

# Functionalization of $\text{Cu}_3\text{BTC}_2@IL$ composites with Pd(II) for catalytic applications

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## Introduction

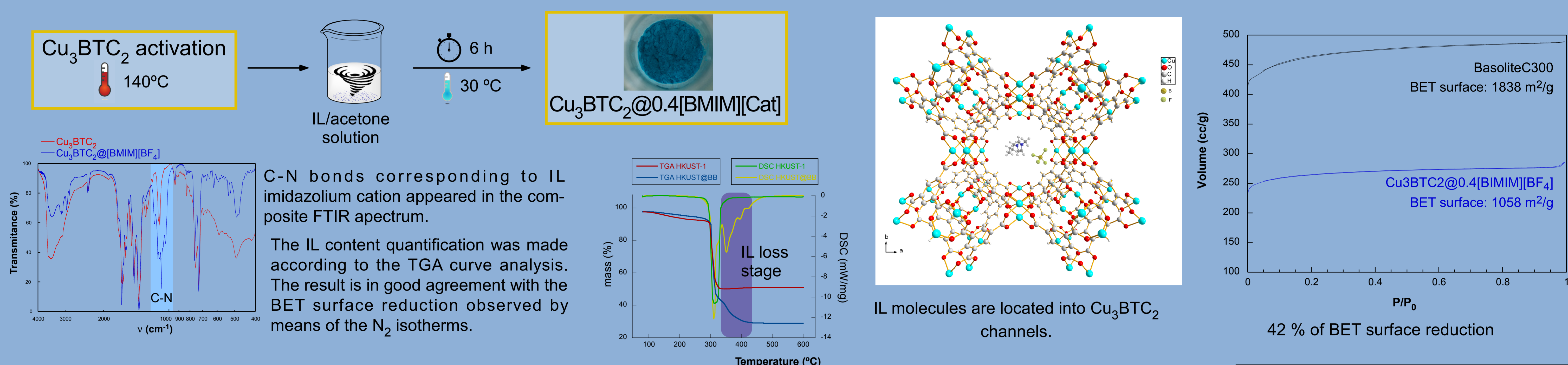
Metal-organic frameworks could be excellent supports for active catalytic species in order to obtain heterogeneous and reusable catalysts, easily removable from the reaction media.[1,2] Additionally, the presence of unsaturated metal centres in their pores provides a superb opportunity to tackle with reactions that requires more than one type of metal centre.[3] In order to obtain heterometallic catalyst, we have immobilized Pd(II) into the pores of the well studied  $\text{Cu}_3\text{BTC}_2$  MOF (BTC= benzene-1,3,5-tricarboxylate) with the help of imidazolium derived ionic liquids (IL).

- [1] P. Valvekens, F. Vermoortele and D. D. Vos, Catal. Sci. Technol., 2013, 3, 1435–1445.  
 [2] E. S. Larrea, R. Fernández de Luis, J. Orive, M. Iglesias and M. I. Arriortua, Eur. J. Inorg. Chem., 2015, 2015, 4699–4707.  
 [3] D. Saha, R. Sen, T. Maity and S. Koner, Langmuir, 2013, 29, 3140–3151.

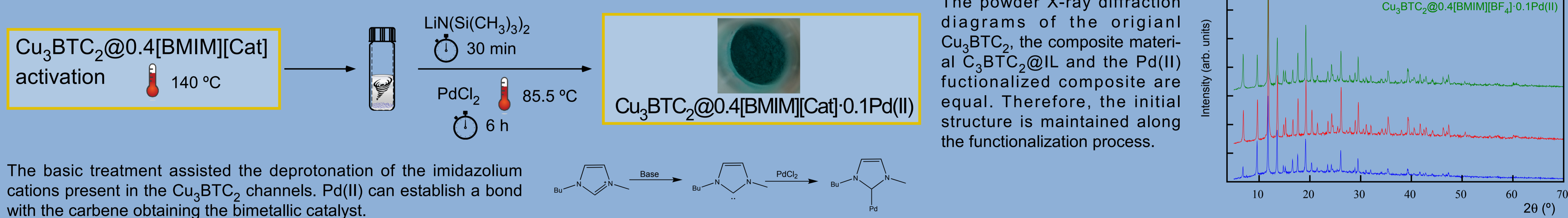
## Preparation method

**Materials:** Basolite C300®, [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>] ionic liquids (BMIM= 1-Butyl-3-methylimidazolium), Lithium bis(trimethylsilyl) amide, Palladium(II) chloride, acetone, toluene, acetonitrile.

### 1<sup>st</sup> step: MOF@IL composite formation



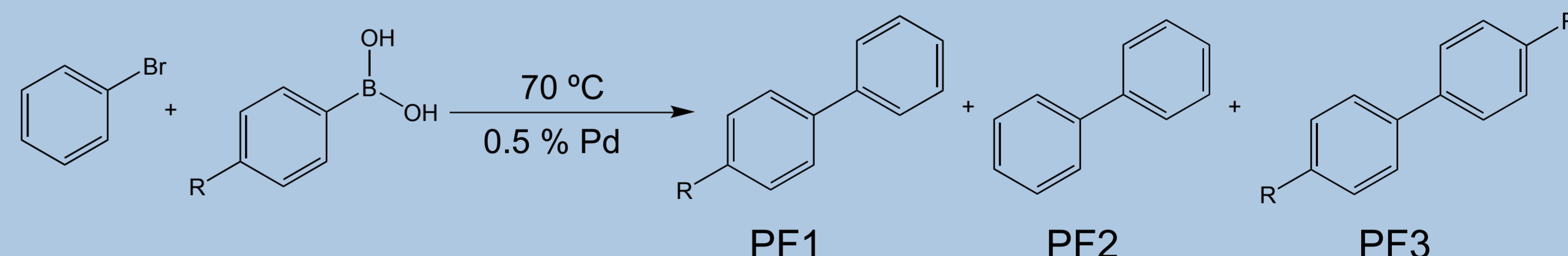
### 2<sup>nd</sup> step: MOF@IL composite functionalization



## Catalytic activity tests

### Suzuki-Miyaura cross-coupling

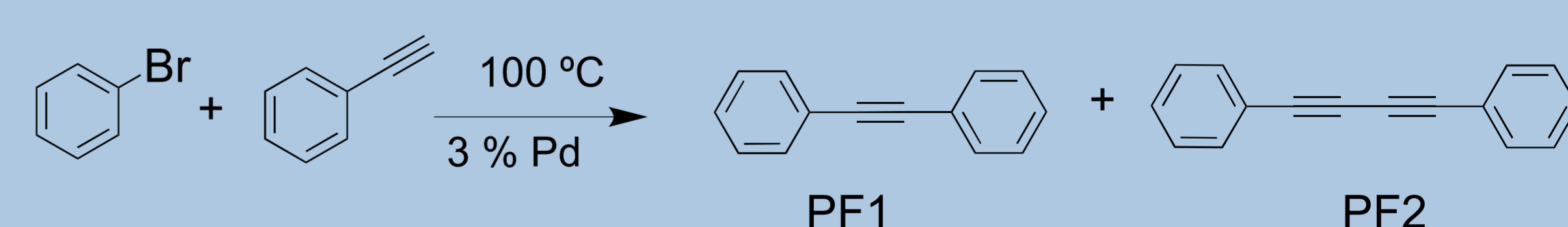
R	Solvent	Base	C <sub>T</sub> (t)	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	S <sub>1</sub>
Me	MeOH	K <sub>2</sub> CO <sub>3</sub>	91% (1.5h)	61%	9%	21%	67%
MeO	MeOH	K <sub>2</sub> CO <sub>3</sub>	67% (4h)	67%	0	0	100%



The catalyst seem to be active for the Suzuki-Miyaura cross-coupling. However, after during the reaction the catalysts suffers a structural transformation. For this reason, we concluded that the catalysis is not heterogenous.

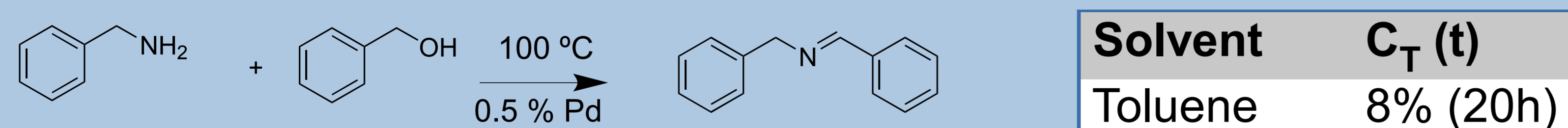
### Sonogashira cross-coupling

Catalyst	Solvent	Base	C <sub>T</sub> (t)	C <sub>1</sub>	C <sub>2</sub>	S <sub>1</sub>
Cu <sub>3</sub> BTC <sub>2</sub> @0.4[BMIM][BF <sub>4</sub> ]-0.1Pd	Toluene	Et <sub>3</sub> N	70% (22h)	0	70%	0%
Cu <sub>3</sub> BTC <sub>2</sub> @0.4[BMIM][BF <sub>4</sub> ]	Toluene	Et <sub>3</sub> N	0% (20 h)			



The reaction with the Pd(II) functionalized MOF@IL composite does not yield the cross-coupling product, but the ethynylbenzene homocoupling reaction one. The not functionalized composite is not active for this reaction. Hence, the active species is the Pd(II)

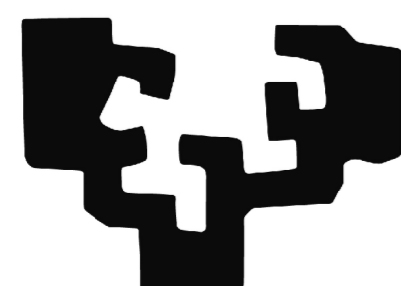
### Amine alkylation



For the alkylation of aniline the catalyst seem to be active but the yield of the reaction is quite low. The recovered catalyst maintained the crystal structure. More work should be done to improve the conversion and to confirm the heterogeneous nature of the catalyst for this reaction.

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