

Supporting information

AIBN/NaBr-promoted aerobic oxidation of benzylic alcohols via a radical process

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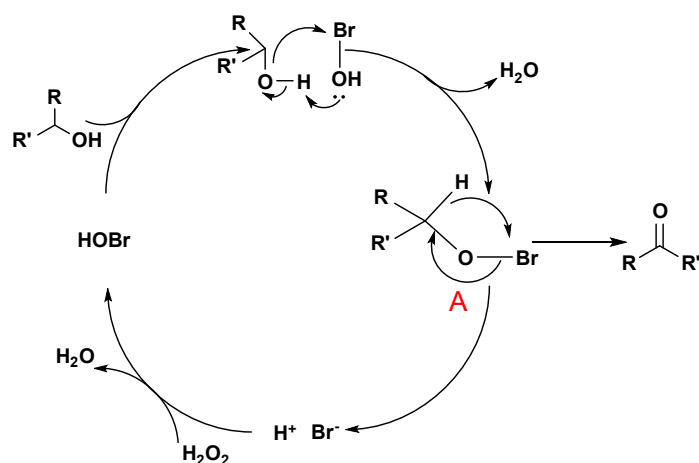
1, General Remarks

Reagents and solvents: Commercially available reagents were used without any further purification. All organic solvents were of reagent grade quality. The dry 1, 4-dioxane was distilled from sodium/benzophenone.

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: ^1H NMR was recorded on magnet system 400'54 ascend purchased from Bruker Biospin AG. ^1H NMR spectra chemical shifts (δ) are reported in parts per million (ppm) referenced to TMS (0ppm). 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.

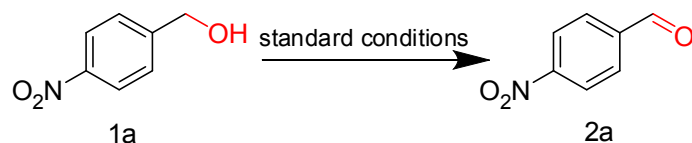
2,



Scheme S1: Proposed mechanism of $\text{H}_2\text{O}_2/\text{Br}^-/\text{H}^+$

Initially, Br^- was oxidized to form the hypobromous acid in the presence of acid and hydrogen peroxide. The generated hypobromous acid subsequently reacted with the corresponding hydroxyl group to form the hypobromite intermediate A, which yielded the corresponding carbonyl compounds via α -hydrogen elimination. Brønsted acid and Br^- were reformatted to maintain the system circularly. ^[1-2]

3, Table S 2: The temperature screening under optimized conditions^a



Entry	Catalyst (equiv)	Additive(equiv)	Solvent	T(°C)	Yield (%) ^b
1	AIBN	NaBr(3)	Dioxane	50	34
2	AIBN	NaBr(3)	Dioxane	60	82
3	AIBN	NaBr(3)	Dioxane	70	95
4	AIBN	NaBr(3)	Dioxane	80	94
5	AIBN	NaBr(3)	Dioxane	90	92

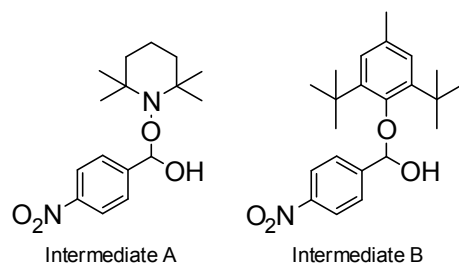
^areaction condition: 1a (1 mmol), AIBN (0.05 mmol), NaBr (3 mmol), solvent (3 mL), T (°C), under O₂ (O₂ balloon). ^byield: isolated yield.

4, General experimental procedure

The specific benzylic alcohols (1 mmol, 1.0 eq) and sodium bromide (3 mmol, 3 eq) were dissolved in dioxane (3 mL), then AIBN (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil bath at 70 °C under O₂ atmosphere (O₂ balloon). The reaction mixtures were diluted with ethyl acetate and washed with brine and water. The separated organic layers were dried over by anhydrous Na₂SO₄ 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.

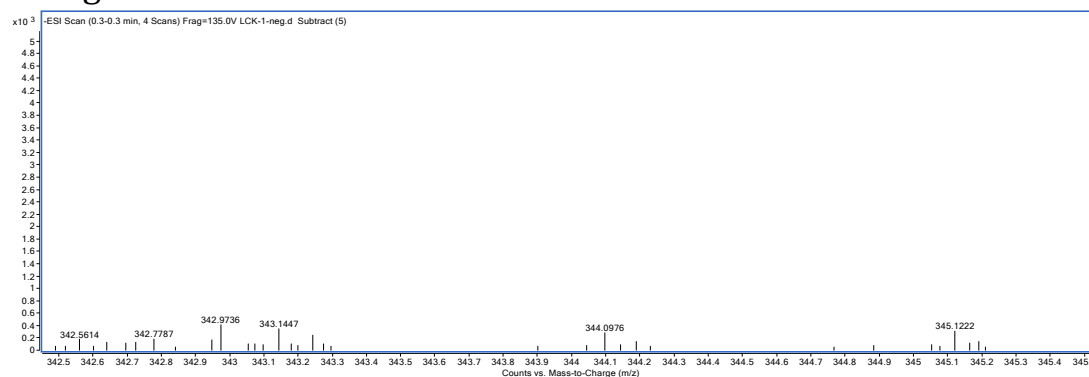
5, proposed mechanism and verification

5.1 Scheme S2: intermediate A and intermediate B



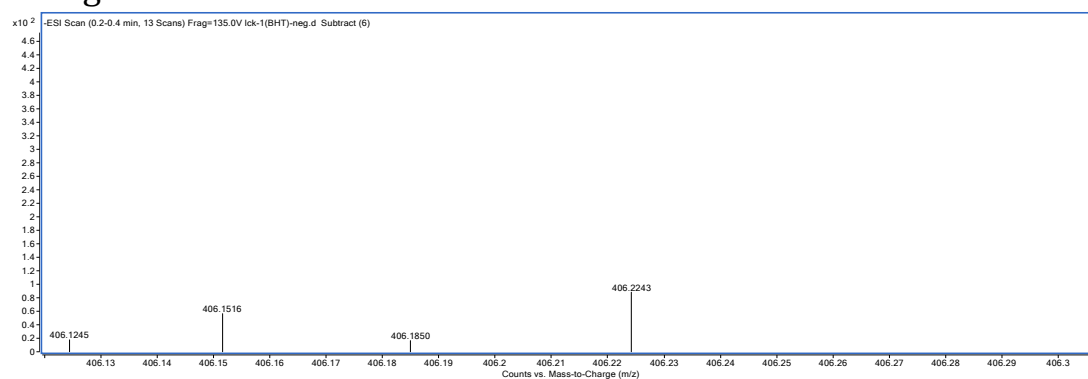
Scheme S2: intermediate A and intermediate B

5.2 Figure S1: MS for intermediate A



HRMS calculated for intermediate A ($C_{16}H_{24}N_2O_4+Cl$): 343.143, found: 343.1447.

5.3 Figure S2: MS for intermediate B

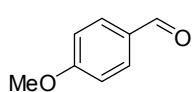


HRMS calculated for intermediate B ($C_{22}H_{29}NO_4+Cl$): 406.1791, found: 406.1850.

6, Characterization Data of the products

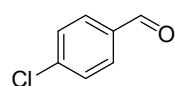
All the products were characterized by 1H NMR spectroscopy and compared with literature reported data.

Anisic aldehyde



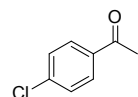
1H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.77 – 7.72 (m, 2H), 6.94 – 6.89 (m, 2H), 3.79 (s, 3H). Spectral data are in accordance with the literature report.^[3-4]

4-Chlorobenzaldehyde



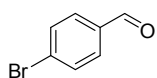
1H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.78 – 7.76 (m, 1H), 7.75 – 7.74 (m, 1H), 7.47 – 7.45 (m, 1H), 7.45 – 7.43 (m, 1H). Spectral data are in accordance with the literature report.^[3]

4'-Chloroacetophenone



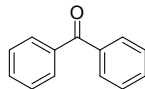
1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 1H), 7.81 – 7.80 (m, 1H), 7.38 – 7.36 (m, 1H), 7.35 – 7.34 (m, 1H), 2.51 (s, 3H).

4-Bromobenzaldehyde



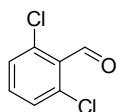
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.91 (s, 1H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H).

Benzophenone (2i)



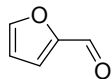
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 – 7.78 (m, 4H), 7.62 – 7.56 (m, 2H), 7.52 – 7.46 (m, 4H). Spectral data are in accordance with the literature report.^[4]

2, 6-Dichlorobenzaldehyde.



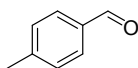
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.43 (s, 1H), 7.33 (s, 3H). Spectral data are in accordance with the literature report.^[3]

Furfural



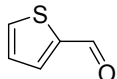
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.59 (s, 1H), 7.64 – 7.62 (m, 1H), 7.19 (dd, $J = 3.6, 0.5$ Hz, 1H), 6.54 (dd, $J = 3.6, 2$ Hz, 1H). Spectral data are in accordance with the literature report.^[5]

p-Tolualdehyde



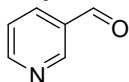
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.88 (s, 1H), 7.69 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 2.36 (s, 3H). Spectral data are in accordance with the literature report.^[3]

2-Thenaldehyde



$^1\text{H NMR}$ (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.^[4]

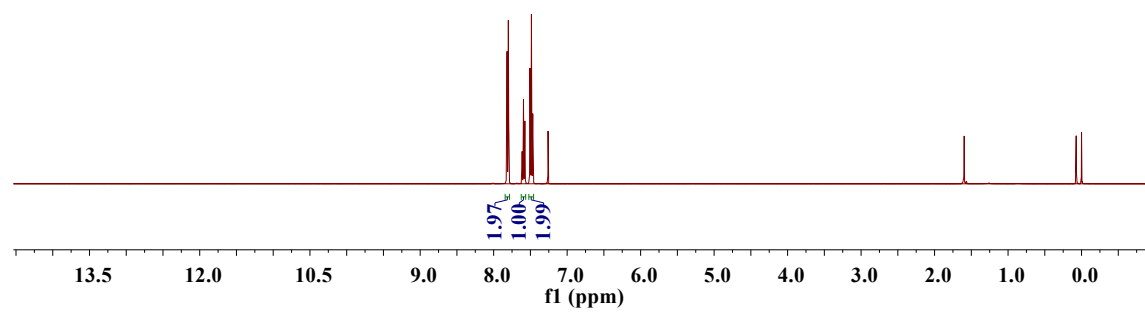
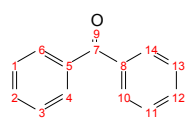
3-Pyridinecarboxaldehyde



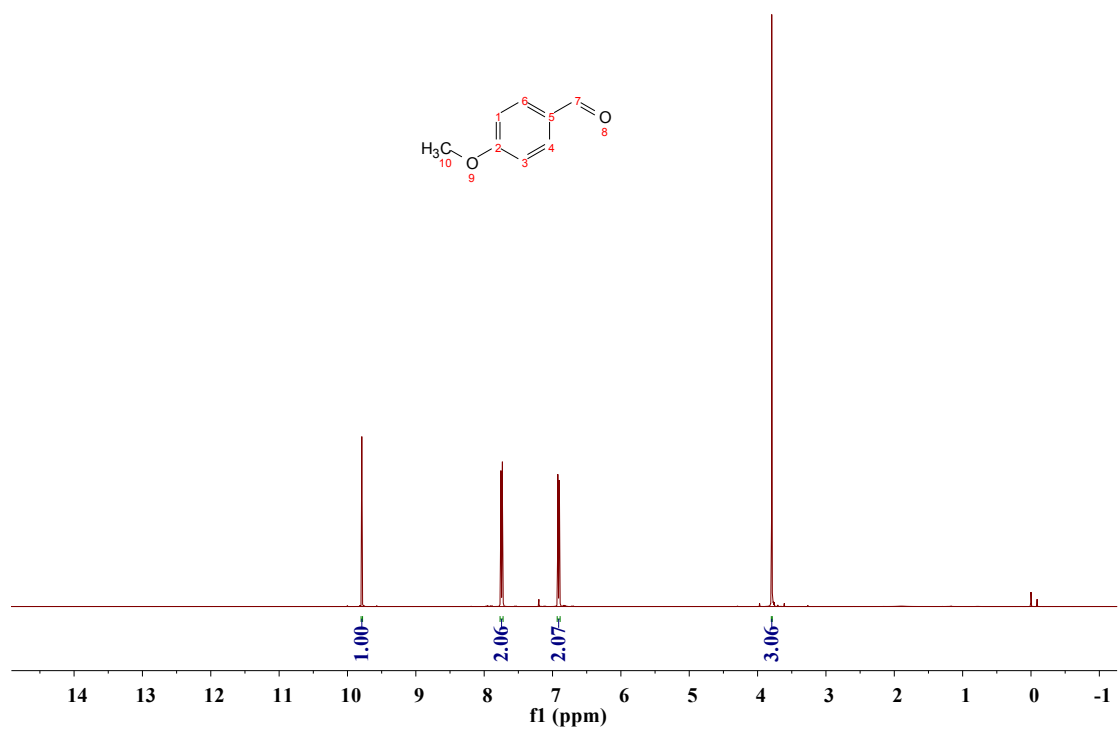
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.06 (s, 1H), 9.02 (dd, $J = 1.6$ Hz, 0.4 Hz, 1H), 8.78 (dd, $J = 4.8, 1.6$ Hz, 1H), 8.11 (dt, $J = 7.9, 2.0$ Hz, 1H), 7.43 (dd, $J = 7.9, 4.8$ Hz, 1H). Spectral data are in accordance with the literature report.^[3]

6, ¹H spectra

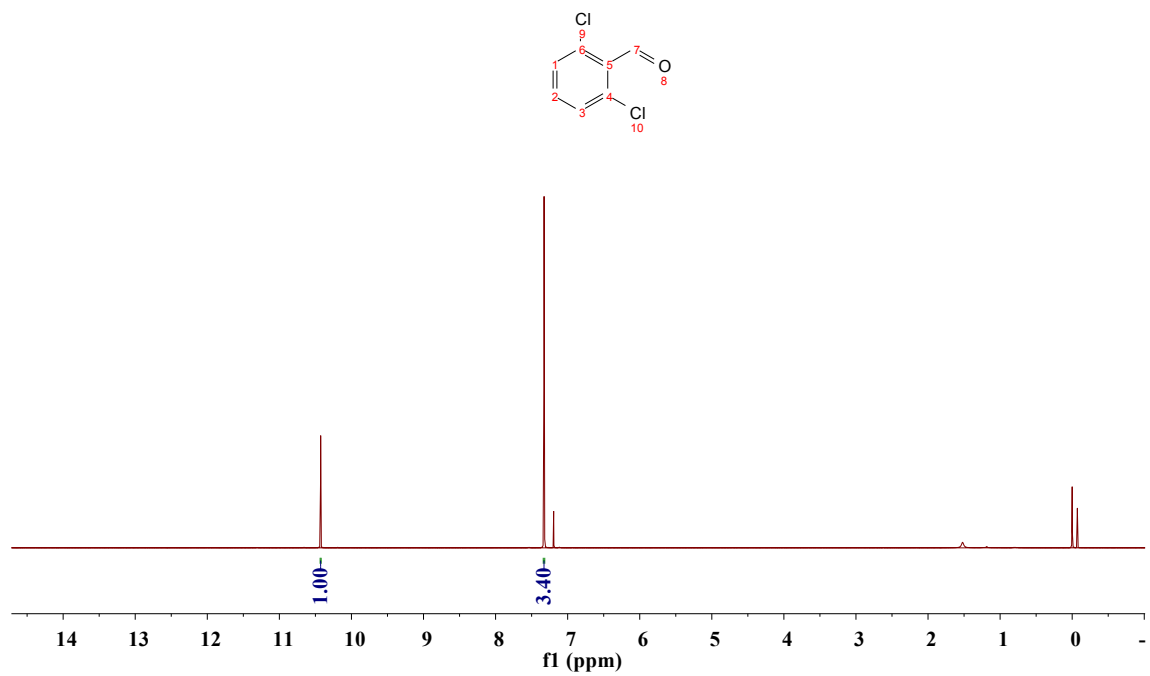
Yu-3
Yu-3



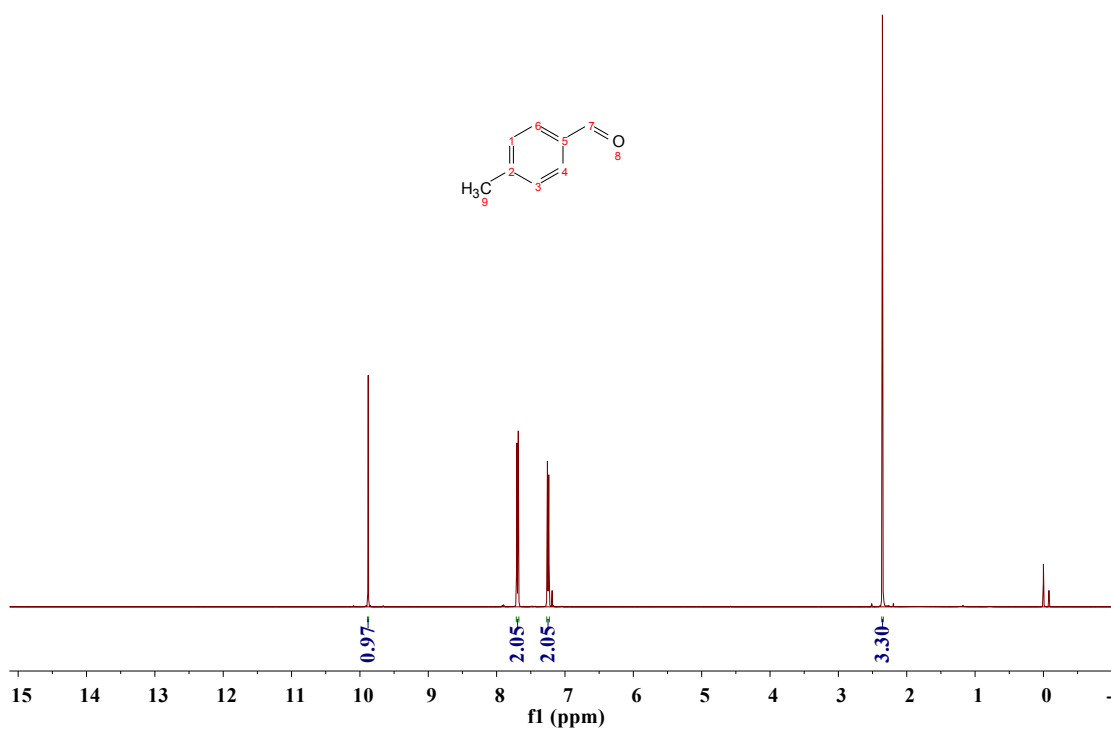
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Yu-4



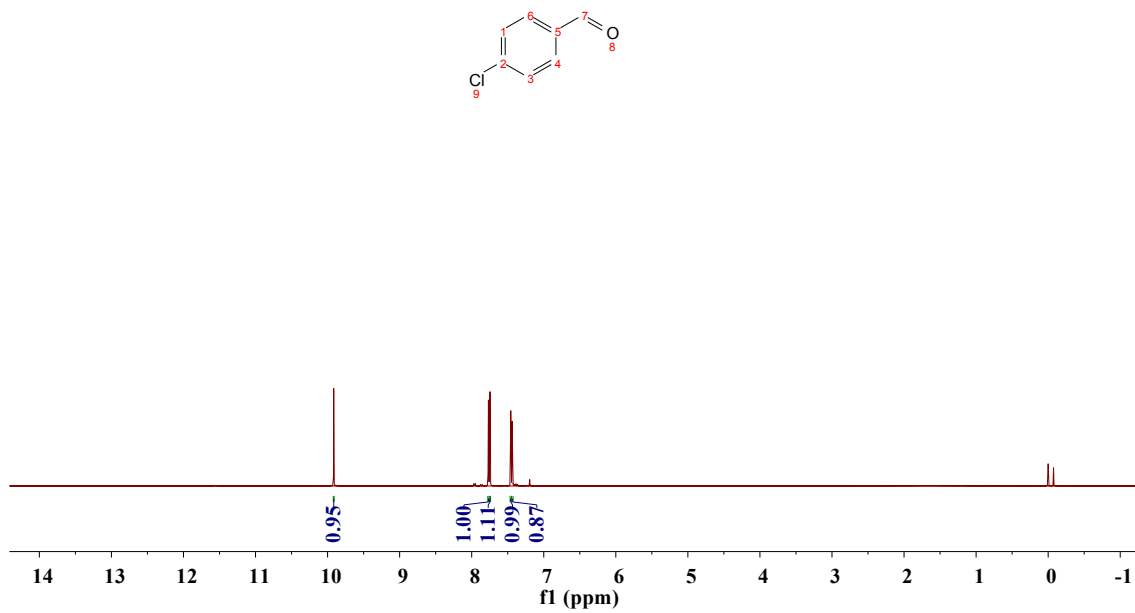
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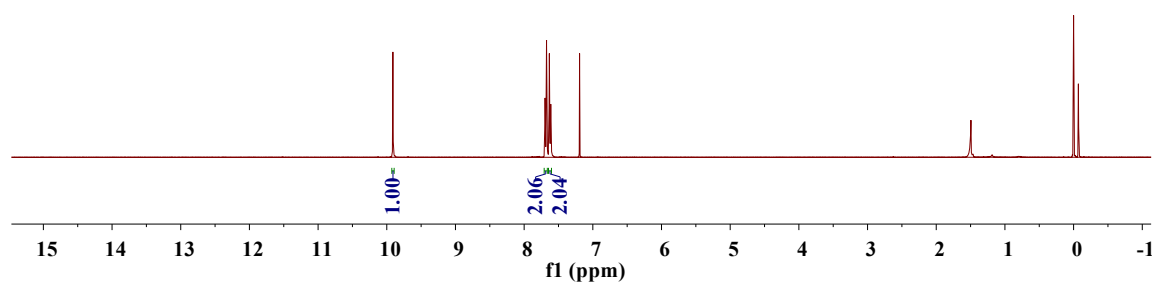
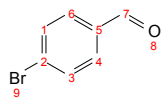
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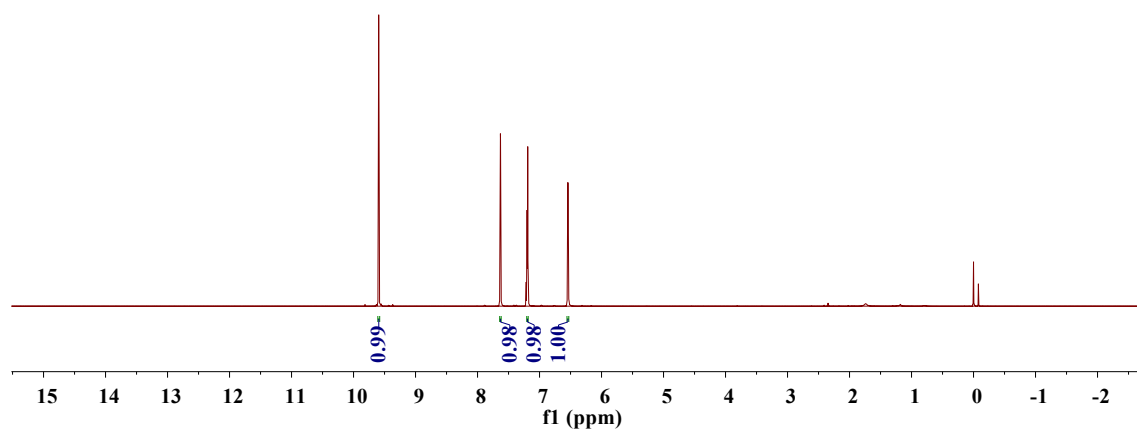
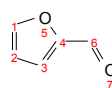
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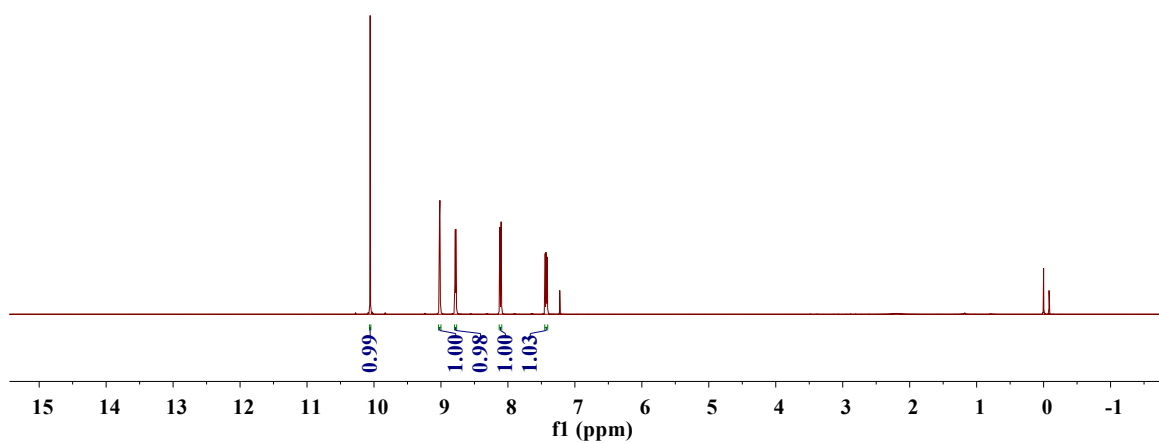
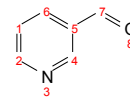
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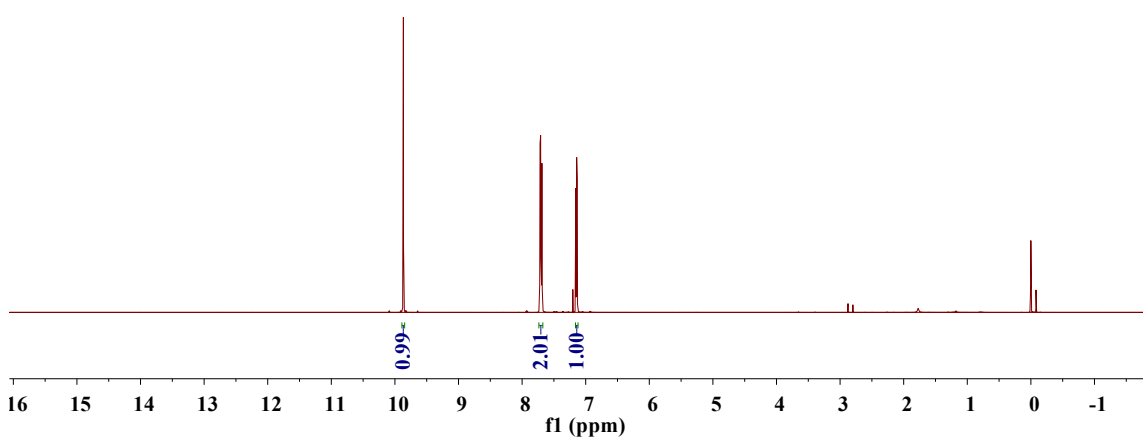
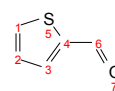
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YH-11



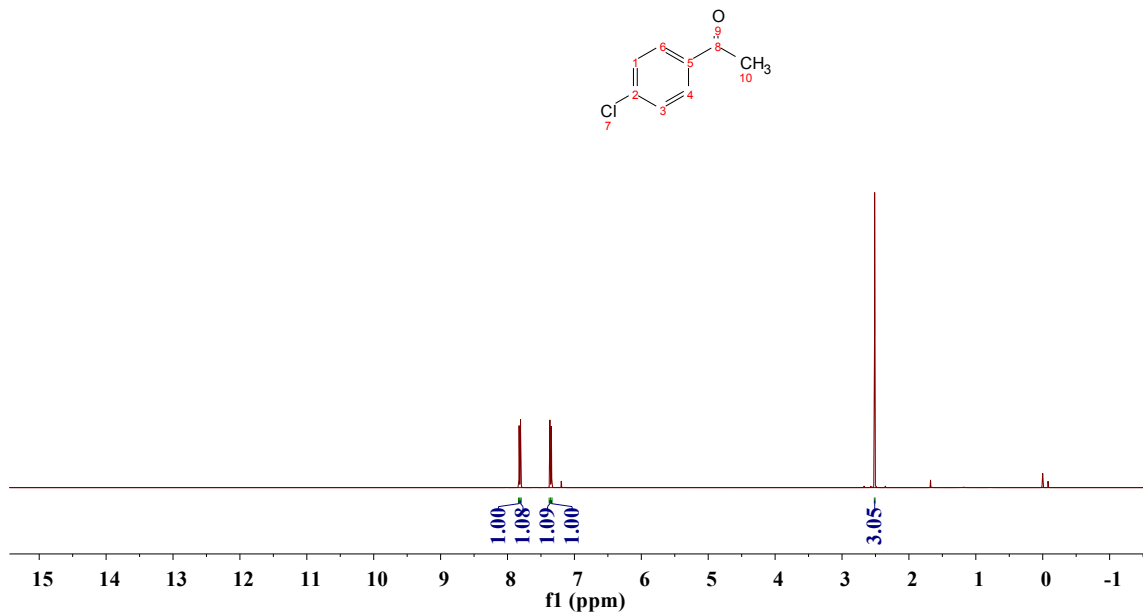
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YH-17



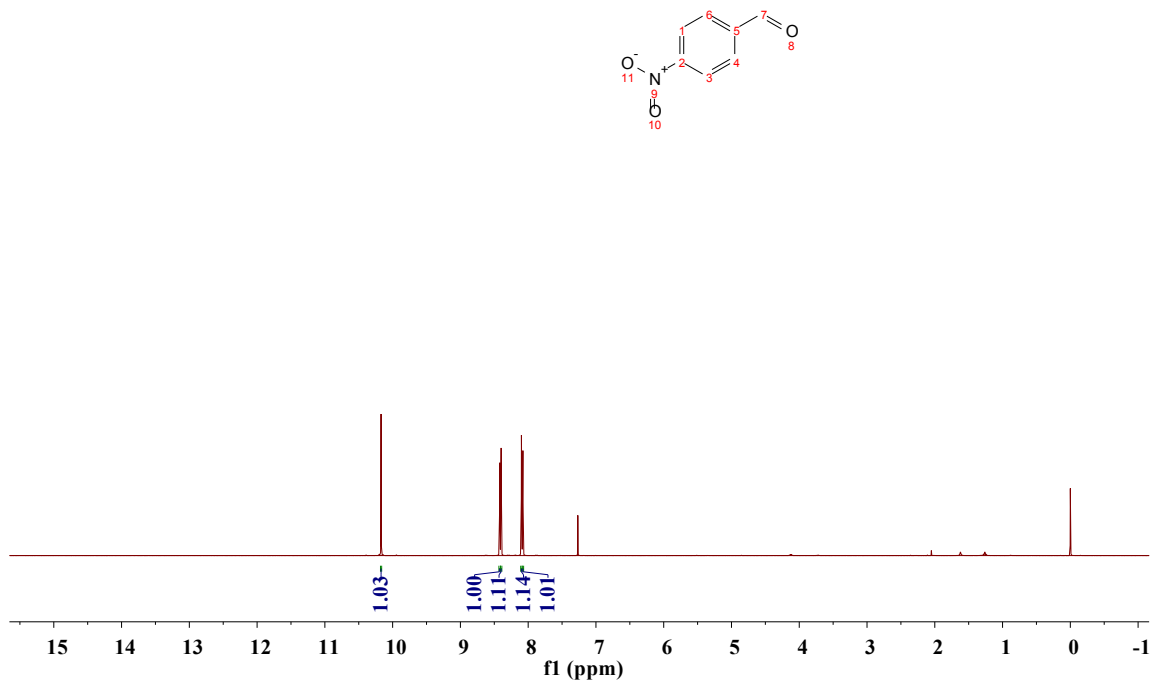
YH-18
YH-18



YH-19
YH-19



LQW-9
LQW-9



7, References

- [1] M. Dey, S. S. Dhar and M. Kalita, *Synthetic Communications*, 2013, 43, 1734-1742.
- [2] G. Joshi, R. D. Patil and S. Adimurthy, *Rsc Advances*, 2012, 2, 2235-2239
- [3] M. M. Hossain, S.-G. Shyu, *Advanced Synthesis & Catalysis* **2010**, 352, 3061-3068.
- [4] M. Inuma, K. Moriyama, H. Togo, *Tetrahedron* **2013**, 69, 2961-2970.
- [5] X. Wang, D. Z. Wang, *Tetrahedron* **2011**, 67, 3406-3411.