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Authors: Antonio Muñoz, Pedro Leo, Gisela Orcajo, Fernando Martinez, and Guillermo Calleja

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URJC-1-MOF as new heterogeneous recyclable catalyst for C-Heteroatom coupling reactions

Dr. Antonio Muñoz,[a] Dr. Pedro Leo,[b] Dr. Gisela Orcajo,[a] Prof. Dr. Fernando Martínez, [b] and Prof. Dr. Guillermo Calleja*[a]

Abstract: The capacity of copper-based URJC-1-MOF as a MOF catalyst in cross-coupling reactions has been evaluated, focusing on the Chan-Lam-Evans arylation-type reactions on amines and alcohols without extra additives or ligands. The extraordinary chemical and structural stability of URJC-1-MOF and its good specific surface, make this material a promising alternative to homogeneous Cu (II) catalysts for cross-coupling reactions. URJC-1-MOF showed a remarkable catalytic activity for cross-coupling C-N and C-O reactions, higher than other heterogeneous and homogeneous copper-based catalyst, such as CuO, HKUST-1, Cu-MOF-74, $Cu(OAc)_2$ and $CuSO_4{\cdot}5H_2O$. Moreover, its easy recovery by simple filtration and reusability in successive runs without any loss of activity and stability, demonstrates the potential of URJC-1-MOF as an alternative catalyst for this kind of reactions in different chemical media of industrial interest.

Introduction

Metal Organic Frameworks (MOFs) have emerged in the last decades as a new class of porous materials with promising properties for gas storage[1] and separation,[2] energy storage,[3] drug delivery,[4] and catalysis.[5] These applications derive from their porous structure with a remarkable pore volume and extended surface area. Moreover, these materials provide a widespread platform of tunable hybrid inorganic-organic frameworks for the inclusion of specific metals with different coordination environments and functional groups in the organic linkers. So, MOF materials have a great potential as heterogeneous catalysts in organic chemistry for different synthetic transformations, becoming environmentally and economically more efficient than classical homogeneous catalysts, facilitating its implementation in multigram scale and industrial scale processes.[6]. Some examples of these reactions are cycloaddition reactions,[7] C-H bond amination reactions,[8] multicomponent reactions,[9] and site-selective sp^3 C-H functionalization reactions such as undirected benzylic C-H borylation, silylation and amination.[10] Of special interest are the cross-coupling procedures for the formation of C-O and C-N bonds in complex organic molecules.[11] Commonly, these methodologies involve the use of homogeneous catalysis with metallic complexes containing Ir, Pd, Rh and other high-cost metals [12], also difficult to recover. Among the procedures to form C-heteroatom bonds in cross-coupling reactions, without the need of a precious metal catalyst, the use of Cu (I), Cu (II) or even Cu (0) shows particular interest. As an example, in the Ullmann-type coupling reaction, a copper source has been commonly used in stoichiometric amount in the presence of additional ligands, resulting in just moderate yields, requiring high temperatures and long reaction times.[13] To face these difficulties some modifications have been proposed, particularly for Chan-Lam-Evans reactions, which include the use of arylboronic acids, instead of arylhalides, and a nucleophile component, usually an amine or an alcohol. This allows the use of the copper source in catalytic amounts, just in the presence of an oxidant, usually atmospheric oxygen which oxidizes the complex metal centers from Cu (II) to Cu (III), favoring the oxidative addition catalyzed by the metal center, as required for the coupling reaction to take place according to the proposed mechanism. [14]

In this work, the copper-based URJC-1-MOF developed in our research group[15] has been extensively tested as heterogeneous catalyst in Chan-Lam-Evans-type coupling reaction, particularly, in C-N and C-O coupling reactions, for a wide variety of substrates. Different reaction conditions such as solvent, type of base, temperature, reaction time and substrates have been studied, observing the effect on the performance of URJC-1-MOF catalyst. In addition, this material was compared with other copper-based heterogeneous and homogeneous catalysts and its reusability was also assessed in consecutive reaction cycles.

Results and Discussion

URJC-1-MOF catalyst used in this work has a crystalline structure formed by Cu(II) linked to 1H-imidazol-4,5-tetrazole ligand, displaying a BET surface area of 408 m^2/g and a pore volume of 0.24 cm^3/g. This material provides open metal sites as active centers (see SI-1) and a remarkable thermal and chemical stability for different organic solvents with different polarity, even in boiling water. [15] This structural robustness contrasts with the limited stability of other MOF materials shown in the literature. This material has been tested as potential catalyst for C-heteroatom coupling reactions using no additives nor precious metals.[16]

Initially, the influence of the type of solvent, base and temperature was evaluated in the N-arylation and O-arylation of benzeneboronic acid (**1**) with aniline (**2**) and phenol (**3**), respectively. The reaction yields are listed in Table 1 (N-arylation) and Table 2 (O-arylation). In general, the catalytic performance were similar for both types of reactions. The coupling reaction practically did not take place for non-polar solvents such as dichloromethane, regardless of the type of the base (entries 1-3 of Table 1 and entries 1-4 of Table 2). Ethers like 1,4-dioxane and THF also evidence a negligible activity of the URJC-1-MOF material (entries 11-12 of Table 1 and Table 2).

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[a] Department of Chemical, Energy and Mechanical Technology,
Rey Juan Carlos University
C/ Tulipán s/n, 28933, Mostoles (Spain)
[b] Department of Chemical and Environmental Technology,
Rey Juan Carlos University
C/ Tulipán s/n, 28933, Mostoles (Spain)
E-mail: guillermo.calleja@urjc.es

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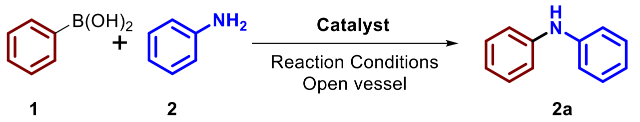
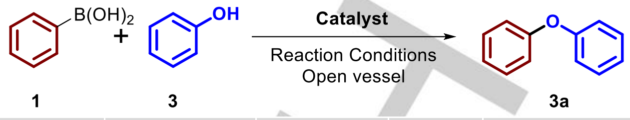
Table 1. Influence of solvent and base for aniline N-arylation reaction catalyzed by URJC-1-MOF and comparison with other catalysts [a]



Entry	Catalyst	Solvent	Base	Isolated Yield (%)
1	URJC-1-MOF	CH_2Cl_2	no	—
2	URJC-1-MOF	CH_2Cl_2	TEA	trace[b]
3	URJC-1-MOF	CH_2Cl_2	KOAc	trace[b]
4	URJC-1-MOF	MeOH	TEA	31
5	URJC-1-MOF	MeOH	K_2CO_3	43
6	URJC-1-MOF	MeOH	KOAc	64
7	URJC-1-MOF	EtOH	K_2CO_3	62
8	URJC-1-MOF	EtOH	KOAc	67
9	URJC-1-MOF	DMF	K_2CO_3	70
10	URJC-1-MOF	DMF	KOAc	84, 76[c]
11	URJC-1-MOF	1,4-Dioxane	KOAc	trace[b]
12	URJC-1-MOF	THF	KOAc	—
13	URJC-1-MOF	DMF/H_2O[d]	K_2CO_3	74, 78[c]
14	URJC-1-MOF	DMF/H_2O[d]	KOAc	79, 77[c]
15	CuO	DMF	KOAc	—
16	CuO	DMF/H_2O[d]	KOAc	—
17	Cu-MOF-74	DMF	KOAc	48
18	Cu-MOF-74	DMF/H_2O[d]	KOAc	17[e]
19	HKUST-1	DMF	KOAc	21
20	HKUST-1	DMF/H_2O[d]	KOAc	13[f]
21	$Cu(OAc)_2$	DMF	KOAc	76
22	$Cu(OAc)_2$	DMF/H_2O[d]	KOAc	63
23	$CuSO_4\cdot 5H_2O$	DMF	KOAc	62
24	$CuSO_4\cdot 5H_2O$	DMF/H_2O[d]	KOAc	56

[a]: Reaction Conditions: Benzeneboronic acid **1** (1.5 eq), aniline **2** (1 eq), **catalyst** (7.5mol% Cu), Base (2 eq), Solvent volume: 3 mL and RT. Reaction time 15h [b]: Product observed in TLC, not isolated. [c]: Reaction temperature 60ºC. [d]: Proportion DMF/H_2O: 2/1. [e]: [Cu^{2+}] in the leachate = 12 ppm. [f]: [Cu^{2+}] in the leachate = 83 ppm.

Table 2. Influence of solvent and base for phenol O-arylation reaction catalyzed by URJC-1-MOF and comparison with other catalysts [a]



Entry	Catalyst	Solvent	Base	Isolated Yield (%)
1	URJC-1-MOF	CH_2Cl_2	no	—
2	URJC-1-MOF	CH_2Cl_2	TEA	trace[b]
3	URJC-1-MOF	CH_2Cl_2	KOAc	21
4	URJC-1-MOF	CH_2Cl_2	K_2CO_3	—
5	URJC-1-MOF	MeOH	TEA	18
6	URJC-1-MOF	MeOH	KOAc	39
7	URJC-1-MOF	EtOH	K_2CO_3	56
8	URJC-1-MOF	EtOH	KOAc	41
9	URJC-1-MOF	DMF	K_2CO_3	72, 76[c]
10	URJC-1-MOF	DMF	KOAc	75, 80[c]
11	URJC-1-MOF	1,4-Dioxane	KOAc	trace[b]
12	URJC-1-MOF	THF	KOAc	trace[b]
13	URJC-1-MOF	DMF/H_2O[b]	K_2CO_3	71, 74[c]
14	URJC-1-MOF	DMF/H_2O[b]	KOAc	73, 71[c]
15	CuO	DMF	KOAc	—
16	CuO	DMF/H_2O[d]	KOAc	—
17	Cu-MOF-74	DMF	KOAc	40
18	Cu-MOF-74	DMF/H_2O[d]	KOAc	15[e]
19	HKUST-1	DMF	KOAc	27
20	HKUST-1	DMF/H_2O[d]	KOAc	9[f]
21	$Cu(OAc)_2$	DMF	KOAc	72
22	$Cu(OAc)_2$	DMF/H_2O[d]	KOAc	70
23	$CuSO_4\cdot 5H_2O$	DMF	KOAc	65
24	$CuSO_4\cdot 5H_2O$	DMF/H_2O[d]	KOAc	69

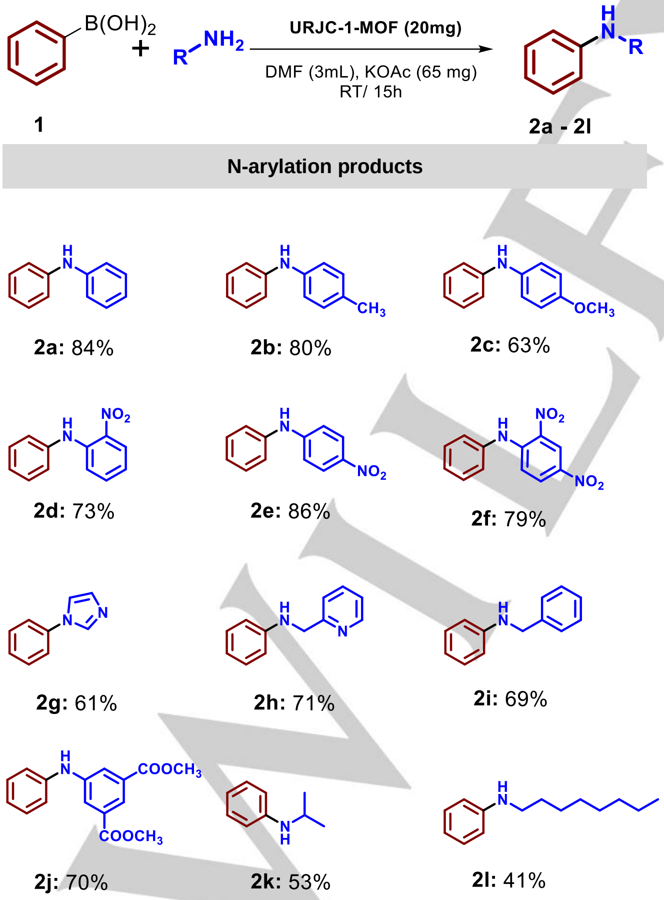
[a] Reaction Conditions: Benzeneboronic acid **1** (1.5 eq), phenol **3** (1 eq), **catalyst** (7.5mol% Cu), Base (2 eq), Solvent volume: 3 mL and RT. Reaction time 15h [b]: Product observed in TLC, not isolated. [c]: Reaction temperature 60ºC. [d]: Proportion DMF/H_2O: 2/1. [e]: [Cu^{2+}] in the leachate = 8 ppm. [f]: [Cu^{2+}] in the leachate = 71 ppm.

In contrast, more polar solvents (methanol, ethanol and DMF) led to higher product yields (entries 4-10 of Table 1 and 5-10 of Table 2). It is well-known that polar solvents can favor the stabilization of the reaction intermediates, promoting their evacuation out of the catalytic centers. Regarding the basic agent, the use of KOAc improves significantly the catalytic activity of both C-heteroatom coupling reactions for polar solvents. The maximum performance was obtained with DMF, achieving remarkable yields of 84% (Table 1, entry 10) and 75% (Table 2, entry 10) using KOAc as a base and room temperature for aniline and phenol, respectively. The increase of the reaction temperature up to 60ºC does not significantly improve the yield of both reactions.

Leaching of the catalytically active metal sites into the reaction media along the reaction test, can partially induce the homogenous catalytic reaction, so that the true heterogeneous contribution of URJC-1-MOF catalyst should be checked (see SI-2). The presence of water in the reaction medium was also tested in order to assess the catalytic activity of URJC-1-MOF under a more sustainable solvent. Additionally, the presence of humidity could favor the reduction of atmospheric oxygen, according to the mechanism proposed by Hardouin et al. [17] The catalytic experiments performed with a mixture of DMF/Water (2/1 volume) hardly affects the activity achieved by DMF alone.

For comparison purposes, other copper-based heterogeneous (CuO, Cu-MOF-74[18] and HKUST-1[19]) and homogeneous catalysts ($Cu(OAc)_2$ and $CuSO_4{\cdot}5H_2O$) were tested using DMF, KOAc as base and room temperature. URJC-MOF-1 displays a higher activity than the heterogeneous system (Table 1 and 2; entries 15, 17 and 19) and the homogeneous system (Table 1 and 2; entries 21 and 23). The basic and donor sites from the tetrazole-based ligands of URJC-1-MOF and the unsaturated copper acid sites seem to have a synergistic catalytic effect as compared to the other MOFs with tereftalic derived ligands (Cu-MOF-74 and HKUST-1) (see SI-4), copper oxide and homogeneous copper salts. Additionally, the crystalline phase of URJC-1-MOF, Cu-MOF-74 and HKUST-1 keeps unaltered (See SI-4) and copper leached-off of the catalyst was not detected in the reaction medium. Interestingly, unlike URJC-1-MOF, the catalytic activity of heterogeneous CuO and MOF-type materials (Table 1 and 2, entries 16, 18 and 20) in the presence of water (DMF/water 2/1, KOAc as base and room temperature) showed a lower activity and stability. Cu-MOF-74 and HKUST-1 evidenced clear signals of structural damage of the framework (see SI-4) and copper concentrations into the reaction media of 12 and 83 mg/L for aniline arylation and 8 and 71 ppm for phenol arylation, respectively. These results demonstrate the high robustness of URJC-1-MOF in aqueous media compared to others MOFs.[20] In the case of homogeneous catalytic systems (Table 1 and 2, entries 22 and 24), the presence of water slightly reduced the product yields.

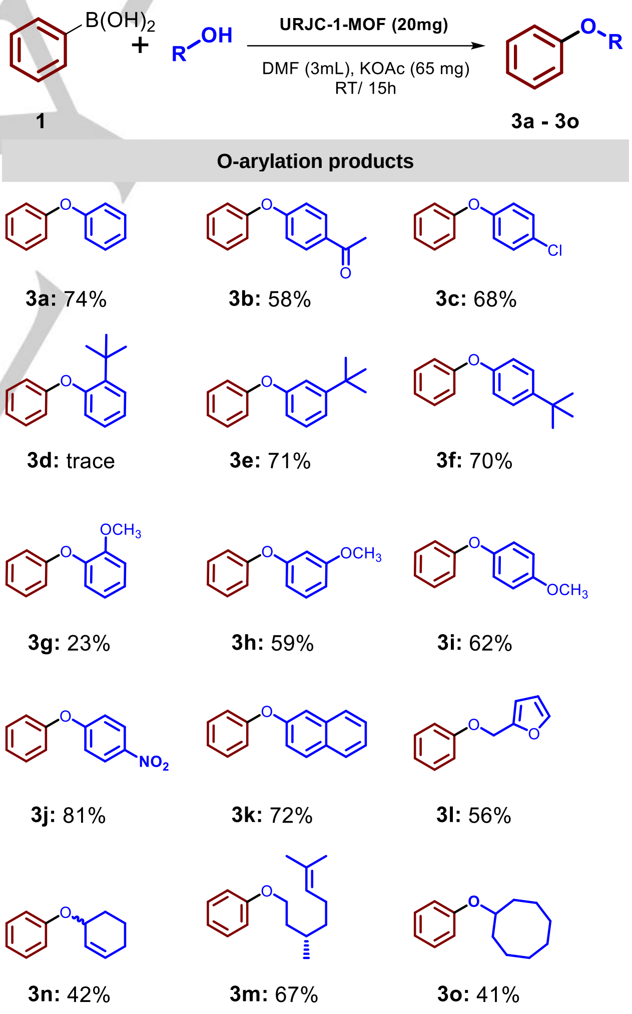
Table 3. N-arylation reactions between benzeneboronic acid (**1**) and different amines at room temperature with URJC-1-MOF as catalyst.



Catalytic activity of URJC-1-MOF was also studied for N-arylation and O-arylation reactions with different types of amine (Table 3) and alcohol compounds (Table 4). All the resulting products were isolated using flash chromatography on silica gel and characterized with usual spectroscopic techniques (see SI-6). Akyl and non-arylamines showed lower product yields than arylamine substrates. A similar trend was also observed for non-aromatic alcohols as compared to phenolic derivative substrates. However, in both cases, the product yields (alkylamines: **2k,** 53% and **2l:** 41%; non-arylamines: **2h,** 71% and **2i,** 69%; and non-aromatic compounds: **3l,** 56%, **3n,** 42%, **3m,** 67%, and **3o:** 41%) were significantly higher than those found in the literature, even using homogeneous catalysts. [21]

In the case of substituted phenol compounds, *meta-* and *para-*substituted compounds displayed higher product yields than the ortho-substituted homologues (Table 4). These results seem to indicate a certain chemo-selectivity of URJC-1-MOF, in particular for bulky substituents, which has not been observed with other heterogeneous catalyst such as (Cu(tpa)-MOF) using also polar solvents and room temperature[22] or even with homogeneous catalysts in Ullmann-type coupling reactions[21].

Table 4. O-arylation reactions between benzeneboronic acid (**1**) and different alcohols at room temperature with URJC-1-MOF as catalyst.



This steric hindrance was evident for bulky functional groups such as the tert-butyl group (**3d** *(ortho-)*, trace; **3e** *(meta-)*, 71%; **3f** *(para-)*, 70%) or the methoxy- group (**3g** (*ortho*-), 23%, **3h** (*meta*-), 59% and **3i** (*para*), 62%). Interestingly, nitro-substituted compounds evidenced the highest product yields in both N-arylation and O-arylation reactions. This increase of reactivity of nitro-substituted compounds was remarkable even for *ortho*-nitroaniline (**2d**, 73%; Table 3).

To evaluate the reusability of URJC-1-MOF catalyst, five succesive reactions of aniline arylation to produce phenylaniline (**2a**; Table 3) in gram-scale were carried out, with partial recovery of the catalyst by simple filtration, washing with DMF, H_2O and EtOH and drying at 60 °C overnight. Concentration values were fixed as: 7.5 mol of Cu (340 mg of catalyst), 1.05 g of benzeneboronic acid (**1**), 0.535 g of aniline (**2**), 1.15 g of KOAc and 35 mL of DMF. There was no significant loss of activity along the five cycles of 15 hours of reaction, maintaining a product yield above 90%. The X-ray diffraction patterns of recovered catalyst after some cycles (first, third and fifth ones, Figure 1) evidenced the stability of pristine URJC-1-MOF crystalline phase. Signals of reactants and/or products retained in the URJC-1-MOF structure were not detected from FT-IR spectra (see SI-5). Moreover, the recovery of the solid catalyst after each cycle was practically total (above 95 %). Finally, the copper leached-off was negligible, showing liquid concentration values below 0.1 mg/L in the reaction medium, as shown by ICP-OES measurements. All these results confirmed the heterogeneous activity, chemical stability and potential reusability of URJC-1-MOF in successive consecutive reaction cycles.

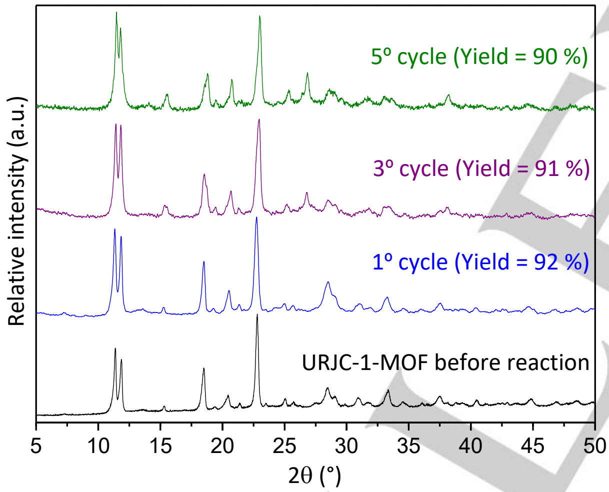


Figure 1: X-ray diffraction patterns of fresh and used URJC-1-MOF catalyst after consecutive reactions and the resulting catalytic yields.

Conclusions

URJC1-MOF material has been evaluated as heterogeneous catalyst for Chan-Lam-Evans-type reactions. The catalyst prompted the formation of C-heteroatom bonds under mild reaction conditions in a straightforward manner using "open flask" conditions without extra additives or ligands. URJC-1-MOF achieved higher yields than other homogeneous and heterogeneous copper-based catalysts, which makes this novel catalyst a very promising material for catalytic applications. URJC-1-MOF-MOF is stable in the presence of water, with no copper leaching into the reaction media. URJC-1-MOF showed a remarkable performance for N- and O-Arylation of benzeneboronic acid with different aniline and phenol derivatives. Its catalytic performance was sensitive to steric hindrance for bulky molecules, showing an interesting chemo-selectivity for arylation in *meta*- and *para*- positions. URJC-1-MOF was easily recovered after reaction, maintaining its crystalline structure and catalytic activity in successive reaction cycles. These results make URJC-1-MOF a promising new catalyst, becoming a greener and cheaper alternative to catalysts for coupling reactions.

Experimental Section

Typical catalytic tests to assess the activity of catalyst for N- or O-Arylation reactions, characterization technique for quantification of product yields and method for catalyst recovery to evaluate the reusability in successive catalytic cycles are described in SI-5. URJC-1-MOF and Cu-MOF-74 were synthesized following the procedure previously reported, [15, 18] and HKUST-1 was purchased to Sigma-Aldrich (Spain).

Acknowledgements

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Keywords: heterogeneous catalysis • URJC-1-MOF• C-N coupling • C-O coupling • Chan-Lam coupling

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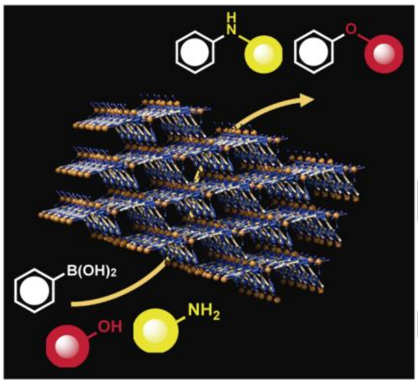
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

URJC-1-MOF is new copper-based material that exhibits high activity in the N and O - arylation reaction of aryl boronic acids with amines and alcohols. The catalyst can be facilely separated and be reused without significant degradation in catalytic activity even in aqueous media.



*Dr. Antonio Muñoz, Dr. Pedro Leo, Dr. Gisela Orcajo, Prof. Dr. Fernando Martínez and Prof. Dr. Guillermo Calleja**

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URJC-1-MOF as new heterogeneous recyclable catalyst for C-Heteroatom coupling reactions

Layout 2:

COMMUNICATION

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