ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2025, **61**, 1882

Received 5th November 2024,
Accepted 23rd December 2024

DOI: 10.1039/d4cc05908e

rsc.li/chemcomm

Transition-metal-free dibenzoxazepinone synthesis by hypervalent iodine-mediated chemoselective arylocyclizations of *N*-functionalized salicylamides†

Naoki Miyamoto,[a] Kotaro Kikushima,[a] Hirotaka Sasa,[ab] Ten Katagiri,[a] Naoko Takenaga,[c] Yasuyuki Kita *[d] and Toshifumi Dohi *[ad]

We have developed transition-metal-free synthetic methodologies for dibenzoxazepinones utilizing salicylamides as starting materials and employing two distinct types of successive hypervalent iodine-mediated arylocyclizations. This synthetic protocol encompasses selective phenol *O*-arylation of salicylamides with diaryliodonium salts, followed by electrophilic aromatic amination utilizing chemically or electronically generated hypervalent iodine reagents in the second stage of the process.

Dibenzoxazepinone, a seven-membered heterocyclic compound, possesses a unique structural motif commonly found in bioactive compounds, pharmaceuticals, and their intermediates (Fig. 1).[1] Various synthetic approaches to dibenzoxazepinones involving diaryl ether and amide moiety formation have been documented (Fig. 2).[2]

The synthesis of dibenzoxazepinones typically involves the formation of diaryl ether bonds as the key step. The condensation of *ortho*-functionalized benzoic acids and aminophenols, along with diaryl ether bond formation *via* a transition-metal-catalyzed coupling or aromatic nucleophilic substitution (S_NAr), represents a straightforward approach (Fig. 2a).[3] Starting with salicylic esters and *ortho*-fluoronitroarenes also provides an efficient combination for the construction of dibenzoxazepinone structures, involving diaryl ether bond formation followed by reductive lactamization with iron (Fig. 2b).[4] Notably, salicylamides undergo a double S_NAr reaction to form both aryl C–O and C–N bonds in a single procedure. However, the starting material is limited to electron-deficient aromatic compounds (Fig. 2c).[5] In contrast, transition-metal-catalyzed coupling reactions address this limitation; the reaction of benzamides and *ortho*-bromophenol derivatives in the presence of a copper catalyst yields dibenzoxazepinones in a single procedure (Fig. 2d).[6] Moreover, transition-metal catalysts enable CO insertion, leading to a three-component coupling for dibenzoxazepinone synthesis (Fig. 2e).[7] However, the use of transition-metal catalysts presents drawbacks, including high cost and toxicity, and efficient transition-metal-free methods are highly desirable, particularly for drug synthesis.

As a transition-metal-free approach to the formation of aryl–heteroatom bonds, the use of diaryliodonium salts as arylating agents represents an attractive strategy,[8] with the initial phenol *O*-arylation using diaryliodonium salts reported in 1953.[9] Over approximately ten years, advanced phenol *O*-arylation methods, incorporating considerations of the base, counter anion, and aryl ligand, have been developed by many researchers and our group.[10,11] The fluoride and acetate counter anions of diaryliodonium salts directly activate phenol nucleophilicities, enabling these reactions to proceed under milder primary conditions. Furthermore, trimethoxyphenyl (TMP)-iodonium salts are readily accessible,[12] exhibit unified selectivity for aryl transfer,[13,14] and have been employed in phenol *O*-arylations.

In this context, we focused on the selective *O*-arylation of salicylamides under transition-metal-free conditions (Fig. 3, step a). Thus, the obtained *O*-arylated salicylamides undergo electrophilic aromatic amination[15] to give dibenzoxazepinones

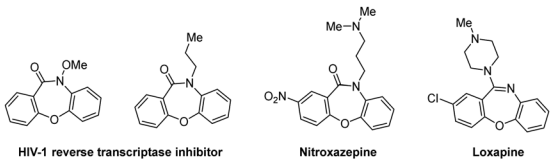


Fig. 1 Bioactive compounds of dibenzoxazepinone derivatives.

[a] *College of Pharmaceutical Sciences, Ritsumeikan University, Kusatsu 525-8577, Shiga, Japan. E-mail: td1203@ph.ritsumei.ac.jp*
[b] *School of Pharmacy and Pharmaceutical Sciences, Mukogawa Women's University, 11-68 Koshien Kyuban-cho, Nishinomiya 663-8179, Hyogo, Japan*
[c] *Faculty of Pharmacy, Meijo University, 150 Yagotoyama, Tempaku-ku, Nagoya 468-8503, Japan*
[d] *Research Organization of Science and Technology, Ritsumeikan University, Kusatsu 525-8577, Shiga, Japan. E-mail: kita@ph.ritsumei.ac.jp*

† Electronic supplementary information (ESI) available: Experimental procedure, characterization date and NMR spectra for all new compounds. See DOI: https://doi.org/10.1039/d4cc05908e

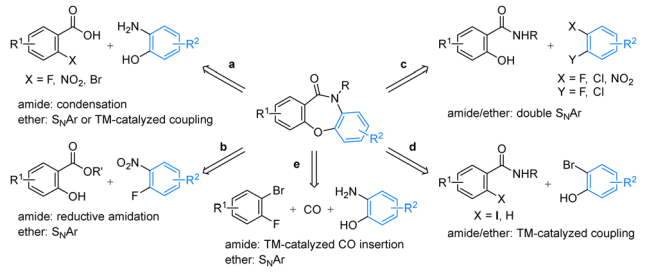


Fig. 2 C–O bond formation approach for dibenzoxazepinone synthesis.

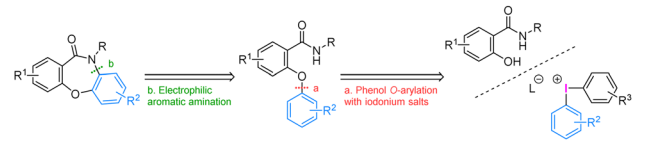


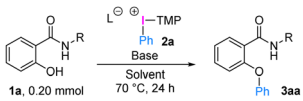
Fig. 3 New approach for dibenzoxazepinone synthesis.

(Fig. 3, step b). This study reports the synthesis of transition-metal-free dibenzoxazepinones *via* chemoselective arylocyclization, leveraging the unique reactivity of diaryliodonium salts. Furthermore, it demonstrates a one-pot strategy for synthesizing dibenzoxazepinone through chemical- or electro-oxidation, utilizing persistent iodoarene as catalyst. The challenge lies in the selective phenol *O*-arylation of salicylamides because of the competitive arylation that can occur at both the nitrogen and oxygen atoms of the amide.[14b,c,16] In fact, the copper-catalyzed coupling of salicylamide and halobenzene has been investigated; this reaction proceeded with selective amide *N*-arylation.[17]

The investigation began with the *O*-arylation of *N*-functionalized salicylamides using TMP-iodonium salts (Table 1 and Table S1, ESI†). The reaction between *N*-methoxy-functionalized salicylamide (**1a**) and phenyl(TMP)-iodonium acetate (**2a**) was conducted in the presence of Na_2CO_3 (1.5 equiv.) in a $(CH_2Cl)_2$–H_2O (1 : 1) mixture at 70 °C for 24 h. The corresponding *O*-arylated salicylamide **3aa** was obtained in 42% yield (entry 1). When *N-tert*-butoxy-functionalized salicylamide was used as the starting material, the corresponding *O*-arylated salicylamide **3aa** was not obtained (entry 2). The starting materials were not recovered in these reactions, suggesting that the previously reported side reactions involving amide *N*- and/or *O*-arylation had occurred.[14f] The introduction of phthalimide group (NPhth) to amide moiety could reduce the reactivity for amide arylation.[14c] In fact, the reaction employing *N*-NPhth-functionalized salicylamide resulted in chemoselective *O*-arylation of hydroxy group generating **3aa** in 41% yield with recovery of the starting material (entry 3). Screening of various bases ($NaHCO_3$, K_2CO_3) and solvents ($(CH_2Cl)_2$, H_2O, $CHCl_3$) revealed that the use of K_2CO_3 in $CHCl_3$ resulted in 74% yield (entries 4–8). The influence of the counter anion of the phenyl(TMP)iodonium salt was investigated, with trifluoroacetate emerging as the optimal counter anion due to its lower nucleophilicity compared to acetate (entry 9). The tosylate counter anion exhibited similar reactivity and produced salicylamide diaryl ether **3aa** in 88% yield (entry 10).

Based on the optimized reaction conditions, we investigated the scope of the chemoselective arylation of *N*-NPhth salicylamide **1** with aryl(TMP)iodonium trifluoroacetate **2** (Fig. 4). Salicylamides bearing 4-(**1d**), 5-(**1b**), 6-methyl (**1c**), and 4-methoxy (**1e**) substituents were used, and the desired *O*-arylated salicylamides **3ba–3ea** were obtained in good yields. The *O*-arylation of halogen-functionalized salicylamides **1f–1i** also proceeded efficiently without dehalogenation, yielding *O*-arylated salicylamides **3fa–3ia** in 63–89% yield. Aryl(TMP) iodonium trifluoroacetate containing electron-donating (methyl (**2b**)), halogen (**2c–2e**), and electron-withdrawing (phenyl (**2f**), methyl ester (**2g**), ketone (**2h**), and cyano (**2i**)) groups were effectively converted into the desired products **3ab–3ai** in moderate to good yields. Cyano-functionalized aryl(TMP) iodonium trifluoroacetate **2i** decomposed more rapidly than it reacted with salicylamide at 70 °C; thus, the reaction yield was improved at 40 °C. *meta*- and *ortho*-functionalized

Table 1 Optimization of reaction conditions for *O*-arylation[a]



Entry	R	Base	Solvent	L	Yield[b] (%)
1	OMe	Na_2CO_3	$(CH_2Cl)_2/H_2O$ (1 : 1)	OAc	42
2	O^{t}Bu	Na_2CO_3	$(CH_2Cl)_2/H_2O$ (1 : 1)	OAc	0
3	NPhth	Na_2CO_3	$(CH_2Cl)_2/H_2O$ (1 : 1)	OAc	41
4	NPhth	$NaHCO_3$	$(CH_2Cl)_2/H_2O$ (1 : 1)	OAc	40
5	NPhth	K_2CO_3	$(CH_2Cl)_2/H_2O$ (1 : 1)	OAc	52
6	NPhth	K_2CO_3	$(CH_2Cl)_2$	OAc	70
7	NPhth	K_2CO_3	H_2O	OAc	Trace
8	NPhth	K_2CO_3	$CHCl_3$	OAc	74
9	NPhth	K_2CO_3	$CHCl_3$	$OCOCF_3$	95 (90)[c]
10	NPhth	K_2CO_3	$CHCl_3$	OTs	88

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (1.2 equiv.), and base (1.5 equiv.) in solvent (2.0 mL) at 70 °C for 24 h. [b] Yields were determined by ^{1}H NMR. [c] Isolated yield. TMP = 2,4,6-trimethoxyphenyl. NPhth = phthalimide.

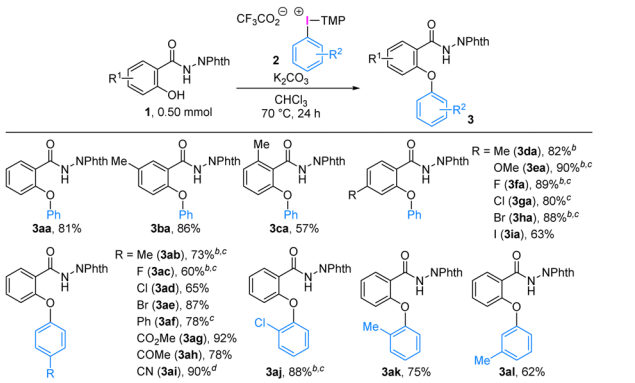


Fig. 4 Substrate scope of *O*-arylation with aryl(TMP)iodonium salts. [a] Reaction conditions: **1** (0.50 mmol), **2** (1.2 equiv.), and K_2CO_3 (1.5 equiv.) in $CHCl_3$ (5.0 mL) at 70 °C for 24 h. [b] For 36 h. [c] At 90 °C. [d] At 40 °C.

aryl(TMP)iodonium trifluoroacetates were also well-tolerated, yielding corresponding salicylamide diaryl ethers **3aj–3al** in 62–88% yields.

The *O*-arylated salicylamides obtained serve as valuable precursors for the intramolecular electrophilic aromatic amination, yielding dibenzoxazepinones (Fig. 5). Hypervalent iodine-mediated electrophilic aromatic amination is an attractive methodology for transition-metal-free C–N bond formation,[18–20] and we applied it to the synthesis of dibenzoxazepinone. Following the evaluation of various iodine catalysts and reaction conditions, the reaction was conducted using 2,2′-diiodo-1,1′-biphenyl (5 mol%), *m*-chloroperbenzoic acid (*m*CPBA, 1.1 equiv.), and trifluoroacetic acid (2.0 equiv.) in CH_2Cl_2–HFIP (1 : 1) at room temperature (Table S2, ESI†). This reaction proceeded efficiently, yielding dibenzoxazepinones with electron-donating (**4ba–4ea** and **4ab**), electron-withdrawing (**4ag–4ai**), and halogen atoms (**4fa–4ia**, **4ac–4ae**) in moderate to good yields. When *O*-(*para*-fluorinated) salicylamide **3ac** was employed, defluoro-spirocyclization occurred,[19b,20e] yielding dibenzoxazepinone **4ac** in low yield. Salycylamides bearing *ortho*-chlorophenyl (**3aj**) and *ortho*-tolyl (**3ak**) groups were also applicable, producing the desired dibenzoxazepinones **4aj** and **4ak**. The C–N coupling reaction of salicylamide having *meta*-tolyl group **3al** yielded the dibenzoxazepinones **4al** and **4al′** in 54% yield as a mixture of two regioisomers.

We subsequently investigated the one-pot synthesis of dibenzoxazepinones **4** from *N*-NPhth salicylamides **1** by combining two successive arylations; *O*-arylation with diaryliodonium salts and intramolecular *N*-cyclization with hypervalent iodine reagents generated under chemical or electrolytic conditions (Fig. 6). Arylation with diaryliodonium salts is typically accompanied by the coproduction of a stoichiometric amount of iodoarenes. To minimize chemical waste, iodoarenes have been utilized as aryl sources in successive transition-metal-catalyzed coupling reactions.[21] However, no examples exist of their use as oxidizing reagents in successive bond-forming

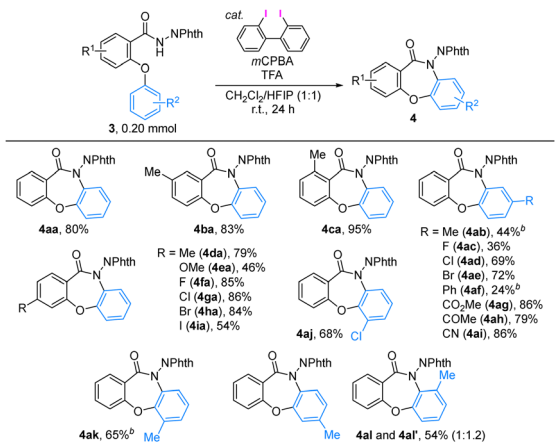


Fig. 5 Substrate scope of *N*-arylation with μ-oxo hypervalent iodine reagents. [a] Reaction conditions: **3** (0.20 mmol), iodine catalyst (5 mol%), *m*CPBA (1.1 equiv.), and TFA (2.0 equiv.) in CH_2Cl_2/HFIP (1 : 1, 2.0 mL) at room temperature for 24 h. [b] Iodine catalyst (10 mol%) and *m*CPBA (1.5 equiv.) were used.

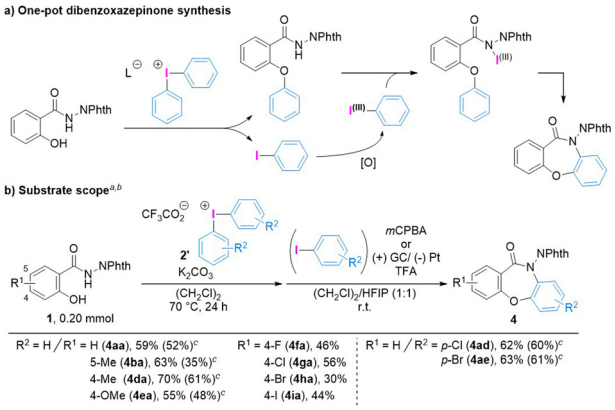


Fig. 6 One-pot dibenzoxazepinone synthesis through chemical and electrolytic conditions. [a] Reaction conditions (*O*-arylation): **1** (0.20 mmol), **2′** (1.2 equiv.), and K_2CO_3 (1.5 equiv.) in $(CH_2Cl)_2$ (2.0–2.5 mL) at 70 °C for 24 h. [b] Reaction conditions (chemical oxidation): *m*CPBA (1.5 equiv.) in $(CH_2Cl)_2$/HFIP (1 : 1, 4.0 mL) at room temperature for 24 h. [c] Reaction conditions (electro-oxidation): TFA (10 equiv.) in $(CH_2Cl)_2$/HFIP (1 : 1, 5.0 mL) at room temperature. Glassy carbon anode, platinum foil cathode, constant current electrolysis (CCE) at 10 mA for 4.5 F mol^{-1}.

steps. In this one-pot dibenzoxazepinone synthesis strategy, the first step involved a chemoselective *O*-arylation of *N*-NPhth salicylamide with diaryliodonium salt, followed by hypervalent iodine-mediated electrophilic aromatic amination, which occurred *via* the chemical- or electro-oxidation of the persistent iodoarene generated in the first step (Fig. 6a). For this purpose, *m*CPBA was employed as a chemical reoxidant for the second amination step, and dibenzoxazepinones **4** were obtained in 30–70% yields (Fig. 6b). Subsequently, the C–N coupling conditions were optimized using salicylamide diaryl ether **3da** under electrolytic conditions (Table S3, ESI†). In this reaction, potassium trifluoroacetate, generated by adding trifluoroacetic acid and potassium bicarbonate, serves as a suitable electrolyte. *N*-NPhth salicylamides **1a**, **1b**, **1d**, and **1e** and diaryliodonium salts containing *para*-chloro (**2d′**) and bromo (**2e′**) were tolerated, and the corresponding dibenzoxazepinones **4** were obtained in acceptable yields, without addition of external iodoarene. Control experiments were conducted under electrolytic conditions using diaryl ether **3da** (Table S4 and Fig. S1, ESI†). The presence of iodobenzene was crucial for this reaction; in its absence, complete decomposition of **3da** was observed. Compared to chemical oxidation, the reaction time was shorter under the electrolytic conditions, likely due to the specific formation of highly reactive μ-oxo PIFA[22] under electrolytic conditions. Indeed, μ-oxo PIFA and PIFA were specifically observed as major species by ^1H and ^{19}F NMR measurements under electrolytic conditions in the absence of diaryl ether **3da**.

In conclusion, we developed efficient synthetic methods for dibenzoxazepinones by combining two distinct types of successive hypervalent-mediated arylocyclization reactions. When aryl(TMP)iodonium salts were employed as arylation agents, *O*-arylated salicylamides were isolated, followed by electrophilic aromatic amination using μ-oxo hypervalent iodine catalyst. Furthermore, successive electrophilic aromatic aminations

could be conducted without adding an external iodoarene under chemical and electrolytic conditions, achieving a one-pot metal-free synthesis of dibenzoxazepinones from salicylamides.

T. D. and K. K. acknowledge support from JSPS KAKENHI grant number 19K05466 (T. D.) and 23K04827 (K. K.), JST CREST grant number JPMJCR20R1, and the Ritsumeikan Global Innovation Research Organization (R-GIRO) project. N. M. thanks JST the establishment of university fellowships towards the creation of science technology innovation grant number JPMJSP2101.

Data availability

The data underlying this study are available in the published article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (*a*) J. M. Klunder, K. D. Hargrave, M. West, E. Cullen, K. Pal, M. L. Behnke, S. R. Kapadia, D. W. McNeil, J. C. Wu, G. C. Chow and J. Adams, *J. Med. Chem.*, 1992, **35**, 1887; (*b*) Y. Liao, B. J. Venhuis, N. Rodenhuis, W. Timmerman, H. Wikström, E. Meier, G. D. Bartoszyk, H. Bottcher, C. A. Seyfried and S. Sundell, *J. Med. Chem.*, 1999, **42**, 2235; (*c*) R. A. Smits, H. D. Lim, B. Stegink, R. A. Bakker, I. J. P. de Esch and R. Leurs, *J. Med. Chem.*, 2006, **49**, 4512.

2 (*a*) K. Brewster, R. J. Clarke, J. M. Harrison, T. D. Inch and D. Utley, *J. Chem. Soc., Perkin Trans.*, 1976, **12**, 1286; (*b*) D. Tsvelikhovsky and S. L. Buchwald, *J. Am. Chem. Soc.*, 2011, **133**, 14228; (*c*) C. W. Cheung, M. L. Ploeger and X. Hu, *Nat. Commun.*, 2017, **8**, 14878; (*d*) S. Zou, Z. Zhang, C. Chen and C. Xi, *Asian J. Org. Chem.*, 2021, **10**, 355.

3 (*a*) X. Ouyang, N. Tamayo and A. S. Kiselyov, *Tetrahedron*, 1999, **55**, 2827; (*b*) A. V. Samet, K. A. Kislyi, V. N. Marshalkin and V. V. Semenov, *Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 549; (*c*) J. Shi, J. Wu, C. Cui and W.-M. Dai, *J. Org. Chem.*, 2016, **81**, 10392.

4 R. A. Bunce and J. E. Schammerhorn, *J. Heterocycl. Chem.*, 2006, **43**, 1031.

5 Y. Liu, C. Chu, A. Huang, C. Zhan, Y. Ma and C. Ma, *ACS Comb. Sci.*, 2011, **13**, 547.

6 (*a*) M. O. Kitching, T. E. Hurst and V. Snieckus, *Angew. Chem., Int. Ed.*, 2012, **51**, 2925; (*b*) Z. Zhang, Z. Dai, X. Ma, Y. Liu, X. Ma, W. Lia and C. Ma, *Org. Chem. Front.*, 2016, **3**, 799.

7 (*a*) C. Shen, H. Neumann and X.-F. Wu, *Green Chem.*, 2015, **17**, 2994; (*b*) Z. Feng, J.-A. Ma and C. W. Cheung, *Org. Chem. Front.*, 2022, **9**, 3869.

8 (*a*) P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123; (*b*) E. A. Merritt and B. Olofsson, *Angew. Chem., Int. Ed.*, 2009, **48**, 9052; (*c*) B. Olofsson, *Top. Curr. Chem.*, 2015, **373**, 135; (*d*) K. Aradi, B. L. Tóth, G. L. Tolnai and Z. Novák, *Synlett*, 2016, 1456; (*e*) K. Kikushima, E. E. Elboray, J. O. C. Jiménez-Halla, C. R. Solorio-Alvarado and T. Dohi, *Org. Biomol. Chem.*, 2022, **20**, 3231; (*f*) D. R. Stuart, *Diaryliodonium salts*, ACS In Focus, Washington, DC, 2024.

9 F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *J. Am. Chem. Soc.*, 1953, **75**, 2708.

10 (*a*) N. Jalalian, E. E. Ishikawa, L. F. Silva Jr. and B. Olofsson, *Org. Lett.*, 2011, **13**, 1552; (*b*) N. Jalalian, T. B. Petersen and B. Olofsson, *Chem. – Eur. J.*, 2012, **18**, 14140; (*c*) E. Lindstedt, R. Ghosh and B. Olofsson, *Org. Lett.*, 2013, **15**, 6070; (*d*) L. Chan, A. McNally, Q. Y. Toh, A. Mendoza and M. J. Gaunt, *Chem. Sci.*, 2015, **6**, 1277; (*e*) R. T. Gallagher, S. Basu and D. R. Stuart, *Adv. Synth. Catal.*, 2020, **362**, 320.

11 K. Kikushima, M. Miyamoto, K. Watanabe, D. Koseki, Y. Kita and T. Dohi, *Org. Lett.*, 2022, **24**, 1924.

12 (*a*) V. Carreras, A. H. Sandtorv and D. R. Stuart, *J. Org. Chem.*, 2017, **82**, 1279; (*b*) E. Lindstedt, M. Reitti and B. Olofsson, *J. Org. Chem.*, 2017, **82**, 11909; (*c*) T. L. Seidl, A. Moment, C. Orella, T. Vickery and D. R. Stuart, *Org. Synth.*, 2019, **96**, 137; (*d*) Y. Chen, Y. Gu, H. Meng, Q. Shao, Z. Xu, W. Bao, Y. Gu, X.-S. Xue and Y. Zhao, *Angew. Chem., Int. Ed.*, 2022, **61**, e202201240; (*e*) N. Miyamoto, D. Koseki, K. Sumida, E. E. Elboray, N. Takenaga, R. Kumar and T. Dohi, *Beilstein J. Org. Chem.*, 2024, **20**, 1020.

13 (*a*) J. Malmgren, S. Santoro, N. Jalalian, F. Himo and B. Olofsson, *Chem. – Eur. J.*, 2013, **19**, 10334; (*b*) T. L. Seidl, S. K. Sundalam, B. McCullough and D. R. Stuart, *J. Org. Chem.*, 2016, **81**, 1998; (*c*) A. H. Sandtorv and D. R. Stuart, *Angew. Chem., Int. Ed.*, 2016, **55**, 15812; (*d*) T. L. Seidl and D. R. Stuart, *J. Org. Chem.*, 2017, **82**, 11765; (*e*) D. R. Stuart, *Chem. – Eur. J.*, 2017, **23**, 15852; (*f*) S. Basu, A. H. Sandtorv and D. R. Stuart, *Beilstein J. Org. Chem.*, 2018, **14**, 1034.

14 (*a*) T. Dohi, D. Koseki, K. Sumida, K. Okada, S. Mizuno, A. Kato, K. Morimoto and Y. Kita, *Adv. Synth. Catal.*, 2017, **359**, 3503; (*b*) K. Kikushima, A. Morita, E. E. Elboray, T. Bae, N. Miyamoto, Y. Kita and T. Dohi, *Synthesis*, 2022, 5192; (*c*) E. E. Elboray, T. Bae, K. Kikushima, Y. Kita and T. Dohi, *Adv. Synth. Catal.*, 2023, **365**, 2703; (*d*) K. Kikushima, K. Komiyama, N. Umekawa, K. Yamada, Y. Kita and T. Dohi, *Org. Lett.*, 2024, **26**, 5347; (*e*) K. Kikushima, T. Tsuda, N. Miyamoto, Y. Kita and T. Dohi, *Chem. Commun.*, 2024, **60**, 10552; (*f*) E. E. Elboray, T. Bae, K. Kikushima, N. Takenaga, Y. Kita and T. Dohi, *J. Org. Chem.*, 2024, **89**, 17518.

15 (*a*) J. Jiao, K. Murakami and K. Itami, *ACS Catal.*, 2016, **6**, 610; (*b*) Y. Park, Y. Kim and S. Chang, *Chem. Rev.*, 2017, **117**, 9247; (*c*) V. C. M. Gasser, S. Makai and B. Morandi, *Chem. Commun.*, 2022, **58**, 9991.

16 (*a*) M. Rovira, M. Soler, I. Güell, M.-Z. Wang, L. Gómez and X. Ribas, *J. Org. Chem.*, 2016, **81**, 7315; (*b*) Y. Wang, H. Xie, K. Liu, J. Li and J.-B. Liu, *Catalysts*, 2022, **12**, 1278.

17 I. Güell and X. Ribas, *Eur. J. Org. Chem.*, 2014, 3188.

18 F. V. Singh, S. E. Shetgaonkar, M. Krishnan and T. Wirth, *Chem. Soc. Rev.*, 2022, **51**, 8102.

19 (*a*) T. Dohi, A. Maruyama, Y. Minamitsuji, N. Takenaga and Y. Kita, *Chem. Commun.*, 2007, 1224; (*b*) T. Dohi, N. Takenaga, K. Fukushima, T. Uchiyama, D. Kato, M. Shiro, H. Fujioka and Y. Kita, *Chem. Commun.*, 2010, **46**, 7697; (*c*) A. P. Antonchick, R. Samanta, K. Kulikov and J. Lategahn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8605; (*d*) X. Guo, D. Zhang-Negreriea and Y. Du, *RSC Adv.*, 2015, **5**, 94732; (*e*) N. Lucchetti, M. Scalone, S. Fantasia and K. Muñiz, *Adv. Synth. Catal.*, 2016, **358**, 2093; (*f*) D. Liang, W. Yu, N. Nguyen, J. R. Deschamps, G. H. Imler, Y. Li, A. D. MacKerell, Jr., C. Jiang and F. Xue, *J. Org. Chem.*, 2017, **82**, 3589; (*g*) T. Dohi, H. Sasa, M. Dochi, C. Yasui and Y. Kita, *Synthesis*, 2019, 1185; (*h*) H. Sasa, K. Mori, K. Kikushima, Y. Kita and T. Dohi, *Chem. Pharm. Bull.*, 2022, **70**, 106; (*i*) H. Sasa, S. Hamatani, M. Hirashima, N. Takenaga, T. Hanasaki and T. Dohi, *Chemistry*, 2023, **5**, 2155.

20 (*a*) K. Inoue, Y. Ishikawa and S. Nishiyama, *Org. Lett.*, 2010, **12**, 436; (*b*) T. Broese and R. Francke, *Org. Lett.*, 2016, **18**, 5896; (*c*) M. Elsherbini, B. Winterson, H. Alharbi, A. A. Folgueiras-Amador, C. Génot and T. Wirth, *Angew. Chem., Int. Ed.*, 2019, **58**, 9811; (*d*) B. L. Frey, M. T. Figgins, G. P. Van Trieste III, R. Carmieli and D. C. Powers, *J. Am. Chem. Soc.*, 2022, **144**, 13913; (*e*) J. C. Bieniek, B. Mashtakov, D. Schollmeyer and S. R. Waldvogel, *Chem. – Eur. J.*, 2024, **30**, e202303388.

21 (*a*) N. A. Bumagin, E. V. Luzikova, L. L. Sukhomlinova, T. P. Tolstaya and L. P. Beletskaya, *Russ. Chem. Bull.*, 1995, **44**, 385; (*b*) S. G. Modha and M. F. Greaney, *J. Am. Chem. Soc.*, 2015, **137**, 1416; (*c*) C. J. Teskey, S. M. A. Sohel, D. L. Bunting, S. G. Modha and M. F. Greaney, *Angew. Chem., Int. Ed.*, 2017, **56**, 5263.

22 (*a*) J. Gallos, A. Varvoglis and N. W. Alcock, *J. Chem. Soc., Perkin Trans. 1*, 1985, 757; (*b*) T. Dohi, T. Uchiyama, D. Yamashita, N. Washimi and Y. Kita, *Tetrahedron Lett.*, 2011, **52**, 2212; (*c*) T. Dohi, T. Nakae, N. Takenaga, T. Uchiyama, K. Fukushima, H. Fujioka and Y. Kita, *Synthesis*, 2012, 1183.