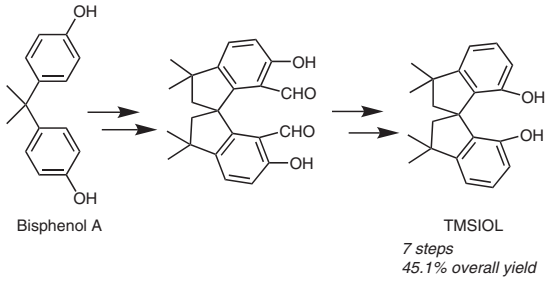
Synthesis Q. Zhou et al. Paper

Synthesis and Optical Resolution of 3,3,3′,3′-Tetramethyl-1,1′-spirobiindane-7,7′-diol

Qiaoxia Zhou
Rihuang Pan
Huanyu Shan
Xufeng Lin*

Laboratory of Asymmetric Catalysis and Synthesis,
Department of Chemistry, Zhejiang University,
Hangzhou 310027, P. R. of China
lxfok@zju.edu.cn



Received: 28.05.2018
Accepted after revision: 30.07.2018
Published online: 04.09.2018
DOI: 10.1055/s-0037-1610831; Art ID: ss-2018-h0371-op

Abstract A novel chiral C_2-symmetric spiro diol, 3,3,3′,3′-tetramethyl-1,1′-spirobiindane-7,7′-diol (TMSIOL), was conveniently prepared via practical seven-step route from Bisphenol A in 45.1% overall yield. L-Menthyl chloroformate is used as optical resolving agent for the separation of the two enantiomers of TMSIOL.

Key words asymmetric catalysis, chiral ligand, chiral diol, spirobiindane, resolution

Optically active C_2-symmetric diols have found many applications as chiral ligands and also as key cores for providing a diverse range of excellent supporting chiral ligands in transition-metal-catalyzed asymmetric reactions, for example, bisphosphines, phosphine-oxazolines, bisoxazolines, diamines, and phosphites.[1] Recently, chiral diols became also a leading motif in organocatalysts design for asymmetric synthesis, such as chiral phosphoric acids.[2] The most prominent C_2-symmetric diols are BINOL,[3] H_8-BINOL,[4] BIPHENOL,[5] TADDOL,[6] and VANOL.[7] Another prevalent class of chiral diols is based on the spiro skeletons, such as SpirOH,[8] SPINOL,[9] SBIFOL,[10] and SBIXOL[11] (Figure 1). It should be noted that the dihedral angles for the axially chiral ligands are a key factor for reactivity and enantioselectivity in asymmetric catalysis.

It is well known that spiro skeleton has been recognized as a privileged chiral backbone for chiral ligands in asymmetric catalysis.[12] In this context, many outstanding contributions have been made by some research groups, such as Chan, Sasai, Zhou, van Leeuwen, and Ding groups.[13] We also developed a novel class of chiral spirocyclic phosphoric acids (SPAs) based on the SPINOL skeleton, and these SPAs catalysts are now widely applied in over 100 asymmetric reactions.[14] More recently, we developed new types of chiral phosphine-oxazoline ligands (HMSI-PHOX) and bisphosphine ligands (HMSI-PHOS) based on a hexamethyl-1,1′-spirobiindane backbone, and demonstrated their successful application in asymmetric reaction.[15] Herein, we report the design, synthesis and optical resolution of a novel chiral C_2-symmetric spiro diol, 3,3,3′,3′-tetramethyl-1,1′-spirobiindane-7,7′-diol (abbreviated as TMSIOL) (Figure 1). We assume that the introduction of double gem-dimethyl substitution in the spiro backbone of SPINOL will remove the active benzyl hydrogen and change the dihedral angle of the conformationally rigid axially chiral diol. Chiral ligands derived from TMSIOL may well keep their stability and improve the enantioselectivity of a reaction in some cases.

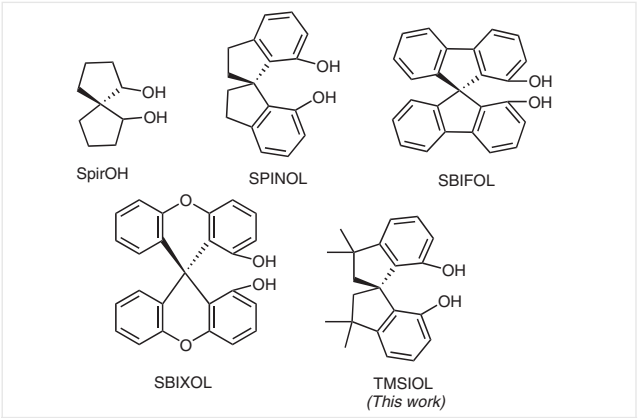
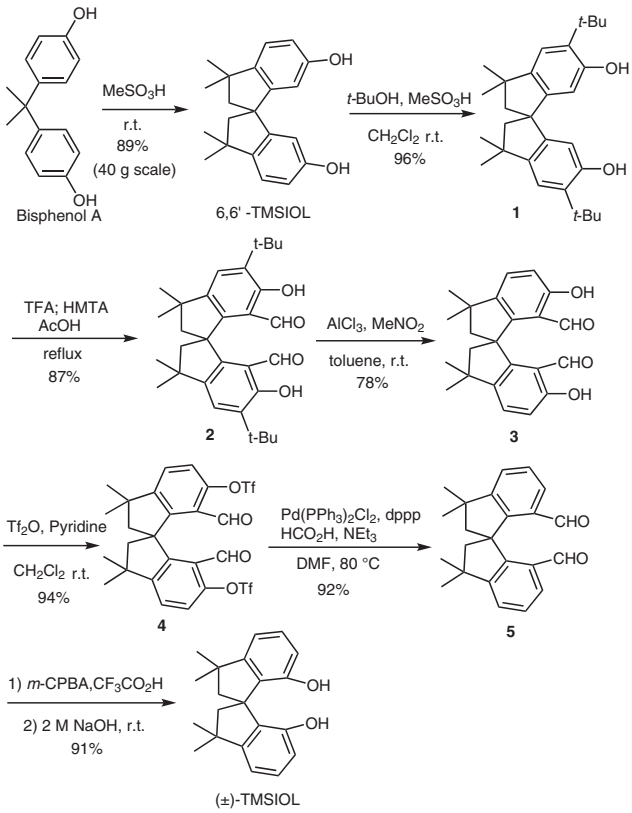


Figure 1 Chiral spiro diols

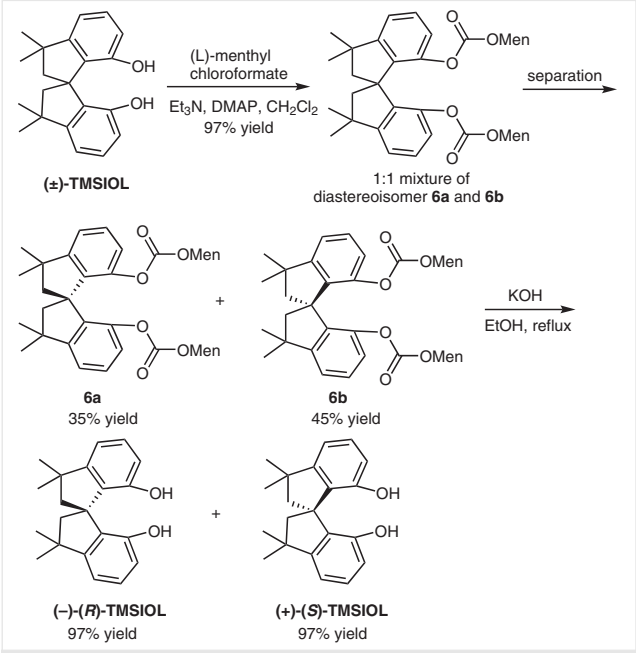
We started the synthesis of TMSIOL from commercially available cheap Bisphenol A ($ 1.5/kg), as shown in Scheme 1. The racemate of tetramethyl-1,1′-spirobiindane-6,6′-diol (6,6′-TMSIOL) was obtained in 89% yield on a 40 g scale by a modified acid-catalyzed rearrangement cyclization reaction of Bisphenol A.[16] The alkylated product **1** was prepared in an almost quantitative yield from 6,6′-TMSIOL under

general Friedel–Crafts reaction conditions and did not need any further purification. Then, aldehyde groups were introduced by Duff reaction to afford the corresponding product **2** in 87% yield. The *tert*-butyl substituents were removed by the retro-Friedel–Crafts reaction to obtain **3** in 78% yield. The following esterification with Tf_2O gave the bistriflate **4** in 94% yield. The subsequent Pd-catalyzed reduction with formic acid afforded spiro-bialdehyde **5** in 92% yield. Finally, the *rac*-TMSIOL was obtained in 91% yield by the Baeyer–Villiger oxidation rearrangement and subsequent hydrolysis. Thus, TMSIOL has been achieved in 7 steps and 45.1% overall yield from Bisphenol A.



Scheme 1 Synthesis of *rac*-TMSIOL

Then, using L-menthyl chloroformate as a resolving agent, efficient chiral resolution of *rac*-TMSIOL was accomplished, as shown in Scheme 2. Treatment of *rac*-TMSIOL with L-menthyl chloroformate in the presence of NEt_3 and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) gave **6a** and **6b** as 1:1 diastereoisomer mixture in 97% yield. Menthol ester of (*R*)-TMSIOL (**6a**) was isolated as a white solid by recrystallization from hexane in 70% yield, based on one diastereomer. Absolute configuration of **6a** was confirmed by X-ray diffraction analysis (Figure 2).[17] Another menthol ester of (*S*)-TMSIOL **6b** was separated as a liquid from mother liquor of recrystallization by silica gel column in 90% yield, based on one diastereomer. Pure enantiomers, (*R*)-TMSIOL and



Scheme 2 Optical resolution of *rac*-TMSIOL

(*S*)-TMSIOL, were obtained by hydrolysis of **6a** and **6b** in almost quantitative yields, respectively. Absolute configuration of (*R*)-TMSIOL was confirmed by X-ray diffraction analysis, which gave the dihedral angle of 77.0° (Figure 3).[18] By comparison, a single crystal of (*S*)-SPINOL was obtained, and X-ray diffraction analysis showed the corresponding dihedral angle of 69.3° (Figure 4).[19] Notably, the dihedral angles of chiral TMSIOL and SPINOL show remarkable difference. It is well established that double gem-dimethyl substitution in SPINOL increases the dihedral angle of the

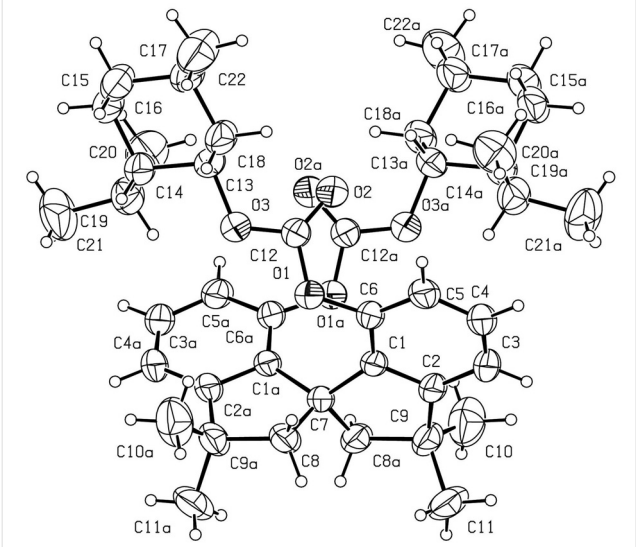


Figure 2 X-ray single-crystal structure of **6a**

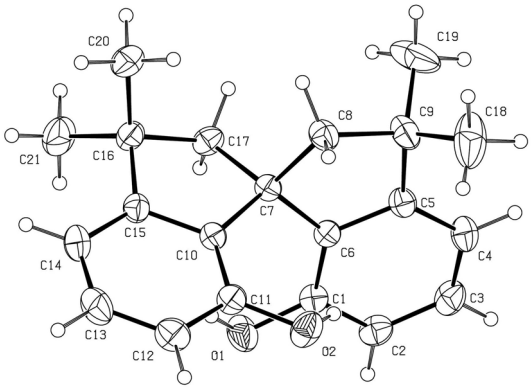


Figure 3 X-ray single-crystal structure of (*R*)-TMSIOL

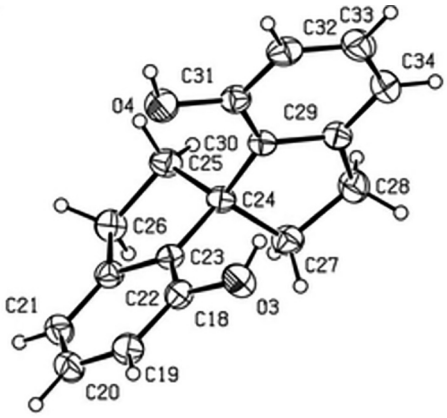
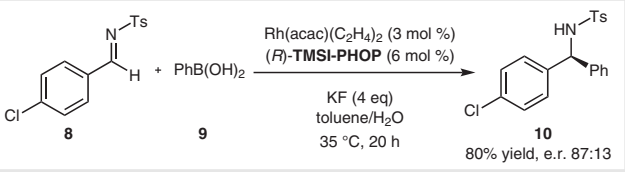


Figure 4 X-ray single-crystal structure of (*S*)-SPINOL



Scheme 4 Asymmetric arylation of imine

axially chiral spiro-diol. Thus, chiral ligands derived from TMSIOL may well improve the enantioselectivity of a reaction in some case.

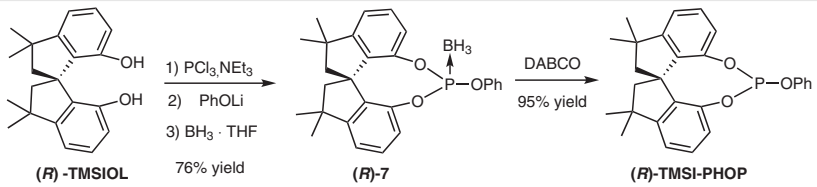
Additionally, spiro phosphite (*R*)-TMSI-PHOP was conveniently derived from chiral sprio diol (*R*)-TMSIOL, as shown in Scheme 3. As a very common oxidation-free relay for catalytic phosphate ligand, air stable borane complex (*R*)-**7** was first obtained in good yield by condensation of chiral spiro diol (*R*)-TMSIOL with PCl_3, followed by treatment with the corresponding lithium phenolate and borane-tetrahydrofuran complex in one-pot procedure. An easy and selective method of decomplexation of (*R*)-**7** by DABCO provided (*R*)-TMSI-PHOP in 95% yield. Further, the efficiency of (*R*)-TMSI-PHOP was tested in the rhodium-catalyzed asymmetric arylation of imines.[20] As shown in Scheme 4, *N*-tosylphenylimine **8** was treated with phenylboronic acid (**9**) in the presence of 3 mol% of $Rh(acac)(C_2H_4)_2$ and 6 mol% of (*R*)-TMSI-PHOP in aqueous KF-toluene at 35 °C for 20 hours. The desired chiral diarylmethylamine product **10** was obtained in 80% yield with e.r. 87:13.

In summary, we have developed a simple and scalable route towards a novel C_2-symmetric spiro diol (TMSIOL) in **7** steps and 45.1% overall yield from Bisphenol A. L-Menthyl chloroformate is used as optical resolving agent for the separation of the two enantiomers of TMSIOL. According to data from X-ray diffraction analysis of chiral TMSIOL and SPINOL, dihedral angles of the axially chiral spiro diols show remarkable difference, and double gem-dimethyl substitution in the spiro backbone of SPINOL increases the dihedral angle. A spiro phosphite (*R*)-TMSI-PHOP and its borane complex were conveniently derived from chiral (*R*)-TMSIOL. Further application of novel chiral TMSIOL for the preparation of new chiral ligands and catalysts in asymmetric catalysis is currently underway.

All reagents and solvents were purchased from commercial sources. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III 400 spectrometer. IR spectra were recorded on Nicolet NEXUS 470 spectrometer. HRMS data were measured on Waters GCT Premier and Bruker Ultraflex. X-ray single crystal diffraction intensity data were recorded on Rigaku Gemini A Ultra instrument. Optical rotations were measured on a PerkinElmer Model 341 polarimeter.

3,3,3′,3′-Tetramethyl-1,1′-spirobiindene-6,6′-diol (6,6′-TMSIOL)

$MeSO_3H$ (440 mL) was added to a flask containing Bisphenol A (100 g, 438 mmol), and the mixture was stirred at r.t. for 3 days. Then the mixture was poured onto 400 g crushed ice, stirred to r.t. and filtered. The filter residue was washed with hot water. To a boiling saturated solution of the crude product in EtOH, hot water was added slowly



Scheme 3 Synthesis of spiro phosphite

until no more precipitation was observed. The product 6,6′-TMSIOL was collected by filtration as a white solid after drying in an oven (105 °C); yield: 40 g (89%); mp 176–178 °C.

IR (film): 3376, 3020, 2953, 2861, 1607, 1492, 1467, 1383, 1149, 1117, 1096, 856, 820, 668, 649 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 7.96 (s, 2 H), 7.05 (d, *J* = 8.2 Hz, 2 H), 6.71 (dd, *J* = 8.2, 2.4 Hz, 2 H), 6.22 (d, *J* = 2.3 Hz, 2 H), 3.04 (s, 2 H), 2.34 (d, *J* = 13.0 Hz, 2 H), 2.21 (d, *J* = 13.0 Hz, 2 H), 1.37 (s, 6 H), 1.31 (s, 6 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 157.77, 152.93, 143.94, 123.29, 115.35, 111.22, 60.58, 58.25, 43.43, 32.21, 30.90.

HRMS (EI, GC-TOF): *m*/*z* [M⁺] calcd for $C_{21}H_{24}O_2$: 308.1776; found: 308.1779.

The analytical and spectral data were in complete agreement with the previously published data.[16]

5,5′-Di-*tert*-butyl-3,3,3′,3′-tetramethyl-1,1′-spirobiindene-6,6′-diol (1)

To a solution of 6,6′-TMSIOL (10.0 g, 32.5 mmol) in CH_2Cl_2 (100 mL) was added *t*-BuOH (10 mL, 109 mmol). The resulting mixture was stirred at r.t. and $MeSO_3H$ (15 mL) was added slowly. The reaction was allowed to proceed 4 h at r.t. Then, the reaction was quenched by adding H_2O. The mixture was evaporated under reduced pressure to remove CH_2Cl_2. The resulting mixture was filtered and the solid was washed with H_2O to give product **1** as a white powder after drying in an oven (105 °C); yield: 13 g (96%); mp 283–284 °C.

IR (film): 3537, 2954, 2866, 1615, 1499, 1464, 1409, 1361, 1250, 1167, 1116, 889, 852, 741 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.05 (s, 2 H), 5.40 (s, 2 H), 3.04 (s, 2 H), 2.29 (d, *J* = 13.0 Hz, 2 H), 2.09 (d, *J* = 13.0 Hz, 2 H), 1.43 (s, 6 H), 1.35 (s, 18 H), 1.28 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.68, 149.14, 144.01, 135.07, 119.72, 111.78, 59.59, 56.69, 43.22, 34.65, 31.81, 30.47, 29.77.

HRMS (EI, GC-TOF): *m*/*z* [M⁺] calcd for $C_{29}H_{40}O_2$: 420.3038; found: 420.3034.

5,5′-Di-*tert*-butyl-6,6′-dihydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobiindene-7,7′-dicarbaldehyde (2)

A solution of hexamethylenetetraamine (HMTA; 10.8 g, 77 mmol) and compound **1** (5.2 g, 12.4 mmol) in trifluoroacetic acid (150 mL) was refluxed for 24 h under an atmosphere of N_2. Then, AcOH (150 mL) was added and the mixture was refluxed for 72 h. Aq 6 M HCl (150 mL) was added, and after refluxing for 24 h, H_2O (300 mL) was added, and the reaction mixture was refluxed for further 24 h and cooled to r.t. The precipitate was collected by filtration, washed with H_2O, and dried to give **2** as a yellow powder; yield: 5.0 g (87%); mp 226–227 °C.

IR (film): 2956, 2925, 2869, 1685, 1637, 1606, 1465, 1430, 1391, 1363, 1303, 1283, 1253, 1201, 1186, 1163 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 12.55 (s, 2 H), 9.60 (s, 2 H), 7.30 (s, 2 H), 2.56 (d, *J* = 13.5 Hz, 2 H), 2.39 (d, *J* = 13.5 Hz, 2 H), 1.42 (s, 18 H), 1.37 (s, 6 H), 1.35 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.17, 163.72, 149.48, 141.37, 139.25, 128.91, 114.19, 77.35, 77.03, 76.71, 60.32, 57.56, 43.19, 35.07, 32.06, 30.13, 29.31.

HRMS (EI, GC-TOF): *m*/*z* [M⁺] calcd for$C_{31}H_{40}O_4$: 476.2927; found: 476.2927.

6,6′-Dihydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobiindene-7,7′-dicarbaldehyde (3)

To a solution of compound **2** (2.0 g, 4.2 mmol) and $AlCl_3$ (10.0 g, 75 mmol) in toluene (30 mL) was added $MeNO_2$ (20 mL) at 0 °C. The reaction mixture was stirred overnight at r.t. under an atmosphere of N_2. Then, aq 3 M HCl was added slowly at 0 °C to quench the reaction. The resulting mixture was stirred at r.t. for 24 h and extracted with EtOAc. The combined organic extracts were washed with H_2O and sat. brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography with 100% CH_2Cl_2. The solid was washed with hexane to give the product **15** as a yellow powder; yield: 1.2 g (78%); mp 219–220 °C.

IR (film): 2961, 2867, 1659, 1604, 1579, 1454, 1392, 1285, 1181, 1165, 1151 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 11.72 (s, 2 H), 9.58 (s, 2 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 6.94 (d, *J* = 8.6 Hz, 2 H), 2.62 (d, *J* = 13.5 Hz, 2 H), 2.43 (d, *J* = 13.5 Hz, 2 H), 1.39 (s, 6 H), 1.37 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.28, 163.97, 152.08, 142.55, 132.07, 118.97, 114.37, 60.20, 58.04, 43.01, 32.01, 30.11.

HRMS (EI, GC-TOF): *m*/*z* [M⁺] calcd for $C_{23}H_{24}O_4$: 364.1675; found: 364.1679.

7,7′-Diformyl-3,3,3′,3′-tetramethyl-1,1′-spirobiindene-6,6′-diyl Bis(trifluoromethanesulfonate) (4)

To a solution of compound **3** (2 g, 5.5 mmol) and pyridine (2.4 mL, 30 mmol) in CH_2Cl_2 (30 mL) was added Tf_2O (3.8 mL) at 0 °C. The resulting mixture was stirred at r.t. for 24 h under an atmosphere of N_2. Then, aq 1 M HCl was added to quench the reaction. The mixture was extracted with CH_2Cl_2, the combined organic extracts were washed with H_2O and sat. brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography with 100% CH_2Cl_2 to give the product **4** as a pale yellow powder; yield: 3.25 g (94%); mp 114–115 °C.

IR (film): 2961, 2870, 1704, 1649, 1600, 1470, 1428, 1365, 1250, 1216, 1140, 869, 841, 805 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 2.53–2.41 (m, 4 H), 1.51 (s, 6 H), 1.43 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.57, 154.89, 151.81, 149.98, 128.90, 123.35, 118.56 (q, *J* = 319 Hz), 59.18, 57.28, 43.22, 32.43, 29.01.

HRMS (EI, GC-TOF): *m*/*z* [M⁺] calcd for $C_{25}H_{22}F_6O_8S_2$: 628.0660; found: 628.0655.

3,3,3′,3′-Tetramethyl-1,1′-spirobiindene-7,7′-dicarbaldehyde (5)

To a solution of compound **4** (628 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (59 mg, 0.084 mmol), dppp (40 mg, 0.96 mmol), and NEt_3 (3.34 mL, 24 mmol) in DMF was added HCO_2H (0.95 mL, 15.5 mmol) at 0 °C. The resulting mixture was stirred at 80 °C for 24 h under an atmosphere of N_2. Then, the mixture was cooled to r.t. and quenched with aq 1 M HCl. The mixture was extracted with EtOAc, the combined organic extracts were washed with H_2O and sat. brine, and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was purified by flash column chromatography (PE/EtOAc 15:1) to give the product **5** as a white powder; yield: 305 mg (92%); mp 203–204 °C.

IR (film): 3788, 3351, 2962, 2861, 2754, 1700, 1685, 1589, 1451, 1394, 1305, 1241, 807 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.58 (s, 2 H), 7.73 (dd, *J* = 7.4, 1.4 Hz, 2 H), 7.50–7.39 (m, 4 H), 2.58 (d, *J* = 13.2 Hz, 2 H), 2.47 (d, *J* = 13.2 Hz, 2 H), 1.48 (s, 6 H), 1.42 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.28, 153.41, 152.39, 130.89, 129.34, 128.45, 128.40, 59.35, 58.05, 43.62, 32.46, 29.58.

HRMS (EI, GC-TOF): *m*/*z* [M$^+$] calcd for $C_{23}H_{24}O_2$: 332.1776; found: 332.1773.

3,3,3′,3′-Tetramethyl-1,1′-spirobiindane-7,7′-diol (TMSIOL)

To a solution of **5** (2 g, 6 mmol) in CH_2Cl_2 was added trifluoroacetic acid (0.9 mL) at 0 °C. The resulting solution was stirred for 10 min at 0 °C under an atmosphere of N_2. Subsequently, *m*-CPBA (4.28 g) was added. The mixture was stirred for 20 min. Then, the reaction was allowed to proceed overnight and quenched by adding sat. aq Na_2SO_3. The mixture was extracted with EtOAc, the combined organic extracts were washed with H_2O and sat. brine, and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was dissolved in MeOH (10 mL), and aq 3 M NaOH (20 mL) was added slowly. The mixture was stirred overnight at r.t. Then, aq 3 M HCl was added until pH 7. The mixture was extracted with EtOAc (3 ×), the combined organic layers were washed with H_2O and sat. brine, and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was purified by flash column chromatography (PE/EtOAc 10:1) to give the product TMSIOL as a white powder; yield: 1.7 g (91%); mp 190–192 °C.

IR (film): 3805, 3746, 3195,2 983, 2925, 1748, 1683, 1585, 1469, 1456, 1360, 1304, 1242, 1201, 1175 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (m, 2 H), 6.83 (d, *J* = 7.5 Hz, 2 H), 6.66 (d, *J* = 8.0 Hz, 2 H), 4.43 (s, 2 H), 2.39 (d, *J* = 13.4 Hz, 2 H), 2.33 (d, *J* = 13.4 Hz, 2 H), 1.41 (s, 6 H), 1.36 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.08, 152.71, 130.36, 130.07, 115.41, 114.59, 77.37, 77.05, 76.74, 55.56, 54.14, 44.26, 31.94, 29.68.

HRMS (EI, GC-TOF): *m*/*z* [M$^+$] calcd for $C_{21}H_{24}O_2$: 308.1776; found: 308.1778.

Chiral Resolution of TMSIOL

To a solution of TMSIOL (2.876 g, 9.35 mmol) and NEt_3 (3.23 mL, 22.4 mmol) in CH_2Cl_2 (140 mL) were added L-menthyl chloroformate (3.53 g, 21.57 mmol) and DMAP (122 mg, 1 mmol) at 0 °C. The reaction mixture was stirred overnight at r.t. under an atmosphere of N_2. Aq 1 M HCl was added to quench the reaction. The mixture was extracted with EtOAc, the combined organic layers were washed with H_2O and sat. brine, and dried (Na_2SO_4). The solvent was removed in vacuo to give **6a** and **6b** as 1:1 diastereoisomer mixture in 97% yield (6.11 g) as light yellow oil, which was dissolved in hexane (20 mL) and cooled to –18 °C to give a white solid (2.42 g) (95% dr). The latter was recrystallized from hexane once to give the diastereomerically pure isomer **6a** (2.2 g) as colorless crystals. The diastereomerically pure isomer **6b** (2.83 g) was obtained by column chromatography (PE/EtOAc 100:1) from the mother liquor.

6a

Yield: 2.2 g (35%); colorless crystals; mp 84–85 °C; $[\alpha]_D^{20}$ –60.9 (*c* 1.00, acetone).

IR (film): 2995, 2867, 1760, 1462, 1234 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (dd, *J* = 8.1, 7.5 Hz, 2 H), 7.04–6.92 (m, 4 H), 4.26 (td, *J* = 10.9, 4.4 Hz, 2 H), 2.46 (d, *J* = 13.2 Hz, 2 H), 2.23 (d, *J* = 13.2 Hz, 2 H), 2.02 (dd, *J* = 7.0, 4.6 Hz, 2 H), 1.65–1.55 (m, 6 H), 1.47–1.28 (m, 14 H), 1.26–1.17 (m, 2 H), 0.99–0.75 (m, 18 H), 0.62 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.07, 152.19, 147.19, 138.48, 128.22, 119.55, 119.12, 56.88, 55.53, 46.77, 44.10, 40.48, 34.07, 32.48, 31.26, 29.54, 25.20, 22.99, 22.00, 20.98, 16.14.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{43}H_{60}O_6Na$: 695.4288; found: 695.4262.

6b

Yield: 2.83 g (45%); liquid; $[\alpha]_D^{20}$ –205.0 (*c* 1.00, acetone).

IR (film): 2995, 2868, 1760, 1462, 1234 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 7.8 Hz, 2 H), 6.97 (dd, *J* = 17.3, 7.8 Hz, 4 H), 4.26 (td, *J* = 10.8, 4.4 Hz, 2 H), 2.46 (d, *J* = 13.2 Hz, 2 H), 2.25 (d, *J* = 13.2 Hz, 2 H), 1.90–1.75 (m, 2 H), 1.69–1.57 (m, 6 H), 1.42–1.17 (m, 16 H), 1.00–0.60 (m, 24 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.16, 151.18, 146.12, 137.85, 127.34, 118.95, 118.29, 77.46, 55.78, 54.48, 45.87, 43.12, 39.26, 33.03, 31.41, 30.13, 28.50, 24.75, 22.13, 20.93, 19.79, 15.32. HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{43}H_{60}O_6Na$: 695.4288; found: 695.4262.

(*R*)-TMSIOL

To a solution of **6a** (672 mg, 1 mmol) in EtOH (10 mL) was added KOH (560 mg, 10 mmol). The mixture was refluxed for 1 h and cooled to r.t. Aq 3 M HCl was added until the solution was acidic. The mixture was extracted with EtOAc, and the combined organic layers were washed with H_2O and sat. brine, and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was purified by flash column chromatography (PE/EtOAc 100:1) to give the product (*R*)-TMSIOL as a white powder; yield: 300 mg (97%); mp 180–181 °C; $[\alpha]_D^{20}$ –130.1 (*c* 1.00, acetone).

(*S*)-TMSIOL

(*S*)-TMSIOL was obtained by the above same procedure from **6b** (672 mg, 1 mmol); yield: 300 mg (97%); white powder; mp 180–181 °C; $[\alpha]_D^{20}$ +130.0 (*c* 1.00, acetone).

Compound [(*R*)-7]

To a solution of (*R*)-TMSIOL (1.54 g, 5 mmol) and NEt_3 (1.72 mL, 12 mmol) in THF (30 mL) was added PCl_3 (2.75 mL) at –78 °C. Then, the mixture was stirred for 30 min under an atmosphere of N_2. The reaction was allowed to proceed for 3 h at r.t. Then, the mixture was cooled to –78 °C, and a solution of lithium phenolate (6 mmol) in THF, which was prepared from phenol (563 mg, 6 mmol) and *n*-BuLi (2 M/THF, 2 mL, 5 mmol) in THF (7 mL), was added The resulting mixture was stirred overnight at r.t.. A 1 M solution of BH_3·THF (20 mL, 20 mmol) in hexane was added at 0 °C. The resulting mixture was stirred 2 h at r.t. and then H_2O was added at 0 °C to quench the reaction. The mixture was extracted with EtOAc, the combined organic layers were washed with H_2O and sat. brine, and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was purified by flash column chromatography (PE/EtOAc 50:1) to give the product (*R*)-**7** as a white powder; yield: 1.65 g (73%); mp 200–201 °C; $[\alpha]_D^{20}$ +164.7 (*c* 1.00, acetone).

IR (film): 3370, 2968, 2924, 2416, 1591, 1489, 1456, 1315, 1200, 1168, 1124, 968, 940, 886, 747 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.22 (m, 4 H), 7.12 (dt, *J* = 14.1, 6.9 Hz, 3 H), 7.04–6.95 (m, 2 H), 6.84 (d, *J* = 8.5 Hz, 2 H), 2.43 (dd, *J* = 12.7, 4.1 Hz, 2 H), 2.06 (dd, *J* = 26.3, 12.7 Hz, 2 H), 1.56 (d, *J* = 3.3 Hz, 6 H), 1.28 (d, *J* = 1.7 Hz, 6 H), 0.52 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.99, 154.62, 150.58, 150.52, 143.31, 142.97, 142.83, 139.57, 138.86, 129.56, 129.12, 125.42, 122.15, 122.11, 121.63, 121.60, 121.10, 120.81, 120.56, 120.53, 57.45, 56.15, 55.63, 42.96, 42.67, 32.60, 32.57, 30.01, 29.99.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 105.44 (br).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{30}BO_3PNa$: 467.1923; found: 467.1930.

Phenyl [(*R*)-3,3,3′,3′-Tetramethyl-1,1′-spirobiindane-7,7′-diyl]phosphite [(*R*)-TMSI-PHOP]

In a three-necked flask, a mixture of (*R*)-**7** (444 mg, 1 mmol), DABCO (112 mg, 1 mmol), and hexane (10 mL) was stirred for 2 h at 40 °C. Then, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc 50:1) to give the product (*R*)-TMSI-PHOP as a white power; yield: 410 mg (95%); mp 100–102 °C; $[\alpha]_D^{20}$ +145.4 (*c* 1.00, acetone).

IR (film): 3355, 2972, 1583, 1460, 1212, 1050, 880, 808, 758, 690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.14 (m, 3 H), 7.13–6.86 (m, 7 H), 6.68 (d, *J* = 7.9 Hz, 1 H), 2.34 (d, *J* = 12.7 Hz, 2 H), 2.00 (d, *J* = 12.5 Hz, 2 H), 1.47 (d, *J* = 11.0 Hz, 6 H), 1.22 (d, *J* = 8.3 Hz, 6 H).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 118.84.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.44, 153.99, 152.34, 152.25, 144.46, 144.41, 142.85, 142.78, 142.71, 139.39, 129.72, 129.08, 129.06, 128.19, 123.84, 121.97, 121.88, 121.82, 120.01, 119.99, 119.77, 119.68, 119.35, 77.37, 77.05, 76.74, 57.05, 56.39, 55.45, 43.09, 42.51, 32.43, 32.09, 30.31, 30.09.

HRMS (EI, GC-TOF): *m*/*z* [M$^+$] calcd for $C_{27}H_{27}O_3P$: 430.1698; found. 430.1725.

(*S*)-*N*-[(4-Chlorophenyl)phenylmethyl]-4-methylbenzenesulfonamide (10)

Under a N_2, $Rh(acac)(C_2H_4)_2$ (0.6 mg, 1.5 μmol), and (*R*)-TMSI-PHOP (1.4 mg, 3 μmol) were dissolved in toluene (0.5 mL) in a dry Schlenk tube. The mixture was stirred at r.t. for 1 h. Then, (*E*)-*N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (**8**; 15 mg, 0.05 mmol), $PhB(OH)_2$ (12 mg, 0.1 mmol), KF (12 mg, 0.2 mmol), and H_2O (0.5 mL) were added sequentially and the reaction mixture was stirred at 35 °C for 20 h. The mixture was cooled to r.t. and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/PE 1:8) to afford the product **10** as a white powder; yield: 15 mg (80%); mp 119–120 °C; e.r. = 87:13; $[\alpha]_D^{20}$ –28.0 (*c* 0.25, CH_2Cl_2).

HPLC analysis: Chiralpak OD-H (hexane/*i*-PrOH (93:7), 0.8 mL/min, 230 nm); t_R (major) = 21.455 min, t_R (minor) = 30.599 min.

IR (film): 3271, 3063, 3031, 2923, 2871, 1911, 1806, 1598, 1491 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.3 Hz, 2 H), 7.24–7.12 (m, 7 H), 7.10–7.01 (m, 4 H), 5.53 (d, *J* = 7.1 Hz, 1 H), 5.18–5.15 (m, 1 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 140.1, 139.0, 137.2, 133.4, 129.4, 128.8, 128.7, 128.6, 127.9, 127.3, 127.2, 60.8, 21.5.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{20}H_{18}ClNO_2S$: 370.0669; found: 370.0665.

Funding Information

We appreciate the National Natural Science Foundation of China (21572200) and the Fundamental Research Funds for the Central Universities (2017QNA3013) for financial support.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609623.

References

(1) (a) Ojima, I. *Catalytic Asymmetric Synthesis*; Wiley-VCH: Weinheim, **2000**. (b) Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, **1999**. (c) Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857. (d) McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809. (e) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.

(2) (a) Akiyama, T.; Itoh, J.; Fuchibe, K. *Adv. Synth. Catal.* **2006**, *348*, 999. (b) Akiyama, T. *Chem. Rev.* **2007**, *107*, 5744. (c) Terada, M. *Chem. Commun.* **2008**, *44*, 4097. (d) Adair, G.; Mukherjee, S.; List, B. *Aldrichimica Acta* **2009**, *41*, 31. (e) Yu, J.; Shi, F.; Gong, L.-Z. *Acc. Chem. Res.* **2011**, *44*, 1156. (f) Parmar, D.; Sugiono, E.; Raja, S.; Rueping, M. *Chem. Rev.* **2014**, *114*, 9047.

(3) (a) Brunel, J. M. *Chem. Rev.* **2007**, *107*, PR1. (b) Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155. (c) Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857. (d) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (e) Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801. (f) Rueping, M.; Kuenkel, A.; Atodiresei, I. *Chem. Soc. Rev.* **2011**, *40*, 4539.

(4) Cramer, N.; Laschat, S.; Baro, A. *Organometallics* **2006**, *25*, 2284.

(5) (a) Hua, Z.; Vassar, V. C.; Ojima, I. *Org. Lett.* **2003**, *5*, 3831. (b) Shi, C.; Chien, C. W.; Ojima, I. *Chem. Asian J.* **2011**, *6*, 674.

(6) (a) Seebach, D.; Beck, A. K.; Heckel, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 92. (b) Seebach, D.; Pichota, A.; Beck, A. K.; Pinkerton, A. B.; Litz, T.; Karjalainen, J.; Gramlich, V. *Org. Lett.* **1999**, *1*, 55.

(7) (a) Wulff, W.; Desai, A. *Synthesis* **2010**, 3670. (b) Bao, J.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3814.

(8) (a) Cram, D. J.; Steinberg, H. *J. Am.Chem. Soc.* **1954**, *76*, 2753. (b) Hardeggar, E.; Maeder, E.; Semarne, H. M.; Cram, D. J. *J. Am. Chem. Soc.* **1959**, *81*, 2729. (c) Chan, A. S. C.; Hu, W.; Pai, C.-C.; Lau, C.-P. *J. Am. Chem. Soc.* **1997**, *119*, 9570. (d) Srivastava, N.; Mital, A.; Kumar, A. *J. Chem. Soc., Chem. Commun.* **1992**, 493.

(9) (a) Birman, V. B.; Rheingold, A. L.; Lam, K.-C. *Tetrahedron: Asymmetry* **1999**, *10*, 125. (b) Li, Z.; Liang, X.; Wu, F.; Wan, B. *Tetrahedron: Asymmetry* **2004**, *15*, 665.

(10) Cheng, X.; Hou, G.-H.; Xie, J.-H.; Zhou, Q.-L. *Org. Lett.* **2004**, *6*, 2381.

(11) (a) Wu, S.; Zhang, W.; Zhang, Z.; Zhang, X. *Org. Lett.* **2004**, *6*, 3565. (b) Zhang, W.; Wang, C.-J.; Gao, W.; Zhang, X. *Tetrahedron Lett.* **2005**, *46*, 6087. (c) Zhang, W.; Wu, S.; Zhang, Z.; Yennawar, H.; Zhang, X. *Org. Biomol. Chem.* **2006**, *4*, 4474.

(12) (a) Xie, J.-H.; Zhou, Q.-L. *Acc. Chem. Res.* **2008**, *41*, 581. (b) Bajracharya, G. B.; Arai, M. A.; Koranne, P. S.; Suzuki, T.; Takizawa, S.; Sasai, H. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 285. (c) Ding, K.; Han, Z.; Wang, Z. *Chem. Asian J.* **2009**, *4*, 32. (d) Xie, J.-H.; Zhou, Q.-L. *Acta Chim. Sinica* **2014**, *72*, 778. (e) Liu, Y.; Li, W.; Zhang, J. *Natl. Sci. Rev.* **2017**, *4*, 326.

(13) (a) Chan, A. S. C.; Hu, W. H.; Pai, C. C.; Lau, C. P. *J. Am. Chem. Soc.* **1997**, *119*, 9570. (b) Arai, M. A.; Kuraishi, M.; Arai, T.; Sasai, H. *J. Am. Chem. Soc.* **2001**, *123*, 2907. (c) Fu, Y.; Xie, J.-H.; Hu, A. G.; Zhou, H.; Wang, L. X.; Zhou, Q.-L. *Chem. Commun.* **2002**, 480. (d) Zoraida, F.; Beentjes, M. S.; Batema, G. D.; Dieleman, C. B.; van Strijdonck, G. P. F.; Joost, N. H. R.; Paul, C. J. K.; Jan, F.; Kees, G.; van Leeuwen, P. W. N. M. *Angew. Chem. Int. Ed.* **2003**, *42*, 1284. (e) Xie, J-H.; Duan, H-F.; Fan, B-M.; Cheng, X.; Wang, L-X.; Zhou, Q-L. *Adv. Synth. Catal.* **2004**, *346*, 625. (f) Han, Z. B.; Wang,

Z.; Zhang, X. M.; Ding, K. L. *Angew. Chem. Int. Ed.* **2009**, *48*, 5345. (g) Li, J.; Chen, G.; Wang, Z.; Zhang, R.; Zhang, X. M.; Ding, K. *Chem. Sci.* **2011**, *2*, 1141. (h) Wang, X. M.; Meng, F. Y.; Wang, Y.; Han, Z. B.; Chen, Y. J.; Liu, L.; Wang, Z.; Ding, K. L. *Angew. Chem. Int. Ed.* **2012**, *51*, 9276.

(14) For recent examples from our group, see: (a) Xu, F.; Huang, D.; Han, C.; Shen, W.; Lin, X.; Wang, Y. *J. Org. Chem.* **2010**, *75*, 8677. (b) Huang, D.; Xu, F.; Lin, X.; Wang, Y. G. *Chem. Eur. J.* **2012**, *18*, 3148. (c) Li, X.; Zhao, Y.; Qu, H.; Mao, Z.; Lin, X. *Chem. Commun.* **2013**, *49*, 1401. (d) Huang, D.; Li, X.; Xu, F.; Li, L.; Lin, X. *ACS Catal.* **2013**, *3*, 2244. (e) Li, X.; Chen, D.; Gu, H.; Lin, X. *Chem. Commun.* **2014**, *50*, 7538. (f) Shen, X.; Wang, Y.; Wu, T.; Mao, Z.; Lin, X. *Chem. Eur. J.* **2015**, *21*, 9039. (g) Lou, H.; Wang, Y.; Jin, E.; Lin, X. *J. Org. Chem.* **2016**, *81*, 2019. (h) Xie, E.; Rahman, A.; Lin, X. *Org. Chem. Front.* **2017**, *4*, 1407. For selected examples by other groups, see: (i) Čorić, I.; Müller, S.; List, B. *J. Am. Chem. Soc.* **2010**, *132*, 17370. (j) Xing, C.; Liao, Y.; Ng, J.; Hu, Q. *J. Org. Chem.* **2011**, *76*, 4125. (k) Xu, B.; Zhu, S.-F.; Xie, X.-L.; Shen, J.-J.; Zhou, Q.-L. *Angew. Chem. Int. Ed.* **2011**, *50*, 11483. (l) Rubush, D. M.; Morges, M. A.; Rose, B. J.; Thamm, D. H.; Rovis, T. *J. Am. Chem. Soc.* **2012**, *134*, 13554. (m) Chen, Z.; Wang, B.; Wang, Z.; Zhu, G.; Sun, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 2027. (n) Wu, J.; Wang, Y.; Drljevic, A.; Rauniyar, V.; Phipps, R.; Toste, F. D. *Proc. Natl. Acad. Sci. U S A* **2013**, *110*, 13729. (o) Wang, S.-G.; You, S.-L. *Angew. Chem. Int. Ed.* **2014**, *53*, 2194. (p) Zhang, Y.; Zhao, J.; Jiang, F.; Sun, S.; Shi, F. *Angew. Chem. Int. Ed.* **2014**, *53*, 13912. (q) Gobé, V.; Guinchard, X. *Chem. Eur. J.* **2015**, *21*, 8511. (r) Rong, Z.; Zhang, Y.; Chua, R. H. B.; Pan, H.; Zhao, Y. *J. Am. Chem. Soc.* **2015**, *137*, 4944. (s) Li, S.; Zhang, J.; Li, X.; Cheng, D.; Tan, B. *J. Am. Chem. Soc.* **2016**, *138*, 16561. For a recent review focusing on SPAs, see: (t) Rahman, A.; Lin, X. *Org. Biomol. Chem.* **2018**, *16*, 4753.

(15) (a) Sun, W.; Gu, H.; Lin, X. *J. Org. Chem.* **2018**, *83*, 4034. (b) Chang, S.; Wang, L.; Lin, X. *Org. Biomol. Chem.* **2018**, *16*, 2239.

(16) (a) Fisher, C. H.; Furlong, R. W.; Grant, M. *J. Am. Chem. Soc.* **1936**, *58*, 820. (b) Molteni, V.; Rhodes, D.; Rubins, K.; Hansen, M.; Bushman, F. D.; Siegel, J. S. *J. Med. Chem.* **2000**, *43*, 2031. (c) Chen, W.-F.; Lin, H.-Y.; Dai, S. A. *Org. Lett.* **2004**, *6*, 2341.

(17) CCDC 1843734 contains the supplementary crystallographic data for compound **6a** reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

(18) CCDC 1845549 contains the supplementary crystallographic data for (*R*)-TMSIOL reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

(19) CCDC 1854445 contains the supplementary crystallographic data for (*S*)-SPINOL reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

(20) For reviews, see: (a) Marques, C. S.; Burke, A. J. *ChemCatChem* **2011**, *3*, 635. (b) Tian, P.; Dong, H.-Q.; Lin, G.-Q. *ACS Catal.* **2012**, *2*, 95. (c) Chen, D.; Xu, M.-H. *Chin. J. Org. Chem.* **2017**, *37*, 1589. For selected examples, see: (d) Duan, H.-F.; Jia, Y.-X.; Wang, L.-X.; Zhou, Q.-L. *Org. Lett.* **2006**, *8*, 2567. (e) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336.