Redox neutral and acid-free Minisci C-H alkylation of heteroarenes enabled by dual photoredox/bromide catalysis in micellar solutions

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Abstract

Microstructured aqueous solutions were employed to engage non-activated alkyl bromides in the visible-light-promoted C-H functionalization of heteroarenes. The reactive carbon-centered alkyl radicals were generated by merging the photoredox approach, bromide anion co-catalysis and spatial pre-aggregation of reacting species in the mixture. The presented methodology allowed obtaining alkylated heteroarenes without stoichiometric radical-promoters, in acid-free conditions and using blue LEDs as the light source.

1. Introduction

C-H alkylation of heteroarenes, known as Minisci reaction, is a well-established synthetic tool for C(sp^2)-C(sp^3) bond formation.[1] It enables direct, late-stage modification of aromatic heterocycles, which are omnipresent structural motifs in various natural products, pharmaceuticals and agrochemicals.[2] The Minisci reaction involves generation of carbon-centered alkyl radicals and their addition to an electron-deficient heteroaromatic ring, which is accompanied by a formal loss of the hydrogen atom.

Various precursors of alkyl radicals have been employed in the Minisci reaction including amino acids,[3] aldehydes,[4–6] ketones,[7] carboxylic acids,[8–10] alkyltrifluoroborate salts,[11] pyridinium salts,[12,13] boronic acids,[14,15] diazonium salts,[16] peroxides,[17–19] alkyl halides[20–27] etc. Among them, alkyl bromides are of particular synthetic potential, as they are readily available and inexpensive starting materials. However, the cleavage of the relatively strong C−Br bond in alkyl bromides, which must occur in the course of the process, presents a major challenge. As a result, only few variants of the Minisci reaction exploiting non-activated alkyl bromides have been reported so far.

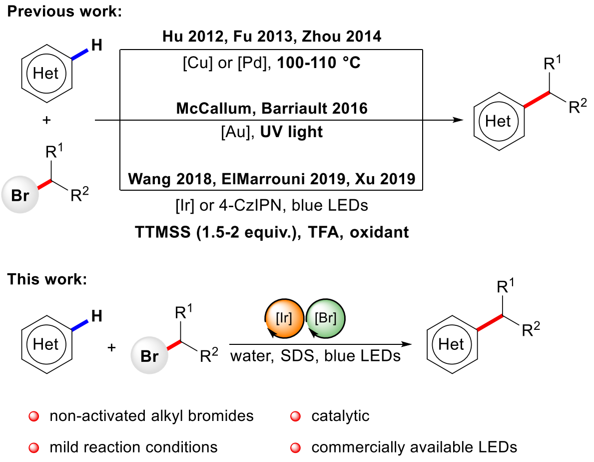


Fig. 1. Strategies for C-H alkylation of heteroarenes with non-activated alkyl bromides.

The established strategies to overcome the challenge of C-Br bond activation involve the use of high temperatures, strong UV-light irradiation or the addition of stoichiometric amounts of silyl radical-promoters (Fig. 1). Accordingly, in 2012 Hu *et al.* developed an efficient method for alkylation of benzoxazoles with secondary alkyl halides.[22] The majority of presented syntheses were realized using alkyl iodides, but few examples with bromides have also been reported. The reaction was performed at elevated temperatures, and with the use of copper-based catalyst. One year later, Fu *et al.* demonstrated the cross-coupling of non-activated secondary and tertiary alkyl bromides with pyridine *N*-oxides in the presence of palladium catalyst and phosphine ligand.[23] The method was further developed by Zhou *et al.*, who extended the palladium-catalyzed Minisci reaction on a broad variety of heteroarenes, including indole- and pyridine derivatives.[24] The photocatalytic alternative towards the activation of alkyl bromides have been presented by McCallum and Barriault.[25] Using gold complexes as catalysts and UV light as the energy source they performed Minisci reactions with various non-activated bromoalkanes and heteroarenes and supported their studies by the detailed investigations of photophysical and electrochemical properties of the photocatalyst.[26] Minisci reactions with non-activated alkyl bromides were also investigated by the groups of Wang, ElMarrouni and Xu, who capitalized on the joined action of the photocatalyst, acid, silyl radical-promoters and visible light irradiation.[27–29]

While these pioneering methods are of unquestionable value, the need for mild, redox-neutral catalytic methods of C-H alkylation of heteroarenes with alkyl bromides still remains. In order to address this challenge we resorted to photocatalysis in aqueous structured solutions. We exploited the pre-aggregation of the reacting species and merged it with the autocatalytic role of bromide anions, which were generated *in situ* from the starting material.[30] This allowed facilitating the C-C coupling of non-activated alkyl bromides with heteroarenes without stoichiometric radical-promoters, in acid-free conditions and with commercial blue LEDs as the light source.

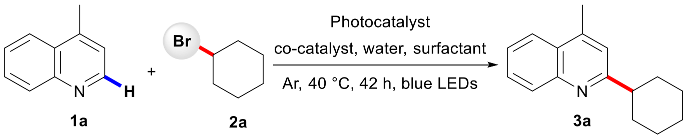
2. Results and discussion

The redox potential of typical photocatalysts in their excited state, including strongly reducing Ir-species, precludes the direct single-electron-transfer (SET) to alkyl bromides (-2.29 V vs. SCE for 1-bromooctane)[31]. However, catalytic species of a much higher reducing power can be generated via the reductive quenching of the catalyst followed by the subsequent excitation with a second visible-light-photon.[30,32–34] Although the typically used reductive quenchers include tertiary amines, Hantzsch esters, alcohols, ascorbate anions etc.,[35] it has recently been shown that the efficient quenching of excited Ir-complexes can also be achieved using simple halide anions, leading to Ir(II)-species and halide radicals.[36–40] We decided to test, if Br^- anions, which are released upon the single-electron-reduction and fragmentation of alkyl bromides, can be recycled and used as mediators in the Minisci reaction - quench the excited Ir(III)-photocatalyst and thus promote the generation of alkyl radicals.

Unique properties of structured solutions of surfactants, combined with operationally simple preparation, render them advantageous media for chemical reactions such as biocatalysis,[41] polymerizations,[42] transition-metal catalyzed cross-coupling reactions,[43] and organocatalytic transformations[44]. Recent reports show that they may also play a vital role in photocatalysis.[30,45–48] From the viewpoint of the designed Minisci reaction, structured aqueous solution could provide the necessary pre-association of the starting materials and the photocatalyst, improve the kinetics of the reaction and thus eliminate the harsh reaction conditions or stoichiometric additives, including radical promotors and acids.

In order to test the working hypothesis, we subjected bromocyclohexane (**2a**) to the reaction with lepidine (**1a**) in the presence of $Ir(dtbby)(ppy)_2PF_6$ (**4**) as photocatalyst, in aqueous solution of surfactant and under irradiation with blue LEDs (Table **1**). We were pleased to see that the reaction proceeded and the desired coupling product **3a** was formed in 31% yield (entry 1). The reaction parameters were then optimized with respect to the surfactant, photocatalyst, co-catalyst, time, as well as the ratio and concentration of reagents (for full optimization studies see SI). The addition of the catalytic amount of NaBr facilitated the process and increased the yield of compound **3a** to 47% (entry 2). Further screening established CBr_4 as a co-catalyst of choice (entries 2-5). The applied conditions, which were called Procedure A, afforded the full conversion of lepidine **1a** and the desired product **3a** in 91% yield. The alkylation occurred selectively at position *C2*. Although the optimal reaction conditions involved 20 mol% of CBr_4 and 42 hours of irradiation, the efficient formation of the product **3a** was observed already after shorter reaction time (52% after 18 h, 78% after 24 h) or using lower co-catalyst loading (5 mol%) (entries 6 and 7, respectively). Among various tested photocatalysts, the highest activity was achieved using Ir(dtbbpy)(ppy)$_2$PF$_6$ (**4**). Other mediators proved inefficient (entries 8, 10-12), or provided the product **3a** in low yield (entry 9). Having catalyst and co-catalyst selected, we evaluated the influence of popular and readily available surfactants. The superior performance of sulfate-based surfactants: sodium dodecyl sulfate (SDS) and sodium lauryl oligoethylene glycol sulfate (SLES) was observed (entries 1 - 13), which is in agreement with previous reports.[30] The satisfactory 41% yield of the desired product **3a** was also detected when zwitterionic surfactant SB3-14 was used (entry 15). The application of anionic potassium dodecanate, cationic dodecyltrimethylammonium chloride (DTAC) or non-ionic Triton X-100 led to less efficient product **3a** formation (entries 14, 16, 17).

Table 1. Optimization studies^a

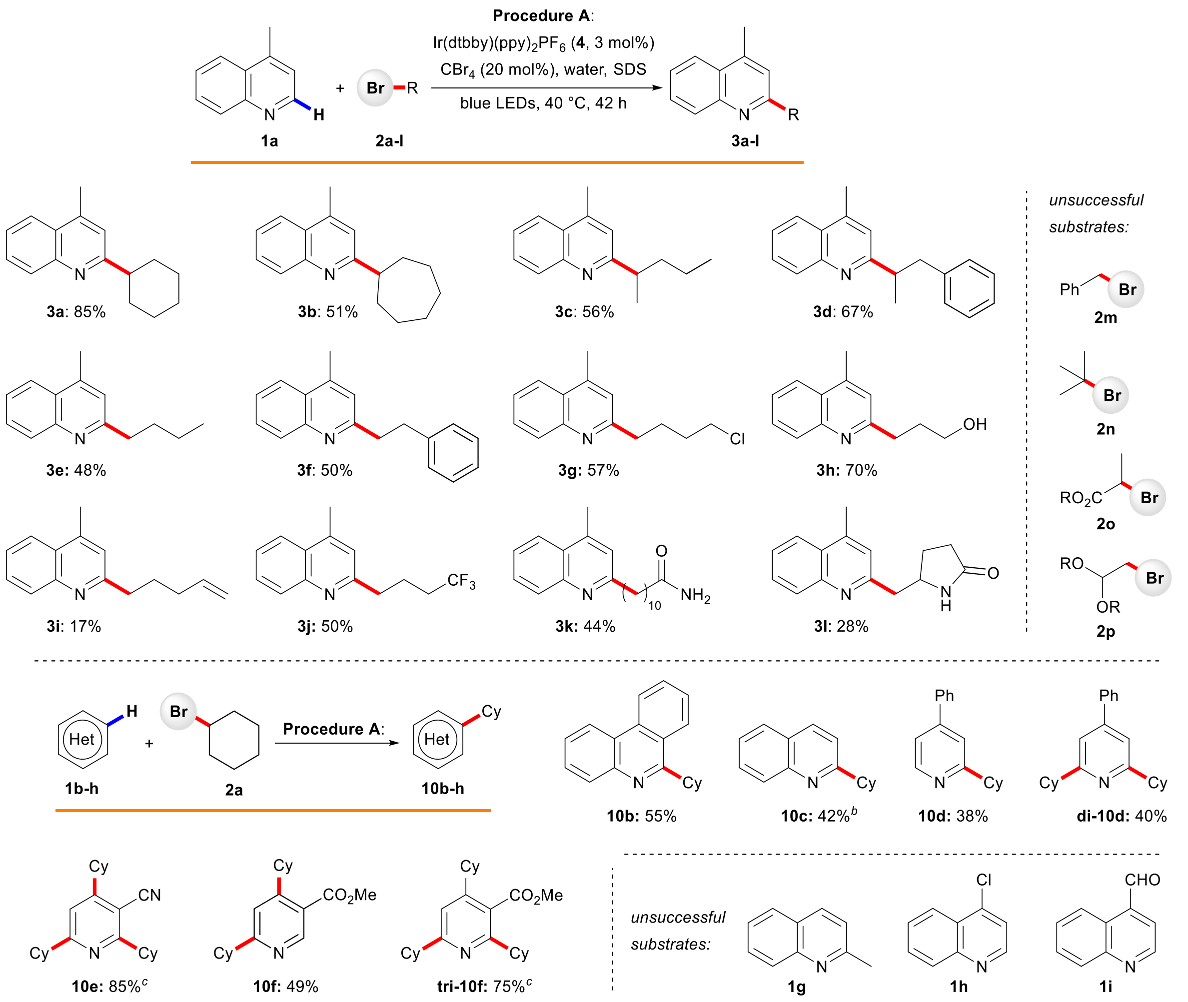


No.	Co-catalyst	Photocatalyst	Time [h]	Surfactant	Yield 3a^b [%]
1	-	[Ir] **4**	42	SDS	31
2	NaBr	[Ir] **4**	42	SDS	47
3	NBS	[Ir] **4**	42	SDS	19
4	CCl$_3$Br	[Ir] **4**	42	SDS	85
5	CBr$_4$	[Ir] **4**	42	SDS	91
6	CBr$_4$	[Ir] **4**	24	SDS	78
7	CBr$_4$ (5 mol%)	[Ir] **4**	42	SDS	48
8	CBr$_4$	[Ir] **5**	42	SDS	0
9	CBr$_4$	[Ir] **6**	42	SDS	16
10	CBr$_4$	Ru(bpy)$_3$PF$_6$ (**7**)	42	SDS	0
11	CBr$_4$	4CzIPn (**8**)	42	SDS	0
12	CBr$_4$	Eosin Y (**9**)	42	SDS	0
13	CBr$_4$	[Ir] **4**	42	SLES	48
14	CBr$_4$	[Ir] **4**	42	C$_{11}$H$_{23}$CO$_2$K	13
15	CBr$_4$	[Ir] **4**	42	SB3-14	41
16	CBr$_4$	[Ir] **4**	42	Triton X-100	24
17	CBr$_4$	[Ir] **4**	42	DTAC	16

^{a}Reaction conditions: lepidine **1a** (0.1 mmol), bromocyclohexane **2a** (0.2 mmol), surfactant (0.25 mmol), co-catalyst (20 mol%), photocatalyst (3 mol%), water (5 mL), 40 °C, 451 nm, 42 h. ^{b}Yields were calculated using GC analysis. *n*-Dodecane was used as internal standard. [Ir] **4** - Ir(dtbbpy)(ppy)$_2$PF$_6$, [Ir] **5** - Ir(ppy)$_3$PF$_6$, [Ir] **6** - Ir[dF(CF$_3$)(ppy)$_2$](dtbby)PF$_6$.

With the reaction conditions established, we next investigated the scope of the developed transformation (Table 2). In general, secondary bromides **2a**-**2d** provided higher yields of the desired products than primary ones **2e**-**2l**, which reflects higher thermodynamic stability of the intermediate radicals. However, the precursors **2m-o** of even more stabilized benzyl, tertiary or α-carbonyl radicals, proved unsuitable, presumably due to the competing oxidation to carbocations and hydrolysis, which led to respective alcohols. Several functional groups in the bromide moiety showed good compatibility with our procedure such as free hydroxyl group (**3h**), primary (**3k**) and secondary amides (**3l**), chlorides (**3g**) or CF$_3$ function (**3j**). Additionally, the product **3i** possessing a terminal double bond was also isolated. Alkyl bromides **2p** decorated with acetal groups proved unstable under the reaction conditions. Evaluation of the aromatic coupling partners showed that the reaction is compatible not only with simple heterocycles such as lepidine **1a**, phenantridine **1b** and quinoline **1c**, but also derivatives, which contain ester or cyano substituents. 4-Phenylpyridine **1d** gave a mixture of mono- and disubstituted products **10d** and **di-10d**, both of which could be selectively isolated (38% and 40% respectively). In the case of nicotinonitrile **1e** and methylnicotinate **1f**, the increase in the amount of alkyl bromide (from 3 to 5 equiv.) led to selective formation of tri-substituted products **10e** and **tri-10f** in very good yields. Alternatively, by keeping the standard reaction conditions, the di-substituted compound **10f** was obtained as the main product. The two alkyl groups were appended selectively at positions *C4* and *C6*, as indicated by 2D NMR studies (see SI). The observed limitations on the side of the heteroaromatic partner included the compounds with blocked position *C2*, heterocycles possessing aldehyde or ketone groups or substrates with halogen substituents, for which the undesired dehalogenation reactions prevailed.

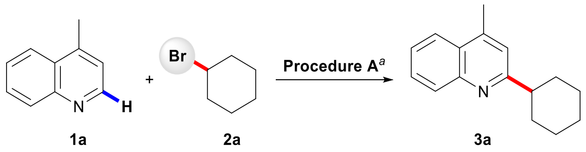
Table 2. Scope of the reaction[a]



[a]Average isolated yield obtained from two separate reactions are given. [b]Isolated in a 3:1 mixture with 2,4-dicyclohexylquinoline. [c]Reactions were carried out for 20 h with 5 equiv. of alkyl bromide.

In order to gain more insights into the studied reaction, a series of mechanistic experiments was conducted. The control reactions showed that light, the photocatalyst and the surfactant are all essential for this Minisci protocol (Table 3, entries 2, 3 and 4). Only small portions of the heteroarene convert in the absence of the alkyl bromide as the second reagent (entry 5). Furthermore, the addition of CBr_4 facilitates the developed reaction and lower yield (31%) of the model product **3a** was obtained in its absence (entry 6). To evaluate the impact of the micellar solution as the reaction environment, the control reaction in acetonitrile was performed. Although a clear solution indicated good solubility of all of the reaction components, the formation of product **3a** was not detected (entry 7). No desired reaction was also observed when 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) was employed under the optimized conditions, which indicates the presence of radical intermediates in the reaction mechanism (entry 8).

Table 3. Control experiments



No.	Variation from optimized conditions^a	Conversion **1a**^{b} [%]	Yield **3a**^{b} [%]
1	-	100	91
2	no photocatalyst **4**	23	0
3	no light	20	0
4	no SDS	22	1
5	no bromocyclohexane (**2a**)	13	0
6	no CBr_4	52	31
7	MeCN instead of aqueous SDS	37	0
8	with the addition of TEMPO^c	13	0

^{a}Optimized conditions: lepidine (**1a**, 0.1 mmol), bromocyclohexane (**2a**, 0.2 mmol), SDS (0.25 mmol), CBr_4 (20 mol%), $\mathrm{Ir(dtbbpy)(ppy)_2PF_6}$ (**4**, 3 mol%), water (5 mL), 40 °C, 451 nm, 42 h. ^{b}Conversion and yield were calculated using GC analysis. *n*-Dodecane was used as internal standard; ^{c}2 equiv. of TEMPO were added to the reaction mixture.

To further examine the mechanistic pathway, we conducted a radical-clock experiment starting from 5-bromo-1-hexene (**2r**) (Fig. 2a). The presence of the cyclopentane ring in the main product **3r** suggests the formation of carbon-centered radicals, which undergo fast 5-exo-trig cyclization and subsequent addition to the heteroarene **1a**. The Stern−Volmer fluorescence quenching experiment was performed, to examine the interactions of the photocatalyst with other reaction components (Fig. 2b).[49] It showed that the excited state of $\mathrm{Ir(dtbbpy)(ppy)_2PF_4}$ (**4**) is quenched effectively by CBr_4, while only low quenching efficiency was observed for the lepidine (**1a**) or the alkyl bromide **2a**. These results are congruent with the high redox potential of alkyl bromides and nitrogen heterocycles.[50] The reaction progress was monitored over time, showing the increasing rate of the process within the first 10 hours of irradiation (Fig. 2c). It supports the concept of the autocatalytic role of bromide anions. Their accumulation in the reaction mixture increases the quenching efficiency and provides higher concentration of the reduced form of the photocatalyst **4**. Moreover, a significant change in the pH of the reaction mixture, from basic (pH = 10) to acidic (pH = 3) was observed over time.

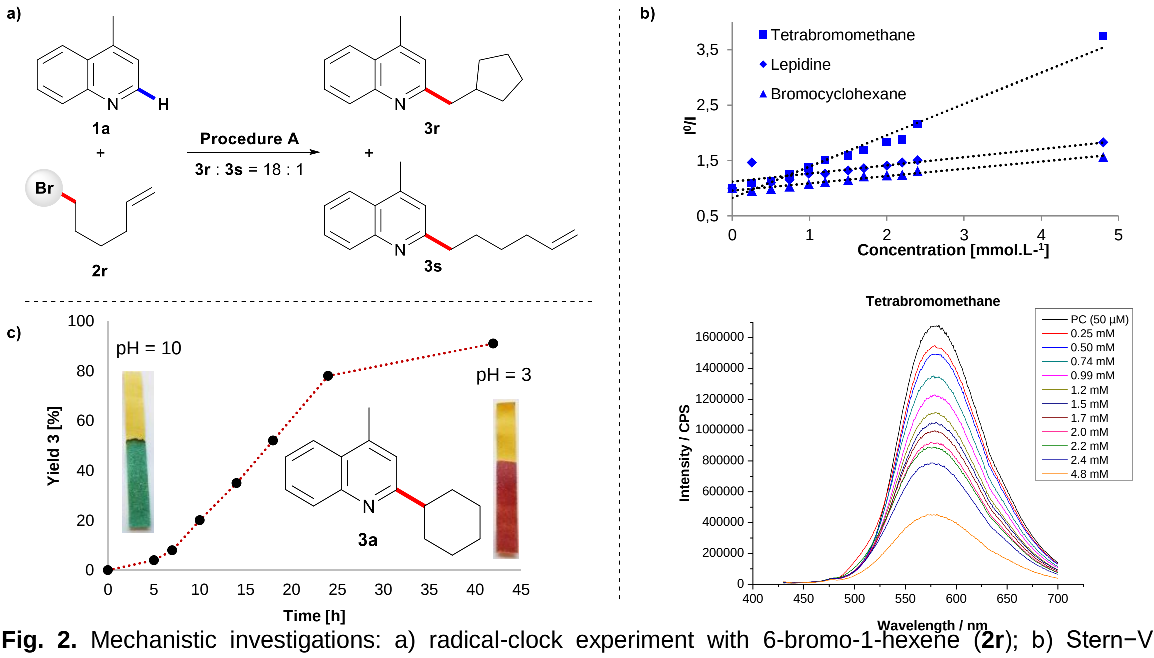


Fig. 2. Mechanistic investigations: a) radical-clock experiment with 6-bromo-1-hexene (**2r**); b) Stern−Volmer fluorescence quenching of $\mathrm{Ir(dtbbpy)(ppy)_2}$ (c = 50 μM) in aqueous SDS; c) Kinetic studies of the model reaction and the change in the pH of the reaction progress.

In accordance with these results, as well as the optimization studies, we propose a mechanism of the developed Minisci reaction (Fig. 3). It has been firmly established that the excited [Ir] **4** photocatalyst ($E_{1/2}$ = -1.51 V vs. SCE in acetonitrile)[51] undergoes reductive quenching by Br^- anions ($E_{1/2}$ = +0.80 V vs. SCE in DME).[36–39] Consequently, a bromine radical and the reduced Ir(II)-complex are generated. The latter species can undergo consecutive absorption of a second photon, resulting in the formation of a strongly reducing form of the iridium-complex[30,32] or a solvated electron.[34] SET to alkyl bromide **A** followed by fragmentation affords alkyl radical **B** and a bromide anion, which participates in subsequent catalytic cycles. An addition of alkyl radical **B** to pyridinium salt **C** provides the radical cation **D**, able to undergo hydrogen-atom-transfer (HAT) with an electrophilic bromine radical. As a result, the protonated form **E** of the final product is produced. Additionally, the contribution of radical propagation through the interaction of radical cation **D** with alkyl bromide **A** should also be considered.

Detailed mechanistic studies on the role of CBr_4 co-catalyst are ongoing, but preliminary results suggest that, through the photosensitized hydrolysis of CBr_4, it may provide the starting concentration of bromide anions at the early stage of the process. Although the light-induced reactivity of this compound is usually associated with mesolytic bond cleavage,[52–55] or homolytic dissociation to CBr_3 and Br radicals,[56,57] it has been shown that in the aqueous conditions the photoinduced hydrolytic pathway to HBr prevails.[58] Alternatively, the reduction of CBr_4 by excited Ir(III)*-photocatalyst can be considered, leading to Br^-, the CBr_3 radical and Ir(IV)-complex. The last two species may undergo SET to recover Ir(III) and produce CBr_3 cation, which reacts with water to give the tribromomethanol and a proton. Finally, tetrabromomethane may contribute to the overall reaction outcome through yet another catalytic mode. Due to the halogen bonding with bromide anions,[59,60] it may decrease their hydrophilic character, slow down the migration to the water bulk and, consequently, render Br^- more accessible to the excited Ir(III)* photocatalyst.

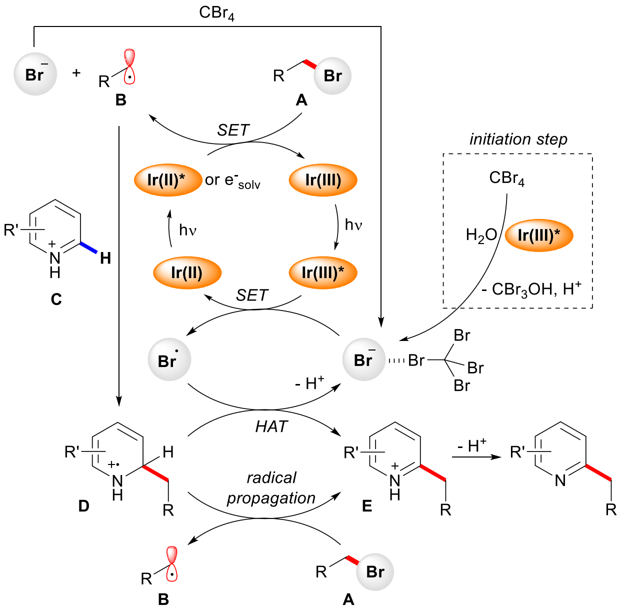
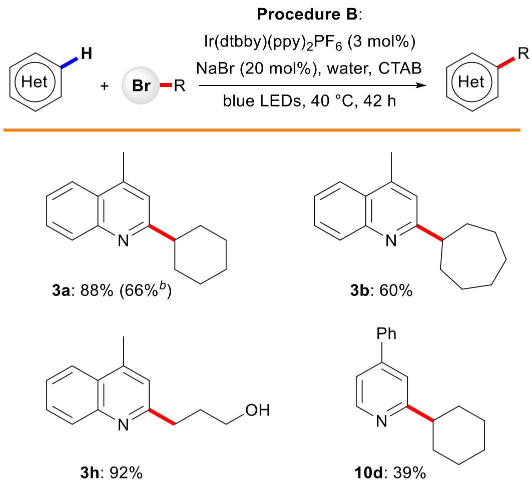


Fig. 3. Proposed mechanistic pathway.

To further examine the decisive role of the solution structuring, in particular the postulated pre-arrangement of bromide anions, we investigated the reaction in the presence of the cationic surfactant cetyltrimethylammonium bromide (CTAB) and catalytic amount of NaBr instead of CBr_4. The positively charged head of the surfactant would retain the bromide counter-anion through ion-pairing interactions and keep it in a close distance to the interface, thus favoring the interaction with the photocatalyst. We were pleased to find, that, under this condition, which were called Procedure B, the compound **3a** was obtained in 88% yield (Table 4). Moreover, the use of CTAB as a sole source of bromide anions, without external NaBr added, also afforded the desired product **3a** in good yield (66%). Finally, we demonstrated that the Procedure B can be successfully implemented to obtain alkylated heterocycles **3b**, **3h** and **10d** from other aliphatic bromides and heteroarenes in good efficiency.

Table 4. The C-H alkylation of heteroarenes using cationic surfactant with bromide counter ion.



3a: 88% (66%[b])

3b: 60%

3h: 92%

10d: 39%

[a]Yields were calculated using NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. [b]The reaction was performed in the absence of NaBr.

3. Conclusions

In summary, we have developed a new photocatalytic procedure for Minisci-type coupling of heteroarenes with various alkyl bromides, which exploits the combination of photoredox catalysis with bromide anion catalysis. With the use of micellar solution as the reaction media, it is possible to carry out the reaction in mild, aqueous conditions, with no need for external oxidant or stoichiometric radical promoter. The coupling products were obtained in the absence of equimolar amounts of acid, a requirement for standard Minisci protocols. The external additives are simple and cost-efficient and they were used in catalytic amounts. The obtained optimization data and mechanistic experiments highlight the critical importance of microstructuring and pre-organization of the components in the reaction mixture.

4. Conflicts of interest

There are no conflicts to declare

5. Acknowledgements

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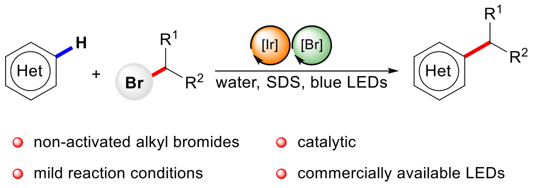

6. Notes and references

1. R. S. J. Proctor and R. J. Phipps, *Angew. Chemie Int. Ed.*, 2019, 2–36.
2. K. C. Majumdar and S. K. Chattopadhyay, Eds., *Heterocycles in Natural Product Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011.
3. D. N. Mai and R. D. Baxter, *Org. Lett.*, 2016, **18**, 3738–3741.
4. K. Matcha and A. P. Antonchick, *Angew. Chemie - Int. Ed.*, 2013, **52**, 2082–2086.
5. Y. Siddaraju, M. Lamani and K. R. Prabhu, *J. Org. Chem.*, 2014, **79**, 3856–3865.
6. Z. Wang, X. Ji, J. Zhao and H. Huang, *Green Chem.*, 2019, **21**, 5512–5516.
7. P. Liu, W. Liu and C. J. Li, *J. Am. Chem. Soc.*, 2017, **139**, 14315–14321.
8. W.-F. Tian, C.-H. Hu, K.-H. He, X.-Y. He and Y. Li, *Org. Lett.*, 2019, **21**, 6930–6935.
9. F. Minisci, R. Bernardi, F. Bertini, R. Galli and M. Perchinummo, *Tetrahedron*, 1971, **27**, 3575–3579.
10. J. Kan, S. Huang, J. Lin, M. Zhang and W. Su, *Angew. Chemie - Int. Ed.*, 2015, **54**, 2199–2203.
11. G. A. Molander, V. Colombel and V. A. Braz, *Org. Lett.*, 2011, **13**, 1852–1855.
12. F. J. R. Klauck, M. J. James and F. Glorius, *Angew. Chemie - Int. Ed.*, 2017, **56**, 12336–12339.
13. X. Ma and S. B. Herzon, *J. Am. Chem. Soc.*, 2016, **138**, 8718–8721.
14. G. X. Li, C. A. Morales-Rivera, Y. Wang, F. Gao, G. He, P. Liu and G. Chen, *Chem. Sci.*, 2016, **7**, 6407–6412.
15. I. B. Seiple, S. Su, R. A. Rodriguez, R. Gianatassio, Y. Fujiwara, A. L. Sobel and P. S. Baran, *J. Am. Chem. Soc.*, 2010, **132**, 13194–13196.
16. D. Xue, Z. H. Jia, C. J. Zhao, Y. Y. Zhang, C. Wang and J. Xiao, *Chem. - A Eur. J.*, 2014, **20**, 2960–2965.
17. D. A. DiRocco, K. Dykstra, S. Krska, P. Vachal, D. V. Conway and M. Tudge, *Angew. Chemie - Int. Ed.*, 2014, **53**, 4802–4806.
18. F. Minisci, C. Giordano, E. Vismara, S. Levi and V. Tortelli, *J. Am. Chem. Soc.*, 1984, **106**, 7146–7150.
19. F. Minisci, E. Vismara, F. Fontana, G. Morini, M. Serravalle and C. Giordano, *J. Org. Chem.*, 1986, **51**, 4411–4416.
20. N. B. Bissonnette, M. J. Boyd, G. D. May, S. Giroux and P. Nuhant, *J. Org. Chem.*, 2018, **83**, 10933–10940.
21. P. Nuhant, M. S. Oderinde, J. Genovino, A. Juneau, Y. Gagné, C. Allais, G. M. Chinigo, C. Choi, N. W. Sach, L. Bernier, Y. M. Fobian, M. W. Bundesmann, B. Khunte, M. Frenette and O. O. Fadeyi, *Angew. Chemie - Int. Ed.*, 2017, **56**, 15309–15313.
22. P. Ren, I. Salihu, R. Scopelliti and X. Hu, *Org. Lett.*, 2012, **14**, 1748–1751.
23. B. Xiao, Z. J. Liu, L. Liu and Y. Fu, *J. Am. Chem. Soc.*, 2013, **135**, 616–619.
24. X. Wu, J. W. T. See, K. Xu, H. Hirao, J. Roger, J.-C. Hierso and J. S. Zhou, *Angew. Chemie*, 2014, **126**, 13791–13795.
25. T. McCallum and L. Barriault, *Chem. Sci.*, 2016, **7**, 4754–4758.
26. C. D. McTiernan, M. Morin, T. McCallum, J. C. Scaiano and L. Barriault, *Catal. Sci. Technol.*, 2016, **6**, 201–207.
27. J. Dong, X. Lyu, Z. Wang, X. Wang, H. Song, Y. Liu and Q. Wang, *Chem. Sci.*, 2019, **10**, 976–982.
28. J. J. Perkins, J. W. Schubert, E. C. Streckfuss, J. Balsells and A. ElMarrouni, *European J. Org. Chem.*, 2019, **4**, 2–10.
29. R. Chang, J. Fang, J.-Q. Chen, D. Liu, G.-Q. Xu and P.-F. Xu, *ACS Omega*, 2019, **4**, 14021–14031.
30. M. Giedyk, R. Narobe, S. Weiß, D. Touraud, W. Kunz and B. König, *Nat. Catal.*, 2020, **3**, 40–47.
31. P. W. Jennings, D. G. Pillsbury, J. L. Hall and V. T. Brice, *J. Org. Chem.*, 1976, **41**, 719–722.
32. T. U. Connell, C. L. Fraser, M. L. Czyz, Z. M. Smith, D. J. Hayne, E. H. Doeven, J. Agugiaro, D. J. D. Wilson, J. L. Adcock, A. D. Scully, D. E. Gómez, N. W. Barnett, A. Polyzos and P. S. Francis, *J. Am. Chem. Soc.*, 2019, **141**, 17646–17658.
33. I. Ghosh, T. Ghosh, J. I. Bardagi and B. König, *Science (80-.).*, 2014, **346**, 725 LP – 728.
34. F. Glaser, C. Kerzig and O. S. Wenger, *Angew. Chemie*, , DOI:10.1002/ange.201915762.
35. D. Petzold, M. Giedyk, A. Chatterjee and B. König, *European J. Org. Chem.*, 2020, **2020**, 1193–1244.
36. P. Zhang, C. C. Le and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2016, **138**, 8084–8087.
37. T. Kawasaki, N. Ishida and M. Murakami, *J. Am. Chem. Soc.*, 2020, **142**, 3366–3370.
38. Z. Wang, X. Ji, T. Han, G.-J. Deng and H. Huang, *Adv. Synth. Catal.*, 2019, **361**, 5643–5647.
39. Z. Wang, Q. Liu, X. Ji, G.-J. Deng and H. Huang, *ACS Catal.*, 2020, **10**, 154–159.
40. M. Zidan, A. O. Morris, T. McCallum and L. Barriault, *European J. Org. Chem.*, , DOI:10.1002/ejoc.201900786.
41. M. Cortes-Clerget, N. Akporji, J. Zhou, F. Gao, P. Guo, M. Parmentier, F. Gallou, J. Y. Berthon and B. H. Lipshutz, *Nat. Commun.*, 2019, **10**, 1–10.
42. I. Capek and T. Kocsisova, *Des. Monomers Polym.*, 2011, **14**, 327–345.
43. S. Handa, B. Jin, P. P. Bora, Y. Wang, X. Zhang, F. Gallou, J. Reilly and B. H. Lipshutz, *ACS Catal.*, 2019, **9**, 2423–2431.
44. L. Baxová, R. Cibulka and F. Hampl, *J. Mol. Catal. A Chem.*, 2007, **277**, 53–60.
45. M. Bu, G. Lu, J. Jiang and C. Cai, *Catal. Sci. Technol.*, 2018, **8**, 3728–3732.
46. T. Kohlmann, C. Kerzig and M. Goez, *Chem. – A Eur. J.*, 2019, **25**, 9991–9996.
47. C. Kerzig and M. Goez, *Chem. Sci.*, 2016, **7**, 3862–3868.
48. R. Naumann, F. Lehmann and M. Goez, *Angew. Chemie Int. Ed.*, 2018, **57**, 1078–1081.
49. M. H. Gehlen, *J. Photochem. Photobiol. C Photochem. Rev.*, 2020, **42**, 100338.
50. H. G. Roth, N. A. Romero and D. A. Nicewicz, *Synlett*, 2016, **27**, 714–723.
51. C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363.
52. M. J. W. Taylor, W. T. Eckenhoff and T. Pintauer, *Dalt. Trans.*, 2010, **39**, 11475–11482.
53. M. Pirtsch, S. Paria, T. Matsuno, H. Isobe and O. Reiser, *Chem. – A Eur. J.*, 2012, **18**, 7336–7340.
54. M. N. C. Balili and T. Pintauer, *Dalt. Trans.*, 2011, **40**, 3060–3066.
55. T. Hou, P. Lu and P. Li, *Tetrahedron Lett.*, 2016, **57**, 2273–2276.
56. Q. Kong, M. Wulff, J. H. Lee, S. Bratos and H. Ihee, *J. Am. Chem. Soc.*, 2007, **129**, 13584–13591.
57. S. Tripathi, S. N. Singh and L. D. S. Yadav, *RSC Adv.*, 2016, **6**, 14547–14551.
58. C. Zhao, X. Lin, W. M. Kwok, X. Guan, Y. Du, D. Wang, K. F. Hung and D. L. Phillips, *Chem. - A Eur. J.*, 2005, **11**, 1093–1108.
59. G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, *Chem. Rev.*, 2016, **116**, 2478–2601.
60. T. Brinck and A. N. Borrfors, *J. Mol. Model.*, , DOI:10.1007/s00894-019-4014-7.