**Palladium-Catalyzed Cross-Coupling of Aryl Triethylammonium Bis(catechol)
Silicates with Aryl Bromides Using Microwave Irradiation**

Supporting Information

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General Experimental

Thin-layer chromatography (TLC) was performed on 0.25 mm Merck silica gel coated plates treated with a UV-active binder with compounds being identified by one or more of the following methods: UV (254 nm), iodine, or vanillin/sulfuric acid charring. Flash chromatography was performed using thick walled columns and medium pressure silica gel (Whatman 200-425 mesh), with column length and diameter being determined by the method of Still.¹ Melting points were taken in Kimax soft glass capillary tubes using a Thomas-Hoover Uni-Melt capillary melting point apparatus (Model 6406K) equipped with a calibrated thermometer. Melting points are corrected. Infrared spectra band positions are reported in reciprocal centimeters (cm^{-1}) and relative intensities are listed as br (broad), s (strong), m (medium), or w (weak). Nuclear magnetic resonance (^1H , ^{13}C NMR) spectra were recorded on a 400 MHz spectrometer. Chemical shift values are reported in parts per million (δ) relative to tetramethylsilane (TMS). Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Low resolution mass spectrometry (LRMS) and high resolution mass spectrometry (HRMS) data are reported in the form of m/z (intensity relative to base peak = 100). The matrix used for fast atom bombardment (FAB) was ethylene glycol. Tetrahydrofuran was distilled from sodium/benzophenone ketyl prior to use. Bis(dibenzylideneacetone)palladium ($\text{Pd}(\text{dba})_2$), and tetrabutylammonium fluoride (1M solution in THF) were purchased from Acros and used as received. 2-(Dicyclohexylphosphino)biphenyl was purchased from Strem and recrystallized from ethanol prior to use.

Microwave reactions were carried out on a CEM Discover microwave reactor with a circular, single mode, self tuning microwave applicator operating at 2450 MHz. The reaction vessel was purged with argon prior to the addition of reagents.

All compounds were determined to be >95% pure by ^1H NMR or GC analysis, unless otherwise noted. Previously reported compounds were characterized *via* ^1H and ^{13}C NMR and IR and compared to literature values.

General procedure for the palladium catalyzed cross-coupling reaction of aryl bromides with aryl bis(catechol) silicates:

Aryl bromide (1.00 mmol), aryl bis(catechol) silicate (1.50 mmol), $\text{Pd}(\text{dba})_2$ (0.05 mmol) and dicyclohexylphosphinobiphenyl (0.05 mmol) were combined in a microwave tube with a magnetic stir bar. The microwave tube was sealed with a septum and 5 mL of THF was added, followed by TBAF (1.0 M in THF, 1.50 mmol). The reaction was stirred briefly to dissolve the reagents and placed into the microwave reactor. The reaction was then heated to a set temperature of 120 °C (50 W) for 10 min. The tube was removed from the reactor and the contents filtered through a short plug (2 cm) of silica gel (CH_2Cl_2 elutant). The solvent was removed *in vacuo* and the biaryl product purified via column chromatography.

Biphenyl. Column chromatography (TLC R_f = 0.54, pentane) yielded a white solid (89%) mp 69-71 °C (lit. 69-70°C). The ^1H and ^{13}C NMR and IR match that reported by Koza.²

2-Methoxybiphenyl. Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.37) yielded a colorless oil (84%). The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Buchwald.³

3-Methoxybiphenyl (Table 7, Entry 5). Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.21) yielded a colorless oil (84%); IR (CCl_4) 3064 (m), 3033 (m), 3005 (w), 2957 (m), 2940 (m), 2833 (m), 1604 (s), 1569 (s), 1480 (s), 1424 (m), 1293 (m), 1214 (s), 1176 (m), 1058 (m); ^{13}C NMR (CDCl_3) δ 55.1, 112.6, 112.6, 112.9, 119.6, 127.2, 127.4, 128.7, 129.7, 141.1, 142.7, 159.9; LRMS (EI^+) m/z 184 (M^+ , 100), 154 (22), 141 (46), 139 (18), 115 (42); HRMS (EI^+) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{O}$ 184.0888, found 184.0884. The spectral data (^1H NMR) was identical to that previously reported by Nielson.⁴

4-Methoxybiphenyl. Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.32) yielded a white solid (81%) mp 87.0-87.5 °C (lit. 87.5 °C).⁵ The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by DeShong.⁵

2-Methylbiphenyl. Column chromatography (pentane, TLC R_f = 0.57) yielded a colorless oil (86%). The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by DeShong.⁵

2,6-Dimethylbiphenyl. Column chromatography (pentane, TLC R_f = 0.47) yielded a colorless oil (80%); IR (CCl_4) 3029, (w), 2992 (w), 2950 (w), 2916 (w), 2829 (w), 1611 (m), 1500 (m), 1241 (m), 1176 (w), 1045 (w). The spectral data (^1H and ^{13}C NMR) were identical to those previously reported by Buchwald.³

4-tert-Butylbiphenyl (Table 4, Entry 8). Column chromatography (pentane, TLC R_f = 0.36) yielded a white solid (88%) mp 49-50 °C (lit. 47-49 °C).³ The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Buchwald.³

4-Acetylbiphenyl. Column chromatography (9:1 hexanes/EtOAc, TLC R_f = 0.31) yielded a white solid (89%) mp 119.0-119.4 °C (lit. 119.0-119.5 °C).⁵ The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by DeShong.⁵

4-Nitrobiphenyl. Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.20) yielded a white solid (93%) mp 114-115 °C (lit. 113-115 °C);⁶ IR (CCl_4) 3064 (w), 3036 (w), 1600 (m), 1552 (m), 1521 (s), 1476 (w), 1341 (s). The spectral data (^1H and ^{13}C NMR) were identical to those previously reported by Novak.⁶

1-Phenylnaphthalene. Column chromatography (pentane, TLC R_f = 0.42) yielded a colorless oil (84%); LRMS (EI^+) m/z 204 (M^+ , 100), 203 (74), 188 (20), 29 (50), 18 (90); HRMS (EI^+) m/z calcd for $C_{16}H_{12}$ 204.0939, found 204.0948. The IR and 1H NMR were identical to those reported by DeShong.⁵ The ^{13}C NMR was identical to that reported by Bergbreiter.⁷

2-Methoxy-biphenyl-4-carboxylic acid ethyl ester. Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.53) yielded a white solid (82%) mp 104.5-105.0 °C (lit. 105 °C);⁸ IR (CCl_4) 3040 (w), 2985 (w), 2957 (w), 2933 (w), 2874 (w), 2833 (w), 1718 (s), 1604 (m), 1500 (m), 1462 (w), 1276 (s), 1245 (m), 1183 (m), 1107 (m), 1045 (m). The spectral data (1H and ^{13}C NMR) were identical to those previously reported by Gosmimi.⁹

2,3,4-Trimethoxybiphenyl. Column chromatography (TLC R_f = 0.31, 9:1 Hexanes/EtOAc) yielded a yellow oil which was recrystallized (hexane) to give a white solid (84%) mp 47.2-47.9 °C (lit. 46-47 °C). The 1H , and ^{13}C NMR, and IR match that reported by Banwell.¹⁰

2,3,4-Trimethoxy-6-carbaldehyde-biphenyl. Column chromatography (TLC R_f = 0.24, 9:1 Hexanes/EtOAc) yielded a white solid (74%) mp 91.2-92.4 °C. IR (CCl_4) 3085 (w), 3067 (w), 3009 (w), 2960 (m), 2933 (m), 2857 (m), 1683 (s), 1587 (m), 1328 (s), 1193 (m), 1141 (s), 1096 (s); 1H NMR ($CDCl_3$) δ 3.59 (s, 3H), 3.94 (s, 3H), 3.99 (s, 3H), 7.30-7.35 (m, 3H), 7.42-7.43 (m, 2H), 9.63 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 56.6, 61.4, 61.5, 105.6, 110.2, 127.5, 128.1, 123.3, 128.4, 129.9, 130.1, 131.4, 133.2, 191.8; LRMS (FAB^+) m/z 273 ($M^+ + H$, 100), 272 (80), 255 (42), 230 (24), 214 (19), 151 (18), 135 (24), 119 (25), 85 (29), 55 (34), 43 (25); HRMS (FAB^+ , M^+) m/z calcd for $C_{16}H_{16}O_4$ 272.1049, found 272.1045.

2,3,4-Trimethoxy-6-carbomethoxy-biphenyl. Column chromatography (TLC R_f = 0.31, 4:1 Hexanes/EtOAc) yielded a white solid (79%) mp 67.2-67.8 °C. IR (CCl_4) 3065 (w), 3002 (w), 2940 (m), 2836 (w), 1718 (s), 1593 (m), 1486 (m), 1435 (m), 1397 (m), 1335 (s), 1224 (m), 1134 (m), 1100 (s), 1045 (m), 1007 (m); 1H NMR ($CDCl_3$) δ 3.54 (s, 3H), 3.57 (s, 3H), 3.94 (s, 3H), 3.96 (s, 3H), 7.22-7.26 (m, 3H), 7.37-7.38 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 51.9, 56.1, 59.9, 60.0, 108.9, 126.4, 126.9, 127.6, 129.3, 130.7, 136.7, 145.3, 151.5, 152.3, 168.1; LRMS (FAB^+) m/z 302 (M^+ , 100), 271 (79), 256 (20); HRMS (FAB^+ , M^+) m/z calcd for $C_{17}H_{20}O_5$ 302.1154, found 302.1148.

2-Methoxy-5-phenylcyclohepta-2,4,6-trien-1-one. 5-Bromotropolone was prepared according to a literature procedure.¹¹ Column chromatography (TLC R_f = 0.38, EtOAc) yielded a light tan solid (76%) mp 139.2-140.4 °C (lit. 140-141 °C).¹² The IR, 1H NMR, and ^{13}C NMR matched that reported by Banwell.¹²

1-Bromo-2,3,4-trimethoxybenzene. Pyridinium tribromide (90%) (4.66 g, 13.1 mmol), was added in small portions over 30 min to a light red solution of 1,2,3-trimethoxybenzene (2.00 g, 11.9 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (50 mg 0.18 mmol) in Ac_2O (35 mL). The deep red solution was then heated at 55 °C for 5 min. The reaction was carefully poured into 100 mL of hot water. After cooling, the mixture was extracted with 50 mL of Et_2O (x4), dried (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.44, 4:1 hexanes/ EtOAc) produced a pale yellow oil (82%). IR (CCl_4) 3009 (m), 2960 (m), 2940 (s), 2898 (m), 2836 (m), 1580 (m), 1486 (s), 1462 (s), 1414 (s), 1293 (s), 1221 (s), 1096 (s), 1017 (s). ^{13}C NMR (CDCl_3) δ 56.2, 61.0, 61.1, 108.4, 108.6, 126.8, 151.0, 153.3. The ^1H NMR matches that reported by Pettit.¹³

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Current Data Parameters

NAME	high
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20040610
Time	13.40
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	65536
SOLVENT	CDCl_3
NS	16
DS	4
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	45.3
DW	60.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

===== CHANNEL f1 =====

NUC1	^1H
P1	9.50 usec
PL1	-4.00 dB
SFO1	399.7324685 MHz

F2 - Processing parameters

SI	32768
SF	399.7300469 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	21.00 cm
CY	12.80 cm
F1P	9.000 ppm
F1	3597.57 Hz
F2P	-0.500 ppm
F2	-199.86 Hz
PPMCM	0.45238 ppm/cm
HZCM	180.83026 Hz/cm

ppm

S12

7.601
7.598
7.582
7.534
7.531
7.478

1.365

ppm

S17

ppm

S19

7.384
7.380
7.366
7.261
7.246
7.242
7.226
7.223
7.217

3.957
3.939
3.571
3.536

1.558

S20

ppm

S21

In CDCl₃