Supporting Information
for Design of *N*-Spiro C_2 -Symmetric Chiral Quaternary Ammonium Bromides
as Novel Chiral Phase-Transfer Catalysts: Synthesis and Application to
Practical Asymmetric Synthesis of α -Amino Acids

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Characterization of Chiral Ammonium Salt (*S*)-10b: (48% yield): ^1H NMR (400 MHz, CDCl_3) δ 7.98 (2H, d, $J = 8.4$ Hz, Ar-H), 7.92 (2H, d, $J = 8.8$ Hz, Ar-H), 7.88 (2H, d, $J = 8.0$ Hz, Ar-H), 7.71 (2H, d, $J = 8.4$ Hz, Ar-H), 7.66 (2H, d, $J = 6.4$ Hz, Ar-H), 7.62 (2H, d, $J = 8.8$ Hz, Ar-H), 7.53 (2H, ddd, $J = 8.4, 6.8, 1.2$ Hz, Ar-H), 7.48 (2H, t, $J = 8.0$ Hz, Ar-H), 7.30-7.38 (4H, m, Ar-H), 7.24-7.28 (2H, m, Ar-H), 7.19 (2H, d, $J = 8.4$ Hz, Ar-H), 6.88 (2H, br d, $J = 8.0$ Hz, Ar-H), 6.39 (2H, d, $J = 13.6$ Hz, Ar- CH_2), 5.50 (2H, d, $J = 12.8$ Hz, Ar- CH_2), 5.30 (2H, d, $J = 13.6$ Hz, Ar- CH_2), 4.50 (2H, d, $J = 12.8$ Hz, Ar- CH_2) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 135.6, 134.0, 133.6, 133.6, 133.2, 131.8, 130.8, 129.3, 129.0, 128.2, 128.2, 127.6, 127.3, 127.2, 126.9, 126.6, 126.4, 125.0, 123.9, 122.9, 62.4, 61.8 ppm; IR (KBr) 3344, 3045, 1686, 1595, 1508, 1458, 1398, 1356, 1215, 1171, 1028, 871, 804, 777, 752 cm^{-1} . HRMS (FAB) Calcd for $\text{C}_{44}\text{H}_{34}\text{N}$: 576.2686 (M^+), Found 576.2686 (M^+). Melted at 104 $^\circ\text{C}$ with decomposition. $[\alpha]_{\text{D}}^{27}$ 132.2 $^\circ$ (c 0.50, CHCl_3).

Representative Procedure for the Synthesis of Chiral Ammonium Salts 11b and 11c

(*S*)-3,3'-Dibromo-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl [(*S*)-20]: To a solution of (*S*)-17 (7.49 g, 20 mmol) in THF (60 mL) was added a 1.6 M hexane solution of *n*-BuLi (30 mL, 48 mmol) dropwise at -78 $^\circ\text{C}$ under argon atmosphere. This mixture was allowed to warm to 0 $^\circ\text{C}$ and stirred there for 1 h, then cooled to -78 $^\circ\text{C}$ again. To this mixture was added a solution of bromine (3.07 mL, 60 mmol) in pentane (15 mL) dropwise over 15 min and the cooling bath was removed. After stirring overnight at room temperature, the resulting mixture was poured into saturated Na_2SO_3 . The organic layer was separated and aqueous phase was extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over Na_2SO_4 . Evaporation of solvents and purification of the residue by column chromatography on silica gel (ethyl acetate/ CH_2Cl_2 /hexane = 1:1:15 as eluant) gave (*S*)-3,3'-dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl [(*S*)-18]¹ (9.59 g, 18 mmol, 90% yield): ^1H NMR (400 MHz, CDCl_3) δ 8.27 (2H, s, Ar-H), 7.80 (2H, d, $J = 8.0$ Hz, Ar-H), 7.44 (2H, ddd, $J = 8.0, 6.8, 1.2$ Hz, Ar-H), 7.30 (2H, ddd, $J = 8.0, 6.8, 1.2$ Hz, Ar-H), 7.18 (2H, d, $J = 8.0$ Hz, Ar-H), 4.83 (2H, d, $J = 9.2$ Hz, OCH_2O), 4.81 (2H, d, $J = 9.2$ Hz, OCH_2O), 2.58 (6H, s, OCH_3) ppm; IR (KBr) 2953, 2827, 1495, 1447, 1418, 1385, 1348, 1234, 1198, 1157, 1084, 1001, 959, 901, 802, 745 cm^{-1} .

A mixture of (*S*)-18 (9.59 g, 18 mmol) and concentrated HCl (1 mL) in 1,4-dioxane (40 mL) was heated to 50 $^\circ\text{C}$ and stirred for 3 h. The resulting mixture was poured into water and

extracted with ethyl acetate. The organic extracts were washed with brine and dried over Na_2SO_4 . After evaporation of solvents, the crude (*S*)-3,3-dibromo-1,1'-bi-2-naphthol [(*S*)-**19**]² was directly used for the following reaction without any purification. Analytical sample of (*S*)-**19** was purified by column chromatography on silica gel (ethyl acetate/hexane = 1:5 as eluant): ¹H NMR (400 MHz, CDCl_3) δ 8.25 (2H, s, Ar-H), 7.81 (2H, d, J = 8.4 Hz, Ar-H), 7.38 (2H, ddd, J = 8.0, 6.8, 1.2 Hz, Ar-H), 7.31 (2H, ddd, J = 8.4, 6.8, 1.2 Hz, Ar-H), 7.09 (2H, d, J = 8.0 Hz, Ar-H), 5.52 (2H, br, OH) ppm; IR (KBr) 3488, 1580, 1499, 1448, 1421, 1379, 1359, 1296, 1267, 1204, 1184, 1143, 1007, 885, 789, 745 cm^{-1} .

Trifluoromethanesulfonylation of crude (*S*)-**19** was performed in a similar manner as described for the conversion of (*S*)-1,1'-bi-2-naphthol to (*S*)-**12**. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 /hexane = 1:10 as eluant) to give (*S*)-3,3'-dibromo-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl [(*S*)-**20**] (12.1 g, 17.1 mmol, 95% yield): ¹H NMR (300 MHz, CDCl_3) δ 8.44 (2H, s, Ar-H), 7.92 (2H, d, J = 8.1 Hz, Ar-H), 7.61 (2H, ddd, J = 8.1, 6.9, 1.2 Hz, Ar-H), 7.41 (2H, ddd, J = 8.1, 6.9, 1.2 Hz, Ar-H), 7.22 (2H, d, J = 8.1 Hz, Ar-H) ppm; ¹³C NMR (100 MHz, CDCl_3) δ 142.6, 135.5, 132.9, 132.4, 128.3, 128.1, 127.3, 127.2, 126.0, 117.9 (q, $J_{\text{C-F}}$ = 319 Hz) ppm; IR (KBr) 1425, 1213, 1132, 987, 947, 893, 842, 808, 766, 750, 694, 638 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{10}\text{Br}_2\text{F}_6\text{NaO}_6\text{S}_2$: 728.8082 ($[\text{M}+\text{Na}]^+$), Found 728.8056 ($[\text{M}+\text{Na}]^+$). Anal. Calcd for $\text{C}_{22}\text{H}_{10}\text{Br}_2\text{F}_6\text{O}_6\text{S}_2$: C, 37.31; H, 1.42; Br, 22.56; F, 16.09. Found C, 37.50; H, 1.23; Br, 22.43; F, 16.34. mp 173 °C. $[\alpha]_{\text{D}}^{29}$ 188.1° (c 0.55, CHCl_3).

(*S*)-3,3'-Diphenyl-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl [(*S*)-21** (Ar = Ph)]**: The Pd-catalyzed Suzuki coupling of (*S*)-**20** and phenylboronic acid was carried out as described for the coupling of (*S*)-**30**. (80% yield): ¹H NMR (300 MHz, CDCl_3) δ 8.12 (2H, s, Ar-H), 7.99 (2H, d, J = 8.1 Hz, Ar-H), 7.34-7.66 (16H, m, Ar-H) ppm; ¹³C NMR (100 MHz, CDCl_3) δ 143.7, 136.0, 134.2, 133.0, 132.6, 132.2, 129.6, 128.3, 128.2, 128.0, 127.4, 127.3, 125.0, 117.4 (q, $J_{\text{C-F}}$ = 321 Hz) ppm; IR (KBr) 3454, 1417, 1211, 1136, 980, 945, 856, 816, 781, 764, 700 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{34}\text{H}_{20}\text{F}_6\text{NaO}_6\text{S}_2$: 725.0498 ($[\text{M}+\text{Na}]^+$), Found 725.0485 ($[\text{M}+\text{Na}]^+$). mp 167 °C. $[\alpha]_{\text{D}}^{26}$ 301.8° (c 0.50, CHCl_3).

(*S*)-3,3'-Bis(2-naphthyl)-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl [(*S*)-21** (Ar = β -Np)]**: (80% yield): ¹H NMR (300 MHz, CDCl_3) δ 8.23 (2H, s, Ar-H), 8.14 (2H, s, Ar-H), 7.94-8.05 (8H, m, Ar-H), 7.77 (2H, dd, J = 8.4, 1.8 Hz, Ar-H), 7.56-7.64 (6H, m, Ar-H) 7.38-7.46 (4H, m, Ar-H) ppm; ¹³C NMR (100 MHz, CDCl_3) δ 144.0, 134.3, 133.7, 133.4, 133.2, 132.9, 132.8, 132.4, 129.1, 128.2, 128.2, 128.1, 127.7, 127.5, 127.4, 126.5, 126.4, 125.2, 117.5 (q, $J_{\text{C-F}}$ = 322 Hz) ppm; IR (KBr) 3429, 3055, 1418, 1209, 1136, 1115, 999, 945, 891, 820, 748 cm^{-1} . HRMS (FAB) Calcd for $\text{C}_{42}\text{H}_{24}\text{F}_6\text{O}_6\text{S}_2$: 802.0919 (M^+), Found 802.0894 (M^+). Anal. Calcd for $\text{C}_{42}\text{H}_{24}\text{F}_6\text{O}_6\text{S}_2$: C, 62.84; H, 3.01, F, 14.20. Found C, 62.96; H, 3.30, F, 13.93. mp 145 °C. $[\alpha]_{\text{D}}^{26}$ 300.7° (c 0.36, CHCl_3).

(*S*)-3,3'-Diphenyl-2,2'-dimethyl-1,1'-binaphthyl [(*S*)-22** (Ar = Ph)]**: To a mixture of (*S*)-**21** (Ar = Ph) (281 mg, 0.40 mmol) and $\text{NiCl}_2(\text{PPh}_3)_2$ (13.1 mg, 5 mol%) in ether (3 mL) was added a 1 M ethereal solution of MeMgI (2.0 mL, 2.0 mmol) dropwise at 0 °C under argon atmosphere. This mixture was then refluxed for 1 day. After cooling to room temperature, the mixture was

poured into ice-cooled 1 N HCl and filtered to remove the catalyst. The filtrate was extracted with ether and the organic extracts were washed with brine, dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography on silica gel (CH₂Cl₂/hexane = 1:20 as eluant) gave (*S*)-3,3'-diphenyl-2,2'-dimethyl-1,1'-binaphthyl [(*S*)-**22** (Ar = Ph)] (163 mg, 0.38 mmol, 94% yield): ¹H NMR (300 MHz, CDCl₃) δ 7.89 (2H, d, *J* = 8.1 Hz, Ar-H), 7.85 (2H, s, Ar-H), 7.36-7.51 (12H, m, Ar-H), 7.23 (2H, dd, *J* = 6.6, 1.2 Hz, Ar-H), 7.12 (2H, d, *J* = 8.4 Hz, Ar-H), 1.95 (6H, s, Ar-CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 142.2, 141.2, 136.4, 132.5, 131.9, 129.4, 129.4, 128.2, 128.1, 128.0, 127.8, 126.8, 126.0, 125.6, 125.3, 18.3 ppm; IR (KBr) 3454, 3053, 2924, 1601, 1493, 1446, 1261, 1072, 1028, 894, 781, 766, 748, 700 cm⁻¹. HRMS (FAB) Calcd for C₃₄H₂₆: 434.2035 (M⁺), Found 434.2033 (M⁺). mp 182 °C. [α]_D²⁷ -80.6° (c 0.49, CHCl₃).

(*S*)-3,3'-Bis(2-naphthyl)-2,2'-dimethyl-1,1'-binaphthyl [(*S*)-**22** (Ar = β-Np)]: (76% yield): ¹H NMR (300 MHz, CDCl₃) δ 7.91-7.98 (12H, m, Ar-H), 7.63 (2H, dd, *J* = 8.4, 1.2 Hz, Ar-H), 7.52-7.56 (4H, m, Ar-H), 7.46 (2H, ddd, *J* = 8.1, 6.9, 1.2 Hz, Ar-H), 7.30 (2H, ddd, *J* = 8.1, 6.9, 1.2 Hz, Ar-H), 7.19 (2H, d, *J* = 8.1 Hz, Ar-H), 2.03 (6H, s, Ar-CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 139.8, 136.5, 133.3, 132.7, 132.3, 132.0, 132.0, 128.5, 128.0, 127.9, 127.9, 127.6, 127.4, 126.2, 126.1, 125.8, 125.7, 125.4, 18.5 ppm; IR (KBr) 3491, 3053, 1599, 1504, 1398, 1269, 1148, 1018, 891, 856, 820, 746 cm⁻¹. HRMS (FAB) Calcd for C₄₂H₃₀: 534.2348 (M⁺), Found 534.2368 (M⁺). mp 222 °C. [α]_D²⁷ -18.1° (c 0.51, CHCl₃).

(*S*)-3,3'-Diphenyl-2,2'-bis(bromomethyl)-1,1'-binaphthyl [(*S*)-**23** (Ar = Ph)]: Radical bromination of (*S*)-**22** (Ar = Ph) was performed in a similar manner as described for the preparation of (*S*)-**14** from (*S*)-**13**. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/hexane = 1:20 as eluant) to afford (*S*)-3,3'-diphenyl-2,2'-bis(bromomethyl)-1,1'-binaphthyl [(*S*)-**23** (Ar = Ph)] (quantitative yield): ¹H NMR (300 MHz, CDCl₃) δ 7.91-7.93 (4H, m, Ar-H), 7.61-7.65 (4H, m, Ar-H), 7.45-7.55 (8H, m, Ar-H), 7.30 (2H, ddd, *J* = 8.4, 6.9, 1.5 Hz, Ar-H), 7.17 (2H, d, *J* = 7.2 Hz, Ar-H), 4.29 (4H, s, Ar-CH₂) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 140.4, 136.2, 133.1, 132.2, 131.8, 130.3, 129.4, 128.1, 127.8, 127.4, 127.2, 127.1, 126.4, 32.1 ppm; IR (KBr) 3427, 3053, 1587, 1495, 1443, 1219, 1026, 899, 866, 795, 752, 725, 702 cm⁻¹. HRMS (FAB) Calcd for C₃₄H₂₄Br₂: 590.0245 (M⁺), Found 590.0259 (M⁺). Anal. Calcd for C₃₄H₂₄Br₂: C, 68.94; H, 4.08; Br, 26.98. Found C, 68.86; H, 4.19; Br, 26.93. mp 189 °C. [α]_D²⁶ -66.1° (c 0.50, CHCl₃).

(*S*)-3,3'-Bis(2-naphthyl)-2,2'-bis(bromomethyl)-1,1'-binaphthyl [(*S*)-**23** (Ar = β-Np)]: (quantitative yield): ¹H NMR (300 MHz, CDCl₃) δ 8.12 (2H, d, *J* = 1.5 Hz, Ar-H), 7.93-8.01 (10H, m, Ar-H), 7.77 (2H, dd, *J* = 8.4, 1.8 Hz, Ar-H), 7.52-7.57 (6H, m, Ar-H), 7.34 (2H, ddd, *J* = 8.1, 6.9, 1.5 Hz, Ar-H), 7.34 (2H, d, *J* = 8.4 Hz, Ar-H), 4.36 (4H, s, Ar-CH₂) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 140.8, 137.9, 136.3, 133.1, 133.1, 132.5, 132.4, 131.8, 130.6, 128.4, 128.0, 127.8, 127.7, 127.6, 127.6, 127.3, 127.2, 126.5, 126.3, 126.1, 32.1 ppm; IR (KBr) 3454, 3053, 2924, 1587, 1504, 1435, 1217, 1128, 1024, 943, 894, 856, 820, 748 cm⁻¹. HRMS (FAB) Calcd for C₄₂H₂₈Br₂: 690.0558 (M⁺), Found 690.0544 (M⁺). Anal. Calcd for C₄₂H₂₈Br₂: C, 72.85; H, 4.08; Br, 23.08. Found C, 72.83; H, 4.28; Br, 22.94. mp 249 °C. [α]_D²⁷ 30.1° (c 0.50, CHCl₃).

Chiral Ammonium Salt (*S,S*)-11b: (*S,S*)-**11b** was prepared in a similar manner as described

for (*S,S*)-**11a**. (87% yield): ^1H NMR (300 MHz, CDCl_3) δ 8.34 (2H, s, Ar-H), 8.11 (2H, d, $J = 8.1$ Hz, Ar-H), 7.84 (2H, d, $J = 8.1$ Hz, Ar-H), 7.74 (2H, br, Ph), 7.63 (2H, ddd, $J = 8.0, 7.1, 1.1$ Hz, Ar-H), 7.49 (2H, ddd, $J = 8.0, 7.1, 1.1$ Hz, Ar-H), 7.31-7.36 (4H, m, Ar-H), 7.09-7.22 (6H, m, Ar-H), 7.20-8.20 (8H, br, Ph), 6.32 (2H, d, $J = 8.4$ Hz, Ar-H), 5.01 (2H, d, $J = 13.7$ Hz, Ar- CH_2), 4.40 (2H, d, $J = 13.2$ Hz, Ar- CH_2), 4.24 (2H, d, $J = 13.7$ Hz, Ar- CH_2), 3.71 (2H, d, $J = 13.2$ Hz, Ar- CH_2) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 139.0, 136.1, 133.8, 133.8, 132.6, 130.9, 130.9, 130.8, 130.0, 128.9, 128.6, 128.4, 128.2, 128.1, 127.4, 127.3, 127.2, 126.8, 126.6, 124.7, 122.3, 62.3, 57.5 ppm; IR (KBr) 3649, 3367, 3053, 1653, 1558, 1491, 1456, 847, 812, 752, 708 cm^{-1} . HRMS (FAB) Calcd for $\text{C}_{56}\text{H}_{40}\text{N}$: 726.3163 (M^+), Found 726.3155 (M^+). Melted at 254°C with decomposition. $[\alpha]_{\text{D}}^{26}$ 86.6° (c 1.00, CHCl_3).

Chiral Ammonium Salt (*S,S*)-11c: (76% yield): ^1H NMR (300 MHz, CDCl_3) δ 8.49 (2H, s, Ar-H), 8.16 (2H, d, $J = 8.4$ Hz, Ar-H), 8.14 (2H, br, Ar-H), 7.79 (2H, br, β -Np), 7.67 (2H, t, $J = 6.9$ Hz, Ar-H), 7.31-7.39 (4H, m, Ar-H), 7.20 (2H, d, $J = 7.5$ Hz, Ar-H), 7.08 (2H, t, $J = 6.8$ Hz, Ar-H), 6.94 (2H, d, $J = 9.0$ Hz, Ar-H), 7.00-8.60 (12H, br, β -Np), 5.05 (2H, br, Ar- CH_2), 4.50 (2H, d, $J = 13.8$ Hz, Ar- CH_2), 4.22 (2H, d, $J = 12.9$ Hz, Ar- CH_2), 3.66 (2H, d, $J = 12.9$ Hz, Ar- CH_2) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 139.2, 139.1, 135.7, 133.9, 133.5, 133.0, 132.6, 131.1, 130.6, 129.8, 128.7, 128.4, 128.3, 128.2, 128.2, 127.8, 127.6, 127.4, 127.3, 127.1, 127.1, 126.6, 126.4, 124.5, 122.6, 62.3, 57.5 ppm; IR (KBr) 3852, 3649, 3367, 3051, 1653, 1558, 1506, 1456, 1361, 853, 833, 749 cm^{-1} . HRMS (FAB) Calcd for $\text{C}_{64}\text{H}_{44}\text{N}$: 826.3476 (M^+), Found 826.3483 (M^+). Melted at 267°C with decomposition. $[\alpha]_{\text{D}}^{26}$ 55.4° (c 1.00, CHCl_3).

Characterization of Alkylation Product 8a.

(*R*)-tert-Butyl 2-[(Diphenylmethylene)amino]pent-4-enoate [8a ($\text{R}' = \text{CH}_2\text{-CH=CH}_2$)]:³ ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.65 (2H, m, Ph), 7.29-7.47 (6H, m, Ph), 7.16-7.20 (2H, m, Ph), 5.72 (1H, ddt, $J = 17.2, 10.4, 7.2$ Hz, CH=CH_2), 5.06 (1H, dd, $J = 17.2, 1.5$ Hz, *cis*- CH=CH_2), 5.01 (1H, dd, $J = 10.4, 1.5$ Hz, *trans*- CH=CH_2), 4.00 (1H, dd, $J = 7.6, 5.6$ Hz, CHC=O), 2.57-2.69 (2H, m, $\text{CH}_2\text{-CH=CH}_2$), 1.44 (9H, s, *t*-Bu) ppm; IR (neat) 2978, 1735, 1624, 1447, 1367, 1286, 1151, 916, 847, 781, 696 cm^{-1} .

(*R*)-tert-Butyl 2-[(Diphenylmethylene)amino]-4-methylpent-4-enoate [8a ($\text{R}' = \text{CH}_2\text{-C(CH}_3\text{)=CH}_2$)]:⁴ ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.64 (2H, m, Ph), 7.28-7.45 (6H, m, Ph), 7.15-7.19 (2H, m, Ph), 4.73 (1H, s, C=CH_2), 4.71 (1H, s, C=CH_2), 4.07 (1H, dd, $J = 8.4, 5.2$ Hz, CHC=O), 2.63 (1H, dd, $J = 13.6, 5.2$ Hz, $\text{CH}_2\text{-C(CH}_3\text{)=CH}_2$), 2.56 (1H, dd, $J = 13.6, 8.4$ Hz, $\text{CH}_2\text{-C(CH}_3\text{)=CH}_2$), 1.52 (3H, s, CH_3), 1.45 (9H, s, *t*-Bu) ppm; IR (neat) 2978, 1735, 1624, 1447, 1367, 1286, 1151, 893, 849, 781, 696 cm^{-1} .

(*R*)-tert-Butyl 2-[(Diphenylmethylene)amino]pent-4-ynoate [8a ($\text{R}' = \text{CH}_2\text{-C}\equiv\text{CH}$)]: ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.67 (2H, m, Ph), 7.30-7.46 (6H, m, Ph), 7.25-7.28 (2H, m, Ph), 4.18 (1H, dd, $J = 7.8, 5.4$ Hz, CHC=O), 2.79 (2H, m, $\text{CH}_2\text{-C}\equiv\text{C}$), 1.95 (1H, t, $J = 2.4$ Hz, $\text{C}\equiv\text{CH}$), 1.45 (9H, s, *t*-Bu) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 169.3, 139.5, 136.1, 130.2, 128.8, 128.5, 128.2, 128.1, 127.8, 81.5, 81.2, 70.0, 64.8, 28.1, 23.4 ppm; IR (neat) 3296, 2978, 1732, 1624, 1578, 1447, 1369, 1286, 1153, 845, 781, 696, 638 cm^{-1} . HRMS (FAB) Calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_3$:

332.1652 ($[M-H]^+$), Found 332.1672 ($[M-H]^+$). $[\alpha]_D^{27}$ 112.4° (*c* 0.89, $CHCl_3$; 99% ee). HPLC analysis: Daicel Chiralcel OD, hexane/2-propanol = 400:1, flow rate = 0.5 mL/min, retention time; 26.3 min (*S*) and 30.5 min (*R*). Absolute configuration was confirmed, after cleavage of benzophenone imine and *tert*-butyl ester (6 N HCl), by comparison of the optical rotation of the amino acid hydrochloride with literature value.⁵

(*R*)-*tert*-Butyl *N*-(Diphenylmethylene)-4-methylphenylalaninate {8a [*R'* = CH_2 -(4- CH_3 -Ph)]}: ¹H NMR (400 MHz, $CDCl_3$) δ 7.56-7.58 (2H, m, Ar-H), 7.26-7.38 (6H, m, Ar-H), 6.98 (2H, d, *J* = 8.4 Hz, Ar-H), 6.93 (2H, d, *J* = 8.4 Hz, Ar-H), 6.63 (2H, br d, *J* = 6.0 Hz, Ar-H), 4.08 (1H, dd, *J* = 9.2, 4.4 Hz, $CHC=O$), 3.19 (1H, dd, *J* = 13.6, 4.4 Hz, Ar- CH_2), 3.10 (1H, dd, *J* = 13.6, 9.2 Hz, Ar- CH_2), 2.28 (3H, s, CH_3), 1.44 (9H, s, *t*-Bu) ppm; IR (neat) 2978, 2928, 1732, 1624, 1516, 1447, 1367, 1286, 1151, 910, 845, 779, 696 cm^{-1} .

(*R*)-*tert*-Butyl *N*-(Diphenylmethylene)-4-fluorophenylalaninate {8a [*R'* = CH_2 -(4-F-Ph)]}: ¹H NMR (400 MHz, $CDCl_3$) δ 7.56-7.58 (2H, m, Ar-H), 7.28-7.39 (6H, m, Ar-H), 6.99-7.03 (2H, m, Ar-H), 6.85-6.89 (2H, m, Ar-H), 6.67 (2H, br d, *J* = 7.2 Hz, Ar-H), 4.08 (1H, dd, *J* = 8.8, 4.8 Hz, $CHC=O$), 3.19 (1H, dd, *J* = 13.6, 4.8 Hz, Ar- CH_2), 3.12 (1H, dd, *J* = 13.6, 8.8 Hz, Ar- CH_2), 1.44 (9H, s, *t*-Bu) ppm; IR (KBr) 2978, 2928, 1728, 1626, 1508, 1447, 1369, 1285, 1221, 1148, 841, 781, 698 cm^{-1} .

(*R*)-*tert*-Butyl 2-[(Diphenylmethylene)amino]-3-(1-naphthyl)propanoate {8a [*R'* = CH_2 -(α -Np)]}: ¹H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, dd, *J* = 8.1, 1.1 Hz, Ar-H), 7.69-7.72 (2H, m, Ar-H), 7.50-7.52 (2H, m, Ar-H), 7.40 (1H, ddd, *J* = 8.7, 6.9, 1.2 Hz, Ar-H), 7.24-7.32 (6H, m, Ar-H), 7.13 (1H, tt, *J* = 7.5, 1.2 Hz, Ar-H), 6.96 (2H, t, *J* = 7.5 Hz, Ar-H), 6.62 (2H, br, Ar-H), 4.31 (1H, dd, *J* = 8.4, 3.9 Hz, $CHC=O$), 3.81 (1H, dd, *J* = 13.5, 3.9 Hz, Ar- CH_2), 3.50 (1H, dd, *J* = 13.6, 8.4 Hz, Ar- CH_2), 1.47 (9H, s, *t*-Bu) ppm; ¹³C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.9, 139.2, 135.7, 134.0, 133.5, 132.1, 129.8, 128.5, 128.2, 128.0, 127.6, 127.6, 127.5, 127.1, 126.9, 125.4, 125.1, 125.0, 123.5, 81.0, 66.5, 36.6, 28.1 ppm; IR (neat) 3059, 2978, 1732, 1622, 1576, 1447, 1367, 1288, 1150, 1074, 1028, 974, 845, 777, 696 cm^{-1} . HRMS (FAB) Calcd for $C_{30}H_{29}NO_2$: 435.2200 (M^+), Found 435.2199 (M^+). $[\alpha]_D^{27}$ 343.7° (*c* 1.19, $CHCl_3$; 99% ee). HPLC analysis: Daicel Chiralcel OD, hexane/2-propanol = 100:1, flow rate = 0.5 mL/min, retention time; 20.9 min (*R*) and 23.1 min (*S*). Absolute configuration was confirmed, after cleavage of benzophenone imine and *tert*-butyl ester (6 N HCl) followed by the reprotection of amine moiety (Boc_2O , *aq* NaOH), by comparison of the HPLC retention time of the *N*-Boc amino acid with literature value.⁷

(*R*)-*tert*-Butyl *N*-(Diphenylmethylene)-2,6-dichlorophenylalaninate {8a [*R'* = CH_2 -(2,6- Cl_2 -Ph)]}: ¹H NMR (400 MHz, $CDCl_3$) δ 7.60-7.62 (2H, m, Ar-H), 7.25-7.36 (6H, m, Ar-H), 7.16 (2H, d, *J* = 8.0 Hz, Ar-H), 7.03 (1H, t, *J* = 8.0 Hz, Ar-H), 6.63 (2H, br d, *J* = 5.2 Hz, Ar-H), 4.48 (1H, dd, *J* = 10.4, 4.0 Hz, $CHC=O$), 3.69 (1H, dd, *J* = 13.6, 10.4 Hz, Ar- CH_2), 3.43 (1H, dd, *J* = 13.6, 4.0 Hz, Ar- CH_2), 1.45 (9H, s, *t*-Bu) ppm; ¹³C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.2, 139.2, 137.5, 136.3, 135.9, 134.4, 129.9, 128.8, 128.2, 128.1, 127.9, 127.9, 127.8, 127.7, 127.5, 81.2, 64.4, 34.4, 28.1 ppm; IR (neat) 2978, 1732, 1661, 1622, 1560, 1437, 1367, 1290, 1151, 1088, 1028, 849, 777, 696 cm^{-1} . HRMS (ESI) Calcd for $C_{26}H_{26}Cl_2NO_2$: 454.1335 ($[M+H]^+$), Found 454.1324 ($[M+H]^+$). $[\alpha]_D^{27}$

238.6° (*c* 1.04, CHCl₃; 96% ee). HPLC analysis: Daicel Chiralcel OD, hexane/2-propanol = 400:1, flow rate = 0.5 mL/min, retention time; 16.5 min (*R*) and 19.1 min (*S*). Absolute configuration was determined, after cleavage of benzophenone imine (1 N HCl) and reprotection of amine moiety [(*R*)- and (*S*)-MTPA-Cl, pyridine, DMAP], by Mosher's method.⁸

(*R*)-*tert*-Butyl *N*-(Diphenylmethylene)-2,6-dimethylphenylalaninate (8a {R' = CH₂-[2,6-(CH₃)₂-Ph]}): ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.59 (2H, m, Ar-H), 7.26-7.36 (4H, m, Ar-H), 7.19 (2H, t, *J* = 8.0, Hz, Ar-H), 6.98 (1H, t, *J* = 8.0 Hz, Ar-H), 6.87 (2H, d, *J* = 8.0, Hz, Ar-H), 6.35 (2H, br, Ar-H), 4.17 (1H, dd, *J* = 10.8, 2.8 Hz, CHC=O), 3.39 (1H, dd, *J* = 14.4, 10.8 Hz, Ar-CH₂), 3.15 (1H, dd, *J* = 14.4, 2.8 Hz, Ar-CH₂), 2.11 (6H, s, Ar-CH₃), 1.46 (9H, s, *t*-Bu) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 169.3, 139.0, 137.5, 135.9, 134.8, 129.8, 128.5, 128.2, 127.8, 127.7, 127.5, 126.3, 126.0, 80.9, 65.6, 32.7, 28.1, 20.3 ppm; IR (neat) 2978, 1732, 1624, 1576, 1447, 1367, 1285, 1150, 1070, 1030, 976, 849, 770, 696 cm⁻¹. HRMS (ESI) Calcd for C₂₈H₃₂NO₂: 414.2428 ([M+H]⁺), Found 414.2428 ([M+H]⁺). [α]_D²⁷ 257.0° (*c* 1.15, CHCl₃; 99% ee). HPLC analysis: Daicel Chiralcel OD, hexane/2-propanol = 300:1, flow rate = 0.5 mL/min, retention time; 15.4 min (*R*) and 18.3 min (*S*). Absolute configuration was assigned, after cleavage of benzophenone imine and *tert*-butyl ester (6 N HCl) and subsequent reprotection of amine moiety (Boc₂O, *aq* NaOH), by comparison of the optical rotation of the *N*-Boc amino acid with literature value.⁹

(*R*)-*tert*-Butyl *N*-(Diphenylmethylene)-4-phenylphenylalaninate {8a [R' = CH₂-(4-Ph-Ph)]}:¹⁰ ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.60 (4H, m, Ar-H), 7.26-7.43 (11H, m, Ar-H), 7.12 (2H, d, *J* = 8.0, Hz, Ar-H), 6.65 (2H, br d, *J* = 6.8 Hz, Ar-H), 4.15 (1H, dd, *J* = 9.2, 4.4 Hz, CHC=O), 3.26 (1H, dd, *J* = 13.6, 4.4 Hz, Ar-CH₂), 3.19 (1H, dd, *J* = 13.6, 9.2 Hz, Ar-CH₂), 1.45 (9H, s, *t*-Bu) ppm; IR (neat) 2976, 2930, 1732, 1624, 1576, 1489, 1447, 1367, 1286, 1151, 1074, 1028, 976, 847, 764, 696 cm⁻¹.

(*R*)-*tert*-Butyl *N*-(Diphenylmethylene)-4-benzoylphenylalaninate {8a [R' = CH₂-(4-Bz-Ph)]}:¹¹ ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.78 (2H, m, Ar-H), 7.59-7.67 (2H, m, Ar-H), 7.54-7.58 (3H, m, Ar-H), 7.43-7.49 (2H, m, Ar-H), 7.28-7.39 (6H, m, Ar-H), 7.19 (2H, d, *J* = 8.4, Hz, Ar-H), 6.70 (2H, br d, *J* = 6.8, Hz, Ar-H), 4.18 (1H, dd, *J* = 8.8, 4.4 Hz, CHC=O), 3.31 (1H, dd, *J* = 13.6, 4.4 Hz, Ar-CH₂), 3.25 (1H, dd, *J* = 13.6, 8.8 Hz, Ar-CH₂), 1.45 (9H, s, *t*-Bu) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 170.4, 170.2, 143.5, 139.2, 137.7, 136.0, 135.4, 132.0, 130.1, 129.8, 129.7, 129.6, 128.6, 128.3, 128.0, 127.8, 127.5, 81.3, 67.4, 39.6, 28.1 ppm; IR (KBr) 2976, 2930, 1732, 1659, 1607, 1578, 1447, 1367, 1277, 1150, 937, 847, 781, 698 cm⁻¹. HRMS (ESI) Calcd for C₃₃H₃₂NO₃: 490.2377 ([M+H]⁺), Found 490.2374 ([M+H]⁺). [α]_D²⁷ 124.1° (*c* 1.02, CHCl₃; 99% ee). HPLC analysis: Daicel Chiralcel OD, hexane/2-propanol = 100:1, flow rate = 0.5 mL/min, retention time; 22.6 min (*S*) and 32.3 min (*R*). Absolute configuration was verified by comparison of the optical rotation of the corresponding amino acid hydrochloride with literature value.¹⁰

(*R*)-*tert*-Butyl *N*-(Diphenylmethylene)alaninate [8a (R' = CH₃)]:⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.63-7.65 (2H, m, Ph), 7.30-7.51 (6H, m, Ph), 7.17-7.20 (2H, m, Ph), 4.03 (1H, q, *J* = 6.8 Hz, CHC=O), 1.44 (9H, s, *t*-Bu), 1.40 (3H, d, *J* = 6.8 Hz, CH₃) ppm; IR (neat) 2978, 1736, 1624,

1447, 1367, 1284, 1153, 1123, 1030, 849, 781, 696 cm^{-1} .

(*R*)-*tert*-Butyl 2-[(Diphenylmethylene)amino]butanoate [**8a** ($\text{R}' = \text{CH}_2\text{CH}_3$)]: ^1H NMR (400 MHz, CDCl_3) δ 7.64–7.66 (2H, m, Ph), 7.30–7.50 (6H, m, Ph), 7.16–7.19 (2H, m, Ph), 3.85 (1H, dd, $J = 7.6, 5.2$ Hz, $\text{CHC}=\text{O}$), 1.86–1.95 (2H, m, $\text{CH}_2\text{-CH}_3$), 1.44 (9H, s, *t*-Bu), 0.87 (3H, t, $J = 7.2$ Hz, CH_3) ppm; IR (neat) 2978, 1734, 1663, 1624, 1447, 1367, 1279, 1153, 696 cm^{-1} .

X-ray Structure Determination

Chiral Ammonium Salt (*S,S*)-11f** (PF_6^-):** Anion exchange of (*S,S*)-**11f** (Br^-) using Amberlyst-A26 (OH^- form) gave (*S,S*)-**11f** (OH^-). The MeOH solution of (*S,S*)-**11f** (OH^-) was treated with 60% HPF_6 aqueous solution (1.2 equiv) at 0 °C. The resulting precipitate was collected by filtration and washed with water to afforded (*S,S*)-**11f** (PF_6^-): ^1H NMR (400 MHz, CDCl_3) δ 8.25 (2H, s, Ar-H), 8.09 (2H, d, $J = 8.8$ Hz, Ar-H), 7.93 (2H, d, $J = 8.4$ Hz, Ar-H), 7.64 (2H, t, $J = 7.2$ Hz, Ar-H), 7.2–7.8 (4H, br, Ar-H), 7.52–7.56 (4H, m, Ar-H), 7.33 (2H, t, $J = 8.0$ Hz, Ar-H), 7.23–7.27 (2H, m, Ar-H), 7.12 (2H, d, $J = 8.8$ Hz, Ar-H), 7.05 (2H, d, $J = 8.8$ Hz, Ar-H), 6.48 (2H, d, $J = 8.4$ Hz, Ar-H), 4.75 (2H, d, $J = 14.0$ Hz, Ar- CH_2), 4.15 (2H, d, $J = 14.0$ Hz, Ar- CH_2), 4.07 (2H, d, $J = 13.2$ Hz, Ar- CH_2), 3.61 (2H, d, $J = 13.2$ Hz, Ar- CH_2) ppm; IR (KBr) 3665, 3582, 3465, 3065, 2955, 1614, 1528, 1450, 1362, 1244, 1049, 845, 750 cm^{-1} .

The single crystals were mounted on a glass capillary [(*S,S*)-**11a**] or a CryoLoop (Hampton Research Co. Ltd.) [(*S,S*)-**11f** (PF_6^-)]. Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å) to a maximum 2θ value of 55°. All of the crystallographic calculations were performed using teXsan software package of the Molecular Structure Corp. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using SIR-92. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The crystallographic data were summarized in the following table.

	(<i>S,S</i>)- 11a	(<i>S,S</i>)- 11f (PF_6^-)
empirical formula	$\text{C}_{50}\text{H}_{44}\text{N}_3\text{Br}$	$\text{C}_{63}\text{H}_{50}\text{F}_{12}\text{NPO}_4\text{Cl}_2$
formula weight	766.82	1214.95
crystal system	orthorhombic	orthorhombic
space group	$\text{I}2_12_12_1$ (No. 24)	$\text{P}2_12_12_1$ (No. 19)
<i>a</i> , Å	14.6723(9)	11.0133(4)
<i>b</i> , Å	25.127(1)	15.2191(8)
<i>c</i> , Å	10.8390(5)	34.881(2)
<i>V</i> , Å ³	3996.1(4)	5846.5(5)
<i>Z</i>	4	4
D_{calc} , g/cm ³	1.274	1.380
<i>T</i> , °C	15	-150
μ ($\text{MoK}\alpha$), cm ⁻¹	10.7	2.25
no. of reflns meased	4311	33632

no. of reflns obsd	2543	7308
no. of variable	249	750
<i>R</i>	0.071	0.084
<i>R_w</i>	0.206	0.234
goodness of fit	1.26	1.49

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