**Supporting Information for**

# Improved Arene Fluorination Methodology for I(III) Salts

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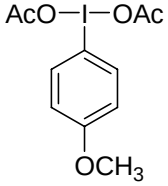
**Materials:** All materials were obtained from commercial sources and used as received unless otherwise noted. Tetramethylammonium fluoride (TMAF) and diphenyliodonium nitrate were dried at 60-80 °C in a drying pistol (charged with $P_2O_5$) under dynamic vacuum for one week. Hexabutyldistannane and chlorotributylstannane were distilled in vacuo into flame-dried storage tubes and stored under dry nitrogen. Acetonitrile and acetonitrile-$d_3$ were heated at reflux over $P_2O_5$, distilled into flame-dried storage tubes, transferred to the glove box, and were stored there over $CaH_2$. Benzene and benzene-$d_6$ were heated at reflux over $CaH_2$ overnight and distilled directly into flame-dried storage tubes under dry nitrogen. Toluene-$d_8$ was distilled over $CaH_2$ into flame-dried storage tubes and stored over molecular sieves. All glassware, syringes, and NMR tubes were oven dried (140 °C) for more than 24 h before they were transferred into the glove box for use. TBAF was synthesized according to our previously reported method.[1] All NMR experiments reported here were performed using a Bruker Avance 400 MHz NMR spectrometer in the NMR laboratory at the University of Nebraska-Lincoln.

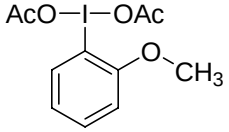
***Procedures***:

**Bis(acetyloxy)-(4-methoxyphenyl)-$\lambda_3$ –iodane; (1-(diacetoxyiodo)-4-methoxybenzene, 1a)**



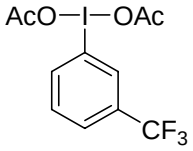

4-Iodoanisole (2.34 g, 10 mmol) was dissolved in 90 mL of glacial acetic acid and the stirred solution was warmed to 40 °C. Sodium perborate tetrahydrate (13.6 g, 110 mmol) was added in portions over the course of one hour. After the addition was complete, the temperature of the reaction mixture was maintained at 40 °C for 8 h before it was allowed to cool to room temperature. Half of the acetic acid (~ 45 mL) was removed by distillation at reduced pressure. The remaining solution was treated with 100 mL of deionized water and the aqueous layer was extracted (3 × 40 mL) with dichloromethane. The combined organic fractions were dried over sodium sulfate, and the solvent was removed by rotary evaporation to give 2.25 g (64%) of 1-(diacetoxyiodo)-4-methoxybenzene, **1a**. This compound was dried in vacuo and used without further purification. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 8.055 (d, J = 9.1 Hz, 2H, H2/H6), 7.053 (d, J = 9.1 Hz, 2H, H3/H5), 3.861 (s, 3H, OMe), 1.905 (s, 6H, $(OCOCH_3)_2$); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 177.73 (CO), 163.73 (C4), 138.75 (C2/C6), 118.00, (C3/C5), 111.97 (C1), 56.85 (OMe), 20.76 ($(OCOCH_3)_2$); HRMS: (HRFAB) calcd. for $C_{14}H_{13}NO_4I$ $[M - 2OAc+3\text{-}NBA]^+$ 385.9889 found 385.9885. (lit. [2,3] $^{13}$C NMR ($CDCl_3$, 50 MHz, 20 °C) δ 162.0 (C4), 137.0 (C2/C6), 116.5 (C3/C5), 111.4 (C1).); $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) δ 176.31 (CO), 111.64 (C1), 20.36 ($(OCOCH_3)_2$).)

**Bis(acetyloxy)-(2-methoxyphenyl)-$\lambda_3$ –iodane; (1-(diacetoxyiodo)-2-methoxybenzene, 3a)**



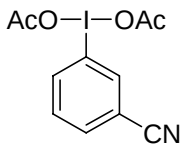
2-Iodoanisole (2.34 g, 10 mmol) was dissolved in 90 mL of glacial acetic acid and the stirred solution was warmed to 40 °C. Sodium perborate tetrahydrate (13.6 g, 110 mmol) was added in portions over the course of one hour. After the addition was complete, the temperature of the reaction mixture was maintained at 40 °C for 8 h before it was allowed to cool to room temperature. Half of the acetic acid (~ 45 mL) was removed by distillation at reduced pressure. The remaining solution was treated with 100 mL of deionized water and the aqueous layer was extracted (3 × 40 mL) with dichloromethane. The combined organic fractions were dried over sodium sulfate, and the solvent was removed by rotary evaporation to give 2.29 g (65%) of 1-(diacetoxyiodo)-2-methoxybenzene. This compound was dried in vacuo and used without further purification. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 8.175 (d, J = 8.0 Hz, 1H, H6), 7.690 (dd, $J_1$ = 7.6, $J_2$= 8.2 Hz 1H, H5), 7.313 (d, J =8.2 Hz, 1H, H3), 7.085 (dd, $J_1$ =8.0, $J_2$=7.6 Hz, 1H, H4), 3.958 (s, 3H, OMe), 1.884(s, 6H, $(OCOCH_3)_2$); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 178.00 (CO), 157.72(C2), 139.09 (C6), 136.34 (C4), 124.17 (C3), 113.91 (C1), 113.87 (C5), 58.20 (OMe), 20.71($(OCOCH_3)_2$); HRMS (HRFAB): calcd. for $C_{14}H_{13}NO_4I$ $[M - 2OAc+3\text{-}NBA]^+$ 385.9889 found 385.9874. (lit.[4] $^1$H NMR δ (270 MHz, $CDCl_3$) 8.10 (1H, d, H6 J = 8 Hz), 7.56 (1H, t, H5 J = 8 Hz), 7.13 (1H, d, H3, J = 8 Hz), 7.00 (1H, t, H4 J = 8 Hz), 3.95 (3H, s, $OCH_3$), 1.93 (6H, s, $(OCOCH_3)_2$); $^{13}$C NMR (68 MHz; $CDCl_3$) δ 176.7 (CO), 156.3 (C3), 137.8, 134.6, 122.9, 113.4 (C1), 112.1, 57.0 (OMe), 20.5 ($(OCOCH_3)_2$).)

**Bis(acetyloxy)-(3-(trifluoromethy)phenyl)-$\lambda_3$ –iodane; (1-(diacetoxyiodo)-3-(trifluoromethyl)benzene, 6a)**



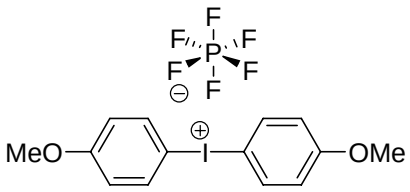

1-(Diacetoxyiodo)-3-(trifluoromethyl)benzene (3.12 g, 80%) was prepared from 3-iodobenzotrifluoride (2.72 g, 10 mmol) using the identical procedure used to prepare **1a**. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 8.492 (s, H1, C2), 8.397 (d, J = 8.3 Hz, 1H, C6), (d, J = 7.9 Hz, 1H, C4), (dd, $J_1$ = 8.3 Hz, $J_2$ = 7.9 Hz, 1H, C5), 1.939 (s, 6H, $(OCOCH_3)_2$); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 178.03 (CO), 140.25 (C6), 133.45 (q, J = 33.5 Hz, C3), 133.24 (q, J = 3.9 Hz, C2), 133.14 (C5), 130.07 (q, J = 3.7 Hz, C4), 123.96 (q, J = 273.1 Hz, $CF_3$), 122.02 (C1), 20.73 ($(OCOCH_3)_2$); $^{19}$F NMR ($CD_3CN$, 376MHz, 25 °C) δ -63.255 ($^1J_{C\text{-}F}$= 273.1 Hz, $^2J_{C\text{-}F}$= 33.5 Hz); HRMS (HRFAB): calcd. for $C_{14}H_{10}NO_3IF_3$ $[M - 2OAc+3\text{-}NBA]^+$ 423.9657 found 423.9645. (lit.[5]: $^1$H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 6 H, $(OCOCH_3)_2$), 7.65 (t, J = 7.9 Hz, 1 H, ArH), 7.85 (d, J = 7.9 Hz, 1H, ArH), 8.28 (d, J = 7.9 Hz, 1 H, ArH), 8.33 (s, 1 H, ArH); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 176.5, 138.1, 132.9 (q, $J_{CF}$ = 33.4 Hz, $CCF_3$), 131.7 (q, $J_{CF}$ = 3.7 Hz, $CCCF_3$), 131.2, 128.4 (q, $J_{CF}$ = 3.7 Hz, CCCF3), 122.7 (q, $J_{CF}$ = 270.8 Hz, $CF_3$), 120.9, 20.2.)

**Bis(acetyloxy)-(3-cyanophenyl)-$\lambda_3$ –iodane; (3-(diacetoxyiodo)benzonitrile, 7a)**



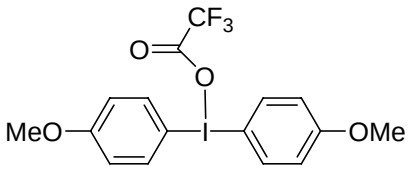
3-(Diacetoxyiodo)benzonitrile (2.43 g, 70%) was prepared from 3-iodobenzonitrile (2.29 g, 10 mmol) using the identical procedure used to prepare **1a**. $^{1}$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 8.515 (s, 1H, H2), 8.406 (d, J = 8.1 Hz, 1H, H6), 7.866 (d, J = 8.1 Hz, 1H, H4), 7.711 (t, J = 8.1 Hz, 1H, H5), 1.954 (s, 6H, $(OCOCH_3)_2$); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 178.25 (CO), 140.65 (C6), 139.69 (C2), 136.88 (C5), 132.95 (C4), 121.84 (C3), 115.82 (CN), 109.99 (C1); HRMS (HRFAB): calcd. for $C_{14}H_{10}N_2O_3I$ $[M - 2OAc+3\text{-}NBA]^+$ 380.9736 found 380.9722. (lit.[6]: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 7.61-8.39(4H, m, ArH), 2.02(6H, s, $MeCO_2$).)

**Bis(4-methoxyphenyl)iodonium hexafluorophosphate (1d)**



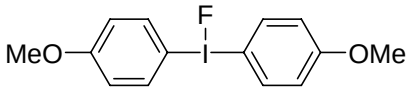

In a glove box under nitrogen, 1-(diacetoxyiodo)-4-methoxybenzene (**1a**) (352 mg, 1 mmol) was weighed into a glass vial and 1.5 mL of dry acetonitrile was added. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, 4-iodoanisole (neat, 0.11 mL, 1 mmol) was added and the vial was sealed and taken out of the glove box; the mixture was allowed to stir at room temperature for 2 h. Water (10 mL) was added and the mixture was transferred to a separatory funnel and extracted (3 × 5 mL) with hexanes. The reserved aqueous layer was treated with 502 mg (3 mmol) of $NaPF_6$. The white precipitate was filtered, dried in vacuo, and recrystallized in a mixture of diethyl ether/dichloromethane to give 391 mg of bis(4-methoxyphenyl)iodonium hexafluorophosphate (80.5%). $^{1}$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 7.973 (d, J = 9.1 Hz, 4H, H2/H2'/H6/H6'), 7.046 (d, J = 9.1 Hz, 4H, H3/H3'/H5/H5'), 3.833 (s, 6H, OMe); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 164.61 (C4/C4'), 138.55 (C2/C2'/C6/C6'), 119.42 (C3/C3'/C5/C5'), 103.36 (C1/C1'), 57.06 (OMe); $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C) δ -72.833 (d, $^{1}J_{P\text{-}F}$ = 707.3 Hz, $PF_6^-$); HRMS (HRFAB): calcd. for $C_{14}H_{14}O_2I$ $[M - PF_6]^+$ 341.0038 found 341.0036.

**Bis(4-methoxyphenyl)-trifluoroacetoxy- $\lambda_3$-iodane; (bis(4-methoxyphenyl)iodonium trifluoroacetate, 1e)**



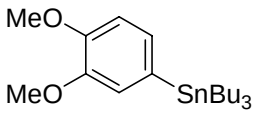
In a nitrogen flushed Schlenk tube equipped with a magnetic stir bar and a rubber septum seal, 1-(diacetoxyiodo)-4-methoxybenzene (**1a**) (1.41 g, 4 mmol) was dissolved in 30 mL of dry dichloromethane and the solution was cooled to -30 °C. Trifluoroacetic acid (0.61 mL, 8 mmol) was added and the solution was allowed to warm slowly to room temperature and stirred for 30 min. Subsequently, the solution was cooled to -30 °C and anisole (0.44mL, 4 mmol) was added dropwise by syringe. When the addition was complete, the mixture was allowed to warm to room temperature and stirred for an additional 1 h. The solvent was removed by rotary evaporation and the residual solid was recrystallized from diethyl ether/dichloromethane to give 1.53 g (71%) of bis(4-methoxyphenyl)iodonium trifluoroacetate. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 7.951 (d, J = 9.1 Hz, 4H, H2/H2'/H6/H6'), 6.981 (d, J = 9.1 Hz, 4H, H3/H3'/H5/H5'), 3.805 (s, 6H, OMe); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 163.84 (C4/C4'), 138.14 (C2/C2'/C6/C6'), 118.69 (C3/C3'/C5/C5'), 106.64 (C1/C1'), 56.86 (OMe); $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C) δ -75.436 ($CF_3^-$, $^1J_{C-F}$ = 297.3 Hz, $^1J_{C-F}$ = 33.3 Hz).

**Bis(4-methoxyphenyl)-fluoro-$\lambda_3$-iodane; (bis(4-methoxyphenyl)iodonium fluoride, 1(F)**



In a glove box under nitrogen, a mixture of 454 mg (1 mmol) bis(4-methoxyphenyl)iodonium trifluoroacetate (**1e**) and 262 mg (1 mmol) anhydrous tetrabutylammonium fluoride (TBAF) was treated with 1 mL of dry tetrahydrofuran (THF). The solution was allowed to stand for 1 h, the white precipitate was collected and washed (3 × 0.5 mL) with THF. Calculated yield: 288.7 mg (80.2%). Iodonium salts were shielded from the light during all operations. $^1$H NMR (saturated solution in $CD_3CN$, 400 MHz, 25 °C): δ 7.739 (d, J = 8.9 Hz, 4H, H2/H2'/H6/H6'), 6.853 (d, J = 8.9 Hz, 4H, H3/H3'/H5/H5'), 3.769 (s, 6H, OMe); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 162.43 (C4/C4'), 136.98 (C2/C2'/C6/C6'), 117.52 (C3/C3'/C5/C5'), 113.20 (C1/C1'), 56.55 (OMe); $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C) δ -17.91 (broad s, I-F).

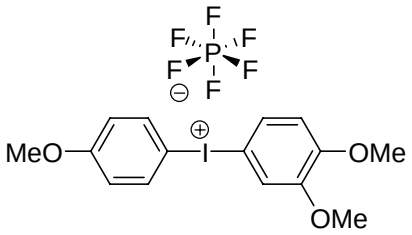
**3,4-Dimethoxyphenyltributyltin (2c)**



In a glove box under nitrogen, 4-bromoveratrole (1.085 g, 5 mmol) and $Pd(PPh_3)_4$ (289 mg , 0.25 mmol) were dissolved in 15 mL of dry toluene. The solution was transferred into a storage tube equipped with PTFE chemcap seal, and hexabutylditin (3.19 g, 5 mmol) was added. The tube was sealed, taken out of

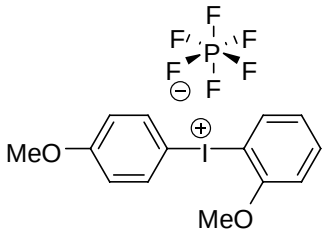
the glove box, and heated at 120 °C for 48 h. The reaction mixture was allowed to cool to room temperature and diluted with hexane (15 mL) before saturated aqueous KF solution (15 mL) was added. The mixture was stirred for 30 min, filtered through celite, and the organic layer was separated. The solvent was removed in vacuo to give the crude product as a yellow oil. The crude product was purified by column chromatography (Rf = 0.4, hexane/dichloromethane 98/2, basic alumina) to give 1.69 g (79.1%) of 3,4-dimethoxyphenyltributyltin. $^{1}$H NMR ($C_6D_6$, 400 MHz, 25 °C): δ 7.097 (d, J = 7.7 Hz, 1H, H6), 7.074 (s, 1H, H2), 6.744 (d, J = 7.7 Hz, 1H, H5), 3.557 (s, 3H, 3-OMe), 3.443 (s, 3H, 4-OMe), 1.632 (m, 6H, β$CH_2$), 1.384 (m, 6H, γ$CH_2$), 1.117 (m, 6H, α$CH_2$), 0.912 (t, J = 7.6 Hz, 9H, $CH_3$), (coupling to $^{117}$Sn and $^{119}$Sn observed, J ranged from 10.7 – 41.3 Hz); $^{13}$C NMR ($C_6D_6$, 100 MHz, 25 °C) δ 151.21 (C4), 150.66 (C6), 132.35 (C1), 130.13 (C3), 120.75 (C5), 113.12 (C2), 56.21 (3-OMe), 55.75 (4-OMe), 29.87 (γC), 28.16 (βC), 14.31 (δC), 10.32 (αC), (coupling to $^{117}$Sn and $^{119}$Sn observed, J ranged from 1.0 – 320.8 Hz); HRMS (HRFAB): calcd. for $C_{20}H_{37}O_2Sn$ $[M + H]^+$ 429.1815 found 429.1799. (lit.[7]: $^{1}$H NMR ($CDCl_3$): δ 6.7 - 7.3 (m, 3H, Ar-H), 3.89 (s, 3H, OMe), 3.86 (s, 3H, OMe), 1.1-1.8 (m, 18H, 9 × $CH_2$), 0.89 (s, 9H, 3 × $CH_3$); b.p. 166-172 °C/0.4mmHg.)

**(3,4-Dimethoxyphenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (2d)**



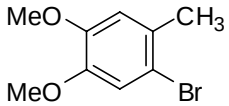

In a glove box under nitrogen, 1-(diacetoxyiodo)-4-methoxybenzene (352 mg, 1 mmol) was dissolved in 1.5 mL of dry acetonitrile and a solution of p-toluenesulfonic acid monohydrate (190 mg, 1 mmol) in 1.5 mL of dry acetonitrile was added. 3,4-Dimethoxyphenyl)tributyltin, **2c** (427 mg, 1 mmol) was added and the mixture was allowed to react at room temperature for 2 h. Water (10 mL) was added and the mixture was extracted (3 × 5 mL) with hexanes. The aqueous layer was treated with $NaPF_6$ (502 mg, 3 mmol) and the white precipitate was filtered, dried in vacuo, and recrystallized with diethylether/dichloromethane to give 370 mg (71.7%) of(3,4-dimethoxyphenyl)(4'-methoxyphenyl)iodonium hexafluorophosphate. $^{1}$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 7.986 (d, J = 9.1 Hz, 2H, H2'/H6'), 7.647 (dd, $J_1$ =8.9 Hz, $J_2$ = 2.2 Hz, 1H, H6), 7.558 (d, J = 2.2 Hz, 1H, H2), 7.049 (d, J = 9.1 Hz, 2H, H3'/H5'), 7.022 (d, J = 8.9 Hz, 1H, H5), 3.845 (s, 3H, 3-OMe), 3.843 (s, 3H, 4'-OMe), 3.834 (s, 3H, 4-OMe); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 164.58 (C4'), 154.62 (C4), 152.50 (C3), 138.49 (C2'/C6'), 130.65 (C6), 119.38 (C2), 119.13 (C3'/C5'), 115.52 (C5), 103.37 (C1), 102.64 (C1'), 57.49 (3-OMe), 57.14 (4'-OMe), 57.05 (4-OMe); $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C) δ -72.786 (d, $^{1}J_{P-F}$ = 705.8 Hz, $PF_6^-$); HRMS (HRFAB): calcd. for $C_{15}H_{16}O_3I$ $[M - PF_6]^+$ 371.0144 found 371.0156.

**(2-Methoxyphenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (3d)**



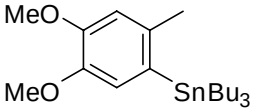
In a glove box under nitrogen, 1-(diacetoxyiodo)-2-methoxybenzene, **3a**, (352 mg, 1 mmol) was weighed into a glass vial and 1.5 mL of dry acetonitrile was added. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, 4-iodoanisole (neat, 0.11 mL, 1 mmol) was added. The vial was sealed and taken out of the glove box; the mixture was allowed to stir at room temperature for 2 h. Water (10 mL) was added and the mixture was transferred to a separatory funnel and extracted (3 × 5 mL) with hexanes. The reserved aqueous layer was treated with 502 mg (3 mmol) of $NaPF_6$. The white precipitate was filtered, dried in vacuo, and recrystallized in a mixture of diethyl ether/dichloromethane to give 405 mg (83.3%) of (2-methoxyphenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 7.988 (d, J = 9.2 Hz, 2H, H2'/H6'), 7.878 (d, J =8.4 Hz, 1H, H6), 7.659 (td, $J_1$ = 8.4 Hz, $J_2$ = 1.3 Hz,1H, H4), 7.232 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.3 Hz, 1H, H5), 7.063 (td, $J_1$ = 8.4 Hz, $J_2$ = 1.3 Hz, 1H, H3), 7.051 (d, J = 9.2, 2H, H3'/H5'), 3.970 (s, 3H, 2-OMe), 3.841 (s, 3H, 4'-OMe); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 164.73 (C4'), 157.90 (C2), 139.52 (C2'/C6'), 137.08 (C4), 136.79 (C6), 125.36 (C3), 119.44 (C3'/C5'), 114.70 (C5), 104.69 (C1), 100.92 (C1'), 58.40 (2-OMe), 57.06 (4'-OMe); $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C) δ -72.675 (d, $^1J_{P-F}$ = 706.2 Hz, $PF_6^-$); HRMS (HRFAB): calcd. for $C_{14}H_{14}O_2I$ $[M - PF_6]^+$ 341.0038 found 341.0035.

**1-Bromo-4,5-dimethoxy-2-methylbenzene (4b)**



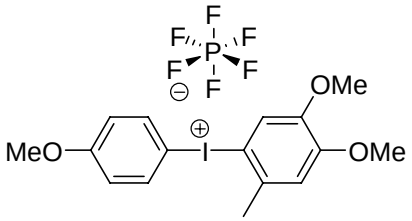
To a stirred solution of 3,4-dimethoxytoluene (3.6 mL, 25 mmol) in 125 mL of acetonitrile was added N-bromosuccinimide (4.9 g, 27.5 mmol). The mixture was stirred at room temperature for 2 h, the solvent was removed by rotary evaporation, and 100 mL of $CCl_4$ was added. The solid was succinimide was removed by filtration, the solvent was removed by rotary evaporation, and the crude product was recrystallized from hexane to afford 5.2 g (90%) of 1-bromo-4,5-dimethoxy-2-methylbenzene. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 7.022 (s, 1H, H6), 6.822 (s, 1H, H3), 3.752 (s, 3H, OMe), 3.744 (s, 3H, OMe), 2.269(s, 3H, Me); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 149.91 (C5), 149.33 (C4), 130.73 (C2), 116.73 (C6), 115.35 (C3), 115.12 (C1); HRMS (HRCI): calcd. for $C_9H_{12}O_2Br$ $[M + H]^+$ 231.0021, 233.0000 found 231.0011, 233.0013. (lit.[8]: $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.000 (s, 1H, Ar-H), 6.731 (s, 1H, Ar-H), 3.874 (s, 3H, -OMe), 3.843 (s, 3H, OMe), 2.327 (s, 3H, -Me).)

**(4,5-Dimethoxy-2-methylphenyl)tributyltin (4c)**



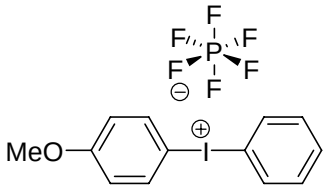
In a glove box under nitrogen, 1-bromo-4,5-dimethoxy-2-methylbenzene (**4b**) (1.155 g, 5 mmol) and $Pd(PPh_3)_4$ (289 mg ,0.25 mmol) were dissolved in 15 mL of dry toluene. The solution was transferred into a storage tube equipped with PTFE chemcap seal and hexabutylditin (3.19 g, 5 mmol) was added. The tube was sealed, removed from the glove box, and heated at 120 °C for 48 h. The reaction mixture was allowed to cool to room temperature and diluted with hexane (15 mL) before saturated aqueous KF solution (15 mL) was added. The mixture was stirred for 30 min, filtered through celite, and the organic layer was separated. The solvent was removed to give the crude product as a yellow oil. The crude product was purified by column chromatography (Rf = 0.4, hexane/dichloromethane 98/2, basic alumina) to give 1.68 g (76.2%) of (4,5-dimethoxy-2-methyl-phenyl)tributyltin. $^1$H NMR ($C_6D_6$, 400 MHz, 25 °C): δ 7.048 (s, 1H, H6), 6.661 (s, 1H, H3), 3.593 (s, 3H, 3-OMe), 3.458 (s, 3H, 4-OMe), 2.358 (s, 3H, 2-Me), 1.615 (m, 6H, β$CH_2$), 1.384 (m, 6H, γ$CH_2$), 1.143 (m, 6H, α$CH_2$), 0.910 (t, J = 7.6 Hz, 9H, $CH_3$), (coupling to $^{117}$Sn and $^{119}$Sn observed, J ranged from 5.4 – 45.6 Hz); $^{13}$C NMR ($C_6D_6$, 100 MHz, 25 °C) δ 151.11 (C4), 148.36 (C2), 137.98 (C5), 131.85 (C1), 121.44 (C3), 114.65 (C6), 56.53 (3-OMe), 55.78 (4-OMe), 30.04 (γC), 28.18 (βC), 25.04 (2-Me), 14.28 (δC), 10.77 (αC), (coupling to $^{117}$Sn and $^{119}$Sn observed, J ranged from 1.0 – 326.2 Hz); HRMS (HRFAB): calcd. for $C_{21}H_{39}O_2Sn$ $[M + H]^+$ 443.1972 found 443.1982.

**(4,5-Dimethoxy-2-methylphenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (4d)**



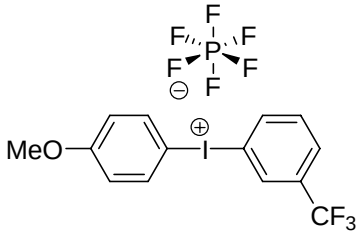

In a glove box under nitrogen, 1-(diacetoxyiodo)-4-methoxybenzene (352 mg, 1 mmol) was dissolved in 1.5 mL of dry acetonitrile. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, (4,5-dimethoxy-2-methylphenyl)tributyltin (**4c**) (441 mg, 1 mmol) added. The vial was sealed and taken out of the glove box and the mixture was allowed to stir at room temperature for 2 h. Water (10 mL) was added and the mixture was transferred to a separatory funnel and extracted (3 × 5 mL) with hexanes. The reserved aqueous layer was treated with 502 mg (3 mmol) of $NaPF_6$. The white precipitate was filtered, dried in vacuo, and recrystallized in a mixture of diethyl ether/dichloromethane to give 397 mg (75%) of (4,5-dimethoxy-2-methylphenyl)(4'-methoxyphenyl)iodonium hexafluorophosphate. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 7.939 (d, J = 9.2 Hz, 2H, H2'/H6'), 7.593 (s, 1H, H6), 7.055 (d, J = 9.2 Hz, 2H, H3'/H5'), 7.026 (s, 1H, H5), 3.835 (s, 6H, 3/4'-OMe), 3.828 (s, 3H, 4-OMe), 2.550 (s, 3H, 2-Me); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 164.45 (C4'), 154.63 (C4), 150.46 (C5), 138.28 (C2'/C6'), 136.71 (C2), 120.59 (C6), 119.41 (C3'/C5'), 115.28 (C3), 107.01 (C1), 102.58 (C1'), 57.51 (3-OMe), 57.14 (4'-OMe), 57.04 (4-OMe); $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C) δ -72.735 (d, $^1J_{P-F}$ = 706.9 Hz, $PF_6^-$); HRMS (HRFAB): calcd. for $C_{16}H_{18}O_3I$ $[M - PF_6]^+$ 3385.0301 found 3385.0313.

**Phenyl-(4-methoxyphenyl)iodonium hexafluorophosphate (5d)**



In a glove box under nitrogen, diacetoxyiodobenzene (322 mg, 1 mmol) was weighed into a glass vial and 1.5 mL of dry acetonitrile was added. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, 4-iodoanisole (neat, 0.11 mL, 1 mmol) was added and the vial was sealed and taken out of the glove box; the mixture was allowed to stir at room temperature for 2 h. Water (10 mL) was added and the mixture was transferred to a separatory funnel and extracted (3 × 5 mL) with hexanes. The reserved aqueous layer was treated with 502 mg (3 mmol) of $NaPF_6$. The white precipitate was filtered, dried in vacuo, and recrystallized in a mixture of diethyl ether/dichloromethane to give 355 mg (77.9%) of phenyl-(4-methoxyphenyl)iodonium hexafluorophosphate. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 8.022 (d, J = 7.6 Hz, 2H, H2/H6), 8.011 (d, J =9.4 Hz, 2H, H2'/H6'), 7.701 (t, J = 7.6 Hz, 1H, H4), 7.734 (t, J = 7.6 Hz, 2H, H3/H5), 7.063 (d, J = 9.4 Hz, 2H, H3'/H5'), 3.839 (s, 6H, OMe); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 164.77 (C4'), 139.04 (C2'/C6'), 136.22 (C2/C6), 134.27 (C4), 133.77 (C3/C5), 119.58 (C3'/C5'), 115.29 (C1), 102.50 (C1'), 57.09 (OMe); $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C) δ -72.754 (d, $^1J_{P\text{-}F}$ = 707.7 Hz, $PF_6^-$); HRMS (HRFAB): calcd. for $C_{13}H_{12}OI$ $[M - PF_6]^+$ 310.9925 found 310.9932.

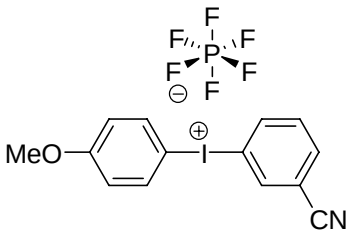
**(3-(Trifluoromethyl)phenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (6d)**



In a glove box under nitrogen, 1-(diacetoxyiodo)-3-(trifluoromethyl)benzene (**6a**) (390 mg, 1 mmol) was weighed into a glass vial and 1.5 mL of dry acetonitrile was added. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, 4-iodoanisole (neat, 0.11 mL, 1 mmol) was added and the vial was sealed and taken out of the glove box; the mixture was allowed to stir at room temperature for 2 h. Water (10 mL) was added and the mixture was transferred to a separatory funnel and extracted (3 × 5 mL) with hexanes. The reserved aqueous layer was treated with 502 mg (3 mmol) of $NaPF_6$. The white precipitate was filtered, dried in vacuo, and recrystallized in a mixture of diethyl ether/dichloromethane to give 503 mg (96.1%) of (3-(trifluoromethyl)phenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 8.384 (s, 1H, H2), 8.266 (d, J = 8.1 Hz, 1H, H6), 8.056 (d, J = 9.2 Hz, 2H, H2'/H6'), 7.996 (d, J = 8.1 Hz, 1H, H4), 7.716 (t, J = 8.1 Hz, 1H, H5), 7.083 (d, J = 9.2, 2H, H3'/H5'), 3.847 (s, 3H, 4'-OMe); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 164.99 (C4'), 139.99 (C6), 139.38 (C2'/C6'), 134.44 (C5), 134.281 (q, J = 33.6 Hz, C3), 133.08 (q, J =

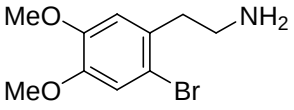
3.7 Hz, C2), 133.05 (q, J = 3.7 Hz, C4), 124.11 (q, J = 272.8 Hz, $CF_3$), 119.71 (C3'/C5'), 114.83 (C1), 102.54 (C1'), 57.13 (4'-OMe); $^{19}F$ NMR ($CD_3CN$, 376 MHz, 25 °C) δ -63.420 ($^1J_{F-C}$= 272.8 Hz, $^2J_{F-C}$= 33.6 Hz, $CF_3$), -72.625 (d, $^1J_{P-F}$ = 707.1 Hz, $PF_6^-$); HRMS (HRFAB): calcd. for $C_{14}H_{11}OIF_3$ $[M - PF_6]^+$ 378.9807 found 378.9817.

**(3-Cyanophenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (7d)**




In a glove box under nitrogen, 3-(diacetoxyiodo)benzonitrile (**7a**) (347 mg, 1 mmol) was weighed into a glass vial and 1.5 mL of dry acetonitrile was added. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, 4-iodoanisole (neat, 0.11 mL, 1 mmol) was added and the vial was sealed and taken out of the glove box. The mixture was allowed to stir at room temperature for 2 h. Water (10 mL) was added and the mixture was transferred to a separatory funnel and extracted (3 × 5 mL) with hexanes. The reserved aqueous layer was treated with 502 mg (3 mmol) of $NaPF_6$. The white precipitate was filtered, dried in vacuo, and recrystallized in a mixture of diethyl ether/dichloromethane to give 354 mg (73.7%) of (3-cyanophenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate. $^1H$ NMR ($CD_3CN$, 400 MHz, 25 °C): δ 8.389 (t, J = 1.6 Hz, 1H, H2), 8.273 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.6 Hz, 1H, H6), 8.038 (d, J = 9.4 Hz, 2H, H2'/H6'), 8.017 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.6 Hz, 1H, H4), 7.665 (t, J = 8.2 Hz, 1H, H5), 7.082 (d, J = 9.4, 2H, H3'/H5'), 3.850 (s, 3H, 4'-OMe); $^{13}C$ NMR ($CD_3CN$, 100 MHz, 25 °C) δ 165.04 (C4'), 140.40 (C6), 139.50 (C2), 139.47 (C2'/C6'), 137.79 (C5), 134.13 (C4), 119.75 (C3'/C5'), 117.63 (C3), 116.75 (CN), 114.53 (C1), 102.56 (C1'), 57.16 (4'-OMe); $^{19}F$ NMR ($CD_3CN$, 376 MHz, 25 °C) δ -72.675 (d, $^1J_{P-F}$ = 707.5 Hz, $PF_6^-$); HRMS (HRFAB): calcd. for $C_{14}H_{11}NOI$ $[M - PF_6]^+$ 335.9885 found 335.9876.

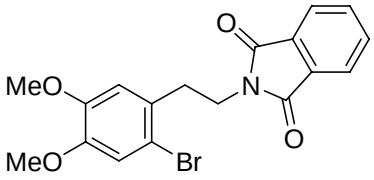
**2-(2-Bromo-4,5-dimethoxyphenyl)ethanamine (8f)**




A solution of bromine (1.1 mL, 22 mmol) in acetic acid (10 mL) was added slowly to a vigorously stirred solution of 2-(3,4-dimethoxyphenyl)ethanamine (3.4 mL, 20 mmol) in 50 mL of acetic acid. The mixture was stirred for two hours, filtered, and the isolated solid was washed with dichloromethane (3 × 10 mL) and petroleum ether (3 × 10 mL). The remaining solid was dissolved in water and the pH was adjusted to 10 with aqueous KOH solution. The aqueous solution was extracted with dichloromethane (3 × 10 mL) and the combined organic layers were evaporated to give 4.12g (78%) of 2-(2-bromo-4,5-

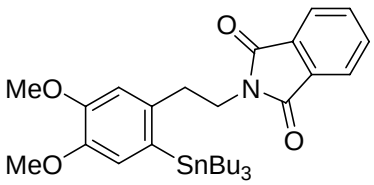
dimethoxyphenyl)ethananamine. The crude product was dried under dynamic vacuum overnight and used without further purification. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 7.00 (s, 1H, H6), 6.73 (s, 1H, H3), 3.85 (s, 3H, OMe), 3.84 (s, 3H, OMe), 2.94 (t, J = 7.17 Hz, 2H, $CH_2$), 2.81 (t, J = 7.17 Hz, 2H, $CH_2$), 1.24 (s, 2H, $NH_2$); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C): δ 148.34 (C5), 148.07 (C4), 131.09 (C2), 115.66 (C6), 114.33 (C1), 113.43 (C3), 56.15 (OMe), 42.40 ($CH_2$), 39.92 ($CH_2$); HRMS (HRFAB): calcd. for $C_{10}H_{14}O_2NBr$ $[M + H]^+$ 262.0266, 260.0286 found 262.0262, 260.0276. (lit.[9]: $^1$H NMR δ 1.38, s, $NH_2$; 2.8-2.9, m, $CH_2Ar$; 2.9-3.0, m, $CH_2N$; 3.85, s, $OCH_3$; 3.86, s, $OCH_3$; 6.74, s, 1H. $^{13}$C NMR δ 39.8, $CH_2$; 42.3, $CH_2$; 56.1, 2× $OCH_3$; 113.4, C3 or C6; 114.3, CBr; 115.6, C6 or C3; 131.0, C1; 148.0, C4 or C5; 148.3, C5 or C4. MS (c.i., $NH_3$) m/z 262 (MH, 98%), 260 (MH, 100), 182 (20), 180 (14).)

**2-Bromo-4, 5-dimethoxyl-1-(2-phthalimidoethyl)benzene (8b)**




2-(2-Bromo-4,5-dimethoxyphenyl)ethanamine (**8f**) (3.5 g, 13.2 mmol) was dissolved in 50 mL of dry acetonitrile and phthaloyl dichloride (2.14 mL, 14.5 mmol) and diisopropylethylamine (7 mL, 39.6 mmol) were added. This mixture was stirred at room temperature for 14 h. The acetonitrile was removed by rotary evaporation and the remaining material was taken up in dichloromethane and washed with alkaline water (pH = 11). The aqueous wash was extracted with dichloromethane (3 × 15 mL), and the organic fractions were combined and dried over sodium sulfate. The solvent was removed by rotary evaporation to give a colorless solid. This crude product was dissolved in dichloromethane and loaded on top of a silica gel column (60 Å silica) and the purified product was eluted with dichloromethane (Rf = 0.2). The solvent was removed by rotary evaporation to give **8b** (1.8 g, 34%). $^1$H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.83 (m, 2H, phthalimide), 7.71 (m, 2H, phthalimide), 7.00 (s, 1H, H6), 6.68 (s, 1H, H3), 3.96 (t, J = 7.02 Hz, 2H, $CH_2$), 3.84 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.08 (t, 2H, J = 7.02 Hz, $CH_2$); $^{13}$C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 168.17 (CO), 148.35 (C5), 148.30 (C4), 133.97 (C3'/C6'), 132.04 (C1'/C2'), 129.30 (C2), 123.24 (C4'/C5'), 115.54 (C6), 114.50 (C1), 113.20 (C3), 56.08 (OMe), 55.95 (OMe), 37.65 ($CH_2$), 34.40 ($CH_2$); HRMS (ESI): calcd. for $C_{18}H_{16}O_4NBr$ $[M + Na]^+$ 412.0160, 414.0140 found 412.0173, 414.0143. (lit.[10]: $^1$H NMR ($CDCl_3$, 200 MHz): δ 2.99 (2H, dd, H-β); 3.63 (3H, S, $OCH_3$); 3.75 (3H, s, $OCH_3$); 3.88 (2H, dd, H-α); 6.65 (1H, s, H-3), 6.91 (1H, s, H-6); 7.64 (2H, tt, H-5', H-6'); 7.75 (2H, dddd, H-4', H-7').)

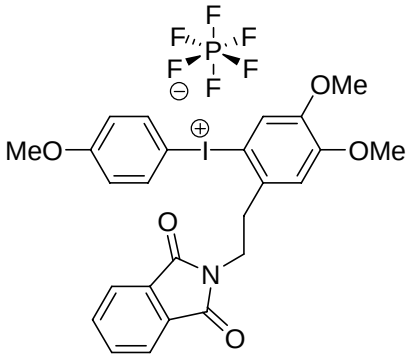
**(4,5-Dimethoxy-2-(2-phthalimido)phenyl)tributyltin (8c)**




In a glove box under nitrogen, 2-bromo-4,5-dimethoxy-1-(2-phthalimidoethyl)benzene (**8b**) (1.945 g, 5 mmol) and $Pd(0)(PPh_3)_4$ (289 mg ,0.25 mmol) was dissolved in 15 mL of dry toluene. The solution was transferred into a storage tube equipped with a PTFE chemcap seal and hexabutylditin (3.19 g, 5 mmol)

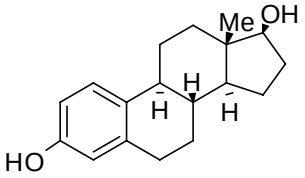
was added. The tube was sealed, removed from the glove box, and heated to at 120 °C for 48 h. The reaction mixture was allowed to cool to room temperature and diluted with hexane (15 mL) before saturated aqueous KF solution (15 mL) was added. The mixture was stirred for 30 min, filtered through celite, and the organic layer was separated. The solvent was removed to give the crude product as a yellow oil. The crude product was purified by column chromatography (Rf = 0.4, hexane/dichloromethane 95/5, basic alumina) to give 0.68 g (22.6%) of (4,5-dimethoxy-2-(2-phthalimido)phenyl)tributyltin. $^{1}$H NMR ($C_6D_6$, 400 MHz, 25 °C): δ 7.41 (m, 2H, phthalimide), 7.10 (s, 1H, H3), 7.01 (s, 1H, H6), 6.84 (m, 2H, phthalimide), 3.93 (t, J= 8.14 Hz, 2H, $CH_2$), 3.56 (s, 3H, OMe), 3.43 (s, 3H, OMe), 3.12 (t, J = 8.14 Hz, 2H, $CH_2$), 1.73 (m, 6H, β$CH_2$), 1.44 (m, 6H, γ$CH_2$), 1.35 (m, 6H, α$CH_2$), 0.960 (t, J = 7 Hz, 9H, $CH_3$), (coupling to $^{117}$Sn and $^{119}$Sn observed, J ranged from 8.14 – 50.48 Hz); $^{13}$C NMR ($C_6D_6$, 100 MHz, 25 °C) δ 167.64 (CO), 150.70 (C4), 147.40 (C2), 137.95 (C5), 133.21 (C3'/C6'), 132.39 (C1'/C2'), 132.00 (C1), 122.73 (C4'/C5'), 120.50 (C6), 55.64 (OMe), 55.05 (OMe), 39.90 ($CH_2$), 37.71 ($CH_2$), 29.54 (γC), 27.66 (βC), 13.76 (δC), 10.66 (αC), (coupling to $^{117}$Sn and $^{119}$Sn observed, J ranged from 1.0 – 322.00 Hz); HRMS (HRCI): calcd. for $C_{30}H_{43}O_4NSn$ $[M + H]^+$ 602.2292, found 602.2281.

**(4,5-Dimethoxy-2-(2-phthalimidoethyl)phenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (8d)**



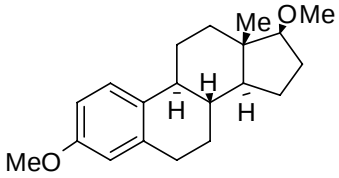

In a glove box under nitrogen, 1-(diacetoxyiodo)-4-methoxybenzene (352 mg, 1 mmol) was dissolved in 1.5 mL of dry acetonitrile. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, (4,5-dimethoxy-2-(2-phthalimido)phenyl)tributyltin (**9c**) (601 mg, 1 mmol) was added and the mixture was allowed to stir at room temperature for 2 h outside the glove box. Water (10 mL) was added and the mixture was transferred to a separatory funnel and extracted (3 × 5 mL) with hexanes. The reserved aqueous layer was treated with 502 mg (3 mmol) of $NaPF_6$. The white precipitate was filtered, dried in vacuo, and recrystallized in a mixture of diethyl ether/dichloromethane to give 379 mg (55%) of (4,5-dimethoxy-2-(2-phthalimidoethyl)phenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate. $^{1}$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 8.00 (d, J = 9.15 Hz, 2H, H2''/H6''), 7.81 (m, 4H, phthalimide), 7.61 (s, 1H, H6), 7.37 (s, 1H, H3), 7.00 (d, J = 9.15 Hz, 2H, H3''/H5''), 3.87 (t, J = 7.52 Hz, $CH_2$), 3.85 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.20 (t, J = 7.52 Hz, $CH_2$); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C) δ 168.21 (CO), 163.08 (C4''), 153.25 (C4), 149.95 (C5), 136.80 (C2''/C6''), 135.06 (C2), 134.41 (C3'/C6'), 132.01 (C1'/C2'), 123.06 (C4'/C5'), 119.54 (C3), 118.06 (C3''/C5''), 113.73 (C6), 106.01 (C1), 101.80 (C1''), 56.22 (OMe), 55.85 (OMe), 55.69 (OMe), 38.04 ($CH_2$), 36.67 ($CH_2$); $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C) δ -72.785 (d, $^{1}J_{P-F}$ = 706.59 Hz, $PF_6^-$) ; HRMS (HRFAB): calcd. for $C_{25}H_{23}O_5NPF_6I$ $[M - PF_6]^+$ 544.0621, found 544.0615.

**β-Estradiol (9g)**[11]



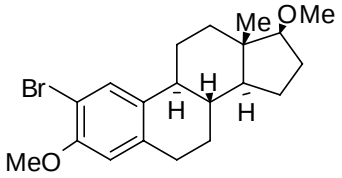

A solution of estrone (2.60 g, 9.62 mmol) in 130 mL of methanol was treated with concentrated aqueous NaOH (1.14 g, 28.5 mmol) and added to a stirred solution of $NaBH_4$ (0.97 g, 25.53 mmol) in 130 mL of methanol. $H_2$ evolution ceased after about 45 min, and the mixture was poured into 200 mL of water and neutralized with 3 M HCl. The precipitate was filtered, washed with water and recrystallized from hot aqueous methanol to give β-estradiol (2.54 g, 97% from two crops). $^1$H NMR (DMSO-$d_6$, 400 MHz, 25 °C): δ 8.983 (s, 1H), 7.044 (d, J = 8.4 Hz, 1H), 6.500 (d, J = 8.4 Hz, 1H), 6.428 (s, 1H), 4.496 (d, J = 4.8 Hz, 1H), 3.52 (m, 1H), 2.697 (m, 2H), 2.229 (m, 1H), 2.065 (m, 1H), 1.94-1.73 (m, 3H), 1.582 (m, 1H), 1.43-1.05 (m, 7H), 0.665 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz, 25 °C): δ 154.89, 137.14, 130.42, 126.05, 114.91, 112.71, 80.06, 49.52, 43.54, 42.82, 38.70, 36.60, 29.90, 29.17, 26.96, 26.09, 22.79, 11.28; HRMS (ESI) calcd. for $C_{18}H_{24}O_2Na$ $[M + Na]^+$ 295.1674 found 295.1668.

**3,17-Dimethoxy-β-estra-1,3,5(10)-triene (9f)**[12]



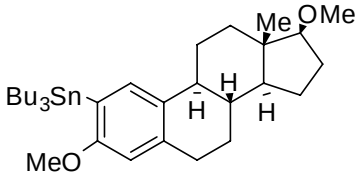

A previously reported procedure[12] was improved slightly. β-Estradiol (9g) (2.54 g, 9.32 mmol) was dissolved in 125 mL of dry THF under $N_2$ and cooled to 0 °C. NaH (1.07 g, 44.58 mmol) was added, and the reaction mixture was stirred for 15 min. $CH_3I$ (5.40 mL, 86.48 mmol) was added by syringe, and the turbid reaction mixture was stirred overnight and allowed to warm slowly to room temperature. The reaction mixture was poured carefully into ice-water. After the effervescence ceased, the organic product was extracted into EtOAc (3 x 125 mL), washed with aqueous $NaHCO_3$ (125 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to afford 3,17-dimethoxy-β-estra-1,3,5(10)-triene (2.33 g, 83%) as an off-white solid. $^1$H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.218 (d, J = 8.6 Hz, 1H), 6.722 (dd, $J_1$ = 8.6 Hz, $J_2$ = 2.6 Hz, 1H), 6.640 (d, J = 2.6 Hz, 1H), 3.787 (s, 3H), 3.391 (s, 3H), 3.327 (t, J = 8.3 Hz, 1H), 2.861 (m, 2H), 2.297 (m, 1H), 2.200 (m, 1H), 2.15-2.00 (m, 2H), 1.94-1.84 (m, 1H), 1.76-1.64 (m, 1H), 1.58-1.15 (m, 7H), 0.800 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 157.61, 138.19, 132.89, 126.55, 113.97, 111.66, 91.01, 58.13, 55.41, 50.49, 44.13, 43.43, 38.81, 38.27, 30.04, 27.98, 27.44, 26.67, 23.26, 11.76; HRMS (ESI) calcd. for $C_{20}H_{28}O_2Na$ $[M + Na]^+$ 323.1987 found 323.1994. (Lit.[12]: $^1$H NMR ($CDCl_3$): δ 7.18 (d, J = 8.63 Hz, 1H), 6.68 (d, J = 8.54 Hz, 1H), 6.60 (s, 1H), 3.75 (s, 3H), 3.36 (s, 3H), 3.29 (t, J = 16.62 Hz, 1H), 2.84 (m, 2H), 2.25 (m, 1H), 2.15 (t, J = 21.87 Hz, 1H), 2.02 (m, 2H), 1.84 (m, 1H), 1.66 (m, 1H), 1.52-1.17 (m, 7H), 0.77 (s, 3H); LRMS (CI): *m/z* (rel intensity) 301 (MH+, 100).)

**2-Bromo-3,17-dimethoxy-β-estra-1,3,5(10)-triene (9b)**[13]



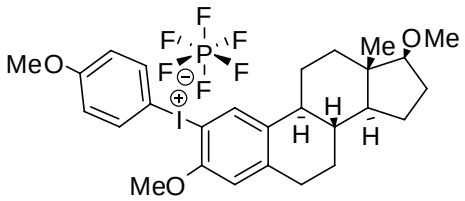

A solution of N-bromosuccinimide (1.51 g, 8.5 mmol) in $CH_3CN$ (30 mL) was added to a $CCl_4$ solution (70 mL) of dimethoxy-β-estra-1,3,5(10)-triene (**9f**) (2.32 g, 7.72 mmol), and the resulting mixture was stirred at room temperature protected from light for 2.5 h. The solvent was removed in vacuo to obtain a residual mixture of a yellow oil and a white solid. $CCl_4$ was added and the solution was filtered and evaporated to give a yellow oil. The oil was triturated in warm methanol to yield a crude solid, which was determined by $^1$H-NMR to be an 80:20 mixture of the 2-bromo and the 4-bromo estradiol dimethyl ethers (2.30 g, 78.5%). Recrystallization of the crude product mixture from hot methanol (1$^{st}$ crop) gave 2-Bromo-3,17-dimethoxy-β-estra-1,3,5(10)-triene (1.40g, 48%) as a white solid in 95% purity, with the 4-bromo isomer as a trace impurity. The solid was carried forward to the next step without further purification. $^1$H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.434 (s, 1H), 6.615 (s, 1H), 3.860 (s, 3H), 3.385 (s, 3H), 3.319 (t, J = 8.4 Hz, 1H), 2.820 (m, 2H), 2.29-2.01 (m, 4H), 1.93-1.85 (m, 1H), 1.75-1.64 (m, 1H), 1.58-1.15 (m, 7H), 0.796 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 153.70, 137.40, 134.47, 130.44, 112.50, 108.74, 90.89, 58.13, 56.40, 50.38, 43.90, 43.39, 38.53, 38.10, 29.82, 27.96,27.26, 26.63, 23.23, 11.34; HRMS (FAB) calcd. for $C_{20}H_{27}O_2Br$ $[M]^+$ 378.1194, 380.1174 found 378.1149, 380.1174.

**2-tributylstannyl-3,17-dimethoxy-β-estra-1,3,5(10)-triene (9c)**[7]




A THF solution of the bromosteroid **9b** (0.7 g, 1.84 mmol in 20 mL) was cooled to -78 °C under $N_2$. n-BuLi (2.47 M in hexanes, 0.78 mL, 1.93 mmol) was added dropwise with stirring, and the resulting solution was stirred at -78 °C for 30 min. $Bu_3SnCl$ (0.52 mL, 1.93 mmol) was then added dropwise at -78 °C, and the resultant mixture allowed to warm to room temperature over 12 h. Diethyl ether (50 mL) was added to the reaction mixture and the organic solvents were was washed with water (3 x 50 mL). The organic layer was mixed with KF (0.1 g in 1 mL EtOH) and stirred for a few minutes to remove any residual $Bu_3SnCl$. The mixture was washed with water, and the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to obtain 2-tributylstannyl-3,17-dimethoxy-β-estra-1,3,5(10)-triene (10c) as a colorless, viscous oil (0.87 g, 80%). $^1$H NMR ($CD_2Cl_2$, 400 MHz, 25 °C): δ 7.229 (s, $^3J_{Sn\text{-}H}$ = 46.4 Hz, 1H), 6.521 (s, $^4J_{Sn\text{-}H}$ = 17.4 Hz, 1H), 3.705 (s, 3H), 3.330 (s, 3H), 3.292 (t, J = 8.3 Hz, 1H), 2.92-2.74 (m, 2H), 2.306 (m, 1H), 2.188 (m, 1H), 2.10-1.96 (m, 2H), 1.93-1.82 (m, 1H), 1.72-1.16 (m, 8H, $H_{alicyclic}$ on steroid overlapping with m centered ~ δ 1.52, 6H, β$CH_2$ and m centered ~ δ 1.32, 6H, γ$CH_2$), 1.001 (m, 6H, α$CH_2$), 0.878 (t, J = 7.3 Hz, 9H, $CH_3$), 0.763 (s, 3H); $^{13}$C NMR ($CD_2Cl_2$, 100 MHz, 25 °C): δ 162.48, 138.91, 134.41, 133.16, 127.03, 109.82, 91.27, 58.07, 55.56, 50.79, 44.69, 43.79, 39.42, 38.68, 30.68, 29.76, 28.25, 27.95, 27.86, 27.14, 23.58, 14.06, 11.95, 10.26; HRMS (FAB) calcd. for $C_{32}H_{54}O_2Sn$ $[M]^+$ 590.3146 found 590.3130.

**(3,17-dimethoxy-β-estra-1,3,5(10)-trien-2-yl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (9d)**



In a glove box under nitrogen, $CH_3CN$ solutions of 1-(diacetoxyiodo)-4-methoxybenzene (65 mg, 0.19 mmol in 1 mL) and tosylic acid monohydrate (35 mg, 0.19 mmol in 1 mL) were mixed together to generate a Koser's type reagent. The yellow reagent mixture was added to a THF solution of 2-tributylstannyl-3,17-dimethoxy-β-estra-1,3,5(10)-triene (**9c**) (112 mg, 0.19 mmol in 1 mL), and the resultant pale yellow reaction mixture was stirred overnight protected from light. The reaction mixture was brought out of the box, and the solvent was removed in vacuo to obtain a white solid residue. The solid was washed with hexanes, redissolved in $CH_3CN$ and extracted with hexanes to remove the alkyltin byproducts. Solvent was removed from the $CH_3CN$ layer to obtain a colorless oil. The oil was dissolved in about 5 mL of $CH_3CN$ and water (25 mL) and $NaPF_6$ (96 mg, 0.57 mmol) were added; the solution turned into a milky suspension. The mixture was extracted with $CH_2Cl_2$ and the organic solvents were removed in vacuo to obtain a colorless oil. The oil was triturated twice with hexanes to afford a pale brown solid. The solid was separated and dissolved in $CH_3CN$ and filtered. The solvent was removed in vacuo and the sticky solid was triturated again with hexanes to give (3,17-dimethoxy-β-estra-1,3,5(10)-trien-2-yl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (**9d**) as a pale brown solid (84 mg, 65%). The solid was collected by filtration and dried under dynamic high vacuum in a $P_2O_5$ drying pistol (3 d) before fluorination was attempted. $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C): δ 7.953 (d, J = 8.8 Hz, 2H), 7.826 (s, 1H), 7.018 (d, J = 8.8 Hz, 2H), 6.933 (s, 1H), 3.895 (s, 3H), 3.828 (s, 3H), 3.36-3.23 (s overlapping with t, 4H), 2.918 (m, 2H), 2.28-2.12 (m, 2H), 2.12-1.81 (m overlapping with solvent, 3H), 1.672 (m, 1H), 1.52-1.14 (m, 7H), 0.743 (s, 3H); $^{13}$C NMR ($CD_3CN$, 100 MHz, 25 °C): δ 164.52, 155.71, 147.38, 139.13, 138.45, 134.81, 119.23, 114.65, 101.98, 101.67, 91.59, 58.27, 58.23, 57.03, 51.15, 44.94, 44.29, 39.15, 38.81, 30.92, 28.69, 27.60, 27.44, 24.01, 12.35; $^{19}$F NMR ($CD_3CN$, 376 MHz, 25 °C): δ -72.876 (d, $^1J_{P-F}$ = 706.9 Hz, $PF_6^-$); $^{31}$P NMR ($CD_3CN$, 162 MHz, 25 °C): δ -144.525 (septet, $^1J_{P-F}$ = 706.9 Hz, $PF_6^-$); HRMS ( FAB) calcd for $C_{27}H_{34}IO_3$ $[M - PF_6]^+$ 533.1553 found 533.1561.

**General procedure for fluorination of diaryliodonium salts in acetonitrile:** In a nitrogen atmosphere glove box, 0.05 mmol of the appropriate aryl(4-methoxyphenyl)-iodonium hexafluorophosphate and 0.05 mmol of TMAF were dissolved in 0.6 mL of dry acetonitrile. The solution was transferred into a J-Young NMR tube, sealed, and taken out of the glove box. The tube was wrapped in aluminum foil and placed in a 140 °C oil bath. After 15 minutes, no remaining starting material was observable by $^1$H NMR spectroscopy. Yields of the reactions are recorded in manuscript table 1.

**General procedure for fluorination of diaryliodonium salts in benzene:** In a nitrogen atmosphere glove box, 0.05 mmol of the appropriate aryl(4-methoxyphenyl)-fluoro-$\lambda^3$-iodane and 0.05 mmol of TMAOTf were dissolved in 0.6 mL of dry $d_6$-benzene. The solution was transferred into a J-Young NMR tube, sealed, and taken out of the glove box. The tube was wrapped in aluminum foil and placed in

a 140 °C oil bath. After 15 minutes, no remaining starting material was observable by $^1$H NMR spectroscopy. Yields of the reactions are recorded in manuscript table 1.

**General procedure for fluorination of diaryliodonium salts in benzene, toluene and acetonitrile under salt-free conditions**: In a nitrogen atmosphere glove box, 0.05 mmol of an appropriate aryl(4-methoxyphenyl)-iodonium hexafluorophosphate was dissolved in 0.3 mL of dry acetonitrile. A solution of 0.05 mmol of TMAF in 0.3 mL of dry acetonitrile was added slowly. The mixture was transferred into a J-Young NMR tube, sealed, and taken out of the glove box. The solvent was evaporated and the tube was taken back into the glove box. Dry benzene-$d_6$ or toluene-$d_8$ (0.6 mL) was added and the solution was passed through a 0.2 mm membrane filter and transferred into a J-Young NMR tube, sealed, and taken out of the glove box. (For decomposition in acetonitrile, regular benzene was used to dissolve the iodonium fluoride, removed by vacuum and $d_3$-acetonitrile was added). The tube was wrapped in aluminum foil and placed in a 140 °C oil bath. After 15 minutes, no remaining starting material was observable by $^1$H NMR spectroscopy. Yields of the reactions are recorded in manuscript tables 2 and S1.

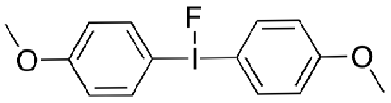
**Table S1**. Yields of fluorinated arenes obtained from decomposition of salts **1-7** after removal of $TMAPF_6$. in $d_8$-toluene.

| **Cmpd.** | $C_7D_8$ (ArF + 4FA)[a] |
|---|---|
| **1** | 83 |
| **2** | (76 + 12) |
| **3** | (53 + 21) |
| **4** | (72 + 17) |
| **5** | (55 + 18) |
| **6** | (89 + 10) |
| **7** | (87 + 0) |

[a] The numbers inside the parentheses indicate the percentage yields of the desired fluorinated arenes followed by the amount of 4-fluoroanisole (4FA) produced during the reaction. All solutions were heated at 140 ºC for 15 minutes in sealed NMR tubes.

Bis(4-methoxyphenyl)-iodonium fluoride (1e)

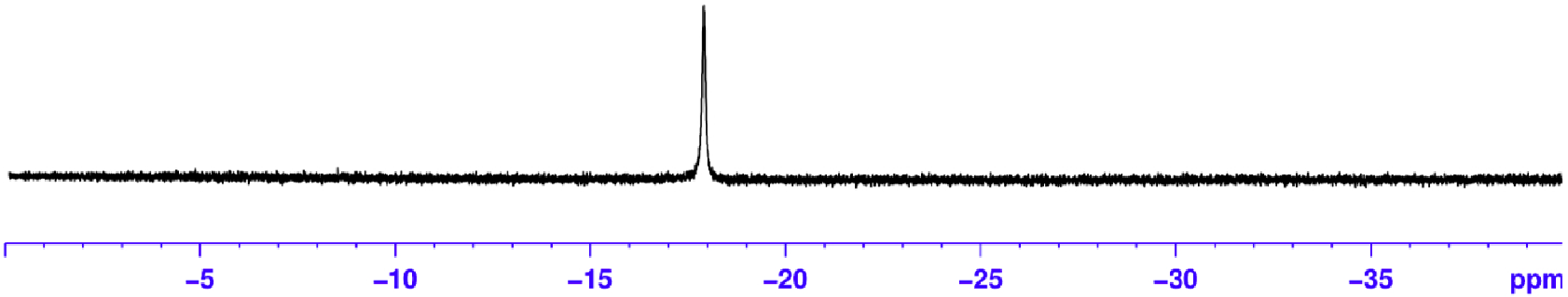
$^{1}$H NMR (400 MHz, $CD_3CN$, 25 °C)



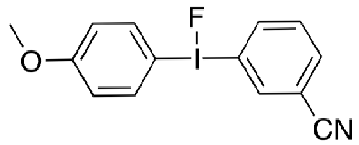




$^{19}$F NMR (376 MHz, $CD_3CN$, 25 °C)



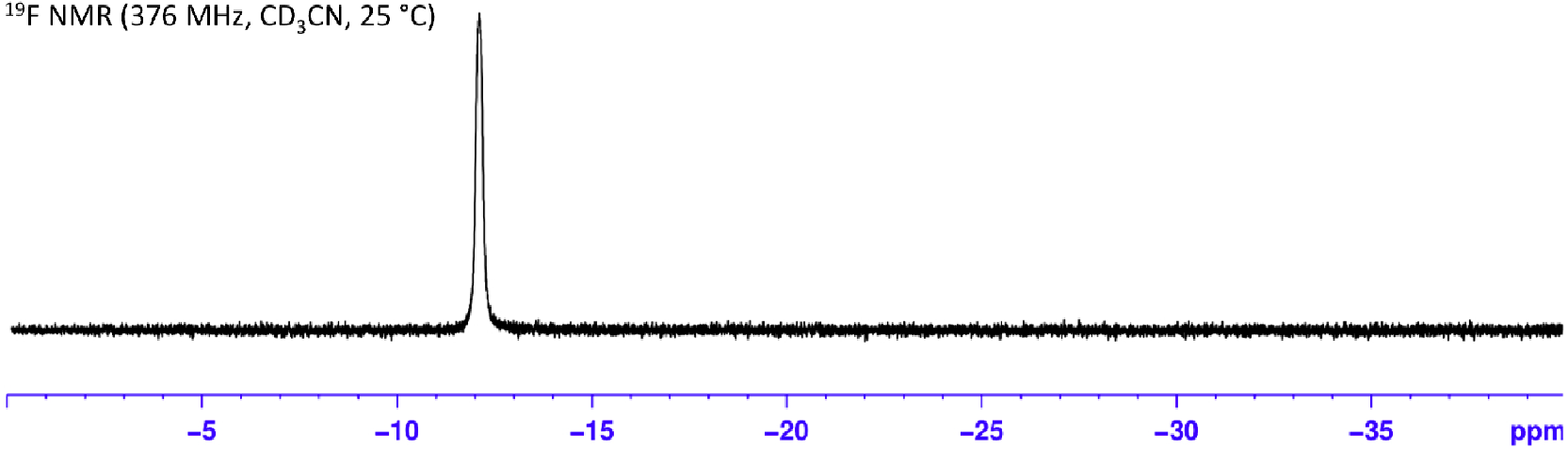
(3-Cyanophenyl)(4′-methoxyphenyl)-iodonium fluoride (3e)




$^{1}$H NMR (400 MHz, $CD_3CN$, 25 °C)

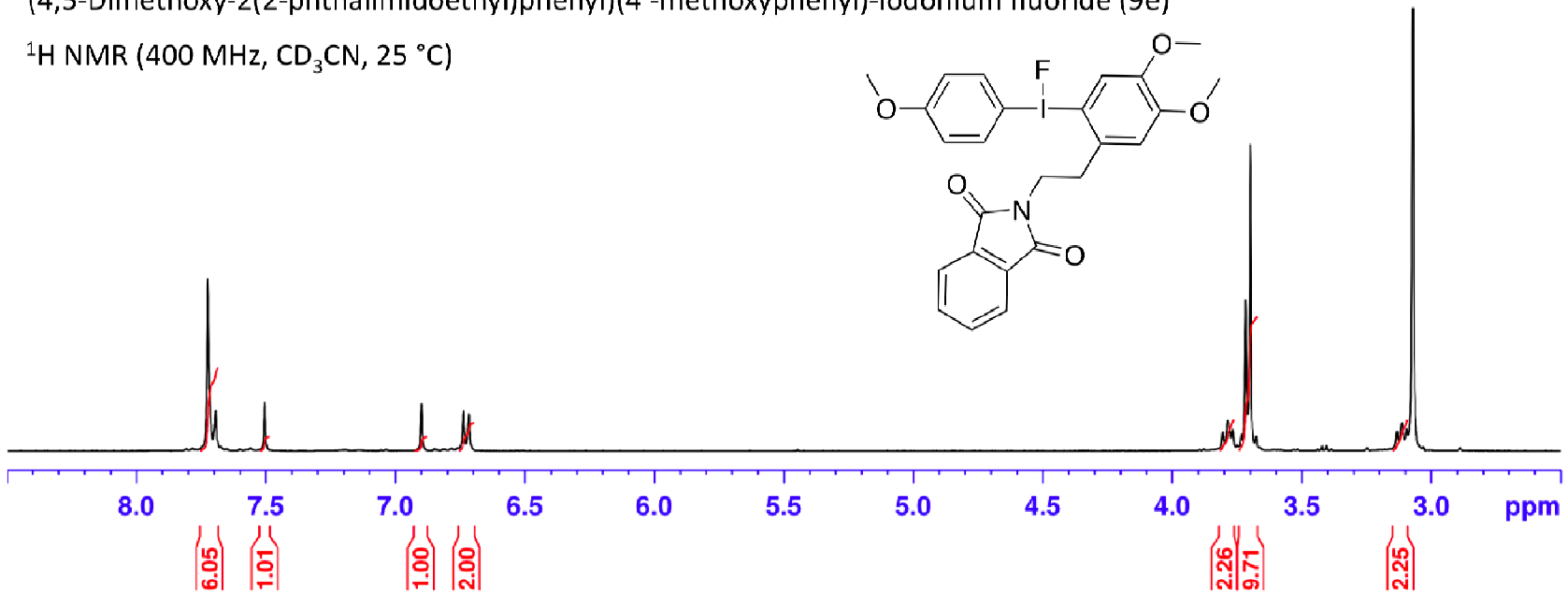



$^{19}$F NMR (376 MHz, $CD_3CN$, 25 °C)

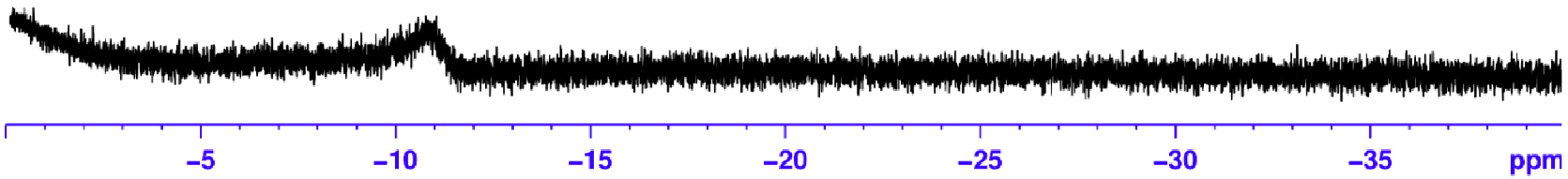


(4,5-Dimethoxy-2(2-phthalimidoethyl)phenyl)(4'-methoxyphenyl)-iodonium fluoride (9e)

$^{1}$H NMR (400 MHz, $CD_3CN$, 25 °C)




$^{19}$F NMR (376 MHz, $CD_3CN$, 25 °C)



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