Supporting Information

Preparation and Structure of Phenolic Aryliodonium Salts

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1. General experimental remarks

All reactions were performed under dry argon atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane and acetonitrile were distilled from CaH$_2$ immediately prior to use. Diethyl ether was distilled from Na/benzophenone. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded as a KBr pellet on a Perkin-Elmer 1600 series FT-IR spectrophotometer. $^1$H NMR spectra were recorded on a Varian Inova 500 and 300 MHz NMR spectrometer; $^{13}$C NMR spectra were recorded on Varian Inova 500 and Varian 300 MHz NMR spectrometers at 125 and 75 MHz, respectively. Chemical shifts are reported in parts per million (ppm). $^1$H and $^{13}$C chemical shifts are referenced relative to tetramethylsilane. Triisopropylsilox benzene 1a$^1$, tert-butyldimethylsilox benzene 1b$^2$, tert-butyldiphenylsilox benzene 1c$^3$, triisopropyl(2-tolyloxy)silane 1f$^4$, and (2-chlorophenoxy)triisopropylsilane 1g$^5$ were prepared according to the reported procedures. Various hydroxy(tosyloxy)iodoarenes 5 (5a,c,e,g,h,i$^6$, 5b$^7$, 5f$^8$, 5j$^9$, 5k$^{10}$, 5l$^{11}$) were prepared according to the reported procedures.

2. Preparation of hydroxy(tosyloxy)iodoarenes

3,5-Dimethyl[hydroxy(tosyloxy)iodo]benzene (5d)

\[
\text{HO} \quad \uparrow \quad \text{Ots} \\
\text{Me} \quad \uparrow \quad \text{Me}
\]

1-Iodo-3,5-dimethyliodobenzene (232mg, 1.0 mmol) was added at room temperature to a stirred mixture of $p$-TsOH•H$_2$O (190 mg, 1.0 mmol) and m-CPBA (173 mg, 1.0 mmol) in dichloromethane (4.0 mL)–2,2,2-trifluoroethanol (4.0 mL). The reaction was stirred at room temperature for 30 minute. After reaction, the mixture was evaporated under reduced pressure, and the crude mixture was washed with diethyl ether several times and
then dried in vacuum to give the 3,5-dimethyl[hydroxy(tosyloxy)iodo]benzene **5d**, 328 mg (78%) isolated as a yellow solid: mp 137.8-138.6 °C; IR (KBr) cm⁻¹ 3450, 2956, 2917, 2856, 1603, 1460, 1310, 1188, 1045; \(^1\)H NMR (500 MHz, CD₃OD): δ 7.93 (s, 2H), 7.64 (d, \(J = 7.8\) Hz, 2H), 7.42 (s, 1H), 7.21 (d, \(J = 7.8\) Hz, 2H), 2.39 (s, 6H), 2.35 (s, 3H); \(^{13}\)C NMR (125 MHz, CD₃OD): δ 141.9, 141.5, 135.0, 132.9, 128.4, 125.5, 120.4, 19.9, 19.8; HRMS (ESI-TOF-positive mode): calcd for C₈H₁₀IO ([M-OTs]⁺): 248.977, found: 248.9775.

**4-Acetoxy[hydroxy(tosyloxy)iodo]benzene (7)**

![Chemical structure](image)

1-Acetoxy-4-iodobenzene (1572mg, 6.00 mmol) was added at room temperature to a stirred mixture of p-TsOH•H₂O (1198 mg, 6.30 mmol) and m-CPBA (1170 mg, 6.78 mmol) in dichloromethane(14.0 mL). The reaction was stirred at room temperature for 2 hours. After reaction, the mixture was evaporated under reduced pressure, and the crude mixture was washed with diethyl ether several times and then dried in vacuum to give the 4-acetoxy[hydroxy(tosyloxy)iodo]benzene **7**, 2101 mg (78%) isolated as a white solid: mp 83.4-83.5 °C; IR (KBr) cm⁻¹ 3419, 3163, 3039, 3023, 2932, 1771, 1481, 1246, 1191, 1045; \(^1\)H NMR (500 MHz, CD₃OD): δ 8.41 (d, \(J = 8.8\) Hz, 2H), 7.70 (d, \(J = 8.3\) Hz, 2H), 7.48 (d, \(J = 8.8\) Hz, 2H), 7.23 (d, \(J = 8.3\) Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H); \(^{13}\)C NMR (125 MHz, CD₃OD): δ 168.7, 154.9, 141.6, 140.5, 137.5, 128.4, 125.5, 125.1, 116.6, 19.9, 19.4; HRMS (APCI-positive mode): calcd for C₈H₁₀IO₃ ([M-OTs]⁺): 278.9518, found: 278.9491.

**3. Preparation of phenyl(4-triisopropylsiloxylphenyl)iodonium tosylate 3a**

Phenyl(4-triisopropylsiloxylphenyl)iodonium tosylate (3a)
Koser’s reagent 2a (392 mg, 1.0 mmol) was added at 0 °C to a stirred mixture of (triisopropylsiloxy)benzene 1a (300 mg, 1.2 mmol) in 2,2,2-trifluoroethanol (2.0 mL). The reaction was stirred at room temperature for 24 hour. After completion of reaction, the solvent was removed under reduced pressure to give solid residue. Then diethyl ether was added to solid residue to prepare the suspended solution, which was filtered, washed with diethyl ether several times, and dried in vacuum to give product the desired phenyl(4-triisopropylsiloxyphenyl)iodonium tosylate 3a; 545 mg (87%) isolated as a white solid: mp 135.2-135.4 °C; IR (KBr) cm\(^{-1}\) 3456, 3076, 3060, 2959, 2894, 2868, 1576, 1484, 1272, 1232, 1167, 1036, 755; \(^1\)H NMR (500 MHz, CD\(_3\)OD): \(\delta\) 7.92 (d, \(J = 7.0\) Hz, 2H), 7.81 (d, \(J = 8.5\) Hz, 2H), 7.53-7.40 (m, 3H), 7.34-7.23 (m, 2H), 7.04-6.95 (m, 2H), 6.83-6.73 (m, 2H), 2.27 (s, 3H), 1.28-1.16 (m, 3H), 1.10-1.01 (m, 18H); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD): \(\delta\) 159.2, 142.8, 139.0, 137.3, 134.7, 131.3, 131.2, 128.3, 125.9, 123.1, 116.0, 104.4, 21.2, 17.7, 12.5; HRMS (ESI-positive mode): calcd for C\(_{21}\)H\(_{30}\)IO\(_2\)Si (\([\text{M-OTs}]^+\))\(^+\): 453.1111, found: 453.1120.

4. **Preparation of Phenolic (Aryl)iodonium Triflates 4**

Hydroxy(tosyloxy)iodoarenes 2 (0.5-2.0 mmol) was added at 0 °C to a stirred mixture of (triisopropylsiloxy)benzene 1a (0.6-2.4 mmol) in 2,2,2-trifluoroethanol (1.0-4.0 mL). The reaction was stirred at room temperature for 24 hour. After the reaction, the mixture was evaporated under reduced pressure, and then trifluoromethanesulfonic acid (113 mg to 452 mg) and acetonitrile (0.50 mL to 2.0 mL) was added at 0 °C to the crude reaction mixture. The reaction was stirred at 0 °C for 2 hours. After completion of reaction, the solvent was removed under reduced pressure to give solid residue. Then diethyl ether was added to solid residue to prepare the suspended solution, which was filtered, washed with diethyl ether several times, and dried in vacuum to give the desired diaryliodonium triflate salts 4a.
Phenyl(4-hydroxyphenyl)iodonium trflate (4a)

Reaction of Koser’s reagent 2a (784 mg, 2.0 mmol) according to the general procedure afforded 864 mg (97%) of product 4a, isolated as a white solid: mp 156.4-157.8 °C (decomp.); IR (KBr) cm⁻¹ 3268, 3099, 3069, 1597, 1576, 1487, 1431, 1284, 1241, 1206, 637; ¹H NMR (500 MHz, CD₃OD): δ 8.09 (d, J = 7.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.56-7.47 (m, 2H), 6.89 (d, J = 8.0 Hz, 2H); ¹³C NMR (75 MHz, CD₃OD): δ 161.9, 137.6, 134.7, 132.2, 120.6 (q, JCF = 318.0 Hz), 119.1, 115.3, 101.3. ¹⁹F NMR (470 MHz, CD₃OD): δ -80.1; Anal. Calcd for C₁₂H₁₀F₃IO₄: C, 35.00; H, 2.26; I, 28.44; S, 7.19. Found: C, 34.79; H, 2.29; I, 28.20; S, 7.44. HRMS (ESI-TOF-positive mode): calcd for C₁₂H₁₀IO ([M-OTf]⁺): 296.9776, found: 296.9784.

Phenyl(4-hydroxyphenyl)iodonium tosylate (4b)

Reaction of Koser’s reagent 2a (392 mg, 1.0 mmol) according to the general procedure for 24 hour stirring using p-TsOH·H₂O (571 mg, 3.0 mmol) instead of TfOH afforded 187 mg (62%) of product 4b, isolated as a white solid: mp 151.4-151.7 °C (decomp.); IR (KBr) cm⁻¹ 3219, 3094, 3067, 2999, 2920, 1593, 1568, 1474, 1445, 1286, 1218, 1032, 813, 681; ¹H NMR (500 MHz, CD₃OD): δ 8.09 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.55-7.49 (m, 1H), 7.23 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 2.37 (s, 3H); ¹³C NMR (75 MHz, CD₃OD): δ 161.7, 142.2, 140.2, 137.4, 134.4, 131.9, 131.6, 128.4, 125.5, 118.8, 115.1, 101.1, 19.9; HRMS (ESI-TOF-positive mode): calcd for C₁₂H₁₀IO ([M-OTs]⁺): 296.9776, found: 296.9796.

Phenyl(4-hydroxyphenyl)iodonium bromide (4c)
Reaction of Koser’s reagent 2a (392 mg, 1.0 mmol) according to the general procedure afforded the crude 4a compound. Then KBr (1190 mg, 10 mmol) was added at room temperature to a stirred mixture of crude mixture 4a in water (3 mL). The reaction was stirred at room temperature for 2 hour. After completion of reaction, the mixture was filtrated and washed with diethyl ether several times and then dried in vacuum to give the desired diaryliodonium bromide salt 4c; 312 mg (83%) isolated as a white solid: mp 180.5-180.6 °C; IR (KBr) cm⁻¹ 3180, 3044, 3004, 1593, 1576, 1489, 1429, 1281, 738, 647; ¹H NMR (500 MHz, CD₃OD): δ 8.13 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 9.0 Hz, 2H), 7.69 (t, J = 7.3 Hz, 1H), 7.57-7.51 (m, 2H), 6.91 (d, J = 9.0 Hz, 2H); ¹³C NMR (75 MHz, CD₃OD): δ 161.6, 137.3, 134.4, 131.9, 131.6, 118.8, 115.7, 101.7; Anal. Calcd for C₁₂H₁₀BrIO: C, 38.23; H, 2.67; I, 33.66. Found: C, 38.17; H, 2.52; I, 33.38. HRMS (ESI-TOF-positive mode): calcd for C₁₂H₁₀IO ([M-Br]⁺): 296.9771, found: 296.9797.

Single crystals of product 4c suitable for X-ray crystallographic analysis were obtained by slow crystallization from the methanol-acetonitrile solution. X-ray diffraction data for 4c were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 123 K. The structure was solved by the Sir 2011¹² and refined by full-matrix least-squares refinement on F² using SHELXL-2014/7.¹³ Crystal data for 4c C₁₂H₁₀BrIO: M 377.01, monoclinic, space group C2/c, a = 21.7877(8), b = 5.8060(2), c = 19.4890(14) Å, α = 90, β = 100.565(8), γ = 90 o, V = 2423.6(2) Å³, Z = 8, 6797 reflections measured, 2139 unique, 1679 I>2σ; final R₁ =
5. Preparation of Phenolic (Aryl)iodonium Triflates 6

Hydroxy(tosyloxy)iodoarenes 2a or 5 (0.5-2.0 mmol) was added at 0 °C to a stirred mixture of (triisopropylsiloxy)benzenes 1 (0.6-2.4 mmol) in 2,2,2-trifluoroethanol (1.0-4.0 mL). The reaction was stirred at room temperature for 24 hour. After the reaction, the mixture was evaporated under reduced pressure, and then trifluoromethanesulfonic acid (113 mg to 452 mg) and acetonitrile (0.50 mL to 2.0 mL) was added at 0 °C to the crude reaction mixture. The reaction was stirred at 0 °C for 2 hours. After completion of reaction, the solvent was removed under reduced pressure to give solid residue. Then diethyl ether was added to solid residue to prepare the suspended solution, which was filtered, washed with diethyl ether several times, and dried in vacuum to give the desired diaryliodonium triflate salts 6.

ortho-Tolyl(4-hydroxyphenyl)iodonium triflate (6a)

Reaction of Koser’s reagent 5a (203 mg, 0.5 mmol) according to the general procedure afforded 204 mg (89%) of product 6a, isolated as a white solid: mp 203.4-203.6 °C (decomp.); IR (KBr) cm⁻¹ 3295, 3100, 3057, 1594, 1576, 1488, 1430, 1287, 1241, 1207, 1024, 752, 635; ¹H NMR (500 MHz, CD₃OD): δ 8.23 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 9.0 Hz, 2H), 7.62-7.53 (m, 1H), 7.34-7.27 (m, 1H), 6.88 (d, J = 9.0 Hz, 2H), 2.67 (s, 3H); ¹³C NMR (75 MHz, CD₃OD): δ 161.5, 140.8, 137.1, 136.7, 132.9, 131.4, 129.2, 120.4 (q, ¹J_CF = 316.5 Hz), 120.0, 100.4, 24.1 ¹⁹F NMR (282 MHz, CD₃OD): δ -80.0; HRMS (ESI-TOF-positive mode): calcd for C₁₃H₁₂IO ([M-OTf]⁺): 310.9933, found: 310.9923.

meta-Tolyl(4-hydroxyphenyl)iodonium triflate (6b)
Reaction of Koser’s reagent 5b (406 mg, 1.0 mmol) according to the general procedure afforded 445 mg (97%) of product 6b, isolated as a white solid: mp 157.7-157.9 °C (decomp.); IR (KBr) cm⁻¹ 3284, 3097, 3063, 2934, 1601, 1576, 1488, 1432, 1283, 1240, 1208, 1023, 787, 636; ¹H NMR (500 MHz, CD₃OD): δ 8.00-7.93 (m, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.42-7.36 (m, 1H), 6.89 (d, J = 8.5 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (75 MHz, CD₃OD): δ 161.6, 142.6, 137.4, 134.6, 132.7, 131.5, 131.3, 120.4 (q, ¹JCF = 316.7 Hz), 118.8, 114.9, 101.0, 19.8. ¹⁹F NMR (282 MHz, CD₃OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for C₁₃H₁₂IO ([M-OTf]⁺): 310.9933, found: 310.9949.

*para*-Tolyl(4-hydroxyphenyl)iodonium triflate (6c)

Reaction of Koser’s reagent 5c (406 mg, 1.0 mmol) according to the general procedure afforded 433 mg (94%) of product 6c, isolated as a white solid: mp 155.4-155.6 °C; IR (KBr) cm⁻¹ 3271, 3100, 3073, 2929, 1600, 1578, 1478, 1432, 1283, 1240, 1207, 836, 799, 637; ¹H NMR (500 MHz, CD₃OD): δ 7.96 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (75 MHz, CD₃OD): δ 161.6, 143.4, 137.2, 134.4, 132.3, 120.4 (q, ¹JCF = 317.1 Hz), 118.8, 111.4, 101.3, 19.9. ¹⁹F NMR (282 MHz, CD₃OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for C₁₃H₁₂IO ([M-OTf]⁺): 310.9933, found: 310.9945.

3,5-Dimethyl-phenyl(4’-hydroxyphenyl)iodonium triflate (6d)
Reaction of Koser’s reagent 5d (420 mg, 1.0 mmol) according to the general procedure afforded 407 mg (86%) of product 6d, isolated as a white solid: mp 151.7-152.0 °C (decomp.); IR (KBr) cm⁻¹ 3294, 3182, 3090, 2926, 1597, 1576, 1489, 1435, 1291, 1237, 1210, 784, 637; ¹H NMR (500 MHz, CD₃OD): δ 7.95 (d, J = 9.0 Hz, 2H), 7.73 (s, 2H), 7.32 (s, 1H), 6.89 (d, J = 9.0 Hz, 2H), 2.35 (s, 6H); ¹³C NMR (75 MHz, CD₃OD): δ 161.6, 142.2, 137.3, 133.6, 131.7, 118.8, 114.7, 100.9, 19.7. ¹⁹F NMR (282 MHz, CD₃OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for C₁₄H₁₄IO ([M·OTf]⁺): 325.0089, found: 325.0095.

2,4,6-trimethyl-phenyl(4’-hydroxyphenyl)iodonium triflate (6e)

Reaction of Koser’s reagent 5e (434 mg, 1.0 mmol) according to the general procedure afforded 433 mg (89%) of product 6e, isolated as a white solid: mp 172.0-172.2 °C (decomp.); IR (KBr) cm⁻¹ 3271, 3100, 3027, 2923, 1578, 1489, 1437, 1275, 1239, 1030, 764, 640; ¹H NMR (500 MHz, CD₃OD): δ 7.76 (d, J = 9.0 Hz, 2H), 7.21 (s, 2H), 6.87 (d, J = 9.0 Hz, 2H), 2.67 (s, 6H), 2.35 (s, 3H); ¹³C NMR (75 MHz, CD₃OD): δ 161.3, 144.1, 141.8, 136.3, 129.8, 121.4, 120.4 (q, ¹JCF = 317.1 Hz), 118.9, 99.3, 25.5, 19.6. ¹⁹F NMR (282 MHz, CD₃OD): δ -80.0; HRMS (ESI-TOF-positive mode): calcd for C₁₅H₁₆IO ([M·OTf]⁺): 339.0240, found: 339.0256.

m-Metoxy-phenyl(4’-hydroxyphenyl)iodonium triflate (6f)
Reaction of Koser’s reagent 5f (422 mg, 1.0 mmol) according to the general procedure afforded 364 mg (76%) of product 6f, isolated as a light pink solid: mp 151.4-151.7 °C (decomp.); IR (KBr) cm⁻¹ 3278, 3094, 3066, 2974, 2943, 1590, 1576, 1480, 1430, 1283, 1245, 1024, 637; ¹H NMR (500 MHz, CD₃OD): δ 7.98 (d, J = 8.5 Hz, 2H), 7.68 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.45-7.39 (m, 1H), 7.21 (dd, J = 8.8 Hz, 2.3 Hz, 1H), 6.90 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H); ¹³C NMR (75 MHz, CD₃OD): δ 161.7, 161.3, 137.4, 132.2, 126.2, 120.4 (q, JCF = 317.0 Hz), 119.7, 118.8, 117.9, 114.8, 101.1, 55.1; ¹⁹F NMR (282 MHz, CD₃OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for C₁₃H₁₂IO₂ ([M-OTf]⁺): 326.9882, found: 326.9888.

*p-Metoxy-phenyl(4’-hydroxyphenyl)iodonium triflate (6g)*

![Structure Image]

Reaction of Koser’s reagent 5g (422 mg, 1.0 mmol) according to the general procedure afforded 137 mg (29%) of product 6g, isolated as a light brown solid: mp 138.1-138.4 °C (decomp.); IR (KBr) cm⁻¹ 3262, 3100, 3070, 2969, 2932, 1590, 1577, 1488, 1432, 1284, 1265, 1241, 1208, 1026, 638; ¹H NMR (300 MHz, CD₃OD): δ 8.01 (d, J = 9.3 Hz, 2H), 7.93 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 9.3 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H); ¹³C NMR (75 MHz, CD₃OD): δ 162.9, 161.5, 137.0, 136.6, 120.4 (q, JCF = 315.9 Hz), 118.7, 117.3, 103.7, 101.8, 54.9; ¹⁹F NMR (282 MHz, CD₃OD): δ -80.2; HRMS (ESI-TOF-positive mode): calcd for C₁₃H₁₂IO₂ ([M-OTf]⁺): 326.9882, found: 326.9873.

*p-Chloro-phenyl(4’-hydroxyphenyl)iodonium triflate (6h)*

![Structure Image]

Reaction of Koser’s reagent 5h (427 mg, 1.0 mmol) according to the general procedure
afforded 468 mg (97%) of product 6h, isolated as a light pink solid: mp 158.7-159.0 °C (decomp.); IR (KBr) cm⁻¹ 3271, 3110, 3098, 3070, 1598, 1578, 1488, 1433, 1284, 1242, 1206, 1092, 638; ¹H NMR (500 MHz, CD₃OD): δ 8.07 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H); ¹³C NMR (75 MHz, CD₃OD): δ 161.8, 138.6, 137.5, 136.1, 131.7, 120.4 (q, J_CF = 316.3 Hz), 118.9, 112.5, 111.4. ¹⁹F NMR (282 MHz, CD₃OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for C₁₂H₉IClO₃ ([M-OTf]⁺): 330.9387, found: 330.9392.

**p-Nitro-phenyl(4-hydroxyphenyl)iodonium triflate (6i)**

![Structure](structure.png)

Reaction of Koser’s reagent 5i (437 mg, 1.0 mmol) according to the general procedure afforded 385 mg (78%) of product 6i, isolated as a light brown solid: mp 163.4-163.7 °C; IR (KBr) cm⁻¹ 3291, 3109, 3060, 3023, 1603, 1579, 1534, 1487, 1440, 1362, 1287, 1223, 852, 637; ¹H NMR (500 MHz, CD₃OD): δ 8.31 (s, 4H), 8.04 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H); ¹³C NMR (75 MHz, CD₃OD): δ 162.0, 150.0, 137.9, 135.6, 125.9, 120.8, 120.4 (q, J_CF = 318.2 Hz), 119.1, 101.1. ¹⁹F NMR (282 MHz, CD₃OD): δ -80.0; HRMS (ESI-TOF-positive mode): calcd for C₁₂H₉INO₃ ([M-OTf]⁺): 341.9627, found: 341.9644.

**2-Thiophene(4’-hydroxyphenyl)iodonium triflate (6j)**

![Structure](structure.png)

Reaction of Koser’s reagent 5j (284 mg, 1.0 mmol) according to the general procedure afforded 246 mg (54%) of product 6j, isolated as a light brown solid: mp 141.3-141.5 °C (decomp.); IR (KBr) cm⁻¹ 3301, 3098, 3073, 1598, 1576, 1487, 1432, 1286, 1243, 1204, 637; ¹H NMR (300 MHz, CD₃OD): δ 7.98 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 3.6 Hz, 1H), 7.86 (d, J = 5.4 Hz, 1H), 7.20-7.12 (m, 1H), 6.88 (d, J = 8.3 Hz, 2H); ¹³C NMR (75 MHz,
Single crystals of product 6j suitable for X-ray crystallographic analysis were obtained by slow crystallization from the acetonitrile-methanol solution. X-ray diffraction data for 6j were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at at 173 K. The structure was solved by Sir 2004 and refined by full-matrix least-squares refinement on F² using SHELXL-2014/7. Crystal data for 6j C₁₁H₈F₃I₂O₆S₂: M 452.19, monoclinic, space group P2₁/c, a = 12.4345(7), b = 10.6515(7), c = 12.6308(9) Å, α = 90, β = 115.594(8), γ = 90 o, V = 1508.75(19) Å³, Z = 4, 13623 reflections measured, 3454 unique, 2720 I>2σ; final R₁ = 0.0321, Rw = 0.0732, S = 1.058. CCDC-1855607.

2-Thiophene(4’-hydroxyphenyl)iodonium bromide (6k)

Reaction of 6j (113 mg, 0.25 mmol) was added to a stirred mixture of KBr (298 mg, 2.5 mmol) in water (1.5 mL). The reaction was stirred at room temperature for 2 hour. After completion of reaction, the mixture was filtrated and washed with diethyl ether several times and then dried in vacuum to give the desired diaryliodonium bromide salt 6k; 44
mg (46%) isolated as a white solid: mp 186.8-187.3 °C; IR (KBr) cm⁻¹ 3198, 3096, 3087, 3048, 1594, 1576, 1489, 1429, 1283, 643; ¹H NMR (500 MHz, CD₃OD): δ 7.98 (d, J = 8.9 Hz, 2H), 7.92 (d, J = 3.3 Hz, 1H), 7.84 (d, J = 5.1 Hz, 1H), 7.18 (m, 1H), 6.87 (d, J = 8.9 Hz, 2H); ¹³C NMR (75 MHz, CD₃OD): δ 161.5, 139.6, 136.7, 136.3, 129.2, 118.6, 105.0, 99.7; HRMS (APCI-positive mode): calcd for C₁₀H₈I₂O₅ ([M-Br])⁺: 302.9341, found: 302.9318.

Single crystals of product 6k suitable for X-ray crystallographic analysis were obtained by slow crystallization from the methanol solution. X-ray diffraction data for 6k were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 173 K. The structure was solved by the Sir 2011¹² and refined by full-matrix least-squares refinement on F² using SHELXL-2014/7.¹³ Crystal data for 6k C₁₀H₈BrI₂O₅: M 383.03, monoclinic, space group C2/c, a = 22.0476(15), b = 5.6780(4), c = 18.9405(13) Å, α = 90, β = 100.965(7), γ = 90 °, V = 2327.8(3) Å³, Z = 8, 14785 reflections measured, 2663 unique, 1923 I>2σ; final R₁ = 0.0504, Rw = 0.1292, S = 1.100. CCDC-1855608.

3-Thiophene(4’- hydroxyphenyl)iodonium triflate (6l)

Reaction of Koser’s reagent 5k (284 mg, 1.0 mmol) according to the general procedure afforded 301 mg (67%) of product 6l, isolated as a white solid: mp 152.6-153.0 °C (decomp.); IR (KBr) cm⁻¹ 3298, 3115, 3100, 3083, 3072, 1600, 1576, 1487, 1432, 1284, 1240, 1208, 634; ¹H NMR (300 MHz, CD₃OD): δ 8.40 (d, J = 3.0 Hz, 1H), 7.96 (d, J =
8.7 Hz, 2H), 7.72-7.65 (m, 1H), 7.57 (d, J = 5.4 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H); $^{13}$C NMR (75 MHz, CD$_3$OD): δ 161.5, 137.1, 134.9, 130.7, 130.1, 120.4 (q, $^1J_{CF}$ = 315.9 Hz), 118.7, 102.1, 98.8. $^{19}$F NMR (282 MHz, CD$_3$OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcld for C$_{10}$H$_8$IOS ([M-Otf])$: 302.9341, found: 302.9332.

Single crystals of product 6l suitable for X-ray crystallographic analysis were obtained by slow crystallization from the acetonitrile-methanol solution. X-ray diffraction data for 6l were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation ($\lambda$ = 0.71073 Å) at 173 K. The structure was solved by Sir 2004$^{14}$ and refined by full-matrix least-squares refinement on $F^2$ using SHELXL-2014/7.$^{13}$ Crystal data for 6l C$_{11}$H$_8$F$_3$IO$_4$S$_2$: M 452.19, monoclinic, space group P2$_1$/c, a = 12.296(3), b = 10.711(2), c = 12.599(2) Å, α = 90, β = 115.117(8), γ = 90 °, V = 1502.5(5) Å$^3$, Z = 4, 18294 reflections measured, 3439 unique, 2897 I>2σ; final R$_1$ = 0.0259, Rw = 0.0552, S = 1.078. CCDC-1855609.

1-(4-hydroxyphenyl)-1H,3-benzo[d][1,2]iodoxol-3(1H)-one (6m)

Reaction of Koser’s reagent 5l (218 mg, 0.5 mmol) according to the general procedure afforded 126 mg (74%) of product 6m, isolated as a light brown solid: mp
169.4-169.9 °C (decomp.); IR (KBr) cm⁻¹ 3334, 3096, 2935, 2868, 1676, 1598, 1580, 1494, 1436, 1230, 634; \(^1\)H NMR (500 MHz, CD\(_3\)OD): \(\delta\) 8.39 (dd, \(J = 7.8\) Hz, 1.8 Hz, 1H), 8.00 (d, \(J = 9.0\) Hz, 2H), 7.78-7.67 (m, 2H), 7.08 (d, \(J = 8.0\) Hz, 1H), 7.07 (d, \(J = 9.0\) Hz, 2H); \(^{13}\)C NMR (75 MHz, CD\(_3\)OD): \(\delta\) 169.5, 162.7, 140.0, 136.3, 132.7, 131.0, 128.9, 119.4, 115.0, 96.6. HRMS (ESI-TOF-positive mode): calcd for C\(_{13}\)H\(_{10}\)IO\(_3\) ([M+H])\(^+\): 340.9675, found: 340.9692.

Single crystals of product 6m suitable for X-ray crystallographic analysis were obtained by slow crystallization from the acetonitrile-methanol solution. X-ray diffraction data for 6m were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoK\(\alpha\) radiation (\(\lambda = 0.71073\) Å) at 123 K. The structure was solved by Sir 2011\(^{12}\) and refined by full-matrix least-squares refinement on \(F^2\) using SHELXL-2014/7.\(^{13}\) Crystal data for 6m C\(_{13}\)H\(_9\)IO\(_3\): M 340.10, hexagonal, space group P6\(_2\), \(a = 15.5268(11), b = 15.5268(11), c = 16.7336(12)\) Å, \(\alpha = 90, \beta = 90, \gamma = 120\) o, \(V = 3493.7(6)\) Å\(^3\), \(Z = 12, 18294\) reflections measured, 3439 unique, 2897 I>2\(\sigma\); final \(R_1 = 0.0259, Rw = 0.0552, S = 1.078\). CCDC-1855610.

**4-Hydroxy-3-methylphenyl(phenyl)iodonium triflate (6n)**

Reaction of Koser’s reagent 2a (196 mg, 0.5 mmol) with triisopropyl(2-tolyloxy)silane 1f (159 mg, 0.6 mmol) according to the general procedure afforded 178 mg (77%) of product 6n, isolated as a light brown solid: mp 146.1-146.6 °C; IR (KBr) cm⁻¹ 3398, 3057,
2929, 1566, 1487, 1283, 1246, 1170, 638; $^1$H NMR (500 MHz, CD$_3$OD): $\delta$ 8.08 (d, $J = 9.0$ Hz, 2H), 7.89 (d, $J = 2.3$ Hz, 1H), 7.81 (dd, $J = 8.5, 2.3$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.54-7.49 (m, 2H), 6.84 (d, $J = 8.5$ Hz, 1H), 2.21 (s, 3H); $^{13}$C NMR (125 MHz, CD$_3$OD): $\delta$ 159.8, 137.5, 134.8, 134.4, 131.9, 131.6, 129.7, 120.4 (q, $^1$J$_{CF} = 316.9$ Hz), 117.4, 115.0, 100.8, 14.6 $^{19}$F NMR (470 MHz, CD$_3$OD): $\delta$ -80.1; HRMS (ESI-TOF-positive mode): calcd for C$_{13}$H$_{12}$IO ([M-OTf]$^+$): 310.9933, found: 310.9935.

3-Chloro-4-hydroxyphenyl(phenyl)iodonium triflate (6o)

Reaction of Koser’s reagent 2a (196 mg, 0.5 mmol) with (2-chlorophenoxy)triisopropylsilane 1g (171 mg, 0.6 mmol) according to the general procedure afforded 182 mg (76%) of product 6o, isolated as a white solid: mp 154.6 °C (decomp.); IR (KBr) cm$^{-1}$ 3302, 3084, 3063, 1566, 1479, 1445, 1283, 1241, 1187, 639; $^1$H NMR (500 MHz, CD$_3$OD): $\delta$ 8.21 (s, 1H), 8.14 (d, $J = 8.0$ Hz, 2H), 7.93 (d, $J = 9.3$ Hz, 1H), 7.69 (t, $J = 7.5$ Hz, 1H), 7.57-7.51 (m, 2H), 7.01 (d, $J = 9.3$ Hz, 1H); $^{13}$C NMR (125 MHz, CD$_3$OD): $\delta$ 157.5, 136.7, 135.5, 134.7, 132.2, 131.7, 123.3, 120.4 (q, $^1$J$_{CF} = 316.9$ Hz), 119.1, 115.3, 100.8. $^{19}$F NMR (470 MHz, CD$_3$OD): $\delta$ -80.1; HRMS (ESI-TOF-positive mode): calcd for C$_{13}$H$_9$ClIO ([M-OTf]$^+$): 330.9387, found: 330.9381.

3,5-Dimethylphenyl(4'-hydroxy-3'-methylphenyl)iodonium triflate (6p)

Reaction of Koser’s reagent 5d (210 mg, 0.5 mmol) with triisopropyl(2-tolyloxy)silane 1f (159 mg, 0.6 mmol) according to the general procedure afforded 182 mg (76%) of
product 60, isolated as a light purple solid: mp 136.9-137.0 °C; IR (KBr) cm⁻¹ 3311, 3199, 3067, 2929, 1575, 1492, 1453, 1283, 1171, 635; ¹H NMR (500 MHz, CD₃OD): δ 7.87 (s, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.72 (s, 2H), 7.31 (s, 1H), 6.84 (d, J = 8.5 Hz, 1H), 2.35 (s, 6H), 2.21 (s, 3H); ¹³C NMR (125 MHz, CD₃OD): δ 159.7, 142.2, 137.4, 134.7, 131.7, 129.6, 120.4 (q, JₙCF = 316.6 Hz), 117.3, 114.7, 100.6, 19.7, 14.6. ¹⁹F NMR (470 MHz, CD₃OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for C₁₅H₁₆IO ([M-OTf])⁺: 339.0246, found: 339.0250.

6. Preparation of 4,4’-diphenolic iodonium salts 8

Koser’s reagent 7 (0.5-2.0 mmol) was added at 0 °C to a stirred mixture of (triisopropylsiloxy)benzenes 1a or 1e (0.6-2.4 mmol) in 2,2,2-trifluoroethanol (1.0-4.0 mL). The reaction was stirred at room temperature for 24 hours. After reaction, the mixture was evaporated under reduced pressure, and then trifluoromethanesulfonic acid (1.0-4.0 mmol) and acetonitrile (0.5-2.0 mL) were added at 0 °C to the crude mixture. The reaction was stirred at 0 °C for 2 hours. After completion of reaction, the solvent was removed under reduced pressure to give solid residue. Then diethyl ether was added to solid residue to prepare the suspended solution, which was filtered, washed with diethyl ether several times, and dried in vacuum to give the desired 4,4’-di(hydroxyphenyl)iodonium triflate 8a or 8d.

4,4’-di(hydroxyphenyl)iodonium triflate (8a)

![Structure of 4,4’-di(hydroxyphenyl)iodonium triflate](image)

Reaction of Koser’s reagent 7 (600 mg, 2.4 mmol) according to the general procedure afforded 873 mg (94%) of product 8a, isolated as a light brown solid: mp 126.5-126.7 °C; IR (KBr) cm⁻¹ 3343, 3096, 3063, 3017, 1594, 1576, 1484, 1439, 1276, 1243, 1207, 640; ¹H NMR (500 MHz, CD₃OD): δ 7.92 (d, J = 9.0 Hz, 4H), 6.88 (d, J = 9.0 Hz, 4H); ¹³C NMR (75 MHz, CD₃OD): δ 161.4, 136.8, 120.5 (q, JₙCF = 318.0 Hz), 118.7, 101.9; ¹⁹F
NMR (282 MHz, CD$_3$OD): δ -80.5; HRMS (ESI-TOF-positive mode): calcd for C$_{12}$H$_{10}$IO$_2$ ([M-OTf]$^+$): 312.9725, found: 312.9732.

**4,4’-di(hydroxyphenyl)iodonium tosylate (8b)**

![Structure of 4,4’-di(hydroxyphenyl)iodonium tosylate (8b)]

Reaction of Koser’s reagent 7 (450 mg, 1.0 mmol) according to the general procedure afforded the crude 8a compound. Then p-TsONa (1940 mg, 10.0 mmol) was added at room temperature to a stirred mixture of crude mixture 8a in water (5.0 mL). The reaction was stirred at room temperature for 2 hour. After completion of reaction, the mixture was filtrated and washed with diethyl ether several times and then dried in vacuum to give the desired 4,4’-diphenol-λ$^3$-iodonium tosylate 8b; 308 mg (64%) isolated as a light brown solid: mp 156.3-156.6 °C; IR (KBr) cm$^{-1}$: 3160, 3090, 3011, 2926, 1600, 1579, 1489, 1440, 1282, 1219, 1030, 681; $^1$H NMR (500 MHz, CD$_3$OD): δ 7.90 (d, $J = 8.8$ Hz, 4H), 7.70 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 4H), 2.36 (s, 3H); $^{13}$C NMR (75 MHz, CD$_3$OD): δ 161.4, 142.2, 140.2, 136.8, 128.4, 125.5, 118.7, 101.9, 19.9; HRMS (ESI-TOF-positive mode): calcd for C$_{12}$H$_{10}$IO$_2$ ([M-OTs]$^+$): 312.9725, found: 312.9735.

**4,4’-di(hydroxyphenyl)iodonium bromide (8c)**

![Structure of 4,4’-di(hydroxyphenyl)iodonium bromide (8c)]

Reaction of Koser’s reagent 7 (450 mg, 1.0 mmol) according to the general procedure afforded the crude 8a compound. Then KBr (1190 mg, 10.0 mmol) was added at room temperature to a stirred mixture of crude mixture 8a in water (3.0 mL). The reaction was stirred at room temperature for 2 hour. After completion of reaction, the mixture was filtrated and washed with diethyl ether several times and then dried in vacuum to give the
desired 4,4’-diphenol-λ³-iodonium bromide 8c; 233 mg (59%) isolated as a white solid: mp 163.4-163.8 °C; IR (KBr) cm⁻¹ 3258, 3060, 2923, 2856, 1597, 1486, 1427, 1280, 640; ¹H NMR (500 MHz, CD₂OD): δ 7.91 (d, J = 9.3 Hz, 4H), 6.87 (d, J = 9.3 Hz, 4H); ¹³C NMR (75 MHz, CD₂OD): δ 161.3, 136.8, 118.6, 101.5; HRMS (ESI-TOF-positive mode): calcd for C₁₂H₁₀I₂⁺: 312.9725, found: 312.9737.

(4-hydroxy-3-methylphenyl)(4’-hydroxyphenyl)iodonium triflate (8d)

Reaction of Koser’s reagent 7 (225 mg, 0.50 mmol) with triisopropyl(2-tolyloxy)silane 1f (159 mg, 0.60 mmol) according to the general procedure afforded 163 mg (68%) of product 8d, isolated as a light brown solid: mp 140.2-140.8 °C; IR (KBr) cm⁻¹ 3244, 3091, 3015, 2929, 1577, 1486, 1427, 1278, 1216, 1171, 642; ¹H NMR (500 MHz, CD₂OD): δ 7.90 (d, J = 8.3 Hz, 2H), 7.83 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 7.8 Hz, 1H), 2.21 (s, 3H); ¹³C NMR (125 MHz, CD₂OD): δ 161.3, 159.5, 137.0, 136.7, 134.2, 129.5, 120.4 (q, ¹JC = 316.9 Hz), 118.7, 117.2, 101.8, 101.6, 14.7; ¹⁹F NMR (470 MHz, CD₂OD): δ -80.2; HRMS (ESI-TOF-positive mode): calcd for C₁₃H₁₂IO₂ ([M-OTf]⁺): 326.9882, found: 326.9884.

7. Preparation of dimeric oxyphenyl(phenyl)iodonium ylidic salts

Reaction of 4c (0.50-0.90 mmol) was added to a stirred mixture of 10%K₂CO₃ solution (5.0-9.0 mL). The reaction was stirred at room temperature for 1 to 24 hour. After completion of reaction, the mixture was filtrated and washed with diethyl ether several times and then dried in vacuum to give the desired oxyphenyl(phenyl)iodonium ylidic bromide salt.

Dimeric oxyphenyl(phenyl)iodonium ylide-HBr (9a)
Reaction of 4c (338 mg, 0.90 mmol) according to the general procedure for 1 hour stirring afforded 187 mg (62%) of product 9a, isolated as a light yellow solid: mp 122.8-123.4 °C; IR (KBr) cm⁻¹: 3453, 3051, 3017, 2929, 1573, 1490, 1445, 680; ¹H NMR (500 MHz, CD₃OD): δ 8.02 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 9.3 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.53-7.47 (m, 2H) 6.72 (d, J = 9.3 Hz, 2H); ¹³C NMR (125 MHz, CD₃OD-DMSO = 20:1): δ 167.3, 137.2, 133.5, 131.3, 131.1, 120.6, 115.3, 95.4.; Anal. Calcd for C₂₄H₁₉BrI₂O₂: C, 42.82; H, 2.85; I, 37.71. Found: C, 42.86; H, 2.73; I, 37.47.

Single crystals of product 9a suitable for X-ray crystallographic analysis were obtained by slow crystallization from the methanol solution. X-ray diffraction data for 9a were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 123 K. The structure was solved by Sir 2004¹⁴ and refined by full-matrix least-squares refinement on F² using SHELXL-2014/7.¹³ Crystal data for 9a C₂₄H₁₉BrI₂O₂: M 673.09, orthorhombic, space group Pbcn, a = 11.0912(3), b = 18.5647(13), c = 10.9748(2) Å, α = 90, β = 90, γ = 90 o, V = 2259.76(17) Å³, Z = 4, 28473 reflections measured, 2586 unique, 2404 I>2σ; final R₁ = 0.0183, Rw = 0.0432, S = 1.073. CCDC-1855611.

**Dimeric oxyphenyl(phenyl)iodonium ylide-KBr (9b)**
Reaction of 4c (189 mg, 0.50 mmol) according to the general procedure for 24 hour stirring afforded 144 mg (81%) of product 9b, isolated as a light yellow solid: mp 143.5 °C (decomp.); IR (KBr) cm⁻¹ 3438, 3084, 3054, 3020, 1568, 1443, 655; ¹H NMR (500 MHz, CD₃OD): δ 7.96 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.62 (t, J = 7.0 Hz, 1H), 7.52-7.45 (m, 2H), 6.58 (d, J = 8.8 Hz, 2H); ¹³C NMR (75 MHz, CD₃OD): δ 172.8, 137.7, 133.3, 131.4, 131.4, 122.8, 115.6, 90.8. Anal. Calcd for C₂₄H₁₉BrI₂KO₂: C, 40.53; H, 2.55; I, 35.69. Found: C, 40.66; H, 2.64; I, 35.45.

8. X-ray crystal structures of phenolic iodonium compounds

Figure S1-X-ray crystal structure of 4c. All non-oxygen hydrogen atoms were removed for clarity. Ellipsoids drawn to the 50% probability level. An additional bromide anion (Br1’) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordination environment of the iodine atom. Selected bond lengths and angles: I(1)-C(1) 2.094(13); I(1)-C(7) 2.137(11); I(1)-Br(1) 3.277(2); O(1)-C(4) 1.379(15); I(1)-Br(1’) 3.280(1); C(1)-I(1)-C(7) 92.7(4); C(1)-I(1)-Br(1) 86.8(3); Br(1)-I(1)-Br(1’) 89.9(1); Br(1’)-I(1)-C(7) 90.5(2). A least-squares plane fit through I1, C1, C7, Br1 and Br1’ resulted in a root-mean square deviation of 0.029 Å.
Figure S2-X-ray crystal structure of 6j. All non-oxygen hydrogen atoms were removed for clarity. Ellipsoids drawn to the 50% probability level. An additional triflate anion (containing O4') from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordination environment of the iodine atom. The thiophenyl group was modeled as positionally disordered over two positions and only one position is displayed for clarity. Selected bond lengths and angles: I(1)-C(1) 2.103(3); I(1)-C(7) 2.071(4); I(1)-O(3) 2.936(2); I(1)-O(4') 2.896(3); C(4)-O(1) 1.363(3); C(1)-I(1)-O(4') 82.0(1); C(7)-I(1)-O(3) 78.9(5); O(3)-I(1)-O(4') 100.5(1); C(1)-I(1)-C(7) 98.6(5). A least-squares plane fit through I1, C1, C7, O3 and O4' resulted in a root-mean square deviation of 0.0097 Å.

Figure S3-X-ray crystal structure of 6k. All non-oxygen hydrogen atoms were removed for clarity. Ellipsoids drawn to the 50% probability level. An additional bromide anion
(Br1’) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordination environment of the iodine atom. Selected bond lengths and angles: I(1)-C(1) 2.123(8); I(1)-C(5) 2.108(8); I(1)-Br(1) 3.180(1); I(1)-Br(1’) 3.3338(9); C(8)-O(1) 1.365(9); C(1)-I(1)-Br(1’) 89.7(2); C(5)-I(1)-Br(1) 87.2(2); Br(1)-I(1)-Br(1’) 89.13(2); C(1)-I(1)-C(5) 94.1(3). A least-squares plane fit through I1, C1, C7, O3 and O4’ resulted in a root-mean square deviation of 0.0501 Å.

**Figure S4** - X-ray crystal structure of 6l. All non-oxygen hydrogen atoms were removed for clarity. Ellipsoids drawn to the 50% probability level. An additional triflate anion (containing O3’) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordination environment of the iodine atom. The thiophenyl group was modeled as positionally disorder over two positions and only one position is displayed for clarity. Selected bond lengths and angles: I(1)-C(1) 2.08(1); I(1)-C(5) 2.102(3); I(1)-O(4) 2.938(2); I(1)-O(3’) 2.914(2); C(8)-O(1) 1.358(3); C(1)-I(1)-O(4) 80(1); C(5)-I(1)-O(3’) 82.1(1); O(3’)-I(1)-O(4) 100.3(1); C(1)-I(1)-C(5) 97(1). A least-squares plane fit through I1, C1, C5, O4 and O3’ resulted in a root-mean square deviation of 0.0206 Å.
**Figure S5**-X-ray crystal structure of 6m. All non-oxygen hydrogen atoms were removed for clarity. Ellipsoids drawn to the 50% probability level. Interestingly, two coordination environments were observed for the iodine atoms: t-shaped and pseudo-square planar. Remarkably, the bond lengths between the two coordination geometries were similar. An additional molecule of 6m (containing O2’) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordination environment of one iodine atom. Selected bond lengths and angles for the pseudo-square planar molecule: I(1)-C(1) 2.122(7); I(1)-C(8) 2.098(7); I(1)-O(1) 2.486(5); I(1)-O(2’) 3.027(5); C(11)-O(3) 1.357(9); C(1)-I(1)-O(1) 74.5(2); C(1)-I(1)-C(8) 96.1(3); O(1)-I(1)-O(2’) 102.3(2); C(8)-I(1)-O(2’) 87.4(2). A least-squares plane fit through I1, C1, C8, O1 and O2’ resulted in a root-mean square deviation of 0.1209 Å. Selected bond lengths and angles for the t-shaped molecule: I(1A)-C(1A) 2.129(7); I(1A)-C(8A) 2.112(7); I(1A)-O(1A) 2.476(5); C(11A)-O(3A) 1.356(9); C(1A)-I(1A)-O(1A) 74.4(3); C(1A)-I(1A)-C(8A) 97.5(3); O(1A)-I(1A)-C(8A) 171.7(2). A least-squares plane fit through I1A, C1A, C8A and O1A resulted in a root-mean square deviation of 0.0132 Å.
Figure S6- X-ray crystal structure of 9a. All non-oxygen hydrogen atoms were removed for clarity. Elliposoids drawn to the 50% probability level. The two halves of 9a are related by a 2-fold axis with the hydrogen atom (joining O1–O1’) and Br1 both located on the 2-fold axis. An additional molecule of 9a (containing O1”) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordination environment of the iodine atom. Selected bond lengths and angles: I(1)-C(1) 2.108(2); I(1)-C(7) 2.106(2); I(1)-Br(1) 3.3076(3); I(1)-O(1’) 2.760(2); C(4)-O(1) 1.326(3); C(1)-I(1)-O(1”) 85.9(1); C(7)-I(1)-Br(1) 81.8(1); O(1”)-I(1)-Br(1) 98.71(3); C(1)-I(1)-C(7) 93.3(1). A least-squares plane fit through I1, C1, C5, O4 and O3’ resulted in a root-mean square deviation of 0.0848 Å.

9. Reaction of 8a with various anionic nucleophiles

*para*-Nitrophenol 10

\[
\text{HO} \quad \begin{array}{c}
\text{NO}_2
\end{array}
\]

4,4’-Diphenolic iodonium triflate 8a (92 mg, 0.20 mmol) was added at room temperature
to a stirred mixture of sodium nitrite (28 mg, 0.40 mmol) and sodium triflate (38 mg, 0.22 mmol) in ethyl acetate (2.0 mL). The reaction was stirred at 70 °C for 17 hour. After reaction, 10% aqueous HCl (5 mL) was added and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 4:1) afforded the analytically pure para-nitrophenol 10; 13 mg (46%) isolated as a light brown solid: mp 107.8-108.6 ºC (lit.\(^1\); mp 112-113 ºC); $^1$H NMR (500 MHz, CDCl$_3$): δ 8.18 (d, $J$ = 6.5 Hz, 2H), 6.91 (d, $J$ = 6.5 Hz, 2H), 5.65 (s, 1H).

**para-Azidephenol 11\(^{16}\)**

![](image)

4,4’-Diphenolic iodonium triflate 8a (92 mg, 0.20 mmol) was added at room temperature to a stirred mixture of sodium azide (65 mg, 1.0 mmol) and sodium triflate (38 mg, 0.22 mmol) in methanol (2.0 mL). The reaction was stirred at reflux for 17 hour. After reaction, water (5 mL) was added and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate-triethyl amine = 3:1:0.1 to 1:1:0.1) afforded the analytically pure para-azidephenol 11; 15 mg (56%) isolated as a light brown oil; $^1$H NMR (500 MHz, CDCl$_3$): δ 6.91 (d, $J$ = 8.3 Hz, 2H), 6.82 (d, $J$ = 8.3 Hz, 2H).

**para-Thiocyanatophenol 12\(^{17}\)**

![](image)

4,4’-Diphenolic iodonium triflate 8a (92 mg, 0.20 mmol) was added at room temperature to a stirred mixture of sodium thiocyanate (97 mg, 1.0 mmol) and sodium triflate (38 mg, 0.22 mmol) in ethylacetate (2.0 mL). The reaction was stirred at reflux for 17 hour. After reaction, water (5 mL) was added and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced
pressure. Purification by preparative TLC (hexane-ethyl acetate = 3:1) afforded the analytically pure para-thiocyanatophenol 12; 14 mg (47%) isolated as a light yellow oil; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.46 (d, $J = 9.0$ Hz, 2H), 6.89 (d, $J = 9.0$ Hz, 2H), 5.41 (brs, 1H).

**para-Selenocyanatophenol 13**

\[
\text{HO} \quad \text{SeCN} \quad \text{HO}
\]

4,4’-Diphenolic iodonium triflate 8a (92 mg, 0.20 mmol) was added at room temperature to a stirred mixture of sodium selenocyanate (144 mg, 1.0 mmol) and sodium triflate (38 mg, 0.22 mmol) in ethylacetate (2.0 mL). The reaction was stirred at reflux for 17 hour. After reaction, water (5 mL) was added and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3:1) afforded the analytically pure para-selenocyanatophenol 13; 36 mg (91%) isolated as a light yellow solid: mp 82.4-83.3 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 5.28 (brs, 1H).

**para-(Phenylsulfonyl)phenol 14**

\[
\text{HO} \quad \text{SO}_2\text{Ph} \quad \text{HO}
\]

4,4’-Diphenolic iodonium triflate 8a (92 mg, 0.20 mmol) was added at room temperature to a stirred mixture of sodium phenylsulfinate (164 mg, 1.0 mmol) and sodium triflate (38 mg, 0.22 mmol) in methanol (2.0 mL). The reaction was stirred at reflux for 17 hour. After reaction, water (5 mL) was added and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by preparative TLC (hexane-ethyl acetate = 3:1) afforded the analytically pure para-(phenylsulfonyl)phenol 14; 5 mg (11%) isolated as a light yellow oil; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J = 8.5$ Hz, 2H), 7.83 (d, $J = 8.5$ Hz, 2H), 7.57-7.46 (m, 3H), 6.91 (d, $J = 8.5$ Hz, 2H), 5.95 (brs, 1H).
10. References

$^1$H NMR (500 MHz, CD$_3$OD)

\[
\text{HO---O}^{\text{Ts}} \\
\text{Me---Me}
\]
$^{13}$C NMR (125 MHz, CD$_3$OH)

![Chemical structure and NMR spectrum]
$^1$H NMR (500 MHz, CD$_3$OH)
$^{13}$C NMR (125 MHz, CD$_3$OH)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (125 MHz, CD$_3$OH)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^1$H NMR (470 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}$F NMR (282 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}F$ NMR (282 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}$F NMR (282 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}$F NMR (282 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}\text{F NMR (282 MHz, CD}_3\text{OD)}$
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}$F NMR (282 MHz, CD$_3$OD)
$^1$H NMR (300 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
${}^{19}$F NMR (282 MHz, CD$_3$OD)

![Diagram of chemical structure](image)
¹H NMR (500 MHz, CD₃OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}$F NMR (282 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}$F NMR (282 MHz, CD$_3$OD)
$^1$H NMR (300 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)

![NMR spectrum image]
$^{19}\text{F NMR (282 MHz, CD$_3$OD)}$

![NMR Spectrum Diagram]
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^1$H NMR (300 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}$F NMR (282 MHz, CD$_3$OD)

\[ \text{Diagram of compound} \]
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (125 MHz, CD$_3$OD)
$^{19}$F NMR (470 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (125 MHz, CD$_3$OD)
$^{19}$F NMR (470 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)

![NMR Spectrum](image)
$^{13}$C NMR (125 MHz, CD$_3$OD)
$^{19}$F NMR (470 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^{19}$F NMR (282 MHz, CD$_3$OD)
$^1\text{H NMR (500 MHz, CD$_3$OD)}$
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (125 MHz, CD$_3$OD)
\(^{19}\text{F} \text{ NMR (470 MHz, CD}_3\text{OD)}\)

![Chemical Structure with NMR Spectrum]
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (125 MHz, CD$_3$OD-DMSO = 20:1)

![C NMR spectrum](image)

Ph\(\text{I}^+\)

Ph\(\text{I}^+\)

\(\text{O}^-\)

\(\text{Br}^-\)

\(\text{H}^-\)

\(\text{Ph}^-\)

\(\text{Ph}^-\)

\(\text{O}^-\)
$^1$H NMR (500 MHz, CD$_3$OD)
$^{13}$C NMR (75 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)