Chan–Lam-Type C–N Cross-Coupling Reactions under Base- and Ligand-Free Cu^I-Zeolite Catalysis

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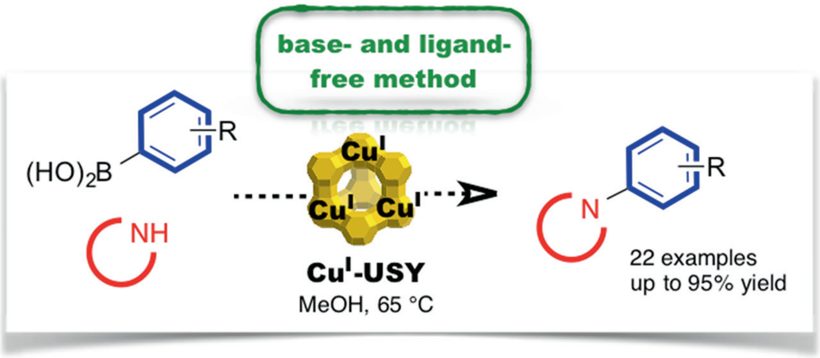

Dedicated to the memory of Prof. J. F. Normant, a brilliant scientist and a wonderful person, and in recognition of his outstanding achievements in organometallic chemistry.

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Abstract Various representative copper(I)-exchanged zeolites were investigated for their catalytic potential in Chan–Lam cross-coupling reactions. Cu^I-USY appeared as the best catalyst and proved to efficiently promote C–N cross-coupling processes under attractive, simple, and practical conditions, namely refluxing in methanol under air and without any base.

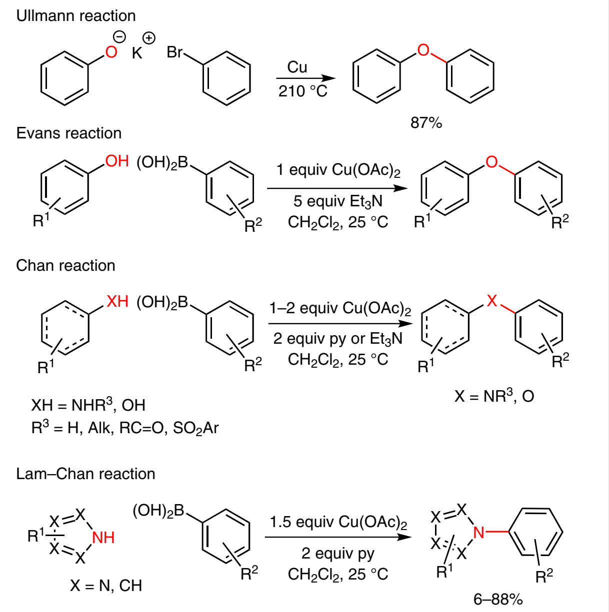
Key words copper, zeolites, heterogeneous catalysis, cross-coupling, Chan–Lam reaction, C–N bond formation

Copper was among the very first metals used to promote organic transformations. This metal indeed contributed to the initiation of the long history of metal-mediated formation of carbon–carbon bonds with the Glaser homocoupling reaction reported as early as the mid-19th century,[1] the Meerwein diazo decarboxylative coupling,[2] and later on the Cadiot–Chodkiewicz cross-coupling in the mid-1950s.[3] These works and others pioneered the tremendous expansion of organocopper chemistry in the 1960s and 1970s. Among them, it is worth mentioning the unique contribution of Prof. J. F. Normant, to whom this paper is dedicated, with, among others, the Normant carbocupration reaction[4] and its developments.[5]

Copper was also involved in the very first coupling reactions producing carbon–heteroatom bonds, the so-called Ullmann reaction,[6] which have again initiated numerous variations.[7]

Due to harsh reaction conditions, the synthetic scope of these Ullmann-type reactions was however restricted to a limited range of substrates (Scheme 1). Nevertheless, at the turn of the 21st century, new combinations of reagents and copper/ligand systems unleashed the power of such coupling reactions in organic synthesis and medicinal chemistry.[7] Among them, the mild conditions concomitantly proposed by Chan,[8] Lam,[9] and Evans[10] for, respectively, C–N and C–O bond formation significantly improved the possibility by allowing the coupling of arylboronic acids with various *N*- or *O*-nucleophiles (Scheme 1). The *N*- or *O*-nucleophiles could be as various phenols, amines, anilines, amides, imides, ureas, carbamates, and sulfonamides, while stannanes, siloxanes, and organobismuth derivatives can replace boronic acids.[11] These reactions are usually induced by a stoichiometric amount of copper(II) in the presence of excess base (Scheme 1). Catalysis could nevertheless be achieved with various copper species, especially copper(II) complexes,[12] if the reaction is performed in air.

Although such homogeneous catalysis provides huge potential, product and catalyst recovery remains a problem for practical and industrial applications. Heterogenization of catalysts has thus become an important issue, especially for the production of fine chemicals, due to the benefits of this catalysis mode (i.e., easier isolation of products/catalyst, recyclability of the catalyst, etc.) and its consequences in industry.[13] Surprisingly, and despite its interest, only a handful of examples of heterogeneously catalyzed Chan–Lam–Evans reactions have so far been reported. Fluorapa-



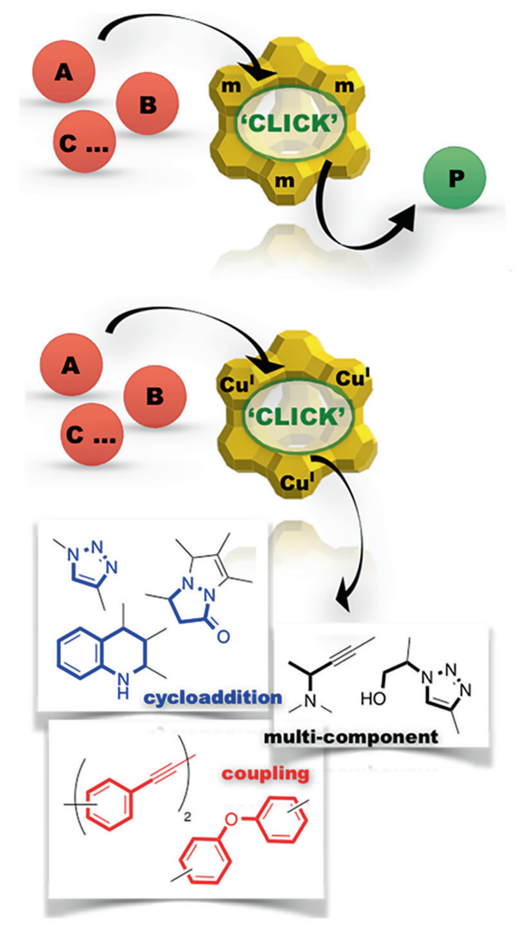
Scheme 1 From the pioneering Ullmann reaction to the Chan–Lam–Evans versions involving arylboronic acids in place of aryl halides

tite in which calcium ions were exchanged for copper(II) ions has been applied to the coupling of imidazole and a few alkylamines with phenylboronic acid.[14] Alternatively, cuprous oxide particles have also been used, either as such[15] or supported on natural natrolite.[16]

In connection with the heterogenization issue and with the 'greening' of organic transformations as a goal,[17,18] we are currently developing the *zeo-click* concept, in which reagents should react through zeolites, metalated or not, benefitting from zeolite size and shape selectivity under conditions as mild as possible (Scheme 2, top).[18] We have already shown that copper(I) is stabilized in zeolites, their framework acting as a polydentate ligand toward the metal ion, and that the resulting Cu^{I}-zeolites are excellent heterogeneous catalysts, easy to handle, recyclable, and shape selective, for a variety of organic transformations, usually without the need for an additional ligand (Scheme 2, bottom).[19]

To further extend this toolbox, we recently reported a new Ullmann-type synthesis of diaryl ethers with Cu^{I}-USY zeolite as a ligand-free and recyclable catalyst.[19k] We now demonstrate here that the Chan–Lam version could also be catalyzed with Cu^{I}-zeolites under very mild conditions without added base.

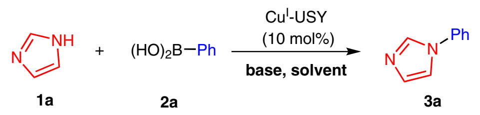
To set up the reaction conditions, we examined the archetypal coupling of imidazole (**1a**) and phenylboronic acid (**2a**), in the presence or absence of base and using Cu^{I}-USY zeolite as the catalyst in various solvents (Table 1). In the solvent commonly used for Chan–Lam–Evans reactions, i.e. dichloromethane, very low conversion occurred in the presence of either pyridine or triethylamine, the bases commonly used in these couplings.[8–11] The yields were accordingly very low, equivalent to those obtained without base (entries 1 and 2 vs 3). Since we aimed to develop a base-free version, we next screened other solvents in the presence of only Cu^{I}-USY as the catalytic system (entries 4–7). Sometimes used with copper(II) complexes, coordinating solvents did not improve these results, except for DMF which allowed for 67% yield to be achieved, even in the absence of base (entry 4). More interestingly, protic solvents drastically changed the reaction course (entries 5–7). Indeed, water, ethanol, and methanol gave good to excellent yields of the expected coupling product in the absence of base. Methanol provided the best results, (entry 7 vs 5 and 6), and neither deborylation nor homocoupling products could be detected, despite their common observation in Chan–Lam–Evans reactions. The ability of methanol to allow this coupling reaction in the presence of Cu^{I}-USY zeolite is quite surprising since the original report mentioned that no reaction occurs in methanol.[9] Remarkably, the addition of a base (pyridine



Scheme 2 The *zeo-click* concept (top) and some reactions achieved with Cu^{I}-zeolites (bottom)[19]

or triethylamine) did not enhance the efficiency of the coupling reaction, pyridine even altering negatively the reaction progress (entries 8 and 9 vs 7).

Table 1 Screening of Conditions for the Cu^I-USY-Catalyzed Coupling of Phenylboronic Acid and Imidazole[a]



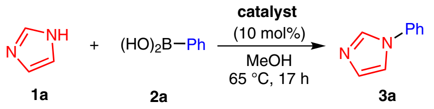
Entry	Solvent	Base	Temp (°C)	Time (h)	Yield (%)[b]
1	CH_2Cl_2	pyridine	45	48	<5
2	CH_2Cl_2	Et_3N	45	48	<5
3	CH_2Cl_2	–	45	48	<5
4	DMF	–	65	17	67
5	H_2O	–	65	17	56
6	EtOH	–	65	17	80
7	MeOH	–	65	17	86
8	MeOH	pyridine	65	17	74
9	MeOH	Et_3N	65	17	85
10	MeOH	–	20	48	<5
11[c]	MeOH	–	65	17	88
12[d]	MeOH	–	65	17	68
13[e]	MeOH	–	65	17	86
14[f]	MeOH	–	65	17	33

[a] Reaction run with phenylboronic acid (1.0 equiv with a 0.17 M concentration) and imidazole (1.5 equiv) under air, unless otherwise stated.
[b] Yields of isolated pure products.
[c] Reaction run with imidazole (2.0 equiv).
[d] Reaction run with imidazole (1.0 equiv) and phenylboronic acid (1.5 equiv).
[e] Reaction run with a 0.5 M concentration of phenylboronic acid.
[f] Reaction run with a 1 M concentration of phenylboronic acid.

In this reaction, heating proved necessary as almost no conversion occurred at room temperature (entry 7 vs 10). In terms of **1a**/**2a** ratio, a slight excess of nucleophile relative to boronic acid provided better results (entries 7 and 11 vs 12). Regarding reagent concentration, the boronic acid concentration proved important with an optimum around 0.2–0.5 M (entries 8 and 12 vs 13), probably due to equilibration with the corresponding boroxine.[20]

Under the so-obtained conditions, the influence of zeolite pore size and shape was examined in the same model coupling reaction (Table 2). Various typical and readily available zeolites were doped with copper(I) ions upon heating in the presence of CuCl,[18,19i] characterized, and then engaged as a catalyst in the Chan–Lam reaction. All of them were able to promote the cross-coupling reaction, but Cu^I-USY was clearly the best catalyst (entry 1 vs 2–4). In agreement with our earlier results,[19] USY zeolite which offers the largest pores (7–11 Å) with a cage shape provided the best results in terms of conversion, yield, and reaction time.

Table 2 Screening of Catalysts for the Coupling of Phenylboronic Acid and Imidazole[a]



Entry	Catalyst	Yield (%)[b]
1	Cu^I-USY	86
2	Cu^I-ZSM5	43[c]
3	Cu^I-MOR	47[c]
4	Cu^I-Beta	54[c]
5	CuCl	15[c]
6	NH_4-USY	0[d]
7	none	0[d]

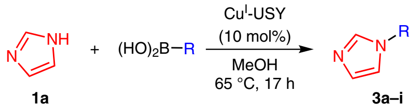
[a] Reaction run with phenylboronic acid (1.0 equiv with a 0.17 M concentration) and imidazole (1.5 equiv) under air, unless otherwise stated.
[b] Yields of isolated pure products.
[c] Incomplete conversion.
[d] No conversion.

Control experiments with native commercial USY zeolite or without any catalyst clearly evidenced the role of copper in this reaction (entries 6 and 7). Interestingly, the use of copper chloride itself only led to marginal reaction, revealing the catalytic ability of copper embedded within the (right) zeolite framework (entry 5 vs 1).

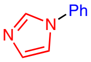
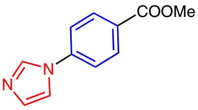
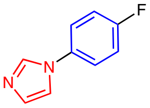
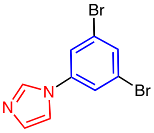
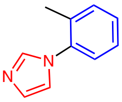
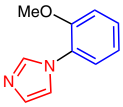
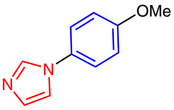
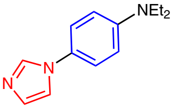
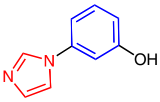
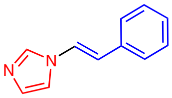
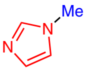
This copper zeolite catalyst can be easily recovered and reused after a simple filtration-washing sequence. With the same model reaction, two cycles could be performed without change in catalyst efficacy (86% and 85% yields for respectively run 1 and 2) but the third run induced a drop in yield, with only 60% yield of isolated product being obtained. Although the lowering of the catalyst amount inherent to its recovery at each cycle could be responsible for such decrease, some leaching might also explain these results. However, a Sheldon test performed under the same conditions, has shown a significantly reduced conversion after 24 hours at 65 °C upon removal of the Cu^I-USY catalyst. Overall, these results suggested a preference for a 'catch and release' mechanism for this heterogeneous catalyst over leaching of catalytically active species in solution.

With these reaction conditions in hand, we then explored the scope of this base-free Cu^I-USY catalyzed Chan–Lam alternative (Tables 3 and 4). In a first series of experiments, the effect of the boronic acid nature was examined (Table 3). Phenylboronic acids carrying electron-deficient groups did not significantly affect the reaction efficacy (entries 2 and 3 vs 1). However, those carrying electron-rich substituents led to contrasted results. Although *o*-tolylboronic acid gave an improved and excellent yield of the corresponding product **3e** (entry 5 vs 1), its *o*-methoxy analogue led to a net decrease in yield (entry 5 vs 6), neverthe-

Table 3 Cu^I-USY-Catalyzed Coupling of Imidazole with Various Boronic Acids[a]



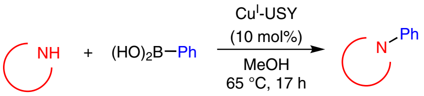
1a **3a–i**

Entry	Product		Yield (%)[b]
1		**3a**	86
2		**3b**	84
3		**3c**	83
4		**3d**	73
5		**3e**	95
6		**3f**	80
7		**3g**	71
8		**3h**	28
9		**3i**	72
10		–	–[c]
11		–	–[c]

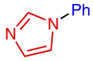
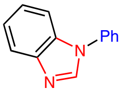
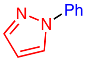
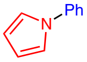
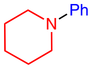
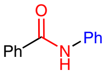
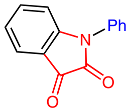
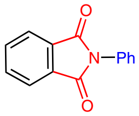
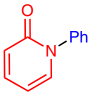
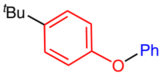
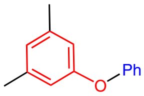
[a] Reaction run with boronic acid (1.0 equiv with a 0.17 M concentration) and imidazole (1.5 equiv) under air, unless otherwise stated.
[b] Yields of isolated pure products.
[c] Complete conversion but no traces of expected product detected.

less these are better than the results obtained by Chan, Lam, and co-workers.[8,9] Surprisingly, the corresponding *p*-methoxy analogue led to another decrease in yield (entry 7 vs 6), while the *p*-diethylamino derivative could only afford

Table 4 Cu^I-USY-Catalyzed Coupling of Phenylboronic Acid with Various Nucleophiles[a]



2a **3a,j–n**

Entry	Product	Number	Yield (%)[b]
1		**3a**	86
2		–	–[c]
3		**3j**	55
4		–	–[c]
5		–	–[c]
6		**3k**	55
7		**3l**	55
8		**3m**	56
9		**3n**	37[d]
10		–	–[c]
11		–	–[c]

[a] Reaction run with boronic acid (1.0 equiv with a 0.17 M concentration) and imidazole (1.5 equiv) under air, unless otherwise stated.
[b] Yields of isolated pure products.
[c] Partial conversion but no traces of expected product detected.
[d] No traces of *O*-arylated product detected.

the expected product **3h** in poor yield (entry 8 vs 7 vs 1). Interestingly, *m*-hydroxyphenylboronic acid reacted as expected, giving 3-(1*H*-imidazol-1-yl)phenol (**3i**) in good yield, without further coupling as a phenol (entry 9). This result suggests an attractive and possibly useful selectivity in *N*- vs *O*-coupling reactions (*vide infra*).

In sharp contrast to arylboronic acids, alkyl- or vinylboronic acids did not furnish the expected coupling products (entries 10 and 11). Their ease of cyclization to boroxine may be one of the reasons.

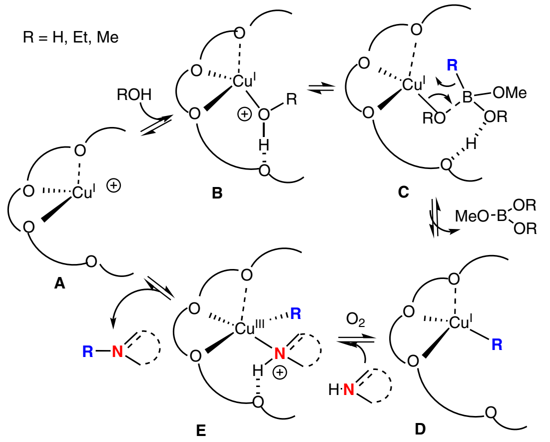
In another series of experiments, the effect of variations in the nucleophile nature was investigated (Table 4). *N*-Heterocycles proved more or less reactive depending on their structure, but often less reactive than imidazole under the present conditions. Usually less reactive than imidazole itself in Chan–Lam coupling, benzimidazole unexpectedly did not produce any coupling under the present conditions (entry 2 vs 1). In contrast, pyrazole could be arylated in good yield, although less than imidazole (entry 3 vs 1).

Although known for its low or lack of reactivity, pyrrole was nevertheless engaged under the present conditions, aiming that a possible confinement effect due to the zeolite framework could force them to react.[21] Pyrrole unfortunately did not lead to the expected coupling products, even in the presence of base (entry 4). Similarly, simple amines such as piperidine also did not form the corresponding *N*-arylated product (entry 5). This lack of Chan–Lam-type couplings could be linked to the basicity of the nucleophile, in reminiscence of Cundy's observations.[22]

Indeed, amides, including cyclic amides such as isatin (entries 6 and 7), and imides (entry 8) readily reacted and gave the expected *N*-arylated products **3k–m** in good yields. However, pyridin-2(1*H*)-one only gave a modest yield of the expected coupling product **3n**. Interestingly, only the *N*-arylated product was formed (entry 9), revealing again the same *N*- vs *O*-selectivity in such coupling reactions.

To get more evidence of this selectivity, we engaged various phenols under the same conditions. In sharp contrast to *N*-nucleophiles, these *O*-nucleophiles did not react at all under the present conditions (entries 10 and 11). Therefore, these conditions are exclusively selective for *N*-nucleophiles, offering numerous opportunities in organic synthesis.

In these Chan–Lam type reactions, the zeolite framework can act as a large ligand, stabilizing copper species. It can also favor proton transfer at various stages (Scheme 3). In this regard, such large oxygenated ligands could help to understand the special role of protic solvents (Scheme 3, intermediates **A** and **B**). Furthermore, the fact that boronic acids are only efficiently converted in protic solvents, particularly methanol, is reminiscent of Jutand's study on the key role that water and related ligands could play in the Suzuki–Miyaura coupling reaction, especially at the transmetalation step.[23] From this background, transmetalation could indeed occur through intermediate **C**. On the other hand, the large oxygenated zeolite framework ligand could play a role similar to the dedicated ligand designed by Stahl and Ribas for the mechanism of the Ullmann coupling reaction.[24] Upon air oxidation and in the presence of a nucleophile, a copper(III) intermediate **E** could be formed, stabilized by the oxygenated zeolite framework and by H-bonding with the incoming nucleophile. Reductive elimination would then lead to the coupling product, while regenerating the zeolite framework coordinated to copper(I).



Scheme 3 Mechanistic proposal for the Cu^{I}-zeolite catalyzed Chan–Lam cross-coupling reaction

In conclusion, we have reported a new ligand-free and base-free Cu-catalyzed protocol for the cross-coupling of arylboronic acids with a variety of *N*-nucleophiles. Among four representative and readily available copper(I)-exchanged zeolites, Cu^{I}-USY proved to be the best catalyst by efficiently promoting the cross-coupling process under attractive, simple, and practical conditions, i.e. refluxing in methanol under air and without any base. This catalyst could be easily recovered and recycled at least three times.

Further works are in progress in our groups to expand the scope of this heterogeneous Chan–Lam cross-coupling version, to decipher its mechanism and to apply it to organic (total) synthesis.

All starting materials were commercially available and were used as received. The reactions were monitored by TLC carried out on silica plates (silica gel 60 F_{254}, Merck) using UV light for visualization. Column chromatography was performed on silica gel 60 (0.040–0.063 mm, Merck) using mixtures of EtOAc and cyclohexane. Evaporation of solvents were conducted under reduced pressure at temperatures less than 30 °C unless otherwise noted. Melting points were measured with a Stuart SMP30 apparatus in open capillary tubes and are uncorrected. IR spectra were obtained from the 'Service Commun de Spectroscopie Infrarouge et Raman' of the Plateforme Technique, Institut de Chimie de Toulouse. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz, respectively relative to residual solvent as an internal standard ($CDCl_3$: δ = 7.26 for ^{1}H and δ = 77.0 for ^{13}C). Carbon multiplicities were determined by DEPT135 experiments. Electrospray (ESI), Atmospheric-Pressure Chemical Ionization (APCI) and Desorption Chemical Ionization (DCI) low/high-resolution mass spectra were obtained from the 'Service Commun de Spectroscopie de Masse' of the Plateforme Technique, Institut de Chimie de Toulouse.

Cu$^{\mathrm{I}}$-USY Catalyzed Cross-Coupling Reaction of Arylboronic Acids with *N*-Nucleophiles; General Procedure

In a 10-mL round-bottom flask were successively added Cu$^{\mathrm{I}}$-USY (ca. 15 mg, 10 mol% of copper species), the nucleophile (0.75 mmol, 1.5 equiv), the boronic acid (0.5 mmol, 1.0 equiv), and MeOH (3.0 mL). The mixture was refluxed under air for 17 h and analyzed by LCMS. After cooling to r.t., the solvent was removed and the desired compound was isolated by purification on a short pad of silica gel (cyclohexane/EtOAc mixture).

1-Phenyl-1*H*-imidazole (3a)

[CAS Reg. No. 7164-98-9]

Pale yellow oil; yield: 62 mg (86%); R_f = 0.30 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3107, 3059, 1600, 1509, 1304, 1058, 760 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.85 (br s, 1 H), 7.51–7.45 (m, 2 H), 7.41–7.34 (m, 3 H), 7.28 (t, J = 1.2 Hz, 1 H), 7.21 (br s, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 137.1, 135.3, 130.2, 129.7, 127.2, 121.2, 118.0.

MS (DCI, +): m/z (%) = 145 (100) [M + H]$^+$.

Methyl 4-(1*H*-Imidazol-1-yl)benzoate (3b)

[CAS Reg. No. 101184-08-1]

White solid; yield: 85 mg (84%); mp 127 °C; R_f = 0.20 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3111, 3005, 2957, 2845, 1712, 1609, 1526, 1266, 1062, 851 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.19–8.15 (m, 2 H), 8.01 (br s, 1 H), 7.51–7.46 (m, 2 H), 7.36 (br t, J = 1.5 Hz, 1 H), 7.26 (br s, 1 H), 3.95 (s, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 165.8, 140.5, 135.2, 131.4, 130.9, 128.8, 120.4, 117.6, 52.2.

MS (DCI, +): m/z (%) = 203 (100) [M + H]$^+$.

1-(4-Fluorophenyl)-1*H*-imidazole (3c)

[CAS Reg. No. 21441-24-7]

Pale yellow oil; yield: 67 mg (83%); R_f = 0.25 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3113, 3072, 1518, 1231, 1058, 837 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.75 (br s, 1 H), 7.32–7.27 (m, 2 H), 7.19–7.17 (m, 2 H), 7.00–6.95 (m, 2 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 161.5 (d, J = 246.7 Hz), 135.6, 133.5 (d, J = 2.2 Hz), 130.3, 123.4 (d, J = 8.2 Hz), 118.5, 116.6 (d, J = 22.7 Hz).

MS (DCI, +): m/z (%) = 163 (100) [M + H]$^+$.

1-(3,5-Dibromophenyl)-1*H*-imidazole (3d)

[CAS Reg. No. 149797-66-0]

White solid; yield: 110 mg (73%); mp 101–103 °C; R_f = 0.45 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3131, 3060, 3015, 1591, 1570, 1497, 1304, 1267, 1103, 1064, 842, 748 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.84 (br s, 1 H), 7.67 (t, J = 1.5 Hz, 1 H), 7.51 (d, J = 1.5 Hz, 2 H), 7.26–7.23 (m, 2 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 139.1, 135.3, 133.0, 131.2, 123.9, 123.2, 117.2.

MS (DCI, +): m/z (%) = 145 (35) [M – Br$_2$ + 2 H]$^+$, 223 (40) [M – ^{81}Br + 2 H]$^+$, 225 (40) [M – ^{79}Br + 2 H]$^+$, 301 (50) [M(^{79}Br,^{79}Br) + H]$^+$, 303 (100) [M(^{79}Br,^{81}Br) + H]$^+$, 305 (50) [M(^{81}Br,^{81}Br) + H]$^+$.

1-(2-Methylphenyl)-1*H*-imidazole (3e)

[CAS Reg. No. 25371-93-1]

Pale yellow oil; yield: 75 mg (95%); R_f = 0.40 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3111, 2960, 1505, 1240, 1059, 765 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.62 (br s, 1 H), 7.39–7.27 (m, 3 H), 7.24–7.21 (m, 2 H), 7.07 (t, J = 1.2 Hz, 1 H), 2.19 (s, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 137.4, 136.5, 133.8, 131.2, 129.2, 128.7, 126.8, 126.4, 120.4, 17.5.

MS (DCI, +): m/z (%) = 159 (100) [M + H]$^+$.

1-(2-Methoxyphenyl)-1*H*-imidazole (3f)

[CAS Reg. No. 10040-93-4]

Pale yellow oil; yield: 70 mg (80%); R_f = 0.25 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3115, 2939, 2839, 1600, 1515, 1250, 1058, 754 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.85 (br s, 1 H), 7.41–7.35 (m, 1 H), 7.29 (dd, J = 1.5, 7.5 Hz, 1 H), 7.22–7.20 (m, 2 H), 7.08–7.02 (m, 2 H), 3.86 (s, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 152.5, 137.7, 128.9, 128.6, 126.4, 125.4, 120.9, 120.2, 112.2, 55.7.

MS (DCI, +): m/z (%) = 175 (100) [M + H]$^+$.

1-(4-Methoxyphenyl)-1*H*-imidazole (3g)

[CAS Reg. No. 10040-95-6]

Beige solid; yield: 62 mg (71%); mp 62–63 °C; R_f = 0.35 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3118, 3005, 2837, 1611, 1520, 1250, 1060, 832 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.75 (br s, 1 H), 7.32–7.27 (m, 2 H), 7.19–7.17 (m, 2 H), 7.00–6.95 (m, 2 H), 3.84 (s, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 158.8, 135.7, 130.6, 129.9, 123.0, 118.6, 114.7, 55.5.

MS (DCI, +): m/z (%) = 175 (100) [M + H]$^+$.

N,*N*-Diethyl-4-(1*H*-imidazol-1-yl)aniline (3h)

[CAS Reg. No. 1269166-04-2]

Brown solid; yield: 30 mg (28%); mp 55–57 °C; R_f = 0.20 (EtOAc).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.71 (br s, 1 H), 7.21–7.15 (m, 4 H), 6.71–6.66 (m, 2 H), 3.37 (q, J = 7.2 Hz, 4 H), 1.18 (t, J = 7.2 Hz, 6 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 147.1, 135.9, 129.4, 125.9, 123.4, 118.9, 111.9, 44.5, 12.4.

MS (DCI, +): m/z (%) = 216 (100) [M + H]$^+$, 186 (70) [M – Et]$^+$.

3-(1*H*-Imidazol-1-yl)phenol (3i)

[CAS Reg. No. 10041-03-9]

White solid; yield: 58 mg (72%); mp 162 °C; R_f = 0.15 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3118, 3005, 2837, 1611, 1520, 1250, 1060, 832 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (s, 1 H), 7.51 (s, 1 H), 7.31 (t, J = 8.1 Hz, 1 H), 7.13 (s, 1 H), 7.00 (ddd, J = 0.9, 2.4, 8.1 Hz, 1 H), 6.94 (t, J = 2.4 Hz, 1 H), 6.82 (ddd, J = 0.9, 2.4, 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 139.5, 136.8, 131.9, 130.0, 119.7, 115.7, 113.1, 109.3.

MS (DCI, +): m/z (%) = 161 (100) $[M + H]^+$.

1-Phenyl-1*H*-pyrazole (3j)

[CAS Reg. No. 1126-00-7]

Pale yellow oil; yield: 40 mg (55%); R_f = 0.80 (cyclohexane/EtOAc 1:4).

FTIR (ATR, neat): 3110, 2922, 1600, 1521, 1501, 1393, 936, 755 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (br d, J = 2.4 Hz, 1 H), 7.73–7.68 (m, 3 H), 7.48–7.43 (m, 2 H), 7.32–7.27 (m, 1 H), 6.47 (br t, J = 2.3 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.0, 140.1, 129.3, 126.7, 126.4, 119.1, 107.5.

MS (DCI, +): m/z (%) = 145 (100) $[M + H]^+$.

N-Phenylbenzamide (3k)

[CAS Reg. No. 93-98-1]

White solid; yield: 54 mg (55%); mp 160–162 °C; R_f = 0.80 (cyclohexane/EtOAc 1:1).

FTIR (ATR, neat): 3343, 3053, 1654, 1599, 1527, 1464, 1321, 749 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.86 (m, 2 H), 7.80 (br s, 1 H), 7.66–7.63 (m, 2 H), 7.59–7.47 (m, 3 H), 7.41–7.35 (m, 2 H), 7.19–7.13 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 137.9, 135.0, 131.8, 129.0, 128.7, 127.0, 124.5, 120.2.

MS (DCI, +): m/z (%) = 198 (100) $[M + H]^+$, 215 (25) $[M + NH_4]^+$.

N-Phenylisatin (3l)

[CAS Reg. No. 723-89-7]

Orange solid; yield: 61 mg (55%); mp 138–139 °C; R_f = 0.40 (cyclohexane/EtOAc 4:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.66 (m, 1 H), 7.58–7.51 (m, 3 H), 7.47–7.39 (m, 3 H), 7.16 (dt, J = 0.9, 7.5 Hz, 1 H), 6.89 (br d, J = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.8, 157.2, 151.5, 138.3, 132.8, 129.9, 128.7, 125.9, 125.5, 124.2, 117.4, 111.2.

MS (DCI, +): m/z (%) = 196 (90) $[M – CO + H]^+$, 167 (100) $[M – 2 CO]^+$.

N-Phenylphthalimide (3m)

[CAS Reg. No. 520-03-6]

Orange solid; yield: 63 mg (56%); mp 207–208 °C; R_f = 0.40 (cyclohexane/EtOAc 4:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98–7.92 (m, 2 H), 7.82–7.75 (m, 2 H), 7.54–7.38 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 134.3, 131.7, 131.6, 129.0, 128.0, 126.5, 123.7.

MS (DCI, +): m/z (%) = 196 (90) $[M – CO + H]^+$, 167 (100) $[M – 2 CO]^+$.

1-Phenylpyridin-2(1*H*)-one (3n)

[CAS Reg. No. 13131-02-7]

White solid; yield: 32 mg (37%); mp 125–126 °C; R_f = 0.15 (cyclohexane/EtOAc 1:1).

FTIR (ATR, neat): 3054, 1660, 1603, 1581, 1529, 1492, 767 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.32 (m, 7 H), 6.66 (ddd, J = 0.9, 1.2, 9.3 Hz, 1 H), 6.23 (dt, J = 1.2, 6.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.3, 140.8, 139.8, 137.9, 129.2, 128.4, 126.4, 121.8, 105.8.

MS (DCI, +): m/z (%) = 172 (100) $[M + H]^+$.

Recycling Procedure

At the end of a run, the zeolite could be recovered by filtration over a polypropylene Millipore membrane and further washed with EtOAc, water, and acetone. After drying under reduced pressure, the so-obtained solid was used as catalyst in the next run.

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Supporting Information

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