Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

A Visible Light Driven Direct Synthesis of Industrially Relevant Glutaric Acid Diesters from Aldehydes

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1. General information:

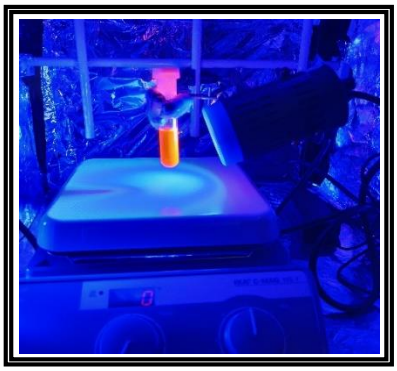
Unless otherwise noted, all the starting materials and reagents were purchased from commercial suppliers (Aldrich, TCI, and Alfa Aesar) and were used without any further purification. Thin-layer chromatography (TLC) was performed using silica gel 60 GF_{254} pre-coated aluminium backed plates (2.5 mm). Visualization was accomplished by the irradiation with UV light at 254 nm. The column chromatography was performed using silica gel (100–200 mesh) eluting with petroleum ether and ethyl acetate. The NMR spectra were recorded using tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 100 MHz (Bruker and Jeol) unless otherwise noted. Chemical shifts (δ) are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.16 ppm) for $^{13}C\{^{1}H\}$ NMR spectroscopy. For ^{1}H NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (*J*) are given in Hz and integration. $^{13}C\{^{1}H\}$ NMR spectra were recorded with complete proton decoupling. ^{19}F NMR spectra were recorded at 377 MHz. Mass samples were analyzed by high-resolution mass spectrometry (HRMS)-ESI TOF. Fluorescence spectra were recorded on Fluoromax-4 spectrofluorometer (Horiba Scientific, U.S.A.). UV absorption was performed using Shimadzu, UV-2600 UV spectrophotometer. All photocatalytic reactions were performed under blue LEDs (Kessil PR160L series Blue LEDs, and IBRA Pure 60 W Blue LED Flood Light, IP Rating: IP66).

2. General procedure for the synthesis of 3 (GP1):

To an oven dried 10 mL crimp capped vial charged with magnetic stir bar was added aldehyde **2** (2 mmol, 2 equiv.), Eosin Y (5 mol%) and DIPEA (2 mmol, 2 equiv.) at room temperature under argon atmosphere. The vial was purged again with argon and sealed with aluminum crimp cap using a crimper. Then anhydrous DMSO (3 mL) was added under argon. Then the reaction mixture was degasified using argon for 30 minutes under constant purging and monitoring. After the degasification acrylates **1** (1 mmol, 1 equiv.) was added under inert atmosphere. Then the reaction mixture was irradiated with 456 nm Kessil Lamp (Blue LED) with 75% intensity (the temperature turns around 60 °C measured by IR-thermometer, by keeping the fan switch off/ No other external heating source was applied) stirred for 24 h. After the completion of the reaction (monitored by TLC), 10 mL of water was added to the reaction mixture and was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were evaporated under

reduced pressure and the crude residue was purified by using column chromatography (Silica gel 100–200 mesh size, using ethyl acetate/Pet-Ether as eluent system).

Reaction setup under visible light (Kessil lamp)



3. General procedure for the synthesis of 3 under sunlight

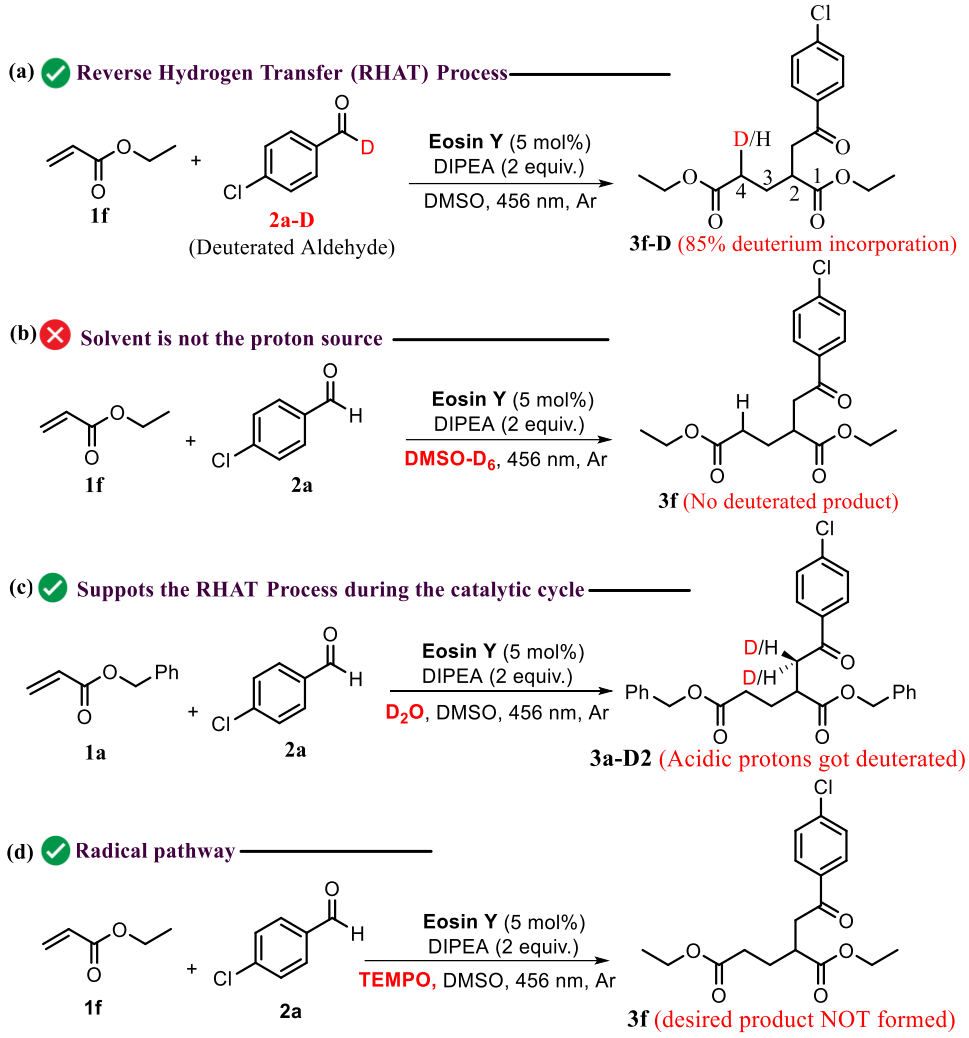
To an oven dried 10 mL reaction tube charged with magnetic stir bar was added aldehyde **2** (2 mmol, 2 equiv.), Eosin Y (5 mol%) and DIPEA (2 mmol, 2 equiv.) at room temperature under argon atmosphere. The reaction tube was purged again with argon and sealed with rubber septum. Then anhydrous DMSO (3 mL) was added under argon. Then the reaction mixture was degasified using argon for 30 minutes under constant purging and monitoring. After the degasification acrylates **1** (1 mmol, 1 equiv.) was added under inert atmosphere. Then the reaction mixture was kept under sunlight (around 40 $^{\circ}$C) for 24 h (8 h x 3 days). After the completion of the reaction (monitored by TLC), 10 mL of water was added to the reaction mixture and was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were evaporated under reduced pressure and the crude residue was purified by using column chromatography (Silica gel 100–200 mesh size, using ethyl acetate/Pet-Ether as eluent system).

Reaction setup under sunlight

Atmospheric Temperature (40 ^{o}C)

4. Controlled Experiments:

4.1 A set of Control Experiments

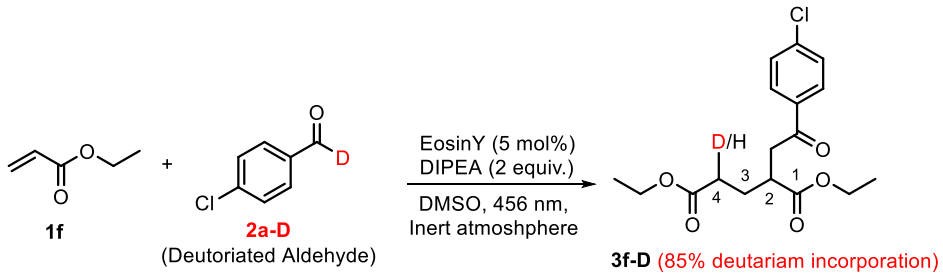


Scheme S1. Control Experiments

4.2 Procedure for the preparation of 3f-D:

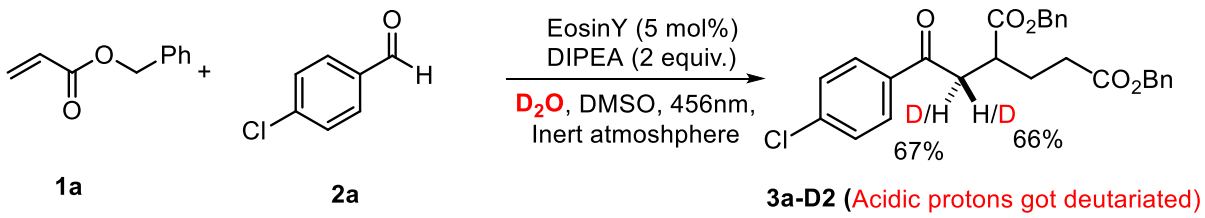
To an oven dried 10 mL crimp cap vial charged with magnetic stir bar was added deuterated 4-chlorobenzaldehyde **2a-D**[1] (2 mmol, 2 equiv., 283 mg), Eosin Y (5 mol%) and DIPEA (2 mmol, 2 equiv.) at room temperature under argon atmosphere. The vial was purged with argon and sealed with an aluminium crimp cap using a crimper. Then anhydrous DMSO (3 mL) was added under argon. Then the reaction mixture was degasified using argon for 30 minutes under constant purging and monitoring. After the degasification ethyl acrylate **1f** (1 mmol, 1 equiv., 100 mg) was added under inert atmosphere. The reaction mixture was irradiated with 456 nm Kessil lamp (Blue LED) with 75% intensity (the temperature turns around 60 ˚C-external temperature-measured by IR-

thermometer, by keeping the fan switched off) stirred for 24 h. After completion of the reaction (monitored by TLC), 10 mL of water was added to the reaction mixture and was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were evaporated under reduced pressure and the crude residue was purified by using column chromatography (Silica gel 100–200 mesh size, using ethyl acetate/Petroleum ether as eluent system) to afford the desired product **3f-D** in 65% yield and the deuterium incorporation was observed in C4-carbon of **3f-D** with 85% yield.



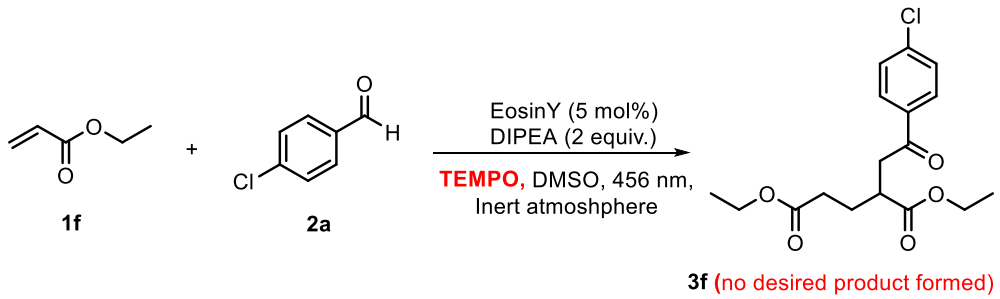
4.3 Procedure for the preparation of 3a-D_2:

To an oven dried 10 mL crimp cap vial charged with magnetic stir bar was added 4-chlorobenzaldehyde **2a** (2 mmol, 2 equiv., 281 mg), Eosin Y (5 mol%), DIPEA (2 mmol, 2 equiv.) and D_2O (300 µL) at room temperature under argon atmosphere. The vial was purged again with argon and then sealed with aluminium crimp cap using a crimper. Then anhydrous DMSO (3 mL) was added under argon. Then the reaction mixture was degasified using argon for 30 minutes under constant purging and monitoring. After the degasification, the benzyl acrylate **1a** (1 mmol, 1 equiv., 162 mg) was added under inert atmosphere. Then the reaction mixture was irradiated with 456 nm Kessil Lamp (Blue LED) with 75% intensity (the temperature turns around 60 °C-external temperature-measured by IR-thermometer, by keeping the fan switched off) and stirred for 24 h. After completion of the reaction (monitored by TLC), 10 mL of water was added to the reaction mixture and was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were evaporated under reduced pressure and the crude residue was purified over column chromatography (Silica gel 100–200 mesh size, using ethyl acetate/Petroleum ether as an eluent system) to afford the desired product **3a-D_2** in 45%.



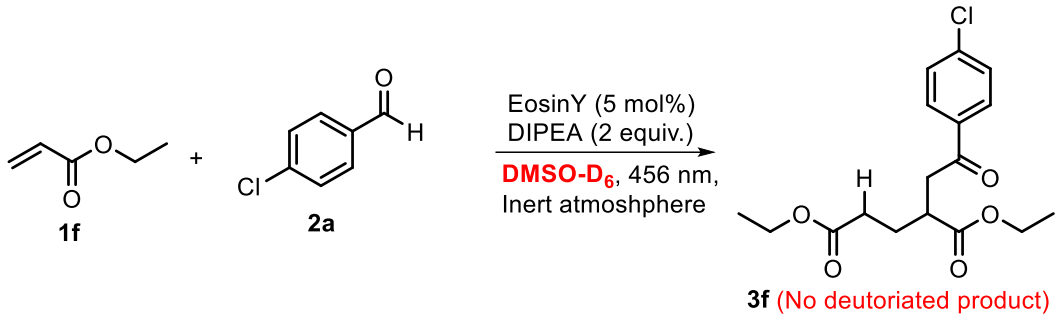
4.4 Procedure for the reaction using TEMPO:

To an oven dried 10 mL crimp cap vial charged with magnetic stir bar was added aldehyde **2a** (2 mmol, 2 equiv., 281 mg), Eosin Y (5 mol%) and DIPEA (2 mmol, 2 equiv.) and TEMPO (2 mmol, 2 equiv.,) at room temperature under argon atmosphere. The vial was then purged again with argon and sealed with aluminium crimp cap using a crimper. Then anhydrous DMSO (3 mL) was added under argon atmosphere. Then the reaction mixture was degasified again using argon for 30 minutes under constant purging and monitoring. After the degasification acrylate **1f** (1 mmol, 1 equiv., 100 mg) was added dropwise under inert atmosphere. Then the reaction mixture was irradiated with 456 nm Kessil lamp (Blue LED) with 75% (the temperature turns around 60 °C-external temperature-measured by IR-thermometer, by keeping the fan switched off) and stirred for 24 h. Even after prolonged reaction time, the compound **3f** was not formed.



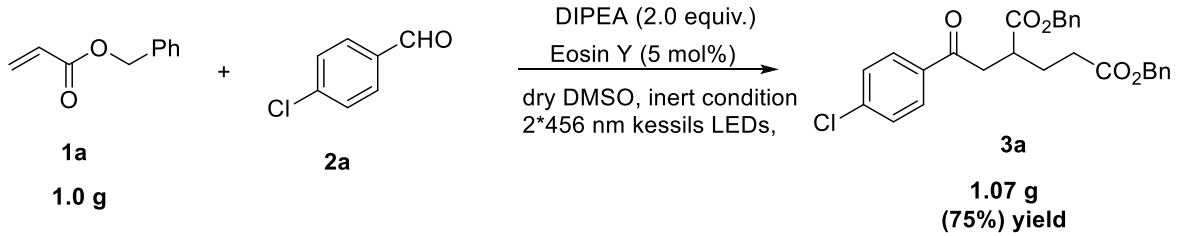
4.5 Procedure for the reaction using DMSO-D_6:

To an oven dried 10 mL crimp cap vial charged with magnetic stir bar was added 4-chlorobenzaldehyde **2a** (2 mmol, 2 equiv., 281 mg), Eosin Y (5 mol%) and DIPEA (2 mmol, 2 equiv.) at room temperature under argon atmosphere. The vial was purged again with argon and sealed with aluminium crimp cap using a crimper. Then anhydrous DMSO-D_6 (3 mL) was added under argon atmosphere. Then the reaction mixture was degasified using argon for 30 minutes under constant monitoring. After the degasification ethyl acrylate **1f** (1 mmol, 1 equiv., 100 mg) was added under inert atmosphere. Then the reaction mixture was irradiated with 456 nm Kessil lamp (Blue LED) with 75% intensity (the temperature turns around 60 °C-external temperature-measured by IR-thermometer, by keeping the fan switched off) stirred for 24 h. After completion of the reaction (monitored by TLC), 10 mL of water was added to the reaction mixture and was extracted with ethyl acetate (3 × 10 mL). The combined organic extract was evaporated under reduced pressure and the crude residue was purified by using column chromatography (Silica gel 100–200 mesh size, using ethyl acetate/Petroleum ether as an eluent system) to afford the product **3f** in 68% yield and the deuterated incorporation was not observed in the product **3f**.



5. Procedure for the gram scale synthesis of 3a:

To an oven dried 100 mL round bottomed flask aldehyde **2a** (12.33 mmol, 2 equiv., 1.73 g), Eosin Y (5 mol%) and DIPEA (12.33 mmol, 2 equiv.) was added at room temperature under argon atmosphere. The round bottomed flask equipped with rubber septum was flushed with argon (three times). Then anhydrous DMSO (30 mL) was added under argon. Then the reaction mixture was degasified using argon for 1 h under constant purging and monitoring. After the degasification benzyl acrylate **1a** (6.17 mmol, 1 equiv., 1 g) was added under inert atmosphere. Then the reaction mixture was irradiated with 2 * 456 nm Kessil Lamps with 75% intensity (the temperature turns around 60 °C-external temperature-measured by IR-thermometer, by keeping the fan switched off) and stirred for 36 h. After the completion of the reaction (monitored by TLC), 100 mL of water was added to the reaction mixture and was extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were evaporated under reduced pressure and the crude residue was purified by using column chromatography over silica gel (100–200 mesh size) using ethyl acetate/petroleum ether as an eluent system).



6. Mechanistic study:

6.1 Fluorescence Quenching Experiment and Stern-Volmer plot:

Fluorescence quenching experiment was carried out using Fluorescence spectrophotometer, using 1.0 µM solution of Eosin Y in dry DMSO and variable concentrations of (2 to 5 mM) of 4-chlorobenzaldehyde **2a** in dry DMSO solvent. The sample was prepared in 3 mL quartz cuvette

and the flask was degasified with Argon before the spectra were recorded. The quenching plot of the experiments are given below in Figure 1.1.

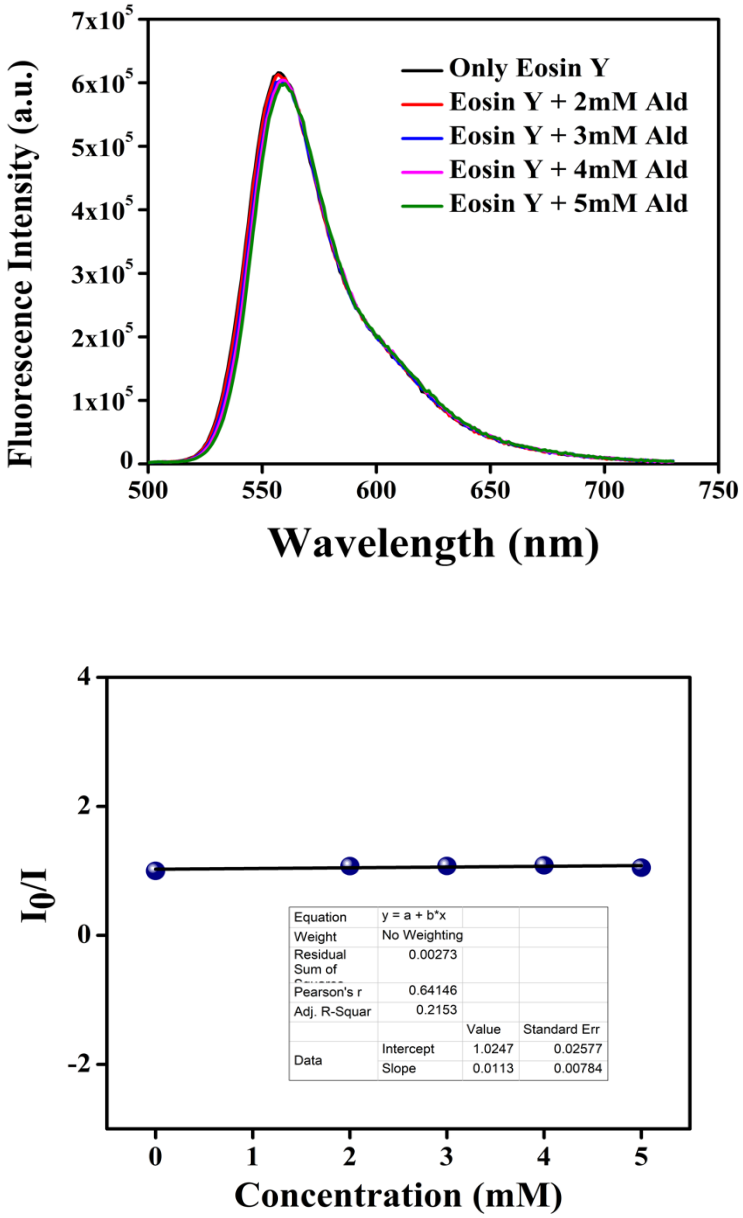


Figure 1.1. Fluorescence quenching experiments and Stern-Volmer plot of Eosin Y in presence of aldehyde **2a**

Fluorescence quenching experiment was carried out using Fluorescence spectrophotometer, using 1.0 µM solution of Eosin Y in dry DMSO and variable concentrations of (2 to 5 mM) of ethyl acrylate **1f** in dry DMSO solvent. The sample was prepared in a 3 mL quartz cuvette and

the flask was degasified with Argon before the spectra were recorded. The quenching plot of the experiments are given below.

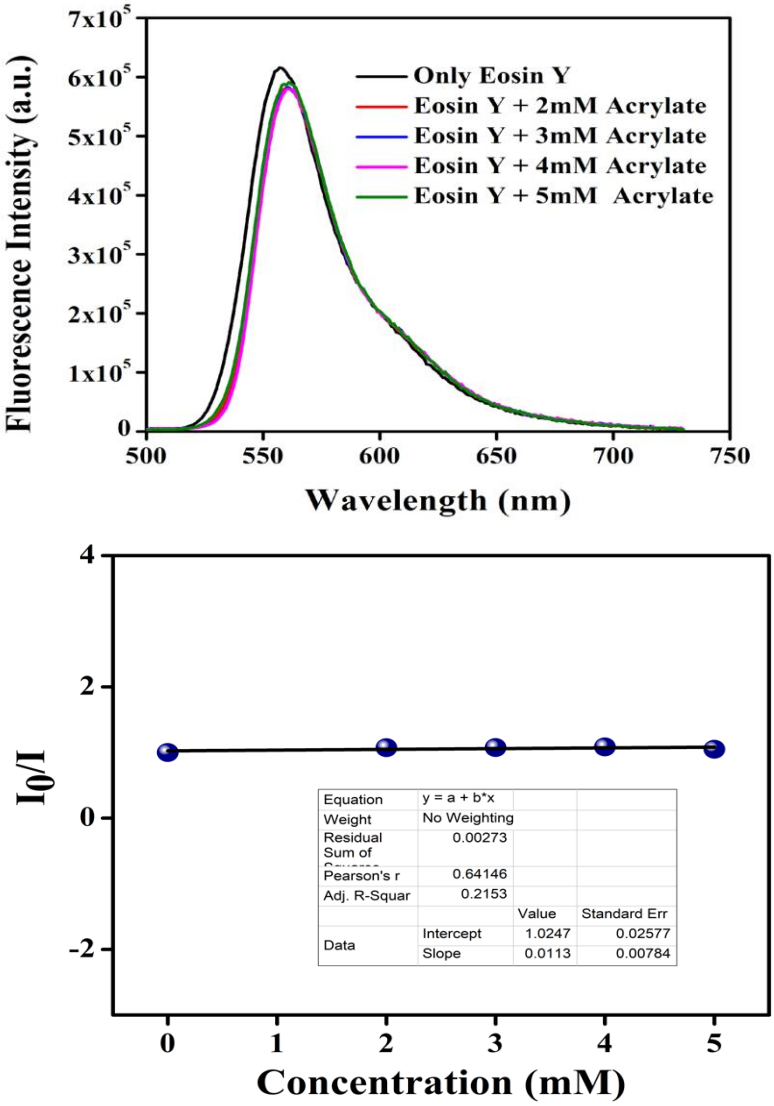


Figure 1.2. Fluorescence quenching experiments and Stern-Volmer plot of Eosin Y in presence of ethyl acrylate **1f**

Fluorescence quenching experiment was carried out using Fluorescence spectrophotometer, using 1.0 µM solution of Eosin Y in dry DMSO and variable concentrations of (2 to 5 mM) of diisopropyl ethylamine (DIPEA) in dry DMSO solvent. The sample was prepared in 3 mL quartz cuvette and the flask was degasified with Argon before the spectra were recorded. The quenching plot of the experiments are given below.

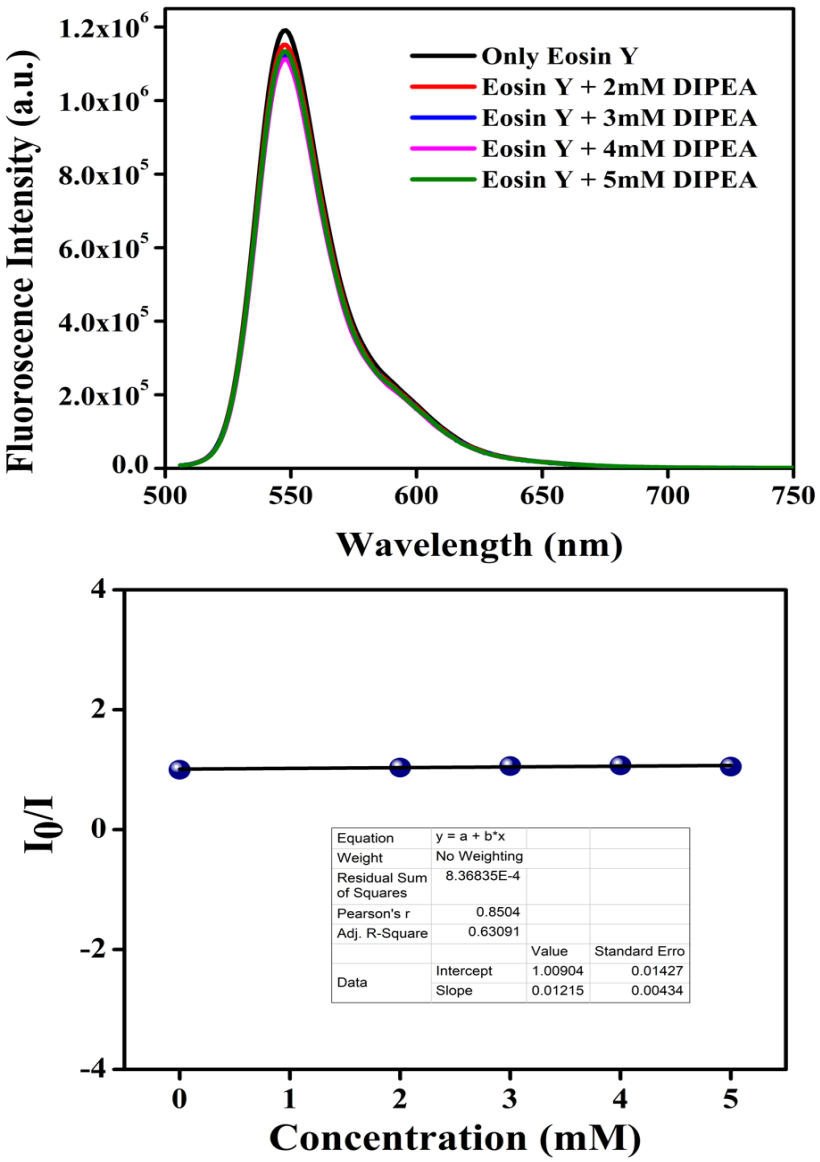


Figure 1.3. Fluorescence quenching experiments and Stern-Volmer plot of Eosin Y in presence of DIPEA

Fluorescence quenching experiment was carried out using Fluorescence spectrophotometer, using 1.0 µM solution of Eosin Y in dry DMSO and variable concentrations of (2 to 5 mM) each of diisopropyl ethylamine (DIPEA) + 4-Chlorobenzaldehyde **2a** in dry DMSO solvent. The sample was prepared in a 3 mL quartz cuvette and the flask was degasified with Argon before the spectra were recorded. The quenching plot of the experiments are given below.

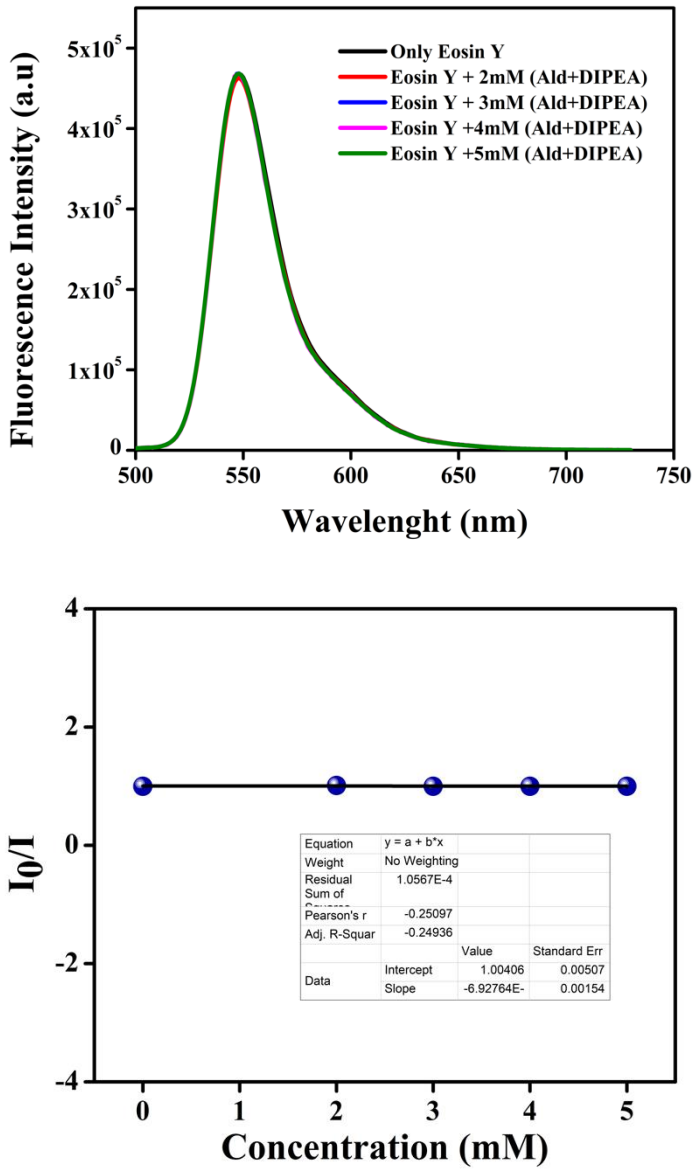


Figure 1.4. Fluorescence quenching experiments and Stern-Volmer plot of Eosin Y in presence of 4-cholorobenzaldehyde + DIPEA

The fluorescence intensity of the Eosin Y was not quenched by 4-chlorobenzaldehyde **2a** or ethyl acrylate **1f** or by DIPEA. Also, fluorescence intensity of Eosin Y was not quenched in presence both aldehyde **2a** and DIPEA. Based on the Stern-Volmer plot data, possibility of PCET (Proton Coupled Electron Transfer) process during the course of reaction pathway has been ruled out (**Figure 1**). The fluorescence quenching experiment and the Stern Volmer plot clearly suggested that neither SET process nor the PCET process is involved during the course of the reaction.

6.2 UV-Visible absorption of Eosin Y and reaction mixture:

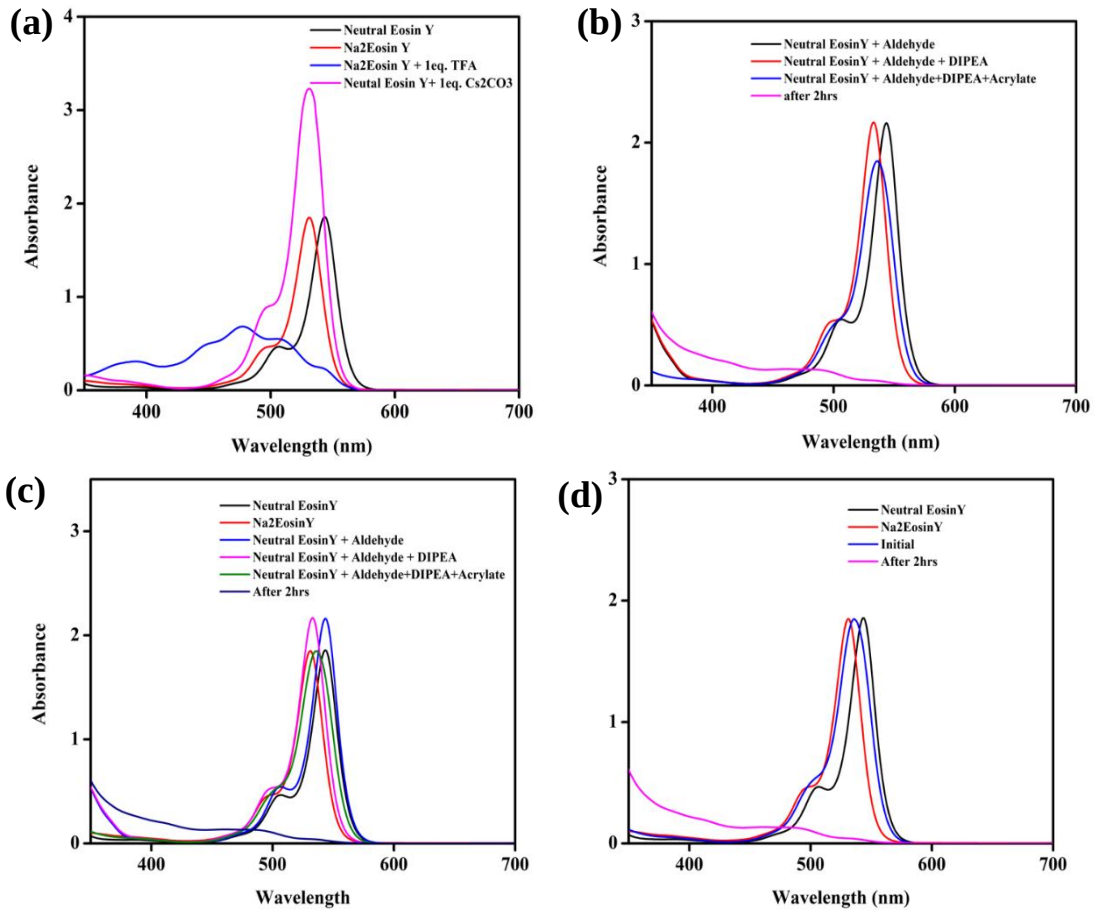


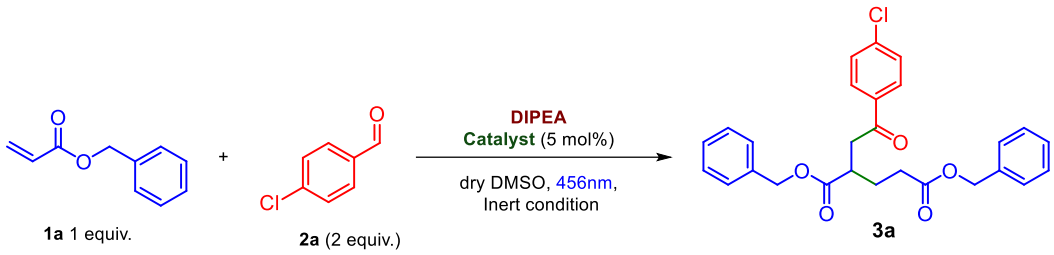
Figure 2. (a) UV-Vis absorption of different form of Eosin Y in DMSO. 20µM neutral Eosin Y, 20µM Na2Eosin Y, 20µM Na2Eosin Y+ 20µM TFA, 20µM neutral Eosin Y + 20µM Cs_2CO_3. **(b)** 20µM neutral Eosin Y + 1 equiv. 4-chloro benzaldehyde, 20µM neutral EosinY + 1 equiv. 4-chloro benzaldehyde + 1 equiv. DIPEA, 20µM neutral Eosin Y+ 1 equiv. 4-chlorobenzaldehyde aldehyde + 1 equiv. DIPEA + 1equiv. ethyl acrylate, after 2 hr of the reaction, in DMSO solvent. **(c)** 20µM neutral Eosin Y, 20µM Na2EosinY, 20µM neutral Eosin Y + 1 equiv. 4-chloro benzaldehyde, 20 µM neutral Eosin Y + 1 equiv. 4-chloro benzaldehyde+ 1equiv. DIPEA, 20 µM neutral Eosin Y + 1 equiv. 4-chlorobenzaldehyde + 1 eq. DIPEA + 1 equiv. Ethyl Acrylate **1f**, after 2 h of the reaction, in DMSO solvent. **(d)** 20 µM neutral Eosin Y, 20 µM Na2EosinY, absorption was recorded before the irradiation of light (reaction at 0 hr). Later, the absorption was recorded after 2 hr of the reaction.

Neutral Eosin Y in DMSO has a maximum absorption at 543 nm. Na_2Eosin Y in DMSO shows maximum absorption at 531 nm. 20μM neutral EosinY + 20μM Cs_2CO_3 in DMSO showed maximum absorption at 531 nm. 20μM Na_2EosinY+ 20 μM TFA in DMSO has maximum absorption at 542 nm. 20μM neutral Eosin Y + 1 equiv. 4-chloro benzaldehyde shows at maximum absorption at 543 nm. 20μM neutral EosinY + 1 equiv. 4-chloro benzaldehyde + 1equiv. DIPEA has a maximum absorption at 533nm. 20 μM neutral EosinY + 1equiv. 4-chloro benzaldehyde + 1 eq. DIPEA + 1 equiv. ethyl acrylate **1f** showed the maximum absorption at 535 nm.

At the beginning the reaction mixture shows maximum absorption at 536 nm. After 2 h of reaction, an absorption hump was observed at 530 nm. It showed that the reaction mixture has maximum absorption nearly equal to the absorption of Na_2Eosin Y and this proved that in the reaction mixture there must be a dianionic form of Eosin Y which is acting as the active form of the catalyst in the catalytic cycle.

6.3 pH study of the reaction mixture during the course of the reaction:

6.3.1 Table 1: pH of different reaction conditions:



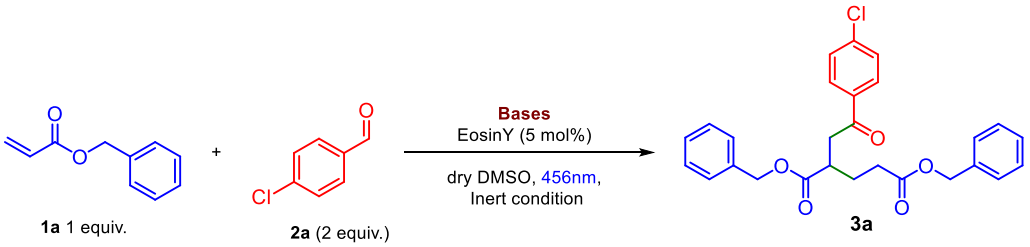
Entry	Reaction condition	pH	Yield (%)
1.	Initially, reaction mixture without DIPEA using Eosin Y	4.33	0
2.	After completion of the reaction, reaction mixture without DIPEA using Eosin Y	2.2	NR
3.	Initially, reaction mixture without DIPEA using Na_2Eosin Y	5.37	0
4.	After completion of the reaction, reaction mixture without DIPEA using Na_2Eosin Y	3.6	10
5.	Initially, reaction mixture with 1 equiv. DIPEA using Eosin Y	7.33	0
6.	After completion of the reaction, reaction mixture with 1 equiv. DIPEA using Eosin Y	4.9	40
7.	Initially, reaction mixture with 1 equiv. DIPEA using Na_2Eosin Y	8.84	0
8.	After completion of the reaction, reaction mixture with 1 equiv. DIPEA using Na_2Eosin Y	5.2	41
9.	Initially, reaction mixture with 2 equiv. DIPEA using Eosin Y	9.25	0
10.	After completion of the reaction, reaction mixture with 2 equiv. DIPEA using Eosin Y	7.2	80
11.	Initially, reaction mixture with 2 equiv. DIPEA using Na_2Eosin Y	8.56	0
12.	After completion of the reaction, reaction mixture with 2 equiv. DIPEA using Na_2Eosin Y	7.1	65

We observed that in the absence of DIPEA, Na_2Eosin Y afforded the product **3a** in 10% yield (Table 1, Entry 4, Page S14). While the reaction in the absence of DIPEA and neutral Eosin Y didn't proceed at all (Table 1, Entry 2, Page S14). Based on the pH values (measured using pH meter), we observed that the during the course of the transformation the pH of the reaction medium is getting lowered. This might be probably due to the hydrogen atom abstraction during

the catalytic cycle. Around pH 7 the maximum yield of the product **3a** was formed (Table 1, Entry 10,12, page S14) as compared to the other conditions having different pH values (see Table 1). Based on these results, we concluded that the DIPEA is essentially maintaining the pH of the reaction to keep the active dianionic form available for the catalytic cycle.

7. Optimisation of The Reaction:

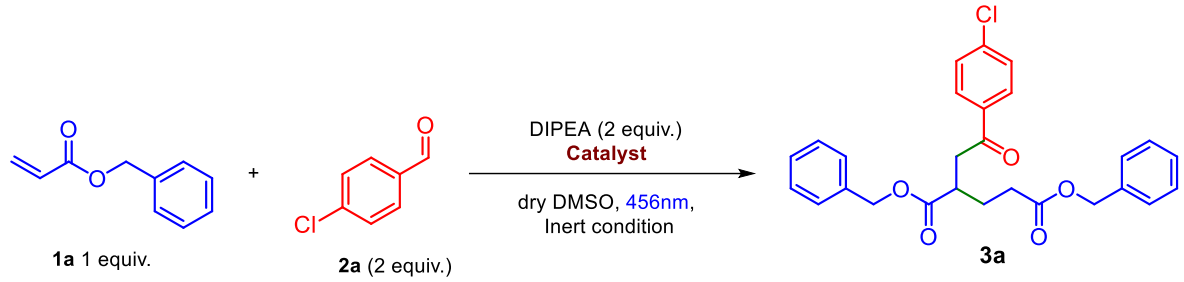
7.1 Table S1: Screening of Bases[a]



Entry	Bases	Yield (%)[b]
1.	DIPEA	80
2.	Triethylamine (TEA)	59
3.	Diisopropyl amine (DIPA)	20
4.	K_2CO_3	<5
5.	Cs_2CO_3	7
6.	DABCO	NR
7.	DBU	40
8.	DMAP	NR
9.	HCO_2Na	Trace

Reaction conditions: [a] Benzyl acrylate **1a** (1 mmol), 4-chlorobenzaldehyde **2**a (2 mmol), Base (2 mmol), Eosin Y (5 mol%), using a single 456 nm Kessil lamp (Blue LED) under inert atmosphere in dry DMSO (temperature around 60 ^{o}C, keeping fan switched off). [b] Yields are calculated after purification using column chromatography.

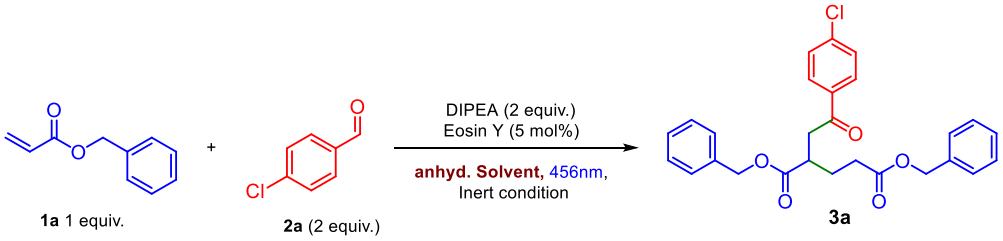
7.2. Table S2: Screening of Catalyst[a]



Entry	Catalyst	Yield (%)[b]
1.	Eosin Y	80
2.	Rhodamine 6G	NR
3.	Ru Catalyst	NR
4.	Ir Catalyst	Trace
5	Rose Bengal	55
6	Na_2EosinY	60
7	9-Fluorenone,	Trace
8	Thioxanthen-9-one	50
9	9H-Xanthen-9-one	10
10	Anthracene-9,10-dione	NR
11	Fluorescein	45

Reaction conditions: [a] Benzyl acrylate **1a** (1 mmol), 4-chloro benzaldehyde **2a** (2 mmol), DIPEA (2 mmol), Catalyst (5 mol%), using a single 456 nm Kessil LED under inert atmosphere in dry DMSO (temperature around 60 ^{o}C, keeping fan switched off). [b] Yields are calculated after purification using column chromatography.

7.3. Table S3: Screening of Solvents[a]



Entry.	Solvents	Yield(%)[b]
1.	DMSO	80
2.	Acetonitrile	60
3.	DMF	62
4.	Acetone	40
5.	THF	43
6.	*Tert*-butanol	41

Reaction conditions: [a] Benzyl acrylate **1a** (1 mmol), 4-chloro benzaldehyde **2a** (2 mmol), DIPEA (2 mmol), Eosin Y (5 mol%), using a single 456 nm Kessil LED under inert atmosphere in dry solvents (temperature around 60 ^{o}C, keeping fan switched off). [b] Yields are calculated after purification using column chromatography.

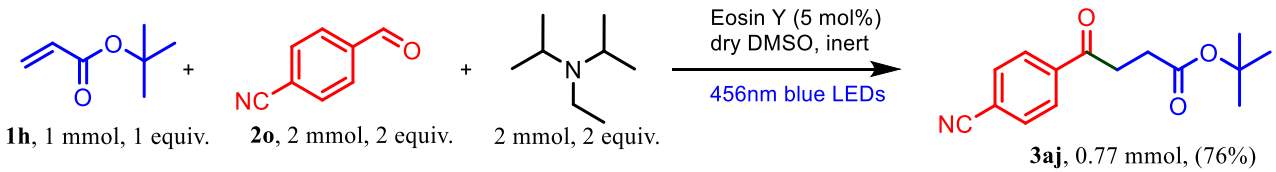
7.4. Table S4: Screening of different Blue LEDs[a]

Entry	Lights	Temperature	Yield(%)[b]
1	525 nm (100% intensity)	40 °C	40
2	467 nm (100% intensity)	55 °C	42
3	456 nm (100% intensity)	70 °C	52
4	440 nm (100% intensity)	80 °C	40
5	456 nm (75% intensity)	60 °C	80
6	456 nm (50% intensity)	50 °C	55
7	456 nm (25% intensity)	40 °C	35
8[c]	2 * 456 nm (75% intensity)	25 °C	20
9[c]	2 * 456 nm (100% intensity)	35 °C	61
10[d]	60 W Blue LEDs	60 °C	76

Reaction conditions: [a] Benzyl acrylate **1a** (1 mmol), 4-chloro benzaldehyde **2a** (2 mmol), DIPEA (2 mmol), Eosin Y (5 mol%), using a single Kessil Lamp (Blue LED) under inert atmosphere in dry DMSO keeping the fan switched off. [b] Yields are calculated after purification using column chromatography. [c] used 2 Kessil LED lamps with fan switched on. [d] 60 W Blue LED has been used with external temperature 60 °C, instead of Kessils light.

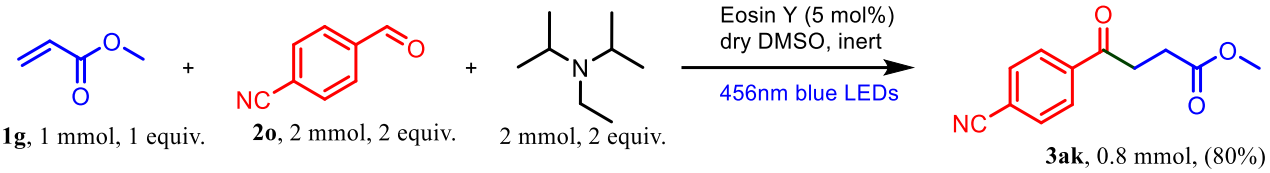
8. Undesired transformation:

It is important to note that surprisingly the reaction of ^{t}butyl acrylate **1h** and 4-cyano benzaldehyde **2o** afforded the unexpected γ-keto ester **3aj** instead of the substituted glutaric acid diester as a final product. The compound **3aj** was obtained as off-white solid following the general procedure (GP1) (199 mg, 76% yield), R_f = 0.25 (Petroleum ether/EtOAc 70:30).



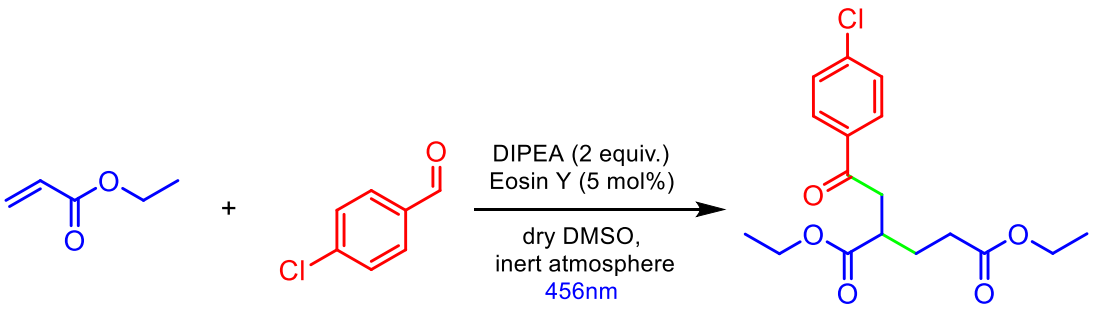
1h, 1 mmol, 1 equiv. **2o**, 2 mmol, 2 equiv. 2 mmol, 2 equiv. **3aj**, 0.77 mmol, (76%)

The reaction of **1g** and **2o** following the general procedure (GP1) afforded the corresponding compound γ-keto ester **3ak** as off-white solid (176 mg, 80% yield), R_f = 0.2 (Petroleum ether/EtOAc 70:30).



1g, 1 mmol, 1 equiv. **2o**, 2 mmol, 2 equiv. 2 mmol, 2 equiv. **3ak**, 0.8 mmol, (80%)

9. Light Switch ON/OFF Experiment:



1f, 1 mmol **2a**, 2 mmol **3f**

In order to understand and evaluate the impact of light and heat on the outcome of the yield of the product **3f** and also examine whether or not the reaction is proceeding via radical chain mechanism Light ON/OFF experiment has been carried out.

To an oven dried 10 mL crimp cap vial charged with magnetic stir bar was added 4-chloro benzaldehyde **2a** (2 mmol, 2 equiv.), Eosin Y (5 mol%) and DIPEA (2 mmol, 2 equiv.) at room temperature under argon atmosphere. The vial was sealed with aluminium crimp cap using a

crimper and was purged again with argon. Then anhydrous DMSO (3 mL) was added under argon. The reaction mixture was degasified using argon for 30 minutes under constant purging and monitoring. After the degasification ethyl acrylate **1f** (1 mmol, 1 equiv.) was added under inert atmosphere. A total of 9 vials containing the above-mentioned reactants were set up. All the 9 vials were irradiated with 456 nm Kessil LED with 75% intensity (the temperature turns around 60 °C-external temperature-measured by IR-thermometer, by keeping the fan switched off).

After stirring the reaction mixture for 2 h, one of the reaction vials was taken out and subjected to purification (following the General Procedure-1, using column chromatography) to calculate the yield (see Fig. 3). While the rest of 8 reaction vials were stirred under dark for next 2 h. After the stirring for a total of 4 h (with and without light), one more vial was taken out and subjected to purification (following the General Procedure-1, using column chromatography) to calculate the yield. While the remaining 7 reaction vials were kept under irradiation again for next 2 h and we followed the same procedure of switching off/on LED for remaining all the vials of an interval 2 h over a period of total 18 h for the last vial. The yield for all the reaction vials were calculated after the purification using column chromatography. The detailed results are given below in a bar diagram.

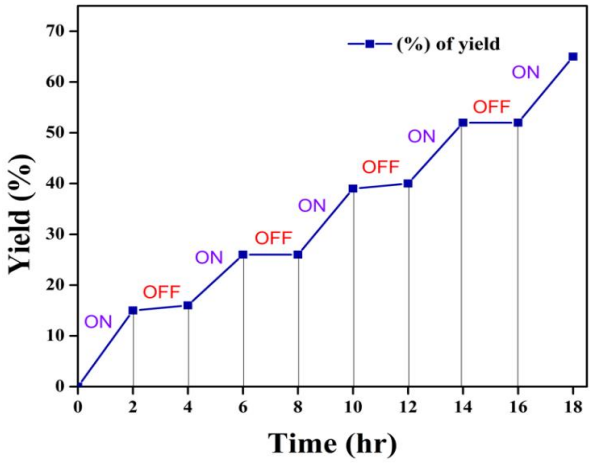


Figure 3: Light Switch ON/OFF experiment

Based on the above results, we concluded that the reaction does not proceed via radical-chain mechanism and in order to support the observation further we calculated the quantum yield of 3f.

10. Quantum yield calculation of 3f:

a) Determination of quantum yield by standard ferrioxalate actinometry

Determination of the light intensity at 450 nm: Yoon's procedure was followed to calculate the photon flux of the spectrophotometer by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored under dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 60 seconds at λ = 456 nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 hour to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using Eq. (1).

$$\text{Mol } Fe^{2+} = \frac{V.\Delta A}{l.\varepsilon} \qquad \text{Eq.(1)}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol–1 cm–1). The photon flux can be calculated using Eq (2)

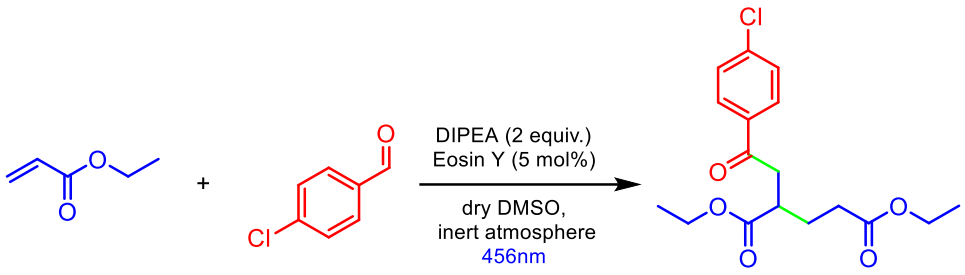
$$\text{Photon flux} = \frac{mol\ Fe^{2+}}{\phi.t.f} \qquad \text{Eq.(2)}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 450 nm), t is the time (60 seconds), and f is the fraction of light absorbed at λ = 450 nm (0.8979, vide infra). The photon flux was calculated (average of three experiments) to be 1.55×10^{-9} einstein s^{-1}.

$$\text{Mol } Fe^{2+} = \frac{0.00235\ L.(1.730-1.332)}{1.00\ cm.11100\ Lcm^{-1}mol^{-1}} = 8.426*10^{-8}\ \text{mol}$$

$$\text{Proton flux} = \frac{8.426*10^{-8}\ mol}{1.01.60s.0.8979} = 1.55*10^{-9}\ \text{einstein } s^{-1}$$

Determination of quantum yield:



The sample was stirred and irradiated (λ = 456 nm, slit width = 10.0 nm) for 14400 s (4 h). After irradiation, the solvent was removed. The yield of product formed was determined as 5% by crude ^{1}H NMR based on a 1,3,5-trimethoxylbenzene standard. The quantum yield was determined using Eq. (3). Essentially all incident light (f > 0.999, vide infra) is absorbed by the eosin Y at the reaction conditions described above. Φ (5% NMR yield of **3f**) = 0.56.

$$\phi = \frac{mol\ product}{flux.t.f} \qquad \text{Eq. (3)}$$

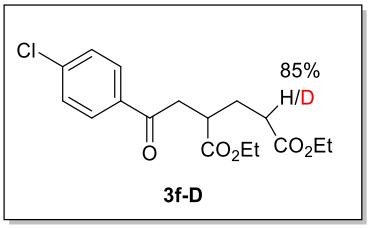
$$= \frac{12.47*10^{-6}}{1.55*10^{-9}\ einstein\ s^{-1}.14400s.1} = \mathbf{0.56}$$

Reference:

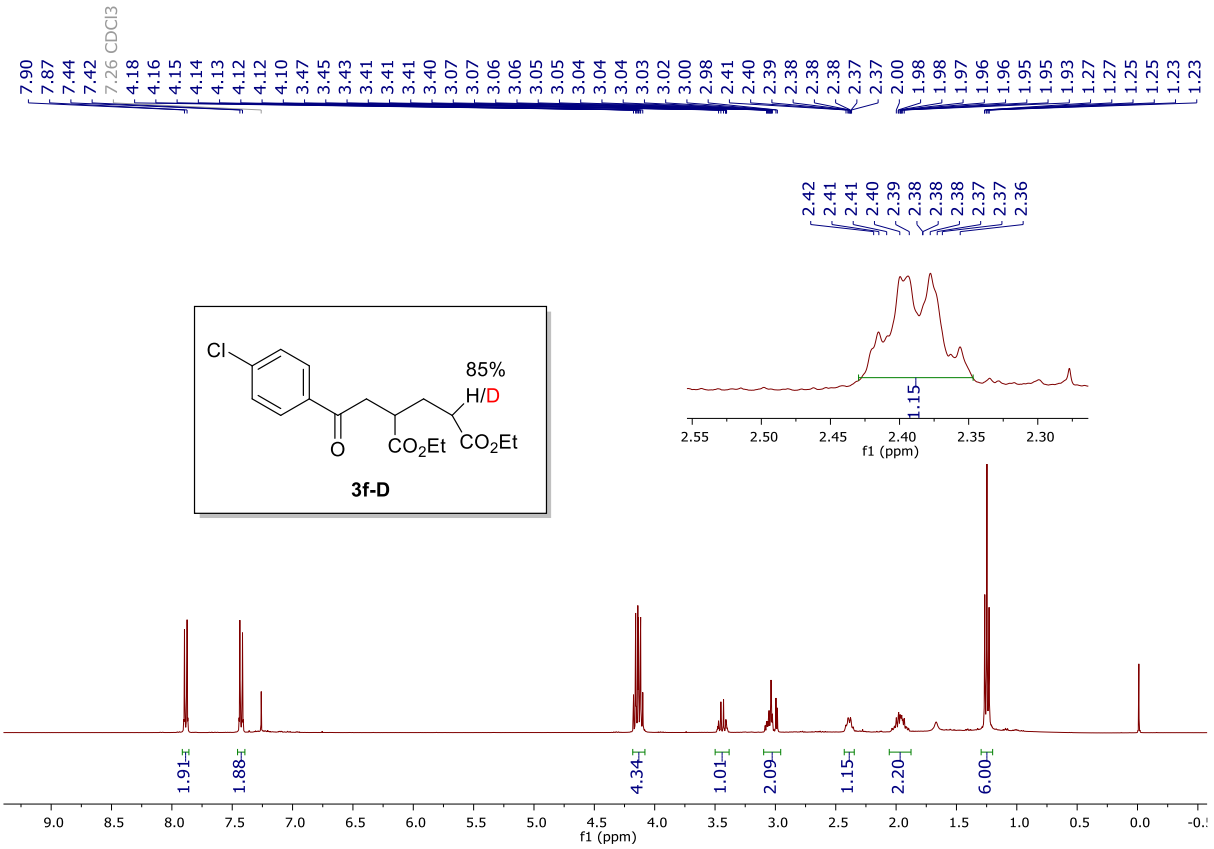
1. Mahesh, S. K.; Nanubolu, J. B.; Sudhakar, G. Tandem Addition/Electrocyclization/Benzylation of Alkyl Aryl-1,3-dienes and Aromatic Aldehydes: Access to Highly Substituted Indenes. *J. Org. Chem*. **2019**, *84*, 7815−7828.

11. NMR data of the compounds obtained through Control experiments:

11.1. NMR data of reaction using deuterated chlorobenzaldehyde (3f-D)



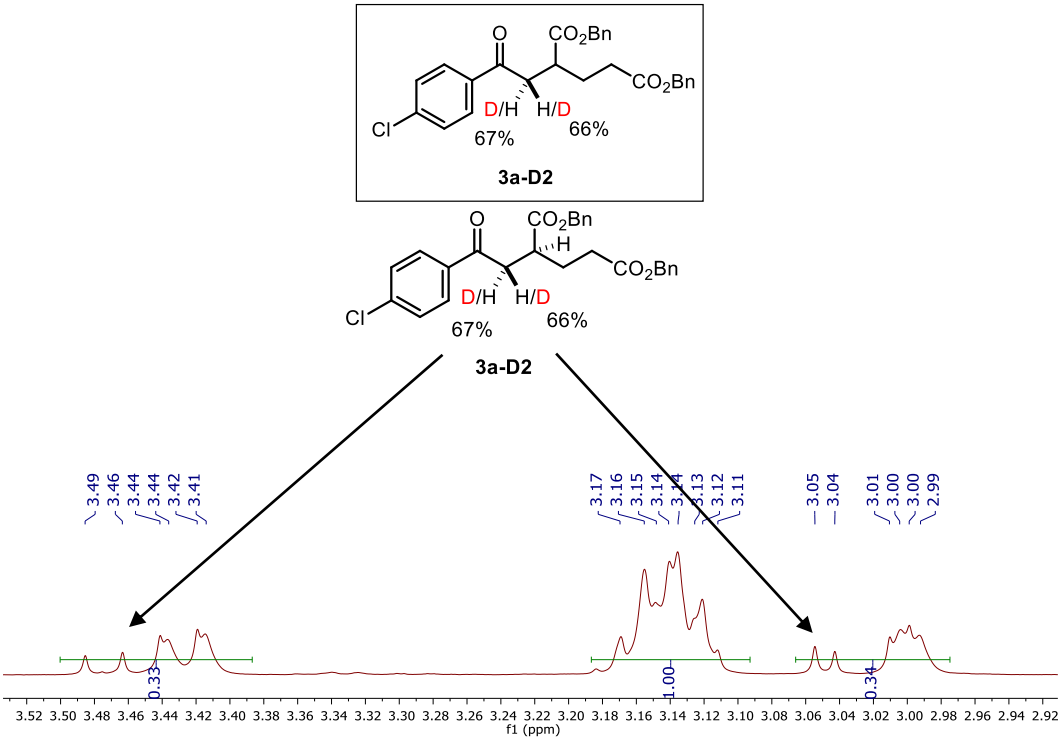
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 4.14 (dq, *J* = 9.3, 7.1 Hz, 4H), 3.50 – 3.38 (m, 1H), 3.10 – 2.96 (m, 2H), 2.43 – 2.35 (m, 1.15H), 2.06 – 1.88 (m, 2H), 1.25 (td, *J* = 7.1, 0.8 Hz, 6H).



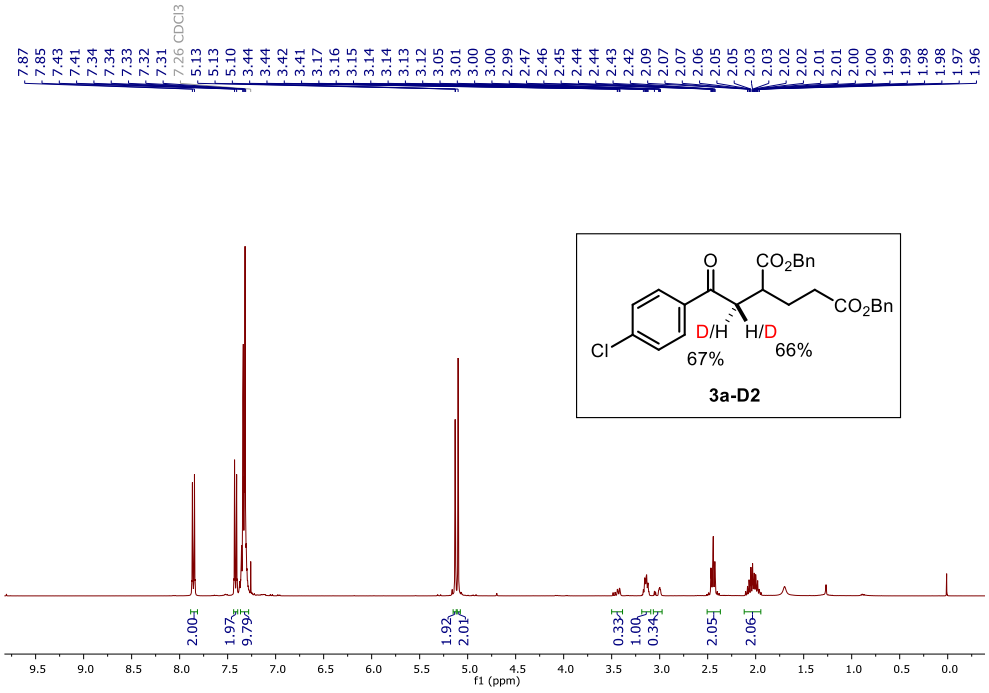
^{1}H NMR spectrum **3f-D** $CDCl_3$, 400 MHz

11.2. NMR data of reaction of 2a and 1a in D_2O (3a-D2):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.58 Hz, 2H), 7.42 (d, *J* = 8.62 Hz, 2H), 7.37 – 7.27 (m, 10H), 5.13 (d, *J* = 1.25 Hz, 2H), 5.10 (s, 2H), 3.44 (m, 0.33H), 3.15 (dt, *J* = 8.06, 5.77 Hz, 1H), 3.02 (m, 0.34H), 2.44 (m, 2H), 2.03 (m, 2H).



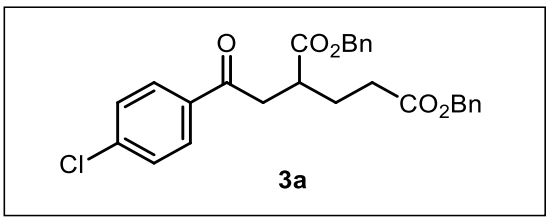
Expansion of **3a-D2**



^{1}H NMR spectrum of **3a-D2,** $CDCl_3$, 400 MHz

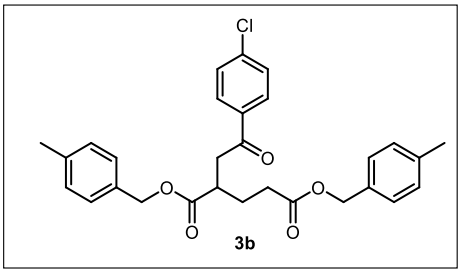
12. Characterization Data:

Dibenzyl 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3a)



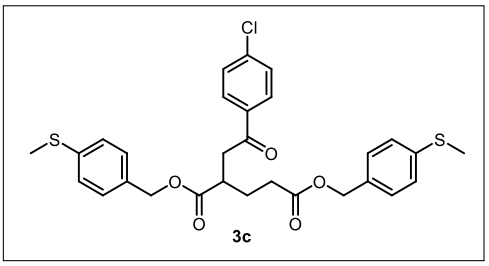
The title compound **3a** was prepared according to the general procedure (GP1) starting from benzyl acrylate **1a** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). White solid (185 mg, 80% yield), R_f = 0.2 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.68 Hz, 2H), 7.32 (d, *J* = 8.68 Hz, 2H), 7.25 (m, 10H), 5.06 (s, 2H), 5.02 (s, 2H), 3.37 (dd, *J* = 17.73, 8.93 Hz, 1H), 3.08 (tt, *J* = 8.44, 4.22 Hz, 1H), 2.94 (dd, *J* = 17.73, 4.65 Hz, 1H), 2.37 (td, *J* = 7.40, 2.14 Hz, 2H), 1.96 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.4, 174.4, 172.4, 139.6, 135.8, 135.7, 134.7, 129.4, 128.8, 128.5, 128.5, 128.2, 128.2, 128.1, 128.1, 66.5, 66.3, 40.2, 39.6, 31.7, 26.9. HRMS (ESI TOF) *m/z* calcd. For $C_{27}H_{26}ClO_5$ $[M + H]^+$ 465.1463 found 465.1468.

Bis(4-methylbenzyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3b)



The title compound **3b** was prepared according to the general procedure (GP1) starting from substituted benzyl acrylate **1b** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). semi solid (209 mg, 85% yield), R_f = 0.22 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.58 Hz, 2H), 7.42 (d, *J* = 8.59 Hz, 2H), 7.22 (dd, *J* = 8.20, 6.70 Hz, 4H), 7.14 (dd, *J* = 13.96, 7.84 Hz, 4H), 5.09 (d, *J* = 1.80 Hz, 2H), 5.06 (s, 2H), 3.44 (dd, *J* = 17.59, 8.80 Hz, 1H), 3.18 – 3.08 (m, 1H), 3.01 (dd, *J* = 17.57, 4.76 Hz, 1H), 2.47 – 2.40 (m, 2H), 2.35 (s, 3H), 2.34 (s, 3H), 2.10 – 1.92 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 174.5, 172.7, 139.8, 138.1, 134.9, 132.9, 132.8, 129.6, 129.4, 129.3, 129.0, 128.5, 128.4, 66.7, 66.5, 40.3, 39.8, 31.9, 27.0, 21.3. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{30}ClO_5$ $[M + H]^+$ 493.1776 found 493.1770.

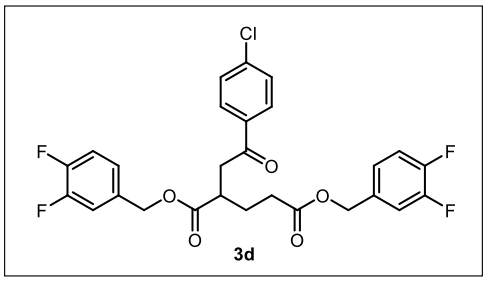
Bis(4-(methylthio)benzyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3c)



3c

The title compound **3c** was prepared according to the general procedure (GP1) starting from substituted benzyl acrylate **1c** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). semi solid (224 mg, 81% yield), R_f = 0.2 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.42 (d, *J* = 8.56 Hz, 2H), 7.25 – 7.21 (m, 6H), 7.20 (s, 2H), 5.07 (s, 2H), 5.04 (s, 2H), 3.43 (dd, *J* = 17.60, 8.82 Hz, 1H), 3.12 (tdd, *J* = 8.33, 5.75, 4.62 Hz, 1H), 3.00 (dd, *J* = 17.60, 4.66 Hz, 1H), 2.47 (s, 3H), 2.47 (s, 3H), 2.45 – 2.38 (m, 2H), 2.09 – 1.90 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 174.5, 172.6, 139.9, 132.6, 132.6, 129.6, 129.1, 129.0, 126.6, 126.6, 66.4, 66.2, 40.4, 39.8, 31.9, 27.0, 15.8. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{30}ClO_5S_2$ $[M + H]^+$ 557.1218 found 557.1221.

Bis (3,4-difluorobenzyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3d)

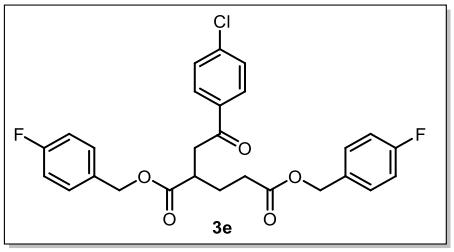


3d

The title compound **3d** was prepared according to the general procedure (GP1) starting from substituted benzyl acrylate **1d** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). semi solid (210 mg, 79% yield), R_f = 0.22 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 2H), 7.47 – 7.41 (m, 2H), 6.86 (ddtd, *J* = 8.94, 6.75, 4.73, 2.40 Hz, 4H), 6.74 (tdq, *J* = 7.96, 6.16, 1.95 Hz, 2H), 5.10 (d, *J* = 4.42 Hz, 2H), 5.07 (s, 2H), 3.51 – 3.41 (m, 1H), 3.20 – 3.11 (m, 1H), 3.08 (dd, *J* = 17.54, 4.53 Hz, 1H), 2.49 (td, *J* = 7.37, 1.51 Hz, 2H), 2.13 – 1.98 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.4, 174.3, 172.2, 163.23 (d, *J* = 250 Hz), 163.22 (d, *J* = 245Hz), 163.1 (d, *J* = 250 Hz), 163.10 (d, *J* = 245 Hz), 140.1, 139.67 (td, *J* = 9.23, 1.10 Hz), 134.7, 129.6, 129.1, 110.73 (d, *J*= 26 Hz), 110.73 (d, *J*= 12 Hz), 110.71 (d, *J*= 25 Hz), 110.71 (d, *J*= 11 Hz), 103.74 (t, *J*= 25 Hz), 103.69 (t, *J*= 25 Hz), 102.82 (t, *J* = 25.39 Hz), 65.3, 65.3, 65.3, 65.1, 65.1, 65.1, 40.5, 39.7, 31.7, 26.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -109.17, -109.20, -109.73. HRMS (ESI TOF) *m/z* calcd. For $C_{27}H_{22}ClF_4O_5$ $[M + H]^+$ 537.1086 found 537.1080.

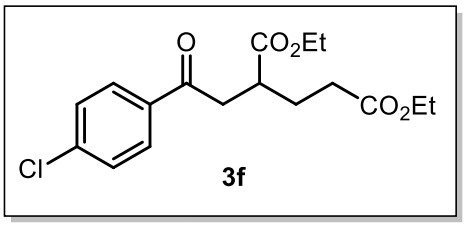
Bis(4-fluorobenzyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3e):



The title compound **3e** was prepared according to the general procedure (GP1) starting from substituted benzyl acrylate **1e** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). semi solid (205 mg, 82% yield), R_f = 0.22 (petroleum ether/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 2H), 7.44 – 7.37 (m, 2H), 7.30 (ddd, *J* = 8.8, 5.3, 2.2 Hz, 4H), 7.01 (dt, *J* = 13.3, 8.7 Hz, 4H), 5.06 (d, *J* = 12.6 Hz, 4H), 3.43 (dd, *J* = 17.6, 8.8 Hz, 1H), 3.16 – 2.96 (m, 2H), 2.45 – 2.36 (m, 2H), 2.07 – 1.91 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.40, 174.40, 172.40, 162.7 (d, *J* = 249 Hz), 162.65 (d, *J* = 241 Hz), 139.85, 134.72, 131.6 (t, *J*= 2.8 Hz), 130.3 (d, *J*= 4 Hz), 130.2 (d, *J*= 4 Hz), 129.44, 129.42, 128.98, 128.95, 128.93, 115.49 (d, *J* = 28 Hz), 115.49 (d, *J*= 15 Hz), 65.92, 65.72, 40.30, 39.63, 31.71, 26.92. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.42, -113.54. HRMS (ESI TOF) *m/z* calcd. For $C_{27}H_{24}ClF_2O_5$ $[M + H]^+$ 501.1275 found 501.1277.

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

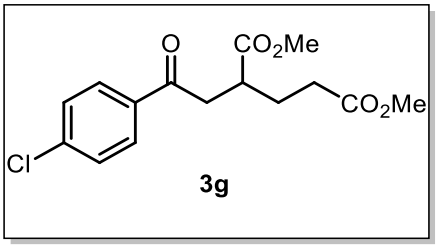


The title compound **3b** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (119 mg, 70% yield), R_f = 0.22 (petroleum ether/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 4.20 – 4.10 (m, 4H), 3.44 (q, J = 8.6, 8.1 Hz, 1H), 3.09 – 2.97 (m, 2H), 2.40 (ddd, J = 7.9, 7.0, 2.1 Hz, 2H), 2.07 – 1.86 (m, 2H), 1.25 (td, J = 7.2, 0.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.7, 174.8,

172.9, 139.9, 135.0, 129.6, 129.1, 60.9, 60.7, 40.5, 39.8, 32.0, 27.2, 14.3, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{17}H_{22}ClO_5$ $[M + H]^+$ 341.1150 found 341.1156.

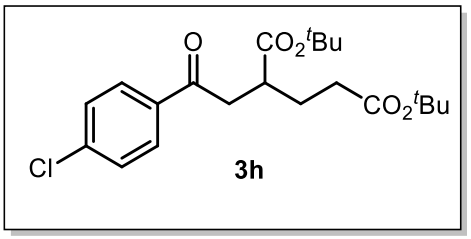
Dimethyl 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3g)



3g

The title compound **3g** was prepared according to the general procedure (GP1) starting from methyl acrylate **1g** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (106 mg, 68% yield), R_f = 0.15 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.46 – 7.42 (m, 2H), 3.71 (s, 3H), 3.68 (s, 3H), 3.54 – 3.36 (m, 1H), 3.17 – 2.97 (m, 2H), 2.52 – 2.33 (m, 2H), 2.11 – 1.89 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 175.2, 173.2, 139.9, 134.8, 129.5, 129.1, 52.1, 51.8, 40.5, 39.6, 31.7, 27.1. HRMS (ESI TOF) *m/z* calcd. For $C_{15}H_{17}ClO_5Na^+$ $[M + Na]^+$ 335.0657 found 335.0664.

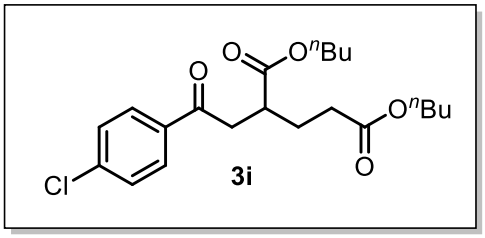
Di-tert-butyl 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3h)



3h

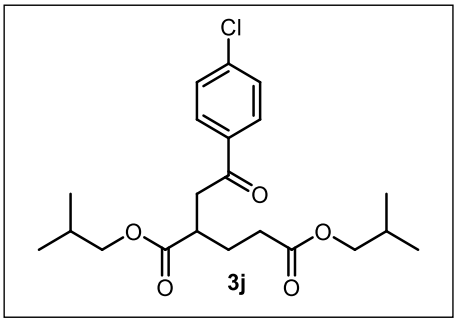
The title compound **3h** was prepared according to the general procedure (GP1) starting from tert-butyl acrylate **1h** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (140 mg, 71% yield), R_f = 0.3 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.44 – 7.39 (m, 2H), 3.37 (dd, *J* = 18.5, 10.1 Hz, 1H), 3.00 – 2.83 (m, 2H), 2.31 (ddd, *J* = 8.3, 7.2, 1.8 Hz, 2H), 1.96 – 1.80 (m, 2H), 1.43 (s, 9H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.9, 174.1, 172.3, 139.7, 135.2, 129.6, 129.0, 81.0, 80.6, 40.7, 40.5, 33.1, 28.2, 28.1, 27.4. HRMS (ESI TOF) *m/z* calcd. For $C_{21}H_{30}ClO_5$ $[M + H]^+$ 397.1776 found 397.1780.

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



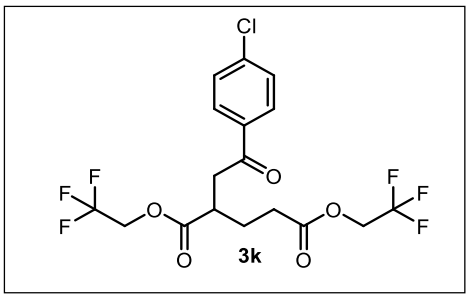
The title compound **3i** was prepared according to the general procedure (GP1) starting from n-butyl acrylate **1i** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (142 mg, 72% yield), R_f = 0.27 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.49 – 7.39 (m, 2H), 4.09 (dt, *J* = 7.8, 6.7 Hz, 4H), 3.50 – 3.41 (m, 1H), 3.13 – 2.97 (m, 2H), 2.42 (ddd, *J* = 7.9, 7.0, 2.1 Hz, 2H), 2.07 – 1.89 (m, 2H), 1.65 – 1.57 (m, 4H), 1.41 – 1.32 (m, 4H), 0.92 (td, *J* = 7.4, 5.3 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.7, 174.9, 173.0, 139.8, 135.0, 129.6, 129.0, 64.8, 64.6, 40.4, 39.8, 32.0, 30.7, 30.7, 27.2, 19.2, 19.2, 13.8, 13.8. HRMS (ESI TOF) *m/z* calcd. For $C_{21}H_{30}ClO_5$ $[M + H]^+$ 397.1776 found 397.1774.

Diisobutyl 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3j)



The title compound **3j** was prepared according to the general procedure (GP1) starting from iso-butyl acrylate **1j** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (140 mg, 71% yield), R_f = 0.28 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.53 Hz, 2H), 7.42 (d, J = 8.53 Hz, 2H), 3.88 – 3.83 (m, 4H), 3.45 (dd, J = 17.34, 8.57 Hz, 1H), 3.12 – 2.96 (m, 2H), 2.47 – 2.39 (m, 2H), 2.07 – 1.83 (m, 4H), 0.92 (d, J = 1.85 Hz, 6H), 0.90 (d, J = 1.86 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 174.8, 172.9, 139.8, 134.9, 129.6, 129.0, 71.1, 70.8, 40.4, 39.9, 32.0, 27.8, 27.2, 19.2, 19.2. HRMS (ESI TOF) *m/z* calcd. For $C_{21}H_{29}ClO_5Na^+$ $[M + Na]^+$ 419.1596 found 419.1600.

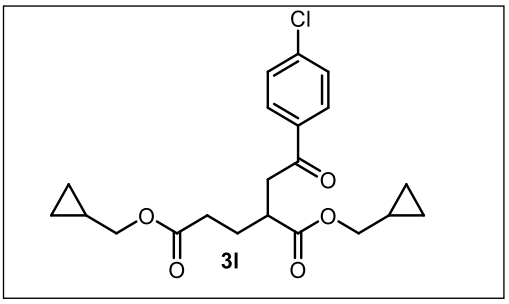
Bis(2,2,2-trifluoroethyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3k)



The title compound **3k** was prepared according to the general procedure (GP1) starting from 2,2,2-trifluoroethyl acrylate **1k** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (154 mg, 69% yield), R_f = 0.25 (petroleum ether/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.66 Hz, 2H), 7.45 (d, *J* = 8.67 Hz, 2H), 4.59 (dq, *J* = 12.59, 8.40 Hz, 1H), 4.52 – 4.40 (m, 3H), 3.54 – 3.40 (m, 1H), 3.22 – 3.09 (m, 2H), 2.60 – 2.54 (m, 2H), 2.11 – 1.99 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.0, 173.1, 171.1, 140.2, 134.6, 129.6, 129.2, 124.4, 124.4, 121.6, 121.6, 118.9, 61.2, 61.1, 60.9, 60.7, 60.5, 60.4, 60.1, 59.9, 40.4, 39.3, 31.1, 26.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.8, -73.9. HRMS (ESI TOF) *m/z* calcd. For $C_{17}H_{16}ClF_6O_5$ $[M + H]^+$ 449.0585 found 449.0588.

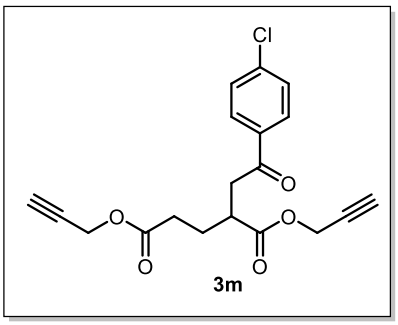
Bis(cyclopropylmethyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3l)



The title compound **3l** was prepared according to the general procedure (GP1) starting from cyclopropylmethyl acrylate **1l** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (141 mg, 71% yield), R_f = 0.25 (petroleum ether/EtOAc 80:20).

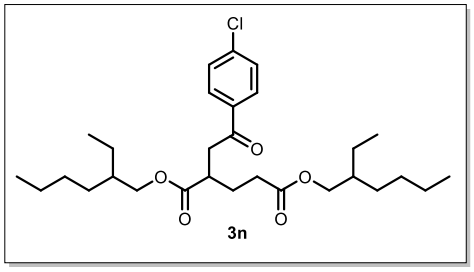
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.46 – 7.38 (m, 1H), 3.99 – 3.85 (m, 4H), 3.46 (dd, *J* = 17.41, 8.66 Hz, 1H), 3.14 – 2.94 (m, 2H), 2.46 (ddd, *J* = 8.37, 7.18, 1.77 Hz, 2H), 2.09 – 1.91 (m, 3H), 1.19 – 1.04 (m, 2H), 0.58 – 0.50 (m, 4H), 0.26 (tdd, *J* = 5.38, 4.17, 2.51 Hz, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.7, 174.91, 173.0, 139.8, 134.9, 129.6, 129.1, 69.7, 69.5, 40.5, 39.9, 31.9, 27.2, 9.9, 9.9, 3.4, 3.4, 3.3. HRMS (ESI TOF) *m/z* calcd. For $C_{21}H_{25}ClO_5Na^+$ $[M + Na]^+$ 415.1283 found 415.1292.

Di(prop-2-yn-1-yl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3m)



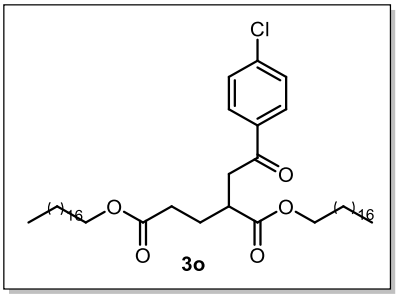
The title compound **3m** was prepared according to the general procedure (GP1) starting from prop-2-yn-1-yl acrylate **1m** (1 mmol) and 4-chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (126 mg, 70% yield), R_f = 0.24 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.74 Hz, 2H), 7.43 (d, *J* = 8.64 Hz, 2H), 4.78 – 4.63 (m, 4H), 3.51 – 3.40 (m, 1H), 3.19 – 2.96 (m, 2H), 2.54 – 2.45 (m, 4H), 2.10 – 1.93 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.3, 174.0, 172.0, 140.0, 134.8, 129.6, 129.1, 77.6, 77.6, 75.2, 75.1, 52.5, 52.2, 40.4, 39.5, 31.6, 26.8. HRMS (ESI TOF) *m/z* calcd. For $C_{19}H_{17}ClO_5Na^+$ $[M + Na]^+$ 383.0662 found 361.0664.

Bis(2-ethylhexyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3n)



The title compound **3n** was prepared according to the general procedure (GP1) starting from 2-ethylhexyl acrylate **1n** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Off-white Semi-solid (182 mg, 72% yield), R_f = 0.35 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9 (d, *J* = 8.5 Hz, 2H), 7.4 (d, *J* = 8.5 Hz, 2H), 4.0 (ddd, *J* = 9.9, 5.8, 3.6 Hz, 4H), 3.4 (dd, *J* = 17.3, 8.5 Hz, 1H), 3.1 – 3.0 (m, 2H), 2.4 (ddd, *J* = 8.2, 7.0, 2.4 Hz, 2H), 2.1 – 1.9 (m, 2H), 1.6 – 1.5 (m, 2H), 1.4 – 1.3 (m, 16H), 0.9 (ddd, *J* = 6.2, 4.0, 1.9 Hz, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 174.9, 173.1, 139.8, 135.0, 129.6, 129.1, 67.3, 67.26, 67.2, 40.4, 39.9, 38.8, 38.8, 32.0, 30.5, 30.5, 30.4, 29.0, 29.0, 27.2, 23.8, 23.1, 23.1, 14.2, 11.1, 11.00. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{46}ClO_5$ $[M + H]^+$ 509.3028 found 509.3033.

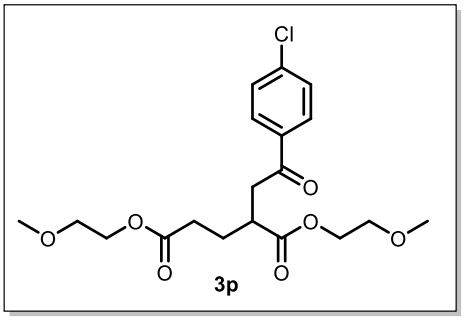
Dioctadecyl 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3o)



The title compound **3o** was prepared according to the general procedure (GP1) starting from Stearyl Acrylate **1o** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). White solid (231 mg, 59% yield), R_f = 0.5 (petroleum ether/EtOAc 85:15).

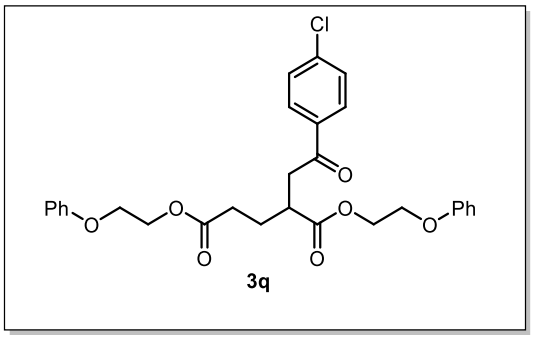
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 4.07 (dt, *J* = 8.0, 6.8 Hz, 4H), 3.45 (dd, *J* = 17.1, 8.4 Hz, 1H), 3.10 – 2.96 (m, 2H), 2.45 – 2.37 (m, 2H), 2.06 – 1.90 (m, 2H), 1.58 (t, *J* = 3.6 Hz, 4H), 1.25 (s, 60H), 0.88 (t, *J* = 8 Hz, 6H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 196.5, 174.7, 172.8, 139.7, 134.9, 129.5, 128.9, 65.0, 64.8, 40.4, 39.8, 31.9, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 28.6, 28.6, 27.1, 25.9, 25.9, 22.7, 14.1. HRMS (ESI TOF) *m/z* calcd. For $C_{49}H_{86}ClO_5$ $[M + H]^+$ 789.6158 found 789.6155.

Bis(2-methoxyethyl) 2-(2-(4-chlorophenyl)-2-oxoethyl) pentanedioate (3p)



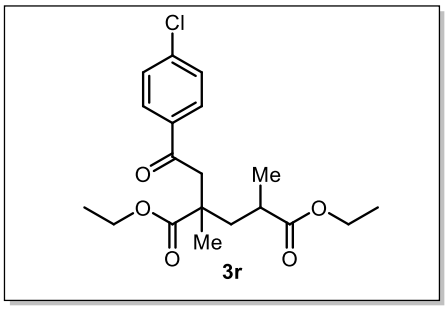
The title compound **3p** was prepared according to the general procedure (GP1) starting from 2-methoxyethyl acrylate **1p** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). White semi-solid (143 mg, 71% yield), R_f = 0.2 (petroleum ether/EtOAc 75:25). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.42 (d, J = 8.6 Hz, 2H), 4.30 – 4.19 (m, 4H), 3.57 (ddd, J = 5.3, 3.8, 2.0 Hz, 4H), 3.44 (dd, J = 17.3, 8.3 Hz, 1H), 3.36 (s, 3H), 3.34 (s, 3H), 3.14 – 2.98 (m, 2H), 2.47 (ddd, J = 8.0, 7.0, 2.3 Hz, 2H), 2.07 – 1.90 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.5, 174.6, 172.8, 139.7, 134.8, 129.5, 128.9, 70.4, 70.3, 63.7, 63.6, 59.0, 58.9, 40.3, 39.6, 31.6, 26.9. HRMS (ESI TOF) *m/z* calcd. For $C_{19}H_{26}ClO_7Na^+$ $[M + Na]^+$ 423.1186 found 423.1189.

Bis(2-phenoxyethyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3q)



The title compound **3q** was prepared according to the general procedure (GP1) starting from 2-phenoxyethyl acrylate **1q** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Off-white solid (196 mg, 75% yield), R_f = 0.23 (petroleum ether/EtOAc 75:25). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 2H), 7.39 (d, *J* = 8.63 Hz, 2H), 7.32 – 7.21 (m, 5H), 6.95 (dt, *J* = 8.62, 1.11 Hz, 2H), 6.90 – 6.83 (m, 3H), 4.55 – 4.36 (m, 4H), 4.16 – 4.10 (m, 4H), 3.45 (dd, *J* = 17.57, 8.64 Hz, 1H), 3.19 – 2.94 (m, 2H), 2.56 – 2.45 (m, 2H), 2.12 – 1.92 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.5, 174.6, 172.8, 158.6, 139.9, 134.8, 129.7, 129.6, 129.6, 129.1, 121.3, 121.2, 114.7, 114.7, 65.8, 65.7, 63.2, 63.1, 40.5, 39.7, 31.7, 27.0. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{30}ClO_7$ $[M + H]^+$ 525.1675 found 525.1678.

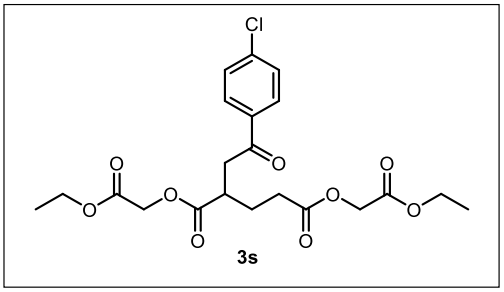
Diethyl 2-(2-(4-chlorophenyl)-2-oxoethyl)-2,4-dimethylpentanedioate (3r)



The title compound **3r** was prepared according to the general procedure (GP1) starting from ethyl methacrylate **1r** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (133 mg, 72% yield), R_f = 0.25 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.63 Hz, 2H), 7.41 (d, *J* = 8.56 Hz, 2H), 4.15 – 4.01 (m, 4H), 3.40 (t, *J* = 17.40 Hz, 1H), 3.08 (dd, *J* = 17.71, 4.75 Hz, 1H), 2.57 (dtd, *J* = 8.79, 7.04, 3.23 Hz, 1H), 2.25 (m, 1H), 1.71 (m, 1H), 1.3-1.1 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.3, 196.2, 177.1, 176.9, 176.3, 176.0, 139.7, 139.6, 135.5, 135.4, 129.4, 129.0, 60.8, 60.8, 60.6, 60.6, 47.4, 46.3, 43.5, 43.5, 42.9, 42.7,

35.9, 35.9, 23.0, 21.5, 20.2, 19.9, 14.3, 14.2, 14.2, 14.1. HRMS (ESI TOF) *m/z* calcd. For $C_{19}H_{25}ClO_5Na^+$ $[M + Na]^+$ 391.1283 found 391.1287.

Bis(2-ethoxy-2-oxoethyl) 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate (3s)

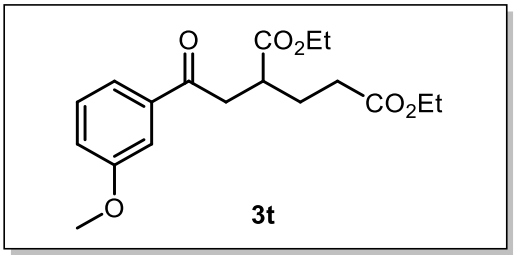


3s

The title compound **3s** was prepared according to the general procedure (GP1) starting from 2-ethoxy-2-oxoethyl acrylate **1s** (1 mmol) and 4-Chlorobenzaldehyde **2a** (2 mmol). Colorless liquid (162 mg, 71% yield), R_f = 0.3 (petroleum ether/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.64 Hz, 2H), 7.44 (d, *J* = 8.59 Hz, 2H), 4.72 (d, *J* = 15.85 Hz, 1H), 4.61 (d, *J* = 2.08 Hz, 2H), 4.56 (d, *J* = 15.88 Hz, 1H), 4.21 (qd, *J* = 7.17, 2.00 Hz, 4H), 3.52 (dd, *J* = 17.84, 8.75 Hz, 1H), 3.29 – 3.18 (m, 1H), 3.10 (dd, *J* = 17.87, 4.74 Hz, 1H), 2.73 – 2.63 (m, 2H), 2.19 – 2.01 (m, 2H), 1.28 (td, *J* = 7.12, 3.63 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 174.2, 172.4, 167.9, 167.8, 139.9, 134.8, 129.6, 129.1, 126.8, 61.6, 61.5, 61.1, 60.9, 40.4, 39.3, 31.3, 26.8, 14.2, 14.2. HRMS (ESI TOF) *m/z* calcd. For $C_{21}H_{26}ClO_9$ $[M + H]^+$ 457.1260 found 457.1264.

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

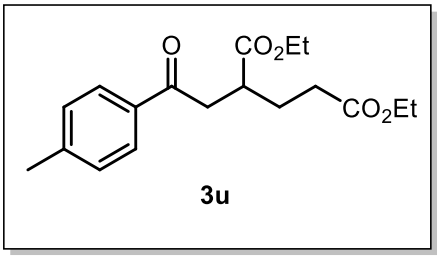


3t

The title compound **3t** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 3-methoxybenzaldehyde **2b** (2 mmol). Colorless liquid (124 mg, 74% yield), R_f = 0.3 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.45 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.08 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 4.12 (dq, *J* = 11.3, 7.1 Hz, 4H), 3.82 (s, 3H), 3.44 (dd, *J* = 18.8, 9.8 Hz, 1H), 3.12 – 2.95 (m, 2H), 2.39 (ddd, *J* = 8.0, 7.1, 2.0 Hz, 2H), 2.03 – 1.88 (m, 2H), 1.23 (td, *J* = 7.2,

2.4 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 197.7, 174.8, 172.8, 159.9, 138.0, 129.7, 120.7, 119.9, 112.2, 60.8, 60.6, 55.5, 40.6, 39.8, 32.0, 27.1, 14.3, 14.2. HRMS (ESI TOF) *m/z* calcd. For $C_{18}H_{25}O_6$ $[M + H]^+$ 337.1646 found 337.1650.

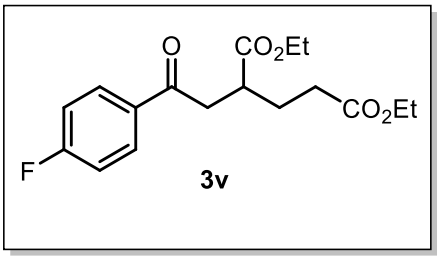
Diethyl 2-(2-oxo-2-(p-tolyl)ethyl)pentanedioate (3u)



3u

The title compound **3u** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 4-methylbenzaldehyde **2c** (2 mmol). Colorless liquid (115 mg, 72% yield), R_f = 0.4 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.14 (dq, *J* = 10.1, 7.1 Hz, 4H), 3.45 (dd, *J* = 18.7, 9.8 Hz, 1H), 3.10 – 2.99 (m, 2H), 2.45 – 2.34 (m, 5H), 2.06 – 1.85 (m, 2H), 1.29 – 1.21 (m, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 197.5, 174.9, 172.9, 144.1, 134.2, 129.4, 128.2, 125.8, 60.8, 60.6, 40.4, 39.9, 32.0, 27.2, 21.7, 14.3, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{18}H_{25}O_5$ $[M + H]^+$ 321.1697 found 321.1699.

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

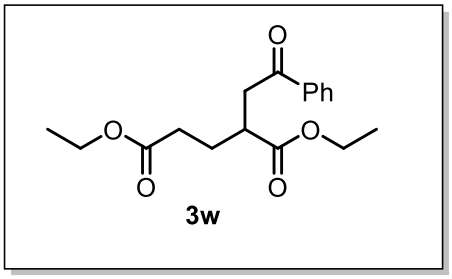


3v

The title compound **3v** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 4-fluorobenzaldehyde **2d** (2 mmol). Colorless liquid (105 mg, 65% yield), R_f = 0.3 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.11 (dd, *J* = 8.9, 8.3 Hz, 2H), 4.16 – 4.09 (m, 4H), 3.48 – 3.39 (m, 1H), 3.09 – 2.96 (m, 2H), 2.40 (ddd, *J* = 7.9, 7.1, 2.1 Hz, 2H), 2.06 – 1.88 (m, 2H), 1.24 (td, *J* = 7.1, 1.3 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ [1] 196.2, 174.7, 172.8, 165.8 (d, *J* = 255.0 Hz), 133.0 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 9.3 Hz), 115.7 (d, *J* = 21.9 Hz), 60.8, 60.5, 40.3, 39.7, 31.9, 27.0, 14.2,

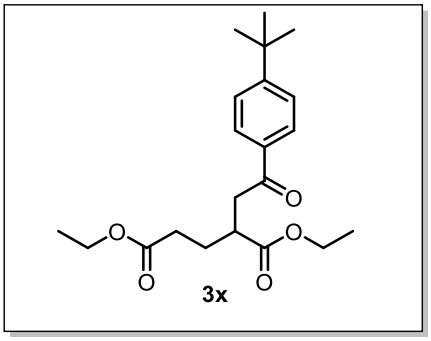
14.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.75. HRMS (ESI TOF) *m/z* calcd. For $C_{17}H_{22}FO_5$ $[M + H]^+$ 325.1446 found 325.1450.

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



The title compound **3w** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and benzaldehyde **2e** (2 mmol). Colorless liquid (108 mg, 71% yield), R_f = 0.3 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (ddd, *J* = 7.51, 1.42, 0.73 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.44 (ddt, *J* = 8.42, 7.74, 0.75 Hz, 2H), 4.13 (dqd, *J* = 10.73, 7.12, 0.77 Hz, 4H), 3.46 (ddd, *J* = 18.78, 9.80, 0.74 Hz, 1H), 3.10 – 3.00 (m, 2H), 2.44 – 2.37 (m, 2H), 2.06 – 1.85 (m, 2H), 1.24 (tdd, *J* = 7.08, 1.29, 0.72 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.8, 174.9, 172.9, 136.6, 133.3, 128.7, 128.1, 60.8, 60.6, 40.5, 39.8, 32.0, 27.1, 14.3, 14.2. HRMS (ESI TOF) *m/z* calcd. For $C_{17}H_{23}O_5$ $[M + H]^+$ 307.1540 found 307.1543.

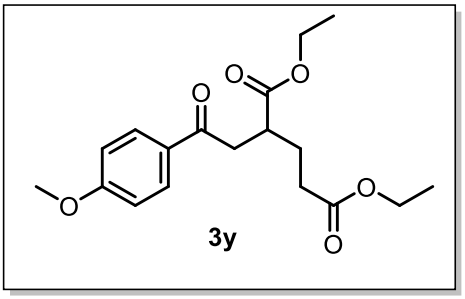
Diethyl 2-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)pentanedioate (3x)



The title compound **3x** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 4-tert-butyl benzaldehyde **2f** (2 mmol). Colorless liquid (126 mg, 70% yield), R_f = 0.2 (petroleum ether/EtOAc 85:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.47 Hz, 2H), 7.46 (d, *J* = 8.60 Hz, 2H), 4.13 (dq, *J* = 9.97, 7.13 Hz, 4H), 3.45 (dd, *J* = 18.73, 9.82 Hz, 1H), 3.11 – 2.99 (m, 2H), 2.40 (ddd, *J* = 8.60, 7.14, 2.28 Hz, 2H), 1.98 (qt, *J* = 13.31, 6.73 Hz, 2H), 1.33 (s, 9H), 1.24 (t, *J* = 7.14 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.5,

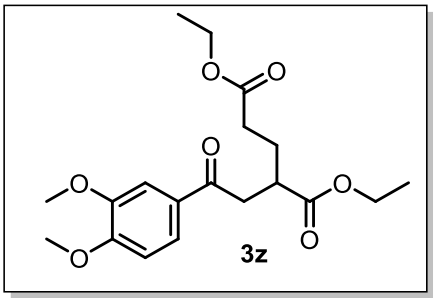
175.0, 172.9, 157.1, 134.1, 128.1, 125.7, 60.8, 60.6, 40.5, 39.9, 35.2, 32.1, 31.2, 27.2. HRMS (ESI TOF) *m/z* calcd. For $C_{21}H_{31}O_5$ $[M + H]^+$ 363.2166 found 363.2169.

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



The title compound **3y** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 4-methoxybenzaldehyde **2g** (2 mmol). Colorless liquid (128 mg, 76% yield), R_f = 0.3 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.62 Hz, 2H), 6.92 (d, *J* = 8.66 Hz, 2H), 4.18 – 4.09 (m, 4H), 3.86 (s, 3H), 3.46 – 3.36 (m, 1H), 3.08 – 2.97 (m, 2H), 2.40 (ddd, *J* = 8.58, 7.01, 2.19 Hz, 2H), 2.05 – 1.89 (m, 2H), 1.24 (tdd, *J* = 7.19, 1.11, 0.54 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.4, 175.0, 172.9, 163.7, 130.4, 129.8, 113.8, 60.8, 60.6, 55.6, 40.2, 39.9, 32.1, 27.2, 14.3, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{18}H_{25}O_6$ $[M + H]^+$ 337.1646 found 337.1648.

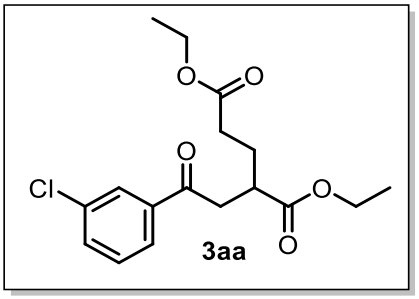
Diethyl 2-(2-(3,4-dimethoxyphenyl)-2-oxoethyl)pentanedioate (3z)



The title compound **3z** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 3,4-dimethoxybenzaldehyde **2h** (2 mmol). Colorless liquid (143 mg, 78% yield), R_f = 0.3 (petroleum ether/EtOAc 65:35). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.36, 2.04 Hz, 1H), 7.49 (d, *J* = 2.01 Hz, 1H), 6.87 (d, *J* = 8.40 Hz, 1H), 4.13 (dq, *J* = 11.69, 7.13 Hz, 4H), 3.93 (s, 3H), 3.91 (s, 3H), 3.42 (dd, *J* = 18.50, 9.89 Hz, 1H), 3.08 – 2.99 (m, 2H),

2.40 (ddd, *J* = 8.12, 7.06, 2.14 Hz, 2H), 2.04 – 1.88 (m, 2H), 1.24 (td, *J* = 7.14, 3.17 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.3, 174.9, 172.8, 153.4, 149.0, 129.8, 122.7, 110.0, 110.0, 60.7, 60.5, 56.0, 56.0, 40.0, 40.0, 32.0, 27.1, 14.2, 14.2. HRMS (ESI TOF) *m/z* calcd. For $C_{19}H_{27}O_7$ $[M + H]^+$ 367.1751 found 367.1755.

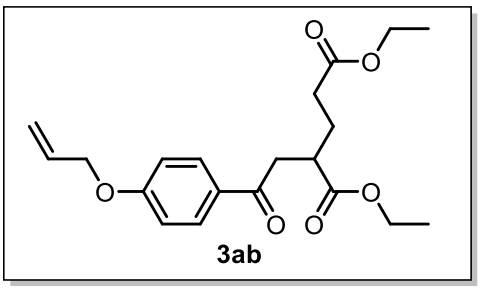
Diethyl 2-(2-(3-chlorophenyl)-2-oxoethyl)pentanedioate (3aa)



The title compound **3aa** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 3-Chlorobenzaldehyde **2i** (2 mmol). Colorless liquid (118 mg, 69% yield), R_f = 0.22 (petroleum ether/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, *J* = 1.88 Hz, 1H), 7.81 (dt, *J* = 7.76, 1.38 Hz, 1H), 7.52 (ddd, *J* = 7.95, 2.10, 1.05 Hz, 1H), 7.39 (t, *J* = 7.87 Hz, 1H), 4.14 (dq, *J* = 8.85, 7.12 Hz, 4H), 3.49 – 3.40 (m, 1H), 3.10 – 2.94 (m, 2H), 2.44 – 2.37 (m, 2H), 2.06 – 1.88 (m, 2H), 1.25 (td, *J* = 7.13, 0.91 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.7, 174.7, 172.8, 138.1, 135.1, 133.3, 130.1, 128.3, 126.2, 61.0, 60.7, 40.6, 39.7, 32.0, 27.1, 14.3, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{17}H_{22}ClO_5$ $[M + H]^+$ 341.1150 found 341.1154.

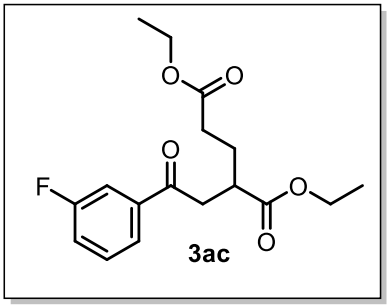
Diethyl 2-(2-(4-(allyloxy)phenyl)-2-oxoethyl)pentanedioate (3ab)



The title compound **3ab** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 4-(allyloxy)benzaldehyde **2j** (2 mmol). Colorless liquid (131 mg, 72% yield), R_f = 0.3 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.96 Hz, 2H), 6.93 (d, *J* = 8.94 Hz, 2H), 6.04 (ddt, *J* = 17.24, 10.54, 5.29 Hz, 1H), 5.48 – 5.26

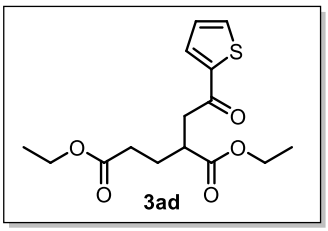
(m, 2H), 4.60 (dt, *J* = 5.27, 1.53 Hz, 2H), 4.19 – 4.10 (m, 4H), 3.48 – 3.35 (m, 1H), 3.10 – 2.96 (m, 2H), 2.40 (ddd, *J* = 8.20, 7.06, 2.12 Hz, 2H), 2.06 – 1.90 (m, 2H), 1.25 (td, *J* = 7.10, 1.01 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 196.4, 175.0, 173.0, 162.7, 132.6, 130.4, 129.8, 118.3, 114.5, 69.0, 60.8, 60.6, 40.2, 39.9, 32.1, 27.2, 14.3, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{20}H_{27}O_6$ $[M + H]^+$ 363.1802 found 363.1805.

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



The title compound **3ac** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 3-fluorobenzaldehyde **2k** (2 mmol). Colorless liquid (108 mg, 67% yield), R_f = 0.22 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dt, *J* = 7.81, 1.19 Hz, 1H), 7.62 (ddd, *J* = 9.41, 2.58, 1.51 Hz, 1H), 7.44 (td, *J* = 8.01, 5.51 Hz, 1H), 7.29 – 7.23 (m, 1H), 4.14 (dq, *J* = 9.68, 7.17 Hz, 4H), 3.51 – 3.38 (m, 1H), 3.12 – 2.97 (m, 2H), 2.45 – 2.37 (m, 2H), 2.05 – 1.89 (m, 2H), 1.25 (td, *J* = 7.11, 1.17 Hz, 6H). $^{13}C\ \{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 196.7, 196.7, 174.8, 172.9, 163.0 (d, *J* = 248.2 Hz), 138.7 (d, *J* = 6.2 Hz), 130.4 (d, *J* = 7.7 Hz), 123.9 (d, *J* = 2.9 Hz), 120.4 (d, *J* = 21.6 Hz), 114.9 (d, *J* = 22.5 Hz), 61.0, 60.7, 40.7, 39.8, 32.0, 27.1, 14.3, 14.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.7. HRMS (ESI TOF) *m/z* calcd. For $C_{17}H_{22}FO_5$ $[M + H]^+$ 325.1446 found 325.1449.

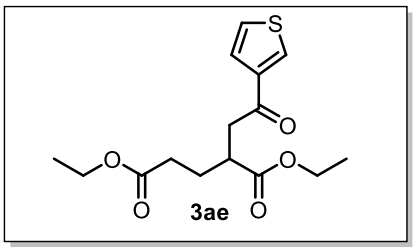
Diethyl 2-(2-oxo-2-(thiophen-2-yl)ethyl)pentanedioate (3ad)



The title compound **3ad** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and thiophene-2-carbaldehyde **2l** (2 mmol). Colorless liquid (100 mg, 64% yield), R_f = 0.3 (petroleum ether/EtOAc 70:30).

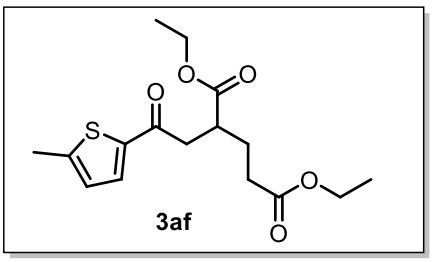
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 3.80, 1.14 Hz, 1H), 7.63 (dd, *J* = 4.92, 1.11 Hz, 1H), 7.12 (dd, *J* = 4.93, 3.79 Hz, 1H), 4.13 (p, *J* = 7.16 Hz, 4H), 3.44 – 3.33 (m, 1H), 3.09 – 2.96 (m, 2H), 2.48 – 2.34 (m, 2H), 1.98 (tt, *J* = 14.18, 6.56 Hz, 2H), 1.24 (td, *J* = 7.10, 3.37 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.8, 174.7, 172.9, 143.8, 133.9, 132.2, 128.3, 61.0, 60.7, 41.0, 39.9, 32.0, 27.1, 14.3, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{15}H_{21}O_5S$ $[M + H]^+$ 313.1104 found 313.1109.

Diethyl 2-(2-oxo-2-(thiophen-3-yl)ethyl)pentanedioate (3ae)



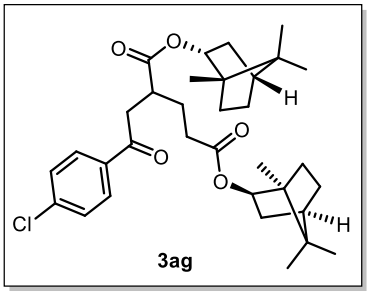
The title compound **3ae** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and thiophene-3-carbaldehyde **2m** (2 mmol). Colorless liquid (101 mg, 65% yield), R_f = 0.3 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 2.87, 1.27 Hz, 1H), 7.53 (dd, *J* = 5.08, 1.25 Hz, 1H), 7.31 (dd, *J* = 5.11, 2.91 Hz, 1H), 4.13 (dq, *J* = 8.68, 7.15 Hz, 4H), 3.37 (dd, *J* = 16.90, 8.22 Hz, 1H), 3.08 – 2.94 (m, 2H), 2.40 (ddd, *J* = 8.06, 7.01, 2.47 Hz, 2H), 2.09 – 1.84 (m, 2H), 1.24 (t, *J* = 7.14 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.2, 174.9, 172.9, 141.9, 132.2, 126.9, 126.6, 60.9, 60.7, 41.6, 39.8, 32.0, 27.1, 14.3, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{15}H_{20}O_5SNa^+$ $[M + Na]^+$ 335.0928 found 335.0926.

Diethyl 2-(2-(5-methylthiophen-2-yl)-2-oxoethyl)pentanedioate (3af)



The title compound **3af** was prepared according to the general procedure (GP1) starting from ethyl acrylate **1f** (1 mmol) and 5-methylthiophene-2-carbaldehyde **2n** (2 mmol). Colorless liquid (103 mg, 63% yield), R_f = 0.32 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.72 Hz, 1H), 6.78 (dd, *J* = 3.79, 1.05 Hz, 1H), 4.17 – 4.13 (m, 2H), 4.12 – 4.09 (m, 2H), 3.32 (dd, *J* = 16.67, 8.39 Hz, 1H), 3.07 – 2.89 (m, 2H), 2.52 (d, *J* = 1.05 Hz, 3H), 2.43 – 2.34 (m, 2H), 2.05 – 1.87 (m, 2H), 1.28 – 1.21 (m, 6H). 13C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.2, 174.6, 172.8, 149.9, 141.5, 132.6, 126.8, 60.8, 60.5, 40.5, 39.9, 31.9, 27.0, 16.0, 14.2, 14.2. HRMS (ESI TOF) *m/z* calcd. For $C_{16}H_{23}O_5S$ $[M + H]^+$ 327.1261 found 327.1258.

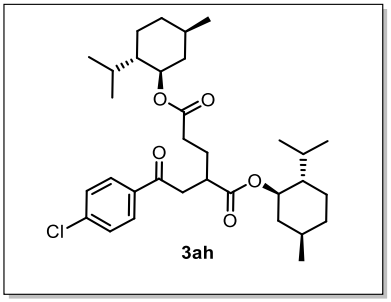
Bis ((1*S*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl) 2-(2-(4-chlorophenyl)-2oxoethyl)pentanedioate (3ag)



The title compound **3ag** was prepared according to the general procedure (GP1) starting from borneol derived acrylate **1t** (1 mmol) and 4-chlorobenzaldehyde **2a** (2 mmol). White solid (103 mg, 63% yield), R_f = 0.3 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.42 (d, *J* = 8.60 Hz, 2H), 4.95 – 4.83 (m, 2H), 3.46 (ddd, *J* = 17.40, 8.90, 4.24 Hz, 1H), 3.16 – 3.04 (m, 1H), 3.05 – 2.97 (m, 1H), 2.50 – 2.42 (m, 2H), 2.34 (dddt, *J* = 13.18, 9.95, 5.16, 2.75 Hz, 2H), 2.10 – 1.83 (m, 4H), 1.74 – 1.65 (m, 4H), 1.35 – 1.00 (m, 6H), 0.90 – 0.87 (m, 6H), 0.86 (d, *J* = 4.14 Hz, 6H), 0.84 – 0.79 (m, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.63, 196.6, 196.6, 175.0, 174.9 173.1, 139.8, 135.0, 129.6, 129.6, 129.1, 80.62, 80.53, 80.26,

80.24, 49.0, 48.9, 48.9, 48.0, 48.0, 45.0, 45.0, 40.4, 40.1, 40.0, 37.0, 36.9, 36.7, 32.4, 32.3, 28.1, 28.1, 28.08, 27.40, 27.35, 27.31, 27.23, 19.81, 19.80, 19.78, 18.95, 13.65, 13.54. HRMS (ESI TOF) *m/z* calcd. For $C_{33}H_{46}ClO_5$ $[M + H]^+$ 557.3028 found 557.3033.

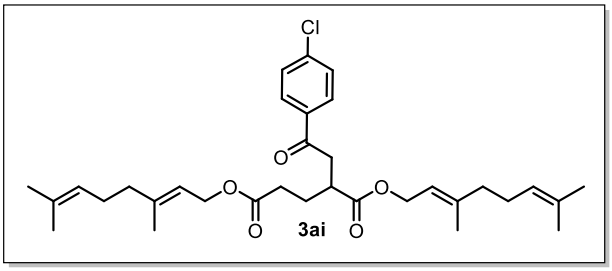
Bis ((1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl) 2-(2-(4-chlorophenyl)-2-oxoethyl) pentanedioate-(3ah)



The title compound **3ah** was prepared according to the general procedure (GP1) starting from menthol derived acrylate **1u** (1 mmol) and 4-chlorobenzaldehyde **2a** (2 mmol). Semi solid (151 mg, 54% yield), R_f = 0.3 (petroleum ether/EtOAc 80:20).

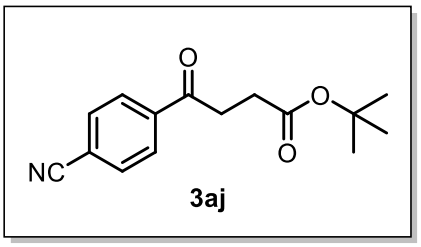
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.43 (dd, *J* = 8.58, 1.44 Hz, 2H), 4.67 (dddt, *J* = 14.35, 6.72, 4.79, 2.44 Hz, 2H), 3.44 (dt, *J* = 17.30, 9.57 Hz, 1H), 3.10 – 2.89 (m, 2H), 2.38 (dddd, *J* = 10.41, 8.12, 4.86, 3.02 Hz, 2H), 2.08 – 1.78 (m, 6H), 1.70 – 1.64 (m, 4H), 1.54 – 1.44 (m, 2H), 1.40 – 1.31 (m, 2H), 1.10 – 0.93 (m, 4H), 0.88 (ddd, *J* = 7.11, 4.00, 2.64 Hz, 12H), 0.83 (d, *J* = 7.01 Hz, 2H), 0.76 – 0.70 (m, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.70, 196.5, 174.3, 174.3, 172.5, 139.8, 139.7, 135.2, 135.1, 129.6, 129.6, 129.0, 129.0, 75.0, 74.8, 74.5, 47.1, 47.1, 47.0, 41.1, 41.1, 40.9, 40.7, 40.4, 40.3, 40.2, 40.1, 34.4, 34.3, 34.4, 32.3, 31.5, 31.5, 31.5, 27.5, 27.2, 26.5, 26.4, 26.2, 26.1, 23.6, 23.5, 23.4, 23.1, 22.2, 22.1, 21.0, 20.9, 20.9, 20.9, 16.5, 16.4, 16.2, 15.9. HRMS (ESI TOF) *m/z* calcd. For $C_{33}H_{50}ClO_5$ $[M + H]^+$ 561.3341 found 561.3344.

Bis((*E*)-3,7-dimethylocta-2,6-dien-1-yl)2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate-(3ai)



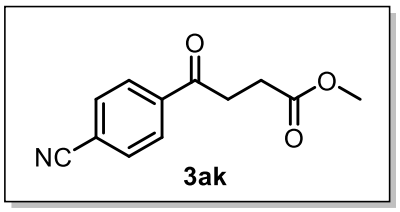
The title compound **3ai** was prepared according to the general procedure (GP1) starting from geraniol derived acrylate **1v** (1 mmol) and 4-chlorobenzaldehyde **2a** (2 mmol). Semi solid (134 mg, 48 % yield), R_f = 0.3 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9 – 7.8 (m, 2H), 7.4 (d, *J* = 8.6 Hz, 2H), 5.3 (tq, *J* = 7.1, 1.4 Hz, 2H), 5.1 (tt, *J* = 6.7, 1.5 Hz, 2H), 4.6 (dd, *J* = 11.3, 6.9 Hz, 4H), 3.4 (dd, *J* = 17.2, 8.3 Hz, 1H), 3.1 – 3.0 (m, 2H), 2.4 (td, *J* = 8.2, 7.5, 2.3 Hz, 2H), 2.1 – 2.0 (m, 10H), 1.7 (dd, *J* = 5.6, 1.4 Hz, 12H), 1.6 (d, *J* = 1.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.7, 174.8, 172.9, 142.6, 142.5, 139.8, 135.0, 132.0, 131.9, 129.6, 129.1, 123.9, 123.9, 118.3, 61.9, 61.7, 40.5, 39.9, 39.7, 39.6, 32.1, 32.0, 29.8, 29.5, 27.2, 26.5, 26.4, 25.8, 22.8, 17.8, 16.6, 16.6, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{33}H_{46}ClO_5$ $[M + H]^+$ 557.3028 found 493.1770.

tert-butyl 4-(4-cyanophenyl)-4-oxobutanoate (3aj)



The compound **3aj** was prepared according to the general procedure (GP1) starting from tert-butyl acrylate **1h** (1 mmol) and 4-cyano benzaldehyde **2o** (2 mmol). Off-white solid (198 mg, 76% yield), R_f = 0.25 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.59 Hz, 2H), 7.74 (d, *J* = 8.60 Hz, 2H), 3.22 (t, *J* = 6.45 Hz, 2H), 2.67 (t, *J* = 6.47 Hz, 2H), 1.41 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.2, 171.8, 139.7, 132.5, 128.5, 118.0, 116.4, 80.9, 33.8, 29.2, 28.1. HRMS (ESI TOF) *m/z* calcd. For $C_{15}H_{18}NO_3$ $[M + H]^+$ 260.1281 found 260.1285.

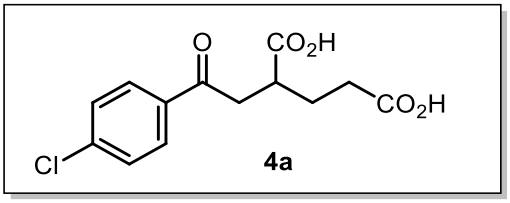
Methyl 4-(4-cyanophenyl)-4-oxobutanoate (3ak)



3ak

The compound **3ak** was prepared according to the general procedure (GP1) starting from methyl acrylate **1g** (1 mmol) and 4-cyano benzaldehyde **2o** (2 mmol). Off-white solid (175 mg, 80% yield), R_f = 0.2 (petroleum ether/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.55 Hz, 1H), 7.86 – 7.58 (m, 1H), 3.70 (s, 2H), 3.30 (t, *J* = 6.48 Hz, 1H), 2.78 (t, *J* = 6.44 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.0, 173.1, 139.5, 132.6, 128.6, 118.0, 116.6, 52.1, 33.8, 27.9. HRMS (ESI TOF) *m/z* calcd. For $C_{12}H_{12}NO_3$ $[M + H]^+$ 218.0812 found 218.0816.

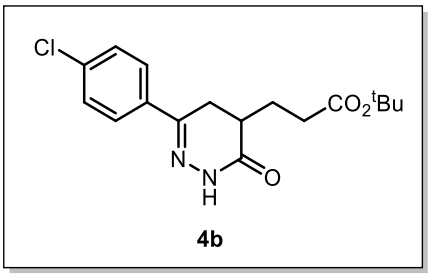
2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioic acid (4a)



4a

To a solution of ester **3h** (100 mg, 0.251mmol) in dichloromethane (3 mL) was added trifluoroacetic acid (3 mL). The mixture was stirred at room temperature for 2 h. The mixture was evaporated and partitioned between dichloromethane and water. The aqueous layer was washed with dichloromethane (10 mL x 3), combined the organic layers, dried over sodium sulfate, then filtered and concentrated in vacuum afford the title compound **4a** as brown solid (57mg, 79% yield). ^{1}H NMR (400 MHz, CD_3OD) δ 7.98 (d, *J* = 8.62 Hz, 1H), 7.50 (d, *J* = 8.60 Hz, 1H), 3.46 (dd, *J* = 18.07, 9.37 Hz, 1H), 3.14 (dd, *J* = 18.02, 4.36 Hz, 1H), 3.00 (dddd, *J* = 9.33, 7.60, 6.22, 4.33 Hz, 1H), 2.44 (ddd, *J* = 8.17, 6.98, 2.97 Hz, 1H), 2.08 – 1.81 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 198.9, 178.4, 176.7, 140.6, 136.6, 130.8, 129.9, 41.3, 41.0, 32.5, 28.1. HRMS (ESI TOF) *m/z* calcd. For $C_{13}H_{14}ClO_5$ $[M + H]^+$ 285.0524 found 285.0520.

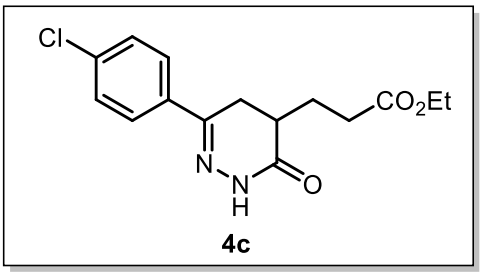
***t*ert-butyl 3-(6-(4-chlorophenyl)-3-oxo-2,3,4,5-tetrahydropyridazin-4-yl)propanoate (4b)**



4b

In 20 mL round bottomed flask the ester derivative **3h** (100 mg, 0.251mmol) was taken. To this 5 mL of hydrazine hydrate was added at room temperature. Then the reaction mixture was reflux for 10 h. After that the solvent was evaporated under reduce pressure. The residue was purified by silica gel column chromatography to give **4b** as white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.65 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.68 Hz, 2H), 3.06 (dd, *J* = 16.51, 6.57 Hz, 1H), 2.69 (dd, *J* = 16.51, 10.65 Hz, 1H), 2.62 – 2.51 (m, 1H), 2.45 (ddd, *J* = 7.92, 6.96, 4.16 Hz, 2H), 2.13 (ddt, *J* = 13.96, 8.01, 6.83 Hz, 1H), 1.81 (tt, *J* = 14.04, 6.74 Hz, 1H), 1.43 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 169.5, 149.6, 136.1, 134.2, 129.0, 127.2, 80.8, 35.2, 32.8, 28.2, 28.2, 25.2. HRMS (ESI TOF) *m/z* calcd. For $C_{17}H_{22}ClN_2O_5$ $[M + H]^+$ 337.1313 found 337.1309.

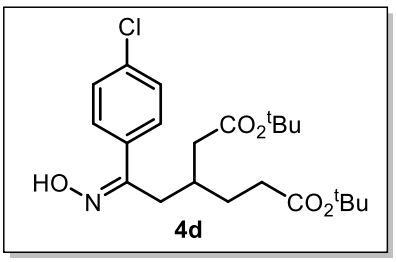
Ethyl 3-(6-(4-chlorophenyl)-3-oxo-2,3,4,5-tetrahydropyridazin-4-yl)propanoate (4c)



4c

In 20 mL round bottomed flask the ester derivative **3f** (100 mg, 0.251mmol) was taken. To this 5 mL of hydrazine hydrate was added at room temperature. Then the reaction mixture was reflux for 10 h. After that the solvent was evaporated under reduce pressure. The residue was purified by silica gel column chromatography to obtain **4d** as white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.68 – 7.62 (m, 2H), 7.40 – 7.35 (m, 2H), 4.12 (q, *J* = 7.16 Hz, 2H), 3.06 (dd, *J* = 16.48, 6.51 Hz, 1H), 2.70 (dd, *J* = 16.45, 10.66 Hz, 1H), 2.65 – 2.49 (m, 3H), 2.16 (dtd, *J* = 14.16, 7.78, 6.73 Hz, 1H), 1.85 (dtd, *J* = 13.86, 7.58, 6.07 Hz, 1H), 1.24 (t, *J* = 7.12 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.1, 169.6, 149.6, 136.1, 134.2, 129.0, 127.2, 60.7, 35.1, 31.7, 28.2, 25.2, 14.3. HRMS (ESI TOF) *m/z* calcd. For $C_{15}H_{18}ClN_2O_3$ $[M + H]^+$ 309.1000 found 309.1004.

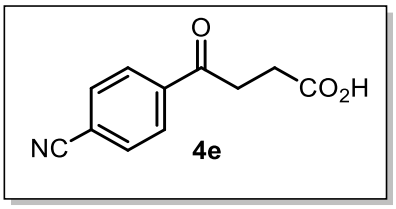
Di-tert-butyl (*Z*)-3-(2-(4-chlorophenyl)-2-(hydroxyimino)ethyl)hexanedioate (4d)



4d

A mixture di-tert-butyl 2-(2-(4-chlorophenyl)-2-oxoethyl)pentanedioate **3h** (0.251 mmol), hydroxylamine hydrochloride (0.753 mmol) and pyridine in (0.753 mmol) in tert-butanol (3 mL) was stirred at 80 °C for 24 h until completion of the reaction as determined by TLC. The solvent was removed in vacuo. Water (10 mL) was added and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure to provide the glutarate substituted ketoximes **4c** as off-white semi solid (56 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.54 (d, *J* = 8.68 Hz, 2H), 7.33 (d, *J* = 8.64 Hz, 2H), 3.04 – 2.94 (m, 2H), 2.72 – 2.62 (m, 1H), 2.35 – 2.12 (m, 2H), 1.94 – 1.84 (m, 1H), 1.84 – 1.73 (m, 2H), 1.45 (dt, *J* = 7.87, 3.13 Hz, 1H), 1.40 (s, 9H), 1.32 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.9, 172.4, 156.7, 135.5, 134.0, 128.9, 128.0, 42.8, 33.1, 28.4, 28.2, 28.0, 27.9. HRMS (ESI TOF) *m/z* calcd. For $C_{22}H_{33}ClNO_5$ $[M + H]^+$ 426.2042 found 426.2038.

4-(4-cyanophenyl)-4-oxobutanoic acid (4e)

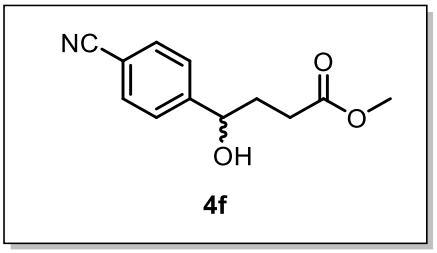


4e

To a solution of ester **3ai** (50 mg, 0.192 mmol) in dichloromethane (1.5 mL) was added trifluoroacetic acid (1.5 mL). The mixture was stirred at room temperature for 2 h. The mixture was evaporated and partitioned between dichloromethane and water. The aqueous layer was washed with dichloromethane (10 mLx3), combined the organic layers, dried over sodium sulfate, then filtered and concentrated in vacuum afford the title compound **4e** as brown solid (30mg, 77% yield). ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.15 – 8.08 (m, 2H), 7.88 – 7.83 (m, 2H), 3.34 – 3.30 (m, 2H), 2.76 – 2.65 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ 199.2,

176.3, 141.2, 133.7, 129.7, 119.0, 117.3, 34.7, 28.7. HRMS (ESI TOF) *m/z* calcd. For $C_{11}H_{10}NO_3$ $[M + H]^+$ 204.0655 found 204.0657.

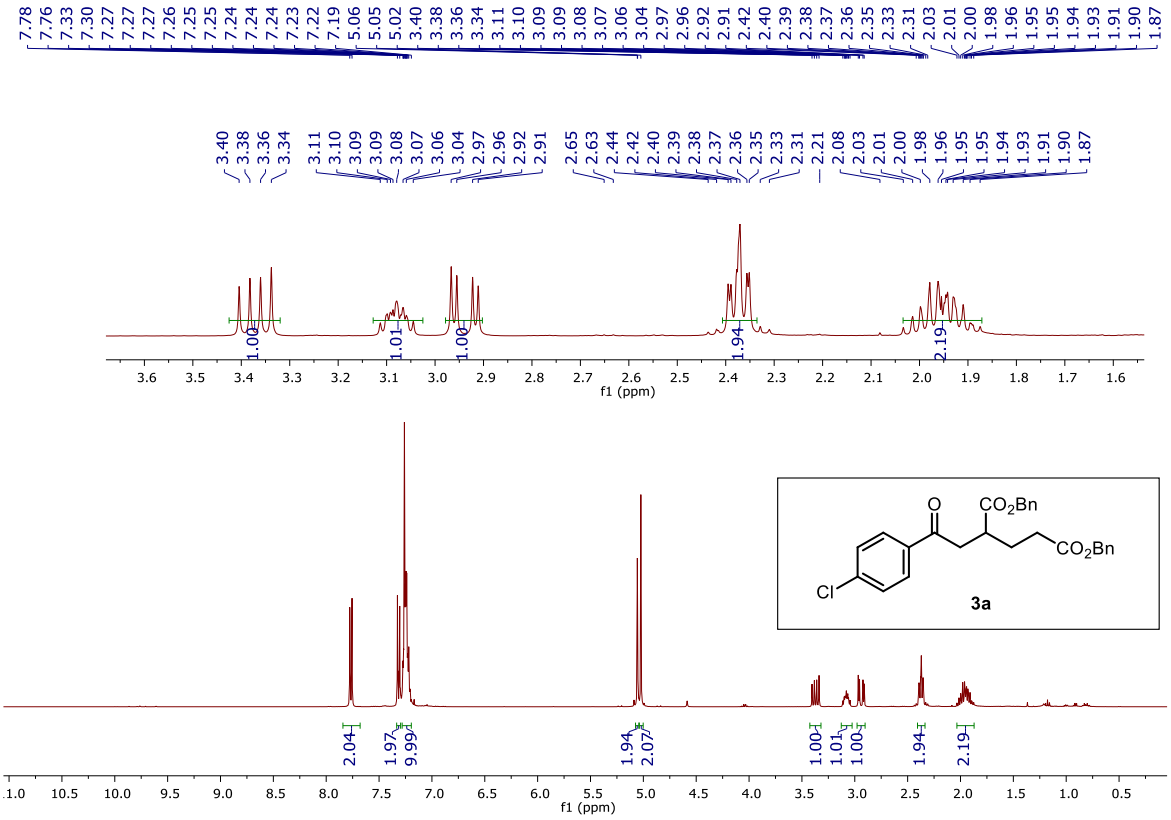
Methyl 4-(4-cyanophenyl)-4-hydroxybutanoate (ANI-AE-AP-11) (4f)



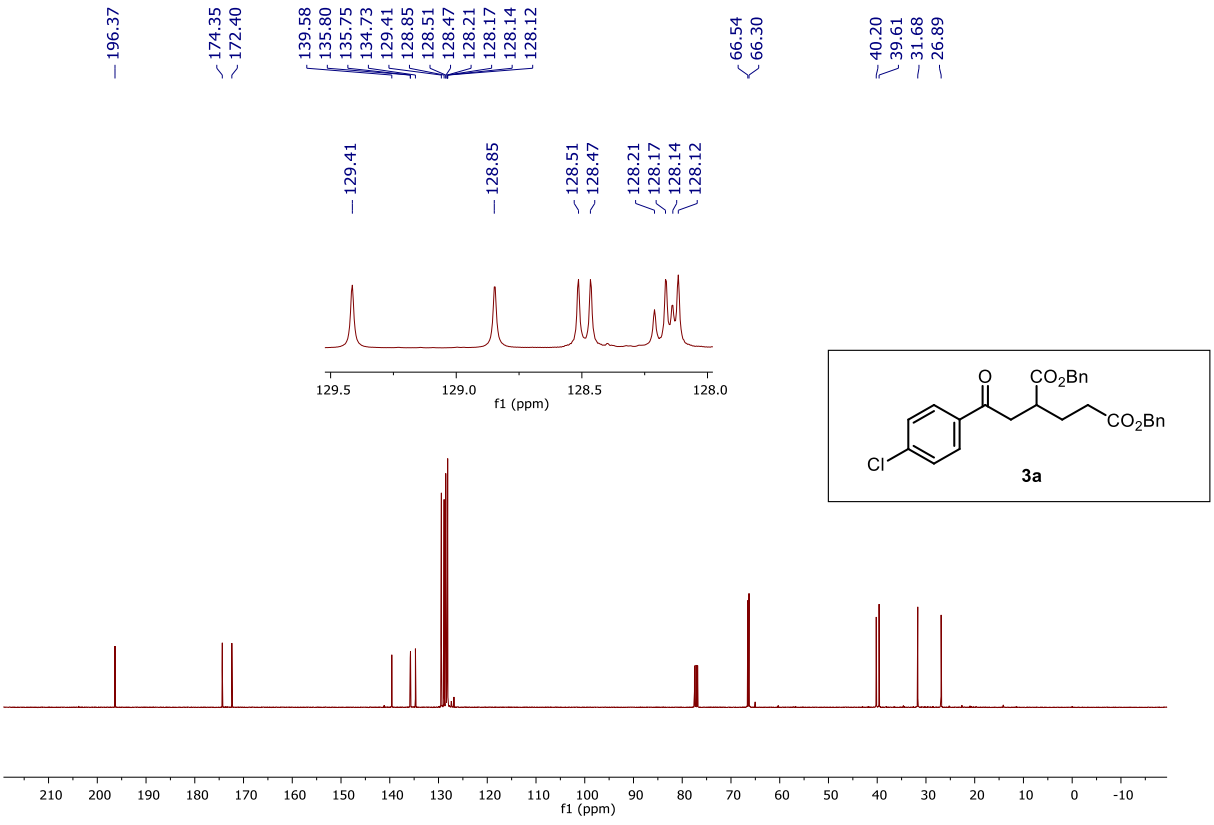
4f

To a solution of the keto ester **3aj** (50 mg, 0.192 mmol) in methanol (2 mL), sodium borohydride (2 equiv.) was added portion wise at 0 ˚C. The reaction mixture was allowed to warm up to room temperature. When the reduction was completed (according to the TLC) the solvent was carefully evaporated under reduced pressure. The residue was purified by silica gel column chromatography to obtain **4f** (36.5 mg, 72% yield, dr= 3:1). (Major diastereomer)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.47 (d, *J* = 8.10 Hz, 2H), 4.85 (dd, *J* = 7.97, 4.37 Hz, 1H), 3.68 (s, 3H), 2.46 (q, *J* = 6.75 Hz, 2H), 2.11 – 1.96 (m, 2H). ^{1}H NMR (400 MHz, $CDCl_3$) (Minor diastereomer) 2.81 – 2.62 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) (Major diastereomer) δ 174.5, 149.6, 132.5, 126.6, 118.9, 111.4, 72.8, 52.1, 33.8, 30.2. ^{13}C NMR (100 MHz, $CDCl_3$) (Minor diastereomer) δ 176.2, 144.8, 132.8, 125.9, 118.5, 112.5, 80.0, 31.0, 28.8. HRMS (ESI TOF) *m/z* calcd. For $C_{12}H_{14}NO_3$ $[M + H]^+$ 220.0968 found 220.0965.

13. Copies of ^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra:



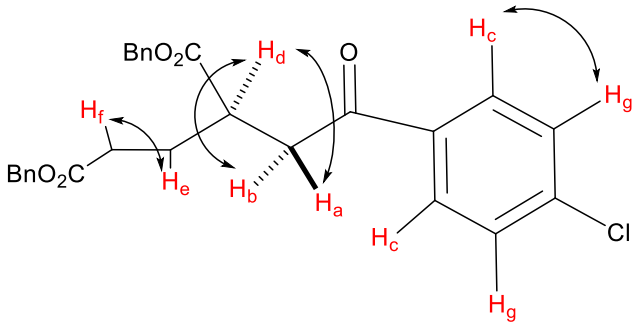
^{1}H NMR spectrum of **3a**, $CDCl_3$, 400 MHz



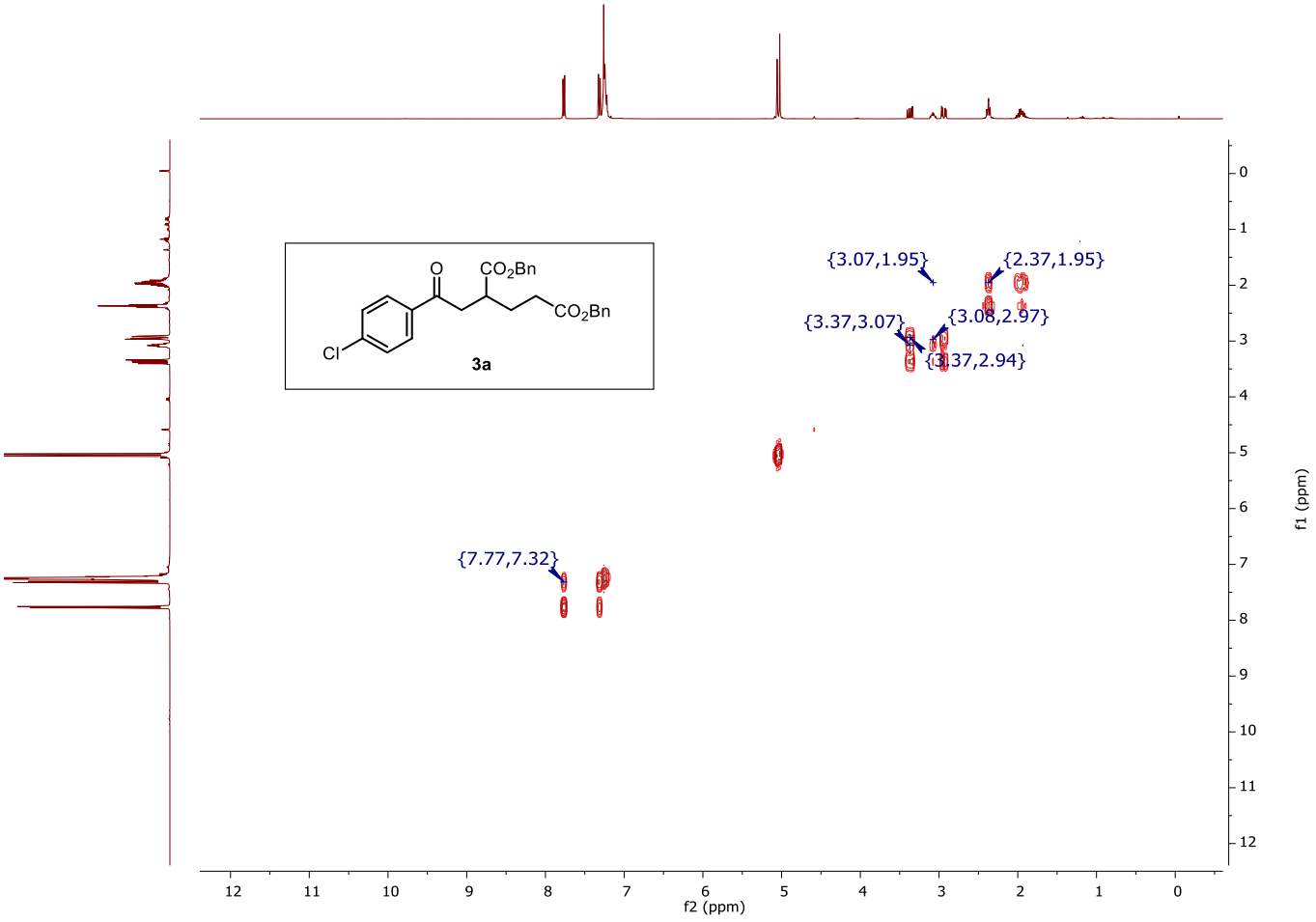
$^{13}C\{^{1}H\}$ NMR spectrum of **3a**, $CDCl_3$, 100 MHz

COSY

^{1}H-^{1}H correlation



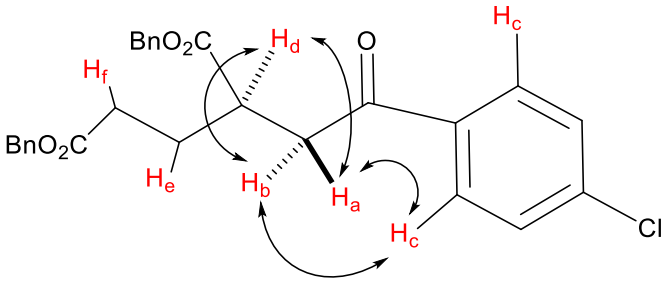
Ha = 3.37 δ ppm
Hb = 2.94 δ ppm
Hc = 7.77 δ ppm
Hd = 3.08 δ ppm
He = 1.95 δ ppm
Hf = 2.37 δ ppm
Hg = 7.32 δ ppm



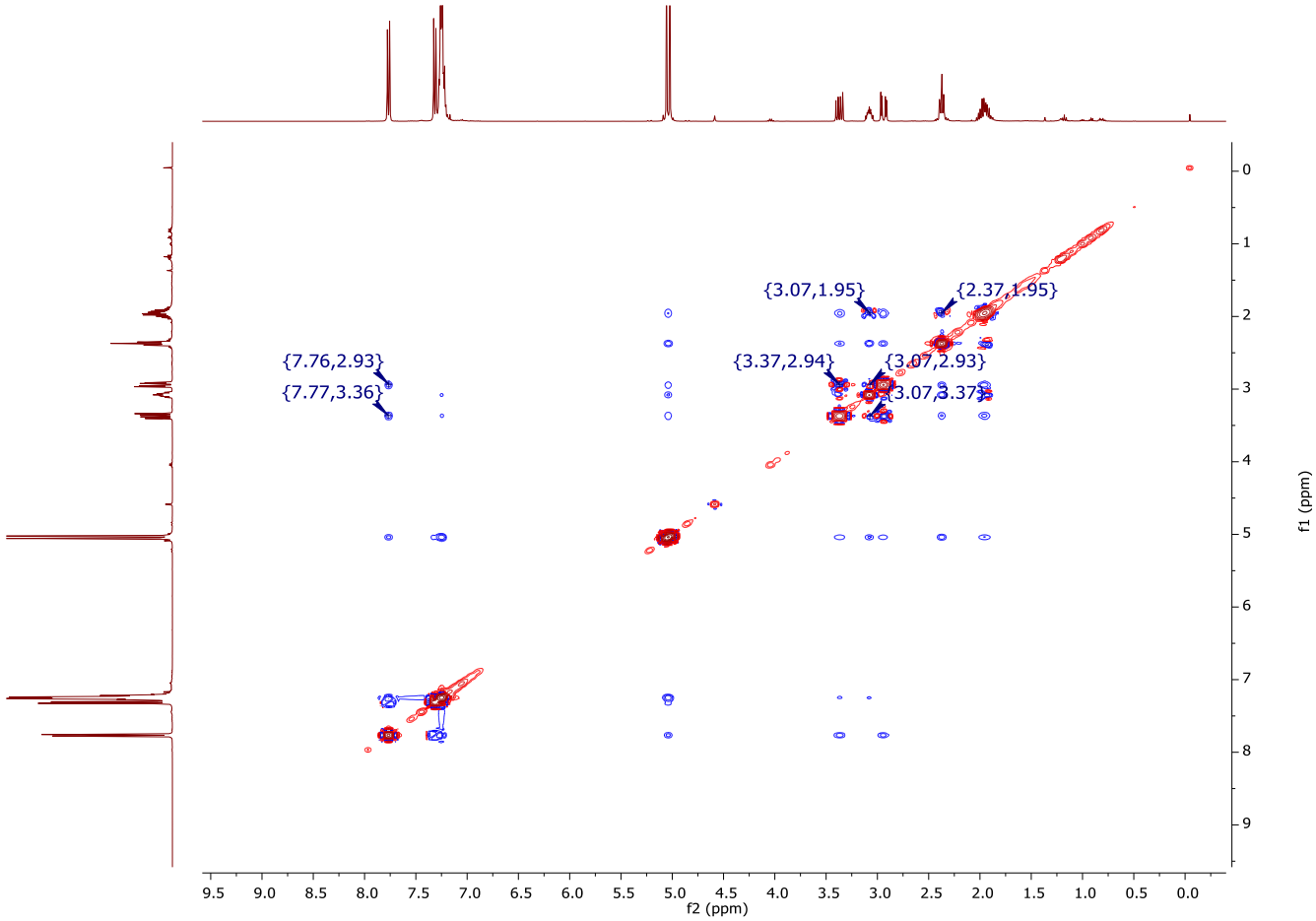
COSY (^{1}H-^{1}H) spectrum of **3a**

NOESY

^{1}H-^{1}H correlation



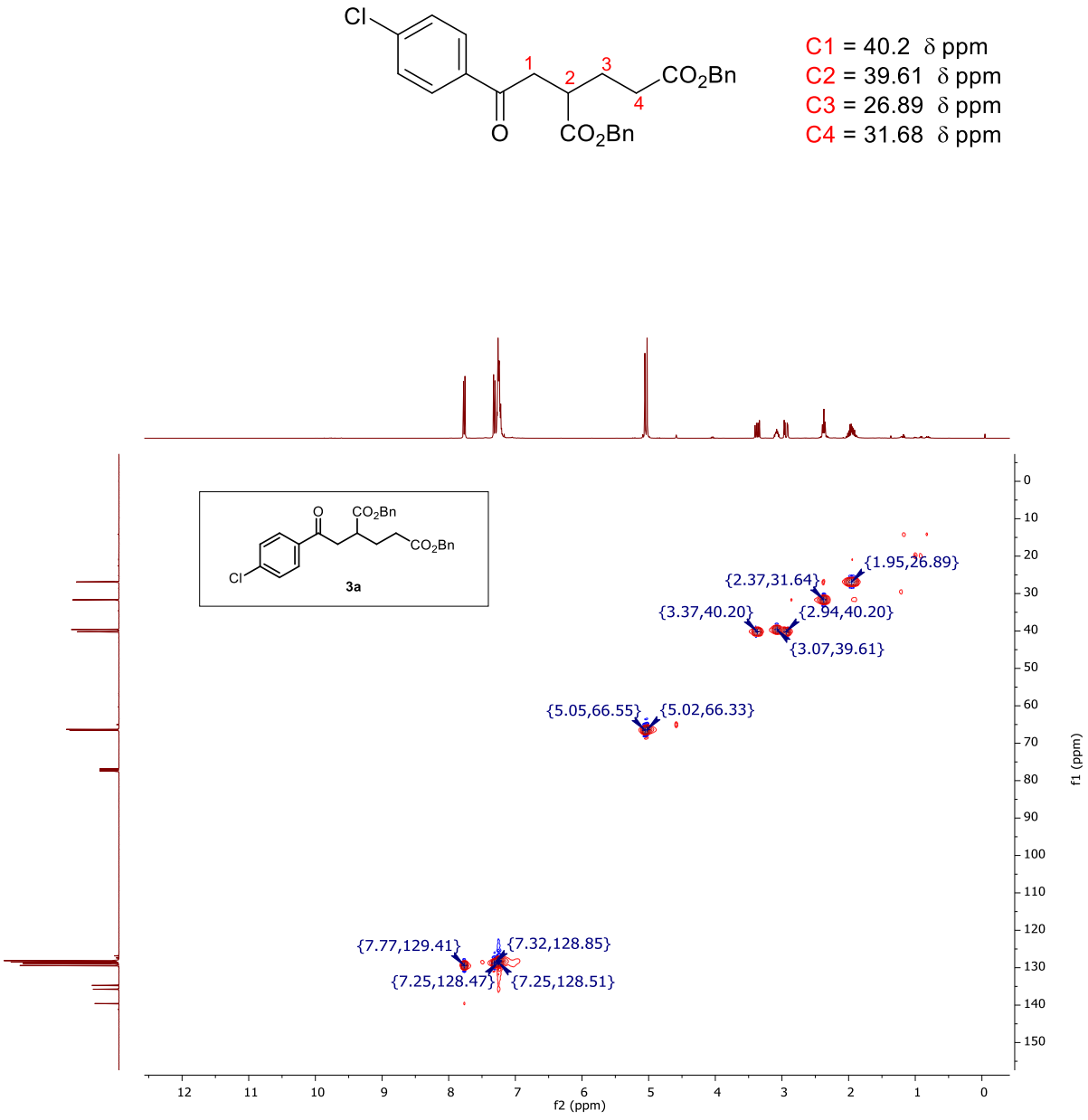
Ha = 3.37 δ ppm
Hb = 2.94 δ ppm
Hc = 7.77 δ ppm
Hd = 3.08 δ ppm
He = 1.95 δ ppm
Hf = 2.37 δ ppm



NOESY (^{1}H-^{1}H) spectrum of **3a**

HSQC

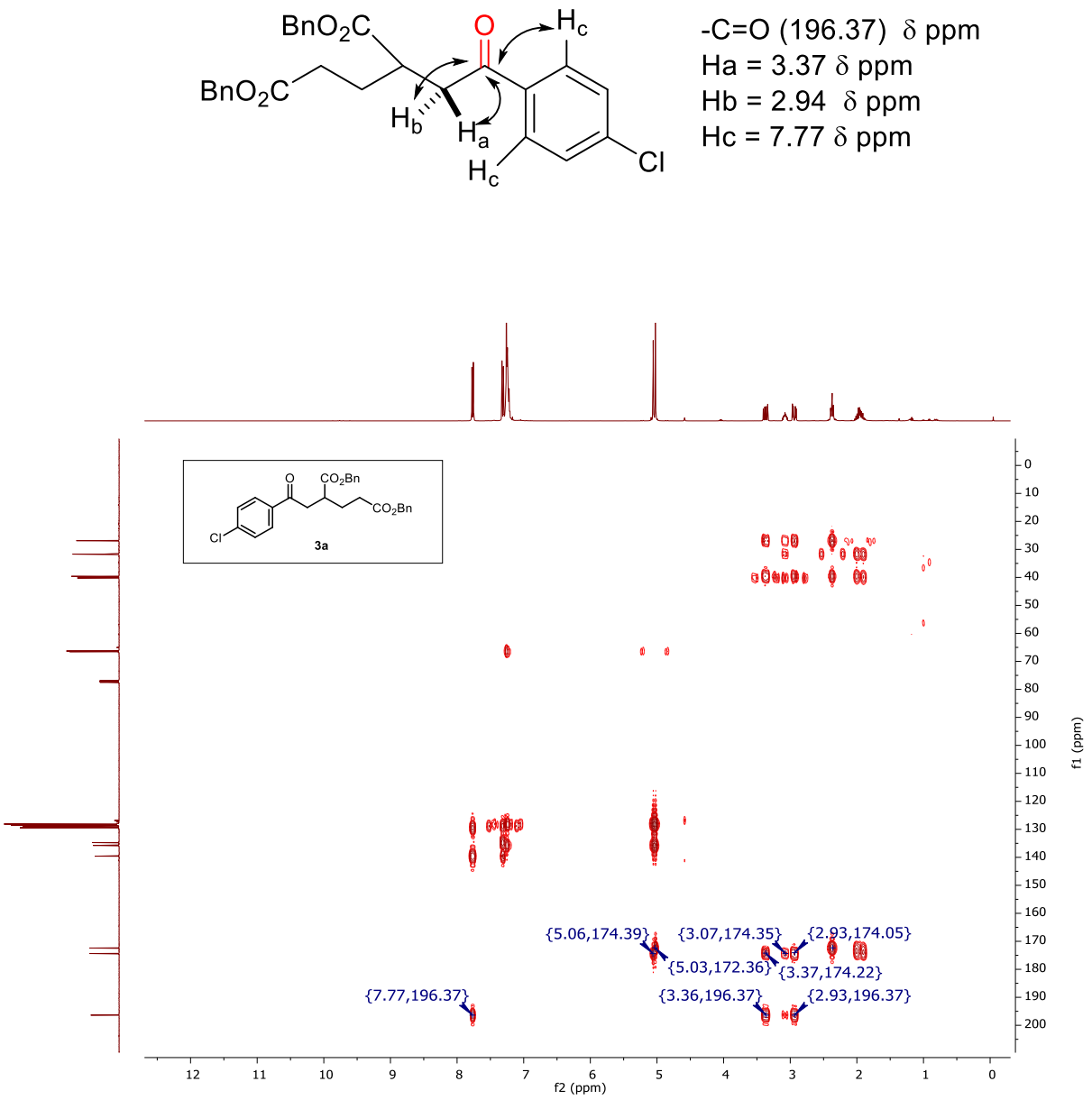
^{1}H-^{13}C correlation



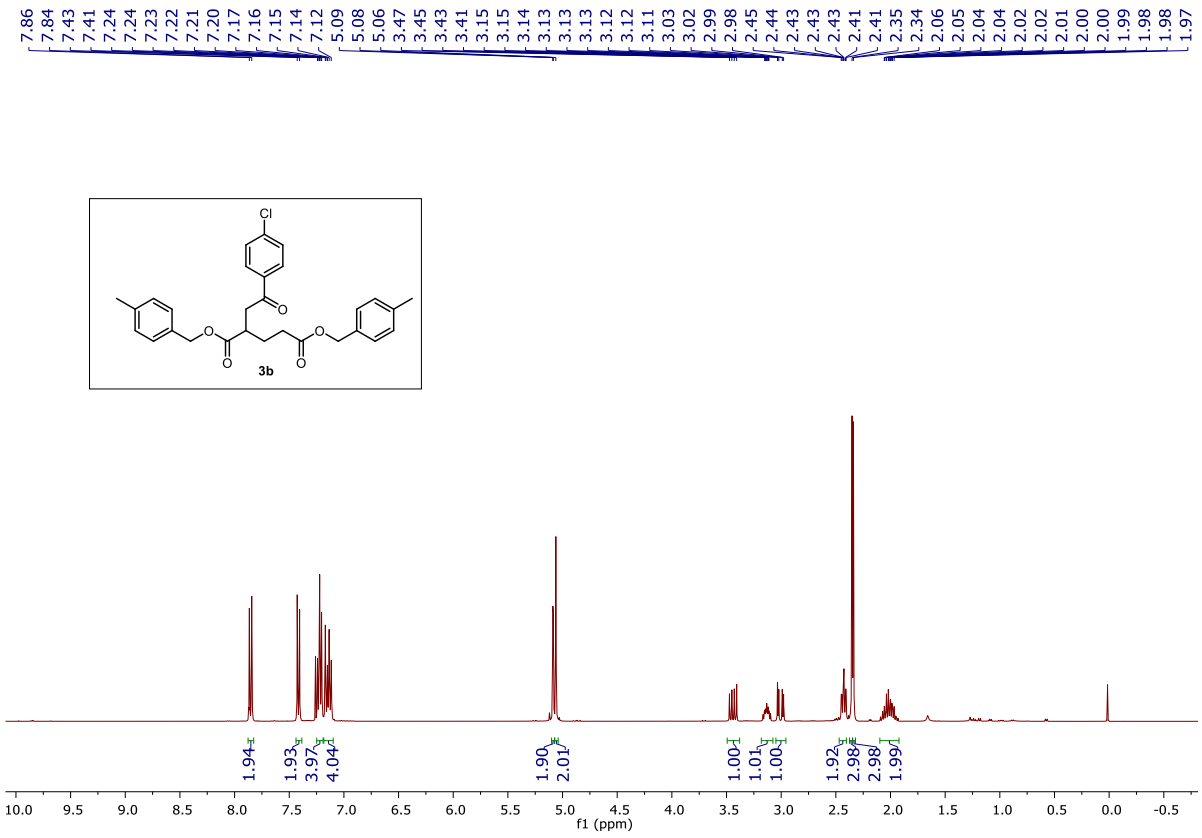
HSQC (^{1}H-^{13}C) spectrum of **3a**

HMBC

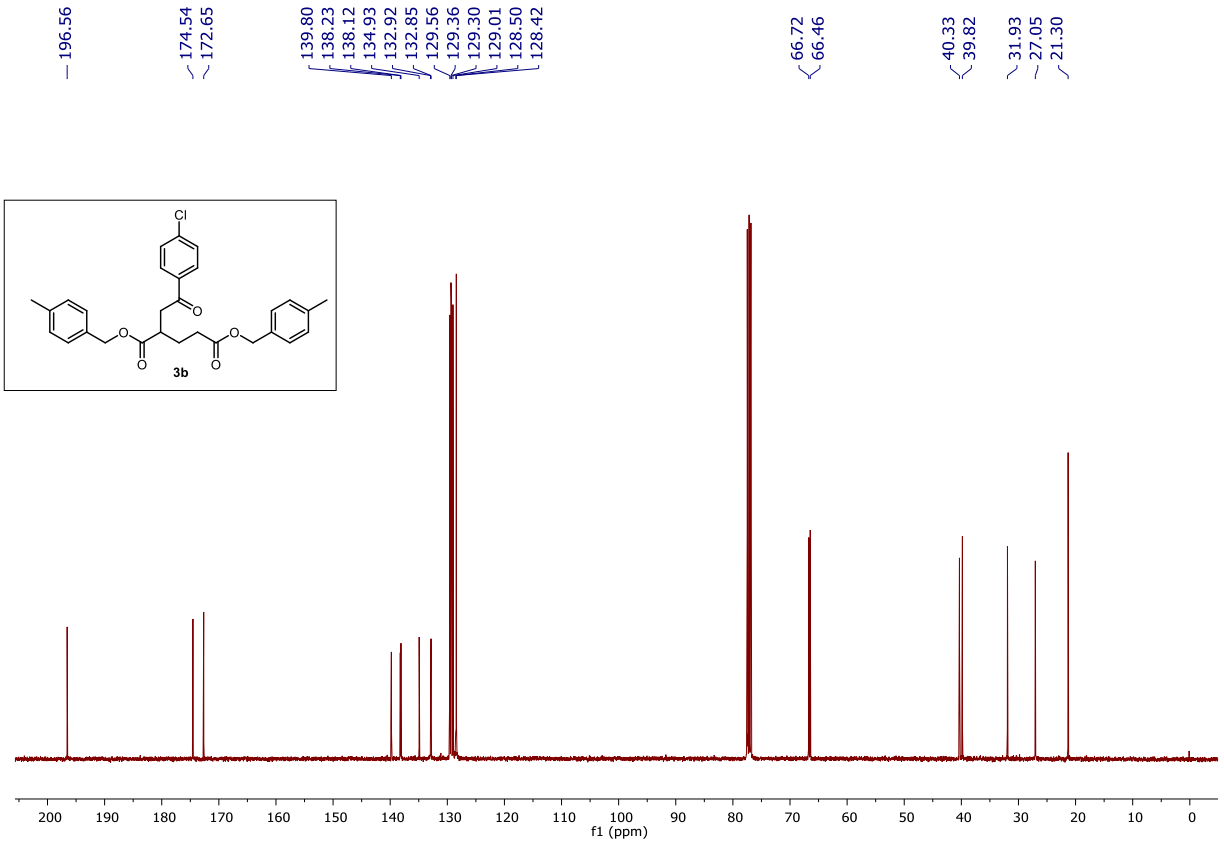
^{1}H-^{13}C correlation



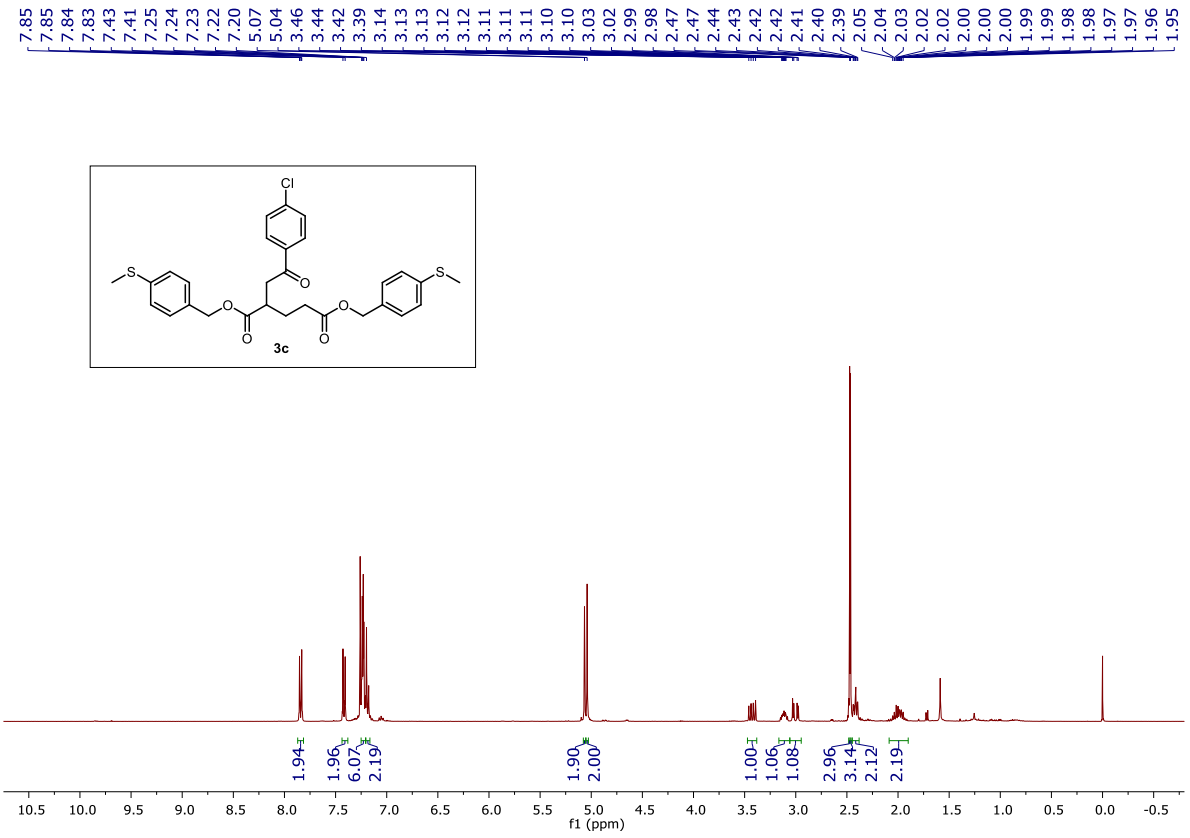
HMBC (^{1}H-^{13}C) spectrum of **3a**



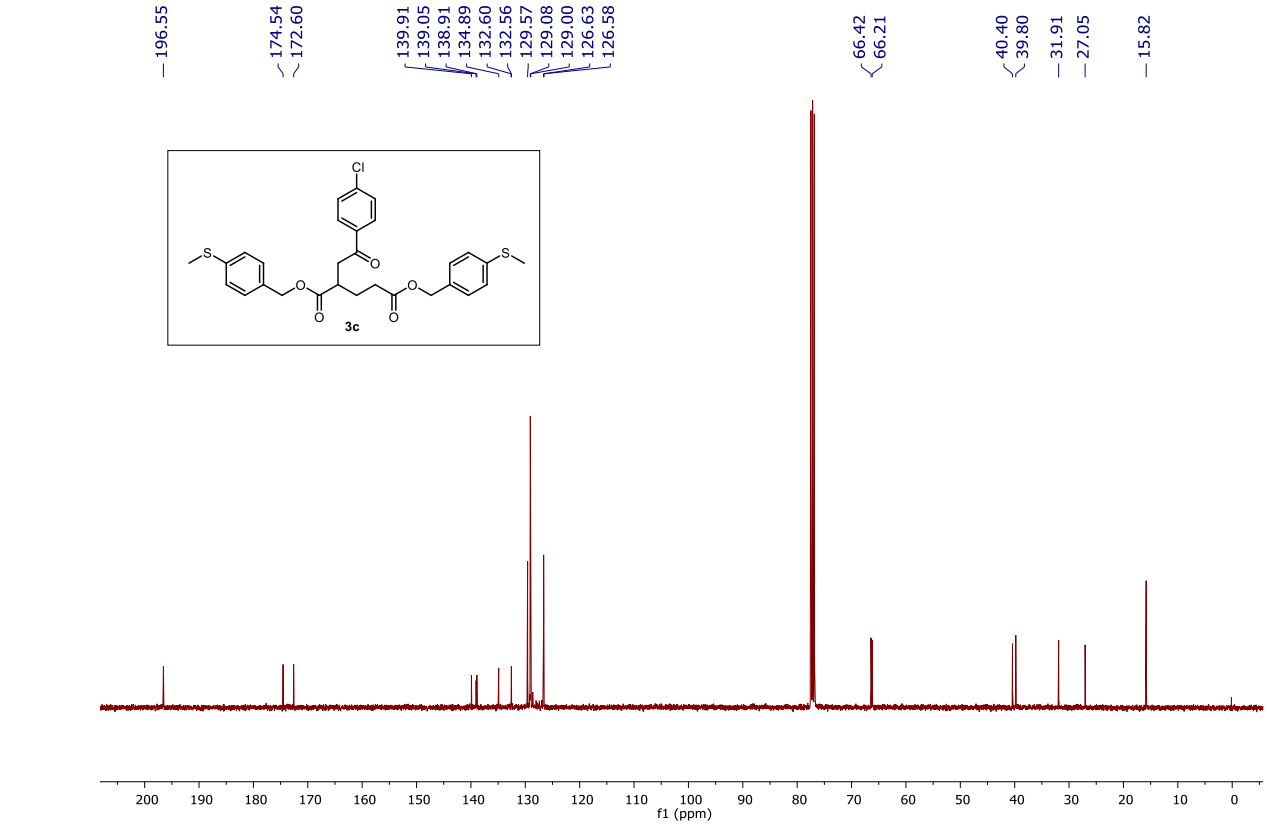
^{1}H NMR spectrum of **3b**, $CDCl_3$, 400 MHz



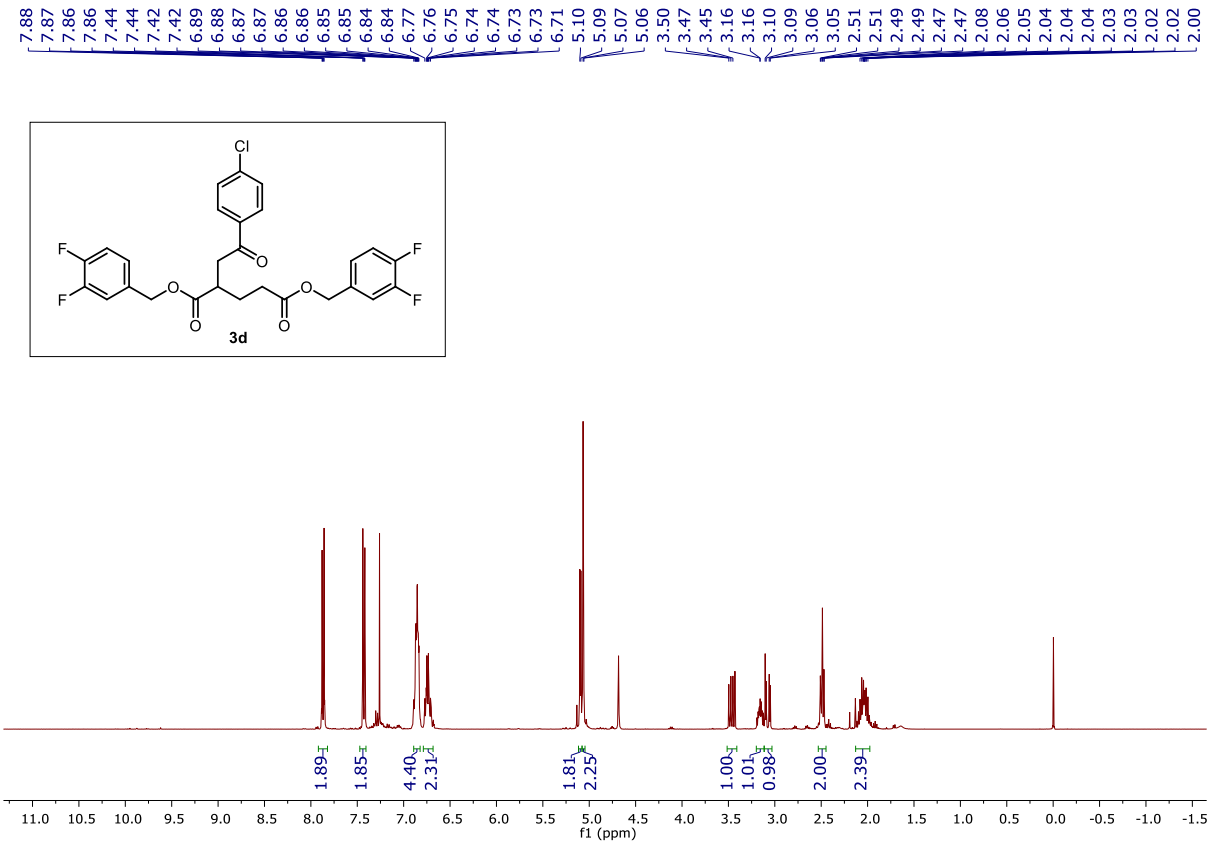
^{13}C {^{1}H} NMR spectrum of **3b**, $CDCl_3$, 100 MHz



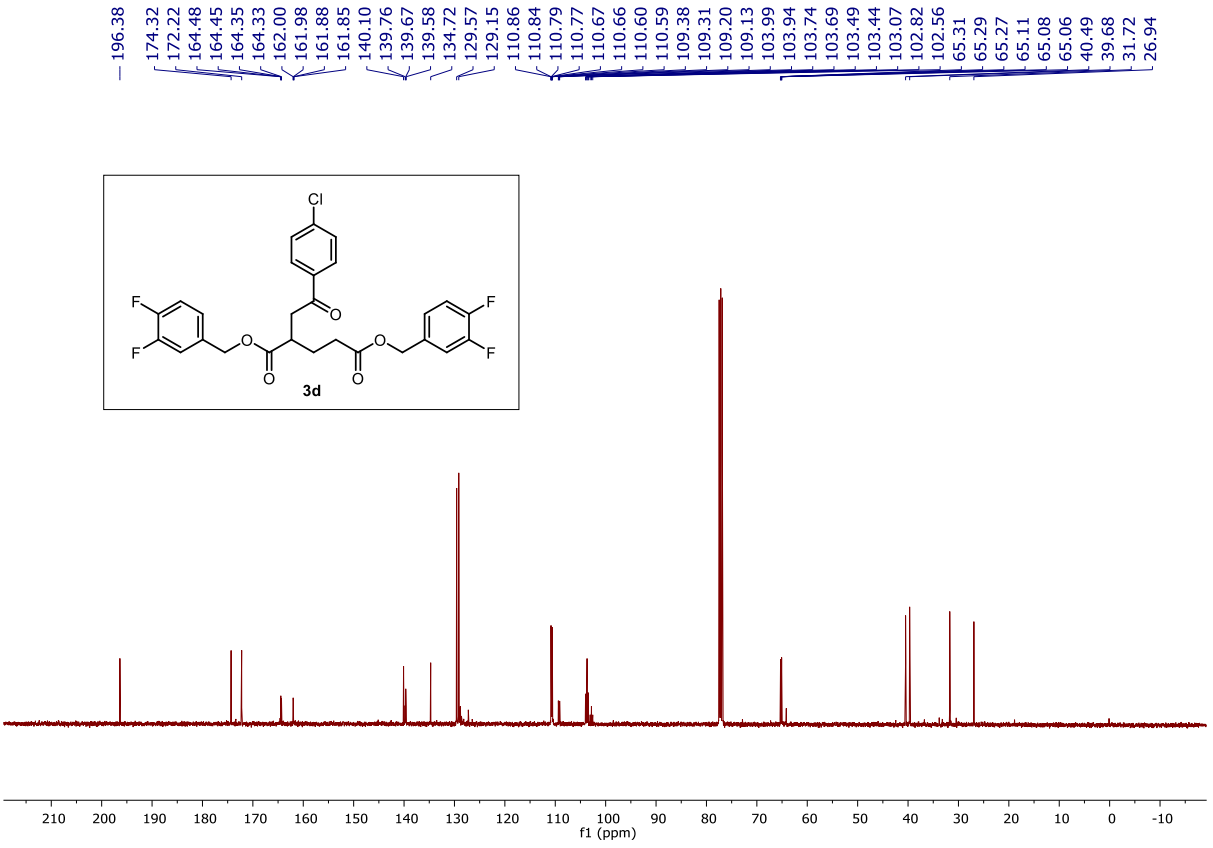
^{1}H NMR spectrum of **3c**, $CDCl_3$, 400 MHz



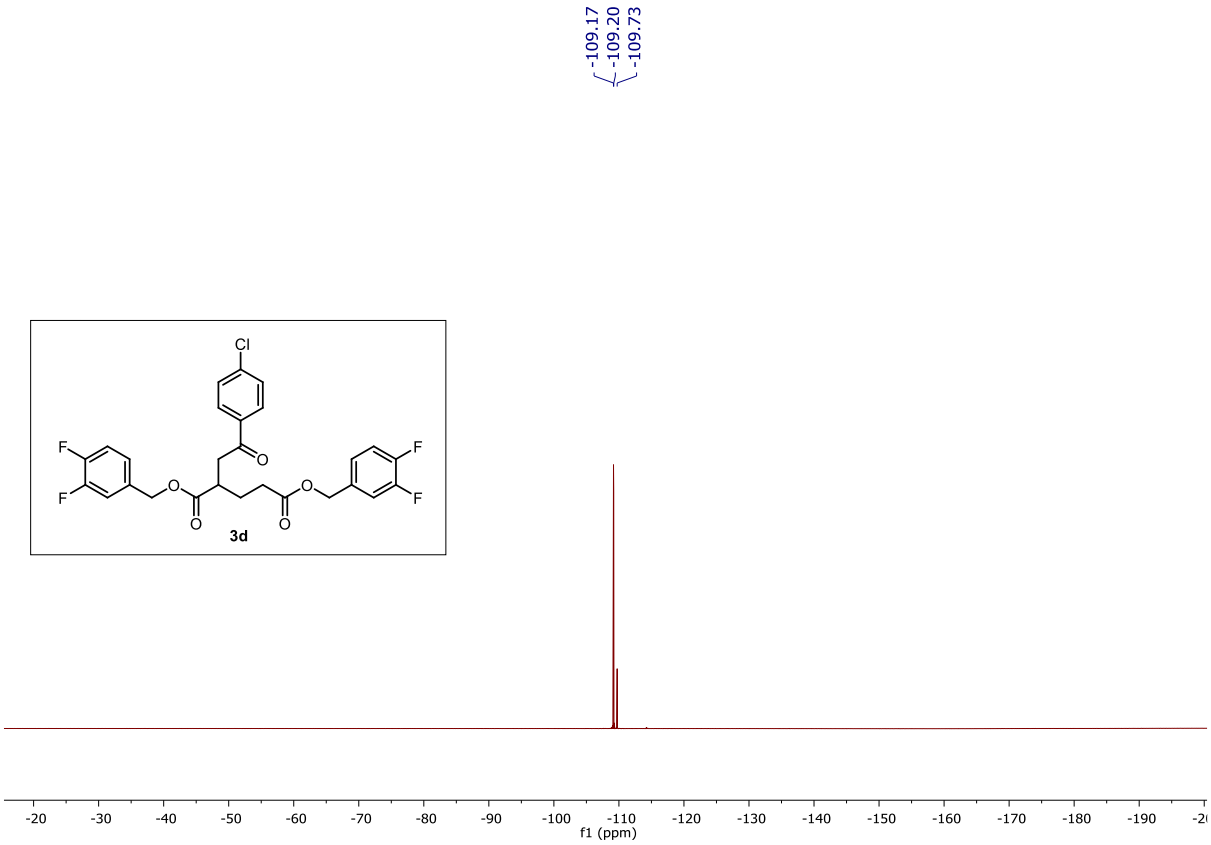
^{13}C {^{1}H} NMR spectrum of **3c**, $CDCl_3$, 100 MHz



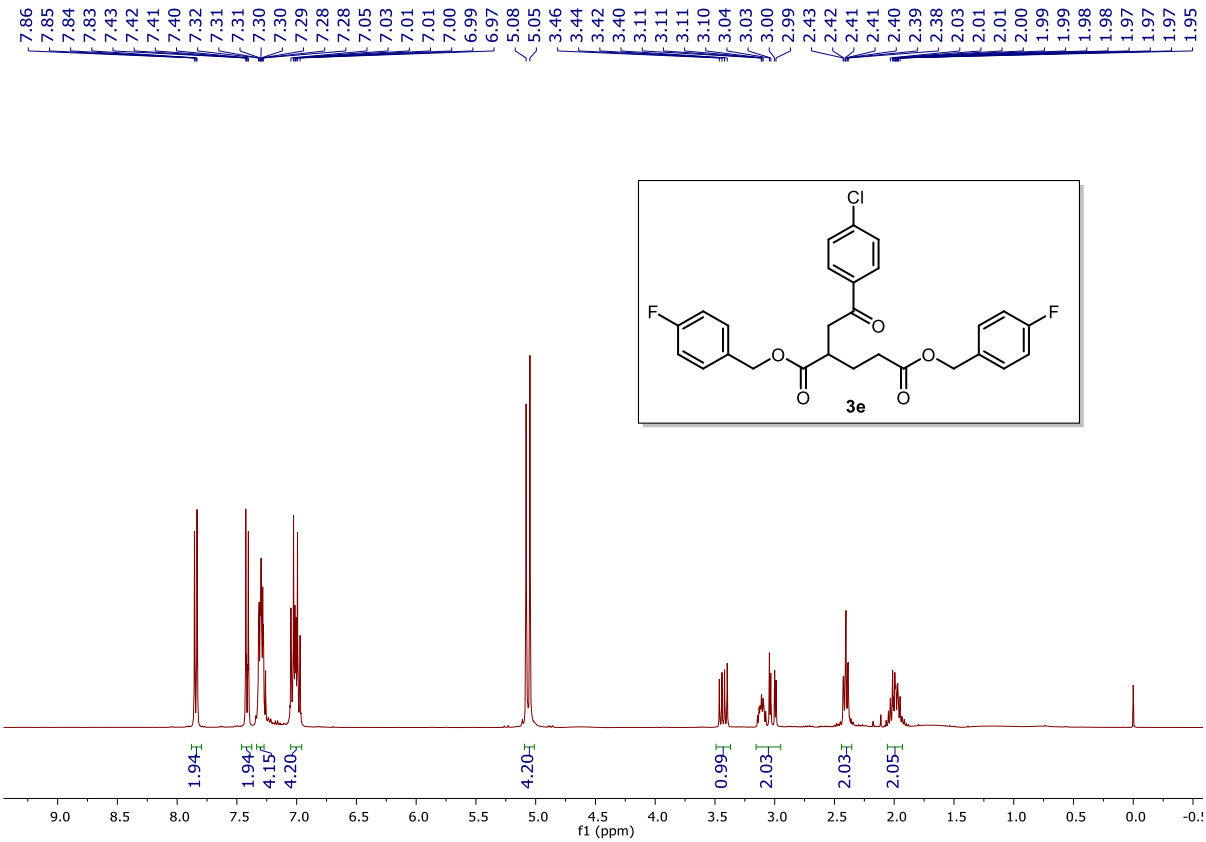
^{1}H NMR spectrum of **3d**, $CDCl_3$, 400 MHz



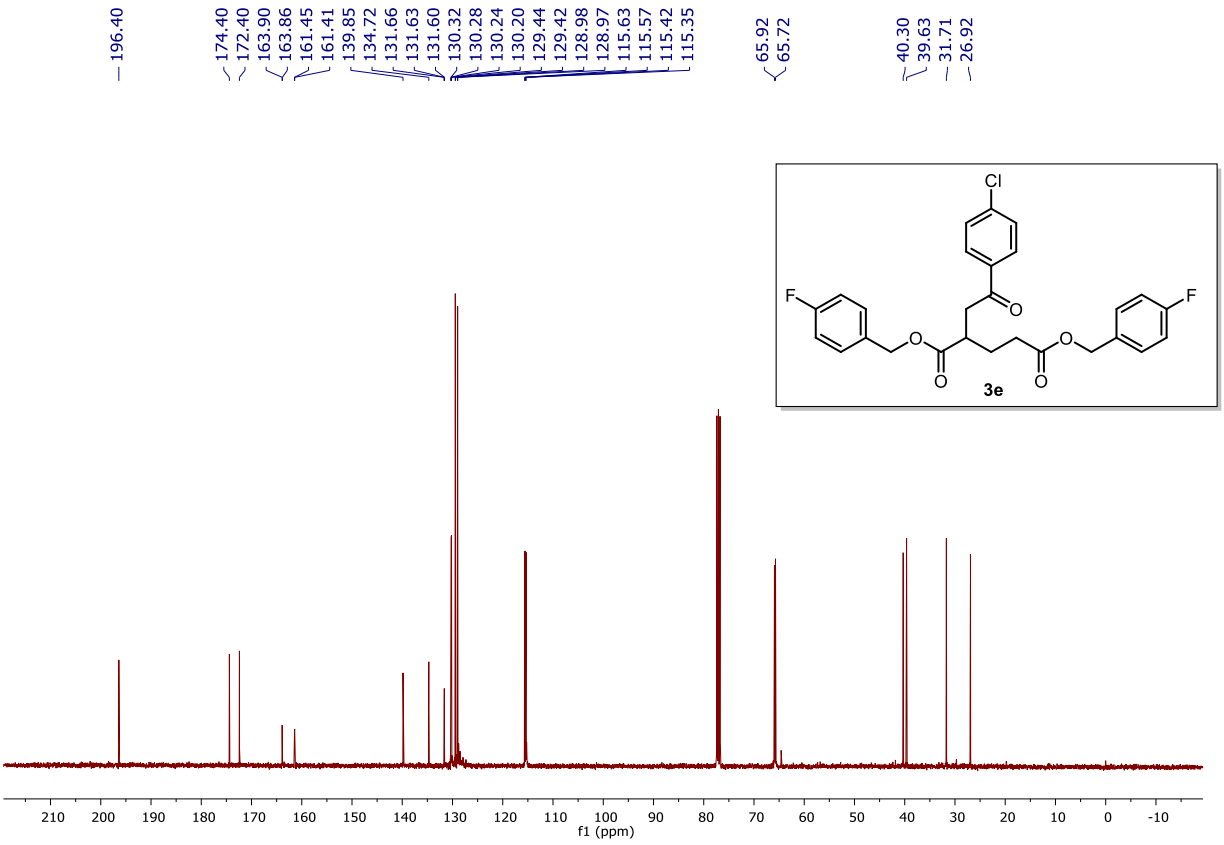
^{13}C {^{1}H} NMR spectrum of **3d**, $CDCl_3$, 100 MHz



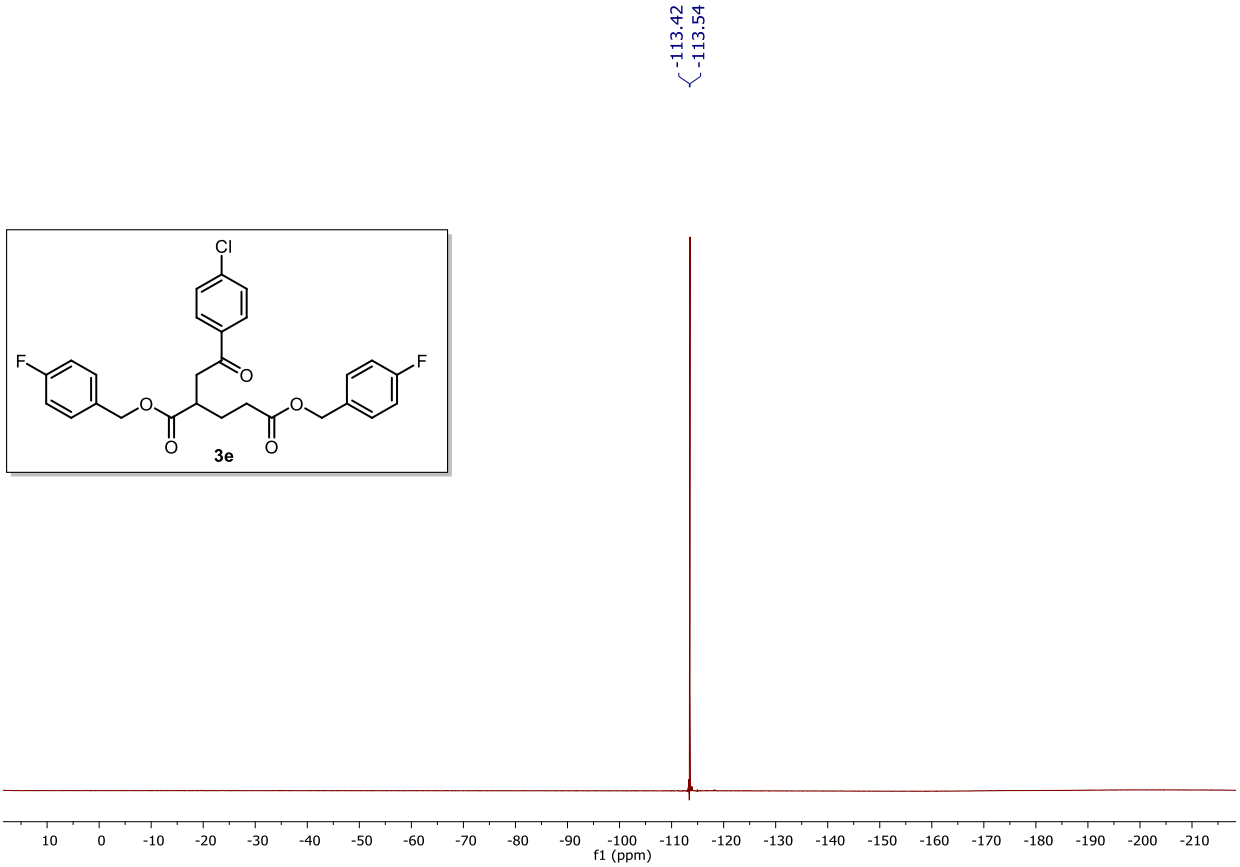
^{19}F NMR spectrum of **3d**, CDCl3, 377 MHz



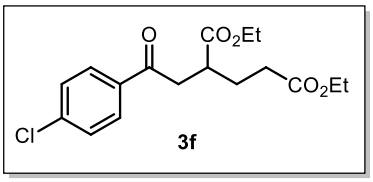
^{1}H NMR spectrum of **3e**, $CDCl_3$, 400 MHz

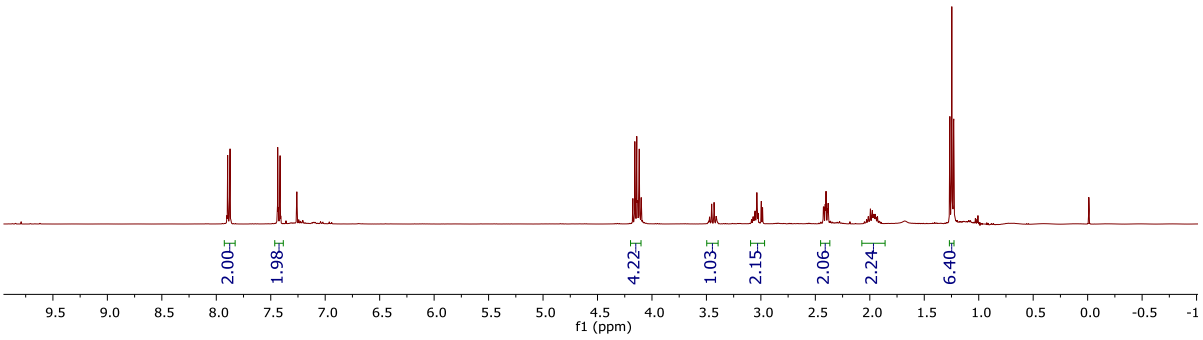


^{13}C{^{1}H} NMR spectrum of 3e, $CDCl_3$, 100 MHz

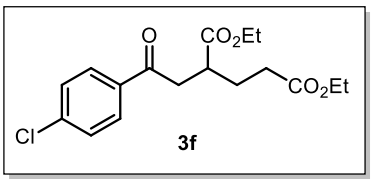


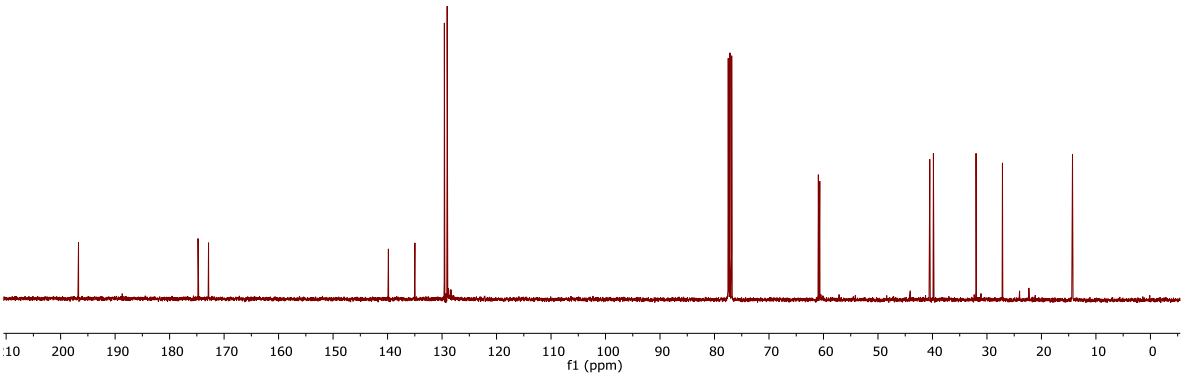
^{19}F NMR spectrum of **3e**, $CDCl_3$, 377 MHz



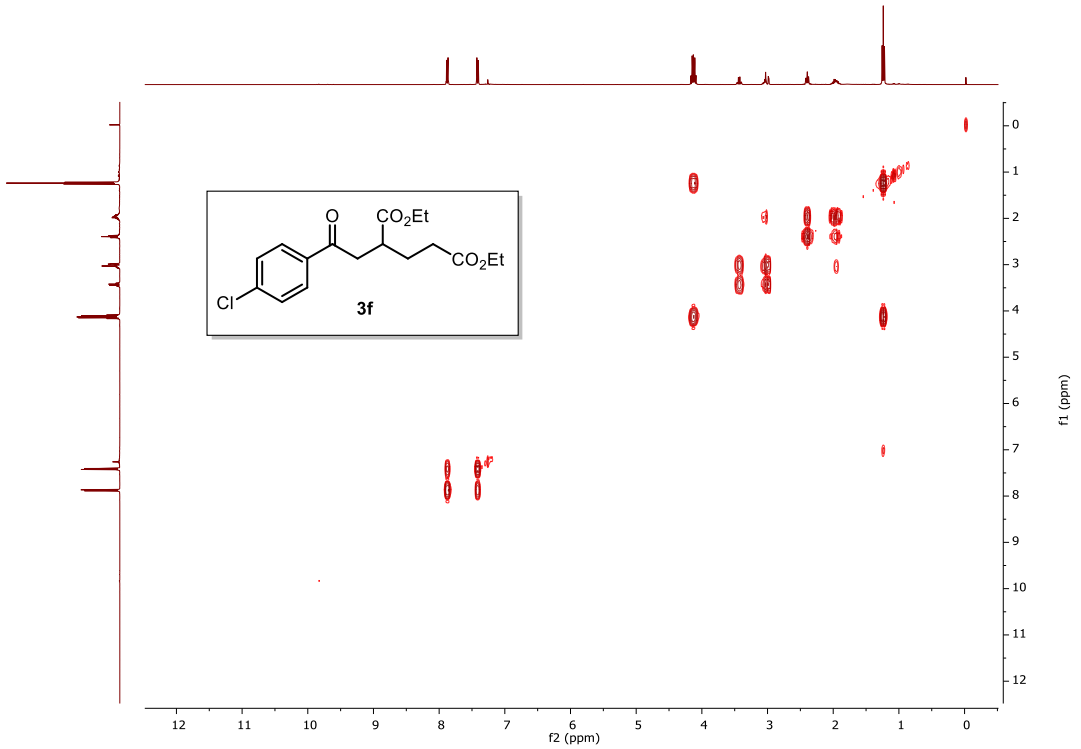


^{1}H NMR spectrum of **3f**, $CDCl_3$, 400 MHz

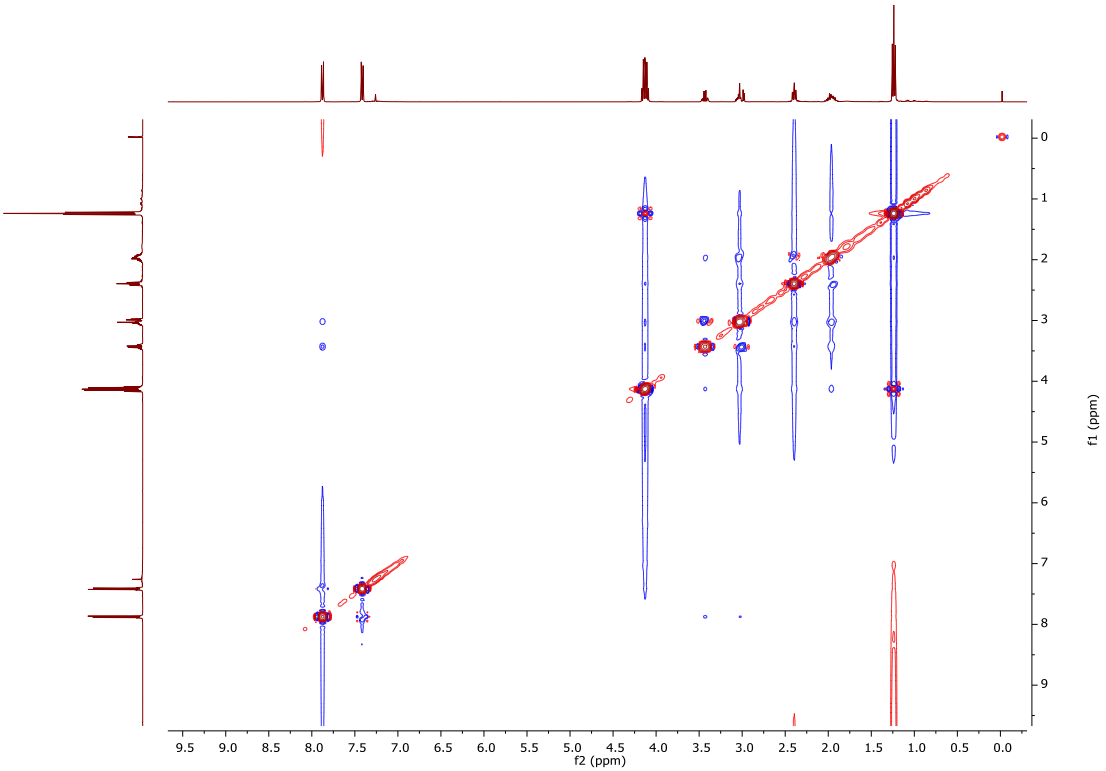




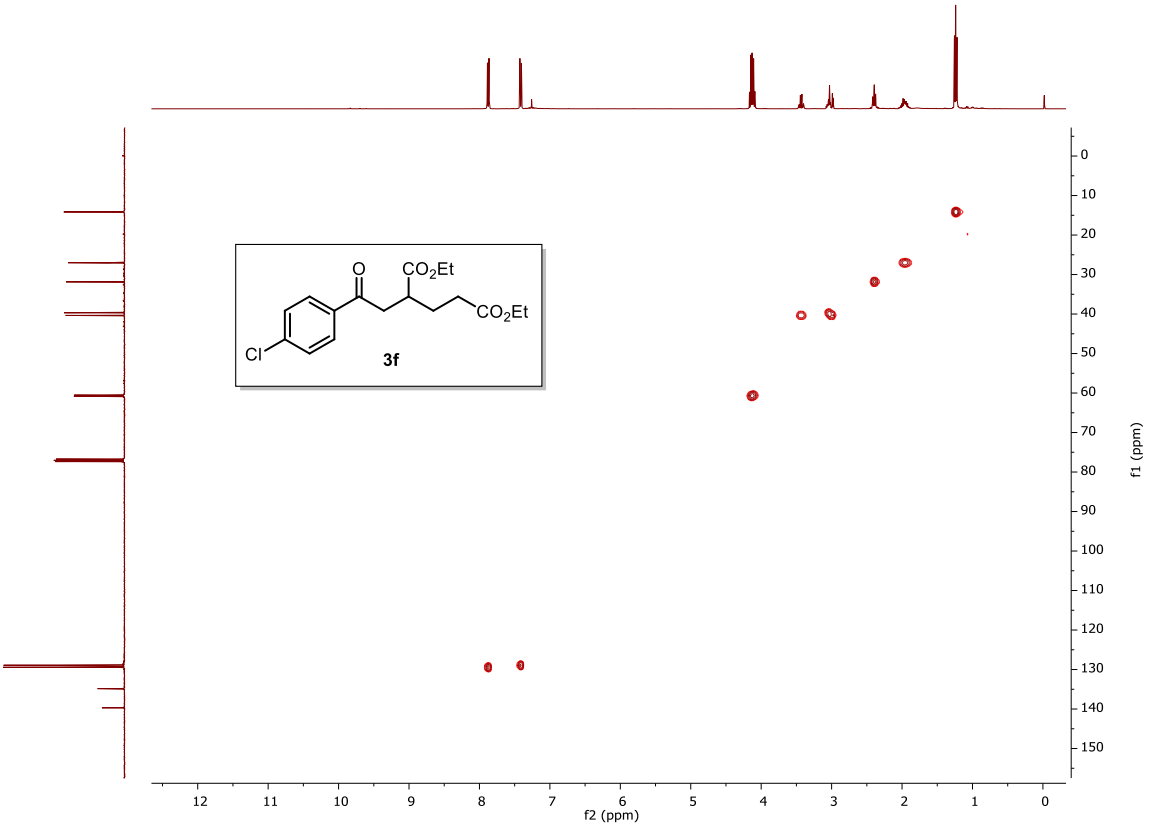
^{13}C {^{1}H} NMR spectrum of **3f**, $CDCl_3$, 100 MHz



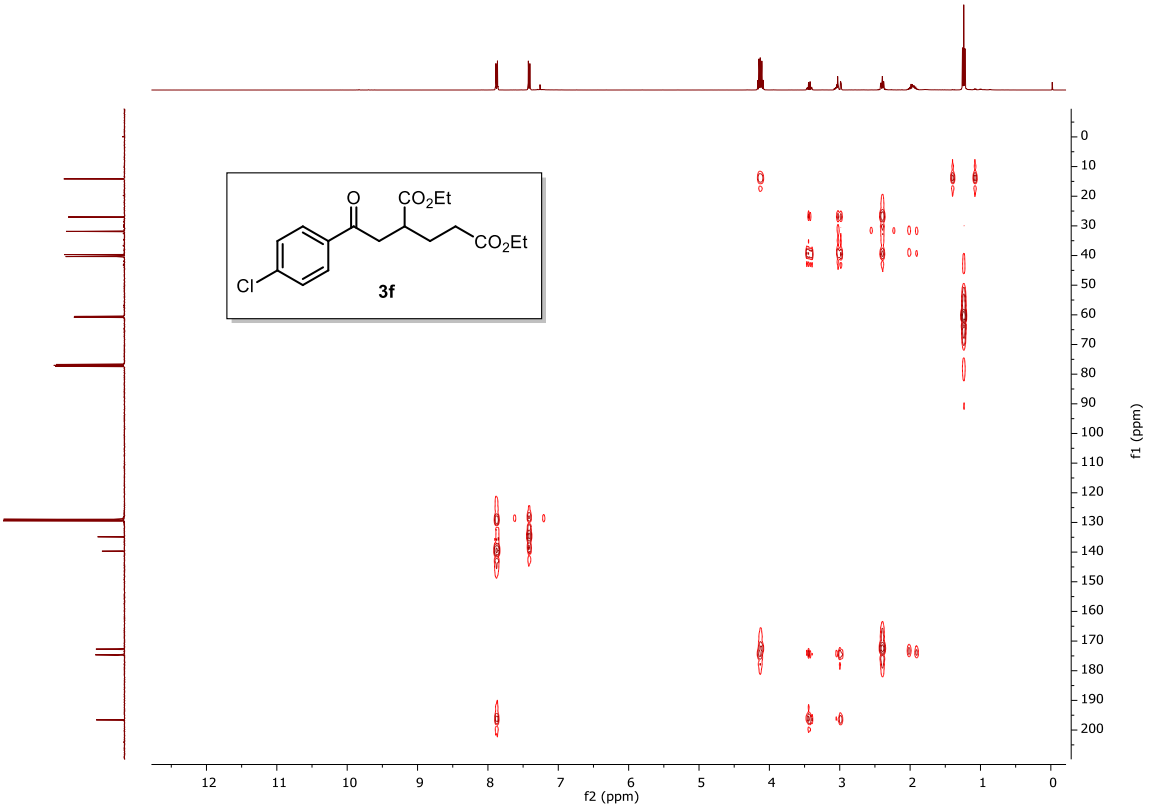
COSY (^{1}H-^{13}C) spectrum of **3f**



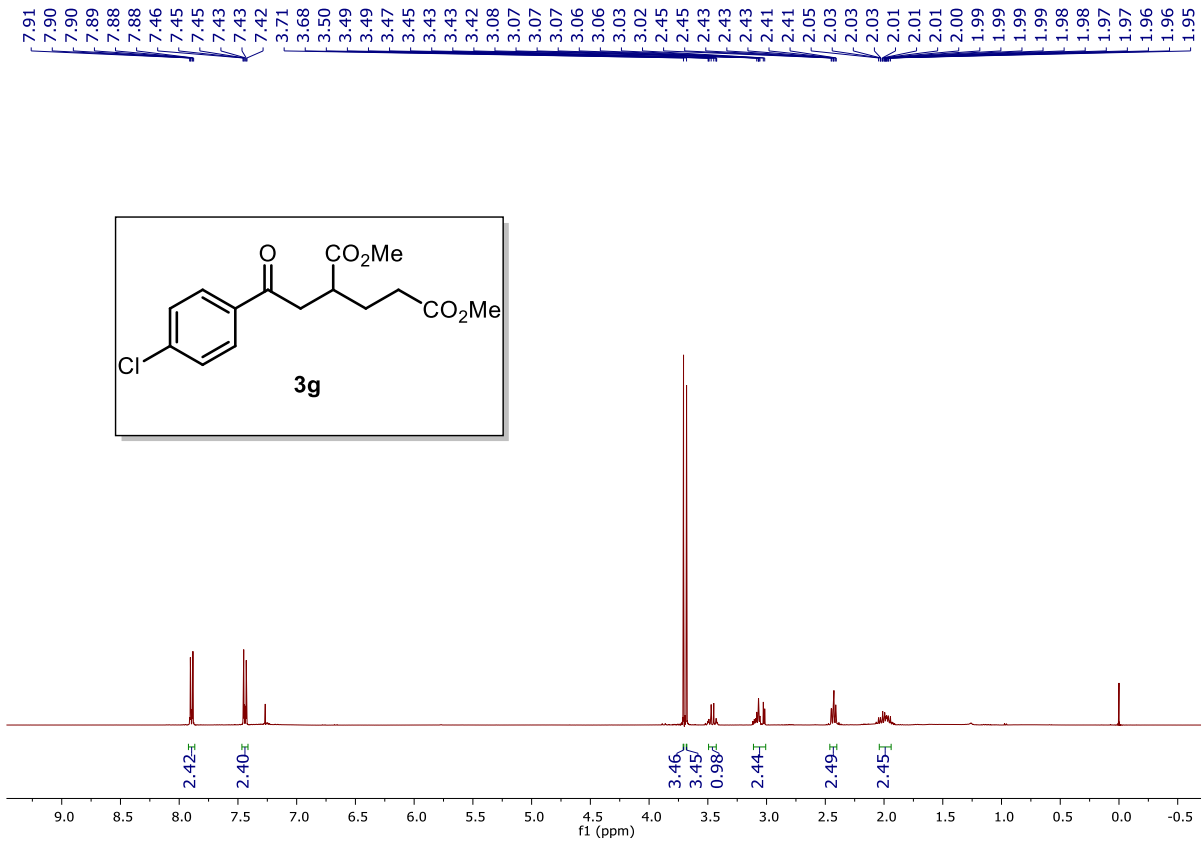
NOESY (^{1}H-^{13}C) spectrum of **3f**



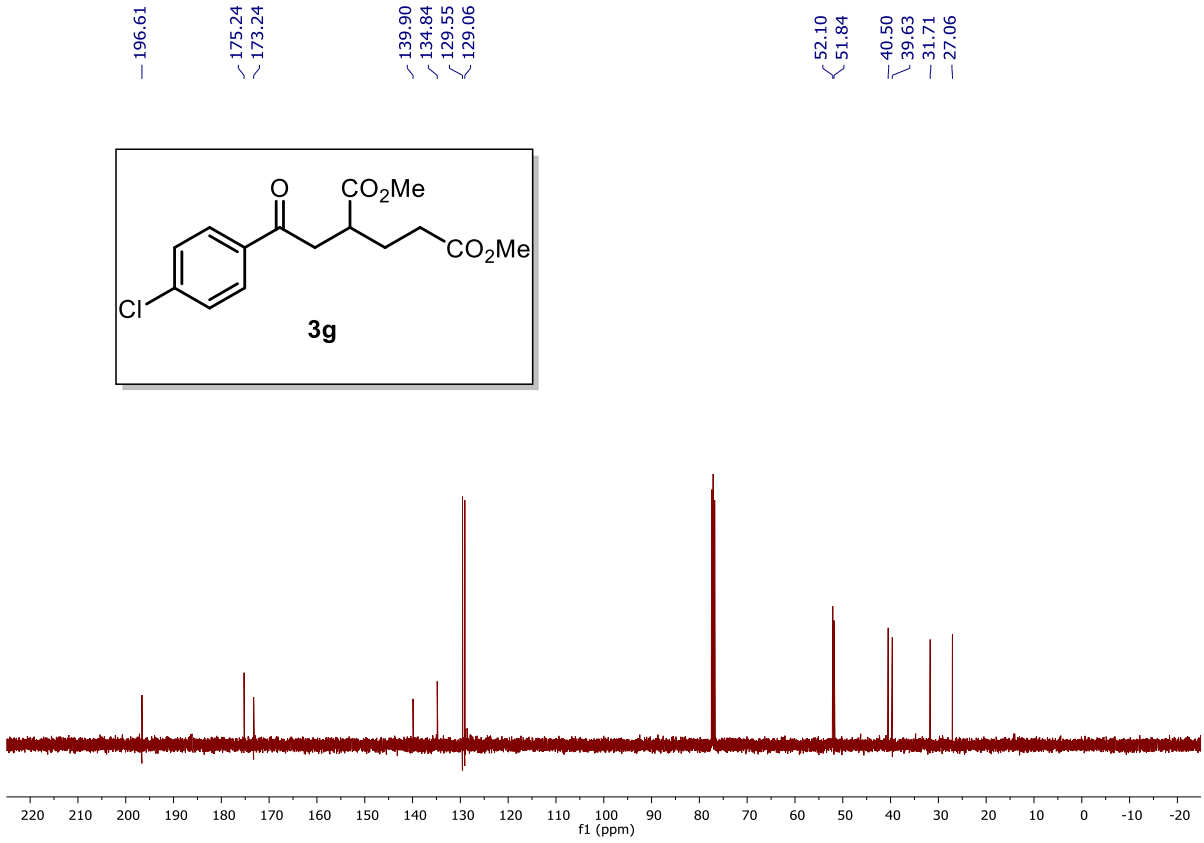
HSQC (^{1}H-^{13}C) spectrum of **3f**



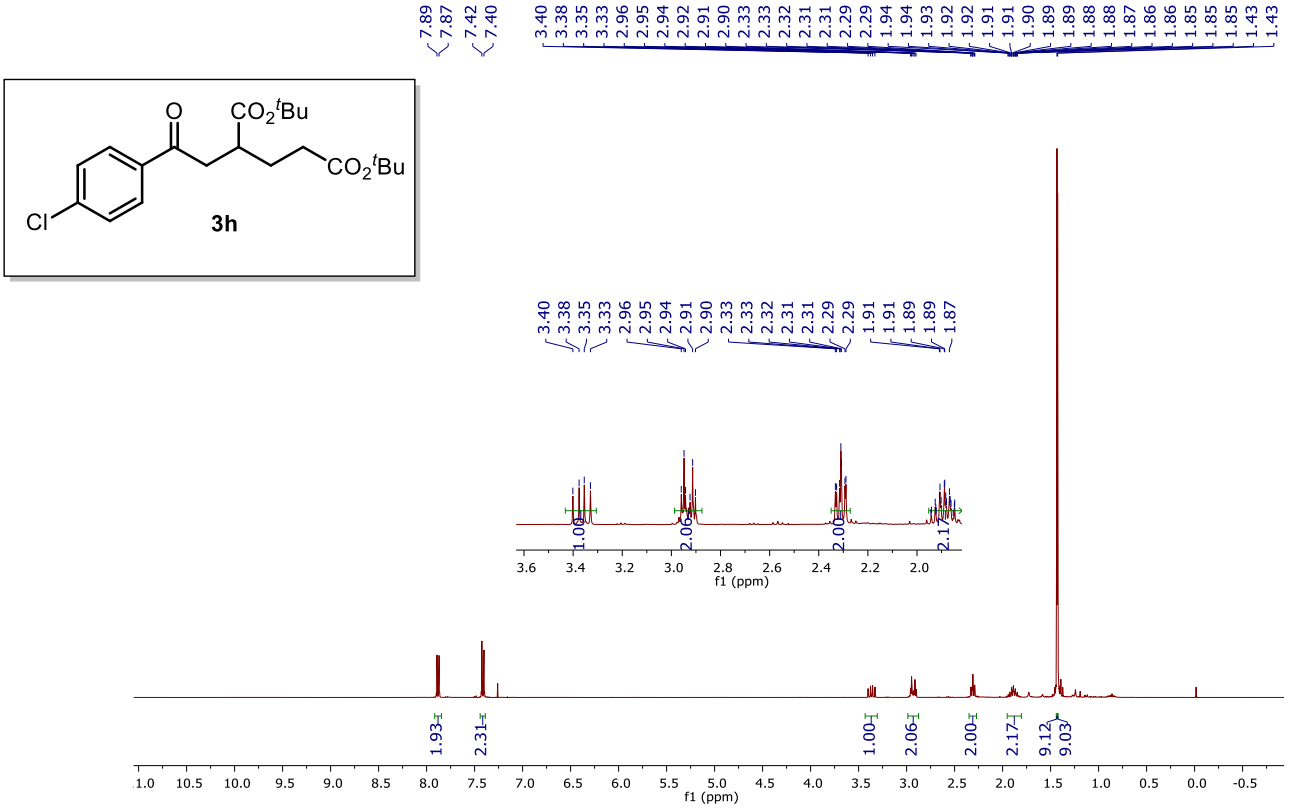
HMBC (^{1}H-^{13}C) spectrum of **3f**



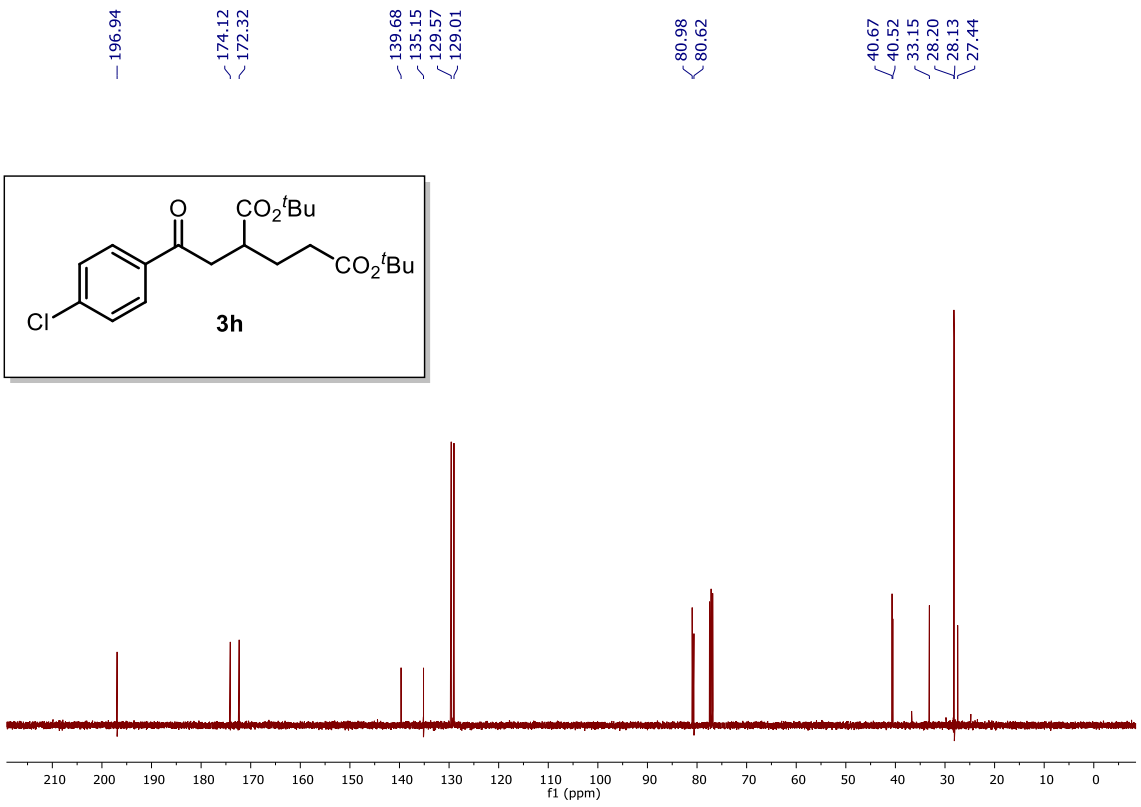
^{1}H NMR spectrum of **3g**, $CDCl_3$, 400 MHz



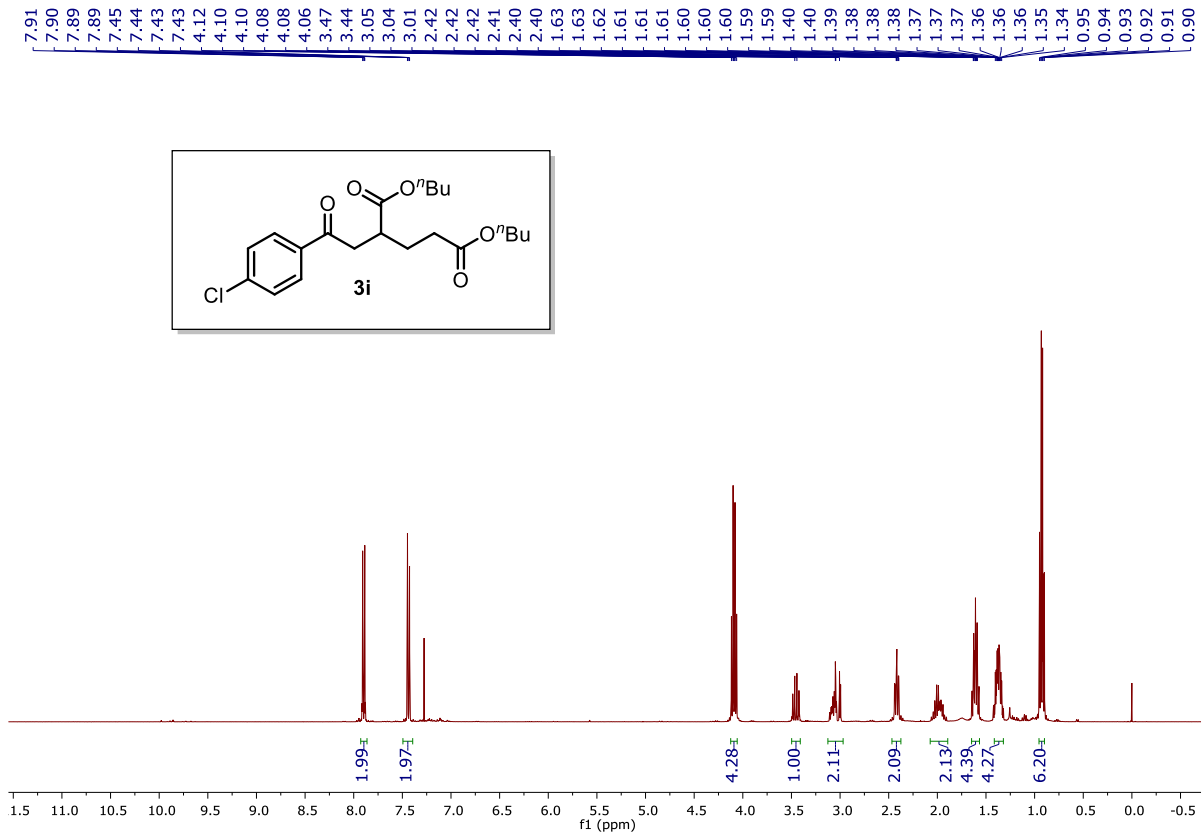
^{13}C{^{1}H} NMR spectrum of **3g**, $CDCl_3$, 100 MHz



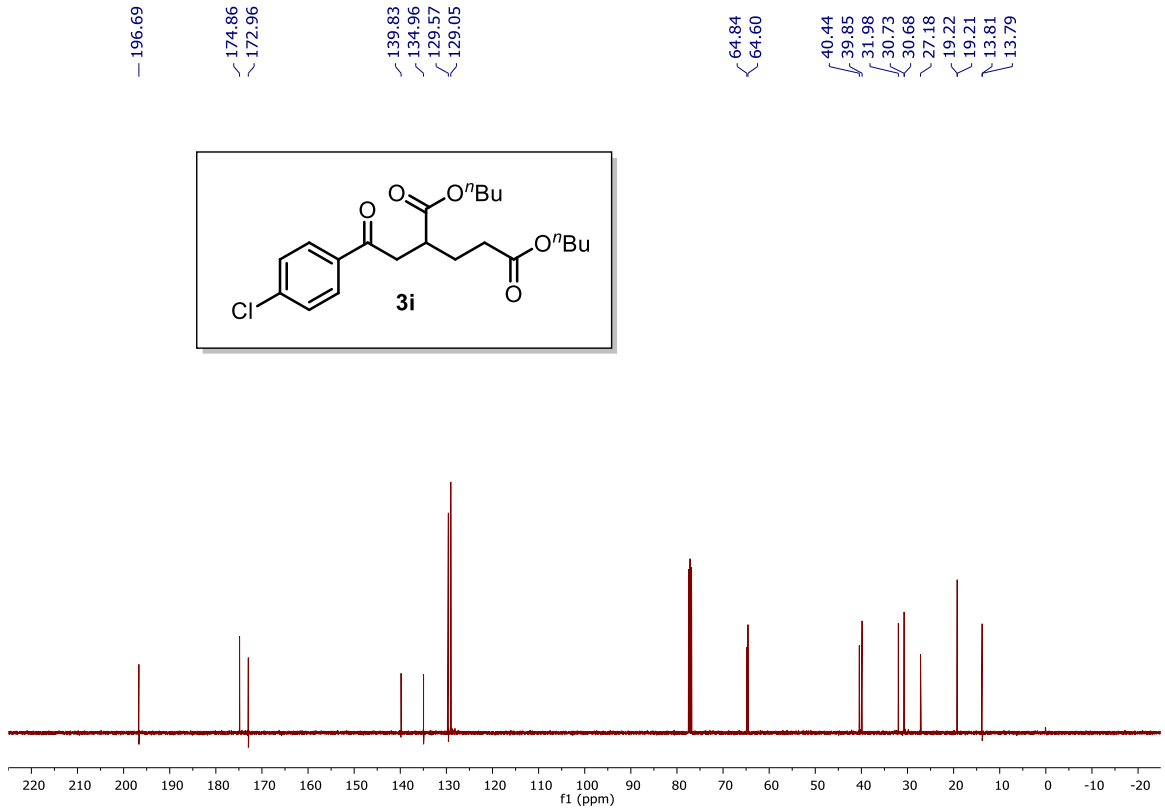
^{1}H NMR spectrum of **3h**, $CDCl_3$, 400 MHz



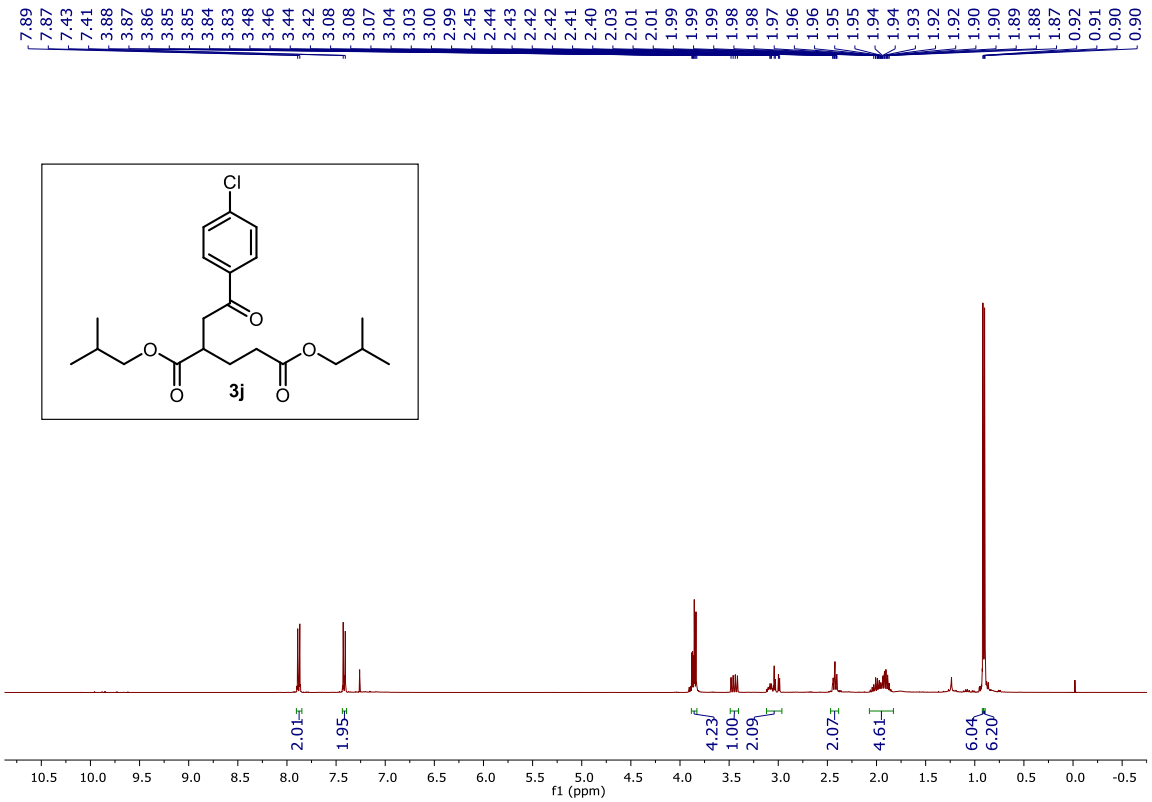
^{13}C {^{1}H} NMR spectrum of **3h**, $CDCl_3$, 100 MHz



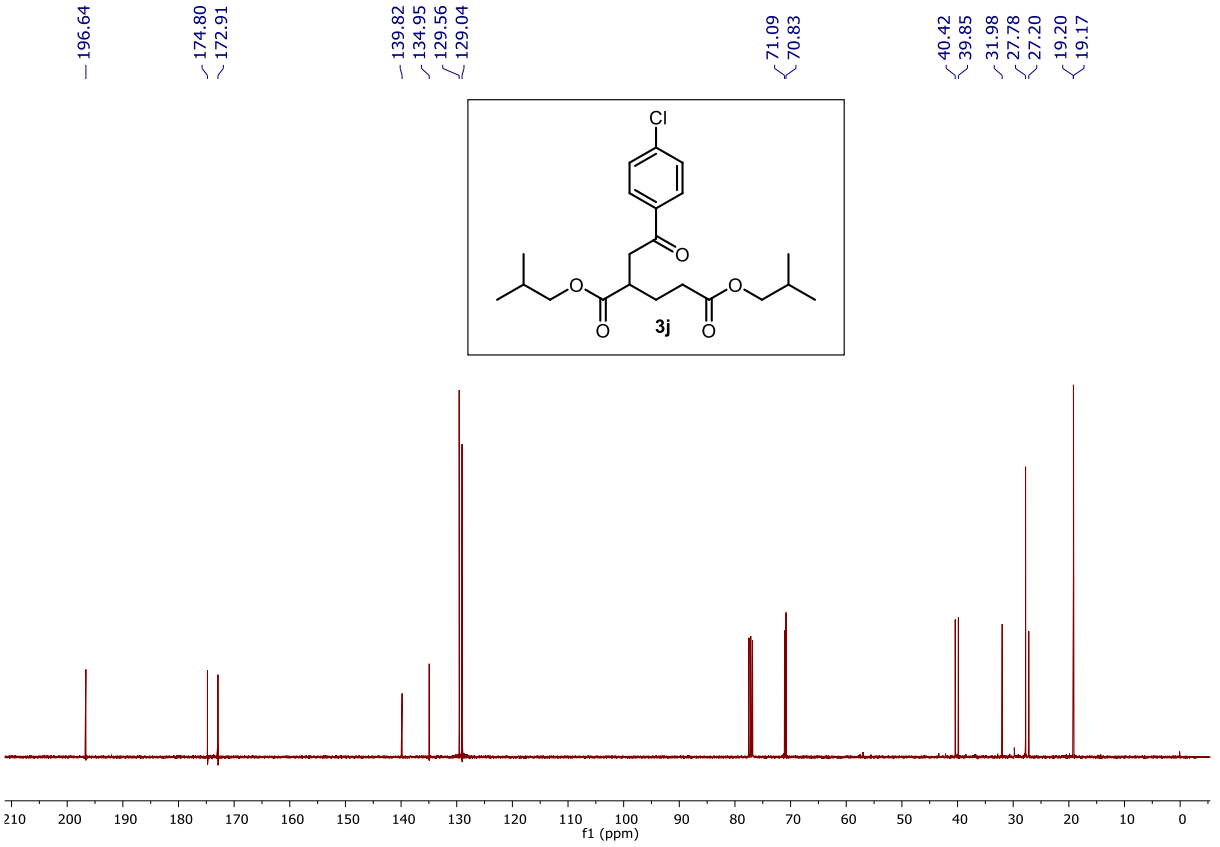
^{1}H NMR spectrum of **3i**, $CDCl_3$, 400 MHz



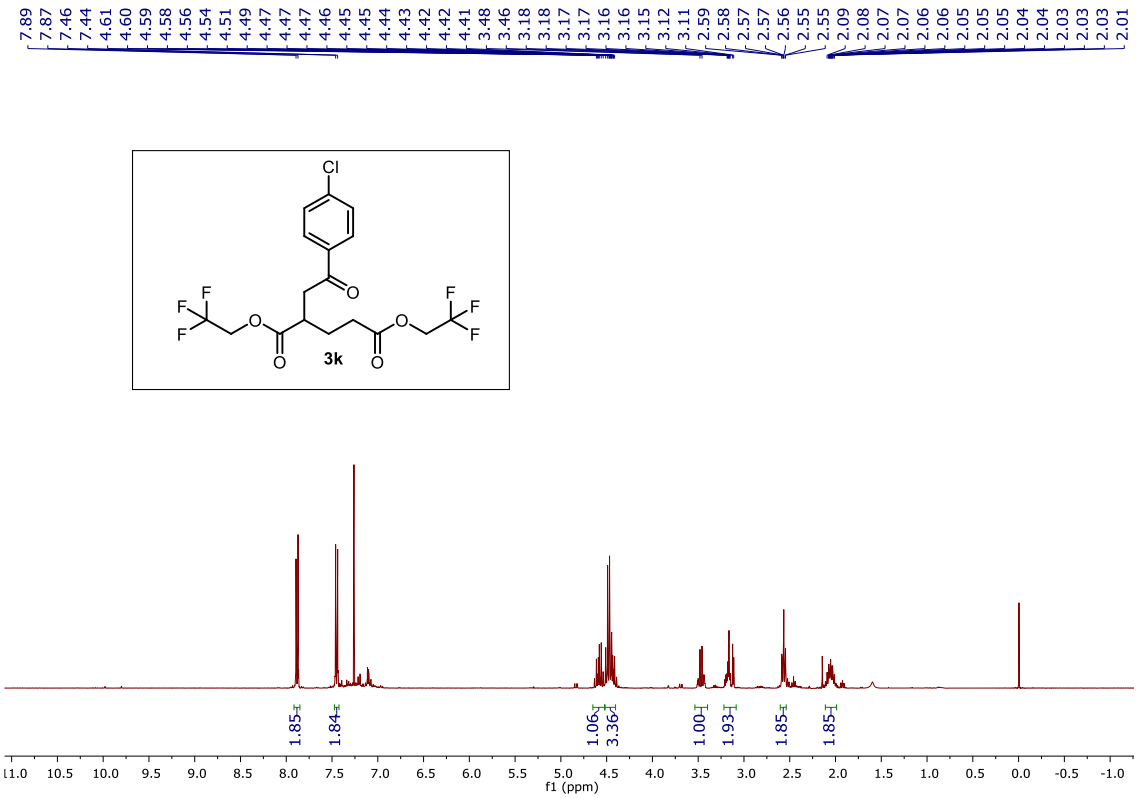
^{13}C{^{1}H} NMR spectrum of **3i**, $CDCl_3$, 100 MHz



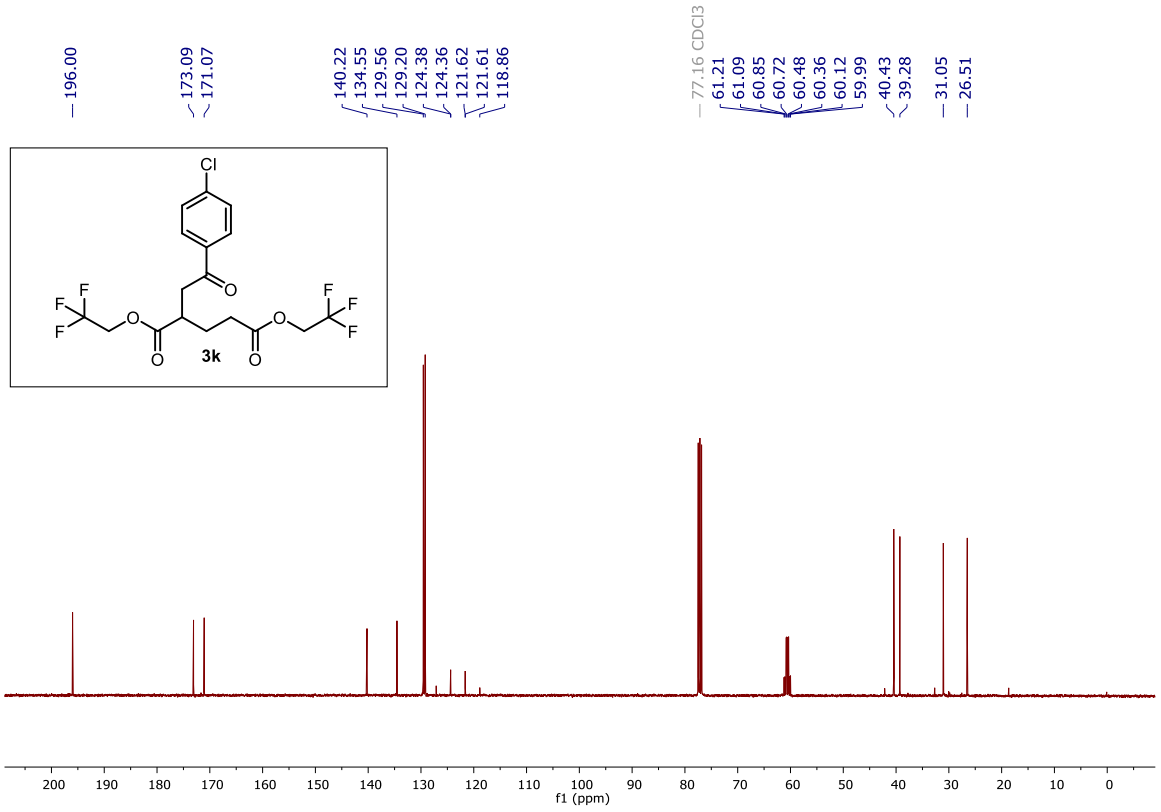
^{1}H NMR spectrum of **3j**, $CDCl_3$, 400 MHz



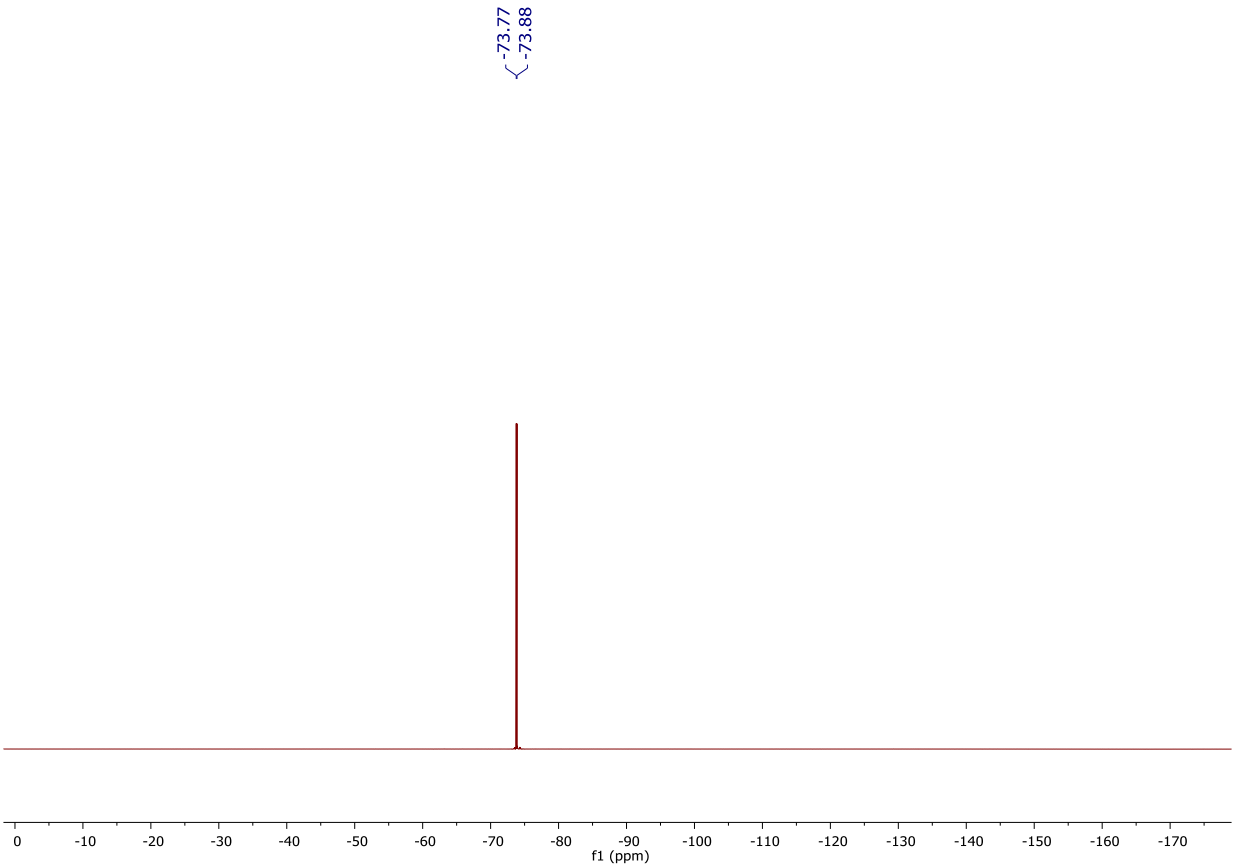
^{13}C{^{1}H} NMR spectrum of **3j**, $CDCl_3$, 100 MHz



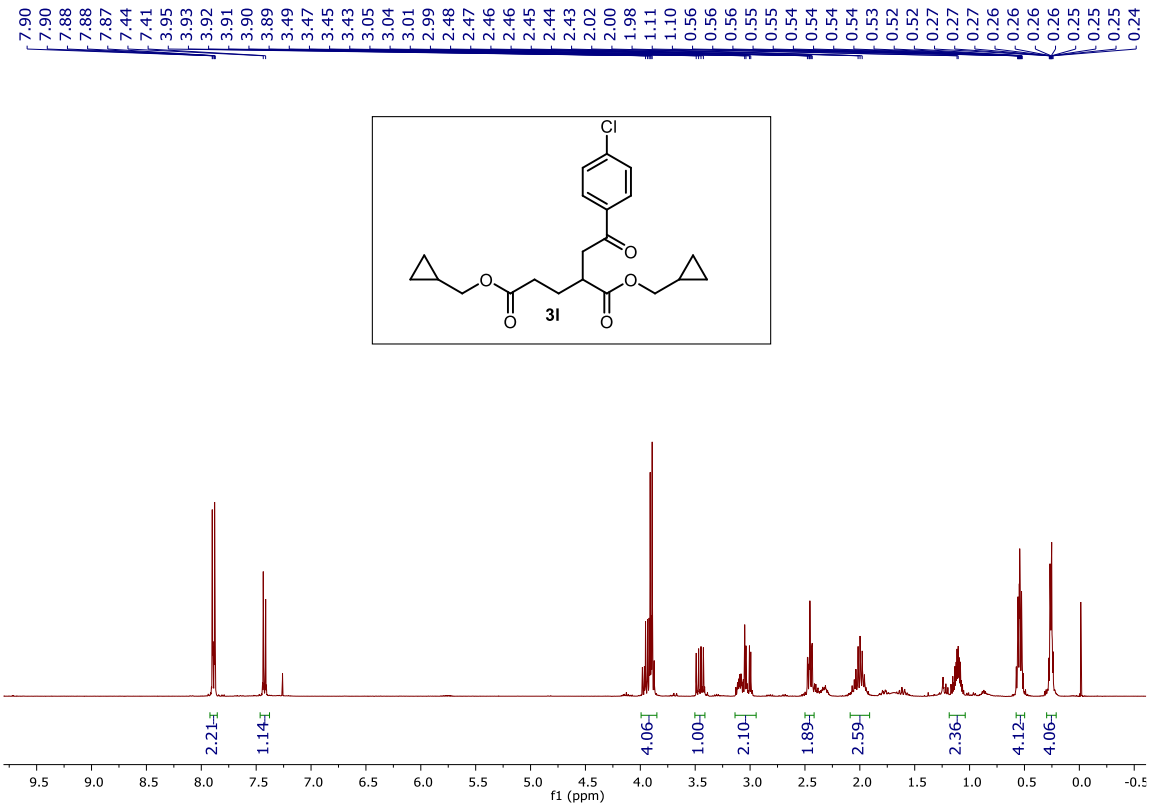
^{1}H NMR spectrum of **3k**, $CDCl_3$, 400 MHz



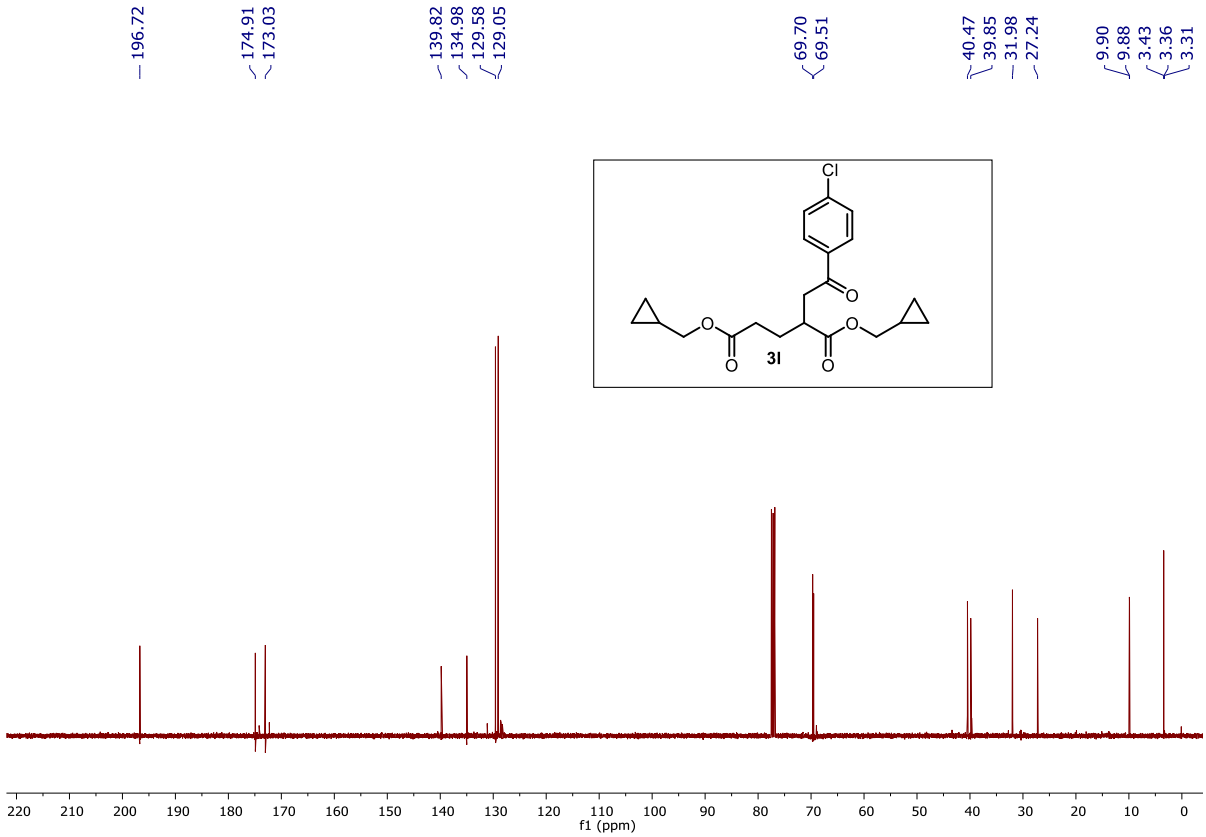
^{13}C {^{1}H} NMR spectrum of **3k**, $CDCl_3$, 100 MHz



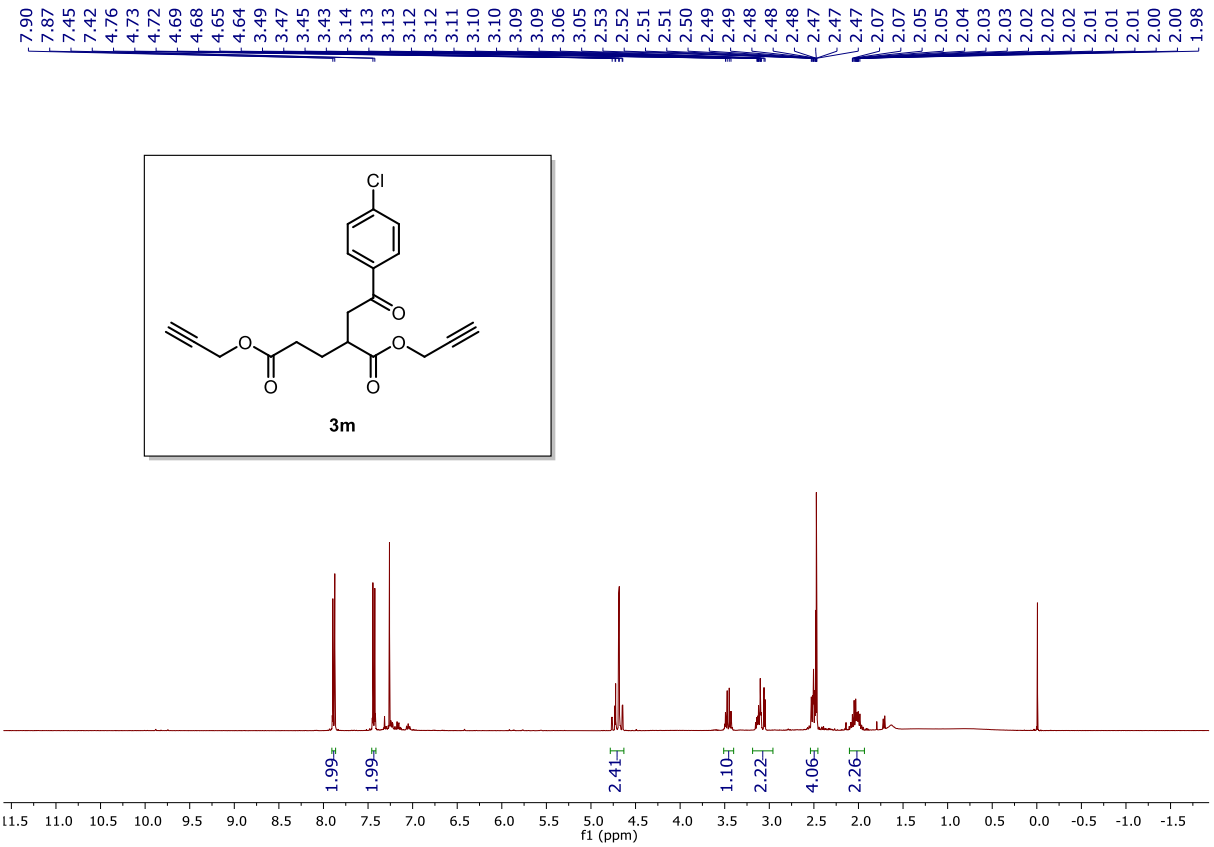
^{19}F NMR spectrum of **3k**, $CDCl_3$, 377 MHz



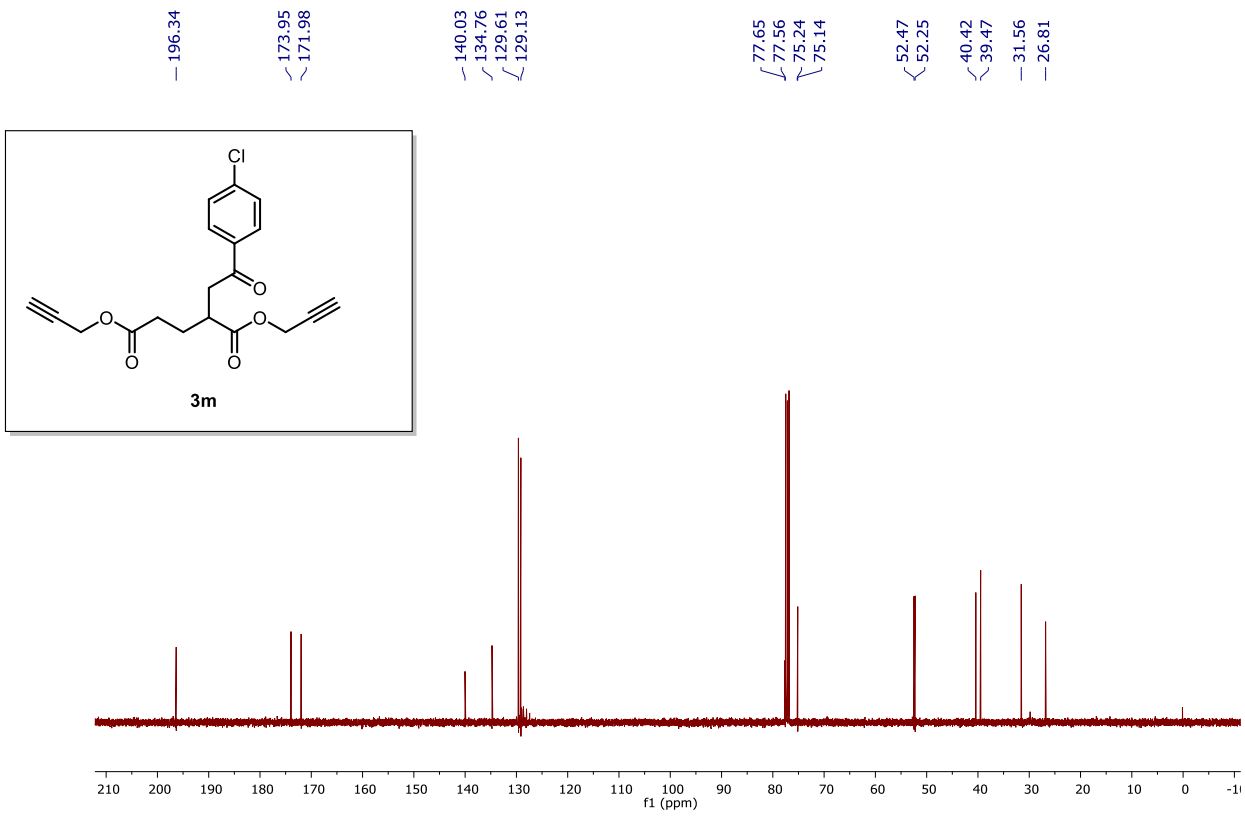
^{1}H NMR spectrum of **3l**, $CDCl_3$, 400 MHz



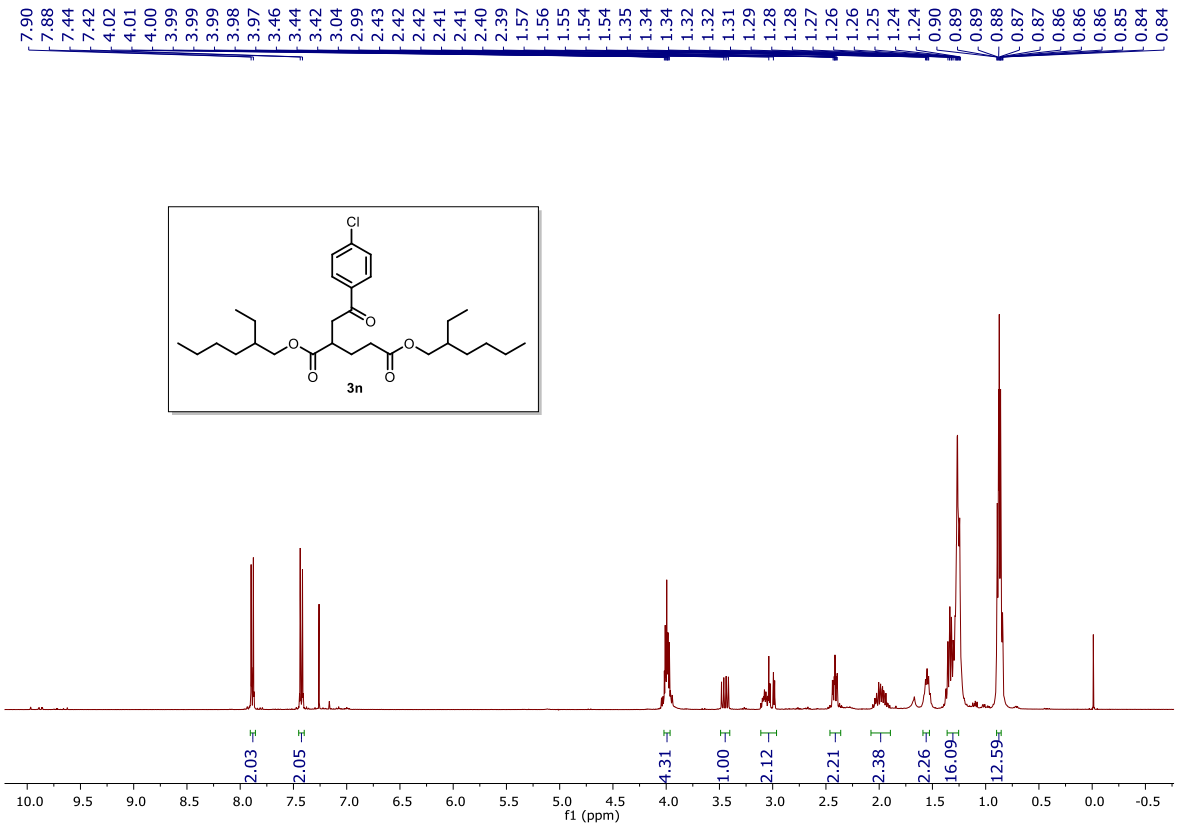
^{13}C{^{1}H} NMR spectrum of **3l**, $CDCl_3$, 100 MHz



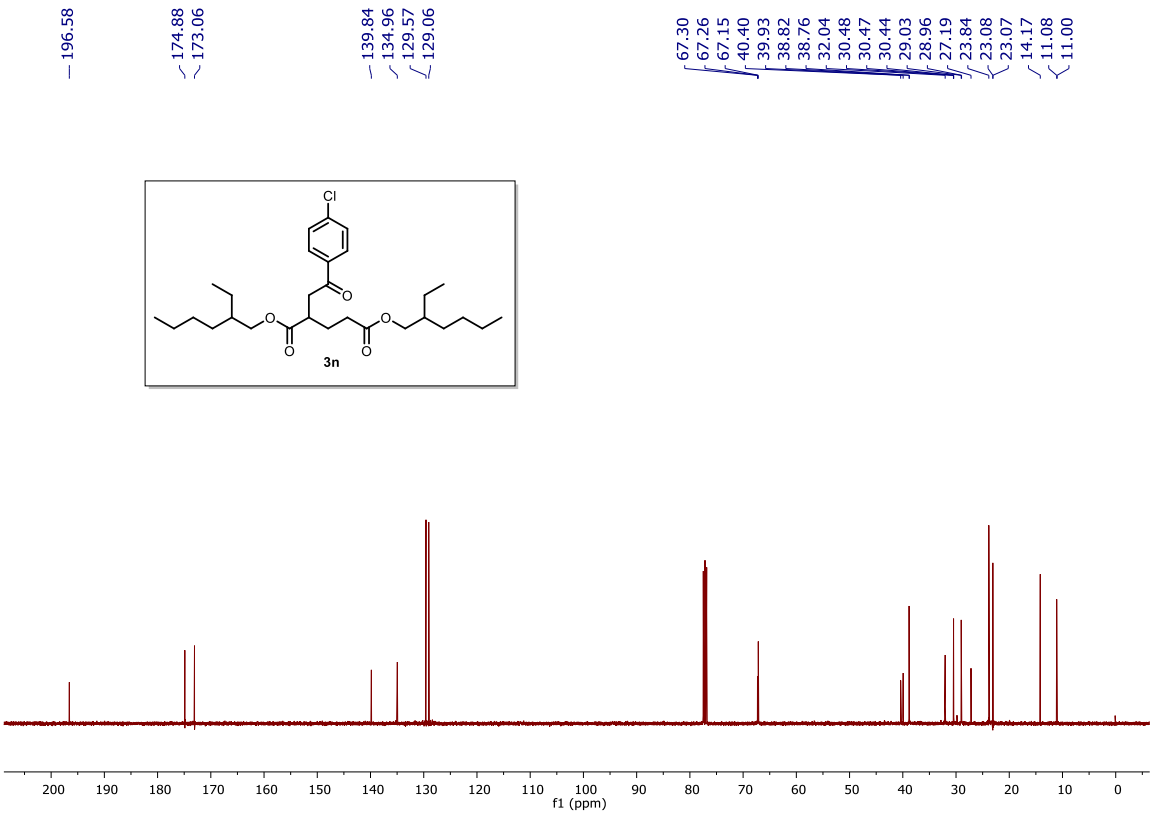
^{1}H NMR spectrum of **3m**, $CDCl_3$, 400 MHz



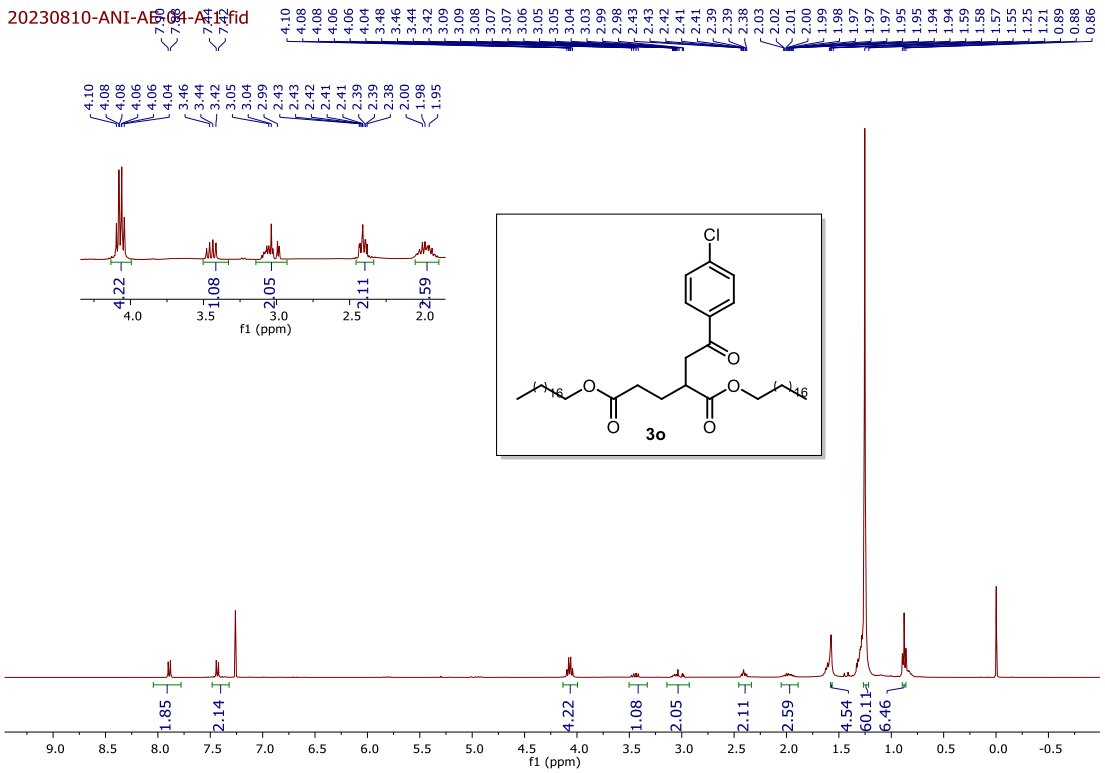
^{13}C {^{1}H} NMR spectrum of **3m**, $CDCl_3$, 100 MHz



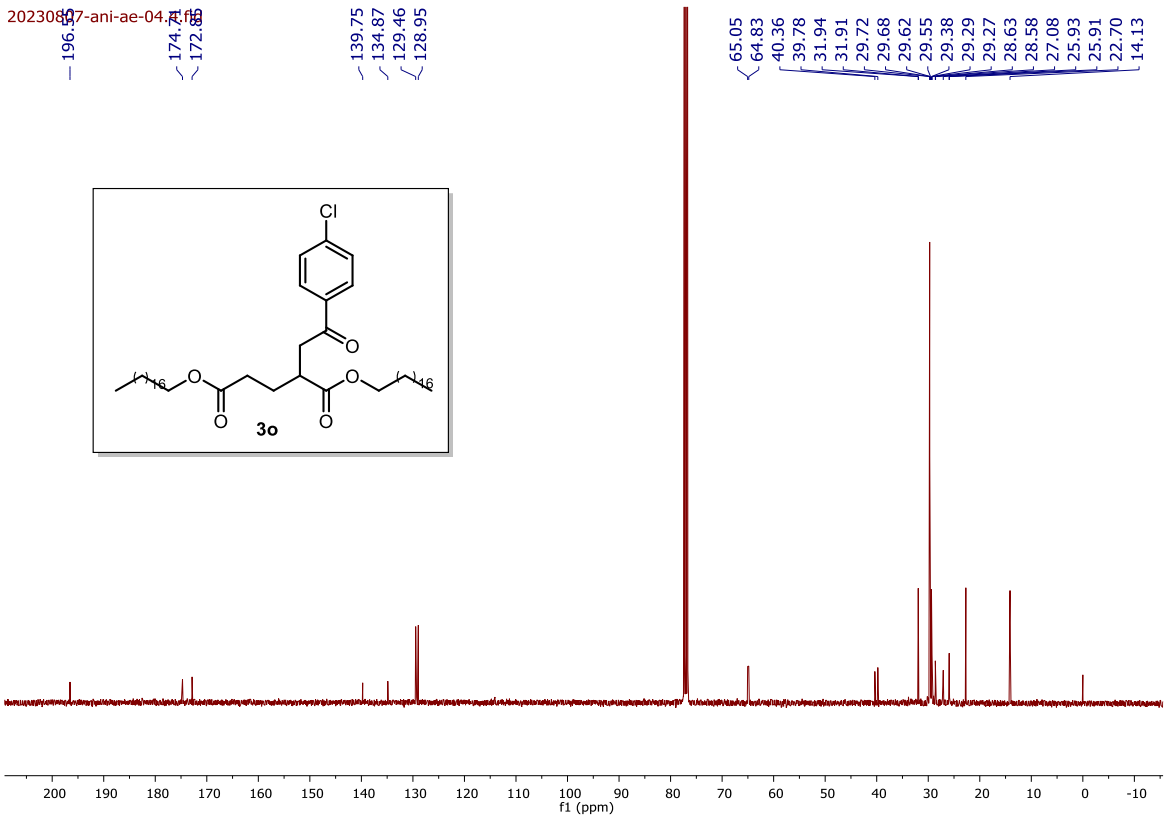
^{1}H NMR spectrum of **3n**, $CDCl_3$, 400 MHz



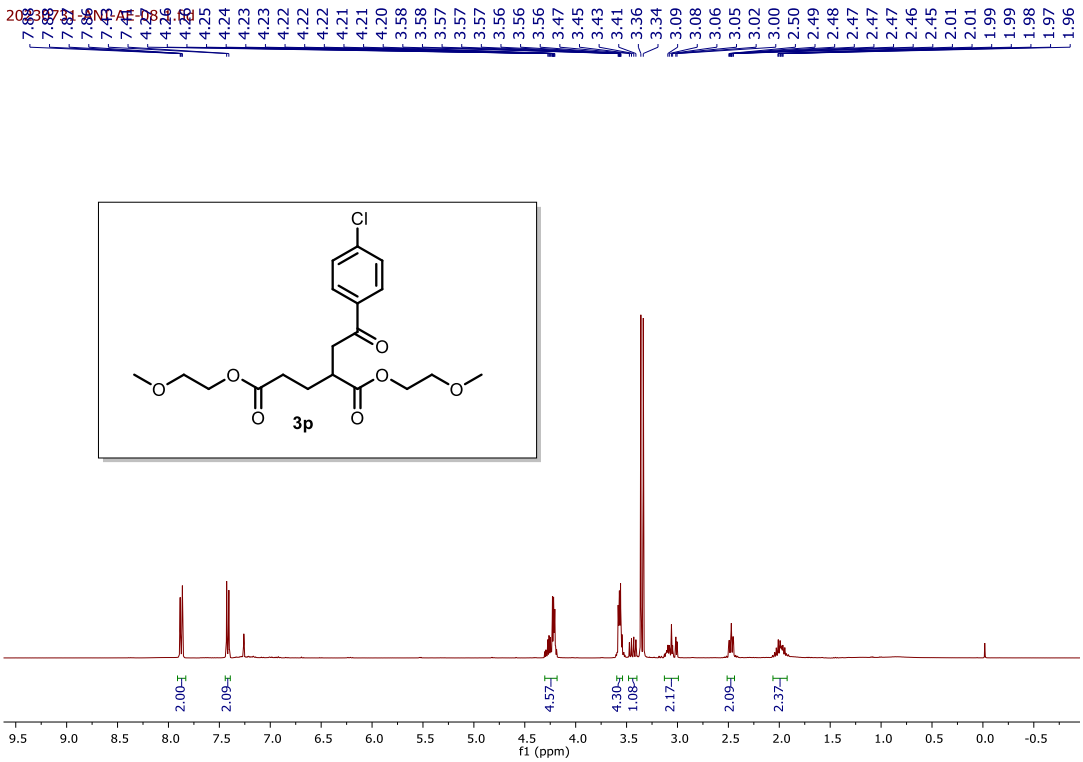
^{13}C{^{1}H} NMR spectrum of **3n**, $CDCl_3$, 100 MHz



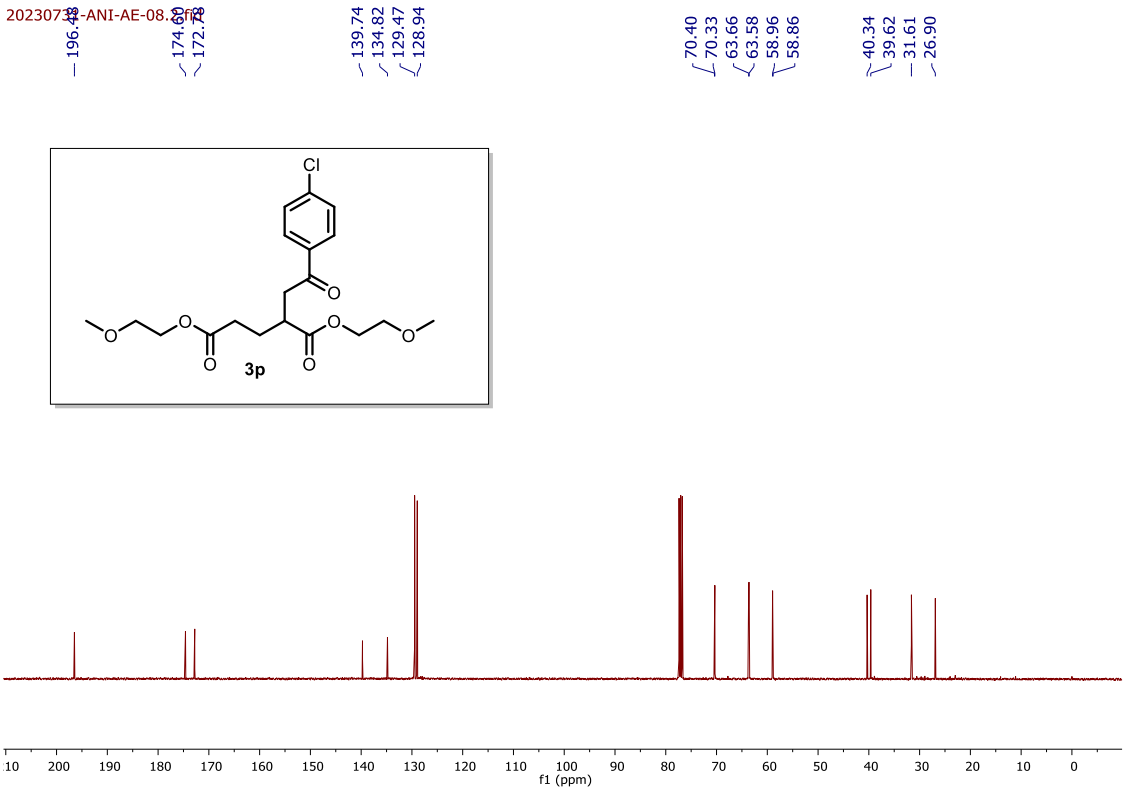
^{1}H NMR spectrum of **3o**, $CDCl_3$, 400 MHz



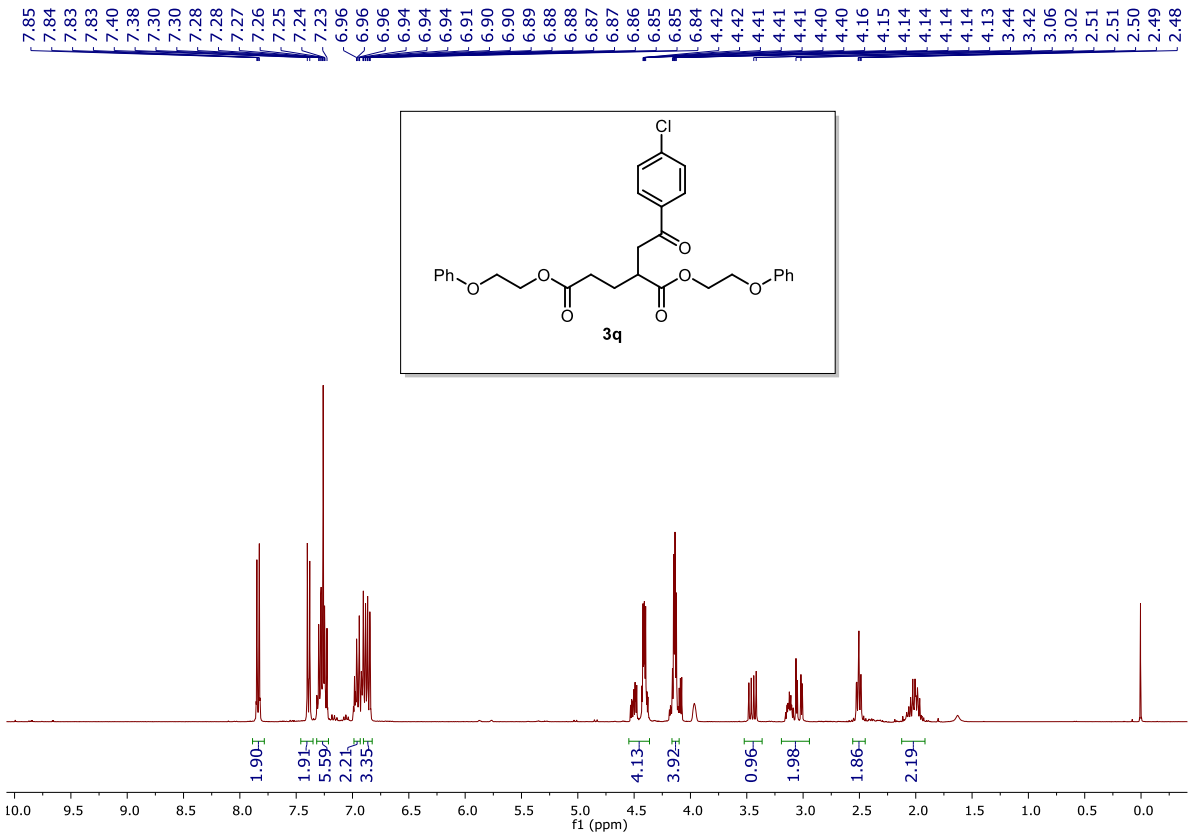
^{13}C {^{1}H} NMR spectrum of **3o**, $CDCl_3$, 100 MHz



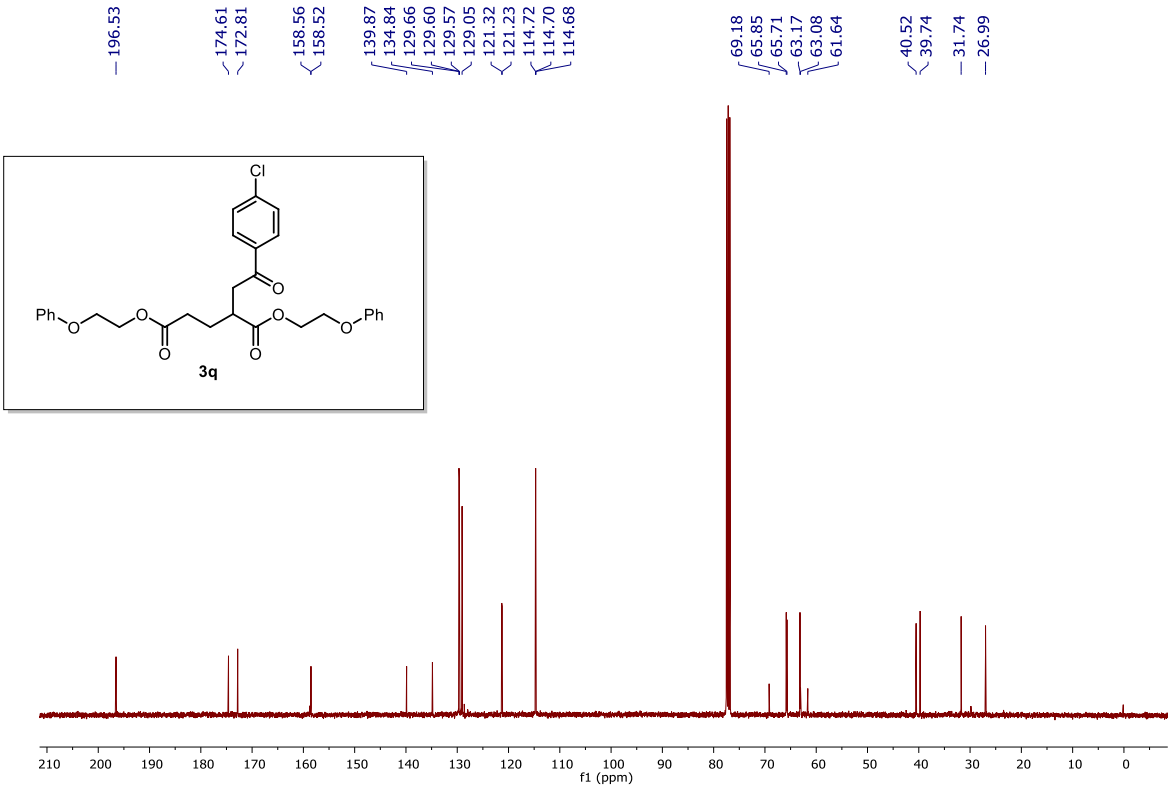
^{1}H NMR spectrum of **3p**, $CDCl_3$, 400 MHz



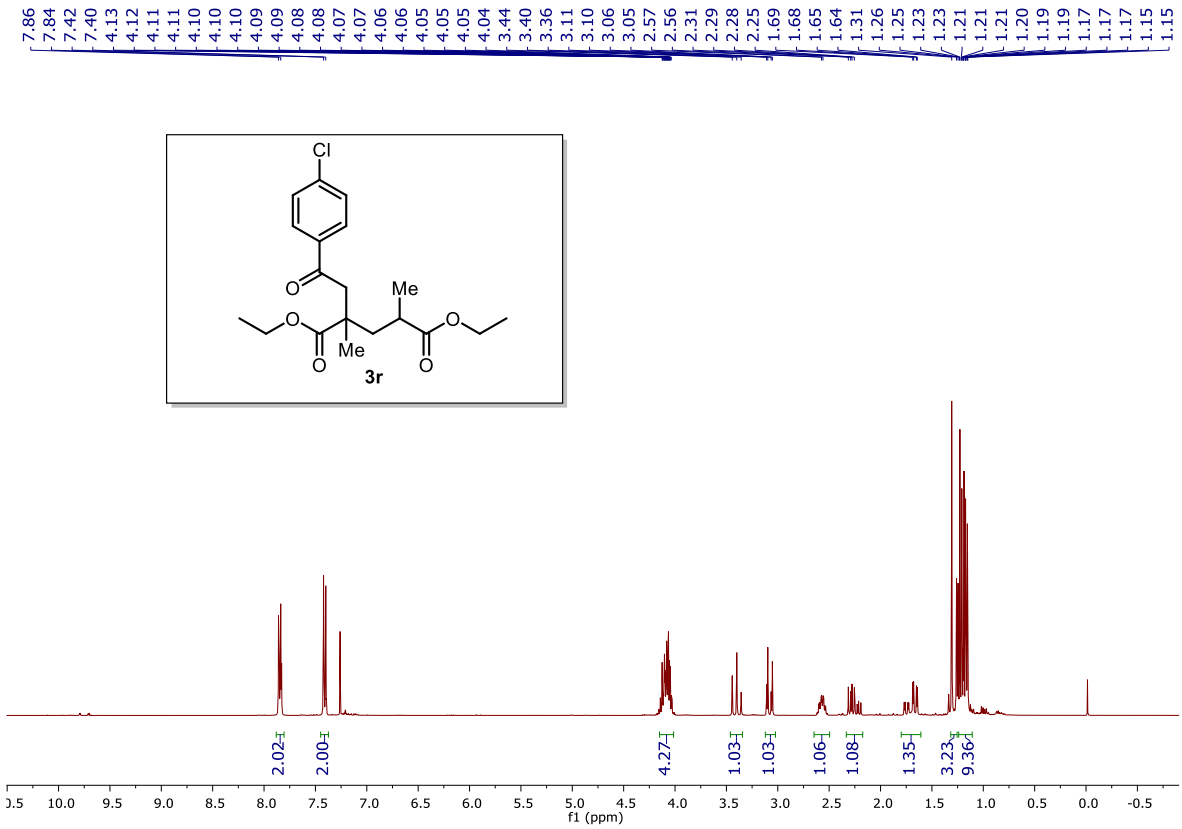
^{13}C{^{1}H} NMR spectrum of **3p**, $CDCl_3$, 100 MHz



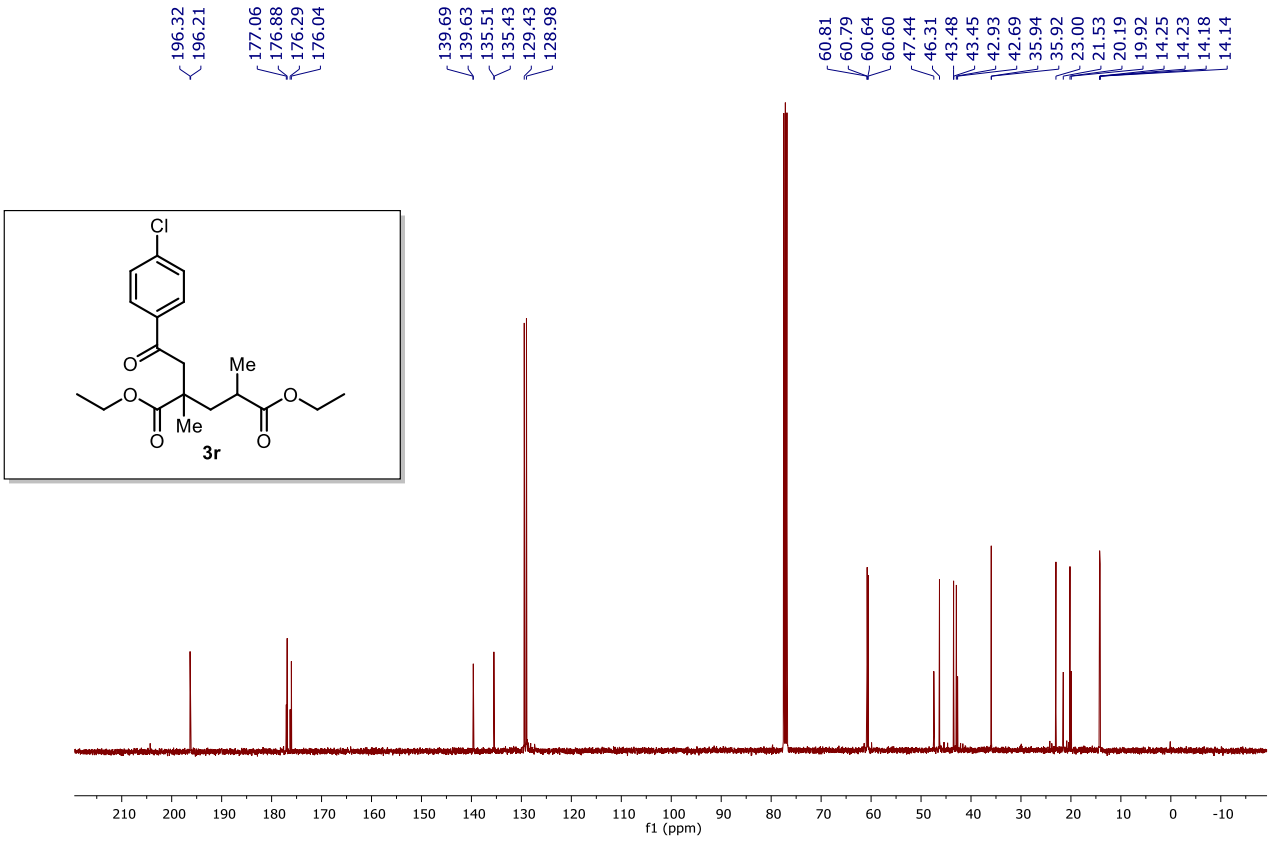
^{1}H NMR spectrum of **3q**, $CDCl_3$, 400 MHz



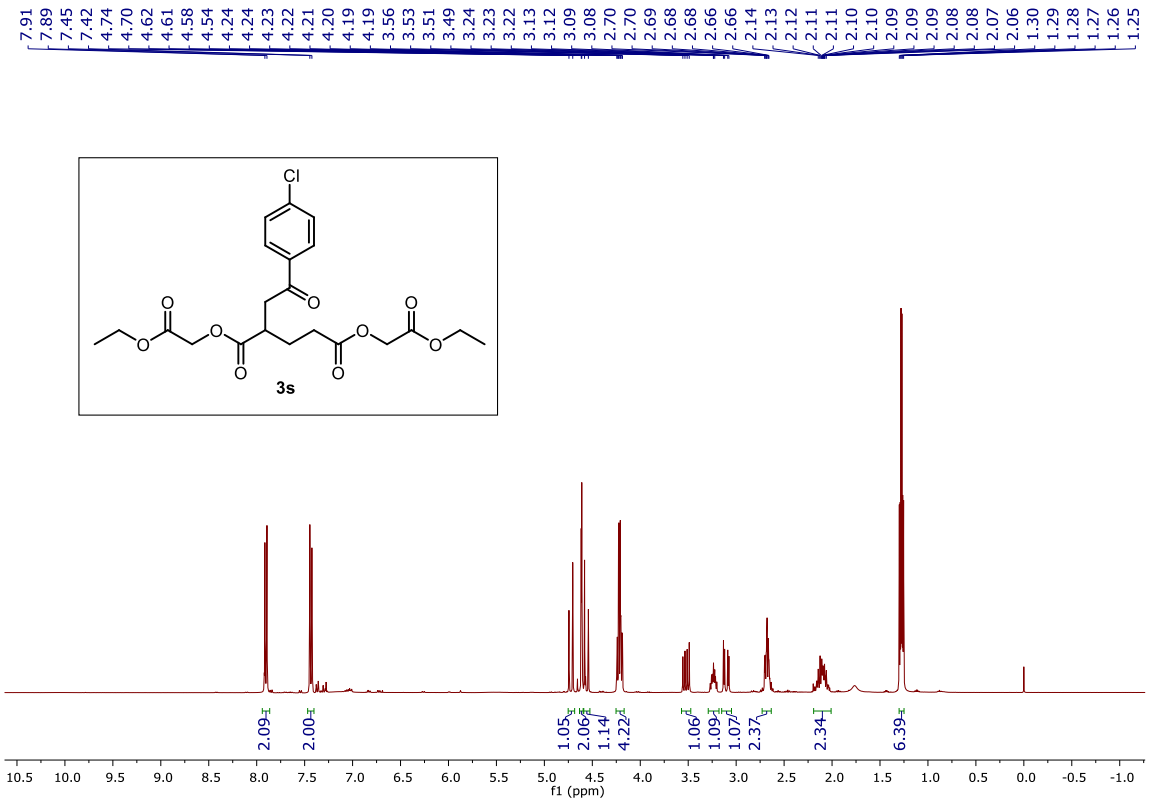
^{13}C{^{1}H} NMR spectrum of **3q**, $CDCl_3$, 100 MHz



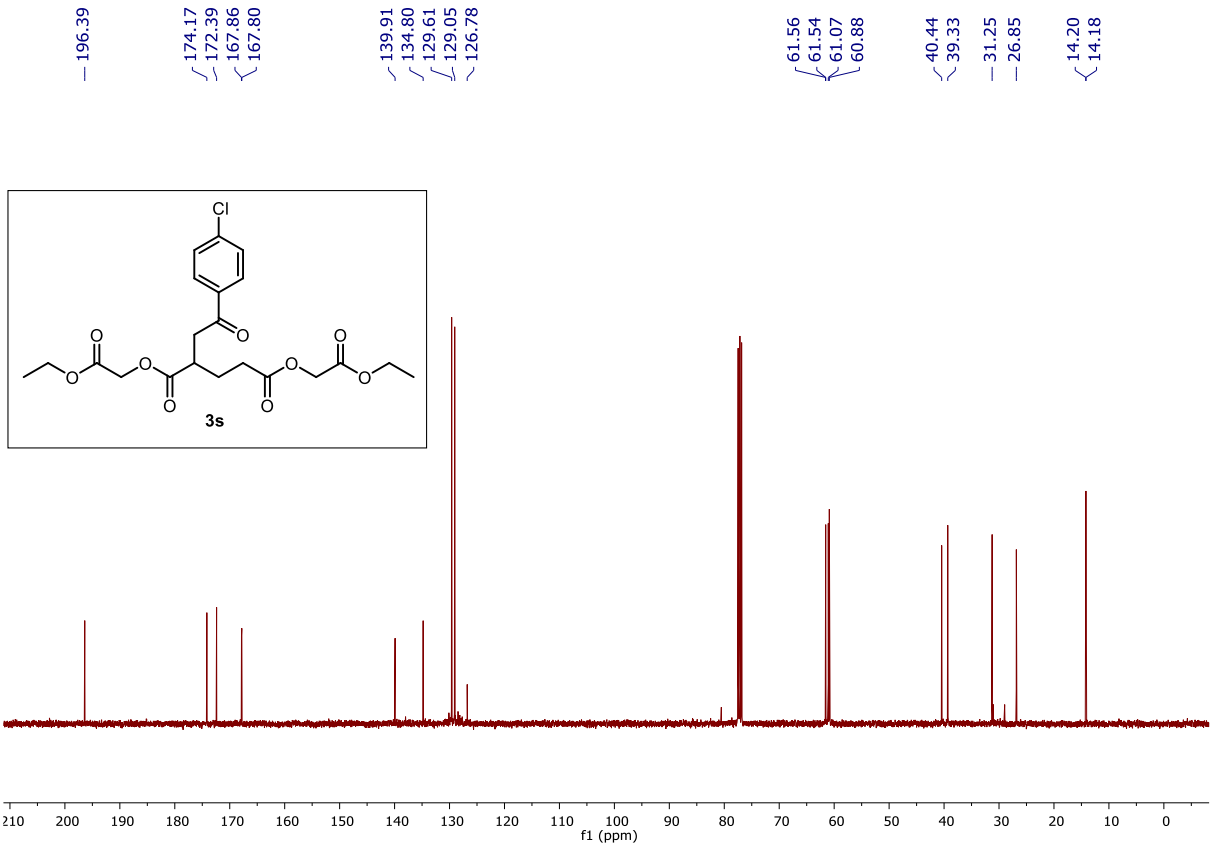
^{1}H NMR spectrum of **3r**, $CDCl_3$, 400 MHz



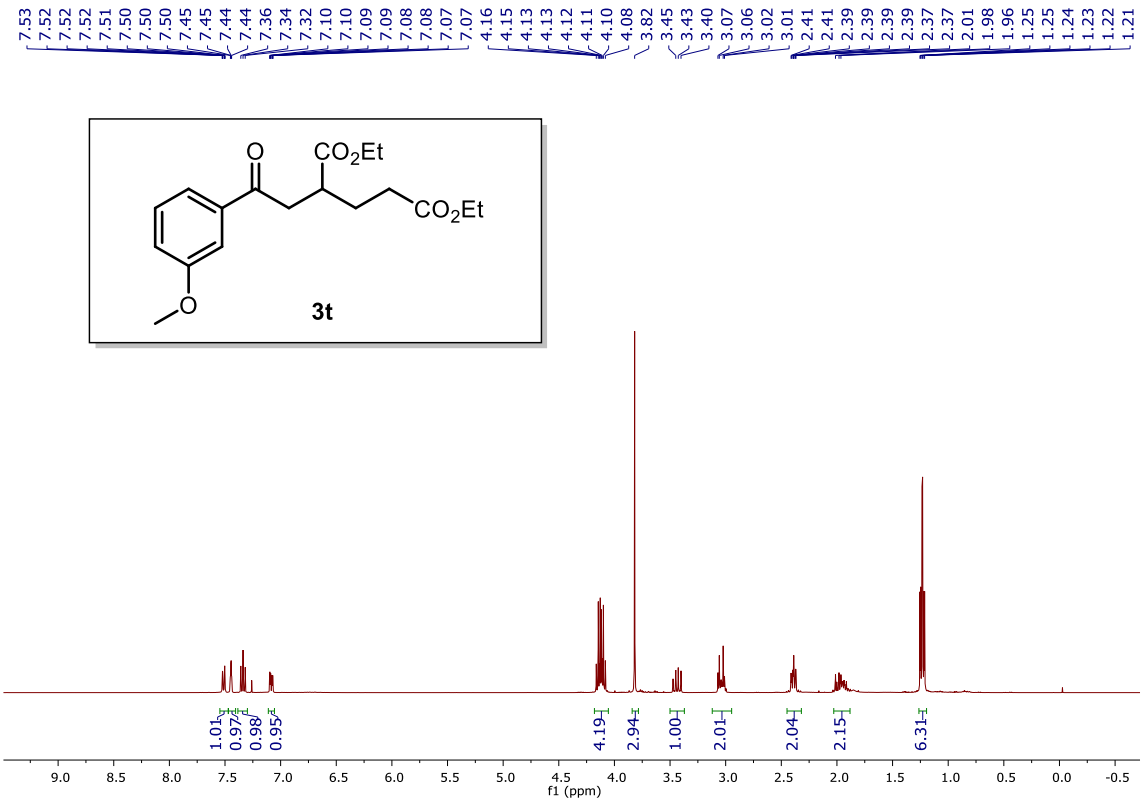
^{13}C {^{1}H} NMR spectrum of **3r**, $CDCl_3$, 100 MHz



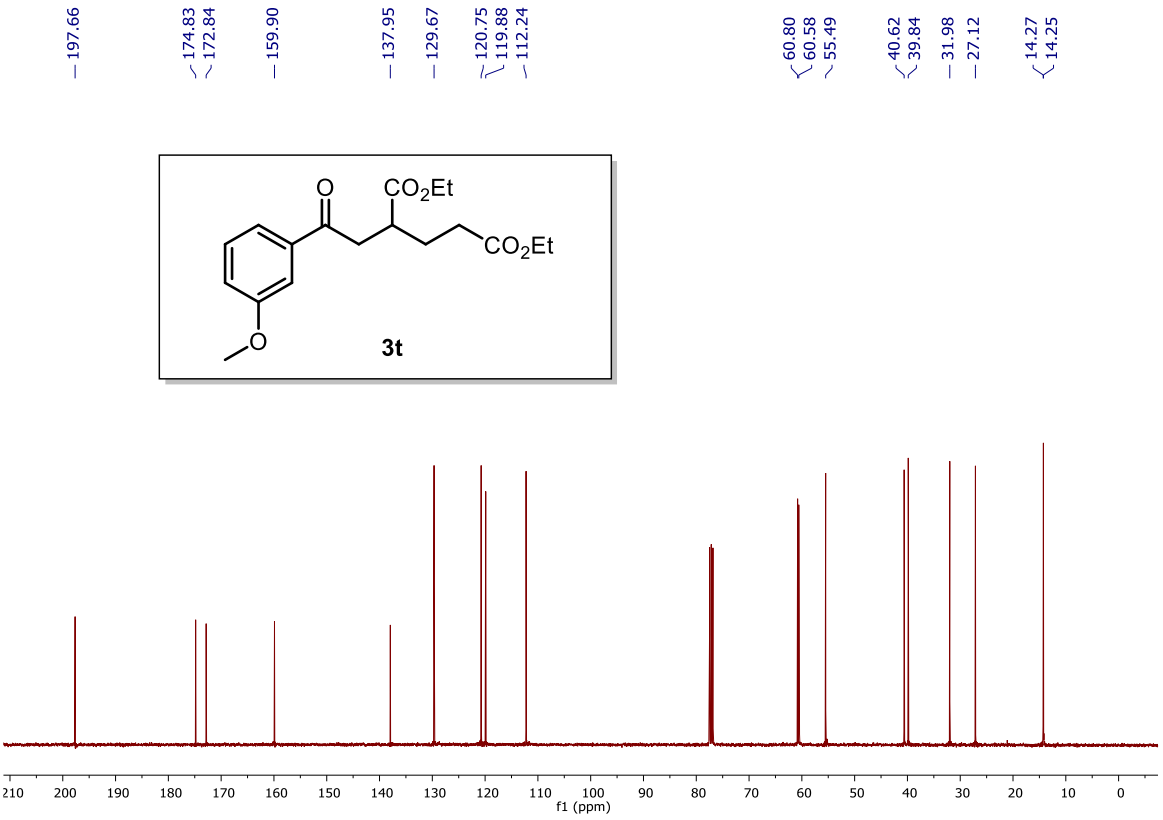
^{1}H NMR spectrum of **3s**, $CDCl_3$, 400 MHz



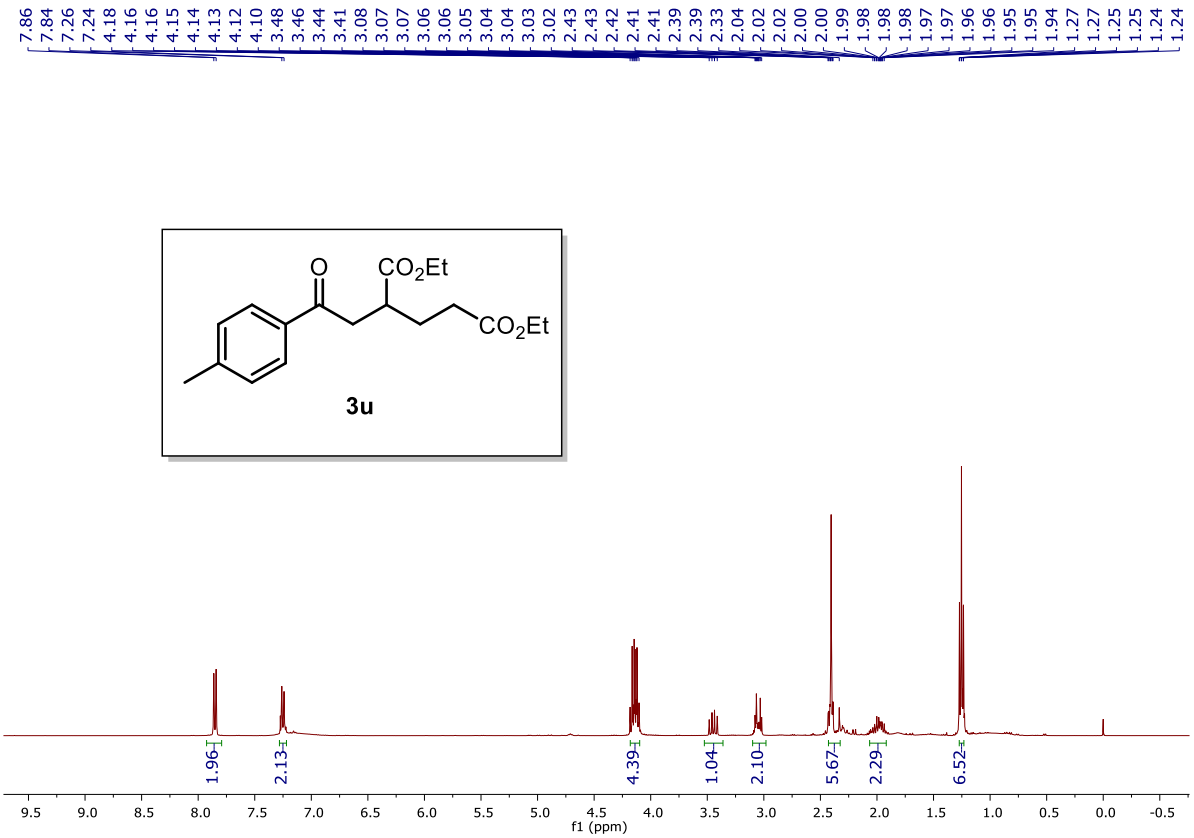
^{13}C{^{1}H} NMR spectrum of **3s**, $CDCl_3$, 100 MHz



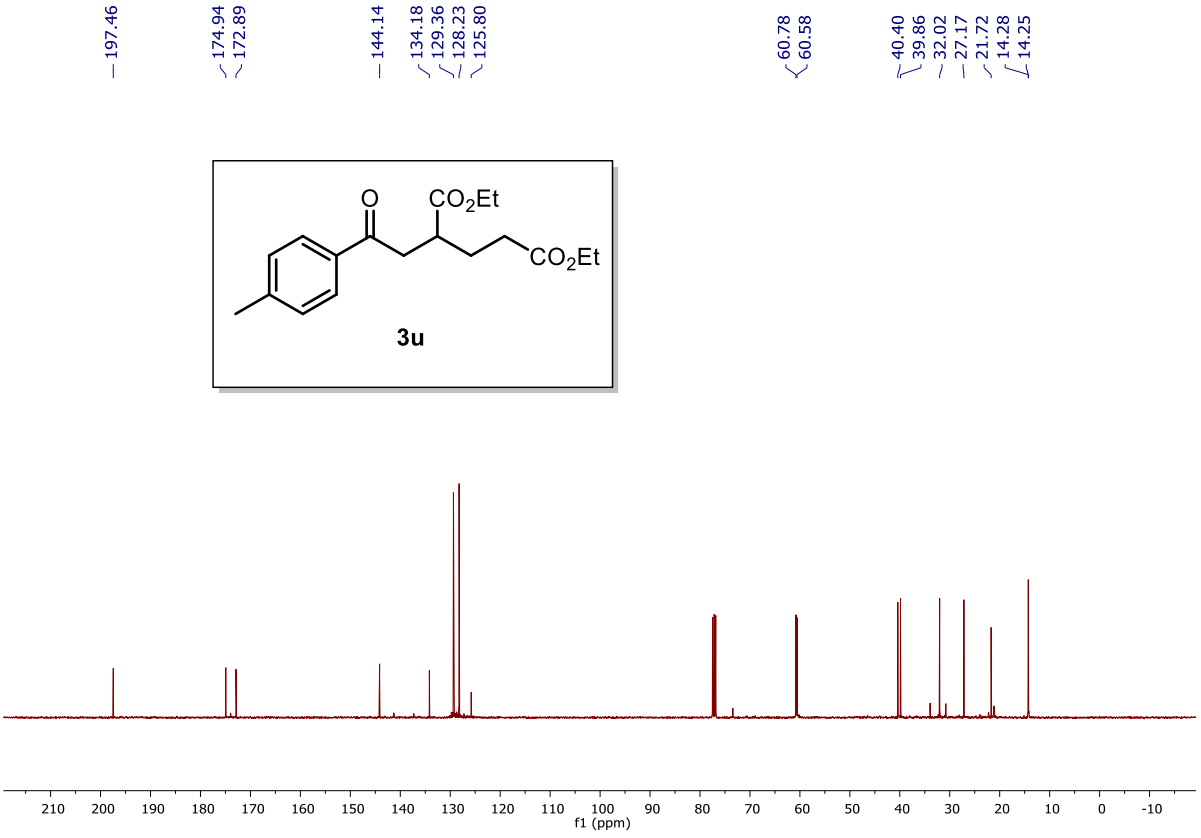
^{1}H NMR spectrum of **3t**, $CDCl_3$, 400 MHz



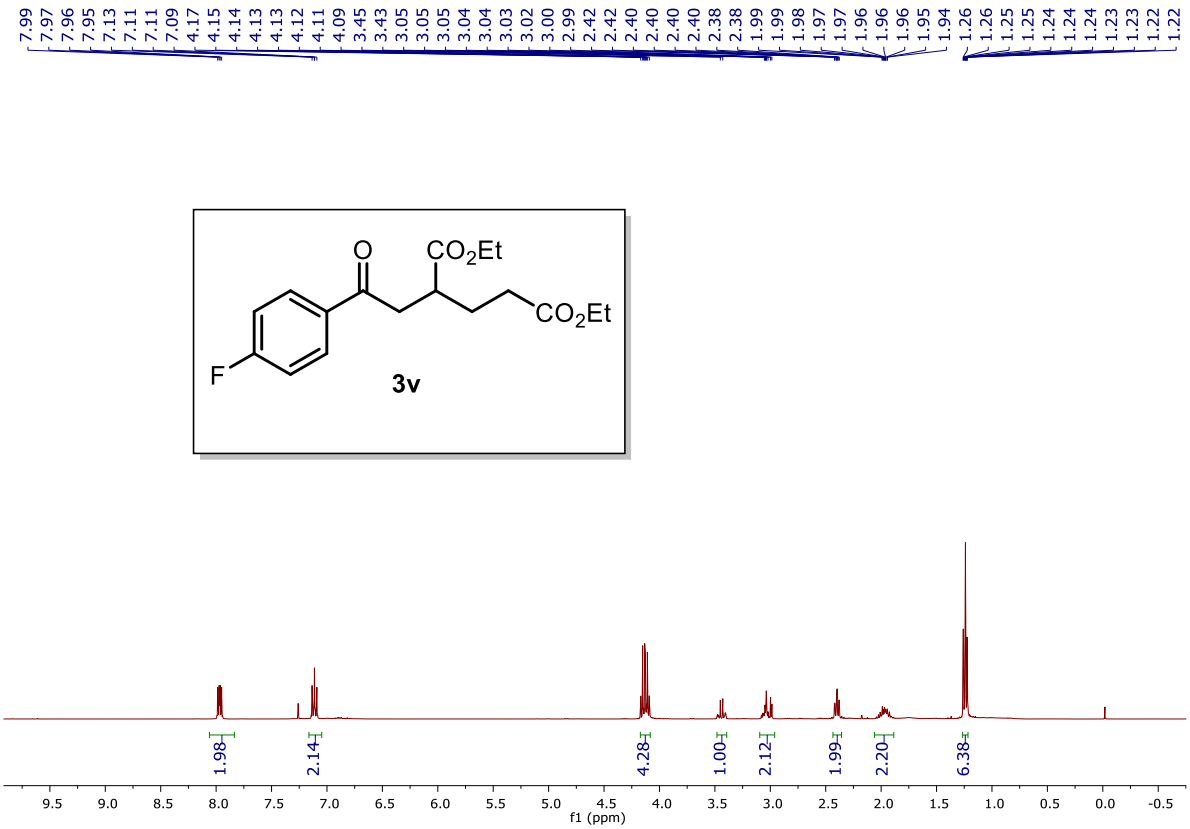
^{13}C{^{1}H} NMR spectrum of **3t**, $CDCl_3$, 100 MHz



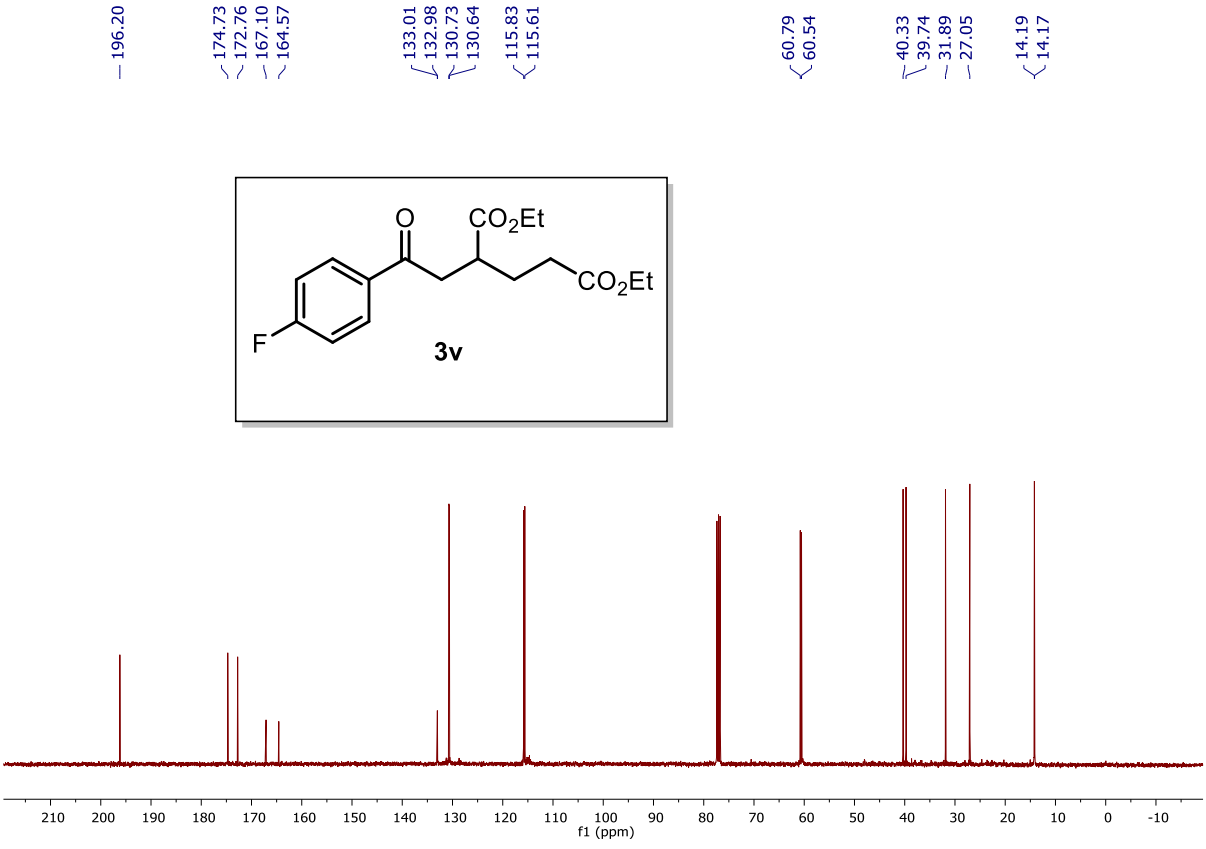
^{1}H NMR spectrum of **3u**, $CDCl_3$, 400 MHz



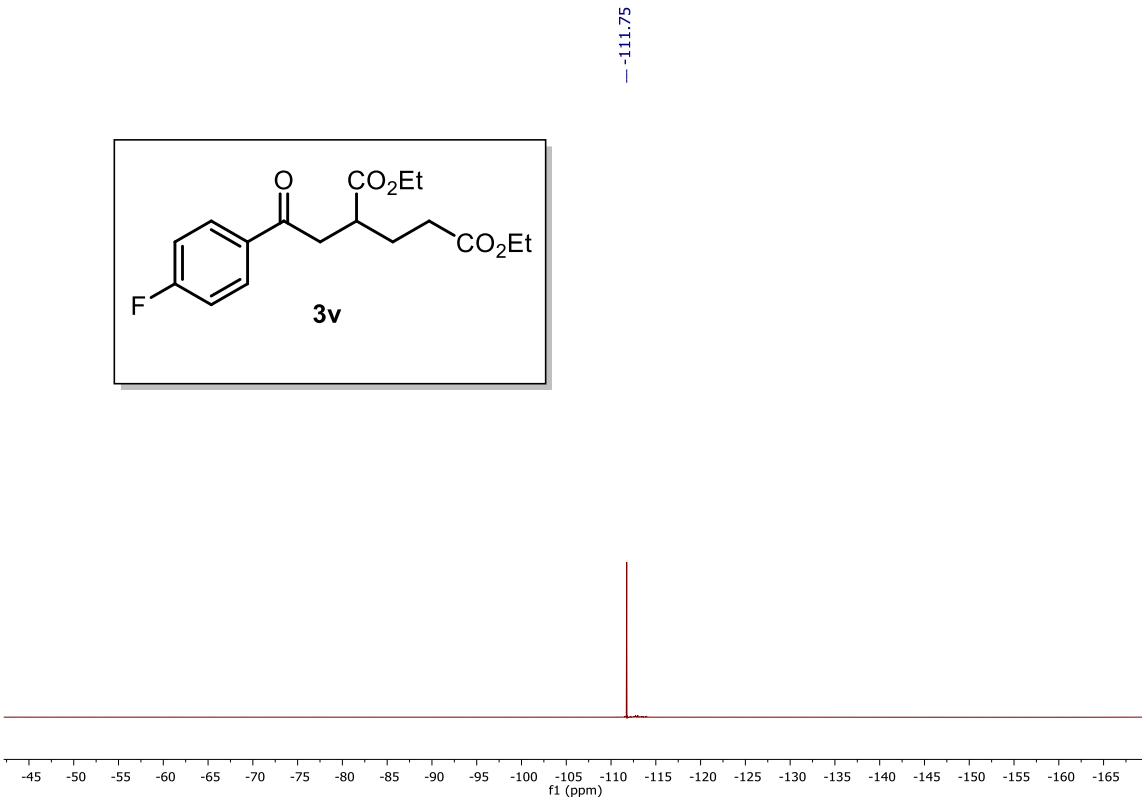
^{13}C{^{1}H} NMR spectrum of **3u**, $CDCl_3$, 100 MHz



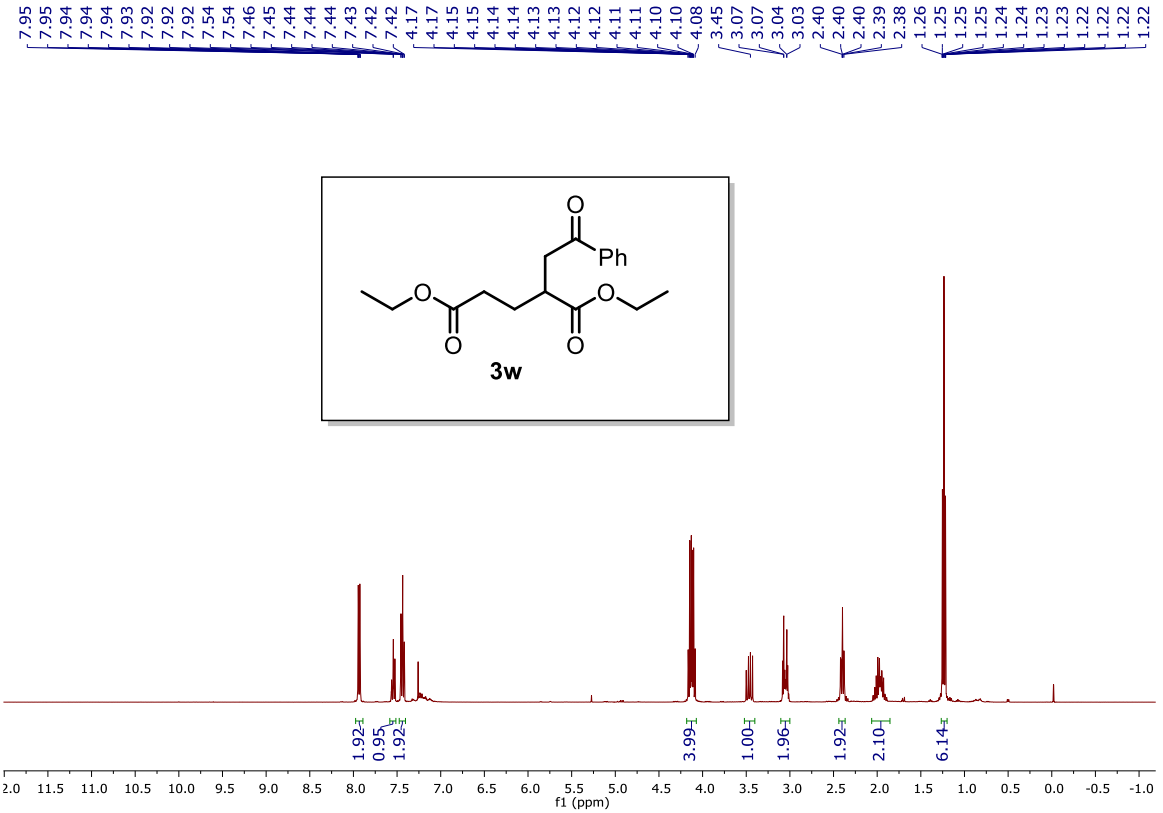
^{1}H NMR spectrum of **3v**, $CDCl_3$, 400 MHz



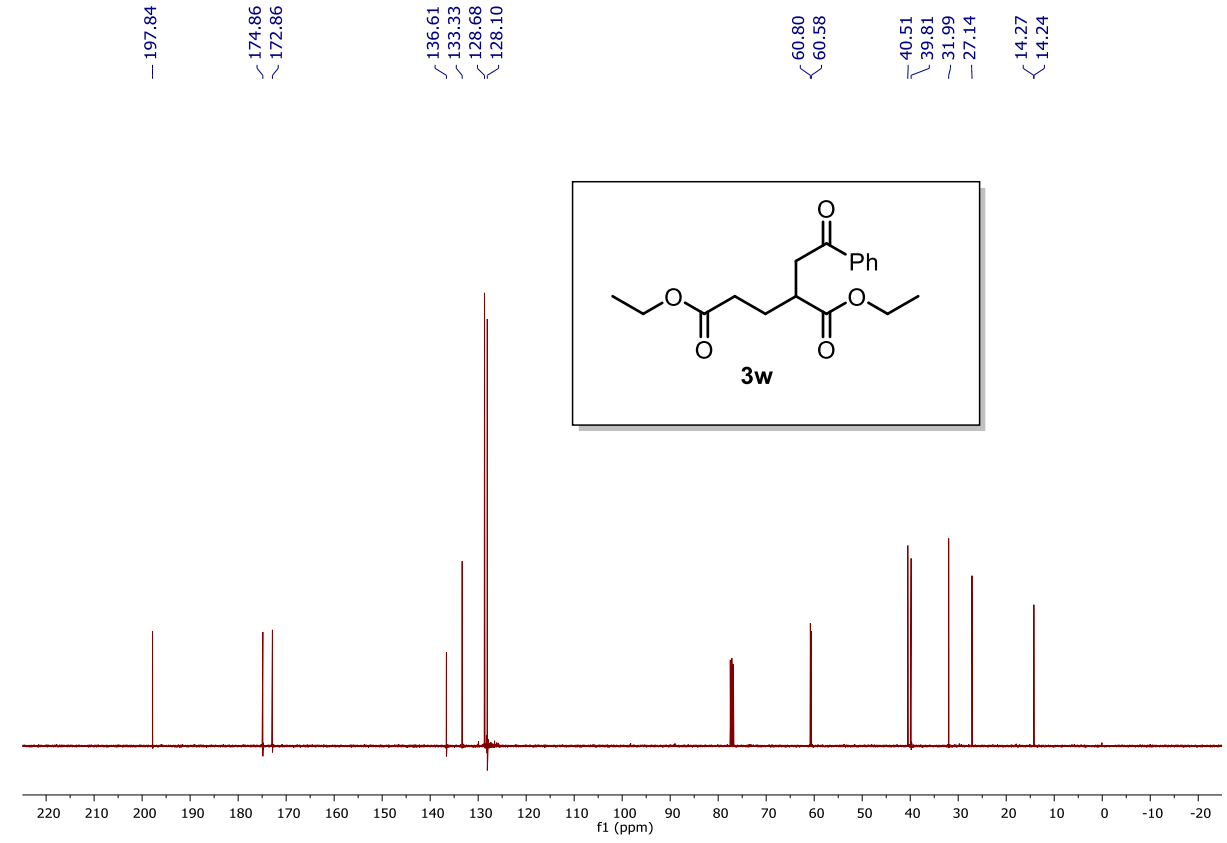
^{13}C{^{1}H} NMR spectrum of **3v**, $CDCl_3$, 100 MHz



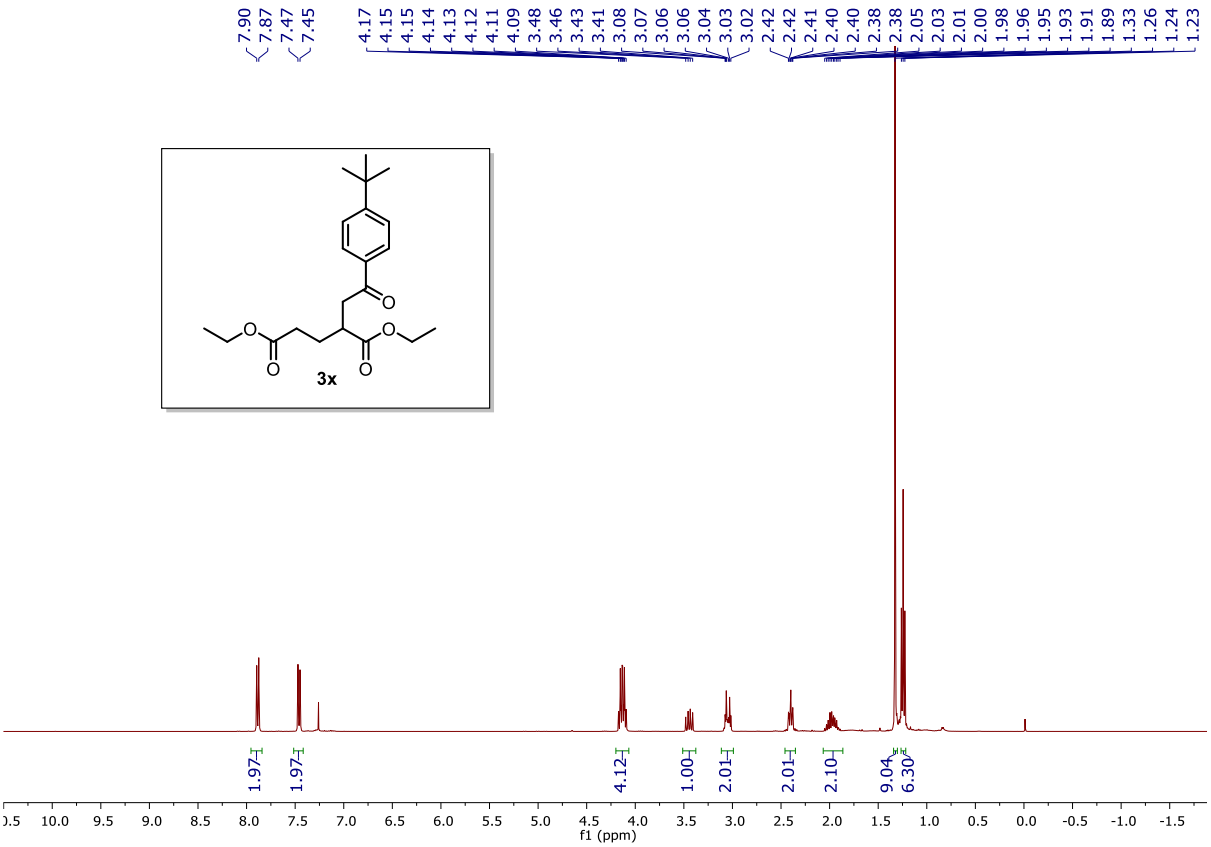
^{19}F NMR spectrum of **3v**, $CDCl_3$, 377 MHz



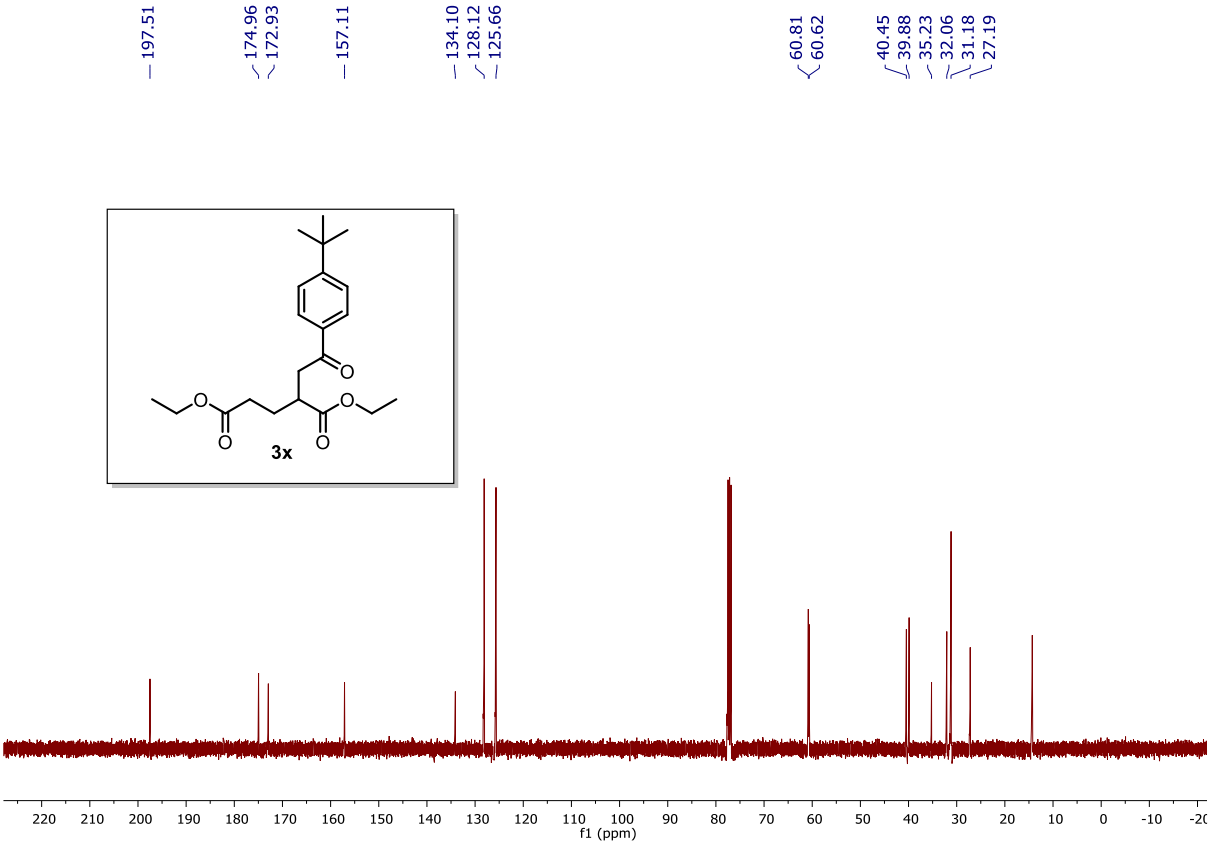
^{1}H NMR spectrum of **3w**, $CDCl_3$, 400 MHz



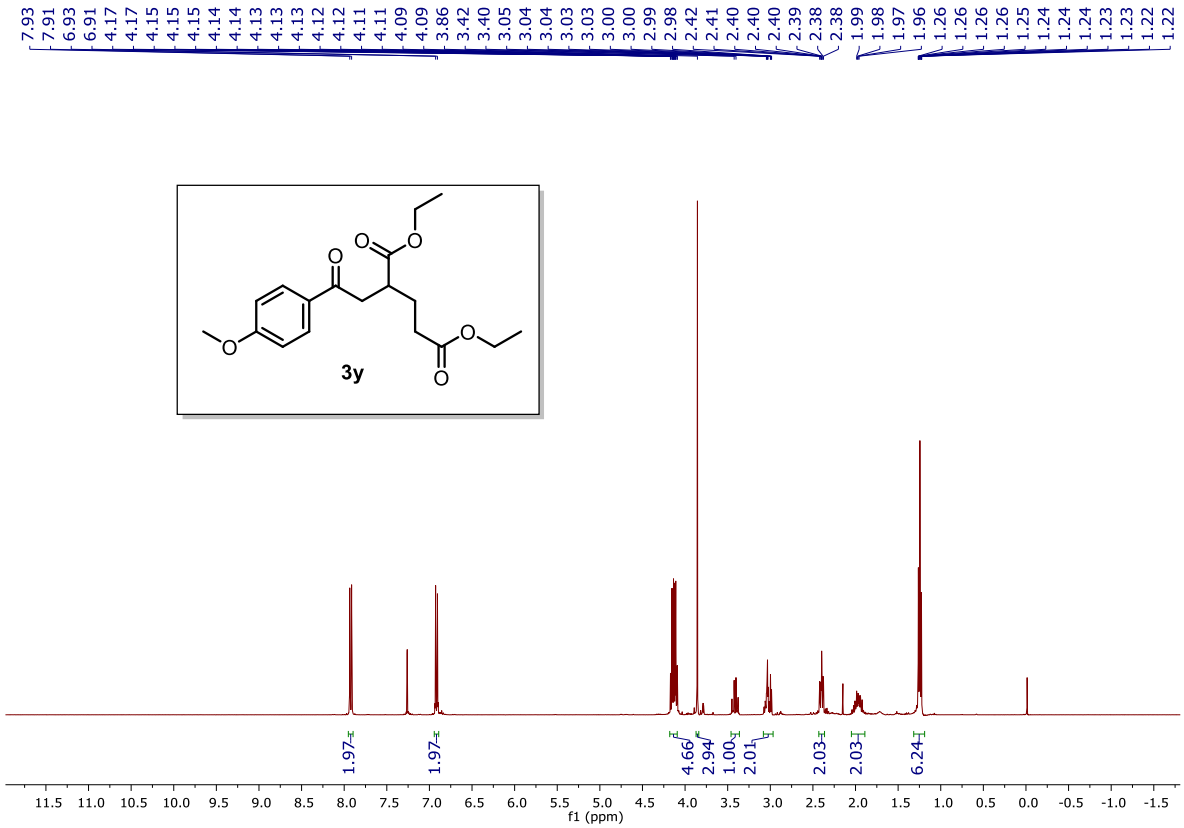
^{13}C{^{1}H} NMR spectrum of **3w**, $CDCl_3$, 100 MHz



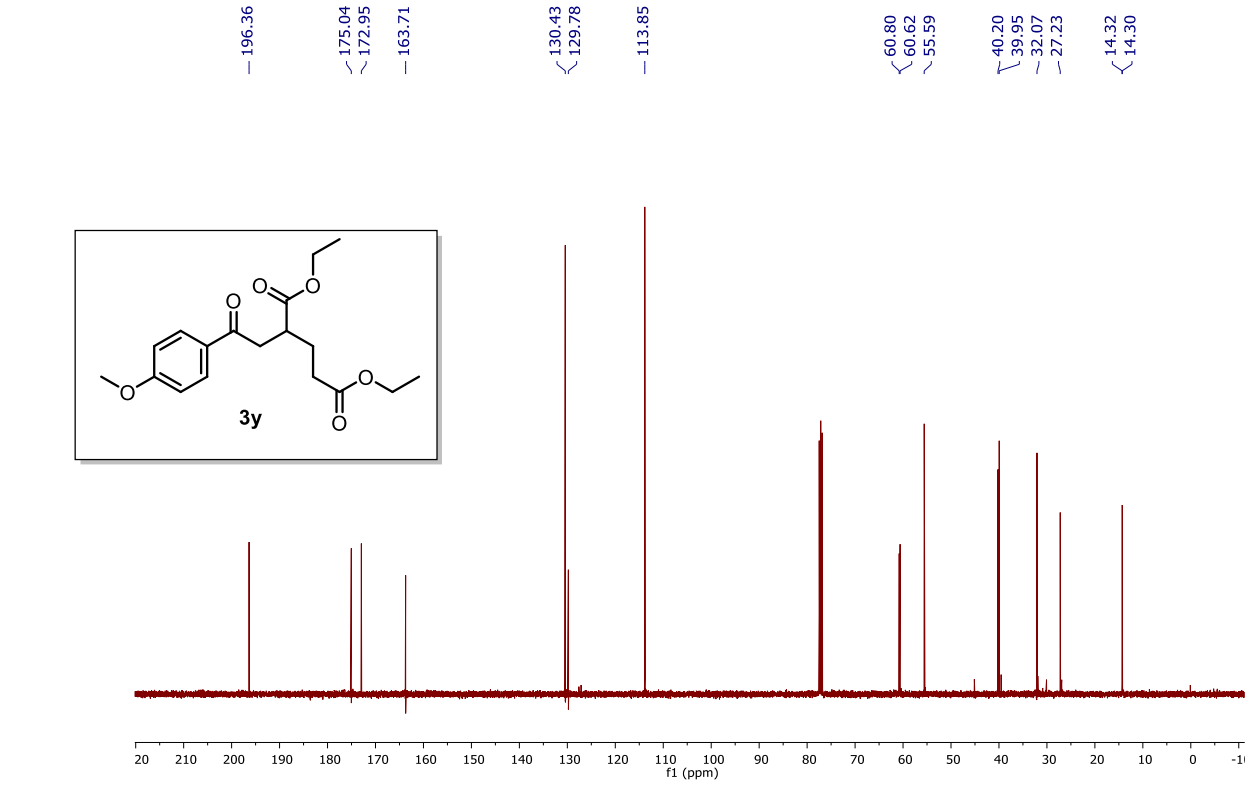
^{1}H NMR spectrum of **3x**, $CDCl_3$, 400 MHz



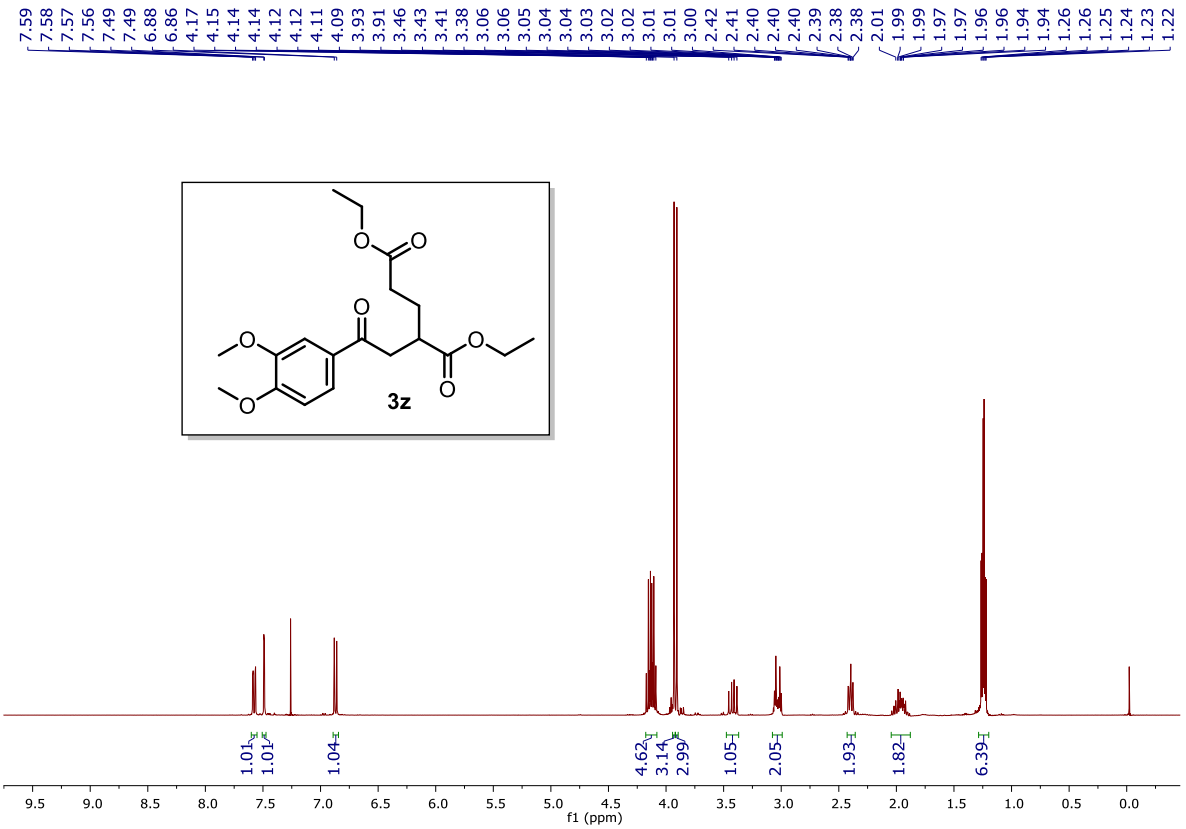
^{13}C{^{1}H} NMR spectrum of **3x**, $CDCl_3$, 100 MHz



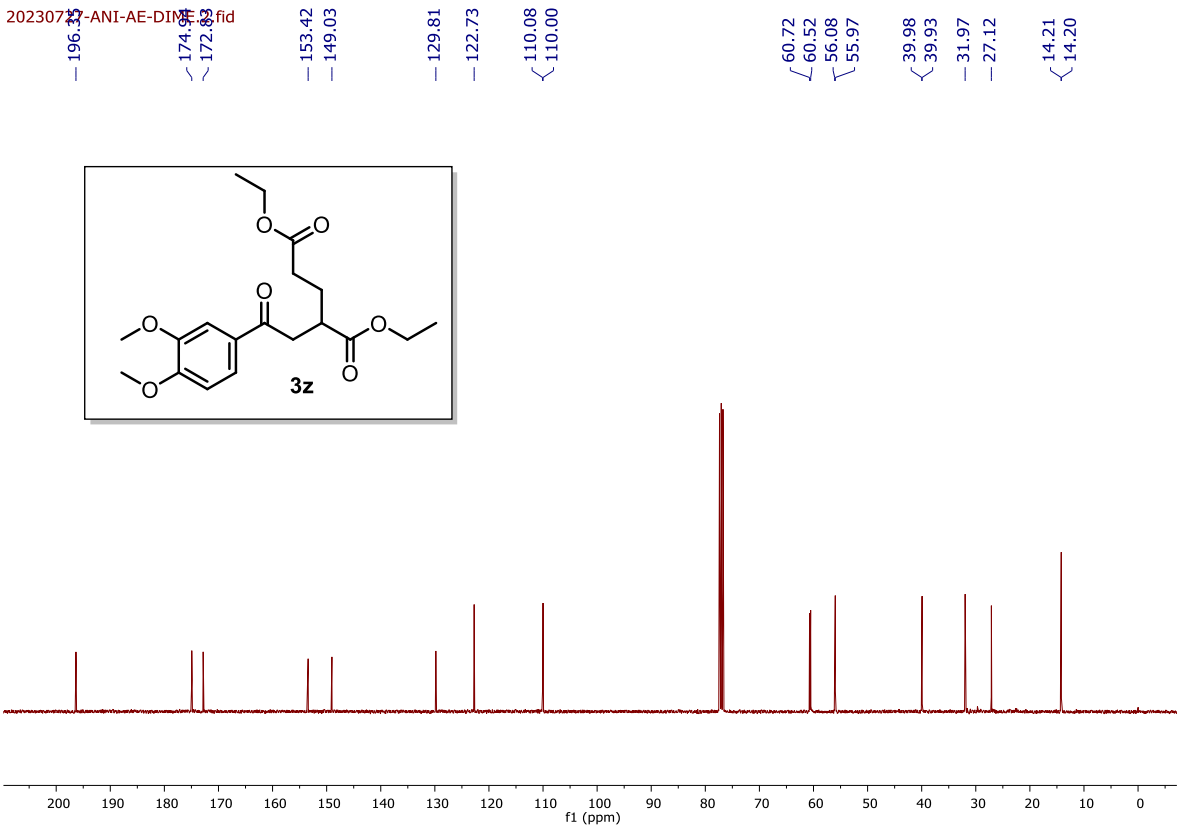
^{1}H NMR spectrum of **3y**, $CDCl_3$, 400 MHz



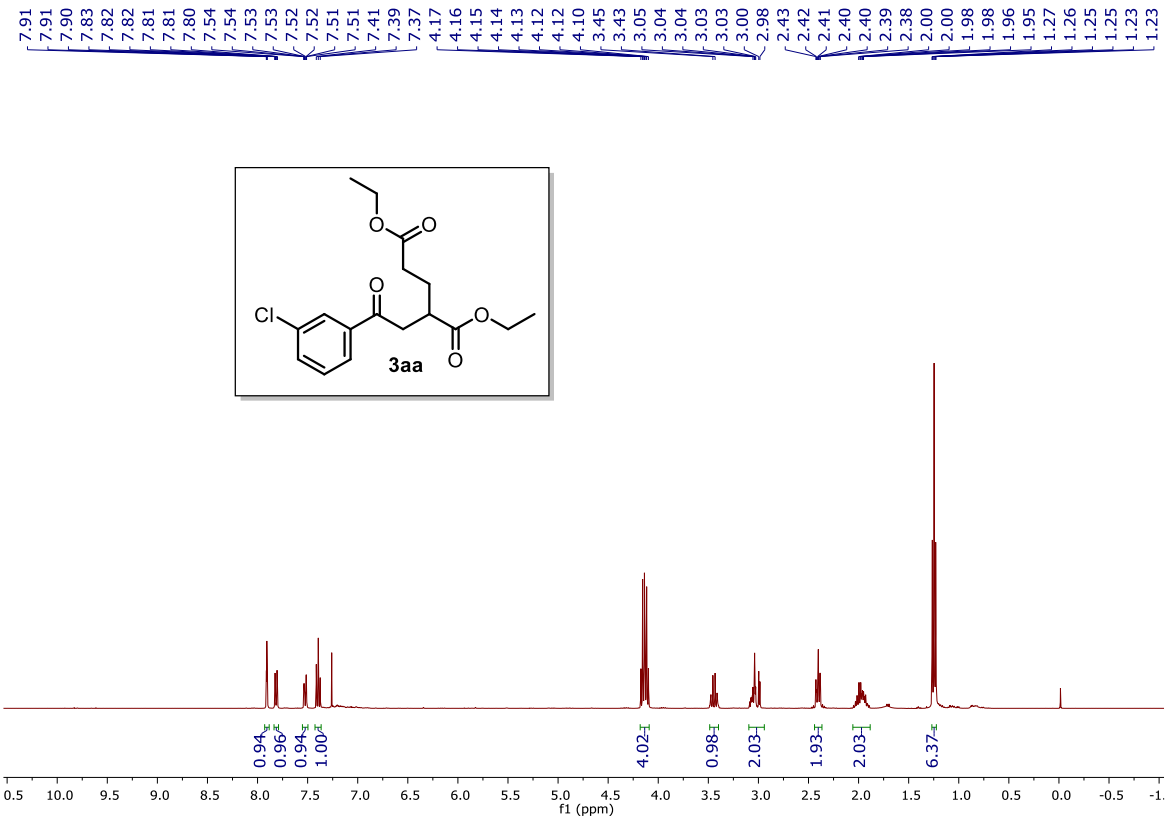
^{13}C {^{1}H} NMR spectrum of **3y**, $CDCl_3$, 100 MHz



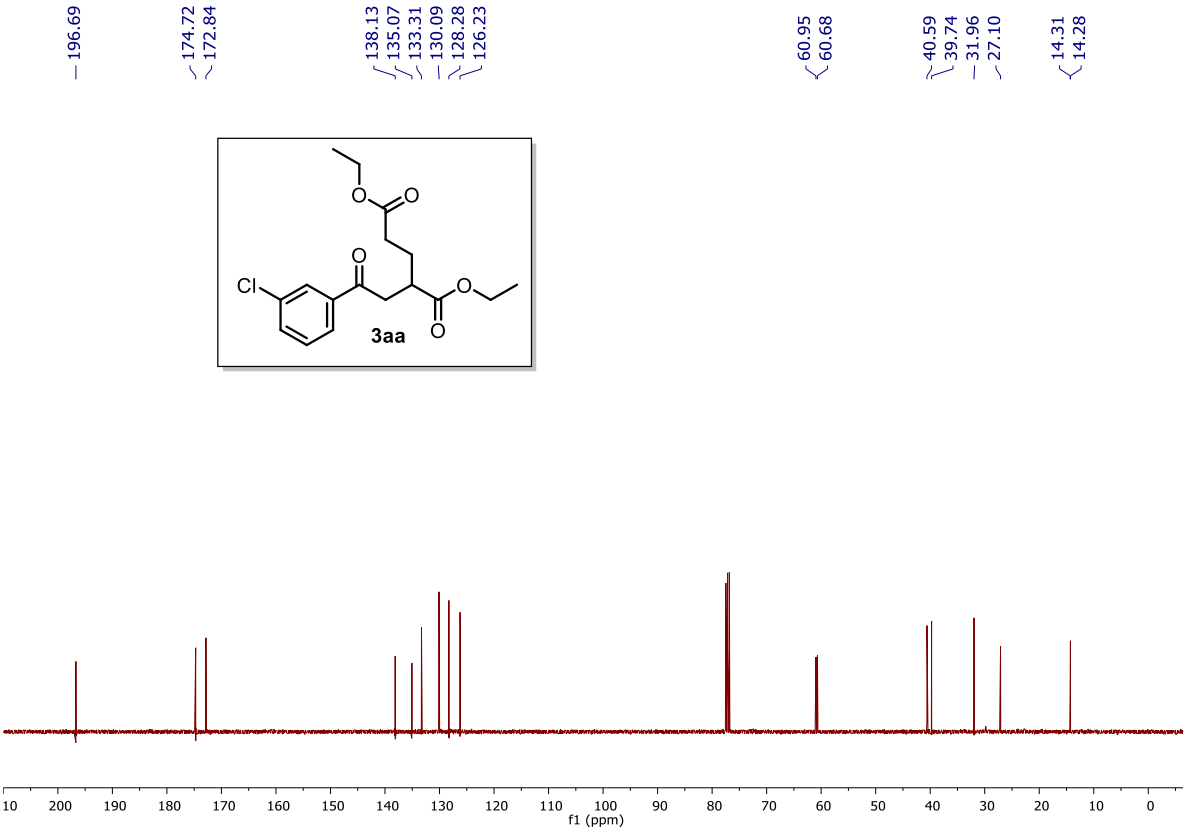
^{1}H NMR spectrum of **3z**, $CDCl_3$, 400 MHz



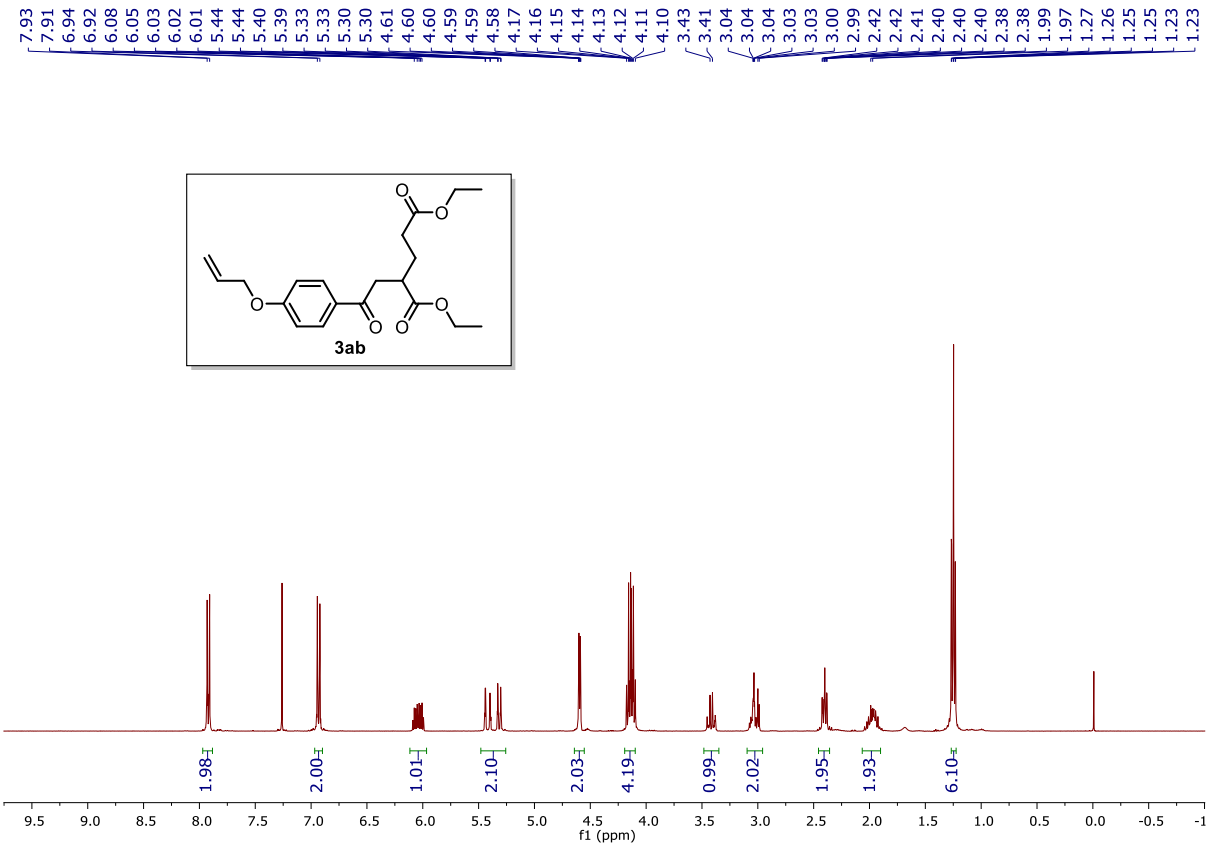
^{13}C{^{1}H} NMR spectrum of **3z**, $CDCl_3$, 100 MHz



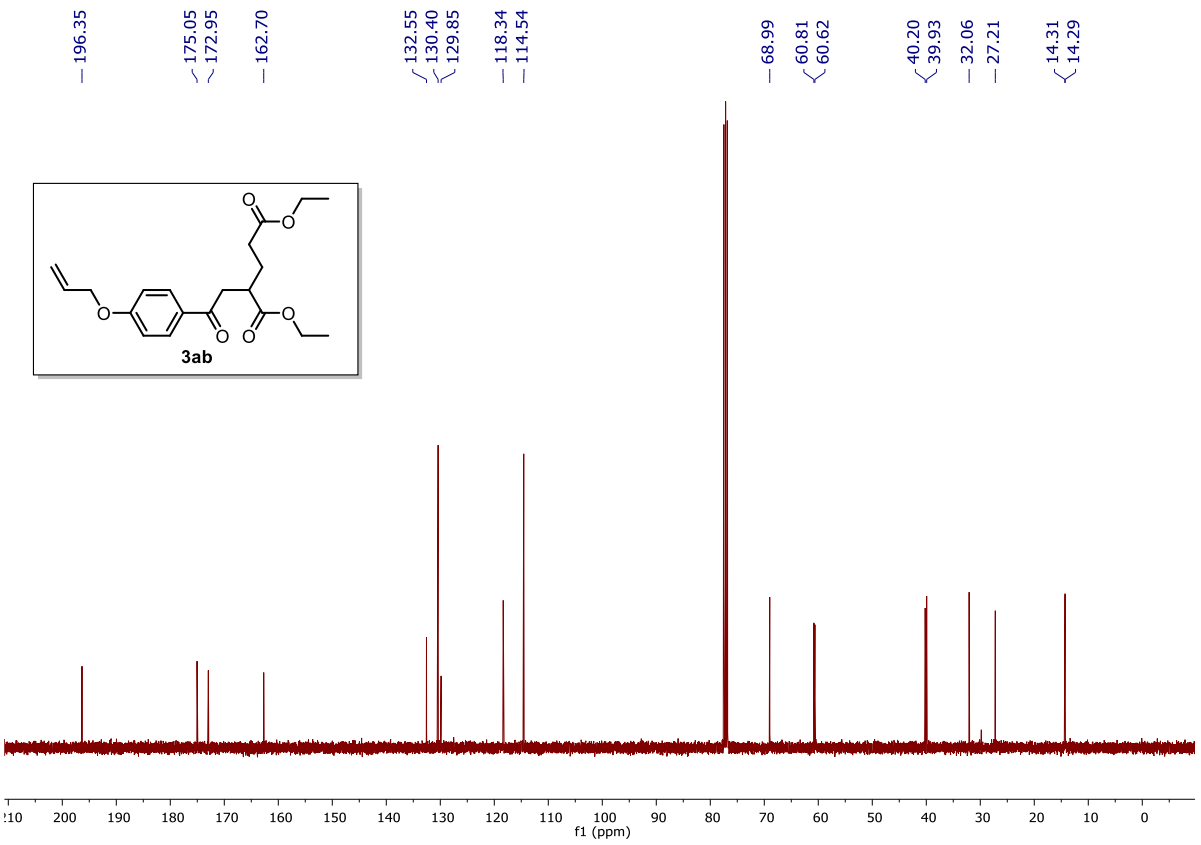
^{1}H NMR spectrum of **3aa**, $CDCl_3$, 400 MHz



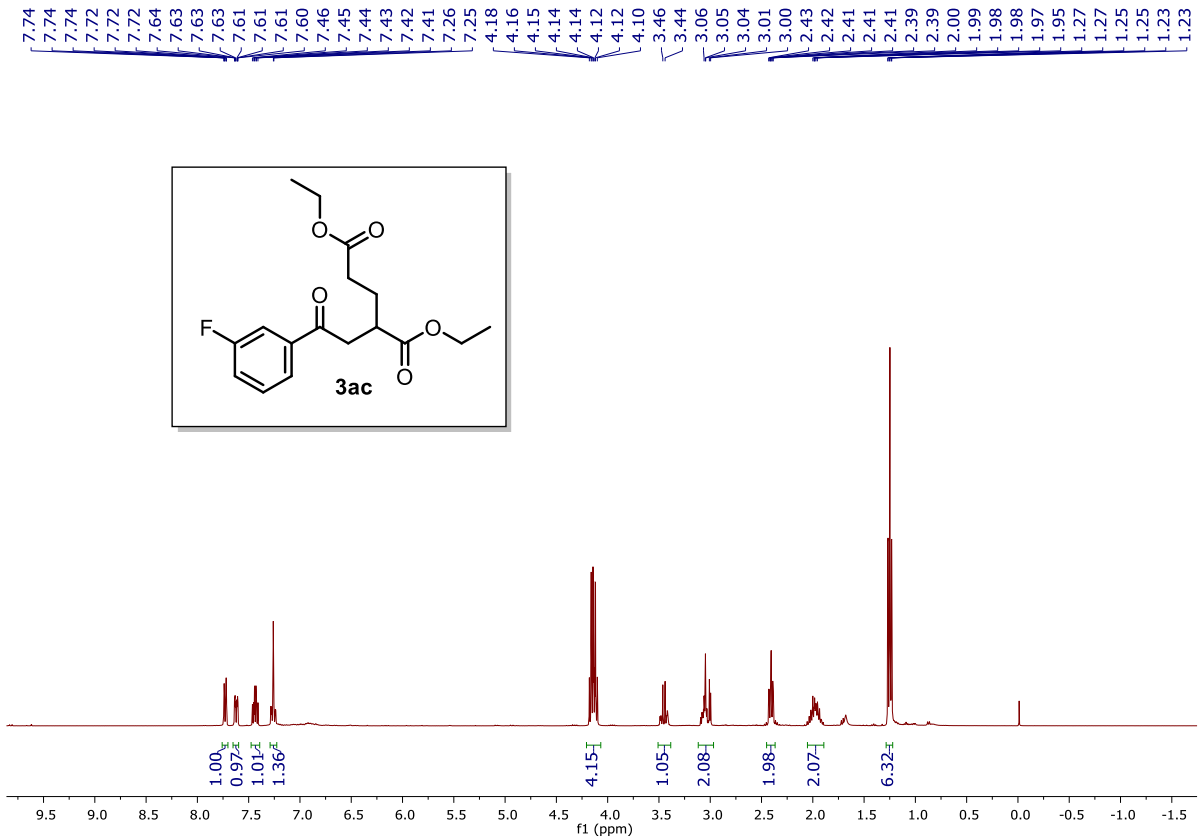
^{13}C{^{1}H} NMR spectrum of **3aa**, $CDCl_3$, 100 MHz



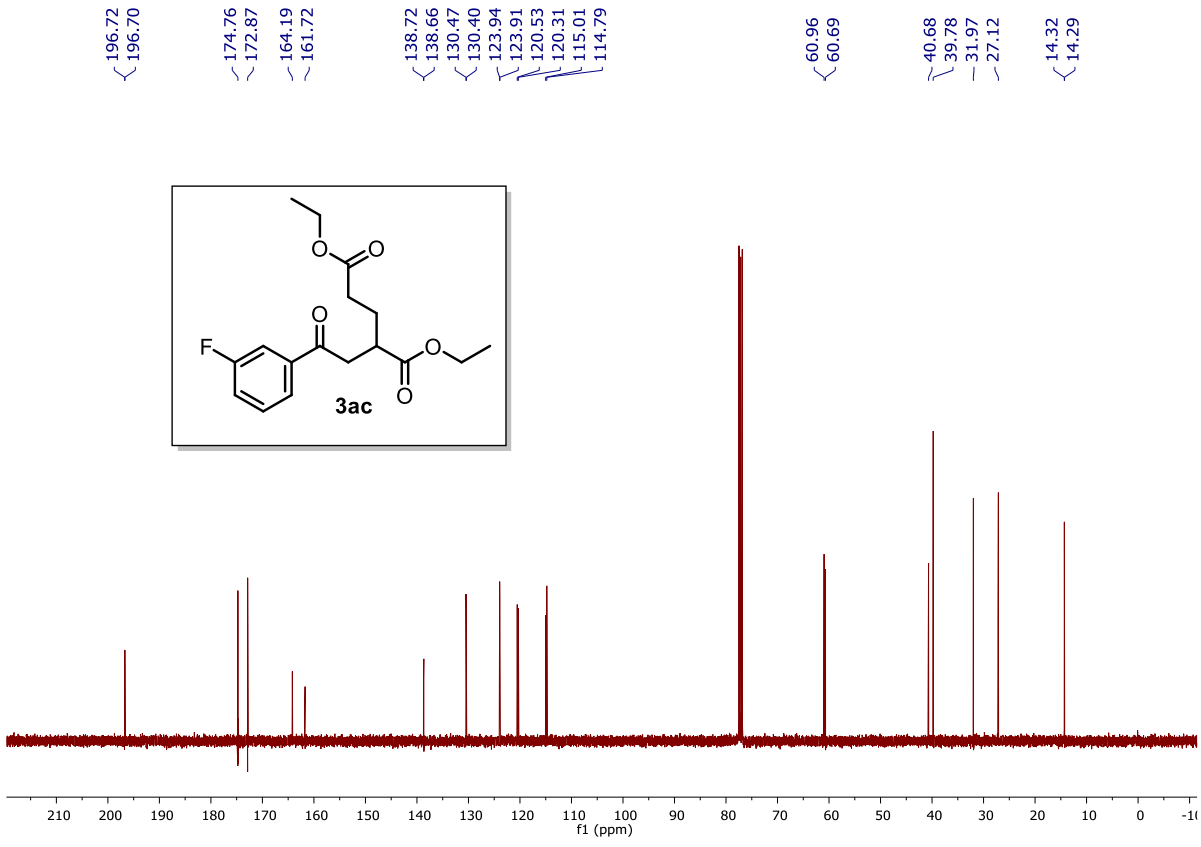
^{1}H NMR spectrum of **3ab**, $CDCl_3$, 400 MHz



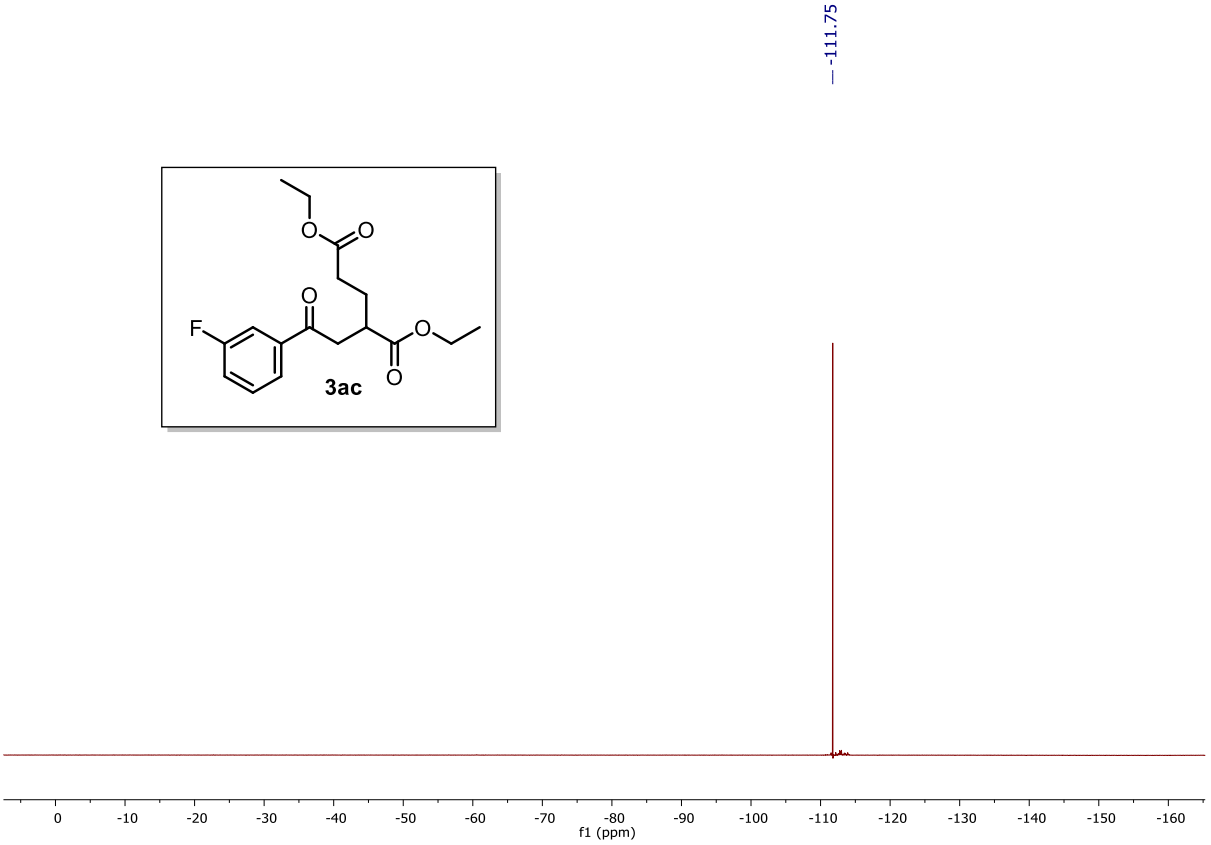
^{13}C{^{1}H} NMR spectrum of **3ab**, $CDCl_3$, 100 MHz



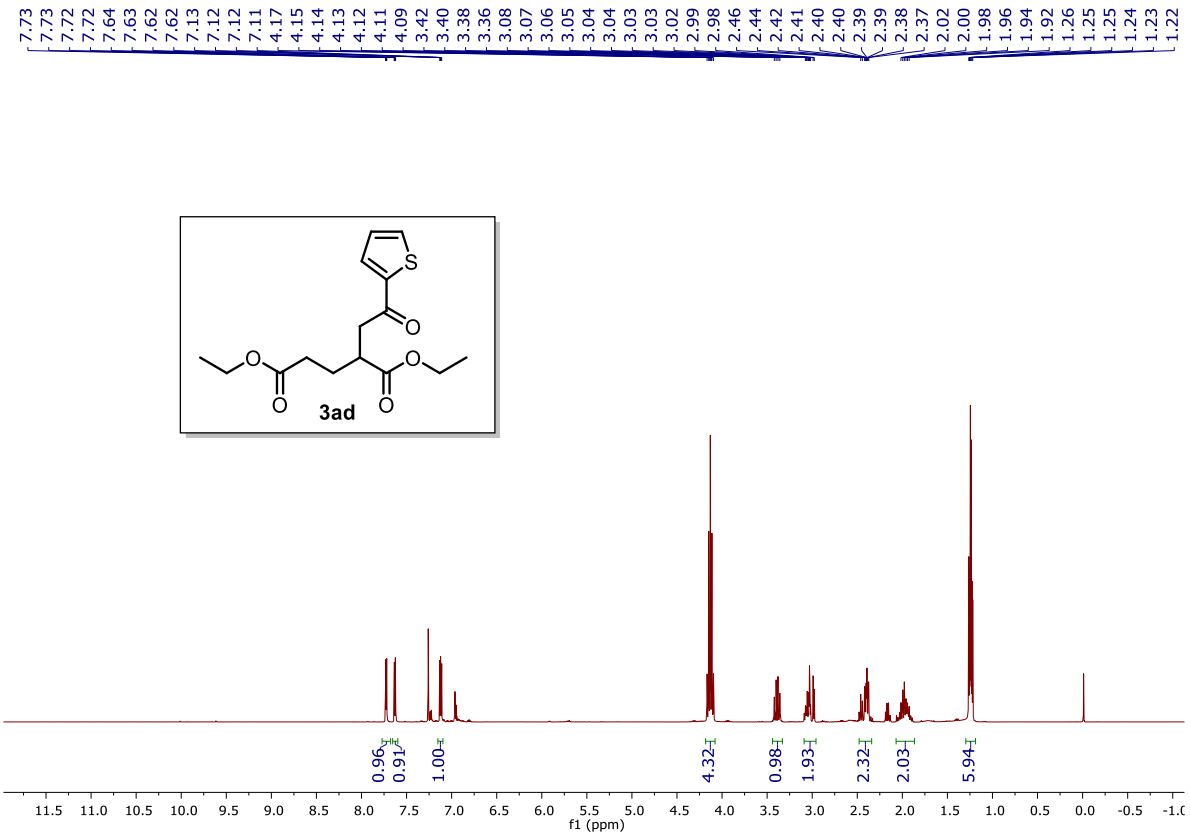
^{1}H NMR spectrum of **3ac**, $CDCl_3$, 400 MHz



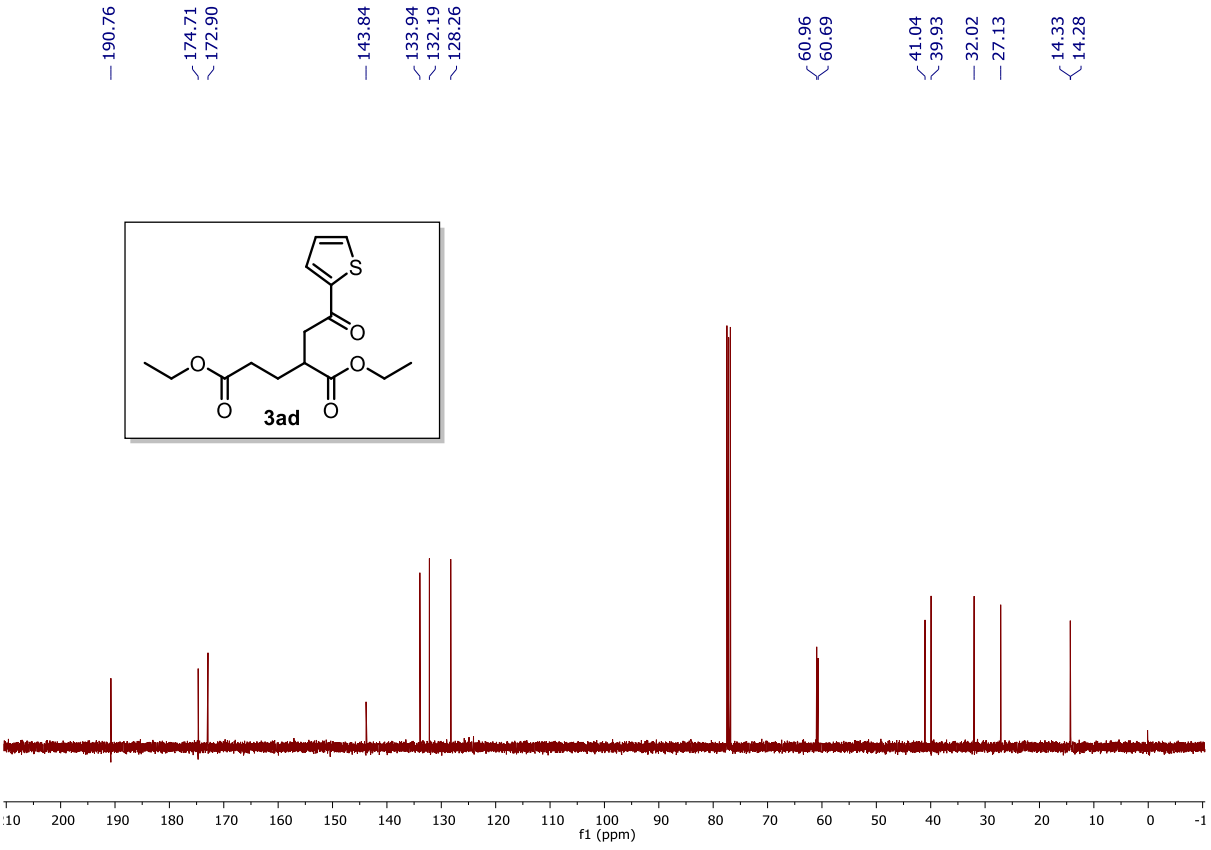
^{13}C {^{1}H} NMR spectrum of **3ac**, $CDCl_3$, 100 MHz



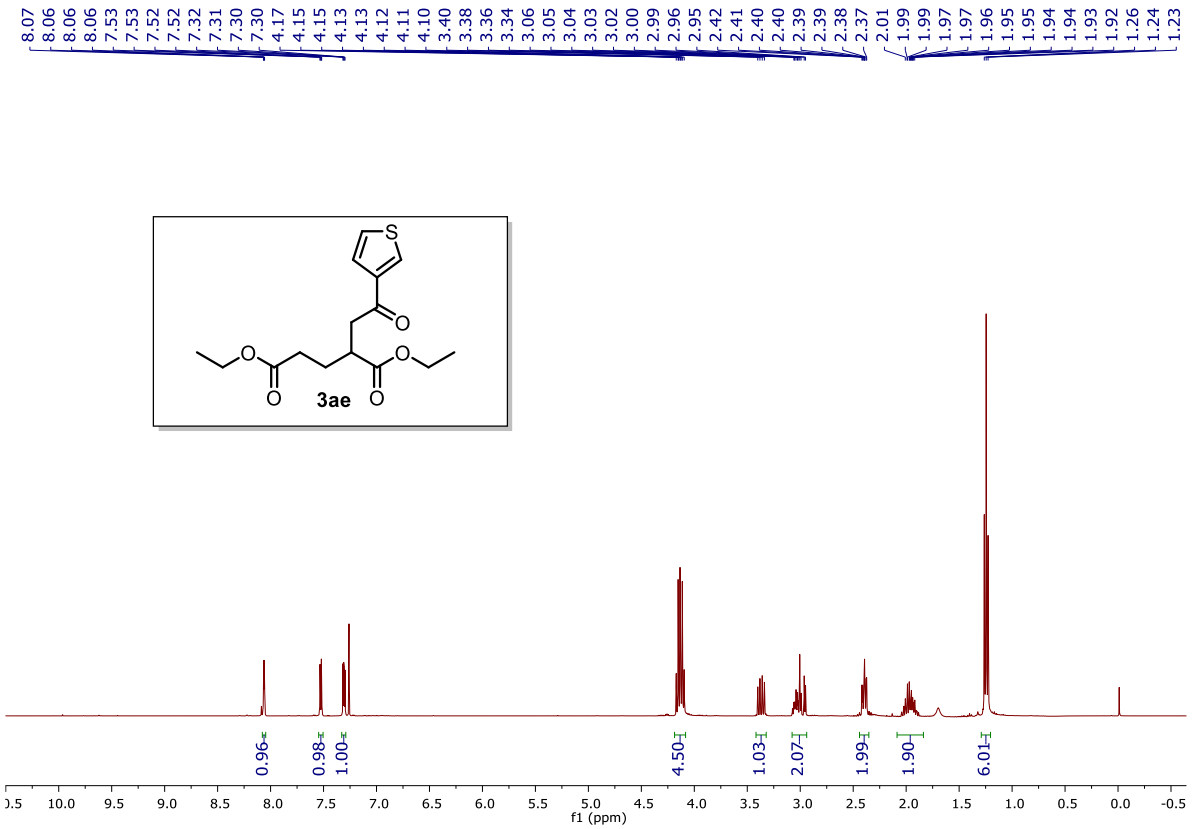
^{19}F NMR spectrum of **3ac**, $CDCl_3$, 377 MHz



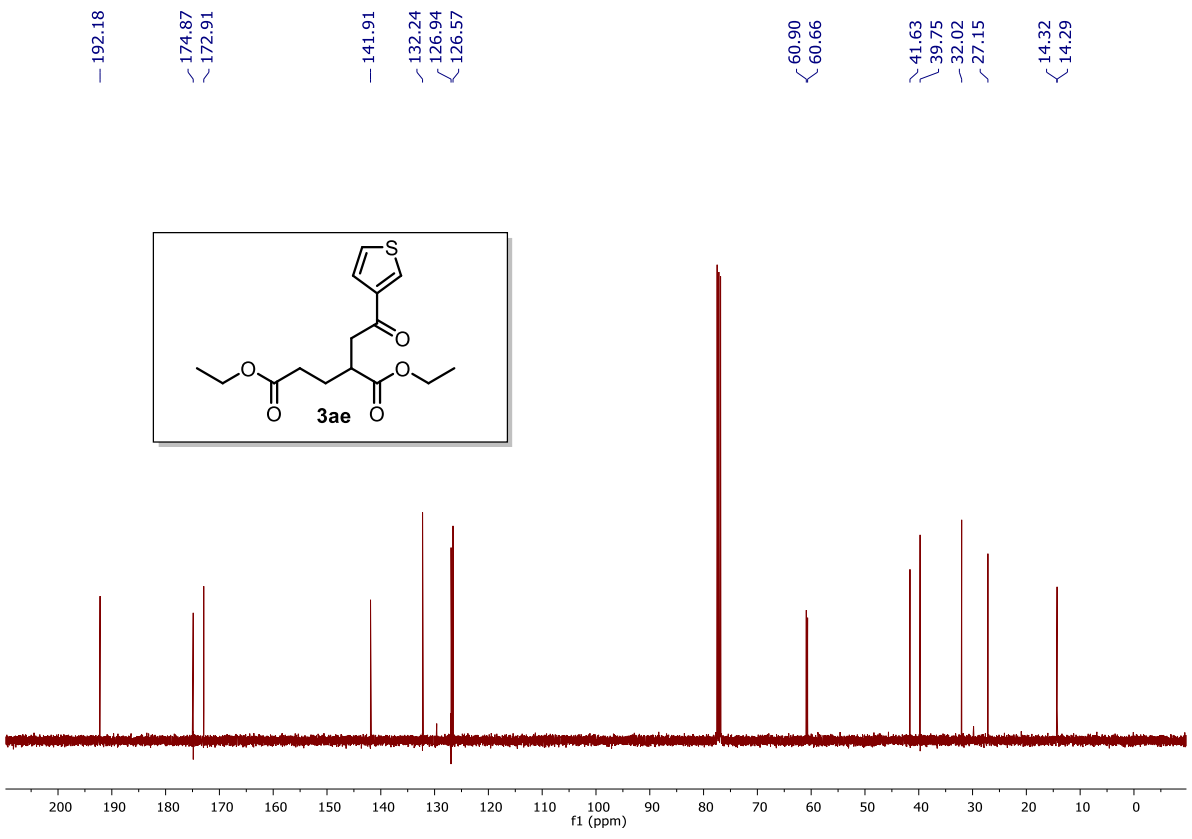
^{1}H NMR spectrum of **3ad**, $CDCl_3$, 400 MHz



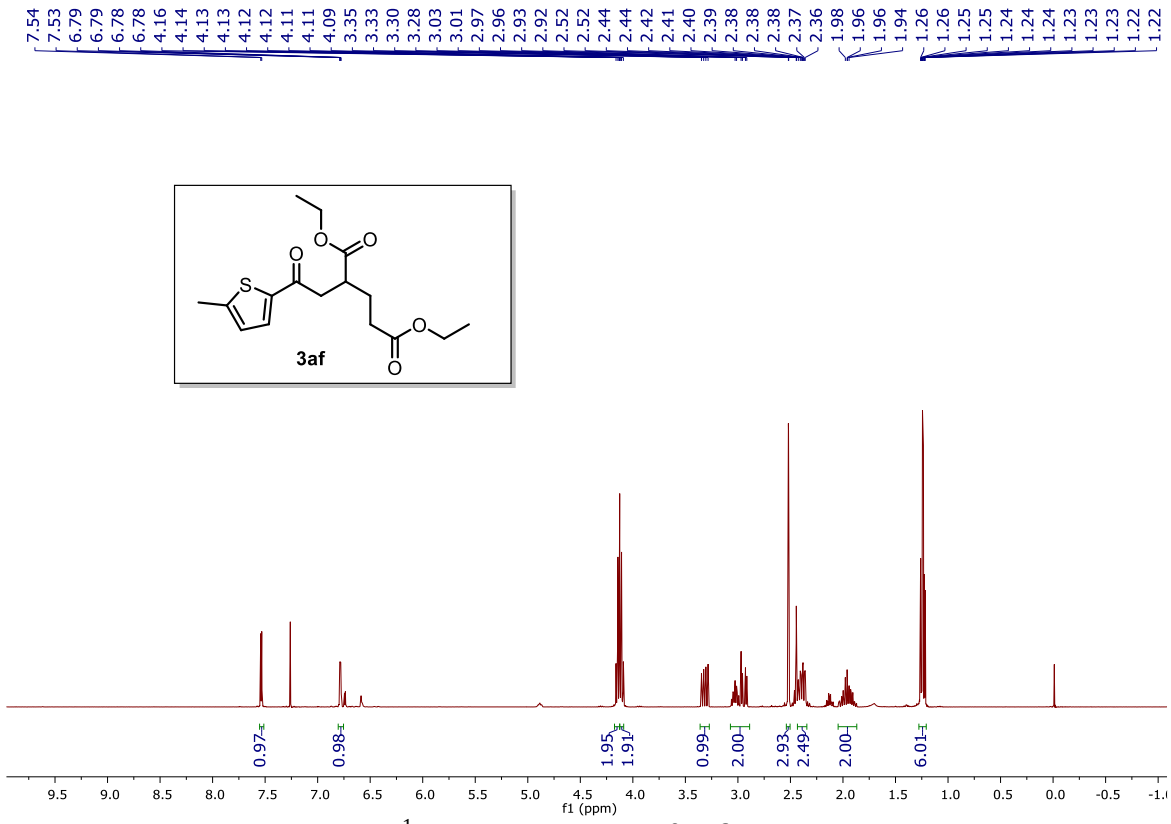
^{13}C {^{1}H} NMR spectrum of **3ad**, $CDCl_3$, 100 MHz



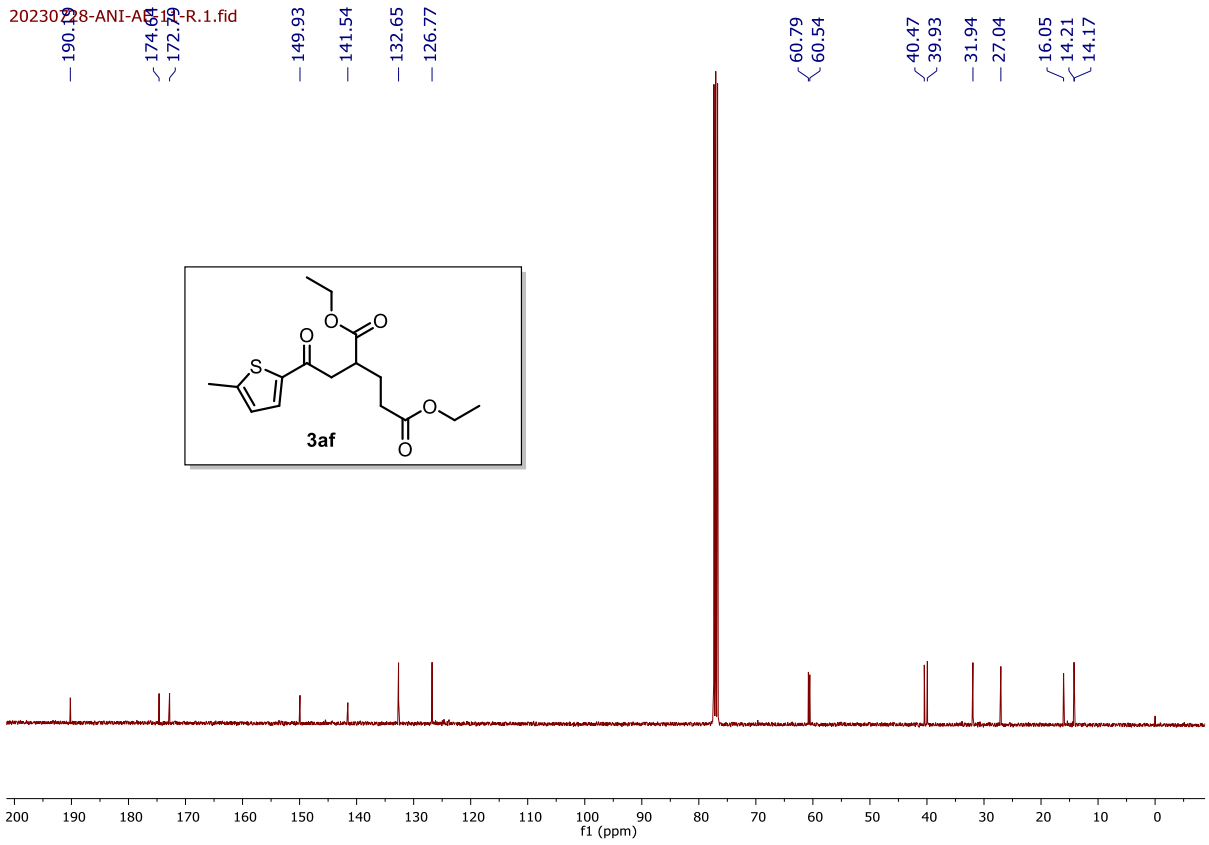
^{1}H NMR spectrum of **3ae**, $CDCl_3$, 400 MHz



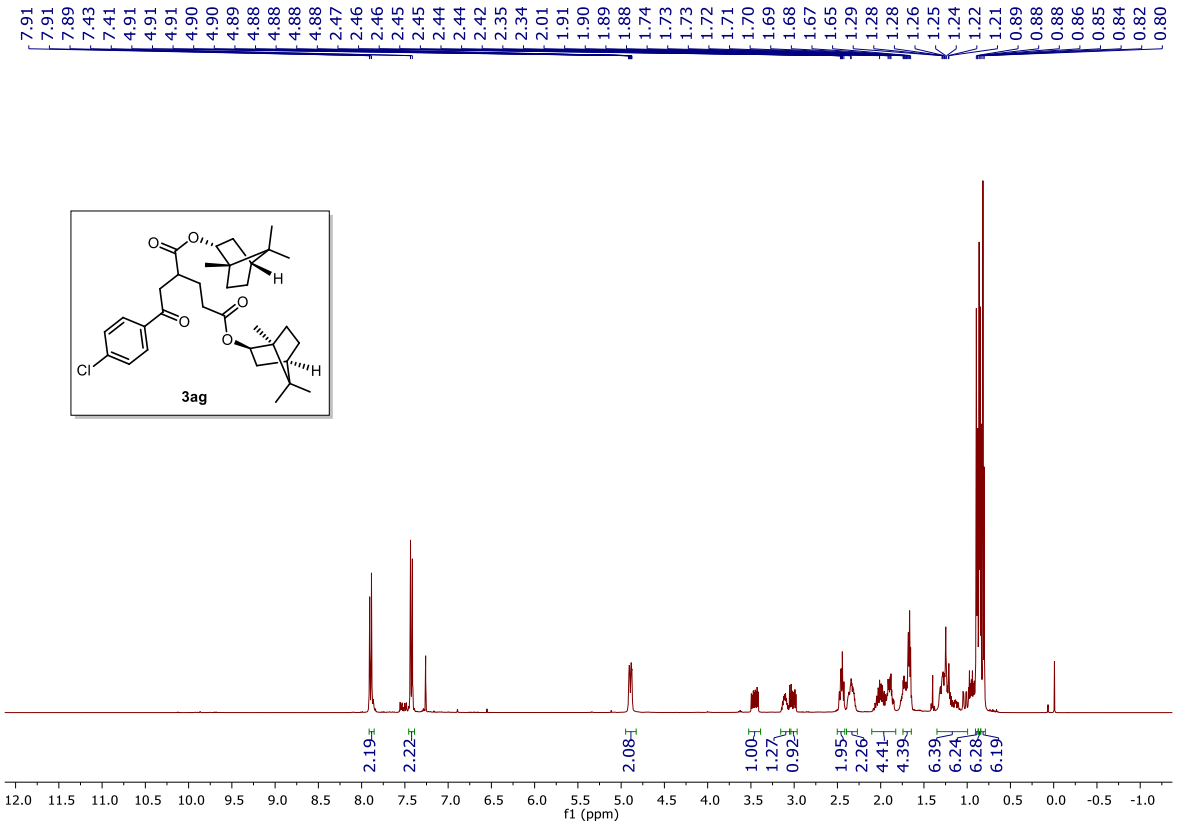
^{13}C{^{1}H} NMR spectrum of **3ae**, $CDCl_3$, 100 MHz



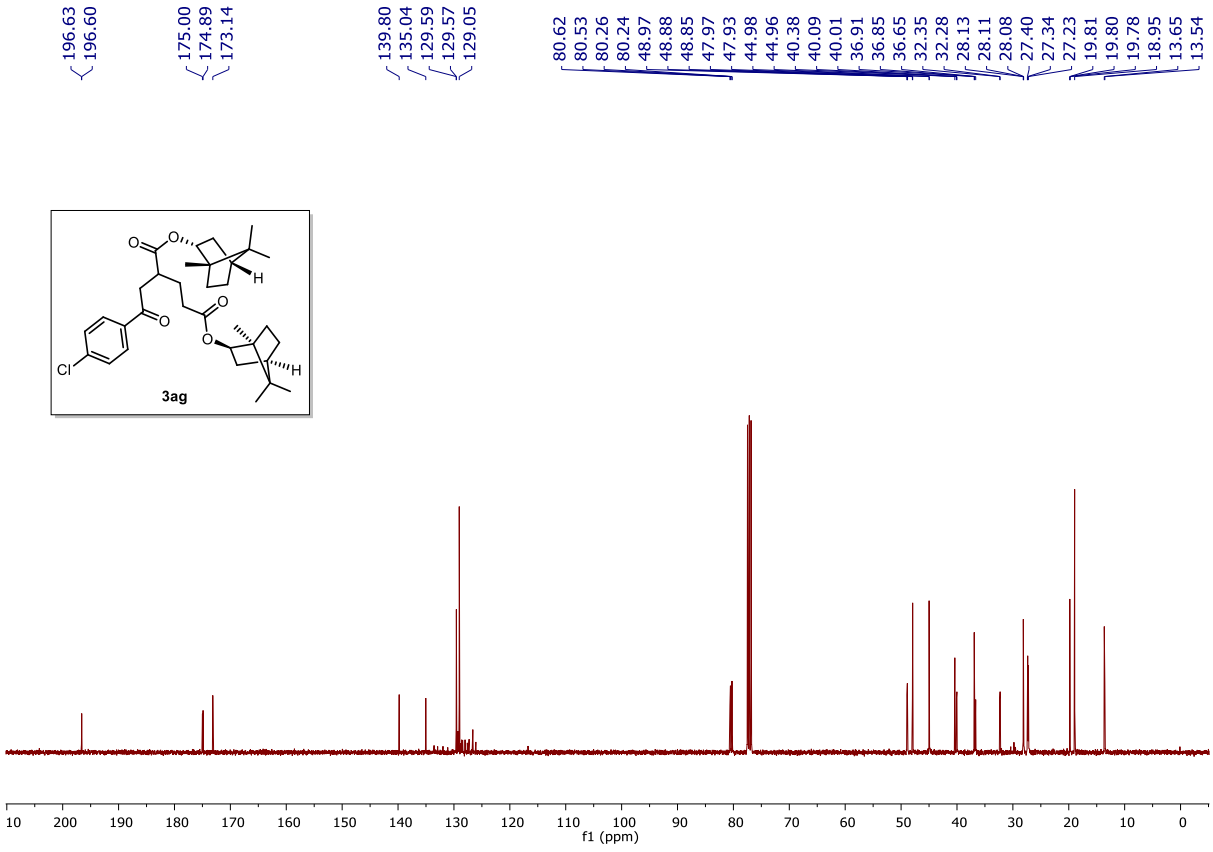
^{1}H NMR spectrum of **3af**, $CDCl_3$, 400 MHz



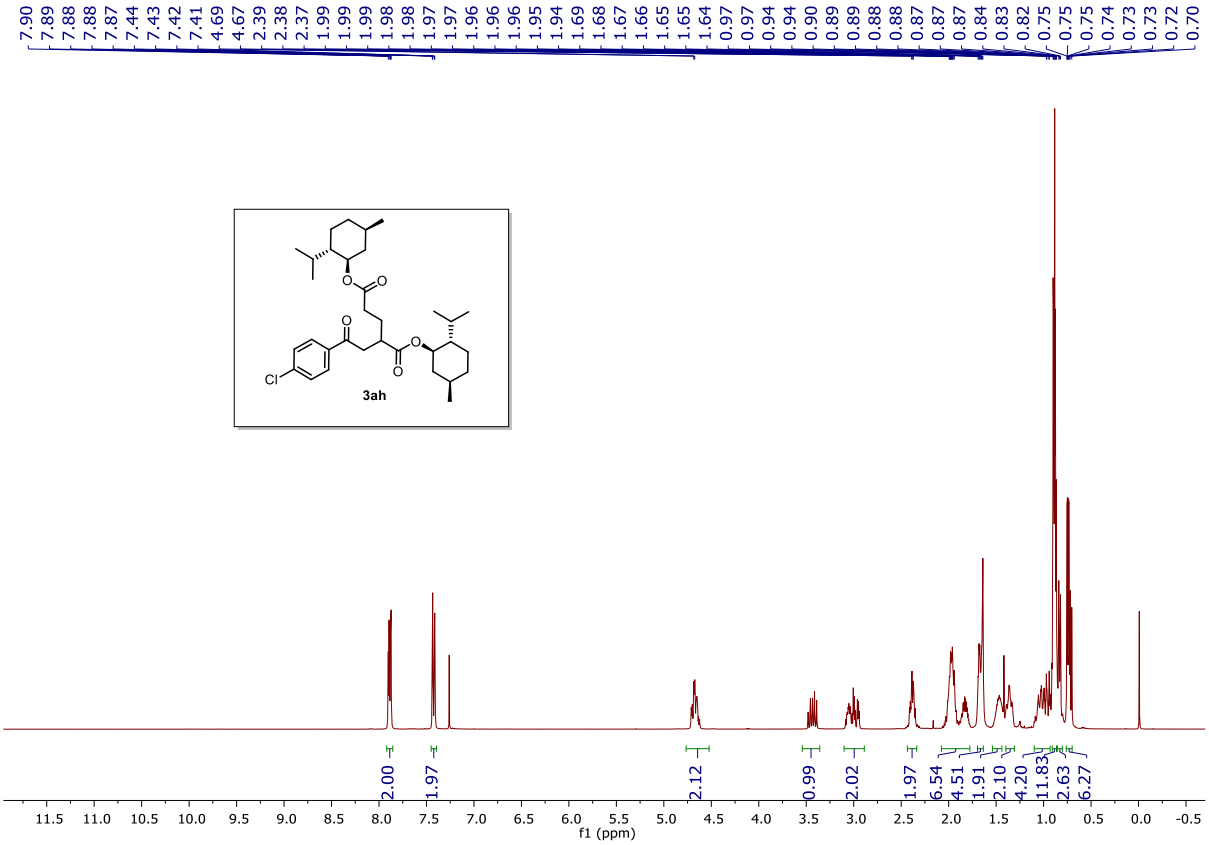
^{13}C{^{1}H} NMR spectrum of **3af**, $CDCl_3$, 100 MHz



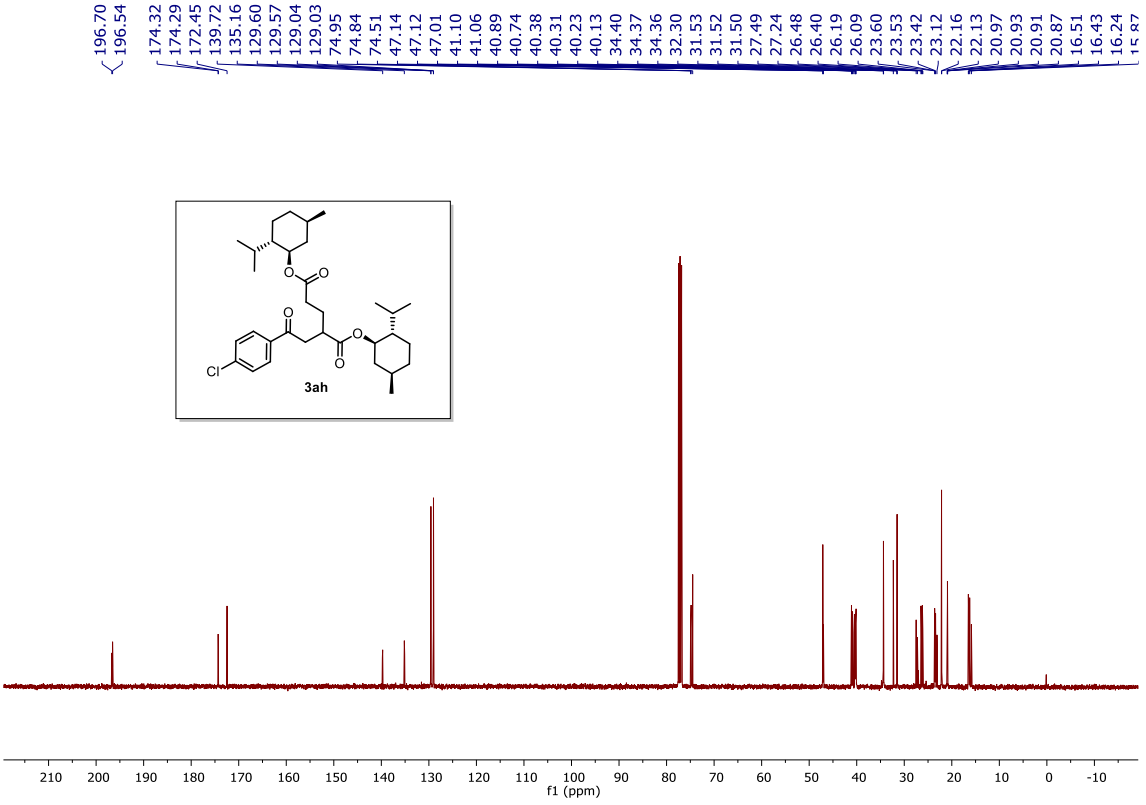
^{1}H NMR spectrum of **3ag**, $CDCl_3$, 400 MHz



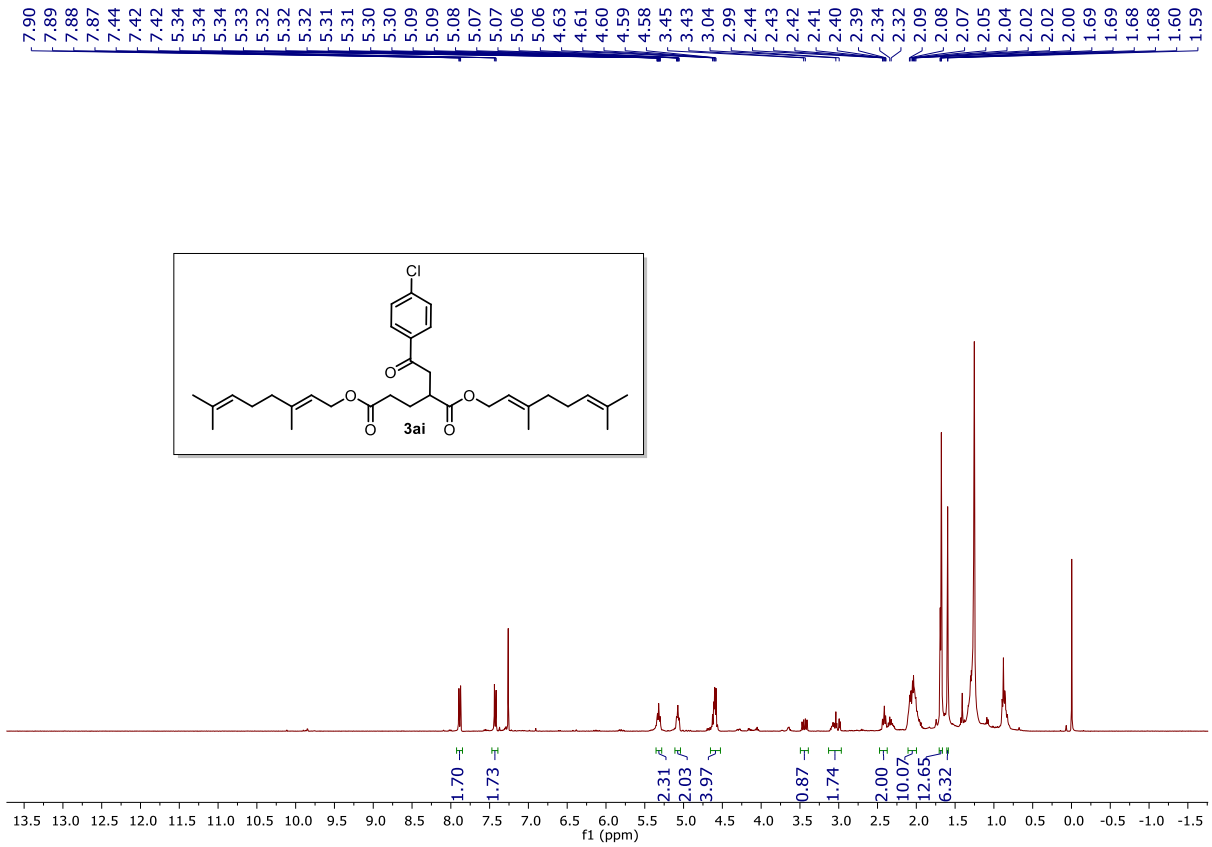
$^{13}C\{^{1}H\}$ NMR spectrum of **3ag**, $CDCl_3$, 100 MHz



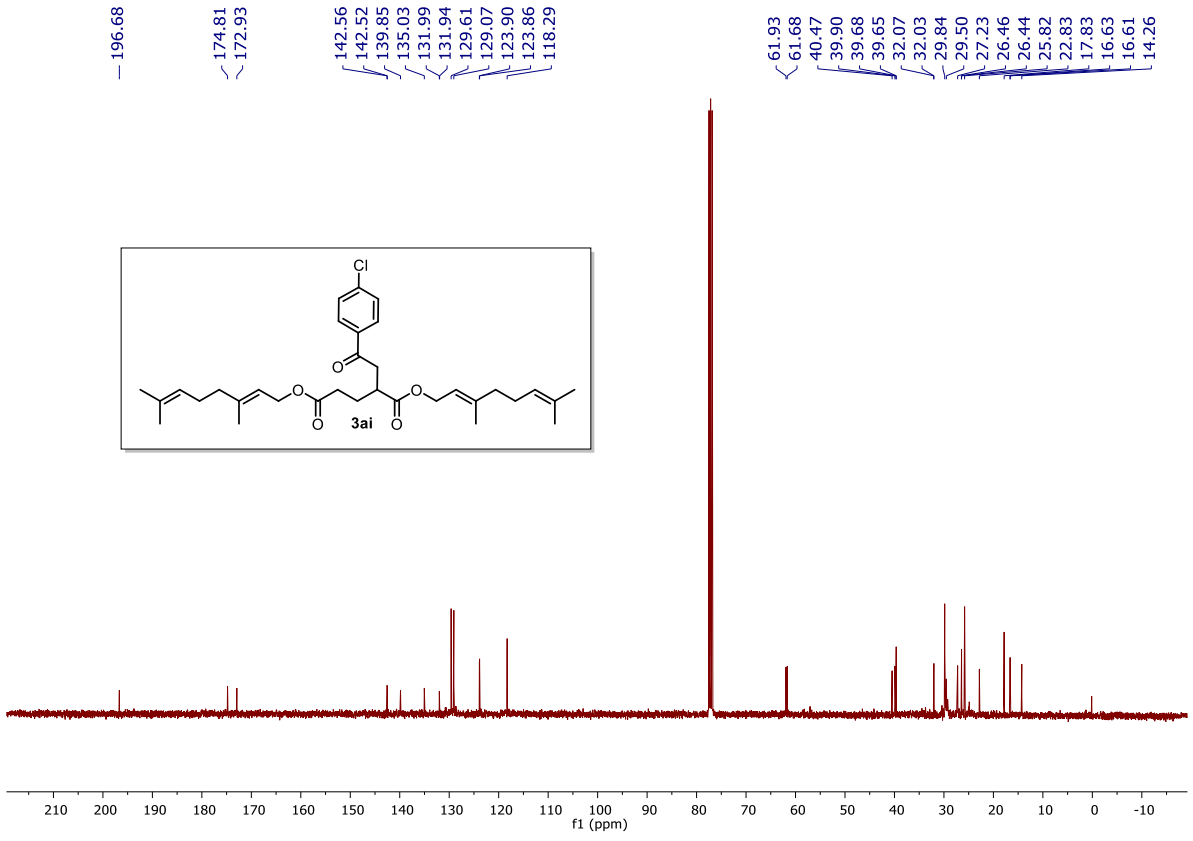
^{1}H NMR spectrum of **3ah**, $CDCl_3$, 400 MHz



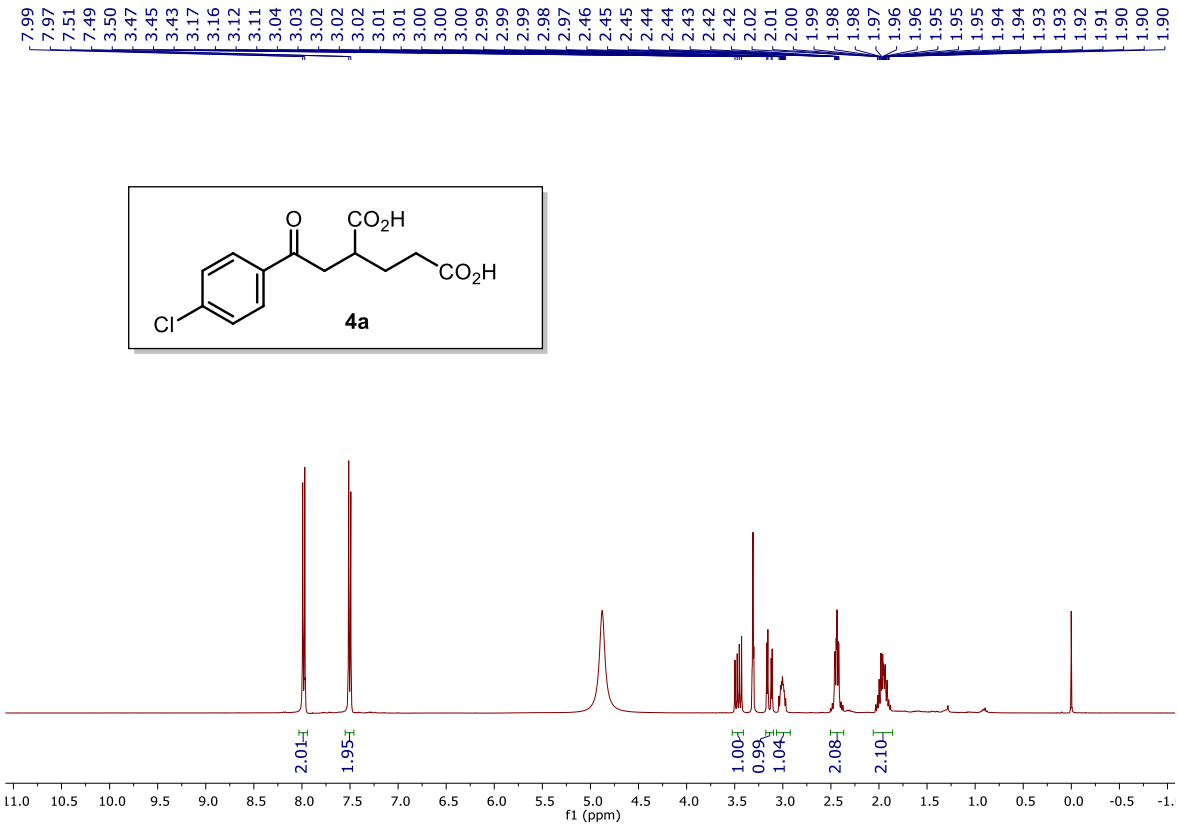
$^{13}C\ \{^{1}H\}$ NMR spectrum of **3ah**, $CDCl_3$, 100 MHz



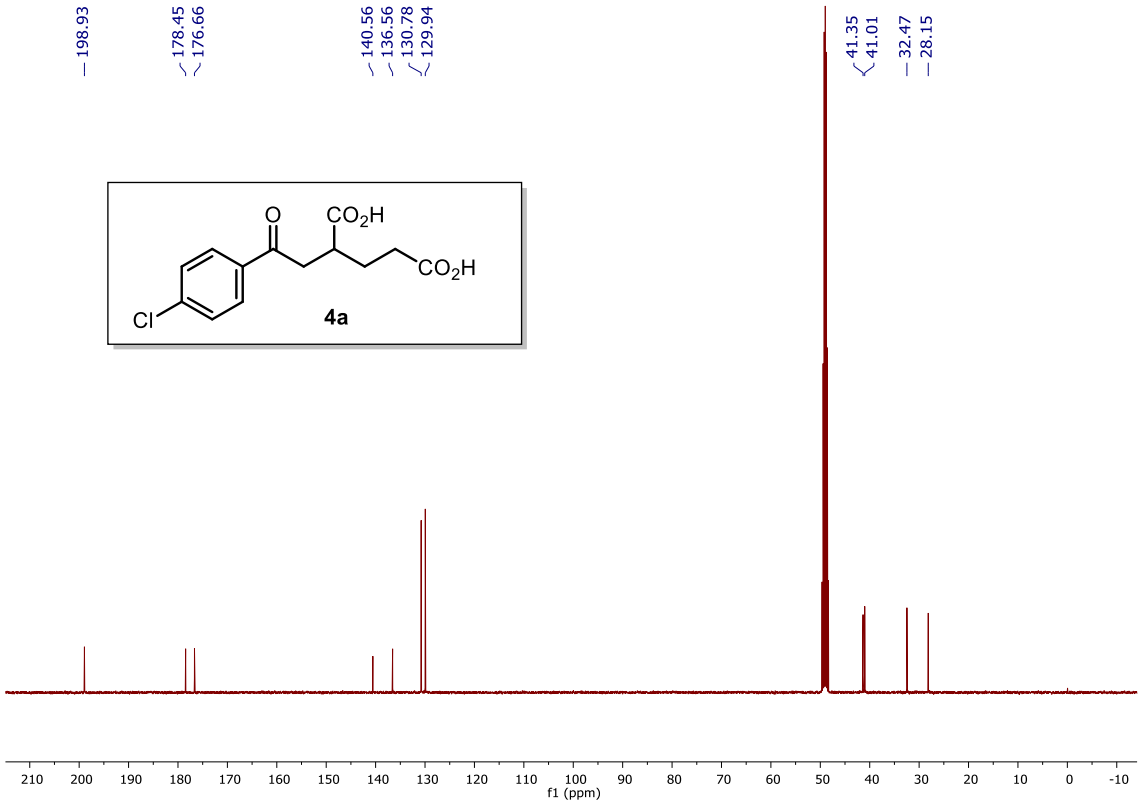
^{1}H NMR spectrum of **3ai**, $CDCl_3$, 400 MHz



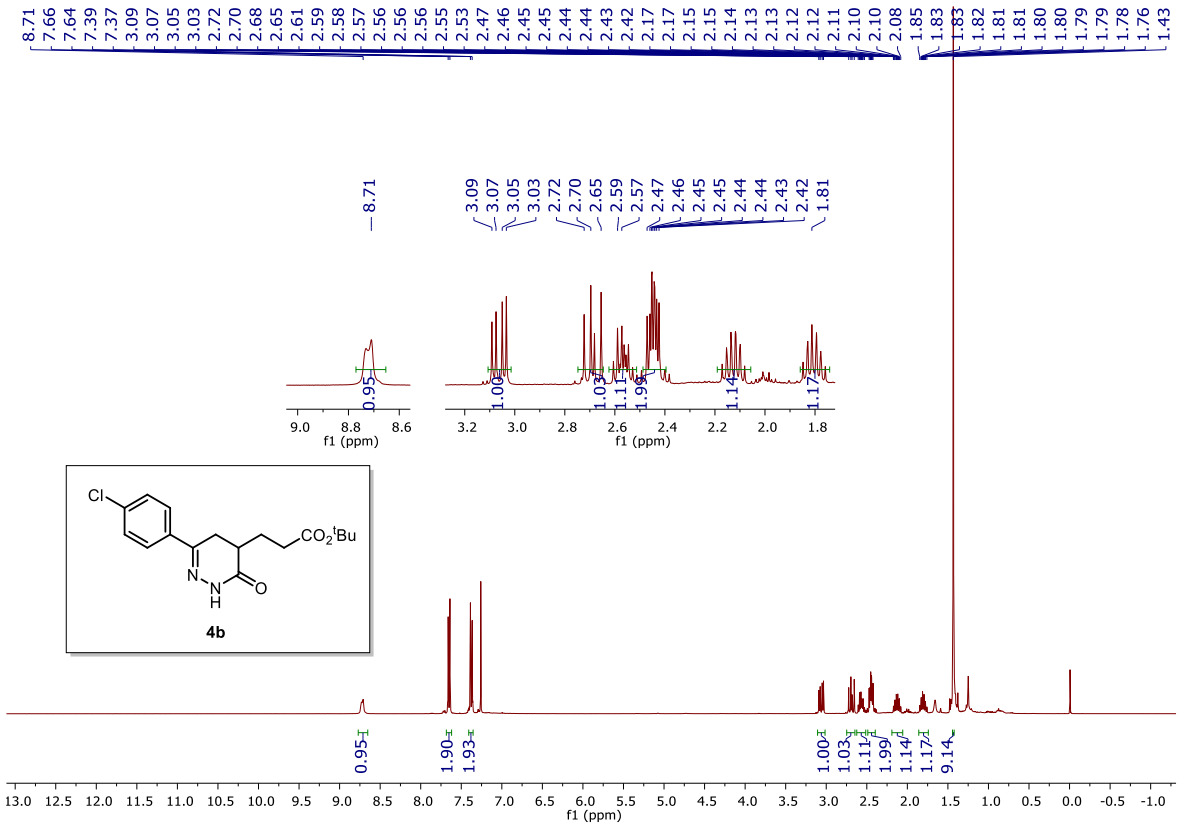
^{13}C{^{1}H} NMR spectrum of **3ai**, $CDCl_3$, 100 MHz



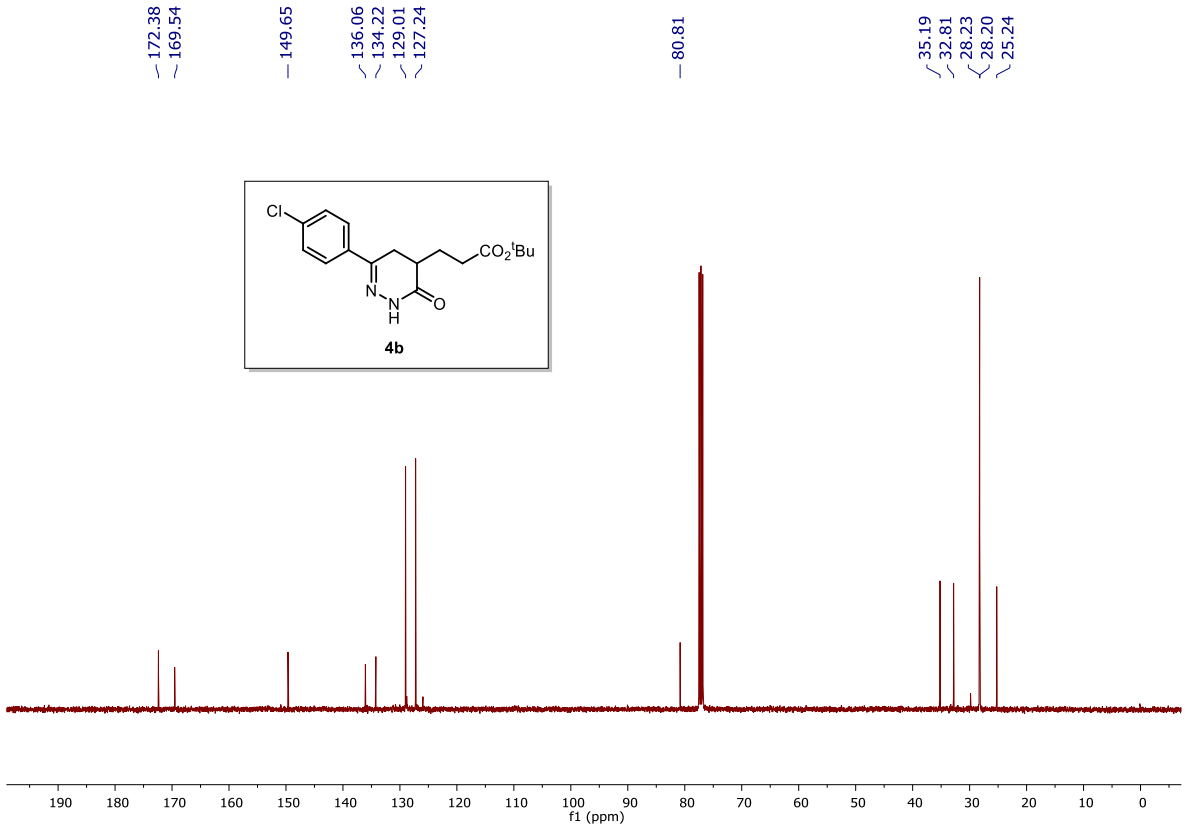
^{1}H NMR spectrum of **4a**, CD_3OD, 400 MHz



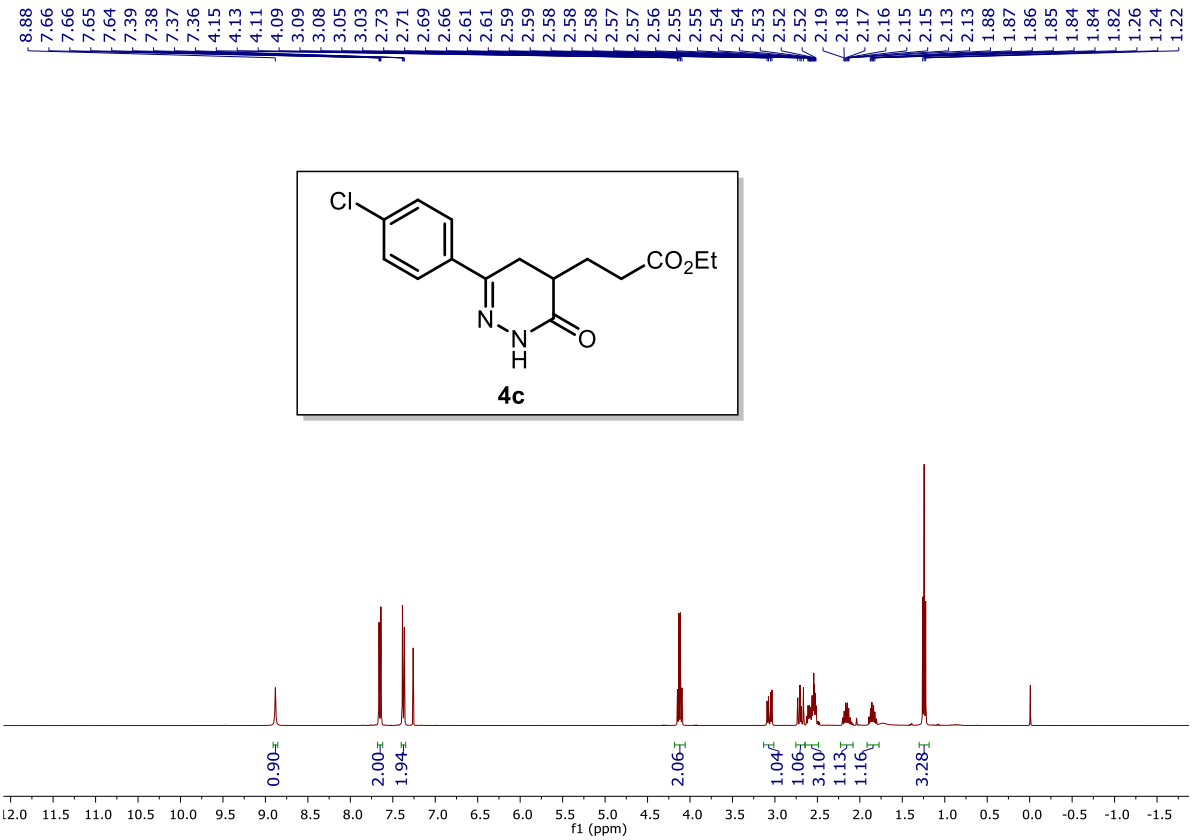
^{13}C{^{1}H} NMR spectrum of **4a**, CD_3OD, 100 MHz



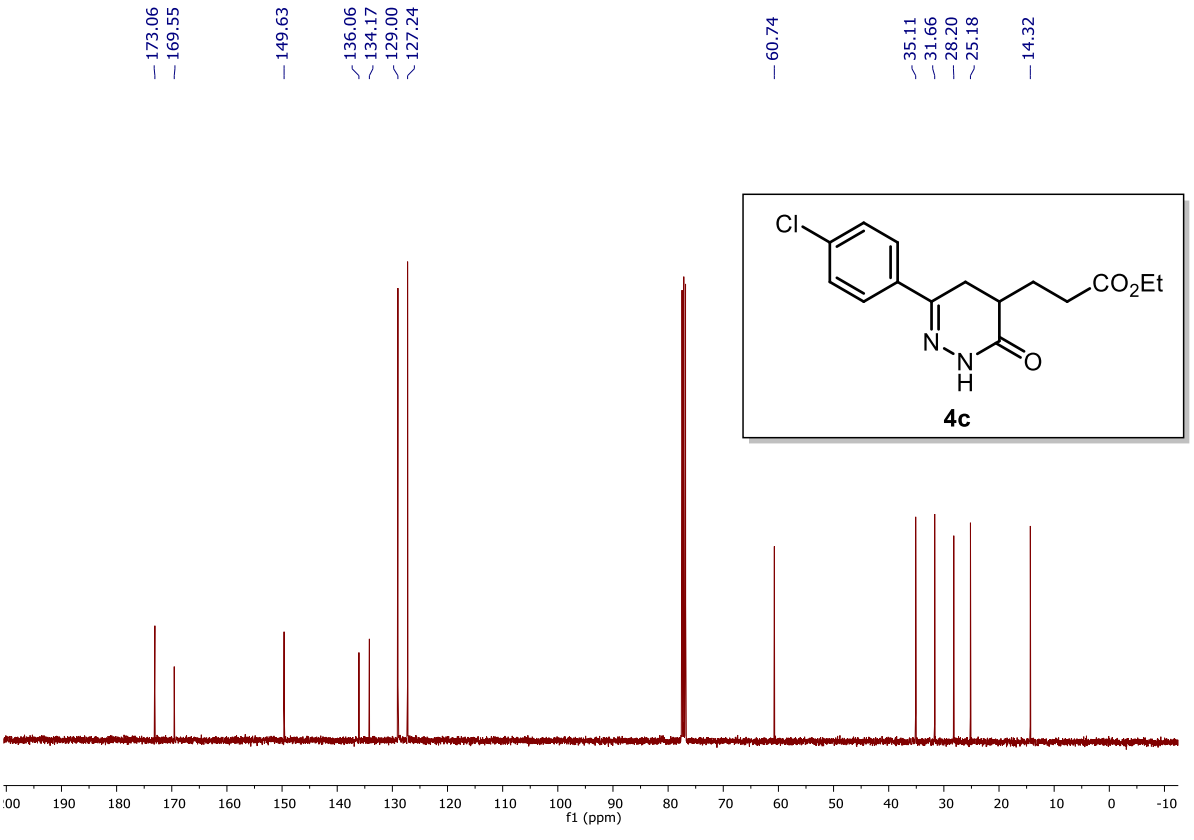
^{1}H NMR spectrum of **4b**, $CDCl_3$, 400 MHz



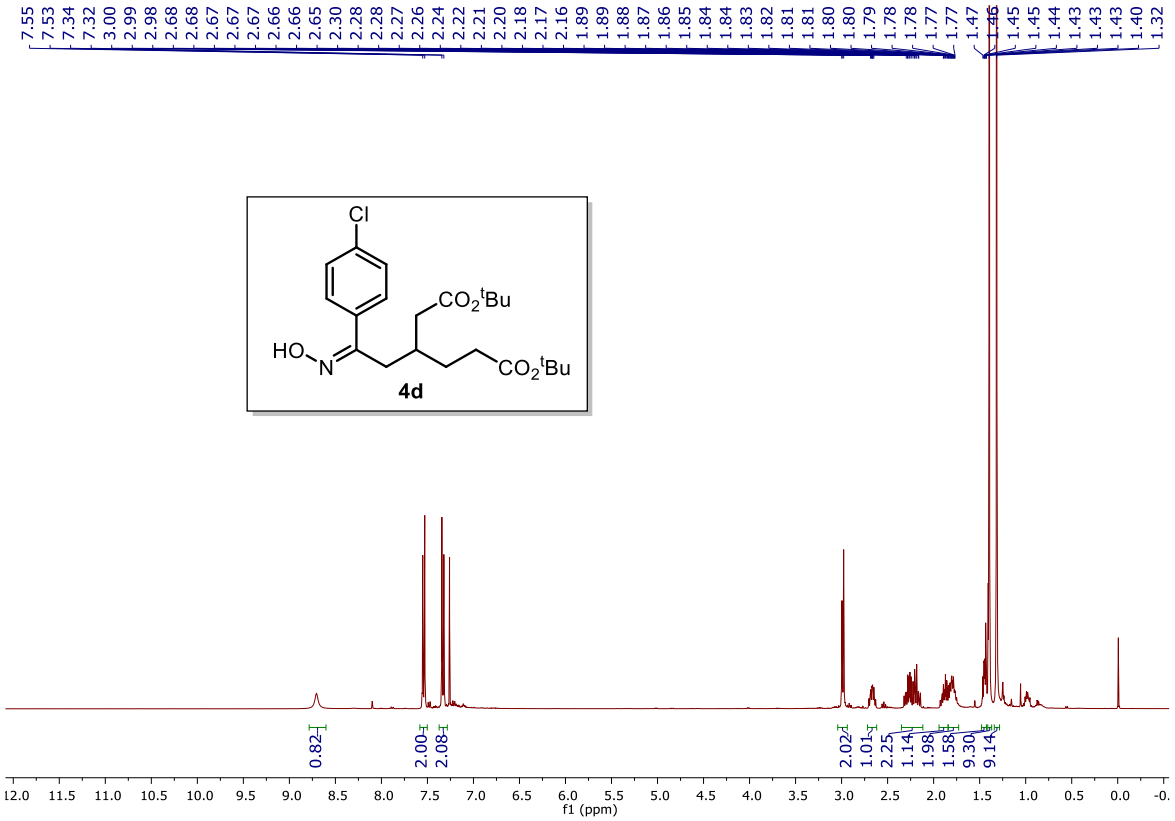
^{13}C{^{1}H} NMR spectrum of **4b**, $CDCl_3$, 100 MHz



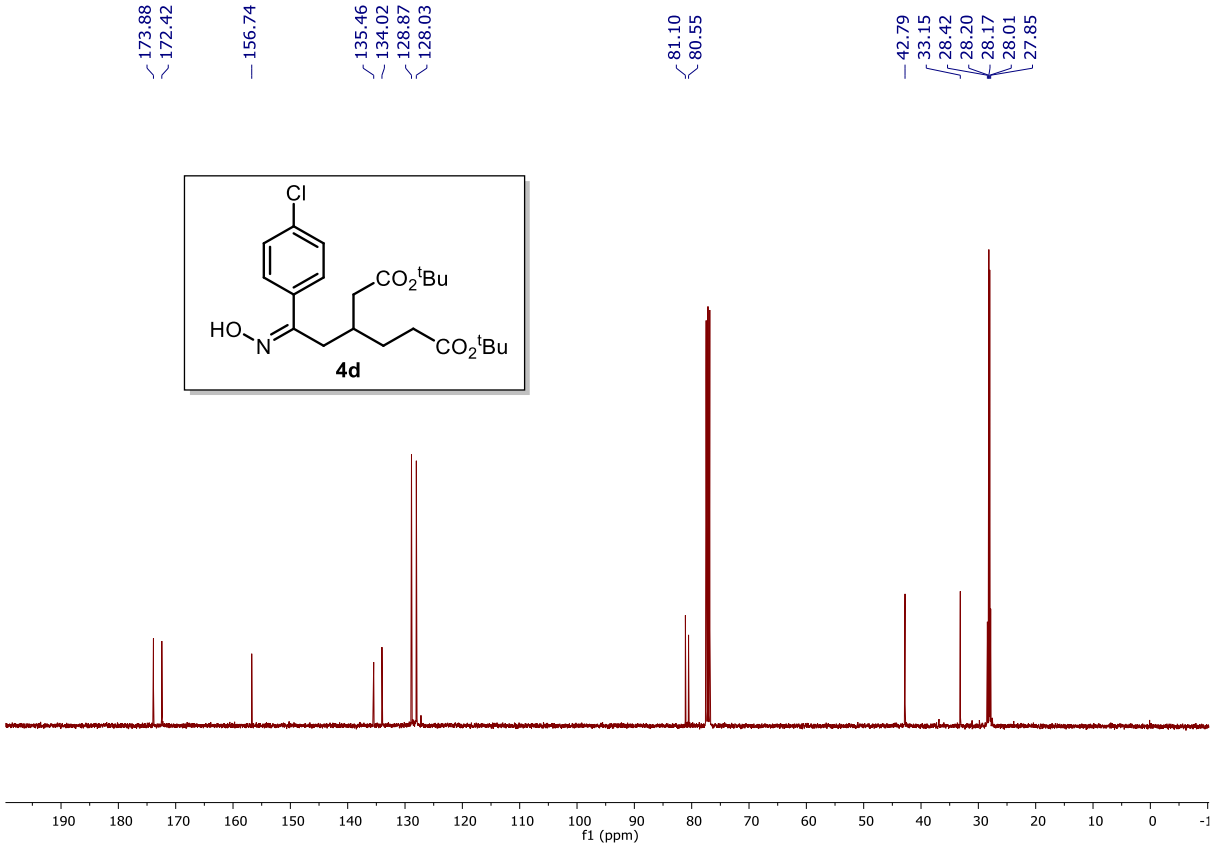
^{1}H NMR spectrum of **4c**, $CDCl_3$, 400 MHz



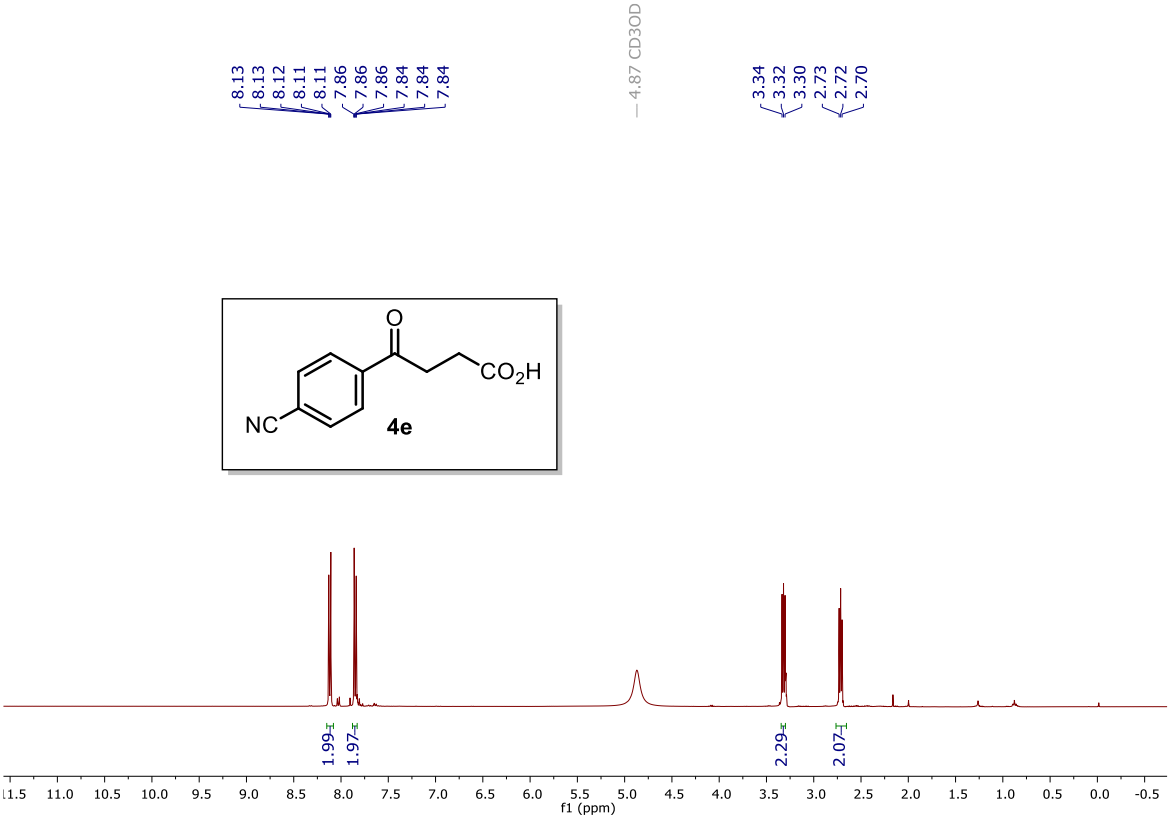
^{13}C{^{1}H} NMR spectrum of **4c**, $CDCl_3$, 100 MHz



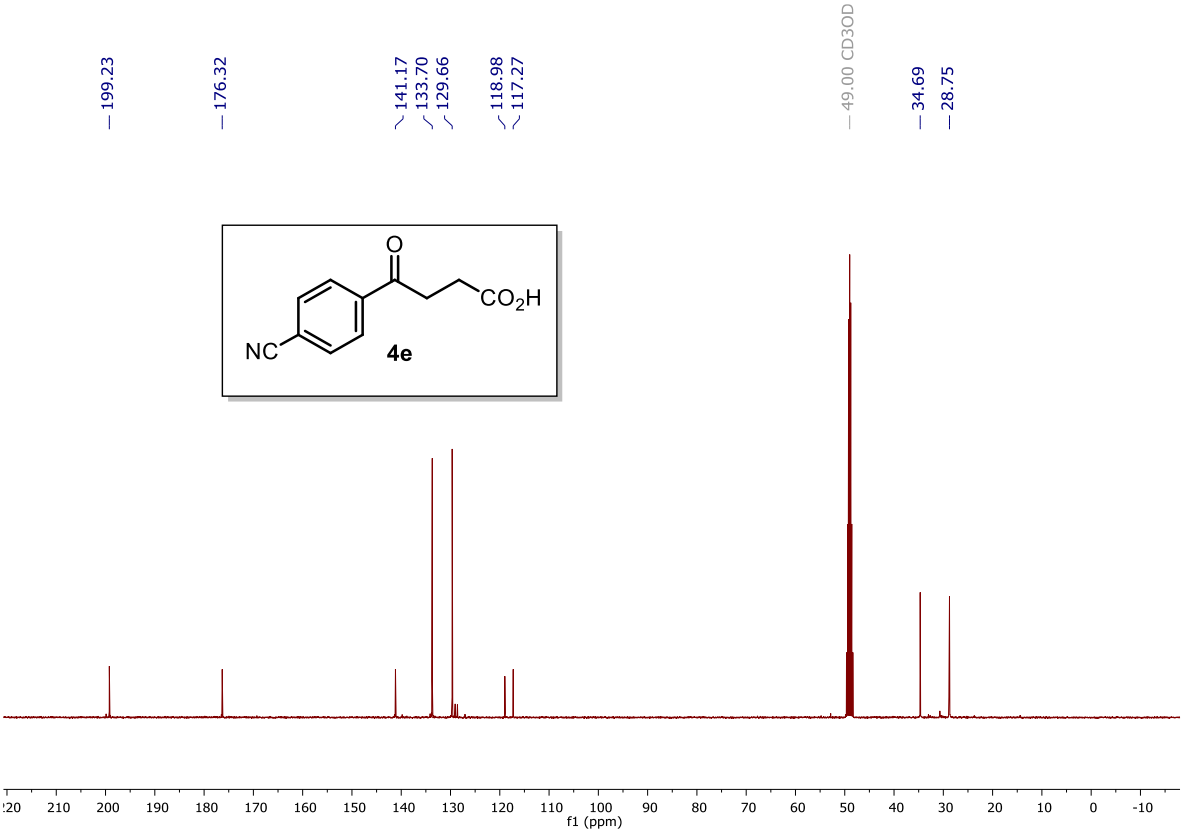
^{1}H NMR spectrum of **4d**, $CDCl_3$, 400 MHz



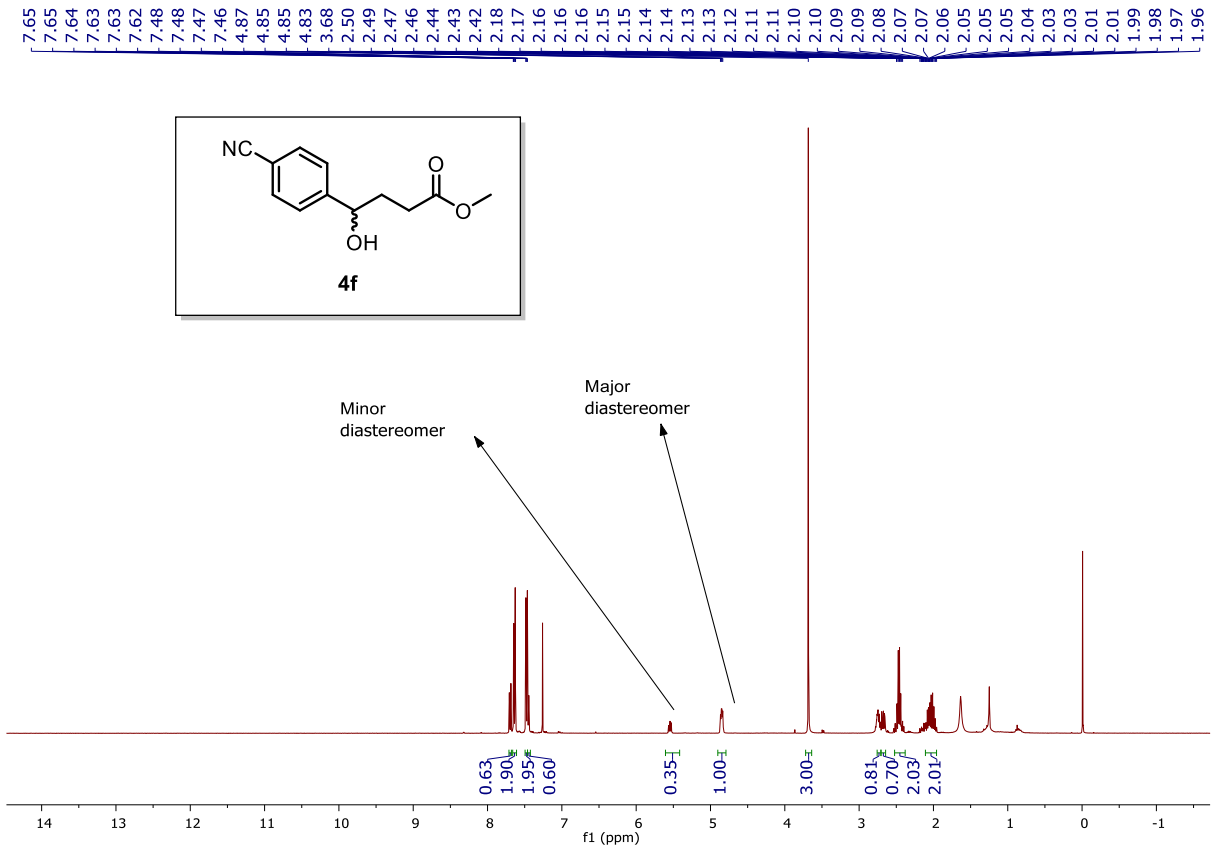
^{13}C {^{1}H} NMR spectrum of **4d**, $CDCl_3$, 100 MHz



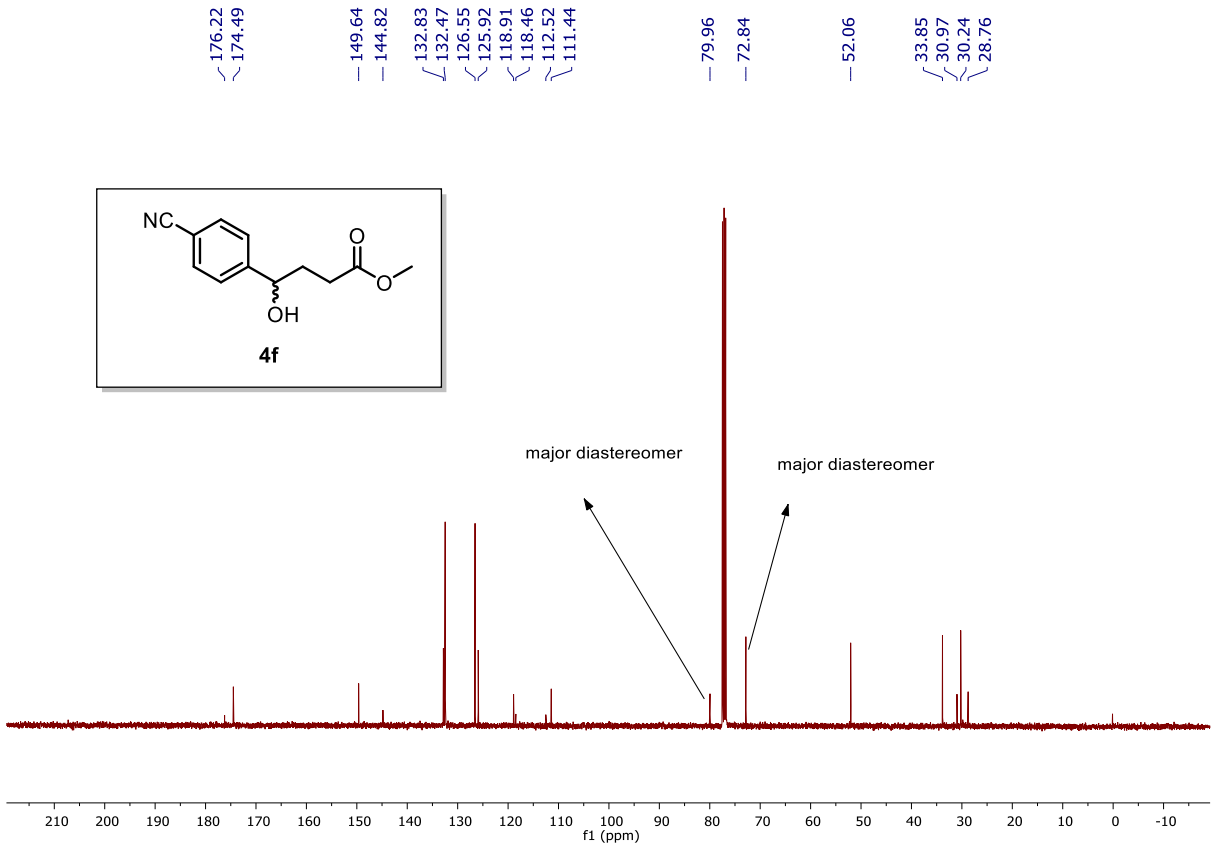
^{1}H NMR spectrum of **4e**, CD_3OD, 400 MHz



^{13}C{^{1}H} NMR spectrum of **4e**, CD_3OD, 100 MHz



^{1}H NMR spectrum of **4f**, $CDCl_3$, 400 MHz



^{13}C {^{1}H} NMR spectrum of **4f**, $CDCl_3$, 100 MHz