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Synthesis of Diaryliodonium Salts with a Sulfamate Counter Anion Mediated by Hypervalent Iodine(III) Reagent (Phenyliodonio)sulfamate

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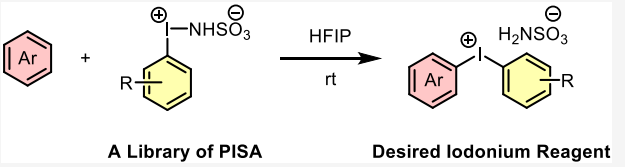
ABSTRACT: Diaryliodonium salts are an important class of hypervalent iodine reagents, widely used as aryl transfer reagents, benzyne precursors, and halogen bond donors in organic synthesis. They also function as photoacid generators and show antibacterial activity. Herein, we report a highly atom-economical strategy for the efficient synthesis of both symmetric and unsymmetric diaryliodonium salts at room temperature, using the readily available (phenyliodonio)sulfamate as a reagent and hexafluoroisopropanol as the solvent. This method demonstrates good functional group compatibility and is scalable to the gram scale. Furthermore, anion exchange enabled the synthesis of commercially available photoacid generators, highlighting the potential of this approach as a viable route for producing photoacid generators. Moreover, sulfamate-containing diaryliodonium salts can react with phenols, amines, and chloride, enabling direct access to the corresponding arylated products.



INTRODUCTION

$[Ar^1–I–Ar^2]^+X^-$, commonly known as diaryliodonium salts due to the presence of two aryl ligands in their structure, represent a prominent class of hypervalent iodine(III) reagents. The synthesis of these reagents was first reported by Meyer and Hartmann as early as 1894.[1] Subsequent in-depth investigations into their properties have uncovered their remarkable versatility in modern organic synthesis, where they act as effective electrophilic arylating agents,[2] benzyne precursors,[3] and halogen bond donors capable of catalyzing several named reactions.[4] Furthermore, their applications extend well beyond traditional synthetic uses into functional materials, such as photoacid generators in 3D printing technology for driving photopolymerization processes.[5] In addition, their antibacterial activity has also been documented by research groups including those led by Goldstein and Han (Figure 1).[6] Given their broad and notable application value, efficient synthetic strategies toward diaryliodonium salts have attracted sustained attention in recent years.

Synthetic routes to diaryliodonium salts primarily rely on either the direct reaction of arenes with hypervalent iodine(III) reagents or the *in situ* oxidation of aryl iodides in the presence of arenes. Among these strategies, the λ^3-iodanation of arene substrates by using hypervalent iodine(III) reagents represents an efficient method for preparing diaryliodonium salts, demonstrating broad applicability for both symmetric and unsymmetric structures (Figure 2). As early as 1964, Beringer et al. pioneered the synthesis of unsymmetric diaryliodonium salts containing *ortho*-carboxyl groups via the coupling of 2-carboxyiodosobenzene with arenes.[7] Then, Widdowson et al. developed various methods for synthesizing unsymmetric diaryliodonium salts, including reactions of $PhI(OAc)_2$ with arenes, coupling of Koser's reagent with arylstannanes, and the combination of $PhI(OAc)_2$ with arylboronic acids.[8] In 2018, Zhdankin et al. reported a direct method for synthesizing *para*-hydroxy-substituted diaryliodonium salts through the reaction of Koser's reagent with triisopropylsiloxybenzene in trifluoroethanol.[9] In 2023, Olofsson et al. further refined existing methods: by using Koser's reagents or $PhI(OAc)_2$ bearing electron-deficient aryl groups to react with electron-rich arenes under acid-free conditions, they achieved high yields of unsymmetric diaryliodonium salts having electron-deficient aryl groups.[10]

(Phenyliodonio)sulfamate (**PISA**) is a two-coordinate hypervalent iodine reagent bearing sulfamic acid as its ligand. Its core structure features a characteristic I−N coordinate

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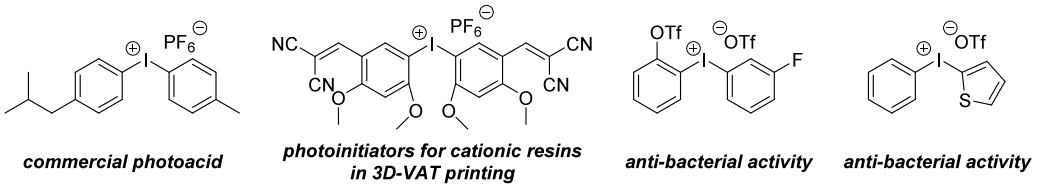


Figure 1. Multifaceted utility of diaryliodonium salts.

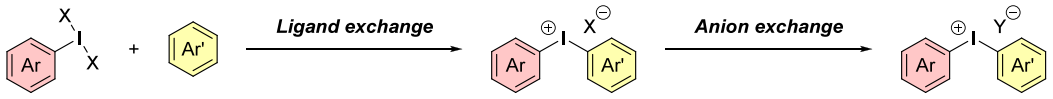


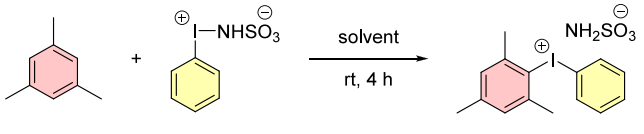
Figure 2. Synthetic routes to diaryliodonium salts via λ^3-iodanation of arenes using hypervalent iodine(III) reagents.

bond, in which the iodine(III) center bears a formal positive charge, while the oxygen atom of the sulfamate ligand carries a negative charge—this results in overall electrical neutrality, eliminating the need for an additional counterion. **PISA** possesses an exposed, highly electrophilic iodine(III) center, offering a distinct advantage over other iodane reagents such as PhIO, $PhI(OAc)_2$, and Koser's reagent. Specifically, **PISA** enables direct attack by nucleophilic substrates and eliminates the requirement for activation via an external Lewis acid, thereby facilitating the formation of a simplified reaction system.[11] Herein, we report a novel method for the synthesis of diaryliodonium salts through the direct $C(sp^2)$–H λ^3-iodination of arenes using **PISA.**

RESULTS AND DISCUSSION

Our preliminary attempt to use trifluoroethanol (TFE) as the solvent for the reaction of **PISA** (**2a**) with 1.5 equiv of mesitylene (**1g**) afforded diaryliodonium salt **3ga** in 37% yield (Table 1, entry 1). This result prompted further solvent screening: switching to hexafluoroisopropanol (HFIP) significantly improved the yield of **3ga** to 91% (entry 2). We next investigated the effect of the loading of reactant **1g** in HFIP. When 1.2 or 2.0 equiv of **1g** were employed, the yield of **3ga** decreased slightly to 85% and 87%, respectively (entries 3 and 4). No target product **3ga** was detected when the reaction was conducted in either isopropanol (*i*-PrOH, entry 5) or hexafluoroisopropyl methyl ether (HFMOP), indicating that the concurrent presence of the hydroxyl group and multiple fluorine atoms in the solvent is critical for the reaction to proceed successfully.[12] Ultimately, we established the optimized reaction conditions for the synthesis of **3ga**: HFIP as the solvent (at a concentration of 0.1 M relative to **PISA**), 1.5 equiv of **1g**, and a reaction time of 4 h at room temperature.

Table 1. Optimization of Reaction Conditions.[a]



entry	**1g** (equiv)	**2a** (equiv)	solvent	yield (%)[b]
1	1.5	1.0	TFE	37
2	1.5	1.0	HFIP	91
3	1.2	1.0	HFIP	85
4	2.0	1.0	HFIP	87
5	1.5	1.0	*i*-PrOH	n.d.
6	1.5	1.0	HFMOP	n.d.

[a]Reaction conditions: substrate **1g**, and **PISA 2a** (0.1 mmol scale, 1.0 equiv) were stirred in 2 mL of solvent for 4 h at room temperature. [b]Yields were determined by ^{1}H NMR spectroscopy with nitrobenzene as an internal standard. Yields were based on **PISA** (0.1 mmol scale, 1.0 equiv). n.d. = not detected. HFMOP is hexafluoroisopropyl methyl ether.

With the optimal reaction conditions established, we subsequently tested the generality and functional group tolerance of the reaction by examining a range of arenes and heteroarenes with **PISA** and its derivatives (Scheme 1). First, **PISA** was reacted with monosubstituted arenes bearing *tert*-butyl, methoxy, and iodo substituents. All these monosubstituted arenes exhibited good tolerance under the optimized reaction conditions, affording the corresponding target products (**3aa**–**ca**) in 63–96% yields within 10 min. Disubstituted electron-rich arenes also reacted smoothly with **PISA**, yielding the corresponding products (**3da**–**3fa**) in a range of 56–84%. Subsequently, we explored the synthesis of diaryliodonium salts derived from trisubstituted arenes with significant steric hindrance. Both trimethylbenzene and trimethoxybenzene were found to readily undergo reaction to form the corresponding diaryliodonium salts (**3ga** and **3ha**) in 83% and 91% yields, respectively. Notably, 1,3,5-triisopropylbenzene which possesses extremely high steric hindrance could also react with **PISA** to afford the target product (**3ia**) in 59% yield. Furthermore, we further investigated the compatibility of heteroarenes with the reaction system. Both easily oxidizable thiophene and basic pyridine derivatives afforded the corresponding diaryliodonium salts (**3ja** and **3ka**) in 96% and 92% yields, respectively. In addition, a series of **PISA** derivatives containing electron-withdrawing groups were synthesized. It was observed that when 4-F-**PISA** (**2b**) and 4-Cl-**PISA** (**2c**) reacted with electron-rich arenes, yielding the desired products (**3bb**–**3lc**) in 63–69% yields. The reaction of 3,5-bis(trifluoromethyl)-**PISA** (**2d**) with the sterically hindered trimethylbenzene and trimethoxybenzene proceeded smoothly, affording the desired products **3gd** and **3hd.**We also investigated the reaction of 4-NO_2-**PISA** (**2e**) with arenes and heteroarenes. When bromobenzene was reacted with **2e** in trifluoroacetic acid, the unsymmetric diaryliodonium salt **3me**—containing two distinct electron-deficient aryl groups—was readily obtained in 41% yield. In the ^{13}C NMR spectrum of **3me**, no relevant peaks corresponding to the trifluoroacetate ion were observed, indicating that even with trifluoroacetic acid as the reaction solvent, the anion remained as the sulfamate. Gratifyingly, electron-rich arenes

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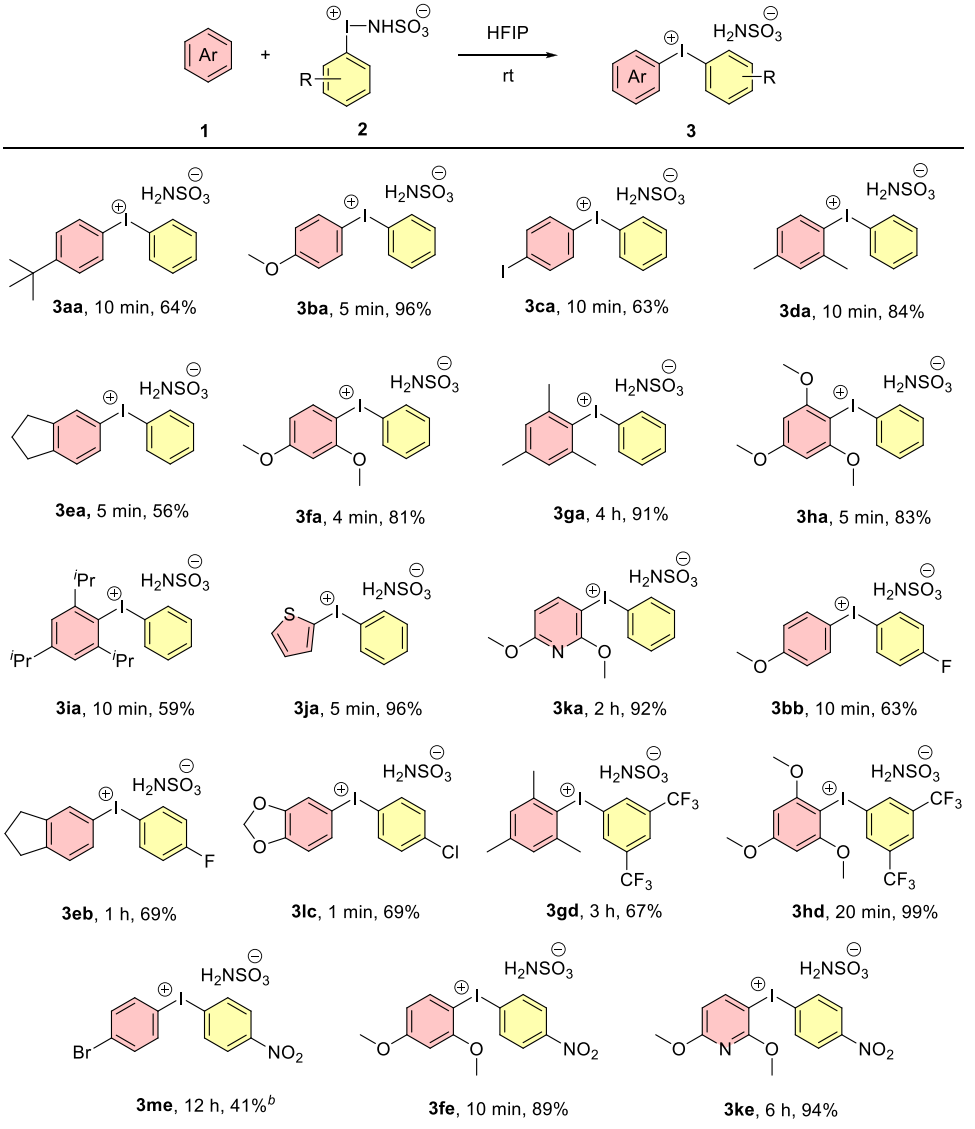
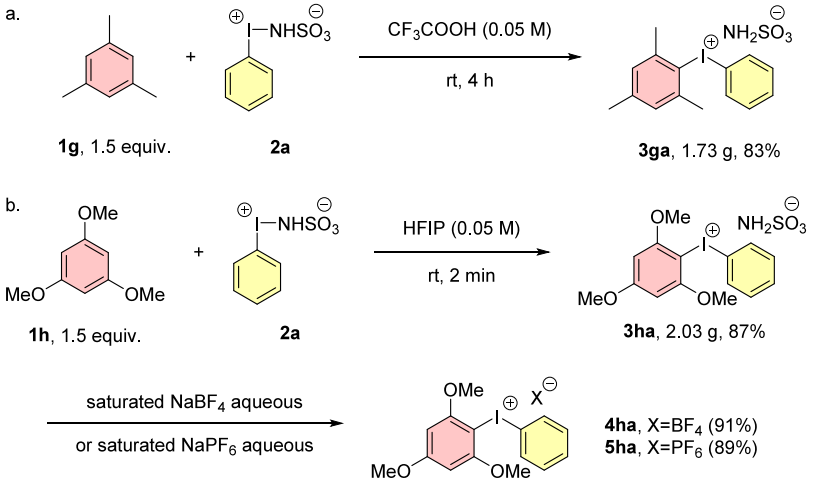
Scheme 1. Substrate Scope of Diaryliodonium Salts with Sulfamate Counterions[a]



[a]Reaction conditions: **PISA** (0.3 mmol scale, 1.0 equiv), and substrate (1.5 equiv) were stirred in 6 mL (0.05 M) HFIP at room temperature under air. [b]CF_3COOH as solvent.

Scheme 2. Gram-Scale and Ion Exchange Reactions



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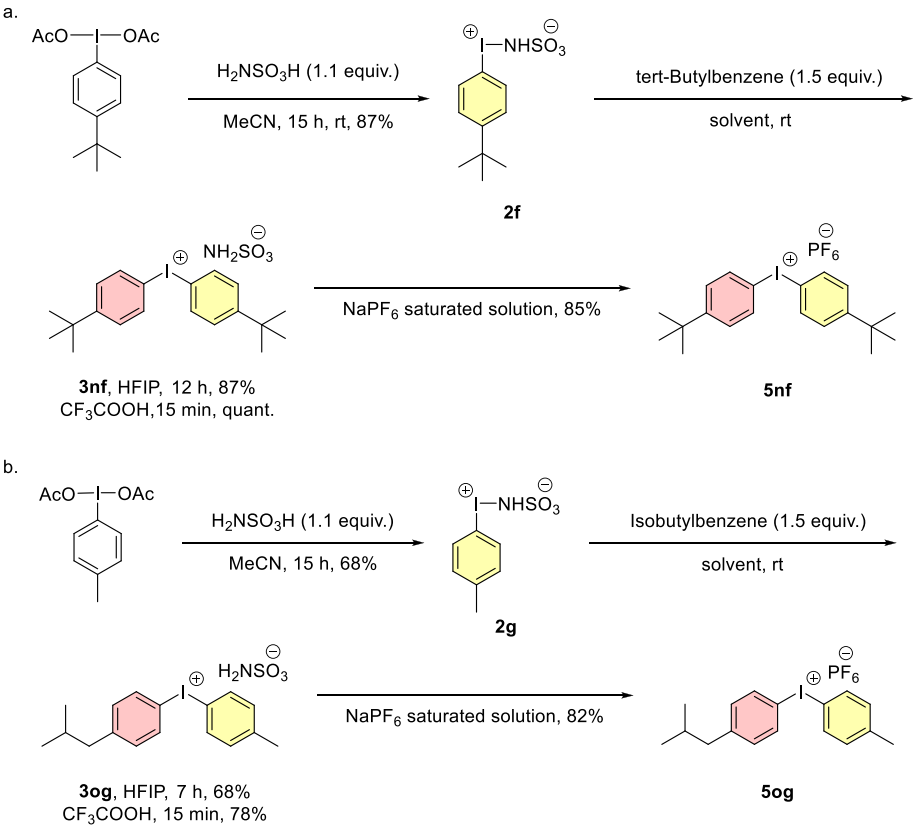
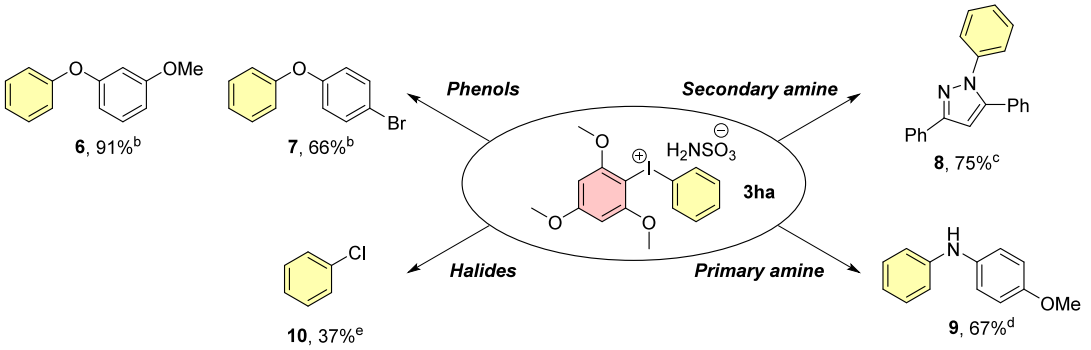
Scheme 3. Access to Two Commercial Photoacids through a PISA-Mediated Diaryliodonium Salt Synthesis



Scheme 4. Arylation Reactions of Various Nucleophiles with 3ha[a]



[a]Isolated yields are reported. [b]Phenols (0.1 mmol), **3ha** (0.12 mmol), Na_2CO_3 (0.15 mmol), CH_2Cl_2 (1 mL), and H_2O (1 mL), 40 °C. [c]Pyrazole (0.1 mmol), **3ha** (0.11 mmol), $NH_3{\cdot}H_2O$ (25 wt %, 1 mL), DCE (1 mL), rt. [d]*p*-Anisidine (0.1 mmol), **3ha** (0.1 mmol), DMF (2 mL), 130 °C. [e]**3ha** (0.2 mmol), CuCl (0.3 mmol), DMF, 120 °C, yield determined by GC.

and pyridine derivatives also reacted with **2e** to afford the target products (**3fe** and **3ke**) in approximately 90% yields.

The practical utility was evaluated through gram-scale reactions (Scheme 2). Scaled-up synthesis via coupling of **PISA** with **1g** and **1h** (5 mmol scale) provided the corresponding products **3ga** and **3ha** in 83% and 87% yield, respectively. Notably, the yields were nearly identical to those achieved under standard small-scale conditions (Scheme 1). Additionally, ion exchange reactions were performed on **3ha** using saturated aqueous solutions of sodium tetrafluoroborate and sodium hexafluorophosphate, respectively. This afforded **4ha** and **5ha** in nearly 90% yield for both the tetrafluoroborate and hexafluorophosphate exchanges.

Furthermore, this methodology was successfully extended to the synthesis of two commercially available photoacids: bis(4-*tert*-butylphenyl)iodonium hexafluorophosphate (**5nf**) and 4-isobutylphenyl-4′-methylphenyliodonium hexafluorophosphate (**5og**), as illustrated in Scheme 3. As a representative example, the photoacid precursor **3nf**, featuring a sulfamate counterion, was isolated in 87% yield under standard reaction conditions. Notably, switching to trifluoroacetic acid as the solvent enabled quantitative formation of **3nf**. Subsequent anion metathesis of precursor **3nf** with a saturated solution of sodium hexafluorophosphate afforded the target photoacid **5nf** in 85% yield. Additionally, using an analogous three-step sequence, we efficiently synthesized 4-isobutylphenyl-4′-methylphenyliodonium hexafluorophosphate (**5og**) in an overall yield of 44%.

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Finally, we explored the reactivity of unsymmetrical diaryliodonium sulfamates as aryl-transfer reagents. Previous studies by Dohi, Olofsson, Novák, and Li have independently reported the use of unsymmetrical diaryliodonium salts in highly polar solvents such as DMF or water for arylation reactions, achieving good to excellent yields.[13] Therefore, we have conducted investigation into the aromatic nucleophilic substitution reactions of unsymmetrical diaryliodonium sulfamates with various nucleophiles containing oxygen, nitrogen, and chlorine atoms (Scheme 4). Using **3ha** as a substrate in a biphasic solvent system of water and dichloromethane with Na_2CO_3 as base, two diaryl ethers **6** and **7** were successfully synthesized from 3-methoxyphenol and 4-bromophenol, yielding the corresponding products in 91% and 66% yield, respectively. Under similar conditions, the *N*-nucleophile 3,5-diphenylpyrazole afforded 1,3,5-triphenyl-*1H*-pyrazole (**8**) in 75% yield. Additionally, when *p*-anisidine was employed as the nucleophile in DMF, the *N*-arylated product **9** was directly obtained from **3ha** in 67% yield. Furthermore, the use of copper(I) chloride as chlorine source provided the corresponding chlorobenzene (**10**) in a yield of 37%. It is noteworthy that in all cases the phenyl group was selectively transferred, while the trimethoxyphenyl moiety served as a dummy ligand and was not incorporated into the final products.

CONCLUSIONS

In summary, we have developed and reported a method for the direct λ^3-iodination of arene C(sp^2)−H bonds using **PISA** as the reagent and HFIP as the solvent, enabling the synthesis of diaryliodonium salts. Compared with traditional synthetic approaches employing other hypervalent iodine reagents, this **PISA**-based strategy produces minimal waste and shows exceptional atom economy—all atoms derived from the starting materials are fully incorporated into the target products. This method is applicable to the synthesis of both symmetric and unsymmetric diaryliodonium salts, thereby demonstrating high synthetic efficiency and excellent broad functional group tolerance. Moreover, it is amenable to gram-scale scaling; via straightforward anion exchange, commercially available photoacids can be readily accessed. It is worth noting that diaryliodonium sulfamates can serve as arylating agents to react with oxygen-, nitrogen-, and halogen-containing nucleophiles, yielding the corresponding arylated products.

EXPERIMENTAL SECTION

General Information. Some chemicals were used as received from commercial suppliers without further purification. Other chemicals were prepared by the reported procedures. All solvents before use were dried and purified according to the standard procedure. NMR spectra were recorded for ^{1}H NMR (400 MHz), ^{1}H NMR (600 MHz) and ^{13}C NMR (100 MHz), ^{13}C NMR (150 MHz) using TMS as an internal standard and Bruker AV 400 and AV 600 as instruments. The following abbreviations were used to describe peak patterns where appropriate: singlet (s), doublet (d), triplet (t), multiplet (m). High-resolution mass spectroscopy (HRMS) was recorded on a high-resolution ESI−FTICR mass spectrometer (Varian 7.0 T). Melting points were determined on a RY-1 electrothermal micromelting point apparatus.

General Procedure for the Synthesis of PISA and Its Analogues (2). To a solution of phenyl-λ^3-iodanediyl diacetate (5 mmol) in anhydrous CH_3CN (0.5 M) was added NH_2SO_3H (5.5 mmol, 1.1 equiv) at room temperature and the reaction mixture was stirred for 12 h. $PhI^+NHSO_3^-$ (**2a**) was obtained after filtration and washed with Et_2O (20 mL). Other analogues were conducted with the corresponding analogues of $PhI(OAc)_2$ according to the standard procedure.

General Procedure for the Synthesis of Diaryliodonium Salts (3). To a dry round-bottom flask containing **2** (0.3 mmol) in HFIP (6 mL) was added (hetero)arenes **1** (0.45 mmol, 1.5 equiv). The mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the organic phase was concentrated *in vacuo*. Then Et_2O was added to the residue, the product was precipitated with vigorously stirring.

The gram scale reactions for the synthesis **3ga** and **3ha** were conducted according to the standard procedure.

General Procedure for Ion Exchange (4 and 5). Diaryliodonium salts **3** was dissolved in 100 mL of dichloromethane and washed three times with saturated sodium tetrafluoroborate or sodium hexafluorophosphate aqueous solution in a funnel, the organic phase was dried with Mg_2SO_4 and concentrated *in vacuo* to obtain the pure products **4** and **5** respectively.

General Procedure for the Synthesis of Diaryl Ether, 6 and 7. Phenol (0.10 mmol) and base (0.15 mmol) were dissolved in the mixed solvent of dichloromethane (1 mL) and water (1 mL) in a round-bottom flask. **3ha** (0.12 mmol, 56.0 mg) was added to the reaction mixture, and then stirred at 40 °C for 17 h. The reaction was quenched with sat. NH_4Cl aq., and the mixture was transferred to a separatory funnel. The organic layer was separated, and the residual aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic fractions were dried over Na_2SO_4, and all volatiles were removed under vacuum. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/petroleum ether = 1:50) to afford **6** and **7**.

General Procedure for the Synthesis of 1,3,5-Triphenyl-1*H*-pyrazole (8). 3,5-diphenyl-*1H*-pyrazole (0.10 mmol) was dissolved in mixed solvent of 1,2-dichloroethane (2 mL) and aqueous ammonia (25 w/w%, 2 mL) in a round-bottom flask. **3ha** (0.12 mmol, 56.0 mg) was added to the reaction mixture, and then stirred at room temperature for 17 h. The reaction was quenched with HCl aq. (*1M*), and the mixture was transferred to a separatory funnel. The organic layer was separated, and the residual aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic fractions were dried over Na_2SO_4, and all volatiles were removed under vacuum. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/petroleum ether = 1:50) to afford 1,3,5-triphenyl-*1H*-pyrazole.

General Procedure for the Synthesis of 4-Methoxy-*N*-phenylaniline (9). *p*-Anisidine (0.10 mmol) were dissolved in DMF (2.0 mL) in a round-bottom flask. **3ha** (0.10 mmol, 46.7 mg) was added to the reaction mixture, and then stirred at 130 °C for 24 h. The reaction was quenched with dichloromethane (20 mL) and sat. LiCl aq., and the mixture was transferred to a separatory funnel. The organic layer was separated, and the residual aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic fractions were dried over Na_2SO_4, and all volatiles were removed under vacuum. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/petroleum ether = 1:10) to afford 4-methoxy-*N*-phenylaniline.

General Procedure for the Synthesis of Chlorobenzene (10). **3ha** (0.20 mmol, 93.4 mg) were dissolved in DMF (0.4 mL) in a round-bottom flask. CuCl (0.30 mmol, 29.7 mg) was added to the reaction mixture, and then stirred at 120 °C for 24 h. The reaction was quenched with dichloromethane (20 mL) and sat. LiCl aq., and the mixture was transferred to a separatory funnel. The organic layer was separated, and the residual aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over Na_2SO_4, and nitrobenzene (0.2 mmol, 20.8 μL) was added as an internal standard, with the yield determined by GC.

Characterization Data of Products. *(Phenyliodonio)sulfamate (**2a**).* White solid; m.p.:117 °C; yield 1.36 g (91%); ^{1}H NMR (400 MHz, D_2O) δ 8.14 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, D_2O) δ 134.7, 133.4,

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131.7, 123.1. HRMS (ESI): m/z calcd for $C_6H_5INO_3S$ $[M-H]^-$: 297.9040, found: 297.9042.

*((4-Fluorophenyl)iodonio)sulfamate (**2b**).* White solid; decomp. 123 °C; yield 1.11g (70%); ^1H NMR (400 MHz, D_2O) δ 8.30−8.21 (m, 2H), 7.32 (t, J = 8.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, D_2O) δ 165.1 (d, J = 254.5 Hz), 138.1 (d, J = 9.6 Hz), 119.2 (d, J = 23.3 Hz), 110.0; ^{19}F NMR (376 MHz, D_2O) δ −103.54 − −103.90 (m). HRMS (ESI): m/z calcd for $C_6H_4FINO_3S$ $[M-H]^-$: 315.8946, found: 315.8944.

*((4-Chlorophenyl)iodonio)sulfamate (**2c**).* Yellow solid; decomp. 125 °C; yield 1.43g (86%); ^1H NMR (400 MHz, $CDCl_3/CF_3CO_2D$, 1:20) δ 8.51 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CF_3CO_2D$, 1:20) δ 136.6, 136.1, 127.3, 117.0. HRMS (ESI): m/z calcd for $C_6H_4ClINO_3S$ $[M-H]^-$: 331.8651, found: 331.8644.

*((3,5-Bis(trifluoromethyl)phenyl)iodonio)sulfamate (**2d**).* White solid; m.p.:135−136 °C; yield 1.87g (86%); ^1H NMR (400 MHz, $CDCl_3/CF_3CO_2D$, 1:20) δ 8.22 (s, 2H), 7.75 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CF_3CO_2D$, 1:20) δ 136.5 (q, J = 35.4 Hz), 135.9, 128.4 (q, J = 3.3 Hz), 123.8, 121.1; ^{19}F NMR (376 MHz, $CDCl_3/CF_3CO_2D$, 1:20) δ: −64.1. HRMS (ESI): m/z calcd for $C_8H_3F_6INO_3S$ $[M-H]^-$: 433.8788, found: 433.8786.

*((4-Nitrophenyl)iodonio)sulfamate (**2e, NISA**).* Pale yellow solid; m.p.:166−167 °C; yield 1.39g (81%); ^1H NMR (400 MHz, $CDCl_3/CF_3CO_2D$, 1:20) δ 7.94 (d, J = 9.2 Hz, 2H), 7.91 (d, J = 9.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CF_3CO_2D$, 1:20) δ 151.2, 137.3, 128.1, 127.5. HRMS (ESI): m/z calcd for $C_6H_4IN_2O_5S$ $[M-H]^-$: 342.8891, found: 342.8895.

*((4-(tert-Butyl)phenyl)iodonio)sulfamate (**2f**).* Pale yellow solid; m.p.:110−112 °C; yield 1.54g (87%); ^1H NMR (600 MHz, D_2O) δ 8.19 (d, J = 4.2 Hz, 2H), 7.69 (d, J = 12.4 Hz, 2H), 1.32 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, D_2O) δ 158.2, 135.0, 129.1, 119.4, 34.8, 30.1. HRMS (ESI): m/z calcd for $C_{10}H_{13}INO_3S$ $[M-H]^-$: 353.9666, found: 353.9674.

*(p-Tolyliodonio)sulfamate (**2g**).* Pale yellow solid; m.p.:107−108 °C; yield 1.42g (91%); ^1H NMR (400 MHz, D_2O) δ 8.13 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 2.42 (d, J = 8.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, D_2O) δ 145.4, 135.1, 132.4, 127.6, 20.8. HRMS (ESI): m/z calcd for $C_7H_7INO_3S$ $[M-H]^-$: 311.9197, found: 311.9195.

*(4-(tert-Butyl)phenyl)(phenyl)iodonium Sulfamate (**3aa**).* Gray powder; m.p.:140−142 °C; yield 83.1 mg (64%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.7 Hz, 4H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.8, 134.8, 134.7, 131.7, 131.7, 129.1, 116.4, 112.6, 35.1, 31.0; HRMS (ESI): calcd for $C_{16}H_{18}I^+$ $[M]^+$: 337.0448, found: 337.0451.

*(4-Methoxyphenyl)(phenyl)iodonium Sulfamate (**3ba**).* Gray powder; m.p.:109−111 °C; yield 117.2 mg (96%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.20−8.05 (m, 4H), 7.67 (t, J = 7.5 Hz, 1H), 7.51 (dd, J = 10.9, 4.8 Hz, 2H), 7.06 (d, J = 9.1 Hz, 2H), 3.85 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 164.5, 138.6, 136.0, 133.35, 133.0, 118.8, 117.0, 105.0, 56.4; HRMS (ESI): calcd for $C_{13}H_{12}IO^+$ $[M]^+$: 310.9927, found: 310.9931.

*(4-Iodophenyl)(phenyl)iodonium Sulfamate (**3ca**).* Brown powder; m.p.:160−166 °C; yield 95 mg (63%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.17 (d, J = 7.9 Hz, 2H), 8.02−7.81 (m, 4H), 7.70 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 142.3, 137.8, 136.5, 133.7, 133.2, 116.6, 115.7, 100.5; HRMS (ESI): calcd for $C_{12}H_9I_2^+$ $[M]^+$: 406.8788, found: 406.8792.

*(2,4-Dimethylphenyl)(phenyl)iodonium Sulfamate (**3da**).* Gray powder; m.p.:70−75 °C; yield 102.1 mg (84%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.15 (d, J = 7.4 Hz, 1H), 8.07 (s, 2H), 7.66 (s, 1H), 7.51 (s, 2H), 7.40 (s, 1H), 7.16 (s, 1H), 2.61 (s, 3H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 146.0, 142.4, 138.6, 135.9, 133.7, 133.4, 133.2, 131.5, 117.2, 115.3, 25.5, 21.2. HRMS (ESI): calcd for $C_{14}H_{14}I^+$ $[M]^+$: 309.0135, found: 309.0138.

*(2,3-Dihydro-1H-inden-5-yl)(phenyl)iodonium Sulfamate (**3ea**).* Gray powder; m.p.:179−183 °C; yield 70 mg (56%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.13 (d, J = 7.7 Hz, 2H), 8.02 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.37 (d, J = 8.0 Hz, 1H), 2.97 (td, J = 7.4, 4.2 Hz, 4H), 2.10 (p, J = 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 151.3, 150.5, 136.2, 134.5, 133.5, 133.1, 132.4, 129.0, 116.2, 113.1, 33.9, 33.7, 26.4. HRMS (ESI): calcd for $C_{15}H_{14}I^+$ $[M]^+$: 321.0135, found: 321.0141.

*(2,4-Dimethoxyphenyl)(phenyl)iodonium Sulfamate (**3fa**).* Gray solid; m.p.:90−92 °C; yield 106.2 mg (81%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 9.3 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.8 Hz, 2H), 6.49 (dd, J = 6.6, 2.4 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.6, 158.8, 137.5, 134.2, 131.2, 131.0, 117.8, 107.9, 99.6, 98.0, 56.5, 55.8. HRMS (ESI): calcd for $C_{14}H_{14}IO_2^+$ $[M]^+$: 341.0033, found: 341.0038.

*Mesityl(phenyl)iodonium Sulfamate (**3ga**).* Gray powder; m.p.: 130−132 °C; yield 114.4 mg (91%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.04 (s, 2H), 2.62 (s, 6H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 142.1, 132.7, 131.7, 130.9, 130.0, 123.14, 115.3, 27.1, 21.1. HRMS (ESI): calcd for $C_{15}H_{16}I^+$ $[M]^+$: 323.0291, found: 323.0295.

*Phenyl(2,4,6-trimethoxyphenyl)iodonium Sulfamate (**3ha**).* Gray powder; m.p.:128−130 °C; yield 116.3 mg (83%); ^1H NMR (400 MHz, MeOH-d_4) δ 7.95 (d, J = 7.9 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 6.42 (s, 2H), 3.98 (s, 6H), 3.90 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 168.8, 161.5, 135.8, 133.1, 132.78, 115.9, 92.9, 86.1, 57.8, 56.7. HRMS (ESI): calcd for $C_{15}H_{16}IO_3^+$ $[M]^+$: 371.0139, found: 371.0147.

*Phenyl(2,4,6-triisopropylphenyl)iodonium Sulfamate (**3ia**).* Viscous solid; m.p.: Viscous; yield 89 mg (59%;) ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.9 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.14 (s, 2H), 3.34 (dt, J = 13.3, 6.6 Hz, 2H), 2.95 (dt, J = 13.8, 6.9 Hz, 1H), 1.24 (dd, J = 25.4, 6.8 Hz, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.7, 152.2, 132.5, 131.7, 131.0, 124.7, 121.1, 113.8, 39.1, 34.04, 24.2, 23.6. HRMS (ESI): calcd for $C_{21}H_{28}I^+$ $[M]^+$: 407.1230, found: 407.1237.

*Phenyl(thiophen-2-yl)iodonium Sulfamate (**3ja**).* Gray powder; m.p.:73−74 °C; yield 110.3 mg (96%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.18 (dd, J = 8.4, 1.0 Hz, 2H), 8.02 (dd, J = 3.8, 1.2 Hz, 1H), 7.89 (dd, J = 5.4, 1.2 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.17 (dd, J = 5.4, 3.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4)) δ 142.2, 138.6, 135.8, 133.7, 133.1, 130.9, 119.1, 99.1. HRMS (ESI): calcd for $C_{10}H_8IS^+$ $[M]^+$: 286.9386, found: 286.9392.

*(2,6-Dimethoxypyridin-3-yl)(phenyl)iodonium Sulfamate (**3ka**).* Gray solid; m.p.: 144−146 °C; yield 120.9 mg (92%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.40 (d, J = 8.6 Hz, 1H), 8.09 (dd, J = 8.3, 0.9 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.51 (dd, J = 10.8, 4.8 Hz, 2H), 6.46 (d, J = 8.6 Hz, 1H), 4.06 (s, 3H), 3.97 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 168.2, 162.1, 149.8, 136.2, 133.4, 133.0, 116.2, 106.8, 87.6, 55.9, 55.0. HRMS (ESI): calcd for $C_{13}H_{13}INO_2^+$ $[M]^+$: 341.9985, found: 341.9989.

*(4-Fluorophenyl)(4-methoxyphenyl)iodonium Sulfamate (**3bb**).* Viscous solid; yield 80.3 mg (63%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.19 (dd, J = 8.0, 4.9 Hz, 2H), 8.11 (d, J = 8.6 Hz, 2H), 7.28 (t, J = 8.5 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H), 3.85 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 167.5, 165.0, 164.5, 139.0, 138.9, 138.6, 120.5, 120.3, 118.9, 110.4, 105.0, 56.4. ^{19}F NMR (376 MHz, MeOH-d_4) δ −103.86. HRMS (ESI): calcd for $C_{13}H_{11}FIO^+$ $[M]^+$: 328.9833, found: 328.9837.

*(2,3-Dihydro-1H-inden-5-yl)(4-fluorophenyl)iodonium Sulfamate (**3eb**).* Gray powder; m.p.:140−144 °C; yield 90 mg (69%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.26−8.16 (m, 2H), 8.04 (s, 1H), 7.97−7.88 (m, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.28 (t, J = 8.7 Hz, 2H), 2.97 (t, J = 7.4 Hz, 4H), 2.10 (p, J = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 167.6, 165.1, 151.3, 150.5, 139.2, 139.1, 134.4, 132.3, 129.0, 120.6, 120.3, 113.4, 110.0, 33.9, 33.7, 26.4; ^{19}F NMR (376 MHz, MeOH-d_4) δ −107.66. HRMS (ESI): calcd for $C_{15}H_{13}FI^+$ $[M]^+$: 339.0040 found: 339.0043.

*Benzo[d][1,3]dioxol-5-yl(4-chlorophenyl)iodonium Sulfamate (**3lc**).* Gray powder; m.p.:146−149 °C; yield 94.2 mg (69%); ^1H

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NMR (400 MHz, MeOH-d_4) δ 8.13 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.7 Hz, 1H), 6.10 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 153.3, 151.6, 140.2, 137.7, 133.2, 132.4, 116.3, 114.2, 112.5, 104.9, 104.4. HRMS (ESI): calcd for $C_{13}H_9ClIO_2^+$ $[M]^+$: 358.9330 found: 358.9335.

(3,5-Bis(trifluoromethyl)phenyl)(mesityl)iodonium Sulfamate (**3gd**). Gray powder; m.p.:134−135 °C; yield 114.6 mg (67%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.42 (s, 2H), 8.31 (s, 1H), 7.32 (s, 2H), 2.68 (s, 6H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, MeOH-d_4) δ 146.7, 143.9, 135.4 (q, J = 34.5 Hz), 135.2, 131.7, 127.1, 123.5 (q, J = 273.0 Hz), 122.7, 115.0, 27.1, 21.1. ^{19}F NMR (376 MHz, MeOH-d_4) δ −64.48. HRMS (ESI): calcd for $C_{17}H_{14}F_6I^+$ $[M]^+$: 459.0039 found: 459.0041.

(3,5-Bis(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)-iodonium Sulfamate (**3hd**). Gray powder; m.p.:150−152 °C; yield 179.1 mg (99%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.57 (s, 2H), 8.28 (s, 1H), 6.47 (s, 2H), 4.01 (s, 6H), 3.92 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, MeOH-d_4) δ 169.4, 161.4, 136.2, 134.9 (q, J = 34.4 Hz), 126.9, 123.6 (q, J = 272.9 Hz), 116.6, 93.2, 86.5, 57.9, 56.9. ^{19}F NMR (376 MHz, MeOH-d_4) δ −64.42. HRMS (ESI): calcd for $C_{17}H_{14}F_6IO_3^+$ $[M]^+$: 506.9886 found: 506.9889.

(4-Bromophenyl)(4-nitrophenyl)iodonium Sulfamate (**3md**). Gray powder; m.p.:163−165 °C; yield 61.5 mg (41%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.44 (d, J = 9.0 Hz, 2H), 8.31 (d, J = 9.0 Hz, 2H), 8.16 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, MeOH-d_4) δ 150.1, 137.1, 136.4, 135.1, 127.5, 126.1, 121.2, 113.8. HRMS (ESI): calcd for $C_{12}H_8BrINO_2^+$ $[M]^+$: 403.8778 found: 403.8779.

(2,4-Dimethoxyphenyl)(4-nitrophenyl)iodonium Sulfamate (**3fe**). Gray powder; m.p.:128−130 °C; yield 128.7 mg (89%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.28 (s, 4H), 8.14 (d, J = 9.0 Hz, 1H), 6.80 (s, 1H), 6.72 (d, J = 8.8 Hz, 1H), 3.97 (s, 3H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 167.7, 160.3, 151.4, 140.0, 137.1, 127.3, 121.8, 110.5, 100.9, 95.1, 57.7, 56.7. HRMS (ESI): calcd for $C_{14}H_{13}INO_4^+$ $[M]^+$: 385.9884 found: 385.9888.

(2,6-Dimethoxypyridin-3-yl)(4-nitrophenyl)iodonium Sulfamate (**3ke**). Yellow powder; m.p.:81−85 °C; yield 136.2 mg (94%); ^1H NMR (400 MHz, MeOH-d_4) δ 8.46 (d, J = 8.6 Hz, 2H), 8.44−8.29 (m, 4H), 4.06 (s, 3H), 3.98 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 168.5, 162.2, 151.4, 150.1, 137.4, 127.4, 121.8, 107.1, 87.8, 56.1, 55.1. HRMS (ESI): calcd for $C_{13}H_{12}IN_2O_4^+$ $[M]^+$: 386.9836 found: 386.9834.

Phenyl(2,4,6-trimethoxyphenyl)iodonium Tetrafluoroborate (**4ha**). Yellow powder; m.p.:110−113 °C; yield 416.8 mg (91%); ^1H NMR (400 MHz, MeOH-d_4) δ 7.95 (d, J = 7.9 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 6.42 (s, 2H), 3.98 (s, 6H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 168.9, 161.5, 135.8, 133.1, 132.8, 115.8, 92.9, 86.0, 57.8, 56.7. ^{11}B NMR (128 MHz, MeOH-d_4) δ −1.12. ^{19}F NMR (375 MHz, MeOH-d_4) δ −154.36 (d, J = 18.9 Hz). HRMS (ESI): calcd for $C_{15}H_{16}IO_3^+$ $[M]^+$: 371.0139 found: 371.0145.

Phenyl(2,4,6-trimethoxyphenyl)iodonium Hexafluorophosphate(V) (**5ha**). Pink powder; m.p.:108−110 °C; yield 459.2 mg (89%); ^1H NMR (400 MHz, MeOH-d_4) δ 7.95 (d, J = 8.0 Hz, 2H), 7.66−7.59 (m, 1H), 7.51−7.41 (m, 2H), 6.41 (s, 2H), 3.98 (d, J = 1.7 Hz, 6H), 3.89 (d, J = 1.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4) δ 168.9, 161.5, 135.8, 133.1, 132.8, 115.8, 92.9, 86.0, 57.8, 56.7. ^{31}P NMR (162 MHz, MeOH-d_4) δ −129.20 − −159.25 (m). ^{19}F NMR (376 MHz, MeOH-d_4) δ −73.67, −75.55. HRMS (ESI): calcd for $C_{15}H_{16}IO_3^+$ $[M]^+$: 371.0139 found: 371.0144; calcd for F_6P^-; $[M]^-$:144.9647 found: 144.9652.

Bis(4-(tert-butyl)phenyl)iodonium Sulfamate (**3nf**). Gray powder; m.p.:74−78 °C; yield 127.6 mg (87%, in HFIP), 146.7 mg (100%, in CF_3COOH); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 4H), 7.42 (d, J = 8.2 Hz, 4H), 1.28 (s, 18H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 156.3, 134.7, 129.4, 110.5, 77.3, 77.1, 76.9, 35.2, 31.0. HRMS (ESI): calcd for $C_{20}H_{26}I^+$ $[M]^+$: 393.1074 found: 393.1082.

Bis(4-(tert-butyl)phenyl)iodonium Hexafluorophosphate(V) (**5nf**). Gray powder; m.p.:144−147 °C; yield 137.2 mg (85%); ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 4H), 7.49 (d, J = 8.2 Hz, 4H), 1.29 (s, 18H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 157.4, 135.2, 130.2, 107.8, 35.3, 31.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ −130.11 − −157.81 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.89, −70.78. HRMS (ESI): calcd for $C_{20}H_{26}I^+$ $[M]^+$: 393.1074 found: 393.1077.

(4-Isobutylphenyl)(p-tolyl)iodonium Sulfamate (**3og**). Viscous solid; yield 91.2 mg (68%, in HFIP), 104.6 mg (78%, in CF_3COOH); ^1H NMR (600 MHz, MeOH-d_4) δ 8.03 (t, J = 7.9 Hz, 4H), 7.34 (dd, J = 15.1, 8.1 Hz, 4H), 2.54 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.91−1.81 (m, 1H), 0.88 (d, J = 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, MeOH-d_4) δ 147.1, 143.7, 135.0, 134.8, 132.5, 132.5, 111.3, 110.9, 30.0, 21.1, 20.0. HRMS (ESI): calcd for $C_{17}H_{20}I^+$ $[M]^+$: 351.0604 found: 351.0608.

(4-Isobutylphenyl)(p-tolyl)iodonium Hexafluorophosphate(V) (**5og**). Viscous solid; yield 112 mg (82%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.5 Hz, 4H), 7.25 (dd, J = 12.4, 8.4 Hz, 4H), 2.48 (d, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.83 (dt, J = 13.5, 6.8 Hz, 1H), 0.87 (d, J = 6.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.1, 144.5, 135.5, 135.2, 133.59, 133.5, 108.3, 108.1, 45.0, 30.1, 22.2, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ −120.57 − −163.62 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ −146.88. HRMS (ESI): calcd for $C_{17}H_{20}I^+$ $[M]^+$: 351.0604 found: 351.0609.

1-Methoxy-3-phenoxybenzene (**6**). Yield 18.2 mg (91%); ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 (t, J = 7.8 Hz, 2H), 7.22 (t, J = 8.1 Hz, 1H), 7.11 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 7.6 Hz, 1H), 6.59 (d, J = 7.6 Hz, 2H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 161.0, 158.5, 157.0, 130.2, 129.8, 123.4, 119.1, 111.0, 108. 9, 104.9, 55.4.

1-Bromo-4-phenoxybenzene (**7**). Yield 16.4 mg (66%); ^1H NMR (600 MHz, CDCl3) δ 7.43 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.13 (t, J = 7.3 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 156.7, 156.6, 132.7, 129.9, 123.7, 120.4, 119.0, 115.6.

1,3,5-Triphenyl-1H-pyrazole (**8**). Yield 22.2 mg (75%), ^1H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 2H), 7.45−7.11 (m, 13H), 6.75 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 150.9, 143.4, 139.1, 132.0, 129.6, 127.9, 127.7, 127.6, 127.4, 127.3, 127.0, 126.4, 124.8, 124.3, 104.2.

4-Methoxy-N-phenylaniline (**9**). Yield 13.3 mg (67%); ^1H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, J = 7.8 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.83 (t, J = 7.3 Hz, 1H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 155.3, 145.2, 135.8, 129.4, 122.3, 119.6, 115.7, 114.7, 55.6.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.5c02442.

Experiment details, selected diaryliodonium sulfamate solubility in common solvents, and NMR spectra for all synthesized compounds (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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