Supporting Information

A New Synthesis of Vaulted Biaryl Ligands via the Snieckus Phenol Synthesis

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Experimental procedures and spectral data.

α -Bromomethylstyrene **15**.

The following procedure was adapted from one reported by Reed.¹ A mixture of 94.4 g (0.8 mol) of α -methylstyrene, 90.0 g (0.5 mol) of NBS, and 50 mL of carbon tetrachloride in a 1 L flask fitted with a reflux condenser and magnetic stirrer was heated to 160-170 °C until the mixture was refluxing and the solids dissolved. As the exothermic reaction subsided, the mixture allowed to cooled down slowly over a period of 3 hours. The precipitated succinimide was separated by filtration, and the carbon tetrachloride and excess α -methylstyrene were removed under reduced pressure. The residue was cooled to 0 °C, and then pre-cooled *n*-pentane (100 mL) was added and succinimide that precipitated was removed by filtration. Addition of additional *n*-pentane (3 x 50 mL) caused precipitation of more succinimide which was removed by filtration. The residue was distilled at 0.4 mm pressure and the fraction in the temperature range of 96 °C - 102 °C was collected to give 73.2 g of a colorless liquid (74 % yield). The ^1H NMR spectrum of this fraction revealed that it is composed of an 81 : 19 mixture of α -bromomethyl styrene **15** and α -methyl- β -bromostyrene **16**. The vinyl bromide **16** was obtained as a single isomer but the stereochemistry was not determined. The mixture was used without further purification in the alkylation step. Spectral data for **15** matched that which has been previously reported:¹ ^1H NMR (400 MHz, CDCl_3)

δ = 4.39 (s, 2 H), 5.49 (s, 1 H), 5.57 (s, 1 H), 7.34-7.51 (m, 5 H). Spectral data for **16**: ^1H NMR (400 MHz, CDCl_3) δ 2.23 (s, 3 H), 6.46 (s, 1 H), 7.34-7.51 (m, 5 H).

Preparation of N,N-diisopropyl-1-naphthamide **13a**.

The following is a modification of the procedure reported by Harvey, et. al., for the synthesis of the corresponding diethylamide.² 1-Naphthoic acid (580 mmol, 100 g), thionyl chloride (640 mmol, 46.7 mL) and benzene (120 mL) was added to a 500 mL three-necked round-bottomed flask fitted with an addition funnel. Dimethylformamide (20 mL) was added dropwise from the addition funnel to the mixture which was stirred magnetically.³ Vigorous gas evolution ensued with gradual dissolution of the solid. After 2 hours, benzene and excess thionyl chloride were evaporated under reduced pressure. The residue was distilled under reduced pressure and 1-naphthoyl chloride **19** (150 - 152 °C/0.15mm) was obtained as light yellow oil (106 g) in 96 % yield.

N,N-diisopropyl-1-naphthamide **13a** was prepared by the Schotten-Baumann method. A mixture of 70.1 mL of di-isopropylamine (500 mmol) and 450 mL of 10 % aqueous sodium hydroxide was placed in a 2-liter three-necked flask equipped with a mechanical stirrer. Then 106 g of 1-naphthoyl chloride was gradually poured into the flask with vigorously stirring. After 30 min, the crude N,N-diisopropyl-1-naphthamide separated as a white solid. The product was collected by filtration on a Büchner funnel under reduced pressure and thoroughly washed with water (5 x 100 mL) and then air-dried. The N,N-di-isopropyl-1-naphthamide **13a** was obtained as a white powder (112 g) in 80 % yield after crystallization by dissolution in 500 mL of boiling ethyl acetate and then cooling to -5 °C. This compound had a ^1H NMR spectrum identical to that which has been reported.⁴

Diisopropyl-6-methynaphthamide **13b**.

To a flask containing 6-methylnaphthoic acid **12b**⁵ (4.14 g, 22.24 mmol) under N_2 was added benzene (9.3 mL, 2.4 M) and the resulting slurry stirred for 5 min. Thionyl chloride (1.78 mL, 24.47 mmol) was added followed by the dropwise addition of DMF (0.758 mL, 9.786 mmol).³ The resulting clear red solution was allowed to stir for 4 h, after which time the solution was concentrated on a rotary evaporator, removing any excess SOCl_2 . The benzene/DMF solution was taken on into the next step. This reaction was assumed to have progressed in quantitative yield. Methylene chloride (5 mL) was added to a flask containing the acid chloride under N_2 . This solution was stirred for 5 min before being transferred *via* canula to a flask containing a stirring solution of $(i\text{-Pr})_2\text{NH}$ (3.74 mL, 26.69 mmol) and NEt_3 (3.72 mL, 26.69 mmol) in CH_2Cl_2 (35 mL, 0.5 M) under N_2 . After stirring overnight, H_2O (25 mL) was added to the reaction. The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 $\times$ 50 mL). The combined organic layers were washed with 2 M HCl (aq) (2 $\times$ 50 mL) and sat NaHCO_3 (aq) (2 $\times$ 50 mL) and then dried with Na_2SO_4 . Concentration under reduced pressure and purification of the product by silica gel column chromatography (10% EtOAc:hexane) gave **13b** as a white solid (4.43 g, 74 %). M.p. 140-142 $^\circ\text{C}$; R_f = 0.19 (10% EtOAc:hexane). Spectral data for **13b**: ^1H NMR (300 MHz, CDCl_3) δ 1.01 (d, 3 H, J = 6.5 Hz), 1.05 (d, 3 H, J = 6.5 Hz), 1.63 (d, 3 H, J = 7.0 Hz), 1.69 (d, 3 H, J = 7.0 Hz), 2.48 (s, 3 H), 3.62-3.54 (m, 2 H) 7.21-7.42 (m, 3 H), 7.60 (s, 1 H), 7.69-7.73 (m, 2 H); ^{13}C NMR (300 MHz, CDCl_3) δ 20.6, 20.6, 20.8, 21.6, 45.9, 51.0, 121.2, 124.7, 125.3, 127.1, 127.4, 127.8, 128.9, 133.7, 136.0, 136.4, 170.0, 1 sp^3 C not located; IR (neat) 3053m, 2976m, 1622s, 1332m, 1265s, 710s, 704s cm^{-1} ; mass spectrum m/z (% rel intensity) 269 M^+ (16), 169 (100), 141.0 (43), 115 (11), 88 (17), 84 (16), calcd for m/z 269.1780, meas 269.1777. Anal calcd for $\text{C}_{18}\text{H}_{23}\text{ON}$: C, 80.26; H, 8.61; N, 5.20. Found: C, 80.02; H, 8.73; N, 5.18.

Preparation of o-(2-phenylallyl)-N,N-diisopropyl-1-naphthamide **17a**.

To a stirred THF (50 mL) solution of N,N-diisopropyl-1-naphthamide **13a** (1.02 g, 4 mmol) at -78 °C under argon was added by syringe 3.4 mL of a 1.3 M *s*-BuLi solution (4.4 mmol). Anion formation was allowed to proceed for 30 min at this temperature. Meanwhile, in a separate flask a solution of MgBr₂-etherate (12 mmol) was freshly prepared. 1,2-Dibromoethane (1.03 mL, 12 mmol) was added dropwise to a stirred suspension of magnesium turnings (0.36 g, 15 mmol) in dry diethyl ether (12 mL) at room temperature. The rate of addition was adjusted so as to maintain gentle reflux. The mixture was stirred for an additional one hour at room temperature. This solution of MgBr₂-etherate was transferred by canula to the anion derived from **13a**. The reaction mixture was allowed to warm to room temperature (*ca.* 45 min) and then re-cooled to -78 °C and then stirred for 40 min. α -Bromomethylstyrene (0.87 g 4.4 mmol: 1.074 g of the mixture of an 81 : 19 mixture of isomers) was then added and the solution was allowed to warm to room temperature overnight. The reaction was quenched by the addition of 50 mL of saturated aqueous ammonium chloride. The aqueous phase was extracted with diethyl ether (3 x 50 mL). The combined organic layers were stripped of solvents under reduced pressure. The residue was purified by flash chromatography (hexane : methylene chloride : ethyl acetate = 10 : 1.5 : 1) to give 1.19 g of o-(2-phenylallyl)-N,N-diisopropyl-naphthamide **17a** as a white solid in 80 % yield. Spectral data for **17a**: ¹H NMR (400 MHz, CDCl₃) δ 0.70 (d, 3 H, *J* = 6.8 Hz), 0.78 (d, 3 H, *J* = 6.8 Hz), 1.35 (d, 3 H, *J* = 6.8 Hz), 1.45 (d, 3 H, *J* = 6.8 Hz), 3.26-3.34 (m, 2 H), 3.55 (d, 1 H, *J* = 16.4 Hz), 3.79 (d, 1 H, *J* = 16.8 Hz), 4.73 (s, 1 H), 5.30 (s, 1 H), 6.95-7.07 (m, 4 H), 7.15-7.22 (m, 4 H), 7.39-7.50 (m, 3 H); ¹³C NMR (125 MHz) δ 20.6, 20.7, 21.0, 21.3, 38.2, 46.2, 51.0, 112.4, 115.2, 124.9, 125.7, 126.0, 126.4, 127.3, 127.5, 127.7, 127.9, 128.2, 128.3, 129.8, 132.1, 132.2, 134.9, 140.6, 145.9, 169.3; mass spectrum *m/z* (% rel intensity) 371 M⁺ (6), 271 (49), 270 (34), 257 (10), 242 (14), 207 (100), 164 (19), 128 (18), 96 (15), 91 (23). Anal Calcd for C₂₆H₂₉NO: C, 84.06; H, 7.87; N, 3.77. Found: C, 84.32; H, 7.52; N, 3.98.

Diisopropyl 6-methyl-2-(2-phenylallyl)naphthalen-1-amide **17b**.

A 1.4 M solution of *s*-BuLi (3.8 mL, 4.899 mmol) in hexanes was added dropwise over 1 min to a solution of diisopropyl-6-methylnaphthamide **13b** (1.199 g, 4.454 mmol) in THF (55 mL, 0.08 M) under N₂ at -78 °C. The resulting orange solution was stirred for 1 h at this temperature. Meanwhile, in a separate flask a solution of freshly prepared MgBr₂-etherate was generated. Dibromoethane (1.151 mL, 13.36 mmol) was added over a 1 h period to a flask fitted with a condenser and containing magnesium turnings (0.406 g, 16.7 mmol) and 20 mL ether under N₂. The resulting reaction was stirred for 2 h before being transferred *via* canular to a solution containing the *ortho*-lithiated naphthamide **13b**. The color of the solution changed from orange to pale green and it was then stirred for a further 15 min before being allowed to warm to rt over a 1 h period. After cooling to -78 °C, α -bromomethyl styrene (mixture of **15** and **16** containing 2.43 g, (8.9 mmol) of **15**) was added dropwise and then the mixture was allowed to warm to room temperature overnight. The reaction was quenched with sat NH₄Cl (50 mL), the layers separated and the aqueous Layer extracted with EtOAc (3 $\times$ 50 mL). The combined organic layers were washed with brine (2 $\times$ 25 mL) and dried with Na₂SO₄. Concentration under reduced pressure and purification of the product by silica gel column chromatography (10% EtOAc:hexane) gave **17b** (1.29 g, 75 %) as a pale yellow foam and the recovery of some of the starting material (0.242 g, 19 %). Spectral data for **17b**: R_f = 0.45 (20 % EtOAc:hexane); ¹H NMR (300 MHz, CDCl₃) δ 1.03 (d, 3 H, J = 6.5 Hz), 1.11 (d, 3 H, J = 6.5 Hz), 1.69 (d, 3 H, J = 6.5 Hz), 1.81 (d, 3 H, J = 6.5 Hz), 2.51 (s, 3 H), 3.54-3.72 (m, 2 H), 3.88 (d, 1 H, J = 16.5 Hz), 4.12 (d, 1 H, J = 16.5 Hz), 5.07 (d, 1 H, J = 1.5 Hz), 5.64 (s, 1 H), 7.26-7.75 (m, 10 H); ¹³C NMR (300 MHz, CDCl₃) δ 20.5, 20.6, 21.0, 21.3, 21.5, 38.0, 46.1, 50.9, 115.8, 124.7, 126.0, 126.9, 127.0, 127.3, 127.5, 128.0, 128.3, 128.6, 131.1, 132.3, 134.7, 135.3, 140.6, 145.9, 169.4; IR (CDCl₃) 3055, 2986, 2936, 1622, 1265 cm⁻¹; mass spectrum *m/z* (% rel intensity) 385 M⁺ (10), 285 (25), 269 (30), 249 (30), 226 (15), 169(70), 141 (30), 88 (100), 71 (75), 57 (65), 51 (100), calcd for *m/z* 385.2406, meas 385.2416.

Preparation of 2-phenyl-4-phenanthrol **2a**.

To a stirred THF (50 mL) solution of *o*-(2-phenylallyl)-*N,N*-diisopropyl-naphthamide **17a** (0.9 g, 2.4 mmol) at -78 °C under argon was added 3.4 mL of a 1.4 M solution of MeLi in ether. The solution turned black immediately. The reaction mixture was allowed to warm to room temperature and stirred at room temperature overnight. The reaction was quenched by the addition of 50 mL of saturated aqueous ammonium chloride. The aqueous phase was extracted with diethyl ether (3 x 50 mL). The organic layers were combined and the solvents removed under reduced pressure. The residue was purified by flash chromatography on silica gel with a 4 : 1 mixture of hexane to ether to give 0.59 g of 2-phenyl-4-phenanthrol **2a** as a light brown solid in 90 % yield. The ¹H NMR spectrum of the product matched that which has been previously reported for **2a**.⁶

7-Methyl-phenylphenanthren-4-ol **2b**.

A solution of 1.4 M MeLi (9.893 mL, 13.988 mmol) in hexanes was added dropwise over a 5 min period to a solution of diisopropyl 6-methyl-2-(2-phenylallyl)naphthalen-1-amide **17b** (2.448 g, 6.358 mmol) in THF (120 mL, 0.05 M) at -78 °C. The resulting solution was stirred for 1 h before it was allowed to warm to room temperature overnight. The reaction was quenched with sat aq NH₄Cl (150 mL), the layers separated and the aqueous layer extracted with EtOAc (3 x 150 mL). The combined organic fractions were washed with brine (2 x 75 mL) and dried with Na₂SO₄. Concentration under reduced pressure and purification of the product by silica gel column

chromatography (10% EtOAc:hexane), resulted in isolation of the desired 3-phenyl-8-methylphenanthrol **2b** (1.433 g, 80 %) as a brown solid (hexane). M.p. 146-147 °C, R_f = 0.36 (20% EtOAc:hexane). Spectral data for **2b**: ^1H NMR (300 MHz, CDCl_3) δ 2.55 (s, 3 H), 7.23 (d, 1 H, J = 1.5 Hz), 7.28 (s, 1 H), 7.42 (d, 1 H, J = 7.5 Hz), 7.51 (t, 3 H, J = 7.5 Hz), 7.73 (t, 6 H, J = 10 Hz), 9.53 (d, 1 H, J = 8.5 Hz); ^{13}C NMR (300 MHz, CDCl_3) δ 21.3, 112.0, 118.6, 119.7, 127.1, 127.2, 127.4, 127.8, 128.1, 128.2, 128.3, 128.8, 132.7, 134.9, 135.6, 138.7, 140.2, 154.4, 1 sp^2 C not located; IR (CDCl_3) 3566w, 3055w, 2988w, 1205s, 710s, 706s cm^{-1} ; mass spectrum m/z (% rel intensity) 284 M^+ (100), 241 (10), 184 (50), 141 (60), 115 (20), 57 (30), calcd for m/z 284.1201, meas 284.1197.

7,7'-Dimethyl-2,2'-diphenyl-(3,3'-biphenanthrene)-4,4'-diol **18**.

A 250 mL Erlenmeyer flask containing 3-phenyl-8-methylphenanthrol **2b** (0.50 g) was heated in an oil bath at 185 °C for 10 h. The dark solid that was formed was dissolved in EtOAc and the polymer was filtered through Celite. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel (10 % EtOAc/Hexanes) to give **18** (0.33g, 67 %) as a white solid. M.p. > 250, R_f = 0.32 (10 % EtOAc / Hexanes). Spectral data for **18**: ^1H NMR (300 MHz, CDCl_3) δ 2.58 (s, 6 H), 6.57 (s, 2 H), 6.68 (d, 4 H, J = 7.5 Hz), 6.95 (t, 4 H, J = 7.2 Hz), 7.06 (t, 2 H, 7.2 Hz), 7.41 (s, 2 H), 7.52 (d, 2 H, 3.00 Hz), 7.63-7.77 (m, 6 H), 9.63 (d, 2 H, J = 8.5 Hz); ^{13}C NMR (300 MHz, CDCl_3) δ 21.3, 115.7, 118.1, 123.1, 126.7, 127.0, 127.5, 128.03, 128.08, 128.68, 128.70, 128.8, 128.9, 133.0, 134.9, 136.1, 139.8, 141.1, 153.2; IR (neat) 3484w, 3026w, 2916w; mass spectrum m/z (% rel intensity) 566 M^+ (100), 384 (13), 283 (83), 244 (28), 154 (18), 105 (12), calcd for m/z 566.2246, meas 566.2245.

S-7,7'-Dimethyl-2,2'-diphenyl-(3,3'-biphenanthrene)-4,4'-diol **18.**

To a 50 mL round-bottomed flask was added 12 mL of MeOH, 64.7 g of CuCl (0.65 mmol) and 0.30 g of (-)-sparteine (1.30 mmol). The flask was sonicated in an ultrasonic bath with air sparged into the solution. The temperature was maintained at or below 25 °C by the addition of ice to the water in the bath. The flask was sealed with a septum after 45 minutes and then purged with argon for 60 minutes in the ultrasonic bath. The green Cu(II)-sparteine solution was transferred via cannula to a solution of racemic 7,7'-dimethyl VAPOL **18** (0.22 g, 0.38 mmol) in 50 mL of CH₂Cl₂ in a 250 mL round-bottomed flask which was had previously been purged with argon and sonicated for 60 minutes. The combined solution was sonicated for 10 minutes and then the flask was removed from ultrasonic bath, covered with aluminum foil and stirred at room temperature for 6 hours under a positive pressure of argon maintained by a slow flow through the head space of the flask. The reaction was quenched by adding 5 mL of concentrated HCl and then stirring for 10 minutes. The two layers were separated. The lower CH₂Cl₂ layer was collected and the upper MeOH/H₂O layer was washed with 3 × 30 mL of CH₂Cl₂. The combined CH₂Cl₂ layers were dried over MgSO₄. Upon removal of solvent, the crude reaction mixture was loaded onto a silica gel column and eluted with a 1:1 mixture of CH₂Cl₂ / hexane to give 0.17 g (0.30 mmol, 79 % yield) S-**18** as a white solid. The optical purity of S-**18** was found to be of ≥ 99 % by HPLC on a Pirkle D-Phenylglycine column with a 75:25 mixture of hexane/isopropanol (260 nm, flow rate: 2 mL/min). Under these conditions the retention time of R-**18** was 14.8 min and that of S-**18** was 19.8 min. $[\alpha]_D^{20} = +155.6$ (c=1, EtOAc).

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