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Supporting Information

2-Iodosylbenzoic acid activated by trifluoromethanesulfonic anhydride: efficient oxidant and electrophilic reagent for preparation of iodonium salts

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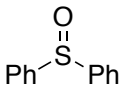
1. General experimental remarks

All reactions were performed in open air with a stopper and oven-dried glassware. All commercial reagents were ACS grade and were used without further purification. NMR spectra was recorded on a Bruker 400 MHz NMR spectrophotometer (^{1}H NMR, ^{13}C NMR and ^{19}F NMR). Meting Points were determined in an open capillary tube with a Mel-temp II meting point apparatus. Infrared spectra were recorded on PerkinElmer Spectrum 1600 series FT-IR spectrometer. Hypervalent iodine reagents **1, 13**[1] and **14**[2] were prepared according to the reported procedure.

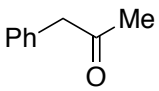
2. Reaction of IBA-Tf_2O with Substrates

Diphenyl sulfoxide 5[4]



Trifluoromethanesulfonic anhydride (42 mg, 0.150 mmol) was added dropwise at 0 °C to a stirred mixture of 2-iodosylbenzoic acid **1** (33 mg, 0.125 mmol) and diphenylsulfide **4** (23 mg, 0.125 mmol) in dichloromethane (1.0 mL). The reaction was stirred for 10 minutes at room temperature. After completion of the reaction, 5% aqueous $Na_2S_2O_3$ (5 mL) and saturated $NaHCO_3$ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by short column chromatography (hexane-ethyl acetate = 3 : 1) afforded 15 mg (58%) of analytically pure diphenyl sulfoxide **5**, colorless oil; IR (neat) cm^{-1}; 3056, 2922, 1580, 1474, 1443, 1042; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.64 (m, 4H), 7.50-7.43 (m, 6H).

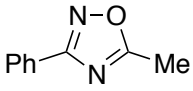
1-Phenyl-2-propanone 6[5]



Trifluoromethanesulfonic anhydride (42 mg, 0.150 mmol) was added dropwise at 0 °C to a stirred mixture of

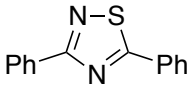
2-iodosylbenzoic acid **1** (33 mg, 0.125 mmol) and α-methyl styrene **6** (15 mg, 0.125 mmol) in dichloromethane (1.0 mL) and water (50 μL). The reaction was stirred at room temperature for 24 hours. After completion of the reaction, 5% aqueous $Na_2S_2O_3$ (5 mL) and saturated $NaHCO_3$ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by short column chromatography (hexane-ethyl acetate = 5 : 1) afforded 7 mg (41%) of analytically pure 1-phenyl-2-propanone **7**, colorless oil; IR (neat) cm^{-1}; 3063, 3030, 2923, 1715, 1602, 1421; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.31 (m, 2H), 7.30-7.27 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.70 (s, 2H), 2.15 (s, 3H).

5-Methyl-3-phenyl-1,2,4-oxadiazole 8[5]



Trifluoromethanesulfonic anhydride (51 mg, 0.180 mmol) was added dropwise at 0 °C to a stirred mixture of 2-iodosylbenzoic acid **1** (40 mg, 0.150 mmol) and benzaoldoxime **8** (18 mg, 0.150 mmol) in acetonitrile (1.0 mL). The reaction was stirred at room temperature for 3 hours. After completion of the reaction, 5% aqueous $Na_2S_2O_3$ (5 mL) and saturated $NaHCO_3$ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by short column chromatography (hexane-ethyl acetate = 3 : 1) afforded 13 mg (55%) of analytically pure 5-methyl-3-phenyl-1,2,4-oxadiazole **9**, colorless oil; IR (neat) cm^{-1}; 3068, 2929, 2854, 1597, 1576, 1447, 1360; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12-8.01 (m, 2H), 7.54-7.42 (m, 3H), 2.66 (s, 3H).

3,5-Diphenyl-1,2,4-thiadiazole 11[5]

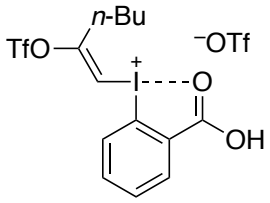


Trifluoromethanesulfonic anhydride (42 mg, 0.150 mmol) was added dropwise at 0 °C to a stirred mixture of 2-iodosylbenzoic acid **1** (33 mg, 0.125 mmol) and thiobenzamide **10** (17 mg, 0.125 mmol) in dichloromethane (1.0 mL). The reaction was stirred at room temperature for 16 hours. After completion of the reaction, 5% aqueous $Na_2S_2O_3$ (5 mL) and saturated $NaHCO_3$ (5 mL) were added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by short column chromatography (hexane-ethyl acetate = 3 : 1) afforded 11 mg (74%) of analytically pure 3,5-diphenyl-1,2,4-thiadiazole **11**, white solid: mp 89.1-89.3 °C (lit.[5], mp 88.3-88.9 °C); IR (KBr) cm^{-1}; 3118, 3046, 1602, 1475; ^1H NMR (400 MHz, $CDCl_3$): δ 8.43-8.36 (m, 2H), 8.10-8.01 (m, 2H), 7.58-7.47 (m, 6H).

3. General procedure for synthesis of pseudocyclic vinyliodonium triflate salts 12

Trifluoromethanesulfonic anhydride (169 mg, 0.60 mmol) was added dropwise at 0 °C to a stirred mixture of 2-iodosylbenzoic acid **1** (0.50 mmol) and alkyne **15** (0.60 mmol) in dichloromethane (2.0 mL). The reaction was stirred for 4 hours at room temperature. After the completion of the reaction, the solvent was removed under reduced pressure and the remaining solid product was washed with hexane and ether several times then dried in vacuum to obtain pure product **12**.

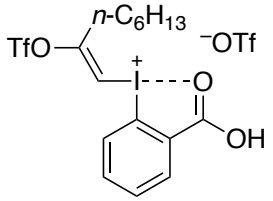
(*E*)-2-((2-(((Trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12a[3]



Reaction with 1-hexyne **15a** (49 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol)according to the general procedure afforded 292 mg (93%) of product **12a**, isolated as a white solid: mp 149.1-149.5 °C

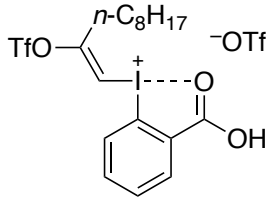
(lit.[3], mp 148.7-149.2 °C); IR (KBr) cm^{-1}; 3097, 2974, 2883, 1669, 1631, 1590, 1415, 1308, 1225, 1200; ^1H NMR (400 MHz, CD_3CN): δ 8.38 (dd, *J* = 7.6 Hz, 1.8 Hz, 1H), 7.95-7.90 (m, 1H), 7.89-7.83 (m, 1H), 7.79 (dd, *J* = 8.2 Hz, 1.0 Hz, 1H), 7.16 (s, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 1.65-1.51 (m, 2H), 1.41-1.26 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, CD_3CN): δ -74.4, -79.4.

(*E*)-2-((2-(((Trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12b[3]



Reaction with 1-octyne **15b** (66 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol)according to the general procedure afforded 312 mg (95%) of product **12b**, isolated as a white solid: mp 153.0-153.2 °C (lit.[3], mp 152.2-153.5 °C); IR (KBr) cm^{-1}; 3087, 2966, 2933, 2864, 1668, 1639, 1417, 1307, 1225, 1200; ^1H NMR (400 MHz, CD_3CN): δ 8.38 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 7.97-7.90 (m, 1H), 7.89-7.83 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 1.67-1.55 (m, 2H), 1.34-1.15 (m, 6H), 0.80 (t, *J* = 7.0 Hz, 3H); ^{19}F NMR (377 MHz, CD_3CN): δ -74.4, -79.4.

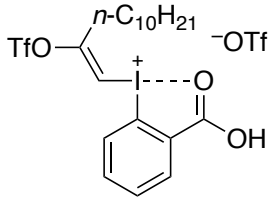
(*E*)-2-((2-(((Trifluoromethyl)sulfonyl)oxy)decy-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12c[3]



Reaction with 1-decyne **15c** (83 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 318 mg (93%) of product **12c**, isolated as a white solid: mp 144.7-145.2 °C (lit.[3], mp 145.1-146.1 °C); IR (KBr) cm^{-1}; 3084, 2931, 2861, 1667, 1638, 1589, 1415, 1306, 1222, 1198; ^1H NMR (400 MHz, CD_3CN): δ 8.39 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 7.96-7.90 (m, 1H), 7.81-7.77 (m, 1H), 7.80 (d,

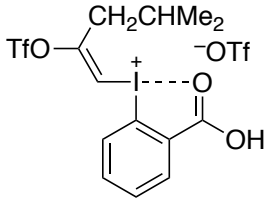
J = 8.0 Hz, 1H), 7.17 (s, 1H), 2.84 (t, *J* = 7.4 Hz, 2H), 1.67-1.50 (m, 2H), 1.32-1.12 (m, 10H), 0.84 (t, *J* = 7.0 Hz, 3H); ^{19}F NMR (376 MHz, CD_3CN) δ -74.4, -79.4.

(*E*)-2-((2-(((Trifluoromethyl)sulfonyl)oxy)dodec-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12d[3]



Reaction with 1-dodecyne **15d** (100 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol)according to the general procedure afforded 379 mg (94%) of product **12d**, isolated as a white solid: mp 136.1-136.4 °C (lit.[3], mp 136,5-138.7 °C); IR (KBr) cm^{-1}; 3085, 2930, 2860, 1667, 1590, 1418, 1307, 1223, 1197; ^{1}H NMR (400 MHz, CD_3CN): δ 8.41 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 8.00-7.93 (m, 1H), 7.92-7.86 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.20 (s, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 1.68-1.54 (m, 2H), 1.41-1.16 (m, 14H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{19}F NMR (376 MHz, CD_3CN) δ -74.4, -79.4.

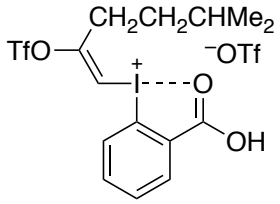
(*E*)-2-((4-Methyl-2-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12e[3]



Reaction with 4-methyl-1-pentyne **15e** (49 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 267 mg (85%) of product **12e**, isolated as a white solid: mp 156.7 °C (decomp.) (lit.[3], mp 157.4-158.6 °C); IR (KBr) cm^{-1}; 3085, 2967, 2878, 1666, 1597, 1419, 1225; ^{1}H NMR (400 MHz, CD_3CN): δ 8.38 (dd, *J* = 7.4Hz, 1.5Hz, 1H), 7.96-7.90 (m, 1H), 7.88-7.83 (m, 1H), 7.83-7.78 (m, 1H), 7.22 (s, 1H), 2.74 (d, *J* = 7.6 Hz, 2H), 2.12-2.00 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 6H); ^{19}F NMR

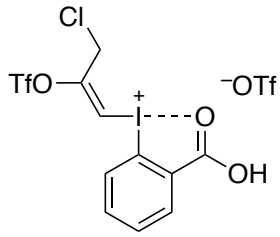
(376 MHz, CD_3CN) δ -74.4, -79.4.

(*E*)-2-((5-Methyl-2-(((trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12f[3]



Reaction with 5-methyl-1-hexyne **15f** (58 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 275 mg (86%) of product **12f**, isolated as a white solid: mp 168.2-168.5 °C (decomp.) (lit.[3], mp 168.7-169.3 °C); IR (KBr) cm^{-1}; 3088, 2968, 2881, 1669, 1648, 1590, 1414, 1308, 1225, 1197; ^1H NMR (400 MHz, CD_3CN): δ 8.38 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 7.96-7.90 (m, 1H), 7.88-7.83 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H), 2.87-2.79 (m, 2H), 1.62-1.45 (m, 3H), 0.84 (d, *J* = 6.4 Hz, 6H); ^{19}F NMR (376 MHz, CD_3CN) δ -74.4, -79.4.

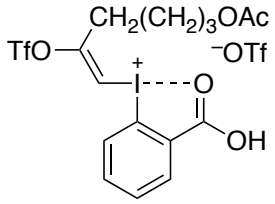
(*E*)-2-((3-Chloro-2-(((trifluoromethyl)sulfonyl)oxy)prop-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12g



Reaction with 3-chloro-1-propyne **15g** (45 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 254 mg (82%) of product **12g**, isolated as a white solid: mp 154.7-155.3 °C; IR (KBr) cm^{-1}; 3096, 2990, 2864, 1662, 1632, 1588, 1425, 1302, 1227; ^1H NMR (400 MHz, CD_3CN): δ 8.39 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 7.98-7.92 (m, 1H), 7.90-7.84 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.45 (s,

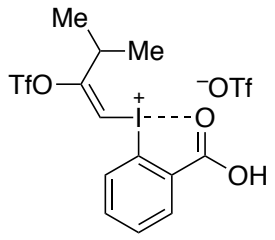
1H), 4.71 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 170.9, 158.2, 138.5, 134.1, 132.9, 130.7, 126.7, 121.5 (q, $^1J_{CF}$ = 318 Hz), 119.0 (q, $^1J_{CF}$ = 318 Hz), 115.0, 43.2; ^{19}F NMR (376 MHz, CD_3CN) δ -73.9, -79.4; HRMS (ESI-positive ionization): calcd for $C_{11}H_8Cl^{35}F_3IO_5S$ ([M-OTf]$^+$): 470.8778, found: 470.8805.

(*E*)-2-((6-Acetoxy-2-(((trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12h



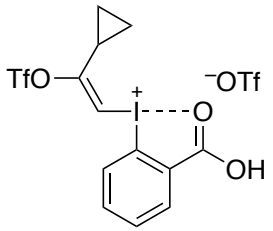
Reaction with 6-acetoxy-1-hexyne **15h** (84 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 227 mg (66%) of product **12h**, isolated as a brown solid: mp 68.3-70.1 °C; IR (KBr) cm^{-1}; 3074, 2963, 2886, 1729, 1660, 1630, 1590, 1425, 1228; ^{1}H NMR (400 MHz, CD_3CN): δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.98-7.89 (m, 1H), 7.89-7.82 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.19 (s, 1H), 4.03-3.89 (m, 2H), 2.95-2.82 (m, 2H), 1.92 (s, 3H), 1.74-1.53 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 174.2, 170.6, 165.3, 138.3, 134.1, 132.7, 130.2, 126.9, 121.3 (q, $^1J_{CF}$ = 313 Hz), 119.0 (q, $^1J_{CF}$ = 318 Hz), 114.6, 92.2, 63.7, 34.8, 27.9, 23.2, 20.6; ^{19}F NMR (376 MHz, CD_3CN) δ -74.3, -79.4; HRMS (ESI-positive ionization): calcd for $C_{16}H_{17}F_3IO_7S$ ([M-OTf]$^+$): 536.9692, found: 536.9715.

(*E*)-2-((3-Methyl-2-(((trifluoromethyl)sulfonyl)oxy)but-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12i



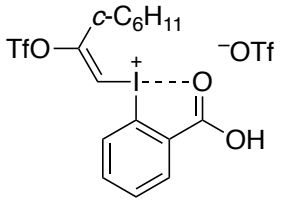
Reaction with 3-methyl-1-butyne **15i** (41 mg, 0.6 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 261 mg (85%) of product **12i**, isolated as a white solid: mp 153.5-154.1 °C (decomp.); IR (KBr) cm^{-1}; 3092, 3001, 2886, 1665, 1619, 1588, 1416, 1259, 1215; ^{1}H NMR (400 MHz, CD_3CN): δ 8.41 (dd, J = 7.6 Hz, 2.0 Hz, 1H), 8.00-7.94 (m, 1H), 7.92-7.82 (m, 2H), 7.08 (s,1H), 3.46-3.33 (m, 1H), 1.19 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 170.5, 169.0, 138.4, 134.1, 132.7, 130.1, 126.9, 121.6 (q, $^{1}J_{CF}$ = 318 Hz), 119.0 (q, $^{1}J_{CF}$ = 318 Hz), 114.8, 88.5, 35.0, 19.0; ^{19}F NMR (376 MHz, CD_3CN) δ -74.3, -79.4; HRMS (ESI-positive ionization): calcd for $C_{13}H_{13}F_3IO_5S$ ($[M\text{-}OTf]^+$): 464.9480, found: 464.9507.

(*E*)-2-((2-Cyclopropyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-λ^3-iodanyl)benzoic acid triflate salt 12j



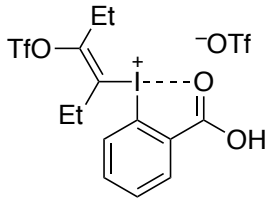
Reaction with cyclopropylacetylene **15j** (40 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 193 mg (63%) of product **12j**, isolated as a light brown solid: mp 101.8-102.3 °C (decomp.); IR (KBr) cm^{-1}; 3094, 2973, 2895, 1669, 1626, 1590, 1415, 1308, 1226; ^{1}H NMR (400 MHz, CD_3CN): δ 8.41 (dd, J = 7.6 Hz, 2.0 Hz, 1H), 8.00-7.93 (m, 1H), 7.92-7.82 (m, 2H), 7.11 (s,1H), 2.38-2.22 (m, 1H), 1.24-0.96 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ 170.4, 165.2, 138.3, 134.2, 132.7, 130.1, 126.9, 118.9 (q, $^{1}J_{CF}$ = 318 Hz), 113.9, 89.9, 16.3, 9.0; ^{19}F NMR (376 MHz, CD_3CN) δ -74.2, -79.4; HRMS (ESI-positive ionization): calcd for $C_{13}H_{11}F_3IO_5S$ ($[M\text{-}OTf]^+$): 462.9324, found: 462.9349.

(*E*)-2-((2-Cyclohexyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-λ^3-iodanyl)benzoic acid triflate salt 12k[3]



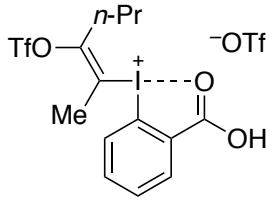
Reaction with ethynylcyclohexane **15k** (65 mg, 0.60 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 258 mg (79%) of product **12k**, isolated as a white solid: mp 155.0-155.9 °C (decomp.) (lit.[3], mp 159.7-161.2 °C); IR (KBr) cm^{-1}; 3087, 2944, 2865, 1669, 1620, 1591, 1414, 1308, 1222; ^1H NMR (400 MHz, CD_3CN): δ 8.39 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.96-7.90 (m, 1H), 7.88-7.78 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.04 (s,1H), 3.09-2.99 (m, 1H), 1.79-1.71 (m, 4H), 1.70-1.60 (m, 1H), 1.53-1.39 (m, 2H), 1.35-1.11 (m, 3H); ^{19}F NMR (376 MHz, CD_3CN) δ -74.3, -79.4.

(*E*)-2-((4-(((Trifluoromethyl)sulfonyl)oxy)hex-3-en-3-yl)-λ^3-iodanyl)benzoic acid triflate salt 12l[3]



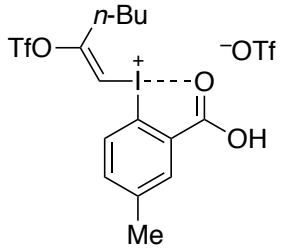
Reaction with 3-hexyne **15l** (49 mg, 0.6 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 311 mg (99%) of product **12l**, isolated a white solid: mp 129.4-130 °C (decomp.); IR (neat) cm^{-1}; 3080, 2991, 2882, 1665, 1591, 1421, 1292, 1223; ^1H NMR (400 MHz, CD_3CN): δ 8.40 (dd, *J* = 7.4 Hz, 1.8 Hz, 1H), 7.98-7.83 (m, 2H), 7.75 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 2.97-2.87 (m, 4H), 1.18 (t, *J* = 7.4 Hz, 6H); ^{19}F NMR (376 MHz, CD_3CN): δ -74.7, -79.4.

(*E*)-2-((3-(((Trifluoromethyl)sulfonyl)oxy)hex-2-en-2-yl)-λ^3-iodanyl)benzoic acid triflate salt 12m[3]



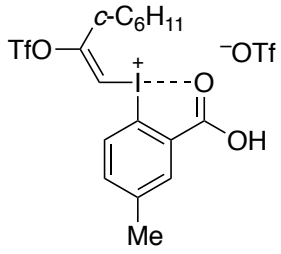
Reaction with 2-hexyne **15m** (49 mg, 1.0 mmol) and 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) according to the general procedure afforded 286 mg (91%) of product **12m**, isolated a white solid: mp 146.5-171.2 °C (lit.[3], mp 146.0-147.0 °C); IR (KBr) cm^{-1}; 3091, 2976, 2883, 1671, 1427, 1292, 1218; ^1H NMR (400 MHz, CD_3CN): δ 8.41 (dd, *J* = 7.4 Hz, 1.8 Hz, 1H), 7.98-7.83 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.76 (s, 3H), 1.71-1.58 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, CD_3CN): δ -74.8, -79.4.

(*E*)-5-Methyl-2-((2-(((trifluoromethyl)sulfonyl)oxy)hex-1-en-2-yl)-λ^3-iodanyl)benzoic acid triflate salt 12n[3]



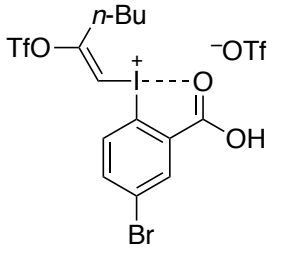
Reaction with 1-hexyne **15a** (49 mg, 0.6 mmol) and 4-methyl-2-iodosylbenzoic acid **13** (139 mg, 0.50 mmol) according to the general procedure afforded 283 mg (88%) of product **12n**, isolated a white solid: mp 121.9-122.7 °C (lit.[3], mp 115.8-116.9 °C); IR (KBr) cm^{-1}; 3082, 2967, 2872, 1661, 1581, 1424, 1223; ^1H NMR (400 MHz, CD_3CN): δ 8.25 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.17 (s, 1H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.53 (s, 3H), 1.62 (quint, *J* = 7.6 Hz, 2H), 1.41-1.30 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, CD_3CN): δ -74.4, -79.4.

(*E*)-2-((2-Cyclohexyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-λ^3-iodanyl)-5-methylbenzoic acid triflate salt 12o



Reaction with ethynylcyclohexane **15k** (65 mg, 0.60 mmol) and 4-methyl-2-iodosylbenzoic acid **13** (139 mg, 0.50 mmol) according to the general procedure afforded 281 mg (84%) of product **12o**, isolated a white solid: mp 130.0-130.3 °C (decomp.); IR (KBr) cm^{-1}; 3085, 2943, 2862, 1641, 1609, 1591, 1424, 1259, 1221; ^1H NMR (400 MHz, CD_3CN): δ 8.25 (d, J = 1.2 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2.0 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.05 (s, 1H), 3.11-3.01 (m, 1H), 2.53 (s, 3H), 1.84-1.73 (m, 4H), 1.73-1.63 (m, 1H), 1.55-1.42 (m, 2H), 1.39-1.17 (m, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 170.6, 168.1, 144.0, 139.0, 134.6, 129.7, 126.6, 121.6 (q, $^1J_{CF}$ = 318 Hz), 118.9 (q, $^1J_{CF}$ = 318 Hz), 111.1, 88.6, 44.4, 29.6, 25.3, 25.1, 20.3; ^{19}F NMR (376 MHz, CD_3CN): δ -74.3, -79.4; HRMS (ESI-positive ionization): calcd for $C_{17}H_{19}F_3IO_5S$ ($[M\text{-}OTf]^+$): 518.9950, found: 518.9975.

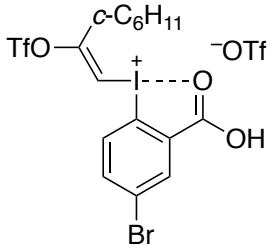
(*E*)-5-Bromo-2-((2-(((Trifluoromethyl)sulfonyl)oxy)hex-1-en-2-yl)-λ^3-iodanyl)benzoic acid triflate salt 12p[3]



Reaction with 1-hexyne **15a** (49 mg, 0.6 mmol) and 4-bromo-2-iodosylbenzoic acid **14** (172 mg, 0.50 mmol) according to the general procedure afforded 293 mg (83%) of product **12p**, isolated a white solid: mp 149.7-150.2 °C (lit.[3], mp 167.5-169.2 °C); IR (KBr) cm^{-1}; 3093, 2970, 2874, 1666, 1624, 1431, 1295, 1226, 1205; ^1H NMR (400 MHz, CD_3CN): δ 8.52 (d, J = 2.4 Hz, 1H), 8.10 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.68 (d, J = 8.8

Hz, 1H), 7.19 (s, 1H), 2.86 (t, J = 7.6 Hz, 2H), 1.62 (quint, J = 7.6 Hz, 2H), 1.42-1.29 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, CD_3CN): δ -74.4, -79.4.

(*E*)-5-Bromo-2-((2-cyclohexyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-λ^3-iodanyl)benzoic acid triflate salt 12q



Reaction with ethynylcyclohexane **15k** (65 mg, 0.60 mmol) and 4-bromo-2-iodosylbenzoic acid **14** (172 mg, 0.50 mmol) according to the general procedure afforded 158 mg (43%) of product **12q**, isolated a light brown solid: mp 137.3-138.2 °C (decomp.); IR (KBr) cm^{-1}; 3104, 2942, 2862, 1667, 1610, 1429, 1284, 1227; ^{1}H NMR (400 MHz, CD_3CN): δ 8.52 (d, J = 2.4 Hz, 1H), 8.10 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.8Hz, 1H), 7.07 (s, 1H), 3.13-2.98 (m, 1H), 1.85-1.73 (m, 4H), 1.72-1.63 (m, 1H), 1.53-1.42 (m, 2H), 1.38-1.22 (m, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 169.4, 168.6, 140.7, 136.5, 131.5, 128.8, 126.7, 118.9 (q, $^1J_{CF}$ = 318 Hz), 113.6, 88.7, 44.5, 29.5, 25.3, 25.1; ^{19}F NMR (376 MHz, CD_3CN): δ -74.3, -79.3; HRMS (ESI-positive ionization): calcd for $C_{16}H_{16}F_3IO_5SBr^{79}$ ([M-OTf]$^+$): 582.8899, found: 582.8916.

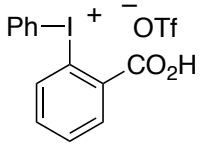
4. Large scale reaction for preparation of (E)-2-((2-(((Trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)-λ^3-iodanyl)benzoic acid triflate salt 12a

Trifluoromethanesulfonic anhydride (705 mg, 3.0 mmol) was added dropwise at 0 °C to a stirred mixture of 2-iodosylbenzoic acid **1** (660 mg, 2.50 mmol) and 1-hexyne **15a** (246 mg, 3.0 mmol) in dichloromethane (10.0 mL). The reaction was stirred for 4 hours at room temperature. After the completion of the reaction, the solvent

was removed under reduced pressure and the remaining solid product was washed with hexane and ether several times then dried in vacuum to afford 1445 mg (92%) of pure product **12a.**

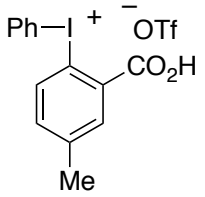
5. Preparation of phenyl benziodoxole derivatives

2-Carboxyphenyl(phenyl)iodonium triflate 15[6]



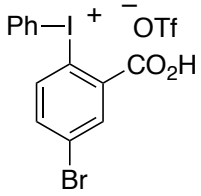
Trifluoromethanesulfonic anhydride (169 mg, 0.60 mmol) was added dropwise at 0 °C to a stirred mixture of 2-iodosylbenzoic acid **1** (132 mg, 0.50 mmol) and benzene (78 mg, 1.0 mmol) in dichloromethane (1.0 mL). The reaction was stirred at room temperature for 12 hours. After the completion of the reaction, the solvent was removed under reduced pressure and the remaining solid product was washed with hexane and ether several times then dried in vacuum to obtain 2-carboxyphenyl(phenyl)iodonium triflate **15** 238 mg (100%) as a white solid: mp 226.7-227.4 °C (lit.[6], mp 230.5-231.4 °C); IR (KBr) cm^{-1}; 3089, 1674, 1584, 1425, 1291, 1217; ^{1}H NMR (400 MHz, CD_3CN): δ 8.40 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 8.00-7.93 (m, 1H), 7.82-7.68 (m, 4H), 7.08 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H); ^{19}F NMR (377 MHz, CD_3CN): δ -79.4.

4-Methyl-2-carboxyphenyl(phenyl)iodonium triflate 16[6]



Trifluoromethanesulfonic anhydride (169 mg, 0.60 mmol) was added dropwise at 0 °C to a stirred mixture of 4-methyl-2-iodosylbenzoic acid **13** (139 mg, 0.50 mmol) and benzene (78 mg, 1.0 mmol) in dichloromethane (1.0 mL). The reaction was stirred at room temperature for 12 hours. After the completion of the reaction, the solvent was removed under reduced pressure and the remaining solid product was washed with hexane and ether several times then dried in vacuum to obtain 4-methyl-2-carboxyphenyl(phenyl)iodonium triflate **16** 224 mg (92%) as a white solid: mp 149.3-149.6 °C (lit.[6], mp 149.3-152.6 °C); IR (KBr) cm^{-1}; 3087, 2986, 1651, 1575, 1256; ^{1}H NMR (400 MHz, CD_3CN): δ 8.22 (d, J = 2.4 Hz, 1H), 8.16-8.08 (m, 2H), 7.97-7.88 (m, 2H), 7.76-7.67 (m, 2H), 7.54-7.47 (m, 1H), 6.90 (d, J = 7.6 Hz, 2H), 2.44 (s, 3H); ^{19}F NMR (377 MHz, CD_3CN): δ -79.4.

4-Bromo-2-carboxyphenyl(phenyl)iodonium triflate 17[6]



Trifluoromethanesulfonic anhydride (42 mg, 0.150 mmol) was added dropwise at 0 °C to a stirred mixture of 4-bromo-2-iodosylbenzoic acid **14** (43 mg, 0.125 mmol) and benzene (20 mg, 0.150 mmol) in dichloromethane (0.250 mL). The reaction was stirred at room temperature for 12 hours. After the completion of the reaction, the solvent was removed under reduced pressure and the remaining solid product was washed with hexane and ether several times then dried in vacuum to obtain 4-bromo-2-carboxyphenyl(phenyl)iodonium triflate **17** 67 mg (97%) as a white solid: mp 189.1-189.5 °C (lit.[6], mp 186.1-187.5 °C); IR (KBr) cm^{-1}; 3085, 1672, 1463, 1385, 1255; ^{1}H NMR (400 MHz, CD_3CN): δ 8.48 (d, J = 2.4 Hz, 1H), 8.14-8.09 (m, 2H), 7.93 (t, J = 7.4 Hz, 1H), 7.80 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.75-7.69 (m, 2H), 6.90 (d, J = 8.8 Hz, 1H); ^{19}F NMR (377 MHz, CD_3CN): δ -79.4.

6. References:

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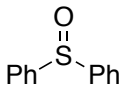
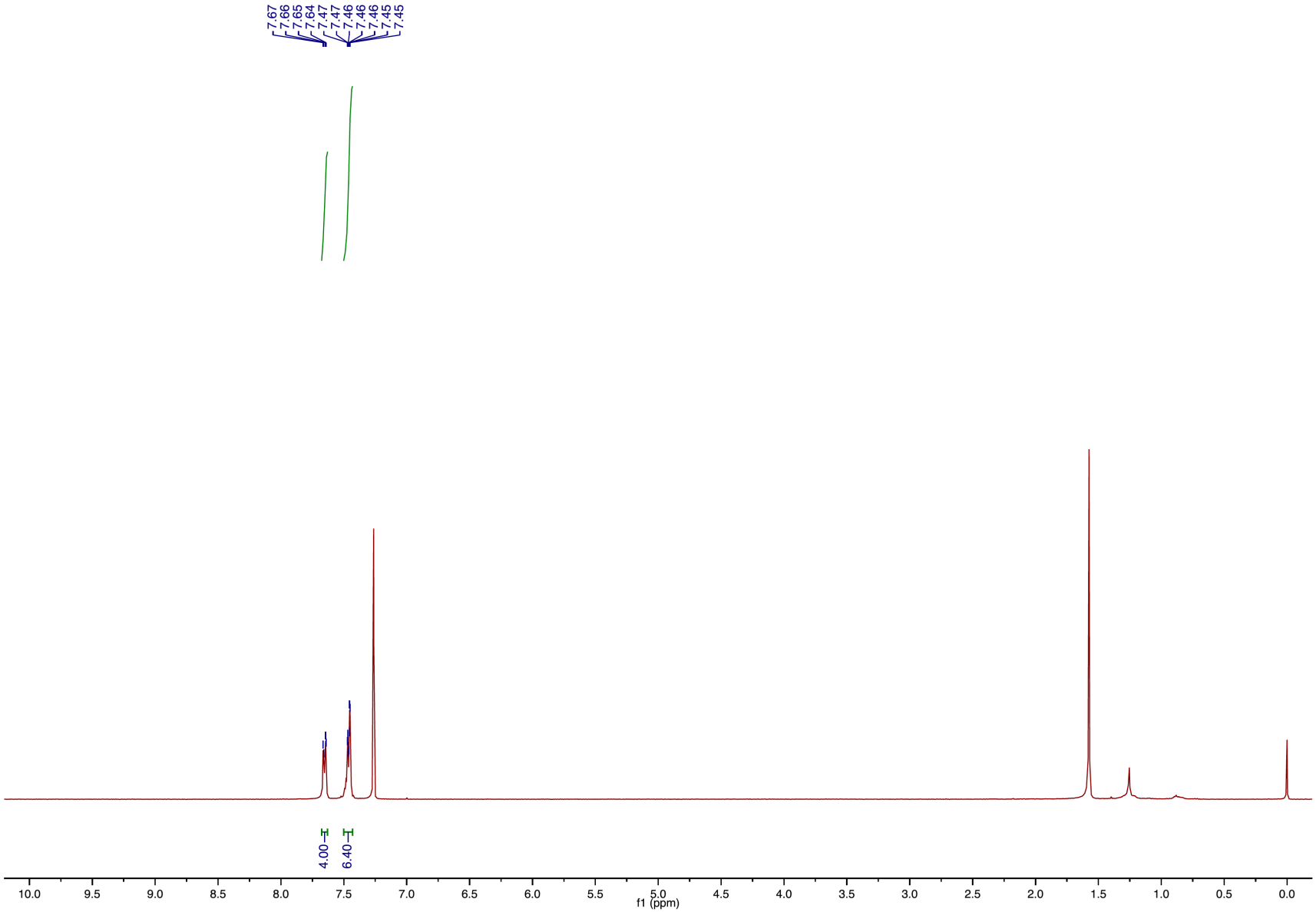
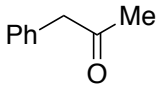
4. A. Yoshimura and V. V. Zhdankin, *ARKIVOC* 2017, DOI: 10.3998/ark.5550190.p009.893, 32-40.
5. A. Yoshimura, K. C. Nguyen, S. C. Klasen, A. Saito, V. N. Nemykin and V. V. Zhdankin, *Chem. Commun.*, 2015, **51**, 7835-7838.
6. A. Yoshimura, S. M. Larson, G. B. Frahm, C. D. Huss, G. T. Rohde, V. N. Nemykin, M. S. Yusubov, A. Saito and V. V. Zhdankin, *ARKIVOC (Gainesville, FL, U. S.)*, 2020, DOI: 10.24820/ark.5550190.p011.324, 35-49.

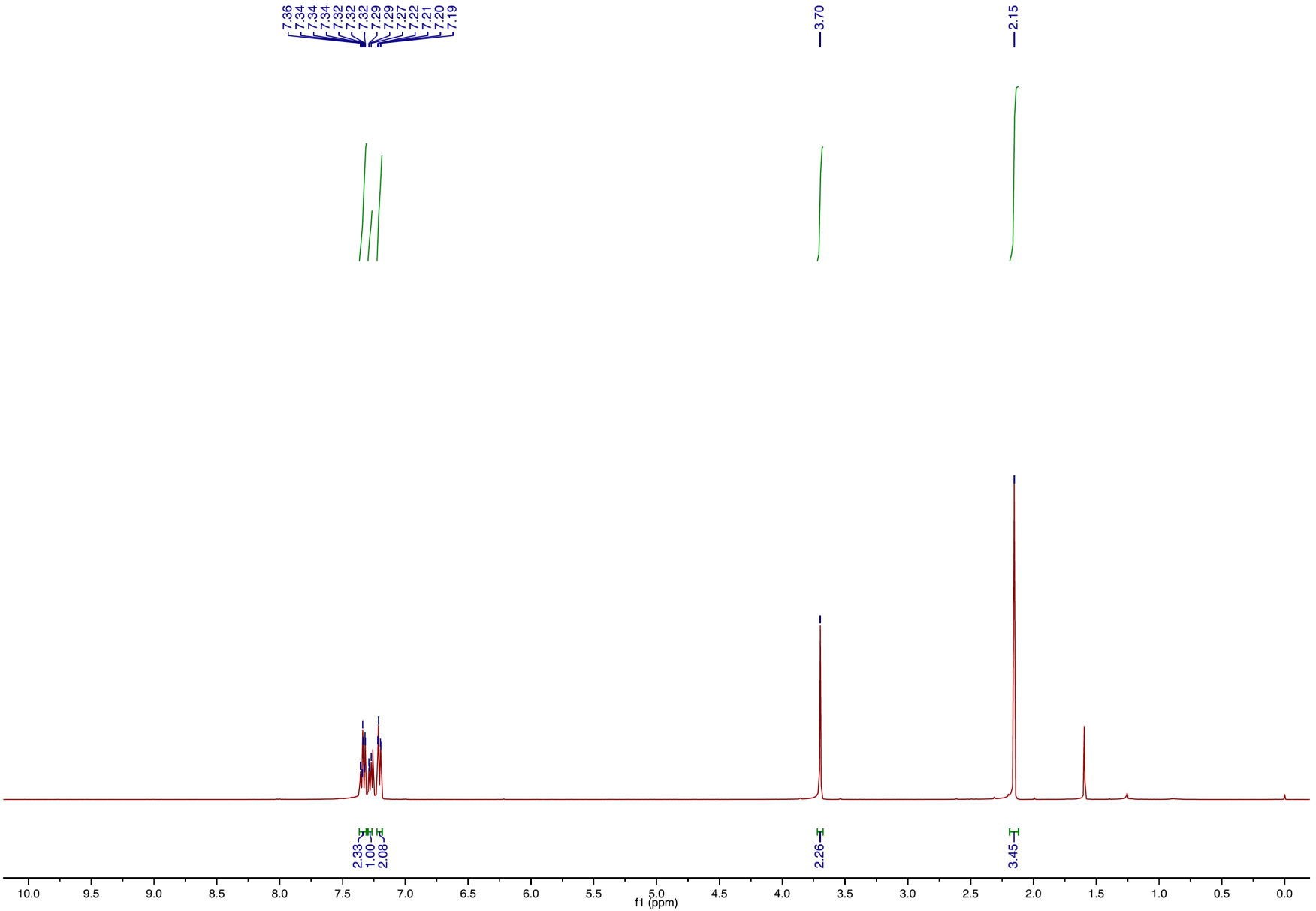
^{1}H NMR (400 MHz, $CDCl_3$)



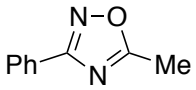


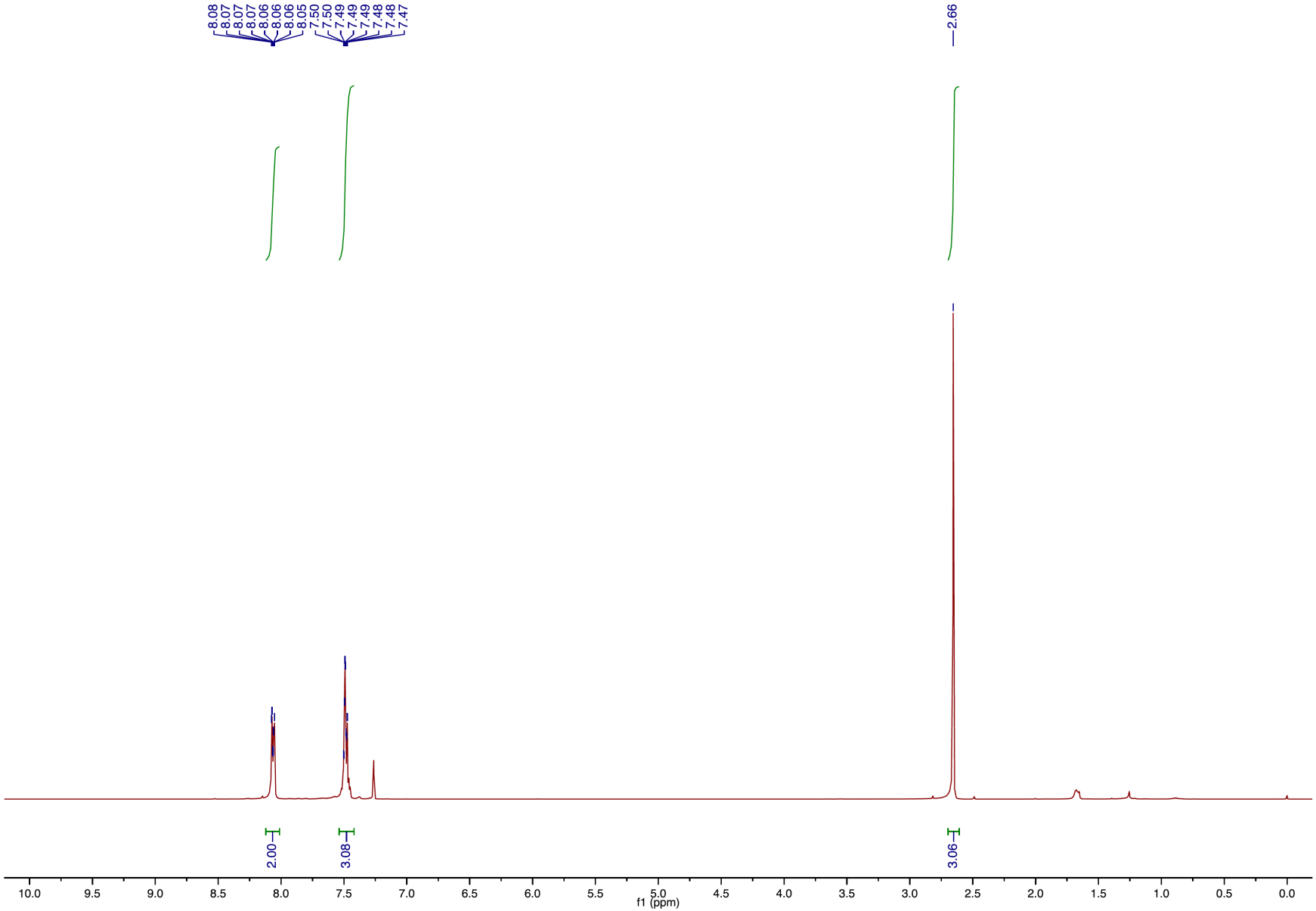
^{1}H NMR (400 MHz, $CDCl_3$)



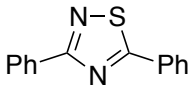


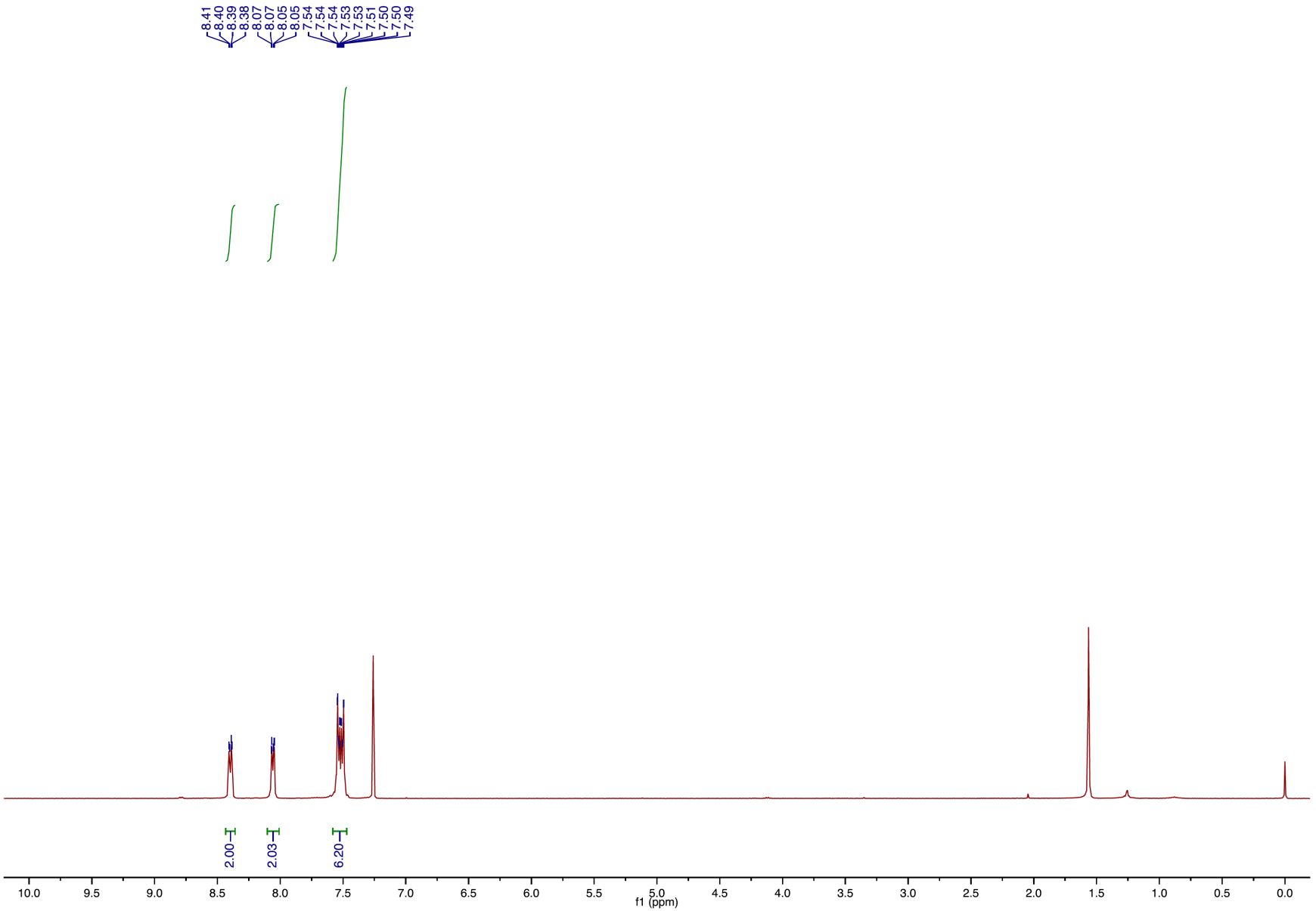
^{1}H NMR (400 MHz, $CDCl_3$)





^{1}H NMR (400 MHz, $CDCl_3$)





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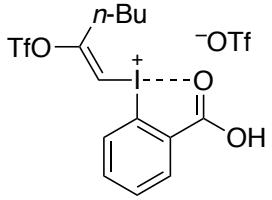
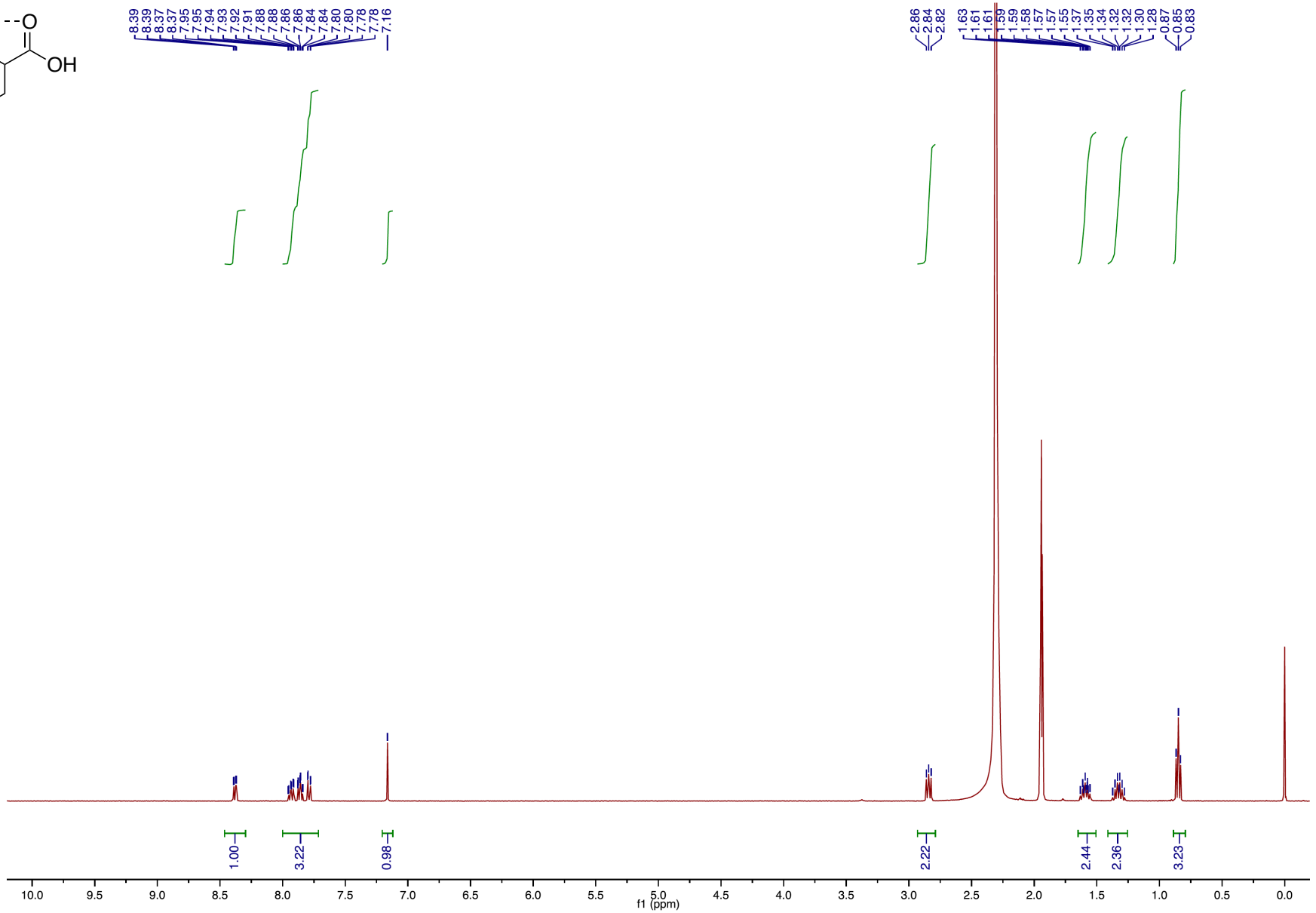
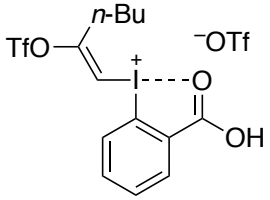
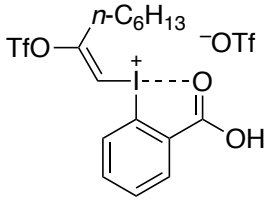




^{19}F NMR (376 MHz, CD_3CN)



^{1}H NMR (400 MHz, CD_3CN)



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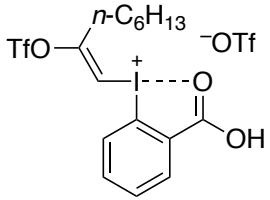

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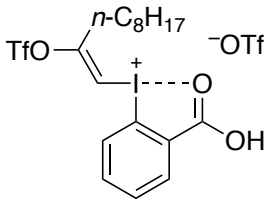

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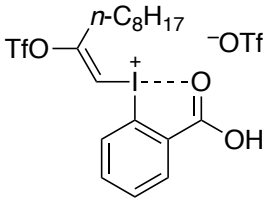

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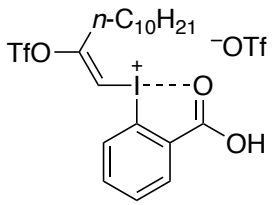

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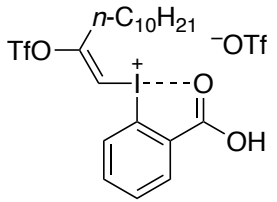
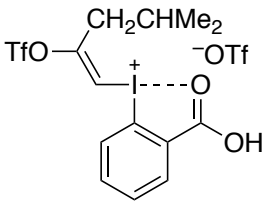
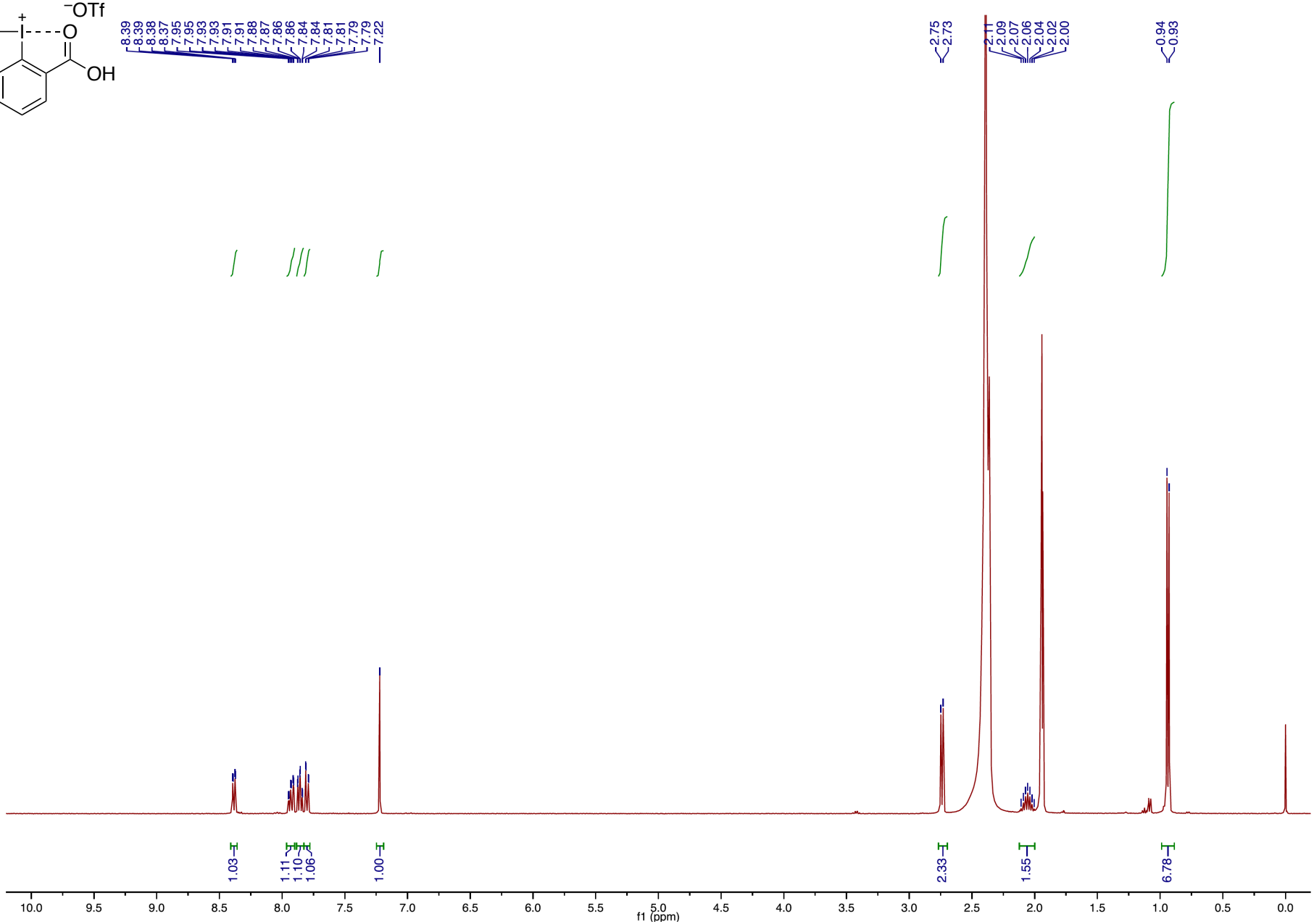
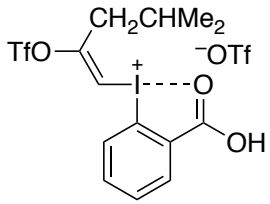


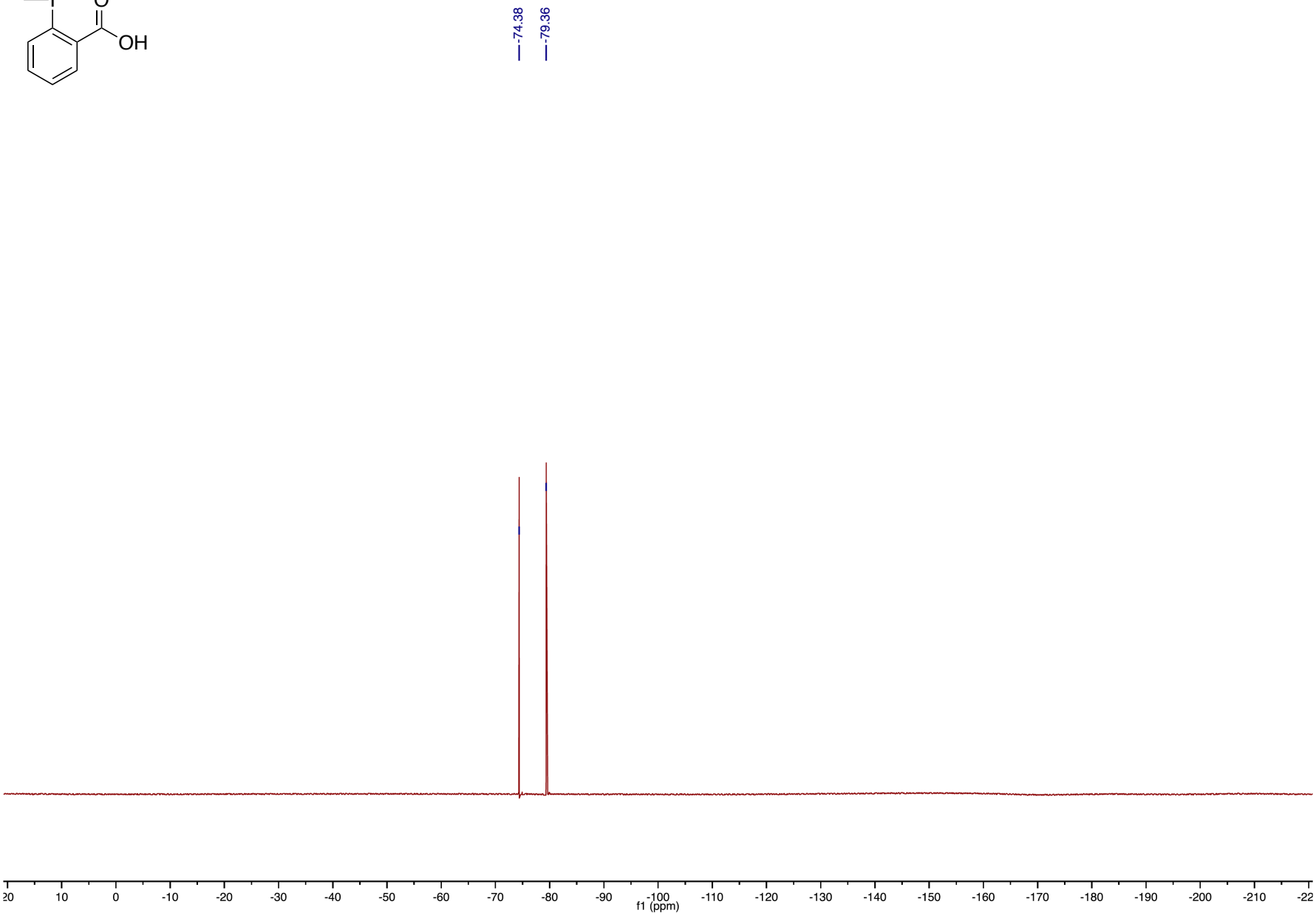
^{1}H NMR (400 MHz, CD_3CN)





^{19}F NMR (376 MHz, CD_3CN)





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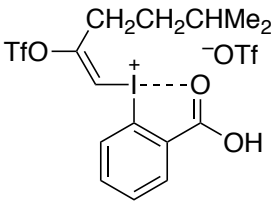
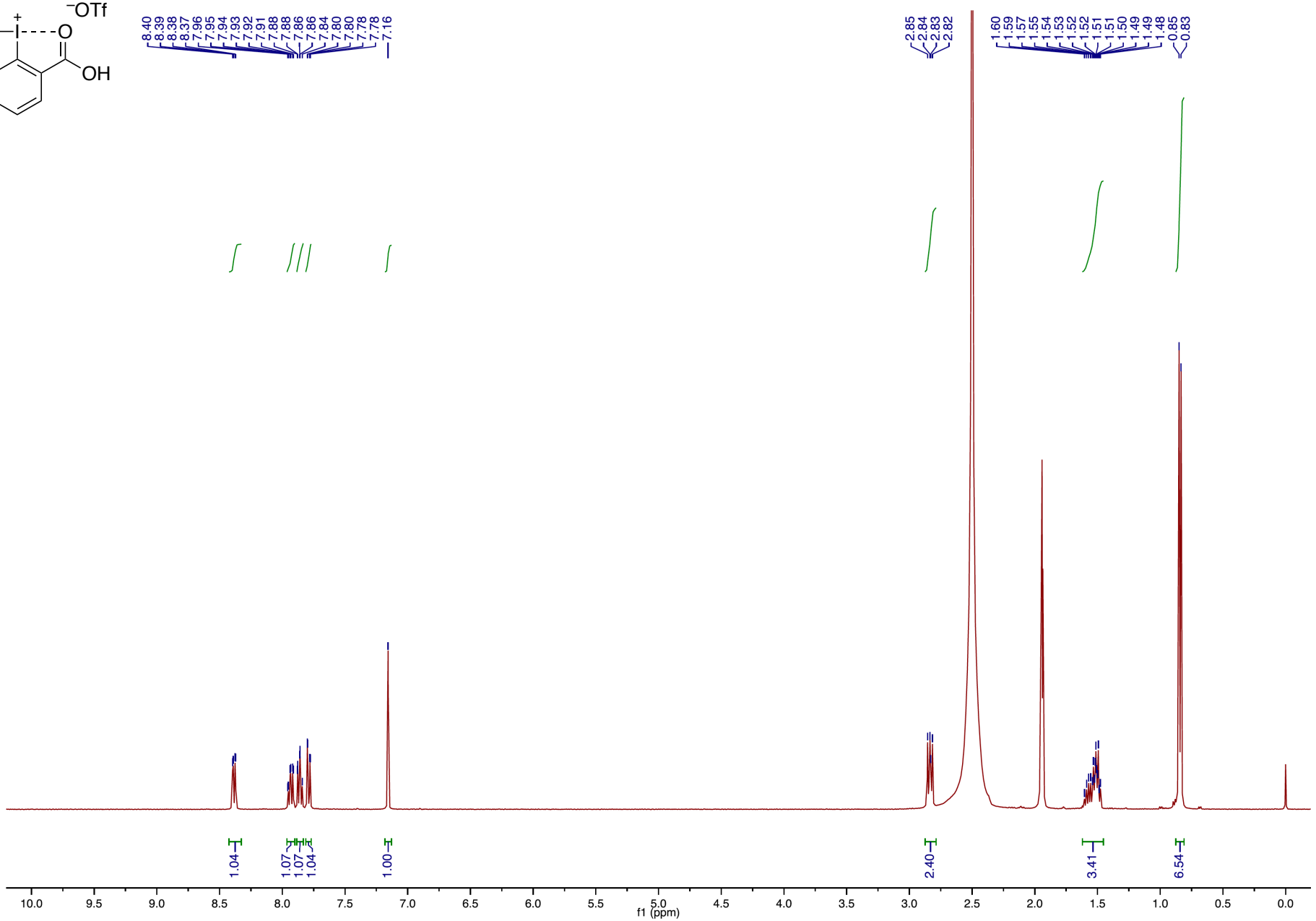
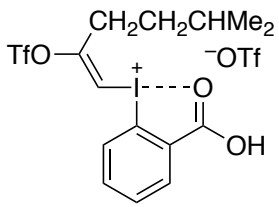
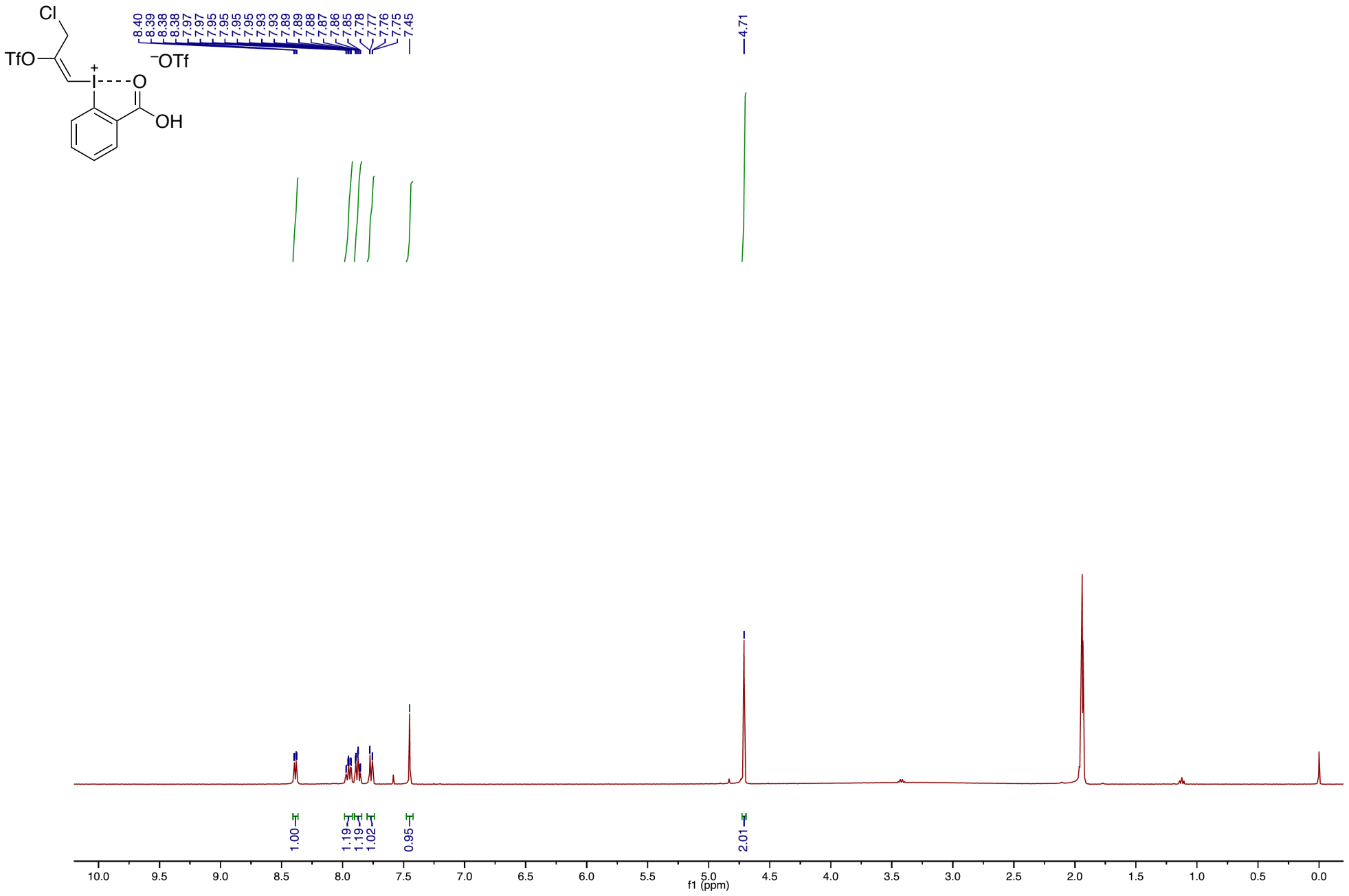




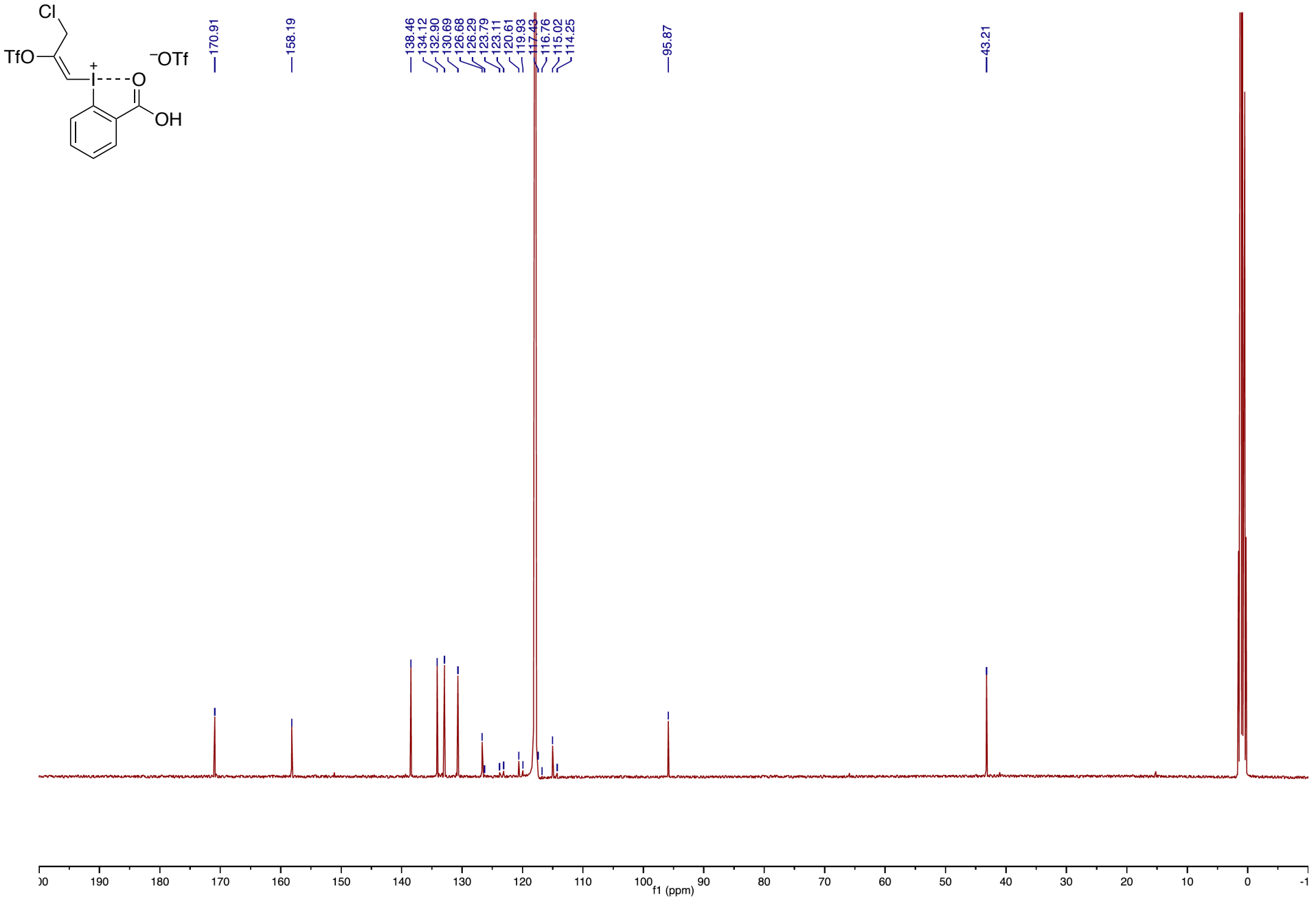
^{19}F NMR (376 MHz, CD_3CN)



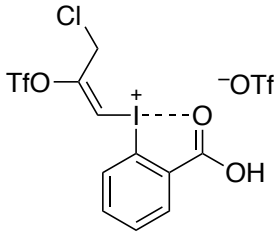
^{1}H NMR (400 MHz, CD_3CN)



^{13}C NMR (100 MHz, CD_3CN)



^{19}F NMR (376 MHz, CD_3CN)



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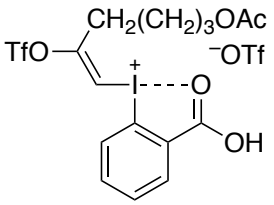

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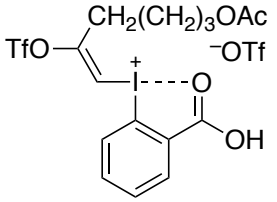

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170.57
165.31
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132.70
130.21
126.89
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123.78
122.89
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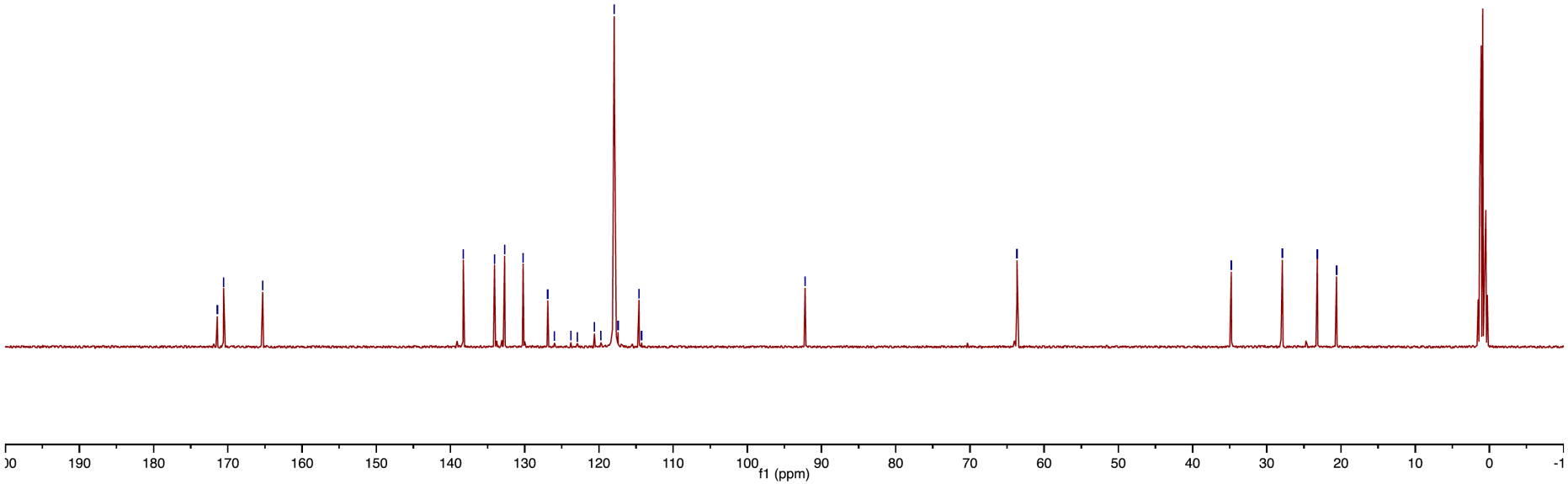

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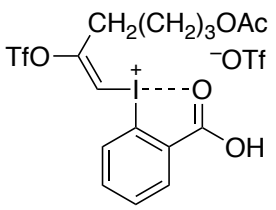

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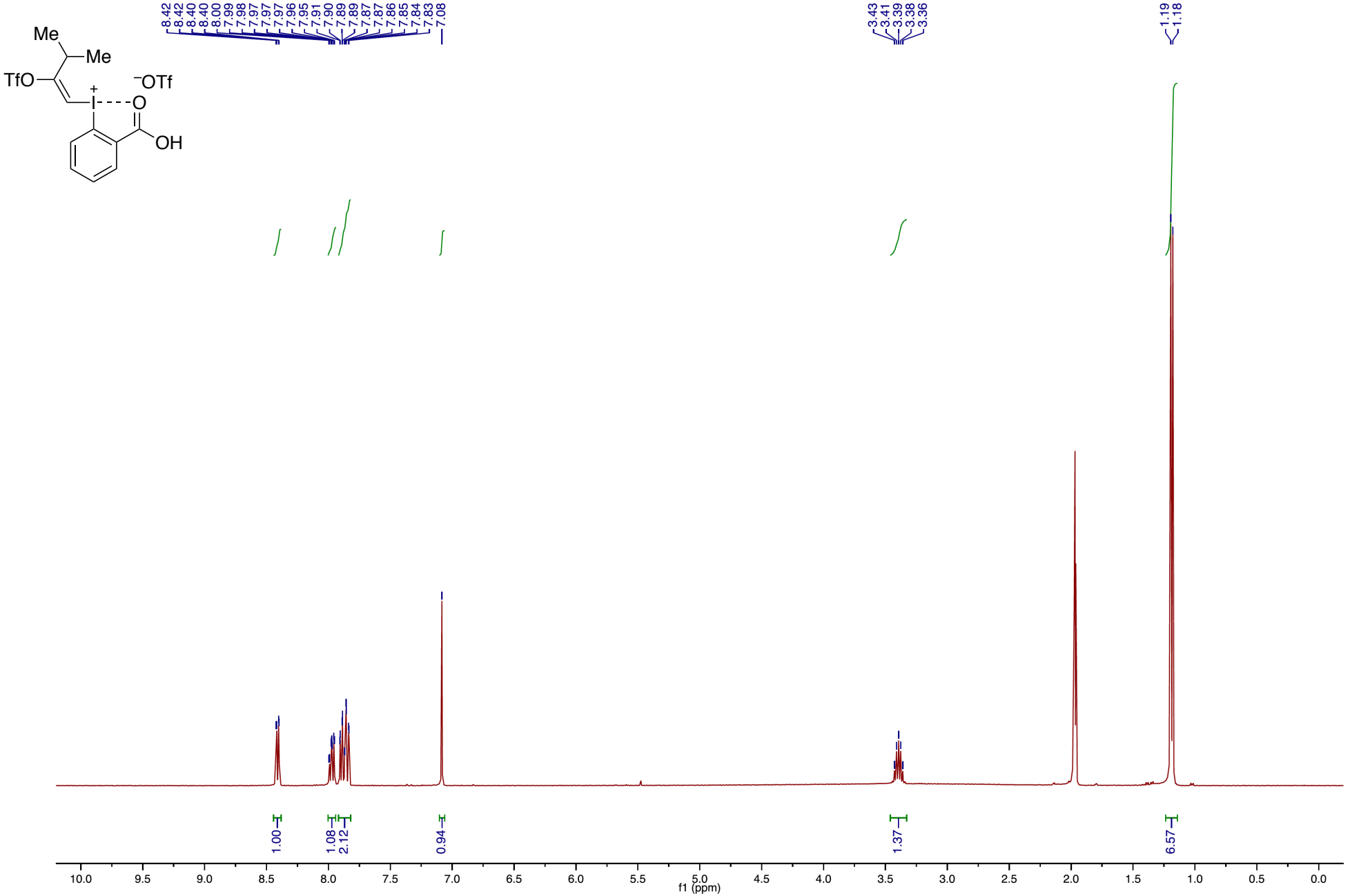
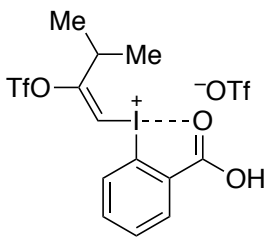
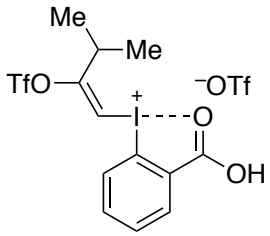


^{13}C NMR (100 MHz, CD_3CN)



^{19}F NMR (376 MHz, CD_3CN)



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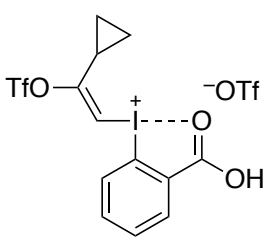

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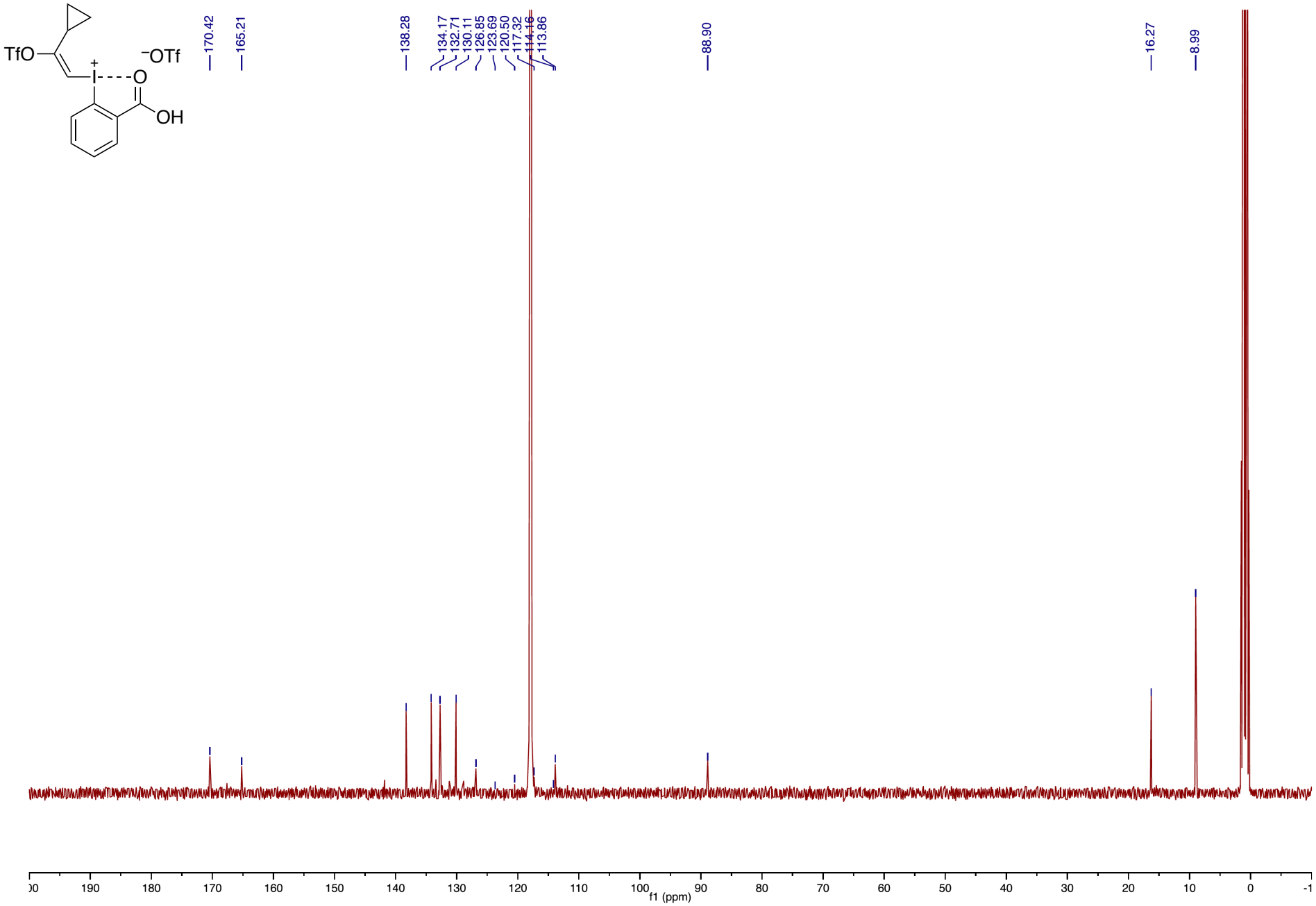

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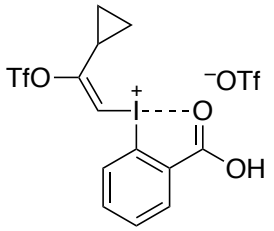

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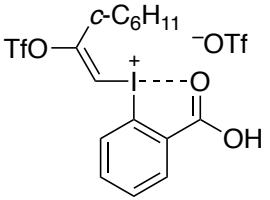

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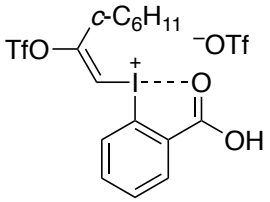

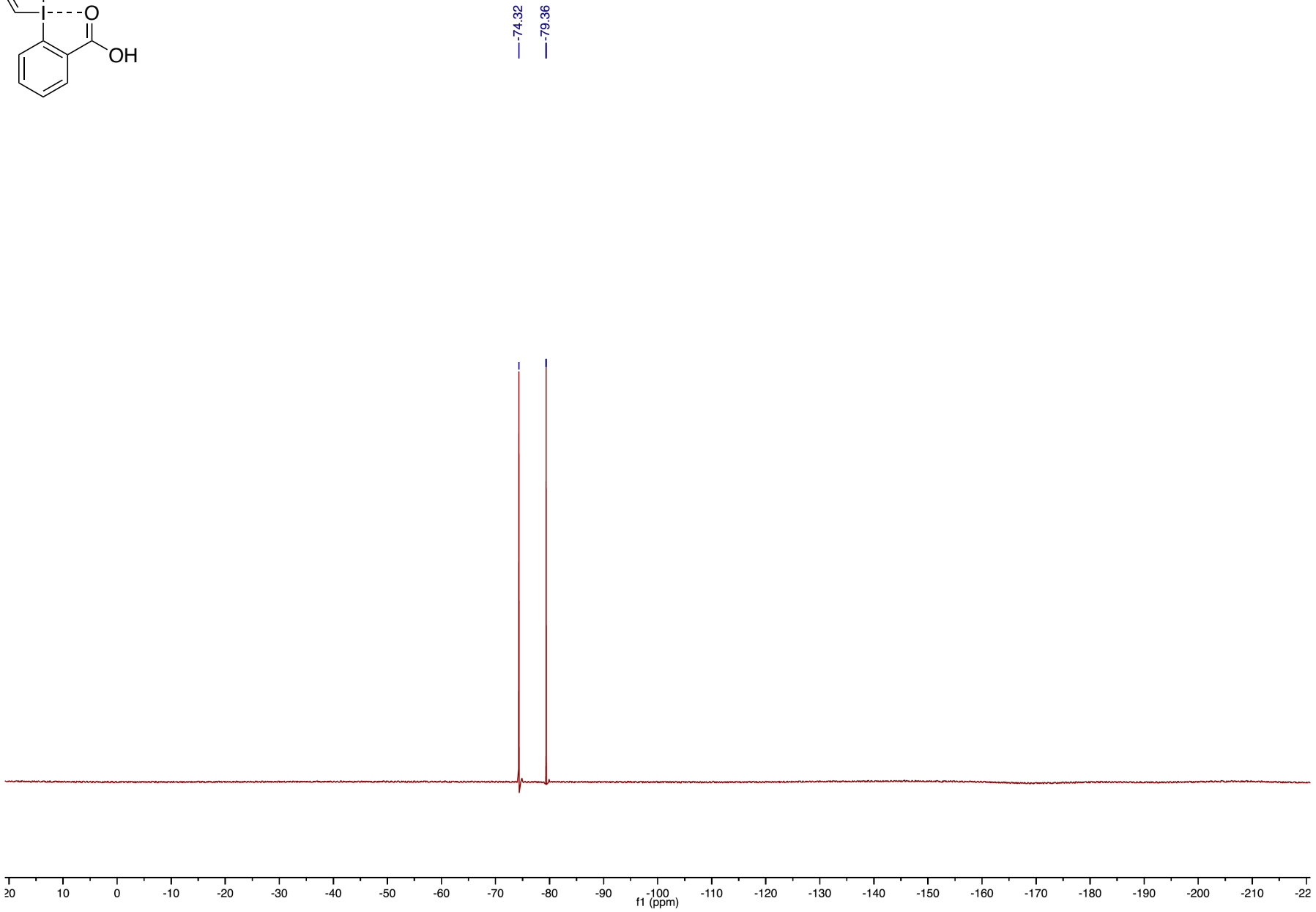

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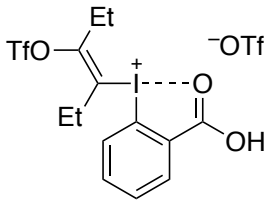

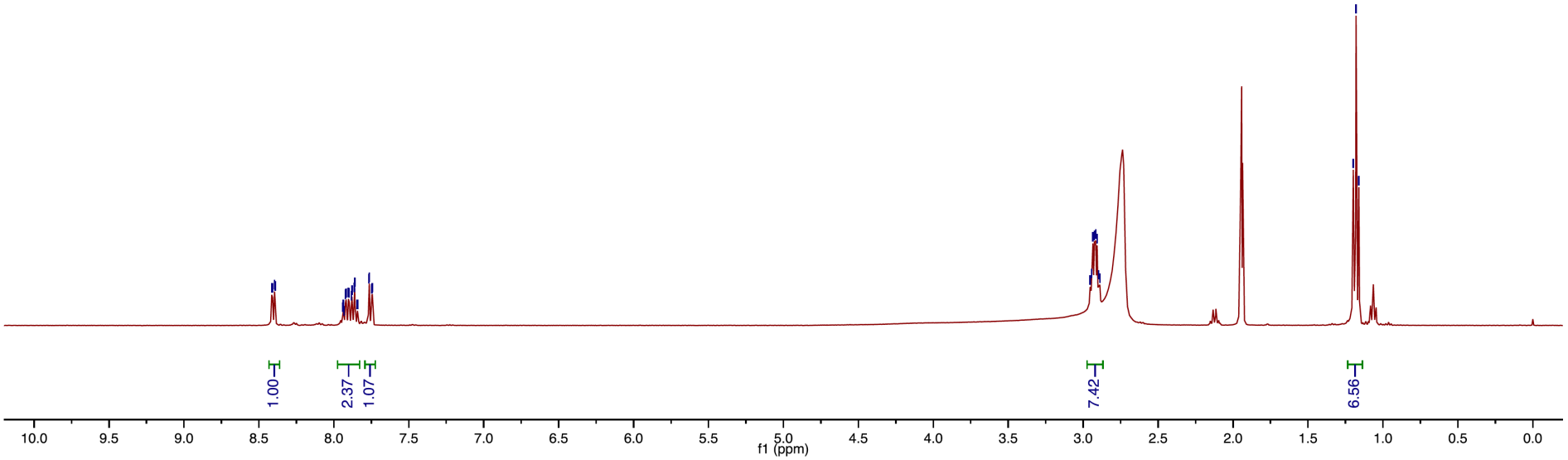

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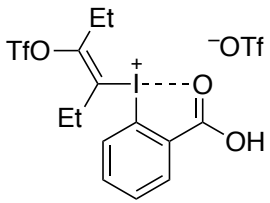

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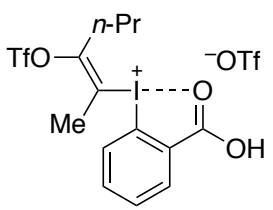

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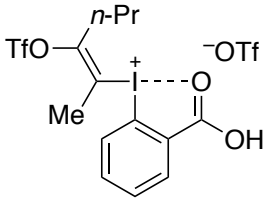

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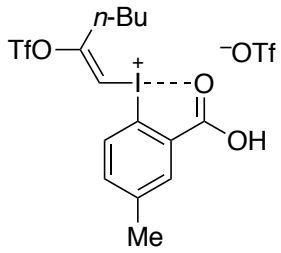

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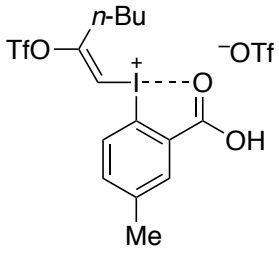

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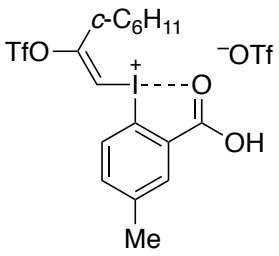

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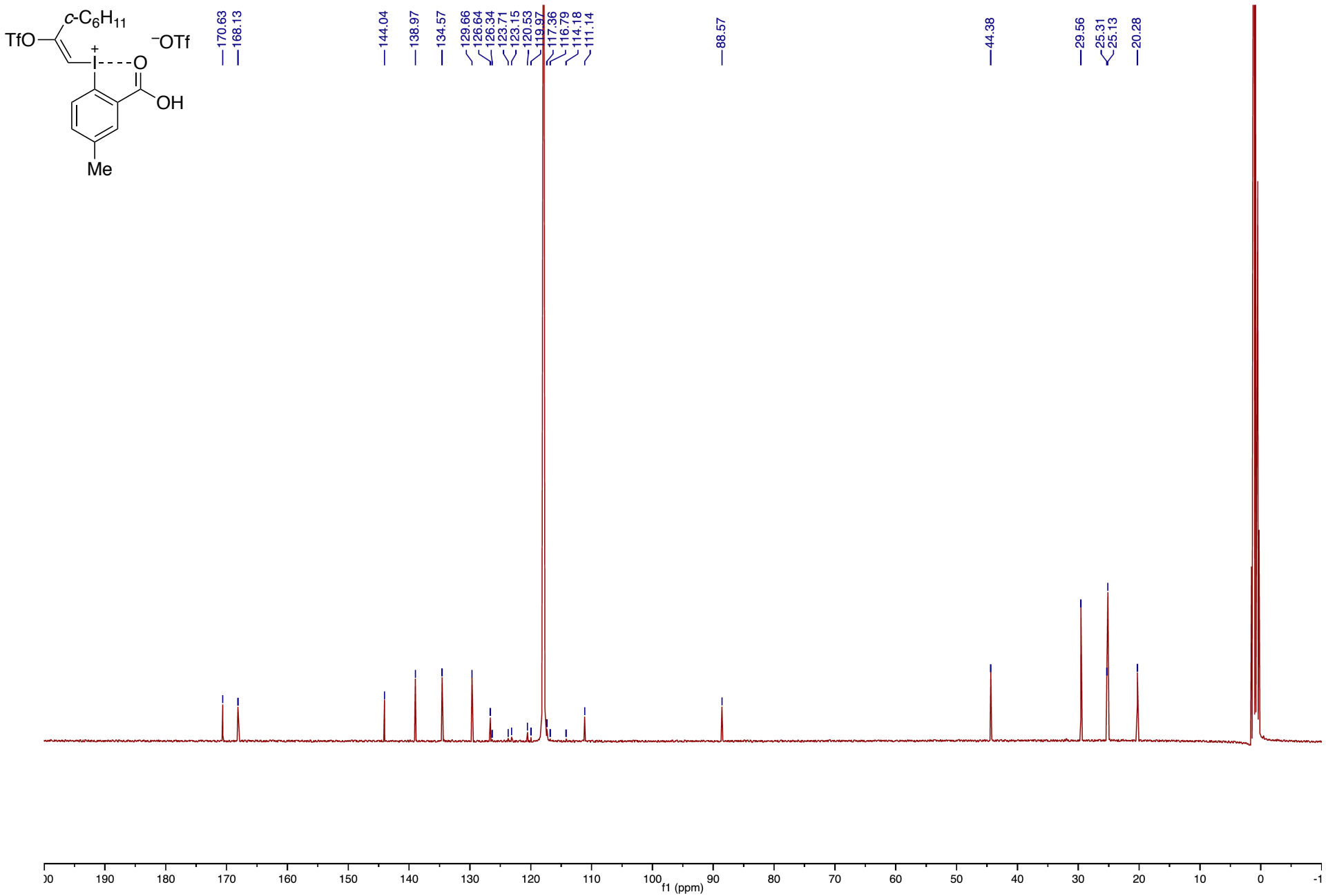

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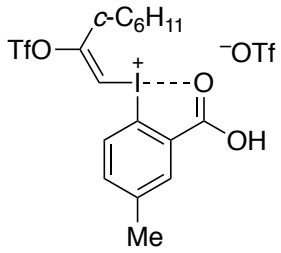

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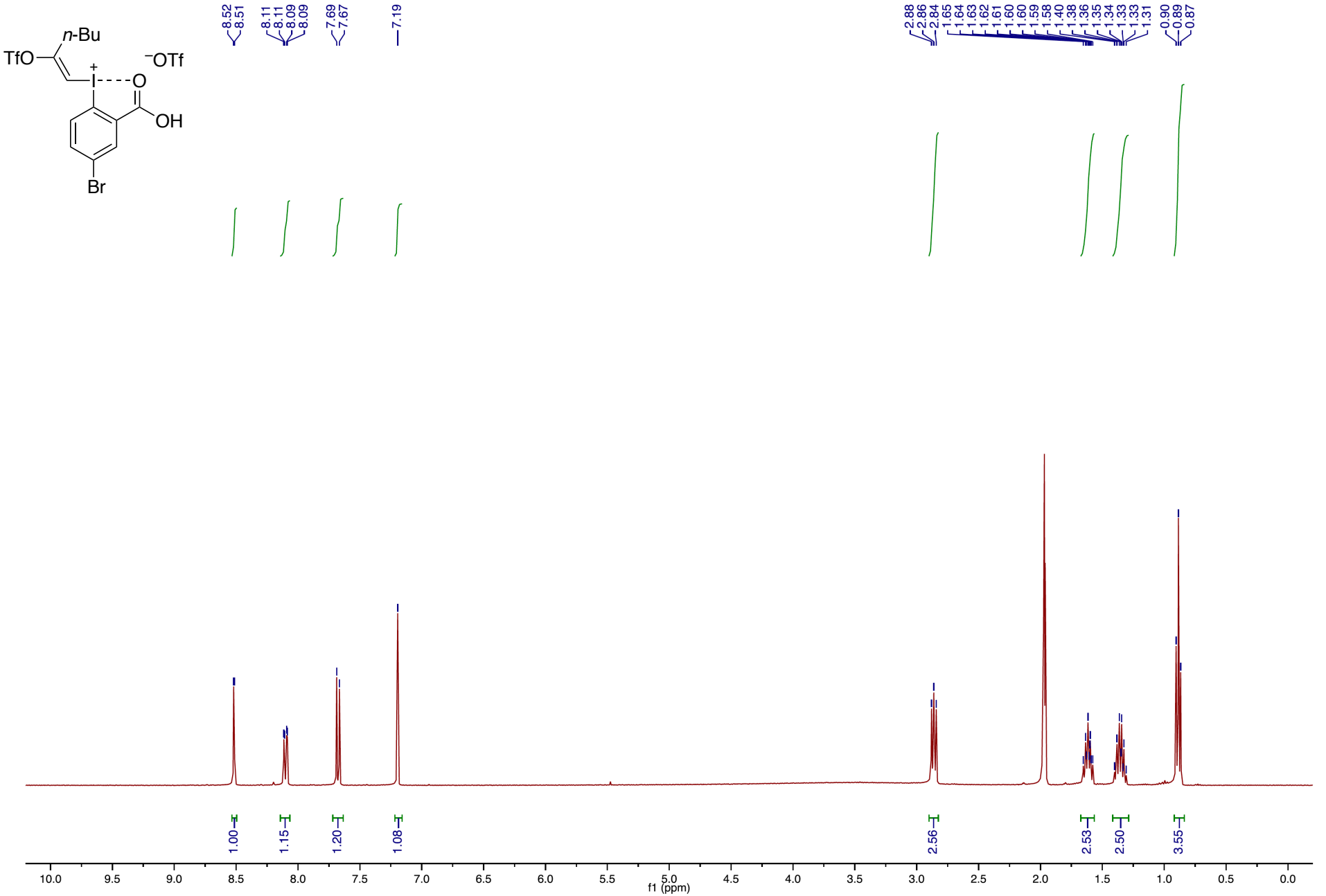

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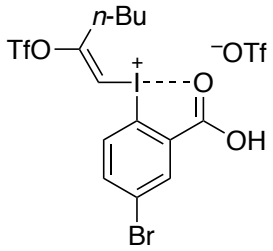

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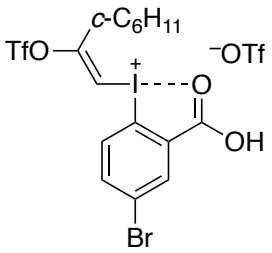

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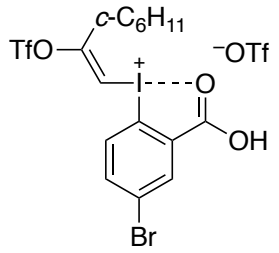

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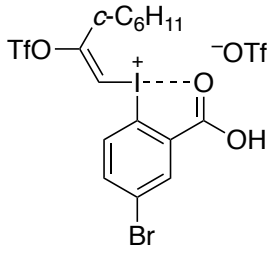

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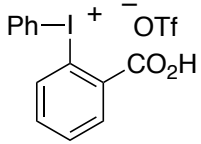

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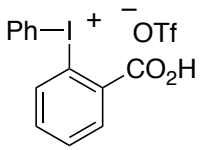

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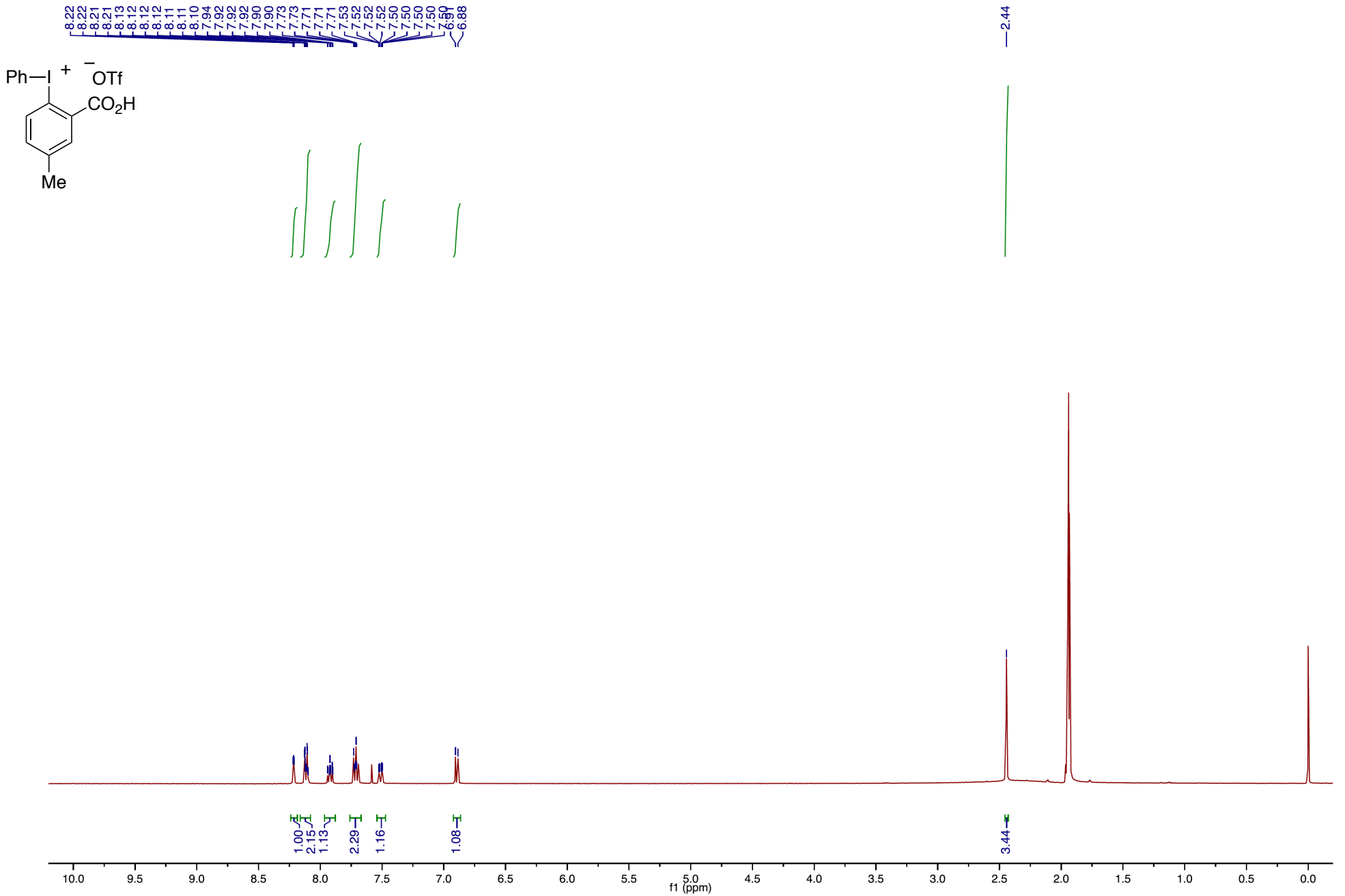

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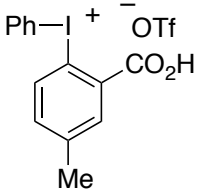

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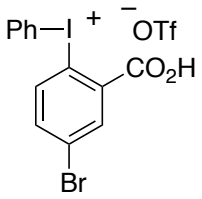

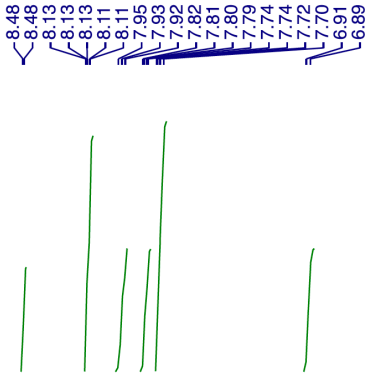

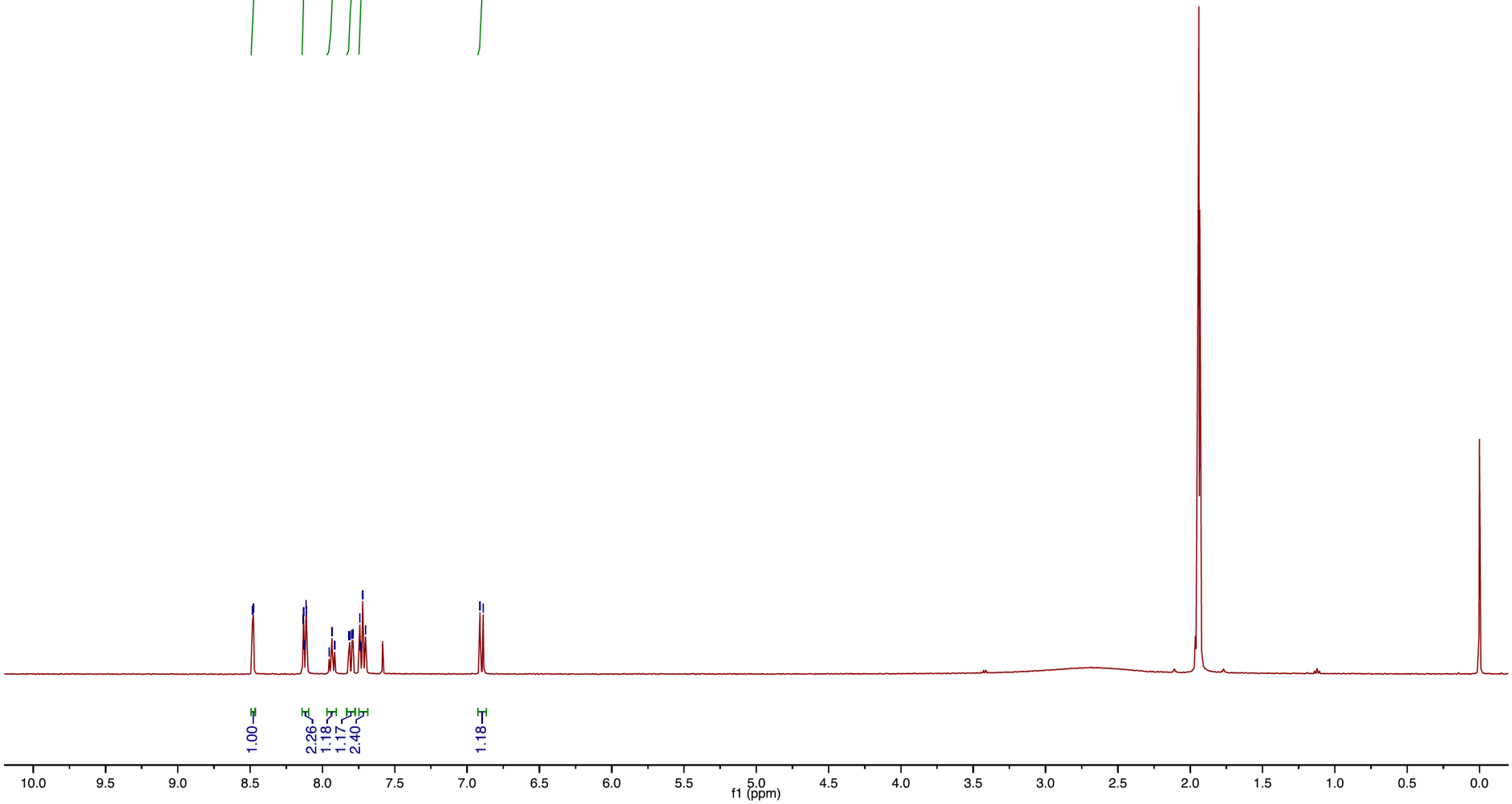

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