SUPPORTING INFORMATION

“Steric Modulation of Chiral Biaryl Diamines via Pd-Catalyzed Directed C–H Arylation”

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Synthesis of 2,2’-diacetylaminobiaryls..........................................................S1

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General considerations. All commercially-available chemicals were used as received. 1H and 13C NMR spectra were obtained on 300 MHz spectrometers. Chemical shift (δ) values are relative to TMS (0.0 ppm) or DMSO-d6 (2.50 ppm) for 1H NMR spectra and relative to deuterated solvent for 13C NMR spectra (77.23 ppm for CDCl3 and 39.52 ppm for DMSO-d6). Flash chromatography was performed using SiliaFlash® P60 (Silicycle, particle size 40 - 63 µm, 230-400 mesh).

Synthesis of 2,2’-diacetylaminobiaryls. A representative synthesis is given for compound 4.1 Diamine 12 (6.51g, 30.7 mmol), DMAP (370mg, 3.03 mmol), and acetic anhydride (35 mL, 371 mmol) were combined and stirred at 75°C for 2h. The resultant suspension was cooled to room temperature and the supernatant was slowly added to 300 mL 0.2M HCl(aq). After stirring for 20 minutes at room temperature, the suspension was extracted 2x with CH2Cl2, dried over MgSO4, filtered and solvent was removed in vacuo. CH2Cl2 was added and removed under vacuum until the scent of acetic acid was no longer detectable. Procedure affords 9.06g pure product, 99.6% yield. 1H NMR (300 MHz, CDCl3) δ 1.90 (s, 6H), δ 1.93 (s, 6H), δ 6.88 (br. s, 2 H), δ 7.15 (d, J = 7.6 Hz, 2H), δ 7.35 (t, J = 7.6 Hz, 2H), δ 8.01 (d, J = 7.6 Hz, 2H). 13C NMR (75MHz, CDCl3) δ 19.9, δ 24.6, δ 120.5, δ 127.0, δ 129.4, δ 136.0, δ 137.4, δ 169.1.
2',2''-diacetylamino-m-quaterphenyl (3). 70% yield, light tan powder. Purified by flash chromatography (3 : 2 EtOAc/hexanes, R_f = 0.15). HRMS: m/z (ESI) calculated [MH]^+ = 421.1911, measured 421.1902 (Δ = 2.1 ppm). ^1H NMR (300 MHz, DMSO-d_6 spiked with CD_3OD) δ 1.48 (s, 6H), δ 7.17 (dd, J = 7.0, 1.7 Hz, 2H), δ 7.29 - 7.45 (m, 14H). ^13C NMR (75MHz, DMSO-d_6) δ 22.2, δ 126.9, δ 127.1, δ 128.0, δ 128.6, δ 129.0, δ 129.4, δ 133.0, δ 139.4, δ 139.5, δ 140.5, δ 169.1.

2',2''-diacetylamino-6',6''-dimethyl-m-quaterphenyl (5a). >99% yield, off-white powder. Purified by flash chromatography (gradient, 1 : 1 Et_2O/toluene to pure Et_2O, R_f = 0.29 in 1:1 Et_2O/toluene). HRMS: m/z (ESI) calculated [MH]^+ = 449.2224, measured 449.2242 (Δ = 4.0 ppm). ^1H NMR (300 MHz, CDCl_3) δ 1.60 (s, 6H), δ 1.94 (s, 6H), δ 7.26 - 7.40 (m, 14H). ^13C NMR (75MHz, CDCl_3) δ 20.1, δ 23.0, δ 127.3, δ 128.4, δ 128.8, δ 129.4, δ 129.8, δ 132.8, δ 138.8, δ 140.2.

2',2''-diamino-6',6''-dimethyl-m-quaterphenyl (6). > 99 % yield, tan solid. HRMS: m/z (ESI) calculated [MH]^+ = 365.2013, measured 365.2027 (Δ = 3.8 ppm). ^1H NMR (300 MHz, CDCl_3) δ 2.04 (s, 6H), δ 3.67 (br. s, 4H), δ 6.79 (dd, J = 7.5, 0.3 Hz, 2H), δ 7.07 (d, J = 7.8 Hz, 2H), δ 7.30 (tt, J = 7.5, 1.5 Hz, 2H), δ 7.39 - 7.44 (m, 4H), δ 7.46 - 7.50 (m, 4H). ^13C NMR (75MHz, CDCl_3) δ 19.9, δ 120.1, δ 122.7, δ 125.5, δ 127.1, δ 128.9, δ 129.4, δ 129.7, δ 137.3, δ 140.2, δ 141.5. (S)-6: [α]_D^{25} = -81.4 (c 8.9, CH_2Cl_2).

2',2''-diacetylamino-4',4''-di-tert-butyl-6',6''-dimethyl-m-quaterphenyl (5b). >99% yield, tan solid. Purified by flash chromatography (3 : 1 Et_2O/hexanes, R_f = 0.35). HRMS: m/z (ESI) calculated [MH]^+ = 583.3295, measured 583.3314 (Δ = 3.3 ppm). ^1H NMR (300 MHz, CDCl_3) δ 1.31 (s, 18H), δ 1.51 (s, 6H), δ 1.85 (br. s, 6H), δ 7.22 - 7.36 (m, 12H). ^13C NMR (75MHz, CDCl_3) δ 19.9, δ 22.4, δ 31.5, δ 34.6, δ 125.2, δ 127.7, δ 128.4, δ 129.5, δ 129.8, δ 132.5, δ 136.9, δ 137.2, δ 138.6, δ 150.0.
2',2''-diacetylamino-4,4''''-dimethoxy-6',6'''-dimethyl-m-quaterphenyl (5c). 76% yield, bronze-colored solid. Purified by flash chromatography (Et₂O, Rᵣ = 0.09). HRMS: m/z (ESI) calculated [MH⁺] = 509.2435, measured 509.2419 (Δ = 3.1 ppm). ¹H NMR (300 MHz, CDCl₃) δ 1.44 (s, 6H), δ 1.81 (s, 6H), δ 3.75 (s, 6H), δ 6.78 (d, J = 9.6 Hz, 4H), δ 7.22 - 7.25 (m, 8H), δ 8.28 (br. s, 2H). ¹³C NMR (75MHz, CDCl₃) δ 19.8, δ 22.6, δ 55.2, δ 113.5, δ 129.1, δ 129.4, δ 129.8, δ 132.6, δ 132.8, δ 136.1, δ 137.7, δ 138.3, δ 158.6.

2',2''-diacetylamino-3,3''',5,5''',6',6'''-hexamethyl-m-quaterphenyl (5d). 93% yield, tan solid. Purified by flash chromatography (gradient, 1 : 3 to 1 : 1 Et₂O/toluene, Rᵣ = 0.11). HRMS: m/z (ESI) calculated [MH⁺] = 505.2850, measured 505.2861 (Δ = 2.2 ppm). ¹H NMR (300 MHz, CDCl₃) δ 1.46 (s, 6H), δ 1.80 (s, 6H), δ 2.25 (s, 12H), δ 6.88 (s, 2H), δ 6.96 (s, 4H), δ 7.20 - 7.27 (m, 4H), δ 8.13 (br. s, 2H). ¹³C NMR (75MHz, CDCl₃) δ 19.9, δ 21.4, δ 22.6, δ 126.4, δ 128.7, δ 129.1, δ 129.5, δ 132.9, δ 136.4, δ 137.5, δ 138.6, δ 140.1.

2',2''-diacetylamino-3,3''',5,5''',6',6'''-hexamethyl-m-quaterphenyl (5e). 68% yield, orange-tan solid. Purified by flash chromatography (Et₂O, Rᵣ = 0.17). HRMS: m/z (ESI) calculated [MH⁺] = 509.2435, measured 509.2428 (Δ = 1.4 ppm). ¹H NMR (300 MHz, CDCl₃) δ 1.50 (s, 6H), δ 1.85 (s, 6H), δ 3.73 (s, 6H), δ 6.80 (br. d, J = 8.8 Hz, 2H), δ 6.90 - 6.93 (m, 4H), δ 7.18 - 7.29 (m, 6H), δ 8.08 (br. s, 2H). ¹³C NMR (75MHz, CDCl₃) δ 19.9, δ 22.7, δ 55.3, δ 113.1, δ 114.0, δ 121.2, δ 129.1, δ 129.3, δ 129.6, δ 132.8, δ 136.7, δ 137.4, δ 138.6, δ 141.5, δ 159.5.

1,1'-binaphthalene-2,2'-diacetylamino-3,3'-diphenyl (7). 89% yield, tan solid. Purified by flash chromatography (1 : 1 Et₂O/toluene, Rᵣ = 0.22). HRMS: m/z (ESI) calculated [MH⁺] = 521.2224, measured 521.2225 (Δ < 1 ppm). ¹H NMR (300 MHz, CDCl₃) δ 1.28 (s, 6H), δ 6.96 (m, 4H), δ 7.04 – 7.61 (m, 14H), δ 7.91 – 7.94 (d, J = 8.3 Hz, 2H), δ 7.97 (s, 2H). ¹³C NMR (75MHz, CDCl₃) δ 22.8, δ 126.0, δ 127.0, δ 127.5, δ 128.2, δ 128.4, δ 129.1, δ 130.0, δ 132.2, δ 132.9, δ 139.1, δ 140.0.
In DMSO-\textsubscript{d}\textsubscript{6} spiked with CD\textsubscript{3}OD

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in DMSO-\textsubscript{d}\textsubscript{6}
HPLC e.e. Determination of (S)-5a.

Column: Chiralcel AD-H
Eluent: iPrOH/Hexanes (10/90)
Flow rate: 1.0 mL/min
Detection: UV 210 nm

(1) Gott, A. L.; Clarke, A. J.; Clarkson, G. J.; Scott, P. Organometallics 2007, 26, 1729-1737.