Electronic Supporting Information

Zn based Metal Organic Framework as a Heterogeneous Catalyst for C-C Bond Formation Reactions

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Synthesis and characterization of Zn-BTC MOF

Synthesis
Reported procedure was followed to obtain Zn-BTC MOF.\(^1\) Zinc (II) chloride (8.4 g, 61.92 mmol) and 1,3,5-trimesic acid (6.5 g, 30.93 mmol) were added in 360 mL of 1:1:1 mixture H\(_2\)O/EtOH/DMF in a 250 mL RB flask. Triethylamine was added drop wise to this solution to maintain the solution pH 7 and then the mixture was stirred at 100 °C for 24 h. The resulting white precipitate was filtered and repeatedly washed with DMF until the unreacted component was completely removed, then immersed in 400 mL of CH\(_2\)Cl\(_2\) overnight. After one day, the precipitate was repeatedly washed with the same solvent and again immersed in 400 mL of CH\(_2\)Cl\(_2\) for 24 h. The product was collected by filtration and dried at 65 °C under vacuum for 18 h. The white powder thus obtained after purification was grinded well with pestle and mortar (yield – 12.8 g).

Scheme S1. Synthesis of Zn-BTC MOF: Reaction conditions; Solvent, H\(_2\)O:EtOH:DMF(1:1:1), 100 °C, 24 h.
C-O-C stretching vibration band appeared at 1097 cm$^{-1}$. Strong absorption bands at 1637 and 1575 cm$^{-1}$ and between 1441 and 1371 cm$^{-1}$ are attributed to bound C–O group, asymmetric and symmetric stretching vibrations respectively. This clearly indicates that the BTC is coordinated to Zn. The presence of broad O–H absorption peak between 3435 cm$^{-1}$ indicates that some of the carboxyl groups are not fully deprotonated which, in turn, accounts for the presence of some free carboxylate are not coordinated to the metal center. Finally the peak at 1637 cm$^{-1}$ confirms that Zn is coordinated with –COO– moieties.
The Zn-BTC MOF shows some characteristic peaks below 20° in 2θ, which is identical to the replicated pattern from its single crystal structure. These peaks with 2θ values are concordant with the reported values (2θ = 10.80, 19.42, 23.86 and 27.85°). The PXRD spectra showed less crystallinity of the material.
**Figure S3.** SEM images of Zn-BTC MOF.

The SEM images of Zn-BTC MOF show perfect cubic morphology.
**EDX**

![EDX Spectrogram](image-url)  

Spectrum: Acquisition 6009  

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**Total: 105.68  100.00  100.00**
Figure S4. TGA of Zn-BTC MOF

The Figure S4 illustrates the weight losses observed in the thermal gravimetric experiment for Zn-BTC MOF in nitrogen environment. Three steps can be seen in the TGA analysis. The first weight loss was detected at 80 °C accounting for a weight loss of 5% due to the loss of solvent molecules in the material. The second weight loss was observed at 207 °C, around 15% is due to the loss of coordinated solvent molecules such as DMF and water from the framework structure. The third weight loss (26%) in 378 °C might be indexed as total collapse and degradation of organic ligand, indicating that this material is very robust. After this point, further increase in temperature led to the formation of metal oxide.3
Figure S5. Study showing the effect of Zn-BTC catalyst loading on product conversion.

With the optimized conditions in hand (optimized for Zn-Bp-BTC), we initially tested the influence of catalyst loading for Zn-BTC catalyst at different levels of catalytic loading. As evident from Figure S5, yield of compound 1 varied with difference in catalyst loading. At 0.01 mmol catalyst loading, 81 % yield was obtained for compound 1 and the duration of the reaction was 9 h. When catalyst loading was increased to 0.03 mmol and 0.06 mmol, the yield of the compound 1 did not vary much i.e., 88, 89% of yields were obtained, however, the duration of the reaction decreased from 8 h - 5 h. Further increase in the catalyst loading had very little effect on the yield and duration. The further reaction was carried out in the absence of catalyst to study the influence of the catalyst in the reaction. It is noteworthy that there is no product formation in the absence of catalyst even the reaction was carried out at elevated temperatures for 24 h. These results clearly indicate that the catalyst is essential in mediating this reaction.
Zn-Bp-BTC MOF

Solid state NMR of Zn-Bp-BTC MOF

Solid state $^{13}$C NMR of Zn-Bp-BTC MOF. * denotes the side bands.

Solid state $^{13}$C CPMAS NMR spectra of Zn-Bp-BTC MOF showed characteristic peaks at various regions. Bipyridine carbons appeared at 127 and 169 ppm. 1,3,5-Benzene tricarboxylate carbons appeared at 137 and 176 ppm respectively. Apart from these, co-ordinated DMF peaks were also seen at 39, 34 ppm (methyl protons), and at 216 ppm (C=O, DMF). In addition to these, side bands appeared at 97 and 59 ppm. To confirm the presence of ‘N’ (bipyridine ‘N’), $^{15}$N-CPMAS was recorded.
Solid state $^{15}$N NMR of Zn-Bp-BTCMOF

Characteristic $^{15}$N peak appeared at 365 ppm corresponding to the ‘N’ of 4,4'-bipyridine.
Figure S6. XRD patterns of Zn-BTC, Zn-Bp-BTC before and after catalysis and the simulated XRD pattern of Zn-Bp-BTC.
### Zn-Bp-BTC MOF Characterization

**EDX**

![EDX Spectrum](image)

**Spectrum: Acquisition 7636**


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Thermogravimetric analysis shows that Zn-Bp-BTC MOF undergoes weight loss at different temperatures as evident from Figure S6. Initial weight loss at 165 °C can be attributed to the loss of coordinated/trapped solvent molecules. Due to the decreased coordination ability of Zn$^{2+}$ion compared to Ni$^{2+}$ and Co$^{2+}$, the decomposing temperature of Zn-Bp-BTC MOF was observed at 266 °C. Possibly this point indicates the instability of organic moiety present in the framework structure. The subsequent increase in temperature led to the decomposition of organic and inorganic moieties finally leading to metal oxide formation.\textsuperscript{3}
Study on the effect of temperature on Zn-Bp-BTC catalyzed Knoevenagel condensation reaction using different substrates

![Chemical reaction](image)

**Table S1.** Temperature effect on product conversion using 4-bromobenzaldehyde.$^a$

<table>
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<tr>
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<th>Yield, %$^b$</th>
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$^a$ Zn-Bp-BTC (0.06 mmol), aldehyde (1 equiv), malononitrile (1.1 equiv) in MeOH.

$^b$ isolated yield.

![Chemical reaction](image)

**Table S2.** Temperature effect on product conversion using 9-anthraldehyde.$^a$

<table>
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$^a$ Zn-Bp-BTC (0.06 mmol), aldehyde (1 equiv), malononitrile (1.1 equiv) in MeOH.

$^b$ isolated yield.
Table S3. Temperature effect on product conversion using 2,5-dimethoxybenzaldehyde.$^a$

<table>
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$^a$ Zn-Bp-BTC (0.06 mmol), aldehyde (1 equiv), malononitrile (1.1 equiv) in MeOH.

$^b$ isolated yield.

Table S4. Temperature effect on product conversion using 3,4,5-trimethoxybenzaldehyde.$^a$

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$^a$ Zn-Bp-BTC (0.06 mmol), aldehyde (1 equiv), malononitrile (1.1 equiv) in MeOH.

$^b$ isolated yield.
Mechanism

**Scheme S2.** Proposed mechanism for Knoevenagel condensation using Zn-Bp-BTC MOF.

A possible mechanism for the formation of \(\alpha,\beta\)-unsaturated dicyano compounds is shown in Scheme S2. The terminal uncoordinated Bp unit acts as a basic site and deprotonates a proton from active methylene group generating a carbanion. The carbanion then attacks the carbonyl carbon. The acidic metal site can stabilise the intermediate and subsequent protonation leads to the formation of hydroxyl compound. Subsequent deprotonation by the basic site of MOF leads to the formation of \(\alpha,\beta\)-unsaturated dicyano compound with the elimination of water molecule.
NMR of Knoevenagel condensation products

All synthesized compounds via Knoevenagel condensation reaction were well characterized by $^1$H and $^{13}$C NMR.

2-benzylidenemalononitrile(1)

Brown color solid, melting point -83°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.75 (s, 1H), 7.37 (s, 3H), 6.89-6.80 (m, 2H).

2-((naphthalen-5-yl)methylene)malononitrile(2)

Yellow color solid, melting point - 163°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.69 (s, 1H), 8.30 (d, $J = 4.0$ Hz, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 2H) 7.74-7.62 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 157.8, 135.0, 133.6, 131.2, 129.5, 128.7, 128.6, 127.4, 125.5, 122.4, 113.8, 112.6, 85.3.

2-(4-bromobenzylidene)malononitrile(3)

Yellow color solid, melting point - 151°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.78-7.76 (m, 2H), 7.72-7.68 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 158.5, 133.2, 131.9, 130.1, 129.7, 113.4, 112.5, 83.6.
2-((anthracen-5-yl)methylene)malononitrile (4)

Orange color solid, melting point - 188 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$: 8.96 (s, 1H), 8.66 (s, 1H), 8.10 (d, $J = 8.0$ Hz, 2H), 7.93 (dd, $J = 12.0$ Hz, 2H) 7.70-7.57 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$: 160.7, 132.7, 131.0, 129.7, 129.2, 128.5, 126.2, 124.0, 112.8, 111.7, 109.6.

2-(1-(4-nitrophenyl)ethylidene)malononitrile (5)

Yellow color solid, melting point - 157 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$: 8.37 (t, $J = 12.0$ Hz, 2H) 7.70 (d, $J = 8.0$ Hz, 2H), 2.69 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$: the tertiary carbon next to the nitro group is not observed, 141.5, 136.9, 128.4, 124.4, 119.4, 114.0, 69.8, 24.6.

4-(2,2-dicyanovinyl)benzoic acid (6)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$: 8.11 (d, $J = 8.0$ Hz, 2H), 7.89 (d, $J = 8.0$ Hz, 2H), 7.83 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$: 168.3, 159.0, 136.2, 134.0, 130.6, 130.4, 112.2, 95.5.

2-(2,5-dimethoxybenzylidene)malononitrile (7)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$: 8.11 (d, $J = 8.0$ Hz, 2H), 7.89 (d, $J = 8.0$ Hz, 2H), 7.83 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$: 168.3, 159.0, 136.2, 134.0, 130.6, 130.4, 112.2, 95.5.
Yellow color solid, melting point - 104 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_{H}$: 8.29 (s, 1H), 7.73 (d, $J = 4.0$ Hz, 1H), 7.16 (dd, $J = 4.0$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H); $^{13}$C NMR(100 MHz, CDCl$_3$) $\delta_{C}$: 154.3, 124.4, 120.3, 114.5, 113.3, 112.9, 111.2, 81.1, 56.4, 56.0.

2-(3,4,5-trimethoxybenzylidene)malononitrile(8)$^{10}$

![Diagram](image1)

Yellow color solid, melting point - 147 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_{H}$: 7.73 (s, 1H), 7.33 (s, 1H), 4.05 (s, 3H), 3.98 (s, 6H); $^{13}$C NMR(100 MHz, CDCl$_3$) $\delta_{C}$: 159.5, 153.5, 144.1, 126.0, 114.1, 113.3, 108.4, 80.7, 61.4, 56.5.

2-(4-hydroxybenzylidene)malononitrile(9)$^5$

![Diagram](image2)

Melting point - 188°C: $^1$H NMR (400 MHz, CDCl$_3$) $\delta_{H}$: 7.39 (d, $J = 8.0$ Hz, 2H), 7.02-6.98 (m, 1H), 6.50 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR(100 MHz, CDCl$_3$) $\delta_{C}$: 163.9, 159.1, 133.5, 122.3, 116.5, 114.5, 113.4.

2-((naphthalen-2-yl)methylene)malononitrile(10)$^{11}$

![Diagram](image3)

Melting point - 139 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_{H}$: 8.30 (s, 1H), 8.10-8.07 (m, 1H), 7.97-7.90 (m, 4H), 7.69-7.61 (m, 2H); $^{13}$C NMR(100 MHz, CDCl$_3$) $\delta_{C}$: 159.9, 136.0, 134.6, 130.1, 129.8, 129.8, 128.6, 128.1, 127.8, 124.3, 114.1, 113.0, 82.4
General procedure for the synthesis of benzimidazole derivatives

A mixture of o-phenylenediamine (0.10 g, 0.92 mmol) and benzaldehyde (0.09 g, 0.92 mmol) was dissolved in 20 ml of EtOH. The reaction mixture was stirred at RT for 5 h. The reaction was carried out using Zn-Bp-BTC MOF as a heterogeneous catalyst. The progress of the reaction was monitored by TLC (EtoAc :PET-80, 2 %). After completion of the reaction the reaction mixture was filtered to remove the catalyst and the solvent was evaporated and resultant crude mixture was kept for recrystallization in EtOH. The recrystallized product was washed two times with EtOH and dried to afford the brown color product 2a (0.15 mg, 84%).

NMR data

2-phenyl-1H-benzo[d]imidazole (11)

Dark brown color solid, melting point – 291 °C. ¹H NMR (500 MHz, DMSO-d₆) δ_H: 12.99 (s, 1H), 8.13-8.10 (m, 2H), 7.77-7.75 (m, 2H), 7.67 (d, J = 10.0 Hz, 1H), 7.53 (d, J = 5.0 Hz, 1H), 7.24-7.20 (m, 3H); ¹³C NMR (125 MHz, DMSO-d₆) δ_C: 150.2, 143.7, 135.0, 131.9, 131.7, 130.9, 129.4, 128.3, 123.2, 122.8, 118.9, 111.4.

2-(4-bromophenyl)-1H-benzo[d]imidazole (12):

Yellow color solid, melting point – 300 ºC. ¹H NMR (500 MHz, CDCl₃+DMSO-d₆) δ_H: 7.92 (d, J = 5.0 Hz, 2H), 7.45 (d, J = 10.0 Hz, 4H), 7.08-7.06 (m, 2H). ¹³C NMR (125 MHz, DMSO-d₆) δ_C: 149.6, 130.8, 130.7, 128.4, 127.2, 122.6, 121.3.
2-(2,5-dimethoxyphenyl)-1H-benzo[d]imidazole (13): brown color solid, melting point – 218 °C. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta_H\): 7.90 (t, \(J = 10.0\) Hz, 3H), 7.59 (s, 2H), 7.59-7.36 (m, 2H), 4.10 (s, 3H), 3.92 (s, 3H); \(^1\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta_C\): 153.3, 151.7, 145.8, 131.7, 125.4, 120.3, 114.2, 114.0, 56.6, 56.07.

![Structure of 2-(2,5-dimethoxyphenyl)-1H-benzo[d]imidazole](image)

2-(4-bromophenyl)-5-chloro-1H-benzo[d]imidazole (14): cream color solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)+DMSO-\(d_6\)) \(\delta_H\): 13.02 (s, 1H), 8.10 (d, \(J = 10.0\) Hz, 2H), 7.78 (d, \(J = 10.0\) Hz, 2H), 7.72 (s, 1H), 7.66 (d, \(J = 5.0\) Hz, 1H), 7.55 (d, \(J = 10.0\) Hz, 1H), 7.26-7.21 (m, 1H); \(^1\)C NMR (125 MHz, CDCl\(_3\)+DMSO-\(d_6\)) \(\delta_C\): 132.5, 132.4, 129.4, 129.0, 129.4, 128.8, 127.5, 14.1, 123.3, 10.7, 118.8, 113.2, 111.6.

**General procedure for the synthesis of 2-amino 4H-chromene**

A mixture of benzaldehyde (0.10 g, 0.94 mmol), malononitrile(0.06 g, 1.03 mmol) and dimeredone (0.13 g, 0.94 mmol) was dissolved in 20 ml of EtOH. The reaction mixture was stirred at 80°C for 5 h. The reaction was carried out using Zn-Bp-BTC MOF as a heterogeneous catalyst. The progress of the reaction was monitored by TLC (Thin layer chromatography) using EtOAc:PET mixture as eluent. After completion of the reaction the reaction mixture was filtered to remove the catalyst and the solvent was evaporated and resultant precipitate was washed three times (10 ml X 3) with petroleum ether and dried using vacuum distillation to afford the final product.

![Structure of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile](image)

2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile(15): Brown color solid, melting point - 235 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta_H\): 7.73-7.18 (m, 5H), 4.52 (s, 2H), 4.40 (s, 1H), 2.22 (d, \(J = 10.0\) Hz, 2H), 1.93 (s, 2H), 1.11 (s, 3H), 1.04 (s, 3H); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta_C\): 196.9, 161.6, 157.6, 143.3, 128.7, 127.6, 127.3, 118.8, 144.2, 63.7, 50.8, 40.8, 35.6, 32.3, 29.6, 27.8.
2-amino-4-(2,5-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (16): Colorless solid, melting point - 214 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ$_H$: 6.79 (d, $J = 10.0$ Hz, 1H), 6.68-6.64 (m, 2H), 4.69 (s, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 3.73 (s, 3H), 2.43 (s, 2H), 2.21 (d, $J = 5.0$ Hz, 2H), 1.11 (s, 3H), 1.06 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ$_C$: 196.0, 162.4, 158.0, 153.7, 151.7, 132.3, 115.5, 113.1, 112.6, 63.7, 56.5, 55.7, 50.8, 40.8, 32.3, 30.7, 29.1, 27.7.

$^1$H and $^{13}$C NMR spectrum of isolated compounds

$^1$H NMR of compound 1 in CDCl$_3$
1H NMR of compound 2 in CDCl₃

13C NMR of compound 2 in CDCl₃
$^1$H NMR of compound 3 in CDCl$_3$

$^{13}$C NMR of compound 3 in CDCl$_3$
H NMR of compound 4 in CDCl₃

^{13}C NMR of compound 4 in CDCl₃
$^1$H NMR of compound 5 in CDCl$_3$

$^{13}$C NMR of compound 5 in CDCl$_3$
$^1$H NMR of compound 7 in CDCl$_3$

$^{13}$C NMR of compound 7 in CDCl$_3$
$^1$H NMR of compound 8 in CDCl$_3$

$^{13}$C NMR of compound 8 in CDCl$_3$
$^{1}H$ NMR of compound 9 in CDCl$_3$-DMSO-$d_6$

$^{13}C$ NMR of compound 9 in CDCl$_3$-DMSO-$d_6$
$^{1}H$ NMR of compound 10 in CDCl$_3$

$^{13}$C NMR of compound 10 in CDCl$_3$
$^1$H, $^{13}$C and Dept NMR spectrum of synthesized 2-amino 4H-chromene and benzimidazole derivatives
DEPT NMR spectrum of compound 11

\[ \text{1H NMR spectrum of compound 12} \]
$^{13}$C NMR spectrum of compound 12

DEPT NMR spectrum of compound 12
H NMR spectrum of compound 13

\[ \text{\textsuperscript{13}C NMR spectrum of compound 13} \]
DEPT NMR spectrum of compound 13

$^1$H NMR spectrum of compound 14
C NMR spectrum of compound 14

DEPT NMR spectrum of compound 14
H NMR spectrum of compound 15

\[ \text{\^{1}H NMR spectrum of compound 15} \]

\[ \text{\^{13}C NMR spectrum of compound 15} \]

38
DEPT NMR spectrum of compound 15

1H NMR spectrum of compound 16
13C NMR spectrum of compound 16

DEPT NMR spectrum of compound 16
Supporting References