Supporting Information
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Supporting Information for

Brønsted Acid-Catalyzed Synthesis of Unsymmetrical Arylbis(3-indolyl)methanes

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General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. 1H and 13C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for 1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for 13C NMR are reported in terms of chemical shift (δ, ppm).

α-(3-Indolyl)benzylamine substrates 2 were prepared according to known method by using an achiral catalyst. [ref: Kang, Q.; Zhao, Z.-A.; You, S.-L. J. Am. Chem. Soc. 2007, 129, 1484.]
Experimental Sections:

General procedure for synthesis of the unsymmetrical triarylmethanes

In a dry Schlenk tube, α-(3-indolyl)benzylamine 2 (0.20 mmol) and phosphorodiamidic acid 1 (4.8 mg, 0.01 mmol) were dissolved in toluene (2 mL) under argon. N-methyl indole (0.30 mmol) was added and the solution was stirred for several hours at room temperature. After the reaction was complete (monitored by TLC), saturated aqueous NaHCO₃ (3 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (10 mL). The organic layer was washed by brine (5 mL), separated, and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/8 ~1/5) to afford the product.

3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole (Table 2, entry 1).

Prepared according to the general procedure A to provide the title compound as a white solid (94% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: H NMR (300 MHz, CDCl₃) δ 3.65 (s, 3H), 5.87 (s, 1H), 6.49 (s, 1H), 6.63 (s, 1H), 6.69-7.02 (m, 2H), 7.13-7.39 (m, 11H), 7.82 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 32.6, 40.1, 109.1, 111.0, 118.0, 118.6, 119.1, 119.7, 119.9, 120.0, 121.4, 121.8, 123.6, 126.0, 127.4, 126.0, 126.9, 127.4, 128.1, 128.2, 128.6, 136.5, 137.3, 144.1; IR (film) 3410, 3053, 2923, 1605, 1456, 1418, 1371, 1329, 1295, 1092, 1011, 740, 703, 580 cm⁻¹. HRMS (EI): Exact mass calcd for C₂₄H₂₀N₂: 336.1626. Found: 336.1628.

3-((1-methyl-1H-indole-3-yl)(4-methoxyphenyl)methyl)-1H-indole (Table 2, entry 2).

Prepared according to the general procedure A to provide the title compound as a white solid (95% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: ¹H NMR (300 MHz, CDCl₃) δ 3.55 (s, 3H), 3.72 (s, 3H), 5.80 (s, 1H), 6.44-6.50 (m, 2H), 6.79 (d, J = 8.4 Hz, 2H), 6.94-6.99 (m, 2H), 7.11-7.22 (m, 6H), 7.37 (d, J = 8.1 Hz, 2H), 7.61 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 32.5, 39.2, 55.1, 109.0, 111.0, 113.5, 118.5, 119.0, 119.9, 120.0, 120.1, 121.3, 121.7, 123.5, 126.9, 127.3, 128.1, 129.5, 136.4, 136.5, 137.3, 157.7; IR (film) 3409, 2951, 1610, 1509, 1456, 1245, 1174, 1033, 796, 740, 425 cm⁻¹; HRMS (EI): Exact mass calcd for C₂₅H₂₂N₂O: 366.1732. Found: 366.1735.
3-(((1-methyl-1H-indol-3-yl)(p-tolyl)methyl)-1H-indole. (Table 2, entry 3). Prepared according to the general procedure A to provide the title compound as a white solid (97% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) δ 2.31 (s, 3H), 3.63 (s, 3H), 5.83 (s, 1H), 6.49 (s, 1H), 6.61 (s, 1H), 6.95-7.00 (m, 2H), 7.08 (d, $J$ = 7.8 Hz, 2H), 7.11-7.30 (m, 6H), 7.40 (dd, $J$ = 2.4, 8.1 Hz, 2H), 7.76 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 21.1, 32.6, 39.6, 109.0, 110.9, 118.2, 118.5, 119.1, 119.9, 120.0, 121.3, 121.8, 123.5, 127.0, 127.4, 128.2, 128.5, 128.9, 135.4, 136.6, 137.3, 141.1; IR (film) 3412, 1510, 1456, 1328, 1092, 1011, 740 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{25}$H$_{22}$N$_2$: 350.1783. Found: 350.1797.

3-(((1-methyl-1H-indol-3-yl)(2-bromophenyl)methyl)-1H-indole (Table 2, entry 4). Prepared according to the general procedure A to provide the title compound as a white solid (97% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) δ 3.55 (s, 3H), 6.28 (s, 1H), 6.41 (s, 1H), 6.45 (s, 1H), 6.96-7.23 (m, 9H), 7.38 (d, $J$ = 5.7 Hz, 2H), 7.59 (d, $J$ = 6.9 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 32.6, 39.4, 109.1, 111.0, 116.6, 118.4, 118.7, 119.2, 119.8, 120.0, 121.5, 121.9, 123.8, 124.7, 126.9, 127.2, 127.3, 127.7, 128.4, 130.4, 132.7, 136.5, 137.4, 143.1. IR (film) 3410, 3058, 2924, 1583, 1457, 1436, 1436, 1371, 1011, 804, 742, 424 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{24}$H$_{19}$N$_2$Br: 416.0711. Found: 416.0713.

3-(((1-methyl-1H-indol-3-yl)(4-bromophenyl)methyl)-1H-indole. (Table 2, entry 5). Prepared according to the general procedure A to provide the title compound as a white solid (95% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) δ 3.62 (s, 3H), 5.82 (s, 1H), 6.46 (s, 1H), 6.56-6.57 (m, 1H), 6.99-7.00 (m, 2H), 7.12-7.20 (m, 4H), 7.26-7.38 (m, 6H), 7.77 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 32.7, 39.6, 109.2, 111.1, 117.5, 118.8, 119.1, 119.3, 119.7, 119.8, 119.9, 121.6, 122.0, 123.6, 126.8, 127.2, 128.2, 130.5, 131.3, 136.6, 137.4, 143.3; IR (film) 3380, 1484, 1457, 1422, 1402, 1371, 1218, 1008, 798, 758, 743, 424 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{24}$H$_{19}$N$_2$Br: 414.0732. Found: 414.0730.
3-((1-methyl-1H-indole-3-yl)(4-nitrophenyl)methyl)-1H-indole. (Table 2, entry 6). Prepared according to the general procedure A to provide the title compound as a white solid (97% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.66 (s, 3H), 5.96 (s, 1H), 6.51 (s, 1H), 6.63-6.64 (m, 1H), 7.00-7.04 (m, 2H), 7.18-7.21 (m, 2H), 7.29-7.35 (m, 4H), 7.48 (d, $J$ = 8.7 Hz, 2H), 7.94 (s, 1H), 8.11 (d, $J$ = 8.7 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 32.7, 40.1, 109.3, 111.2, 116.4, 118.1, 119.0, 119.5, 119.6, 121.8, 122.2, 123.5, 123.6, 126.6, 126.9, 128.2, 129.4, 136.6, 137.3, 146.4, 152.1; IR (film) 3410, 3052, 2925, 1594, 1516, 1456, 1418, 1372, 1345, 1012, 793, 740, 424 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{24}$H$_{19}$N$_3$O$_2$: 381.1477. Found: 381.1476.

3-((1-methyl-1H-indole-3-yl)(3-nitrophenyl)methyl)-1H-indole. (Table 2, entry 7). Prepared according to the general procedure A to provide the title compound as a white solid (83% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.62 (s, 3H), 5.95 (s, 1H), 6.49 (s, 1H), 6.59 (d, $J$ = 2.4 Hz, 1H), 7.97-7.02 (m, 2H), 7.16-7.39 (m, 7H), 7.65 (d, $J$ = 7.5 Hz, 1H), 7.86 (s, 1H), 8.01-8.04 (m, 1H), 8.18-8.19 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 32.6, 49.9, 109.3, 111.2, 116.5, 118.2, 118.9, 119.40, 119.5, 121.4, 121.7, 122.2, 123.5, 123.7, 126.5, 126.9, 128.2, 129.0, 134.8, 136.6, 137.4, 146.5, 148.3. IR (film) 3410, 3055, 2927, 1594, 1526, 1457, 1348, 1095, 798, 740, 424 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{24}$H$_{19}$N$_3$O$_2$: 381.1477. Found: 381.1476.

5-methoxy-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole. (Table 2, entry 8). Prepared according to the general procedure A to provide the title compound as a white solid (93% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.59 (s, 3H), 3.66 (s, 3H), 5.80 (s, 1H), 6.48 (s, 1H), 6.54 (s, 1H), 6.79-6.81 (m, 2H), 6.95-6.99 (m, 1H), 7.12-7.36 (m, 9H), 7.62 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 32.6, 40.1, 55.8, 101.7, 109.7, 111.6, 111.8, 118.7, 119.4, 120.0, 121.4, 126.0, 127.3, 128.1, 128.2, 128.6, 131.7, 137.3, 144.1, 153.6; IR (film) 3412, 2932, 2827, 1583, 1483, 1439, 1328, 1207, 1171, 1047, 742 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{25}$H$_{22}$N$_2$O [M]$^+$: 366.1732 Found: 366.1734.
5-methyl-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole. (Table 2, entry 9). Prepared according to the general procedure A to provide the title compound as a yellow solid (92% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.32 (s, 3H), 3.55 (s, 3H), 5.82 (s, 1H), 6.44-6.46 (m, 2H), 6.94-6.99 (m, 2H), 7.10-7.36 (m, 10H), 7.48 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 21.4, 32.5, 40.0, 109.0, 110.7, 118.2, 118.6, 119.1, 119.3, 120.0, 121.4, 123.4, 123.8, 126.0, 127.2, 127.4, 128.1, 128.2, 128.3; 128.6, 134.8, 137.4, 144.3; IR (film) 3411, 2918, 1482, 1421, 1371, 793, 741, 703, 589 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{25}$H$_{22}$N$_2$: 350.1783. Found: 350.1779.

5-bromo-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole. (Table 2, entry 10). Prepared according to the general procedure A to provide the title compound as a colorless solid (74% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.64 (s, 3H), 5.80 (s, 1H), 6.45 (s, 1H), 6.64 (s, 1H), 7.00 (t, $J$ = 7.3 Hz, 1H), 7.13-7.34 (m, 10H), 7.51 (s, 1H), 7.85 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 32.6, 39.9, 109.1, 112.5, 117.7, 118.7, 119.4, 119.9, 121.5, 122.2, 124.7, 126.2, 127.2, 128.2, 128.3, 128.5, 128.7, 135.2, 137.4, 143.7; IR (film) 3411, 2926, 1614, 1456, 1437, 1327, 1094, 793, 741, 702 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{24}$H$_{19}$N$_2$Br: 416.0711. Found: 416.0712.

5-fluoro-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole. (Table 2, entry 11). Prepared according to the general procedure A to provide the title compound as a white solid (72% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.59 (s, 3H), 5.77 (s, 1H), 6.46 (s, 1H), 6.61 (d, $J$ = 2.1 Hz, 1H), 6.85-7.01 (m, 3H), 7.11-7.36 (m, 9H), 7.71 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 32.6, 39.9, 109.1, 110.9, 110.3, 111.5, 111.6, 117.7, 118.7, 119.9, 121.5, 125.3, 126.2, 127.3, 128.2, 128.3, 128.6, 133.1, 137.4, 143.8, 155.9, 159.0; IR (film) 3414, 1582, 1483, 1451, 1328, 1165, 938, 795, 742, 703, 425 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{24}$H$_{19}$N$_2$F: 354.1532. Found: 354.1530.

6-(benzyloxy)-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole. (Table 2, entry 12). Prepared according to the general procedure A to provide the title compound as a white solid (74% yield) following silica gel chromatography (ethyl acetate/petroleum ether =
6-bromo-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole.

(Table 2, entry 13). Prepared according to the general procedure A to provide the title compound as a yellow solid (98% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/5, v/v).

Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.57 (s, 3H), 5.79 (s, 1H), 6.43-6.45 (m, 2H), 6.96-7.05 (m, 2H), 7.15-7.34 (m, 10H), 7.48 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 32.6, 40.0, 109.2, 113.9, 115.3, 117.7, 118.7, 119.7, 119.8, 121.1, 121.5, 122.4, 124.1, 125.8, 126.2, 127.3, 128.1, 128.2, 128.5, 137.3, 137.3, 143.8; IR (film) 3408, 3051, 2926, 1491, 14571, 1423, 1408, 1371, 1329, 1093, 1047, 804, 740, 703, 423 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{24}$H$_{19}$N$_2$Br: 414.0732. Found: 414.0729.

4-methyl-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole.

(Table 2, entry 14). Prepared according to the general procedure A to provide the title compound as a pale yellow solid (66% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/6, v/v).

Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.45 (s, 3H), 2.64 (s, 3H), 6.14 (s, 1H), 6.36 (s, 1H), 6.50 (d, $J$ = 1.8 Hz, 1H), 6.79 (d, $J$ = 7.5 Hz, 1H), 6.95-7.08 (m, 2H), 7.16-7.29 (m, 8H), 7.36 (d, $J$ = 7.8 Hz, 1H), 7.81 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 22.2, 32.6, 41.0, 108.9, 109.0, 118.6, 119.7, 120.0, 120.3, 120.9, 121.4, 121.9, 124.4, 125.6, 125.9, 127.1, 128.1, 128.7, 128.9, 131.4, 137.0, 137.4, 145.0; IR (film) 3399, 3051, 2926, 1491, 14571, 1423, 1408, 1371, 1229, 1223, 1155, 1114, 775, 742, 704, 424 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{25}$H$_{22}$N$_2$: 350.1783. Found: 350.1784.

2-methyl-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-1H-indole. (Table 2, entry 15). Prepared according to the general procedure A to provide the title compound as a pale yellow solid (88% yield) following silica gel chromatography (ethyl acetate/petroleum ether = 1/4, v/v).

Analytical data: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.13 (s, 3H), 3.56 (s, 3H), 5.88 (s, 1H), 6.50
(s, 1H), 6.84-7.03 (m, 3H), 7.13-7.31 (m, 10H), 7.54 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 12.1, 32.6, 39.2, 109.0, 110.0, 114.0, 117.3, 118.6, 118.9, 119.3, 119.8, 120.5, 121.4, 125.8, 127.8, 128.0, 128.4, 128.7, 131.4, 135.1, 137.3, 144.1; IR (film) 3402, 3053, 2917, 1614, 1459, 1328, 1012, 740, 701 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{25}$H$_{22}$N$_2$: 350.1783. Found: 350.1780.

3-(phenyl(2,4,6-trimethoxyphenyl)methyl)-1H-indole (eq 1, Figure 2)

61% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ 3.56 (s, 6H), 3.77 (s, 3H), 6.15 (s, 2H), 6.28 (s, 1H), 6.84 (d, $J = 1.2$ Hz, 1H), 6.96-7.01 (m, 1H), 7.08-7.28 (m, 7H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.82 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 36.3, 55.2, 55.7, 91.7, 110.8, 114.3, 117.9, 118.9, 119.7, 121.3, 123.6, 124.9, 127.9, 128.5, 136.0, 144.6, 159.0, 159.7; IR (film) 3394, 3047, 2936, 1608, 1493, 1495, 1332, 1204, 1153, 1105, 950, 838, 737 cm$^{-1}$; HRMS (EI): Exact mass calcd for C$_{24}$H$_{23}$NO$_3$: 373.1678. Found: 373.1680;