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Supporting Online Material for

**Chiral Organic Ion Pair Catalysts Assembled Through a Hydrogen-Bonding Network**

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## Supporting Online Material for Chiral Organic Ion Pair Catalysts Assembled through a Hydrogen-Bonding Network

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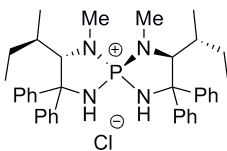
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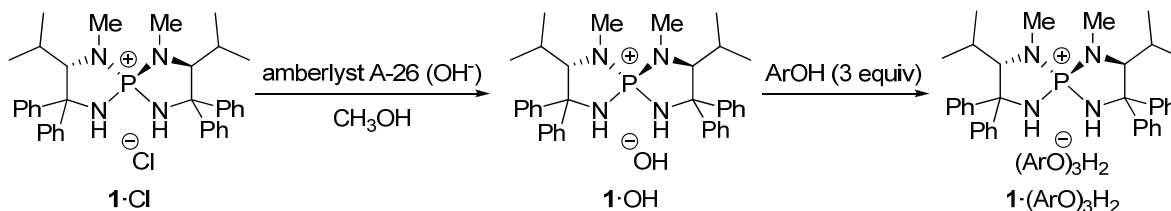
**General Information:** Infrared spectra were recorded on a JASCO FT/IR-300E spectrometer.  $^1\text{H}$  NMR spectra were recorded on a Varian INOVA-500 (500 MHz) or INOVA-700 (700 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance ( $\text{CD}_3\text{OD}$ ; 3.31 ppm) or tetramethylsilane (0.0 ppm) resonance as the internal standard ( $\text{CDCl}_3$ ). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sept = septet, oct = octet, m = multiplet, and br = broad) and coupling constants (Hz).  $^{13}\text{C}$  NMR spectra were recorded on a Varian INOVA-500 (126 MHz) or INOVA-700 (175 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ( $\text{CDCl}_3$ ; 77.16 ppm,  $\text{CD}_3\text{OD}$ ; 49.0 ppm).  $^{31}\text{P}$  NMR spectra were recorded on a Varian Mercury-300BB (121 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from  $\text{H}_3\text{PO}_4$  (0.0 ppm) resonance as the external standard. Optical rotations were measured on a JASCO DIP-1000 polarimeter. The high resolution mass spectra were measured on an BRUKER DALTONICS microTOF focus-KR spectrometer. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF<sub>254</sub>, 0.25 mm). Flash column chromatography was performed on silica gel 60 (spherical, 40-50  $\mu\text{m}$ ; Kanto Chemical Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns ( $\phi$  4.6 mm x 250 mm, DAICEL CHIRALCEL OD-H (ODH), CHIRALPAK IA (IA) or CHIRALPAK IC (IC)) with hexane (H), isopropyl alcohol (IPA), and ethanol (EtOH) as eluent.

Toluene and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Tetraaminophosphonium salts **1a**·Cl and **1b**·Cl (*S1-3*), azlactone **2** (*S4*), and  $\alpha,\beta$ -unsaturated *N*-acylbenzotriazoles **3a-k** (*S5*) were prepared by following the literature procedures. Other simple chemicals were purchased and used as such.

### Experimental Section:

#### Characterization of Tetraaminophosphonium Salts 1:

**1b**·Cl:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (2H, d,  $J = 16.5$  Hz), 7.68 (4H, br), 7.59 (4H, dd,  $J = 7.5$ , 1.0 Hz), 7.39 (4H, t,  $J = 7.5$  Hz), 7.32 (4H, brt,  $J = 7.5$  Hz), 7.28 (2H, t,  $J = 7.5$  Hz), 7.20 (2H, t,  $J = 7.5$  Hz), 3.79 (2H, dd,  $J_{\text{P-H}} = 21.0$  Hz,  $J_{\text{H-H}} = 5.0$  Hz), 1.95-1.85 (2H, m), 1.85-1.77 (2H, m), 1.80 (6H, d,  $J_{\text{P-H}} = 10.0$  Hz), 0.94-0.82 (2H, m), 0.84 (6H, t,  $J = 7.0$  Hz), 0.56 (6H, d,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ )  $\delta$  148.0, 139.5 (d,  $J_{\text{P-C}} = 11.4$  Hz), 128.7, 128.6, 128.0, 127.7, 127.6, 127.0, 73.4 (d,  $J_{\text{P-C}} = 12.6$  Hz), 70.9 (d,  $J_{\text{P-C}} = 9.3$  Hz), 36.1, 32.2 (d,  $J_{\text{P-C}} = 6.0$  Hz), 25.2, 18.9, 12.1;  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  37.7; IR (KBr): 3059, 2967, 2874, 1495, 1446, 1358, 1334, 1191, 1035, 751  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{38}\text{H}_{48}\text{N}_4\text{P}^+$  ( $[\text{M}-\text{Cl}]^+$ ) 591.3611. Found 591.3608;  $[\alpha]_{\text{D}}^{24}$  -268.8 ( $c = 0.95$ ,  $\text{CHCl}_3$ ).



**Counter Anion Exchange Procedure to Prepare Chiral Tetraaminophosphonium Phenoxide 1·(ArO)<sub>3</sub>H<sub>2</sub> (*S6*):** Chiral tetraaminophosphonium chloride **1**·Cl was transformed into the corresponding phosphonium hydroxide **1**·OH by passing a methanolic solution of **1**·Cl through an ion-exchange resin (amberlyst A-26, OH<sup>-</sup> form). The resulting **1**·OH was then treated with phenol (3.0 equiv) in methanol at room temperature. The resulting mixture was co-evaporated with benzene

three times, and subsequent crystallization of the residue from hexane and diethyl ether afforded white solids, which were collected by filtration and dried under reduced pressure to give the title compound.

**1a·(PhO)<sub>3</sub>H<sub>2</sub>:** <sup>1</sup>H NMR (700 MHz, CD<sub>3</sub>OD) δ 7.62 (4H, d, *J* = 7.0 Hz), 7.45 (4H, t, *J* = 7.0 Hz), 7.34 (2H, t, *J* = 7.7 Hz), 7.33 (4H, br), 7.32 (4H, t, *J* = 7.7 Hz), 7.28 (2H, t, *J* = 7.7 Hz), 7.09 (6H, t, *J* = 7.0 Hz), 6.71 (6H, d, *J* = 7.0 Hz), 6.66 (3H, t, *J* = 7.0 Hz), 4.00 (2H, dd, *J*<sub>P-H</sub> = 19.6 Hz, *J*<sub>H-H</sub> = 6.3 Hz), 1.89 (6H, d, *J*<sub>P-H</sub> = 9.8 Hz), 1.87 (2H, oct, *J* = 6.3 Hz), 0.95 (6H, d, *J* = 6.3 Hz), 0.49 (6H, d, *J* = 6.3 Hz), N-H and O-H protons were not found due to deuteration; <sup>13</sup>C NMR (175 MHz, CD<sub>3</sub>OD) δ 161.6, 148.9, 141.6 (d, *J*<sub>P-C</sub> = 12.8 Hz), 130.2, 130.0, 129.2, 129.0, 128.9, 128.7, 127.9, 118.6, 117.4, 72.5 (d, *J*<sub>P-C</sub> = 10.7 Hz), 71.6 (d, *J*<sub>P-C</sub> = 10.7 Hz), 32.8 (d, *J*<sub>P-C</sub> = 6.1 Hz), 30.9, 22.7, 19.8; <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ 36.4.

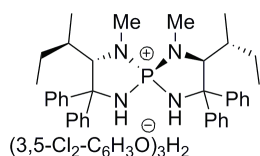
**1a·(4-Me-C<sub>6</sub>H<sub>4</sub>O)<sub>3</sub>H<sub>2</sub>:** <sup>1</sup>H NMR (700 MHz, CD<sub>3</sub>OD) δ 7.62 (4H, d, *J* = 7.7 Hz), 7.45 (4H, t, *J* = 7.7 Hz), 7.35 (2H, t, *J* = 7.7 Hz), 7.33 (4H, br), 7.32 (4H, t, *J* = 7.7 Hz), 7.28 (2H, t, *J* = 7.7 Hz), 6.90 (6H, d, *J* = 8.4 Hz), 6.61 (6H, d, *J* = 8.4 Hz), 4.01 (2H, dd, *J*<sub>P-H</sub> = 19.6 Hz, *J*<sub>H-H</sub> = 6.3 Hz), 2.19 (9H, s), 1.89 (6H, d, *J*<sub>P-H</sub> = 9.8 Hz), 1.87 (2H, oct, *J* = 6.3 Hz), 0.95 (6H, d, *J* = 6.3 Hz), 0.49 (6H, d, *J* = 6.3 Hz), N-H and O-H protons were not found due to deuteration; <sup>13</sup>C NMR (175 MHz, CD<sub>3</sub>OD) δ 159.0, 148.9, 141.7 (d, *J*<sub>P-C</sub> = 13.3 Hz), 130.6, 130.0, 129.2, 129.0, 128.9, 128.7, 127.9, 127.6, 117.1, 72.5 (d, *J*<sub>P-C</sub> = 10.6 Hz), 71.7 (d, *J*<sub>P-C</sub> = 10.0 Hz), 32.8 (d, *J*<sub>P-C</sub> = 6.1 Hz), 30.9, 22.7, 20.5, 19.8; <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ 36.4.

**1a·(4-Cl-C<sub>6</sub>H<sub>4</sub>O)<sub>3</sub>H<sub>2</sub>:** <sup>1</sup>H NMR (700 MHz, CD<sub>3</sub>OD) δ 7.62 (4H, d, *J* = 7.7 Hz), 7.44 (4H, t, *J* = 7.7 Hz), 7.34 (2H, t, *J* = 7.7 Hz), 7.33 (4H, br), 7.32 (4H, t, *J* = 7.7 Hz), 7.28 (2H, t, *J* = 7.7 Hz), 7.07 (6H, d, *J* = 8.4 Hz), 6.68 (6H, d, *J* = 8.4 Hz), 4.00 (2H, dd, *J*<sub>P-H</sub> = 19.6 Hz, *J*<sub>H-H</sub> = 6.3 Hz), 1.89 (6H, d, *J*<sub>P-H</sub> = 9.8 Hz), 1.86 (2H, oct, *J* = 6.3 Hz), 0.95 (6H, d, *J* = 6.3 Hz), 0.49 (6H, d, *J* = 6.3 Hz), N-H and O-H protons were not found due to deuteration; <sup>13</sup>C NMR (175 MHz, CD<sub>3</sub>OD) δ 160.0, 148.9, 141.6 (d, *J*<sub>P-C</sub> = 12.6 Hz), 130.0, 129.2, 129.0, 128.9, 128.7, 127.9, 123.4, 118.6, 72.5 (d, *J*<sub>P-C</sub> = 11.4 Hz), 71.6 (d, *J*<sub>P-C</sub> = 10.0 Hz), 32.8 (d, *J*<sub>P-C</sub> = 6.1 Hz), 30.9, 22.7, 19.8, one carbon was not found probably due to overlapping; <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ 36.4.

**1a·(2-Cl-C<sub>6</sub>H<sub>4</sub>O)<sub>3</sub>H<sub>2</sub>:** <sup>1</sup>H NMR (700 MHz, CD<sub>3</sub>OD) δ 7.62 (4H, d, *J* = 7.7 Hz), 7.45 (4H, t, *J* = 7.7 Hz), 7.34 (2H, t, *J* = 7.7 Hz), 7.33 (4H, br), 7.32 (4H, t, *J* = 7.7 Hz), 7.28 (2H, t, *J* = 7.7 Hz), 7.17 (3H, dd, *J* = 7.7, 1.4 Hz), 6.98 (3H, td, *J* = 7.7, 1.4 Hz), 6.80 (3H, dd, *J* = 7.7, 1.4 Hz), 6.54 (3H, td, *J* = 7.7, 1.4 Hz), 4.00 (2H, dd, *J*<sub>P-H</sub> = 19.6 Hz, *J*<sub>H-H</sub> = 6.3 Hz), 1.89 (6H, d, *J*<sub>P-H</sub> = 10.5 Hz), 1.87 (2H, oct, *J* = 6.3 Hz), 0.95 (6H, d, *J* = 6.3 Hz), 0.49 (6H, d, *J* = 6.3 Hz), N-H and O-H protons were not found due to deuteration; <sup>13</sup>C NMR (175 MHz, CD<sub>3</sub>OD) δ 159.1, 148.9, 141.6 (d, *J*<sub>P-C</sub> = 12.8 Hz), 130.5, 130.0, 129.2, 129.0, 128.9, 128.7, 128.6, 127.9, 123.1, 119.4, 118.1, 72.5 (d, *J*<sub>P-C</sub> = 10.7 Hz), 71.7 (d, *J*<sub>P-C</sub> = 10.0 Hz), 32.8 (d, *J*<sub>P-C</sub> = 6.0 Hz), 30.9, 22.7, 19.8; <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ 36.4.

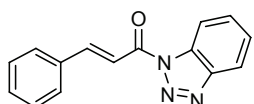
**1a·(3-Cl-C<sub>6</sub>H<sub>4</sub>O)<sub>3</sub>H<sub>2</sub>:** <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 7.62 (4H, d, *J* = 7.5 Hz), 7.45 (4H, t, *J* = 7.5 Hz), 7.35 (2H, t, *J* = 7.5 Hz), 7.34 (4H, br), 7.32 (4H, t, *J* = 7.5 Hz), 7.30-7.26 (2H, m), 7.05 (3H, t, *J* = 8.0 Hz), 6.71 (3H, t, *J* = 2.0 Hz), 6.65 (3H, d, *J* = 8.0 Hz), 6.62 (3H, d, *J* = 8.0 Hz), 4.01 (2H, dd, *J*<sub>P-H</sub> = 20.0 Hz, *J*<sub>H-H</sub> = 6.5 Hz), 1.89 (6H, d, *J*<sub>P-H</sub> = 10.0 Hz), 1.87 (2H, oct, *J* = 6.5 Hz), 0.95 (6H, d, *J* = 6.5 Hz), 0.49 (6H, d, *J* = 6.5 Hz), N-H and O-H protons were not found due to deuteration; <sup>13</sup>C NMR (175 MHz, CD<sub>3</sub>OD) δ 163.1, 148.9, 141.6 (d, *J*<sub>P-C</sub> = 13.4 Hz), 135.5, 131.1, 130.0, 129.2, 129.0, 128.9, 128.7, 127.9, 118.4, 117.7, 116.1, 72.5 (d, *J*<sub>P-C</sub> = 10.7 Hz), 71.6 (d, *J*<sub>P-C</sub> = 10.2 Hz), 32.8 (d, *J*<sub>P-C</sub> = 6.1 Hz), 30.9, 22.7, 19.8; <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ 36.4.

**1a·(3,5-Cl<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>H<sub>2</sub>:** <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 7.62 (4H, d, *J* = 7.5 Hz), 7.45 (4H, t, *J* = 7.5 Hz), 7.35 (2H, t, *J* = 7.5 Hz), 7.34 (4H, br), 7.32 (4H, t, *J* = 7.5 Hz), 7.30-7.26 (2H, m), 6.68 (3H, t, *J* = 2.0 Hz), 6.64 (6H, d, *J* = 2.0 Hz), 4.01 (2H, dd, *J*<sub>P-H</sub> = 20.0 Hz, *J*<sub>H-H</sub> = 6.5 Hz), 1.89 (6H, d, *J*<sub>P-H</sub> = 10.0 Hz), 1.87 (2H, oct, *J* = 6.5 Hz), 0.95 (6H, d, *J* = 6.5 Hz), 0.49 (6H, d, *J* = 6.5 Hz), N-H and O-H protons were not found due to deuteration; <sup>13</sup>C NMR (175 MHz, CD<sub>3</sub>OD) δ 164.0, 148.9, 141.6 (d, *J*<sub>P-C</sub> = 12.8 Hz), 136.1, 130.0, 129.2, 129.0, 128.9, 128.7, 127.9, 118.1, 116.5, 72.5 (d, *J*<sub>P-C</sub> = 10.7 Hz), 71.7 (d, *J*<sub>P-C</sub> = 10.0 Hz), 32.8 (d, *J*<sub>P-C</sub> = 6.0 Hz), 30.9, 22.7, 19.8; <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ 36.4; IR (KBr): 2964, 1578, 1446, 1423, 1370, 1269, 1019, 936, 797, 753 cm<sup>-1</sup>.

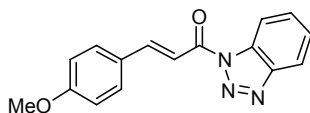


**1b**·(3,5-Cl<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>H<sub>2</sub>: <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 7.61 (4H, d, *J* = 7.5 Hz), 7.45 (4H, t, *J* = 7.5 Hz), 7.35 (2H, t, *J* = 7.5 Hz), 7.34 (4H, br), 7.33 (4H, t, *J* = 7.5 Hz), 7.31-7.26 (2H, m), 6.68 (3H, t, *J* = 2.0 Hz), 6.64 (6H, d, *J* = 2.0 Hz), 4.09 (2H, dd, *J*<sub>P-H</sub> = 19.0 Hz, *J*<sub>H-H</sub> = 4.0 Hz), 1.89 (6H, d, *J*<sub>P-H</sub> = 10.0 Hz), 1.78 (2H, dqd, *J* = 13.0, 7.0, 2.5 Hz), 1.42 (2H, qtd, *J* = 7.0, 4.0, 2.5 Hz), 0.93 (2H, dqd, *J* = 13.0, 7.0, 4.0 Hz), 0.76 (6H, t, *J* = 7.0 Hz), 0.62 (6H, d, *J* = 7.0 Hz), N-H and O-H protons were not found due to deuteration; <sup>13</sup>C NMR (175 MHz, CD<sub>3</sub>OD) δ 163.9, 148.9, 141.7 (d, *J*<sub>P-C</sub> = 12.6 Hz), 136.0, 130.0, 129.1, 129.0, 128.8, 128.7, 127.9, 118.1, 116.5, 72.8 (d, *J*<sub>P-C</sub> = 10.7 Hz), 71.5 (d, *J*<sub>P-C</sub> = 10.7 Hz), 37.7, 32.6 (d, *J*<sub>P-C</sub> = 6.0 Hz), 26.0, 18.8, 12.2; <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>OD) δ 36.8; IR (KBr): 2971, 1581, 1424, 1374, 1210, 1034, 936, 827, 796, 752 cm<sup>-1</sup>.

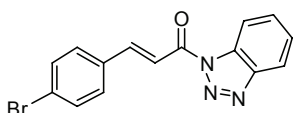
### Characterization of α,β-Unsaturated *N*-Acybenzotriazoles 3:



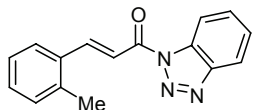
**3a** (*S5*): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.43 (1H, d, *J* = 7.5 Hz), 8.17 (1H, d, *J* = 16.0 Hz), 8.16 (1H, d, *J* = 7.5 Hz), 8.14 (1H, d, *J* = 16.0 Hz), 7.78-7.76 (2H, m), 7.70 (1H, t, *J* = 7.5 Hz), 7.54 (1H, t, *J* = 7.5 Hz), 7.51-7.46 (3H, m).



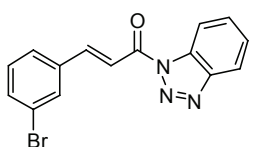
**3b** (*S7*): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.43 (1H, dt, *J* = 8.0, 1.0 Hz), 8.15 (1H, dt, *J* = 8.0, 1.0 Hz), 8.12 (1H, d, *J* = 15.0 Hz), 8.00 (1H, d, *J* = 15.0 Hz), 7.73 (2H, d, *J* = 9.0 Hz), 7.68 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz), 7.53 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz), 6.99 (2H, d, *J* = 9.0 Hz), 3.89 (3H, s).



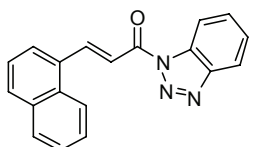
**3c**: <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 8.40 (1H, dt, *J* = 8.4, 1.4 Hz), 8.15 (1H, dt, *J* = 8.4, 1.4 Hz), 8.11 (1H, d, *J* = 15.4 Hz), 8.06 (1H, d, *J* = 15.4 Hz), 7.68 (1H, ddd, *J* = 8.4, 7.0, 1.4 Hz), 7.63-7.58 (4H, m), 7.53 (1H, ddd, *J* = 8.4, 7.0, 1.4 Hz); <sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>) δ 163.8, 147.4, 146.5, 133.1, 132.6, 131.5, 130.5, 130.4, 126.5, 126.1, 120.4, 116.8, 114.9; IR (KBr): 1699, 1618, 1486, 1450, 1405, 1389, 1072, 995, 790, 753 cm<sup>-1</sup>; HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>11</sub>BrN<sub>3</sub>O<sup>+</sup>Na<sup>+</sup> ([M+Na]<sup>+</sup>) 349.9899, 351.9880. Found 349.9898, 351.9894.



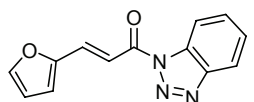
**3d** (*S7*): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.48 (1H, d, *J* = 15.5 Hz), 8.42 (1H, d, *J* = 8.0 Hz), 8.16 (1H, d, *J* = 8.0 Hz), 8.07 (1H, d, *J* = 15.5 Hz), 7.86 (1H, d, *J* = 7.5 Hz), 7.69 (1H, t, *J* = 8.0 Hz), 7.54 (1H, d, *J* = 8.0 Hz), 7.37 (1H, t, *J* = 7.5 Hz), 7.31 (1H, t, *J* = 7.5 Hz), 7.28 (1H, d, *J* = 7.5 Hz), 2.56 (3H, s).



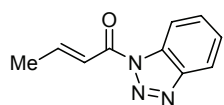
**3e**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (1H, d, *J* = 8.0 Hz), 8.17 (1H, d, *J* = 8.0 Hz), 8.13 (1H, d, *J* = 16.0 Hz), 8.06 (1H, d, *J* = 16.0 Hz), 7.90 (1H, t, *J* = 1.0 Hz), 7.70 (1H, t, *J* = 8.0 Hz), 7.67 (1H, dd, *J* = 8.0, 1.0 Hz), 7.60 (1H, dd, *J* = 8.0, 1.0 Hz), 7.55 (1H, t, *J* = 8.0 Hz), 7.35 (1H, t, *J* = 8.0 Hz); <sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>) δ 163.6, 146.9, 146.5, 136.3, 134.3, 131.7, 131.5, 130.7, 130.6, 127.6, 126.5, 123.4, 120.4, 117.6, 114.9; IR (KBr): 1704, 1628, 1452, 1372, 1175, 1074, 998, 984, 758 cm<sup>-1</sup>; HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>11</sub>BrN<sub>3</sub>O<sup>+</sup> ([M+H]<sup>+</sup>) 328.0080, 330.0061. Found 328.0066, 330.0003.



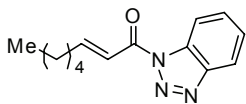
**3f**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.04 (1H, d, *J* = 15.5 Hz), 8.46 (1H, dt, *J* = 8.0, 1.0 Hz), 8.34 (1H, d, *J* = 8.0 Hz), 8.25 (1H, d, *J* = 15.5 Hz), 8.17 (1H, dt, *J* = 8.0, 1.0 Hz), 8.09 (1H, d, *J* = 8.0 Hz), 8.00 (1H, d, *J* = 8.0 Hz), 7.93 (1H, d, *J* = 8.0 Hz), 7.71 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz), 7.65 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz), 7.58<sub>2</sub> (1H, t, *J* = 8.0 Hz), 7.57<sub>9</sub> (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz), 7.55 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz); <sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>) δ 164.0, 146.5, 145.5, 133.9, 132.0, 131.8, 131.6, 131.3, 130.5, 129.1, 127.5, 126.6, 126.4, 126.2, 125.7, 123.3, 120.3, 118.3, 115.0; IR (KBr): 1700, 1605, 1572, 1449, 1376, 1352, 1169, 982, 768, 746 cm<sup>-1</sup>; HRMS (ESI-TOF) Calcd for C<sub>19</sub>H<sub>14</sub>N<sub>3</sub>O<sup>+</sup> ([M+H]<sup>+</sup>) 300.1131. Found 300.1132.



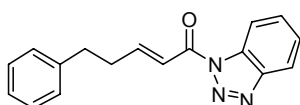
**3g** (*S8*): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (1H, dd, *J* = 8.0, 1.0 Hz), 8.15 (1H, dd, *J* = 8.0, 1.0 Hz), 7.98 (1H, d, *J* = 16.0 Hz), 7.88 (1H, d, *J* = 16.0 Hz), 7.68 (1H, t, *J* = 8.0 Hz), 7.62 (1H, d, *J* = 2.0 Hz), 7.53 (1H, t, *J* = 8.0 Hz), 6.87 (1H, d, *J* = 3.5 Hz), 6.57 (1H, dd, *J* = 3.5, 2.0 Hz).



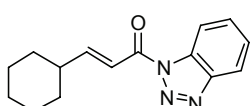
**3h** (*S*):  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (1H, d,  $J = 8.0$  Hz), 8.13 (1H, d,  $J = 8.0$  Hz), 7.66 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 7.57-7.46 (3H, m), 2.13 (3H, d,  $J = 5.5$  Hz).



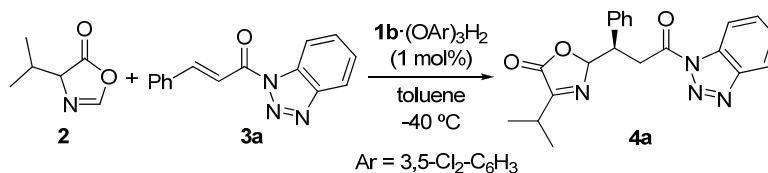
**3i**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (1H, dt,  $J = 8.0, 1.0$  Hz), 8.14 (1H, dt,  $J = 8.0, 1.0$  Hz), 7.66 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 7.53 (1H, d,  $J = 15.0$  Hz), 7.52 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 2.44 (2H, dtd,  $J = 7.5, 5.0, 2.5$  Hz), 1.61 (2H, quin-t,  $J = 7.5, 2.5$  Hz), 1.42-1.32 (4H, m), 0.93 (3H, t,  $J = 7.5$  Hz);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 155.2, 146.4, 131.6, 130.3, 126.3, 120.3, 119.9, 114.9, 33.2, 31.5, 27.7, 22.6, 14.1; IR (KBr): 2956, 2929, 1716, 1637, 1485, 1450, 1377, 1286, 988, 751  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}^+$  ( $[\text{M}+\text{H}]^+$ ) 244.1444. Found 244.1446.



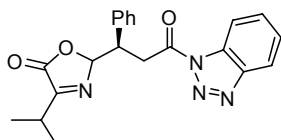
**3j**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (1H, dd,  $J = 8.0, 1.0$  Hz), 8.13 (1H, dd,  $J = 8.0, 1.0$  Hz), 7.66 (1H, td,  $J = 8.0, 1.0$  Hz), 7.56 (1H, d,  $J = 16.0$  Hz), 7.52 (1H, td,  $J = 8.0, 1.0$  Hz), 7.51 (1H, dt,  $J = 16.0, 5.0$  Hz), 7.32 (2H, t,  $J = 7.5$  Hz), 7.24 (2H, d,  $J = 7.5$  Hz), 7.23 (1H, t,  $J = 7.5$  Hz), 2.93 (2H, t,  $J = 8.0$  Hz), 2.77 (2H, td,  $J = 8.0, 5.0$  Hz);  $^{13}\text{C NMR}$  (175 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 153.4, 146.3, 140.5, 131.5, 130.3, 128.7, 128.4, 126.4, 126.2, 120.5, 120.2, 114.8, 34.7, 34.3; IR (KBr): 3029, 2904, 1711, 1632, 1450, 1380, 1077, 995, 957, 819, 754, 716  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}^+$  ( $[\text{M}+\text{H}]^+$ ) 278.1288. Found 278.1295.



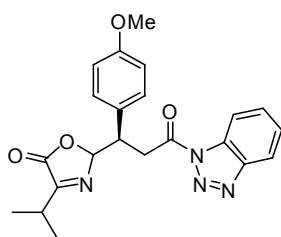
**3k**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (1H, dt,  $J = 8.5, 1.0$  Hz), 8.13 (1H, dt,  $J = 8.5, 1.0$  Hz), 7.66 (1H, ddd,  $J = 8.5, 7.0, 1.0$  Hz), 7.51 (1H, ddd,  $J = 8.5, 7.0, 1.0$  Hz), 7.47 (1H, dd,  $J = 19.0, 3.5$  Hz), 7.44 (1H, d,  $J = 19.0$  Hz), 2.39 (1H, tq,  $J = 12.5, 3.5$  Hz), 1.92 (2H, brd,  $J = 12.5$  Hz), 1.83 (2H, dq,  $J = 12.5, 3.5$  Hz), 1.73 (1H, dq,  $J = 12.5, 3.5, 1.5$  Hz), 1.37 (2H, qt,  $J = 12.5, 3.5$  Hz), 1.32 (2H, q,  $J = 12.5$  Hz), 1.27 (2H, qt,  $J = 12.5, 3.5$  Hz);  $^{13}\text{C NMR}$  (175 MHz,  $\text{CDCl}_3$ )  $\delta$  164.2, 159.7, 146.4, 131.6, 130.3, 126.2, 120.2, 117.7, 114.9, 41.4, 31.7, 26.0, 25.8; IR (KBr): 2926, 2852, 1715, 1634, 1449, 1378, 987, 959, 826, 750  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}^+$  ( $[\text{M}+\text{H}]^+$ ) 256.1444. Found 256.1443.



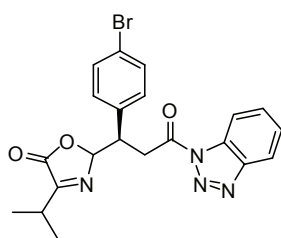
**Representative Procedure for Chiral Tetraaminophosphonium Phenoxide  $1\cdot(\text{ArO})_3\text{H}_2$ -Catalyzed Asymmetric Conjugate Addition of Azlactone 2:**  $\alpha,\beta$ -Unsaturated *N*-acylbenzotriazole **3a** (49.9 mg, 0.2 mmol) and **1b**·(3,5- $\text{Cl}_2$ - $\text{C}_6\text{H}_3\text{O}$ ) $_3\text{H}_2$  (0.01 equiv, 2.16 mg, 2.0  $\mu\text{mol}$ ) were placed in a dried test tube and dissolved into toluene (0.2 mL) under Ar atmosphere. Azlactone **2a** (28.0 mg, 0.22 mmol) was then introduced dropwise slowly at  $-40$   $^\circ\text{C}$  and the stirring was continued for 4 hours. A solution of trifluoroacetic acid in toluene (0.5 M, 20  $\mu\text{L}$ ) was added to the reaction mixture. The mixture was poured into ice-cooled 1 *N* HCl aqueous solution and the aqueous phase was extracted with ethyl acetate (EA). The combined organic phase was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and filtered. All volatiles were removed by evaporation and the diastereomeric ratio was determined by  $^1\text{H NMR}$  analysis of the crude aliquot. Purification of the residue by column chromatography on silica gel (H/EA = 5:1 as eluent) afforded **4a** in 95% yield (71.5 mg, 0.19 mmol), whose enantiomeric excess was determined to be 95% ee by HPLC analysis. **4a**: IC, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda = 210$  nm, 24.5 min (minor diastereomer), 27.5 min (major; major diastereomer), 30.5 min (minor; major diastereomer), 38.0 min (minor diastereomer);  $^1\text{H NMR}$  (700 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (1H, dt,  $J = 8.4, 0.7$  Hz), 8.12 (1H, dt,  $J = 8.4, 0.7$  Hz), 7.64 (1H, ddd,  $J = 8.4, 7.0, 0.7$  Hz), 7.51 (1H, ddd,  $J = 8.4, 7.0, 0.7$  Hz), 7.30-7.26 (2H, m), 7.26-7.22 (3H, m), 6.28 (1H, dd,  $J = 4.2, 2.1$  Hz), 4.24 (1H, td,  $J = 7.0, 4.2$  Hz), 4.18 (1H, dd,  $J = 17.5, 7.0$  Hz), 4.09 (1H, dd,  $J = 17.5, 7.0$  Hz), 2.79 (1H, sept-d,  $J = 7.0, 2.1$  Hz), 1.18 (3H, d,  $J = 7.0$  Hz), 1.04 (3H, d,  $J = 7.0$  Hz);  $^{13}\text{C NMR}$  (175 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 169.9, 164.5, 146.3, 134.5, 131.1, 130.8, 129.7, 128.4, 128.2, 126.5, 120.4, 114.5, 44.1, 99.7, 36.1, 28.1, 18.9, one carbon was not found probably due to overlapping; IR (liq. film): 2973, 1781, 1737, 1451, 1390, 1167, 1064, 995, 965, 752  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 399.1428. Found 399.1429.



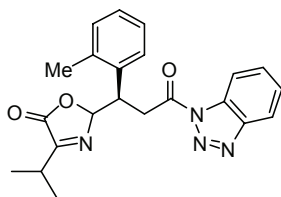
**4a**: IC, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda = 210$  nm, 24.5 min (minor diastereomer), 27.5 min (major; major diastereomer), 30.5 min (minor; major diastereomer), 38.0 min (minor diastereomer);  $^1\text{H NMR}$  (700 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (1H, dt,  $J = 8.4, 0.7$  Hz), 8.12 (1H, dt,  $J = 8.4, 0.7$  Hz), 7.64 (1H, ddd,  $J = 8.4, 7.0, 0.7$  Hz), 7.51 (1H, ddd,  $J = 8.4, 7.0, 0.7$  Hz), 7.30-7.26 (2H, m), 7.26-7.22 (3H, m), 6.28 (1H, dd,  $J = 4.2, 2.1$  Hz), 4.24 (1H, td,  $J = 7.0, 4.2$  Hz), 4.18 (1H, dd,  $J = 17.5, 7.0$  Hz), 4.09 (1H, dd,  $J = 17.5, 7.0$  Hz), 2.79 (1H, sept-d,  $J = 7.0, 2.1$  Hz), 1.18 (3H, d,  $J = 7.0$  Hz), 1.04 (3H, d,  $J = 7.0$  Hz);  $^{13}\text{C NMR}$  (175 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 169.9, 164.5, 146.3, 134.5, 131.1, 130.8, 129.7, 128.4, 128.2, 126.5, 120.4, 114.5, 44.1, 99.7, 36.1, 28.1, 18.9, one carbon was not found probably due to overlapping; IR (liq. film): 2973, 1781, 1737, 1451, 1390, 1167, 1064, 995, 965, 752  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 399.1428. Found 399.1429.



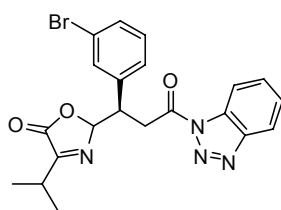
**4b:** IC, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda$  = 210 nm, 33.6 min (minor diastereomer), 39.5 min (minor; major diastereomer), 41.8 min (major; major diastereomer), 53.9 min (minor diastereomer);  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (1H, dt,  $J$  = 8.4, 0.7 Hz), 8.13 (1H, dt,  $J$  = 8.4, 0.7 Hz), 7.65 (1H, ddd,  $J$  = 8.4, 7.7, 0.7 Hz), 7.51 (1H, ddd,  $J$  = 8.4, 7.7, 0.7 Hz), 7.15 (2H, d,  $J$  = 8.4 Hz), 6.80 (2H, d,  $J$  = 8.4 Hz), 6.26 (1H, dd,  $J$  = 4.2, 2.1 Hz), 4.19 (1H, td,  $J$  = 7.7, 4.2 Hz), 4.16 (1H, dd,  $J$  = 17.5, 7.7 Hz), 4.04 (1H, dd,  $J$  = 17.5, 7.7 Hz), 3.75 (3H, s), 2.81 (1H, sept-d,  $J$  = 7.7, 2.1 Hz), 1.19 (3H, d,  $J$  = 7.7 Hz), 1.08 (3H, d,  $J$  = 7.7 Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 169.8, 164.6, 159.3, 146.3, 131.1, 130.8<sub>1</sub>, 130.7<sub>6</sub>, 126.5, 126.2, 120.4, 114.5, 113.8, 99.8, 55.3, 43.4, 36.3, 28.1, 19.0, one carbon was not found probably due to overlapping; IR (liq. film): 2972, 1779, 1738, 1515, 1451, 1389, 1254, 1065, 996, 966, 753  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_4\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 429.1533. Found 429.1535.



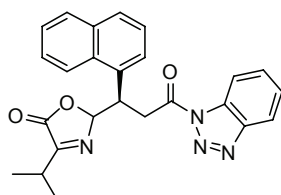
**4c:** IA, H/EtOH = 2:1, flow rate = 0.5 mL/min,  $\lambda$  = 210 nm, 26.4 min (major; major diastereomer), 33.9 min (minor diastereomer), 45.4 min (minor diastereomer), 68.9 min (minor; major diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (1H, dt,  $J$  = 8.0, 1.0 Hz), 8.13 (1H, dt,  $J$  = 8.0, 1.0 Hz), 7.66 (1H, ddd,  $J$  = 8.0, 7.0, 1.0 Hz), 7.53 (1H, ddd,  $J$  = 8.0, 7.0, 1.0 Hz), 7.42 (2H, dt,  $J$  = 8.5, 2.5 Hz), 7.14 (2H, dt,  $J$  = 8.5, 2.5 Hz), 6.25 (1H, dd,  $J$  = 4.0, 2.0 Hz), 4.20 (1H, ddd,  $J$  = 7.5, 6.0, 4.0 Hz), 4.16 (1H, dd,  $J$  = 17.0, 7.5 Hz), 4.05 (1H, dd,  $J$  = 17.0, 6.0 Hz), 2.83 (1H, sept-d,  $J$  = 7.0, 2.0 Hz), 1.20 (3H, d,  $J$  = 7.0 Hz), 1.08 (3H, d,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 169.9, 164.3, 146.4, 133.6, 131.6, 131.3, 131.1, 130.9, 126.6, 122.4, 120.5, 114.4, 99.4, 43.7, 36.0, 28.2, 19.0<sub>1</sub>, 19.0<sub>0</sub>; IR (liq. film): 2973, 1782, 1738, 1487, 1450, 1389, 1167, 1065, 968, 753  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_4\text{O}_3\text{BrNa}$  ( $[\text{M}+\text{Na}]^+$ ) 477.0533, 479.0515. Found 477.0537, 479.0527.



**4d:** IA, H/IPA/EtOH = 36:1:3, flow rate = 0.5 mL/min,  $\lambda$  = 210 nm, 26.3 min (major; major diastereomer), 32.3 min (minor diastereomer), 34.6 min (minor diastereomer), 38.4 min (minor; major diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (1H, dd,  $J$  = 8.0, 1.0 Hz), 8.12 (1H, dd,  $J$  = 8.0, 1.0 Hz), 7.64 (1H, ddd,  $J$  = 8.0, 7.0, 1.0 Hz), 7.51 (1H, ddd,  $J$  = 8.0, 7.0, 1.0 Hz), 7.18-7.08 (4H, m), 6.25 (1H, dd,  $J$  = 5.0, 2.0 Hz), 4.52 (1H, ddd,  $J$  = 8.0, 7.0, 5.0 Hz), 4.20 (1H, dd,  $J$  = 18.0, 8.0 Hz), 4.06 (1H, dd,  $J$  = 18.0, 7.0 Hz), 2.85 (1H, sept-d,  $J$  = 7.0, 2.0 Hz), 1.22 (3H, d,  $J$  = 7.0 Hz), 1.13 (3H, d,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 169.7, 164.4, 146.2, 138.1, 133.3, 131.0, 130.9, 130.7, 128.3, 127.8, 126.4, 125.6, 120.3, 114.4, 100.4, 39.1, 36.9, 28.2, 20.2, 19.0<sub>2</sub>, 19.0<sub>0</sub>; IR (liq. film): 2972, 1780, 1738, 1450, 1390, 1064, 968, 911, 752, 730  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 413.1584. Found 413.1584.

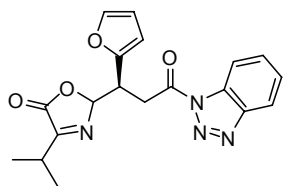


**4e:** IC, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda$  = 210 nm, 24.5 min (minor diastereomer), 27.5 min (major; major diastereomer), 31.0 min (minor; major diastereomer), 36.5 min (minor diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (1H, dt,  $J$  = 8.5, 1.0 Hz), 8.14 (1H, dt,  $J$  = 8.5, 1.0 Hz), 7.67 (1H, ddd,  $J$  = 8.5, 7.0, 1.0 Hz), 7.53 (1H, ddd,  $J$  = 8.5, 7.0, 1.0 Hz), 7.39 (1H, dt,  $J$  = 8.0, 1.5 Hz), 7.37 (1H, t,  $J$  = 1.5 Hz), 7.21 (1H, dt,  $J$  = 8.0, 1.5 Hz), 7.17 (1H, t,  $J$  = 8.0 Hz), 6.27 (1H, dd,  $J$  = 4.5, 2.0 Hz), 4.21 (1H, td,  $J$  = 7.0, 4.0 Hz), 4.14 (1H, dd,  $J$  = 18.0, 7.0 Hz), 4.10 (1H, dd,  $J$  = 18.0, 7.0 Hz), 2.84 (1H, sept-d,  $J$  = 7.0, 2.0 Hz), 1.22 (3H, d,  $J$  = 7.0 Hz), 1.10 (3H, d,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 169.8, 164.3, 146.3, 136.9, 132.4, 131.3, 131.0, 130.8, 130.0, 128.8, 126.6, 122.4, 120.4, 114.4, 99.2, 43.7, 36.1, 28.2, 19.0, 18.9; IR (liq. film): 2973, 1781, 1737, 1450, 1391, 1065, 998, 965, 733, 708  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_4\text{O}_3\text{BrNa}$  ( $[\text{M}+\text{Na}]^+$ ) 477.0533, 479.0515. Found 477.0530, 479.0503.

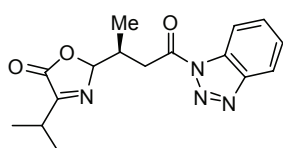


**4f:** IC, H/IPA = 3:1, flow rate = 0.5 mL/min,  $\lambda$  = 210 nm, 24.4 min (minor diastereomer), 30.1 min (major; major diastereomer), 33.5 min (minor; major diastereomer), 43.1 min (minor diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (1H, d,  $J$  = 8.0 Hz), 8.18 (1H, d,  $J$  = 8.0 Hz), 8.12 (1H, dt,  $J$  = 8.0, 1.0 Hz), 7.85 (1H, dt,  $J$  = 8.0, 1.0 Hz), 7.77 (1H, d,  $J$  = 8.0 Hz), 7.61 (2H, t,  $J$  = 8.0 Hz), 7.51 (1H, t,  $J$  = 8.0 Hz), 7.50 (1H, t,  $J$  = 8.0 Hz), 7.47 (1H, d,  $J$  = 8.0 Hz), 7.41 (1H, t,  $J$  = 8.0 Hz), 6.38 (1H, dd,  $J$  = 4.5, 2.0 Hz), 5.22 (1H, brs), 4.23 (1H, dd,  $J$  = 17.5, 7.5 Hz), 4.13 (1H, dd,  $J$  = 17.5, 6.5 Hz), 2.84 (1H, sept-d,  $J$  = 7.0, 2.0 Hz), 1.20 (3H, d,  $J$  = 7.0 Hz), 1.08 (3H, d,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 169.7, 164.3, 146.2, 134.0, 132.2, 131.9, 131.0, 130.7, 129.1, 128.8, 126.8, 126.5, 126.3, 126.0, 124.8, 123.1, 120.3, 114.4, 100.3, 38.0, 36.3, 28.2, 19.0, one carbon was not found

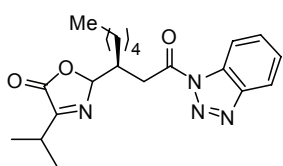
probably due to overlapping; IR (liq. film): 2973, 1781, 1738, 1450, 1391, 1055, 969, 910, 782, 733  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{25}\text{H}_{22}\text{N}_4\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 449.1584. Found 449.1583.



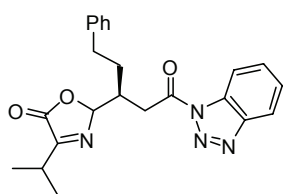
**4g:** IC, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda = 210$  nm, 30.8 min (minor diastereomer), 33.2 min (major; major diastereomer), 38.5 min (minor; major diastereomer), 47.7 min (minor diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (1H, dt,  $J = 8.0, 1.0$  Hz), 8.15 (1H, dt,  $J = 8.0, 1.0$  Hz), 7.68 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 7.54 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 7.31 (1H, dd,  $J = 2.0, 1.0$  Hz), 6.29 (2H, dd,  $J = 4.0, 2.0$  Hz), 6.23 (1H, d,  $J = 4.0$  Hz), 4.34 (1H, td,  $J = 7.0, 4.0$  Hz), 4.20 (1H, dd,  $J = 18.0, 7.0$  Hz), 4.03 (1H, dd,  $J = 18.0, 7.0$  Hz), 2.87 (1H, sept-d,  $J = 7.0, 2.0$  Hz), 1.21 (3H, d,  $J = 7.0$  Hz), 1.10 (3H, d,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 169.8, 164.5, 148.8, 146.3, 142.6, 131.1, 130.8, 126.6, 120.4, 114.5, 110.6, 109.5, 98.7, 38.5, 34.6, 28.2, 19.1, 18.9; IR (liq. film): 2973, 1782, 1738, 1451, 1393, 1167, 1063, 1000, 966, 736  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 389.1220. Found 389.1211.



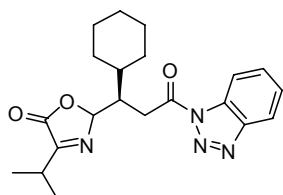
**4h:** IC, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda = 210$  nm, 25.1 min (minor diastereomer), 28.3 min (minor; major diastereomer), 34.4 min (major; major diastereomer), 36.9 min (minor diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (1H, dt,  $J = 8.0, 1.0$  Hz), 8.14 (1H, dt,  $J = 8.0, 1.0$  Hz), 7.69 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 7.54 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 6.03 (1H, dd,  $J = 5.0, 2.0$  Hz), 3.66 (1H, dd,  $J = 17.0, 6.0$  Hz), 3.50 (1H, dd,  $J = 17.0, 7.5$  Hz), 3.00 (1H, sept-d,  $J = 6.5, 2.0$  Hz), 2.93 (1H, quin-dd,  $J = 7.0, 6.0, 5.0$  Hz), 1.28 (3H, d,  $J = 6.5$  Hz), 1.26 (3H, d,  $J = 7.0$  Hz), 1.12 (3H, d,  $J = 6.5$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 169.5, 164.9, 146.3, 131.1, 130.8, 126.5, 120.4, 114.5, 101.4, 37.4, 33.7, 28.3, 19.4, 19.1, 14.0; IR (liq. film): 2973, 1781, 1739, 1485, 1451, 1392, 1059, 984, 937, 752  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 337.1271. Found 337.1271.



**4i:** IC, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda = 210$  nm, 14.4 min (minor diastereomer), 16.7 min (minor; major diastereomer), 19.9 min (major; major diastereomer), 20.8 min (minor diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (1H, d,  $J = 8.0$  Hz), 8.14 (1H, d,  $J = 8.0$  Hz), 7.68 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 7.53 (1H, ddd,  $J = 8.0, 7.0, 1.0$  Hz), 6.09 (1H, dd,  $J = 5.0, 2.0$  Hz), 3.50 (1H, dd,  $J = 17.5, 7.0$  Hz), 3.46 (1H, dd,  $J = 17.5, 7.0$  Hz), 2.95 (1H, sept-d,  $J = 7.0, 2.0$  Hz), 2.86 (1H, quin-d,  $J = 7.0, 5.0$  Hz), 1.60 (1H, ddd,  $J = 10.0, 7.0, 5.0$  Hz), 1.53-1.40 (3H, m), 1.38-1.26 (4H, m), 1.24 (3H, d,  $J = 7.0$  Hz), 1.19 (3H, d,  $J = 7.0$  Hz), 0.88 (3H, t,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 169.2, 164.9, 146.3, 131.1, 130.7, 126.4, 120.4, 114.5, 100.6, 38.3, 34.8, 31.7, 29.1, 28.3, 26.6, 22.5, 19.1, 19.0, 14.1; IR (liq. film): 2931, 1781, 1737, 1450, 1389, 1168, 1057, 975, 771, 752  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 393.1897. Found 393.1889.

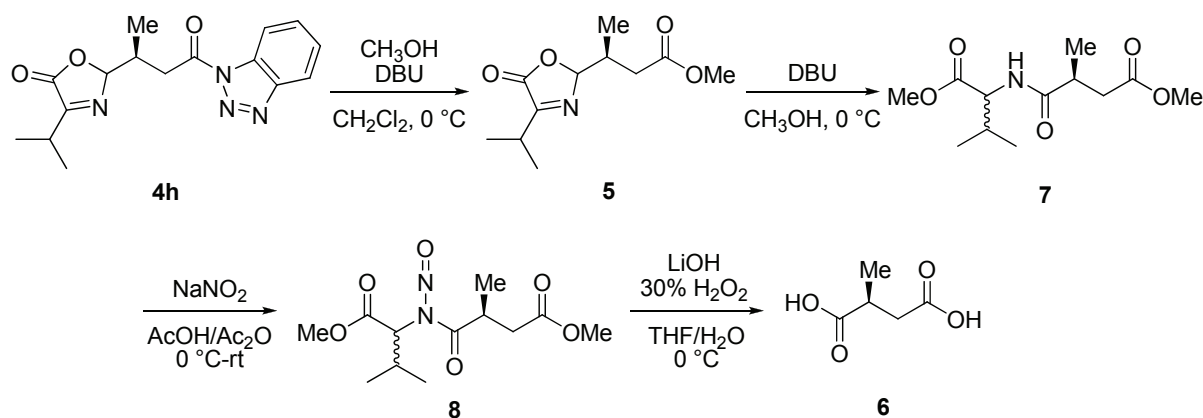


**4j:** IC, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda = 210$  nm, 21.0 min (minor diastereomer), 24.7 min (minor; major diastereomer), 29.6 min (minor diastereomer), 31.6 min (major; major diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (1H, d,  $J = 8.0$  Hz), 8.14 (1H, d,  $J = 8.0$  Hz), 7.68 (1H, t,  $J = 8.0$  Hz), 7.53 (1H, t,  $J = 8.0$  Hz), 7.27 (2H, t,  $J = 7.0$  Hz), 7.19 (2H, d,  $J = 7.0$  Hz), 7.17 (1H, t,  $J = 7.0$  Hz), 6.11 (1H, dd,  $J = 5.0, 2.0$  Hz), 3.56 (1H, dd,  $J = 17.5, 7.0$  Hz), 3.51 (1H, dd,  $J = 17.5, 6.0$  Hz), 2.99 (1H, sept-d,  $J = 7.0, 2.0$  Hz), 2.89 (1H, brs,  $J = 6.5$  Hz), 2.84 (1H, ddd,  $J = 18.0, 14.0, 6.5$  Hz), 2.80 (1H, ddd,  $J = 18.0, 14.0, 6.5$  Hz), 1.97 (1H, ddt,  $J = 14.0, 9.5, 6.5$  Hz), 1.81 (1H, ddt,  $J = 14.0, 9.5, 6.5$  Hz), 1.24 (3H, d,  $J = 7.0$  Hz), 1.18 (3H, d,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 169.4, 164.8, 146.3, 140.9, 131.1, 130.7, 128.6, 128.4, 126.4, 126.3, 120.4, 114.5, 100.6, 38.1, 34.8, 33.3, 30.8, 28.3, 19.1, 19.0; IR (liq. film): 2972, 2932, 1780, 1737, 1485, 1451, 1389, 1060, 974, 910, 733  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{23}\text{H}_{24}\text{N}_4\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 427.1741. Found 427.1744.



**4k:** IA, H/EtOH = 10:1, flow rate = 0.5 mL/min,  $\lambda = 210$  nm, 21.5 min (minor diastereomer), 25.9 min (minor diastereomer), 29.8 min (major; major diastereomer), 33.5 min (minor; major diastereomer);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (1H, dt,  $J = 8.5, 1.0$  Hz), 8.14 (1H, dt,  $J = 8.5, 1.0$  Hz), 7.67 (1H, ddd,  $J = 8.5, 7.0, 1.0$  Hz), 7.53 (1H, ddd,  $J = 8.5, 7.0, 1.0$  Hz), 6.09 (1H, dd,  $J = 5.0, 2.0$  Hz), 3.41 (1H, dd,  $J = 17.0, 5.0$  Hz), 3.32 (1H, dd,  $J = 17.0, 7.5$  Hz), 2.89 (1H, sept-d,  $J = 7.0, 2.0$  Hz), 2.83 (1H, dq,  $J = 7.5, 5.0$  Hz), 1.93-1.66 (6H, m), 1.36-1.14 (5H, m), 1.22 (3H, d,  $J = 7.0$  Hz), 1.11 (3H, d,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 169.0, 165.0, 146.4, 131.2, 130.7, 126.4, 120.4, 114.5, 100.1, 43.6, 38.8, 31.9, 30.9, 30.4, 28.3, 26.6, 26.5, 26.4, 19.1, 18.9; IR (liq.

film): 2928, 2853, 1780, 1738, 1450, 1389, 1062, 964, 751, 733  $\text{cm}^{-1}$ ; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{26}\text{N}_4\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 405.1897. Found 405.1898.



### Derivatization of 4h to Methylsuccinic Acid 6:

**Methanolysis of 4h:** To a solution of **4h** (157.2 mg, 0.5 mmol, 96% ee) in dichloromethane (5 mL) was added methanol (40.5  $\mu\text{L}$ , 1.0 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (74.8  $\mu\text{L}$ , 0.5 mmol) dropwise at  $0\text{ }^\circ\text{C}$ . The reaction mixture was stirred for 5 min and diluted with 1 *N* HCl aqueous solution to quench the reaction. The resulting aqueous phase was extracted with EA three times. The combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$  and filtered. After concentration, the residue was purified by column chromatography on silica gel (H/EA = 5:1 as eluent) to give **5** in 98% yield and its diastereomeric ratio was >20:1. The enantiomeric purity of **5** was determined to be 96% ee by chiral stationary phase HPLC analysis. **5**: IC, H/EtOH = 20:1, flow rate = 0.5 mL/min,  $\lambda = 210\text{ nm}$ , 24.5 min (minor diastereomer), 28.4 min (major; major diastereomer), 29.4 min (minor diastereomer), 30.9 min (minor; major diastereomer);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.85 (1H, dd,  $J = 5.0, 2.0\text{ Hz}$ ), 3.70 (3H, s), 2.99 (1H, sept-d,  $J = 7.0, 2.0\text{ Hz}$ ), 2.59-2.51 (1H, m), 2.52 (1H, dd,  $J = 15.5, 6.0\text{ Hz}$ ), 2.30 (1H, dd,  $J = 15.5, 7.5\text{ Hz}$ ), 1.29 (3H, d,  $J = 7.0\text{ Hz}$ ), 1.28 (3H, d,  $J = 7.0\text{ Hz}$ ), 0.98 (3H, d,  $J = 7.0\text{ Hz}$ ).

**Isomerization and Methanolysis of 5:** A solution of **5** (111.4 mg, 0.49 mmol) and DBU (73.3  $\mu\text{L}$ , 0.49 mmol) in methanol (10 mL) was stirred at  $0\text{ }^\circ\text{C}$  for 30 min. 1 *N* HCl aqueous solution was then added to the mixture to quench the reaction. The mixture was extracted with EA three times and organic phases were washed with brine. The combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$  and filtered. After evaporation, the residue was purified by column chromatography on silica gel (H/EA = 2:1 as eluent) to furnish **7** as a mixture of diastereomers in 87% yield. **7**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.25 (0.5H, d,  $J = 8.5\text{ Hz}$ ), 6.18 (0.5H, d,  $J = 8.5\text{ Hz}$ ), 4.57 (0.5H, dd,  $J = 8.5, 5.0\text{ Hz}$ ), 4.54 (0.5H, dd,  $J = 8.5, 5.0\text{ Hz}$ ), 3.74<sub>3</sub> (1.5H, s), 3.73<sub>5</sub> (1.5H, s), 3.68 (1.5H, s), 3.67 (1.5H, s), 2.86-2.72 (2H, m), 2.42-2.35 (1H, m), 2.17<sub>0</sub> (0.5H, sept-d,  $J = 7.0, 5.0\text{ Hz}$ ), 2.16<sub>6</sub> (0.5H, sept-d,  $J = 7.0, 5.0\text{ Hz}$ ), 1.23 (1.5H, d,  $J = 7.0\text{ Hz}$ ), 1.20 (1.5H, d,  $J = 7.0\text{ Hz}$ ), 0.94 (1.5H, d,  $J = 7.0\text{ Hz}$ ), 0.93 (1.5H, d,  $J = 7.0\text{ Hz}$ ), 0.91 (3H, d,  $J = 7.0\text{ Hz}$ ).

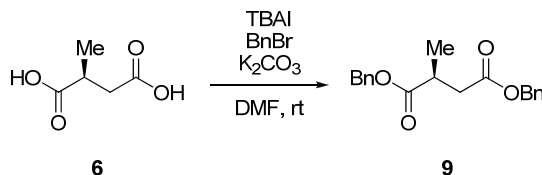
***N*-Nitrosation of 7 (S<sub>9</sub>):** To a solution of **7** (77.8 mg, 0.3 mmol) in glacial acetic acid (1 mL) and acetic anhydride (2 mL) was added  $\text{NaNO}_2$  (207.0 mg, 3.0 mmol) at  $0\text{ }^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature and stirred for 18 hours. The resulting solution was poured onto ice and the aqueous phase was extracted with diethyl ether twice. The organic phase was washed with water, saturated  $\text{NaHCO}_3$  aqueous solution, and brine. The combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. Purification of the residue by column chromatography on silica gel (H/EA = 10:1 as eluent) afforded **8** as a mixture of diastereomers in 77% yield. **8**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.94 (0.5H, d,  $J = 9.0\text{ Hz}$ ), 4.86 (0.5H, d,  $J = 9.0\text{ Hz}$ ), 4.32-4.23 (1H, m), 3.67<sub>2</sub> (1.5H, s), 3.66<sub>6</sub> (1.5H, s), 3.62 (1.5H, s), 3.61 (1.5H, s), 3.08 (1H, dd,  $J = 17.0, 10.0\text{ Hz}$ ), 2.57 (1H, dd,  $J = 17.5, 5.0\text{ Hz}$ ), 2.49 (1H, d-sept,  $J = 9.0, 7.0\text{ Hz}$ ), 1.35 (1.5H, d,  $J = 7.0\text{ Hz}$ ), 1.33 (1.5H, d,  $J = 7.0\text{ Hz}$ ), 1.11 (3H, d,  $J = 7.0\text{ Hz}$ ), 0.61 (1.5H, d,  $J = 7.0\text{ Hz}$ ), 0.59 (1.5H, d,  $J = 7.0\text{ Hz}$ ).

**Hydrolysis of 8 (S<sub>9</sub>):** A solution of **8** (66.3 mg, 0.23 mmol) in THF (23 mL) was treated with 30%  $\text{H}_2\text{O}_2$  solution (1.3 mL) and a 1.0 *M* aqueous solution of  $\text{LiOH}$  (2.3 mL, 2.3 mmol) at  $0\text{ }^\circ\text{C}$  for 4 hours. Then, a saturated aqueous solution of  $\text{NaHSO}_3$  was added to the resulting solution until peroxides were completely reduced. After concentration, the residual



aqueous phase was washed with diethyl ether, acidified with *conc.* HCl and extracted with EA twice. The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure to give (*S*)-**6** in 75 % yield. (*S*)-**6**: <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 2.83 (1H, dqd, *J* = 8.0, 7.0, 6.0), 2.66 (1H, dd, *J* = 17.0, 8.0 Hz), 2.39 (2H, dd, *J* = 17.0, 6.0 Hz), 1.21 (3H, d, *J* = 7.0 Hz); [α]<sub>D</sub><sup>27</sup> -14.4 (c = 1.18, EtOH) [lit. (*S*10) [α]<sub>D</sub><sup>24.2</sup> -15.0 (c = 1.89, EtOH) for *S* isomer, 99% ee].

**Conservation of Enantiomeric Purity:** The enantiomeric purity of **6** was determined by HPLC analysis after esterification.



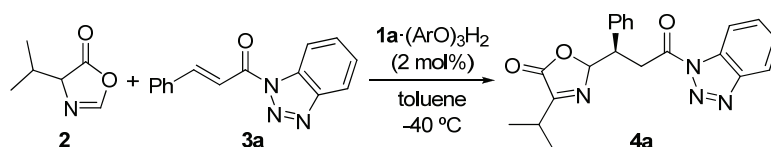
**Esterification of 6:** To a solution of **6** (21.0 mg, 0.16 mmol), tetrabutylammonium iodide (TBAI) (5.9 mg, 0.01 mmol) and K<sub>2</sub>CO<sub>3</sub> (132.7 mg, 0.96 mmol) in *N,N*-dimethylformamide (DMF) (2 mL) was added benzyl bromide (57.1 μL, 0.48 mmol) dropwise at room temperature. The reaction mixture was vigorously stirred for 8 hours and diluted with H<sub>2</sub>O. The resulting aqueous solution was extracted with diethyl ether three times. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Evaporation of solvents and purification of the residue by column chromatography on silica gel (H/EA = 10:1 as eluent) gave **9** in 83% yield. The enantiomeric purity of **9** was determined to be 95% ee by chiral stationary phase HPLC analysis. **9**: ODH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 16.1 min (*R*), 21.1 min (*S*); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 7.36-7.33 (4H, m), 7.33-7.30 (6H, m), 5.12 (1H, d, *J* = 12.6 Hz), 5.10 (1H, d, *J* = 11.9 Hz), 5.08 (1H, d, *J* = 12.6 Hz), 5.07 (1H, d, *J* = 11.9 Hz), 3.00 (1H, sex, *J* = 7.0 Hz), 2.81 (1H, dd, *J* = 16.1, 7.0 Hz), 2.48 (1H, dd, *J* = 16.1, 7.0 Hz), 1.24 (3H, d, *J* = 7.0 Hz).

## Additional Experimental Data and Discussion:

**Effect of Phenol Structure on the Selectivity:**  $\alpha,\beta$ -Unsaturated *N*-acylbenzotriazole **3a** (24.9 mg, 0.10 mmol) and **1a**·(ArO)<sub>3</sub>H<sub>2</sub> (0.02 equiv, 2.0  $\mu$ mol) were placed in a dried test tube and dissolved into toluene (1.0 mL) under Ar atmosphere. Azlactone **2** (14.0 mg, 0.11 mmol) was then introduced dropwise slowly at  $-40$  °C and the stirring was continued for indicated hours. A solution of trifluoroacetic acid in toluene (0.5 M, 20  $\mu$ L) was added to the mixture at  $-40$  °C to quench the reaction. The resulting mixture was poured into ice-cooled 1 *N* HCl aqueous solution and the aqueous phase was extracted with EA. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. After removing all volatiles by evaporation, purification of the residue by column chromatography on silica gel (H/EA = 5:1 as eluent) afforded **4a**, whose enantiomeric excess was determined by HPLC analysis.

The results with a series of catalysts that possess different phenols are listed in Table S1. Although it seems to be difficult to see any tendency of correlation between the phenol structure and enantioselectivity, the use of 3,5-Cl<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>OH leads to the highest selectivity so far.

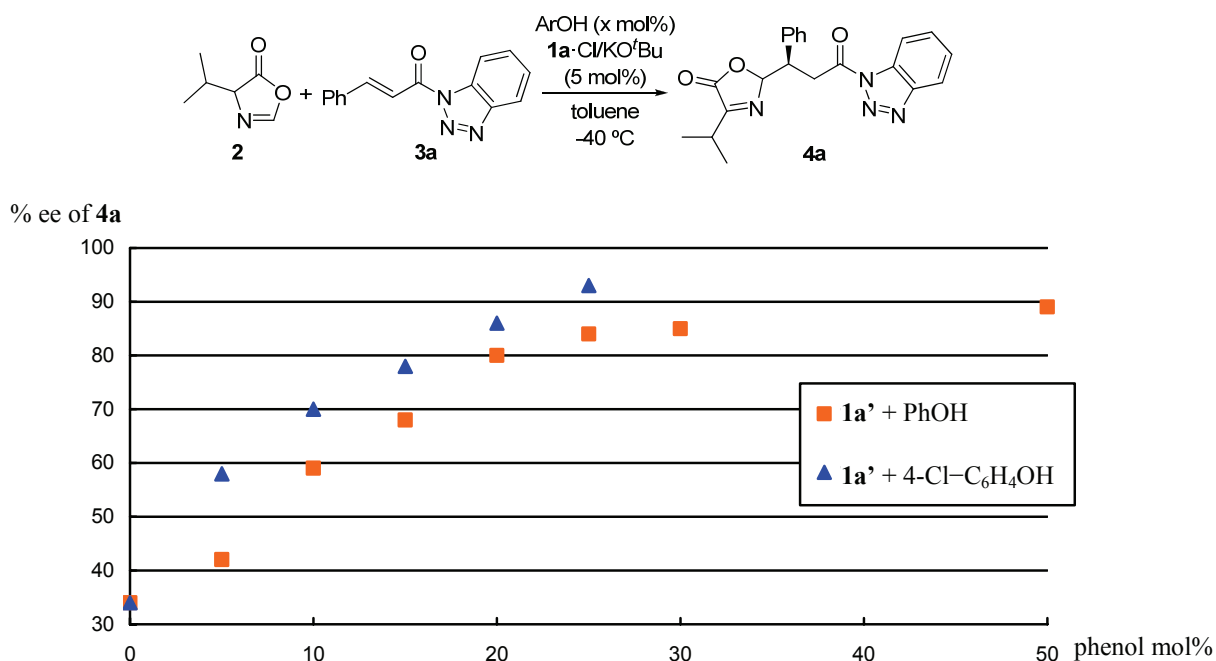
**Table S1.** Optimization of Phenol Structure



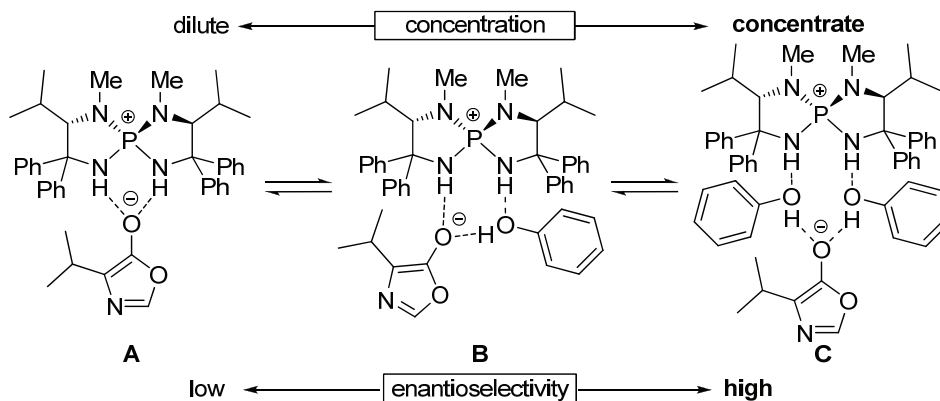
entry	catalyst	time (h)	yield (%)	ee (%)
1	<b>1a</b> ·(PhO) <sub>3</sub> H <sub>2</sub>	9	98	67
2	<b>1a</b> ·(4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	12	91	74
3	<b>1a</b> ·(4-F-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	8	99	71
4	<b>1a</b> ·(4-Cl-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	10	94	77
5	<b>1a</b> ·(4-Br-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	15	95	75
6	<b>1a</b> ·(4-Me-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	8	95	65
7	<b>1a</b> ·(4-MeO-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	36	54	76
8	<b>1a</b> ·(2-naphthoxide) <sub>3</sub> H <sub>2</sub>	12	93	45
9	<b>1a</b> ·(2-Cl-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	18	95	65
10	<b>1a</b> ·(2-Me-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	6	90	67
11	<b>1a</b> ·(2-Ph-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	10	96	43
12	<b>1a</b> ·(3-Cl-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	8	97	75
13	<b>1a</b> ·(3,5-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> O) <sub>3</sub> H <sub>2</sub>	24	99	85
14	<b>1a</b> ·(3,5-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> O) <sub>3</sub> H <sub>2</sub>	13	90	58
15	<b>1a</b> ·(2,4-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> O) <sub>3</sub> H <sub>2</sub>	12	97	68
16	<b>1a</b> ·(2,6-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> O) <sub>3</sub> H <sub>2</sub>	12	99	37
17	<b>1b</b> ·(PhO) <sub>3</sub> H <sub>2</sub>	12	99	85
18	<b>1b</b> ·(4-Cl-C <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> H <sub>2</sub>	18	95	91

**Selectivity Dependence on Phenol Concentration:** To a solution of **1a**·Cl (8.24 mg, 13.75  $\mu$ mol) in toluene (2.4 mL) was introduced a 1.0 M THF solution of KO<sup>t</sup>Bu (12.5  $\mu$ L, 12.5  $\mu$ mol) at  $-78$  °C and the mixture was stirred there for 30 min. After addition of a solution of phenol (PhOH or 4-Cl-C<sub>6</sub>H<sub>4</sub>OH) in 0.1 mL of toluene at  $-40$  °C, the resulting catalyst solution was aged for 30 min. Then, *N*-acylbenzotriazole **3a** (62.3 mg, 0.25 mmol) and azlactone **2** (35.0 mg, 0.275 mmol) were added sequentially, and stirring was continued at  $-40$  °C. The reaction was quenched by the addition of a solution of trifluoroacetic acid (0.5 M, 150  $\mu$ L) at  $-40$  °C and the whole mixture was poured into ice-cooled 1 N HCl aqueous solution. After extractive workup with EA and evaporation of solvents, the crude residue was purified by silica gel column chromatography (H/EA = 5:1 as eluent) to give the adduct **4a**, whose enantiomeric excess was determined by HPLC analysis.

The enantioselectivity of the reaction was plotted against the concentration of phenol under the influence of **1a** as a cationic component of the catalyst (Fig. S1). The form of each plotting clearly showed the strong dependence of the selectivity on the phenol concentration. In consideration of this observation and the effect of the catalyst concentration described in the manuscript, there would be an equilibrium in the assembly of an enolate ion pair such as shown in Fig. S2. The lower enantioselectivity observed under lower phenol concentration might stem from the intervention of the enolate assembly of either **A** or **B**. Higher concentration of phenol should push this equilibrium to right and increased population of the assembly **C** would lead to the higher selectivity [30 mol% of phenol (30 mM of phenol concentration) corresponds to that of the optimized reaction conditions, which is 0.2 mmol scale with 1 mol% of **1a**·(OPh)<sub>3</sub>H<sub>2</sub> in 0.2 mL of toluene].



**Fig. S1.** Selectivity Dependence on Phenol Concentration



### Crystallographic Structure Determination:

**Recrystallization of 1a·(PhO)<sub>3</sub>H<sub>2</sub> (CCDC 741902):** Tetraaminophosphonium phenoxide 1a·(PhO)<sub>3</sub>H<sub>2</sub> was recrystallized from hexane/diethyl ether solvent system at room temperature.

The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on  $F^2$  by using SHELXTL (*SII*). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen and oxygen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions. The crystallographic data were summarized in Table S2, S3 and ORTEP diagram was shown in Fig. S3.

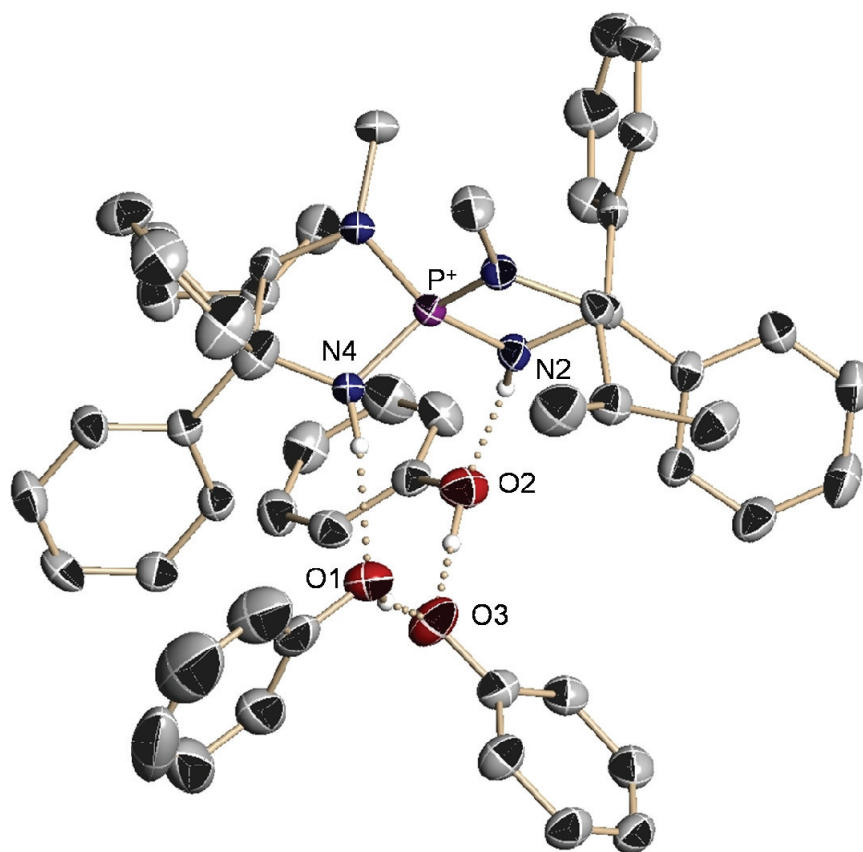
**Table S2.** Crystal Data and Structure Refinement for 1a·(PhO)<sub>3</sub>H<sub>2</sub>.

Empirical formula	C <sub>54</sub> H <sub>61</sub> N <sub>4</sub> O <sub>3</sub> P	
Formula weight	845.04	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.5801(5) Å	$\alpha = 90^\circ$ .
	b = 21.0028(10) Å	$\beta = 90^\circ$ .
	c = 21.1066(11) Å	$\gamma = 90^\circ$ .
Volume	4690.1(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.197 Mg/m <sup>3</sup>	
Absorption coefficient	0.106 mm <sup>-1</sup>	
F(000)	1808	
Crystal size	0.60 x 0.20 x 0.10 mm <sup>3</sup>	
Theta range for data collection	1.37 to 28.30°.	
Index ranges	-11<=h<=14, -28<=k<=22, -27<=l<=28	
Reflections collected	35732	
Independent reflections	11630 [R(int) = 0.0576]	
Completeness to theta = 28.30°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9895 and 0.9390	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	11630 / 0 / 581	
Goodness-of-fit on F <sup>2</sup>	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0559, wR2 = 0.1171	
R indices (all data)	R1 = 0.0838, wR2 = 0.1328	
Absolute structure parameter	0.13(8)	
Largest diff. peak and hole	0.358 and -0.224 e.Å <sup>-3</sup>	

**Table S3.** Hydrogen Bonds for 1a·(PhO)<sub>3</sub>H<sub>2</sub> [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(58)...O(3)#1	0.95(4)	1.60(4)	2.539(3)	168(4)
O(2)-H(57)...O(3)#2	0.94(4)	1.58(4)	2.506(3)	167(3)
N(4)-H(56)...O(1)#3	0.89(3)	2.00(3)	2.881(3)	172(2)
N(2)-H(55)...O(2)#4	0.89(3)	1.97(3)	2.838(3)	163(2)

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z; #2 x,y-1,z+1; #3 x-1,y,z; #4 x-1,y,z-1.



**Fig. S3.** Molecular Structure of Tetraaminophosphonium Phenoxide **1a**·(PhO)<sub>3</sub>H<sub>2</sub>. All calculated hydrogen atoms are omitted for clarity. Purple = phosphorus, blue = nitrogen, red = oxygen, black = carbon.

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