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P-Chiral, *N*-phosphoryl sulfonamide Brønsted acids with an intramolecular hydrogen bond interaction that modulates organocatalysis†

Minglei Yuan,‡ Ifenna I. Mbaezue, ‡ Zhi Zhou, Filip Topic and Youla S. Tsantrizos *

Brønsted acids exemplified by OttoPhosa I (5c) were designed and evaluated in the asymmetric transfer hydrogenation of quinolines. Their catalytic properties are modulated by an intramolecular hydrogen bond that rigidifies their catalytic cavity, accelerates the reaction rate and improves enantioselectivity.

Phosphorus-based Brønsted acids have emerged as a highly promising class of organocatalysts. Many molecular designs have contributed to this field, including the most valuable BINOL-based Brønsted acids **1** and **2** (Fig. 1).[1] Brønsted acids **1** were first reported by Akiyama[2] and Terada,[3] and have been shown to efficiently catalyse a plethora of asymmetric reactions, including Mannich-type[2a,3,4] and Diels–Alder reactions,[5] the enantioselective hydrophosphonylation of imines,[6] reductive aminations,[7] imine transfer hydrogenations,[8] Friedel–Crafts alkylations,[9] intramolecular Michael additions,[10] the *N*,*O*-acetalization of aldehydes[11] and the transfer hydrogenation of various heterocyclic compounds.[12] These Brønsted acids were also reported to catalyse metal-free asymmetric 6π-electrocyclization reactions, leading to enantiomerically enriched 1,4-dihydropyridazines.[13] Recently, List reported the design of BINOL-based dimeric and sterically highly confined imidodiphosphorimidate analogs (IDPi; **2**, Fig. 1).[14] IDPi analogs were shown to catalyse the protonation of olefins, which then react with intramolecular hydroxyl groups to form chiral 5- and 6-membered ring ethers.[14a] Additionally, they can catalyse enantioselective C–C bond formation in Mukaiyama aldol-type reactions with a remarkably low concentration of the catalyst.[14b]

N-Phosphoryl sulfonamide derivatives of **1** (*e.g.* **1f**) were first introduced by Yamamoto and shown to possess greater ability to activate substrates with low reactivity, such as aldehydes, ketones and silyl enol ethers.[5,15] This observation is consistent with the higher acidity of the *N*-triflyl Brønsted acid;[16] the pK_a values of many analogs of **1** have been determined in acetonitrile[17] and DMSO.[18] However, the higher reaction rates observed with the *N*-triflyl Brønsted acid, as compared to the corresponding phosphoric acids, were often also associated with lower enantioselectivity.[4b,c] For example, List reported that direct asymmetric *N*,*O*-acetalization of aldehydes with Brønsted acids **1e** and **1g** resulted in products with 61%

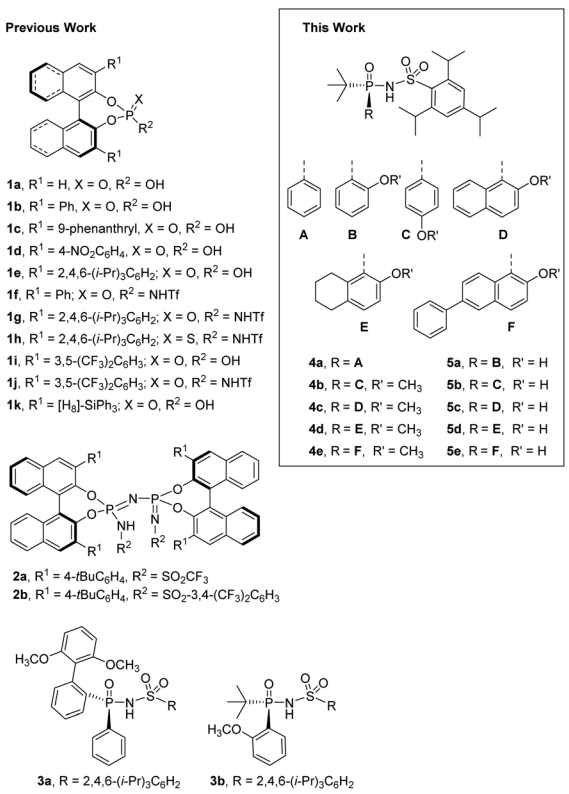

Fig. 1 Phosphorus-based Brønsted acid organocatalysts.

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 0B8. E-mail: Youla.tsantrizos@mcgill.ca

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‡These authors contributed equally.

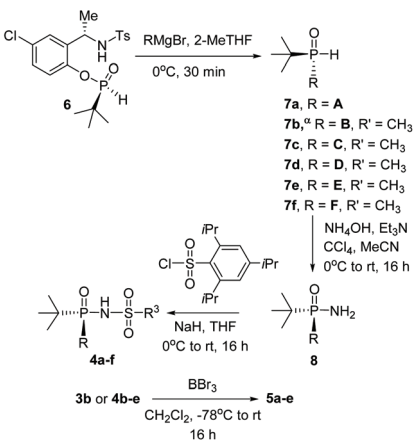
ee and 14% ee, respectively.[19a] Similarly, asymmetric methanolysis of *cis*-1,2-cyclohexanedicarboxylic anhydride with a phosphinic acid and its corresponding phosphoramide led to 22% ee and 0% ee, respectively.[19b] Recently, Han reported the synthesis of *P*-stereogenic analogs **3** (*e.g.* **3a**,**b**) and observed that these compounds catalyzed the transfer hydrogenation of 2-phenylquinolines in only 30–36% enantiomeric excess.[20]

Based on the collective knowledge in this field, we decided to explore the impact of an intramolecular non-covalent interaction that could potentially participate in stabilizing the reaction intermediates in the transfer hydrogenation of heterocyclic compounds. We aimed to combine the higher catalytic activity of phosphoramides with the steric effect of *t*-butyl-substituted *P*-chiral phosphines into a new class of Brønsted acids, typified by analog **5c** (Fig. 1). In the design of these compounds, we presumed that a hydrogen bond between a heteroatom attached to the backbone of the catalyst and the acidic NH could (a) further increase the acidity of the catalyst, (b) rigidify the catalytic cavity, (c) stabilize the transition state of the reaction, and (d) potentially recruit the Hantzsch ester, thus leading to faster conversion at RT and good enantioselectivity. Herein we report the properties of a prototype, analog **5c** (OttoPhosa I), having a strategically placed phenolic moiety, as a key structural element (Fig. 1).

Recently, we reported a library synthesis of structurally diverse *t*-butyl-substituted *P*-chiral secondary phosphine oxides (SPOs) in high enantiomeric purity, starting from precursor **6** (Scheme 1).[21] Preparation of analogs **7a**, **7c** and **7d** was reported and the same methodology was used for the syntheses of **7e** and **7f** in good yields and high enantiomeric purity.[21] In order to probe the impact of the intramolecular hydrogen bond characterizing Brønsted acids **5** in a head-to-head comparison with analogs missing only that feature, we also synthesized the previously disclosed SPO **7b** (the precursor to Brønsted acid **3b**) using the method previously reported.[22] Intermediates **7** were treated with aqueous ammonia in the presence of Et_3N and CCl_4 to obtain the phosphinamides **8** *via* an Atherton–Todd-type reaction.[23] These intermediates were treated with 2,4,6-triisopropylbenzenesulfonyl chloride under basic conditions to give the *P*-chiral, *N*-phosphoryl sulfonamides **3b** and **4**. Finally, analogs **3b** and **4b–e** were treated with BBr_3 to cleave the methyl ether and obtain the phenolic Brønsted acids **5a–e** (Fig. 1). Due to the polarity of these compounds (**4** and **5**), chiral HPLC analysis proved to be very challenging. Consequently, the reported enantiomeric purities of analogs **4** were based on the enantiomeric purity of the corresponding phosphinamides **8**. However, in cases where both compounds **8** and the corresponding analogs **4** could be analyzed by chiral HPLC, a negligible difference in enantiomeric excess was observed (*e.g.* for **8a** and **4a**, 96.6% ee and 96.0% ee, respectively).

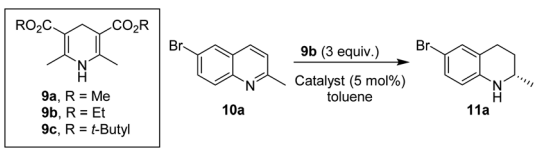
As a proof of concept, we decided to study the ability of our compounds to catalyze the asymmetric transfer hydrogenation of quinolines, which is an extensively investigated reaction with many BINOL-based Brønsted acids **1**. Rueping first reported using Brønsted acids **1** (Fig. 1)[24] as a greener approach for the preparation of chiral 1,2,3,4-tetrahydroquinolines (as compared to the classical metal-mediated hydrogenation under high pressure of H_2). The hydride source for these reactions is derived from the Hantzsch ester **9** (Table 1), a bioisostere of NADH/NADPH.[25] Chiral tetrahydroquinolines are valuable scaffolds for the synthesis of many biologically active compounds, including natural products[26,27] and human therapeutics (Fig. 2).[28]

The transfer hydrogenation of the 6-bromo-2-methylquinoline (**10a**) to the 1,2,3,4-tetrahydroquinoline **11a** was first investigated using the previously reported Brønsted acid **3b** (Table 1; entry 3). In parallel, the same reaction was carried out in the absence of a catalyst at 60 °C, 40 °C and 22 °C, to exclude the possibility of any competing reaction. Surprisingly, a significant amount of **11a** was formed at high temperatures even in the absence of a catalyst (entry 1), which was suppressed at RT (entry 2). To the best of our knowledge, this



Scheme 1 Synthesis of Brønsted acids ([a]prepared as previously reported[22]).

Table 1 Asymmetric transfer hydrogenation of quinolines



Entry	Catalyst	Temp./°C	Time/h	Yield/%	**11a** %ee[a]
1	None	60	48	50	—
2	None	22	48	—	—
3	**3b**	22	48	75	40
4	**4a**	22	48	72	40
5	**5a**	22	2	99	58
6	**5b**	22	24	99	40
7	**5c**	22	2	99	80(93[b])
8[c]	**5c**	22	0.5	99	80
9[d]	**5c**	22	5	99	89
10	**5d**	22	2	99	60
11	**5e**	22	2	99	84

[a] %ee of the crude product. [b] %ee of the isolated crystalline product. [c] Reaction was run in $CHCl_3$. [d] Reaction was run in cyclohexane.

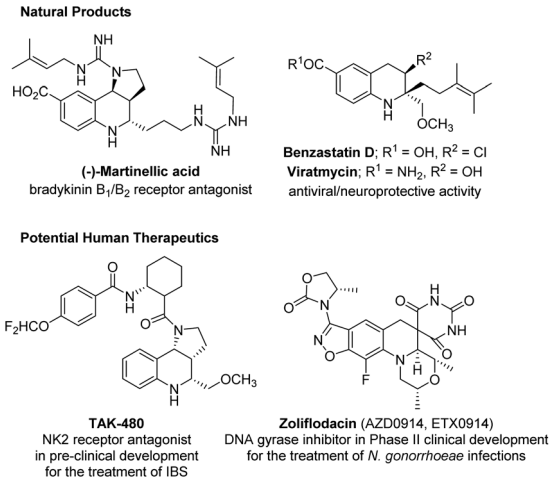


Fig. 2 Examples of bioactive tetrahydroquinolines.

observation has not been previously reported. Although the 2-methoxy group in Brønsted acid **3b** could potentially hydrogen-bond with the NH, the rate of the reaction and enantioselectivity were identical to those of the simple phenyl analog **4a** (entry 3 *vs.* 4). In contrast, the corresponding phenolic Brønsted acid **5a** led to quantitative conversion in 2 h and higher enantioselectivity (entry 3 *vs.* 5). A much slower reaction rate was observed with the 4-phenol derivative **5b** and the enantioselectivity was also reduced to that observed with **3b** and **4a** (entry 6 *vs.* 3 and 4, respectively). These results strongly support our hypothesis of a beneficial intramolecular cooperative interaction.

Extension of the π-system to the naphthalen-2-ol derivative **5c** led to further improvement in enantioselectivity, giving a crude product in a 1 : 9 *R* : *S* ratio and a quantitative yield after 2 h at RT; enantiomeric purity was increased to a 3.5 : 96.5 *R* : *S* ratio upon crystallization of the product (entry 7). Furthermore, the same reaction could be completed in only 30 min if run in $CHCl_3$ without any loss in enantioselectivity (entry 8). The best enantioselectivity was observed when the reaction was run in cyclohexane (89% ee); however, the reaction time was a little longer (entry 9). Interestingly, the corresponding 5,6,7,8-tetrahydronaphthalen-2-ol derivative **5d** gave very similar results to the simple phenol **5a** (entry 5 *vs.* 10), suggesting that π-stacking interactions between the catalyst and the substrate play a significant role in this reaction. Extension of the π-system to the 6-phenylnaphthalen-2-ol analog **5e** provided some further improvement in enantioselectivity (entry 7 *vs.* 11); this aspect of our catalyst design merits further investigation in future studies.

The absolute stereochemistries of the (*S*)-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (**11a**) and the Brønsted acids R_p-**5a** and R_p-**5c** were confirmed by their single-crystal X-ray structures (Fig. 3a–c, respectively). The structures of R_p-**5a** and R_p-**5c** also clearly showed the presence of a hydrogen bond between the phenolic oxygen and the acidic NH and provided a molecular view of a small substrate-binding cavity (*e.g.* Fig. 3d; **5c**).

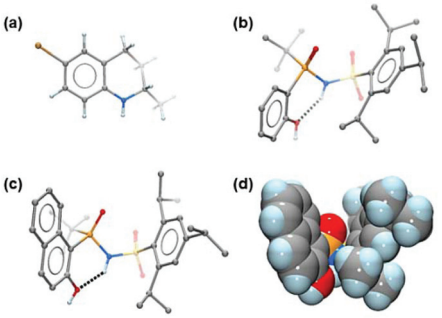


Fig. 3 (a) (*S*)-**11a**; (b) R_p-**5a**; (c) R_p-**5c**; (d) space-filling model based on the X-ray of R_p-**5c**.

Optimization of the reaction conditions for the solvent and the Hantzsch ester effects in the presence of catalyst **5c** were also studied (ESI Tables 1 and 2†). The effects of the Hantzsch esters (**9a–c**) investigated so far did not result in any major differences. The substrate scope was subsequently explored and the results were compared to those reported for BINOL-based Brønsted acids **1b** and **1c** (Table 2); the objective of this study was to simply gain further insight into the catalytic properties of catalyst **5** in comparison to BINOL-based Brønsted acids **1** that have similar size (or slightly larger) substrate-binding cavities. Although catalyst optimization is often required for each different type of reaction, certain structural trends are well known about organocatalysts **1**.[1] For example, large substituents at the 3,3′-positions of the BINOL-based Brønsted acids **1** typically provide better enantioselectivity, due to higher steric bulk and larger substrate-binding catalytic cavities (*e.g.* Table 2, entry 8 *vs.* 9).[24]

Table 2 Substrate scope and catalyst effect

Entry	Catalyst	R^2	$R^3/R^4/R^6$	Time/h	Yield/%	**11**%ee[a]
1	**5c**	Me	H/H/H	16	73	88
2	**5c**	Me	H/H/Br	5	99	88(93[b])
3	**5c**	Me	H/H/NO_2	3	83	86(96[b])
4	**5c**	Me	H/H/OMe	168	<5	—
5	**5c**	Et	H/H/H	9	72	75
6	**5c**	i-Pr	H/H/H	22	77	66
7	**5c**	Ph	H/H/H	12	95	59
8[c]	**1b**	Ph	H/H/H	—	nd	5
9[c]	**1c**	Ph	H/H/H	12	92	97
10	**5c**	H	H/Me/H	96	70	30
11[c]	**1b**	H	H/Me/H	35–60	nd	35
12	**5c**	H	Me/H/H	16	71	14
13	**5c**	H	Ph/H/H	86	51[d]	4
14[c]	**1c**	H	Ph/H/H	22–48	nd	Racemic
15[e]	**5c**	CO_2Me	H/H/H	4	71	30

Most reactions catalyzed by **5c** were run at RT. [a] %ee of the product. [b] %ee after crystallization. [c] Data obtained at 60 °C.[24,30] [d] Yield based on the recovered starting material. [e] Data obtained at 50 °C.

Screening of various substituents at the C-2 position of the quinoline substrate revealed that substituents with larger steric bulk led to lower enantioselectivity (Table 2; entry 1 *vs.* 5 and 6). Substitution with an electron-withdrawing group at C-6 accelerated the reaction rate (entries 2 and 3), whereas an electron-donating group dramatically reduced the rate of the reaction (entry 4). These observations are consistent with the general mechanism for this type of reaction.[1,24] Hydrogenation of the 2-phenylquinoline resulted in lower enantioselectivity than expected (59% ee; entry 7), suggesting a possible competing π-stacking interaction between the catalyst and the C-2 phenyl group, instead of the quinoline core. It is noteworthy that in spite of its small cavity size, compound **5c** catalyzed the transfer hydrogenation of the 2-phenylquinoline with significantly higher enantioselectivity than catalyst **1b** (entry 7 *vs.* 8),[24] whereas hydrogenation of the 4-methylquinoline catalyzed by **5c** results in a similar enantioselectivity to that reported with catalyst **1b**[29] (entry 10 *vs.* 11). We also examined the hydrogenation of the 3-methyl and 3-phenyl substituted quinolines but observed low enantioselectivity and slower reaction rates (entries 12 and 13, respectively). Our observations are consistent with those reported by Rueping for the 3-substituted *vs.* the 2-substituted quinoline. For example, whereas hydrogenation of the 2-phenylquinoline with catalyst **1c** leads to 97% ee of the tetrahydroquinoline **11** (entry 9),[24] the 3-phenylquinoline was reported to give a racemic mixture of the corresponding product (entry 14). However, sterically more congested catalysts, such as **1k**, were shown to lead to the formation of the 3-phenyl-1,2,3,4-tetrahydroquinoline in 74% ee, under the same reaction conditions.[30] Finally, we examined the transfer hydrogenation of methylquinoline-2-carboxylate (entry 15). A strongly electron-withdrawing substituent at C-2 is expected to decrease the electron density on the quinoline nitrogen and significantly decrease the rate of this reaction.[31] In fact, the transfer hydrogenation of methylquinoline-2-carboxylate catalyzed by a Brønsted acid has not been previously reported. We were pleased to see quantitative conversion in 4 hours, albeit in modest enantioselectivity (the isolated yield of the pure product was only 71% due to partial co-elution of the Hantzsch esters with the product during chromatography). It is reasonable to assume that the high acidity of Brønsted acid **5c** is able to compensate for the electronic effects of the C-2 carboxylate moiety.

Although we have not yet fully explored the mechanistic differences between catalyst **5c** and the BINOL-based Brønsted acids **1**, our current data are generally consistent with the established mechanism for this reaction.[1,24,29] The rate acceleration and enantioselectivity differences observed between catalysts **3b** and **5a** (Table 1; entry 3 *vs.* 5) are consistent with our original hypothesis, which presumed that protonation of the quinoline by the catalyst could lead to an intramolecular cooperative ion pair (Fig. 4; **II**), stabilizing the conjugate base of the catalyst. Whether the shared proton in the ionized form **II** is derived from the OH or the NH of the original catalyst (**I**) is inconsequential to the proposed intermediate **II**. Additionally, once the protonated quinoline is bound to the catalyst, it is likely that the OH moiety recruits the Hantzsch ester, leading to a more stable trimolecular complex (**III**) and guiding the delivery of the hydride species from the side of the naphthol ring (**IV**). Binding of the 2-methylquinoline to **5c** through favorable π-stacking interactions and placement of the quinoline nitrogen near the acidic NH of the catalyst necessitates that the 2-methyl group becomes buried in the catalytic pocket and near the *t*-butyl substituent on the phosphorus. Therefore, entrance of the hydride from the side of the naphthol would simultaneously push the 2-methyl group away from the steric bulk of the *t*-butyl group.

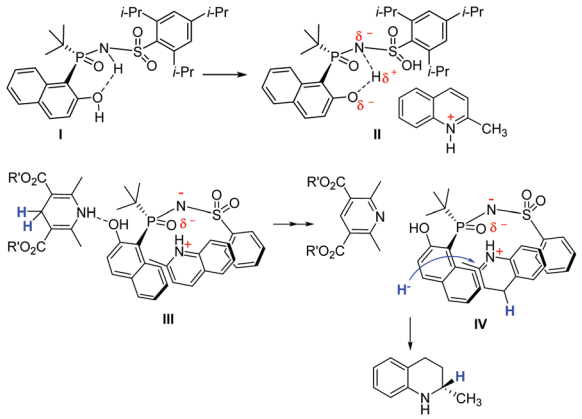


Fig. 4 Proposed catalytic mechanism of Brønsted acid **5c**.

In summary, we aimed to demonstrate that the incorporation of an intramolecular H-bond between a phenolic substituent on a *P*-stereogenic center of a Brønsted acid and the NH of its *N*-phosphoryl sulfonamide can stabilize the conformation of the catalytic cavity, accelerate the reaction rate and increase enantioselectivity for the transfer hydrogenation of quinolines. OttoPhosa I (**5c**) represents a prototype of this new class of Brønsted acid organocatalysts. Its catalytic properties compare favorably with those of BINOL-based Brønsted acids **1** having a similarly small substrate-binding pocket. The synthesis of analogues **5** and fine-tuning of their catalytic properties for different chemical transformations can be easily achieved in a modular library mode[21] and is currently in progress.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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References

1 For an extensive review see: D. Parmar, E. Sugiono, S. Raja and M. Rueping, Chem. Rev., 2014, **114**, 9047; Additions and Corrections: *Chem. Rev.* 2017, **117**, 10608.

2 (*a*) T. Akiyama, J. Itoh, K. Yokota and K. Fuchibe, *Angew. Chem., Int. Ed.*, 2004, **43**, 1566; (*b*) T. Akiyama, *Chem. Rev.*, 2007, **107**, 5744.

3 D. Uraguchi and M. Terada, *J. Am. Chem. Soc.*, 2004, **126**, 5356.

4 (*a*) M. Rueping, E. Sugiono and F. R. Schoepke, *Synlett*, 2007, 1441; (*b*) Q.-X. Guo, H. Liu, C. Guo, S.-W. Luo, Y. Gu and L.-Z. Gong, *J. Am. Chem. Soc.*, 2007, **129**, 3790; (*c*) I. D. Gridnev, M. Kouchi, K. Sorimachi and M. Terada, *Tetrahedron Lett.*, 2007, **48**, 497.

5 D. Nakashima and H. Yamamoto, *J. Am. Chem. Soc.*, 2006, **128**, 9626.

6 T. Akiyama, H. Morita, J. Itoh and K. Fuchibe, *Org. Lett.*, 2005, **7**, 2583.

7 R. I. Storer, D. E. Carrera, Y. Ni and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2006, **128**, 84.

8 (*a*) S. Hoffmann, A. M. Seayad and B. List, *Angew. Chem., Int. Ed.*, 2005, **44**, 7424; (*b*) M. Rueping, E. Sugiono, C. Azap, T. Theissmann and M. Bolte, *Org. Lett.*, 2005, **7**, 3781; (*c*) T. B. Nguyen, H. Bousserrouel, Q. Wang and F. Guéritte, *Org. Lett.*, 2010, **12**, 4705; (*d*) J. Greindl, J. Hioe, N. Sorgenfrei, F. Morana and R. M. Gschwind, *J. Am. Chem. Soc.*, 2016, **138**, 15965.

9 (*a*) J. Itoh, K. Fuchibe and T. Akiyama, *Angew. Chem., Int. Ed.*, 2008, **47**, 4016; (*b*) M. Zeng, Q. Kang, Q.-L. He and S.-L. You, *Adv. Synth. Catal.*, 2008, **350**, 2169; (*c*) J.-W. Zhang, Q. Cai, X.-X. Shi, W. Zhang and S.-L. You, *Synlett*, 2011, 1239.

10 L.-D. Zhang, L.-R. Zhong, J. Xi, X. L. Yang and Z.-J. Yao, *J. Org. Chem.*, 2016, **81**, 1899.

11 S. Vellalath, I. Čorić and B. List, *Angew. Chem., Int. Ed.*, 2010, **49**, 9749.

12 For recent reviews see: (*a*) M. Rueping, J. Dufour and F. R. Schoepke, *Green Chem.*, 2011, **13**, 1084; (*b*) A. M. F. Phillips and A. J. L. Pombeiro, *Org. Biomol. Chem.*, 2017, **15**, 2307.

13 A. Das, C. M. R. Volla, I. Atodiresei, W. Bettray and M. Rueping, *Angew. Chem., Int. Ed.*, 2013, **52**, 8008.

14 (*a*) N. Tsuji, J. L. Kennemur, T. Buyck, S. Lee, S. Prévost, P. S. J. Kaib, D. Bykov, C. Farès and B. List, *Science*, 2018, **359**, 1501; (*b*) H. Y. Bae, D. Höfler, P. S. J. Kaib, P. Kasaplar, C. K. De, A. Döhring, S. Lee, K. Kaupmees, I. Leito and B. List, *Nat. Chem.*, 2018, **10**, 888.

15 (*a*) C. H. Cheon and H. Yamamoto, *J. Am. Chem. Soc.*, 2008, **130**, 9246; (*b*) C. H. Cheon and H. Yamamoto, *Org. Lett.*, 2010, **12**, 2476.

16 M. Rueping, C. Azap, E. Sugiono and T. Theissmann, *Synlett*, 2005, 2367.

17 K. Kaupmees, N. Tolstoluzhsky, S. Raja, M. Rueping and I. Leito, *Angew. Chem., Int. Ed.*, 2013, **52**, 11569.

18 (*a*) P. Christ, A. G. Lindsay, S. S. Vormittag, J.-M. Neudörfl, A. Berkessel and A. M. C. O'Donoghue, *Chem. – Eur. J.*, 2011, **17**, 8524; (*b*) C. Yang, X.-S. Xue, J.-L. Jin, X. Li and J.-P. Cheng, *J. Org. Chem.*, 2013, **78**, 7076.

19 (*a*) S. Vellalath, I. Čorić and B. List, *Angew. Chem., Int. Ed.*, 2010, **49**, 9749; (*b*) V. N. Wakchaure and B. List, *Angew. Chem., Int. Ed.*, 2010, **49**, 4136.

20 Z. S. Han, H. Wu, B. Qu, Y. Wang, L. Wu, L. Zhang, Y. Xu, L. Wu, Y. Zhang, H. Lee, F. Roschangar, J. J. Song and C. H. Senanayake, *Tetrahedron Lett.*, 2019, **60**, 1834.

21 S.-G. Li, M. Yuan, F. Topic, Z. S. Han, C. H. Senanayake and Y. S. Tsantrizos, *J. Org. Chem.*, 2019, **84**, 7291.

22 Z. S. Han, H. Wu, Y. Xu, Y. Zhang, B. Qu, Z. Li, D. R. Caldwell, K. R. Fandrick, L. Zhang, F. Roschangar, J. J. Song and C. H. Senanayake, *Org. Lett.*, 2017, **19**, 1796.

23 (*a*) F. R. Atherton, H. T. Openshaw and A. R. Todd, *J. Chem. Soc.*, 1945, 660; (*b*) S. S. Le Corre, M. Berchel, H. Couthon-Gourvès, J.-P. Haelters and P.-A. Jaffrès, *Beilstein J. Org. Chem.*, 2014, **10**, 1166.

24 M. Rueping, A. P. Antonchick and T. Theissmann, *Angew. Chem., Int. Ed.*, 2006, **45**, 3683.

25 (*a*) D. Mauzerall and F. H. Westheimer, *J. Am. Chem. Soc.*, 1955, **77**, 2261; (*b*) R. Abeles and F. H. Westheimer, *J. Am. Chem. Soc.*, 1958, **80**, 5459; (*c*) D. Richter and H. Mayr, *Angew. Chem., Int. Ed.*, 2009, **48**, 1958.

26 (*a*) B. B. Snider, Y. Ahn and S. M. O'Hare, *Org. Lett.*, 2001, **3**, 4217; (*b*) S. G. Davies, A. M. Fletcher, J. A. Lee, T. J. A. Lorkin, P. M. Roberts and J. E. Thomson, *Org. Lett.*, 2013, **15**, 2050.

27 H. Tsutsumi, Y. Katsuyama, M. Izumikawa, M. Takagi, M. Fujie, N. Satoh, K. Shinya and Y. Ohnishi, *J. Am. Chem. Soc.*, 2018, **140**, 6631.

28 (*a*) G. S. Basarab, P. Doig, V. Galullo, G. Kern, A. Kimzey, A. Kutschke, J. P. Newman, M. Morningstar, J. Mueller, L. Otterson, K. Vishwanathan, F. Zhou and M. Gowravaram, *J. Med. Chem.*, 2015, **58**, 6264; (*b*) S. N. Taylor, J. Marrazzo, B. E. Batteiger, E. W. Hook III, A. C. Seña, J. Long, M. R. Wierzbicki, H. Kwak, S. M. Johnson, K. Lawrence and J. Mueller, *N. Engl. J. Med.*, 2018, **379**, 1835.

29 M. Rueping, T. Theissmann, M. Stoeckel and A. P. Antonchick, *Org. Biomol. Chem.*, 2011, **9**, 6844.

30 M. Rueping, T. Theissmann, S. Raja and J. W. Bats, *Adv. Synth. Catal.*, 2008, **350**, 1001.

31 D. Y. Park, S. Y. Lee, J. Jeon and C.-H. Cheon, *J. Org. Chem.*, 2018, **83**, 12486.