

Supporting Information

Palladium-catalyzed direct reductive cross-coupling of aryltrimethylammonium salts with aryl bromides

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General Information

Analytical thin layer chromatography (TLC) was performed using silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Flash chromatography was performed using Merck silica gel (200-300 mesh) for column chromatography with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^1H , ^{19}F , and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker Avance or Jeol 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ^1H , ^{19}F , and ^{13}C NMR analysis. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI or EI Source).

Optimization of Reaction Conditions

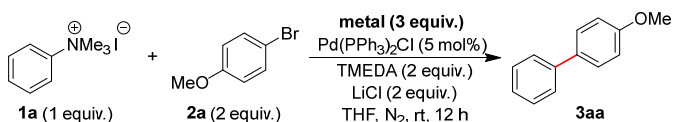
Table S1. Optimization of Reaction Conditions by Using Different Solvents



entry	solvent	yield (%) ^a	entry	solvent	yield (%) ^a
1	DMF	0	6	^t BuOMe	0
2	DMA	0	7	THF	94 (29) ^b
3	MeCN	0	8	DME	0
4	DMSO	0	9	Et ₂ O	0
5	1,4-dioxane	0	10	CpOMe	0

^a Yields were determined by using 1,4-dimethoxybenzene as an internal standard. ^b Reaction was performed under 60 °C.

Table S2. Optimization of Reaction Conditions by Using Different Metals



entry	metal	yield (%) ^a	entry	metal	yield (%) ^a
1	Mg	94	6	Ga	0
2	Al	0	7	Bi	0
3	Zn	0	8	Fe	0
4	Mn	0	9	Sn	0
5	In	0	10	Pb	0

^a Yields were determined by using 1,4-dimethoxybenzene as an internal standard.

Table S3. Optimization of Reaction Conditions by Using Different Catalysts

entry	catalyst	yield (%) ^a
1	Pd(PPh ₃) ₂ Cl ₂	94
2	Co(PPh ₃) ₂ Cl ₂	<5
3	Ni(PPh ₃) ₂ Cl ₂	0
4	CuCl ₂	<5
5	FeCl ₃	<5
6	CrCl ₂	0

^a Yields were determined by using 1,4-dimethoxybenzene as an internal standard.

Table S4. Optimization of Reaction Conditions by Using Different Aryltrimethylammonium Salts

entry	X	yield (%) ^a
1	I	94
2	Cl	77
3	Br	80
4	OTf	78

^a Yields were determined by using 1,4-dimethoxybenzene as an internal standard.

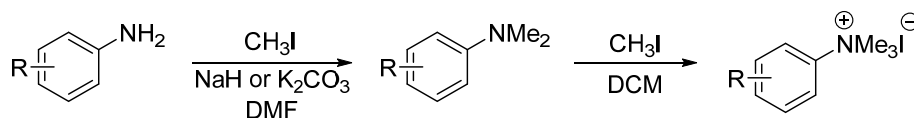
Experimental Procedure

Typical procedures for the cross-coupling reaction between aryltrimethylammonium salts with aryl bromides (taking product 3aa as an example)

To an oven-dried sealed tube equipped with a magnetic stir bar was added magnesium turnings (72.9 mg, 3 mmol) and LiCl (84.8 mg, 2 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling to room temperature, dry THF (3 mL) was added and the sealed tube was backfilled with nitrogen (x3). Then aryltrimethylammonium iodide (**1a**, 263.1 mg, 1 mmol) and Pd(PPh₃)₂Cl₂ (35.1 mg, 0.05 mmol) were weighed into the tube, after which 4-bromoanisole (**2a**, 374.1 mg, 2 mmol) and TMEDA (232.4 mg, 2 mmol) were added by syringe. Then the mixture was stirred at room temperature for 12 h. The resulting mixture was then quenched with saturated NH₄Cl solution and extracted with EtOAc (20 mL x3). The organic layers were

combined and washed with brine, dried over Na₂SO₄. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3aa** as a white solid.

Typical procedures for the synthesis of different aryltrimethylammonium salts



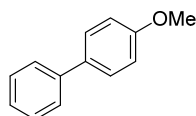
The aryltrimethylammonium salts were synthesized according to reported methods by a two-step procedure.

Step 1:¹⁻² Aniline (10 mmol, 1 equiv.), K₂CO₃ (30 mmol, 4.14 g) and DMF (50 mL) were added to a 100 mL round-bottomed flask equipped with a magnetic stir bar under N₂. The mixture was stirred at room temperature and iodomethane (1.25 mL, 20 mmol, 2 equiv.) was added dropwise. After completion of the reaction (monitored by TLC), the resulting mixture was diluted with water and the solution was extracted with DCM, washed with brine, dried over Na₂SO₄. Solvents were removed under reduced pressure and the crude product was purified by silica gel column chromatography.

Step 2:³⁻⁵ To a solution of the above amine in DCM (10 mL) was dropwise added iodomethane (1.5 equiv.). The resulting mixture was stirred at room temperature and monitored by TLC. After completion of the reaction, solvent was removed under reduced pressure and the residue was filtered, washed with petroleum ether to yield the salt.

Characterization data of products

4-Methoxy-1,1'-biphenyl (**3aa**)



Yield = 90%, 165.4 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2a**). White solid.

M.p.: 83.5-85.1 °C.

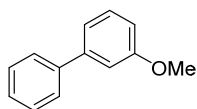
¹H NMR (400 MHz, CDCl₃): δ 7.65–7.56 (m, 4H), 7.51–7.44 (m, 2H), 7.39–7.34 (m, 1H), 7.06–7.01 (m, 2H), 3.89 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 159.0, 140.7, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.3 ppm.

IR (KBr): ν = 2961, 2836, 1606, 1522, 1488, 1288, 1252, 1035, 834, 760, 688 cm⁻¹.

HRMS (m/z): calcd for C₁₃H₁₃O [M+H]⁺ 185.0961, found: 185.0965.

3-Methoxy-1,1'-biphenyl (**3ab**)



Yield = 70%, 128.2 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2b**). Yellow oil.

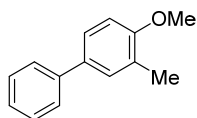
¹H NMR (400 MHz, CDCl₃): δ 7.51–7.46 (m, 2H), 7.35–7.29 (m, 2H), 7.26–7.20 (m, 2H), 7.07 (ddd, *J* = 7.6, 1.6, 1.0 Hz, 1H), 7.04–7.01 (m, 1H), 6.78 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.73 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 159.8, 142.7, 141.0, 129.7, 128.7, 127.4, 127.1, 119.6, 112.8, 112.6, 55.2 ppm.

IR (KBr): ν = 3031, 2937, 2834, 1599, 1478, 1421, 1296, 1213, 1054, 757, 713, 698 cm⁻¹.

HRMS (m/z): calcd for C₁₃H₁₃O [M+H]⁺ 185.0961, found: 185.0970.

4-Methoxy-3-methyl-1,1'-biphenyl (**3ac**)



Yield = 93%, 185.2 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2c**). White solid.

M.p.: 74.8–75.8 °C.

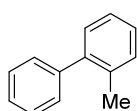
¹H NMR (400 MHz, CDCl₃): δ 7.66–7.62 (m, 2H), 7.52–7.45 (m, 4H), 7.40–7.34 (m, 1H), 6.98–6.93 (m, 1H), 3.93 (s, 3H), 2.38 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 157.3, 141.0, 133.2, 129.4, 128.6, 126.8, 126.7, 126.5, 125.3, 110.1, 55.3, 16.4 ppm.

IR (KBr): ν = 1608, 1512, 1490, 1467, 1439, 1243, 1135, 1023, 887, 763, 752 cm⁻¹.

HRMS (m/z): calcd for C₁₄H₁₅O [M+H]⁺ 199.1117, found: 199.1123.

2-Methyl-1,1'-biphenyl (**3ad**)



Yield = 78%, 131.2 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2d**). Colorless Oil.

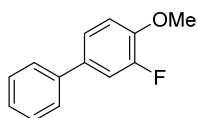
¹H NMR (400 MHz, CDCl₃): δ 7.56–7.51 (m, 2H), 7.48–7.44 (m, 3H), 7.41–7.36 (m, 4H), 2.41 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 141.9, 141.9, 135.3, 130.3, 129.8, 129.1, 128.0, 127.2, 126.7, 125.7, 20.4 ppm.

IR (KBr): ν = 3059, 3019, 1479, 1438, 1010, 748, 701, 618, 562, 455 cm⁻¹.

HRMS (m/z): calcd for C₁₃H₁₂ [M+H]⁺ 169.1012, found: 169.1013.

3-Fluoro-4-methoxy-1,1'-biphenyl (**3ae**)



Yield = 86%, 173.9 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2e**). White solid.

M.p.: 88.2-89.3 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.58–7.53 (m, 2H), 7.48–7.42 (m, 2H), 7.39–7.37 (m, 1H), 7.36–7.32 (m, 2H), 7.04 (t, *J* = 8.6 Hz, 1H), 3.94 (s, 3H) ppm.

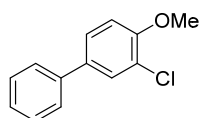
¹³C NMR (100 MHz, CDCl₃): δ 152.5 (d, *J* = 245.3 Hz), 146.9 (d, *J* = 10.8 Hz), 139.6 (d, *J* = 2.1 Hz), 134.3 (d, *J* = 6.6 Hz), 128.8, 127.2, 126.6, 122.6 (d, *J* = 3.5 Hz), 114.7 (d, *J* = 18.9 Hz), 113.5 (d, *J* = 2.6 Hz), 56.2 ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ -134.88–135.16 (m) ppm.

IR (KBr): ν = 2976, 2844, 1617, 1584, 1530, 1494, 1414, 1313, 1296, 1136, 1015, 872, 754 cm⁻¹.

HRMS (m/z): calcd for C₁₃H₁₂FO [M+H]⁺ 203.0867, found: 203.0869.

3-Chloro-4-methoxy-1,1'-biphenyl (**3af**)



Yield = 54%, 116.9 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2f**). Colorless oil.

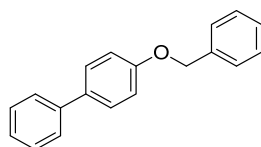
¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.51–7.37 (m, 4H), 7.13 (d, *J* = 7.7 Hz, 2H), 3.98 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 155.0, 141.2, 140.3, 130.3, 128.8, 127.6, 127.0, 121.5, 120.0, 110.9, 56.0 ppm.

IR (KBr): ν = 3030, 2938, 2853, 1593, 1567, 1479, 1396, 1306, 1226, 1072, 855, 760, 717 cm⁻¹.

HRMS (m/z): calcd for C₁₃H₁₂ClO [M+H]⁺ 219.0571, found: 219.0575.

4-(Benzyloxy)-1,1'-biphenyl (**3ag**)



Yield = 81%, 210.4 mg (1 mmol scale with the use of 3 equiv. of aryl bromide **2g**). White solid.

M.p.: 128.8-130.1 °C.

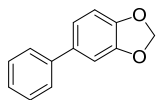
¹H NMR (400 MHz, CDCl₃): δ 7.61–7.54 (m, 4H), 7.51–7.48 (m, 2H), 7.47–7.41 (m, 4H), 7.40–7.31 (m, 2H), 7.11–7.06 (m, 2H), 5.14 (s, 2H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 158.3, 140.7, 136.9, 133.9, 128.7, 128.6, 128.1, 128.0, 127.5, 126.7, 126.7, 115.1, 70.0 ppm.

IR (KBr): ν = 2923, 2907, 2865, 1608, 1523, 1488, 1468, 1453, 1377, 1249, 1198, 1021, 825, 760, 717, 695, 688 cm⁻¹.

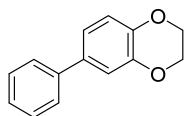
HRMS (m/z): calcd for C₁₉H₁₇O [M+H]⁺ 261.1274, found: 261.1275.

5-Phenylbenzo[d][1,3]dioxole (**3ah**)



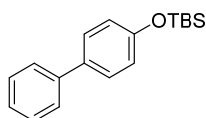
Yield = 91%, 179.7 mg (1 mmol scale with the use of 3 equiv. of aryl bromide **2h**). Yellow oil.
¹H NMR (400 MHz, CDCl₃): δ 7.58–7.51 (m, 2H), 7.47–7.40 (m, 2H), 7.37–7.31 (m, 1H), 7.13–7.06 (m, 2H), 6.91 (dd, *J* = 7.8, 0.5 Hz, 1H), 6.01 (s, 2H) ppm.
¹³C NMR (100 MHz, CDCl₃): δ 148.0, 147.0, 140.9, 135.5, 128.7, 126.9, 126.8, 120.9, 108.5, 107.6, 101.1 ppm.
IR (KBr): ν = 1510, 1478, 1429, 1249, 1224, 1106, 1040, 937, 889, 812, 759, 712, 697 cm⁻¹.
HRMS (m/z): calcd for C₁₃H₁₁O₂ [M+H]⁺ 199.0754, found: 199.0756.

6-Phenyl-2,3-dihydrobenzo[*b*][1,4]dioxine (**3ai**)



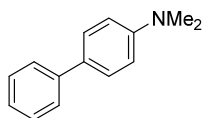
Yield = 86%, 183.0 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2i**). Colorless oil.
¹H NMR (400 MHz, CDCl₃): δ 7.59–7.55 (m, 2H), 7.47–7.41 (m, 2H), 7.36–7.31 (m, 1H), 7.16 (d, *J* = 2.2 Hz, 1H), 7.12 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 4.31 (s, 4H) ppm.
¹³C NMR (100 MHz, CDCl₃): δ 143.6, 143.1, 140.5, 134.7, 128.7, 126.8, 126.7, 120.1, 117.5, 115.8, 64.4, 64.4 ppm.
IR (KBr): ν = 1590, 1574, 1518, 1485, 1309, 1283, 1246, 1226, 1070, 896, 764, 717, 698 cm⁻¹.
HRMS (m/z): calcd for C₁₄H₁₃O₂ [M+H]⁺ 213.0910, found: 213.0914.

[(1,1'-Biphenyl)-4-yloxy](*tert*-butyl)dimethylsilane (**3aj**)



Yield = 75%, 212.6 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2j**). White solid.
M.p.: 57.1–58.4 °C.
¹H NMR (400 MHz, CDCl₃): δ 7.60 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.54–7.50 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38–7.32 (m, 1H), 6.99–6.94 (m, 2H), 1.07 (s, 9H), 0.29 (s, 6H) ppm.
¹³C NMR (100 MHz, CDCl₃): δ 155.2, 140.8, 134.2, 128.7, 128.1, 126.7, 126.6, 120.3, 25.7, 18.2, -4.4 ppm.
IR (KBr): ν = 2957, 2927, 2857, 1602, 1487, 1404, 1251, 1172, 1110, 916, 847, 777, 692 cm⁻¹.
HRMS (m/z): calcd for C₁₈H₂₅OSi [M+H]⁺ 285.1669, found: 285.1668.

N,N-Dimethyl-[1,1'-biphenyl]-4-amine (**3ak**)



Yield = 76%, 150.2 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2k**). White solid.

M.p.: 122.7-123.2 °C.

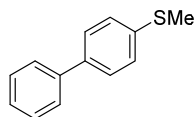
¹H NMR (400 MHz, CDCl₃): δ 7.73–7.69 (m, 2H), 7.67–7.63 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 6.97–6.89 (m, 2H), 3.09 (s, 6H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 149.8, 141.1, 129.2, 128.6, 127.6, 126.2, 125.9, 112.7, 40.5 ppm.

IR (KBr): ν = 1610, 1528, 1491, 1447, 1354, 1229, 956, 818, 760, 692 cm⁻¹.

HRMS (m/z): calcd for C₁₄H₁₆N [M+H]⁺ 198.1277, found: 198.1277.

[1,1'-Biphenyl]-4-yl(methyl)sulfane (3al)



Yield = 66%, 132.1 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2l**). White solid.

M.p.: 110.6-111.2 °C.

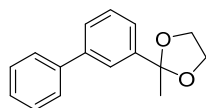
¹H NMR (400 MHz, CDCl₃): δ 7.63–7.54 (m, 4H), 7.47 (td, *J* = 6.9, 1.7 Hz, 2H), 7.40–7.34 (m, 3H), 2.55 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 140.4, 137.9, 137.5, 128.8, 127.4, 127.1, 126.8, 126.8, 15.8 ppm.

IR (KBr): ν = 2916, 1592, 1479, 1400, 1257, 1168, 1098, 1003, 954, 824, 754, 686 cm⁻¹.

HRMS (m/z): calcd for C₁₃H₁₃S [M+H]⁺ 201.0732, found: 201.0734.

2-([1,1'-Biphenyl]-3-yl)-2-methyl-1,3-dioxolane (3am)



Yield = 91%, 220.0 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2m**). Colorless oil.

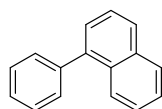
¹H NMR (400 MHz, CDCl₃): δ 7.76 (t, *J* = 1.7 Hz, 1H), 7.67–7.61 (m, 2H), 7.59–7.53 (m, 1H), 7.52–7.42 (m, 4H), 7.37 (tt, *J* = 6.7, 1.2 Hz, 1H), 4.08 (td, *J* = 6.1, 4.2 Hz, 2H), 3.89–3.78 (m, 2H), 1.74 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 143.8, 141.1, 141.0, 128.7, 128.7, 127.3, 127.2, 126.6, 124.2, 124.0, 108.8, 64.4, 27.7 ppm.

IR (KBr): ν = 2987, 2887, 1599, 1478, 1452, 1413, 1373, 1220, 1200, 1038, 871, 759, 708 cm⁻¹.

HRMS (m/z): calcd for C₁₆H₁₇O₂ [M+H]⁺ 241.1223, found: 241.1233.

1-Phenylnaphthalene (3an)



Yield = 74%, 151.1 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2n**). Colorless oil.

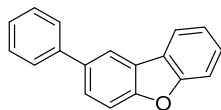
¹H NMR (400 MHz, CDCl₃): δ 8.12 – 7.99 (m, 3H), 7.70 – 7.54 (m, 9H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 140.7, 140.2, 133.7, 131.5, 130.0, 128.2, 128.2, 127.6, 127.2, 126.9, 126.0, 126.0, 125.7, 125.3 ppm.

IR (KBr): ν = 3055, 1591, 1507, 1395, 1182, 1117, 1030, 1019, 802, 778, 760, 703, 615 cm⁻¹.

HRMS (m/z): calcd for C₁₆H₁₃ [M+H]⁺ 205.1012, found: 205.1016.

2-Phenyldibenzo[*b,d*]furan (3ao)



Yield = 66%, 153.4 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2o**). White solid.

M.p.: 181.8-182.9 °C.

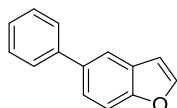
¹H NMR (400 MHz, CDCl₃): δ 8.16 (dd, *J* = 1.9, 0.6 Hz, 1H), 8.01 (ddd, *J* = 7.6, 1.3, 0.6 Hz, 1H), 7.70 (dt, *J* = 8.2, 1.4 Hz, 3H), 7.66–7.60 (m, 2H), 7.54–7.47 (m, 3H), 7.44 – 7.36 (m, 2H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 156.6, 155.7, 141.3, 136.4, 128.8, 127.4, 127.3, 127.0, 126.6, 124.7, 124.2, 122.8, 120.7, 119.2, 111.7 ppm.

IR (KBr): ν = 3054, 1603, 1471, 1446, 1202, 1187, 1121, 1022, 891, 843, 759, 747, 696, 573, 604, 429 cm⁻¹.

HRMS (m/z): calcd for C₁₈H₁₃O [M+H]⁺ 245.0961, found: 245.0960.

5-Phenylbenzofuran (3ap)



Yield = 38%, 74.7 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2p**). White solid.

M.p.: 65.9-67.2 °C.

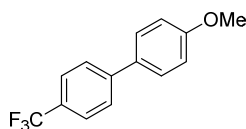
¹H NMR (400 MHz, CDCl₃): δ 7.83–7.80 (m, 1H), 7.69–7.62 (m, 3H), 7.61–7.53 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39–7.34 (m, 1H), 6.84 (dd, *J* = 2.2, 0.8 Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 154.5, 145.5, 141.6, 136.4, 128.7, 127.9, 127.4, 126.8, 123.9, 119.7, 111.5, 106.8 ppm.

IR (KBr): ν = 3144, 2923, 1536, 1462, 1428, 1233, 1163, 1107, 1026, 886, 823, 780, 696 cm⁻¹.

HRMS (m/z): calcd for C₁₄H₁₁O [M+H]⁺ 195.0804, found: 195.0810.

4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3ba)



Yield = 95%, 120.3 mg (0.5 mmol scale with the use of 3 equiv. of aryl bromide **2a**). White solid.

M.p.: 121.4-122.3 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.75–7.63 (m, 4H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H) ppm.

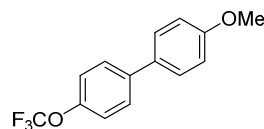
¹³C NMR (100 MHz, CDCl₃): δ 159.8, 144.2, 132.1, 128.6 (q, *J* = 32.5 Hz), 128.3, 126.8, 124.4 (q, *J* = 271.8 Hz), 125.6 (q, *J* = 3.8 Hz), 114.4, 55.3 ppm.

¹⁹F NMR (376 MHz, CDCl₃): δ -62.15 (s, 3F) ppm.

IR (KBr): ν = 2965, 2937, 2844, 1604, 1502, 1337, 1298, 1277, 1261, 1122, 1076, 1036, 1012, 830, 816, 719, 703 cm^{-1} .

HRMS (m/z): calcd for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$ 253.0835, found: 253.0843.

4-Methoxy-4'-(trifluoromethoxy)-1,1'-biphenyl (3ca)



Yield = 92%, 247.9 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2a**). White solid.

M.p.: 97.9-99.8 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3): δ 7.42-7.34 (m, 4H), 7.13 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 3.71 (s, 3H) ppm.

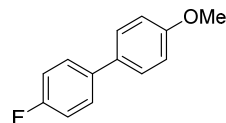
^{13}C NMR (100 MHz, CDCl_3): δ 159.4, 148.1, 139.6, 132.5, 128.1, 127.9, 121.2, 120.5 (q, J = 256.8 Hz), 114.3, 55.2 ppm.

^{19}F NMR (376 MHz, CDCl_3): δ -57.70 (s, 3F) ppm.

IR (KBr): ν = 2845, 1610, 1499, 1465, 1445, 1293, 1210, 1158, 1036, 1014, 828, 814 cm^{-1} .

HRMS (m/z): calcd for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 269.0784, found: 269.0784.

4-Fluoro-4'-methoxy-1,1'-biphenyl (3da)



Yield = 95%, 192.4 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2a**). White solid.

M.p.: 91.1-91.6 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3): δ 7.56-7.49 (m, 4H), 7.18-7.11 (m, 2H), 7.04-6.99 (m, 2H), 3.88 (s, 3H) ppm.

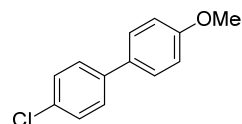
^{13}C NMR (100 MHz, CDCl_3): δ 162.0 (d, J = 245.4 Hz), 159.0, 136.9 (d, J = 3.3 Hz), 132.7, 128.1 (d, J = 8.0 Hz), 127.9, 115.5 (d, J = 21.4 Hz), 114.2, 55.2 ppm.

^{19}F NMR (376 MHz, CDCl_3): δ -116.46 ppm.

IR (KBr): ν = 3414, 1607, 1600, 1496, 1291, 1236, 1160, 1038, 1012, 826, 810, 791, 540 cm^{-1} .

HRMS (m/z): calcd for $\text{C}_{13}\text{H}_{12}\text{FO}$ $[\text{M}+\text{H}]^+$ 203.0867, found: 203.0871.

4-Chloro-4'-methoxy-1,1'-biphenyl (3ea)



Yield = 98%, 214.3 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2a**). White solid.

M.p.: 112.1-113.5 $^{\circ}\text{C}$.

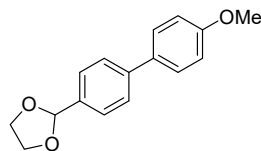
^1H NMR (400 MHz, CDCl_3): δ 7.55-7.48 (m, 4H), 7.44-7.39 (m, 2H), 7.05-6.99 (m, 2H), 3.88 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 159.2, 139.1, 132.5, 132.3, 128.7, 127.9, 127.8, 114.2, 55.2 ppm.

IR (KBr): ν = 2962, 2936, 2839, 1606, 1485, 1309, 1263, 1199, 1132, 1037, 845, 821 cm^{-1} .

HRMS (m/z): calcd for $\text{C}_{13}\text{H}_{12}\text{ClO}$ $[\text{M}+\text{H}]^+$ 219.0571, found: 219.0575.

2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-1,3-dioxolane (3fa)



Yield = 99%, 127.7 mg (0.5 mmol scale with the use of 3 equiv. of aryl bromide **2a**). Brown solid.

M.p.: 105.4-106.8 $^{\circ}\text{C}$.

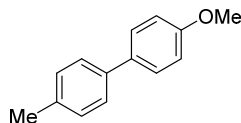
^1H NMR (400 MHz, CDCl_3): δ 7.63-7.56 (m, 6H), 7.01 (d, J = 8.7 Hz, 2H), 5.89 (s, 1H), 4.20-4.13 (m, 2H), 4.12-4.03 (m, 2H), 3.86 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 159.1, 141.5, 136.0, 133.0, 128.0, 126.7, 126.5, 114.0, 103.4, 65.1, 55.1 ppm.

IR (KBr): ν = 2891, 2836, 1607, 1499, 1465, 1310, 1254, 1195, 1089, 1036, 960, 813, 698 cm^{-1} .

HRMS (m/z): calcd for $\text{C}_{16}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$ 257.1172, found: 257.1176.

4-Methoxy-4'-methyl-1,1'-biphenyl (3ga)



Yield = 94%, 186.8 mg (1 mmol scale with the use of 3 equiv. of aryl bromide **2a**). White solid.

M.p.: 109.3-109.8 $^{\circ}\text{C}$.

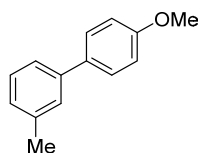
^1H NMR (400 MHz, CDCl_3): δ 7.52-7.48 (m, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 6.98-6.93 (m, 2H), 3.82 (s, 3H), 2.37 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 158.8, 137.9, 136.3, 133.6, 129.4, 127.9, 126.5, 114.1, 55.3, 21.0 ppm.

IR (KBr): ν = 2957, 2913, 2839, 1608, 1441, 1289, 1252, 1182, 1038, 1013, 842, 808, 498 cm^{-1} .

HRMS (m/z): calcd for $\text{C}_{14}\text{H}_{15}\text{O}$ $[\text{M}+\text{H}]^+$ 199.1117, found: 199.1122.

4'-Methoxy-3-methyl-1,1'-biphenyl (3ha)



Yield = 94%, 186.9 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2a**). White solid.

M.p.: 52.4-53.7 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3): δ 7.68-7.62 (m, 2H), 7.53-7.47 (m, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.27-7.23 (m, 1H), 7.11-7.06 (m, 2H), 3.92 (s, 3H), 2.53 (s, 3H) ppm.

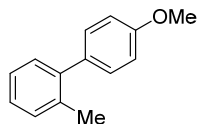
^{13}C NMR (100 MHz, CDCl_3): δ 159.0, 140.7, 138.2, 133.7, 128.6, 128.0, 127.4, 127.3, 123.7,

114.0, 55.1, 21.5 ppm.

IR (KBr): $\nu = 2955, 2837, 1605, 1516, 1486, 1441, 1295, 1252, 1195, 1028, 838, 787, 696, 578, 438 \text{ cm}^{-1}$.

HRMS (m/z): calcd for $\text{C}_{14}\text{H}_{15}\text{O}$ $[\text{M}+\text{H}]^+$ 199.1117, found: 199.1124.

4'-Methoxy-2-methyl-1,1'-biphenyl (3ia)



Yield = 79%, 157.5 mg (1 mmol scale with the use of 3 equiv. of aryl bromide **2a**). Colorless oil.

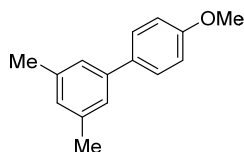
^1H NMR (400 MHz, CDCl_3): δ 7.39–7.32 (m, 6H), 7.08–7.04 (m, 2H), 3.93 (s, 3H), 2.39 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 158.4, 141.4, 135.4, 134.2, 130.2, 130.2, 129.8, 126.9, 125.7, 113.4, 55.1, 20.5 ppm.

IR (KBr): $\nu = 2953, 2834, 1613, 1516, 1483, 1464, 1441, 1267, 1244, 1176, 1039, 1018, 834, 787, 761, 586 \text{ cm}^{-1}$.

HRMS (m/z): calcd for $\text{C}_{14}\text{H}_{15}\text{O}$ $[\text{M}+\text{H}]^+$ 199.1117, found: 199.1125.

4'-Methoxy-3,5-dimethyl-1,1'-biphenyl (3ja)



Yield = 82%, 173.3 mg (1 mmol scale with the use of 3 equiv. of aryl bromide **2a**). White solid.

M.p.: 45.3–47.1 °C.

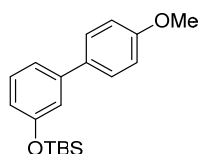
^1H NMR (400 MHz, CDCl_3): δ 7.61–7.56 (m, 2H), 7.26–7.23 (m, 2H), 7.03 (dt, $J = 6.6, 2.6$ Hz, 3H), 3.89 (s, 3H), 2.44 (s, 6H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 140.7, 138.1, 133.9, 128.3, 128.1, 124.6, 114.0, 55.2, 21.4 ppm.

IR (KBr): $\nu = 2953, 2834, 1613, 1516, 1483, 1294, 1267, 1244, 1176, 1039, 834, 761, 731 \text{ cm}^{-1}$.

HRMS (m/z): calcd for $\text{C}_{15}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$ 213.1274, found: 213.1279.

tert-Butyl((4'-methoxy-[1,1'-biphenyl]-3-yl)oxy)dimethylsilane (3ka)



Yield = 84%, 264.5 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2a**). Colorless oil.

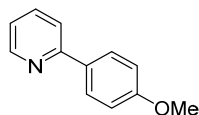
^1H NMR (400 MHz, CDCl_3): δ 7.56–7.51 (m, 2H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.17 (ddd, $J = 7.7, 1.7, 1.0$ Hz, 1H), 7.08–7.05 (m, 1H), 7.02–6.97 (m, 2H), 6.82 (ddd, $J = 8.0, 2.4, 1.0$ Hz, 1H), 3.87 (s, 3H), 1.04 (s, 9H), 0.26 (s, 6H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 159.1, 155.9, 142.2, 133.5, 129.6, 128.1, 119.8, 118.5, 118.3, 114.1, 55.3, 25.7, 18.2, -4.4 ppm.

IR (KBr): ν = 2956, 2930, 2857, 1601, 1586, 1518, 1479, 1441, 1289, 1249, 1211, 1180, 940, 834, 784, 697, 573 cm⁻¹.

HRMS (m/z): calcd for C₁₉H₂₇O₂Si [M+H]⁺ 315.1775, found: 315.1774.

2-(4-Methoxyphenyl)pyridine (3la)



Yield = 44%, 82.0 mg (1 mmol scale with the use of 2 equiv. of aryl bromide **2a**). Yellow solid.

M.p.: 53.3-54.7 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.65 (ddd, *J* = 4.8, 1.7, 1.0 Hz, 1H), 8.00–7.90 (m, 2H), 7.77–7.62 (m, 2H), 7.17 (ddd, *J* = 7.1, 4.8, 1.4 Hz, 1H), 7.06–6.93 (m, 2H), 3.86 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 160.4, 157.1, 149.5, 136.6, 132.0, 128.1, 121.4, 119.8, 114.1, 55.3 ppm.

IR (KBr): ν = 2999, 2837, 1628, 1605, 1515, 1463, 1434, 1247, 1179, 1037, 840, 779, 739 cm⁻¹.

HRMS (m/z): calcd for C₁₂H₁₂NO [M+H]⁺ 186.0913, found: 186.0918.

Reference

1. R. S. Lewis, M. F. Wisthoff, J. Grissmerson and W. J. Chain, Metal-Free Functionalization of *N,N*-Dialkylanilines via Temporary Oxidation to *N,N*-Dialkylaniline *N*-Oxides and Group Transfer. *Org. Lett.*, 2014, **16**, 3832-3835.
2. T. Saitoh, S. Yoshida and J. Ichikawa, 1,8-Bis(diphenylmethyl)naphthalenediyl Dication as an Organic Oxidant: Synthesis of Benzidines via Self-Coupling of *N,N*-Dialkylanilines. *Org. Lett.*, 2004, **6**, 4563-4565,
3. L.-G. Xie and Z.-X. Wang, Nickel-Catalyzed Cross-Coupling of Aryltrimethylammonium Iodides with Organozinc Reagents. *Angew. Chem. Int. Ed.*, 2011, **50**, 4901-4904.
4. X.-Q. Zhang and Z.-X. Wang, Cross-Coupling of Aryltrimethylammonium Iodides with Arylzinc Reagents Catalyzed by Amido Pincer Nickel Complexes. *J. Org. Chem.*, 2012, **77**, 3658-3663.
5. S. B. Blakey and D. W. C. MacMillan, The First Suzuki Cross-Couplings of Aryltrimethylammonium Salts. *J. Am. Chem. Soc.*, 2003, **125**, 6046-6047.

¹H, ¹³C, and ¹⁹F NMR spectra of products

