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# New 1D chiral Zr-MOFs based on in situ imine linker formation as catalysts for asymmetric C-C coupling reactions

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## ABSTRACT

A novel chiral diimine Zr-MOF (DUT-136, DUT - Dresden University of Technology) is synthesized in a one-pot reaction from  $ZrCl_4$ , 4-formylbenzoic acid, and (*R*,*R*)-1,2-diphenylethylenediamine as an enantiopure core. Inspired by the versatile chemistry of the C=N bond, a variety of post-synthetic derivatizations were performed. Oxidation, reduction, and metalation effectively generated the chiral amide-, amine-, and Ni containing DUT-136 MOFs, respectively. The catalytic activity of these postsynthetically modified materials was systemically evaluated in a wide range of asymmetric organic transformations, including the Friedel Crafts alkylation, Michael addition, aldol reaction, and the Nicatalyzed C-C coupling.

## **INTRODUCTION**

Schiff-base chemistry has emerged as a simple and useful tool in designing various types of porous materials, including metal-organic frameworks (MOFs),<sup>[1-4]</sup> covalent organic frameworks (COFs),<sup>[5-7]</sup> and porous organic polymers (POPs).<sup>[8, 9]</sup> These imine-based networks generally exhibit high stabilities in most organic solvents, while their nitrogen atoms can coordinate to various transition metal ions, offering ideal platforms for catalytic applications.<sup>[10, 11]</sup> In fact, metal complexes, based on dynamic imine chemistry could be employed as effective catalysts for several organic reactions. More importantly, the Shiff-base reactions also are an efficient and environmentally benign approach to generate homochirality.<sup>[11]</sup> Recently, numerous reports dedicated to preparation of chiral porous materials based on formations of chiral imine have been published.<sup>[12-15]</sup> These materials have not only been applied as effective catalysts for asymmetric base-catalyzed reactions, but also offer vast possibilities for postsynthetic transformations via chemical conversion of imine groups and metalation.<sup>[16-18]</sup> However, their stability is still an intrinsic drawback, hindering practical applications. Therefore, the incorporation of chiral imine containing ligands into Zr-based frameworks is a promising approach to obtain crystalline porous materials, possessing high activities as well as outstanding stable structures.<sup>[11, 19]</sup> Assembling the Zr<sub>6</sub>-node and chiral imine ligands into a solid framework structure faces two major challenges: i) formation of amorphous phases due to rapid nucleation and precipitation, and ii) decomposition of imine groups in the acidic environment during Zr-MOFs synthesis. This issue was for the first time mentioned by Zhou and co-workers, reporting formation of pure phase of PCN-160 in a synthesis containing mixture of 4-[(E)-(4-carboxybenzylidene)amino]benzoic acid (CBAB) and azobenzene (4,4'-stilbenedicarboxylic acid (AZDC)) linkers.<sup>[2]</sup> This result could be rationalized assuming that the imine bonds in CBAB linkers were broken up during Zr-MOF synthesis, which require either a high temperature (120 °C) or an excess amount of acid modulators.<sup>[2]</sup> A similar observation was reported by Jiang et al. and Cui et al. in 2018.<sup>[20,</sup> <sup>21]</sup> Particularly, chiral Zr-MOFs based on salen ligands could only be obtained through a precious

modulated process, while the introduction of these chiral salen linkers could be only carried out by oneor two-step ligand exchange.<sup>[20]</sup> In addition, the solubility of chiral diimine linkers is also a certain obstacle to introduce them into metal-organic frameworks.<sup>[22]</sup> However, these hindrances could be overcome by employing one-pot synthesis, in which formation of imine organic linkers and of MOF occur at the same time, limiting the acidic influence of zirconium ion, and of monocarboxylic acid modulator, as well as eliminating the low solubility problem. Actually, a series of Ti-MOFs based on imine linkages was successfully synthesized *via in situ* generation of titanium clusters and imine ligands.<sup>[1, 3]</sup>

In the following, the synthesis of a new chiral Zr-MOF, DUT-136, *via in situ* formation of Zr-clusters and chiral imine-organic building blocks is described, and its catalytic activity is evaluated in a wide range of asymmetric C-C coupling reactions.

## **RESULTS AND DISSCUSION**

## Materials synthesis and characterization

In the first attempts to synthetize chiral imine Zr-MOF, we decided to utilize (R,R)-1,2diaminocyclohexane and 3-formyl-4-hydroxybenzoic acid as building blocks for *in situ* synthesis (**Figure 1b**). Unfortunately, all efforts following this approach resulted in unknown amorphous phases, as indicated by powder X-ray diffraction (PXRD). The presence of acidic reagents, such as Zr<sup>4+</sup>, HCl, and modulators in MOF syntheses process are a serious hindrance to generate imine linkers.<sup>[21]</sup> To limit this negative impact, a strategy using hydrophobic and bulky groups protecting the imine groups from acidic reagents is proposed. In particular, the diimine ligand, built from 4-formylbenzoic acid and (R,R)-1,2diphenylethylenediamine was aimed, in which the phenyl groups are employed as imine protectors. This strategy provided an efficient way to synthesize chiral Zr-MOF, DUT-136, *via* one-pot synthesis method (**Figure 1a**).

To obtain the desired products of good crystallinity, a series of various modulators in varying concentrations was utilized in initial experiments. The reactions were carried out in DMF as solvent at 80 °C in the presence of CH<sub>3</sub>COOH as modulator in the concentration range from 0 to 150 equivalents (based on ZrCl<sub>4</sub> amount). However, the syntheses with less than 40 equiv. of CH<sub>3</sub>COOH only produced amorphous powders, while materials with highest crystallinity were obtained with 80 equiv. of CH<sub>3</sub>COOH. Higher amount of modulator does not lead to further crystallinity improvement (**Figure S1a**).



**Figure 1.** Combination of Zr-clusters and some chiral linkers to achieve chiral Zr-MOFs. Color scheme of cluster: Zr (green); O (red); C (black).

Besides, the crystallinity was found to be affected also by the nature of modulator. Only poorly crystalline phases were particularly formed in case of benzoic acid or formic acid as additives, while the crystallization was not observed in the presence of CF<sub>3</sub>COOH (**Figure S1b**). Although, the monocarboxylic acids play a key role in improving the crystallinity of Zr-MOFs, an excess amount of acids could promote the hydrolysis of imine to the corresponding precursors. This explains the formation of the poorly crystalline products in the case of using either a strong acid such as CF<sub>3</sub>COOH or high concentrations of modulators. In addition, the fragility of such imine bonds in the acidic environment has also been a major reason for forming non-crystalline powders when imine linkers are applied directly in zirconium framework assembly.<sup>[2, 23]</sup> Therefore, the one-pot reaction of three components, including 1, 2-diphenylethylenediamine, 4-formylbenzoic acid, and zirconium chloride (**Figure 1a**) has been found as

an advantageous approach to avoid these inherent drawbacks in the self-assembly synthesis of chiral Zr-

MOF containing diimine linkers



Figure 2. PXRD patterns of as-synthesized and activated DUT-136 at room temperature ( $\lambda = 1.5405$  Å).

Although, the resulting DUT-136 material is highly crystalline according to PXRD (**Figure 2**), the regular spherical particles with approximately 500 nm in size were observed in the corresponding SEM images (**Figure S7a**). The size of this particles is not sufficient for single crystal X-ray diffraction analysis. Consequently, an attempt to increase the size of crystals was undertaken by varying temperature as well as solvent in the presence of 80 equiv. of  $CH_3COOH$  with stoichiometric ratio of  $ZrCl_{4,4}$ -formylbenzoic acid, and 1,2-diphenylethylenediamine of 2:2:1. However, these conditions also lead to poorly crystalline phases. In particular, amorphous powders with broadened peak profiles were found if conducting the reaction at 60 °C in DMF, while further increase of temperature up to 100 °C or 120 °C produced only particles, for which no reflections were detected in XRD pattern (**Figure S2a**). The change of solvent to DEF or NMP also resulted in a slightly reduced crystallinity (**Figure S2b**).



**Figure 3.** Structure of DUT-136: a) Organic linker (4,4'-(((1,2-diphenylethane-1,2-diyl)bis(azaneylylidene))bis(methaneylylidene))dibenzoate) formed*in situ*from 4-formylbenzoic acid and (*R*,*R* $)-1,2-diphenylethylenediamine; b) <math>Zr_6O_4(OH)_4(CH_3OO)_{12}$  cluster; c) Interconnection of  $Zr_6O_4(OH)_4Zr$ -clusters by organic linkers into chain (the pore is represented by yellow sphere with the radius of 3 Å); d) View on the crystal structure along *c* direction. Color scheme: Zr (green); O (red); C (black); N (blue). H atoms are omitted for clarity.

Due to the microcrystalline nature of the resulting product, its structure was solved from PXRD data. In the structure of DUT-136, the interconnection of the well-known hexanuclear cluster  $Zr_6O_4(OH)_4$  and diimine building blocks results in a 6-connected one-dimensional chain (**Figure 3c**). Thus, each inorganic SBU is connected to six diimine linkers, and each of these linkers is coordinated to two Zr-clusters. Six acetate anions are additionally coordinated to the remaining coordination sites of the Zr-node. As a result,

the internal pore with diameters of about 6 Å is formed, restricted by zirconium cluster at vertices and the diimine ligand as the edges of the pore.

The microporosity of crystalline material was confirmed by nitrogen physisorption at 77 K. The specific BET surface area and total pore volume derived from the isotherm amount to 795 m<sup>2</sup>/g and 0.35 cm<sup>3</sup>/g, respectively (in the case of *R*,*R*-configuration of linker) (**Figure S4a**). The pore size distribution calculated by de quench solid density functional theory (QSDFT) for slit/cylindrical pore geometry is shown in **Figure S4b**. The sharp peak at 3 Å appearing in the distribution, is close to the pore radius of the cage obtained from crystallographic data. A similar isotherm was also recorded for a material containing *S*,*S*-configuration of the linker, which showed 730 m<sup>2</sup>/g and 0.32 cm<sup>3</sup>/g for specific BET surface area and total pore volume, respectively.

The thermal stability of the material was investigated by thermogravimetric analysis (TGA) and in situ thermo-PXRD measurements (Figure S8). The PXRD patterns remained virtually unchanged up to 250 °C, after that the appearance of amorphous phase was observed following by the decomposition of organic linker starting from 300 °C (Figure S8b). According to TGA, the decomposition of DUT-136 in air proceed in two steps. The first weight loss of 8.57% at 200 °C corresponds to the residual DMF solvent and acetate anions. The next weight decrease of 53.57% observed at 490 °C corresponds to the decomposition of the organic building blocks. This oxidation reaction leads to ZrO<sub>2</sub> as the final product (35.76%), which matches well with zirconium content found by ICP-OES measurement (27.34%). Together with NMR results of digested samples, chemical formula а  $Zr_6O_6(L)_{2.45}(OH)_2(CH_3COO)_{2.1} \cdot 2.3DMF$  (L = 4,4'-(((1,2-diphenylethane-1,2-diyl)bis(azaneylylidene))bis(methaneylylidene))dibenzoate) is proposed for "as made" material.

#### Post-synthetic derivatization

Utilization of the diimine linkers as organic struts in DUT-136 also offers various possibilities for functionalization *via* chemical conversion of its imine groups. In fact, the post synthetic amidation and amination of linker in DUT-136 could be carried out under mild conditions, giving DUT-136\_amide and DUT-136\_amine, respectively.



**Figure 4.** NMR spectra and the corresponding linker in DUT-136\_imine (black), DUT-136\_amine (blue), and DUT-136 amide (red).

The reaction to synthesize DUT-136\_amine was performed in the presence of sodium borohydride as a reducing reagent in methanol as solvent at room temperature. The successful reduction was confirmed by Fourier transform infrared (FT-IR) spectroscopy (**Figure 6**). The spectrum of reduced material (DUT-

136\_amine) exhibits a broad signal at 3640 cm<sup>-1</sup>, which can be assigned to the free N-H stretching vibrations. This conversion of imine linkers was quantified by NMR analysis of digested samples (**Figure 4 and S14**). In the NMR spectrum of DUT-136\_amine, a new signal, attributed to the proton on carbon at position 2 (**Figure 4**), appears at 5.4 ppm instead of signal at 5.2 ppm, characteristic for the parent DUT-136 (**Figure 4**).



**Figure 5.** a) PXRD patterns ( $\lambda = 1.5405$  Å) and b) nitrogen physisorption isotherms at 77 K of DUT-136\_imine (black), DUT-136\_ amine (blue) and DUT-136\_amide (red).

By comparing the area of these proton peaks, the conversion of the material from imine to amine was calculated to be approx. 92%. In addition, the transformation of –C=N to –C-NH groups was also recorded in solid state <sup>13</sup>C-NMR. A new peak, belonging to amine carbon, was observed at 190 ppm along with the signal of imine carbon at 175 ppm, indicating the formation of amine linkages (**Figure S15**).For the formation of DUT-136\_amide, the oxidation reaction was performed using sodium chlorite as oxidizing reagent in dioxane as solvent, giving DUT-136\_amide. The free N-H stretching at 3654 cm<sup>-1</sup> was also observed in the FT-IR spectrum of oxidized material (**Figure 6**), however, only 70% conversion of imine linkers was achieved after 24 hours of reaction, according to the NMR data (**Figure 4 and S13**).



Figure 6. DFTIR spectra of DUT-136 imine and its derivatives.

The crystallinity of DUT-136\_amide as well as of DUT-136\_amine was confirmed by PXRD measurements (**Figure 5a**), showing no substantial structural rearrangement of the material during the course of chemical transformation. Although, the shape as well as the thermal stability of crystals still maintained (**Figure S7b-f; Figure S9 and S10**), the nitrogen adsorption capacity at 77 K of oxidized and

reduced materials was significantly decreased from 795 m<sup>2</sup>/g to 364 m<sup>2</sup>/g (0.16 cm<sup>3</sup>/g) and 198 m<sup>2</sup>/g (0.11 cm<sup>3</sup>/g), respectively (**Figure 5b**). Similar capacity drop was also found for CO<sub>2</sub> at 25 °C. A moderate CO<sub>2</sub> uptake of 20.4 cm<sup>3</sup>/g at 1 bar was found for DUT-136\_imine, while this value decreased to 10.6 and 6.5 cm<sup>3</sup>/g for the reduced and oxidized material, respectively (**Figure S16**).

## Catalytic studies

To emphasize the catalytic activity of DUT-136 series, a wide range of organic transformations, including acid-base and transition metal catalyzed C-C coupling reactions were investigated.

## Friedel–Crafts alkylation reaction

As the first model reaction, the Friedel–Crafts alkylation between trans-β-nitrostyrene and indole (**Figure** 7) was employed to assess the catalytic behavior of DUT-136.

![](_page_12_Figure_6.jpeg)

Figure 7. Asymmetric Friedel–Crafts alkylation between trans-β-nitrostyrene and indole.

This reaction is not only an advantageous approach to obtain enantiopure aromatic derivatives with perfect atom economy, but also allow to evaluate efficiency of acidic active sites of chiral catalytic systems.<sup>[24]</sup> In fact, much effort in recent years has been devoted to the development of Brønsted and Lewis acids with chiral environment to achieve improved performances in the Friedel–Crafts alkylation of arenes with nitroalkenes.<sup>[24-26]</sup>

In this work, the effect of DUT-136 on reaction performance was studied in toluene with *trans*- $\beta$ -nitrostyrene/indole molar ratio of 1:1.5 at 50 °C.

A moderate conversion was achieved after 3 days of the reaction in the presence of 5 mol%, and 10 mol% (based on Zr content) of DUT-136 catalyst, (33%, and 65%, respectively). The conversion increases to

88% using 15 mol% of catalyst (**Table 1**). DUT-136 with 6-connected Zr-clusters has higher activity than DUT-67 (a typical 8-connected Zr-MOF) (**Entry 1-Table 1**),<sup>[27]</sup> which required 7 days to achieve a comparable conversion (90%).

| Table | 1. | Perfc | ormance o | f | various | catal | ysts | in | the | Frie | del- | -Crat | fts | alky | vlation |  |
|-------|----|-------|-----------|---|---------|-------|------|----|-----|------|------|-------|-----|------|---------|--|
|       |    |       |           |   |         |       | -1   |    |     |      |      |       |     |      | /       |  |

|   | Entry | Catalyst <sup>a</sup> | Reaction | Yield            | ee               |
|---|-------|-----------------------|----------|------------------|------------------|
| _ | Entry | Catalyst              | time (h) | (%) <sup>b</sup> | (%) <sup>c</sup> |
|   | 1     | DUT-67                | 168      | 90               | 0                |
|   | 2     | RR-DUT-136_imine      | 72       | 88               | 0                |
|   | 3     | RR_DUT-136_amine      | 72       | 81               | 0                |
|   | 4     | RR DUT-136 amide      | 72       | 85               | 0                |

<sup>a</sup> Reaction conditions: 50 °C, 15 mol% catalyst based on zirconium content, 1.0 mmol trans-β-nitrostyrene, 1.5 mmol indole, 4 mL toluene; <sup>b</sup> Determined by GC; <sup>c</sup> *ee* value determined by HPLC.

However, no enantioselectivity at all was found for all catalysts investigated. The absence of enantioselective induction indicates the contribution of acidic Zr-clusters as active species.<sup>[28, 29]</sup> Despite DUT-136 contains chiral diimine linkers, they are not sufficiently active (in comparison to Zr) to produce enantiomeric excess of the product.

## Aldol addition reaction

In an effort to demonstrate the function of enantiopure sites in DUT-136, its basic activity based on diimine linkers was investigated *via* an acid-base catalyzed aldol addition of cyclohexanone and 4-nitrobenzaldehyde in presence of benzoic acid as additive (**Figure 8**).<sup>[28]</sup>

![](_page_13_Figure_8.jpeg)

Figure 8. Asymmetric aldol addition reaction of 4-nitrobenzaldehyde and cyclohexanone.

**Table 2.** Performance of various catalysts in the aldol reaction.

| Entry | Catalyst <sup>a</sup> | Amount<br>(mol%) | Yield (%) <sup>b</sup> | syn/anti <sup>c</sup> | ee <sup>c</sup> (%) |
|-------|-----------------------|------------------|------------------------|-----------------------|---------------------|
| 1     | RR-DUT-               | 5                | 32                     | -                     | 0                   |
|       | 136_imine             | 5                | 52                     |                       | Ŭ                   |
| 2     | RR-DUT-               | 10               | 27                     |                       | 0                   |
| 2     | 136_imine             | 10               | 37                     | -                     | 0                   |
| 2     | RR-DUT-               | 15               | 41                     | -                     | 0                   |
| 3     | 136_imine             | 15               |                        |                       | 0                   |
|       | RR-DUT-               | 20               | 12                     | 72.22                 | -                   |
| 4     | 136 imine             | 20               | 43                     | /3:23                 | 5                   |
| -     | RR-DUT-               | •                |                        |                       | 0                   |
| 5     | 136 amine             | 20               | 55                     | 77:23                 | 9                   |
|       |                       |                  |                        |                       | _                   |
| 6     | 136 amide             | 20               | 48                     | 78:22                 | 7                   |

<sup>a</sup> Reaction conditions: 25 °C, 0.05 mmol benzoic acid, 0.25 mmol 4-nitrobenzaldehyde, 4 mmol cyclohexanone, 1 mL DMSO, reaction time 168h; <sup>b</sup> determined by GC; <sup>c</sup>*ee* value for *syn*-isomers was determined by HPLC.

As expected from our recent investigation of RR-DUT-136\_imine, a modest enantioselectivity of 5% *ee* for syn-isomers (77:23 *dr* (*syn:anti*)) was observed in the reaction carried out in DMSO at 25 °C with 20 mol% catalyst (based on diimine linkers) in 7 days (**Entry 4 - Table 2**). Although there was a gradual rise in aldolisation yield from 32% to 43% by increasing the catalyst amount from 5 mol% to 20 mol%, respectively, further increase up to 30 mol% DUT-136 does not lead to further improvement. However, the utilization of the post-synthetically functionalized DUT-136 provided a minor enhancement in stereoselectivity. The reaction catalyzed by 20 mol% of oxidized material, DUT-136\_amide, reaches up to 48% yield and 7% *ee* for *syn*-isomers (**Entry 6 - Table 2**), while this enantiomeric excess for DUT-136\_amine, was 9% (*syn*-isomers) in line with 55% yield and 77:23 *dr* (*syn:anti*) (**Entry 5 - Table 2 and Figure S23**). In addition, due to the steric effect of Zr-clusters,<sup>[28]</sup> DUT-136 and its derivatives showed a unprecedentedly high *syn*-diastereoselectivity (*syn* over *anti*), which was rarely observed in previous reports.<sup>[28, 30, 31]</sup>

#### Michael addition reaction

Since the achiral Zr-MOFs are not active in Michael addition reaction,<sup>[29]</sup> the performance of new materials was investigated in addition reaction of *trans*- $\beta$ -nitrostyrene and cyclohexanone (**Figure 9**).<sup>[29]</sup>

![](_page_15_Figure_3.jpeg)

Figure 9. Asymmetric Michael addition of trans-β-nitostyrene and cyclohexanone.

The reaction involving chiral DUT-136\_ imine catalysts in the mixture of isopropanol and methanol at 50 °C proceeds slowly to only 12% yield and 5% *ee* for *syn*-isomers after 7 days. A minor improvement (17% yield and 17% *ee*) was achieved in the presence of trifluoroacetic acid (TFA) as additive (**Entry 3** - **Table 3**). This value could be further improved, if the post synthetically modified DUT-136 materials were used as catalysts.

A yield of 27% and 23% *ee* were obtained with chiral RR-DUT-136\_amide material, and 28% yield and 31% *ee* in the case of DUT-136\_amine (Entry 7-8 - Table 3 and Figure S24). As mentioned above, although the acidic defect sites on Zr-cluster are not active in the Michael reaction, their presence can have a negative effect on the performance of the nitrogen-containing functional groups.<sup>[29]</sup> Hence, the application of acid additives not only enhances the formation rate of enamine intermediates, but also improves the ability of DUT-136 and its derivatives to catalyze the Michael addition of *trans*-βnitrostyrene and cyclohexanone. Similarly, by transformation of DUT-136 into amide- as well as amine derivatives, the basicity of the material is enhanced, which is reflected in clear improvement in enaminecatalyzed reactions.

 Table 3. Performance of various catalysts in the Michael reaction.

| Entry | Catalyst <sup>a</sup> | Amount<br>(mol%) | Additive | Yield<br>(%) <sup>b</sup> | syn/<br>anti<br>c | ee <sup>c</sup><br>(%) |   |
|-------|-----------------------|------------------|----------|---------------------------|-------------------|------------------------|---|
| 1     | RR-DUT-               | 5                | TEA      | 0                         |                   |                        |   |
| 1     | 136_imine             | 5                | IFA      | 0                         | -                 | -                      |   |
| 2     | RR-DUT-               | 10               | TEA      | 0                         |                   |                        |   |
| 2     | 136_imine             | 10               | IFA      | 0                         | -                 | -                      |   |
| 2     | RR-DUT-               | 20               | TEA      | 17                        | 02.9              | 17                     |   |
| 3     | 136_imine             | 20               | IFA      | 1 /                       | 92.8              | 17                     |   |
| 4     | RR-DUT-               | 20               | Formic   | 10                        |                   |                        |   |
| 4     | 136_imine             | 20               | acid     | 10                        | -                 | -                      | - |
| 5     | RR-DUT-               | 20               | Acetic   | 11                        |                   |                        |   |
| 3     | 136_imine             | 20               | acid     | 11                        | -                 | -                      |   |
| 6     | RR-DUT-               | 20               | Benzoic  | 0                         |                   |                        |   |
| 0     | 136_imine             | 20               | acid     | 0                         | -                 | -                      |   |
| 7     | RR-DUT-               | 20               | TEA      | 20                        | 95.15             | 21                     |   |
| /     | 136_amine             | 20               | IFA      | 28                        | 83.13             | 51                     |   |
| 0     | RR-DUT-               | 20               | TEA      | 27                        | 96.14             | 22                     |   |
| ð     | 136 amide             | 20               | IFA      | 27                        | 80:14             | 23                     |   |

<sup>a</sup> Reaction conditions: 50 °C, 0.05 mmol additives, 0.25 mmol trans-β-nitrostyrene, 5 mmol cyclohexanone, 4 mL isopropanol:methanol (1:1, v:v); <sup>b</sup> Determined by GC; <sup>c</sup> *ee* value for *syn*-isomers determined by HPLC.

## Ni(II)-catalyzed asymmetric Michael addition

The DUT-136\_diimine offer many possibilities for post-synthetic metalation to afford organometallic catalysts. In this context, the DUT-136 and its derivatives were also utilized as support to immobilize nickel(II) catalytic sites. The materials were then applied as catalysts in a cross C-C coupling reaction of diethyl malonate and *trans*-β-nitrostyrene (**Figure 10**).

![](_page_16_Figure_5.jpeg)

**Figure 10.** Asymmetric Ni-catalyzed Michael reaction of *trans*-β-nitrostyrene and iethyl malonate.

The addition of malonates to electron deficient alkenes (conjugate addition reactions) is a well-known tool to construct optically active 1,3-carbonyl compounds.<sup>[32]</sup> A series of significant breakthroughs, reported by Evans and coworkers from 2005 to 2007, demonstrates the vital role of chiral Ni(II) complexes based on diamine derivatives in asymmetric additions of 1,3-dicarbonyl compounds to nitroalkenes.<sup>[32-34]</sup>

Post-synthetic Ni-metalation of DUT-136 and its derivatives was performed by immersing them in methanol solution of Ni(OAc)<sub>2</sub> at 25 °C. The resulting materials were washed several times with methanol to remove unreacted chemicals before activation under vacuum at 100 °C for 24 h. The presence of metal was confirmed by ICP-OES, indicating that the immobilization of Ni(II) significantly relied on the nitrogen-containing functional groups in DUT-136. The highest Ni content was found in the DUT-136\_amide\_Ni material with 2.1 wt%, while in case of DUT-136\_imine\_Ni and DUT-136\_amine\_Ni the loadings of 1.4 wt% and 1.7 wt%, respectively, were reached. To verify the crystallinity of all resulting samples, PXRD analysis was employed. It showed no significant changes in the structures after post synthetic metalation (**Figure S5**).

The asymmetric cross C-C coupling reaction of *trans*- $\beta$ -nitrostyrene and diethyl malonate was typically carried out in toluene as solvent in the presence of 3 mol% catalyst (based on Ni) at 25 °C. It should be noted that no traces of product were detected after 240 hours of reaction, if the parent DUT-136 materials, as well as homogeneous Ni(OAc)<sub>2</sub> catalysts were utilized (**Entry 2, Table 4**). If DUT-136\_imine\_Ni was used, a yield of 36% was obtained (**Entry 6, Table 4**). The performance of Ni-catalyzed Michael addition could be significantly improved (to 63%, and 67% yield), if DUT-136\_amide\_Ni, and DUT-136\_amine\_Ni were applied (**Entry 7 and 8, table 4**). Moreover, a gradual increase in enantioselectivity toward formation of *R*-isomer was observed. This value increases from 6% *ee* in the reactions catalyzed by Ni-DUT-136\_imine\_Ni materials to 16%, and 12% *ee* in reaction catalyzed by DUT-136\_amide\_Ni, and DUT-136\_amide\_Ni, respectively.

| Entry | Catalyst <sup>a</sup>                | Solvent               | Reaction time (h) | Yield (%) <sup>b</sup> | ee °           |
|-------|--------------------------------------|-----------------------|-------------------|------------------------|----------------|
| 1     | -                                    | Toluene               | 240               | 0                      | 0              |
| 2     | Ni(OAc) <sub>2</sub>                 | Toluene               | 240               | 0                      | 0              |
| 3     | RR-amine core + Ni(OAc) <sub>2</sub> | Toluene               | 72                | 100                    | -34 (S-isomer) |
| 4     | SS-amine core + Ni(OAc) <sub>2</sub> | Toluene               | 72                | 100                    | 26 (R-isomer)  |
| 5     | RR-DUT-136_imine                     | Toluene               | 240               | 0                      | 0              |
| 6     | RR-DUT-136_imine_Ni                  | Toluene               | 240               | 36                     | 6              |
| 7     | RR-DUT-136_amine_Ni                  | Toluene               | 240               | 67                     | 12             |
| 8     | RR-DUT-136_amide_Ni                  | Toluene               | 240               | 63                     | 16             |
| 9     | SS-DUT-136_amide_Ni                  | Toluene               | 240               | 61                     | 18             |
| 10    | RR-DUT-136_amide_Ni                  | Toluene               | 240               | 63                     | 18             |
| 11    | RR-DUT-136_amide_Ni                  | THF                   | 240               | 48                     | 6              |
| 12    | RR-DUT-136_amide_Ni                  | 1,4-dioxane           | 240               | 59                     | 8              |
| 13    | RR-DUT-136_amide_Ni                  | Methanol              | 240               | 100                    | 4              |
| 14    | RR-DUT-136_amide_Ni                  | Ethanol               | 240               | 100                    | 5              |
| 15    | RR-DUT-136_amide_Ni                  | Toluene/Ethanol (1%)  | 240               | 100                    | 16             |
| 16    | RR-DUT-136_amide_Ni                  | Toluene/Ethanol (5%)  | 240               | 65                     | 18             |
| 17    | RR-DUT-136_amide_Ni                  | Toluene/Ethanol (10%) | 240               | 83                     | 19             |
| 18    | RR-DUT-136_amide_Ni                  | Toluene/Ethanol (15%) | 240               | 98                     | 22             |
| 19    | RR-DUT-136_amide_Ni                  | Toluene/Ethanol (20%) | 240               | 100                    | 6              |

**Table 4.** Performance of various catalysts in the Ni-catalyzed Michael reaction.

aReaction conditions: 25 °C, 3 mol% catalyst based Ni content, 0.25 mmol trans-β-nitrostyrene, 2.5 mmol diethyl malonate,

3 mL toluene; <sup>b</sup> determined by GC; <sup>c</sup> ee value was determined by HPLC.

More importantly, the utilization of DUT-136\_amide\_Ni causes a reversal in enantioselectivity in comparison with the reaction catalyzed by respective homogeneous Ni-complex.

In the presence of an organometallic catalyst, obtained from (R,R)-1, 2-diphenylethylenediamine and Ni(OAc)<sub>2</sub>, the reaction proceeds to a complete conversion with 34% *ee* for *S*-enantiomer, while the *ee* value toward generating *R*-product was observed to be 26% with the Ni-complex derived from (*S*,*S*)-diamine core (**Entry 3-4** - **Table 4** and **Figures S25** - **S26**). Although, RR-DUT-136\_amine\_Ni was synthesized from (*R*,*R*)-1, 2-diphenylethylenediamine precursor, it promotes the preferable formation of *R*-enantiomer as product. To confirm this observation, an additional reaction using *SS*-DUT-136\_amide\_Ni as catalyst was investigated under optimized conditions. Interestingly, the enantioselectivity was observed with 18% *ee* for *R*-isomer (**Entry 9 - Table 4**).

Recently, Kobayashi and co-workers also reported a novel chial heterogeneous system, obtained by wet impregnation of chiral nickel–diamine complexes into MCM-41. These catalysts showed excellent performances (90% yield and 90% *ee*) for asymmetric addition of dimethyl malonate and *trans*- $\beta$ -nitrostyrene, however, the inverse enantioselectivity was not observed in all experiments.<sup>[35]</sup> A basic difference between chiral MCM-41 catalysts and *RR*-DUT-136 is the presence of bulky Zr<sub>6</sub>-clusters in framework, which could induce a reversed stereoselectivity.<sup>[28]</sup> Clearly, the steric effect of Zr<sub>6</sub>-nodes on stereoselectivity in asymmetric reactions is complex, and the issue still needs further investigations.

In the next step, the influence of various solvents was investigated to optimize the reaction conditions. It was found that the product formation significantly relies on polarity of the reaction medium. In particular, the conversion of *trans*- $\beta$ -nitrostyrene proceeds slowly in polar aprotic solvents, such as THF, 1,4-dioxane, only affording 48% and 59% yield with modest *ee* values of 6% and 8%, respectively. A conversion up to 100% was observed if methanol or ethanol was applied as solvent (**Entry 11-14 - Table 4**). Although the reaction yield could be significantly improved in polar protic solvents, unexpected low enantioselectivity (*ee* values below 5%) was detected by HPLC.

![](_page_19_Figure_3.jpeg)

**Figure 11.** The leaching test carried out at room temperature. Kinetic progress of the reaction with catalyst (black cycles) and after filtration of catalyst after 72 h (red diamond).

By adjusting the content of ethanol and toluene in reaction mixture, the polarity was systematically changed to evaluate the best conditions for catalysis. In fact, the yield of reaction gradually increases from 65% to 98% as the ethanol content was changed from 1% to 15%, but also *ee* value just increases up to 22% (Entry 18 - Table 4 and Figure S27). However, further increasing of ethanol content leads to an abrupt decrease in enantioselectivity, though the conversion of reaction still reaches excellent values.

Utilization of metalated materials as heterogeneous catalysts often leads to the leaching of metal species into the liquid phase. In this context, the leaching test were performed, carrying out the reaction under optimized conditions. The reaction progress was monitored by GC, and the DUT-136\_imine\_Ni catalyst was removed by centrifugation after the first 72 h of reaction. Approximately 42% yield was obtained after 72 h, and no further conversion of main product takes place after the solid catalyst was removed (**Figure 11**). ICP-OES measurements indicates, that the nickel content in the DUT-136 sample used in the reaction still maintained at 2.1 wt%, showing high stability as well as activity of DUT-136\_amide\_Ni after 72h reaction time.

![](_page_20_Figure_3.jpeg)

Figure 12. Catalyst recycling test.

The main advantage of heterogeneous catalyst is the possibility to reuse the catalyst several times. Therefore, the catalyst recycling experiment was conducted. The catalyst was separated from reaction mixture after every 240 h of reaction, washed, and activated at 100 °C for 8 hours and then applied again. The catalyst shows stable performance, with the reaction yield of 62% and 18% *ee* for *R*-isomer after three cycles (**Figure 12**). However, a sudden drop was observed in the 4<sup>th</sup> run, as the reaction only produced 49% yield, while this value has decreased to 33% with 10% *ee* in the next cycle (**Figure 12**). The nickel loading of the catalyst dropped to about 1.6 wt%, according to ICP-OES analysis, although its high crystallinity remained (**Figure S6**). This shows that the stability as well as activity of DUT-136\_amide\_Ni is maintained under these conditions only for three cycles.

## CONCLUSIONS

A new chiral metal-organic framework, DUT-136, was synthesized in a one-pot reaction, promoting the *in situ* formation of the chiral diimin linker and the MOF simultaneously. As linker precursors 4-formylbenzoic acid and (*R*,*R*)-1,2-diphenylethylenediamine (as an enantiopure core) were applied. Although, the crystal size of DUT-136 obtained was insufficient for single crystal X-ray analysis, its structure was solved and refined from the experimental PXRD data. In the structure, each hexanuclear Zr-cluster,  $[Zr_6O_4(OH)_4]^{12+}$ , is coordinated by six diimine linkers, connecting the clusters into a one-dimensional chain. The material is porous after desolvation, showing BET surface area of 795 m<sup>2</sup>/g.

Post-synthetic derivatization effectively converts DUT-136\_imine to amide-, and aminecontaining frameworks. The oxidized and reduced materials were obtained *via* amidation or amination under mild conditions, which allowed preservation the original structure. The resulting

materials, DUT-136\_imine, DUT-136\_amine, and DUT-136\_amide were applied in a series of asymmetric catalytic reactions: Friedel–Crafts alkylation reaction, Aldol addition reaction, Michael addition reaction and carbon-carbon cross coupling reaction.

The materials obtained post-synthetically, showed improved performance in asymmetric basecatalyzed reactions. In the presence of the *RR*-DUT-136\_amine as catalyst yields up to 55% and 9% *ee* for *syn*-isomers in aldol reaction could be achieved. A 28% yield with 31% *ee* was obtained in the Michael addition of trans- $\beta$ -nitrostyrene and cyclohexanone.

No enantioselectivity was found for these chiral materials, if used in a typical acid-catalyzed reaction, such as the Friedel Crafts alkylation, indicating the dominating role of Zr-clusters as highly catalytically active species, overacting the activity of the chiral linker. Thus, enantiopure active sites located at the nitrogen-containing functional groups provide a moderate enantioselectivity for enamine-catalyzed reactions.

The immobilization of Ni(II) active sites through a simple post-synthetic metalation resulted in catalysts highly active in asymmetric carbon-carbon cross coupling reactions of *trans*-β-nitrostyrene and diethyl malonate. Especially, the Ni-containing chiral -DUT-136\_amide material shows excellent performance, affording high conversions (up to 100 %). However, the chiral environment resulted again in modest enantiomeric excess values only. Interestingly, inversion of enantioselectivities as compared to the reactions catalyzed by the corresponding homogenous Ni-complex catalysts was observed. The materials could be easily reused at least three times without any significant degradation in catalytic activity.

In overall, the poor performance of DUT-136 could originate from limited reaction space in the pore due to the steric demand of phenyl groups on organic building block and new strategies to increase the pore size are needed for the possible performance improvement.

## **EXPERIMENTAL SECTION**

## Materials and instrumentation

All reagents and starting materials were purchased from Sigma-Aldrich, and were used as received without any further purification. Nitrogen physisorption measurements were carried out using a BELSORP-max (MicrotacBEL, Japan) apparatus at 77 K up to 1 bar and high purity nitrogen gas (99.999 %). The samples were heated in vacuum at 393 K for 24 h prior to adsorption experiments. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX 500 P.

All room temperature solid-state NMR experiments were carried out on a Bruker AVANCE III HD spectrometer operating at 14 T (<sup>1</sup>H frequency of 600.12 MHz), equipped with a Bruker 3.2 mm probe. <sup>13</sup>C CP MAS NMR spectra were recorded with <sup>1</sup>H excitation pulses of 2.5 µs, a contact time of 2 ms, a repetition delay of 4 s, a MAS spinning rate of 14 kHz and up to 2000 scans. <sup>1</sup>H MAS NMR spectra were measured using single-pulse excitation of 2.5 MHz, a MAS spinning rate of 22 kHz and up to 32 scans.

Scanning electron microscopy (SEM) images were recorded on a HITACHI SU 8020. The zirconium content in the samples was determined by Inductively Coupled Plasma Mass spectrometry (ICP-OES) using an Optima 7000 DV instrument. Gas chromatography (GC) analyses were performed using a Shimadzu GC 17 A equipped with a flame ionization detector (FID) and a BPX5 column (30 m length, 0.25 mm in inner diameter, and 0.25 mm film thickness). The following temperature program for GC analysis was used: the samples were heated from 313 to 321 K with a heating rate of 4 K/min; then from 321 K to 373 K with 15 K/min and held at 373 K for 4 min; after that continuously heated from 373 to 543 K with 30 K/min and held at 543 K for 5 min. Inlet and detector temperatures were set constant at 543 K. The *n*-dodecane was used as

an internal standard to calculate reaction yields. Mass spectra were collected using a Shimadzu GCMS-QP5000, and were compared with database of NIST library.

Enantiomeric excess was determined by HPLC (Elite LaChrom System from VWR/HITACHI using a UV L2400 detector) using a Lux Amylose-1 chiral column (0.5 μm, 75/25 v/v).

The Fourier-transform infrared (FT-IR) spectra were obtained on a Vertex 70 instrument, with samples dispersed on potassium bromide pellets. The measurements were carried out in 2 scans with a resolution of  $2 \text{ cm}^{-1}$ .

Powder X-ray diffraction (PXRD) patterns were collected on a STOE STADI P diffractometer equipped with  $\omega$ -2 $\theta$  goniometer, Cu-K $\alpha$ 1 radiation ( $\lambda$  = 1.54056 Å) and MYTHEN® (DECTRIS) detector. All routine measurements were performed at room temperature using spinning flatbed sample holders in transmission geometry within range  $2\theta = 3 - 30^{\circ}$  with increment of 0.015°. PXRD patterns of the solvent free powder of DUT-136 was measured in the glass capillary (d =0.3 mm) at room temperature in range  $2\theta = 3 - 70^{\circ}$ . Unit cell parameters and crystal symmetry were determined by ab initio indexing of PXRD patterns in X-Cell program, implemented in Materials Studio 5.0 program.<sup>[36]</sup> The unit cell parameters and PXRD profile were refined using Pawley fit option of the Reflex module. Further the  $Zr_6O_4(OH)_4$  cluster was inserted in the random position of the obtained unit cell containing symmetry elements of P3 space group. The structure was solved by simulating annealing method, implemented in Materials Studio. The starting model for the refinement was obtained using visualization module of Materials Studio by introducing of the organic ligand to the model, obtained from solution. The composition of building blocks was based on chemical formula of the material derived from elemental analysis, TGA and NMR data (Figure S12 and S14). The model was optimized using geometry optimization tool with implemented Universal Force Field (UFF). As a last step, the Rietveld refinement with energy

increment (1% UFF) was applied on the model. Because of low data / parameter ratio, rigid bodies were defined. Zirconium and oxygen atoms in the cluster were refined as separate structural units while phenyl rings and carboxylates moieties were defined as rigid units, which allowed to reduce the overall motion group to 18 units with 94 allowed degrees of freedom. The final Into each unit cell, one Zr6O8 cluster was combined with organic linkers and modulator molecules. Rietveld refinement plot is shown in **Figure S3**.

Experimental data from Rietveld refinement of DUT-136:  $Zr_6O_{32}N_6C_{102}H_{84}$ , M = 2453.07 g mol<sup>-1</sup>, trigonal *P*3 (No 143), *a* =19.7780 Å, *c* = 12.5744 Å, *V* = 4259.7 Å3, *Z* = 1, *d*<sub>calc</sub> = 0.956 g cm<sup>-3</sup>, zero point shift -0.00118, profile function Thompson-Cox-Hastings, U = 0.23279, W = -0.00227, V = 0.02966, X = 0.48528, Y = 0.01153, asymmetry correction function Berar-Baldinozzi, P1 = 0.29958, *P2* = -2.21946, *P3* = -0.88470, *P4* = 4.38592, Final *Rwp* = 6.54 %, *Rp* = 4.74%.

## Material synthesis

**DUT-136**: In a representative procedure, a mixture of  $ZrCl_4$  (0.92 g, 3.95 mmol) and 4formylbenzoic acid (0.54 g, 3.60 mmol, 0.91 equiv.) was dissolved in 100 mL of DMF and 15 mL of CH<sub>3</sub>COOH (262.5 mmol, 66.5 equiv.). A solution of (1*R*,2*R*)-1,2-diphenylethylenediamine or (1*S*,2*S*)-1,2-diphenylethylenediamine (0.38 g, 1.80 mmol, 0.45 equiv.) in 50 mL of DMF was added dropwise to the ZrCl<sub>4</sub> solution. The resulting solution was then sonicated for 10 min before distributing into 30 different vials (10 mL in volume). These vials were then heated at 80 °C for 168 hours. The solid product was consequently collected by decanting the mother liquor and washed with DMF (3 × 100 mL). The DMF solvent was exchanged with acetone (5 × 100 mL) at room temperature. The resulting product was then activated at 100 °C for 12 h under vacuum, yielding white solid powders of DUT-136.

Yield: 0.91 g (71% based on (1R,2R)-1,2-diphenylethylenediamine).

Crystal data for DUT-136 ( $Zr_6C_{102}O_{32}N_6H_{84}$ ): M = 2453.07 g/mol, trigonal *P*3, *a* = 19.7780 Å, *c* = 12.5744 Å, *V* = 4259.74 Å<sup>3</sup>.

Elemental analysis for Zr<sub>6</sub>O<sub>6</sub>(imine-L)<sub>3</sub>.6(CH3COO)·6.8DMF: calcd: C 50.4%, H 4.72%, N 6.15%; found: C 49.1%, H 4.83%, N 6.21%.

<sup>1</sup>H NMR spectrum after MOF digestion: (500 MHz, DMSO-d6/DCl):  $\delta$ (ppm): 10.0 (s, 2H, proton in aldehyde groups of 4-formylbenzoic acid), 7.99 (m, 8H, benzyl groups of 4-formylbenzoic acid), 7.57 (m, 2H, benzyl groups of 1,2-diphenylethylenediamine), 5.21(s, 2H, CH groups of 1,2-diphenylethylenediamine).

**DUT-136\_amine**: 0.04 g of DUT-136 (0.013 mmol) was slowly stirred in 1.5 mL of methanol for 5 minutes at room temperature before NaBH<sub>4</sub> (3 x 0.0025 g, 0.2 mmol, 15.3 equiv.) was added. After 24 h, the liquid was removed, and the product was washed with 10 mL of water, 5 times with 5 mL of acetone, and desolvated at 100 °C for 12 h under vacuum.

Elemental analysis for Zr<sub>6</sub>O<sub>6</sub>(amine-L)<sub>3</sub>(OH)<sub>5.86</sub>·0.14CH<sub>3</sub>COO: calcd: C 48.6% H 4.05% N 3.8%; found: C 47.2% H 3.98% N 3.75%.

<sup>1</sup>H NMR spectrum after MOF digestion: (500 MHz, DMSO-d6/DCl): δ(ppm): 8.22 (m, 4H, benzyl group of 4-formylbenzoic acid), 7.76 (m, 4H, benzyl groups of 4-formylbenzoic acid), 7.98 (m, 5H, benzyl group of 1,2-diphenylethylenediamine), 7.56 (m, 5H, benzyl groups of 1,2-diphenylethylenediamine), 5.45 (s, 2H, CH groups of 1,2-diphenylethylenediamine).

**DUT-136\_amide**: 0.04 g of DUT-136 (0.013 mmol) was dispersed in a mixture of 1,4-dioxane (1 mL) and 2-methyl-2-butene (0.62 mL, 5.9 mmol, 450 equiv). 100  $\mu$ L of aqueous sodium chlorite solution (3.3 M, 0.33 mmol, 25 equiv) and 35  $\mu$ L of acetic acid (0.6 mmol, 47 equiv.) were added slowly to the mixture without stirring. The reaction was carried out in dark for 24 h. The resulting

powder was then washed with water (2 times, 5 mL) acetone (5 imes,10 mL) and desolvated at 100 °C for 12 h under vacuum, producing white solid of DUT-136 amide.

Elemental analysis for Zr<sub>6</sub>O<sub>6</sub>(amide-L)<sub>3</sub>(OH)<sub>5.86</sub>·0.14CH<sub>3</sub>COO: calcd: C 47.8%, H 3.45%, N 3.7%; found: C 47.2%, H 4.01%, N 3.63%.

<sup>1</sup>H NMR spectrum after MOF digestion: (500 MHz, DMSO-d6/DCl): δ(ppm): 8.12 (m, 8H, benzyl groups of 4-formylbenzoic acid), 7.95(m, 10H, benzyl groups of 1,2-diphenylethylenediamine), 5.40 (s, 2H, CH groups of 1,2-diphenylethylenediamine).

**DUT-136**\_**Ni**: 0.05 g of DUT-136 or its derivatives were dispersed in 5 mL of ethanol containing 0.21 g of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O. for 24 hours at room temperature. The resulting solid samples were collected by centrifuging, washed with ethanol (5 times,10 mL) and desolvated at 100 °C for 12 h under vacuum. The nickel contents were further confirmed by ICP-OES analysis.

## Catalytic studies

## Asymmetric Friedel Craft alkylation

In a typical experiment, a mixture of a trans- $\beta$ -nitrostyrene (0.0375 g, 0.25 mmol), indole (0.0585 g, 0.5 mmol) and *n*-hexadecane (0.05 mL) as an internal standard were placed into a 10 mL Schlenk tube containing toluene (4 mL) and the catalyst. The reaction was performed at 50 °C for 7 days. The conversion was monitored by sampling periodically the reaction mixture. The organic constituents were then diluted with ethyl acetate (1mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and analyzed by GC and HPLC.

GC temperature programme used: Initial heating from 40 to 48 °C with a heating rate of 4 °C/min; then from 48 °C to 100 °C with 15 °C/min and held at 100 °C for 4 min; after that continuously heated from 100 to 270 °C with 30 °C/min and held at 270 °C for 10 min. Inlet and

detector temperatures were set constant at 270 °C. The *n*-hexadecane was used as an internal standard to calculate reaction conversion. The retention time of the product was 20.27 min.

Enantiomeric excess was analyzed by HPLC Elite LaChrom System with a UV L2400 detector and a Lux Amylose-1 chiral column. The mobile phase was a mixture of hexane and isopropanol (85:15, v:v) with flow rate of 0.5 mL/min. The product was detected by UV detector operated at  $\lambda$ = 250 nm. The retention times of two enantiomers were 25.161 and 27.510 min, respectively.

## **Asymmetric Aldol addition reaction**

In a typical experiment, a mixture of 4-nitrobenzaldehyde (0.0375 g, 0.25 mmol) and *n*-dodecane (0.05 mL, 0.22 mmol) was placed into a 10-mL Schlenk tube containing 1.00 mL of dimethyl sulfoxide (DMSO) and catalysts. After that, 20 equiv of cyclohexanone (0.50 mL, 5 mmol) and 0.2 equiv of benzoic acid were added. The resulting mixture was stirred at 298 K for 7 days. The pure product, 2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one as an orange solid, was isolated (in 95% yield) by column chromatography (silica gel, ethyl acetate/isohexane = 1:3). This product was used as standard compound to record a calibration curve for the determination of the yield by GC.

For kinetic studies, reaction progress was monitored by GC/MS as followed: Aliquots (0.02 mL) were removed from the reaction mixture, diluted with ethyl acetate (1.00 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting samples were heated from 40 to 48 °C with a heating rate of 4 °C/min; then from 48 °C to 100 °C with 15 °C/min and held at 100 °C for 4 min; after that continuously heated from 100 to 270 °C with 30 °C/min and held at 270 °C for 5 min. Inlet and detector temperatures were set constant at 270 °C. The yield was identified by comparing the area of product peak (t = 17.398 min) with the area of *n*-dodecane peak (t = 10.555 min).

In the recycling test, the catalyst was separated by centrifugation, washed intensively with ethanol to remove any undesired compounds, and dried in vacuum at 120 °C for 24 h, and reused for a new catalytic run. To ensure the heterogeneity of the catalyst, the solid catalyst was removed after 72 h of the reaction. The remaining reaction solution was stirred for further 5 h. Reaction progress was monitored by GC as previously described.

Enantiomeric excess of 2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one in product mixture was determined by HPLC (Elite LaChrom System from VWR/HITACHI using a UV L2400 detector) using a Lux Amylose-1 chiral column (0.5  $\mu$ m, 75/25 (v/v) hexane/isopropanol, 0.5 mL/min,  $\lambda = 225$  nm), retention times:  $t_{((S)-2-((S)-hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one)} = 19.0432$  min (major),  $t_{((R)-2-((R)-hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one)} = 17.223$  min,  $t_{((S)-2-((R)-hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one)} = 21.103$ min.

## Asymmetric Michael addition reaction

In a standard preparation, trans- $\beta$ -nitrostyrene (0.0375 g, 0.25 mmol), *n*-hexadecane as internal standard (0.05 mL, 0.17 mmol), and catalysts (15 mol%) were placed into a 10-mL Schlenk tube containing 3 mL of a solvent mixture of isopropanol and ethanol (1:1 v:v). 20 equiv of cyclohexanone (0.50 mL, 5 mmol) was added to the reaction Schlenk tube. The resulting mixture was consequently stirred for 3 min before heating up to 50 °C. Reaction progress was monitored by GC as followed: Aliquots (0.20 mL) were removed from the reaction mixture, diluted with isopropanol (1.00 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The samples were analysed by GC and HPLC.

For the recycling test, the catalyst was collected by centrifugation, washed intensively with DMF and ethanol to remove any undesired compounds, activated in vacuum at 120 °C for 24 h, and reused for a new catalytic run. To ensure the heterogeneity of the catalyst, the MOF catalyst was

removed after 72 h of the reaction. The remaining reaction solution was stirred for further 5 h. Reaction progress, if any, was monitored by GC as previously described.

For determination of reaction yield, the samples were injected into GC device at 40 °C and heated up to 48 °C in 2 minutes. The temperature was continuously increased to 100 °C with 15 °C/min heating rate and maintained at this point for 4 min before elevating up to 270 °C with a rate of 30 °C/min and held at 270 °C for 4 min. The yields were calculated by comparing the area of product peak ( $t_{major} = 16.242$  min and  $t_{minor} = 16.334$  min) with the area of *n*-hexadecane peak (t= 13.935 min). The product, 2-(2-nitro-1-phenylethyl) cyclohexanone, was isolated by column chromatography (silica gel, ethyl acetate/hexane = 1:4) as a white solid.

Enantiomeric excesses of 2-(2-nitro-1-phenylethyl)cyclohexanone in product mixtures were determined by HPLC (ELITE LACHROM System from VWR/HITACHI using a UV L2400 detector) using a Lux Amylose I chiral column (0.5  $\mu$ m, 98/2 (v/v) hexane/isopropanol, 1 mL/min,  $\lambda$ = 225 nm, retention times: t<sub>(S)-2((R)-2-nitro-1-phenylethyl)</sub>cyclohexan-1-one = 48.437 min (major), t<sub>(R)-2((S)-2-nitro-1-phenylethyl)</sub>cyclohexan-1-one = 40.887 min, and t<sub>(R)-2((R)-2-nitro-1-phenylethyl)</sub>cyclohexan-1-one = 40.887 min, and t<sub>(R)-2((R)-2-nitro-1-phenylethyl)</sub>cyclohexan-1-one = 33.123 min.

## Nickel-catalyzed asymmetric Michael addition

In a representative preparation, a mixture of trans-β-nitrostyrene (0.0375 g, 0.25 mmol), *n*-hexadecane as internal standard (0.05 mL, 0.17 mmol), and DUT-136\_Ni (20 mol% based on Ni content) was placed into a 10 mL Schlenk tube containing 3 mL of toluene. The resulting mixture was stirred for 3 min before 0.4 mL of diethylmalonate (2.625 mmol, 10.5 equiv.) was added. Reaction progress was monitored by removing the aliquots from the reaction mixture. Organic components were diluted with ethyl acetate (1 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and analyzed using GC and HPLC.

A GC temperature program: the samples were heated from 40 to 48 °C with a heating rate of 4 °C/min; then from 48 °C to 100 °C with 15 °C/min and held at 100 °C for 4 mins; after that continuously heated from 100 to 270 °C with 30 °C/min and held at 270 °C for 5 mins. The product signal was observed at 15.897 min.

For determination of enantiomeric purity, HPLC Elite LaChrom System with a UV L2400 detector and a Lux Amylose-1 chiral column was employed. A mixture of hexane and isopropanol (80:20, v:v) was employed as mobile phase to analyze the samples. With a flow rate of 0.5, the retention time of product detected by UV detector operated at  $\lambda$ = 254 nm, was 23.747 min for *R*-enantiomer and 67.677 min for *S*-enantiomer, respectively.

## ASSOCIATED CONTENT

**Supporting Information**. The detailed procedure for synthesis of DUT-136 and its derivatives; PXRD patterns; adsorption isotherms, NMR data for DUT-136 as well as for the products of the reactions; thermogravimetric analysis data; HPLC chromatograms; These materials are available free of charge *via* the Internet at http://

## AUTHOR INFORMATION

## **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Notes

The authors declare no competing financial interest.

## **ABBREVIATIONS**

DUT, Dresden University of Technology; NIST, National Institute of Standards and Technology;

MAS NMR, magic angle spinning nuclear magnetic resonance spectroscopy; SEM, scanning

electron microscopy.

## REFERENCES

- H. L. Nguyen, T. T. Vu, D. Le, T. L. H. Doan, V. Q. Nguyen, N. T. S. Phan, ACS Catal., 2017, 7, 338-342, DOI: 10.1021/acscatal.6b02642.
- [2] S. Yuan, L. Zou, J.-S. Qin, J. Li, L. Huang, L. Feng, X. Wang, M. Bosch, A. Alsalme, T. Cagin, H.-C. Zhou, *Nat. Commun.*, 2017, 8, 15356 DOI: 10.1038/ncomms15356.
- [3] H. L. Nguyen, F. Gándara, H. Furukawa, T. L. H. Doan, K. E. Cordova, O. M. Yaghi, *J. Am. Chem. Soc.*, **2016**, 138, 4330-4333, DOI: 10.1021/jacs.6b01233.
- [4] S. Yuan, P. Zhang, L. Zhang, A. T. Garcia-Esparza, D. Sokaras, J.-S. Qin, L. Feng, G. S. Day, W. Chen, H. F. Drake, P. Elumalai, S. T. Madrahimov, D. Sun, H.-C. Zhou, *J. Am. Chem. Soc.*, **2018**, 140, 10814-10819, DOI: 10.1021/jacs.8b04886.
- [5] M. S. Lohse, T. Bein, Adv. Funct. Mater., 2018, 28, 1705553, DOI: 10.1002/adfm.201705553.
- [6] J. L. Segura, M. J. Mancheño, F. Zamora, *Chem. Soc. Rev.*, **2016**, 45, 5635-5671, DOI: 10.1039/C5CS00878F.
- [7] X. Feng, X. Ding, D. Jiang, *Chem. Soc. Rev.*, 2012, 41, 6010-6022, DOI: 10.1039/C2CS35157A.
- [8] T. Hasell, A. I. Cooper, *Nat. Rev. Mater.*, **2016**, 1, 16053, DOI: 10.1038/natrevmats.2016.53.
- [9] A. G. Slater, A. I. Cooper, *Science*, **2015**, 348, aaa8075, DOI: 10.1126/science.aaa8075.
- [10] Y. Jin, Y. Zhu, W. Zhang, *CrystEngComm*, **2013**, 15, 1484-1499, DOI: 10.1039/C2CE26394G.
- [11] M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.*, **2012**, 112, 1196-1231, DOI: 10.1021/cr2003147.
- [12] X. Han, Q. Xia, J. Huang, Y. Liu, C. Tan, Y. Cui, J. Am. Chem. Soc., 2017, 139, 8693-8697, DOI: 10.1021/jacs.7b04008.
- [13] Z. Li, Y. Liu, Q. Xia, Y. Cui, Chem. Commun., 2017, 53, 12313-12316, DOI: 10.1039/C7CC06979K.
- [14] H.-S. Xu, S.-Y. Ding, W.-K. An, H. Wu, W. Wang, J. Am. Chem. Soc., 2016, 138, 11489-11492, DOI: 10.1021/jacs.6b07516.
- [15] J. Zhang, X. Han, X. Wu, Y. Liu, Y. Cui, J. Am. Chem. Soc., 2017, 139, 8277-8285, DOI: 10.1021/jacs.7b03352.

- [16] F. Song, C. Wang, J. M. Falkowski, L. Ma, W. Lin, J. Am. Chem. Soc., 2010, 132, 15390-15398, DOI: 10.1021/ja1069773.
- [17] C. Zhu, Q. Xia, X. Chen, Y. Liu, X. Du, Y. Cui, ACS Catal., 2016, 6, 7590-7596, DOI: 10.1021/acscatal.6b02359.
- [18] Q. Xia, Z. Li, C. Tan, Y. Liu, W. Gong, Y. Cui, J. Am. Chem. Soc., 2017, 139, 8259-8266, DOI: 10.1021/jacs.7b03113.
- [19] C. Wang, M. Zheng, W. Lin, J. Phys. Chem. Lett., 2011, 2, 1701-1709, DOI: 10.1021/jz200492d.
- [20] J. Jiao, C. Tan, Z. Li, Y. Liu, X. Han, Y. Cui, J Am Chem Soc, 2018, 140, 2251-2259, DOI: 10.1021/jacs.7b11679.
- [21] J. Li, Y. Ren, C. Yue, Y. Fan, C. Qi, H. Jiang, ACS Appl. Mater. Interfaces, 2018, 10, 36047-36057, DOI: 10.1021/acsami.8b14118.
- [22] P. Deria, J. E. Mondloch, O. Karagiaridi, W. Bury, J. T. Hupp, O. K. Farha, *Chem. Soc. Rev.*, 2014, 43, 5896-5912, DOI: 10.1039/C4CS00067F.
- [23] C. Tan, X. Han, Z. Li, Y. Liu, Y. Cui, J. Am. Chem. Soc., 2018, 140, 16229-16236, DOI: 10.1021/jacs.8b09606.
- [24] S.-L. You, Q. Cai, M. Zeng, Chem. Soc. Rev., 2009, 38, 2190-2201, DOI: 10.1039/B817310A.
- [25] Y.-X. Jia, S.-F. Zhu, Y. Yang, Q.-L. Zhou, J. Org. Chem., 2006, 71, 75-80, DOI: 10.1021/jo0516537.
- [26] G. Bartoli, M. Bosco, A. Carlone, F. Pesciaioli, L. Sambri, P. Melchiorre, *Org. Lett.*, 2007, 9, 1403-1405, DOI: 10.1021/ol070309o.
- [27] V. Bon, I. Senkovska, I. A. Baburin, S. Kaskel, *Cryst. Growth Des*, **2013**, 13, 1231-1237, DOI: 10.1021/cg301691d.
- [28] K. D. Nguyen, C. Kutzscher, S. Ehrling, I. Senkovska, V. Bon, M. de Oliveira, T. Gutmann, G. Buntkowsky, S. Kaskel, J. Catal., 2019, 377, 41-50, DOI: https://doi.org/10.1016/j.jcat.2019.07.003.
- [29] K. D. Nguyen, C. Kutzscher, F. Drache, I. Senkovska, S. Kaskel, *Inorg. Chem.*, 2018, 57, 1483-1489, DOI: 10.1021/acs.inorgchem.7b02854.
- [30] C. Kutzscher, G. Nickerl, I. Senkovska, V. Bon, S. Kaskel, *Chem. Mater.*, **2016**, 28, 2573-2580, DOI: 10.1021/acs.chemmater.5b04575.
- [31] W. Notz, F. Tanaka, C. F. Barbas, Acc. Chem. Res., 2004, 37, 580-591, DOI: 10.1021/ar0300468.
- [32] K. Zheng, X. Liu, X. Feng, Chem. Rev., 2018, 118, 7586-7656 DOI: 10.1021/acs.chemrev.7b00692.
- [33] D. A. Evans, D. Seidel, J. Am. Chem. Soc., **2005**, 127, 9958-9959, DOI: 10.1021/ja052935r.
- [34] D. A. Evans, S. Mito, D. Seidel, J. Am. Chem. Soc., 2007, 129, 11583-11592, DOI: 10.1021/ja0735913.
- [35] H. Ishitani, K. Kanai, W.-J. Yoo, T. Yoshida, S. Kobayashi, *Angew. Chem. Int. Ed.*, 2019, 58, 13313-13317, DOI: 10.1002/anie.201906349.
- [36] Materials Studio. Accelrys Software Inc.: San Diego 2009.

# Graphical abstract

![](_page_34_Figure_2.jpeg)

## Highlights

- In situ formation of diimin linker and MOF gives DUT-136 based on Zr-clusters
- Post-synthetic reactions converts DUT-136 to amide-, and amine-containing frameworks
- Catalytic activity of DUT-136 series was studied in a wide range of organic transformations
- DUT-136 and its derivatives were utilized as support to immobilize nickel(II)
- Ni(II) containing catalysts are active in asymmetric carbon-carbon cross coupling reactions
- Ni containing catalysts show enantioselectivities inversed to homogenous Ni-complex

## **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

![](_page_36_Picture_4.jpeg)