

# Synthesis of a new chiral amino phosphine ligand and its application in the asymmetric allylic alkylation (AAA) reaction

Jianqing Feng, D. Scott Bohle and Chao-Jun Li\*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6

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**Abstract**—This article describes the synthesis of a new chiral amino phosphine ligand based on an amino naphthol starting material, which is resolved efficiently by using L-tartaric acid. The asymmetric induction of the ligand in the Pd(0)-catalyzed allylic substitution of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate was investigated. Good yields and enantiomeric excesses up to 78% of the product were obtained.

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## 1. Introduction

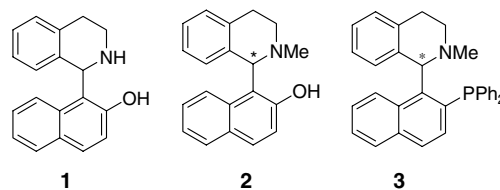
The development of novel chiral ligands remains one of the most attractive areas in the field of transition metal-catalyzed asymmetric reactions.<sup>1</sup> Chiral *N,P*-ligands represent an important type of chirality transfer agents for asymmetric catalysis.<sup>2</sup>

Meanwhile, palladium-catalyzed asymmetric allylic substitution reactions through the use of chiral ligands have been the subject of extended interest in the synthetic community due to their wide synthetic scope, practical simplicity, and potential for asymmetric syntheses.<sup>3</sup> Recently, non-symmetrical heterobidentate ligands were found to be efficient chiral sources for asymmetric allylic substitutions. These ligands regulate the enantioselectivity through their steric and ligand effects. In particular, the coordination of ligands with different donor ability affects the susceptibility of the  $\pi$ -allyl terminal carbons *trans* to the metal center differently towards nucleophiles (*trans*-effect) and results in high regioselectivity in the nucleophilic attack.<sup>4</sup> Some successful examples include 2-(phosphinoaryl)oxazolines<sup>4a-c</sup> and (phosphinonaphthyl) isoquinoline (QUINAP).<sup>4d</sup>

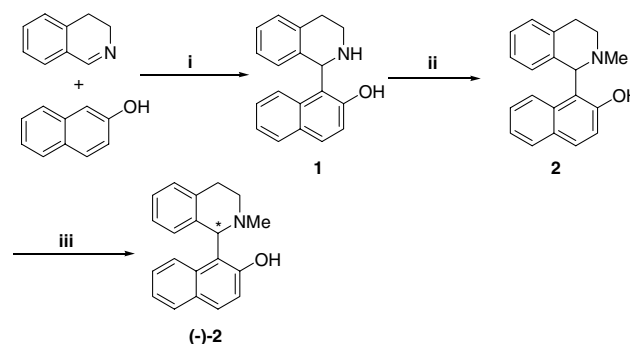
As part of our continuous effort to develop nitrogen-containing ligands for enantioselective catalysis,<sup>5</sup> we herein report the synthesis of a new amino phosphine ligand mTHIQ-NAP, **3** based on **1**, and the application of ligand **3** in the Pd-catalyzed asymmetric allylic alkylation.

## 2. Results and discussions

In our previous report, a novel amino phenol, THIQNOL **1** can be prepared efficiently from dihydroisoquinoline and 1-naphthol (Scheme 1).<sup>5</sup>



A self-catalytic aza-Friedel–Crafts method was employed to generate a 1-naphtholyl tetrahydroisoquinoline product

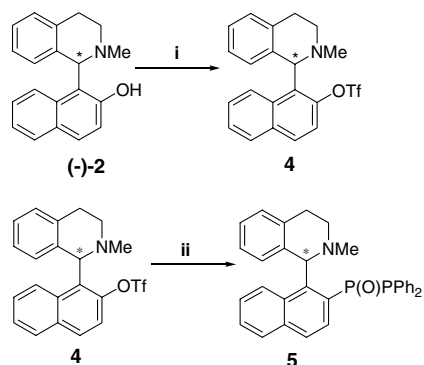


**Scheme 1.** Reagents and conditions: (i) Neat, 60 °C, 92%; (ii) MeI, KHCO<sub>3</sub>, DMF, rt, 98%; (iii) 0.5 equiv L-tartaric acid, DCM, EtOH, >99% ee.

\* Corresponding author. Tel.: +1 514 398 8457; e-mail: cj.li@mcgill.ca

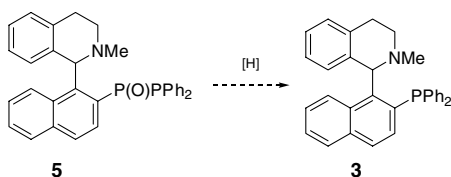
in near-quantitative yield under neat conditions. Subsequently, compound **1** was methylated with  $\text{CH}_3\text{I}$  in the presence of  $\text{KHCO}_3$  to give **2** (mTHIQNOL) in high yield. Racemic compound **2** can be readily resolved by *L*-tartaric acid in more than 99% enantiomeric purity.

Treatment of (–)-**2** with trifluoromethanesulfonic anhydride in the presence of pyridine gave its triflate derivative **4** in 98% yield. The coupling reaction of **4** with  $\text{Ph}_2\text{P}(\text{O})\text{H}$  catalyzed by  $\text{Pd}(\text{OAc})_2/\text{dppp}$  [dppp = 1,3-bis(diphenylphosphino)propane] gave compound **5** in 44% yield (Scheme 2).



**Scheme 2.** Reagents and conditions: (i)  $\text{Tf}_2\text{O}$ , pyridine, DCM, 0 °C, 98%; (ii)  $\text{Ph}_2\text{P}(\text{O})\text{H}$ ,  $\text{Pd}(\text{OAc})_2$ , dppp, DMSO, 100 °C,  $^t\text{Pr}_2\text{EtN}$ , 44%.

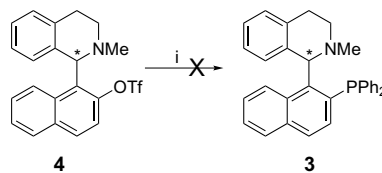
With phosphine oxide **5** in hand, we attempted to synthesize tertiary phosphine **3** through reduction of the phosphine oxygen double bond (Scheme 3). Various reducing systems were screened. For example, by using  $\text{HSiCl}_3/\text{Et}_3\text{N}$ ,  $\text{LiAlH}_4$ , or  $\text{DIBAL-H}$ , we could only isolate the compound derived from the breaking of carbon–phosphine bond of diphenylphosphine oxide. The  $\text{SmI}_2\text{-HMPT}$  and  $\text{LiAlH}_4\text{-CeCl}_3$  systems were also examined. Unfortunately, all these attempts failed to afford the anticipated product **3**.



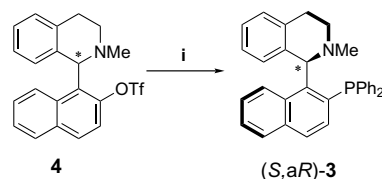
**Scheme 3.**

Subsequently, we changed our strategy to phosphinate the triflate directly with diphenylphosphine following the reported method (Scheme 4).<sup>6</sup> Heating a mixture of chiral triflate **4**, diphenylphosphine, and 10 mol % [bis(diphenylphosphino)ethane]nickel dichloride with DABCO in DMF at 100 °C for 2 days did not provide the desired phosphine **3**.

Finally, inspired by the method published by Chan,<sup>7</sup> we realized the key step, phosphination, by using the  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2/\text{Zn}/\text{Ph}_2\text{PCL}$  system (Scheme 5). With **4** as the starting material, the chiral *N,P*-ligand (*S,aR*)-**3** was



**Scheme 4.** Reagents and conditions: (i)  $\text{HPPH}_2$ ,  $\text{NiCl}_2(\text{dpppe})$ , DABCO, DMF, 100 °C, 2 d.



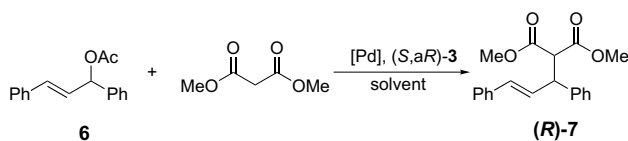
**Scheme 5.** Reagents and conditions: (i)  $\text{Ph}_2\text{PCL}$ ,  $\text{NiCl}_2(\text{PPh}_3)_2$ , Zn, DMF, 110 °C, 12 h, 47%, >98% ee.

isolated in the 47% yield. The structure and configuration was confirmed by X-ray single crystal analysis. The ee of the ligand was retained at more than 98%, and was confirmed by chiral HPLC.

With the new *N,P*-ligand in hand, its use as a chiral ligand for asymmetric reactions was briefly examined. The  $\text{Pd}(0)$ -catalyzed allylic substitution of racemic 1,3-diphenylprop-2-en-1-yl acetate **6** with dimethyl malonate was taken as a model reaction. Table 1 shows the details of our results. The reaction carried out in  $\text{CH}_2\text{Cl}_2$  at 25 °C with  $[\text{Pd}(\text{C}_3\text{H}_5\text{Cl})_2]$  as a catalyst precursor, (*S,aR*)-**3** as chiral ligand, and  $\text{KOAc}/N,O$ -bis(trimethylsilyl)acetamide (BSA) as base gave (*R*)-**7** in 91% yield and 68% ee (entry 1). Decreasing the temperature led to a significant improvement in the enantioselectivity of the reaction (entry 2 vs 1). Using  $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$  as the catalyst precursor, decreased the enantioselectivity; however the product yield did increase (entries 3 vs 2). Substitution of the reaction solvent with toluene or THF did not improve either the yield or enantioselectivity (entries 4 and 5). The yields remained similar (74–85% isolated yields) upon changing the base (entries 6 and 7); however, the enantioselectivity decreased significantly.<sup>8</sup> The (*R*)-configuration of the allylic substitution product was assigned by comparing the retention time of the major enantiomer with literature reports.<sup>9</sup> It should be noted that when  $\text{Cs}_2\text{CO}_3$  was used as the base, the absolute configuration of the product obtained, switched from (*R*) to (*S*) (entry 8).

### 3. Conclusion

In conclusion, we have designed and synthesized a new chiral amino phosphine ligand from an amino naphthol starting material which can be efficiently resolved by *L*-tartaric acid. The application of the ligand in the asymmetric allylic alkylation reaction has been investigated briefly; and good yields and enantiomeric excesses up to 78% of the product were obtained. Further studies on the modifications of the

**Table 1.** Asymmetric Pd(0)-catalyzed substitution of **6** with dimethyl malonate

Entry	Conditions	Time	Yield <sup>a</sup> (%)	ee <sup>b</sup> (%)
1	CH <sub>2</sub> Cl <sub>2</sub> , BSA, KOAc, [(allyl)PdCl] <sub>2</sub> , rt	48	91	68
2	CH <sub>2</sub> Cl <sub>2</sub> , BSA, KOAc, [(allyl)PdCl] <sub>2</sub> , –25 °C	48	74	78
3	CH <sub>2</sub> Cl <sub>2</sub> , BSA, KOAc, Pd <sub>2</sub> (dba) <sub>3</sub> CHCl <sub>3</sub> , –25 °C	48	82	53
4	THF, BSA, KOAc, [(allyl)PdCl] <sub>2</sub> , –25 °C	48	68	15
5	Toluene, BSA, KOAc, [(allyl)PdCl] <sub>2</sub> , –25 °C	48	Trace	nd
6	CH <sub>2</sub> Cl <sub>2</sub> , BSA, LiOAc, [(allyl)PdCl] <sub>2</sub> , –25 °C	48	85	37
7	CH <sub>2</sub> Cl <sub>2</sub> , BSA, CsOAc, [(allyl)PdCl] <sub>2</sub> , –25 °C	48	79	40
8	CH <sub>2</sub> Cl <sub>2</sub> , Cs <sub>2</sub> CO <sub>3</sub> , [(allyl)PdCl] <sub>2</sub> , –25 °C	48	95	–44

<sup>a</sup> Isolated yield.

<sup>b</sup> Determined by HPLC on Chiralpak AD column; the absolute configuration of the product was assigned as (*R*) (by comparing the retention time with the reported value).

ligand and their applications to other asymmetric reactions are currently in progress in our laboratory.

## 4. Experimental

### 4.1. General information

<sup>1</sup>H NMR spectra were recorded on Varian 300 and 400 MHz spectrometers and the chemical shifts are reported in parts per million ( $\delta$ ) relative to the internal standard TMS (0 ppm) for CDCl<sub>3</sub>. The coupling constants, *J*, are reported in Hertz (Hz). <sup>13</sup>C NMR spectra were obtained at 75 and 100 MHz and referenced to the internal solvent signals (central peak is 77.00 ppm in CDCl<sub>3</sub>). HRMS analyses were obtained on a Kratos MS25RFA Mass Spectrometer. IR spectra were recorded by using an ABB Bomem MB100 instrument. Melting points were recorded with Melting Point Apparatus, Gallenkamp. All reagents were weighed and handled in air at room temperature. All reagents were purchased from Aldrich Chemical Company except for 3,4-dihydroisoquinoline, which was prepared from 1,2,3,4-tetrahydroisoquinoline according to literature methods.<sup>10</sup> All reagents were used without further purification. X-ray diffraction was measured on a Bruker D8 diffractometer with Mo K $\alpha$  radiation at room temperature.

### 4.2. 1-(1,2,3,4-Tetrahydro-isoquinolin-1-yl)-naphthalen-2-ol 1 (THIQNOL)

The compound was synthesized by our reported method.<sup>5</sup> Mp: 148–150 °C; IR (KBr pellet):  $\nu_{\max}$  3289, 3056, 3018, 2954, 2921, 2886, 2834, 1622, 1597, 1462, 1230, 807, 738 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$  8.01 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.08 (m, 3H), 6.87 (m, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.03 (s, 1H), 3.53 (m, 1H), 3.28 (m, 2H), 2.89 (d, *J* = 14 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm)  $\delta$  155.9, 136.2, 133.9, 133.4, 129.7, 128.8, 128.7, 128.3, 126.9 (2x), 126.7, 126.2,

122.6, 121.4, 120.2, 118.2, 55.6, 43.8, 29.2; MS (EI) *m/z* (%) 275 (M<sup>+</sup>, 100), 258, 229, 215; HRMS Calcd for C<sub>19</sub>H<sub>17</sub>NO: 275.1310. Found: 275.1307.

### 4.3. Procedure for synthesizing 1-(2-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-2-ol 2 (mTHIQNOL)

Powdered KHCO<sub>3</sub> (690 mg, 6.9 mmol) was added to a solution of **1** (1.85 g, 6.73 mmol) in DMF (60 mL). After stirring for 10 min, CH<sub>3</sub>I (1.05 g, 7.40 mmol) in DMF (20 mL) was added into the slurry. After an additional 8 h of stirring, the mixture was filtered and the solid was washed consecutively with water and acetone to give a white powder (1.7 g, 5.9 mmol, 87%). Mp: 210–212 °C; IR (KBr pellet)  $\nu_{\max}$  2956, 1622, 1516, 821 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$  8.06 (d, *J* = 8.0 Hz, 1H), 7.85–7.71 (m, 2H), 7.52–7.48 (m, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.10–7.03 (m, 3H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 5.37 (s, 1H), 3.43–3.38 (m, 1H), 3.34–3.30 (m, 1H), 2.91–2.77 (m, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm)  $\delta$  155.3, 135.8, 134.0, 133.2, 129.5, 128.9, 128.4, 128.1, 127.3, 126.9, 126.5, 126.2, 122.5, 121.4, 119.7, 117.7, 64.1, 52.9, 43.8, 29.3; HRMS Calcd for C<sub>20</sub>H<sub>20</sub>NO: 290.1539. Found: 290.1541.

### 4.4. Procedure for resolving 1-(2-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-2-ol 2

(2*R*,3*R*)-Tartaric acid (114 mg, 0.76 mmol) in EtOH (15 mL) was added into a solution of racemic **2** (440 mg, 1.52 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). Stirring the reaction mixture at room temperature overnight led to the formation of a white solid. After stirring for another 24 h, the solution was filtered to afford a colorless solid (300 mg, 0.68 mmol, 45%). This solid was treated with aqueous NaHCO<sub>3</sub> solution, and then extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under a reduced pressure to afford a white powder 182 mg (0.63 mmol, 41%). The enantiomeric purity of the product was determined by chiral HPLC (Daicel Chiralcel OD-H, hexane–isopropanol =

97.5:2.5, flow rate 1.0 mL/min): enantiomeric excess >99%;  $[\alpha]_{\text{D}}^{20} = -304.7$  ( $c$  0.4,  $\text{CH}_2\text{Cl}_2$ ). The mother solution was evaporated to dryness under a reduced pressure to give a residue, which was crystallized from hexane/ethyl acetate to afford a white powder (172 mg, 0.60 mmol, 39% yield). The enantiomeric purity was determined by chiral HPLC (Daicel Chiralcel OD-H, hexane–isopropanol = 97.5:2.5, flow rate 1.0 mL/min) to be 92% ee.

#### 4.5. (–)-1-(1,2,3,4-Tetrahydro-2-methylisoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate 4

Trifluoromethanesulfonic anhydride (0.7 mL, 4.15 mmol) was slowly added into a solution of (–)-2 (1.0 g, 3.46 mmol) and pyridine (0.5 mL, 5.12 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (20.0 mL) at 0 °C. The reaction mixture was stirred for 1 h and then warmed to room temperature. After removal of the solvent under reduced pressure, the resulting residue was subjected to chromatographic separation on silica gel with hexane–EtOAc (10:1) as eluent to give 4 as a light yellow oil (1.42 g, 98%);  $[\alpha]_{\text{D}}^{20} = -81.55$  ( $c$  1.8,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.39 (d,  $J = 8.1$  Hz, 1H), 7.93–7.83 (m, 2H), 7.48–7.09 (m, 4H), 6.92 (t,  $J = 7.7$  Hz, 1H), 6.59 (s, 1H), 5.27 (s, 1H), 3.55–3.50 (m, 1H), 3.32–3.27 (m, 1H), 2.99–2.75 (m, 2H), 2.22 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$  147.1, 133.9, 137.3, 133.5, 131.6, 130.9, 130.5, 128.5, 128.3, 128.0, 126.6, 126.2, 123.3, 120.1, 118.5, 116.9, 113.7, 64.0, 54.1, 44.3, 29.7; HRMS Calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_3\text{SF}_3$  (M+1): 422.1032. Found: 422.1026.

#### 4.6. 1,2,3,4-Tetrahydro-2-methyl-1-(2-(diphenylphosphino)naphthalen-1-yl)isoquinoline 5

To a mixture of 4 (421 mg, 1 mmol), diphenylphosphine oxide (404 mg, 2 mmol),  $\text{Pd}(\text{OAc})_2$  (22 mg, 0.1 mmol), and dppp (62 mg, 0.15 mmol), DMSO (5 mL) and diisopropylethylamine (0.9 mL, 5 mmol) were added, and the mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, washed twice with water, then brine, dried over  $\text{Na}_2\text{SO}_4$ , and then concentrated under a reduced pressure. The resulting residue was subjected to chromatographic separation on silica gel with hexane–EtOAc (1:1) as eluent to give 5 as a white solid (208 mg, 44%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08 (d,  $J = 8.4$  Hz, 1H), 7.97 (d,  $J = 8.1$  Hz, 1H), 7.85 (d,  $J = 8.1$  Hz, 1H), 7.59–6.93 (m, 15H), 6.70–6.61 (m, 1H), 5.50 (s, 1H), 4.11–3.92 (m, 1H), 3.68–3.55 (m, 1H), 2.48 (dd,  $J = 4.5, 17.4$ , 1H), 1.82 (s, 1H).  $^{31}\text{P}$  NMR (121.46 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.5; HRMS Calcd for  $\text{C}_{32}\text{H}_{29}\text{NOP}$  (M+1): 474.1981. Found: 474.1976.

#### 4.7. (S,aR)-1,2,3,4-Tetrahydro-2-methyl-1-(2-(diphenylphosphino)naphthalen-1-yl)isoquinoline 3 (mTHIQ-NAP)

To a solution of 1-(1,2,3,4-tetrahydro-2-methylisoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate 4 (920 mg, 2.2 mmol) and bis(triphenylphosphine) nickel(II) chloride (720 mg, 1.1 mmol) in dry DMF (8 mL) under nitrogen in a Schlenk flask, chlorodiphenylphosphine (0.4 mL, 2.2 mmol) was added after which zinc (100 mg  $\times$  3,

4.6 mmol) was then added in three portions. The color of the solution gradually changed from blue to dark red. The solution was heated to 110 °C under nitrogen for 12 h. The reaction mixture was then cooled down to room temperature and the solvent removed in vacuo. The residue was redissolved in  $\text{CH}_2\text{Cl}_2$  and purified by a short column chromatography on silica gel using ethyl acetate as eluent to obtain the crude product. Further purification by column chromatography on silica gel with eluent (ethyl acetate–hexane, 1:1) afforded the product (472 mg, 47% yield) as a colorless solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.44 (d,  $J = 8.1$  Hz, 1H), 7.71–6.76 (m, 16H), 6.42 (s, 1H), 3.52 (m, 1H), 3.25 (m, 1H), 2.96–2.80 (m, 2H), 2.05 (s, 3H);  $[\alpha]_{\text{D}}^{20} = -130.5$  ( $c$  1.4,  $\text{CHCl}_3$ );  $^{31}\text{P}$  NMR (121.46 MHz,  $\text{CDCl}_3$ ):  $\delta$  –16.0; HRMS Calcd for  $\text{C}_{32}\text{H}_{29}\text{NP}$  (M+1): 458.2032. Found: 458.2025. The enantiomeric purity was determined by HPLC (Chiralcel OD-H, flow rate = 0.5 mL/min, hexane–*iso*-propanol = 90:10,  $t_{\text{R}} = 14.4$  min).

#### 4.8. Typical procedure for Pd(0)-catalyzed asymmetric allylic alkylation reaction

In a Schlenk tube containing 1,3-diphenylprop-2-en-1-yl acetate ( $\pm$ )-6 (252 mg, 1.0 mmol),  $[\text{Pd}(\text{C}_3\text{H}_5\text{Cl})_2]$  (3.7 mg, 0.01 mmol, 1 mol %), and (*S,aR*)-3 (9.0 mg, 0.02 mmol, 2 mol %) in  $\text{CH}_2\text{Cl}_2$  (2 mL) were added. The mixture was stirred at room temperature for 30 min. Dimethyl malonate (396 mg, 3.0 mmol), KOAc (2.8 mg, 0.02 mmol), and BSA (613 mg, 3.0 mmol) were then added at –78 °C. The reaction mixture was stirred at –25 °C for 48 h and then quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  and extracted with EtOAc (3  $\times$  5 mL). The organic phase was washed with saturated aqueous  $\text{NaHCO}_3$  and brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under a reduced pressure. The residue was purified by flash chromatography on silica gel with hexane–EtOAc (6:1) as eluent to produce (*R*)-7<sup>9</sup> (240 mg, 74%) as a colorless oil with 78% ee.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 3.54 (s, 3H), 3.70 (s, 3H), 3.96 (d,  $J = 10.8$  Hz, 1H), 4.25 (dd,  $J = 10.8, 8.7$  Hz, 1H), 6.33 (dd,  $J = 15.4, 8.6$  Hz, 1H), 6.46 (d,  $J = 15.8$  Hz, 1H), 7.17–7.24 (m, 10H). The enantiomeric excess was determined by HPLC (Chiralpak AD, flow rate = 1 mL/min, hexane:*iso*-propanol = 90:10,  $t_{\text{R}} = 9.4$  min,  $t_{\text{S}} = 12.7$  min).

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