(revised)

Rhodium-Catalyzed Asymmetric Arylation of Imines with Organostannanes. Asymmetric Synthesis of Diarylmethylamines

Supporting Data

Preparation of Imines (1a-e, 2a, 3a, and 9).

A general procedure is shown below: A sulfonamide, an aldehyde (1.1 eq.), and tetraethyl orthosilicate (1.1 eq.) were combined in a flask equipped with a Dean-Stark, and the mixture was heated at 160 °C under nitrogen for 6 h. After cooling to room temperature, the reaction mixture was dissolved in warm ethyl acetate, treated with *n*-hexane, and allowed to stand at room temperature. The crystals were collected by filtration, washed with *n*-hexane, and dried. ***N*-(4-Trifluoromethylphenyl)methylidene-4-nitrobenzenesulfonamide (1a)**: ^{1}H NMR ($CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 8.09 (d, J = 8.3 Hz, 2H), 8.23 (d, J = 8.3 Hz, 2H), 8.41 (d, J = 8.3 Hz, 2H), 9.19 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 123.20 (q, J = 273 Hz), 124.48, 126.33 (q, J = 3.6 Hz), 129.59, 131.74, 134.87, 136.55 (q, J = 33 Hz), 143.57, 150.86, 170.72. Anal. Calcd for $C_{14}H_9O_4N_2SF_3$: C, 46.93; H, 2.53. Found: C, 46.92; H, 2.32. ***N*-(4-Trifluoromethylphenyl)methylidene-4-chlorobenzenesulfonamide (2a)**: ^{1}H NMR ($CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 8.3 Hz, 2H), 8.06 (d, J = 8.3 Hz, 2H), 9.12 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 123.23 (q, J = 272 Hz), 126.14 (q, J = 3.5 Hz), 129.61, 129.63, 131.46, 135.11, 136.04 (q, J = 33 Hz), 136.13, 140.67, 169.24. Anal. Calcd for $C_{14}H_9O_2NSClF_3$: C, 48.36; H, 2.61. Found: C, 48.07; H, 2.41. ***N*-(4-Trifluoromethylphenyl)methylidene-4-methylbenzenesulfonamide (3a)**: ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H), 7.37 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.90 (d, J = 8.3 Hz, 2H), 8.05 (d, J = 8.3 Hz, 2H), 9.08 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.09, 123.36 (q, J = 272 Hz), 126.10 (d, J = 3.6 Hz), 128.30, 129.97, 131.38, 134.54, 135.42, 135.77 (q, J = 33 Hz), 145.11, 168.46. Anal. Calcd for $C_{15}H_{12}O_2NSF_3$: C, 55.04; H, 3.70. Found: C, 54.87; H, 3.90. ***N*-(4-Methoxycarbonylphenyl)methylidene-4-nitrobenzenesulfonamide (1b)**: ^{1}H NMR ($CDCl_3$) δ 3.96 (s,

3H), 8.03 (d, J = 8.3 Hz, 2H), 8.17 (d, J = 8.3 Hz, 2H), 8.23 (d, J = 8.3 Hz, 2H), 8.41 (d, J = 8.3 Hz, 2H), 9.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 52.70, 124.42, 129.53, 130.29, 131.38, 135.33, 136.05, 143.72, 150.80, 165.67, 171.13. Anal. Calcd for $C_{15}H_{12}O_6N_2S$: C, 51.72; H, 3.47. Found: C, 51.75; H, 3.36. ***N*-(4-Fluorophenyl)methylidene-4-nitrobenzenesulfonamide (1c)**: ^{1}H NMR ($CDCl_3$) δ 7.22 (t, J = 8.6 Hz, 2H), 7.99 (dd, J = 8.6, 5.4 Hz, 2H), 8.21 (d, J = 9.1 Hz, 2H), 8.41 (d, J = 9.1 Hz, 2H), 9.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 117.19 (d, J = 22 Hz), 124.36, 128.38, 129.35, 134.29 (d, J = 10 Hz), 144.12, 150.65, 167.36 (d, J = 260 Hz), 170.68. Anal. Calcd for $C_{13}H_9O_4N_2SF$: C, 50.65; H, 2.94. Found: C, 50.68; H, 2.85. ***N*-(4-Chlorophenyl)methylidene-4-nitrobenzenesulfonamide (1d)**: ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J = 8.3 Hz, 2H), 7.90 (d, J = 8.3 Hz, 2H), 8.21 (d, J = 8.3 Hz, 2H), 8.40 (d, J = 8.3 Hz, 2H), 9.09 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 124.40, 129.42, 129.89, 130.38, 132.73, 142.50, 143.99, 150.71, 170.84. Anal. Calcd for $C_{13}H_9O_4N_2SCl$: C, 48.08; H, 2.79. Found: C, 48.19; H, 2.73. ***N*-4-Phenylmethylidene-4-nitrobenzenesulfonamide (1e)**: ^{1}H NMR ($CDCl_3$) δ 7.53 (t, J = 7.6 Hz, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.96 (d, J = 8.1 Hz, 2H), 8.22 (d, J = 8.8 Hz, 2H), 8.40 (d, J = 8.8 Hz, 2H), 9.13 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 124.35, 129.36, 129.39, 131.72, 131.97, 135.82, 144.23, 150.62, 172.39. Anal. Calcd for $C_{13}H_{10}O_4N_2S$: C, 53.79; H, 3.47. Found: C, 53.67; H, 3.66. ***N*-[(*E*)-2-Phenylethenyl]methylidene-4-nitrobenzenesulfonamide (9)**: ^{1}H NMR ($CDCl_3$) δ 7.01 (dd, J = 15.5, 9.3 Hz, 1H), 7.43-7.51 (m, 3H), 7.58-7.62 (m, 3H), 8.17 (d, J = 8.8 Hz, 2H), 8.38 (d, J = 8.8 Hz, 2H), 8.86 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 124.32, 124.35, 128.96, 129.23, 129.33, 132.26, 133.88, 144.47, 155.94, 172.98. Anal. Calcd for $C_{15}H_{12}O_4N_2S$: C, 56.95; H, 3.82. Found: C, 56.69; H, 3.85.

Preparation of (*R*)-2-(Diphenylphosphino)-2'-(3,5-dimethyl-4-methoxyphenyl)-1,1'-binaphthyl (Ar*-MOP).

A mixture of (*R*)-2-(diphenylphosphino)-2'-(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (1.12 g, 1.91 mmol), dichloro[1,3-bis(diphenylphosphino)propane]nickel (0.202 g, 0.38 mmol), and 3,5-dimethyl-4-methoxyphenylmagnesium bromide (1.5 M, 9 mL, in tetrahydorofuran) was refluxed for 24 h under nitrogen. After cooling to room temperature, the reaction mixture was quenched with saturated ammonium chloride (20 mL) on ice bath, and extracted with diethyl ether. The extract was dried over anhydrous $MgSO_4$, and evaporated. The residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1) to give 0.634 g (58% yield) of (*R*)-2-(diphenylphosphino)-2'-(3,5-dimethyl-4-methoxyphenyl)-1,1'-binaphthyl (Ar*-MOP): ^{1}H-NMR ($CDCl_3$) : 1.83 (s, 6H), 3.61 (s, 3H), 6.61 (s, 2H), 6.65 (t, *J* = 6.8 Hz, 2H), 6.83 (d, *J* = 8.3Hz , 1H), 6.90 (t, *J* = 6.8 Hz, 2H), 7.00 (t, *J* = 7.3Hz , 1H), 7.04 (t, *J* = 7.3 Hz , 2H), 7.09 (t, *J* = 6.8 Hz , 2H), 7.12 (t, *J* = 7.8Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.9 Hz, 1H), 7.35 (t, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 3.9 Hz , 1H), 7.45 (d, *J* = 8.8 Hz , 1H), 7.50 (t, *J* = 6.8 Hz , 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H); ^{31}P{^{1}H}NMR δ -19.54 (s). Anal. Calcd for $C_{41}H_{33}PO$: C, 85.99; H, 5.81. Found: C, 85.71; H, 5.91.

Rhodium-Catalyzed Asymmetric Arylation of Imines with Organostannanes.

The results including specific rotation data and methods for the determination of enantiomeric purities are shown in Table 1. A typical procedure is given for the preparation of ***N*-[(4-trifluoromethylphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (5am)** (entry 1, Table 1): Phenyltrimethylstannane (482 mg, 2.00 mmol; **4m**) and 1,4-dioxane (0.6 mL) were added to a pressure bottle charged with lithium fluoride (104 mg, 4.00 mmol), $Rh(acac)(C_2H_4)_2$ (3.1 mg, 12 μmol), (*R*)-MeO-MOP (12.4 mg, 26 μmol), and *N*-(4-trifluoromethylphenyl)methylidene-4-nitrobenzenesulfonamide (143 mg, 0.40 mmol; **1a**). The bottle was sealed under nitrogen. The mixture was stirred at 110 °C for 12 h and concentrated in vacuo. The residue was dissolved in dichloromethane, washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was chromatographed on a silica gel column

(COSMOSIL 75SL-II-PREP, 18 mmϕ x 30 mm, pretreated with methanol and dried) with ethyl acetate as an eluent to give 143 mg (82% yield) of *N*-[(4-trifluoromethylphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (**5am**). ^{1}H NMR ($CDCl_3$) δ 5.59 (d, *J* = 7.8 Hz, 1H), 5.75 (d, *J* = 7.8 Hz, 1H), 7.05-7.06 (m, 2H), 7.21-7.27 (m, 3H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 8.15 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 61.38, 123.73 (q, *J* = 272 Hz), 123.98, 125.69 (q, *J* = 3.6 Hz), 127.31, 127.78, 128.30, 128.53, 129.07, 130.35 (q, *J* = 33 Hz), 138.67, 143.55, 145.94, 149.84. Anal. Calcd for $C_{20}H_{15}O_4N_2SF_3$: C, 55.04; H, 3.46. Found: C, 55.11; H, 3.53. ***N*-[(4-Trifluoromethylphenyl)phenylmethyl]-4-chlorobenzenesulfonamide (6am)**: ^{1}H NMR ($CDCl_3$) δ 5.55 (d, *J* = 7.4 Hz, 1H), 5.65 (d, *J* = 7.4 Hz, 1H), 7.02-7.07 (m, 2H), 7.20-7.31 (m, 7H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 61.14, 123.86 (q, *J* = 272 Hz), 125.55 (q, *J* = 3.6 Hz), 127.29, 127.75, 128.28, 128.52, 128.97, 129.09, 130.05 (q, *J* = 33 Hz), 138.63, 139.24, 139.25, 143.97. Anal. Calcd for $C_{20}H_{15}O_2NSClF_3$: C, 56.41; H, 3.55. Found: C, 56.20; H, 3.72. ***N*-[(4-Trifluoromethylphenyl)phenylmethyl]-4-methylbenzenesulfonamide (7am)**: ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H), 5.02 (d, *J* = 6.9 Hz, 1H), 5.62 (d, *J* = 6.9 Hz, 1H), 7.03-7.06 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.22-7.28 (m, 5H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.34, 61.03, 123.99 (q, *J* = 271 Hz), 124.36 (q, *J* = 3.6 Hz), 127.12, 127.29, 127.79, 127.93, 128.78, 129.39, 129.58 (q, *J* = 32 Hz), 137.11, 136.75, 143.48, 144.44. Anal. Calcd for $C_{21}H_{18}O_2NSF_3$: C, 62.21; H, 4.47. Found: C, 61.92; H, 4.56. ***N*-[(4-Methoxycarbonylphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (5bm)**: ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H), 5.40 (d, *J* = 7.4 Hz, 1H), 5.74 (d, *J* = 7.4 Hz, 1H), 7.04-7.07 (m, 2H), 7.20-7.26 (m, 5H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 52.30, 61.39, 123.90, 127.37, 127.38, 128.23, 128.30, 128.90, 129.71, 129.91, 138.84, 144.55, 146.07, 146.69, 166.49. Anal. Calcd for $C_{21}H_{18}O_6N_2S$: C, 59.15; H, 4.25. Found: C, 59.40; H, 4.39. ***N*-[(4-Fluorophenyl)phenylmethyl]-4-nitrobenzenesulfonamide (5cm)**: ^{1}H NMR ($CDCl_3$) δ 5.49 (d, *J* = 7.3 Hz, 1H), 5.70 (d, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H),

7.03-7.08 (m, 2H), 7.12 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.20-7.24 (m, 3H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 61.04, 115.67 (d, *J* = 22 Hz), 123.90, 127.28, 128.22, 128.29, 128.87, 129.16 (d, *J* = 8.3 Hz), 135.48 (d, *J* = 3.6 Hz), 139.19, 146.15, 149.76, 162.30 (d, *J* = 247 Hz). Anal. Calcd for $C_{19}H_{15}O_4N_2SF$: C, 59.06; H, 3.91. Found: C, 58.78; H, 4.03. ***N*-[(4-Chlorophenyl)phenylmethyl]-4-nitrobenzenesulfonamide (5dm)**: ^{1}H NMR ($CDCl_3$) δ 5.20 (d, *J* = 7.3 Hz, 1H), 5.69 (d, *J* = 7.3 Hz, 1H), 7.03-7.07 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.20-7.25 (m, 5H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 61.08, 123.93, 127.28, 128.28, 128.30, 128.77, 128.89, 128.91, 134.08, 138.15, 138.97, 146.07, 149.76. Anal. Calcd for $C_{19}H_{15}O_4N_2SCl$: C, 56.65; H, 3.75. Found: C, 56.67; H, 3.59. ***N*-[(4-Trifluoromethylphenyl)(4-methoxyphenylmethyl]-4-nitrobenzenesulfonamide (5an)**: ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3H), 5.41 (d, *J* = 7.3Hz, 1H), 5.70 (d, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.34, 60.84, 114.37, 123.33 (q, *J* = 271 Hz), 123.97, 125.63 (q, *J* = 7.3 Hz), 127.69, 128.33, 128.64, 130.26 (q, *J* = 33 Hz), 130.77, 143.81, 146.05, 149.85, 159.66. Anal. Calcd for $C_{21}H_{17}O_5N_2SF_3$: C, 54.08; H, 3.67. Found: C, 54.20; H, 3.81. ***N*-[phenyl(4-Methoxyphenyl)methyl]-4-nitrobenzenesulfonamide (5en)**: ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3H), 5.25 (d, *J* = 7.4 Hz, 1H), 5.68 (d, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 7.07-7.14 (m, 2H), 7.18-7.25 (m, 3H), 7.74 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.31, 61.23, 114.08, 114.85, 116.04, 123.79, 126.41, 127.32, 127.93, 127.97, 128.33, 128.70, 131.58, 146.36, 159.36. Anal. Calcd for $C_{20}H_{18}O_5N_2S$: C, 60.29; H, 4.55. Found: C, 60.21; H, 4.60. ***N*-[(*E*)-2-phenylethenyl)phenylmethyl]-4-nitrobenzenesulfonamide (10)**: ^{1}H NMR ($CDCl_3$) δ 5.18 (s, 1H), 5.25 (t, *J* = 6.9 Hz, 1H), 6.09 (dd, *J* = 15.5, 6.9 Hz, 1H), 6.41 (d, *J* = 15.7 Hz, 2H), 7.16-7.21 (m, 4H), 7.22-7.29 (m, 6H), 7.85 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 60.28, 123.92, 126.46, 127.11, 127.29, 128.33, 128.44,

128.45, 128.68, 128.91, 133.08, 135.46, 138.67, 146.67, 149.67. Anal. Calcd for $C_{21}H_{18}O_4N_2S$: C, 63.94; H, 4.60. Found: C, 63.70; H, 4.65.

Deprotection of Sulfonamides.

A typical procedure is given for the reaction of *N*-[(4-trifluoromethylphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (**5am**) giving **(4-trifluoromethylphenyl)phenylmethylamine (8am)**: A mixture of benzenethiol (40 mg, 0.36 mmol), anhydrous potassium carbonate (124 mg, 0.90 mmol), and *N*-[(4-trifluoromethylphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (131 mg, 0.30 mmol, **5am**) in 0.5 mL of *N,N*-dimethylformamide was stirred at 20 °C for 3 h. The reaction mixture was dissolved in diethyl ether, washed with saturated sodium bicarbonate and water, dried over anhydrous $MgSO_4$, and evaporated. The residue was chromatographed on silica gel (preparative thin-layer, hexane/ethyl acetate = 2/1) to give 60 mg (80% yield) of (4-trifluoromethylphenyl)phenylmethylamine (**8am**): ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 2H), 5.27 (s, 1H), 7.25 (br t, J = 6.9 Hz, 1H), 7.30-7.37 (m, 4H), 7.51 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 59.49, 122.06 (q, J = 270 Hz), 125.42 (q, J = 3.6 Hz), 126.87, 127.24, 127.38, 128.71, 129.20 (q, J = 32 Hz), 144.85, 149.49. Anal. Calcd for $C_{14}H_{12}NF_3$: C, 66.93; H, 4.81. Found: C, 66.81; H, 4.88.

Preparation of *N*-[(4-Trifluoromethylphenyl)phenylmethyl]-4-methylbenzenesulfonamide (7am) from (4-Trifluoromethylphenyl)phenylmethylamine (8am).

A mixture of p-toluenesulfonyl chloride (12 mg, 0.062 mmol), triethylamine (13 mg, 0.12 mmol), 4-dimethylaminopyridine (0.4 mg, 3.1 μmol), and (4-trifluoromethylphenyl)-phenylmethylamine (**8am**) in 1,4-dioxane (0.6 mL) was stirred at 20 °C for 24 h at room temperature. The mixture was evaporated and the residue was chromatographed on silica gel (preparative thin-layer, hexane/ethyl acetate = 5/1) to give 22 mg (87% yield) of *N*-[(4-Trifluoromethylphenyl)phenylmethyl]-4-methylbenzenesulfonamide (**7am**).