Electronic Supporting Information

Synthesis of phenol esters by direct C-H activation of aldehydes using highly efficient and reusable copper immobilized polyimide covalent organic framework (Cu@PI-COF)

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Table of Contents

Instrumentation

The synthesized catalyst was characterized by various physio-chemical techniques. To determine the functional groups, present in the material Fourier-transform infrared spectroscopic absorption peaks were observed on PerkinElmer Spectrum 2000 using KBr pellet in scanning range of 4000-400 cm^{-1}. For crystal structure and phase purity determination, X-ray diffractograms were recorded on Rigaku MiniFlex Diffractometer at a scanning rate of 2° min^{-1} in the 2θ range of 10-45°. For shape and morphology, scanning electron micrographs were obtained on Digital Scanning Electron Microscope JEOL, JSM 6610LV. For this, prior to imaging finely crushed powdered samples were mounted on carbon taped metal stubs. Sample was further sputter-coated with JEOL JEC-3000 FC auto fine coater platinum sputtering machine. SEM-coupled EDAX was used to examine the elements present in the catalyst. Transmission electron micrographs were attained on CRYO-TEM Talos microscope operated at 200 kV by dispersing the samples in ethanol. Further, samples were casted on carbon coated copper grids. Energy dispersive X-ray spectroscopy (EDX) was performed on Ametek EDAX system. Atomic absorption spectroscopy was used to examine the copper content present in the catalyst using a PerkinElmer Optima 2100 DV. To gain knowledge about thermal stability, thermogravimetric curves were attained under nitrogen atmosphere using a Linseis TGA from room temperature to 500 °C at heating rate of 10 °C min^{-1} with a gas flow of 2 L h^{-1}. The N_2 adsorption-desorption isotherm was measured using NOVA touch 4LX [s/n:1050020628] surface area analyzer instrument at liquid nitrogen temperature (77 K). The specific surface area was obtained by Brunauer-Emmett–Teller (BET) equation and the pore

width distribution was calculated using DFT method. The optimization of the reaction conditions was carried out using Agilent gas chromatograph (6850 GC) having a HP-5MS capillary column (stationary phase: 5% phenyl methyl siloxane; column length: 30 m; internal diameter: 0.25 mm; film thickness: 0.25 µm) and a quadrupole mass filter equipped 5975C mass selective detector (MSD) using helium as a carrier gas. Finally, analysis of the organic compounds was confirmed by ^{1}H (400 MHz) and ^{13}C (100 MHz) Bruker-400 nuclear magnetic resonance spectrophotometer. Spectra were recorded in $CDCl_3$. Chemical shifts (δ) for proton and carbon are reported in parts per million (ppm) units downfield from internal standard, tetramethylsilane (TMS).

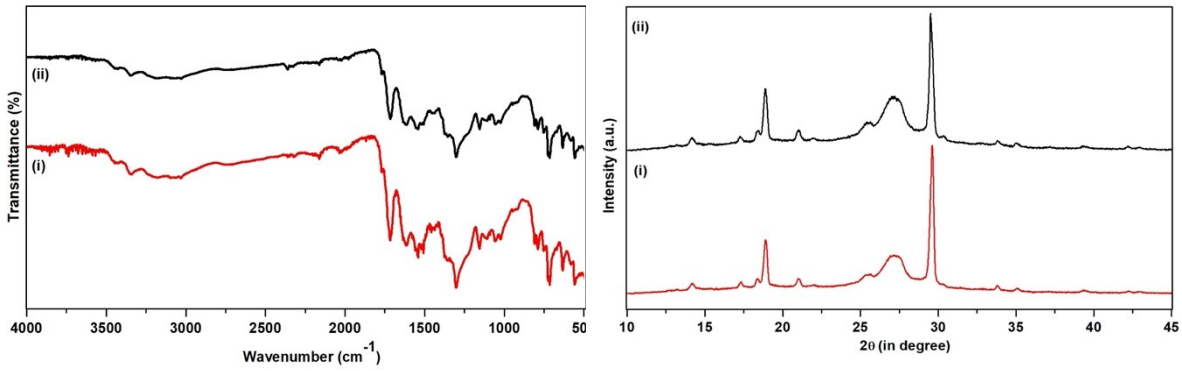


Fig. S1 a) FT-IR spectra and b) XRD curves of i) fresh Cu@PI-COF & ii) recovered Cu@PI-COF.

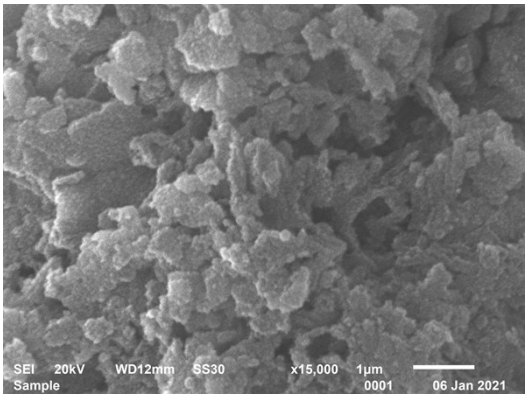
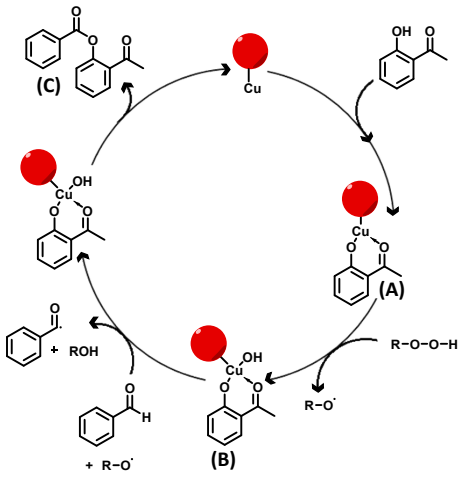


Fig. S2 SEM image of recovered Cu@PI-COF.

Plausible Reaction Mechanism

On the grounds of literature investigations, a possible reaction mechanism has been proposed for the synthesis of phenol esters using 2-hydroxyacetophenone and benzaldehyde (**Scheme S1**). The presence of a carbonyl group adjacent to the hydroxy group is essential for the success of the oxidative C-O coupling. In the present transformation it was found that the selected product did not form in the absence of catalyst. It was Cu@PI-COF which led to formation of phenol esters. The first step involves the formation of coordination complex (A) between the enol-tautomer of 2-hydroxyacetophenone and transition metal.[1] In the next step, coordination complex of Cu (A) catalyzes the decomposition of TBHP to give Cu-enolate (B) and RO· which then reacted with benzaldehyde to give benzoyl radical.[2] Further, benzoyl radical reacted with

the enolate of copper to produce targeted product (C) and regenerated Cu@PI-COF for further reactions.



Scheme S1 Proposed reaction mechanism for the formation of phenol esters.

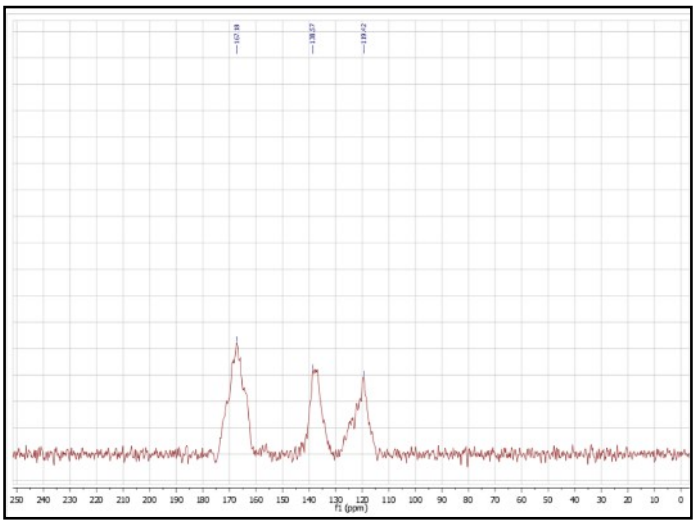


Fig. S3 ^{13}C solid-state NMR spectra of PI-COF.

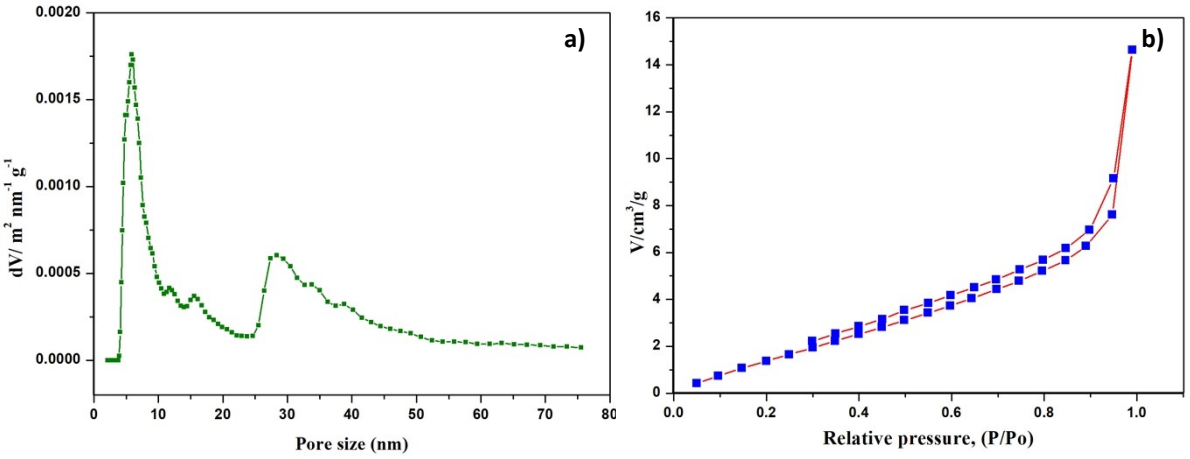


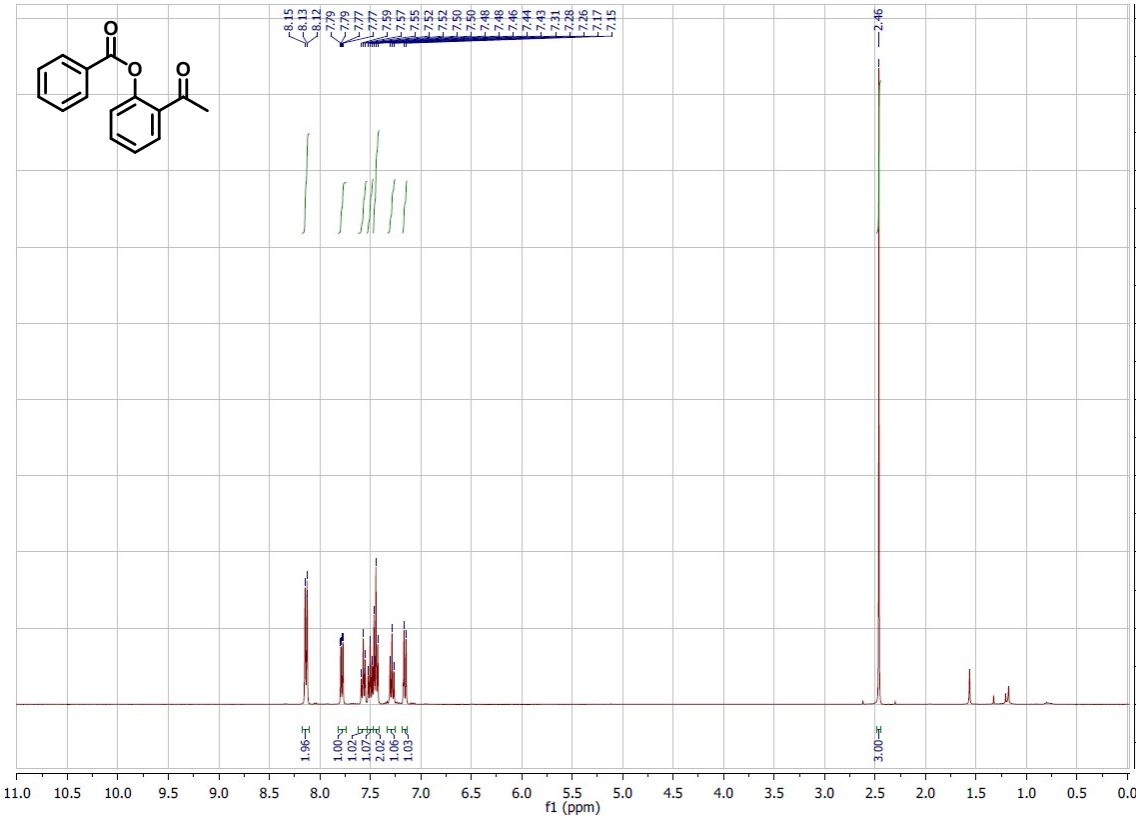
Fig. S4 a) Pore size distributions & b) adsorption-desorption isotherm of PI-COF.

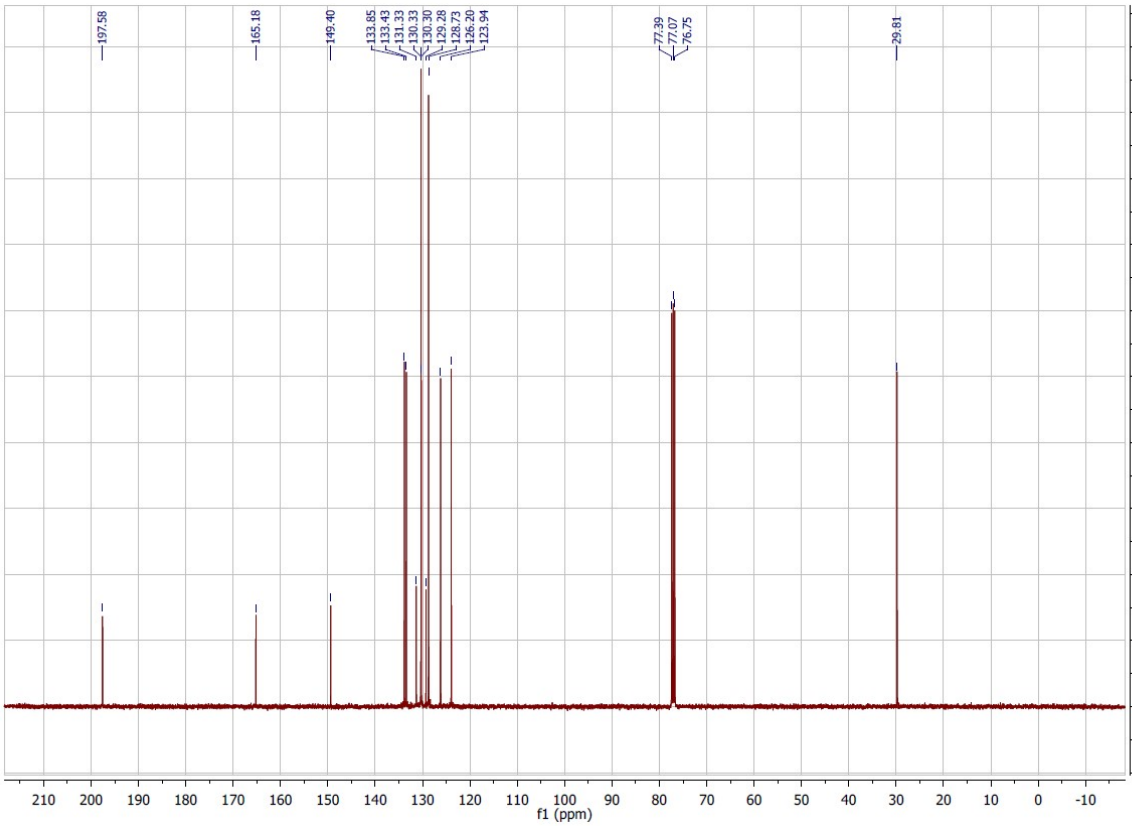
NMR Spectra of isolated products

^{1}H and ^{13}C NMR spectra of isolated phenol esters.

Scheme 2, Entry 3a

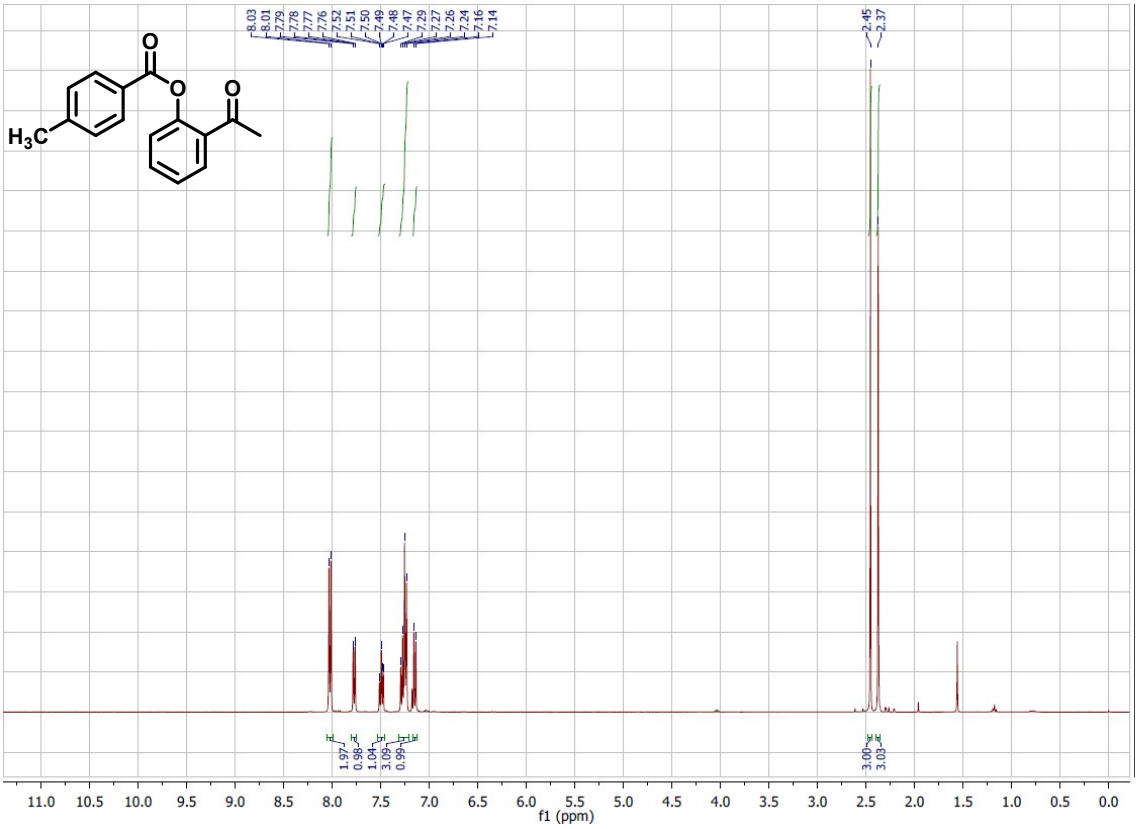
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 2H), 7.78 (dd, J = 7.8, 1.5 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.50 (td, J = 8.0, 1.6 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 8.0 Hz, 1H), 7.16 (d, J = 8.1 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.6, 165.2, 149.4, 133.8, 133.4, 131.3, 130.3, 130.3, 129.3, 128.7, 126.2, 123.9, 29.8.

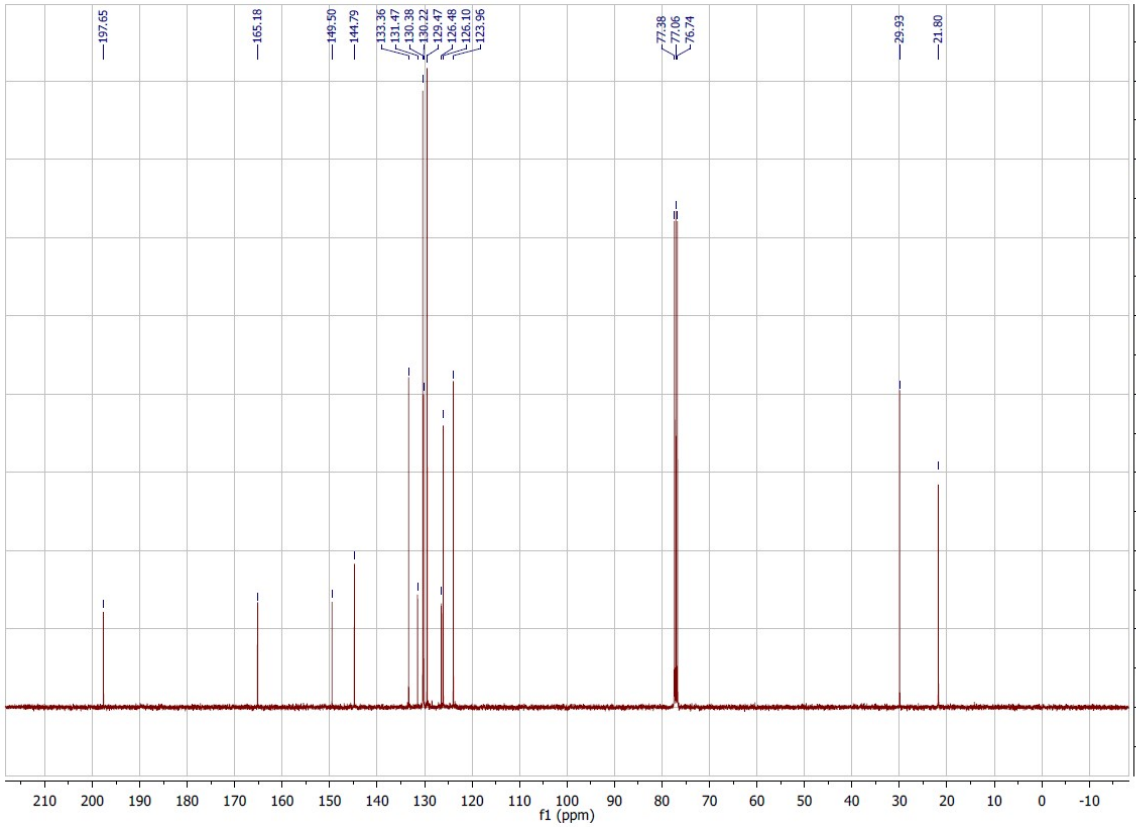




Scheme 2, Entry 3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J =8.1 Hz, 2H), 7.77 (dd, J = 7.8, 1.4 Hz, 1H), 7.49 (td, J = 8.0, 1.5 Hz, 1H), 7.26 (dd, J = 15.6, 7.8 Hz, 3H), 7.15 (d, J = 8.1 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.6, 165.2, 149.5, 144.8, 133.4, 131.5, 130.4, 130.2, 129.5, 126.5, 126.1, 124.0, 29.9, 21.8.

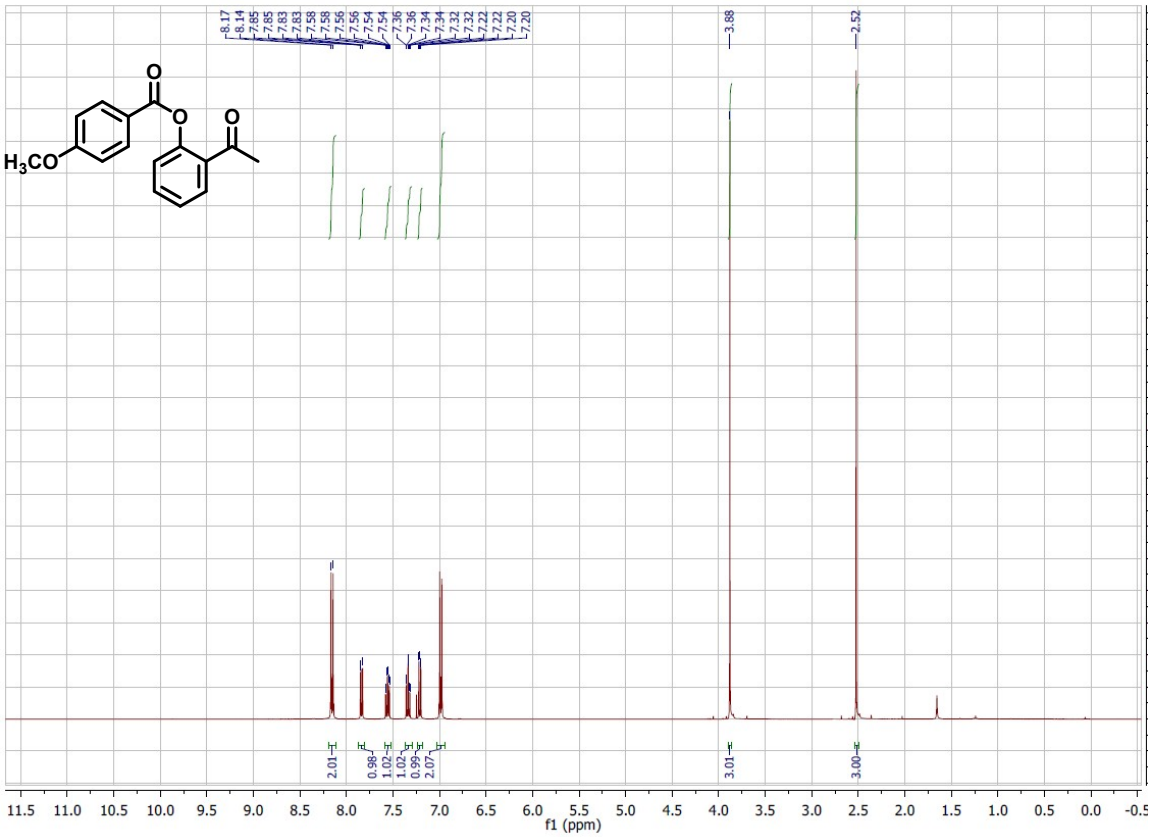


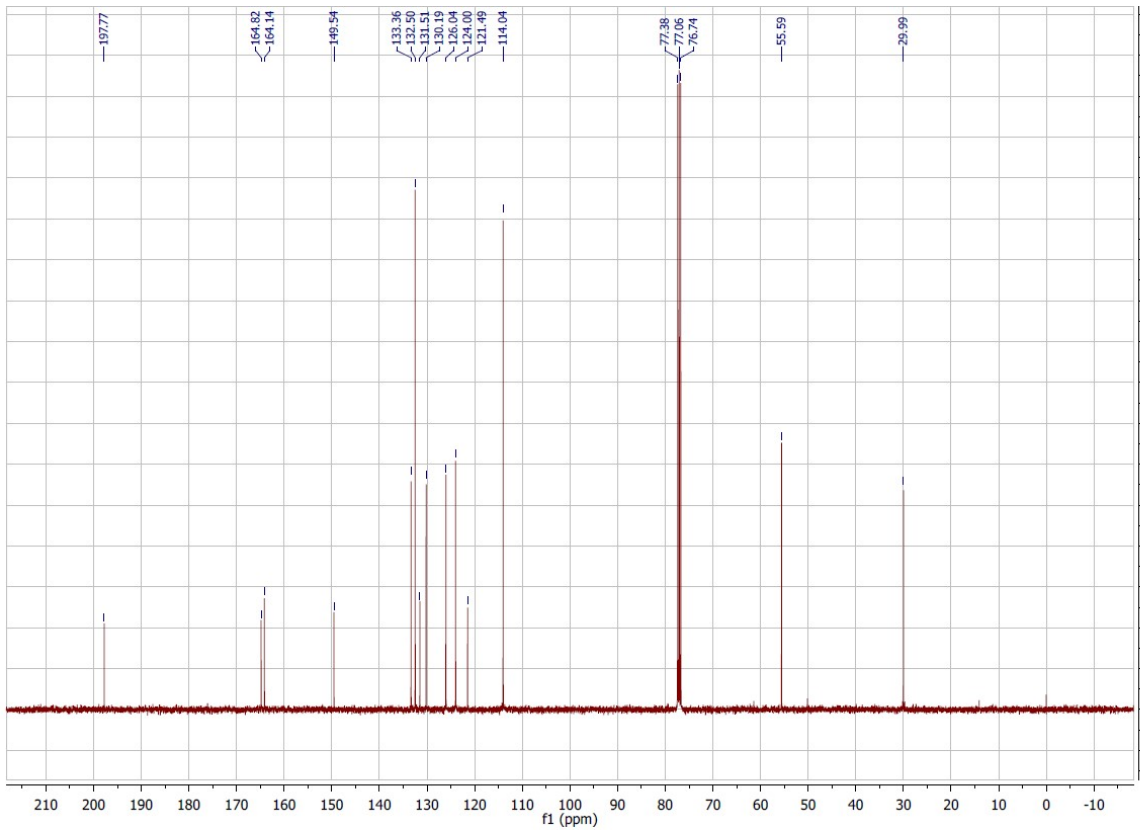


Scheme 2, Entry 3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J=8.9 Hz, 2H), 7.84 (dd, J = 7.8, 1.7 Hz, 1H), 7.56 (m, 1H), 7.34 (td, J = 7.6, 1.1 Hz, 1H), 7.21 (dd, J = 8.1, 0.9 Hz, 1H), 6.99 (m, 2H), 3.88 (s, 3H),

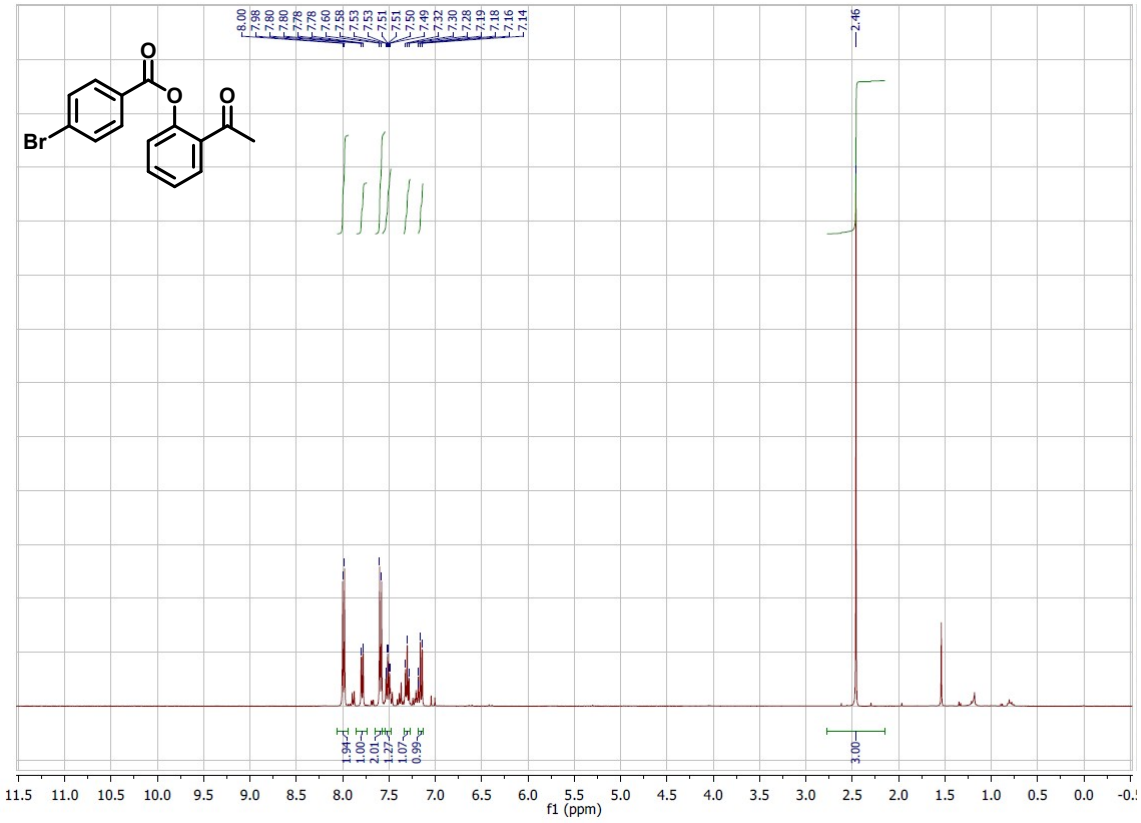
2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.8, 164.8, 164.1, 149.5, 133.4, 132.5, 131.5, 130.2, 126.0, 124.0, 121.5, 114.0, 55.6, 30.0

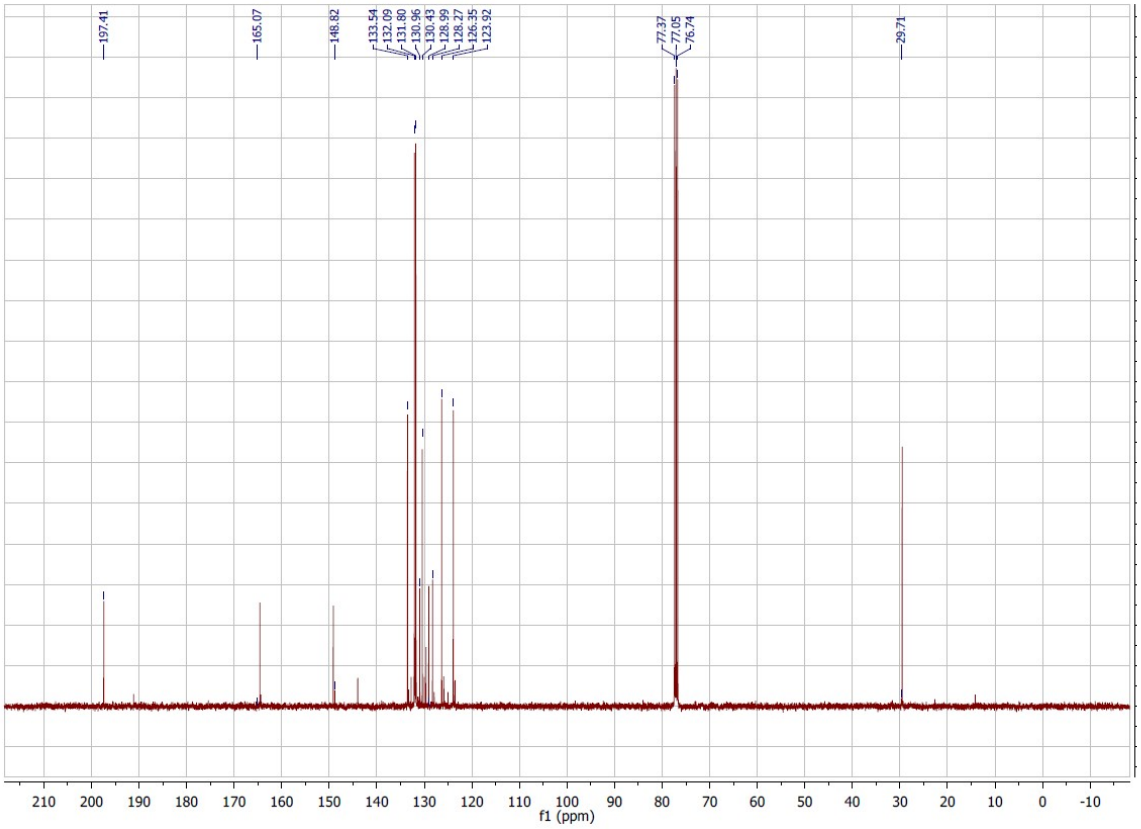




Scheme 2, Entry 3d

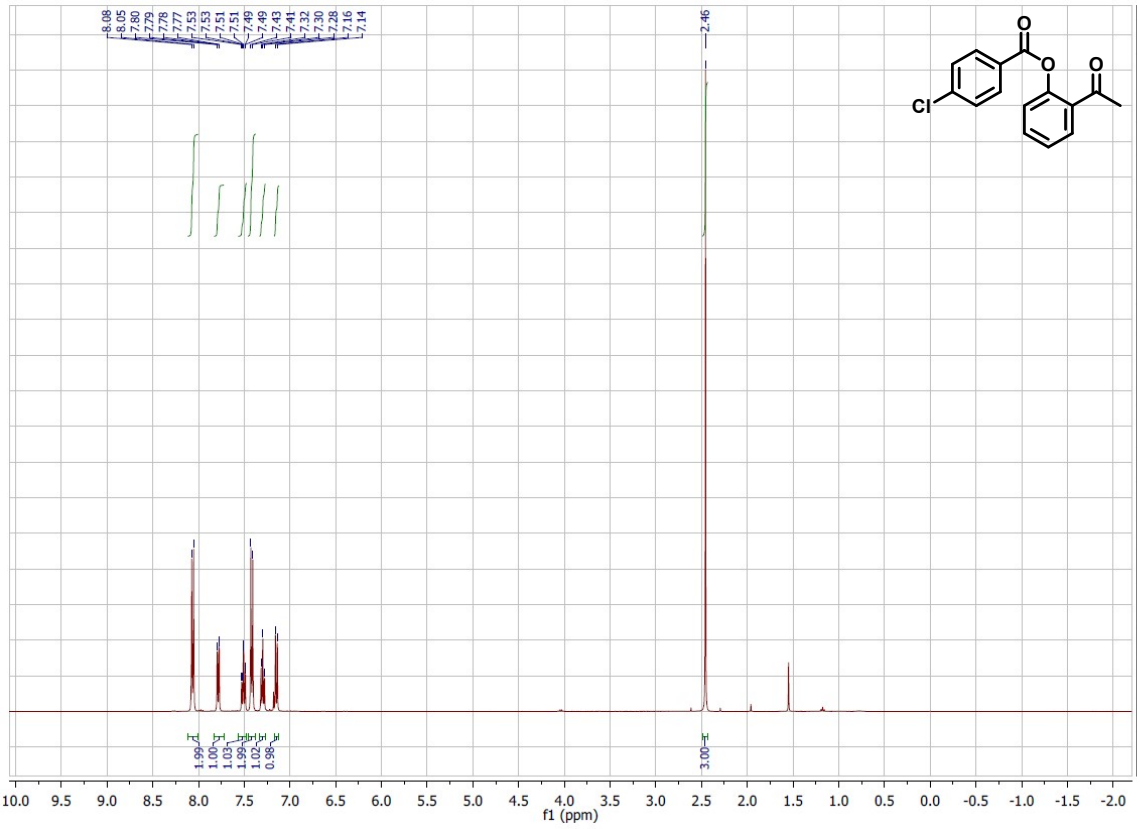
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.5 Hz, 2H), 7.79 (dd, J = 7.8, 1.4 Hz, 1H), 7.59 (d, J = 8.5 Hz, 2H), 7.51 (td, J = 8.0, 1.5 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 2,46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.4, 165.1, 148.8, 133.5, 132.1, 131.8, 131.0, 130.4, 129.0, 128.3, 126.3, 123.9, 29.7.





Scheme 2, Entry 3e

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 8.6 Hz, 2H), 7.79 (dd, J = 7.8, 1.4 Hz, 1H), 7.51 (td, J = 8.0, 1.5 Hz, 1H), 7.42 (d, J = 8.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.4, 164.4, 149.2, 140.3, 133.5, 131.7, 131.0, 130.4, 129.1, 127.8, 126.3, 123.9, 29.5.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7.30
7.28
7.16
7.14
2.46
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O
O
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1.00
1.03
1.99
1.02
0.98
3.00
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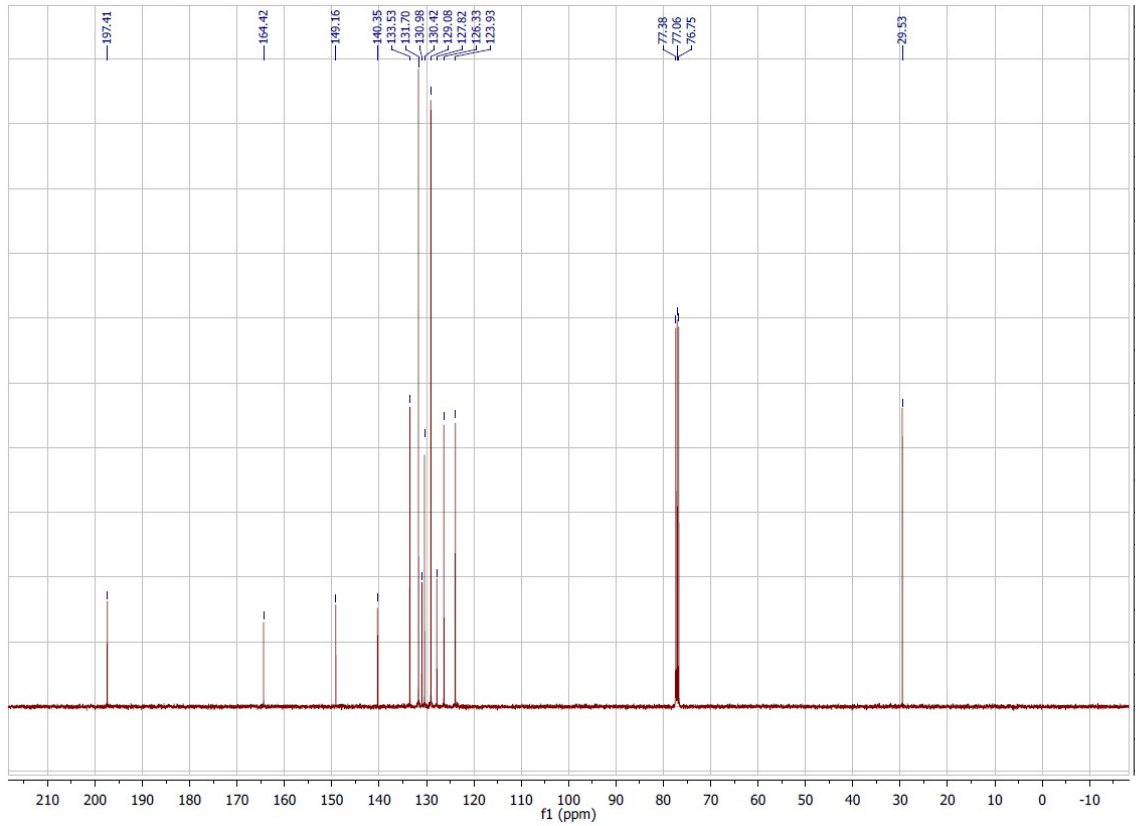
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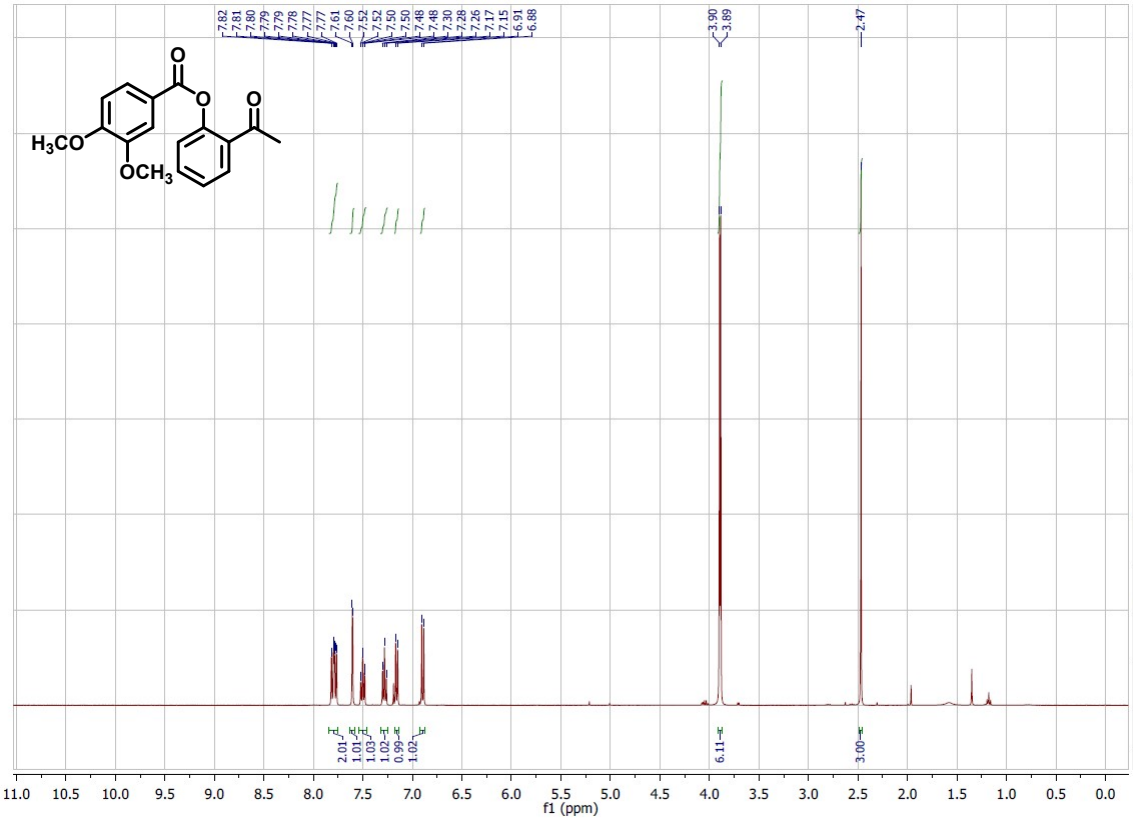
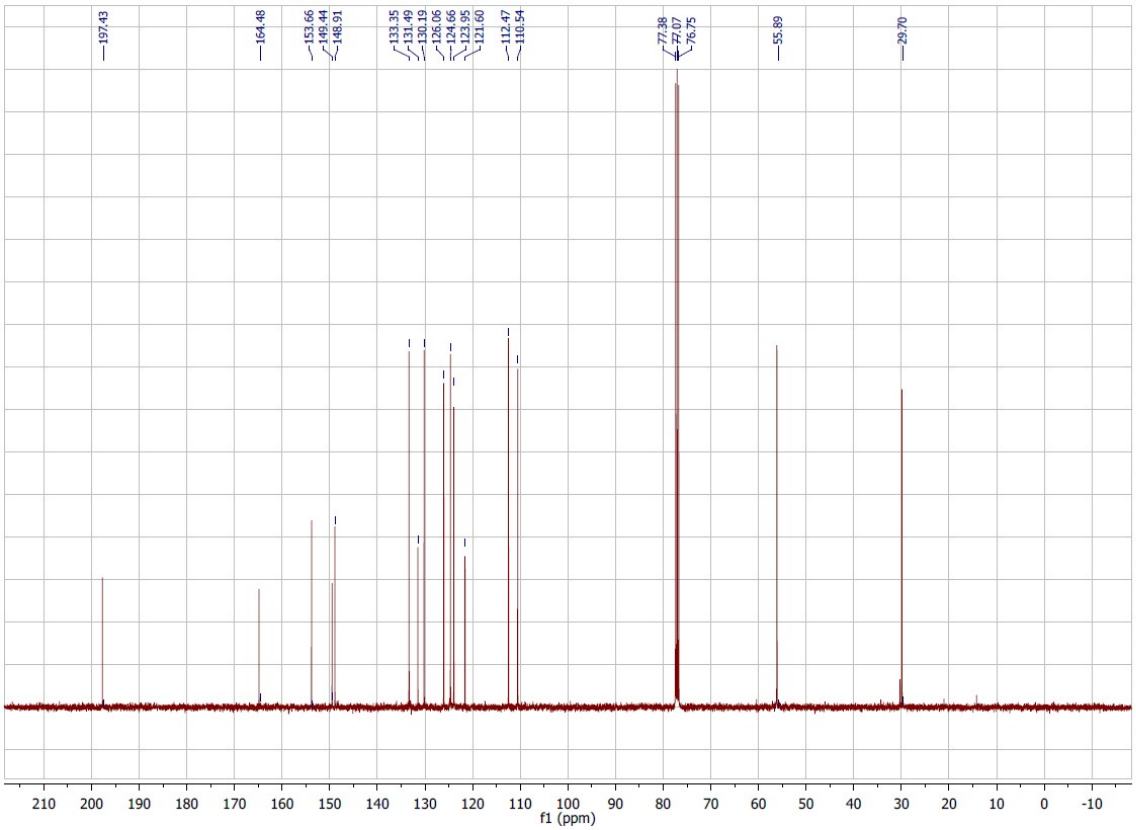
76.75
29.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Scheme 2, Entry 3f

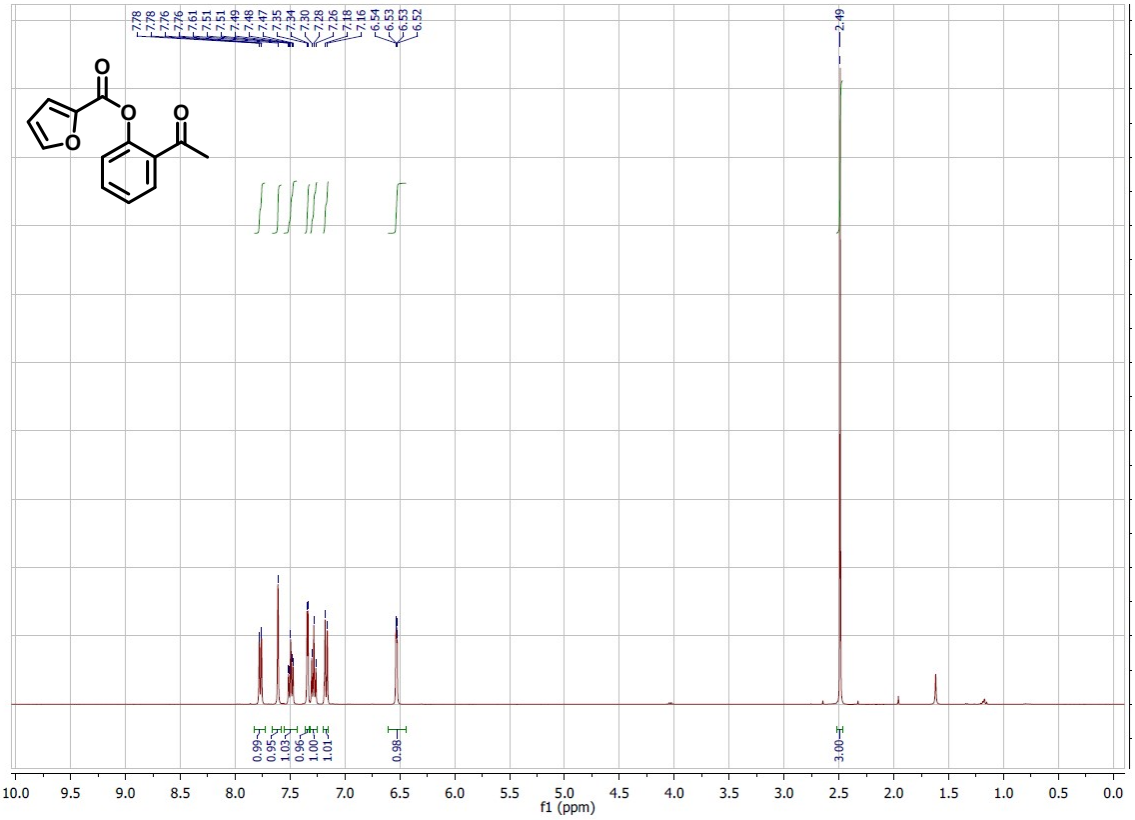
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (ddd, J = 9.4, 8.1, 1.7 Hz, 2H), 7.60 (d, J = 1.8 Hz, 1H), 7.50 (td, J = 8.0, 1.6 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.16 (d, J = 8.1 Hz, 1H), 6.9 (d, J = 8.5 Hz, 1H), 3.89 (d, J = 5.0 Hz, 6H), 2.47 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) 197.4, 164.5, 153.7, 149.4, 148.9, 133.3, 131.5, 130.2, 126.1, 124.7, 123.9, 121.6, 112.5, 110.5, 55.9, 29.7.





Scheme 2, Entry 3g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 7.8, 1.3 Hz, 1H), 7.61 (s, 1H), 7.49 (m, 1H), 7.34 (d, J = 3.5 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 8.1 Hz, 1H), 6.53 (dd, J = 3.4, 1.6 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.5, 156.6, 148.5, 147.5, 143.8, 133.4, 131.2, 130.3, 126.4, 123.8, 120.0, 112.4, 29.8.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7.18
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6.53
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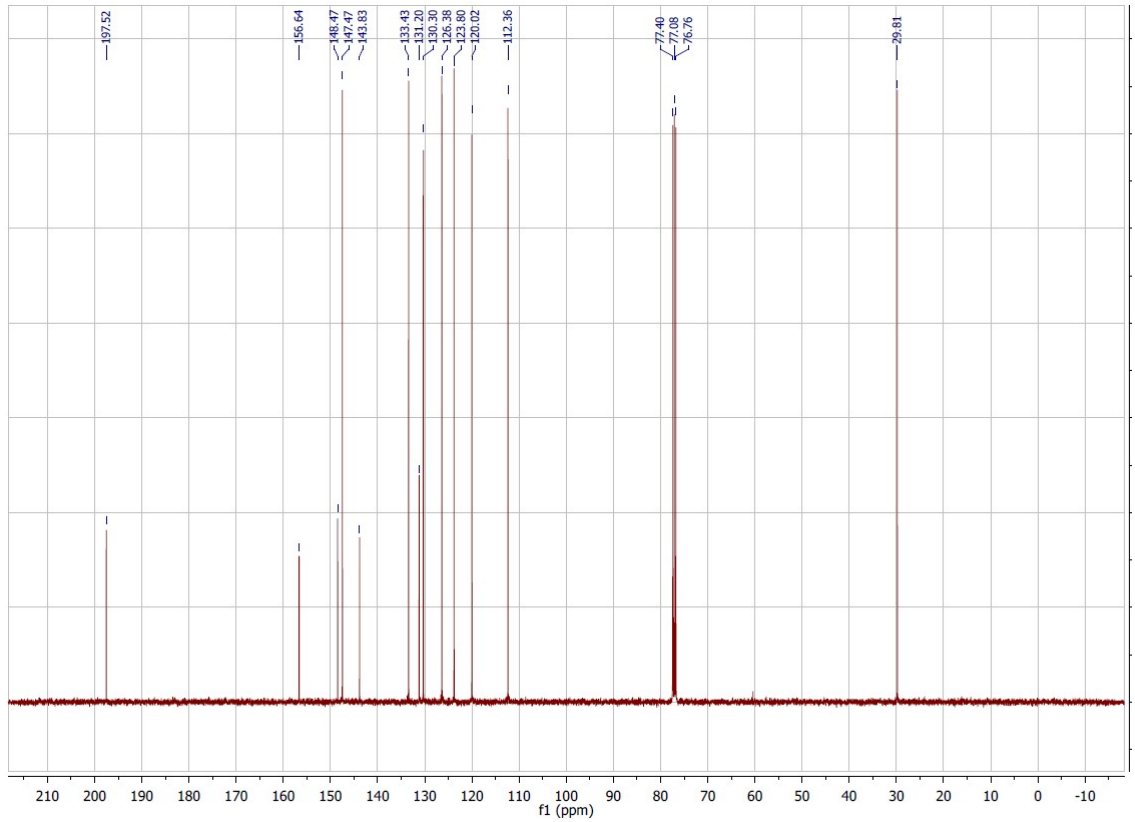
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120.02
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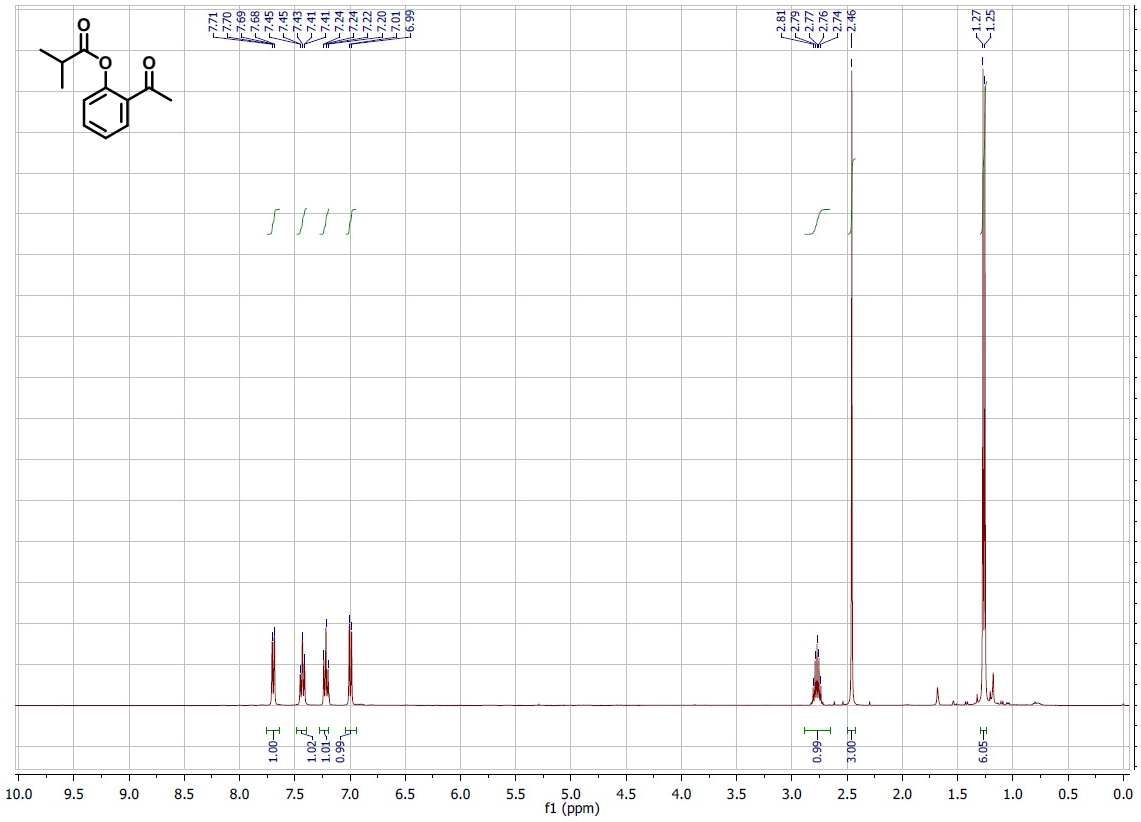
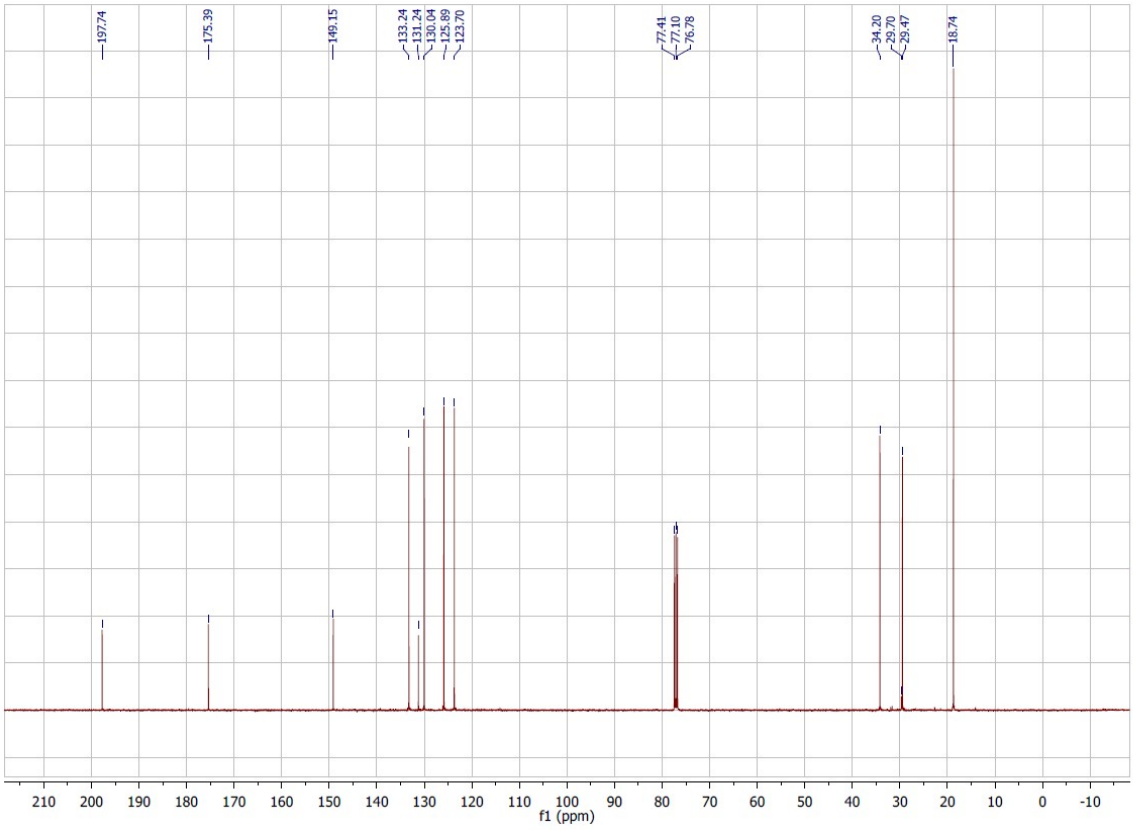
77.40
77.08
76.76
29.81
f1 (ppm)

Scheme 2, Entry 3j

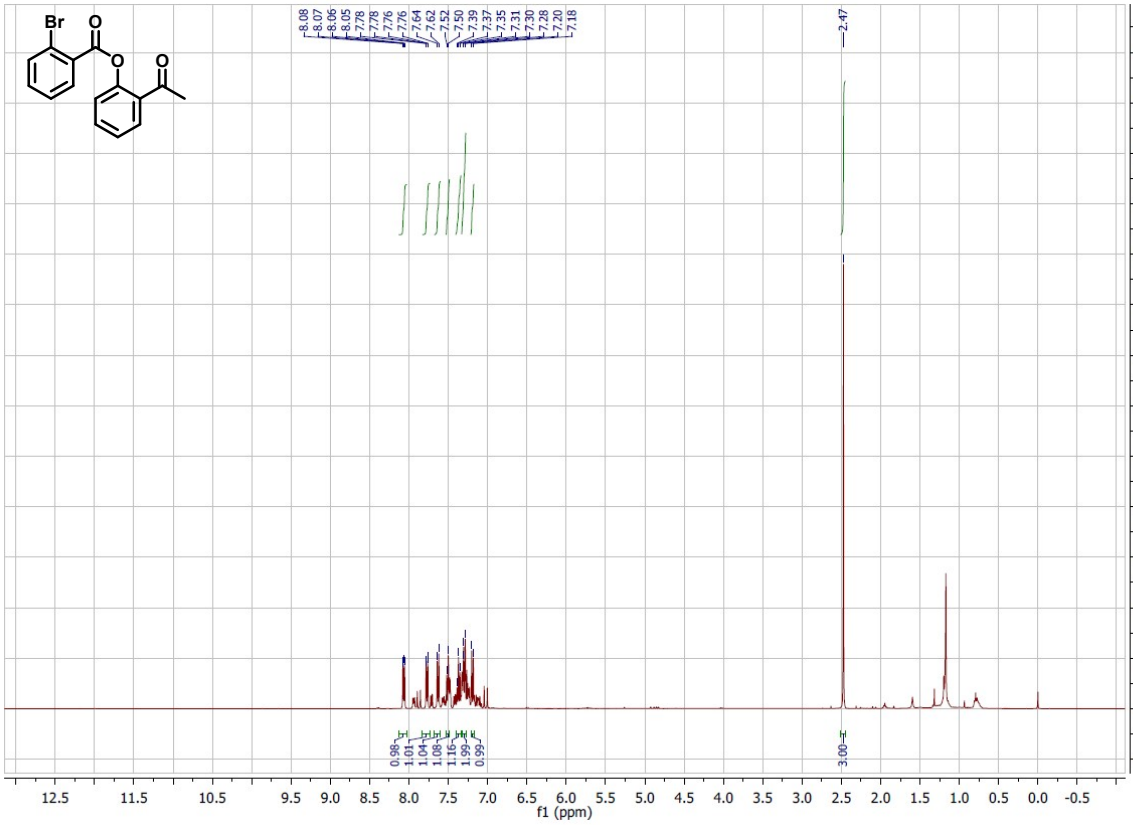
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 7.8, 1.3 Hz, 1H), 743 (m, 1H), 7.22 (dd, J = 11.7, 4.2 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H), 2.77 (dt, J = 14.0, 7.0 Hz, 1H), 2.46 (s, 3H), 1.26 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.7, 175.4, 149.1, 133.2, 131.2, 130.0, 125.9, 123.7, 34.2, 29.7, 29.5, 18.7.





Scheme 2, Entry 3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.6, 1.7 Hz, 1H), 7.77 (dd, J = 7.8, 1.4 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.30 (m, 2H), 7.19 (d, J = 8.1 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.4, 164.5, 149.1, 143.4, 134.5, 133.6, 133.3, 132.1, 131.1, 130.9, 130.4, 127.5, 126.4, 123.9, 122.3, 29.2.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7.28
7.20
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1.04
1.08
1.16
1.99
0.99
3.00
12.5 11.5 10.5 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
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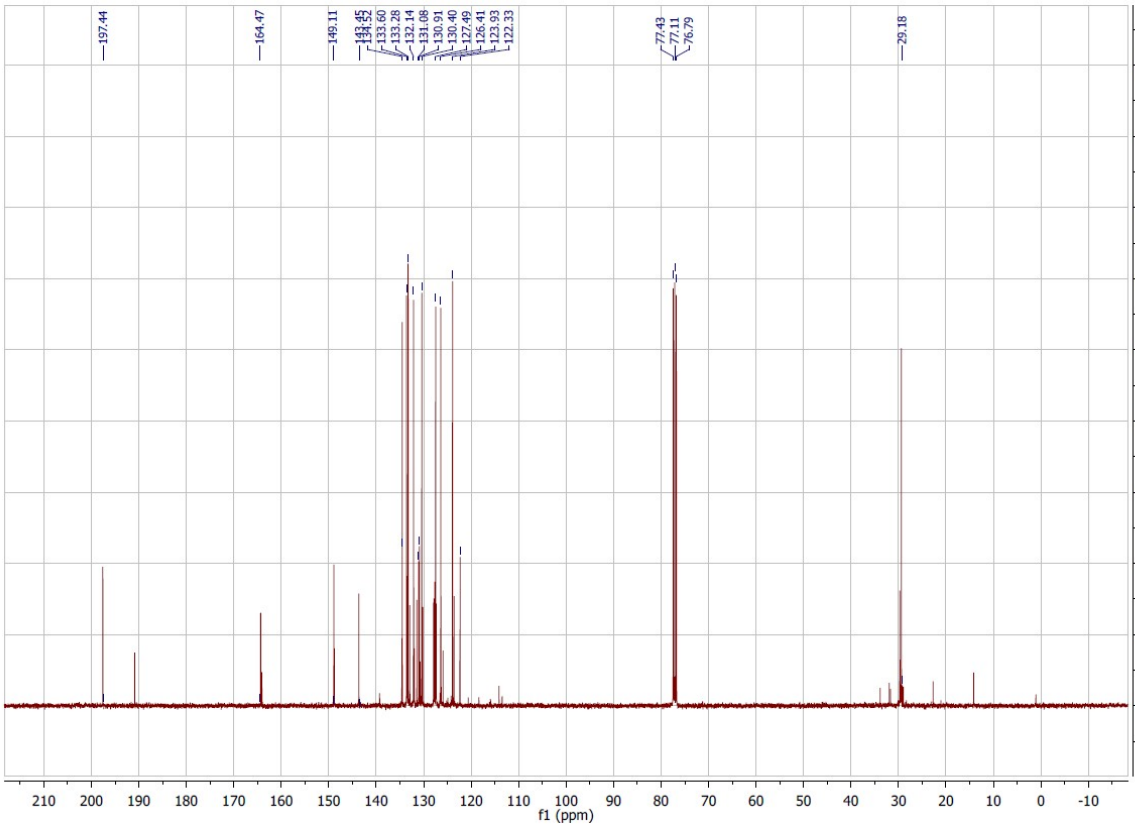
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76.79
29.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

[1] I. Luz, A. Corma, F. L. i Xamena, *Catalysis Science & Technology* **2014**, *4*, 1829-1836.
[2] aC.-J. Li, *Accounts of chemical research* **2009**, *42*, 335-344; bW.-J. Yoo, C.-J. Li, *The Journal of Organic Chemistry* **2006**, *71*, 6266-6268.