

A novel modified MIL-101-NH₂ ligand for CuI-catalyzed and air promoted oxidation of secondary alcohols

Hui Liu,^a Daniele Ramella,^b Peng Yu*,^a and Yi Luan*,^c

^a Science College of Hunan Agricultural University, Hunan, 410128, China, E-mail: pengy7505@hunau.net

^b Temple University-Beury Hall, 1901, N. 13th Street, Philadelphia PA 19122, United States

^c School of Materials Science and Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, P. R. China, yiluan@ustb.edu.cn

Supporting Information

General Information. All ^1H NMR, and ^{13}C NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG, ^1H 400 MHz) spectrometer at ambient temperature in CDCl_3 . Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and integration. The structure and phase of the samples were evaluated by X-ray powder diffraction (XRD, Rigaku DMAX-RB 12 KW) with Cu $K\alpha$ radiation ($\lambda=0.15406$ nm). The morphology of the as-obtained product was characterized by scanning electron microscopy (SEM, ZEISS SUPRA55). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were conducted on a TEI Tecnai F20. The samples for the SEM, TEM and HRTEM measurements were dispersed in ethanol and sonicated for a few minutes and supported onto the silicon slice and the holey carbon film on a Cu grid, respectively. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distributions were derived from the adsorption branches of isotherms by using the Barrett–Joyner–Halenda (BJH) model. Infrared spectra were recorded on a NICOLET 6700 infrared spectrophotometer. Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel.

General procedure for the aerobic oxidation of alcohols

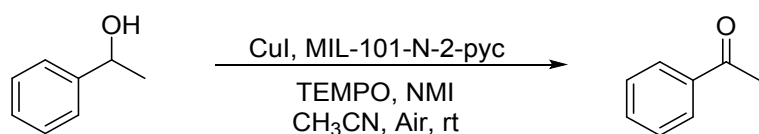


Fig. S1 General procedure for the Aerobic Oxidation of Alcohols

In a typical procedure, 1.0 mmol of 1-phenylethanol, 0.05 mmol of TEMPO, 0.1 mmol of NMI were mixed in the presence of 0.05 mmol of MIL-101-N-2-pyc ligand. were added in a 25 mL round-bottom flask. Without sealing the flask, the solution was stirred at room temperature (23 °C) for the desired time until the reaction was completed. The filtered liquid samples were examined by GC-MS using *n*-Dodecane as the internal standard.

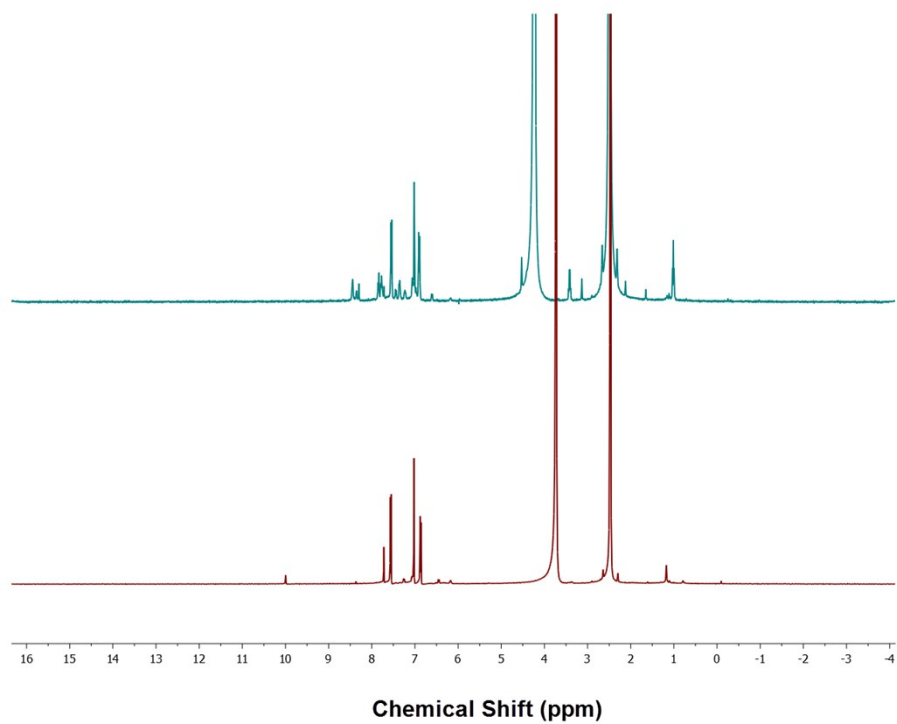


Fig. S2 Full ¹H NMR spectra of digested MIL-101-NH₂ (bottom) and MIL-101-N-2-pyc (top).

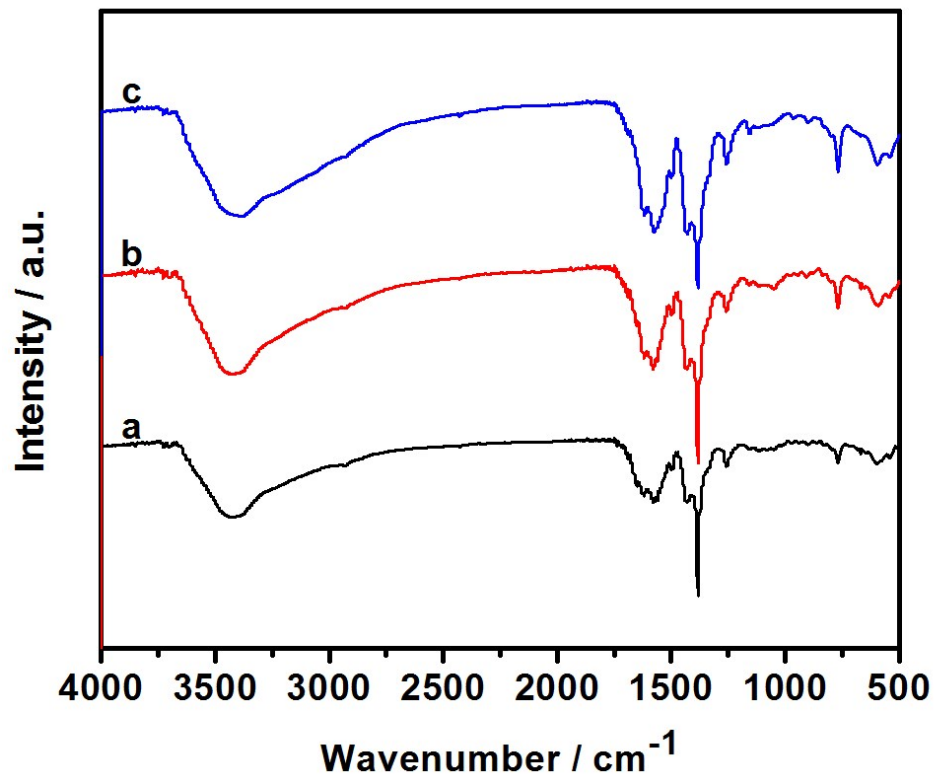


Fig. S3 FTIR of (a) MIL-101-NH₂, (b) modified MIL-101-N-2-pyc, (c) MIL-101-N-sal.

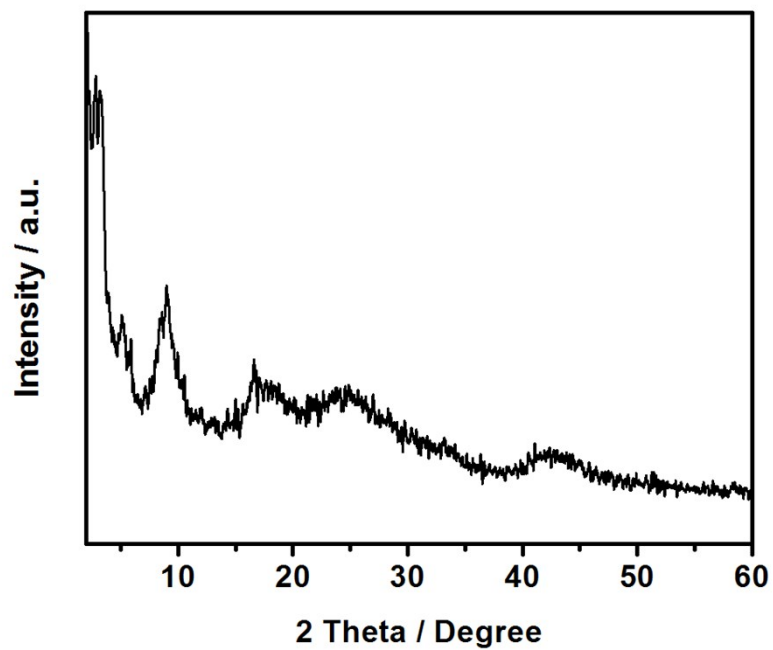


Fig. S4 Powder XRD of recycled MIL-101-N-2-pyc ligand

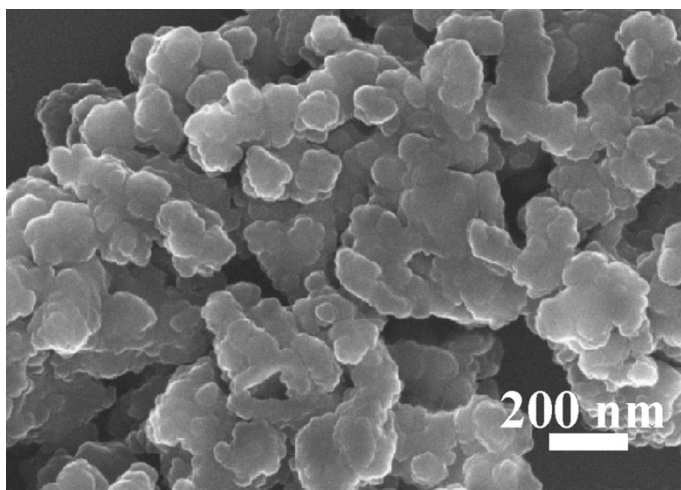


Fig. S5 SEM of recycled MIL-101-N-2-pyc ligand.

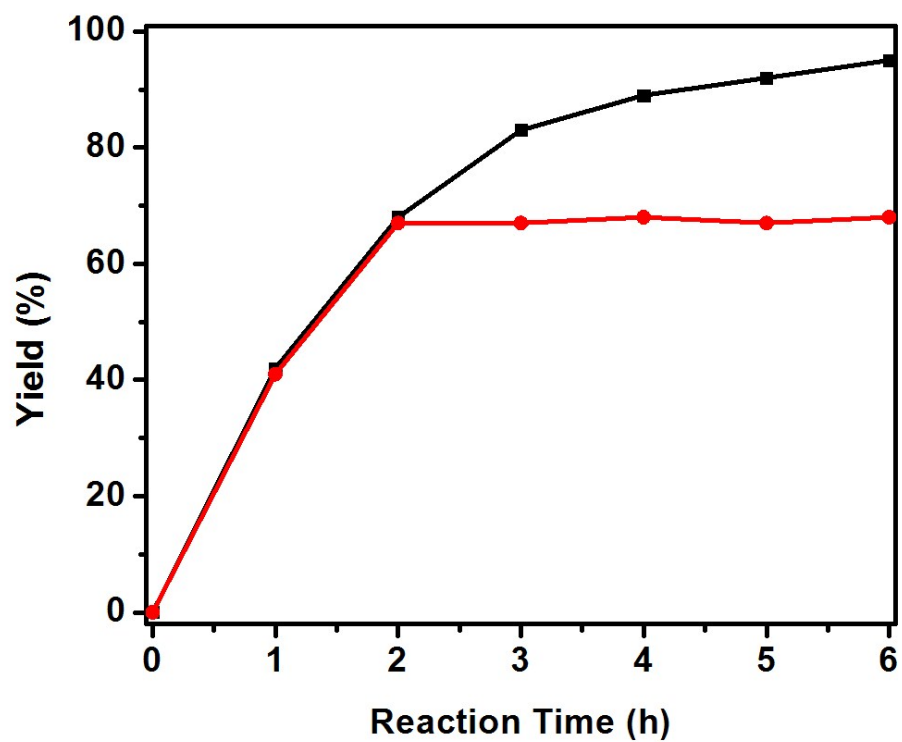


Fig. S6 Conversion *versus* time in the aerobic oxidation of alcohol catalyzed by CuI/MIL-101-N-2-pyc. a) normal reaction, b) solid ligand was filtered at 2 h.

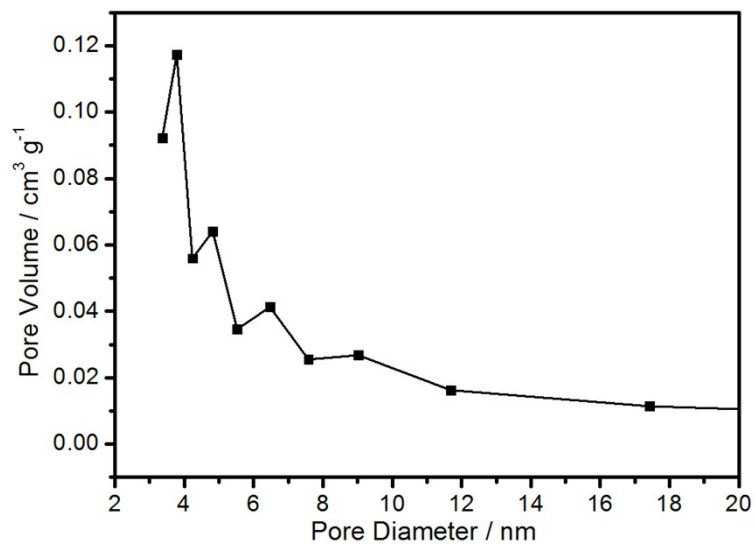


Fig. S7 BJH pore size distribution for MIL-101-NH₂.

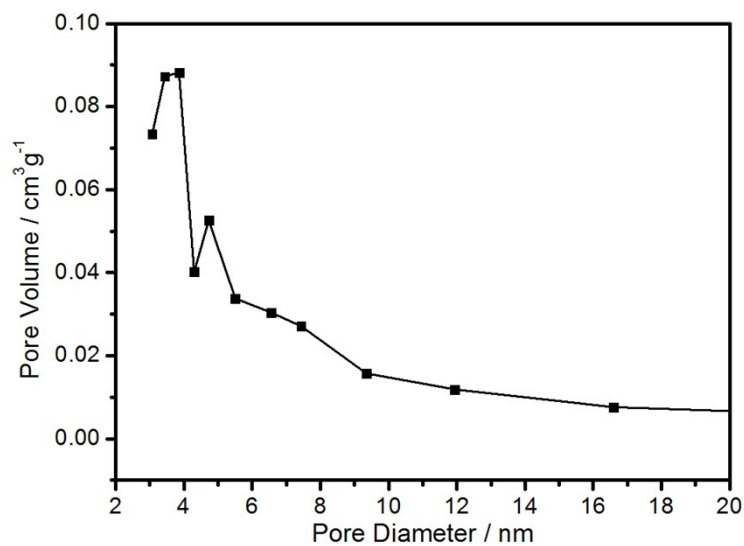


Fig. S8 BJH pore size distribution for MIL-101-N-2-pyc.

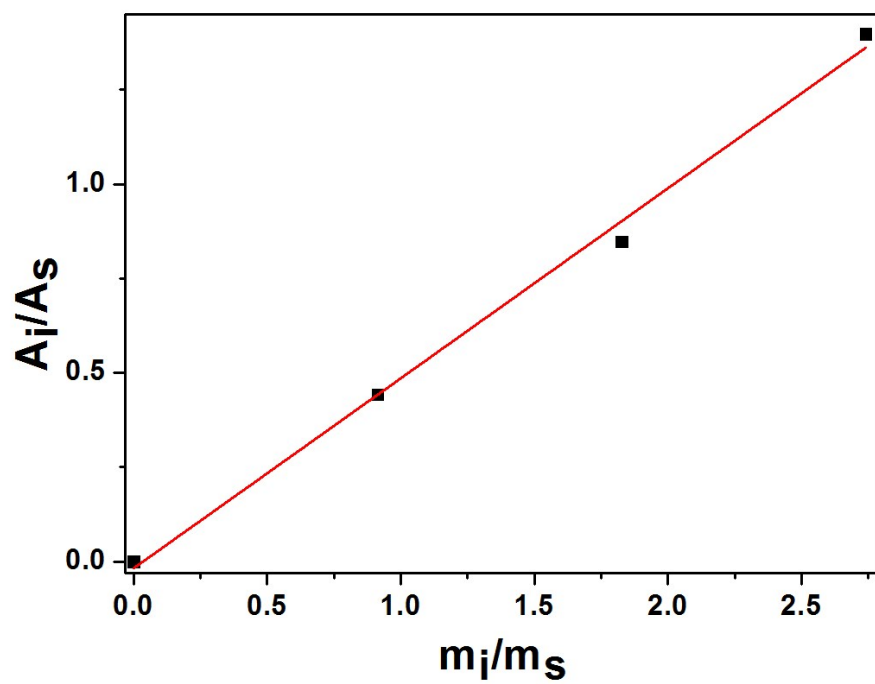
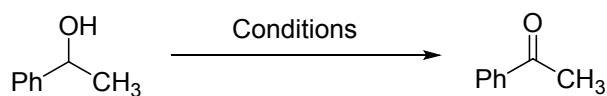


Fig. S9. Linear fit calibration of standard data to analyze unknown concentration of acetophenone

Table S1. Literature comparison for secondary alcohol oxidation.



Catalyst	Loading	Reaction time	T (°C)	Solvent	Yield	Reference
Cu/HT	7.3 mol%	3 h	130	<i>p</i> -xylene	98%	1
Cu(0)/Al ₂ O ₃	8 wt%	2 h	120	DMF	99%	2
Cellulose-Cu-NP	20 mol%	0.5	60	CH ₃ CN	99%	3
Pd@MIL-88B-NH ₂ @ nano-SiO ₂	2 mol%	10 h	150	<i>p</i> -xylene	98%	4
CuI/MIL-101-N-2-pyc	5 mol%	6 h	rt (23)	CH ₃ CN	99%	This work
CuI/MIL-101-N-2-pyc	1 mol%	1 h	120	<i>p</i> -xylene	99%	This work

[1] T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawaa and K. Kaneda, *Chem. Commun.*, 2008, **39**, 4804–4806.

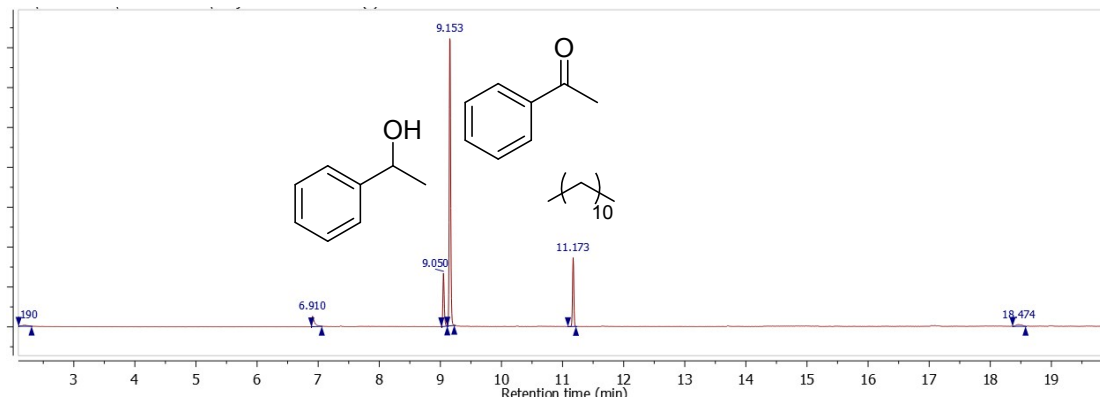
[2] D. Damodara, R. Arundhathi and PR. Likhar, *Adv. Synth. Catal.*, 2014, **356**, 189–198.

[3] D. Baruah, FL. Hussaina, M. Suria, UP. Saikia, P. Senguptab, DK. Duttab, and D. Konwara, *Catal. Commun.*, 2016, **77**, 9-12.

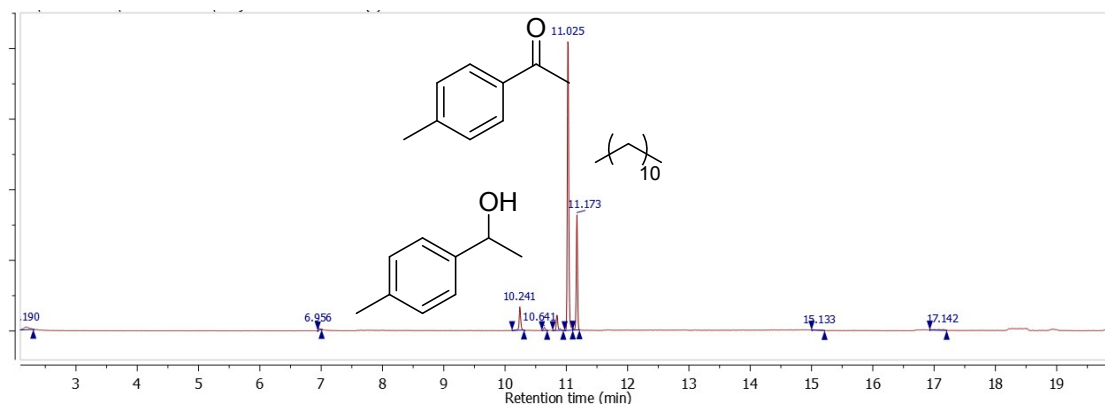
[4] V. Pascanu, AB. Gomez, C. Ayats, AE. Platero-Prats, F. Carson, J. Su, QX. Yao, MA. Pericas, XD. Zou and B Martin-Matute, *ACS Catal.*, 2015, **5**, 472-479.

GC-MS result of aerobic oxidation reaction.

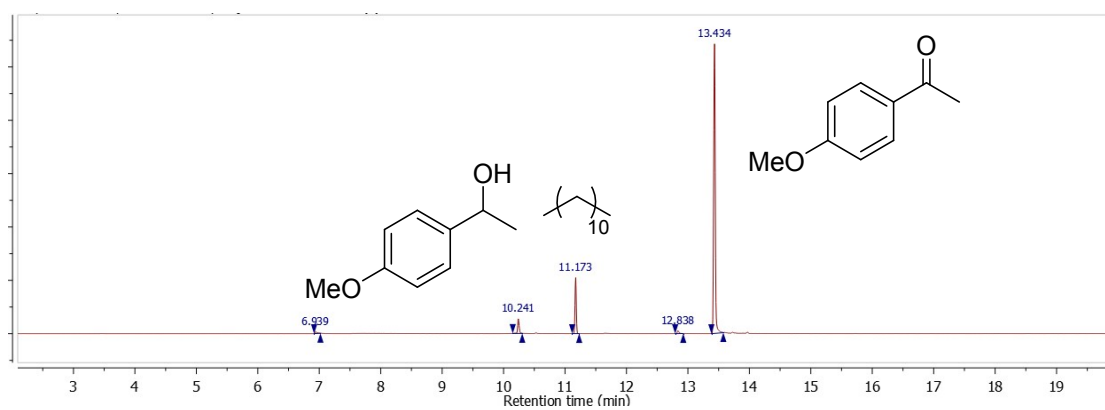
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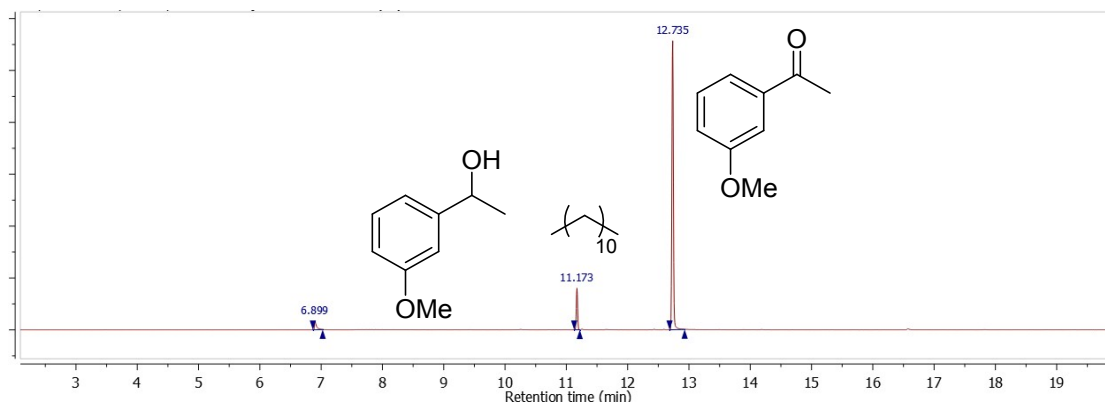
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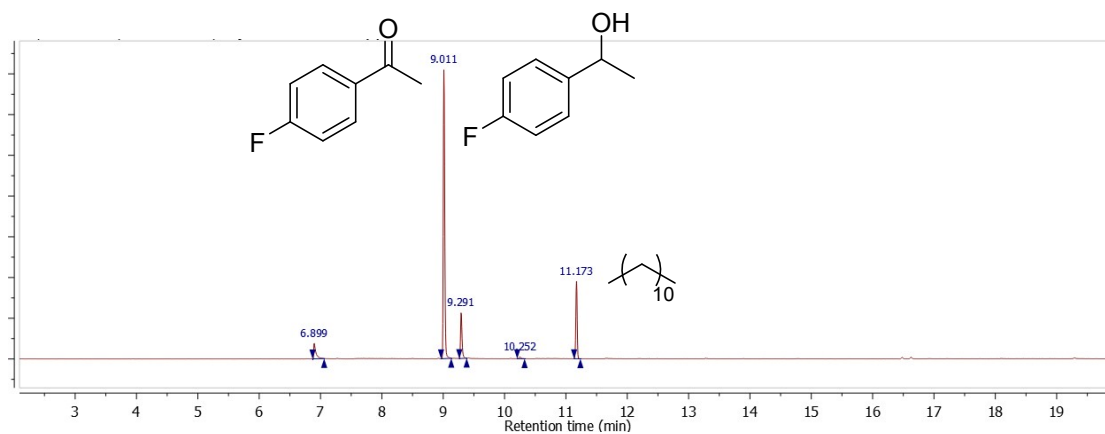
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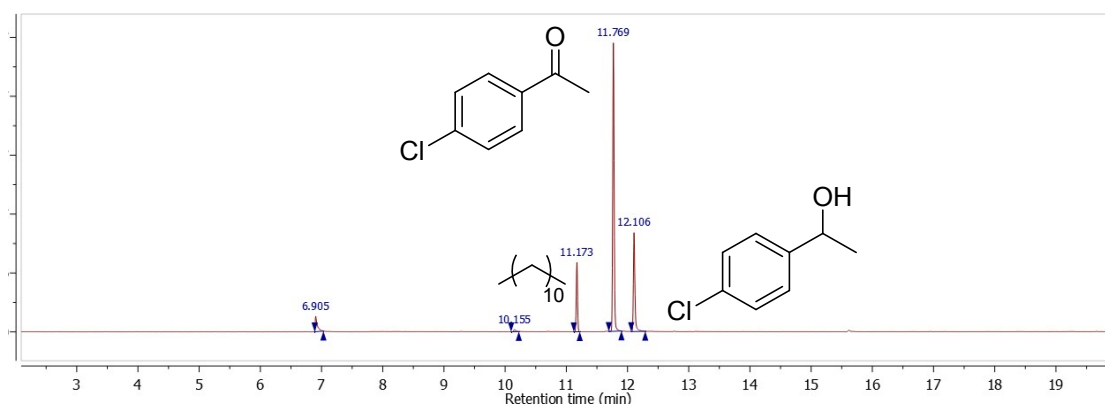
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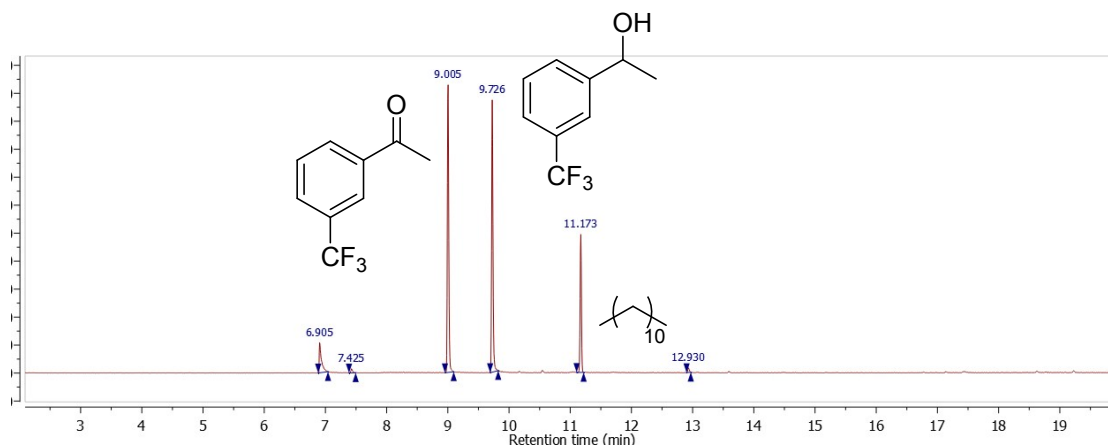
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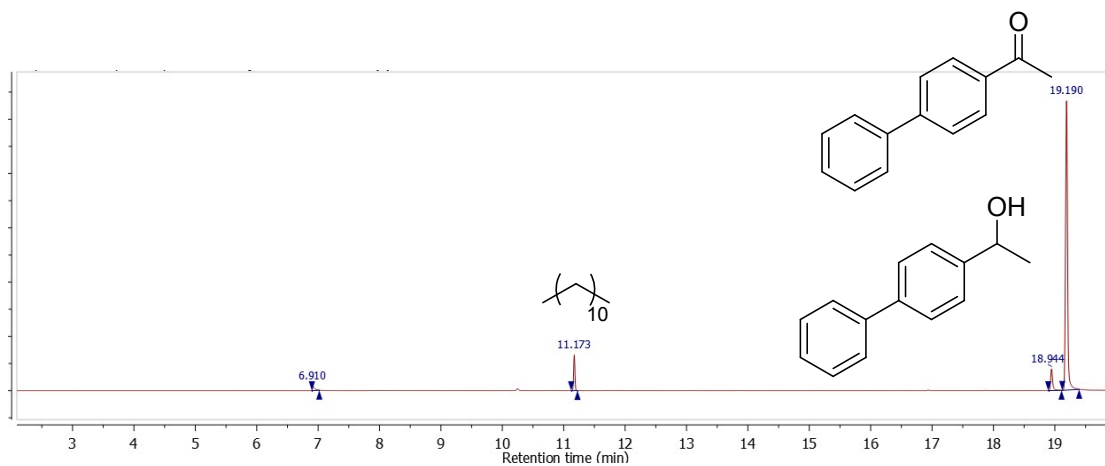
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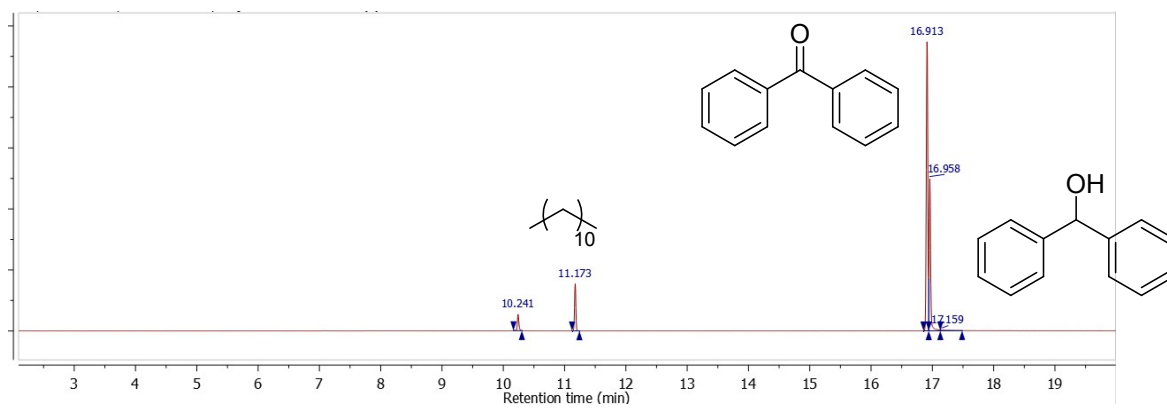
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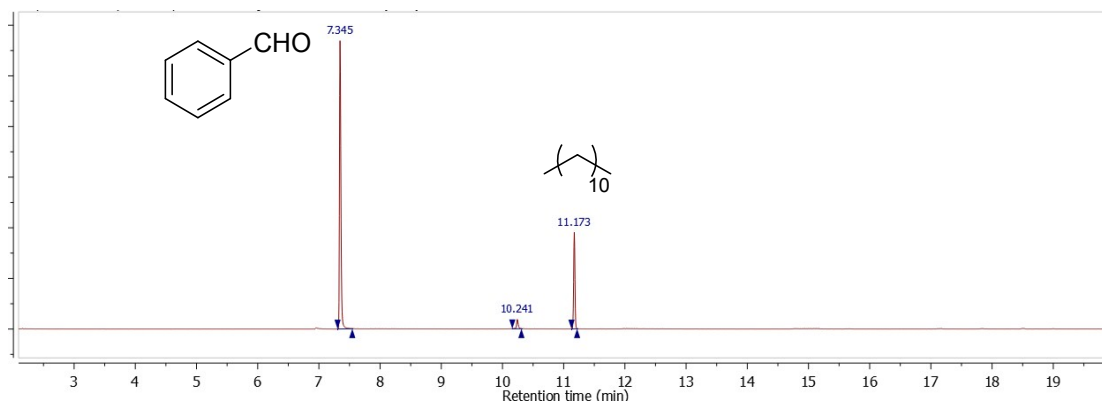
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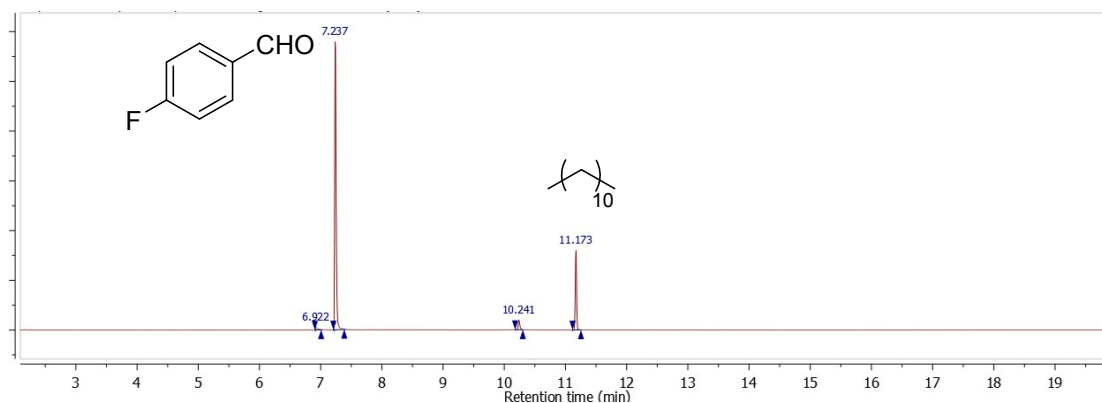
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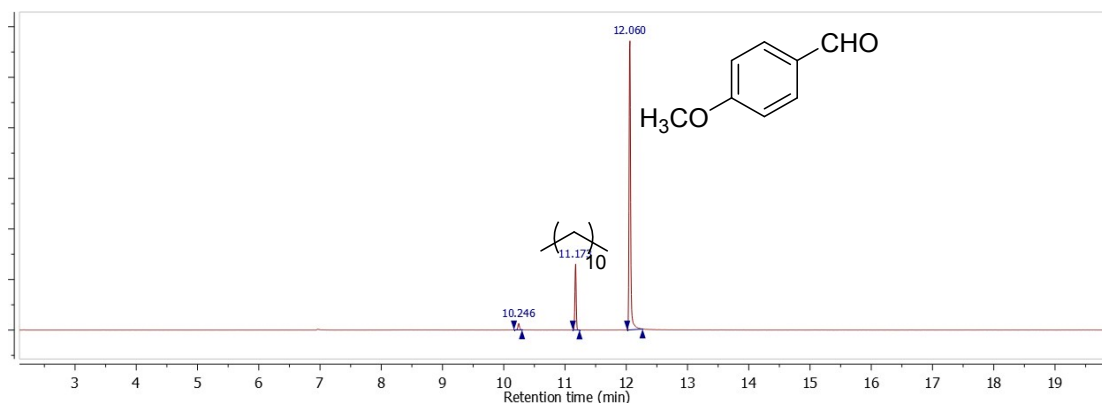
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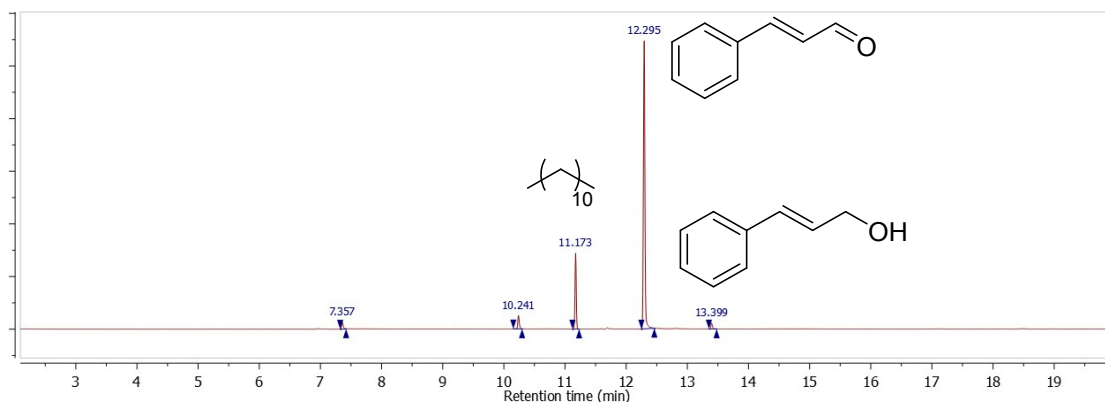
For Fig. 8, Compound **a2**



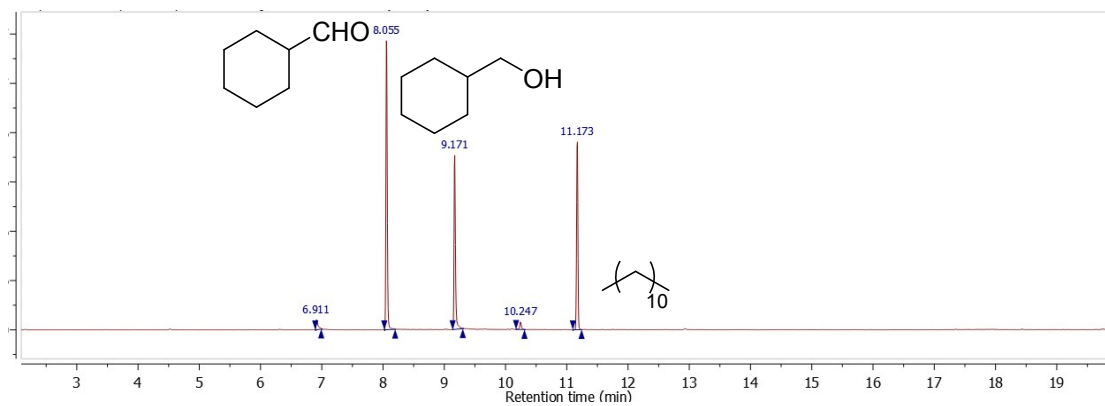
For Fig. 8, Compound **a3**



For Fig. 8, Compound **a4**



For Fig. 8, Compound **a5**



For Fig. 8, Compound **a6**

