Preparation and Palladium-Catalyzed Cross Coupling of Aryl Triethylammonium (Bis)catechol Silicates With Aryl Triflates

W. Michael Seganish and Philip DeShong*

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 above 200°C were taken with a Mel-Temp apparatus using a calibrated thermometer. Melting points are corrected.

Samples used for obtaining infrared spectra were either dissolved in carbon tetrachloride or prepared as a potassium bromide pellet. 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 shifts 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), br s (broad singlet).

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, diethyl ether, and dioxane were distilled from sodium/benzophenone ketyl. Methylene chloride and pyridine were distilled from calcium hydride. Dimethylformamide and triethylamine were distilled from calcium sulfate. Methanol was fractionally distilled from calcium chloride.

2-(Dicyclohexylphosphino)biphenyl and 2-(di-*tert*-butylphosphino)biphenyl were recrystallized from ethanol prior to use. Catechol and triphenylphosphine were each recrystallized from hexanes prior to use.

All glassware used in these reactions was either oven dried at 120 °C for 12 hours or flame dried prior to use. All reactions were conducted under an atmosphere of anhydrous argon.

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. All new compounds were fully characterized using ^1H NMR, ^{13}C NMR, IR, low resolution and high resolution mass spectrometry.

Synthesis and Characterization of Aryl Catecholates.

Triethylammonium bis(1,2-benzenediolato)phenylsilicate (Table 1 Entry 1). To a maroon colored solution of catechol (13.1 g, 120 mmol) in EtOH (30 mL) was added $\text{PhSi}(\text{OMe})_3$ (11.2 mL, 60.0 mmol) and NEt_3 (8.36 mL, 60.0 mmol). The reddish-brown solution was stirred for 15 minutes during which time a white precipitate formed. The catecholate complex was further precipitated by the addition of 10 mL of ether. The reaction mixture was then filtered and the filter cake was washed with ether to yield a white powder which was dried under vacuum at 60 °C for two days to give 22.4 g (88 %) of the title compound as a white powder mp 218-220 °C (lit. 220-230 °C).² IR (KBr) 3421 (m), 3064 (w), 3040 (m), 2943 (s), 2802 (m), 2722 (m), 2360 (s), 2329 (s), 1597 (s), 1493 (s), 1359 (s), 1241 (s), 1110 (s), 1014 (s); LRMS (FAB⁺) m/z 321 (M^+ - HNEt_3 , 56), 319 (12), 239 (30), 118 (16), 102 (100), 85 (9); HRMS (FAB⁺, M^+ - NHet_3) m/z calcd for $\text{C}_{18}\text{H}_{13}\text{O}_4\text{Si}$ 321.0564, found 321.0563. The spectral data (^1H , ^{13}C NMR) were identical to those previously reported by Woolins.³

General procedure for the synthesis and characterization of triethylammonium (bis)catechol arylsilicates.

To a maroon solution of catechol (15.5 mmol) in MeOH (10 mL) was added the aryl siloxane (7.40 mmol) and NEt_3 (8.10 mmol). Reaction was stirred overnight at room temperature, during which time some precipitation of the arylsilicate occurred. The arylsilicate was further precipitated with 20 mL of ether. The solid was filtered and the filter cake washed with 50 mL of ether. The arylsilicate was dried under vacuum at 60 °C overnight.

Triethylammonium bis(1,2-benzenediolato)-(2-methoxyphenyl)silicate (Table 1 Entry 2). White crystals (82%) mp 195-199 °C; IR (KBr) 3426 (m), 3064 (m), 3036 (m), 1487 (s), 1242 (s), 1013 (m), 831 (s); ^1H NMR (DMSO- d_6) δ 1.15 (t, $J=7.6$, 9H), 3.07 (q, $J=7.6$, 6H), 3.27 (s, 3H), 6.44-6.53 (m, 8H), 6.66-6.69 (m, 2H), 7.03-7.08 (m, 2H), 8.8 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 10.7, 47.6, 56.8, 111.2, 112.0, 118.9, 121.3, 130.2, 134.0, 134.6, 152.8, 163.4; LRMS (FAB $^-$) m/z 351 ($\text{M}^- - \text{NHEt}_3$, 100), 339 (30), 325 (20), 323 (9); HRMS (FAB $^-$, $\text{M}^- - \text{HNEt}_3$) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{O}_5\text{Si}$ 351.0689, found 351.0688.

Triethylammonium bis(1,2-benzenediolato)-(3-methoxyphenyl)silicate (Table 1, Entry 3). Precipitation from ether produced a white powder which was recrystallized from methanol to yield colorless needles (94%) mp 219-220 °C; IR (KBr) 3423 (m), 3095 (s), 3057 (m), 3002 (m), 2936 (m), 2878 (m), 2836 (m), 2733 (w), 1566 (s), 1483 (s), 1407 (s), 1355 (s), 1252 (s), 1107 (m), 1048 (m), 1014 (s), 827 (s); ^1H NMR (DMSO- d_6) δ 1.15 (t, $J=7.2$, 9H), 3.06 (t, $J=7.2$, 6H), 3.62 (s, 3H), 6.48 (m, 4H), 6.59-6.62 (m, 4H), 6.71-6.74 (m, 1H), 7.06-7.08 (m, 3H), 8.70 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 9.0, 46.1, 54.9, 110.1, 113.0, 117.9, 121.0, 127.4, 128.2, 143.7, 150.7, 158.4; LRMS (FAB $^-$) m/z 351 ($\text{M}^- - \text{NHEt}_3$, 100), 259 (9); HRMS (FAB $^-$, $\text{M}^- - \text{HNEt}_3$) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{O}_5\text{Si}$ 351.0689, found 351.0679.

Triethylammonium bis(1,2-benzenediolato)-(4-methoxyphenyl)silicate (Table 1, Entry 4). White crystals (86%) mp 184-185 °C; IR (KBr) 3430 (m), 3040 (w), 2943 (s), 2831 (s), 2900 (s), 2831 (w), 2730 (s), 2077 (s), 2046 (s), 1910 (s), 1860 (s), 1751 (s), 1596 (s), 1487 (s), 1363 (s), 1246 (s), 1180 (s), 1114 (s), 1017 (s); ^1H NMR (DMSO- d_6) δ 1.24 (t, $J=7.3$, 9H), 3.22 (q, $J=7.3$, 6H), 3.69 (s, 3H), 6.66-6.74 (m, 10H), 7.54 (d, $J=3.2$, 2H), 9.51 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 8.4, 46.2, 54.8, 110.7, 112.8, 118.8, 130.8, 136.6, 149.6, 160.1; LRMS (FAB $^-$) m/z 351 ($\text{M}^- - \text{NHEt}_3$, 40), 251 (100), 138 (30), 122 (26), 46 (22); HRMS (FAB $^+$) ($\text{M}^- - \text{HNEt}_3 + \text{Li}$) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{O}_5\text{SiLi}$ 358.0849, found 358.0841.

Triethylammonium bis(1,2-benzenediolato)-(2-methylphenyl)silicate (Table 1, Entry 5). White crystals (83%) mp 194-196 °C; IR (KBr) 3429 (m), 3029 (s), 3002 (s), 2702 (s), 2536 (m), 2494 (m), 1590 (m), 1486 (s), 1355 (m), 1241 (s), 834 (s); ^1H NMR (DMSO- d_6) δ 1.15 (t, $J=8.0$, 9H), 2.32 (s, 3H), 3.06 (q, $J=8.0$, 6H), 6.61-6.72 (m, 8H), 6.92-6.95 (m, 2H), 7.00-7.02 (m, 1H), 7.43-7.45 (m, 1H), 9.45 (br s, 1H);

^{13}C NMR (DMSO- d_6) δ 8.2, 22.9, 46.1, 110.8, 118.7, 124.0, 128.0, 129.3, 133.8, 140.1, 142.2, 149.5;

LRMS (FAB $^+$) m/z 335 (M^+ - NHEt_3 , 100) 153 (10); HRMS (FAB $^+$) (M^+ - NHEt_3) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{Si}$ 335.0740, found 335.0750.

Triethylammonium bis(1,2-benzenediolato)-(3-methylphenyl)silicate (Table 1, Entry 6). White powder (90%) mp 177-179 $^{\circ}\text{C}$; IR (KBr) 3432 (m), 3064 (m), 1490 (s), 1355 (m), 1245 (s), 824 (s); ^1H NMR (DMSO- d_6) δ 1.14 (t, $J=7.2$, 9H), 2.17 (s, 3H), 3.05 (q, $J=7.2$, 6H), 6.24-6.25 (m, 1H), 6.45-6.50 (m, 4H), 6.58-6.62 (m, 4H), 6.95-7.03 (m, 2H), 7.30-7.33 (m, 2H), 8.95 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 8.7, 21.3, 45.8, 109.8, 117.5, 126.7, 128.4, 131.9, 135.1, 135.3, 141.7, 150.4; LRMS (FAB $^+$) m/z 335 (M^+ - NHEt_3 , 100), 297 (23), 148 (69), 146 (10); HRMS (FAB $^+$, M^+ - NHEt_3) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{Si}$ 335.0740, found 335.0742.

Triethylammonium bis(1,2-benzenediolato)-(4-methylphenyl)silicate (Table 1, Entry 7). Compound was contaminated with a small amount of catechol despite repeated recrystallizations from THF. White crystals (88%) mp 190-194 $^{\circ}\text{C}$; IR (KBr) 3431 (m), 3040 (s), 2971 (s), 2809 (m), 2777 (m), 2746 (m), 1600 (m), 1493 (s), 1359 (s), 1238 (s), 1103 (s), 1017 (s), 831 (s); ^1H NMR (DMSO- d_6) δ 1.14 (t, $J=7.2$, 9H), 2.18 (s, 3H), 3.05 (q, $J=7.2$, 6H), 6.22-6.28 (m, 4H), 6.47-6.50 (m, 2H), 6.58-6.61 (m, 2H), 6.94 (d, $J=7.6$, 2H), 7.41 (d, $J=7.6$, 2H), 8.87 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 8.7, 21.0, 45.7, 109.0, 109.7, 115.4, 117.4, 127.4, 135.1, 150.5; LRMS (FAB $^+$) m/z 335 (M^+ - NHEt_3 , 100), 243 (9); HRMS (FAB $^+$, M^+ - NHEt_3) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{Si}$ 335.0740, found 335.0738.

Triethylammonium bis(1,2-benzenediolato)-(3,4-benzodioxole)silicate (Table 1, Entry 8). Precipitation from ether produced a light red solid which was recrystallized from methanol to yield light brown plates (82%) mp 219.0-219.5 $^{\circ}\text{C}$; IR (KBr) 3430 (m), 3052 (m), 2994 (m), 2877 (m), 2772 (m), 2726 (w), 1479 (s), 1411 (m), 1352 (m), 1246 (s), 1034 (s), 1014 (m), 893 (s), 827 (s); ^1H NMR (DMSO- d_6) δ 1.14 (t, $J=7.2$, 9H), 3.05 (t, $J=7.2$, 6H), 5.85 (s, 2H), 6.48-6.52 (m, 4H), 6.60-6.62 (m, 4H), 6.72 (d, $J=7.6$, 1H), 6.99 (s, 1H), 7.07 (d, $J=7.6$, 2H), 8.70 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 9.1, 46.1, 100.2, 107.9, 110.1, 114.9, 117.9, 129.4, 135.3, 146.5, 147.4, 150.7; LRMS (FAB $^+$) m/z 365 (M^+ - NHEt_3 , 100), 298 (9), 148 (45); HRMS (FAB $^+$, M^+ - NHEt_3) m/z calcd for $\text{C}_{19}\text{H}_{13}\text{O}_6\text{Si}$ 365.0481, found 365.0480.

Triethylammonium bis(1,2-benzenediolato)-(4-carboethoxyphenyl)silicate (Table 1, Entry 9). White crystals (89%) mp 230-240 °C (decomp.); IR (KBr) 3433 (m), 3043 (m), 2981 (m), 2736 (w), 1721 (s), 1486 (s), 1279 (s), 1245 (s), 1089 (m), 1020 (m), 824 (s); ^1H NMR (DMSO- d_6) δ 1.13 (t, $J=7.2$, 9H), 1.26 (t, $J=6.8$, 3H), 2.99-3.00 (m, 6), 4.24 (q, $J=6.8$, 2H), 6.47-6.50 (m, 4H), 6.59-6.62 (m, 4H), 7.68 (d, $J=8.0$, 2H), 7.71 (d, $J=8.0$, 2H), 8.70 (br, 1H); ^{13}C NMR (DMSO- d_6) δ 9.1, 14.2, 45.7, 60.4, 109.9, 115.7, 117.7, 127.3, 129.1, 134.5, 150.1; LRMS (FAB $^+$) m/z 393 ($\text{M}^+ - \text{NHEt}_3$, 100), 320 (11); HRMS (FAB $^+$, $\text{M}^+ - \text{NHEt}_3$) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{O}_6\text{Si}$ 393.0794, found 393.0791.

Triethylammonium bis(1,2-benzenediolato)-3-(4-methoxy)pyridylsilicate (11). White powder, recrystallization from methanol yielded white flakes (94%); mp 173-174 °C; IR (KBr) 3405 (w), 3056 (s), 3013 (s), 2932 (m), 2833 (m), 2730 (m), 1583 (s), 1491 (s), 1355 (s), 1234 (s), 1110 (s), 1020 (s), 819 (s); ^1H NMR (DMSO- d_6) δ 1.15 (t, $J=7.1$, 9H), 3.10 (q, $J=7.1$, 6H), 3.73 (s, 3H), 6.19-6.25 (m, 4H), 6.48-6.50 (m, 2H), 6.58-6.63 (m, 2H), 7.71-7.74 (m, 2H), 8.22 (s, 1H), 8.89 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 10.1, 47.2, 54.2, 111.4, 116.7, 119.2, 147.5, 151.7, 153.5, 155.1, 165.1; LRMS (FAB $^+$) m/z 352 ($\text{M}^+ - \text{NHEt}_3$, 100), 169 (60); HRMS (FAB $^+$, $\text{M}^+ - \text{NHEt}_3$) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}_5\text{NSi}$ 352.0641, found 352.0648.

General Procedure for the synthesis and characterization of aryl triflates.

Method A

In a modified procedure of Ritter,⁴ triflic anhydride (11 mmol) was added dropwise to the corresponding phenol (10 mmol) in pyridine (10 mL) at 0 °C and stirred for 10 minutes at 0 °C. The reaction was then allowed to stir at room temperature for 12 h. The solution was diluted with 25 mL of ether and extracted with a 1M solution of CuSO_4 (25 mL x3). The organic layer was then washed with water (25 mL), dried (MgSO_4), and concentrated *in vacuo*. The aryl triflate was then purified *via* silica gel chromatography.

Method B

Triflate was prepared according to a modified procedure of Barf.⁵ Phenyl trifluoromethanesulfonamide (11 mmol), triethylamine (11 mmol) and the corresponding phenol (10 mmol) were combined in 20 mL of CH_2Cl_2 and stirred at room temperature for 12 h. The solution was then poured into 50 mL of water and extracted twice with 50 mL of CH_2Cl_2 . The organic layer was dried (MgSO_4), and concentrated *in vacuo*. The aryl triflate was then purified *via* silica gel chromatography.

Method C

The following is a modified procedure of Genet.⁶ 4-aminophenol (5 mmol) and triethylamine (5 mmol) were added to CH₂Cl₂ (20 mL) and stirred at room temperature for 30 minutes. The solution was cooled to -40 °C and trifluoromethanesulfonyl chloride (5 mmol) in 3 mL of CH₂Cl₂ was added over 10 minutes. The resulting solution was stirred at -40 °C for 30 min, followed by 1 hour at room temperature. Diethyl ether was added (50 mL) and the mixture was filtered. The filtrate was washed with brine (50 mL), dried (MgSO₄), and evaporated. The triflate was then purified *via* silica gel chromatography.

4-Methoxyphenyl trifluoromethanesulfonate (Table 4, Entry 1). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.49) yielded a pale yellow oil (94%); ¹³C NMR (CDCl₃) δ 55.4, 114.0, 119.0 (q, *J*_{CF} = 322), 122.2, 143.0, 159.1. The spectral data (IR, ¹H NMR) were identical to those previously reported by Stille.⁷

2-Methoxyphenyl trifluoromethanesulfonate (Table 4, Entry 2). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.46) yielded a colorless oil (83%); ¹³C NMR (CDCl₃) δ 56.2, 113.36, 119.0 (q, *J*_{CF} = 321), 121.0, 122.6, 129.5, 139.0, 151.6. The spectral data (IR, ¹H NMR) were identical to those previously reported by Cabri.⁸

4-Phenylcarbaldehyde trifluoromethanesulfonate (Table 4, Entry 3). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.46) yielded a white solid mp 140-142 °C (86%); IR (CCl₄) 2826 (m), 2791 (w), 2729 (m), 1714 (s), 1593 (s), 1500 (m), 1438 (s), 1210 (s), 1141 (s), 886 (s); ¹H NMR (CDCl₃) δ 7.51 (m, 2H), 8.01-8.04 (m, 2H), 10.06 (s, 1H); ¹³C NMR (CDCl₃) δ 118.7 (q, *J*_{CF} = 320), 123.3, 131.6, 135.8, 153.0, 190.1; LRMS (EI⁺) *m/z* 254 (M⁺, 80), 253 (12), 189 (100), 161 (10), 95 (18), 69 (10), 65 (25); HRMS (EI⁺) *m/z* for C₈H₄O₄F₃S calcd 252.9782, found 252.9790.

2-Acetylphenyl trifluoromethanesulfonate (Table 4, Entry 4). Commercially available from Aldrich.

2-Acetylphenyl trifluoromethanesulfonate (Table 4, Entry 5). Triflate was prepared according to method

A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.33) yielded a pale yellow oil (91%); ^{13}C NMR (CDCl_3) δ 29.3, 118.2 (q, J_{CF} = 319), 122.9, 128.9, 131.1, 132.0, 134.0, 146.9, 196.9; LRMS (EI^+) m/z 268 (M^+ , 35), 253 (100), 189 (10), 120 (75), 107 (17), 92 (39), 77 (28), 69 (39), 63 (23), 43 (19); HRMS (EI^+) m/z calcd for $\text{C}_9\text{H}_7\text{O}_4\text{F}_3\text{S}$ 268.0017, found 268.0027. The spectral data (IR, ^1H NMR) were identical to those previously reported by Cabri.⁸

4-Carbomethoxyphenyl trifluoromethanesulfonate (Table 4, Entry 6). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.51) yielded a colorless oil (95%); The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by DeShong.⁹

4-Acetamidophenyl trifluoromethanesulfonate (Table 4, Entry 7). Triflate was prepared according to method A. Crude compound was isolated as a red solid. Recrystallization from toluene yielded colorless needles (92%) mp 125.5-126.0 °C (lit. 120-124 °C);¹⁰ IR (KBr) 3306 (s), 3202 (w), 3130 (w), 3081 (w), 3040 (w), 2795 (w), 1673 (s), 1535 (s), 1428 (s), 1221 (s), 1138 (s) 896 (s); ^1H NMR (DMSO) δ 2.06 (s, 3H), 7.41 (d, J =8.1, 2H), 7.72 (d, J =8.1, 2H). 10.23 (s, 1H); ^{13}C NMR (DMSO) δ 24.0, 118.3 (q, J_{CF} = 322), 120.3, 121.8, 139.7, 144.0, 168.7; LRMS (EI^+) m/z 283 (M^+ , 51), 150 (33), 108 (100), 43 (34); HRMS (EI^+) m/z for $\text{C}_9\text{H}_9\text{O}_4\text{NF}_3\text{S}$ calcd 284.0204, found 284.0202.

4-tert-Butyl phenyl trifluoromethanesulfonate (Table 4, Entry 8). Triflate was prepared according to method A. Column chromatography (19:1 hexane/EtOAc, TLC R_f = 0.52) yielded a colorless oil (87%); IR (CCl_4) 3064 (w), 2967 (s), 2905 (m), 2867 (m), 1504 (s), 1424 (s), 1214 (s), 1145 (s), 889 (s); ^{13}C NMR (CDCl_3) δ 31.3, 34.8, 118.7 (q, J_{CF} = 319), 120.9, 123.8, 127.3, 147.7, 151.8; LRMS (EI^+) m/z 282 (M^+ , 15), 267 (100), 175 (20), 134 (11), 91 (17); HRMS (EI^+) m/z for $\text{C}_{11}\text{H}_{13}\text{O}_3\text{F}_3\text{S}$ calcd 282.0538, found 282.0534. The spectral data (^1H NMR) was identical to that previously reported by Zhu.¹¹

4-Aminophenyl trifluoromethanesulfonate (Table 4, Entry 9). Triflate was prepared according to method C. Column chromatography (1:1 hexane/EtOAc, TLC R_f = 0.52) yielded a light brown oil (92%);

IR (CCl₄) 3496 (m), 3402 (m), 3054 (w), 3023 (w), 1618 (m), 1545 (m), 1504 (s), 1421 (s), 1252 (m), 1214 (s), 1145 (s), 889 (s); ¹H NMR (CDCl₃) δ 3.58 (br s, 2H), 6.56 (d, *J*=8.8, 2H), 7.99 (d, *J*=8.8, 2H); ¹³C NMR (CDCl₃) δ 115.6, 118.6 (q, *J*_{CF} = 320), 122.3, 141.6, 147.2; LRMS (EI⁺) *m/z* 241 (M⁺, 40), 108 (100), 80 (15); HRMS *m/z* calcd for C₇H₆O₃NF₃S 241.0020 found 241.0018.

4-Cyanophenyl trifluoromethanesulfonate (Table 4, Entry 10). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.43) yielded a colorless oil (84%); IR (CCl₄) 3105 (w), 3074 (w), 2236 (s), 1600 (s), 1504 (s), 1421 (s), 1245 (s), 1210 (s), 1155 (s), 882 (s); ¹³C NMR (CDCl₃) δ 113.2, 117.3, 118.5 (q, *J*_{CF} = 320), 122.9, 134.9, 152.3. The spectral data (¹H NMR) was identical to that previously reported by Cabri.⁸

2-Cyanophenyl trifluoromethanesulfonate (Table 4, Entry 11). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.40) yielded a colorless oil (77%); ¹³C NMR (CDCl₃) δ 107.4, 113.8, 118.7 (q, *J*_{CF} = 319), 122.8, 123.6, 129.2, 134.6, 135.2, 149.8; LRMS (EI⁺) *m/z* 251 (M⁺, 55), 187 (35), 159 (100), 139 (11), 90 (45), 69 (85), 63 (15); HRMS (EI⁺) *m/z* for C₈H₄O₃NF₃S calcd 250.9864, found 250.9869. The spectral data (IR, ¹H NMR) were identical to those previously reported by Cabri.⁸

4-Nitrophenyl trifluoromethanesulfonate (Table 4, Entry 12). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.56) yielded a white solid (96%) mp 51.0-51.9 °C (lit. 50.5-52 °C).⁹ The spectral data (IR, ¹H and ¹³C NMR) were identical to those previously reported by DeShong.⁹

1-Naphthyl trifluoromethanesulfonate (Table 4, Entry 13). Triflate was prepared according to method A. Column chromatography (19:1 hexane/EtOAc, TLC R_f = 0.36) yielded a colorless oil (81%). The spectral data (IR, ¹H and ¹³C NMR) were identical to those previously reported by DeShong.⁹

2,6-Dimethoxyphenyl trifluoromethanesulfonate (Table 4, Entry 14). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.39) yielded a colorless oil (94%). The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Saa.¹²

2-Methylphenyl trifluoromethanesulfonate (Table 4, Entry 15). Triflate was prepared according to method A. Column chromatography (19:1 hexane/EtOAc, TLC R_f = 0.49) yielded a colorless oil (83%); ^{13}C NMR (CDCl_3) δ 118.9 (q, J_{CF} = 318), 121.4, 123.7, 128.5, 131.1, 132.4, 148.8. The spectral data (IR, ^1H NMR) were identical to those previously reported by Cabri.⁸

2,6-Dimethylphenyl trifluoromethanesulfonate (Table 4, Entry 16). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.66) yielded a colorless oil (87%). The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Saa.¹³

2-Formyl-6-methoxyphenyl trifluoromethanesulfonate (Table 4, Entry 17). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.26) yielded white crystals (88%) mp 37.9-38.5 °C (lit. 36-38 °C);¹³ IR (CCl_4) 3023 (w), 2964 (w), 2947 (m), 2888 (w), 2843 (m), 2757 (w), 1704 (s), 1583 (s), 1486 (s), 1431 (s), 1221 (s), 1148 (s), 1076 (s), 882 (s). The spectral data (^1H and ^{13}C NMR) were identical to those previously reported by Saa.¹³

2-Pyridyl trifluoromethanesulfonate (Table 5, Entry 1). Triflate was prepared according to method A. Triflate was isolated in 96% yield and 97% purity (GC) without purification as a colorless oil; ^{13}C NMR (CDCl_3) δ 118.9 (q, J_{CF} = 320), 115.4, 124.6, 141.4, 148.9, 156.2. The spectral data (IR, ^1H NMR) were identical to those previously reported by Umemoto.¹⁴

3-Pyridyl trifluoromethanesulfonate (Table 5, Entry 2). Triflate was prepared according to method A. Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.30) yielded a colorless oil (89%); IR (CCl_4) 3064 (w), 1593 (s), 1569 (s), 1466 (s), 1428 (s), 1228 (s), 1165 (s), 1141 (s), 893 (s); ^1H NMR (CDCl_3) δ 7.43-7.46 (m, 1H), 7.66-7.69 (m, 1H), 8.64-8.67 (m, 2H); ^{13}C NMR (CDCl_3) δ 118.9 (q, J_{CF} = 319), 124.9,

129.2, 143.1, 147.1, 149.8; LRMS (EI⁺) m/z 228 (M⁺, 10), 227 (100), 163 (32), 94 (18), 66 (44), 39 (31); HRMS (EI⁺) m/z for C₆H₅O₃NF₃S calcd 227.9942, found 227.9939.

5-Indole trifluoromethanesulfonate (Table 5, Entry 3). Triflate was prepared according to method B.

Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.24) yielded a colorless oil (76%); IR (CCl₄) 3489 (s), 1428 (s), 1221 (s), 1145 (s), 1100 (s), 941 (s), 879 (s); ¹H NMR (CDCl₃) δ 6.49 (s, 1H), 6.98-7.01 (m, 1H), 7.15-7.21 (m, 2H), 7.49 (s, 1H), 8.26 (br s, 1H); ¹³C NMR (CDCl₃) δ 103.1, 112.1, 112.8, 114.8, 118.6 (q, J_{CF} = 318), 126.9, 128.0, 129.5, 134.6, 143.6; LRMS (EI⁺) m/z 265 (M⁺, 67), 132 (100), 104 (64); HRMS (EI⁺) m/z for C₉H₆O₃NF₃S calcd 265.0020, found 265.0019.

2-Quinolyl trifluoromethanesulfonate (17). Triflate was prepared according to method A. Triflate was isolated in 97% yield and 98% purity (GC) without purification as a pale yellow oil; ¹³C NMR (CDCl₃) δ 113.1, 118.8 (q, J_{CF} = 320), 127.8, 128.8, 131.3, 142.1, 145.9, 153.8. The spectral data (IR, ¹H NMR) were identical to those previously reported by Stille.⁷

Phenyl trifluoromethanesulfonate (Table 7 Entries 1,4-6). Triflate was prepared according to method A.

Column chromatography (4:1 hexane/EtOAc, TLC R_f = 0.63) yielded a colorless oil (85%). The spectral data (IR, ¹H and ¹³C NMR) were identical to those previously reported by DeShong.⁹

2-(((Trifluoromethyl)sulfonyl)oxy)-2,4,6-cycloheptatrienone (4). Triflate was prepared according to method A. Column chromatography (1:1 hexane/EtOAc, TLC R_f = 0.34) yielded a yellow oil (64%). The spectral data (IR, ¹H and ¹³C NMR) were identical to those previously reported by Stille.¹⁵

α -Tocopherol trifluoromethanesulfonate (6). Triflate was prepared according to method A. Column chromatography (pentane, TLC R_f = 0.44) yielded a viscous colorless oil (85%); IR (CCl₄) 2957 (s), 2929 (s), 2867 (m), 1466 (m), 1421 (m), 1404 (s), 1380 (m), 1221 (s), 1145 (s), 1111 (w), 1035 (w), 879 (m); ¹H NMR (CDCl₃) δ 0.84-0.87 (m, 13H), 1.07-1.54 (m, 23H), 1.72-1.80 (m, 2H), 2.10 (s, 3H), 2.19 (s, 3H), 2.22 (s, 3H), 2.57-2.59 (m, 2H); ¹³C NMR (CDCl₃) δ 12.0, 13.2, 14.0, 19.7, 19.8, 20.7, 21.0, 22.7, 22.8,

23.9, 24.5, 24.9, 28.0, 32.8, 32.9, 37.3, 37.4, 37.5, 39.4, 75.7, 77.4, 118.5, 119.0 (q, $J_{CF} = 321$), 124.4, 126.7, 128.1, 139.7, 151.0; LRMS (FAB⁺) m/z 562 (M⁺, 6), 429 (60), 428 (15), 337 (16), 297 (64), 203 (22), 165 (100), 149 (44), 55 (34), 43 (33); HRMS (FAB⁺) m/z calcd for C₃₀H₄₉O₄F₃S 562.3304, found 562.3303.

4-Trifluoromethanesulfonyloxy coumarin (8). Triflate was prepared according to method A. Filtration through a short pad of silica gel yielded pale yellow crystals (88%) mp 59.5-60.9 °C (lit. 59-60 °C);¹⁶ ¹³C NMR (CDCl₃) δ 105.9, 113.9, 117.4, 118.6 (q, $J_{CF} = 320$), 122.6, 125.3, 134.2, 153.5, 157.2, 159.6; LRMS (EI⁺) m/z 294 (M⁺, 76) 202 (100), 133 (98), 116 (11), 105 (70), 92 (31), 69 (92), 63 (24), 51 (18); HRMS (EI⁺) m/z calcd for C₁₀H₅O₄F₃S 293.9807, found 293.9798. The spectral data (IR, ¹H NMR) were identical to those previously reported by Wattanasin.¹⁶

General procedure for the palladium catalyzed cross coupling of pentavalent aryl (bis)catechol complexes of silicon.

Aryl triflate (1.0 mmol), catechol complex (1.5 mmol), Pd(dba)₂ (0.050 mmol), and dicyclohexyl phosphinobiphenyl (0.050 mmol) were combined in a 50 mL round bottom flask equipped with a magnetic stir bar and placed under argon. THF was added *via* syringe (10 mL), followed by 1.5 mmol of TBAF (1.0 M solution in THF). The deep red-brown solution was subjected to one freeze-pump-thaw cycle followed by heating at reflux for 6 h. The crude reaction mixture was diluted with ether (50 mL), and poured into 50 mL of an aqueous 1.0 M NaOH solution. The aqueous layer was then washed twice with 50 mL of ether. The combined ethereal extracts were dried (MgSO₄), and evaporated *in vacuo*. The coupled products were purified *via* column chromatography.

4-Methoxybiphenyl (Table 4, Entry 1). Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.32) yielded a white solid (95%) mp 87.0-87.5 °C (lit. 87.5 °C).⁹ The spectral data (IR, ¹H and ¹³C NMR) were identical to those previously reported by DeShong.⁹

2-Methoxybiphenyl (Table 4, Entry 2). Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.37) yielded a colorless oil (95%). The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Buchwald.¹⁷

4-Phenylbenzaldehyde (Table 4, Entry 3). Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.49) yielded a yellow solid. Recrystallization from petroleum ether yielded a white powder (98%) mp 60.5-61.0 °C (lit. 60-61 °C);¹⁸ IR (CCl_4) 3064 (w), 3029 (w), 2822 (w), 2726 (w), 1707 (s), 1604 (m), 1549 (m), 1210 (w), 1165 (w). The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Leadbeater.¹⁸

4-Acetylbiphenyl (Table 4, Entry 4). Column chromatography (9:1 hexanes/EtOAc, TLC R_f = 0.31) yielded a white solid (96%) mp 119.0-119.4 °C (lit. 119.0-119.5 °C).⁹ The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by DeShong.⁹

2-Acetylbiphenyl (Table 4, Entry 5). Column chromatography (9:1 hexanes/EtOAc, TLC R_f = 0.43) yielded a slight yellow oil (93%). The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Clive.¹⁹

4-Carbomethoxybiphenyl (Table 4, Entry 6). Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.32) yielded a white solid (93%) mp 115-116 °C (lit. 116-117 °C);⁹ ^{13}C NMR (CDCl_3) δ 52.1, 127.1, 127.3, 128.1, 128.8, 128.9, 130.1, 140.0, 145.6, 167.0. The spectral data (IR, ^1H NMR) were identical to those previously reported by DeShong.⁹

N-Acetyl-4-aminobiphenyl (Table 4, Entry 7). Column chromatography (1:1 hexanes/EtOAc, TLC R_f = 0.27) yielded a white solid (92%) mp 152-153 °C (lit. 150-153 °C).¹⁷ The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Buchwald.¹⁷

4-*tert*-Butylbiphenyl (Table 4, Entry 8). Column chromatography (pentane, TLC R_f = 0.36) yielded a white solid (95%) mp 49-50 °C (lit. 47-49 °C).¹⁷ The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by Buchwald.¹⁷

4-Cyanobiphenyl (Table 4, Entry 10). Column chromatography (1:1 hexanes/EtOAc, TLC R_f = 0.40) yielded a white solid (91%) mp 85.6-86.2 °C (lit. 86-87 °C);¹⁷ IR (CCl_4) 3064 (w), 3033 (w), 2232 (m), 1545 (m). The spectral data (^1H and ^{13}C NMR) were identical to those previously reported by Buchwald.¹⁷

2-Cyanobiphenyl (Table 4, Entry 11). Column chromatography (9:1 hexanes/EtOAc, TLC R_f = 0.32) yielded a pale yellow oil (89%); IR (CCl_4) 3067 (w), 3036 (w), 2933 (w), 2853 (w), 2229 (m), 1480 (m). The spectral data (^1H and ^{13}C NMR) were identical to those previously reported by Lemaire.²⁰

4-Nitrobiphenyl (Table 4, Entry 12). Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.20) yielded a white solid (49%) mp 114-115 °C (lit. 113-115 °C);²¹ 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.²¹

1-Phenylnaphthalene (Table 4, Entry 13). Column chromatography (pentane, TLC R_f = 0.42) yielded a colorless oil (86%); LRMS (EI^+) m/z 204 (M^+ , 100), 203 (74), 188 (20), 29 (50), 18 (90); HRMS (EI^+) m/z calcd for $\text{C}_{16}\text{H}_{12}$ 204.0939, found 204.0948. The IR and ^1H NMR were identical to those reported by DeShong.⁹ The ^{13}C NMR was identical to that reported by Bergbreiter.²²

2-Methylbiphenyl (Table 4, Entry 15). Column chromatography (pentane, TLC R_f = 0.57) yielded a colorless oil (92%). The spectral data (IR, ^1H and ^{13}C NMR) were identical to those previously reported by DeShong.⁹

2,6-Dimethylbiphenyl (Table 4, Entry 16). Reaction was run in refluxing dioxane. Column chromatography (pentane, TLC R_f = 0.47) yielded a colorless oil (96%); 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.¹⁷

2-Methoxy-6-formyl-biphenyl (Table 4, Entry 17). Reaction was run in refluxing dioxane. Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.23) yielded a pale yellow oil (86%); IR (CCl_4) 3064 (w), 3033 (w), 3005 (w), 2960 (w), 2933 (w), 2864 (w), 2833 (w), 2746 (w), 1694 (s), 1593 (m), 1576 (m), 1469 (m), 1259 (s), 1065 (m), 910 (m); ^1H NMR (CDCl_3) δ 3.77 (s, 3H), 7.18 (d, J =8.4, 1H), 7.31-7.33 (m, 2H), 7.42-7.46 (m, 4H), 7.62 (d, J =7.6, 1H), 9.73 (s, 1H); ^{13}C NMR (CDCl_3) δ 56.0, 115.8, 119.0, 127.9, 128.0, 128.7, 131.0, 133.1, 134.9, 135.4, 157.0, 192.5; LRMS (EI^+) m/z 212 (M^+ , 100), 211 (50), 197 (19), 180 (25), 169 (27), 152 (26), 139 (28), 115 (18); HRMS (EI^+) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$ 212.0837, found 212.0831.

2-Phenylpyridine (Table 5, Entry 1). Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.39) yielded a pale yellow oil (50%); IR (CCl_4) 3088 (w), 3067 (m), 3037 (w), 3009 (w), 1580 (s), 1566 (s), 1466 (s), 1445 (s), 1424 (m). The spectral data (^1H and ^{13}C NMR) were identical to those previously reported by Furukawa.²³

3-Phenylpyridine (Table 5, Entry 2). Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.24) yielded a yellow oil (53%); IR (CCl_4) 3095 (w), 3061 (w), 3029 (w), 2929 (w), 2853 (w), 1476 (m), 1455 (m), 1411 (s), 1007 (m); ^{13}C NMR (CDCl_3) δ 123.5, 127.1, 128.1, 129.1, 134.3, 136.6, 137.8, 148.3, 148.4; LRMS m/z (EI^+) 155 (M^+ , 100), 154 (39), 127 (11), 76 (15), 63 (9), 43 (23); HRMS (EI^+) m/z for $\text{C}_{11}\text{H}_9\text{N}$ calcd 155.0735, found 155.0725. The spectral data (^1H NMR) was identical to that previously reported by Sakamoto.²⁴

5-Phenylindole (Table 5, Entry 3). Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.24) yielded a light brown oil (76%); IR (CCl_4) 3485 (m), 3067 (w), 3029 (w), 907 (m); ^1H NMR (CDCl_3) δ 6.56 (s, 1H), 7.10-7.12 (m, 1H), 7.27-7.44 (m, 5H), 7.64 (d, J =7.6, 2H), 7.85 (s, 1H), 7.99 (br s, 1H); ^{13}C NMR (CDCl_3) δ 102.8, 111.3, 119.2, 121.8, 124.9, 126.3, 127.3, 128.3, 128.6, 133.3, 135.2, 142.5; LRMS

(FAB⁺) m/z 194 (M⁺, 100), 193 (70), 165 (10); HRMS (FAB⁺) m/z calcd for C₁₄H₁₁N 193.0891, found 193.0900.

2-Phenylquinoline (Table 5, Entry 4). Column chromatography (9:1 hexanes/EtOAc, TLC R_f = 0.36) yielded a white solid (91%) mp 82.0-83.0 °C (lit. 82.0-82.5 °C);²⁵ IR (CCl₄) 3061 (m), 3033 (m), 1604 (m), 1552 (s). The spectral data (¹H and ¹³C NMR) were identical to those previously reported by Miyaura.²⁵

2-Methyl-4-methoxybiphenyl (Table 7, Entry 1). Column chromatography (4:1 hexanes/CH₂Cl₂, TLC R_f = 0.27) yielded a colorless oil (20%); IR (CCl₄) 3064 (w), 3002 (w), 2954 (w), 2933 (w), 2909 (w), 2840 (w), 1614 (w), 1545 (s), 1248 (m); LRMS (FAB⁺) m/z 198 (M⁺, 24), 133 (22), 89 (35), 73 (35), 45 (35); HRMS (FAB⁺) m/z calcd for C₁₄H₁₄O 198.1045, found 198.1052. The spectral data (¹H and ¹³C NMR) were identical to those previously reported by Lipshutz.²⁶

3-Methyl-4-methoxybiphenyl (Table 7, Entry 2). Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.47) yielded a white solid (97%) mp 52.0-53.2 °C (lit. 54 °C);²⁷ IR (CCl₄) 3057 (w), 3033 (w), 2995 (w), 2957 (w), 2936 (w), 2840 (w), 1614 (s), 1514 (s), 1252 (s), 1170 (m), 1038 (m); ¹³C NMR (CDCl₃) δ 21.6, 55.3, 114.1, 123.8, 127.4, 127.6, 128.2, 128.6, 133.9, 138.3, 140.8, 159.0; LRMS (FAB⁺) m/z 198 (M⁺, 100), 184 (5), 183 (5); HRMS (FAB⁺) m/z calcd for C₁₄H₁₄O 198.1045, found 198.1036. The spectral data (¹H NMR) was identical to that previously reported by Rao.²⁷

4-Methyl-4-methoxybiphenyl (Table 7, Entry 3). Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.40) yielded a white solid (92%) mp 107.4-108.1 °C (lit. 105-107 °C);²⁸ IR (CCl₄) 3064 (w), 3019 (w), 2957 (w), 2919 (w), 2857 (w), 1462 (w), 1448 (w); ¹³C NMR (CDCl₃) δ 21.1, 55.3, 114.1, 126.6, 128.0, 129.4, 133.7, 136.3, 138.0, 158.9. The spectral data (¹H NMR) was identical to that previously reported by Roth.²⁸

3-Methoxybiphenyl (Table 7, Entry 5). Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.21) yielded a colorless oil (87%); 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.²⁹

2-Methoxy-biphenyl-4-carboxylic acid ethyl ester (Table 7, Entry 7). Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.53) yielded a white solid (94%) mp 104.5-105.0 °C (lit. 105 °C),³⁰ 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.³¹

5-(4-Methoxy-phenyl)-1,3-benzodioxole (Table 7, Entry 8). Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.24) yielded a sticky white solid. The solid was recrystallized from Et_2O /hexanes to yield colorless plates (89%) mp 95.6-96.2 °C (lit 95-96 °C);³² IR (CCl_4) 3071 (w), 3040 (w), 3006 (w), 2961 (m), 2930 (m), 2888 (w), 2833 (w), 2775 (w), 1611 (m), 1480 (s), 1256 (s), 1218 (s), 1183 (m), 1045 (s), 945 (m). The spectral data (^1H and ^{13}C NMR) were identical to those previously reported by Bannwarth.³²

2-Phenylcyclohepta-2,4,6-triene-1-one (5). Column chromatography (4:1 hexanes/EtOAc, TLC R_f = 0.27) yielded a slightly yellow solid (89%) mp 83.5-84.2 °C (lit. 84.5-85.5 °C);³³ IR (CCl_4) 3065 (w), 3030 (w), 2930 (w), 2850 (w), 1632 (m), 1595 (s); ^{13}C NMR (CDCl_3) δ 128.1, 128.4, 129.1, 133.3, 133.7, 135.3, 136.5, 139.9, 142.4, 152.6, 186.6; LRMS (EI^+) m/z 182 (M^+ , 25), 181 (100), 154 (56), 153 (38), 76 (15); HRMS (EI^+) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{O}$ 183.0732, found 182.0727. The spectral data (^1H NMR) was identical to that previously reported by Mann.³⁴

Phenyl- α -tocopherol (7). Column chromatography (pentane, TLC R_f = 0.35) yielded a viscous, colorless oil (90%); IR (CCl_4) 3085 (w), 3057 (w), 3026 (w), 2957 (s), 2926 (s), 2864 (s), 1562 (m), 1459 (m) 1155 (m), 1103 (s); ^1H NMR (CDCl_3) δ 0.84-0.87 (m, 14H), 1.07-1.60 (m, 21H), 1.80 (m, 3H), 1.86 (s, 3H), 1.90 (s, 3H), 2.15 (m, 1H), 2.19 (s, 3H), 2.61-2.65 (m, 2H), 7.12 (m, 2H), 7.30 (t, J =8.0, 1H), 7.38 (t, J =8.0, 2H); ^{13}C NMR (CDCl_3) δ 11.9, 16.7, 17.7, 19.7, 20.8, 22.6, 22.7, 24.0, 24.5, 24.8, 27.9, 32.7, 37.4, 37.5, 39.4, 75.0, 116.6, 121.7, 126.1, 128.1, 130.1, 130.2, 131.6, 133.1, 133.4, 142.7, 150.7; LRMS (FAB^+) m/z 490 (M^+ , 19), 265 (11), 225 (100), 223 (18), 55 (16); HRMS (FAB^+) m/z calcd for $\text{C}_{35}\text{H}_{54}\text{O}$ 490.4175, found 490.4176.

5-(4-Methoxybenzene)-2-methoxypyridine (13). Column chromatography (19:1 hexanes/EtOAc, TLC R_f = 0.26) yielded a white solid (96%) mp 75.0-75.9 $^\circ\text{C}$; IR (CCl_4) 3043 (m), 3016 (m), 2981 (m), 2847 (m), 2902 (m), 2840 (m), 1604 (s), 1486 (s), 1373 (m), 1290 (s), 1279 (s), 1245 (s), 1172 (m), 1055 (m), 1020 (m); ^1H NMR (CDCl_3) δ 3.85 (s, 3H), 3.97 (s, 3H), 6.79 (d, J =12.0, 1H), 6.98 (d, J =8.0, 2H), 7.45 (d, J =8.0, 2H), 7.73-7.76 (m, 1H), 8.34 (s, 1H); ^{13}C NMR (CDCl_3) δ 53.5, 55.4, 110.7, 114.4, 127.7, 129.8, 130.4, 137.2, 144.5, 159.1, 163.2; LRMS (FAB^+) m/z 216 (M^+ , 100), 215 (30); HRMS (FAB^+) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}$ 216.1025, found 216.1033.

5-(2-Quinoyl)-2-methoxypyridine (15). Column chromatography (9:1 hexanes/EtOAc, TLC R_f = 0.31) yielded a white solid (97%) mp 78.5-79.0 $^\circ\text{C}$; IR (CCl_4) 3067 (w), 3040 (w), 3016 (w), 2981 (w), 2947 (w), 2905 (w), 2850 (w), 1604 (s), 1490 (s), 1390 (m), 1286 (m), 1020 (m); ^1H NMR (CDCl_3) δ 4.03 (s, 3H), 6.90 (d, J =8.4, 1H), 7.53 (m, 1H), 7.73 (m, 1H), 7.82 (d, J =8.4, 2H), 8.13 (d, J =8.8, 1H), 8.21 (d, J =8.8, 1H), 8.47-8.50 (m, 1H), 8.91 (s, 1H); ^{13}C NMR (CDCl_3) δ 54.3, 111.6, 118.7, 126.8, 127.6, 128.0, 129.4, 130.1, 130.4, 137.5, 138.5, 146.7, 148.8, 155.3, 165.4; LRMS (EI^+) m/z 236 (M^+ , 100), 235 (79), 207 (33), 192 (22); HRMS (EI^+) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{ON}_2$ 236.0950, found 236.0940.

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