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Selective One-Pot Two-Step C–C Bond Formation using Metal–Organic Frameworks with Mild Basicity as Heterogeneous Catalysts

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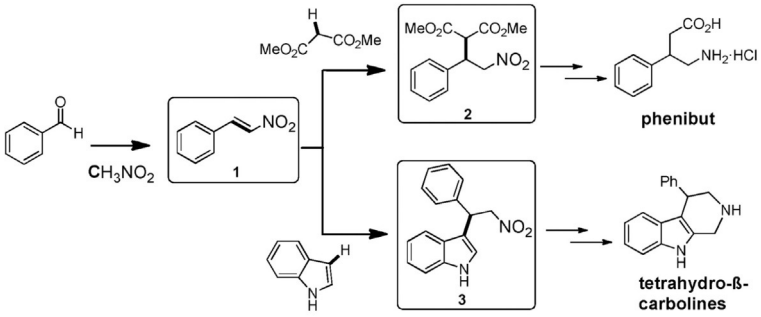
Copper-ion-exchanged nickel pyrazolate frameworks behave as selective heterogeneous catalysts for the one-pot, two-step (Henry reaction/Michael type addition) synthesis of neuroactive pharmaceutical intermediates starting from nitromethane and benzaldehyde. Tuning the basicity of multifunctional metal–organic framework catalysts through ion exchange with copper(II) cations allows the tandem C–C bond-forming process to be selectively directed towards the desired pharmaceutical intermediate.

Serotonin reuptake inhibitors and GABA (γ-aminobutyric acid) receptor agonists have found potential pharmacological applications in the treatment of multiple neurological pathologies. Different synthetic strategies and new homogeneous catalysts have been proposed to access these types of compounds.[1] In particular, the use of multistep cascade reactions reduces the number of synthetic steps and chemical waste. For example, simple components such as nitromethane, benzaldehyde, indole, and dimethyl malonate produce compounds **1**, **2**, and **3** through a "one-pot", two-step reaction (Scheme 1).[2] These molecules are intermediates in the synthesis of β-phenyl-γ-aminobutyric acid (phenibut), tryptamine analogues, and tetrahydro-β-carboline drugs.

The process starts with a nitroaldol condensation between benzaldehyde and nitromethane to form β-nitrostyrene (**1**). Then, the addition of dimethyl malonate or indole to the reaction mixture produces Michael adduct **2** or indole derivative **3**. Finally, the nitro groups can be further reduced to obtain the GABA or tryptamine scaffold, respectively. The replacement of soluble catalysts[1b–g,3] by heterogeneous counterparts simplifies the removal of the catalyst from the reaction mixture and may allow its reuse.[4] Herein, a new family of post synthetically modified metal–organic frameworks is employed to selectively direct the different C–C bond-forming reactions towards desired products **2** and **3** starting from benzaldehyde and nitromethane as starting materials.

Metal–organic frameworks (MOFs) are interesting heterogeneous catalysts because they contain a large amount of well-positioned metal sites (nodes) in a periodic porous framework constructed by multitopic organic molecules (linkers).[5] In particular, our group prepared the $[Ni_8(OH)_4(H_2O)_2(BDP)_6]$ (NiBDP) metal–organic framework in sizeable amounts by treating the relatively inexpensive H_2BDP [1,4-bis(pyrazol-4-yl)benzene] linker with nonprecious first-row nickel salts. The resulting MOF has a porous, non-interpenetrated FCU crystalline framework based on octanuclear nickel(II) clusters connected by BDP linkers, and it shows high thermal and chemical stability in basic media.[6] We also studied the formation of the linker-defective $K[Ni_8(OH)_6(BDP\_X)_{5.5}]$ (NiBDP_X@K) MOF, in which BDP_X = benzene-1,4-bispyrazolate-2-X; X = H, OH, or NH_2. The density functional theory (DFT)-energy-minimized structure of the secondary building unit (SBU), modeled as anionic $[Ni_8(OH)_6(pyrazolate)_{11}]^-$ moieties, contains exposed hydroxides replacing the pyrazolate vacancies. It was proposed that the exposed hydroxides of the metal cluster and the polar functional groups of the organic linkers behaved as active adsorption sites. Moreover, the presence of extraframework K^+ cat-



Scheme 1. Multistep synthesis of neuroactive pharmaceutical intermediates starting from benzaldehyde, nitromethane, and indole or dimethyl malonate precursors.

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ions opens the way to ion-exchange processes, as recently demonstrated with Ba^{2+} ions, to yield defective ion-exchanged materials. Both the extraframework cations and the defects are responsible for the excellent CO_2 and SO_2 adsorption and ion-conductive properties of these multifunctional MOFs.[7]

In view of these results, we now explore the impact of post synthetic modification of the NiBDP_X@K materials by cation exchange with copper ions on the catalytic properties. Exposure of the NiBDP_X@K materials to a methanol 0.1 M $Cu(ClO_4)_2$ solution led to new ion-exchanged solids NiBDP@Cu, NiBDP_OH@Cu, and NiBDP_NH_2@Cu (Figure 1). The nickel, copper and hydroxide ions of the inorganic clusters are bridged by 1,4-bis (pyrazol-4-yl)benzene linkers, and this creates a site isolation in the nodes of the framework. This approach prevents the deactivation of incompatible active sites, such as copper and nickel Lewis acid centers and basic centers, by means of keeping them apart in the crystalline metal–organic framework support.

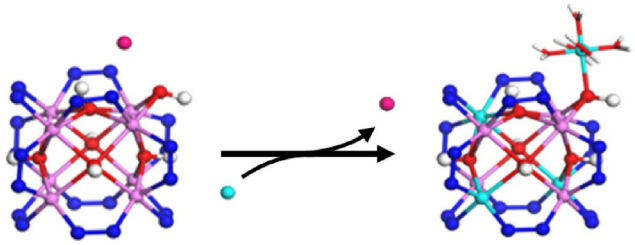


Figure 1. Schematic representation of the transformation of $K[Ni_8(OH)_6(BDP\ X)_{5.5}]$ by ion exchange with $Cu(ClO_4)_2$ to produce $[Cu(H_2O)_5]_{0.5}[Ni_5Cu_3(OH)_6(BDP\ X)_{5.5}]$. For simplicity, only the secondary building unit is shown. Ni, pink; K, magenta; Cu, cyan; N, blue; O, red; H, white.

Inductively coupled plasma mass spectrometry (ICP-MS) analysis is indicative of the ion-exchange process in the NiBDP_OH@Cu and NiBDP_NH_2@Cu materials together with some encapsulation of $Cu(ClO_4)_2$ ion pairs. Notably, NiBDP@Cu contains a considerably higher copper concentration, which is indicative of probable partial replacement of the nickel ions in the octanuclear metal hydroxide cluster framework nodes (see Figures S17 and S18 in the Supporting Information). We find that the K concentration diminishes by approximately 90% in NiBDP@Cu, which shows that the exchange process is quite efficient (see Table S1). Furthermore, UV/Vis spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) seem to indicate the presence of Cu^{II} inside the metal clusters (Figures S14, S17, and S18).

Herein, we used these MOFs as heterogeneous catalysts for the first step of Scheme 1. This consisted of the Henry reaction between benzaldehyde and nitromethane followed by dehydration of the nitroaldol adduct to produce β-nitrostyrene (**1**).[8] On the one hand, upon using nitromethane as a solvent, the selectivity to desired product **1** was never higher than 70% owing to the addition of a second molecule of nitromethane to β-nitrostyrene.[9] As we will demonstrate below, the selectivity towards the desired nitroalkene versus the dinitroalkane can be used as a diagnostic tool to investigate the basic strength of these MOFs. On the other hand, the benzaldehyde conversion was very low in the presence of aprotic solvents, such as toluene (< 40% after 72 h of reaction). In this sense, 2-butanol was selected as the optimal reaction solvent. The best selectivity to desired Henry reaction product **1** was obtained with the unfunctionalized MOF catalysts (i.e., NiBDP, NiBDP@K, and NiBDP@Cu). In this case, benzaldehyde reacted with nitromethane to produce desired β-nitrostyrene (**1**) as the main product after 48 h (> 90% selectivity). For the KOH-treated NiBDP@K catalyst, the benzaldehyde conversion further increased (56% conversion) relative to that obtained with the pristine NiBDP material (39% conversion). Upon measuring the pH of an aqueous suspension of the MOFs (after 1 h of stirring at room temperature),[10] there was an increase in the pH on passing from NiBDP (pH 7.8) to NiBDP@K (pH 8.3). This suggested the presence of basic sites in the K-exchanged material, as also reported for hydrotalcites.[11]

Upon using NiBDP@Cu as the catalyst, 81% conversion of benzaldehyde and 94% selectivity to **1** were obtained after 48 h, which supported the use of Cu as a catalyst for the nitroaldol reaction.[12] NiBDP@Cu clearly outperformed the other copper MOFs such as CuBTC, which only converted 2% of the aldehyde after 60 h of reaction with an excess amount of nitromethane at 100 °C.[13] A hot-filtration test confirmed the heterogeneous nature of the catalytic process, as the reaction stopped completely after the removal of NiBDP@Cu from the liquid reaction mixture (Figure S20). Copper-exchanged NiBDP@Cu gave rise to higher benzaldehyde conversion and selectivity to **1** than NiBDP and NiBDP@K. In general, the selectivity to product **1** was higher for all the NiBDP_X@Cu catalysts than for the ones without Cu (see Figure 2).

The benzaldehyde conversion after 48 h increased on passing from NiBDP (39% conversion) to the NiBDP_OH (81% conversion) and NiBDP_NH_2 (93% conversion) functionalized materials. This indicated that the hydrophilic NH_2- and OH-functionalized materials had higher activity. Although these functional groups have been proposed to activate acid hydrogen atoms in C–C bond-forming reactions involving carbonyls and enolates, such as aldol condensations and additions,[5f–k] in our hands, the use of the pure amino- and hydroxy-functionalized linkers (i.e., BDP NH_2 and BDP OH) as catalysts did not en-

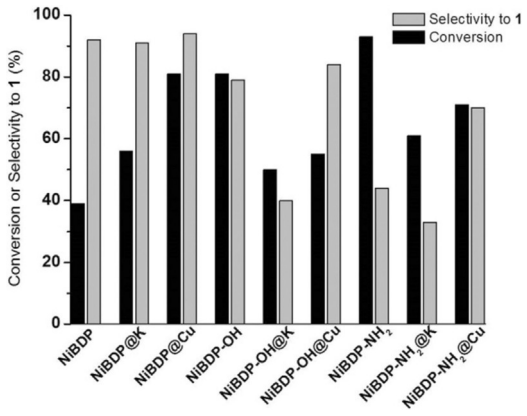


Figure 2. Benzaldehyde conversion and selectivity to product **1** (after 48 h of reaction) for the Henry reaction between benzaldehyde (0.1 mmol) and nitromethane (1 mmol) by using MOF (10 mg).

hance the conversion of benzaldehyde relative to that of the blank reaction. One important observation for this acid–base-catalyzed process was that the selectivity towards desired Henry product **1** (at the maximum benzaldehyde conversion after 48 h of reaction, see Figure S24) decreased as the basicity of the MOF increased, and this resulted in a mixture of nitro and dinitro products. This is related to the formation of (1,3-dinitropropan-2-yl)benzene (**1b**) resulting from the Michael addition of a second molecule of nitromethane to nitroalkene **1**. The further consumption of intermediate **1** towards **1b** is favored in the presence of the amino- (NH_2) and hydroxy- (OH) functionalized solids.[9,14]

Thus, although the benzaldehyde conversions and reaction rates were higher for the functionalized materials, the further consumption of **1** to form **1b** decreased the selectivity to desired product **1** (see Figure 3a). The higher selectivity to **1** upon using the Cu-exchanged materials may be attributed to the lower basicity of the Cu-exchanged MOFs. In contrast with the polar NH_2/OH groups, the presence of (Lewis acid) copper sites in the MOF seems to decrease the basicity of the material.

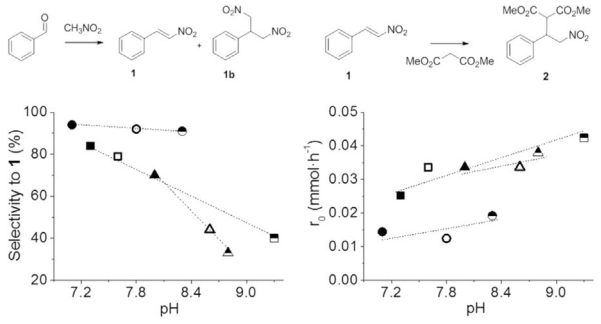


Figure 3. Effect of basicity (pH of a suspension of 4 mg of MOF in 10 mL of water stirring for 1 h) of the NiBDP_X@M materials, for which X = H (●), OH (■), NH_2 (▲), M = no exchanged metal (○), K (half empty), Cu (full), on the catalytic activity of Michael-type additions. Both the addition of a) nitromethane and b) dimethyl malonate to **1** increases with the basicity of the MOF. Dashed line serves as a guide to the eye.

The catalytic performance of the solid MOFs for this first reaction step was compared with those of the homogeneous metal precursors of the MOF, that is, nickel acetate [$Ni(OAc)_2$] and copper perchlorate [$Cu(ClO_4)_2$] (see Table S2). On the one hand, upon using $Ni(OAc)_2$ as the catalyst, the yield of **1** was slightly higher than that obtained with NiBDP after 48 h (48 vs. 36%).[15] However, the TOF (turnover frequency) values for both NiBDP and $Ni(OAc)_2$ were similar ($\approx 0.04\ h^{-1}$). On the other hand, the $Cu(ClO_4)_2$ salt produced only a moderate yield of product **1** (27%), in contrast to other copper Lewis acid catalysts in the presence of N-containing ligands.[12] This seemed to indicate that the encapsulated ion pairs that may have remained after washing treatment did not significantly contribute to the catalytic activity of the MOF. Notably, if $Cu(ClO_4)_2$ was used in combination with $Ni(OAc)_2{\cdot}H_2O$, the TOF value ($0.02\ h^{-1}$) was lower than that obtained upon using NiBDP@Cu ($0.08\ h^{-1}$).

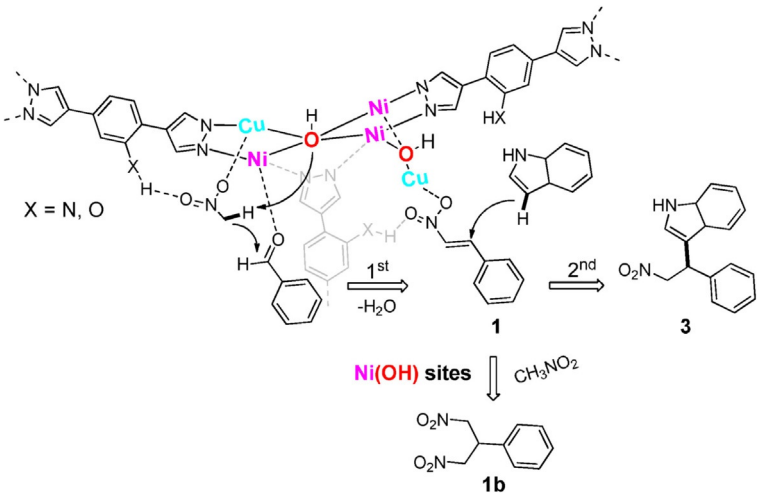
Furthermore, we aimed to proceed with a second reaction step by adding dimethyl malonate or indole to the reactor after the Henry reaction (see Scheme 1) in one pot. Given that NiBDP@Cu did not readily induce further reaction of intermediate **1** with nitromethane, this catalyst was employed to convert **1** further into pharmaceutical intermediates **2** and **3** in a second step. Regarding the synthesis of **2**, upon adding dimethyl malonate to β-nitrostyrene (**1**) formed during the first step in the presence of NiBDP@Cu as a heterogeneous catalyst, Michael adduct **2** was quantitatively obtained (full conversion of **1** and 100% selectivity to **2**) after 12 h. On the contrary, only 29 and 64% of pure β-nitrostyrene (**1**) was converted into **2** for the blank and NiBDP, respectively. Unfortunately, in contrast to the high selectivity to **1** obtained with NiBDP@Cu, it was not possible to obtain high yields of **2** in a "one-pot" manner by using the polar NH_2- or OH-functionalized materials owing to the low yield of β-nitrostyrene (**1**) obtained in the Henry reaction (50 and 64% yield, respectively).

To compare all the MOFs already studied in the first reaction step in the Michael addition reaction (**1**→**2**), we performed the addition of dimethyl malonate to pure β-nitrostyrene (**1**) by employing other vessel than the one used for the Henry reaction. The TOF values obtained were higher for the NH_2- and OH-functionalized solids ($\approx 1\ h^{-1}$) than for NiBDP ($0.4\ h^{-1}$), as was observed for the Henry reaction. The parallel trend between pH of the MOF suspension and the catalytic activity was particularly clear for this reaction (see Figure 3b), and the K-exchanged materials were the most basic and active ones. Interestingly, the basicity of the suspensions increased upon decreasing the size of the NiBDP_X@Cu MOF particles (see Figures S8–S10), which could be related to exposed hydroxide groups on the external surface of the particles. For instance, the small size (< 1 μm) of NiBDP_NH_2@Cu gave rise to basic suspensions (pH ≈ 8) showing a relatively high TOF value ($\approx 1\ h^{-1}$) for the Michael addition of dimethyl malonate to pure **1**.

To prove the feasibility of the tandem process for the production of substituted indoles, a stoichiometric amount of indole was added to the reaction mixture after 48 h of the Henry reaction. β-Nitrostyrene (**1**) formed during the first Henry reaction step was quantitatively converted (in one pot) after an additional 12 h into 3-(2-nitro-1-phenylethyl)-1*H*-indole (**3**) in the presence of the NiBDP@Cu MOF catalyst (full conversion of **1** and 100% selectivity to **3**). It is important to highlight that none of the homogeneous catalysts, that is, $Ni(OAc)_2$, KOH, or $Cu(ClO_4)_2$, converted more than 40% of **1** into **3** after 12 h [starting from pure β-nitrostyrene (**1**) in a different pot, but under the same reaction conditions]. The catalytic activity of the MOFs for this reaction (**1**→**3**) showed no direct correlation with their basicity (pH of the suspension), although the NiBDP material and the homogeneous $Ni(OAc)_2$ catalyst had TOF values that were 10 times lower ($\approx 0.15\ h^{-1}$) than those of the other exchanged (Cu, K) or functionalized (NH_2, OH) materials (Table S2 and Figure S28). At present, we cannot fully explain why the activity of the NH_2/OH-functionalized MOFs (NiBDP_NH_2, NiBDP_OH) is higher than that of NiBDP. One hypothesis may be hydrogen-bonding activation of β-nitrostyrene by the hydrophilic NH_2 and OH functional groups in the linker, as recently described for 1,3-disiloxanediols.[16]

Moreover, the copper ions introduced into defective NiBDP@K increased the catalytic activity of NiBDP@Cu for this reaction (see Figure S28), which was proven to be catalyzed by MOFs with Lewis acid sites.[17] However, in contrast to the fact that $Cu_3(btc)_2$ (H_3btc = benzene-1,3,5-tricarboxylic acid) shows better performance in toluene than in 2-butanol, for NiBDP@Cu, the reaction was favored in the alcohol solvent. Again, this was probably a result of hydrogen-bonding activation of the nitro group of β-nitrostyrene by the 2-butanol solvent at 100 °C, which gave approximately 30% yield of **3** after 12 h in the absence of a catalyst. In contrast, if the reaction was performed in toluene in the absence of a catalyst, no trace amount of **3** was detected after 12 h.

The catalytic results for the one-pot synthesis of substituted indole **3** were compared to those obtained by using different nickel- and copper-containing solids (see Table 1). In our hands, NiBDP@Cu outperformed the nickel and copper MOFs (Table 1, entries 6 and 9) as well as the pyrazolate (Table 1, entries 4 and 6) and hydroxide (Table 1, entries 5 and 8) catalysts tested. The performance of basic nickel pyrazolate, $Ni(pz)_2$ (Table 1, entry 4), in the one-pot, two-step process was better than that of the copper analogue (Table 1, entry 7). An excess amount of basic sites favored the generation of byproducts, such as the reaction of **1** into **1b**, which occurred in the case of solids with high basicity such as NiBDP@K (Table 1, entry 2) and $Ni(OH)_2$ (Table 1, entry 5). Copper pyrazolate, $Cu(pz)_2$, showed high activity for the second step, which is in line with the performance of NiBDP@Cu for this particular reaction. For all NiBDP materials, the crystalline structure and surface area were maintained after the first and second steps of the tandem process, with only a slight decrease for NiBDP@Cu. A tentative reaction mechanism of the tandem process using this type of MOF is shown in Scheme 2.



Scheme 2. Representation of the binuclear bridged cluster (some linkers were intentionally omitted for clarity), for which the nickel, copper, or basic sites cooperatively activate both the carbonyl group of the benzaldehyde and the nitro group of the nitromethane and nitrostyrene molecules.

In conclusion, the NiBDP_X@Cu [H_2BDP = 1,4-bis(pyrazol-4-yl)benzene] metal–organic framework (MOF) presented higher selectivity to compound **1**, owing to its milder basicity, than either of the NiBDP_X@K or NiBDP_X parent solids, with higher activity for Michael-type additions. The best results in terms of activity and selectivity were obtained for NiBDP@Cu owing to the simultaneous presence of copper(II) ions at the nickel–oxo clusters and adequate basicity to avoid consecutive Michael addition of a second molecule of nitromethane to intermediate **1**. This allowed for the coupling of a second C–C bond-forming reaction step with the aim to obtain important pharmaceutical precursors (i.e., compounds **2** and **3**) from simple molecules. The novel NiBDP@Cu material described here allows the optimal performance of the one-pot Henry reaction/Michael-type addition as a high yielding (70%) tandem process, directing the benzaldehyde starting product towards pharmaceutical intermediates **2** and **3**. This work showed the potential catalytic applications of nickel pyrazolate type highly porous and stable MOFs as basic catalysts for multi C–C bond-forming reactions, as they present higher activities than copper and nickel carboxylate, pyrazolate, and hydroxide solids. Future efforts in the synthesis, characterization, and new catalytic applications of these materials are expected, with particular interest in the characterization of the copper sites in the crystal structure.

Table 1. TOFs for the individual steps and yield of **3** after 60 h of the one-pot, two-step process by using different MOF catalysts.[a]

Entry	Catalyst	$TOF_{1st\ step}$[b] [$10^{-2}\,h^{-1}$]	$TOF_{2nd\ step}$[b] [$10^{-2}\,h^{-1}$]	Yield of $\mathbf{3}_{one\text{-}pot}$ [%]
1	NiBDP@Cu	8	120	70
2	NiBDP@K	5	100	49
3	NiBDP	4	40	22
4	$Ni(pz)_2$	5	41	39
5	$Ni(OH)_2$	1	16	21
6	Ni_2(dhtp)	1	15	2
7	$Cu(pz)_2$	2	64	13
8	$Cu(OH)_2$	1	13	22
9	$Cu_3(btc)_2$	1	14	3

[a] First step: benzaldehyde to **1**; second step: **1** to **3**; two-step process: benzaldehyde to **3**. Conditions: benzaldehyde or **1** (0.1 mmol), catalyst (10 mg), 2-butanol (0.5 mL), 100 °C. Hpz = pyrazole, H_4dhtp = benzene-1,4-dicarboxylic-2,5-dihydroxy acid, H_3btc = benzene-1,3,5-tricarboxylic acid. [b] TOF = mmol of **1** or **3** obtained per mmol of Cu and/or Ni and time (for conversions < 30%).

Experimental Section

The NiBDP, NiBDP-OH, and NiBDP-NH_2 MOF samples were prepared according to the procedure reported by our group.[6] NiBDP X@K MOFs were prepared by suspending NiBDP_X (0.055 mmol) in a 0.35 M absolute ethanol solution of KOH (5.5 mL), and the mixture was stirred overnight. NiBDP_X@Cu was prepared by suspending NiBDP_X@K (100 mg) in a 0.1 M methanol solution of $Cu(ClO_4)_2$ (12 mL) and stirring for 16 h at room temperature. Catalytic tests were performed by stirring the substrate(s) (1 mmol, 10 equiv. of nitromethane for the Henry reaction) and the MOF catalyst (10 mg) in a round-bottomed flask at reflux in 2-butanol (0.5 mL). The consumption of the starting material was monitored by GC-FID by

using decane as an internal standard. The reaction products were characterized by NMR spectroscopy and MS (see the Supporting Information for more details).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: tunable basicity · C–C bond formation · domino reactions · heterogeneous catalysis · metal–organic frameworks

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