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Fluoroalcohols: versatile solvents in hypervalent iodine chemistry and syntheses of diaryliodonium(III) salts

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ABSTRACT

We first introduced 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and 2,2,2-trifluoroethanol (TFE) as unique solvents for reactions involving hypervalent iodine-mediated phenolic oxidations in the 1980s, in which the fluoroalcohols have been successfully utilized as stabilizing solvents of the reactive cationic intermediates, generated in situ by the action of phenyliodine(III) diacetate (PIDA) and phenyliodine bis (trifluoroacetate) (PIFA). This pioneering study produced a breakthrough in hypervalent iodine chemistry, and many synthetic applications that enable a variety of transformations have appeared utilizing this unique medium. For example, the single-electron-transfer (SET) oxidation ability of PIFA toward phenyl ethers has been discovered for the first time in HFIP and TFE, taking advantage of the unique acid-like behaviors to stabilize the aromatic cation radicals. More recently, the catalytic strategy of hypervalent iodine reagents has found extensive applications with the aid of the fluoroalcohols to produce highly reactive catalytic species under mild conditions. The fluoroalcohols are now widely used as versatile solvents not only in hypervalent iodine chemistry, but also in other organic syntheses. This manuscript for the Special Issue deals with the background of the hypervalent iodine chemistry and a new topic concerning the utility of fluoroalcohols for the synthesis of diaryliodonium(III) salts.

1. Introduction

Most chemical transformations known to date in organic synthesis were carried out in the solution phase using solvents. The solvents employed would work to break the self-association between the molecules and dissolve the reactants and reagents, allowing the opportunity for all components to react on a molecular level in one flask. In exothermic processes, the heat transport ability of the medium is particularly important, and reactions would often result in proceeding disorderly, and sometimes even explosively, in the absence of solvents. Many other properties of solvents have been summarized as macroscopic physical parameters and constants, such as the boiling point, density, dipole moment, hydrogen-bond donor and acceptor capability, etc., by which the solvent effect on organic reactions would be now quantitatively estimated.[1] 'A reaction cannot be separated from the medium in which it is performed',[2] and no one can neglect this long-live theme when performing the reactions.

For this objective, the selection of an appropriate solvent is indispensable for enhancing the efficiency of most chemical processes. Even recently, progress regarding a new solvent foundation is active and the number of available solvents is increasing. In particular, the use of fluorous liquids,[3] ionic liquids,[4] and supercritical fluids[5] as solvents is actively being promoted with the growing impetus of greener synthetic processes.

The fluoroalcohols, i.e., 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and 2,2,2-trifluoroethanol (TFE), appear as a group of solvents with unique properties (Fig. 1). These are significantly different from classic alcohols, and the presence of the fluoroalkyl groups provides many specific properties that no other solvents show. The highly polar [$E_T(30)$=69.3 for HFIP, 59.8 for TFE],[6a] but low nucleophilic [N=−4.23 (HFIP), −2.78 (TFE)][7] fluoroalcohols are unique solvents that exhibits a high ionizing power [Y=3.8 (HFIP), 1.8 (TFE)][7] with a pK_a higher [9.3 (HFIP), 12.4 (TFE)][6b] than that of acetic acid [pK_a=5.2]. In addition, HFIP, and TFE have quite excellent hydrogen-bond donor abilities [α=1.96 (HFIP), 1.51 (TFE)].[6c] Due to these

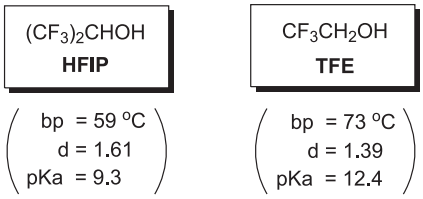

Figure 1. Fluorinated alcohols as solvents in organic synthesis.

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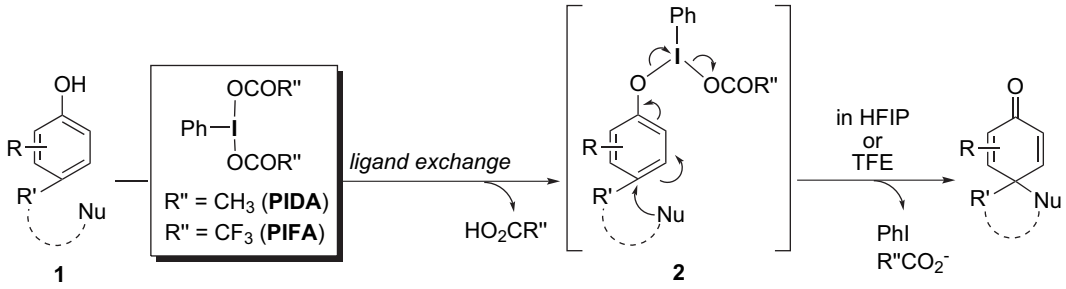
unique properties, the fluoroalcohols sometimes dramatically direct the course of reactions as the solvent. That is, the synthetic potential of fluoroalcohols as an attractive and unique alternative to ordinary commercially available solvents has been growing in interest in modern organic synthesis.[8]

Although the solvents show the characteristic properties, the reports that applied the unique solvents were relatively sporadic in organic synthesis until recently. In the 1980s, the authors introduced for the first time these alcohols as polar, but less nucleophilic solvents, in hypervalent iodine chemistry to perform the oxidation of phenols for the purpose of synthesizing spirodienones,[9] and applied the reaction to the synthesis of natural products having the spirodienone moiety.[10] Thereafter, the ability to stabilize aromatic cation radicals was first established for HFIP and TFE during our continuing study of the single-electron-transfer (SET) oxidations of aromatic compounds using hypervalent iodine reagents.[11] These two cases are good examples that the fluoroalcohols directed the reactive intermediates and the course of the reactions as solvents.

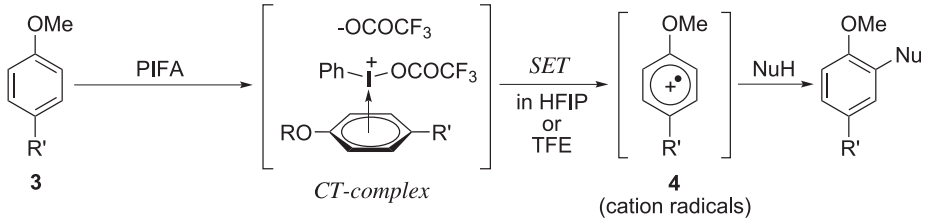
For the oxidation of phenols **1** using hypervalent iodine reagents, i.e., PIDA and PIFA, the reactions are typically explained by the two-electron-transfer processes that involve the initial ligand exchange at the iodine centers (Scheme 1).[12] Thus, the iodine(III) centers of PIDA and PIFA would react with phenolic oxygens to give the phenoxyiodine(III) intermediates **2**. The excellent leaving ability of the high-valent iodine atoms may smoothly generate the phenoxenium ions in the solvents, HFIP and TFE,[13] which were trapped by various concomitant types of nucleophiles,[9] thus a new mechanism should apparently be involved. A few years later, we determined the generation of aromatic cation radicals **4** produced by the SET oxidation through the charge-transfer (CT)-complex of phenyl ethers **3** and PIFA (Scheme 2), based on detailed UV and ESR spectroscopic measurements.[11b] This is the first strong evidence that clarified the SET oxidation ability of hypervalent iodine reagents toward aromatic rings, the success of which has found further applications for the synthesis as the method of C–H functionalization to directly introduce a wide range of nucleophiles (AcO, ArS, SCN, CN, β-dicarbonyl compounds, etc.)[11b–g] into aromatic compounds and for the oxidative biaryl couplings.[18] Applications of HFIP as a solvent for the spectroscopic studies of cation radicals have now become the reasonable choice.[8b]

The pioneering works including ours have triggered a recent rapid promotion of their use as solvent in hypervalent iodine chemistry as well as in the vast field of organic synthesis, and the utility seems to go beyond the initial perspective as new unique outcomes are revealed.

Recently, during our study of hypervalent iodine chemistry, we found a remarkable rate enhancement caused by the addition of fluoroalcohols for the condensation of aromatic compounds and hypervalent iodine reagents.[19] This finding has given rise to the opportunity for realizing a highly efficient dehydrative approach for diaryliodonium(III) salts. Notably, the fluoroalcohols were indispensable for the success of each reaction, while other typical solvents were unsatisfactory in terms of the reaction rate and yield of the products, which seems to support involvement of the Wheland type of cationic σ-complexes suggested in the related



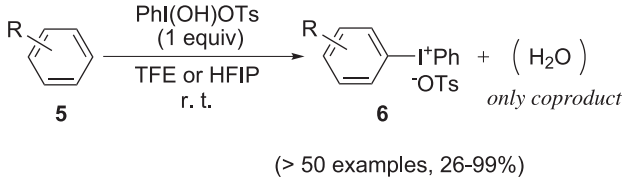
Scheme 1. Hypervalent iodine(III)-mediated oxidations of phenols in HFIP and TFE.



Scheme 2. Aromatic cation radical generation in HFIP and TFE in the hypervalent iodine-induced SET processes.

completing the oxidations. Based on the combination of the versatility of the reactions with the excellent features of the reagents as safe and low-toxic alternatives to heavy metal oxidizers, such as lead, mercury, cadmium, and thallium-based agents,[14] the oxidation of phenols basis of the umpolung of aromatic rings using hypervalent iodine reagents is recognized, for natural product synthesis, as the most practical and important biomimetic dearomatization process.[15–17]

On the other hand, the hypervalent iodine(III) reagents also act as excellent SET oxidizing agents in the fluoroalcohol solvents. In 1991, we reported the aromatic azidation of phenyl ethers by the treatment of PIFA in HFIP in the presence of $TMSN_3$.[11a] Interestingly, the novel aromatic azidation only proceeded in the fluoroalcohol solvents. For the novel aromatic substitution process, therefore, studies of diaryliodonium(III) synthesis.[20] In the following sections, we discuss the versatility of our new dehydrative approach to diaryliodonium(III) salts in fluoroalcohol solvents (Scheme 3). The method is very clean, only producing water as the sole coproduct.



Scheme 3. Direct dehydrative approach to diaryliodonium(III) salts in fluoroalcohol solvents, TFE and HFIP.

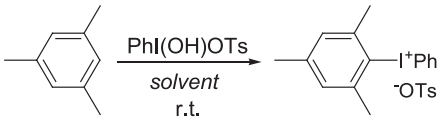
2. Results and discussion

2.1. Remarkable influence of the solvents in direct dehydrative approach for diaryliodonium(III) salts

The dehydrative condensation of hypervalent iodine(III) reagents and aromatic compounds is considered to be a simple and clean approach to diaryliodonium(III) salts.[21] Typically, such direct methods were achieved using the activated iodine(III) compounds with strong acids[21a,b] or Koser's reagent [PhI(OH)OTs][21c] for limited types of products and counterions in moderate yields and/or with poor regioselectivities. In these studies, the effect of the solvent has never been evaluated.

To elucidate the solvent effect on the dehydrative iodonium(III) salts formations, we screened a number of solvents for the reaction of mesitylene **5a** and Koser's reagent (Table 1). As reported by Koser and Margida,[21c] neat conditions (entry 1) as well as the use of dichloromethane (entry 2), acetonitrile (entry 3), and methanol (entry 4) as solvents did not produce the desired iodonium(III) salt **6a** in the case of the alkylbenzene **5a**. In contrast, a remarkable effect of the solvent was clearly observed in fluoroalcohols. Surprisingly, the dehydrative condensation smoothly proceeded at room temperature to give the salt **6a** in nearly quantitative yields (entries 5 and 6). The reactions in TFE and HFIP were completed in a few hours with no excess reagent, and the product was obtained as the pure form after precipitation by adding Et_2O. Thus, the only coproduct from the reactions is water after the dehydration. Apparently, the fluoroalcohols played a critical role in the enhanced reactivity of Koser's reagent.

Table 1
Solvent effect in the reaction of **5a** and Koser's reagent[a]



5a **6a-OTs**

Entry	Solvent	Yield[b] (%)
1	—[c]	n.r.[d]
2	CH_2Cl_2	15[e]
3	CH_3CN	n.r.[d]
4	MeOH	n.d.[f]
5	TFE	97
6	HFIP	94

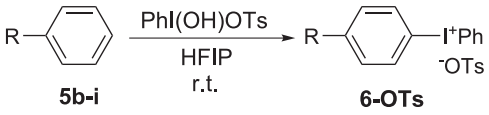
[a] All reactions were performed using an equimolar amount of **5a** and Koser's reagent, [PhI(OH)OTs], for 24 h.
[b] Isolated yield after precipitation.
[c] Mesitylene **5a** was used as solvent.
[d] No reaction was observed with the recovery of PhI(OH)OTs.
[e] Product was obtained as a mixture including large amount of inseparable impurities.
[f] n.d.=not determined.

2.2. Direct synthesis of diaryliodonium(III) salts from aromatic compounds and hypervalent iodine reagents: Scope and limitations

The diaryliodonium(III) salts, $ArI^+Ar'X^-$ (where, Ar and Ar′=aryl, X=counterion), represent one of the most useful and important classes of hypervalent iodine compounds, which show a wide range of applicability, such as arylating agents and benzyne precursors in organic synthesis, active bactericides, a photoacid generator (PAG) for cationic polymerization processes, etc.[22] These beneficial chemical and physical properties highly depend on both the structure of the iodonium(III) part and anionic counterion, X^-, and hence the development of general methods for diaryliodonium salts with a large structural diversity is strongly desired.[23] To alleviate the limitation of the direct methodology, stepwise approaches using organometallic compounds, i.e., lithio-, silyl-, stannyl-, and boryl-functionalized aromatic compounds, should be prepared and used for this purpose.[20] The situation prompted us to examine the versatility and scope of our method utilizing fluoroalcohol medium in diaryliodonium salt syntheses.

To determine the influence of the substituent on the benzene ring, we first examined the reactions of benzene derivatives **5b**–**i**. Table 2 represents the results and Hammet σ constants of substituents. In this screening, the yield of the iodonium salts obtained from the reactions seems to show a good correlation with the σ_P constants to support the intermediacy of the cationic species toward the diaryliodonium salts.[20] Thus, methoxybenzene **5b** having a negative σ_P value (σ_P=−0.12) smoothly reacted, and the presence of the methoxy group controlled the regioselectivity to give a *para*-

Table 2
Substitution effect of the benzene ring[a]

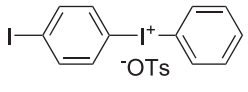


5b-i **6-OTs**

Entry	R	σ_P	Product	Yield[b] (%)
1[c]	OMe (**5b**)	−0.12	**6b-OTs**	89
2	H (**5c**)	0	**6c-OTs**	89
3	Cl (**5d**)	0.24	**6d-OTs**	57[d]
4	Br (**5e**)	0.26	**6e-OTs**	51[d]
5	OAc (**5f**)	0.31	**6f-OTs**	n.d.[e]
6	COMe (**5g**)	0.47	**6g-OTs**	n.d.[e]
7	CF_3 (**5h**)	0.53	**6h-OTs**	n.r.
8	NO_2 (**5i**)	0.81	**6i-OTs**	n.r.

[a] Reactions were examined using equimolar amount of **5b**–**i** and Koser's reagent for 24 h at room temperature.
[b] Isolated yield of pure product after precipitation.
[c] TFE was used as solvent.
[d] Products were obtained as a mixture of two regioisomers.
[e] Yield was not determined due to contamination of *p*-TsOH to the product.

substituted iodonium salt **6b-OTs** (entry 1). In contrast, the substituents having positive σ_P values, such as halogens, diminished both the regioselectivity and the yield compared to benzene **5c** itself (entries 2–4). As the results, the products **6d-OTs** and **6e-OTs** were obtained in lower yields as a mixture of regioisomers. As the electron-withdrawing character of the substituent increases, the reactions would hardly occur. The reactions of the electron-deficient aryl moieties were quite slow, which also made isolation of the products troublesome because of the contamination of *p*-TsOH and other impurities (entries 5 and 6). Trifluoromethylbenzene **5h** and nitrobenzene **5i** did not react at all under these conditions (entries 7 and 8). Instead, the reagent-derived iodonium salt **A**, which is considered to be a condensation product of the in situ formed iodobenzene and Koser's reagent, was detected (Fig. 2).

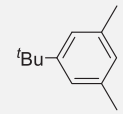
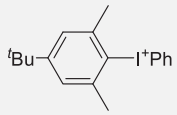
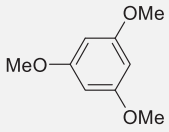
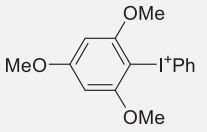
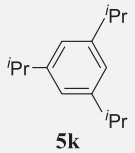
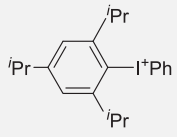
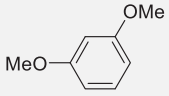
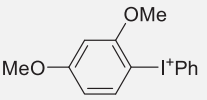
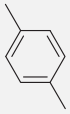
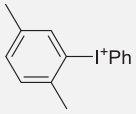
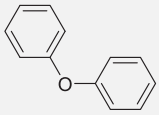
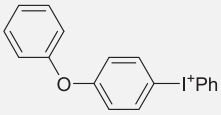
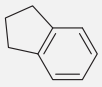
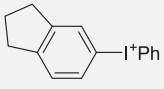
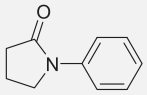
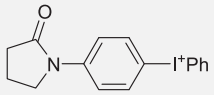
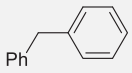
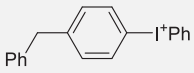
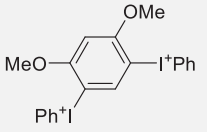
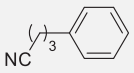
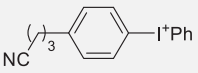
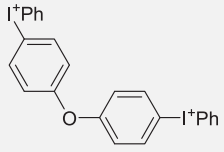
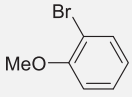
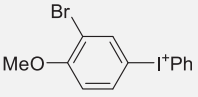
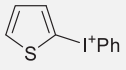
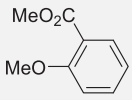
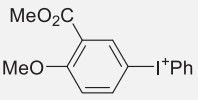
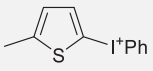
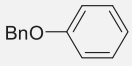
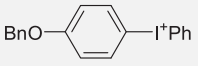
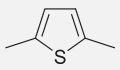
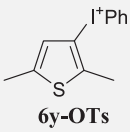


A

Figure 2. Potential byproduct **A** from Koser's reagent.

For the alkylbenzenes, phenyl ethers, and other electron-rich aromatic and heteroaromatic compounds, the new protocol provided a facile access to a wide range of diaryliodonium salts **6-OTs** (Table 3, see the Experimental section). Under the optimized conditions, the reaction of **5j** afforded **6j-OTs** in quantitative yield as a single isomer (entry 1). The result clearly suggests that the reaction might be dependent on the steric environments of the reactive sites, although the sterically congested product **6k-OTs** could be obtained in an acceptable yield (entry 2). The *para*-disubstituted

Table 3
Selected examples of substrates[a]

Entry	Substrate (**5**)	Product (**6-OTs**)	Yield[b] (%)	Entry	Substrate (**5**)	Product (**6-OTs**)	Yield[b] (%)
1	 **5j**	 **6j-OTs**	99	10	 **5s**	 **6s-OTs**	97
2	 **5k**	 **6k-OTs**	62	11	 **5t**	 **6t-OTs**	88
3	 **5l**	 **6l-OTs**	88	12	 **5u**	 **6u-OTs**	99
4	 **5m**	 **6m-OTs**	81	13	 **5v**	 **6v-OTs**	72
5	 **5n**	 **6n-OTs**	72	14[c]	**5t**	 **6t'-OTs**	99
6	 **5o**	 **6o-OTs**	93	15[c]	**5u**	 **6u'-OTs**	99
7	 **5p**	 **6p-OTs**	96	16	 **5w**	 **6w-OTs**	86
8	 **5q**	 **6q-OTs**	94	17	 **5x**	 **6x-OTs**	93
9	 **5r**	 **6r-OTs**	96	18	 **5y**	 **6y-OTs**	62

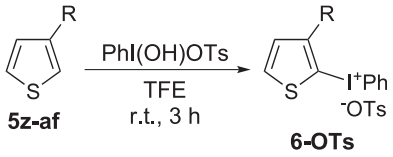
[a] Reactions were performed using equimolar amount of aromatic compounds **5** and Koser's reagent (1 equiv) in TFE at room temperature unless otherwise noted.
[b] Isolated yield after purification.
[c] Koser's reagent (2 equiv) was used.

benzene **5l** reacted at the *ortho* position producing the iodonium salt **6l-OTs** (entry 3). Similar results were obtained in other electron-rich aromatic compounds with or without some functional groups (entries 4–13). In substrates **5t** and **5u**, perfect control of the products, **6t-OTs** versus **6t′-OTs** or **6u-OTs** versus **6u′-OTs**, was attained by the amounts of the added reagent (entries 11, 12, 14, and 15).[24] The α-thienyliodonium salts were obtained from the thiophenes, **5w** and **5x** (entries 16 and 17), while the α-disubstituted thiophene **5y** produced the β-thienyl salt **6y-OTs** in good yield (entry 18). All of the products **6** were precipitated as solids after replacement of TFE with Et_2O, and did not contain other iodine(III) impurities and regioisomeric products.

For the 3-substituted thiophenes **5z-af**, the condensation should preferentially occur at the α-positions of the sulfur atom, among

which the 2-positions were more reactive (Table 4). Even **5ad-af** containing an aryl, alkoxy, and halogen at the 3-position were converted to the products in good yields with complete regioselectivity (entries 5–7). It should be noted that a serious background side reaction of uncontrollable polymerization[25] caused by the highly electron-rich alkoxy thiophene moiety in **5ae** was excluded under the stated conditions. A remarkable solvent effect was clearly observed in each case, and the reactions finished within a shorter reaction time (by 3 h) when compared to other solvents, such as CH_2Cl_2.[21c] The iodonium salts having thienyl moieties have found new applications as organic non-linear optic materials,[26a] active bacteriocides,[26b,c] precursors of fluorinated aromatic compounds,[26d] etc.

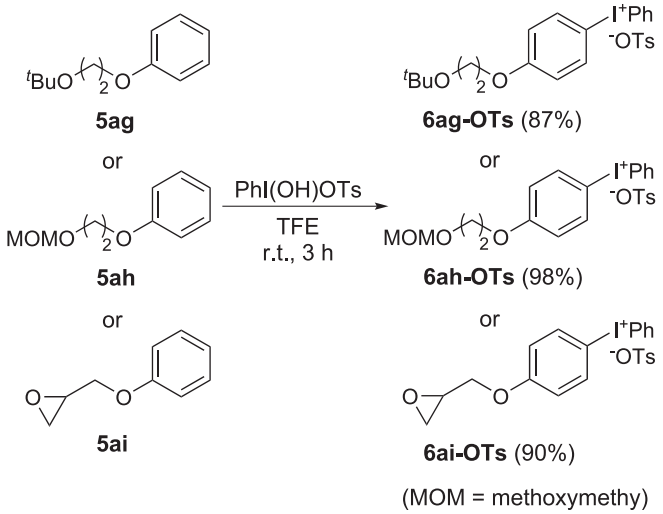
Table 4
Reactivity of 3-substitituted thiophenes **5z-af**



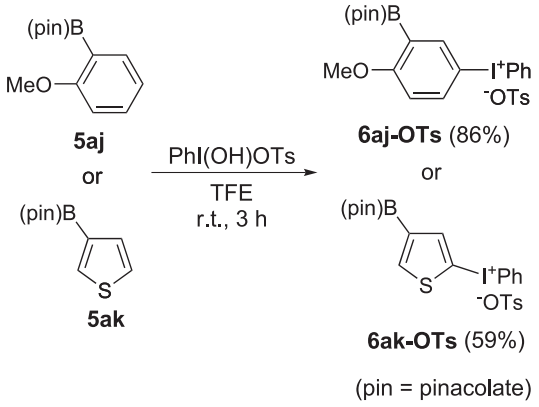
Entry	R	Product	Yield[a] (%)
1	Me (**5z**)	**6z-OTs**	98
2	Hex (**5aa**)	**6aa-OTs**	84
3	*c*-Hex (**5ab**)	**6ab-OTs**	74
4	*i*-Bu (**5ac**)	**6ac-OTs**	93
5	Ph (**5ad**)	**6ad-OTs**	88
6	OMe (**5ae**)	**6ae-OTs**	89
7	Br (**5af**)	**6af-OTs**	95

[a] Isolated yield of pure product after precipitation.

Our method is particularly valuable when performing the reactions of substrates with acid-sensitive functional groups. The reactions of protected alcohols and the epoxide **5ag-ai** in Scheme 4 are good examples in which the advantage was highlighted. In this examination, deprotection of the ^{t}Bu and MOM groups as well as the ring-opening of the epoxide were not observed. In addition, the reactions of **5aj** and **5ak** proceeded with retention of the metalloid element and furnished the organoborane moieties in iodonium(III) salts that are potentially suitable for further applications (Scheme 5).[27] To our knowledge, report on the iodonium salts containing such the acid-labile moieties and metalloid elements are quite limited[28] this should account for the significant synthetic merit of our method utilizing the fluoroalcohols for expanding the structural diversity of the diaryliodonium(III) salts.

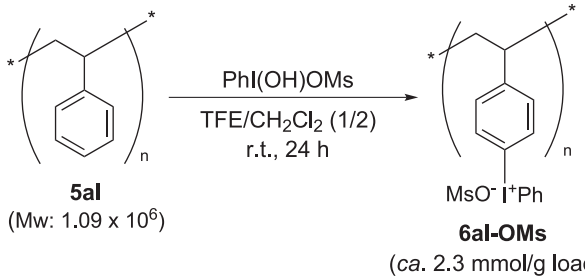


Scheme 4. Substrates having acid-labile functional groups.



Scheme 5. Reactions of organoborane compounds **5aj** and **5ak**.

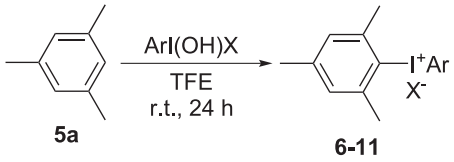
As described above, a new condensation method utilizing fluoroalcohols is quite simple and versatile. The high efficiency of the method made polymer functionalization possible by the incorporation of the iodonium(III) group. The synthesis of the iodonium(III)-supported poly(styrene)s was reported more than forty years ago to control the physical and chemical properties of the polymers,[29] but multistep transformations (typically, iodination, oxidation followed by conversion to the iodonium(III) forms) starting from poly(styrene)s should be employed for this purpose, resulting in the unsatisfactory loading of the function sites (~1.5 mmol loading of I(III) sites per gram). It became clear in our study that our straightforward procedure was applicable for the low-reactive polymers (Scheme 6). The use of a mixed solvent system, TFE, and CH_2Cl_2, was plausible for solving the solubility issue of the initial polymer, and accordingly, after stirring the dissolved solution of the linear poly(styrene) **5al** (100 mg, Mw: 1.09×10^6) and PhI(OH)OMs (317 mg, 1.0 mmol)[30] at ambient temperature, the iodine(III)-containing polymer **6al-OMs** (369 mg, ca. 85% incorporation of the iodine(III) reagent) was obtained by precipitation of the crude mixture in Et_2O. Elemental analysis of the polymer **6al-OMs** revealed that it contains ca. 2.3 mmol/g of the functionalized iodine(III) sites. The high loading of the iodonium (III) site in **6al-OMs** allowed the umpolung of the polarity, leading to the high solubility of the polymer in MeOH that is compatible with the monomeric diphenyl iodonium mesylate,[31] thus we called this comcept, 'polymer reforming'.

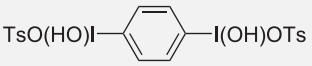


Scheme 6. Application of the method for a poly(styrene) reforming.

A large number of Koser's-type iodine(III) derivatives are now readily available,[32] and the variation of the reagents in the reaction could also expand the structural diversity of the obtained products. Selected examples utilizing these types of iodine compounds are shown in Table 5. Iodonium salts **6a**–**12a** having different kind of aryl rings were obtained from a single substrate **5a** and Koser's type of iodine derivatives. Regarding the reagents, ArI(OH)X, both the electron-rich and deficient aryl moieties were applicable (entries 4–9). One of the significant advantages of using fluoroalcohol

Table 5
Reactions using Koser's reagent derivatives[a]

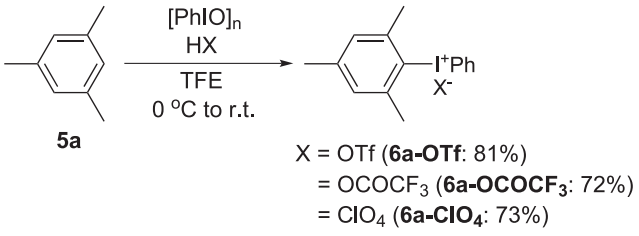


Entry	ArI(OH)X	Product	Yield[b] (%)
1	PhI(OH)OTs	**6a-OTs**	97
2	PhI(OH)OMs	**6a-OMs**	87
3	PhI(OH)OCs	**6a-OCs**	98
4	$C_6F_5I(OH)OTs$	**7a-OTs**	81
5	$(p\text{-}CF_3)C_6H_4I(OH)OTs$	**8a-OTs**	92
6	$(p\text{-}NO_2)C_6H_4I(OH)OTs$	**9a-OTs**	86
7	$(p\text{-}MeO)C_6H_4I(OH)OTs$	**10a-OTs**	62
8	(Mesityl)I(OH)OTs	**11a-OTs**	62
9[c]		**12a-OTs**	93

OMs=methanesulfonyloxy. OCs=(+)-10-camphorsulfonyloxy.
[a] Reactions were performed using equimolar amount of **5a** and ArI(OH)X.
[b] Isolated yield of pure product after precipitation.
[c] ArI(OH)OTs (0.5 equiv) was used.

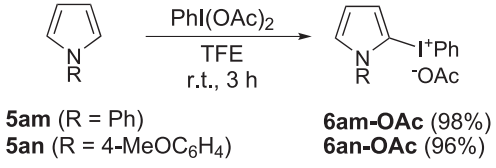
solvents in the reactions is that various types of reagents can be used in these ways.

The chemical and physical properties of the diaryliodonium(III) salts also highly depend on the nature of the anionic counterpart. Modification of the counterions was easily attainable using iodosobenzene, $[PhIO]_n$, instead of Koser's reagent, and Brønsted acids (Scheme 7). A variety of counterions, X^-, were thus conveniently introduced into the products **6a** by this strategy. This can avoid the circuitous anion metatheses work-ups.[20,21,23]



Scheme 7. Incorporation of other counterions, X^-.

Unfortunately, an attempt to prepare iodonium salts from 1*H*-pyrrole was unsuccessful. However suitably *N*-substituted pyrroles **5am** and **5an** formed the corresponding iodonium salts **6am-OAc** or **6an-OAc** in nearly quantitative yields with PIDA (Scheme 8).



Scheme 8. Preparation of pyrrole iodonium(III) salts.

The presence of an electron-withdrawing group apparently interferes with the dehydrative condensation as shown in Table 2 (vide ante). Other limitations of our method are also present. The synthesis of highly congested iodonium salts was difficult, and *tert*-alkyl groups at the *ortho* position to the reactive site retarded the condensation as shown by the 1,3-di(*tert*-butyl)benzene (Fig. 3). Similarly, the trimethysilyl group did not positively affect the yield of **6ao-OTs**, a benzyne precursor.[33] The polycyclic aromatic rings,

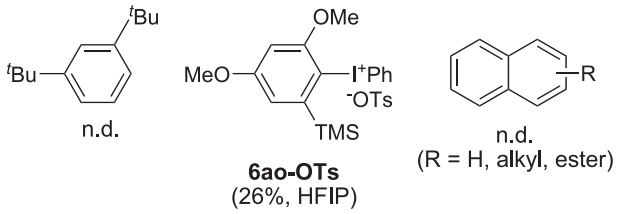


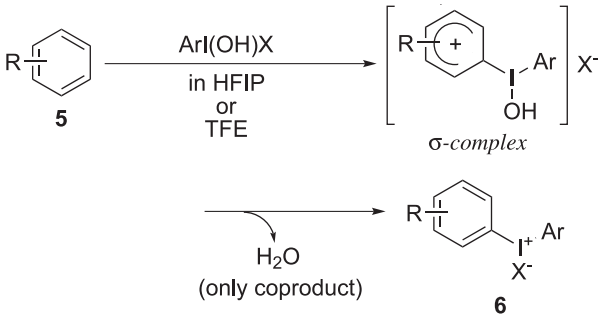
Figure 3. Limitation of substrate types.

such as naphthalene, could be used in the oxidations, rather than the iodonium salt formation, resulting in the formation of unidentified oxidized products.

After discovering that the fluoroalcohols work as excellent promoters for the direct dehydrative condensation, they became a promising solvent in exploiting the diaryliodonium(III) salts synthesis. For example, the solvent was partially utilized for the new straightforward synthesis of diaryl iodonium(III) salts from iodoarenes with stoichiometric oxidants in recent studies.[23d,e]

2.3. Mechanistic remarks

In previous reports on the dehydrative condensation of aromatic compounds and hypervalent iodine(III) reagents, the Wheland σ-complexes were typically considered to be the key intermediate.[20,21] The clear dependence between the product yield and aryl-ring substituent shown in Table 2 is also consistent with the reaction mechanism involving the σ-complexes, the formation of which should be further accelerated by using the cation-stablizing solvents, TFE, and HFIP, in our case. Thus, one plausible explanation of the reaction mechanism leading to the diaryliodonium (III) salts should be the formation of the σ-complexes by electrophilic attack of the iodine(III) centers on aromatic rings, followed by the elimination of water (Scheme 9).



Scheme 9. Reaction mechanism involving the σ-complexes.

Nevertheless, based on the principle for the cation radical generation from the electron-rich aromatic compounds, i.e., alkylarenes, phenyl ethers, and thiophenes, by the iodine(III)-induced SET oxidation in the fluoroalcohols[8a] as well as the recent participation of Koser's reagent in that chemistry,[34] the involvement of the aromatic cation radicals shown in Scheme 2 as an alternative possible reaction intermediate is not perfectly excluded. Indeed, the spectroscopic study of the intermediate for the reaction of 3-methylthiophene **5z** and Koser's reagent (Eq. 1) in the fluoroalcohol solvent suggested the generation of the aromatic cation radicals of **5z**. Based on the UV–vis measurement, the spectrum of the reaction mixture showed a good agreement with the known absorption band between the wavelengths of 500 and 600 nm for the cation radical species of **5z** (Fig. 4).[35,36] This is the first establishment of the SET oxidation ability of Koser's reagent by successful spectroscopic detection of the aromatic cation radicals. We thus strongly propose the aromatic cation radicals as potential

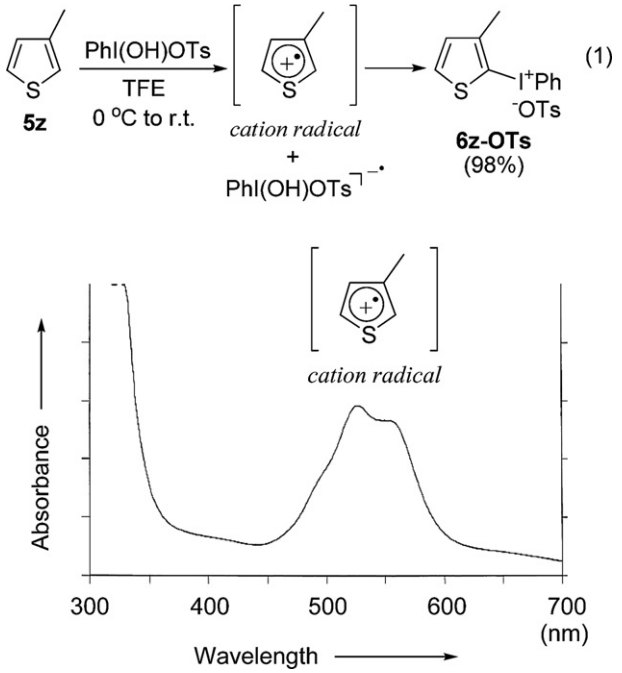
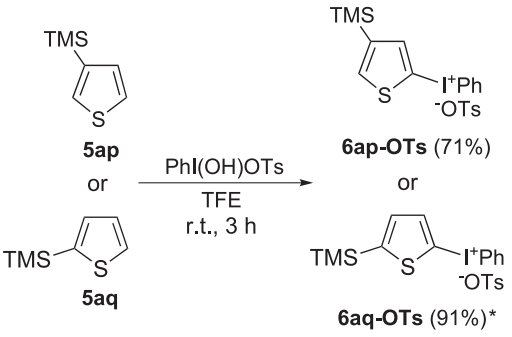


Figure 4. UV–vis spectrum of the reaction of 3-methylthiophene **5z** and Koser's reagent in TFE.

intermediates leading to the diaryliodonium(III) salts, especially in the electron-rich phenyl ethers and thiophenes.

A unique selectivity was observed for the organo-silicon compounds **5ap** and **5aq** in our method (Scheme 10). The *ipso*-substitution products at the silicon-bound carbon atoms as a result of the silicon-iodine(III) exchange via the Wheland type of σ-complex[20d,37] were not obtained at all, but the dehydrative condensation products **6ap-OTs** and **6aq-OTs**, in which the carbon–silicon bonds are maintained, were instead produced. This clarifies the difference in our strategy to other reported methods.



Scheme 10. Unique reactivities in organosilanes **5ap** and **5aq** **6aq-OTs** obtained included small amount of its regioisomer.

From these observations, it is very difficult to define the real reaction intermediates involved during the reactions in each case. In any way, the fluoroalcohols can work for the generation and stabilization of both the σ-complexes and aromatic cation radicals,[8] which seems to be a key to the effective reaction progress.

3. Conclusion

The present study revealed that the fluoroalcohols, i.e., TFE and HFIP, can positively affect the initiation of the dehydrative condensation of hypervalent iodine reagents toward aromatic and heteroaromatic compounds by taking advantage of their unique characteristics as highly polar, but low nucleophilic solvents, to stabilize the cationic intermediates involved during the reactions. In the reactions, a remarkable rate-acceleration effect of the fluoroalcohol solvents was clearly observed, and thus the diaryliodonium(III) salts were directly obtained using a variety of electron-rich aromatic compounds including the non-activated benzene and thiophene using only 1 equiv of hypervalent iodine (III) reagents with or without Brønsted acids in shorter reaction times and higher yields when compared with other classical solvents. The present dehydrative approach is, therefore, very clean because it produces only water as a coproduct, and versatile because it is capable of affording a variety of the diaryliodonium(III) salts. In addition, the use of fluoroalcohols in the direct dehydrative approach for diaryliodonium(III) salts can avoid the preparation of metalated substrates, and reduce byproducts and metal waste. As a result, a direct greener method for the synthesis of diaryliodonium(III) salts has been established by using the fluoroalcohol solvents without the production of any harmful byproducts.

The diaryliodonium(III) salts prepared by our methods and others are not only useful compounds as the classical arylating agents, but also have found some new attractive applications.[22a] In this study, we have recently developed a metal-free cross-coupling reaction of electron-rich aromatic compounds to give biaryls, utilizing the diaryliodonium salts(III) as the selective heteroaryl transfer agents.[38] With further innovation to synthesize these classes of compounds, the design of iodonium salts as stoichiometric reagents and catalysts will be extensively studied for the purpose of realizing more environmentally friendly reactions as well as asymmetric transformations.[39] Hence, the application of a variety of salts would become one of the exciting areas in hypervalent iodine chemistry and organic synthesis in the forthcoming decade, which has a significant potential to partially replace conventional methods using transition metals in view of green sustainable chemistry.

In this paper, we described the versatility of fluoroalcohol solvents for the synthesis of diaryliodonium(III) salts along with a brief introduction of their historical background and importance in hypervalent iodine chemistry. It has also found significant activity in the new area of hypervalent iodine chemistry as organocatalysts,[14m] and the scope of the catalytic strategy is expanding with the aid of the fluoroalcohols.[40,41] The promising ability to produce highly reactive hypervalent iodine species under mild conditions should not only contribute to the development of new catalytic transformations, but also improve the known methods by replacing the originally developed catalytic systems.

Typically, the solvent exists as a major component in most homogeneous systems, but it is often regarded to take a secondary role for the reactions on the basis of only few physical factors, such as solubility and polarity, etc., once a new solvent is accepted as a common tool in organic synthesis. The fluoroalcohols are beyond the success up to ordinary solvents in hypervalent iodine chemistry. The uses of these solvents are sometimes indispensable for initiating chemical transformations, which is the major reason for the so-called 'magic solvent' by many researchers engaged in the field of chemistry. Despite their unique characteristics, it seems that they no longer belong to an unusual choice of solvent in modern organic synthesis. Based on the unique characteristics thus far revealed, further synthetic applications highlighting the fluoroalcohols as unique solvents and additives should be encouraged in future studies.

4. Experimental

4.1. General

Melting points (mp) are uncorrected. The ^{1}H NMR (and ^{13}C NMR) spectra were recorded by a JEOL JMN-300 spectrometer

operating at 300 MHz (75.3 MHz for ^{13}C NMR) in $CDCl_3$ at 25 °C with tetramethylsilane as the internal standard. The data are reported as follows: chemical shift in parts per million (δ), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br s=broad singlet, m=multiplet), and coupling constant (Hz). The infrared spectra (IR) were obtained using a Hitachi 270-50 spectrometer. The high resolution mass spectra were performed by the Elemental Analysis Section of Osaka University. PhI(OH)OTs (HTIB, Koser's reagent) is a commercially available compound and was used as received. Solvents were obtained from commercial suppliers and were used without further purification.

4.2. General procedure for direct dehydrative approach to diaryliodonium(III) salts in fluoroalcohol solvents

To a stirred solution of arene **5** (1.0 mmol) in 2,2,2-trifluoroethanol (5 mL), HTIB (392 mg, 1.0 mmol) was added in one portion at room temperature under air, and it was stirred for 1–24 h. MeOH was then added to the reaction mixture when the solvents were removed under vacuum. The resulting oily crude product **6-OTs** was precipitated by addition of Et_2O with stirring. The precipitate was filtered and dried in vacuo to give pure **6** as a powder.

*4.2.1. (4-Bromophenyl)(phenyl)iodonium tosylate (**6e-OTs**, including a small amount of regioisomer).* A slightly yellow solid. IR (KBr) cm^{-1}: 3066, 3045, 2990, 1635, 1564, 1469, 1440, 1394, 1377, 1195, 1132, 1107, 1063, 1043, 1014, 988, 818, 738, 696. ^1H NMR (400 MHz, CD_3OD) δ 2.35 (s, 3H), 7.00 (d, 2H, J=9.3 Hz), 7.21 (d, 2H, J=8.0 Hz), 7.52 (t, 2H, J=8.0 Hz), 7.67 (d, 4H, J=8.0 Hz), 7.86 (d, 1H, J=4.8 Hz), 8.05 (d, 2H, J=8.0 Hz), 8.17 (d, 2H, J=8.0 Hz) ppm. ^{13}C NMR (100.53 MHz, CD_3OD) δ 21.3, 126.9, 129.8, 133.1, 133.2, 133.8, 133.9, 136.2, 136.4, 136.5, 138.1, 141.7, 142.3 ppm.

*4.2.2. (4-Benzylphenyl)(phenyl)iodonium tosylate (**6n-OTs**).* A colorless solid, mp 147–148 °C. IR (KBr) cm^{-1}: 3027, 2920, 1715, 1658, 1600, 1577, 1495, 1470, 1452, 1439, 1400, 1312, 1190, 1132, 1045, 1014, 1001, 991, 923, 816, 786, 740, 696. ^1H NMR (400 MHz, CD_3OD) δ 2.34 (s, 3H), 4.00 (s, 2H), 7.15–7.19 (m, 5H), 7.24(d, 1H, J=8.0 Hz), 7.34 (d, 2H, J=8.0 Hz), 7.49 (t, 2H, J=8.0 Hz), 7.63–7.69 (m, 4H), 8.04 (d, 2H, J=8.0 Hz), 8.12 (d, 2H, J=8.0 Hz) ppm. ^{13}C NMR (100.5 MHz, CD OD) δ 21.3, 42.3, 113.0, 116.1, 127.0, 127.6, 129.7, 129.8, 130.0, 133.1, 133.6(×2), 136.3, 136.4, 136.6, 141.1, 141.7, 148.5 ppm. HRMS (FAB) calcd for $C_{19}H_{16}IO$ $[M-OTs]^+$ 371.0297, found 371.0299.

*4.2.3. [4-(3-Cianopropyl)phenyl](phenyl)iodonium tosylate (**6o-OTs**).* A colorless solid, mp 131–133 °C. IR (KBr) cm^{-1}: 3048, 3028, 2936, 2866, 2243, 1566, 1483, 1470, 1441, 1424, 1402, 1323, 1190, 1132, 1107, 1045, 1015, 991, 816, 789, 745, 694, 682. ^1H NMR (300 MHz, $CDCl_3$) δ 1.91 (quin, 2H, J=7.8 Hz), 2.30 (t, 2H, J=7.8 Hz), 2.31 (s, 3H), 2.74 (t, 2H, J=7.8 Hz), 7.01 (d, 2H, J=7.8 Hz), 7.15 (d, 2H, J=7.8 Hz), 7.32 (t, 2H, J=7.8 Hz), 7.45–7.52 (m, 3H), 7.89 (d, 2H, J=7.8 Hz), 7.95 (d, 2H, J=7.8 Hz) ppm. ^{13}C NMR (75.5 MHz, CD_3OD) δ 16.3, 21.2, 26.3, 33.9, 112.7, 115.3, 119.1, 125.8, 128.4, 131.4, 131.5, 134.4, 135.1, 135.6, 139.4, 142.3, 144.0 ppm.

*4.2.4. (3-Bromo-4-methoxyphenyl)(phenyl)iodonium tosylate (**6p-OTs**).* A colorless solid, mp 158–159 °C. IR (KBr) cm^{-1}: 3050, 3015, 2936, 1566, 1476, 1439, 1379, 1292, 1271, 1255, 1207, 1192, 1155, 1132, 1045, 1015, 991, 816, 758, 692. ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.84 (s, 3H), 6.80 (d, 1H, J=7.8 Hz), 7.00 (d, 2H, J=7.8 Hz), 7.30 (t, 2H, J=7.8 Hz), 7.40–7.47 (m, 3H), 8.11–8.15 (m, 3H), 8.37 (d, 1H, J=2.1 Hz) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.3, 56.4, 104.3, 113.8, 114.3, 116.2, 125.9, 128.5, 130.7, 131.4, 131.5, 134.9, 136.9, 139.1, 139.6, 158.6 ppm. HRMS (FAB) calcd for $C_{13}H_{11}BrIO$ $[M-OTs]^+$ 388.9038, found 388.9038.

*4.2.5. (4-Benzyloxylphenyl)(phenyl)iodonium tosylate (**6r-OTs**).* A colorless solid, mp 183–185 °C. IR (KBr) cm^{-1}: 3071, 3046, 2934, 1578, 1567, 1482, 1454, 1442, 1402, 1381, 1291, 1235, 1193, 1131, 1043, 1013, 1003, 858, 832, 314, 756, 736, 696. ^1H NMR (400 MHz, CD_3OD) δ 2.34 (s, 3H), 5.13 (s, 2H), 7.11 (d, 2H, J=8.0 Hz), 7.20(d, 2H, J=8.0 Hz), 7.33–7.41 (m, 5H), 7.50 (t, 2H, J=8.0 Hz), 7.67 (t, 3H, J=8.0 Hz), 8.05–8.11 (m, 4H) ppm. ^{13}C NMR (75.5 MHz, CD_3OD) δ 21.3, 71.5, 104.7, 116.5, 119.7, 127.0, 128.7, 129.3, 129.6, 129.8, 133.0, 133.5, 136.0, 137.5, 138.5, 141.6, 143.6, 163.5 ppm. HRMS (FAB) calcd for $C_{19}H_{16}IO$ $[M-OTs]^+$ 387.0246, found 387.0257.

*4.2.6. (2,4-Dimethoxylphenyl)(phenyl)iodonium tosylate (**6t-OTs**).* A colorless solid, mp 203–206 °C. IR (KBr) cm^{-1}: 3009, 2942, 1578, 1468, 1439, 1410, 1308, 1285, 1254, 1211, 1190, 1165, 1132, 1045, 1015, 833, 816, 746, 694. ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.81 (s, 3H×2), 6.48 (d, 2H, J=2.7 Hz), 7.05 (d, 2H, J=7.8 Hz), 7.30 (t, 2H, J=7.8 Hz), 7.46 (t, 1H, J=7.8 Hz), 7.58 (d, 2H, J=7.8 Hz), 7.84–7.90 (m, 3H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.2, 55.8, 56.7, 93.4, 99.7, 108.5, 115.0, 126.0, 128.4, 131.3, 131.4, 134.3, 138.5, 139.4, 142.4, 158.6, 165.1 ppm. HRMS (FAB) calcd for $C_{14}H_{14}IO_2$ $[M-OTs]^+$ 341.0039, found 341.0060.

*4.2.7. Bis(iodonium) tosylate (**6t′-OTs**).* A slightly brown solid, mp 49–50 °C. IR (KBr) cm^{-1}: 3051, 2988, 2943, 2922, 1568, 1470, 1440, 1370, 1283, 1215, 1190, 1132, 1107, 1045, 1013, 991, 816, 739, 696. ^1H NMR (300 MHz, CD_3OD) δ 2.36 (s, 6H), 4.05 (s, 6H), 6.93 (s, 1H), 7.19 (d, 4H, J=7.8 Hz), 7.46 (t, 4H, J=7.8 Hz), 7.61–7.68 (m, 6H), 8.08 (d, 4H, J=7.8 Hz), 9.12 (s, 1H) ppm. ^{13}C NMR (75.5 MHz, CD_3OD) δ 21.4, 58.5, 97.3, 98.6, 116.2, 126.8, 129.7, 132.9, 133.4, 136.3, 141.5, 143.3, 146.0, 164.1 ppm. HRMS (FAB) calcd for $C_{27}H_{25}I_2O_5S$ $[M-OTs]^+$ 714.9507, found 714.9525.

*4.2.8. [{4-(2-tert-Buthoxy)ethoxy}phenyl](phenyl)iodonium tosylate (**6ag-OTs**).* A colorless solid, mp 164–168 °C. IR (KBr) cm^{-1}: 3047, 2973, 2937, 2872, 1580, 1486, 1471, 1452, 1441, 1403, 1363, 1297, 1254, 1193, 1131, 1095, 1043, 1013, 990, 969, 915, 816, 709, 693. ^1H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 9H), 2.30 (s, 3H), 3.67 (t, 2H, J=5.2 Hz), 4.04 (t, 2H, J=5.2 Hz), 6.87 (d, 2H, J=8.0 Hz), 7.05 (d, 2H, J=8.0 Hz), 7.31 (t, 2H, J=8.0 Hz), 7.45 (t, 1H, J=8.0 Hz), 7.57 (d, 2H, J=8.0 Hz), 7.81 (d, 2H, J=8.0 Hz), 7.87 (d, 2H, J=8.0 Hz) ppm. ^{13}C NMR (100.53 MHz, CD_3OD) δ 21.3, 27.7, 61.3, 61.5, 69.8, 116.5, 119.4 (×2), 126.9, 129.8, 133.0, 133.4, 136.0, 138.5, 141.6, 143.6, 163.8 ppm.

*4.2.9. [{4-(2-Methoxymethoxy)ethoxy}phenyl](phenyl)iodonium tosylate (**6ah-OTs**).* A colorless solid, mp 156–158 °C. IR (KBr) cm^{-1}: 2939, 1580, 1485, 1442, 1403, 1297, 1254, 1173, 1155, 1118, 1044, 991, 913, 827, 742, 683. ^1H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.34 (s, 3H), 3.89 (t, 2H, J=4.4 Hz), 4.14 (t, 2H, J=4.4 Hz), 4.69 (s, 2H), 6.90 (d, 2H, J=8.8 Hz), 7.07 (d, 2H, J=7.6 Hz), 7.36 (t, 2H, J=7.6 Hz), 7.51 (t, 1H, J=7.6 Hz), 7.59 (d, 2H, J=7.6 Hz), 7.85–7.90 (m, 4H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 21.2, 65.5, 67.8, 77.2, 96.6, 118.1, 118.2, 126.0, 128.6, 131.7, 131.8, 134.3, 134.4, 137.3, 137.4, 139.5, 161.8 ppm. HRMS (FAB) calcd for $C_{16}H_{18}IO_3$ $[M-OTs]^+$ 385.0301, found 385.0279.

*4.2.10. (4-Oxiranylmethoxyphenyl)(phenyl)iodonium tosylate (**6ai-OTs**).* A colorless solid, mp 143–146 °C. IR (KBr) cm^{-1}: 3028, 1572, 1485, 1440, 1251, 1188, 1132, 1045, 1014, 987, 815, 767, 696. ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.73 (dd, 1H, J=4.5, 2.7 Hz), 2.91 (t, 1H, J=4.5 Hz), 3.32 (m, 1H), 3.86 (dd, 1H, J=10.8, 6.0 Hz), 4.26 (dd, 1H, J=10.8, 2.7 Hz), 6.87 (d, 2H, J=7.5 Hz), 7.03 (d, 2H, J=8.1 Hz), 7.33 (t, 2H, J=7.5 Hz), 7.46–7.52 (m, 3H), 7.85–7.92 (m, 4H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 21.1, 44.3, 49.7, 69.0, 104.2, 115.6, 117.9,

125.7, 128.4, 131.3, 131.4, 134.6, 137.4, 139.3, 142.4, 161.0 ppm. HRMS (FAB) calcd for $C_{15}H_{14}IO_2$ $[M-OTs]^+$ 353.0039, found 353.0035.

*4.2.11. (3-Boronpinacolate-4-methoxyphenyl)(phenyl)iodonium tosylate (**6aj-OTs**).* A colorless solid, mp 171–172 °C. IR (KBr) cm^{-1}: 3048, 2978, 2938, 2845, 1584, 1555, 1481, 1460, 1441, 1398, 1339, 1317, 1256, 1190, 1144, 1134, 1065, 1045, 1015, 963, 860, 816, 752, 696. ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 12H), 2.31 (s, 3H), 3.83 (s, 3H), 6.84 (d, 1H, J=7.8 Hz), 7.05 (d, 2H, J=7.8 Hz), 7.33 (t, 2H, J=7.8 Hz), 7.48 (t, 1H, J=7.8 Hz), 7.56 (d, 2H, J=7.8 Hz), 7.91 (d, 2H, J=7.8 Hz), 8.11 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.2, 24.7, 56.0, 84.1, 103.2, 113.9, 115.6, 125.9, 128.4, 131.2, 131.4, 134.2, 134.8, 139.2, 140.7, 142.5, 143.8, 166.6 ppm.

*4.2.12. (4-Boronpinacolate-2-thienyl)(phenyl)iodonium tosylate (**6ak-OTs**).* A colorless solid, mp 165–168 °C. IR (KBr) cm^{-1}: 3054, 2979, 1563, 1511, 1469, 1314, 1269, 1192, 1135, 1088, 1048, 1014, 990, 966, 951, 854, 815, 737, 697, 684. ^1H NMR (400 MHz, CD_3OD) δ 1.32 (s, 12H), 2.36 (s, 3H), 7.21 (d, 2H, J=8.0 Hz), 7.52 (d, 2H, J=8.0 Hz), 7.68 (t, 3H, J=8.0 Hz), 8.15 (t, 3H, J=8.0 Hz), 8.25 (d, 1H, J=1.2 Hz) ppm. ^{13}C NMR (100.53 MHz, CD_3OD) δ 21.3, 25.1, 85.8, 118.8, 127.0, 129.8, 133.1, 133.2, 133.7, 135.7, 135.8, 141.6, 143.6, 146.5, 148.2 ppm. HRMS (FAB) calcd for $C_{16}H_{19}BIO_2S$ $[M-OTs]^+$ 413.0238, found 413.0240.

4.3. General procedure for dehydrative condensation of mesitylene 5a and iodosobenzene in the presence of Brönsted acids (Scheme 7)

To a stirred solution of mesitylene **5a** (105 mg, 1.0 mmol) in 2,2,2-trifluoroethanol (5 mL), iodosobenzene (220 mg, 1.0 mmol) and perchloric acid aqueous solution (60%, 334 μL) were added at 0 °C under air, and it was stirred for 2 h at room temperature. After the reaction was completed, CH_2Cl_2 was added to the mixture. The organic layer was separated and aqueous phase was extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and evaporated. The resulting oily crude product **6a–ClO$_4$** was precipitated by adding Et_2O with stirring. The precipitate was filtered off and dried in vacuo to give **6a–ClO$_4$** (298 mg, 73%) as a colorless powder.

*4.3.1. Phenyl(2,4,6-trimethylphenyl)iodonium perchlorate (**6a–ClO$_4$**)[19].* A colorless solid, mp 79 °C. IR (KBr) cm^{-1}: 3057, 2983, 1564, 1469, 1379, 1300, 1267, 1110, 989, 746, 680, 624. ^1H NMR (300 MHz) δ 2.34 (s, 3H), 2.65 (s, 6H), 7.23 (s, 2H), 7.50 (t, 2H, J=7.8 Hz), 7.63 (t, 1H, J=7.8 Hz), 7.90 (d, 2H, J=7.8 Hz) ppm. ^{13}C NMR (75.5 MHz) δ 21.0, 27.1, 114.0, 122.2, 131.3, 133.2, 133.3, 135.3, 143.5, 145.8 ppm.

4.4. General procedure for dehydrative condensation using Koser's reagent derivatives and PIDA (Table 5, Schemes 6 and 8)

To a stirred solution of arene **5** (1.0 mmol) in 2,2,2-trifluoroethanol (5 mL), Koser's reagent derivatives (100 mol % I(III)) or PIDA (322 mg, 1.0 mmol) was added in one portion at room temperature under air, and it was stirred for 3–24 h. MeOH was then added to the reaction mixture when the solvents were removed under vacuum. The resulting oily crude product was precipitated by addition of Et_2O with stirring. The precipitate was filtered and dried in vacuo to give pure product as a powder.

*4.4.1. (4-Trifluoromethylphenyl)(2,4,6-trimethylphenyl)iodonium tosylate (**8a-OTs**).* A colorless solid, mp 165–166 °C. IR (KBr) cm^{-1}: 3034, 2969, 2920, 1593, 1449, 1393, 1323, 1300, 1188, 1132, 1103, 1067, 1045, 1015, 1003, 991, 853, 827, 816, 772, 754, 696. ^1H NMR (300 MHz, CD_3OD) δ 2.34 (s, 3H×2), 2.63 (s, 6H), 7.18 (d, 2H, J=7.8 Hz), 7.22 (s, 2H), 7.62 (d, 2H, J=7.8 Hz), 7.76 (d, 2H, J=7.8 Hz), 8.06 (d, 2H, J=7.8 Hz). ^{13}C NMR (100.53 MHz, CD_3OD) δ 21.1, 21.3, 27.1, 118.1, 122.5, 124.7 (q, J=271 Hz), 126.9, 129.7 (q, J=3.8 Hz), 129.8, 131.4, 134.6 (q, J=33.6 Hz), 135.9, 141.6, 143.5, 143.6, 146.1 ppm. HRMS (FAB) calcd for $C_{16}H_{15}F_3I$ $[M-OTs]^+$ 391.0171, found 391.0157.

*4.4.2. (4-Nitrophenyl)(2,4,6-trimethylphenyl)iodonium tosylate (**9a-OTs**).* A colorless solid, mp 163–165 °C. IR (KBr) cm^{-1}: 2969, 1601, 1568, 1530, 1468, 1350, 1343, 1312, 1300, 1192, 1132, 1043, 1005, 849, 816, 752, 734, 696. ^1H NMR (300 MHz, CD_3OD) δ 2.34 (s, 3H), 2.35 (s, 3H), 2.63 (s, 6H), 6.39 (d, 2H, J=7.8 Hz), 7.24 (s, 2H), 7.62 (d, 2H, J=7.8 Hz), 8.09 (d, 2H, J=7.8 Hz), 8.24 (d, 2H, J=7.8 Hz). ^{13}C NMR (75.5 MHz, CD_3OD) δ 21.1, 21.3, 27.1, 120.0, 122.6, 126.9, 127.5, 129.8, 131.5, 136.3, 141.7, 143.5, 143.7, 146.3, 151.3 ppm. HRMS (FAB) calcd for $C_{15}H_{15}INO_2$ $[M-OTs]^+$ 368.0148, found 368.0137.

*4.4.3. (4-Methoxyphenyl)(2,4,6-trimethylphenyl)iodonium tosylate (**10a-OTs**).* A colorless solid, mp 159–160 °C. IR (KBr) cm^{-1}: 3460, 3428, 3059, 3020, 2947, 2920, 2866, 2835, 1581, 1570, 1485, 1458, 1398, 1300, 1251, 1190, 1130, 1044, 1014, 993, 851, 820, 750, 694. ^1H NMR (300 MHz, CD_3OD) δ 2.31 (s, 3H), 2.33 (s, 3H), 2.63 (s, 6H), 3.79 (s, 3H), 7.00 (d, 2H, J=7.8 Hz), 7.15 (s, 2H), 7.17 (d, 2H, J=7.8 Hz), 7.64 (d, 2H, J=7.8 Hz), 7.83 (d, 2H, J=7.8 Hz). ^{13}C NMR (100.53 MHz, CD_3OD) δ 21.0, 21.1, 27.0, 56.3, 102.7, 118.8, 122.9, 126.9, 129.8, 131.1, 137.5, 141.6, 143.2, 143.5, 145.3, 164.0 ppm.

*4.4.4. Bis(iodonium) tosylate (**12a-OTs**).* A colorless solid, mp 201–202 °C. IR (KBr) cm^{-1}: 3051, 2988, 2943, 2922, 1568, 1470, 1440, 1370, 1283, 1215, 1190, 1132, 1107, 1045, 1013, 991, 816, 739, 696. ^1H NMR (400 MHz, CD_3OD) δ 2.35 (s, 6H×2), 2.58 (s, 12H), 7.21 (s, 4H×2), 7.63 (s, 4H), 7.92 (s, 4H) ppm. ^{13}C NMR (100.53 MHz, CD_3OD) δ 21.1, 21.3, 27.1, 66.9, 117.8, 122.5, 126.9, 129.8, 131.5, 137.9, 141.7, 143.7, 146.3 ppm.

*4.4.5. Iodonium polymer (**6al-OMs**)[19].* White powder. IR (KBr): 3020, 1471, 1438, 1330, 1265, 1217, 1056, 1014, 941, 899, 779, 752, 700 cm^{-1}. Elemental Anal. Found: S, 7.32; I, 29.07 (theoretical loading of I: 291 mg I/g **6al-OMs**=2.28 mmol I/g **6al-OMs**).

*4.4.6. (1-Phenylpyrrol-2-yl)(phenyl)iodonium acetate (**6am-OAc**).* A colorless solid, mp 155–156 °C. IR (KBr) cm^{-1}: 2926, 1714, 1516, 1402, 1381, 1282, 1253, 1180, 1099, 839, 736, 615. ^1H NMR (400 MHz, $CDCl_3$) δ 1.87 (s, 3H), 6.54–6.57 (m, 1H), 7.25 (dd, 2H, J=6.6, 1.8 Hz), 7.31–7.36 (m, 2H), 7.39–7.43 (m, 2H), 7.55–7.60 (m, 6H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 24.2, 94.5, 114.0, 119.5, 126.6, 128.0, 130.6, 130.9, 131.2, 113.2, 133.0, 134.8, 140.2, 180.1 ppm.

*4.4.7. [1-(4-Methoxyphenyl)pyrrol-2-yl](phenyl)iodonium tosylate (**6an-OAc**).* A colorless solid, mp 150–151 °C. IR (KBr) cm^{-1}: 3055, 1716, 1556, 1537, 1496, 1402, 1384, 1321, 1282, 1261, 1213, 1180, 1139, 1099, 841, 763, 734, 650, 605. ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3H), 3.88 (s, 3H), 6.51 (t, 1H, J=3.4 Hz), 7.05 (d, 2H, J=7.2 Hz), 7.13 (d, 2H, J=7.2 Hz), 7.25 (t, 1H, J=2.1 Hz), 7.29 (m, 1H), 7.42 (t, 2H, J=7.8 Hz), 7.60 (m, 3H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 24.2, 56.2, 94.3, 113.8, 115.8, 119.1, 126.2, 129.4, 131.7, 132.8, 132.9, 133.2, 134.8, 162.0, 180.2 ppm.

4.5. Reactions of organo-silicon compounds with Koser's reagent (Fig. 3 and Scheme 10)

The corresponding diaryliodonium(III) salts were obtained according to the procedure described in Experimental section, 4.2.

*4.5.1. Phenyl(2-trimethylsilyl-4,6-dimethoxyphenyl)iodonium tosylate (**6ao-OTs**).* A colorless solid, mp 158–159 °C. IR (KBr) cm^{-1}: 3053, 3009, 2949, 2897, 2843, 1566, 1387, 1310, 1271, 1252, 1217, 1190, 1161, 1132, 1065, 1044, 1013, 991, 864, 841, 816, 758, 696. ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H), 1.95 (s, 3H), 3.45 (s, 3H), 3.52 (s, 3H),

6.24 (s, 1H), 6.38 (s, 1H), 6.73 (d, 2H, J=8.0 Hz), 6.96 (t, 2H, J=8.0 Hz), 7.08 (t, 1H, J=8.0 Hz), 7.34 (d, 4H, J=8.0 Hz) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 0.0, 21.2, 55.7, 57.0, 99.2, 99.4, 115.1, 116.0, 125.9, 128.4, 131.0, 131.6, 131.9, 139.3, 142.8, 150.6, 159.2, 164.7 ppm.

4.6. Measurement of UV–vis absorption spectrum (Fig. 4)[36]

To a stirred solution of 3-methylthiophene (1.0 mg, 1.0×10^{-2} mmol) in CF_3CH_2OH (5 mL) was added HTIB (3.9 mg, 1.0×10^{-2} mmol) in one portion at room temperature under air. The UV–vis absorption spectrum of the reaction mixture was measured on SHIMADZU 2200 UV–vis spectrometer.

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