JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

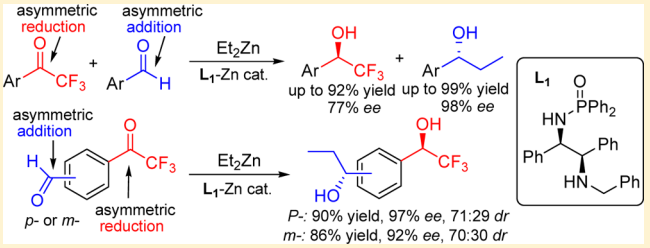
Chemo- and Enantioselective Addition and β-Hydrogen Transfer Reduction of Carbonyl Compounds with Diethylzinc Reagent in One Pot Catalyzed by a Single Chiral Organometallic Catalyst

Huayin Huang,[†] Hua Zong,[†] Guangling Bian, and Ling Song*

The Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

Supporting Information

ABSTRACT: Using a single chiral phosphoramide−Zn(II) complex as the catalyst, the asymmetric β-H transfer reduction of aromatic α-trifluoromethyl ketones and enantioselective addition of aromatic aldehydes with Et_2Zn in one pot were successfully realized, affording the corresponding additive products of secondary alcohols in high yields (up to 99%) with excellent enantioselectivities (up to 98% *ee*) and the reduction products of α-trifluoromethyl alcohols in good to excellent yields with up to 77% *ee*.

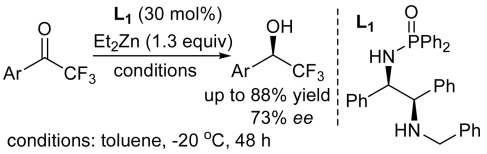


Asymmetric reactions promoted by chiral organometallic catalysts have provided us with powerful transformations for the preparation of optically active compounds.[1−5] In general, one catalyst is commonly used to only catalyze one reaction. However, the increasing demand for efficient synthetic processes drives the development of organometallic catalysts that are capable of catalyzing multiple reactions with distinct mechanisms in one pot.[6−17] Since the chiral environments suitable for two distinct organometallic catalyzed asymmetric reactions are generally different, the development of multiple reactions in one pot with a single organometallic catalyst is highly challenging.[14−17]

In 2000, Pu and co-workers[14] reported their pioneering work on a poly(BINOL−BINAP)ruthenium complex as a single catalyst in a tandem catalytic enantioselective ethylation and asymmetric hydrogenation of dicarbonyl compounds to generate chiral diols, affording the corresponding products with excellent yields, *ee* and *de* values. In 2002, Shibasaki and co-workers[15] reported a successful example of asymmetric sequential cyanation−nitroaldol reaction using a single catalyst of multifunctional [YLi_3{tris(binaphthoxide)}]. In 2003, Ding and co-workers[16,17] used a 1,1′-bi-2-naphthol (BINOL-Zn) complex as a single catalyst to promote an asymmetric hetero-Diels−Alder reaction and enantioselective ethylation in one pot with high efficiency and excellent stereoselectivity.

Chiral 1,2-diamino phosphoramide ligands are very efficient in the catalytic asymmetric addition reactions of organozinc reagents to aldedhydes and ketones or organocatalyzed asymmetric reactions.[18−32] Our recent research findings showed that diethylzinc reagent could be used as a hydrogen source for the asymmetric β-H reduction of α-trifluoromethyl ketones in the presence of a catalytic ammount of chiral 1,2-diamino phosphoramide ligand $\mathbf{L_1}$, affording the corresponding reduction product with up to 88% yield and 73% enantioselectivity (Scheme 1).[33] As an effort to explore the application of chiral phosphoramide-Zn(II) catalyzed asymmetric reactions, we herein report the one-pot catalytic asymmetric ethylation and enantioslective β-H transfer reduction of carbonyl compounds with a diethylzinc reagent using phosphoramide $\mathbf{L_1}$ as a single chiral ligand.

Scheme 1. Catalytic Asymmetric β-Hydrogen Transfer Reduction of α-Trifluoromethyl Aromatic Ketones with Diethylzinc Reagent Using $\mathbf{L_1}$ as the Chiral Ligand



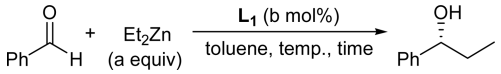
To carry out two distinct asymmetric reactions in one pot, finding reaction conditions that are suitable for both reactions is the key point. With the developed reaction conditions for catalytic asymmetric β-hydrogen transfer reduction reaction between α-trifluoroacetophenone and a diethylzinc reagent shown in Scheme 1 in hand, we first investigated if the same reaction conditions could be used for the asymmetric addition of a diethylzinc reagent to benzaldehyde. The results are listed in Table 1.

To our delight, chiral ligand $\mathbf{L_1}$ was found to be highly efficient in the asymmetric addition reaction of diethylzinc reagent to benzaldehyde. Upon changing the amount of the diethylzinc reagent, the loading of chiral ligand $\mathbf{L_1}$ and reaction temperature had little effect on enantioselectivity (Table 1,

Received: August 12, 2015
Published: November 18, 2015

DOI: 10.1021/acs.joc.5b01871
J. Org. Chem. 2015, 80, 12614−12619

Table 1. Catalytic Asymmetric Addition of Diethylzinc Reagent to Benzaldehyde Using L_1 as the Chiral Ligand[a]



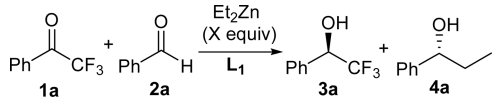
entry	*a*	*b*	temp	time	yield[b]	*ee*[c]
1	1.3	10	0 °C−rt	3 h	92%	96%
2	2.0	10	0 °C−rt	3 h	98%	96%
3	3.0	10	0 °C−rt	3 h	99%	97%
4	1.3	10	0 °C	6 h	96%	96%
5	1.3	10	−20 °C	12 h	68%	96%
6	1.3	30	−20 °C	12 h	97%	98%

[a]Unless otherwise noted, all reactions were carried out with benzaldehyde in 1 mmol scale. [b]Isolated yields. [c]Determined by chiral GC analysis.

entries 1−5). The optimized reaction conditions for the asymmetric β-hydrogen reduction reaction between α-trifluoromethylketone and the diethylzinc reagent were also suitable for the asymmetric ethylation of benzaldehyde with the diethylzinc reagent, providing the corresponding addition product with 97% yield and 98% *ee* (Table 1, entry 6).

On the basis of the above results, we next explored the possibility of carrying out the one-pot asymmetric β-H transfer reduction of α-trifluoromethyl ketone **1a** and enantioselective ethylation of benzaldehyde **2a** with diethylzinc reagent in the presence of L_1. The results are listed in Table 2.

Table 2. Catalytic Asymmetric β-H Transfer Reduction of Trifluoroacetophenone and Catalytic Asymmetric Addition of Diethylzinc Reagent to Benzaldehyde Using L_1 as the Chiral Ligand[a]

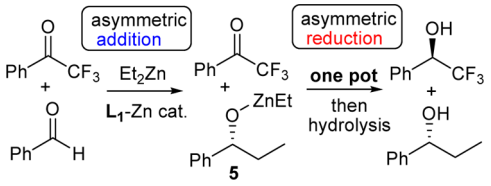


		3a		4a	
entry	*X*	yield[b]	*ee*[c]	yield[b]	*ee*[c]
1	2.6	91%	66%	99%	98%
2	3	89%	27%	97%	95%
3	2.0	67%	65%	97%	95%
4	1.3	trace	–	89%	96%

[a]Unless otherwise noted, L_1 (30 mol %), α-fluorolated ketone (1 mmol), and aldehyde (1 mmol) were used; all reactions were carried out at −20 °C for 48 h in toluene. [b]Isolated yields. [c]Determined by chiral GC analysis.

Because each of the two asymmetric reactions needs 1.3 equiv of the diethylzinc reagent respectively, we first used 2.6 equiv of the diethylzinc reagent for the one-pot reaction. Under optimized conditions, addition product **4a** was obtained with excellent yield (up to 99%) and *ee* (up to 98%), while reduction product **3a** was afforded with a 91% yield and 66% enantioselectivity (Table 2, entry 1). By increasing the use of the diethylzinc reagent, the addition product was obtained with almost the same level of yield and *ee*, but the enantioselectivity of the reduction product decreased significantly (Table 2, entry 2). For the asymmetric ethylation reaction, the addition reaction between benzylaldehyde and the diethylzinc reagent is very slow in the absence of the chiral ligand.[34−39] However, for the asymmetric β-hydrogen transfer reduction, the diethylzinc reagent can reduce the α-trifluoromethyl ketone without the chiral ligand.[40−45] Therefore, an excessive amount of the diethylzinc reagent has a great influence on the enantioselectivity of the asymmetric β-hydrogen transfer reduction while it has little effect on the asymmetric ethylation. When 2.0 equiv of the diethylzinc reagent was used, the yield of the reduction product was only 67% with 65% *ee* (Table 2, entry 3). Further decreasing the amount of diethylzinc reagent to 1.3 equiv only afforded the addition product with an 89% yield and 96% *ee* (Table 2, entry 4). These results indicated that the diethylzinc reagent first reacted with benzaldehyde to form addition product **5** in the presence of L_1-Zn and then reacted with α-trifluoromethyl ketone to form the reduction product in one pot (Scheme 2).

Scheme 2. L_1-Zn Catalyzed Two Asymmetric Reactions in One Pot

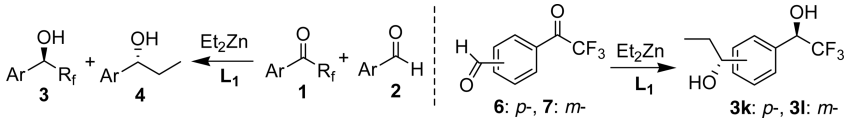


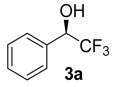
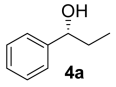
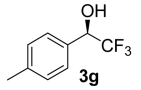
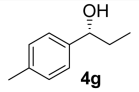
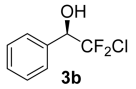
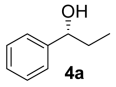
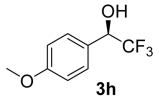
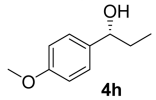
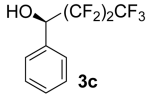
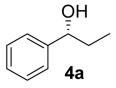
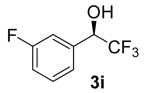
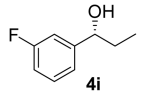
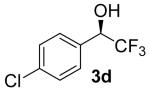
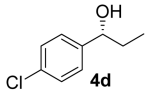
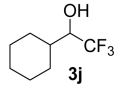
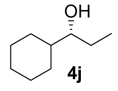
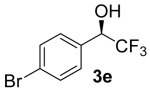
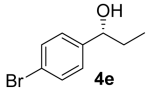
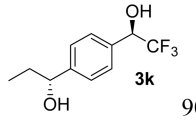
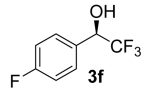
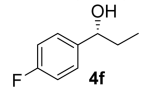
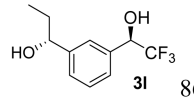
To examine the effectiveness of the developed one-pot catalytic asymmetric β-H transfer reduction and enantioselective addition reaction system, various 1:1 mixtures of aldehydes and α-fluoro-contained ketones were used as the substrates. The results are listed in Table 3.

When this protocol was applied for the asymmetric addition of benzaldehyde and β-H transfer reduction of α-fluorolated aromatic ketones (Table 3, entries 1−3), the corresponding addition products were obtained with excellent yields and *ee* values. If an R_f group was CF_2Cl, the corresponding reduction product was afforded with 77% *ee* and 90% yield. If the R_f group was $(CF_2)_2CF_3$, the *ee* value of the reduction product was decreased to 46% with an 81% yield. High yields (up to 98%) and *ee* values (up to 98%) of the corresponding addition alcohol products were obtained with electron-rich and electron-deficient substrates, and the reduction products could also be afforded with high yields and moderate to good enantioselectivities (Table 3, entries 4−9). When a 1:1 ratio of cyclohexanecarbaldehyde and 1-cyclohexyl-2,2,2-trifluoroethane-1-one was used as the substrates, the aliphatic addition product could be obtained with an 82% yield and 74% *ee*, but the aliphatic reduction product was obtained in 65% yield without any enantioselectivity (0% *ee*, entry 10). In the end, we applied the optimized catalytic system to investigate the two distinct asymmetric reactions of aromatic compounds **6** and **7** containing one aldehyde carbonyl group and one trifluoromethyl carbonyl group in the same molecule. As shown in entry 11 of Table 3, for compound **6** (aldehyde carbonyl group is at the para position of trifluoromethyl carbonyl group), the asymmetric addition of the aldehyde carbonyl group and reduction of the trifluoromethyl carbonyl group were carried out to give the desired diol product in 90% yield and 97% *ee* with a 71:29 *dr* value. When the aldehyde carbonyl group is at the meta position of the trifluoromethyl carbonyl group as shown in compound **7**, the corresponding diol product could be obtained with an 86% yield, 92% *ee*, and a 70:30 *dr* value (entry 12). The configurations of two chiral centers in products **3k** and **3l** were assigned to be *R* and *R* as shown in entries 11 and 12 of Table 3 on the basis of the results obtained using

DOI: 10.1021/acs.joc.5b01871
J. Org. Chem. 2015, 80, 12614−12619

Table 3. Catalytic Asymmetric β-H Transfer Reduction of α-Fluoro-Contained Ketones and Catalytic Asymmetric Addition of Diethylzinc Reagent to Aldehydes in One Pot Using L_1 as the Chiral Ligand[a]



Entry	yield[b] (ee[c]) of 3	yield[b] (ee[c]) of 4	Entry	yield[b] (ee[c]) of 3	yield[b] (ee[c]) of 4
1	 91% (66%)	 99%(98%)	7	 82% (61%)	 87% (96%)
2	 90% (77%)	 99% (97%)	8	 75% (52%)	 93% (92%)
3	 81% (46%)	 98% (98%)	9	 94% (60%)	 97% (98%)
4	 87% (64%)	 95% (94%)	10[d]	 65% (0%)	 82% (74%)
5	 92% (52%)	 98% (93%)	11	 90% (97%), 71: 29 *dr*[c]	
6	 81% (59%)	 98% (97%)	12	 86% (92%), 70: 30 *dr*[c]	

[a]Unless otherwise noted, L_1 (30 mol %), Et_2Zn (2.6 equiv), α-fluorolated ketone (1 mmol), and aldehyde (1 mmol) were used; all reactions were carried out at −20 °C for 48 h in toluene. [b]Isolated yields. [c]Determined by chiral GC or HPLC analysis. [d]Conducted at 0 °C.

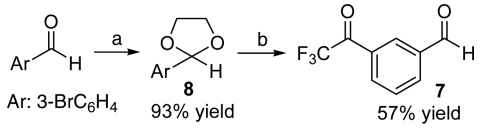
benzaldehyde and trifluoroacetophenone as substrates mentioned above.

In summary, we have found that chiral 1,2-amino phosphoramide ligand L_1 is efficient in both the asymmetric β-H transfer reduction of α-trifluoro ketones and enantioselective ethylation of aldehydes with a diethylzinc reagent under the same reaction conditions. Our investigation has demonstrated the ability of a single organometallic catalyst to promote two distinct asymmetric reactions with a single reagent in one pot, which might provide the possibility for a more efficient and environmentally benign synthesis of optically active complex molecules.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all experiments were carried out under an atmosphere of dry nitrogen with magnetic stirring. All solvents were purified and dried prior to use according to literature.[46] All other commercial reagents were used as received without further purification unless otherwise stated. ^1H (NMR 400 MHz), ^{13}C (NMR 100 MHz), and ^{19}F (NMR 376 MHz) spectra were recorded in $CDCl_3$ solutions using a 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm, δ) relative to residual $CDCl_3$ (δ 7.26 for ^1H NMR), or $CDCl_3$ (δ 77.0 for ^{13}C NMR). Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and brs (broad singlet). Optical rotations were measured on a polarimeter and reported as follows: $[\alpha]_D^T$ (*c* g/100 mL, solvent). The *ee* values of the products were determined using chiral HPLC with an OD-H column or chiral GC with a Chirasil Dex CB column. Chiral ligands L_1[27] and compound **6**[47] were synthesized according to the reported methods.

Representative Procedure for Preparing 3-(Trifluoroacetyl)-benzaldehyde (7). Anhydrous ethylene glycol (10.85 g, 175 mmol)



and a catalytic amount of *p*-toluenesulfonic acid monohydrate (450 mg, 2.5 mmol) were added to a solution of 3-bromobenzaldehyde (9.25 g, 50 mmol) in anhydrous toluene (100 mL), and the reaction mixture was refluxed (oil bath 135 °C) for 24 h with a Dean−Stark trap. Then the reaction mixture was cooled to room temperature, washed with brine (50 mL × 3), dried over anhydrous $MgSO_4$, and concentrated in vacuo to give 10.64 g (93%) of crude product **8** which was used in the next step without further purification. 2-(3-Bromophenyl)-1,3-dioxolane (**8**):[48] ^1H NMR (400 MHz, $CDCl_3$): δ 3.97−4.12 (m, 4H), 5.77 (s, 1H), 7.20−7.28 (m, 1H), 7.37−7.43 (m, 1H), 7.45−7.54 (m, 1H), 7.61−7.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.3, 102.6, 122.4, 125.2, 129.5, 130.0, 132.2, 140.4.

To a solution of **8** (4.58 g, 20 mmol) in Et_2O (30 mL), *n*-BuLi (1.6 M in hexane, 14.4 mL, 23 mmol) was added dropwise at −78 °C. After stirring the resulting mixture at that temperature for 1 h, ethyl trifluoroacetate (3.69 g, 26 mmol) in ether (10 mL) was added slowly at −78 °C over 10 min. The reaction mixture was allowed to warm to

DOI: 10.1021/acs.joc.5b01871
J. Org. Chem. 2015, 80, 12614−12619

0 °C slowly and stirred for 8 h. After that, the mixture was hydrolyzed with HCl (1 M, 50 mL) at 0 °C and extracted by EtOAc (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give a residue, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to give 2.30 g (57%) of product.

*3-(Trifluoroacetyl)benzaldehyde (**7**).* Light brown oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (t, J = 7.8 Hz, 1H), 8.25 (m, 1H), 8.34 (d, J = 7.9 Hz, 1H), 8.56 (s, 1H), 10.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 116.4 (q, J = 291.0 Hz), 130.1, 130.7, 131.4 (d, J = 2.1 Hz), 135.2 (d, J = 1.9 Hz), 135.4, 137.0, 179.7 (q, J = 36.0 Hz), 190.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −71.7 (s, 3F). Anal. Calcd for $C_9H_5F_3O_2$: C, 53.48; H, 2.49. Found: C, 53.52; H, 2.53.

Typical Procedure for the Catalytic Asymmetric β-H Transfer Reduction of α-Fluorolated Ketones and Asymmetric Addition of Diethylzinc Reagent to Aldehydes Using L_1 as the Chiral Ligand. A solution of chiral ligand $\mathbf{L_1}$ (160 mg, 0.30 mmol) in dry toluene (2.6 mL) was stirred under an atmosphere of N_2 in a Schlenk tube at 0 °C for 15 min. Then diethylzinc reagent (2.6 mL, 2.6 mmol, 1.0 *M* in toluene) was added dropwise and the reaction mixture was stirred for 30 min at 0 °C. Then the reaction mixture was cooled to −20 °C before a mixture of benzaldehyde (106 mg, 1.0 mmol) and trifluoroacetophenone (174 mg, 1.0 mmol) was added. After being stirred for 48 h, the reaction was quenched by saturated NH_4Cl solution (30 mL) and extracted with EtOAc (30 mL × 3), dried over $MgSO_4$, filtered, and concentrated in vacuum to give the crude product that was purified by flash chromatography using EtOAc/*n*-hexane mixture to afford the corresponding alcohol products. The enantiomeric excess was determined by chiral GC or chiral HPLC analysis.

*(R)-2,2,2-Trifluoro-1-phenylethanol (**3a**).*[49] Colorless oil, 160 mg (91% yield); 66% *ee* value was determined by Chiral GC Chirasil Dex CB [column temperature: 130 °C, t_R = 10.09 min (minor, *S*), t_R = 10.53 min (major, *R*)]. $[\alpha]_D^{25.5}$ −12.8 (*c* 0.50, CH_2Cl_2) [Literature[49] $[\alpha]_D^{25}$ −13.1 (*c* 0.28, CH_2Cl_2) for 60% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.73 (s, 1H), 5.02 (q, J = 6.6 Hz, 1H), 7.38−7.54 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.9 (q, J = 32.2 Hz), 124.3 (q, J = 281.0 Hz), 127.5, 128.6, 129.6, 134.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.2 (d, J = 6.7 Hz, 3F).

*(R)-1-Phenylpropan-1-ol (**4a**).*[50] Colorless oil (135 mg, 99% yield); 98% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 130 °C, t_R = 8.56 min (major, *R*), t_R = 9.01 min (minor, *S*)]. $[\alpha]_D^{20.9}$ +21.9 (*c* 1.00, $CHCl_3$) [Literature[50] $[\alpha]_D^{26.0}$ +40.3 (*c* 1.21, $CHCl_3$) for 96% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, 3H), 1.71−1.92 (m, 2H), 1.96 (br, 1H), 4.51−4.72 (m, 1H), 7.25−7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.1, 31.8, 75.9, 125.9, 127.4, 128.4, 144.6.

*(R)-2-Chloro-2,2-difluoro-1-phenylethanol (**3b**).*[51] Colorless oil, 173 mg (90% yield); the 77% *ee* value was determined by Chiral GC Chirasil Dex CB [column temperature: 125 °C, t_R = 28.21 min (minor, *S*), t_R = 28.70 min (major, *R*)]. $[\alpha]_D^{30.1}$ −9.3 (*c* 0.50, $CHCl_3$) [literature[51] $[\alpha]_D^{21}$ −13.8 (*c* 1.01, $CHCl_3$) for 73% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.07 (s, 1H), 5.07 (t, J = 6.6 Hz, 1H), 7.32−7.62 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 77.6, 126.0, 127.8, 128.4, 129.0 (t, J = 297.0 Hz), 129.6, 131.9, 134.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.3 (dd, J = 7.4 Hz, 164.0 Hz, 1F), −64.3 (dd, J = 8.4 Hz, 164.0 Hz, 1F).

*(R)-2,2,3,3,4,4,4-Heptafluoro-1-phenylbutan-1-ol (**3c**).*[52,53] Colorless oil, 224 mg (81% yield); the 46% *ee* value was determined by Chiral GC Chirasil Dex CB [column temperature: 145 °C, t_R = 6.27 min (major, *R*), t_R = 6.90 min (minor, *S*)]. $[\alpha]_D^{30.1}$ −8.9 (*c* 1.00, EtOH) [literature[52] $[\alpha]_D^{22}$ +23.02 (*c* 2.32, EtOH) for 86% *ee* (*S*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (s, 1H), 5.20 (dd, J = 6.3 Hz, 17.7 Hz, 1H), 7.37−7.58 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.2 (dd, J = 22.2 Hz, 28.6 Hz), 105.0−119.4 (m), 127.9, 128.0, 128.1, 128.4, 128.5, 128.7, 129.4,129.6, 129.7, 134.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.9 (t, J = 10.8 Hz, 3F), −118.1−(−127.2) (m, 4F).

*(R)-1-(4-Chlorophenyl)-2,2,2-trifluoroethanol (**3d**).*[49] Colorless oil, 183 mg (87% yield); the 64% *ee* value was determined by Chiral GC Chirasil Dex CB [column temperature: 130 °C, t_R = 22.26 min (minor, *S*), t_R = 24.73 min (major, *R*)]. $[\alpha]_D^{30.6}$ −11.0 (*c* 0.50, CH_2Cl_2) [literature[49] $[\alpha]_D^{25}$ −18.3 (*c* 0.13, CH_2Cl_2) for 51% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.01 (s, 1H), 5.01 (q, J = 6.6 Hz, 1H), 7.34−7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.1 (q, J = 32.0 Hz), 124.1 (q, J = 283.5 Hz), 128.8 (d, J = 1.5 Hz), 129.6, 132.4, 135.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.5 (d, J = 6.8 Hz, 3F).

*(R)-1-(4-Chlorophenyl)-1-propanol (**4d**).*[50] Colorless oil (162 mg, 95% yield); 94% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 130 °C, t_R = 20.63 min (major, *R*), t_R = 23.44 min (minor, *S*)]. $[\alpha]_D^{30.1}$ +38.9 (*c* 1.20, $CHCl_3$) [Literature[50] $[\alpha]_D^{26.0}$ + 30.6 (*c* 2.08, $CHCl_3$) for 96% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.5 Hz, 3H), 1.65−1.84 (m, 2H), 2.38 (br, 1H), 4.55 (t, J = 6.8 Hz, 1H), 7.20−7.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.9, 31.8, 75.2, 127.3, 128.4, 132.9, 142.9.

*(R)-1-(4-Bromophenyl)-2,2,2-trifluoroethanol (**3e**).*[49] Colorless oil, 234 mg (92% yield); the 52% *ee* value was determined by Chiral GC Chirasil Dex CB [column temperature: 145 °C, t_R = 20.52 min (minor, *S*), t_R = 21.98 min (major, *R*)]. $[\alpha]_D^{27.5}$ −10.5 (*c* 0.50, CH_2Cl_2) [literature[49] $[\alpha]_D^{25}$ −11.5 (*c* 0.24, CH_2Cl_2) for 57% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.22 (s, 1H), 4.98 (q, J = 6.6 Hz, 1H), 7.31−7.41 (m, 2H), 7.49−7.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.2 (q, J = 32.1 Hz), 123.8, 124.0 (q, J = 282.0 Hz), 129.1, 131.8, 132.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.4 (d, J = 6.8 Hz, 3F).

*(R)-1-(4-Bromophenyl)propan-1-ol (**4e**).*[54] Colorless oil, 211 mg (98% yield); the 93% *ee* value was determined by Chiral GC Chirasil Dex CB [column temperature: 145 °C, t_R = 19.36 min (major, *R*), t_R = 21.39 min (minor, *S*)]. $[\alpha]_D^{28.0}$ +16.9 (*c* 1.20, C_6H_6) [literature[54] $[\alpha]_D^{26.0}$ + 13.33 (*c* 1.00, C_6H_6) for 76% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 7.4 Hz, 3H), 1.60−1.81 (m, 2H), 2.80 (br, 1H), 4.48 (t, J = 6.5 Hz, 1H), 7.12−7.20 (m, 2H), 7.41−7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0, 31.8, 75.2, 121.1, 127.8, 131.4, 143.6.

*(R)-2,2,2-Trifluoro-1-(4-fluorophenyl)ethanol (**3f**).*[49] Colorless oil, 157 mg (81% yield); the 59% *ee* value was determined by Chiral GC Chirasil Dex CB [column temperature: 125 °C, t_R = 13.48 min (minor, *S*), t_R = 14.68 min (major, *R*)]. $[\alpha]_D^{28.6}$ −12.3 (*c* 0.50, CH_2Cl_2) [literature[49] $[\alpha]_D^{19}$ −11.5 (*c* 0.07, CH_2Cl_2) for 45% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.12 (s, 1H), 5.01 (q, J = 6.5 Hz, 1H), 7.00−7.17 (m, 2H), 7.35−7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.2 (q, J = 32.2 Hz), 115.6 (d, J = 21.9 Hz), 124.1 (q, J = 282.1 Hz), 129.3 (d, J = 8.2 Hz), 129.7 (d, J = 1.7 Hz), 163.4 (d, J = 248.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.6 (d, J = 6.7 Hz, 3F), −112.4 (m, 1F).

*(R)-1-(4-Fluorophenyl)propan-1-ol (**4f**).*[55] Colorless oil (151 mg, 98% yield); 97% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 130 °C, t_R = 11.83 min (major, *R*), t_R = 12.88 min (minor, *S*)]. $[\alpha]_D^{31.1}$ +37.0 (*c* 1.00, $CHCl_3$) [Literature[55] $[\alpha]_D^{24}$ −40.6 (*c* 0.67, $CHCl_3$) for 90% *ee* (*S*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 7.5 Hz, 3H), 1.55−1.85 (m, 2H), 2.80 (br s, 1H), 4.51 (t, J = 6.6 Hz, 1H), 6.91−7.06 (m, 2H), 7.15−7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0 (d, J = 27.4 Hz), 31.9, 75.2, 115.1 (d, J = 21.0 Hz), 127.6 (d, J = 8.1 Hz), 140.3 (d, J = 2.7 Hz), 162.1 (d, J = 243 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.4 (s, 1F).

*(R)-2,2,2-Trifluoro-1-p-tolylethanol (**3g**).*[49] Colorless oil, 156 mg (82% yield); the 61% *ee* value was determined by Chiral GC Chirasil Dex CB [column temperature: 125 °C, t_R = 10.13 min (minor, *S*), t_R = 10.57 min (major, *R*)]. $[\alpha]_D^{28.5}$ −14.7 (*c* 0.50, CH_2Cl_2) [literature[49] $[\alpha]_D^{25}$ −12.7 (*c* 0.18, CH_2Cl_2) for 68% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.87 (br, 1H), 4.98 (m, 1H), 7.16−7.30 (m, 2H), 7.33−7.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 72.6 (q, J = 31.8 Hz), 124.4 (q, J = 281.1 Hz), 127.4, 129.3, 131.1, 139.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.4 (d, J = 6.9 Hz, 3F).

*(R)-1-p-Tolylpropan-1-ol (**4g**).*[54] Colorless oil (131 mg, 87% yield); 96% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 130 °C, t_R = 11.11 min (major, *R*), t_R = 12.12 min (minor, *S*)]. $[\alpha]_D^{32.0}$ +31.5 (*c* 1.00, C_6H_6) [Literature[54] $[\alpha]_D^{21}$ +28.9 (*c* 1.00, C_6H_6) for 74% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.4 Hz, 3H), 1.68−1.93 (m, 2H), 2.31 (br s, 1H), 2.39 (s, 3H), 4.55 (t, J = 6.6 Hz, 1H), 7.16−7.23 (m, 2H), 7.24−7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.2, 21.1, 31.8, 75.8, 126.0, 129.1, 137.0, 141.7.

DOI: 10.1021/acs.joc.5b01871
J. Org. Chem. 2015, 80, 12614−12619

*(R)-2,2,2-Trifluoro-1-(4-methoxyphenyl)ethanol (**3h**).*[49] Colorless oil (155 mg, 75% yield); 52% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 130 °C, t_R = 25.83 min (minor, *S*), t_R = 27.77 min (major, *R*)]. $[\alpha]_D^{32.0}$ −10.2 (*c* 0.50, $CHCl_3$) [Literature[49] $[\alpha]_D^{25.0}$ −13.6 (*c* 0.27, CH_2Cl_2) for 67% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (s, 1H), 3.84 (s, 3H), 4.88−5.09 (m, 1H), 6.90−7.06 (m, 2H), 7.39−7.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 72.4 (q, *J* = 32.2 Hz), 113.5, 114.1, 124.4 (q, *J* = 281.5 Hz), 126.3, 128.8, 160.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.7 (d, *J* = 6.9 Hz, 3F).

*(R)-1-(4-Methoxyphenyl)-1-propanol (**4h**).*[50] Colorless oil (154 mg, 93% yield); 92% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 130 °C, t_R = 25.20 min (major, *R*), t_R = 27.77 min (minor, *S*)]. $[\alpha]_D^{30.1}$ +37.4 (*c* 1.30, $CHCl_3$) [Literature[50] $[\alpha]_D^{26.0}$ +38.9 (*c* 1.23, $CHCl_3$) for 96% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.4 Hz, 3H), 1.69−1.82 (m, 2H), 2.51 (br, 1H), 3.80 (s, 3H), 4.50 (s, 1H), 6.87−7.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.2, 31.8, 55.2, 75.5, 113.7, 127.2, 136.9, 158.9.

*(R)-2,2,2-Trifluoro-1-(3-fluorophenyl)ethanol (**3i**).*[49] Colorless oil (182 mg, 94% yield); 60% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 125 °C, t_R = 11.28 min (minor, *S*), t_R = 12.24 min (major, *R*)]. $[\alpha]_D^{32.0}$ −11.5 (*c* 0.50, $CHCl_3$) [Literature[49] $[\alpha]_D^{19}$ −19.3 (*c* 0.13, CH_2Cl_2) for 52% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (br, 1H), 5.04 (q, *J* = 6.5 Hz, 1H), 7.08−7.19 (m, 1H), 7.20−7.32 (m, 2H), 7.34−7.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.2 (q, *J* = 32.5 Hz), 114.6 (d, *J* = 23.0 Hz), 116.5 (d, *J* = 21.2 Hz), 123.1 (d, *J* = 2.2 Hz), 124.0 (q, *J* = 282.1 Hz), 130.2 (d, *J* = 8.1 Hz), 136.2 (d, *J* = 7.3 Hz), 162.8 (d, *J* = 246.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.1 (d, *J* = 6.8 Hz, 3F), −112.6−(−112.7) (m, 1F).

*(R)-1-(3-Fluorophenyl)propan-1-ol (**4i**).*[56] 149 mg (97% yield); Colorless oil, 98% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 125 °C, t_R = 9.72 min (major, *R*), t_R = 10.72 min (minor, *S*)]. $[\alpha]_D^{25.8}$ +21.6 (*c* 1.00, $CHCl_3$) [Literature[56] $[\alpha]_D^{25}$ +32.7 (*c* 1.61, $CHCl_3$) for 92% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.4 Hz, 3H), 1.65−1.85 (m, 2H), 2.71 (br, 1H), 4.55 (t, *J* = 6.5 Hz, 1H), 6.91−7.01 (m, 1H), 7.01−7.11 (m, 2H), 7.22−7.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.9, 31.8, 75.2 (d, *J* = 1.52 Hz), 112.8 (d, *J* = 21.4 Hz), 114.2 (d, *J* = 21.2 Hz), 121.6 (d, *J* = 2.9 Hz), 129.8 (d, *J* = 8.1 Hz), 147.4 (d, *J* = 6.6 Hz), 162.9 (d, *J* = 245.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −113.2 (s, 1F).

*1-Cyclohexyl-2,2,2-trifluoroethanol (**3j**).*[57] 118 mg (65% yield); Colorless oil, 0% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 100 °C, t_R = 19.12 min, t_R = 20.25 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10−1.30 (m, 5H), 1.64−1.94 (m, 6H), 3.34 (d, *J* = 6.7 Hz, 1H), 3.62−3.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7, 25.9, 26.0, 26.9, 29.2 (d, *J* = 1.0 Hz), 38.3, 74.2 (q, *J* = 29.5 Hz), 125.4 (q, *J* = 283.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −75.6 (d, *J* = 7.8 Hz, 3F).

*(R)-1-Cyclohexylpropan-1-ol (**4j**).*[50] 118 mg (82% yield); Colorless oil, 74% *ee* value was determined by Chiral GC Chirasil Dex CB [Inlet temperature: 100 °C, t_R = 28.32 min (minor, *S*), t_R = 29.06 min (major, *R*)]. $[\alpha]_D^{25.6}$ +10.1 (*c* 1.20, $CHCl_3$) [Literature[50] $[\alpha]_D^{26.0}$ +5.4 (*c* 0.61, $CHCl_3$) for 93% *ee* (*R*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.4 Hz, 3H), 0.91−1.16 (m, 6H), 1.29−1.38 (m, 1H), 1.43−1.53 (m, 1H), 1.56−1.61 (m, 2H), 1.66−1.77 (m, 3H), 1.99 (br, 1H), 3.17−3.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.2, 26.2, 26.4, 26.5, 26.7, 27.8, 29.3, 43.1, 77.5.

*1-(4-(2,2,2-Trifluoro-1-hydroxyethyl)phenyl)propan-1-ol (**3k**).* 211 mg (90% yield); white solid, mp 88−89 °C. 97% *ee* value was determined by Chiarl HPLC [Chiralcel OD-H, column temperature: 40 °C, 210 nm, *i*-PrOH/*n*-hexane = 12:88, $t_{(R, S)}$ = 7.95 min, $t_{(S, R)}$ = 9.63 min, $t_{(R, R)}$ = 11.54 min, $t_{(S, S)}$ = 15.31 min; $[\alpha]_D^{29.1}$ +17.2 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_3CN): δ 0.89 (t, *J* = 7.4 Hz, 3H), 1.64−1.77 (m, 2H), 2.69 (s, 1H), 4.56 (t, *J* = 6.4 Hz, 2H), 5.09 (q, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 9.5, 31.9, 71.1 (q, *J* = 35.8 Hz), 74.3 (d, *J* = 3.9 Hz), 125.0 (q, *J* = 281.3 Hz), 125.9, 127.4, 133.9, 146.7; ^{19}F NMR (376 MHz, CD_3CN): δ −78.7 (d, *J* = 6.8 Hz, 3F). Anal. Calcd for $C_{11}H_{13}F_3O_2$: C, 56.41; H, 5.59. Found: C, 56.52; H, 5.62.

*1-(3-(2,2,2-Trifluoro-1-hydroxyethyl)phenyl)propan-1-ol (**3l**).* 201 mg (86% yield); Colorless oil. 92% *ee* value was determined by Chiarl HPLC [Chiralcel AD-H, column temperature: 40 °C, 210 nm, *i*-PrOH/*n*-hexane = 5:95, $t_{(R, S), (S, R)}$ = 38.03 min, $t_{(S, S)}$ = 46.29 min, $t_{(R, R)}$ = 48.00 min; $[\alpha]_D^{24.8}$ +14.0 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.4 Hz, 3H), 1.64−1.84 (m, 2H), 2.43−3.24 (br, 1H), 3.48−4.38 (br, 1H), 4.50−4.60 (m, 1H), 4.83−4.98 (m, 1H), 7.29−7.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.9, 31.6, 72.5 (q, *J* = 31.7 Hz), 75.8 (d, *J* = 3.6 Hz), 124.3 (q, *J* = 282.6 Hz), 125.1, 126.7, 127.1, 128.5, 144.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.1 (d, *J* = 6.7 Hz, 3F). Anal. Calcd for $C_{11}H_{13}F_3O_2$: C, 56.41; H, 5.59. Found: C, 56.54; H, 5.65.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01871.

Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra, and chiral GC or HPLC analysis for all alcohol products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: songling@fjirsm.ac.cn.

Author Contributions

†H.H. and H.Z. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial supports from National Nature Science Foundation of China (No. 21207131); The Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences.

■ REFERENCES

(1) Walsh, P. J.; Kozlowski, M. C. *Fundamentals of Asymmetric Catalysis*; University Science Books: Sausalito, CA, 2009.

(2) Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds. *Comprehensive Asymmetric Catalysis I–III*; Springer Verlag: New York, 1999; Vols. *1–3*.

(3) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley-Interscience: New York, 1994.

(4) Yamamoto, H. *Lewis Acids in Organic Synthesis*; Wiley-VCH: New York, 2001.

(5) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106−112.

(6) Ambrosini, L. M.; Lambert, T. H. *ChemCatChem* **2010**, *2*, 1373−1380.

(7) Ajamian, A.; Gleason, J. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3754−3760.

(8) Heutling, A.; Pohlki, F.; Bytschkov, I.; Doye, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2951−2954.

(9) Louie, J.; Bielawski, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312−11313.

(10) Bielawski, C. W.; Louie, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 12872−12873.

(11) Orita, A.; Nagano, Y.; Nakazawa, K.; Otera, J. *Adv. Synth. Catal.* **2002**, *344*, 548−555.

(12) Chen, J.; Otera, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 91−93.

(13) Drouin, S. D.; Zamanian, F.; Fogg, D. E. *Organometallics* **2001**, *20*, 5495−5497.

(14) Yu, H. B.; Hu, Q. S.; Pu, L. *J. Am. Chem. Soc.* **2000**, *122*, 6500−6501.

(15) Tian, J.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3636−3638.

DOI: 10.1021/acs.joc.5b01871
J. Org. Chem. 2015, 80, 12614−12619

(16) Du, H. F.; Ding, K. L. *Org. Lett.* **2003**, *5*, 1091−1093.
(17) Du, H. F.; Zhang, X.; Wang, Z.; Ding, K. L. *Tetrahedron* **2005**, *61*, 9465−9477.
(18) Hatano, M.; Miyamoto, T.; Ishihara, K. *Org. Lett.* **2007**, *9*, 4535−4538.
(19) Hatano, M.; Mizuno, T.; Ishihara, K. *Synlett* **2010**, *2010*, 2024−2028.
(20) Hatano, M.; Mizuno, T.; Ishihara, K. *Chem. Commun.* **2010**, *46*, 5443−5445.
(21) Hatano, M.; Mizuno, T.; Ishihara, K. *Tetrahedron* **2011**, *67*, 4417−4424.
(22) Hatano, M.; Gouzu, R.; Mizuno, T.; Abe, H.; Yamada, T.; Ishihara, K. *Catal. Sci. Technol.* **2011**, *1*, 1149−1158.
(23) Huang, H. Y.; Zong, H.; Bian, G. L.; Song, L. *J. Org. Chem.* **2012**, *77*, 10427−10434.
(24) Shen, B.; Huang, H. Y.; Bian, G. L.; Zong, H.; Song, L. *Chirality* **2013**, *25*, 561−566.
(25) Zong, H.; Huang, H. Y.; Bian, G. L.; Song, L. *Tetrahedron Lett.* **2013**, *54*, 2722−2725.
(26) Yue, H. F.; Huang, H. Y.; Bian, G. L.; Zong, H.; Li, F. L.; Song, L. *Tetrahedron: Asymmetry* **2014**, *25*, 170−180.
(27) Huang, H. Y.; Zong, H.; Shen, B.; Yue, H. F.; Bian, G. L.; Song, L. *Tetrahedron* **2014**, *70*, 1289−1297.
(28) Huang, H. Y.; Zong, H.; Yue, H. F.; Bian, G. L.; Song, L. *J. Org. Chem.* **2014**, *79*, 9455−9464.
(29) Liu, Y. L.; Zhou, F.; Cao, J. J.; Ji, C. B.; Ding, M.; Zhou, J. *Org. Biomol. Chem.* **2010**, *8*, 3847−3850.
(30) Ding, M.; Zhou, F.; Liu, Y. L.; Wang, C. H.; Zhao, X. L.; Zhou, J. *Chem. Sci.* **2011**, *2*, 2035−2039.
(31) Gao, W. M.; Yu, J. S.; Zhao, Y. L.; Liu, Y. L.; Zhou, F.; Wu, H. H.; Zhou, J. *Chem. Commun.* **2014**, *50*, 15179−15182.
(32) Yu, J. S.; Liao, F. M.; Gao, W. M.; Liao, K.; Zuo, R. L.; Zhou, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 7381−7385.
(33) Huang, H. Y.; Zong, H.; Bian, G. L.; Song, L. *Tetrahedron: Asymmetry* **2015**, *26*, 835−839.
(34) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833−856.
(35) Pu, L.; Yu, H. B. *Chem. Rev.* **2001**, *101*, 757−824.
(36) Binder, C. M.; Singaram, B. *Org. Prep. Proced. Int.* **2011**, *43*, 139−208.
(37) Knochel, P., Jones, P., Eds. *Organic Reagents: A Practical Approach*; Oxford University Press: New York, 1999.
(38) Werner, T.; Riahi, A. M.; Schramm, H. *Synthesis* **2011**, *2011*, 3482−3490.
(39) Werner, T.; Bauer, M.; Riahi, A. M.; Schramm, H. *Eur. J. Org. Chem.* **2014**, *2014*, 4876−4883.
(40) Sasaki, S.; Yamauchi, T.; Kubo, H.; Kanai, M.; Ishii, A.; Higashiyama, K. *Tetrahedron Lett.* **2005**, *46*, 1497−1500.
(41) Yearick, K.; Wolf, C. *Org. Lett.* **2008**, *10*, 3915−3918.
(42) Genov, M.; Martinez-Ilarduya, J. M.; Calvillo-Barahona, M.; Espinet, P. *Organometallics* **2010**, *29*, 6402−6407.
(43) Hevia, E.; Kennedy, A. R.; Klett, J.; Livingstone, Z.; Mccall, M. D. *Dalton Trans.* **2010**, *39*, 520−526.
(44) Calvillo-Barahona, M.; Cordovilla, C.; Genov, M. N.; Martinez-Ilarduya, J. M.; Espinet, P. *Dalton Trans.* **2013**, *42*, 14576−14582.
(45) Calvillo-Barahona, M.; Casares, J. A.; Cordovilla, C.; Genov, M. N.; Martinez-Ilarduya, J. M.; Espinet, P. *Chem. - Eur. J.* **2014**, *20*, 14800−14806.
(46) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth Heinemann: Oxford, 2003.
(47) Chen, L. S.; Chen, G. J.; Tamborski, C. *J. Organomet. Chem.* **1983**, *251*, 139−148.
(48) Lee, A. S. Y.; Cheng, C. L. *Tetrahedron* **1997**, *53*, 14255−14262.
(49) Wu, S. X.; Guo, J. Y.; Sohail, M.; Cao, C. Y.; Chen, F. X. *J. Fluorine Chem.* **2013**, *148*, 19−29.
(50) Zhong, J. C.; Guo, H. C.; Wang, M. A.; Yin, M. M.; Wang, M. *Tetrahedron: Asymmetry* **2007**, *18*, 734−741.
(51) Kitazume, T.; Asai, M.; Tsukamoto, T.; Yamazaki, T. *J. Fluorine Chem.* **1992**, *56*, 271−284.
(52) Ramachandran, P. V.; Teodorovic, A. V.; Brown, H. C. *Tetrahedron* **1993**, *49*, 1725−1738.
(53) Mikami, K.; Murase, T.; Itoh, Y. *J. Am. Chem. Soc.* **2007**, *129*, 11686−11687.
(54) Chaloner, P. A.; Langadianou, E.; Perera, S. A. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2731−2735.
(55) Prasad, K. R.; Revu, O. *Tetrahedron* **2013**, *69*, 8422−8428.
(56) Bisai, A.; Singh, P. K.; Singh, V. K. *Tetrahedron* **2007**, *63*, 598−601.
(57) Krishnamurti, R.; Bellew, D. R.; Prakash, G. K. S. *J. Org. Chem.* **1991**, *56*, 984−989.

DOI: 10.1021/acs.joc.5b01871
J. Org. Chem. 2015, 80, 12614−12619