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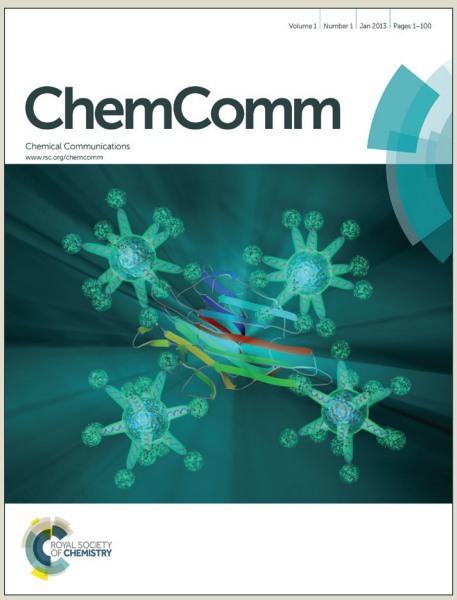

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DOI: 10.1039/C5CC05985B

Journal Name

COMMUNICATION

Azobenzene-Containing Metal-Organic Framework as an Efficient Heterogeneous Catalyst for Direct Amidation of Benzoic Acids: Synthesis of Bioactive Compounds

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hanh T. H. Nguyen,[a] Linh T. M. Hoang,[a] Long H. Ngo,[b] Ha L. Nguyen,[b] Chung K. Nguyen,[a] Binh T. Nguyen,[b] Quang T. Ton,[c] Hong K. D. Nguyen,[d] Kyle E. Cordova,[b] and Thanh Truong[a,*]

An azobenzene-containing zirconium metal-organic framework was demonstrated to be an effective heterogeneous catalyst for the direct amidation of benzoic acids in tetrahydrofuran at 70 °C. This finding was applied to the synthesis of several important, representative bioactive compounds.

The formation of amide bonds has attracted much interest due to its pervasiveness in biologically active compounds, industrially-relevant polymers, and pharmaceutical products.[1-3] Methodologies based on reactions of amines with alcohols, aldehydes, nitriles, and aryl halides/CO have been reported, often with poor atom economy and toxic/corrosive by-products.[1,4,5] However, the direct condensation of a carboxylic acid with an amine remains the most desirable pathway as the only side product is water. Due to the high activation barrier of this route, protocols have been developed to employ homogeneous biocatalysts, Lewis acid catalysts based on boron reagents, or metal complexes to successfully form amides from carboxylic acids.[4-6] The success of these homogeneous catalysts has led a push to develop heterogeneous catalytic systems, including metal-based catalysts,[7] Lewis acidic zeolites,[8] solid-supported boronic acids,[9] and immobilized enzymes.[10] However, there remain significant drawbacks as a result of harsh conditions employed during the reaction, unavoidable by-products, complex synthesis of catalysts, or limitations of heterogeneous systems with respect to substrate scope.[4-10] Therefore, the direct amidation of carboxylic acids, especially with less active substrates such as benzoic acids, catalyzed by more efficient heterogeneous catalysts remains an underdeveloped field.

Metal-organic frameworks (MOFs) are a class of crystalline, porous materials whose architectures can be designed and characterized at the atomic level.[11] MOFs are constructed by linking inorganic secondary building units (SBUs) and organic linkers, in which both components can be tailored to suit particular applications.[11] As a result of the modular approach to MOF synthesis, these materials have emerged as a class of promising heterogeneous catalysts for organic transformations.[12] It is worth noting that low stability towards moisture as well as various harsh chemical environments often limits MOFs in catalysis.[11,12] However, MOFs based on $Zr_6O_4(OH)_4(CO_2)_{12}$ clusters are advantageous for such applications as the resulting structures are typically moisture- and chemically-stable and integrate Lewis acidic zirconium sites within the backbone of the architecture.[13,14]

By taking advantage of the chemically stable SBUs as well as modifying the linker, we were able to change the stability as well as the reactivity of a MOF toward cross coupling reactions.[15] Herein, we report the synthesis and characterization of a zirconium-based MOF, termed Zr-AzoBDC (where AzoBDC = azobenzene-4,4′-dicarboxylate), and its application as a heterogeneous catalyst for direct amidation reactions. The design strategy was based on the hypothesis that a zirconium-based MOF with an azobenzene backbone would provide large enough pore space for the substrates to react, better affinity of reagents, and potentially promote direct coupling through a cooperative effect between the Lewis acidic SBUs and azo functionalities.[14] Indeed, Zr-AzoBDC demonstrated superior catalytic activity for amide formation under significantly milder conditions when compared to other zirconium-based MOFs, common Lewis and Brønsted acids, and other catalytically-active MOFs.

Zr-AzoBDC was solvothermally synthesized with slight modifications to previous reports.[16] Specifically, H_2-AzoBDC and zirconium oxychloride octahydrate were reacted in *N,N*-dimethylformamide (DMF) with acetic acid added as a modulator (Figure 1a).[16] The resulting solution was heated at

[a]*Faculty of Chemical Engineering, HCMC University of Technology, VNU-HCM, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam. Email: tvthanh@hcmut.edu.vn*
[b]*Center for Molecular and NanoArchitecture, VNU-HCM, Ho Chi Minh City, Vietnam.*
[c]*Department of Chemistry, HCMC University of Science, VNU-HCM, 05 Nguyen Van Cu, District 5, Ho Chi Minh City, Vietnam.*
[d]*School of Chemical Engineering, C4-306, Hanoi University of Science and Technology, Hanoi, Vietnam*
†Electronic Supplementary Information (ESI) available: Synthesis and characterization of Zr-AzoBDC, additional catalytic data, and recycling studies. See DOI: 10.1039/b000000x/

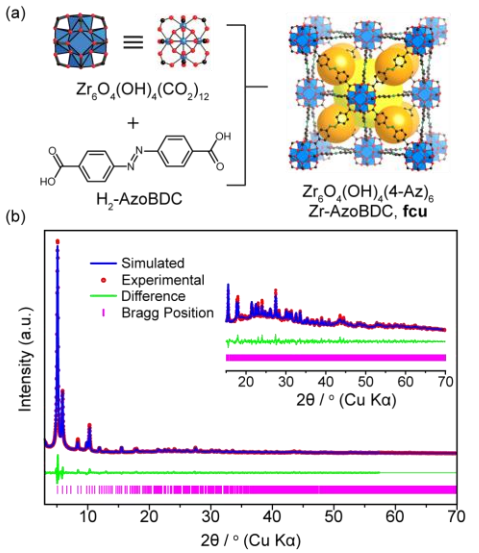


Fig. 1. (a) Building units used to generate Zr-AzoBDC with a **fcu** net. Zr-AzoBDC (right) results from $Zr_6O_4(OH)_4(CO_2)_{12}$ secondary building units (left) joined by azobenzene-4,4′-dicarboxylic acid (H_2-AzoBDC) linkers (left). Orange and yellow spheres represent the tetrahedral and octahedral pore cavities, respectively. Atom colors: Zr, blue polyhedra; C, black; N, green; O, red. H atoms are omitted for clarity. (b) PXRD analysis showing the experimental pattern (red circles), simulated pattern (blue), and the difference plot (green). The Bragg positions are shown in pink. Inset: Satisfactory agreement extends to diffraction at higher angles.

85 °C for three days, yielding an orange microcrystalline solid, which was subsequently activated and characterized (see ESI).[†] Scanning electron microscopy analysis revealed homogeneity with respect to the shape of the microcrystalline particles, which provides support to a singular phase synthesized (see Fig. S1, ESI).[†]

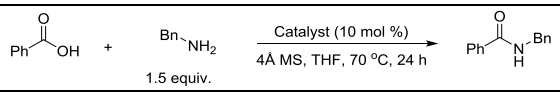
To elucidate the structural features of Zr-AzoBDC, powder X-ray diffraction (PXRD) analysis on an activated sample, in conjunction with structural modelling, was carried out (see ESI).[†] Specifically, from the unit cell parameters of the indexed PXRD pattern, a structural model was generated by linking the primarily observed cuboctahedral-shaped, 12-connected (12-c) $Zr_6O_4(OH)_4(CO_2)_{12}$ SBU with the linear AzoBDC linkers into a 12,2-c **fcu** net (see ESI).[†] A full profile pattern refinement was performed against the experimental PXRD pattern leading to refined unit cell parameters (*Fm*-3, a = 29.3994 Å) and satisfactory residual values (R_p = 8.48%, R_{wp} = 11.24%) (Figure 1b, see Tables S1 and S2, ESI).[†] The three-dimensional structure of Zr-AzoBDC is described as face-centered cubic composed of both tetrahedral and octahedral cavities with internal pore diameters of *ca*. 14.8 Å and 16.8 Å, respectively, which are in turn connected by *ca*. 9.2 Å triangular windows. It is noted that these diameters are in line with those measured for the isoreticular (having the same topology) MOFs, UiO-66, -67, -68 as well as MOF-806.[13] The potential solvent accessible void, as calculated by *PLATON*,[17] is 74%. This was supported by N_2 isotherm measurements at 77 K, in which Zr-AzoBDC exhibited significant uptake in the low-pressure region, resulting in calculated Brunauer-Emmett-Teller and Langmuir surface areas of 3200 and 3500 $m^2\ g^{-1}$, respectively (see Fig. S4, ESI).[†]

After structural characterization, the catalytic activity of Zr-AzoBDC for amidation reactions was investigated using a model coupling reaction of benzylamine (Bn-NH_2) with benzoic acid. Specifically, optimization of the catalytic activity with respect to solvent, temperature, and catalyst loading was undertaken (see Table S3, ESI).[†] During this process, molecular sieves were added to the reaction with the realized expectation that lower reaction temperatures would be obtained. Optimal results were obtained in tetrahydrofuran (THF) at 70 °C, with 10 mol% Zr-AzoBDC catalyst loading, when 82% gas chromatography (GC) yield was remarkably achieved (see Table S3, entry 1, ESI).[†] In particular, the role of solvent was found to play an important role in reaction efficiency. Notably, in 1,4-dioxane, acetonitrile, and toluene, the model coupling reaction was inefficient with <20% yield (see Table S3, entries 2-4, ESI).[†] It was observed that by decreasing Zr-AzoBDC catalyst loading, the reaction efficiency significantly dropped (see Table S3, entries 1,5,6, ESI).[†] Catalytic reaction taken place at 60 °C afforded only 50% yield while reactions at increased temperatures (80 °C) produced similar results as the optimal reaction conditions (see Table S3, entries 1,7,8, ESI).[†] Additionally, formation of an ammonium carboxylate salt, which retarded the nucleophilic attack by the amine nitrogen atom are likely to result in poor yields when benzoic acid was used in excess (see Table S3, entries 1,10, ESI). As expected, reactions without molecular sieve offered < 2% and 42 % at 70 °C and 110 °C, respectively (see Table S3, entries 11, 12, ESI).[†] Previous reports for the amidation of benzoic acid suffered either forcing conditions, low reaction yields, or stoichiometric amounts of waste by-product derived from coupling reagents.[18-21] Moreover, the lowest temperature reported for the amidation of benzoic acid, using metal- or borane-based heterogeneous catalysts, is 110 °C.[7,9] Clearly, Zr-AzoBDC considerably improves upon all of these drawbacks. As expected, only trace amount of desired product was observed when reactions were carried out without added catalyst (see Table S3, entry 9, ESI).[†]

The suitability of Zr-AzoBDC as an effective heterogeneous catalyst was evaluated by comparative studies on the catalytic activity of two isoreticular Zr-MOFs, UiO-66 and UiO-67, which are built from the same Zr SBU and have the same underlying topology as Zr-AzoBDC.[13,16] As is shown in Table 1, UiO-66 exhibited no appreciable catalytic (entry 2). This observation is attributed to the triangular pore windows (*ca*. 6 Å) and octahedral pore cavity (*ca*. 11 Å) being too small to accommodate the substrates within the UiO-66 structure.[13,14] This points to the likelihood that catalytic amide formation does not occur solely on the surface of Zr-AzoBDC, but rather within the pores. When using UiO-67 as a catalyst, the yield noticeably increases (41% yield), as the adverse pore size effect is minimized (entry 3). However, the activity of UiO-67 remains much lower than Zr-AzoBDC. Interestingly, Zr-AzoBDC also exhibited significantly higher activity than previously used amidation catalysts, $ZrCl_4$ and $ZrOCl_2$ (entries 4,5).[18] Other acid catalysts and catalytically active MOFs were also evaluated as shown in Table 1 (entries 6-15).[22]

In order to highlight the role of the azo functionality in promoting the catalytic activity of Zr-AzoBDC, an amidation

Table 1. Comparative study of catalysts[a]

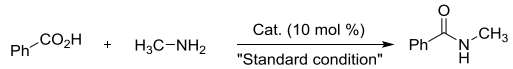


Entry	Type	Catalyst	GC Yield (%)
1	**Zr-MOFs**	Zr-AzoBDC	82 (76)
2		UiO-66	trace
3		UiO-67	41 (33)
4	**Zr salts**	$ZrCl_4$	31
5		$ZrOCl_2$	28
6	**Other acids**	H_2-AzoBDC	6
7		Triflic acid	4
8		TFA	7
9		pTSA	12
10		ZSM-5	8
11		HY Zeolite	<2
12	**Other MOFs**	Co-ZIF-67	<2
13		$Ni_2(BDC)_2(DABCO)$	<2
14		Zn-ZIF-8	<2
15		$Cu_2(BDC)_2(DABCO)$	<2

[a]Volume of solvent, 2 mL; 0.2 mmol scale. Bn-NH_2, benzylamine; MS, molecular sieves; TFA, trifluoroacetic acid; *p*TSA, *p*-toluenesulfonic acid; ZIF, zeolitic imidazolate framework; BDC, benzene-1,4-dicarboxylate; DABCO, 1,4-diazabicyclo[2.2.2]octane. Numbers in parenthesis indicate isolated yields.

control reaction was performed, in which the resulting product is sufficiently small in molecular size (Scheme 1).

As is shown, the varying pore sizes of UiO-66 and UiO-67 did not significantly affect the reactivity. Thus, the high yield obtained with Zr-AzoBDC confirms the positive impact of the azo group on the catalyst activity. This finding was further supported by reactions using AzoBDC linker and $ZrOCl_2$ metal cluster.



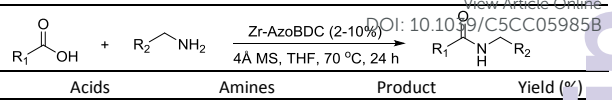
Catalyst	UiO-66	UiO-67	Zr-AzoBDC	H_2-AzoBDC	$ZrOCl_2$
Yield	17	28	66	<2	32

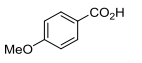
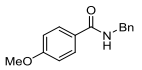
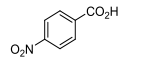
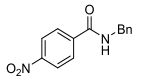
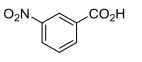
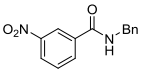
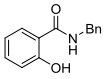
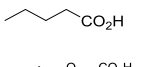
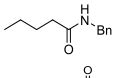
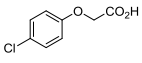
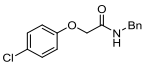
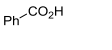
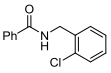
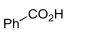
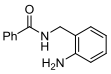
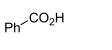
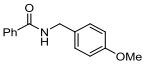
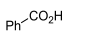
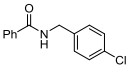
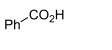
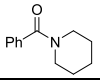
Scheme 1. Reactions of benzoic acid with methylamine.

Control experiments, using the model amidation reaction with the corresponding optimized conditions, were subsequently performed to ensure that the catalytic activity did not originate from any leaching of Zr^{4+} ions from Zr-AzoBDC into the reaction mixture. As expected, there was no conversion detected in the catalyst-free reaction mixture after ZrAzoBDC was removed (see ESI).† In addition, inductively coupled plasma mass spectrometry revealed the concentration of Zr^{4+} to be <10 ppm in the filtrate (see ESI).† Encouraged by these results, recycling studies were undertaken. At the end of each reaction period (24 h), Zr-AzoBDC was recovered from the reaction mixture, washed with solvent, and re-used. This process was performed 5 times (see Fig. S13, ESI).† PXRD analysis of Zr-AzoBDC revealed that the crystallinity of this material was retained (see Figs. S14 and S15, ESI).† Clearly, the exceptional catalytic activity of Zr-AzoBDC was maintained without significant degradation.

To assess the substrate scope of the Zr-AzoBDC heterogeneous catalyst, we applied the optimized conditions to a variety of carboxylic acid and amine coupling derivatives. The isolated product yields are presented in Table 2.

Table 2. Reaction scope with respect to coupling partners[a]

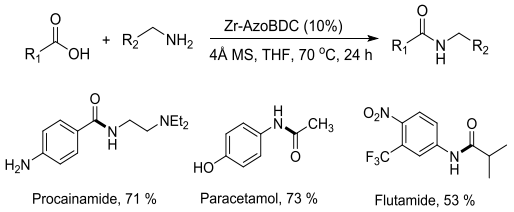


Entry	Acids	Amines	Product	Yield (%)
1				78
2				37
3				39
4				55
5[b]				97
6[c]				81
7				75
8				80
9		4-MeO-Bn-NH_2		68
10		4-Cl−Bn-NH_2		71
11				48

[a]Reaction conditions: carboxylic acid derivatives (1 mmol), amine derivatives (1.1 mmol), catalyst (10 mol%), and activated 4 Å molecular sieves (0.5 g) in dry solvent at 70 °C in a sealed tube under Ar atmosphere. [b]catalyst (5 mol %). [c]catalyst (2 mol %).

Reasonable yields were achieved for acid derivatives with both activating and deactivating substituents at different substituted positions (entries 1-4). The amidation of more reactive acids (i.e. aliphatic carboxylic acids) achieved excellent yields even at 2-5 mol% catalyst loading (entries 5, 6). Additionally, cross-coupling reactions of benzoic acid with substituted benzylamine derivatives were also investigated. As is shown, desired products were also obtained in relatively high yields (entries 7-10). Finally, the optimized catalytic conditions were extended to the direct amidation of benzoic acid with piperidine, a secondary amine source. The desired product was realized in 48% yield (entry 11), thus, effectively demonstrating the exceptional catalytic activity of Zr-AzoBDC over a wide range of substrates.

The use of homogeneous catalysts in pharmaceutical synthesis often represents a major problem regarding the removal of contaminated metals.[23] To further expand on the potential of Zr-AzoBDC to be used in practical applications, we utilized this heterogeneous catalyst in the synthesis of pharmaceutically relevant amides possessing bioactivity (Scheme 2). Specifically, Procainamide, an antiarrhythmic agent, was efficiently synthesized from the respective carboxylic acid. Previously, either the protection of the aromatic amine group or a 2-step synthetic process, including



Scheme 2. Synthesis of bioactive amide-containing compounds by the heterogeneous Zr-AzoBDC catalyst.

amidation of nitroarenes followed by hydrogenation, was required.[24] Similarly, Paracetamol was obtained directly from acetic acid and 4-aminophenol in 73% yield through utilization of Zr-AzoBDC. Finally, a reasonable yield was achieved in the synthesis of Flutamide, an oral and non-steroidal antiandrogen drug mainly used for prostate cancer treatment. It is noted that these drugs were previously synthesized by reacting amines with acid anhydride or acyl halides.[25] One can argue that increased efficiency in such reactions makes the chemical processes more "green" by reducing the amount of steps in the synthetic sequences and the resulting purification.

In conclusion, we have reported the synthesis of Zr-AzoBDC constructed from an azobenzene-4,4'-dicarboxylate (4-Az) linker and $Zr_6O_4(OH)_4(CO_2)_{12}$ cluster. This structure exhibited exceptional catalytic activity toward direct amidation of benzoic acids under mild conditions (10 mol% catalyst loading, THF, 70 °C). The heterogeneous nature of Zr-AzoBDC enabled it to be recycled and re-applied to new reactions (5 times) without degradation in catalytic activity. Furthermore, the substrate scope of Zr-AzoBDC was demonstrated to be widely applicable to various substituted carboxylic acid and amine derivatives for the synthesis of bioactive amide compounds.

Vietnam National University – Ho Chi Minh City (VNU-HCM) is acknowledged for financial support via grant No. B2015-20-04. Catalyst synthesis and characterization were supported by B2011-50-01TĐ. We thank Dr. H. Furukawa, Prof. H. T. Nguyen, Mr. T. T. Vu, Ms. A. M. Osborn, and Mr. H. Q. Pham for their valuable discussions and assistance. Prof. O. M. Yaghi is gratefully acknowledged for supporting MANAR.

Notes and references

1 V. R. Pattabiraman and J. W. Bode, *Nature*, 2011, **480**, 471-479.
2 E. Valeur and M. Bradley, *Chem. Soc. Rev.*, 2009, **38**, 606-631.
3 A. K. Ghose, V. N. Viswanadhan, and J. J. Wendoloski, *J. Comb. Chem.*, 1999, **1**, 55-68.
4 (a) C. L. Allen and J. M. J. Williams, *Chem. Soc. Rev.*, 2011, **40**, 3405-3415. (b) S. Roy, S. Roy, and G. W. Gribble, *Tetrahedron*, 2012, **68**, 9867-9923.
5 H. Charville, D. Jackson, G. Hodges, and A. Whiting, *Chem. Commun.*, 2010, **46**, 1813-1823.
6 A. Goswami and S. G. Van Lanen, *Mol. BioSyst.*, 2015, **11**, 338-353.
7 (a) M. Hosseini-Sarvari and H. Sharghi, *J. Org. Chem.*, 2006, **71**, 6652-6654. (b) H. Thakuria, B. M. Borah, and G. Das, *J. Mol. Catal. A: Chem.*, 2007, **274**, 1-10. (c) S. M. Coman, M. Florea, V. I. Parvulescu, V. David, A. Medvedovici, D. De Vos, P. A. Jacobs, G. Poncelet, and P. Grange, *J. Catal.*, 2007, **249**, 359-369. (d) L. Ma'mani, M. Sheykhan, A. Heydari, M. Faraji, and Y. Yamini, *Appl. Catal., A*, 2010, **377**, 64-69.
8 (a) N. Narender, P. Srinivasu, S. J. Kulkarni, and K. V. Raghavan, *Green Chem.*, 2000, **2**, 104-105. (b) J. W. Comerford, J. H. Clark, D. J. Macquarrie, and S. W. Breeden, *Chem. Commun.*, 2009, 2562-2564. (c) S. Ghosh, A. Bhaumik, J. Mondal, A. Mallik, S. Sengupta, and C. Mukhopadhyay, *Green Chem.*, 2012, **14**, 3220-3229. (d) Nagarajan, P. Ran, P. Shanmugavelan, M. Sathishkumar, A. Ponnuswamy, K. S. Nahm, and G. G. Kumar, *New J. Chem.*, 2012, **36**, 1312-1319.
9 (a) R. Latta, G. Springsteen, and B. H. Wang, *Synthesis*, 2001, 1611. (b) T. Maki, K. Ishihara, and H. Yamamoto, *Org. Lett.*, 2005, 5043-5046. (c) T. Maki, K. Ishihara, and H. Yamamoto, *Tetrahedron*, 2007, **63**, 8645-8657.
10 (a) T. Maugard, M. Remaud-Simeon, D. Petre, and P. Monsan, *Tetrahedron*, 1997, **53**, 5185-5194. (b) F. Le Joubioux, O. Achour, N. Bridiau, M. Graber, and T. Maugard, *J. Mol. Catal. B: Enzym.*, 201 **70**, 108-113.
11 (a) H. Furukawa, K. E. Cordova, M. O'Keeffe, and O. M. Yaghi, *Science*, 2013, **341**, 1230444. (b) Y. Chen, Z. Li, Q. Liu, Y. Shen, X. Wu, D. Xu, X. Ma, L. Wang, Q.-H. Chen, Z. Zhang, and S. Xiang, *Cryst. Growth Des.*, 2015, **15**, 3847-3852. (c) Y. Shen, Z. Li, L. Wang, Y. Y Q. Liu, X. Ma, Q. Chen, Z. Zhang, and S. Xiang, *J. Mater. Chem.* 2015, **3**, 593-599. (d) Z. Zhang, Z.-Z. Yao, S. Xiang, and B. Chen *Energy Environ. Sci.*, 2014, **7**, 2868-2899.
12 (a) A. Corma, H. García, and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606-4655. (b) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, and Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011-6061. (c) Z.-Y Gu, J. Park, A. Raiff, Z. Wei, H.-C. Zhou, *ChemCatChem* 2014, **6**, 67-75. (d) I. Lu Corma, and F. X. Llabrés i. Xamena, *Catal. Sci. Technol.* 2014, **4**, 1829-1836.
13 (a) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, Bordiga, and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 1385 13851. (b) H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **13** 4369-4381.
14 (a) L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M. H. Nilson Jakobsen, K. P. Lillerud, and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700-1718. (b) F. Vermoortele, R. Ameloot, A. Vimont, C. Serre, and D. E. De Vos, *Chem. Commun.*, 2011, **47**, 1521-1523. (c) Vermoortele, M. Vandichel, B.Van de Voorde, R. Ameloot, M Waroquier, V. Van Speybroeck, and D. E. De Vos, *Angew. Chem. Int. Ed.*, 2012, **51**, 4887-4890. (d) F. Vermoortele, B. Bueken, G. Le Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock, and D. E. De Vos, *Am. Chem. Soc.*, 2013, **135**, 11465-11468.
15 (a) H. T. N. Le, T. V. Tran, N. T. S. Phan, and T. Truong, *Catal. Sci. Technol.*, 2015, **5**, 851-859. (b) N. T. T. Tran, Q. H. Tran, and T. Truong. *J. Catal.,* 2014, **320**, 9-15. (c) G. H. Dang, T. T. Dang, D. T. Le T. Truong, and N. T. S. Phan, *J. Catal.*, 2014, **319**, 258-264.
16 (a) A. Schaate, S. Dühnen, G. Platz, S. Lilienthal, A. M. Schneider, and P. Behrens, *Eur. J. Inorg. Chem.*, 2012, 790-796. (b) Q. Yang, V. Guillerm, F. Ragon, A. D. Wiersum, P. L. Llewellyn, C. Zhong, T. Devic C. Serre, and G. Martin, *Chem. Commun.*, 2012, **48**, 9831-9833. (c) Rogan, H. Chevreau, T. Devic, C. Serre, and P. Horcajada, *Chem. –Eur. J.*, 2015, **21**, 7135-7143. (d) A. Schaate, P. Roy, A. Godt, J. Lippke, Waltz, M. Wiebcke, and P. Behrens, *Chem. –Eur. J.*, 2011, **17**, 6643 6651.
17 A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148-155.
18 C. L. Allen, A. R. Chhatwal, and J. M. J. Williams, *Chem. Commun* 2012, **48**, 666-668.
19 L. J. Gooßen, D. M. Ohlmann, and P. P. Lange, *Synthesis*, 2009, 16 164.
20 R. M. Lanigan, P. Starkov, and T. D. Sheppard, *J. Org. Chem.*, 20 **78**, 4512-4523.
21 H. Lundberg, F. Tinnis, and H. Adolfsson, *Synlett.*, 2012, **23**, 22 2204.
22 (a) J. Gascon, A. Corma, F. Kapteijn, and F. X. Llabrés i Xamena, *ACS Catal.*, 2014, **4**, 361-378. (b) A. Dhakshinamoorthy, M. Opanasenk J. Cejka, and H. Garcia, *Catal. Sci. Technol.*, 2013, **3**, 2509-2540. (c) Valvekens, F. Vermoortele, and D. E. De Vos, *Catal. Sci. Technol* 2013, **3**, 1435-1445.
23 C. E. Garrett and K. Prasad, *Adv. Synth. Catal.*, 2004, **346**, 889-900.
24 S. M. Kelly and B. H. Lipshutz, *Org. Lett.*, 2014,**16**, 98-101.
25 (a) A. S. Travis, The Chemistry of Anilines. Wiley, 2007. (b) P Stabile and A. P. Dicks *J. Chem. Educ.*, 2003, **80**, 1439.