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Synthesis, Characterization, and Reaction of a Both Inter- and Intramolecularly Coordinated Pseudocyclic Iodosylbenzene–Trifluoroacetic Acid Complex

Masaharu Yudasaka,[a] Toshifumi Maruyama,[b] Eiji Yamaguchi,[a] Norihiro Tada*[a] and Akichika Itoh*[a]

Abstract: An *ortho*-substituted ether-oxygen-coordinated pseudocyclic iodosylbenzene-trifluoroacetic acid (pcISB-TFA) complex was synthesized and characterized by X-ray crystallographic analysis. TFA suppresses the disproportionation by both coordination of the oxygen atom to the iodine (III) center through secondary bonding and hydrogen bonding to the oxygen anion. This bench-stable reagent is highly soluble in common organic solvents and reacts with various organic substrates under mild reaction conditions to give the corresponding products in good yields.

Introduction

Organohypervalent iodine compounds have been widely used as mild, selective, and environmentally friendly reagents for various synthetic oxidative reactions.[1] Recently, pseudocyclic hypervalent iodine compounds including asymmetric catalysts and reagents have attracted a great deal of attention because of the intramolecular secondary bonding that regulates the stability, solubility, and enantioselectivity of the compounds.[2] Thus, many types of pseudocyclic hypervalent iodine compounds such as aryliodonium, alkynyl iodonium, hydroxy iodonium, iodonium ylide, iminoiodane, and iodylbenzene adopting various *ortho*-substituted coordination groups such as ether, ester, amide, nitro, sulfonamide, and sulfone have been reported to date.[2]

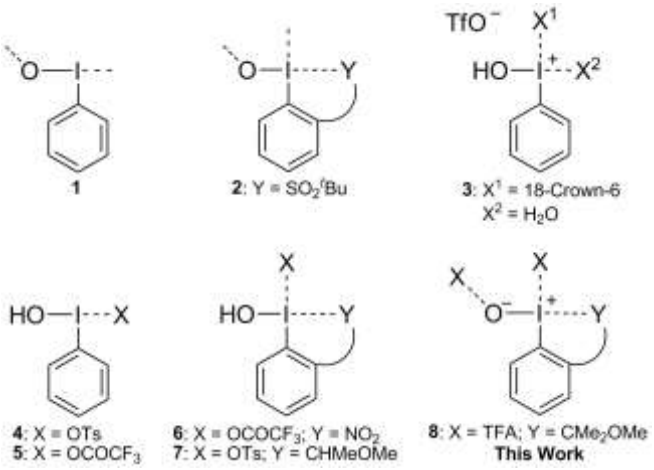
Iodosylbenzene (**1**: ISB, Scheme 1), a versatile oxygen-atom transfer agent in synthetic and biomimetic syntheses, is the simplest and most useful reagent. However, the I•••O hypervalent interactions make ISB a polymer, which is essentially insoluble in all nonreactive organic solvents.[3] In 1999, Protasiewicz and co-workers solved this problem by introducing *tert*-butylsulfone at the *ortho*-position.[4] In pseudocyclic iodosylbenzene **2**, the intramolecular I•••O hypervalent interaction of the sulfonyl oxygen redirects the intermolecular interaction from the backside of the I–O bond to the I–C bond. Because the redirected intermolecular secondary bonding is weak, **2** is soluble in common organic solvents. However, soluble pseudocyclic iodosylarenes are fairly limited because they readily disproportionate to more stable iodylarenes and iodoarenes probably through intermolecular coordination.[4] Thus, disruption of the weak intermolecular secondary bonding should make iodosylarenes resistive to disproportionation.

Intermolecular secondary bonding has also been used to improve the solubility and stability of hypervalent iodine compounds. In 1998, Protasiewicz and co-workers reported soluble imino-λ^3-iodanes by adding organic *N*-oxides.[5] Ochiai and co-workers demonstrated that intermolecular secondary bonding with 18-crown-6 stabilized various organic λ^3-iodanes, such as aqua(hydroxy)(aryl)iodonium ions **3**, in which the conjugate base of the strong acid (TfOH) does not coordinate and instead the oxygen atom of the crown ether coordinates to the iodine (III) center.[6] However, to the best of our knowledge, there has been no attempt to apply both inter- and intramolecular coordination to improve the stability and solubility of hypervalent iodine compounds.

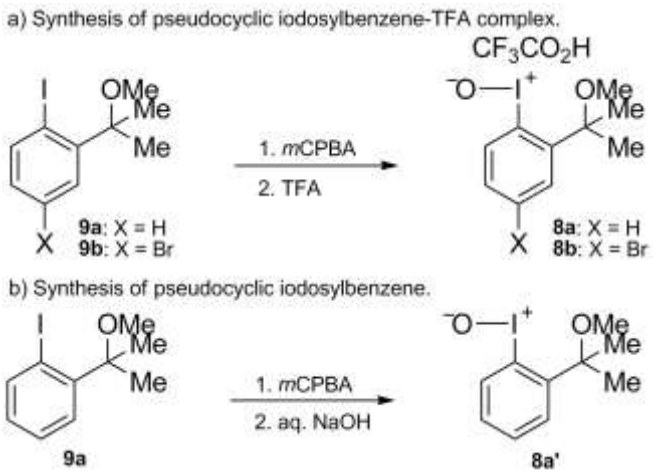
Organohypervalent iodine compounds with trifluoroacetate as a ligand, such as bis(trifluoroacetoxy)iodobenzene (PIFA) and μ-oxobis[trifluoroacetato(phenyl)iodine], have been used as effective reagents in various reactions.[1,7] Trifluoroacetate is also a useful ligand for alkynyl- and diaryl-λ^3-iodane.[8] On the other hand, [hydroxy(tosyloxy)iodo]benzene (**4**; Koser's reagent; Ts = *p*-toluenesulfonyl) is a useful stable activated iodosylbenzene,[9] whereas [hydroxy(trifluoroacetoxy)iodo]benzene **5** has no well-established precedents,[10] which can be explained by the unmatched trans influences of the hydroxy and trifluoroacetoxy groups.[11] Notwithstanding the unique and useful character of trifluoroacetoxy hypervalent iodine, there are few studies of pseudocyclic hypervalent iodane with trifluoroacetate.[2] Nikiforov and co-workers have reported pseudocyclic hydroxy iodonium **6**, the structure of which is similar to that of Wirth's reagent **7**, with a strong electron-withdrawing *ortho*-nitro group; however, the reactivity of **6** was not reported.[12,13] Over the course of our studies of the unique reactivity of trifluoroacetoxy ligands in hypervalent iodine compounds, both inter- and intramolecularly coordinated iodosylarene was revealed. Herein, we report for the first time a both inter- and intramolecularly stabilized pseudocyclic iodosylbenzene–trifluoroacetic acid complex (**8**; pcISB-TFA).

[a] Gifu Pharmaceutical University 1-25-4, Daigaku-nishi, Gifu 501-1196, Japan.
E-mail: ntada@gifu-pu.ac.jp
Itoha@gifu-pu.ac.jp
http://sv1.gifu-pu.ac.jp/lab/gousei/
[b] Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan.

Supporting information and ORCID(s) from the authors(s) for this article are available on the WWW under http:



Scheme 1. Inter- and Intramolecular coordination in organo-λ^3-iodane.



Scheme 2. a) Synthesis of pseudocyclic iodosylbenzene-TFA complex. b) Synthesis of pseudocyclic iodosylbenzene.

Results and Discussion

The oxidation of 1-iodo-2-(1-methoxy-1-methylethyl)benzene **9a** by *meta*-chloroperbenzoic acid (*m*CPBA) in dichloromethane/trifluoroethanol at room temperature under argon and the addition of TFA gave pseudocyclic iodosylbenzene–TFA 1:1 complex **8a** in 60% yield as a white powder after decantation and washing with diethyl ether at 0 °C (Scheme 2; a). Complex **8b** was prepared in a similar way from 4-bromo-1-iodoarene **9b** in 50% yield. Compound **8b** is soluble in dichloromethane, chloroform (0.33 M), acetonitrile, acetone, methanol, and water but not in the less polar solvents diethyl ether and hexane. Interestingly, **8b** is stable in the solid state at room temperature; no decomposition was detected when it was left standing in air at room temperature for two weeks. On the other hand, treatment with aq. NaOH at room temperature for 30 minutes after evaporation of solvent instead of TFA gave pale yellow oil containing **8a'** (48% yield), **9a** (8% yield), and iodylarene (4% yield) by ^{1}H NMR, and the half-life ($t_{1/2}$) of **8a'** at room temperature was about 12 hours (Scheme 2; b). As a solution in $CDCl_3$, the half-life ($t_{1/2}$) of **8b** at room temperature was found to be approximately 100 h. This is considered to be fairly stable compared with the half-life of **2** (6 h) and **8a'** (2.5 h).

Recrystallization from dichloromethane/diethyl ether/hexane at room temperature gave single crystals of **8b** suitable for X-ray crystallographic analysis (Fig. 1).[14] Figure 1 illustrates a T-shaped structure, ligated by the internal ether oxygen atoms (O2, O4) and oxygen anions (O1, O3) apical site of the iodine center with near-linear O1–I1–O2 (167.6°) and O3–I2–O4 (167.4°). The TFA oxygen atoms (O5 and O6) also coordinate to the hypervalent iodine center, resulting in a near-linear C1–I1–O5 (171.8°) and C2–I2–O6 (169.7°) arrangement. Including the TFA oxygen atoms (O5 and O6) and the iodine center, the complex adopts a distorted square planar geometry around the iodine atom. Root-mean-square deviations of 0.031Å (I1, C1, O1, O2, and O5) and 0.062Å (I2, C2, O3, O4, and O6) were observed from their least-squares plane, and the sums of the iodine-centered bond angles are Σ°I1=360.0° and Σ°I2=360.2°, respectively. Another feature of complex **8b** is that the linear O1–I1–O2 and O3–I2–O4 hypervalent bonding is highly unsymmetrical, as observed in other related compounds.[15] The oxygen anion ligand in **8b** is tightly bound to the iodine (III) center with the O1–I1 and O3–I2 distances of 1.913 and 1.911 Å, respectively, which are slightly shorter than that predicted for covalent radii (1.99 Å), whereas the internal ether oxygen is loosely bound to the iodine (III) center (O2–I1, 2.401Å; O4–I2, 2.387 Å). Intriguingly, the oxygen anions (O1 and O3) are stabilized by hydrogen bonding with TFA. The crystal structure of **8b** indicates that TFA is a stronger acid (pK_a=0.23) than aqua(hydroxy)(phenyl)iodonium (pK_a=4.30) but not sufficient to convert the complex to the hydroxy iodonium like Wirth's reagent **7**.[13,16] Furthermore, the TFA oxygen atoms coordinate to the iodine (III) center with the O5–I1 and O6–I2 distances of 2.897 and 2.903 Å, respectively. These interactions are weak but strong enough to disrupt the weak intermolecular secondary bonding. This result is different from that for the iodylbenzene-TFA complex, in which TFA is only a hydrogen bond donor to the oxygen atom, like $CDCl_3$ in complex **2**.[4b,17] All of these close

contacts are responsible for the thermal stability and high solubility of complex **8**.

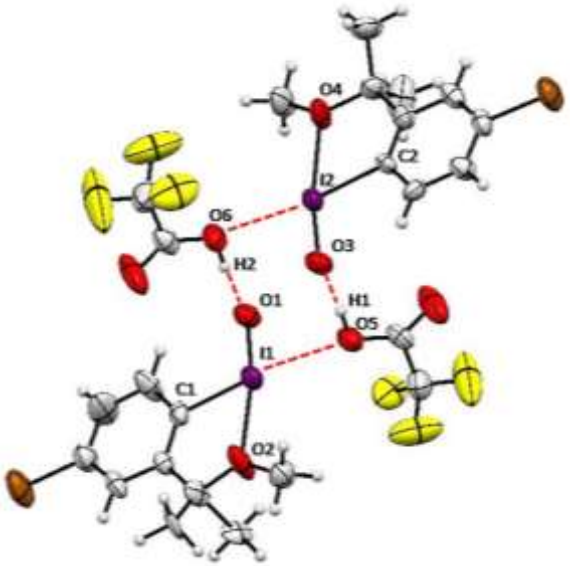
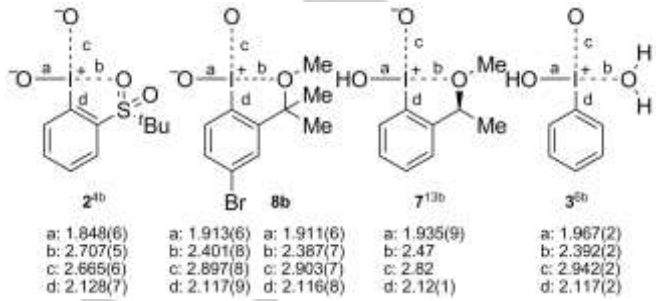


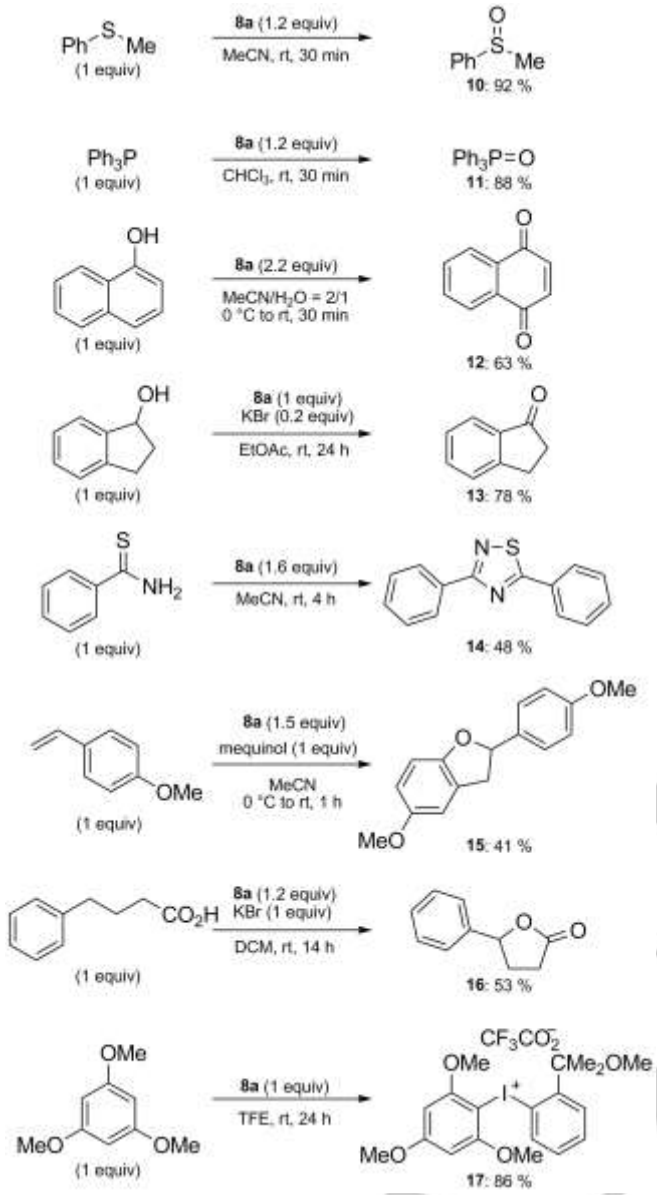
Figure 1. ORTEP drawing of **8b** (thermal ellipsoids set at 50% probability). Selected bond lengths (Å) and angles (°): I(1)–C(1) 2.117(9); I(1)–O(1) 1.913(6); I(1)–O(2) 2.401(8); I(1)–O(5) 2.897(8); O(1)–H(2) 1.758; H(2)–O(6) 0.841; O(2)–I(1)–C(1) 72.3(3); O(1)–I(1)–C(1) 95.4(3); O(1)–I(1)–O(2) 167.6(3); C(1)–I(1)–O(5) 171.8(3); I(1)–O(1)–H(2) 100.6; I(2)–C(2) 2.116(8); I(2)–O(3) 1.911(6); I(2)–O(4) 2.387(7); I(2)–O(6) 2.903(7); O(3)–H(1) 1.722; H(1)–O(5) 0.840; O(4)–I(2)–C(2) 71.9(3); C(2)–I(2)–O(3) 95.9(3); O(3)–I(2)–O(4) 167.4(3); C(2)–I(2)–O(6) 169.7(3); I(2)–O(3)–H(1) 102.2.

Scheme 3 shows the bond lengths of hypervalent and other secondary bonding in the known iodosylarene and hydroxy-λ^3-iodanes.[4b,6b,13b] The ⁻O–I bond of **8b** is longer than that of **2** (bond length *a* of **2** and **8b**); this is probably because the oxygen atom of the *tert*-butylsulfonyl group of **2** is farther from iodine than the oxygen atom of the ether group of **8b** (bond length *b* of **2** and **8b**). Moreover, the ⁻O–I bond is shorter than the HO–I bond (bond length *a* of **8b**, **7** and **3**). On the other hand, the secondary bond to the oxygen atom of TFA is longer than that to the anionic oxygen of **2** and **7** but is comparable to that to an oxygen atom of the crown ether of **3**, albeit with similar C–I bond distances (bond lengths *c* and *d*).



Scheme 3. Bond lengths of hypervalent iodine compounds.

Complex **8** can serve as a versatile oxidizing agent in various solvents. The reactions shown in Scheme 4 illustrate the range of applications of **8a**. The oxidation of sulfide and phosphine produced sulfoxide **10** and phosphine oxide **11** in high yields, respectively. 1-Naphthol was oxidized to naphthoquinone **12** in aqueous solution in good yield. 1-Indanol was oxidized to 1-indanone **13** in good yield in the presence of KBr.[18] The oxidative dimerization of thiobenzamide and coupling of phenol with alkene were also performed to afford 3,5-diphenyl-1,2,4-thiadiazole **14** and dihydrobenzofuran **15** in moderate yield, respectively. Furthermore, **8a** was applied to lactonization of carboxylic acid to give lactone **16** in good yield.[19] The exposure of 1,3,5-trimethoxybenzene to **8a** in trifluoroethanol at room temperature resulted in facile ligand exchange at the iodine center and afforded the diaryl-λ^3-iodane trifluoroacetate **17** in high yield. All of these reactions proceeded smoothly without adding an external acid catalyst.



Scheme 4. Reactions of pcISB-TFA **8a**.

Conclusions

In summary, we have synthesized and characterized a pseudocyclic iodosylbenzene–trifluoroacetic acid complex, and the structure was unambiguously determined by single-crystal X-ray analysis. The results indicate that trifluoroacetic acid is not acidic enough to convert pseudocyclic iodosylbenzene to hydroxy iodonium, but it disrupts the intermolecular coordination by using hydrogen bonding and secondary coordination. The synthesized complex is stable in the solid state and can be used as a versatile oxidant in various solvents. The reactivity of pcISB-TFA is lower than μ-oxobis[trifluoroacetato(phenyl)iodine] for the applied reactions probably because *ortho*-substituted coordination group is bulky.

Experimental Section

General Remarks: All reactants and reagents including dry solvents were obtained from commercial suppliers and used as received. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained on a JEOL ECA500 spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR, and 470 MHz for ^{19}F NMR) and a JEOL AL400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR). Chemical shifts (δ) are expressed in parts per million and are internally referenced [0.00 ppm (tetramethylsilane) for ^{1}H NMR and 77.0 ppm ($CDCl_3$) for ^{13}C NMR]. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, td = triplet of doublets). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD and Shimadzu hybrid IT-TOF mass spectrometer and are reported as m/z (relative intensity). IR spectra were recorded on a Perkin Elmer FT-IR spectrometer Frontier in ATR mode and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F254). Flash column chromatography was performed with Kanto silica gel 60N (Spherical, Neutral, 40–50 mm). Visualization of the developed chromatogram was performed by UV lamp (254 nm) and *p*-anisaldehyde or basic potassium permanganate stain. Melting points were measured on a Yanagimoto micro melting point apparatus without correlation.

Synthesis of 5-bromo-2-iodobenzoic acid methyl ester (Procedure A)[20,21]: 2-iodobenzoic acid (6.20 g, 25.0 mmol, 1.00 eq.) was taken up in concentrated H_2SO_4 (50 mL), and heated to 60 °C. The solid *N*-bromosuccinimide (5.34 g, 30.0 mmol, 1.20 eq.) was added a small amount to the reaction mixture during 15 minutes and stirred for 2 hours. The reaction was monitored by TLC. After the reaction was completed, a crushed ice was poured into the reaction mixture to precipitate the solid. The precipitated solid was filtered and washed with cold water. The solid was dissolved in ethyl acetate and the organic layer was washed with water and brine, dried with Na_2SO_4. The organic layer was filtered and concentrated in vacuo. The solid residue was used in the next step without any purification. To the solid residue in DMF (25 mL) at room temperature was added K_2CO_3 (4.15 g, 30.0 mmol 1.20 eq.). After gas evolution ceased, methyl iodide (1.71 mL, 27.5 mmol, 1.10 eq.) was added dropwise and the reaction mixture was stirred at room temperature for 16 hours. H_2O (50 mL) was added to the reaction mixture and the aqueous phase was extracted with diethyl ether (3 × 100 mL). The organic layers were combined, washed with H_2O, brine, and dried with $MgSO_4$. The organic layer was filtered and concentrated in vacuo. The residue was purified by column chromatography (Hex : EtOAc = 10 : 1) to afford 5-bromo-2-iodobenzoic acid methyl ester (7.38 g, 86 %, 2 steps). Rf: 0.53 (Hex : EtOAc = 10 : 1). Physical state: Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 2.4 Hz, 1 H), 7.84 (d, *J* = 8.2 Hz, 1 H), 7.28 (dd, *J* = 8.2, 2.4 Hz, 1 H), 3.94 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 142.6, 136.4, 135.7, 133.9, 122.2, 92.2, 52.7. HRMS (DART, positive) calcd for $C_8H_7BrIO_2$ $[M + H]^+$ 340.8596, Found 340.8575.

2-iodobenzoic acid methyl ester: Following the Procedure A without bromination, 2-iodobenzoic acid (6.2g, 25 mmol) was used. Without purification by column chromatography, 2-iodobenzoic acid methyl ester (6.28 g, 96 %) was obtained. Rf: 0.56 (Hex : EtOAc = 10 : 1). Physical state: pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 1 H), 7.81 (d, *J* = 7.7 Hz, 1 H), 7.39-7.45 (m, 1 H), 7.14-7.20 (m, 1 H), 3.94 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 141.3, 135.0, 132.7, 130.9,

127.9, 94.0, 52.4. HRMS (DART, positive) calcd for $C_8H_8IO_2$ $[M + H]^+$ 262.9491, Found 262.9516.

Synthesis of 5-bromo-2-iodo-α,α-dimethylbenzenemethanol (Procedure B)[21]: A 50 mL two-necked, round-bottomed flask equipped with a reflux condenser, an argon inlet, a Teflon-coated magnetic stir bar and a rubber septum was charged with magnesium turnings (1.59 g, 66.3 mmol, 3.1 eq.). The vessel was flame dried under vacuum and maintained under an atmosphere of argon during the course of the reaction. The flask was charged with diethyl ether (4.2 mL). The methyl iodide (2.93 mL, 47.1 mmol, 2.20 eq.) in diethyl ether (4.2 mL) was added dropwise to the magnesium turnings. The reaction was initiated, as evidenced by reflux, then, the reaction mixture was immediately diluted with additional diethyl ether (5.9 mL) through the septum of the flask using a syringe. The addition of methyl iodide was continued at a rate of 1 mL/min to maintain a gentle reflux. After the addition was completed, the reaction mixture was allowed to cool to ambient temperature. The brownish reaction mixture was allowed to stand until the remaining magnesium turnings was settled, then the supernatant was transferred via a cannula through the septum into a 100 mL round-bottomed flask equipped with argon inlet, a large Teflon-coated magnetic stir bar, and a rubber septum. The magnesium turnings were rinsed with diethyl ether (4.2 mL) and transferred to the reaction flask via a cannula, and the solution was cooled to 0 °C. A solution of 5-bromo-2-iodobenzoic acid methyl ester (7.30 g, 21.4 mmol, 1.00 eq.) in diethyl ether (3.4 mL) was added dropwise under vigorous stirring over 10 min. The reaction mixture was left in the cooling bath and allowed to warm to ambient temperature for 18 hours. The reaction mixture was treated carefully with a saturated NH_4Cl aq. (25 mL). A thick yellow precipitate was formed and water (2 × 25 mL) was added until most of the solid material dissolved, and then the yellow suspension was filtered through a pad of celite. The organic phase was separated from the aqueous phase, and the aqueous phase was extracted with diethyl ether (4 ×35 mL). The combined ethereal phases were dried over potassium carbonate, filtered, the solvent was evaporated and the residue is dried under vacuum. The residue was purified by column chromatography (Hex : EtOAc = 10 : 1) to afford 5-bromo-2-iodo-α,α-dimethyl benzenemethanol (3.57 g, 49 %). Rf: 0.33 (Hex : EtOAc = 10 : 1). Physical state: Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.82 (m, 2 H), 7.04 (dd, *J* = 10.1, 1.9 Hz, 1 H), 2.32 (br s, 1 H), 1.75 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 143.9, 131.6, 130.0, 122.9, 91.0, 73.3, 29.4. HRMS (DART, positive) calcd for $C_9H_{11}BrIO$ $[M + H]^+$ 340.8960, Found 340.8932.

2-Iodo-α,α-dimethylbenzenemethanol: Following the Procedure B, 2-iodobenzoic acid methyl ester (5.32g, 20.3 mmol) was used. Purification by column chromatography (Hex : EtOAc = 10 : 1) to afford 2-iodo-α,α-dimethylbenzenemethanol (2.82 g, 53 %). Rf: 0.38 (Hex : EtOAc = 10 : 1). Physical state: pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.7 Hz, 1 H), 7.63 (dd, *J* = 8.2, 1.5 Hz, 1 H), 7.30-7.36 (m, 1 H), 6.88-6.93 (m, 1 H), 2.55 (br s, 1 H), 1.76 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 142.8, 128.7, 128.2, 126.8, 93.2, 73.6, 29.7. HRMS (IT-TOF, positive) calcd for $C_9H_{11}INaO$ $[M + Na]^+$ 284.9747, Found 284.9762.

Synthesis of 4-bromo-1-iodo-2-(1-methoxy-1-methylethyl)benzene (9b) (Procedure C)[22]: Sodium hydride (0.41g, 10.4 mmol, 1.77 eq.) was diluted with dry THF (7 mL), and 5-bromo-2-iodo-α,α-dimethylbenzenemethanol (2.0 g, 5.86 mmol, 1.0 eq.) in THF (7 mL) was slowly added under stirring. After the gas evolution ceased, methyl iodide (2.62 mL, 42.2 mmol, 7.2 eq.) was added and placed at 50 °C. After 2 days, the reaction mixture was diluted with diethyl ether and washed with water, then the organic phase was separated from the aqueous phase, and the aqueous phase was extracted with diethyl ether (3 × 30 mL). The combined ethereal phases were dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (Hex : EtOAc = 30 : 1) to afford **9b** (1.70 g, 82 %). Rf: 0.33 (Hex : EtOAc = 30 : 1). Physical state: Colorless solid. m.p.: 65.4-68.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.2 Hz, 1 H), 7.46 (d, *J* = 2.4 Hz, 1 H), 7.05 (dd, *J* = 8.2, 2.4 Hz, 1 H), 3.05 (s, 3 H), 1.65 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 144.5, 131.7, 131.5, 122.6, 91.0, 77.5, 50.4, 26.7. HRMS (DART, positive) calcd for $C_{10}H_{13}BrIO$ $[M + H]^+$ 354.9116, Found 354.9135.

1-Iodo-2-(1-methoxy-1-methylethyl)benzene (9a): Following the Procedure C, 2-iodo-α,α-dimethylbenzenemethanol (1.87 g, 7.13 mmol) was used. Purification by column chromatography (Hex : EtOAc = 30 : 1) to afford **9a** (1.38 g, 70 %). Rf: 0.47 (Hex : EtOAc = 30 : 1). Physical state: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.7 Hz, 1 H), 7.29-7.38 (m, 2 H), 6.88-6.94 (m, 1 H), 3.04 (s, 3 H), 1.67 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 143.3, 128.7, 128.4, 127.9, 93.2, 77.8, 50.3, 26.9. HRMS (IT-TOF, positive) calcd for $C_{10}H_{13}INaO$ $[M + Na]^+$ 298.9903, Found 298.9899.

Synthesis of 4-bromo-2-(1-methoxy-1-methylethyl)iodosylbenzene-trifluoroacetic acid complex (8b) (Procedure D)[23]: 4-Bromo-1-iodo-2-(1-methoxy-1-methylethyl)benzene (1.07 g, 3.0 mmol, 1.00 eq.) was dissolved in CH_2Cl_2 (4.5 mL), and CF_3CH_2OH (5.5 mL) and *m*CPBA (0.52 g, 2.25 mmol, 0.75 eq.) were added to the stirred solution and stirred 40 minutes, followed by the addition of TFA (0.34 g, 3.0 mmol, 1.00 eq.) in CH_2Cl_2 (1.0 mL). The resulting solution was stirred at room temperature for 4 hours, and the solvent was removed in vacuo. Diethyl ether was added to the resulting solid and the white solid was formed. The white solid was decanted with diethyl ether and dried under vacuum to afford **8b** (0.72g, 50%). The starting material **9b** was recovered by column chromatography (Hex : EtOAc = 30 : 1)(0.42 g, 40 %). Physical state: Colorless solid. m.p.: 117.3-120.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.7 Hz, 1 H), 7.71 (dd, *J* = 8.7, 1.9 Hz, 1 H), 7.46 (d, *J* = 1.9, 1 H), 3.56 (s, 3 H), 1.63 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7(q, *J* = 36.0 Hz), 145.8, 133.6, 130.5, 128.4, 125.8, 115.9 (q, *J* = 291.5 Hz), 110.2, 82.8, 51.4, 25.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ -75.5. HRMS (DART, positive) calcd for $C_{10}H_{13}BrIO_2^+$ 370.9138, Found 370.9146. Anal. calcd for $C_{12}H_{13}BrF_3IO_4$ H=2.70 %, C=29.72 %, Found H= 2.67%, C= 29.57 %

2-(1-methoxy-1-methylethyl)iodosylbenzene-trifluoroacetic acid complex (8a): Following the Procedure D, 1-iodo-2-(1-methoxy-1-methylethyl)benzene (0.55g, 2.0 mmol) was used. Decantation by diethyl ether at 0 °C to afford **8a** (0.49 g, 60 %). Physical state: Colorless solid. m.p.: 103.8-107.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.58-7.63 (m, 1 H), 7.48-7.53 (m, 1 H), 7.35 (dd, *J* = 7.7, 1.5 Hz, 1 H), 3.57 (s, 3 H), 1.64 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7 (q, *J* = 36.0 Hz), 143.7, 130.9, 130.7, 127.6, 126.5, 116.0 (q, *J* = 291.5Hz), 111.4, 83.2, 51.1, 25.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ -75.4. HRMS (DART, positive) calcd for $C_{10}H_{14}IO_2^+$ 293.0033, Found 293.0035.

Hydroxy[2-(1-methoxy-1-methylethyl)phenyl]iodonium *p*-toluenesulfonate (S1): Following the Procedure D, 1-iodo-2-(1-methoxy-1-methylethyl)benzene (55.2 mg, 0.2 mmol) and $TsOH•H_2O$ (38 mg, 0.2 mmol) were used. Decantation by diethyl ether at 0 °C and the solid was recrystallized from $CHCl_3/Et_2O$/Hexane at room temperature to afford **S1** (44.8 mg, 48 %). Physical state: Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.78 (d, *J* = 7.7 Hz, 2 H), 7.55 (td, *J* = 7.2, 1.5 Hz, 1 H), 7.47 (m, 1 H), 7.31 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 3.64 (s, 3 H), 2.33 (s, 3 H), 1.60 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 141.2, 140.3, 130.9, 130.8, 128.8, 127.4, 126.5, 126.1, 111.8, 83.7, 51.6, 25.1, 21.3. HRMS (IT-TOF, positive) calcd for $C_{10}H_{14}IO_2^+$ 293.0033, Found 293.0045.

Synthesis of 2-iodo-*N*,*N*-dimethylbenzamide (Procedure E)[24]: A 30 mL flask was charged with a magnetic stir bar, 2-iodobenzoic acid (0.49 g, 2.0 mmol, 1.0 eq.), $CuSO_4 \cdot 5H_2O$ (50 mg, 0.2 mmol, 0.1 eq.) and DMF (6 mL). TBHP in water (70 wt %) (0.772 mL, 6.0 mmol, 3.0 eq.) was added dropwise under stirring at room temperature for 10 min. The temperature was raised gradually to 85 °C and the reaction was stirred for overnight. The reaction mixture was then allowed to cool to room temperature, diluted with 20 mL of ethyl acetate and filtered. The filtrate was washed with excess water and extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude products which was purified by flash column chromatography (Hex : EtOAc = 2 : 1) to afford 2-iodo-*N*,*N*-dimethylbenzamide (0.35 g, 64 %). Rf: 0.20 (Hex : EtOAc = 2 : 1). Physical state: pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.85 (m, 1 H), 7.33-7.43 (m, 1 H), 7.15-7.24 (m, 1 H), 7.00-7.10 (m, 1 H), 3.13 (s, 3 H), 2.84 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 142.7, 138.9, 130.0, 128.3, 126.9, 92.3, 38.3, 34.6. HRMS (DART, positive) calcd for $C_9H_{10}INO$ $[M + H]^+$ 275.9807, Found 275.9835.

Hydroxy[2-(*N*,*N*-dimethylaminocarbonyl)phenyl]iodonium trifluoroacetate (S2): Following the Procedure D, 2-iodo-*N*,*N*-dimethylbenzamide (0.055g, 0.2 mmol) was used. The crude solid was dissolved in diethyl ether and then hexane was added to form the solid. The solid was collected and recrystallized from $CHCl_3$/Hexane at -30 °C to afford **S2** (11.4 mg, 18 %). Physical state: Colorless solid. m.p.: 107.2-107.8. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.0 Hz, 1 H), 8.06 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.89 (td, *J* = 8.6, 1.2 Hz, 1 H), 7.65-7.73 (m, 1 H), 3.00-3.80 (br, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 163.0 (q, *J* = 34.8 Hz), 135.3, 131.3, 129.9, 128.9, 126.9, 122.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ -75.3. Anal. calcd for $C_{11}H_{11}F_3INO_4$ H=2.74 %, C=32.61 %, N= 3.46 %, Found H= 2.71%, C= 32.41 %, N= 3.41 %

(Methylsulfinyl)benzene (10): A solution of **8a** (60.9 mg, 0.15 mmol, 1.20 eq.) in MeCN (0.5 mL) was added to thioanisole (16 mg, 0.125 mmol, 1.00 eq.) in MeCN (0.5 mL). The reaction was stirred at room temperature for 30 minutes. The $Na_2S_2O_3$ aq. and saturated $NaHCO_3$ aq. were added, and the mixture was extracted with CH_2Cl_2. The organic phase was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography (Hex : EtOAc = 1 : 1) to afford **10** (16.2 mg, 92 %). Rf: 0.22 (Hex : EtOAc = 1 : 1)**.** Physical state: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.68 (m, 2 H), 7.49-7.57 (m, 3 H), 2.74 (s, 3 H)**.** ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 131.1, 129.4, 123.5, 43.9**.** HRMS (IT-TOF, positive) calcd for C_7H_8NaOS $[M + Na]^+$ 163.0188, Found 163.0161.

Triphenylphosphine oxide (11): A solution of **8a** (60.9 mg, 0.15 mmol, 1.20 eq.) in $CHCl_3$ (0.5 mL) was added to triphenyl phosphine (32.7 mg, 0.125 mmol, 1.00 eq.) in $CHCl_3$ (0.5 mL). The reaction was stirred at room temperature for 30 minutes. The solvent was removed in vacuo. Purification by column chromatography (Hex : EtOAc = 1 : 1 to EtOAc only) to afford **11** (30.5 mg, 88 %). Rf: 0.39 (Hex : EtOAc = 1: 1)**.** Physical state: Colorless solid**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.69 (m, 6 H), 7.46-7.52 (m, 3 H), 7.36-7.40 (m, 6 H)**.** ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.0, 132.2, 132.1, 132.0, 131.97, 131.95, 128.6, 128.5**.** HRMS (DART, positive) calcd for $C_{18}H_{16}OP$ $[M + H]^+$ 279.0861, Found 279.0864.

1,4-Naphthalenedione (12): To a stirred solution of 1-naphthol (14.4 mg, 0.1 mmol, 1.00 eq.) in MeCN (0.5 mL) and H_2O (0.5 mL), **8a** (89.3 mg, 0.22 mmol, 2.20 eq.) in MeCN (0.5 mL) was added at 0°C. The reaction was stirred at room temperature for 3 hours. The saturated $NaHCO_3$ aq. was added to the mixture and it was then extracted with EtOAc several times. The combined organic phases were washed with brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by preparative TLC (Hex : EtOAc = 10 : 1) to afford **12** (9.9 mg, 63 %). Rf: 0.56 (Hex : EtOAc = 10 : 1)**.** Physical state: Yellow solid**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.13 (m, 2 H), 7.75-7.82 (m, 2 H), 6.98-7.02 (m, 2H)**.** ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.1, 138.7, 134.0, 131.9, 126.5**.** HRMS (DART, positive) calcd for $C_{10}H_7O_2$ $[M + H]^+$ 159.0368, Found 159.03731.

2,3-Dihydro-1H-inden-1-one (13): To a stirred solution of 2,3-dihydro-1H-inden-1-ol (13.4 mg, 0.1 mmol, 1.00 eq.) and KBr (2.4 mg, 0.02 mmol, 0.2 eq.) in EtOAc (1.0 mL), **8a** (40.6 mg, 0.1 mmol, 1.00 eq.) was added at room temperature. The reaction was stirred for 24 hours. The resulting mixture was concentrated under reduced pressure. Purification by preparative TLC (Hex : EtOAc = 10 : 1) to afford **13** (10.3 mg, 78 %). Rf: 0.38 (Hex : EtOAc = 10 : 1)**.** Physical state: Colorless oil**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.7 Hz, 1 H), 7.56-7.62 (m, 1 H), 7.49 (dd, *J* = 7.7, 1.0 Hz, 1 H), 7.35-7.40 (m, 1 H), 3.16 (t, *J* = 6.0 Hz, 2H), 2.66-2.72 (m, 2H)**.** ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 155.2, 137.11, 134.6, 127.3, 126.7, 123.8, 36.2, 25.7**.** HRMS (IT-TOF, positive) calcd for C_9H_8NaO $[M + Na]^+$ 155.0467, Found 155.0447.

3,5-Diphenyl-1,2,4-thiadiazole (14): Benzthioamide (17.2 mg, 0.125 mmol, 1.00 eq.) was added to a solution of **8a** (81.2 mg, 0.2 mmol, 1.60 eq.) in MeCN (1 mL). The reaction was stirred at room temperature for 4 hours. The $Na_2S_2O_3$ aq. and saturated $NaHCO_3$ aq. were added, and the mixture was extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuo and the residue was purified by preparative TLC (Hex : EtOAc = 50 : 1) to afford **14** (7.1 mg, 48 %). Rf: 0.31 (Hex : EtOAc = 50: 1)**.** Physical state: Colorless solid**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (dd, *J* = 7.7, 2.4 Hz, 2 H), 8.06 (dd, *J* = 7.2, 1.9 Hz, 2 H), 7.46-7.58 (m, 6 H)**.** ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.2, 173.9, 132.9, 132.0, 130.8, 130.4, 129.3, 128.7, 128.4, 127.5**.** HRMS (DART, positive) calcd for $C_{14}H_{11}N_2S$ $[M + H]^+$ 239.0565, Found 239.0540.

2,3-Dihydro-5-methoxy-2-(4-methoxyphenyl)benzofuran (15): To an ice-cooled solution of 4-methoxyphenol (24.8 mg, 0.2 mmol, 1.00 eq.) and 4-methoxystyrene (26.8 mg, 0.2 mmol, 1.00 eq.) in MeCN (0.25 mL), **8a** (121.8 mg, 0.3 mmol, 1.50 eq.) in MeCN (0.5 mL) was added in one portion at room temperature. The reaction was stirred for 1 hour and then it was quenched with solid sodium hydrogen carbonate. After filtration, the solvent was removed in vacuo and the residue was purified by column chromatography (Hex : EtOAc = 10 : 1) to afford **15** (21.1 mg, 41 %). Rf: 0.48 (Hex : EtOAc = 10 : 1)**.** Physical state: Colorless solid**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.2 Hz, 2 H), 6.90 (d, *J* = 8.7 Hz, 2 H), 6.66-6.80 (m, 3 H), 5.68 (t, *J* = 8.7 Hz, 1 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 3.54 (dd, *J* = 15.5, 9.2 Hz, 1 H), 3.19 (dd, *J* = 15.5, 8.2 Hz, 1 H)**.** ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 154.2, 153.8, 133.9, 127.7, 127.3, 114.0, 112.9, 111.2, 109.2, 84.1, 56.0, 55.2, 38.6**.** HRMS (DART, positive) calcd for $C_{16}H_{17}O_3$ $[M + H]^+$ 257.1099, Found 257.1088.

2,3-Dihydro-5-phenyl-2-flanone (16): To a stirred suspension of 4-phenylbutyric acid (16.4 mg, 0.1 mmol, 1.00 eq.) and KBr (11.9 mg, 0.1 mmol, 1.00 eq.) in dry CH_2Cl_2 (0.5 mL), **8a** (48.7 mg, 0.12 mmol, 1.20 eq.) in dry CH_2Cl_2 (0.5 mL) was added at room temperature and vigorously stirred for 14 hours. After completion of the reaction, saturated $NaHCO_3$ aq. was added to the mixture and then stirred for additional 5 minutes. The organic layer was separated, washed with $NaHCO_3$ aq., $Na_2S_2O_3$ aq. and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuo and the residue was purified by preparative TLC (Hex : EtOAc = 5 : 1) to afford **16** (8.6 mg, 53 %). Rf: 0.14 (Hex : EtOAc = 5 : 1)**.** Physical state: Colorless oil**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.44 (m, 5 H), 5.52 (t, *J* = 7.0 Hz, 1 H), 2.63-2.72 (m, 3 H), 2.14-2.28 (m, 1 H)**.** ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 139.4, 128.8, 128.5, 125.3, 81.2, 30.9, 28.9**.** HRMS (DART, positive) calcd for $C_{10}H_{11}O_2$ $[M + H]^+$ 163.0681, Found 163.0689.

[2-(1-methoxy-1-methylethyl)phenyl] (2,4,6-Trimethoxyphenyl) iodonium trifluoroacetate (17): 1,3,5-Trimethoxybenzene (16.8 mg, 0.1 mmol, 1.00 eq.) was added to a solution of **8a** (40.6 mg, 0.1 mmol, 1.00 eq.) in CF_3CH_2OH. The reaction mixture was stirred at room temperature for 24 hours. The mixture was evaporated under reduced pressure and the crude oil was decanted with diethyl ether several times at room temperature and then dried in vacuum to afford **17** (47.8 mg, 86 %). Physical state: Colorless solid**.** m.p: 171.8-174.0 °C**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.43 (m, 2 H), 7.12-7.15 (td, *J* = 7.4, 1.7 Hz 1H), 6.98 (d, *J* = 8.0 Hz, 1 H), 6.26 (s, 2 H), 3.91 (s, 3 H), 3.86 (s, 6 H), 3.57 (s, 3 H), 1.67 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.2, 161.1, 160.9 (q, *J* = 32.4 Hz), 145.4, 130.3, 130.2, 129.3, 128.1, 117.0 (q, *J* = 296.3 Hz), 110.4, 91.6, 84.8, 79.2, 56.93, 56.91, 55.91, 55.89, 50.0, 25.4**.** ^{19}F NMR (470 MHz, $CDCl_3$): δ -74.8. HRMS (DART, positive) calcd for $C_{19}H_{24}IO_4^+$ 443.0714, Found 443.0707.

Keywords: iodosylbenzene • trifluoroacetic acid • pseudocyclic • coordination • oxidation

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[14] Crystallographic data for **8b**: $C_{12}H_{13}BrF_3IO_4$, *Mr* = 485.03, *T* = 173 K, monoclinic, space group $P2_1/c$, *a* = 16.403(6) Å, *b* = 11.229(4) Å, *c* = 17.248(6) Å, β = 93.877(4)°, *V* = 3169.7(19) Å^3, *Z* = 8, μ (Mo *K*α) = 4.58 mm^{-1}. 7271 reflections were collected. *R* = 0.082, *wR* = 0.223, GOF = 1.097. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: deposition number CCDC-1569951.

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[16] The IR experiment also suggests that the character of H···O bond of **8b** is different from H-O bonds of other hydroxy iodonium because it has peak of 2283 cm^{-1} instead of around 2400 cm^{-1} of other hydroxy iodonium; see supporting information.

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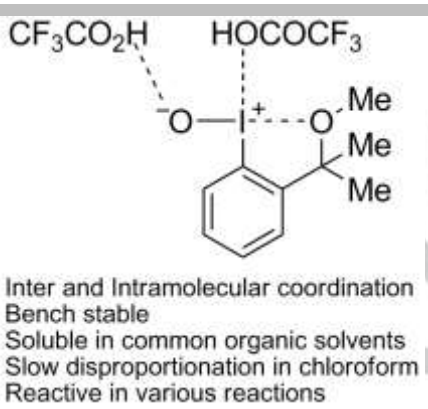
An *ortho*-substituted ether-oxygen-coordinated pseudocyclic iodosylbenzene–trifluoroacetic acid (pcISB-TFA) complex was synthesized and characterized by X-ray crystallographic analysis. TFA suppresses the disproportionation by both coordination of the oxygen atom to the iodine (III) center through secondary bonding and hydrogen bonding to the oxygen anion.



Hypervalent iodine

Masaharu Yudasaka, Toshifumi Maruyama, Eiji Yamaguchi, Norihiro Tada, Akichika Itoh**

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Synthesis, Characterization, and Reaction of a Both Inter- and Intramolecularly Coordinated Pseudocyclic Iodosylbenzene–Trifluoroacetic Acid Complex