ORGANIC CHEMISTRY FRONTIERS

RESEARCH ARTICLE

Cite this: *Org. Chem. Front.*, 2019, **6**, 3956

Synthesis of paracyclophanes with planar and central chirality: kinetic resolution of [2.2] paracyclophane aldimines *via* palladium-catalyzed addition of arylboronic acids†

Yang Zhao, [a,b] Han Wang,[a] Bo Wu[a] and Yong-Gui Zhou *[a,c]

Received 13th August 2019,
Accepted 26th October 2019

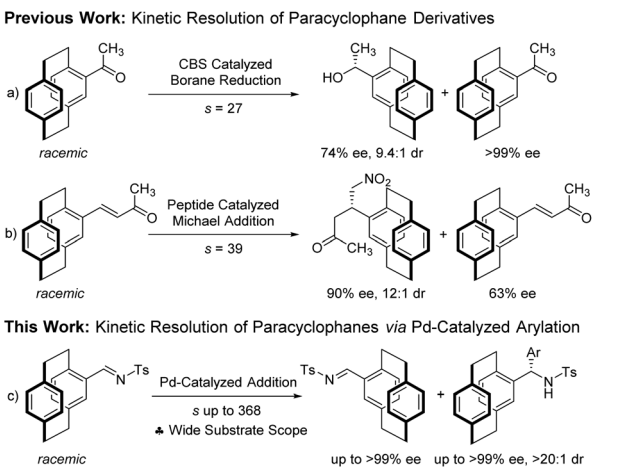
DOI: 10.1039/c9qo01011d

rsc.li/frontiers-organic

Kinetic resolution of [2.2]paracyclophane aldimines was achieved through palladium-catalyzed enantioselective arylation with arylboronic acids. The catalytic process provided reliable access to enantiopure paracyclophane derivatives with planar and central chirality as well as the recovered chiral aldimines with a selectivity factor up to 368. Furthermore, the synthetic utility of the [2.2]paracyclophane aldimines has been demonstrated by converting them into useful chiral building blocks.

[2.2]Paracyclophane and its derivatives have a privileged three-dimensional framework which was first discovered by Brown and Farthing in 1949.[1] Structurally, two stacked benzene rings are distorted into a boat conformation, which is locked by two ethylene bridges at their *para*-positions.[2] Owing to their rigid scaffold, substituted paracyclophanes can show planar chirality.[3] Planar-chiral paracyclophanes can be used in various chiral materials,[4] and also serve as ligands or auxiliaries in asymmetric catalysis and stereoselective synthesis.[5,6] Various methods for the synthesis of enantiopure paracyclophanes have been developed including classical stoichiometric resolution methods, chromatographic separation on chiral stationary phases[7,8] and catalytic asymmetric processes.[9,10]

Monosubstituted [2.2]paracyclophanes have been employed as chiral ligands in asymmetric dialkylzinc additions to aldehydes, asymmetric cyclopropanation reactions and asymmetric epoxidation reactions.[5b,6] Monosubstituted [2.2]paracyclophanes bearing chiral substituents were proved to control the enantioselectivity of the reaction effectively because of the interplay between the planar chirality of the [2.2]paracyclophane and the central chirality of the substituents.[6b] Catalytic synthesis of paracyclophane derivatives with planar and central chirality has been less explored. In 2001, the group of Kagan realized the kinetic resolution of 4-acetyl[2.2]paracyclophane by borane reduction in the presence of a CBS catalyst, giving 1-[4-[2.2]-paracyclophan-yl]-ethan-1-ol with 74% ee and 9.4 : 1 dr (Scheme 1a).[10a] Recently, the kinetic resolution of enone-substituted [2.2]paracyclophane by peptide-catalyzed Michael addition of nitromethane was developed by Kudo and co-workers; the ee value of the recovered material was moderate (63%) (Scheme 1b).[10b] However, these examples of the construction of paracyclophanes with planar and central chirality featured limited substrate scope. Hence, the development of a facile approach to prepare paracyclophane derivatives with an excellent selectivity factor and broad substrate scope is highly desirable.



Scheme 1 Synthesis of [2.2]paracyclophane derivatives with planar and central chirality *via* kinetic resolution.

[a]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China. E-mail: ygzhou@dicp.ac.cn; http://www.lac.dicp.ac.cn/*
[b]*University of Chinese Academy of Sciences, Beijing 100049, P. R. China*
[c]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China*

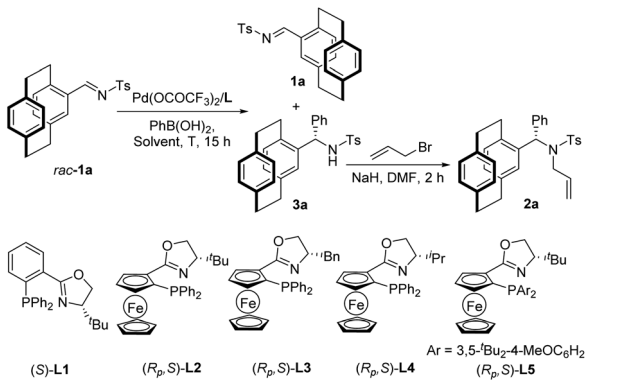
†Electronic supplementary information (ESI) available: Experimental details, compound characterization, and NMR and HPLC spectra. CCDC 1891926 (**2a**), 1910494 (**2l**) and 1917426 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9qo01011d

Metal-catalyzed addition of arylboron reagents to activated imines has achieved great success in the construction of chiral amine compounds.[11,12] Due to the high efficacy and robustness of palladium catalysts, much attention has been directed to the development of palladium-catalyzed enantioselective addition of arylboronic acids.[12] We envisaged that palladium-catalyzed asymmetric addition could be applied to the kinetic resolution of [2.2]paracyclophane aldimines for the facile synthesis of paracyclophane derivatives with planar and central chirality. Herein, we report the kinetic resolution of [2.2]paracyclophane aldimines *via* palladium-catalyzed addition of arylboronic acids, providing a series of paracyclophane derivatives with planar and central chirality with an excellent selectivity factor (Scheme 1c).

To begin our investigation, racemic *N*-tosyl[2.2]paracyclophane-4-methanimine **1a** and phenylboronic acid were chosen as model substrates. Our previous work showed that bidentate phosphine-oxazoline ligands are effective for the Pd-catalyzed asymmetric addition of arylboronic acids to aldimine.[12k,l] Based on the previous reports, (*S*)-^{t}Bu-Phox was chosen as the initial ligand. This kinetic resolution of *rac*-**1a** was conducted in the presence of the $Pd(OCOCF_3)_2$/(*S*)-^{t}Bu-Phox catalyst at 60 °C. Satisfyingly, the reaction proceeded smoothly, giving the desired addition adduct **3a**. The obtained product **3a** was *in situ* allylated with allyl bromide to furnish less polar tertiary *N*-allyl amine **2a** which was more easily separable. At 55% conversion of the substrate *rac*-**1a**, the recovered aldimine **1a** and product **2a** could be resolved to 96.0% ee and 97.7% ee, respectively, albeit with only 4 : 1 dr (Table 1, entry 1, *s* factor was 32). Therefore, the main challenge is to improve the diastereoselectivity. A series of planar chiral phosphinooxazoline ligands were examined (Table 1, entries 2–5). Ferrocene-derived **L2** was the favourable ligand in terms of diastereoselectivity and kinetic resolution efficiency. Solvents also played an important role in the reaction. The reaction was shut down in 1,2-dichloroethane or 1,4-dioxane (Table 1, entries 6 and 7). When the addition was conducted in HFIP, the conversion of the substrate *rac*-**1a** decreased dramatically and only 13% conversion was obtained (Table 1, entry 8). Subsequently, the effect of temperature was evaluated. On decreasing or increasing the reaction temperature, the kinetic resolution efficiency diminished (Table 1, entries 9 and 10). The *s* factor was cooperatively affected by the conversion of the substrate and enantioselectivity of the recovered aldimine **1a**. When the conversion was over 50%, the *s* factor was lower with a higher conversion. When the quantity of $PhB(OH)_2$ was decreased to one equivalent, the reaction proceeded successfully with high kinetic resolution efficiency (Table 1, entry 11, *s* factor was 115). Therefore, the optimal conditions were established as: $Pd(OCOCF_3)_2$/**L2**/$PhB(OH)_2$ (1.0 eq.)/TFE (2.0 mL)/60 °C.

With the optimized conditions in hand, we evaluated the substrate scope and generality (Table 2). Firstly, the effect of the substituent on the benzene ring of arylboronic acid was examined. The diastereoselectivity could be influenced unfavourably by steric effects. In comparison with the reactions of the substrates bearing a *meta*-substituted or *para*-substituted aryl group, a slightly lower diastereomeric ratio was obtained for the *ortho*-substituent on the benzene ring (Table 2, entries 2–4). It was also found that the electronic properties of the arylboronic acids had an obvious influence on the kinetic resolution efficiency. Electron-withdrawing substituents (–F, $–CF_3$) on the aromatic ring were accommodated with excellent kinetic resolution efficiency (Table 2, entries 5, 6 and 8). Halogens such as 4-Cl and 3-Cl were also suitable, which allow further potential functionalization (Table 2, entries 7 and 9). The reaction conditions were compatible with a methoxy group, albeit with lower enantioselectivity of the recovered aldimine (−)-**1a** (Table 2, entry 10, *s* factor was 39). Moreover, a naphthalene-derived boronic acid also provided the desired product (+)-**2k** (Table 2, entry 11). For aliphatic boronic acids including methylboronic acid, *n*-butylboronic acid and *trans*-2-phenylvinylboronic acid, when the reaction was conducted under the standard conditions for 15 h, unfortunately, no reaction occurred. We next focused on expanding the aldimine scope. *para*-Substituted [2.2]paracyclophane aldimine *rac*-**1b** underwent the kinetic resolution process

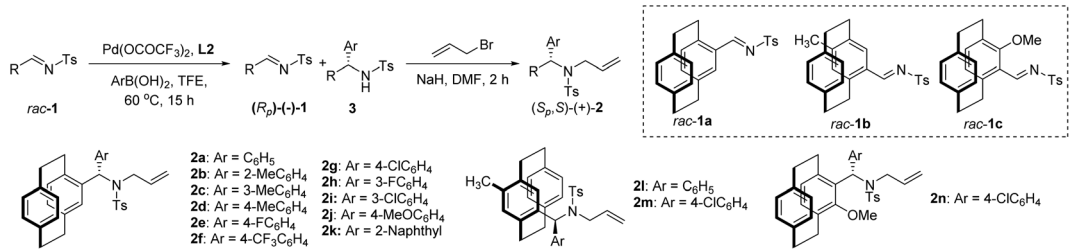
Table 1 Optimization of the kinetic resolution[a]



Entry	L	Solvent	*rac*-**1a** conv.[b] (%)	**1a** ee[c] (%)	**2a** ee[c] (dr)[d]	*s*[e]
1	**L1**	TFE	55	96.0	97.7 (04 : 1)	32
2	**L2**	TFE	52	95.1	98.0 (12 : 1)	57
3	**L3**	TFE	50	85.9	94.0 (16 : 1)	36
4	**L4**	TFE	58	92.6	88.2 (09 : 1)	16
5	**L5**	TFE	48	76.1	95.1 (13 : 1)	24
6	**L2**	DCE	<5	—	—	—
7	**L2**	Dioxane	<5	—	—	—
8	**L2**	HFIP	13	8.1	97.3 (12 : 1)	4
9[f]	**L2**	TFE	48	76.0	99.1 (15 : 1)	23
10[g]	**L2**	TFE	56	93.8	97.6 (13 : 1)	23
11[h]	**L2**	TFE	50	94.0	97.8 (12 : 1)	115
12[i]	**L2**	TFE	49	81.6	98.6 (11 : 1)	31

[a] Conditions: *rac*-**1a** (0.10 mmol), $PhB(OH)_2$ (0.15 mmol), $Pd(OCOCF_3)_2$ (5.0 mol%), **L** (5.0 mol%), solvent (2.0 mL), 60 °C, 15 h. [b] Determined by ^{1}H NMR analysis using benzyl ether as the internal standard. [c] Determined by chiral HPLC analysis. [d] Determined by ^{1}H NMR spectroscopy. [e] Calculated selectivity factors: C = conv., $s = \ln[(1 - C)(1 - \text{ee of } \mathbf{1a})]/\ln[(1 - C)(1 + \text{ee of } \mathbf{1a})]$. [f] The reaction was carried out at 40 °C. [g] The reaction was carried out at 80 °C. [h] Using 1.0 equiv. $PhB(OH)_2$ (0.10 mmol). [i] Using 0.6 equiv. $PhB(OH)_2$ (0.06 mmol).

Table 2 Substrate scope for the kinetic resolution of [2.2]paracyclophane aldimines **1** [a]

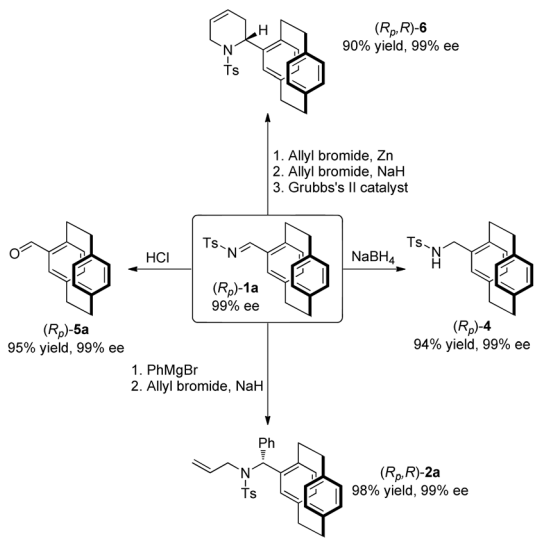


Entry	*rac*-**1** conv.[b] (%)	**1** yield[c] (%)	**1** ee[d] (%)	**2**	**2** yield[c] (%)	**2** ee[d] (%)	**2** dr[b]	*s*[e]
1	50	39	93.7	**2a**	48	98.8	12 : 1	108
2	50	38	80.1	**2b**	50	98.7	7 : 1	22
3	56	28	91.2	**2c**	49	98.1	12 : 1	19
4	55	36	88.0	**2d**	53	98.3	13 : 1	17
5	51	43	99.2	**2e**	49	96.3	16 : 1	229
6	51	37	98.5	**2f**	51	98.7	>20 : 1	177
7	51	40	99.6	**2g**	50	98.9	>20 : 1	281
8	51	41	97.4	**2h**	50	98.9	>20 : 1	131
9	51	42	98.4	**2i**	50	99.4	>20 : 1	172
10	49	45	83.9	**2j**	48	96.5	13 : 1	39
11	50	41	82.3	**2k**	48	98.4	12 : 1	26
12[f]	51	40	99.4	**2l**	50	97.9	8 : 1	251
13[f]	51	42	99.9	**2m**	47	97.9	17 : 1	368
14[g]	15	85	13.2	**2n**	12	99.4	>20 : 1	8

[a] Conditions: *rac*-**1** (0.20 mmol), $ArB(OH)_2$ (0.20 mmol), $Pd(OCOCF_3)_2$ (5.0 mol%), **L2** (5.0 mol%), TFE (4.0 mL), 60 °C, 15 h. [b] Determined by ^1H NMR spectroscopy. [c] Isolated yield. [d] Determined by HPLC. [e] Calculated selectivity factors: C = conv., $s = \ln[(1 - C)(1 - \text{ee of } \mathbf{1})]/\ln[(1 - C)(1 + \text{ee of } \mathbf{1})]$. [f] *rac*-**1b** (0.20 mmol). [g] *rac*-**1c** (0.20 mmol).

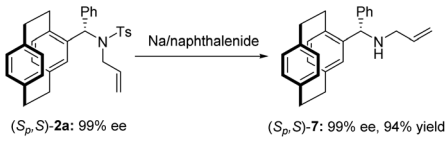
smoothly under the optimized reaction conditions (Table 2, entries 12 and 13). It is worth noting that by employing 4-chlorophenylboronic acid in this transformation, aldimine (−)-**1b** was isolated with 42% yield and 99.9% ee together with the addition product (+)-**2m** with 47% yield and 97.9% ee (*s* factor was 368, 17 : 1 dr). But for the *ortho*-substituted [2.2] paracyclophane aldimine *rac*-**1c**, only a small amount of the product was observed, and the *s* factor was low; the reason might be the obvious steric effect (Table 2, entry 14). In addition, we investigated the aldimine of [2.2]paracyclophane-derived α,β-unsaturated aldehyde; the reaction system was complicated. The vinylogous substrate might be unstable under these conditions. The absolute configuration of (+)-**2a** and (+)-**2l** was unambiguously confirmed as (S_p,*S*) by X-ray crystallographic analysis; the configuration of the recovered aldimines (−)-**1a** and (−)-**1b** was assigned R_p configuration by comparison with X-ray crystallographic data of the compounds (+)-**2a** and (+)-**2l**.

To demonstrate the synthetic versatility of the recovered aldimine (R_p)-**1a**, a variety of transformations of (R_p)-**1a** were conducted (Scheme 2). Reduction of aldimine (R_p)-**1a** with sodium borohydride delivered amine **4** in 94% yield without loss of optical purity. (R_p)-**1a** was also converted into the corresponding aldehyde **5a** by hydrolysis in the presence of hydrochloric acid. Significantly, treatment of (R_p)-**1a** with a phenyl Grignard reagent afforded the desired adduct with high diastereoselectivity, followed by allyl protection, giving the enantiomer (R_p,*R*)-**2a** with 99% ee and 98% yield. In addition,



Scheme 2 Derivatizations of the recovered material (R_p)-**1a**.

the Barbier reaction of (R_p)-**1a** worked well to provide the addition product with high diastereoselectivity, followed by protection of the secondary amino group to form the allylamine. Ring-closing metathesis with the Grubbs catalyst successfully gave the heterocycle **6** with 99% ee and 90% yield over two steps. For the planar-chiral addition product (S_p,*S*)-**2a**, the selective removal of the tosyl group was achieved using



Scheme 3 Desulfonylation of (S_p,S)-**2a**.

sodium naphthalenide, providing the free amine **7** with 99% ee and 94% yield (Scheme 3).

Conclusion

In summary, an efficient method for the kinetic resolution of racemic [2.2]paracyclophane aldimines has been developed *via* palladium-catalyzed addition of arylboronic acids, giving a variety of paracyclophane derivatives with planar and central chirality as well as the recovered chiral aldimines with an excellent selectivity factor. Moreover, the synthetic utility of the recovered aldimines was demonstrated by converting them into useful chiral [2.2]paracyclophane-based building blocks. This protocol provides new access to paracyclophane derivatives with planar and central chirality. Further studies toward new approaches to synthesize chiral [2.2]paracyclophanes will be reported in due course.

Experimental

A typical procedure for kinetic resolution of [2.2] paracyclophane aldimines

A Schlenk tube was charged with $Pd(OCOCF_3)_2$ (3.3 mg, 0.01 mmol) and (R_p,S)-**L2** (5.0 mg, 0.01 mmol) under nitrogen, and degassed anhydrous acetone (1.5 mL) was added. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum to obtain the catalyst. Then the substrate *rac*-**1a** (0.20 mmol), arylboronic acid (0.20 mmol) and 2,2,2-trifluoroethanol (4.0 mL) were added into the tube under nitrogen. The mixture was heated to 60 °C. After stirring at 60 °C for 15 h, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The resulting mixture was dried under vacuum and the conversion of *rac*-**1a** was confirmed by ^{1}H NMR analysis with benzyl ether as an internal standard. The solvent was removed *in vacuo*; the recovered material (−)-**1a** (30.7 mg, 50% conv., 39% yield, 93.7% ee) and the addition product **3a** were isolated by column chromatography on silica gel using hexanes and ethyl acetate as an eluent. Enantiomeric excess of the recovered material (−)-**1a** was determined by HPLC (AD-3 column, *n*-hexane/i-PrOH 80/20, 0.8 mL min^{-1}, 254 nm, 30 °C), t_1 = 16.6 min (minor), t_2 = 18.9 min (major).

To a solution of the addition product **3a** in dry *N*,*N*-dimethylformamide (DMF, 1.0 mL), sodium hydride (15 mg, 0.38 mmol, 60% wt.) was added at 0 °C, and then allyl bromide (36 mg, 26.0 μL, 0.30 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred at room temperature for 2 h. Water (5.0 mL) was added, and the reaction mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried using anhydrous sodium sulfate and filtered, concentrated *in vacuo* and analyzed by crude ^{1}H NMR to determine the diastereomeric ratio. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel using hexanes and ethyl acetate as an eluent to afford the product (+)-**2a** (48.9 mg, 48% yield, 12 : 1 dr, 98.8% ee). Enantiomeric excess of the product (+)-**2a** was determined by HPLC (AD-H column, *n*-hexane/i-PrOH 90/10, 1.0 mL min^{-1}, 254 nm, 30 °C), t_1 = 6.9 min (major), t_2 = 7.5 min (minor).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the National Natural Science Foundation of China (21532006, 21690074) and the Chinese Academy of Sciences (XDB17020300) is acknowledged.

References

1 C. J. Brown and A. C. Farthing, *Nature*, 1949, **164**, 915.
2 H. Hope, J. Bernstein and K. N. Trueblood, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 1733.
3 D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, 1955, **77**, 6289.
4 (*a*) Y. Morisaki, M. Gon and Y. Chujo, *Polym. Chem.*, 2013, **51**, 2311; (*b*) M. Cakici, Z.-G. Gu, M. Nieger, J. Bürck, L. Heinke and S. Bräse, *Chem. Commun.*, 2015, **51**, 4796; (*c*) Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh and Y. Chujo, *J. Am. Chem. Soc.*, 2014, **136**, 3350; (*d*) Y. Morisaki, K. Inoshita and Y. Chujo, *Chem. – Eur. J.*, 2014, **20**, 8386; (*e*) M. Gon, Y. Morisaki and Y. Chujo, *J. Mater. Chem. C*, 2015, **3**, 521; (*f*) M. Gon, Y. Morisaki and Y. Chujo, *Eur. J. Org. Chem.*, 2015, 7756; (*g*) Y. Morisaki, R. Sawada, M. Gon and Y. Chujo, *Chem. – Asian J.*, 2016, **11**, 2524; (*h*) Y. Morisaki and Y. Chujo, *Bull. Chem. Soc. Jpn.*, 2019, **92**, 265.
5 (*a*) V. I. Rozenberg, E. V. Sergeeva and H. Hopf, *Modern Cyclophane Chemistry*, Wiley-VCH, Weinheim, 2004; (*b*) S. E. Gibson and J. D. Knight, *Org. Biomol. Chem.*, 2003, **1**, 1256; (*c*) G. J. Rowlands, *Isr. J. Chem.*, 2012, **52**, 60; (*d*) O. R. P. David, *Tetrahedron*, 2012, **68**, 8977; (*e*) F. Fringuelli, O. Piermatti, F. Pizzo and R. Ruzziconi, *Chem. Lett.*, 2000, 38; (*f*) T. M. Konrad, J. T. Durrani, C. J. Cobley and M. L. Clarke, *Chem. Commun.*, 2013, **49**, 3306; (*g*) J. F. Schneider, F. C. Falk, R. Fröhlich and

J. Paradies, *Eur. J. Org. Chem.*, 2010, 2265; (*h*) C. Beemelmanns, R. Husmann, D. K. Whelligan, S. Özçubukçu and C. Bolm, *Eur. J. Org. Chem.*, 2012, 3373; (*i*) D. Enders, M. Ludwig and G. Raabe, *Chirality*, 2012, **24**, 215; (*j*) S. Kitagaki, T. Ueda and C. Mukai, *Chem. Commun.*, 2013, **49**, 4030.

6 (*a*) S. Tanji, A. Ohno, I. Sato and K. Soai, *Org. Lett.*, 2001, **3**, 287; (*b*) S. Sugiyama, Y. Aoki and K. Ishii, *Tetrahedron: Asymmetry*, 2006, **17**, 2847; (*c*) D. S. Masterson and D. T. Glatzhofer, *J. Mol. Catal. A: Chem.*, 2000, **161**, 65; (*d*) C. Bolm and T. Kühn, *Synlett*, 2000, 899; (*e*) S. Banfi, A. Manfredi, F. Montanari, G. Pozzi and S. Quici, *J. Mol. Catal. A: Chem.*, 1996, **113**, 77.

7 (*a*) D. Enders, S. Noll and J. W. Bats, *Synlett*, 2005, 2679; (*b*) B. Jiang and X.-L. Zhao, *Tetrahedron: Asymmetry*, 2004, **15**, 1141; (*c*) L. Minuti, A. Taticchi and A. Marrocchi, *Tetrahedron: Asymmetry*, 2000, **11**, 4221; (*d*) J. J. P. Kramer, C. Yildiz, M. Nieger and S. Bräse, *Eur. J. Org. Chem.*, 2014, 1287; (*e*) D. C. Braddock, I. D. MacGilp and B. G. Perry, *J. Org. Chem.*, 2002, **67**, 8679.

8 (*a*) Y. Wang, H. Yuan, H. Lu and W.-H. Zheng, *Org. Lett.*, 2018, **20**, 2555; (*b*) M. Toda, Y. Inoue and T. Mori, *ACS Omega*, 2018, **3**, 22; (*c*) C. Braun, S. Bräse and L. L. Schafer, *Eur. J. Org. Chem.*, 2017, 1760; (*d*) G. Meyer-Eppler, R. Sure, A. Schneider, G. Schnakenburg, S. Grimme and A. Lützen, *J. Org. Chem.*, 2014, **79**, 6679; (*e*) D. Enders, S. Noll, G. Raabe and J. Runsink, *Synthesis*, 2008, 1288; (*f*) H. Hopf, W. Gruhn, D. G. Barrett, A. Gerdes, J. Hibner, J. Hucker, Y. Okamoto and Y. Kaida, *Chem. Ber.*, 1990, **123**, 841.

9 (*a*) K. Rossen, P. J. Pye, A. Maliakal and R. P. Volante, *J. Org. Chem.*, 1997, **62**, 6462; (*b*) M.-L. Delcourt, S. Turcaud, E. Benedetti and L. Micouin, *Adv. Synth. Catal.*, 2016, **358**, 1213; (*c*) M.-L. Delcourt, S. Felder, E. Benedetti and L. Micouin, *ACS Catal.*, 2018, **8**, 6612; (*d*) M.-L. Delcourt, S. Felder, S. Turcaud, C. H. Pollok, C. Merten, L. Micouin and E. Benedetti, *J. Org. Chem.*, 2019, **84**, 5369.

10 (*a*) P. Dorizon, C. Martin, J.-C. Daran, J.-C. Fiauda and H. B. Kagana, *Tetrahedron: Asymmetry*, 2001, **12**, 2625; (*b*) K. Akagawa, N. Nishi, I. Yoshikawa and K. Kudo, *Eur. J. Org. Chem.*, 2015, 5055.

11 For some reviews, see: (*a*) G. K. Friestad and A. K. Mathies, *Tetrahedron*, 2007, **63**, 2541; (*b*) C. S. Marques and A. J. Burke, *ChemCatChem*, 2011, **3**, 635; (*c*) S. Kobayashi, Y. Mori, J. S. Fossey and M. M. Salter, *Chem. Rev.*, 2011, **111**, 2626; (*d*) P. Tian, H.-Q. Dong and G.-Q. Lin, *ACS Catal.*, 2012, **2**, 95.

12 For some reviews, see: (*a*) Y.-W. Sun, P.-L. Zhu, Q. Xu and M. Shi, *RSC Adv.*, 2013, **3**, 3153; (*b*) M. Quan, L. Wu, G. Yang and W. Zhang, *Chem. Commun.*, 2018, **54**, 10394. For selected examples, see: (*c*) H. Dai and X. Lu, *Org. Lett.*, 2007, **9**, 3077; (*d*) H. Dai, M. Yang and X. Lu, *Adv. Synth. Catal.*, 2008, **350**, 249; (*e*) H. Dai and X. Lu, *Tetrahedron Lett.*, 2009, **50**, 3478; (*f*) G. Yang and W. Zhang, *Angew. Chem., Int. Ed.*, 2013, **52**, 7540; (*g*) M. Quan, G. Yang, F. Xie, I. D. Gridnev and W. Zhang, *Org. Chem. Front.*, 2015, **2**, 398; (*h*) Q. He, L. Wu, X. Kou, N. Butt, G. Yang and W. Zhang, *Org. Lett.*, 2016, **18**, 288; (*i*) C. Jiang, Y. Lu and T. Hayashi, *Angew. Chem., Int. Ed.*, 2014, **53**, 9936; (*j*) X. Gao, B. Wu, Z. Yan and Y.-G. Zhou, *Org. Biomol. Chem.*, 2016, **14**, 55; (*k*) Z. Yan, B. Wu, X. Gao and Y.-G. Zhou, *Chem. Commun.*, 2016, **52**, 10882; (*l*) Z.-B. Zhao, L. Shi, F.-J. Meng, Y. Li and Y.-G. Zhou, *Org. Chem. Front.*, 2019, **6**, 1572.

