Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Merging metal-organic framework catalysis with organocatalysis: Thiourea functionalized heterogeneous catalyst at nanoscale

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Supporting Information

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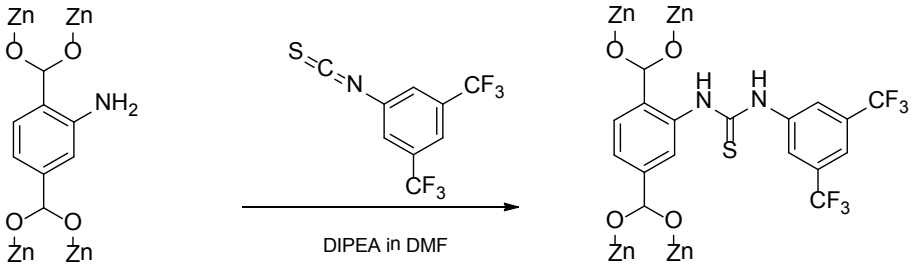
General Information. All ^{1}H NMR, and ^{13}C NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG, ^{1}H 400 MHz) spectrometer at ambient temperature in $CDCl_3$. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, 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 Kα radiation (λ=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. All reactions were performed under nitrogen, in oven dried or flame dried glassware with magnetic stirring.

The synthesis of nano IRMOF-3

Synthesis of nano-IRMOF-3 was achieved using modified literature procedure.[1] $Zn(NO_3)_2 \cdot 4H_2O$ (1.44 g, 5.5 mmol), 2-aminoterephtalic acid (0.37 g, 2 mmol), and 50 mL *N*,*N*-dimethylformamide (DMF) were mixed at room temperature. The thus obtained mother solution was sealed and placed in the oven at 55 °C for 96 h. 10 mL of the incubated mother solution were used, 2 mmol (0.728 g) CTAB were added with stirring at 55 °C until the CTAB was completely dissolved. The mother solution was then transferred to another oven at 105 °C and heated for 1.5 h. After that, TEA was added (278 μL, 2 mmol) under strong stirring for 10 min. Products were separated, well washed with DMF three times, chloroform three times, then immersed into chloroform over night to remove DMF guest molecules from IRMOF-3 crystals, and finally dried under vacuum.

[1] M. Y. Ma, D. Zacher, X. N. Zhang, R. A. Fischer, N. Metzler-Nolte, *Cryst. Growth Des.*, 2011, **11**, 185.

The synthesis of IRMOF-3-thiourea catalyst.



IRMOF-3 **IRMOF-3-thiourea**

Isothiocyanate modification of IRMOF-3:

Approximately 400 mg of nano-scaled IRMOF-3 (0.492 mmol based on MW of 813 g/mol) was suspended in 10 mL of $CHCl_3$, then 2 equiv. of 3,5-bis(trifluoromethyl)phenyl isothiocyanate and diisopropylethylamine (0.33 mL,4 mmol). The mixture was stirred slowly at 40 ºC for 24 h, after which the solvent was decanted, and fresh DMF (10 mL) was added once a day for three days and then $CHCl_3$ was used to rinse the crystals once a day for twice. The crystals were dried under vacuum at 40 ºC before use. All samples were vacuumed at 100 ºC before characterizations.

For catalyst recycle:

At the end of each reaction cycle, the catalyst was recovered by centrifugation of the solution mixture followed by washing with a solvent (5 - 10 ml). After being immersed in the solvent for 12 h and dried at 40 ºC under vacuum for 12 h, the catalyst was reused.

Table S1. Reaction condition details for the synthesis of catalyst **C6**, **C7** and **C8**.

Entry	Catalyst	Temperature	Rxn Time	Equiv.	Thioura loading
1	**C6**	40 ºC	1 h	2	4%
2	**C7**	40 ºC	24 h	2	17%
3	**C8**	80 ºC	24 h	4	26%

Characterizatios of as-synthesized IRMOF-3-thiourea catalyst.

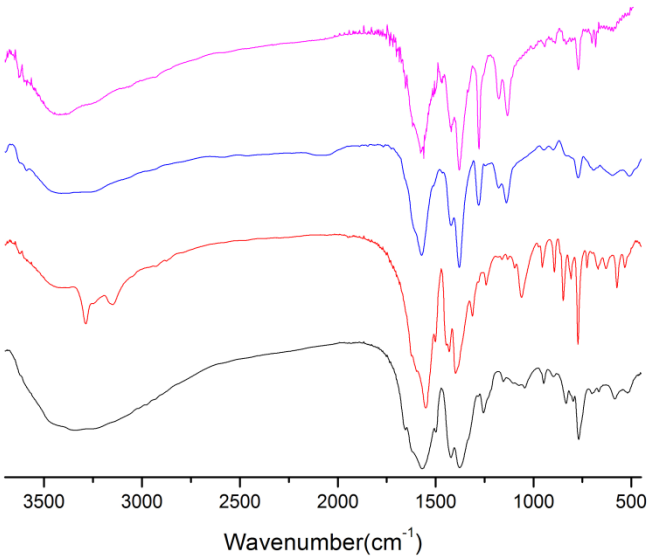


Figure S1. FTIR spectra of IRMOF-3 and IRMOF-3-thourea. From bottom to top, IRMOF-3, 4% modified IRMOF-3 (**C6**), 17% modified IRMOF-3 (**C7**), 26% modified IRMOF-3 (**C8**).

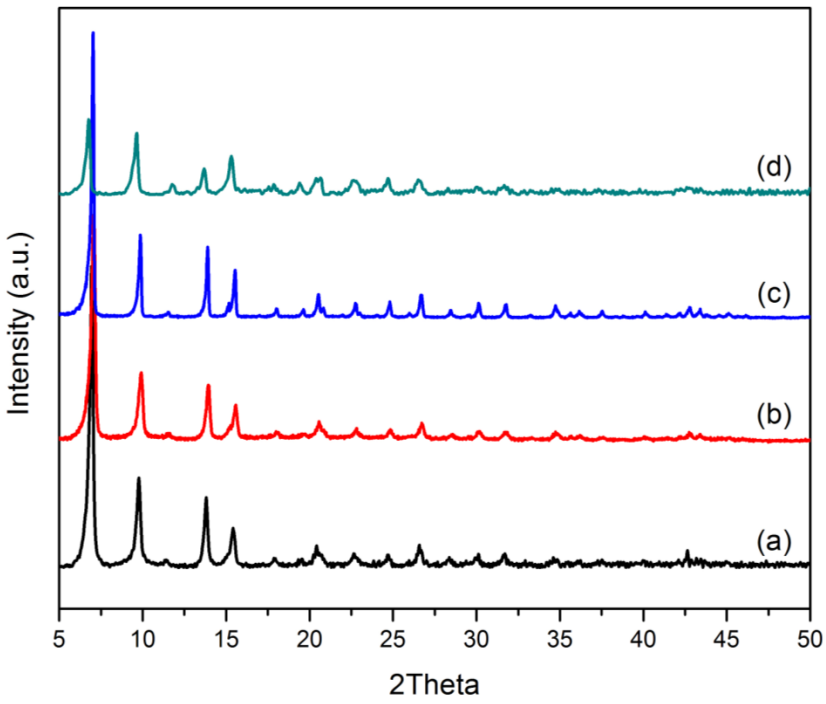


Figure S2. PXRD patterns of MOFs. (a) IRMOF-3 (b) nanosized IRMOF-3 (c) nanosized IRMOF-3-thiourea (26% modified, **C8**), (d) Recycled IRMOF-3-thiourea catalyst.

Brunauer−Emmer−Teller (BET) Surface Areas Analysis

To confirm the modification of the MOF and investigate its effect on porosity, the Brunauer-Emmett-Teller (BET) surface area of two modified samples were meansured via nitrogen adoption at 77 K. The surface area is reduced relative to 351.631 in comparison to IRMOF-3 (~ 600 m^2g^{-1} under our condition), which is expected as a result of large functional group modification. Considering the high crystallinity (from PXRD and SEM), the trapping of the guest molecules inside the pores may be caused by steric hindrance of the pendant amino groups on the thiourea-phenyl linkers, which may serve to block accessibility of the otherwise open pores.

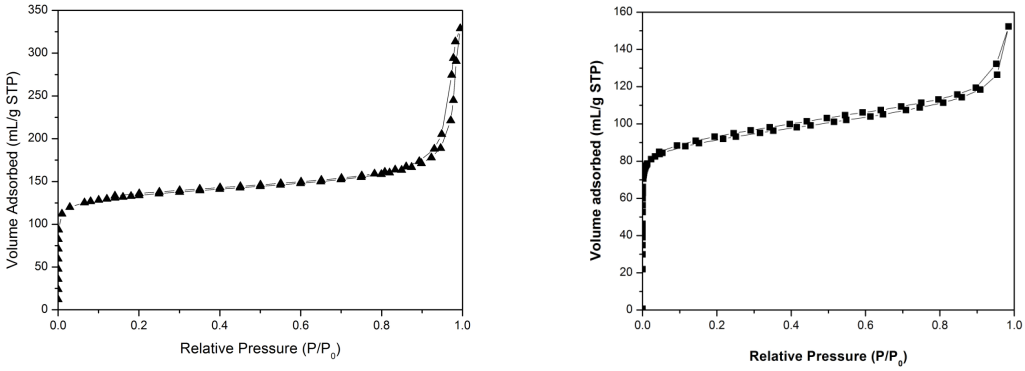


Figure S3. N_2 adsorption isotherms for IRMOF-3 (left) and IRMOF-3-thiourea (**C8**, right).

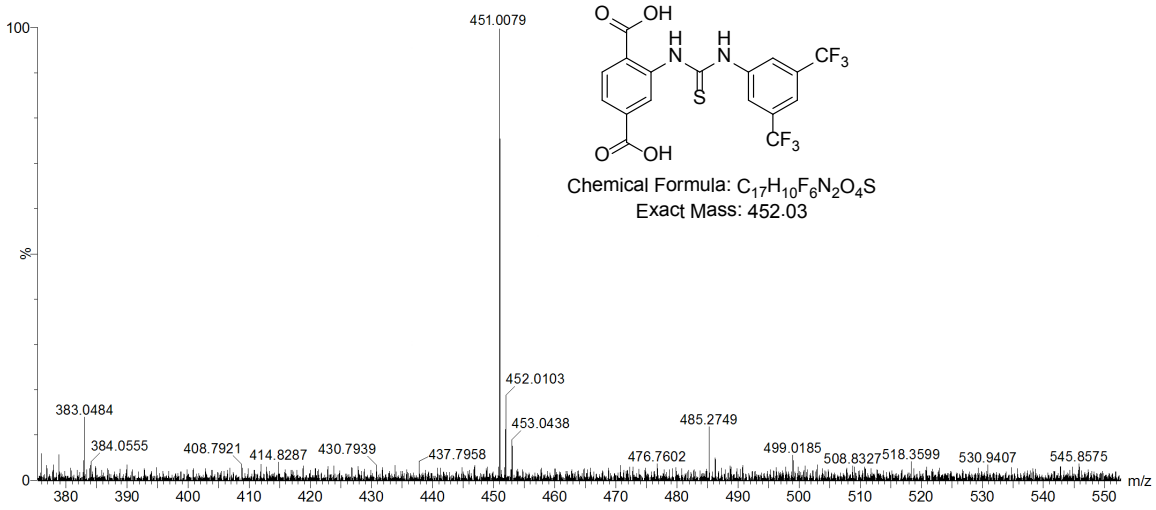


Figure S4. ESI-MS (negative mode) of IRMOF-3-thiourea catalyst **C8**.

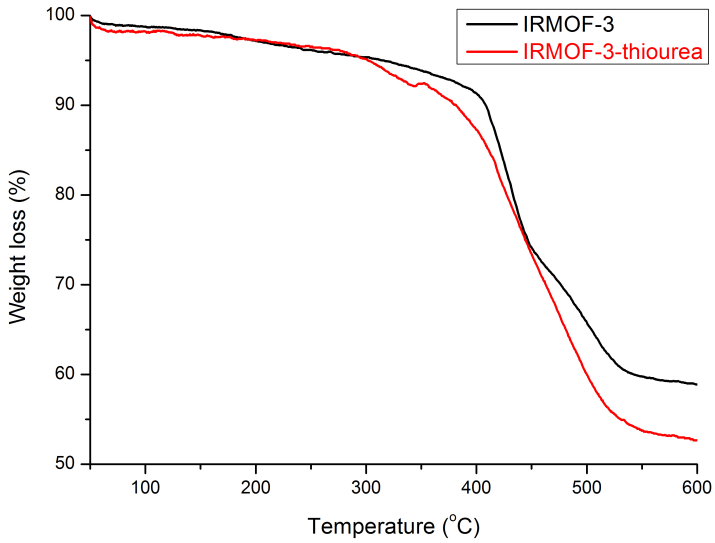


Figure S5. TG spectra of IRMOF-3 (Black) and IRMOF-3-thiourea catalyst **C8** (Red).

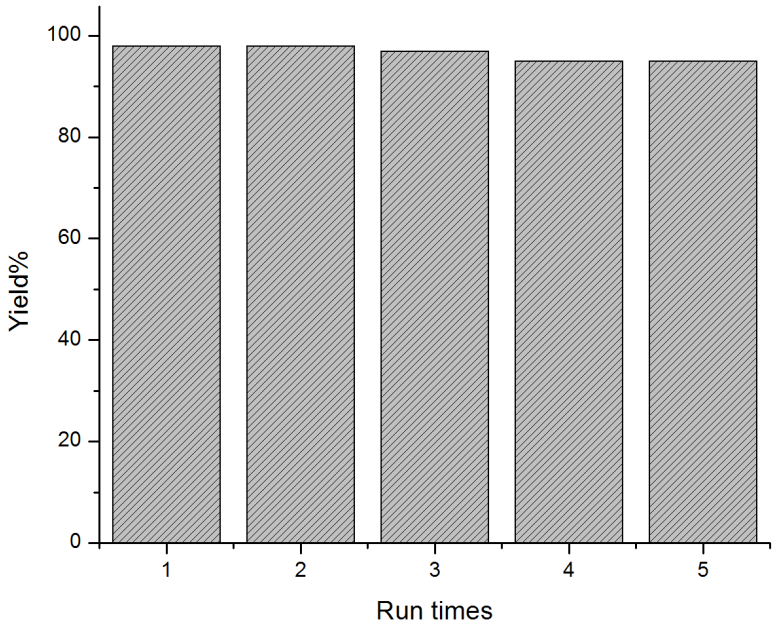


Figure S6. The recyclable results of IRMOF-3-thiourea catalyzed acetalization of benzaldehyde

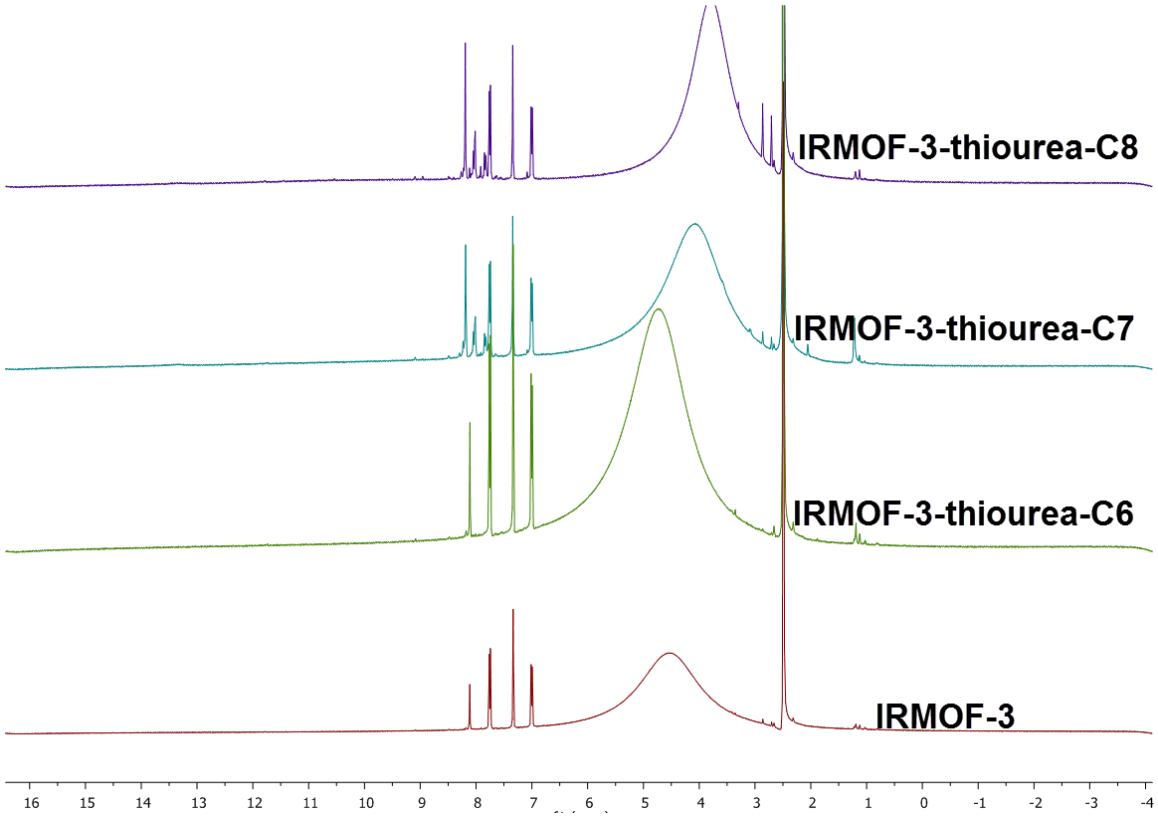
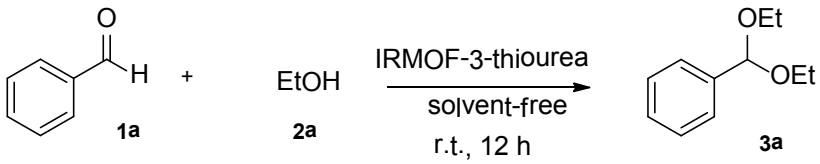


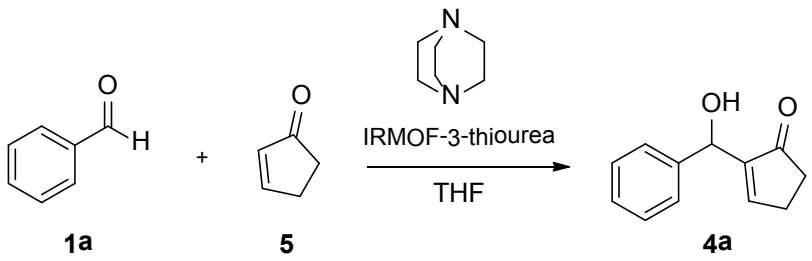
Figure S7. Full ^{1}H NMR spectra of digested IRMOF-3 and IRMOF-3-thiourea.

General procedure for acetalization of aldehydes using IRMOF-3-thiourea catalyst (Table 1 and 2)



A 10-mL reaction vessel (oven dried) was charged with 0.2 mol% **C8** catalyst (based on 26 mol% thiourea, 0.002 mmol, 6.8 mg) in dry ethanol (184 mg, 4.0 mmol), and benzaldehyde substrate (106 mg, 1.0 mmol). The reaction mixture was stirred under N_2 atmosphere at room temperature (23 ºC) for 12 h. After the reaction was over, the reaction mixture was centrifuged. The yield of desired product was analyzed by GC-MS using nitrobenzene as internal standard.

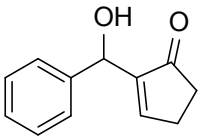
General procedure for the MBH reaction



1a **5** **4a**

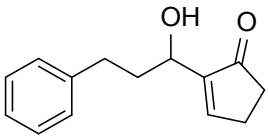
A 10-mL reaction vessel was charged with 2 mol% **C8** catalyst (based on 26 mol% thiourea, 0.02 mmol, 68 mg), benzaldehyde substrate (106 mg, 1.0 mmol), 2-cyclopenten-1-one (164 mg, 2.0 mmol), 1,4-diazabicyclo [2.2.2]octane (56 mg, 0.5 mmol) in 2 mL of tetrahydrofuran under N_2 atmosphere. The reaction was stirred at 4 ºC for 24 h. After dilution with hexanes, the reaction mixture was directly subjected to flash chromatography on silica gel and eluted with a hexanes:ethyl acetate solution (9:1 - 1:1) to yield 2-(hydroxy(phenyl)methyl)cyclopent-2-enone **4a** as a colorless oil.

2-(Hydroxy-phenyl-methyl)-cyclopent-2-enone (4a)



White solid (44 mg, 0.235 mmol, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 5H), 5.50 (s, 1H), 3.34 (d, J = 3.4 Hz, 1H), 2.61 – 2.47 (m, 2H), 2.47 – 2.29 (m, 2H). Other spectral data is in agreement with previous report.[2]

2-(1-Hydroxy-3-phenyl-propyl)-cyclopent-2-enone (4b)



Colorless oil (54 mg, 0.25 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (td, J = 2.7, 1.1 Hz, 1H), 7.28 – 7.16 (m, 2H), 7.16 – 7.07 (m, 3H), 4.41 (t, J = 6.0 Hz, 1H), 2.90 (s, 1H), 2.83 – 2.70 (m, 1H), 2.63 (dt, J = 13.9, 8.0 Hz, 1H), 2.57 – 2.47 (m, 2H), 2.35 (ddd, J = 17.0, 9.6, 3.2 Hz, 2H), 2.00 – 1.86 (m, 2H). Other spectral data is in agreement with previous report.[3]

[2] M. Shi, Y.-M. Xu, G.-L.Zhao and X.-F. Wu, *Eur. J. Org. Chem*. 2002, 3666.

[3] C. M. Marson, D. W. M. Benzies and A. D. Hobson, *Tetrahedron* 1991, **47**, 5491.

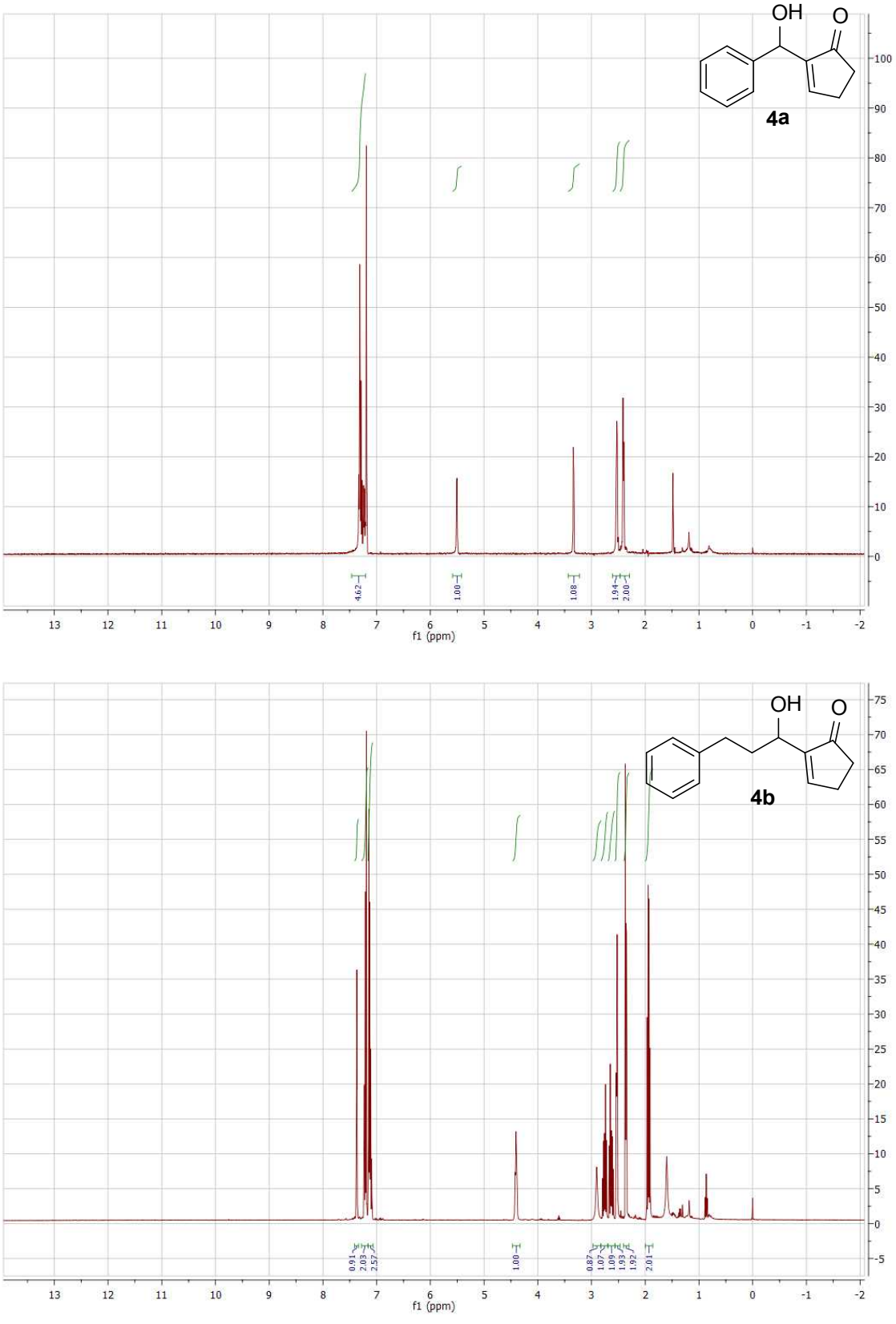


Figure S8. ^{1}H spectrum of MBH reaction products.