



HAL
open science

Syntheses of new chiral chimeric photo-organocatalysts

Jiyaun Lyu, Matteo Leone, Aurélie Claraz, Clémence Allain, Luc Neuville,
Géraldine Masson

► **To cite this version:**

Jiyaun Lyu, Matteo Leone, Aurélie Claraz, Clémence Allain, Luc Neuville, et al.. Syntheses of new chiral chimeric photo-organocatalysts. RSC Advances, 2021, 11 (58), pp.36663 - 36669. 10.1039/d1ra06885g . hal-03799120v1

HAL Id: hal-03799120

<https://hal.science/hal-03799120v1>

Submitted on 12 Apr 2023 (v1), last revised 5 Oct 2022 (v2)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

COMMUNICATION

Syntheses of New Chiral Chimeric Photo-Organocatalysts

Jiyaun Lyu,^a Matteo Leone,^a Aurélie Claraz,^a Clémence Allain,^b Luc Neuville,^a Géraldine Masson*^aReceived 00th January
20xx,
Accepted 00th January
20xx

DOI: 10.1039/x0xx00000x

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 photocatalysis^{1,2} has been recognized as powerful methods 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 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, early example documented by Bach's *et al.*⁸ using chiral bifunctional organocatalysts **A** (Figure 1) have 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.

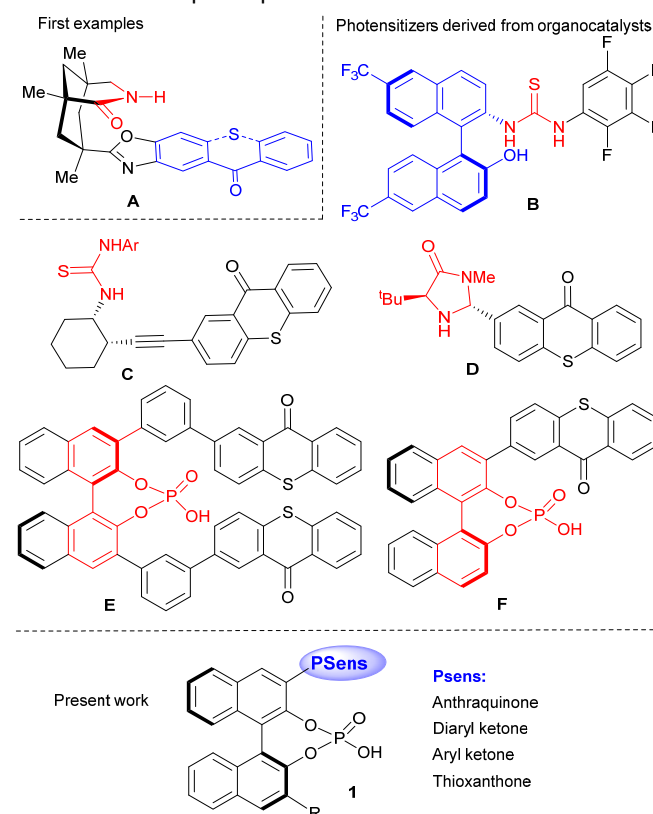


Figure 1 Chiral chimeric photo-organocatalysts.

^a Institut de Chimie des Substances Naturelles CNRS, Univ. Paris-Saclay, 1 Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France. E-mail: Geraldine.masson@cnrs.fr

^b Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, 91190, Gif-sur-Yvette, France.

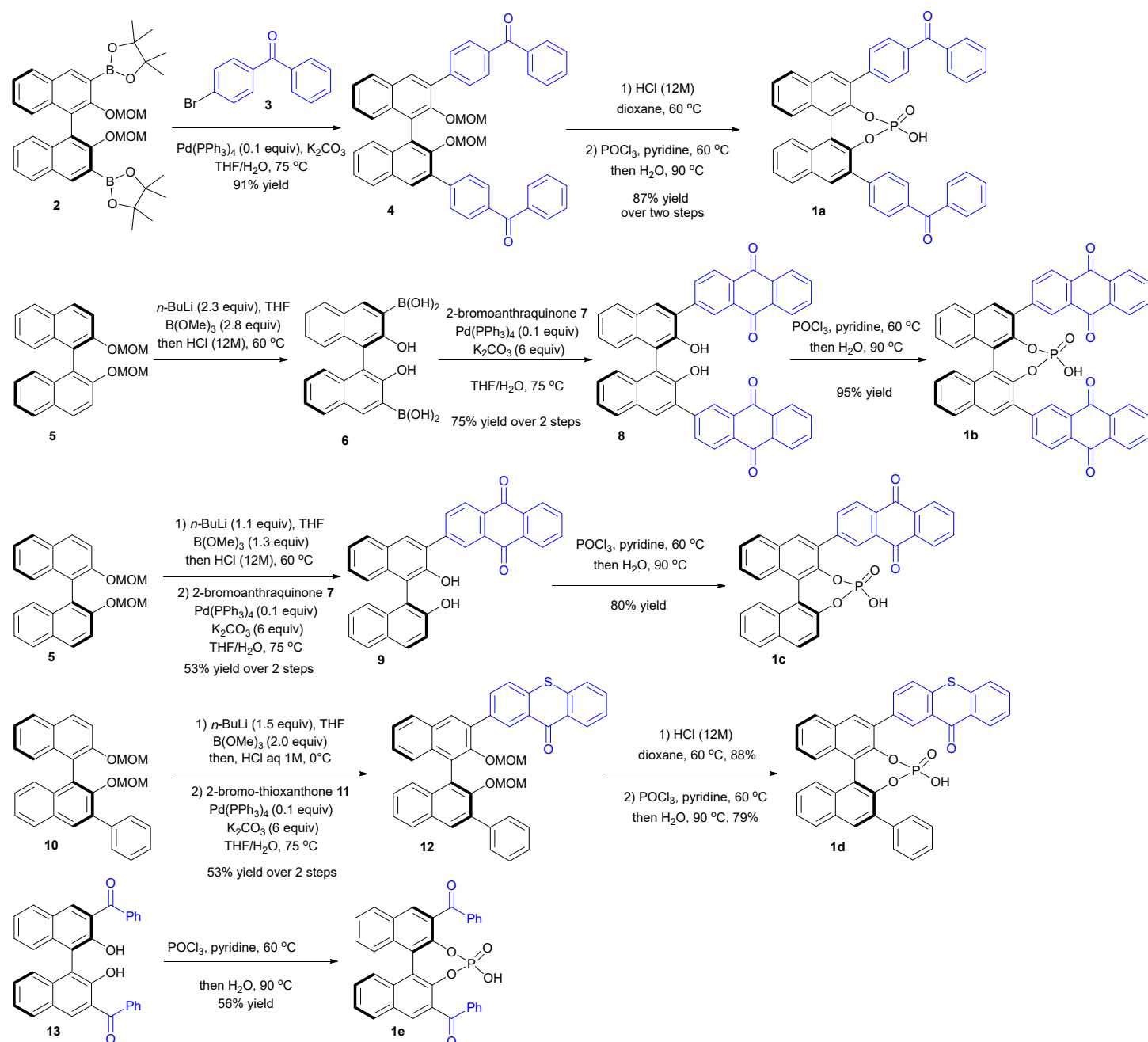
† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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.¹⁶ Nearly at the same time, our group found that chiral BINOL phosphoric acid **F** with one thioxanthone unit in the 3-position (Figure 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.¹⁸ 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,²⁰ thioxanthone^{18a} and anthraquinone²¹ have longly 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.

**Scheme 1** Syntheses of chiral phosphoric acid photocatalysts**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 catalyst **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-bromobenzophenone **3**, furnished compound **4** in high yields (91%). 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 catalyst **1b**. Double *ortho*-lithiation of protected BINOL **5** followed by trapping with cheap $\text{B}(\text{OMe})_3$ and subsequent hydrolysis lead to phenol-free bis boronic acid **6**.²³ 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.²⁴ In our preliminary report, we reported that the C₁-symmetric thioxanthone catalyst **1a** was superior to the corresponding C₂-symmetric in terms of reactivity.¹⁷ 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**,²⁵ 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.*,²⁶ we also prepared phosphoric acid **1e** by simple phosphorylation for comparative purpose.

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 Supporting Information). Photosensitizers expected to be activated by visible light were evaluated first.

Chiral phosphoric acid-thioxanthone photocatalyst **1d** exhibits absorption maxima λ_{\max} at 256 nm and 397 nm in DCM. The bis-substituted anthraquinone catalyst **1b** and mono-anthraquinone photocatalyst **1c** showed an absorption λ_{\max} at 267 and 259 nm, respectively. However, the monosubstituted photocatalyst **1c** has an additional burst at 329 nm. It should be mentioned that absorption was still significant for thioxanthone **1d** and both anthraquinones **1b**, **1c** up to 448 nm meaning that they could work in the visible light region. The absorbance λ_{\max} 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 exhibit 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 mono-substituted anthraquinone catalyst **1c** indicating much less quenching occurred in this structure.

entry	PCat	λ_{abs} nm ($\epsilon / \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)	λ_{em} nm	ϕ_{f}
1	1a	296 (4.3x10 ⁴)		<0.01
2	1b	267 (7.8x10 ⁴) 335 (sc)		<0.01
3	1c	259 (5.1x10 ⁴) 325 (1.4x10 ⁴)	580	0.01
4	1d	256 (5.8x10 ⁴) 397 (3.2x10 ⁴)	448	0.054

5	1e	262 (4.7x10 ⁴)	<0.01
---	-----------	----------------------------	-------

Table 1: Spectroscopic data in DCM for chiral photocatalyst **1a**, **1c-e** and in DMSO for **1b** (molar absorption coefficient ϵ , absorption maxima λ_{abs} , fluorescence emission quantum yield ϕ_{f} determined using quinine sulphate as a reference and emission maxima λ_{em}).

PCat	$E_{1/2}(\mathbf{1}/\mathbf{1}^{\bullet-})$ V vs Ag^+/Ag	$E_{1/2}(\mathbf{1}^{\bullet-}/\mathbf{1}^{2-})$ V vs Ag^+/Ag	$E_{1/2}(\mathbf{1}^*/\mathbf{1}^{\bullet-})$ V vs Ag^+/Ag ^a	$E_{1/2}(\mathbf{1}^{\bullet-}/\mathbf{1}^{2-})$ V vs Ag^+/Ag ^a
1a	-1.96		+1.10	
1b	-1.10	-1.48	+1.70	+1.32
1c	-1.09	-1.53	+1.71	+1.27
1d	-1.70		+1.17	
1e	-1.72 ^b	-2.04		+1.22

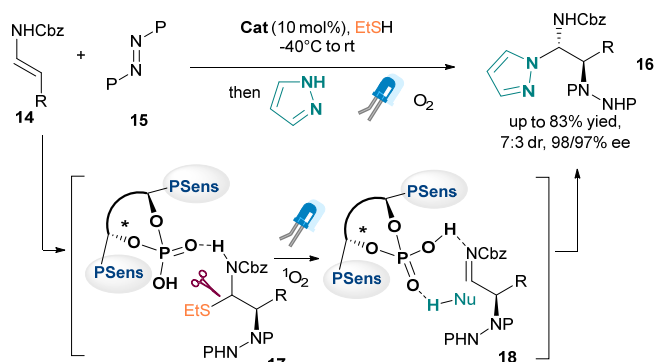
Table 2: Electrochemical data for chiral photocatalyst **1c-g** in DCM. Cyclic voltammetry of photocatalysts (V vs Ag^+/Ag), in dichloromethane (with 0.1 M Bu_4NPF_6 as electrolyte) on glassy carbon electrode. Concentrations are about 2.10⁻³ mmol/mL. ^a Calculated using the relationship $E^\circ(\text{Pcat } \mathbf{1}^*/\mathbf{1}^{\bullet-}) = E_{1/2}(\text{Pcat } \mathbf{1}^*/\mathbf{1}^{\bullet-}) + E_{0,0}(\text{Pcat } \mathbf{1}^*/\mathbf{1}^{\bullet-})$ and $E_{0,0}$ values were estimated spectroscopically from the position of the long wavelength tail of the absorption spectrum (Table S1 in the Supporting Information). ^b No oxidation peak.

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 -1.96V 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 -1.72V and -2.04V, respectively, and only one oxidation process was observed. This result indicates that **1e** can be partially reversibly reduced. Finally, the estimation of the $E_{0,0}$ from absorption spectra of **1** allowed us to evaluate the excited state oxidation potential of **1***. The values decreased in the order **1c** > **1b** > **1d** > **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.²⁷ The process involves the β -addition of an enecarbamate **14** to azodicarboxylate **15** in presence of EtSH²⁸ followed by the photoinduced coupling of an azole with the *in situ* generated α -carbamoysulfide **17**.²⁹ 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 photocatalysts).

However, as demonstrated in our recent publication,¹⁷ a bifunctional chiral chimeric photocatalyst, such as **1F** 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 this reaction constitute a perfect benchmark reaction to evaluate chiral chimeric photocatalysts.



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

Therefore, we examined the reaction of (*E*)-benzylprop-1-enylcarbamate (**14a**) with dibenzyl azodicarboxylate (**15a**), one equivalent of EtSH in the presence of 10 mol% of the newly synthesized catalysts (Table 3). With **1d** under a 405 nm irradiation, we were delighted to find that desired 1,2-diamide **16a** was produced in good yield in a 1:1.5 diastereomeric ratio and with high enantioselectivity. Compared to our previous work performed with catalyst **F**,¹⁷ only marginal differences were noted, demonstrating that substitution at the 3' position in such structure is not determinant, but interestingly, is possible. To our surprise, only trace of α -carbamoylsulfide **17a** was observed when the bis-substituted anthraquinone catalyst **1b** was used. The lack of reactivity might be due to the presence of multiple H-bond hydrogen-acceptor sites in the structure of **1b**, thereby disturbing the dual activation of both reaction partners with such structure. Interestingly, when the mono-substituted anthraquinone **1c** was evaluated, a little reactivity was recovered, allowing the formation of **16a** in moderate yield and enantioselectivity. Acyclic ketone photocatalysts **1a** and **1e** were also investigated under near UV (365 nm) or visible light (405 nm) irradiation and afforded a contrasting result, since the first catalyst **1a** gave a good enantioselectivity, whereas the second one **1e** led to racemic product.

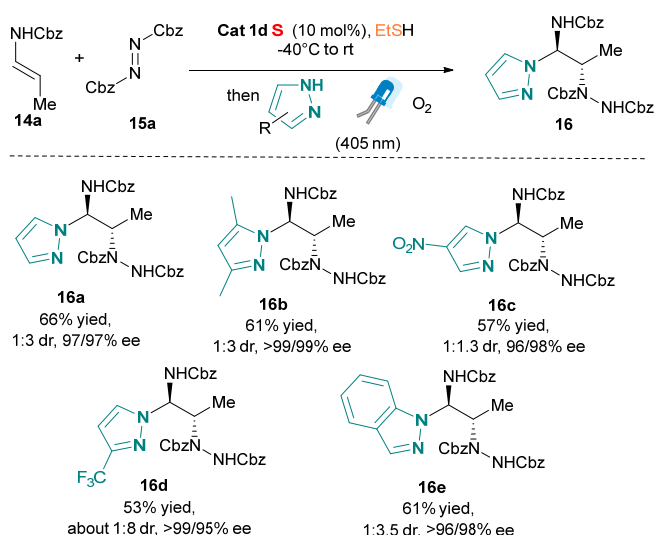
In order to verify the generality of the result obtained with catalyst **1d**, several 1-(hetero)aryl-1,2-diamines **16** were subsequently synthesized by changing the pyrazole partners (scheme 3). As such, compound **16a-e** were all obtained with good yields and excellent enantioselectivities. Diastereoselectivity was modest for compound **16c** (1:1.3), significant for compounds **16a, b** and **16e** (close to 1:3) and quite important for compound **16d** (1:8). Except for the later

one, diastereoselectivity follows the same trend as the one obtained in our previous work with catalyst **F**,¹⁷ 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.

Table 3 Evaluation of organophoto-catalytic activity^a

Entry	Pcat 1	λ nm ^b	Yield (%) ^c	<i>dr</i> ^d	<i>ee</i> (%) ^{e,f}
1 ^{a,c}	1a(s)	365	60	1:2	(-) 92/93 ^e
2 ^a	1bR	405	–	–	–
3 ^{a,c}	1cS	405	31	1:2.5	(-) 37/43
4 ^a	1d(S)	405	72	1:1.5	(-) 97/97 ^e
5 ^d	1eR	405	63	1:1.3	0/0

^a 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 16h. ^b wavelength of irradiation. ^c Isolated yield after column chromatography. ^d *dr* was determined by ¹H-NMR analysis and *anti*-diastereoselectivity assumed by analogy with our previous work. ^e Enantiomeric excess was determined by HPLC analysis on chiral stationary phase. ^f (+) 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.

Conclusions

In summary, we have developed an efficient reaction sequence providing a short and efficient syntheses of new chimeric photo-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

- For selected recent review on recent asymmetric visible-light photocatalysis, see (a) J. Großkopf, T. Kratz, T. Rigotti and T. Bach, *Chem. Rev.*, 2021, doi:acs.chemrev.1c00272 (b) T. Rigotti and J. Alemán, *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, *John Wiley & Sons*, 2018, 335; (j) A. F. Garrido-Castro, M. C. Maestro and J. Alemán, *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. Brimiouille, 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.
- 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, C. R. and J. Stephenson, *Acc. Chem. Res.*, 2016, **49**, 2295; (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, *Acc. Catal.*, 2013, **3**, 895; (j) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322; (k) J. Xuan and W.-J. Xiao *Angew. Chem., Int. Ed.*, 2012, **51**, 6828.
- 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. Jurberg, A. Álvarez-Fernández and P. Melchiorre, *Nat. Chem.*, 2013, **5**, 750.
- 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 David 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.
- 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.
- 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, 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, 1486; (e) C. B. Roos, J. Demaerel, D. E. Graff, R. R. Knowles, *J. Am. Chem. Soc.*, 2020, **142**, 5974; (f) Y. J. Li, M. Lei, and L. Gong, *Nat. Catalysis*, 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, W. J. Xiao, *Angew. Chem., Int. Ed.*, 2019, **58**, 13375; (i) G. K. Zeng, Y. Q. Li, B. K. Qiao, X. W. Zhao, 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 Z. Y. Jiang, *Chem. Commun.*, 2019, **55**, 7534–7537; (m) M. Hou, L. Lin, X. Chai, X. Zhao, B. Qiao, Z. Jiang *Chem. Sci.*, 2019, **10**, 6629; (n) J. J. Zhao, H. H. Zhang, X. Shen and S. Y. Yu, *Org. Lett.*, 2019, **21**, 913; (o) K. Cao, S. Tan, R. Lee, S. Yang, H. Jia, X. Zhao, B. Qiao and Z. Jiang, *J. Am. Chem. Soc.*, 2019, **141**, 5437.
- For a recent review, see: M. J. Genzink, J. B. Kidd, W. B. Swords and T. P. Yoon, *Chem. Rev.* 2021, doi: [acs.chemrev.1c00467](https://doi.org/10.1039/c1cy00467g); for leading examples, see (b) K. L. Skubi, J. B. Kidd, H. Jung, I. A. Guzei, M.-H. Baik and T. P. Yoon, *J. Am. Chem. Soc.* 2017, **139**, 17186; (c) W. Ding, L.-Q. Lu, Q.-Q. Zhou, Y. Wei, J.-R. Chen and W.-J. Xiao, *J. Am. Chem. Soc.* 2017, **139**, 63.
- First example of catalytic enantioselective chemistry merging hydrogen bonding organocatalysis with organic UV-light photocatalysis, see: (a) A. Bauer, F. Westkämper, S. Grimme, T. Bach, *Nature*, 2005, **436**, 1139; Visible Light Induced enantioselective cycloadditions: (b) A. Tröster, R. Alonso, A. Bauer and T. Bach, *J. Am. Chem. Soc.* 2016, **138**, 7808; (b) H. Guo, E. Herdtweck and T. Bach, *Angew. Chem. Int. Ed.* 2010, **49**, 7782; (d) R. Brimiouille, H. Guo and T. Bach, *Chem. Eur. J.* 2012, **18**, 7752; (d) 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.
- Selected examples: (a) Kimura, Y.; Uruguchi, D.; Ooi, T. *Org. Biomol. Chem.*, 2021, **19**, 1744; (b) D. Uruguchi, 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; (g) Z. Yang, H. Li, S. Li, M. T. Zhang and S. Luo, *Org. Chem. Front.*, 2017, **4**, 1037; (h) P. D. Morse, T. M. Nguyen, C. L. Cruz, D. A. Nicewicz, *Tetrahedron*, 2018, **74**, 3266.
- 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, E. Meggers, *Nature*, 2014, **515**, 100.
- 11 N. Vallavoju, 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, 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. Sugiono, 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, 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, B. Tan, *Chin. J. Chem.*, 2020, **38**, 213.
- 16 (a) F. Pecho, Y.-Q. Zou, J. Gramüller, T. Mori, S. M. Huber, A. Bauer, R. M. Gschwind, T. Bach, *Chem. – Eur. J.*, 2020, **26**, 5190; (b) F. Pecho, Y. Sempere, J. Gramüller, F. M. Hörmann, R. M. Gschwind, 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. Voutyritsa 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. Albinì, *Chem. Soc. Rev.*, 2013, **42**, 97.
- 19 (a) C. Chatgililoglu, D. Crich, M. Komatsu and I. Ryu, *Chem. Rev.*, 1999, **99**, 1991; (b) C. B. Tripathi, T. Ohtani, M. T. Corbett, 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. Gemayel, C. Emmelin, S. Perrier, S. Tomaz, V. J. Baboornian, D. A. Fishman, S. A. Nizkorodov, S. Dumasa 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, S. Guo, *Chem. Soc. Rev.*, 2013, **42**, 5323.
- 21 J. Cervantes-González, D. A. Vosburg, 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; (a) He, Z. Bian 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, K. Kanda, Kousou, *Org. Lett.*, 2006, **8**, 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. Chausset-Boissarie and I. Gillaizeau, *Chem. – Eur. J.*, 2014, **20**, 7548-7564; (d) K. Gopalaiah 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; (b) C. Lalli, A. Dumoulin, C. Lebé, F. Drouet, V. Guérineau, 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, G. Masson, *J. Org. Chem.* 2016, **81**, 7230; (e) C. Lebé, M. Languet, C. Allain and G. Masson, *Org. Lett.*, 2016, **18**, 1478.