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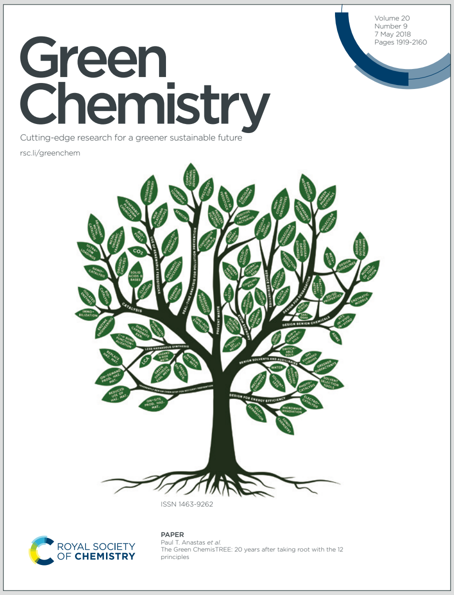

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ARTICLE

MOFs Come up to Scratch: An Environmentally Benign Route to Oxidative [4+2] Cycloaddition on Maleimides Solely via MOF in Water

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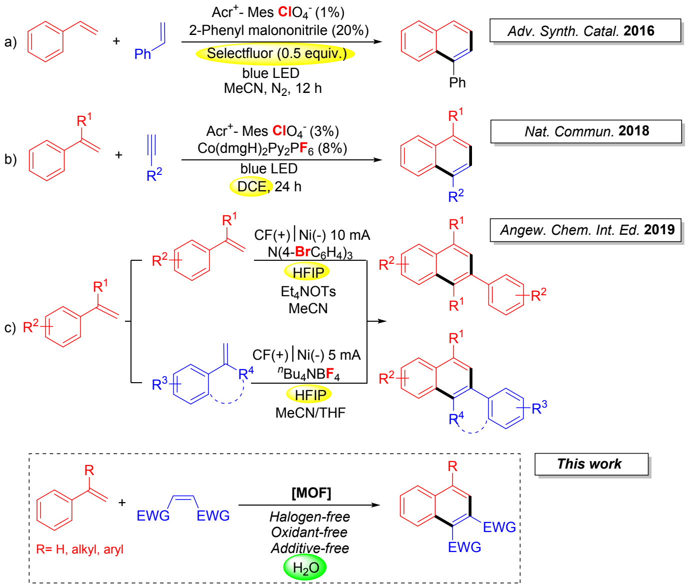
The first Diels-Alder reaction of vinyl arenes with ene systems catalyzed by MOFs is reported. Maleimides and maleic anhydride were annulated/dehydrogenated on styrenes in the presence of a mixed-metal (FeNi)MIL-88A catalyst. Neither additional oxidant nor a source of halogen is needed to drive this oxidative [4+2] cyclization reaction. Kinetic evidence such as activation entropy corroborates the proposed concerted mechanism. The reaction proceeds merely through a cost-effective catalyst in water as the greenest solvent. The product of annulation of styrene with maleic anhydride was used for the first L-selective annulative π-extension on naphthalene.

Introduction

Fusion of a ring segment through formation of two new bonds at the expense of two other bonds is a transformation which has always appealed to organic chemists. Given the fact that maleimides have a high aspiration for involvement of both their olefinic carbons in their reactions, myriads of reactions have been emerged concerning maleimides as one of coupling partners in cyclization reactions.[1] However, in most cases the double bond of maleimides cannot be preserved thus usually succinimides, rather than maleimides, are present in the structure of the products formed. In our previous work, we succeeded in retaining the maleimide core in annulation with styrenes via a Pd-catalyzed consecutive C-H activation.[2] Subsequent to our work, Antonchick *et al.* reported a novel dehydrogenative Diels-Alder (D-A) reaction of alkylarenes on benzoquinone which could successfully be extended to styrenes.[3] But, when it was applied to maleimides, as mentioned earlier, the double bond of maleimide converted to a single bond even using a twofold excess of an oxidant oxidant. Diels-Alder (D-A) reaction is known as a robust transformation for the synthesis of six-membered rings in organic chemistry.[4] Therefore, when construction of an arene ring is demanded,[5] D-A reactions have always been a sought-after method. Among dienes used in D-A reactions, styrenes are of the most challenging cases. This is mainly due to the competitive unwanted reactions of styrenes, i.e. [2+2] cycloaddition,[6] and polymerization.[7] It is for this reason that all reports concerning engagement of styrene in an annulation reaction with another coupling partner, thus suppressing side-reactions of styrenes, are considered as notable achievements. In this context, Liang *et al.* managed to couple two styrenes in a metal-free reaction without observing considerable polymerization (Scheme 1a).[8] Having followed their lead, two years later Lei used yne systems, which are far more active than double bonds, to trap styrenes with the aid of a metal catalyst (Scheme 1b).[9] Also lately, a report on electrochemical [4+2] annulation of styrenes has been published which led to naphthalenes after going through a rearrangement (Scheme 1c).[10] All the foregoing research work had a feature in common: *"using two or more halogenated reagents in their reactions"*.



Scheme 1. [4+2] reactions of styrenes

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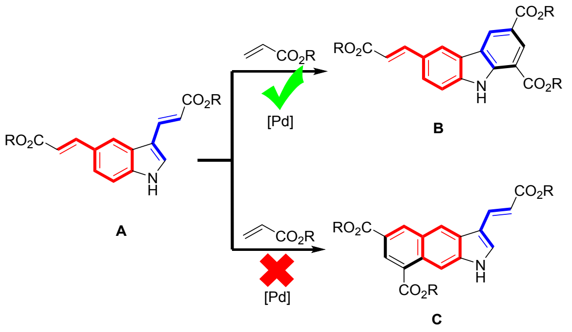
It is worth mentioning that despite all efforts in this field, D-A reaction on styrenes (as a diene system rather than an ene system) has still remained challenging. To give a better insight into this, a comparison between a styrenyl system and a dienyl system in terms of their reactivity in D-A reaction was made in Verma's work. In this study, when Pd-catalyzed reaction of 5-vinyl substituted indoles **A** with acrylates was studied, the reaction led to 5-substituted carbazoles **B** instead of benzoindoles **C** confirming that it was diene systems which won this competition over styrenes in D-A reaction (Scheme 2).[11c]

Metal-organic frameworks have been shown to be powerful catalysts in a vast area of chemistry. They owe their catalytic properties to coordinatively unsaturated sites (CUS) around their metal-nodes.[12] Catalysis of both oxidation [13] and reduction reactions [14] is the most common reactivity patterns reported for MOFs. As well as these reactions, there have been copious examples of MOF-catalyzed organic coupling reactions.[15] Recently, inspired by Mukherjee *et al.* a few reports on D-A annulations catalyzed by MOFs have been reported. However, all are either hetero-D-A or D-A by using simple/real dienes.[16] Herein, we will describe the first D-A reaction of styrenes with ene systems catalyzed by an MOF, which preserved the ene's double bond. The reaction is free from any toxic additive and can be conducted in water as the greenest solvent. Use of water as a non-toxic medium is the most preferred option among chemists. Preference for this solvent over others also rises from its low cost and widespread availability. Yet, despite its advantageous features since most of organic compounds show poor solubility in water, use of this environmentally benign solvent is limited in organic reactions. Plus, water is infamous for deactivating most metal catalysts due to which transition-metal catalysts often work inefficiently in this solvent. Given all the afformentioned, contriving reactions which are feasible in water as the sole medium of the reaction is of great value.[17]



Scheme 2. A dienyl system eclipsing a styrenyl system

Results and Discussion

The MOF MIL-88A was prepared according to the literature.[18] Because of the key role of metal nodes in MOF structures, catalytic property as well as chemical stability of MOFs can be tuned by the synthesis of "mixed-metal MOFs". It is noteworthy that in conventional (single-metal) MIL-88 MOFs, anions fill the pores, thereby preventing the structure from being porous. As a solution, proper "mixed-metal MOFs" were designed which introduced porosity into the framework by neutralization of structure and therefore the need for the presence of counterions within the pores was obviated.[19] Given the powerful catalytic activities of Ni(II) complexes in various D-A annulations [20] and since the preparation of trimeric mixed-metal acetate of Fe(III) and Ni(II) has been previously reported,[21] in this paper, we focused on the synthesis of hypothetical neutral/porous (FeNi)MIL-88A, ($Fe_2NiO(O_2CCH{=}CHCO_2)_3.nH_2O$) as the catalyst of choice. As the first step toward this end (and according to reference 18), 2.8 mmol of iron(III) chloride hexahydrate, 1.4 mmol of nickel nitrate hexahydrate and 4.2 mmol fumaric acid were dissolved in 30 mL of water and stirred for 15 minutes. The mixture was transferred into a Teflon-lined autoclave and heated at 100 °C for 15 h. After filtration and washing with water, the product was analyzed by various spectroscopic methods. Then, regarding literature reports about Ag(I),[22] we chose it as another candidate to check its efficiency/synergistic effect in the D-A reaction when deposited on the structure of MIL-88A. Therefore, Ag-deposited MIL-88A nanoparticles were prepared by a post-synthetic exchange (PSE) of Ag(I) source with the prepared MIL-88A. XRD, FTIR, SEM, TEM, EDAX-elemental mapping, N_2 adsorption/desorption isotherm, BET and BJH were used to characterize the synthesized compounds (Figures 1-4 and S1-4). In addition, the thermal stability of the synthesized material was analyzed by Thermogravimetry/Differential Thermal Analyzer (Figure 5). XRD patterns of the Ag-deposited MIL-88A and (FeNi)MIL-88A in Co anode have been shown in Figure S1. In the case of MIL-88A and (FeNi)MIL-88A, diffraction patterns can be clearly seen at 2Ɵ: 12.6°, 14.0° which are related to the pure MIL-88A structure regarding literature reports on Cu anode.[18b,23] No detectable difference was observed between XRD of Ni modified structure and that of the parent compound confirming that the structure of MIL-88A remained intact (Figure S1a-b). When Ag was deposited on MIL-88A, a different scenario happened due to the presence of Cl^- anions in the pores of MIL-88A which was consistent with Liu's report.[24] In its XRD, there were three additional diffractions at 32.4°, 37.6° and 54.2° related to 111, 200 and 220 patterns of AgCl (JCPDS no. 31-1238) confirming the precipitation of AgCl in the pores of MIL-88A (Figure S1c).

Figure S2 depicts the FTIR spectra of the prepared compounds. The bands at 1394 cm^{-1} and 1601 cm^{-1} are generated by the symmetric and asymmetric stretching of the C=O bonds of carboxylate groups of the fumarate linkers. The bands at 1219 cm^{-1} can be assigned to the C-O vibration of the fumarate groups. Broad band at around 3000-3600 cm^{-1} indicates O-H stretching mode of adsorbed water which overlaps with stretching of C-H bonds. In addition, forming Fe-Oxo clusters can be proved by the band at around 577 cm^{-1}, the characteristic band of Fe-O bonds. The bands at 644 cm^{-1} and 677 cm^{-1} are related to the carbonyl group [23,25] and C-H bending mode, respectively. As is clear, no detectable changes were found in the FTIR spectrum of mixed-metal FeNi nor in that of the Ag-deposited MIL-88A proving that the structures

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did not change considerably after introducing Ag(I) and Ni(II) into the parent compound.

Porosity and morphology of the prepared MOFs have been outlined in Figure 1. SEM images recorded by a Zeiss instrument ensured the porous structures of the prepared MOFs. As was expected, both of the prepared samples showed hexagonal spindle-like morphology and the surface of the samples was not smooth due to the porous structure.

The results of TEM (Figure 2) are accurately in agreement with the SEM ones showing uniform sizes of spindles in both the prepared materials.

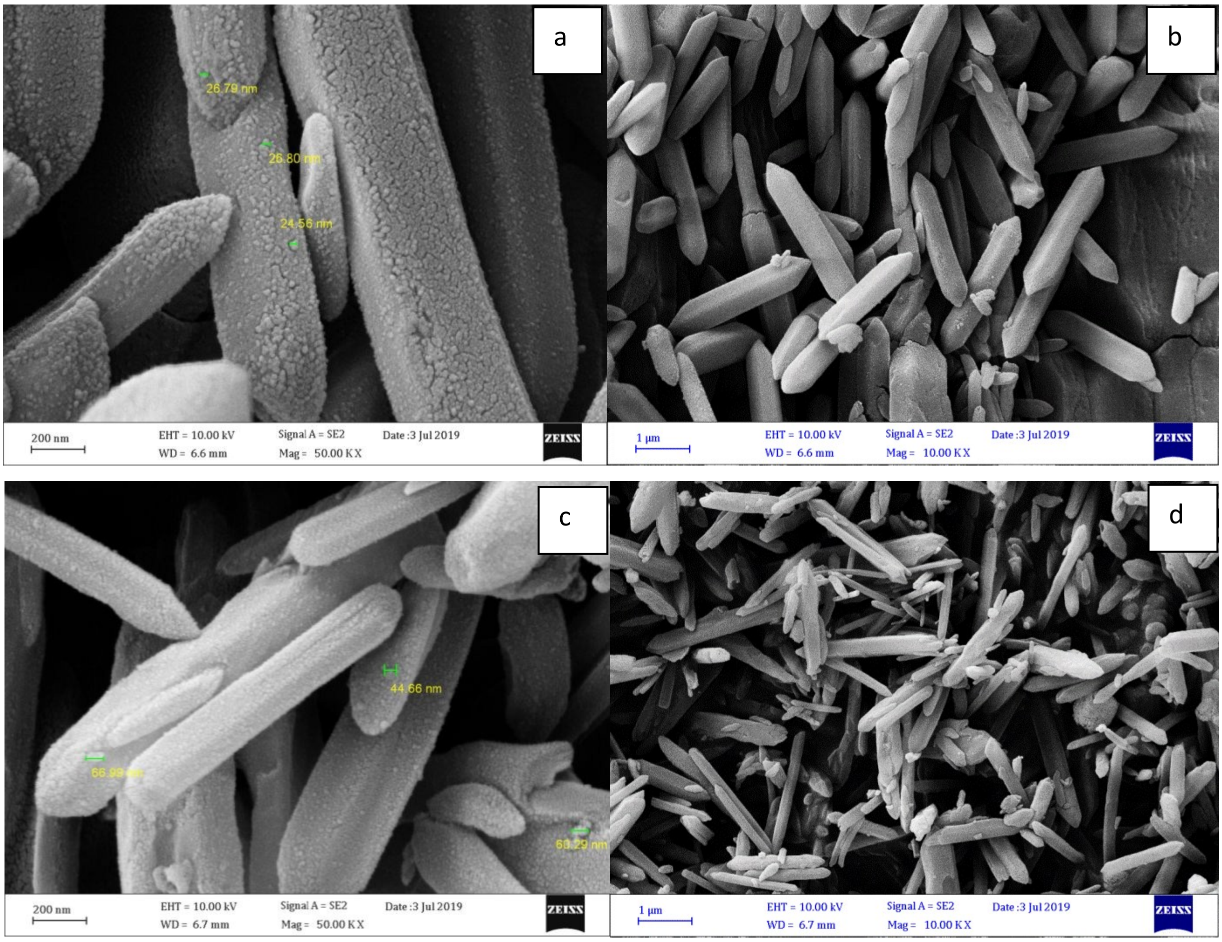

Figure 1. SEM images of (FeNi)MIL-88A (a-b) and Ag-deposited MIL-88A (c-d)

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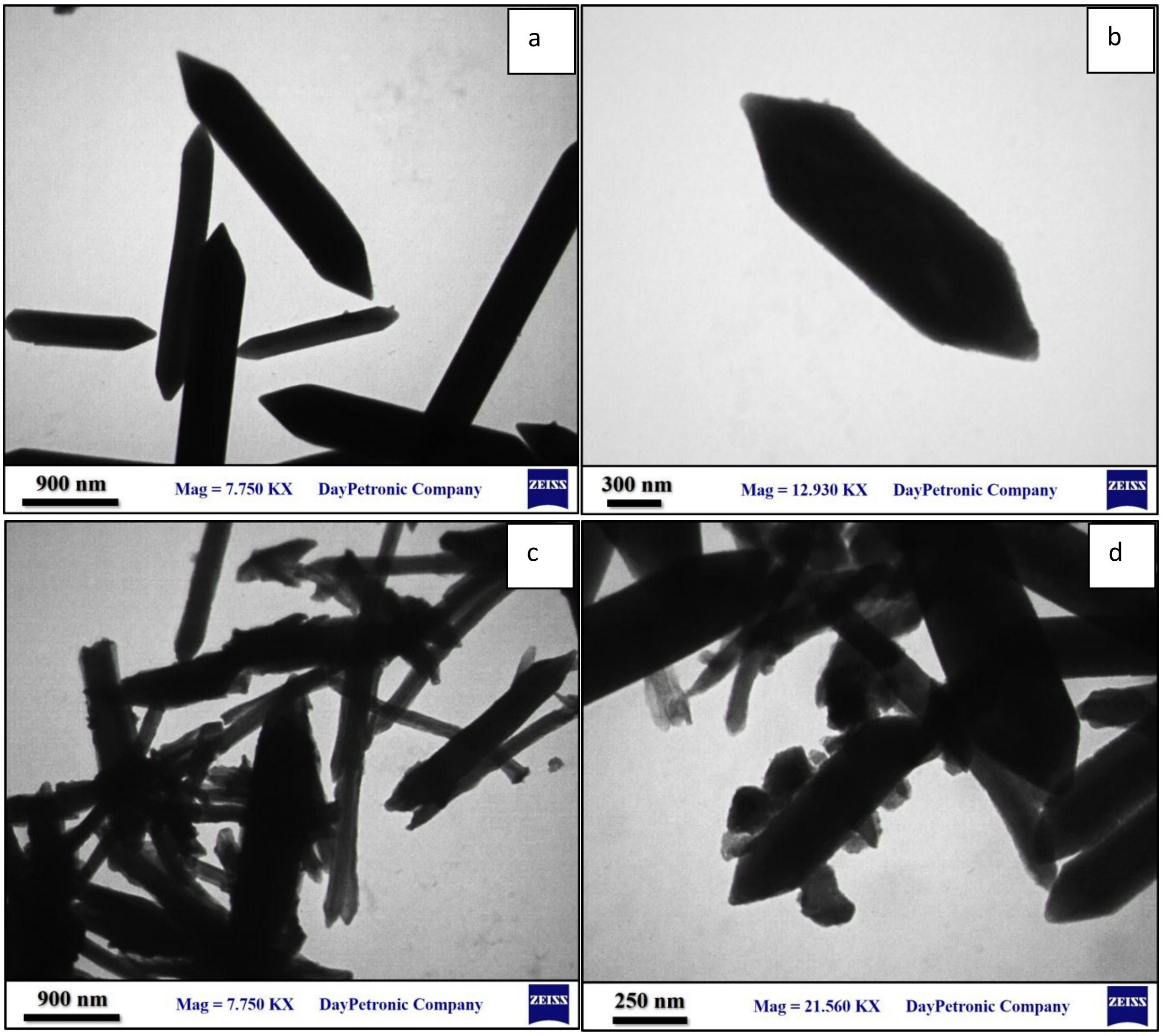

Figure 2. TEM images of (FeNi)MIL-88A (a-b) and Ag-deposited MIL-88A (c-d)

The quantitative amounts of the metal content were measured by the energy dispersive X-ray spectroscopy (EDAX) elemental mapping (Figure S3-S4). Analyses indicated the presence of Fe, C, Ni and Cl for the (FeNi)MIL-88A; and Fe, C, Ag, and Cl and for Ag-deposited MIL-88A; the presence of Cl^- in the structure of (FeNi)MIL-88A confirmed the partial exchanging of Ni in the structure. Elemental mapping demonstrates the uniform distribution of all elements (O, Cl, Fe and Ni in the case of (FeNi)MIL-88A and O, Cl, Fe and Ag in the case of Ag-deposited MIL-88A) within the MOF structures.

To give more precise information, the structures were analyzed by ICP. In the case of Ag-deposited MIL-88A, the elemental contents were shown to be 2.59 mmol/g Fe and 0.22 mmol/g Ag. Thus, the molar ratio of Fe/Ag is about 12. As a result, it can be noted as $Fe_{2.77}Ag_{0.23}O(O_2CCH{=}CHCO_2)_3$. For the (FeNi)MIL-88A the analysis confirmed the content of Fe and Ni about 2.97 mmol/g and 8.8×10^{-4} mmol/g, respectively. This indicates that the molar ratio of Fe/Ni is about 3300/1. Therefore, despite the hypothesized formula $Fe_2NiO(O_2CCH{=}CHCO_2)_3$, it had better be denoted as (FeNi)MIL-88A. On the basis of such low exchanging value of Ni (about 0.03%), it can be inferred that as opposed to our initial intent for the synthesis of neutral-porous (FeNi)MIL-88A, the

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prepared mixed-metal compound is not neutral and must have contained counterion (Cl^-) in its pores (as can be seen in EDAX). Due to the low Ni uptake (as confirmed by ICP about <0.001 mmol/g) and insufficient accuracy of EDAX, the amount of Ni cannot be measured, whereas for Ag-deposited MIL-88A, EDAX showed 3.8 wt.% Ag (equal to 0.35 mmol Ag/g of catalyst). Higher Ag impregnation on the structure is due to deposition of AgCl in the pores which was also confirmed by XRD.

Specific surface areas of the catalysts and properties of their pores were investigated by the N_2 adsorb-desorb isotherm, BET and BJH (Figures 3-4). It was previously reported that the specific surface area of MIL-88A was below 30 m^2/g;[26] therefore we expected to obtain a lower value than those of other MOFs.[27] This low surface area of MIL-88A was explained by its flexible structure and probably closed pores during the pre-treatment degassing for N_2 adsorb/desorb measurement.[28] As was envisaged, specific surface areas of the prepared (FeNi)MIL-88A and Ag-deposited MIL-88A were calculated to be about 7.5 and 6.7 m^2/g, respectively. N_2 adsorption/desorption isotherms of the prepared Ag-deposited MIL-88A (Figure 3a) confirmed a combination of type II and III isotherms, mostly like type II, in agreement with the literature.[18b] In contrast, (FeNi)MIL-88A showed a type III isotherm (Figure 3b). It can be deduced that together with mesopores, some micropores are present in the former structure which are filled at very low pressures. To determine the pore diameters of the materials, the structures were analyzed by the BJH analysis (Figure 4). Based on findings, pore volume was increased from 0.05 cm^3/g for Ag-deposited MIL-88A to 0.11 cm^3/g for (FeNi)MIL-88A. This is maybe due to what is explained as the partial neutralization and therefore removal of counterions from the pores of MIL-88 [19] which is in agreement with its type III N_2 adsorb/desorb isotherm.

It is notable that while (FeNi)MIL-88A includes only mesopores over 18 nm, in Ag-deposited MOF together with these mesopores, there are also micro scale pores with diameters of about 1.8 nm. The observation confirms that the precipitation of AgCl within the pores of the structure reduces some pore diameters to the micropores scale (consequently leads to a reduction in the total pore volume).

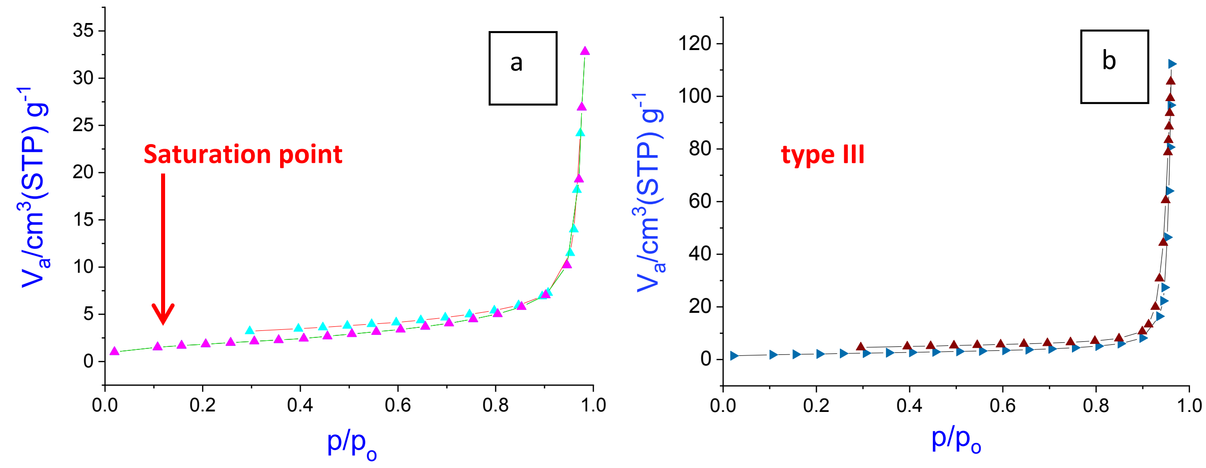

Figure 3. N_2 Adsorption/desorption isotherm of (a) Ag-deposited MIL-88A and (b) (FeNi)MIL-88A

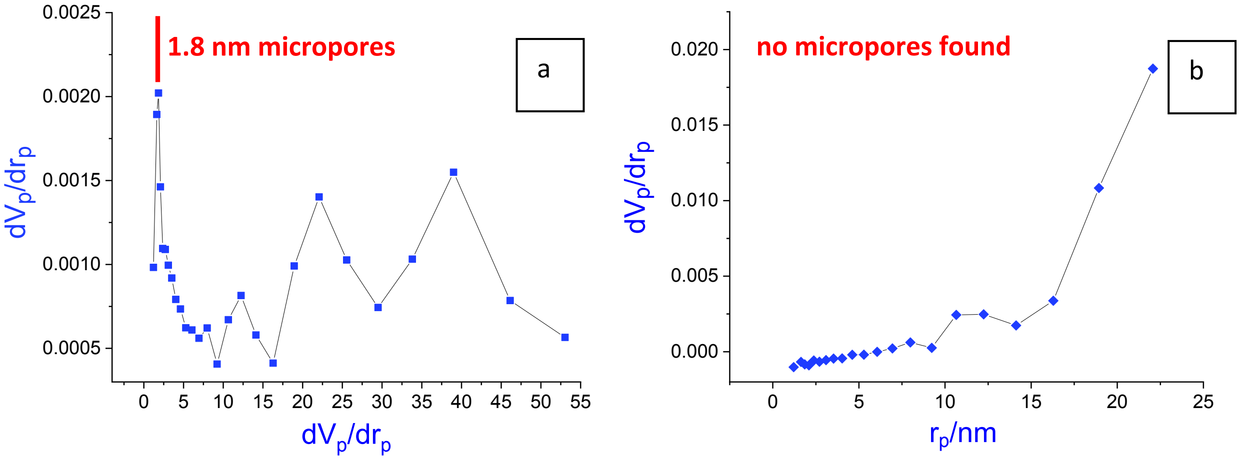

Figure 4. BJH analysis of (a) Ag-deposited MIL-88A and (b) (Fe-Ni)MIL-88A

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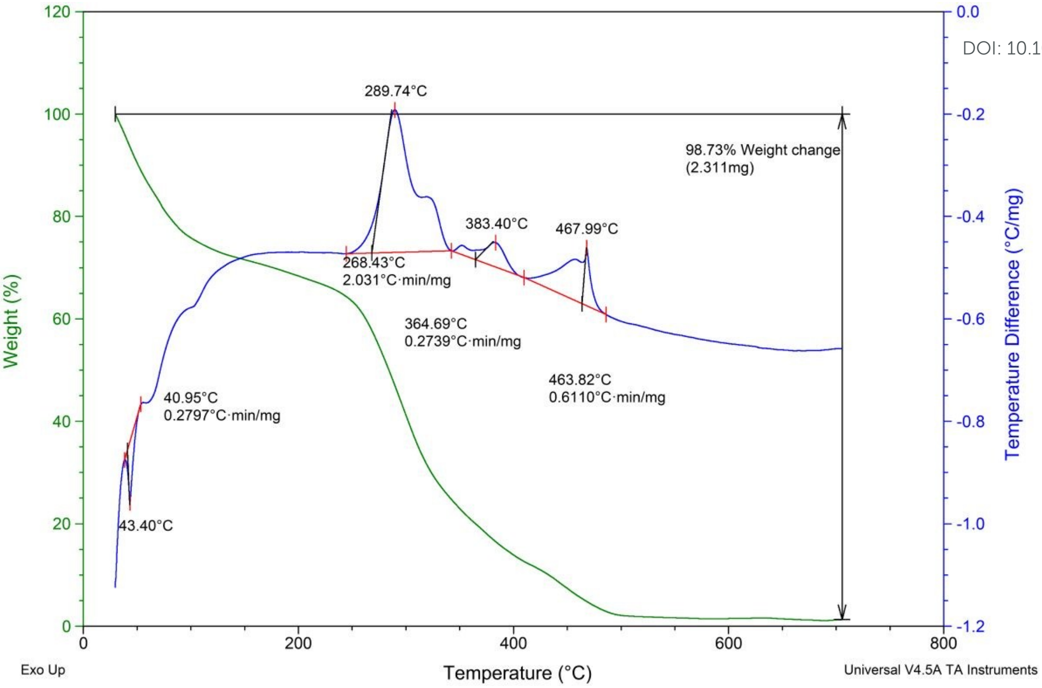

Figure 5. TGA-DTA analysis of (Fe-Ni)MIL-88A

TGA results are also in agreement with that of MIL-88A in the literature [29] (see Figure 5). As can be seen, the as-prepared (Fe-Ni)MIL-88A is fully stable under 250 °C and experiences only one weight loss of about 30% due to evaporation of water. Above 250 °C, a three step weight-loss of exothermic processes occurs each of which is overlapping with one another and consecutive. An exothermic process takes place at about 270-360 °C together with about 50% weight loss related to sublimation of fumarate and the collapse of the framework.[30] There are also two other exothermic processes at 383 and 468 °C. According to the study of XRD of MIL-88A framework at different temperatures in Yang's work [29] at around 400 °C, MIL-88A is converted to γ-Fe_2O_3. Upon increasing the temperature to 450-500 °C, *in situ* conversion of γ-Fe_2O_3 into α-Fe_2O_3 occurs and finally MIL-88A is converted to carbon-coated α-Fe_2O_3 nanospindles. Therefore, it can be concluded that the peaks at 383 and 468 °C may be related to the formation of γ-Fe_2O_3 and α-Fe_2O_3, respectively.

Having characterized our prepared catalysts, we then set out to put their efficiency in promoting organic reactions into test. For this purpose, the reaction of styrene **1**, as diene, and *N*-methyl malemide **2** in the presence of the synthesized MIL-88A as catalyst in acetonitrile was chosen as the model reaction. The reaction led to a trace amount of benzo[e]isoindole-1,3-dione **3** (<5% by GC) (Table 1, entry 1). Since we sought out the construction of a naphthalene ring, an oxidation step seemed to be essential, thus the reaction was tested in the presence of additional oxidants (entries 2-4). $AgNO_3$ as a metal oxidizing agent increased the yield to 38% (entry 2), by the same token, CuCl gave a relatively high yield (entry 3). However, use of TBHP, as a non-metallic oxidant, totally suppressed the reaction and only a trace amount of the product was obtained (entry 4). This may be due to the tendency of styrenes to be oxidized when exposed to TBHP and generation of undesirable by-products resulting from the foregoing side reaction.[31] Using NaClO and $NaClO_4$ gave the similar results (entries 5,6). With this result, CuCl seemed to be the best choice as an external oxidant, so optimization of catalyst loading was then taken into consideration. As expected, decreasing the amount of the catalyst had a destructive effect on the yield, whereas increasing it to 15 mg built up the yield, albeit rather inconsiderably (entries 7,8). As the next step, we replaced MIL-88A with our prepared mixed-metal MOFs. This time in the presence of Ag-deposited MIL-88A and (FeNi)MIL-88A the reaction proceeds smoothly and led to the similar yields (entries 9,10). Next, we went further and executed the reaction merely by use of mixed-metal MOFs and eliminated the oxidant from the reaction (entries 11,12). To our delight, even in the absence of additional oxidant, the reactions led to the desired D-A/aromatization product in 41 and 46% yields, respectively. Compared with the entry 1 in which used unmodified MIL-88A, it can be concluded that silver and nickel must have a synergistic effect when added into the framework. Therefore, (FeNi)MIL-88A (10 mg, about 0.017 mol% according to ICP) was chosen as the best catalyst in the absence of any oxidant. In continuation, the effect of various solvents in the reaction was studied (entries 13-17). Among all solvents used, best yield was obtained in water. No product was formed in the presence of acetic acid as an additive confirming that the only requirement to promote the reaction is our prepared catalyst (entry 18). Accomplishing the reaction in water as a safe solvent apart from exclusion of the oxidant is quite an achievement meeting Green Chemistry postulates. Lowering the reaction time to 6 h led to a drop in the yield (entry 19).

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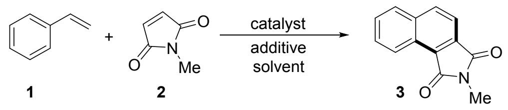
Table 1. Screening the reaction conditions [a]



entry	catalyst	additive	solvent	yield%
1	MIL-88A(10 mg)	-	acetonitrile	trace
2	MIL-88A(10 mg)	$AgNO_3$	acetonitrile	38
3	MIL-88A(10 mg)	CuCl	acetonitrile	43
4	MIL-88A(10 mg)	TBHP	acetonitrile	trace
5	MIL-88A(10 mg)	NaClO[b]	acetonitrile	trace
6	MIL-88A(10 mg)	$NaClO_4$[b]	acetonitrile	trace
7	MIL-88A(5 mg)	CuCl	acetonitrile	13
8	MIL-88A(15 mg)	CuCl	acetonitrile	48
9	Ag-MIL-88A (10 mg)	CuCl	acetonitrile	45
10	(FeNi)MIL-88A(10 mg)	CuCl	acetonitrile	52
11	Ag-MIL-88A(10 mg)	-	acetonitrile	41
12	(FeNi)MIL-88A(10 mg)	-	acetonitrile	46
13	(FeNi)MIL-88A(10 mg)	-	toluene	55
14	(FeNi)MIL-88A(10 mg)	-	Ethyl acetate	53
15	(FeNi)MIL-88A(10 mg)	-	DCE	trace
16	(FeNi)MIL-88A(10 mg)	-	ethanol	60
17	(FeNi)MIL-88A(10 mg)	-	H_2O	80
18	(FeNi)MIL-88A(10 mg)	AcOH	H_2O	trace [c]
19	(FeNi)MIL-88A(10 mg)	-	H_2O	45[d]
20	$Ni(NO_3)_2.6H_2O$(10 mg)	-	H_2O	no rxn
21	recovered from #17 [e]		H_2O	78(79,76, 77,75) [f]

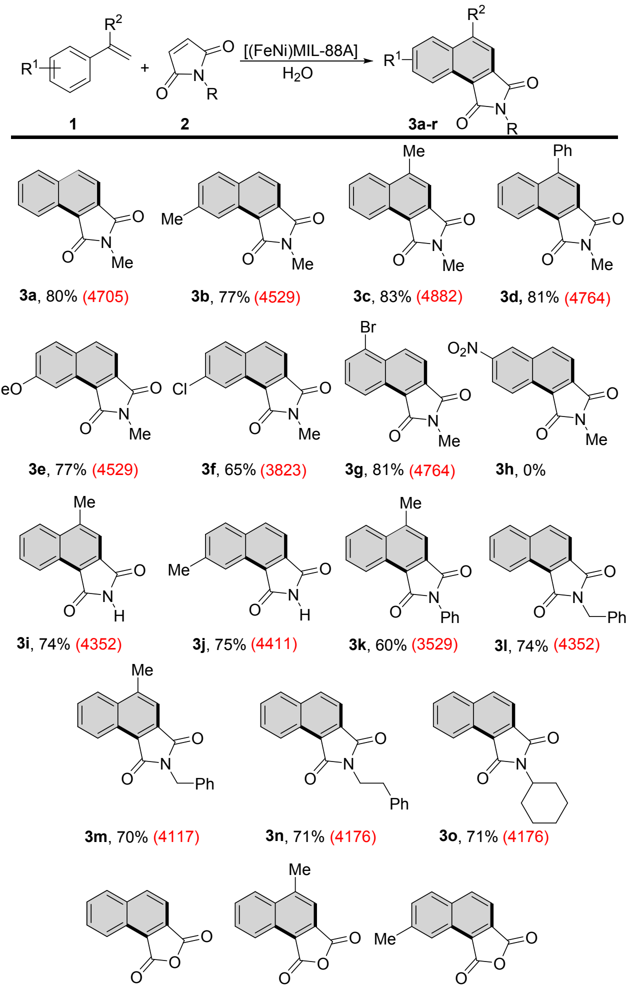
[a] Reaction conditions: styrene (3 equiv), *N*-methyl maleimide (0.05 mmol), additive (1 equiv), solvent (0.3 mL), 100 °C, 20 h. [b] as a 2M solution. [c] 0.05 mL AcOH. [d] Quenched after 6 h. [e] The reaction of entry 15 was repeated in a twofold scale. [f] Reusing of the catalyst in 2nd, 3rd, 4th and 5th runs.

When the reaction was tested in the presence of homogeneous nickel source, no reaction occurred after 20 h (entry 20). The experiment illustrates the heterogeneous type of catalysis and the role of single-site Ni-Fe catalytic centers inside the pores of the prepared MOF (see also supporting information S4; the catalyst *hot filtration test*). Recoverability of the prepared MOF was also tested which showed it could be recovered and reused in successive runs with a slight loss of activity (entry 21, Figure S5). Also, no leaching of Ni or Fe was detected by evaluation of reaction solution using ICP.

Eventually, we found 0.017 mol% (FeNi)MIL-88A in water as the best condition to the desired benzo[e]isoindole-1,3-dione. With the optimized conditions in hand, we then investigated the scope of the reaction (Table 2).

Therefore, miscellaneous styrenes were reacted with *N*-methyl maleimide. *p*-Methyl styrene readily gave the D-A product albeit in a slightly lower yield than styrene (**3a,b**). However, when styrenes possessing substituents at *α*-position were used, an increase in the yields of the corresponding products was observed (**3c,d**). Appending an electron-releasing methoxy group at C4 position furnished the desired product in a 77% isolated yield (**3e**). Gratifyingly, halogen-containing styrenes that can be potential substrates for subsequent reactions were also reacted effectively with their halide segment being remained intact (**3f-3g**).

Table 2. (FeNi)MIL-88A catalyzed annulation of styrenes on maleimides [a]



3a, 80% (4705)
3b, 77% (4529)
3c, 83% (4882)
3d, 81% (4764)
3e, 77% (4529)
3f, 65% (3823)
3g, 81% (4764)
3h, 0%
3i, 74% (4352)
3j, 75% (4411)
3k, 60% (3529)
3l, 74% (4352)
3m, 70% (4117)
3n, 71% (4176)
3o, 71% (4176)
3p, 68% [b] (4000)
3q, 64% [b] (3764)
3r, 66% [b] (3882)

[a] Reactions were run under the following conditions: Styrene (3 mmol), maleimide (1 mmol), (FeNi)MIL-88A (200 mg, 0.017 mol%), water (5 mL), 100 °C, 20 h. The numbers in parentheses are the turnover numbers based on the yield of the products. [b] 5 equiv of maleic anhydride in acetonitrile as solvent was used.

The reaction was also tested for *N*-H-, *N*-phenyl-, *N*-benzyl-, *N*-phenethyl and *N*-cyclohexyl maleimides which resulted in corresponding benzo[e]isoindole-1,3-diones in good yields (**3i-3o**). Maleic anhydride was also used as the dienophile instead of maleimide, generating naphtho[1,2-c]furan-1,3-dione derivatives in 64-68% yields (**3p-r**). In comparison with our previous report which took advantage of homogeneous Pd, the present report is based on a heterogeneous cost-effective catalyst. As an additional benefit, the reaction is also environmentally benign due to the following privileges: (a) no leaching was observed by the catalyst according to ICP; (b) the reaction proceeds in water as the greenest solvent without any need for an organic co-solvent; (c) it works under oxidant-free conditions; and (d) the TON by the (FeNi)MIL-88A is between 3500 to 4800 for various derivatives. According to the recoverability test of the catalyst (Table 1, entry 19), a TON over 27000 was obtained for **3a** during 6 consecutive runs.

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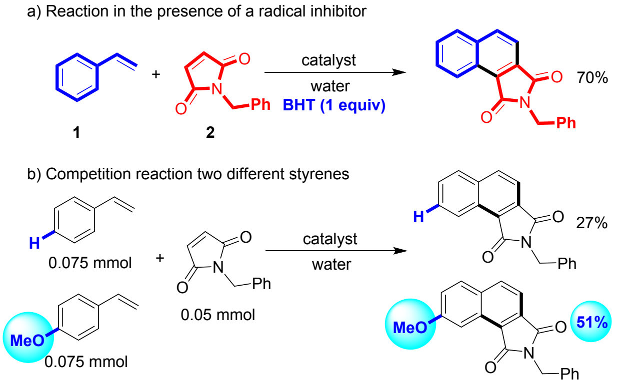
To confirm whether the reaction proceeded through a chain radical pathway or a D-A mechanism, the reaction of styrene **1** and *N*-benzyl maleimide **2** was tested in the presence of BHT as a radical inhibitor which did not bring about a marked change in the yield of the desired product (Scheme 3a). Control experiment proved that a chain radical mechanism might be unlikely. Additionally, the competition reaction between two different styrenes was conducted (Scheme 3b). Evaluation showed that electron-rich *p*-methoxystyrene reacts more efficiently, verifying that electrons must have been released from vinyl arene during the reaction.



Scheme 3. Control experiments

Mechanistic studies: To determine the order of reaction and gain more insight into its mechanism, the changes in concentration of maleimide over time (d[maleimide]/dt) in the reaction of *N*-benzyl maleimide with styrene under the standard conditions were studied by HPLC. In this reaction, aliquots (0.05 mL) were removed every 90 minutes and this was continued for 6 hours. HPLC was used to determine the concentration of *N*-benzyl maleimide at each time by using a calibration plot. Two plots were recorded. The first one was recorded to check the fist-order kinetic and the other for the second-order kinetic reaction. The ln[maleimide] and 1/[maleimide] were plotted versus time (Figure S6a-b). The second plot shows a straighter line with a correlation value of 0.989, which is indicative of a second-order reaction. From the slope of the line, a rate constant of 2.9×10^{-3} L.mol^{-1} sec^{-1} is obtained at 100 ^{o}C. In contrast, when the data is plotted in a first-order manner a much lower correlation value (= 0.964) is obtained. From the plot of Figure S6b it is easily seen that the reaction demonstrates simple second-order reaction kinetics. To determine kinetic parameters of the reaction by Eyring plot and Arrhenius plot, the reaction rate constants were measured at three different temperatures.

The related reaction rate constants k at 80 and 120 ^{o}C were measured as 1.0×10^{-3} and 8.2×10^{-3} L/mol.sec, respectively (Table 3, Figure 6).

Table 3. 1/[maleimide] *vs* time in the reaction of styrene with *N*-benzyl maleimide at 80, 100 and 120 ^{o}C

t (sec)	1/[maleimide] (L/mol) Reaction temperature (K)		
	353	373	393
5400	42.6949	33.0999	22.2135
10800	48.7527	51.7598	60.2159
16200	52.9852	64.6616	110.482

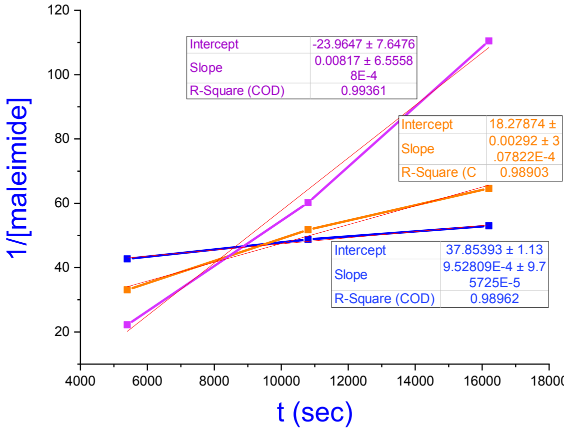


Figure 6. Plot of 1/[maleimide] *vs* time in the reaction of styrene with *N*-benzyl maleimide at 80, 100 and 120 ^{o}C

Also, the kinetic reaction parameters (activation entropy, activation enthalpy, activation Gibbs energy and activation energy) were measured using Eyring- and Arrhenius plots to check whether the reaction proceeded through a Diels-Alder reaction or not. To this end, the concentrations of *N*-benzyl maleimide in reaction coordination were determined at three different temperatures (80, 100 and 120 ^{o}C) and the plots of lnk versus 1/T and ln(k/T) versus 1/T were recorded (Figure 7, Table 4).

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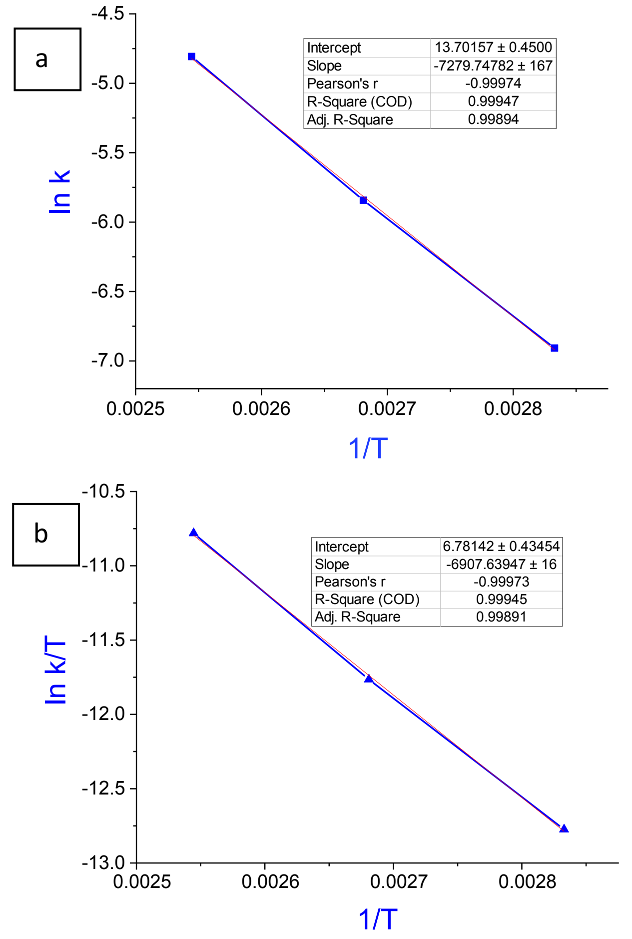


Figure 7. Arrhenius (a) and Eyring (b) plots of the reaction of styrene with *N*-benzyl maleimide in water

Table 4. The kinetic parameters of the reaction of styrene and N-benzyl maleimide[a]

$\Delta S^{\ddagger}$ (J/mol.K)	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta G^{\ddagger}$ (kJ/mol)	E_a (kJ/mol)
-141.1	**57.4**	**110.0[a]**	**60.5**

[a] The activation free energy $\Delta G^{\ddagger}$ was estimated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at 100 °C.

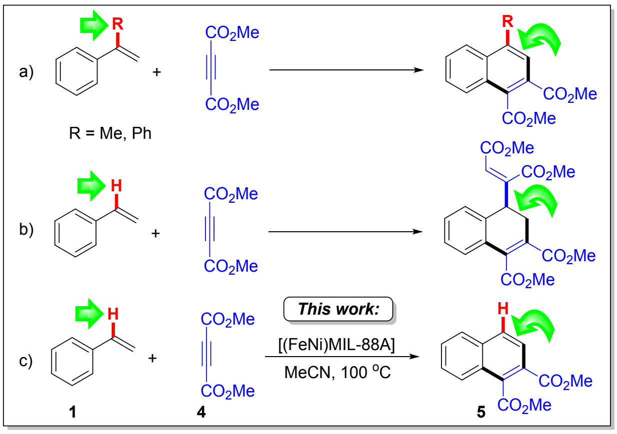
According to Eyring plot, the activation entropy of the reaction is about -141.1 e.u, in the range of that typical of D-A reactions (from -120 to -175 e.u) [32] and more negative than that of stepwise organic reactions.[33] Furthermore, to rule out the probable ionic/polar transition states, reaction constant k of the reaction was measured in various solvents (Table 5).

Table 5. Solvent effect in the reaction of *N*-benzyl maleimide with styrene on the optimal conditions

entry	solvent	$10^3\times$ second-order rate constant k, L/mol.sec
1	H_2O	2.9
2	EtOH	2.4
3	toluene	2.1
4	EtOAc	1.9
5	MeCN	1.6

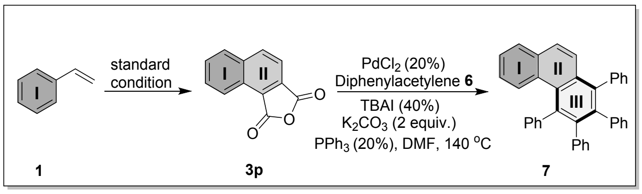
Based on the data acquired it was found that the reaction constant changed only slightly over the change of solvent. The slight acceleration of the reaction in the protic solvents may results from hydrogen-bonding of water and/or EtOH to the polarized activated T.S.[34] Thus, considering that no intermediate was observed in the reaction and on the basis of experimentally found large negative value of activation entropy [35] it can be proposed that the reaction proceeded through a D-A mechanism. Therefore, in line with the recently published work by Bickelhaupt's group demonstrating that Lewis acids catalyze D-A reactions by reduction of repulsion between the π-systems of diene and incoming dienophile,[36] it can be presumed that in this reaction the MOF catalyst acts as a Lewis acid to promote D-A cyclization within its mesopores.

Although the number of publications concerning the reaction of styrene with triple bonds has been more prevalent than those reporting its reaction with double bonds, it still falls into the category of the least developed reactions. Among the few examples that have been released so far, only α-substituted styrenes in which the active α position was blocked by a substituent furnished the expected aromatic D-A products (Scheme 4a).[37] However, when styrene with accessible double bond position was utilized, two molecules of alkynes got involved and dihydronaphthalene was obtained (Scheme 4b).[37b,38] Here, to further expand the versatility of this approach, maleimide was replaced with dimethyl acetylene dicarboxylate **4** (DMAD) the reaction of which gave rise to dimethyl naphthalene-1,2-dicarboxylate **5** in 66% yield through an annulation/oxidative aromatization process (Scheme 4c). Satisfyingly, as opposed to prior reports we managed to gain naphthalene without occupying the active α-site of styrene substantiating the efficiency of this approach. This procedure can be a suitable alternative to the prevailing methods which need either as high a temperature as 180 ˚C or commercially unavailable starting materials to yield similar product.[39]



Scheme 4. Annulation of styrenes on DMAD

PAHs, main component of OLEDs and TFTs, are classically synthesized using pre-functionalized molecules during stepwise methods.[40] As an alternative way to the synthesis of PAHs, newly one-shot APEX reactions have received significant attention by use of a 'template arene' and a 'π-extending reagent'.[41] Recently, Itami *et al.* reported the first K-selective π-extension on phenanthrene for the synthesis of nanographene.[42] However, despite all efforts, APEX reactions on naphthalene have been rarely studied.[41] The only report on this front was disclosed by Cramer *et al.* in which annulation took place in the K-region of naphthalene.[43] Having said that, L-selective π-extension on naphthalene has not been explored so far. Previously, it was shown that phthalic anhydrides can be used as precursors of PAHs.[44] Yet, the number of phenanthrenes possessing aryl substituents at peripheral rings, due to unavailability of cyclic anhydride as its starting material, was only limited. Hence, the products of our reaction can be used as starting materials for further functionalization. To showcase the indirect broad application of our products both in the organic synthesis and nanotubes, we reacted cyclic anhydride **3p** with diphenyl acetylene **6** with manipulation of the previous report which successfully led to the synthesis of 1,2,3,4-tetraphenylphenanthrene **7**, a readily convertible compound to other PAHs, in 41% isolated yield (Scheme 5).



Scheme 5. The three Rings: Synthetic utility of product **3p** in the synthesis of unsymmetrical highly-substituted phenanthrene

Conclusion

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In conclusion, the first MOF-catalyzed D-A type annulation of vinyl arenes as diene on maleimides has been introduced. The reaction is also applicable to the electron-poor triple bonds leading to naphthalenes bearing electron-withdrawing substituents. Also, the synthetic utility of the product successfully led to a PAH target molecule, ensuring that simple styrenes can be a parent molecule of PAHs. To the best of our knowledge this is the first example of π-extension of styrene to PAH families.

Experimental section

The synthesis of nickel-exchanged MIL-88A ((FeNi)MIL-88A)

$FeCl_3.6H_2O$ (2.8 mmol, 0.757 g) and $Ni(NO_3)_2.6H_2O$ (1.4 mmol, 0.4 g) were added to a vessel and 30 mL deionized water was added. Then fumaric acid (4.2 mmol, 0.487 g) was added and the resulted mixture was stirred for 15 minutes. The mixture was transferred into a Teflon-lined autoclave and heated at 100 °C for 15 h. After filtration and washing with hot water, 0.35 g mustard color powder was obtained. The product was analyzed by various spectroscopic methods.

The synthesis of silver-deposited on MIL-88A

MIL-88A was prepared according to the literature. Fumaric acid (4.2 mmol, 0.487 g) and $FeCl_3.6H_2O$ (4.2 mmol, 1.13 g) were added to a vessel containing 21 mL deionized water. The mixture was stirred for 1 h at room temperature and then transferred into a 70 mL Teflon-lined autoclave. The autoclave was placed in an oven and heated to 70 °C for 8 h. After cooling to room temperature and centrifugation, the resulted solid was washed thoroughly with hot water and ethanol and dried at 100 °C to yield MIL-88A. $AgNO_3$ (0.25 mmol, 37 mg) was dissolved in a 35 mL 1:1 solution of deionized water and ethanol. 0.25 g of the as-prepared MIL-88A was added to the resulting solution and heated to 85 °C for 1 day. The solid was washed with water and ethanol and dried at room temperature which finally resulted in a yellowish-orange powder (0.2 g).

General procedure for the synthesis of Benzo[e]isoindole-1,3-diones

In a vial equipped with a stir bar, vinyl arene (3 mmol), maleimide (1 mmol) and (FeNi)MIL-88A (0.2 g, 0.017 mol%) were dissolved in water (5 mL) and capped. The resulting mixture was heated in an oil bath at 100 °C for 20 h. After extraction with dichloromethane and drying the organic layer over sodium sulfate, the solution was evaporated under reduced pressure. The organic residue was purified by column chromatography. Pure benzo[e]isoindole-1,3-dione was obtained after recrystallization of the product from *n*-hexane.

General procedure for the synthesis of Naphtho[1,2-c]furan-1,3-diones

Vinyl arene (1 mmol), maleic anhydride (5 mmol, 0.49 g) and (FeNi)MIL-88A (0.2 g, 0.017 mol%) in acetonitrile (5 mL), was stirred at 100 °C for 20 h in a capped vessel. After extraction with dichloromethane and drying over sodium sulfate, the organic layer evaporated under reduced pressure. The organic residue was purified by a silica loaded column chromatography. Recrystallization of the product using *n*-hexane gave pure products.

The synthesis of 1,2,3,4-tetraphenylphenanthrene (7)

Naphtho[1,2-c]furan-1,3-dione **3p** (1mmol), diphenyl acetylene 6 (2 equiv), $PdCl_2$ (20 mol%), *tetra-n*-butylammonium iodide (40 mol%), triphenylphosphine (20 mol%) and K_2CO_3 (2 equiv) were dissolved in DMF (5 mL) and capped. The mixture was heated at 140 ^oC for 20 h. The resulted mixture was extracted with dichloromethane and the organic layer was dried over sodium sulfate. The solution was evaporated under reduced pressure and the organic residue was purified by column chromatography.

Hot filtration test of the catalyst

To study the homogeneous or heterogeneous type of the catalyst, the reaction of styrene **1** and *N*-benzyl maleimide **2** in the optimal condition was quenched after 6 h when it resulted in 32% yield of **3a**. The catalyst (FeNi)MIL-88A was filtered from the hot reaction solution and the reaction was allowed to continue for further 14 h by the filtrate. The reaction led to 35% yield at the end of 20 h. Experiment confirms that the reaction proceeds inside the (FeNi)MIL-88A as a heterogeneous catalyst not by the homogeneous solution.

Conflicts of interest

There are no conflicts to declare.

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