

Development of a Novel Brønsted acid UiO-66 Metal-Organic Framework Catalyst by Postsynthetic Modification and its Application in Catalysis

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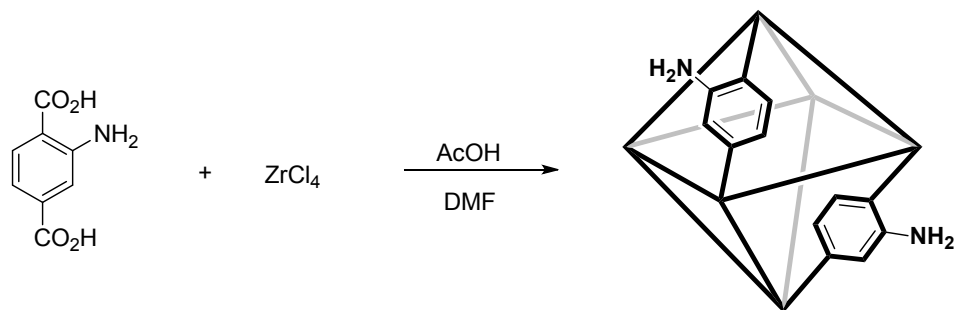
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Supporting Information

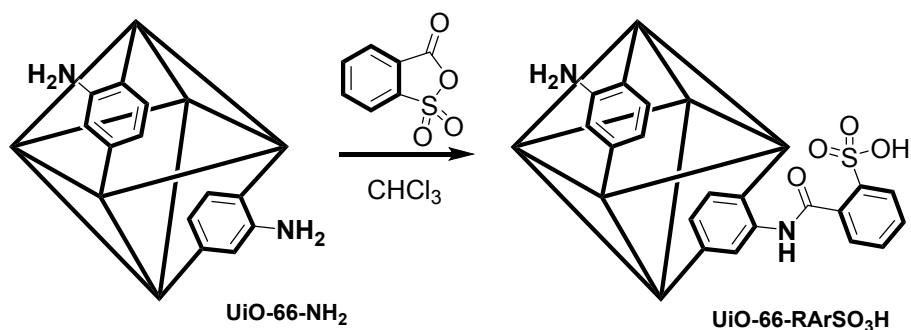
General Information. All ^1H NMR, and ^{13}C NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG, ^1H 400 MHz) spectrometer at ambient temperature in CDCl_3 . Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet,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

The synthesis procedure of UiO-66-NH₂ metal-organic framework at nanoscale



ZrCl₄ (1.6 g, 6.8 mmol) in DMF (150 mL) was stirred with acetic acid (11.4 mL, 3.4 mol) at 55 °C. A DMF solution (50 mL) of 2-aminoterephthalic acid (1.2 g, 6.8 mmol) was added to the previous mixture solution. Then, water (0.5 mL, 0.028 mmol) was added to the solution as well and the solution was sonicated at 60 °C. The mixture solution was further kept in a bath at 120 °C for 24 h. After 24 h, the solution was cooled to room temperature and the precipitate was collected by centrifugation. The obtained solid was washed with DMF (2 x 20 mL), ethanol (3 x 20 mL) and dried under reduced pressure (80 °C, 3 h).

The synthesis procedure of UiO-66-NH-RSO₃H catalyst.



Post-synthetic modification of UiO-66-NH₂:

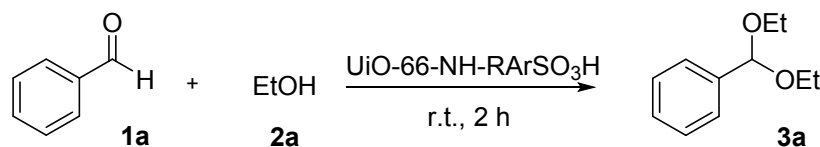
1.77 g of nano-scaled UiO-66-NH₂ (1.0 mmol based on MW of 1766 g/mol) was suspended in 20 mL of CHCl₃, then 1.0 equiv. of *o*-sulfobenzoic acid anhydride (184 mg, 1.0 mmol) was added. The mixture was stirred slowly at 25 °C for 12 h, after which the solvent was decanted. Fresh DMF (10 mL) was added once a day for three days and then CHCl₃ was used to rinse the crystals once a day for two days. The crystals were dried under vacuum at 40 °C before use.

For catalyst recycling:

At the end of each reaction cycle, the catalyst was recovered by centrifugation of the solution mixture followed by washing with 5 - 10 mL ethanol (acetalization reaction) or

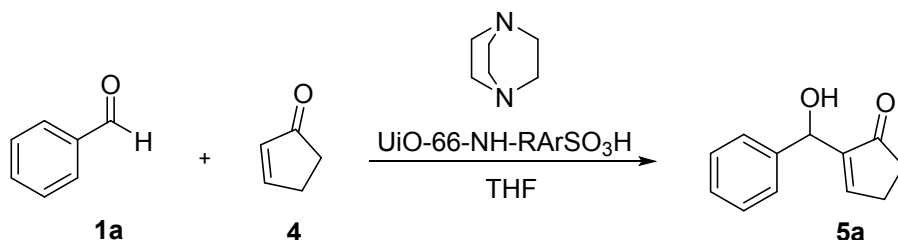
THF (MBH reaction). After being immersed in the solvent for 12 h and dried at 40 °C under vacuum for 12 h, the catalyst was reused.

General procedure for acetalization of aldehydes using UiO-66-NH-RArSO₃H catalyst



A 10-mL reaction vessel (oven dried) was charged with UiO-66-NH-RArSO₃H catalyst (based on 20 mol% aromatic sulfonic acid, MW of UiO-66-NH-RArSO₃H = 1803, 0.001 mmol, 1.80 mg in Table 1) in 0.5 mL dry ethanol and benzaldehyde substrate (106 mg, 1.0 mmol). The reaction mixture was stirred under N₂ atmosphere at room temperature (23 °C) for 2 h. After the reaction was complete, the reaction mixture was centrifuged. The yield of desired acetal product was determined by GC-MS using nitrobenzene as internal standard.

General procedure for the Morita-Baylis-Hillman reaction using UiO-66-NH-RArSO₃H catalyst



A 10-mL reaction vessel was charged with 0.001 mol% UiO-66-NH-RArSO₃H catalyst (0.001 mmol, 1.80 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 2.0 mL of tetrahydrofuran under N₂ atmosphere. The reaction was stirred at 23 °C for 6 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 **5a** as a colorless oil.

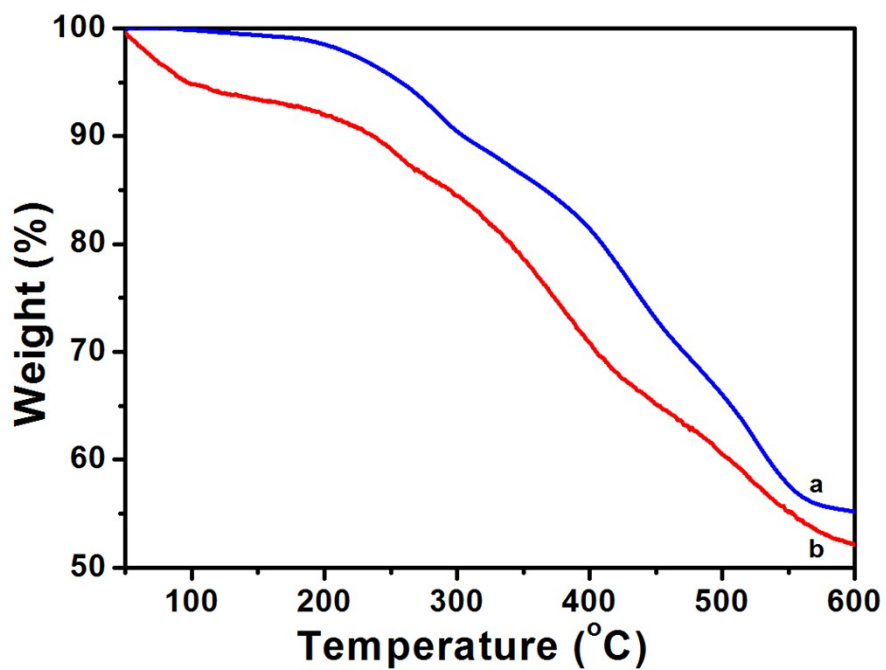


Fig. S1 TGA spectra of (a) UiO-66-NH₂ and (b) UiO-66-RArSO₃H catalyst.

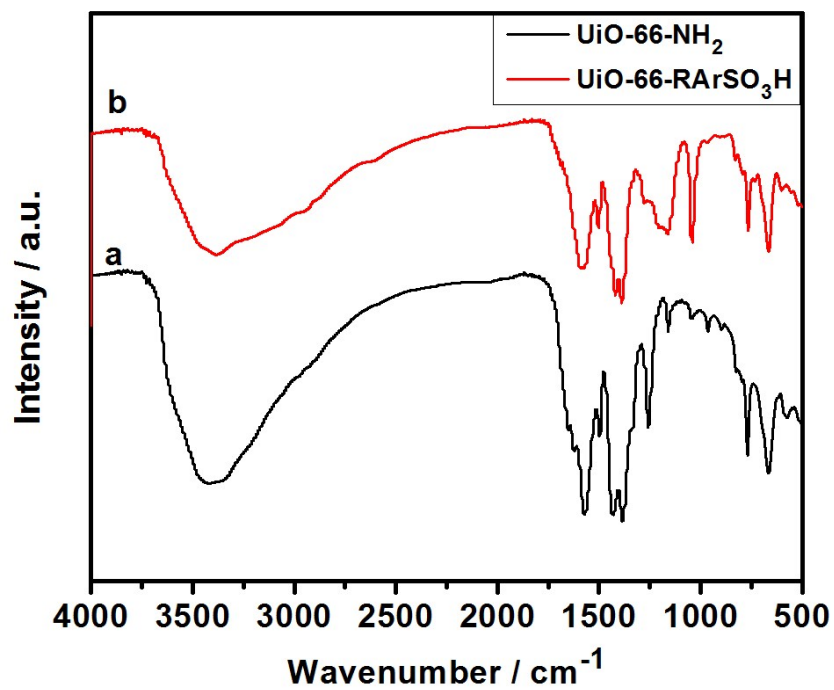


Fig. S2 FTIR spectra of UiO-66-NH₂ (Black, bottom) and UiO-66-RArSO₃H catalyst (Red, top).

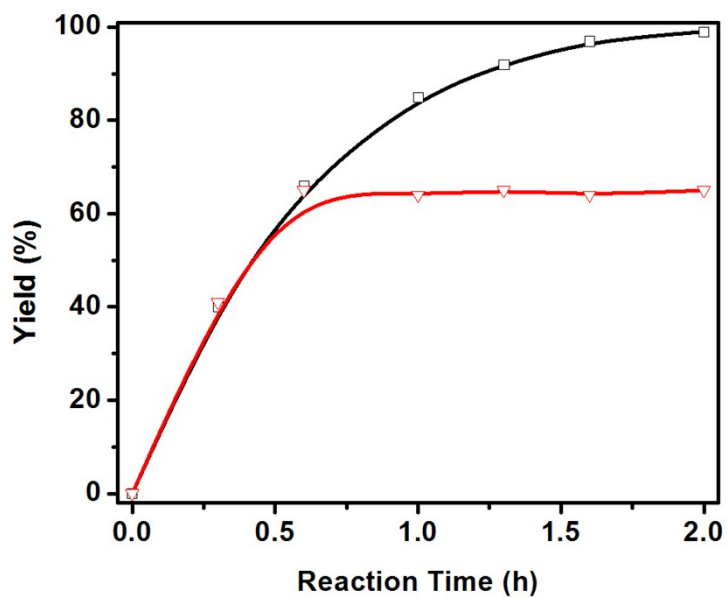


Fig. S3 Conversion *versus* time in the acetalization of benzaldehyde catalyzed by UiO-66-NH-RSO₃H (Black). Catalyst was filtered at 40 min (Red).

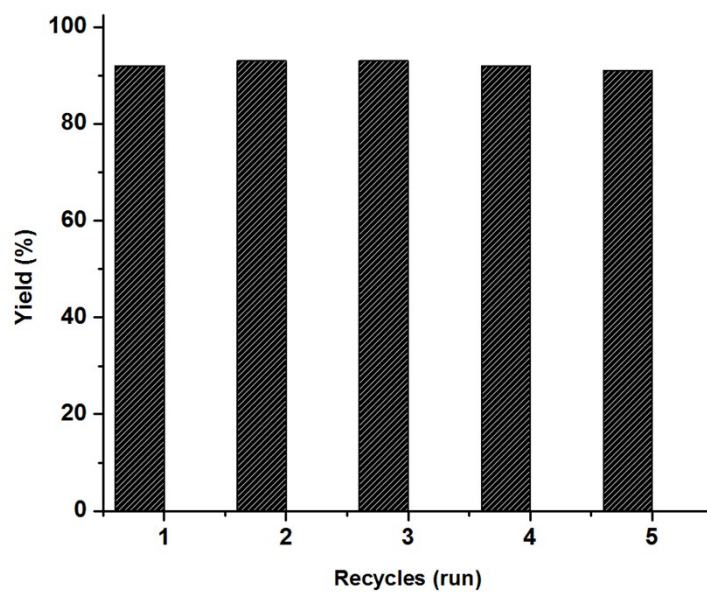


Fig. S4. The catalyst recycling of UiO-66-RArSO₃H in MBH reaction.

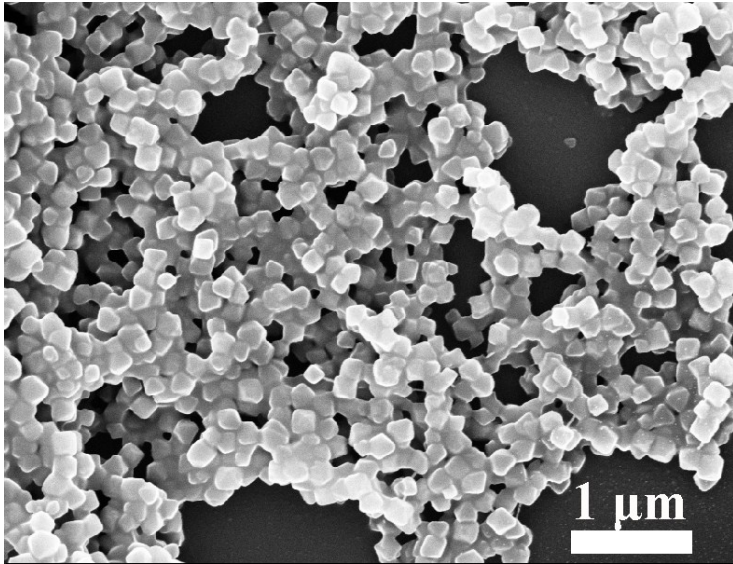


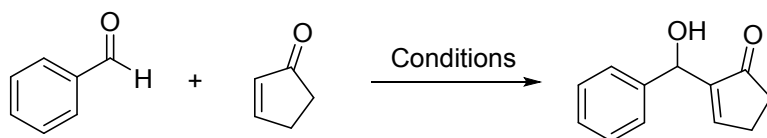
Fig. S5 SEM image of recycled UiO-66-RArSO₃H.

Table S1. Control reaction for UiO-66-RSO₃H catalyzed Morita-Baylis-Hillman reaction.

Entry	Catalyst	Additive	Yield
1	-	-	0%
2	-	DABCO (0.5 eq.)	23%
3	UiO-66-RArSO ₃ H	-	11%
4	UiO-66-RArSO ₃ H	DABCO (0.5 eq.)	92%

Reaction conditions: aldehyde (1.0 mmol), 2-cyclopenten-1-one (2.0 mmol), 1,4-diazabicyclo [2.2.2]octane (0.5 mmol), UiO-66-RArSO₃H catalyst (0.1 mol%), were stirred at 23 °C for 6 h.

Table S2. Literature comparison for MBH reaction of 2-cyclohexene-1-one.



Catalyst	Loading	Reaction time	T (°C)	Solvent	Yield	Reference
Bis(thio)urea	20 mol% with 4 eq. of enone	72 h	10	neat	99	1
NMP and Ba(OH) ₂	5 mol% and 1.5 mol%	9 h	0	CH ₃ OH/ CH ₂ Cl ₂	73%	2
EtAlI	120 mol%	24 h	0	CH ₂ Cl ₂	56%	3
TMG/azole	10 mol%/10 mol%	24 h	23	THF	94%	4
UiO-66-RArSO ₃ H	0.1 mol%	6 h	23	THF	92%	This work

1. Albrecht Berkessel, Katrin Roland, Jörg M. Neudörfl, Asymmetric Morita-Baylis-Hillman Reaction Catalyzed by Isophoronediamine-Derived Bis(thio)urea Organocatalysts, *Org. Lett.*, 2006, 8 (19), 4195-4198.

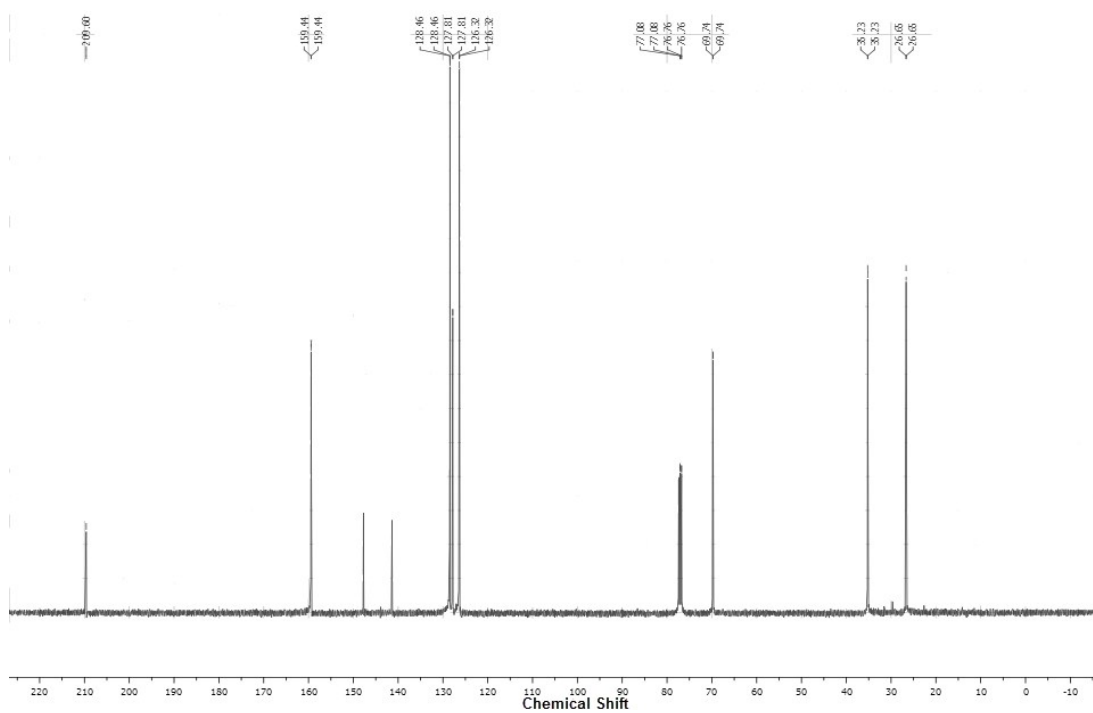
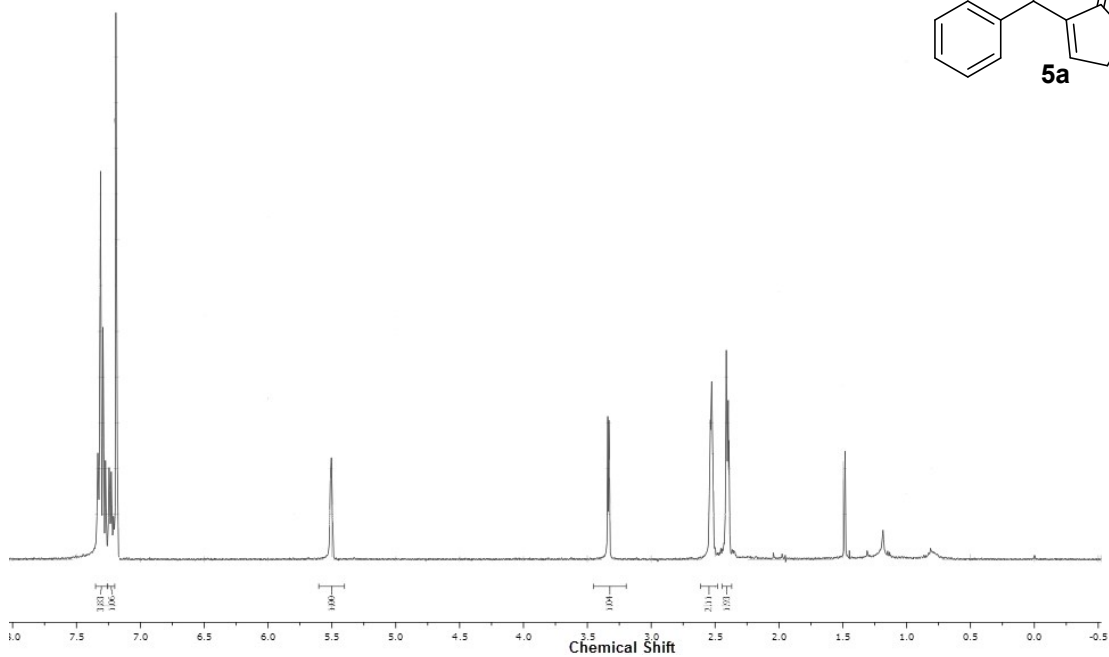
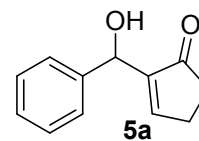
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3. Wei Pei, Han-Xun Wei and Guigen Li, The Baylis-Hillman condensation of a,b-conjugate cycloketones with aldehydes using diethylaluminum iodide alone as the promoter, *Chem. Commun.*, 2002, 2412-2413.

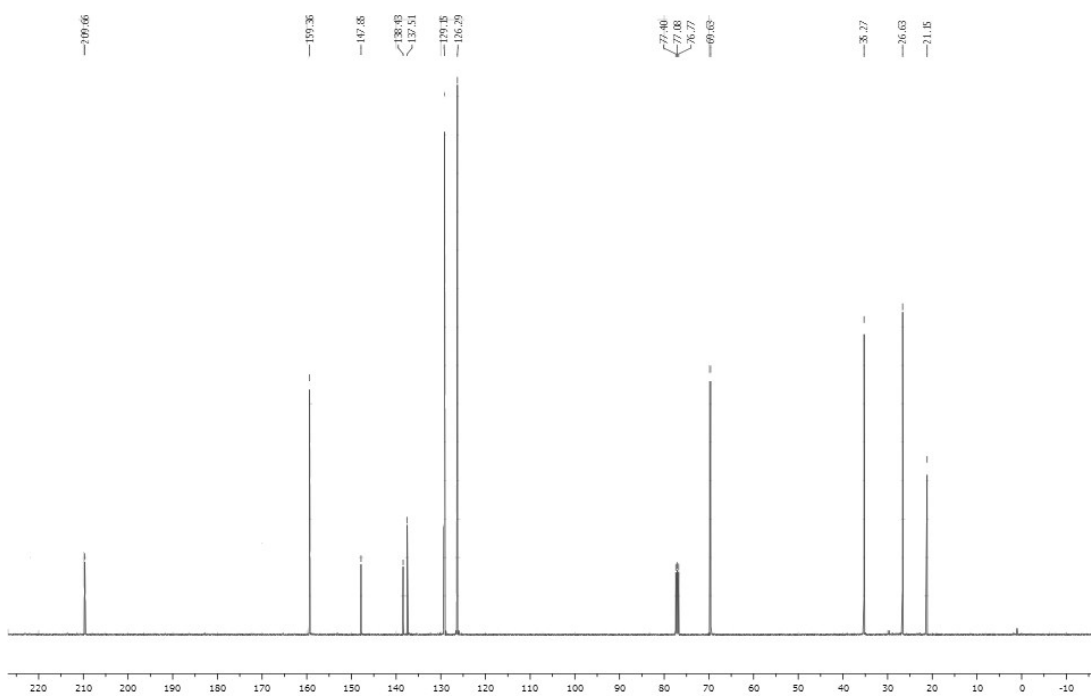
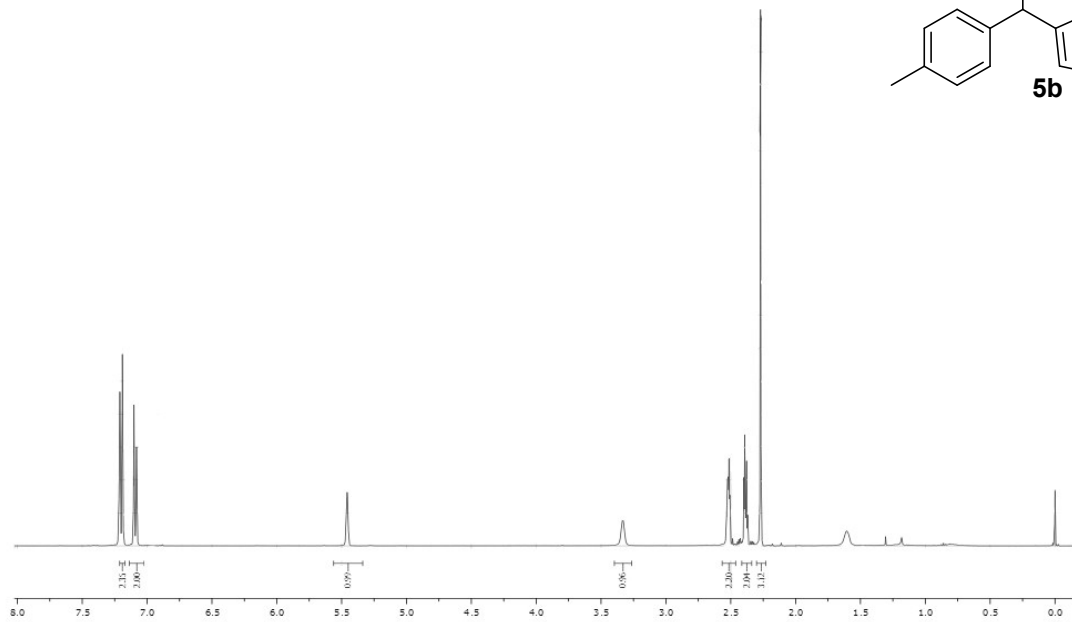
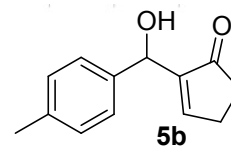
4. Masahiro Terada, Satoko Fukuchi, Kei Amagai, Megumi Nakano, Hitoshi Ube, Guanidine/Azole Binary System as an Efficient Catalyst for Morita-Baylis-Hillman Reaction, *ChemCatChem*, 2012, 4, 963-967.

Fig. S6 ^1H and ^{13}C NMR spectra of MBH reaction products.

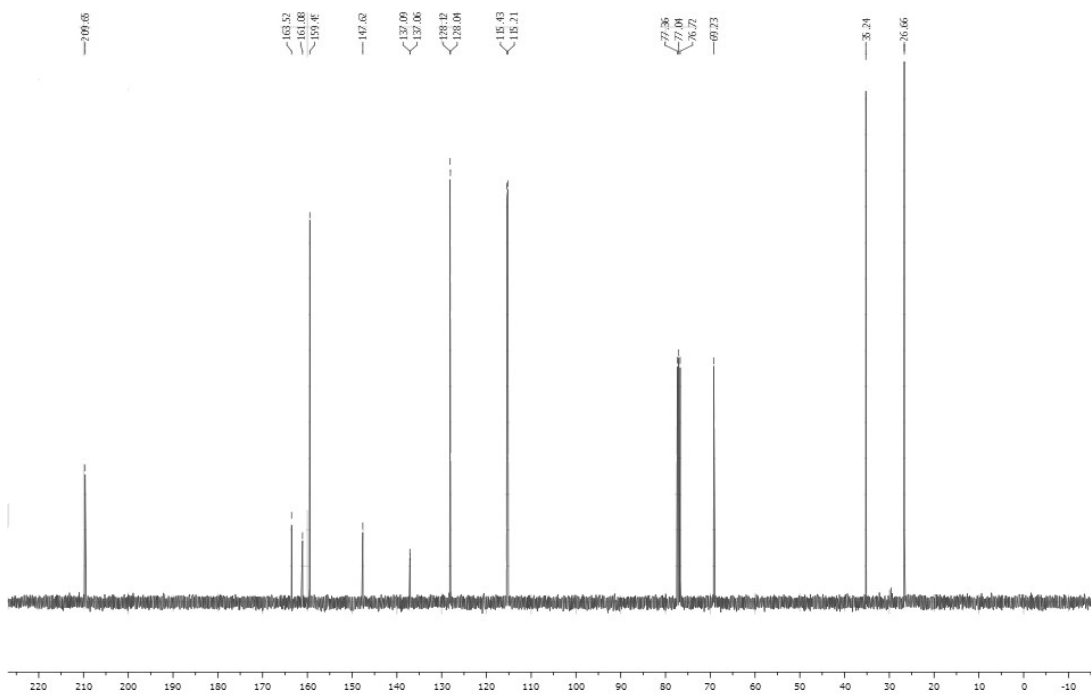
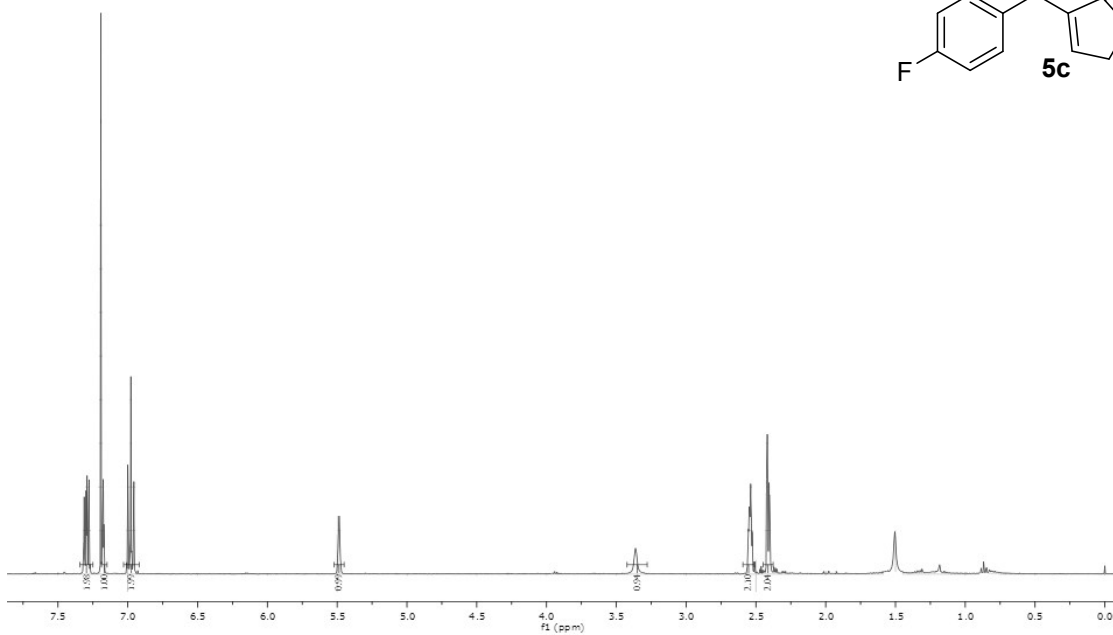
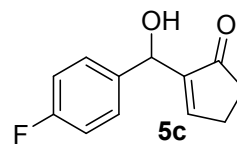
2-(Hydroxy-phenyl-methyl)-cyclopent-2-enone (5a)



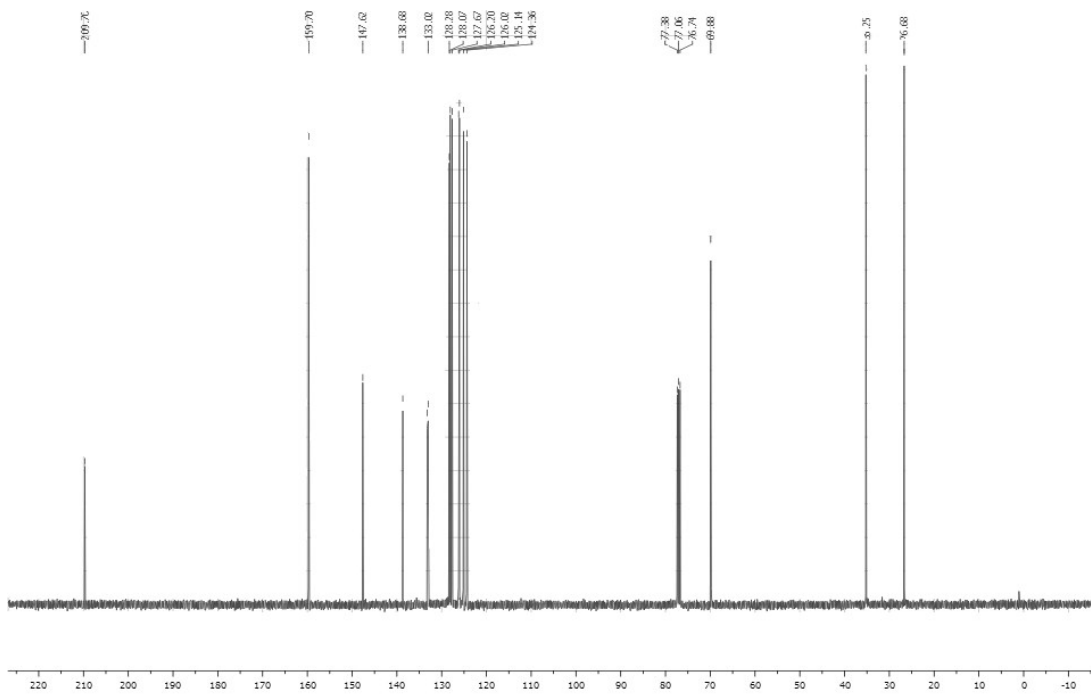
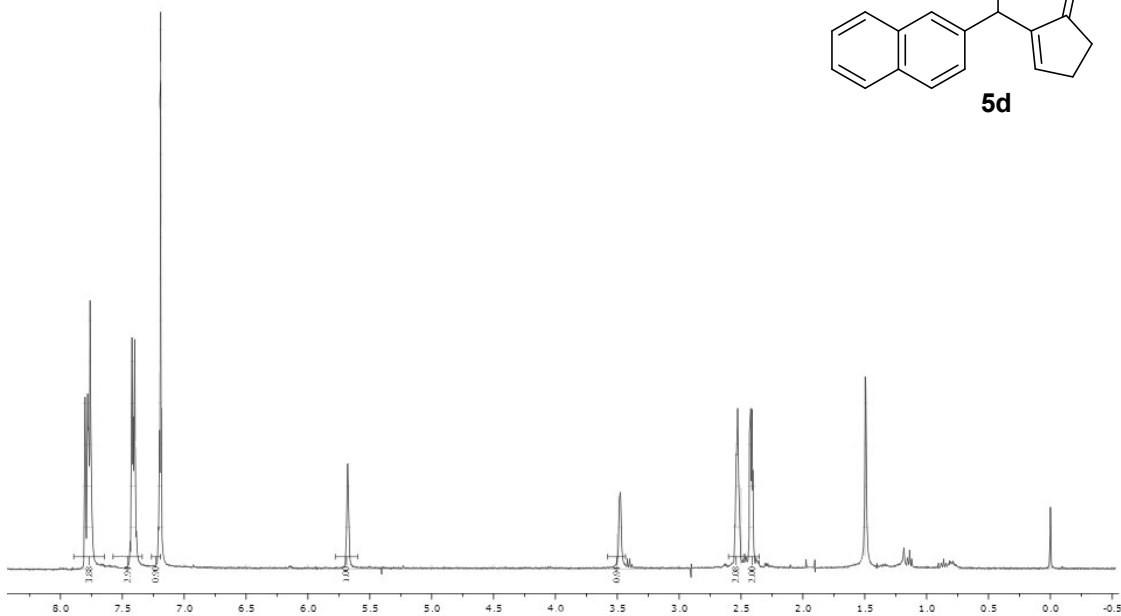
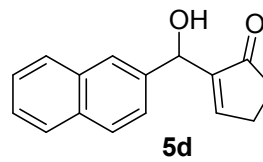
2-(Hydroxy-*p*-tolyl-methyl)-cyclopent-2-enone (5b)



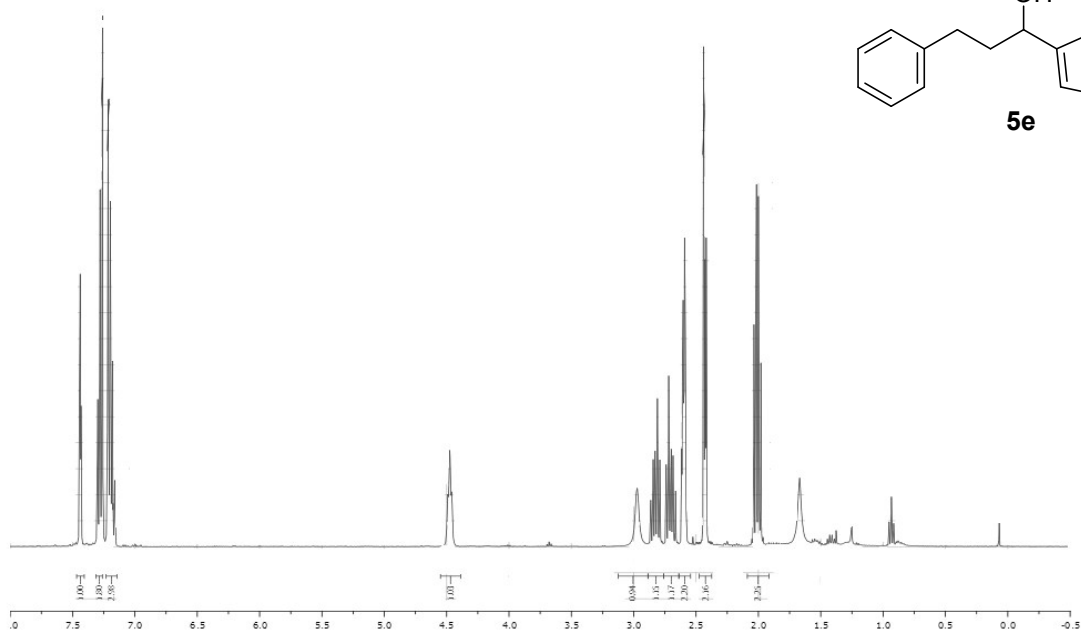
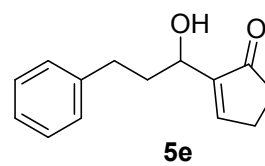
2-[(4-Fluoro-phenyl)-hydroxy-methyl]-cyclopent-2-enone (5c)



2-(Hydroxy-naphthalen-2-yl-methyl)-cyclopent-2-enone (5d)



2-(1-Hydroxy-3-phenyl-propyl)-cyclopent-2-enone (5f)



Chemical shift values (ppm): 10.20, 88.10, 67.43, 64.13, 61.00, 28.88, 25.88, 67.18, 37.12, 35.22, 31.66, 26.56

