Supplementary Information

Versatile Direct Dehydrative Approach for Diaryliodonium Salts in Fluoroalcohol Media

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General Information

^{1}H NMR and ^{13}C NMR spectra were recorded by a JEOL JMN-300 or EX-270 spectrometer in CD_3OD otherwise noted. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad singlet, m = multiplet), integration, and coupling constant (Hz). Infrared spectra (IR) were obtained using a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters for strong and structurally important peaks. Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. High resolution mass spectra and elemental analyses were performed by the Elemental Analysis Section of Osaka University.

Materials

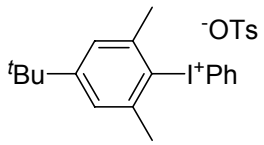
PhI(OH)OCs, 2,4,6-$CH_3C_6H_2I(OH)OTs$ and $C_6F_5I(OH)OTs$ was synthesized according to the literature procedure.[1), 2)] 3-Trimethylsilylthiophene **1l** was obtained from

commercially available 3-bromothiophene by the known method.[3)] Linear poly(styrene) **4** (TSK standard class, Type F-128 (TS-206), Mol. Wt: 1.09 x 10^6) was purchased from TOSOH COOPORATION and used as received. All other starting materials are commercially available. They were used without further purification.

Representative experimental procedure for dehydrative diaryliodonium(III) salts formation in 2,2,2-trifluoroethanol

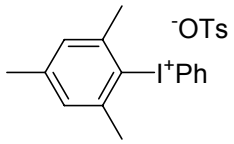
To a stirred solution of arene **1b** (162 mg, 1 mmol) in 2,2,2-trifluoroethanol (5 mL), [hydroxyl(tosyloxy)iodo]benzene (392 mg, 1 mmol) was added in one portion at room temperature under air, and it was stirred overnight. MeOH was then added to the reaction mixture when the solvents were removed under vacuum. The resulting oily crude product **2b** was precipitated by the addition of Et_2O with stirring. The precipitate was filtered and dried *in vacuo* to give **2b** (531 mg, 99%) as a white powder.

Phenyl(4-tert-Butyl-2,6-dimethylphenyl)iodonium tosylate (2b)



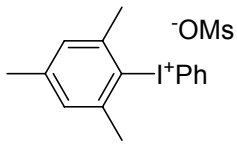
White powder; m.p. 157 ^oC; ^1H NMR (300 MHz,): δ = 1.30 (s, 9H), 2.34 (s, 3H), 2.68 (s, 6H), 7.18 (d, 2H, *J* = 8.4 Hz), 7.42-7.50 (m, 4H), 7.57-7.66 (m, 3H), 7.90 (d, 2H, *J* = 8.4 Hz) ppm; ^{13}C NMR (67.8 MHz): δ = 21.3, 27.3, 31.3, 35.8, 114.1, 122.5, 126.9, 127.9, 129.8, 133.2, 133.3, 135.3, 141.5, 143.2, 143.6, 158.3 ppm; IR (KBr): 3018, 2968, 1568, 1472, 1219, 1132, 1045, 928, 772, 665, 627 cm^{-1}; HRMS (FAB): calcd for $C_{18}H_{22}I$ $[M - OTs]^+$: 365.0761, found 365.0777.

Phenyl(2,4,6-trimethylphenyl)iodonium tosylate (2a)



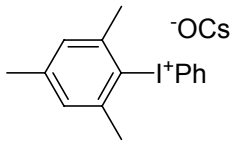
White powder; m.p. 153-157 ^{o}C ; ^{1}H NMR (300 MHz): δ = 2.32 (s, 3H), 2.33 (s, 3H), 2.62 (s, 6H), 7.16-7.18 (m, 4H,), 7.45 (d, 1H, *J* = 7.5 Hz), 7.48 (d, 1H, *J* = 7.5 Hz), 7.58-7.65 (m, 3H), 7.87 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 21.0, 21.3, 27.0, 114.1, 122.4, 126.9, 129.8, 131.2, 133.1, 133.2, 135.2, 141.5, 143.4, 143.6, 145.6 ppm; IR (KBr): 3045, 2951, 1566, 1469, 1438, 1230, 1192, 1132, 1045, 989, 737, 696 cm^{-1}; HRFABMS (FAB): Calcd for $C_{15}H_{16}I$ $[M - OTs]^{+}$: 323.0297, Found 323.0311.

Phenyl(2,4,6-trimethylphenyl)iodonium mesylate (2a-OMs)



White powder; m.p. 135-136 ^{o}C; ^{1}H NMR (300 MHz): δ = 2.34 (s, 3H,), 2.53 (s, 3H), 2.65 (s, 6H), 7.08 (s, 2H), 7.38 (t, 2H, *J* = 7.5 Hz), 7.49 (t, 1H, *J* = 7.5 Hz), 7.75 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (75.5 MHz,): δ = 21.0, 26.9, 39.0, 113.3, 121.7, 129.8, 131.0, 131.6, 132.9, 142.1, 143.5 ppm; IR (KBr): 3018, 2950, 1566, 1438, 1218, 1058, 995, 750 cm^{-1}; HRFABMS (FAB): Calcd for $C_{15}H_{16}I$ $[M - OMs]^{+}$: 323.0297, Found 323.0287.

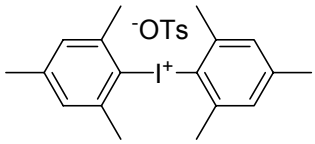
Phenyl(2,4,6-trimethylphenyl)iodonium (+)-10-campharsulfonate (2a-OCs)



White powder; m.p. 173-174 ^{o}C; ^{1}H NMR (300 MHz,): δ = 0.81 (s, 3H), 1.09 (s, 3H),

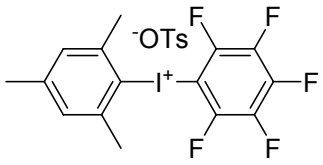
1.32-1.39(m, 1H), 1.50-1.58(m, 1H), 1.85(d, 1H, *J* = 18.3 Hz), 1.98-2.02 (m, 2H), 2.28-2.35 (m, 4H), 2.57-2.72 (m, 8H), 3.26 (d, 1H, *J* = 15 Hz), 7.23 (s, 2H), 7.50 (t, 2H, *J* = 7.8 Hz), 7.64 (t, 1H, *J* = 7.5 Hz), 7.91 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 20.1, 20.5, 21.0, 25.7, 27.1, 27.8, 43.6, 44.0, 48.1, 59.5, 114.2, 122.4, 131.3, 133.2, 133.2, 135.3, 143.5, 145.7, 218.1 ppm; IR (KBr): 2955, 1741, 1566, 1454, 1415, 1265, 1190, 1045, 995, 750 cm^{-1}; HRFABMS (FAB): Calcd for $C_{25}H_{32}IO_4S$ $[M + H]^+$: 555.1066, Found 555.1093.

Bis(2,4,6-trimethylphenyl)iodonium tosylate (2aa)



White powder; m.p. 138-142 °C; ^{1}H NMR (300 MHz): δ = 2.33 (s, 6H), 2.35 (s, 3H), 2.51 (s, 12H), 7.17-7.22 (m, 6H), 7.66 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (125.7 MHz): δ = 20.8, 21.3, 26.1, 119.1, 126.9, 129.7, 131.7, 141.5, 143.6, 143.6, 145.2 ppm; IR (KBr): 3022, 2976, 1454, 1191, 1132, 1045, 985, 732, 694 cm^{-1}; HRFABMS (FAB): Calcd for $C_{18}H_{22}I$ $[M – OTs]^+$: 365.0766, Found 365.0780.

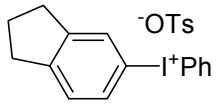
Pentafluorophenyl(2,4,6-trimethylphenyl)iodonium tosylate (2ab)



White powder; m.p. 162°C; ^{1}H NMR (300 MHz): δ = 2.33 (s, 3H), 2.36 (s, 3H), 2.68 (s, 6H,), 7.18-7.21 (m, 4H,), 7.58 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (125.7 MHz): δ = 21.0, 21.3, 26.9, 123.3, 126.8, 129.8, 131.4, 141.8, 143.3, 143.9, 146.4, 154.6, 154.9, 155.0, 155.2 ppm; IR (KBr): 3018, 2972, 1510, 1487, 1454, 1190, 1132, 1078, 1045, 974, 738, 694 cm^{-1}; HRFABMS (FAB): Calcd for $C_{22}H_{19}F_5IO_3S$ $[M + H]^+$: 555.0026,

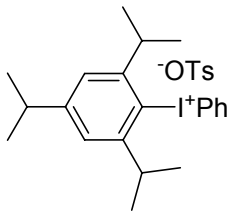
Found 555.0012.

Phenyl(Indan-5-yl)iodonium tosylate (2c)



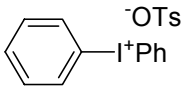
White powder; m.p. 143-146°C; ^{1}H NMR (300 MHz,): δ = 2.02 (quintet, 2H, *J* = 7.5 Hz), 2.32 (s, 3H), 2.90 (t, 4H, *J* = 7.5 Hz), 7.17 (d, 2H, *J* = 7.8 Hz,), 7.30 (d, 1H, *J* = 7.8 Hz), 7.45 (t, 2H, *J* = 7.8 Hz), 7.58-7.68 (m, 3H), 7.88 (d, 1H, *J* = 7.8 Hz), 7.99 (s, 1H), 8.12 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 21.3, 26.3, 33.6, 33.8, 113.0, 116.1, 126.9, 128.9, 129.8, 132.4, 133.0, 133.1, 133.3, 134.5, 136.2, 141.5, 150.2, 150.9 ppm; IR (KBr): 3020, 2962, 1471, 1440, 1261, 1217, 1132, 1045, 744 cm^{-1}; HRFABMS (FAB): Calcd for $C_{15}H_{14}I$ $[M - OTs]^+$: 321.0140, Found 321.0127.

Phenyl(2,4,6-triisopropylphenyl)iodonium tosylate (2d)



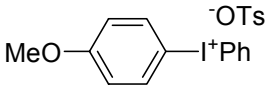
White powder; m.p. 137-140 °C; ^{1}H NMR (300 MHz): δ = 1.25-1.28 (m, 18H), 2.35 (s, 3H), 3.00 (septet, 1H, *J* = 6.9 Hz), 3.39 (m, 2H), 7.20 (d, 2H, *J* = 8.1 Hz), 7.32 (s, 2H), 7.46-7.51 (m, 2H), 7.56-7.69 (m, 3H,), 7.82 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 21.3, 24.1, 24.5, 35.4, 40.6, 114.9, 123.3, 126.3, 126.9, 129.8, 133.1, 133.3, 134.7, 141.6, 143.6, 153.3, 156.8 ppm; IR (KBr): 3039, 2964, 1469, 1257, 119, 1132, 1045, 740, 694 cm^{-1}; HRFABMS (FAB): Calcd for $C_{21}H_{28}I$ $[M - OTs]^+$: 407.1236, Found 407.1250.

Diphenyliodonium tosylate (2e)[4)]



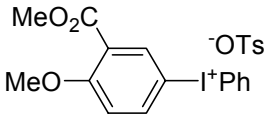
White powder; m.p. 179-180 °C; ^{1}H NMR (360 MHz, DMSO-d_6): δ = 2.29 (s, 3H), 7.11 (d, 2H, *J* = 7.9 Hz), 7.48 (d, 2H, *J* = 7.9Hz,), 7.53 (t, 4H, *J* = 7.3 Hz), 7.67 (t, 2H, *J* = 7.3 Hz), 8.25 (d, 4H, *J* = 7.7 Hz) ppm; ^{13}C NMR (90.0 MHz, DMSO-d_6): δ = 24.7, 120.5, 129.5, 132.0, 135.7, 136.0, 139.1, 141.5, 149.8 ppm; IR (KBr): 3045, 2989, 1471 , 1438, 1267, 1193, 1130, 1041, 1012, 989, 817, 750, 690 cm^{-1}.

Phenyl (4-Methoxyphenyl)iodonium tosylate (2f)[5)]



White powder; m.p. 143-146 °C; ^{1}H NMR (300 MHz,): δ = 2.33 (s, 3H,), 3.79 (s, 3H), 7.00 (d, 2H, *J* = 9.3 Hz), 7.19 (d, 2H, *J* = 7.8Hz), 7.46 (t, 2H, *J* = 7.5 Hz), 7.62 (t, 1H, *J* = 7.5 Hz,), 7.68 (d, 2H, *J* = 7.8 Hz), 8.04-8.11 (m, 4H) ppm; ^{13}C NMR (75.5 MHz): δ = 21.3, 56.3, 104.5, 116.5, 118.8, 126.9, 129.8, 133.0, 133.3, 136.0, 138.6, 141.6, 143.6, 164.3 ppm; IR (KBr): 3026, 1730, 1573, 1487, 1440, 1257, 1298, 1180, 1132, 1043, 817, 742, 692 cm^{-1}.

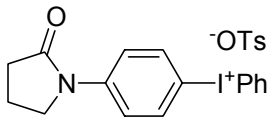
Phenyl(4-Methoxy-3-methoxycarbonylphenyl)iodonium tosylate (2g)



White powder; m.p. 170 °C; ^{1}H NMR (300 MHz): δ = 2.34 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 7.21 (t, 3H, *J* = 8.7 Hz), 7.50 (t, 2H, *J* = 7.8Hz,), 7.67 (d, 3H, *J* = 7.8 Hz), 8.15 (d, 2H, *J* = 7.8 Hz), 8.28 (d, 1H, *J* = 9.0 Hz), 8.49 (d, 1H, *J* = 1.8 Hz) ppm; ^{13}C NMR (75.5 MHz,): δ = 21.3, 53.1, 57.1, 104.1, 116.7, 117.1, 124.5, 126.9, 129.8, 133.1,

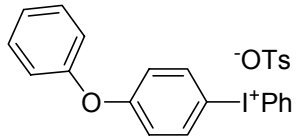
133.6, 136.2, 139.5, 141.6, 142.0, 143.6, 163.2, 166.0 ppm; IR (KBr): 3018, 1585, 1487, 1434, 1265, 1218, 771, 667 cm^{-1}; HRFABMS (FAB): Calcd for $C_{22}H_{21}INaO_6S$ $[M + Na]^+$: 563.0001, Found 562.9987.

Phenyl[4-(2-Oxo-pyrrolidin-1-yl)-phenyl]iodonium tosylate (2h)



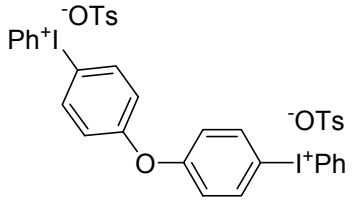
White powder; m.p. 79 ^oC; ^1H NMR (300 MHz): δ = 2.13 (m, 2H), 2.34 (s, 3H), 2.58 (t, 2H, *J* = 8.1 Hz), 3.86 (t, 2H, *J* = 6.9 Hz), 7.20 (d, 2H, *J* = 7.8 Hz), 7.49 (t, 2H, *J* = 7.8 Hz), 7.63-7.69 (m, 3H), 7.80 (d, 2H, *J* = 8.7 Hz,), 8.13 (d, 4H, *J* = 8.7 Hz) ppm; IR (KBr): 3051, 2981, 1693, 1579, 1487, 1384, 1303, 1191, 1130, 1043, 817, 746, 694 cm^{-1}.

Phenyl(4-Phenoxyphenyl)iodonium tosylate (2i)



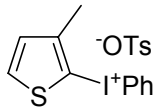
White powder; m.p. 138-139 ^oC; ^1H NMR (300 MHz): δ = 2.30 (s, 3H), 6.94-7.02 (m, 4H), 7.16-7.24 (m, 3H), 7.37-7.49 (m, 4H), 7.59-7.70 (m, 3H), 8.08-8.15 (m, 4H) ppm; ^{13}C NMR (75.5 MHz): δ = 21.3, 106.9, 116.5, 121.3, 121.5, 126.3, 126.9, 129.8, 131.4, 133.0, 133.4, 136.2, 138.8, 141.6, 143.6, 156.1, 162.8 ppm; IR (KBr): 3020, 1568, 1479, 1440, 1217, 1132, 1043, 815, 752, 692 cm^{-1}; HRFABMS (FAB): Calcd for $C_{18}H_{14}IO$ $[M – OTs]^+$: 373.0089, Found 373.0085.

(Oxydi-4,1-phenylene)-bis(phenyl)iodonium tosylate (2i-bis)



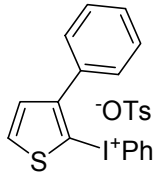
White powder; m.p. 122 °C; ^{1}H NMR (300 MHz,): δ = 2.31 (s, 6H), 7.05-7.19 (m, 8H), 7.45-7.68 (m, 10H), 8.15-8.18 (m, 8H) ppm; ^{13}C NMR (75.5 MHz): δ = 21.3, 109.3, 116.5, 123.4, 126.9, 129.8, 133.1, 133.5, 136.4, 139.1, 141.7, 143.5, 160.4 ppm; IR (KBr): 3018, 2966, 1566, 1479, 1440, 1217, 1132, 1043, 1014, 817, 767, 696 cm^{-1}; HRFABMS (FAB): Calcd for $C_{31}H_{25}I_2O_2S$ [M - OTs]$^{+}$: 746.9557, Found 746.9570.

Phenyl(3-Methyl-2-thienyl)iodonium tosylate (2j)[6)]



White powder; m.p. 165 °C; ^{1}H NMR (300 MHz): δ = 2.33 (s, 3H), 2.49 (s, 3H), 7.03 (d, 1H, *J* = 5.1Hz), 7.19 (d, 2H, *J* = 7.2 Hz), 7.46-7.49 (m, 2H), 7.59-7.67(m, 3H), 7.83 (d, 1H, *J* = 5.1 Hz), 8.05 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 17.5, 21.3, 98.4, 118.4, 126.9, 129.8, 131.0, 133.0, 133.1, 133.4, 135.4, 137.7, 141.6, 150.0 ppm; IR (KBr): 3051, 1575, 1469, 1440, 1191, 1132, 1045, 1014, 991, 815, 746, 680 cm^{-1}.

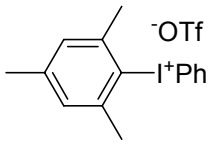
Phenyl(3-phenyl-2-thieyl)iodonium tosylate (2k)



White powder; m.p. 122-123 °C; ^{1}H NMR (300 MHz): δ = 2.31 (s, 3H), 7.12-7.24 (m, 3H), 7.31 (t, 2H, *J* = 7.5 Hz), 7.37-7.47 (m, 2H), 7.48-7.62 (m, 6H), 7.65 (d, 2H, *J* = 7.8 Hz), 8.00 (d, 1H, *J* = 5.1 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 21.3, 98.7, 118.7, 126.9,

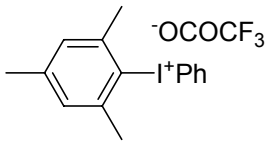
129.8, 130.2, 130.4, 130.5, 132.7, 133.3, 135.2, 135.6, 138.5, 141.6, 143.3, 153.2 ppm; IR (KBr): 3053, 1485, 1469, 1440, 1265, 1197, 1132, 1045, 1014, 991, 815, 748, 696 cm^{-1}; HRFABMS (FAB): Calcd for $C_{16}H_{12}IS$ $[M - OTs]^+$: 362.9704, Found 362.9702.

Phenyl(2,4,6-trimethyl-phenyl)iodonium triflate (2a-OTf)[7)]



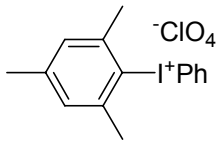
White powder; m.p. 148 °C; ^1H NMR (300 MHz): δ = 2.35 (s, 3H), 2.65 (s, 6H), 7.23 (s, 2H), 7.50 (t, 2H, *J* = 7.5 Hz), 7.63 (t, 1H, *J* = 7.5 Hz), 7.90 (d, 2H, *J* = 7.5 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 21.0, 27.0, 114.0, 119.7, 122.2, 131.3, 133.2, 133.3, 135.2, 143.5, 145.8 ppm; IR (KBr): 3053, 2983, 1622, 1566, 1469, 1379, 1259, 1163, 1029, 989, 746, 638 cm^{-1}.

Phenyl(2,4,6-trimethyl-phenyl)iodonium trifluoroacetate (2a-$OCOCF_3$)



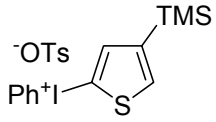
White powder; m.p. 133-136 °C; ^1H NMR (300 MHz): δ = 2.35 (s, 3H), 2.65 (s, 6H), 7.23 (s, 2H), 7.50 (t, 2H, *J* = 7.5 Hz), 7.64 (t, 1H, *J* = 7.5 Hz), 7.89 (d, 2H, *J* = 7.5 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 21.0, 27.0, 114.1, 119.4, 122.4, 131.3, 133.2, 133.3, 135.1, 143.5, 145.8, 162.7 ppm; IR (KBr): 2968, 1666, 1614, 1469, 1379, 1299, 1217, 1130, 1031, 991, 769, 665 cm^{-1}; HRFABMS (FAB): Calcd for $C_{15}H_{16}I$ $[M - OCOCF_3]^+$: 323.0297. Found 323.0300.

Phenyl(2,4,6-trimethyl-phenyl)iodonium perchlorate (2a-ClO_4)



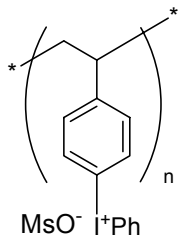
White powder; m.p. 79 ^{o}C; ^{1}H NMR (300 MHz): δ = 2.34 (s, 3H,), 2.65 (s, 6H), 7.23 (s, 2H), 7.50 (t, 2H, *J* = 7.8 Hz), 7.63 (t, 1H, *J* = 7.8 Hz), 7.90 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = 21.0, 27.1, 114.0, 122.2, 131.3, 133.2, 133.3, 135.3, 143.5, 145.8 ppm; IR (KBr): 3057, 2983, 1564, 1469, 1379, 1300, 1267, 1110, 989, 746, 680, 624 cm^{-1}.

Phenyl(4-trimethylsilanyl-2-thieyl)iodonium tosylate (2l)



White powder; m.p. 121 ^{o}C; ^{1}H NMR (300 MHz,): δ = 0.32 (s, 9H), 2.40 (s, 3H), 7.26 (d, 2H, *J* = 7.8 Hz), 7.54 (t, 2H, *J* = 7.5 Hz), 7.67-7.74 (m, 3H), 7.99 (s, 1H, *J* = 1.2 Hz), 8.11 (s, 1H, *J* = 1.2 Hz), 8.19 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C NMR (75.5 MHz): δ = -0.59, 21.6, 119.1, 127.2, 130.1, 133.4, 133.9, 136.1, 136.4, 141.9, 143.8, 144.4, 146.5, 147.0 ppm; IR (KBr): 3051, 2954, 1566, 1469, 1440, 1253, 1199, 1132, 1103, 1043, 1014, 991, 883, 842, 750, 680 cm^{-1}; HRFABMS (FAB): Calcd for $C_{18}H_{26}O_2NS$ $[M + H]^{+}$: 358.9781, Found 358.9792.

Iodonium polymer (5-OMs)



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 **5-OMs** = 2.28 mmol I/g **5-OMs**)

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