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Supplementary Material to

Sulfonium Salts. Participants *Par Excellence* in Metal-Catalyzed Carbon-carbon Bond Forming Reactions.

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General Methods

All solvents were dried and stored over 4 Å molecular sieves prior to use. Capillary GLC analysis was performed on a Hewlett Packard 5890 with helium as the carrier gas (flow rate 0.64 mL/min, 20 m fused silica column). Analytical TLC was accomplished with glass plates precoated with Merck F_{254} silica gel 60 and visualized by UV light or iodine stain. Rotary chromatography was performed with a Chromatotron from Harrison Research using 4 mm PF_{254} silica rotors, eluting with mixtures of hexanes and ether. The arylboronic acids were prepared from the corresponding organolithium or magnesium reagent according to published procedures.[1] 1,4-Dibromobutane, *n*-BuLi (2.5 M in hexanes), and thiophene were purchased from Acros Chemicals and used as received. 2-Methoxy-5-aminopyridine, 2-mercaptopyridine, thiophenol, 2-bromobenzyl bromide, 4-bromobenzyl bromide, 2-fluorobenzyl chloride, 4-nitrobenzyl bromide and 2-tri-*n*-butylstannylthiophene were purchased from Aldrich Chemical Company and used as received. 4-Fluorothiophenol was purchased from Oakwood Chemicals. 2-Mercaptonaphthalene was purchased from Lancaster. $NH_4PF_6$was purchased from PCR.

Starting Materials

The following were prepared according to known procedures:

3,4-Dimethoxybenzyl bromide,[2] 3-thienylmethyl bromide,[3] 3-bromomethylpyridinium hydrobromide,[4] 6-bromomethyl-2*H*-1-benzopyran-2-one,[5] 1-tri-*n*-butylstannyl-2-phenylethylene,[6] tri-*n*-butylstannylbenzofuran.[7]

***N*-(2-Bromophenyl)pyrrole**: Under nitrogen, 2,5-dimethoxytetrahydrofuran (1.32 g, 10.00 mmol) was added drop-wise to 2-bromoaniline (1.72 g, 9.99 mmol) in acetic acid (15 mL. The reaction mixture was stirred for 12 h at 80 °C. After cooling to room temperature, the reaction mixture was diluted with Et_2O (40 mL) and washed several times with water then with a saturated solution of sodium bicarbonate until the pH of the water layer was basic. Activated carbon and anhydrous $MgSO_4$ were added to the Et_2O layer. After filtration and evaporation, the liquid residue waspurified by column chromatography (SiO_2, hexane-Et_2O gradient as eluent)giving product as a viscous oil (2.10 g, 9.46 mmol, 95%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, J = 7.6 Hz, 1 H), 7.39 (m, 2 H), 7.34 (m, 1 H), 6.89 (t, J = 2.0 Hz, 2 H), 6.35 (t, J = 2.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 109.1, 119.9, 122.2, 128.1, 128.3, 128.7, 133.8. HRMS (EI) Calcd for $C_{10}H_8BrN$: 220.9840. Found: 222.982.

1-(*N*-Pyrollyl)-2-(tri-*n*-butylstannyl)benzene: Under nitrogen hexa-*n*-butyldistannane (1.160 g, 2.00 mmol) was added to N-(2-bromophenyl)pyrrole (0.444 g, 2.00 mmol) in DMF (10 mL). After addition of $PdCl_2(PPh_3)_2$ (0.02 g, 0.02 mmol), the reaction mixture was stirred at 70 °C for 12 h. It was cooled to room temperature, diluted with Et_2O (30 mL), and washed with water (3 x 30 mL). The organic layer was dried over magnesium sulfate, filtered, and evaporated to leave a yellow residue that was purified by column chromatography (SiO_2, hexanes). The product was obtained as a colorless, viscous liquid (0.72 g, 1.67 mmol, 84%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 7.2 Hz, 1 H), 7.38 (m, 3 H), 6.80 (t, J = 2.0 Hz, 2 H), 6.29 (t, J = 2.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 10.2, 13.6, 27.3, 29.1, 109.3, 121.8, 125.7, 126.8, 128.9, 137.6. HRMS (EI) Calcd for $C_{22}H_{35}NSn$: 433.1791. Found: 376.1087 (M^+ - C_4H_9 mass).

Preparation of Sulfonium Salts

Benzylic and Heterobenzylic Salts.

***S*-(Benzyl) Tetramethylenesulfonium ClO_4^-** was prepared using the procedure of Aggarwal, et. al.[8]

***S*-(2-Bromobenzyl) Tetramethylenesulfonium PF_6^-.** 2-Bromobenzyl bromide (2.50 g, 10.000 mmol, 1.00 equiv) was dissolved in acetone (10 mL) then THT (1.00 g, 11.340 mmol, 1.13 equiv) and NH_4PF_6 (1.79 g, 11.00 mmol, 1.1 equiv) were added. A white solid immediately began to precipitate. After stirring at room temperature for 12 h, the solid was filtered and washed with acetone. Et_2O was added to the filtrate to induce crystallization of *S*-(2-bromobenzyl) tetramethylenesulfonium PF_6^- as white crystals (2.82 g, 70 %): Mp 155-156 °C (acetone/Et_2O, 5:1); ^1H NMR ($(CD_3)_2SO$, 300 MHz): δ 7.75 (d, J = 6.2 Hz, 1 H), 7.64 (d, J = 6.2 Hz, 1 H), 7.32-7.47 (m, 2 H), 4.59 (s, 2 H), 3.35-3.55 (m, 4 H), 2.09-2.19 (m, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 28.8, 43.8, 45.9, 125.1, 129.2, 129.9, 132.3, 133.7, 134.0. Anal. Calcd for $C_{11}H_{14}BrF_6PS$: C, 32.77; H, 3.50; Br, 19.82; F, 28.27; P, 7.68; S, 7.95. Found: C, 32.91; H, 3.58; S, 8.03.

***S*-(2-Fluorobenzyl) Tetramethylenesulfonium PF_6^-.** By the same procedure, 2-fluorobenzyl chloride (2.90 g, 20.060 mmol, 1.00 equiv), THT (2.00 g, 22.680 mmol, 2.26 equiv), and NH_4PF_6 (3.58 g, 22.00 mmol, 2.2 equiv) in acetone (10 mL) after 48 h at 55 °C gave product as white platelets (3.64 g, 52 %): Mp 231-232 °C (acetone/Et_2O, 5:1); ^1H NMR ($(CD_3)_2SO$, 300 MHz): δ 7.17- 7.65 (m, 4 H), 4.58 (s, 2 H), 3.22-3.56 (m, 4 H), 2.08-2.35 (m, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 28.6, 39.5, 43.7, 116.6 (d, $J_{(CF)}$ = 21.14 Hz), 117.4 (d, $J_{(CF)}$ = 14.34 Hz), 125.9 (d, $J_{(CF)}$ = 3.77 Hz), 132.7 (d, $J_{(CF)}$ = 8.305 Hz), 133.3 (d, $J_{(CF)}$ = 2.265 Hz), 161.1 (d, $J_{(CF)}$ = 265 Hz). Anal. Calcd for $C_{11}H_{14}F_7PS$: C, 38.60; H, 4.12; F, 38.86; P, 9.05; S, 9.37. Found: C, 38.68; H, 4.18; S, 9.44.

***S*-(4-Fluorobenzyl) Tetramethylenesulfonium PF_6^-.** To a 100 mL round-bottomed flask containing 4-fluorobenzyl chloride (10.0 g, 69.17 mmol), tetrahydrothiophene (18.29 g, 207.5 mmol), and acetone (10 mL) was added a solution of NH_4PF_6 (20.3 g, 124.5 mmol) in ~ 50 mL of acetone. After stirring at 35 °C for 16 h, the precipitated NH_4Cl was removed by filtration and washed with acetone. Solvents were evaporated and the resulting solid was dissolved in a minimal amount of acetone and crystallized by the addition of Et_2O giving analytically pure *S*-(4-fluorobenzyl)tetramethylenesulfonium PF_6^- as colorless crystals (15.71 g, 66 %): Mp

118-120 °C (acetone/hexanes); IR (KBr pellet, cm^{-1}): 3018, 2968, 1602, 1510, 1424, 1225, 827. ^1H NMR ($(CD_3)_2SO$, 300 MHz): δ 7.55 (app q, J = 2.0, 5.5 Hz, 2 H), 7.26 (app t, J = 8.8 Hz, 2 H), 4.47 (s, 2 H), 3.31 (m, 4 H), 2.13 (m, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 161.2 (d, C4 - 246 Hz), 133.1 (d, C2,C6 - 8.7 Hz), 126.5 (d, C1 - 2.62 Hz), 116.8 (d, C3,C5 - 21.81 Hz), 44.7 (s, benzylic CH_2), 43.0 (s, α-to sulfonium), 28.5 (s, β-to sulfonium). Anal. Calcd for $C_{11}H_{14}F_7PS$: C, 38.60; H, 4.12; F, 38.86; P, 9.05; S, 9.37. Found: C, 38.66; H, 4.16; S, 9.33.

***S*-(4-Nitrobenzyl) Tetramethylenesulfonium PF_6^-.** By the same procedure, 4-nitrobenzyl bromide (2.20 g, 10.190 mmol, 1.00 equiv), THT (1.00 g, 11.340 mmol, 1.11 equiv), and NH_4PF_6 (1.79 g, 11.00 mmol, 1.1 equiv) in acetone (10 mL) for 12 h at 40 °C gave crystalline product (2.95 g, 80 %): Mp 123-125 °C (acetone/Et_2O, 5:1); IR (KBr pellet, cm^{-1}): 1609 (m), 1516 (s), 1424 (m), 1346(s). ^1H NMR ($(CD_3)_2CO$, 300 MHz): δ 8.28 (d, J = 6.1 Hz, 2 H), 7.95 (d, J = 6.1 Hz, 2 H), 4.88 (s, 2 H), 3.71 (m, 4 H), 2.30-2.58 (m, 4 H). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 28.5, 43.5, 44.7, 124.3, 132.0, 136.9, 205.5. Anal. Calcd for $C_{11}H_{14}F_6NO_2PS$: C, 35.78; H, 3.82; F, 30.87; N, 3.79; O, 8.67; P, 8.39; S, 8.68. Found: C, 35.84; H, 3.86; N, 3.78; S, 8.81.

***S*-(3,4-Dimethoxybenzyl) Tetramethylenesulfonium ClO_4^-.** By the same procedure, 3,4-dimethoxybenzyl bromide (2.29 g, 9.910 mmol, 1.00 equiv), THT (1.30 g, 14.740 mmol, 1.49 equiv) and $NaClO_4$ (1.30 g, 10.620 mmol, 1.07 equiv) in acetone (10 mL) for 12 h at room temperature gave *S*-(3,4-dimethoxybenzyl)tetramethylenesulfonium ClO_4^- as a white microcrystalline solid (2.1 g, 6.200 mmol, 63 %): Mp 112-113 °C (acetone/Et_2O); ^1H NMR ($(CD_3)_2SO$, 300 MHz): δ 6.94-7.19 (m, 3 H), 4.41 (s, 2 H), 3.72 (s, 6 H), 3.20-3.30 (m, 4 H), 2.00-2.30 (m, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 28.6, 42.8, 45.8, 56.0, 56.0, 112.6, 114.0, 121.9, 123.5, 149.5, 150.2. Anal. Calcd for $C_{13}H_{19}ClO_6S$: C, 46.09; H, 5.65; Cl, 10.46; O, 28.33; S, 9.46. Found: C, 46.21; H, 5.63; S, 9.36.

***S*-(3-Thienylmethyl) Tetramethylenesulfonium PF_6^-.** By the same procedure, 3-thienylmethyl bromide[3] (3.54 g, 19.990 mmol, 1.00 equiv), THT (1.80 g, 20.410 mmol, 1.02

equiv), and NH_4PF_6 (3.58 g, 22.000 mmol, 1.1 equiv) in acetone -THF (1:1, 20 mL) for 12 h at 40 °C gave *S*-(3-thienylmethyl) tetramethylenesulfonium PF_6^- as white crystals (3.85 g, 13.520 mmol, 58 %): Mp 104-106 °C (EtOH); IR (KBr pellet, cm^{-1}): 1623 (s), 1410 (s), 1253 (m). ^1H NMR ($(CD_3)_2CO$, 300 MHz): δ 8.86 (s, 1 H), 7.59 (m, 1 H), 7.33 (d, J = 4.3 Hz, 1 H), 4.77 (s, 2 H), 3.50-3.70 (m, 4 H), 2.20-2.40 (m, 4 H). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 28.4, 40.5, 42.6, 104.9, 128.2, 128.5, 128.6, 128.9. Anal. Calcd for $C_9H_{13}F_6PS_2$: C, 32.73; H, 3.97; F, 34.51; P, 9.38; S, 19.42. Found: C, 32.76; H, 4.01; S, 19.53.

***S*-(3-Pyridylmethyl) Tetramethylenesulfonium PF_6^-.** A solution of 3-bromomethylpyridinium hydrobromide[4] (1.27 g, 5.020 mmol, 1.00 equiv) in water (15%) was treated with THT (1.00 g, 11.340 mmol, 2.26 equiv) and NH_4PF_6 (1.75 g, 10.740 mmol, 2.14 equiv) for 8 h at room temperature. The white microcrystalline solid which gradually precipitated was filtered and air-dried (2.27 g) then dissolved in acetone and titrated with saturated aqueous sodium bicarbonate to pH 7.4 using a pH meter. Solvents were evaporated under reduced pressure and the resulting solid was triturated 3 times with water (10 mL). The remaining solid was air-dried and recrystallized from acetone-Et_2O giving *S*-(3-pyridylmethyl) tetramethylenesulfonium PF_6^- as a white solid (1.5 g, 4.610 mmol, 92%): Mp 87-89 °C (water); IR (KBr pellet, cm^{-1}): 3032 (s), 1595 (m), 1573 (m), 1481 (m), 1424 (s). ^1H NMR ($(CD_3)_2SO$, 300 MHz): δ 8.69 (s, 1 H), 8.59 (s, 1 H), 7.92 (d, J = 7.4 Hz, 1 H), 7.46 (m, 1 H), 4.51 (s, 2 H), 3.30-3.52 (m, 4 H), 2.02-2.14 (m, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 28.6, 42.9, 43.5, 124.8, 126.0, 138.9, 150.6, 151.1. Anal. Calcd for $C_{10}H_{14}F_6NPS$: C, 36.93; H, 4.34; F, 35.05; N, 4.31; P, 9.52; S, 9.86. Found: C, 36.91; H, 4.36; N, 4.27; S, 9.76.

***S*-(2*H*-1-Benzopyran-2-one-6-methyl) Tetramethylenesulfonium PF_6^-.** 6-Bromomethyl-2*H*-1-benzopyran-2-one[5] (2.39 g, 10.000 mmol, 1.00 equiv) in acetone (10 mL) was treated with THT (1.20 g, 13.610 mmol, 1.36 equiv) and NH_4PF_6 (1.79g, 11.000 mmol, 1.1 equiv) for 12 h at room temperature. The precipitated solid was filtered and washed with acetone and the resulting solution was treated with Et_2O to crystallize *S*-(2*H*-1-benzopyran-2-one-6-methyl) tetramethylenesulfonium PF_6^- from solution (3.13 g, 8.790 mmol, 80 %): Mp 202-203

°C (acetone/Et_2O, 5:1); IR (KBr pellet, cm^{-1}): 3062 (w), 2986 (w), 1716 (s), 1431 (w). ^1H NMR ($(CD_3)_2SO$, 300 MHz): δ 8.02 (d, J = 6.4 Hz, 1 H), 7.84 (s, 1 H), 7.75 (d, J = 6.2 Hz, 1 H), 7.45 (d, J = 6.2 Hz, 1 H), 6.53 (d, J = 6.4 Hz, 1 H), 4.58 (s, 2 H), 3.29-3.50 (m, 4 H), 2.00-2.30 (m, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 28.5, 43.1, 44.6, 117.4, 117.9, 119.6, 126.5, 130.9, 134.2, 144.2, 154.3, 160.1. Anal. Calcd for $C_{14}H_{15}ClO_6S$: C, 48.49; H, 4.36; Cl, 10.22; O, 27.68; S, 9.25. Found: C, 48.35; H, 4.34; S, 9.15.

Aryl and Heteroaryl Sulfonium Salts

Preparation of *S*-(Phenyl) Tetramethylenesulfonium PF_6^-. Triethylamine (27.5 g, 272.3 mmol, 1.5 equiv) was slowly added to a 500 mL round-bottom flask containing thiophenol (20 g, 181.5 mmol), 1,4-dibromobutane (78.4 g, 363 mmol, 2.0 equiv) and Et_2O (200 mL). The reaction mixture was stirred for 30 min then diluted with Et_2O (200 mL) and washed with 1.2 N HCl (2 x 200 mL) and brine. The organic layer was dried ($MgSO_4$), the solvents were evaporated, and the crude material was dissolved in acetone (40 mL) and treated with NH_4PF_6 (44.4 g, 272.3 mmol). After stirring overnight at room temperature, the reaction mixture was filtered through a medium porosity fritted-glass funnel, the filtrate was concentrated under reduced pressure, and Et_2O (200 mL) was added producing colorless crystals. The crystals were collected on a coarse fritted-glass funnel and washed with water (200 mL), ethanol (200 mL), and Et_2O (200 mL). The product was purified by recrystallization from acetone/Et_2O to give 42.8 g (76 %) of analytically pure colorless crystals:[9] Mp 140-144 °C (acetone/Et_2O); IR (KBr pellet, cm^{-1}): 3075 (w), 3025 (w), 2954 (w), 1581 (w), 1453 (s), 841 (br, s). ^1H NMR ($(CD_3)_2SO$, 360 MHz): δ 7.94 (d, J = 6.8 Hz, 2 H), 7.73 (d, J = 6.8 Hz, 1 H), 7.68 (app t, J = 6.8 Hz, 2 H), 3.92 (m, 2 H), 3.76 (app q, J = Hz, 2 H), 2.30 (app q, J = 6.8 Hz, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 133.5 (s), 130.9 (s), 130.2 (s), 127.8 (s), 48.0 (s), 28.7 (s). Anal. Calcd for $C_{10}H_{13}F_6PS$: C, 38.72; H, 4.22; S, 10.34. Found: C, 38.62; H, 4.26; S, 10.25.

***S*-(4-Fluorophenyl) Tetramethylenesulfonium PF_6^-.** Using the same procedure, 4-fluorothiophenol (10.0 g, 78.0 mmol), NH_4PF_6 (15.3 g, 93.6 mmol) and 1,4-dibromobutane (50.5 g, 234.1 mmol) gave *S*-(4-fluorophenyl) tetramethylenesulfonium PF_6^- as a colorless microcrystalline solid (12.5 g, 28.2 mmols, 49 %): Mp 108-109 °C (acetone/hexanes); IR (KBr pellet, cm^{-1}): 3111 (w), 3033 (w), 2969 (w), 1588 (m), 1496 (m), 1403 (m), 1240 (m), 841 (br, s). ^1H NMR ($(CD_3)_2SO$, 360 MHz): δ 8.03 (dd, J = 8.6, 3.4 Hz, 2 H), 7.57 (app t, J = 8.5 Hz, 2 H), 3.91 (m, 2 H), 3.75 (m, 2 H), 2.29 (app q, J = 6.8, 15.4 Hz, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 162.4 (d, 248 Hz), 133.4 (d, 8. 52 Hz), 123.6 (s), 118.1 (d, 21.8 Hz), 48.4 (s, α-to sulfonium), 28.7 (s, β-to sulfonium). Anal. Calcd for $C_{10}H_{12}F_7SP$: C, 36.59; H, 3.69; F, 40.52; S, 9.77; P, 9.44. Found: C, 36.66; H, 3.75; S, 9.70.

***S*-(2-Pyridyl) Tetramethylenesulfonium PF_6^-.** By the same procedure (but using 5 % NaOH instead of 1.2 N HCl to wash the Et_2O layer), 2-mercaptopyridine (10 g, 90.0 mmol) and 1,4-dibromobutane (58.3 g, 270.0 mmols) gave 15.5 g product (54 %): Mp 128-132 °C (acetone/Et_2O); IR (KBr pellet, cm^{-1}): 3082 (w), 3033 (w), 2961 (w), 1574 (m), 1425 (m), 827 (br, s). ^1H NMR ($(CD_3)_2SO$, 360 MHz): δ 8.80 (d, J = 5.1 Hz, 1 H), 8.18 (app t, J = 6.8 Hz, 2 H), 7.77 (m, 1 H), 3.92 (m, 2 H), 3.83 (m, 2 H), 2.24 (m, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 151.5 (s), 147.8 (s), 140.1 (s), 127.9 (s), 127.7 (s), 46.7 (s), 29.1 (s). Anal. Calcd for $C_9H_{12}NSPF_6$: C, 34.73; H, 3.89; N, 4.50; S, 10.30. Found: C, 34.78; H, 3.89; N, 4.49; S, 10.25.

***S*-(2-Thienyl) Tetramethylenesulfonium PF_6^-.** A 250 mL round-bottomed flask equipped with a magnetic stirring bar was charged with thiophene (8.00 g, 91.1 mmol) and THF (100 mL) then flushed with nitrogen and cooled to 0 °C. *n*-BuLi (86.5 mmol, 34.58 mL, 2.5 M in hexanes) was added slowly via syringe. After stirring for 20 min, the reaction mixture was treated with small portions of powdered sulfur (2.77 g, 86.5 mmol). The resulting pale yellow solution was stirred for 10 min and then transferred by cannula into a solution of 1,4-dibromobutane (46.7 g, 216.3 mmol, 2.5 equiv) in THF (100 mL) maintained at 0 °C. After 20 min the mixture was diluted with Et_2O (200 mL) and washed with water (200 mL) and brine

(200 mL). The organic phase was collected and the solvent removed *in vacuo*. The resultant crude oil was diluted with acetone (50 mL) and treated with NH_4PF_6 (23 g, 138.4 mmol, 1.6 equiv) at 23 °C for 48 h. The suspended NH_4Br was removed by filtration, the filter cake was washed with acetone, and the solvent was removed *in vacuo*. The crude solid was triturated with Et_2O and the Et_2O layer decanted from the solid. The solid was triturated with water and collected on a coarse frit by filtration. The solid was then washed with water, ethanol, and then Et_2O and air-dried to give a colorless microcrystalline solid that was purified by recrystallization form acetone/hexanes to give 13.8 g (49 %) of analytically pure product: Mp 160-163 °C (acetone/hexanes); IR (KBr pellet, cm^{-1}): 3111 (m), 3025 (w), 2947 (w), 1453 (m), 1396 (s), 1225 (m), 841 (br, s). ^1H NMR ($(CD_3)_2SO$, 360 MHz): δ 8.22 (d, J = 5.1 Hz, 1 H), 7.99 (d, J = 4.3 Hz, 1 H), 7.34 (app t, J = 4.3 Hz, 1 H), 3.96 (app p, J = 6.8, 12.8 Hz, 2 H), 3.65 (app p, J = 5.1, 12.0 Hz, 2 H), 2.40 (m, 2 H), 2.31 (m, 2 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 138.4 (s), 136.8 (s), 129.0 (s), 124.3 (s), 51.7 (s, α-to sulfonium), 28.9 (s, β-to sulfonium). Anal. Calcd for $C_8H_{11}S_2F_6P$: C, 30.38; H, 3.51; S, 20.28. Found: C, 30.45; H, 3.56; S, 20.34.

***S*-(2-Methoxy-5-pyridyl) Tetramethylenesulfonium PF_6^-.** A 250 mL round-bottom flask was charged with 1.2 N HCl (100 mL, 120 mmol) and 2-methoxy-5-aminopyridine (5.00 g, 40.28 mmol) and cooled to 0 °C. $NaNO_2$ (2.92 g, 42.29 mmol, 1.05 equiv) was added in small portions to produce the diazonium salt. The red/purple solution was stirred for 30 min and then thiourea (3.68 g, 48.33 mmol, 1.2 equiv) was added in small portions. After stirring for 10 min the mixture was allowed to warm to 23 °C and stirred until gas evolution ceased (~ 3 h). Sodium bicarbonate (4 equiv) was slowly added until the solution was basic and the mixture was heated to 100 °C to hydrolyze the isothiouronium salt. After stirring at 100 °C for 30 min the mixture was cooled to 23 °C and stirred for an additional 36 h. Then, 1,4-dibromobutane (26.1 g, 120.84 mmol, 3.0 equiv) in acetone (75 mL) was added quickly in one portion and the mixture was stirred at 23 °C for 30 min. The crude thioether product was extracted into Et_2O (200 mL) and washed with water (200 mL) and brine (200 mL). The

organic layer was collected, solvents were removed *in vacuo*, and then NH_4PF_6 (10.0 g, 61.3 mmol 1.5 equiv) in acetone (50 mL) was added to the crude oil. The mixture was stirred at 23 °C for 48 h then the resulting suspension was filtered on a coarse frit to remove precipitated ammonium bromide. The filter cake was washed with acetone and the filtrate was condensed *in vacuo*. The resulting solid was triturated with Et_2O and the solid was collected on a coarse frit and washed with water, ethanol, and Et_2O. After air-drying the red solid was purified by recrystallization 3 times from acetone/hexanes to give 2.65 g (19 %) of an analytically pure, microcrystalline, colorless solid: Mp 144-146 °C (acetone/hexanes); IR (KBr pellet, cm^{-1}): 3025 (w), 2969 (w), 1581 (s), 1481 (s), 1375 (s), 1289 (s), 1005 (s), 848 (s). ^1H NMR ($(CD_3)_2SO$, 300 MHz): δ 8.67 (s, 1 H), 8.19 (dd, J = 2.7, 9.0 Hz, 1 H), 7.09 (d, J = 9.0 Hz, 1 H), 3.92 (s, 3 H), 3.83 (m, 2 H), 3.70 (m, 2 H), 2.31 (app t, J = 7.3 Hz, 2 H), 2.25 (app t, J = 8.9 Hz, 2 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 166.6 (s, C2), 150.4 (s, C6), 140.6 (s), 117.2 (s), 113.1 (s), 54.7 (s, OCH3), 48.4 (s, α-to sulfonium), 28.9 (s, β-to sulfonium). Anal. Calcd for $C_{10}H_{14}NOSPF_6$: C, 35.20; H, 4.14; N, 4.10; O, 4.69; S, 9.40. Found: C, 35.33; H, 4.14; N, 4.07; S, 9.34.

Preparation of Alkenylsulfonium Salts.

S-(1-Phenylethene-1-yl) Tetramethylenesulfonium PF_6^-. Against a flow of nitrogen, Br_2 (0.80 g, 5.010 mmol, 1.02 equiv) in CH_2Cl_2 (5 mL) was added dropwise to styrene (0.51 g, 4.890 mmol, 1.00 equiv) and THT (1.99 g, 22.560 mmol, 4.61 equiv) in CH_2Cl_2 (30 mL) at 0 °C. A white solid immediately precipitated. After the addition was complete (30 min), the reaction mixture was allowed to warm to the room temperature and filtered to give 1.141 g of a white solid. This was immediately dissolved in water (10 mL) and treated with silver(I) oxide (1.28 g, 5.520 mmol, 1.13 equiv). The reaction mixture was stirred for 10 min, filtered, and NH_4PF_6 (1.14 g, 5.520 mmol, 1.43 equiv) as an aqueous solution was added. The product immediately precipitated and was filtrated, air-dried, and washed with Et_2O giving *S*-(1-phenylethene-1-yl) tetramethylenesulfonium PF_6^- (1.07 g, 3.180 mmol, 65 %) as white

crystals: Mp 62-63 °C (EtOH) ^{1}H NMR ($(CD_3)_2CO$, 300 MHz): δ 7.61 (m, 2 H), 7.51 (m, 3 H), 6.42 (s, 1 H), 6.39 (s, 1 H), 3.89-4.01 (m, 4 H), 2.22-2.42 (m, 4 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 28.3, 45.4, 126.4, 128.2, 129.8, 130.9, 133.6, 135.7. Anal. Calcd for $C_{12}H_{15}F_6PS$: C, 42.86; H, 4.50; F, 33.90; P, 9.21; S, 9.53. Found: C, 42.96; H, 4.49; S, 9.44.

***E-S*-(4-Octene-4-yl) Tetramethylenesulfonium PF_6^-.** Bromine (6.50 g, 40.680 mmol, 1.14 equiv) was added dropwise to tetrahydrothiophene (10.00 g, 113.380 mmol, 3.18 equiv) in acetonitrile (40 mL) at -40 °C. After 1 h at -40 °C, the yellow precipitate was treated with *cis*-4-octene (4.00 g, 35.650 mmol, 1.00 equiv) then with $AlCl_3$ (0.10 g, 24.540 mmol, 0.02 equiv). The reaction mixture was warmed to the 0 °C, held there for another hour, then warmed to room temperature and treated with hexanes-Et_2O (3:1) until two layers separated. The upper layer was removed and the bottom layer was washed 3 times by swirling with a hexane - Et_2O mixture (30 mL). Volatiles were evaporated under reduced pressure and the residual material was dissolved in water (60 mL) and treated with silver oxide (2.23 g, 9.620 mmol, 0.27 equiv). The gray suspension was stirred for 10 min at room temperature, then filtered. Upon addition of NH_4PF_6 (2.23 g, 9.620 mmol, 0.27 equiv) to the filtrate a white solid precipitated. It was filtered off, dried, dissolved in acetone, filtered again and treated with hexane- Et_2O (3:1; *Caution - this compound very soluble in Et_2O*) to give *E-S*-(4-octene-4-yl) tetramethylenesulfonium PF_6^- as a white solid (2.65 g, 22 %): Mp 82-84 °C (acetone). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.31-6.38 (t, J = 7.3 Hz, 1 H), 3.66-3.73 (m, 2 H), 3.34-3.47 (m, 2 H), 2.21-2.49 (m, 8 H), 1.42-1.65 (m, 4 H), 0.87-1.09 (m, 6 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 13.2, 13.5, 21.1, 22.0, 29.6, 31.1, 31.9, 43.3, 125.0, 148.6, 148.9. Anal. Calcd for $C_{12}H_{23}F_6PS$: C, 41.86; H, 6.73; F, 33.10; P, 8.99; S, 9.31 Found: C, 41.78; H, 6.71; S, 9.20.

***Z-S*-(4-Octene-4-yl) Tetramethylenesulfonium PF_6^-.** The same procedure using *trans*-4-octene (4.00 g, 35.650 mmol, 1.00 equiv), THT (10.00 g, 113.380 mmol, 3.18 equiv), bromine (6.50 g, 40.680 mmol, 1.14 equiv), $AlCl_3$ (0.10 g, 0.750 mmol, 0.02 equiv) and NH_4PF_6 (4.00 g, 0.750 mmol, 0.69 equiv)] gave *Z-S*-(4-octene-4-yl) tetramethylenesulfonium PF_6^- as a white

solid (2.13 g, 6.190 mmol, 17 %): Mp 72 °C decomp (acetone). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89-1.04 (m, 6 H), 1.22-1.43 (m, 4 H), 2.24 (q, J = 7.4 Hz, 2 H), 2.27-2.48 (m, 6 H), 3.38-3.51 (m, 2 H), 3.67-3.82 (m, 2 H), 6.43 (t, J = 6.8 Hz, 1 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): d 13.8, 21.5, 22.8, 28.6, 30.5, 31.8, 44.3, 125.7, 148.6. Anal. Calcd for $C_{12}H_{23}F_6PS$: C, 41.86; H, 6.73; F, 33.10; P, 8.99; S, 9.31. Found: C, 41.81; H, 6.70; S, 9.25. Determination of the stereochemistry of the *E*- and *Z*- isomers: *Z*, *S*-(4-octene-4-yl) tetramethylenesulfonium PF_6^- was treated with $NaBH_4$ in the presence of 5 % of $NiCl_2(PPh_2Me)_2$ to give *Z*-4-octene (compared with authentic sample). In the same way, *E*-4-octene was obtained by reduction of *E-S-*(4-octene-4-yl) tetramethylenesulfonium PF_6^-.

Benzylic Cross-coupling Reactions

Via Organostannanes

Tetra-*n*-butylammonium Diphenylphosphinate. A 100 mL round-bottomed flask was charged with MeOH (20 mL) and diphenylphosphinic acid (4.0 g, 18.33 mmol). Tetra-*n*-butylammonium hydroxide (18.33 mL of 1.0 M solution in MeOH) was added and the mixture was shaken briefly. The resulting cloudy solution was filtered through Celite™. The solvent was removed *in vacuo* leaving a pale yellow oil. This was placed under high vacuum overnight, giving a semi-solid. The product was purified by recrystallization from ether/hexanes to give colorless, hygroscopic plates (7.71 g, 91%): Mp 53-63 °C (ether/hexanes). IR (CH_2Cl_2, KBr, cm^{-1}): 2961 (m), 1268 (w), 1190 (w), 1119 (w), 1040 (w), 705 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87 (m, 2 H), 7.22 (m, 8 H), 3.27 (app t, J = 8.4 Hz, 8 H), 1.56 (m, 8 H), 1.33 (q, J = 7.4 Hz, 8 H), 0.92 (t, J = 7.3 Hz, 12 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 131.8 (m), 128.3 (m), 127.1 (m), 58.4 (s), 23.9 (s), 19.5 (s), 13.7 (s).

Phenyl-2-thienylmethane, 1a. Under nitrogen, *S*-(benzyl) tetramethylenesulfonium ClO_4^- (0.14 g, 0.500 mmol, 1.00 equiv) and 2-tri-*n*-butylstannylthiophene (0.19 g, 0.500 mmol, 1.00 equiv) in EtOH (2 mL) were treated with tetra-*n*-butylammonium diphenylphosphinate (0.25 g, 0.540 mmol, 1.08 equiv) and 0.2 mol% of a palladium catalyst prepared *in situ* from Pd_2dba_3

and 8 equiv of TFP. The reaction mixture was stirred at 42-45 °C for 12 h, allowed to cool, then treated with Et_2O to precipitate salts. After filtration and evaporation of the filtrate, the residue was subjected to chromatography (Chromatotron®, 4 mm, silica gel, hexanes) to give 2-benzylthiophene as a colorless oil (0.071 g, 0.410 mmol, 82 %).[10] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.18-7.35 (m, 5 H), 7.13 (d, J = 4.4 Hz, 1 H), 6.91 (m, 1 H), 6.78 (s, 1 H), 4.15 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 36.0, 123.9, 125.1, 126.4, 126.8, 128.5, 128.6.

1-Bromo-2-(*E*-3-phenyl-2-propenyl)benzene, 1b. By the same procedure and workup, *S*-(2-bromobenzyl) tetramethylenesulfonium PF_6^- (0.40 g, 1.000 mmol, 1.00 equiv), 1-tri-*n*-butylstannyl-2-phenylethylene (0.39 g, 1.000 mmol, 1.00 equiv), tetra-*n*-butylammonium diphenylphosphinate (0.50 g, 1.090 mmol, 1.09 equiv) and 0.2 mol% of a palladium catalyst prepared *in situ* from Pd_2dba_3 and 8 equiv of TFP in EtOH (6 mL) after 8 h at 55 °C gave, after chromatography (Chromatotron®, 4 mm, silica gel, hexanes), 1-bromo-2-(*E*-3-phenyl-2-propenyl)benzene as a colorless oil (0.217 g, 0.80 mmol, 80 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.03-5.55 (m, 9 H), 6.27-6.47 (m, 2 H), 3.65 (d, J = 7.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 39.5, 126.2, 127.3, 127.3, 127.6, 127.9, 128.0, 128.3, 128.6, 129.1, 131.8, 132.8, 132.9, 137.4, 139.6. Anal. Calcd for $C_{15}H_{13}Br$: C, 65.95; H, 4.80; N, 4.49. Found: C, 65.88; H, 4.81.

2-(3-Thienylmethyl)benzofuran, 1c. By the same procedure and workup, *S*-(3-thienylmethyl) tetramethylenesulfonium PF_6^- (0.17 g, 0.500 mmol, 1.00 equiv), 2-tri-*n*-butylstannylbenzofuran (0.20 g, 0.500 mmol, 1.00 equiv), tetra-*n*-butylammonium diphenylphosphinate (0.28 g, 0.600 mmol, 1.20 equiv), and 0.2 mol% of palladium catalyst prepared *in situ* from Pd_2dba_3 and 8 equiv of TFP in EtOH (4 mL) after 12 h at 42-45 °C gave, after chromatography (Chromatotron®, silica gel, 4 mm hexanes- Et_2O gradient), 2-(3-thienylmethyl)benzofuran as a colorless oil (0.081 g, 0.380 mmol, 76 %).[11] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.00-7.56 (m, 7 H), 6.39 (s, 1 H), 4.12 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 29.6, 103.1, 110.9, 120.4, 122.1, 122.6, 123.5, 125.8, 128.3, 157.2.

1-Phenyl-3-(3-pyridyl)-(*E*)-1-propene, 1d. By the same procedure and workup, *S*-(3-pyridylmethyl) tetramethylenesulfonium PF_6^- (0.16 g, 0.500 mmol, 1.00 equiv), 1-tri-*n*-

butylstannyl-2-phenyl ethylene (0.20 g, 0.500 mmol, 1.00 equiv), tetra-*n*-butylammonium diphenylphosphinate (0.25 g, 0.540 mmol, 1.08 equiv) and 0.2 mol% of a palladium catalyst prepared *in situ* from Pd_2dba_3 and 8 equiv of TFP in EtOH (2 mL) after 12 h at 42-45 °C gave, after chromatography (Chromatotron®, silica gel, 4 mm hexanes- Et_2O gradient), 3-(3-phenyl-2-propenyl) pyridine,[12] as a colorless viscous oil (0.041 g, 0.210 mmol, 42 %). IR (CD_2Cl_2, KBr, cm^{-1}): 1650 (s), 1598 (m), 1577 (m). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.40-8.60 (m, 2 H), 7.45-7.55 (m, 1 H), 7.15-7.40 (m, 6 H), 6.20-6.49 (m, 2 H), 3.63 (d, J = 6.3 Hz, 2 H).

1,2-Dimethoxy-4-(3-phenyl-2-propenyl) benzene, 1e. By the same procedure and workup, *S*-(3,4-dimethoxybenzyl) tetramethylenesulfonium ClO_4^- (0.17 g, 0.510 mmol, 1.00 equiv), 1-tri-*n*-butylstannyl-2-phenyl ethylene (0.20 g, 0.510 mmol, 1.00 equiv), tetra-*n*-butylammonium diphenylphosphinate (0.25 g, 0.540 mmol, 1.06 equiv) and 0.2 mol% of a palladium catalyst prepared *in situ* from Pd_2dba_3 and 8 equiv of TFP in EtOH (2 mL) after 10 h at 42-45 °C gave, after chromatography (Chromatotron®, silica gel, 4 mm, hexanes), 1,2-dimethoxy-4-(3-phenyl-2-propenyl) benzene as a colorless oil (0.097 g, 0.380 mmol, 75 %).[13] ^1H NMR ($CDCl_3$, 300 MHz): δ 7.19-7.38 (m, 5 H), 6.71-6.82 (m, 3 H), 6.28-6.46 (m, 2 H), 3.83 (s, 6 H), 2.46 (d, J = 5.8 Hz, 2 H).

6-(2-Benzofuranylmethyl)-2*H*-1-benzopyran-2-one, 1f. By the same procedure and workup, *S*-(2*H*-1-benzopyran-2-one-6-methyl) tetramethylenesulfonium PF_6^- (0.20 g, 0.500 mmol, 1.00 equiv), 2-tri-*n*-butylstannylbenzofuran (0.20 g, 0.500 mmol, 1.00 equiv), tetra-*n*-butylammonium diphenylphosphinate, 0.25 g, 0.540 mmol, 1.08 equiv), and 0.2 mol% of palladium catalyst prepared *in situ* from Pd_2dba_3 and 8 equiv of TFP in EtOH (8 mL) after 14 at 42-45 °C gave, after chromatography (Chromatotron®, silica gel, 4 mm, hexanes/Et_2O), 6-(2-benzofuranylmethyl)-2*H*-1-benzopyran-2-one as a white solid (0.106 g, 0.380 mmol, 76 %): Mp 106-107 °C (hexanes/Et_2O); IR (KBr, cm^{-1}): 1708 (s, C=O). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.13-7.68 (m, 8 H), 6.34-6.44 (m, 2 H), 4.13 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5MHz): δ 34.2, 103.8, 110.9, 116.9, 117.1, 120.5, 122.7, 123.8, 127.7, 132.5, 143.2. Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38; O, 17.37. Found: C, 78.23; H, 4.43.

1-(1-Pyrrolyl)-2-(2-bromophenylmethyl)benzene, 1g. By the same procedure and workup, *S*-(2-bromobenzyl) tetramethylenesulfonium PF_6^- (0.20 g, 0.500 mmol, 1.00 equiv), 1-(1-pyrrolyl)-2-tri-*n*-butylstannylbenzene (0.22 g, 0.510 mmol, 1.02 equiv), tetra-*n*-butylammonium diphenylphosphinate, 0.25 g, 0.540 mmol, 1.08 equiv), and 0.1 mol% of a palladium catalyst prepared *in situ* from Pd_2dba_3 and 8 equiv of TFP in EtOH (2 mL) was treated with a slow-release "Copper pill". This was made from copper diphenylphosphinate (0.014g, 0.1mmol) and polyvinylalcohol (80 % hydrolyzed, 0.180 g) mixed using a ball mill and then formed into a homogeneous pellet with a KBr press. After 5 h at 40 °C, chromatography (Chromatotron®, 4 mm, hexane/Et_2O) gave 1-(1-pyrrolyl)-2-(2-bromophenylmethyl)benzene as a colorless oil (0.12 g, 0.405 mmol, 81 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.92-7.57 (m, 8 H), 6.78 (m, 2 H), 6.29 (m, 2 H), 3.97 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 37.1, 109.1, 110.1, 122.2, 125.0, 127.2, 127.2, 127.5, 127.9, 128.1, 130.4, 131.0, 132.9, 135.4, 139.7, 140.6, 148.3. Anal. Calcd for $C_{17}H_{14}BrN$: C, 65.40; H, 4.52; N, 4.49. Found: C, 65.37; H, 4.50; N, 4.51.

1-(1-Pyrrolyl)-2-(3-pyridylmethyl)benzene, 1h. By the same procedure and workup, *S*-(3-pyridylmethyl) tetramethylenesulfonium PF_6^- (0.16 g, 0.500 mmol, 1.00 equiv), 1-(1-pyrrolyl)-2-tri-*n*-butylstannylbenzene (0.22 g, 0.510 mmol, 1.02 equiv), tetra-*n*-butylammonium diphenylphosphinate (0.270 g, 0.588 mmol, 1.17 equiv), and 0.1 mol% of a palladium catalyst prepared *in situ* from Pd_2dba_3 and 8 equiv of TFP in EtOH (2 mL) was treated with a slow-release "Copper pill" made from copper diphenylphosphinate (0.014g, 0.1 mmol) and polyvinylalcohol (80 % hydrolyzed, 0.180 g) as in the example above. After 5 h at 40 °C, chromatography (Chromatotron®, 4 mm, hexane/Et_2O) gave 1-(1-pyrrolyl)-2-(3-pyridylmethyl)benzene as a yellow oil (0.071 g, 0.300 mmol, 60 %). IR (CD_2Cl_2, KBr, cm^{-1}): 1662 (s), 1600 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.38 (s, 1 H), 8.22 (s, 1 H), 7.05-7.35 (m, 6 H), 6.64 (s, 2 H), 6.23 (s, 2 H), 4.82 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 34.5, 109.2, 122.1, 123.3, 127.6, 128.2, 130.7, 136.0, 136.1, 147.5, 149.9. HRMS (EI) Calcd for $C_{16}H_{14}N_2$: 234.1157. Found: 234.1157.

VIA BORONIC ACIDS

1-Nitro-4-[(4-methylthiophenyl)methyl] benzene, 1i. Under nitrogen, *S*-(4-nitrobenzyl) tetramethylenesulfonium PF_6^- (0.37 g, 1.000 mmol, 1.00 equiv), 4-methylthiobenzyl boronic acid (0.17 g, 0.990 mmol, 0.99 equiv), $PdCl_2$dppf (0.004 g, 0.005 mmol; dppf = diphenylphosphinoferrocene) in THF (8 mL) with K_2CO_3 (0.80 g, 5.790 mmol, 5.79 equiv) was stirred for 6 h at 45 °C. After cooling to room temperature, solids were removed by filtration, the filtrate was condensed, and the residues were subjected to chromatography (Chromatotron®, silica gel, 4 mm, hexane/Et_2O gradient) to give 1-nitro-4-[(4-methylthiophenyl)methyl] benzene as a yellow solid (0.174 g, 0.670 mmol, 67 %): Mp 89-93 °C (hexanes/Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.0-8.2 (m, 2 H), 7.0-7.4 (m, 6 H), 3.98 (s, 2 H), 2.43 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 15.9, 41.1, 123.8, 127.1, 129.4, 129.6, 136.0, 148.8. Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40; O, 12.34; S, 12.36. Found: C, 64.85; H, 5.05; N, 5.43; S, 12.31.

1-Fluoro-2-[(4-methylphenyl)methyl] benzene, 1j. By the same procedure, *S*-(2-fluorobenzyl) tetramethylenesulfonium PF_6^- (0.171 g, 0.500 mmol, 1.00 equiv), *p*-tolylboronic acid (0.07 g, 0.500 mmol, 1.00 equiv), $PdCl_2$dppf (0.004 g, 0.005 mmol) with K_2CO_3 (0.80 g, 5.790 mmol, 11.58 equiv) in 90% EtOH (4 mL) after 6 h at 45 °C gave, after chromatography (Chromatotron®, silica gel, 4 mm, hexane/Et_2O gradient), 1-fluoro-2-[(4-methylphenyl)methyl] benzene as a transparent viscous oil (0.074 g, 0.370 mmol, 74 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.99-7.25 (m, 8 H), 3.98 (s, 2 H), 2.34 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.0, 34.4, 115.5 (d, $J_{(CF)}$ = 22 Hz), 124.1 (d, $J_{(CF)}$ = 25 Hz), 127.0, 128.0 (d, $J_{(CF)}$ = 8.3 Hz), 128.5, 128.6, 128.9, 129.4, 129.7, 131.2 (d, $J_{(CF)}$ = 4.6 Hz), 136.5 (d, $J_{(CF)}$ = 107 Hz), 161.2 (d, $J_{(CF)}$ = 244 Hz). Anal. Calcd for $C_{14}H_{13}F$: C, 83.97; H, 6.54;. Found: C, 83.92; H, 6.54.

1,2-Dimethoxy-4-[(4-methylphenyl)methyl] benzene, 1k. By the same procedure, *S*-(3,4-dimethoxybenzyl) tetramethylenesulfonium ClO_4^- (0.17 g, 0.500 mmol, 1.00 equiv), *p*-tolylboronic acid (0.07 g, 0.500 mmol, 1.00 equiv), and $PdCl_2$dppf (0.004 g, 0.005 mmol) with K_2CO_3 (0.80 g, 5.790 mmol, 11.58 equiv) in 90 % EtOH (4 mL) after 8 h at 45 °C gave, after

chromatography (Chromatotron®, silica gel, 4 mm, hexane Et_2O gradient), 1,2-dimethoxy-4-[(4-methylphenyl)methyl]benzene as a colorless viscous oil (0.088 g, 0.360 mmol, 72 %).[14] ^1H NMR ($CDCl_3$, 300 MHz): δ 7.08 (s, 4 H), 6.69-6.82 (m, 3 H), 3.87 (s, 2 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 2.32 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.0, 41.1, 55.8, 55.9, 111.2, 112.2, 120.8, 128.6, 129.1, 133.9, 135.5, 138.3, 147.3, 148.9.

6-(4-Methylphenylmethyl)-2*H*-1-benzopyrane-2-one, 1l. By the same procedure, *S*-(2*H*-1-benzopyrane-2-one-6-methyl) tetramethylenesulfonium PF_6^- (0.20 g, 0.500 mmol, 1.00 equiv), *p*-tolylboronic acid (0.07 g, 1.00 M, 0.500 mmol, 1.00 equiv), $PdCl_2$dppf (0.002 g, 6 x 10^{-4} mmol, 0.41 mol%) and K_2CO_3 (0.80 g, 5.790 mmol, 11.58 equiv) in DME (4 mL) after 14 h at 45 °C gave, after chromatography (Chromatotron®, silica gel, 4 mm, hexane Et_2O gradient), 6-(4-methylphenylmethyl)-2*H*-1-benzopyrane-2-one as a white solid (0.072 g, 0.290 mmol, 58 %): Mp 67-68 °C (hexanes /Et_2O); IR (CD_2Cl_2, KBr, cm^{-1}): 3056 (w), 1612 (s, C=O). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, *J* = 7.4 Hz, 1 H), 6.98-7.36 (m, 7 H), 6.37 (d, *J* = 7.4 Hz, 1 H), 3.95 (s, 2 H), 2.29 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.0, 40.6, 116.6, 116.9, 127.5, 128.7, 129.4, 132.6, 143.4. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64; O, 12.78. Found: C, 81.12; H, 5.76.

(*E*)-2-Heptenylbenzene, 1m. Under nitrogen, *S*-(benzyl) tetramethylenesulfonium ClO_4^- (0.28 g, 1.000 mmol, 1.00 equiv) was partially dissolved in dry EtOH (4 mL) and treated with 1-hexenyl-1-boronic acid (0.13 g, 1.000 mmol, 1.00 equiv) and $Pd(PPh_3)_4$ (10 mg, 0.0086 mmol). With stirring, a solution of tetra-*n*-butylammonium fluoride in THF (1.00 mL, 1.00 M, 1.000 mmol, 1.00 equiv) was added via syringe. After 8 h at 42 °C the reaction mixture was extracted with Et_2O (2 x 10 mL) and dried over $MgSO_4$. Solvents were evaporated under reduced pressure and the oily residue was purified by chromatography (Chromatotron®, 4 mm, silica/hexanes) to give *E*-1-benzyl-1-hexene as a yellow, oily liquid (0.131 g, 0.750 mmol, 75 %).[15] ^1H NMR ($CDCl_3$, 300 MHz): δ 7.10-7.36 (m, 5 H), 5.42-5.62 (m, 2 H), 3.32 (d, *J* = 4.5 Hz, 2 H), 1.90-2.10 (m, 2 H), 1.20-1.45 (m, 4 H), 0.86 (t, *J* = 3.6 Hz, 3 H). ^{13}C

NMR ($CDCl_3$, 75.5 MHz): δ 14.0, 22.2, 31.7, 32.2, 39.1, 125.8, 128.3, 128.4, 128.7, 131.0, 132.1, 141.1.

VIA an Organozinc Reagent

2-(4-Fluorobenzyl)thiophene, 1n. *n*-BuLi (2.19 mmol, 1.14 mL of 2.5 M solution in hexanes) was added by syringe to a solution of thiophene (0.19 g, 2.22 mmol) in THF (7 mL) in a 25 mL Schlenk flask cooled to 0 °C. After stirring for 15 min, $ZnCl_2$ (2.22 mmol, 2.22 mL of 1.0 M in ether) was added and the mixture was allowed to warm to room temperature. After 10 min, Ni(dppf)Cl_2 (2 %, 0.02 g, 0.030 mmol; dppf = diphenylphosphinoferrocene) and *S*-(4-fluorobenzyl) tetramethylenesulfonium hexafluorophosphate (0.506 g, 1.48 mmol) were added. The resulting mixture was stirred at room temperature for 6 h then diluted with ether (100 mL) and washed with water (2 x 100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4, solvents were removed under reduced pressure, and the crude product was purified by chromatography (Chromatotron®, 4 mm SiO_2 rotor, 100 % hexanes) to give 0.212 g (75 %) of product as a colorless oil with spectroscopic data identical to that published.[16]

Aryl Sulfonium Cross-coupling Reactions

4-Methylbiphenyl, 2a. Under nitrogen, a 25 mL test tube with a side-arm was charged with *S*-(phenyl) tetramethylenesulfonium PF_6^- (0.50 g, 1.61 mmol), *p*-tolylboronic acid (0.31 g, 2.26 mmol), freshly ground K_2CO_3 (1.0 g), and Pd(dppf)Cl_2 (0.047 g, 4 mol %). THF (5 mL) was added and the mixture was stirred at 40 °C for 14 h. The reaction mixture was diluted with Et_2O (100 mL) and treated with decolorizing carbon. The mixture was filtered through Celite™ and the solvent was removed under reduced pressure. The crude product was purified by chromatography (Chromatotron®, 4 mm SiO_2, 100 % hexanes) to give 0.257 g (95 %) of a crystalline solid: Mp 45-46 °C (*Lit. mp.* 44-47 °C, Aldrich catalog). The product was identical to an authentic sample obtained from Aldrich Chemical Co.

2-(4-Tolyl)pyridine, 2b. By the same procedure, *S*-(2-pyridyl) tetramethylenesulfonium PF_6^- (0.60 g, 1.93 mmol), *p*-tolylboronic acid (0.22 g, 1.61 mmol), freshly ground K_2CO_3 (1.0 g), and Pd(dppf)Cl_2 (0.047 g, 4 mol %) in THF with 50 μL of added water after 14 h at 40 °C gave, after chromatography (Chromatotron® rotor, silica gel, 4 mm, 50% Et_2O/hexanes), a colorless oil (0.21 g, 1.24 mmol, 77%). This product was identical in all respects to an authentic sample obtained from Aldrich.

2-(4-Fluorophenyl)thiophene, 2c. Under nitrogen, a 50 mL Schlenk flask was charged with *S*-(4-fluorophenyl) tetramethylenesulfonium PF_6^- (0.86 g, 2.61 mmol), thiophene-2-boronic acid (0.40 g, 3.13 mmol), freshly ground K_2CO_3 sesquihydrate (1.5 g), and Pd(dppf)Cl_2 (0.038 g, 2 mol %). Degassed 95% EtOH (8 mL) was added and the reaction mixture was stirred at 40 °C for 3 h. It was diluted with Et_2O (100 mL), washed with water (2 x 100 mL) and brine (100 mL), and the organic layer was collected and dried over Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified by chromatography (Chromatotron®, 4 mm SiO_2, 100 % hexanes) to give 0.345 g (74 %) of a crystalline solid: Mp 48-49 °C (EtOH); IR (CH_2Cl_2, KBr, cm^{-1}): 3047 (w), 1496 (s), 1225 (m). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.56 (dd, *J* = 2.1, 5.4 Hz, 2 H), 7.23 (dd, *J* = 2.1, 9.1 Hz, 2 H), 7.07 (d, *J* = 2.1 Hz, 1 H), 7.05 (app s, *J* = Hz, 1 H), 7.03 (app d, *J* = 4.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 162.3 (d, *J* = 246 Hz), 128.1 (s), 127.7 (d, *J* = 8.46 Hz), 127.5 (s), 124.8 (s), 123.1 (s), 115.8 (d, *J* = 21.72 Hz). Anal. Calcd for $C_{10}H_7FS$: C, 67.39; H, 3.96; F, 10.66; S, 17.99. Found: C, 67.11; H, 3.99; S, 18.22.

2-Methoxy-5-(3-thienyl)pyridine, 2d. By the same procedure, *S*-(2-methoxy-5-pyridyl) tetramethylenesulfonium PF_6^- (0.60 g, 1.76 mmol) and 3-thiopheneboronic acid (0.36 g, 2.81 mmol) after 3 h at 40 °C gave, after chromatography (Chromatotron® rotor, silica gel, 4 mm, 50% Et_2O/hexanes), product as a colorless oil (0.269 g, 1.41 mmol, 80%). IR (CH_2Cl_2, KBr, cm^{-1}): 3011 (w), 2947 (w), 1602 (s), 1489 (s), 1382 (s), 1289 (s), 1019 (s). ^1H NMR ($(CD_3)_2SO$, 360 MHz): δ 8.42 (d, *J* = 2.4 Hz, 1 H), 7.77 (dd, *J* = 2.4, 8.5 Hz, 1 H), 7.27 (d, *J* = 4.9 Hz, 1 H), 7.21 (d, *J* = 3.7 Hz, 1 H), 7.08 (app t, *J* = 4.3 Hz, 1 H), 6.77 (d, *J* = 8.5 Hz, 1 H),

3.96 (s, 3 H). ^{13}C NMR ($(CD_3)_2SO$, 75.5 MHz): δ 163.5 (s), 144.2 (s), 140.7 (s), 136.4 (s), 128.1 (s), 124.6 (s), 124.1 (s), 122.9 (s), 110.9 (s), 53.6 (s, OCH_3). Anal. Calcd for $C_{10}H_9NOS$: C, 62.80; H, 4.74; N, 7.32; S, 16.77. Found: C, 62.86; H, 4.80; N, 7.31; S, 16.74.

2-*(E)*-Styrylthiophene, 2e. A 25 mL Schlenk flask was charged with *S*-(2-thienyl) tetramethylenesulfonium PF_6^- (0.50 g, 1.58 mmol), (Z) β-styrylboronic acid (0.30 g, 2.37 mmol), freshly ground K_2CO_3 sesquihydrate (1.2 g), and Pd(dppf)Cl_2 (0.023 g, 2 mol %). THF (6 mL) was added and the reaction mixture was stirred at 50 °C for 9 h. It was diluted with Et_2O (100 mL) and treated with decolorizing carbon and anhydrous sodium sulfate. After filtration through Celite™, the solvents were removed under reduced pressure and the crude product was purified by chromatography (Chromatotron®, 4 mm SiO_2, 100 % hexanes) to give 0.210 g (71 %) of a colorless solid: Mp = 110-111 °C (hexanes). *Lit.*[17] *Mp.* = 111 °C.

Alkenyl Sulfonium Cross-coupling Reactions

1-Methylthio-4-(1-phenylethenyl)benzene, 3a. Under nitrogen with stirring, a mixture of *S*-(1-phenylethene-1-yl) tetramethylenesulfonium PF_6^- (0.17 g, 0.500 mmol, 1.00 equiv) and 3-thiomethylphenylboronic acid (0.08 g, 0.500 mmol, 1.00 equiv) was treated with K_2CO_3 (0.80 g, 5.790 mmol, 11.58 equiv) and $PdCl_2$dppf (0.004 g, 0.005 mmol) in THF (4 mL). The reaction color changed from red to yellow within 5 min. After 8 h at 40 °C the reaction mixture was filtered, the solid was washed with Et_2O (2 x 20 mL), the filtrate was evaporated and the residues were subjected to chromatography (Chromatotron®, silica gel, 4 mm, hexanes-Et_2O gradient) giving 1-methylthio-4-(1-phenylethenyl)benzene as a white solid (0.084 g, 0.370 mmol, 74 %): Mp 59 °C (hexanes/Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.16-7.37 (m, 9 H), 5.42 (s, 1 H), 5.39 (s, 1 H), 2.46 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 15.8, 113.9, 126.2, 127.8, 128.2, 128.3, 128.6, 138.0, 138.3, 141.4, 149.4. Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.17. Found: C, 79.46; H, 6.33; S, 14.08.

1-Methyl-4-(1-phenylethenyl)benzene, 3b. By the same procedure, *S*-(1-phenylethene-1-yl) tetramethylenesulfonium PF_6^- (0.17 g, 0.500 mmol, 1.00 equiv), *p*-tolylboronic acid (0.09 g,

0.650 mmol, 1.30 equiv) with K_2CO_3 (0.80 g, 5.790 mmol, 11.58 equiv) and $PdCl_2$dppf (0.004 g, 0.005 mmol) in THF (4 mL) after 8 h at 40 °C gave, after chromatography (Chromatotron®, silica gel, 4mm, hexanes), 1-methyl-4-(1-phenylethenyl)benzene as a transparent oil (0.08 g, 0.410 mmol, 82 %).[18] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.30 (s, 3 H), 5.39 (s, 1 H), 5.42 (s, 1 H), 6.89-7.47 (m, 9 H).

α-Methylstyrene, 3c. Under nitrogen, *S*-(1-phenylethene-1-yl) tetramethylenesulfonium PF_6^- (0.168 g, 0.500 mmol) and $NiCl_2(PPh_2Me)_2$ (0.012 g, 0.022 mmol) in THF (6 mL) were treated dropwise over 2 min with dimethyl zinc (0.5 mL of 2M solution in toluene, 1.000 mmol). The temperature of the reaction mixture was increased to 45 °C and the reaction was monitored by GLC. After 12 h, quantitative GLC (decane as internal standard) indicated a 97% yield of α-methylstyrene.

***Z*-1-Methoxy-3-(1-propyl-1-pentenyl) benzene, 3d.** By the same procedure, *Z*-*S*-(4-octene-4-yl) tetramethylenesulfonium PF_6^- (0.17 g, 0.500 mmol, 1.00 equiv), 3-methoxyphenylboronic acid (0.08 g, 0.500 mmol, 1.00 equiv) with K_2CO_3 (0.80 g, 5.790 mmol, 11.58 equiv) and $PdCl_2$dppf (0.004 g, 0.005 mmol) in THF (4 mL) after 8 h at 40 °C gave, after chromatography (Chromatotron®, silica gel, 4mm, hexanes), *Z*-1-methoxy-3-(1-propyl-1-pentenyl) benzene as a transparent viscous oil (0.078 g, 0.360 mmol, 72 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J = 7.3 Hz, 3 H), 0.95 (t, J = 7.3 Hz, 3 H), 2.25-2.61 (m, 4 H), 2.17 (q, J = 7.4 Hz, 2 H), 2.45 (t, J = 7.3 Hz, 2 H), 3.79 (s, 3 H), 5.64 (t, J = 7.4 Hz, 1 H), 6.78 (d, J= 6.9, 1H), 6.87 (s,1H), 6.95 (d, J =6.9, 1H), 7.20 (t, J =6.9, 1 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 14.0, 14.0, 21.8, 23.1, 30.6, 31.8, 55.2, 111.4, 119.0, 129.0, 129.3, 139.9, 145.1, 159.4. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16; Found: C,82.47; H,10.12. NOE difference experiment: irradiation of the aromatic proton at the 2-position of benzene ring (singlet at 6.87) resulted in the increase of the absorbance at 5.64 (triplet, vinyl proton; 3.4%); irradiation at 5.64 (vinyl proton) resulted in an increase at 5.64 ppm.

***Z*-2-(1-Propyl-1-pentenyl) thiophene, 3e.** By the same procedure, *Z*-*S*-(4-octene-4-yl) tetramethylenesulfonium PF_6^- (0.17 g, 0.500 mmol, 1.00 equiv), 2-thienylboronic acid (0.06 g,

0.500 mmol, 1.00 equiv) with K_2CO_3 (0.80 g, 5.790 mmol, 11.58 equiv) and $PdCl_2$dppf (0.004 g, 0.005 mmol) in THF (4 mL) after 8 h at 40 °C gave, after chromatography (Chromatotron®, silica gel, 4mm, hexanes), 2-(1-propyl-1-pentenyl) as a yellow viscous oil (0.08 g, 0.410 mmol, 82 %).[19] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.08 (m, 1 H), 6.96-6.94 (m, 2 H), 5.89 (t, J = 7.3 Hz, 1 H), 2.44 (t, J = 7.3 Hz, 2 H), 2.16 (q, J = 7.4 Hz, 2 H), 1.39-1.58 (m, 4 H), 0.85-0.98 (m, 6 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 14.0, 14.0, 14.1, 22.2, 22.3, 22.9, 30.3, 30.5, 32.4, 121.9, 122.7, 127.1, 128.1, 133.6, 147.5.

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