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Improved Arene Fluorination Methodology for I(III) Salts

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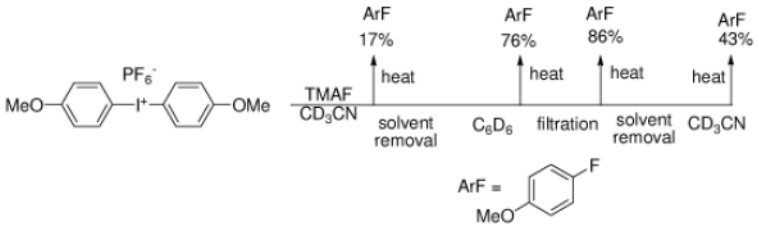
Abstract



The use of low polarity aromatic solvents (benzene or toluene) and/or the removal of inorganic salts results in dramatically improved yields of fluorinated arenes from diaryliodonium salts. This methodology is shown to “scale down” to the conditions used typically for radiotracer synthesis.

The inability to functionalize electron-rich arenes with fluoride ion sources narrows the scope and increases the expense of practical ^{18}F-labeled imaging agents for positron emission tomography.1 Two fluoride-based approaches to fluoroarenes have been heavily investigated of late: 1) transition-metal-catalyzed fluorination,2-6 and 2) elimination of aryl fluorides from diaryliodonium salts.7,8 Stang and coworkers have stressed the similarities of iodonium ion and late transition metal ion chemistries,9 thus we thought that the use of low polarity, non-coordinating media, which often suppresses ionic (disproportionation, ligand exchange, electron transfer) side reactions of transition metal complexes,10 might be a strategy to improve diaryliodonium fluoride chemistry. Here we show that the use of benzene solvent and/or removal of “inert” electrolyte is associated with substantially improved yields of fluorinated aromatic compounds from the decomposition of diaryliodonium fluorides. These results have significant ramifications for the preparation of fluorinated radiotracers.

Previously we reported the preparation of phenyliodonium difluoride from anhydrous tetrabutylammonium fluoride11 (TBAF) and phenyliodonium diacetate.12 In the course of this work we noted that excess fluoride ion led to the eventual reduction of $PhIF_2$ to PhI and bifluoride ion by an unknown mechanism. This reaction was largely suppressed in nonpolar solvents such as benzene. Similarly, if bis(4-methoxyphenyl)iodonium hexafluorophosphate **1** is treated with excess anhydrous TBAF or anhydrous tetramethylammonion fluoride13 (TMAF) in acetonitrile at ambient temperature, 4-iodoanisole is formed without the generation of any fluorinated arenes. If substoichiometric amounts of fluoride are present the decomposition reaction is largely suppressed at room temperature, but upon heating of the

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Supporting Information Available: Experimental procedures and analytical data for all new compounds and synthetic intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

acetonitrile solution **1** undergoes thermal decomposition to form 4-fluoroanisole (4FA) in poor yield (17%) along with 4-iodoanisole and anisole. Given that the redox chemistry of $PhIF_2$ was suppressed in benzene, we investigated the thermal decomposition of diaryliodonium fluoride salts in nonpolar media as well. Initial experiments (Figure 1) indicated that this approach might be fruitful.

To test the generality of this approach, diaryliodonium hexafluorophosphates **2-7** (Figure 2) were prepared by two established methods: **3** and **5-7** were prepared by TsOH catalyzed electrophilic aromatic substitution of anisole by $ArI(OAc)_2$, 14,15 and compounds **2** and **4** were prepared from the corresponding tributylstannanes and *p*-OMePhI(OH)(OTs) (Figure 3).16,17 The iodonium salts were isolated by precipitation from aqueous solutions using $NaPF_6$. (Full experimental procedures are provided in the Supporting Information.)

Several procedures for diaryliodonium fluoride decomposition were investigated. In the first, compounds **1-7** were treated with 1 equivalent of anhydrous TMAF in CD_3CN and heated (140 °C, 15 min) in sealed NMR tubes. Yields of fluorinated arenes were determined by ^1H NMR spectroscopy and confirmed by GC-MS analysis. In the second method, ion exchange with TMAF was performed in acetonitrile, the solvent was evaporated, and the remainder was suspended in d_6-benzene and heated (140 °C, 15 min) in sealed NMR tubes. A comparison of the results from these two procedures is given in Table 1. In all cases, the yields of fluorinated arenes were superior for the reactions conducted in benzene. In acetonitrile, the formation of HF_2^- and BF_4^- (from the borosilicate NMR tube) was observed, whereas no inorganic fluoride byproducts were seen when benzene was the reaction solvent. Inspection of the results shows that the 4-methoxyphenyl group strongly directs the fluoride nucleophile to the electron-poor aromatic ring, as is generally observed when diaryliodonium salts are fluorinated with cyclotron-derived ^{18}F-fluoride ion.1

In addition to reducing the solvent polarity, the use of benzene as the reaction solvent effectively removes the inorganic spectator ions (tetramethylammonium and hexafluorophosphate) from solution. While these salts are not expected to participate directly in the thermal decomposition reaction, their presence might facilitate ligand exchange reactions and increase the I-F dissociation rate and dissociation constants. To probe whether the observed improvement in fluorination yield was a function of solvent polarity or extraneous salt, the thermal decomposition of the diaryliodonium fluorides was also conducted under “salt free” conditions in both solvents.

Salt removal was performed by a simple solvent exchange process; compounds **2-7** were dissolved in CH_3CN, treated with TMAF and the solvent was evaporated. The remaining salts were dissolved in benzene and passed through a 0.20 μm PTFE syringe filter (Scheme 1). Upon evaporation of the benzene, clean samples of the diaryliodonium salts were obtained. ^1H and ^{19}F NMR spectra of the isolated diaryliodonium fluorides showed no residual $TMAPF_6$ in the samples of diaryliodonium fluorides prepared using this solvent exchange method.

The results of thermal decomposition reactions (140 °C, 15 min) of the “salt free” diaryliodonium fluorides are summarized in Table 2. For reactions conducted in benzene, salt-free conditions were associated with a modest enhancement in the yields of fluorinated arenes. In contrast, the yields of reactions conducted in CD_3CN improved dramatically after the salt was removed; in some instances the yields obtained for the thermal decomposition of salt-free diaryliodonium fluorides in acetonitrile approached those seen for reactions conducted in benzene. These results suggest that fluoride ion dissociation may be responsible for some degradation of the arene fluorination efficiency observed in polar aprotic solvents.

Deuterated benzene is a particularly convenient and relatively inexpensive solvent for conducting these iodonium salt decomposition experiments, but its carcinogenicity makes benzene unattractive for practical preparations. Thus, we also investigated the thermal decomposition reactions of compounds **1-7** in d_8-toluene under salt free conditions. The yields and selectivities for formation of fluorinated arenes from **1-7** (Table S1, Supporting Information) were essentially identical to those obtained for reactions conducted in C_6D_6, indicating that a wide range of nonpolar aromatic solvents might be readily used for this process.

Compounds **8** and **9**, suitably protected precursors of previously investigated radiotracers ^{18}F-6-fluorodopamine18 and ^{18}F-2-fluoroestradiol,19 respectively, were decomposed to the corresponding fluorinated arenes in excellent (80% for **8**) and fair (42% for **9**) yields in benzene. The reduced fluorination yield for the latter compound is accompanied by a concomitant increase in the amount of 4-fluoroanisole produced, consistent with the similar “directing group” abilities of the 2-methoxy and 4-methoxy substituted arenes. (Recently, our laboratory reported a potential solution to this directing group problem.20) Successful fluorination of these arenes indicates that the methodology is sufficiently broad to tolerate suitably protected alcohol and amine functionality.

To more closely mimic the conditions of radiotracer synthesis, we examined the thermal decomposition reactions of **1** at three concentrations (1 mM, 5 μM, and 5 nM); radiotracer synthesis is typically conducted in the nM-μM ^{18}F-fluoride concentration range. Since our studies were conducted exclusively with ^{19}F-fluoride, we needed an appropriate analytical tool to test the impact of dilution upon the yield of fluorinated arenes. For product analysis we used a GC-TOF-MS; this technique was sufficiently sensitive to detect and quantify reproducibly 500 femtograms of injected 4-fluoroanisole. To minimize fluoride losses due to adsorption on glass surfaces during the dilution process, **1** was first treated with TBAF and the bis(4-methoxyphenyl)iodonium fluoride **1(F)** was isolated.

Under standard thermal decomposition conditions (140 °C, 15 min, 0.5 mL of benzene) the yield of 4-fluoroanisole declined sharply with the concentration of **1(F)**: 1 mM – 90%, 5 μM – 30%, 5 nM – 0%. In contrast, thermal decomposition of a mixture of 5 ng **1(F)** and excess (1 mg) bis(4-methoxyphenyl)iodonium trifluoroacetate under standard conditions gave excellent and reproducible yields of 4-fluoroanisole (80 ± 10% by GC-TOF-MS). (Control experiments in which bis(4-methoxyphenyl)iodonium trifluoroacetate was heated in benzene without added **1(F)** produced no detectable fluoroanisole.)

Taken together, the results reported here show that the perhaps counterintuitive choice of nonpolar media for the pyrolysis of highly polar diaryliodonium fluorides has an important and practical impact on the success of arene fluorination, and that these new conditions give excellent yields of fluorinated arenes. Even when the total concentration of fluoride ion is vanishingly small, as it is when ^{18}F-fluorinated radiotracers are synthesized, the presence of excess diaryliodonium substrate leads to excellent conversion to the fluorinated arene. In addition to suppressing deleterious side reactions, an important role of the nonpolar solvent is to precipitate inorganic salts that may catalyze ligand exchange, electron transfer, and disproportionation reactions. These new conditions have their genesis in the hypothesis that I(III) behaves like a transition metal ion, and long-standing observations of fluoride's propensity to promote the disproportionation of low-valent transition metal ions. Studies to demonstrate the direct application of these new reaction conditions in ^{18}F-radiotracer synthesis are currently underway.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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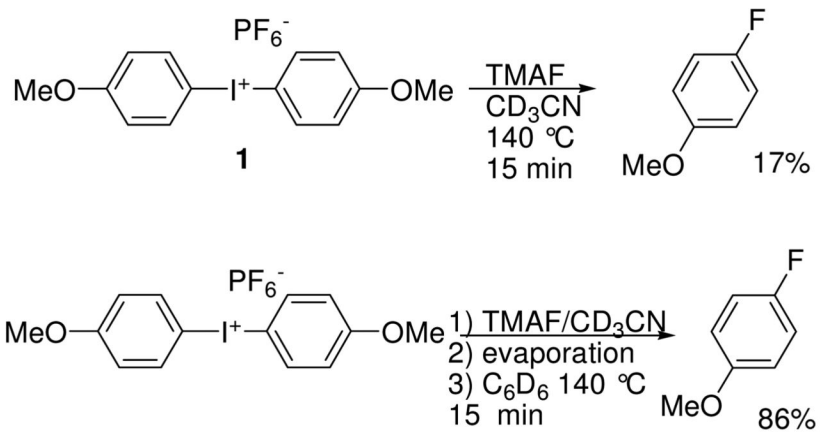

Figure 1.
Solvent effect upon the decomposition of bis(4-methoxyphenyl)iodonium fluoride.

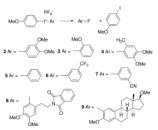

Figure 2.
Direct decomposition of diaryliodonium fluorides in C_6D_6 and CD_3CN at 140 °C.

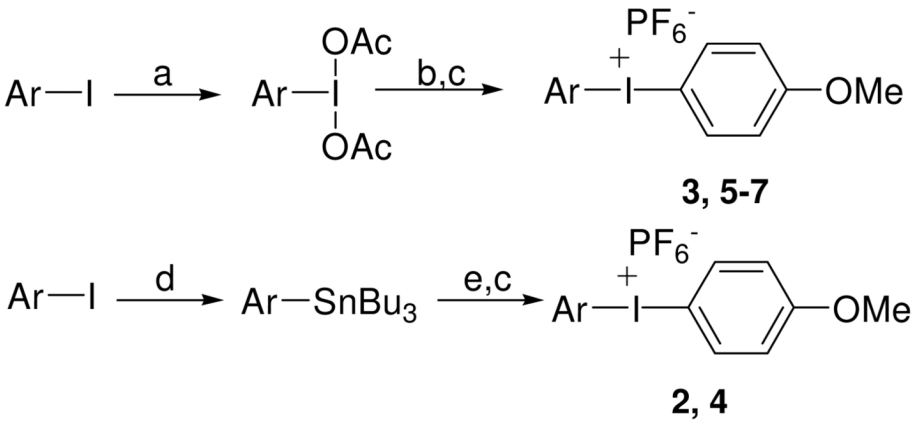

Figure 3.

Preparation of diaryliodonium salts **2-7.** a) $NaBO_3$, AcOH, 40 °C, 8 h; b) $TsOH \cdot H_2O$, anisole, CH_3CN; c) H_2O, $NaPF_6$; d) $Pd_2(dba)_3$, P(*t*-Bu)$_3$, benzene, Sn_2Bu_6, 100 °C; e) *p*-(OMe)PhI(OTs)(OH), CH_3CN.

Scheme 1.
Salt removal by solvent exchange process.

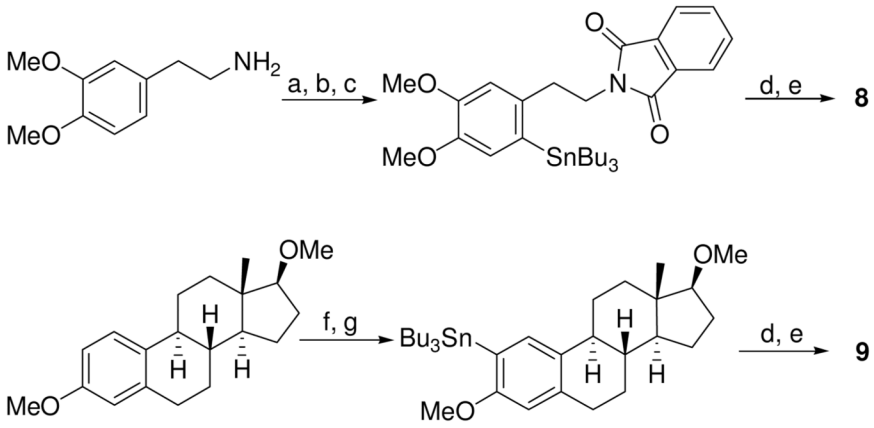

Figure 4.

Syntheses of compounds **8** and **9**. a) Br_2, AcOH, rt, KOH; b) diisopropylethylamine, phthaloyl dichloride, CH_3CN, rt; c) $Pd_2(dba)_3$, *t*-Bu_3P, benzene, Sn_2Bu_6, 100 °C; d) *p*-OMePhI(OTs)(OH), CH_3CN; e. H_2O, $NaPF_6$; f) NBS, CH_3CN/CCl_4 (3:7) ; g) n-BuLi, Bu_3SnCl, THF, −78 °C to rt.

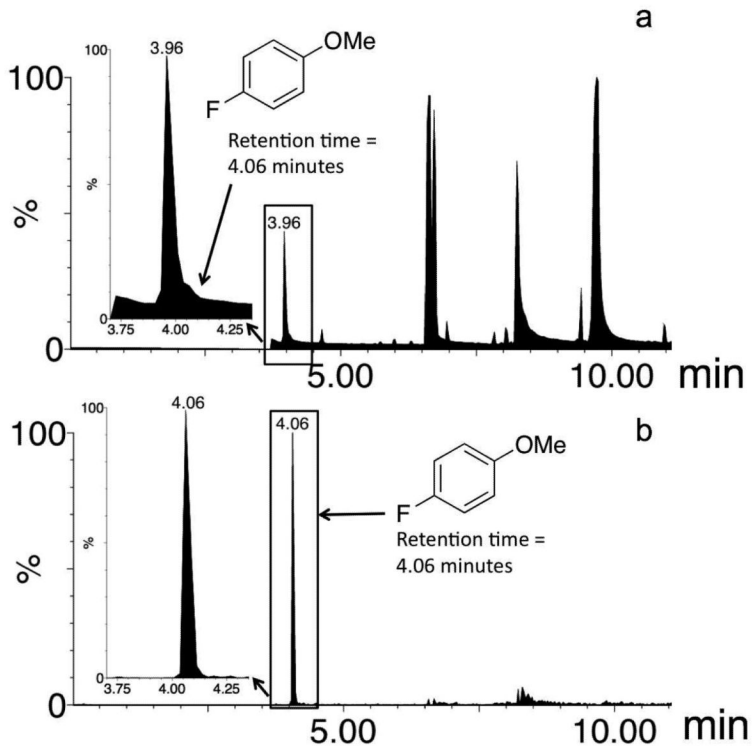

Figure 5.
a) Total ion chromatogram of the decomposition reaction mixture of **1(F)** in acetonitrile; b) Selected ion chromatogram of the same reaction mixture (mass range = 126.03-126.04).

Table 1

Yields of fluorinated arenes obtained from direct decomposition of salts **1**-**7**.

Cmpd.	C_6D_6 (ArF + 4FA)[a]	CD_3CN (ArF + 4FA)
1	76	17
2	(59 + 19)	(2 + 1)
3	(59 + 25)	(2 + 1)
4	(76 + 14)	(2 + 1)
5	(41 + 10)	(3 + 1)
6	(86 + 0)	(33 + 0)
7	(93 + 5)	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 °C for 15 minutes in sealed NMR tubes.

Table 2

Yields of fluorinated arenes obtained from decomposition of salts **1-7** after removal of $TMAPF_6$.

	"Salt Free" Conditions	
Cmpd.	**C_6D_6 (ArF + 4FA)[a]**	**CD_3CN (ArF + 4FA)**
1	86	43
2	(77 + 14)	(30 + 8)
3	(49 + 23)	(40 + 20)
4	(78 + 12)	(49 + 32)
5	(57 + 20)	(40 + 15)
6	(85 + 10)	(68 + 0)
7	(89 + 0)	(78 + 0)

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

Supporting Information for

Improved Arene Fluorination Methodology for I(III) Salts

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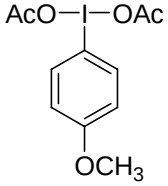
Supplementary Information Table of Contents

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.

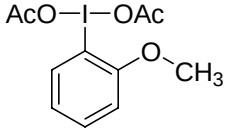
Procedures:

Bis(acetyloxy)-(4-methoxyphenyl)-λ_3 –iodane; (1-(diacetoxyiodo)-4-methoxybenzene, 1a)



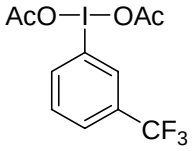
4-Iodoanisole (2.34 g, 10 mmol) was dissolved in 90 mL of glacial acetic acid and the stirred solution was warmed to 40 °C. Sodium perborate tetrahydrate (13.6 g, 110 mmol) was added in portions over the course of one hour. After the addition was complete, the temperature of the reaction mixture was 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)-λ_3 –iodane; (1-(diacetoxyiodo)-2-methoxybenzene, 3a)



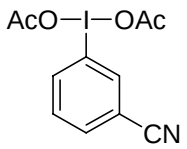
2-Iodoanisole (2.34 g, 10 mmol) was dissolved in 90 mL of glacial acetic acid and the stirred solution was warmed to 40 °C. Sodium perborate tetrahydrate (13.6 g, 110 mmol) was added in portions over the course of one hour. After the addition was complete, the temperature of the reaction mixture was 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)-λ_3 –iodane; (1-(diacetoxyiodo)-3-(trifluoromethyl)benzene, 6a)



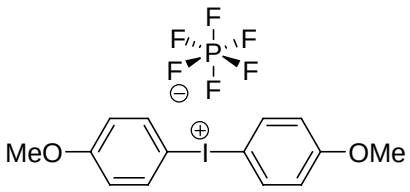
1-(Diacetoxyiodo)-3-(trifluoromethyl)benzene (3.12 g, 80%) was prepared from 3-iodobenzotrifluoride (2.72 g, 10 mmol) using the identical procedure used to prepare **1a**. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.492 (s, H1, C2), 8.397 (d, J = 8.3 Hz, 1H, C6), (d, J = 7.9 Hz, 1H, C4), (dd, J_1 = 8.3 Hz, 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)-λ_3 –iodane; (3-(diacetoxyiodo)benzonitrile, 7a)



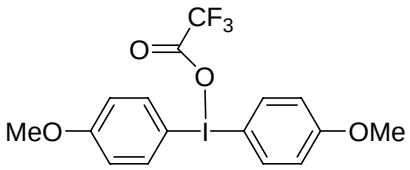
3-(Diacetoxyiodo)benzonitrile (2.43 g, 70%) was prepared from 3-iodobenzonitrile (2.29 g, 10 mmol) using the identical procedure used to prepare **1a**. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.515 (s, 1H, H2), 8.406 (d, J = 8.1 Hz, 1H, H6), 7.866 (d, J = 8.1 Hz, 1H, H4), 7.711 (t, J = 8.1 Hz, 1H, H5), 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)



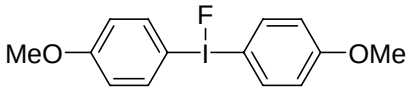
In a glove box under nitrogen, 1-(diacetoxyiodo)-4-methoxybenzene (**1a**) (352 mg, 1 mmol) was weighed into a glass vial and 1.5 mL of dry acetonitrile was added. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. 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- λ_3-iodane; (bis(4-methoxyphenyl)iodonium trifluoroacetate, 1e)



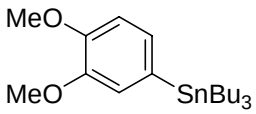
In a nitrogen flushed Schlenk tube equipped with a magnetic stir bar and a rubber septum seal, 1-(diacetoxyiodo)-4-methoxybenzene (**1a**) (1.41 g, 4 mmol) was dissolved in 30 mL of dry dichloromethane and the solution was cooled to -30 °C. Trifluoroacetic acid (0.61 mL, 8 mmol) was added and the solution 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-λ_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).

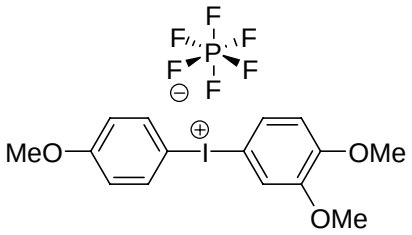
3,4-Dimethoxyphenyltributyltin (2c)



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

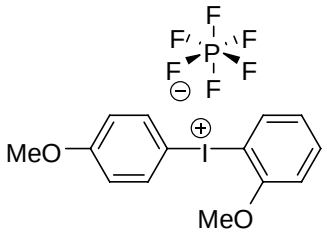
the glove box, and heated at 120 °C for 48 h. The reaction mixture was allowed to cool to room temperature and diluted with hexane (15 mL) before saturated aqueous KF solution (15 mL) was added. The mixture was stirred for 30 min, filtered through celite, and the organic layer was separated. The solvent 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, βCH_2), 1.384 (m, 6H, γCH_2), 1.117 (m, 6H, αCH_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)



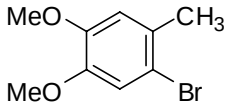
In a glove box under nitrogen, 1-(diacetoxyiodo)-4-methoxybenzene (352 mg, 1 mmol) was dissolved in 1.5 mL of dry acetonitrile and a solution of p-toluenesulfonic acid monohydrate (190 mg, 1 mmol) in 1.5 mL of dry acetonitrile was added. 3,4-Dimethoxyphenyl)tributyltin, **2c** (427 mg, 1 mmol) was added 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)



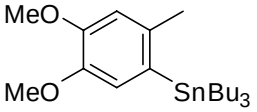
In a glove box under nitrogen, 1-(diacetoxyiodo)-2-methoxybenzene, **3a**, (352 mg, 1 mmol) was weighed into a glass vial and 1.5 mL of dry acetonitrile was added. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. 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)



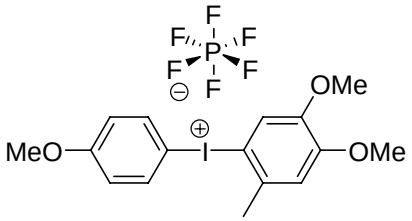
To a stirred solution of 3,4-dimethoxytoluene (3.6 mL, 25 mmol) in 125 mL of acetonitrile was added N-bromosuccinimide (4.9 g, 27.5 mmol). The mixture was stirred at room temperature for 2 h, the solvent was removed by rotary evaporation, and 100 mL of CCl_4 was added. The solid was succinimide was removed 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)



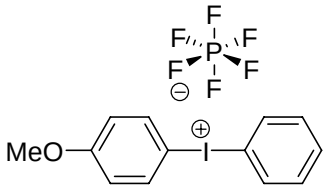
In a glove box under nitrogen, 1-bromo-4,5-dimethoxy-2-methylbenzene (**4b**) (1.155 g, 5 mmol) and $Pd(PPh_3)_4$ (289 mg ,0.25 mmol) were dissolved in 15 mL of dry toluene. The solution was transferred into a storage tube equipped with PTFE chemcap seal and hexabutylditin (3.19 g, 5 mmol) was added. 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, βCH_2), 1.384 (m, 6H, γCH_2), 1.143 (m, 6H, αCH_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)



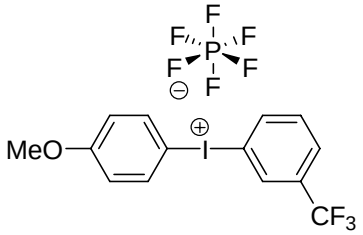
In a glove box under nitrogen, 1-(diacetoxyiodo)-4-methoxybenzene (352 mg, 1 mmol) was dissolved in 1.5 mL of dry acetonitrile. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, (4,5-dimethoxy-2-methylphenyl)tributyltin (**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.

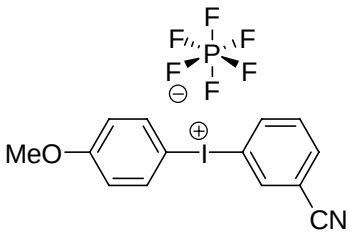
(3-(Trifluoromethyl)phenyl)-(4'-methoxyphenyl)iodonium hexafluorophosphate (6d)



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 =

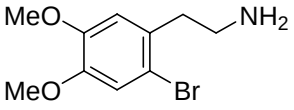
3.7 Hz, C2), 133.05 (q, J = 3.7 Hz, C4), 124.11 (q, J = 272.8 Hz, CF_3), 119.71 (C3'/C5'), 114.83 (C1), 102.54 (C1'), 57.13 (4'-OMe); ^{19}F NMR (CD_3CN, 376 MHz, 25 °C) δ -63.420 ($^1J_{F-C}$= 272.8 Hz, $^2J_{F-C}$= 33.6 Hz, CF_3), -72.625 (d, $^1J_{P-F}$ = 707.1 Hz, PF_6^-); HRMS (HRFAB): calcd. for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

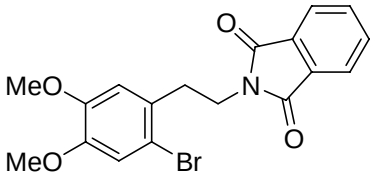
2-(2-Bromo-4,5-dimethoxyphenyl)ethanamine (8f)



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-

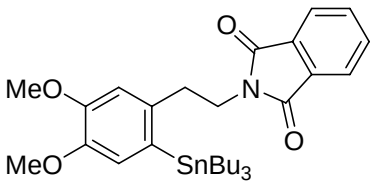
dimethoxyphenyl)ethananamine. The crude product was dried under dynamic vacuum overnight and used without further purification. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.00 (s, 1H, H6), 6.73 (s, 1H, H3), 3.85 (s, 3H, OMe), 3.84 (s, 3H, OMe), 2.94 (t, J = 7.17 Hz, 2H, CH_2), 2.81 (t, J = 7.17 Hz, 2H, CH_2), 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').)

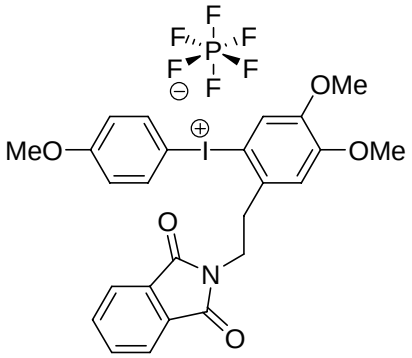
(4,5-Dimethoxy-2-(2-phthalimido)phenyl)tributyltin (8c)



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)

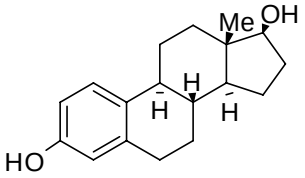
was added. The tube was sealed, removed from the glove box, and heated to at 120 °C for 48 h. The reaction mixture was allowed to cool to room temperature and diluted with hexane (15 mL) before saturated aqueous KF solution (15 mL) was added. The mixture was stirred for 30 min, filtered through celite, 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, βCH_2), 1.44 (m, 6H, γCH_2), 1.35 (m, 6H, αCH_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)



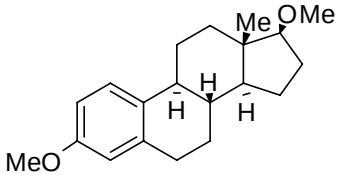
In a glove box under nitrogen, 1-(diacetoxyiodo)-4-methoxybenzene (352 mg, 1 mmol) was dissolved in 1.5 mL of dry acetonitrile. A solution containing *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) dissolved in 1.5 mL of dry acetonitrile was added by syringe. Upon completion of the addition, (4,5-dimethoxy-2-(2-phthalimido)phenyl)tributyltin (**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]



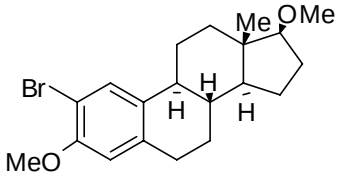
A solution of estrone (2.60 g, 9.62 mmol) in 130 mL of methanol was treated with concentrated aqueous NaOH (1.14 g, 28.5 mmol) and added to a stirred solution of $NaBH_4$ (0.97 g, 25.53 mmol) in 130 mL of methanol. H_2 evolution ceased after about 45 min, and the mixture was poured into 200 mL of water 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]



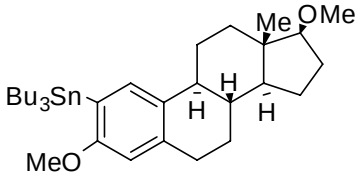
A previously reported procedure[12] was improved slightly. β-Estradiol (9g) (2.54 g, 9.32 mmol) was dissolved in 125 mL of dry THF under N_2 and cooled to 0 °C. NaH (1.07 g, 44.58 mmol) was added, and the reaction mixture was stirred for 15 min. CH_3I (5.40 mL, 86.48 mmol) was added by syringe, and the 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]



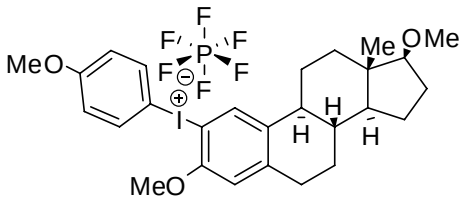
A solution of N-bromosuccinimide (1.51 g, 8.5 mmol) in CH_3CN (30 mL) was added to a CCl_4 solution (70 mL) of dimethoxy-β-estra-1,3,5(10)-triene (**9f**) (2.32 g, 7.72 mmol), and the resulting mixture was stirred at room temperature protected from light for 2.5 h. The solvent was removed in vacuo to 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 (1st 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, βCH_2 and m centered ~ δ 1.32, 6H, γCH_2), 1.001 (m, 6H, αCH_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-λ^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.

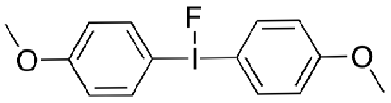
Table S1. Yields of fluorinated arenes obtained from decomposition of salts **1-7** after removal of $TMAPF_6$. in d_8-toluene.

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)

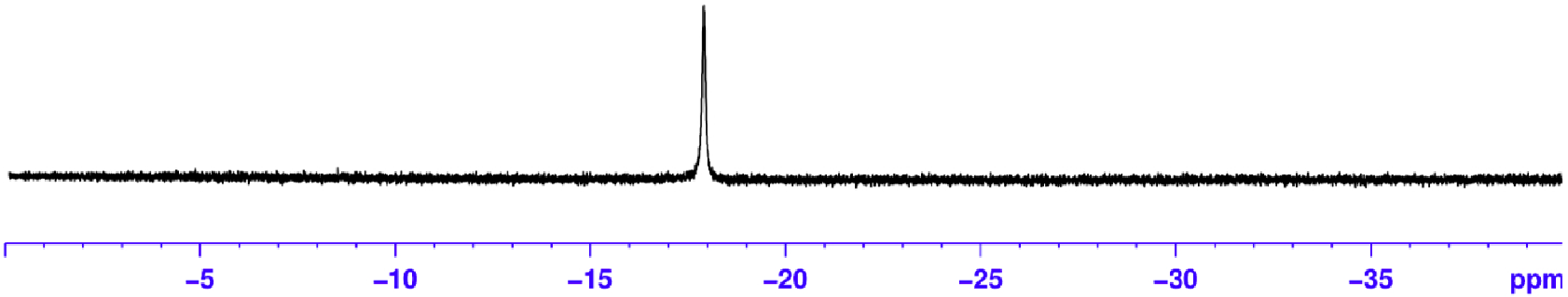
[a] The numbers inside the parentheses indicate the percentage yields of the desired fluorinated arenes followed by the amount of 4-fluoroanisole (4FA) produced during the reaction. All solutions were heated at 140 ºC for 15 minutes in sealed NMR tubes.

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

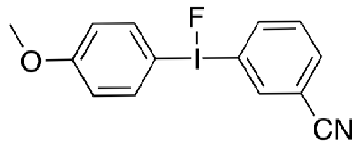
^{1}H NMR (400 MHz, CD_3CN, 25 °C)



^{19}F NMR (376 MHz, CD_3CN, 25 °C)

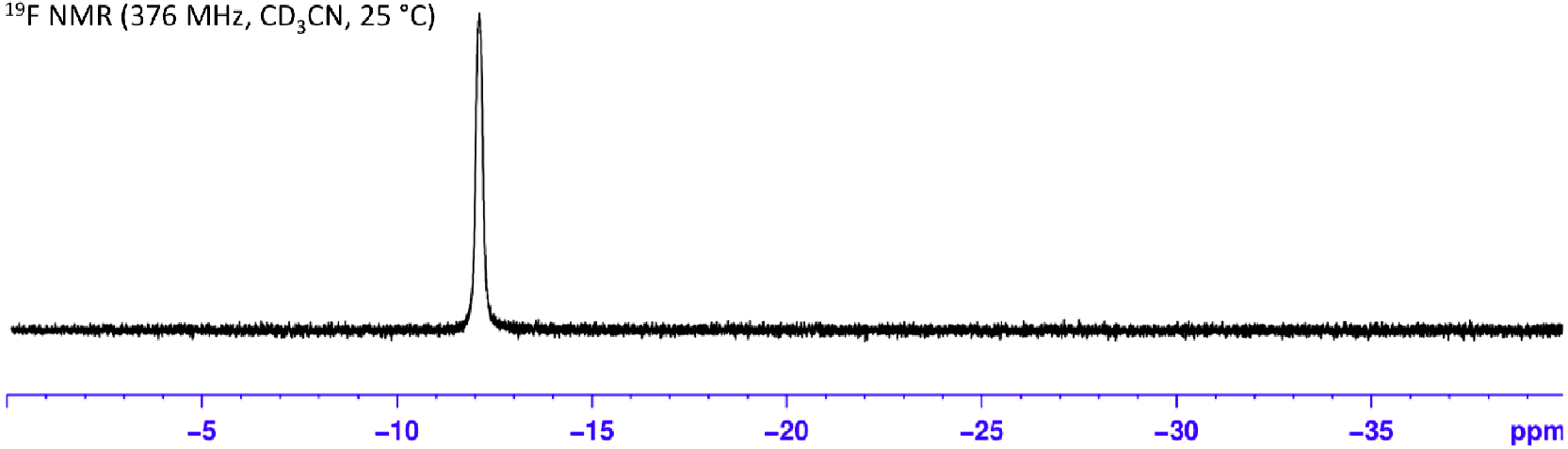


(3-Cyanophenyl)(4′-methoxyphenyl)-iodonium fluoride (3e)



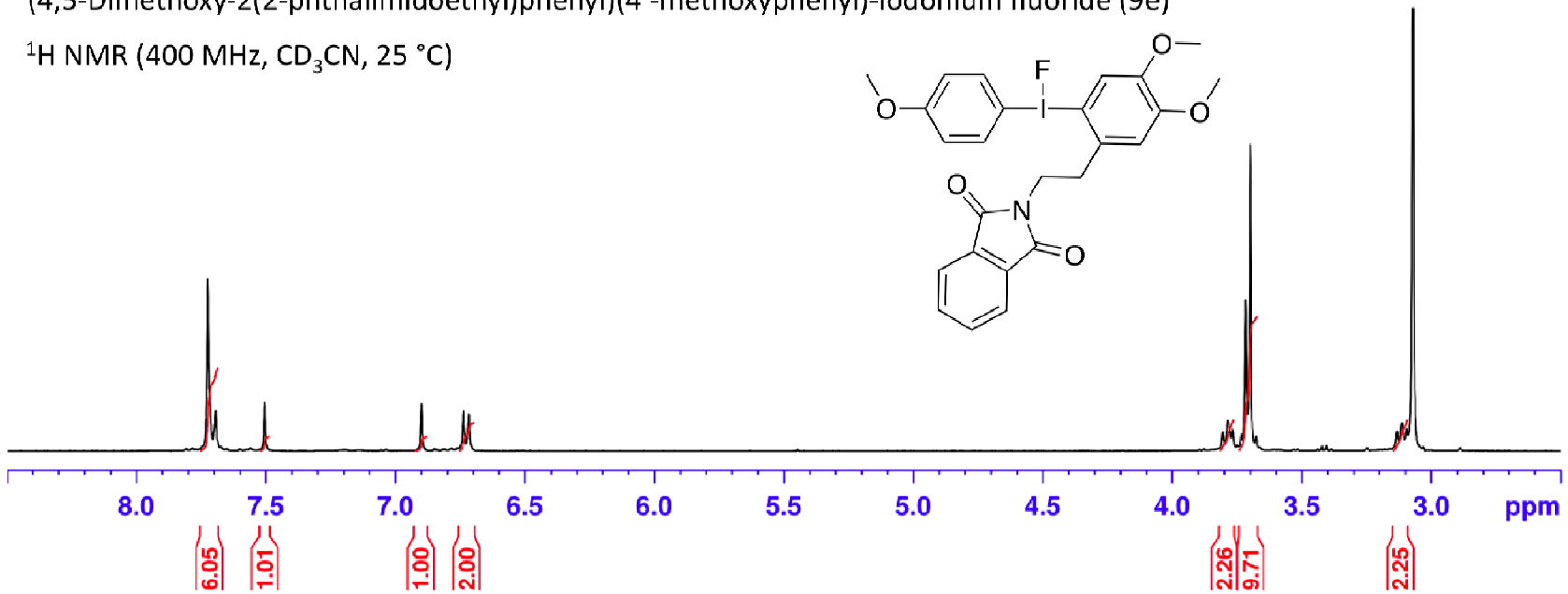
^{1}H NMR (400 MHz, CD_3CN, 25 °C)

^{19}F NMR (376 MHz, CD_3CN, 25 °C)

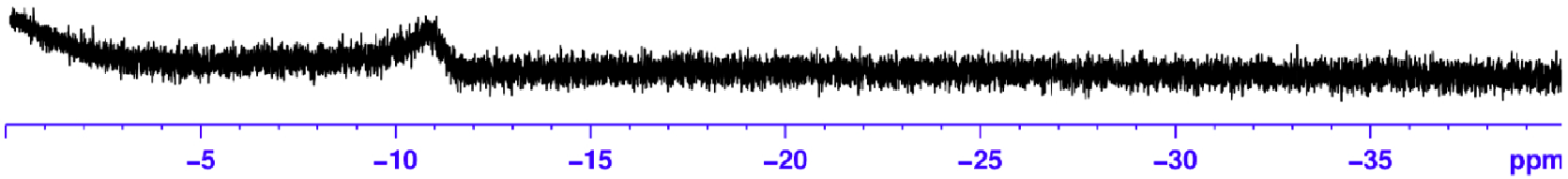


(4,5-Dimethoxy-2(2-phthalimidoethyl)phenyl)(4'-methoxyphenyl)-iodonium fluoride (9e)

^{1}H NMR (400 MHz, CD_3CN, 25 °C)



^{19}F NMR (376 MHz, CD_3CN, 25 °C)



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