Chemistry
A European
Journal

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

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To be cited as: *Chem. Eur. J.* 10.1002/chem.202004234

Link to VoR: https://doi.org/10.1002/chem.202004234

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10.1002/chem.202004234

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Visible light promoted, catalyst-free radical carbohydroxylation and carboetherification under mild biomimetic conditions

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Dedication ((optional))

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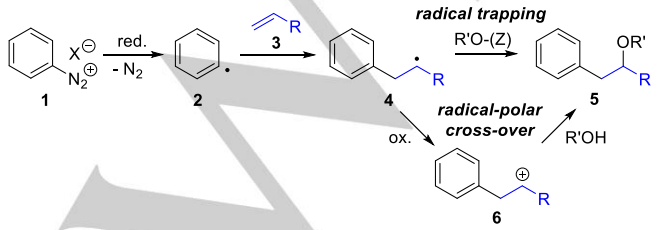
Abstract: Metal and catalyst-free carbohydroxylations and carboetherifications at room temperature have been achieved by a combination of beneficial factors including high aryl diazonium concentration and visible light irradiation. The acceleration of the reaction by visible light irradiation is particularly remarkable against the background that neither the aryldiazonium salt nor the alkene show absorptions in the respective range of wavelength. These observations point to weak charge transfer interactions between diazonium salt and alkene, which are nevertheless able to considerably influence the reaction course. As highly promising perspective, many more aryldiazonium-based radical arylations might benefit from simple light irradiation without requiring a photocatalyst or particular additive.

Introduction

Radical alkene functionalizations[1] have become increasingly popular over the last two decades, especially due to the development of a great variety of novel metal-free,[2] photocatalyzed[3] or even catalyst-free reactions.[4] An important subgroup within this general reaction type are carbooxygenations,[5] whereat a carbon moiety and an oxygen-centered functional group are attached to the original alkene unit. Such transformations, which include radical carbohydroxylations[6] and carboetherifications[7] as most prominent examples, can proceed via two major reaction mechanisms. In Scheme 1, this is shown for intermolecular Meerwein-type[8,9] carbooxygenations, where an aryldiazonium salt is used as radical precursor.



Scheme 1. Reaction mechanisms for Meerwein-type radical carbooxygenations.

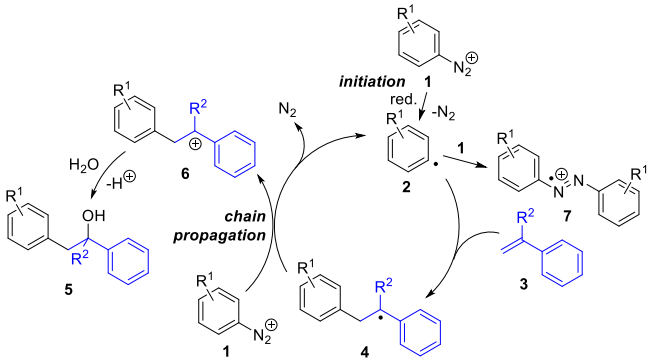
Following the reductive formation of an aryl radical **2** from the diazonium salt **1**, addition to the alkene **3** gives the central alkyl intermediate **4**. While in classical reactions, the C-O bond in **5** is formed via ligand transfer from a copper complex[10] or by trapping of radical **4** by a persistent oxygen-centered radical such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO),[11] C-O bond formation may also be achieved via intermediate oxidation of radical **4** to cation **6**. Not surprisingly, the radical polar cross-over pathway[12] is highly dependent on the stabilization of cation **6** (e.g. R = aryl, Oalkyl),[13] whereat the final carbooxygenation product **5** then arises from the attack of an oxygen-centered nucleophile. Remarkably, the scope of Meerwein carbooxygenations could be significantly broadened by exploiting the radical polar cross-over pathway, as such simple compounds as water or aliphatic alcohols may now be used for C-O bond formation, and thus to determine the nature of the OR' group in **5**.[14]

Within our recent research in the field of Meerwein arylation chemistry,[15] a novel variant could be developed, in which the carbohydroxylation of styrenes was achieved in metal- and catalyst-free reactions under thermal conditions (70 °C).[16] The facts that no additives besides the diazonium salt and the styrene are required, and that the solvent mixture already comprises water to introduce the hydroxyl group, are important pre-requisites to further develop this reaction type towards an arylation under biomimetic conditions. Regarding so far proposed biocompatible arylations,[17] there is still room for improvement, as many of these transformations have either to be conducted at elevated temperatures, in a non-natural pH environment, or they comprise non-natural additives.[17] In this work, it will be shown which particular and partially surprising effects can be exploited to conduct the carbohydroxylation at room temperature, and how these findings can be extended towards a particularly mild, metal- and catalyst-free carboetherification.

Results and Discussion

To assess how the previously developed carbohydroxylation could be conducted under biomimetic conditions, particularly at room temperature, a closer look at the underlying mechanism is helpful (Scheme 2). As the initiation step from diazonium ion **1** to radical **2** will be much slower at room temperature than at

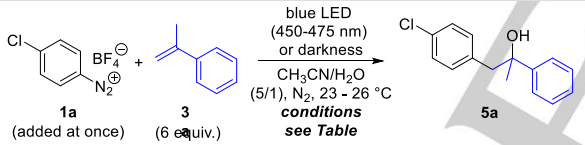
70°C,[18] we thought to evaluate whether this drawback can be counterbalanced by visible light irradiation. Although none of the reactants shows absorptions in the range of 450-475 nm, increased initiation might nevertheless occur via the formation of weak charge-transfer complexes.[19]



Scheme 2. Mechanistic background of the carbohydroxylation of styrenes.

In addition, the chain propagation is likely to be improved by a faster or even at once addition of the diazonium salt to the reaction mixture, given that the homocoupling of radical **2** to diazonium ion **1**[20] to give **7** remains slower than the desired addition of aryl radical **2** to styrene **3**.[21] The results of selected preliminary experiments are summarized in Table 1.

Table 1. Optimization of reaction conditions at room temperature.



entry	conditions	yield **5a**[a]
1	darkness, N_2, 1 h (23°C)	1%
2	darkness, N_2, 3 h (23 °C)	20%
3	darkness, N_2, 19 h (23 °C)	73%
4	LED, N_2, 1 h (26 °C)	72%
5	**LED, N_2, 3 h (26 °C)**	**79%**
6	**LED, N_2, 19 h (26 °C)**	**79%**

[a] Yields determined by ^{1}H-NMR using 1,4-dimethoxybenzene as internal standard.

While the "at once addition" of the diazonium salt **1a** to the reaction mixture was shown to be feasible, it still led to a comparably long reaction times (entries 1-3). Additional irradiation with blue LEDs (450-475 nm) then resulted in a remarkable increase of the reaction rate (entries 4-6). The strongest relative effect was found at a reaction time of 1 hour (c.f. entries 1 and 4). Additional attempts with the corresponding diazonium chloride pointed to a higher reactivity of the tetrafluoroborate salt **1a** in the carbohydroxylation (see Supporting Information).

The beneficial effect of performing the carbohydroxylation under visible light irradiation (450-475 nm) was confirmed in additional experiments with 4-fluoro-, 3-bromo- and 4-bromophenyl-diazonium tetrafluoroborate **1b-d** under otherwise identical conditions (Figure 1). Having observed that visible light irradiation raises the temperature of the reaction mixture (23 °C) by around 3 °C, we further conducted a series of control experiments at a slightly further increased temperature of 28 °C to exclude that the accelerating effect attributed to visible light irradiation would be solely caused by the temperature effect.

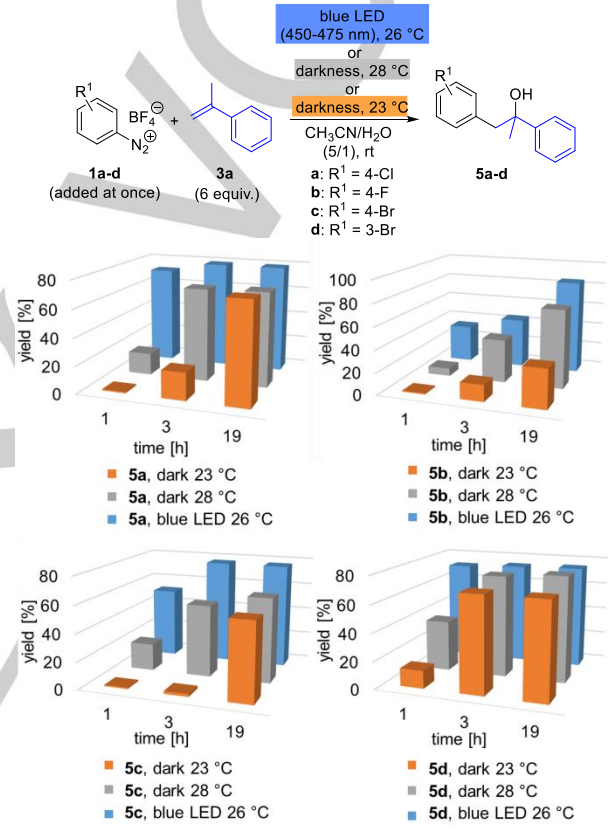


Figure 1. Comparison of the reaction course under blue LED irradiation with reactions in darkness.

Comparing the yields of **5a-d** under irradiation (blue) and in darkness (orange and grey) after one hour, the strongest relative effects were found for 4-chloro, 4-fluoro and 4-bromo substitution **5a-c**, where the yield under irradiation exceeded the one in darkness by factors of 34 to 72 (at 23 °C) and 2.6 to 4.9 (at 28 °C), respectively. The reaction with the 3-bromophenyldiazonium salt **5d** was found to be the fastest in darkness, which points to a somehow higher reactivity of this particular diazonium ion (see below) or related to mechanism, possibly also a more effective chain propagation step (c.f. Scheme 2) under the present conditions. Regarding the final yield after 19 h, the largest increase upon irradiation was observed for the 4-fluoro-substituted derivative **5b**. In a further control experiment on the effect of irradiation, the reaction mixture containing **1a** and **3a** (to give **5a**) was cooled to 10°C.

While almost no formation of **5a** (1%) was observed at 23°C after 1 h (in the dark), and the reaction should be even slower at 10°C, irradiation of this particular mixture now gave 6% of **5a** after 1 h, thereby underlining the benefit of irradiation.

To get insights why particular reactions might initially benefit more from irradiation than others, UV spectra of the diazonium salts **1a-d**, of α-methylstyrene (**3a**), and of the four individual reaction mixtures were recorded (Figure 2). Due to the very weak absorptions of the reactants **1a-d** and **3a**, the spectra could be obtained at comparably high concentrations, which were identical to those in the real reaction mixtures (Table 1, Figure 1).

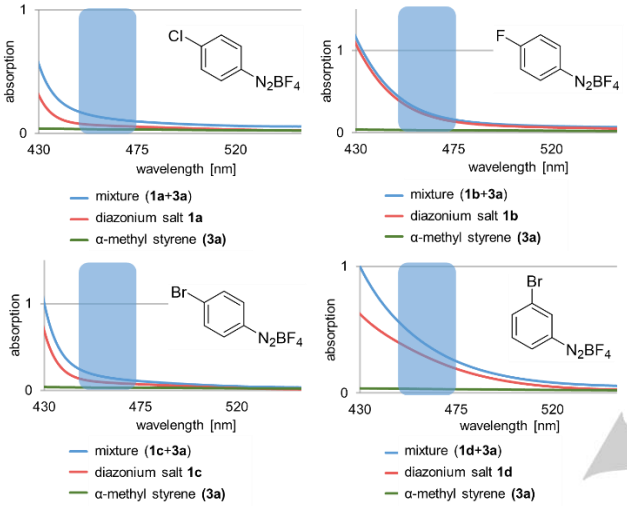


Figure 2. UV-Vis spectra of **1a-d**, α-methylstyrene (**3a**) and the 4 related reaction mixtures.

As expected, the formation of a strong CT complex between one of the diazonium ions **1a-d** and **3a** could not be observed for any of the four combinations. As even minor differences between the reactions are hardly detectable, it appears not to be possible to directly correlate the stronger acceleration in the reactions to **5a-c** to an increased absorption of the particular reaction mixture. Most importantly, all measured absorptions in the visible irradiation range from 450 to 475 nm are very weak, as indicated by the very low ε values determined for the reaction mixtures comprising a diazonium salt from **1a-d** and styrene **3a** (**1a/3a:** 1.50-0.88 $M^{-1}cm^{-1}$, **1b/3a:** 3.92-1.46 $M^{-1}cm^{-1}$, **1c/3a:** 1.88-0.97 $M^{-1}cm^{-1}$, **1d/3a:** 4.83-2.29 $M^{-1}cm^{-1}$). On this basis, the observed sensitivity of the carbohydroxylation to irradiation is surprising, and most likely due to an increased initiation rate via very weak, hardly detectable, but still effective intermolecular CT interactions.[19a]

Further support for such interactions could be obtained from three experiments, in which diazonium salt **1a** was once irradiated in the solvent mixture without further additive, then in the presence of benzene (6 equiv.) and finally together with the typical substrate α-methylstyrene (**3a**) (Figure 3).

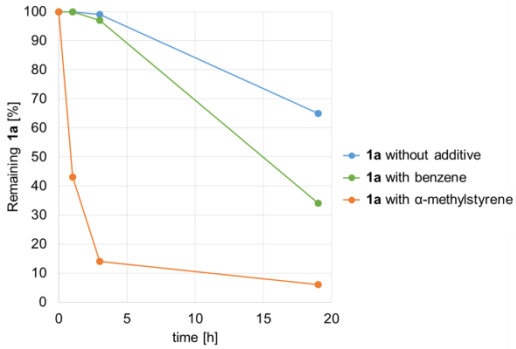


Figure 3. Decomposition of the diazonium salt **1a** upon irradiation at 450-475 nm with no additive, benzene or α-methylstyrene (**3a**).

With no additive being present, **1a** decomposes slowly. The addition of benzene (6 equiv.) was already able to slightly accelerate the decay, which points to a weak interaction with the diazonium ion, and which is in agreement with earlier results.[19a] Due to a most likely stronger interaction, and accelerated by the chain mechanism (Scheme 2), the by far fastest consumption of **1a** was observed in combination with styrene **3a** (6 equiv.).

As the overall reaction rate of the carbohydroxylation not only depends on initiation, but also on the chain transfer step (Scheme 2), we further investigated the four diazonium salts **1a-d** using Differential Pulse Voltammetry (DPV) (Figure 4). The main question thereby was whether **1a-d** might differ in their reduction potentials, which could explain facilitated initiation as well as chain transfer.

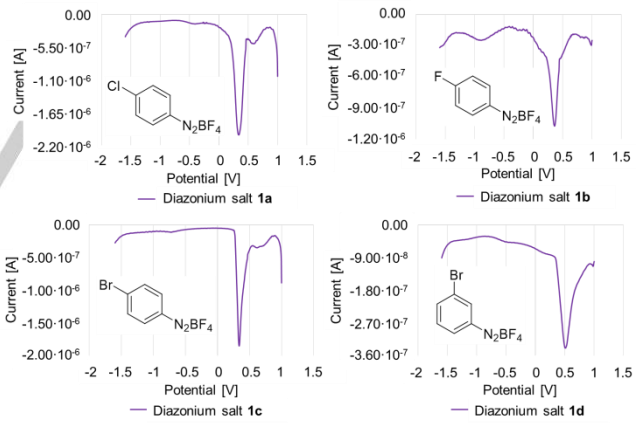


Figure 4. Differential pulse voltammetry measurements for **1a-d**.

The results from these experiments demonstrate that the reduction of the 3-bromo derivative **1d** (0.51 V) is slightly easier than that of the three 4-substituted diazonium ions **1a-1c** (0.34 V, 0.36 V, 0.34 V, respectively). The reaction with **1d** might thus benefit from a facilitated initiation and chain transfer, which is in agreement with Figure 1, where **1d** shows the fastest reactions in the dark at 23°C and at 28°C. The fact that among the "electrochemically identical" diazonium ions **1a-c**, the fastest arylation of styrene **3a** was observed for the 4-chloro derivative **1a**, can be a hint to a slightly more effective CT interaction of this particular diazonium ion with **3a**.

With insights into the mechanism and optimized conditions now available (Table 1), we continued with an evaluation of the substrate scope (Scheme 3). Within this study, we focused on the variation of the diazonium ion, since this is known as the more critical component regarding initiation and chain transfer, and thus the overall reaction course.[16]

5a: R^1 = 4-Cl, R^2 = Me 77% (79%)
5b: R^1 = 4-F, R^2 = Me 82% (85%)[c]
5c: R^1 = 4-Br, R^2 = Me 70% (77%)
5d: R^1 = 3-Br, R^2 = Me 74% (75%)
5e: R^1 = 3-F, R^2 = Me, 71% (80%)
5f: R^1 = 4-CO_2Me, R^2 = Me 50% (55%)
5g: R^1 = 2-CO_2Me, R^2 = Me 82% (n.d.)
5h: R^1 = 4-OMe, R^2 = Me 0% (0%)
5i: R^1 = 4-Cl, R^2 = Ph 25% (n.d.)

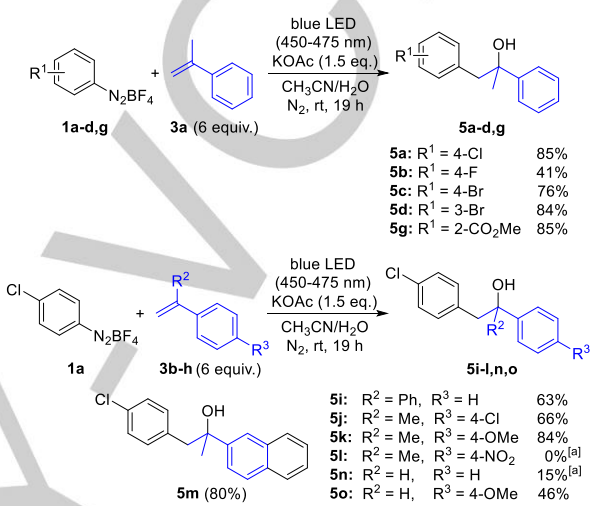
Scheme 3. Scope of carbohydroxylation at room temperature. Yields determined after column chromatography. Yields given in brackets determined by ^{1}H-NMR using 1,4-dimethoxybenzene as internal standard. [c]Reaction mixture neutralized during work-up and before column chromatography.

Synthetically useful yields were obtained for most diazonium salts in combination with α-methylstyrene (**3a**). Only the 4-methoxy derivative **5h** turned out as too unreactive, at which the low reactivity resulting from donor substitution could not be overcome by irradiation.[19a] A low yield of 25% was observed for the functionalization of 1,1-diphenylethene (**3b**), which can partly be explained by insufficient solubility and ineffective phase transfer of the aryl radical.[22]

Regarding the desired biocompatibility of the carbohydroxylation, measurements of the pH value during the synthesis of **5a** (Scheme 3) revealed that the pH value drops from an initial value of 3 to values around 1.5 over the reaction course. While the initially acidic conditions can be attributed to traces of tetrafluoroboric acid in the diazonium tetrafluoroborate salt, the increasing acidity during product formation is caused by the mechanism, which liberates protons (**6**→**5**, Scheme 2). This drawback can however be balanced by the addition of potassium acetate (1.5 equiv.) to the reaction mixture. For the synthesis of **5a**, the pH value then changes from 6 to 5, and thus remains in a fully biocompatible region. Moreover, the presence of potassium acetate led to an even slightly improved yield for **5a** (85%) under irradiation and to a yield of 79% from the control reaction in darkness at 28 °C. The now lower impact of irradiation can be explained by the basically facilitated aryl radical formation at higher pH values, so that the effect of irradiation and the importance of the weak CT interaction is then reduced. Notably, and besides typical reductants, less acidic conditions as well as nucleophiles can have a strong influence on the rate of aryl radical formation from diazonium ions.[18]

Regarding the general mechanism depicted in Scheme 2, and in agreement with previous studies,[18] we assume that the effect of potassium acetate, which is a base and nucleophile, will be largely limited to the initiation step (**1**→**2**, Scheme 2). The aryl radical addition to styrene **3** (**2**→**4**, Scheme 2), for which the rate can be estimated to around 3×10^8 $M^{-1}s^{-1}$[23], is unlikely to be altered significantly by the presence of the acetate. The final chain transfer step (**4**→**6**, Scheme 2) could basically be influenced if some adduct of the nucleophile (or base) with the diazonium ion would significantly reduce its free concentration.[15c]

Regarding the results from further reactions combining irradiation and the presence of potassium acetate, it turned out that upon variation of the diazonium salt (Scheme 4, upper part), most yields were slightly improved compared to the base-free conditions (Scheme 3), with the only exception of the 4-fluoro derivative **5b**. This deviation can however be rationalized by the low stability of the 4-fluorophenyl diazonium ion under less acidic conditions, as it may undergo substitution at the 4-position.[24]



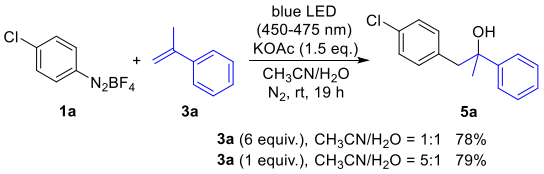
5a: R^1 = 4-Cl 85%
5b: R^1 = 4-F 41%
5c: R^1 = 4-Br 76%
5d: R^1 = 3-Br 84%
5g: R^1 = 2-CO_2Me 85%

5i: R^2 = Ph, R^3 = H 63%
5j: R^2 = Me, R^3 = 4-Cl 66%
5k: R^2 = Me, R^3 = 4-OMe 84%
5l: R^2 = Me, R^3 = 4-NO_2 0%[a]
5n: R^2 = H, R^3 = H 15%[a]
5o: R^2 = H, R^3 = 4-OMe 46%

Scheme 4. Scope of carbohydroxylation in the presence of potassium acetate. Yields determined after column chromatography; [a] Yield determined by ^{1}H-NMR using 1,4-dimethoxybenzene as internal standard.

The variations of the styrene (Scheme 4, lower part) not only show an enlarged scope, but also support the reaction mechanism depicted in Scheme 2. While the 4-methoxy substitution on the styrene increases the yield (**5k**: 84%), the corresponding 4-nitro derivative does not give any product **5l** due to the strongly destabilizing effect of the nitro group on the related cation **6** (Scheme 2). In line with that, unsubstituted styrene leads to a low yield (**5n**: 15%) due to the lack of the methyl group, which can to some extent be counterbalanced by a 4-methoxy substituent (**5o**: 46%) that again stabilizes the cation **6**. Such significant deviations were not likely to occur if the mechanism proceeded via some coupling of radical **4** (c.f. pathway **4**→**5**, Scheme 1). From the absence of dimerization products related to the stabilized, benzylic radical **4**,[25] one can even conclude that the oxidation step to cation **6** has to be quite efficient.

Finally, and also directed towards a future application under biomimetic conditions, we performed the arylation of α-methylstyrene (**3a**) with diazonium salt **1a** in a reaction mixture with a higher water content (water/acetonitrile = 1:1, v/v) (Scheme 5). In a separate experiment, the amount of **3a** was reduced to only one equivalent.



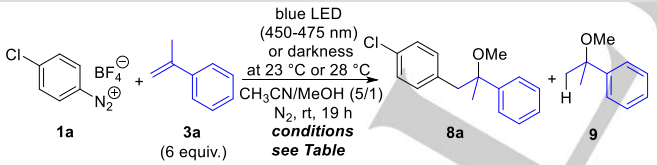
Scheme 5. Carbohydroxylation conducted with higher water content or reduced amount of styrene **3a**. Yields determined by ^{1}H-NMR using 1,4-dimethoxybenzene as internal standard.

The fact that both reactions provided the desired alcohol **5a** in only slightly lower yields of 78% and 79% (c.f. **5a**: 85%, Scheme 4), respectively, further underlines the excellent suitability of α-methylstyrenes as highly effective aryl radical acceptors for future applications. The biological compatibility of tetrafluoroborate has been outlined in a number of previous studies.[26]

Based on the exceptionally mild and biocompatible conditions now available for the carbohydroxylation, we turned to investigate whether the novel procedure could also be extended to carboetherification. As for the previous modification, namely the addition of potassium acetate, the presence of methanol can influence the overall mechanism. In contrast to the previously used nucleophile water, alcohols can enable hydrogen atom transfer to aryl radicals, which in the case of methanol would lead to the •CH_2OH radical.[18] As this particular radical is known to be capable of reducing diazonium ions to aryl radicals and dinitrogen along with the formation of formaldehyde, an undesired reduction of the diazonium salt to the parent aromatic compound can basically occur in the presence of alcohols via these two steps in the sense of a chain reaction.[27]

Results from initial experiments are summarized in Table 2, at which the optimized conditions from Table 1 (entry 6) were only varied in the way that water was replaced by methanol, and the effect of potassium acetate was studied in this early stage.

Table 2. Optimization of reaction conditions for carboetherification.



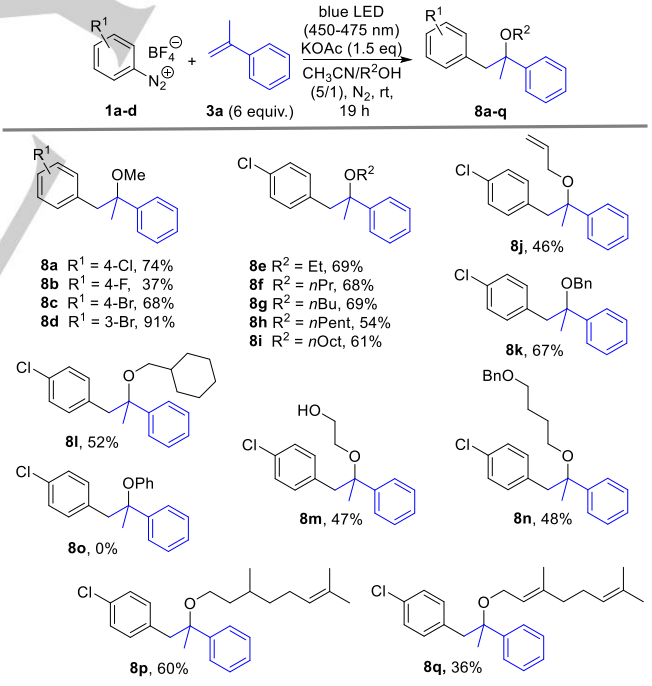
entry	conditions	yield **8a**[a]	yield **9**[b]
1	darkness, 23 °C	8%	0%
2	darkness, 28 °C	27%	24%
3	blue LED (26°C)	70%	44%
4	KOAc (1.5 eq.), darkness, 23 °C	64%	0%
5	KOAc (1.5 eq.), darkness, 28 °C	66%	0%
6	KOAc (1.5 eq.), blue LED (26°C)	72%	0%

[a]Yields of **8a** determined by ^{1}H-NMR using 1,4-dimethoxybenzene as internal standard based on diazonium salt **1a.** [b]Yields of **9** determined by ^{1}H-NMR using 1,4-dimethoxybenzene as internal standard based on α-methylstyrene (**3a**).

Although the reaction mixture containing **1a** and **3a** in methanol and acetonitrile does show even weaker absorptions in the range from 450 to 475 nm (ε values from 0.86 to 0.38 $M^{-1}cm^{-1}$) than in water and acetonitrile (1.50-0.88 $M^{-1}cm^{-1}$), a remarkable effect of visible light irradiation was also observed for carboetherification (Table 2, entries 1-3) in the absence of potassium acetate. This can be attributed, as for carbohydroxylation, to a weak but nevertheless effective CT complexation, resulting in an improved initiation step and an increased reaction rate. However, the absence of potassium acetate again leads to an acidic reaction mixture with pH values ranging from 3 to 1.5 over the reaction course, which results in the concomitant formation of methanol adduct **9**. The fact that a comparable side reaction with that to **9** was not observed during carbohydroxylation can be explained by the increased basicity of water compared to methanol,[28] which is apparently able to sufficient reduce the acidity in the reaction mixture.

With the addition of potassium acetate (entries 4-6), the pH change over the reaction course was again shifted to a region between 6 and 5, and the acid-induced formation of **9** was fully suppressed. As observed for the carbohydroxylation, the less acidic reaction mixture now basically favors radical formation from the diazonium ion and the beneficial effect of light irradiation is thus reduced.

With practicable conditions for carboetherification available, we turned to evaluate the substrate scope regarding the diazonium salt and the alcohol (Scheme 6).



Scheme 6. Reaction scope of carboetherification. [a]Yields determined after column chromatography.

Among the four diazonium salts leading to the methyl ethers **8a-d**, only the 4-fluoro derivative gave a moderate yield of **8b** (37%), which is due to the known sensitivity of the 4-fluoro-phenyldiazonium ion to less acidic conditions (c.f. Scheme 4).[24] The successful variation of the alcohols included increased

chain length and cyclic moieties (**8e-i**,**l**), allyl and benzyl alcohol (**8j** and **8k**) as well protected and unprotected diols (**8m** and **8n**), and gave yields in the range of 46 to 69%. Allylic and benzylic positions, which are often troublesome in radical arylations,[29] are thus well tolerated in the present functionalization. Only phenol failed to give the desired carboetherification product **8o**, which can be attributed to the fast hydrogen atom transfer from phenols to highly reactive aryl radicals under non-aqueous conditions.[30] Particularly remarkable are the successful reactions with citronellol and geraniol, which provided **8p** and **8q** in yields of 60% and 36% respectively. The mild biomimetic conditions of the carboetherification, which proceeds at room temperature and in a pH range from 5 to 6, are thus also applicable to more sensitive alcohols.

Conclusion

In summary, it has been shown that radical carbohydroxylations and carboetherifications can be carried out under hitherto unknown, exceptionally mild and biomimetic conditions. Besides the fact that no particular catalyst is required, the reactions further benefit from their feasibility in the absence of non-natural additives and at ambient temperature. Particularly remarkable is the accelerating effect of visible light irradiation, which is surprising as the individual reaction mixtures show only very weak absorptions in the applied wavelength range from 450 to 475 nm. This accelerating effect was found useful to increase the initiation rate when the overall conditions enable only slow initiation, as for example under acidic conditions. This general observation may be useful for many other aryldiazonium-based radical arylations, which can possibly be improved through visible light irradiation although only weak absorptions of the reaction mixture can be measured. All in all, these new results pave the way for a successful future application of aryldiazonium ions in radical reactions under biomimetic conditions and in biological systems.

Experimental Section

General Experimental

Solvents and reagents were obtained from commercial sources and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded using *Bruker Avance* 400 MHz (13C: 101 MHz), and *Bruker Avance* 600 MHz (13C: 151 MHz) spectrometers. For ^{1}H NMR spectra, $CDCl_3$, CD_3CN, D_2O, DMSO were used as solvents referenced to TMS (0 ppm), $CDCl_3$ (7.26 ppm), CD_3CN (1.94 ppm), D_2O (4.79 ppm), DMSO (2.50 ppm). Chemical shifts are in parts per million (ppm). Coupling constants are reported in hertz (Hz). The following abbreviations are used for the description of signals: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad singlet). ^{13}C NMR spectra were recorded in $CDCl_3$, CD_3CN and MeOH using $CDCl_3$ (77.0 ppm), CD_3CN (118.3 ppm) and MeOH (49.0 ppm) as standard. Chemical shifts are reported in parts per million (ppm). Mass spectra were recorded using electron spray ionization (ESI) and a sector field mass analyzer or time of flight (TOF) for HRMS measurements. Analytical TLC was carried out on Merck silica gel plates using short wave (254 nm) UV light to visualize components. Silica gel (Kieselgel 60, 40-63mm, Merck) was used for flash column chromatography. UV-vis spectra were recorded on a Specord 200 Plus device. For UV and UV-vis irradiation a 250 W iron lamp with either black glass filter (315-420nm) or without filter (315-700nm) was used. For visible light irradiation a 10 W blue LED lamp was used. Differential pulse voltammetry was conducted in a classical three-electrode cell from Deutsche Metrohm GmbH & Co. KG, which was connected to Metrohm Autolab PGSTAT 101, controlled by NOVA 2.1 software which was running on a personal computer. A gold electrode was used as a working electrode and was combined with a platinum sheet (1.0 cm^2) which served as a counter electrode. All potentials are provided relative to a Ag/AgCl (2 M lithium chloride in ethanol) reference electrode with a potential of 0.164 V vs SHE at 21±1°C. Spectra were measured in acetonitrile (LC-MS grade) at 21±1°C with NBu_4PF_6 (0.1 M) as a supporting electrolyte and **1a-d** (1 mM). Differential pulse voltammetry was performed with a scan rate of v = 10 mVs^{-1}. All measurements were done under nitrogen atmosphere.

General Procedures

*Aryldiazonium salts (**1a-h**):*
Aryldiazonium tetrafluoroborate salts (**1a-h**) were prepared according to literature procedures.[31]
Before use of the aryldiazonium tetrafluoroborate salts **1a-h**, the remaining water content was determined by ^{1}H-NMR to correct the actual amount of the tetrafluoroborate salts for further reactions.

Alkenes **3c-3f**:
Alkenes **3c**[32], **3d**[32], **3e**[33], **3f**[34] were prepared according to literature procedures.

General procedure for carbohydroxylation or carboetherification without base (GP1):
The alkene (**3**, 6.0 eq.) was dissolved in a mixture of acetonitrile and water or alcohol (5/1, 5 mL) under nitrogen atmosphere in a reaction tube. The tetrafluoroborate diazonium salt **1** (1.0 eq.) was dissolved in a mixture of acetonitrile and water or alcohol (5/1, 4 mL) and added to the reaction mixture. The reaction was stirred under nitrogen atmosphere and either under blue LED irradiation, in the dark at 23 °C or 28 °C for 19 h. Water (50 mL) was added to the mixture and it was extracted with diethylether (3 x 20 mL). The combined organic phases were dried over sodium sulfate and the solvent was removed under reduced pressure.
For NMR analysis, 1,4-dimethoxybenzene (69 mg, 0.5 mmol) was added and dissolved in $CDCl_3$.

General procedure for carbohydroxylation or carboetherification with base (GP2):
Potassium acetate (1.5 eq.) was added to a reaction tube and the tube was set under nitrogen atmosphere. The alkene (**3**, 6.0 eq.) was dissolved in a mixture of acetonitrile and water or alcohol (5/1, 5 mL) and added to the reaction. The tetrafluoroborate diazonium salt **1** (1.0 eq.) was dissolved in a mixture of acetonitrile and water or alcohol (5/1, 4 mL) and added to the reaction mixture. The reaction was stirred under nitrogen atmosphere and either under blue LED irradiation, in the dark at 23 °C or 28 °C for 19 h. Water (50 mL) was added to the mixture and it was extracted with diethylether (3 x 20 mL). The combined organic phases were dried over sodium sulfate and the solvent was removed under reduced pressure.
For NMR analysis, 1,4-dimethoxybenzene (69 mg, 0.5 mmol) was added and dissolved in $CDCl_3$.

Synthetic procedure and characterization data

*1-(4-Chlorophenyl)-2-phenylpropan-2-ol (**5a**)*. a) Compound **5a** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and water according to GP1 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 6/1 → 4/1) to give **5a** (191 mg, 0.77 mmol, 77%) as a yellow oil. b) Compound **5a** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol) and α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 4/1) to give **5a** (209 mg, 0.85 mmol, 85%) as a yellow oil. c) Compound **5a** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol) and α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) according to GP2 in the dark at 28 °C. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 10/1) to give **5a** (195 mg, 0.79 mmol, 79%) as a yellow oil. R_f = 0.7 (isohexane/ethyl acetate = 4:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.36 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.05 (d, *J* = 13.4 Hz, 1H), 2.96 (d, *J* = 13.4 Hz, 1H), 1.91 (bs, 1H), 1.53 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 147.2, 135.4, 132.6, 132.0, 128.2, 128.1, 126.9, 125.1, 74.6, 49.9, 29.3. The analytical data are in agreement with those reported in literature.[15]

*1-(4-Fluorophenyl)-2-phenylpropan-2-ol (**5b**)*. a) Compound **5b** was prepared from 4-fluorophenyl diazonium tetrafluoroborate (**1b**, 210 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and water according to GP1 under blue LED irradiation. Before workup potassium acetate (147 mg, 1.50 mmol) was added to the mixture. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 20/1 → 10/1 → 6/1) to give **5b** (188 mg, 0.82 mmol, 82%) as an orange oil. b) Compound **5b** was prepared from 4-fluorophenyl diazonium tetrafluoroborate (**1b**, 210 mg, 1.00 mmol) and α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 20/1) to give **5b** (94 mg, 0.41 mmol, 41%) as an orange oil. R_f = 0.7 (isohexane/ethyl acetate = 4:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.39 – 7.29 (m, 4H), 7.28 – 7.22 (m, 1H), 6.95 – 6.85 (m, 4H), 3.09 (d, *J* = 13.5 Hz, 1H), 2.99 (d, *J* = 13.5 Hz, 1H), 1.57 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 163.2, 160.7, 147.3, 132.1 (d, *J* = 7.8 Hz), 128.2, 126.9, 125.1, 114.9 (d, *J* = 21.1 Hz), 74.6, 49.8, 29.5. The analytical data are in agreement with those reported in literature.[15]

*1-(4-Bromophenyl)-2-phenylpropan-2-ol (**5c**)*. a) Compound **5c** was prepared from 4-bromophenyl diazonium tetrafluoroborate (**1c**, 271 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and water according to GP1 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 6/1) to give **5c** (205 mg, 0.70 mmol, 70%) as a red oil. b) Compound **5c** was prepared from 4-bromophenyl diazonium tetrafluoroborate (**1c**, 271 mg, 1.00 mmol) and α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 20/1 → 10/1) to give **5c** (244 mg, 0.84 mmol, 84%) as a red oil. R_f = 0.7 (isohexane/ethyl acetate = 4:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.38 – 7.29 (m, 6H), 7.27 – 7.22 (m, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.07 (d, *J* = 13.4 Hz, 1H), 2.97 (d, *J* = 13.4 Hz, 1H), 1.68 (bs, 1H), 1.57 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 147.1, 135.8, 132.3, 131.1, 128.2, 126.9, 125.0, 120.7, 74.5, 49.9, 29.4. The analytical data are in agreement with those reported in literature.[15]

*1-(3-Bromophenyl)-2-phenylpropan-2-ol (**5d**)*. a) Compound **5d** was prepared from 3-bromophenyl diazonium tetrafluoroborate (**1d**, 271 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and water according to GP1 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 6/1) to give **5d** (216 mg, 0.74 mmol, 74%) as a red oil. b) Compound **5d** was prepared from 3-bromophenyl diazonium tetrafluoroborate (**1d**, 271 mg, 1.00 mmol) and α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 20/1 → 10/1) to give **5d** (222 mg, 0.76 mmol, 76%) as a red oil. R_f = 0.7 (isohexane/ethyl acetate = 4:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.41 – 7.30 (m, 5H), 7.29 – 7.24 (m, 1H), 7.17 (t, *J* = 1.7 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.92 – 6.88 (m, 1H), 3.07 (d, *J* = 13.3 Hz, 1H), 2.97 (d, *J* = 13.3 Hz, 1H), 1.69 (bs, 1H), 1.57 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 147.3, 139.4, 133.7, 129.8, 129.6, 129.3, 128.3, 127.1, 125.0, 122.2, 74.6, 50.3, 29.4. The analytical data are in agreement with those reported in literature.[15]

*1-(3-Fluorophenyl)-2-phenylpropan-2-ol (**5e**)*. Compound **5e** was prepared from 3-fluorophenyl diazonium tetrafluoroborate (**1e**, 210 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and water according to GP1 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 8/1) to give **5e** (164 mg, 0.71 mmol, 71%) as a yellow oil. R_f = 0.7 (isohexane/ethyl acetate = 4:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.41 – 7.31 (m, 4H), 7.28 – 7.23 (m, 1H), 7.17 (td, *J* = 7.9, 6.1 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.72 – 6.68 (m, 1H), 3.11 (d, *J* = 13.3 Hz, 1H), 3.01 (d, *J* = 13.3 Hz, 1H), 1.58 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 163.8, 161.4, 147.3, 129.4 (d, *J* = 8.3 Hz), 128.3, 127.0, 126.4 (d, *J* = 2.8 Hz), 125.0, 117.6 (d, *J* = 21.0 Hz), 113.6 (d, *J* = 21.0 Hz), 74.6, 50.3 (d, *J* = 1.6 Hz), 29.5. The analytical data are in agreement with those reported in literature.[15]

*Methyl 4-(2-hydroxy-2-phenylpropyl)benzoate (**5f**)*. Compound **5f** was prepared from 4-(methoxycarbonyl)phenyldiazonium tetrafluoroborate (**1f**, 250 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and water according to GP1 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 6/1) to give **5f** (134 mg, 0.50 mmol, 50%) as an orange oil. R_f = 0.4 (isohexane/ethyl acetate = 4:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.89 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.30 – 7.24 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H), 3.19 (d, *J* = 13.1 Hz, 1H), 3.10 (d, *J* = 13.1 Hz, 1H), 1.61 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 167.2, 147.2, 142.5, 130.8, 129.3, 128.6, 128.3, 127.0, 125.1, 74.7, 52.2, 50.7, 29.6. The analytical data are in agreement with those reported in literature.[15]

*3-Methyl-3-phenylisochroman-1-one (**5g**)*. a) Compound **5g** was prepared from 2-(methoxycarbonyl)phenyldiazonium tetrafluoroborate (**1g**, 250 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and water according to GP1 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 6/1) to give **5g** (196 mg, 0.82 mmol, 82%) as a yellow oil. b) Compound **5g** was prepared from 2-(methoxycarbonyl)phenyldiazonium tetrafluoroborate (**1g**, 250 mg, 1.00 mmol) and α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 10/1) to give **5g** (189 mg, 0.79 mmol, 79%) as a yellow oil. R_f = 0.3 (isohexane/ethyl acetate = 6:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.04 (ddd, *J* = 7.8, 1.4, 0.6 Hz, 1H), 7.54 – 7.40 (m, 3H), 7.34 –

7.28 (m, 3H), 7.26 – 7.19 (m, 2H), 3.55 (d, *J* = 16.3 Hz, 1H), 3.43 (d, *J* = 16.2 Hz, 1H), 1.78 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 165.4, 143.7, 138.0, 134.0, 130.1, 128.6, 127.7, 127.6, 127.5, 125.3, 124.8, 83.7, 39.2, 30.3. The analytical data are in agreement with those reported in literature.[15]

*2-(4-Chlorophenyl)-1,1-diphenylethan-1-ol (**5i**)*. Compound **5i** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), 1,1-diphenyl ethylene (**3b**, 1.06 mL, 6.00 mmol) and water according to GP1 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1 → 30/1) to give **5i** (76 mg, 0.25 mmol, 25%) as a light orange oil. Compound **5i** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), 1,1-diphenyl ethylene (**3b**, 1.06 mL, 6.00 mmol) and water according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1 → 30/1) to give **5i** (196 mg, 0.63 mmol, 63%) as a light orange oil. R_f = 0.3 (isohexane/ethyl acetate = 10:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.46 – 7.40 (m, 4H), 7.37 – 7.31 (m, 4H), 7.32 – 7.23 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.62 (s, 2H), 2.30 (bs, 1H). DEPTQ ($CDCl_3$, 151 MHz) δ (ppm) = 146.4, 134.6, 132.7, 132.3, 128.2, 128.1, 127.2, 126.3, 78.1, 47.4.The analytical data are in agreement with those reported in literature.[15]

*1,2-Bis(4-chlorophenyl)propan-2-ol (**5j**)*. Compound **5j** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 180 mg, 0.78 mmol), 1-chloro-4-(prop-1-en-2-yl)benzene (**3c**, 711 mg, 4.66 mmol) and water according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 10/1) to give **5j** (144 mg, 0.51 mmol, 66%) as an orange oil. R_f = 0.3 (isohexane/ethyl acetate = 10:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.28 (s, 4H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 3.03 (d, *J* = 13.4 Hz, 1H), 2.96 (d, *J* = 13.4 Hz, 1H), 1.54 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 145.7, 135.0, 132.7, 132.6, 131.9, 128.2, 128.2, 126.6, 74.3, 49.8, 29.4.The analytical data are in agreement with those reported in literature.[15]

*1-(4-Chlorophenyl)-2-(4-methoxyphenyl)propan-2-ol (**5k**)*. Compound **5k** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 199 mg, 0.86 mmol), 1-methoxy-4-(prop-1-en-2-yl)benzene (**3d**, 760 mg, 5.13 mmol) and water according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 5/1) to give **5k** (199 mg, 0.72 mmol, 84%) as an orange oil. R_f = 0.2 (isohexane/ethyl acetate = 5:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.27 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.05 (d, *J* = 13.3 Hz, 1H), 2.97 (d, *J* = 13.3 Hz, 1H), 1.54 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) =158.5, 139.4, 135.6, 132.6, 132.0, 128.2, 126.3, 113.5, 74.4, 55.4, 50.1, 29.5.The analytical data are in agreement with those reported in literature.[15]

*1-(4-Chlorophenyl)-2-(naphthalen-2-yl)propan-2-ol (**5m**)*. Compound **5m** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), 2-(prop-1-en-2-yl)naphthalene (**3f**, 1009 mg, 6.00 mmol) and water according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 6/1) to give **5m** (238 mg, 0.80 mmol, 80%) as a yellow oil. R_f = 0.3 (isohexane/ethyl acetate = 4:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.98 – 7.80 (m, 4H), 7.59 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.23 (d, *J* = 13.4 Hz, 1H), 3.13 (d, *J* = 13.4 Hz, 1H), 2.26 (bs, 1H), 1.70 (s, 3H).DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.6, 135.3, 133.2, 132.6, 132.4, 132.0, 128.3, 128.2, 128.0, 127.6, 126.2, 126.0, 123.8, 123.6, 74.8, 49.6, 29.6.The analytical data are in agreement with those reported in literature.[15]

*2-(4-Chlorophenyl)-1-phenylethan-1-ol (**5n**)*. Compound **5n** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), styrene (**3g**, 0.92 mL, 6.00 mmol) and water according to GP2 under blue LED irradiation. The yield was determined by 1H NMR spectroscopy using 1,4-dimethoxybenzene (69 mg, 0.5 mmol) yielding in 15% of compound **5n**. The analytical data is in agreement with those reported in literature.[35]

*2-(4-Chlorophenyl)-1-(4-methoxyphenyl)ethan-1-ol (**5o**)*. Compound **5o** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), 1-methoxy-4-vinylbenzene (**3h**, 0.80 mL, 6.00 mmol) and water according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ ethyl acetate : 6/1 → 4/1) to give **5o** (120 mg, 0.46 mmol, 46%) as an orange oil. R_f = 0.5 (isohexane/ethyl acetate = 2:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.30 – 7.21 (m, 4H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.82 (dd, *J* = 7.7, 5.6 Hz, 1H), 3.83 (s, 3H), 3.07 – 2.93 (m, 2H), 2.05 (bs, 1H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 159.2, 136.7, 135.8, 132.33, 131.0, 128.5, 127.3, 113.9, 75.0, 55.4, 45.4. The analytical data are in agreement with those reported in literature.[15]

*1-Chloro-4-(2-methoxy-2-phenylpropyl)benzene (**8a**)*. Compound **8a** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and methanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 2/1) to give **8a** (194 mg, 0.74 mmol, 74%) as a yellow oil. R_f = 0.4 (isohexane/ethyl acetate = 10:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.34 – 7.22 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.10 (s, 3H), 2.98 (d, *J* = 13.2 Hz, 1H), 2.92 (d, *J* = 13.3 Hz, 1H), 1.48 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.0, 136.0, 132.1, 128.2, 127.7, 127.2, 126.8, 79.7, 50.7, 50.3, 21.3. The analytical data are in agreement with those reported in literature.[15]

*1-Fluoro-4-(2-methoxy-2-phenylpropyl)benzene (**8b**)*. Compound **8b** was prepared from 4-fluorophenyl diazonium tetrafluoroborate (**1b**, 210 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and methanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 20/1) to give **8b** (91 mg, 0.37 mmol, 37%) as a yellow oil. R_f = 0.6 (isohexane/ethyl acetate = 20:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.34 – 7.20 (m, 5H), 6.94 – 6.59 (m, 4H), 3.10 (s, 3H), 2.98 (d, *J* = 13.3 Hz, 1H), 2.93 (d, *J* = 13.3 Hz, 1H), 1.49 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 162.4, 160.8, 144.0, 133.1 (d, *J* = 3.2 Hz), 132.1 (d, *J* = 7.7 Hz), 128.0, 127.0, 126.7, 114.3 (d, *J* = 20.7 Hz), 79.6, 50.5, 45.0, 21.2. HRMS (ESI): calculated for $C_{15}H_{14}F$ [M-CH_3OH+H^+]: 213.1074, found: 213.1075.

*1-Bromo-4-(2-methoxy-2-phenylpropyl)benzene (**8c**)*. Compound **8c** was prepared from 4-bromophenyl diazonium tetrafluoroborate (**1c**, 271 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and methanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1 → 50/1) to give **8c** (208 mg, 0.68 mmol, 68%) as an orange oil. R_f = 0.4 (isohexane/ethyl acetate = 50:1) [UV]. ^{1}H-NMR

($CDCl_3$, 400 MHz) δ (ppm) = 7.40 – 7.22 (m, 7H), 6.77 (d, *J* = 8.7 Hz, 2H), 3.13 (s, 3H), 3.00 (d, *J* = 13.2 Hz, 1H), 2.94 (d, *J* = 13.2 Hz, 1H), 1.52 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 143.9, 136.5, 132.5, 130.6, 128.2, 127.2, 126.7, 120.3, 79.6, 50.6, 50.3, 21.3. HRMS (ESI): calculated for $C_{15}H_{14}Br$ [M-CH_3OH+H^+]: 273.0273, found: 273.0272.

*1-Bromo-3-(2-methoxy-2-phenylpropyl)benzene (**8d**)*. Compound **8d** was prepared from 3-bromophenyl diazonium tetrafluoroborate (**1d**, 271 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and methanol according to GP2 under blue LED irradiation. The crude product purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1) to give **8d** (278 mg, 0.91 mmol, 91%) as a brown oil. R_f = 0.4 (isohexane/ethyl acetate = 100:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.36 – 7.22 (m, 5H), 7.04 (t, *J* = 1.9 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 3.10 (s, 3H), 2.98 (d, *J* = 13.3 Hz, 1H), 2.90 (d, *J* = 13.3 Hz, 1H), 1.50 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 143.9, 139.9, 133.7, 129.3, 129.2, 129.0, 128.1, 127.1, 126.6, 121.6, 79.5, 50.5, 50.5, 21.2. HRMS (ESI): calculated for $C_{15}H_{14}Br$ [M-CH_3OH+H^+]: 273.0273, found: 273.0272.

*1-Chloro-4-(2-ethoxy-2-phenylpropyl)benzene (**8e**)*. Compound **8e** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and ethanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 200/1 → 100/1 → 20/1) to give **8e** (190 mg, 0.69 mmol, 69%) as an orange oil. R_f = 0.8 (isohexane/ethyl acetate = 10:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.33 – 7.22 (m, 5H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 3.35 (dq, *J* = 8.8, 6.9 Hz, 1H), 3.13 (dq, *J* = 8.8, 7.0 Hz, 1H), 2.98 (d, *J* = 13.2 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 1.48 (s, 3H), 1.17 (t, *J* = 7.0 Hz, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.8, 136.2, 132.2, 132.1, 128.1, 127.7, 127.1, 126.6, 79.3, 58.0, 50.6, 21.9, 15.9. HRMS (ESI): calculated for $C_{17}H_{19}ClNaO$ [M+Na]: 297.1017, found: 297.1021.

*1-Chloro-4-(2-phenyl-2-propoxypropyl)benzene (**8f**)*. Compound **8f** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and propanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1) to give **8f** (196 mg, 0.68 mmol, 68%) as a yellow oil. R_f = 0.4 (isohexane/ethyl acetate = 100:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.36 – 7.21 (m, 5H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.23 (dt, *J* = 8.7, 6.7 Hz, 1H), 3.05 (dt, *J* = 8.7, 6.7 Hz, 1H), 2.99 (d, *J* = 13.2 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 1.59 (dtd, *J* = 14.1, 7.4, 6.6 Hz, 2H), 1.50 (s, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.9, 136.3, 132.2, 132.0, 128.1, 127.6, 127.1, 126.6, 78.9, 64.2, 50.8, 23.7, 21.8, 11.0. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-C_3H_8O+H^+]: 229.0779, found: 229.0781.

*1-(2-Butoxy-2-phenylpropyl)-4-chlorobenzene (**8g**)*. Compound **8g** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and butanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1) to give **8g** (209 mg, 0.69 mmol, 69%) as an orange oil. R_f = 0.3 (isohexane/ethyl acetate = 100:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.33 – 7.22 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.26 (dt, *J* = 8.8, 6.6 Hz, 1H), 3.08 (dt, *J* = 8.8, 6.6 Hz, 1H), 2.98 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 1.55 (ddt, *J* = 12.1, 8.8, 4.0 Hz, 2H), 1.48 (s, 3H), 1.37 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.9, 136.3, 132.2, 132.0, 128.1, 127.6, 127.1, 126.7, 79.0, 62.2, 50.8, 32.6, 21.8, 19.6, 14.2. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-$C_4H_{10}O$+H^+]: 229.0779, found: 229.0782.

*1-Chloro-4-(2-(pentyloxy)-2-phenylpropyl)benzene (**8h**)*. Compound **8h** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and pentanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1) to give **8h** (172 mg, 0.54 mmol, 54%) as an orange oil. R_f = 0.3 (isohexane/ethyl acetate = 100:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.33 – 7.21 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.25 (dt, *J* = 8.7, 6.7 Hz, 1H), 3.06 (dt, *J* = 8.7, 6.7 Hz, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.88 (d, *J* = 13.2 Hz, 1H), 1.59 – 1.51 (m, 2H), 1.48 (s, 3H), 1.29 (tdd, *J* = 11.0, 6.0, 3.6 Hz, 4H), 0.89 (t, *J* = 7.1 Hz, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 145.0, 136.3, 132.2, 132.1, 128.1, 127.7, 127.1, 126.7, 79.0, 62.6, 50.8, 30.2, 28.6, 22.7, 21.9, 14.2. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-$C_5H_{12}O$+H^+]: 229.0779, found: 229.0781.

*1-Chloro-4-(2-(octyloxy)-2-phenylpropyl)benzene (**8i**)*. Compound **8i** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and octanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1) to give **8i** (220 mg, 0.61 mmol, 61%) as an orange oil. R_f = 0.3 (isohexane/ethyl acetate = 100:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.33 – 7.21 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.25 (dt, *J* = 8.7, 6.7 Hz, 1H), 3.06 (dt, *J* = 8.7, 6.7 Hz, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.88 (d, *J* = 13.2 Hz, 1H), 1.59 – 1.51 (m, 2H), 1.48 (s, 3H), 1.29 (tdd, *J* = 11.0, 6.0, 3.6 Hz, 4H), 0.89 (t, *J* = 7.1 Hz, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.8, 136.2, 132.1, 132.0, 128.0, 127.5, 127.0, 126.5, 78.9, 62.4, 50.7, 31.9, 30.4, 29.5, 29.4, 26.3, 22.7, 21.7, 14.2. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-$C_8H_{18}O$+H^+]: 229.0779, found: 229.0781.

*1-(2-(Allyloxy)-2-phenylpropyl)-4-chlorobenzene (**8j**)*. Compound **8j** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and allyl alcohol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1) to give **8j** (132 mg, 0.46 mmol, 46%) as a red oil. R_f = 0.3 (isohexane/ethyl acetate = 100:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.38 – 7.24 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.93 (ddt, *J* = 17.2, 10.5, 5.0 Hz, 1H), 5.34 (dd, *J* = 17.2, 1.9 Hz, 1H), 5.16 (dd, *J* = 10.4, 1.8 Hz, 1H), 3.86 (ddt, *J* = 12.9, 5.2, 1.6 Hz, 1H), 3.69 (ddt, *J* = 12.8, 4.8, 1.7 Hz, 1H), 3.07 – 2.92 (m, 2H), 1.55 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.3, 136.0, 135.6, 132.2, 132.1, 128.2, 127.7, 127.3, 126.6, 115.5, 79.8, 63.9, 50.7, 22.0. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-C_3H_6O+H^+]: 229.0779, found: 229.0781.

*1-(2-(Benzyloxy)-2-phenylpropyl)-4-chlorobenzene (**8k**)*. Compound **8k** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and benzyl alcohol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1 → 50/1) to give **8k** (227 mg, 0.67 mmol, 67%) as a yellow oil. R_f = 0.2 (isohexane 100%) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.44 – 7.31 (m, 10H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.26 (d, *J* = 11.5 Hz, 1H), 3.14 (d, *J* = 13.3 Hz, 1H), 3.05 (d, *J* = 13.3 Hz, 1H), 1.67 (s, 3H).). DEPTQ ($CDCl_3$,

101 MHz) δ (ppm) = 144.3, 139.4, 136.0, 132.2, 132.1, 128.4, 128.2, 127.7, 127.3, 127.2, 127.2, 126.6, 79.8, 64.8, 50.8, 21.9. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-C_7H_8O+H^+]: 229.0779, found: 229.0779.

1-Chloro-4-(2-(cyclohexylmethoxy)-2-phenylpropyl)benzene ***(8l)***. Compound **8l** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and cyclohexylmethanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 50/1) to give **8l** (177 mg, 0.52 mmol, 52%) as a light orange oil. R_f = 0.4 (isohexane/ethyl acetate = 100:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.36 – 7.25 (m, 5H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.10 (dd, *J* = 8.6, 6.4 Hz, 1H), 3.02 (d, *J* = 13.2 Hz, 1H), 2.96 – 2.88 (m, 2H), 1.87 – 1.69 (m, 5H), 1.66 – 1.54 (m, 1H), 1.51 (s, 3H), 1.37 – 1.16 (m, 3H), 1.03 – 0.90 (m, 2H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.9, 136.3, 132.3, 132.0, 128.0, 127.6, 127.0, 126.7, 78.6, 68.1, 50.8, 38.7, 30.5, 26.9, 26.2, 21.8. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-$C_7H_{14}O$+H^+]: 229.0779, found: 229.0781.

2-((1-(4-Chlorophenyl)-2-phenylpropan-2-yl)oxy)ethan-1-ol ***(8m)***. Compound **8m** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and ethylene glycol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 4/1) to give **8m** (138 mg, 0.47 mmol, 47%) as an orange oil. R_f = 0.3 (isohexane/ethyl acetate = 4:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.34 – 7.23 (m, 5H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.77 – 3.66 (m, 2H), 3.39 (ddd, *J* = 9.8, 6.3, 3.5 Hz, 1H), 3.24 (ddd, *J* = 9.6, 5.4, 3.5 Hz, 1H), 3.02 (d, *J* = 13.3 Hz, 1H), 2.94 (d, *J* = 13.3 Hz, 1H), 1.88 (bs, 1H), 1.52 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 143.9, 135.8, 132.2, 132.0, 128.2, 127.7, 127.3, 126.5, 79.2, 63.4, 62.4, 50.5, 21.8. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-$C_2H_6O_2$+H^+]: 229.0779, found: 229.0780.

1-(2-(4-(Benzyloxy)butoxy)-2-phenylpropyl)-4-chlorobenzene ***(8n)***. Compound **8n** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and 4-benzyloxy-1-butanol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 50/1 → 25/1) to give **8n** (197 mg, 0.48 mmol, 48%) as an orange oil. R_f = 0.3 (isohexane/ethyl acetate = 50:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.39 – 7.24 (m, 10H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.52 (s, 2H), 3.50 (t, *J* = 6.3 Hz, 2H), 3.29 (dt, *J* = 8.7, 6.3 Hz, 1H), 3.12 (dt, *J* = 8.7, 6.2 Hz, 1H), 2.99 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 1.77 – 1.62 (m, 4H), 1.49 (s, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.8, 138.7, 136.2, 132.2, 132.0, 128.5, 128.1, 127.7, 127.6 (x2), 127.1, 126.6, 79.0, 72.97, 70.4, 62.2, 50.7, 27.1, 26.8, 21.8. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-$C_{11}H_{16}O_2$+H^+]: 229.0779, found: 229.0781; calculated for $C_{11}H_{17}O_2$ [M-$C_{15}H_{13}Cl$+H^+]: 181.1223, found: 181.1224.

1-Chloro-4-(2-((3,7-dimethyloct-6-en-1-yl)oxy)-2-phenylpropyl)benzene ***(8p)***. Compound **8p** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and β-citronellol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 100/1) to give **8p** (230 mg, 0.60 mmol, 60%) as a red oil. R_f = 0.2 (isohexane/ethyl acetate = 100:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.33 – 7.19 (m, 5H), 7.10 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.81 (dd, *J* = 8.4, 4.1 Hz, 2H), 5.09 (dp, *J* = 5.7, 1.5 Hz, 1H), 3.34 – 3.22 (m, 1H), 3.14 – 3.02 (m, 1H), 2.96 (d, *J* = 13.3 Hz, 1H), 2.87 (dd, *J* = 13.2, 5.3 Hz, 1H), 1.97 (dt, *J* = 14.6, 7.8 Hz, 2H), 1.68 (d, *J* = 1.3 Hz, 2H), 1.60 (dd, *J* = 6.5, 1.3 Hz, 3H), 1.56 (s, 3H), 1.50 – 1.46 (m, 3H), 1.42 – 1.20 (m, 2H), 1.18 – 1.07 (m, 1H), 0.87 – 0.80 (m, 3H). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.9 (d), 136.3, 132.2, 132.0, 128.1, 127.6, 127.1, 126.6 (d), 125.0, 79.0, 60.8, 60.7, 50.8 (d), 37.6, 37.5, 37.4, 37.3, 29.9, 29.7 (d), 25.9 (d), 25.7, 25.6, 21.8, 19.9, 19.7, 17.8 (d). HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-$C_{10}H_{20}O$ +H^+]: 229.0779, found: 229.0777.

1-Chloro-4-(2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-2-phenylpropyl)benzene ***(8q)***. Compound **8q** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and geraniol according to GP2 under blue LED irradiation. The crude product was purified *via* column chromatography (isohexane/ dichloromethane : 6/1) to give **8q** (139 mg, 0.36 mmol, 36%) as an orange oil. R_f = 0.2 (isohexane/dichloromethane = 5:1) [UV]. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.38 – 7.25 (m, 5H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.39 (ddd, *J* = 6.6, 5.9, 1.3 Hz, 1H), 5.14 (ddt, *J* = 7.0, 5.5, 1.4 Hz, 1H), 3.88 (ddd, *J* = 11.2, 6.6, 0.8 Hz, 1H), 3.67 (ddd, *J* = 11.2, 6.5, 0.9 Hz, 1H), 3.04 (d, *J* = 13.2 Hz, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.17 – 2.03 (m, 4H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.57 (d, *J* = 1.3 Hz, 3H), 1.54 (s, 3H).). DEPTQ ($CDCl_3$, 101 MHz) δ (ppm) = 144.4, 138.7, 136.0, 132.1, 132.0, 131.6, 128.0, 127.6, 127.1, 126.7, 124.1, 121.6, 79.5, 59.8, 50.5, 39.7, 26.4, 25.8, 21.7, 17.8, 16.5. HRMS (ESI): calculated for $C_{15}H_{14}Cl$ [M-$C_{10}H_{18}O$ +H^+]: 229.0779, found: 229.0777.

(2-Methoxypropan-2-yl)benzene ***(9)***. Compound **9** was prepared from 4-chlorophenyl diazonium tetrafluoroborate (**1a**, 226 mg, 1.00 mmol), α-methylstyrene (**3a**, 0.78 mL, 6.00 mmol) and methanol according to GP1 under blue LED irradiation. The crude product was purified *via* column chromatography (100% isohexane → isohexane/ ethyl acetate : 10/1). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.44-7.20 (m, 5H), 3.07 (s, 3H), 1.54 (s, 6H). The analytical data are in agreement with those reported in literature.[36]

Acknowledgements

The authors would like to thank Elisabeth Eckenberger for technical assistance. L.-M.A. is also grateful for support by the Graduate School Molecular Science (GSMS). The DPV measurements supported by Pascal Gazetas and Prof. Dr. Norbert Jux, (FAU Erlangen-Nürnberg) are gratefully acknowledged.

Keywords: Meerwein • Arylation • Diazonium • Styrene • Biomimetic

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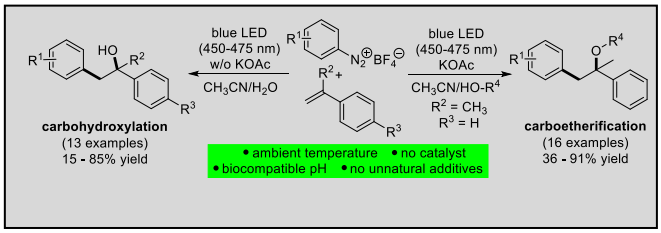

As shown in this work, Meerwein-type carbooxygenations can be conducted under fully biocompatible conditions, including ambient temperature and the absence of catalysts or unnatural additives. Surprisingly, the reactions can be further promoted by visible light irradiation, although the reaction mixtures show only very weak absorptions in the respective wavelength range.

Institute and/or researcher Twitter usernames: ((optional))

10.1002/chem.202004234