Supporting Information

Palladium-Catalyzed Direct Arylation of Aryl(azaaryl)methanes with Aryl Halides Providing Triarylmethanes

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Instrumentation and Chemicals

¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were taken on Varian Mercury 500 spectrometers and were recorded in CDCl₃. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ¹H and relative to CDCl₃ at 77.0 ppm for ¹³C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Xylene was purchased from Wako Pure Chemical Co. and stored over slices of sodium. Di(acetonitrile)dichloropalladium and cesium hydroxide monohydrate were purchased from Aldrich. Tricyclohexylphosphine was purchased from Strem. All reactions were carried out under argon atmosphere. Preparations of aryl(azaaryl)methanes **1** are shown below. 2-Benzylquinoline (**1f**) was prepared according to the method in the literature¹.

¹ Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Chem. Lett.* **2004**, 33, 1240–1241.

Experimental Procedure

Synthesis of 2-Benzylpyrimidine (**1a**)

Benzylmagnesium chloride (0.76 M in THF, 28 mL, 21 mmol) was slowly added to a solution of 2-chloropyrimidine (2.2 g, 19 mmol), nickel acetylacetonate (250 mg, 1.0 mmol), and triphenylphosphine (1.0 g, 4.0 mmol) in THF (40 mL) at 0 °C. The reaction mixture was stirred for 2 h at 20 °C. Water (60 mL) was added, and the product was extracted with ethyl acetate (40 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane : ethyl acetate = 1 : 1) afforded 2-benzylpyrimidine (**1a**, 2.4 g, 13 mmol) in 70% yield.

Synthesis of 2-Benzylbenzothiazole (**1h**)

Phenylacetyl chloride (1.3 mL, 12 mmol) was added to a solution of 2-aminothiophenol (1.1 mL, 10 mmol) and magnesium sulfate (5.0 g) in toluene (20 mL) at 0 °C. The resulting mixture was heated at reflux for 6 h. NaHCO₃ aq. was added, and the product was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane:ethyl acetate = 2:1) provided 2-benzylbenzothiazole (**1h**, 2.1 g, 9.3 mmol) in 93% yield.

Typical Procedure for Palladium-catalyzed Direct Arylation of Aryl(azaaryl)methanes **1**

Cesium hydroxide monohydrate (0.17 g, 1.0 mmol) and di(acetonitrile)dichloropalladium (6.5 mg, 0.025 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser under Ar atmosphere. Tricyclohexylphosphine (0.5 M in toluene, 0.15 mL, 0.075 mmol), xylene (1.0 mL), 2-benzylpyrimidine (**1a**, 85 mg, 0.50 mmol), and chlorobenzene (**2a**, 68 mg, 0.60 mmol) were sequentially added at ambient temperature. The resulting mixture was heated at reflux for 3 h. After the mixture was cooled to room temperature, water (10 mL) was added. The product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Purification on silica gel (hexane : ethyl acetate = 1 : 1) afforded 2-diphenylmethylpyridine (**3a**, 0.11 g, 0.43 mmol) in 86% yield.

Optimization of Reaction Conditions

The yields shown in this page are NMR yields.

Table S1. Effect of Base

entry	base	time	3a	1a
1	$\text{CsOH}\cdot\text{H}_2\text{O}$	2 h	87%	—
2	KOH	3 h	76%	—
3	NaOH	6 h	65 %	22%
4	Cs_2CO_3	3 h	6%	84%

Table S2. Screening of Ligand

entry	Ligand	3a	1a
1	15 mol% PCy_3	87	—
2	15 mol% P^tBu_3	5	84
3	15 mol% PPh_3	41	39
4	15 mol% PMe_3	trace	91
5	15 mol% $\text{P}(o\text{-tol})_3$	2	62
6	7.5mol% DPPE	63	25
7	7.5mol% DPPP	43	40
8	7.5mol% DPPF	35	49
9	7.5mol% BINAP	86	4

Characterization Data for Compounds

2-Benzylpyrimidine (1a): IR (neat) 699, 746, 1419, 1496, 1561, 3032 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.30 (s, 2H), 7.12 (dd, $J = 5.0, 5.0$ Hz, 1H), 7.21–7.24 (m, 1H), 7.29–7.32 (m, 2H), 7.36–7.37 (m, 2H), 8.68 (d, $J = 5.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 46.2, 118.8, 126.8, 128.7, 129.3, 138.3, 157.5, 170.2. Found: C, 77.87; H, 6.02; N, 16.37%. Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2$: C, 77.62; H, 5.92; N, 16.46%.

2-(2-Pyridylmethyl)pyridine (1e): ^1H NMR (CDCl_3) δ 4.35 (s, 2H), 7.14 (dd, $J = 8.0, 5.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.62 (ddd, $J = 8.0, 8.0, 2.0$ Hz, 2H), 8.55–8.56 (m, 2H); ^{13}C NMR (CDCl_3) δ 47.3, 121.7, 123.8, 136.8, 149.5, 159.5.

2-Benzylquinoline (1f): IR (nujol) 714, 747, 1425, 1453, 1505, 1598, 1618 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.35 (s, 2H), 7.21–7.25 (m, 2H), 7.28–7.32 (m, 4H), 7.49 (ddd, $J = 7.0, 7.0, 1.0$ Hz, 1H), 7.70 (ddd, $J = 7.0, 7.0, 1.0$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 45.7, 121.7, 126.1, 126.7, 126.9, 127.7, 128.8, 129.2, 129.4, 129.6, 136.7, 139.4, 148.0, 161.4.

2-Benzylbenzoxazole (1g): IR (neat) 695, 721, 746, 842, 1003, 1141, 1242, 1455, 1570, 3032 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.27 (s, 2H), 7.25–7.31 (m, 3H), 7.33–7.39 (m, 4H), 7.39–7.47 (m, 1H), 7.67–7.70 (m, 1H); ^{13}C NMR (CDCl_3) δ 35.5, 110.6, 120.0, 124.4, 124.9, 127.5, 129.0, 129.2, 135.0, 141.5, 151.2, 165.4. Found: C, 80.38; H, 5.48; N, 6.69%. Calcd for $\text{C}_{14}\text{H}_{11}\text{NO}$: C, 80.36; H, 5.30; N, 6.69%.

2-Benzylbenzothiazole (1h): IR (nujol) 702, 730, 759, 1437, 1454, 1495, 1517 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.44 (s, 2H), 7.28–7.38 (m, 6H), 7.45 (dd, $J = 8.0, 8.0$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 40.8, 121.7, 123.0, 125.0, 126.1, 127.5, 129.0, 129.3, 135.8, 137.4, 153.4, 171.3.

2-(Diphenylmethyl)pyrimidine (3a): IR (nujol) 624, 704, 1377, 1415, 1452, 1560, 2855, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.80 (s, 1H), 7.11 (t, $J = 5.0$ Hz, 1H), 7.20–7.24 (m, 2H), 7.28–7.33 (m, 8H), 8.71 (d, $J = 5.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 60.7, 118.9, 126.9, 128.5, 129.3, 141.9, 157.5, 171.9. Found: C, 82.87; H, 6.03; N, 11.33%. Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2$: C, 82.90; H, 5.73; N, 11.37%. m.p.: 65–68 $^{\circ}\text{C}$.

2-[(1-Naphthyl)phenylmethyl]pyrimidine (3b): IR (nujol) 700, 801, 1418, 1559, 2855, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.56 (s, 1H), 7.13 (t, $J = 5.0$ Hz, 1H), 7.18 (d, $J = 7.0$ Hz, 1H),

² Dyker, G.; Muth, O. *Eur. J. Org. Chem.* **2004**, 4319–4322.

³ Florio, S.; Capriati, V.; Colli, G. *Tetrahedron* **1997**, 53, 5839–5846.

7.24–7.27 (m, 1H), 7.29–7.34 (m, 4H), 7.38–7.45 (m, 3H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.84–7.86 (m, 1H), 8.04 (d, $J = 8.0$ Hz, 1H), 8.73 (d, $J = 5.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 57.2, 118.8, 124.1, 125.6, 125.6, 126.4, 127.0, 127.2, 127.8, 128.7, 129.0, 129.8, 132.1, 134.2, 138.2, 141.4, 157.6, 172.3. Found: C, 85.03; H, 5.64; N, 9.43%. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2$: C, 85.11; H, 5.44; N, 9.45%. m.p.: 124–126 °C.

2-[(2-Methylphenyl)phenylmethyl]pyrimidine (3c): IR (nujor) 703, 1378, 1413, 1462, 1559, 2855, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.25 (s, 3H), 5.98 (s, 1H), 7.06–7.08 (m, 1H), 7.10–7.18 (m, 4H), 7.20–7.24 (m, 3H), 7.28–7.31 (m, 2H), 8.71 (d, $J = 5.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 20.2, 57.4, 118.7, 126.1, 126.8, 126.9, 128.5, 129.1, 129.6, 130.6, 136.7, 140.3, 141.3, 157.5, 172.0. Found: C, 83.17; H, 6.22; N, 10.72%. Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2$: C, 83.04; H, 6.19; N, 10.76%. m.p.: 96–98 °C.

2-[(4-Methoxyphenyl)phenylmethyl]pyrimidine (3d): IR (nujor) 700, 1033, 1178, 1250, 1414, 1511, 1562, 2933, 3031 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.78 (s, 3H), 5.74 (s, 1H), 6.84–6.86 (m, 2H), 7.14 (dd, $J = 5.0, 5.0$ Hz, 1H), 7.23–7.25 (m, 3H), 7.29–7.30 (m, 4H), 8.73 (d, $J = 5.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 55.4, 60.0, 114.0, 118.9, 126.8, 128.5, 129.2, 130.4, 134.1, 142.3, 157.5, 158.5, 172.2.

2-[(4-Dimethylaminophenyl)phenylmethyl]pyrimidine (3e): IR (nujor) 1377, 1417, 1452, 1523, 1561, 2855, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.91 (s, 6H), 5.70 (s, 1H), 6.67–6.70 (m, 2H), 7.12 (t, $J = 4.5$ Hz, 2H), 7.19–7.20 (m, 3H), 7.28–7.30 (m, 4H), 8.72 (d, $J = 4.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 40.8, 60.0, 112.8, 118.7, 126.6, 128.4, 129.3, 129.9, 130.0, 142.7, 149.6, 157.4, 172.6. Found: C, 78.74; H, 6.68; N, 14.47%. Calcd for $\text{C}_{19}\text{H}_{19}\text{N}_3$: C, 78.86; H, 6.62; N, 14.52%. m.p.: 124–126 °C.

2-[(4-Ethenylphenyl)phenylmethyl]pyrimidine (3f): IR (neat) 700, 730, 909, 1416, 1495, 1510, 1561, 1569, 3032 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.20 (dd, $J = 11.0, 1.0$ Hz, 1H), 5.70 (dd, $J = 12.5, 1.0$ Hz, 1H), 5.78 (s, 1H), 6.68 (dd, $J = 12.5, 11.0$ Hz, 1H), 7.15 (t, $J = 5.0$ Hz, 1H), 7.21–7.25 (m, 1H), 7.27–7.31 (m, 6H), 7.34–7.36 (m, 2H), 8.74 (d, $J = 5.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 60.5, 113.8, 118.9, 126.4, 126.9, 128.6, 129.3, 129.5, 136.3, 136.7, 141.6, 141.9, 157.5, 171.9. Found: C, 83.91; H, 5.79; N, 10.20%. Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2$: C, 83.79; H, 5.92; N, 10.29%. m.p.: 68–70 °C.

***tert*-Butyl 4-[phenyl(2-pyrimidyl)methyl]benzoate (3g):** IR (nujor) 734, 1121, 1166, 1294, 1413, 1562, 1711 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.56 (s, 9H), 5.83 (s, 1H), 7.16 (t, $J = 5.0$ Hz, 1H), 7.22–7.32 (m, 5H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.93 (d, $J = 8.0$ Hz, 2H), 8.73 (d, $J = 5.0$ Hz, 2H);

^{13}C NMR (CDCl_3) δ 28.4, 60.7, 81.0, 119.1, 127.1, 128.7, 129.3, 129.3, 129.7, 130.7, 141.4, 146.6, 157.6, 165.8, 171.4.

2-(Diphenylmethyl)pyridine (4a): IR (nujor) 698, 1377, 1430, 1466, 1585, 2855, 2924 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.70 (s, 1H), 7.08 (d, $J = 5.0$ Hz, 1H), 7.13 (ddd, $J = 7.5, 4.5, 1.0$ Hz, 1H), 7.16–7.18 (m, 4H), 7.20–7.24 (m, 2H), 7.28–7.31 (m, 4H), 7.60 (ddd, $J = 7.5, 7.5, 2.0$ Hz, 1H), 8.60 (d, $J = 5.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 59.6, 121.6, 123.9, 126.7, 128.6, 129.5, 136.6, 142.9, 149.8, 163.4. Found: C, 88.21; H, 6.27; N, 5.55%. Calcd for $\text{C}_{18}\text{H}_{15}\text{N}$: C, 88.13; H, 6.16; N, 5.71%. m.p.: 68–70 $^\circ\text{C}$.

4-(Diphenylmethyl)pyridine (4b):⁴ IR (nujor) 607, 700, 1031, 1378, 1416, 1448, 1591, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.50 (s, 1H), 7.03–7.04 (m, 2H), 7.09–7.11 (m, 4H), 7.23–7.27 (m, 2H), 7.29–7.33 (m, 4H), 8.50–8.51 (m, 2H); ^{13}C NMR (CDCl_3) δ 56.4, 124.8, 127.0, 128.8, 129.5, 142.3, 150.0, 152.9. Found: C, 88.32; H, 6.40; N, 5.65%. Calcd for $\text{C}_{18}\text{H}_{15}\text{N}$: C, 88.13; H, 6.16; N, 5.71%. m.p.: 74–75 $^\circ\text{C}$.

2-[Phenyl(2-pyridyl)methyl]pyridine (4d): IR (nujor) 1431, 1464, 1586, 2855, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.82 (s, 1H), 7.13 (ddd, $J = 8.0, 5.0, 1.0$ Hz, 2H), 7.23–7.31 (m, 7H), 7.62 (ddd, $J = 8.0, 8.0, 3.0$ Hz, 2H), 8.59 (ddd, $J = 5.0, 1.5, 1.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 61.9, 121.7, 124.2, 126.9, 128.7, 129.5, 136.6, 141.9, 149.6, 162.3. Found: C, 83.02; H, 5.94; N, 11.30%. Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2$: C, 82.90; H, 5.73; N, 11.37%. m.p.: 95–97 $^\circ\text{C}$.

2-Diphenylmethylquinoline (4e): IR (nujor) 722, 757, 824, 1450, 1494, 2855, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.92 (s, 1H), 7.21–7.25 (m, 6H), 7.28–7.32 (m, 5H), 7.51 (ddd, $J = 7.0, 7.0, 1.5$ Hz, 1H), 7.69 (ddd, $J = 7.0, 7.0, 1.5$ Hz, 1H), 7.78 (dd, $J = 8.5, 1.5$ Hz, 1H), 8.07 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 60.3, 122.1, 126.4, 126.7, 127.0, 127.6, 128.5, 128.6, 129.6, 129.6, 136.5, 142.8, 148.1, 163.3. Found: C, 89.22; H, 5.74; N, 4.59%. Calcd for $\text{C}_{22}\text{H}_{17}\text{N}$: C, 89.46; H, 5.80; N, 4.74%. m.p.: 120–122 $^\circ\text{C}$.

2-Diphenylmethylbenzoxazole (4f):⁵ IR (nujor) 748, 909, 1003, 1141, 1243, 1455, 1496, 1564, 1602 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.77 (s, 1H), 7.25–7.35 (m, 12H), 7.45–7.47 (m, 1H), 7.72–7.74 (m, 1H); ^{13}C NMR (CDCl_3) δ 51.7, 110.8, 120.4, 124.4, 125.0, 127.6, 128.9, 128.9, 139.4, 141.4, 151.1, 166.8.

2-Diphenylmethylbenzothiazole (4g):⁶ IR (nujor) 746, 1140, 1313, 1494, 1599, 3027, 3061

⁴ 4-(Diphenylmethyl)pyridine is available from Aldrich.

⁵ Bywater, W. G.; Coleman, W. R.; Kamm, O.; Merritt, H. H. *J. Am. Chem. Soc.* **1945**, 67, 905.

⁶ Alt, G. H. *J. Org. Chem.* **1968**, 33, 2858.

cm⁻¹; ¹H NMR (CDCl₃) δ 5.95 (s, 1H), 7.27–7.37 (m, 11H), 7.46 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 56.0, 121.7, 123.4, 125.1, 126.2, 127.5, 128.9, 129.3, 135.8, 141.5, 153.6, 174.4.

1,4-Bis[di(2-pyridyl)methyl]benzene (6a): IR (nujor) 1433, 1467, 1587, 2855, 2925 cm⁻¹; ¹H NMR (CDCl₃) δ 5.78 (s, 2H), 7.12 (dd, *J* = 7.5, 5.0 Hz, 4H), 7.21 (s, 4H), 7.24 (d, *J* = 7.5 Hz, 4H), 7.60 (dd, *J* = 7.5, 7.5 Hz, 4H), 8.56 (d, *J* = 5.0 Hz, 4H); ¹³C NMR (CDCl₃) δ 61.6, 121.7, 124.3, 129.6, 136.6, 140.3, 149.6, 162.3. Found: C, 81.00; H, 5.23; N, 13.26%. Calcd for C₂₈H₂₂N₄: C, 81.13; H, 5.35; N, 13.52%.

1,3,5-Tris[di(2-pyridyl)methyl]benzene (6b): IR (nujor) 1432, 1465, 1585, 2855, 2924 cm⁻¹; ¹H NMR (CDCl₃) δ 5.70 (s, 3H), 7.01 (s, 3H), 7.07 (ddd, *J* = 8.0, 5.0, 1.0 Hz, 6H), 7.10 (d, *J* = 8.0 Hz, 6H), 7.53 (ddd, *J* = 8.0, 8.0, 1.0 Hz, 6H), 8.47 (d, *J* = 5.0 Hz, 6H); ¹³C NMR (CDCl₃) δ 61.8, 121.6, 124.2, 129.1, 136.5, 142.0, 149.4, 162.2.

Figure 1. ^1H NMR spectrum of **3d**

Figure 2. ^{13}C NMR spectrum of **3d**

Figure 3. ^1H NMR spectrum of **3g**

Figure 4. ^{13}C NMR spectrum of **3g**

Figure 6. ^{13}C NMR spectrum of **4f**

Figure 7. ^1H NMR spectrum of **4g**

Figure 8. ^{13}C NMR spectrum of **4g**

Figure 9. ^1H NMR spectrum of **6b**

Figure 10. ^{13}C NMR spectrum of **6b**