Revised

Supporting Information

Asymmetric Carbon-Carbon Coupling of Phenols or Anilines with Aryllead Triacetates

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General. Infrared (IR) spectra were recorded on a Shimazu FTIR-8100 spectrometer. ^{1}H-NMR spectra were measured on a Varian Gemini-300 (300 MHz) at ambient temperature. Data are recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, and m = multiplet), coupling constant (Hz), integration, and assignment. ^{13}C-NMR spectra were recorded on Varian Gemini-300 (75 MHz) spectrometer at ambient temperature. Chemical shifts are recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.07 ppm). Chiral high-performance liquid chromatography (chiral HPLC) analyses were conducted using a Shimazu LC-10AD coupled with a diode array–detector SPD-MA10A-VP and a chiral column of CHIRALCEL OD-H (Daicel Chemical Industries, LTD.). All experiments were carried out under an atmosphere of dry argon. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (E. Merck Art. 9385). Microanalysis was performed at the Faculty of Agriculture, Nagoya University. High-resolution mass spectra analyses were recorded at the Faculty of Technology, Nagoya University.

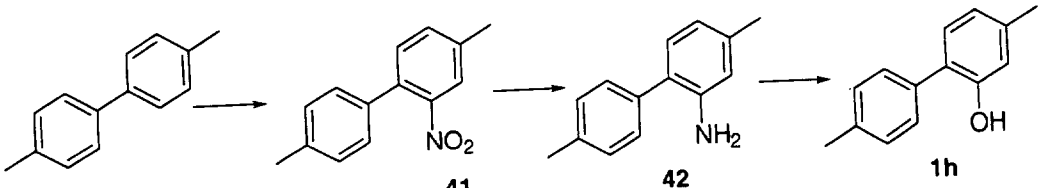
In experiments that required dry solvent, toluene and CH_2Cl_2 were freshly distilled from calcium hydride, and tetrahydrofuran (THF) and hexane were freshly distilled from sodium metal using benzophenone ketyl as an indicator. Organic substrates, phenols **1a**, **1e**, **1f**, and **1i**, and amines **5–9**, **12**, sparteine, dehydroabietylamine, eburnamonine, ajmalicine, $(DHQD)_2PHAL$, strychnine, and brucine, **16a** and **16e-h**, were all obtained commercially, and used without further purification. DABCO and quinuclidine were

purified by recrystallization from hexane before use. Lead compound **2d**,[1] **2f**,[1] **2h**,[1] and **2i**,[2] and amines **10**,[3] and **11**,[4] and phenol **1g**[5] were all known compounds and prepared as described in the literature. Phenols (*R*)- and (*S*)-**3a-b**,[6] *meso*-**3a-b**,[6] **3l**,[7] **3m**,[8] and **3n**[9] are all known compounds. Lead compounds[10] **2a-i** and dimetal anilides **16b**,[11] **16c**,[12] and **16d**[11] were prepared as described in the literature and by treatment of **16a** with BuLi (hexane solution, 0 °C, 0.5h), *t*-BuMgCl (THF solution, 0 °C, 1h), MeMgCl (THF solution, r.t., 1h), MeMgBr (ether solution, r.t., 1h), MeMgI (ether solution, r.t., 1h), or MeZnCl (THF solution, 70 °C, 1h). Aniline **32**[13] is a known compound.

3,5-Dimethyl-2-phenylphenol (**1g**). IR (KBr) 3495, 1624, 1474, 1304, 1188 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.42-7.37 (m, 1H), 7.29-7.24 (m, 2H), 6.69 (s, 1H), 6.68 (s, 1H), 4.70 (s, 1H, OH), 2.32 (s, 3H, CH_3), 2.04 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 138.5, 136.9, 135.3, 130.4, 129.3, 128.0, 125.2, 122.8, 113.2. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81, H, 7.12; Found: C, 84.82, H, 7.26.

3-Methyl-6-(4-methylphenyl)phenol (**1h**). IR (KBr) 3497, 1615, 1503, 1399, 1285, 1119 cm-1; 1H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.12 (d, 1H, J = 7.8 Hz), 6.813 (s, 1H), 6.806 (d, 2H, J = 7.8 Hz), 5.16 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 139.0, 137.3, 134.0, 129.91, 129.85, 128.9, 125.2, 121.6, 116.2, 21.1 (two peaks overlap). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81, H, 7.12; Found: C, 84.72, H, 7.18. This phenol **1h** was prepared from commercially available 4,4'-dimethylbiphenyl (**40**) as described in the literature [regarding the following procedures (1) and (2)]:[14] (1) Regioselective mono-nitration at the 2-position of **40** to give 2-nitro-4,4'-dimethylbiphenyl (**41**); (2) Reduction of the obtained mono-nitro compound **41** to 2-amino-4,4'-dimethylbiphenyl (**42**); (3) Sandmyer reaction of **42** to give the corresponding 4-diazo compound, followed by hydration with H_2O: To an aqueous H_2SO_4 (5.4 mL of H_2SO_4 in 15.0 mL of H_2O) solution of the amine (5.94 g, 30 mmol) was added an aqueous solution of $NaNO_2$ (2.50 g, 36 mmol in 100 mL of H_2O) dropwise at 0 °C, followed by sequential treatment with urea (300 mg) and iced H_2O (ca. 30 g of ice + 30 mL of H_2O). This mixture was slowly warmed to 50 °C over 1h, stirred for 1h, and extracted with diethyl ether. The organic layer was dried over Na_2SO_4. Evaporation of solvents and

purification by column chromatography on silica gel gave the desirable phenol **1h** (14.78 mmol, 49%) as a colorless solid.



40 **41** **42** **1h**

General Procedure for the preparation of Aryllead Triacetate.[1] The arylboronic acid (10.0 mmol) was added over 15 min to a stirred mixture of lead tetraacetate (4.43 g, 10.0 mmol) and mercury(II) acetate (0.5 mmol) in chloroform (15.2 mL) at 40 °C. The mixture was stirred at 40°C for 1h and then at room temperature overnight. The reaction mixture was filtered through Celite, which was then washed with chloroform (2 × 30 mL). The chloroform filtrate was washed with water (40 ml), and the aqueous layer was then extracted with chloroform (2 × 80 mL). The combined chloroform solutions were filtered through Celite and then concentrated to a volume of 100 ml at 40 °C. Light petroleum (600 mL) was added and the mixture was kept at 0 °C overnight. Crystals of the aryllead triacetate were deposited and collected at the pump.

2-Isopropylphenyllead triacetate (**2a**). mp 124-127°C; IR (KBr) 2967, 1572, 1374, 995 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, 1H, J = 8.4 Hz, ^{207}Pb satellites gave $J_{2\text{-Pb}}$ = 405 Hz), 7.89-7.09 (m, 3H), 3.03 (m, 1H), 2.10 (s, 9H, 3 x $C{=}OCH_3$), 1.34 (d, 6H, J = 6.6 Hz, 2 x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.3, 162.9, 150.7, 132.1, 130.5, 129.4, 128.8, 37.0, 24.3, 20.4. Anal. Calcd for $C_{15}H_{20}O_6Pb$: C, 35.78, H, 4.00; Found: C, 35.78, H, 4.10.

2-Methylphenyllead triacetate (**2b**). mp 118-121 °C; IR (KBr) 3048, 1572, 1374, 994 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, 1H, J = 7.8 Hz, ^{207}Pb satellites gave $J_{2\text{-Pb}}$ = 405 Hz), 7.76-6.98 (m, 3H), 2.61 (s, 3H, $C{=}CCH_3$ ^{207}Pb satellites gave $J_{\text{Me-Pb}}$ = 33.3 Hz), 2.11 (s, 9H, 3 x $C{=}OCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.5, 163.2, 140.2, 132.8, 131.9, 130.8, 128.5, 21.9, 20.6. Anal. Calcd for $C_{13}H_{16}O_6Pb$: C, 32.84, H, 3.39; Found: C, 32.80, H, 3.44.

2-Phenylphenyllead triacetate (**2c**). mp 145-147 °C; IR (KBr) 3048, 1561, 1374, 994 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, 1H, J = 8.1 Hz, ^{207}Pb satellites gave $J_{2\text{-Pb}}$ = 403

Hz), 7.90-7.17 (m, 8H), 1.93 (s, 9H, 3 x O=CCH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 179.8, 164.9, 144.9 ,140.4, 131.7, 131.4, 130.0, 129.4, 128.8, 128.7, 128.6, 20.1. Anal. Calcd for $C_{18}H_{18}O_6Pb$: C, 40.22, H, 3.38; Found: C, 40.23, H, 3.32.

2-Methylnaphthyllead triacetate (**2e**). mp 138-141 °C; IR (KBr) 2977, 1759, 1547, 1427, 1264 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.35 (dd, 1H, J = 8.7, 4.5), 8.05-7.04 (m, 5H), 2.85 (s, 3H, ^{207}Pb satellites gave $J_{Me\text{-}Pb}$ = 21.3 Hz), 2.09 (s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 180.4, 164.2, 139.7, 134.5, 134.1, 131.9, 130.1, 128.5, 128.4, 126.4, 124.5, 22.5, 20.5. Anal. Calcd for $C_{17}H_{18}O_6Pb$: C, 38.85, H, 3.45; Found: C, 38.89, H, 3.43.

2-Methoxynaphthyllead triacetate (**2g**). mp 121-124 °C; IR (film) 3750, 1559, 1507, 1399, 1343, 1262 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.36 (d, 1H, J = 8.4), 8.00 (d, 1H, J = 8.4, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 18.6 Hz), 7.85 (dd, 1H, J = 8.4, 0.6, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 43.5 Hz), 7.65 (td, 1H, J = 7.2, 1.5), 7.45 (td, 1H, J = 8.1, 1.2), 7.34 (d, 1H, J = 8.7, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 105.0 Hz), 4.04 (s, 3H), 2.11 (s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 180.0, 156.0, 147.5, 134.5, 134.3, 131.5, 128.9, 128.4, 125.0, 124.4, 113.0, 57.3, 20.2. HRMS (FAB+) *m/z*: Calcd for $C_{17}H_{18}O_7Pb$-CH_3CO_2: 483.0686; Found: 483.0733.

2-Isopropylphenyllead tribenzoate (**13**). IR (film) 2967, 1597, 1543, 1451, 1370, 1177 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.12 (d, 6H, J = 7.2 Hz), 8.00-7.96 (m, 1H), 7.62-7.38 (m, 12H), 3.35-3.26 (m, 1H), 1.32 (d, 6H, J = 6.6 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 175.0, 163.5, 150.9, 133.4, 132.1, 131.0, 130.8, 130.1, 129.5, 128.9, 128.2, 37.2, 24.5. HRMS (FAB+) *m/z*: Calcd for $C_{30}H_{26}O_6Pb$-$C_6H_5CO_2$: 569.1206; Found: 569.1238. Aryllead **13** was prepared according to the procedure described above, except that lead tetrabenzoate[15] was used instead of lead tetraacetate.

General Procedure for the Asymmetric Coupling of Phenols with Arylleads. *dl*-3,5-Dimethyl-2,6-bis(2-isopropylphenyl)phenol (*dl*-**3a**). To a solution of phenol **1a** (6.10 g, 50.0 mmol) in toluene (650 mL) was added a 1.59 M hexane solution of *n*-BuLi (31.4 mL) at 0 °C under argon, and the mixture was stirred for 15 min. After the mixture was cooled to -78 °C, brucine [39.4 g, 100 mmol; *Caution!* EXTREMELY POISONOUS (oral LD_{50} in rats = 1 mg kg^{-1}) Handle in well-ventilated hood only], aryllead **2a** (50.4 g, 100 mmol; *Caution!* Poisonous. Handle in well-ventilated hood only) and molecular sieves 4A powder

(150 g) were added sequentially. The mixture was stirred at -20 °C for 21h, and filtered through a celite pad. The obtained cake was washed with CH_2Cl_2, and the filtrate was concentrated. The residue was purified by column chromatography, where non-polar products came off the column initially (diethyl ether/hexane = 1/10 to 1/1 as the eluent) to give **3a** (15.6 g, 88%), **4a** (0.84 g, 7%), and **1a** (0.31 g, 5%), whereas brucine remained at almost the starting point of the column. The next eluent (Et_3N/MeOH = 1/10) allowed >90% recovery of brucine, which can be reused after being washed with 10% NH_4OH and then diethyl ether, and dried (100 °C for 12h at 3 mmHg). **3a**: mp 148-149 °C (**3a**, >99% ee)

2-(2-Isopropylphenyl)-3,5-dimethylphenol (**4a**). IR (KBr) 3495, 2963, 1624, 1570, 1302, 1183 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.38 (m, 2H), 7.31-7.25 (m, 1H), 7.10 (d, 1H, *J* = 7.8 Hz), 6.68 (d, 2H, J = 4.8 Hz), 4.46 (s, 1H, OH), 2.68 (m, 1H), 2.33 (s, 3_H, CH3), 1.95 (s, 3^H, CH3), 1.12 (d, 3H, J = 6.9 Hz, CHCH3), 1.11 (d, 3H, J = 6.9 Hz, CHCH3); 13C NMR (75 MHz, CDCl3) δ 152.7, 148.9, 138.3, 137.1, 132.9, 130.9, 129.0, 126.6, 126.3, 124.3, 122.7, 112.9, 30.0, 24.4, 23.6, 21.3, 20.2. Anal. Calcd for $C_{17}H_{20}O$: C, 84.96, H, 8.39; Found: C, 84.97, H, 8.44. HPLC analysis (column: OD-H): retention times of two enantiomers of **4a**: t_R = 11.4 (major) and 15.6 (minor) min using *i*-PrOH/hexane (1/400) as the eluent at a flow rate of 1.0 mL/min.

dl-3,5-Dimethyl-2,6-bis(2-phenylphenyl)phenol (*dl*-**3c**). mp 44 -45°C (**3c**, >99% ee); IR (KBr) 3544, 1448, 1291, 1225, 1150, 1051 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49-7.36 (m, 6H), 7.21 (s, 10H), 7.04-7.01 (m, 2H), 6.39 (s, 1H, MeC=CH-CMe), 4.58 (s, 1H, OH), 1.76 (s, 6H, 2 x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 142.4, 141.2, 135.7, 134.8, 131.3, 130.3, 128.8, 128.1, 127.6 (two peaks overlap), 126.7, 124.9, 123.0, 20.0. Anal. Calcd for $C_{32}H_{26}O$: C, 90.11, H, 6.14; Found: C, 90.09, H, 6.39. HPLC analysis (column: OD-H): retention times of two enantiomers of *dl*-**3c**: t_R = 20.5 (major) and 25.3 (minor) min using *i*-PrOH/hexane (1/200) as the eluent at a flow rate of 1.0 mL/min.

3,5-Dimethyl-2-(2-phenylphenyl)phenol (**4b**) (Table 5, entry 3). IR (KBr) 3438, 1622, 1570, 1302, 1188 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.41 (m, 3H), 7.29-7.24 (m, 1H), 7.13-7.22 (m, 5H), 6.56 (s, 1H), 6.49 (s, 1H), 4.68 (s, 1H, OH), 2.24 (s, 3H, CH_3), 1.79 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 142.8, 140.6, 138.4, 136.8, 133.4, 131.5,

130.9, 128.7, 128.6, 128.1, 127.8, 126.9, 124.6, 122.7, 112.9, 21.2, 20.1. Anal. Calcd for $C_{20}H_{18}O$: C, 87.56, H, 6.61; Found: C, 87.55, H, 6.62. HPLC analysis (column: OD-H): retention times of two enantiomers of **4b**: t_R = 10.0 (major) and 12.4 (minor) min using *i*-PrOH/hexane (1/40) as the eluent at a flow rate of 1.0 mL/min.

dl- and *meso*-3,5-Dimethyl-2,6-bis(1-naphthyl)phenol (*dl*- and *meso*-**3d**). IR (KBr) 3546, 1509, 1389, 1289, 1238, 1055 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91-7.87 (m, 4H), 7.68-7.42 (m, 10H), 6.96 (*dl*) (s, 1H, MeC=CH-CMe), 6.98 (*meso*) (s, 1H, MeC=CH-CMe), 4.49 (*dl*) (s, 1H, OH), 4.50 (*meso*) (s, 1H, OH), 2.02 (*dl*) (s, 6H, CH_3), 2.03 (*meso*) (s, 6H, 2 x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) for *dl*-isomer: δ 151.0, 137.5, 134.1, 133.9, 132.3, 128.4, 128.2, 128.0, 126.4,126.0 (two peaks overlap), 125.7 (two peaks overlap), 125.6, 123.7, 123.3, 20.1. for *meso*-isomer: δ 151.0, 137.7, 134.0, 133.9, 132.3, 128.4, 128.3, 128.2, 126.4, 126.0 (two peaks overlap), 125.7 (two peaks overlap), 125.4, 123.6, 123.4, 20.1. Anal. Calcd for $C_{28}H_{22}O$: C, 89.81, H, 5.92; Found: C, 89.80, H, 6.03. HPLC analysis (column: OD-H): retention times of two enantiomers of *dl*-**3d**: t_R = 5.0 (minor) and 10.6 (major) min; *meso*-**3d**: t_R = 5.40 using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 1.0 mL/min.

3,4,5-Trimethyl-2,6-bis(2-phenylphenyl)phenol (**3e**). mp 44-45 °C (**3e**, >99% ee); IR (KBr) 3649, 1418, 1287, 1227, 1042 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.35 (m, 6H), 7.20 (s, 10H), 7.02-6.99 (m, 2H), 4.41 (s, 1H, OH), 1.90 (s, 3H, CH_3), 1.72 (s, 6H, 2 x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 142.6, 141.4, 135.8, 133.9, 131.4, 130.2, 128.8, 127.9, 127.6 (two peaks overlap), 126.5, 126.4, 125.0, 17.6, 15.8. Anal. Calcd for $C_{33}H_{28}O$: C, 89.96, H, 6.41; Found: C, 89.95, H, 6.69. HPLC analysis (column: OD-H): retention times of two enantiomers of *dl*-**3e**: t_R = 6.3 (minor) and 6.8 (major) min using *i*-PrOH/hexane (1/20) as the eluent at a flow rate of 1.0 mL/min.

3,4,5-Trimethyl-2-(2-phenylphenyl)phenol (**4c**) (Table 5, entry 5). IR (KBr) 3511, 1466, 1293, 1181, 1038 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53-7.43 (m, 3H), 7.27-7.24 (m, 1H), 7.20-7.12 (m, 5H), 6.58 (s, 1H), 4.52 (s, 1H, OH), 2.21 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.75 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 142.9, 140.7, 136.7, 134.9, 134.3, 131.7, 130.8, 128.6, 128.5, 128.0, 127.8, 126.8, 126.7, 125.2, 113.7, 20.8, 17.6, 15.2. Anal. Calcd for $C_{21}H_{20}O$: C, 87.46, H, 6.99; Found: C, 87.23, H,7.21. HPLC analysis

(column: OD-H): retention times of two enantiomers of **4c**: t_R = 41.7 (major) and 66.1 (minor) min using *i*-PrOH/hexane (1/400) as the eluent at a flow rate of 1.0 mL/min.

2,6-Bis(2-isopropylphenyl)-3,5-dimethoxyphenol (**3f**). IR (KBr) 3532, 2961, 1624, 1337, 1206, 1109 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44-7.14 (m, 8H), 6.26 (s, 1H, MeOC=CH-COMe), 4.60 (s, 1H, OH), 3.77 (s, 6H, 2 x OCH_3), 2.84 (m, 2H), 1.19 (d, 6H, J = 6.9 Hz, $CH(CH_3)_2$), 1.12 (d, 6H, J = 6.9 Hz, $CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 151.8, 149.1, 131.5, 131.3, 128.4, 125.9, 125.6, 109.3, 87.4, 55.5, 30.4, 24.1, 23.7. Anal. Calcd for $C_{26}H_{30}O_3$: C, 79.97, H, 7.74; Found: C, 79.98, H, 7.87. HPLC analysis (column: OD-H): retention times of two enantiomers of *dl*-**3f**: t_R = 9.9 (minor) and 11.3 (major) min using *i*-PrOH/hexane (1/400) as the eluent at a flow rate of 1.0 mL/min.

3,5-Dimethoxy-2,6-bis(2-phenylphenyl)phenol (**3g**). IR (KBr) 3534, 1619, 1462, 1337, 1204, 1105 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) common peaks for *dl*- and *meso*-isomer: δ 7.46-7.32 (m, 6H), 7.24-7.03 (m, 12H), 5.77 (s, 1H), for *dl*-isomer: 4.77 (s, 1H, OH), 3.36 (s, 6H, 2 x OCH_3), for *meso*-isomer: 4.98 (s, 1H, OH), 3.31 (s, 6H, 2 x OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) for *dl*-isomer: δ 157.0, 151.1, 143.1, 141.7, 131.6, 129.9, 128.5, 127.9, 124.4, 127.3, 126.3, 109.6, 87.6, 55.2. for *meso*-isomer: δ 157.0, 151.0, 143.2, 141.8, 131.9, 131.4, 130.2, 128.5, 128.0, 127.4 (two peaks may overlap), 126.3, 109.6, 87.6, 55.1. Anal. Calcd for $C_{32}H_{26}O_3$: C, 83.82, H, 5.71; Found: C, 83.85, H, 5.75. HPLC analysis (column: OD-H): retention times of two enantiomers of *dl*-**3g**: t_R = 21.1 (major) and 28.4 (minor) min; *meso*-**3g**: t_R = 32.0 using *i*-PrOH/hexane (1/100) as the eluent at a flow rate of 1.0 mL/min.

3,5-Dimethoxy-2-(2-phenylphenyl)phenol (**4d**) (Table 5, entry 7). IR (KBr) 3534 ,1622, 1586, 1208, 1152, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52-7.41 (m, 3H), 7.37-7.31 (m, 1H), 7.24-7.13 (m, 5H), 6.09 (d, 1H, J = 2.4 Hz), 5.93 (d, 1H, J = 2.1 Hz), 4.93 (s, 1H, OH), 3.74 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 157.9, 154.1, 143.6, 141.1, 131.9, 130.6, 130.5, 128.6, 128.4, 128.0, 127.6, 126.7, 109.5, 92.3, 91.3, 55.3, 55.2. Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41, H, 5.92; Found: C, 78.41, H, 6.04. HPLC analysis (column: OD-H): retention times of two enantiomers of **4d**: t_R = 7.4 (major) and 8.3 (minor) min; using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 1.0 mL/min.

6-(2-Isopropylphenyl)-3,5-dimethyl-2-phenylphenol (**3h**). IR (KBr) 3544, 2961, 1458,

1401, 1291, 1051 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.24 (m, 8H), 7.15-7.12 (m, 1H), 6.82 (s, 1H, MeC=CH-CMe), 4.55 (s, 1H, OH), 2.76 (m, 1H), 2.13 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.16 (d, 3H, J = 6.9 HZ, CHCH_3), 1.13 (d, 3H, J = 6.9 Hz, CHCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 148.3, 136.6, 136.3, 136.0, 134.1, 130.5, 130.3, 128.7, 128.5, 127.3, 126.3, 125.9, 125.6, 125.1, 123.2, 30.2, 24.3, 23.7, 20.4, 20.1. Anal. Calcd for $C_{23}H_{24}O$: C, 87.30, H, 7.64; Found: C, 87.31, H, 7.92. HPLC analysis (column: OD-H): retention times of two enantiomers of **3h**: t_R = 9.0 (minor) and 10.6 (major) min using *i*-PrOH/hexane (1/400) as the eluent at a flow rate of 1.0 mL/min.

2-(2-Isopropylphenyl)-3-methyl-6-(4-methylphenyl)phenol (**3i**). IR (KBr) 3530, 2963, 1458, 1395, 1242, 1117 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49-7.40 (m, 4H), 7.33-7.15 (m, 5H), 6.92 (d, 1H, J = 7.8 Hz), 4.80 (s, 1H, OH), 2.73 (m, 1H), 2.38 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.15 (d, 3H, J = 6.9 Hz, CHCH_3), 1.14 (d, 3H, J = 6.9 Hz, CHCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 148.5, 136.74, 136.67, 135.2, 133.4, 130.5, 129.19, 129.16, 129.1, 128.9, 127.8, 126.6, 126.3, 125.4, 121.8, 30.1, 24.4, 23.7, 21.2, 20.3. Anal. Calcd for $C_{23}H_{24}O$: C, 87.30, H, 7.64; Found: C, 87.22, H, 7.94. HPLC analysis (column: OD-H): retention times of two enantiomers of **3i**: t_R = 12.2 (minor) and 21.6 (major) min using *i*-PrOH/hexane (1/400) as the eluent at a flow rate of 1.0 mL/min.

3-Methyl-2-(2-methylphenyl)-6-(4-methylphenyl)phenol (**3j**). IR (KBr) 3528, 1541, 1509, 1397, 1246 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, 2H, J = 8.1 Hz), 7.37-7.18 (m, 7H), 6.92 (d, 1H, J = 8.1 Hz), 4.82 (s, 1H, OH), 2.38 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.00 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 137.6, 136.7, 136.4, 135.0, 134.9, 130.6, 130.3, 129.2 (two peaks overlap), 129.0, 128.4, 127.8, 126.6, 125.4, 121.9, 21.2, 19.9, 19.5. Anal. Calcd for $C_{21}H_{20}O$: C, 87.46, H, 6.99; Found: C, 87.46, H, 7.12. HPLC analysis (column: OD-H): retention times of two enantiomers of **3j**: t_R = 15.6 (minor) and 25.8 (major) min using *i*-PrOH/hexane (1/400) as the eluent at a flow rate of 1.0 mL/min.

1-(2-Isopropylphenyl)-2-naphthol (**3k**). IR (KBr) 3490, 2961, 1619, 1462, 1389, 1181 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85-7.79 (m, 2H), 7.58-7.48 (m, 2H), 7.39-7.16 (m, 6H), 4.89 (s, 1H, OH), 2.61 (m, 1H), 1.11 (d, 3H, J = 6.9 Hz, CHCH_3), 1.02 (d, 3H, J = 6.9 Hz, CHCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 149.8, 133.6, 131.6 (two peaks overlap), 129.4, 129.3, 128.8, 128.0, 126.8, 126.6., 126.4, 124.7, 123.3, 120.1, 117.2, 30.2, 24.3, 23.9.

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99, H, 6.92; Found: C, 86.98, H, 7.06. HPLC analysis (column: OD-H): retention times of two enantiomers of **3k**: t_R = 15.7 (major) and 18.3 (minor) min using *i*-PrOH/hexane (1/400) as the eluent at a flow rate of 1.0 mL/min.

1-(2-Phenylphenyl)-2-naphthol (**3l**). IR (KBr) 3507, 1620, 1540, 1389, 1181 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73-7.66 (m, 2H), 7.62-7.48 (m, 3H), 7.40-7.22 (m, 4H), 7.10-6.99 (m, 6H), 4.97 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 143.4, 140.2, 133.5, 132.7, 132.2, 131.0, 129.5, 129.2, 128.7, 128.4, 128.3, 128.0, 127.8, 127.1, 126.4, 124.7, 123.2, 120.4, 117.1. Anal. Calcd for $C_{22}H_{16}O$: C, 89.16, H, 5.44; Found: C, 89.13, H, 5.48. HPLC analysis (column: doubly-arrayed OD-H): retention times of two enantiomers of **3l**: t_R (*S*-**3l**: minor isomer) = 39.8 and t_R (*R*-**3l**: major isomer) = 41.5 min using *i*-PrOH/hexane (1/20) as the eluent at a flow rate of 0.5 mL/min.

2-Hydroxy-1,1'-binaphthyl (**3m**). HPLC analysis (column: OD-H): retention times of two enantiomers of **3m**: t_R (*S*-**3m**: minor isomer) = 9.3 and t_R (*R*-**3m**: major isomer) = 15.5 min using *i*-PrOH/hexane (1/20) as the eluent at a flow rate of 1.0 mL/min.

2-Hydroxy-2'-methoxy-1,1'-binaphthyl (**3n**). HPLC analysis (column: triply-arrayed OD-H): retention times of two enantiomers of **3n**: t_R (*S*-**3n**: minor isomer) = 59.8 and t_R (*R*-**3n**: major isomer) = 62.3 min using *i*-PrOH/hexane (1/20) as the eluent at a flow rate of 0.5 mL/min.

10-Benzyloxy-11-methoxystrychnine (**14**). To a suspension of 10-hydroxy-11-methoxystrychnine[16] (1.6 g, 4.2 mmol) in DMSO (160 ml) at 80 °C was added NaH (110 mg, 4.6 mmol) under Ar. After 30 min, benzyl bromide (547 µl, 4.6 mmol) was added, and the mixture was then stirred at 80 °C for 1 h. To the whole mixture was added CH_2Cl_2 (500 ml) and then washed with water (100 ml). The organic layer was dried over Na_2SO_4 and filtered, and the solvents were removed via rotary evaporation. The product was purified by flash chromatography (methanol/Et_3N = 10/1 as the eluent) to give 395 mg (20%) of **14**. IR (film) 2861, 2361, 1665, 1497, 1451, 1401, 1283 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.42-7.28 (m, 5H), 6.64 (s, 1H), 5.89 (bs, 1H), 5.10 (s, 2H), 4.30-7.25 (m, 1H), 4.25-4.01 (m, 2H), 3.91 (s, 3H), 3.80 (d, 1H, J = 10.2 Hz), 3.74 (bs, 1H), 3.68 (d, 1H, J = 14.4 Hz), 3.19-3.06 (m, 3H), 2.86-2.77 (m, 1H), 2.71 (d, 1H, J = 15.0 Hz), 2.64 (dd, 1H, J = 17.7, 3.3 Hz), 2.31 (dt, 1H, J = 14.4, 4.2 Hz), 1.82-1.74 (m, 2H), 1.39 (d,

1H, J = 14.4 Hz), 1.28-1.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 150.3, 144.9, 140.3, 137.1, 136.6, 128.4, 127.8, 127.6, 127.5, 123.3, 109.6, 101.2, 77.7, 72.1, 64.5, 60.3, 59.9, 56.2, 52.6, 51.7, 50.1, 48.2, 42.4, 42.3, 31.5, 26.6. HRMS (FAB+) *m/z*: Calcd for $C_{29}H_{30}N_2O_4$+H$^+$: 471.2284; Found: 471.2270. $[\alpha]^{25}_D$ = -69.3° (*c* 1.63, $CHCl_3$).

10-*t*-Butyldiphenylsiloxy-11-methoxystrychnine (**15**). To a suspension of 10-hydroxy-11-methoxystrychnine[16] (380 mg, 1.0 mmol) in DMSO (20 ml) at 80 °C was added NaH (26 mg, 1.1 mmol) under Ar. After 30 min, *t*-butylchlorodiphenylsilane (572 µl, 2.2 mmol) was added, and the mixture was then stirred at 60 °C for 5 h. To the whole mixture was added CH_2Cl_2 (50 ml) and then washed with water (50 ml). The organic layer was dried over Na_2SO_4 and filtered, and the solvents were removed via rotary evaporation. The product was purified by flash chromatography (methanol as the eluent) to give 62 mg (10%) of **15**. IR (film) 2857, 2361, 1665, 1497, 1449, 1401, 1287 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.65 (m, 5H), 7.40-7.26 (m, 6H), 6.33 (s, 1H), 5.84 (bs, 1H), 4.26-4.21 (m, 1H), 4.16-3.98 (m, 2H), 3.70 (d, 1H, J = 10.8 Hz), 3.67 (s, 3H), 3.61 (bd, 1H, J = 15.0 Hz), 3.37 (bs, 1H), 3.11-3.02 (m, 3H), 2.77-2.56 (m, 3H), 2.18 (dt, 1H, J = 15.0, 6.0 Hz), 1.71-1.65 (m, 1H), 1.58-1.47 (m, 1H), 1.22-1.13 (m, 2H), 1.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 150.4, 141.8, 140.6, 136.1, 135.50, 135.45, 133.33, 133.30, 129.7, 129.6, 127.5, 127.4, 127.2, 123.3, 114.0, 101.2, 77.7, 64.5, 60.3, 59.7, 55.7, 52.5, 51.4, 50.1, 48.1, 42.3, 42.1, 31.4, 26.7, 26.5, 19.7. HRMS (FAB+) *m/z*: Calcd for $C_{38}H_{42}N_2O_4Si$+H$^+$: 619.2992; Found: 619.2964. $[\alpha]^{25}_D$ = -66.6° (*c* 0.56, $CHCl_3$).

Typical Procedure for Coupling reaction of Magnesium Anilides with Aryllead Triacetates: Synthesis of Arylamine 17. To a solution of 3,5-dimethylaniline (162 µL, 1.3 mmol) in toluene (6.50 mL) was added a 1.0 M THF solution of *t*-BuMgCl (1.30 mL, 1.3 mmol) at 0 °C under argon. The mixture was stirred for 3h at room temperature. To a solution of 2-isopropylphenyllead triacetate (504 mg, 1.0 mmol) and DABCO (112 mg, 1.0 mmol) in toluene (20.0 mL) was added the above solution of the Mg-amide at room temperature. The mixture was stirred for 2h and subjected directly to the column chromatography on silica gel (diethyl ether/hexane = 1/50 to 1/9 as the eluent) to give 2-(2-isopropylphenyl)-3,5-dimethylaniline **17** (211 mg, 88%) and 2,6-bis(2-isopropylphenyl)-3,5-dimethylaniline **18** (14 mg, 8%). These yields are based on the initial amount of the

Pb-reagent. Thus, 96% of the Pb species was converted into **17** and **18**.

2-(2-Isopropylphenyl)-3,5-dimethylaniline (**17**). IR (film) 3472, 3378, 1617, 1574, 1480, 1443, 1329 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, 1H, J = 7.5 Hz), 7.36 (t, 1H, J = 7.2 Hz), 7.24 (td, 1H, J = 7.2, 2.1 Hz), 7.06 (d, 1H, J = 7.5 Hz), 6.54 (s, 1H), 6.45 (s, 1H), 3.29 (s, 2H), 2.76-2.67 (m, 1H), 2.28 (s, 3H), 1.90 (s, 3H), 1.15 (d, 3H, J = 6.9 Hz), 1.11(d, 3H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 144.1, 137.4, 136.9, 136.1, 130.3, 128.0, 126.4, 125.9, 124.2, 120.7, 113.1, 29.9, 24.4, 23.9, 21.2, 20.4. Anal. Calcd for $C_{17}H_{19}N$: C, 85.30, H, 8.84, N, 5.95; Found: C, 85.31, H, 9.01, N, 5.95.

2-(2-Isopropylphenyl)-3,5-dimethoxyaniline (**19**). IR (film) 3478, 3382, 2959, 1611, 1204, 1157, 1082 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.33 (m, 2H), 7.24(t, 1H, J = 7.2 Hz), 7.12 (d, 1H, J = 7.2 Hz), 6.01 (s, 1H), 5.99 (s, 1H), 3.81 (s, 3H), 3.65 (s, 3H), 3.44 (s, 2H), 2.81-2.71 (m, 1H), 1.12 (d, 6H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 158.5, 149.0, 145.7, 133.1, 131.1, 127.9, 126.0, 125.5, 108.4, 92.4, 88.7, 55.2, 55.0, 30.0, 24.1, 23.7. HRMS (EI+) *m/z*: Calcd for $C_{17}H_{21}NO_2$: 271.1573; Found: 271.1596.

1-(2-Isopropylphenyl)-2-naphthylamine (**20**). IR (film) 3478, 3384, 2961, 1620, 1514, 1387, 1352 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75-7.69 (m, 2H), 7.52(d, 1H, J = 7.8 Hz), 7.45 (t, 1H, J = 7.8 Hz), 7.33 (t, 1H, J = 7.5 Hz), 7.25-7.09 (m, 4H), 7.04 (d, 1H, J = 9.0 Hz), 3.60 (s, 2H), 2.71-2.57 (m, 1H), 1.14 (d, 3H, J = 6.9 Hz), 1.00 (d, 3H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 141.2, 134.9, 134.0, 131.1, 128.5, 128.4, 127.8 (two peaks overlap), 126.6, 126.2, 126.1, 124.3, 122.0, 119.0, 117.9, 30.1, 24.2, 24.1. HRMS (EI+) *m/z*: Calcd for $C_{19}H_{19}N$: 261.1519; Found: 261.1559.

2-Amino-1-(2-isopropylphenyl)anthracene (**21**). IR (film) 3384, 2961, 1624, 1460, 1408, 1343 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.93-7.87 (m, 2H), 7.71-7.68(m, 1H), 7.58-7.48 (m, 3H), 7.40-7.35 (m, 1H), 7.33-7.29 (m, 2H), 7.24-7.21 (m, 1H), 7.08 (d, 1H, J = 9.0 Hz), 3.67 (s, 2H), 2.73-2.64 (m, 1H), 1.14 (d, 3H, J = 6.9 Hz), 0.99 (d, 3H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 140.2, 135.0, 132.8, 132.3, 131.4, 129.3, 129.0, 128.4, 127.94, 127.86, 127.6, 126.8, 126.4, 126.3, 125.1, 123.9, 121.6, 119.7, 116.5, 30.1, 24.3, 24.1. HRMS (EI+) *m/z*: Calcd for $C_{23}H_{21}N$: 311.1675; Found: 311.1657.

9-Amino-10-(2-isopropylphenyl)phenanthrene (**22**). IR (film) 3384, 2963, 1622, 1496, 1435, 1399, 1266 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, 1H, J = 7.8 Hz), 8.62 (d,

1H, J = 8.1 Hz), 7.94-7.93 (d, 1H, J = 6.9 Hz), 7.69-7.60 (m, 2H), 7.56-7.32 (m, 5H), 7.20 (d, 1H, J = 6.9 Hz), 3.91 (s, 2H), 2.73-2.64 (m, 1H), 1.11 (d, 3H, J = 6.9 Hz), 0.99 (d, 3H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 136.7, 135.4, 133.2, 131.3, 130.6, 128.5, 126.73, 126.69, 126.5 (two peaks overlap), 126.3, 125.7, 125.1, 125.0, 123.3, 123.1, 122.3, 121.5, 117.1, 30.1, 24.4, 24.0. HRMS (EI+) *m/z*: Calcd for $C_{23}H_{21}N$: 311.1675; Found: 311.1701.

2-(2-Methoxyphenyl)-3,5-dimethylaniline (**23**). IR (film) 3374, 2942, 1617, 1574, 1482, 1460, 1258 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (td, 1H, J = 7.8, 2.1 Hz), 7.14 (dd, 1H, J = 7.5, 1.8 Hz), 7.05-6.99 (m, 2H), 6.55 (s, 1H), 6.47 (s, 1H), 3.76 (s, 3H), 3.38 (s, 2H), 2.27 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 144.1, 137.7, 137.5, 131.7, 128.9, 126.4, 121.4, 121.1, 120.9, 113.5, 111.3, 55.6, 21.3, 20.1. HRMS (FAB+) *m/z*: Calcd for $C_{15}H_{17}NO$: 227.1311; Found: 227.1334.

2,6-(2-Methoxyphenyl)-3,5-dimethylaniline (**24**) (*dl* or *meso*). IR (film) 2923, 1601, 1507, 1478, 1266, 1252 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (td, 2H, J = 7.8, 1.8 Hz), 7.20 (dd, 2H, J = 7.5, 1.8 Hz), 7.05-6.99 (m, 4H), 6.68 (s, 1H), 3.79 (s, 6H), 3.24 (s, 2H), 1.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 142.1, 136.2, 131.9, 128.8, 126.9, 121.6, 121.1, 121.0, 111.2, 55.6, 20.2. HRMS (FAB+) *m/z*: Calcd for $C_{22}H_{23}NO_2$+H^+: 334.1808; Found: 334.1793. The diastereomer of **24** (*meso* or *dl*). IR (film) 2923, 1601, 1491, 1456, 1435, 1267, 1244 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (td, 2H, J = 7.8, 1.8 Hz), 7.20 (dd, 2H, J = 7.5, 1.8 Hz), 7.04 (d, 2H, J = 6.9 Hz), 7.00 (d, 2H, J = 7.8 Hz), 6.68(s, 1H), 3.77 (s, 6H), 3.25 (s, 2H), 2.00 (s, 6H); 13C NMR (75 MHz, $CDCl_3$) δ 157.3, 142.1, 136.2, 131.9, 128.9, 126.9, 121.7, 121.12, 121.06, 111.4, 55.5, 20.3. HRMS (FAB+) *m/z*: Calcd for $C_{22}H_{23}NO_2$: 333.1730; Found: 333.1719.

2-(2-Methoxyphenyl)-3,5-dimethoxyaniline (**25**). IR (film) 3378, 3002, 1622, 1458, 1242, 1204, 1154 cm-1; 1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.32 (m, 1H), 7.26-7.21 (m, 1H), 7.05-6.99 (m, 2H), 6.04 (d, 1H, J = 2.4 Hz), 6.00 (d, 1H, J = 2.1 Hz), 3.80 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 3.56 (s, 2H); 13C NMR (75 MHz, $CDCl_3$) δ 160.5, 158.8, 157.6, 145.9, 132.7, 128.8, 123.5, 120.9, 111.5, 106.0, 92.9, 89.5, 55.8, 55.7, 55.1. HRMS (EI+) *m/z*: Calcd for $C_{15}H_{17}NO_3$: 259.1209; Found: 259.1214.

1-(2-Methoxyphenyl)-2-aminonaphthalene (**26**). IR (film) 3380, 3056, 1622, 1493, 1431,

1242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74-7.67 (m, 2H), 7.46-7.41 (m, 1H), 7.26-7.19 (m, 4H), 7.14-7.02 (m, 3H), 3.69 (s, 3H), 3.62 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 141.4, 133.8, 132.7, 129.3, 128.7, 128.0, 127.9, 126.1, 125.3, 124.2, 122.0, 121.4, 118.1, 116.6, 111.7, 55.7. HRMS (EI+) *m/z*: Calcd for $C_{17}H_{15}NO$: 249.1155; Found: 249.1169.

2-Amino-1-(2-methoxyphenyl)anthracene (**27**). IR (film) 3382, 2928, 1624, 1491, 1462, 1244 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.93-7.88 (m, 2H), 7.73-7.68 (m, 2H), 7.51 (td, 1H, *J* = 7.8, 1.8 Hz), 7.34-7.28 (m, 3H), 7.20-7.09 (m, 3H), 3.78 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 140.3, 133.0, 132.5, 132.2, 129.4, 129.3, 129.2, 128.0, 127.9, 127.8, 126.4, 125.5, 125.0, 123.8, 121.5 (two peaks overlap), 120.0, 114.1, 112.0, 55.9. HRMS (FAB+) *m/z*: Calcd for $C_{21}H_{17}NO$: 299.1311; Found: 299.1307.

9-Amino-10-(2-methoxyphenyl)phenanthrene (**28**). IR (film) 2834, 1619, 1489, 1433, 1399, 1254 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.72 (dd, 1H, *J* = 8.7, 1.2 Hz), 8.60 (dd, 1H, *J* = 8.4, 2.1 Hz), 7.91 (dd, 1H, *J* = 8.7, 1.2 Hz), 7.66-7.55 (m, 2H), 7.48-7.32 (m, 3H), 7.28-7.18 (m, 2H), 7.13 (d, 1H, *J* = 7.2 Hz), 7.08 (d, 1H, *J* = 8.4 Hz) 3.98 (s, 2H), 3.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 136.9, 132.9, 132.8, 130.7, 129.5, 126.6, 126.4, 126.3, 125.8 (two peaks overlap), 125.2, 124.9, 123.2, 123.0, 122.3, 121.6, 121.5, 114.7, 111.8, 55.7. HRMS (FAB+) *m/z*: Calcd for $C_{21}H_{17}NO+H^+$: 300.1389; Found: 300.1361.

2-Amino-1-(2'-methyl-1'-naphthalenyl)anthracene (**30**). IR (film) 3384, 3050, 1624, 1429, 1343, 1266 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.96-7.88 (m, 4H), 7.57 (d, 1H, *J* = 8.1 Hz), 7.52 (d, 1H, *J* = 7.8 Hz), 7.42-7.37 (m, 2H), 7.31-7.18 (m, 4H), 7.12 (d, 1H, *J* = 9.3 Hz), 3.53 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 136.2, 132.8, 132.7, 132.4, 132.2, 132.1, 129.4, 129.2, 128.04, 127.99, 127.94, 127.85, 127.83, 126.594, 126.587, 126.4, 125.6, 125.2, 125.1, 123.9, 121.2, 119.8, 113.7, 20.0. HRMS (FAB+) *m/z*: Calcd for $C_{25}H_{19}N$: 333.1519; Found: 333.1479.

9-Amino-10-(2'-methyl-1'-naphthalenyl)phenanthrene (**31**). IR (film) 3056, 1622, 1541, 1509, 1404, 1267 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, 1H, *J* = 7.8 Hz), 8.67 (d, 1H, *J* = 8.4 Hz), 7.96-7.89 (m, 3H), 7.74-7.62 (m, 2H), 7.55 (d, 1H, *J* = 8.1 Hz), 7.42-7.37 (m, 2H), 7.32-7.17 (m, 3H), 6.92 (d, 1H, *J* = 8.1 Hz), 3.85 (s, 2H), 2.15 (s, 3H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 137.1, 136.3, 132.7, 132.6 (two peaks overlap), 132.4, 130.9, 129.1, 128.1, 128.0, 127.1, 126.6, 126.5 (two peaks overlap), 125.9, 125.6, 125.2, 125.1, 124.7, 123.4, 123.2, 122.5, 121.6, 114.3, 20.0. Anal. Calcd for $C_{25}H_{19}N$: C, 90.06, H, 5.74, N, 4.20; Found: C, 89.91, H, 5.96, N, 4.23.

2-Phenyl-3,5-dimethylaniline (**33**). IR (film) 3376, 2921, 1617, 1482, 1458, 1329 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (app.t, 2H, J = 7.5 Hz), 7.34 (app.t, 1H, J = 7.5 Hz), 7.24 (d, 2H, J = 7.5 Hz), 6.54 (s, 1H), 6.47 (s, 1H), 3.40 (s, 2H), 2.27 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 138.2, 137.7, 136.8, 130.1, 129.0, 127.1, 125.1, 120.9, 113.4, 21.2, 20.5. HRMS (EI+) *m/z*: Calcd for $C_{14}H_{15}N$: 197.1206; Found: 197.1247.

2-(3,4,6-Trimethoxyphenyl)-3,5-dimethylaniline (**34**). IR (film) 3007, 1609, 1456, 1418, 1266, 1127 cm-1; 1H NMR (300 MHz, $CDCl_3$) δ 6.54 (s, 1H), 6.46 (s, 1H), 6.24 (s, 2H), 3.86 (s, 3H), 3.71 (s, 6H), 3.37 (s, 2H), 2.26 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 158.7, 144.6, 138.3, 137.4, 120.9, 117.2, 113.5, 106.89, 90.9, 55.9, 55.3, 21.4, 19.9. HRMS (EI+) *m/z*: Calcd for $C_{17}H_{21}NO_3$: 287.1522; Found: 287.1510.

2,6-Bis(3,4,6-trimethoxyphenyl)-3,5-dimethylaniline (**35**). IR (film) 2938, 1509, 1458, 1339, 1225, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.67 (s, 1H), 6.23 (s, 4H), 3.85 (s, 6H), 3.72 (s, 12H), 3.61 (s, 2H), 1.96 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 158.9, 136.8 (two peaks overlap), 121.2, 117.3, 108.0, 91.2, 56.0, 55.3, 20.2. HRMS (FAB+) *m/z*: Calcd for $C_{26}H_{33}NO_6$: 453.2152; Found: 453.2192.

1-(3,4,6-Trimethoxyphenyl)-2-naphthylamine (**36**). IR (film) 3370, 1605, 1462, 1221, 1156, 1127 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72-7.66 (m, 2H), 7.27-7.15 (m, 3H), 7.05 (d, 1H, J = 9.0 Hz), 6.32 (s, 2H), 3.90 (s, 3H), 3.66 (s, 2H), 3.63 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 159.5, 142.0, 134.2, 128.5, 128.1, 127.9, 125.8, 124.2, 121.8, 118.1, 112.7, 105.7, 91.3, 56.0, 55.4. Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77, H, 6.19, N, 4.53; Found: C, 73.63, H, 6.37, N, 4.56.

Typical Procedure for the Asymmetric Coupling Reaction of Magnesium Anilides with Aryllead Triacetates: Synthesis of Arylamine 29. To a solution of β-naphthylamine **16f** (186 mg, 1.3 mmol) in toluene (6.50 mL) was added a 1.0 M THF solution of *t*-BuMgCl (1.30 mL, 1.3 mmol) at 0 °C under argon. The mixture was stirred for 3h at room temperature. To a solution of 2-methylnaphthyllead triacetate (526 mg, 1.0

mmol) and brucine (395 mg, 1.0 mmol) in toluene (20.0 mL) was added the above solution of the Mg-amide at –78 °C. The mixture was stirred for 14h at –78 °C and for 3h at –40 °C, and subjected directly to the column chromatography on silica gel (diethyl ether/hexane = 1/5 to 1/1 as the eluent) to give 2'-methyl-(1,1'-binaphthalen)-2-amine **29** (255 mg, 90%). These yields are based on the initial amount of the Pb-reagent: IR (film) 3384, 3054, 1619, 1509, 1381, 1266 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (app. d, 2H, J = 8.1 Hz), 7.78 (app. d, 2H, J = 8.4 Hz), 7.53 (d, 1H, J = 8.4 Hz), 7.43-7.37 (m, 1H), 7.24-7.09 (m, 5H), 6.88 (d, 1H, J = 8.1 Hz), 3.48 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 136.0, 133.7, 132.7, 132.6, 132.0, 129.1, 128.9, 128.1, 128.01, 127.99, 127.9, 126.5, 126.4, 125.5, 125.1, 124.0, 122.2, 118.0, 116.2, 20.0. HRMS (EI+) *m/z*: Calcd for $C_{21}H_{17}N$: 283.1362; Found: 283.1363. HPLC analysis (column: OD-H): retention times of two enantiomers of **29**: t_R=6.6 (major) and 7.4 (minor) min using *i*-PrOH/hexane (1/9) as the eluent at a flow rate of 1.0 mL/min.

Arylamine **32**.[13] HPLC analysis (column: OD-H): retention times of two enantiomers of **32**: t_R=23.8 (major) and 29.3 (minor) min using *i*-PrOH/hexane (1/50) as the eluent at a flow rate of 1.0 mL/min.

References

(1) Morgan, J.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 715.

(2) Barton, D. H. R.; Donnelly, D. M. X.; Guiry, P. J.; Finet, J.-P. *J. Chem. Soc. Perkin Trans. 1* **1994**, 2921.

(3) Hoffmann, H. M. R.; Plessner, T.; von Riesen, C. *Synlett* **1996**, 690.

(4) The synthesis of (+)-bis[(*R*)-1-phenylethyl]amine: Marshall, J. A.; Lebreton, J. *J. Am. Chem. Soc.* **1988**, *110*, 2925. This procedure was followed by an usual reductive methylation by sequential treatment with formaldehyde and formic acid to give **11**. CAS Registry No. 210367-14-9.

(5) Kaumi, T.; Murata , C.; Sasaki, Y.; Kitajima, H. *Synthesis*, **1980**, 634.

(6) Saito, S.; Kano, T.; Hatanaka, K.; Yamamoto, H. *J. Org. Chem.* **1997**, *62*, 5651.

(7) Nishikori, H.; Katsuki, T. *Tetrahedron Lett.* **1996**, *37*, 9245.

(8) Tamai, Y.; Nakano, T.; Koike, S.; Kawahara, K.; Miyano, S. *Chem. Lett.* **1989**, 1135.

(9) Pirkle, W. H.; Schreiner, J. L. *J. Org. Chem.* **1981**, *46*, 4988.

(10) For the preparation of aryllead triacetates, see: Kozyrod, R. P.; Morgan, J.; Pinhey, J. T. *Aust. J. Chem.* **1985**, *38*, 1147. See also ref. 1.

(11) Abel E. W.; Willey, G. R. *J. Chem. Soc.* **1964**, 1528.

(12) Dilithiated anilines: Ooi, T.; Tayama, E.; Yamada, M.; Maruoka, K. *Synlett* **1999**, 729.

(13) Wilson J. M.; Cram, D. J. *J. Org. Chem.* **1984**, *49*, 4930.

(14) Whitesides, G. M.; Eisenhut, M.; Bunting, W. M.; *J. Am. Chem. Soc.* **1974**, *96*, 5398.

(15) Hey, D. H.; Stirling, C. J. M.; Williams, G. H. *J. Chem. Soc.* **1954**, 2747.

(16) Verpoorte, R.; van Beek, T. A.; Riegman, R. L. M. *Org. Magn. Reson.* **1984**, *22*, 345.