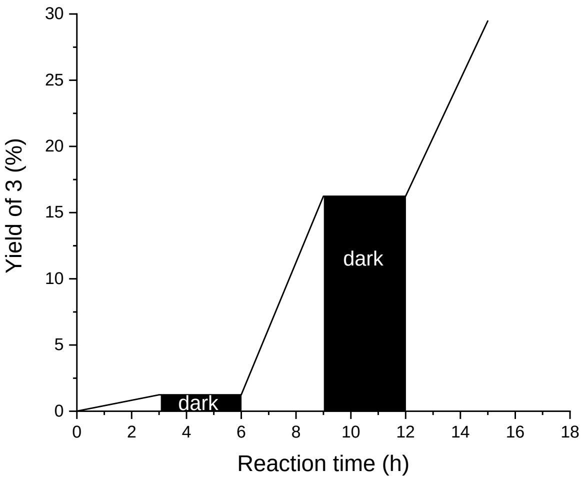
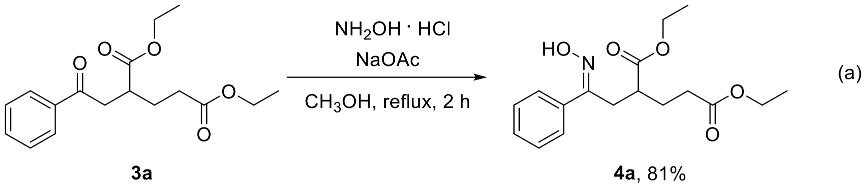
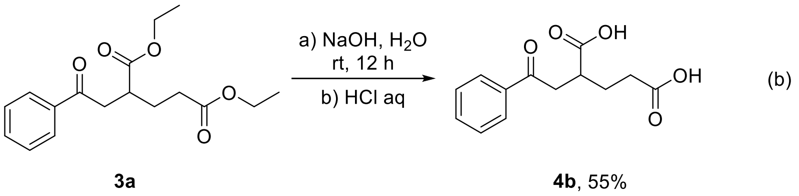


Figure S15. Plot of light on-off experiments

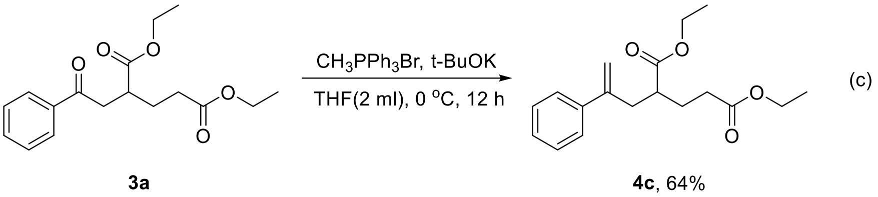
5. Late-stage derivation and application



(a) A 100 mL single-necked round-bottomed flask equipped with an egg-shaped Teflon-coated magnetic stir bar was charged with hydroxylamine hydrochloride (20.0 mg, 0.3 mmol, 1.5 equiv) and sodium acetate anhydrous (41.0 mg, 0.2mmol, 2.5 equiv). **3a** (61.2 mg, 0.2 mmol, 1.0 equiv) was added by syringe and anhydrous methanol (4 mL) was added. The flask was fitted with a water-cooled reflux condenser and brought to reflux by placement onto a pre-heated oil bath (80 °C, oil bath temperature) for 2 h. Upon cooling to room temperature, water (60 mL) was added, and the mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were combined, dried over anhydrous MgSO$_4$, and filtered. The filtrate was concentrated with a rotary evaporator under reduced pressure to yield the **4a** (52.1 mg, 81%).



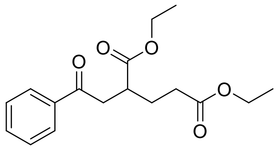
(b) The **3a** (61.2 mg, 0.2 mmol, 1.0 equiv) was added onto an aqueous solution (1 mL) of NaOH (0.2 mmol, 8.0mg, 1.0 equiv). The mixture was stirred under air atmosphere at room temperature over 12 h. Et$_2$O (5 mL) was then added. The layers were separated, and the aqueous one was washed with Et$_2$O (2 x 5 mL) before to be acidified with a concentrated solution of HCl (37% w:w in H$_2$O) to reach pH 1. The product was then extracted with EtOAc (3 x 5 mL). The combined organic layers were dried onto anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give the desired **4b** (27.5 mg, 55%).



(c) Methyltriphenylphosphonium iodide (108.0 mg, 0.3 mmol, 1.5 equiv) and anhyd THF (2.0 mL) was added to a round bottom flask. The flask was placed under an N$_2$ atmosphere and cooled to 0 °C using an ice-water bath. After cooling for 5 min, the flask was charged with KO^{t}Bu (34.0 mg, 0.3 mmol, 1.5 equiv). The suspension was stirred at 0 °C for 30 min. After this time, the flask was charged with **3a** (61.2 mg, 0.2 mmol, 1.0 equiv) in anhyd THF (1.0 mL) via dropwise addition. The reaction mixture was allowed to stir at this temperature for 12 h. After confirmation of reaction completion by HPLC. The filtrate was collected, and the solvent was removed in vacuo by rotary evaporation. The residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether (1/10) to afforded the desired **4b** (38.9 mg, 64%).

6. Characterization data of all products

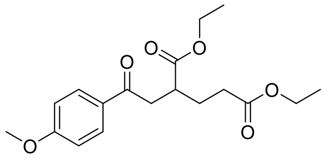
Diethyl 2-(2-oxo-2-phenylethyl)pentanedioate (3a)



The reaction was conducted with benzaldehyde (21.0 µL, 0.2 mmol) and ethyl acrylate (57.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield **3a** (36.7 mg, 60%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.85 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.47 (d, J = 7.7 Hz, 2H), 4.14 (dd, J = 10.8, 7.1 Hz, 4H), 3.48 (dd, J = 18.7, 9.9 Hz, 1H), 3.07 (dt, J = 12.9, 4.9 Hz, 2H), 2.41 (td, J = 8.2, 7.5, 2.0 Hz, 2H), 1.98 (dd, J = 11.4, 6.7 Hz, 2H), 1.25 (td, J = 7.1, 1.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.79, 174.82, 172.82, 136.55, 133.29, 128.63, 128.05, 60.77, 60.55, 40.46, 39.75, 31.95, 27.09, 14.22, 14.20. HRMS (ESI) m/z calcd for $C_{17}H_{22}NaO_5^+$ $(M+Na)^+$ 329.1359, found 329.1366.

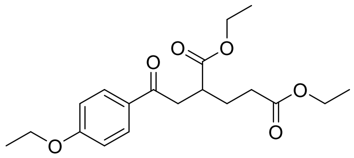
Diethyl 2-(2-(4-methoxyphenyl)-2-oxoethyl)pentanedioate (3b)



The reaction was conducted with 4-methoxybenzaldehyde (25.0 µL, 0.2 mmol) and ethyl acrylate (57.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield **3b** (43.0 mg, 64%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 4.13 (dd, J = 10.3, 7.1 Hz, 4H), 3.86 (s, 3H), 3.47–3.35 (m, 1H), 3.09 – 2.94 (m, 2H), 2.40 (td, J = 8.2, 7.5, 2.1 Hz, 2H), 2.03–1.88 (m, 2H), 1.24 (td, J = 7.2, 1.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.26, 174.94, 172.84, 163.61, 130.32, 129.67, 113.74, 60.71, 60.52, 55.48, 40.10, 39.85, 31.97, 27.12, 14.22, 14.20. HRMS (ESI) m/z calcd for $C_{18}H_{24}NaO_6^+$ $(M+Na)^+$ 359.1465, found 359.1467.

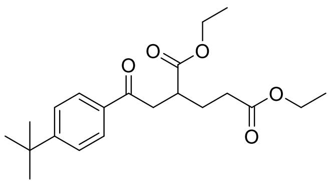
Diethyl 2-(2-(4-ethoxyphenyl)-2-oxoethyl)pentanedioate (3c)



The reaction was conducted with 4-ethoxybenzaldehyde (28.0 µL, 0.2 mmol) and ethyl acrylate (57.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate =10/1) to yield **3c** (39.2 mg, 56%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 4.18–4.04 (m, 6H), 3.47–3.36 (m, 1H), 3.08–2.97 (m, 2H), 2.44–2.35 (m, 2H), 2.05–1.89 (m, 2H), 1.43 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.25, 174.94, 172.84, 163.04, 130.32, 129.49, 114.17, 63.76, 60.69, 60.50, 40.07, 39.86, 31.97, 27.12, 14.66, 14.21, 14.19. HRMS (ESI) m/z calcd for $C_{19}H_{26}NaO_6^+$ $(M+Na)^+$ 373.1622, found 373.1622.

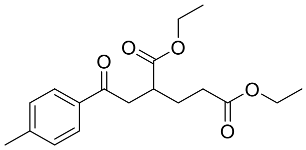
Diethyl 2-(2-(4-(*tert*-butyl)phenyl)-2-oxoethyl)pentanedioate (3d)



The reaction was conducted with 4-(tert-butyl)benzaldehyde (34.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield **3d** (38.4 mg, 53%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 4.14 (dd, J = 9.8, 7.1 Hz, 4H), 3.45 (dd, J = 18.8, 9.8 Hz, 1H), 3.05 (d, J = 13.8 Hz, 2H), 2.40 (t, J = 8.2 Hz, 2H), 2.07–1.87 (m, 2H), 1.33 (s, 9H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.43, 174.87, 172.85, 157.03, 134.01, 128.02, 125.57, 60.73, 60.53, 40.36, 39.80, 35.13, 31.97, 31.08, 27.10, 14.22, 14.19. HRMS (ESI) m/z calcd for $C_{21}H_{30}NO_5^+$ (M+Na)$^+$ 385.1985, found 385.1992.

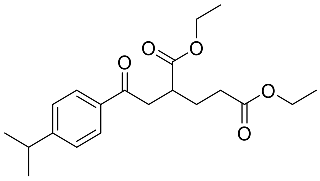
Diethyl 2-(2-oxo-2-(*p*-tolyl)ethyl)pentanedioate (3e)



The reaction was conducted with 4-methylbenzaldehyde (24.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield **3e** (34.0 mg, 53%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.31–7.20 (m, 2H), 4.14 (dq, J = 10.4, 7.1 Hz, 4H), 3.45 (dd, J = 18.7, 9.8 Hz, 1H), 3.05 (d, J = 13.8 Hz, 2H), 2.41 (s, 5H), 2.05–1.88 (m, 2H), 1.28–1.22 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.40, 174.89, 172.84, 144.09, 134.09, 129.30, 128.16, 60.74, 60.54, 40.35, 39.78, 31.96, 27.11, 21.67, 14.22, 14.20. HRMS (ESI) m/z calcd for $C_{18}H_{24}NaO_5^+$ (M+Na)$^+$ 343.1516, found 343.1520.

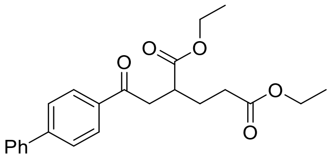
Diethyl 2-(2-(4-isopropylphenyl)-2-oxoethyl)pentanedioate (3f)



The reaction was conducted with 4-isopropylbenzaldehyde (30.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield **3f** (29.9 mg, 43%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.14 (dd, J = 10.0, 7.1 Hz, 4H), 3.45 (dd, J = 18.7, 9.8 Hz, 1H), 3.05 (d, J = 14.0 Hz, 2H), 3.00–2.89 (m, 1H), 2.39 (d, J = 7.3 Hz, 2H), 2.05–1.90 (m, 2H), 1.26 (d, J = 7.1 Hz, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.41, 174.88, 172.84, 154.81, 134.45, 128.31, 126.71, 60.73, 60.53, 40.36, 39.79, 34.27, 31.97, 27.10, 23.67, 14.22, 14.20. HRMS (ESI) m/z calcd for $C_{20}H_{28}NaO_5^+$ (M+Na)$^+$ 371.1829, found 371.1829.

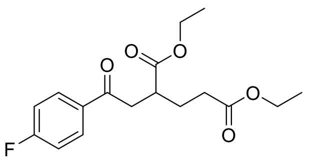
Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)pentanedioate (3g)



The reaction was conducted with [1,1'-biphenyl]-4-carbaldehyde (37.0 µL, 0.2 mmol) and ethyl acrylate (57.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield **3g** (26.7 mg, 35%) as a white solid (mp 90-97 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.76–7.56 (m, 4H), 7.52–7.36 (m, 3H), 4.16 (dd, J = 12.8, 7.1 Hz, 4H), 3.52 (dd, J = 18.7, 9.9 Hz, 1H), 3.10 (d, J = 14.2 Hz, 2H), 2.43 (td, J = 8.2, 7.5, 2.1 Hz, 2H), 2.08–1.92 (m, 2H), 1.27 (td, J = 7.2, 3.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.38, 174.83, 172.83, 145.96, 139.85, 135.27, 128.97, 128.66, 128.28, 127.29, 60.79, 60.56, 40.49, 39.82, 31.97, 27.12, 14.23, 14.22. HRMS (ESI) m/z calcd for $C_{23}H_{25}NaO_5^+$ $(M+Na)^+$ 405.1672, found 405.1689.

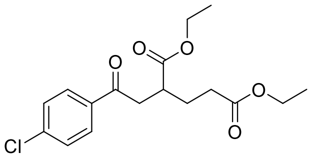
Diethyl 2-(2-(4-fluorophenyl)-2-oxoethyl)pentanedioate (3h)



The reaction was conducted with 4-fluorobenzaldehyde (22.0 µL, 0.2 mmol) and ethyl acrylate (57.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield **3h** (32.4mg, 50%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.7, 5.6 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 4.14 (dd, J = 9.9, 7.2 Hz, 4H), 3.52–3.37 (m, 1H), 3.14–2.91 (m, 2H), 2.52 – 2.31 (m, 2H), 2.07–1.86 (m, 2H), 1.28 – 1.21 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.22, 174.76, 172.78, 130.74, 130.65, 115.86, 115.64, 60.82, 60.57, 40.35, 39.74, 31.91, 27.06, 14.22, 14.19; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.89. HRMS (ESI) m/z calcd for $C_{17}H_{21}FNaO_5^+$ $(M+Na)^+$ 347.1265, found 347.1265.

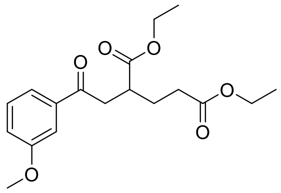
Diethyl 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3i)



The reaction was conducted with 4-chlorobenzaldehyde (24.0 µL, 0.2 mmol) and ethyl acrylate (57.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **3i** (31.3 mg, 46%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.80 (m, 2H), 7.42 (d, J = 8.5 Hz, 2H), 4.14 (dd, J = 9.3, 7.1 Hz, 4H), 3.44 (q, J = 7.8 Hz, 1H), 3.02 (d, J = 16.2 Hz, 2H), 2.51–2.32 (m, 2H), 1.97 (dd, J = 11.6, 6.5 Hz, 2H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.58, 174.63, 172.72, 139.73, 134.92, 129.45, 128.94, 60.80, 60.54, 40.36, 39.74, 31.90, 27.05, 14.20, 14.17. HRMS (ESI) m/z calcd for $C_{17}H_{21}ClNaO_5^+$ $(M+Na)^+$ 363.0970, found 363.0970.

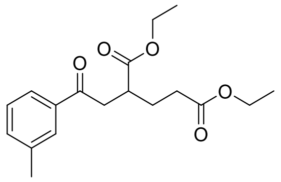
Diethyl 2-(2-(3-methoxyphenyl)-2-oxoethyl)pentanedioate (3j)



The reaction was conducted with 3-methoxybenzaldehyde (25.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield **3j** (31.0 mg, 46%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.7 Hz, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 4.14 (dd, J = 11.1, 7.1 Hz, 4H), 3.84 (s, 3H), 3.43 (d, J = 10.0 Hz, 1H), 3.05 (d, J = 13.8 Hz, 2H), 2.48–2.29 (m, 2H), 1.97 (dd, J = 12.4, 6.6 Hz, 2H), 1.28–1.22 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.59, 174.74, 172.77, 159.87, 137.95, 129.60, 120.69, 119.82, 112.23, 60.74, 60.51, 55.44, 40.56, 39.82, 31.95, 27.08, 14.20, 14.18. HRMS (ESI) m/z calcd for $C_{18}H_{24}NaO_6^+$ $(M+Na)^+$ 359.1465, found 359.1467.

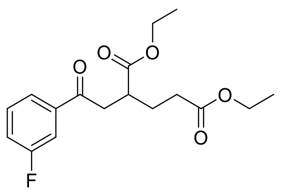
Diethyl 2-(2-oxo-2-(*m*-tolyl)ethyl)pentanedioate (3k)



The reaction was conducted with 3-methylbenzaldehyde (24.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield **3k** (32.6 mg, 51%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.44–7.29 (m, 2H), 4.14 (dq, J = 10.4, 7.1 Hz, 4H), 3.46 (dd, J = 18.8, 9.8 Hz, 1H), 3.06 (d, J = 14.0 Hz, 2H), 2.40 (s, 5H), 2.06–1.90 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.99, 174.86, 172.83, 138.42, 136.58, 134.04, 128.58, 128.50, 125.26, 60.75, 60.55, 40.50, 39.76, 31.95, 27.09, 21.36, 14.22, 14.20. HRMS (ESI) m/z calcd for $C_{18}H_{24}NaO_5^+$ $(M+Na)^+$ 343.1516, found 343.1531.

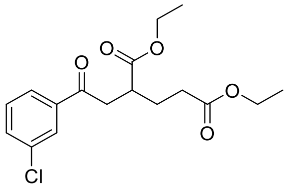
Diethyl 2-(2-(3-fluorophenyl)-2-oxoethyl)pentanedioate (3l)



The reaction was conducted with 3-fluorobenzaldehyde (21.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ethyl acetate = 5/1) to yield **3l** (22.0 mg, 34%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 9.3 Hz, 1H), 7.44 (d, J = 5.5 Hz, 1H), 7.26 (d, J = 3.6 Hz, 1H), 4.14 (dd, J = 9.8, 7.1 Hz, 4H), 3.51–3.41 (m, 1H), 3.10–2.99 (m, 2H), 2.45–2.34 (m, 2H), 2.04 – 1.91 (m, 2H), 1.26 (td, J = 7.2, 1.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.59, 174.63, 172.75, 164.09, 161.62, 138.58, 130.29, 123.80, 120.42, 114.69, 60.85, 60.58, 40.58, 39.69, 31.89, 27.03, 14.22. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.73. HRMS (ESI) m/z calcd for $C_{17}H_{21}FNaO_5^+$ $(M+Na)^+$ 344.1265, found 347.1265.

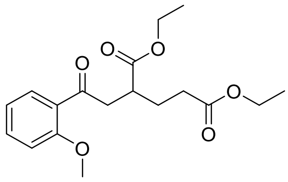
Diethyl 2-(2-(3-chlorophenyl)-2-oxoethyl)pentanedioate (3m)



The reaction was conducted with 3-chlorobenzaldehyde (24.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield **3m** (19.0 mg, 28%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 2.2 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 4.14 (dd, J = 8.7, 7.1 Hz, 4H), 3.50–3.39 (m, 1H), 3.09–2.95 (m, 2H), 2.46–2.35 (m, 2H), 1.98 (dd, J = 13.2, 6.0 Hz, 2H), 1.26 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.55, 174.56, 172.71, 138.12, 135.01, 133.18, 129.97, 128.19, 126.11, 60.84, 60.56, 40.49, 39.70, 31.89, 27.03, 14.20, 14.17. HRMS (ESI) m/z calcd for $C_{17}H_{21}ClNaO_5^+$ $(M+Na)^+$ 363.0970, found 363.0977.

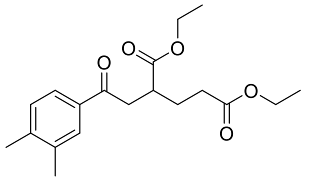
Diethyl 2-(2-(2-methoxyphenyl)-2-oxoethyl)pentanedioate (3n)



The reaction was conducted with 2-ethoxybenzaldehyde (28.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield a mixture of **3n** (23.0 mg, 33%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.8, 1.8 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 6.97 (q, J = 7.8 Hz, 2H), 4.13 (dd, J = 10.1, 7.1 Hz, 4H), 3.90 (s, 3H), 3.42 (dd, J = 18.2, 8.9 Hz, 1H), 3.13 (dd, J = 18.2, 4.9 Hz, 1H), 3.00 (d, J = 5.2 Hz, 1H), 2.38 (t, J = 7.9 Hz, 2H), 1.94 (dq, J = 15.2, 7.4 Hz, 2H), 1.29–1.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.61, 175.07, 172.95, 158.79, 133.78, 130.51, 127.53, 120.68, 111.53, 60.57, 60.46, 55.50, 45.84, 40.12, 32.02, 27.08, 14.21. HRMS (ESI) m/z calcd for $C_{18}H_{24}NaO_6^+$ $(M+Na)^+$ 359.1465, found 359.1469.

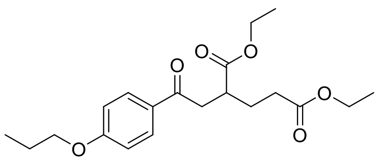
Diethyl 2-(2-(3,4-dimethylphenyl)-2-oxoethyl)pentanedioate (3o)



The reaction was conducted with 3,4-dimethylbenzaldehyde (27.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 10/1) to yield **3o** (40.0 mg, 60%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74–7.63 (m, 2H), 7.19 (d, J = 7.9 Hz, 1H), 4.13 (dq, J = 10.0, 7.1 Hz, 4H), 3.43 (dd, J = 18.7, 9.8 Hz, 1H), 3.04 (d, J = 13.8 Hz, 2H), 2.40 (td, J = 8.1, 7.5, 2.2 Hz, 2H), 2.30 (s, 6H), 2.04–1.89 (m, 2H), 1.27–1.21 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.64, 174.92, 172.85, 142.82, 136.94, 134.48, 129.82, 129.17, 125.77, 60.71, 60.53, 40.34, 39.79, 31.97, 27.11, 20.05, 19.79, 14.22, 14.20. HRMS (ESI) m/z calcd for $C_{19}H_{26}NaO_5^+$ (M+Na)$^+$ 357.1672, found 357.1687.

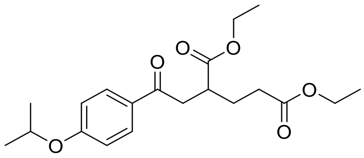
Diethyl 2-(2-oxo-2-(4-propoxyphenyl)ethyl)pentanedioate (3p)



The reaction was conducted with 4-propoxybenzaldehyde (32.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 15/1) to yield **3p** (42.2 mg, 58%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 4.13 (dd, J = 9.9, 7.0 Hz, 4H), 3.97 (t, J = 6.6 Hz, 2H), 3.46–3.35 (m, 1H), 3.09–2.96 (m, 2H), 2.44–2.35 (m, 2H), 2.03–1.88 (m, 2H), 1.82 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 6H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.26, 174.95, 172.85, 163.25, 130.30, 129.44, 114.19, 69.73, 60.70, 60.51, 40.07, 39.87, 31.98, 27.12, 22.44, 14.21, 14.19, 10.45. HRMS (ESI) m/z calcd for $C_{20}H_{28}NaO_6^+$ (M+Na)$^+$ 387.1778, found 387.1785.

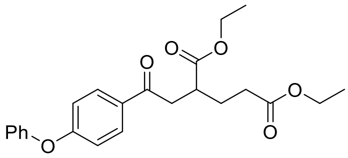
Diethyl 2-(2-(4-isopropoxyphenyl)-2-oxoethyl)pentanedioate (3q)



The reaction was conducted with 4-isopropoxybenzaldehyde (32.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield **3q** (36.3 mg, 50%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 4.69–4.56 (m, 1H), 4.13 (dd, J = 10.2, 7.1 Hz, 4H), 3.49–3.32 (m, 1H), 3.01 (d, J = 14.7 Hz, 2H), 2.44–2.33 (m, 2H), 2.04–1.89 (m, 2H), 1.35 (d, J = 6.1 Hz, 6H), 1.26–1.22 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.22, 174.97, 172.86, 162.13, 130.36, 129.22, 115.10, 70.10, 60.70, 60.52, 40.06, 39.86, 31.98, 27.12, 21.90, 14.21, 14.20. HRMS (ESI) m/z calcd for $C_{20}H_{28}NaO_6^+$ (M+Na)$^+$ 387.1778, found 387.1782.

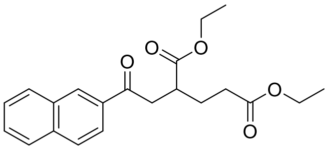
Diethyl 2-(2-oxo-2-(4-phenoxyphenyl)ethyl)pentanedioate (3r)



The reaction was conducted with (E)-N,2-dimethyl-N-phenylbut-2-enamide (35.0 μL, 0.2 mmol) and ethyl acrylate (57.0 μL, 0.52 mmol). Purification by column chromatography was performed

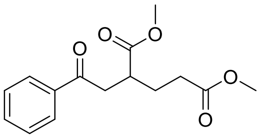
(petroleum ether/ ethyl acetate = 5/1) to yield a mixture of **3r** (26.3 mg, 33%) as a colorless liquid.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 29.4, 8.2 Hz, 4H), 4.14 (dd, *J* = 11.2, 7.1 Hz, 4H), 3.43 (q, *J* = 10.2 Hz, 1H), 3.18–2.88 (m, 2H), 2.50–2.34 (m, 2H), 2.06–1.88 (m, 2H), 1.26 (dt, *J* = 7.2, 3.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.34, 174.88, 172.83, 162.13, 155.43, 131.22, 130.34, 130.08, 124.67, 120.21, 117.32, 60.77, 60.55, 40.23, 39.81, 31.95, 27.10, 14.23, 14.21. HRMS (ESI) m/z calcd for $C_{23}H_{26}NaO_6^+$ $(M+Na)^+$ 421.1622, found 421.1622.

Diethyl 2-(2-(naphthalen-2-yl)-2-oxoethyl)pentanedioate (3s)



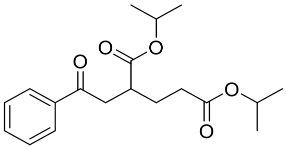
The reaction was conducted with 2-naphthaldehyde (31.2 mg, 0.2 mmol) and ethyl acrylate (57.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield **3s** (22.1 mg, 31%) as a colorless liquid.
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.49 (d, *J* = 1.8 Hz, 1H), 8.05–7.84 (m, 4H), 7.64–7.52 (m, 2H), 4.16 (dd, *J* = 13.8, 7.0 Hz, 4H), 3.63 (dd, *J* = 17.6, 8.8 Hz, 1H), 3.28–3.08 (m, 2H), 2.45 (td, *J* = 8.1, 7.5, 2.3 Hz, 2H), 2.11–1.94 (m, 2H), 1.26 (dt, *J* = 7.2, 3.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.72, 174.88, 172.84, 135.68, 133.89, 132.48, 129.81, 129.60, 128.56, 128.51, 127.80, 126.84, 123.74, 60.80, 60.57, 40.52, 39.87, 31.99, 27.16, 14.23. HRMS (ESI) m/z calcd for $C_{21}H_{24}NaO_5^+$ $(M+Na)^+$ 379.1516, found 379.1512.

Dimethyl 2-(2-oxo-2-phenylethyl)pentanedioate (3t)



The reaction was conducted with benzaldehyde (21.0 µL, 0.2 mmol) and methyl acrylate (47.0µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield a mixture of **3t** (23.4 mg, 42%) as a colorless liquid.
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01–7.87 (m, 2H), 7.63–7.51 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 3.68 (d, *J* = 11.5 Hz, 6H), 3.52–3.44 (m, 1H), 3.08 (d, *J* = 13.9 Hz, 2H), 2.48–2.32 (m, 2H), 2.06–1.88 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.71, 175.29, 173.21, 136.44, 133.35, 128.65, 128.05, 51.97, 51.75, 40.49, 39.60, 31.68, 27.02. HRMS (ESI) m/z calcd for $C_{15}H_{18}NaO_5^+$ $(M+Na)^+$ 301.1046, found 301.1046.

Diisopropyl 2-(2-oxo-2-phenylethyl)pentanedioate (3u)

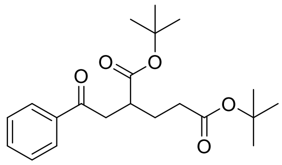


The reaction was conducted with benzaldehyde (21.0 µL, 0.2 mmol) and isopropyl acrylate (67.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate

= 5/1) to yield a mixture of **3u** (32.7 mg, 49%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, J = 7.0 Hz, 2H), 7.55 (d, J = 7.3 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 5.09–4.92 (m, 2H), 3.50–3.40 (m, 1H), 3.11–2.96 (m, 2H), 2.44–2.31 (m, 2H), 1.96 (dd, J = 9.4, 6.9 Hz, 2H), 1.26–1.18 (m, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.82, 174.31, 172.35, 136.66, 133.21, 128.60, 128.03, 68.10, 67.84, 40.45, 39.95, 32.24, 27.19, 21.84, 21.83, 21.79, 21.75. HRMS (ESI) m/z calcd for $C_{19}H_{26}NaO_5^+$ (M+Na)$^+$ 357.1677, found 357.1674.

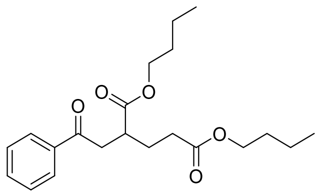
Di-*tert*-butyl 2-(2-oxo-2-phenylethyl)pentanedioate (3v)



The reaction was conducted with benzaldehyde (21.0 μL, 0.2 mmol) and tert-butyl acrylate (76.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/acetone = 5/1) to yield **3v** (25.3 mg, 35%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (dd, J = 8.3, 7.0 Hz, 2H), 3.48–3.34 (m, 1H), 3.04–2.89 (m, 2H), 2.36–2.27 (m, 2H), 1.96–1.84 (m, 2H), 1.44 (d, J = 1.5 Hz, 18H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.03, 174.15, 172.29, 136.73, 133.16, 128.59, 128.04, 80.78, 80.49, 40.62, 40.51, 33.11, 28.11, 28.05, 27.40. HRMS (ESI) m/z calcd for $C_{21}H_{30}NaO_5^+$ (M+Na)$^+$ 362.2093, found 362.2096.

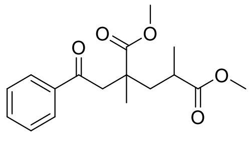
Dibutyl 2-(2-oxo-2-phenylethyl)pentanedioate (3w)



The reaction was conducted with benzaldehyde (21.0 μL, 0.2 mmol) and butyl acrylate (75.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield **3w** (18.1 mg, 25%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03–7.85 (m, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.08 (dt, J = 9.2, 6.7 Hz, 4H), 3.53–3.42 (m, 1H), 3.06 (d, J = 14.2 Hz, 2H), 2.46–2.34 (m, 2H), 2.06–1.90 (m, 2H), 1.64–1.58 (m, 4H), 1.36 (ddd, J = 10.3, 7.5, 3.9 Hz, 4H), 0.92 (td, J = 7.4, 5.9 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.76, 174.86, 172.91, 136.57, 128.62, 128.04, 64.69, 64.48, 40.41, 39.82, 31.96, 30.65, 30.61, 27.13, 19.13, 13.70, 13.68. HRMS (ESI) m/z calcd for $C_{21}H_{30}NaO_5^+$ (M+Na)$^+$ 385.1985, found 385.1988.

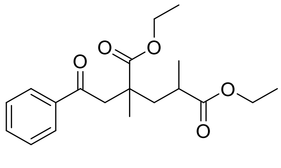
Dimethyl 2,4-dimethyl-2-(2-oxo-2-phenylethyl)pentanedioate (3x)



The reaction was conducted with benzaldehyde (21.0 μL, 0.2 mmol) and methyl methacrylate (56.0 μL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield **3x** (24.5 mg, 40%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99–7.84 (m, 2H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.72–3.53 (m, 6H), 3.51–3.39 (m, 1H), 3.15 (dd, *J* = 17.8, 3.9 Hz, 1H), 2.69–2.55 (m, 1H), 2.27 (ddd, *J* = 27.7, 14.3, 9.1 Hz, 1H), 1.72–1.60 (m, 1H), 1.29 (d, *J* = 16.1 Hz, 3H), 1.17 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.32, 177.15, 176.50, 136.91, 133.17, 128.60, 127.92, 51.76, 46.79, 43.09, 35.61, 22.50, 21.54, 20.04. HRMS (ESI) m/z calcd for $C_{17}H_{22}NaO_5^+$ (M+Na)$^+$ 329.1359, found 329.1361.

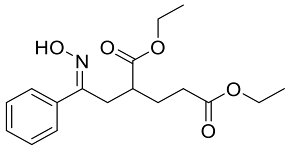
Diethyl 2,4-dimethyl-2-(2-oxo-2-phenylethyl)pentanedioate (3y)



The reaction was conducted with benzaldehyde (21.0 µL, 0.2 mmol) and ethyl methacrylate (65.0 µL, 0.52 mmol). Purification by column chromatography was performed (petroleum ether/ ethyl acetate = 5/1) to yield **3y** (28.7 mg, 43%) as a colorless liquid.

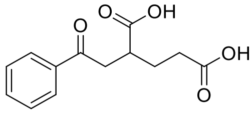
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.18–4.02 (m, 4H), 3.44 (t, *J* = 17.7 Hz, 1H), 3.14 (dd, *J* = 17.8, 4.2 Hz, 1H), 2.59 (s, 1H), 2.34–2.19 (m, 1H), 1.70–1.64 (m, 1H), 1.32–1.14 (m, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.39, 176.85, 176.09, 137.07, 133.08, 128.57, 127.88, 60.65, 60.63, 60.52, 60.48, 47.49, 46.33, 43.30, 42.85, 42.67, 35.81, 22.81, 21.37, 20.09, 19.82, 14.13, 14.11, 14.08, 14.03. HRMS (ESI) m/z calcd for $C_{19}H_{26}NaO_5^+$ (M+Na)$^+$ 357.1672, found 357.1678.

Diethyl (*Z*)-2-(2-(hydroxyimino)-2-phenylethyl)pentanedioate (4a)



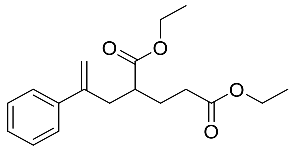
^{1}H NMR (400 MHz, CDCl$_3$) δ 9.24 (s, 1H), 7.59–7.55 (m, 2H), 7.37 (dd, *J* = 4.9, 1.9 Hz, 3H), 4.10–4.04 (m, 2H), 3.94 (ddd, *J* = 10.3, 7.1, 1.0 Hz, 2H), 3.14–3.03 (m, 2H), 2.84–2.77 (m, 1H), 2.32 (ddd, *J* = 20.9, 8.7, 6.2 Hz, 2H), 1.99–1.85 (m, 2H), 1.22–1.17 (m, 3H), 1.13–1.08 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 174.51, 172.94, 157.19, 135.30, 129.37, 128.59, 126.48, 60.71, 60.46, 41.86, 31.85, 28.47, 27.07, 14.15, 13.99.HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO_5^+$ (M+Na)$^+$ 288.0842, found 288.0846.

2-(2-oxo-2-Phenylethyl)pentanedioic acid (4b)



^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 8.10–7.95 (m, 2H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 3.53 (dd, *J* = 18.0, 9.3 Hz, 1H), 3.23–3.16 (m, 1H), 3.08 (dd, *J* = 4.7, 2.3 Hz, 1H), 2.48 (dt, *J* = 8.9, 6.7 Hz, 2H), 2.04–1.87 (m, 2H); ^{13}C NMR (100 MHz, Acetone-*d*$_6$) δ 205.44, 197.71, 175.35, 173.42, 137.09, 132.93, 128.55, 127.89, 39.98, 39.37, 31.05, 26.96. HRMS (ESI) m/z calcd for $C_{13}H_{14}NaO_5^+$ (M+Na)$^+$ 273.0733, found 273.0738.

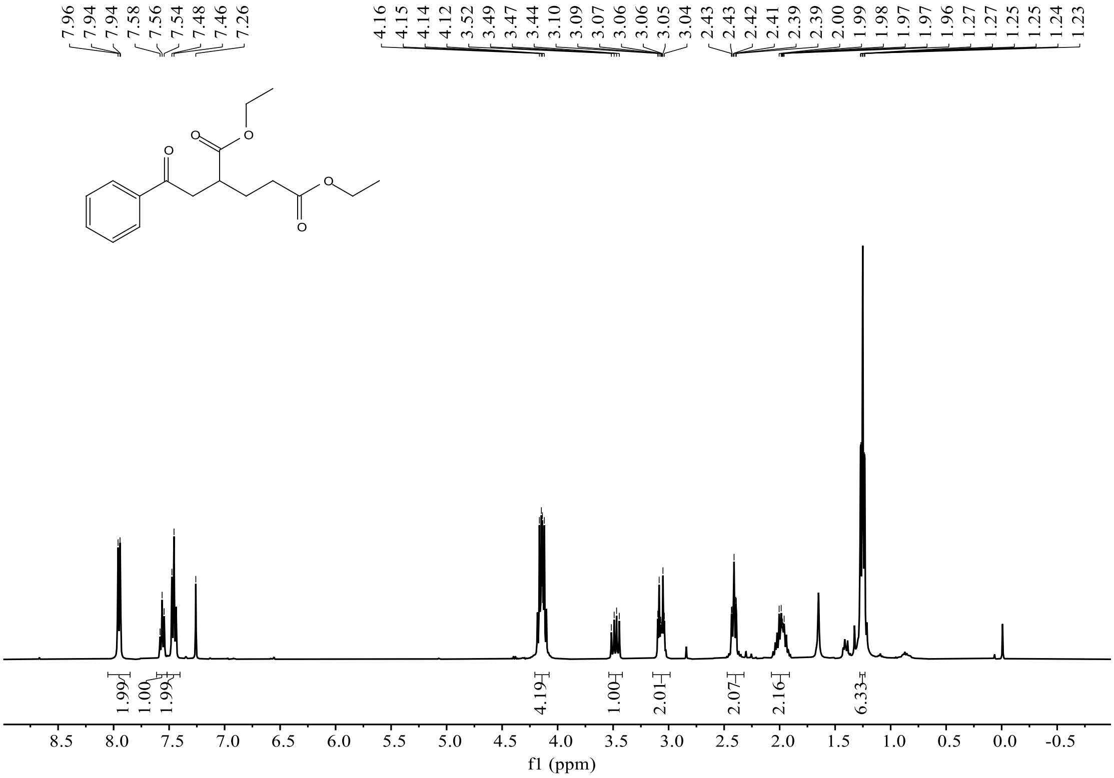
Diethyl 2-(2-phenylallyl)pentanedioate (4c)



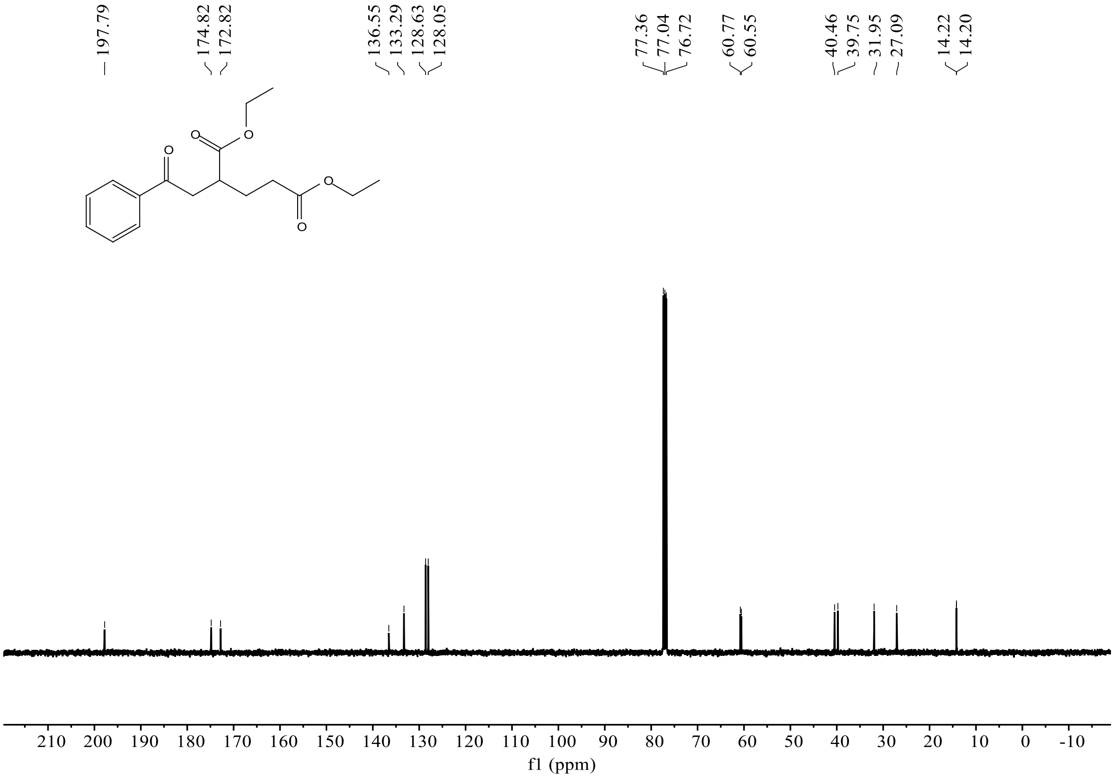
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39–7.25 (m, 5H), 5.29 (d, J = 1.4 Hz, 1H), 5.10 (d, J = 1.3 Hz, 1H), 4.19–3.97 (m, 4H), 2.96–2.82 (m, 1H), 2.72–2.59 (m, 1H), 2.51 (s, 1H), 2.34–2.17 (m, 2H), 1.89 (d, J = 8.2 Hz, 2H), 1.21 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 174.95, 172.89, 145.65, 140.45, 128.38, 127.62, 126.26, 114.72, 60.40, 60.37, 43.46, 38.15, 31.91, 26.91, 14.25, 14.17. HRMS (ESI) m/z calcd for $C_{18}H_{24}NaO_4^+$ (M+Na)$^+$ 278.1539, found 278.1541.

7. Copies of NMR spectra of all products

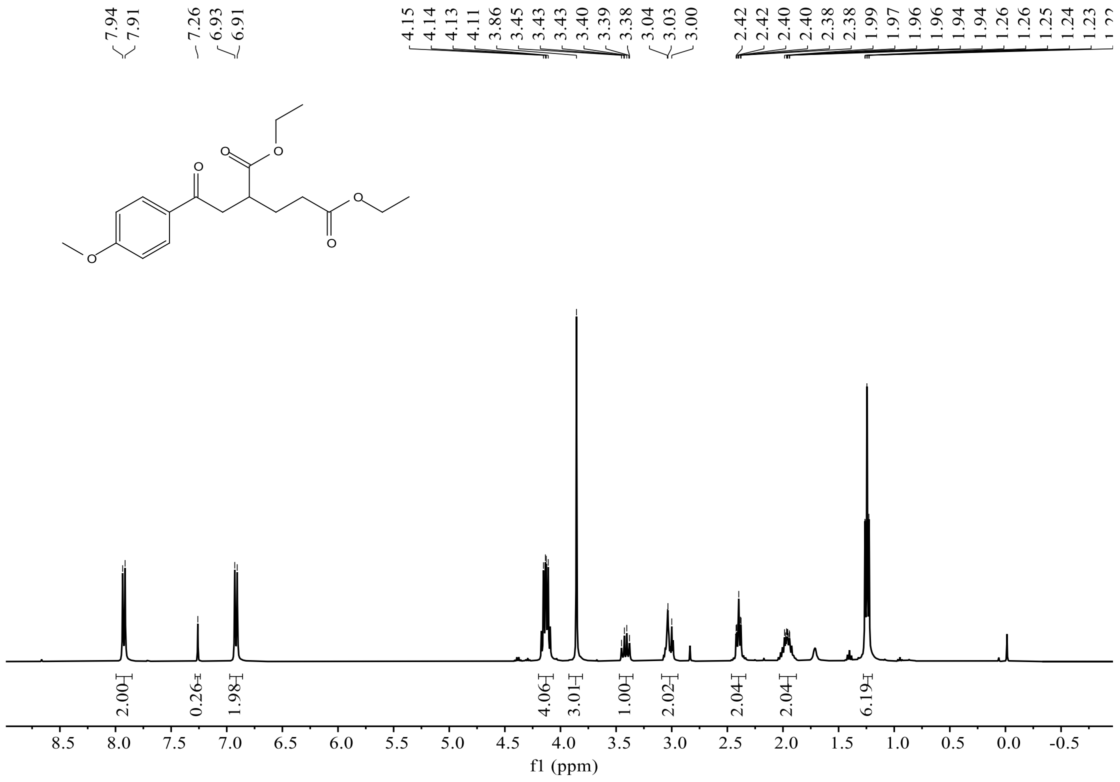
^{1}H NMR spectra of 3a (400 MHz, CDCl$_3$)



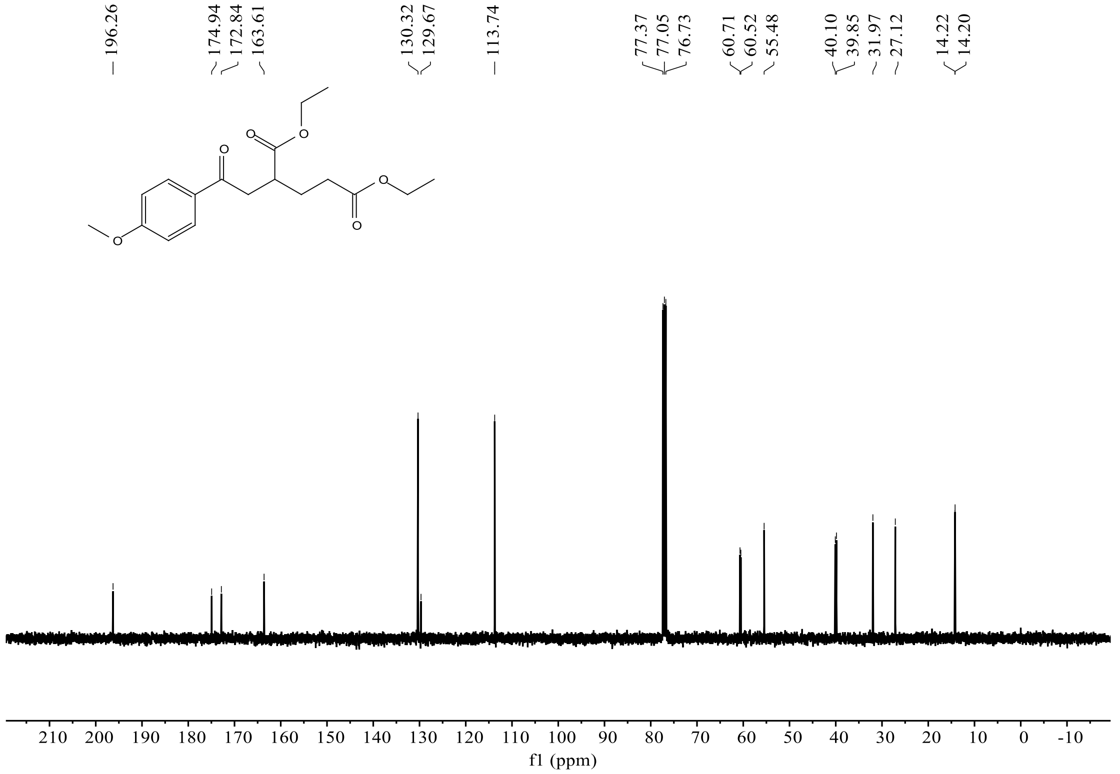
^{13}C NMR spectra of 3a (100 MHz, CDCl$_3$)



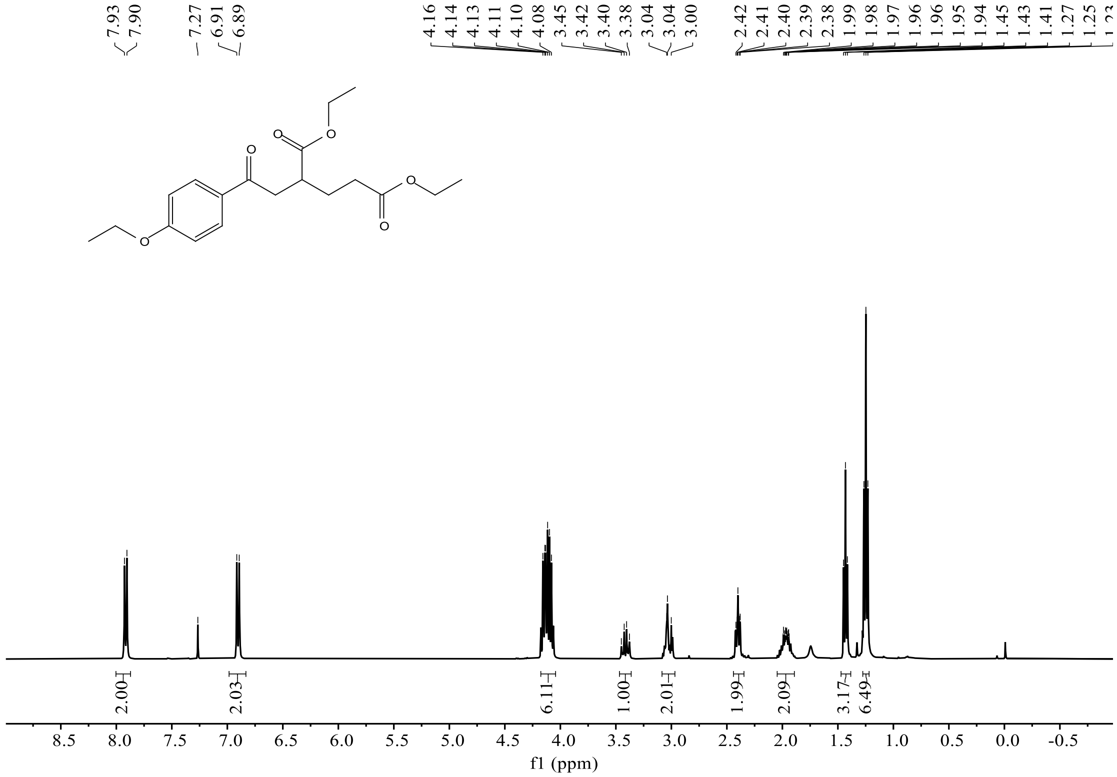
^{1}H NMR spectra of 3b (400 MHz, CDCl$_3$)



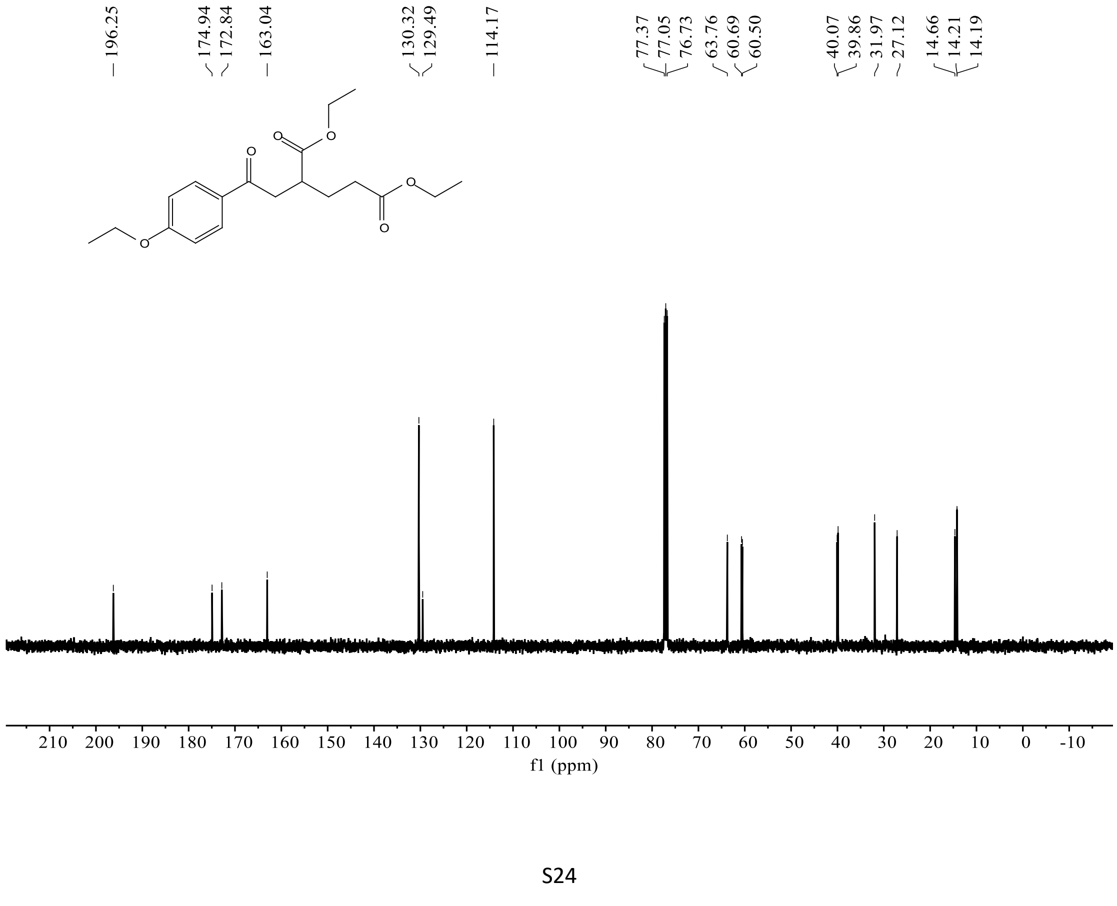
^{13}C NMR spectra of 3b (100 MHz, CDCl$_3$)



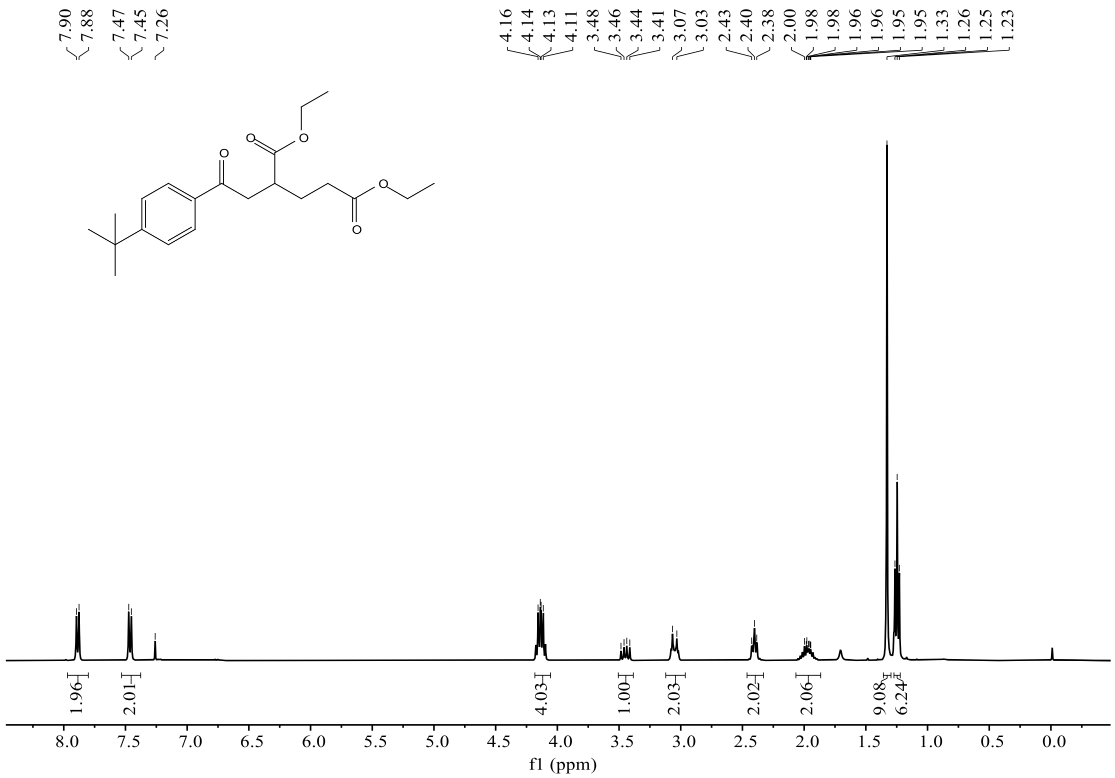
^1H NMR spectra of 3c (400 MHz, $CDCl_3$)



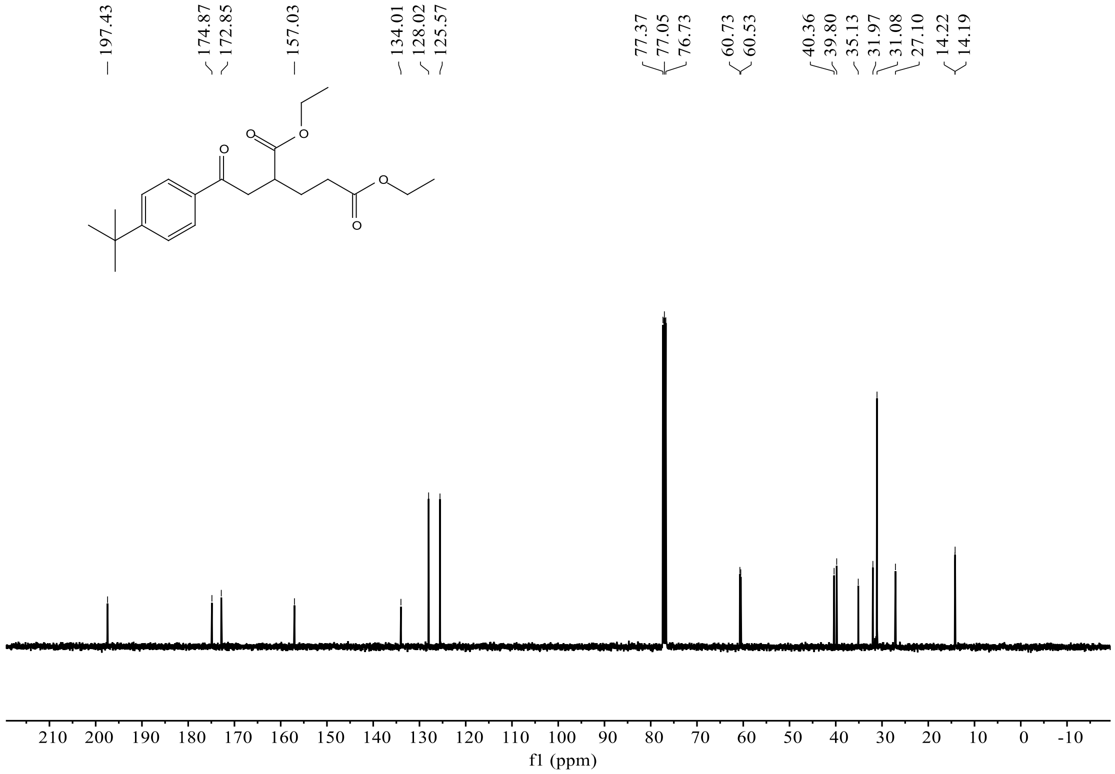
^{13}C NMR spectra of 3c (100 MHz, $CDCl_3$)



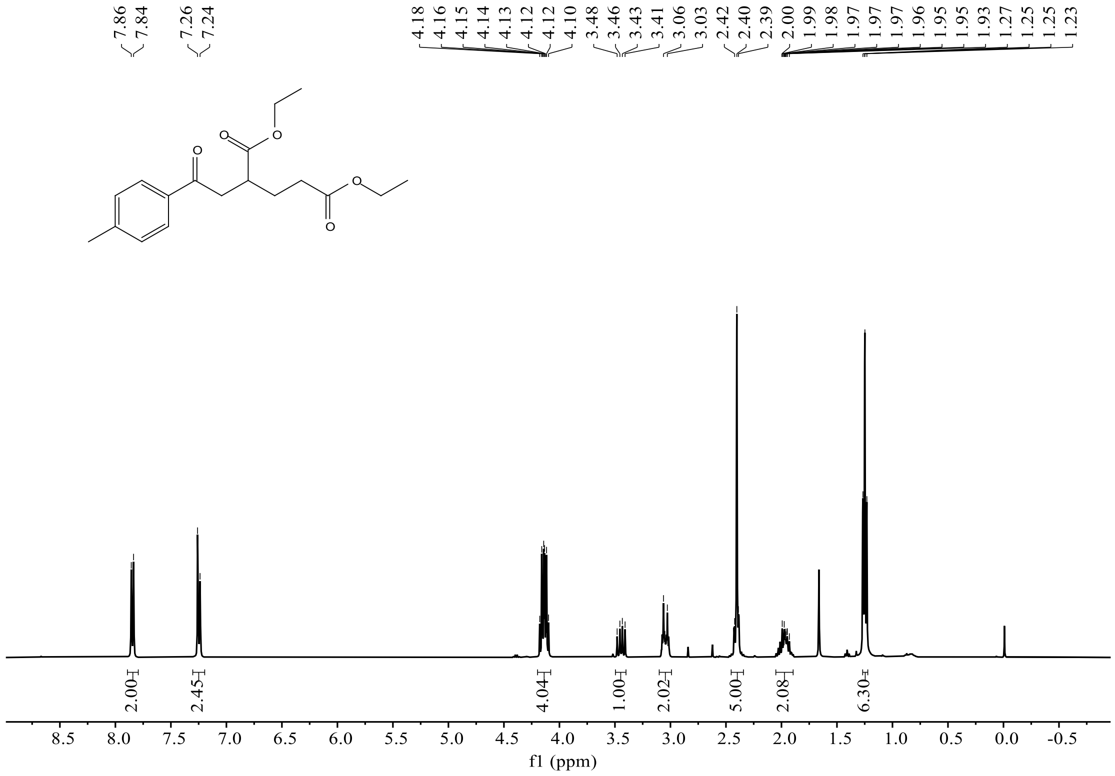
^{1}H NMR spectra of 3d (400 MHz, CDCl$_3$)



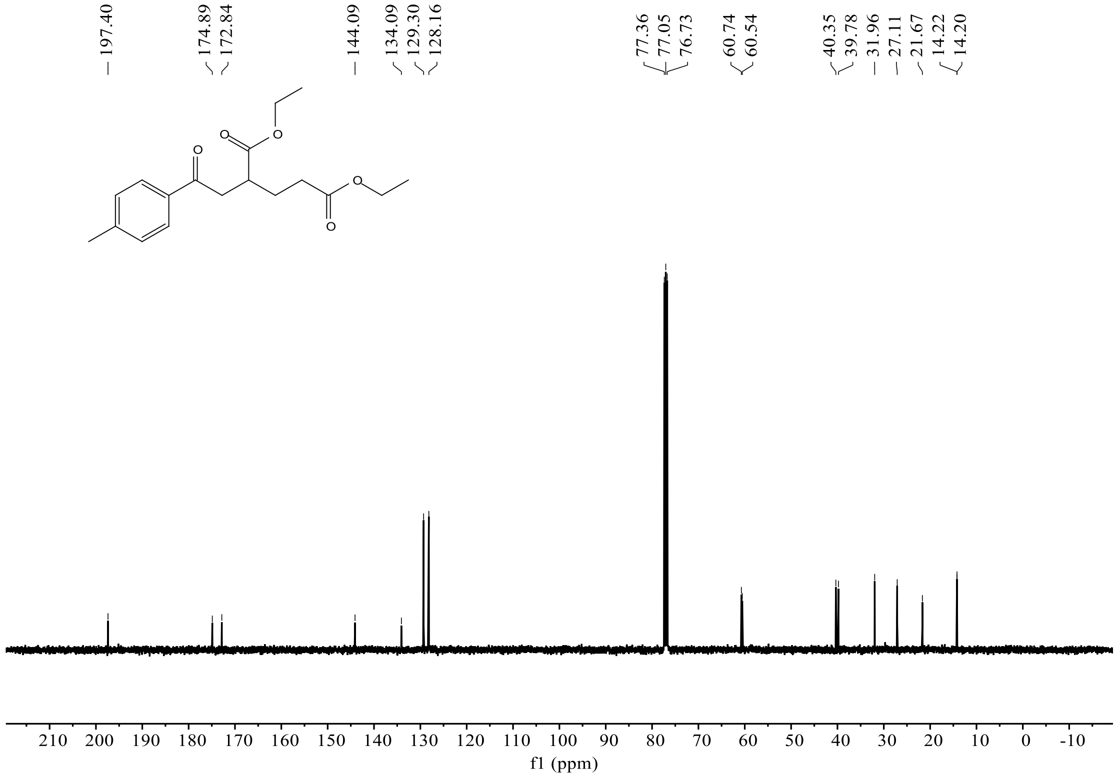
^{13}C NMR spectra of 3d (100 MHz, CDCl$_3$)



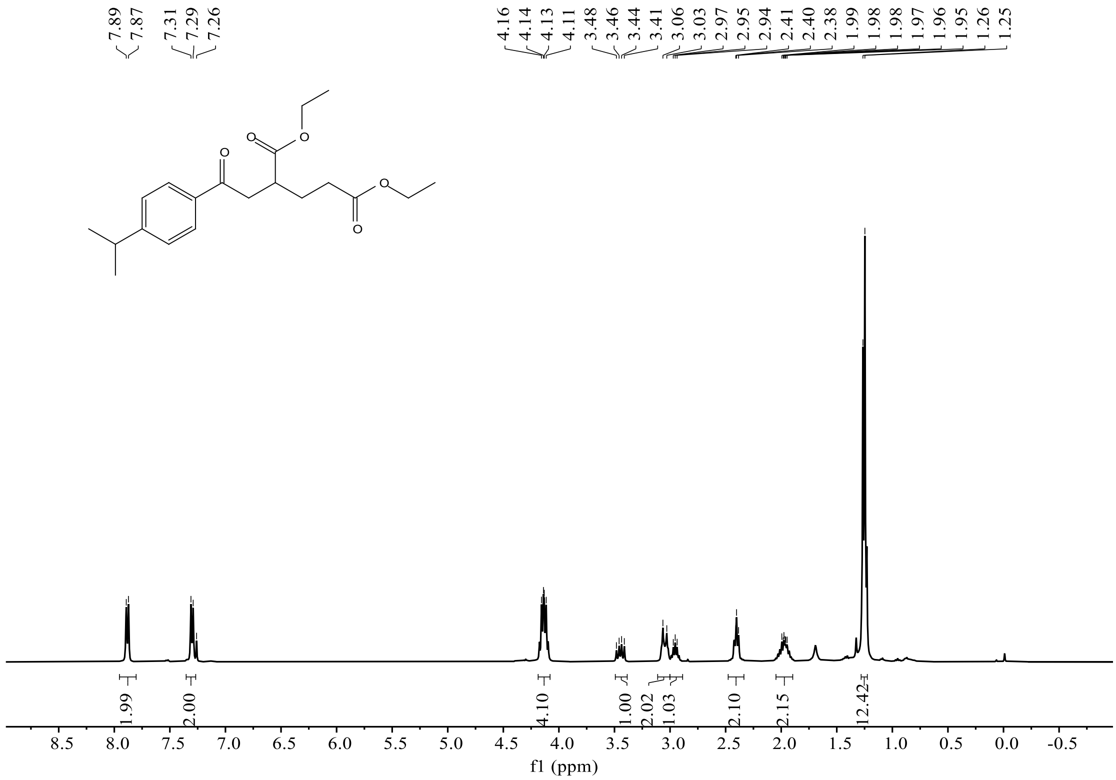
^{1}H NMR spectra of 3e (400 MHz, CDCl$_3$)



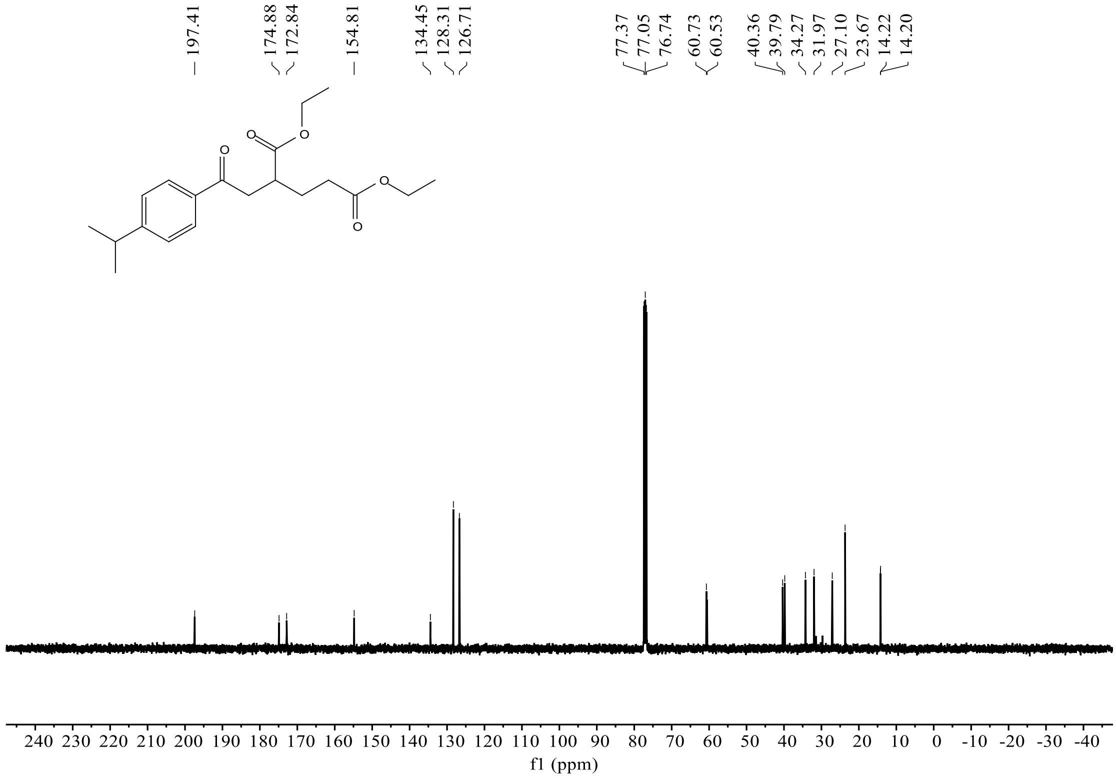
^{13}C NMR spectra of 3e (100 MHz, CDCl$_3$)



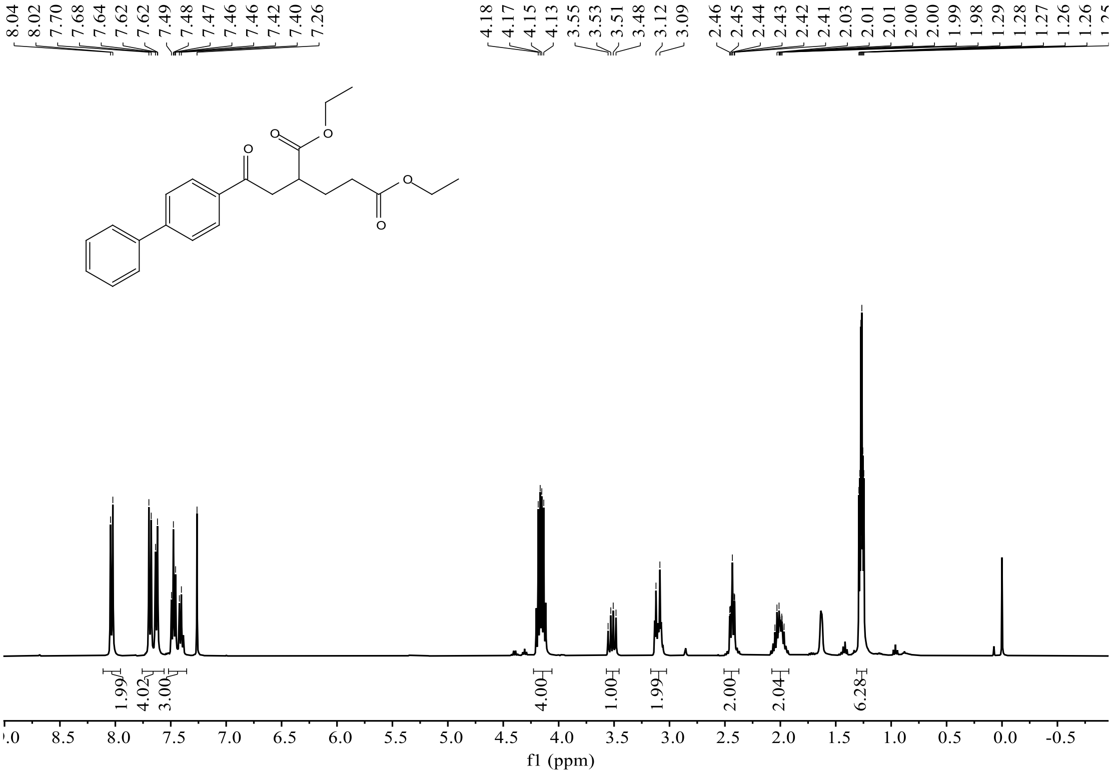
^{1}H NMR spectra of 3f (400 MHz, CDCl$_3$)



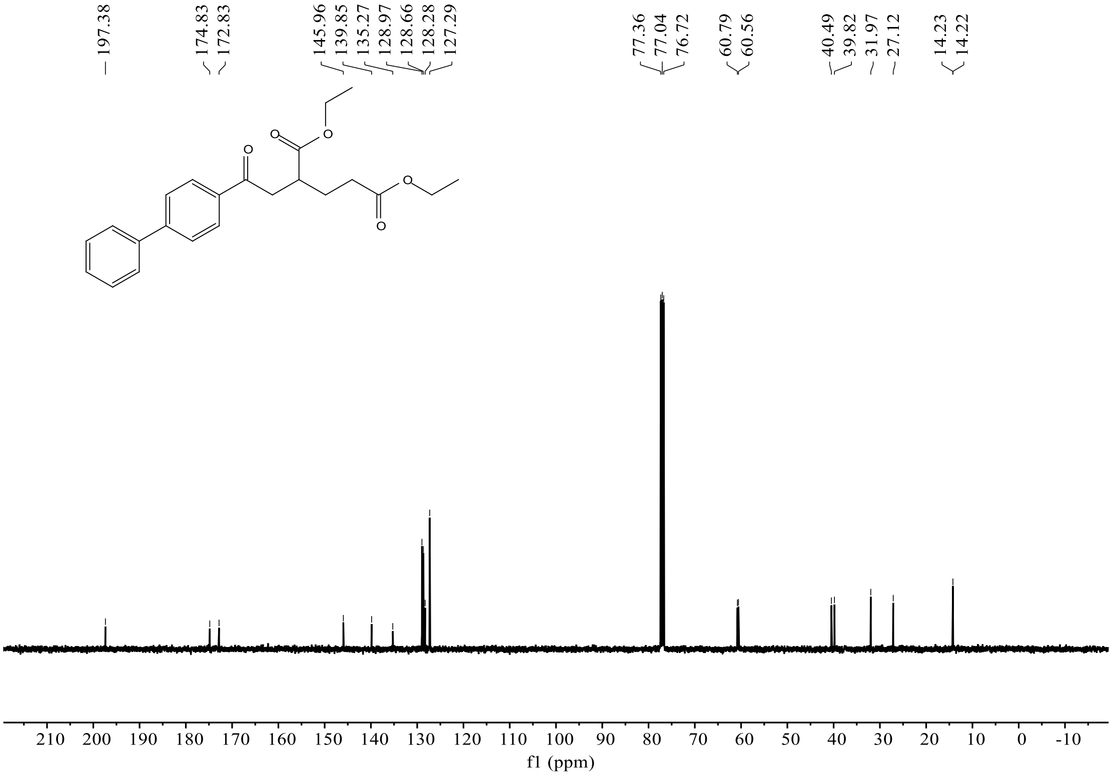
^{13}C NMR spectra of 3f (100 MHz, CDCl$_3$)



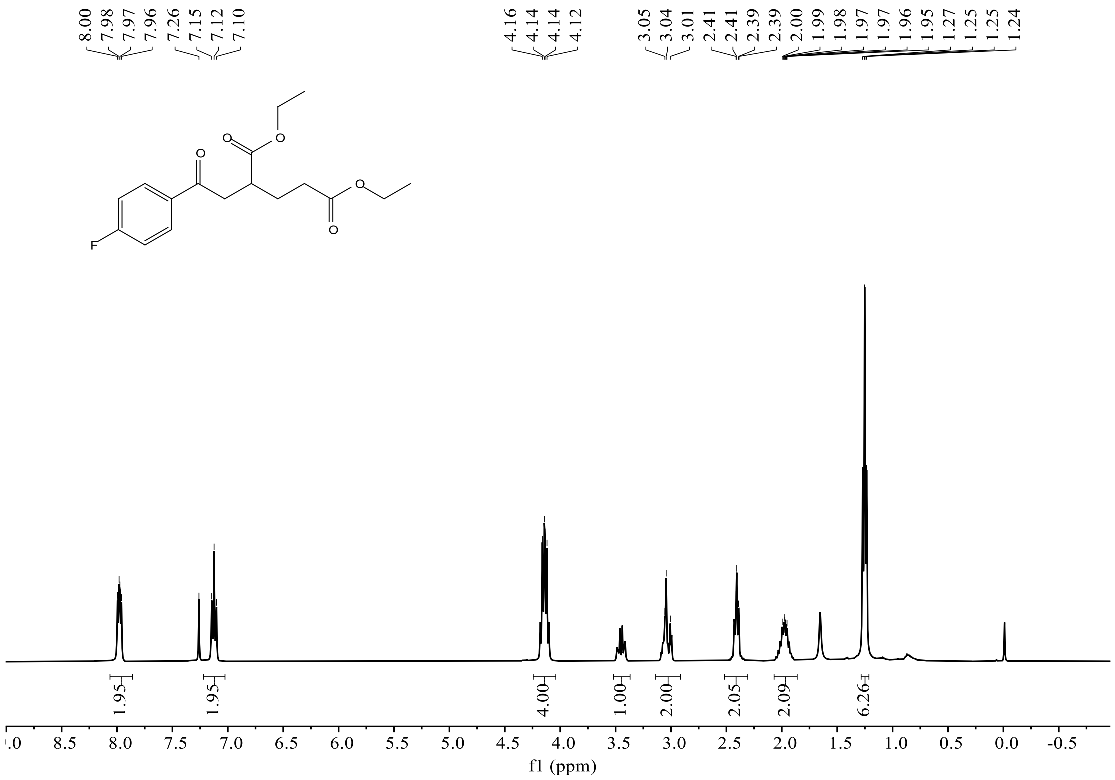
^1H NMR spectra of 3g (400 MHz, $CDCl_3$)



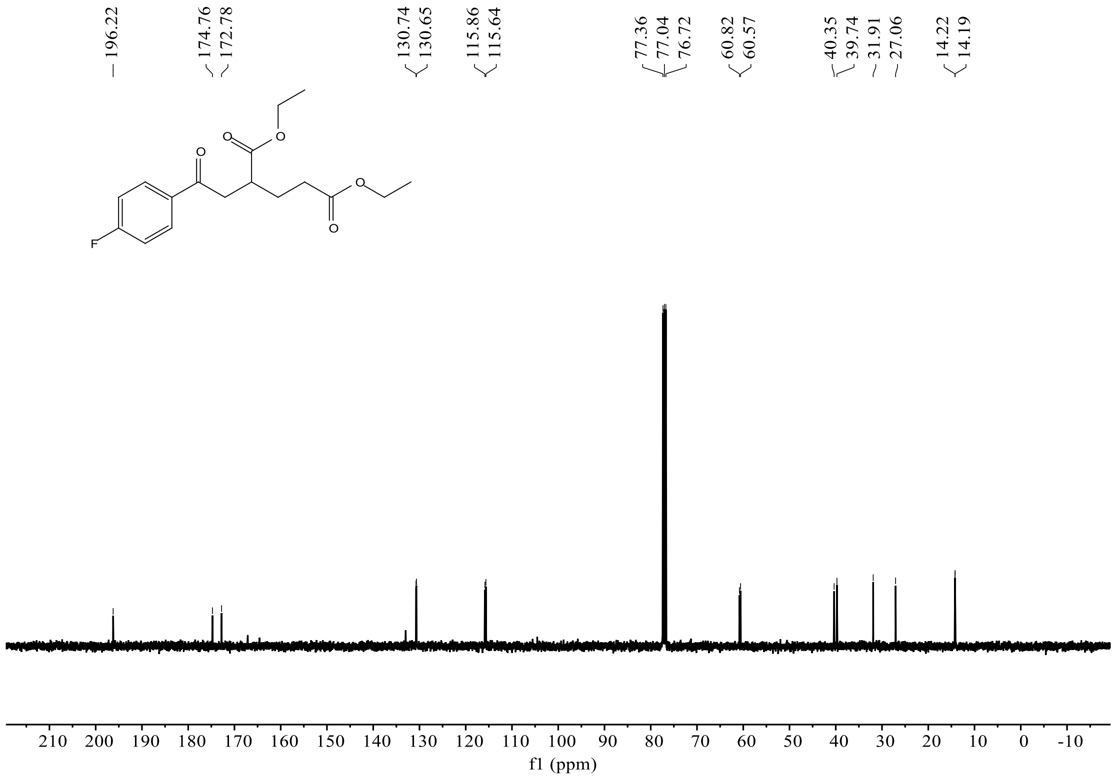
^{13}C NMR spectra of 3g (100 MHz, $CDCl_3$)



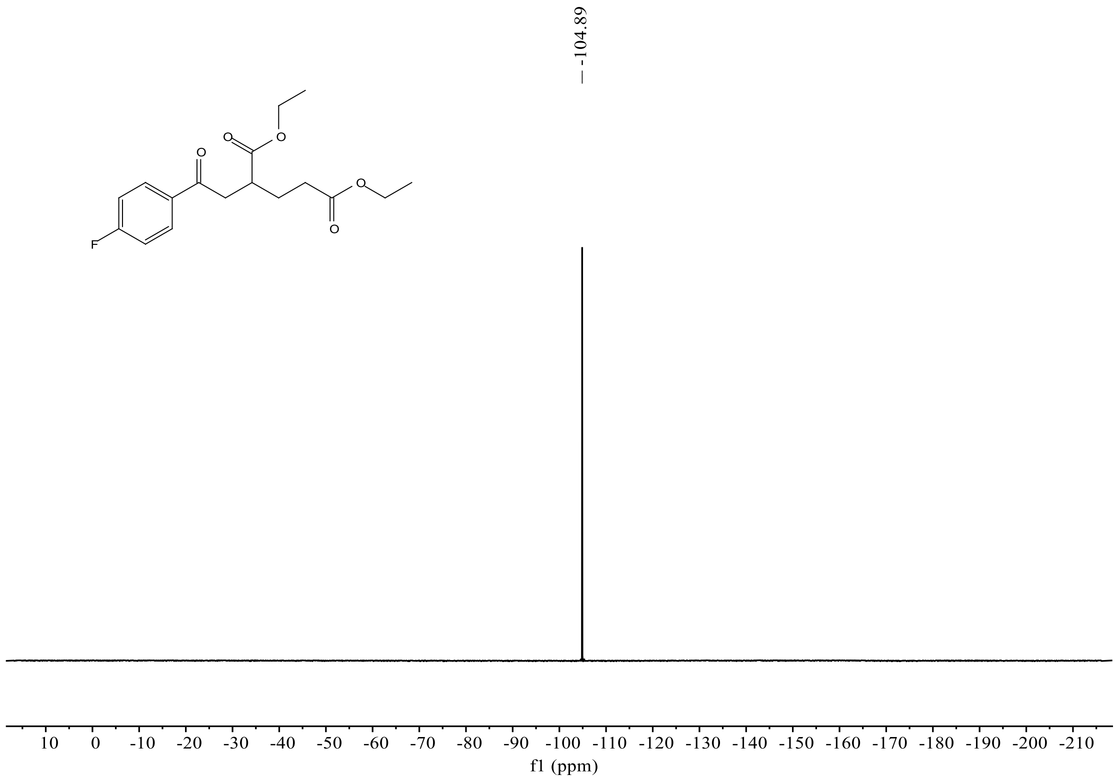
^{1}H NMR spectra of 3h (400 MHz, $CDCl_3$)



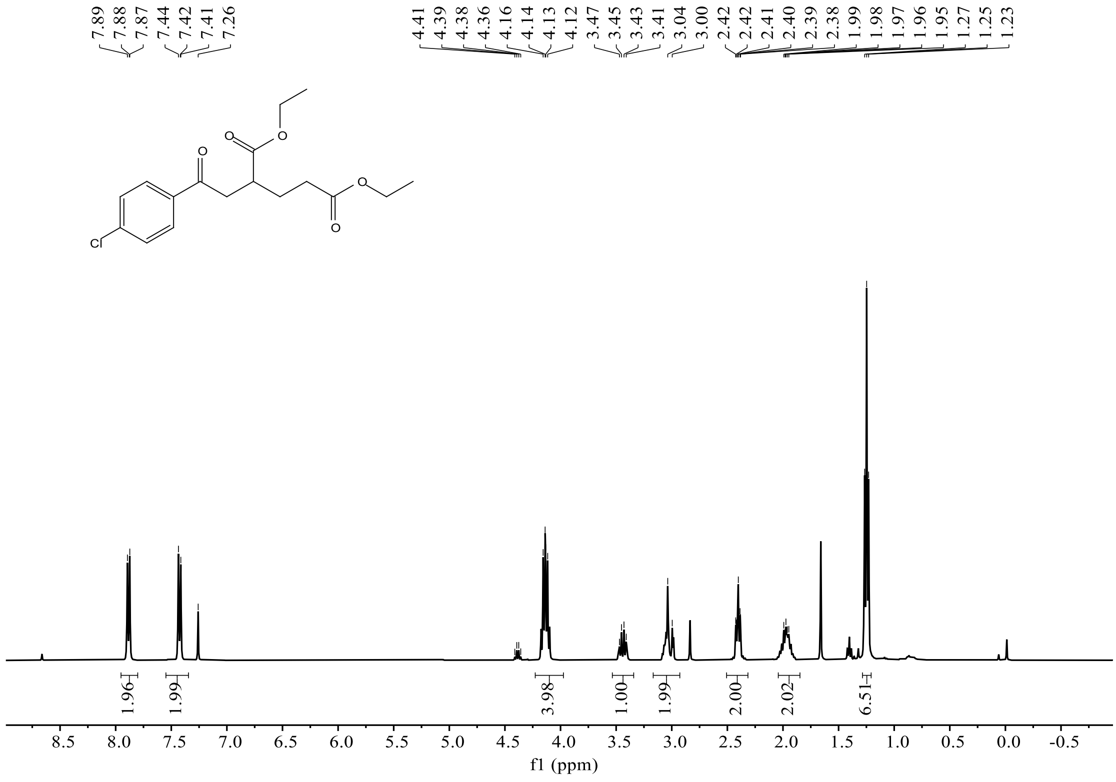
^{13}C NMR spectra of 3h (100 MHz, $CDCl_3$)



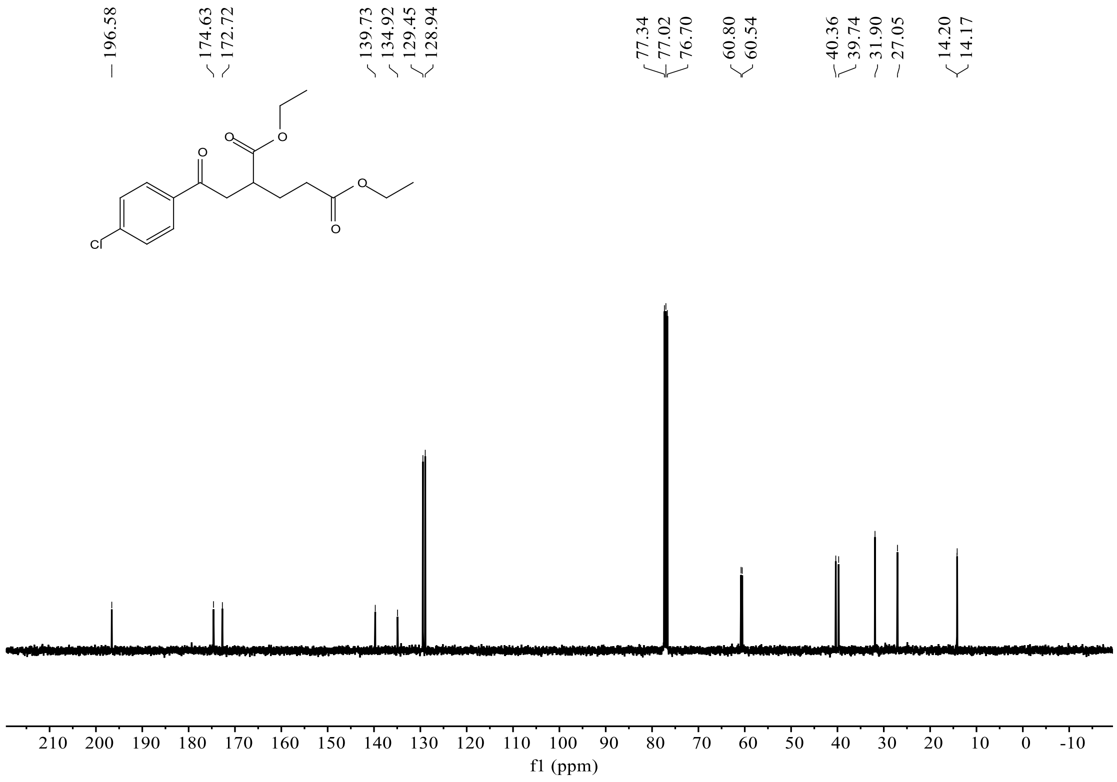
^{19}F NMR spectra of 3h (376 MHz, CDCl$_3$)



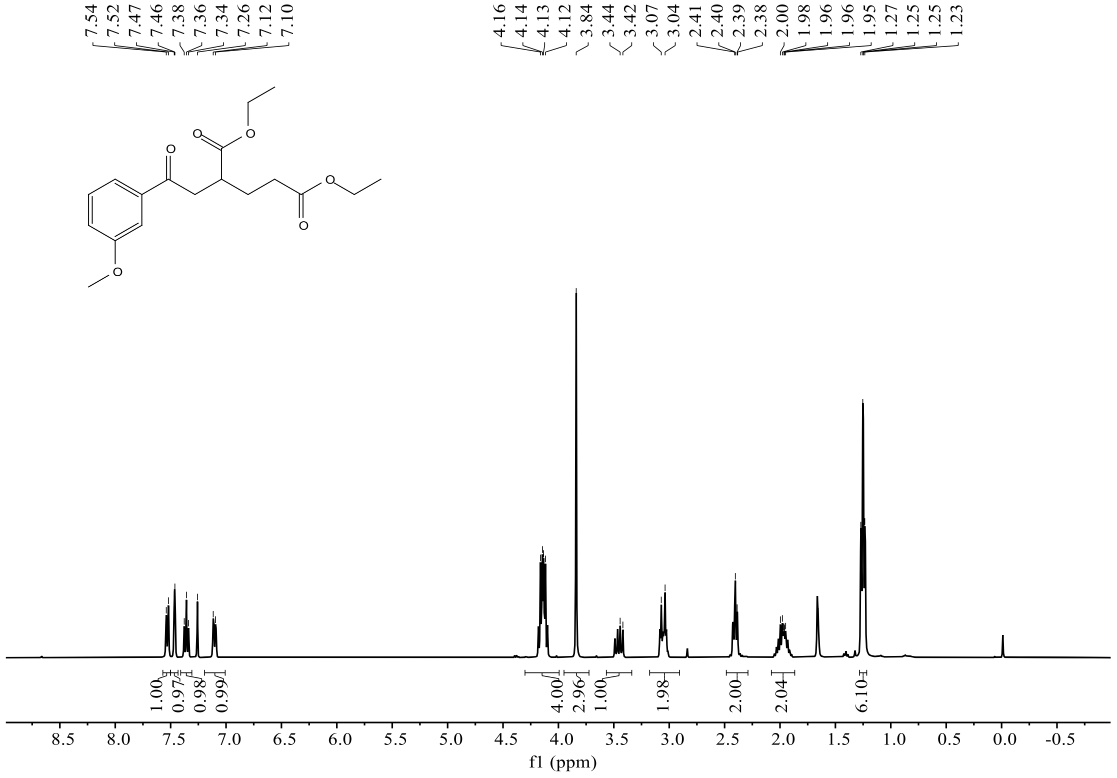
^{1}H NMR spectra of 3i (400 MHz, CDCl$_3$)



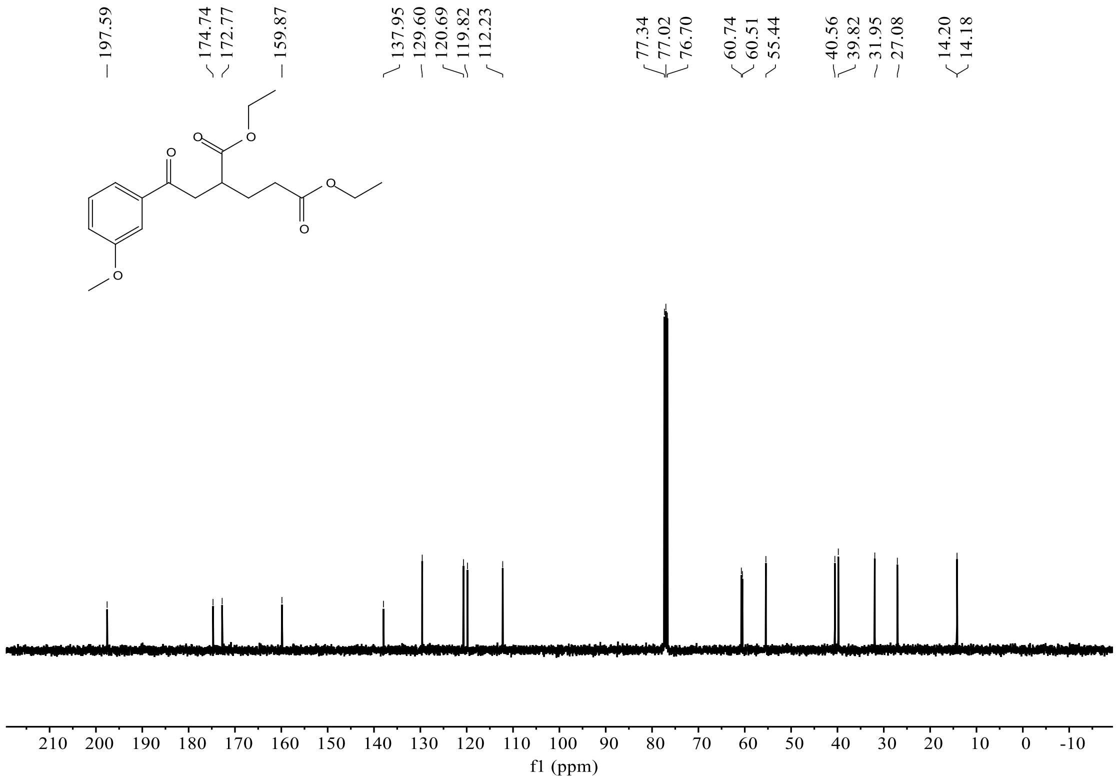
^{13}C NMR spectra of 3i (100 MHz, CDCl$_3$)



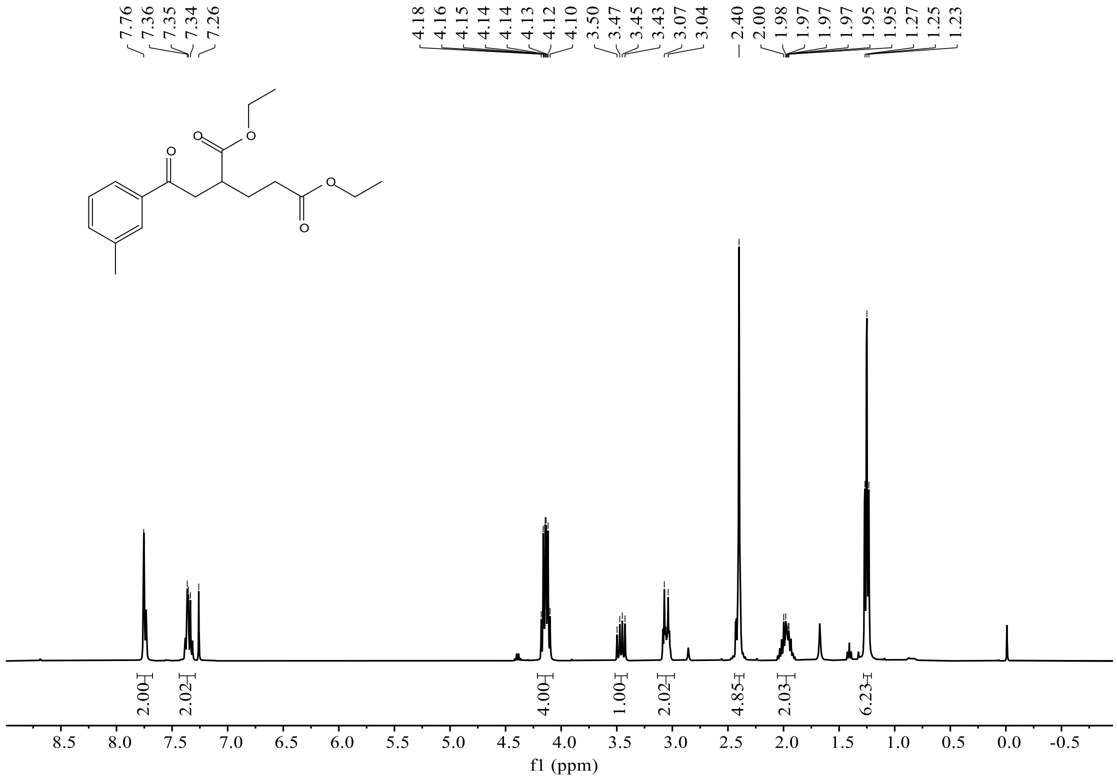
^{1}H NMR spectra of 3j (400 MHz, CDCl$_3$)



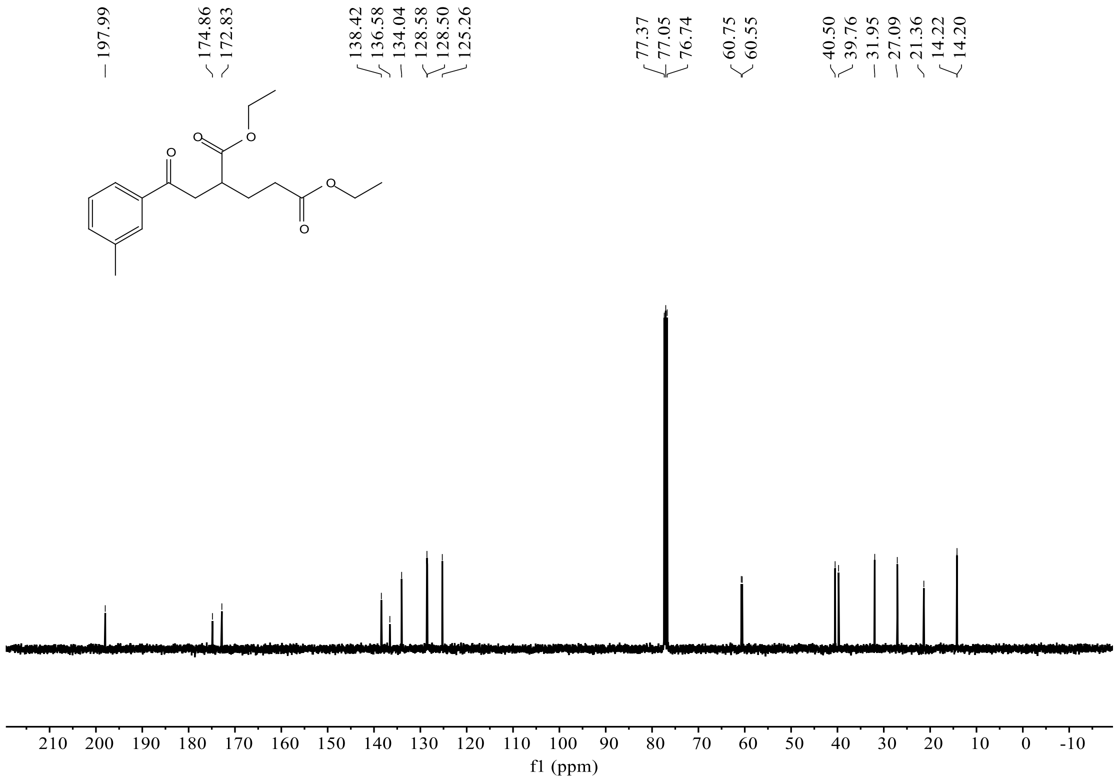
^{13}C NMR spectra of 3j (100 MHz, $CDCl_3$)



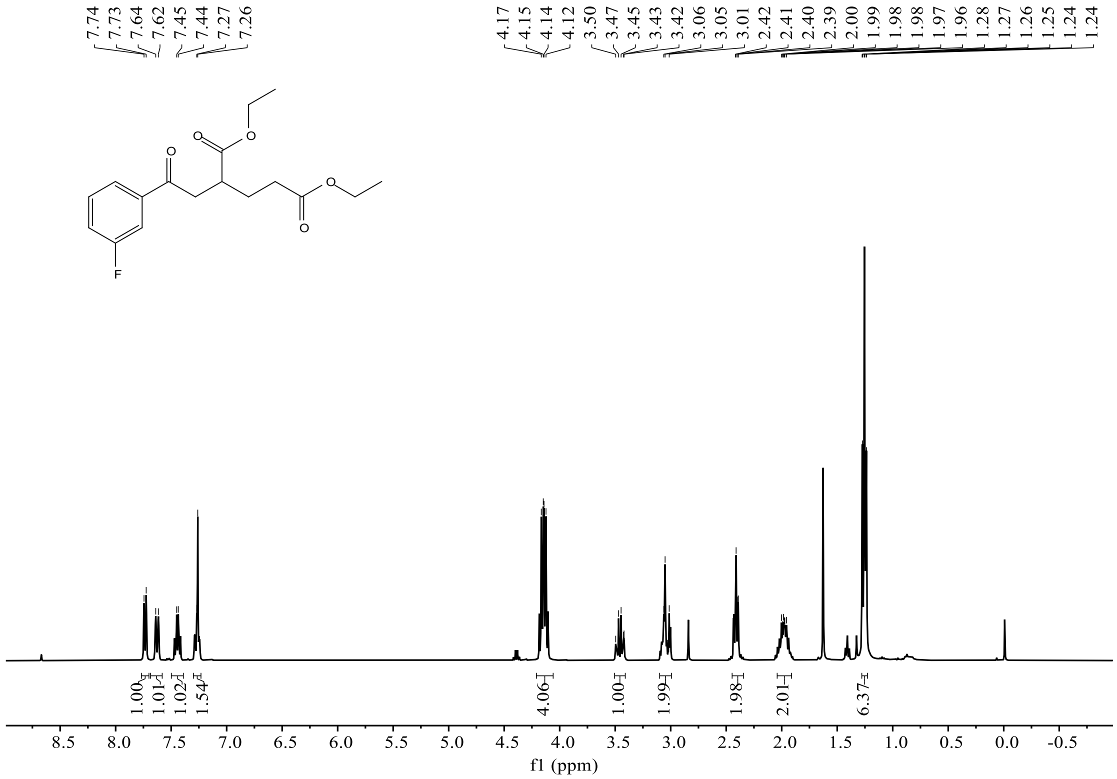
^{1}H NMR spectra of 3k (400 MHz, $CDCl_3$)



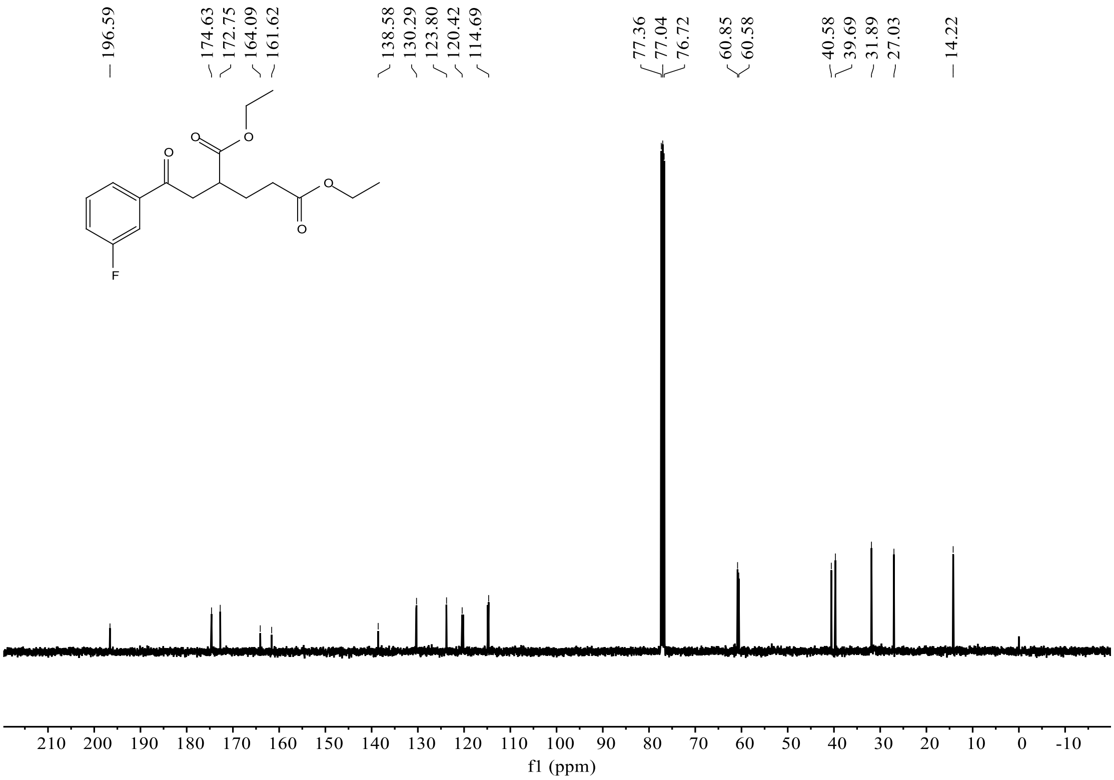
^{13}C NMR spectra of 3k (100 MHz, $CDCl_3$)



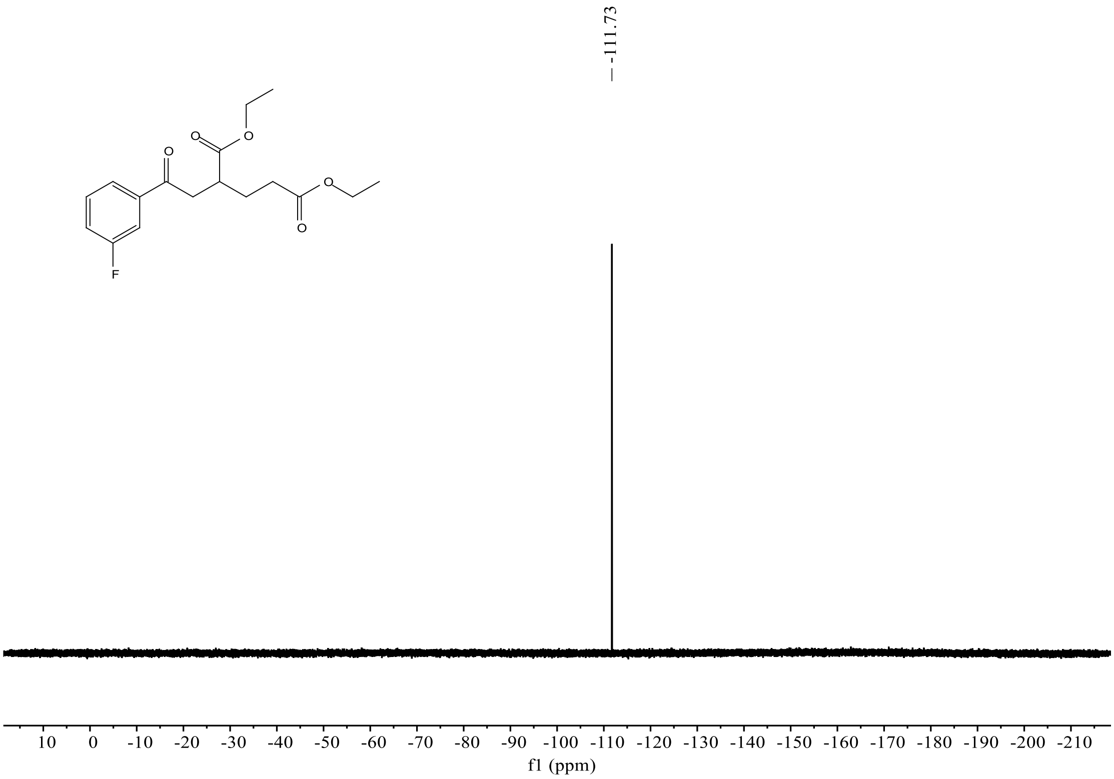
^{1}H NMR spectra of 3l (400 MHz, $CDCl_3$)



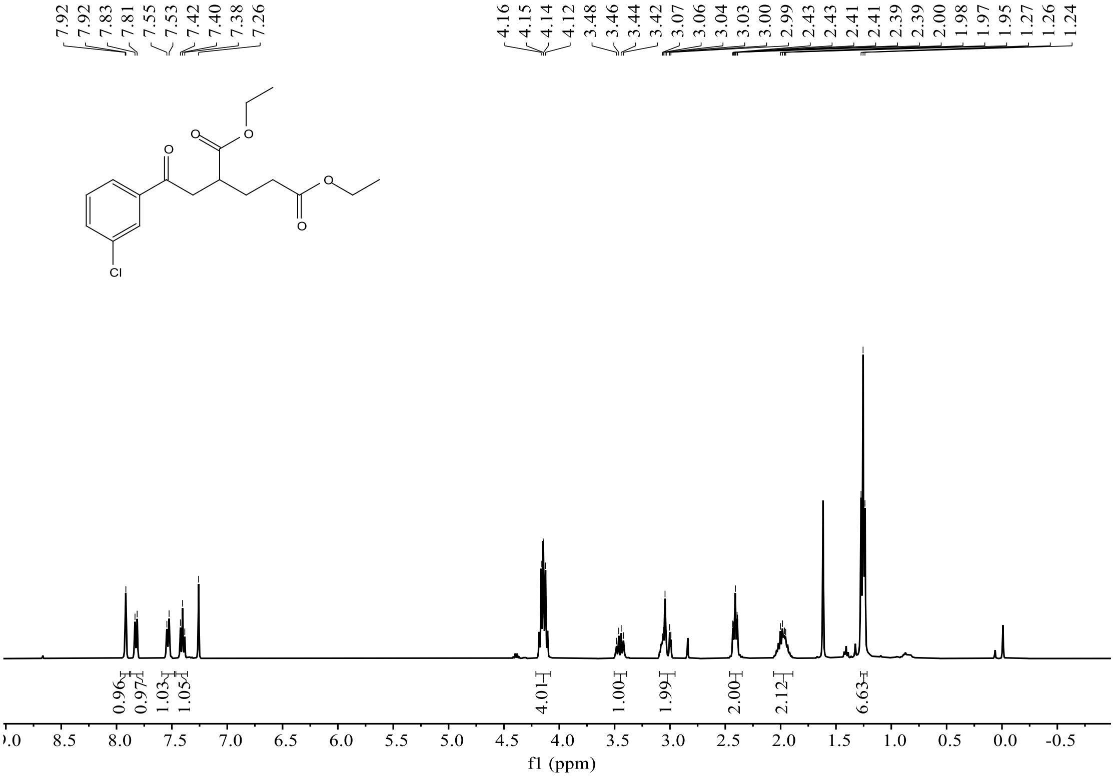
^{13}C NMR spectra of 3l (100 MHz, $CDCl_3$)



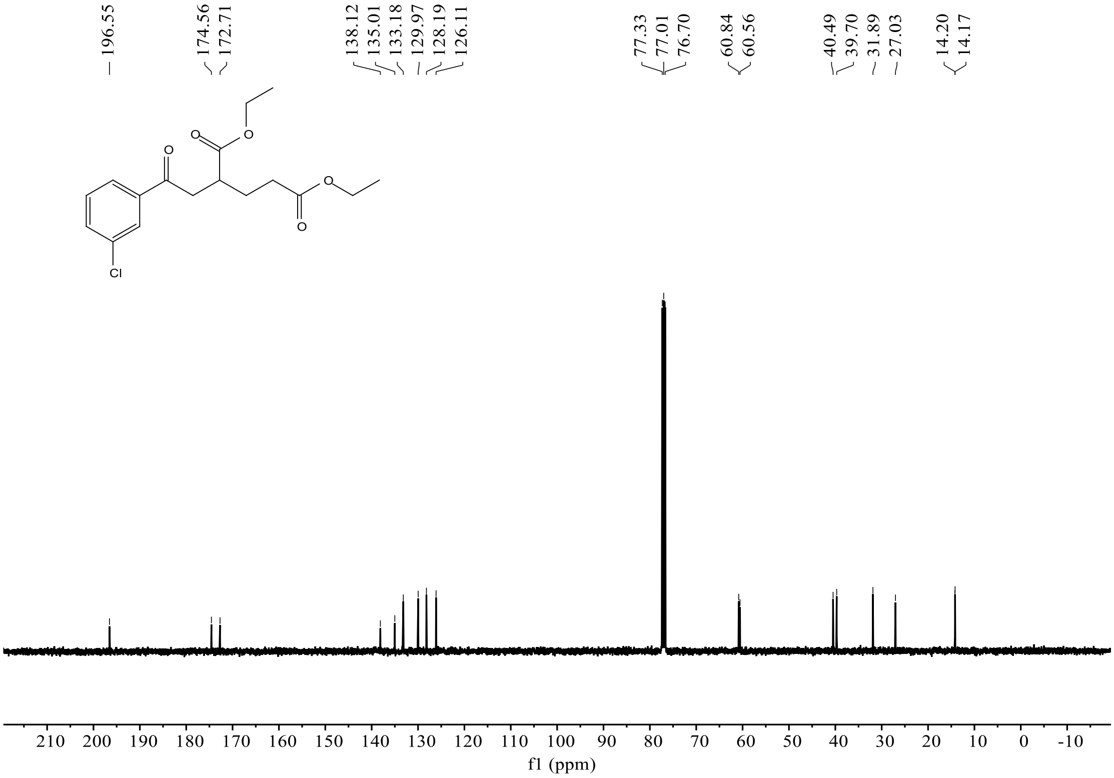
^{19}F NMR spectra of 3l (376 MHz, $CDCl_3$)



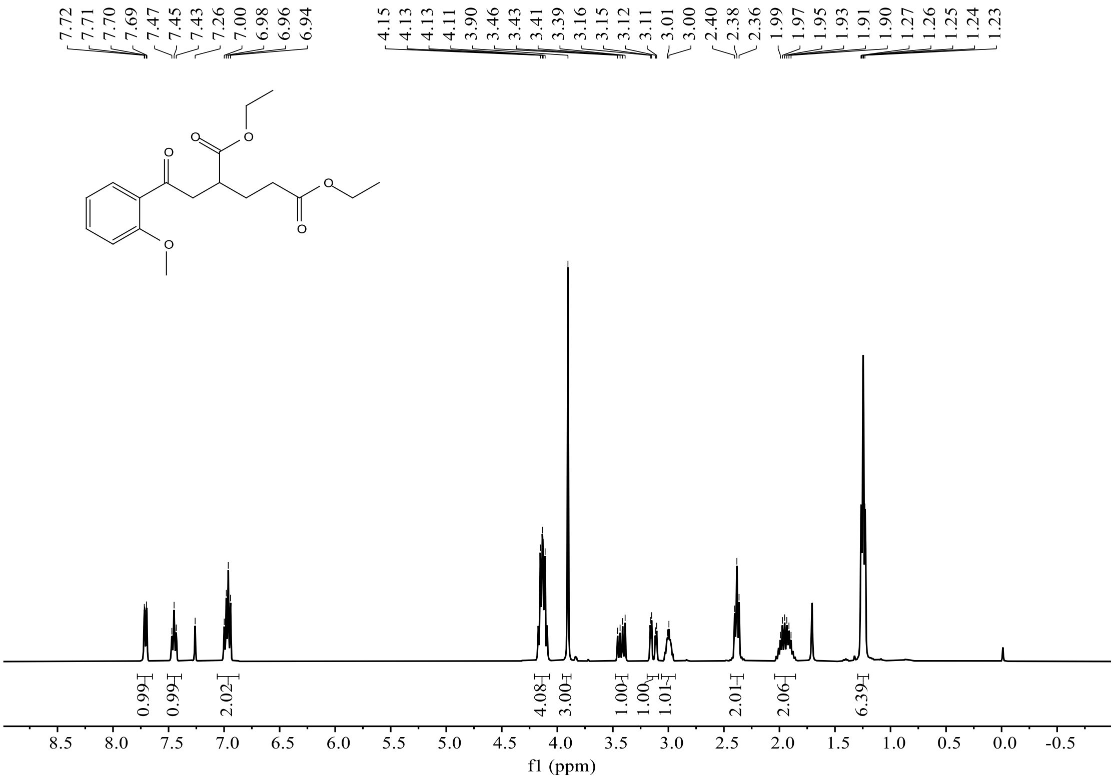
^{1}H NMR spectra of 3m (400 MHz, $CDCl_3$)



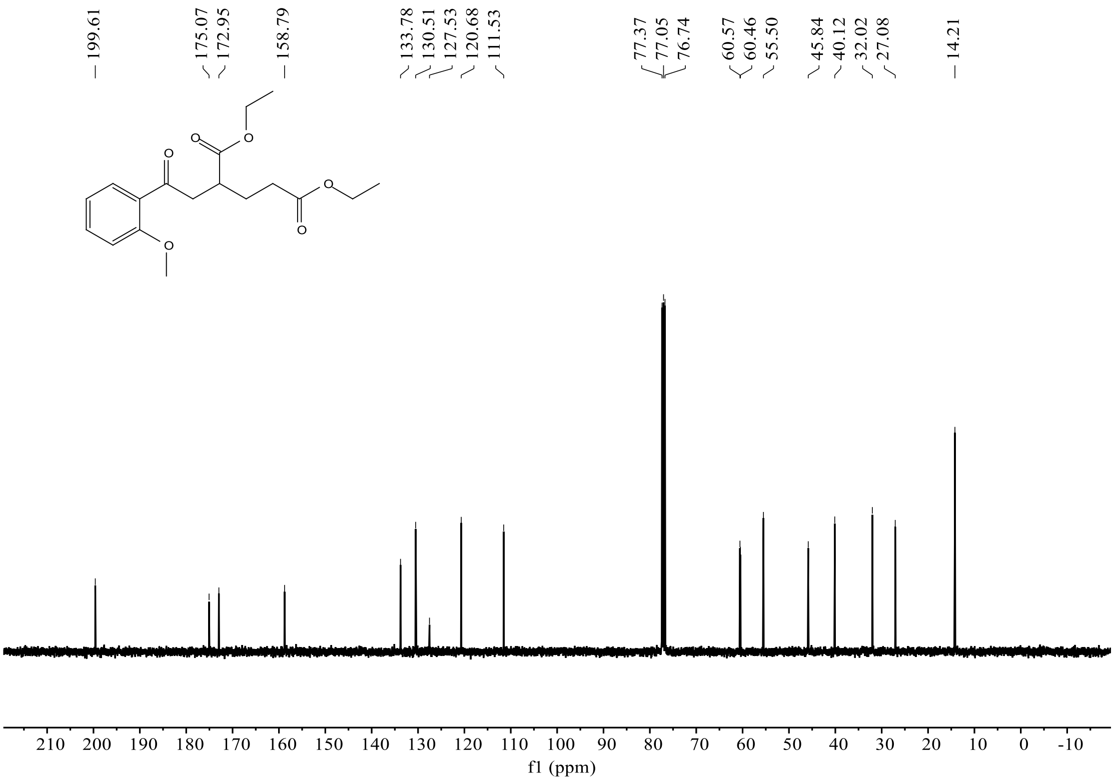
^{13}C NMR spectra of 3m (100 MHz, $CDCl_3$)



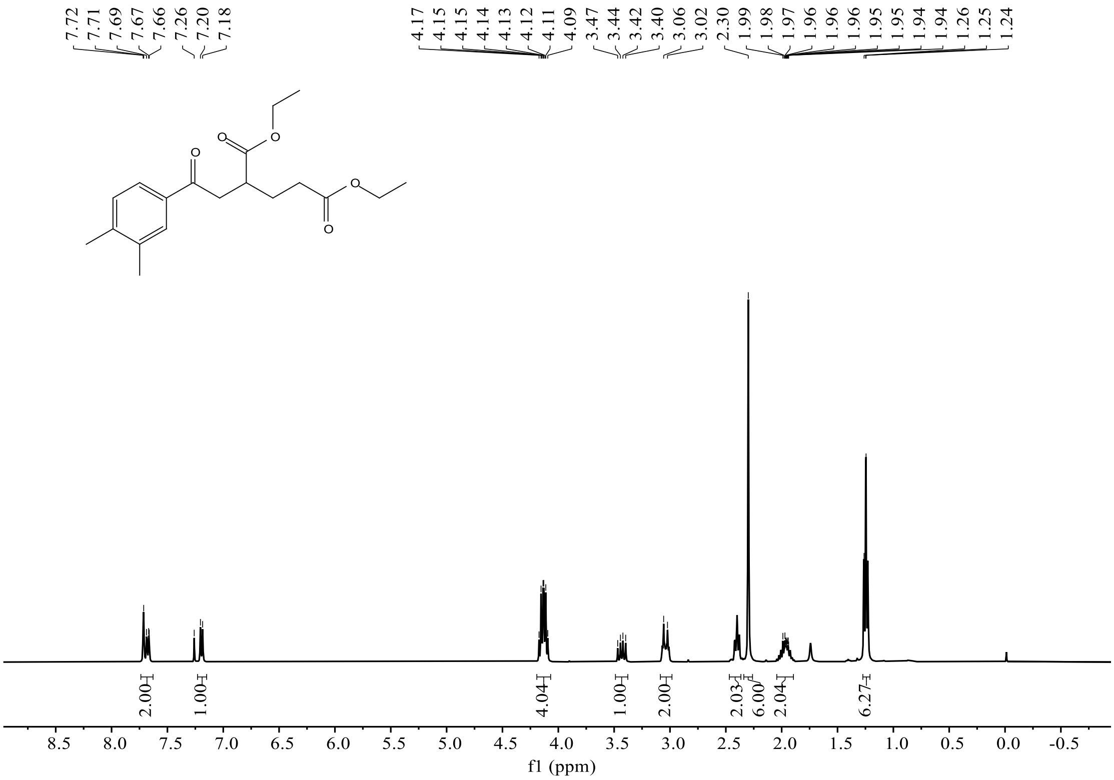
^{1}H NMR spectra of 3n (400 MHz, $CDCl_3$)



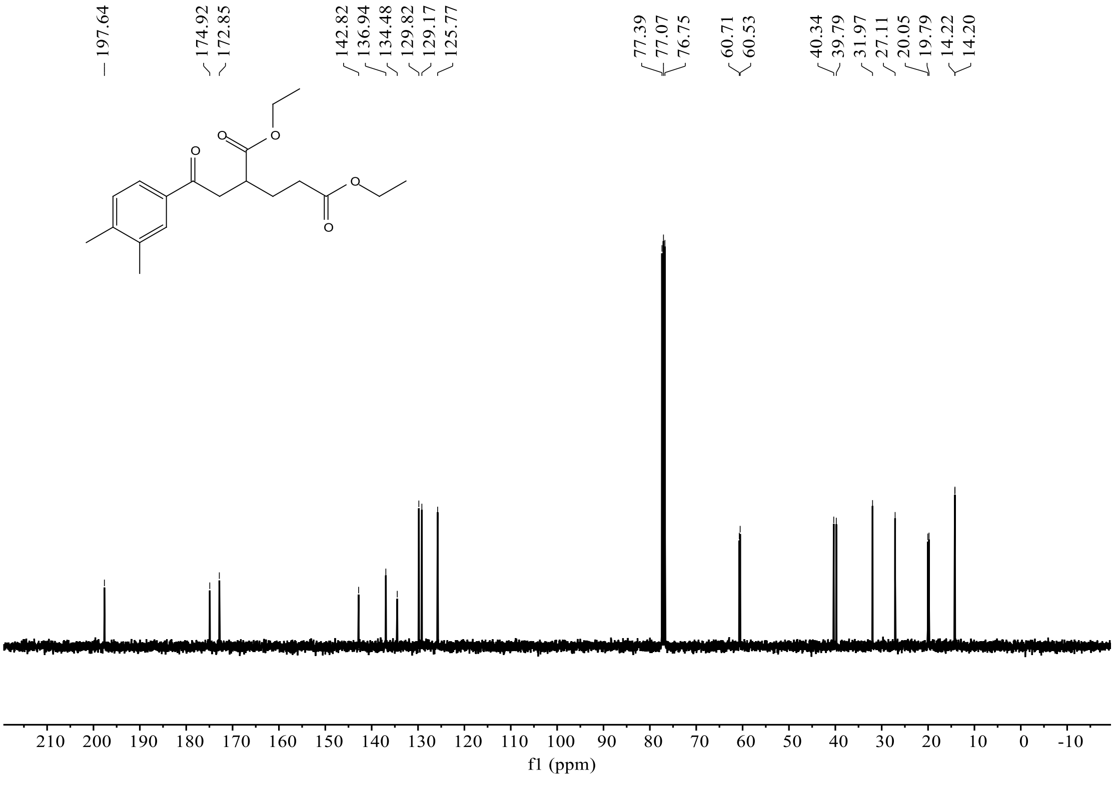
^{13}C NMR spectra of 3n (100 MHz, $CDCl_3$)



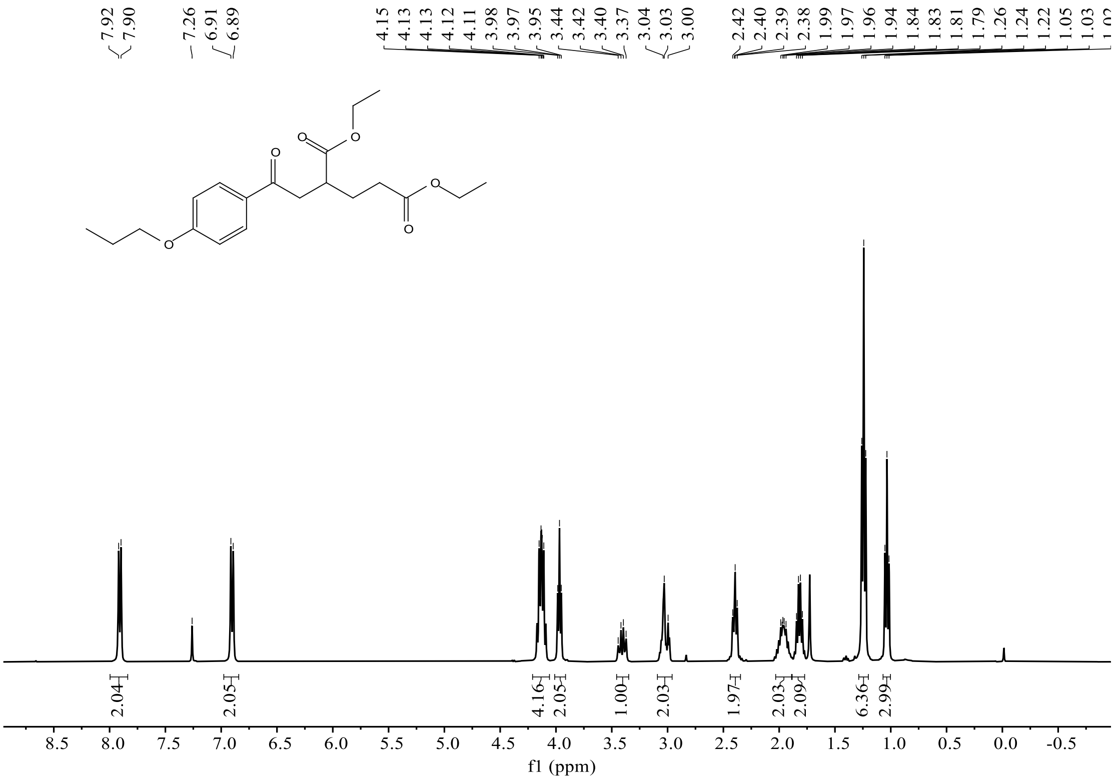
^{1}H NMR spectra of 3o (400 MHz, $CDCl_3$)



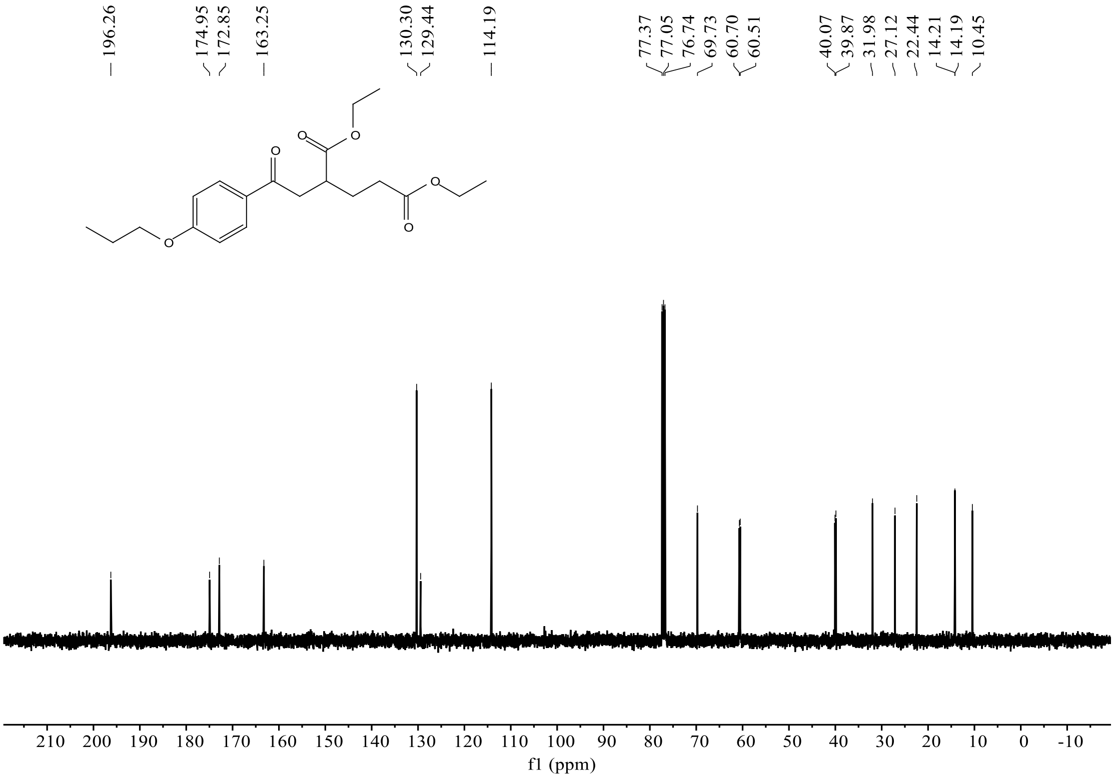
^{13}C NMR spectra of 3o (100 MHz, $CDCl_3$)



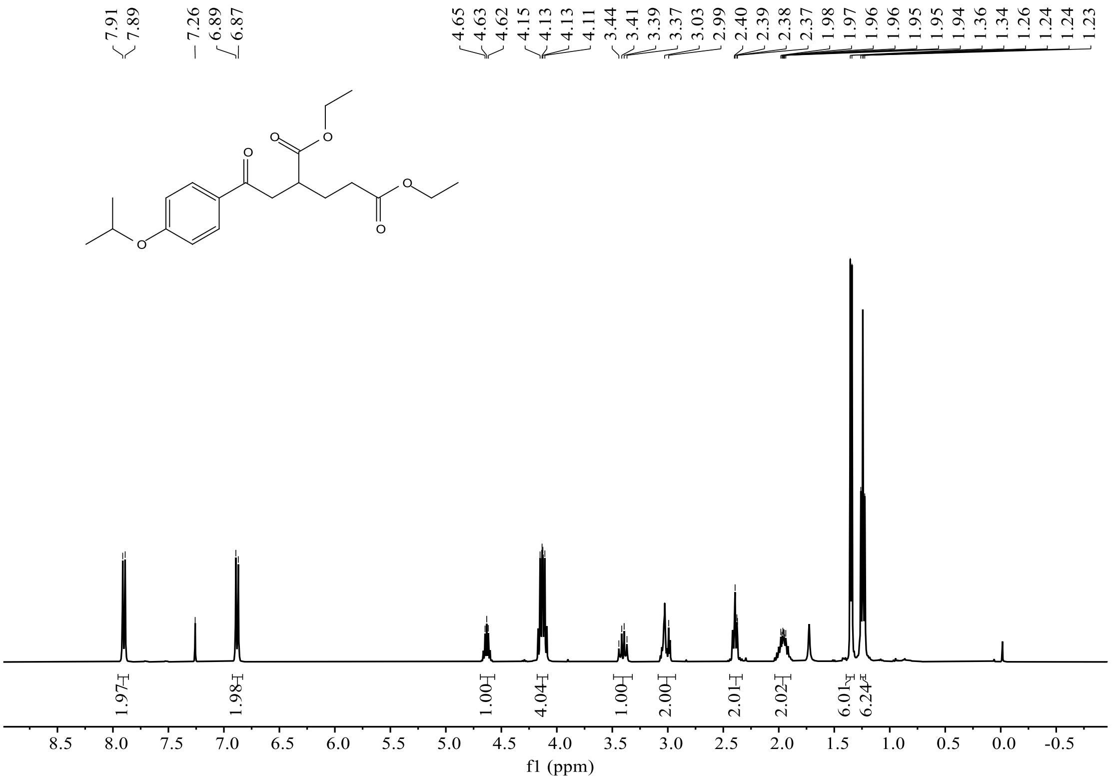
^1H NMR spectra of 3p (400 MHz, $CDCl_3$)



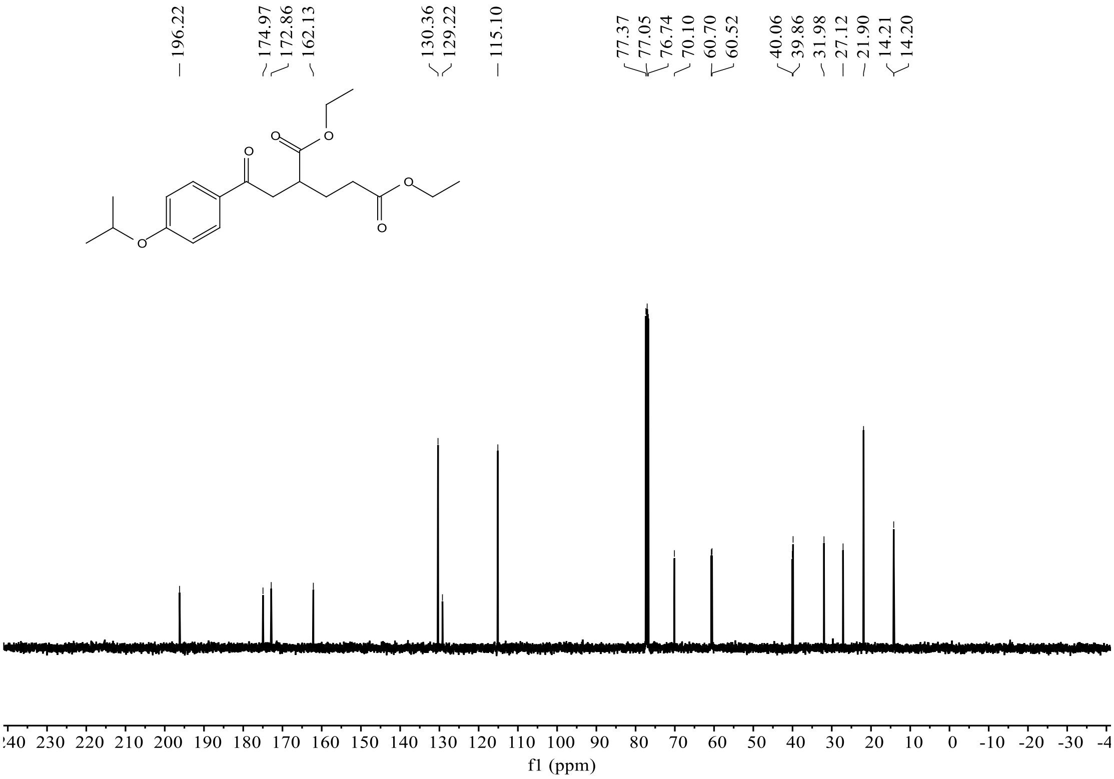
^{13}C NMR spectra of 3p (100 MHz, $CDCl_3$)



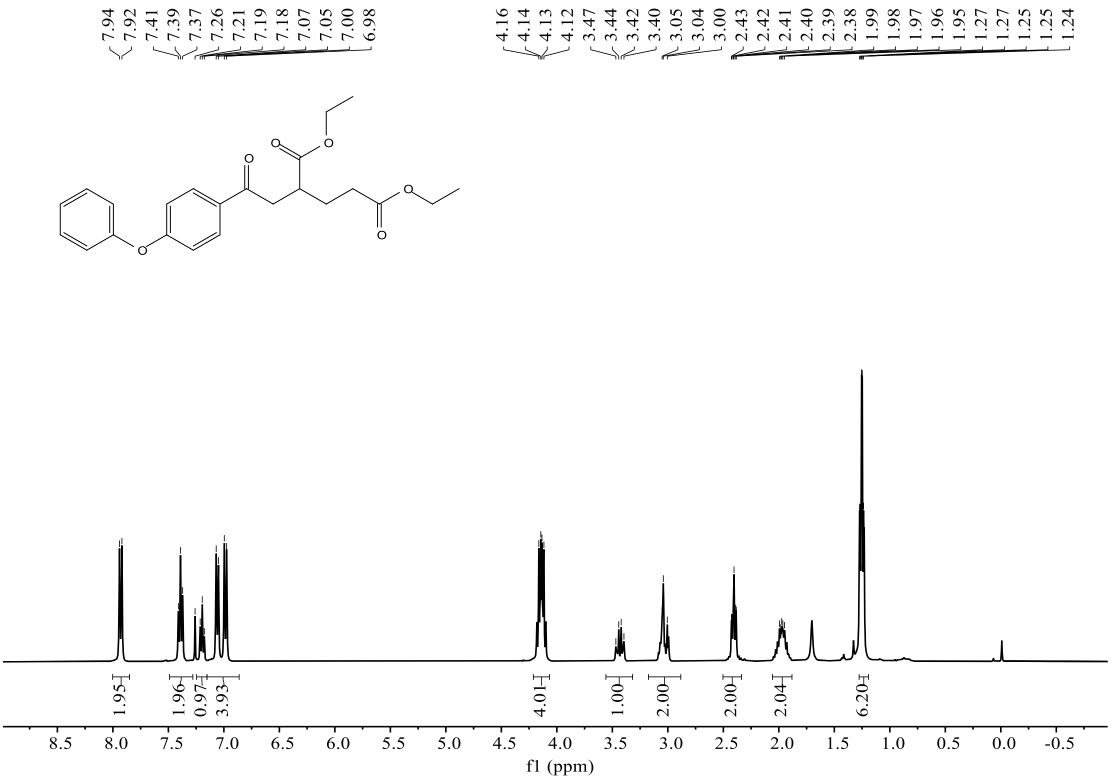
^{1}H NMR spectra of 3q (400 MHz, CDCl$_3$)



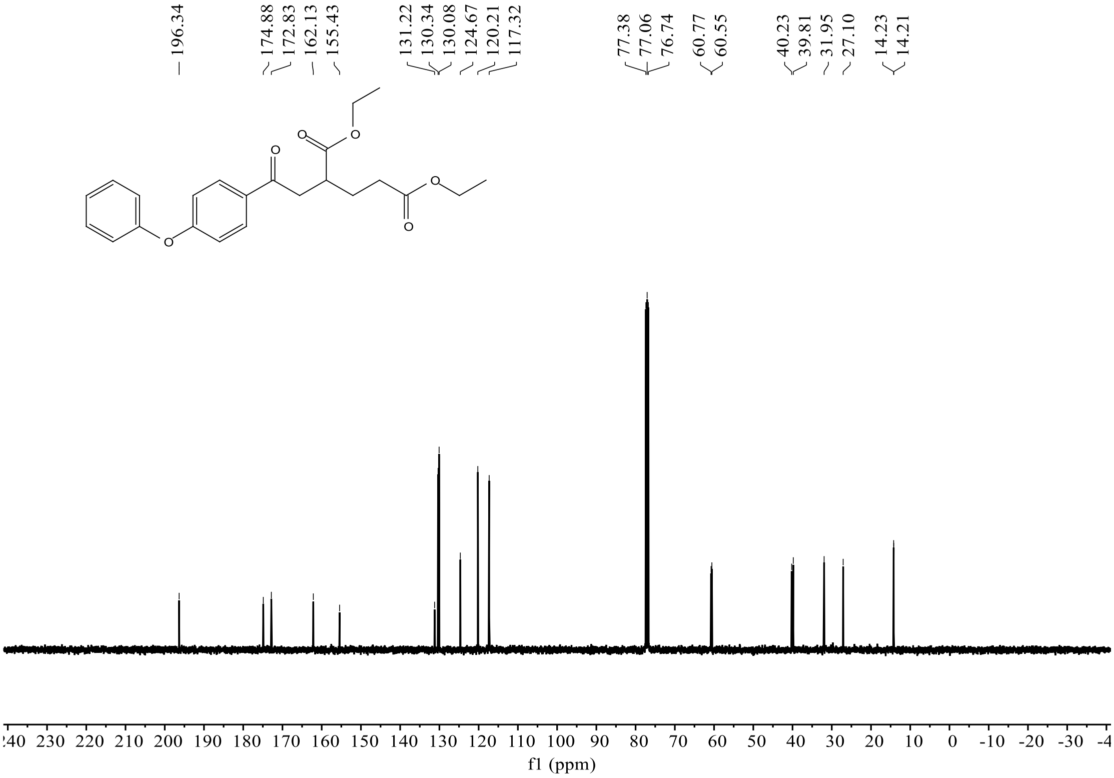
^{13}C NMR spectra of 3q (100 MHz, CDCl$_3$)



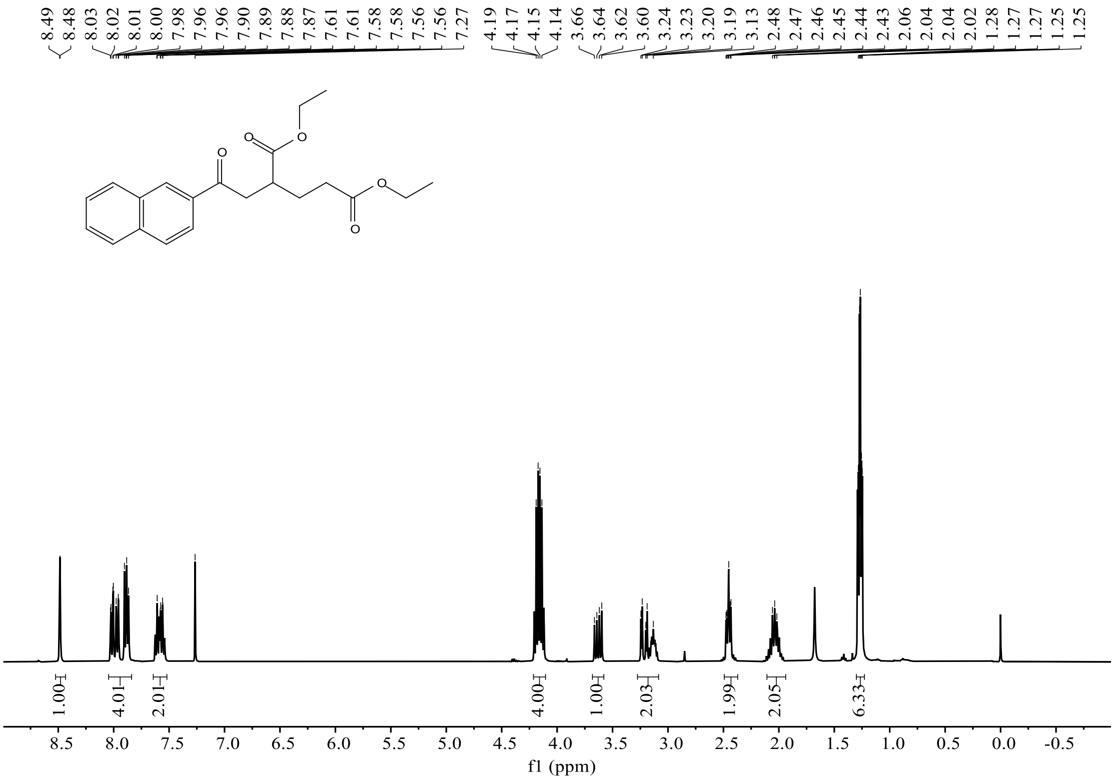
^{1}H NMR spectra of 3r (400 MHz, $CDCl_3$)



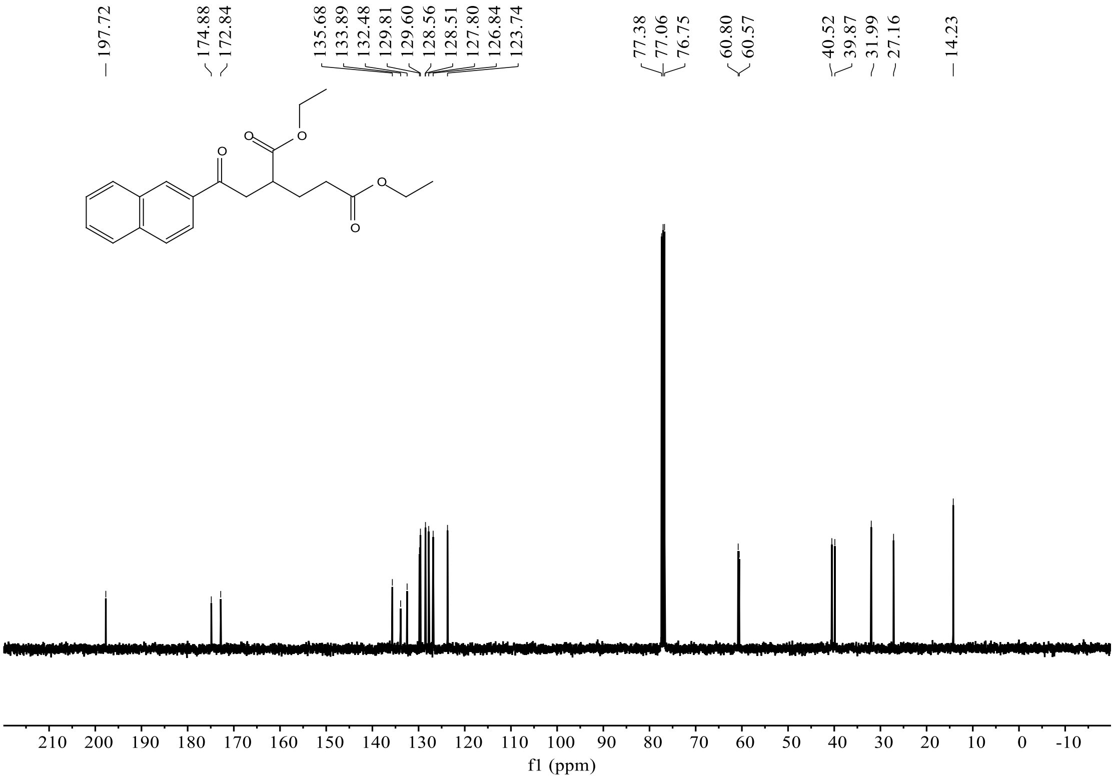
^{13}C NMR spectra of 3r (100 MHz, $CDCl_3$)



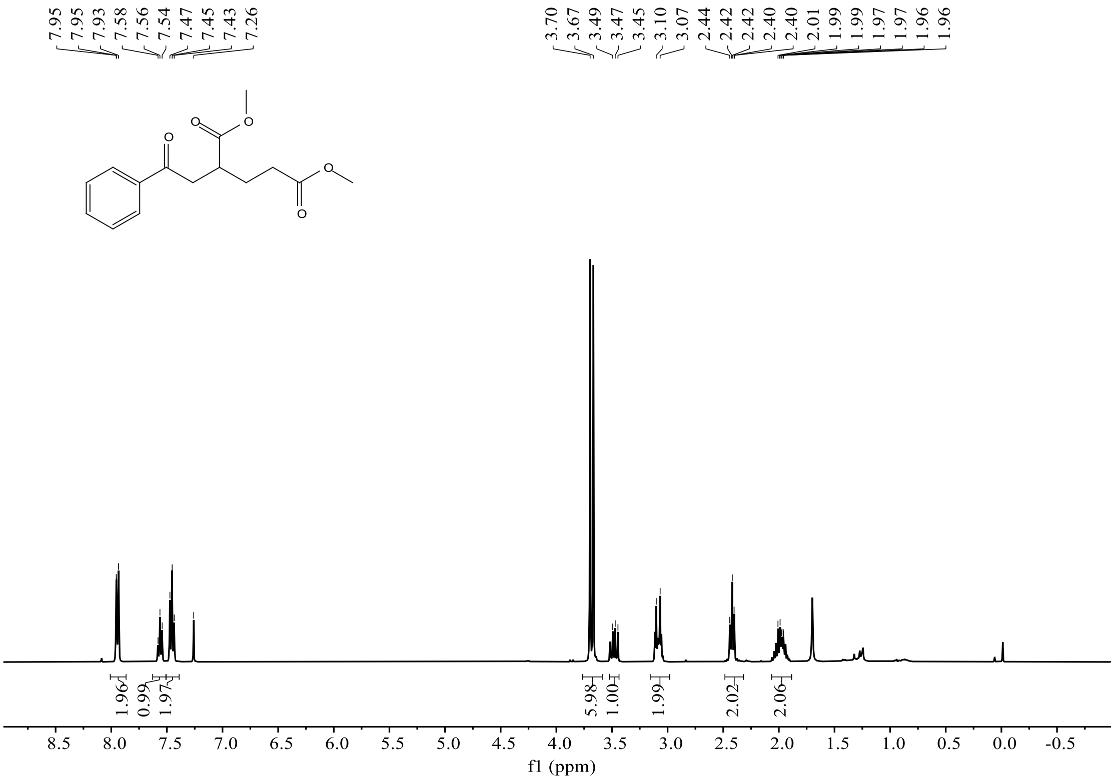
^{1}H NMR spectra of 3s (400 MHz, CDCl$_3$)



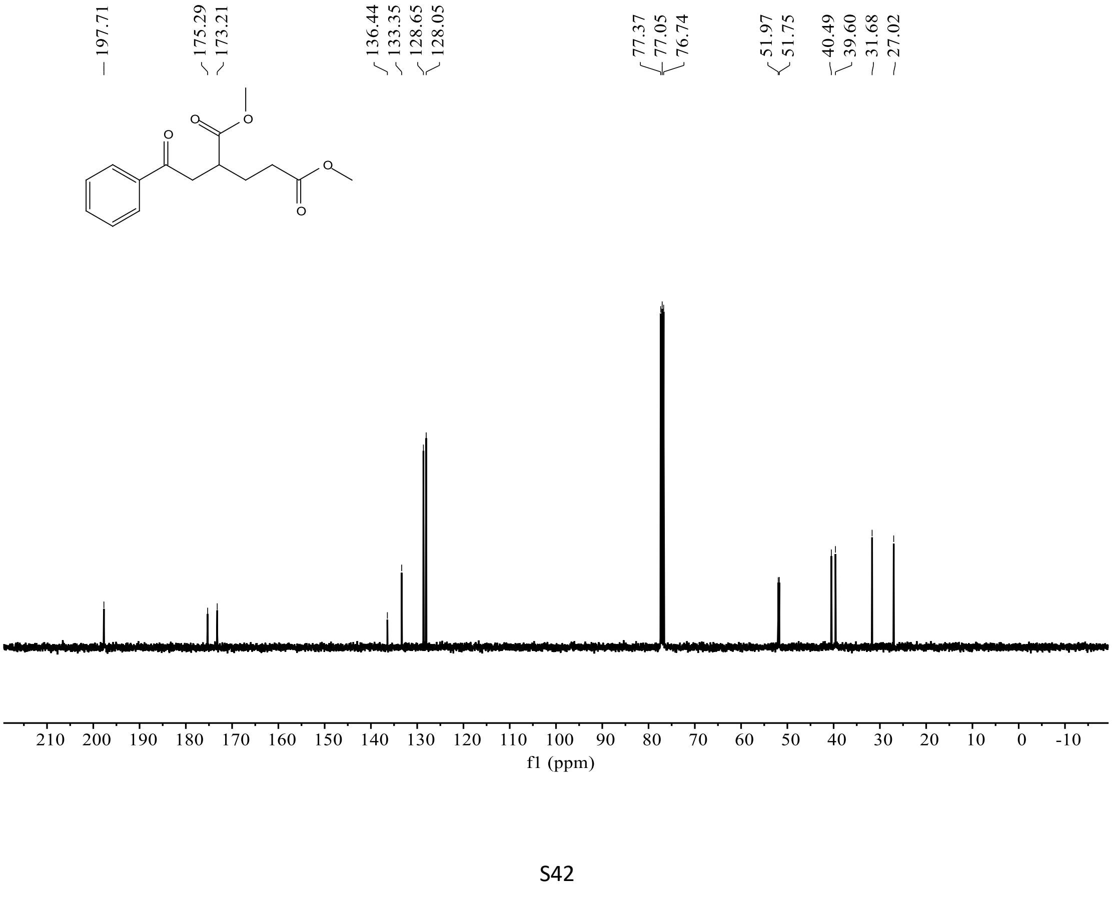
^{13}C NMR spectra of 3s (100 MHz, CDCl$_3$)



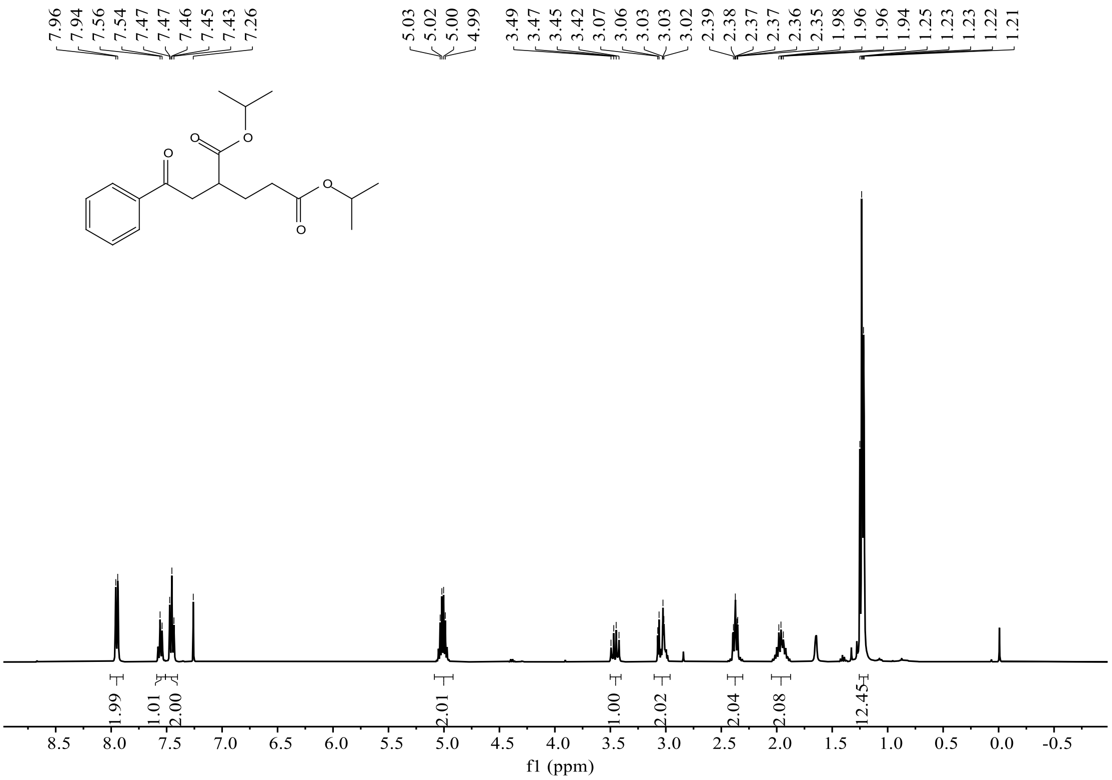
^{1}H NMR spectra of 3t (400 MHz, CDCl$_3$)



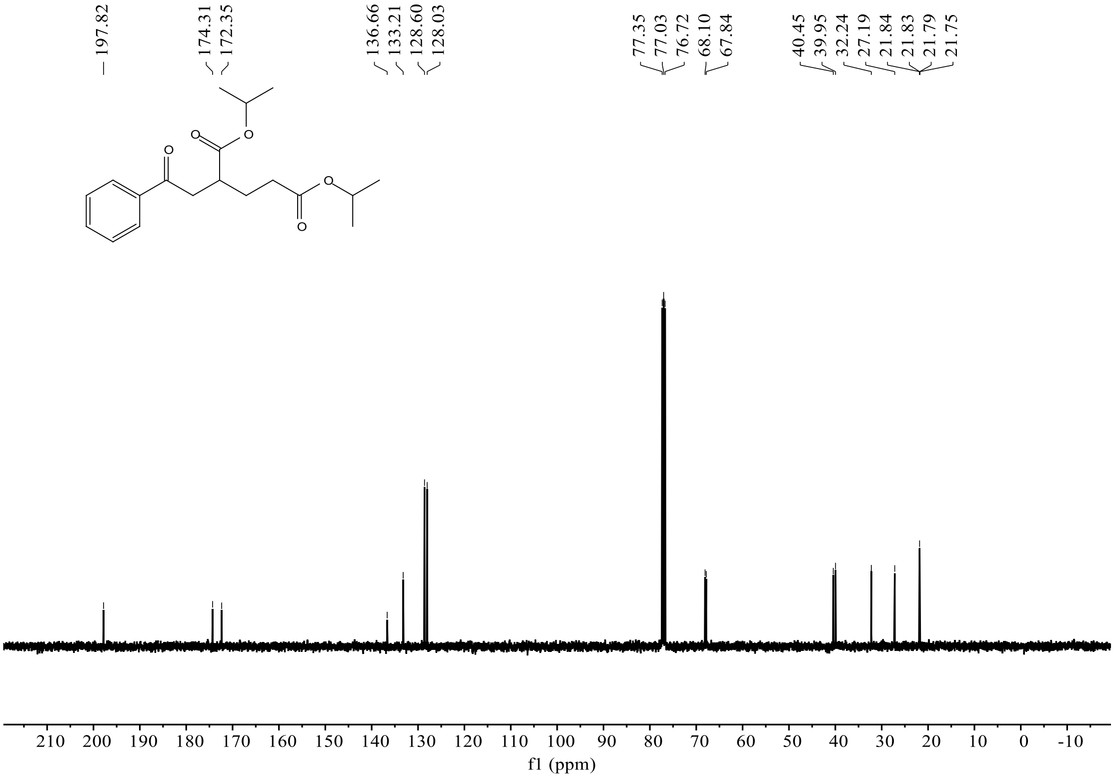
^{13}C NMR spectra of 3t (100 MHz, CDCl$_3$)



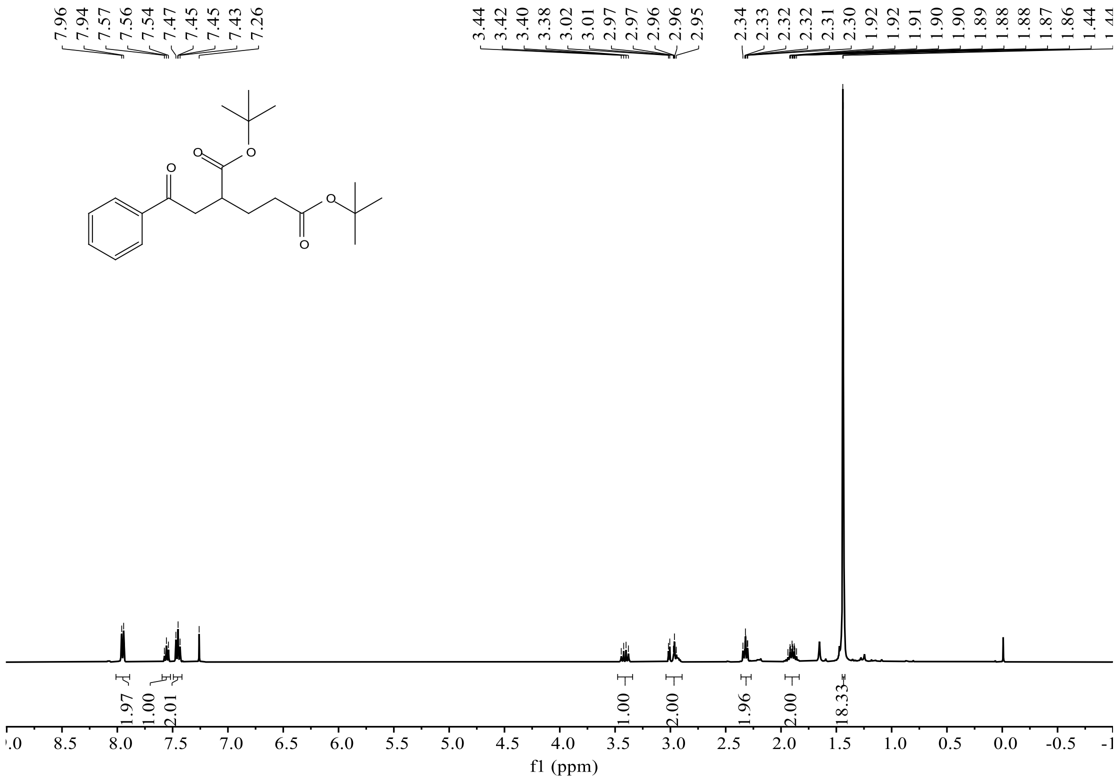
^{1}H NMR spectra of 3u (400 MHz, CDCl$_3$)



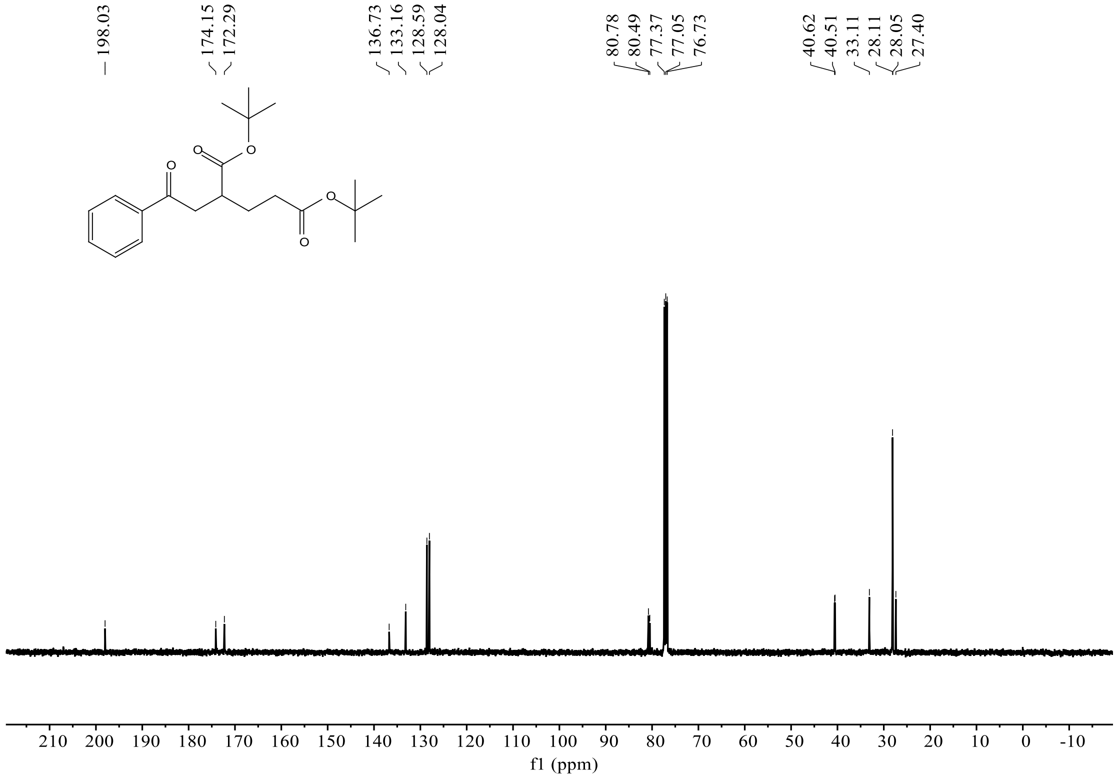
^{13}C NMR spectra of 3u (100 MHz, CDCl$_3$)



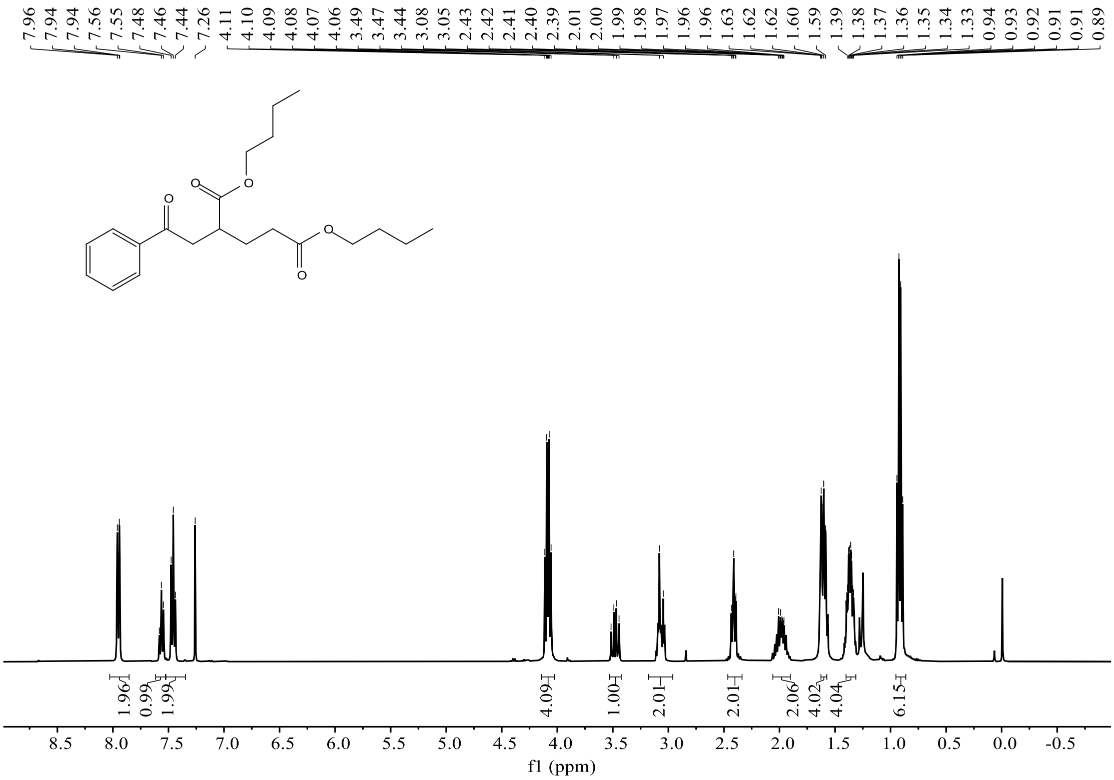
^{1}H NMR spectra of 3v (400 MHz, $CDCl_3$)



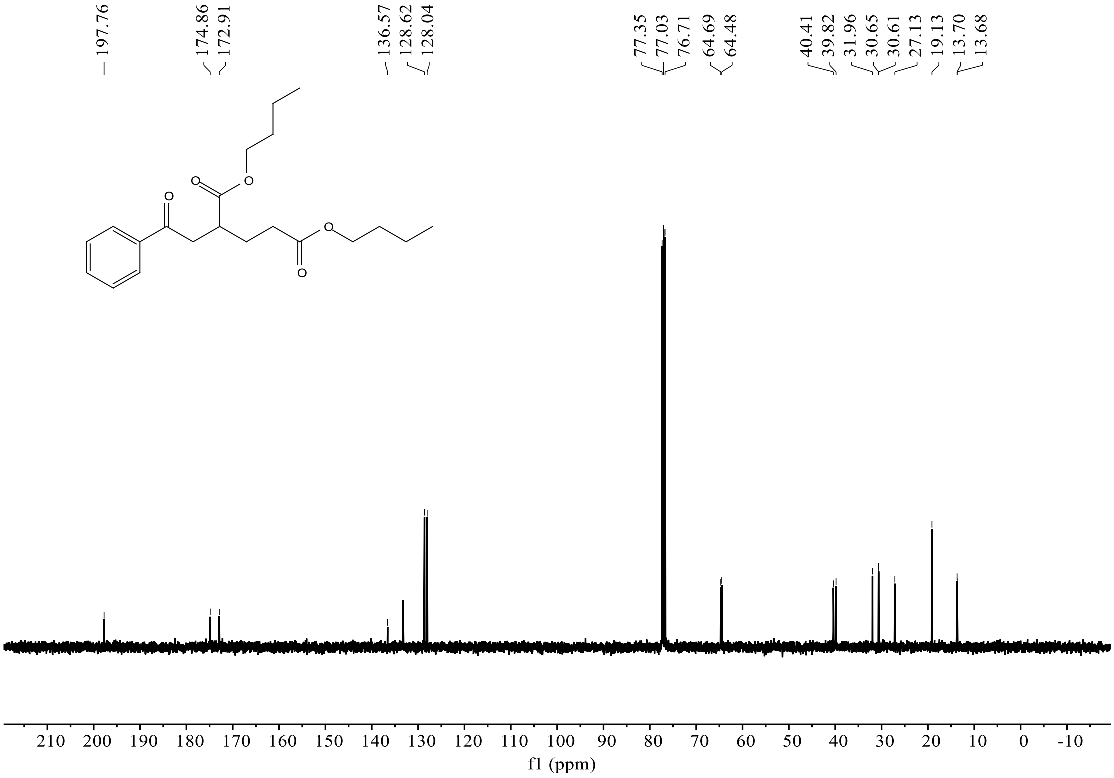
^{13}C NMR spectra of 3v (100 MHz, $CDCl_3$)



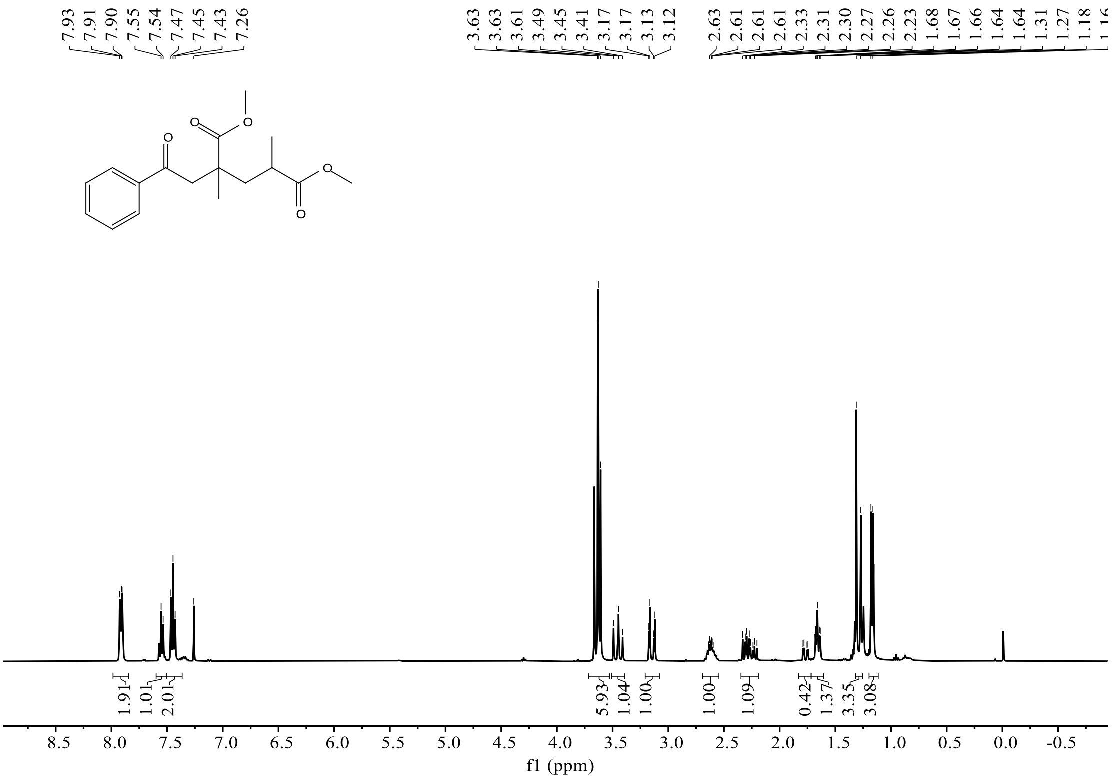
^{1}H NMR spectra of 3w (400 MHz, CDCl$_3$)



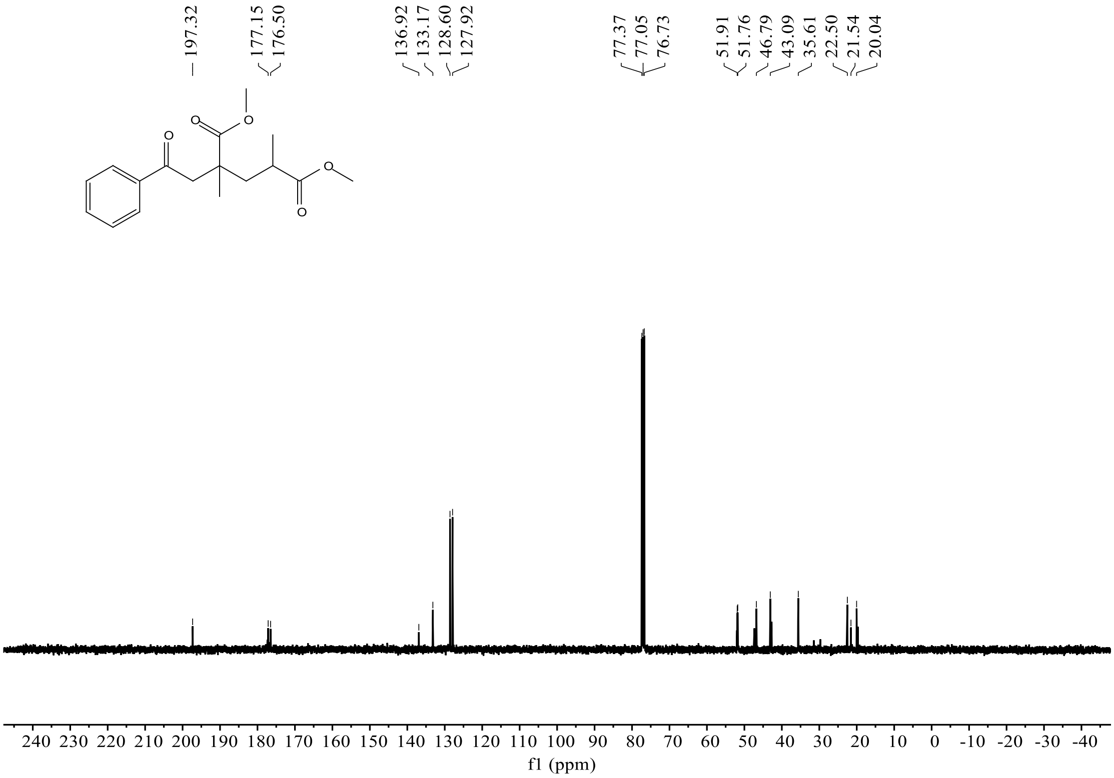
^{13}C NMR spectra of 3w (100 MHz, CDCl$_3$)



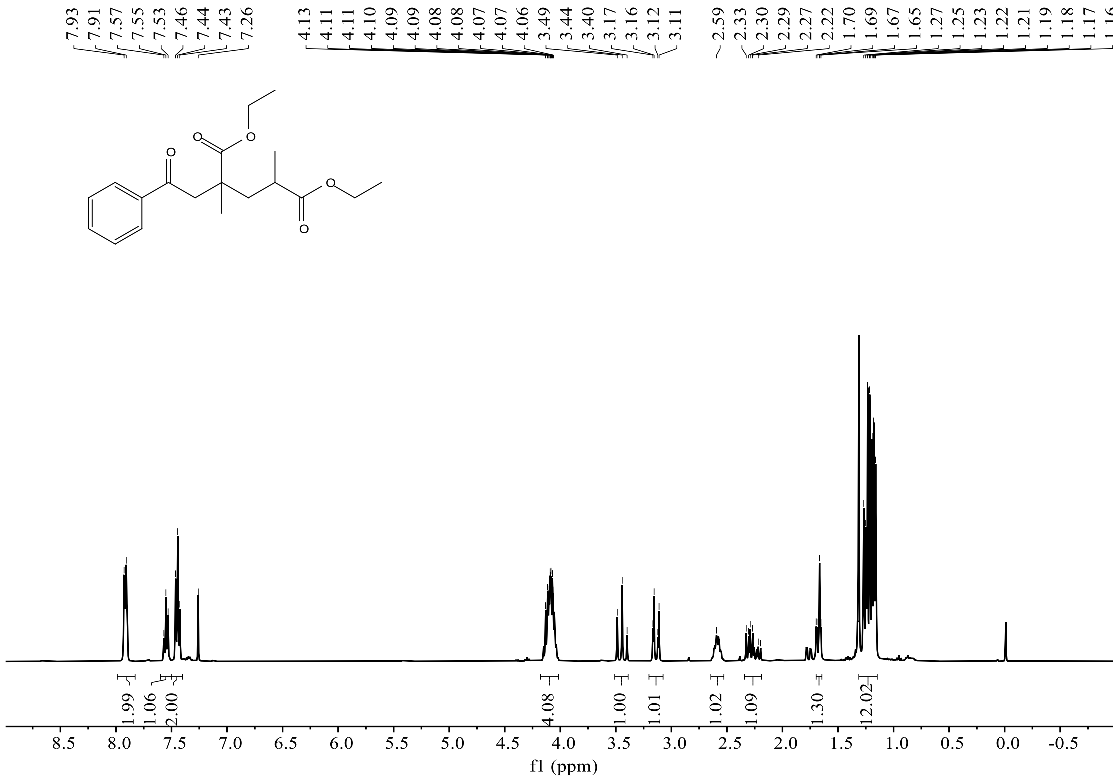
^{1}H NMR spectra of 3x (400 MHz, CDCl$_3$)



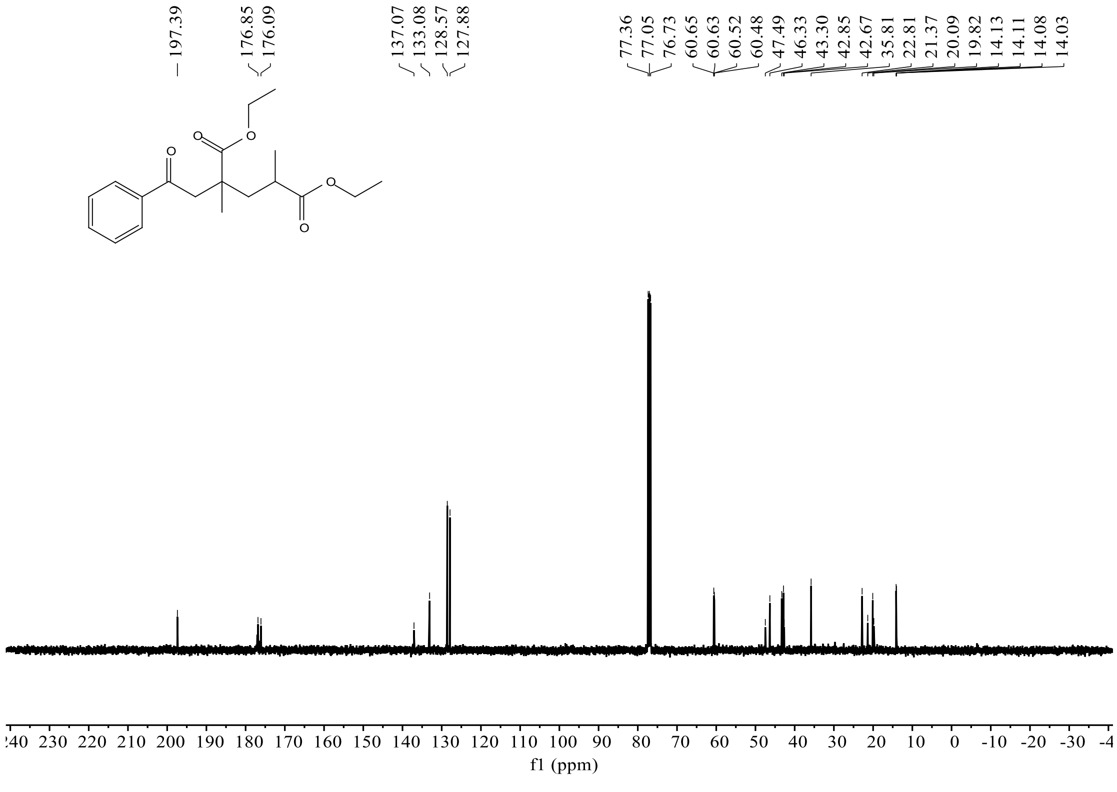
^{13}C NMR spectra of 3x (100 MHz, CDCl$_3$)



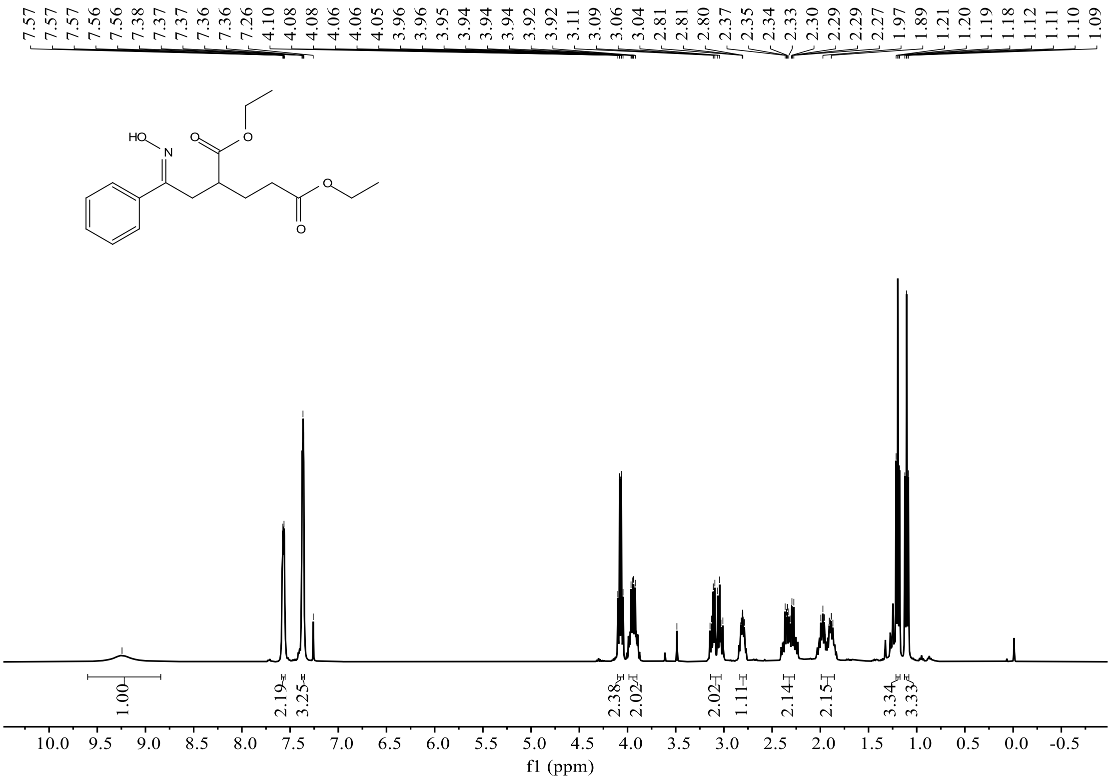
^{1}H NMR spectra of 3y (400 MHz, CDCl$_3$)



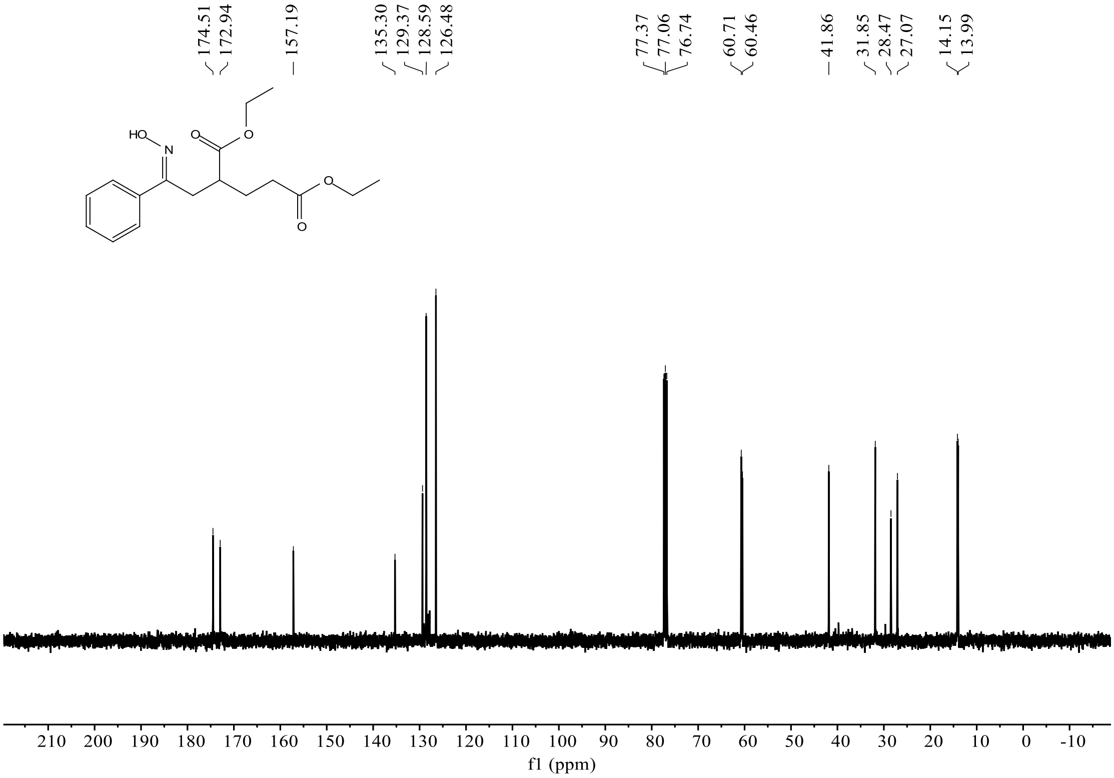
^{13}C NMR spectra of 3y (100 MHz, CDCl$_3$)



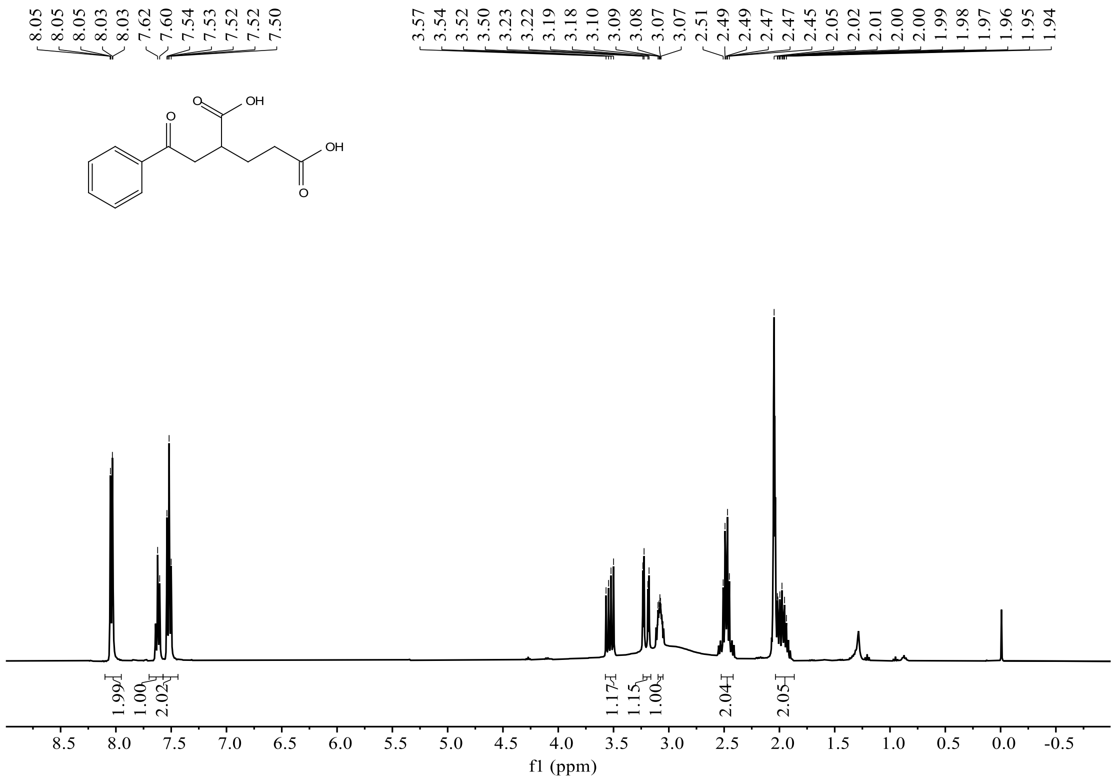
^{1}H NMR spectra of 4a (400 MHz, $CDCl_3$)



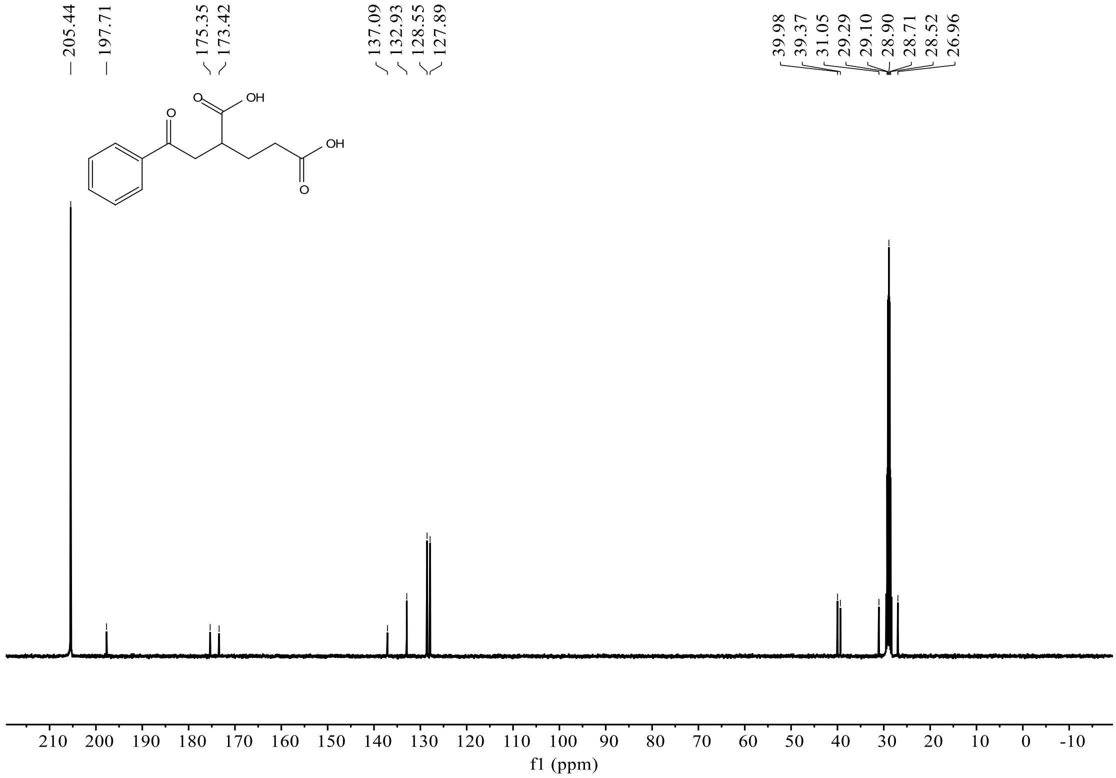
^{13}C NMR spectra of 4a (100 MHz, $CDCl_3$)



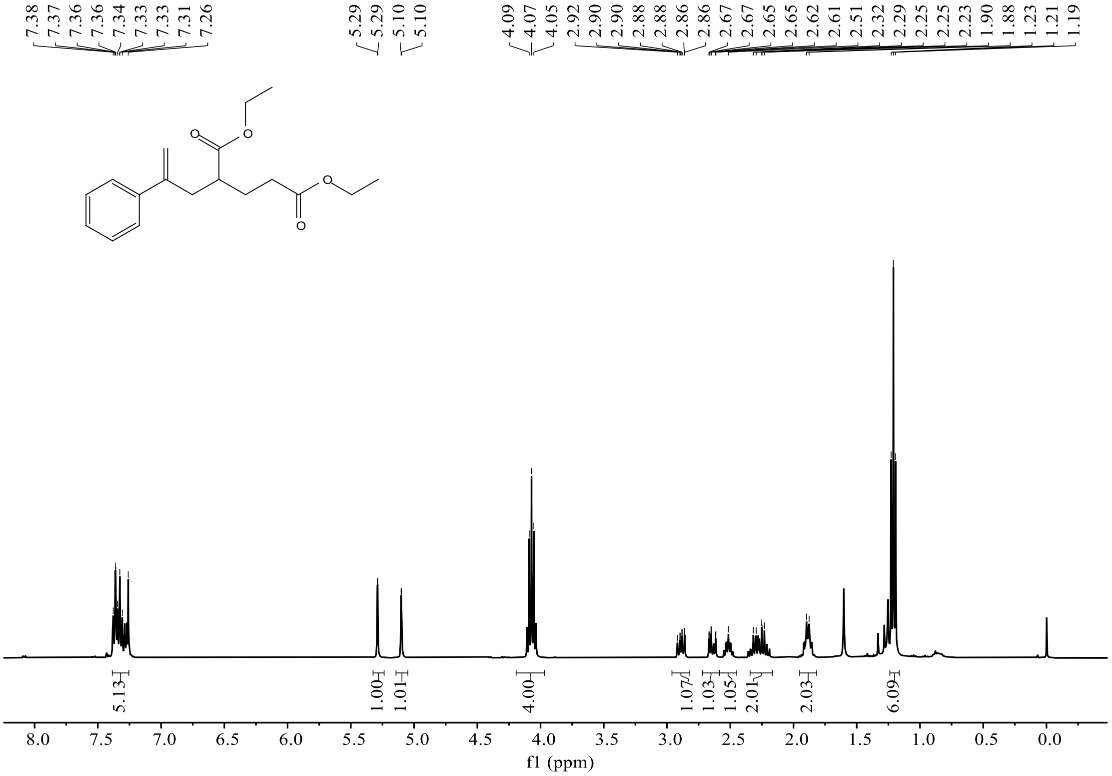
^{1}H NMR spectra of 4b (400 MHz, Acetone-d_6)



^{13}C NMR spectra of 4b (100 MHz, Acetone-d_6)



^{1}H NMR spectra of 4c (400 MHz, CDCl$_3$)



^{13}C NMR spectra of 4c (100 MHz, CDCl$_3$)