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Photocatalytic activation of *N*-chloro compounds for the chlorination of arenes

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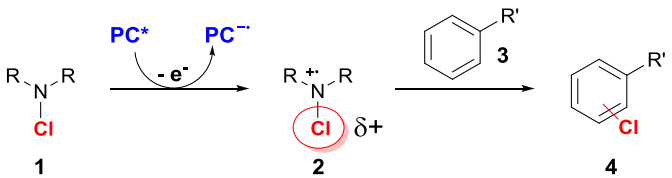
ABSTRACT

Photoredox catalysis activates *N*-chloramines and *N*-chloro-succinimide (NCS) for the electrophilic chlorination of arenes. The photooxidation of the nitrogen atom to a radical cation induces a positive polarization on the chlorine atom, which results in a higher reactivity in electrophilic aromatic chlorination reactions.

1. Introduction

Chlorinated aromatic compounds can be found in many pharmaceuticals, agrochemicals, and polymers and serve as starting materials for the synthesis of organometallic reagents. Moreover, they are versatile synthetic precursors for metal catalyzed cross-couplings.[1–4] Due to the importance of aromatic chlorides the development of efficient strategies for the electrophilic chlorination of arenes under mild conditions is still of great interest. Since chloride usually does not undergo electrophilic aromatic substitution, but rather reacts as a nucleophile these transformations require the use of a 'Cl^+' reagent. Traditional electrophilic chlorination reagents as Cl_2, SO_2Cl_2 and ^{t}BuOCl have a high reactivity, but are also rather unselective.[1,5,6] Their hazardous properties make them difficult to handle and limit practical applications. *N*-Chloro compounds, such as *N*-chlorosuccinimide (NCS), *N*-chloramines or modern guanidine based reagents (Palau'chlor)[7] are valuable alternatives as they contain positively polarized chlorine atoms and are inexpensive and easy to handle. However, except for Palau'-chlor, which requires a multi-step synthesis, they show only moderate reactivity and often need activation by redox active metals,[8–10] Lewis[11–13] or Brønsted acids[14,15] or radical initiators.[16] Most of these activations rely on an increase of the N–Cl bond polarization by decreasing the electron density on the nitrogen, e.g., by coordination of a Lewis acid or protonation of the nitrogen. An analogous effect can be achieved by photocatalytic oxidation of the nitrogen atom to a radical cation **2** as depicted in Scheme 1. The resulting radical cation **2** has a significantly enhanced reactivity compared to the neutral *N*-chloro compound **1** since the positive charge on the nitrogen pulls electron density from the chlorine and induces a strong positive polarization ($\delta+$). This cation radical **2** contains an electrophilic chlorine atom and can react in an electrophilic aromatic substitution with suitable arenes to give chlorinated compounds **4** (Scheme 1).



Scheme 1. General scheme of the oxidative activation of *N*-chloro compounds by photoredox catalysis (PC=photocatalyst).

The use of photoredox catalysis to oxidize **1** would offer a mild way to catalytically activate *N*-chloramines/-amides by visible light at room temperature. This strategy offers a practical alternative to conventional activation pathways.

2. Results and discussion

There are few reports known using *N*-chloramines as starting materials in photoredox catalysis. However, these examples are not based on the oxidation of *N*-chloramines to activate them for

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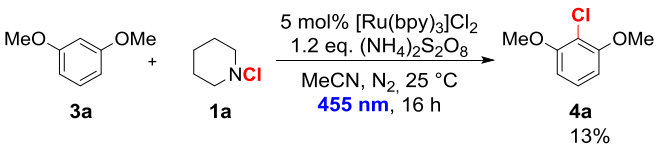
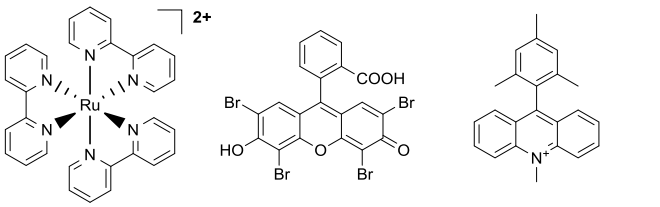
0040-4020/

electrophilic chlorination, but rather on the reduction to induce a cleavage of Cl^- yielding a nitrogen atom centered radical, which reacts further to form a C–N-bond.[17,18] Even though in some examples chloride is later incorporated into the product, it always reacts as a nucleophile and not as an electrophile. To investigate whether *N*-chloramines (**1**) can also be activated by photocatalytic oxidation to undergo electrophilic aromatic substitution (S_EAr), we chose the chlorination of an electron rich arene, namely dimethoxybenzene (**3a**) as a model reaction (Scheme 2): A solution of **3a** (0.25 mmol), the *N*-chloramine **1a** (1.2 equiv), the photocatalyst $[Ru(bpy)_3]Cl_2$ (5 mol %) and ammonium peroxodisulfate (1.2 equiv) to reoxidize the photocatalyst in MeCN was irradiated under N_2-atmosphere over night with blue LEDs (λ_{max}=455 nm). The photocatalytic reaction yielded 13% of the chlorinated arene **4a** whereas without irradiation no chlorination was observed.



Scheme 2. Test reaction for the photocatalytic chlorination of dimethoxybenzene (**3a**) with 1-chlororpiperidine (**1a**).

Even though the yield of chlorination was low, these initial results showed that *N*-chloramines can be activated for S_EAr by photocatalytic oxidation. Next, the reaction conditions were optimized. First we investigated whether the metal based photocatalyst $[Ru(bpy)_3]Cl_2$ can be replaced by cheap organic dyes such as eosin Y or 9-mesityl-10-methylacridinium perchlorate (Acr^+–Mes) (Scheme 3). The redox properties of eosin Y ($E^0_{(EY^*/EY^{\bullet-})}$=0.79 V vs SCE) are similar to $[Ru(bpy)_3]Cl_2$ ($E^0_{(Ru(II)^*/Ru(I))}$=0.77 V vs SCE),[19] nevertheless only traces of chlorination could be obtained when using 10 mol % eosin Y instead of $[Ru(bpy)_3]Cl_2$ (yield **4a**<5%). Next we tested Acr^+–Mes, which is a very strong oxidant in its excited state ($E^0_{(MA^{+*}/MA^{\bullet})}$=2.08 V vs SCE),[20] but despite this high oxidative power the catalyst was less efficient in this transformation than $[Ru(bpy)_3]Cl_2$ (yield **4a** 7%). A possible complication with this catalyst could be that its oxidation potential is sufficiently high to oxidize dimethoxybenzene (**3a**) directly and thus leads to undesired side reactions.[21]



Scheme 3. Employed photocatalyst and the wavelength used for irradiation.

Next, we varied the *N*-chloramine to investigate the influence of the substituents on the nitrogen. The results of this screening are depicted in Table 1. The highest yields of chlorinated dimethoxybenzene **4a** were obtained using 1-chloromorpholine (**1b**) (74%, entry 2), which is except for the heteroatom structurally very similar to the previously employed piperidine derivative (**1a**, entry 1).[†]

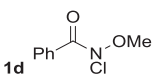
[†] In reported aromatic chlorinations with *N*-chloramines the morpholine derivative showed higher efficiency than *N*-chloropiperidine, see Ref. 14.

The *N*-chloro compounds with benzyl groups **1c** and with 'push-pull' substituents **1d** (entries 3, 4) gave comparable yields, but are unfavourable with respect to atom economy. Further optimization of the reaction was therefore carried out using 1-chloromorpholine (**1b**).

Having identified the suitable *N*-chloramine, we continued with varying the solvent of the reaction (Table 2). All polar solvents and DCM (entries 1–4) showed conversion to the desired product **4b**, whereas the non-polar solvents toluene and 1,2-dichloroethane (1,2-DCE) gave only minor product formation (entries 5, 6). This observation can be explained by the different solubility of the photocatalyst, which poorly dissolves in non-polar solvents. The reaction was most efficient in a mixture of MeCN and water (entry 4), which even led to double chlorination. The enhanced reactivity when water is added to the reaction presumably results from a higher solubility of peroxodisulfate ensuring a quicker regeneration of the photocatalyst.

For further studies the substrate was changed from dimethoxybenzene (**3a**) to the less electron rich anisole (**3b**) since this will circumvent the problem of double chlorination. Table 3 summarizes the results of the reaction optimization. First, we continued the solvent screening and tested different MeCN/H_2O ratios (Table 3, entries 1–3). The reaction using a 4:1 mixture of MeCN and H_2O showed an excellent yield of 95%. Using this solvent mixture the catalyst loading could be lowered to 2 mol % without a change in the yield. A further decrease to 1 mol % showed a slightly decreased yield of 80% (entries 2, 4, 5). Neither the addition of base

Table 1
Variation of the *N*-chloro compound using the reaction conditions depicted in Scheme 2[a]

Entry	*N*-chloro compound	Yield (%)[b]	Conversion (%)[b]
1	 **1a**	13	26
2	 **1b**	**74**	>**99**
3	 **1c**	62	>99
4	 **1d**	61	>99

[a] Reactions were carried out using 0.25 mmol **3a**, 1.2 equiv of the respective *N*-chloro compound, 1.2 equiv $(NH_4)_2S_2O_8$, and 5 mol % $[Ru(bpy)_3]Cl_2\times6H_2O$ in 1.5 mL MeCN. The irradiation time (λ_{max}=455 nm) was 16 h.
[b] Determined by GC analysis using anisole as the internal standard.

Table 2
Results of the solvent screening[a]

Entry	Solvent	Yield (%)[b]	Conversion (%)[b]
1	MeCN	74	>99
2	MeOH	42	60
3	DCM	45	45
4	MeCN/H_2O 3:1	48+DC[c]	>99
5	Toluene	<5	<5
6	1,2-DCE	7	22

[a] Reactions were carried out using 0.25 mmol **3a**, 1.2 equiv **1b**, 1.2 equiv $(NH_4)_2S_2O_8$, and 5 mol % $[Ru(bpy)_3]Cl_2\times6H_2O$ in 1.5 mL of the respective solvent. The irradiation time (λ_{max}=455 nm) was 16 h.
[b] Determined by GC analysis using anisole as the internal standard.
[c] DC=double chlorination.

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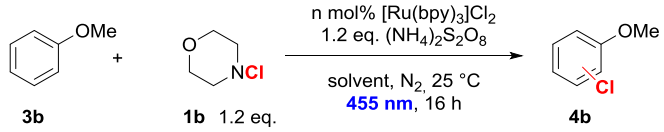
Table 3
Reaction optimization with anisole (**3b**) as the substrate

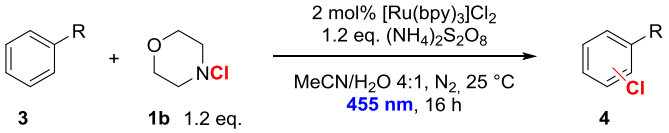


3b **1b** 1.2 eq. **4b**

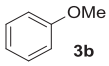
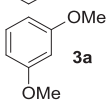
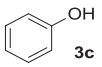
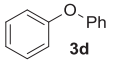
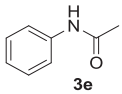
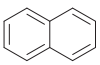
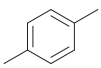
Entry	Reaction condition	Yield (%)[a] (p:o ratio)	Conv. (%)[a]
1[b]	5 mol % $Ru(bpy)_3Cl_2$, MeCN	26 (11:1)	46
2[b]	5 mol % $Ru(bpy)_3Cl_2$, MeCN/H_2O 9:1	88 (5:1)	>99
3	5 mol % $Ru(bpy)_3Cl_2$, MeCN/H_2O 4:1	95 (5:1)	95
4[b]	2 mol % $Ru(bpy)_3Cl_2$, MeCN/H_2O 9:1	90 (5:1)	90
5[b]	1 mol % $Ru(bpy)_3Cl_2$, MeCN/H_2O 9:1	80 (5:1)	83
6	5 mol % $Ru(bpy)_3Cl_2$, MeCN, NaOAc	70 (6:1)	83
7	5 mol % $Ru(bpy)_3Cl_2$, MeCN, pyridine	13 (5:1)	32
8	5 mol % $Ru(bpy)_3Cl_2$, MeCN, HCl 2 M	76 (6:1)	88
9	5 mol % $Ru(bpy)_3Cl_2$, MeCN/H_2O 9:1, 2 equiv **1b**	76 (5:1)	>99
10	5 mol % $Ru(bpy)_3Cl_2$, MeCN/H_2O 9:1, **no $(NH_4)_2S_2O_8$**	0	0
11	**No $Ru(bpy)_3Cl_2$**, MeCN/H_2O 9:1	27 (4:1)	48
12	5 mol % $Ru(bpy)_3Cl_2$, MeCN/H_2O 9:1, **no light**	18 (3:1)	33

[a] Determined by GC analysis using toluene as the internal standard.
[b] Average over two reactions.

Table 4
Scope of the visible light mediated chlorination of arenes with *N*-chloramines[a]



3 **1b** 1.2 eq. **4**

Entry	Substrate	Conversion (%)[b]	Yield (%)[b]	Selectivity (p:o)
1	 **3b**	95	95	5:1
2[c]	 **3a**	>99	74	100:0
3[d]	 **3c**	100	66	2:1
4	 **3d**	55	41	13:1
5	 **3e**	83	75	2:1
6	 **3f**	100	39	1:1
7	 **3g**	20	20	100:0[e]
8	 **3h**	24	9	2:1[f]
9	 **3i**	23	<5	—
10	 **3j**	0	0	—
11	 **3k**	14	<5	—

[a] Reactions were carried out using 0.25 mmol of the arene **3**, 1.2 equiv **1b**, 1.2 equiv $(NH_4)_2S_2O_8$, and 2 mol % $[Ru(bpy)_3]Cl_2 \times 6H_2O$ in 1.5 mL MeCN/H_2O 4:1. The irradiation time (λ_{max}=455 nm) was 16 h.
[b] Determined by GC analysis.
[c] In MeCN.
[d] 3 mL solvent.
[e] 1-Chloronaphthalene.
[f] 2-Chloroxylene: α-chloroxylene.

(entries 6, 7) nor acid (entry 8) or a higher amount of the *N*-chloramine **1b** (entry 9) improved the yield further. The conducted control reactions (entries 10–12) showed that no efficient reaction is observed without light, without the catalyst or without $(NH_4)_2S_2O_8$, respectively. Low amounts of product obtained in the reaction without light and without the catalyst (entries 11, 12) indicate that $(NH_4)_2S_2O_8$ is to some extend able to oxidize the *N*-chloramine **1b**. The *N*-chloro compound **1b** itself cannot chlorinate anisole directly (entry 10).

Having optimized the reaction conditions, we explored the scope of the reaction towards different arenes (Table 4). Electron rich substrates with a +M-substituent such as anisole, dimethoxybenzene, phenol and acetanilide can be chlorinated in good yields (entries 1–5). The aromatic amine **3f** (entry 6) showed only a moderate yield of 39%. The chlorination yield is probably diminished by an unproductive direct oxidation of the amine by the excited photocatalyst.[22] Unfortunately, the reaction is limited to electron rich arenes with +M-substituents, arenes with +I-substituents such as xylene and toluene gave only little chlorinated product (entries 8, 9). No chlorination could be observed for more electron poor substrates as chlorobenzene (entry 10). This suggests that the polarization of the N–Cl-bond induced by photocatalytic oxidation of the nitrogen atom is not strong enough to obtain highly electrophilic chlorine. Hence, the reaction only proceeds with very electron rich substrates. Furthermore, we tried to use the developed method for the α-chlorination of acetophenone, but could only detect traces of chloroacetophenone (entry 11).[‡]

N-Chlorosuccinimide (NCS) is a well-known and widely used chlorination reagent; it generally requires activation. The electron density on the nitrogen atom is significantly reduced by two electron withdrawing groups compared to *N*-chloramines. Accordingly, the chlorine atom on NCS is more electrophilic leading to a higher reactivity in S_EAr. With photocatalytically activated NCS it should therefore be possible to chlorinate also less electron rich substrates as xylene and toluene, which were not accessible by *N*-chloramines. On the other hand, the electron withdrawing groups make the oxidative activation of NCS more challenging as they increase the oxidation potential significantly. To investigate whether the oxidation potential is still within the range of the photocatalyst $[Ru(bpy)_3]Cl_2$, cyclic voltammetry was measured (see Supplementary data). The obtained potential for the oxidation of NCS of 1.10 V versus SCE would be too high for an oxidation from the excited state of the photocatalyst (Scheme 4) as proposed in the previous paragraph for *N*-chloramines. However, the potential of Ru(III), which can be accessed by oxidative quenching of the excited catalyst Ru(II)* would be sufficient to perform the oxidation of NCS. Ru(II)* can be oxidized to Ru(III) by $(NH_4)_2S_2O_8$,[23] which was also employed in the reactions with *N*-chloramines to re-oxidize Ru(I).

[‡] A reaction with alkenes to obtain aminochlorination by incorporation of the chlorine as well as the morpholine part was not successful as mainly chlorohydrins were observed.

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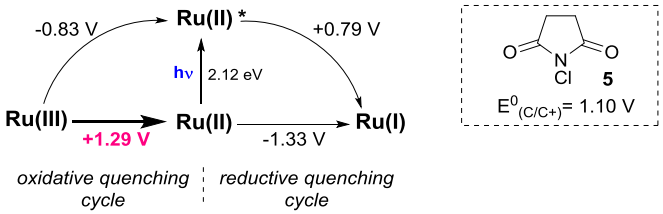


Scheme 4. Redox properties of the photocatalyst $[Ru(bpy)_3]Cl_2$ and oxidation potential of NCS. Potentials are given versus SCE.[23]

Based on the redox potentials it is likely that the previously described photocatalytic activation of the easily oxidizable *N*-chloramines proceeds via the reductive quenching of Ru(II)* (reductive quenching cycle) while the more challenging oxidation of NCS has to proceed via the oxidative quenching cycle where Ru(II)* is first quenched by $(NH_4)_2S_2O_8$ to give the strongly oxidizing Ru(III). From a thermodynamic point the photocatalytic activation of NCS by the developed system is therefore feasible. This would be, to the best of our knowledge, the first photocatalytic activation of NCS for S_NAr. Cho et al. recently reported visible light mediated in situ formation of acid chlorides using NCS as a reagent.[24] However, this reaction proceeds via the transfer of a chlorine radical to a photocatalytically formed acyl radical and does not involve a direct interaction of the photocatalyst and NCS.

To test whether the developed reaction conditions indeed lead to an enhanced activity of NCS for electrophilic chlorination of arenes, we monitored the reaction of NCS with anisole with and without the activation by photoredox catalysis over a period of 180 min. The results are summarized in Fig. 1. For the photocatalytic reaction a solution of anisole (**3b**), NCS (**5**, 1.2 equiv), $(NH_4)_2S_2O_8$ (1.2 equiv) and 2 mol % of the photocatalyst in 2 mL MeCN/water 4:1 was irradiated with 455 nm under N_2-atmosphere. Samples were taken after 30 min, 75 min, 120 min and 180 min. For comparison a parallel reaction with only anisole (**3b**) and NCS (1.2 equiv) in 2 mL MeCN/water 4:1 was performed and samples were taken at the same time intervals. Fig. 1 shows a clear enhancement of the chlorination yield in the photocatalytic reaction (blue curve) compared to the non-catalyzed reaction (red curve). Thereby we could show that NCS is activated for electrophilic chlorination by photocatalytic oxidation at room temperature.

As it has been successfully demonstrated that the reactivity of NCS in the electrophilic aromatic chlorination of anisole is significantly enhanced by photoredox catalysis, we next aimed to explore the effect on a variety of different arenes. To quantify the effect we compared the yields of chlorination obtained with just NCS to the yields obtained using the photocatalytic activation. The results are compiled in Table 5. For almost all tested arenes the photocatalytic system enabled reactions, which failed to deliver any notable amount of product in the absence of the photocatalyst under the tested reaction conditions. Only for aromatic amines or amides (entries 7, 8) the reactivity of NCS could not be increased. Xylene and toluene, which were inaccessible using *N*-chloramines can be chlorinated as well (entries 5, 6). The yields are, however, moderate.

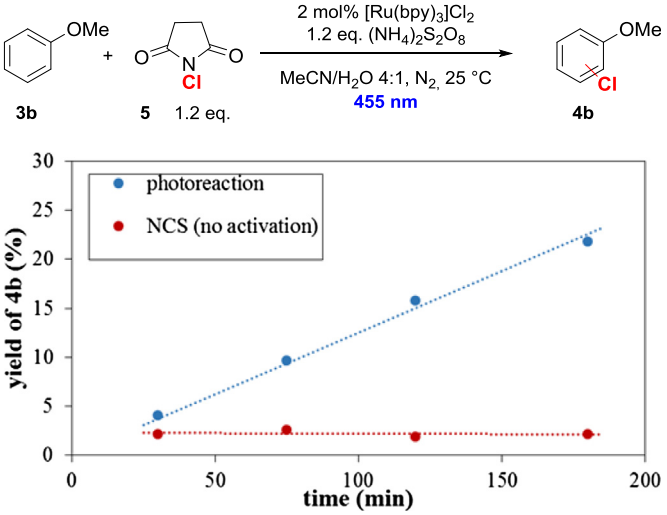
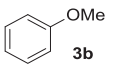
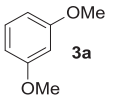
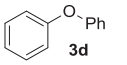
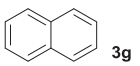
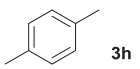
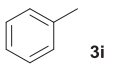
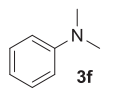
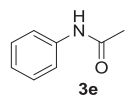
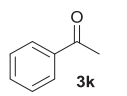


Fig. 1. Monitoring of the chlorination of anisole (**3b**) by NCS without any activation (red curve) and using the photocatalytic activation shown above (blue curve).

3. Conclusion

In conclusion we demonstrated the applicability of visible light photoredox catalysis to activate *N*-chloramines and NCS for electrophilic aromatic chlorination of arenes. The activation proceeds as proposed by oxidation of the nitrogen atom of the *N*-chloro compound inducing a positive polarization on the chlorine atom. The method was applied for the chlorination of a variety of electron rich arenes. While a +M substituent on the aromatic substrate was necessary to observe chlorination with the *N*-chloramine, the stronger chlorination reagent NCS also allowed the use of less

Table 5
Comparison of the electrophilic chlorination using NCS with and without photocatalytic activation[a]

Entry	Substrate	Conv. (%)[b]	Yield (%)[b,c]	Selectivity (p:o)	NCS, no photocat. (%)[a,d]
1	 **3b**	100	92	100:0	<5
2	 **3a**	96	69	100:0	8 (57)
3	 **3d**	58	79	14:1	0
4	 **3g**	100	44	100:0[e]	<1
5	 **3h**	85	59	6:1[f]	0
6	 **3i**	29	38	1:1	0
7	 **3f**	100	21	1:1	44 (44)
8	 **3e**	93	25	2:1	23 (25)
9	 **3k**	13	<5	—	0

[a] Photocatalytic reactions were carried out using 0.25 mmol of substrate, 1.2 equiv NCS, 1.2 equiv $(NH_4)_2S_2O_8$ and 2 mol % $[Ru(bpy)_3]Cl_2$ in 1.5 mL solvent under N_2 atmosphere. The reactions were irradiated for 16 h.
[b] Determined by quantitative GC analysis using an internal standard.
[c] Yields based on conversion.
[d] Yields in brackets are based on conversion.
[e] 1-Chloronaphthalene.
[f] 2-Chloroxylene:α-chloroxylene.

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electron rich substrates as xylene and toluene. The photocatalytic activation can serve as a valuable catalytic alternative to conventional activations; the spatial resolution of light activation may be beneficial for some applications, e.g., in surface science. Using a similar concept for the activation of other oxidizable reagents in organic synthesis may be envisaged.

4. Experimental section

4.1. General

Photocatalytic reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs, λ_{em}=455 nm (±15 nm), 3.5 V, 700 mA). Reaction vials (5 mL crimp cap vials) were illuminated from the bottom with LEDs and cooled from the side using custom made aluminum cooling block connected to a thermostat. NMR spectroscopy was carried out on either a Bruker Avance 400 (^{1}H: 400.13 MHz, ^{13}C: 101 MHz, T=300 K) or a Bruker Avance 300 (^{1}H: 300.13 MHz, ^{13}C: 75 MHz, T=295 K). The solvent residual peak (δ ($CDCl_3$): H 7.26; C 77.0) was used as an internal reference. Standard flash chromatography was performed on an Isolera™ Spektra Systems automated with high performance flash purification system.

4.2. Synthesis of *N*-chloramines

All *N*-chloramines were synthesized according to a literature known procedure described by Bella et al.[25] 1-Chloropiperidine (**1a**) ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.14 (br s, 4H), 1.81–1.63 (m, 4H), 1.46 (br s, 2H). 4-Chloromorpholine (**1b**)[26] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (br s, 2H), 3.14 (br s, 2H). *N*-Benzyl-*N*-chloro-1-phenylmethanamine (**1c**)[27]m ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.27 (m, 5H), 4.16 (s, 2H). *N*-Chloro-*N*-methoxy-benzamide (**1d**)[28] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.74 (m, 2H), 7.63–7.52 (m, 1H), 7.49–7.41 (m, 2H), 3.88 (s, 3H).

4.3. General procedure for the photocatalytic activation of *N*-chloro compounds

In a 5 mL crimp cap vial 0.25 mmol of the respective substrate, together with 0.3 mmol (1.2 equiv) of the *N*-chloramine or NCS, 0.3 mmol (1.2 equiv) $(NH_4)_2S_2O_8$, and 2 mol% (0.005 mmol) $[Ru(bpy)_3]Cl_2\times6H_2O$ were dissolved in 2 mL of MeCN/water 4:1. The reaction mixture was degassed by three cycles of freeze-pump-thaw and irradiated for 16 h with blue LEDs (λ_{max}=455 nm). For GC analysis 500 μL of the reaction mixture was added to 500 μL of the standard solution (0.1 M), anisole for dimethoxybenzene, toluene for anisole, mixed, filtered and submitted to GC analysis. For Tables 4 and 5: After the irradiation the internal standard (0.01 mmol *n*-pentadecane) was added to the reaction and the reaction was immediately quenched with satd Na_2CO_3-solution and brine. The mixture was extracted with ethyl acetate and subjected to GC–FID analysis.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.06.028.

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