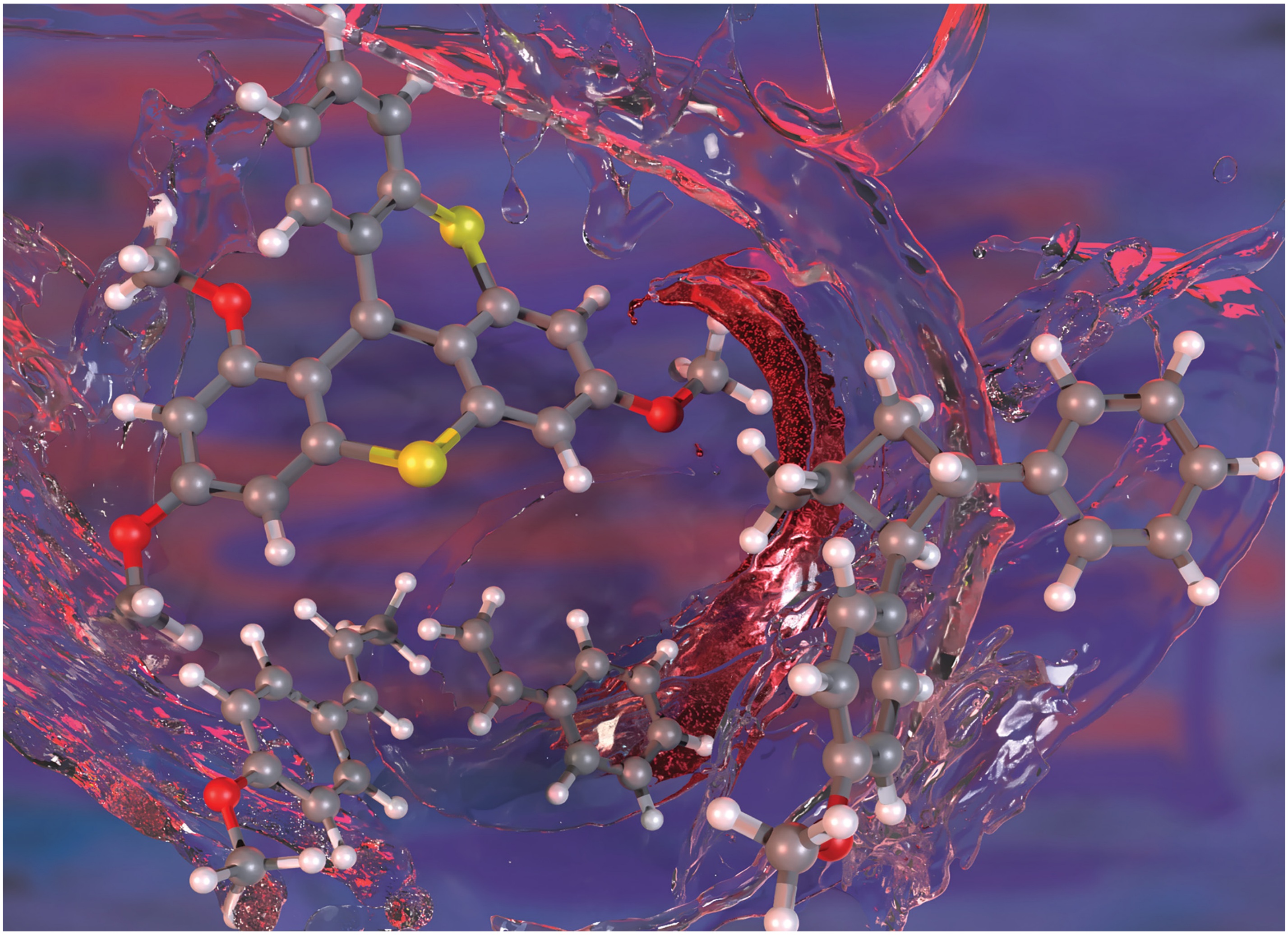


Showcasing research from Professor Yujiro Hoshino and Professor Kenta Tanaka's laboratory, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, JAPAN.

Synthesis of sulfur- and oxygen-bridged cationic [4]-helicenes mediated by Friedel–Crafts-S_NAr tandem reactions for red-light-driven organophotoredox catalysis

The synthesis of sulfur- and oxygen-bridged cationic [4]-helicenes *via* a tandem Friedel–Crafts–S_NAr reaction has been developed. The sulfur-bridged cationic [4]-helicenes are suitable as catalysts for photoredox reactions under low-energy light sources such as red LED light.

Image reproduced by permission of Yujiro Hoshino from *Chem. Commun.*, 2026, **62**, 8404.

As featured in:

See Isao Kadota, Kenta Tanaka, Yujiro Hoshino *et al.*,
Chem. Commun., 2026, **62**, 8404.

ROYAL SOCIETY
OF CHEMISTRY

rsc.li/chemcomm

ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.*, 2026, **62**, 8404

Received 29th December 2025,
Accepted 28th March 2026

DOI: 10.1039/d5cc07398g

rsc.li/chemcomm

Synthesis of sulfur- and oxygen-bridged cationic [4]-helicenes mediated by Friedel–Crafts-S$_\mathrm{N}$Ar tandem reactions for red-light-driven organophotoredox catalysis

Ryoga Hasebe,[a] Rumi Hanada,[a] Yuta Tanaka,[a] Yuta Goto,[b] Mio Takeuchi,[a]
Hiroyoshi Takamura,[b] Isao Kadota,*[b] Kenta Tanaka*[c] and Yujiro Hoshino*[a]

The synthesis of sulfur- and oxygen-bridged cationic [4]-helicenes *via* a tandem Friedel–Crafts–S$_\mathrm{N}$Ar reaction of a diaryl sulfide or a diaryl ether with a (thio)salicylic acid has been developed. The sulfur-bridged cationic [4]-helicenes are suitable as catalysts for photoredox reactions under low-energy light sources such as red LED light.

Cationic helicenes, originating from the pioneering studies on cationic triarylmethyl organic dyes by Hofmann, Verguin, and Lauth, have attracted considerable attention in organic chemistry owing to their unique structural and electronic properties.[1] Oxygen- and nitrogen-bridged cationic helicenes are typically synthesized *via* S$_\mathrm{N}$Ar reactions of triarylmethyl cations, which are prepared from 1,3-dimethoxybenzene and diethyl carbonate (Fig. 1(a)).[2] In contrast to the numerous reports on oxygen- and nitrogen-bridged cationic helicenes, only two examples of sulfur-bridged cationic helicenes have been described, both synthesized *via* a two-step route starting from thioxanthone (Fig. 1(b)).[3] Moreover, the physical properties of sulfur-bridged cationic helicenes remain underexplored; for example, to date, no reports have addressed their application as photoredox catalysts. Therefore, the development of efficient synthetic routes to sulfur-bridged cationic helicenes as well as the investigation of their physical properties and potential applications are highly desirable.

Visible-light-mediated photoredox catalysis has seen widespread development, particularly in the context of sustainable energy-conversion systems.[4] Conventional photoredox reactions often rely on the use of high-energy light sources such as blue LED light; however, recent advances in energy-efficient systems have prompted a shift in attention toward lower-energy light sources such as red LED light. Although metal-based photoredox catalysts that are activated by red light have been extensively studied, red-light-activated organophotoredox catalysts remain relatively underexplored (Fig. 1 (c)).[5] In particular, although Gianetti and co-workers reported a cationic helicene photocatalyst, $[^{n}\mathrm{Pr\text{-}DMQA}^{+}][\mathrm{BF}_4^{-}]$, that functions as a red-light-driven photoredox catalyst in 2020,[5b] only a few examples of cationic helicene photocatalysts have been reported to date.

Recently, we have reported the design and synthesis of thioxanthylium-based organophotoredox catalysts (Fig. 1, '*Our previous work*') which were prepared from diaryl sulfides and aryl-acid chlorides in the presence of trifluoromethanesulfonic acid (TfOH) *via* a Friedel–Crafts reaction.[6] These catalysts can be activated by green LED light to efficiently promote a variety of photoredox reactions.[7] Accordingly, we hypothesized that using (thio)salicylaldehyde instead of aryl-acid chloride could allow performing a Friedel–Crafts–S$_\mathrm{N}$Ar tandem reaction to yield cationic helicenes. Here, we report the synthesis of sulfur- and oxygen-bridged cationic helicenes *via* Friedel–Crafts–S$_\mathrm{N}$Ar tandem reactions and their application as organophotoredox catalysts under red-light irradiation (Fig. 1, '*This work*').

To evaluate the relationship between their structural and physical properties, various cationic [4]-helicenes (**TXTH-1–4**) were initially synthesized in moderate to good yield *via* Friedel–Crafts–S$_\mathrm{N}$Ar tandem reactions between diaryl (thio)ether **1** and (thio)salicylic acid **2** in chlorobenzene at 120 °C (24 h) in the presence of TfOH (Table 1).[6] The as-obtained cationic [4]-helicenes **TXTH-1–4** exhibit moderate excited-state reduction potentials ($E_{1/2}(\mathrm{C}^*/\mathrm{C}^{\bullet-})$ = +1.51 to +1.76 V *vs.* SCE) and an absorption band in the visible spectrum. Compared with **TXT** (Fig. 1), the cyclic voltammograms of **TXTH-1** revealed slightly negatively shifted reduction potentials (Fig. 2). Furthermore, the absorption spectrum is markedly red-shifted relative to that

---

[a] *Graduate School of Environment and Information Sciences, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan. E-mail: hoshino-yujiro-hy@ynu.ac.jp*

[b] *Graduate School of Environmental, Life, Natural Science and Technology, Okayama University, 3-1-1 Tsushima-Naka, Kitaku, Okayama 700-8530, Japan. E-mail: kadota-i@okayama-u.ac.jp*

[c] *Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushima-Naka, Kitaku, Okayama 700-8530, Japan. E-mail: ktanaka@okayama-u.ac.jp*

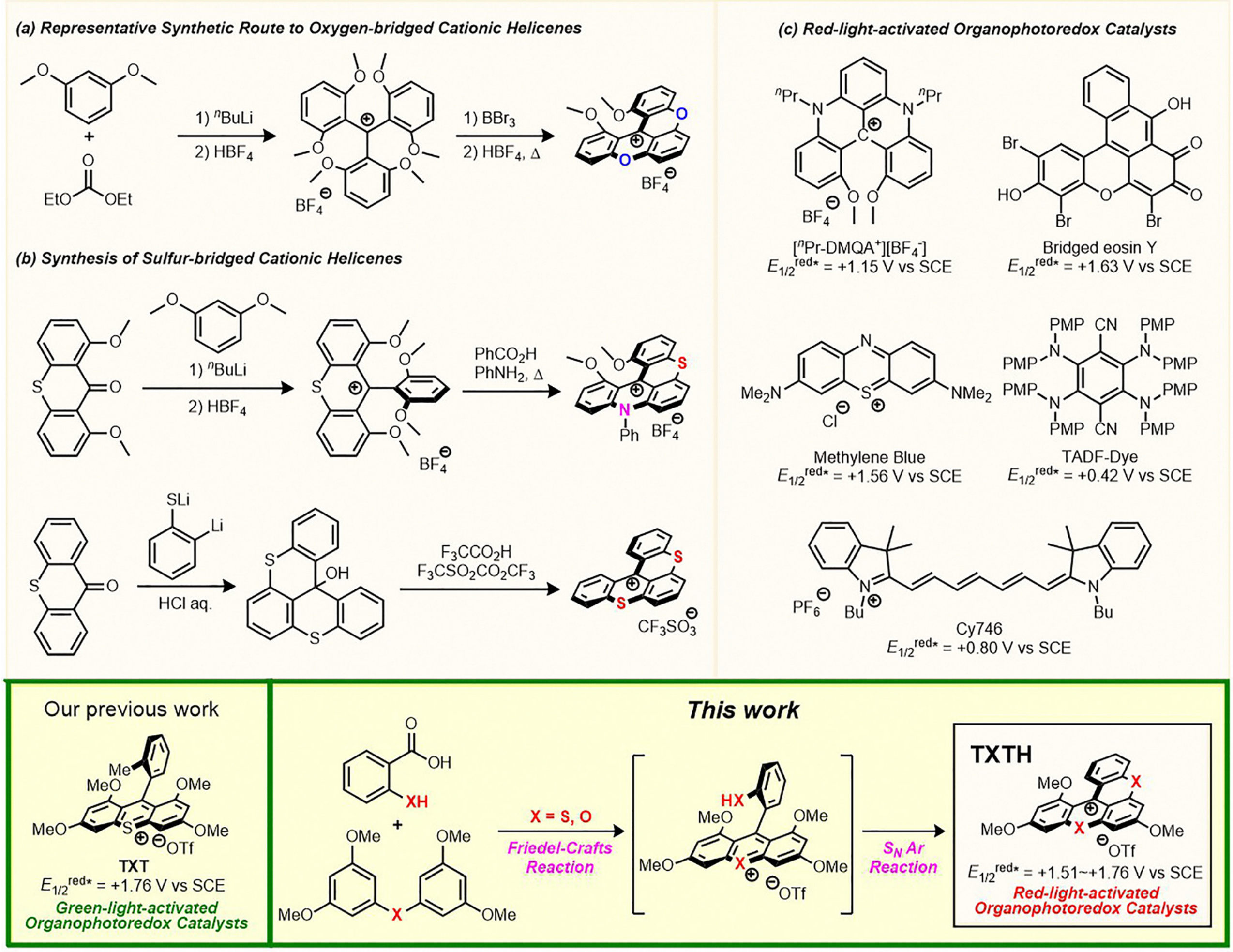


Fig. 1 Representative synthetic routes to cationic helicenes and red-light-activated organophotoredox catalysts.

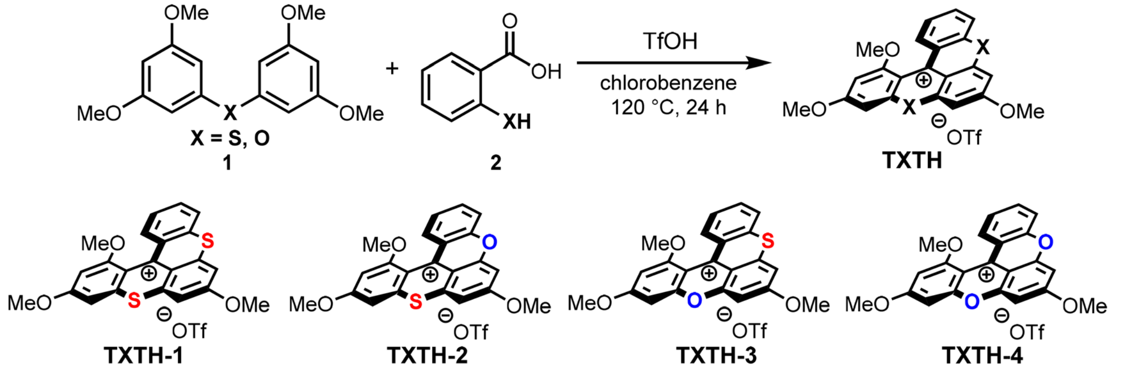
of **TXT** (Fig. 3), which can be attributed to the π-extension of the framework. In particular, **TXTH-1** exhibits a broad absorption band extending to the red region of the visible spectrum ($\lambda_{\text{abs}} <$ 700 nm), suggesting that it could be activated by lower-energy irradiation sources such as red light.

Encouraged by these promising results, we investigated **TXTH-1** as a catalyst in photoredox reactions (Scheme 1). When the [2+2] cycloaddition reaction of *trans*-anethole (**3**) with styrene (**4**) was conducted in the presence of **TXTH-1** under red-LED-light irradiation, the desired product (**5**) was obtained in high yield.[7c] Since the excited-state reduction potential of **TXTH-1** is higher than that of *trans*-anethole (**3**), one-electron oxidation efficiently occurs (**TXTH-1**: $E_{1/2}(\text{C}^*/\text{C}^{\bullet-})$ = +1.51 V *vs.* SCE; **3**: $E_{p/2}$ = +1.24 V *vs.* SCE). Notably, **TXTH-1** also catalyzed a radical-cation Diels–Alder reaction, affording the desired cyclohexene derivative (**7**) in high yield.[6a] Finally, *p*-quinone methide (**9**) underwent efficient trifluoromethylation to give the corresponding product (**10**) in 85% yield.[8] This transformation proceeds *via* oxidation of the Langlois reagent (**8**; $E_{p/2}$ = +1.05 V *vs.* SCE) by **TXTH-1** to generate a trifluoromethyl radical, which subsequently adds to *p*-quinone methide (**9**). These results demonstrate that **TXTH-1** can serve as an effective catalyst for various photoredox reactions under red-LED-light irradiation.

In summary, we have developed a synthetic route to cationic sulfur and oxygen-bridged [4]-helicenes based on Friedel–Crafts–S$_\text{N}$Ar tandem reactions. The reactions of a diaryl (thio)ether with a (thio)salicylic acid in the presence of TfOH successfully yield the cationic [4]-helicenes in good yield. These catalysts exhibit moderate excited-state reduction potentials ($E_{1/2}(\text{C}^*/\text{C}^{\bullet-})$ = +1.51 to +1.76 V *vs.* SCE) and an absorption band in the visible spectrum. Especially **TXTH-1** produces an absorption band that extends to the red region of the visible spectrum, thus enabling the efficient promotion of [2+2] cycloaddition, radical-cation Diels–Alder reaction, and trifluoromethylation under red-LED-light irradiation. The present reaction provides a promising platform for the synthesis of cationic helicenes and the development of red-light-driven organophotoredox catalysis.

This work was supported by Murata Science Foundation, Ichiju Industrial Science and Technology Promotion Foundation, Foundation for Interaction in Science & Technology, ENEOS Tonen General Research/Development Encouragement

Table 1 Synthesis and physical properties of cationic [4]-helicenes



Catalyst	Yield[a] (%)	$E_{1/2}(\mathrm{C}^*/\mathrm{C}^{\bullet-})$[b] (V)	$E_{1/2}(\mathrm{C}/\mathrm{C}^{\bullet-})$[c] (V)	$E_{0,0}$ (eV)	Excitation λ_{max} (nm)	Emission λ_{max} (nm)
TXTH-1	71	+1.51	−0.42	1.93	517	682
TXTH-2	72	+1.63	−0.46	2.09	481	647
TXTH-3	69	+1.54	−0.56	2.10	477	630
TXTH-4	72	+1.76	−0.58	2.34	457	600
TXT[d]	—	+1.76	−0.39	2.15	464	630

[a] All reactions were conducted using diaryl (thio)ether **1** (0.2 mmol), (thio)salicylaldehyde acid **2** (0.6 mmol), and TfOH (0.6 mmol) in chlorobenzene (120 °C; N_2 atmosphere; 24 h). [b] Excited-state oxidation potentials were estimated on the basis of the ground-state redox potentials and the intersection of the absorption and emission bands. [c] Determined by cyclic voltammetry in CH_3CN *vs.* SCE. [d] The values for **TXT** were extracted from previous reports.[6a]

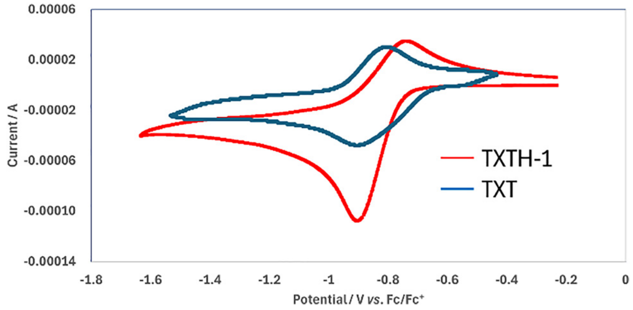
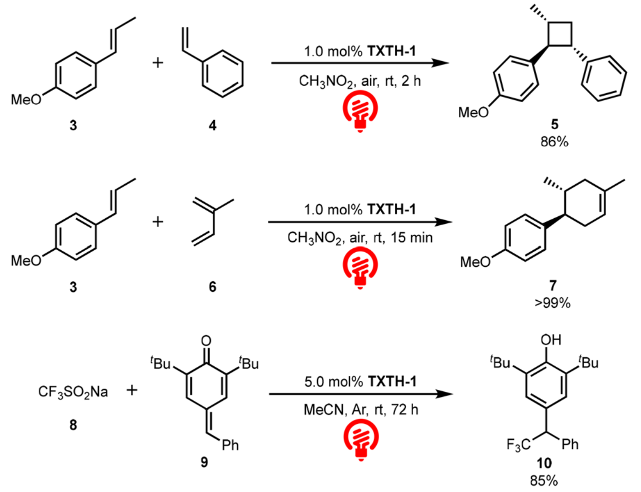


Fig. 2 Cyclic voltammograms of **TXTH-1** and **TXT** (10 mM); supporting electrolyte: *tetra-n*-butylammonium perchlorate (100 mM); in CH_3CN.



Scheme 1 Photoredox reactions catalyzed by **TXTH-1** under red-LED-light irradiation.

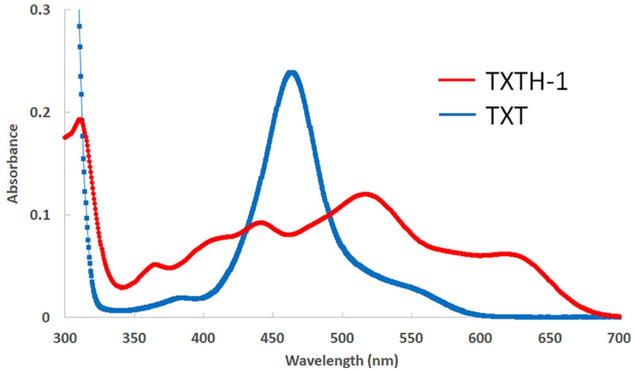


Fig. 3 Absorption spectra of **TXTH-1** and **TXT** in CH_3CN (10 μM).

& Scholarship Foundation, The Yakumo Foundation for Environmental Science, Okayama Foundation for Science and Technology, JKA and its promotion funds from KEIRIN RACE, Amano Institute of Technology, Casio Science Promotion Foundation, Wesco Scientific Promotion Foundation, and JSPS Program for Forming Japan's Peak Research Universities (J-PEAKS) Grant Number JPJS00420230010.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5cc07398g.

References

1 (*a*) J. Bosson, J. Gouin and J. Lacour, *Chem. Soc. Rev.*, 2014, **43**, 2824; (*b*) D. F. Duxbury, *Chem. Rev.*, 1993, **93**, 381–433.

2 (*a*) J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, 1964, **86**, 2252–2256; (*b*) F. Torricelli, J. Bosson, C. Besnard, M. Chekini, T. Bürgi and J. Lacour, *Angew. Chem., Int. Ed.*, 2013, **52**, 1796–1800; (*c*) B. W. Laursen and F. C. Krebs, *Angew. Chem., Int. Ed.*, 2000, **39**, 3432–3434; (*d*) G. M. Labrador, C. Besnard, T. Bürgi, A. I. Poblador-Bahamonde, J. Bosson and J. Lacour, *Chem. Sci.*, 2019, **10**, 7059–7067; (*e*) J. Guin, C. Besnard and J. Lacour, *Org. Lett.*, 2010, **12**, 1748–1751; (*f*) T. J. Sørensen, A. Ø. Madsen and B. W. Laursen, *Tetrahedron Lett.*, 2013, **54**, 587–590; (*g*) M. Marinova, S. Pascal, L. Guénée, C. Besnard, B. Shivachev, K. Kostova, C. Villani, R. Franzini, V. Dimitrov and J. Lacour, *J. Org. Chem.*, 2020, **85**, 11908–11923; (*h*) J. Gouin, T. Bürgi, L. Guénée and J. Lacour, *Org. Lett.*, 2014, **16**, 3800–3803; (*i*) M. Rosenberg, M. Santella, S. A. Bogh, A. V. Muñoz, H. O. B. Andersen, O. Hammerich, I. Bora, K. Lincke and B. W. Laursen, *J. Org. Chem.*, 2019, **84**, 2556–2567; (*j*) R. Kaur, J. Moutet, D. D. Mills and T. L. Gianetti, *Chem. – Eur. J.*, 2025, **31**, e202404135; (*k*) P. Huszthy, K. Lempert and G. Simig, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1351–1354.

3 (*a*) G. D. Figuly, C. K. Loop and J. C. Martin, *J. Am. Chem. Soc.*, 1989, **111**, 654–658; (*b*) C. Nicolas, G. Bernardinelli and J. Lacour, *J. Phys. Org. Chem.*, 2010, **23**, 1049–1056.

4 (*a*) D. A. Nicewicz and D. W. C. MacMillan, *Science*, 2008, **322**, 77–80; (*b*) N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166; (*c*) M. H. Shaw, J. Twilton and J. D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898–6926.

5 (*a*) M. M. Hossain, A. C. Shaikh, R. Kaur and T. L. Gianetti, *J. Am. Chem. Soc.*, 2024, **146**, 7922–7930; (*b*) L. Mei, J. M. Veleta and T. L. Gianetti, *J. Am. Chem. Soc.*, 2020, **142**, 12056–12061; (*c*) A. H. Schade and L. Mei, *Org. Biomol. Chem.*, 2023, **21**, 2472–2485; (*d*) N. Sellet, J. Frey, M. Cormier and J.-P. Goddard, *Chem. Sci.*, 2024, **15**, 8639–8650; (*e*) K. Rybicka-Jasińska, T. Wdowik, K. Łuczak, A. J. Wierzba, O. Drapała and D. Gryko, *ACS Org. Inorg. Au*, 2022, **2**, 422–426; (*f*) L. R. Beck, K. A. Xie, S. L. Goldschmid, S. K. Kariofillis, C. L. Joe, T. C. Sherwood, M. Sezen-Edmonds and T. Rovis, *SynOpen*, 2023, **07**, 76–87; (*g*) Y. Miyamoto, K. Muraoka, S. Murakami, T. Matsudaira and H. Ohmiya, *J. Am. Chem. Soc.*, 2025, **147**, 41185–41192; (*h*) R. P. Pandian, T. K. Chandrashekar, G. S. S. Saini and A. L. Verma, *Faraday Trans.*, 1993, **89**, 677; (*i*) A. Gizatullin, T. Yuan, S. Grotjahn, L. Cavallo, B. König, C. Zhu and M. Rueping, *Angew. Chem., Int. Ed.*, 2026, e26086; (*j*) M. Tanioka, A. Kuromiya, R. Ueda, T. Obata, A. Muranaka, M. Uchiyama and S. Kamino, *Chem. Commun.*, 2022, **58**, 7825–7828.

6 (*a*) K. Tanaka, M. Kishimoto, Y. Tanaka, Y. Kamiyama, Y. Asada, M. Sukekawa, N. Ohtsuka, T. Suzuki, N. Momiyama, K. Honda and Y. Hoshino, *J. Org. Chem.*, 2022, **87**, 3319–3328; (*b*) K. Tanaka, Y. Tanaka, M. Kishimoto, Y. Hoshino and K. Honda, *Beilstein J. Org. Chem.*, 2019, **15**, 2105–2112; (*c*) K. Tanaka, K. D. Omata, Y. Asada, Y. Hoshino and K. Honda, *J. Org. Chem.*, 2019, **84**, 10669–10678; (*d*) K. Tanaka, M. Kishimoto, M. Sukekawa, Y. Hoshino and K. Honda, *Tetrahedron Lett.*, 2018, **59**, 3361–3364; (*e*) A. Mizutani, M. Kondo, S. Itakura, H. Takamura, Y. Hoshino, M. Nishikawa, I. Kadota, K. Kusamori and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 2025, **98**, uoaf044.

7 (*a*) S. Nohara, S. Iwai, N. Yamaguchi, Y. Asada, Y. Kamiyama, Y. Tanaka, K. Tanaka and Y. Hoshino, *Synlett*, 2023, 2525–2529; (*b*) K. Tanaka, Y. Asada and Y. Hoshino, *Chem. Commun.*, 2022, **58**, 2476–2479; (*c*) K. Tanaka, Y. Iwama, M. Kishimoto, N. Ohtsuka, Y. Hoshino and K. Honda, *Org. Lett.*, 2020, **22**, 5207–5211; (*d*) K. Tanaka, Y. Asada, Y. Hoshino and K. Honda, *Org. Biomol. Chem.*, 2020, **18**, 8074–8078; (*e*) H. Ando, H. Takamura, I. Kadota and K. Tanaka, *Chem. Commun.*, 2024, **60**, 4765–4768; (*f*) M. R. El-kholany, T. Senoo, A. Mizutani, H. Takamura, T. Suzuki, I. Kadota and K. Tanaka, *Org. Lett.*, 2025, **27**, 4870–4874; (*g*) S. Kodaki, H. Ando, H. Takamura, I. Kadota and K. Tanaka, *Precis. Chem.*, 2025, **3**, 801–805; (*h*) Y. Goto, H. Ando, H. Takamura, I. Kadota and K. Tanaka, *Org. Lett.*, 2026, **28**, 147–151.

8 K. G. Ghosh, P. Chandu, S. Mondal and D. Sureshkumar, *Tetrahedron*, 2019, **75**, 4471–4478.