Supplementary Material (ESI) for Chemical Communications

Supplementary Material

Stereospecific change in conformation upon complexation of an exoditopic tetraamide host with a bis(ammonium) guest: chiral recognition and strong CD signaling

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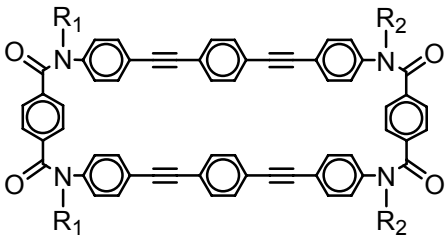
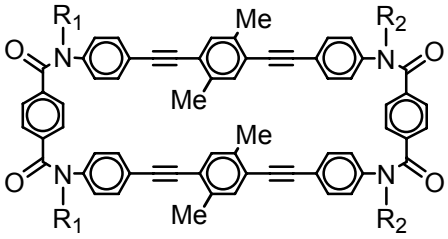


1a : $R_1 = R_2 = {}^{n}Bu$

1a

To a solution of $Pd(PPh_3)_4$ (28 mg, 0.024 mmol) and CuI (6.3 mg, 0.033 mmol) in Et_3N (30 mL), under an argon atmosphere, was added a solution of **5a** (59 mg, 0.12 mmol) and **6a** (100 mg, 0.11 mmol) in THF (10 mL) over 12 h at 40-45°C by using a syringe pump. After removal of precipitates by filtration and evaporation of the solvent, the remaining solid was suspended in 1N HCl aq and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel ($CHCl_3$) and gel permeation chromatography ($CHCl_3$, detected by UV 254 nm) gave **1a** (23 mg) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from AcOEt.

mp 295.0-297.0 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.318 (8H, d, J = 8.4 Hz), 7.142 (8H, s), 7.136 (8H, s), 6.855 (8H, d, J = 8.4 Hz), 3.887 (8H, t, J = 7.2 Hz), 1.544 (8H, qn, J = 7.2 Hz), 1.335 (8H, sx, J = 7.2 Hz), 0.896 (12H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.47, 143.07, 137.41, 132.15, 131.17, 127.97, 127.43, 122.66, 121.08, 89.84, 89.82, 49.89, 29.69, 20.12, 13.78; IR (KBr) 3040, 2956, 2929, 2870, 2217, 1638, 1599, 1518, 1384, 1296, 837 cm^{-1}; FD-MS m/z 1100 (M^+, BP), 550 (M^{2+}), 367 (M^{3+}), 275 (M^{4+}); UV-Vis (CH_2Cl_2) λ_{max} 317 (log ε 4.99); FD-HRMS Calcd for $C_{76}H_{68}N_4O_4$ 1100.5241, Found 1100.5214

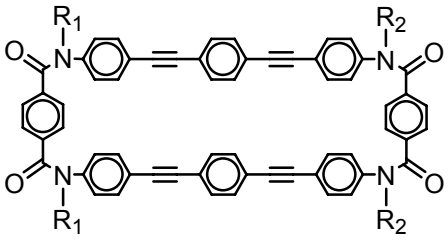


1b : $R_1 = R_2 = {}^{n}Bu$

1b

To a solution of $Pd(PPh_3)_4$ (25 mg, 0.022 mmol) and CuI (6 mg, 0.032 mmol) in Et_3N (30 mL), under an argon atmosphere, was added a suspension of **5a** (50 mg, 0.10 mmol) and **6b** (98 mg, 0.10 mmol) in THF (8 mL) and DMF (2 mL) at 50-55°C. After removal of precipitates by filtration and evaporation of the solvent, the remaining solid was suspended in 1N HCl aq and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel ($CHCl_3$) and gel permeation chromatography ($CHCl_3$, detected by UV 254 nm) gave **1b** (6 mg) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from AcOEt.

mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.307 (8H, d, J = 8.4 Hz), 7.146 (8H, s), 6.984 (4H, s), 6.856 (8H, d, J = 8.4 Hz), 3.890 (8H, t, J = 7.5 Hz), 2.290 (12H, s), 1.536 (8H, qn, J = 7.5 Hz), 1.341 (8H, sx, J = 7.5 Hz), 0.903 (12H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.39, 142.95, 137.36, 136.82, 132.21, 131.98, 128.07, 127.37, 1222.44, 121.51, 93.01, 89.21, 49.98, 29.71, 20.15, 20.03, 13.80; IR (KBr) 3040, 2955, 2929, 2871, 2206, 1648, 1599, 1511, 1384, 1294, 1217, 1121, 837 cm^{-1}; FD-MS m/z 1156 (M^+, BP); UV-Vis (CH_2Cl_2) λ_{max} 317 (log ε 4.96); FD-HRMS Calcd for $C_{80}H_{76}N_4O_4$ 1156.5867, Found 1156.5886

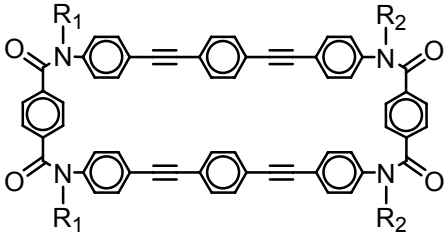


(*R*,*R*,*R*,*R*)-**1c** : $R_1 = R_2 =$ (*R*)-$CH(CH_3)Ph$

(*R*,*R*,*R*,*R*)-**1c**

To a solution of $Pd(PPh_3)_4$ (47 mg, 0.041 mmol) and CuI (11 mg, 0.058 mmol) in Et_3N (40 mL), under an argon atmosphere, was added a solution of (*R*,*R*)-**5c** (108 mg, 0.19 mmol) and (*R*,*R*)-**6c** (184 mg, 0.19 mmol) in THF (10 mL) over 12 h at 40-45°C by using a syringe pump. After removal of precipitates by filtration and evaporation of the solvent, the remaining solid was suspended in 1N HCl aq and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel ($CHCl_3$) and gel permeation chromatography ($CHCl_3$, detected by UV 254 nm) gave (*R*,*R*,*R*,*R*)-**1c** (70 mg) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from benzene/cyclohexane.

mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.373-7.268 (20H, m), 7.123 (8H, d, *J* = 8.7 Hz), 7.095 (8H, s), 7.045 (8H, s), 6.382 (8H, d, *J* = 8.7 Hz), 6.349 (4H, q, *J* = 7.2 Hz), 1.421 (12H, d, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 170.24, 140.90, 139.29, 137.70, 131.43, 131.12, 130.11, 128.44, 127.91, 127.71, 127.39, 122.63, 121.72, 90.08, 89.94, 53.13, 16.52; IR (KBr) 3086, 3063, 3035, 2975, 2933, 2216, 1645, 1598, 1517, 1330, 837, 699 cm^{-1}; FD-MS m/z 1293.6 (M^+, BP); UV-Vis (CH_2Cl_2) λ_{max} 306 (log ε 4.98); $[\alpha]^{20}_D$ = -1250 (c 0.072, $CHCl_3$); CD (CH_2Cl_2) λ 333 (Δε -68.1), 311 (-48.8), 291 (-70.4), 267 (-6.85), 249 (-67.4) nm; FD-HRMS Calcd for $C_{92}H_{68}N_4O_4$ 1292.5241, Found 1292.5215

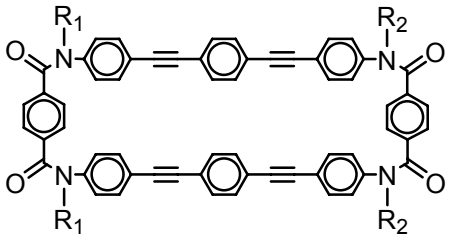


(*S*,*S*,*S*,*S*)-**1c** : $R_1 = R_2 =$ (*S*)-$CH(CH_3)Ph$

(*S*,*S*,*S*,*S*)-**1c**

To a solution of $Pd(PPh_3)_4$ (42 mg, 0.036 mmol) and CuI (14 mg, 0.074 mmol) in Et_3N (40 mL), under an argon atmosphere, was added a solution of (*S*,*S*)-**5c** (111 mg, 0.19 mmol) and (*S*,*S*)-**6c** (188 mg, 0.19 mmol) in THF (10 mL) over 12 h at 40-45°C by using a syringe pump. After removal of precipitates by filtration and evaporation of the solvent, the remaining solid was suspended in 1N HCl aq and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel ($CHCl_3$) and gel permeation chromatography ($CHCl_3$, detected by UV 254 nm) gave (*S*,*S*,*S*,*S*)-**1c** (33 mg) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from benzene/cyclohexane.

mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.373-7.268 (20H, m), 7.123 (8H, d, J = 8.7 Hz), 7.095 (8H, s), 7.045 (8H, s), 6.382 (8H, d, J = 8.7 Hz), 6.350 (4H, q, J = 7.2 Hz), 1.421 (12H, d, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 170.22, 140.91, 139.32, 137.72, 131.44, 131.12, 130.12, 128.44, 127.92, 127.69, 127.40, 122.64, 121.73, 90.08, 89.95, 53.15, 16.53; IR (KBr) 3062, 2978, 2939, 2217, 1645, 1517, 1387, 1332, 840, 698, 581 cm^{-1}; FD-MS m/z 1293.5 (M^+, BP); UV-Vis (CH_2Cl_2) λ_{max} 306 (log ε 4.98); $[\alpha]^{20}_D$ = -1240 (c 0.085, $CHCl_3$); CD (CH_2Cl_2) λ 333 (Δε +68.3), 313 (+49.0), 290 (+71.0), 267 (+7.97), 251 (+67.0) nm; FD-HRMS Calcd for $C_{92}H_{68}N_4O_4$ 1292.5241, Found 1292.5271

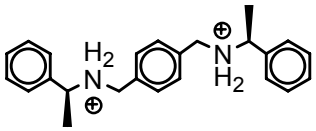


(*R*,*R*)-**1d** : R_1 = (*R*)-$CH(CH_3)Ph$, R_2 = ^{n}Bu

(*R*,*R*)-**1d**

To a solution of $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) and CuI (3 mg, 0.016 mmol) in Et_3N (15 mL), under an argon atmosphere, was added a solution of (*R*,*R*)-**5c** (37 mg, 0.065 mmol) and **6a** (58 mg, 0.066 mmol) in THF (10 mL) over 12 h at 40-45°C by using a syringe pump. After removal of precipitates by filtration and evaporation of the solvent, the remaining solid was suspended in 1N HCl aq and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel ($CHCl_3$) and gel permeation chromatography ($CHCl_3$, detected by UV 254 nm) gave (*R*,*R*)-**1d** (7 mg) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from benzene/hexane.

mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.320-7.287 (14H, m), 7.136 (4H, s), 7.130 (4H, d, *J* = 8.7 Hz), 7.115 (8H, s), 7.043 (4H, s), 6.854 (4H, d, *J* = 8.4 Hz), 6.401 (4H, d, *J* = 8.7 Hz), 6.346 (2H, q, *J* = 6.9 Hz), 3.959-3.807 (4H, m), 1.542 (4H, qn, *J* = 7.2 Hz), 1.453 (6H, d, *J* = 6.9 Hz), 1.306 (4H, sx, J = 7.2 Hz), 0.893 (6H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 170.16, 169.47, 143.10, 140.81, 139.27, 137.65, 137.46, 132.16, 131.42, 131.16, 131.15, 130.18, 128.39, 127.99, 127.92, 127.67, 127.41, 122.71, 122.60, 121.80, 121.03, 90.19, 89.96, 89.85, 89.70, 53.23, 49.92, 29.70, 20.12, 16.74, 13.79; IR (KBr) 2926, 2934, 2874, 2213, 1653, 1517, 1386, 841 cm^{-1}; FD-MS m/z 1196 (M^+, BP); UV-Vis (CH_2Cl_2) λ_{max} 313 (log ε 4.95); $[\alpha]^{13}_D$ = -601.5 (c 0.060, $CHCl_3$); CD (CH_2Cl_2) λ 337 (Δε -30.1), 318 (-16.1), 299 (-28.9), 269 (-0.716), 250 (-26.2) nm; FD-HRMS Calcd for $C_{84}H_{68}N_4O_4$ 1196.5241, Found 1196.5247



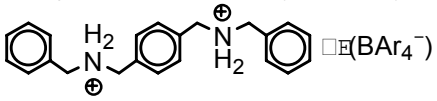
□□(BF$_4^-$)□□(BAr$_4^-$)

(*S*,*S*)-**2** (BF$_4^-$)(BAr$_4^-$) [Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$]

(*S*,*S*)-**2** (BF$_4^-$)(BAr$_4^-$) [Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$]

A mixture of (*S*,*S*)-**2** (BF$_4^-$)$_2$ (108 mg, 0.21 mmol) and NaBAr$_4$ (184 mg, 0.21 mmol) was dissolved in MeOH (5 mL). After evaporation of the solvent in vacuo, the remaining solid was suspended in CH_2Cl_2 (15 mL). Removal of $NaBF_4$ by filtration and concentration of the filtrate gave a colorless solid of (*S*,*S*)-**2** (BF$_4^-$)(BAr$_4^-$).

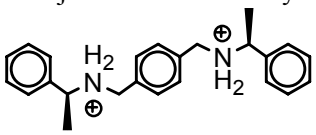
mp could not be measured due to its hygroscopicity; ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm 7.715 (8H, s), 7.552-7.425 (14H, m), 7.334 (4H, s), 4.440 (2H, q, *J* = 6.9 Hz), 4.077 (2H, d, *J* = 12.9 Hz), 3.956 (2H, d, *J* = 12.9 Hz), 1.779 (6H, d, *J* = 6.9 Hz); IR (KBr) 3197, 2990, 2832, 1611, 1459, 1356, 1279, 1124, 887, 838, 682 cm^{-1}; FD-MS m/z 1209 [M-(BF$_4^-$)]$^+$ (74), 433 [M-(BAr$_4^-$)]$^+$ (50), 345 [M-(BF$_4^-$)-(BAr$_4^-$)]$^+$ (BP); UV-Vis (CH_2Cl_2) λ_{max} 274 (log ε 3.59), 269 (log ε 3.70), 261 (log ε 3.65); $[\alpha]^{17}_D$ = +12.9 (c 0.147, $CHCl_3$); CD (CH_2Cl_2) λ 268 (Δε +0.61), 261 (+0.68), 255 (+0.51) nm; Anal. Calcd for $C_{56}H_{42}N_2B_2F_{28}$□H_2O : C, 51.17, H, 3.37, N, 2.13. Found : C, 51.09, H, 3.64, N, 2.54.



achiral guest $(BAr_4^-)_2$ [Ar = 3,5-$(CF_3)_2C_6H_3$]

achiral guest (Ph-CH_2-NH_2^+-CH_2-*p*-C_6H_4-CH_2-NH_2^+-CH_2-Ph) $(BAr_4^-)_2$ [Ar = 3,5-$(CF_3)_2C_6H_3$]

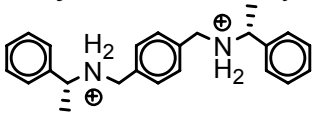
A mixture of achiral guest $(BF_4^-)_2$ (61.8 mg, 0.126mmol) and $NaBAr_4$ (222 mg, 0.251 mmol) was dissolved in MeOH (20 mL). After evaporation of the solvent in vacuo, the remaining solid was suspended in CH_2Cl_2 (50 mL). Removal of $NaBF_4$ by filtration and concentration of the filtrate gave a colorless solid of achiral guest $(BAr_4^-)_2$.
mp 111.0-113.0 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm 7.715 (16H, br. s), 7.707-70362 (22H, m), 4.378 (8H, br. s); IR (KBr) 1703, 1610, 1356, 1281, 1141, 886, 838, 713, 681, 671 cm^{-1}; FD-MS m/z 1181 $[M-(BAr_4^-)]^+$ (BP), 317 $[M-(BAr_4^-)_2]^+$ (15), 227 (22); UV-Vis (CH_2Cl_2) λ_{max} 270.5 (log ε 3.93), 278 (log ε 3.92); Anal. Calcd for $C_{86}H_{50}N_2B_2F_{48}\cdot(H_2O)_2$: C, 49.64, H, 2.62, N, 1.35. Found : C, 49.93, H, 2.87, N, 1.40.



□□(BF$_4^-$)$_2$ (*S*,*S*)-**2** (BF$_4^-$)$_2$

(*S*,*S*)-**2** (BF$_4^-$)$_2$

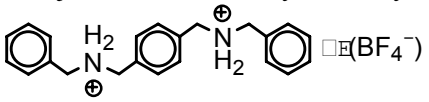
To a solution of (1-phenylethyl)-{4-[(1-phenylethylamino)methyl]benzyl}amine (0.921 g, 2.67 mmol) in MeOH (15 mL) was added 42% HBF_4 aq (0.81 mL, 5.35 mmol). After evaporation of solvent, the remaining solid was purified by recrystallization from CH_3CN/benzene to give (*S*,*S*)-**2** (BF$_4^-$)$_2$ (0.96 g) as colorless crystals in 69% yield. mp 243.5-244.0 °C; ^{1}H NMR (300 MHz, CD_3CN) δ/ppm 7.478 (10H, s), 7.405 (4H, s), 4.456 (2H, q, J = 6.9 Hz), 4.135 (2H, d, J = 13.2 Hz), 3.935 (2H, d, J = 13.2 Hz), 1.681 (6H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, CD_3CN) δ/ppm 136.35, 132.92, 131.48, 130.74, 130.28, 128.80, 60.64, 50.35, 19.37; IR (KBr) 3183, 3128, 2955, 1609, 1453, 1429, 1388, 1058, 766, 700, 553, 521 cm^{-1}; FAB-MS m/z 433 [M-(BF$_4^-$)]$^+$ (4.4), 345 [M-(BF$_4^-$)$_2$]$^+$ (23), 224 (16), 105 (BP); $[\alpha]^{24}_D$ = +2.51 (c 0.271, CH_3CN); Anal. Calcd for $C_{24}H_{30}N_2B_2F_8$: C, 55.42, H, 5.81, N, 5.39. Found : C, 55.64, H, 5.95, N, 5.44.



□□(BF4−)2 (R,R)-2 (BF4-)2

(*R*,*R*)-**2** (BF_4^-)$_2$

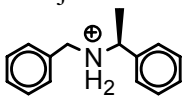
To a solution of (1-phenylethyl){4-[(1-phenylethylamino)methyl]benzyl}amine (1.051 g, 3.05 mmol) in MeOH (17 mL) was added 42% HBF_4 aq (0.93 mL, 6.11 mmol). After evaporation of solvent, the remaining solid was purified by recrystallization from CH_3CN/benzene to give (*R*,*R*)-**2** (BF_4^-)$_2$ (1.24 g) as colorless crystals in 78% yield. mp 246.0-246.5 °C; ^{1}H NMR (300 MHz, CD_3CN) δ/ppm 7.489 (10H, s), 7.410 (4H, s), 4.465 (2H, q, J = 6.9 Hz), 4.142 (2H, d, J = 13.2 Hz), 3.939 (2H, d, J = 13.2 Hz), 1.685 (6H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, CD_3CN) δ/ppm 136.26, 132.84, 131.51, 130.76, 130.29, 128.81, 60.67, 50.34, 19.32; IR (KBr) 3182, 3127, 2929, 2778, 2420, 1607, 1455, 1428, 1388, 1059, 766, 700, 553, 522 cm^{-1}; FAB-MS m/z 433 [M-(BF_4^-)]$^+$ (2.7), 345 [M-(BF_4^-)$_2$]$^+$ (12), 224 (9.3), 105 (BP); $[\alpha]^{24}_D$ = -2.62 (c 0.663, CH_3CN); Anal. Calcd for $C_{24}H_{30}N_2B_2F_8$: C, 55.42, H, 5.81, N, 5.39. Found : C, 55.49, H, 5.84, N, 5.41.



achiral guest $(BF_4^-)_2$

achiral guest (Ph-CH_2-NH_2^+-CH_2-*p*-C_6H_4-CH_2-NH_2^+-CH_2-Ph) $(BF_4^-)_2$

To a solution of benzyl-{(4-benzylaminomethyl)benzyl}amine (0.884 g, 2.79 mmol) in MeOH (25 mL) was added 42% HBF_4 aq (0.85 mL, 5.61 mmol). After evaporation of solvent, the remaining solid was purified by recrystallization from CH_3CN/benzene to give achiral guest $(BF_4^-)_2$ (1.06 g) as a colorless crystals in 77% yield. mp 257.0-293.0 °C (decomp.); ^{1}H NMR (300 MHz, CD_3CN) δ/ppm 7.542 (4H, s), 7.510-7.403 (10H, m), 7.151 (4H, s), 4.266 (8H, s); ^{13}C NMR (75 MHz, CD_3CN) δ/ppm 132.83, 131.69, 131.14, 130.72, 129.99, 52.56, 51.75; IR (KBr) 3191, 3134, 2941, 2791, 2715, 2590, 1554, 1457, 1418, 10.5, 698 cm^{-1}; FAB-MS m/z 405.2 $[M-(BF_4^-)]^+$ (2.1), 317 $[M-(BF_4^-)-1]^+$ (25), 210 (43), 107 (2.2), 91 (BP); Anal. Calcd for $C_{22}H_{26}N_2B_2F_8$: C, 53.70, H, 5.33, N, 5.69. Found : C, 53.65, H, 5.42, N, 5.67.

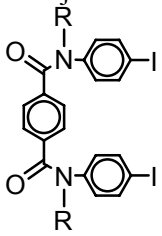


□□(BF$_4^-$) (*S*)-**3** (BF$_4^-$)

(*S*)-**3** (BF$_4^-$)

To a solution of (*S*)-benzyl-(1-phenylethyl)amine (1.082 g, 5.12 mmol) in MeOH (2 mL) was added 42% HBF_4 aq (0.78 mL, 5.15 mmol). After evaporation of solvent, the remaining solid was purified by recrystallization from benzene/hexane to give (*S*)-**3** (BF$_4^-$) as a white solid in quantitative yield.

mp 97.0-98.0 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm 7.527-7.295 (10H, m), 4.307-4.198 (1H, m), 4.073-3.870 (2H, m), 1.667 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm 135.10, 130.38, 130.28, 130.12, 129.79, 129.70, 127.82, 59.02, 50.26, 19.95; IR (KBr) 3190, 3117, 3040, 2931, 2824, 2797, 2761, 2653, 2420, 1588, 1496, 1460, 1446, 1066, 696, 521 cm^{-1}; FAB-MS m/z 212 [M-(BF$_4^-$)]$^+$ (79), 105 (BP), 91 (35), 77 (6.5); UV-Vis (CH_2Cl_2) λ_{max} 268 (log ε 2.49), 262 (log ε 2.69), 257 (log ε 2.68); $[\alpha]^{22}_D$ = -60.7 (c 1.45, $CHCl_3$); CD (CH_2Cl_2) λ 268 (Δε +0.18), 261 (+0.21), 255 (+0.13) nm; Anal. Calcd for $C_{15}H_{18}NBF_4$: C, 60.23, H, 6.07, N, 4.68. Found : C, 60.11, H, 6.05, N, 4.71.

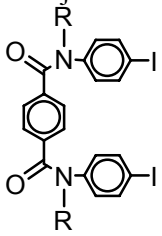


4a : R = ^{n}Bu

4a

To a solution of butyl-4-iodoaniline (5.956 g, 21.7 mmol) and Et_3N (3.0 mL, 21.6 mmol) in THF (150 mL), under an argon atmosphere, was added terephthaloyl chloride (2.198 g, 10.8 mmol). After evaporation of the solvent, the remaining solid was suspended in H_2O and filtration of the precipitates gave **4a** (6.892 g) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from benzene.

mp 193.0-193.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.515 (4H, d, J = 8.4 Hz), 7.083 (4H, s), 6.672 (4H, d, J = 8.4 Hz), 3.821 (4H, t, J = 7.5 Hz), 1.536 (4H, qn, J = 7.5 Hz), 1.320 (4H, sx, J = 7.5 Hz), 0.890 (6H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.28, 142.83, 138.31, 137.09, 129.53, 128.10, 91.58, 50.12, 29.71, 20.10, 13.77; IR (KBr) 2957, 2926, 2862, 1632, 1581, 1564, 1500, 1483, 1406, 1308, 1006, 608 cm^{-1}; FD-MS m/z 680 (M^{+}, BP); Anal. Calcd for $C_{28}H_{30}N_2O_2I_2$: C, 49.43, H, 4.44, N, 4.12, I, 37.31. Found : C, 49.60, H, 4.41, N, 4.03, I, 37.37.

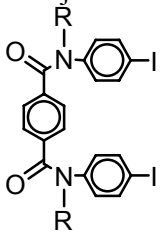


(*R*,*R*)-**4c** : R = (*R*)-CH(CH$_3$)Ph

(*R*,*R*)-**4c**

To a solution of (*R*)-*N*-(1-phenylethyl)-4-iodoaniline (2.55 g, 7.89 mmol) and Et_3N (1.1 mL, 7.91 mmol) in THF (50 mL), under an argon atmosphere, was added terephthaloyl chloride (0.963 g, 4.74 mmol). After evaporation of the solvent, the remaining solid was suspended in H_2O and filtration of the precipitates gave (*R*,*R*)-**4c** (2.67 g) as a white solid.

mp 89.5-91.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.346 (4H, d, *J* = 7.8 Hz), 7.316-7.220 (10H, m), 7.003 (4H, s), 6.316 (2H, q, *J* = 7.2 Hz), 6.192 (4H, d, *J* = 7.8 Hz), 1.433 (6H, d, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.64, 140.63, 138.80, 137.52, 137.20, 132.01, 128.38, 127.90, 127.70, 127.65, 92.91, 53.12, 16.53; IR (KBr) 3087, 3060, 3030, 2974, 2933, 2875, 1645, 1484, 1324, 1007, 720, 577 cm^{-1}; FD-MS m/z 776 (M^+, BP); $[\alpha]^{25}_D$ = -222.8 (c 0.840, $CHCl_3$); FD-HRMS Calcd for $C_{36}H_{30}N_2O_2I_2$ 776.0397, Found 776.0420

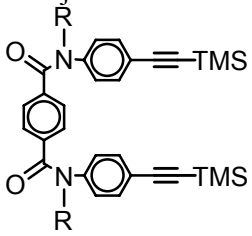


(*S*,*S*)-**4c** : R = (*S*)-CH(CH$_3$)Ph

(*S*,*S*)-**4c**

To a solution of (*S*)-*N*-(1-phenylethyl)-4-iodoaniline (5.255 g, 16.3 mmol) and Et_3N (2.26 mL, 16.2 mmol) in THF (80 mL), under an argon atmosphere, was added terephthaloyl chloride (1.65 g, 8.13 mmol). After evaporation of the solvent, the remaining solid was suspended in H_2O and filtration of the precipitates gave (*S*,*S*)-**4c** (4.99 g) as a white solid.

mp 89.5-91.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.380-7.180 (14H, m), 7.003 (4H, s), 6.384-6.250 (2H, br), 6.190 (4H, d, *J* = 7.8 Hz), 1.431 (6H, d, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.70, 140.70, 138.86, 137.58, 137.26, 132.07, 128.47, 127.97, 127.76, 127.71, 92.94, 53.16, 16.57; IR (KBr) 3087, 3060, 3030, 2975, 2935, 2875, 1645, 1484, 1324, 1007, 720, 577 cm^{-1}; FD-MS m/z 776 (M^+, BP); $[\alpha]^{25}_D$ = +219.6 (c 0.840, $CHCl_3$); FD-HRMS Calcd for $C_{36}H_{30}N_2O_2I_2$ 776.0397, Found 776.0382

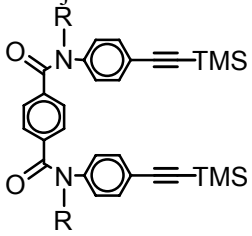


5a (TMS-protected) : R = ^{n}Bu

5a (TMS-protected)

To a suspension of **4a** (4.16 g, 6.12 mmol) and ethynyltrimethylsilane (8.6 mL, 60.9 mmol) in Et_3N (150 mL) and benzene (85 mL), under an argon atmosphere, was added $Pd(PPh_3)_4$ (710 mg, 0.615 mmol) and CuI (117 mg, 0.614 mmol), and the mixture was allowed to warm 55°C. After removal of precipitates by filtration and evaporation of the solvent, chromatographic separation on silica gel ($CHCl_3$) gave TMS-protected **5a** (3.557 g) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from EtOH.

mp 195.5-196.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.278 (4H, d, J = 8.4 Hz), 7.043 (4H, s), 6.833 (4H, d, J = 8.4 Hz), 3.841 (4H, t, J = 7.5 Hz), 1.524 (4H, qn, J = 7.5 Hz), 1.318 (4H, sx, J = 7.5 Hz), 0.881 (6H, t, J = 7.5 Hz), 0.240 (18H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.30, 143.09, 137.12, 132.76, 128.08, 127.43, 121.52, 103.95, 95.46, 49.95, 29.76, 20.11, 13.77, -0.12; IR (KBr) 2958, 2932, 2872, 2157, 1646, 1600, 1504, 864, 840 cm^{-1}; FD-MS m/z 620 (M^+, BP); Anal. Calcd for $C_{38}H_{48}N_2O_2Si_2$: C, 73.50, H, 7.79, N, 4.51. Found : C, 73.31, H, 7.77, N, 4.53.

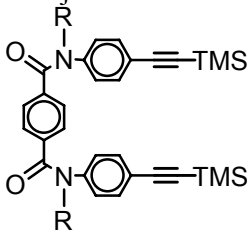


(*R*,*R*)-**5c** (TMS-protected) : R = (*R*)-CH(CH_3)Ph

(*R*,*R*)-**5c** (TMS-protected)

To a suspension of (*R*,*R*)-**4c** (2.60 g, 3.35 mmol) and ethynyltrimethylsilane (4.7 mL, 33.3 mmol) in Et_3N (80 mL) and benzene (40 mL), under an argon atmosphere, was added $Pd(PPh_3)_4$ (390 mg, 0.338 mmol) and CuI (64 mg, 0.336 mmol), and the mixture was allowed to warm 50°C. After removal of precipitates by filtration and evaporation of the solvent, chromatographic separation on silica gel ($CHCl_3$) gave TMS-protected (*R*,*R*)-**5c** (1.80 g) as a white solid.

mp 103.5-104.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.330-7.219 (10H, m), 7.108 (4H, d, *J* = 8.4 Hz), 6.960 (4H, s), 6.458-6.250 (6H, m), 1.430 (6H, d, *J* = 6.9 Hz), 0.230 (18H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.65, 140.75, 139.14, 137.20, 131.97, 130.08, 128.32, 127.93, 127.62, 127.58, 122.07, 103.93, 95.68, 53.16, 16.56, -0.18; IR (KBr) 3064, 3034, 2958, 2899, 2157, 1653, 1599, 1504, 1323, 1250, 865, 843, 699 cm^{-1}; FD-MS m/z 716 (M^+, BP); $[\alpha]^{25}_D$ = -317.1 (c 0.920, $CHCl_3$); FD-HRMS Calcd for $C_{46}H_{48}N_2O_2Si_2$ 716.3254, Found 716.3243

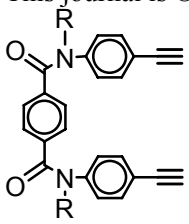


(*S*,*S*)-**5c** (TMS-protected) : R = (*S*)-CH(CH$_3$)Ph

(*S*,*S*)-**5c** (TMS-protected)

To a suspension of (*S*,*S*)-**4c** (4.78 g, 6.16 mmol) and ethynyltrimethylsilane (8.70 mL, 61.6 mmol) in Et_3N (150 mL) and benzene (75 mL), under an argon atmosphere, was added $Pd(PPh_3)_4$ (711 mg, 0.616 mmol) and CuI (134 mg, 0.704 mmol), and the mixture was allowed to warm 42°C. After removal of precipitates by filtration and evaporation of the solvent, chromatographic separation on silica gel ($CHCl_3$) gave TMS-protected (*S*,*S*)-**5c** (3.90 g) as a white solid.

mp 103.5-104.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.330-7.216 (10H, m), 7.109 (4H, d, *J* = 8.4 Hz), 6.961 (4H, s), 6.480-6.240 (6H, br), 1.429 (6H, d, *J* = 7.2 Hz), 0.230 (18H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.70, 140.81, 139.19, 137.25, 132.03, 130.13, 128.37, 127.98, 127.67, 127.65, 122.12, 103.97, 95.74, 53.20, 16.60, -0.13; IR (KBr) 3064, 3034, 2959, 2899, 2158, 1653, 1600, 1504, 1322, 1250, 865, 843, 699 cm^{-1}; FD-MS m/z 716 (M^+, BP); $[\alpha]^{25}_D$ = +318.9 (c 0.950, $CHCl_3$); FD-HRMS Calcd for $C_{46}H_{48}N_2O_2Si_2$ 716.3254, Found 716.3243

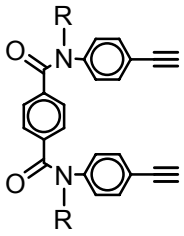


5a : R = ^{n}Bu

5a

To a solution of TMS-protected **5a** (2.74 g, 4.40 mmol) in THF (100 mL) was added a 1M solution of TBAF (2.20 mL, 2.20 mmol) in THF. The mixture was diluted by 1N HCl aq. (120 mL) and extracted with ether (200 mL). The organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel ($CHCl_3$) gave **5a** (1.93 g) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from benzene.

mp 180.0-180.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.305 (4H, d, *J* = 8.4 Hz), 7.070 (4H, s), 6.860 (4H, d, *J* = 8.4 Hz), 3.847 (4H, t, *J* = 7.5 Hz), 3.093 (2H, s), 1.557 (4H, qn, *J* = 7.5 Hz), 1.323 (4H, sx, *J* = 7.5 Hz), 0.888 (6H, t, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.29, 143.42, 137.13, 132.92, 128.11, 127.49, 120.49, 82.59, 78.25, 50.03, 29.76, 20.11, 13.79; IR (KBr) 3296, 2950, 2872, 2108, 1634, 1601, 1506, 1312, 1131, 848, 604 cm^{-1}; FD-MS m/z 476 (M^{+}, BP); Anal. Calcd for $C_{32}H_{32}N_2O_2$: C, 80.64, H, 6.77, N, 5.88. Found : C, 80.69, H, 6.72, N, 5.72.

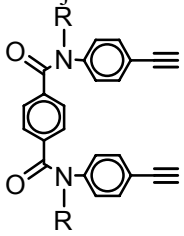


(*R*,*R*)-**5c** : R = (*R*)-CH(CH_3)Ph

(*R*,*R*)-**5c**

To a solution of TMS-protected (*R*,*R*)-**5c** (1.74 g, 2.43 mmol) in THF (50 mL) was added a 1M solution of TBAF (1.20 mL, 1.20 mmol) in THF. The mixture was diluted by 1N HCl aq. (30 mL) and extracted with ether (50 mL). The organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel ($CHCl_3$) gave (*R*,*R*)-**5c** (1.04 g) as a white solid.

mp 156.0-164.0 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.350-7.195 (10H, br), 7.128 (4H, d, *J* = 8.4 Hz), 6.987 (4H, s), 6.399 (4H, d, *J* = 8.4 Hz), 6.322 (2H, q, *J* = 6.6 Hz), 3.089 (2H,s), 1.440 (6H, d, *J* = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.64, 140.71, 139.50, 137.23, 132.13, 130.09, 128.33, 127.88, 127.63, 127.60, 121.09, 82.52, 78.55, 53.25, 16.61; IR (KBr) 3276, 3252, 3060, 2977, 2936, 1640, 1601, 1502, 1326, 837, 698 cm^{-1}; FD-MS m/z 572 (M^+, BP); $[\alpha]^{25}_D$ = -318.7 (c 0.610, $CHCl_3$); FD-HRMS Calcd for $C_{40}H_{32}N_2O_2$ 572.2464, Found 572.2478

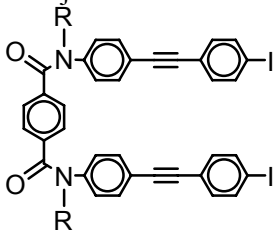


(*S*,*S*)-**5c** : R = (*S*)-CH(CH$_3$)Ph

(*S*,*S*)-**5c**

To a solution of TMS-protected (*S*,*S*)-**5c** (3.71 g, 5.17 mmol) in THF (110 mL) was added a 1M solution of TBAF (2.60 mL, 2.60 mmol) in THF. The mixture was diluted by 1N HCl aq. (200 mL) and extracted with ether (250 mL). The organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel ($CHCl_3$) gave (*S*,*S*)-**5c** (2.32 g) as a white solid.

mp 151.0-163.0 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.348-7.212 (10H, m), 7.128 (4H, d, *J* = 8.7 Hz), 6.987 (4H, s), 6.398 (4H, d, *J* = 8.7 Hz), 6.323 (2H, q, *J* = 6.9 Hz), 3.090 (2H,s), 1.440 (6H, d, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.72, 140.78, 139.57, 137.29, 132.20, 130.15, 128.40, 127.95, 127.70, 127.67, 121.15, 82.58, 78.55, 53.31, 16.66; IR (KBr) 3276, 3252, 3060, 2977, 2936, 1640, 1601, 1502, 1326, 837, 698 cm^{-1}; FD-MS m/z 572 (M^+, BP); $[\alpha]^{25}_D$ = +323.5 (c 0.580, $CHCl_3$); FD-HRMS Calcd for $C_{40}H_{32}N_2O_2$ 572.2464, Found 572.2444

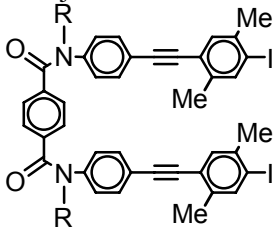


6a : R = ^{n}Bu

6a

To a solution of 1,4-diiodobenzene (1.99 g, 6.02 mmol) in Et_3N (50 mL), under an argon atmosphere, was added $Pd(PPh_3)_4$ (70 mg, 0.061 mmol) and CuI (13 mg, 0.068 mmol), and the mixture was allowed to warm 55°C. To the mixture was added a solution of **5a** (287 mg, 0.602 mmol) in THF (50 mL) over 21 h. After removal of precipitates by filtration and evaporation of the solvent, chromatographic separation on silica gel ($CHCl_3$) gave **6a** (355 mg) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from benzene.

mp 227.5-228.0 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.655 (4H, d, *J* = 8.4 Hz), 7.336 (4H, d, *J* = 8.4 Hz), 7.199 (4H, d, *J* = 8.4 Hz), 7.078 (4H, s), 6.879 (4H, d, *J* = 8.4 Hz), 3.860 (4H, t, *J* = 7.5 Hz), 1.554 (4H, qn, *J* = 7.5 Hz), 1.331 (4H, sx, *J* = 7.5 Hz), 0.888 (6H, t, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.39, 143.12, 137.57, 137.21, 133.01, 132.36, 128.06, 127.65, 122.38, 121.29, 94.42, 89.77, 89.51, 49.94, 29.80, 20.13, 13.78; IR (KBr) 2954, 2857, 1633, 1601, 1510, 1316, 1005, 816 cm^{-1}; FD-MS m/z 880 (M^{+}, BP); Anal. Calcd for $C_{44}H_{38}N_2O_2I_2$: C, 60.01, H, 4.35, N, 3.18, I, 28.82. Found : C, 60.47, H, 4.53, N, 3.33, I, 28.42.

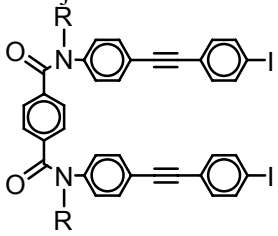


6b : R = ^{n}Bu

6b

To a solution of 2,5-diiodo-*p*-xylene (708 mg, 1.98 mmol) in Et_3N (60 mL), under an argon atmosphere, was added $Pd(PPh_3)_4$ (57 mg, 0.049 mmol) and CuI (10 mg, 0.053 mmol), and the mixture was allowed to warm 45-50°C. To the mixture was added a solution of **5b** (240 mg, 0.495 mmol) in THF (50 mL) over 21 h. After removal of precipitates by filtration and evaporation of the solvent, chromatographic separation on silica gel ($CHCl_3$) gave **6b** (192 mg) as a white solid. An analytical sample was obtained as colorless crystals by recrystalization from benzene.

mp 230.0-231.0 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.669 (2H, s), 7.334 (4H, d, J = 8.4 Hz), 7.275 (2H,s), 7.100 (4H, s), 6.885 (4H, d, J = 8.4 Hz), 3.863 (4H, t, J = 7.5 Hz), 2.375 (6H, s), 2.334 (6H, s), 1.560 (4H, qn, J = 7.5 Hz), 1.333 (4H, sx, J = 7.5 Hz), 0.891 (6H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.39, 142.95, 137.36, 136.82, 132.21, 131.98, 128.07, 127.37, 122.44, 121.51, 93.01, 89.21, 49.98, 29.71, 20.15, 20.03, 13.80; IR (KBr) 3046, 2950, 2869, 2212, 1633, 1602, 1510, 1396, 1315, 1113, 948, 847, 739, 611 cm^{-1}; FD-MS m/z 936 (M^{+}, BP); Anal. Calcd for $C_{28}H_{30}N_2O_2I_2$: C, 61.55, H, 4.95, N, 2.99, I, 27.10. Found : C, 62.28, H, 5.01, N, 3.02, I, 29.88.

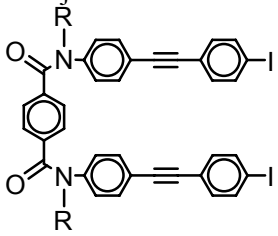


(*R*,*R*)-**6c** : R = (*R*)-CH(CH$_3$)Ph

(*R*,*R*)-**6c**

To a solution of 1,4-diiodobenzene (1.70 g, 5.15 mmol) in Et_3N (45 mL), under an argon atmosphere, was added $Pd(PPh_3)_4$ (61 mg, 0.053 mmol) and CuI (11 mg, 0.058 mmol), and the mixture was allowed to warm 45-50°C. To the mixture was added a solution of (*R*,*R*)-**5c** (300 mg, 0.524 mmol) in THF (45 mL) over 10 h. After removal of precipitates by filtration and evaporation of the solvent, chromatographic separation on silica gel ($CHCl_3$) gave (*R*,*R*)-**6c** (276 mg) as a white solid.

mp 249.0-250.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.643 (4H, d, *J* = 8.7 Hz), 7.334-7.230 (10H, m), 7.181 (4H, d, *J* = 8.7 Hz), 7.167 (4H, d, *J* = 8.4 Hz), 6.993 (4H, s), 6.414 (4H, d, *J* = 8.4 Hz), 6.323 (2H, q, *J* = 7.2 Hz), 1.449 (6H, d, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.79, 140.72, 139.21, 137.54, 137.33, 132.92, 131.57, 130.31, 128.36, 127.93, 127.67, 127.54, 122.23, 121.83, 94.49, 89.81, 89.78, 53.23, 16.66; IR (KBr) 3060, 3030, 2973, 2933, 1648, 1600, 1508, 1321, 1005, 698 cm^{-1}; FD-MS m/z 976 (M^+, BP); $[\alpha]^{17}_D$ = -358.0 (c 0.500, $CHCl_3$); FD-HRMS Calcd for $C_{52}H_{38}N_2O_2I_2$ 976.1023, Found 976.1025

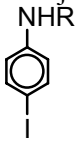


(*S*,*S*)-**6c** : R = (*S*)-$CH(CH_3)Ph$

(*S*,*S*)-**6c**

To a solution of 1,4-diiodobenzene (1.81 g, 5.48 mmol) in Et_3N (60 mL), under an argon atmosphere, was added $Pd(PPh_3)_4$ (72 mg, 0.062 mmol) and CuI (30 mg, 0.158 mmol), and the mixture was allowed to warm 45°C. To the mixture was added a solution of (*S*,*S*)-**5c** (347 mg, 0.607 mmol) in THF (60 mL) over 16 h. After removal of precipitates by filtration and evaporation of the solvent, chromatographic separation on silica gel ($CHCl_3$) gave (*S*,*S*)-**6c** (253 mg) as a white solid.

mp 249.0-250.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.641 (4H, d, *J* = 8.4 Hz), 7.334-7.213 (10H, m), 7.180 (4H, d, *J* = 8.4 Hz), 7.167 (4H, d, *J* = 8.4 Hz), 6.993 (4H, s), 6.414 (4H, d, *J* = 8.4 Hz), 6.323 (2H, q, *J* = 7.2 Hz), 1.449 (6H, d, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.77, 140.71, 139.20, 137.53, 137.32, 132.90, 131.56, 130.29, 128.35, 127.92, 127.65, 127.52, 122.22, 121.83, 94.48, 89.81, 89.78, 53.23, 16.65; IR (KBr) 3061, 3029, 2974, 2934, 1632, 1600, 1509, 1324, 1005, 697 cm^{-1}; FD-MS m/z 976 (M^+, BP); $[\alpha]^{16}_D$ = +360.5 (c 0.193, $CHCl_3$); FD-HRMS Calcd for $C_{52}H_{38}N_2O_2I_2$ 976.1023, Found 976.1049

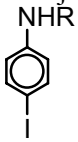


(*R*)-*N*-(1-phenylethyl)-4-iodoaniline

(*R*)-*N*-(1-phenylethyl)-4-iodoaniline

To a suspension of 1,4-diiodobenzene (1.00 g, 3.03 mmol), CuI (58 mg, 0.305 mmol), L-proline (70 mg, 0.606 mmol) and K_2CO_3 (840 mg, 6.09 mmol) in DMSO (6 mL) was added (*R*)-alpha-methylbenzylamine (0.58 mL, 4.55 mmol). The mixture was allowed to warm 84°C. The mixture was diluted with H_2O (30 mL) and AcOEt (40 mL). After extraction with AcOEt (30 mL ×3), the combined organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel (CH_2Cl_2/hexane 1 : 4) to give (*R*)-*N*-(1-phenylethyl)-4-iodoaniline (520 mg) as a white solid.

mp 71.0-72.0 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm 7.404-7.164 (7H, m), 6.303 (2H, d, J = 9.0 Hz), 4.427 (1H, q, J = 6.6 Hz), 4.226 (1H, s), 1.494 (3H, d, J = 6.6 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm 147.29, 145.20, 137.88, 128.99, 127.32, 126.13, 115.86, 77.74, 53.59, 25.07; IR (KBr) 3412, 3058, 3029, 2978, 2964, 2918, 2863, 1591, 1494, 1315, 1295, 813, 763, 703, 509 cm^{-1}; EI-MS m/z 324 (17), 323 (M^+, 100), 308 (40), 219 (34), 105 (89); $[\alpha]^{26}_D$ = +30.11 (c 1.10, $CHCl_3$); Anal. Calcd for $C_{14}H_{14}NI$: C, 52.03, H, 4.37, N, 4.33, I, 39.27. Found : C, 51.97, H, 4.29, N, 4.23, I, 39.42.



(*S*)-*N*-(1-phenylethyl)-4-iodoaniline

(*S*)-*N*-(1-phenylethyl)-4-iodoaniline

To a suspension of 1,4-diiodobenzene (10.0 g, 30.3 mmol), CuI (577 mg, 3.03 mmol), L-proline (699 mg, 6.08 mmol) and K_2CO_3 (8.36 g, 60.6 mmol) in DMSO (60 mL) was added (*S*)-alpha-methylbenzylamine (5.8 mL, 45.5 mmol). The mixture was allowed to warm 100°C. The mixture was diluted with H_2O (200 mL) and AcOEt (200 mL). After extraction with AcOEt (60 mL ×3), combined organic layer was washed with brine and dried over $MgSO_4$. Chromatographic separation on silica gel (CH_2Cl_2/hexane 1 : 4) to give (*S*)-*N*-(1-phenylethyl)-4-iodoaniline (5.807 g) as a white solid.

mp 71.5-72.5 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm 7.328-7.213 (7H, m), 6.303 (2H, d, *J* = 9.0 Hz), 4.428 (1H, q, *J* = 6.6 Hz), 4.237 (1H, s), 1.493 (3H, d, *J* = 6.6 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm 147.27, 145.19, 137.88, 128.98, 127.32, 126.12, 115.86, 77.74, 53.59, 25.06; IR (KBr) 3412, 3058, 3029, 2977, 2964, 2918, 2862, 1591, 1494, 1315, 1295, 813, 763, 703, 509 cm^{-1}; EI-MS m/z 324 (16), 323 (M^+, 100), 308 (40), 219 (28), 105 (68); $[\alpha]^{26}_D$ = -29.9 (c 1.07, $CHCl_3$); Anal. Calcd for $C_{14}H_{14}NI$: C, 52.03, H, 4.37, N, 4.33, I, 39.27. Found : C, 52.13, H, 4.29, N, 4.27, I, 39.00.