Supporting Information

Chiral Tertiary Sulfonium Salts as Effective Catalysts for Asymmetric Base-Free Neutral Phase-Transfer Reactions

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Author Contributions

S.L. Data curation: Equal; Formal analysis: Equal; Writing—review & editing: Supporting

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S.S. Conceptualization: Lead; Data curation: Equal; Formal analysis: Equal; Funding acquisition: Lead; Investigation: Lead; Methodology: Lead; Project administration: Lead; Resources: Lead; Writing—original draft: Lead.

General Information

^1H and ^{13}C NMR spectra were measured on a JEOL JNM-AL 400 NMR instrument (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^1H NMR, and CDCl_3 served as the internal standard (77.0 ppm) for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700N. Infrared spectra (IR) were measured on a JASCO FT/IR-4200 spectrometer. Optical rotations were measured on a JASCO P-2100 polarimeter. High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AT and SPD-20A instruments using Daicel Chiralpak AD-3 or IB-3 (4.6 mm $\times$ 250 mm) columns. All reactions were monitored by thin-layer chromatography using Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), with visualization by the use of UV lamp (254 nm), or dyes such as KMnO_4 . The products were purified by flash column chromatography on silica gel. Dehydrated solvents were purchased from Kanto Chemical.

Scheme S1. Effect of water amount.

Scheme S2. Larger scale reactions.

Experimental Section

1. Synthesis of catalysts.

1-1. Synthesis of catalysts 1.

To the ice-cooled solution of **8**^[1] (0.30 mmol) in CH_2Cl_2 (5 mL) was added SBU_2 (3.0 mmol) at $0\text{ }^\circ\text{C}$ under nitrogen atmosphere. The mixture was stirred for 5 min at $0\text{ }^\circ\text{C}$, then AgOTf (1.8 mmol) was added to the solution. The generation of AgBr precipitate could be observed. The reaction mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was then filtered over celite. The filtrate as a CH_2Cl_2 solution was washed with H_2O . The CH_2Cl_2 solution was separated and dried over Na_2SO_4 . After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 2:1–0:1 as eluent) to afford catalyst **1**. The isolated catalyst **1** was once again purified by flash column chromatography on silica gel to obtain pure catalyst **1**.

1a: 51% yield. $[\alpha]_{\text{D}}^{27} -21.3$ ($c = 1.00$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 9.6$ Hz, 1H), 8.05 (d, $J = 8.8$ Hz, 1H), 7.97 (m, 2H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.51–7.57 (m, 2H), 7.42 (dt, $J = 1.2$, 8.0 Hz, 1H), 7.28–7.36 (m, 2H), 7.20 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 4.60 (d, $J = 13.2$ Hz, 1H), 4.35 (d, $J = 13.2$ Hz, 1H), 3.80 (s, 3H), 3.19–3.25 (m, 4H), 1.03–1.40 (m, 8H), 0.78 (t, $J = 7.2$ Hz, 3H), 0.74 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 136.4, 134.2, 133.1, 133.0, 131.3, 129.5, 129.1, 128.45, 128.42, 128.36, 127.9, 127.3, 127.2, 126.1, 124.39, 124.37, 123.9, 120.6 (q, $J = 319$ Hz), 118.1, 113.1, 56.2, 44.9, 40.3, 26.4, 26.3, 21.2, 21.1, 13.14, 13.10; IR (neat): 3060, 2964, 2934, 2874, 1273, 1237, 1226, 1162, 1028, 730, 635 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{35}\text{OS}$: 443.2409 ($[\text{M}]^+$), found 443.2411.

1b: 65% yield. $[\alpha]_D^{29} +18.8$ ($c = 1.20$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.8$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.50–7.56 (m, 2H), 7.29–7.34 (m, 3H), 7.20 (dt, $J = 1.2, 7.2$ Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 1H), 4.52 (d, $J = 13.2$ Hz, 1H), 4.26 (d, $J = 13.2$ Hz, 1H), 2.90–3.11 (m, 4H), 0.92–1.34 (m, 8H), 0.70 (t, $J = 7.2$ Hz, 3H), 0.67 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.4, 136.7, 134.2, 133.3, 133.1, 130.9, 129.3, 128.8, 128.4, 128.3, 127.9, 127.4, 127.3, 126.5, 124.4, 123.6, 123.5, 120.4 (q, $J = 318$ Hz), 119.1, 115.2, 44.9, 40.3, 40.2, 26.1, 25.9, 21.2, 21.1, 13.01, 12.96; IR (neat): 3277, 3060, 2963, 2934, 2874, 1276, 1239, 1164, 1029, 637 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{33}\text{OS}$: 429.2252 ($[\text{M}]^+$), found 429.2252.

1-2. Synthesis of catalysts 2, 3, and 7.

1-2-1. Synthesis of intermediate 11.

To a mixture of **9**^[2] (2.3 mmol) and K_2CO_3 (4.6 mmol) in THF/ H_2O (5 mL/5 mL) was added Boc_2O (4.6 mmol) at room temperature. The reaction mixture was then refluxed for 12 h. The mixture was cooled to room temperature and quenched by saturated aqueous NH_4Cl . After evaporation of THF, the resulting solution was extracted with ethyl acetate for three times. The organic extracts were washed with brine and dried over Na_2SO_4 . After evaporation of solvents, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 40:1–30:1 as eluent) to afford **10**.

10: 51% yield. $[\alpha]_D^{26} -47.1$ ($c = 1.00$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, $J = 9.2$ Hz, 1H), 7.95 (m, 3H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.4$ Hz, 1H), 7.43 (dt, $J = 1.6, 7.4$ Hz, 1H), 7.35 (dt, $J = 1.2, 7.4$ Hz, 1H), 7.25 (dt, $J = 1.2, 7.6$ Hz, 1H), 7.18 (dt, $J = 1.2, 7.8$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 6.05 (br s, 1H), 2.09 (s, 3H),

1.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 136.0, 134.3, 132.8, 132.6, 132.4, 130.5, 130.3, 128.9, 128.62, 128.58, 128.01, 127.96, 126.6, 126.4, 125.4, 125.3, 125.1, 124.3, 122.3, 119.5, 80.5, 28.1, 20.0; IR (neat): 3414, 3055, 2979, 2927, 1728, 1499, 1155 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_2$: 384.1964 ($[\text{M}+\text{H}]^+$), found 384.1959.

To a solution of **10** (0.30 mmol) in benzene (6 mL) was added *N*-bromosuccinimide (NBS) (0.33 mmol) and 2,2'-azobisisobutyronitrile (AIBN) (0.045 mmol). The reaction mixture was then refluxed for 6 h. The mixture was cooled to room temperature and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 20:1–15:1 as eluent) to afford **11**.

11: 90% yield. $[\alpha]_D^{27} -154.0$ ($c = 1.00$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, $J = 8.8$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 8.01 (d, $J = 8.8$ Hz, 1H), 7.95 (d, $J = 7.2$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.23–7.34 (m, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.12 (d, $J = 8.4$ Hz, 1H), 6.84 (d, $J = 8.8$ Hz, 1H), 6.02 (br s, 1H), 4.34 (d, $J = 10.0$ Hz, 1H), 4.19 (d, $J = 10.0$ Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 135.3, 135.0, 133.6, 132.8, 132.5, 132.0, 130.3, 129.7, 129.3, 128.2, 128.0, 127.9, 127.3, 126.9, 126.6, 126.1, 125.0, 124.6, 120.8, 120.4, 80.5, 31.8, 28.2; IR (neat): 3416, 3056, 2979, 1726, 1496, 1226, 1152, 821, 747 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{26}\text{H}_{25}\text{BrNO}_2$: 462.1069 ($[\text{M}+\text{H}]^+$), found 462.1071.

1-2-2. Synthesis of catalysts **2** and **3** from intermediate **11**.

To a solution of **11** (1.3 mmol) in CH_2Cl_2 (10 mL) was added trifluoroacetic acid (TFA) (3.9 mmol) at room temperature. The reaction mixture was then refluxed for 12 h. The mixture was cooled to room temperature and quenched by saturated aqueous NaHCO_3 . The resulting solution was extracted with CH_2Cl_2 for three times. The organic extracts were dried over Na_2SO_4 , and the solvents were evaporated. The crude product

was dried under vacuo and used for next step. To a solution of the crude product in THF (8 mL) was added aryl isocyanate (ArNCO) (3.9 mmol). The mixture was stirred at room temperature for 4 h. The mixture was concentrated, and the residue was quickly purified by flash column chromatography on silica gel (hexane/ethyl acetate = 5:1–3:1 as eluent) to afford **12**. The isolated compound **12** was quickly used for the next step due to the instability of **12**.

To the ice-cooled solution of **12** (0.30 mmol) in CH₂Cl₂ (5 mL) was added SR₂ (3.0 mmol) at 0 °C under nitrogen atmosphere. The mixture was stirred for 5 min at 0 °C, then AgOTf (1.8 mmol) was added to the solution. The generation of AgBr precipitate could be observed. The reaction mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was then filtered over celite. The filtrate as a CH₂Cl₂ solution was washed with H₂O. The CH₂Cl₂ solution was separated and dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 2:1–0:1 as eluent) to afford catalyst **2** (or **3**). The isolated catalyst **2** (or **3**) was once again purified by flash column chromatography on silica gel to obtain pure catalyst **2** (or **3**).

2a: 25% yield (from **11**). $[\alpha]_D^{27} -19.7$ ($c = 0.90$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, $J = 9.2$ Hz, 1H), 8.08 (d, $J = 8.8$ Hz, 1H), 8.02 (d, $J = 9.6$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.70 (br s, 1H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.16–7.27 (m, 4H), 7.08 (t, $J = 7.6$ Hz, 2H), 6.90 (t, $J = 7.2$ Hz, 1H), 6.78–6.81 (m, 2H) 4.55 (d, $J = 13.2$ Hz, 1H), 4.38 (d, $J = 13.2$, 1H), 2.94–3.11 (m, 4H), 0.92–1.32 (m, 8H), 0.78 (t, $J = 7.2$ Hz, 3H), 0.69 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.1, 138.3, 136.1, 135.1, 134.5, 132.7, 132.4, 130.6, 130.4, 129.7, 128.8, 128.7, 128.5, 128.2, 128.0, 127.9, 127.3, 125.9, 125.1, 124.4, 123.2, 122.4, 120.4, 120.3 (q, $J = 318$ Hz), 120.0, 44.7, 40.4, 40.0, 26.05, 25.96, 21.3, 21.2, 13.13, 13.11; IR (neat): 3344, 2962, 2931, 2873, 1691, 1596, 1546, 1496, 1243, 1162, 1028, 752, 636 cm⁻¹; HRMS (FAB) calcd for C₃₆H₃₉N₂OS: 547.2783 ($[M]^+$), found 547.2792.

2b: 37% yield (from **11**). $[\alpha]_D^{20} +41.2$ ($c = 1.10$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.50–8.54 (m, 2H), 8.14 (d, $J = 8.8$ Hz, 1H), 8.06 (d, $J = 9.2$ Hz, 1H), 7.94–7.99 (m, 4H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 6.8$ Hz, 1H), 7.32–7.37 (m, 2H), 7.23–7.26 (m, 2H), 7.12 (s, 1H), 6.82 (d, $J = 8.8$ Hz, 1H), 4.75 (d, $J = 14.0$ Hz, 1H), 4.28 (d, $J = 13.2$ Hz, 1H), 2.83–3.17 (m, 4H), 0.91–1.41 (m, 8H), 0.82 (t, $J = 7.2$ Hz, 3H), 0.72 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 140.8, 135.7, 135.0, 134.5, 132.7, 132.5, 131.6 (q, $J = 32.9$ Hz), 130.7, 130.6, 129.8, 128.6, 128.5, 128.0, 127.9, 127.8, 127.4, 125.9, 125.3, 124.8, 124.4, 123.3 (q, $J = 272$ Hz), 122.7, 121.7, 121.3, 118.5 (m), 115.2 (m), 44.9, 40.3, 39.9, 26.0, 25.8, 21.3, 21.1, 13.0; IR (neat): 3344, 2965, 2934, 2876, 1712, 1570, 1276, 1171, 1131, 1028, 752, 636 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{38}\text{H}_{37}\text{F}_6\text{N}_2\text{OS}$: 683.2531 ($[\text{M}]^+$), found 683.2526.

2c: 30% yield (from **11**). $[\alpha]_D^{26} +43.7$ ($c = 1.00$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.37–8.42 (m, 2H), 8.15 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 9.2$ Hz, 1H), 7.93–8.03 (m, 4H), 7.80 (d, $J = 8.8$, 1H), 7.59 (t, $J = 6.8$ Hz, 1H), 7.55 (d, $J = 9.2$ Hz, 2H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.19–7.29 (m, 3H), 6.79 (d, $J = 8.4$ Hz, 1H), 4.68 (d, $J = 13.6$ Hz, 1H), 4.30 (d, $J = 13.6$ Hz, 1H), 2.78–3.15 (m, 4H), 0.88–1.48 (m, 8H), 0.82 (t, $J = 7.6$ Hz, 3H), 0.71 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 145.5, 141.8, 135.2, 135.1, 134.4, 132.8, 132.5, 130.8, 130.4, 129.7, 128.4, 127.9, 127.30, 127.25, 126.7, 125.9, 125.33, 125.25, 124.8, 124.5, 122.5, 122.1, 120.0 (q, $J = 317$ Hz), 118.1, 44.7, 40.3, 40.0, 26.0, 25.8, 21.3, 21.1, 13.0; IR (neat): 3346, 2962, 2929, 2873, 1712, 1558, 1498, 1329, 1245, 1175, 1029, 751 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{36}\text{H}_{38}\text{N}_3\text{O}_3\text{S}$: 592.2634 ($[\text{M}]^+$), found 592.2633.

3a: 22% yield (from **11**). $[\alpha]_D^{18} -147.5$ ($c = 0.59$, EtOH); ^1H NMR (400 MHz, CD_3OD) δ 8.30 (d, $J = 9.2$ Hz, 1H), 8.25 (d, $J = 8.0$ Hz, 1H), 8.07–8.19 (m, 4H), 8.02 (dd, $J = 2.0, 8.4$ Hz, 1H), 7.87 (d, $J = 8.8$ Hz, 1H), 7.64 (dt, $J = 2.4, 7.4$ Hz, 1H), 7.38–7.57 (m, 4H), 7.30 (dt, $J = 2.0, 7.6$ Hz, 1H), 7.17 (d, $J = 8.4$ Hz, 1H), 6.84 (d, $J =$

8.0 Hz, 1H), 4.52 (d, $J = 13.2$ Hz, 1H), 4.42 (d, $J = 13.2$, 1H), 2.79–3.30 (m, 4H), 1.27–2.16 (m, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 154.5, 146.8, 143.6, 136.3, 136.2, 135.9, 134.4, 134.2, 132.5, 131.6, 131.0, 129.9, 129.7, 129.11, 129.05, 128.96, 128.6, 127.0, 126.9, 126.8, 125.95, 125.90, 124.2, 124.1, 121.7 (q, $J = 317$ Hz), 118.8, 43.9, 38.2, 37.6, 23.4, 22.2, 22.0; IR (neat): 3349, 3060, 2928, 2856, 1709, 1557, 1497, 1328, 1243, 1173, 1029, 736, 636 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{33}\text{H}_{30}\text{N}_3\text{O}_3\text{S}$: 548.2008 ($[\text{M}]^+$), found 548.2009.

3b: 21% yield (from **11**). $[\alpha]_{\text{D}}^{18} -86.5$ ($c = 1.00$, EtOH); ^1H NMR (400 MHz, CD_3OD) δ 8.25–8.30 (m, 2H), 8.10–8.22 (m, 4H), 8.04 (d, $J = 8.0$ Hz, 1H), 7.88 (dd, $J = 2.8, 8.4$ Hz, 1H), 7.65 (dt, $J = 1.2, 7.4$ Hz, 1H), 7.40–7.58 (m, 4H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 4.68 (d, $J = 13.6$ Hz, 1H), 4.58 (d, $J = 13.2$, 1H), 4.00–4.10 (m, 1H), 3.68–3.80 (m, 2H), 3.41–3.50 (m, 1H), 3.30–3.35 (m, 1H), 3.12–3.23 (m, 2H), 2.82–2.92 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 154.6, 146.7, 143.7, 136.7, 136.2, 136.0, 134.5, 134.2, 132.6, 131.7, 131.1, 129.9, 129.8, 129.2, 129.1, 129.0, 128.7, 127.1, 127.0, 126.3, 126.0, 124.5, 124.3, 121.8 (q, $J = 317$ Hz), 118.8, 63.5, 63.1, 44.2, 35.6, 35.2; IR (neat): 3350, 3058, 2929, 2857, 1711, 1561, 1496, 1329, 1246, 1173, 1109, 1028, 735, 635 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{32}\text{H}_{28}\text{N}_3\text{O}_4\text{S}$: 550.1801 ($[\text{M}]^+$), found 550.1788.

1-2-3. Synthesis of catalyst 7.

To a solution of intermediate **12c** (0.060 mmol) in CH_3CN (5 mL) was added K_2CO_3 (0.30 mmol) and BuSH (0.30 mmol). The mixture was then warmed to 55 °C and stirred for 3 h. The mixture was cooled to room temperature and quenched by saturated aqueous NH_4Cl . The resulting solution was extracted with ethyl acetate for three times. The organic extracts were dried over Na_2SO_4 and evaporated. The residue

was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 4:1–3:1 as eluent) to afford **7**.

7: 38% yield (from **11**). $[\alpha]_D^{25} -106.2$ ($c = 1.10$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 9.2$ Hz, 1H), 7.96–8.05 (m, 4H), 7.88–7.94 (m, 2H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.41 (dt, $J = 1.2, 7.6$ Hz, 1H), 7.19–7.31 (m, 4H), 7.10–7.18 (m, 2H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.80 (s, 1H), 3.66 (d, $J = 12.8$ Hz, 1H), 3.36 (d, $J = 12.0$ Hz, 1H), 2.33 (dt, $J = 1.6, 7.2$ Hz, 2H), 1.12–1.35 (m, 4H), 0.75 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.7, 144.6, 142.5, 136.5, 134.5, 133.0, 132.9, 132.8, 131.3, 130.8, 129.3, 129.2, 128.2, 128.1, 127.7, 127.3, 126.9, 126.4, 125.7, 125.2, 125.1, 125.0, 123.5, 121.0, 118.3, 34.8, 32.8, 31.3, 21.8, 13.5; IR (neat): 3355, 3057, 2957, 2927, 1683, 1559, 1498, 1328, 1249, 1177, 751 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{32}\text{H}_{30}\text{N}_3\text{O}_3\text{S}$: 536.2008 ($[\text{M}+\text{H}]^+$), found 536.2004.

2. General procedure of asymmetric conjugate additions of 3-substituted oxindoles **4** and maleimides **5**.

To a solution of 3-substituted oxindole **4** (0.070 mmol), maleimide **5** (0.084 mmol), and catalyst **2c** (5 mol %, 0.0035 mmol) in toluene (0.20 mL) was added H_2O (2.0 mL) at $25\text{ }^\circ\text{C}$. The reaction mixture was vigorously stirred for 24 h at $25\text{ }^\circ\text{C}$, and then diluted with H_2O . The organic materials were extracted with ethyl acetate (5.0 mL $\times$ 3). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 5:1–3:1 as eluent) to give product **6**. The diastereomeric ratio of the product **6** was determined by ^1H NMR and HPLC analyses. The enantiomeric excess of the product **6** was determined by chiral HPLC analysis. The racemic sample of product **6** was prepared by using a triethylamine as a promoter for the reaction.

6aa:^[3] 64% yield (21.6 mg), d.r. 92:8, 91% *ee*. $[\alpha]_D^{22} -134.4$ ($c = 1.20$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 37.9 min (minor) and 41.4 min (major), minor

diastereomer 16.0 min and 19.0 min. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.16–7.51 (m, 11H), 6.70–6.74 (m, 2H), 4.42 (dd, $J = 4.2, 10.2$ Hz, 1H), 3.09 (dd, $J = 10.0, 19.2$ Hz, 1H), 2.79 (dd, $J = 4.2, 19.2$ Hz, 1H), 1.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.8, 174.42, 174.36, 149.1, 141.3, 136.8, 131.2, 130.0, 129.2, 129.1, 128.7, 128.5, 127.7, 126.3, 124.5, 123.7, 116.4, 84.6, 57.0, 47.9, 32.6, 28.0; IR (neat): 3061, 2981, 2930, 1762, 1711, 1498, 1480, 1462, 1389, 1343, 1297, 1251, 1181, 1147, 749, 724, 693 cm^{-1} .

6ab: 42% yield (15.1 mg), d.r. 86:14, 86% *ee*. $[\alpha]^{25}_{\text{D}} -118.0$ ($c = 0.90$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 27.9 min (minor) and 50.1 min (major), minor diastereomer 20.1 min and 32.6 min. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.4$ Hz, 1H) 7.23–7.51 (m, 8H), 6.83 (d, $J = 9.2$ Hz, 2H), 6.62 (d, $J = 8.8$ Hz, 2H), 4.42 (dd, $J = 4.4, 10.0$ Hz, 1H), 3.76 (s, 3H), 3.10 (dd, $J = 10.0, 19.2$ Hz, 1H), 2.79 (dd, $J = 4.4, 19.6$ Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.1, 174.7, 174.4, 159.6, 149.1, 141.3, 136.8, 129.9, 129.2, 128.5, 127.7, 127.5, 126.3, 124.4, 123.8, 123.7, 116.4, 114.5, 84.6, 57.0, 55.4, 47.8, 32.5, 28.0; IR (neat): 2979, 2931, 1764, 1712, 1513, 1299, 1251, 1150 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_6$: 513.2026 ($[\text{M}+\text{H}]^+$), found 513.2025.

6ac: 60% yield (23.1 mg), d.r. 87:13, 86% *ee*. $[\alpha]^{26}_{\text{D}} -110.9$ ($c = 1.00$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 17.3 min (minor) and 41.1 min (major), minor diastereomer 13.1 min and 24.6 min. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.4$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.46–7.51 (dt, $J = 2.0, 7.8$ Hz, 1H), 7.32–7.42 (m, 5H), 7.20–7.28 (m, 2H), 6.87 (d, $J = 8.4$ Hz 2H), 4.46 (dd, $J = 4.2, 10.0$ Hz, 1H), 3.14 (dd, $J = 10.0, 19.2$ Hz, 1H), 2.81 (dd, $J = 4.0, 19.6$ Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.5, 174.3, 173.9, 149.0, 141.3, 136.5, 134.3, 130.7 (q, $J = 32.9$ Hz), 130.1, 129.2, 128.6, 127.7, 126.6, 126.2 (m), 124.5, 123.6, 123.5 (q, $J = 271$ Hz), 116.5, 84.8, 57.1, 47.9, 32.5, 28.0; IR (neat): 2981, 2930,

1792, 1766, 1716, 1390, 1325, 1300, 1252, 1171, 1150 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_5$: 551.1794 ($[\text{M}+\text{H}]^+$), found 551.1783.

6ad: 17% yield (5.0 mg), d.r. 89:11, 86% *ee*. $[\alpha]_{\text{D}}^{25} -129.7$ ($c = 0.45$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 17.2 min (minor) and 19.5 min (major), minor diastereomer 13.4 min and 24.0 min. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 8.4$ Hz, 1H), 7.42 (dt, $J = 1.2, 7.8$ Hz, 1H), 7.25–7.36 (m, 5H), 7.10–7.20 (m, 2H), 4.28 (dd, $J = 4.4, 9.6$ Hz, 1H), 2.90 (dd, $J = 9.6, 19.2$ Hz, 1H), 2.69 (s, 3H), 2.63 (dd, $J = 4.8, 19.2$ Hz, 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.8, 175.4, 174.6, 149.1, 141.1, 136.9, 129.8, 129.1, 128.4, 127.6, 126.3, 124.4, 123.5, 116.2, 84.6, 56.5, 47.8, 32.4, 28.1, 24.6; IR (neat): 2980, 2925, 2853, 1764, 1730, 1702, 1479, 1463, 1440, 1345, 1284, 1252, 1151 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_5$: 421.1763 ($[\text{M}+\text{H}]^+$), found 421.1762.

6ba:^[3] 45% yield (15.6 mg), d.r. 85:15, 83% *ee*. $[\alpha]_{\text{D}}^{24} -108.6$ ($c = 1.10$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 32.7 min (minor) and 29.1 min (major), minor diastereomer 14.1 min. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.47 (dt, $J = 1.6, 7.4$ Hz, 1H), 7.14–7.43 (m, 9H), 6.68–6.73 (m, 2H), 4.40 (dd, $J = 4.0, 10.0$ Hz, 1H), 3.10 (dd, $J = 10.0, 19.2$ Hz, 1H), 2.80 (dd, $J = 4.0, 18.8$ Hz, 1H), 2.34 (s, 3H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.9, 174.51, 174.50, 149.1, 141.3, 138.5, 133.8, 131.2, 129.88, 129.86, 129.1, 128.7, 127.5, 126.4, 126.3, 124.4, 123.6, 116.3, 84.5, 56.7, 47.8, 32.6, 28.0, 21.0; IR (neat): 2981, 2928, 1764, 1710, 1500, 1479, 1463, 1389, 1343, 1298, 1286, 1250, 1180, 1147, 748 cm^{-1} .

6bc: 54% yield (21.3 mg), d.r. 85:15, 83% *ee*. $[\alpha]_{\text{D}}^{22} -86.1$ ($c = 1.00$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 5:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 25.9 min (minor) and 50.8

min (major), minor diastereomer 16.8 min and 19.8 min. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.47 (dt, J = 2.0, 7.6 Hz, 1H), 7.15–7.25 (m, 6H), 6.87 (d, J = 8.0 Hz, 2H), 4.43 (dd, J = 4.0, 9.6 Hz, 1H), 3.13 (dd, J = 9.6, 19.6 Hz, 1H), 2.82 (dd, J = 4.0, 19.6 Hz, 1H), 2.34 (s, 3H), 1.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.5, 174.4, 174.0, 149.0, 141.3, 138.6, 134.3, 133.5, 130.6 (q, J = 32.1 Hz), 130.0, 129.9, 127.5, 126.5, 126.2 (m), 124.5, 123.54, 123.51 (q, J = 272 Hz), 116.4, 84.7, 56.8, 47.8, 32.6, 28.0, 21.0; IR (neat): 2981, 2928, 1789, 1762, 1713, 1387, 1323, 1300, 1250, 1167, 1147, 1128, 1065, 737 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{31}\text{H}_{28}\text{F}_3\text{N}_2\text{O}_5$: 565.1950 ($[\text{M}+\text{H}]^+$), found 565.1948.

6ca: 28% yield (9.7 mg), d.r. 83:17, 88% *ee*. $[\alpha]_{\text{D}}^{25}$ –100.2 (c = 1.00, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 29.4 min (minor) and 31.8 min (major), minor diastereomer 13.4 min and 14.1 min. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8.4 Hz, 1H), 7.08–7.55 (m, 10H), 6.68–6.79 (m, 2H), 4.42 (dd, J = 4.4, 10.0 Hz, 1H), 3.11 (dd, J = 10.0, 19.6 Hz, 1H), 2.81 (dd, J = 4.4, 19.6 Hz, 1H), 2.33 (s, 3H), 1.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.9, 174.5, 174.4, 149.1, 141.3, 138.9, 136.7, 131.2, 129.9, 129.3, 129.1, 129.0, 128.7, 128.2, 126.4, 126.3, 124.8, 124.5, 123.7, 116.4, 84.6, 56.9, 47.8, 32.6, 28.0, 21.6; IR (neat): 2980, 2926, 1763, 1712, 1498, 1481, 1463, 1390, 1343, 1298, 1251, 1150 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_5$: 497.2076 ($[\text{M}+\text{H}]^+$), found 497.2061.

6da:^[3] 59% yield (20.7 mg), d.r. 90:10, 83% *ee*. $[\alpha]_{\text{D}}^{23}$ –112.4 (c = 1.30, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 37.2 min (minor) and 29.9 min (major), minor diastereomer 14.9 min. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8.4 Hz, 1H), 7.49 (dt, J = 2.4, 7.4 Hz, 1H), 7.22–7.41 (m, 7H), 7.06 (t, J = 8.4 Hz, 2H), 6.66–6.73 (m, 2H), 4.39 (dd, J = 4.0, 10.0 Hz, 1H), 3.11 (dd, J = 10.0, 19.6 Hz, 1H), 2.77 (dd, J = 4.0, 19.6 Hz, 1H), 1.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 174.3, 174.2, 162.7 (d, J = 248 Hz), 149.0, 141.2, 132.5 (d, J = 3.3 Hz), 131.1, 130.2,

129.5 (d, $J = 8.2$ Hz), 129.1, 128.8, 126.2, 126.0, 124.6, 123.5, 116.5, 116.1 (d, $J = 21.4$ Hz), 84.8, 56.4, 47.9, 32.4, 28.0; IR (neat): 2982, 1790, 1765, 1711, 1504, 1389, 1341, 1298, 1247, 1183, 1148 cm^{-1} .

6fa: 46% yield (16.0 mg), d.r. 87:13, 83% *ee*. $[\alpha]_D^{24} -98.6$ ($c = 1.30$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 27.7 min (minor) and 32.1 min (major), minor diastereomer 13.4 min and 19.7 min. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.8$ Hz, 1H), 7.25–7.48 (m, 9H), 7.06 (s, 1H), 6.69–6.78 (m, 2H), 4.41 (dd, $J = 4.0, 10.0$ Hz, 1H), 3.10 (dd, $J = 10.0, 19.2$ Hz, 1H), 2.79 (dd, $J = 4.0, 19.2$ Hz, 1H), 2.35 (s, 3H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.8, 174.6, 174.5, 149.1, 138.9, 136.9, 134.3, 131.3, 130.4, 129.14, 129.12, 128.7, 128.5, 127.7, 126.3, 126.2, 124.0, 116.2, 84.4, 57.1, 47.8, 32.6, 28.0, 21.1; IR (neat): 2981, 2930, 1763, 1712, 1492, 1390, 1335, 1301, 1280, 1251, 1181, 1153 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_5$: 497.2076 ($[\text{M}+\text{H}]^+$), found 497.2067.

6ga:^[3] 81% yield (28.4 mg), d.r. 88:12, 90% *ee*. $[\alpha]_D^{24} -136.7$ ($c = 1.10$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 20.0 min (minor) and 39.7 min (major), minor diastereomer 14.2 min and 14.9 min. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (dd, $J = 4.4, 8.8$ Hz, 1H), 7.30–7.44 (m, 8H), 7.17 (dt, $J = 2.4, 8.8$ Hz, 1H), 7.01 (dd, $J = 2.4, 7.6$ Hz, 1H), 6.82–6.87 (m, 2H), 4.45 (dd, $J = 4.8, 10.0$ Hz, 1H), 3.11 (dd, $J = 10.0, 19.6$ Hz, 1H), 2.73 (dd, $J = 4.8, 19.6$ Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 174.1, 173.9, 159.6 (d, $J = 245$ Hz), 149.0, 137.3, 136.2, 131.1, 129.3, 129.2, 128.8, 128.7, 128.0 (d, $J = 7.4$ Hz), 127.5, 126.2, 117.8 (d, $J = 8.2$ Hz), 116.5 (d, $J = 22.2$ Hz), 111.1 (d, $J = 23.8$ Hz), 84.8, 57.0, 47.7, 32.3, 28.0; IR (neat): 2982, 2936, 1765, 1713, 1483, 1389, 1298, 1269, 1248, 1200, 1148 cm^{-1} .

6gc: 70% yield (27.9 mg), d.r. 96:4, 93% *ee*. $[\alpha]_D^{29} -99.9$ ($c = 1.00$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol

= 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 16.2 min (minor) and 49.1 min (major), minor diastereomer 13.2 min and 23.5 min. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (dd, J = 4.8, 9.2 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.34–7.42 (m, 3H), 7.28–7.33 (m, 2H), 7.17 (dt, J = 2.4, 8.8 Hz, 1H), 6.97–7.03 (m, 3H), 4.47 (dd, J = 4.4, 10.0 Hz, 1H), 3.14 (dd, J = 10.0, 19.6 Hz, 1H), 2.75 (dd, J = 4.4, 19.6 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.3, 174.0, 173.4, 159.6 (d, J = 245 Hz), 148.9, 137.3 (d, J = 2.4 Hz), 136.0, 134.3 (d, J = 21.4 Hz), 130.8 (q, J = 33.0 Hz), 129.4, 128.9, 127.9 (d, J = 7.4 Hz), 127.5, 126.4, 126.3 (q, J = 3.3 Hz), 123.5 (q, J = 271 Hz), 117.9 (d, J = 7.4 Hz), 116.6 (d, J = 22.2 Hz), 111.2, 110.9, 85.0, 57.1, 47.7, 32.4, 28.0; IR (neat): 2981, 2927, 2855, 1793, 1770, 1717, 1483, 1390, 1326, 1299, 1269, 1249, 1166, 1148, 1067 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{25}\text{F}_4\text{N}_2\text{O}_5$: 569.1700 ($[\text{M}+\text{H}]^+$), found 569.1702.

6ha:^[3] 66% yield (23.9 mg), d.r. 92:8, 88% *ee*. $[\alpha]_{\text{D}}^{25}$ –128.0 (c = 1.20, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 22.4 min (minor) and 36.9 min (major), minor diastereomer 15.2 min and 17.3 min. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 2.0 Hz, 1H), 7.16–7.45 (m, 10H), 6.76–6.82 (m, 2H), 4.43 (dd, J = 4.4, 10.4 Hz, 1H), 3.10 (dd, J = 10.0, 19.6 Hz, 1H), 2.74 (dd, J = 4.4, 19.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 174.1, 174.0, 148.8, 142.3, 136.3, 136.0, 131.1, 129.3, 129.2, 128.9, 128.7, 127.5, 126.2, 124.7, 124.5, 124.4, 117.2, 85.2, 56.7, 47.8, 32.4, 28.0; IR (neat): 2981, 2935, 1766, 1712, 1390, 1340, 1282, 1247, 1183, 1148 cm^{-1} .

6ia: 61% yield (21.4 mg), d.r. 88:12, 83% *ee*. $[\alpha]_{\text{D}}^{25}$ –118.6 (c = 1.40, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 67.5 min (minor) and 45.6 min (major), minor diastereomer 17.6 min and 20.5 min. ^1H NMR (400 MHz, CDCl_3) δ 7.06–7.46 (m, 11H), 6.74–6.80 (m, 2H), 4.43 (dd, J = 4.4, 10.0 Hz, 1H), 3.11 (dd, J = 10.0, 19.2 Hz, 1H), 2.77 (dd, J = 4.4, 18.6 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.4, 174.2, 174.0, 149.4 (d, J = 253 Hz), 147.1, 136.1, 131.2, 129.7, 129.3, 129.0, 128.7,

127.5, 127.1, 126.3, 126.1, 125.6 (d, $J = 6.6$ Hz), 119.6 (d, $J = 3.3$ Hz), 118.4 (d, $J = 20.6$ Hz), 85.1, 57.6, 47.8, 32.4, 27.7; IR (neat): 2982, 2932, 1788, 1756, 1711, 1490, 1389, 1251, 1182, 1144, 753, 737, 694 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{26}\text{FN}_2\text{O}_5$: 501.1826 ($[\text{M}+\text{H}]^+$), found 501.1819.

6ic: 73% yield (29.1 mg), d.r. 89:11, 84% *ee*. $[\alpha]_{\text{D}}^{26} -107.0$ ($c = 1.00$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 22.2 min (minor) and 48.8 min (major), minor diastereomer 15.2 min and 27.3 min. ^1H NMR (400 MHz, CDCl_3) δ

7.60 (d, $J = 8.0$ Hz, 2H), 7.18–7.44 (m, 7H), 7.07 (dd, $J = 1.6, 8.4$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 2H), 4.45 (dd, $J = 4.4, 10.4$ Hz, 1H), 3.15 (dd, $J = 10.4, 19.6$ Hz, 1H), 2.80 (dd, $J = 4.4, 19.6$ Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.1, 174.0, 173.7, 149.4 (d, $J = 252$ Hz), 147.0, 135.8, 134.2, 130.6 (q, $J = 32.9$ Hz), 129.6 (d, $J = 1.3$ Hz), 129.3, 128.8, 127.4, 126.4, 126.1 (q, $J = 4.1$ Hz), 125.7 (d, $J = 7.4$ Hz), 123.5 (q, $J = 271$ Hz), 119.6 (d, $J = 4.2$ Hz), 118.4 (d, $J = 20.5$ Hz), 85.3, 57.6 (d, $J = 1.7$ Hz), 47.8, 32.4, 27.7; IR (neat): 2983, 2934, 1788, 1714, 1389, 1325, 1171, 1145 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{25}\text{F}_4\text{N}_2\text{O}_5$: 569.1700 ($[\text{M}+\text{H}]^+$), found 569.1689.

6ja: 66% yield (23.8 mg), d.r. 90:10, 86% *ee*. $[\alpha]_{\text{D}}^{24} -103.7$ ($c = 0.70$, CHCl_3); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 38.3 min (minor) and 24.1 min (major), minor diastereomer 13.8 min and 17.8 min. ^1H NMR (400 MHz, CDCl_3) δ

8.06 (dd, $J = 4.4, 8.8$ Hz, 1H), 7.32–7.39 (m, 3H), 7.15–7.21 (m, 5H), 7.00 (dd, $J = 3.2, 8.0$ Hz, 1H), 6.83–6.87 (m, 2H), 4.43 (dd, $J = 4.4, 10.0$ Hz, 1H), 3.11 (dd, $J = 10.4, 19.6$ Hz, 1H), 2.74 (dd, $J = 4.4, 19.2$ Hz, 1H), 2.35 (s, 3H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 174.2, 174.0, 159.6 (d, $J = 245$ Hz), 149.0, 138.7, 137.3, 133.2, 131.1, 123.0, 129.2, 128.8, 128.2 (d, $J = 7.4$ Hz), 127.3, 126.2, 117.7 (d, $J = 8.2$ Hz), 116.4 (d, $J = 22.3$ Hz), 111.0 (d, $J = 23.8$ Hz), 84.7, 56.8, 47.6, 32.4, 28.0, 21.0; IR (neat): 2981, 2931, 1764, 1714, 1485, 1388, 1298, 1268, 1198, 1148 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{28}\text{FN}_2\text{O}_5$: 515.1982 ($[\text{M}+\text{H}]^+$), found 515.1986.

6ka: 85% yield (30.9 mg), d.r. 89:11, 84% *ee*. $[\alpha]_D^{24} -98.3$ ($c = 0.80$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 21.9 min (minor) and 28.6 min (major), minor diastereomer 13.5 min and 14.0 min. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (dd, $J = 4.4, 8.8$ Hz, 1H), 7.28–7.46 (m, 5H), 7.19 (dt, $J = 2.4, 8.8$ Hz, 1H), 7.09 (dt, $J = 2.8, 8.8$ Hz, 2H), 7.01 (dd, $J = 2.4, 8.0$ Hz, 1H), 6.81–6.86 (m, 2H), 4.41 (dd, $J = 4.4, 10.0$ Hz, 1H), 3.10 (dd, $J = 10.4, 19.6$ Hz, 1H), 2.71 (dd, $J = 4.4, 19.6$ Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.4, 174.0, 173.8, 162.8 (d, $J = 249$ Hz), 159.7 (d, $J = 245$ Hz), 148.9, 137.3 (d, $J = 2.4$ Hz), 132.0 (d, $J = 2.5$ Hz), 131.1, 129.4 (d, $J = 8.2$ Hz), 129.2, 128.9, 127.7 (d, $J = 8.2$ Hz), 126.1, 117.9 (d, $J = 7.4$ Hz), 116.7 (d, $J = 22.3$ Hz), 116.3 (d, $J = 21.4$ Hz), 111.0 (d, $J = 23.9$ Hz), 85.0, 56.4, 47.7, 32.2, 28.0; IR (neat): 2981, 2929, 1764, 1711, 1483, 1389, 1298, 1266, 1244, 1196, 1146, 737 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{25}\text{F}_2\text{N}_2\text{O}_5$: 519.1732 ($[\text{M}+\text{H}]^+$), found 519.1724.

6kc: 56% yield (23.0 mg), d.r. 92:8, 85% *ee*. $[\alpha]_D^{29} -109.7$ ($c = 1.10$, CHCl_3); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 5:1, flow rate = 0.5 mL/min, 220 nm; retention time: major diastereomer; 27.6 min (minor) and 45.8 min (major), minor diastereomer 19.2 min and 21.3 min. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (dd, $J = 4.4, 8.8$ Hz, 1H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.29–7.34 (m, 2H), 7.19 (dt, $J = 2.8, 8.8$ Hz, 1H), 7.10 (t, $J = 8.4$ Hz, 2H), 6.97–7.04 (m, 3H), 4.42 (dd, $J = 4.8, 10.0$ Hz, 1H), 3.14 (dd, $J = 10.4, 19.6$ Hz, 1H), 2.74 (dd, $J = 4.8, 19.6$ Hz, 1H), 1.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.1, 173.9, 173.2, 162.8 (d, $J = 249$ Hz), 159.7 (d, $J = 245$ Hz), 148.8, 137.3 (d, $J = 1.6$ Hz), 134.1, 131.7 (d, $J = 3.3$ Hz), 130.8 (q, $J = 32.9$ Hz), 129.4 (d, $J = 9.1$ Hz), 127.6 (d, $J = 7.4$ Hz), 126.4, 126.3 (q, $J = 4.1$ Hz), 123.5 (q, $J = 271$ Hz), 118.0 (d, $J = 7.4$ Hz), 116.9 (d, $J = 22.3$ Hz), 116.4 (d, $J = 22.2$ Hz), 110.9 (d, $J = 24.7$ Hz), 85.2, 56.5, 47.8, 32.2, 28.0; IR (neat): 2983, 2933, 1789, 1765, 1716, 1483, 1387, 1325, 1300, 1246, 1147 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{24}\text{F}_5\text{N}_2\text{O}_5$: 587.1605 ($[\text{M}+\text{H}]^+$), found 587.1599.

3. Determination of the absolute configuration of products **6**.

The absolute configurations of products **6** were confirmed by comparison of the retention times in HPLC, the optical rotation values, and NMR spectra, for products **6aa**, **6ba**, **6da**, **6ga**, **6ha** with the literature.^[3]

4. Procedure for deuteration experiments (Scheme 2).

To a mixture of 3-phenyloxindole **4a** (0.050 mmol) and **2c** (5 mol %, 0.0025 mmol) in toluene (0.50 mL) was added D₂O (1.0 mL) at 5 °C, and the mixture was vigorously stirred at 5 °C for 2 h. The resulting mixture was extracted with ethyl acetate (5.0 mL × 3), dried over Na₂SO₄ and concentrated. The H/D ratio of **4a** was determined by ¹H NMR spectroscopy.

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