

Supporting Information

“Click” Post-Functionalization of Metal-Organic Framework for Engineering Active Single-Site Heterogeneous Ru(III) Catalysts

Suntao Wu, Liyu Chen, Biaolin Yin and Yingwei Li*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

* To whom correspondence should be addressed. E-mail: liyw@scut.edu.cn

This PDF file includes:

Experimental

Figs. S1 to S6

GC-MS and NMR spectra

Experimental

1. General information

All chemicals and reagents are commercially available and used as received without further purification. 4'-Ethyneyl-2,2':6',2''-terpyridine was prepared according to the literature procedures.^{1,2}

The powder X-ray diffraction patterns of the samples were measured on a Rigaku diffractometer (D/MAX-III A, 3 kW) using Cu K α radiation (40 kV, 30 mA, 0.1543 nm). N₂ adsorption isotherms were obtained on a Micromeritics ASAP 2020M instrument at 77 K. Solution ¹H-NMR data were identified by a Bruker Avance III 400 spectrometer. The residual solvent peak was used as the reference value. HRMS data were recorded on a MAT95XP high resolution mass spectrometry using Electron Spray Ionization (ESI) as ionization source.

Liquid chromatography-mass spectrometry (LC-HRMS) analyses were performed on an Agilent 1290 Infinity LC interfaced to the Bruker maXis impact. The flow rate of the LC-HRMS analyses was held steadily at 1 mL/min and the methanol: water ratio was kept constant at 40:60 for the entire 10 min running time.

TEM micrographs were recorded on a JEM-2010HR (JEOL) instrument. The ruthenium contents of the samples were investigated quantitatively by atomic absorption spectroscopy (AAS) on a Hitachi Z-2300 instrument. IR spectrum was recorded on a Thermo Fisher iS10 FTIR spectrometer with potassium bromide pellets.

2. Materials preparation

Preparation of MIL-101(Cr)-NH₂. MIL-101(Cr)-NH₂ was prepared according

to the reported procedures. Typically, 300 mg activated MIL-101(Cr) was added to a mixture of 7 mL conc. sulfuric acid and 5 mL conc. nitric acid, which was then stirred for 5 h at 0 °C. The mixture was poured into ca. 50 mL ice. The isolated solid was then heated in 30 mL water at 80 °C for 6 h. The resulting green solid was dried at 120 °C under vacuum for 12 h to yield the MIL-101(Cr)-NO₂. Subsequently, 0.9 g of the as-prepared MIL-101(Cr)-NO₂ and 9.78 g of SnCl₂•2H₂O were suspended in 100 mL ethanol. The mixture was heated at 80 °C for 12 h. The green powder was centrifuged and suspended in 20 mL conc. hydrochloric acid. Afterward, the solid was centrifuged and washed with plenty of water until the filtrate pH value was neutral. Finally, the solid material was dried at 120 °C under vacuum for 12 h to give MIL-101(Cr)-NH₂.

Preparation of MIL-101(Cr)-N₃. 300 mg of freshly dried MIL-101(Cr)-NH₂ was placed into a glass tube with 5 mL THF, 0.28 mL tBuONO, and 0.3 mL TMSN₃. The reaction mixture was stirred at room temperature overnight. The green solid was obtained by filtration, washed with THF, and then dried under vacuum to remove the solvents at 65 °C for 12 h. Elemental analysis: Cr₃F(H₂O)₂O(BDC-N₃)₃•5H₂O. Calculated: C, 30.90; H, 2.46; N, 13.51%. Found: C, 31.09; H, 2.44; N, 13.23%. ¹H NMR (DMSO-d₆, 400 MHz), δ: 7.83 (1H, d, J=8.3 Hz), 7.76-7.74 (2H, m). HRMS (ESI) m/z: calcd for C₈H₅N₃O₄ [2M-H]⁻, 413.0482; found [2M-H]⁻, 413.0465.

Preparation of MIL-101(Cr)-tpy. 100 mg of MIL-101-N₃ and 5 mg CuI were placed in the nitrogen-degassed 5 mL toluene solution with 30 mg 4'-ethynyl-2,2':6',2''-terpyridine (0.12 mmol). The reaction mixture was stirred at 80 °C for 12 h.

The resultant precipitate was collected by filtration, washing with toluene and THF to remove unreacted substrates, and finally drying at 65 °C for 12 h under vacuum. $\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{BDC}-\text{N}_3)_{2.54}(\text{BDC}-\text{tpy})_{0.46}\cdot 5\text{H}_2\text{O}$ (corresponding to ca. 14.8% azide functionalization): Calculated: C, 36.38; H, 2.66; N, 13.81%. Found: C, 36.09; H, 2.34; N, 13.83%.

Preparation of $\text{RuCl}_3@$ MIL-101(Cr)-tpy. Typically, 300 mg MIL-101(Cr)-tpy was placed into a glass tube with 10 mL methanol solution containing 30 mg $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$. The reaction mixture was refluxed and stirred for 6 h. The resulting brown solid was collected by filtration and washed with abundant methanol, water, and diethyl ether until the washings became colorless. The solid was finally dried at 65 °C for 12 h under vacuum. $\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{BDC}-\text{N}_3)_{2.54}(\text{BDC}-\text{tpy})_{0.46}(\text{RuCl}_3)_{0.11}\cdot 5\text{H}_2\text{O}$: Calculated: C, 35.75; H, 2.61; N, 13.55%. Found: C, 35.22; H, 2.32; N, 13.37%. The amount of ruthenium in the final solid (determined by AAS) was 0.97 wt%.

3. Digestion and analysis of the MIL-101(Cr) derivatives by mass spectrometry and ^1H NMR

Approximately 50 mg of the MIL-101(Cr) derivative was decomposed using 1 mol/L aqueous NaOH (2 mL) and removing the $\text{Cr}(\text{OH})_3$ solid by filtration, then the terephthalic acid derivative could be precipitated in the filtrate under neutral conditions (pH~7) using 1 mol/L HCl solution. After centrifugation and washing with acetone, the solid was dried at 338 K under vacuum. The terephthalic acid derivative

was obtained for the NMR and HRMS analyses.

Approximately 10 mg of the terephthalic acid derivative was dissolved in deuterated dimethyl sulphoxide (DMSO-d₆) for the solution ¹H NMR spectra. Then approximately 6 mg of terephthalic acid derivative was dissolved using methanol for the HRMS and LC-HRMS analyses.

4. General procedures for the oxidation of alcohols

Alcohol (0.5 mmol), H₂O₂ (0.75 mmol), and RuCl₃@MIL-101(Cr)-tpy (50 mg, 1 mol%) were added to 2 mL of H₂O. The reaction mixture was stirred at 100 °C. Upon reaction completion, the solid catalyst was isolated from the solution by filtration and washed with ethyl acetate. The supernatant was extracted with ethyl acetate and subsequently analyzed by GC/MS (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column).

For the recyclability tests, the reactions were performed under the same reaction conditions as described above, except using the recovered catalyst. Each time, the catalyst was isolated from the solution at the end of the reaction, washed with ethyl acetate, dried at 65 °C under vacuum, and then reused in the next run.

References:

1. S. Li, C. N. Moorefield, C. D. Shreiner, P. S. Wang, R. Sarkar and G. R. Newkome, *New J. Chem.*, 2011, **35**, 2130.
2. V. Grosshenny, F. M. Romero and R. Ziessel, *J. Org. Chem.*, 1997, **62**, 1491.

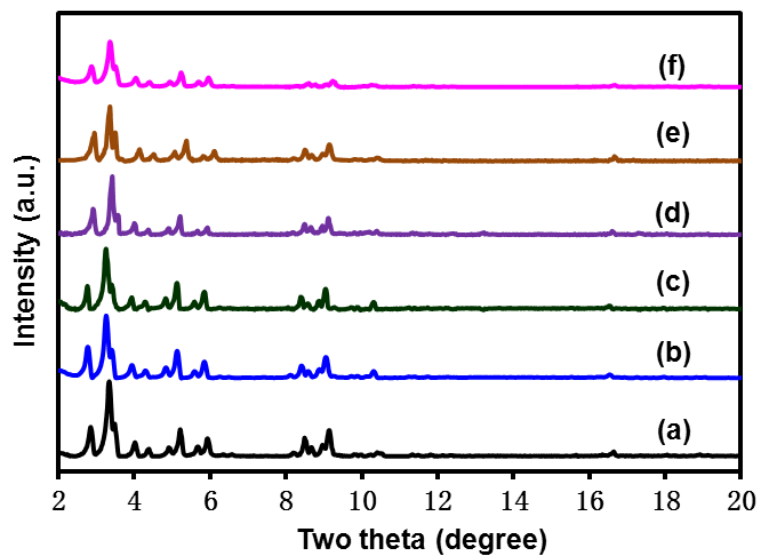


Figure S1. Powder X-ray diffraction patterns of simulated MIL-101(Cr) (a), MIL-101(Cr)-NH₂ (b), MIL-101(Cr)-N₃ (c), MIL-101(Cr)-tpy (d), and RuCl₃@MIL-101(Cr)-tpy before (e) and after (f) reaction.

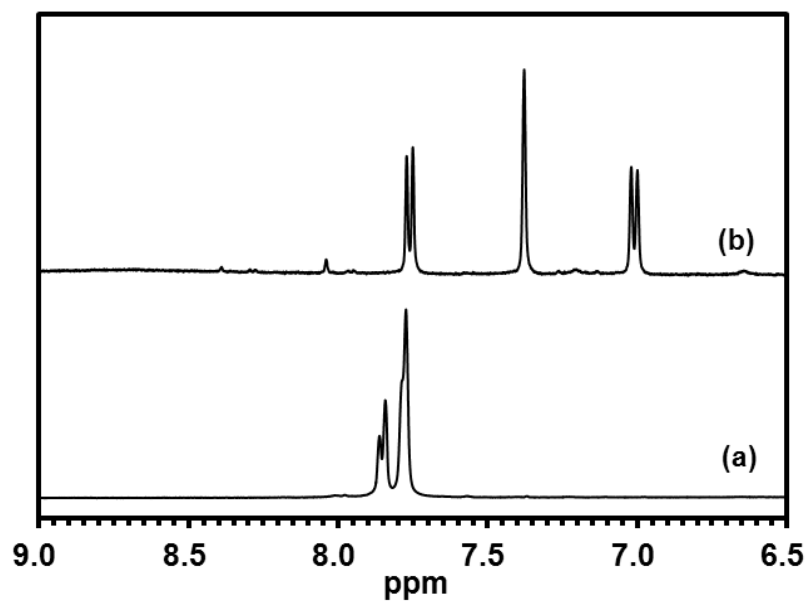


Figure S2. ¹H-NMR comparison between digested MIL-101(Cr)-N₃ (a), and digested MIL-101(Cr)-NH₂ (b).

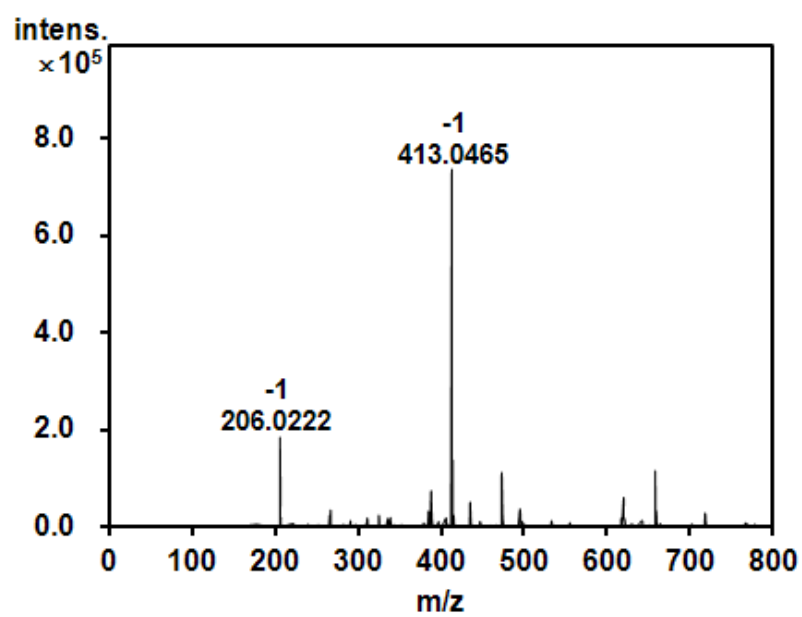


Figure S3. HRMS spectrogram of the linker molecule of the digested MIL-101(Cr)-N₃ (negative mode).

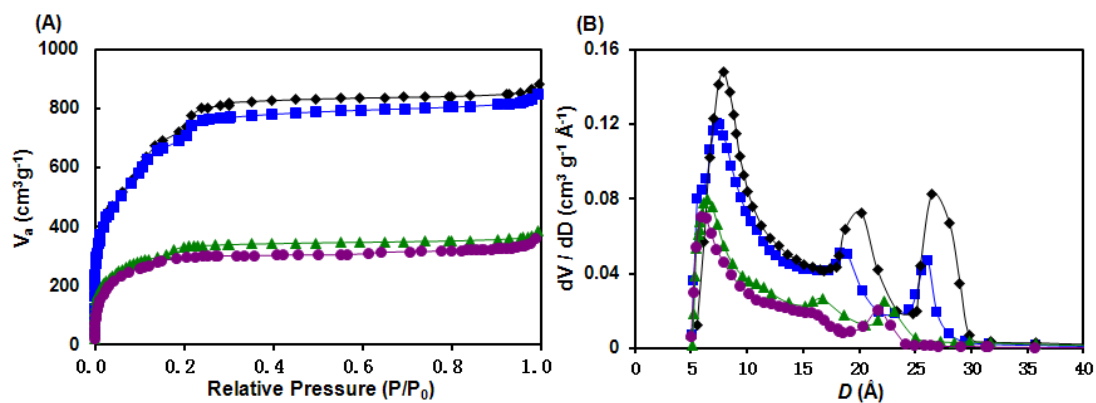


Figure S4. Nitrogen adsorption isotherms at 77 K (A) and pore size distribution (B) of the MIL-101(Cr)-NH₂ (◆), MIL-101(Cr)-N₃ (■), MIL-101(Cr)-tpy (▲), and RuCl₃@MIL-101(Cr)-tpy (●).

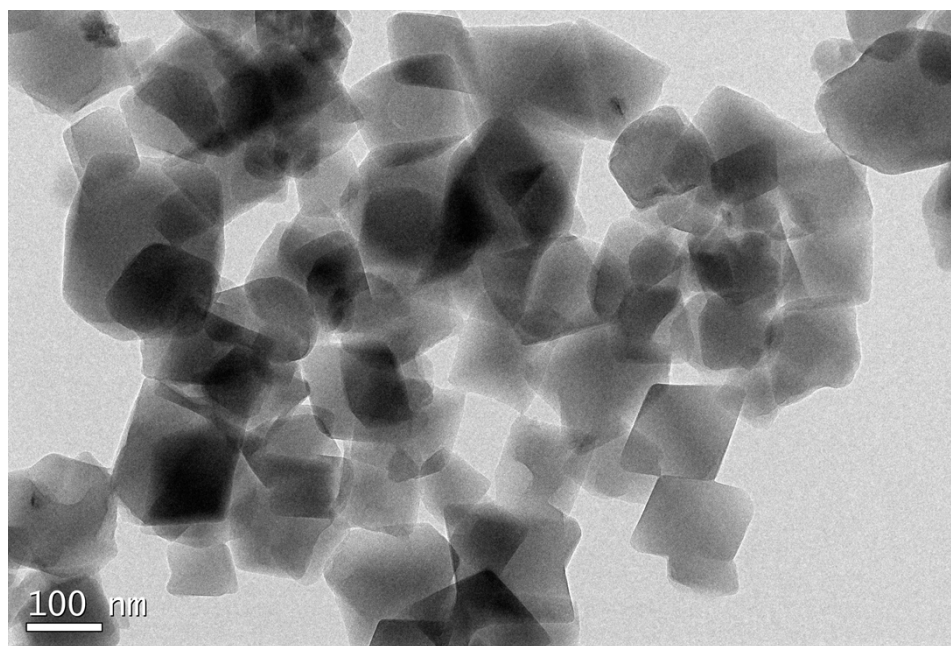


Figure S5. TEM micrograph of the RuCl₃@MIL-101(Cr)-tpy material.

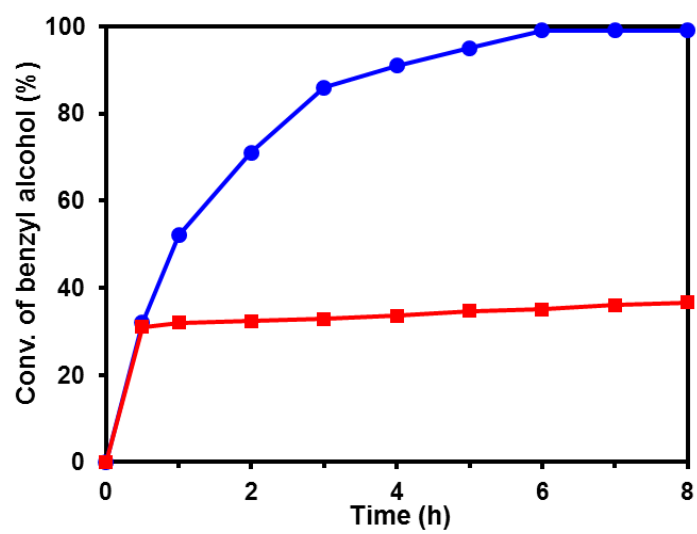
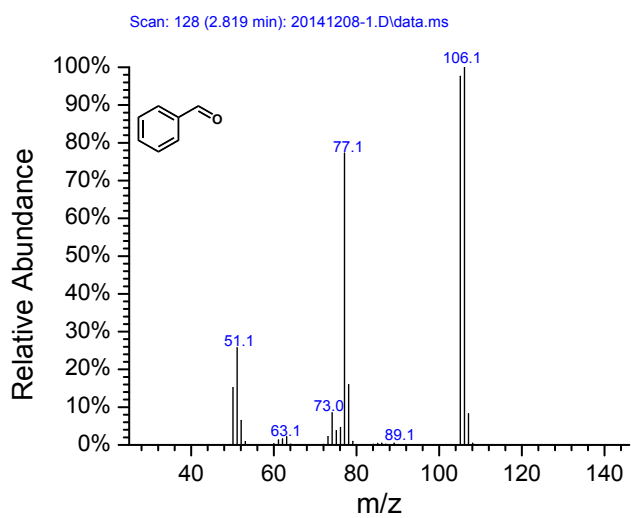
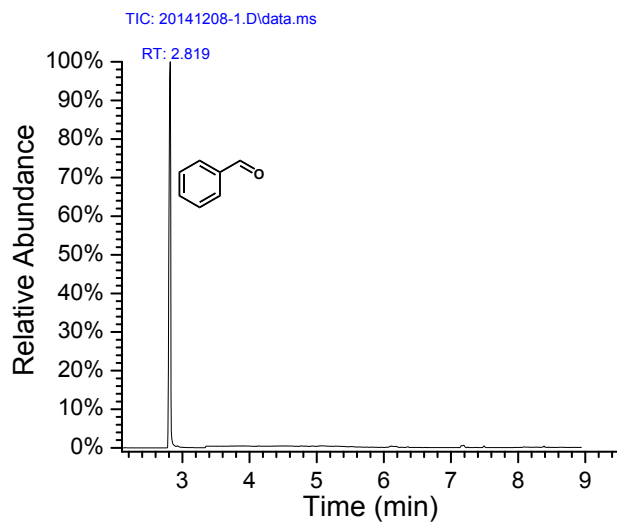


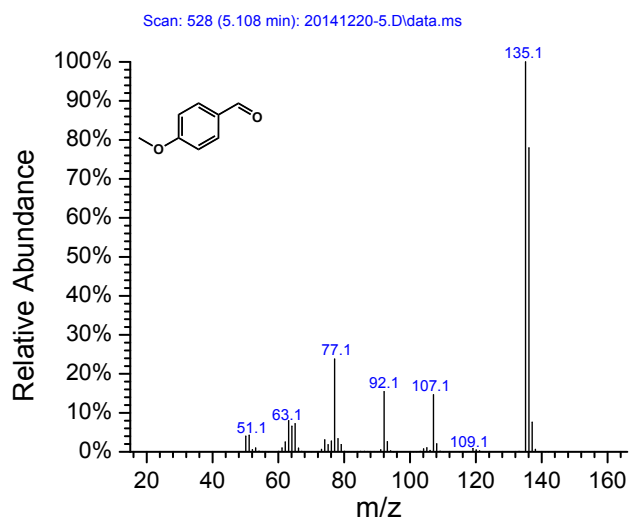
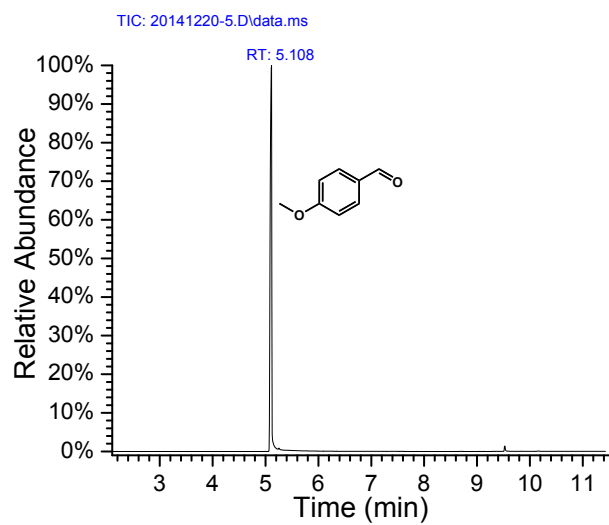
Figure S6. Conversion vs. time plot for the oxidation of benzyl alcohol. (●) With $\text{RuCl}_3@MIL-101(\text{Cr})\text{-tpy}$; (■) with filtrate.

The GC-MS or NMR spectra for the reactions listed in Table 2

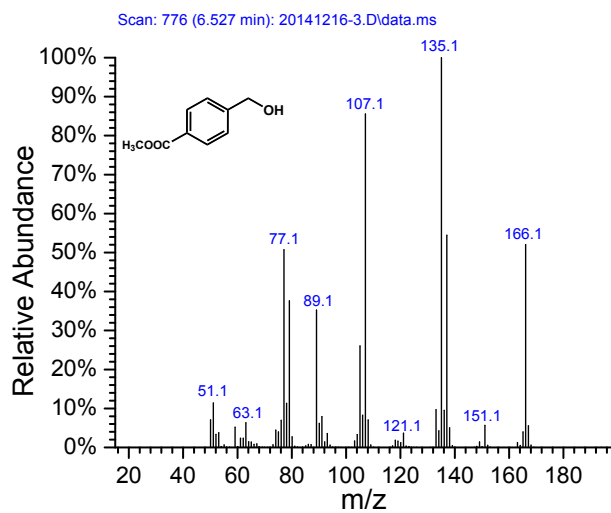
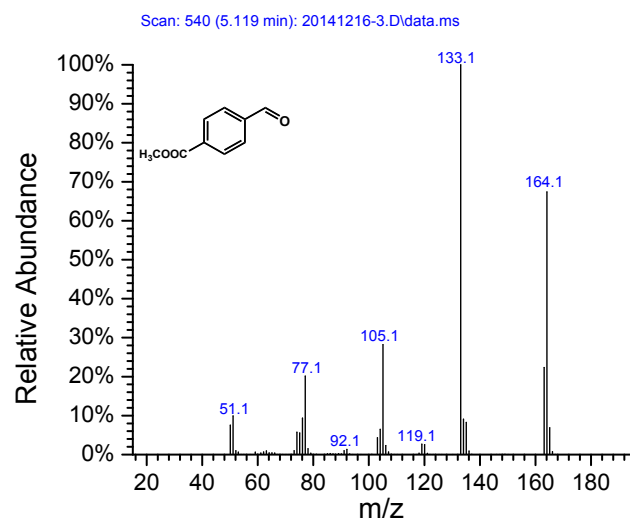
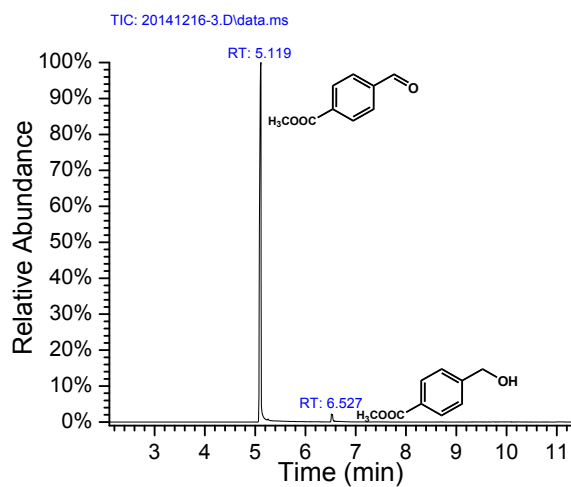
Entry 1



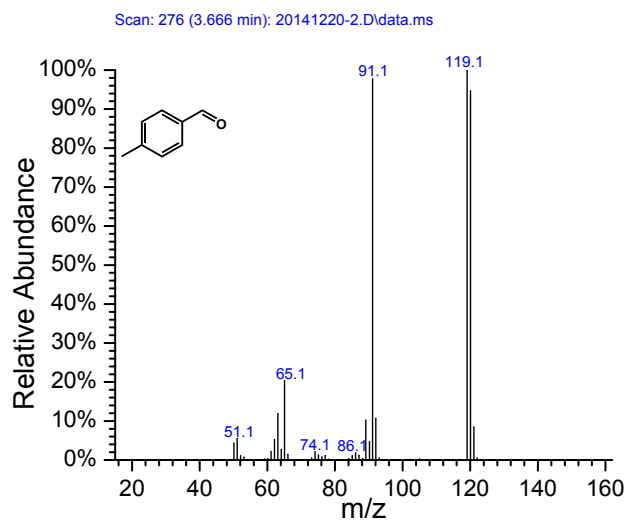
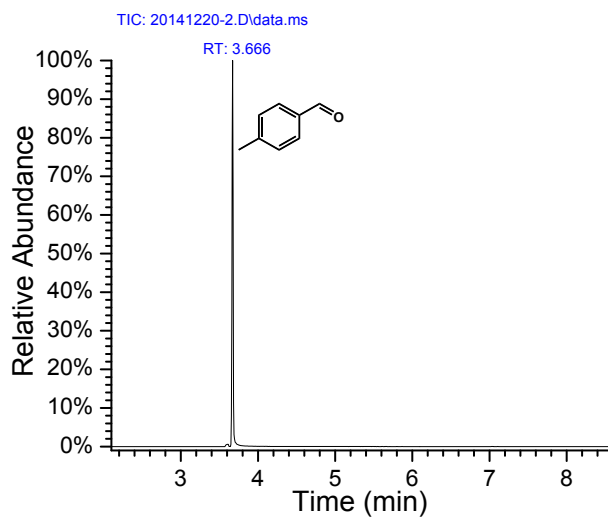
Entry 2



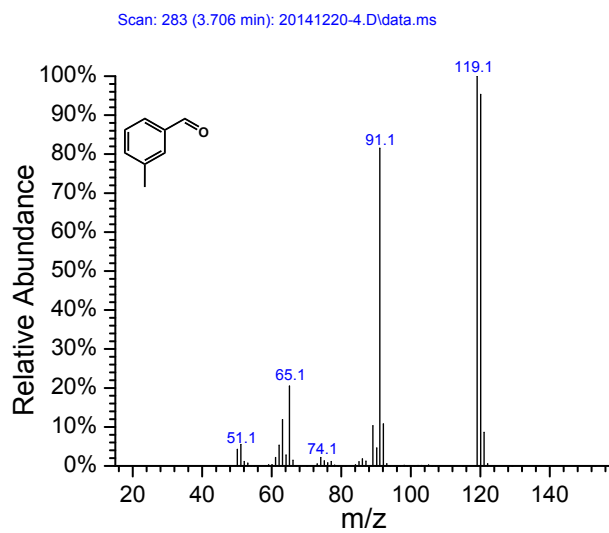
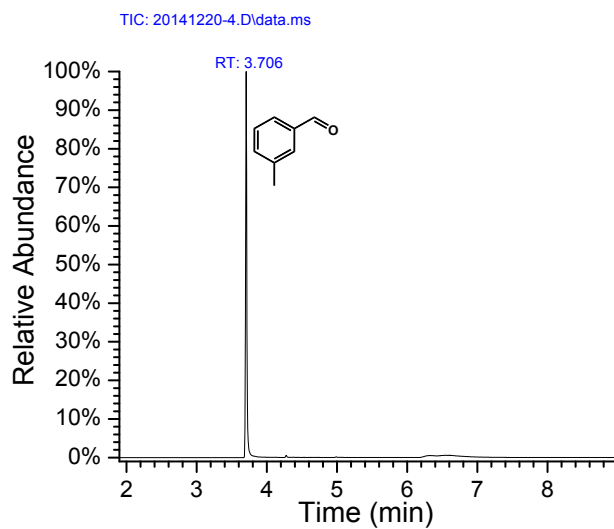
Entry 3



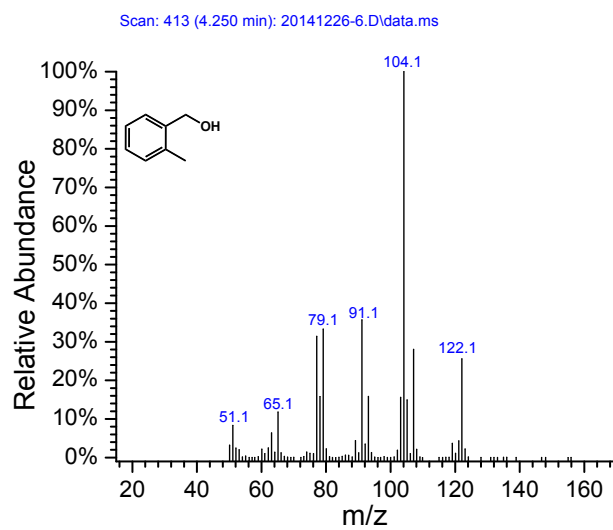
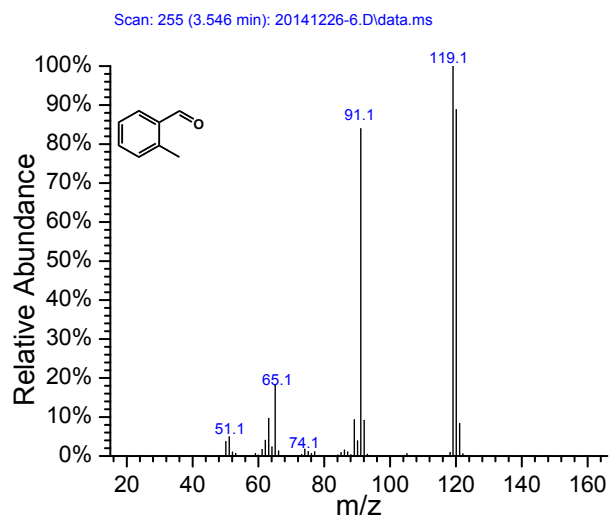
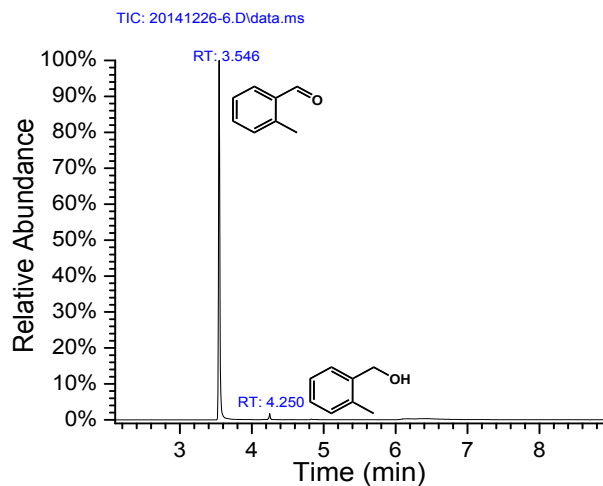
Entry 4



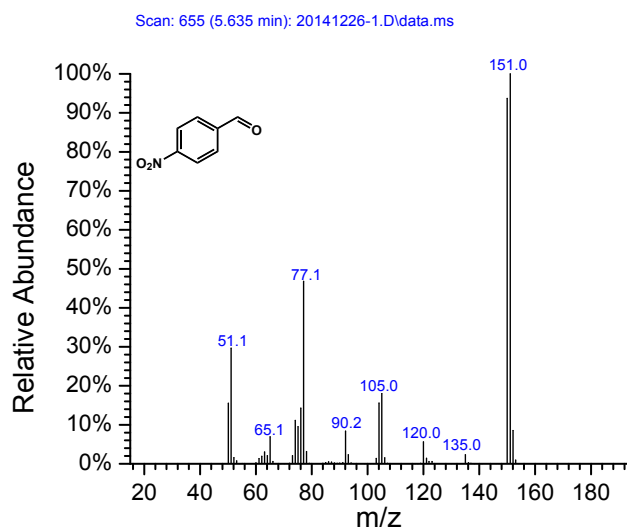
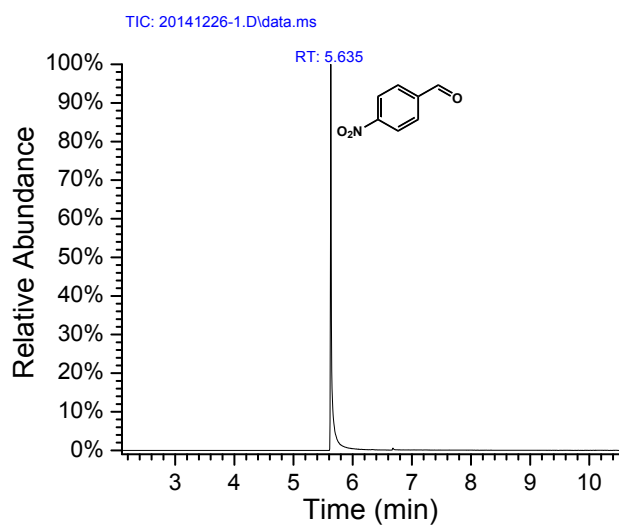
Entry 5



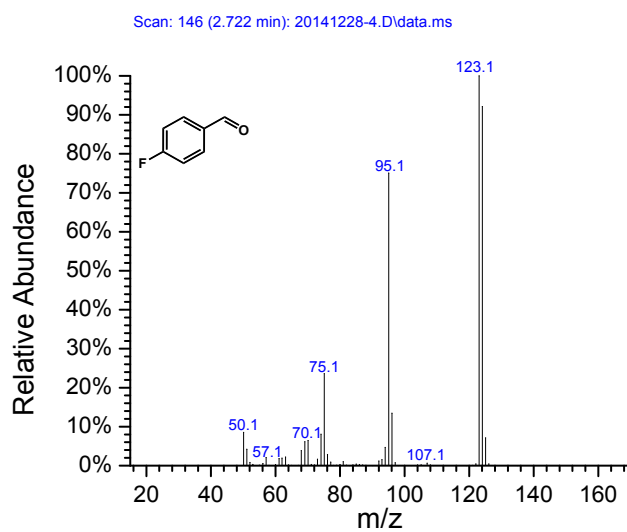
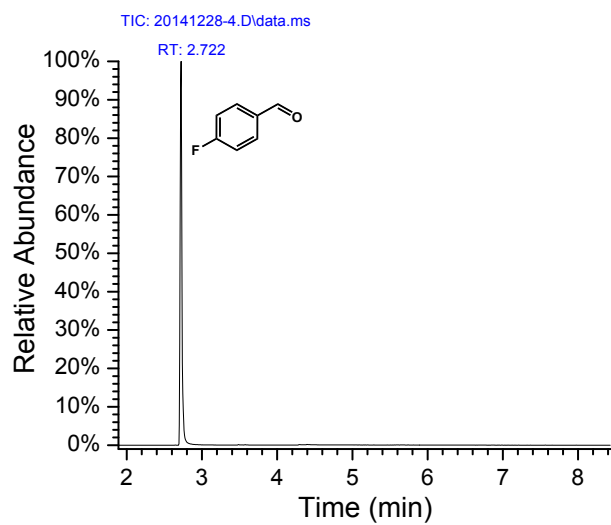
Entry 6



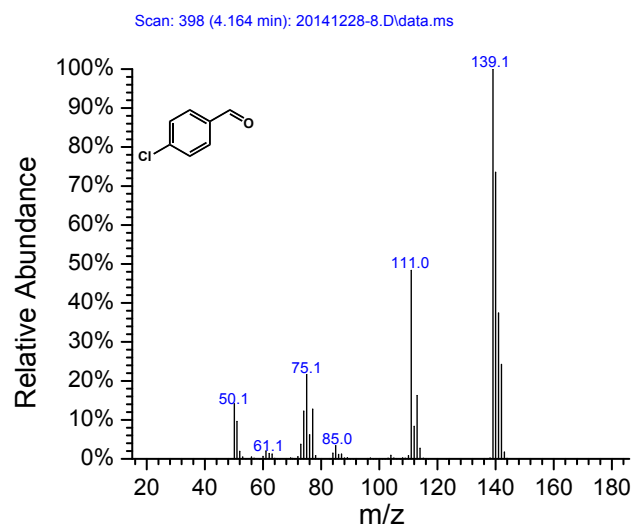
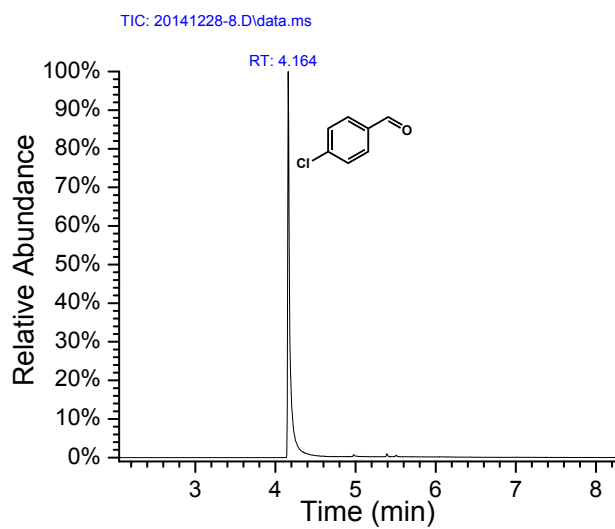
Entry 7



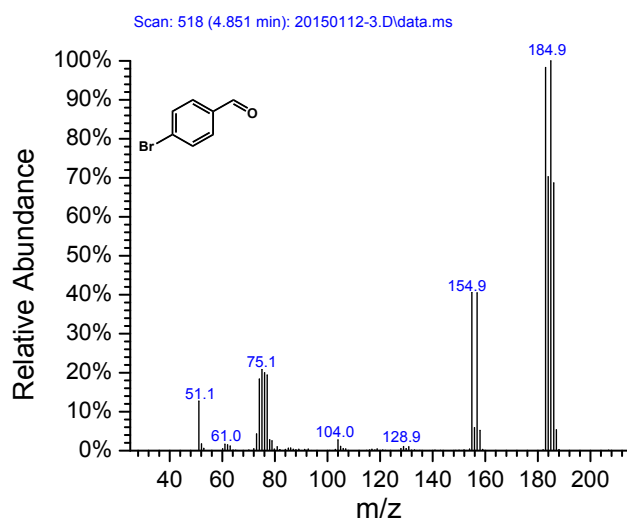
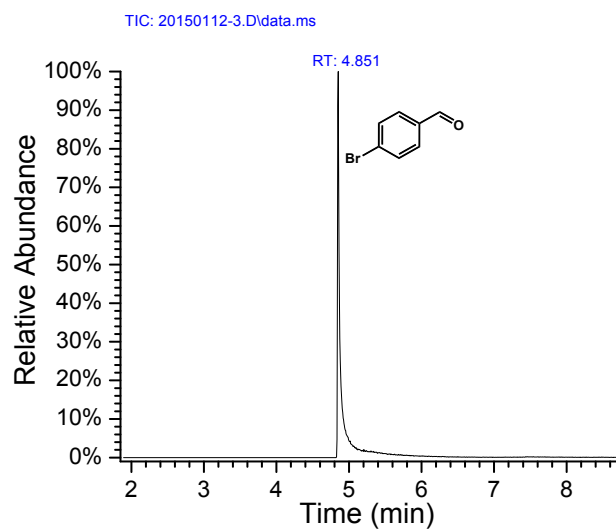
Entry 8



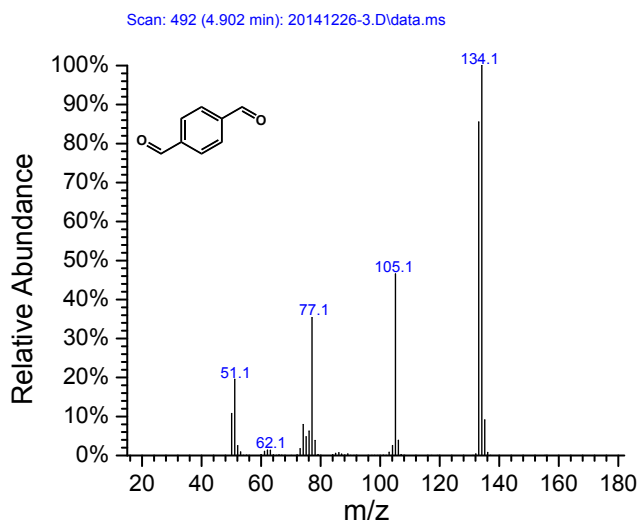
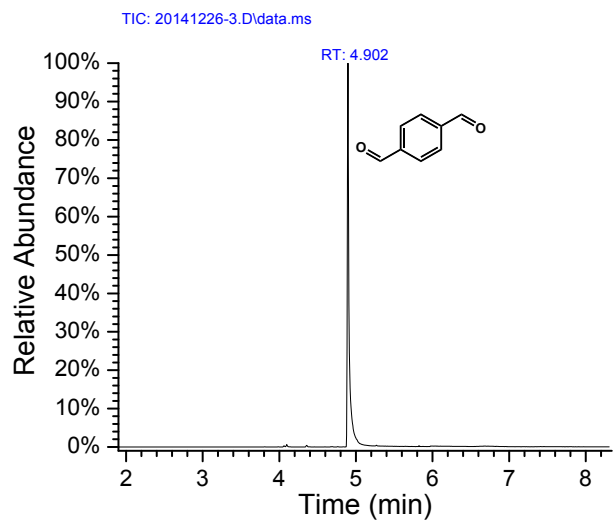
Entry 9



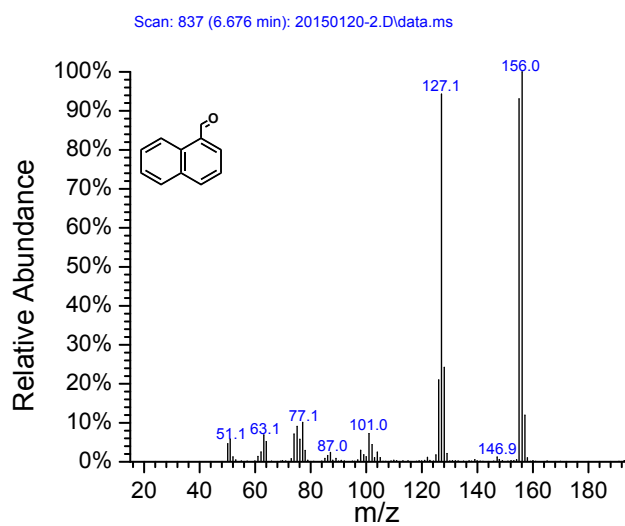
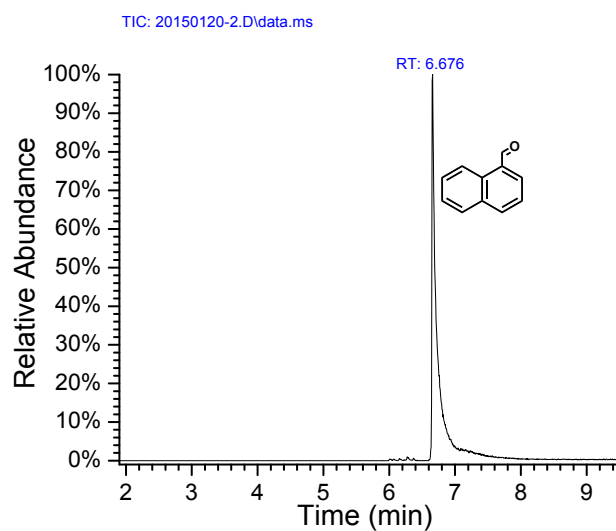
Entry 10



Entry 11



Entry 12



Entry 13

