Supporting information

Highly Practical Sodium(Ⅰ)/ Azobenzene Catalyst System for Aerobic Oxidation of benzylic Alcohols

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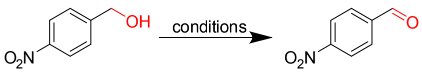
1, General Remarks

Reagents and solvents: Commercially available reagents were used without any further purification. All organic solvents were of reagent grade quality without any further purification.
Chromatography: Flash column chromatography was performed using Silicycle silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 nm or 365 nm).
Nuclear Magnetic Resonance Spectroscopy: ^{1}H NMR was recorded on magnet system 400'54 ascend purchased from Bruker Biospin AG. ^{1}H NMR spectra chemical shifts (δ) are reported in parts per million (ppm) referenced to TMS (0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, m = multiplet, br = broad), coupling constant (J) in Hertz (Hz), and integration.

2, Table S1: The equivalent of NaBr screening



1a 2a

Entry	Catalyst (mol%)	Co-catalyst (equiv.)	T (℃)	Solvent	T(h)	Yield (%)
1	Azobenzene(5)	NaBr(0.2)	80	1,4-Dioxane	48	trace
2	Azobenzene(5)	NaBr(0.5)	80	1,4-Dioxane	48	10
3	Azobenzene(5)	NaBr(1)	80	1,4-Dioxane	48	38
4	Azobenzene(5)	NaBr(2)	80	1,4-Dioxane	48	88
5	Azobenzene(5)	NaBr(3)	80	1,4-Dioxane	48	92

3, General procedure for the oxidation of benzylic alcohols to ketones and aldehydes

The specific benzylic alcohols (1 mmol, 1.0 eq) and sodium bromide (2 mmol, 2 eq) were dissolved in dioxane (3 mL), then azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80℃ under O_2 atmosphere (O_2 balloon). The reaction mixtures were diluted with ethyl acetate and washed with brine and water. The separated organic layers were dried over by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using hexane/ethyl acetate to afford the desired product.

4, General procedure for the oxidation of benzylic 1° alcohols to acids

The specific benzylic 1° alcohols (1 mmol, 1.0 eq) and sodium hydroxide (2 mmol, 2 eq) were dissolved in dioxane (3 mL). Then, azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80℃ under O_2 atmosphere (O_2 balloon). The reaction mixtures were diluted with H_2O and regulated the pH to 1-2 by hydrochloric acid (10%, aq). The product was extracted by ethyl acetate or dichloromethane from the solution before. The separated organic layers were dried over by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using hexane/ethyl acetate or dichloromethane/methanol to afford the desired product.

Benzoic acid (3a), p-toluic acid (3e), 2-furoic acid (3f), 2-thiophenecarboxylic acid (3g)
The specific benzylic 1° alcohols (1 mmol, 1.0 eq) and sodium hydroxide (2 mmol, 2 eq) were dissolved in dioxane (3 mL). Then, azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80℃ under O_2 atmosphere (O_2 balloon). The reaction mixtures were diluted with H_2O and regulated the pH to 1-2 by hydrochloric acid (10%, aq). The product was extracted by ethyl acetate from the solution before. The separated organic layers were dried over by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using hexane/ethyl acetate (2:1) to afford the desired product.

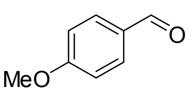
p-Nitrobenzoic acid (3b), 4-Chlorobenzoic acid (3c), 4-Bromobenzoic acid (3d)
The specific benzylic 1° alcohols (1 mmol, 1.0 eq) and sodium hydroxide (2 mmol, 2 eq) were dissolved in dioxane (3 mL). Then, azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80℃ under O_2 atmosphere (O_2 balloon). The reaction mixtures were diluted with H_2O and regulated the pH to 1-2 by hydrochloric acid (10%, aq). The product was extracted by dichloromethane from the solution before. The separated organic layers were dried over by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using dichloromethane/methanol (30:1) to afford the desired product.

Nicotinic acid (3h)
3-Pyridinemethanol (1 mmol, 1.0 eq) and sodium hydroxide (2 mmol, 2 eq) were dissolved in dioxane (3 mL). Then, azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80℃ under O_2 atmosphere (O_2 balloon). The reaction mixtures were diluted with H_2O and regulated the pH to 3-4 by hydrochloric acid (10%, aq). The product was extracted by dichloromethane from the solution before. The separated organic layers were dried over by anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using dichloromethane/methanol (10:1) to afford the desired product.

5, Characterization Data of the products

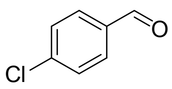
All the products were characterized by ^{1}H NMR spectroscopy and compared with literature reported data.

Anisic aldehyde



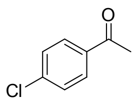
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.77 – 7.72 (m, 2H), 6.94 – 6.89 (m, 2H), 3.79 (s, 3H). Spectral data are in accordance with the literature report.[1-2]

4-Chlorobenzaldehyde



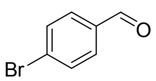
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.78 – 7.76 (m, 1H), 7.75 – 7.74 (m, 1H), 7.47 – 7.45 (m, 1H), 7.45 – 7.43 (m, 1H). Spectral data are in accordance with the literature report.[1]

4'-Chloroacetophenone



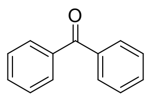
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 1H), 7.81 – 7.80 (m, 1H), 7.38 – 7.36 (m, 1H), 7.35 – 7.34 (m, 1H), 2.51 (s, 3H).

4-Bromobenzaldehyde



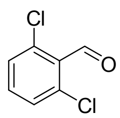
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H).

Benzophenone



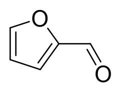
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 4H), 7.62 – 7.56 (m, 2H), 7.52 – 7.46 (m, 4H). Spectral data are in accordance with the literature report.[2]

2, 6-Dichlorobenzaldehyde.



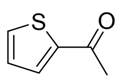
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.33 (s, 3H). Spectral data are in accordance with the literature report.[1]

Furfural



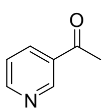
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.64 – 7.62 (m, 1H), 7.19 (dd, *J* = 3.6, 0.5 Hz, 1H), 6.54 (dd, *J* = 3.6, 2 Hz, 1H). Spectral data are in accordance with the literature report.[3]

2-Acetylthiophene



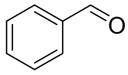
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.06 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.50 (s, 3H). Spectral data are in accordance with the literature report.[3]

3-Acetylpyridine



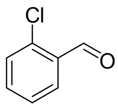
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 2.1 Hz, 1H), 8.71 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.16 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.36 (dd, *J* = 8.0, 4.8 Hz, 1H), 2.57 (s, 3H). Spectral data are in accordance with the literature report.[4]

Benzaldehyde



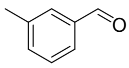
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.83 – 7.78 (m, 2H), 7.58 – 7.53 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H). Spectral data are in accordance with the literature report.[1]

2-Chlorobenzaldehyde



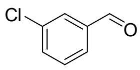
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.84 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.37 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H).

m-Tolualdehyde



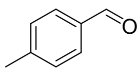
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.58 (m, 2H), 7.37 – 7.30 (m, 2H), 2.33 (s, 3H).

3-Chlorobenzaldehyde



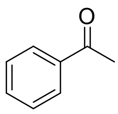
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.77 (t, *J* = 1.6 Hz, 1H), 7.69 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.0, 2.4, 1.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H).

p-Tolualdehyde



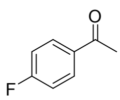
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 3H). Spectral data are in accordance with the literature report.[1]

Acetophenone



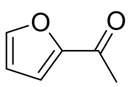
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.41 – 7.35 (m, 2H), 2.52 (s, 3H). Spectral data are in accordance with the literature report.[1]

4-Fluoroacetophenone



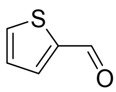
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.04 (m, 2H), 2.51 (s, 3H).

2-Acetylfuran



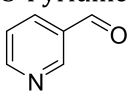
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 1H), 7.12 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.47 (dd, *J* = 3.5, 1.7 Hz, 1H), 2.41 (s, 3H). Spectral data are in accordance with the literature report.[3]

2-Thenaldehyde



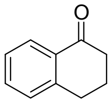
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (d, *J* = 1.2 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.14 (dd, *J* = 4.8, 3.8 Hz, 1H). Spectral data are in accordance with the literature report.[2]

3-Pyridinecarboxaldehyde



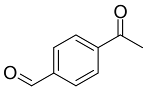
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 9.02 (dd, *J* = 1.6 Hz,0.4 Hz,1H), 8.78 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.11 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.43 (dd, *J* = 7.9, 4.8 Hz, 1H). Spectral data are in accordance with the literature report.[1]

1-Tetralone



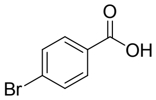
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 6.4 Hz, 1H), 2.88 (t, *J* = 6.1 Hz, 2H), 2.61 – 2.53 (t, *J* = 6 Hz, 2H), 2.10 – 2.01 (m, 2H).

1-Acetyl-4-formylbenzene



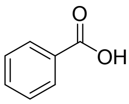
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.93 – 7.90 (m, 2H), 2.60 (s, 3H).

4-Bromobenzoic acid



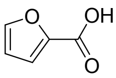
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.57 – 7.53 (m, 2H).

Benzoic acid



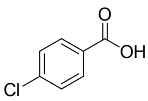
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H).

2-Furoic acid



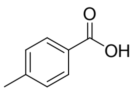
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.59 – 7.57 (m, 1H), 7.28 – 7.26 (m, 1H), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H).

4-Chlorobenzoic acid



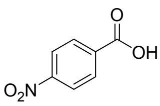
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H).

p-Toluic acid



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 2.36 (s, 3H).

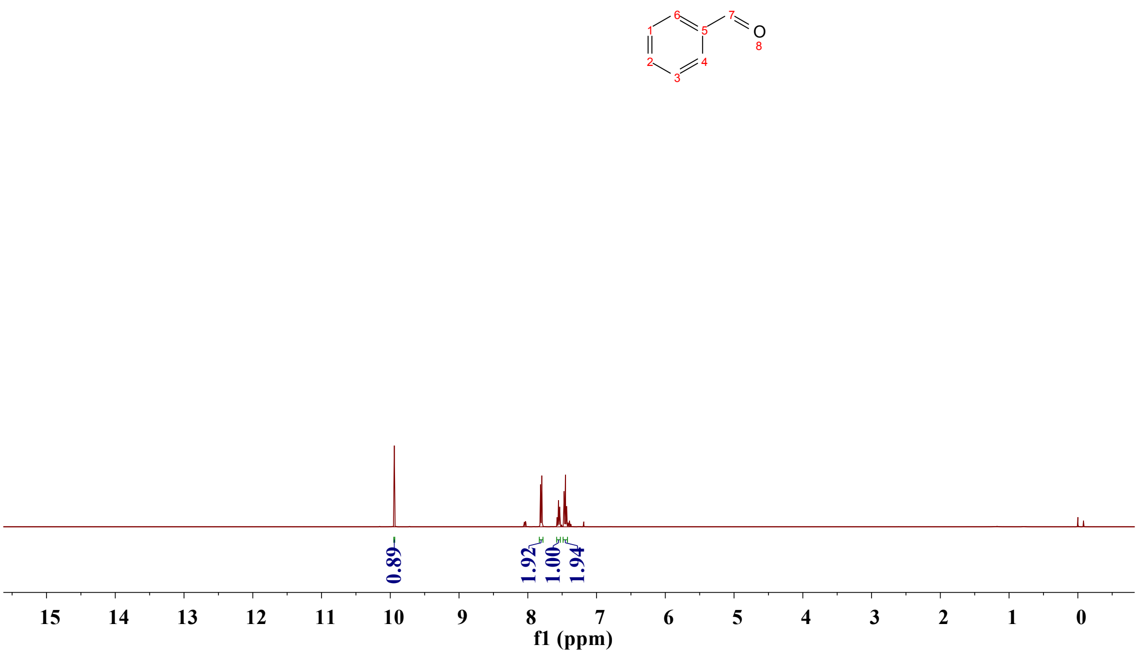
p-Nitrobenzoic acid



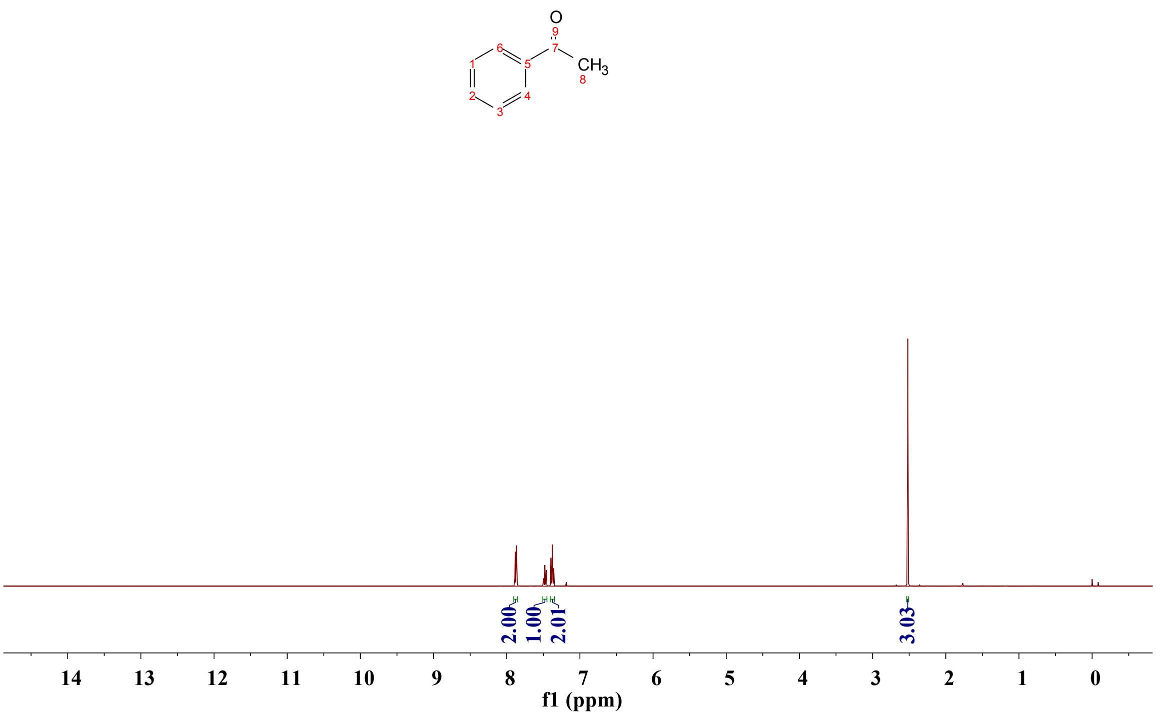
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (m 2H), 8.23 – 8.19 (m, 2H).

6, ^{1}H spectra

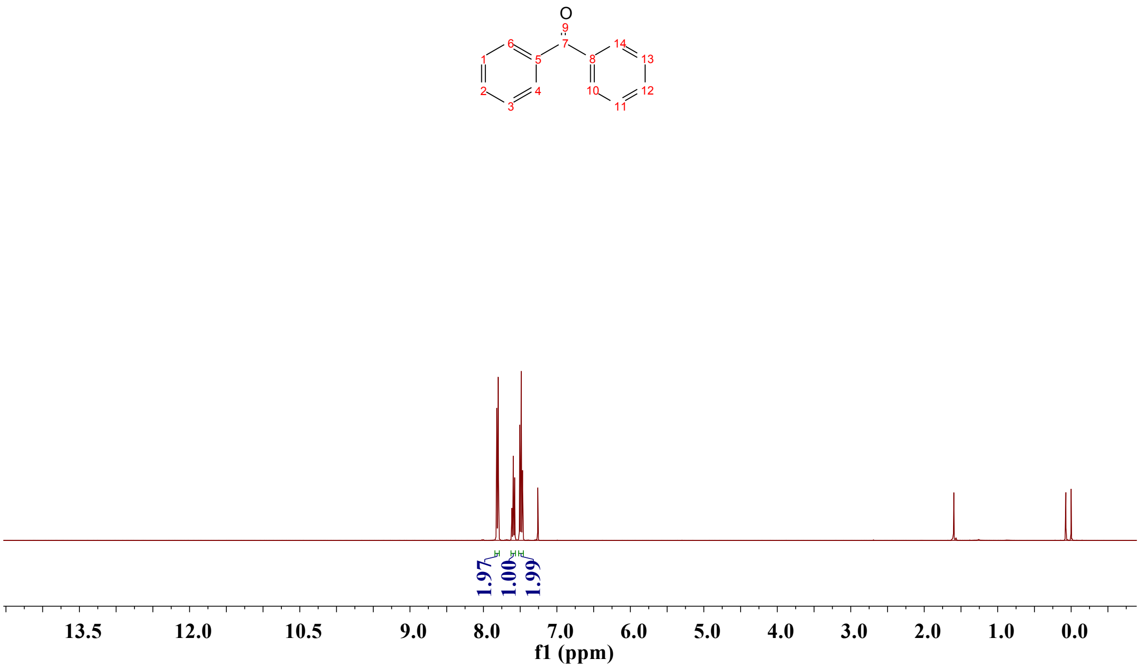
Yu-1
Yu-1



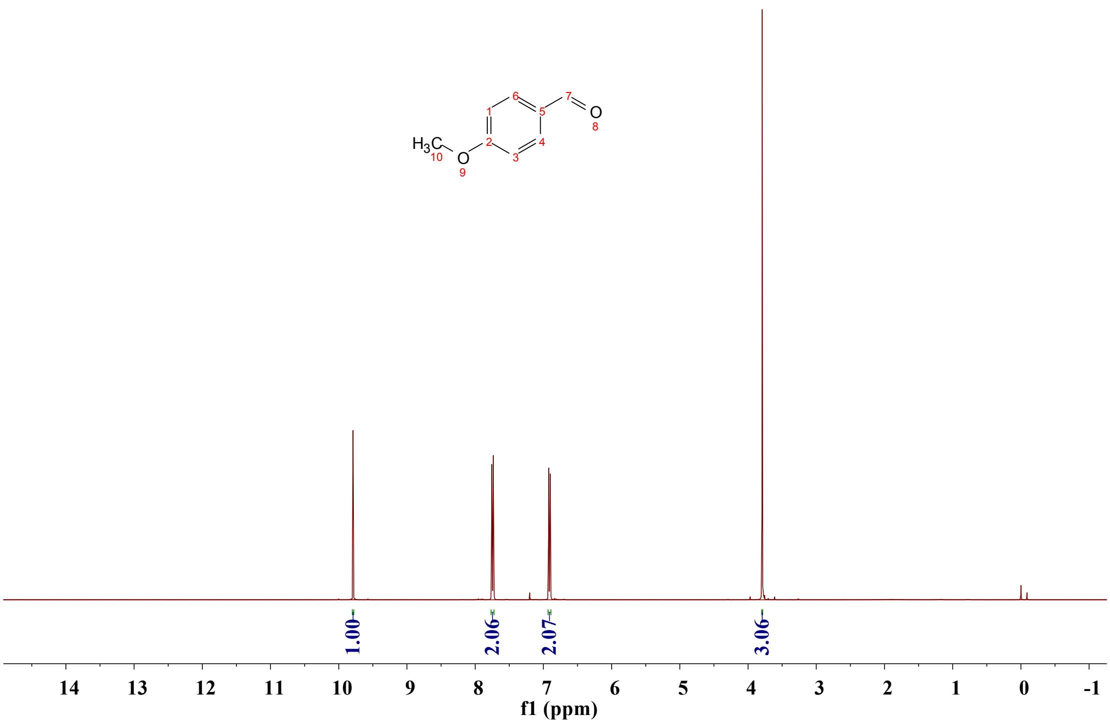
Yu-2
Yu-2



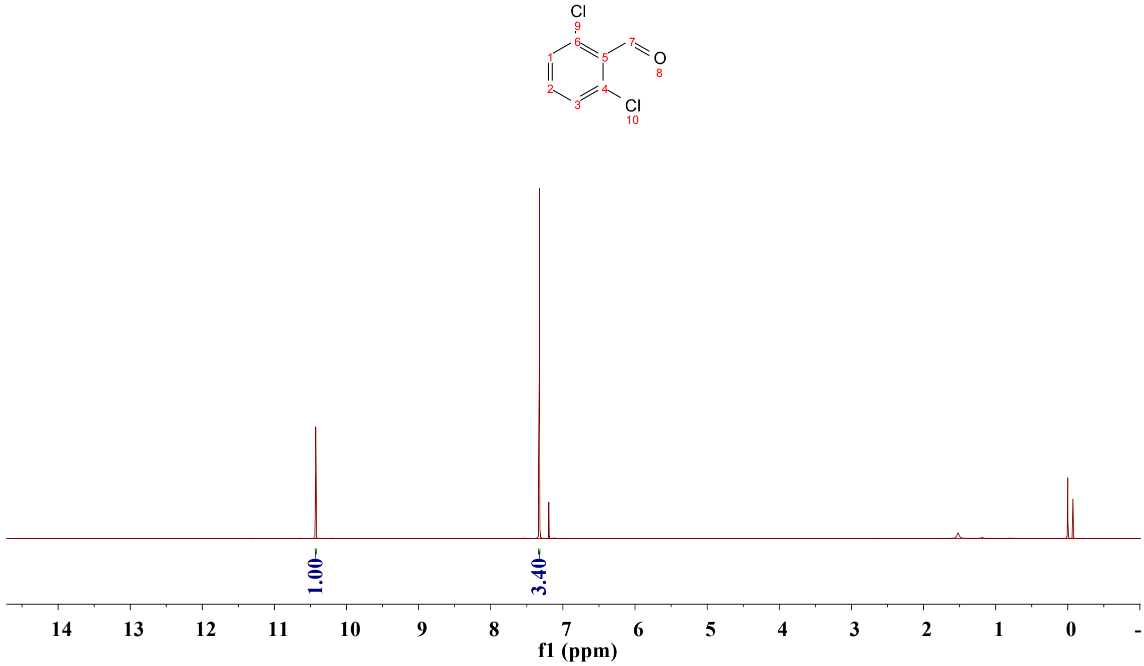
Yu-3
Yu-3



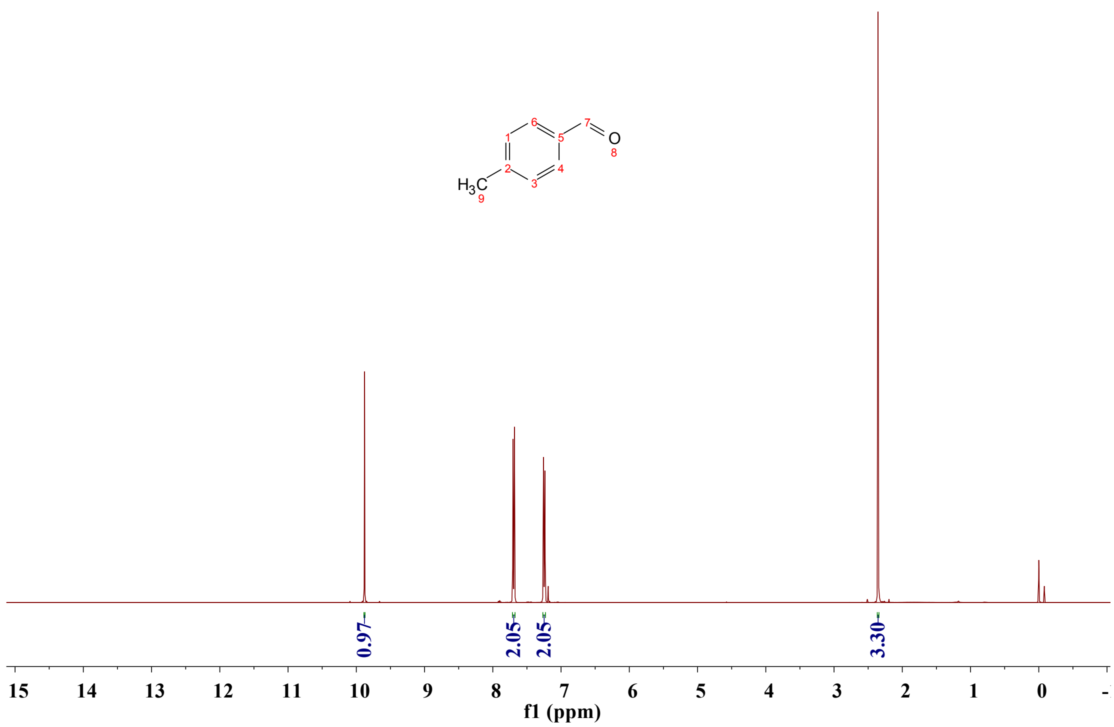
Yu-4
Yu-4



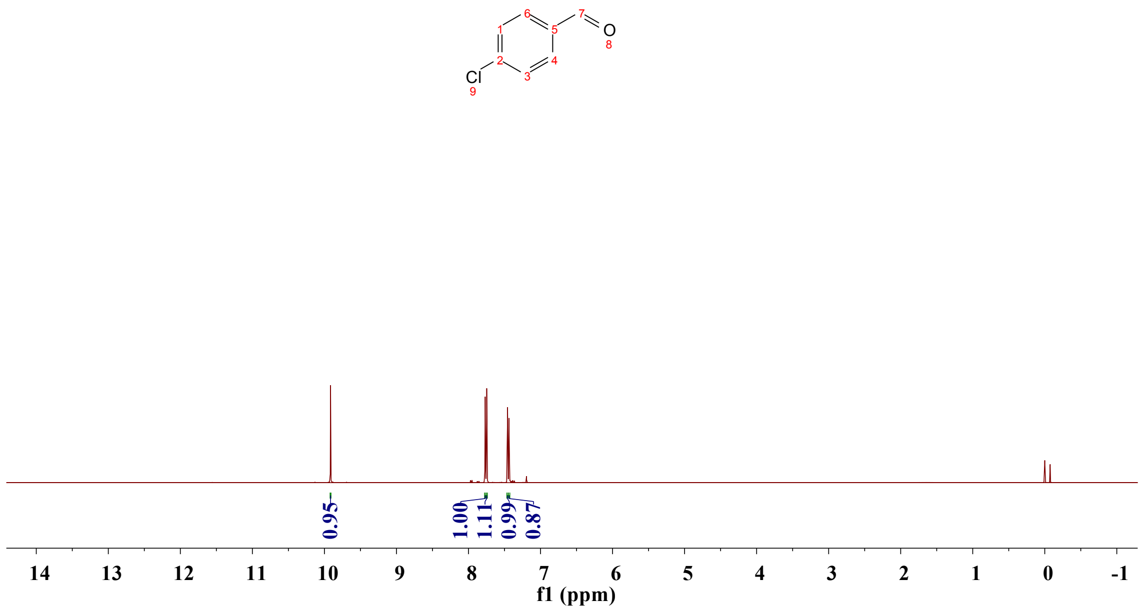
Yu-5
Yu-5



Yu-6
Yu-6



Yu-7
Yu-7



Yu-8
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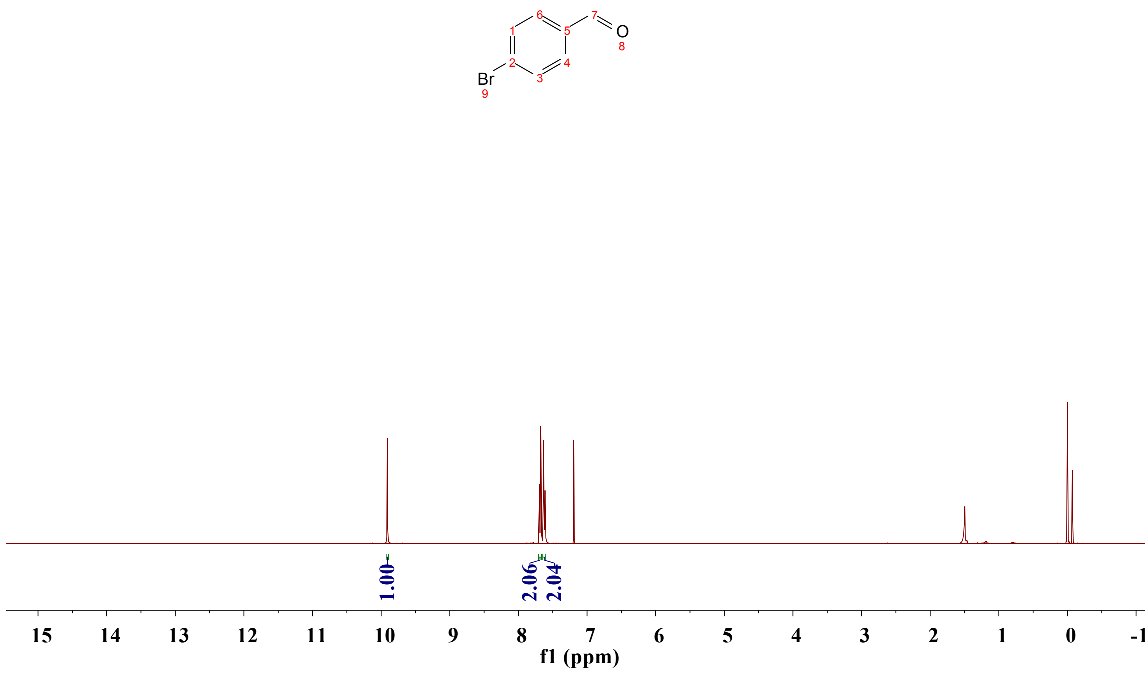
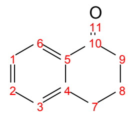
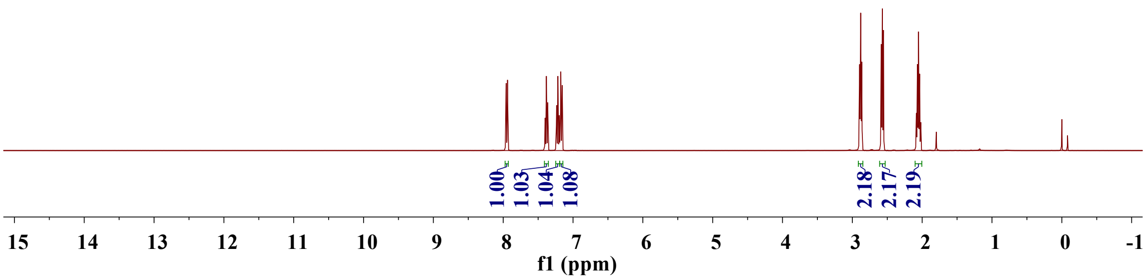


Yu-9
Yu-9





YH-11
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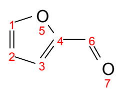

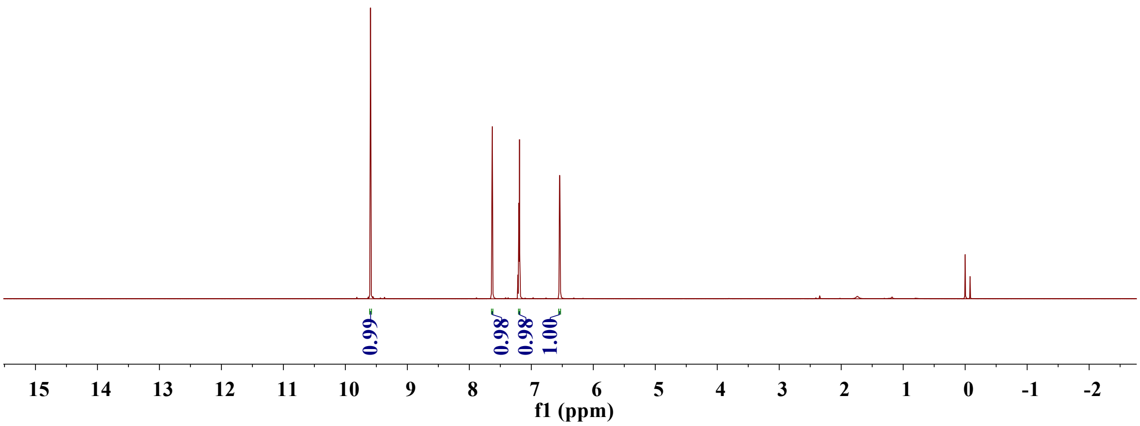

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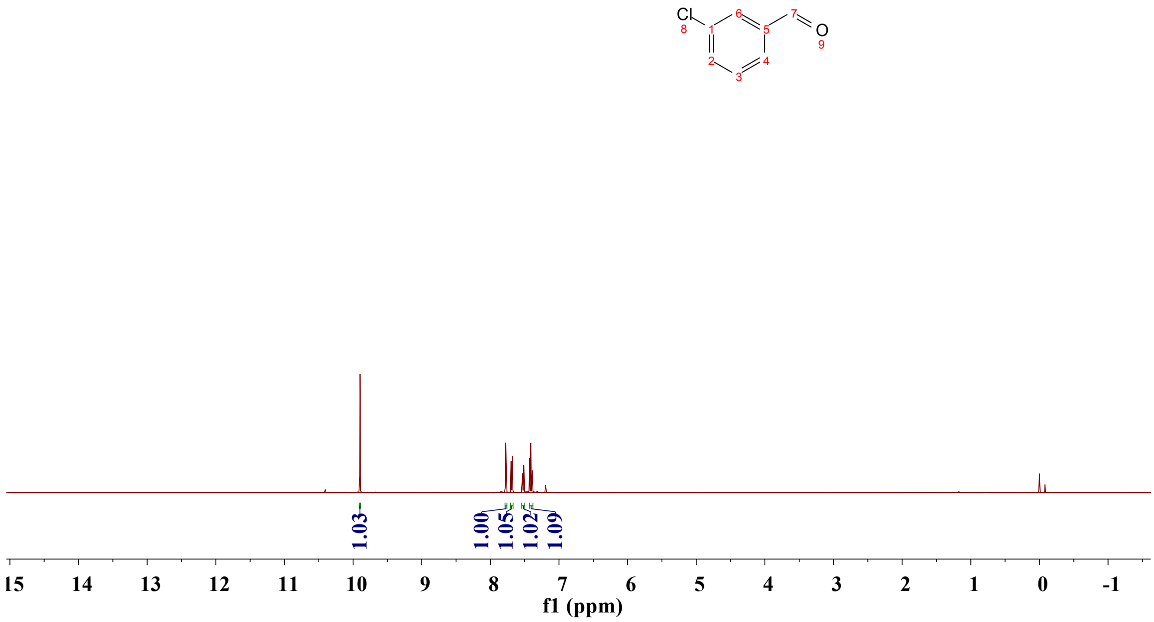
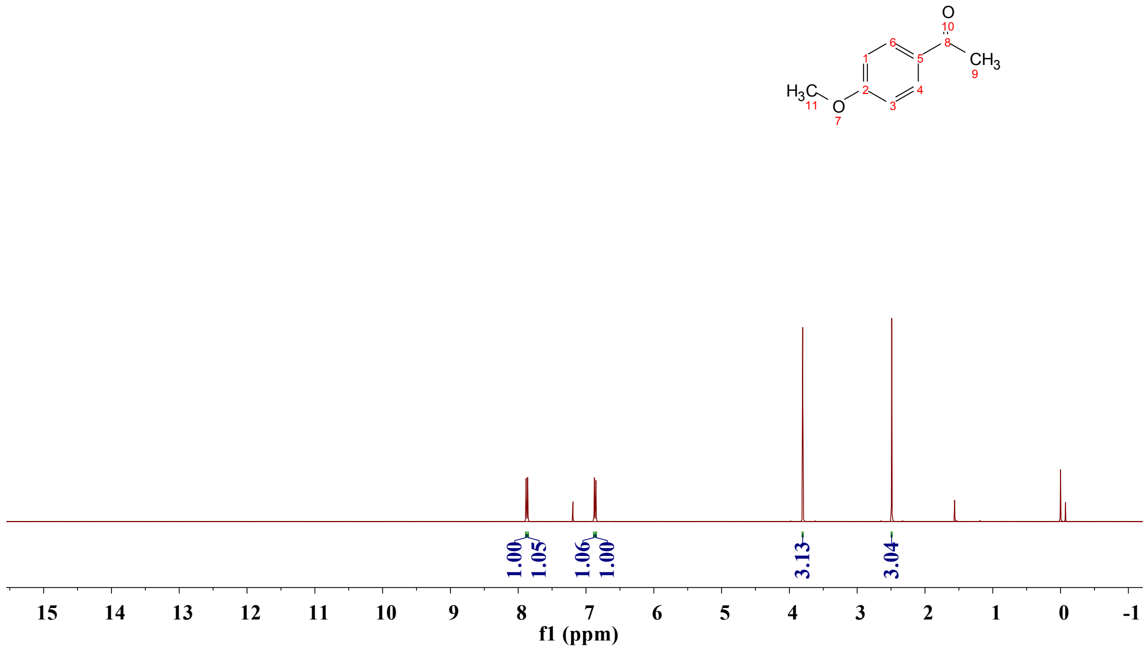


YH-13
YH-13



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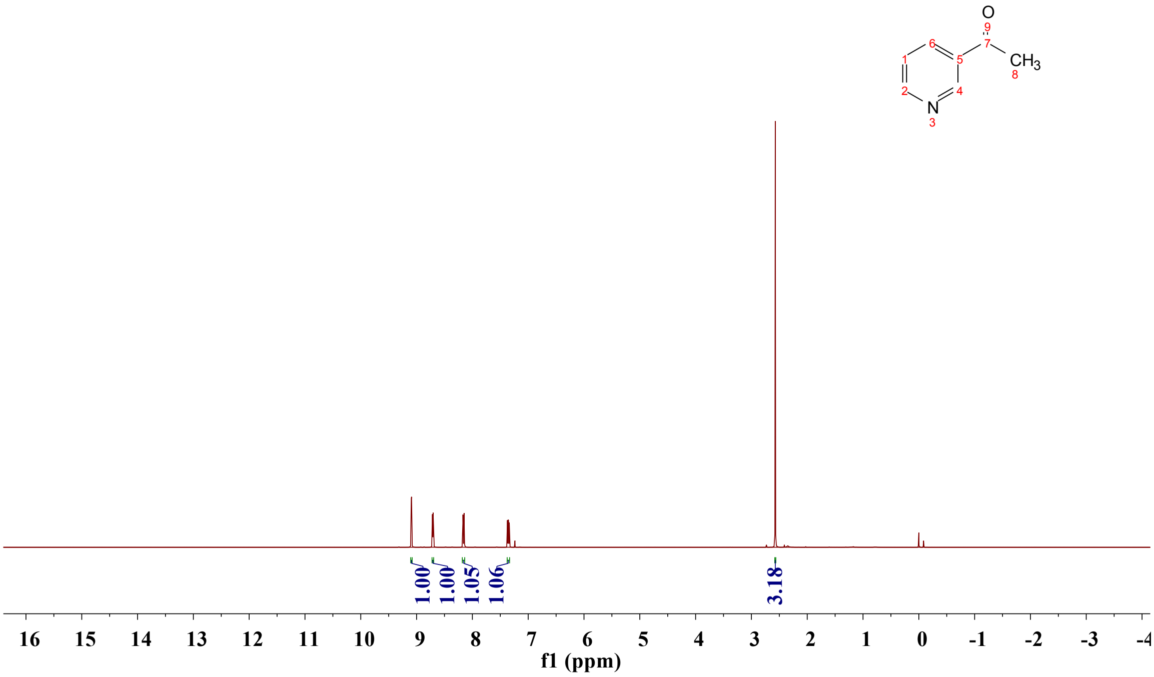
YH-14



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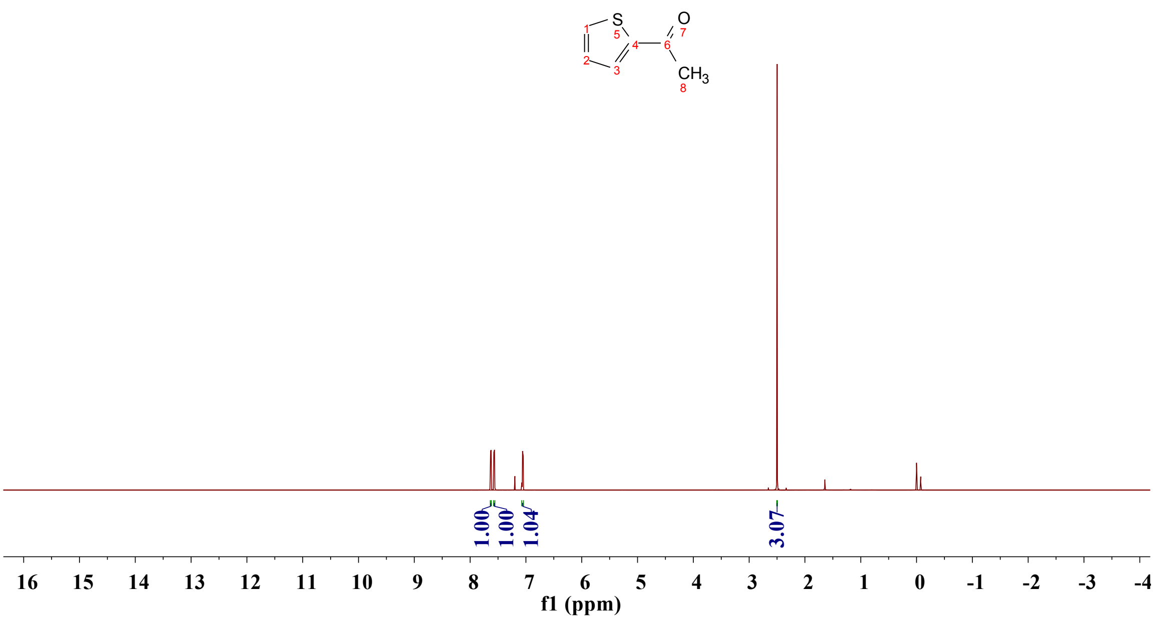
YH-15



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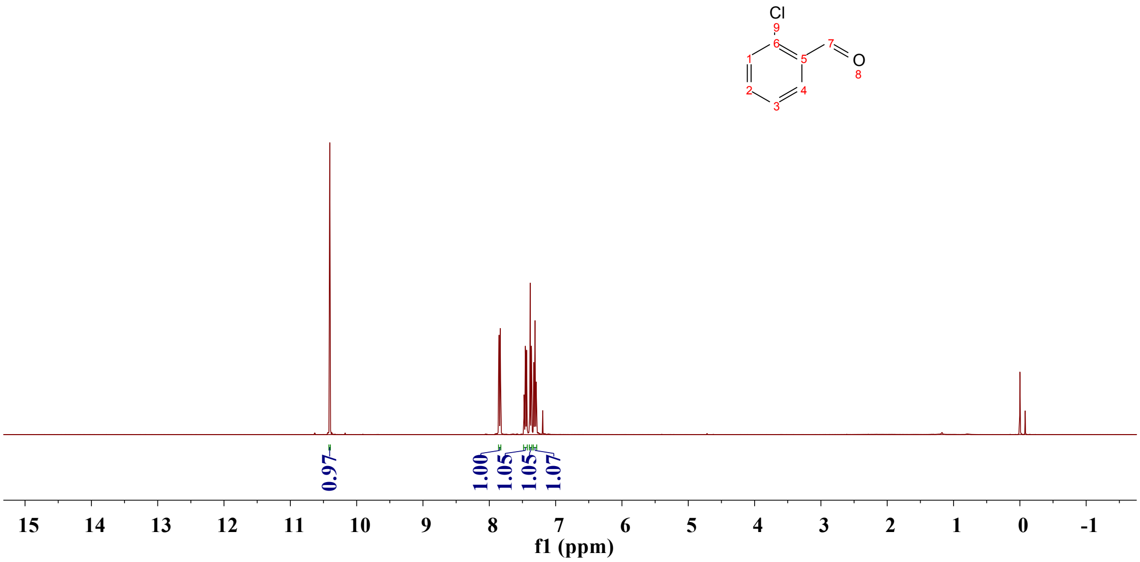
YH-16



YH-17
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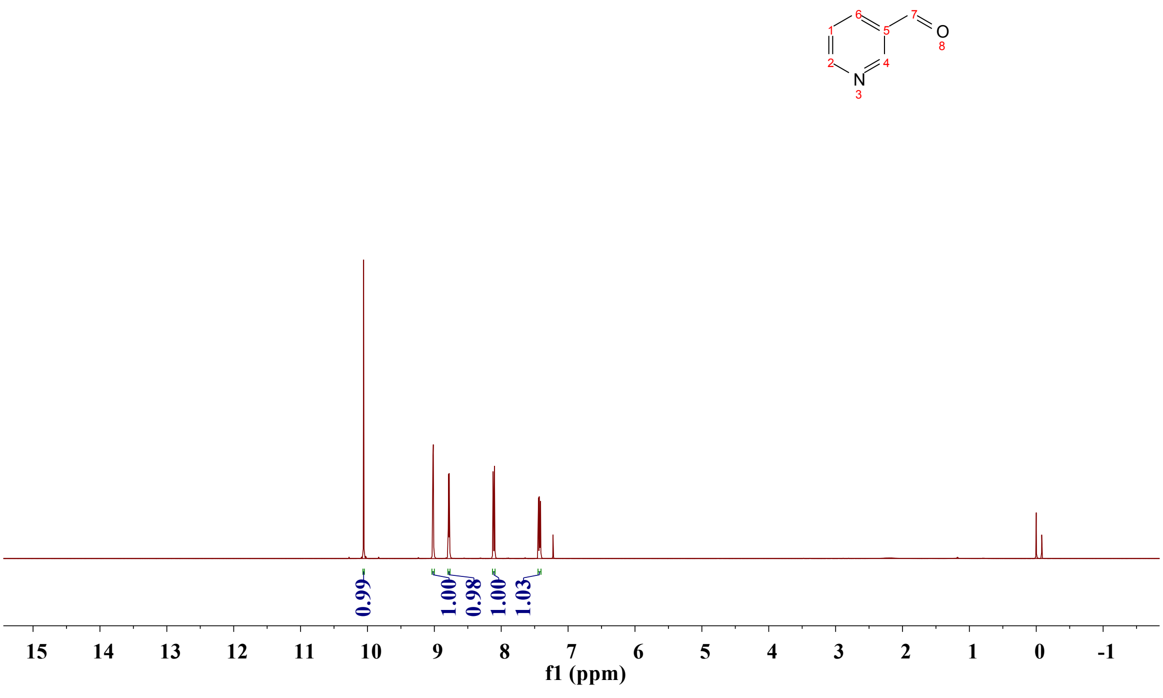

YH-18
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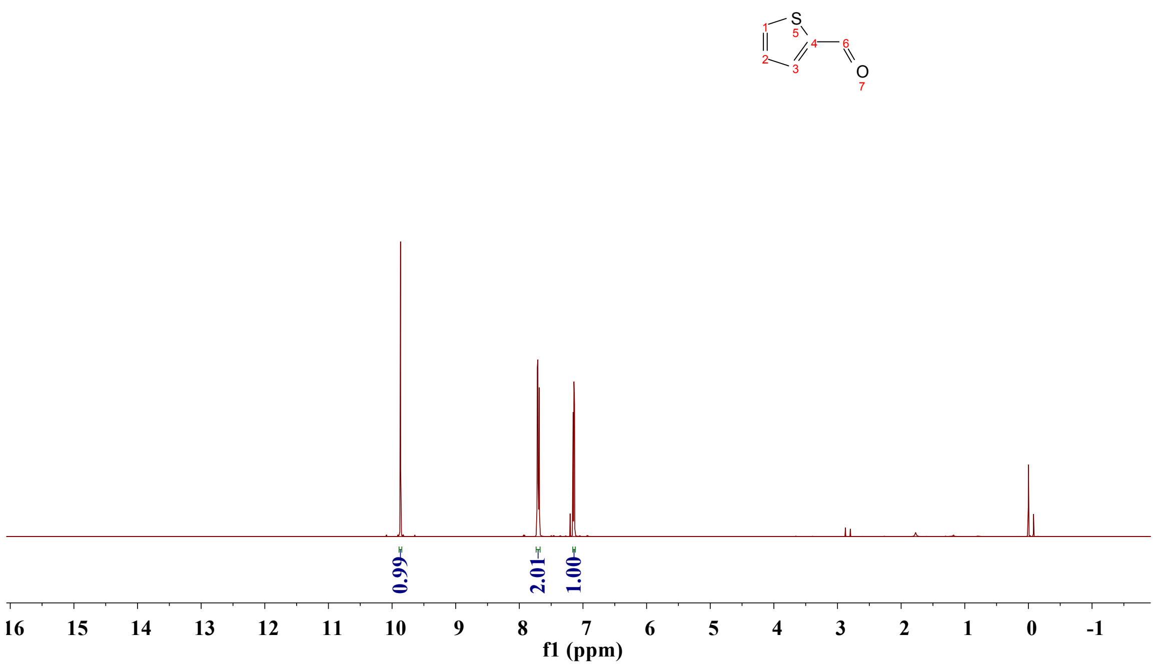

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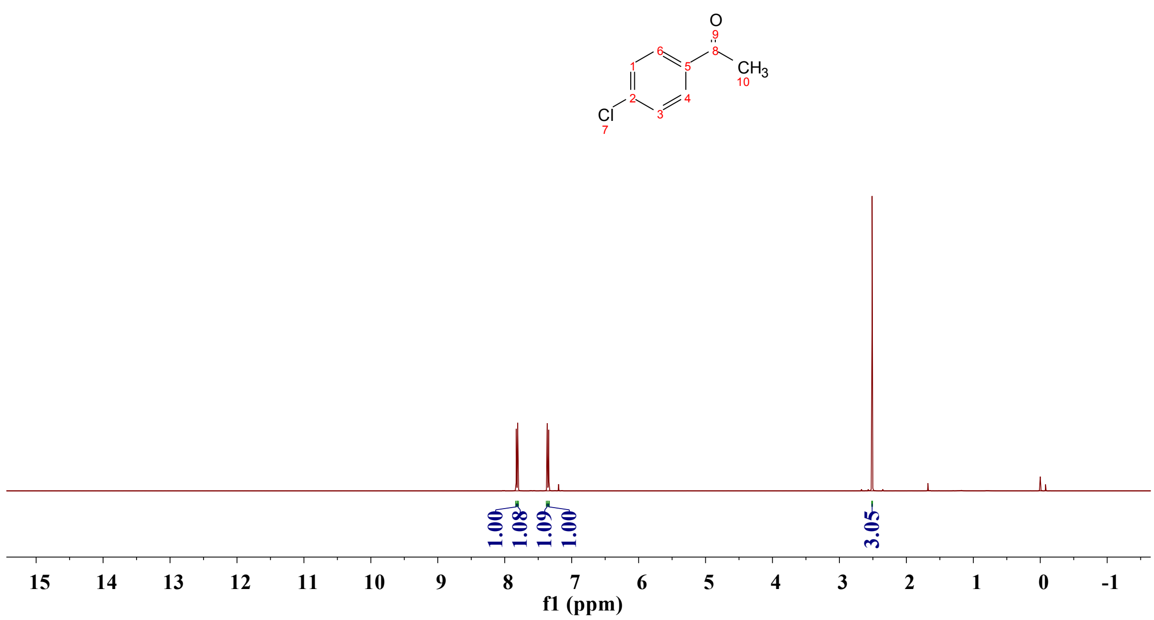

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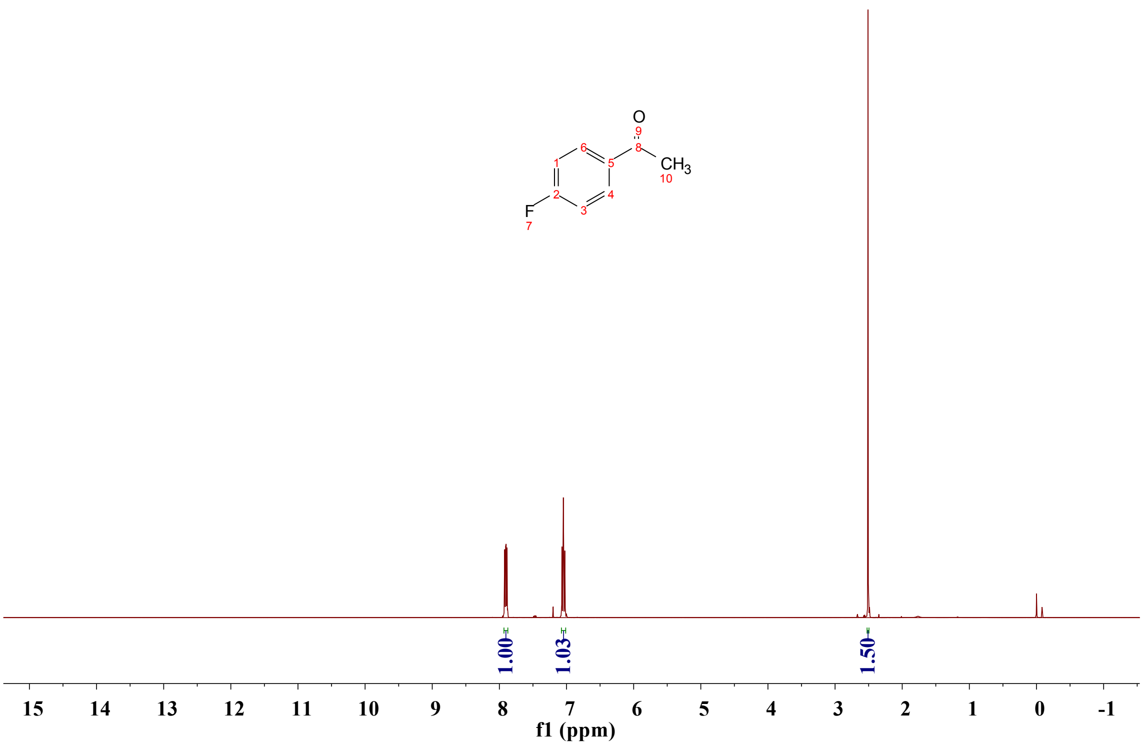

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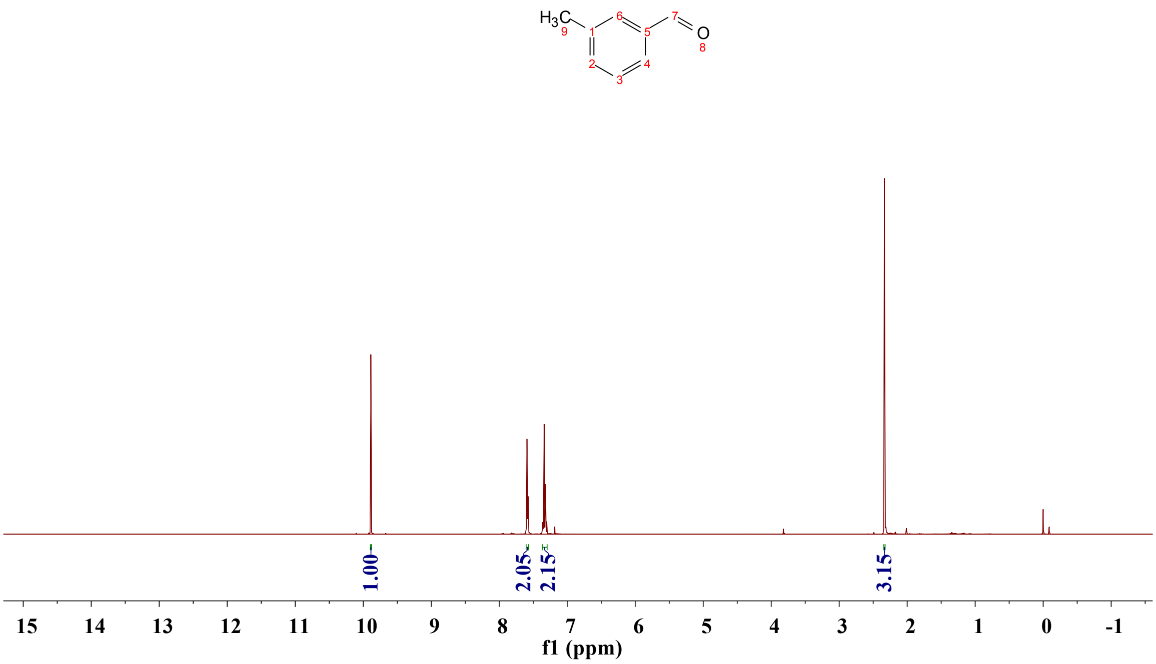

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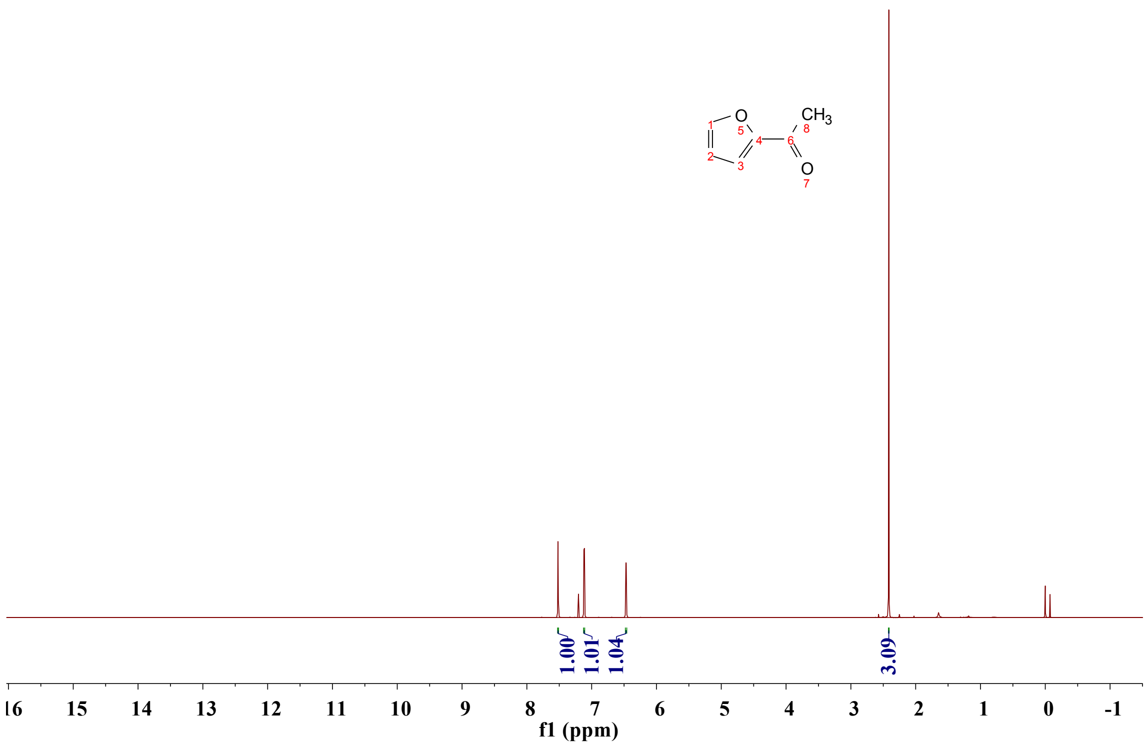

YH-23
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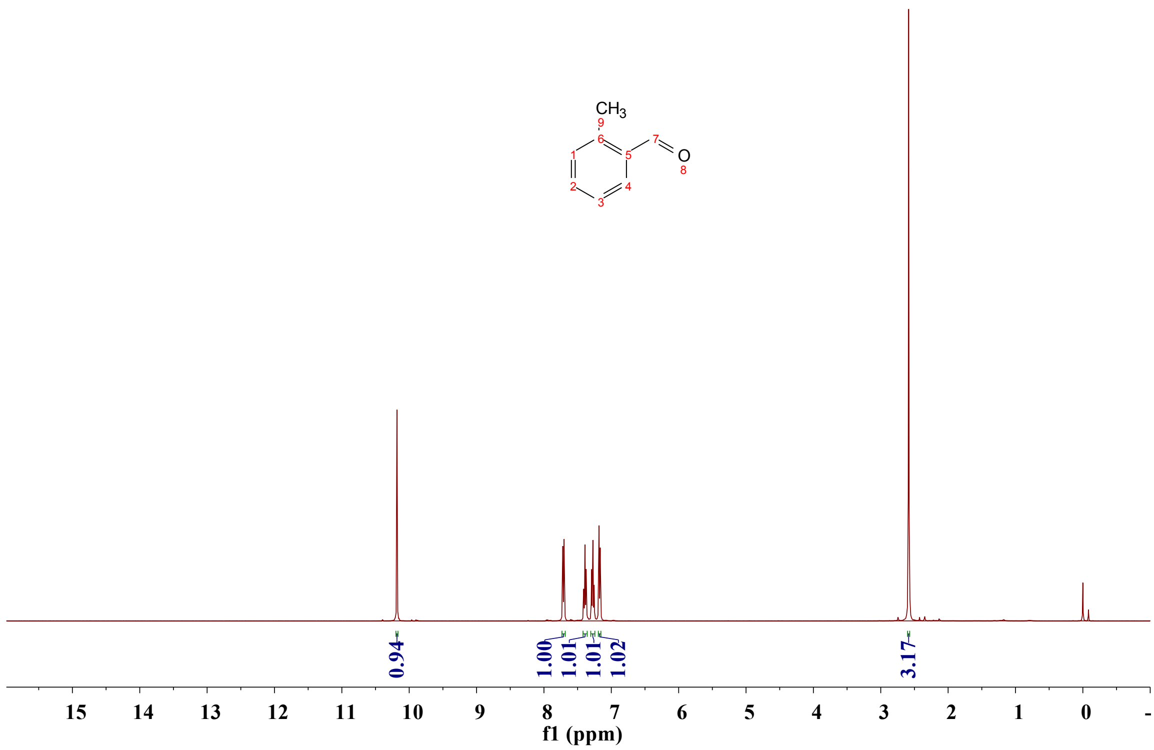

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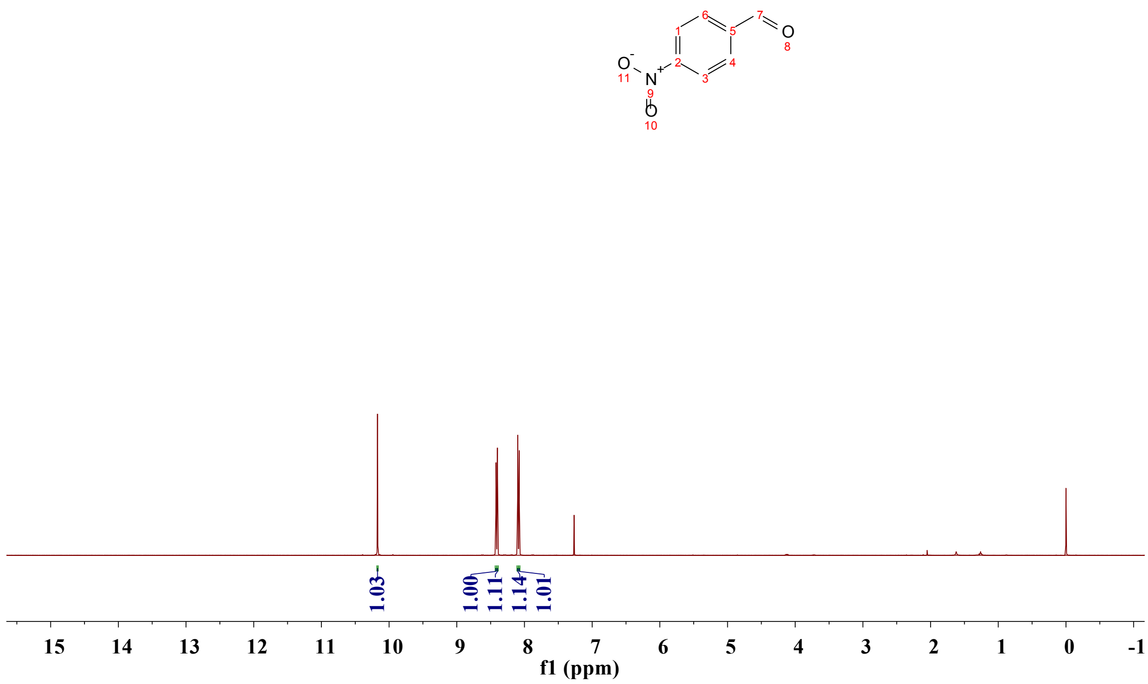

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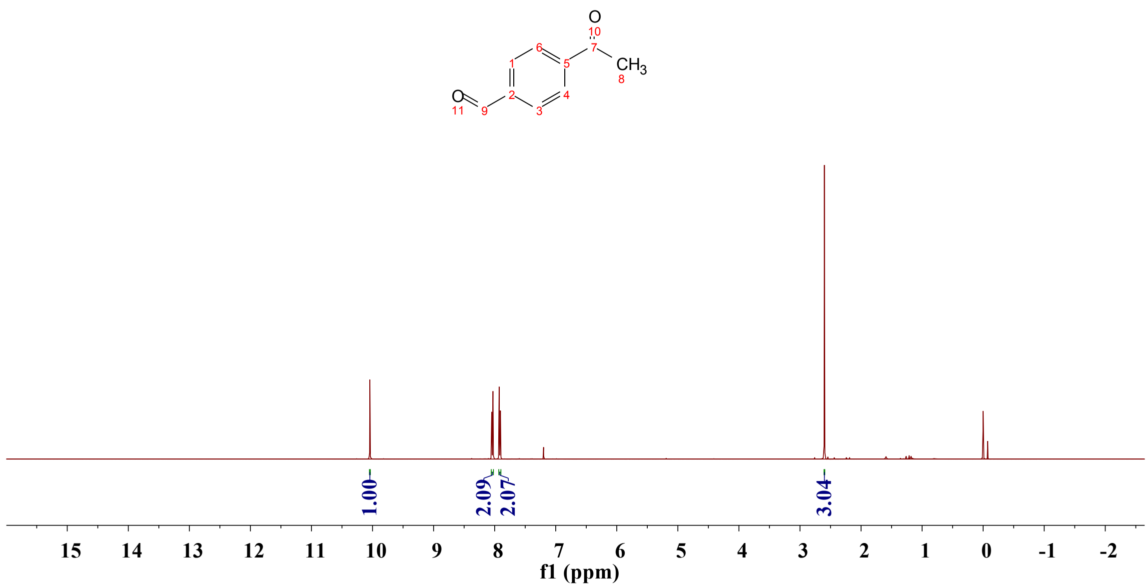
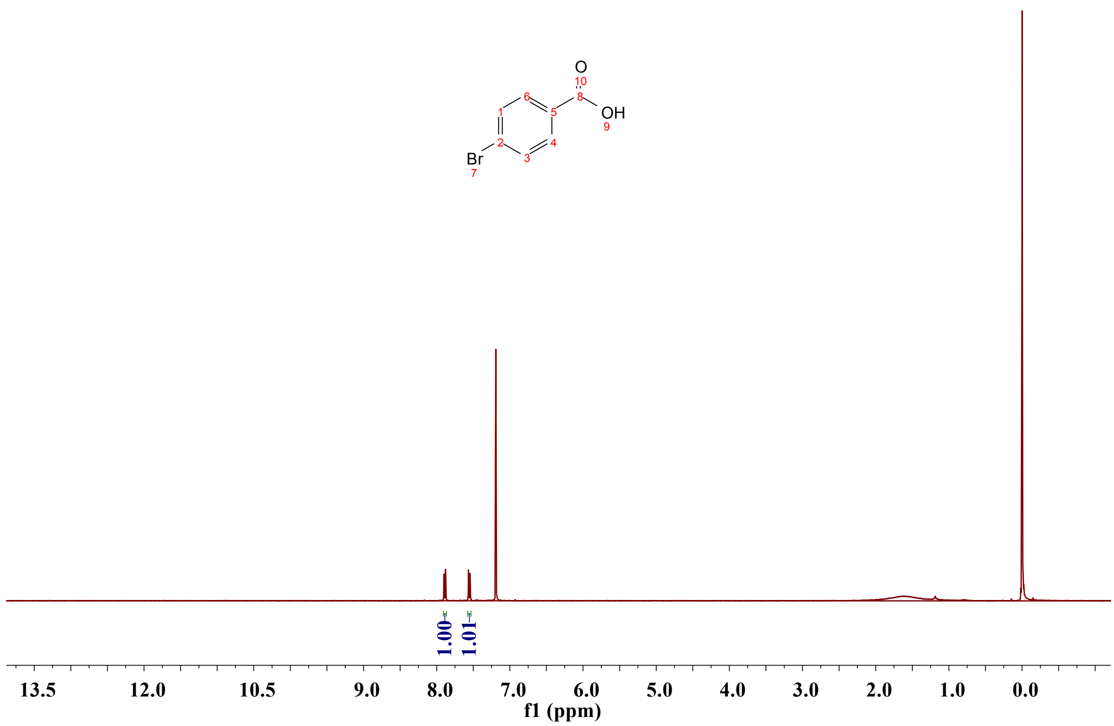
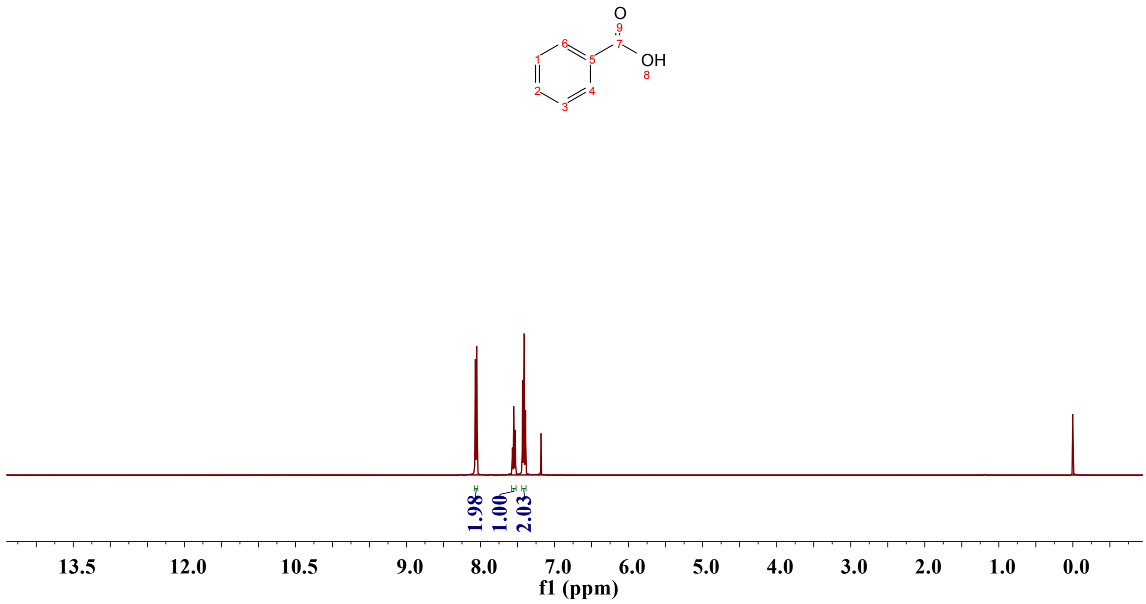


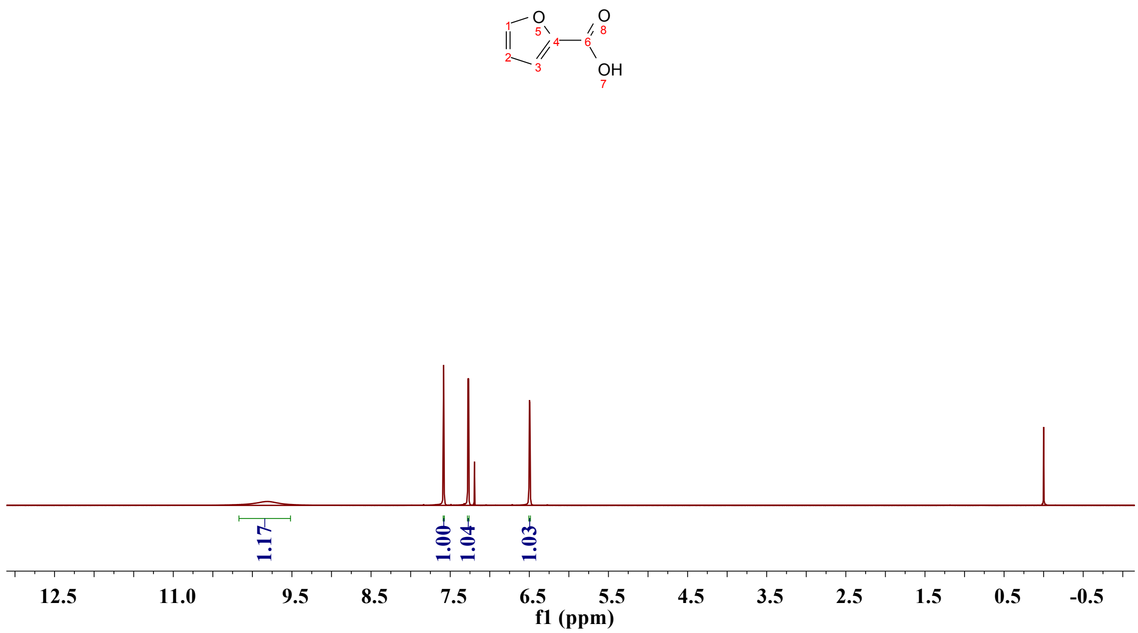
LG-1
LG-1



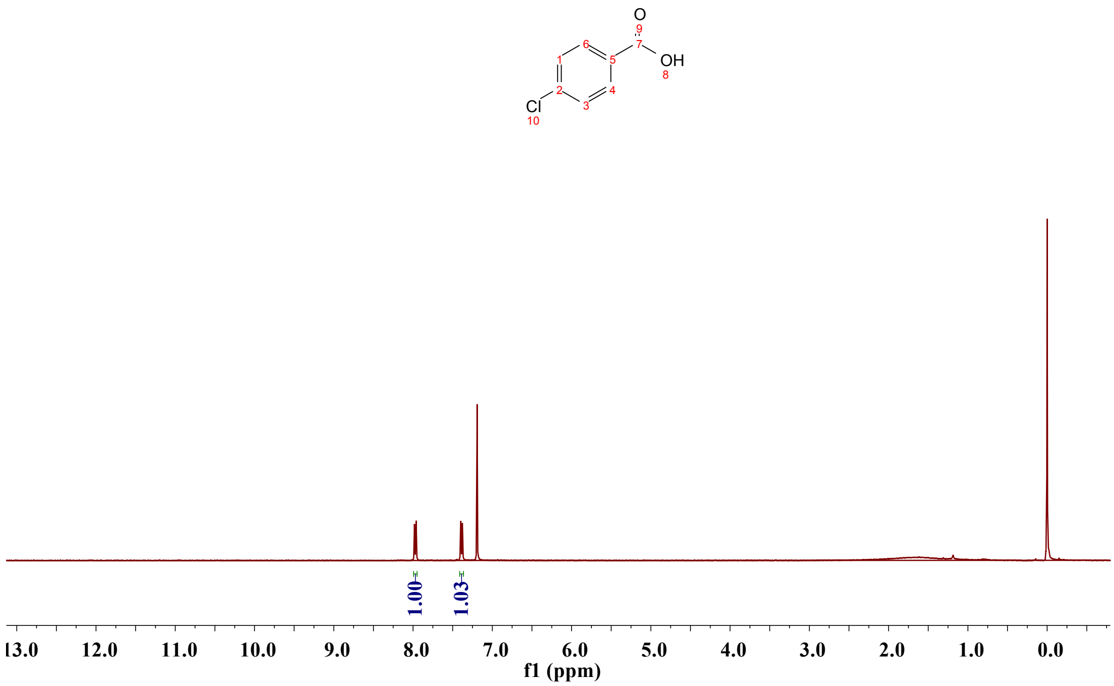
LG-2
LG-2



LG-3
LG-3



LG-4
LG-4



LG-6
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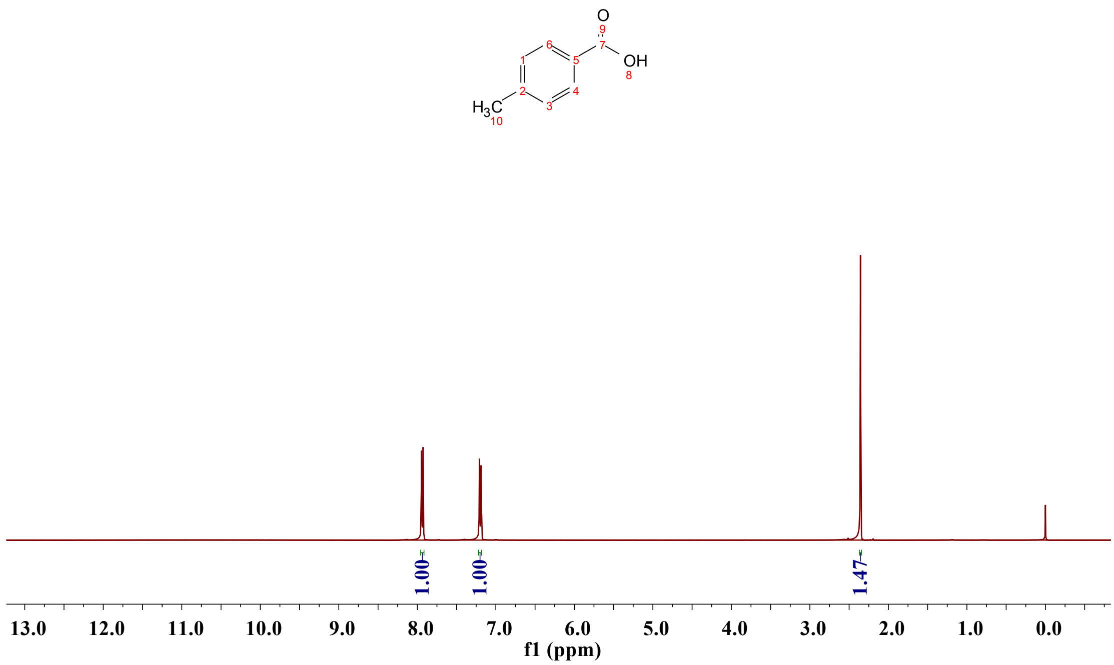
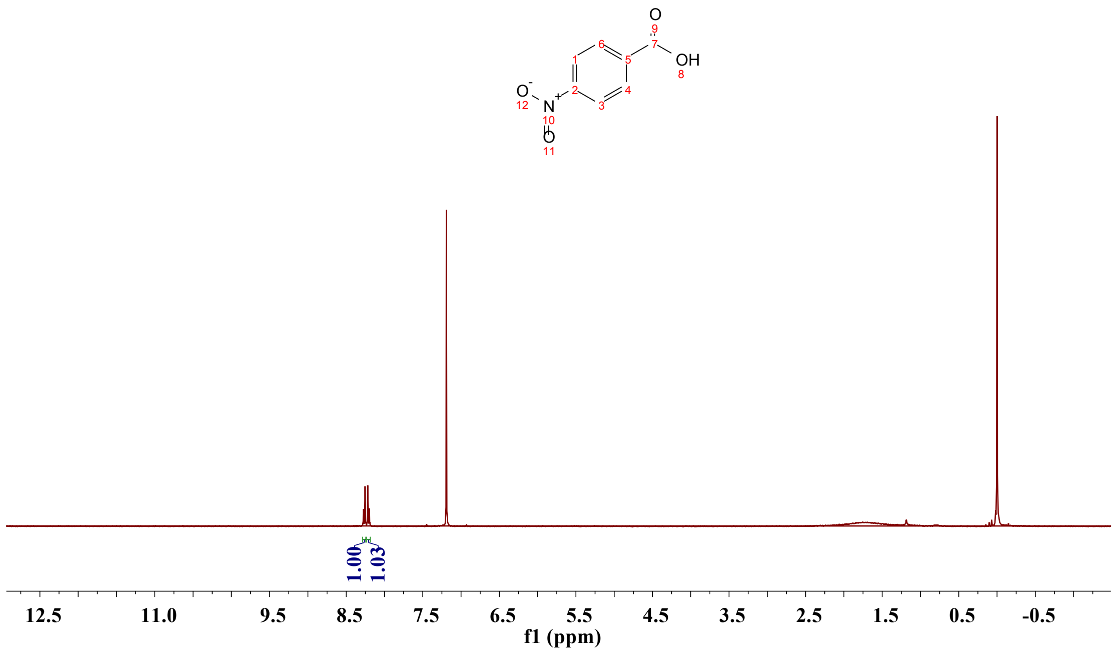


LG-7
LG-7



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