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Aerobic oxidative alkynylation of H-phosphonates and amides: an efficient route for the synthesis of alkynylphosphonates and ynamides using a recyclable Cu–MnO catalyst†

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An atom-economical and efficient route for the synthesis of alkynylphosphonates and ynamides by aerobic oxidative alkynylation of H-phosphonates and amides with both aliphatic and aromatic alkynes using our synthesized recyclable heterogeneous Cu–MnO catalyst has been developed. The phosphorylation was carried out under base- and ligand-free conditions, and in the presence of air as the sole oxidant. The reaction is compatible with a wide variety of functional groups and generates alkynylphosphonate and ynamide products in good to excellent yields. Both reactions can be scaled up to the gram scale without any decrease in the reaction yield and the reaction time is less compared to literature reports. The catalyst is recyclable and reused several times without any significant loss of reactivity.

Introduction

Direct functionalization of the C(sp)–H bond of the terminal alkyne for the construction of the C(sp)–P bond and C(sp)–N bond is highly demanded due to their great interest in chemistry and biology.[1–15] The importance of phosphorous compounds in organic synthesis and their presence in bioactive molecules motivated chemists to develop new methodologies for C(sp)–P bond forming reactions.[8–15] Alkynylphosphonates, containing reactive triple bonds and phosphoryl groups, are a very important class of functional molecules. Therefore, considerable effort has been made for the synthesis of alkynylphosphonates. Traditionally, the reaction of $(RO)_2P(O)Cl$ as a phosphorus electrophile with Li or Mg acetylides is one of the most common and effective methods used for the synthesis of alkynylphosphonates.[16,17] However, it has several limitations like a) the use of hazardous chemicals and generation of toxic waste, and b) poor functional group tolerance. Other alternative strategies for the synthesis of alkynylphosphonates are the reaction of 1,1-dibromo-1-alkenes with H-phosphites,[18,19] oxidative decarboxylative coupling of aryl propiolic acids with dialkyl H-phosphonates,[20,21] cross-coupling with alkynylcopper reagents and 1-alkynyl sulfones[22] and others.[23] On the other hand, the atom economical strategy of coupling terminal alkynes with H-phosphonates to synthesize alkynylphosphonates was not fully explored. In 2009, Zhao and Han *et al.* first reported this strategy using CuI as a catalyst and Et_3N as a base in DMSO solvent.[24,25] Zhao and Chen *et al.* reported a similar reaction using $CuSO_4{\cdot}5H_2O$ as a catalyst and Et_3N as a base.[26] Lu and co-workers reported Cu/Cu_2O nanoparticles supported on Nb_2O_5 as catalyst and tri-*n* butylamine as a base.[27] A base is required for their system to deprotonate the terminal alkyne to prepare the intermediate copper acetylide species. Base free approaches were reported by Wang *et al.* using a silica-supported carbene–Cu(II) catalyst,[28] but the catalyst preparation was not so straightforward, and by Moglie *et al.* using homogeneous Cu_2O as a catalyst.[29] Other than copper, expensive palladium catalyzed, silver mediated dehydrogenative coupling of terminal alkynes with secondary phosphine oxides was reported by Han *et al.*[30] and Lei *et al.*[31] More recently, Han *et al.* reported the same reaction in the absence of silver with only a palladium catalyst.[32] Despite the advancement of C(sp)–H bond preparation, the majority of the reactions were carried out under homogeneous conditions, with limitations like the use of an expensive catalyst, poor recyclability, and chances of metal contamination in the final product which is mostly undesired in the synthesis of pharmaceutical molecules. Hence, the development of an atom-economical, environmentally benign and sustainable heterogeneous catalyst for C(sp)–P bond preparation is still demanded for the advancement of this area. As part

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of our ongoing research on heterogeneous catalysis, we have reported lotus shaped Cu–MnO catalyzed direct C(sp^2)–H halogenation and amination reaction,[33–35] and drawn our attention to the field of C(sp)–P bond and C(sp)–N bond construction. Herein, we wish to report an efficient catalytic system for the oxidative coupling reaction of terminal alkynes with H-phosphonates to synthesize alkynylphosphonates using our recently developed reusable spherical Cu–MnO catalyst; the same catalyst also works for the synthesis of ynamides from amide and alkyne coupling.

Results and discussion

Catalyst preparation

The spherical γ-MnO_2 was prepared by our reported procedure.[36] First, $MnCO_3$ was synthesized under hydrothermal conditions, using $Mn(OAc)_2$, $4H_2O$, ammonium carbonate, and oxalic acid as a chelating agent. After that, the material was calcined at 350 °C under aerobic conditions to get spherical shaped γ-MnO_2. Later, copper [$Cu(OAc)_2{\cdot}H_2O$] impregnation was carried out by evaporation to dryness[33] followed by calcination at 350 °C under 10% H_2 in N_2 flow for 6 h. The synthesized Cu–MnO catalyst was fully characterized by SEM, TEM, XRD, and XPS. During calcination, under a hydrogen atmosphere, manganese(IV) oxide was reduced to manganese(II) oxide. SEM and TEM images (Fig. 1a–d) revealed that the Cu–MnO catalyst is spherical in nature with a diameter of 3–4 μm. In the XRD pattern of 5% Cu–MnO, a tiny peak of metallic Cu was observed (Fig. 1e), which indicates that upon calcination under a reducing environment Cu(II) is reduced to a Cu(0) species and homogeneously distributed over the MnO moiety as confirmed by elemental mapping in EDS-SEM analysis (see the ESI† for details). XPS spectra confirmed the presence of both Cu(0) and Cu(II) species in the surface of the catalyst.[33]

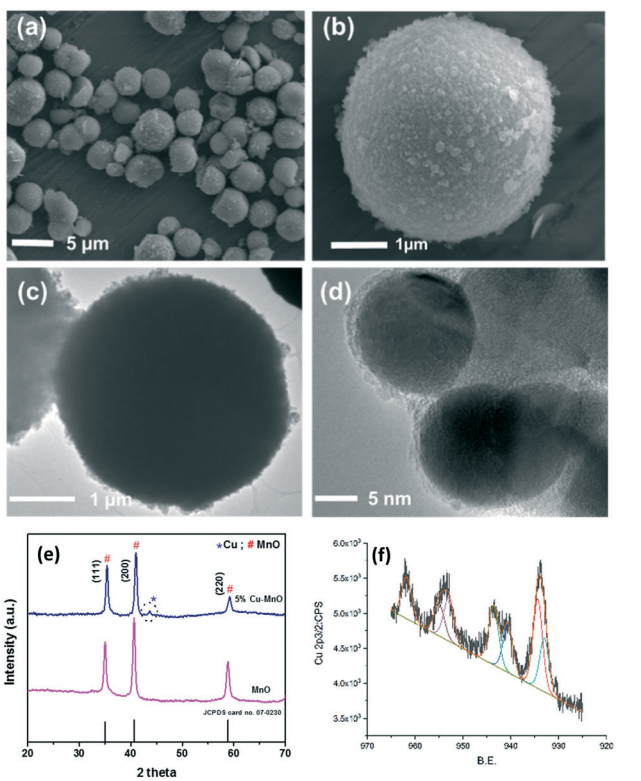


Fig. 1 (a) and (b) SEM images and (c) and (d) TEM images of the synthesized Cu–MnO catalyst; (e) XRD pattern of synthesized Cu–MnO and MnO catalysts; (f) Cu 2p XPS spectra of the 5% Cu–MnO catalyst.

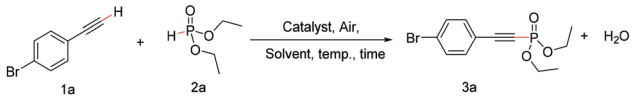
Reaction optimization

After the synthesis and complete characterization of the Cu–MnO catalyst, we started our investigation, and C–P bond formation between 4-bromophenylacetylene (**1a**) and diethyl phosphite (**2a**) was selected as the model reaction to optimize the reaction conditions (Table 1). Our initial investigation started by using our developed catalyst, 5 wt% Cu on MnO. **1a** reacted with **2a** (2 equiv.) in toluene solvent at 100 °C in a closed carousel reaction tube with air for 1.5 h. 40% consumption of **1a** was observed and produced the desired coupled product diethyl ((4-bromophenyl)ethynyl)phosphonate, 3a, in 32% isolated yield (Table 1, entry 1). Encouraged by the result, we first screen solvents for this coupling reaction, as it has been reported[29] that solvents also play a crucial role in this reaction. However, THF and acetonitrile did not work well (entries 2 and 3), whereas DMF showed a similar reactivity, and 38% of the desired product was obtained (entry 4). To our delight, when DMSO was used as the solvent, the reaction went smoothly, and an excellent yield of **3a** (94%, entry 5) was observed. We tried to reduce the reaction temperature to 50 °C and only 56% was obtained, whereas at room temperature a trace amount of the product was obtained. When we reduced the loading of phosphite to 1 equiv. (1 : 1 ratio), we observed 58% of **3a**. Then, we checked the reaction without Cu, in both MnO and MnO_2 under similar reaction conditions, and no reaction took place, so copper is essential for the reaction. As expected, in the absence of a catalyst, no reaction was observed (entry 11). After that, we carried out the reaction under inert conditions to check the role of oxygen, and no reaction took place, so oxygen is also essential for the reaction. Instead of using air, we carried out the reaction under oxygen, and a similar reactivity was observed (entry 13).

With the optimized conditions in hand (Table 1, entry 5), we next examined the scope and limitations of the substituted phenylacetylene. As shown in Table 2, various functional groups including electron donating groups and electron withdrawing groups at the *para* position of the phenyl ring worked well and provided the alkynylphosphonate products in good to excellent yields.

Simple phenyl acetylene worked very well, and an excellent yield was observed (93%, entry **3b**), while other moderate to weak electron withdrawing groups and electron donating groups like bromo, fluoro, methyl, and *tert*-butyl showed high reactivity and furnished the desired products in excellent yields (entries **3a–3e**). The derivatives with a strong electron donating group such as methoxy (78%, **3f**) and dimethylamine (83%, **3g**) produced the desired products in

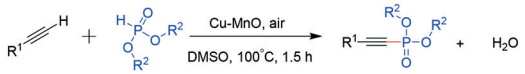
Table 1 Optimization of alkynylation of dialkyl phosphites[a]

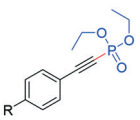


Entry	Catalyst	Solvent	T (°C)	Yield (%)
1	5 wt% Cu–MnO	Toluene	100	32
2	5 wt% Cu–MnO	THF	100	Trace
3	5 wt% Cu–MnO	CH_3CN	100	Trace
4	5 wt% Cu–MnO	DMF	100	38
5	5 wt% Cu–MnO	DMSO	100	94
6	5 wt% Cu–MnO	DMSO	50	56
7	5 wt% Cu–MnO	DMSO	rt	Trace
8	5 wt% Cu–MnO	DMSO	100	58[b]
9	MnO	DMSO	100	NR
10	γ-MnO_2	DMSO	100	NR
11	—	DMSO	100	NR
12	5 wt% Cu–MnO	DMSO	100	NR[c]
13	5 wt% Cu–MnO	DMSO	100	94[d]

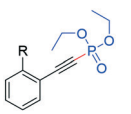
[a] Standard reaction conditions: 0.25 mmol, H-phosphonates 2 equiv., solvent 1 ml, catalyst 12 mg (3.75 mol% Cu), temp: as mentioned in the table, in air, for 1.5 h. [b] Diethyl phosphite 1 equiv. [c] Reaction in a N_2 atmosphere. [d] Oxygen atmosphere.

Table 2 Substrate scope of alkynylation of H-phosphonates[a]

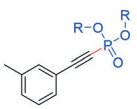




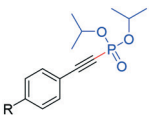
3a, 94%, R = Br
3b, 93%, R = H
3c, 94%, R = F
3d, 97%, R = Me
3e, 95%, R = ^{t}Bu
3f, 78%, R = OMe
3g, 83%, R = NMe_2
3h, 88%, R = CN



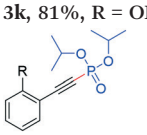
3i, 87%, R = CF_3
3j, 94%, R = Cl
3k, 81%, R = OMe



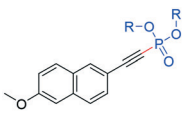
3l, 94%, R = –Et
4l, 91%, R = –iPr



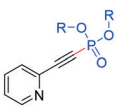
4a, 93%, R = Br
4b, 92%, R = H
4c, 90%, R = F
4d, 95%, R = Me
4e, 94%, R = ^{t}Bu
4f, 81%, R = OMe
4g, 79%, R = NMe_2
4h, 72%, R = CN



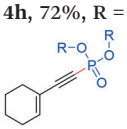
4i, 86%, R = CF_3
4j, 92%, R = Cl
4k, 79%, R = OMe



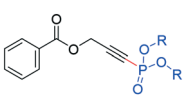
3m, 62%, R = –Et
4m, 63%, R = –iPr



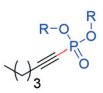
3n, 38% R = –Et
4n, 37%, R = –iPr



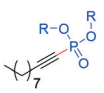
3o, 89% R = –Et
4o, 90%, R = –iPr



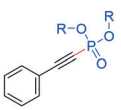
3p, 91% R = –Et
4p, 92%, R = –iPr
4q, 88%, R = –butyl



3r, 95% R = –Et
4r, 94%, R = –iPr



3s, 94% R = –Et
4s, 91% R = –iPr



3t, 90% R = –Me
4t, 92%, R = –butyl

[a] Standard reaction conditions: 0.25 mmol, H-phosphonates 2 equiv., DMSO 1 ml, 5% Cu–MnO catalyst 12 mg (3.75 mol% Cu), 100 °C, in air, for 1.5 h.

good yields. Meanwhile the strong electron withdrawing group nitrile works well, as an excellent yield (88%, **3h**) of the desired product was observed. Placing the functional groups, *e.g.*, trifluoromethyl, chloro, methoxy, and methyl, at the *ortho* and *meta* positions of the phenyl ring resulted in a similar reactivity (81–94%, entries **3i**–**3l**). Other aromatic and heteroaromatic alkynes were also tested and found to be good substrates, as the phosphorylation took place with

moderate to good yields. A low yield of the pyridine derivative (**3n**, 38%) was achieved, which may be due to the coordination of copper with pyridine. Aliphatic terminal alkynes were also successfully phosphorylated in our advanced catalytic system and gave excellent yields of the desired alkynylphosphonate products (**3o–3s**, 89–95%). Next, we examined diisopropyl phosphite as the phosphorylating agent for all the substrates, and to our delight, the phosphorylation proceeds smoothly and furnished the corresponding alkynylphosphonates in good to excellent yields (up to 95%, entries **4a–4s**) for both aromatic and aliphatic alkynes. Besides diethyl phosphite and diisopropyl phosphite, other alkyl H-phosphonates like dimethyl phosphite and dibutyl phosphite were also tested in a coupling reaction with phenylacetylene, and we got excellent yields (**3t**, 90% and **4t**, 92%) of the corresponding alkynylphosphonate products. One interesting thing we have observed is that when a free lone pair is available in the aryl substituent, like the presence of an OMe, NMe_2 or CN functional group (**3f–h**, **k**, **m** and **4f–h**, **k**, **m**) on the aromatic ring, a little lower yield was observed, which might be due to it acting as a ligand (Lewis base donor) and coordinating with the copper.

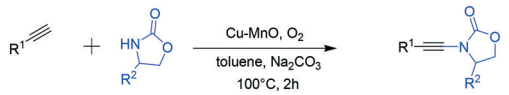
On the other hand, ynamides are also essential synthetic intermediates in organic synthesis, and they are also useful substrates in several organic transformations.[37–48] Cu-Catalyzed oxidative direct amidation of a terminal alkyne with an amide for the synthesis of ynamides was first reported by Stahl and co-workers using 5 equivalents of amide, 20 mol% catalyst loading and a ligand.[49] $Cu(OH)_2$ catalyzed cross-coupling of a terminal alkyne with amides (3 equivalents) was reported by Mizuno and co-workers,[50,51] who mentioned that highly dispersed $Cu(OH)_2$ species supported on Al_2O_3 and TiO_2 as a catalyst were not effective for cross coupling. Several groups also reported the Cu catalyzed oxidative amidation of a terminal alkyne with an N-nucleophile.[52,53] We believe that our developed heterogeneous Cu–MnO catalyst could be a suitable catalyst for the cross-coupling reaction of a terminal alkyne with an amide. We began to investigate the reaction of phenylacetylene and oxazolidin-2-one (2 equiv.) in the presence of our developed 5 wt% Cu–MnO catalyst under an oxygen atmosphere in toluene at 100 °C, but unfortunately the desired ynamide was not obtained. We realized that a Brønsted base might be required for this reaction, which could help to abstract the proton from the alkyne to generate reactive copper acetylides and also abstract the proton from amide derivatives to make them more reactive, so we planned to use Na_2CO_3 and $NaHCO_3$ as bases. To our delight, in the presence of a suitable base, the reaction proceeds excellently, and an almost quantitative yield of ynamide was obtained (97–98%, entries 2 and 3, Table 3). Further screening of solvents revealed that toluene was the best solvent (ESI,† Table S1). We run the reaction in the presence of air instead of pure oxygen, and a slightly lower yield (75%, entry 4) was observed. In contrast, in an inert atmosphere, no ynamide product was obtained, which indicates that molecular oxygen as an oxidant is essential for this reaction. Further decreasing the amount of nucleophile leads to a decrease in the ynamide yield and an increase in the yield of the Glaser coupling product. The coupling of several oxazolidinones and other nitrogen nucleophiles with various aryl and alkyl acetylene derivatives was next investigated with our optimized conditions. The results are summarized in Table 4. Aromatic alkynes consisting of both electron donating and electron withdrawing functional groups, such as Me, OMe, NMe_2, ^{t}Bu, Br, F, and CN, on the *para*-position of the phenyl ring reacted with oxazolidin-2-one very well and produced the corresponding ynamides in good to excellent yields (Table 4, entries **5a–5h**). We next investigated other cyclic carbamates like 4-(chloromethyl)-oxazolidin-2-one and (*S*)-4-benzyloxazolidin-2-one, which showed a similar reactivity and gave the desired ynamides in good to excellent yields (entries **5i–5p**). Other aromatic alkynes, such as 2-ethynyl-6-methoxynaphthalene, react well with oxazolidin-2-one and derivatives leading to good yields of the corresponding ynamides (entries **5q–5s**). The substitution of the functional group at the *ortho* and *meta* positions in the phenyl ring does not have much effect in the coupling reactions, as high yields of the desired ynamides were obtained (entries **5v–5x**). Another nitrogen nucleophile, *N*-methyl-*p*-toluenesulfonamide, is also a viable substrate,

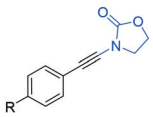
Table 3 Optimization for ynamide synthesis[a]

Entry	Catalyst	Solvent	Base	T (°C)	Yield (%)
1	5 wt% Cu–MnO	Toluene	—	100	0
2	5 wt% Cu–MnO	Toluene	Na_2CO_3	100	98
3	5 wt% Cu–MnO	Toluene	$NaHCO_3$	100	97
4	5 wt% Cu–MnO	Toluene	Na_2CO_3	100	75[b]
5	5 wt% Cu–MnO	Toluene	Na_2CO_3	100	Trace[c]
6	5 wt% Cu–MnO	Toluene	Na_2CO_3	100	58[d]

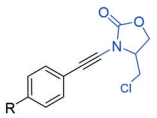
[a] Standard reaction conditions: 0.25 mmol phenylacetylene, 2-oxazolidone (2 equiv., 0.5 mmol), solvent 1 ml, catalyst 12 mg (3.75 mol% Cu), base (2 equiv.), 100 °C, under O_2 atm., for 2 h. [b] Reaction in air atm. [c] Reaction in a N_2 atmosphere. [d] 2-Oxazolidone 1.2 equiv.

Table 4 Substrate scope of amidation[a]

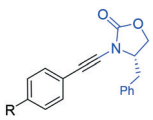




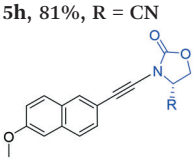
5a, 95%, R = H
5b, 91%, R = Me
5c, 93%, R = OMe
5d, 82%, R = NMe_2
5e, 90%, R = ^{t}Bu
5f, 88%, R = Br
5g, 90%, R = F
5h, 81%, R = CN



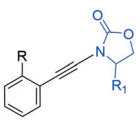
5i, 96%, R = H
5j, 92%, R = Me
5k, 85%, R = OMe
5l, 82%, R = NMe_2
5m, 90%, R = F



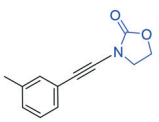
5n, 75%, R = Me
5o, 82%, R = OMe
5p, 68%, R = Br



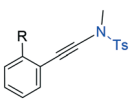
5q, 78%, R = H
5r, 80%, R = CH_2Cl
5s, 75%, R = Bn



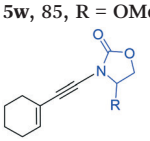
5vt, 89%, R = Cl, R_1 = H
5u, 81%, R = CF_3, R_1 = H
5v, 84%, R = OMe, R_1 = H
5w, 85, R = OMe, R_1 = CH_2Cl



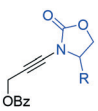
5x, 94%



5y, 80%, R = H
5z, 71%, R = CF_3



5aa, 96%, R = H
5ab, 90%, R = CH_2Cl



5ac, 85%, R = H
5ad, 82%, R = CH_2Cl

[a] Standard reaction conditions: 0.25 mmol, amide 2 equiv., Na_2CO_3 2 equiv., toluene 1 ml, 5% Cu–MnO catalyst 12 mg (3.75 mol% Cu), 100 °C, in air, for 2 h.

affording ynamides in good yields (entries **5y** and **5z**). Next, we investigated the reaction scope of alkyl substituted terminal alkynes with different oxazolidinone coupling partners, affording ynamides in good to excellent yields (entries **5aa**–**5ad**).

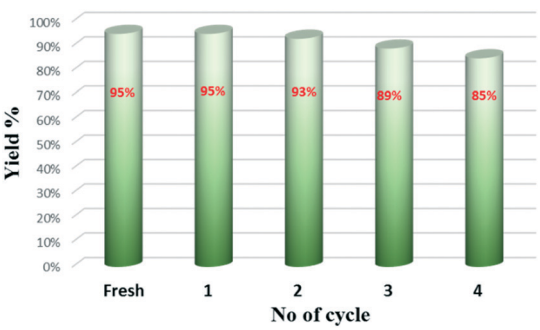
The reaction of phenylacetylene and oxazolidinone is scaled up to the gram scale, and the ynamide (**5a**) was successfully synthesized in a comparable yield (92%). Similarly, the phosphorylation was also scaled up to a 1 gram scale, and the alkynylphosphonate (**3b**) was successfully prepared with a similar yield (93%).

The hot filtration test confirmed the heterogeneity of the reaction. We monitored the reaction progress after taking out the reaction mixture *via* cannula to remove the catalyst, no further reaction was observed, which suggests that the active catalyst was not leached out to the solution and the reaction is heterogeneous in nature. ICP-AES analysis of the filtrate of the standard reaction (synthesis of **3a** and **5a**) was also carried out to analyze catalyst leaching after completion of the reaction, and a negligible amount of Cu (<2 ppm) leached in the filtrate for both cases. After completion of the reaction, the catalyst was filtered, washed and calcined for recycling, and it exhibited good reusability (Table 5).

Kinetic study

In order to better understand the reaction profile, kinetic studies were performed using phenylacetylene and diethyl H-phosphonate as a reactant. The production of alkynylphosphonates and the Glaser coupling product[54] diyne was monitored by HPLC analysis. When 2 equiv. of H-phosphonates (Fig. 2A) was used in the reaction, the reaction went very fast at the beginning, almost 75% product was obtained within 20 min, and the reaction was completed in 90 min; 94% of the desired alkynylphosphonate was obtained with *ca.* 2% diyne. Upon reducing the amount of H-phosphonates to 1.2 equivalents (Fig. 2B), within 10 min, 12% diyne and 55% of the desired alkynylphosphonate were identified. Finally, we observed that with a low amount of the coupling partner, the production of the unwanted

Table 5 Reusability of the catalyst



The catalyst was filtered, thoroughly washed with water and acetone, and dried under vacuum, followed by calcination at 350 °C under 10% H_2 in N_2 flow for 6 h, then reuse.

homocoupled dimer product (~15%) increased and subsequently, the yield of the desired product diminished. In the case of ynamide synthesis (Fig. 2C and D), using phenyl acetylene and oxazolidin-2-one as a substrate, a similar result was observed, where reducing the amount of the N-nucleophile to 1.2 equivalents increased the production of the Glaser coupling diyne product.[54] Also, the amidation reaction rate is a little slower than the phosphorylation reaction as observed from the reaction kinetics. From the kinetic studies, it was confirmed that an excess of the nucleophile is required for both reactions to prevent homocoupled diyne product formation.

To get some insight into the reaction mechanism, we carried out some control experiments. Both reactions went smoothly in the presence of a radical scavenger like BHT and TEMPO (Scheme 1, eqn (1)), and similar yields of the desired coupling products were observed, which clearly indicates that the reactions do not proceed through the radical pathway. With decreasing the amount of the phosphorylation or amidation reagent, the yield of the C–P (60%) and C–N (51%) coupled products decreases, whereas the C–C homo-coupled Glaser coupling product formation increases (19–24%) under these conditions as reported by others.[49] However, under completely inert conditions both reactions do not proceed, and these results suggest that oxygen is essential for these reactions.

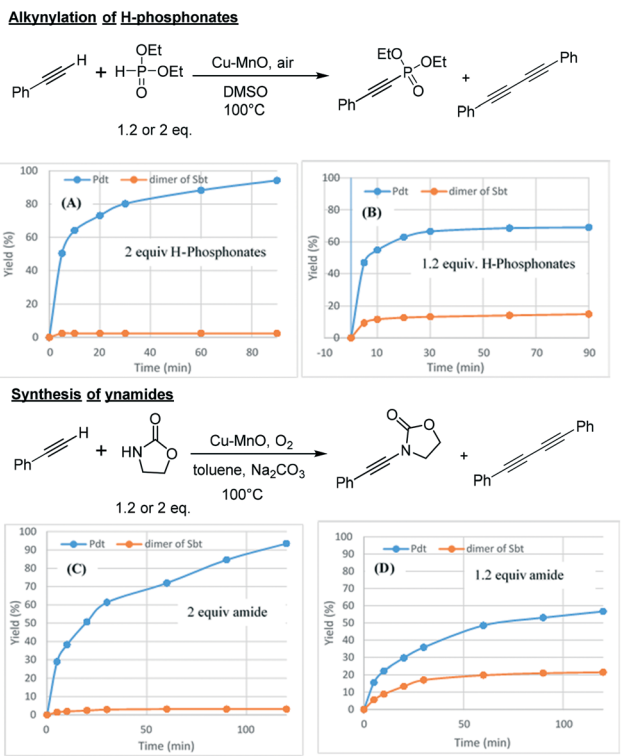


Fig. 2 Kinetics for alkynylation of H-phosphonates (A) with 2 equiv. H-phosphonates and (B) with 1.2 equiv. H-phosphonates and synthesis of ynamides (C) with 2 equiv. amides and (D) with 1.2 equiv. amides. Reaction progress was monitored by HPLC.

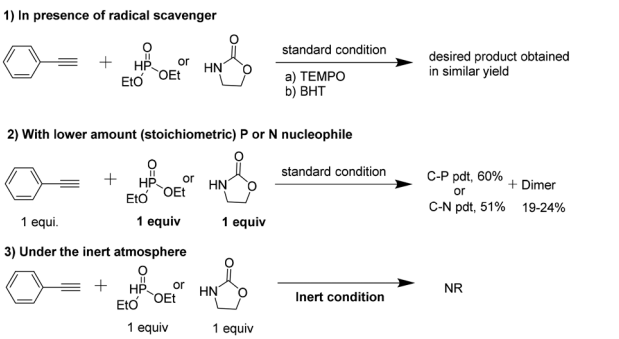
Conclusions

In conclusion, we have developed a very efficient and reusable heterogeneous Cu–MnO catalyst for the aerobic oxidative coupling of a terminal alkyne with H-phosphonates and amides to synthesize alkynylphosphonates and ynamides respectively in excellent yields. A variety of terminal alkynes including electron rich and electron poor aromatics, as well as aliphatic alkynes with several H-phosphonates, delivered the corresponding alkynylphosphonates in very good to excellent yields. Our catalyst is highly reactive, as revealed by the kinetics study, for both cases as the reaction time is shorter compared to literature reports,[23–32,49] where it takes mostly more than 12 h, but in our case, the reaction was completed within 2 h. The added advantage is that the phosphorylation reaction is base and additive free. For ynamide synthesis, a variety of terminal alkynes and different oxazolidinones were successfully utilized and generated the desired products in good to excellent yields. Other nitrogen nucleophiles such as *N*-methyl-*p*-toluenesulfonamide were also viable substrates and afforded the C–N coupled products in good yields. This methodology could be scaled up to the gram scale and tolerate several functional groups. In addition, the catalyst showed very good reusability; up to the fifth recycle it showed a similar productivity.

Experimental section

General procedure I for phosphorylation

In a carousel reaction tube, the Cu–MnO catalyst (12 mg) was placed, and the terminal alkyne (0.25 mmol), dialkyl phosphate (0.5 mmol) and 1 mL DMSO were added to it. The reaction mixture was stirred at 100 °C for 1.5 h under an air atmosphere. After completion of the reaction, the crude reaction mixture was filtered and washed with ethyl acetate (25 mL). The organic layer was washed with water, and then the water layer was re-extracted with ethyl acetate (2 × 25 mL). The combined organic layer was washed with brine solution, dried over Na_2SO_4, and then concentrated under reduced pressure. The resulting residue was purified by flash chromatography (ethyl acetate : hexane) to afford the desired alkynylphosphonate.



Scheme 1 Control experiments to understand the mechanism.

General procedure II for ynamide synthesis

In a carousel reaction tube, the Cu–MnO catalyst (12 mg) and Na_2CO_3 (53 mg, 0.5 mmol) were placed, and then the tube was evacuated and refilled with oxygen three times. Next, the terminal alkyne (0.25 mmol), oxazolidin-2-one (0.5 mmol) and 1 mL toluene were added to it *via* a syringe. The reaction mixture was stirred at 100 °C for 2 h under an oxygen atmosphere. After completion of the reaction, the crude reaction mixture was filtered and washed with ethyl acetate (25 mL). The organic layer was washed with water and brine solution, dried over Na_2SO_4, and then concentrated under reduced pressure. The resulting residue was purified by flash chromatography (ethyl acetate : hexane) to afford the desired ynamide.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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