Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2021

Supporting Information

Direct Access to α-Acyloxycarbonyl Compounds and Esters via Oxidative Esterification of Aldehydes under Visible Light

Anindita Bhowmick,[a] Prakash K. Warghude,[a†] Pankaj D. Dharpure[a†] and Ramakrishna G. Bhat* [a]

[a]Department of Chemistry, Indian Institute of Science Education and Research (IISER) Pune, Dr. Homi Bhabha Road, Pashan, 411008, Maharashtra, India

Email: rgb@iiserpune.ac.in

[†]These authors contributed equally to this work.

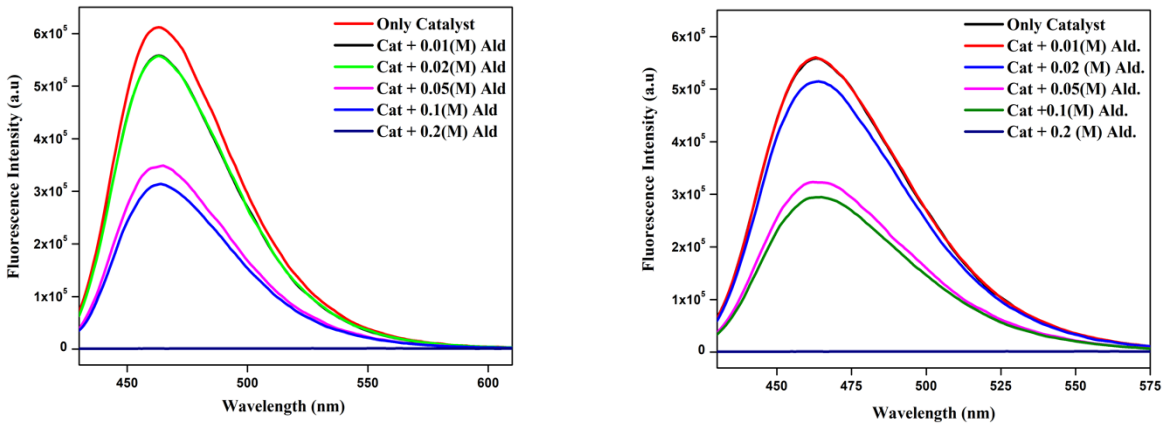
1. General Information

Unless otherwise noted, all the starting materials and reagents were purchased from commercial suppliers (Aldrich, TCI, and Alfa Aesar) and were used without further purification. Thin-layer chromatography (TLC) was performed using silica gel 60 GF_{254} pre-coated aluminum backed plates (2.5 mm). Visualization was accomplished by irradiation with UV light at 254 nm. 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 and ^{13}C NMR were recorded on 400 MHz instrument (Bruker and Jeol). 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 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. Mass samples were analyzed by high-resolution mass spectrometry (HRMS)-ESI TOF. Melting points were measured using BÜCHI M-560 melting point instrument and were uncorrected. Fluorescence spectra were recorded on Fluoromax-4 spectrofluorometer (Horiba Scientific, U.S.A.). All photocatalytic reactions were performed under blue LEDs (IBRA Pure30 W Blue LED Flood Light, IP Rating: IP66).

2. Mechanistic studies:

A. Fluorescence Quenching Experiment:

Fluorescence quenching experiment was carried out using Fluorescence spectrophotometer**,** using 2.5 µM solution of 2, 4, 6-triphenylpyrylium tetrafluoroborate (TPPT) and variable concentrations of (0.01, 0.02, 0.05, 0.1, 0.2 M) of 4-chlorobenzaldehyde **1a** in acetonitrile solvent. The sample was prepared in a 3 mL quartz cuvette and the flask was degasified with Argon before the spectra were recorded. Again, the same procedure was carried out in presence of oxygen. The quenching plots of both the experiments are given below.



(a) (b)

Figure 1. Fluorescence quenching experiment using catalyst and aldehyde under (a) Argon and (b) Oxygen

Fluorescence quenching experiment was carried out using Fluorescence spectrophotometer**,** using 2.5 µM solution of 2, 4, 6-triphenylpyrylium tetrafluoroborate (TPPT) and variable concentrations of (0.01, 0.02, 0.05, 0.1, 0.2 M) of Ethyl bromoacetate **2a** in acetonitrile solvent. The sample was prepared in a 3 mL quartz cuvette and the flask was degasified with Argon before the spectra were recorded. Again, the all the experiments were carried out using similar procedure while in presence of oxygen. The quenching plots of both the experiments are given below.

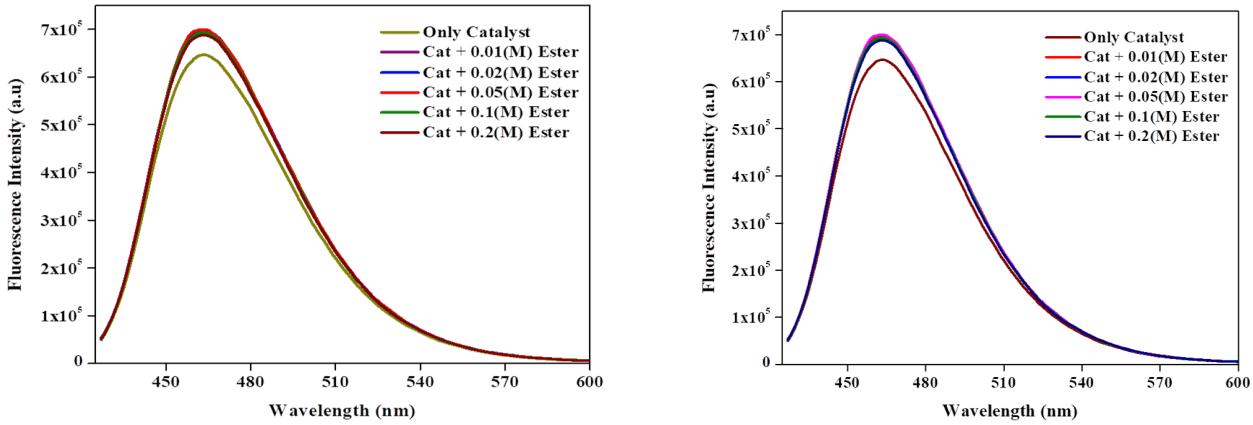


Figure 2. Fluorescence quenching experiment using catalyst and ethyl bromoacetate (ester) under (a) Argon and (b) Oxygen

B. Controlled Experiments:

i). Radical quenching experiment

To a solution of 4-chlorobenzaldehyde **1a** (50 mg, 1 equiv.) in 3 mL acetonitrile, ethyl bromoacetate (1.5 equiv.), Na_2CO_3 (2 equiv.) $AgBF_4$ (1 equiv.), TEMPO (2 equiv.) and photocatalyst TPPT (5 mol%) were added at room temperature under O_2 atmosphere using balloon and the reaction mixture was kept for stirring under Blue LED for 24 h. After the completion of the reaction (monitored by TLC), reaction mixture was filtered, the solvent was evaporated under vacuum and the residue was directly submitted for HRMS analysis. Based on the HRMS spectra we observed the TEMPO trapped radical intermediates. These results supported the radical pathway during the course of the reaction.

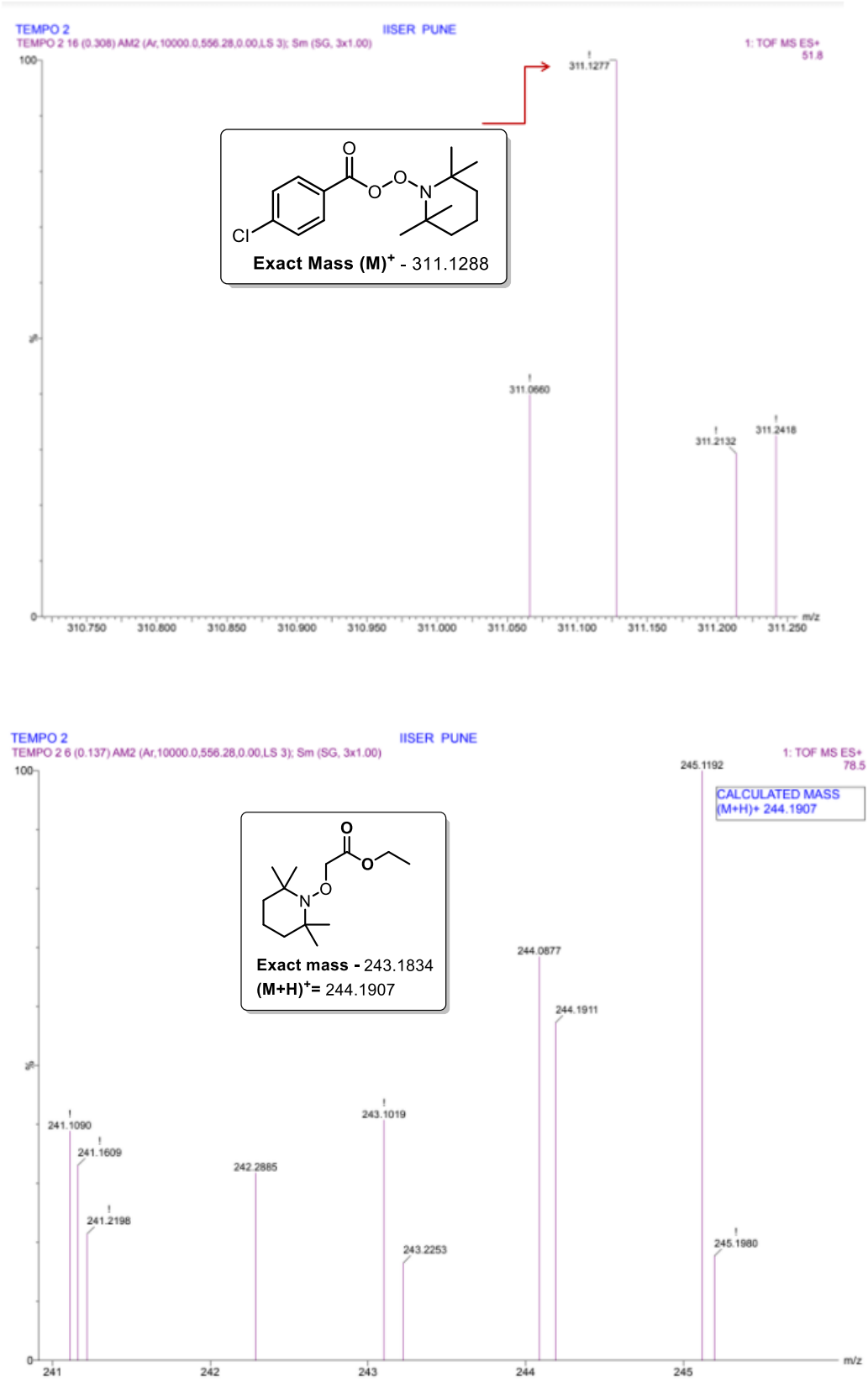


Figure 3. HRMS data of TEMPO trapped radical intermediates

ii). $^{18}O_2$ labeling experiment:

To a solution of 4-chlorobenzaldehyde **1a** (50 mg, 1 equiv.) in 3 mL acetonitrile, 2-bromo-1-phenylethan-1-one **2f** (1.1 equiv.), Na_2CO_3 (2 equiv.) $AgBF_4$ (1 equiv.) and photocatalyst TPPT (5 mol%) were added at room temperature and the reaction mixture was degasified by purging with Argon. Afterwhich, $^{18}O_2$ was purged into the reaction mixture ($^{18}O_2$ cylinder) and the reaction mixture was kept for stirring under Blue LED for 24 h. After the completion of the reaction (monitored by TLC) the reaction mixture was filtered and immediately the solvent was reduced under vacuum. The residue was purified by column chromatography using silica gel 100-200 mesh using ethyl acetate/petroleum ether mixture (1:10) as an eluent to obtain the corresponding ^{18}O labelled product (**3m'**).

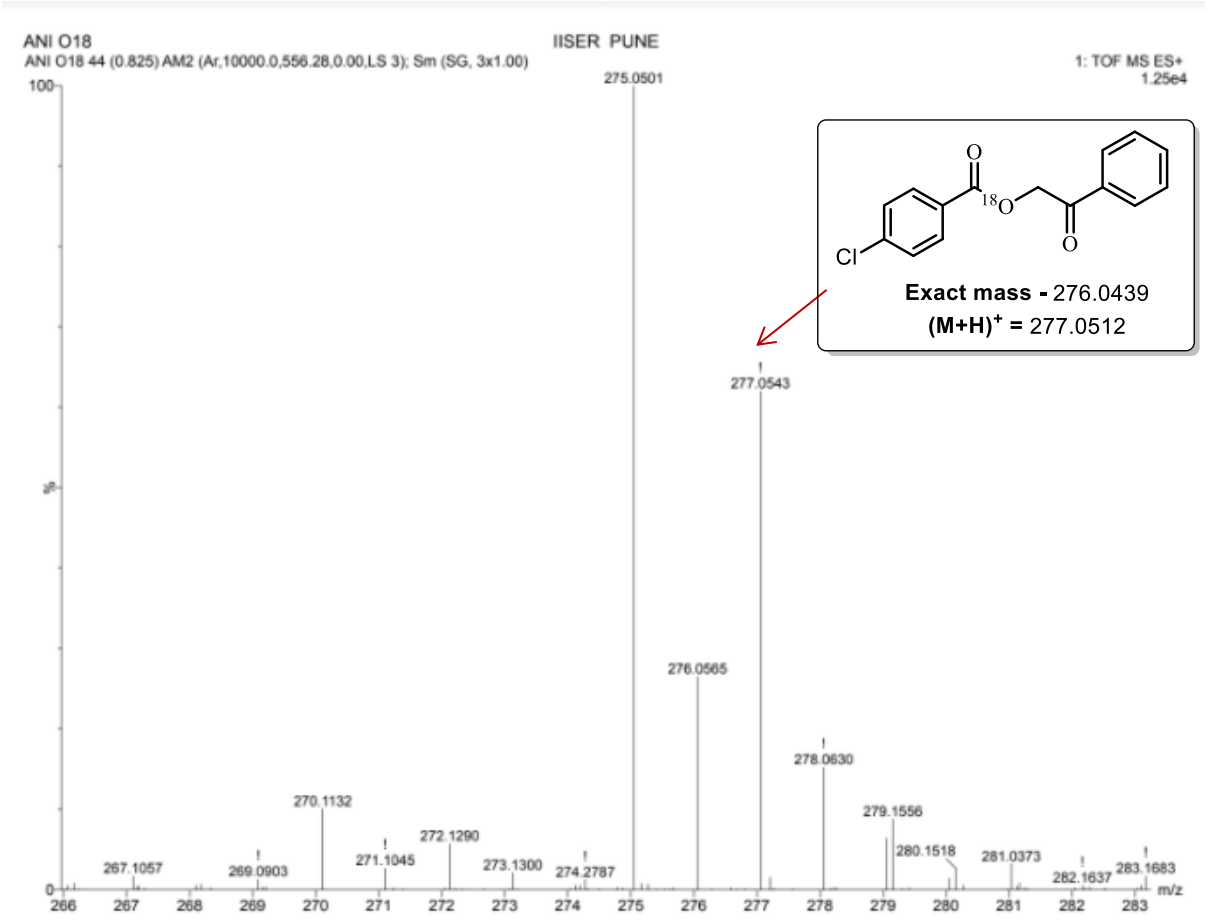
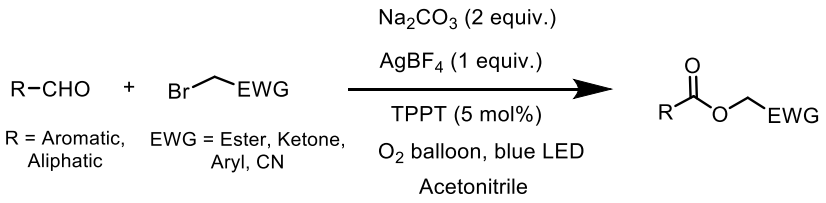


Figure 4. HRMS spectrum of $^{18}O_2$ labeled product **3m′**

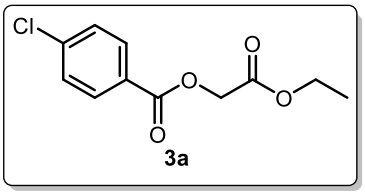
3. General Procedure for the synthesis of α–acyloxy carbonyl compounds:



To the round bottom flask containing solution of Aldehyde (50 mg, 1 equiv.) in 3 mL, acetonitrile, α–bromoester (1.5 equiv.)/ketone (1.1 equiv.)/substituted benzyl bromide (1.5 equiv.)/α–bromo acetonitrile (1.5 equiv.), Na_2CO_3 (2 equiv.) $AgBF_4$ (1 equiv.) and photocatalyst (TPPT, PC-7) (5 mol%) were added at room temperature under O_2 atmosphere and the reaction was kept for stirring under Blue LED for 15-24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the solvent was immediately evaporated under vacuum. The resultant residue was purified by column chromatography using silica gel 100-200 mesh using petroleum ether/ethyl acetate as an eluent system to obtain the corresponding α–acyloxy carbonyl compound.

4. Experimental Data:

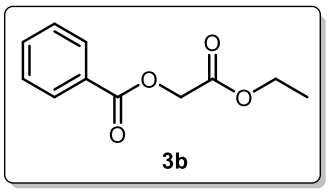
(2-ethoxy-2-oxoethyl 4-chlorobenzoate) (3a)



3a

The compound **3a** was synthesized following the general procedure, starting from 4-chlorobenzadehyde **1a** (50 mg, 0.356 mmol, 1equiv.) and ethyl bromoacetate **2a** (59 µL, 0.534 mmol, 1.5 equiv.). The compound **3a** was obtained as yellow oil, 73.5 mg, 85% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 4.83 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)**: δ 167.7, 165.2, 140.0, 131.4, 128.9, 127.7, 61.6, 61.4, 14.2. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{11}H_{12}ClO_4$ $(M+H)^+$ 243.0424; found 243.0421.

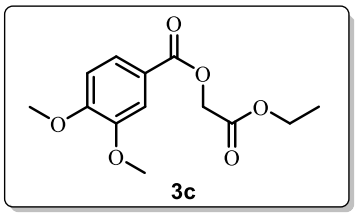
(2-ethoxy-2-oxoethyl benzoate) (3b)[12,13]



The compound **3b** was synthesized following the general procedure, starting from benzaldehyde **1b** (50 mg, 0.471 mmol, 1 equiv.) and ethyl bromoacetate **2a** (78 μL,0.707 mmol, 1.5 equiv.). The **3b** was obtained as colorless oil, 74 mg, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.84 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 167.9, 166.1, 133.5, 130.0, 129.3, 128.5, 61.6, 61.3, 14.2. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{11}H_{12}O_4Na$ $(M+Na)^+$ 231.0633; found 231.0614.

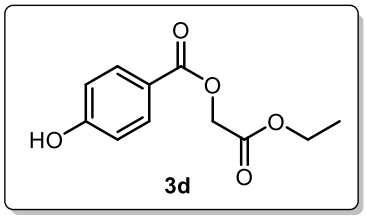
2-ethoxy-2-oxoethyl 3,4-dimethoxybenzoate (3c)



The compound **3c** was synthesized following the general procedure, starting from 3,4-dimethoxybenzaldehyde **1c** (50 mg, 0.301 mmol, 1 equiv.) and ethyl bromoacetate **2a** (50 μL, 0.451 mmol, 1.5 equiv.). The reaction mixture was stirring for 16 h. The compound **3c** was obtained as yellow oil, 69.5 mg, 86% yield.

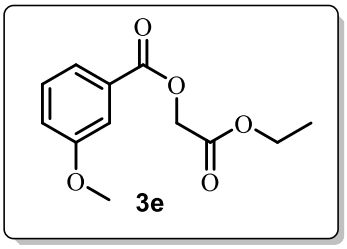
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.81 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 3.92 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 168.1, 165.9, 153.5, 148.8, 124.3, 121.7, 112.3, 110.4, 61.6, 61.2, 56.2, 56.1, 14.3. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{13}H_{17}O_6$ $(M+H)^+$ 269.1025; found 269.1031.

2-ethoxy-2-oxoethyl 4-hydroxybenzoate (3d)



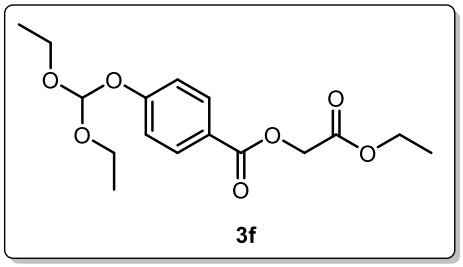
The compound **3d** was synthesized following the general procedure, starting from 4-hydroxybenzaldehyde **1d** (50 mg, 0.409 mmol, 1 equiv.) and ethyl bromoacetate **2a** (68 µL, 0.614 mmol, 1.5 equiv.). The compound **3d** was obtained as colorless oil, 78 mg, 85% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.85 (s, 1H), 7.81 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.67 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 190.8, 168.1, 162.7, 132.0, 130.8, 115.0, 65.3, 61.7, 14.2. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{11}H_{13}O_5$ $(M+H)^+$ 225.0763; found 225.0758.

2-ethoxy-2-oxoethyl 3-methoxybenzoate (3e)



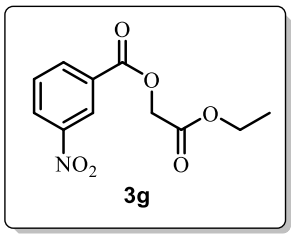
The compound **3e** was synthesized following the general procedure, starting from 3-methoxybenzaldehyde **1e** (50 mg, 0.367mmol, 1 equiv.) and ethyl bromoacetate **2a** (61 µl, 0.551 mmol, 1.5 equiv.). The compound **3e** was obtained as Colorless oil, 71 mg, 81% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (ddd, *J* = 7.7, 1.5, 1.0 Hz, 1H), 7.60 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.36 (ddd, *J* = 8.2, 7.7, 0.4 Hz, 1H), 7.13 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 4.83 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 167.9, 166.0, 159.7, 130.6, 129.6, 122.5, 120.2, 114.3, 61.6, 61.4, 55.6, 14.3. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{12}H_{15}O_5$ $(M+Na)^+$ 261.0739; found 261.0735.

2-ethoxy-2-oxoethyl 4-(diethoxymethoxy)benzoate (3f)



The compound **3f** was synthesized following the general procedure, starting from 4-(diethoxymethoxy)benzaldehyde **1f** (50 mg, 0.223 mmol, 1 equiv.) and ethyl bromoacetate **2a** (37 □L, 0.334 mmol, 1.5 equiv.). The compound **3f** was obtained as colorless oil, 38 mg, 52% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 4.84 (t, *J* = 5.2 Hz, 1H), 4.80 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.06 (d, *J* = 5.2 Hz, 2H), 3.77 (dq, *J* = 9.4, 7.1 Hz, 2H), 3.63 (dq, *J* = 9.4, 7.0 Hz, 2H), 1.26 (dt, *J* = 17.0, 7.1 Hz, 9H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 168.1, 165.7, 162.9, 132.1, 122.0, 114.5, 100.5, 68.8, 63.0, 61.5, 61.2, 15.4, 14.3. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{16}H_{23}O_7$ $(M+H)^+$ 327.1444; found 327.1442.

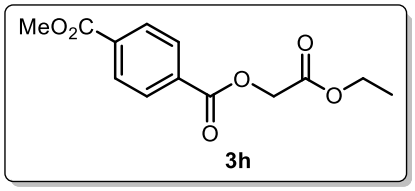
2-ethoxy-2-oxoethyl 3-nitrobenzoate (3g)



The compound **3g** was synthesized following the general procedure, starting from 3-nitrobenzaldehyde **1g** (50 mg, 0.331 mmol, 1 equiv.) and ethyl 2-bromoacetate **2a** (55 μL, 0.496 mmol, 1.5 equiv.). The reaction mixture was stirring for 16hrs. The compound **3g** was obtained as colorless liquid, 43 mg, 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (td, *J* = 1.8, 0.9 Hz, 1H), 8.46 – 8.39 (m, 2H), 7.72 – 7.63 (m, 1H), 4.89 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):**δ 167.4, 164.0, 148.4, 135.7, 131.1, 129.9, 128.0, 125.0, 61.9, 61.8, 14.2. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{11}H_{12}NO_6$ $(M+H)^+$ 254.0665; found 254.0658.

2-ethoxy-2-oxoethyl methyl terephthalate (3h)

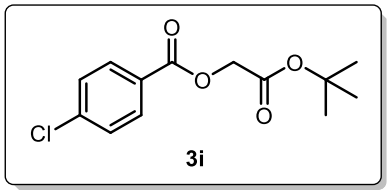


3h

The compound **3h** was synthesized following the general procedure, starting from methyl 4-formylbenzoate **1h** (50 mg, 0.305 mmol, 1 equiv.) and ethyl bromoacetate **2a** (37 μL, 0.457 mmol, 1.5 equiv.). The **3h** was obtained as colorless liquid, 39 mg, 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.9 Hz, 1H), 4.86 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 1H), 3.95 (s, 1H), 1.30 (t, *J* = 7.1 Hz, 1H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 167.7, 166.3, 165.3, 134.5, 133.1, 130.0, 129.8, 61.8, 61.6, 52.6, 14.3. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{13}H_{15}O_6$ $(M+H)^+$ 267.0869; found 267.0868.

2-(tert-butoxy)-2-oxoethyl 4-chlorobenzoate (3i)

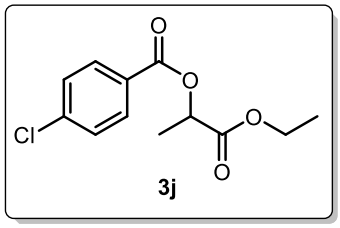


3i

The compound **3i** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and *tert*-butyl bromoacetate **2b** (104 mg, 0.534 mmol, 1.5 equiv.). The **3i** was obtained as colorless liquid, 82 mg, 85% yield.

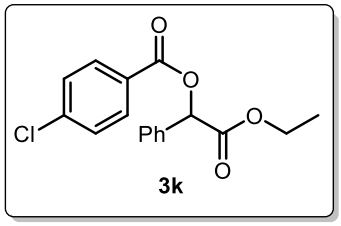
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 4.75 (s, 2H), 1.51 (s, 9H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.8, 165.3, 140.0, 131.4, 128.9, 128.0, 82.8, 61.9, 28.2. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{13}H_{15}ClO_4Na$ $(M+Na)^+$ 293.0557; found 293.0554.

1-ethoxy-1-oxopropan-2-yl 4-chlorobenzoate (3j)[5]



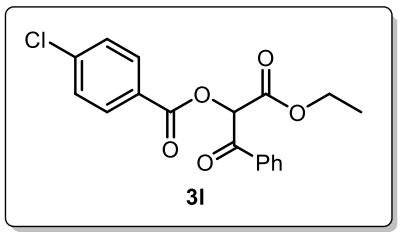
The compound **3j** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and ethyl 2-bromopropanoate **2c** (105 mg, 0.534 mmol, 1.5 equiv.). The **3j** was obtained as colorless liquid, 75 mg, 82% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 5.29 (q, *J* = 7.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.61 (d, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 170.7, 165.2, 139.9, 131.3, 128.9, 128.1, 69.5, 61.6, 17.1, 14.2. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{12}H_{13}ClO_4Na$ $(M+Na)^+$ 279.0400; found 279.0387.

2-ethoxy-2-oxo-1-phenylethyl 4-chlorobenzoate (3k)[6]



The compound **3k** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol 1 equiv.) and ethyl 2-bromo-2-phenylacetate **2d** (130 mg, 0.534 mmol, 1.5 equiv.). The **3k** was obtained as colorless oil, 80 mg, 70% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.57 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.48 – 7.38 (m, 5H), 6.13 (s, 1H), 4.30 – 4.12 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ (ppm) 168.8, 165.2, 140.1, 134.0, 131.5, 129.4, 129.0, 128.95, 127.9, 127.8, 75.3, 62.0, 14.1. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{17}H_{16}ClO_4$ $(M+H)^+$ 319.0737; found 319.0744.

1-ethoxy-1,3-dioxo-3-phenylpropan-2-yl 4-chlorobenzoate (3l)[7]

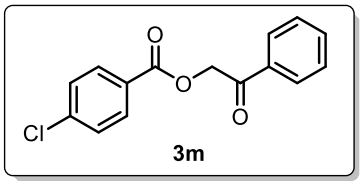


3l

The compound **3l** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and ethyl 2-bromo-3-oxo-3-phenylpropanoate **2e** (145 mg, 0.534 mmol, 1.5 equiv.). The compound **3l** was obtained as colorless oil, 69 mg, 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.08 (m, 2H), 8.07 (d, *J* = 1.4 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.52 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 189.9, 178.9, 165.4, 165.2, 134.4, 134.0, 132.9, 130.3, 130.2, 129.5, 129.4, 129.0, 128.7, 75.1, 62.7, 14.1. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{18}H_{16}ClO_5$ $(M+H)^+$ 347.0686; found 347.0687.

2-oxo-2-phenylethyl 4-chlorobenzoate (3m)[13]

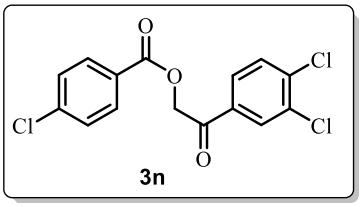


3m

The compound **3m** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (78 mg, 0.391 mmol, 1.1 equiv.). The compound **3m** was obtained as white solid, 72 mg, 74% yield. M.P. 70 -72 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.07 (m, 2H), 7.99 – 7.94 (m, 2H), 7.65 – 7.60 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.43 (m, 2H), 5.58 (s, 2H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 192.0, 165.3, 140.0, 134.3, 134.1, 134, 133.5, 131.5, 130.1, 129.1, 129.04, 129, 128.6, 128, 127.98, 127.96, 66.7. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{15}H_{12}ClO_3$ $(M+H)^+$ 275.0475; found 275.0479.

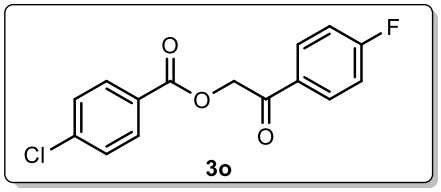
2-(3,4-dichlorophenyl-2-oxoethyl 4-chlorobenzoate (3n)



The compound **3n** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 2-bromo-1-(3, 4-dichlorophenyl)ethan-1-one **2g** (105 mg, 0.391 mmol, 1.1 equiv.). The compound **3n** was obtained as white solid, 104 mg, 85% yield. M.P. 93-95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 8.05 – 8.02 (m, 2H), 7.78 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 5.50 (s, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 190.1, 165.2, 140.2, 138.9, 133.9, 133.8, 131.5, 131.2, 130.1, 130.0, 129.0, 128.7, 127.7, 126.9, 66.5. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{15}H_9Cl_3O_3Na$ $(M+Na)^+$ 364.9509; found 364.9441.

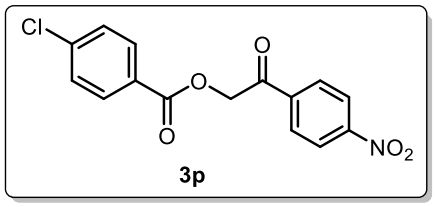
2-(4-fluorophenyl)-2-oxoethyl 4-chlorobenzoate (3o)



The Compound **3o** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 2-bromo-1-(4-fluorophenyl)ethan-1-one **2h** (85 mg, 0.391 mmol, 1.1 equiv.). The compound **3o** was obtained as white solid, 94 mg, 90% yield. M.P. 110-111 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.99 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.18 (t, *J* = 8.5 Hz, 2H), 5.53 (s, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 190.5, 166.3(d, $J_{(C-F)}$ = 255 Hz), 165.3, 140.1, 131.5, 130.8, 130.67 (d, $J_{(C-F)}$ = 9.5 Hz), 130.1, 129.0, 128.6, 127.9, 116.32 (d, $J_{(C-F)}$ = 22.1 Hz), 66.5. **^{19}F NMR (400 MHz, $CDCl_3$):** -103.1. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{15}H_{11}ClFO_3$ $(M+H)^+$ 293.0381; found 293.0334.

2-(4-nitrophenyl)-2-oxoethyl 4-chlorobenzoate (3p)

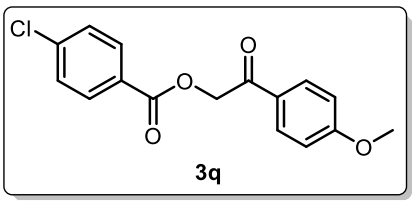


3p

The Compound **3p** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 2-bromo-1-(4-nitrophenyl)ethan-1-one **2i** (96 mg, 0.391 mmol, 1.1 equiv.). The **3p** was obtained as light yellow solid, 104 mg, 91% yield. M.P. 128-130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.9 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 5.57 (s, 2H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 191.0, 165.2, 151.0, 140.4, 138.7, 131.5, 130.1, 129.13, 129.11, 128.7, 127.5, 124.3, 66.8. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{15}H_{11}ClNO_5$ $(M+H)^+$ 320.0326; found 320.0329.

2-(4-methoxyphenyl)-2-oxoethyl 4-chlorobenzoate (3q)[8]

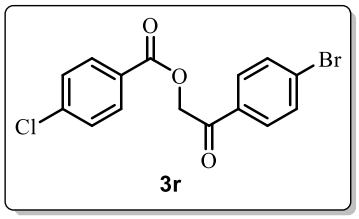


3q

The compound **3q** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 2-bromo-1-(4-methoxyphenyl)ethan-1-one **2j** (90 mg, 0.391 mmol, 1.1 equiv.). The **3q** was obtained as white solid, 81.5 mg, 75% yield. M.P. 124-126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.05 (m, 2H), 7.97 – 7.92 (m, 2H), 7.47 – 7.41 (m, 2H), 7.00 – 6.95 (m, 2H), 5.53 (s, 2H), 3.89 (s, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 190.4, 165.4, 164.3, 139.9, 131.5, 130.3, 128.9, 128.1, 127.3, 114.3, 66.5, 55.7. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{16}H_{14}ClO_4$ $(M+H)^+$ 305.0581; found 305.0587.

2-(4-bromophenyl)-2-oxoethyl 4-chlorobenzoate (3r)

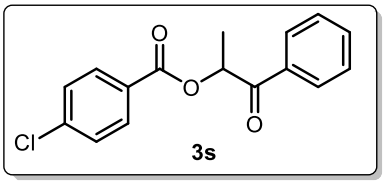


3r

The compound **3r** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 2-bromo-1-(4-bromophenyl)ethan-1-one **2k** (109 mg, 0.391 mmol, 1.1 equiv.). The compound **3r** was obtained as White solid, 101 mg, 80% yield. M.P. 119-121 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 7.96 (m, 2H), 7.91 – 7.77 (m, 2H), 7.69 – 7.61 (m, 2H), 7.44 (d, *J* = 8.6 Hz, 1H), 5.52 (s, 2H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 191.1, 165.2, 140.1, 133.0, 132.4, 132.37, 131.5, 130.1, 129.4, 129.39, 129.0, 128.6, 127.8, 66.5. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{15}H_{11}BrClO_3$ $(M+H)^+$ 352.9580; found 352.9582.

1-oxo-1-phenylpropan-2-yl 4-chlorobenzoate (3s)[15]

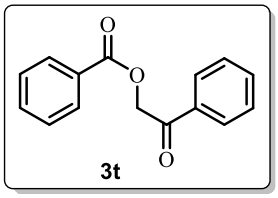


3s

The compound **3s** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 2-bromo-1-phenylpropan-1-one **2l** (83 mg, 0.391 mmol, 1.1 equiv.). The compound **3s** was obtained as white solid, 93 mg, 90% yield. M.P. 98-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 7.96 (m, 4H), 7.63 – 7.55 (m, 1H), 7.52 – 7.40 (m, 4H), 6.24 – 6.16 (m, 1H), 1.67 (dd, *J* = 7.0, 2.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 196.9, 196.6, 166.1, 165.3, 139.9, 134.6, 134.5, 133.8, 133.7, 133.4, 131.4, 130.0, 129.6, 129.0, 128.94, 128.91, 128.7, 128.6, 128.5, 128.1, 72.2, 72.0, 17.4, 17.3. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{16}H_{14}ClO_3$ $(M+H)^+$ 289.0631; found 289.0639.

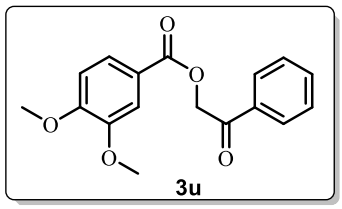
2-oxo-2-phenylethyl benzoate (3t)[12]



The compound **3t** was synthesized following the general procedure, starting from benzaldehyde **1b** (50 mg, 0.471 mmol, 1equiv.) and 2-bromo-1-phenylethan-1-one **2f** (103 mg, 0.518 mmol, 1.1 equiv.). The compound **3t** was obtained as white solid, 91 mg, 80% yield. M.P. 115 - 117 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.98 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.67 – 7.56 (m, 1H), 7.49 (dt, *J* = 13.9, 7.7 Hz, 2H), 5.58 (s, 1H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 192.2, 166.2, 134.4, 134.0, 133.5, 130.1, 129.5, 129, 128.6, 128, 66.6. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{15}H_{12}O_3Na$ $(M+Na)^+$ 263.0684; found 263.0683.

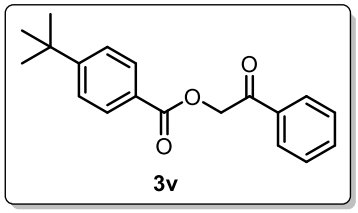
2-oxo-2-phenylethyl 3,4-dimethoxybenzoate (3u)



The compound **3u** was synthesized following the general procedure, starting from 3,4-dimethoxybenzaldehyde **1c** (50 mg, 0.301 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (66 mg, 0.331 mmol, 1.1 equiv.). The **3u** was obtained as white solid, 81 mg, 90% yield. M.P. 108-110°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 – 7.95 (m, 2H), 7.80 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.53 – 7.48 (m, 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 5.55 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ (ppm) 192.5, 165.9, 153.4, 148.7, 134.4, 134.0, 129.0, 128.0, 124.3, 112.3, 110.4, 66.5, 56.2, 56.1. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{17}H_{17}O_5$ $(M+H)^+$ 301.1076; found 301.1078.

2-oxo-2-phenylethyl 4-(tert-butyl)benzoate (3v)[9]

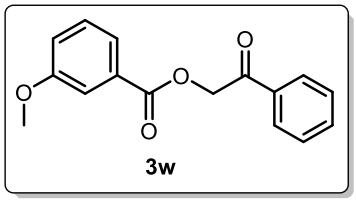


3v

The compound **3v** was synthesized following the general procedure, starting from 4-(tert-butyl)-benzadehyde **1i** (50 mg, 0.308 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (68 mg, 0.339 mmol, 1.1 equiv.). The compound **3v** was obtained as white solid, 79 mg, 86% yield. M.P. 64-66 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.07 (m, 2H), 7.97 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.51 – 7.46 (m, 4H), 5.57 (s, 2H), 1.35 (s, 9H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 192.3, 166.1, 157.1, 134.4, 133.9, 129.9, 128.9, 127.92, 127.91, 127.90, 127.89, 127.88, 126.7, 125.5, 66.4, 35.2, 31.2, 31.19, 31.18, 31.17, 31.16, 31.15, 31.14. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{19}H_{21}O_3$ $(M+H)^+$ 297.1491; found 297.1479.

2-oxo-2-phenylethyl 3-methoxybenzoate (3w)[14]

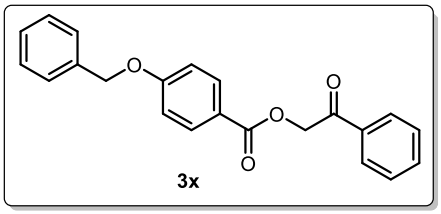


3w

The compound **3w** was synthesized following the general procedure, starting from 3-methoxybenzadehyde **1e** (50 mg, 0.367 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (80 mg, 0.404 mmol, 1.1 equiv.). The compound **3w** was obtained as white solid, 89.5 mg, 90% yield. M.P. 80-81 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.57 (s, 2H), 3.86 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 192.2, 166.1, 159.7, 134.4, 134.0, 130.8, 130.0, 129.6, 129.1, 129.03, 129.0, 128.5, 128.0, 122.6, 120.2, 118.4, 114.3, 66.7, 55.6. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{16}H_{14}O_4Na$ $(M+Na)^+$ 293.0790; found 293.0790.

2-oxo-2-phenylethyl 4-(benzyloxy)benzoate (3x)

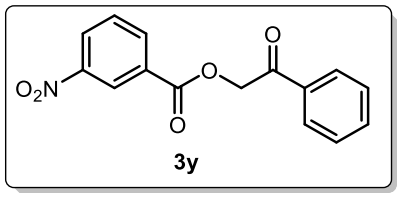


3x

The compound **3x** was synthesized following the general procedure, starting from 4-(benzyloxy)benzaldehyde **1j** (50 mg, 0.236 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (52 mg, 0.259 mmol, 1.1 equiv.). The compound **3x** was obtained as white solid, 71mg, 87%yield. M.P. 122-124 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.07 (m, 2H), 7.97 (dt, *J* = 8.4, 1.7 Hz, 2H), 7.67 – 7.58 (m, 1H), 7.56 – 7.47 (m, 2H), 7.47 – 7.34 (m, 5H), 7.05 – 7.00 (m, 2H), 5.55 (s, 2H), 5.14 (s, 2H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 192.5, 165.8, 163.0, 136.3, 134.5, 134.0, 132.2, 129.0, 128.8, 128.4, 128.0, 127.6, 122.1, 114.7, 70.3, 66.4. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{22}H_{18}O_4Na$ $(M+Na)^+$ 369.1103; found 369.1096.

2-oxo-2-phenylethyl 3-nitrobenzoate (3y)[10]

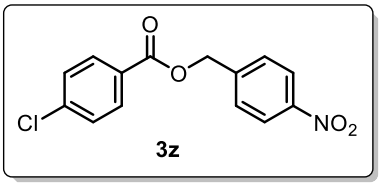


3y

The compound **3y** was synthesized following the general procedure, starting from 3-nitrobenzadehyde **1g** (50 mg, 1equiv.) and 2-bromo-1-phenylethan-1-one **2f** (73 mg, 1.1equiv.). The compound **3y** was obtained as off-white solid, 61 mg, 65%. M.P. 87-89 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (t, *J* = 1.8 Hz, 1H), 8.49 – 8.45 (m, 2H), 8.01 – 7.93 (m, 2H), 7.74 – 7.61 (m, 2H), 7.58 – 7.49 (m, 2H), 5.66 (s, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 191.4, 164.2, 148.5, 135.8, 134.3, 134.1, 131.4, 129.9, 129.2, 128.0, 127.9, 125.2, 67.2. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{15}H_{12}NO_5$ $(M+H)^+$ 286.0715; found 286.0721.

4-nitrobenzyl 4-chlorobenzoate (3z)[11]

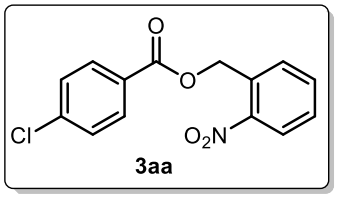


3z

The compound **3z** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1equiv.) and 1-(bromomethyl)-4-nitrobenzene **2m** (116 mg, 0.534 mmol, 1.5 equiv.). The compound **3z** was obtained as white solid, 62 mg, 60%yield. M.P. 122-124 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.7 Hz, 2H), 8.02 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 5.45 (s, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 165.4, 147.9, 143.1, 140.1, 131.2, 129.0, 128.5, 128.0, 124.0, 65.5. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{14}H_{10}ClNO_4Na$ $(M+Na)^+$ - 314.0196; Found - 314.0194.

2-nitrobenzyl 4-chlorobenzoate (3aa)

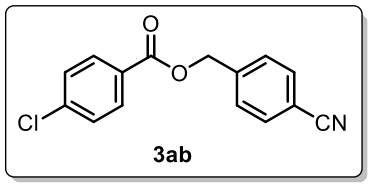


3aa

The compound **3aa** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1equiv.) and 1-(bromomethyl)-2-nitrobenzene **2n** (115 mg, 0.534 mmol, 1.5 equiv.). The compound **3aa** was obtained as grey colored solid, 68 mg, 65% yield. M.P. 90-92 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.09 (m, 1H), 8.06 – 7.91 (m, 2H), 7.72 – 7.59 (m, 2H), 7.56 – 7.46 (m, 1H), 7.46 – 7.40 (m, 2H), 5.77 (s, 2H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 165.2, 147.8, 140.1, 133.9, 132.1, 131.3, 129.9, 129.2, 129.1, 129.07, 128.7, 128.1, 125.3, 63.7. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{14}H_{10}ClNO_4Na$ $(M+Na)^+$ 314.0196; found 314.0186.

4-cyanobenzyl 4-chlorobenzoate (3ab)

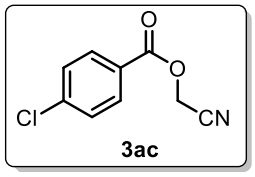


3ab

The compound **3ab** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 1-(bromomethyl)-4-cyanobenzene **2o** (105 mg, 0.534 mmol, 1.5 equiv.). The compound **3ab** was obtained as white solid, 64 mg, 66% yield. M.P. 80-82 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.73 – 7.64 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 5.41 (s, 2H). **^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz):** δ (ppm) 165.4, 141.2, 140.1, 133.6, 132.6, 131.2, 129.9, 129.0, 128.5, 118.6, 112.3, 77.5, 77.2, 76.8, 65.8. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{15}H_{11}ClNO_2$ $(M+H)^+$ 272.0478; found 272.0482.

Cyanomethyl 4-chlorobenzoate (3ac)[2]

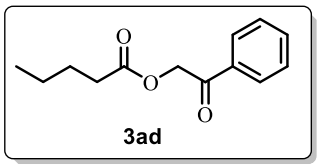


3ac

The compound **3ac** was synthesized following the general procedure, starting from 4-chlorobenzaldehyde **1a** (50 mg, 0.356 mmol, 1 equiv.) and 2-bromoacetonitrile **2p** (64 mg, 0.534 mmol, 1.5 equiv.). The **3ac** was obtained as light yellow liquid, 29 mg, 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 4.96 (s, 2H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ (ppm) 164.3, 141.0, 131.5, 130.2, 129.3, 128.8, 126.4, 114.4, 49.1. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_9H_7ClNO_2$ $(M+H)^+$ 196.0165; found 196.0172.

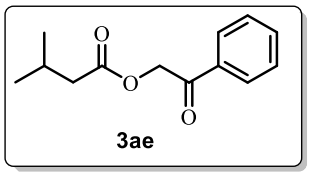
2-oxo-2-phenylethyl pentanoate (3ad)[3]



The compound **3ad** was synthesized following the general procedure, starting from pentanal **1k** (50 mg, 0.580 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (127 mg, 0.638 mmol, 1.1 equiv.). The compound **3ad** was obtained as yellow liquid, 108 mg, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 7.82 (m, 2H), 7.61 (ddt, *J* = 8.6, 6.9, 1.3 Hz, 1H), 7.48 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 2H), 5.34 (s, 2H), 2.67 – 2.28 (m, 2H), 1.87 – 1.58 (m, 2H), 1.50 – 1.34 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 192.5, 173.4, 134.4, 134.0, 129.0, 127.9, 66.0, 33.8, 27.1, 22.4, 13.9. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{13}H_{16}O_3Na$ $(M+Na)^+$ 243.0997; found 243.1005.

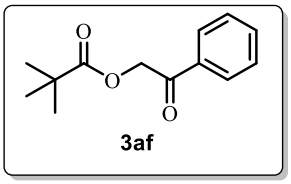
2-oxo-2-phenylethyl 3-methylbutanoate (3ae)



The compound **3ae** was synthesized following the general procedure, starting from 3-methylbutanal **1l** (50 mg, 0.580 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (127 mg, 0.638 mmol, 1.1 equiv.). The compound **3ae** was obtained as light yellow liquid, 111 mg, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.87 (m, 2H), 7.66 – 7.58 (m, 1H), 7.49 (ddt, *J* = 7.9, 6.7, 0.6 Hz, 2H), 5.35 (s, 2H), 2.38 (d, *J* = 7.1 Hz, 2H), 2.21 (ddq, *J* = 13.2, 7.4, 6.6 Hz, 1H), 1.05 (s, 3H), 1.03 (s, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 192.4, 172.6, 134.4, 133.9, 128.9, 127.9, 65.9, 43.1, 25.8, 22.5. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{13}H_{16}O_3Na$ $(M+Na)^+$ 243.0997; found 243.1002.

(2-oxo-2-phenylethyl pivalate (3af)[14]

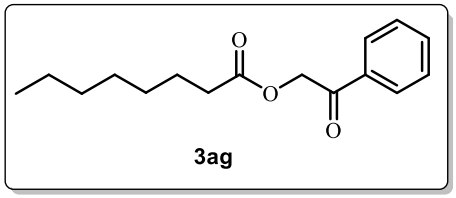


3af

The compound **3af** was synthesized following the general procedure, starting from pivalaldehyde **1m** (50 mg, 0.580 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (127 mg, 0.638 mmol, 1.1 equiv.). The compound **3af** was obtained as white solid, 109 mg, 85% yield. M.P. 54 - 55 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.83 (m, 2H), 7.65 – 7.54 (m, 1H), 7.48 (m, 2H), 5.31 (s, 2H), 1.30 (s, 9H). **^{13}C {^{1}H} NMR (100MHz, $CDCl_3$):** δ 192.6, 178.2, 134.5, 133.9, 129.0, 128.96, 127.9, 66.0, 39.0, 27.4. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{13}H_{17}O_3$ $(M+H)^+$ 221.1178; found 221.1159.

2-oxo-2-phenylethyl octanoate (3ag)[4]

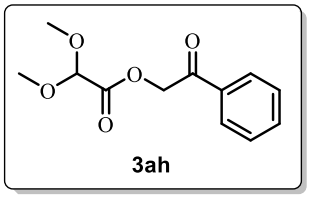


3ag

The compound **3ag** was synthesized following the general procedure, starting from octanal **1n** (50 mg, 0.390 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (85 mg, 0.429 mmol, 1.1 equiv.). The **3ag** was obtained as colorless liquid, 90 mg, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.88 (m, 2H), 7.63 – 7.57 (m, 1H), 7.52 – 7.44 (m, 2H), 5.33 (s, 2H), 2.48 (t, *J* = 7.6 Hz, 2H), 1.69 (dd, *J* = 15.0, 7.3 Hz, 2H), 1.40 – 1.22 (m, 9H), 0.94 – 0.83 (m, 3H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ (ppm) 192.5, 173.4, 134.4, 133.9, 129.0, 128.9, 127.9, 66.0, 34.1, 31.8, 29.2, 29.0, 25.0, 22.7, 14.2. HRMS (ESI TOF) *(m/z)* Calculated Mass $C_{16}H_{22}O_3Na$ $(M+Na)^+$ 285.1467; found 285.1470.

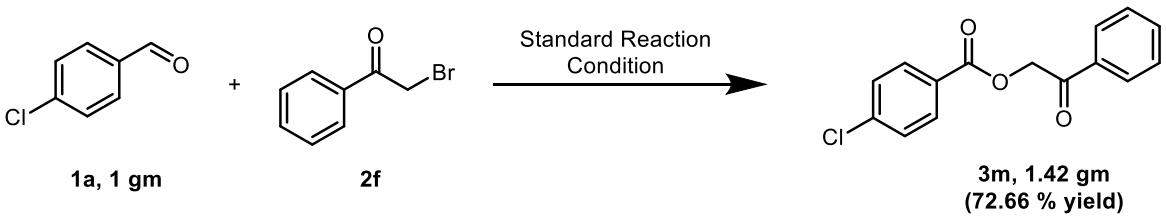
2-oxo-2-phenylethyl 2,2-dimethoxyacetate (3ah)



The compound **3ah** was synthesized following the general procedure, starting from 2,2-dimethoxyacetaldehyde **1o** (50 mg, 0.480 mmol, 1 equiv.) and 2-bromo-1-phenylethan-1-one **2f** (105 mg, 0.582 mmol, 1.1 equiv.). The compound **3ah** was obtained as light yellow liquid, 46 mg, 40% yield.

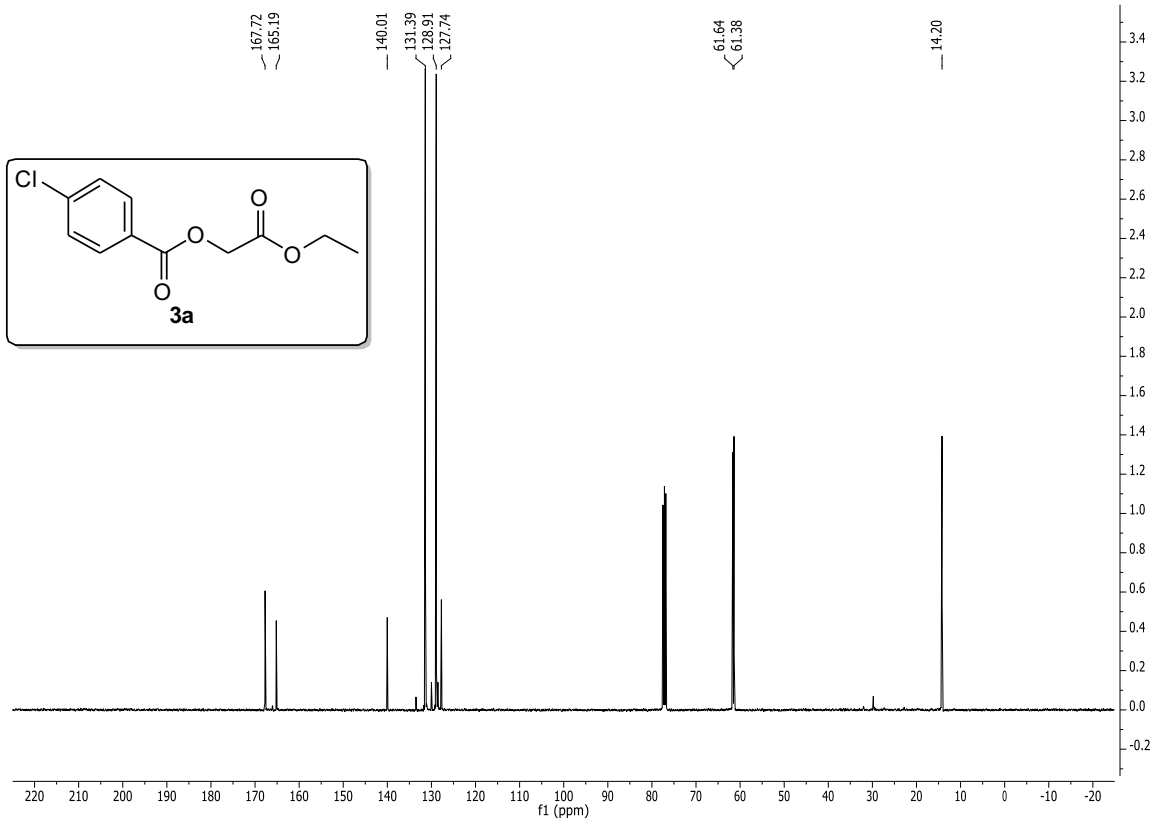
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 5.45 (s, 2H), 5.01 (s, 1H), 3.50 (s, 6H). **^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$):** δ 191.0, 166.7, 134.2, 134.0, 129.0, 127.9, 98.7, 66.7, 54.0. HRMS (ESI TOF) *(m/z)* Calculated mass $C_{12}H_{14}O_5Na$ $(M+Na)^+$ 261.0739; found 261.0735.

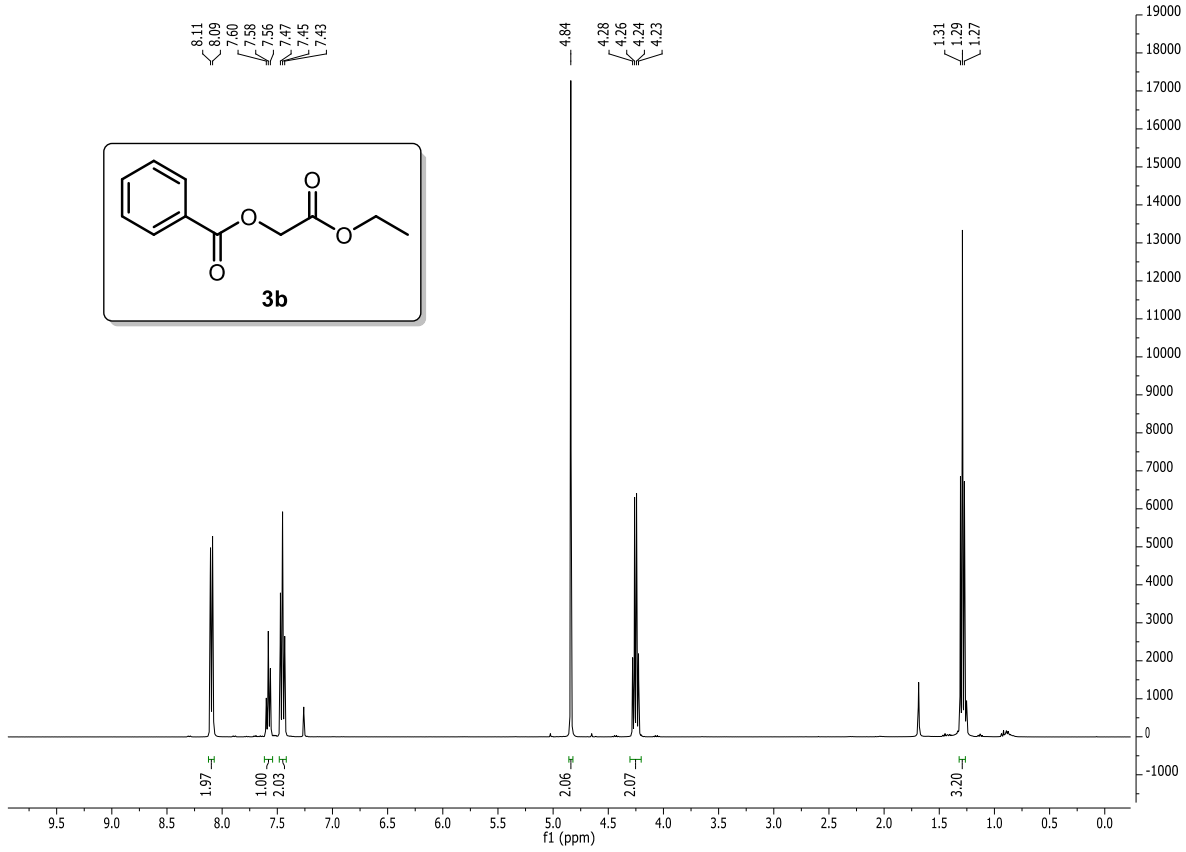
5. Gram Scale Synthesis:

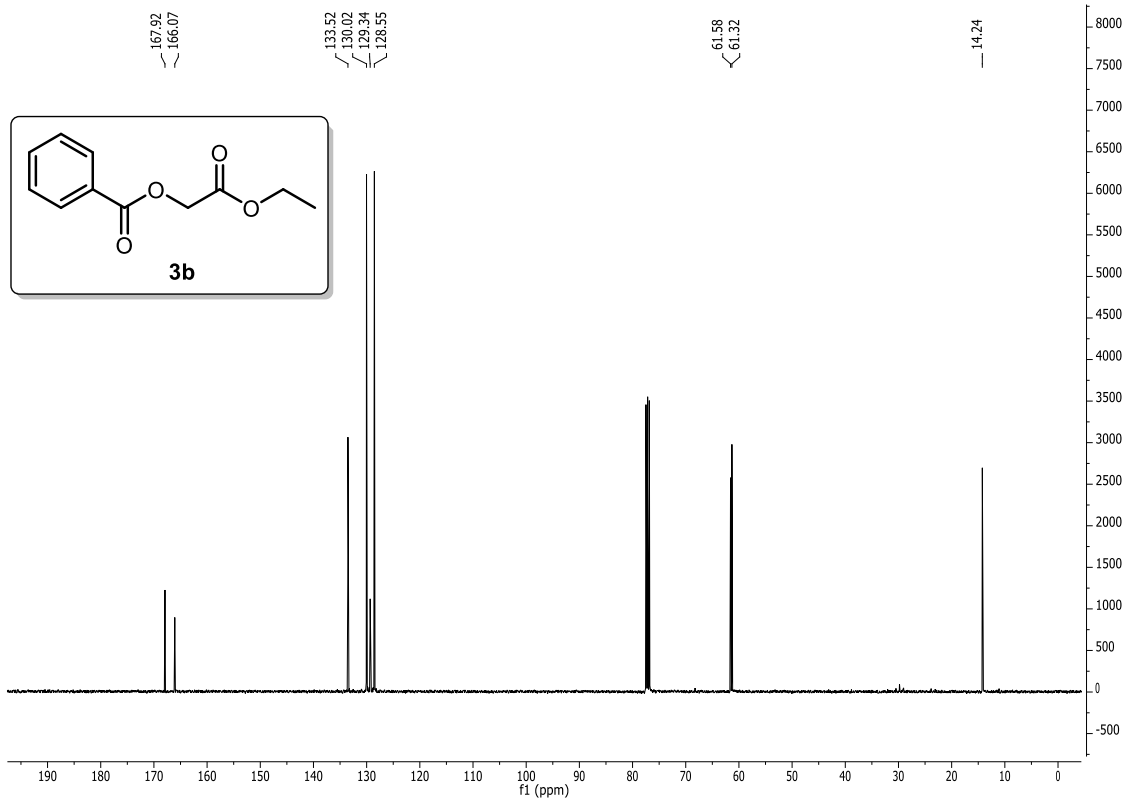


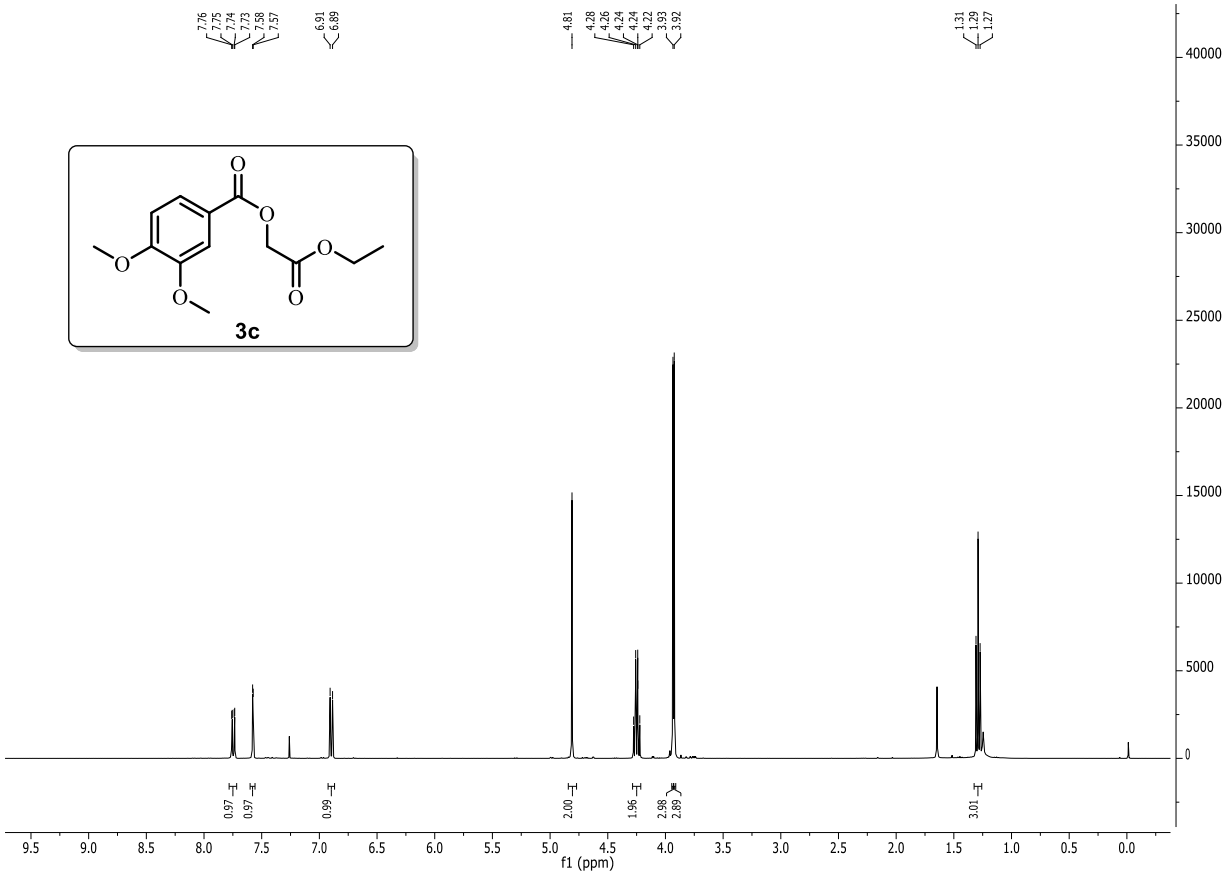
To a solution of 4-chlorobenzaldehyde **1a** (1 g, 1 equiv.) in 50 mL acetonitrile, 2-bromo-1-phenylethan-1-one **2f** (1.1 equiv.), Na_2CO_3 (2 equiv.) $AgBF_4$ (1 equiv.) and photocatalyst TPPT (5 mol%) were added at room temperature and the reaction mixture was kept for stirring under Blue LED (2 × 15 W) for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the solvent was removed under vacuum and the residue was purified by column chromatography using silica gel 100-200 mesh in petroleum ether/ethyl acetate as an eluent system to obtain the corresponding **3m** compound as white solid, 1.42 g, 72.66% yield .

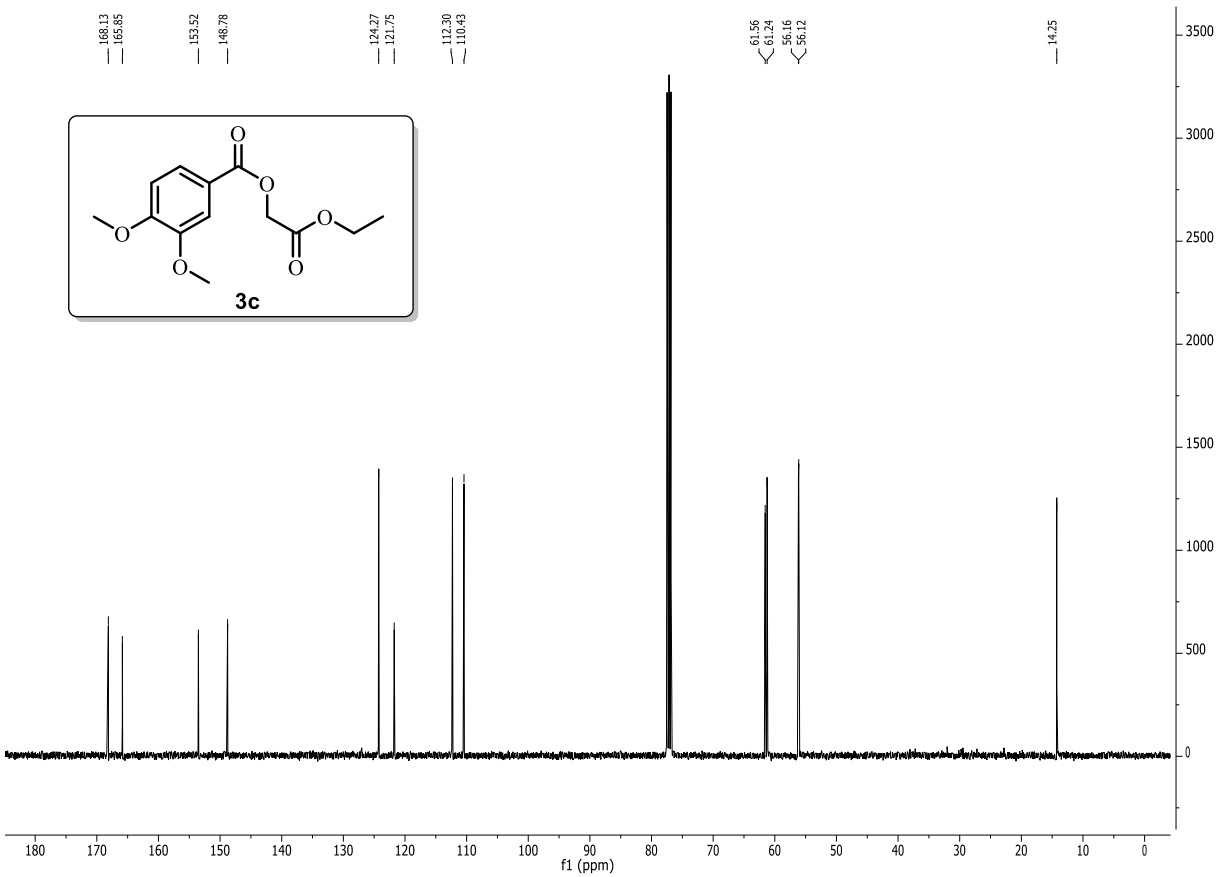
6. Copies of ^{1}H and ^{13}C NMR Spectra:

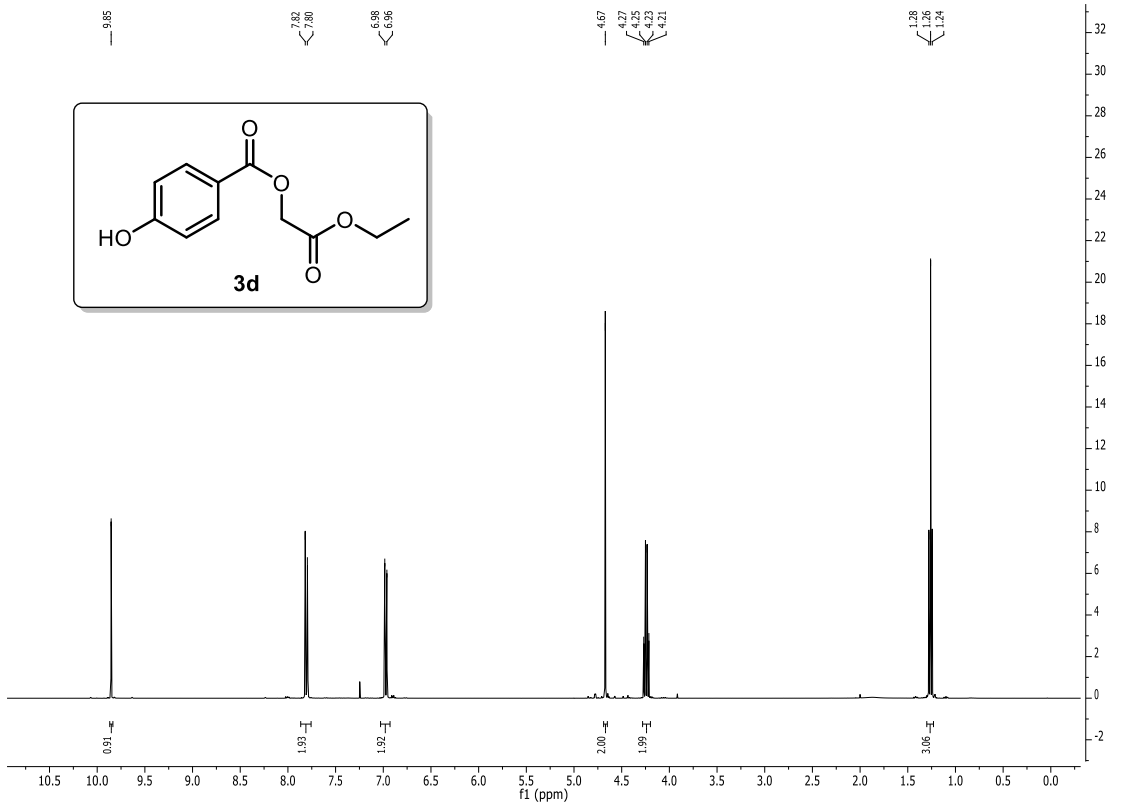


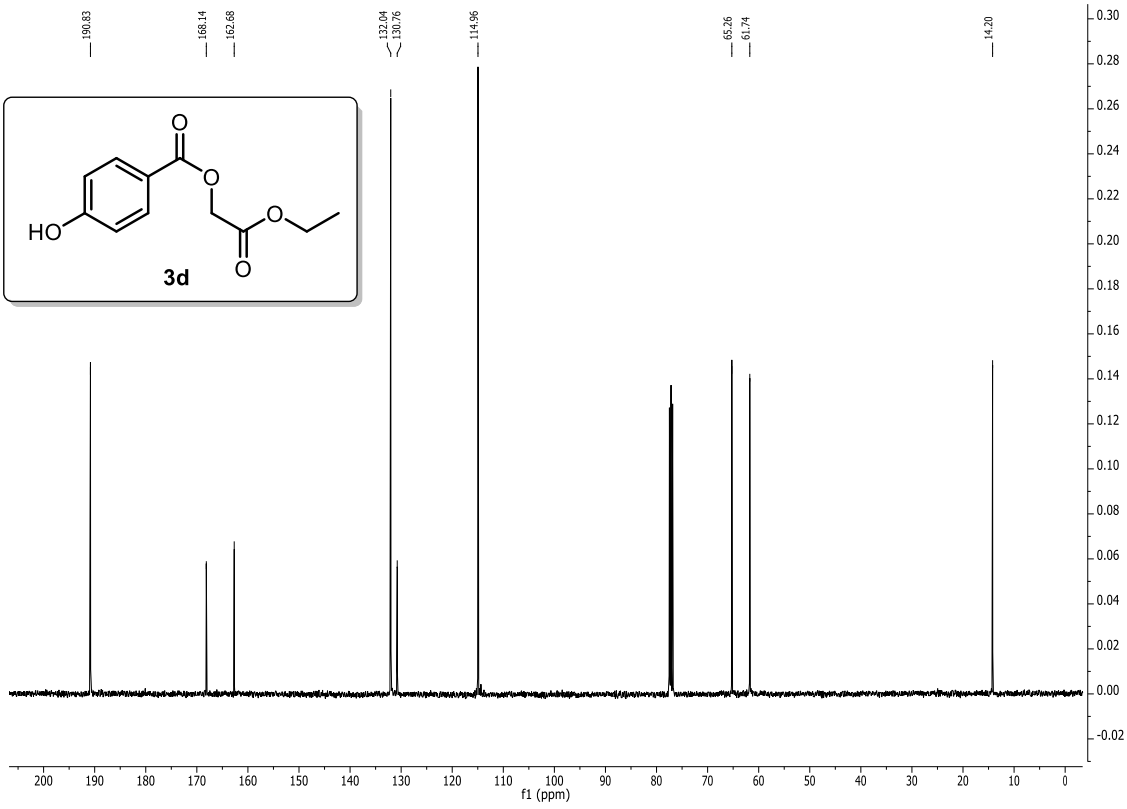

8.11
8.09
7.60
7.58
7.56
7.47
7.45
7.43
4.84
4.28
4.26
4.24
4.23
1.31
1.29
1.27
3b
1.97
1.00
2.03
2.06
2.07
3.20
f1 (ppm)

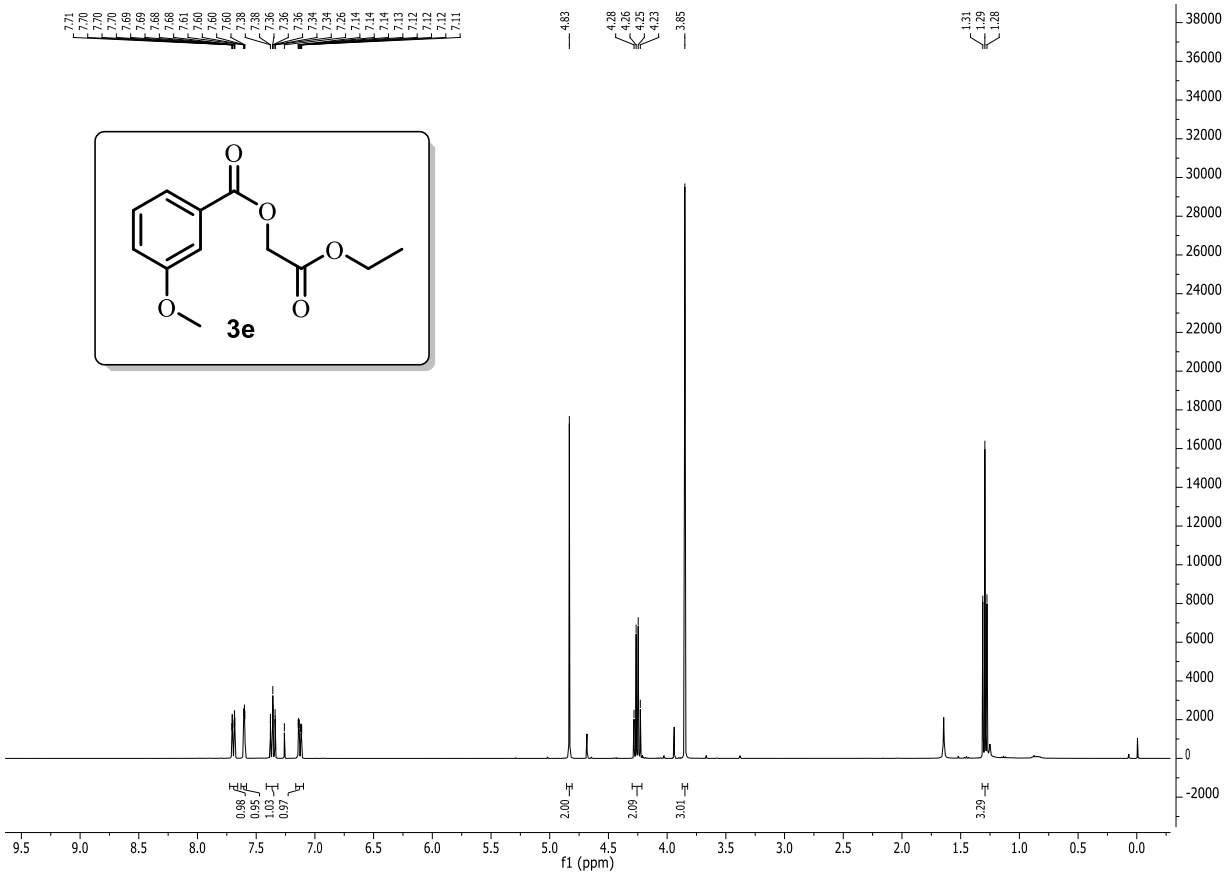

167.92
166.07
133.52
130.02
129.34
128.55
61.58
61.32
14.24
3b
f1 (ppm)

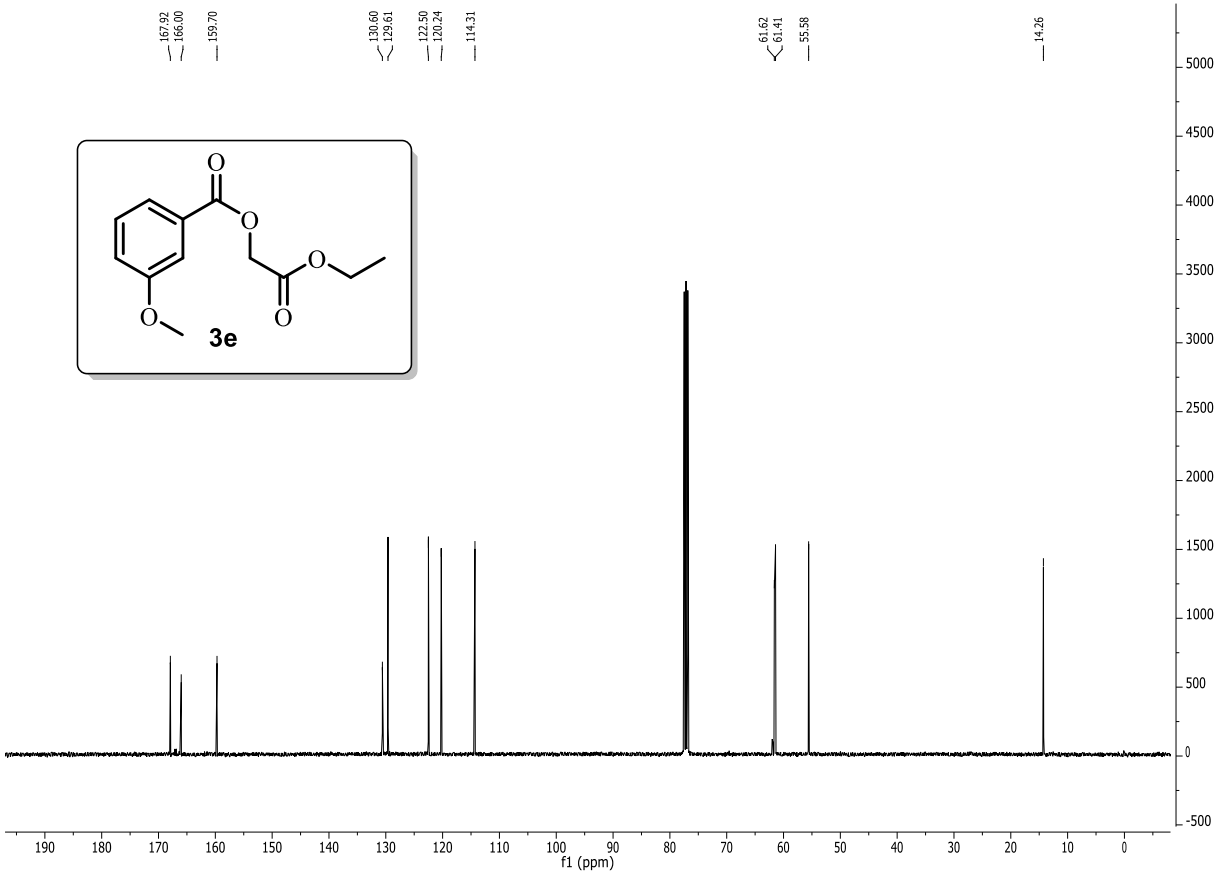

7.76
7.75
7.74
7.73
7.58
7.57
6.91
6.89
4.81
4.28
4.26
4.24
4.24
4.22
3.93
3.92
1.31
1.29
1.27
3c
0.97
0.97
0.99
2.00
1.96
2.98
2.89
3.01
f1 (ppm)

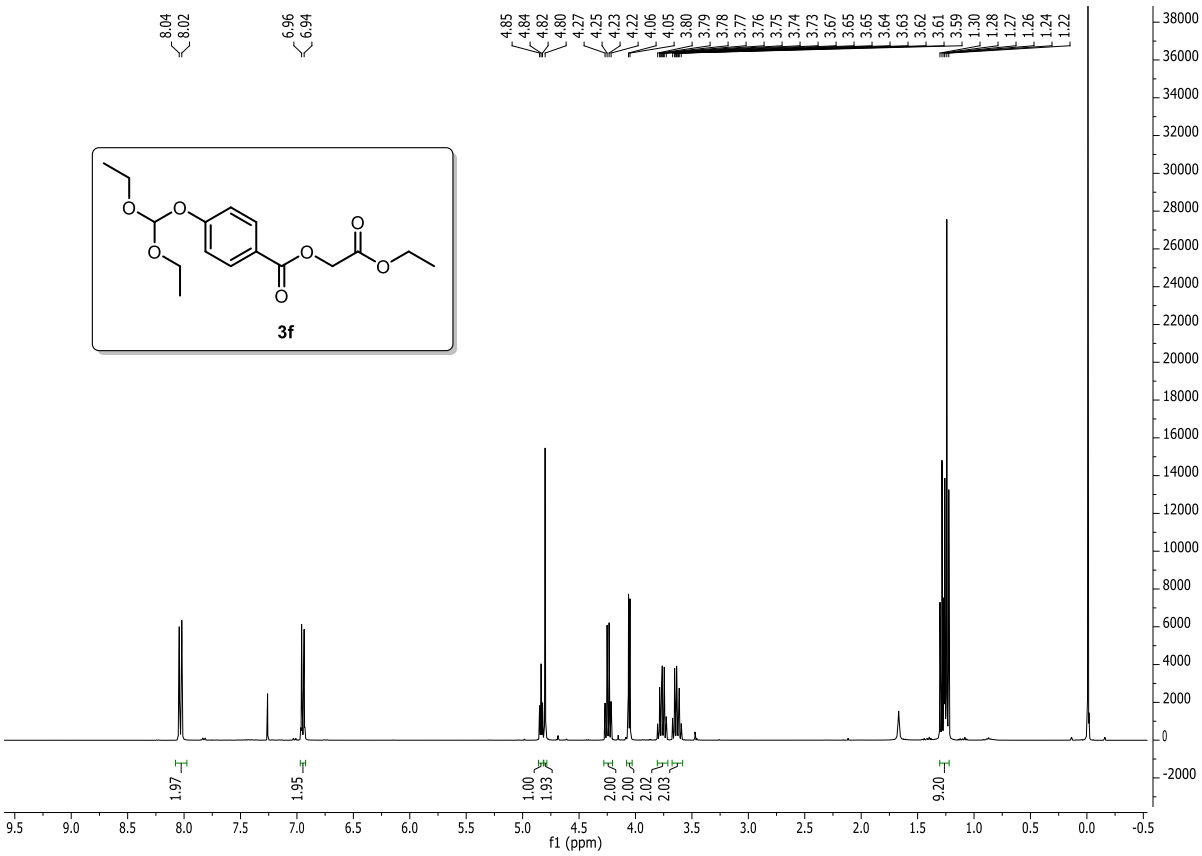

168.13
165.85
153.52
148.78
124.27
121.75
112.30
110.43
61.56
61.24
56.16
56.12
14.25
3c
f1 (ppm)

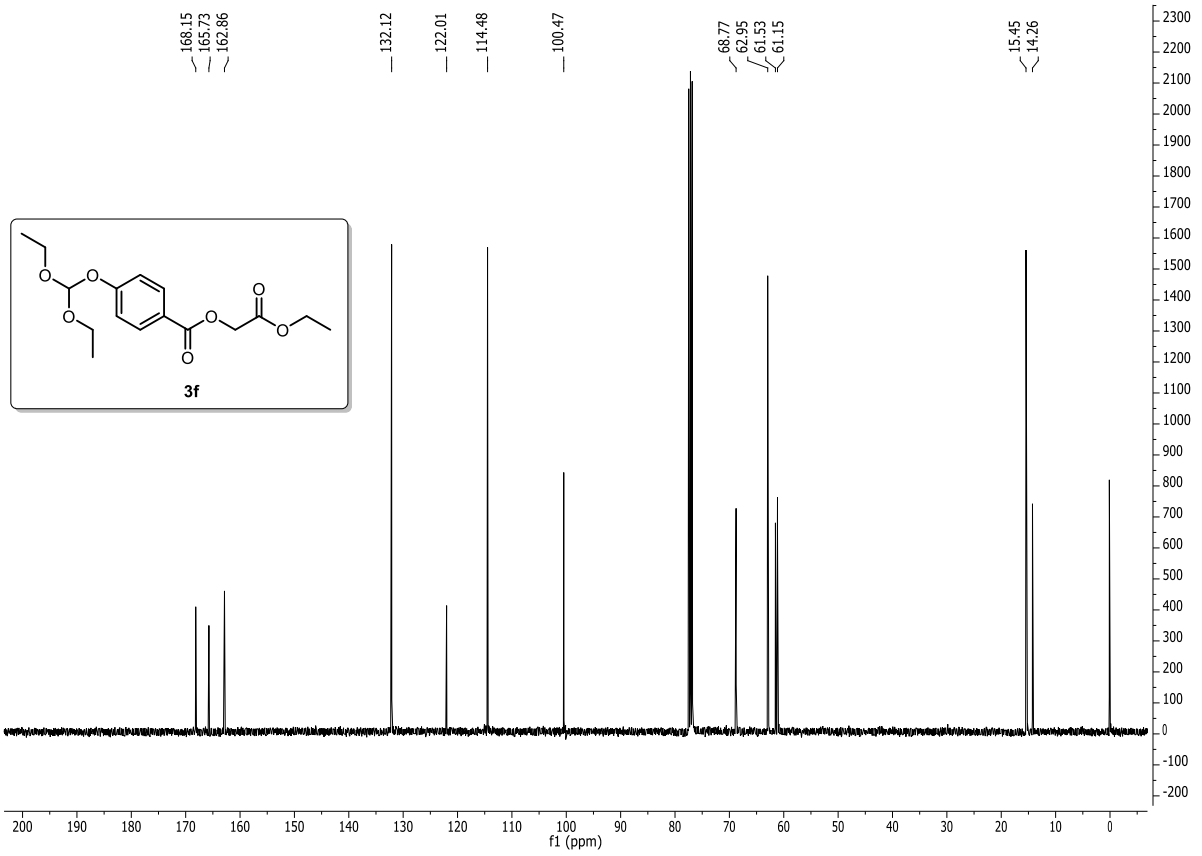

9.85
7.82
7.80
6.98
6.96
4.67
4.27
4.25
4.23
4.21
1.28
1.26
1.24
HO
O
O
O
O
3d
0.91
1.93
1.92
2.00
1.99
3.06
f1 (ppm)

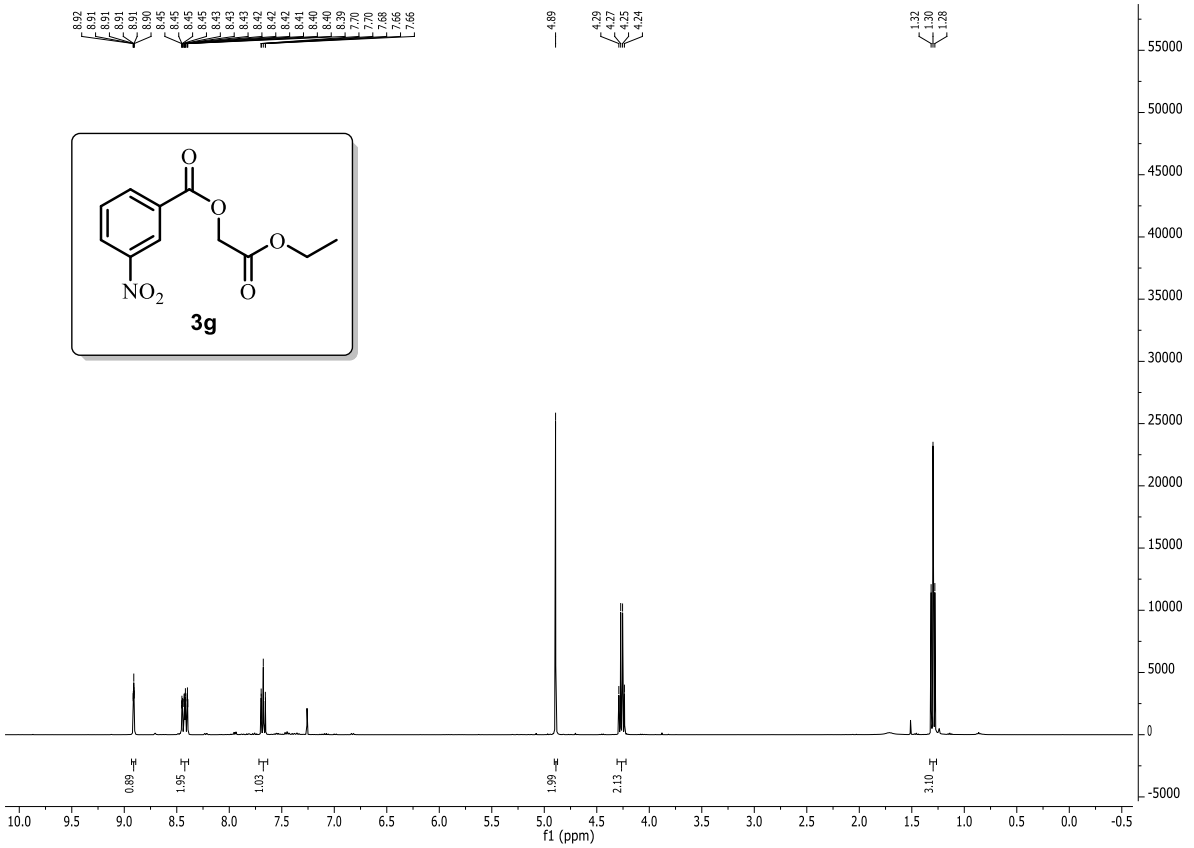

190.83
168.14
162.68
132.04
130.76
114.96
65.26
61.74
14.20
HO
O
O
O
O
3d
f1 (ppm)

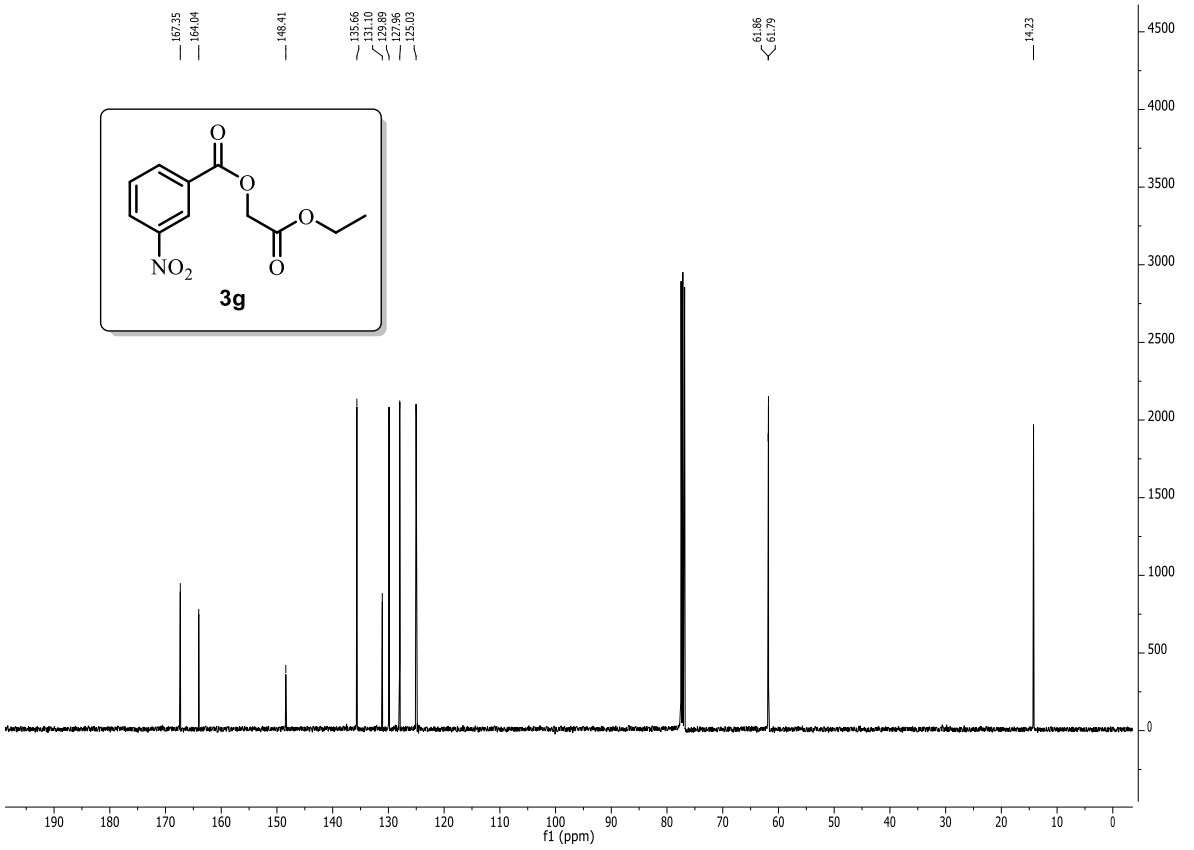

3e
f1 (ppm)

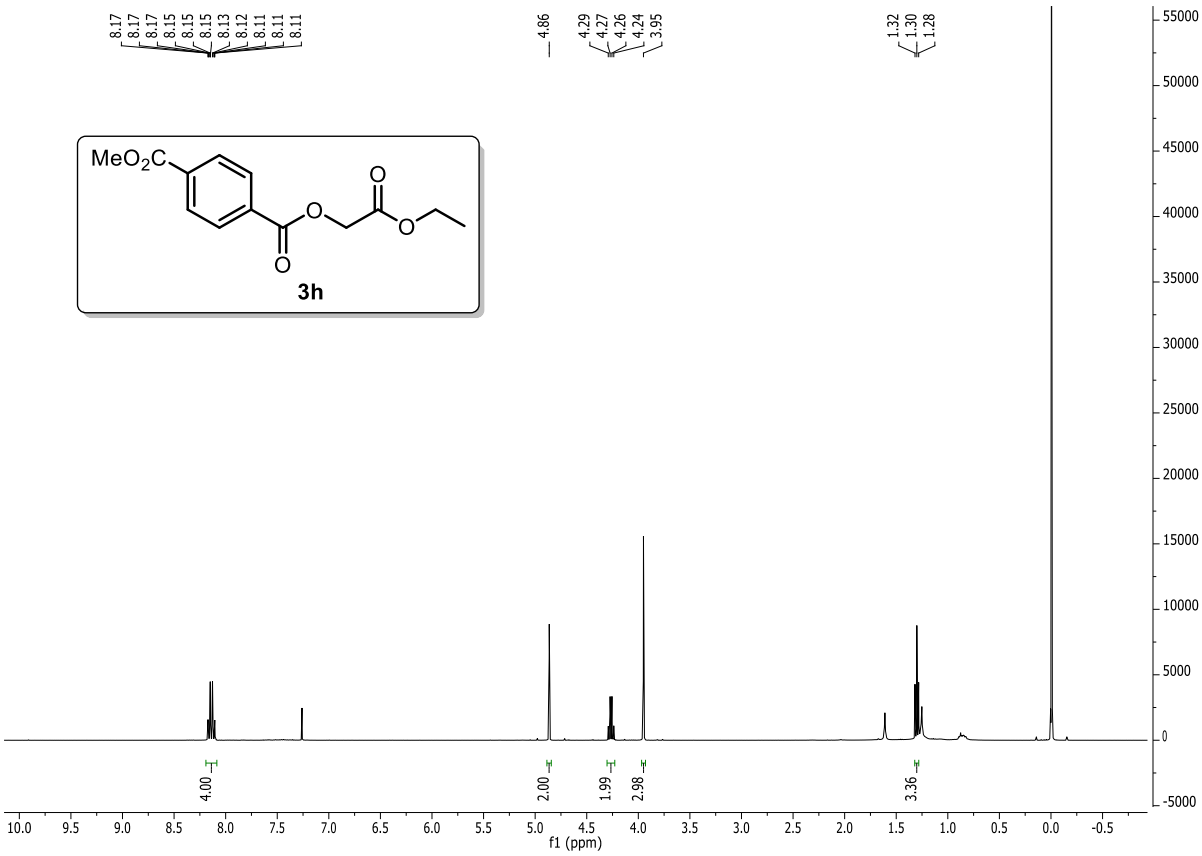

3e
f1 (ppm)

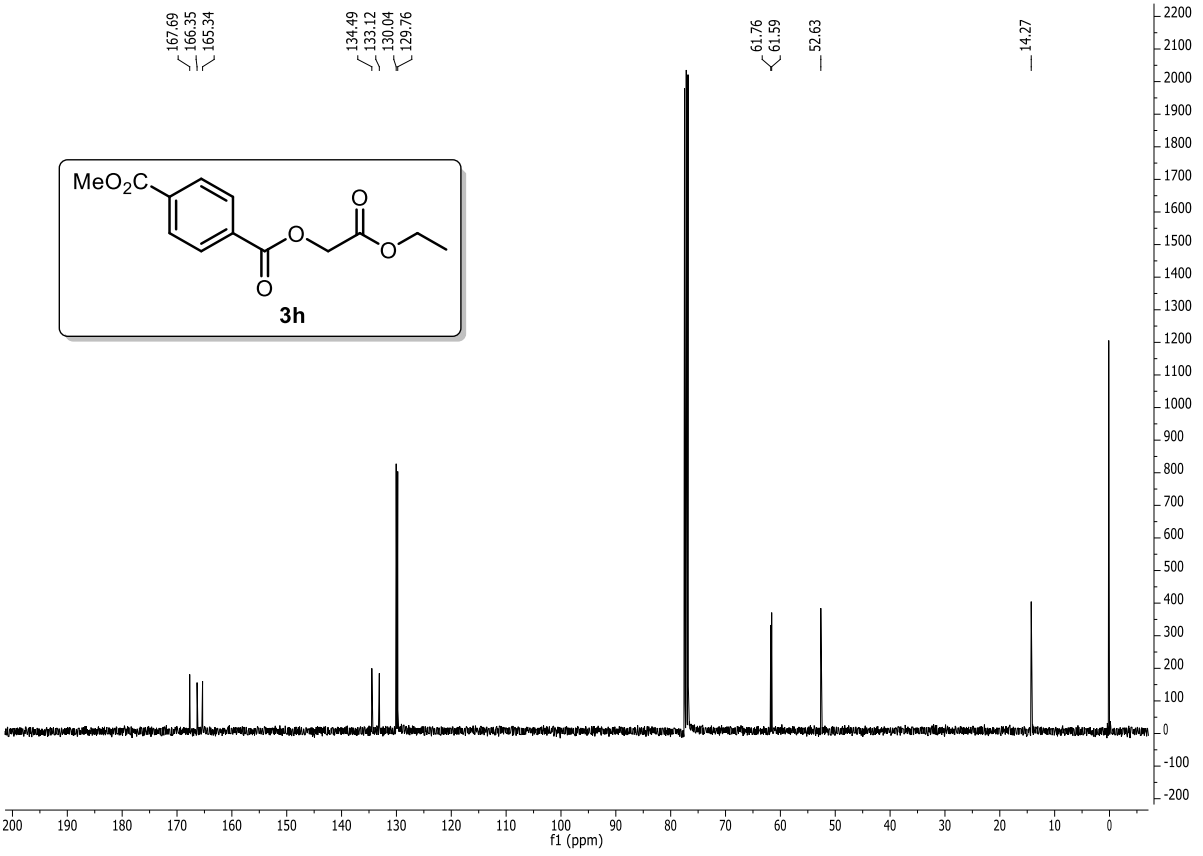

8.04
8.02
6.96
6.94
4.85
4.84
4.82
4.80
4.27
4.25
4.23
4.22
4.06
4.05
3.80
3.79
3.78
3.77
3.76
3.75
3.74
3.73
3.67
3.65
3.64
3.63
3.62
3.61
3.59
1.30
1.28
1.27
1.26
1.24
1.22
3f
1.97
1.95
1.00
1.93
2.00
2.00
2.02
2.03
9.20
f1 (ppm)


168.15
165.73
162.86
132.12
122.01
114.48
100.47
68.77
62.95
61.53
61.15
15.45
14.26
3f
f1 (ppm)

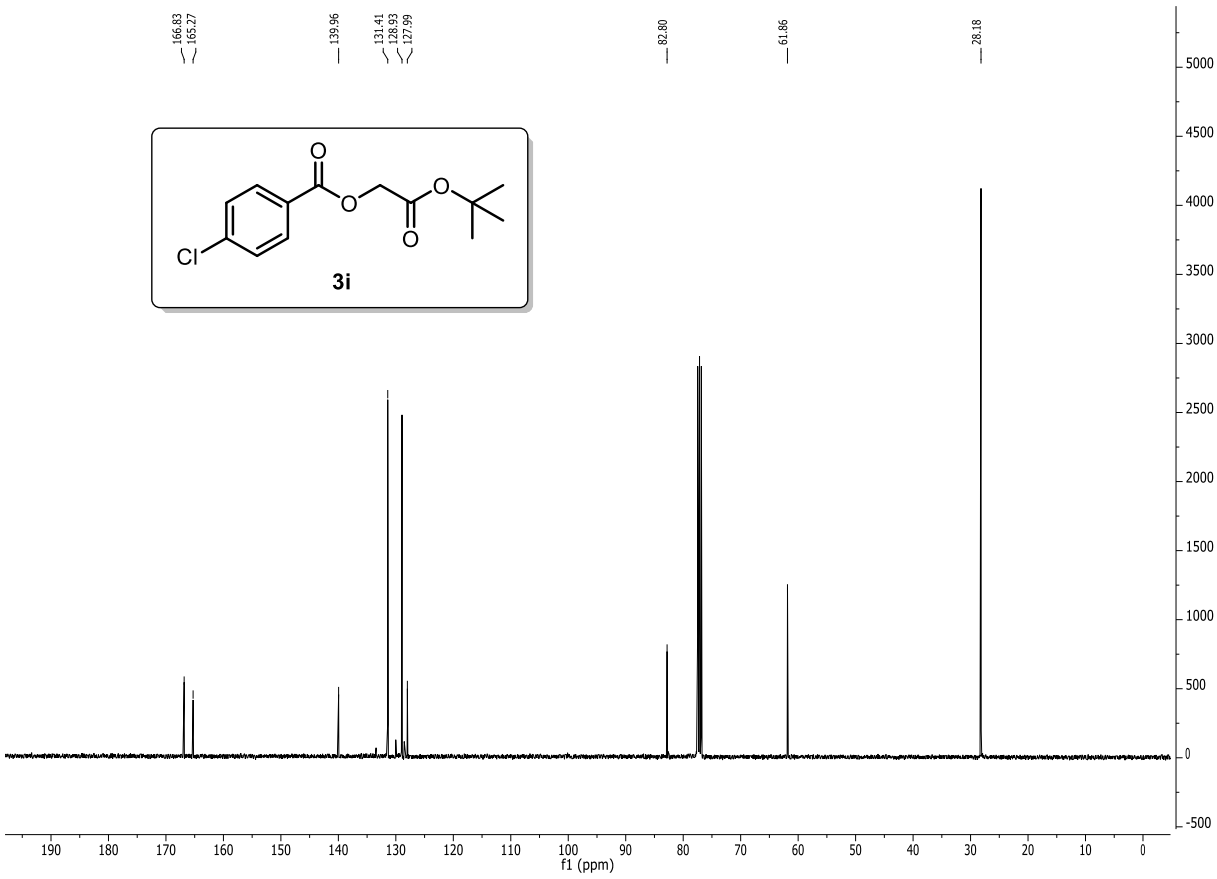

8.92
8.91
8.91
8.91
8.91
8.90
8.45
8.45
8.45
8.45
8.43
8.43
8.43
8.42
8.42
8.42
8.41
8.40
8.40
8.39
7.70
7.70
7.68
7.66
7.66
4.89
4.29
4.27
4.25
4.24
1.32
1.30
1.28
O
O
O
O
NO2
3g
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0.89
1.95
1.03
1.99
2.13
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

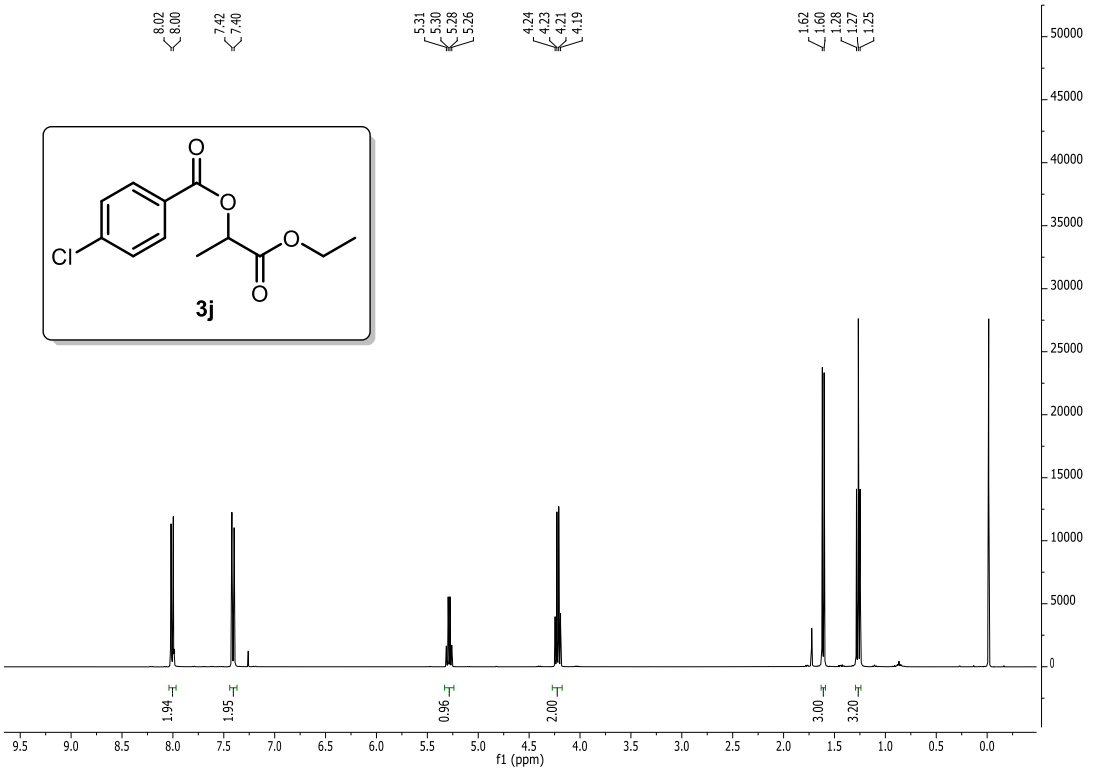

167.35
164.04
148.41
135.66
131.10
129.89
127.96
125.03
61.86
61.79
14.23
O
O
O
O
NO2
3g
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

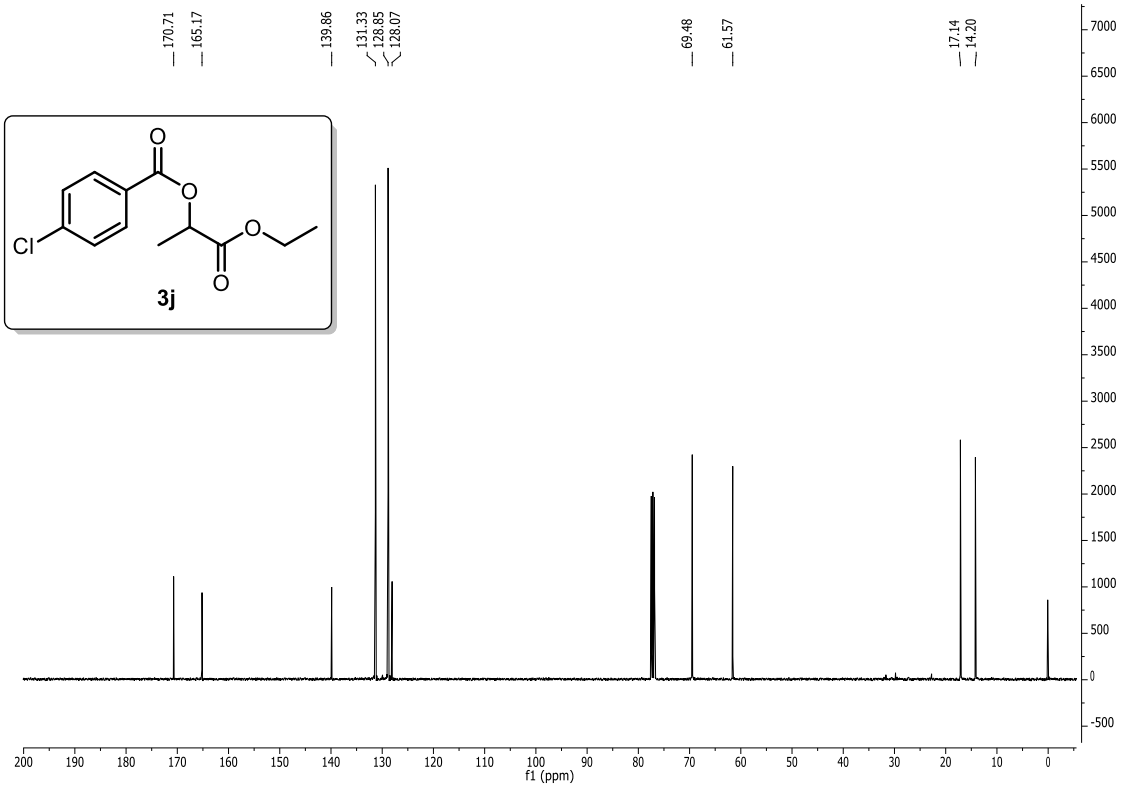

8.17
8.17
8.17
8.15
8.15
8.15
8.13
8.12
8.11
8.11
8.11
4.86
4.29
4.27
4.26
4.24
3.95
1.32
1.30
1.28
MeO2C
O
O
O
O
3h
4.00
2.00
1.99
2.98
3.36
f1 (ppm)

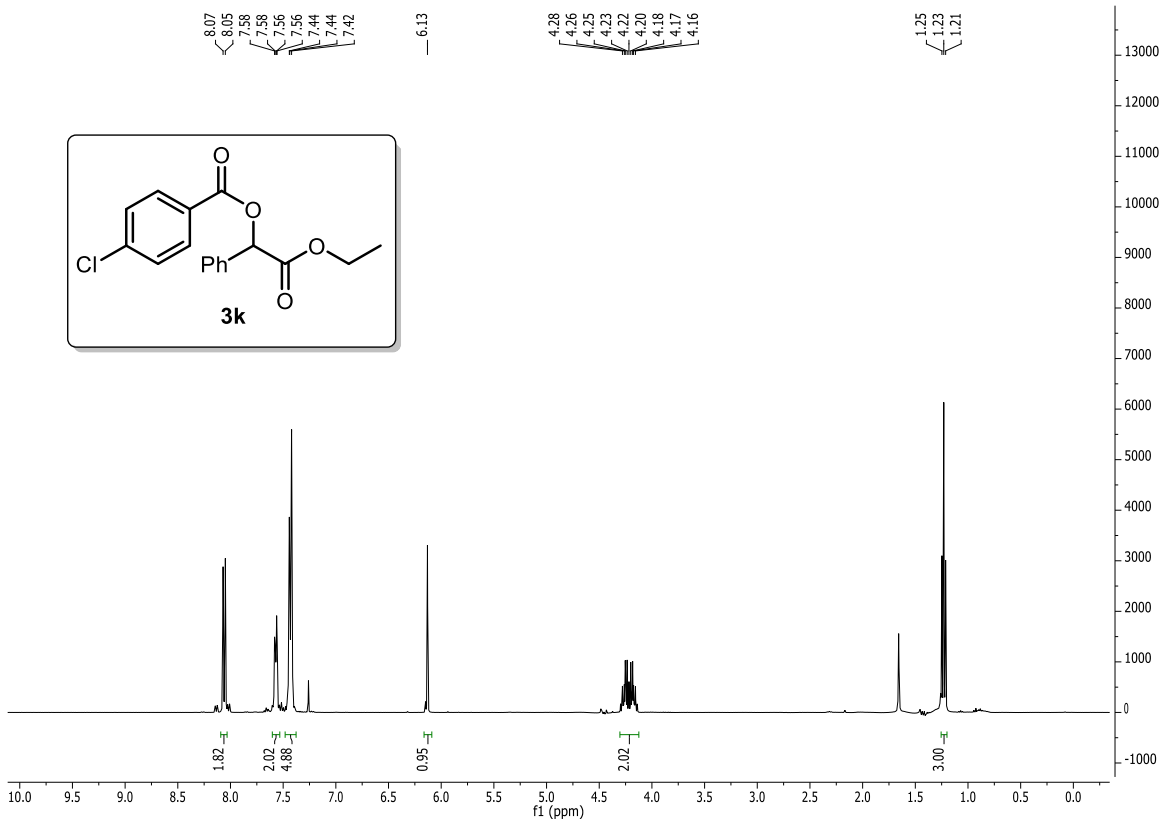

167.69
166.35
165.34
134.49
133.12
130.04
129.76
61.76
61.59
52.63
14.27
MeO2C
O
O
O
O
3h
f1 (ppm)

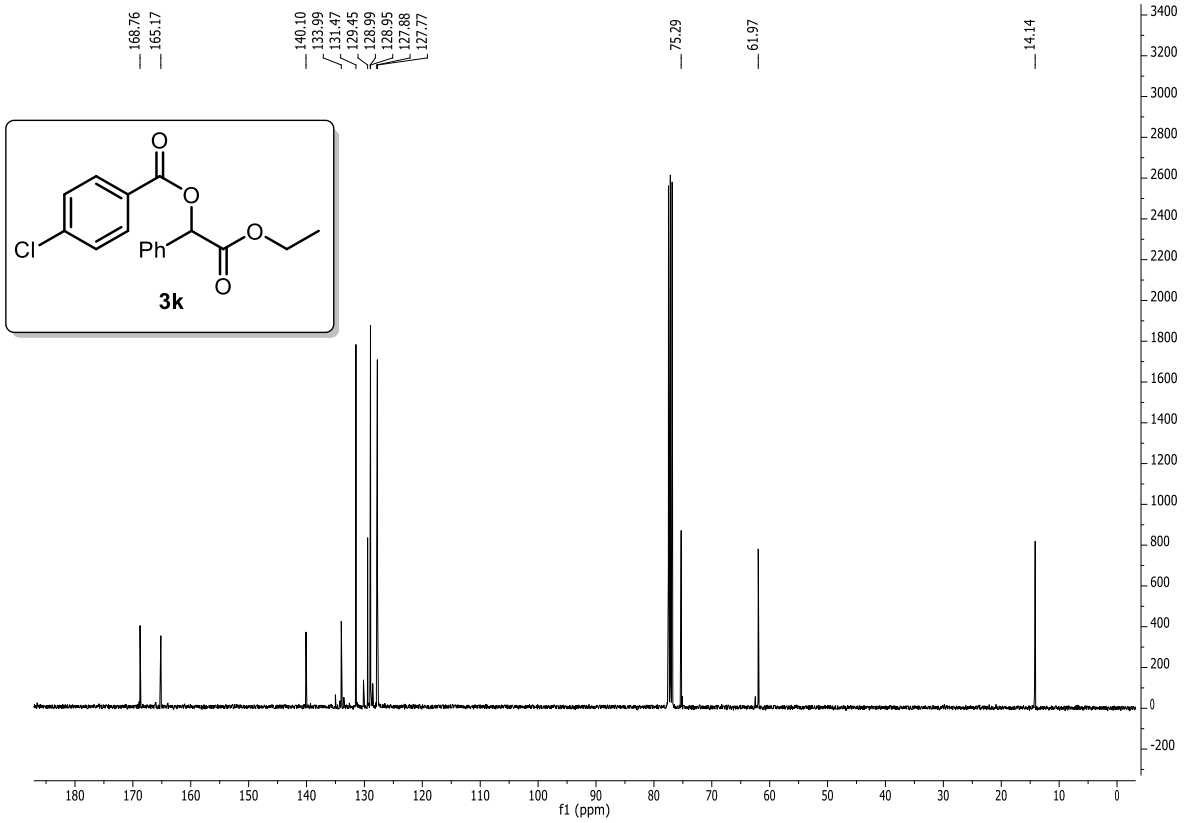

8.06
8.04
7.46
7.44
4.75
1.51
3i
1.88
1.99
2.00
9.22
f1 (ppm)

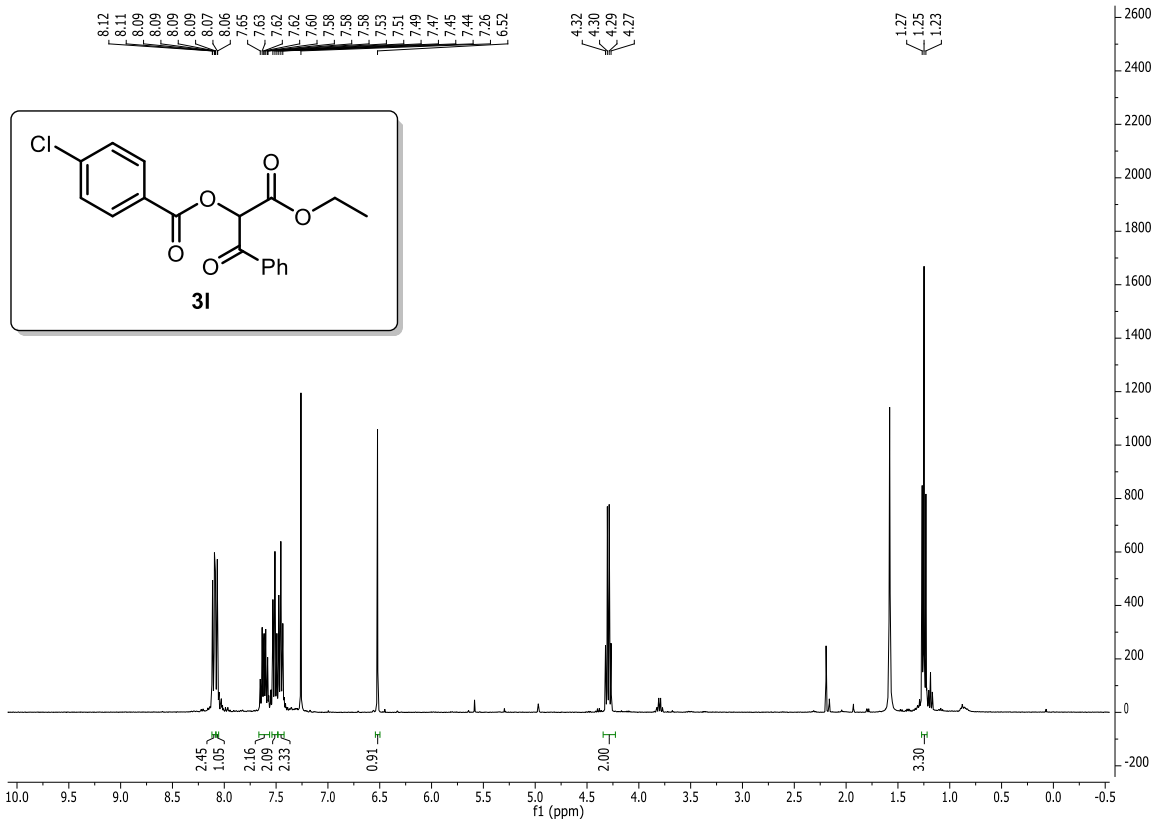

166.83
165.27
139.96
131.41
128.93
127.99
82.80
61.86
28.18
3i
f1 (ppm)

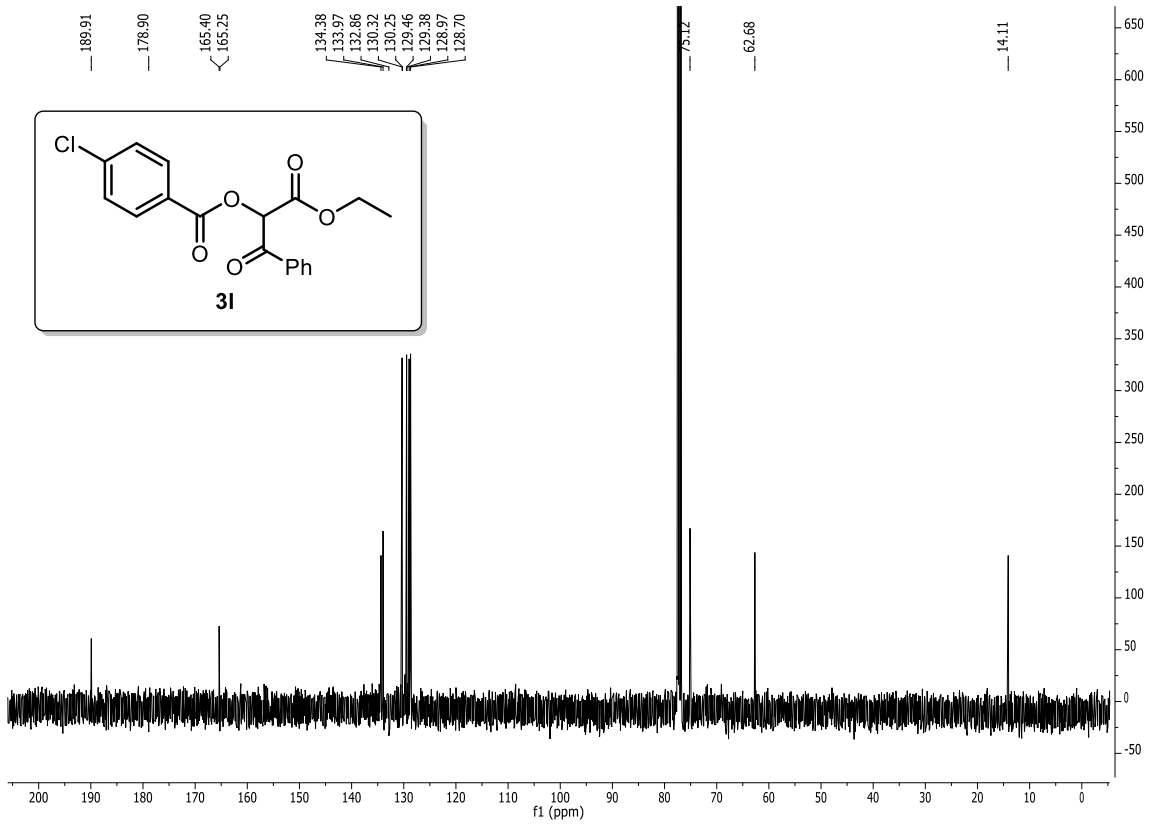

8.02
8.00
7.42
7.40
5.31
5.30
5.28
5.26
4.24
4.23
4.21
4.19
1.62
1.60
1.28
1.27
1.25
Cl
O
O
O
O
3j
1.94
1.95
0.96
2.00
3.00
3.20
f1 (ppm)

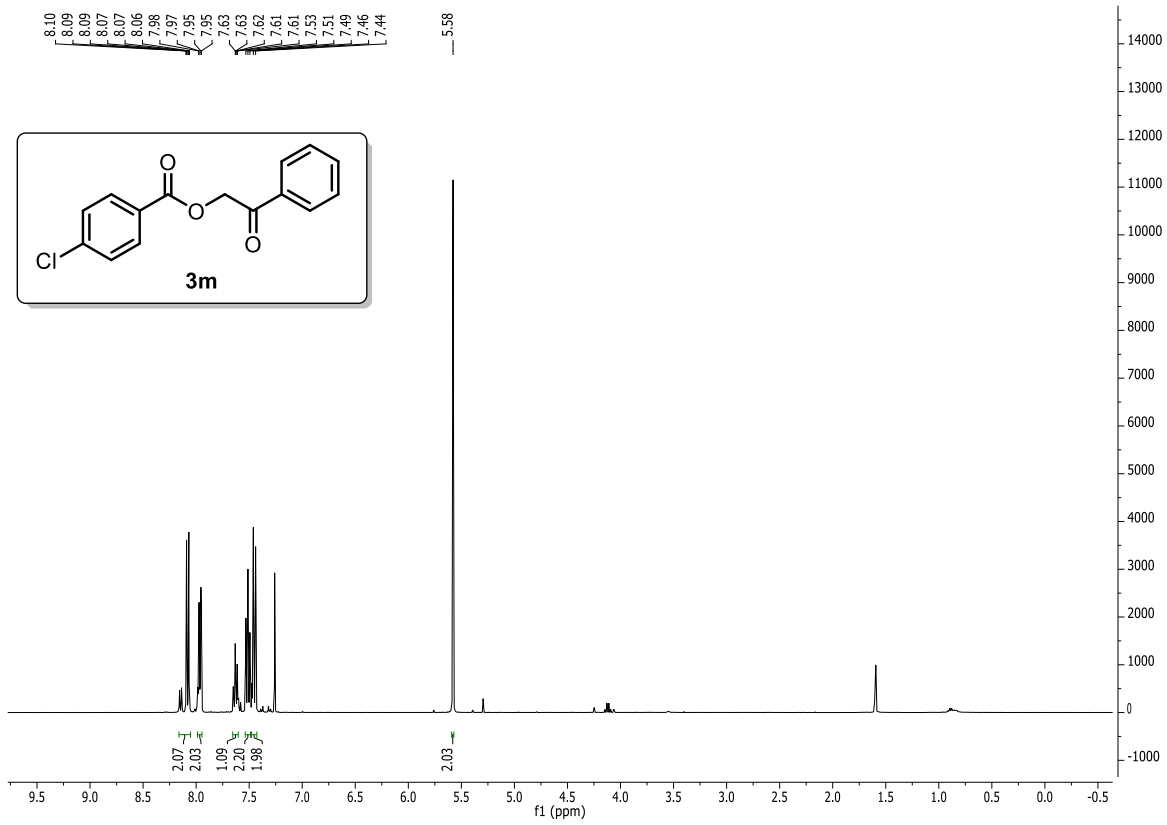

170.71
165.17
139.86
131.33
128.85
128.07
69.48
61.57
17.14
14.20
Cl
O
O
O
O
3j
f1 (ppm)

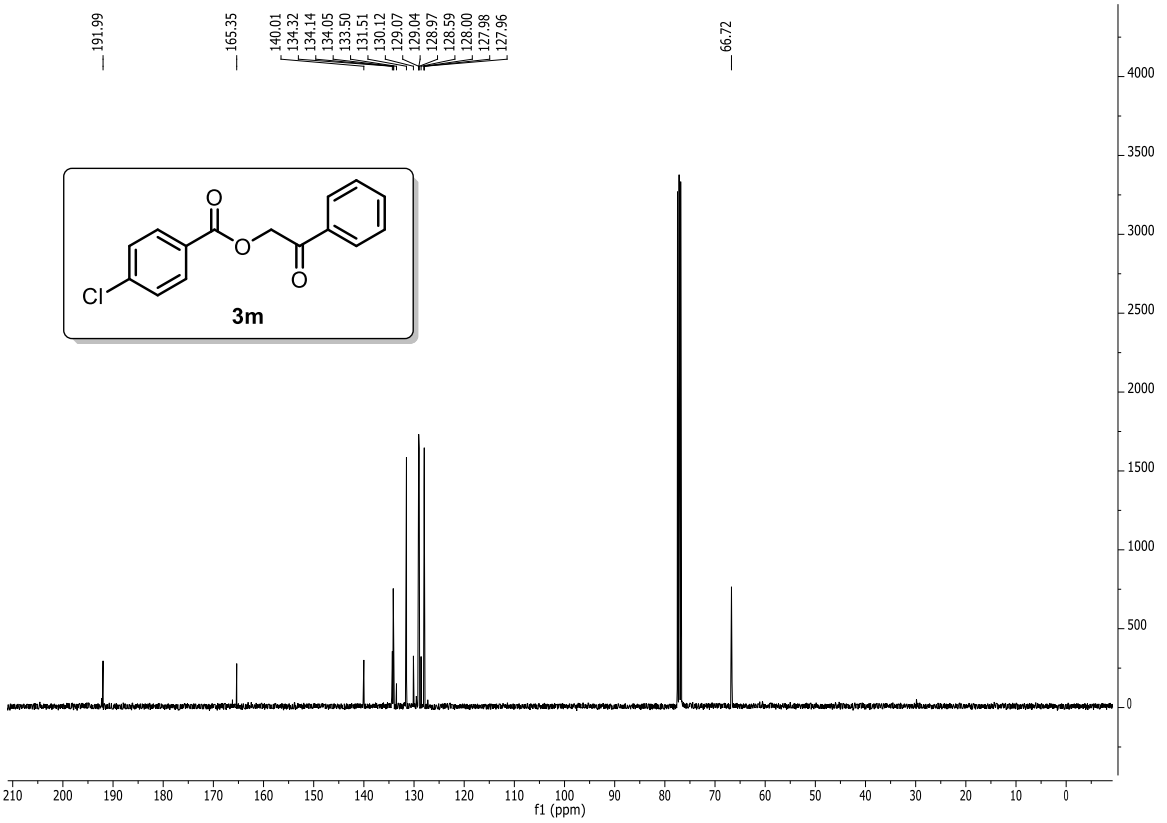

8.07
8.05
7.58
7.58
7.56
7.56
7.44
7.44
7.42
6.13
4.28
4.26
4.25
4.23
4.22
4.20
4.18
4.17
4.16
1.25
1.23
1.21
Cl
Ph
O
O
O
O
3k
1.82
2.02
4.88
0.95
2.02
3.00
f1 (ppm)

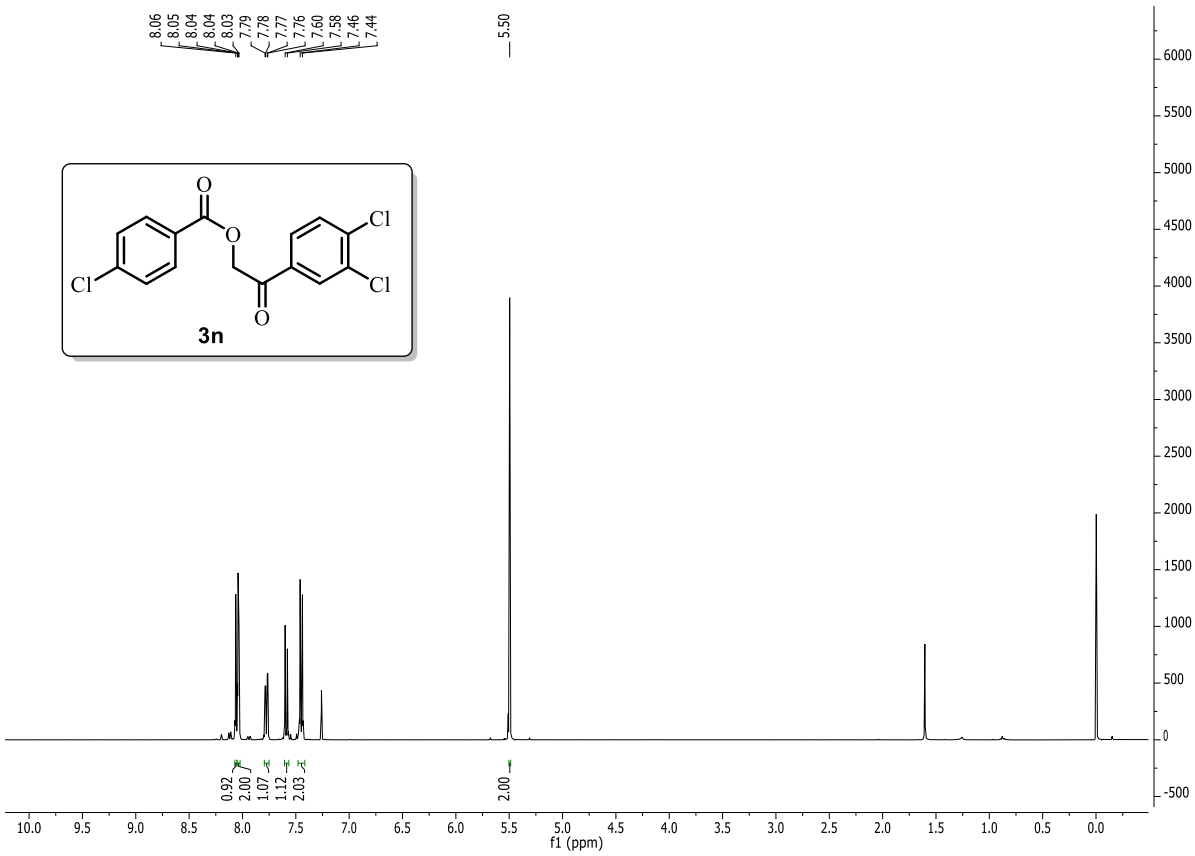

168.76
165.17
140.10
133.99
131.47
129.45
128.99
128.95
127.88
127.77
75.29
61.97
14.14
Cl
Ph
O
O
O
O
3k
f1 (ppm)

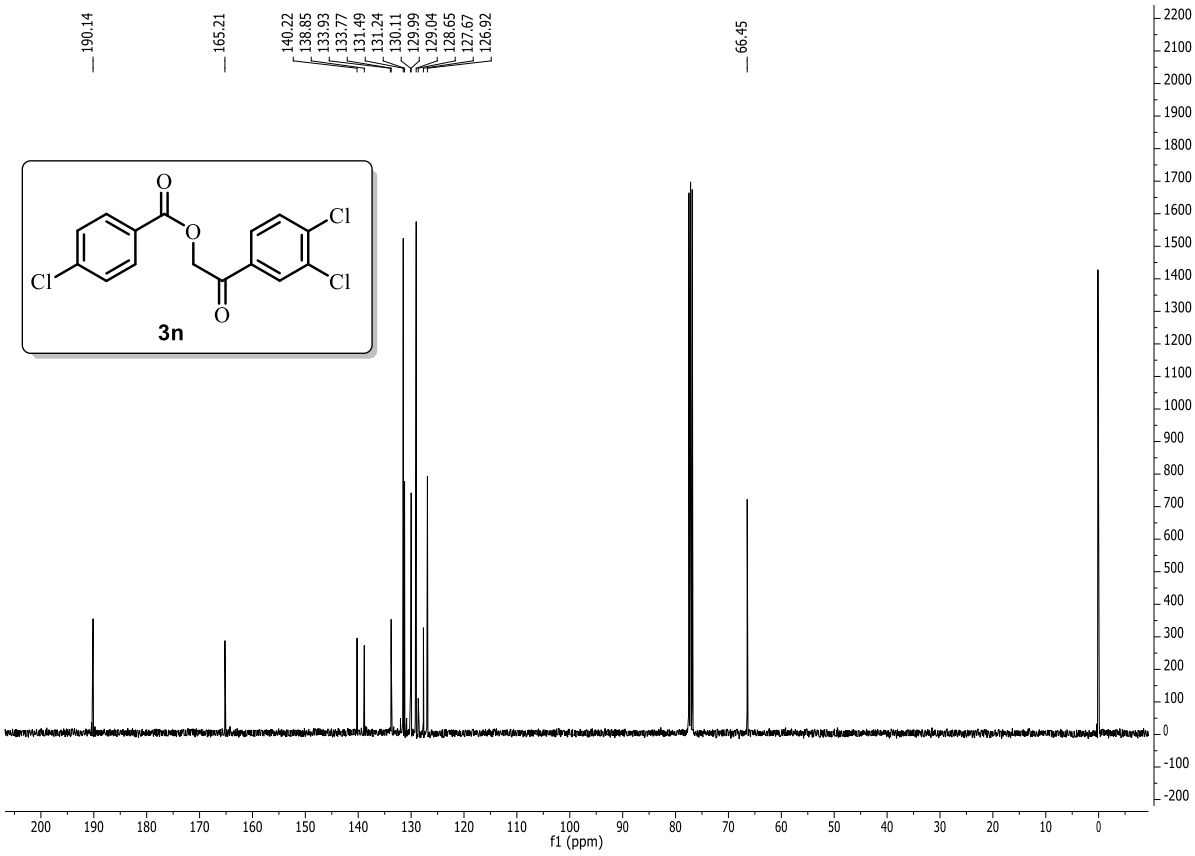

8.12
8.11
8.09
8.09
8.09
8.09
8.07
8.06
7.65
7.63
7.62
7.62
7.60
7.58
7.58
7.58
7.53
7.51
7.49
7.47
7.45
7.44
7.26
6.52
4.32
4.30
4.29
4.27
1.27
1.25
1.23
Cl
O
O
O
O
O
Ph
3l
2.45
1.05
2.16
2.09
2.33
0.91
2.00
3.30
f1 (ppm)

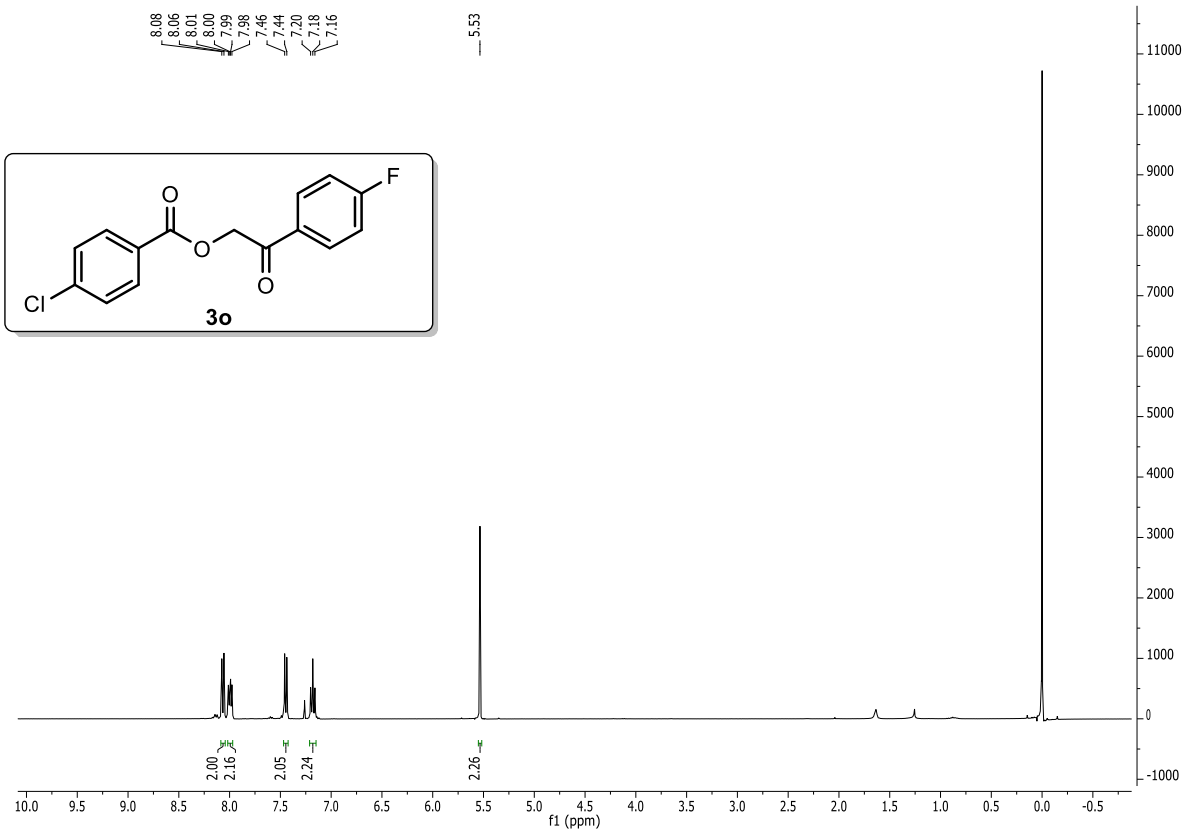

189.91
178.90
165.40
165.25
134.38
133.97
132.86
130.32
130.25
129.46
129.38
128.97
128.70
75.12
62.68
14.11
Cl
O
O
O
O
O
Ph
3l
f1 (ppm)

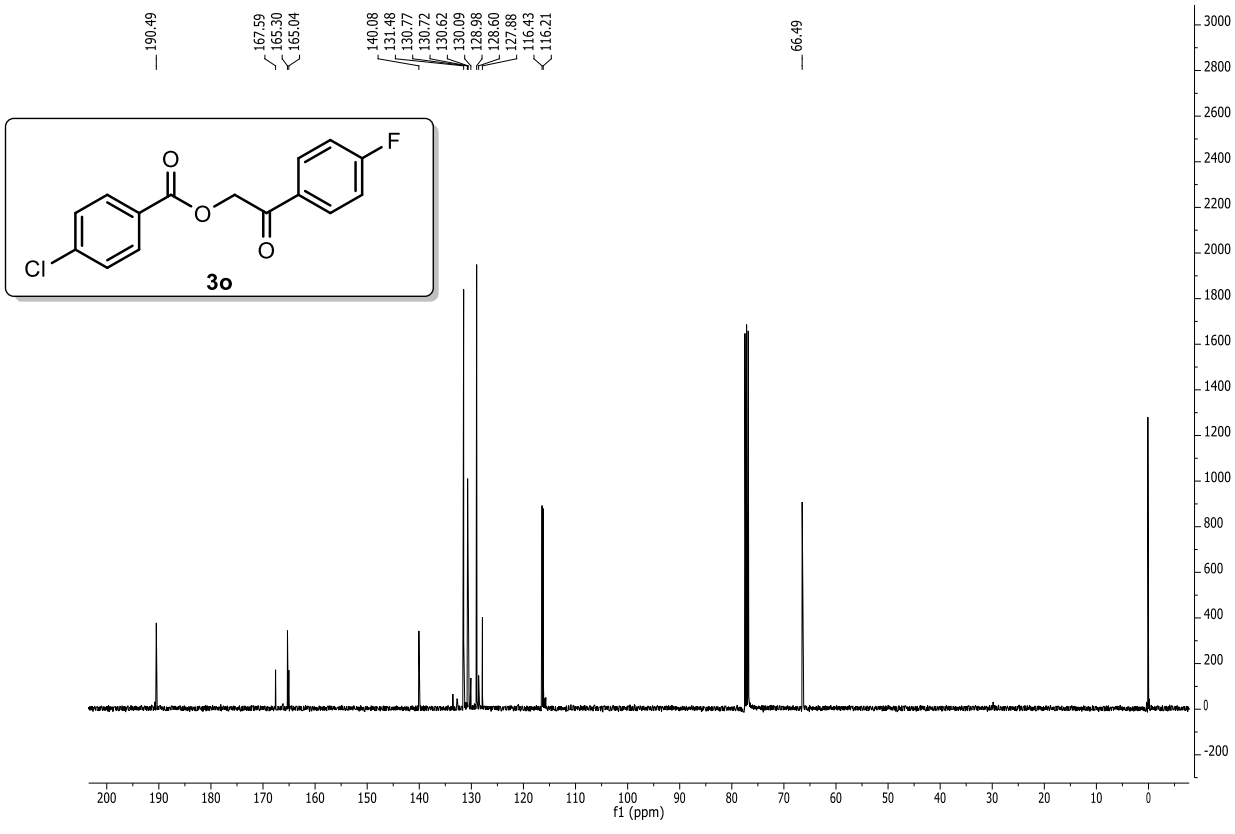

8.10
8.09
8.09
8.07
8.07
8.06
7.98
7.97
7.95
7.95
7.63
7.63
7.62
7.61
7.61
7.53
7.51
7.49
7.46
7.44
5.58
Cl
3m
2.07
2.03
1.09
2.20
1.98
2.03
f1 (ppm)

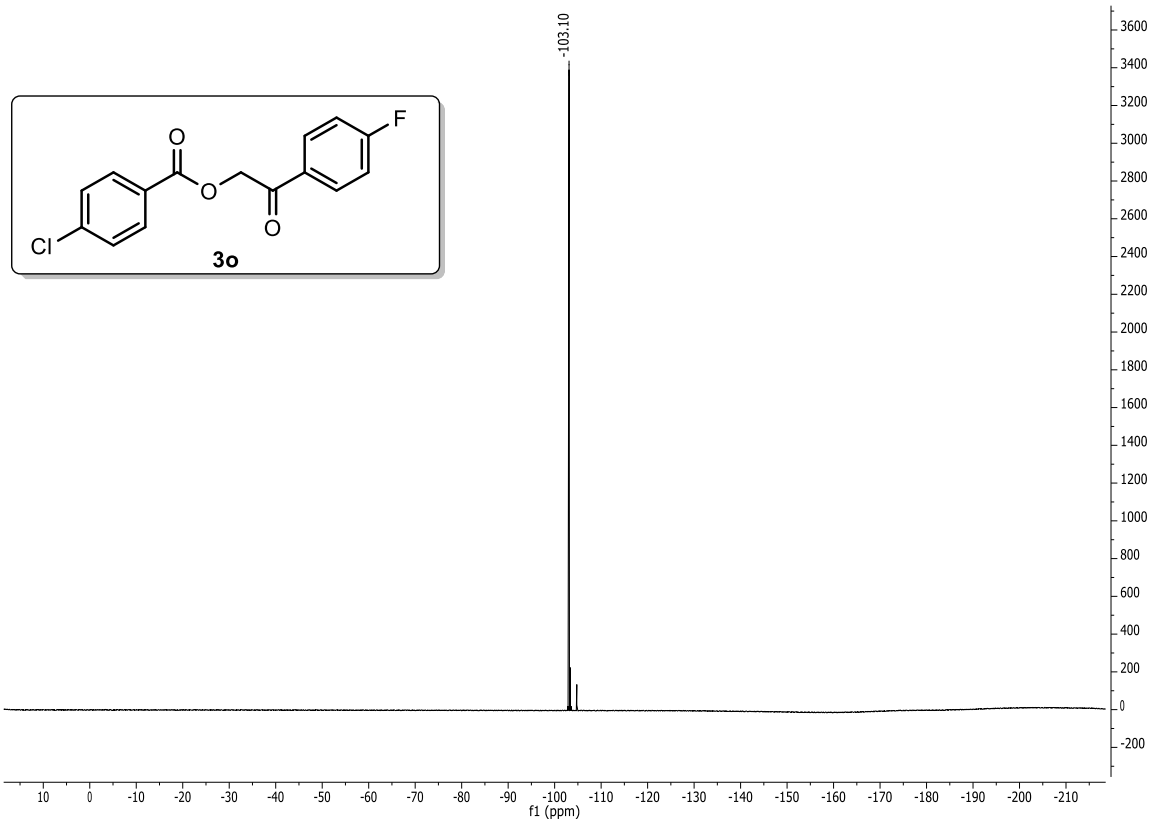

191.99
165.35
140.01
134.32
134.14
134.05
133.50
131.51
130.12
129.07
129.04
128.97
128.59
128.00
127.98
127.96
66.72
Cl
3m
f1 (ppm)


8.06
8.05
8.04
8.04
8.03
7.79
7.78
7.77
7.76
7.60
7.58
7.46
7.44
5.50
Cl
Cl
Cl
O
O
O
3n
0.92
2.00
1.07
1.12
2.03
2.00
f1 (ppm)

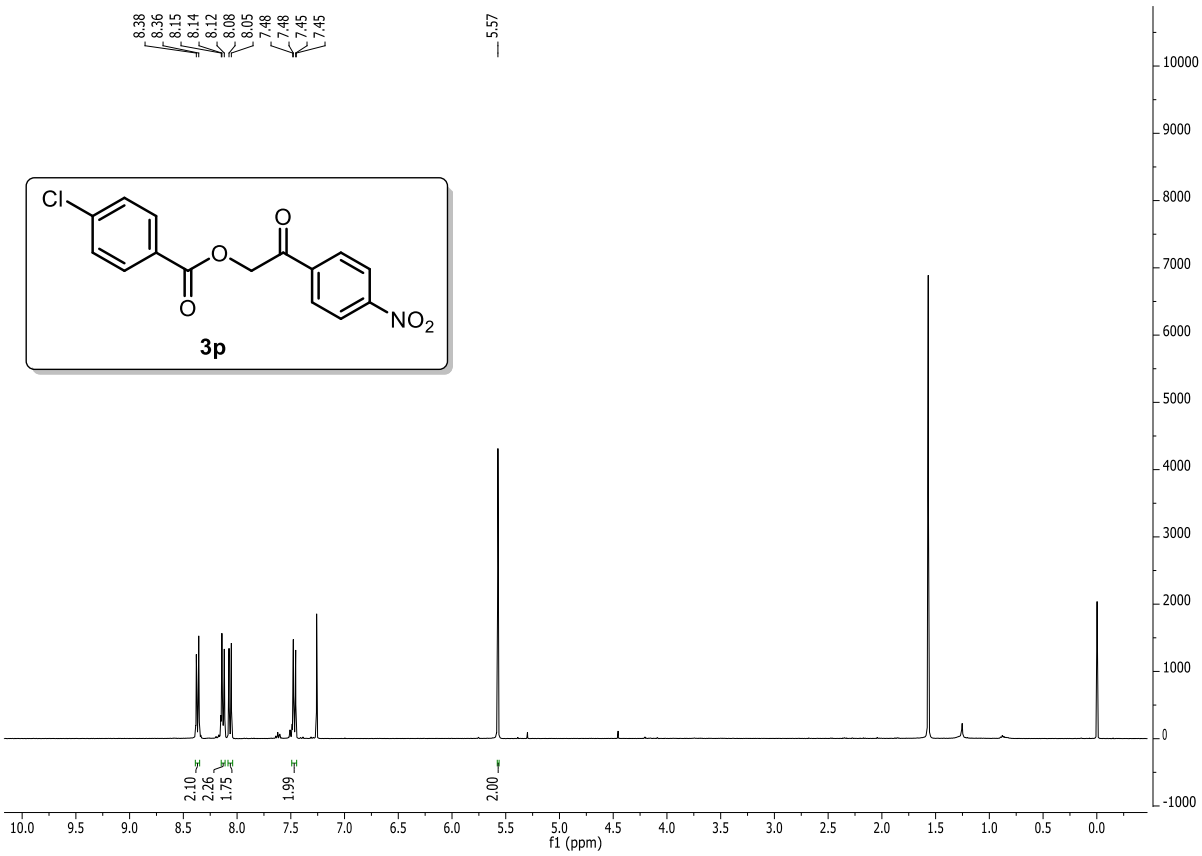

190.14
165.21
140.22
138.85
133.93
133.77
131.49
131.24
130.11
129.99
129.04
128.65
127.67
126.92
66.45
Cl
Cl
Cl
O
O
O
3n
f1 (ppm)

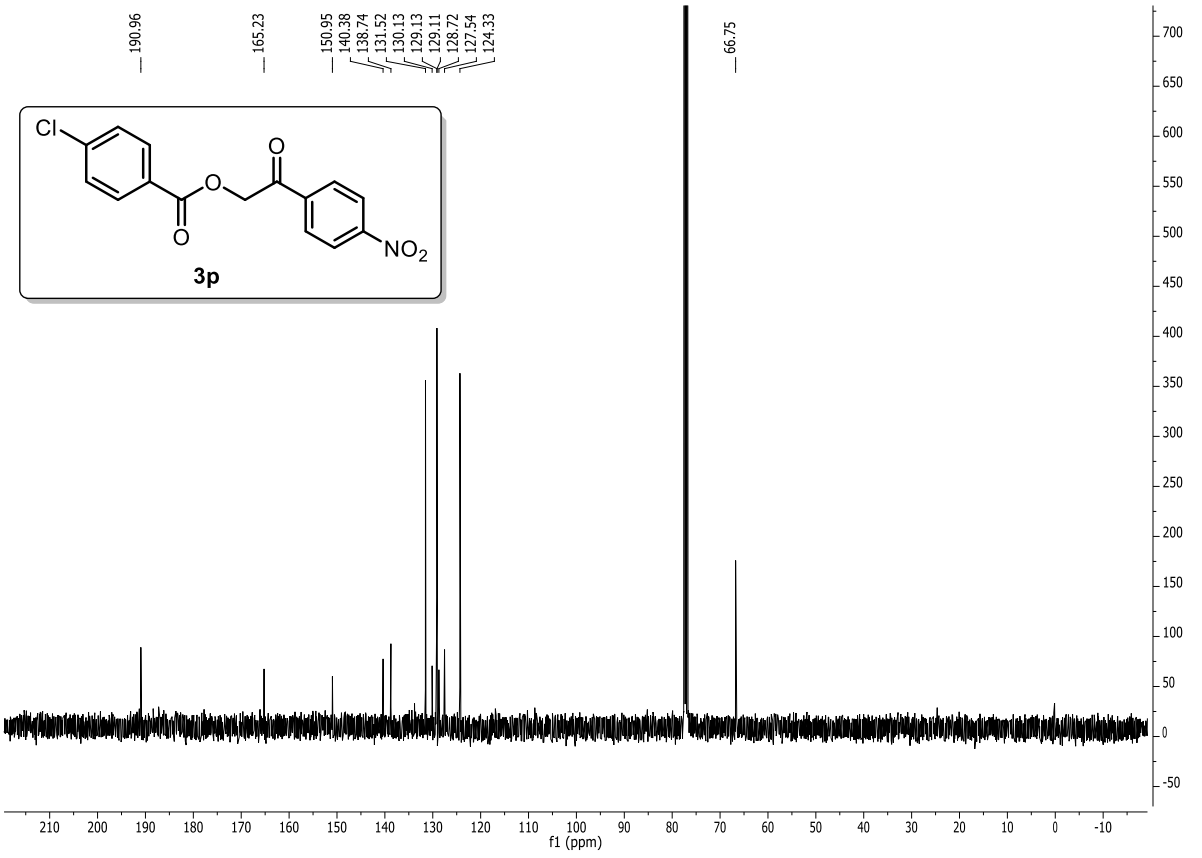

8.08
8.06
8.01
8.00
7.99
7.98
7.46
7.44
7.20
7.18
7.16
5.53
F
O
O
O
Cl
3o
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.00
2.16
2.05
2.24
2.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


190.49
167.59
165.30
165.04
140.08
131.48
130.77
130.72
130.62
130.09
128.98
128.60
127.88
116.43
116.21
66.49
F
O
O
O
Cl
3o
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

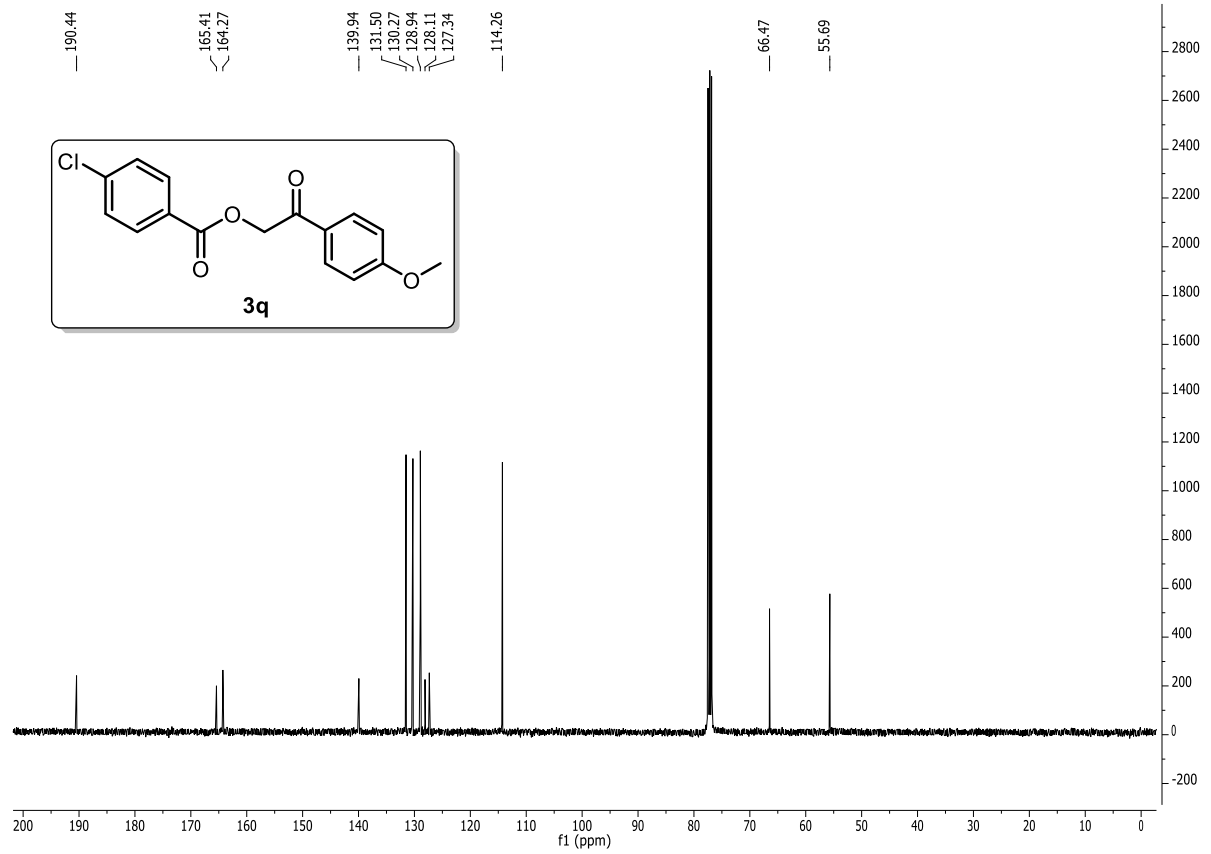


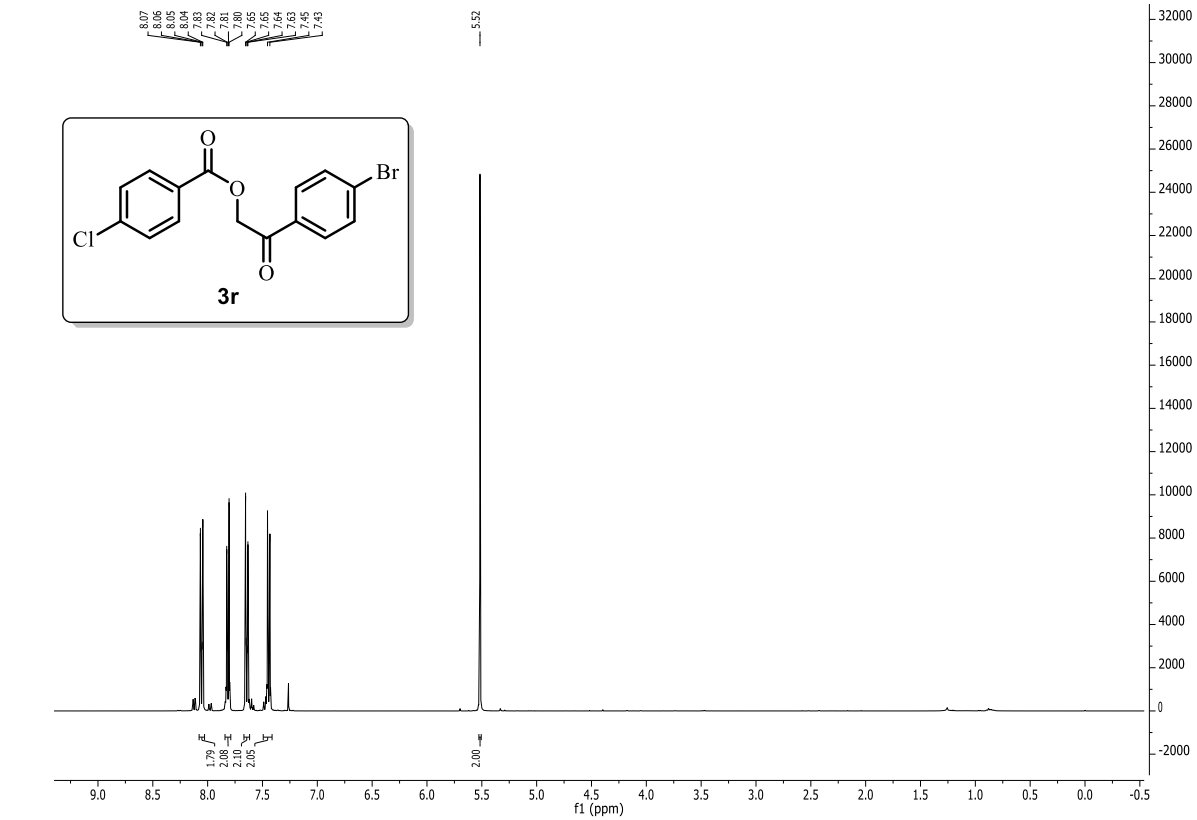
^{19}F NMR spectrum

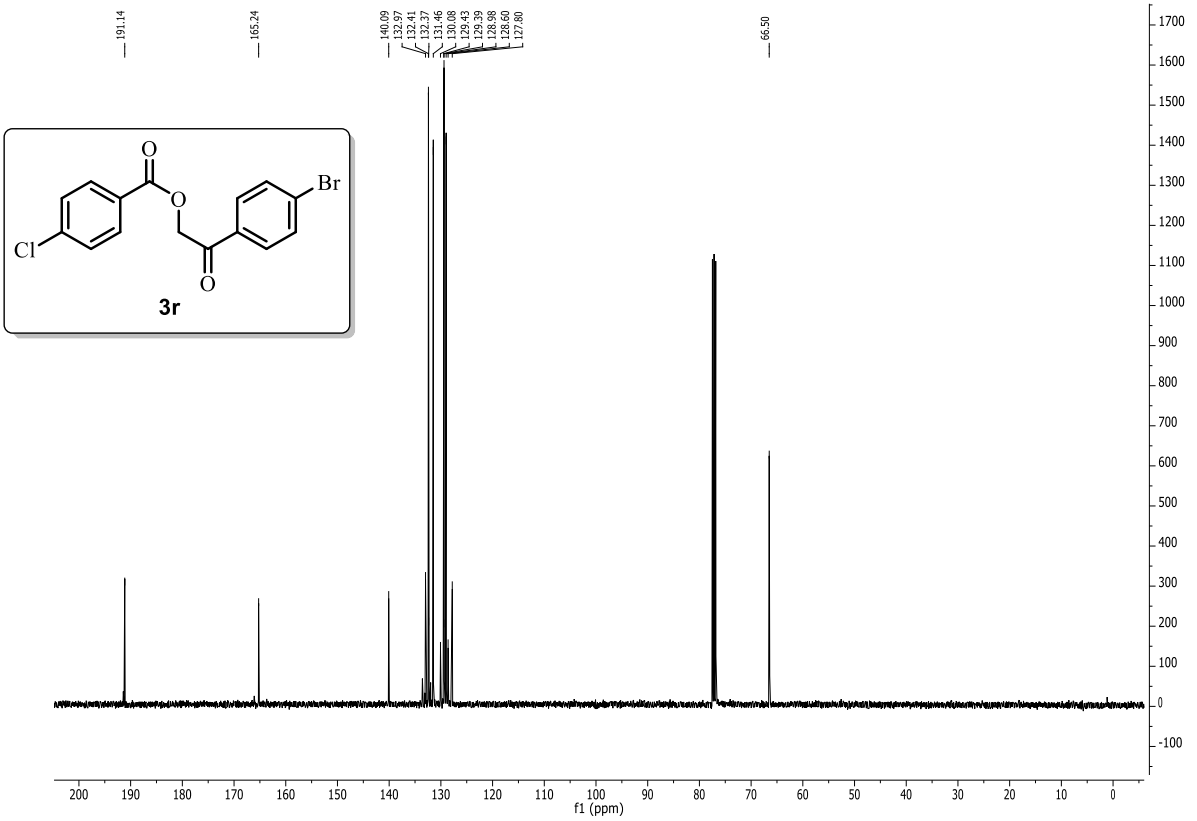

8.38
8.36
8.15
8.14
8.12
8.08
8.05
7.48
7.45
7.45
5.57
Cl
O
O
O
O
NO2
3p
2.10
2.26
1.75
1.99
2.00
f1 (ppm)


190.96
165.23
150.95
140.38
138.74
131.52
130.13
129.13
129.11
128.72
127.54
124.33
66.75
Cl
O
O
O
O
NO2
3p
f1 (ppm)

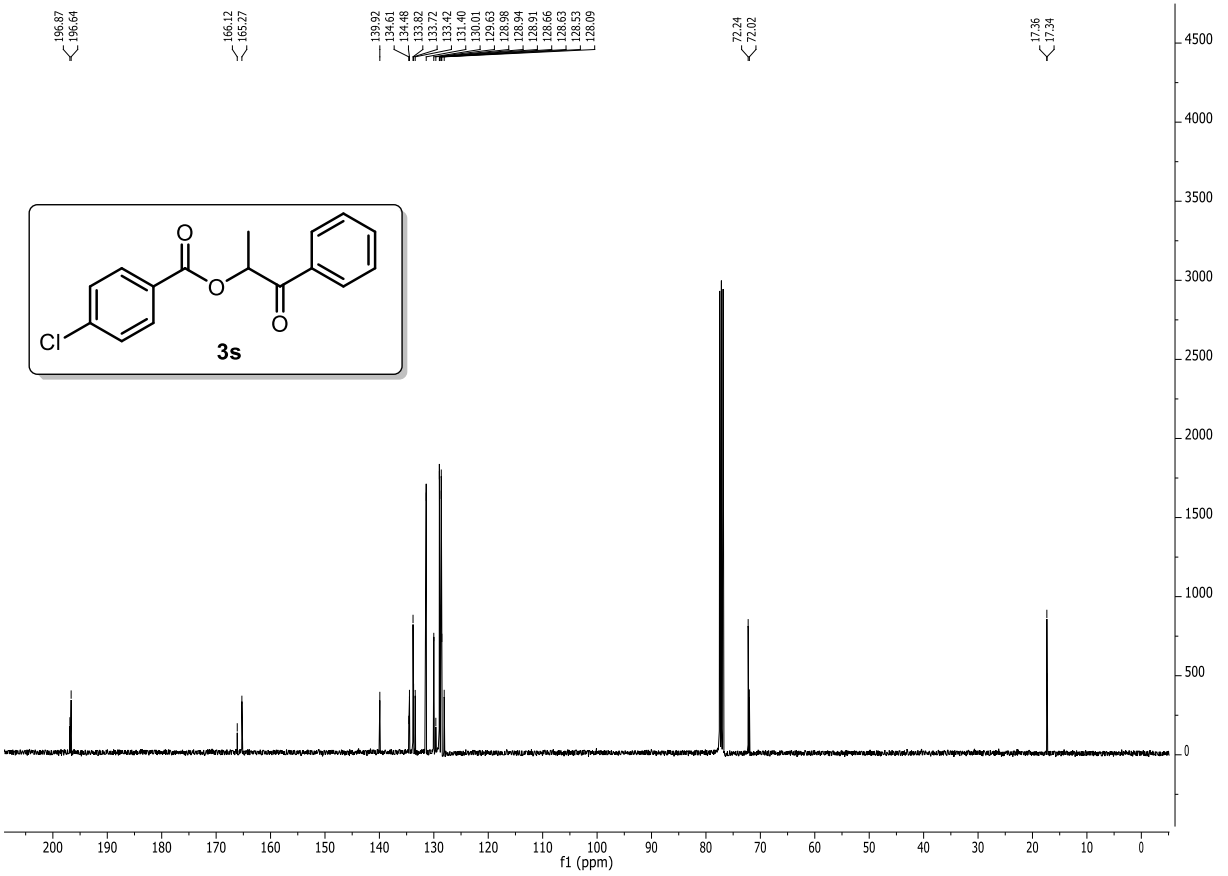

8.09
8.08
8.07
8.06
7.95
7.95
7.94
7.93
7.45
7.45
7.44
7.43
6.99
6.98
6.96
5.53
3.89
Cl
O
O
O
O
3q
1.97
2.01
1.98
2.01
2.00
3.02
f1 (ppm)

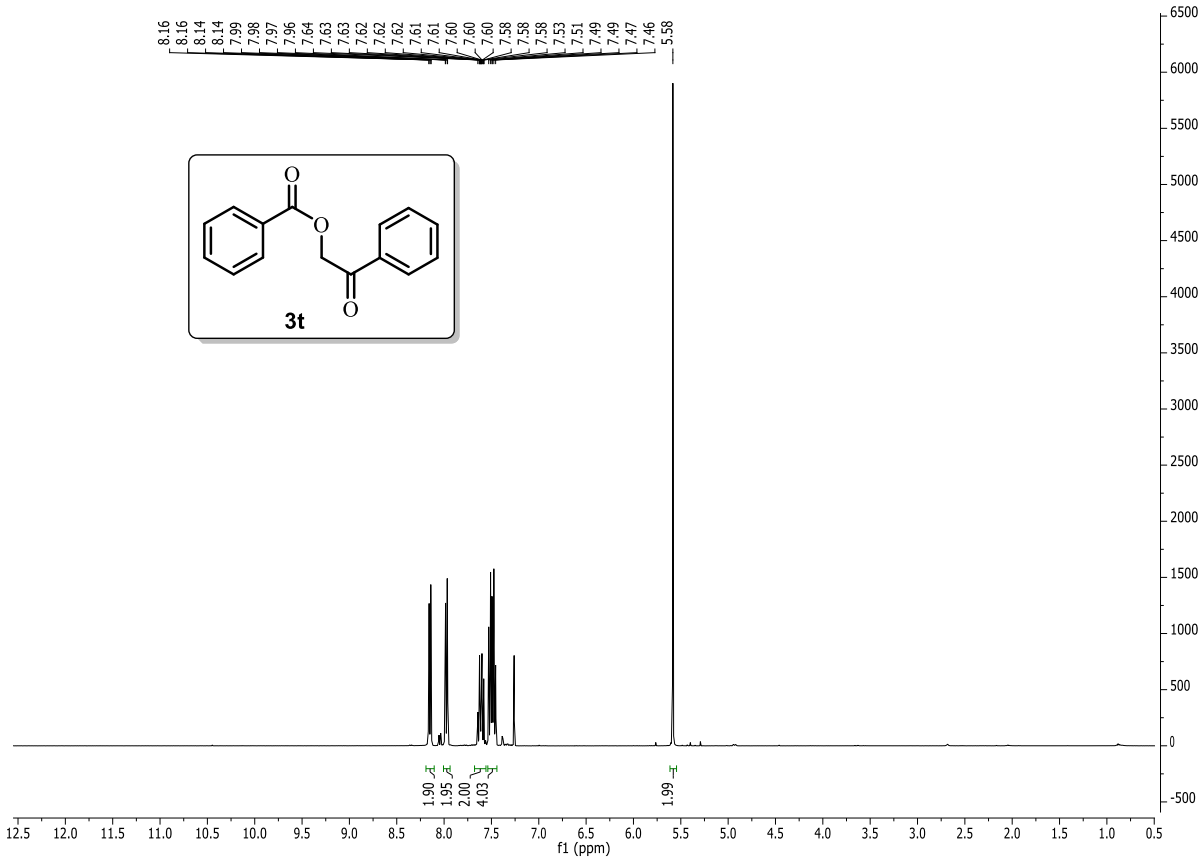

190.44
165.41
164.27
139.94
131.50
130.27
128.94
128.11
127.34
114.26
66.47
55.69
Cl
O
O
O
O
3q
f1 (ppm)

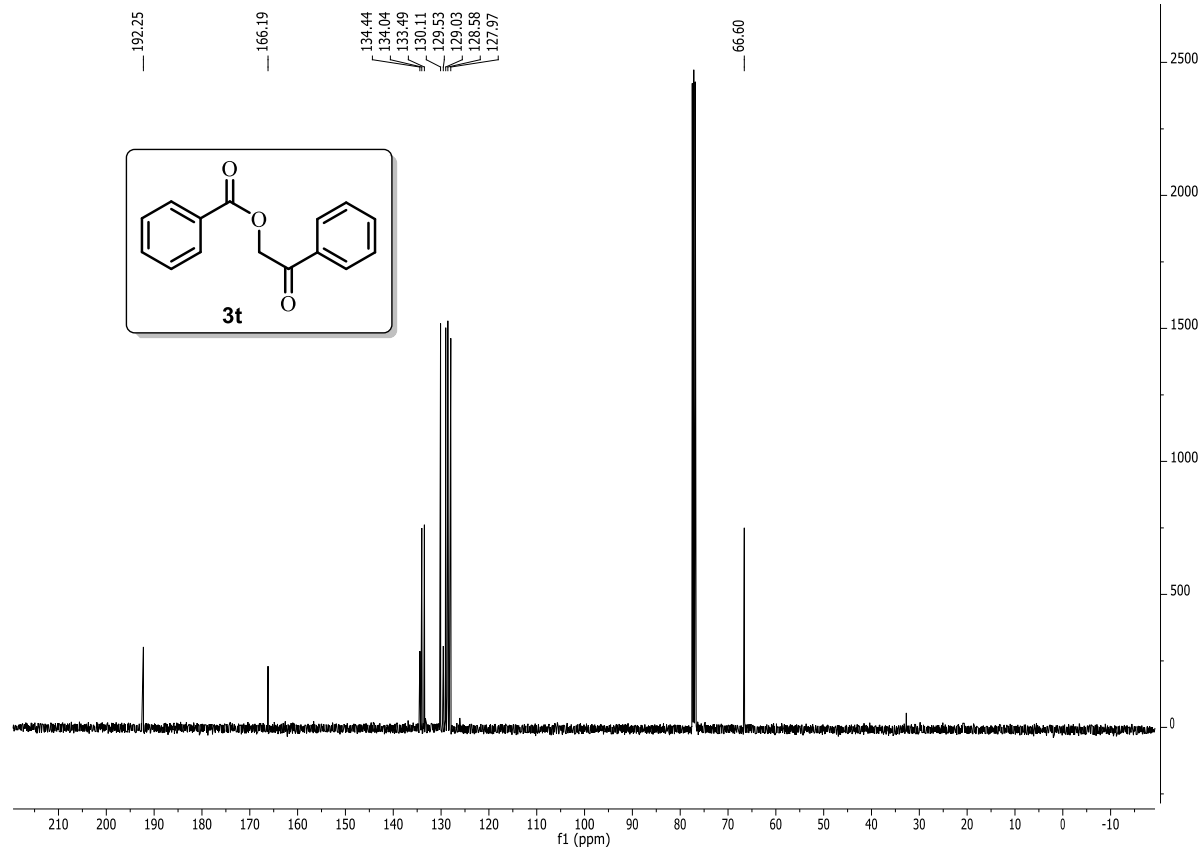

8.07
8.06
8.05
8.04
7.83
7.82
7.81
7.80
7.65
7.65
7.64
7.63
7.45
7.43
5.52
Br
Cl
O
O
O
3r
1.79
2.08
2.10
2.05
2.00
f1 (ppm)

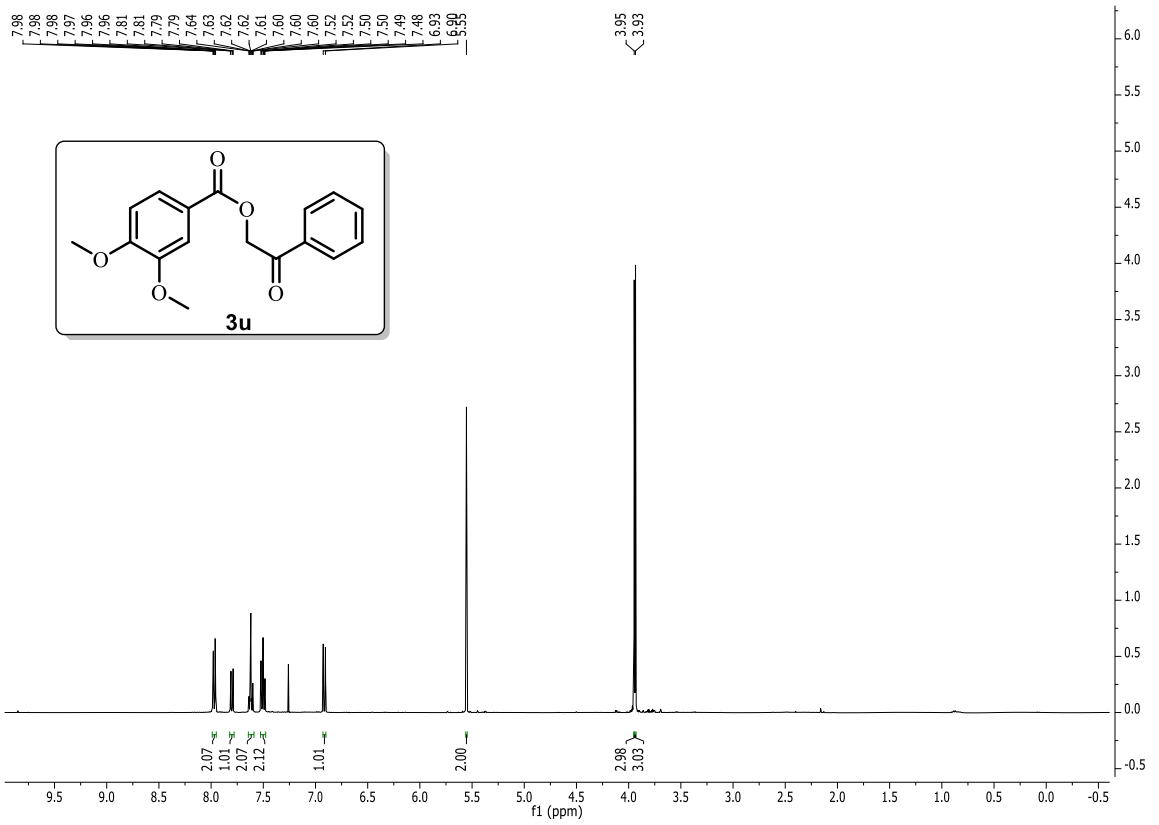

191.14
165.24
140.09
132.97
132.41
132.37
131.46
130.08
129.43
129.39
129.08
128.66
127.80
66.50
Br
Cl
O
O
O
3r
f1 (ppm)

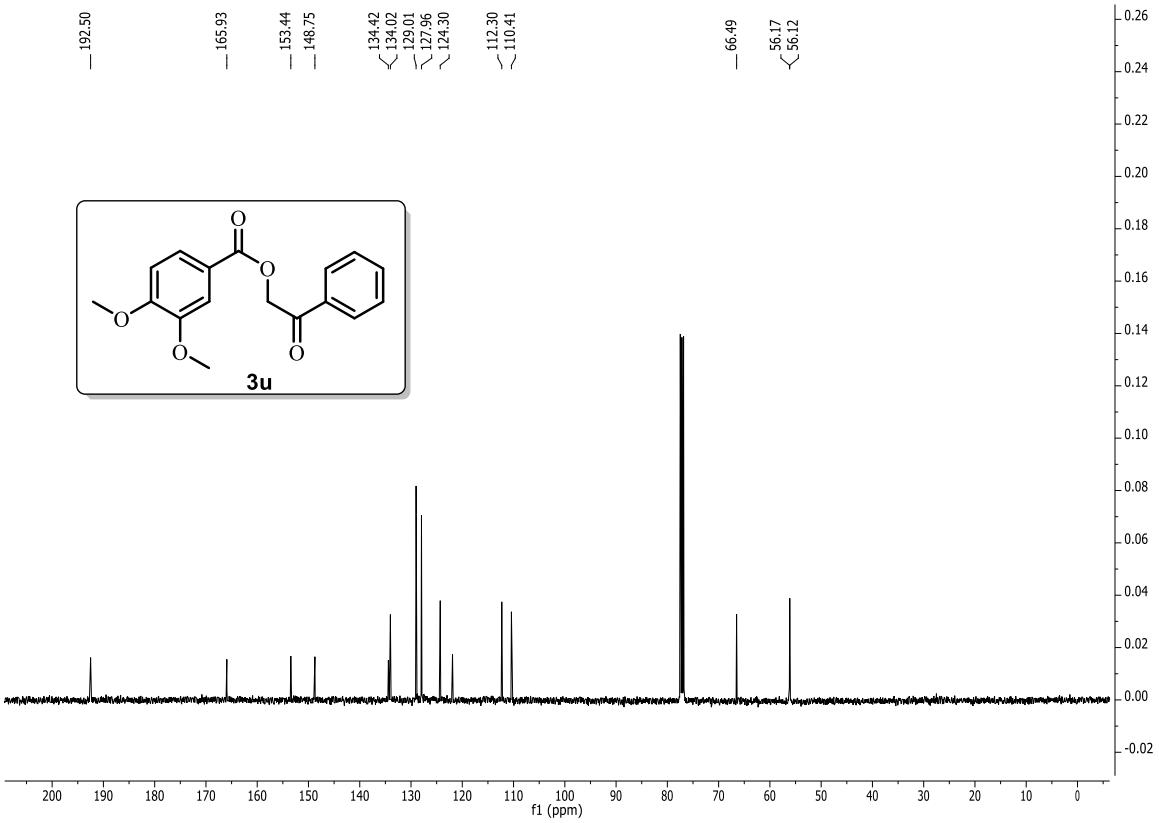

3s
4.00
1.32
4.06
1.01
3.05
f1 (ppm)

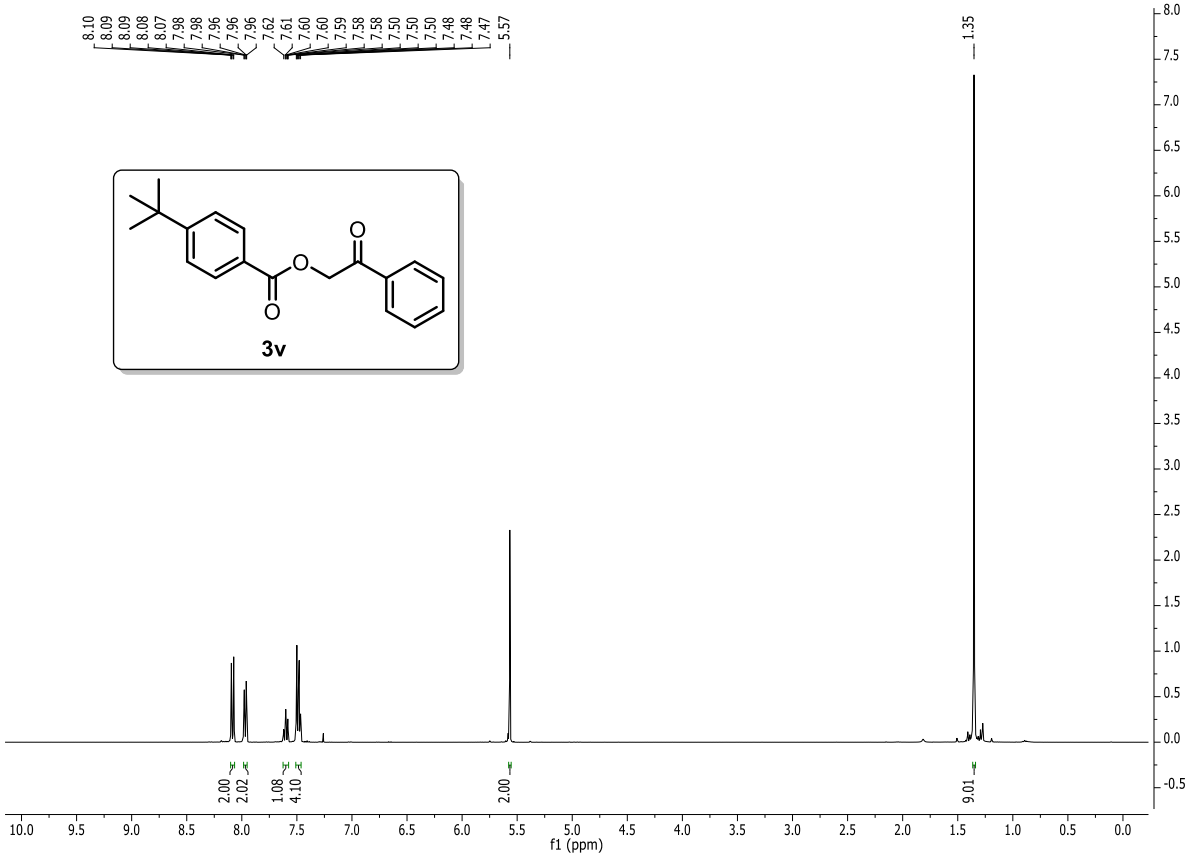

3s
f1 (ppm)

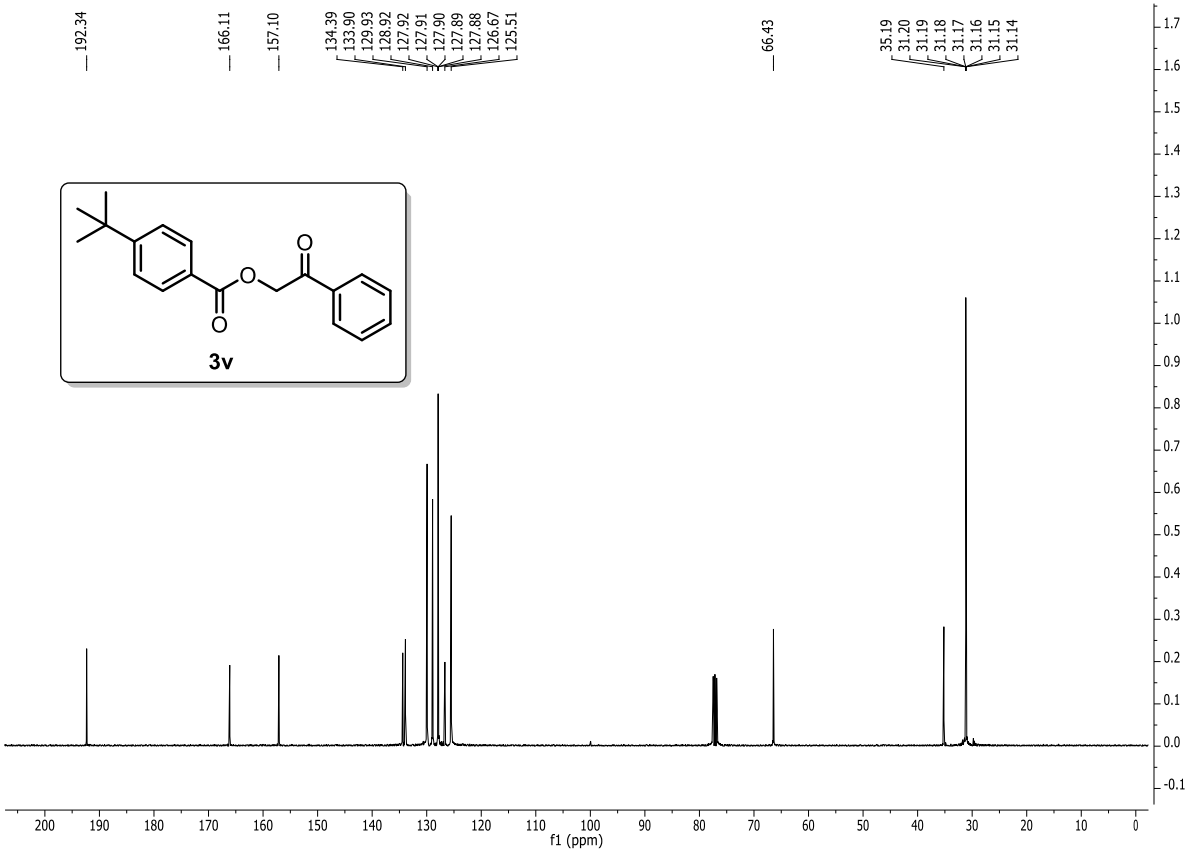

8.16
8.16
8.14
8.14
7.99
7.98
7.97
7.96
7.64
7.63
7.63
7.62
7.62
7.62
7.61
7.61
7.60
7.60
7.60
7.58
7.58
7.58
7.53
7.51
7.49
7.49
7.47
7.46
5.58
3t
1.90
1.95
2.00
4.03
1.99
f1 (ppm)

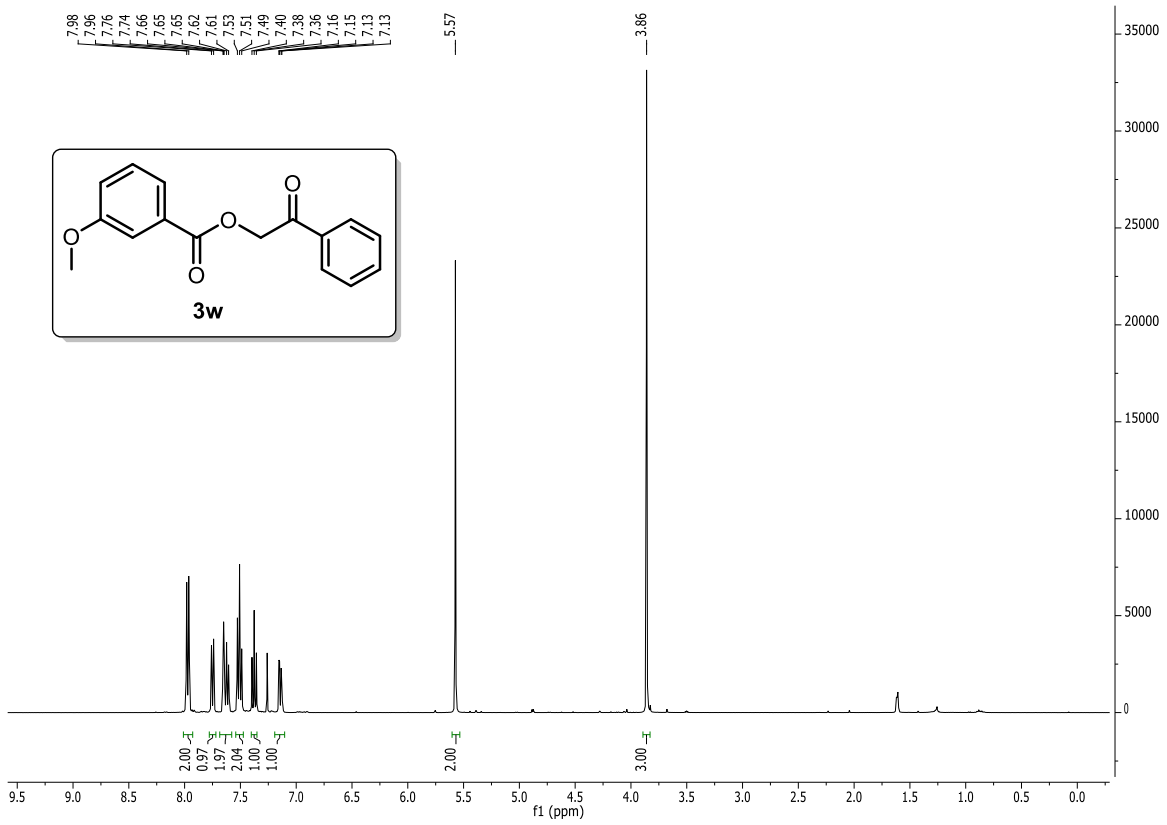

192.25
166.19
134.44
134.04
133.49
130.11
129.53
129.03
128.58
127.97
66.60
3t
f1 (ppm)

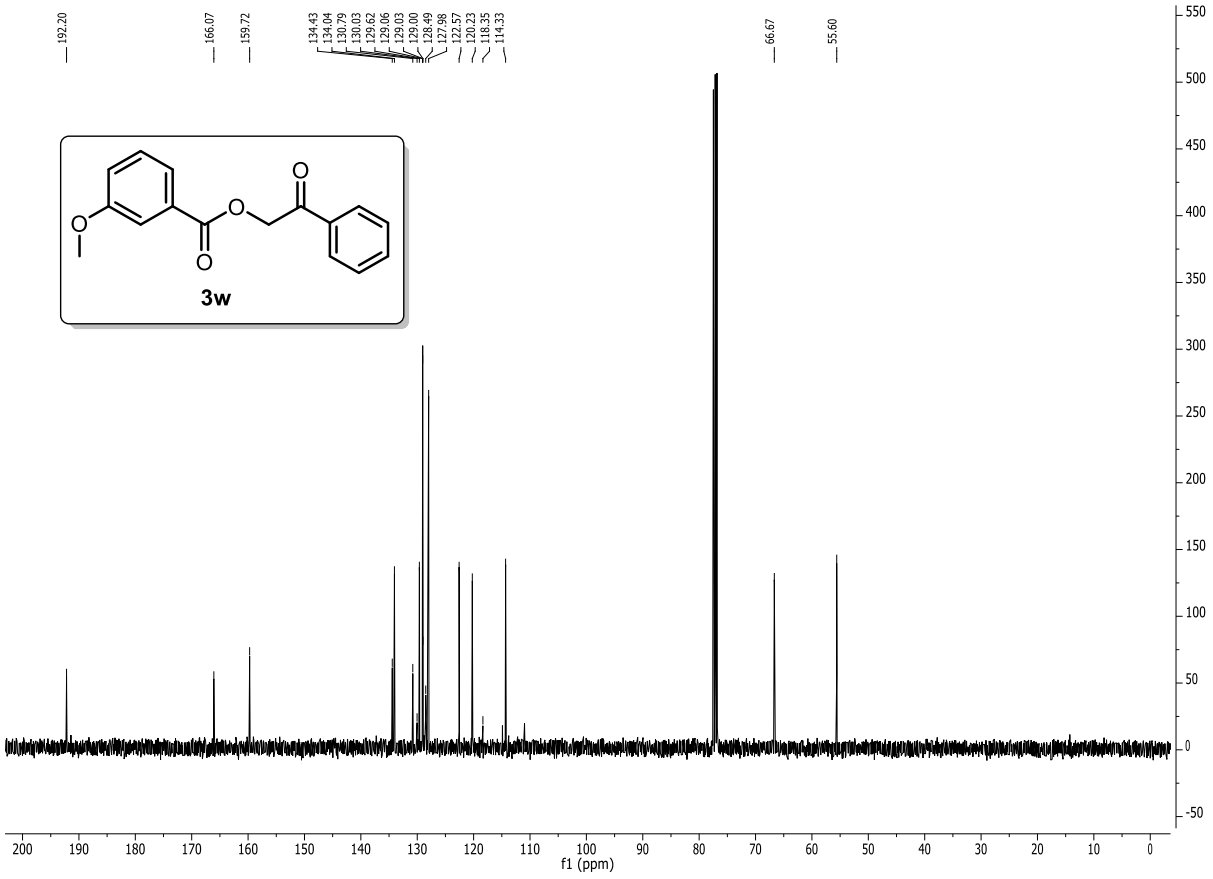

7.98
7.98
7.98
7.97
7.96
7.96
7.81
7.81
7.79
7.79
7.64
7.63
7.62
7.62
7.61
7.60
7.60
7.60
7.52
7.52
7.50
7.50
7.49
7.48
6.93
6.90
5.55
3.95
3.93
3u
2.07
1.01
2.07
2.12
1.01
2.00
2.98
3.03
f1 (ppm)

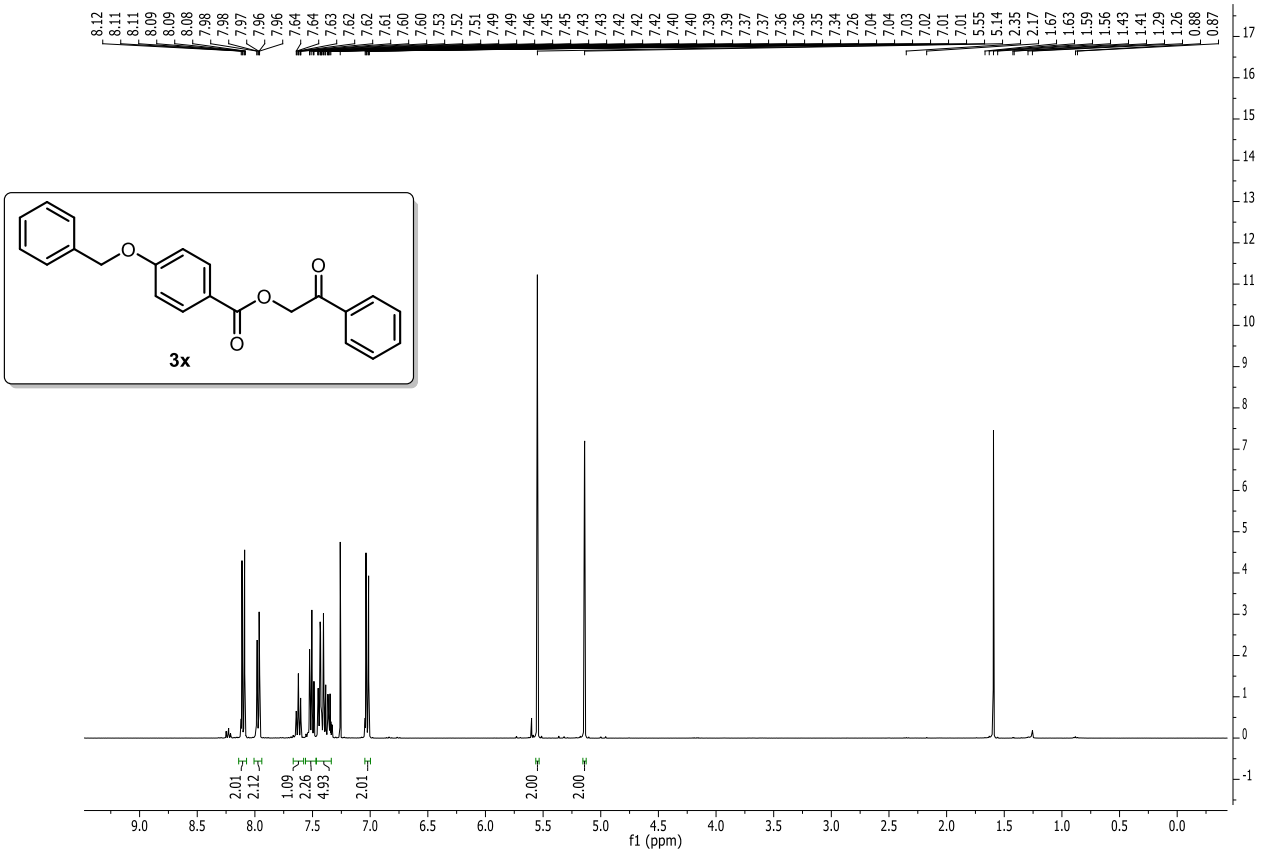

192.50
165.93
153.44
148.75
134.42
134.02
129.01
127.96
124.30
112.30
110.41
66.49
56.17
56.12
3u
f1 (ppm)

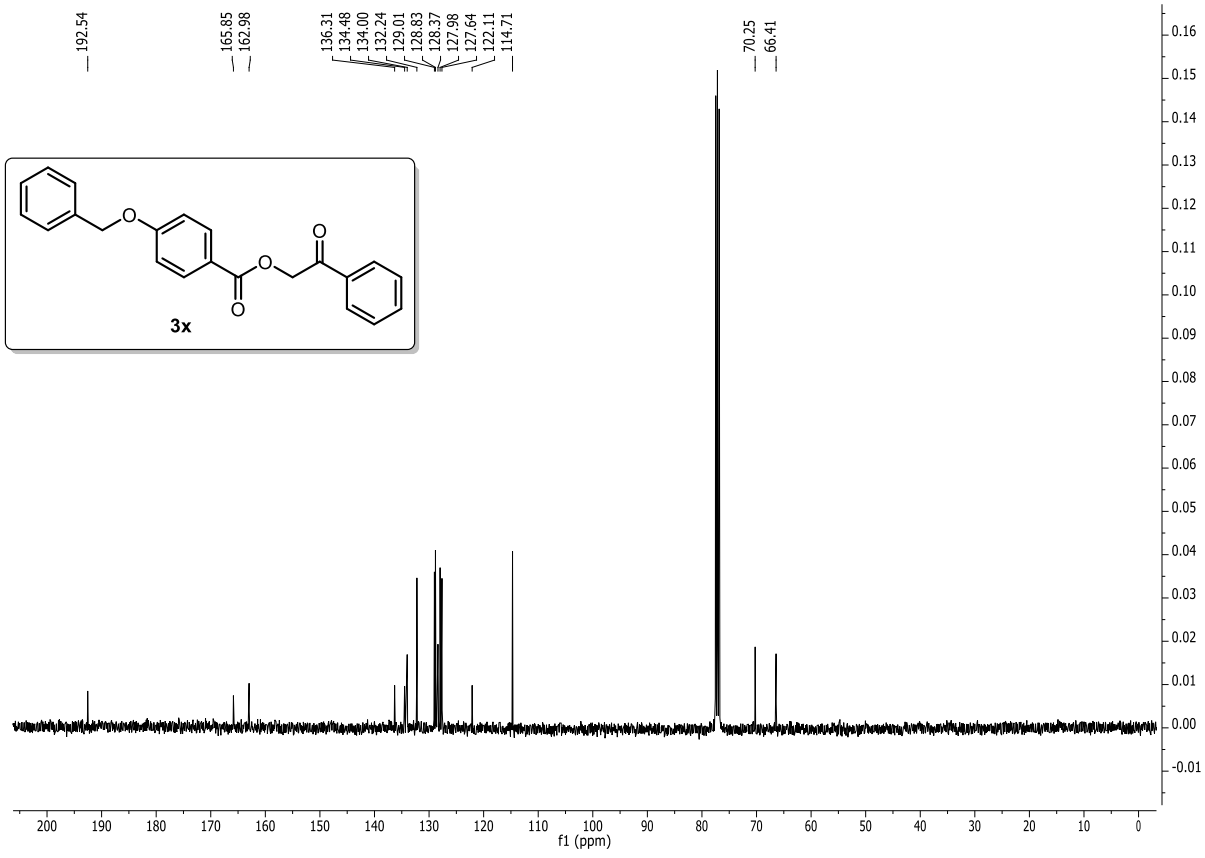

8.10
8.09
8.09
8.08
8.07
7.98
7.98
7.96
7.96
7.96
7.62
7.61
7.60
7.60
7.59
7.58
7.58
7.50
7.50
7.50
7.48
7.48
7.47
5.57
1.35
3v
2.00
2.02
1.08
4.10
2.00
9.01
f1 (ppm)

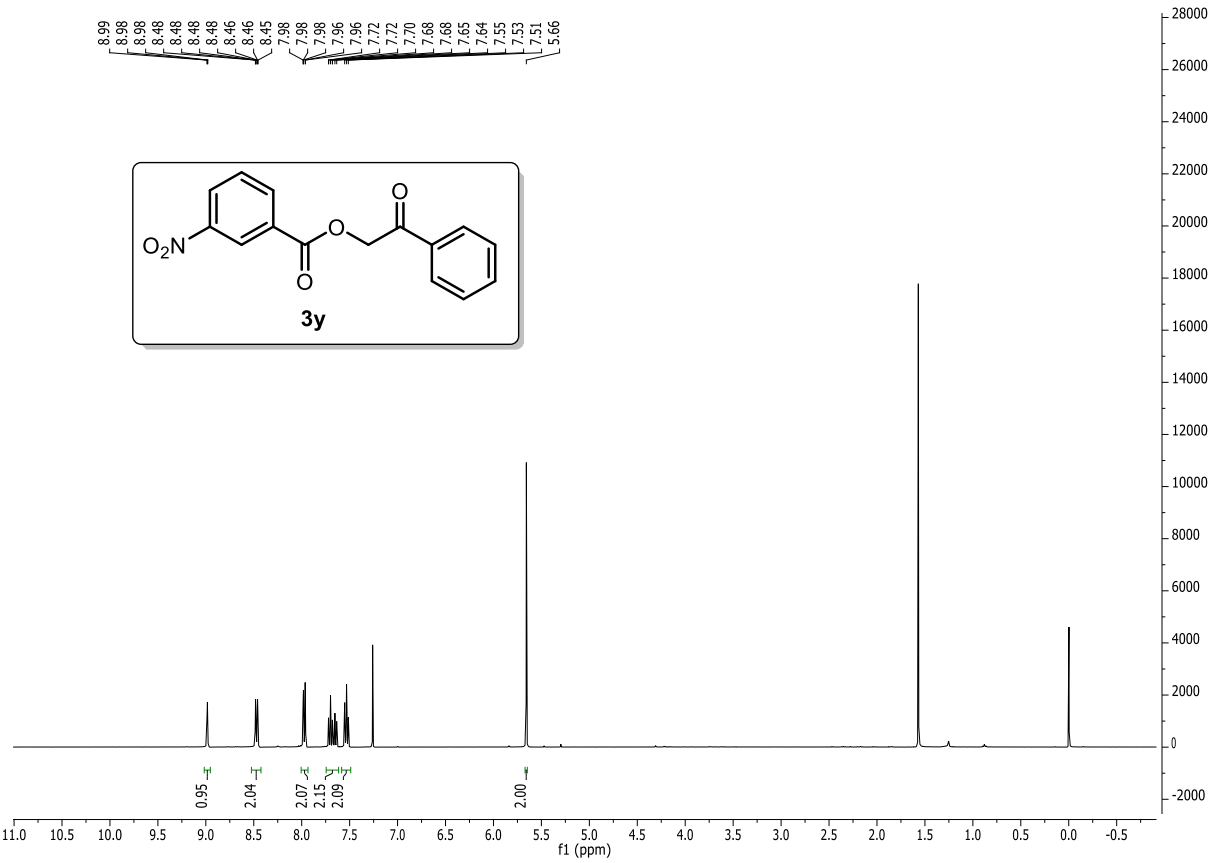

192.34
166.11
157.10
134.39
133.90
129.93
128.92
127.92
127.91
127.90
127.89
127.88
126.67
125.51
66.43
35.19
31.20
31.19
31.18
31.17
31.16
31.15
31.14
3v
f1 (ppm)

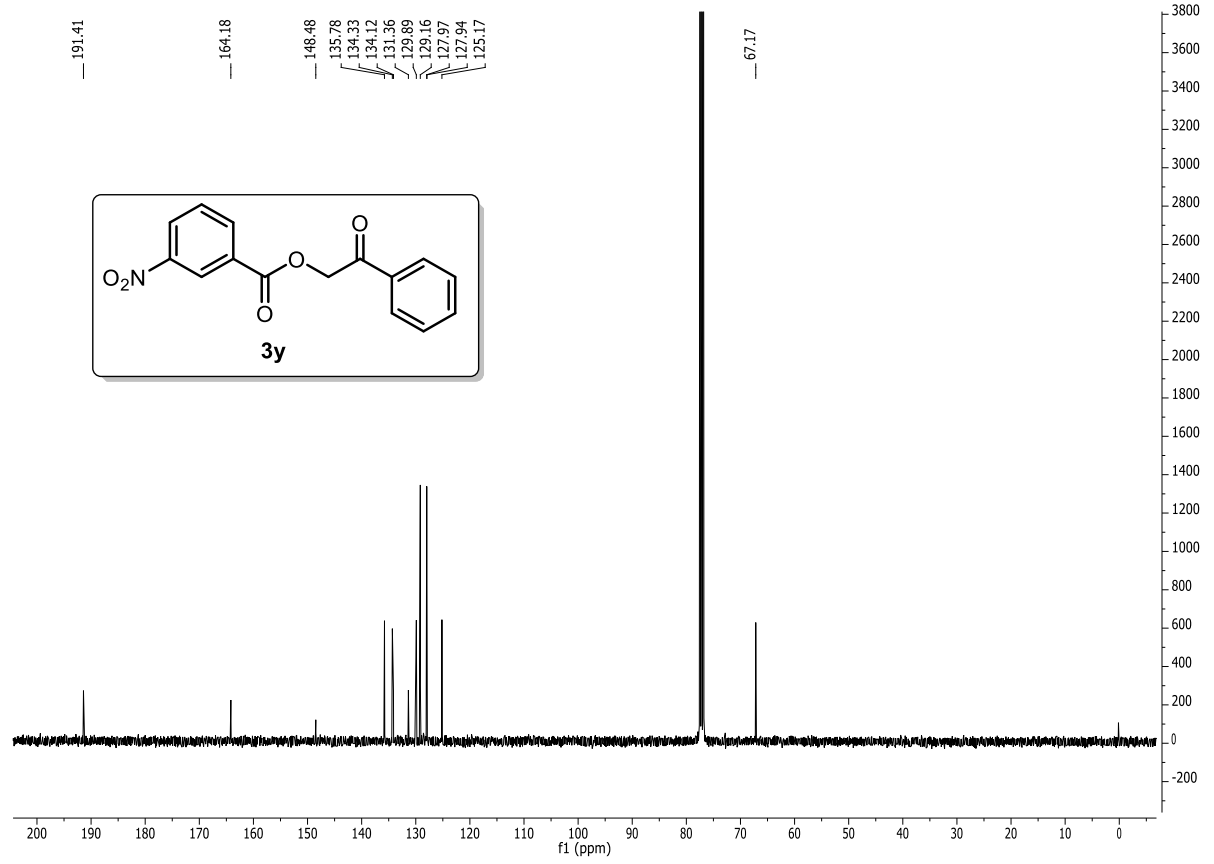

7.98
7.96
7.76
7.74
7.66
7.65
7.65
7.62
7.61
7.53
7.51
7.49
7.40
7.38
7.36
7.16
7.15
7.13
7.13
5.57
3.86
3w
2.00
0.97
1.97
2.04
1.00
1.00
2.00
3.00
f1 (ppm)

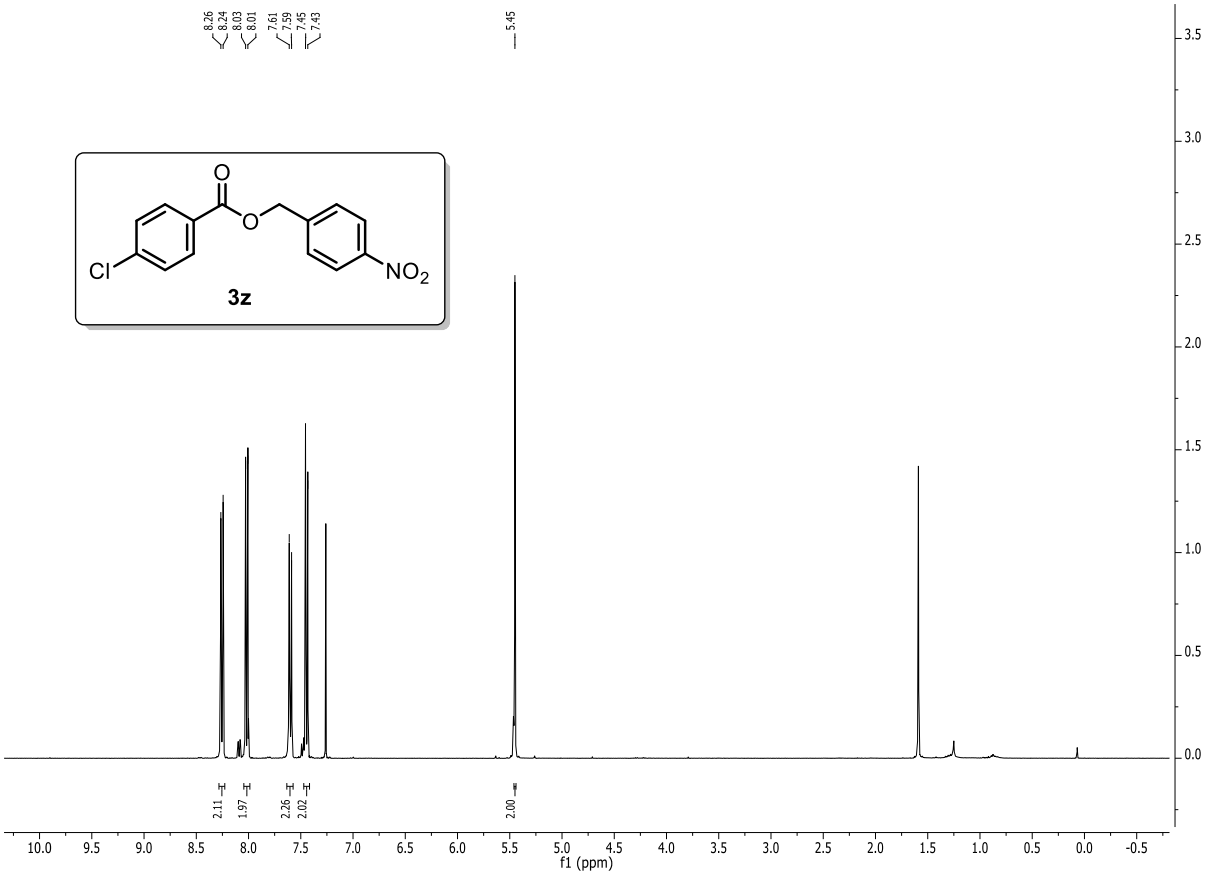

192.20
166.07
159.72
134.43
134.04
130.79
130.03
129.62
129.06
129.03
129.00
128.49
127.88
122.57
120.23
118.35
114.33
66.67
55.60
3w
f1 (ppm)

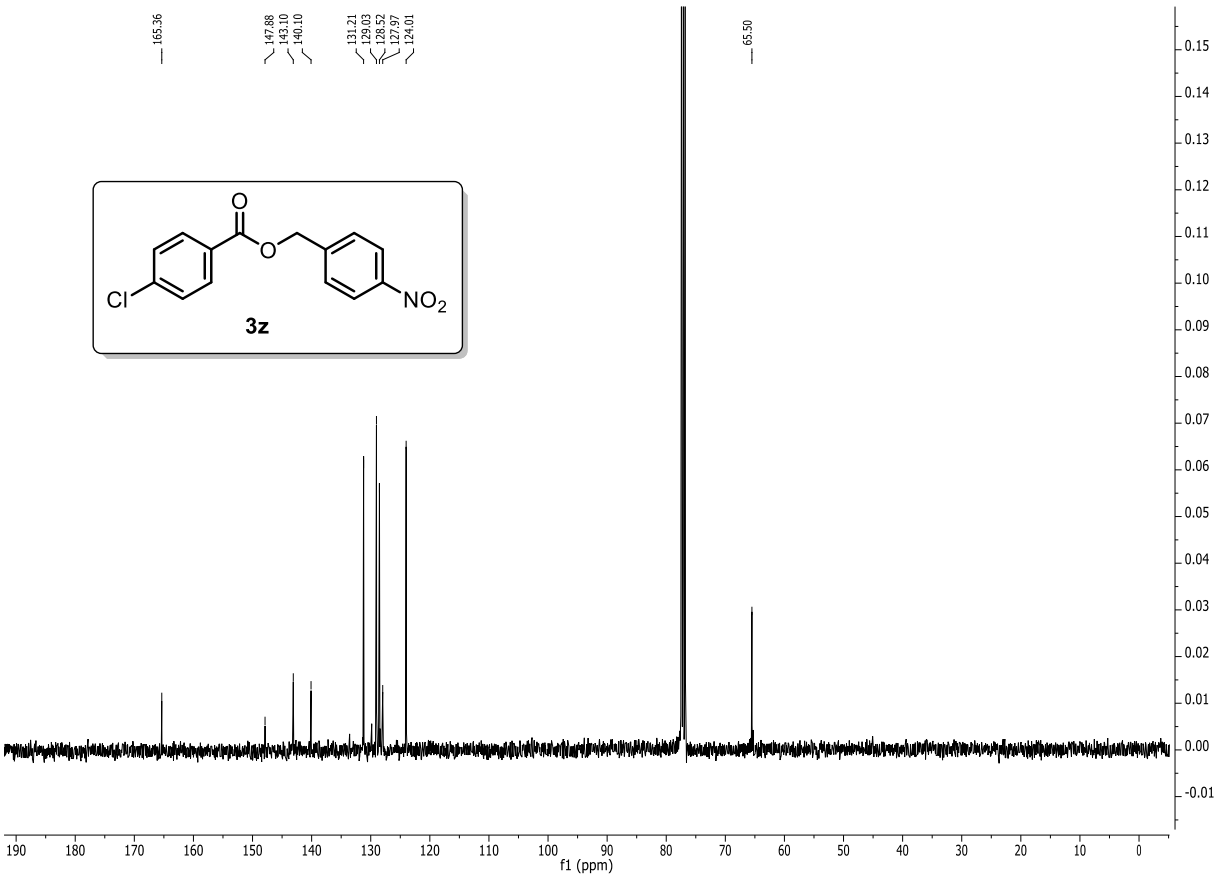

3x
f1 (ppm)

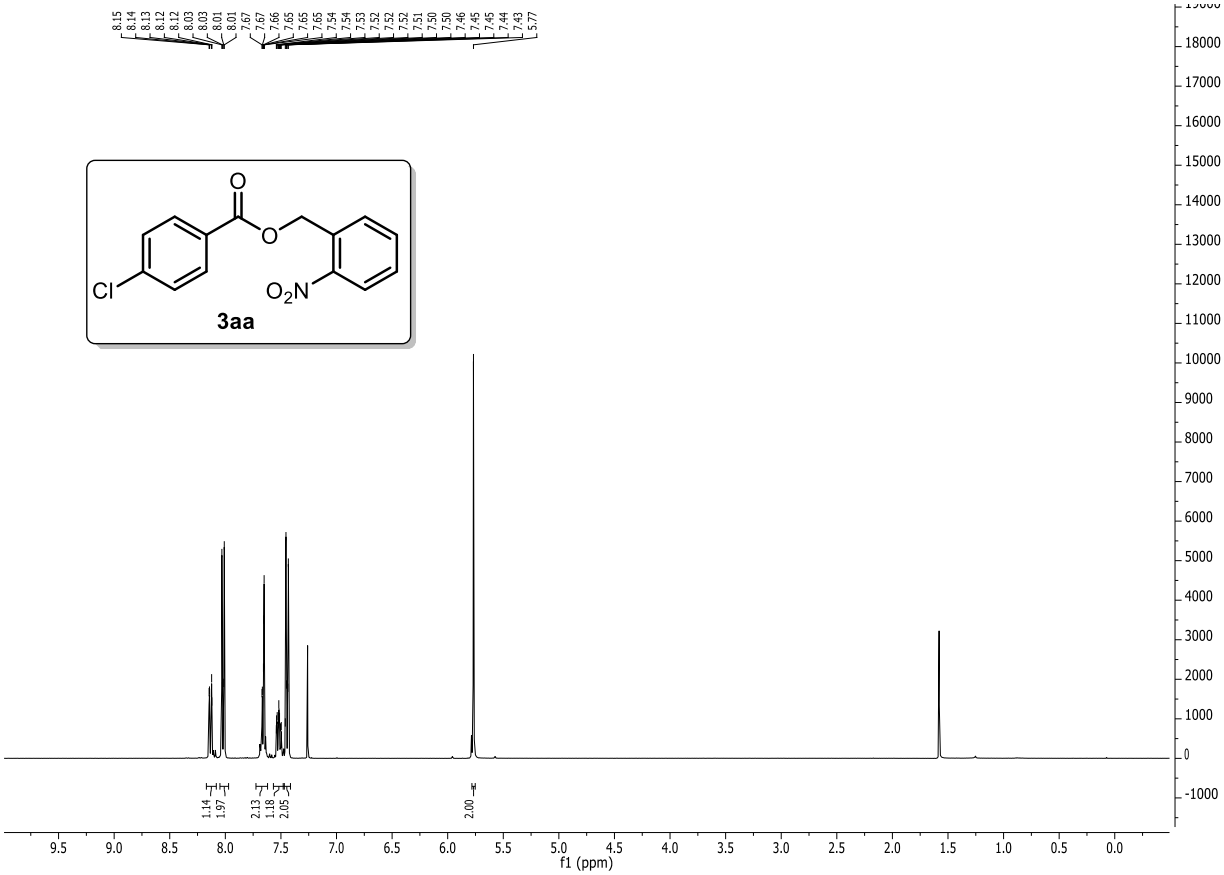

3x
f1 (ppm)

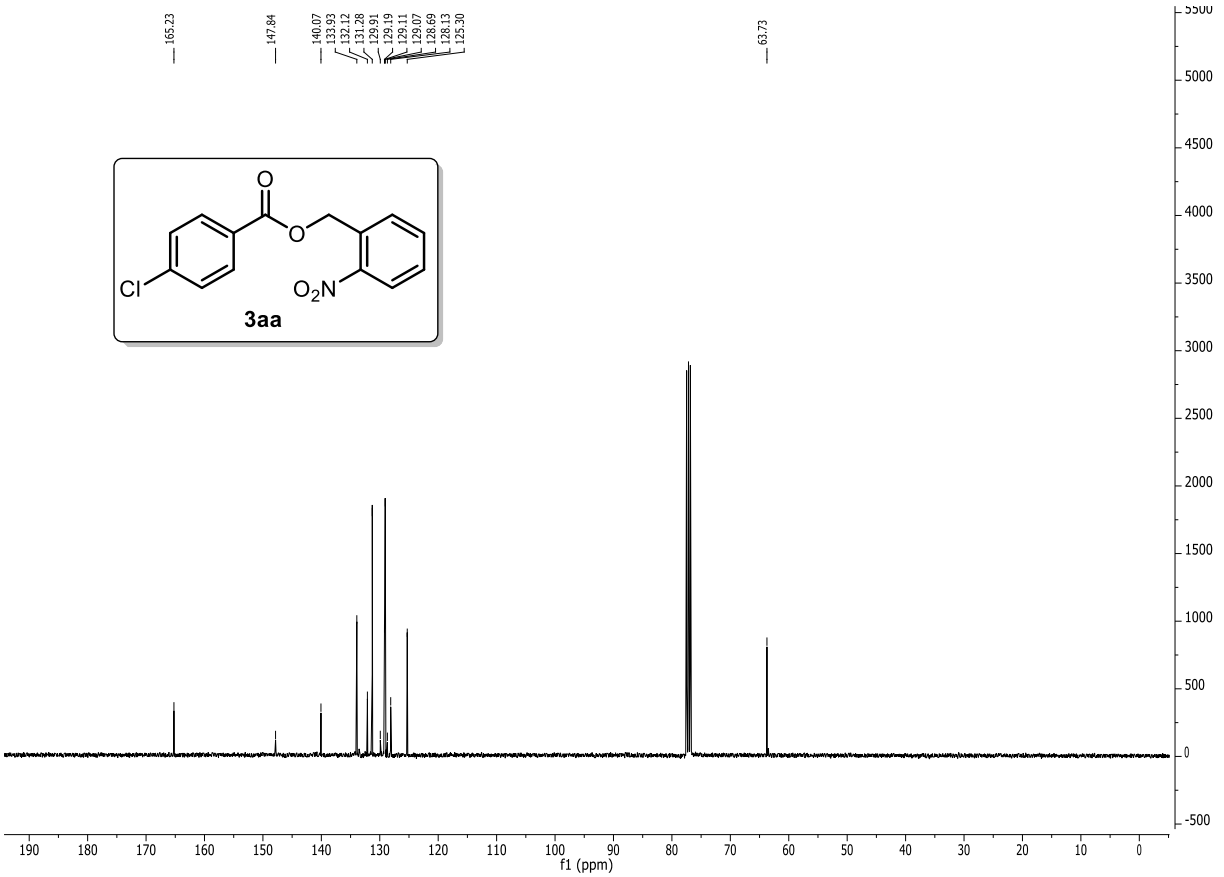

8.99
8.98
8.98
8.48
8.48
8.48
8.48
8.46
8.46
8.45
7.98
7.98
7.98
7.96
7.96
7.72
7.72
7.70
7.68
7.68
7.65
7.64
7.55
7.53
7.51
5.66
O2N
O
O
O
3y
0.95
2.04
2.07
2.15
2.09
2.00
f1 (ppm)

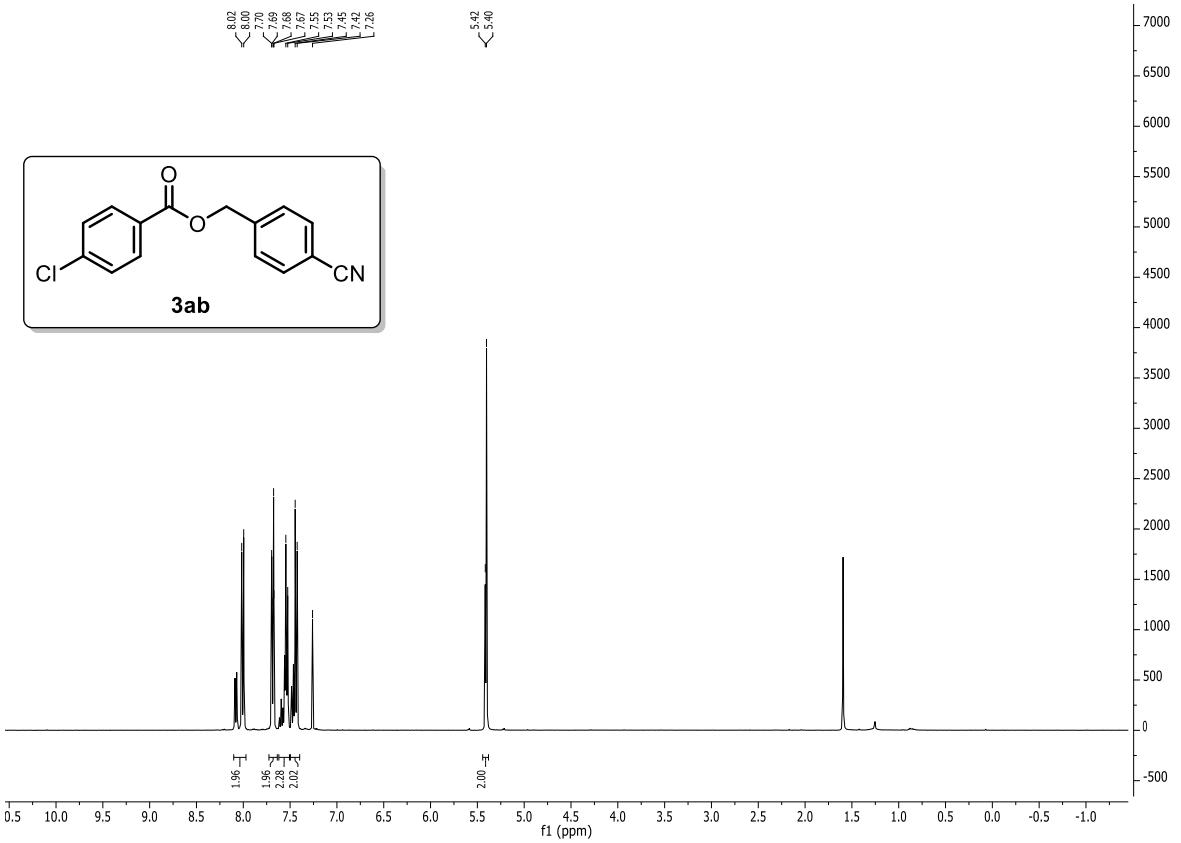

191.41
164.18
148.48
135.78
134.33
134.12
131.36
129.89
129.16
127.97
127.94
125.17
67.17
O2N
O
O
O
3y
f1 (ppm)

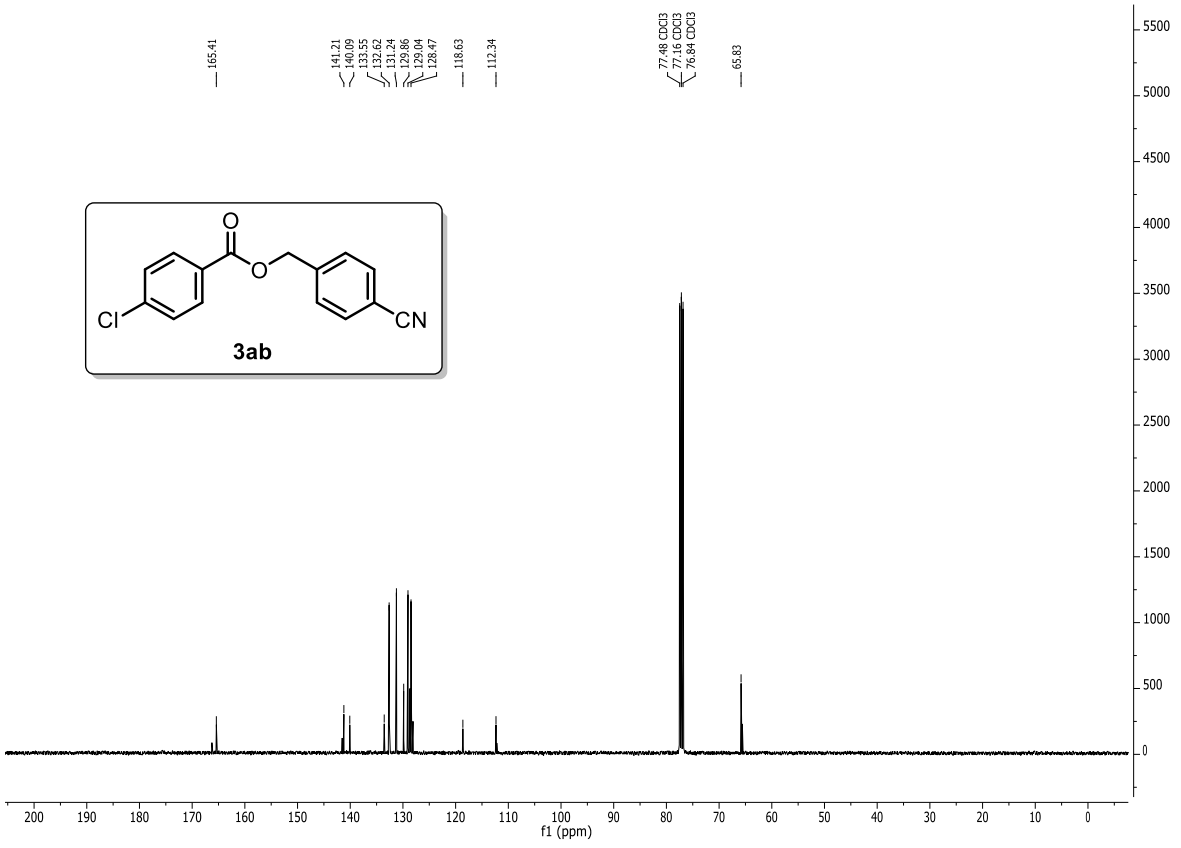

8.26
8.24
8.03
8.01
7.61
7.59
7.45
7.43
5.45
O
O
Cl
NO2
3z
2.11
1.97
2.26
2.02
2.00
f1 (ppm)

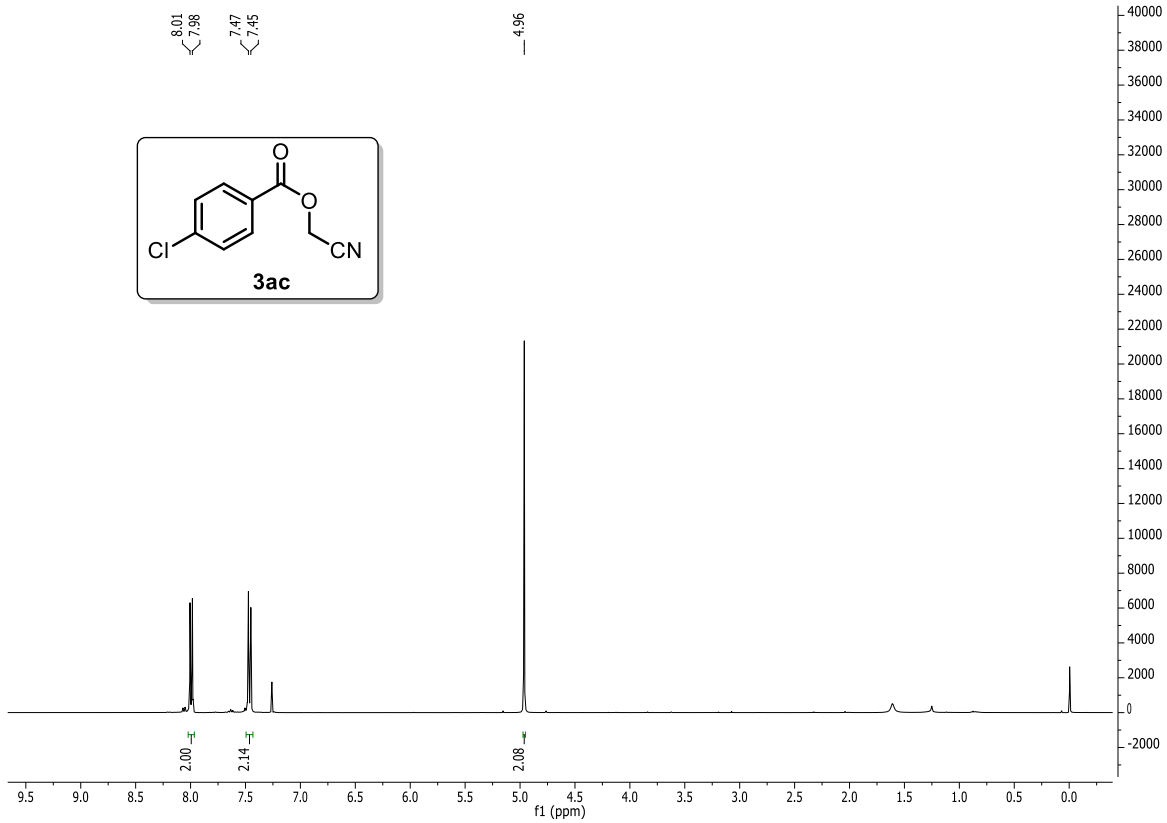

165.36
147.88
143.10
140.10
131.21
129.03
128.52
127.97
124.01
65.50
O
O
Cl
NO2
3z
f1 (ppm)

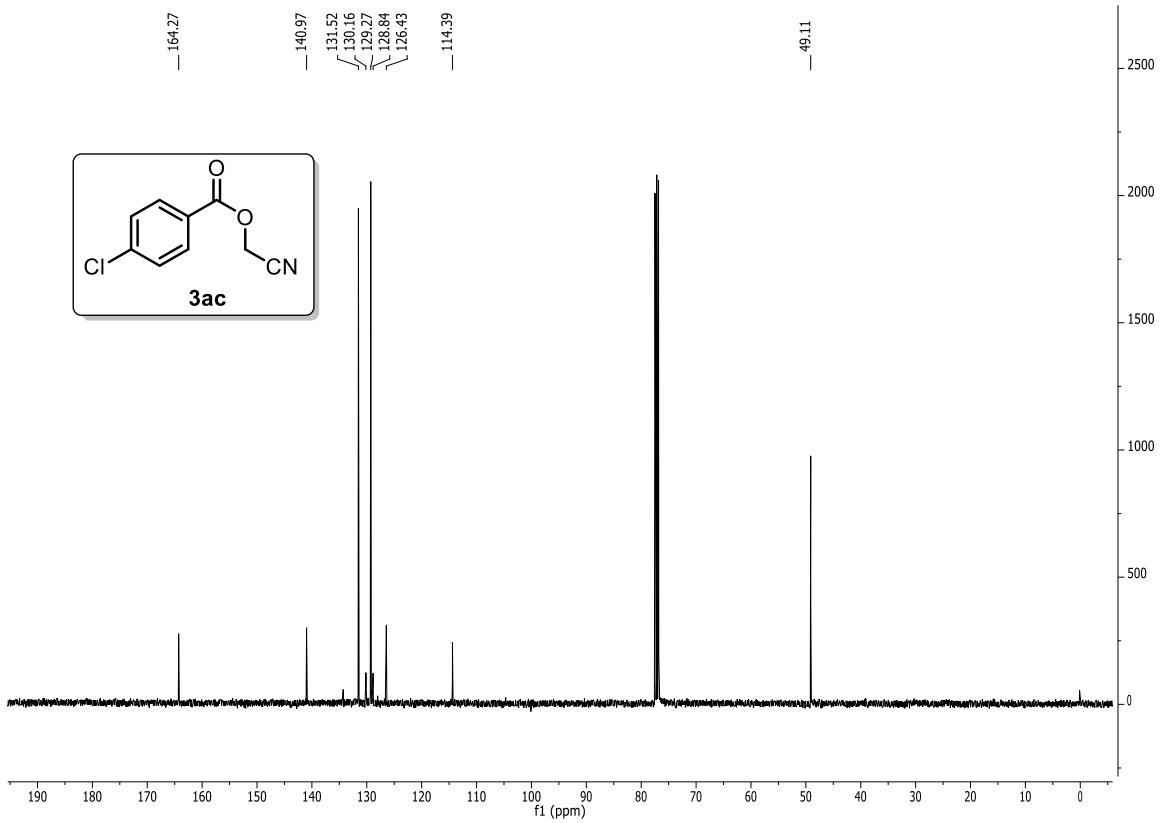

8.15
8.14
8.13
8.12
8.12
8.03
8.03
8.01
8.01
7.67
7.67
7.66
7.65
7.65
7.54
7.54
7.53
7.52
7.52
7.52
7.51
7.50
7.50
7.46
7.45
7.45
7.44
7.43
5.77
O
O
Cl
O2N
3aa
1.14
1.97
2.13
1.18
2.05
2.00
f1 (ppm)

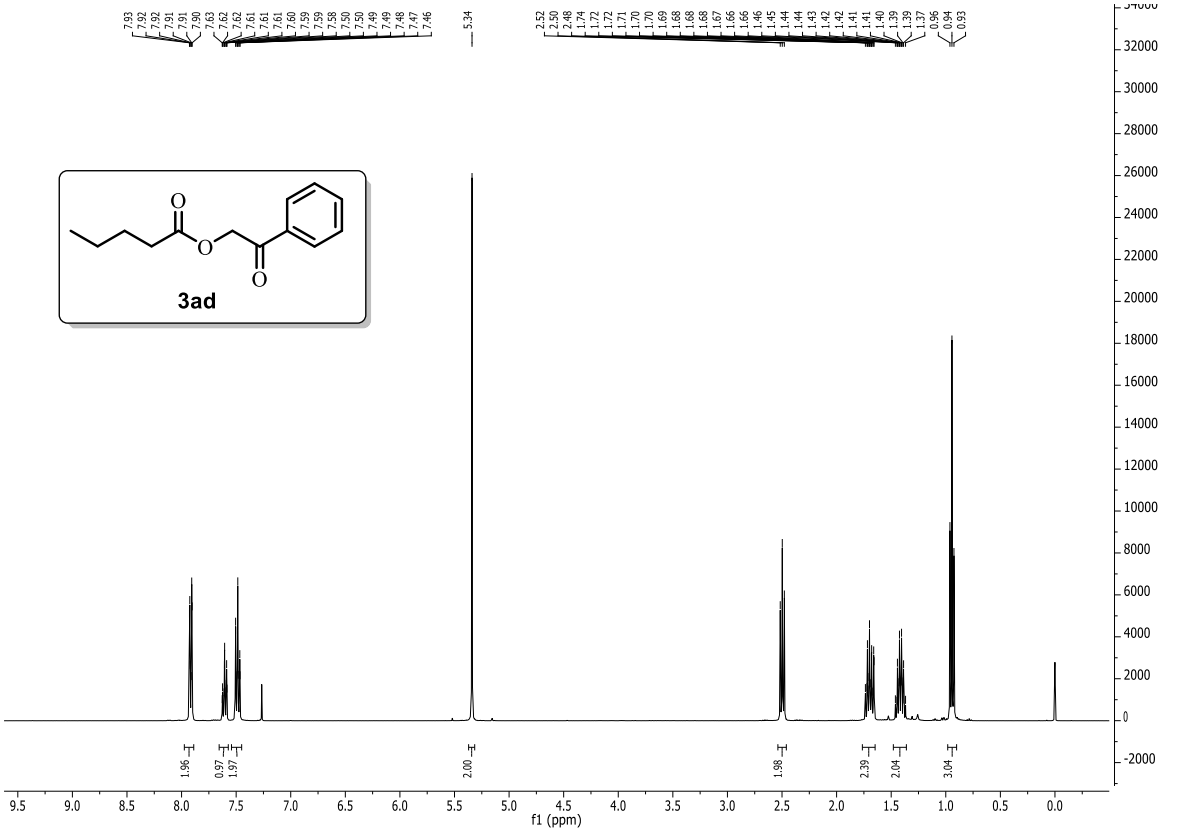

165.23
147.84
140.07
133.93
132.12
131.28
129.91
129.19
129.11
129.07
128.69
128.13
125.30
63.73
O
O
Cl
O2N
3aa
f1 (ppm)

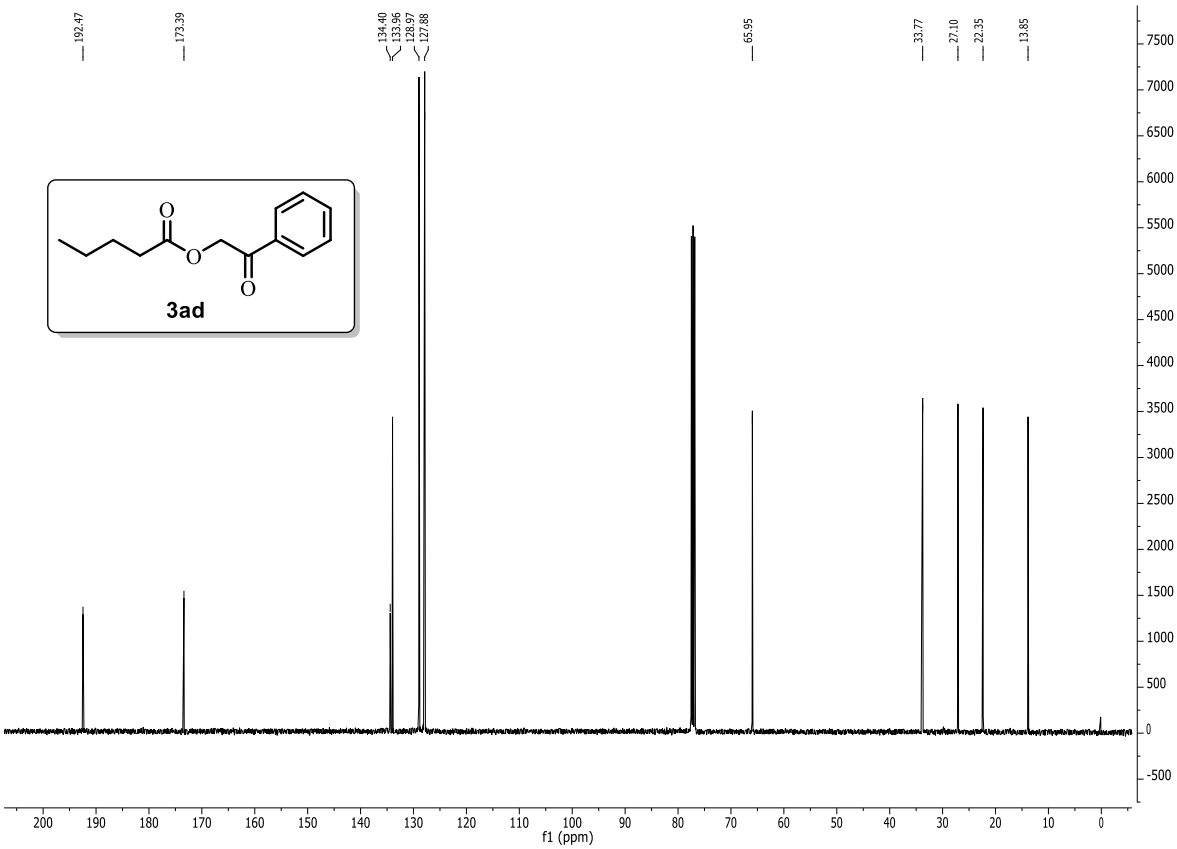

8.02
8.00
7.70
7.69
7.68
7.67
7.55
7.53
7.45
7.42
7.26
5.42
5.40
O
O
Cl
CN
3ab
1.96
1.96
2.28
2.02
2.00
f1 (ppm)

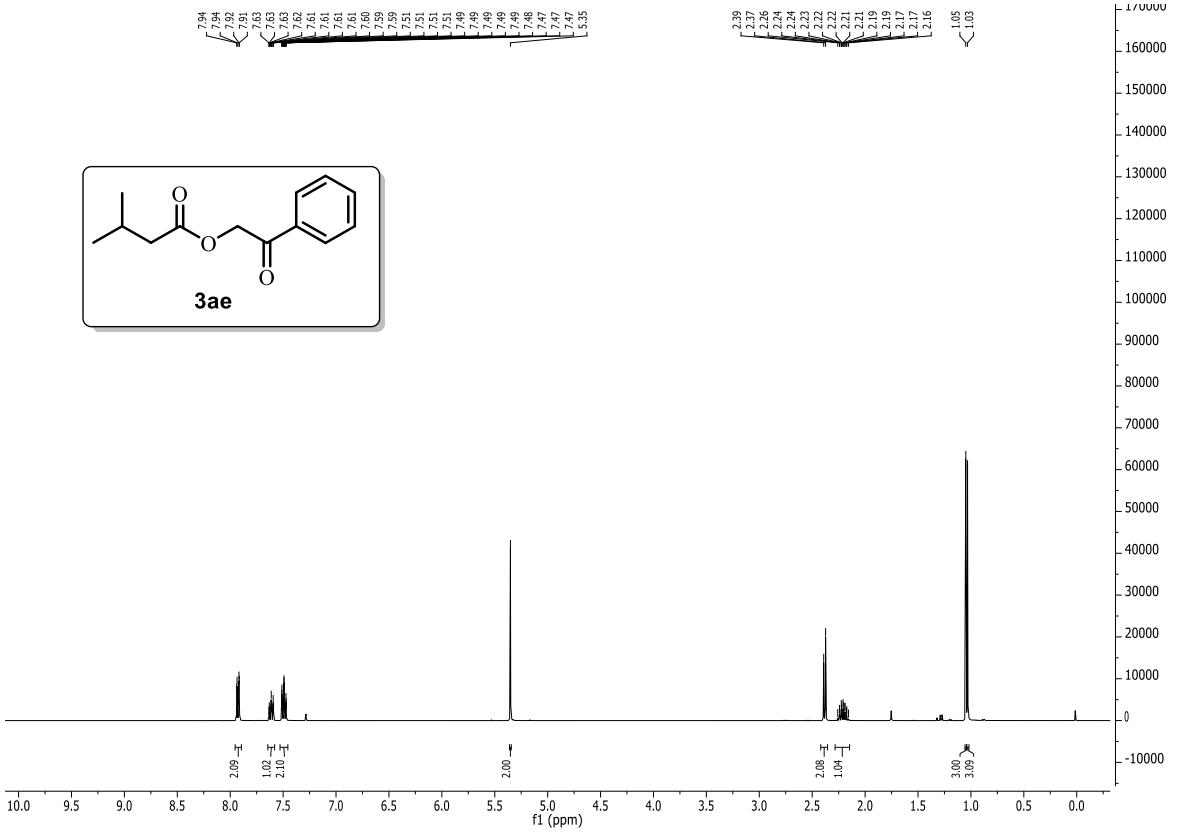

165.41
141.21
140.09
133.55
132.62
131.24
129.86
129.04
128.47
118.63
112.34
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.83
O
O
Cl
CN
3ab
f1 (ppm)

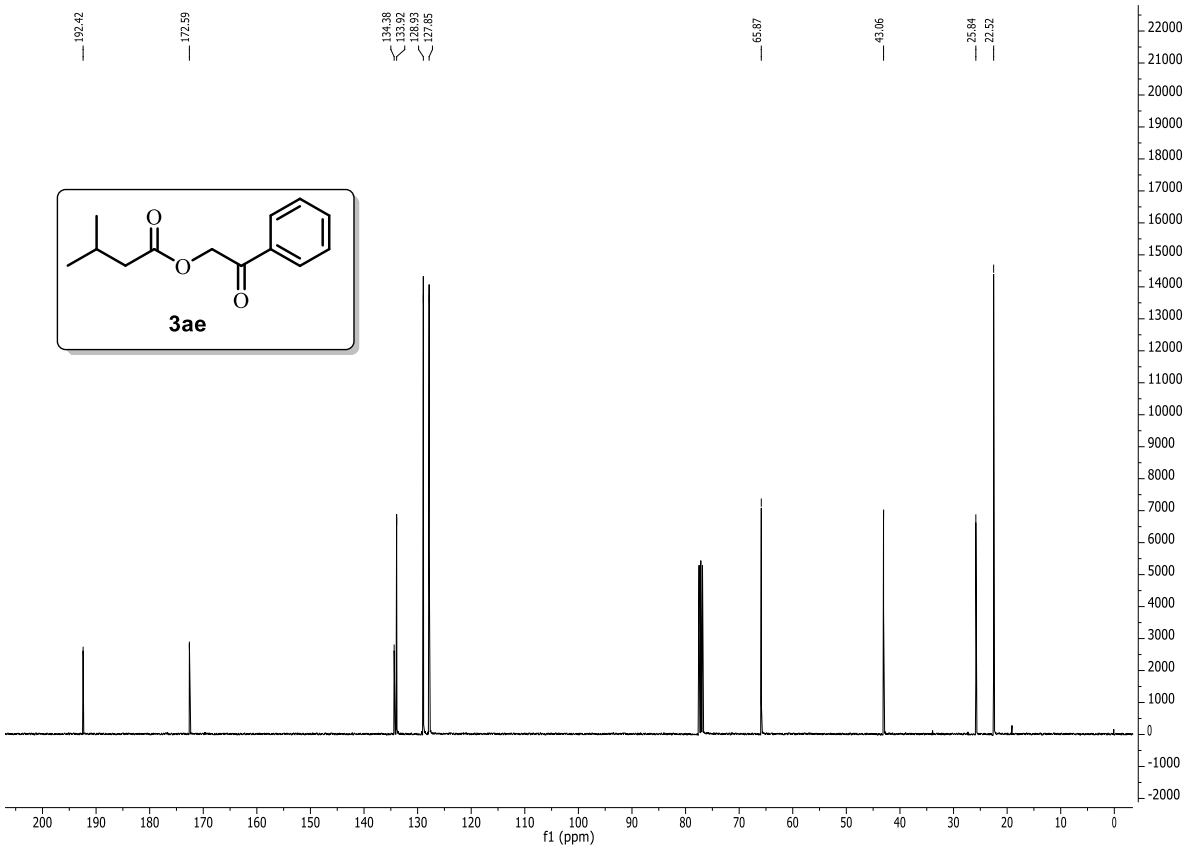

8.01
7.98
7.47
7.45
4.96
O
O
Cl
CN
3ac
2.00
2.14
2.08
f1 (ppm)


164.27
140.97
131.52
130.16
129.27
128.84
126.43
114.39
49.11
O
O
Cl
CN
3ac
f1 (ppm)

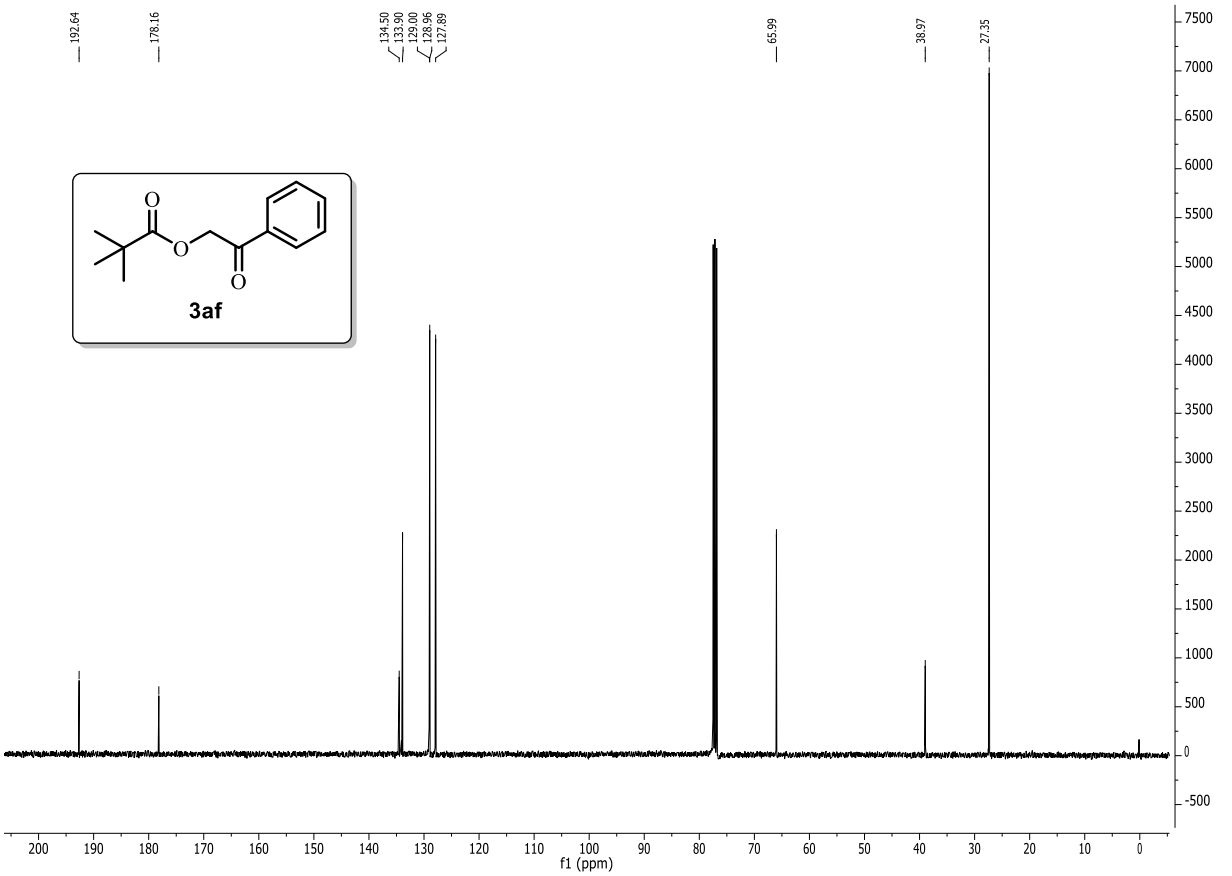

3ad
f1 (ppm)

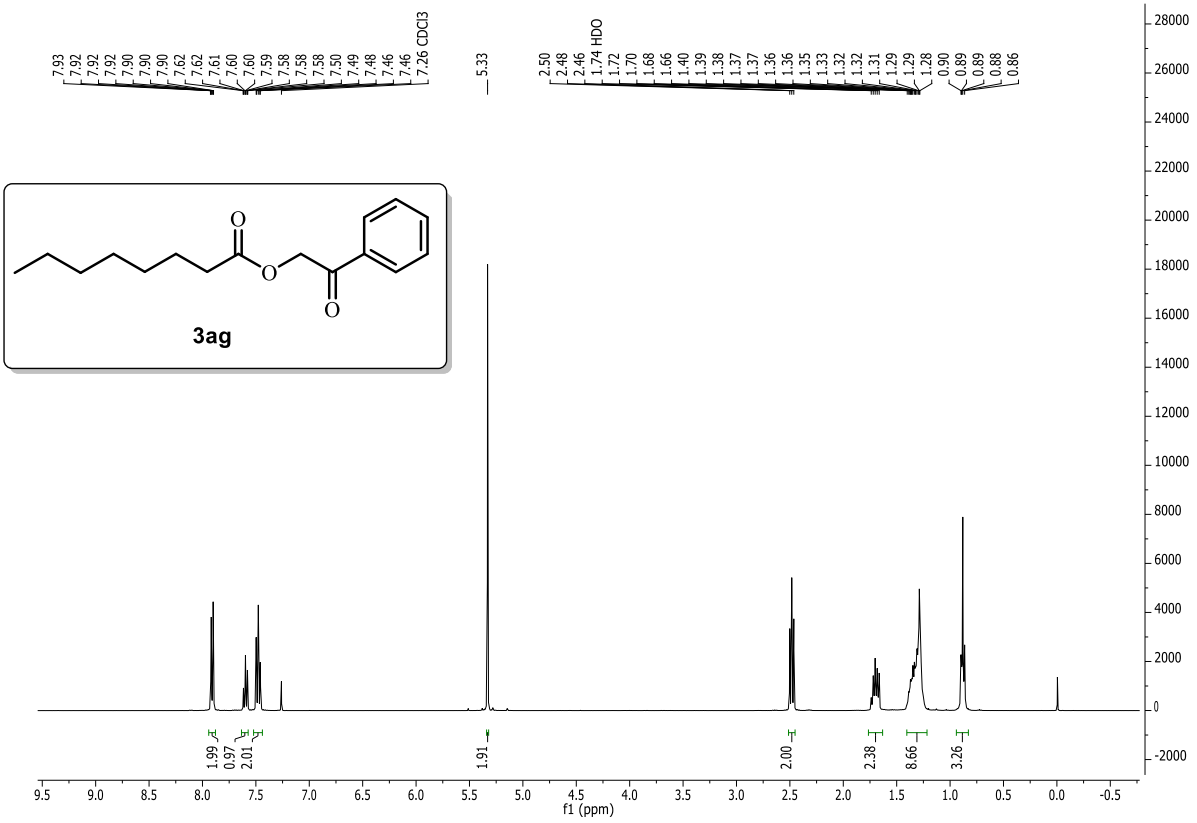

3ad
f1 (ppm)


3ae
f1 (ppm)

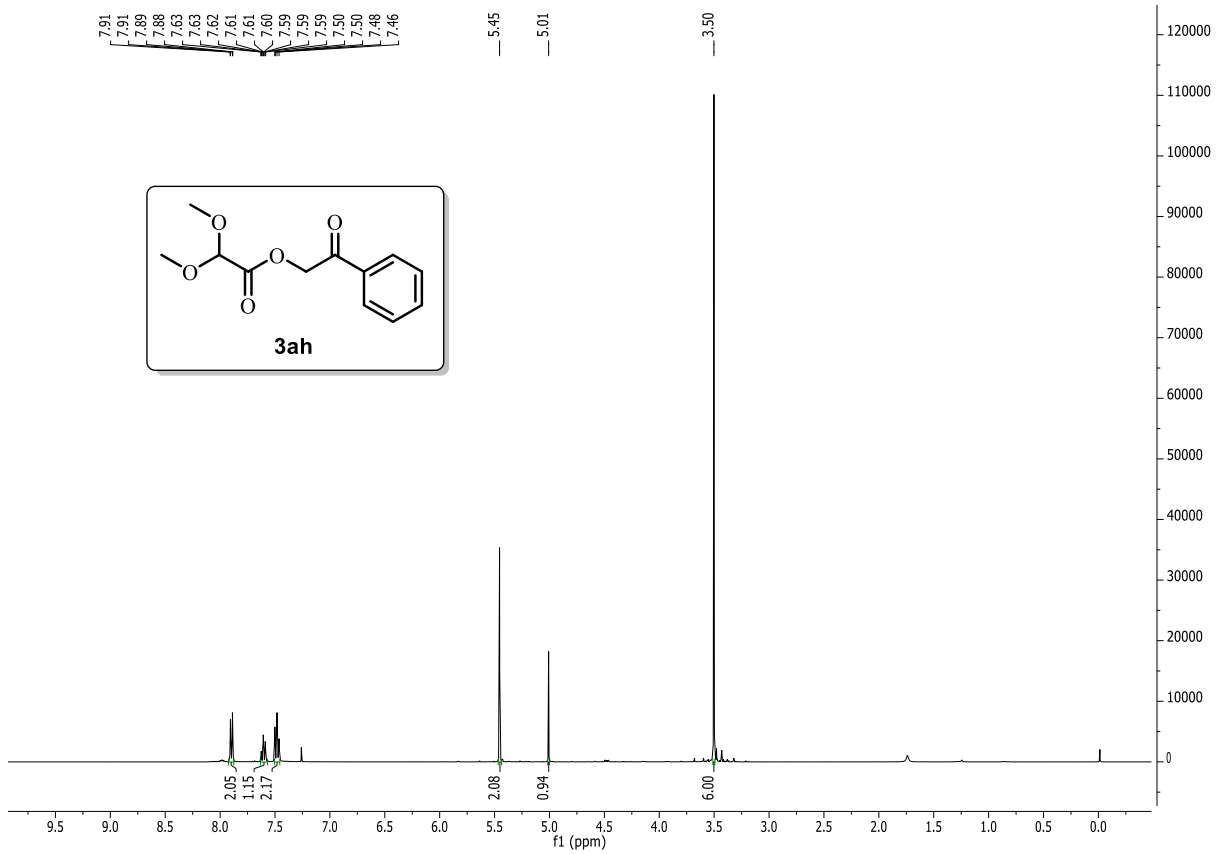

3ae
f1 (ppm)


7.92
7.92
7.90
7.89
7.62
7.62
7.61
7.60
7.60
7.60
7.60
7.59
7.58
7.58
7.58
7.50
7.50
7.50
7.50
7.48
7.48
7.48
7.48
7.48
7.46
7.46
7.46
5.31
1.30
O
O
O
3af
1.98
1.03
2.05
2.00
9.05
f1 (ppm)


192.64
178.16
134.50
133.90
129.00
128.96
127.89
65.99
38.97
27.35
O
O
O
3af
f1 (ppm)


7.93
7.92
7.92
7.92
7.90
7.90
7.90
7.62
7.62
7.61
7.60
7.60
7.60
7.59
7.58
7.58
7.58
7.50
7.49
7.48
7.46
7.46
7.26 CDCl3
5.33
2.50
2.48
2.46
1.74 HDO
1.72
1.70
1.68
1.66
1.40
1.39
1.38
1.37
1.37
1.36
1.36
1.35
1.33
1.32
1.32
1.31
1.29
1.29
1.28
0.90
0.89
0.89
0.88
0.86
3ag
1.99
0.97
2.01
1.91
2.00
2.38
8.66
3.26
f1 (ppm)


192.45
173.38
134.41
133.94
128.95
128.93
127.88
65.95
34.05
31.77
29.18
29.05
25.03
22.73
14.19
3ag
f1 (ppm)


7.91
7.91
7.89
7.88
7.63
7.62
7.61
7.61
7.60
7.59
7.59
7.59
7.50
7.50
7.48
7.46
5.45
5.01
3.50
3ah
2.05
1.15
2.17
2.08
0.94
6.00
f1 (ppm)


191.04
166.69
134.16
134.02
129.03
127.86
98.75
66.72
54.02
3ah
f1 (ppm)

7. References:

1.(a) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev*. **2016**, *116*, 10075−10166. And references cited therein. (b) Alfonzo, E.; Alfonso, F. S.; Beeler, A. B. Redesign of a Pyrylium Photoredox Catalyst and Its Application to the Generation of Carbonyl Ylides. *Org. Lett*. **2017**, *19*, 2989−2992.

2. Gonclaves MST, Oliveira-Campos AMF, Rodrigues LM, Proenca MFRP (2012) Synthesis of 4-Amino- 3, 5- dicyano-arylpyrazoles. Part 2: Isolation and characterization of by-products. *Synth Commun 42*, 1695–1703.

3. Mo, D.-L.; Dai, L.-X.; Hou, X.-L. The Reaction of Terminal Alkynes with PhI(OAc)2: A Convenient Procedure for the Preparation of α-Acyloxy Ketones. *Tetrahedron Lett*. **2009**, 50 , 5578−5581.

4. Ruzicka, R.; Zabadal, M.; Klan, P. Synth. Commun. 2002, 32, 2581 Photolysis of phenacyl esters in a two-phase system, *Synth. Commun*. **2002**, *32*, 2581.

5. Maity, P. K.; Rolfe, A.; Samarakoon, T. B.; Faisal, S.; Kurtz, R. D.; Long, T. R.; Schatz, A.; Flynn, D. L.; Grass, R. N.; Stark,¨ W. J.; Reiser, O.; Hanson, P. R. Monomer-on-Monomer (MoM) Mitsunobu Reaction: Facile Purification Utilizing Surface-Initiated Sequestration. *Org. Lett*. **2011**, *13*, 8−10.

6. Zeng, L.; Sajiki, H.; Cui, S. One-Pot Reaction of Carboxylic Acids, Ynol Ethers, and m-CPBA for Synthesis of α-Carbonyloxy Esters. *Org. Lett*. **2019**, *21*, 6423−6426.

7. Li, X. Q.; Zhou, C.; Xu, X. S. TBAI-catalyzed oxidative coupling of β-ketoesters with carboxylic acid: synthesis of α-carboxylic-β-ketoesters ARKIVOC 2012, 150-158.

8. Forte, G.; Chiarotto, I.; Inesi, A.; Loreto, M. A.; Feroci, M. Electrogenerated N-Heterocyclic Carbene in Ionic Liquid: An Insight into the Mechanism of the Oxidative Esterification of Aromatic Aldehydes. *Adv. Synth. Catal*. **2014**, *356*, 1773−1781.

9. M. Thorat , R. Mane , M. Jagdale & M. Salunkhe (1986) synthesis of phenacyl esters via polymer supported reagents, Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 18:3, 203-205.

10. M. Nallu, M. Subramanian, N. Vembu, A. Akber Hussain, Effect of binaryaqueous-organic solvents on the reaction of phenacyl bromide withnitrobenzoic acid(s) in the presence of triethylamine, *Int. J. Chem. Kinet*. **2004**, *36*, 401–409.

11. Y.-D. Kwon, M. T. La, H.-K. Kim, Aerobic oxidative esterification and thioesterification of aldehydes using dibromoisocyanuric acid under mild conditions: no metal catalysts required. *New J. Chem*. **2018**, *42*, 10833–10841.

12. L. Liu, S. Feng and C. Li, Practical Approach for Quantitative Green Esterifications *ACS Sustain. Chem. Eng*., **2016**, *4*, 6754-6762.
13. R. N. Reddi, P. K. Prasad and S. Arumugam, I_2-Catalyzed Regioselective Oxo- and Hydroxy-acyloxylation of Alkenes and Enol Ethers: A Facile Access to α-Acyloxyketones, Esters, and Diol Derivatives *Org. Lett*., **2014**, *16*, 5674-5677
14. J. Chen, D. Liu, N. Butt, C. Li, D. Fan, Y. Liu and W. Zhang, Palladium-Catalyzed Asymmetric Hydrogenation of α-Acyloxy-1-arylethanones. *Angew. Chem. Int. Ed*., **2013**, *52*, 11632 –11636.
15. S. Guo, J. T. Yu, Q. Dai, H. Yang and J. Cheng, The Bu_4NI-catalyzed alfa-acyloxylation of ketones with benzylic alcohols *Chem. Commun*. **2014**, *50*, 6240-6242.