Supporting Information

An environmentally benign hydration of alkynes catalyzed by gallic acid/tannic acid in water

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1. Experimental Section

1.1 General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX500 (500 MHz) spectrometer and tetramethylsilane (TMS) was used as a reference. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, quin = quintuplet, sex = sextet and br = broad), coupling constant (J values) in Hz and integration. Gallic acid and tannic acid from ALDRICH were used. All of the products were known compounds and were identified by comparison of their physical and spectra data with those of authentic samples.

1.2 General procedure for the synthesis of 2 (2a as an example)

In a sealed tube, a mixture of phenylacetylene **1a** (1.0 mmol), gallic acid (2.0 mmol) and H_2O (2 mL) was stirred at 60 °C for 6 h. After disappearance of the starting material (monitored by TLC), the reaction mixture was poured into 20 mL H_2O and extracted with ethyl acetate (3 × 10 mL). The combined extract was over anhydrous MgSO4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10:1) to yield the desired product **2a** as a colorless oil.

1.3 General procedure for recovery of the catalytic system (1a as an example)

At room temperature, gallic acid and alkynes are insoluble in the reaction mixture (see in Figure 1). When the temperature rised, they can dissolve well in this reaction system (see in Figure 2). After the reaction was finished, hexane was added to the system (see in Figure 3) and then followed with extraction (see in Figure 4). The clearly separated hexane layer has been removed and concentrated to get the desired crude product. The next run was then started by directly adding the phenylacetylene to the recovered catalyst system. Figure 5 shows the recycled system with hexane after 5 cycles.

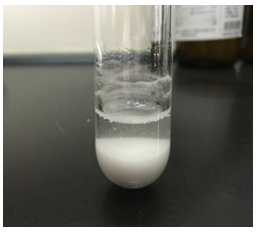


Figure 1

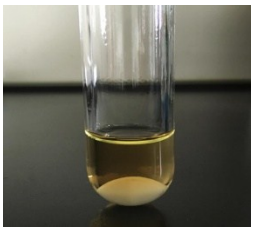


Figure 2

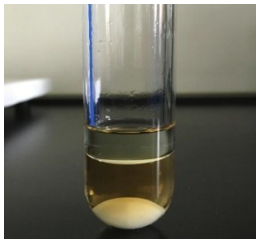


Figure 3

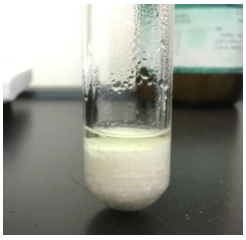


Figure 4

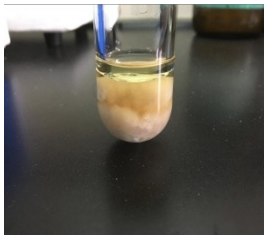


Figure 5

2. Characterization of compounds

*Acetophenone (**2a**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 0.9 Hz, 1H), 7.93 (d, *J* = 1.2 Hz, 1H), 7.56-7.53 (m, 1H), 7.46-7.43 (m, 2H), 2.58 (s, 3H).

*1-(4-chlorophenyl)ethan-1-one (**2b**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.42 - 7.40 (m, 2H), 2.57 (d, *J* = 2.5 Hz, 3H).

*1-(4-bromophenyl)ethan-1-one (**2c**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 2.58 (s, 3H).

*1-(4-nitrophenyl)ethan-1-one (**2d**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32-8.31 (m, 2H), 8.13 (d, *J* = 8.9 Hz, 2H), 2.71 (s, 3H).

*1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2e**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 2.65 (s, 3H).

*1-(4-tolyl)ethan-1-one (**2f**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.55 (d, *J* = 0.6 Hz, 3H), 2.39 (s, 3H).

*1-(4-ethylphenyl)ethan-1-one (**2g**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 -7.84 (m, 2H), 7.27- 7.23

(m, 2H), 2.70-2.67 (m, 2H), 2.56-2.53 (m, 3H), 1.26- 1.22 (m, 3H).

*1-(4-methoxyphenyl)ethan-1-one (**2h**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 2.54 (s, 3H).

*1-(4-hydroxyphenyl)ethan-1-one (**2i**)*. ^{1}H NMR (500 MHz, CDCl3) δ 7.91 (d, *J = 8.7* Hz, 2H), 6.95 (d, *J = 8.7* Hz, 2H), 2.59 (s, 3H).

*1-(4-aminophenyl)ethan-1-one(**2j**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.23 (s, 2H), 2.50 (s, 3H).

*1-(2-methyphenyl)ethan-1-one (**2k**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 1H), 7.36- 7.33 (m, 1H), 7.25-7.20 (m, 2H), 2.55 (s, 3H), 2.52 (s, 3H).

*1-(3-aminophenyl)ethan-1-one(**2l**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 2H), 6.87 (d, *J* = 6.9 Hz, 1H), 3.83 (s, 2H), 2.56 (s, 3H).

*1-(3,4-dichlorophenyl)ethan-1-one (**2m**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.6 Hz, 1H), 7.78-7.76 (m, 1H), 7.55-7.54 (m, 1H), 2.59 (s, 3H).

*1-(3,4-dimethoxyphenyl)ethan-1-one(**2n**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 1H), 6.53-6.50 (m, 1H), 6.46 (d, *J* = 2.3 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 2.57 (s, 3H).

*1-(naphthalen-2-yl)ethan-1-one(**2o**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.03-8.02 (m, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.90-7.87 (m, 2H), 7.62-7.54 (m, 2H), 2.73 (s, 3H).

*1-([1, 1'-biphenyl]-4-yl)ethan-1-one(**2p**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.49-7.46 (m, 2H), 7.42-7.39 (m, 1H), 2.64 (s, 1H).

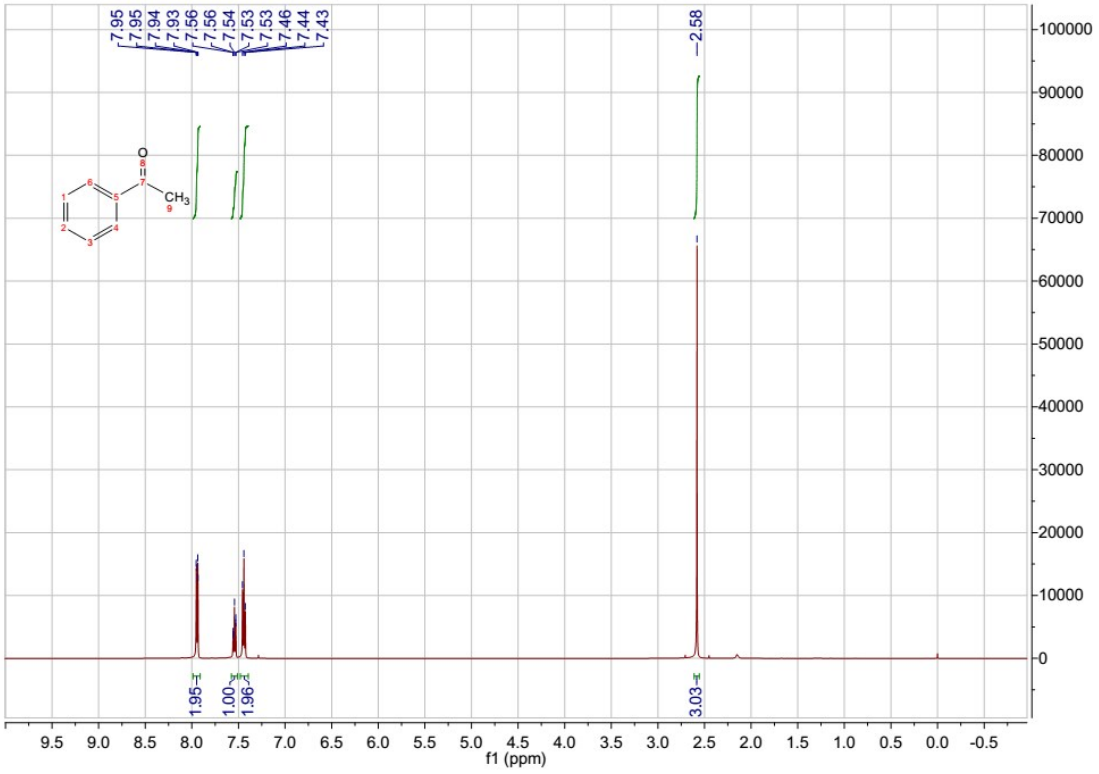
*decan-2-one(**2q**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43-2.40 (m, 2H), 2.13 (s, 3H), 1.58-1.55 (m, 2H), 1.31-1.28 (m, 10H), 0.89-0.86 (m, 3H).

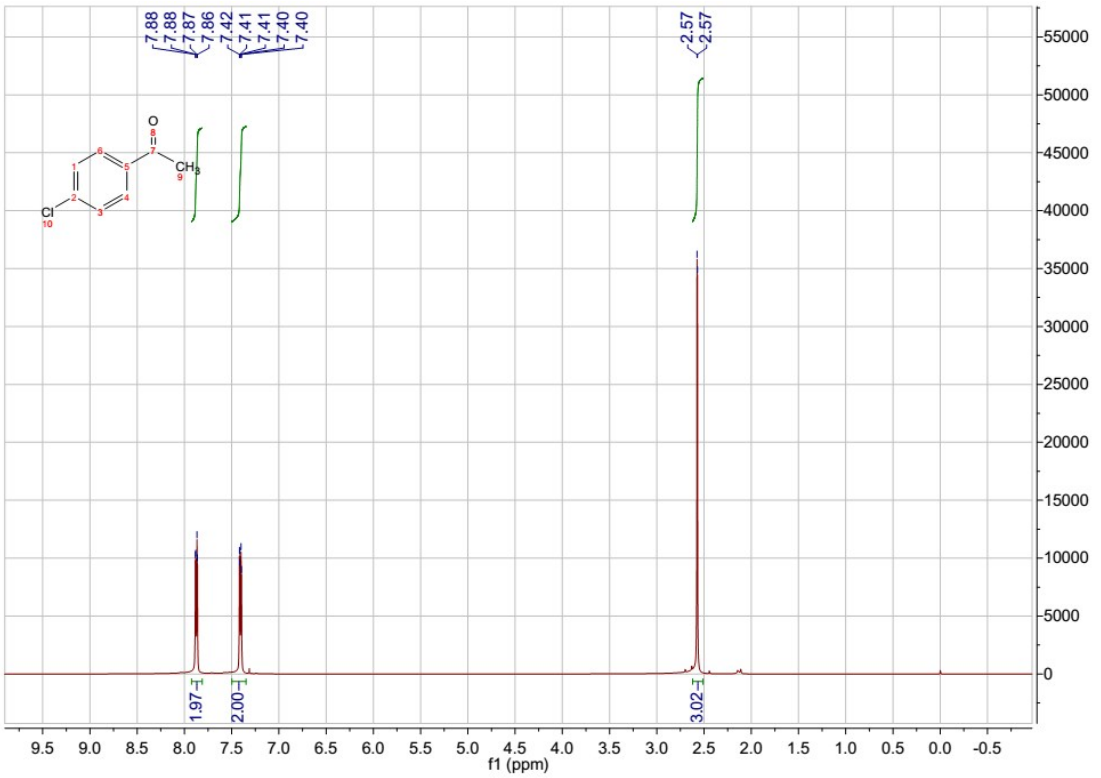
*4-oxopentanoic acid(**2r**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.29 (s, 1H), 2.78-2.75 (m, 2H), 2.63-2.60 (m, 2H), 2.20 (s, 3H).

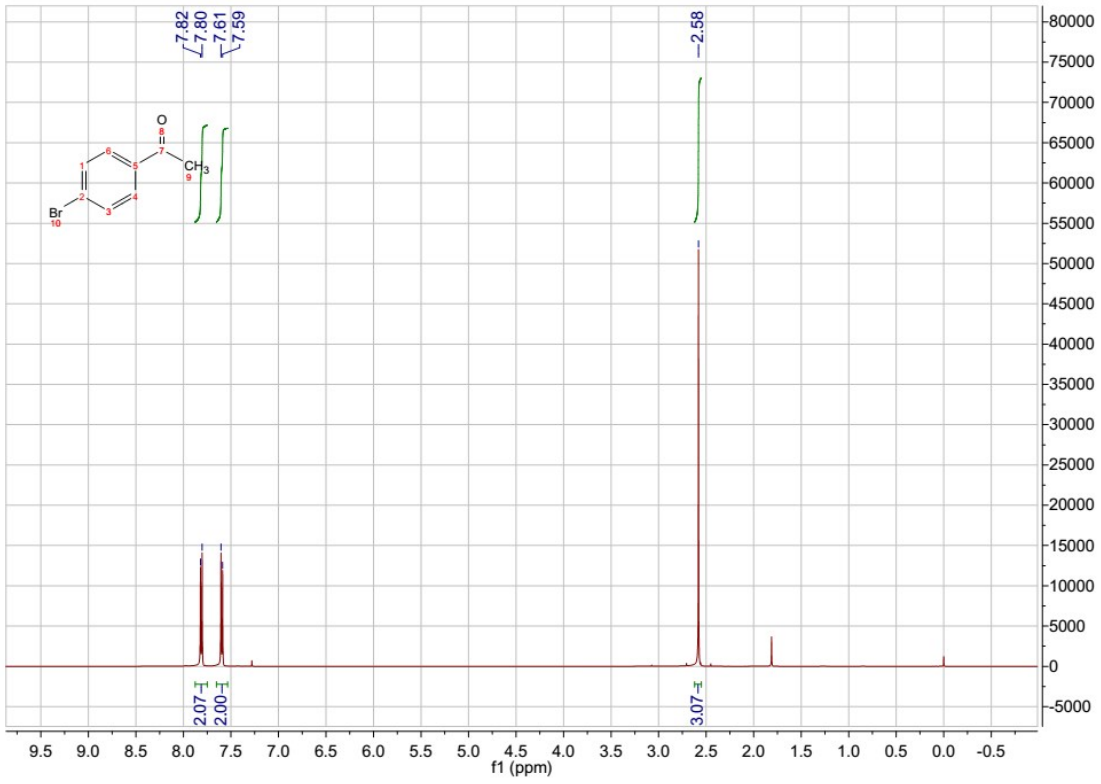
*3-hydroxybutan-2-one(**2s**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.28-4.24 (m, 1H), 3.65 (s, 1H), 2.21 (s, 3H), 1.40 (d, *J* = 7.1 Hz, 3H).

*1-cyclopropylethan-1-one(**2t**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3H), 1.97-1.92 (m, 1H), 1.04-1.00 (m, 2H), 0.90-0.87 (m, 2H).

3. NMR spectra



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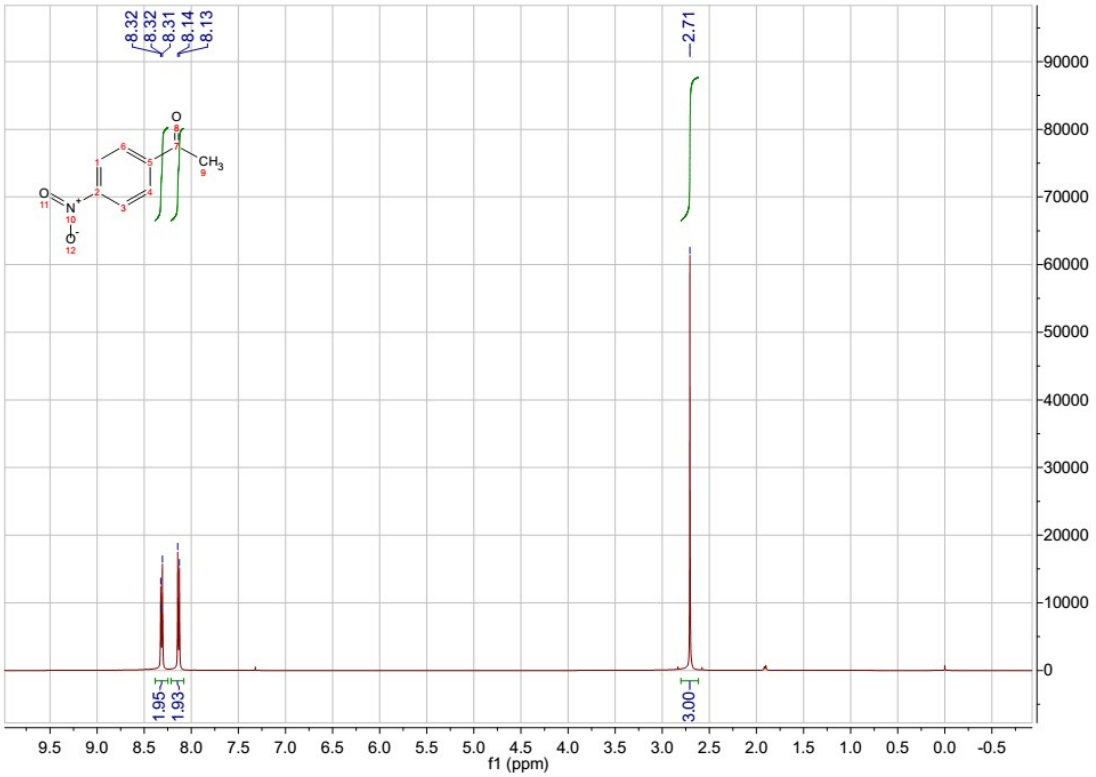
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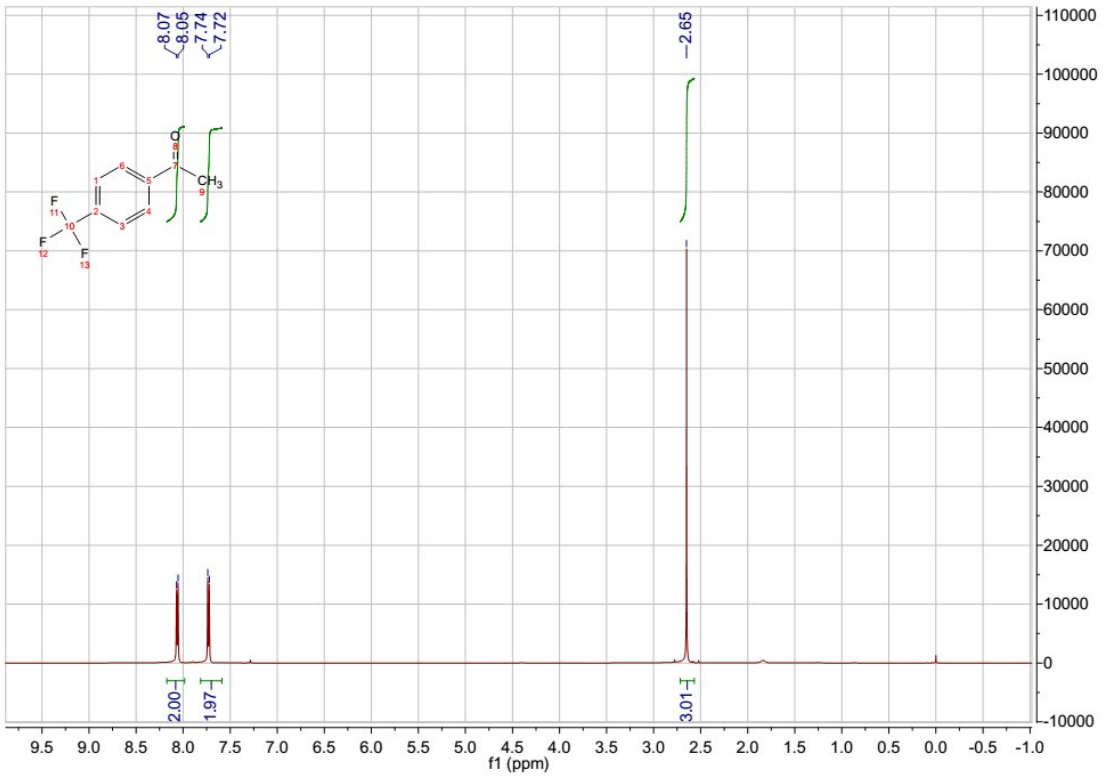
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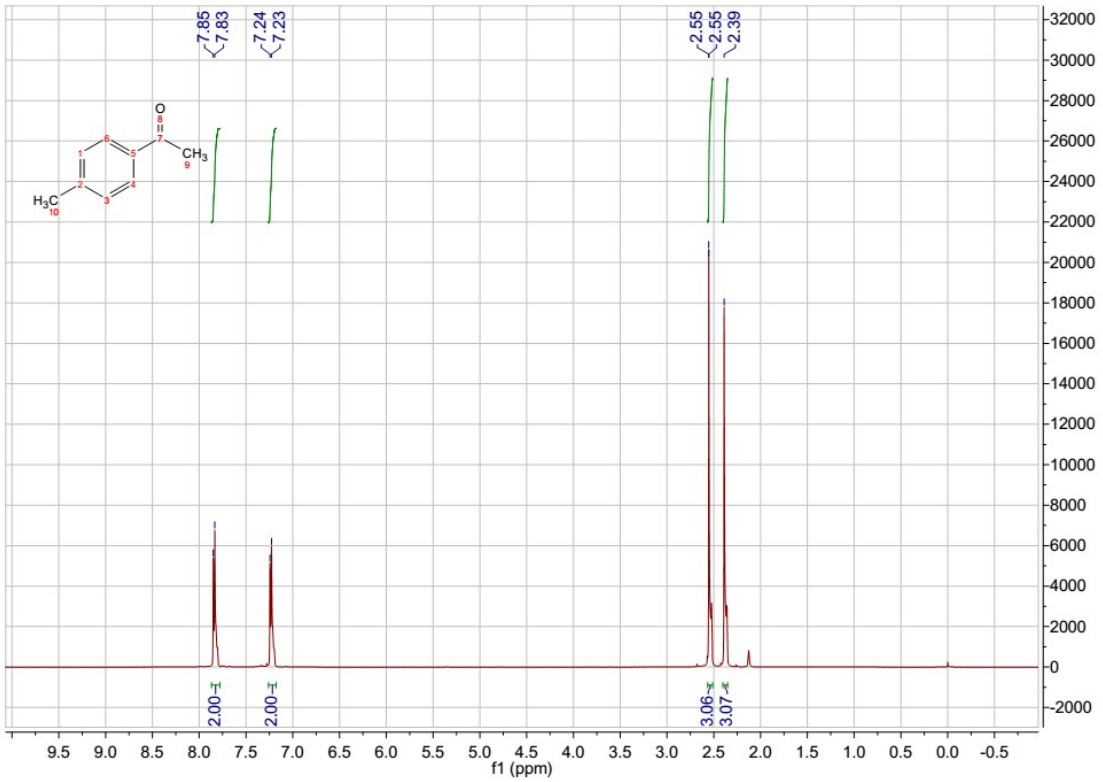
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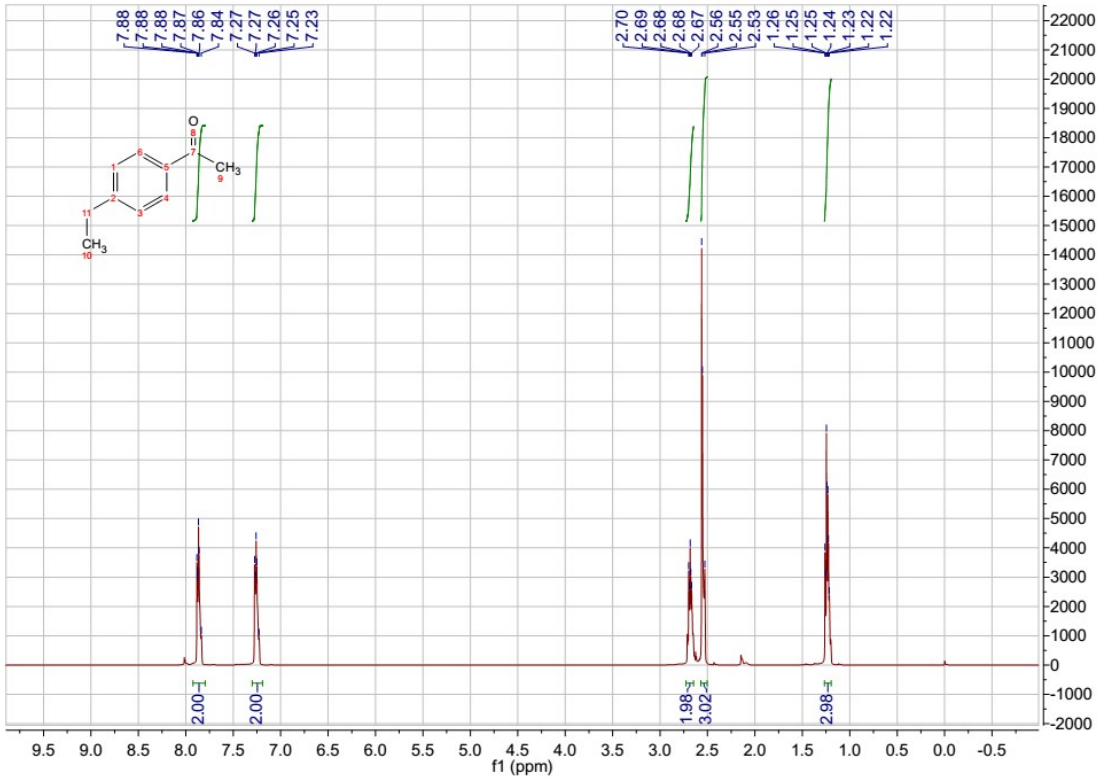
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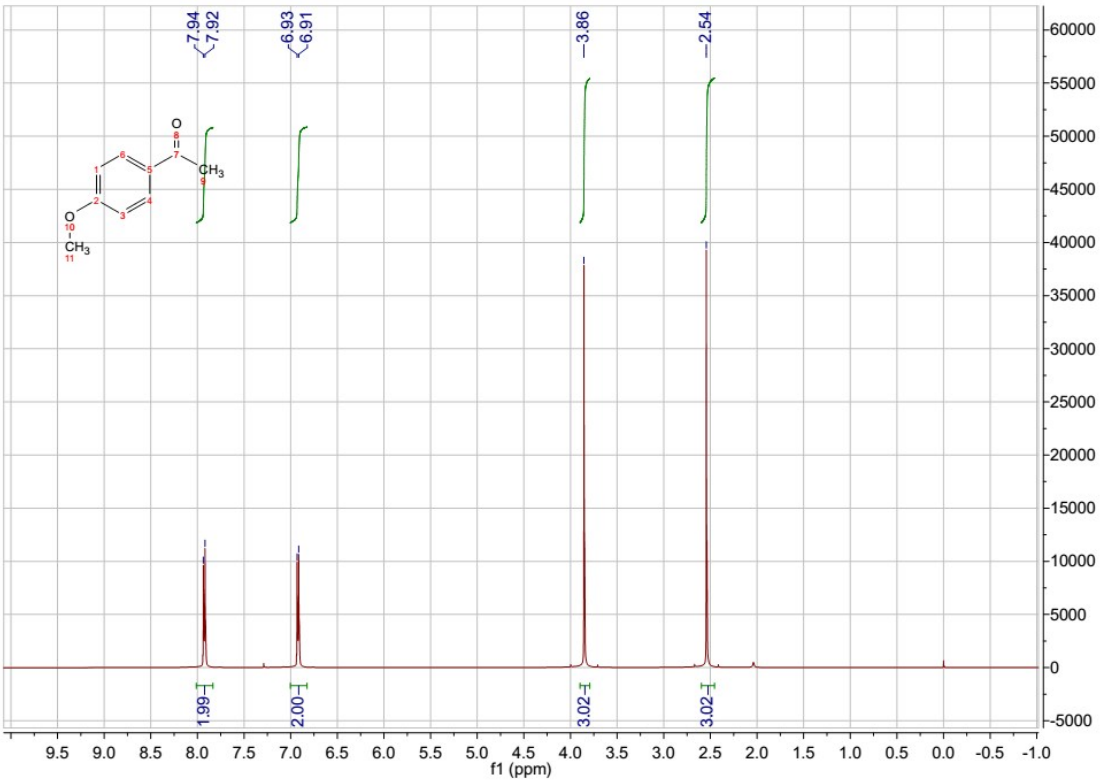
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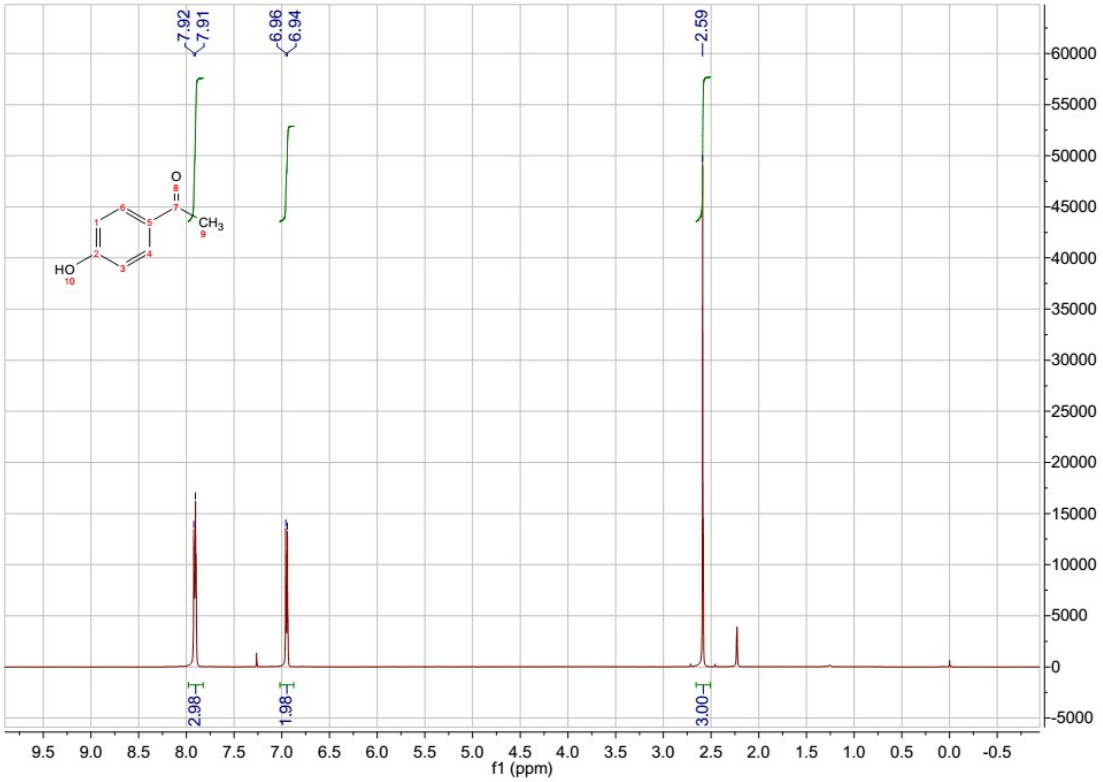
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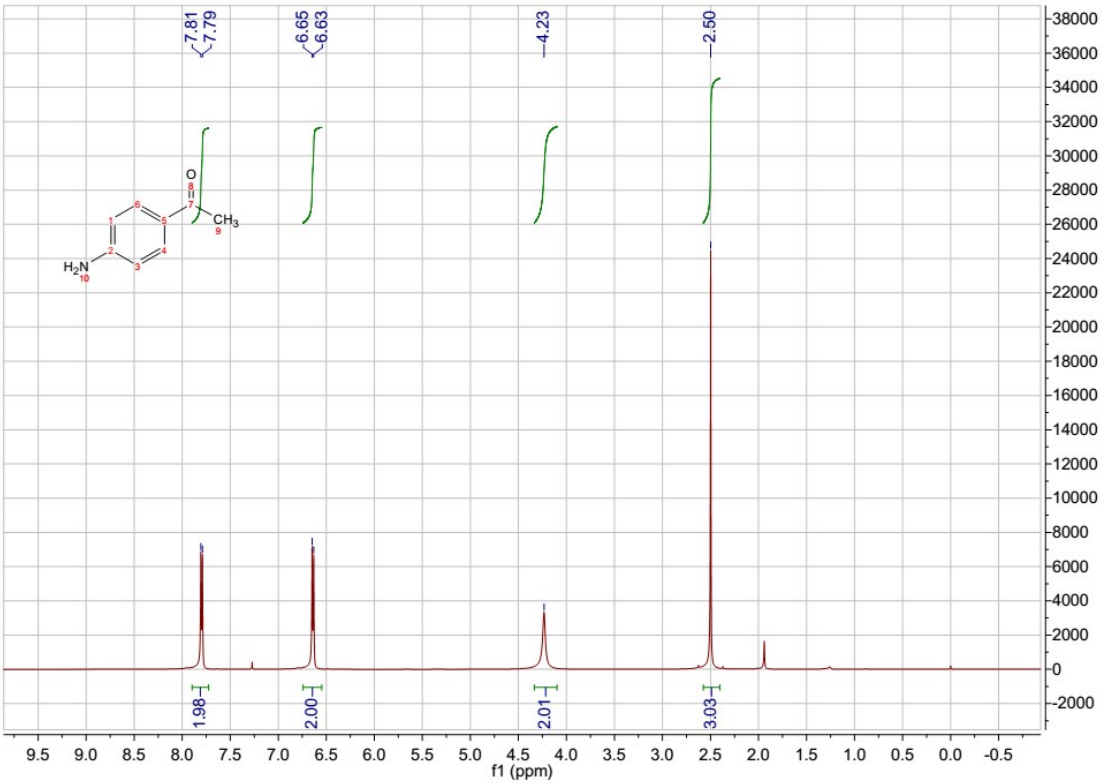
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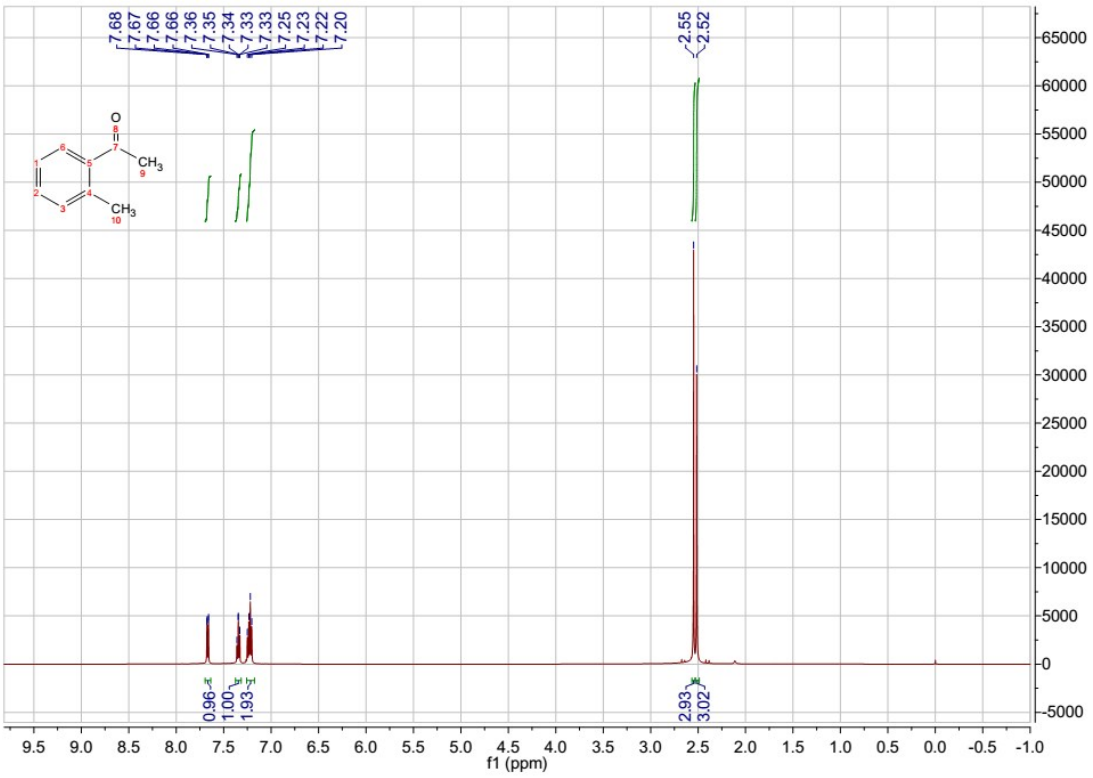
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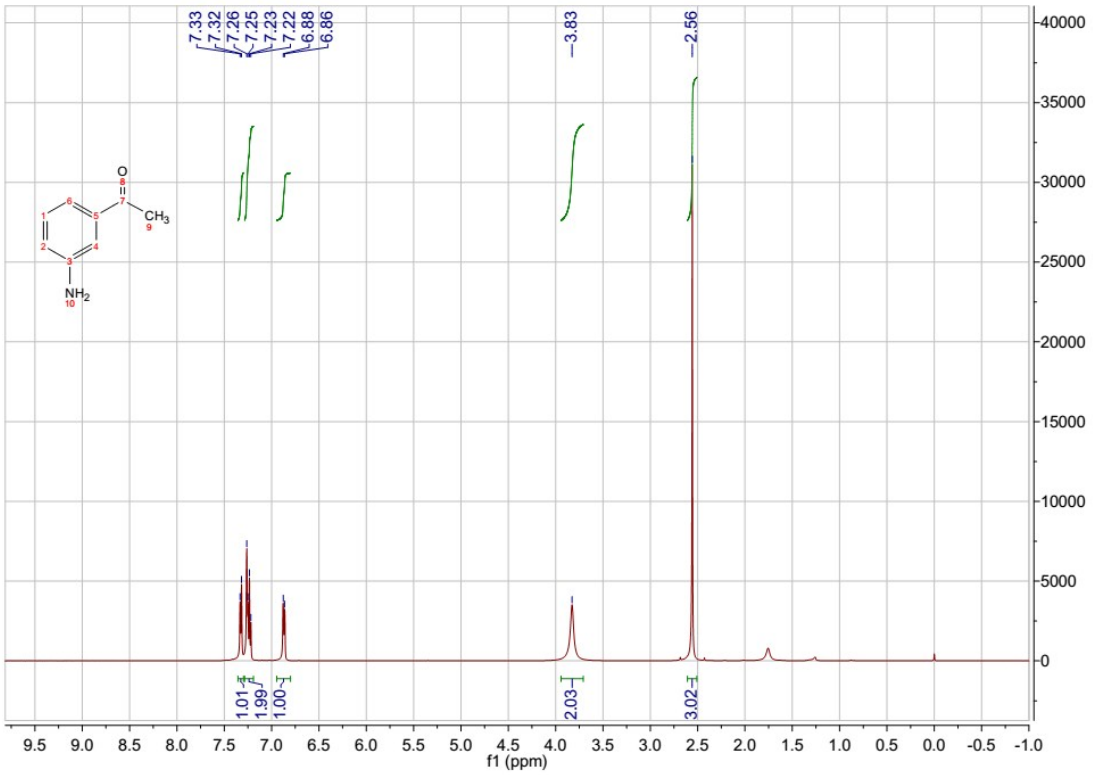
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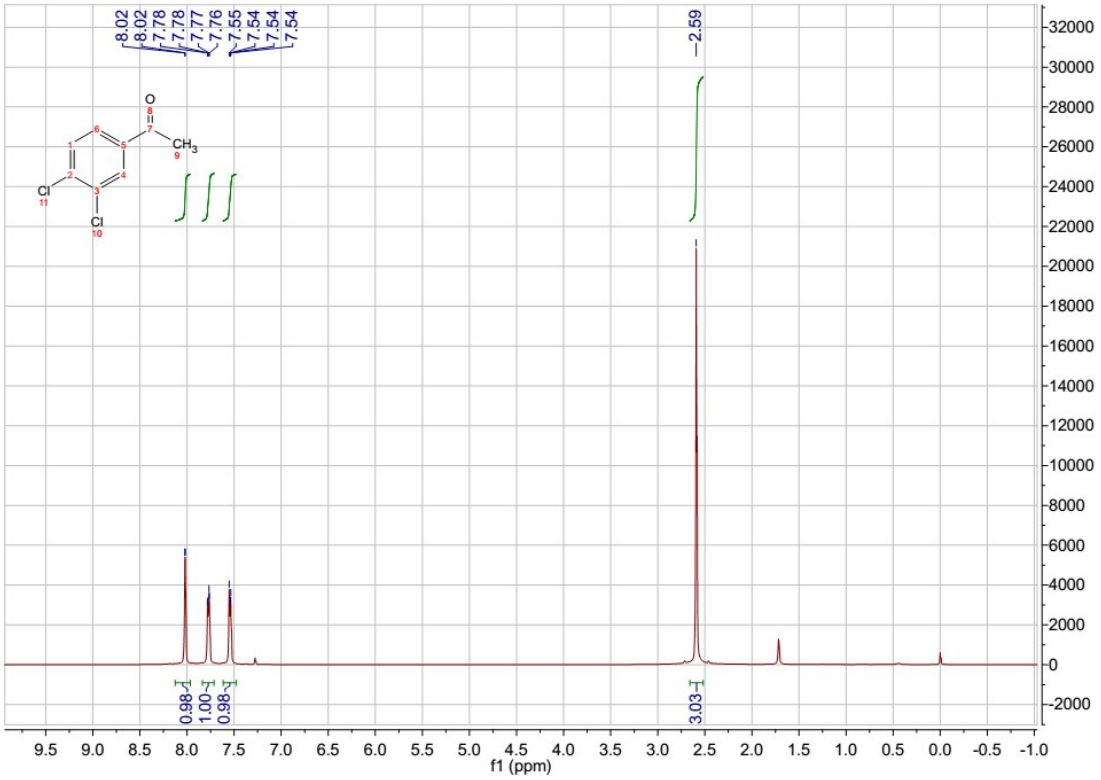
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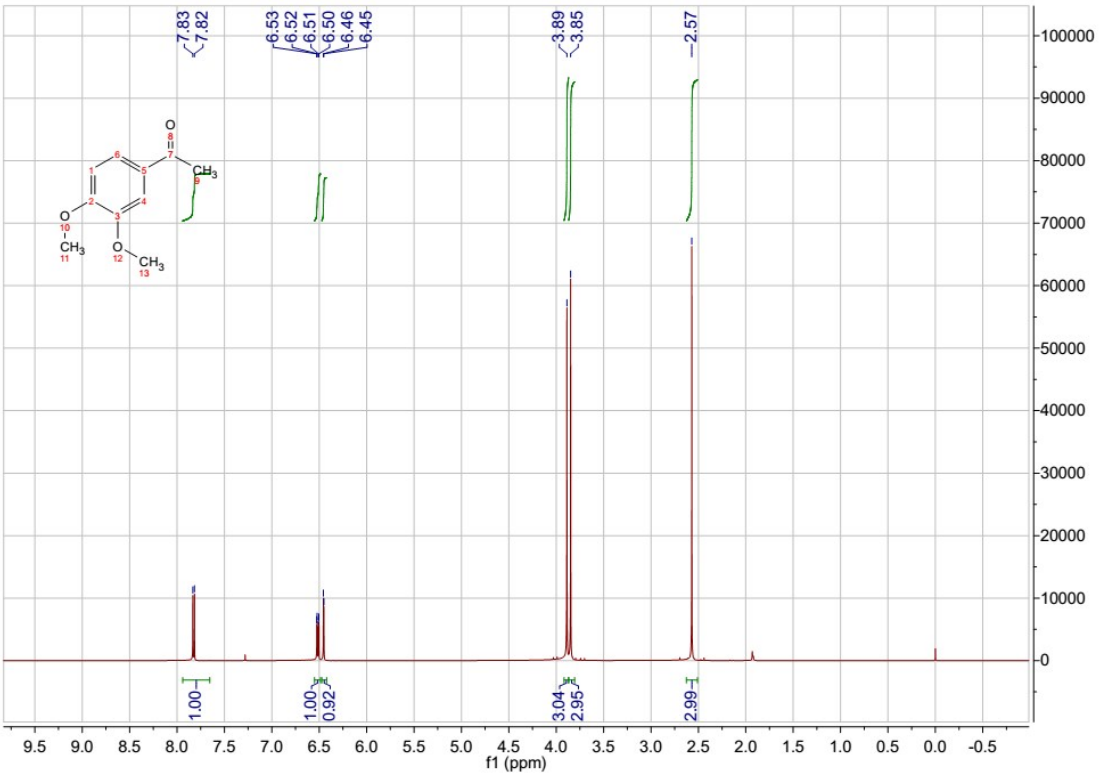
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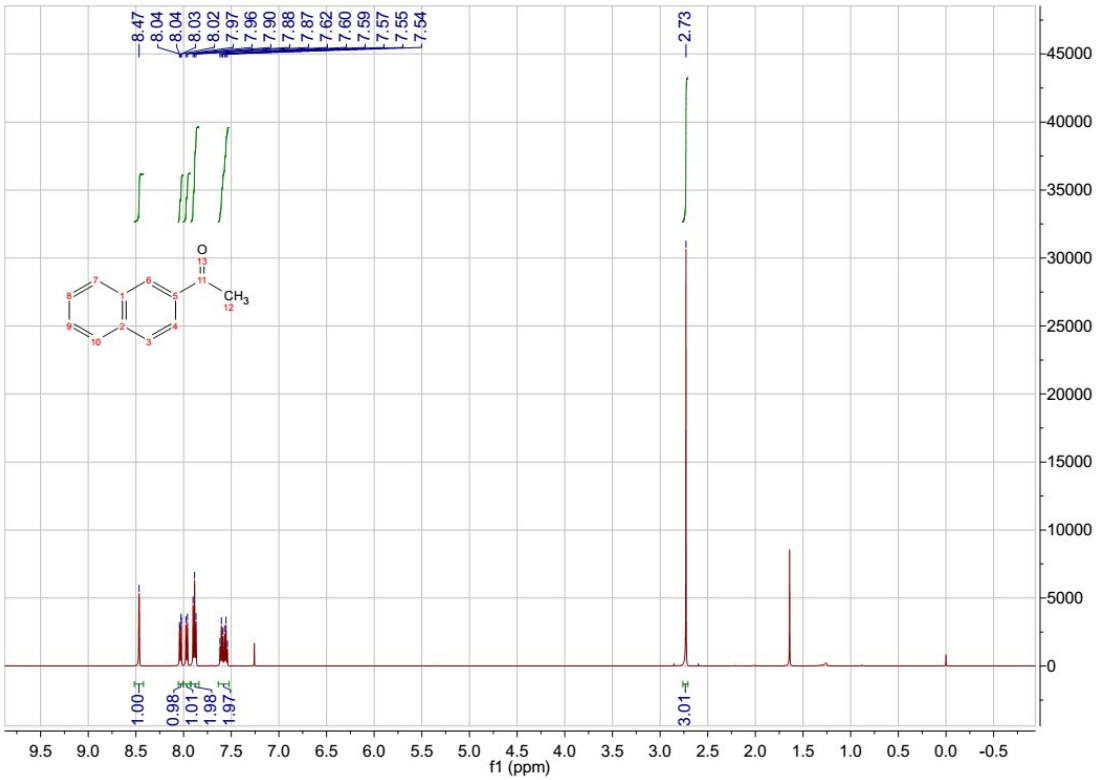
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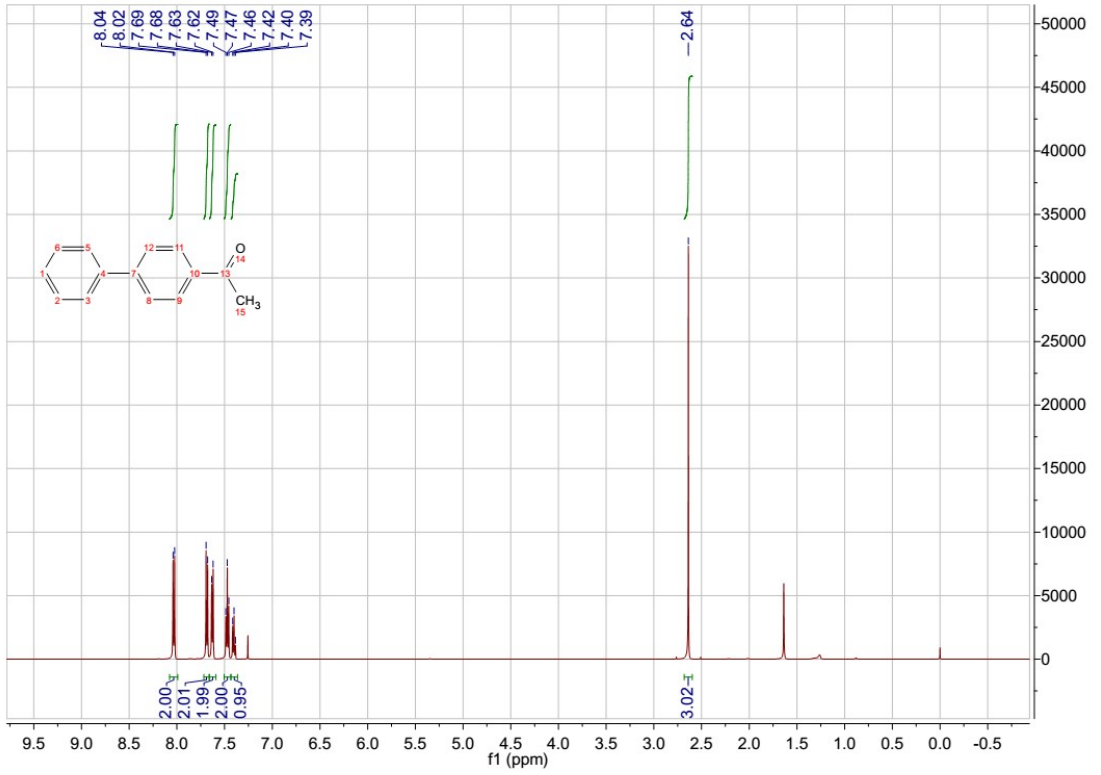
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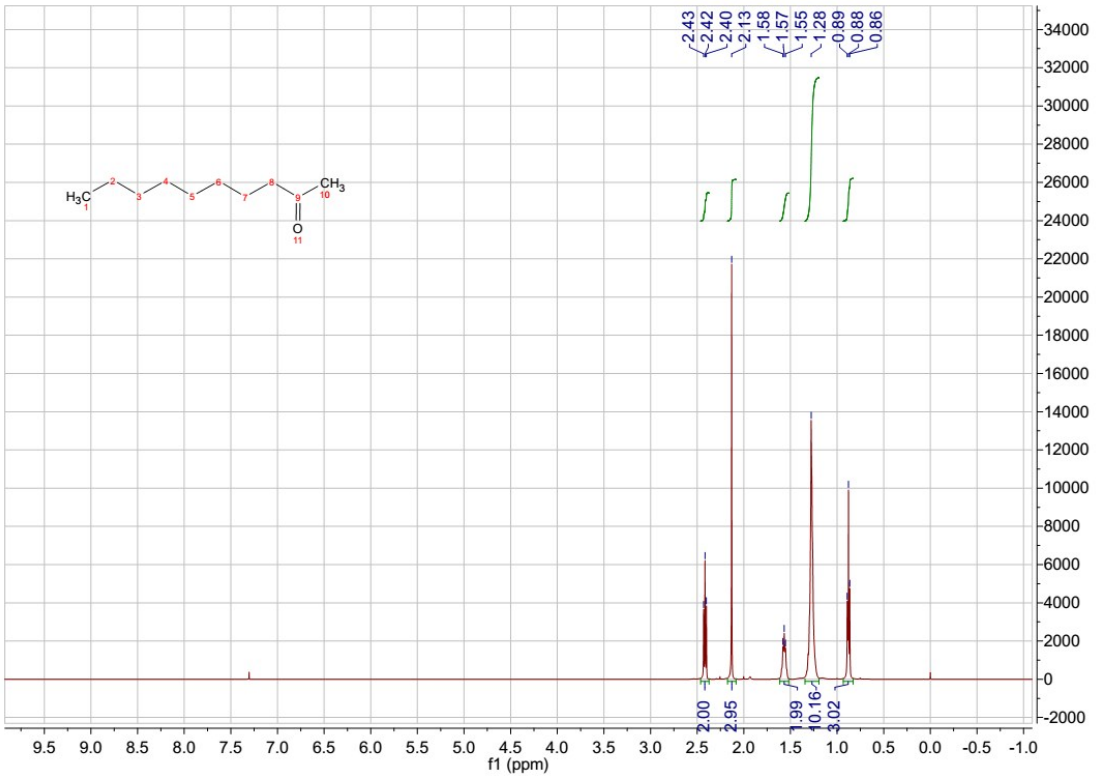
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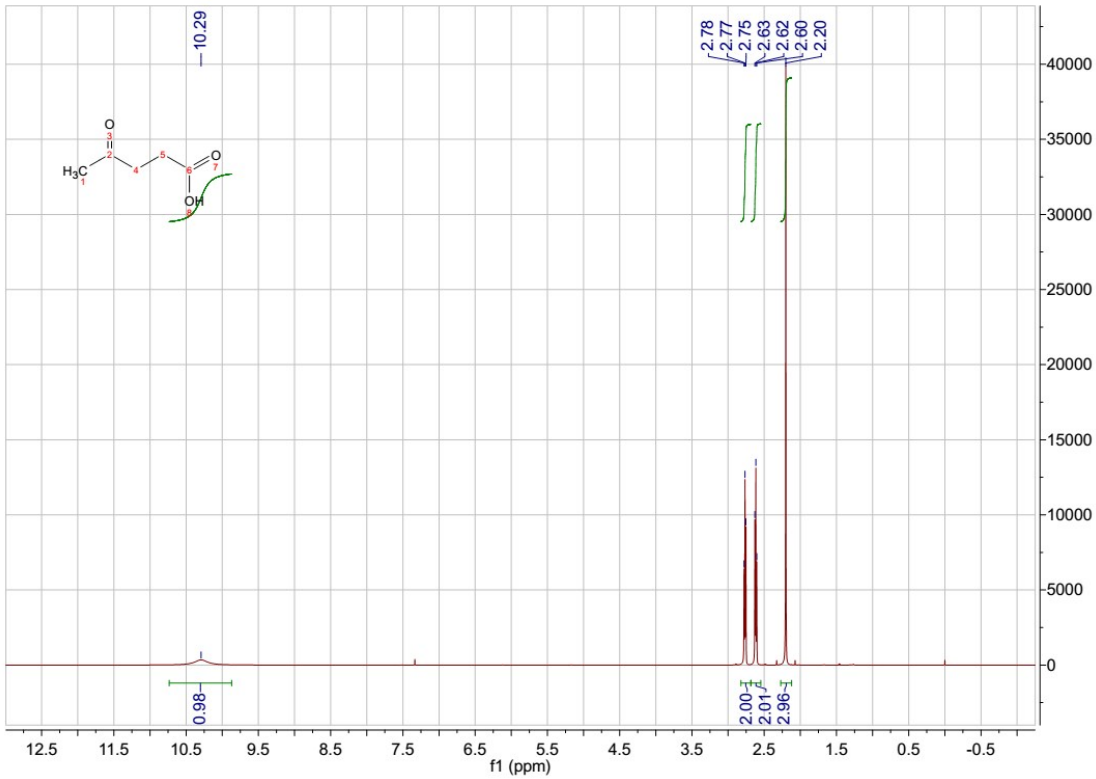
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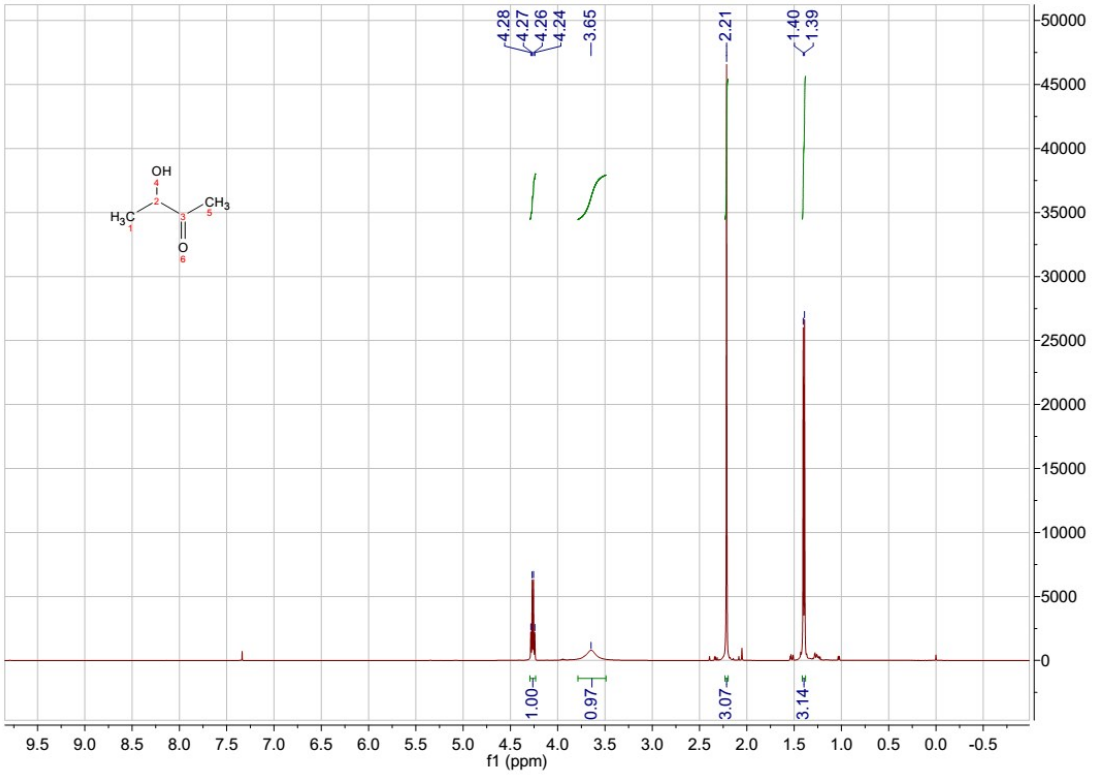
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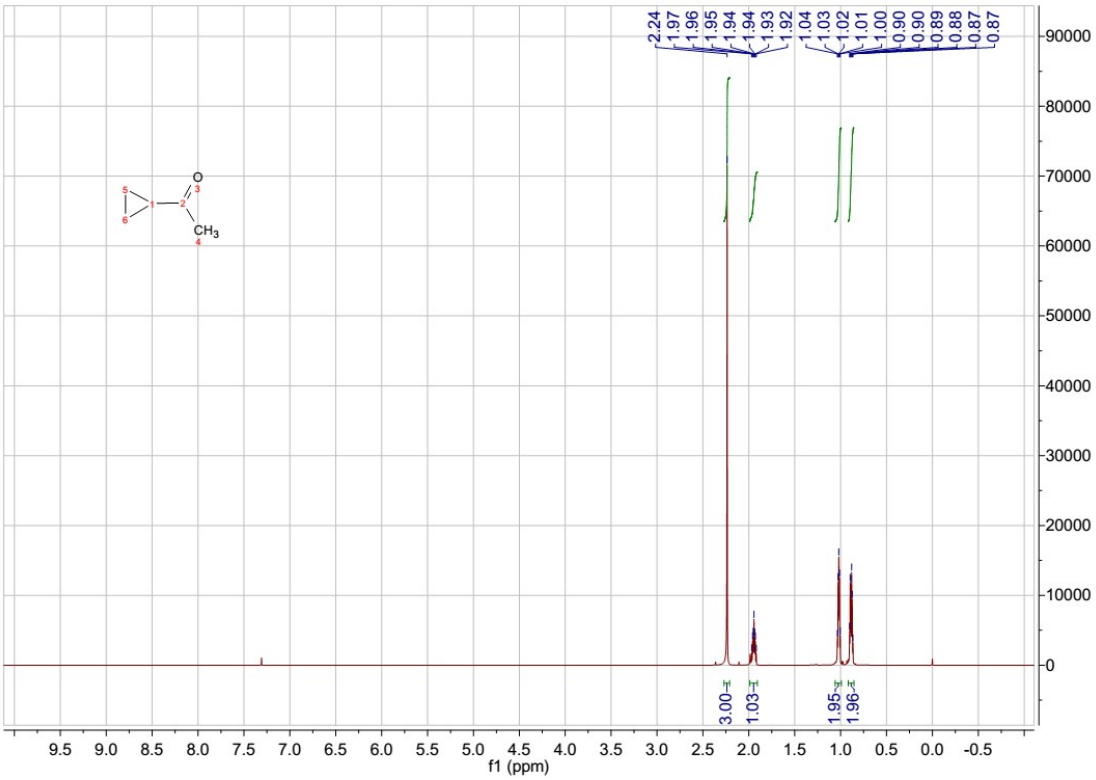
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