SUPPLEMENTARY INFORMATION

Cooperative Catalysis in a Metal-Organic Framework via Post-Synthetic Immobilisation

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Experimental

General methods

All reagents unless otherwise stated were obtained from commercial sources and were used without further purification. Co(salen) was synthesized with the reported procedure.[1] X-ray powder diffraction data were collected on a Rigaku RINT-2200 Right System (Ultima IV) diffractometer with CuKα radiation. Thermogravimetric analyses were recorded on a Rigaku Thermo plus TG-8120 apparatus in the temperature range between 298 and 773 K at a heating rate of 5 $Kmin^{-1}$. The TEM observations were performed with a JEOL JEM-1400 transmission electron microscopy (TEM) system operating at 120 kV. ICP analyses were conducted by ICP AES (SPS 7800, Seiko Instruments). ^1H NMR spectra were recorded on a JEOL JNM-A500 spectrometer. The ^1HNMR chemical shifts are referenced to the residual internal DMSO-d_6.

Synthesis of MIL-101(SO_3H)

Monosodium 2-sulfoterephthalic acid (3.35 g, 12.5 mmol), CrO_3 (1.25 g, 12.5 mmol) and concentrated aqueous hydrochloric acid (0.91 g (12 N), 25 mmol) were dissolved in water (50 ml), then transferred to Teflon-lined stainless steel autoclave. The resulting solution was heated at 453 K for 6 days under hydrothermal conditions. The reaction product was finally obtained after washing three times with DMF under sonication.

Synthesis of Co(salen)(x)@MIL-101(SO_3H)

To 750 mL of Co(salen) methanol solutions (0.56 mM, 1.1 mM, 2.2 mM) were added 450 mg of MIL-101(SO_3H) and stirred at r.t. for 18 hrs under shaded condition. Then, the resulting solids were collected by filtration, followed by the thorough washing with methanol for 18 hrs with Soxhlet apparatus. Co(salen)(x)@MIL-101(SO_3H) (x = 0.13, 0.27, 0.43; x were determined from the results of ICP measurements) were finally obtained after drying in vacuo.

Hydration reaction of phenylacetylene

To 1ml of MeOH were added phenylacetylene (80 mg, 0.76 mmol), H_2O (60 μl, 3.3 mmol) and Co(salen)(x)@MIL-101(SO_3H) (1mol% or 10mol% [Co]). Then, the resulting suspensions were heated at 80 °C to start the reaction. The reactions were checked by ^1HNMR with DMSO-d6 to monitor their progresses. The reaction yield of each step was determined as ^1HNMR yields using the integrals of both reactant and product. Each reaction was executed three times and the average value of the resulting yields were plotted in Fig 3 and Fig 4 with error bar.

Hydration reaction of phenylacetylene derivatives

To 1ml of MeOH were added phenylacetylene derivative (4-ethynylaniline, 4-ethynylanisole, 1-chloro-4-ethynylbenzene or 2-ethynyl-1,3,5-trimethylbenzene)(0.76 mmol), H_2O (60 μl, 3.3 mmol) and Co(salen)(0.27)@MIL-101(SO_3H) (10mol% [Co]). Then, the resulting suspensions were heated at 80 ^{o}C to start the reaction. The reaction yields were determined as ^{1}HNMR yields with DMSO-d6 using the integrals of both reactant and product and shown in Table 1.

Supporting data

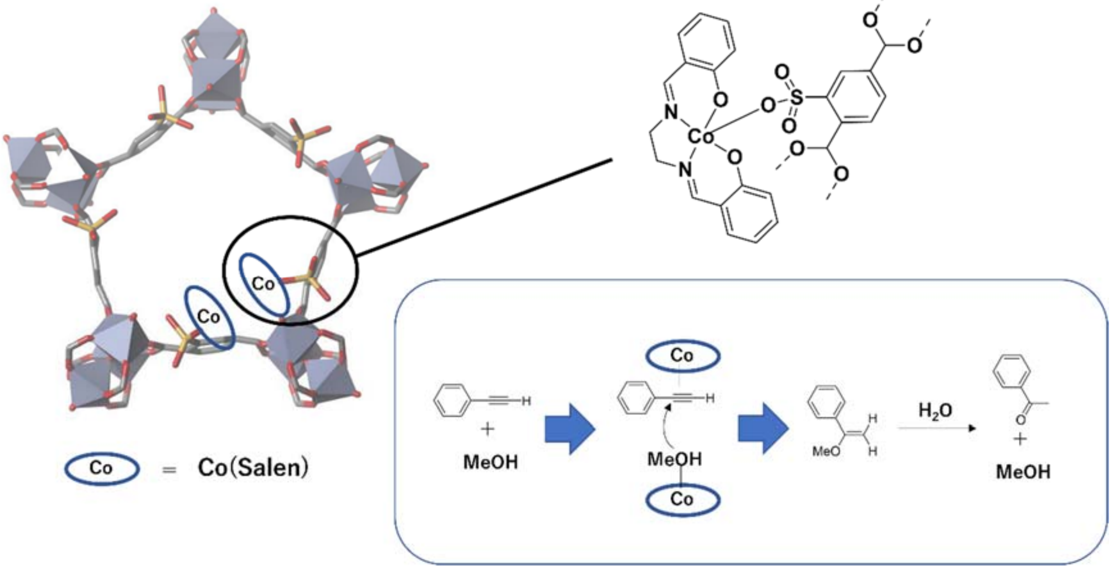


Fig. S1. Schematic image of Co(salen)@MIL-101(SO_3H) and proposed mechanism of Co(salen)-catalyzed hydration of phenylacetylene with cooperative activation

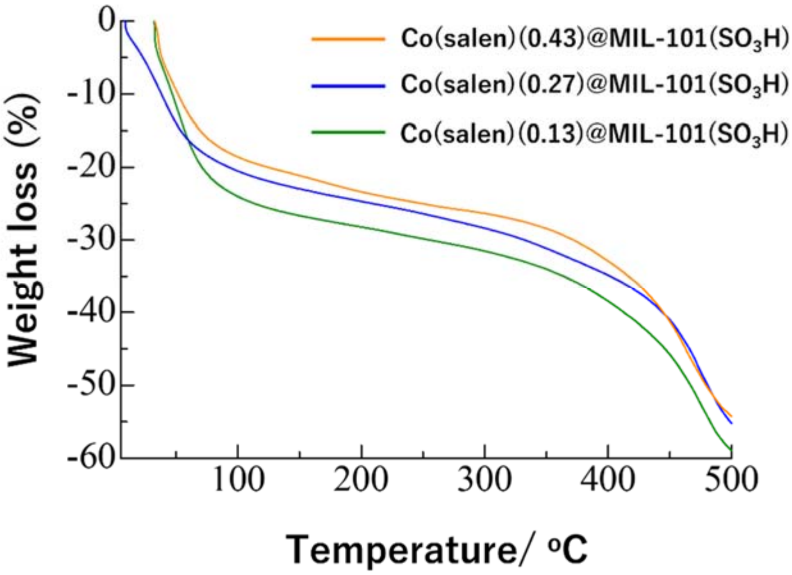


Fig. S2. TG profiles of Co(salen)@MIL-101(SO_3H) filled with EtOH guests

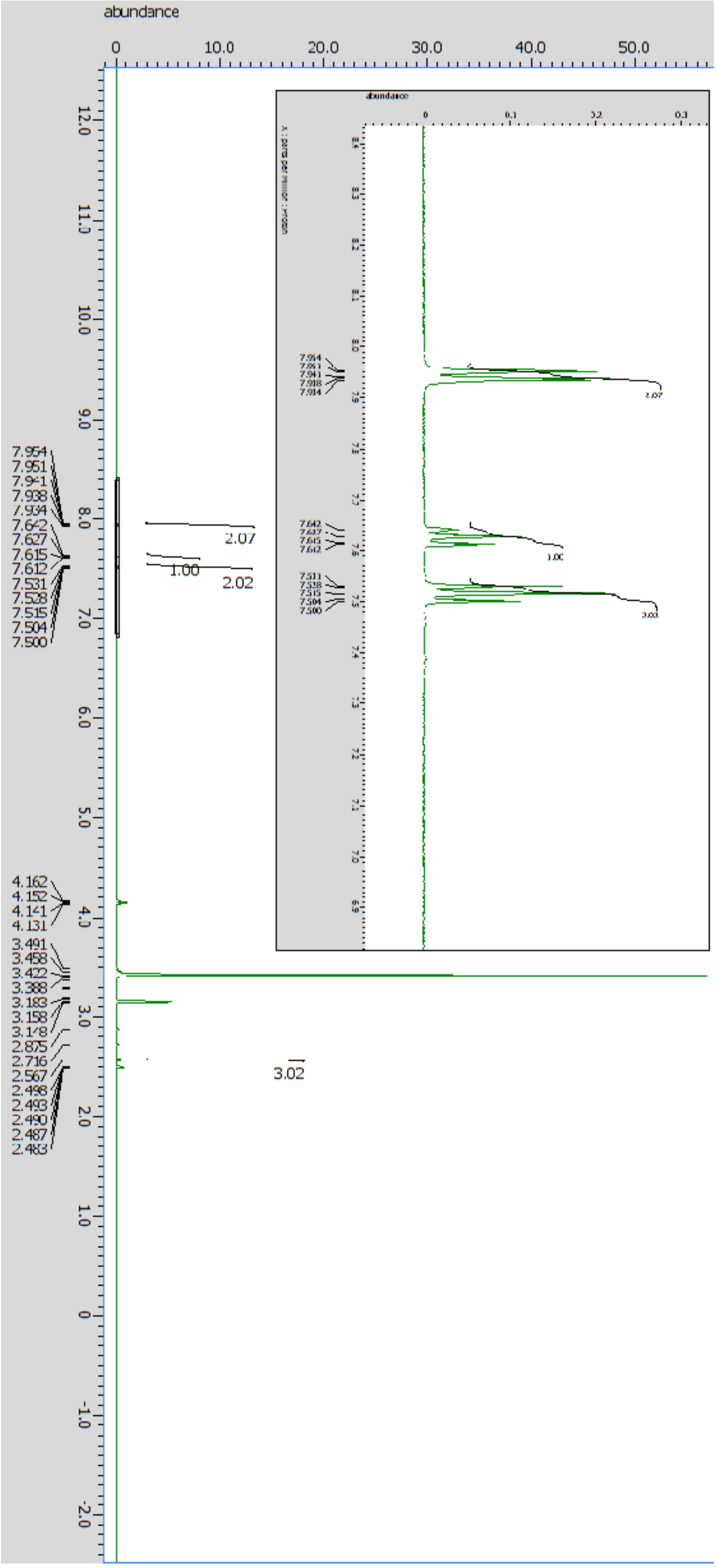


Fig. S3. ^{1}HNMR chart of the reaction solution after the hydration reaction with phenylacetylene. Except for the peaks of target product, the peaks corresponding to MeOH, H_2O and NMR solvent residue were also observed.

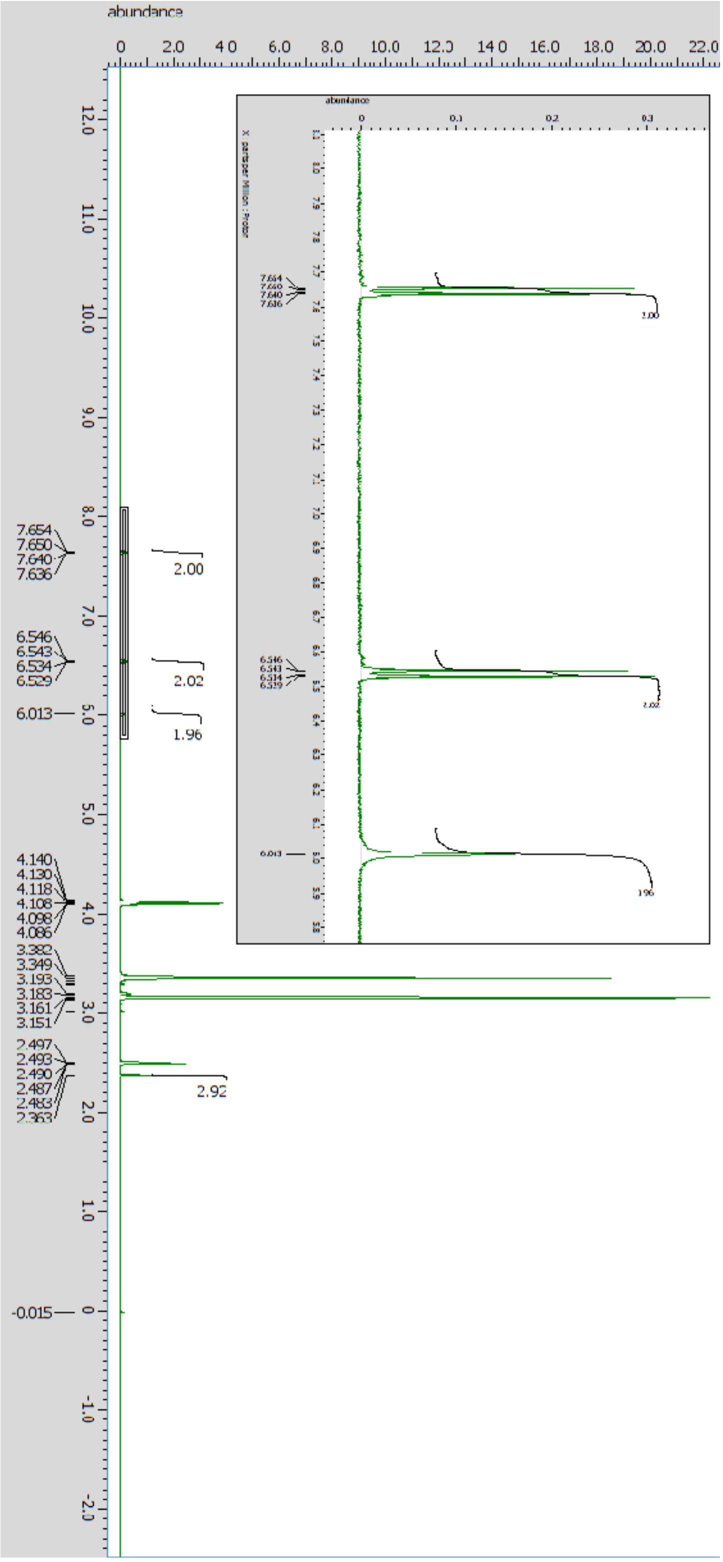


Fig. S4. ^{1}HNMR chart of the reaction solution after the hydration reaction with 4-ethynylaniline. Except for the peaks of target product, the peaks corresponding to MeOH, H_2O and NMR solvent residue were also observed.

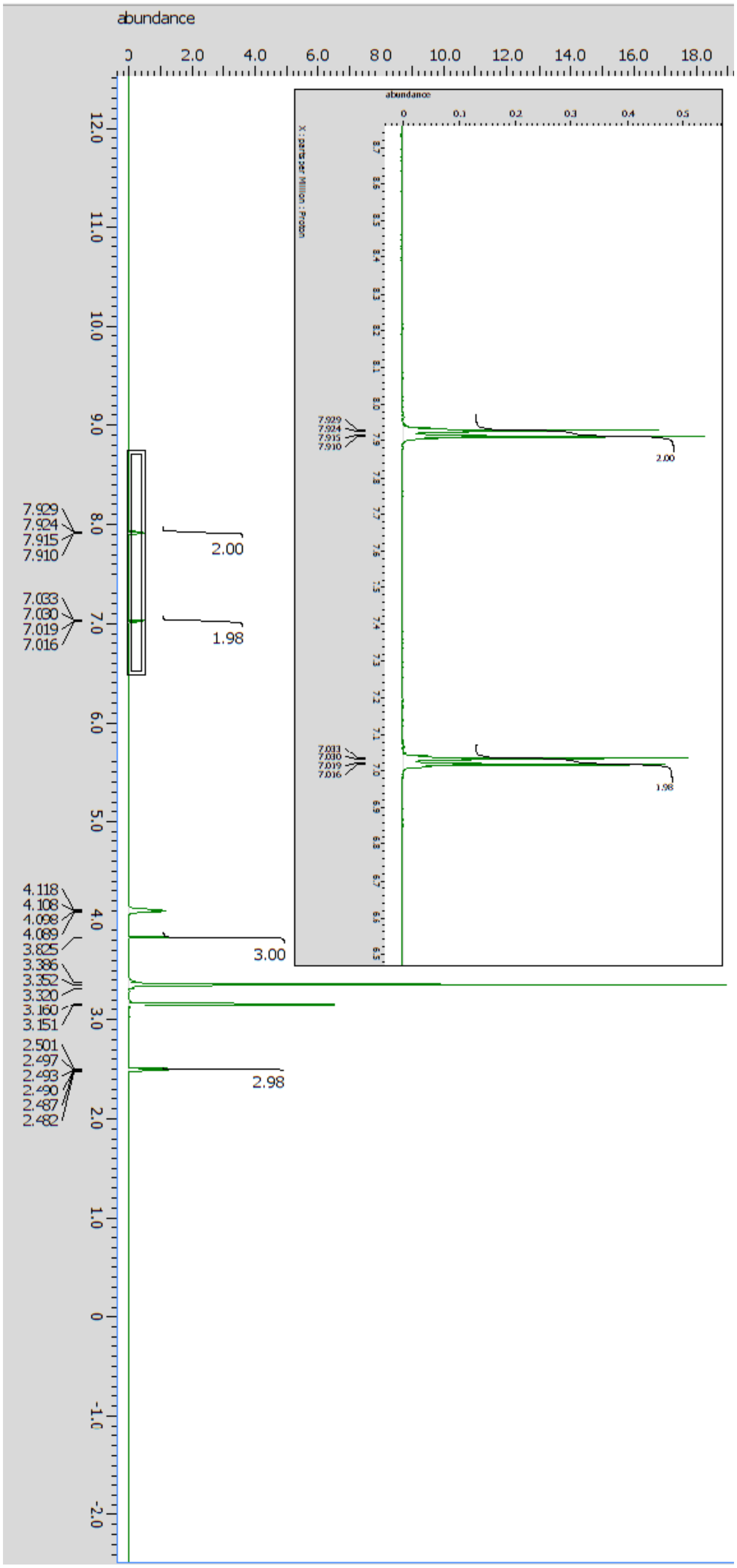


Fig. S5. ^{1}HNMR chart of the reaction solution after the hydration reaction with 4-ethynylanisole. Except for the peaks of target product, the peaks corresponding to MeOH, H_2O and NMR solvent residue were also observed.

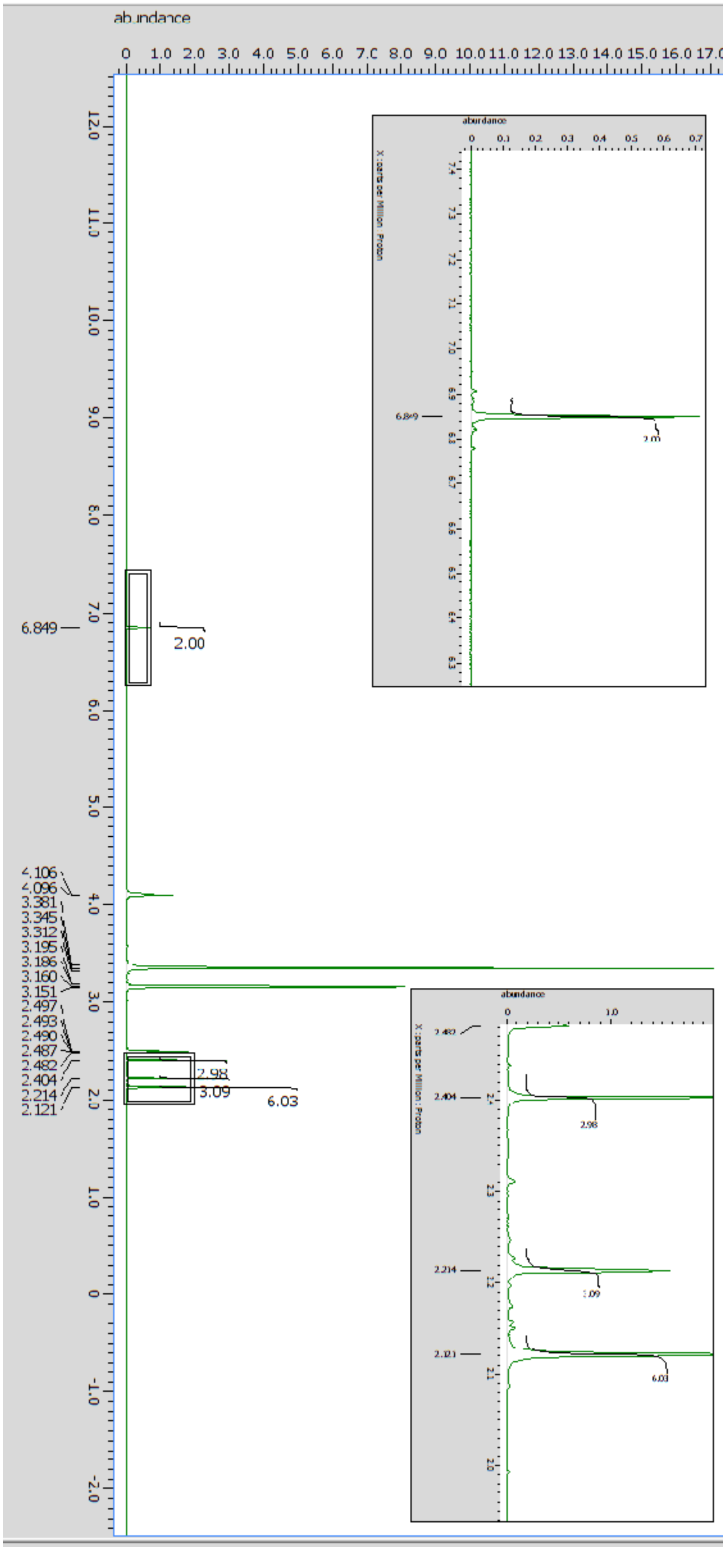


Fig. S6. ^{1}HNMR chart of the reaction solution after the hydration reaction with 2-ethynyl-1,3,5-trimethylbenzene. Except for the peaks of target product, the peaks corresponding to MeOH, H_2O and NMR solvent residue were also observed.

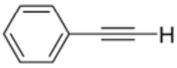
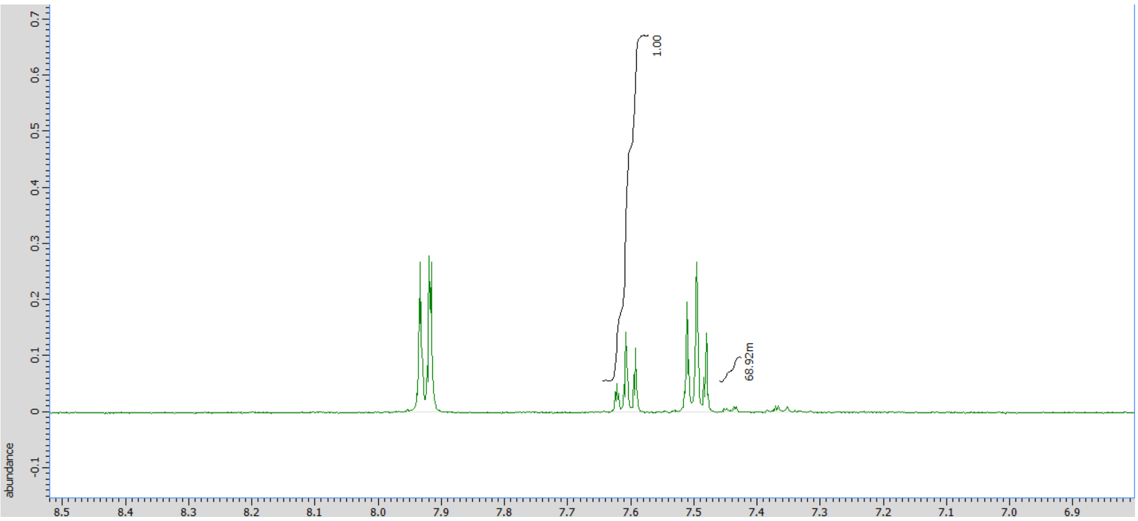
substate	Run	reaction yield (%)
	1	>99
	2	97
	3	96

Table S1. Recycling of Co(salen)(0.27)@MIL-101(SO$_3$H) for the hydration reaction with phenylacetylene. Reaction condition: phenylacetylene (80 mg, 0.76 mmol), MeOH 1ml, H_2O (60 µl, 3.3 mmol) and Co(salen)(0.27)@MIL-101(SO$_3$H) (10mol% [Co]) were mixed and heated at 80 ^{o}C for 24hrs. After the reaction, Co(salene)(0.27)@MIL-101(SO$_3$H) was recovered by filtration and dried in vacuo for reuse.

(a)



(b)

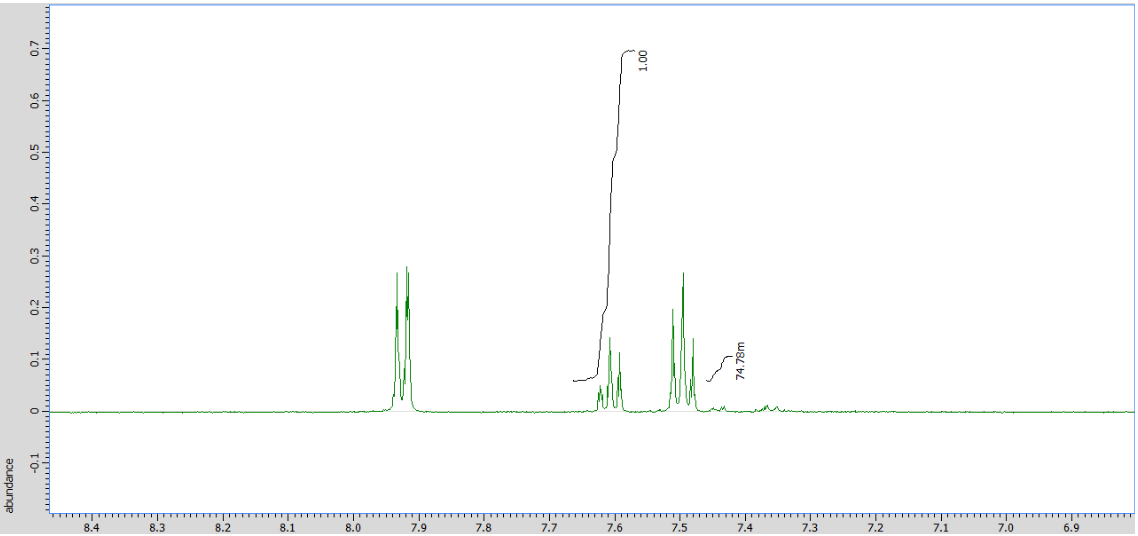


Fig. S7. ^{1}HNMR chart of the reaction solution after the hydration reaction of phenylacetylene with recycled Co(salen)(0.27)@MIL-101(SO_3H): (a) Run 2 and (b) Run 3. Integrals for phenylacetylene and acetophenone to determine reaction yields were shown, respectively.