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Heterogeneous visible-light-induced Meerwein hydration reaction of alkenes in water using mpg-C₃N₄ as a recyclable photocatalyst†

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A green and efficient visible light induced Meerwein hydration reaction of alkenes in aqueous medium using mpg-C₃N₄ as a recyclable photocatalyst has been disclosed. This protocol provides a direct approach for the preparation of racemic alcohols *via* a free radical mechanism. Water acted as both a solvent and a reagent without any additives or co-solvents. The metal-free heterogeneous semiconductor is found to be fully recyclable at least 5 times without any significant reduction in activity. The Meerwein hydration reaction has an excellent substrate scope and gave the desired products in moderate to high yields. Furthermore, this reaction could be carried out under solar light irradiation and is applicable for large-scale reactions with satisfactory results.

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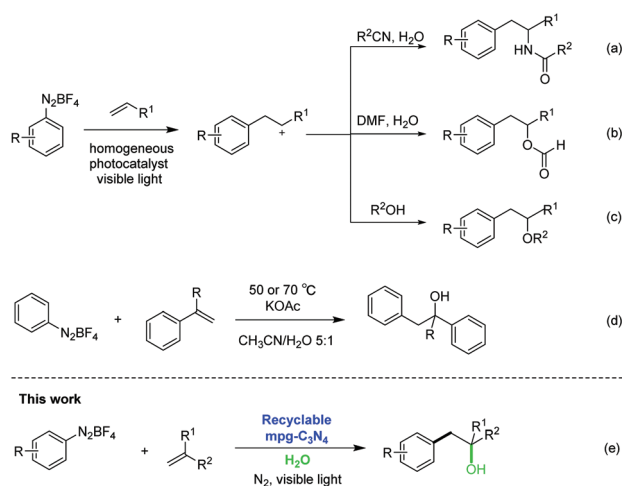
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Introduction

Over the past decade, visible light-induced reactions became a promising route to achieve a wide array of chemical transformations with distinctive energy and environmental merits, which are usually inaccessible with conventional thermal processes.¹ So far, great progress has been achieved with homogeneous photoredox catalysts, such as ruthenium- or iridium-based transition metal complexes² or organic dyes.³ However, these catalysts are usually difficult to recover from the reaction mixture. Thus, growing interest has been focused on using metal-free and recyclable materials as photocatalysts in visible light promoted reactions. On the other hand, water is a cheap, safe, non-toxic and clean reaction medium.⁴ After years of development, using water as a solvent is one of the simplest strategies in sustainable synthetic chemistry.⁵ However, few examples have been reported involving photocatalysis conducted solely in water. Although water has been utilized as a solvent for visible light-mediated reactions, in most cases, organic solvents are required as co-solvents to assist with substrate solubilization.⁶ Recently, the Lipshutz group developed a PQS-enabled visible-light iridium photoredox catalysis, which enabled homogeneous photo-reactions in water.⁷ Notwithstanding the novelty of this approach, challenges still remain. A simple and heterogeneous photocatalytic reaction using water as a solvent is still highly desirable.

In the past few decades, Meerwein type difunctionalization of alkenes has received continuous interest as it provides a synthetically useful route to introduce vicinal substituents.⁸ Besides the classic metal catalyzed reactions, in recent years, visible-light-induced Meerwein reactions have received much attention.⁹ In these processes, the difunctionalization products were obtained by the nucleophilic addition of a carbocation intermediate which was generated by the addition of radicals with alkenes or alkynes. The scope has been increased through the introduction of new aryl radical sources and radical acceptors. For instance, in 2014, the König group successfully achieved intermolecular amino-arylation of alkenes *via* photocatalyzed Meerwein addition (Scheme 1a).¹⁰ Later,



Scheme 1 Meerwein hydration reaction of alkenes.

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they developed a three-component formyloxyarylation of alkenes *via* a similar process (Scheme 1b).¹¹ In 2018, Itoh and co-workers reported a photoredox-catalyzed Meerwein aryl alkoxylation of alkenes with aryl diazonium salts and alcohols to generate substituted ethers (Scheme 1c).¹² Recently, our group also reported a visible-light-induced Meerwein type radical/oxidative addition domino process to access α,α -difunctionalized ketones from alkynes.¹³ Although these methods provided the desired products in attractive routes, most of them use homogeneous photocatalysts that were expensive and unrecoverable. Moreover, the known protocols use potentially toxic organic solvents such as DMF, DMSO, and CH₃CN which do not meet the green chemistry principle.¹⁴

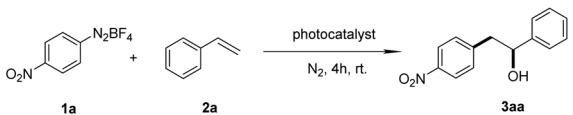
Recent years, graphite phase carbon nitride (C₃N₄)¹⁵ has emerged as a recyclable semiconductor capable of mediating photocatalysis under visible-light irradiation.¹⁶ It is noted that this polymeric material could be investigated in solar water splitting and degradation of pollutants in water.¹⁷ On the other hand, water could be employed as a nucleophilic reagent in Meerwein difunctionalization. In 2016, Kindt *et al.* reported a thermally induced radical carbohydroxylation of alkenes with aryldiazonium salts and water to generate secondary alcohols (Scheme 1d).¹⁸ However, this strategy still uses CH₃CN as a solvent, and some substitutes even need a base as an additive. We envisioned whether mpg-C₃N₄ could catalyze the Meerwein hydration reaction in water without any additives or organic co-solvents and whether racemic alcohols could be delivered. Herein, we develop a visible light promoted Meerwein hydration reaction of alkenes in aqueous medium using mpg-C₃N₄ as a photocatalyst *via* a radical addition/hydration process at room temperature (Scheme 1e).

Results and discussion

Our initial studies began with the attempted reaction of diazonium salt **1a** (0.5 mmol) with 1.2 equiv. of alkene **2a** using 20 mg of g-C₃N₄ as the catalyst in 3 mL of water under 250 W xenon short arc lamp (Xe lamp) irradiation for 4 h at room temperature. To our delight, the desired product **3aa** was obtained with 52% yield (Table 1, entry 1). In order to obtain the optimum yield, a wide variety of photocatalysts were screened. The best result was obtained when mesoporous graphite phase carbon nitride (mpg-C₃N₄) was used which provided **3aa** in 76% yield (Table 1, entry 2). Other metal-doped g-C₃N₄ such as Fe@g-C₃N₄ and Cu@g-C₃N₄ showed lower catalytic activities (Table 1, entries 3 and 4). It is noticed that typical homogeneous photocatalysts such as Ru(bpy)₃Cl₂, Ir(ppy)₃, Eosin Y and Rhodamine B were not able to provide any significant Meerwein hydration reaction of alkenes in water (Table 1, entries 5–8). Organic solvents such as CH₃CN, CH₃OH and THF have also been applied and the results showed relatively lower yields (Table 1, entries 9–11). When the amount of water was increased, higher yields were obtained (Table 1, entries 12 and 13). The best yield was obtained when water was used as the solvent. Furthermore, increasing the amount of mpg-C₃N₄ to 30 mg cannot increase the yield (Table 1, entry 14), in contrast, reducing the amount of mpg-C₃N₄ to 10 mg led to a decreased yield (Table 1, entry 15). Finally, the model reaction was carried out without light or any photocatalyst. As expected, no desired product was observed respectively (Table 1, entries 16 and 17).

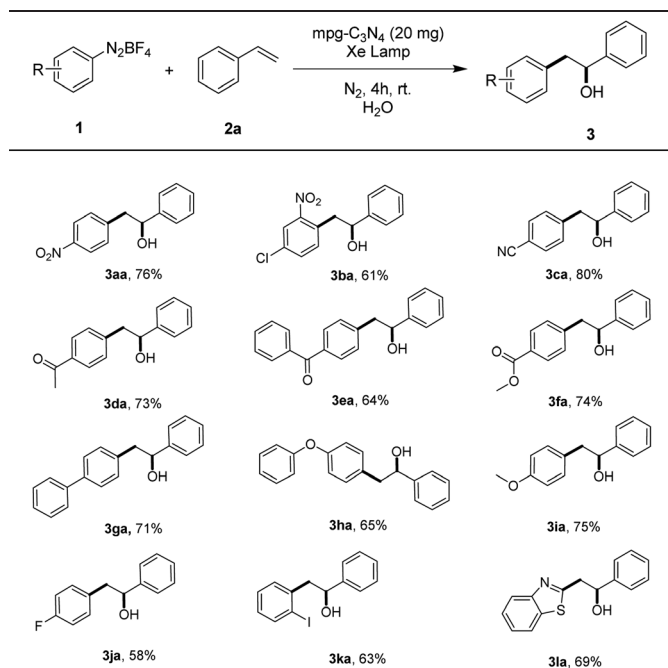
With the optimized conditions in hand, the scope of aryl diazonium derivatives for the Meerwein hydration reaction was

Table 1 Optimization of the reaction conditions^a



Entry	Cat.	Light	Solvent	Yield ^b /%
1	g-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	H ₂ O	52
2	mpg-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	H ₂ O	76
3	Fe@g-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	H ₂ O	64
4	Cu@g-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	H ₂ O	68
5	Ru(bpy) ₃ Cl ₂ (2 mol%)	Blue LED (5 W)	H ₂ O	Trace
6	Ir(ppy) ₃ (2 mol%)	Blue LED (5 W)	H ₂ O	Trace
7	Eosin Y (2 mol%)	Blue LED (5 W)	H ₂ O	Trace
8	Rhodamine B (2 mol%)	Blue LED (5 W)	H ₂ O	Trace
9	Mpg-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	CH ₃ CN/H ₂ O (9 : 1)	52
10	Mpg-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	CH ₃ OH/H ₂ O (9 : 1)	46
11	Mpg-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	THF/H ₂ O (9 : 1)	49
12	Mpg-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	CH ₃ CN/H ₂ O (3 : 1)	66
13	Mpg-C ₃ N ₄ (20 mg)	Xe lamp (250 W)	CH ₃ CN/H ₂ O (1 : 1)	70
14	Mpg-C ₃ N ₄ (30 mg)	Xe lamp (250 W)	H ₂ O	72
15	Mpg-C ₃ N ₄ (10 mg)	Xe lamp (250 W)	H ₂ O	51
16	Mpg-C ₃ N ₄ (20 mg)	No	H ₂ O	0
17	No	Xe lamp (250 W)	H ₂ O	0

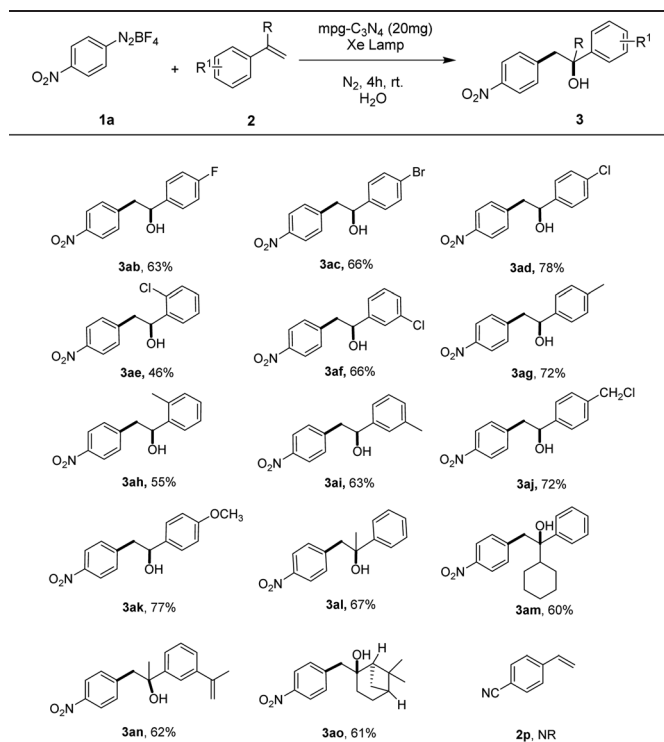
^a Reaction conditions: at room temperature, under a 250 W Xe lamp, light distance 10 cm, solvent (3 mL), substrate **1a** (0.5 mmol), **2a** (0.6 mmol), mpg-C₃N₄ as the catalyst, N₂ atmosphere, reaction for 4 hours. ^b Isolated yield.

Table 2 Scope of diazonium salts^a

^a Reaction conditions: at room temperature, under a 250 W Xe lamp, light distance 10 cm, water (3 mL), substrate **1a** (0.5 mmol), **2a** (0.6 mmol), mpg-C₃N₄ (20 mg), nitrogen atmosphere, reaction for 4 hours. Isolated yield.

examined (Table 2). The expected Meerwein hydration reaction products **3** were obtained using diazonium salts bearing various electron-withdrawing substituents on the aryl ring such as nitro (**3aa**), cyanide (**3ca**), acyl (**3da**, **3ea**) and ester groups (**3fa**) in moderate to good yields. While, diazonium salts bearing electron-donating groups also performed well, affording the corresponding products **3ga–3ia** in 64%–72% yields, which indicated that the electronic effect had slight influence on this reaction. In addition, halogen atoms such as fluoro (**3ja**), iodine (**3ka**) and 4-chloro-2-nitro (**3ba**) were tolerated in the present photocatalytic transformation. Steric hindrance for alkenes were not significant, and aryl alkenes with an *ortho*-nitro or iodine substituent were successfully converted into the corresponding products (**3ba**, **3ka**). Moreover, heterocyclic diazonium derivative **2l** also performed well under these conditions, and the desired product **3la** was obtained in moderate yield.

The scope of various alkenes was then investigated. As shown in Table 3, aryl alkenes containing functional groups such as F, Cl, Br, methyl, CH₂Cl and MeO were well tolerated under the standard conditions. The steric hindrance of the substituents had a significant influence on the reaction, and aryl alkenes with *para*-, *meta*- or *ortho*-chloride substituents were successfully converted into the corresponding products in 78%, 66% and 46%, respectively (**3ad–3af**). Besides, α , β -substituted alkenes (**2l–2m**) could also participate in this reaction, and moderate yields were obtained. In addition, the 1,3-bis(1-methylvinyl) substituent also performed well in this

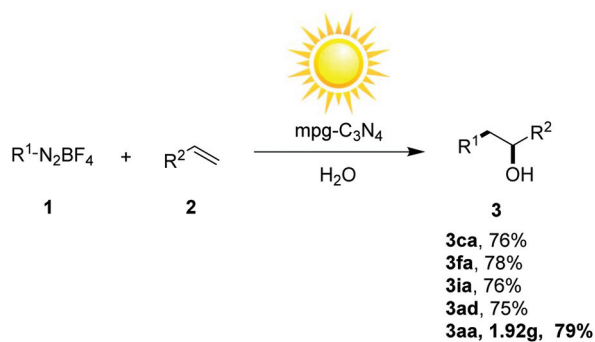
Table 3 Scope of alkenes^a

^a Reaction conditions: at room temperature, under a 250 W Xe lamp, light distance 10 cm, water (3 mL), substrate **1a** (0.5 mmol), **2a** (0.6 mmol), mpg-C₃N₄ (20 mg), nitrogen atmosphere, reaction for 4 hours. Isolated yield.

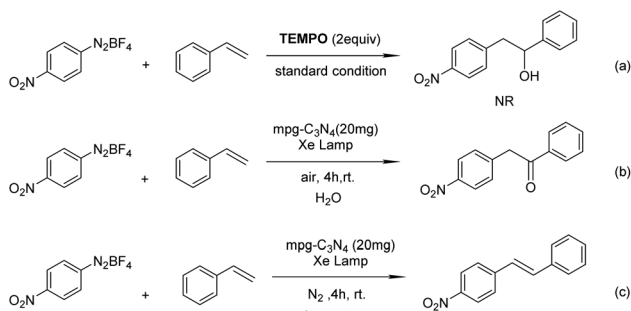
Meerwein hydration, and only a mono-substituted product **3an** was obtained in moderate yield. Besides aryl alkenes, natural aliphatic alkenes such as β -pinene **2o** also showed good tolerance in this reaction and afforded the corresponding product in moderate yield (**3ao**). However, electron-withdrawing substituted alkenes such as **2p** were not suitable for this transformation.

Furthermore, this visible-light-promoted Meerwein hydration reaction of alkenes could be driven by sunlight with better results compared with the model reaction conditions with Xe light irradiation (Fig. S5[†]). The use of solar energy makes it suitable for large-scale application. The reaction of **1a** (10 mmol scale) with **2e** proceeded smoothly under the optimized conditions to provide product **3aa** in 79% yield (1.92 g) using 400 mg of mpg-C₃N₄ within 7 h irradiation under sunlight (Scheme 2).

To further explore the mechanism of the reaction, a group of controlled experiments has been conducted. When 2 equivalents of a free radical inhibitor (TEMPO) were added, the hydroxylation reaction was absolutely inhibited, suggesting that the reaction might have undergone a free radical process (Scheme 3a). In addition, when the reaction was carried out in the presence of oxygen, the by-product 1,2-diacetophenone (Scheme 3b) was obtained. When the reaction was carried out in an anhydrous solvent with nitrogen, the coupling product



Scheme 2 Visible-light-promoted Meerwein hydration reaction of alkenes by sunlight and scale-up reaction. Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), mpq-C₃N₄ (20 mg), water (3 mL), nitrogen atmosphere, ambient temperature (27 °C), under sunlight irradiation, reaction for 4 hours (from 10 a.m. to 2 p.m). Reaction conditions for large-scale application: **1a** (10 mmol), **2e** (12 mmol), mpq-C₃N₄ (400 mg), water (30 mL), nitrogen atmosphere, ambient temperature (27 °C), under sunlight irradiation, reaction for 7 hours (from 9 a.m. to 4 p.m). Isolated yield.



Scheme 3 Controlled experiments.

alkyl olefin was obtained (Scheme 3c). These results indicated that the reaction may undergo a radical addition process of aryl radicals and olefin.

Based on the control experiments and previous literature reports,¹⁹ a plausible reaction mechanism is shown in Fig. 1. Initially, mpq-C₃N₄ is excited upon irradiation with visible light, which undergoes a single electron transfer (SET) to generate aryl radical I from diazonium salt **1**. Adding I to alkene **2** generates the corresponding benzyl radical II, which is oxidized by the valence band of mpq-C₃N₄ to form a carbanion III. Then H₂O as a nucleophilic reagent attacked intermediate III, followed by dehydrogenation to afford the corresponding product **3**.

Finally, the reusability of this catalyst system has been checked. The catalyst was evaluated in the following reaction: 4-nitro-benzene-diazonium tetrafluoroborate **1a** (0.5 mmol) was reacted with alkene **2a** (0.6 mmol) using mpq-C₃N₄ (20 mg) in 3 mL of water under Xe lamp irradiation for 4 h at room temperature. Once the reaction was complete, mpq-C₃N₄ began to precipitate. Therefore, the final product was obtained by extraction with ethyl acetate. The separated mpq-C₃N₄/water

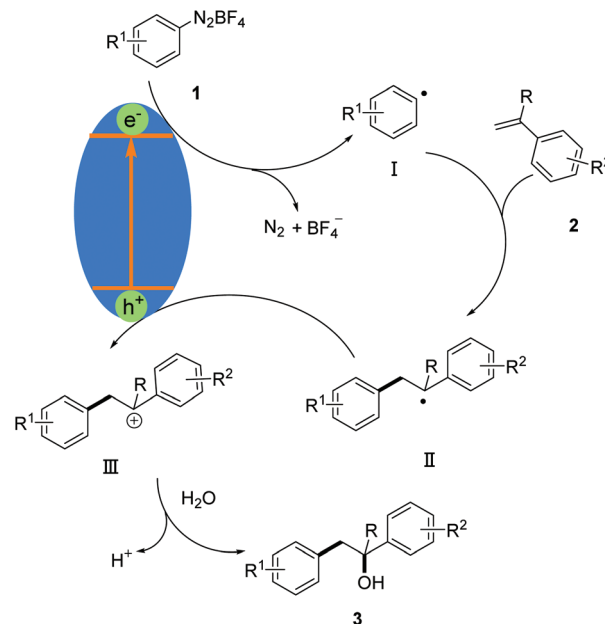


Fig. 1 Plausible reaction mechanism.

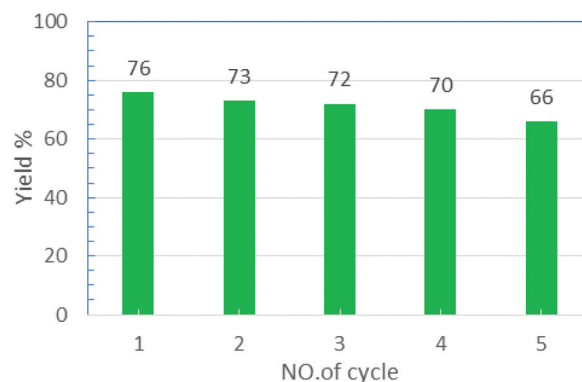


Fig. 2 Recyclability of mpq-C₃N₄ for the synthesis of 2-(4-nitrophenyl)-1-phenylethan-1-ol **3aa**.

system can be reused again directly. The results of the reuse test are shown in Fig. 2. It was obvious that mpq-C₃N₄/water still showed excellent performance for the Meerwein hydration reaction after being reused five times.

Conclusions

In summary, we have developed an environmentally-friendly and effective visible-light-induced Meerwein hydration reaction using mpq-C₃N₄ as a recyclable catalyst in water. Compared with the previous reports,^{18,20} this protocol provides a direct approach for the preparation of racemic alcohols under very mild reaction conditions. Water was used as both a solvent and a reagent without any additives or co-solvents. Notably, the mpq-C₃N₄/water catalyst system could be recycled and

reused five times with satisfactory yield without a significant loss of its activity. Moreover, this reaction could be carried out under solar light irradiation and is applicable for large-scale reactions. This reaction system allowed accessing a variety of products in moderate to high yields. These features make this reaction a potential green and sustainable approach for both academic and industrial applications.

Experimental

Instruments and reagents

^1H NMR spectra were recorded on a Bruker DRX (400 MHz) and ^{13}C NMR spectra were recorded on a Bruker DRX (100 MHz) spectrometer, using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, and the coupling constants J are given in Hz. Mass spectra were recorded on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. All reactions were carried out in oven-dried glassware under a nitrogen atmosphere, unless stated otherwise. For quantitative flash chromatography, technical grade solvents were used. All chemicals were commercially available and used without further purification. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm). The plates were visualized by exposure to ultraviolet light. All solvents were obtained from commercial suppliers. Diazonium salts **1a–1k** were prepared according to the literature.¹⁶

Experimental method

Synthesis of $\text{mpg-C}_3\text{N}_4$. 5 g of cyanamide and 12.5 g of LUDOX HS40 silica were mixed together until complete dissolution of cyanamide. The mixture was heated in an oil bath at 100 °C upon stirring for 3 h until the removal of water and the formation of a white solid. The powder was then ground in a mortar, transferred into a crucible and heated under air at 2.3 °C min^{-1} (4 h) up to 550 °C and then treated at 550 °C for 4 h. The as-obtained yellow powder was ground in a mortar and then stirred in a 4 mol per L NH_4HF_2 solution for 24 h to remove the silica template. The dispersion was filtered, and then the precipitate was washed with water and ethanol. After filtering, the yellow powder was dried under vacuum at 100 °C overnight.

Preparation of racemic alcohols (3). A 25 mL clean and dry Schlenk reaction tube with a magnetic stirring rotor was equipped with diazoniumtetrafluoroborate (0.5 mmol), alkene (0.6 mmol), $\text{mpg-C}_3\text{N}_4$ (20 mg) and H_2O (3 mL). The mixture was irradiated with a Xe lamp (250 W) and stirred at r.t. under a nitrogen atmosphere for 4 h. The distance of the reaction vial from light was about 10 centimeters. After the reaction, $\text{mpg-C}_3\text{N}_4$ was filtered out of the mixture, and the solvent was removed under reduced pressure. Purification of the crude product was achieved by flash column chromatography using

petrol *n*-hexane/ethyl acetate (3 : 1–10 : 1) as the eluent to give product **3**.

Conflicts of interest

There are no conflicts to declare.

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