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Efficient Enantioselective Synthesis of Oxahelicenes Using Redox/Acid Cooperative Catalysts

Makoto Sako,[†] Yoshiki Takeuchi,[†] Tetsuya Tsujihara,[‡] Junpei Kodera,[†] Tomikazu Kawano,[‡] Shinobu Takizawa,*[,†] and Hiroaki Sasai*[,†]

[†]The Institute of Scientific and Industrial Research (ISIR), Osaka University, Mihogaoka, Ibaraki-shi, Osaka 567-0047, Japan
[‡]Department of Medicinal and Organic Chemistry, School of Pharmacy, Iwate Medical University, Yahaba, Iwate 028-3694, Japan

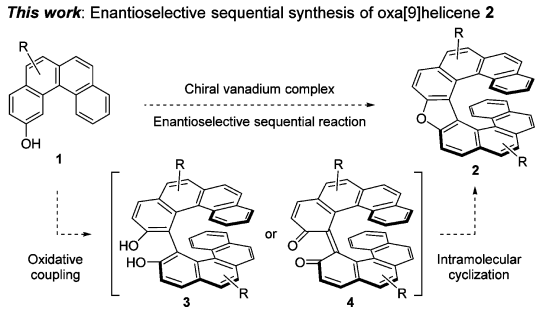
Supporting Information

ABSTRACT: An efficient and enantioselective synthesis of oxa[9]helicenes has been established via vanadium(V)-catalyzed oxidative coupling/intramolecular cyclization of polycyclic phenols. A newly developed vanadium complex cooperatively functions as both a redox and Lewis acid catalyst to promote the present sequential reaction and afford oxa[9]helicenes in good yields with up to 94% ee.

Helicenes are polycyclic aromatic compounds with non-planar screw-shaped skeletons formed from ortho-fused benzene or other aromatic rings. Optically active helicenes and other related helical molecules have received considerable attention as a result of their high potential[1] as chiral ligands,[1a] auxiliaries,[1b] organocatalysts,[1c] liquid crystals,[1d,e] and molecular motors.[1f] Helicene derivatives have classically been synthesized via photocyclization of stilbene units followed by dehydrogenation.[1g,2] This method generally affords trans/cis isomers and is difficult to apply to the asymmetric synthesis of helicene derivatives. Since Stará and Starý reported a synthesis of helicene-like molecules using transition-metal-catalyzed [2 + 2 + 2] cycloadditions of alkynes,[3a] cycloaddition methodologies have principally been utilized for the construction of helicene and helicene-like molecules;[3] however, syntheses of heterohelicenes, which have at least one heteroaromatic ring in the helical chain, and oxahelicenes based on furan rings in particular, are still scarce. In 2005, Nozaki reported the preparation of an optically active oxa[7]helicene via oxidative coupling of phenol derivatives catalyzed by an achiral Cu complex followed by optical resolution of the coupling product and Pd-catalyzed intramolecular cyclization.[4] Recently, Karikomi[5] and Bedekar[6] independently reported that oxa[9 or 11]helicene derivatives could be synthesized from π-expanded phenol derivatives in a few steps. Although the construction of oxahelicenes via oxidative coupling has been achieved, to our knowledge the catalytic and enantioselective preparation of their derivatives has not been reported.

Vanadium catalysis is intriguing from an environmental viewpoint because of the abundant natural availability of vanadium as well as the relatively low toxicity of this metal compared with other heavy metals.[7] The redox characteristics of vanadium complexes have been utilized for asymmetric reactions[8] including, for example, epoxidation,[8f] sulfoxidation,[8g] oxidative coupling of 2-naphthols,[8h,i] and oxidation of α-hydroxy carbonyl compounds.[8j] In addition, the Lewis acidity of vanadium complexes[9] can be used to promote Diels–Alder reactions,[9a] cyanations,[9b] ring opening of *meso*-epoxides,[9c] and Friedel–Crafts-type reactions.[9d] However, there are few reports describing the cooperative effect of these two properties in vanadium-catalyzed sequential reactions.[10] The enantioselective sequential reaction using a chiral vanadium complex with *tert*-butyl hydroperoxide as the primary oxidant was first reported by Toste[10a] in 2006, with further contributions by Liu[10b] and You.[10b,c] These groups succeeded in the development of both epoxidation reactions and ring-opening cascades. As part of our effort to explore chiral vanadium catalysis,[9d,11] we were interested in designing novel vanadium-mediated sequential reactions to access important structural motifs. We assumed that if the chiral vanadium complex could function as both a redox and Lewis acid catalyst for the coupling of 2-hydroxybenzo[*c*]phenanthrenes (**1**), oxa[9]helicenes (**2**) would be obtained in a single operation via aerobic oxidative coupling and subsequent Lewis acid-mediated intramolecular cyclization (Scheme 1).

Scheme 1. Synthesis of Oxahelicenes



We initially tested the reaction of **1a** (R = H)[12] with the chiral dinuclear vanadium complex (R_a,*S*,*S*)-**5**, which efficiently catalyzes the enantioselective oxidative coupling reaction of 2-naphthols.[11b] Among the reaction conditions screened (solvent, temperature, and co-oxidant; see Table S1), we found that the desired oxa[9]helicene **2a** was formed in 81% yield with 58% ee at 60 °C in CCl_4 under a molecular oxygen atmosphere (Table 1, entry 1). Some starting material **1a** remained after the reaction period, but no diol **3a** or quinone **4a** was detected. During further investigation of suitable vanadium complexes, we found that the

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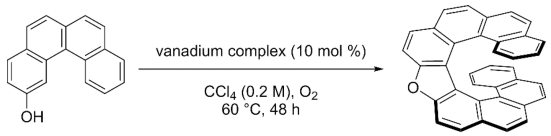
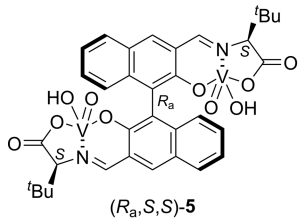
Table 1. Screening of Chiral Vanadium Complexes[a]



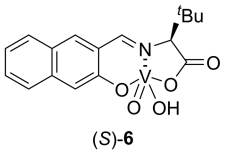
1a 2a

entry	catalyst	yield (%)[b]	ee (%)[c]
1[d]	(R_a,S,S)-**5**	81	58
2	(S)-**6**	61	19
3	(R_a,S)-**7**	71	60
4	(R_a,S)-**8**	72	58
5	(R_a,S)-**9**	87	58
6	(S_a,S)-**9**	91	41
7	(R_a,S)-**10**	90	41
8	(R_a,S)-**11**	86	66
9	(R_a,S)-**12**	95	75
10	(R_a,S)-**13**	52	42
11	(R_a,S)-**14**	99	75
12[e]	(R_a,S)-**14**	95	78 (99[f])

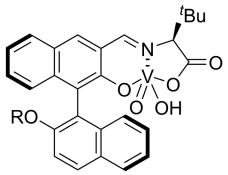
[a]The reaction of **1a** (0.04 mmol) with 10 mol % vanadium complex (0.004 mmol) was carried out in CCl_4 (0.2 mL) at 60 °C under O_2 (1 atm). [b]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined using HPLC (DAICEL CHIRALPAK AD-H). [d]5 mol % (R_a,S,S)-**5** (0.002 mmol), 72 h. [e]50 °C. [f]After a single recrystallization.



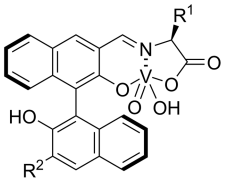
(R_a,S,S)-**5**



(S)-**6**



(R_a,S)-**7** (R = Me)
(R_a,S)-**8** (R = ^{i}Pr)
(R_a,S)-**9** (R = H)



(R_a,S)-**10** (R^1 = Bn, R^2 = H)
(R_a,S)-**11** (R^1 = ^{t}Bu, R^2 = Ph)
(R_a,S)-**12** (R^1 = ^{t}Bu, R^2 = 3,5-$Me_2C_6H_3$)
(R_a,S)-**13** (R^1 = ^{t}Bu, R^2 = 9-anthryl)
(R_a,S)-**14** (R^1 = ^{t}Bu, R^2 = 3,5-$Ph_2C_6H_3$)

mononuclear vanadium complex (S)-**6** also promoted this sequential process. The reaction employing catalyst (S)-**6**, which possesses a naphthyl skeleton, yielded **2a** in 61% yield with 19% ee (entry 2); catalysts (R_a,S)-**7** and (R_a,S)-**8**, both of which bear a binaphthyl unit, resulted in an improved yield and ee of helicene **2a** (entries 3 and 4). Catalyst (R_a,S)-**9**, which has a free hydroxy group on the binaphthyl unit, increased the chemical yield of **2a** without decreasing the ee (87% yield, 58% ee; entry 5). The phenolic hydroxy group in the catalyst could cooperatively activate **1a** with the vanadium metal to accelerate the present sequential reaction.[13] The diastereomeric complex (S_a,S)-**9** was found to be a mismatched catalyst, affording **2a** with lower enantioselectivity (entry 6). Catalyst (R_a,S)-**10**, having a benzyl group instead of a *tert*-butyl group on the amino acid unit, did not show any improvement (entry 7). Among the catalysts that were screened, the presence of a substituent at the 3′ position of the binaphthyl unit proved effective in improving the enantioselectivity. The phenyl-substituted catalyst (R_a,S)-**11** afforded **2a** in 86% yield with 66% ee (entry 8). This result prompted us to examine the effect of substituents at the 3′ position of the binaphthyl moiety. The 3,5-dimethylphenyl-substituted catalyst (R_a,S)-**12** increased the chemical yield and ee to 95% and 75%, respectively (entry 9), while the 9-anthryl-substituted catalyst (R_a,S)-**13** resulted in a decreased yield and ee, probably as a result of steric hindrance between the substituents (entry 10). When the 3,5-diphenylphenyl-substituted catalyst (R_a,S)-**14** was employed, **2a** was obtained in quantitative yield with 75% ee (entry 11). Finally, **2a** was obtained in 95% yield with 78% ee in the reaction that employed 10 mol % catalyst (R_a,S)-**14** at 50 °C (entry 12).

Furthermore, optically pure **2a** was readily accessible by single recrystallization of the enantioenriched product from CH_2Cl_2 and hexane. The optical rotation value of optically pure **2a** showed the characteristic value $[\alpha]_D^{19} = -2647$ (c 0.32, $CHCl_3$). X-ray crystallographic analysis of **2a** unambiguously demonstrated its helical structure, and the absolute configuration of **2a** was definitely determined to be *M* on the basis of the Flack parameter (Figure 1).

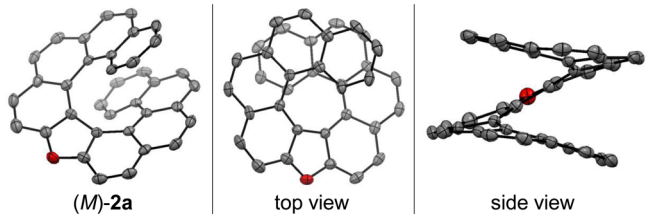


Figure 1. X-ray structure of (*M*)-oxa[9]helicene (**2a**) with ellipsoids at 50% probability. H atoms have been omitted for clarity. Only one of the two independent molecules present in the unit cell is shown.

With the optimal conditions in hand, the substrate scope and limitations of the reaction were investigated using analogues of **1** containing various substituents (Table 2). Phenyl-, *p*-tolyl-, and *p*-fluorophenyl-substituted substrates (**1b–d**, respectively) were converted to the corresponding products **2b–d** in good yields with ca. 50% ee. Alkyl-substituted substrates, such as those with methyl or hexyl groups at the 6-position, afforded coupling products **2e** and **2f** in moderate yields with 88% and 76% ee, respectively. In the coupling reaction of the bromo-substituted substrate **1g** at 60 °C for 72 h, the desired dibrominated helicene **2g** was obtained in 56% yield with 94% ee. We next examined the effect of substitution at positions 9–12 on the terminal aromatic ring. The reaction of **1h** smoothly proceeded to provide **2h** in 68% yield with 80% ee. In contrast, substrate **1i** showed low reactivity, affording **2i** in only 32% yield with 30% ee. When 10 mol % TMSCl[8i] was added to the reaction of **1i** at 60 °C, an improvement in both the yield and ee of **2i** was observed (84% yield, 60% ee). The reaction of **1j**, with a methyl group at the 12 position, did not form the desired product, probably as a result of steric hindrance during the coupling.

To further demonstrate the introduction of substituents on oxa[9]helicenes **2**, several transformations were carried out (Scheme 2). Oxa[9]helicene (**2a**) could be further modified by regioselective bromination; bromination was conducted using 1.05 or 2.1 equiv of pyridinium tribromide ($PyHBr_3$) to yield mono- and dibrominated oxa[9]helicenes **2k** and **2l**, respectively, in good yields (Scheme 2a). Pd-catalyzed Suzuki–Miyaura coupling of dibrominated oxa[9]helicene **2g** with phenylboronic acid ($PhB(OH)_2$) smoothly proceeded to give **2b** in 81% yield with retention of the enantiomeric excess (Scheme 2b).

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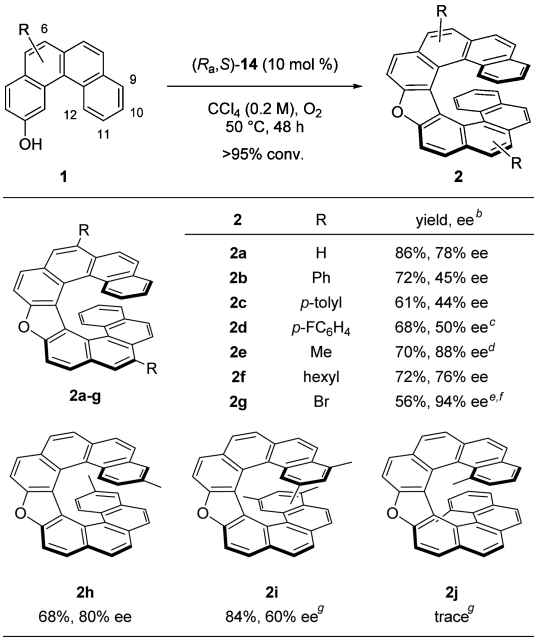
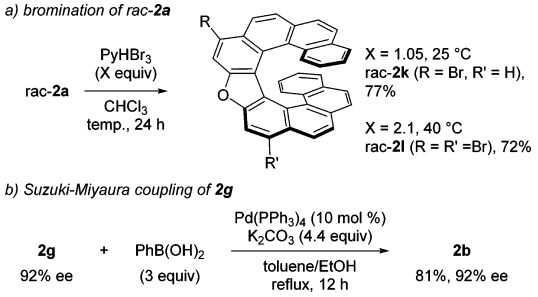
Table 2. Substrate Scope and Limitations[a]



2	R	yield, ee[b]
2a	H	86%, 78% ee
2b	Ph	72%, 45% ee
2c	*p*-tolyl	61%, 44% ee
2d	*p*-FC_6H_4	68%, 50% ee[c]
2e	Me	70%, 88% ee[d]
2f	hexyl	72%, 76% ee
2g	Br	56%, 94% ee[e,f]

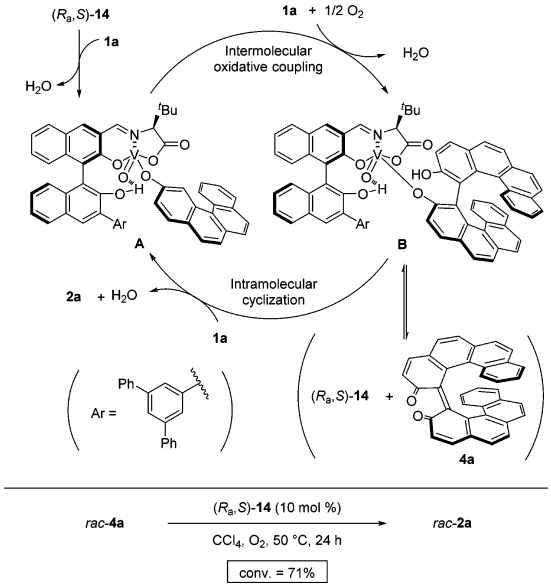
[a]The reaction of **1** (0.04 mmol) with 10 mol % catalyst (R_a,*S*)-**14** (0.004 mmol) was carried out in CCl_4 (0.2 mL) at 50 °C under O_2 (1 atm) for 48 h. [b]Yields of isolated products; ee values were determined by HPLC (DAICEL CHIRALPAK AD-H). [c]72 h. [d]94% NMR yield. [e]60 °C, 72 h. [f]61% NMR yield. [g]60 °C, 10 mol % TMSCl.

Scheme 2. Synthetic Transformations



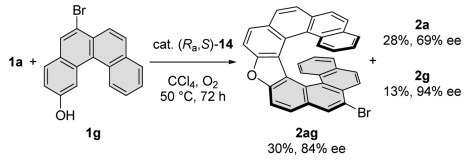
To gain insight into the reaction mechanism, the reaction order with respect to the vanadium catalyst was investigated by calculating the initial rate of the reaction using catalyst loadings of 5, 10, and 15 mol %; the reaction was found to be first order in catalyst (R_a,*S*)-**14** (see the Supporting Information (SI)). This result rules out a dual activation mechanism involving radical–radical coupling mediated by two molecules of the vanadium complex.[11,14] The present oxidative coupling likely occurs through a radical–anion coupling with one molecule of the vanadium complex.[15] A plausible catalytic cycle for the sequential synthesis of oxa[9]helicenes is shown in Scheme 3. The reaction of the mononuclear vanadium(V) complex (R_a,*S*)-**14** with substrate **1a** generates intermediate **A**, which then undergoes an intermolecular coupling with another molecule of **1a** after a single electron transfer to a vanadium(V) species. This is followed by oxidation of vanadium(IV) by O_2 to form intermediate **B**. Finally, intramolecular cyclization assisted by the Lewis acidity of vanadium(V) affords the desired product **2a**, and intermediate **A** is regenerated. It is likely that the hydroxy group on the binaphthyl ligand in the vanadium complex increases the Lewis acidity of vanadium metal through an

Scheme 3. Plausible Catalytic Cycle



intramolecular hydrogen bond in intermediates **A** and **B**. When racemic quinone derivative **4a**[5a] was treated with 10 mol % catalyst (R_a,*S*)-**14**, **2a** was produced in racemic form with 71% conversion; the remaining **4a** was also racemic (Scheme 3). Kinetic resolution was not observed in the reaction of **4a** to yield **2a**, which implies that the enantiodetermining step is the oxidative coupling step of intermediate **A** to intermediate **B**. Quinone **4a** might be outside of the catalytic cycle and in an equilibrium with intermediate **B**. The radical–anion coupling mechanism is also supported by the fact that treatment of electron-rich **1a** (0.02 mmol) and electron-poor **1g** (0.02 mmol) with (R_a,*S*)-**14** (0.004 mmol) afforded a mixture of oxa[9]-helicenes, including the heterocoupling product **2ag** (30% yield, 84% ee) and the homocoupling products **2a** (28% yield, 69% ee) and **2g** (13% yield, 94% ee) (Scheme 4), whereas the radical–radical coupling would preferentially form **2a**.[14−16]

Scheme 4. Oxidative Heterocoupling of 1a with 1g[a]



[a]The reaction of **1a** (0.02 mmol) and **1g** (0.02 mmol) with catalyst (R_a,*S*)-**14** (0.004 mmol) was carried out in CCl_4 (0.2 mL) at 50 °C under O_2 (1 atm) for 72 h.

In conclusion, we have developed an efficient and enantioselective sequential synthesis of oxa[9]helicenes catalyzed by a newly developed chiral vanadium complex. In this process, the vanadium complex works as both a redox catalyst and a Lewis acid catalyst, allowing the sequential reaction via an oxidative coupling/intramolecular cyclization sequence. Additional investigations into the reaction mechanism and the substrate generality in other heterocouplings are now in progress. Furthermore, synthetic studies on other heterohelicenes containing nitrogen, silicon, and/or sulfur are in process in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07424.

Procedures and characterization data (PDF)
X-ray data for (*M*)-**2a** (CCDC 1493624) (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*sasai@sanken.osaka-u.ac.jp
*taki@sanken.osaka-u.ac.jp

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Selected reports: Ligand: (a) Aillard, P.; Voituriez, A.; Dova, D.; Cauteruccio, S.; Licandro, E.; Marinetti, A. *Chem. - Eur. J.* **2014**, *20*, 12373. Auxiliary: (b) Ben Hassine, B.; Gorsane, M.; Pecher, J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1986**, *95*, 557. Organocatalyst: (c) Ben Hassine, B.; Gorsane, M.; Geerts-Evrard, F.; Pecher, J.; Martin, R. H.; Castelet, D. *Bull. Soc. Chim. Belg.* **1986**, *95*, 547. Liquid crystal: (d) Saito, N.; Kanie, K.; Matsubara, M.; Muramatsu, A.; Yamaguchi, M. *J. Am. Chem. Soc.* **2015**, *137*, 6594. (e) Miah, M. J.; Shahabuddin, M.; Karikomi, M.; Salim, M.; Nasuno, E.; Kato, N.; Iimura, K. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 203. Molecular motor: (f) Chen, W.-C.; Lee, Y.-W.; Chen, C.-T. *Org. Lett.* **2010**, *12*, 1472. Recent reviews: (g) Shen, Y.; Chen, C.-F. *Chem. Rev.* **2012**, *112*, 1463. (h) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 1051. (i) Aillard, P.; Voituriez, A.; Marinetti, A. *Dalton Trans.* **2014**, *43*, 15263. (j) Shigeno, M.; Kushida, Y.; Yamaguchi, M. *Chem. Commun.* **2016**, *52*, 4955.

(2) Selected reviews: (a) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 968. (b) Gingras, M.; Félix, G.; Peresutti, R. *Chem. Soc. Rev.* **2013**, *42*, 1007.

(3) Recent reviews: (a) Stará, I. G.; Starý, I. *Sci. Synth.* **2010**, *45b*, 885. (b) Tanaka, K. Synthesis of Helically Chiral Aromatic Compounds via [2 + 2 + 2] Cycloaddition. In *Transition-Metal-Mediated Aromatic Ring Construction*; Tanaka, K., Ed.; Wiley: Hoboken, NJ, 2013; p 281. (c) Tanaka, K.; Kimura, Y.; Murayama, K. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 375. Recent reports: (d) Shibata, T.; Uchiyama, T.; Yoshinami, Y.; Takayasu, S.; Tsuchikama, K.; Endo, K. *Chem. Commun.* **2012**, *48*, 1311. (e) Sawada, Y.; Furumi, S.; Takai, A.; Takeuchi, M.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.* **2012**, *134*, 4080. (f) Jančařík, A.; Rybáček, J.; Cocq, K.; Vacek Chocholoušová, J.; Vacek, J.; Pohl, R.; Bednárová, L.; Fiedler, P.; Císařová, I.; Stará, I. G.; Starý, I. *Angew. Chem., Int. Ed.* **2013**, *52*, 9970. (g) Heller, B.; Hapke, M.; Fischer, C.; Andronova, A.; Starý, I.; Stará, I. G. *J. Organomet. Chem.* **2013**, *723*, 98. (h) Šámal, M.; Chercheja, S.; Rybáček, J.; Vacek Chocholoušová, J.; Vacek, J.; Bednárová, L.; Šaman, D.; Stará, I. G.; Starý, I. *J. Am. Chem. Soc.* **2015**, *137*, 8469. (i) Tsujihara, T.; Inada-Nozaki, N.; Takehara, T.; Zhou, D.-Y.; Suzuki, T.; Kawano, T. *Eur. J. Org. Chem.* **2016**, DOI: 10.1002/ejoc.201600677.

(4) Nakano, K.; Hidehira, Y.; Takahashi, K.; Hiyama, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7136.

(5) (a) Karikomi, M.; Yamada, M.; Ogawa, Y.; Houjou, H.; Seki, K.; Hiratani, K.; Haga, K.; Uyehara, T. *Tetrahedron Lett.* **2005**, *46*, 5867. (b) Salim, M.; Akutsu, A.; Kimura, T.; Minabe, M.; Karikomi, M. *Tetrahedron Lett.* **2011**, *52*, 4518. (c) Salim, M.; Ubukata, H.; Kimura, T.; Karikomi, M. *Tetrahedron Lett.* **2011**, *52*, 6591. (d) Salim, M.; Kimura, T.; Karikomi, M. *Heterocycles* **2013**, *87*, 547. (e) Karikomi, M.; Toda, M.; Sasaki, Y.; Shibuya, M.; Yamada, K.; Kimura, T.; Minabe, M.; Hiratani, K. *Tetrahedron Lett.* **2014**, *55*, 7099.

(6) Sundar, M. S.; Bedekar, A. V. *Org. Lett.* **2015**, *17*, 5808.

(7) Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 148.

(8) Reviews: (a) Bolm, C. *Coord. Chem. Rev.* **2003**, *237*, 245. (b) Volcho, K. P.; Salakhutdinov, N. F. *Russ. Chem. Rev.* **2009**, *78*, 457. (c) Plass, W. *Coord. Chem. Rev.* **2011**, *255*, 2378. (d) Pellissier, H. *Coord. Chem. Rev.* **2015**, *284*, 93. (e) Takizawa, S.; Gröger, H.; Sasai, H. *Chem. - Eur. J.* **2015**, *21*, 8992. Selected examples (pioneering work): Epoxidation: (f) Michaelson, R. C.; Palermo, R. E.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 1990. Sulfoxidation: (g) Nakajima, K.; Kojima, M.; Fujita, J. *Chem. Lett.* **1986**, *15*, 1483. Oxidative coupling of 2-naphthols: (h) Hon, S.-W.; Li, C.-H.; Kuo, J.-H.; Barhate, N. B.; Liu, Y.-H.; Wang, Y.; Chen, C.-T. *Org. Lett.* **2001**, *3*, 869. (i) Chu, C.-Y.; Hwang, D.-R.; Wang, S.-K.; Uang, B.-J. *Chem. Commun.* **2001**, 980. Oxidation of α-hydroxy carbonyl compounds: (j) Radosevich, A. T.; Musich, C.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 1090.

(9) Selected examples (pioneering work): Diels–Alder reaction: (a) Togni, A. *Organometallics* **1990**, *9*, 3106. Cyanation of aldehydes: (b) Belokon', Y. N.; North, M.; Parsons, T. *Org. Lett.* **2000**, *2*, 1617. Ring opening of *meso*-epoxides: (c) Sun, J.; Dai, Z.; Yang, M.; Pan, X.; Zhu, C. *Synthesis* **2008**, *2008*, 2100. Friedel–Crafts-type reaction: (d) Takizawa, S.; Arteaga, F. A.; Yoshida, Y.; Kodera, J.; Nagata, Y.; Sasai, H. *Dalton Trans.* **2013**, *42*, 11787.

(10) (a) Blanc, A.; Toste, F. D. *Angew. Chem., Int. Ed.* **2006**, *45*, 2096. (b) Han, L.; Liu, C.; Zhang, W.; Shi, X.-X.; You, S.-L. *Chem. Commun.* **2014**, *50*, 1231. (c) Han, L.; Zhang, W.; Shi, X.-X.; You, S.-L. *Adv. Synth. Catal.* **2015**, *357*, 3064.

(11) (a) Takizawa, S. *Chem. Pharm. Bull.* **2009**, *57*, 1179. (b) Sako, M.; Takizawa, S.; Yoshida, Y.; Sasai, H. *Tetrahedron: Asymmetry* **2015**, *26*, 613.

(12) A new synthetic method for **1a** was developed (see the SI) because the synthesis reported by Wilds and Werth gave a low overall yield. See: Wilds, A. L.; Werth, R. G. *J. Org. Chem.* **1952**, *17*, 1154.

(13) Selected reviews and papers: (a) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1236. (b) Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2000**, *122*, 12021. (c) Okino, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12672. (d) Chu, C.-Y.; Uang, B.-J. *Tetrahedron: Asymmetry* **2003**, *14*, 53. (e) Ma, J.-A.; Cahard, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4566. (f) Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1566. (g) Uraguchi, D.; Terada, M. *J. Am. Chem. Soc.* **2004**, *126*, 5356. (h) Matsui, K.; Takizawa, S.; Sasai, H. *J. Am. Chem. Soc.* **2005**, *127*, 3680. (i) Akiyama, T.; Itoh, J.; Fuchibe, K. *Adv. Synth. Catal.* **2006**, *348*, 999. (j) Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713. (k) Paull, D. H.; Abraham, C. J.; Scerba, M. T.; Alden-Danforth, E.; Lectka, T. *Acc. Chem. Res.* **2008**, *41*, 655. (l) Sodeoka, M.; Hamashima, Y. *Chem. Commun.* **2009**, 5787. (m) Terada, M. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 101. (n) Rueping, M.; Kuenkel, A.; Atodiresei, I. *Chem. Soc. Rev.* **2011**, *40*, 4539. (o) Park, J.; Hong, S. *Chem. Soc. Rev.* **2012**, *41*, 6931. (p) Sohtome, Y.; Nagasawa, K. *Chem. Commun.* **2012**, *48*, 7777. (q) Brière, J.-F.; Oudeyer, S.; Dalla, V.; Levacher, V. *Chem. Soc. Rev.* **2012**, *41*, 1696. (r) Liu, F. *Chirality* **2013**, *25*, 675. (s) Matsunaga, S.; Shibasaki, M. *Chem. Commun.* **2014**, *50*, 1044. (t) Chen, D.-F.; Han, Z.-Y.; Zhou, X.-L.; Gong, L.-Z. *Acc. Chem. Res.* **2014**, *47*, 2365. (u) Kim, H.; Oh, K. *Synlett* **2015**, *26*, 2067.

(14) Guo, Q.-X.; Wu, Z.-J.; Luo, Z.-B.; Liu, Q.-Z.; Ye, J.-L.; Luo, S.-W.; Cun, L.-F.; Gong, L.-Z. *J. Am. Chem. Soc.* **2007**, *129*, 13927.

(15) (a) Egami, H.; Matsumoto, K.; Oguma, T.; Kunisu, T.; Katsuki, T. *J. Am. Chem. Soc.* **2010**, *132*, 13633. (b) Libman, A.; Shalit, H.; Vainer, Y.; Narute, S.; Kozuch, S.; Pappo, D. *J. Am. Chem. Soc.* **2015**, *137*, 11453.

(16) From cyclic voltammetry (CH_2Cl_2/MeCN (10:1 v/v) with Bu_4NPF_6, ν = 100 mV s^{-1}, vs Fc/Fc^+): $E_{1a(ox)}$ = 1.04 V; $E_{1g(ox)}$ = 0.84 V.

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