Syntheses of new chiral chimeric photo-organocatalysts†

Jiyaun Lyu,a Matteo Leone,a Aurélie Claraz,a Clémence Allain,b Luc Neuville,b and Géraldine Masson*a

A new family of chiral chimeric photo-organocatalysts derived from phosphoric acid were synthesized and their spectroscopic and electrochemical properties were investigated. Then, the ability of these photo-activable molecules to catalyse an asymmetric tandem electrophilic β-amination of enecarbamates was evaluated.

Introduction

Enantioselective photocatalysis1,2 has been recognized as a powerful method for the construction of useful enantiomerically enriched compounds. The past two decades have witnessed tremendous progress using mainly two approaches.3 The first one relies on the combination of two separated catalytic species, one acting as a photosensitizer, the second one bringing chiral information in a dual or cooperative way.1,4-6 The second approach employs bifunctional catalysts in which a single molecule contains both a photoactive group and a chiral unit. This strategy has allowed the development of chiral metallic complexes bearing either an ancillary organic binding domain or an ancillary organo photosensitized or purely bifunctional organocatalysts.7 In the last strategy, an early example documented by Bach et al.8 using chiral bifunctional catalysts A (Fig. 1) has paved the way for further developments of chiral chimeric photo-organocatalysts.1,9,10 For instance, Sibi and Sivaguru et al.11 proposed a chiral catalyst B which merges a thiourea unit and a photoactive binaphthyl moiety, for enantioselective (2 + 2) photocycloaddition. Thiourea was also chosen as organocatalytic part and connected to thioxanthone C to deliver a modestly effective chiral catalyst for photocyclization.12 Combining thioxanthone with chiral secondary amine furnished an effective bifunctional photocatalyst D for enantioselective alkylation of aldehydes.13 Given the diverse classes of organocatalysts, whether chiral or photosensitive, many novel merged structures can be expected. 1,1′-Bi-2-naphthol (BINOL)-derived chiral phosphoric acids occupy a central place in organocatalysis14 and have found application in dual catalysis in combination with redox photosensitizers.1,15 As such, building phosphoric acid centered photosensitizer could provide an avenue to diverse enantioselective photo promoted reactions.

Indeed, two independent reports have recently presented new chiral organophotocatalysts in which a BINOL-derived phosphoric acid was attached to thioxanthone dyes. Bach et al. showed that C2-symmetric catalyst E containing a phenyl linker between BINOL and thioxanthone unit was competent...
catalyst for enantioselective [2 + 2] cycloadditions. Nearly at the same time, our group found that chiral BINOL phosphoric acid F with one thioxanthone unit in the 3-position (Fig. 1) could promote a tandem three-component electrophilic amination of enecarbamates with dibenzyl azodicarboxylate and pyrazoles with high enantioselectivity.17

During this work we also considered other chimeric chiral photocatalysts, derived from a phosphoric acid scaffold and known active photosensitizers. Among them, ketones have a long history in photochemistry and, not only in pure organic synthesis, but also in environmental chemistry.19 In particular, aryl ketones, such as benzophenone, thioxanthone and anthraquinone23 have long been appreciated for their long-lived triplet states and ability to act as effective photosensitizers in a wide number of photochemical transformations. Herein, we report the synthesis, the photophysical properties as well as some photocatalytic capabilities of these new chiral BINOL phosphoric acid photocatalysts bearing different photoactivable aromatic ketones at the 3 or 3,3' positions.

### Results & discussion

The synthesis of targeted bifunctional molecules incorporating diphenyl ketone, anthraquinone, aryl ketone as well as thioxanthone was undertaken. The C2-symmetric (4-phenyl)[phenyl] methanone photocatalyst 1a was easily prepared in high yield through a three-step procedure. Performed under classical conditions, the Suzuki–Miyaura coupling of known 3,3'-substituted BINOL bis pinacol boronate ester 2 with 4-bromo benzophenone 3, furnished compound 4 in high yield (91%).22 HCl promoted MOM-hydrolysis, gave a crude bis-phenol...
derivative that was directly converted to phosphoric acid in an overall 70% yield for two steps. A related but modified sequence in which phenol deprotection would be performed prior to the arylation was adopted for the synthesis of C2-symmetric anthraquinone photocatalyst 1b. Double ortho-lithiation of protected BINOL 5 followed by trapping with cheap B(OMe)_3 and subsequent hydrolysis led to phenol-free bis boronic acid 6. Interestingly, while purification was difficult, engaging the crude extract in the subsequent cross coupling with 2-bromoanthraquinone 7 proved to be highly effective. Final phosphorylation delivered compound 1b in 71% over the entire sequence. In our preliminary report, we reported that the C1-symmetric thioxanthone catalyst 1a was superior to the corresponding C2-symmetric in terms of reactivity. Based on this observation, we became interested in the synthesis of C1-symmetric derivatives. Mono-substituted anthraquinone 1c was therefore synthesized following a similar route to its C2-symmetric counterpart. By reducing the amount of BuLi used in the initial ortho-lithiation step from 2.8 to 1.5 equivalent, a relatively selective monoborylation could be obtained. Subsequent hydrolysis, cross coupling and phosphorylation went uneventfully to deliver compound 1c. A newly designed C1-symmetric thioxanthone having a phenyl substituent at the 3-position 1d was also considered. Synthesis began from easily accessible 3-mono-phenyl-substituted BINOL derivative 10, which could be borylated. Controlled hydrolysis (HCl at 0 °C) at the end of this first step allowed to isolate MOM-protected bis boronic acid that then participated in the Suzuki–Miyaura coupling with 2-bromo-thioxanthone 11 to afford the C1-symmetric product 12 in 53% yield over two steps. Then, MOM deprotection and phosphorylation gave the desired product 1d in good yield. Since phenylmethanone bearing BINOL derived 13 was available following the procedure reported by Wang et al., we also prepared phosphoric acid 1e by simple phosphorylation for comparative purpose (Scheme 1).

With these diverse chiral chimeric organophotocatalysts 1 in hand, we next turned our attention to their photophysical properties by recording UV-vis and emission spectra in DCM as shown in Table 1 (for absorbance and fluorescence spectra, see in the ESIF). Photonsensitizers expected to be activated by visible light were evaluated first.

### Table 1 Spectroscopic data in DCM for chiral photocatalyst 1a, 1c–e and in DMSO for 1b (molar absorption coefficient ε, absorption maxima λ_m, fluorescence emission quantum yield Φ_f, determined using quinine sulphate as a reference and emission maxima λ_em)

| Entry | PCat | λ_m/nm (ε/L mol⁻¹ cm⁻¹) | λ_em/µm | Φ_f |
|-------|------|--------------------------|--------|-----|
| 1     | 1a   | 296 (4.3 × 10^6)         | <0.01  |     |
| 2     | 1b   | 267 (7.8 × 10^6)         | <0.01  |     |
| 3     | 1c   | 259 (3.1 × 10^6)         | 580    | 0.01|
| 4     | 1d   | 325 (1.4 × 10^6)         |         |     |
| 5     | 1e   | 262 (4.7 × 10^6)         | <0.01  |     |

Chiral phosphoric acid-thioxanthone photocatalyst 1d exhibits absorption maxima λ_m at 256 nm and 397 nm in DCM. The bis-substituted anthraquinone catalyst 1b and monoanthraquinone photocatalyst 1c showed an absorption λ_m at 267 and 259 nm, respectively. However, the monosubstituted photocatalyst 1e has an additional burst at 329 nm. It should be mentioned that absorption was still significant for thioxanthone 1d and both anthraquinones 1b, 1e up to 448 nm meaning that they could work in the visible light region. The absorbance λ_m values of catalysts bearing acyclic ketones 1a and 1e were at 262 and 296 nm, respectively. While 1a absorbed only below 380 nm, 1e could exhibited residual absorption up to 430 nm.

The fluorescence emission spectrum of 1d displayed a peak centered at 448 nm with a moderate fluorescence quantum yield. There are nearly no fluorescence of acyclic ketones 1a and 1e as well as for substituted bis-anthraquinone 1b. On the contrary, a slight emission intensity was observed for the monosubstituted anthraquinone catalyst 1e indicating much less quenching occurred in this structure.

The electrochemical activity of the chiral photocatalysts was determined by cyclic voltammetry analyses in DCM using ferrocene as internal reference (Table 2). The C1 symmetric thioxanthone catalyst 1d exhibits a reversible one-electron reduction around −1.70 V. The cyclic voltammogram of C2- and C1-symmetric anthraquinone-based catalyst 1b and 1c showed two reduction peaks which correspond to two single-electron reductions of each ketone on the anthraquinone dye. On the other hand, one reduction peak at −1.96 V was observed for the C2-symmetric benzophenone-based catalyst 1a. Differently, the C2-symmetric photocatalyst bearing ketone 1e exhibits two successive one-electron reduction processes with the redox peaks at −1.72 V and −2.04 V, respectively, and only one oxidation process was observed. This result indicates that 1e can be partially reversibly reduced. Finally, the estimation of the E_{red} from absorption spectra of 1 allowed us to evaluate the excited state oxidation potential of 1e. The values decreased in the order 1d > 1b > 1c > 1e > 1a.

In order to evaluate the ability of the novel objects to act as chiral chimeric photocatalysts, the asymmetric electrophilic amination of α-unsubstituted enecarbamates was chosen as a benchmark reaction. The process involves the β-addition of an enecarbamate 14 to azodicarboxylate 15 in presence of EtSH followed by the photoinduced coupling of an azole with the in situ generated α-carbamoylsulfide 17. Partial racemization of the imine intermediate 18 was observed when the reaction with pyrazole was performed with two distinct catalysts (a chiral phosphoric acid and a distinct photocatalyst).

However, as demonstrated in our recent publication, a bifunctional chiral chimeric photocatalyst, such as F is able to (1) promote the generation of imine from 17 by photooxidation of sulfur atom involving the participation of singlet oxygen but also to (2) bring nucleophile and electrophile in close proximity via a pseudo intramolecular hydrogen-bonding transition state 18, and thereby favors a rapid addition of pyrazole to imine (Scheme 2). This approach overcomes the partial racemization and leads to product 16 with high enantioselectivity. As such
Electrochemical data for chiral photocatalysts 1c–g in DCM. Cyclic voltammetry of photocatalysts (V vs. Ag+/Ag), in dichloromethane (with 0.1 M Bu4NPF6 as electrolyte) on glassy carbon electrode. Concentrations are about 2 \times 10^{-3} \text{ mmol mL}^{-1}.

| PCat | \(E_{1/2}\) (1/1\(^-\), V vs. Ag+/Ag) | \(E_{1/2}\) (1\(^-\)/1\(^2\), V vs. Ag+/Ag) | \(E_{1/2}\) (1\(^+\)/1\(^-\), V vs. Ag+/Ag) | \(E_{1/2}\) (1\(^+\)/1\(^2\), V vs. Ag+/Ag) |
|------|-----------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1a   | -1.96                             | -1.53                           | 1.48                            | 1.10                            |
| 1b   | -1.10                             | -1.53                           | 1.70                            | 1.32                            |
| 1c   | -1.09                             | -1.53                           | 1.71                            | 1.27                            |
| 1d   | -1.70                             | -2.04                           | 1.17                            |                                 |
| 1e   | -1.72<sup>2</sup>                 | -2.04                           | -                              | 1.22                            |

<sup>a</sup> Calculated using the relationship \(E^* = E_{0.0} - E_{0.0}^*\). Values were estimated spectrophotically from the position of the long wavelength tail of the absorption spectrum (Table S1 in the ESI).<sup>b</sup> No oxidation peak.

In order to verify the generality of the result obtained with catalyst 1c, several 1-heteroaryl-1,2-diamines 16 were subsequently synthesized by changing the pyrazole partners (Scheme 3).

**Scheme 2** Enantioselective tandem three-component electrophilic amination of enecarbamates for bifunctional catalyst evaluation.

**Table 3** Evaluation of organophoto-catalytic activity<sup>a</sup>

| Entry | Pcat 1<sup>a</sup> | \(\lambda\) (nm) | Yield<sup>b</sup> (%) | dr<sup>c</sup> | ee<sup>d</sup> (%)<sup>e</sup> |
|-------|-------------------|-----------------|----------------------|----------|-----------------|
| 1<sup>a</sup> | 1a                | 365             | 60                   | 1 : 2    | (−) 92/93<sup>e</sup> |
| 2<sup>a</sup> | 1b                | 405             | —                    | —        | —               |
| 3<sup>a</sup> | 1c                | 405             | 31                   | 1 : 2.5  | (−) 37/43       |
| 4<sup>a</sup> | 1d                | 405             | 72                   | 1 : 1.5  | (−) 97/99<sup>e</sup> |
| 5<sup>a</sup> | 1e                | 405             | 63                   | 1 : 1.3  | 0/0             |

<sup>a</sup> Reaction conditions: 14a (0.1 mmol), 15a (0.15 mmol) and EtSH (0.25 mmol) and 1 (0.01 mmol) in 1 mL of CH2Cl2, at −40°C for 20 hours; then 1H-pyrazole (0.3 mmol), LED, rt under O2 atmosphere for 16 h. <sup>b</sup> Wavelength of irradiation. <sup>c</sup> Isolated yield after column chromatography. <sup>d</sup> dr was determined by \(^1\)H-NMR analysis and antidiastereoselectivity assumed by analogy with our previous work. <sup>e</sup> Enantiomeric excess was determined by HPLC analysis on chiral stationary phase. <sup>f</sup> (−) refers to absolute S configuration, (−) refers to R configuration, assigned based on our previous work (ref. 17).

**Scheme 3** Enantioselective tandem three-component electrophilic amination of enecarbamate 14a and dibenzyl azodicarboxylate 15a with various azoles.
As such, compound 16a–e were all obtained with good yields and excellent enantioselectivities. Diastereoselectivity was modest for compound 16c (1 : 1.3), significant for compounds 16a, 16b and 16e (close to 1 : 3) and quite important for compound 16d (1 : 8). Except for the latter one, diastereoselectivity follows the same trend as the one obtained in our previous work with catalyst F, but with slight improvement. Overall, this implies that tuning the nature of the substituent at the 3′ position of C1-symmetric thioxanthone catalyst (1d vs. F), also not decisive, offers opportunities for further design.

Conclusions

In summary, we have developed an efficient reaction sequence providing a short and efficient syntheses of new chimeric photoredox organocatalysts with C1 and C2 symmetry. Photophysical properties were recorded for each new object. Contrasting photocatalytic activities have been established in asymmetric electrophilic amination of α-unsubstituted enecarbamates providing hints for further studies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge CNRS, ICSN for financial support. J. L. thanks the China Scholarship Council for the doctoral fellowship. M. L. received funding from the European Union H2020 research and innovation program under the Marie S. Curie Grant Agreement No. 956324 (MSCA ITN: Photoreact).

Notes and references

1 For selected recent review on recent asymmetric visible-light photocatalysis, see: (a) J. Groškof, T. Kratz, T. Rigotti and T. Bach, Chem. Rev., 2021, DOI: 10.1021/acs.chemrev.1c00272; (b) T. Rigotti and J. Aleman, Chem. Commun., 2020, 56, 11169; (c) R. Takagi and C. Tabuchia, Org. Biomol. Chem., 2020, 18, 9261; (d) D. Saha, Chem.–Asian J., 2020, 15, 2129; (e) Y. L. Yin, X. W. Zhao, B. K. Qiao and Z. Y. Jiang, Org. Chem. Front., 2020, 7, 1283; (f) Q. Q. Zhou, Y. Q. Zou, L.-Q. Lu and W.-J. Xiao, Angew. Chem., Int. Ed., 2019, 58, 1586; (g) C. J. Seel and T. Gulder, ChemBioChem, 2019, 20, 1871; (h) C. Jiang, W. Chen, W. H. Zheng and H. F. Lu, Org. Biomol. Chem., 2019, 17, 8673; (i) S. C. Coote and T. Bach, Visible Light Photocatalysis in Organic Chemistry, John Wiley & Sons, 2018, p. 335; (j) A. F. Garrido-Castro, M. C. Maestro and J. Aleman, Tetrahedron Lett., 2018, 59, 1286; (k) M. Silvi and P. Melchiorre, Nature, 2018, 554, 41; (l) C. Wang and Z. Lu, Org. Chem. Front., 2015, 2, 179; (m) E. Meggers, Chem. Commun., 2015, 51, 3290; (n) R. Brimioule, D. Lenhart, M. M. Maturi and T. Bach, Angew. Chem., Int. Ed., 2015, 54, 3872; (o) C. Wang and Z. Lu, Org. Chem. Front., 2015, 2, 179.

2 For selected recent review on photocatalysis: (a) J. D. Bell and J. A. Murphy, Chem. Soc. Rev., 2021, 50, 9540; (b) D. Petzold, M. Giedyk, A. Chatterjee and B. König, Eur. J. Org. Chem., 2020, 1486; (c) F. Strieth-Kalthoff, M. J. James, M. Teders, L. Pitzer and F. Glorius, Chem. Soc. Rev., 2018, 47, 7190; (d) L. Marzo, S. K. Pagire, O. Reiser and B. König, Angew. Chem., Int. Ed., 2018, 57, 10034; (e) D. Staveness, I. Bosque and C. R. J. Stephenson, Acc. Chem. Res., 2016, 49, 2259; (f) K. Nakajima, Y. Miyake and Y. Nishibayashi, Acc. Chem. Res., 2016, 49, 1946; (g) M. H. Shaw, J. Twilton and D. W. C. MacMillan, J. Org. Chem., 2016, 81, 6898; (h) R. A. Angnes, Z. Li, C. R. D. Correia and G. B. Hammond, Org. Biomol. Chem., 2015, 13, 9152; (i) T. P. Yoon, ACS Catal., 2013, 3, 895; (j) C. K. Prier, D. A. Rankie and D. W. C. MacMillan, Chem. Rev., 2013, 113, 5322; (k) J. Xuan and W.-J. Xiao, Angew. Chem., Int. Ed., 2012, 51, 6828.

3 A third strategy avoids the use of photocatalyst, see: (a) G. E. M. Crisenza, D. Mazzarella and P. Melchiorre, J. Am. Chem. Soc., 2020, 142, 5461; selected examples ; (b) Z. Y. Cao, T. Ghosh and P. Melchiorre, Nat. Commun., 2018, 9, 3274; (c) A. Bahamonde and P. Melchiorre, J. Am. Chem. Soc., 2016, 138, 8019; (d) E. Arceo, I. D. Jurbur, A. Alvarez-Fernández and P. Melchiorre, Nat. Chem., 2013, 5, 750.

4 The first example of merging photoredox catalysis and asymmetric organocatalysis: (a) D. A. Nicewicz and D. W. C. MacMillan, Science, 2008, 322, 77. See also: (b) D. A. Nagib, M. E. Scott and D. W. C. MacMillan, J. Am. Chem. Soc., 2009, 131, 10875; (c) J. A. Terrett, M. D. Clift and D. W. C. MacMillan, J. Am. Chem. Soc., 2014, 136, 6858; (d) E. R. Welin, A. A. Warkentin, J. C. Conrad and D. W. C. MacMillan, Angew. Chem., Int. Ed., 2015, 54, 9668.

5 Selected recent reviews: (a) K. L. Skubi, T. R. Blum and T. P. Yoon, Chem. Rev., 2016, 116, 10035; (b) M. N. Hopkinson, B. Sahoo, J.-L. Li and F. Glorius, Chem.–Eur. J., 2014, 20, 3874.

6 Selected recent examples: (a) C. Che, Y. N. Li, X. Cheng, Y. N. Lu and C. J. Wang, Angew. Chem., Int. Ed., 2021, 60, 4698; (b) Z. Y. Dai, Z. S. Nong and P. S. Wang, ACS Catal., 2020, 10, 4786; (c) Y. L. Yin, Y. Q. Li, T. P. Gonçalves, Q. Q. Zhan, G. G. Wang, X. W. Zhao, B. K. Qiao, K. W. Huang and Z. Y. Jiang, J. Am. Chem. Soc., 2020, 142, 19451; (d) A. Gualandi, M. Marchini, L. Mengozzi, H. T. Kidanu, A. Franc, P. Ceroni and P. G. Cozzi, Eur. J. Org. Chem., 2020, 2014, 1846; (e) C. B. Roos, J. Demaerel, D. E. Graff and R. R. Knowles, J. Am. Chem. Soc., 2020, 142, 5974; (f) Y. J. Li, M. Lei and L. Gong, Nat. Catal., 2019, 2, 1016; (g) Y. L. Kuang, K. Wang, X. C. Shi, X. Q. Huang, E. Meggers and J. Wu, Angew. Chem., Int. Ed., 2019, 58, 16859; (h) K. Zhang, L. Q. Lu, Y. Jia, Y. Wang, F. D. Lu, F. F. Pan and W. J. Xiao, Angew. Chem., Int. Ed., 2019, 58, 13375; (i) G. K. Zeng, Y. Q. Li, B. K. Qiao, X. W. Zhao and Z. Y. Jiang, Chem. Commun., 2019, 55, 11362; (j) Y. Z. Cheng, Q. R. Zhao, X. Zhang and S. L. You, Angew. Chem., Int. Ed., 2019, 58, 18069; (k) N. Y. Shin, J. M. Ryss, X. Zhang, S. J. Miller and R. R. Knowles, Science, 2019, 366, 364; (l) B. K. Qiao, C. Y. Li, X. W. Zhao, Y. L. Yin and
8 First example of catalytic enantioselective chemistry merging hydrogen bonding organocatalysis with organic UV-light photocatalysis, see: (a) A. Bauer, F. Westkämper, S. Grimme and T. Bach, Nature, 2005, 436, 1139; visible light induced enantioselective cyclodadditions; (b) A. Tröster, R. Alonso, A. Bauer and T. Bach, J. Am. Chem. Soc., 2016, 138, 7808; (c) H. Guo, E. Herdweck and T. Bach, Angew. Chem., Int. Ed., 2010, 49, 7782; (d) R. Brimioulle, H. Guo and T. Bach, Chem.-Eur. J., 2012, 18, 7752; (e) A. Hözl-Hobmeier, A. Bauer, A. V. Silva, S. M. Huber, C. Bannwarth and T. Bach, Nature, 2018, 564, 240; (f) R. Alonso and T. Bach, Angew. Chem., Int. Ed., 2014, 53, 4368.

9 Selected examples: (a) Y. Kimura, D. Uraguchi and T. Ooi, Org. Biomol. Chem., 2021, 19, 1744; (b) D. Uraguchi, Y. Kimura, F. Ueoka and T. Ooi, J. Am. Chem. Soc., 2020, 142(46), 19462; (c) T. Rigotti, A. Casado-Sánchez, S. Cabrera, R. Pérez-Ruiz, M. Liras, V. A. de la Peña O’Shea and J. Alemán, ACS Catal., 2018, 8, 5928; (d) Z. Yang, H. Li, S. Li, M. T. Zhang and S. Luo, Org. Chem. Front., 2017, 4, 1037; (e) P. D. Morse, T. M. Nguyen, C. L. Cruz and D. A. Nicewicz, Tetrahedron, 2018, 74, 3266.

10 Selected examples of organometallic photocatalysts: (a) Y. J. Li, K. X. Zhou, Z. R. Wen, S. Cao, X. Shen, M. Lei and L. Gong, J. Am. Chem. Soc., 2018, 140, 15850; (b) L. Zhang and E. Meggers, Acc. Chem. Res., 2017, 50, 320; (c) Q. M. Kainz, C. D. Matier, A. Bartoszewicz, S. L. Zultanski, J. C. Peters and G. C. Fu, Science, 2016, 351, 681; (d) H. Huo, X. Shen, C. Wang, L. Zhang, P. Röse, L. A. Chen, K. Harms, M. Marsch, G. Hilt and E. Meggers, Nature, 2014, 515, 100.

11 N. Vallavoujo, S. Selvakumar, S. Jockusch, M. P. Sibi and J. Sivaguru, Angew. Chem., Int. Ed., 2014, 53, 5604.

12 F. Mayr, L.-M. Mohr, E. Rodriguez and T. Bach, Synthesis, 2017, 49, 5238.

13 T. Rigotti, A. Casado-Sánchez, S. Cabrera, R. Pérez-Ruiz, M. Liras, V. A. de la Peña O’Shea and J. Alemán, ACS Catal., 2018, 8, 5928.

14 Selected recent reviews on chiral phosphoric acid catalysis: (a) Y.-D. Shao and D.-J. Cheng, ChemCatChem, 2021, 13, 1271; (b) J. Merad, C. Lalli, G. Bernadat, J. Maury and G. Masson, Chem. Eur. J., 2018, 24, 3925; (c) D. Parmar, E. Sugino, S. Raja and M. Rueping, Chem. Rev., 2017, 117, 10608; Chem. Rev., 2014, 114, 9047; (d) T. Akiyama and K. Mori, Chem. Rev., 2015, 115, 9277; (e) S. Schenker, A. Zamfir, M. Freund and S. B. Tsogoeva, Eur. J. Org. Chem., 2011, 2209; (f) M. Rueping, A. Kuenkel and I. Atodiresei, Chem. Soc. Rev., 2011, 40, 4539; (g) D. Kampen, C. M. Reisinger and B. List, Top. Curr. Chem., 2010, 291, 395.

15 S. Li, S.-H. Xiang and B. Tan, Chin. J. Chem., 2020, 38, 213.

16 (a) F. Pecho, Y. -Q. Zou, J. Grammüller, T. Mori, S. M. Huber, A. Bauer, R. M. Gschwind and T. Bach, Chem.-Eur. J., 2020, 26, 5190; (b) F. Pecho, Y. Semperè, J. Grammüller, F. M. Hörmann, R. M. Gschwind and T. Bach, J. Am. Chem. Soc., 2021, 143, 9350.

17 J. Lyu, A. Claraz, M. R. Vitale, C. Allain and G. Masson, J. Org. Chem., 2020, 85, 12843.

18 (a) I. K. Sideri, E. Voutyrtsita and C. G. Kokotos, Org. Biomol. Chem., 2018, 16, 4596; (b) N. A. Romero and D. A. Nicewicz, Chem. Rev., 2016, 116, 10075; (c) D. Ravelli, M. Fagnoni and A. Albini, Chem. Soc. Rev., 2013, 42, 97.

19 (a) C. Chatgilialoglu, D. Crich, M. Komatsu and I. Ryu, Chem. Rev., 1999, 99, 1991; (b) C. B. Tripathi, T. Ohtani, M. T. Corbett and T. Ooi, Chem. Sci., 1986, 8, 5622; (c) J. Coyle and H. Carless, Chem. Soc. Rev., 1972, 1, 465; for selected example involving environmental chemistry, see; (d) R. Genayel, C. Emmelin, S. Perrier, S. Tomaz, V. J. Baboomian, D. A. Fishman, S. A. Nizkorodov, S. Dumasas and C. George, Environ. Sci.: Atmos., 2021, 1, 31; (e) Z. Liu, P. Xie and J. Ma, Environ. Sci.: Nano, 2016, 3, 707.

20 J. Zhao, W. Wu, J. Sun and S. Guo, Chem. Soc. Rev., 2013, 42, 5323.

21 J. Cervantes-González, D. A. Vosborg, S. E. Mora-Rodriguez, M. A. Vázquez, L. G. Zepeda, C. Villegas Gómez and S. Lagunas-Rivera, ChemCatChem, 2020, 12, 3811.

22 (a) Y. Yue, M. Turlington, X.-Q. Yu and L. Pu, J. Org. Chem., 2009, 74, 8681; (b) Y. He, Z. Bian, C. Kang and L. Gao, Chem. Commun., 2010, 46, 5695.

23 J. M. Jiao, G. Wei, F. Li, X. R. Mao, Y. X. Cheng and C. J. Zhu, RSC Adv., 2014, 4, 5887.

24 Free phenol is long known to be compatible in Suzuki-Miyaura-type coupling, for one example: G. Pousse, A. Devineau, V. Dalla, L. Humphreys, M.-C. Lasne, J. Rouden and J. Blanchet, Tetrahedron, 2009, 65, 10617.

25 T. Harada and K. Kanda, Org. Lett., 2006, 5, 3817.

26 K. X. Xu, Z. Qiu, J. J. Zhao, J. Zhao and C. J. Wang, Tetrahedron: Asymmetry, 2009, 20, 1690.

27 For selected reviews on utilisation of enamides, see:(a) F. Beltran and L. Miesch, Synthesis, 2020, 52, 2497; (b) T. Zhu, S. Xie, P. Rojsitthisak and J. Wu, Org. Biomol. Chem., 2020, 18, 1504; (c) N. Gigant, L. Chaussset-Boissarie and I. Gillaizeau, Chem.-Eur. J., 2014, 20, 7548–7564; (d) K. Gopalaiyah and H. B. Kagan, Chem. Rev., 2011, 111, 4599; (e) R. Matsubara and S. Kobayashi, Acc. Chem. Res., 2008, 41, 292.

28 (a) A. Dumoulin, G. Bernadat and G. Masson, J. Org. Chem., 2017, 82, 1775; (b) A. Dumoulin, C. Lalli, P. Retailleau and G. Masson, Chem. Commun., 2015, 51, 5383; (c) C. Lalli, A. Dumoulin, C. Lebée, F. Drouet, V. Guérineau, K. Gopalaiah and H. B. Kagan, Chem. Rev., 2011, 115, 9277; (e) S. Schenker, A. Zamfir, M. Freund and S. B. Tsogoeva, Eur. J. Org. Chem., 2011, 2209; (f) M. Rueping, A. Kuenkel and I. Atodiresei, Chem. Soc. Rev., 2011, 40, 4539; (g) D. Kampen, C. M. Reisinger and B. List, Top. Curr. Chem., 2010, 291, 395.
D. Touboul, V. Gandon, J. Zhu and G. Masson, Chem.–Eur. J., 2014, 21, 1704.

29 (a) G. Levitre, C. Audubert, A. Dumoulin, N. Goual, P. Retailleau, X. Moreau and G. Masson, ChemCatChem, 2019, 11, 5723; (b) T. Le, T. Courant, J. Merad, C. Allain, P. Audebert and G. Masson, J. Org. Chem., 2019, 84, 16139; (c) M. Lanzi, J. Merad, D. Boyarskaya, G. Maestri, C. Allain and G. Masson, Org. Lett., 2018, 20, 5247; (d) L. Jarrige, G. Levitre and G. Masson, J. Org. Chem., 2016, 81, 7230; (e) C. Lebée, M. Languet, C. Allain and G. Masson, Org. Lett., 2016, 18, 1478.