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# Heterogeneous Catalytic Method for the Copper(II)-Catalysed Addition of *H*-Phosphinates and Secondary Phosphine Oxides to Phenylacetylene

**Kinga Juhász[1] · Bence Varga[1] · Péter Bagi[1] · Zoltán Hell[1]**

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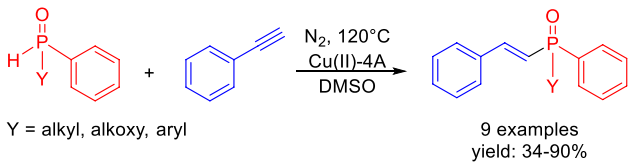
**Abstract**
Copper(II) on 4 Å molecular sieve was found to be an efficient heterogeneous catalyst in the addition of different *H*-phosphinates and secondary phosphine oxides to phenylacetylene. All hydrophosphinylation reactions were completely regioselective, as only β-isomers were formed, and the *E*-alkenylphosphinates and *E*-alkenylphosphine oxides were synthesized in moderate to excellent yields. The catalyst could be reused multiple times in the reaction.

**Graphic Abstract**




**Keywords** Hydrophosphinylation · Heterogeneous catalysis · Copper · Molecular sieve · Alkenylphosphine oxides

## 1 Introduction

Alkenylphosphine oxides represent a group of important compounds in organic, medicinal and agricultural chemistry [1–4]. They are commonly used as building blocks in the preparation of carbo- and heterocyclic compounds [5–8]. The olefinic bond can be modified further to prepare various phosphine ligands [9–12]. Alkenylphosphine oxide scaffolds can also be found in numerous biologically active products or used as such compounds [13–16].

The synthesis of alkenylphosphine oxides usually requires the presence of a transition metal in form of transition metal salts, complexes or the immobilized metals on some kind of support [17–23]. The transition metals most frequently used for the hydrophosphinylation are copper [24–27], nickel [28, 29], palladium [20, 30–32] and rhodium [19–21, 33, 34]. Microwave irradiation has also been used to promote the addition of secondary phosphine oxides to alkynes [35]. Han et al. elaborated the metal-free generation of the alkenylphosphorus non-selective anti-Markovnikov adducts under radical conditions [36]. Radical conditions have also been applied for the selective synthesis of *Z*-alkenylphosphine oxides by Lei and co-workers [37]. Schmidt et al. elaborated the hydrophosphinylation of alkynes under mild conditions in the presence of a lanthanum-based *N,N*-dimethylbenzylamine complex [38]. The earth abundant cobaloxime was used to convert the *H*-phosphine oxide into its reactive radical species under visible light irradiation [39]. The metal-free hydrophosphorylation of ynamides was achieved by the in situ generation of electrophilic phosphorus species to prepare β-aminovinylphosphine oxides [40].

Most of the metal-catalysed reactions mentioned above used homogeneous catalysts for hydrophosphinylations, consequently ligands played an important role in the transformations. Only several among them were

✉ Zoltán Hell
hell.zoltan@vbk.bme.hu

[1] Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest 1111, Hungary

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heterogeneous catalytic process, such as immobilized rhodium catalyst on MSC-41 support [17, 19] or immobilized Rh, Pd, or Ni catalyst on polystyrene bound triphenylphosphane [20, 22]. A related reaction has also been described using heterogeneous catalyst, $Cu/Cu_2O$ nanoparticles supported on $Nb_2O_5$, for the direct synthesis of alkynylphosphonates from alkynes and phosphite esters [41].

Reusability of the catalytic system and the separation of product are the key concerns of the catalytic procedures. The use of suitable heterogeneous catalysts may ease the separation and enable the recycling of the catalyst. Therefore, the development of a heterogeneous catalytic method may be a good alternative in hydrophosphinylation reactions.

In the last decades, our research group has been working on the preparation of different supported metal catalysts. 4 Å molecular sieves and mixed oxides served as solid supports which were impregnated with transition metal salts such as copper and nickel. Supported nickel catalyst showed good activity in the Kumada-coupling [42]. The molecular sieves supported copper(II) catalyst was used in the preparation of propargylamines via $A_3$-coupling [43] and the selective 1,4-addition of arylmagnesium compounds to chalcones [44]. As copper [24–27] and nickel [28, 29] catalysts can be used in homogeneous hydrophosphinylation reactions, we thought that developing the heterogeneous version of such P–C coupling reaction is an idea worth pursuing.

Herein, we present our results achieved in the heterogeneous catalytic hydrophosphinylation of phenylacetylene in the presence of a molecular sieve supported copper(II) catalyst [Cu(II)-4A].

## 2 Experimental

Phenylacetylene, ethyl phenylphosphinate and diphenyl phosphine oxide were purchased from Sigma Aldrich Ltd. The reagents were used without further purification. The solvents were purchased from Merck Chemicals Ltd., and they were used without further purification.

Other *H*-phosphinates (**1a–c**) and secondary phosphine oxides (**4a–f**) were synthesized as described in the literature [45–52].

Thin layer chromatography (TLC) was performed on Merck pre-coated Silica gel 60 $F_{254}$ aluminium plates and visualized by UV irradiation.

Column chromatography was performed on Silica gel 60 with a particle size of 0.063–0.200 mm supplied by Merck.

Surface area of 4A and Cu(II)-4A were measured to investigate their changes after metal deposition. Specific surface areas of samples were measured by nitrogen adsorption and desorption at − 196 °C with BET surface analyser (Micromeritics Model TRISTAR 3000) using BET-BJH method. Prior to the adsorption measurement, the samples were evacuated at 110 °C for 24 h [53].

LC-MS measurements were performed using an Agilent 1100 and Agilent 6130 LC-MS system in positive and negative electrospray mode. $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were made on BRUKER Avance-300 instrument using TMS as an internal standard in $CDCl_3$ for $^1H$ and $^{13}C$ NMR measurements. 85% Solution of $H_3PO_4$ was the external reference for $^{31}P$ NMR chemical shifts.

### 2.1 Preparation of the Catalysts

A suspension of 4 Å molecular sieves (2 g) in deionized water (200 mL) containing the corresponding metallic salt ($CuCl_2$*$2H_2O$, $MnCl_2$*$4H_2O$, $NiCl_2$*$6H_2O$) (0.34 g, 2 mmol) was stirred for 12 h at room temperature. The solid was filtered, washed with deionized water (50 mL) and acetone (20 mL), then dried in an oven at 120 °C for 1 h [43].

### 2.2 Characterization of the Cu(II)-4A Catalyst

The copper content was 5.8 wt%, determined by ICP-OES, which is in good correlation with the theoretical value (6.3 wt%). The original surface area of the molecular sieves (810 $m^2/g$) dropped to 360 $m^2/g$ after the impregnation. During the impregnation copper ions replaces the sodium ions in the synthetic microporous sodium aluminosilicate. But because of the microporous structure of 4A these ions take place on the support's surface. Surface analysis by scanning electron microscope (SEM) showed that the zeolite crystals retained their cubooctahedral form (Fig. 1). Energy-Dispersive X-ray Spectroscopy (EDS) showed that copper evenly covered the support's surface. The size of the particles was in the 2.5–5 µm range [54].

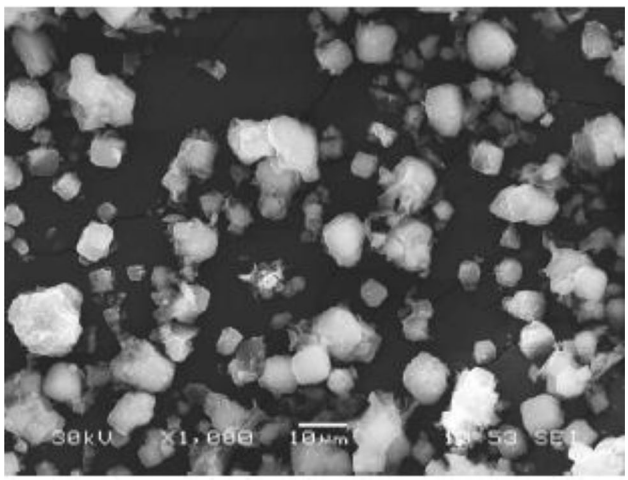



**Fig. 1** SEM image of the Cu(II)-4A catalyst [54]

TPR profile of the catalyst (Fig. 2) showed two peaks, at about 200 °C and at 525 °C. The first corresponds to the reduction of Cu(II) to Cu(I), while the second to the reduction of Cu(I) to Cu(0), verifying the presence of Cu(II) on the catalyst's surface [53]. The measured values are in good agreement with the published data; 155–270 °C for the first, while 360–600 °C for the second reduction step [55, 56].

## 2.3 General Procedure for the Preparation of Compounds 3a–c and 5a–f

The desired products were obtained by the reaction of the corresponding *H*-phosphinate (**1a–c**, 1 mmol) or secondary phosphine oxide (**4a–f**, 1 mmol) and phenylacetylene (**2**, 1 mmol) in DMSO (2 mL) in the presence of Cu(II)-4A catalyst (0.1 g) under nitrogen atmosphere at 120 °C for 12 h. After completion of the reaction the catalyst was filtered and washed with EtOAc. Then, the reaction mixture was diluted with $H_2O$, and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over $Na_2SO_4$, and the solvents were evaporated. The crude product was purified via column chromatography (silica gel, hexane:EtOAc 1:1).

### 2.3.1 Characterization of the Products

*(E)-1-Ethoxylphenylphosphinyl-2-phenylethene* (***3a***) [26]; $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.35–1.38 (t, *J* = 6.9 Hz, 3H), 4.02–4.19 (m, 2H), 6.45–6.53 (dd, *J* = 20.5, 17.4 Hz, 1H), 7.35 (s, 3H), 7.48–7.56 (m, 6H), 7.83–7.87 (dd, J = 12.2, 7.5 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 16.5, 60.9, 117.4, 118.5, 127.8, 128.7, 130.2, 131.4, 131.5, 132.3, 135.0, 147.9. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 31.4. ESI-MS: m/z: 273 $(M+H)^+$.

*(E)-1-Cyclohexylphenylphosphinyl-2-phenylethene* (***3b***) [26]; $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.26 (d, *J* = 9.5 Hz, 1H), 1.44–1.58 (m, 2H), 1.64 (dd, *J* = 13.1, 9.8 Hz, 3 H), 1.69–1.80 (m, 2H), 1.82–1.90 (m, 2H), 1.97–2.05 (m, 1H), 6.49 (dd, *J* = 20.3, 17.4 Hz, 1H), 7.33–7.38 (m, 3H), 7.45–7.51 (m, 4H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.85 (dd, *J* = 12.2, 7.7 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 23.6, 25.2, 33.9, 74.9, 118.1, 119.2, 127.7, 128.8, 130.1, 131.4, 132.1, 147.4. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 29.6. ESI-MS: m/z: 327 $(M+H)^+$.

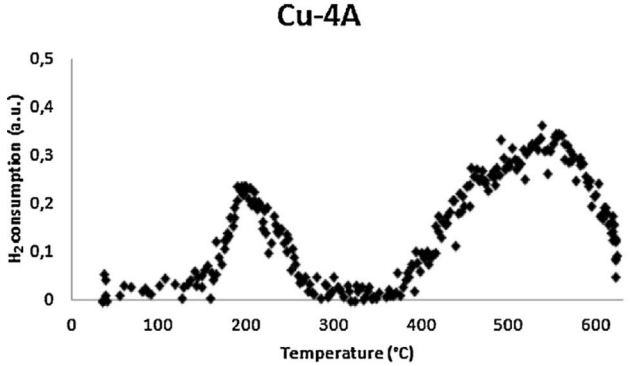



**Fig. 2** TPR profile of the Cu(II)-4A catalyst [53]

*(E)-1-Menthyloxylphenylphosphinyl-2-phenylethene* (***3c***); $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.54 (d, *J* = 6.8 Hz, 1H), 0.81 (d, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 2H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 1.28 (q, *J* = 11.1, 10.7 Hz, 1H), 1.42 (dt, *J* = 22.1, 11.2 Hz, 2H), 1.65 (q, *J* = 15.9 Hz, 2H), 2.24 (m, 1H), 4,12–4.34 (m, 1H), 6.50 (dd, *J* = 20.4, 17.4 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 3H), 7.48 (dt, *J* = 17.0, 9.0 Hz, 5H), 7.56 (dd, *J* = 20.7, 17.7 Hz, 1H), 7.85 (dd, *J* = 12.4, 7.5 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 15.8, 21.2, 21.9, 22.8, 25.7, 31.5, 34.1, 43.7, 48.9, 117.9, 118.9, 127.7, 128.5, 128.8, 130.1, 131.1, 131.4, 131.9, 147.9. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 29.1 (50%), 29.2 (50%). ESI-MS: m/z: 383 $(M+H)^+$.

*(E)-1-Diphenylphosphinyl-2-phenylethene* (***5a***) [26]; $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.84 (dd, *J* = 22.3, 17.4 Hz, 1H), 7.36 (d, *J* = 6.3 Hz, 4H), 7.45–7.54 (m, 8H), 7.76 (dd, *J* = 11.9, 7.8 Hz, 4H). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 118.9, 119.7, 127.9, 128.1, 128.6, 128.7, 128.8, 128.9, 130.2, 131.5, 131.6, 132.0, 147.8. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 24.6. ESI-MS: m/z: 305 $(M+H)^+$.

*(E)-1-(2-Methyoxyphenyl)phenylphosphinyl-2-phenylethene* (***5b***); $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.68 (s, 3H), 6.90 (dd, *J* = 8.3, 5.4 Hz, 1H), 7.05 (dd, *J* = 24.2, 17.5 Hz, 1H), 7.14 (m, 2H), 7.30–7.42 (m, 5H), 7.53 (m, 3H), 7.65–7.73 (m, 3H), 8.07 (dd, *J* = 13.2, 7.5 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 55.4, 118.8, 119.7, 121.2, 121.3, 127.7, 128.2, 128.3, 128.8, 129.7, 130.6, 130.7, 131.3, 134.0, 146.9. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 22.0. ESI-MS: m/z: 335 $(M+H)^+$.

*(E)-1-(2-Trifluoromethylphenyl)phenylphosphinyl-2-phenylethene* (***5c***); $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.94–7.03 (dd, *J* = 25.2, 17.3 Hz, 1H), 7.36 (s, 3H), 7.42–7.43 (dd, *J* = 7.6, 2.9 Hz, 2H), 7.48–7.50 (m, 2H), 7.55–7.56 (m, 2H), 7.59–7.63 (dd, *J* = 12.9, 7.7 Hz, 2H), 7.69–7.71 (m, 1H), 7.72–7.74 (m, 1H), 7.77–7.80 (dd, *J* = 8.3, 4.1 Hz, 1H), 8.41–8.54 (dd, *J* = 13.6, 7.6 Hz, 1H).$^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 117.7, 118.6, 121.9, 122.8, 124.9, 128.0, 128.6, 128.7, 129.0, 130.4, 130.8, 130.9, 132.0, 132.2, 132.6, 135.4, 149.5. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 24.0. ESI-MS: m/z: 373 $(M+H)^+$.

*(E)-1-(Biphenyl-2-yl)phenylphosphinyl-2-phenylethene* (***5d***); $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.19 (dd, *J* = 25.1, 17.3 Hz, 1H); 7.10–7.13 (m, 2H), 7.14–7.17 (m, 3H), 7.19–7.24 (m, 2H), 7.31 (s, 6H), 7.40–7.44 (m, 3H),

7.44–7.48 (m, 2H), 7.56 (t, 1H), 8.04 (dd, $J = 13.4$, 7.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 118.6, 119.4, 126.9, 127.1, 127.5, 127.6, 128.2, 128.3, 128.6, 129.7, 129.9, 130.5, 130.7, 130.8, 131.2, 131.6, 133.3, 133.4, 140.7, 146.8. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 23.7.ESI-MS: m/z: 381 $(M+H)^+$.

*(E)-1-Butylphenylphosphinyl-2-phenylethene (**5e**);* $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.89 (t, $J = 7.3$ Hz, 3H), 1.43 (m, 2H), 1.51–1.71 (m, 2H), 2.00–2.14 (m, 2H), 6.62 (dd, $J = 23.8$, 17.4 Hz, 1H), 7.35 (m, 2H), 7.46–7.54 (m, 6H), 7.73–7.83 (m, 3H). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 13.6, 23.5, 23.9, 30.1, 118.8, 119.6, 127.6, 128.7, 128.8, 129.9, 130.4, 131.6, 132.5, 146.8. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 31.0. ESI-MS: m/z: 285 $(M+H)^+$.

*(E)-1-Cyclohexylphenylphosphinyl-2-phenylethene (**5f**);* $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.02–1.31 (m, 5 H), 1.60–1.89 (m, 6H), 6.68 (dd, $J = 24.6$, 17.3, 1H), 7.30–7.42 (m, 4H), 7.46–7.56 (m, 5H), 7.76 (td, $J = 7.9$, 3.8 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ (ppm): 24.8, 25.8, 26.2, 39.3, 116.9, 117.7, 127.6, 128.5, 128.8, 129.9, 130.7, 131.5, 132.4, 147.7. $^{31}$P NMR (202.4 MHz, $CDCl_3$) δ (ppm): 33.6. ESI-MS: m/z: 311 $(M+H)^+$.

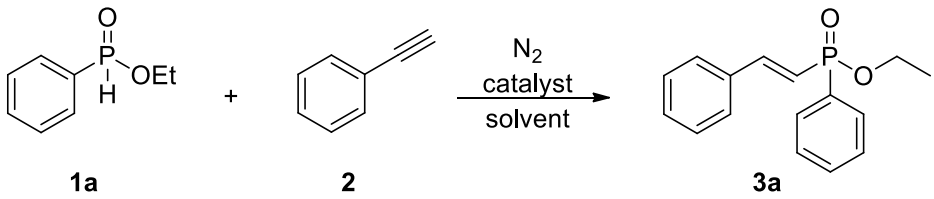
## 3 Results and Discussion

We studied the reaction of different *H*-phosphinates and secondary phosphine oxides with phenylacetylene (**2**) in the presence of molecular sieve supported transition metal catalysts. The reaction of ethyl phenylphosphinate (**1a**) and phenylacetylene (**2**) was chosen for optimization purposes, and the effect of the catalyst, solvent and the reaction time was studied. $^1$H and $^{31}$P NMR spectroscopy and LC-MS were used to follow the progress of the reaction during the optimization study.

According to the literature copper and nickel, further manganese catalysts were tested, all three on 4 Å molecular sieve support. The catalysts were prepared in our research group by the proven impregnation method of 4 Å molecular sieves with the corresponding metal salt in deionized water, followed by filtration and drying [43]. Due to the fact, that *H*-phosphinates and secondary phosphine oxides are prone to oxidation in air at elevated temperatures, the reactions were carried out under nitrogen atmosphere. The results showed, that if the Cu(II)-4A catalyst was changed to Mn(II)-4A or Ni(II)-4A the yields of **3a** decreased significantly (Compare Table 1, Entries 1, 2 and 3). Thus, the Cu(II)-4A catalyst was used for the further experiments.

Next the effect of four different solvents was studied. The reaction temperature was set to 120 °C, unless the boiling point of the corresponding solvent required lower temperature. The reaction time was 12 h. In DMSO and DMF the desired product (**3a**) was prepared in moderate yields (52% or 45%) (Table 1, Entries 3 and 6), but DMSO gave somewhat better results. In contrast, the reactions in 1,4-dioxane and acetonitrile provided the product (**3a**) only in poor yields (5% or 25%) (Table 1, Entries 4 and 5). Analysis of the crude products revealed that complete conversion was not reached

**Table 1** Optimization of the reaction conditions in the reaction of ethyl phenylphosphinate (**1a**) and phenylacetylene (**2**)




**1a** **2** **3a**

| Entry | Catalyst | Solvent | Time (h) | Temperature (°C) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | Mn(II)-4A | DMSO | 12 | 120 | 22 |
| 2 | Ni(II)-4A | DMSO | 12 | 120 | 17 |
| 3 | Cu(II)-4A | DMSO | 12 | 120 | 52 |
| 4 | Cu(II)-4A | 1,4-dioxane | 12 | 100 | 5 |
| 5 | Cu(II)-4A | MeCN | 12 | 80 | 25 |
| 6 | Cu(II)-4A | DMF | 12 | 120 | 45 |
| 7 | Cu(II)-4A | DMSO | 6 | 120 | 38 |
| 8 | Cu(II)-4A | DMSO | 3 | 120 | 25 |

[a]Reagents and conditions: ethyl phenylphosphinate (1 mmol), phenylacetylene (1 mmol), catalyst (0.1 g, 9 mol% Cu), DMSO (2 mL), 120 °C, 12 h

[b]Isolated yield

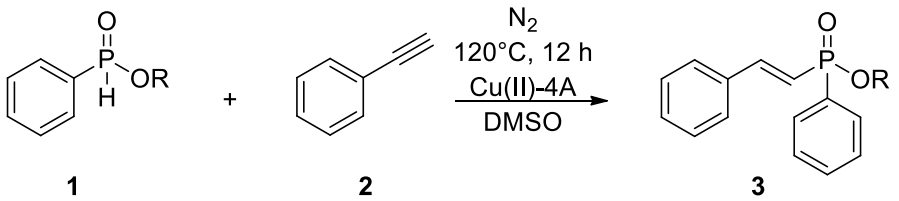
in these instances. A reason for the significantly lower conversions and yields could be the lower reaction temperature. Therefore, the optimization of the catalysts was carried on in DMSO at 120 °C.

Finally, we examined, if the reaction time could be reduced without any deterioration of the yields. Reducing the reaction time to 3 h (Table 1, Entry 8), the yield was also cut in half. With 6 h of reaction time (Table 1, Entry 7) a decrease in the yield was also observed. In both cases, full conversion was not achieved, as unreacted ethyl phenylphosphinate (**1a**) could be identified in the $^{31}$P NMR spectra of the crude product.

In order to demonstrate the need for the catalyst, two control experiments were carried out. In one case, ethyl phenylphosphinate (**1a**) and phenylacetylene (**2**) was heated in DMSO at 120 °C for 12 h, and in a separate experiment the same reaction was carried out in the presence of 4 Å molecular sieve. In both cases, no product formation could be detected by spectroscopic methods, indicating that the Cu(II) dispersed on the surface of the molecular sieve was responsible for the catalytic transformation.

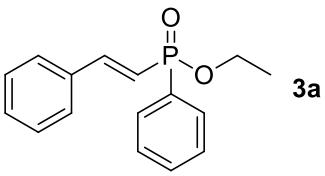
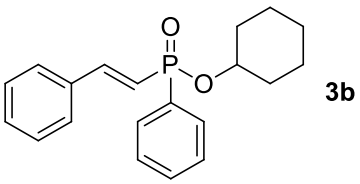
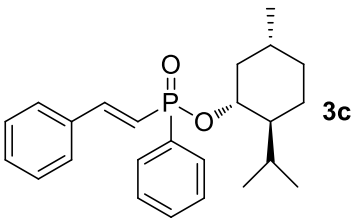
As the result of the optimization studies, the subsequent reactions investigating the substrate scope were carried out in DMSO at 120 °C for 12 h in the presence of the Cu(II)-4A catalyst under nitrogen atmosphere. After the completion of the reaction, the catalyst was removed by filtration, and the crude product obtained after extraction was purified further by column chromatography. The structure of the alkenylphosphinates (Tables 2 and 3) was elucidated by NMR and MS spectroscopy. First, the reaction of various *H*-phosphinates (**1a–d**) with phenylacetylene (**2**) was examined. As a result of the optimization

**Table 2** Reaction of different *H*-phosphinates (**1a–c**) with phenylacetylene (**2**)




**1** **2** **3**

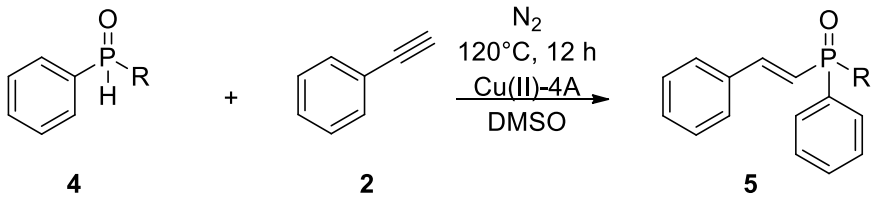
R = Et, cyclohexyl, menthyl

| Entry | R | Product | Yield (%)[b] |
|---|---|---|---|
| 1 | Et **1a** |  **3a** | 52 |
| 2 | cyclohexyl **1b** |  **3b** | 88 |
| 3 | menthyl **1c** |  **3c** 1:1 mixture of 2 diastereomers | 90 |

[a]Reagents and conditions: *H*-phosphinate (1 mmol), phenylacetylene (1 mmol), catalyst (0.1 g, 9 mol% Cu), DMSO (2 mL), 120 °C, 12 h

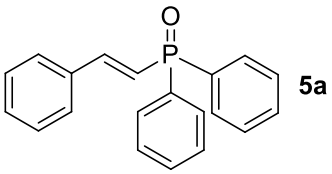
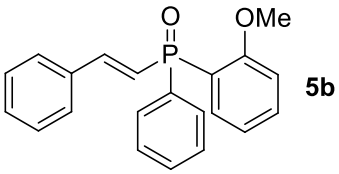
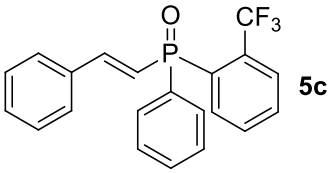
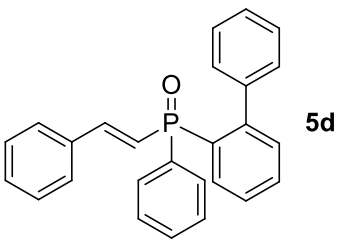
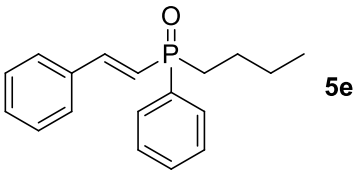
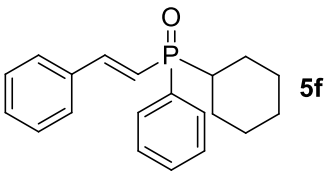
[b]Isolated yield

**Table 3** The addition of secondary phosphine oxides (**4a–f**) to phenylacetylene (**2**)




**4** **2** **5**

R = Ph, 2-MeO-$C_6H_4$, 2-$CF_3$-$C_6H_4$, biphenyl, Bu, cyclohexyl

| Entry | R | Product | Yield (%)[b] |
|---|---|---|---|
| 1 | Ph **4a** |  **5a** | 50 |
| 2 | 2-MeO-$C_6H_4$ **4b** |  **5b** | 67 |
| 3 | 2-$CF_3$- $C_6H_4$ **4c** |  **5c** | 81 |
| 4 | biphenyl-2-yl **4d** |  **5d** | 34 |
| 5 | Bu **4e** |  **5e** | 65 |
| 6 | cyclohexyl **4f** |  **5f** | 87 |

[a]Reagents and conditions: phosphine oxide (1 mmol), phenylacetylene (1 mmol), catalyst (0.1 g, 9 mol% Cu), DMSO (2 mL), 120 °C, 12 h

[b]Isolated yield

studies the (*E*)-1-ethoxylphenylphosphinyl-2-phenylethene (**3a**) was prepared with a yield of 52%, while in case of the cyclohexyl and menthyl substituents the desired products (**3b** and **3c**) were obtained in excellent yields (88% or 90%) (Table 2, Entries 2 and 3). It is noteworthy, that the menthyl phenyl-*H*-phosphinate derived from (-)-menthol was used as a 1:1 mixture of the ($R_P$)- and ($S_P$)-diastereomers. Thus, alkenylphosphinate **3c** was obtained as a 1:1 mixture of two diastereomers. However, in the reaction of *tert*-butyl phenylphosphinate (**1d**) the yield of the (*E*)-1-*tert*-butoxylphenylphosphinyl-2-phenylethene was significantly lower (< 5%), indicating that the increased steric bulk of the *tert*-butoxy group hinders the reaction, which leads to low conversion.

Next, the addition of different secondary phosphine oxides (**4a–f**) to phenylacetylene (**2**) was elaborated. Generally, the desired products (**5a–f**) were prepared in good to excellent yields (50–87%). The only exception was the biphenyl substituted product (**5d**), which phosphine oxide was prepared only in a yield of 34% (Table 3, Entry 4). The reason for this low yield can be attributed to the increased steric hindrance of the given phenyl-(biphenyl-2-yl) phosphine oxide (**4d**), which is in accordance with the observations obtained in the reaction of phenylacetyene (**2**) with the *tert*-butyl phenyl-*H*-phosphinate. Table 3 shows, that 1-diphenylphosphinyl-2-phenylethene (**5a**) could be prepared in a yield of 50%, and the presence of small electron donating or withdrawing groups (OMe or $CF_3$) in the *ortho* position of the phenyl ring was also tolerated, as alkenylphosphine oxides **5b** or **5c** were prepared in yields of 67% or 81% (Table 3, Entries 2 and 3). Alkyl-arylphosphine oxides, such as butyl- or cyclohexyl-phenylphosphine oxide (**4e** or **4f**) could also be coupled with phenylacetylene and the desired product (**5e** and **5f**) could be prepared in 65% and 87% yield (Table 3, Entries 5 and 6).

All hydrophosphinylation reactions of phenylacetylene (**2**) with various H-phosphinates (**3**) or secondary phosphine oxides (**4**) were completely regioselective, as only the anti-Markovnikov β-isomers were formed, and the corresponding products (**3** or **5**) were isolated as sole (*E*) stereoisomers.

The addition of various phosphites, such as diethyl-, di(*i*-propyl), dibutyl and diphenyl phosphite to phenylacetylene (**2**) was also attempted under the standard conditions. However, the spectroscopic analysis of the reaction mixtures showed that the desired dialkyl vinyl-phosphonates were not formed.

There were no determinant by-product detected in the reactions, but more or less tarry by-products were formed which required the purification of the crude products by column chromatography. The stability of the given phosphorous compound might affect the amount of this tarry material. This can explain the lower yield obtained in some cases. The side reaction, which may often occur in the reaction of alkynes in the presence of copper catalyst, yielding the homo-coupled product (in this case 1,4-diphenyl-but-1,3-diin) was not observed. This is in agreement with our previous observations, that this Glaser-type side reaction occurs only if a nitrogen-containing compound (mostly an amine or an ammonium salt) is present in the reaction mixture [see *e.g.* 43].

XRF studies showed that the no copper was found in the crude product. The catalyst has been heated in DMSO, and the catalyst was filtered out from the hot mixture. Based on the XRF analysis, the filtrate did not contain copper either. These results can verify the real heterogeneous catalytic nature of the reaction. Similar results were observed generally in our previous experiments with metal-impregnated molecular sieve catalysts, verifying that there is no leaching of metal during these reactions.

Based on our previous experiments, and in agreement with the literature data [23, 34], a mechanism similar to the metal catalysed cross-coupled reactions is assumed with copper insertion and then elimination (Fig. 3).

The reusability or recyclability is an important property of a heterogeneous catalyst. Thus, the reusability of the Cu(II)-4A catalyst was tested in the reaction of ethyl phenylphosphinate (**1a**) and phenylacetylene (**2**). After filtration from the reaction mixture the catalyst was washed with ethyl acetate and dried at 120 °C for 1 h. Then the recovered catalyst was used in a second experiment. The reusability was tested in two successive runs, and it was found, that the Cu(II)-4A catalyst can be reused one time without significant loss of activity (Table 4). In the third run, the yield of

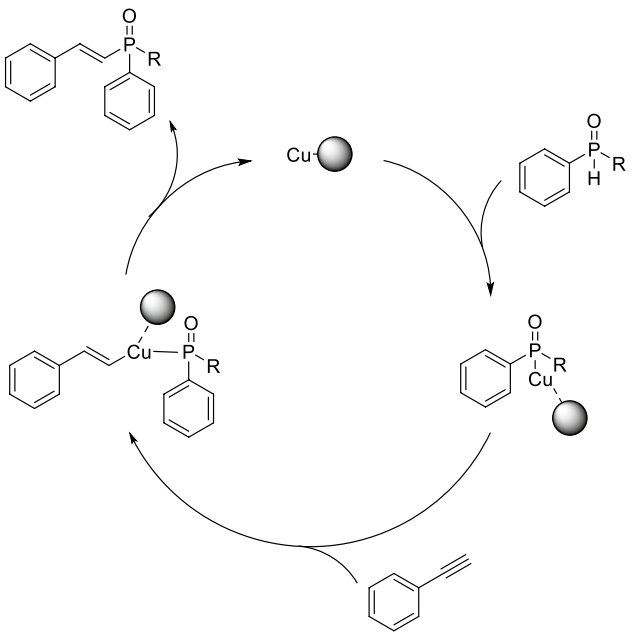



**Fig. 3** Proposed mechanism of the reaction

**Table 4** Reusability of the catalyst in the reaction of ethyl phenylphosphinate (**1a**) and phenylacetylene (**2**)

| Entry | Number of uses | Yield 3a (%)[b] |
|---|---|---|
| 1 | 1 | 52 |
| 2 | 2 | 50 |
| 3 | 3 | 49 |

Reagents and conditions: ethyl phenylphosphinate (1 mmol), phenylacetylene (1 mmol), catalyst (0.1 g, 9 mol% Cu), DMSO (2 mL), 120 °C, 12 h

[b]Isolated yield

**3a** decreased from 52 to 49%. The ICP-OES analysis showed no noticeable change in the copper content of the catalyst.

## 4 Conclusion

In conclusion, copper(II) on 4 Å molecular sieve support was found to be efficient in the hydrophosphinylation of phenylacetylene (**2**). Different *H*-phosphinates (**1a–c**) and secondary phosphine oxides (**4a–f**) were tested, and the desired products were obtained in moderate to excellent yields. The catalyst could be reused at least in two more experiments without significant less of activity.

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