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Haruyasu Asahara *et al.*

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Visible-light-induced upcycling of perchloroethylene into trichloroacetamides using chlorine dioxide

Shohei Ohno,[a] Genta Taniguchi,[a] Minami Fukuhara,[a] Yuki Itabashi,[b] Tsuyoshi Inoue,[ab] Kei Ohkubo[bc] and Haruyasu Asahara*[ab]

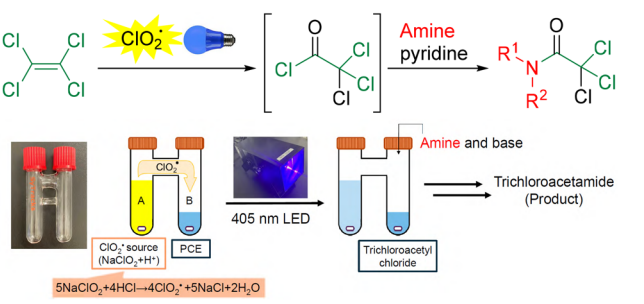
Herein, we report the visible-light-induced upcycling of environmentally problematic perchloroethylene into valuable trichloroacetamides using chlorine dioxide ($ClO_2^{\bullet}$). The reaction proceeds with stoichiometric amounts of reagents; under mild conditions, this enables broad applicability to the synthesis of aromatic trichloroacetamides, carbamates, urea, and heterocycles, offering a sustainable strategy for transforming an environmental pollutant into useful building blocks.

Perchloroethylene (PCE) is a chlorinated solvent widely used in industrial processes such as dry cleaning and metal degreasing. Owing to its high stability and resistance to degradation, PCE persists in the environment, raising concerns about its potential mutagenicity and carcinogenicity.[1–3] In response, its production and use have been progressively restricted by environmental regulations.[4] Nevertheless, PCE is still generated in various industrial processes.[5] Accordingly, chemical upcycling technologies that convert PCE into valuable organic molecules represent a sustainable approach for reducing its environmental impact.[6–8]

Furthermore, PCE decomposes upon photo-oxidation to yield a complex mixture, including chlorine gas, carbon oxides (CO and CO_2), phosgene, epoxides, and trichloroacetyl chloride.[9–15] Recently, photochemical oxidation of PCE was reported, wherein irradiation with deep ultraviolet light (UV-C, $\lambda < 280$ nm) under an oxygen atmosphere produced trichloroacetyl chloride, which upon addition of alcohols or amines afforded trichlorocarbonates or trichloroacetamides.[16,17] In 2024, a visible-light protocol using a small amount of chlorine gas as a radical initiator was reported.[18] These methods have attracted considerable attention as chemical upcycling strategies. However, the method using deep ultraviolet light generates large amounts of highly toxic byproducts, such as phosgene, and requires a large amount of solvent for the substrate. The visible-light protocol overcomes some of these drawbacks but still requires chlorine gas, which presents safety and handling challenges. By contrast, chlorine dioxide ($ClO_2^{\bullet}$) can generate both chlorine radicals and singlet oxygen under visible light irradiation; hence, we have been working on developing oxidation reactions utilizing this property.[19–22] $ClO_2^{\bullet}$ can be used as an oxidant under mild conditions, enabling improved reaction control and reducing safety risks.

Herein, we report the visible light-induced photooxidation of PCE using $ClO_2^{\bullet}$ and establish a one-pot method for the synthesis of valuable trichloroacetamide[23–27] derivatives (Scheme 1). The use of *p*-chlorobenzotrifluoride (PCBTF), which is inert to chlorine radicals and exhibits high solubility, as a solvent enables the reaction to be performed using stoichiometric amounts of PCE. The reaction proceeds under visible light at room temperature (25 °C), which not only minimizes the formation of highly toxic by-products such as phosgene but also expands the reaction scope to include a variety of aromatic trichloroacetamides.

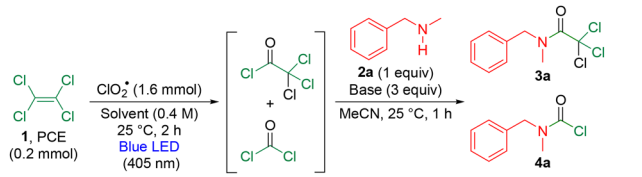
An H-shaped reaction glass tube (COware) was employed as a two-chamber system.[28–30] One side of the system (chamber A) contained an aqueous $ClO_2^{\bullet}$ solution prepared by mixing sodium chlorite ($NaClO_2$) with HCl, and the other side



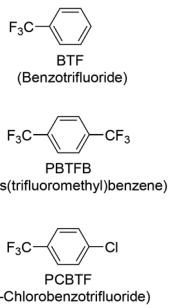
Scheme 1 Visible-light-induced upcycling of PCE into trichloroacetamides using $ClO_2^{\bullet}$.

[a] *Graduate School of Pharmaceutical Sciences, The University of Osaka, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan. E-mail: asahara@phs.osaka-u.ac.jp*
[b] *Institute for Open and Transdisciplinary Research Initiatives (OTRI), The University of Osaka, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan*
[c] *Organization for Carbon Neutrality Collaboration (OCNC), The University of Osaka, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan*

Table 1 Optimization of the reaction conditions



Entry	Solvent	Base	Yield[a] (%) 3a	4a[b]
1	Neat	Pyridine	18	1
2	MeCN	Pyridine	22	2
3	Toluene	Pyridine	25	2
4	BTF	Pyridine	63	4
5	PBTFB	Pyridine	65	4
6	PCBTF	Pyridine	68	4
7	PCBTF	NEt_3	36	2
8	PCBTF	DIPEA	54	9
9	PCBTF	Cs_2CO_3	40	3
10	PCBTF	2,6-Lutidine	51	6
11[c]	PCBTF	Pyridine	55	3
12[d]	PCBTF	Pyridine	76	4
13[e]	PCBTF	Pyridine	80	4



[a] NMR yield based on PCE. [b] Yield was calculated based on two molecules of phosgene per **1**. [c] PCE (0.5 mmol), amine (1 equiv.), pyridine (2 equiv.). [d] PCE (0.5 mmol), amine (1.2 equiv.), pyridine (2 equiv.). [e] PCE (0.5 mmol), amine (1.2 equiv.), pyridine (2 equiv.), PCBTF (0.2 M).

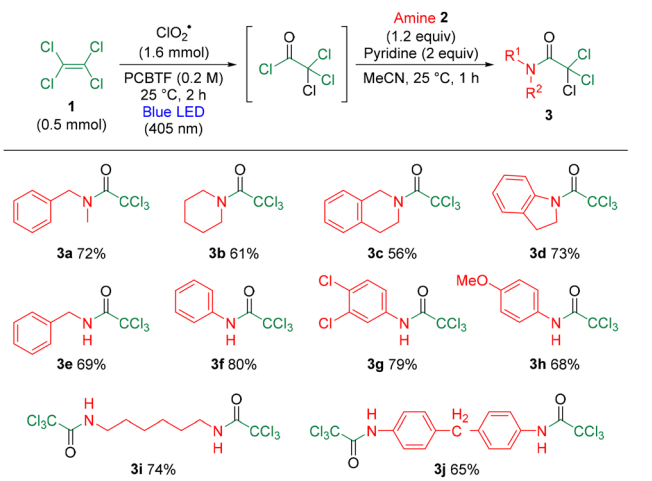
(chamber B) was filled with a solution containing PCE. Upon irradiation of the entire vessel with a blue LED, $ClO_2^•$ in chamber A was activated, resulting in gas formation. The gases passed through the glass-tube bridge connecting the two chambers and dissolved in the PCE-containing solution in chamber B. Subsequent treatment of chamber B with an amine and base afforded trichloroacetamide as the major product, which is regarded as a valuable intermediate for the synthesis of pharmaceuticals and agrochemicals.[23–27]

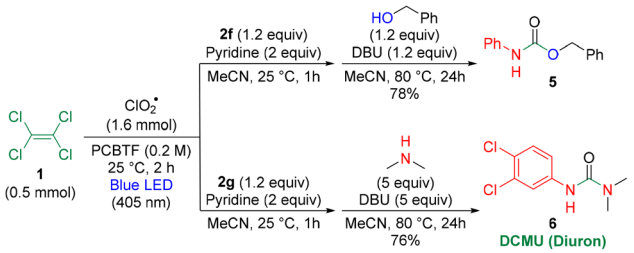
We conducted optimization studies of the visible-light-induced upcycling of PCE **1** to trichloroacetamide **3a** (Table 1). PCE **1** was treated with $ClO_2^•$ (8.0 equiv. relative to PCE),[31] amine (1.0 equiv.), and a base (3.0 equiv.) under irradiation with a 405-nm blue LED. Under solvent-free conditions, using pyridine as a base, **3a** and the phosgene-derived by-product **4a** were obtained in a combined yield of 19% at an 18 : 1 ratio (entry 1).

Using acetonitrile as the solvent afforded a combined yield of 24% in a 11 : 1 ratio (entry 2), and toluene afforded a combined yield of 27% in a 12.5 : 1 ratio (entry 3). However, the reactions between the solvent and $ClO_2^•$ also yielded side products. To suppress such the side reactions, benzotrifluoride (BTF)[32–34] was employed as a solvent that is less reactive toward chlorine radicals; this improved the combined yield to 67% with a 15.8 : 1 ratio (entry 4). Further improvement was achieved using *p*-bis(trifluoromethyl)benzene (PBTFB), affording a 69% combined yield in 16.3 : 1 ratio (entry 5). The best result was achieved with *p*-chlorobenzotrifluoride (PCBTF), which afforded a combined yield of 72% in a 17 : 1 ratio (entry 6). A screening of green solvents and other electron-deficient aromatic solvents was conducted (Table S1). However, these alternative solvents resulted in significantly lower yields than PCBTF. Subsequently, we examined the effects of the base. When the base was changed to triethylamine, **3a** and **4a** were obtained in a combined yield of 38% in an 18 : 1 ratio (entry 7). Using diisopropylethylamine as the base gave a combined yield of 63% in a 6 : 1 ratio (entry 8). Changing the base to Cs_2CO_3 afforded a combined yield of 43% in a 13.3 : 1 ratio (entry 9). The use of 2,6-lutidine afforded a combined yield of 57% at an 8.5 : 1 ratio (entry 10). Subsequently, on using PCBTF as a solvent and pyridine as a base, the reaction of PCE (0.5 mmol) with amine (1.0 equiv.) and pyridine (2.0 equiv.) provided **3a** and **4a** in a combined yield of 58% in an 18.3 : 1 ratio (entry 11). When the amine loading was increased to 1.2 equiv. under identical conditions, the combined yield improved to 80% in a 19 : 1 ratio (entry 12). Further improvement was achieved when twice the amount of PCBTF was used, giving a combined yield of 84% and a 20 : 1 ratio (entry 13). Therefore, the conditions in entry 13 were identified as optimal.

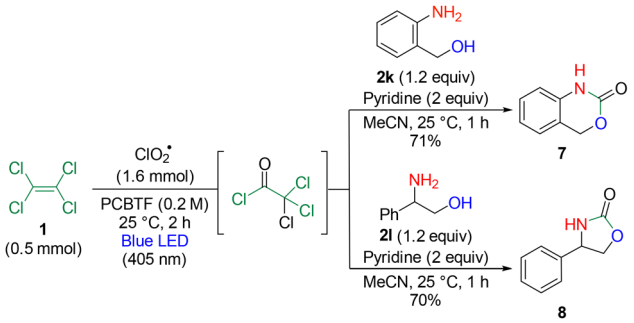
Next, the substrate scope with respect to the amines was investigated under the optimized conditions (Table 2). The reaction with methylbenzylamine afforded **3a** in 72% yield. With an aliphatic heterocycle piperidine, **3b** was obtained in 61% yield, whereas an aromatic heterocyclic tetrahydroisoquinoline gave **3c** in 56% yield and dihydroindole provided **3d** in 73% yield. In the case of primary amines, benzylamine furnished **3e** in 69% yield, and aniline gave **3f** in 80% yield. Additionally, the reaction with dichloroaniline afforded **3g**, which is useful as an intermediate in the synthesis of pharmaceuticals and agrochemicals, in 79% yield. This reaction was also applicable to 4-methoxy aniline, affording **3h** in 68% yield. Furthermore, long-chain aliphatic diamines underwent a smooth transformation to give **3i** in 74% yield, and aromatic diamines afforded **3j** in 65% yield. Notably, the reaction proceeded efficiently with a wide variety of aromatic amines under mild conditions, which was challenging in previous reports.

Table 2 Substrate scope for the visible-light-induced upcycling of PCE into trichloroacetamides





Scheme 2 Visible-light-induced upcycling of PCE into carbamate and urea.



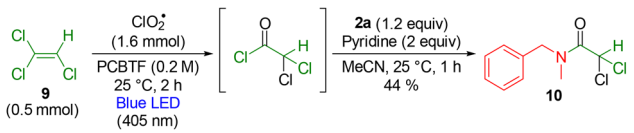
Scheme 3 Visible-light-induced upcycling of PCE into heterocyclic compounds.

After the photooxidation of PCE **1** with $ClO_2^{\bullet}$, the addition of amine **2f** and subsequent heating with benzyl alcohol in the presence of DBU afforded carbamate **5** without the isolation of trichloroacetamide (Scheme 2). Similarly, the reaction with amine **2g**, followed by heating with dimethylamine and DBU, furnished herbicide DCMU **6**.

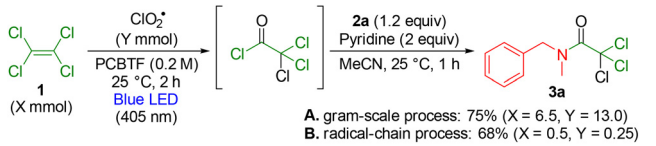
Additionally, when an amino alcohol was used as the substrate, the formation of trichloroacetamide, followed by intramolecular cyclization accompanied by the elimination of the trichloro group, occurred sequentially, affording valuable heterocyclic scaffolds **7** and **8** for drug synthesis in 71% and 70% yields, respectively (Scheme 3).

Furthermore, trichloroethylene **9** was converted to dichloroacetamide **10** under the optimized conditions (Scheme 4). In this reaction, two types of intermediates were considered; however, the product derived from the other possible intermediate was not observed, which was likely due to the higher stability of the radical intermediate, leading to **10**.[35]

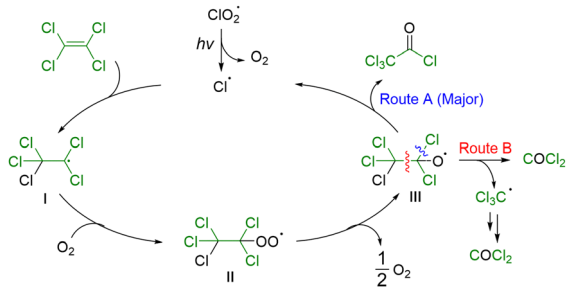
We conducted the reaction using 1.1 g (6.5 mmol) of PCE **1** under the optimized conditions, affording the corresponding amide product **3a** in 75% isolated yield (Scheme 5A). This result suggests that the reaction efficiency is maintained upon scale-up to the gram scale. Furthermore, when the reaction was



Scheme 4 Visible-light-induced upcycling of trichloroethylene.



Scheme 5 Gram-scale experiment and verification of the radical-chain mechanism in the visible-light-induced upcycling of PCE.



Scheme 6 Plausible mechanism for the visible-light-induced upcycling of PCE.

performed with 0.5 equivalents of $ClO_2^{\bullet}$ relative to **1**, **3a** was obtained in 68% yield (Scheme 5B). This result indicates that the reaction proceeded *via* a radical-chain process.

The proposed reaction mechanism is illustrated in Scheme 6. First, a chlorine radical generated by the photoirradiation of $ClO_2^{\bullet}$ adds to PCE to form radical intermediate **I**. Oxygen is added to this radical to afford peroxyl radical intermediate **II**, which is subsequently converted into alkoxyl radical intermediate **III**. From intermediate **III**, two pathways are possible: cleavage of the C–Cl bond affords the desired trichloroacetyl chloride (route A), whereas cleavage of the C–C bond yields the byproduct phosgene (route B).

A radical intermediate was detected by electron spin resonance (ESR) analysis performed at −120 °C. (Fig. S1).[36] In dark, the ESR spectrum showed an anisotropic signal with four hyperfine lines owing to a chlorine nucleus (I = 3/2) corresponding to the $ClO_2^{\bullet}$. The average g value (g_{ave}) was consistent with the reported value of 2.014.[37] After light irradiation and rapid freezing, a new signal was observed at g_{zz} = 2.0337, with the disappearance of the signal owing to $ClO_2^{\bullet}$. A large g_{zz} value was assigned to the corresponding peroxyl radical intermediate **II**.[38]

To elucidate the mechanistic origin of the observed selectivity, density functional theory (DFT) calculations were performed at the B3LYP/6-311+(2d) level, using the pentachloroethoxy radical as the reference state (0 kJ mol^{-1}) (Fig. 1). Along route A, a transition state corresponding to chlorine radical dissociation was observed at a low activation free energy of 2.87 kJ mol^{-1}. Structural analyses revealed substantial elongation of the cleaving C–Cl bond from 1.85 Å in the reactant to 2.07 Å at the transition state, consistent with a homolytic bond-cleavage process. The resulting product was significantly stable, lying 90.2 kJ mol^{-1} lower in energy than the reference state. By contrast, route B proceeded *via* C–C bond scission and exhibited a markedly higher activation barrier of 8.91 kJ mol^{-1}. In the corresponding transition state, the C–C bond

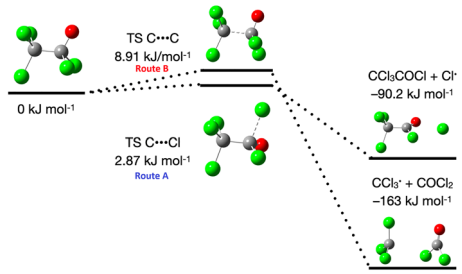


Fig. 1 Transition states and energy profiles of the two competing pathways.

is elongated from 1.58 Å to 1.77 Å, accompanied by contraction of the adjacent C–O bond from 1.30 Å to 1.25 Å, indicating substantial bond reorganization and the development of carbonyl character. Although the product formed *via* route B is thermodynamically more stable (−163 kJ mol^{-1}), the significantly lower activation barrier associated with route A clearly indicates that chlorine-radical dissociation is kinetically favored. This kinetic preference is fully consistent with the experimentally observed high selectivity toward the products derived from route A.

We developed a sustainable and environmentally friendly upcycling strategy that transforms PCE, a harmful pollutant, into valuable trichloroacetamides under visible-light irradiation with $ClO_2^{\bullet}$. Trichloroacetamides can be used directly in subsequent reactions without isolation, allowing for the efficient synthesis of various derivatives such as carbamate, urea, and heterocyclic compounds. When PCBTF was used as the solvent, the reaction proceeded with stoichiometric amounts of reagent. Under mild conditions, the formation of highly toxic byproducts such as phosgene was minimized. This protocol provides access to valuable trichloroacetamides, including challenging aromatic products and heterocycles. The reaction mechanism was clarified by DFT calculations and ESR measurements. These results demonstrate that our method is a practical strategy for the chemical upcycling of PCE and provides fundamental insights that can support the design of future transformations.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article are included in the supplementary information (SI). Supplementary information: experimental details, characterization data for new compounds, and copies of NMR spectra (PDF). See DOI: https://doi.org/10.1039/d6cc00273k.

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References

1 P. G. Tratnyek, E. Edwards, L. Carpenter and S. Blossom, *Environ. Sci.: Processes Impacts*, 2020, **22**, 465–471.
2 M. Di Cicco, A. Tabilio Di Camillo, W. Di Marzio, M. E. Sáenz, D. M. P. Galassi, G. Pieraccini, A. Galante, D. Di Censo and T. Di Lorenzo, *Environ. Toxicol. Chem.*, 2024, **43**, 2515–2527.
3 J. H. Lee, A. K. Bryant, M. Alajlouni, B. E. Boor, A. Tasoglou and S. Liu, *J. Breath Res.*, 2024, **18**, 046008.
4 D. M. Ceballos, K. M. Fellows, A. E. Evans, P. A. Janulewicz, E. G. Lee and S. G. Whittaker, *Front. Public Health*, 2021, **9**, 638082.
5 Perchloroethylene (PCE) can be generated as a side product in industrial chlorination and oxychlorination processes, for example during the production of trichloroethylene or other chlorinated hydrocarbons. Examples see: (*a*) S. Handa, M. Hiraoka, K. Yokoyama and T. Nakamura, *Method for Producing Trichloroethylene and Tetrachloroethylene*, *JP Pat.*, JP4573147, 2010; (*b*) I. W. Sutherland, N. G. Hamilton, C. C. Dudman, P. Jones, D. Lennon and J. M. Winfield, *Appl. Catal., A*, 2011, **399**, 1–11.
6 P. A. Kots, B. C. Vance, C. M. Quinn, C. Wang and D. G. Vlachos, *Nat. Sustainability*, 2023, **6**, 1258–1267.
7 A. Jordan, *Nat. Chem.*, 2024, **16**, 676–677.
8 M. Liu, X. Wu and P. J. Dyson, *Nat. Chem.*, 2024, **16**, 700–708.
9 R. G. Dickinson and J. A. Leermakers, *J. Am. Chem. Soc.*, 1932, **54**, 3852–3862.
10 R. G. Dickinson and J. L. Carrico, *J. Am. Chem. Soc.*, 1934, **56**, 1473–1480.
11 D. M. Frankel, C. E. Johnson and H. M. Pitt, *J. Org. Chem.*, 1957, **22**, 1119–1120.
12 W. L. Dilling, C. J. Bredeweg and N. B. Tefertiller, *Environ. Sci. Technol.*, 1976, **10**, 351–356.
13 A. Yasuhara, *Chemosphere*, 1993, **26**, 1507–1512.
14 S. Kutsuna, T. Ibusuki and K. Takeuchi, *Environ. Sci. Technol.*, 2000, **34**, 2484–2489.
15 P. B. Amama, K. Itoh and M. Murabayashi, *J. Mol. Catal. A: Chem.*, 2004, **217**, 109–115.
16 A. Zhang, Y. Kuwahara, Y. Hotta and A. Tsuda, *Asian J. Org. Chem.*, 2013, **2**, 572–578.
17 T. Akamatsu, M. Shele, A. Matsune, Y. Kashiki, F. Liang, T. Okazoe and A. Tsuda, *ACS Omega*, 2023, **8**, 2669–2684.
18 I. Higashimura, M. Shele, T. Akamatsu, R. Ohmura, F. Liang, T. Okazoe and A. Tsuda, *J. Org. Chem.*, 2024, **89**, 1864–1872.
19 K. Ohkubo and K. Hirose, *Angew. Chem., Int. Ed.*, 2018, **57**, 2126–2129.
20 S. Ohno, H. Asahara, T. Inoue and K. Ohkubo, *RSC Adv.*, 2022, **12**, 31412–31414.
21 H. Asahara, N. Takao, M. Moriguchi, T. Inoue and K. Ohkubo, *Chem. Commun.*, 2022, **58**, 6176–6179.
22 Y. Itabashi, H. Asahara and K. Ohkubo, *Chem. Commun.*, 2023, **59**, 7506–7517.
23 A. Fantinati, V. Zanirato, P. Marchetti and C. Trapella, *ChemistryOpen*, 2020, **9**, 100–170.
24 Q. Zhao, B. Li, X. Zhou, Z. Wang, F. L. Zhang, Y. Li, X. Zhou, Y. Fu and Y. F. Wang, *J. Am. Chem. Soc.*, 2022, **144**, 15275–15285.
25 F. Diaba and G. Trenchs, *Org. Biomol. Chem.*, 2023, **22**, 388–394.
26 M. Bandyopadhyay, B. Bera, S. Pathak, D. Bhunia, S. Bhadra, S. Patra, M. Pal Chowdhury, J. Escorihuela and M. K. Bera, *Adv. Synth. Catal.*, 2024, **366**, 2696–2704.
27 T. T. Vo, M. Naher, C. M. Williams and P. V. Bernhardt, *J. Org. Chem.*, 2025, **90**, 12709–12716.
28 X. Jia, S. Kramer, T. Skrydstrup and Z. Lian, *Angew. Chem., Int. Ed.*, 2021, **60**, 7353–7359.
29 L. Chen, M. Zhou, L. Shen, X. He, X. Li and X. Zhang, *Org. Lett.*, 2021, **23**, 4991–4996.

30 K. Nozawa-Kumada, K. Noguchi, T. Akada, M. Shigeno and Y. Kondo, *Org. Lett.*, 2021, **23**, 6659–6663.
31 Based on the amount of sodium nitrite (0.8 equivalent of $ClO_2^{\bullet}$ was generated from ClO_2^- by dismutation reaction).
32 A. Ogawa and D. P. Curran, *J. Org. Chem.*, 1997, **62**, 450–451.
33 M. Kirihara, Y. Sakamoto, S. Yamahara, A. Kitajima, N. Kugisaki and Y. Kimura, *Synlett*, 2022, 1670–1674.
34 M. Kirihara, T. Kawai, A. Kitajima, S. Yamahara, N. Mori and Y. Kimura, *ChemistrySelect*, 2024, **9**, e202403692.
35 Y. Tian and Z. Q. Liu, *RSC Adv.*, 2014, **4**, 64855–64859.
36 A $ClO_2^{\bullet}$ aqueous solution (0.10–0.20 M) was prepared from sodium chlorite and hydrochloric acid, and the gaseous portion in the headspace was collected using a syringe. The gas was introduced directly into an ESR tube containing tetrachloroethylene. Introduction of $ClO_2^{\bullet}$ was continued until the solution turned yellow. The sample tube was then sealed with a rubber septum and subjected to ESR analysis.
37 K. Ohkubo, K. Hirose, T. Shibata, K. Takamori and S. Fukuzumi, *J. Phys. Org. Chem.*, 2017, **30**, e3619.
38 K. Ohkubo, K. Suga, K. Morikawa and S. Fukuzumi, *J. Am. Chem. Soc.*, 2003, **125**, 12850–12859.