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Note

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Experimental and Theoretical Quantification of the Lewis Acidity of Iodine(III) Species

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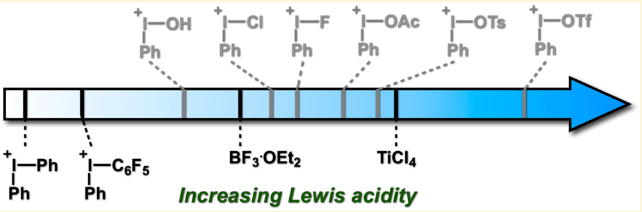
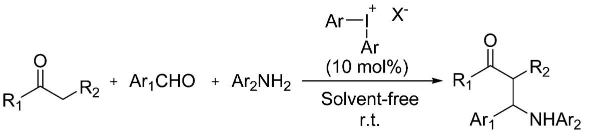
Supporting Information



ABSTRACT: The role of hypervalent iodine reagents as oxidants has been widely recognized for more than 20 years. As electrophilic species, they could also play the role of Lewis acids. While not surprising, this aspect of these reagents has not been fully considered and exploited in the literature. The experimental quantification of the Lewis acidity of a small series of diaryliodonium salts was performed using the Gutmann–Beckett method. Validation of a theoretical model using the experimental data was done in order to predict the Lewis acidity of other cationic iodine(III) species. Comparison with known common Lewis acids is presented.

Hypervalent iodine chemistry has greatly impacted the field of oxidative synthetic methodologies.[1] In the past 20 years it has progessed and become in numerous cases the strategy of choice for certain types of oxidation reactions. In particular, phenolic dearomatization has greatly benefited from the advances of iodine(III)-mediated transformations.[2] Numerous progresses in the field of stereoselective chemistry have also been noted.[3] The role of iodine(III) reagents as oxidants has thus been undoubtly recognized. As such, their electron-deficient character is also well accepted. Despite this, their potential as Lewis acids to promote reactions has not been widely exploited. To the best of our knowledge, only one example of their use as a sole Lewis acid to promote a reaction was reported by Liu, Han, and co-worker in 2015 (eq 1).[4]

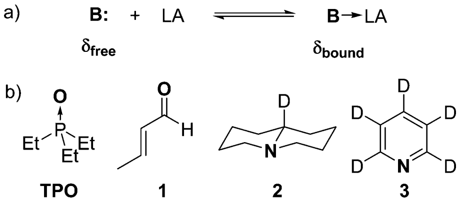


(1)

We have also recently proposed that in the α-tosyloxylation of ketones mediated by [hydroxy(tosyloxy)iodo]benzene (HTIB), the latter initially acts as a Lewis acid to promote the enolization of the ketone starting material, prior to the oxidation process.[5] Despite these few reports, hypervalent iodine reagents are greatly underexploited in this context. This is due in part by the fact that it is currently not known how they compare to more common Lewis acids. In this note we report the first experimental quantification of the Lewis acidity of diaryliodonium salts, their comparison with known Lewis acids, and the use of a computational model to predict the expected Lewis acidity of other cationic iodine(III) species.

In contrast to Brønsted acidity, for which the pK_a scale is widely accepted as a quantitative measurement, there is no universal scale for Lewis acidity. This is mainly due to competing steric and electronic effects that complicate the overall quantification. This picture can be even more complex due to the Pearson's hard and soft acids and bases principle (HSAB).[6] Nevertheless, numerous methods have been developed and accepted for the quantification of Lewis acidity. The measurement of NMR chemical shift displacements ($\Delta\delta$) on a Lewis base probe upon complexation with studied Lewis acids has been one of the most common and practical strategies used (Scheme 1). Once complete association of the probe is achieved, the maximum chemical shift displacement ($\Delta\delta_{max}$) is considered to be quantitative assessment of the capacity of the Lewis acid to accept the electron pair of the probe.

Scheme 1. (a) Concept of the Quantification of Lewis Acidity by NMR and (b) Common Lewis Base Probes Used



In the context of organic chemistry, the method developed initially by Gutmann[7] and generalized by Beckett[8] has been used frequently. It uses triethylphosphine oxide (**TPO**) as a Lewis base probe, measured using ^{31}P{^{1}H} NMR. The method of Childs involves the use of α,β-unsatured carbonyl compounds, such as crotonaldehyde (**1**), as probes, measured using ^{1}H and ^{13}C NMR.[9] More recently, Hilt et al. have

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reported the use of deuterated amine **2** and pyridine **3** as Lewis base probes, enabling measurement using ^{2}H NMR.[10]

We elected to use the Gutmann−Beckett method due to its wide recognition in the field, as it has been used with success for a large and varied range of Lewis acids involved in catalysis. A single displacement is easily measured by ^{31}P{^{1}H} NMR. There is no overlap by ^{1}H NMR in terms of the probe signals to be measured and the electrophilic species studied, making precise stoichiometry determination possible. Additionally, due to the structure of **TPO**, steric effects should be minimal, facilitating comparison with other Lewis acids. The method involves the formation of a **TPO**·Lewis acid adduct and measurement of the ^{31}P chemical shift displacement compared to free **TPO**. To ensure precise calibration of each spectrum, a capillary insert containing 85% aqueous H_3PO_4 is used as an external standard.

The first iodine(III) reagents we investigated were diphenyliodonium hexafluorophosphate (**4a**) and tosylate (**4b**) due to their stability and ease of manipulation (Figure 1). They were also selected to evaluate the counterion effect.

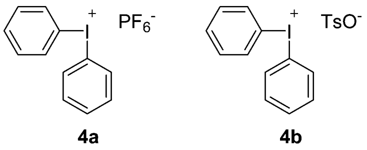


Figure 1. Initial iodine(III) reagents studied.

The noncoordinating nature of the hexafluorophosphate counterion[11] would basically make **4a** a naked iodonium center, preventing the need to take into account competitive association of the counterion and **TPO**. In contrast, the association of **TPO** with **4b** was expected to be more difficult due to competing complexation of the TsO$^-$ counterion to the iodinium center. Since the actual binding affinity of **TPO** to these electrophilic reagents was not known, titrations were performed. Deuterated chloroform ($CDCl_3$) was found to be not suitable for the titration study, due to the low solubility of **4a** and **4b**. Deuterated dichloromethane (CD_2Cl_2) and acetonitrile (CD_3CN) were found to be suitable solvents for **4a** and in part for **4b**. The results are illustrated in Figure 2.

Only marginal chemical shift displacement was observed with **4b** in CD_2Cl_2, even with 6 equiv with respect to **TPO**. Full titration was thus not possible; it demonstrates the strong association of the TsO$^-$ counterion to the iodonium center. Furthermore, the lower solubility of **4b** prevented titration in CD_3CN. For iodonium salt **4a**, full titration was possible and followed a 1:1 binding behavior in both solvents. A slight decrease in binding affinity was observed in CD_3CN, as could be expected from this more polar and complexing solvent. Curve fitting analysis for a 1:1 complex was performed; the results are described in Table 1.

The free energies of binding were calculated from the equilibrium constants. They represent, at room temperature, free energies of −3.1 kcal/mol and −2.3 kcal/mol, respectively. Using DFT calculations, we computed the theoretical binding free energies. By assuming complete dissociation of the PF$_6^-$ counterion, we predicted free energies of −3.5 kcal/mol and −1.7 kcal/mol for CD_2Cl_2 and CD_3CN, respectively. These theoretical results are in good agreement with the experimentally determined values and support the assumption of the noncoordinating nature of PF$_6^-$. The maximum chemical shifts measured ($\Delta\delta_{max}$) at saturation concentration of **4a** were of 6.3 and 6.7 ppm in CD_2Cl_2 and CD_3CN, respectively. The small difference in $\Delta\delta_{max}$ is in line with other observations of the Gutmann−Beckett method, typically enabling comparison of values obtained from different solvents. For comparison, we measured the Lewis acidity of $TiCl_4$, BF_3·OEt_2 as well as thiourea **5**, for which $\Delta\delta_{max}$ was previously measured by Hilt et al. using tributylphosphine oxide.[12] The thioureas are a class of mild but highly useful Lewis acids promoting a wide range of organic transformations.[13] The values are reported in Table 2. The $\Delta\delta_{max}$ obtained, in comparison to these widely different Lewis acids, put into perspective the mild Lewis acidity of **4a**.

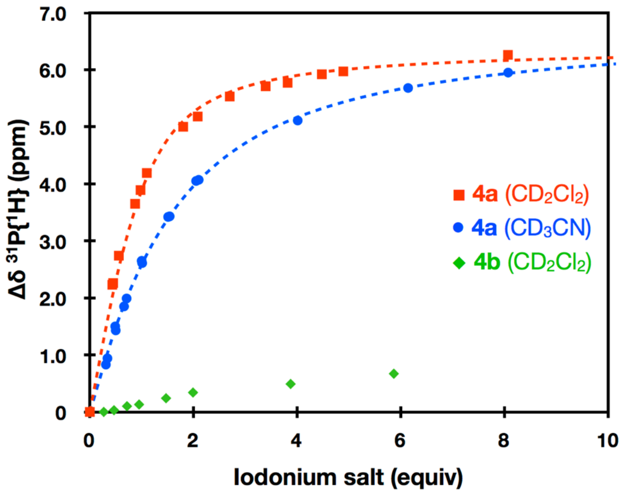


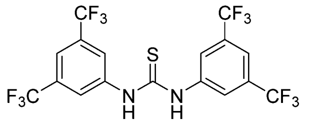
Figure 2. Titration of **TPO** using **4a** and **4b**. NMR performed at 25 °C. Dashed lines were obtained using a numerical fitting for a 1:1 binding model.

Table 1. Experimental and Theoretical Binding Properties of 4a with TPO

solvent	$\Delta\delta_{max}$[a] (ppm)	K_{bind}[b] (M^{-1})	expt. $\Delta G°_{bind}$[c] (kcal/mol)	calcd $\Delta G°_{bind}$[d] (kcal/mol)
CD_2Cl_2	6.3	174.8	−3.1	−3.5
CD_3CN	6.7	46.1	−2.3	−1.7

[a] Chemical shift compared to free **TPO** (at 25 °C), obtained at saturation concentration in **4a** (8 equiv in CD_2Cl_2, 53 equiv in CD_3CN). [b] Determined using curve fitting of the experimental data. [c] Determined using $\Delta G°_{bind} = -RT\ln(K_{bind})$. [d] Calculated at the M06/6-31+G(d,p)-LANL2DZdp(I) level.

Table 2. Evaluation of the Lewis acidity of $TiCl_4$, BF_3·OEt_2, 5, and 4a



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Lewis acid	$\Delta\delta_{max}$ CD_2Cl_2[a] (ppm)	$\Delta\delta_{max}$ CD_3CN (ppm)
$TiCl_4$	44.2	
BF_3·OEt_2	28.0	
5	7.3	
4a	6.3	6.7

[a] Chemical shift compared to free **TPO** (at 25 °C), obtained at saturation concentration of the Lewis acid.

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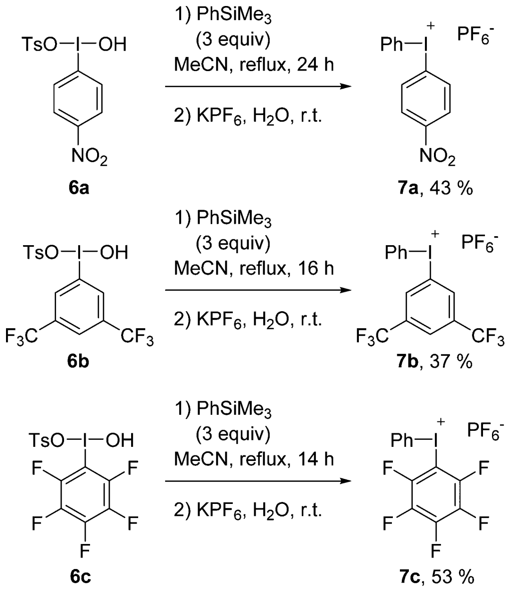
To evaluate the effect of the substitution of diaryliodonium salts on Lewis acidity, we chose three derivatives with different electron-withdrawing groups. Numerous methods have been reported to access nonsymmetric diaryliodonium salts.[14] We selected the arylation of Koser-type reagents (**6a**−**c**) with phenyltrimethylsilane,[15] followed by counterion exchange,[16] to access the desired compounds. Their synthesis is illustrated in Scheme 2.

Scheme 2. Synthesis of Nonsymmetric Diaryliodonium Salts 7a−c



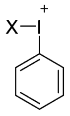
The method proceeded well to furnish modest to fair yields of the desired compound **7a**−**c** as white solids. These derivatives were found to have lower solubility in CD_3CN and very low solubility in CD_2Cl_2. For this reason, the NMR experiments were only performed in CD_3CN at lower concentration (4−5 mM), using >35 equiv to obtain $\Delta\delta_{max}$. The chemical shifts obtained experimentally in CD_3CN are presented in Table 3. Introduction of the *para*-nitro group led to a small increase in Lewis acidity. The inductive effect of the two trifluoromethyl group in **7b** led to a stronger enhancement. Consequently, the highest Lewis acidity was obtained with the perfluorophenyl derivative **7c**. While measurable differences were observed with **4a** and **7a**−**c**, the accessible range of $\Delta\delta_{max}$ with diaryliodonium salts remains fairly small, making them mild Lewis acids.

Table 3. Evaluation of the Lewis Acidity of 7a−c

Lewis acid	$\Delta\delta_{max}$ CD_3CN[a] (ppm)
4a	6.7
7a	7.6
7b	8.6
7c	11.7

[a] Chemical shift compared to free **TPO** (at 25 °C [TPO] = 4−5 mM), obtained at saturation concentration of the Lewis acid.

The diaryliodonium salts are an important and representive class of hypervalent iodine reagents with cationic character. However, cationic iodonium intermediates bearing an electronegative group on the iodine, such as species **8a**−**f**, have often been reported in proposed reaction mechanisms.[17] Using the experimental values obtained from **4a**, **7a**−**c**, $BF_3{\cdot}OEt_2$, and $TiCl_4$, we decided to predict, using computational chemistry, the Lewis acidity of cationic iodine(III) species **8a**−**f** (Figure 3).

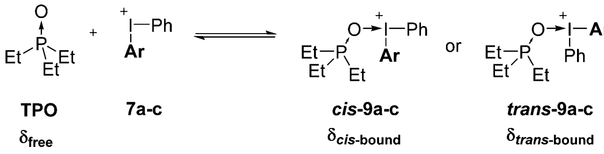


8a, X = OH
8b, X = OAc
8c, X = Cl
8d, X = F
8e, X = OTs
8f, X = OTf

Figure 3. Cationic iodine(III) species **8a**−**f** studied.

We elected to use calculated chemical shifts using the GIAO method[18] as a predictor, since we could easily validate the model with our direct experimental measurements ($^{31}P\{^1H\}$ chemical shift displacements). The theoretical method selected (PBE1PBE/6-311++G(3df,3pd)) was validated recently by Latypov et al. for a wide range of phosphorus-containing compounds.[19] Free **TPO** and the **TPO**·Lewis acid complexes geometries were optimized at the M06/6-31+G(d,p)-LANL2DZdp(I) level, and the ^{31}P chemical shift displacements were computed for these species using single point calculations at the described level (see Computational Methods). The situation is more complicated for nonsymmetric iodonium salts **7a**−**c**, as two complexes are accessible (Scheme 3). Even at saturation concentration, the measured $\Delta\delta_{max}$ will be affected by the relative stabilities, and hence populations, of the two complexes (***cis*-9** and ***trans*-9**).

Scheme 3. Binding Modes of Iodonium Salts 7a−c



The structures of all the complexes were optimized, and the relative free energies obtained. From the relative free energies, populations for ***cis*-9** and ***trans*-9** complexes were calculated. The results are presented in Table 4.

Table 4. Predicted Populations of *cis*-9 and *trans*-9 Complexes

iodonium	$\Delta G_{cis-trans}$[a] (kcal/mol)	***trans*-9**: ***cis*-9**
7a	+0.9	83:17
7b	+1.7	94:6
7c	+3.9	99.9:0.1

[a] Calculated at the M06/6-31+G(d,p)-LANL2DZdp(I) level.

As could be expected, a preference for the complexation *trans* to the more electron-withdrawing aryl moiety, with an increased selectivity going from **7a** to **c**, was observed. The populations were used to obtain the Boltzmann-averaged ^{31}P chemical shifts displacements for **7a**−**c**. The computed $\Delta\delta_{max}$ of all the Lewis acids were then plotted against the experimentally obtained $\Delta\delta_{max}$. The results are illustrated in Figure 4.

We observed a very good linear correlation between the experimental and computed values, despite the different nature

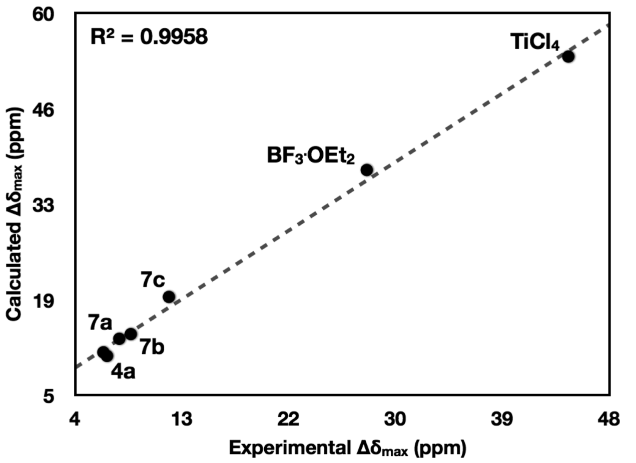


Figure 4. Plot of experimental $\Delta\delta_{max}$ vs calculated $\Delta\delta_{max}$ at the PBE1PBE/6-311++G(3df,3pd) level.

of the Lewis acids and solvents used for the NMR experiments. Using the linear regression data,[20] we computed the predicted displacements for species **8a−f**; the results are presented in Table 5. These predictions show that these cationic iodonium species offer a tremendous range of Lewis acidity, even surpassing compounds such as $TiCl_4$ ($\Delta\delta_{max}(CD_2Cl_2)$ = 44.2 ppm). They could thus promote a wide variety of Lewis acid-promoted transformations.

Table 5. Predicted $\Delta\delta_{max}$ (CD_3CN) for Species 8a−f

iodonium	$\Delta\delta_{max}$ (predicted) (ppm)
8a	22.6
8b	31.5
8c	34.2
8d	38.9
8e	42.5
8f	57.6

In summary, we have reported the first experimental quantification of the Lewis acidity of diaryliodonium salts, using the Gutmann−Beckett method. The values measured finally put into perspective the potential of these hypervalent iodine reagents as Lewis acids. Using the experimental values, we have validated a small theoretical model that enabled the prediction of the Lewis acidity of cationic iodonium species that could be derived from a variety of common hypervalent iodine reagents. The predicted values put into light the possibility of these intermediates to act as proficient Lewis acids in reaction processes. With this in mind, it will now be interesting for researchers to either use these species as catalysts or design reaction methodologies that will initially exploit their Lewis acidic nature prior to their oxidative nature.

COMPUTATIONAL METHODS

The geometry optimizations were done using the Gaussian 09 software package[21] with the M06[22] density functional, including the DFT-D3 London-dispersion correction of Grimme et al.,[23] in combination with the 6-31+G(d,p) basis set[24] for all atoms except titanium, for which LANL2DZ + ECP was used, and iodine, for which LANL2DZdp + ECP was used.[25] The structures were optimized with a solvation model (SMD) for either acetonitrile or dichloromethane.[26] Unless otherwise stated, a fine grid density was used for numerical integration in the calculations. Exhaustive conformational searches were done on all the species described. Harmonic vibrational frequencies were computed for all optimized structures to verify that they were minima, possessing zero imaginary frequency. The free energies are reported in kcal/mol and incorporate unscaled thermodynamic corrections based on the vibrational analyses and temperature of 298 K. A free energy change of +1.89 kcal/mol was applied to all free energies for their conversion from gas phase (1 atm) to liquid phase (1 M). For the reported free energies of the iodonium salt−**TPO** complexes, the basis set superposition error (BSSE) was corrected using the counterpoise method.[27] The ^{31}P NMR chemical shifts calculations were done with the GIAO method[18] by doing single point calculations on the previously optimized geometries using the PBE1PBE density functional,[28] in combination with the 6-311++G(3df,3pd) basis set for all atoms except titanium, for which LANL2DZ + ECP was used, and iodine, for which LANL2DZdp + ECP was used. The single point calculations included a solvation model (SMD) for either acetonitrile or dichloromethane, depending if the experimental chemical shifts were obtained in CD_3CN or CD_2Cl_2, respectively.

EXPERIMENTAL SECTION

General Remarks. All nonaqueous reactions involving air- or moisture-sensitive compounds were run under an inert atmosphere (argon) with rigid exclusion of moisture from reagents and glassware using standard techniques.[29] All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by distillation over sodium (ether) or over calcium hydride (CH_2Cl_2). Flash column chromatography was performed using 230−400 mesh silica (EM Science or Silicycle) of the indicated solvent system according to standard technique.[30] Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel (Merck 60 F_{254}). Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on a FTIR instrument and are reported in reciprocal centimeters (cm^{-1}). Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{19}F, ^{31}P, DEPT, COSY, HMQC) were recorded on a 300 MHz spectrometer. $CDCl_3$ was kept over anhydrous K_2CO_3 but not thoroughly dried. CD_3CN and CD_2Cl_2 were used as received. Chemical shifts for ^1H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm; dichloromethane, δ 5.32 ppm; acetonitrile, δ 1.94 ppm). Chemical shifts for $^{31}P\{^1H\}$ NMR spectra are recorded in parts per million from 85% aqueous H_3PO_4 as the external standard (capillary insert). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext = sextuplet, m = multiplet and br = broad), coupling constant in Hz, integration. Chemical shifts for $^{13}C\{^1H\}$ NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuteroacetonitrile (1.32 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, NOESY, HMQC, and DEPT experiments. High-resolution mass spectra were performed using an UPLC-Q-TOF (ESI) mass spectrometer. The [hydroxy(tosyloxy)iodo]arenes **6a−b**[31] and **6c**[32] as well as thiourea **5**[12] were prepared using literature procedures. Triethylphosphine oxide (**TPO**), **4a**, and **4b** were bought from Sigma-Aldrich and were used as received.

General Procedure for Nonsymmetric Diaryliodonium Salt Synthesis. (4-Nitrophenyl)(phenyl)iodonium Hexafluorophosphate (7a). 1-[Hydroxy(tosyloxy)iodo]-4-nitrobenzene (302 mg, 0.69 mmol) was added to acetonitrile (4 mL) in a round-bottom flask. To this suspension was added phenyltrimethylsilane (350 uL, 2.06 mmol, 3 equiv). The resulting mixture was stirred at reflux under argon for 24 h, at which point the reaction mixture was now a clear solution. The reaction mixture was cooled to room temperature, the solvent was removed by rotary evaporation, and the resulting solid was triturated thrice with diethyl ether (5 mL). The solid was dissolved in dichloromethane (50 mL) and extracted (5 × 4 mL) with an aqueous 1 M KPF_6 solution. The organic phase was then concentrated by rotary evaporation, and the crude solid was stirred with anhydrous diethyl ether (10 mL) for 30 min. The solid was filtered, washed with anhydrous diethyl ether, and dried under vacuum to furnish the title compound as a pale yellow solid (140 mg, 43% yield); T_{fus} 131−140 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 8.33−8.19 (m, 4H), 8.14 (d, J = 8.2 Hz, 2H), 7.77 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, CD_3CN) δ 151.8 (s), 137.4 (s), 137.0 (s), 134.6 (s), 133.8 (s), 127.9 (s), 119.5 (s), 114.4 (s); ^{19}F NMR (283 MHz, CD_3CN) δ −72.84 (d, J = 706.4 Hz); ^{31}P NMR (122 MHz, CD_3CN) δ −147.52 (hept, J = 706.3 Hz); IR (neat) 3113, 1603, 1573, 1512, 1470, 1445, 1350 cm^{-1}; HRMS ESI (m/z) calcd for $C_{12}H_9INO_2$ $[M - PF_6^-]^+$ 325.9672, found 325.9674.

*(3,5-Bis(trifluoromethyl)phenyl)(phenyl)iodonium Hexafluorophosphate (**7b**).* The title compound was obtained as a white solid (273 mg, 37% yield) according to the General Procedure for Nonsymmetric Diaryliodonium Salt Synthesis; T_{fus} 187−189 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 8.53 (s, 2H), 8.25 (s, 1H), 8.05 (d, J = 8.0 Hz, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.9 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, CD_3CN) δ 136.7 (s), 136.4 (s), 134.4 (q, J = 34.5 Hz), 133.9 (s), 133.4 (s), 127.5 (s), 123.2 (q, J = 273.0 Hz), 117.0 (s), 116.5 (s); ^{19}F NMR (283 MHz, CD_3CN) δ −63.52 (s), −72.84 (d, J = 706.5 Hz); ^{31}P NMR (122 MHz, CD_3CN) δ −144.6 (hept, J = 706.5 Hz); IR (neat) 3103, 1567, 1474, 1445, 1343, 1277, 1198, 1130 cm^{-1}; HRMS ESI (m/z) calcd for $C_{14}H_8F_6I$ $[M - PF_6^-]^+$ 416.9569, found 416.9574.

*(Perfluorophenyl)(phenyl)iodonium Hexafluorophosphate (**7c**).* The title compound was obtained as a white solid (510 mg, 53% yield) according to the General Procedure for Nonsymmetric Diaryliodonium Salt Synthesis; T_{fus} 164−168 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 7.96 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, CD_3CN)* δ 135.6 (s), 133.5 (s), 133.2 (s), 120.1 (s) (** The carbon signals from the C_6F_5 aryl group are not visible due to the extensive C−F coupling.*) ^{19}F NMR (283 MHz, CD_3CN) δ −72.96 (d, J = 706.5 Hz), −124.92 (m), −147.45 (t, J = 19.9 Hz), −158.72 (m); ^{31}P NMR (122 MHz, CD_3CN) δ −147.54 (hept, J = 706.5 Hz); IR (neat) 1638, 1509, 1493, 1279, 1093, 1072 cm^{-1}; HRMS ESI (m/z) calcd for $C_{12}H_5F_5I$ $[M - PF_6^-]^+$ 370.9351, found 370.9356.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01616.

> Additional experimental details and NMR spectra for all new compounds. Full Gaussian reference, Cartesian coordinates, electronic and zero-point vibrational energies (PDF)

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Notes

The authors declare no competing financial interest.

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