Regiospecific Syntheses of Functionalized Diaryliodonium Tosylates via [Hydroxy(tosyloxy)iodo]arenes Generated in Situ from (Diacetoxyiodo)arenes

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Supporting Information

ABSTRACT: Ready access to ¹⁸F-labeled aryl synthons is required for preparing novel radiotracers for molecular imaging with positron emission tomography. Diaryliodonium salts react with cyclotron-produced no-carrier-added [¹⁸F]fluoride ion to produce [¹⁸F]aryl fluorides. We aimed to prepare functionalized diaryliodonium salts to serve as potential precursors for producing useful ¹⁸F-labeled aryl



synthons, such as ¹⁸F-labeled halomethylbenzenes, benzaldehydes, and benzoic acid esters. Such salts were designed to have one functionalized aryl ring, one relatively electron-rich ring, such as 4-methoxyphenyl or 2-thienyl, and a nonfluorine containing weakly nucleophilic anion. Generation of a [hydroxy(tosyloxy)iodo]arene from a functionalized (diacetoxyiodo)arene in situ followed by treatment with an electron-rich arene, such as anisole or thiophene, or with a functionalized arylstannane gave expedient regiospecific access to a wide range of functionally diverse diaryliodonium tosylates in moderate to high yields (44–98%). The described methodology broadens the scope for producing new functionalized diaryliodonium salts for diverse applications.

INTRODUCTION

Diaryliodonium salts are hypervalent compounds that are classified as diaryl- λ^3 -iodanes.¹ They are of increasing interest in organic synthesis as effective arylating agents.^{2–4} Moreover, diaryliodonium salts have gained particular value for introducing the short-lived positron-emitter fluorine-18 ($t_{1/2} = 109.7$ min) into radiotracers for molecular imaging in animal and human subjects with positron emission tomography (PET).⁵ Uniquely, reactions of diaryliodonium salts with cyclotron-produced [¹⁸F]fluoride ion can efficiently introduce fluorine-18 onto electron-rich or electron-deficient aromatic rings at any desired carbon position in a rapid single step (Scheme 1).^{6–9}

Scheme 1. General Utility of Diaryliodonium Salts for Preparing [¹⁸F]Fluoroarenes from Cyclotron-Produced [¹⁸F]Fluoride Ion



We are further interested in exploiting the radiofluorination of diaryliodonium salts for rapid access to functionalized $[^{18}F]$ fluoroarenes that might serve as labeling synthons in the preparation of PET radiotracers. These synthons include ^{18}F -

labeled benzoic acid esters, benzyl halides, and benzaldehydes. Several methods exist for the preparation of diaryliodonium salts, and these have recently been categorized and reviewed.³ The vast majority of such methods are applicable to preparing diaryliodonium salts bearing relatively unreactive substituents, such as alkyl, alkoxy, or phenyl, and some of these are also known to be suitable for preparing salts with more reactive substituents, such as halo or nitro. However, diaryliodonium salts bearing halomethyl functionality have not been reported. In addition, literature precedent on the syntheses of diaryliodonium salts with formyl substituents is sparse^{10–17} and in some cases has entailed the use of undesirable reagents, such as organomercury compounds^{10,11} or strong acids^{12,13}

Here we report that variously functionalized diaryliodonium tosylates were readily accessed as their tosylates in moderate to high yields by generating a [hydroxy(tosyloxy)iodo]arene (HTIA) from a prepared (diacetoxyiodo)arene in situ for subsequent treatment with either an electron-rich arene or an arylstannane. This convenient methodology, as well as meeting our particular needs, will also be generally useful to others for preparing functionalized diaryliodonium salts for use as reagents or for their other potential applications (e.g., as photoinitiators or bactericides).^{2,3}

We particularly wished to prepare functionalized diaryliodonium salts in which one aryl ring is especially electron-rich, such as a 4-methoxyphenyl or 2-thienyl ring, because such a

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ring confers high selectivity for radiofluorination at a functionalized partner ring that is relatively less electronrich.^{6-9,18} Moreover, we wished to avoid salts with strongly nucleophilic or fluorine-containing counterions because nucleophilic anions might compete in subsequent radiofluorination reactions and fluorine-containing anions might undesirably release nonradioactive fluoride ion to dilute the specific radioactivity of the [18 F]fluoride ion.⁵ Therefore, tosylate was considered to be an acceptably benign counterion for our specific purpose.

An attractive approach for the single-step syntheses of diaryliodonium tosylates is treatment of an electron-rich arene¹⁷ or an organometallic reagent, such as an arylsilane,¹⁹ arylboronic acid,²⁰ or arylstannane,²¹ with the hypervalent- λ^3 -iodane, [hydroxy(tosyloxy)iodo]benzene,²² especially as the latter is commercially available as Koser's reagent. We considered that the synthetic scope of such useful methods might be expanded for general access to unsymmetrical diaryliodonium salts that would be useful precursors to functionalized [¹⁸F]fluoroarenes as labeling synthons. The use of Koser's reagent restricts the synthesis of diaryliodonium salts to those in which one ring is phenyl. Moreover, highly electronrich derivatives of Koser's reagent, such as 4-[hydroxy-(tosyloxy)iodo]anisole^{23,24} and 2-[hydroxy(tosyloxy)iodo]thiophene,²⁵ are unstable, and sometimes violently so,²³ when isolated. Therefore, we aimed to explore whether such derivatives might instead be prepared and used safely and effectively in situ.

RESULTS AND DISCUSSION

We were attracted to the use of congeneric (diacetoxyiodo)arenes (λ^3 -iodane diacetates) as starting materials to prepare the required [hydroxy(tosyloxy)iodo]arenes (HTIAs) as reactive intermediates, since these diacetates are generally found to be stable microcrystalline solids.^{2,26} We envisaged a synthetic approach in which an iodoarene would first be oxidized to a (diacetoxyiodo)arene with peracetic acid in acetic acid^{27,28} or sodium perborate tetrahydrate in acetic acid²⁷ and in which the isolated diacetate would then be treated with *p*-TsOH·H₂O plus an electron-rich arene or arylstannane. The required (diacetoxyiodo)arenes (1–13) were readily obtained, and the outlined approach was rapidly successful in producing a wide range of the targeted functionalized diaryliodonium tosylates, as we now describe.

In the use of this method with electron-rich anisole (Scheme 2), electrophilic substitution by the functionalized HTIA intermediate occurred exclusively at the para position, and gave the target diaryliodonium tosylates in moderate to very high yields (46-90%), as exemplified in 12 examples (21-32;Table 1). Thus, this method was effective for introducing chloromethyl or bromomethyl groups into ortho, meta or para position, methoxycarbonyl or ethoxycarbonyl into the meta position, acetyl groups into the meta and/or para position, and (diacetoxy)methyl into the ortho position. The regiospecificity of the HTIA intermediates for electrophilic substitution at the para position of anisole was remarkable but also fully consistent with earlier findings. For example, the reagent formed between $PhI(OAc)_2$ and triflic acid is known to react exclusively at the 4position of anisole to produce (4-methoxyphenyl)phenyliodonium triflate.²⁹ We further found that the use of highly electron-rich 1,3,5-trimethoxybenzene with 4chloromethyl(diacetoxyiodo)benzene (Scheme 2) gave the

Scheme 2. Synthesis of Diaryliodonium Tosylates via the Generation of HTIAs in Situ Followed by Treatment with an Electron-Rich Arene^a



"Reagents and conditions: (i) sodium perborate in $MeCO_2H$ or peracetic acid in $MeCO_2H$; (ii) *p*-TsOH·H₂O, $MeCN/CHCl_3$, reflux; (iii) reflux.

corresponding iodonium salt (33) in excellent yield (98%, Table 1).

The halomethyl iodonium tosylates (21-26) are potential precursors to $[{}^{18}F]$ fluorobenzyl halides. $[{}^{18}F]$ 4-Fluorobenzyl bromide has already proved to be a useful labeling synthon for producing PET radiotracers,⁵ including radiotracers for imaging cannabinoid subtype 1,³⁰ histamine subtype 3,³¹ and delta opioid receptors.³² However, the radiosynthesis of this synthon has previously used three steps.³⁰ $[{}^{18}F]$ 3-Fluorobenzyl bromide was recently used to label $[{}^{18}F]$ lapatinib, a potential radiotracer of ERb81/ErbB2 tyrosine kinase.³³ In this case, the $[{}^{18}F]$ (3bromomethyl)fluorobenzene was prepared for the first time from an iodonium salt in two radiosynthetic steps. The syntheses of the diaryliodonium salts (21–26) allow us to explore whether such $[{}^{18}F]$ fluorobenzyl halides can be prepared more efficiently and simply in a single radiosynthetic step.

We further demonstrated that potential diaryliodonium tosylate precursors to $[^{18}F]$ 3-fluorobenzyl bromide that have either 2-thienyl (**34**) or 5-methyl-2-thienyl (**35**) as the electronrich aryl ring could be prepared similarly from thiophene or 2-methylthiophene (Scheme 2) in high and moderate yield (83% and 57%, respectively; Table 1). When the more electron-rich 2-methoxythiophene was used as arene, the target diaryliodonium salt (**36**) was formed in high yield (~78%, preceding drying attempt) (Table 1) but proved unstable to drying under vacuum at room temperature. This salt was the only one arising from this study showing instability.

Thiophene was also used as the electron-rich arene to prepare diaryliodonium tosylates bearing a 3-methoxycarbonyl (37) or 4-methoxycarbonyl (38) substituent on a phenyl ring with a 2-thienyl partner ring in good yields (58% and 83%, respectively; Table 1). The regioselectivity was as expected for

Entry	(Diacetoxyiodo)arene		Electron-rich arene	Product		Yield
1	$\frac{R^{2}}{2CH_{1}Cl}$	<u> R²</u> ц	Anisolo	21	CI	<u>(%)</u> 82
1	2-CH ₂ CI	п	Amsole	41	✓ → I ⁺ → OMe	83
2	3-CH ₂ Cl	Н	Anisole	22		84
3	4-CH ₂ Cl	Н	Anisole	23		90
4	2-CH ₂ Br	Н	Anisole	24		46
5	3-CH ₂ Br	Н	Anisole	25		78
6	4-CH ₂ Br	Η	Anisole	26		81
7	3-MeOCO	Н	Anisole	27		63
8	3-EtOCO	Н	Anisole	28		69
9	3-AcO	Н	Anisole	29		88
10	4-AcO	Н	Anisole	30		88
11	3-AcO	4-AcO	Anisole	31		86
12	2-CH(OAc) ₂	Η	Anisole	32		77
13	4-CH ₂ Cl	Н	1,3,5-Trimethoxybenzene	33		98
14	3-CH ₂ Br	Η	Thiophene	34	Br→S	83
15	3-CH ₂ Br	Н	2-Methylthiophene	35		57
16	3-CH ₂ Br	Η	2-Methoxythiophene	36	Br S OMe	~ 78
17	3-MeOCO	Н	Thiophene	37		58
18	4-MeOCO	Н	Thiophene	38	MeOCO	83

Table 1. Yields of Substituted Diaryliodonium Tosylates $(ArI^+4-MeOC_6H_4OTs^-)$ from (Diacetoxy)iodoarenes $(R^1R^2ArI(OAc)_2)$ and Electron-Rich Arenes

attack of an electrophilic agent on thiophene and is in accord with the report that HTIAs react with thiophene at the 2-position.¹⁷ Although esters of $[^{18}F]$ 4-fluorobenzoic acid may be prepared in a single radiosynthetic step by aromatic nucleophilic substitution with $[^{18}F]$ fluoride ion in *p*-nitro

precursors, radiochemical yields are low.³⁴ Use of a 4-trimethylammonium leaving group improves radiochemical yield.³⁵ However, such aromatic nucleophilic substitution reactions are not expected to be applicable to preparing $[^{18}F]$ 3-fluorobenzoic acid esters in acceptable yields.⁵ Ready

access to iodonium salts bearing alkoxycarbonyl groups such as 37 and 38 will allow us to explore whether they are superior precursors for the radiosyntheses of $[^{18}F]$ 3-fluoro- and $[^{18}F]$ 4-fluorobenzoic acid esters.

We wished to prepare (4-methoxyphenyl)aryliodonium tosylates bearing electron-withdrawing functional groups, such as formyl, since such salts might serve as useful precursors to [¹⁸F]fluorobenzaldehydes, which have been demonstrated to be useful labeling agents.³⁶ Although (diacetoxyiodo)arenes and HTIAs may react well and regioselectively with highly electronrich arenes and heteroarenes they generally show low reactivity toward moderately electron-rich arenes. For example, Koser's reagent fails to react even with benzene or toluene in acetonitrile.¹⁹ By contrast, Koser's reagent reacts readily with organometallic reagents, such as arylstannanes,²¹ to produce the corresponding phenylaryliodonium tosylates. Stannylated benzaldehydes proved readily accessible (Scheme 3). We were

Scheme 3. Synthesis of Functionalized Diaryliodonium Tosylates by Treating 4-[Hydroxy(tosyloxy)iodo]anisole, Generated in Situ, With Arylstannanes^a



^{*a*}Reagents and conditions: (i) sodium perborate in MeCO₂H; (ii) *p*-TsOH·H₂O, MeCN, reflux; (iii) R_6Sn_2 , Pd(PPh₃)₄, 1,4-dioxane, reflux; (iv) CHCl₃, reflux (R = Me for **29** and R= *n*-Bu for **39–42**).

therefore able to explore the synthesis of functionalized (4methoxyphenyl)aryliodonium tosylates through treatment of 4methoxy-(diacetoxyiodo)benzene with tosic acid followed by a stannylated benzaldehyde. This approach (Scheme 3) gave 3formylphenyl(4'-methoxyphenyl)iodonium tosylate (39), the 4formyl analogue (40), and the 6-methoxy derivative of 39 (41)in moderate yields (44-50%; Table 2). Similarly, use of 2-(diacetoxyiodo)thiophene with a stannylated benzaldehyde (Scheme 4) gave the 3-formylphenyl(2'-thienyl)iodonium tosylate (43) and the 6-methoxy analogue (44) in moderate yields (48%) (Table 2). Clearly, the formyl groups in the meta or para position to the tin substituent resisted oxidation in these syntheses. Curiously, in contrast to our success in preparing diaryliodonium tosylates with meta or para formyl groups, all attempts to prepare the o-formyl analogues of 39 or 43 failed. The reason is at present unclear but may be related to the potential for an o-formyl group to form a stable fivemembered benzoiodoxole compound. No o-formyl diaryliodonium salt has yet been reported. Nonetheless, we envisage that the prepared (2-diacetoxymethyl)diaryliodonium tosylate (32) can serve as a precursor to $[{}^{18}F]$ 2-fluorobenzaldehyde in two steps, namely radiofluorination to [18F](2diacetoxymethyl)fluorobenzene followed by hydrolysis.

We were interested to see how well arylstannanes bearing a less electron-withdrawing substituent might perform in our method of diaryliodonium tosylate synthesis. We found that the iodonium tosylate bearing a 3-acetoxy group (29) could be prepared in 79% yield from 3-(tri-*n*-butylstannyl)phenyl acetate and 4-methoxy(diacetoxyiodo)benzene (Table 2), which is very comparable to the yield achieved from the treatment of 3-acetoxy(diacetoxyiodo)benzene with anisole (83%, Table 1). Similarly, the iodonium tosylate bearing a 3-methylamido group (42) was obtained from the arylstannane in high yield (65%) (Table 2).

In summary, diaryliodonium tosylates having one aryl ring bearing chloromethyl, bromomethyl, ester, aldehyde, or amide functionality and another relatively electron-rich ring can be conveniently prepared in moderate to high yields (44–98%) by treating HTIAs, generated in situ, with either electron-rich arenes or organostannanes.

EXPERIMENTAL SECTION

Methods. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded at room temperature. ¹H and ¹³C chemical shifts are reported in δ units (ppm) downfield relative to the signal for tetramethylsilane. High resolution mass spectra (HRMS) were acquired under electron ionization conditions using a double-focusing high-resolution mass spectrometer. Melting points are uncorrected.

Preparation of (Diacetoxyiodo)arenes. (Diacetoxyiodo)arenes (1-15) were prepared by oxidation of iodoarenes with either peracetic acid in acetic acid²⁶ or sodium perborate²⁷ in acetic acid, as follows.

3-Chloromethyl/(diacetoxyiodo)benzene (1). Peracetic acid in acetic acid (32 wt %; 5 mL) was added dropwise to 3-iodobenzyl chloride (2.8 mmol, 0.71 g) at -10 °C (ice–salt bath), and the mixture was slowly warmed to rt and stirred overnight (ca. 14 h). Consumption of 3-iodobenzyl chloride was monitored by TLC (silica gel, hexane $R_f = 0.38$). Aqueous acetic acid (10% v/v) was added to the yellow solution. The precipitate was recovered by filtration, washed with water (10 mL) and then diethyl ether (10 mL × 3), and dried in vacuo for 4 h to give 1 (0.62 g; 59%): mp =143–144 °C; ¹H NMR (CDCl₃) δ 8.12 (t, J = 1.6 Hz, 1H), 8.04 (d, J = 8 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 8 Hz, 1H), 4.63 (s, 2H), 2.02 (s, 6H); ¹³C NMR (CDCl₃) δ 176.5, 140.5, 134.7, 134.6, 131.7, 131.1, 121.4, 44.7, 20.4.

The following compounds 2-13 were prepared likewise. In syntheses where addition of aqueous acetic acid gave no precipitate, the yellow solution was extracted with dichloromethane. The organic layers were then dried over MgSO₄ and evaporated to give a yellow oil which solidified when triturated with diethyl ether.

2-Chloromethyl(diacetoxyiodo)benzene (2): white solid (84%); mp = 151–152 °C; ¹H NMR (CDCl₃) δ 8.25 (dd, *J* = 0.8, 8 Hz, 1H), 8.04 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.66 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.42 (dt, *J* = 1.6, 7.6 Hz, 1H), 4.89 (s, 2H), 1.99 (s, 6H); ¹³C NMR (CDCl₃) δ 176.5, 138.8, 137.7, 133.0, 130.9, 125.1, 47.8, 20.3.

4-Chloromethyl(diacetoxyiodo)benzene (3): white solid (52%); mp = 142–145 °C; ¹H NMR (CDCl₃) δ 8.09 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 4.62 (s, 2H), 2.02 (s, 6H); ¹³C NMR (CDCl₃) δ 176.5, 141.3, 135.3, 130.9, 120.9, 44.8, 20.4.

2-Bromomethyl-(diacetoxyiodo)benzene (4): white solid (45%); mp = 113–115 °C; ¹H NMR (CDCl₃) δ 8.23 (d, *J* = 6.4 Hz, 1H), 7.75 (dd, *J* = 2, 8.4 Hz, 1H), 7.63 (dt, *J* = 2, 7.6 Hz, 1H), 7.39 (dt, *J* = 2.8, 8.8 Hz, 1H), 4.78 (s, 2H), 2.00 (s, 6H); ¹³C NMR (CDCl₃) δ 175.9, 138.6, 137.3, 132.5, 132.4, 130.8, 130.3, 124.8, 33.8, 19.7.

3-Bromomethyl(diacetoxyiodo)benzene (5): white solid (73%); mp = 130–132 °C; ¹H NMR (CDCl₃) δ 8.11 (t, *J* = 1.6 Hz, 1H), 8.01 (dt, *J* = 1.2, 8 Hz, 1H), 7.62 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 4.50 (s, 2H), 2.02 (s, 6H); ¹³C NMR (CDCl₃) δ 176.5, 140.8, 135.1, 134.6, 132.3, 131.2, 121.3, 31.3, 20.4.

4-Bromomethyl(diacetoxyiodo)benzene (6): pale yellow solid (42%); mp = 131-133 °C; ¹H NMR (CDCl₃) δ 8.06 (dd, J = 2, 6.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 4.49 (s, 2H), 2.02 (s, 6H); ¹³C

Entry	$R^{1}R^{2}ArSn(R^{3})_{3}$			(Diacetoxyiodo)arene	Product		Yield
	\mathbf{R}^1	\mathbf{R}^2	R ³				· (%)
1	3-OAc	Н	Me	4-MeOC ₆ H ₄ I(OAc) ₂	29	AcO	79
2	3-СНО	Н	Bu	4-MeOC ₆ H ₄ I(OAc) ₂	39	CHO	44
3	4-CHO	Н	Bu	$4-MeOC_6H_4I(OAc)_2$	40	OHC	52
4	3-СНО	6-MeO	Bu	4-MeOC ₆ H ₄ I(OAc) ₂	41	CHO	50
5	3-MeNHCO	Н	Bu	4-MeOC ₆ H ₄ I(OAc) ₂	42	MeNHCO	65
6	3-СНО	Н	Bu	2-Thienyliodo(OAc) ₂	43	OHC	48
7	3-СНО	6-MeO	Bu	2-Thienyliodo(OAc) ₂	4		48

Table 2. Yields of Substituted Diaryliodonium Tosylates from a (Diacetoxyiodo)arene Treated with a Substituted Arylstannane

Scheme 4. Synthesis of 2-Thienylaryliodonium Salts Bearing an Aldehyde Group on the Non-Thienyl Ring^{a}



"Reagents and conditions: (i) sodium perborate in MeCO₂H, 50 °C; overnight; (ii) *p*-TsOH·H₂O, MeCN, reflux; (iii) CHCl₃, reflux.

NMR (CDCl₃) δ 176.5, 141.7, 138.0, 135.4, 131.5, 130.8, 120.8, 31.4, 20.4.

3-Methoxycarbonyl(diacetoxyiodo)benzene (7): pale yellow solid (30%); mp = 163–165 °C; ¹H NMR (CDCl₃) δ 8.75 (t, *J* = 1.6 Hz, 1H), 8.28–8.25 (m, 2H), 7.59 (t, *J* = 8 Hz, 1H) 3.97 (s, 3H), 2.02 (s, 6H); ¹³C NMR (CDCl₃) δ 176.5, 165.0, 138.9, 136.1, 132.6, 130.8, 123.1, 121.2, 52.3, 20.3.

3-Ethoxycarbonyl(diacetoxyiodo)benzene (8): white solid (19%); mp = 113–115 °C; ¹H NMR (CDCl₃) δ 8.74 (t, *J* = 1.6 Hz, 1H), 8.26 (dd, *J* = 1.6, 8 Hz, 2H), 7.58 (t, *J* = 8 Hz, 1H), 4.42 (q, *J* = 7.2, 2H), 2.02 (s, 6H), 1.43 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (CDCl₃) δ 176.6, 164.5, 138.9, 136.0, 133.2, 132.6, 130.8, 121.1, 61.9, 20.4, 14.3.

3-Acetoxy(diacetoxyiodo)benzene (9): white solid (51%); mp =121-123 °C; ¹H NMR (CDCl₃) δ 7.95-7.92 (m, 1H), 7.89 (t, *J* = 2 Hz, 1H), 7.52 (t, *J* = 8 Hz, 1H), 7.36-7.33 (m, 1H), 2.34 (s, 3H), 2.02

(s, 6H); $^{13}{\rm C}$ NMR (CDCl_3) δ 176.5, 168.5, 151.3, 132.0, 131.3, 128.3, 125.3, 120.5, 21.0, 20.4.

4-Acetoxy(diacetoxyiodo)benzene (**10**): white solid (49%); mp = 153–155 °C; ¹H NMR (CDCl₃: δ 8.09 (dd, *J* = 2.4, 7.2 Hz, 2H), 7.23 (dd, *J* = 2, 8.8 Hz, 2H), 2.34 (s, 3H), 2.02 (s, 6H); ¹³C NMR (CDCl₃) δ 176.5, 168.6, 153.4, 136.5, 124.4, 117.3, 21.1, 20.4.

3,4-Diacetoxy(diacetoxyiodo)benzene (11): pale yellow solid (47%); mp = 140–142 °C; ¹H NMR (CDCl₃) δ 7.97–7.93 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 2.33 (s, 6H), 2.02 (s, 6H); ¹³C NMR (CDCl₃) δ 176.6, 167.4, 167.3, 144.9, 143.1, 133.1, 130.4, 125.6, 116.2, 20.6, 20.5, 20.3.

4-Methoxycarbonyl(diacetoxyiodo)benzene (12): pale yellow solid (19%); mp = 136–138 °C (lit.³⁷ mp =150.0–153.3 °C); ¹H NMR (CDCl₃) δ 8.17–8.12 (m, 4H), 3.97 (s, 3H), 2.02 (s, 6H); ¹³C NMR (CDCl₃) δ 176.5, 165.5, 134.9, 133.1, 131.8, 125.7, 52.7, 20.4.

2-(Diacetoxymethyl)(diacetoxyiodo)benzene (13): white solid (43%); mp = 140–143 °C; ¹H NMR (CDCl₃) δ 8.32 (d, *J* = 7.6 Hz, 1H), 7.85 (s, 1H), 7.79 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.51 (dt, *J* = 1.6, 7.6 Hz, 1H), 2.13 (s, 6H), 1.98 (s, 6H); ¹³C NMR (CDCl₃) δ 176.5, 168.3, 168.1, 138.5, 136.4, 132.5, 132.3, 130.0, 121.5, 91.1, 20.6, 20.2.

2-(Diacetoxyiodo)thiophene (14). Sodium perborate tetrahydrate (7.69 g, 50 mmol) was added portionwise over 30 min to a solution of 2-iodothiophene (1.05 g, 5 mmol) in acetic acid (50 mL). The temperature was raised to 50 °C and the mixture stirred at this temperature overnight (ca. 14 h). The resulting solid was filtered off, and the filtrate was concentrated in vacuo. The product was extracted with dichloromethane (30 mL × 3) and washed with water (100 mL × 2). The organic layers were dried over MgSO₄ and concentrated to a pale yellow oil. Trituration of this oil with Et₂O gave solids that were filtered off, washed with Et₂O, and dried under vacuum to give 14 as a white solid (0.58 g, 35%): mp = 115–118 °C (lit.³⁸ mp = 120–122 °C; lit.³⁹ mp = 112–119 °C). ¹H NMR (CDCl₃) δ 7.78 (dd, *J* = 1.2, 3.6 Hz, 1H), 7.64 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.15–7.13 (m, 1H), 2.02 (s, 6H); ¹³C NMR (CDCl₃) δ 177.0, 139.1, 134.9, 128.7, 106.3, 20.4.

4-Methoxy(diacetoxyiodo)benzene (15).²⁸ This compound was prepared in the same manner as 14 and obtained as a white solid (34%): mp = 85–88 °C (lit.⁴⁰ mp =88–90 °C); ¹H NMR (CDCl₃) δ 8.01 (d, J = 9.2 Hz, 2H), 6.97 (d, J = 9.2 Hz, 2H), 3.87 (s, 3H), 2.00

(s, 6H); $^{13}{\rm C}$ NMR (100 MHz, CDCl₃) δ 176.34, 162.2, 137.1, 116.6, 111.7, 55.6, 20.4.

Preparation of Arylstannanes. Arylstannanes **16–20** were prepared from iodoarenes by treatment with either hexamethylditin⁴¹ or hexa-*n*-butylditin⁴² over palladium catalyst, as follows.

N-Methyl-3-(trimethylstannyl)benzamide (**16**). 3-Iodo-*N*-methylbenzamide (0.73 g, 2.8 mmol) bis(trimethylditin) (1.00 g, 3.1 mmol) and Pd(PPh₃)₄ catalyst (0.068 g, 0.05 mmol) were added to toluene (20 mL) under argon. This mixture was refluxed overnight and the precipitate then filtered off. The filtrate was concentrated in vacuo, and the remaining crude oil was purified with column chromatography (silica gel, 50% EtOAc/hexane) to give **16** (R_f = 0.35) as a white solid (0.39 g, 44%): mp = 91–92 °C; ¹H NMR (CDCl₃) δ 7.88 (d, *J* = 1.2 Hz, 1H), 7.67–7.65 (m, 1H), 7.62–7.60 (m, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 6.14 (s, br, 1H), 3.02 (d, *J* = 4.8 Hz, 3H), 0.31 (s, 9H); ¹³C NMR (CDCl₃) δ 168.8, 143.2, 138.8, 134.1, 128.0, 126.5, 26.9, –7.77.

4-Tri-n-butylstannylbenzaldehyde (17). Bis(tri-n-butylditin) (2.61 g, 4.5 mmol) and Pd(PPh₃)₄ (0.084 g, 0.07 mmol) were added to a solution of 4-iodobenzaldehyde (1.03 g, 4.4 mmol) in 1,4-dioxane (20 mL) under argon. This mixture was refluxed for 8 h. The resulting dark precipitate was filtered off on a Celite pad, and the filtrate was concentrated in vacuo. Column chromatography (silica gel; 5% EtOAc/hexane) of the crude oil gave 17 (R_f = 0.43) as a colorless oil (1.10 g, 63%): ¹H NMR (CDCl₃) δ 9.99 (s, 1H), 7.81–7.77 (m, 2H), 7.67–7.60 (m, 2H), 1.57–1.51 (m, 6H), 1.36–1.31 (m, 6H), 1.13–1.09 (m, 6H), 0.89 (t, J = 7.6 Hz, 9H); ¹³C NMR (CDCl₃) δ 192.7, 152.5, 136.9, 135.9, 128.4, 29.0, 27.3, 13.6, 9.7. Spectroscopic data correspond to reported data.⁴³

3-Tri-n-butylstannylbenzaldehyde (18). This was prepared as described for 17: colorless oil (61%); ¹H NMR (CDCl₃): δ 10.02 (s, 1H), 8.02–7.92 (m, 1H), 7.81–7.77 (m, 1H), 7.74–7.72 (m, 1H), 7.51–7.75 (m, 1H), 1.57–1.51 (m, 6H), 1.37–1.31 (m, 6H), 1.13–1.09 (m, 6H), 0.89 (t, J = 7.2 Hz, 9H); ¹³C NMR (CDCl₃) δ 193.1, 143.5, 142.5, 137.6, 135.5, 129.4, 128.3, 29.0, 27.3, 13.6, 9.6. Spectroscopic data correspond to reported data.⁴⁴

4-Methoxy-3-(tri-n-buty/stannyl)benzaldehyde (19). Bis-(tributylditin) (1.94 g, 3.3 mmol) and Pd(PPh₃)₄ (0.034 g, 0.03 mmol) were added to a solution of 3-iodo-4-methoxybenzaldehyde (0.79 g, 3.0 mmol) in toluene (20 mL) at rt under argon. This mixture was refluxed overnight. The resulting dark precipitate was removed by filtration on Celite pad, and the filtrate toluene solution was concentrated in vacuo. Column chromatography (silica gel; 20% EtOAc/hexane) of the crude oil gave 19 (R_f = 0.5) as a pale yellow oil (1.12 g, 87%): ¹H NMR (CDCl₃) δ 9.89 (s, 1H), 7.90 (d, J = 2 Hz, 1H), 7.83 (dd, J = 2.4, 8.8 Hz, 1H), 6.90 (dd, J = 6.8, 15.2 Hz, 1H), 3.86 (s, 3H), 1.55–1.50 (m, 6H), 1.36–1.30 (m, 6H), 1.11–1.07 (m, 6H), 0.89 (t, J = 7.2 Hz, 9H); ¹³C NMR (CDCl₃) δ 191.1, 168.6, 138.8, 133.2, 131.7, 130.1, 108.7, 55.4, 29.0. 27.2, 13.4, 9.8.

3-(Tri-n-butylstannyl)phenyl Acetate (20). This was prepared as described for **19**: colorless oil (60%); ¹H NMR (CDCl₃) δ 7.35–7.29 (m, 2H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.02–6.99 (m, 1H), 2.29 (s, 3H), 1.57–1.49 (m, 6H), 1.37–1.30 (m, 6H), 1.08–1.04 (m, 6H), 0.88 (t, *J* = 7.6 Hz, 9H); ¹³C NMR (CDCl₃) δ 169.5, 150.3, 143.9, 133.8, 128.7, 121.1, 28.9, 27.3, 21.2, 13.6, 9.6.

Synthesis of Functionalized Diaryliodonium Salts by Treating HTIAs with Electron-Rich Arenes. Chloromethylphenyl(4'-methoxyphenyl)iodonium tosylate (21). p-TsOH·H₂O (0.15 g, 0.8 mmol) was added to a suspension of 2chloromethyl(diacetoxyiodo)benzene (0.31 g, 0.8 mmol) in MeCN (2 mL), giving an intense yellow solution, which was immediately diluted with chloroform (20 mL). Anisole (0.22 g, 2 mmol) was added, and the resultant pale yellow solution was then refluxed for 4 h. The consumption of HTIA was monitored with KI-starch paper. Solvent was then removed under reduced pressure, and the yellow oily residue was triturated with Et₂O (30 mL). Precipitate was filtered off, washed with Et2O, dried under vacuum for 4 h, and recrystallized from MeOH/Et₂O to give 21 as a white solid (0.38 g, 83%): mp =172-174 °C; ¹H NMR (MeOD- d_4) δ 8.33 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.8 Hz, 2H), 7.77-7.67 (m, J = 8.8 Hz, 2Hz), 7.77-7.67 (m, J = 8.8 Hz, 2Hz), 7.77-7.67 (m, J = 8.8 Hz, 2Hz), 7.77-7.67 (m, J = 8.8 Hz), 7.77-7.67

4H), 7.45 (t, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 4.98 (s, 2H), 3.84 (s, 3H), 2.36 (s, 3H); 13 C NMR (MeOD-*d*₄) δ 164.7, 143.7, 141.8, 141.2, 139.1, 138.6, 134.9, 133.5, 133.4, 129.9, 127.1, 120.2, 119.0, 104.7, 56.5, 21.5; HRMS [M - OTs]^{•+} calcd for C₁₄H₁₃OCII 358.9700, found 358.9697.

The following compounds (22-38) were prepared likewise from the appropriate functionalized HTIA and an electron-rich arene (anisole, 1,3,5-trimethoxybenzene, thiophene, 2-methylthiophene, or 2-methoxythiophene).

3-Chloromethylphenyl(4'-methoxyphenyl)iodonium tosylate (22): yield 84%; mp = 170–171 °C; ¹H NMR (CDCl₃) δ 8.00 (s, 1H), 7.89 (dd, *J* = 2, 7.2 Hz, 2H), 7.82 (d, *J* = 8 Hz, 1H), 7.51 (d, *J* = 8 Hz, 3H), 7.31 (t, *J* = 8 Hz, 1H), 7.04 (d, *J* = 8 Hz, 2H), 6.84 (dd, *J* = 2, 7.2 Hz, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 2.32 (s, 3H); ¹³C NMR (CDCl₃) δ 162.5, 142.4, 141.2, 139.6, 137.5, 134.3, 134.1, 131.7, 131.5, 128.5, 126.0, 117.6, 115.7, 103.6, 55.6, 44.5, 21.3; HRMS [M – OTs]^{•+} calcd for C₁₄H₁₃OCII 358.9700, found 358.9694.

4-Chloromethylphenyl(4' methoxyphenyl)iodonium tosylate (23): yield 90%; mp = 191–193 °C; ¹H NMR (MeOD- d_4) δ 8.09 (t, *J* = 8 Hz, 4H), 7.69 (d, *J* = 8 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 4.67 (s, 2H), 3.84 (s, 3H), 2.36 (s, 3H); ¹³C NMR (MeOD- d_4) δ 164.7, 144.3, 143.7, 141.8, 138.8, 136.5, 133.2, 130.0, 127.1, 119.0, 115.9, 104.8, 56.5, 45.5, 21.5; HRMS [M – OTs]⁹⁺ calcd for C₁₄H₁₃OCII 358.9700, found 358.9700.

2-Bromomethylphenyl(4'-methoxyphenyl)iodonium tosylate (24): yield 46%. mp = 135–137 °C; ¹H NMR (MeOD- d_4): δ 8.30 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.77 (dd, *J* = 2, 7.6 Hz, 1H), 7.70–7.65 (m, 3H), 7.42 (dt, *J* = 2.4, 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 4.89 (s, 2H), 3.85 (s, 3H), 2.37 (s, 3H); ¹³C NMR (MeOD- d_4): δ 164.8, 143.7, 141.8, 141.7, 139.1, 138.7, 134.9, 133.5, 133.4, 130.0, 127.1, 120.2, 119.0, 104.6, 56.5, 35.3, 21.5; HRMS [M – OTs]^{•+} calcd for C₁₄H₁₃OBrI 402.9195, found 402.9195.

3-Bromomethylphenyl(4'-methoxyphenyl)iodonium tosylate (25): yield 78%; mp = 171–173 °C; ¹H NMR (CDCl₃) δ 8.00 (s, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8 Hz, 1H), 7.51 (t, J = 8.4 Hz, 3H), 7.29 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8 Hz, 2H), 6.85 (d, J = 9.2 Hz, 2H), 4.35 (s, 2H), 3.81 (s, 3H), 2.32 (s, 3H); ¹³C NMR (CDCl₃) δ 162.5, 142.6, 141.5, 139.4, 137.5, 134.7, 134.0, 132.8, 131.7, 128.5, 126.0, 117.6, 115.8, 103.6, 55.6, 31.2, 21.3; HRMS [M – OTs]^{•+} calcd for C₁₄H₁₃OBrI 402.9195, found 402.9192.

4-Bromomethylphenyl(4'-methoxyphenyl)iodonium tosylate (**26**): yield 81%; mp =139–141 °C; ¹H NMR (CDCl₃) δ 7.88 (t, *J* = 7.2 Hz, 4H), 7.48 (d, *J* = 8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 9.2 Hz, 2H), 4.38 (s, 2H), 3.79 (s, 3H), 2.31 (s, 3H); ¹³C NMR (CDCl₃) δ 162.4, 142.4, 141.4, 139.4, 137.5, 135.0, 131.9, 128.5, 126.0, 117.5, 115.2, 103.8, 55.6, 31.3, 21.3; HRMS [M – OTs]^{•+} calcd for C₁₄H₁₃OBrI 402.9195, found 402.9199.

[3-(Methoxycarbonyl)phenyl](4'-methoxyphenyl)iodonium tosylate (**27**): yield 63%; mp = 155–157 °C; ¹H NMR (MeOD- d_4) δ 8.71 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 8.12 (d, *J* = 10 Hz, 2H), 7.68 (d, *J* = 5.6 Hz, 2H), 7.62 (t, *J* = 6 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 3.83 (s, 3H), 2.35 (s, 3H); ¹³C NMR (MeOD- d_4) δ 166.2, 164.8, 143.7, 141.8, 140.2, 138.9, 136.7, 134.9, 134.1, 133.3, 129.9, 127.1, 119.1, 116.7, 104.8, 56.5, 53.4, 21.4; HRMS [M – OTs]^{•+} calcd for C₁₅H₁₄O₃I 368.9988, found 368.9984.

3-(Ethoxycarbonyl)phenyl(4'-methoxyphenyl)iodonium tosylate (**28**): yield 69%; mp = 173–175 °C; ¹H NMR (CDCl₃) δ 8.44 (s, 1H), 8.22 (d, *J* = 8 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8 Hz, 2H), 7.42 (t, *J* = 8 Hz, 1H), 7.02 (d, *J* = 8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 2.31 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃) δ 164.3, 162.6, 142.4, 139.6, 138.8, 137.4, 135.1, 133.6, 132.3, 131.4, 128.5, 126.0, 117.6, 115.9, 104.0, 61.8, 55.6, 21.3, 14.2; HRMS [M – OTs]^{•+} calcd for C₁₆H₁₆O₃I 383.0144, found 383.0133.

3-Acetoxyphenyl(4'-methoxyphenyl)iodonium tosylate (29): yield 88%; mp = 149–150 °C; ¹H NMR (MeOD- d_4) δ 8.08 (dd, J = 3.2, 9.2 Hz, 2H), 8.00–7.96 (m, 2H), 7.69 (dd, J = 0.8, 8 Hz, 2H), 7.54 (t, J = 8 Hz, 1H), 7.43–7.40 (m, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.08–7.05 (m, 2H), 3.85 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H); 13 C NMR (MeOD- d_4) δ 170.4, 164.7, 153.5, 143.8, 141.8, 138.8, 133.7, 133.3, 130.0, 129.7, 127.3, 127.1, 119.4, 115.6, 104.8, 56.5, 21.5, 20.9; HRMS [M – OTs]^{•+} calcd for C₁₅H₁₄O₃I 368.9988, found 368.9986.

4-Acetoxyphenyl(4'-methoxyphenyl)iodonium tosylate (**30**): yield 88%; mp 157–159 °C; ¹H NMR (CDCl₃) δ 7.94 (dd, J = 2, 7.2 Hz, 2H), 7.88 (dd, J = 2, 7.2 Hz, 2H), 7.94 (dd, J = 1.6, 4.8 Hz, 2H), 7.05–7.00 (m, 4H), 6.80 (dd, J = 2, 9.2 Hz, 2H), 3.78 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H); ¹³C NMR (CDCl₃) δ 168.5, 162.3, 152.9, 142.5, 139.3, 137.5, 136.1, 128.5, 126.0, 124.8, 117.4, 111.4, 104.3, 55.5, 21.2, 21.1; HRMS [M – OTs]^{•+} calcd for C₁₅H₁₄O₃I 368.9988, found 368.9986.

3, 4-Diacetoxyphenyl(4'-methoxyphenyl)iodonium tosylate (**31**): yield 86%; mp 155–156 °C; ¹H NMR (CDCl₃) δ 7.91–7.88 (m, 3H), 7.83 (dd, *J* = 2, 8.8 Hz, 1H), 7.41 (d, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H); ¹³C NMR (CDCl₃) δ 167.5, 167.4, 162.4, 144.9, 143.3, 142.3, 139.4, 137.7, 133.1, 130.2, 128.5, 126.1, 126.0, 117.4, 110.6, 104.4, 55.6, 21.3, 20.6, 20.5; HRMS [M – OTs]^{•+} calcd for C₁₇H₁₆O₅I 427.0043, found 427.0044.

[2-(Diacetoxymethyl)phenyl](4'-methoxyphenyl)iodonium tosylate (**32**): yield 77%; mp 150–153 °C; ¹H NMR (MeOD- d_4) δ 8.28 (dd, J = 0.8, 8 Hz, 1H), 8.07 (dd, J = 2, 7.2 Hz, 2H), 7.86–7.84 (m, 2H), 7.77 (dt, J = 0.8, 7.6 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.56 (dt, J = 1.6, 8 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 9.2 Hz, 2H), 3.84 (s, 3H), 2.36 (s, 3H), 2.12 (s, 6H); ¹³C NMR (MeOD- d_4) δ 170.3, 164.8, 143.8, 141.8, 138.7, 138.6, 138.3, 135.9, 134.6, 131.9, 129.9, 127.1, 119.1, 116.7, 104.7, 92.7, 56.6, 21.5, 20.7; HRMS [M – OTs]^{•+} calcd for C₁₈H₁₈O₅I 441.0199, found 441.0192.

4-Chloromethylphenyl(2',4',6'-trimethoxyphenyl)iodonium tosylate (**33**): yield 98%; mp = 185–187 °C; ¹H NMR (MeOD- d_4) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8 Hz, 2H), 6.41 (s, 2H), 4.65 (s, 2H), 3.97 (s, 6H), 3.89 (s, 3H), 2.36 (s, 3H); ¹³C NMR (MeOD- d_4) δ 169.0, 161.6, 143.9, 143.8, 141.8, 136.3, 132.9, 129.9, 127.1, 115.3, 93.1, 86.4, 57.9, 56.8, 45.6, 21.5; HRMS [M – OTs]^{•+} calcd for C₁₆H₁₇O₃ClI 418.9911, found 418.9906.

3-Bromomethylphenyl(2'-thienyl)iodonium tosylate (**34**): yield 83%; mp = 138–140 °C; ¹H NMR (CDCl₃) δ 8.01 (t, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.81 (dd, *J* = 1.2, 4 Hz, 1H), 7.58 (dd, *J* = 0.8, 5.2 Hz, 1H), 7.50–7.47 (m, 3H), 7.29 (t, *J* = 8 Hz, 1H), 7.07–7.02 (m, 3H), 4.33 (s, 2H), 2.32 (s, 3H); ¹³C NMR (CDCl₃) δ 142.1, 141.5, 140.7, 139.7, 136.2, 134.3, 133.6, 132.1, 131.7, 129.6, 128.6, 125.9, 118.7, 99.2, 31.2, 21.3; HRMS [M – OTs]^{*+} calcd for C₁₁H₉SBrI 378.8653, found 378.8651.

3-Bromomethylphenyl(5'-methyl-2'-thienyl)iodonium tosylate (**35**): yield 57%; mp = 163–165 °C; ¹H NMR (CDCl₃) δ 8.00 (t, *J* = 1.6 Hz, 1H), 7.82 (dq, *J* = 0.8, 8.4 Hz, 1H), 7.61 (d, *J* = 4 Hz, 1H), 7.53 (dd, *J* = 2, 6.4 Hz, 2H), 7.49 (d, *J* = 8 Hz, 1H), 7.30 (t, *J* = 8 Hz, 1H), 7.07 (dd, *J* = 0.4, 8 Hz, 2H), 6.71–6.70 (m, 1H), 4.34 (s, 2H), 2.57 (s, 3H), 2.33 (s, 3H); ¹³C NMR (CDCl₃) δ 152.4, 142.2, 141.5, 141.4, 139.7, 134.0, 133.3, 132.1, 131.7, 128.6, 128.2, 126.0, 118.8, 94.6, 31.2, 21.3, 15.5; HRMS [M – OTs]^{•+} calcd for C₁₂H₁₁SBrI 392.8810, found 392.8807.

3-Bromomethylphenyl(5'-methoxy-2'-thienyl)iodonium tosylate (**36**): yield 78%; mp = 58–59 °C; ¹H NMR (CDCl₃) δ 7.97 (t, *J* = 2 Hz, 1H), 7.81 (dd, *J* = 1.2, 8 Hz, 1H), 7.64 (dd, *J* = 1.6, 8 Hz, 2H), 7.55–7.51 (m, 2H), 7.35 (t, *J* = 8 Hz, 1H), 7.12 (d, *J* = 8 Hz, 2H), 6.22 (d, *J* = 4.4 Hz, 1H), 4.37 (s, 2H), 3.95 (s, 3H), 2.34 (s, 3H); ¹³C NMR (CDCl₃) δ 176.0, 142.3, 141.8, 141.6, 139.8, 133.3, 132.5, 132.2, 131.9, 128.7, 126.0, 119.1, 107.2, 61.0, 31.1, 21.3. This compound decomposed to a black tar during drying under vacuum at room temperature.

[3-(Methoxycarbonyl)phenyl](2'-thienyl)iodonium tosylate (**37**): yield 58%; mp = 140–141 °C; ¹H NMR (MeOD- d_4) δ 8.76 (s, 1H), 8.37 (d, *J* = 7.2 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 2.8 Hz, 1H), 7.90 (d, *J* = 5.6 Hz, 1H), 7.69–7.62 (m, 3H), 7.22–7.17 (m, 3H), 3.94 (s, 3H), 2.36 (s, 3H); ¹³C NMR (MeOD- d_4) δ 166.1, 143.7, 142.7, 141.8, 139.9, 139.1, 136.5, 134.9, 134.3, 133.4, 131.1, 130.0, 127.1, 119.1, 99.3, 53.5, 21.5; HRMS $[M - OTs]^{\bullet+}$ calcd for $C_{12}H_{10}O_2SI$ 344.9446, found 344.9447.

[4-(*Methoxycarbonyl*)phenyl](2'-thienyl)iodonium tosylate (**38**): yield 83%; mp = 188–190 °C; ¹H NMR (MeOD- d_4) δ 8.26 (dd, J = 2, 7.2 Hz, 2H), 8.32 (dd, J = 1.6, 6.8 Hz, 2H), 8.05 (dd, J = 1.2, 3.6 Hz, 1H), 7.92 (dd, J = 1.2, 5.2 Hz, 1H), 7.69 (d, J = 5.6 Hz, 2H), 7.23– 7.18 (m, 3H), 3.92 (s, 3H), 2.36 (s, 3H); ¹³C NMR (MeOD- d_4) δ 166.8, 143.7, 142.8, 141.8, 139.2, 136.0, 135.2, 133.7, 131.1, 130.0, 127.1, 123.4, 99.1, 53.4, 21.5; HRMS [M – OTs]*+ calcd for C₁₂H₁₀O₂SI 344.9446, found 344.9442.

Syntheses of Functionalized Diaryliodonium Salts through Reaction of the HTIA from 4-Methoxy(diacetoxyiodo)benzene with Functionalized Arylstannanes. 3-Formylphenyl(4'methoxyphenyl)iodonium Tosylate (39). p-TsOH·H₂O (0.10 g, 0.53 mmol) was added to a suspension of 4-methoxy-(diacetoxyiodo)benzene (0.19 g, 0.53 mmol) in MeCN (2 mL) while the mixture was cooled to 0 °C. The resultant yellow solution was diluted with chloroform (15 mL). 3-Formyl-3-(trin-butylstannyl)benzaldehyde (0.21 g, 0.52 mmol) in chloroform (5 mL) was added in portions and the mixture gradually heated to reflux for 2 h. The consumption of organotin compound was monitored by TLC (silica gel, 5% EtOAc/ hexane; $R_i = 0.4$), and disappearance of HTIA was confirmed with KI-starch paper. The reaction mixture was then cooled to rt, and solvent was removed in vacuo to give a pale yellow oil which was triturated with Et₂O. Solid was filtered off, washed with Et₂O, and dried under vacuum to give 39 as a white solid: yield 44%; mp = 156–159 °C; ¹H NMR (CDCl₃) δ 9.81 (s, 1H), 8.41 (s, 1H), 8.22 (d, J = 8 Hz, 1H), 7.94–7.90 (m, 3H), 7.47–7.40 (m, 3H), 6.98 (d, J = 8 Hz, 2H), 6.81 (d, J = 9.2 Hz, 2H), 3.78 (s, 3H), 2.29 (s, 3H); 13 C NMR (CDCl₃) δ 189.9. 162.5, 142.2, 140.0, 139.7, 138.5, 137.7, 136.0, 131.8, 131.2, 128.5, 125.9, 117.51, 116.9, 104.1, 55.6, 21.2; HRMS [M -OTs]⁺⁺ calcd for $C_{14}H_{12}O_2I$ 338.9882, found 338.9880.

The following compounds (40-44) were prepared similarly.

4-Formylphenyl(4'-methoxyphenyl)iodonium tosylate (**40**): yield 52%; mp = 184–187 °C; ¹H NMR (CDCl₃) δ 9.93 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 9.2 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2H), 6.99 (d, *J* = 8 Hz, 2H), 6.81 (d, *J* = 9.2 Hz, 2H), 3.78 (s, 3H), 2.29 (s, 3H); ¹³C NMR (CDCl₃) δ 190.7, 162.5, 142.1, 139.7, 137.8, 137.6, 135.2, 131.6, 128.5, 125.9, 122.2, 117.5, 104.1, 55.6, 21.3; HRMS [M – OTs]^{•+} calcd for C₁₄H₁₂O₂I 338.9882, found 338.9878.

3-Formyl-6-methoxyphenyl(4'-methoxyphenyl)iodonium tosylate (**41**): yield 50%; mp = 185–187 °C; ¹H NMR (CDCl₃) δ 9.77 (s, 1H), 8.16 (d, *J* = 2 Hz, 1H), 7.99 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.91 (dd, *J* = 2, 6.8 Hz, 2H), 7.51 (d, *J* = 2 Hz, 2H), 7.10–7.03 (m, 3H), 6.87 (dd, *J* = 2, 6.8 Hz, 2H), 4.02 (s, 3H), 3.82 (s, 3H), 2.31 (s, 3H); ¹³C NMR (CDCl₃) δ 188.4, 162.7, 160.8, 142.4, 139.6, 137.8, 136.8, 135.3, 132.2, 128.5, 126.0, 117.7, 112.2, 106.6, 102,1, 57.6, 55.6, 21.3; HRMS [M – OTs]^{•+} calcd for C₁₅H₁₄O₃I 368.9988, found 368.9982.

[3-(Methylcarbamoyl)phenyl](4'-methoxyphenyl)iodonium tosylate (**42**): yield 65%; mp =172–173 °C; ¹H NMR (MeOD- d_4) δ 8.53 (t, *J* = 1.6 Hz, 1H), 8.24 (dq, *J* = 0.8, 8 Hz, 1H), 8.10 (dd, *J* = 2, 7.6 Hz, 2H), 8.04 (dq, *J* = 1.2, 8 Hz, 1H), 7.68 (dd, *J* = 1.6, 8 Hz, 2H), 7.59 (t, *J* = 8 Hz, 1H), 7.21 (d, *J* = 8 Hz, 2H), 7.06 (dd, *J* = 3.2, 10.4 Hz, 2H), 3.84 (s, 3H), 2.91 (s, 3H), 2.36 (s, 3H); ¹³C NMR (MeOD- d_4) δ 167.9, 164.8, 143.7, 141.8, 139.2, 138.9, 138.6, 135.1, 133.2, 131.7, 130.0, 127.1, 119.1, 116.8, 104.7, 56.5, 27.2, 21.5; HRMS [M – OTs]^{•+} calcd for C₁₅H₁₅NO₂I 368.0148, found 368.0150.

3-Formylphenyl(2'-thienyl)iodonium tosylate (**43**): yield 48%; mp = 153–156 °C; ¹H NMR (CDCl₃) δ 9.82 (s, 1H), 8.40 (t, *J* = 1.6 Hz, 1H), 8.25 (dq, *J* = 1.2, 8 Hz, 1H), 7.94 (dt, *J* = 1.2, 7.6, 1H), 7.86 (dd, *J* = 1.2, 4 Hz, 1H), 7.58 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.49 (t, *J* = 4.8 Hz, 1H), 7.43 (d, *J* = 8 Hz, 2H), 7.04–7.02 (m, 3H), 2.32 (s, 3H); ¹³C NMR (CDCl₃) δ 189.5, 141.1, 140.2, 139.4, 138.6, 136.5, 135.3, 132.0, 131.6, 131.5, 129.8, 128.7, 125.9, 119.5, 21.3; HRMS [M – OTs]^{•+} calcd for C₁₁H₈OSI 314.9341, found 314.9340.

3-Formyl-6-methoxyphenyl(2'-thienyl)iodonium tosylate (44): yield 48%; mp = 178-179 °C; ¹H NMR (CDCl₃) δ 9.73 (s, 1H),

7.97 (dd, J = 2, 8.4 Hz, 1H), 7.76 (dd, J = 1.2, 4 Hz, 1H), 7.51 (dd, J = 1.2, 5.2 Hz, 1H), 7.41 (dd, J = 1.6, 8.4 Hz, 2H), 7.06–7.01 (m, 3H), 6.97 (dd, J = 3.6, 5.2 Hz, 1H), 4.02 (s, 3H), 2.31 (s, 3H); ¹³C NMR $(CDCl_3)$ δ 188.4, 160.6, 142.1, 140.4, 139.7, 138.9, 135.5, 135.0, 131.8, 129.2, 128.5, 125.9, 112.2, 110.2, 98.5, 57.4, 21.3; HRMS [M -OTs]^{•+} calcd for C₁₂H₁₀O₂SI 344.9446, found 344.9441.

ASSOCIATED CONTENT

S Supporting Information

¹H NMR and ¹³C NMR spectra of synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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