Supporting Information

Preparation and Structure of Phenolic Aryliodonium Salts

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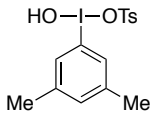
1. General experimental remarks

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. Triisopropylsiloxybenzene **1a**[1], *tert*-butyldimethylsiloxybenzene **1b**[2], *tert*-butyldiphenylsiloxybenzene **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

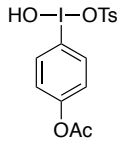
3,5-Dimethyl[hydroxy(tosyloxy)iodo]benzene (5d)



1-Iodo-3,5-dimethyliodobenzene (232mg, 1.0 mmol) was added at room temperature to a stirred mixture of *p*-TsOH•H_2O (190 mg, 1.0 mmol) and *m*-CPBA (173 mg, 1.0 mmol) in dichloromethane (4.0 mL)–2,2,2-trifluoroetahnol (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, CD_3OD): 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, CD_3OD): 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 $C_8H_{10}IO$ $([M\text{-}OTs])^+$: 248.9776, found: 248.9775.

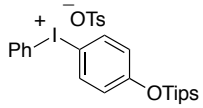
4-Acetoxy[hydroxy(tosyloxy)iodo]benzene (7)



1-Acetoxy-4-iodobenzene (1572mg, 6.00 mmol) was added at room temperature to a stirred mixture of *p*-TsOH•H_2O (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, CD_3OD): 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, CD_3OD): 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 $C_8H_{10}IO_3$ $([M\text{-}OTs])^+$: 278.9518, found: 278.9491.

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

Phenyl(4-triisopropylsiloxyphenyl)iodonium tosylate (3a)

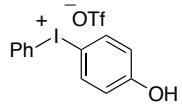


Koser's reagent **2a** (392 mg, 1.0 mmol) was added at 0 °C to a stirred mixture of (triisopropylsiloxy)benzene **1a** (300 mg, 1.2 mmol) in 2,2,2-trifluoroethanol (2.0 mL). The reaction was stirred at room temperature for 24 hour. After completion of reaction, the solvent was removed under reduced pressure 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_3OD): δ 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_3OD): δ 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 $C_{21}H_{30}IOSi$ $([M\text{-}OTs])^{+}$: 453.1111, found: 453.1120.

4. Preparation of Phenolic (Aryl)iodonium Triflates 4

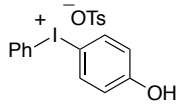
Hydroxy(tosyloxy)iodoarenes **2** (0.5-2.0 mmol) was added at 0 °C to a stirred mixture of (triisopropylsiloxy)benzene **1a** (0.6-2.4 mmol) in 2,2,2-trifluoroethanol (1.0-4.0 mL). The reaction was stirred at room temperature for 24 hour. After the reaction, the mixture was evaporated under reduced pressure, 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 triflate (4a)



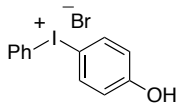
Reaction of Koser's reagent **2a** (784 mg, 2.0 mmol) according to the general procedure afforded 864 mg (97%) of product **4a**, isolated as a white solid: mp 156.4-157.8 °C (decomp.); IR (KBr) cm^{-1} 3268, 3099, 3069, 1597, 1576, 1487, 1431, 1284, 1241, 1206, 637; ^{1}H NMR (500 MHz, CD_3OD): δ 8.09 (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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.9, 137.6, 134.7, 132.2, 120.6 (q, $^{1}J_{CF}$ = 318.0 Hz), 119.1, 115.3, 101.3. ^{19}F NMR (470 MHz, CD_3OD): δ -80.1; Anal. Calcd for $C_{13}H_{10}F_3IO_4$.: 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 $C_{12}H_{10}IO$ $([M\text{-}OTf])^{+}$: 296.9776, found: 296.9784.

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

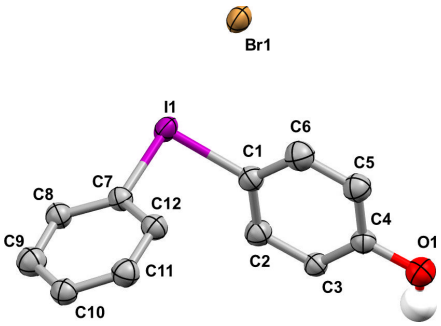


Reaction of Koser's reagent **2a** (392 mg, 1.0 mmol) according to the general procedure for 24 hour stirring using *p*-$TsOH{\cdot}H_2O$ (571 mg, 3.0 mmol) instead of TfOH afforded 187 mg (62%) of product **4b**, isolated as a white solid: mp 151.4-151.7 °C (decomp.); IR (KBr) cm^{-1} 3219, 3094, 3067, 2999, 2920, 1593, 1568, 1474, 1445, 1286, 1218, 1032, 813, 681; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): 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 $C_{12}H_{10}IO$ $([M\text{-}OTs])^{+}$: 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; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.6, 137.3, 134.4, 131.9, 131.6, 118.8, 115.7, 101.7; Anal. Calcd for $C_{12}H_{10}BrIO$.: 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 $C_{12}H_{10}IO$ $([M-Br])^{+}$: 296.9771, found: 296.9797.



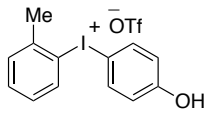
Single crystals of product **4c** suitable for X-ray crystallographic analysis were obtained by slow crystallization from the methanol-acetonitrile solution. X-ray diffraction data for **4c** were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 123 K. The structure was solved by the Sir 2011[12] and refined by full-matrix least-squares refinement on F^2 using SHELXL-2014/7.[13] Crystal data for **4c** $C_{12}H_{10}BrIO$: 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) $Å_3$, Z = 8, 6797 reflections measured, 2139 unique, 1679 I>2σ; final R_1 =

0.0591 , Rw = 0.1786, S = 1.193. CCDC-1855606.

5. Preparation of Phenolic (Aryl)iodonium Triflates 6

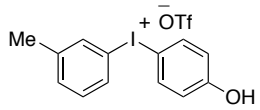
Hydroxy(tosyloxy)iodoarenes **2a** or **5** (0.5-2.0 mmol) was added at 0 °C to a stirred mixture of (triisopropylsiloxy)benzenes **1** (0.6-2.4 mmol) in 2,2,2-trifluoroethanol (1.0-4.0 mL). The reaction was stirred at room temperature for 24 hour. After the reaction, the mixture was evaporated under 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)**



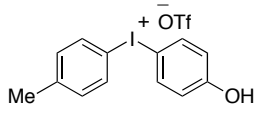
Reaction of Koser's reagent **5a** (203 mg, 0.5 mmol) according to the general procedure afforded 204 mg (89%) of product **6a**, isolated as a white solid: mp 203.4-203.6 °C (decomp.); IR (KBr) cm^{-1} 3295, 3100, 3057, 1594, 1576, 1488, 1430, 1287, 1241, 1207, 1024, 752, 635; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.5, 140.8, 137.1, 136.7, 132.9, 131.4, 129.2, 120.4 (q, $^{1}J_{CF}$ = 316.5 Hz), 120.0, 100.4, 24.1 ^{19}F NMR (282 MHz, CD_3OD): δ -80.0; HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{12}IO$ ($[M\text{-}OTf]$)$^{+}$: 310.9933, found: 310.9923.

***meta*-Tolyl(4-hydroxyphenyl)iodonium triflate (6b)**



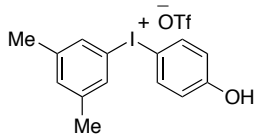
Reaction of Koser's reagent **5b** (406 mg, 1.0 mmol) according to the general procedure afforded 445 mg (97%) of product **6b**, isolated as a white solid: mp 157.7-157.9 °C (decomp.); IR (KBr) cm^{-1} 3284, 3097, 3063, 2934, 1601, 1576, 1488, 1432, 1283, 1240, 1208, 1023, 787, 636; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.6, 142.6, 137.4, 134.6, 132.7, 131.5, 131.3, 120.4 (q, $^{1}J_{CF}$ = 316.7 Hz), 118.8, 114.9, 101.0, 19.8. ^{19}F NMR (282 MHz, CD_3OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{12}IO$ $([M\text{-}OTf])^{+}$: 310.9933, found: 310.9949.

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



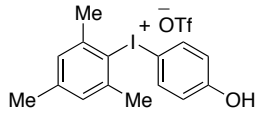
Reaction of Koser's reagent **5c** (406 mg, 1.0 mmol) according to the general procedure afforded 433 mg (94%) of product **6c**, isolated as a white solid: mp 155.4-155.6 °C; IR (KBr) cm^{-1} 3271, 3100, 3073, 2929, 1600, 1578, 1478, 1432, 1283, 1240, 1207, 836, 799, 637; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.6, 143.4, 137.2, 134.4, 132.3, 120.4 (q, $^{1}J_{CF}$ = 317.1 Hz), 118.8, 111.4, 101.3, 19.9. ^{19}F NMR (282 MHz, CD_3OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{12}IO$ $([M\text{-}OTf])^{+}$: 310.9933, found: 310.9945.

3,5-Dimethyl-phenyl(4'-hydroxyphenyl)iodonium triflate (6d)



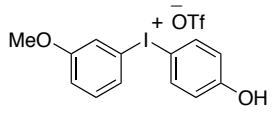
Reaction of Koser's reagent **5d** (420 mg, 1.0 mmol) according to the general procedure afforded 407 mg (86%) of product **6d**, isolated as a white solid: mp 151.7-152.0 °C (decomp.); IR (KBr) cm^{-1} 3294, 3182, 3090, 2926, 1597, 1576, 1489, 1435, 1291, 1237, 1210, 784, 637; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.6, 142.2, 137.3, 133.6, 131.7, 118.8, 114.7, 100.9, 19.7. ^{19}F NMR (282 MHz, CD_3OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for $C_{14}H_{14}IO$ $([M\text{-}OTf])^{+}$: 325.0089, found: 325.0095.

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



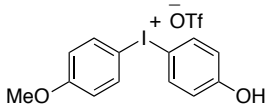
Reaction of Koser's reagent **5e** (434 mg, 1.0 mmol) according to the general procedure afforded 433 mg (89%) of product **6e**, isolated as a white solid: mp 172.0-172.2 °C (decomp.); IR (KBr) cm^{-1} 3271, 3100, 3027, 2923, 1578, 1489, 1437, 1275, 1239, 1030, 764, 640; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.3, 144.1, 141.8, 136.3, 129.8, 121.4, 120.4 (q, $^{1}J_{CF}$ = 317.1 Hz), 118.9, 99.3, 25.5, 19.6. ^{19}F NMR (282 MHz, CD_3OD): δ -80.0; HRMS (ESI-TOF-positive mode): calcd for $C_{15}H_{16}IO$ $([M\text{-}OTf])^{+}$: 339.0240, found: 339.0256.

***m*-Metoxy-phenyl(4'-hydroxyphenyl)iodonium triflate (6f)**



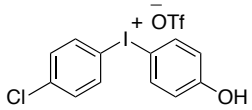
Reaction of Koser's reagent **5f** (422 mg, 1.0 mmol) according to the general procedure afforded 364 mg (76%) of product **6f**, isolated as a light pink solid: mp 151.4-151.7 °C (decomp.); IR (KBr) cm^{-1} 3278, 3094, 3066, 2974, 2943, 1590, 1576, 1480, 1430, 1283, 1245, 1206, 1024, 637; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.7, 161.3, 137.4, 132.2, 126.2, 120.4 (q, $^{1}J_{CF}$ = 317.0 Hz), 119.7, 118.8, 117.9, 114.8, 101.1, 55.1. ^{19}F NMR (282 MHz, CD_3OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{12}IO_2$ $([M\text{-}OTf])^+$: 326.9882, found: 326.9888.

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



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; ^{1}H NMR (300 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 162.9, 161.5, 137.0, 136.6, 120.4 (q, $^{1}J_{CF}$ = 315.9 Hz), 118.7, 117.3, 103.7, 101.8, 54.9. ^{19}F NMR (282 MHz, CD_3OD): δ -80.2; HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{12}IO_2$ $([M\text{-}OTf])^+$: 326.9882, found: 326.9873.

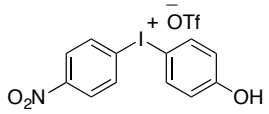
***p*-Chloro-phenyl(4'-hydroxyphenyl)iodonium triflate (6h)**



Reaction of Koser's reagent **5h** (427 mg, 1.0 mmol) according to the general procedure

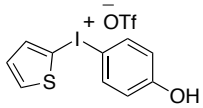
afforded 468 mg (97%) of product **6h**, isolated as a light pink solid: mp 158.7-159.0 °C (decomp.); IR (KBr) cm^{-1} 3271, 3110, 3098, 3070, 1598, 1578, 1488, 1433, 1284, 1242, 1206, 1092, 638; ^{1}H NMR (500 MHz, CD_3OD): δ 8.07 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ 161.8, 138.6, 137.5, 136.1, 131.7, 120.4 (q, $^{1}J_{CF}$ = 316.3 Hz), 118.9, 112.5, 101.4. ^{19}F NMR (282 MHz, CD_3OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for $C_{12}H_9ICl^{35}O$ ($[M\text{-}OTf]$)$^+$: 330.9387, found: 330.9392.

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



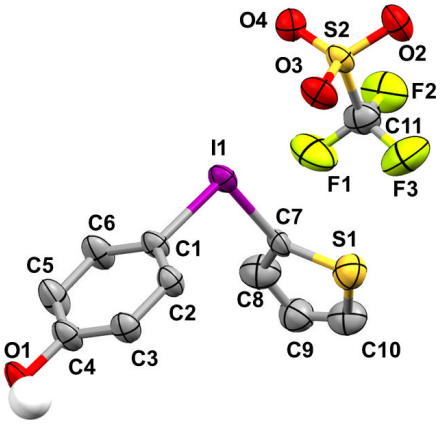
Reaction of Koser's reagent **5i** (437 mg, 1.0 mmol) according to the general procedure afforded 385 mg (78%) of product **6i**, isolated as a light brown solid: mp 163.4-163.7 °C; IR (KBr) cm^{-1} 3291, 3109, 3060, 3023, 1603, 1579, 1534, 1487, 1440, 1362, 1287, 1223, 852, 637; ^{1}H NMR (500 MHz, CD_3OD): δ 8.31 (s, 4H), 8.04 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ 162.0, 150.0, 137.9, 135.6, 125.9, 120.8, 120.4 (q, $^{1}J_{CF}$ = 318.2 Hz), 119.1, 101.1. ^{19}F NMR (282 MHz, CD_3OD): δ -80.0; HRMS (ESI-TOF-positive mode): calcd for $C_{12}H_9INO_3$ ($[M\text{-}OTf]$)$^+$: 341.9627, found: 341.9644.

2-Thiophene(4'-hydroxyphenyl)iodonium triflate (6j)



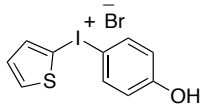
Reaction of Koser's reagent **5j** (284 mg, 1.0 mmol) according to the general procedure afforded 246 mg (54%) of product **6j**, isolated as a light brown solid: mp 141.3-141.5 °C (decomp.); IR (KBr) cm^{-1} 3301, 3098, 3073, 1598, 1576, 1487, 1432, 1286, 1243, 1204, 637; ^{1}H NMR (300 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz,

CD_3OD): δ 161.6, 139.9, 136.8, 136.6, 129.2, 120.4 (q, $^1J_{CF}$ = 317.1 Hz), 118.7, 104.3, 98.4 ^{19}F NMR (282 MHz, CD_3OD): δ -80.0; HRMS (ESI-TOF-positive mode): calcd for $C_{10}H_8IOS$ ([M-OTf])$^+$: 302.9341, found: 302.9332.



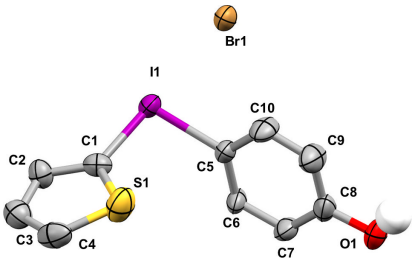
Single crystals of product **6j** suitable for X-ray crystallographic analysis were obtained by slow crystallization from the acetonitrile-methanol solution. X-ray diffraction data for **6j** were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at at 173 K. The structure was solved by Sir 2004[14] and refined by full-matrix least-squares refinement on F^2 using SHELXL-2014/7.[13] Crystal data for **6j** $C_{11}H_8F_3IO_4S_2$: M 452.19, monoclinic, space group $P2_1/c$, 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) Å^3, Z = 4, 13623 reflections measured, 3454 unique, 2720 I>2σ; final R_1 = 0.0321, Rw = 0.0732, S = 1.058. CCDC-1855607.

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



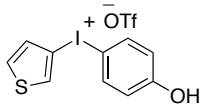
Reaction of **6j** (113 mg, 0.25 mmol) was added to a stirred mixture of KBr (298 mg, 2.5 mmol) in water (1.5 mL). The reaction was stirred at room temperature for 2 hour. After completion of reaction, the mixture was filtrated and washed with diethyl ether several times and then dried in vacuum to give 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; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 161.5, 139.6, 136.7, 136.3, 129.2, 118.6, 105.0, 99.7; HRMS (APCI-positive mode): calcd for $C_{10}H_8IOS$ $([M-Br])^+$: 302.9341, found: 302.9318.



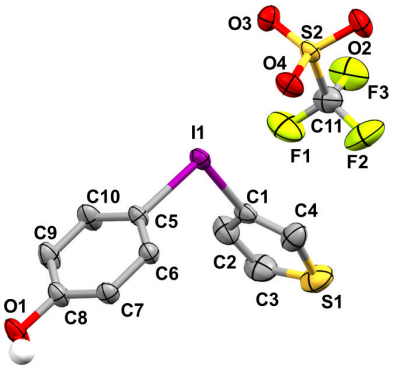
Single crystals of product **6k** suitable for X-ray crystallographic analysis were obtained by slow crystallization from the methanol solution. X-ray diffraction data for **6k** were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 173 K. The structure was solved by the Sir 2011[12] and refined by full-matrix least-squares refinement on F^2 using SHELXL-2014/7.[13] Crystal data for **6k** $C_{10}H_8BrIOS$: 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 o, V = 2327.8(3) $Å_3$, Z = 8, 14785 reflections measured, 2663 unique, 1923 I>2σ; final R_1 = 0.0504, Rw = 0.1292, S = 1.100. CCDC-1855608.

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



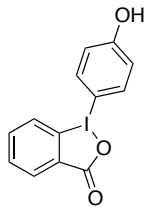
Reaction of Koser's reagent **5k** (284 mg, 1.0 mmol) according to the general procedure afforded 301 mg (67%) of product **6l**, isolated as a white solid: mp 152.6-153.0 °C (decomp.); IR (KBr) cm^{-1} 3298, 3115, 3100, 3083, 3072, 1600, 1576, 1487, 1432, 1284, 1240, 1208, 634; ^{1}H NMR (300 MHz, CD_3OD): 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_3OD): 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_3OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for $C_{10}H_8IOS$ ([M-OTf])$^+$: 302.9341, found: 302.9332.



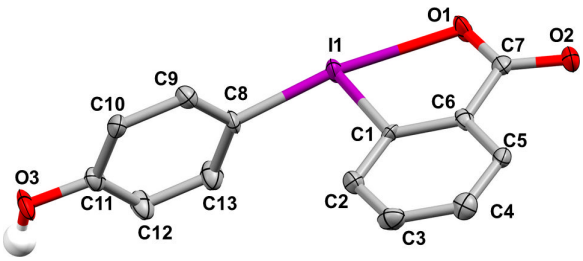
Single crystals of product **6l** suitable for X-ray crystallographic analysis were obtained by slow crystallization from the acetonitrile-methanol solution. X-ray diffraction data for **6l** were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoKα radiation (λ = 0.71073 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** $C_{11}H_8F_3IO_4S_2$: 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)-1λ^3-benzo[*d*][1,2]iodoxol-3(1*H*)-one (6m)



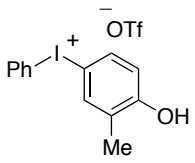
Reaction of Koser's reagent **5l** (218 mg, 0.5 mmol) according to the general procedure afforded 126 mg (74%) of product **6m**, isolated as a light brown solid: mp

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_3OD): δ 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_3OD): δ 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 MoKα radiation (λ = 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** $C_{13}H_9IO_3$: M 340.10, hexagonal, space group $P6_2$, a = 15.5268(11), b = 15.5268(11), c = 16.7336(12) Å, α = 90, β = 90, γ = 120 o, V = 3493.7(6) $Å^3$, Z = 12, 18294 reflections measured, 3439 unique, 2897 I>2σ; final R_1 = 0.0259, Rw = 0.0552, S = 1.078. CCDC-1855610.

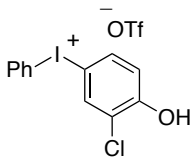
4-Hydroxy-3-methylphenyl(phenyl)iodonium triflate (6n)



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,

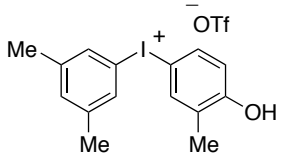
2929, 1566, 1487, 1448, 1283, 1246, 1170, 638; ^{1}H NMR (500 MHz, CD_3OD): δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 2.3 Hz, 1H), 7.81 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54-7.49 (m, 2H), 6.84 (d, *J* = 8.5 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD): δ 159.8, 137.5, 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_3OD): δ -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_3OD): δ 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_3OD): δ 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_3OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for $C_{12}H_9ClIO$ ([M-OTf])$^{+}$: 330.9387, found: 330.9381.

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



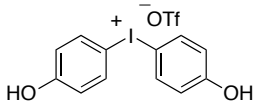
Reaction of Koser's reagent **5d** (210 mg, 0.5 mmol) with triisopropyl(2-tolyloxy)silane **1f** (159 mg, 0.6 mmol) according to the general procedure afforded 182 mg (76%) of

product **6o**, 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; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (125 MHz, CD_3OD): δ 159.7, 142.2, 137.4, 134.7, 131.7, 129.6, 120.4 (q, $^{1}J_{CF}$ = 316.6 Hz), 117.3, 114.7, 100.6, 19.7, 14.6. ^{19}F NMR (470 MHz, CD_3OD): δ -80.1; HRMS (ESI-TOF-positive mode): calcd for $C_{15}H_{16}IO$ $([M\text{-}OTf])^{+}$: 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 hour. 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**.

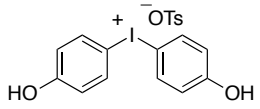
4,4'-di(hydroxyphenyl)iodonium triflate (8a)



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; ^{1}H NMR (500 MHz, CD_3OD): δ 7.92 (d, J = 9.0 Hz, 4H), 6.88 (d, J = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, CD_3OD): δ 161.4, 136.8, 120.5 (q, $^{1}J_{CF}$ = 318.0 Hz), 118.7, 101.9; ^{19}F

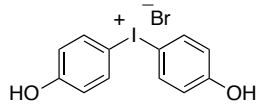
NMR (282 MHz, CD_3OD): δ -80.5; HRMS (ESI-TOF-positive mode): calcd for $C_{12}H_{10}IO_2$ ([M-OTf])$^+$: 312.9725, found: 312.9732.

4,4'-di(hydroxyphenyl)iodonium tosylate (8b)



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_3OD): 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_3OD): 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.

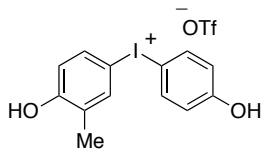
4,4'-di(hydroxyphenyl)iodonium bromide (8c)



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-λ^3-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, CD_3OD): δ 7.91 (d, J = 9.3 Hz, 4H), 6.87 (d, J = 9.3 Hz, 4H); ^{13}C NMR (75 MHz, CD_3OD): δ 161.3, 136.8, 118.6, 101.5; HRMS (ESI-TOF-positive mode): calcd for $C_{12}H_{10}IO_2$ $([M-Br])^+$: 312.9725, found: 312.9737.

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

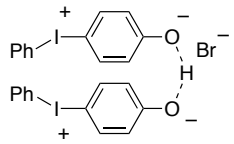


Reaction of Koser's reagent **7** (225 mg, 0.50 mmol) with triisopropyl(2-tolyloxy)silane **1f** (159 mg, 0.60 mmol) according to the general procedure afforded 163 mg (68%) of product **8d**, isolated as a light brown solid: mp 140.2-140.8 °C; IR (KBr) cm^{-1} 3244, 3091, 3015, 2929, 1577, 1486, 1427, 1278, 1216, 1171, 642; ^1H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (125 MHz, CD_3OD): δ 161.3, 159.5, 137.0, 136.7, 134.2, 129.5, 120.4 (q, $^1J_{CF}$ = 316.9 Hz), 118.7, 117.2, 101.8, 101.6, 14.7; ^{19}F NMR (470 MHz, CD_3OD): δ -80.2; HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{12}IO_2$ $([M-OTf])^+$: 326.9882, found: 326.9884.

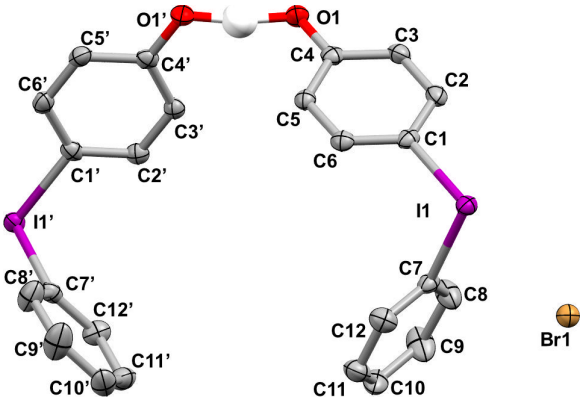
7. Preparation of dimeric oxyphenyl(phenyl)iodonium ylidic salts

Reaction of **4c** (0.50-0.90 mmol) was added to a stirred mixture of 10%K_2CO_3 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)

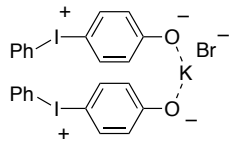


Reaction of **4c** (338 mg, 0.90 mmol) according to the general procedure for 1 hour stirring afforded 187 mg (62%) of product **9a**, isolated as a light yellow solid: mp 122.8-123.4 °C; IR (KBr) cm^{-1} 3453, 3051, 3017, 2929, 1573, 1490, 1445, 680; ^{1}H NMR (500 MHz, CD_3OD): δ 8.02 (d, *J* = 7.5 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); ^{13}C NMR (125 MHz, CD_3OD-DMSO = 20:1): δ 167.3, 137.2, 133.5, 131.3, 131.1, 120.6, 115.3, 95.4.; Anal. Calcd for $C_{24}H_{19}BrI_2O_2$.: 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 2004[14] and refined by full-matrix least-squares refinement on F^2 using SHELXL-2014/7.[13] Crystal data for **9a** $C_{24}H_{19}BrI_2O_2$: 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) $Å^3$, Z = 4, 28473 reflections measured, 2586 unique, 2404 I>2σ; final R_1 = 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, 1488, 1443, 655; ^{1}H NMR (500 MHz, CD_3OD): 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); ^{13}C NMR (75 MHz, CD_3OD): δ 172.8, 137.7, 133.3, 131.4, 131.4, 122.8, 115.6, 90.8. Anal. Calcd for $C_{24}H_{18}BrI_2KO_2$.: 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

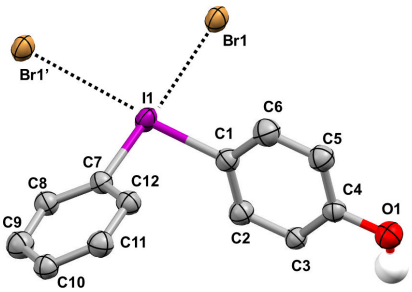


Figure S1-X-ray crystal structure of **4c**. All non-oxygen hydrogen atoms were removed for clarity. Elliposoids drawn to the 50% probability level. An additional bromide anion (Br1‘) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordniation environment of the 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.

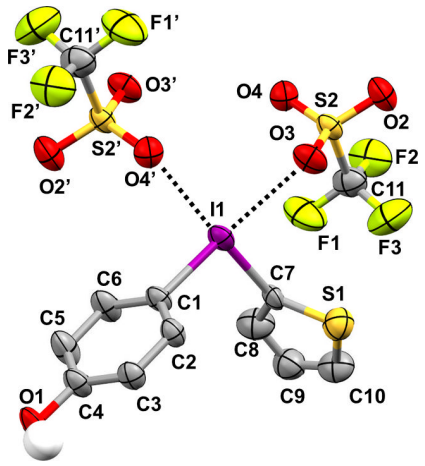


Figure S2-X-ray crystal structure of **6j**. All non-oxygen hydrogen atoms were removed for clarity. Elliposoids drawn to the 50% probability level. An additional triflate anion (containing O4‘) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordniation environment 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.

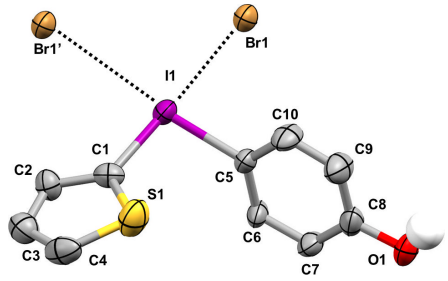


Figure S3-X-ray crystal structure of **6k**. All non-oxygen hydrogen atoms were removed for clarity. Elliposoids drawn to the 50% probability level. An additional bromide anion

(Br1‘) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordniation 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.

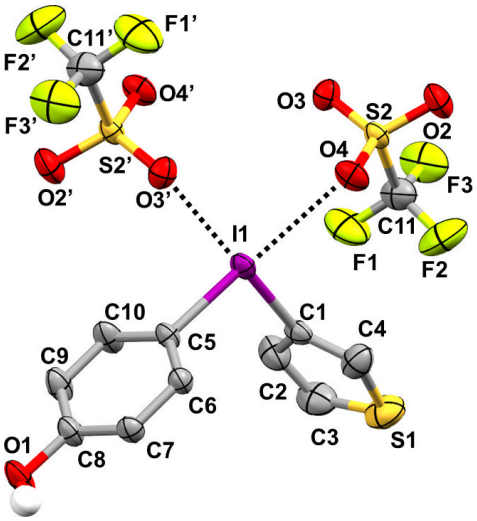


Figure S4-X-ray crystal structure of **6l**. All non-oxygen hydrogen atoms were removed for clarity. Elliposoids drawn to the 50% probability level. An additional triflate anion (containing O3‘) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordniation environment 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.

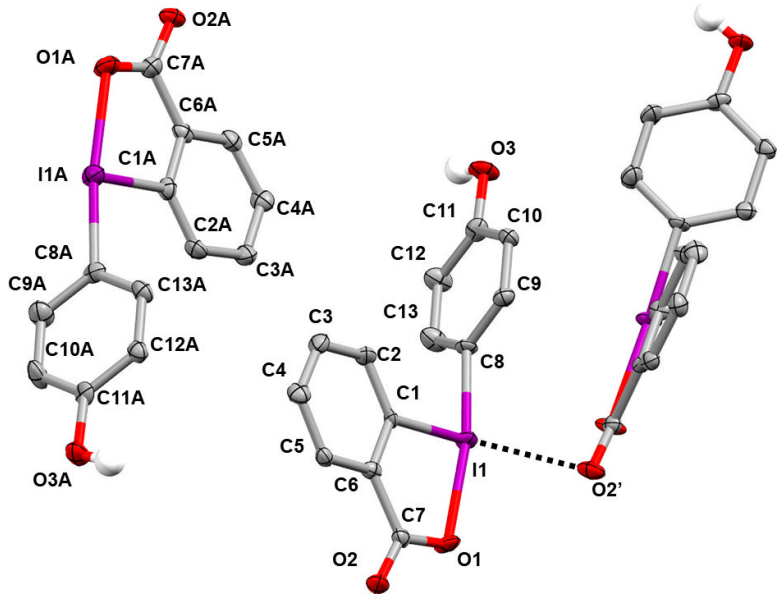


Figure S5-X-ray crystal structure of **6m**. All non-oxygen hydrogen atoms were removed for clarity. Elliposoids drawn to the 50% probability level. Interestingly, two coordination environments were observed for the iodine atoms: t-shaped and pseudo-square planar. Remarkably, the bond lengths between 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 coordniation 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.

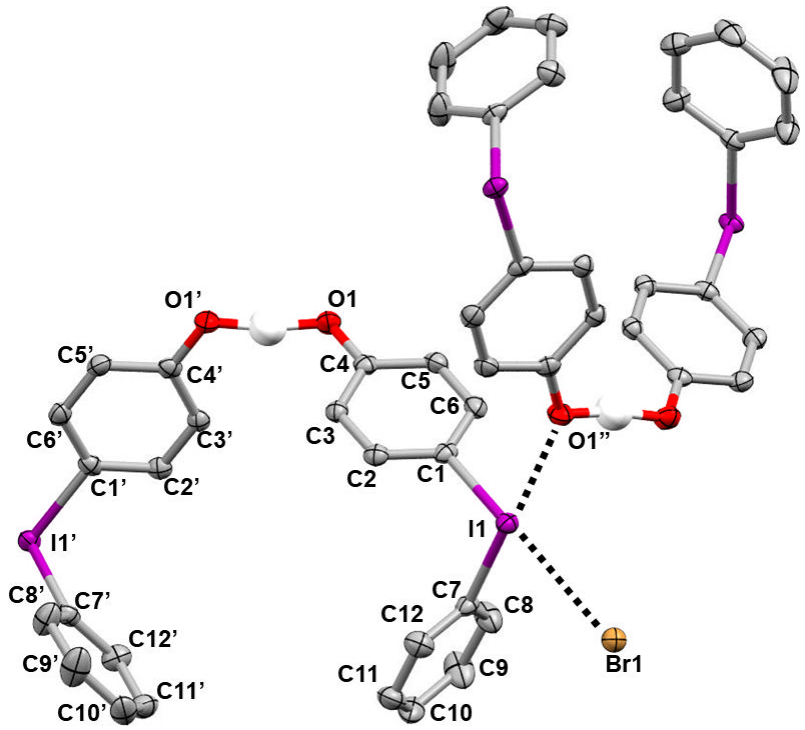
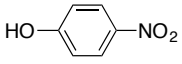


Figure S6-X-ray crystal structure of **9a**. All non-oxygen hydrogen atoms were removed for clarity. Elliposoids drawn to the 50% probability level. The two halves of **9a** are related by a 2-fold axis with the hydrogen atom (joining O1–O1‘) and Br1 both located on the 2-fold axis. An additional molecule of **9a** (containing O1“) from an adjacent asymmetric unit is displayed to illustrate the pseudo-square planar coordniation 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

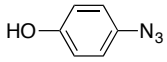
para-Nitrophenol **10**[15]



4,4’-Diphenolic iodonium triflate **8a** (92 mg, 0.20 mmol) was added at room temperature

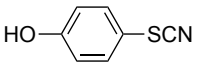
to a stirred mixture of sodium nitrite (28 mg, 0.40 mmol) and sodium triflate (38 mg, 0.22 mmol) in ethyl acetate (2.0 mL). The reaction was stirred at 70 °C for 17 hour. After reaction, 10% aqueous HCl (5 mL) was added and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_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 °C (lit.[10]; mp 112-113 °C); ^{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]



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_2SO_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).

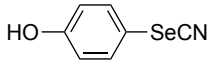
***para*-Thiocyanatophenol 12**[17]



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_2SO_4 and concentrated under reduced

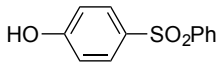
pressure. Purification by preparative TLC (hexane-ethyl acetate = 3:1) afforded the analytically pure *para*-thiocyanatophenol **12**; 14 mg (47%) isolated as a light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 5.41 (brs, 1H).

***para*-Selenocyanatophenol 13**[18]



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_2SO_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, $CDCl_3$): δ 7.56 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 5.28 (brs, 1H).

***para*-(Phenylsulfonyl)phenol 14**[19]



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_2SO_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, $CDCl_3$): δ 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).

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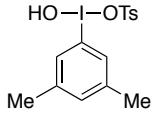
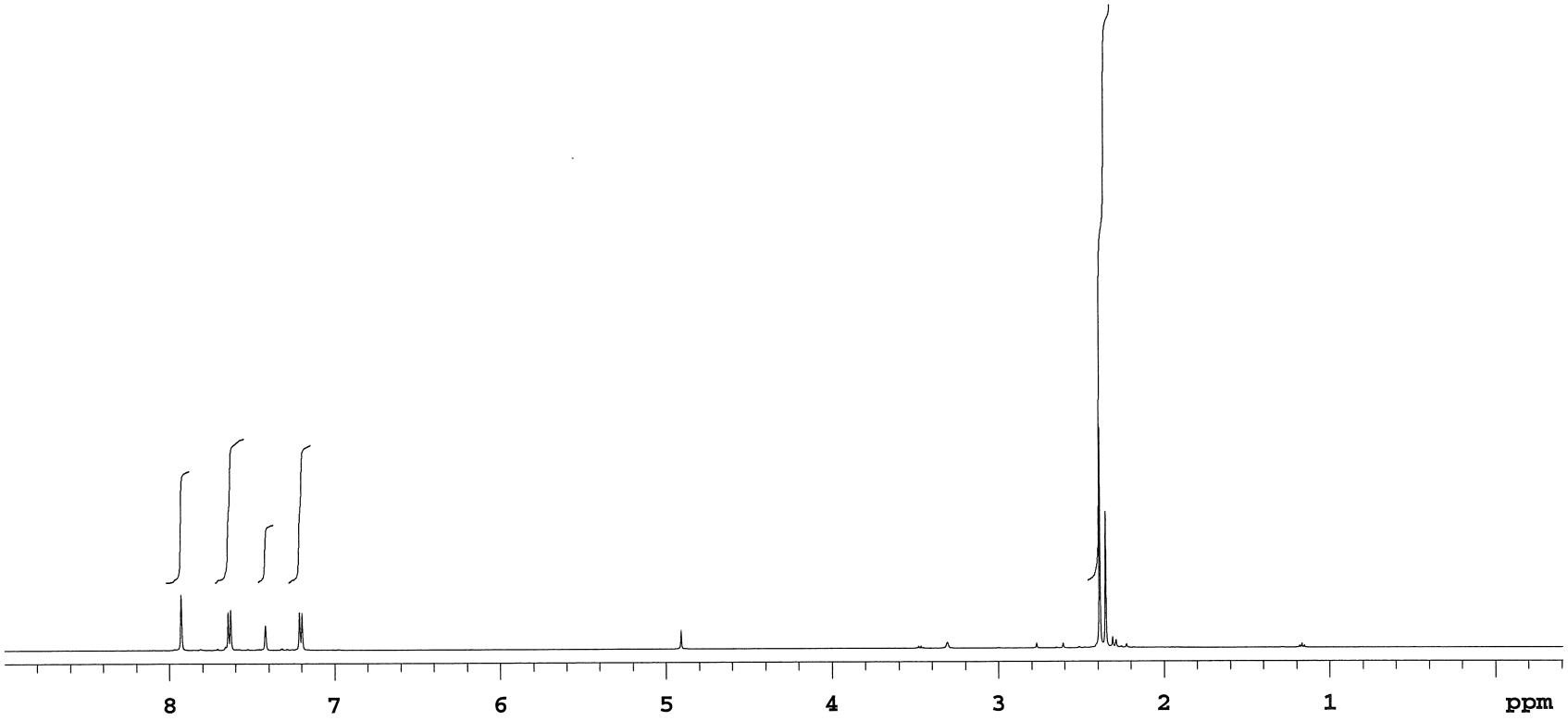
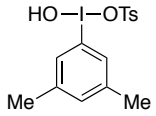
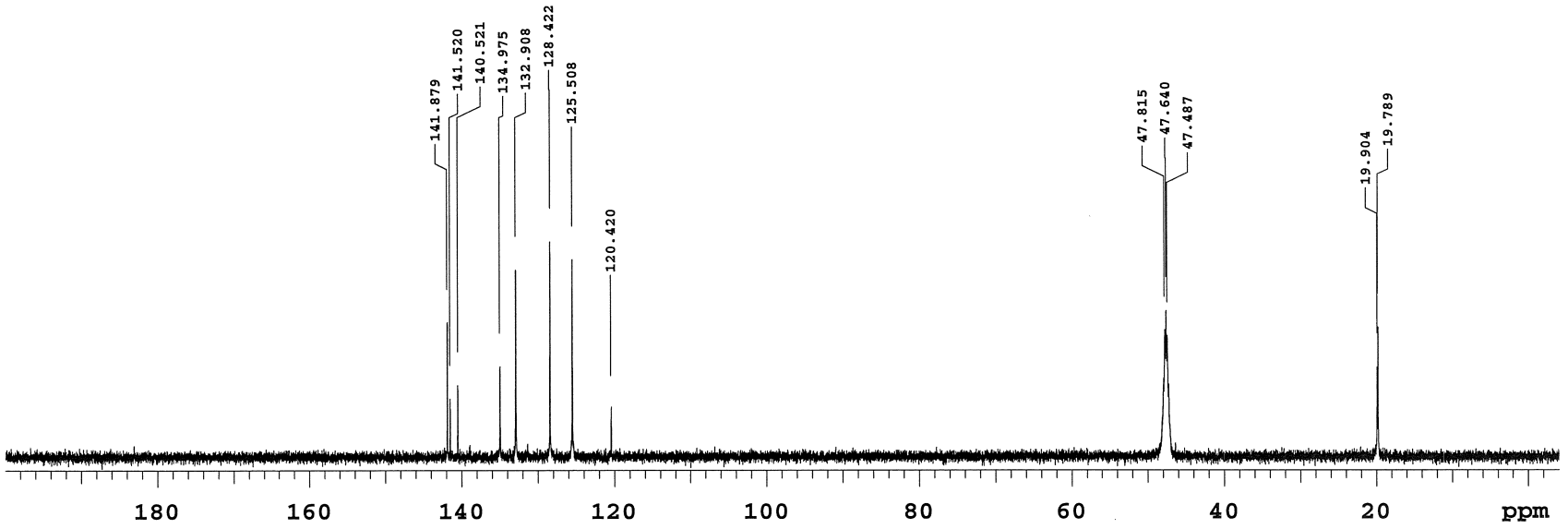
^{1}H NMR (500 MHz, CD_3OD)



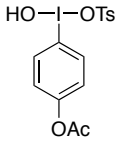


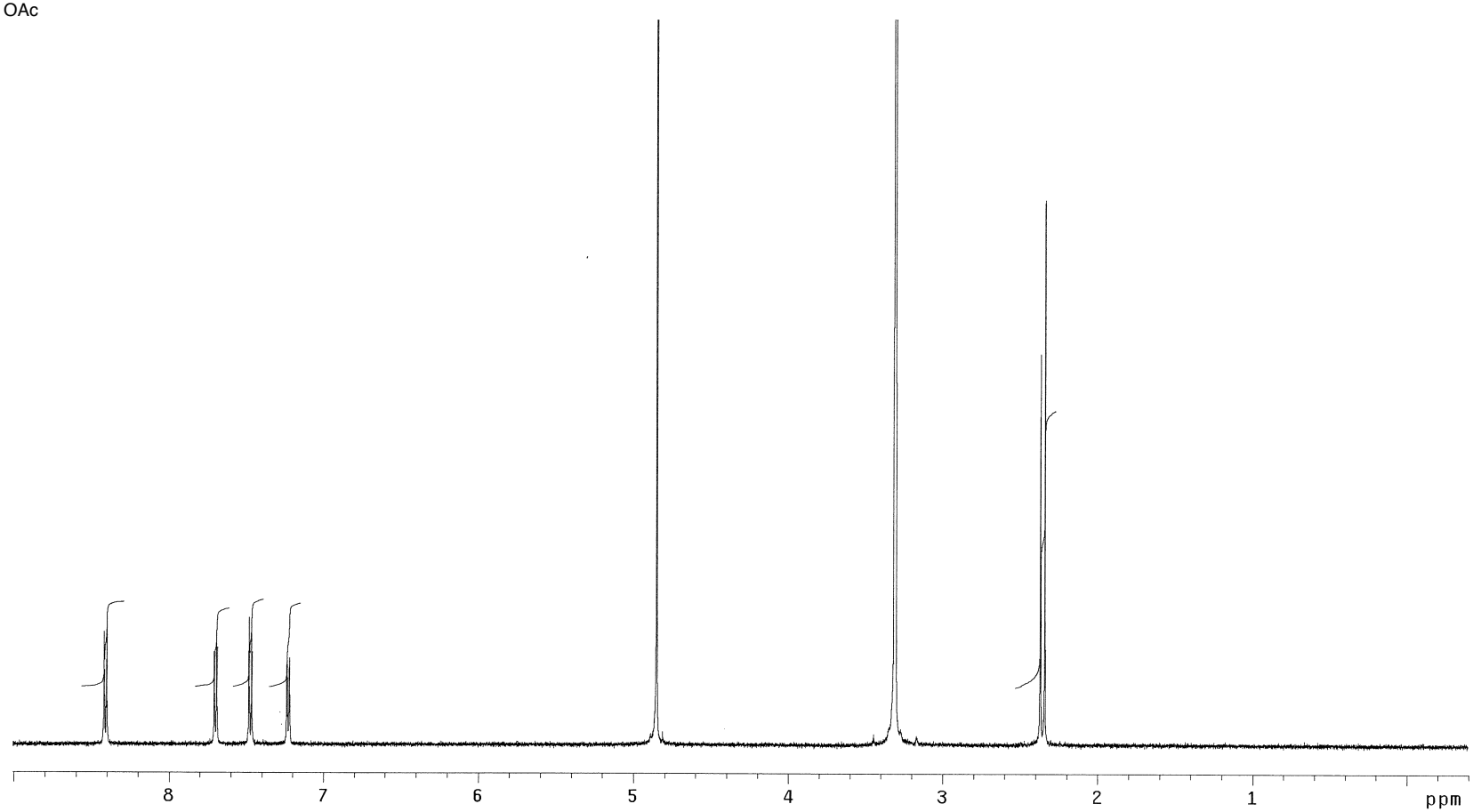
^{13}C NMR (125 MHz, CD_3OH)



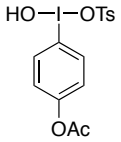


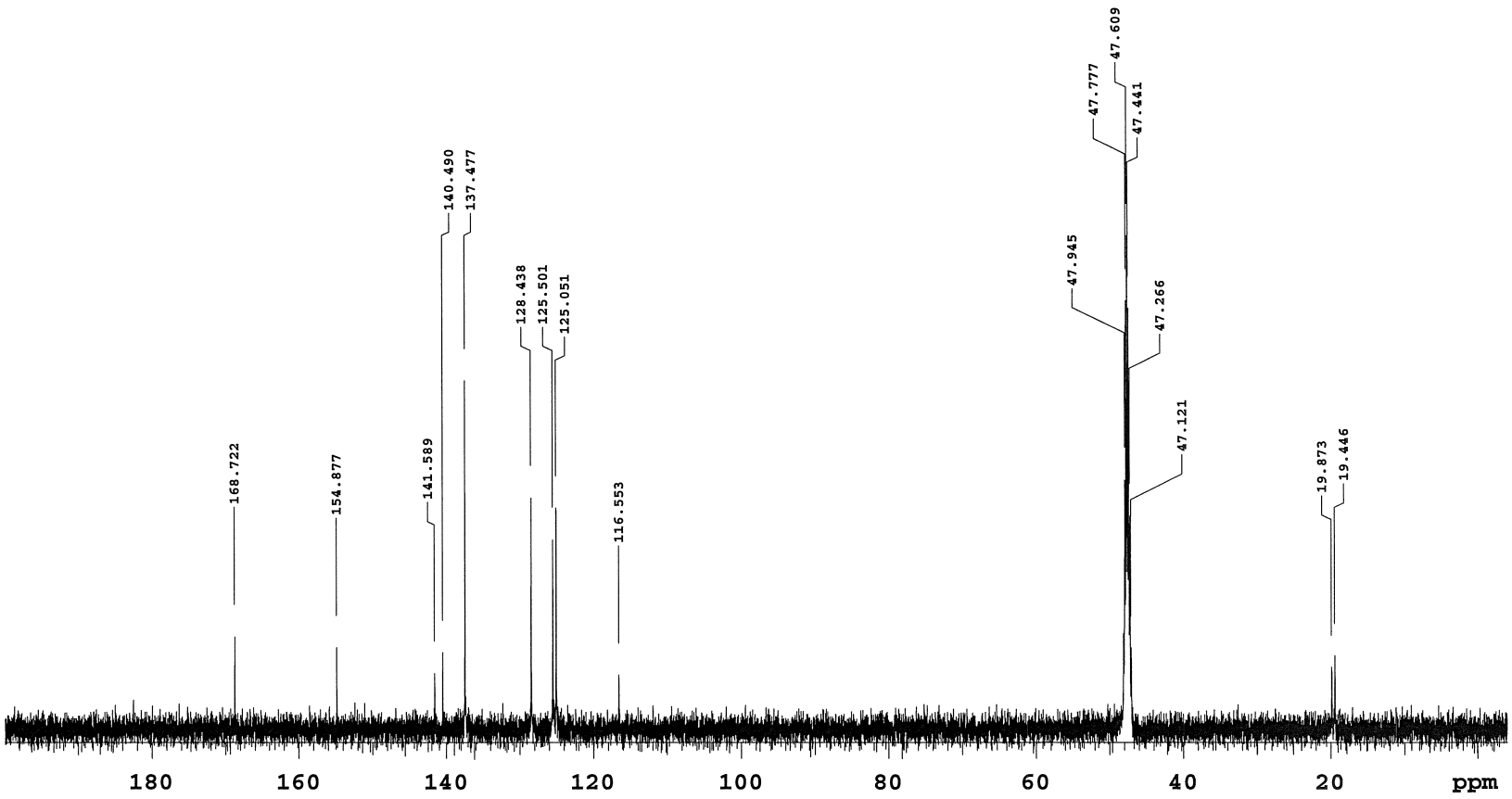
^{1}H NMR (500 MHz, CD_3OH)



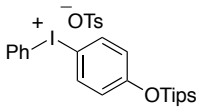


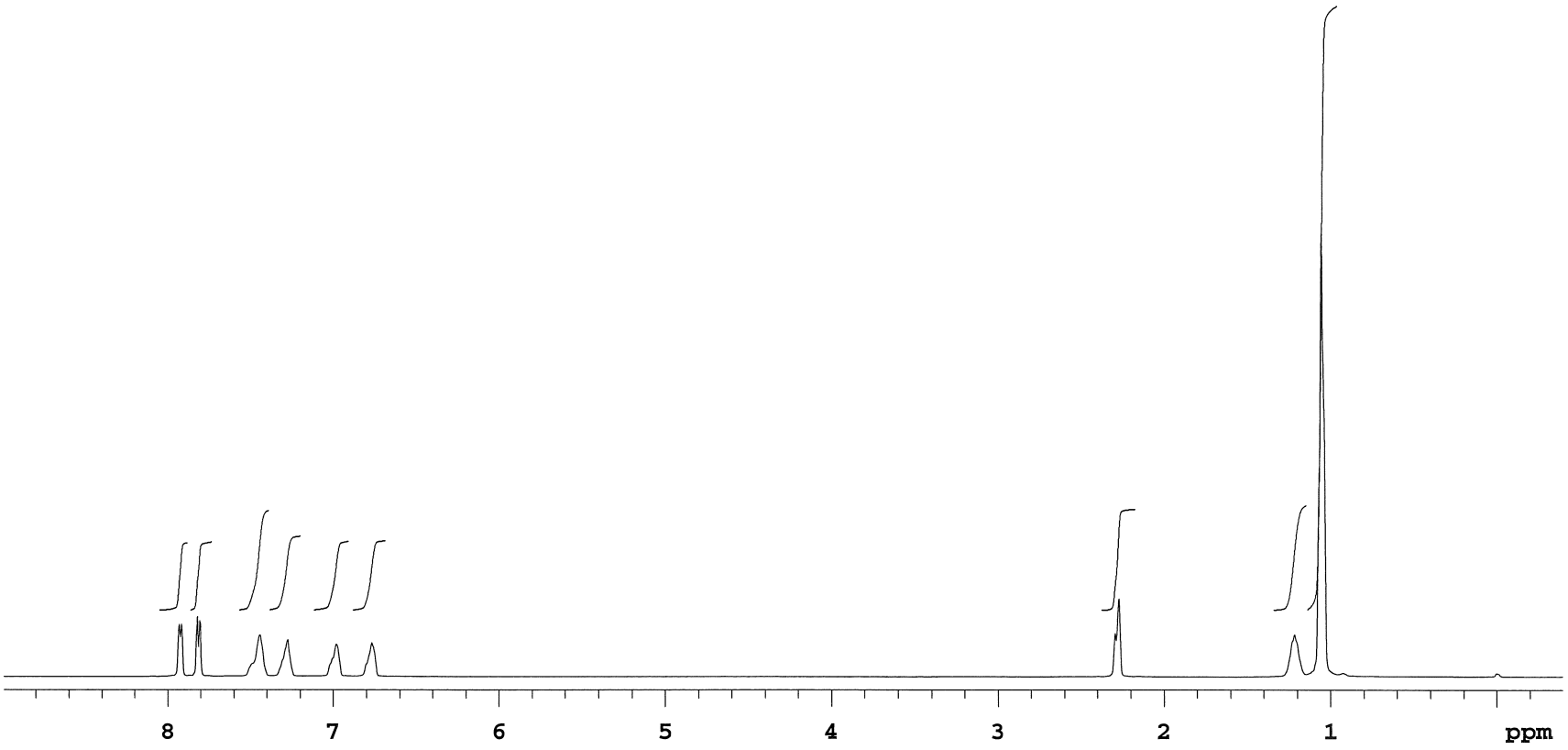
^{13}C NMR (125 MHz, CD_3OH)



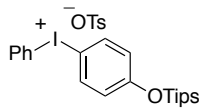


^{1}H NMR (500 MHz, CD_3OD)

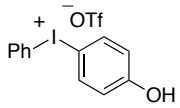


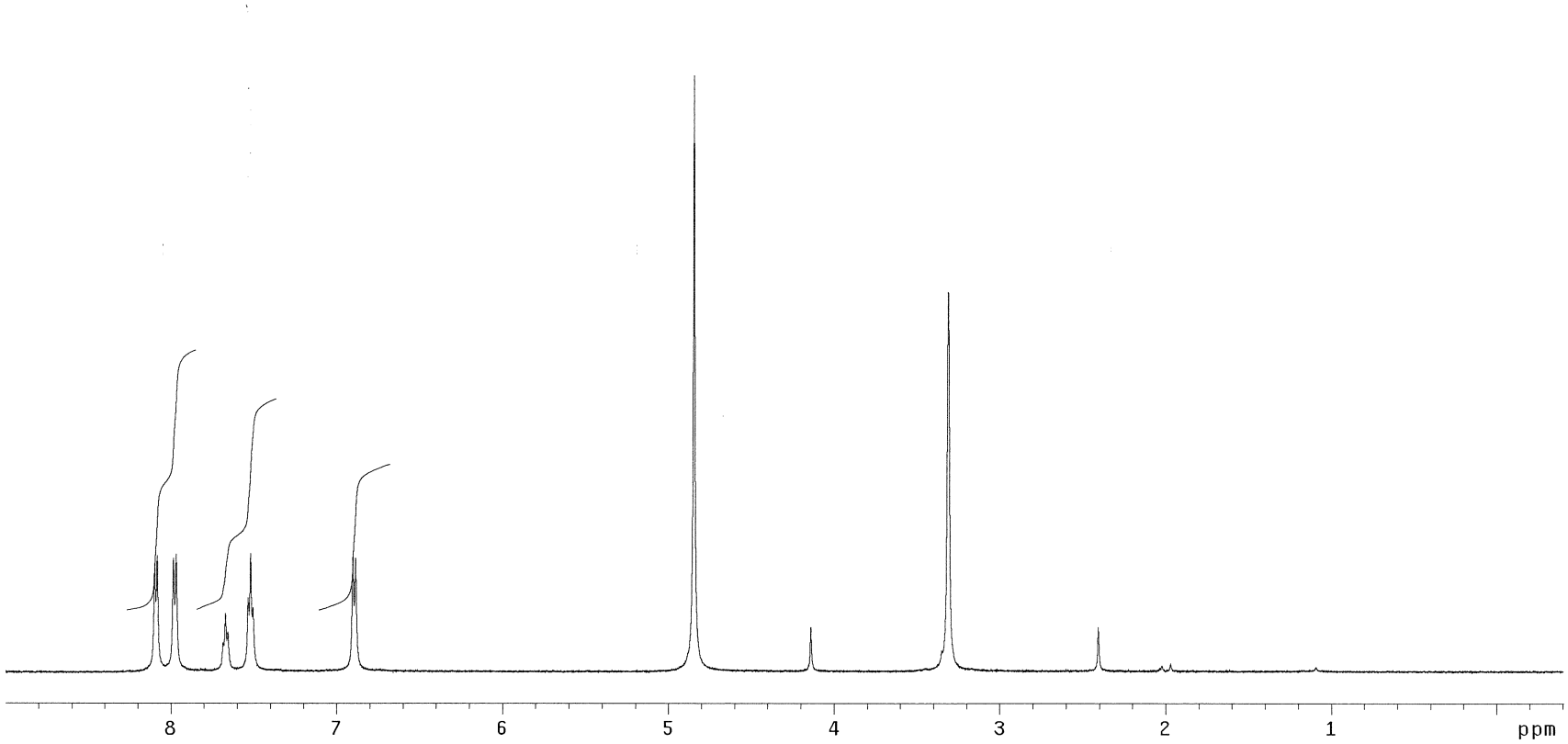


^{13}C NMR (125 MHz, CD_3OH)

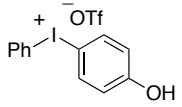


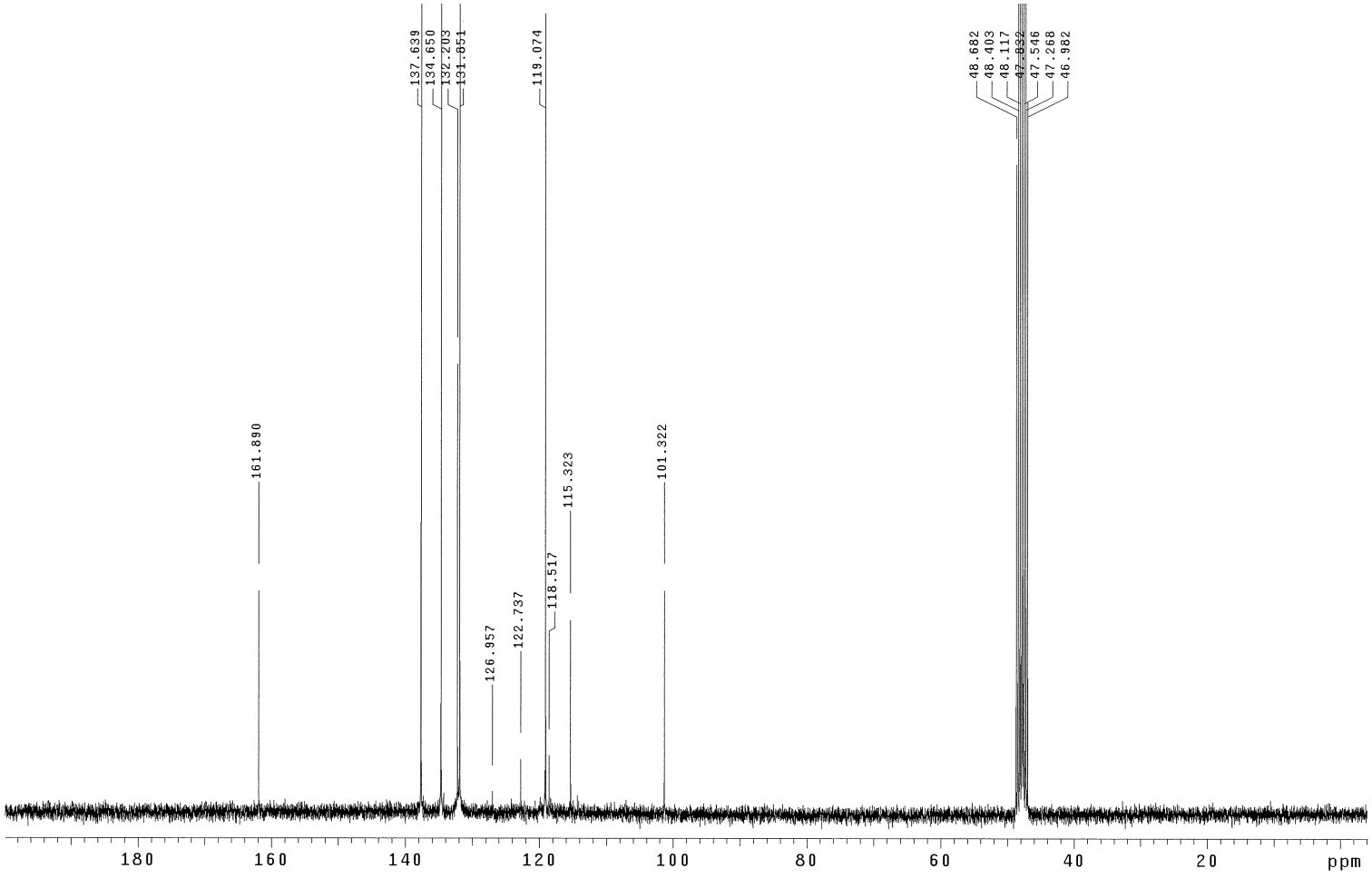
^{1}H NMR (500 MHz, CD_3OD)



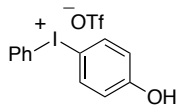


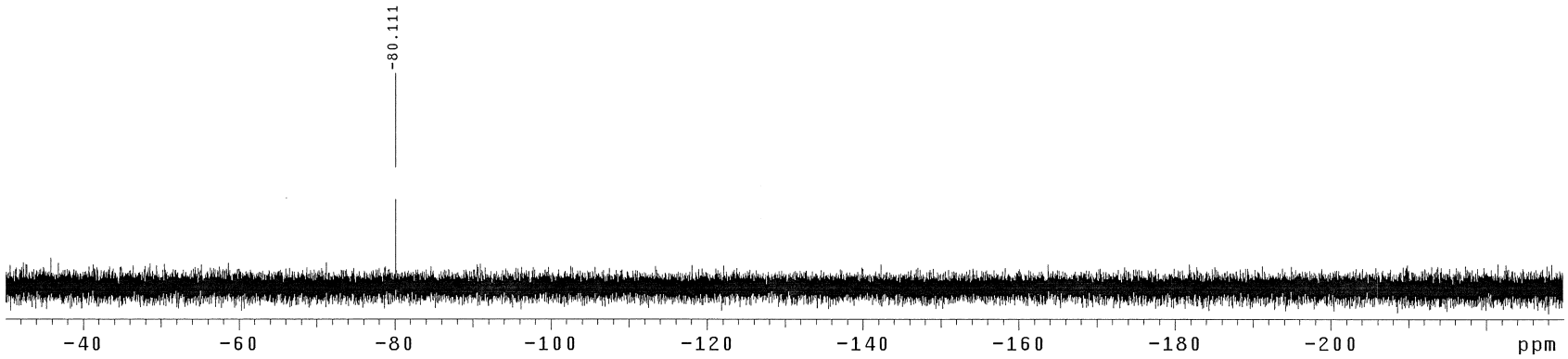
^{13}C NMR (75 MHz, CD_3OD)



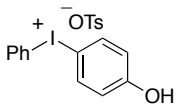


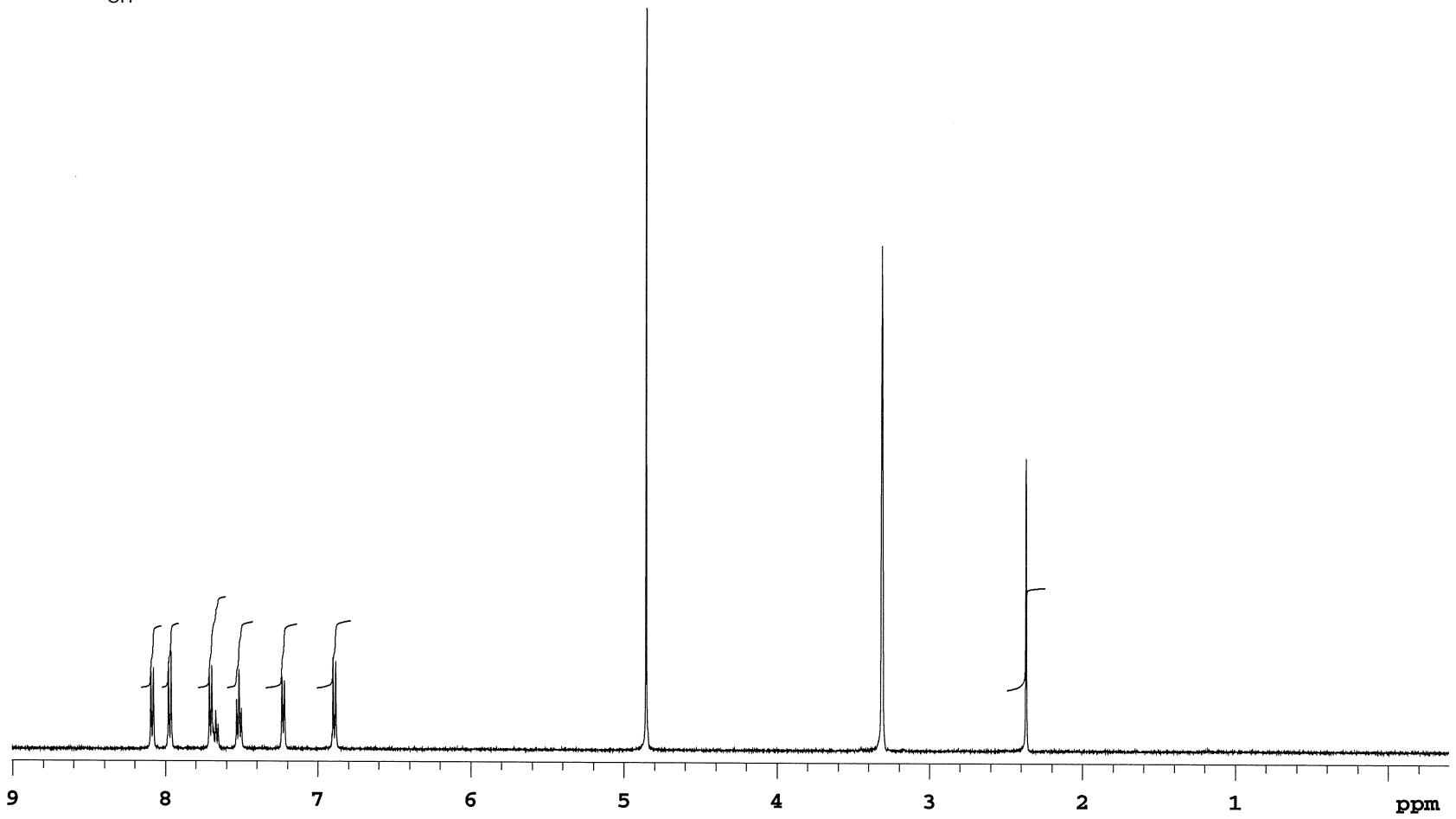
^{1}H NMR (470 MHz, CD_3OD)



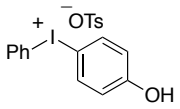


^{1}H NMR (500 MHz, CD_3OD)

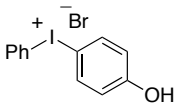


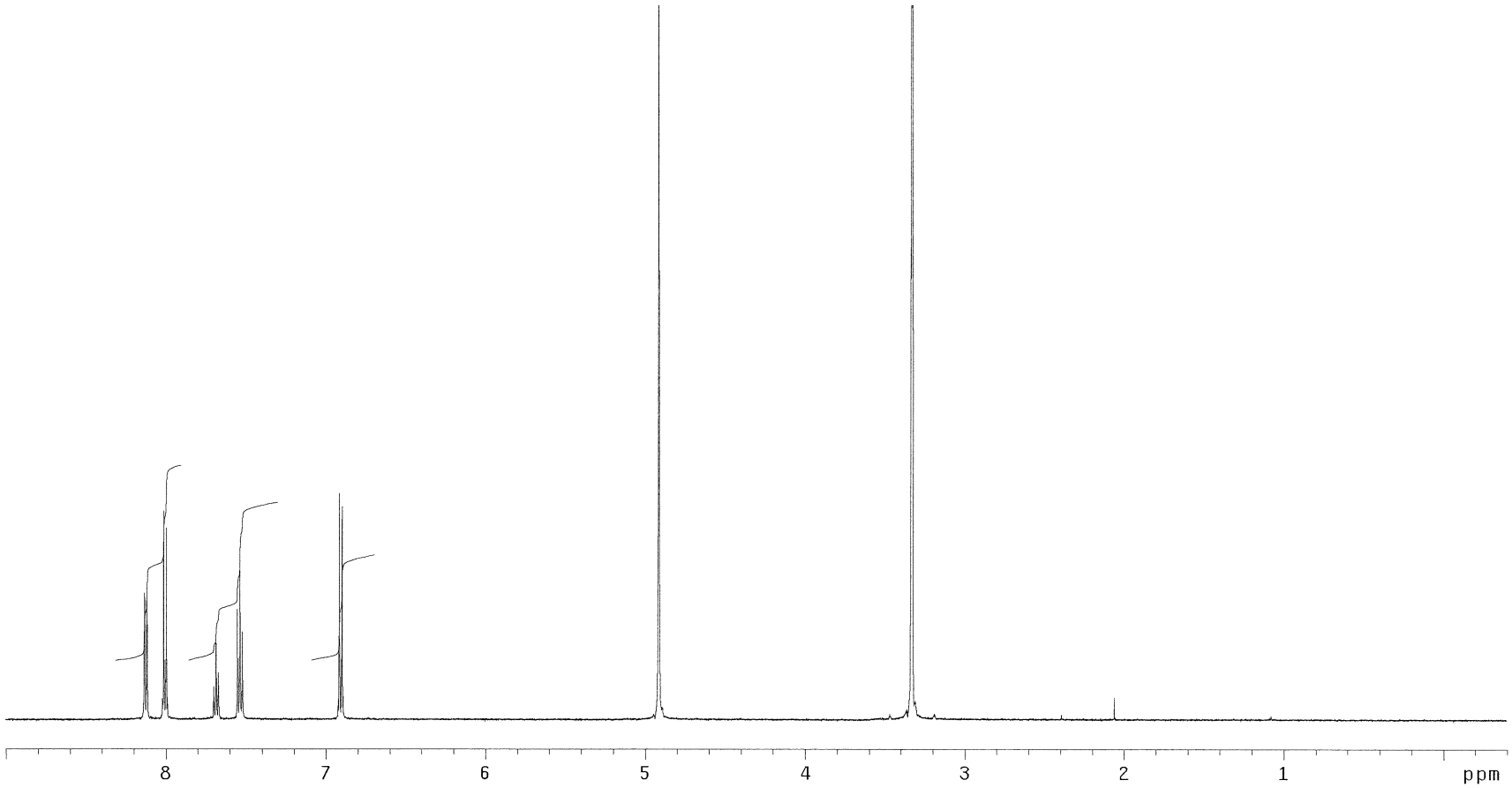


^{13}C NMR (75 MHz, CD_3OD)

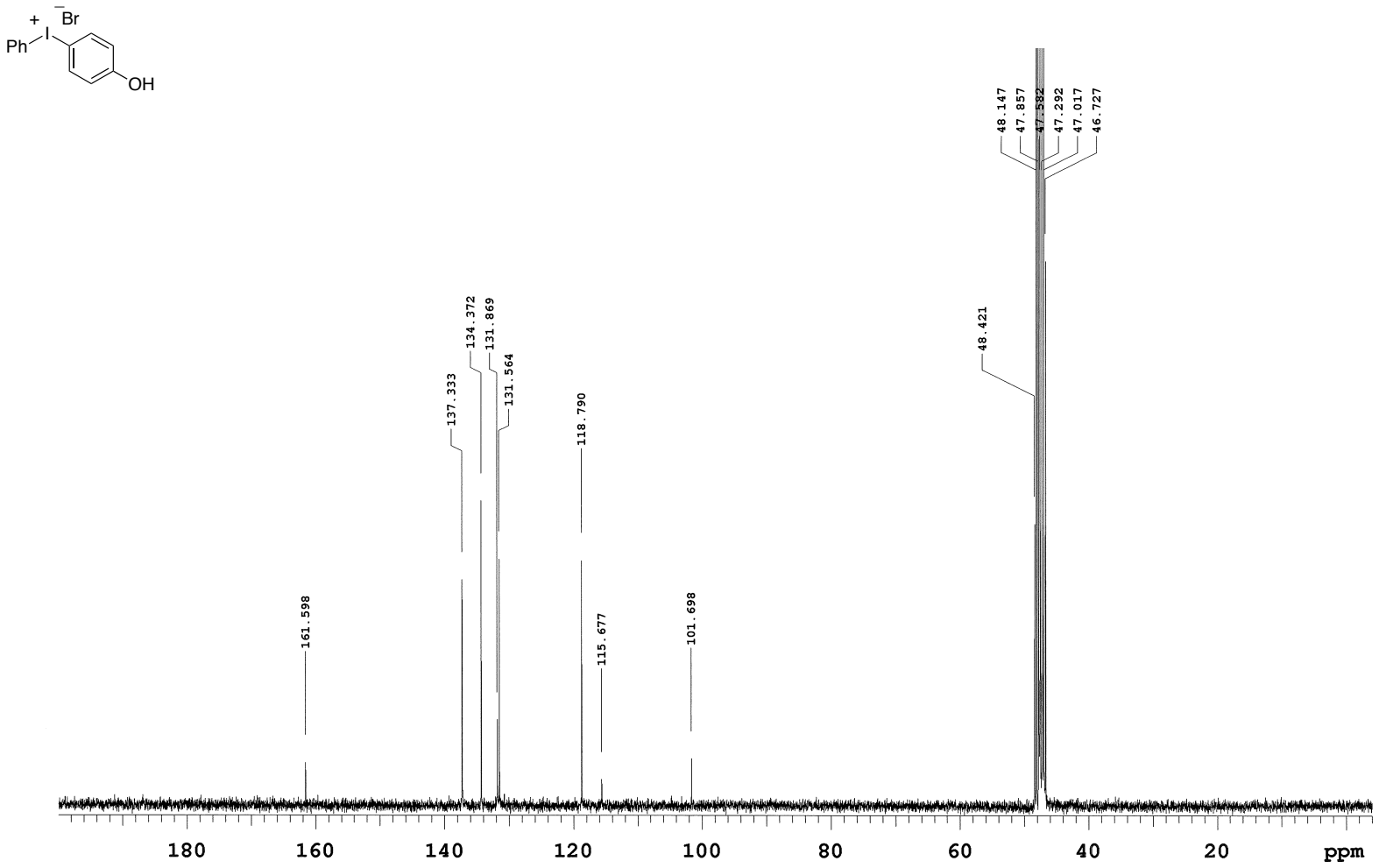


^{1}H NMR (500 MHz, CD_3OD)

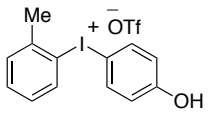


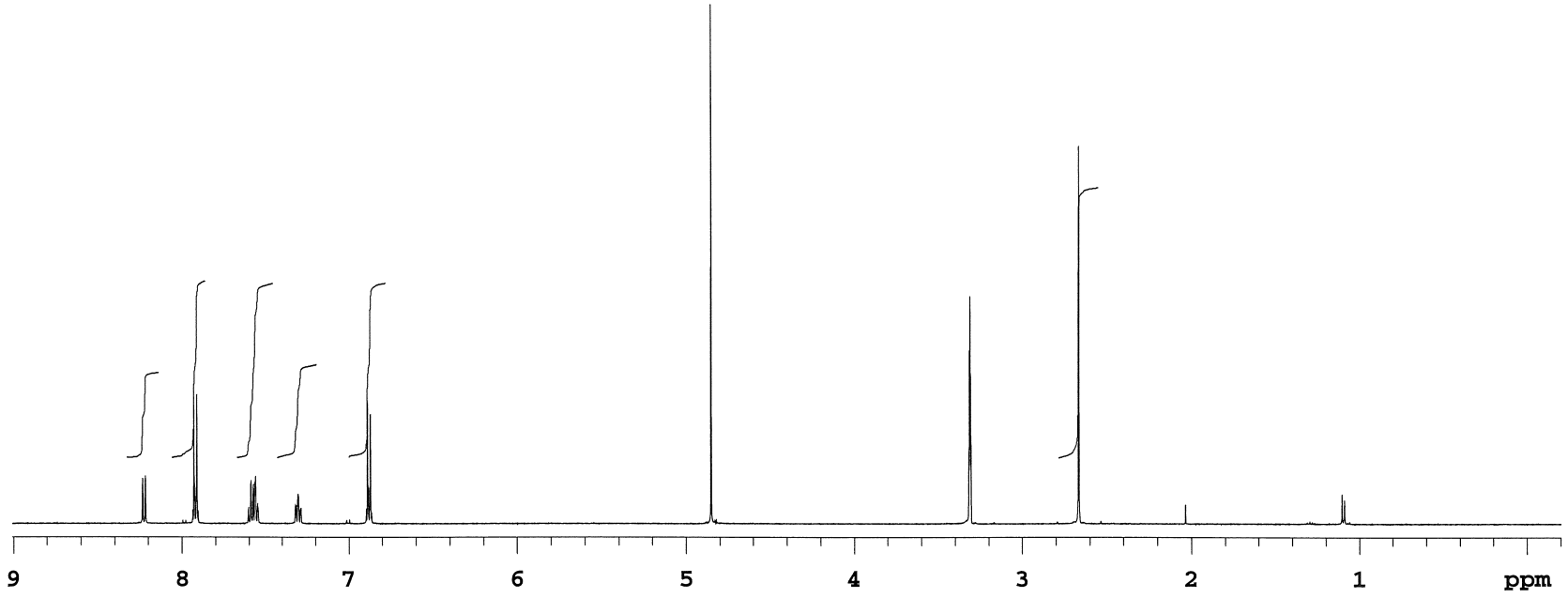


^{13}C NMR (75 MHz, CD_3OD)

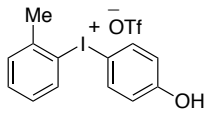


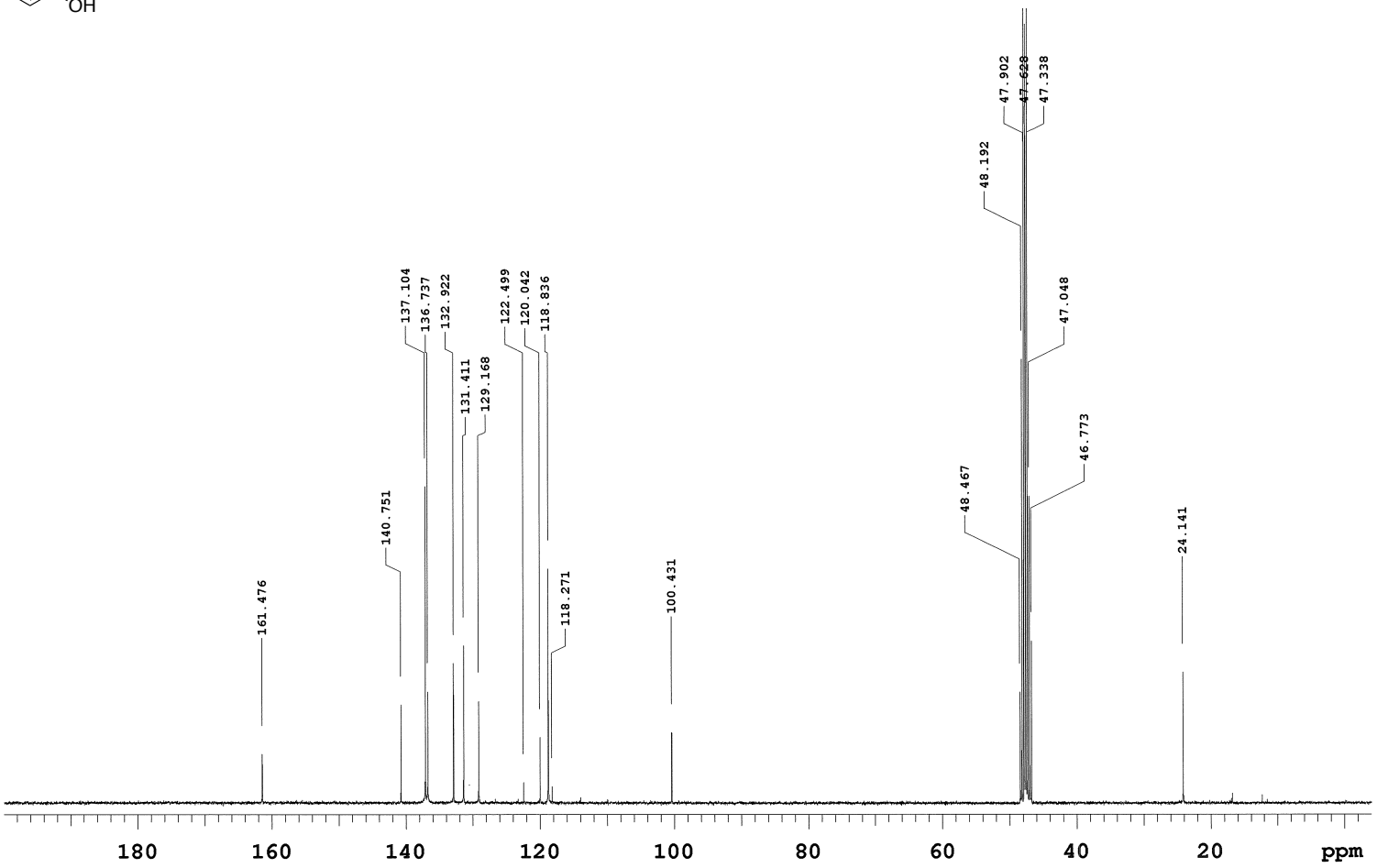
^{1}H NMR (500 MHz, CD_3OD)



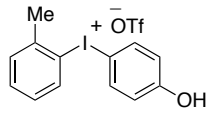


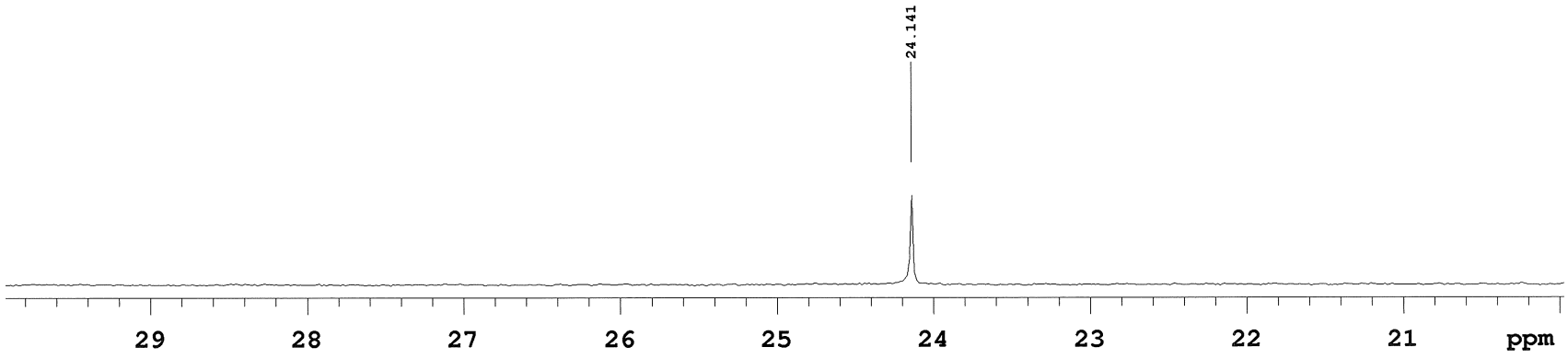
^{13}C NMR (75 MHz, CD_3OD)



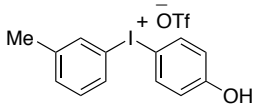


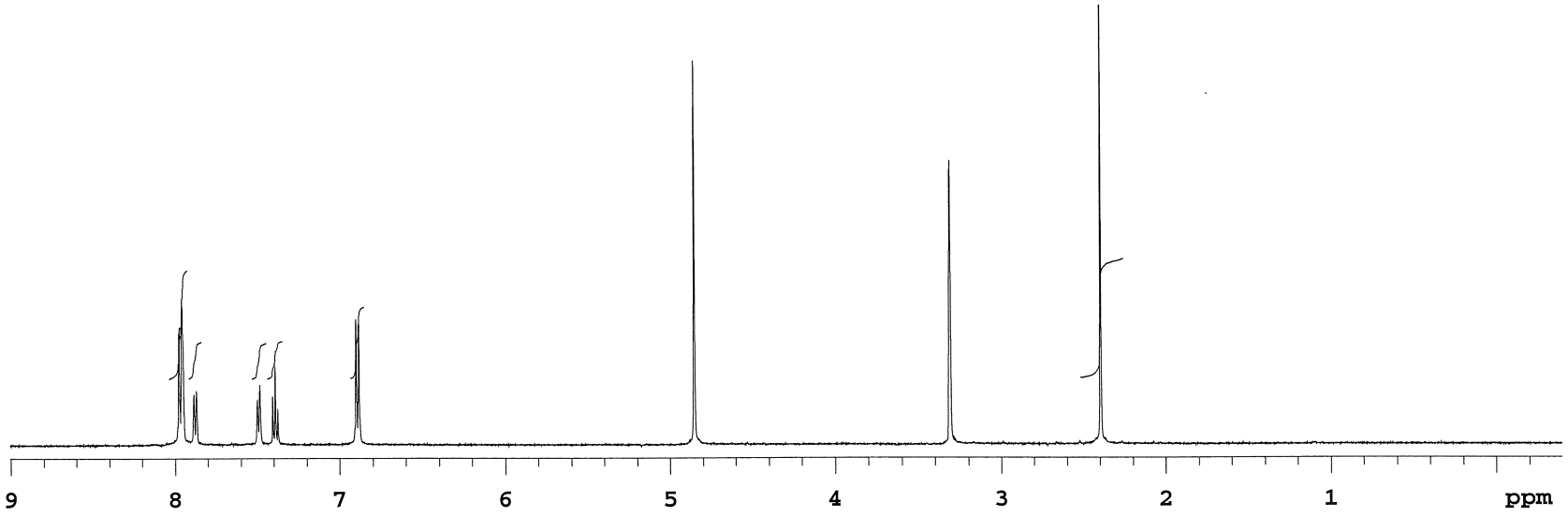
^{19}F NMR (282 MHz, CD_3OD)



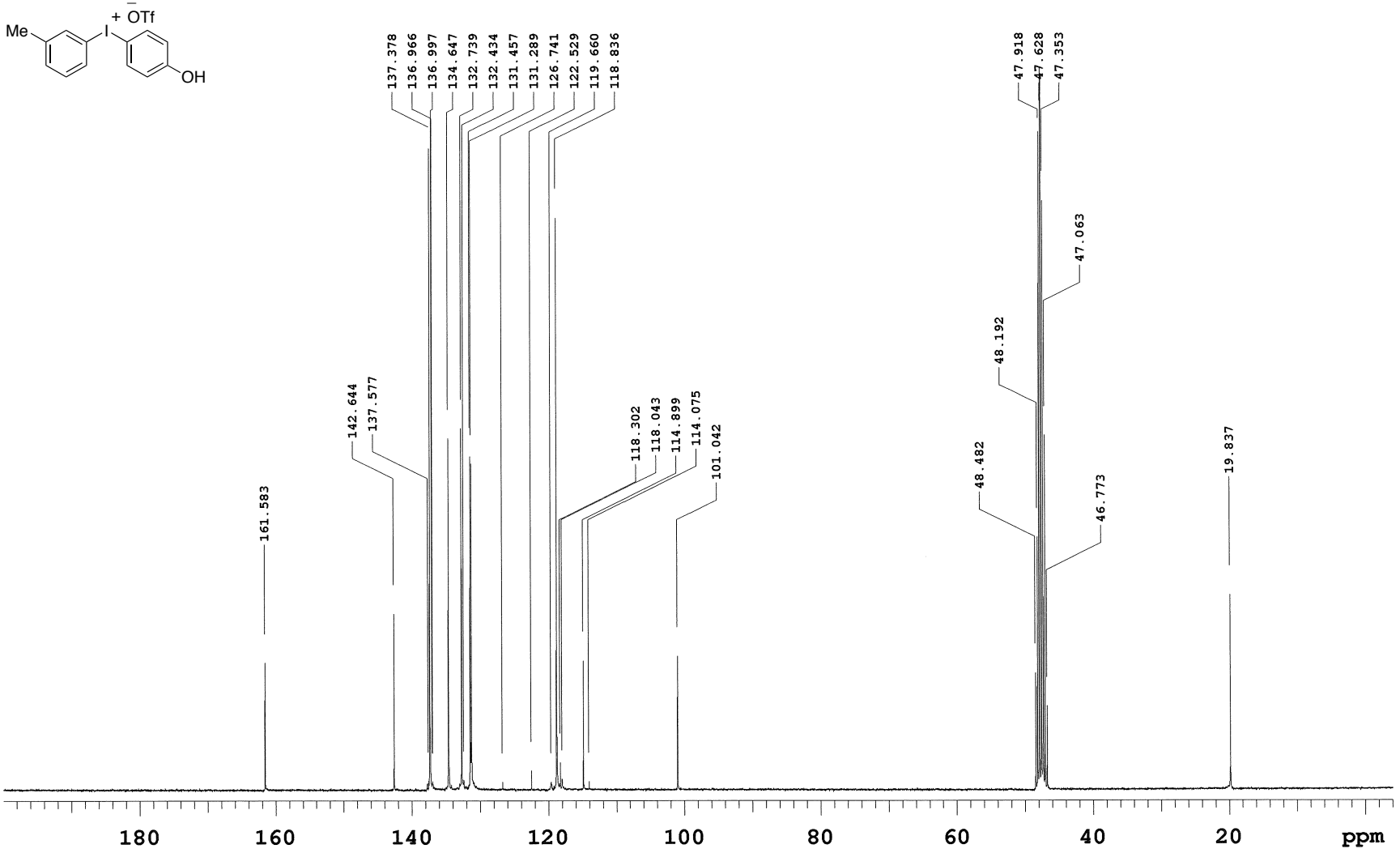


^{1}H NMR (500 MHz, CD_3OD)

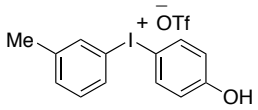


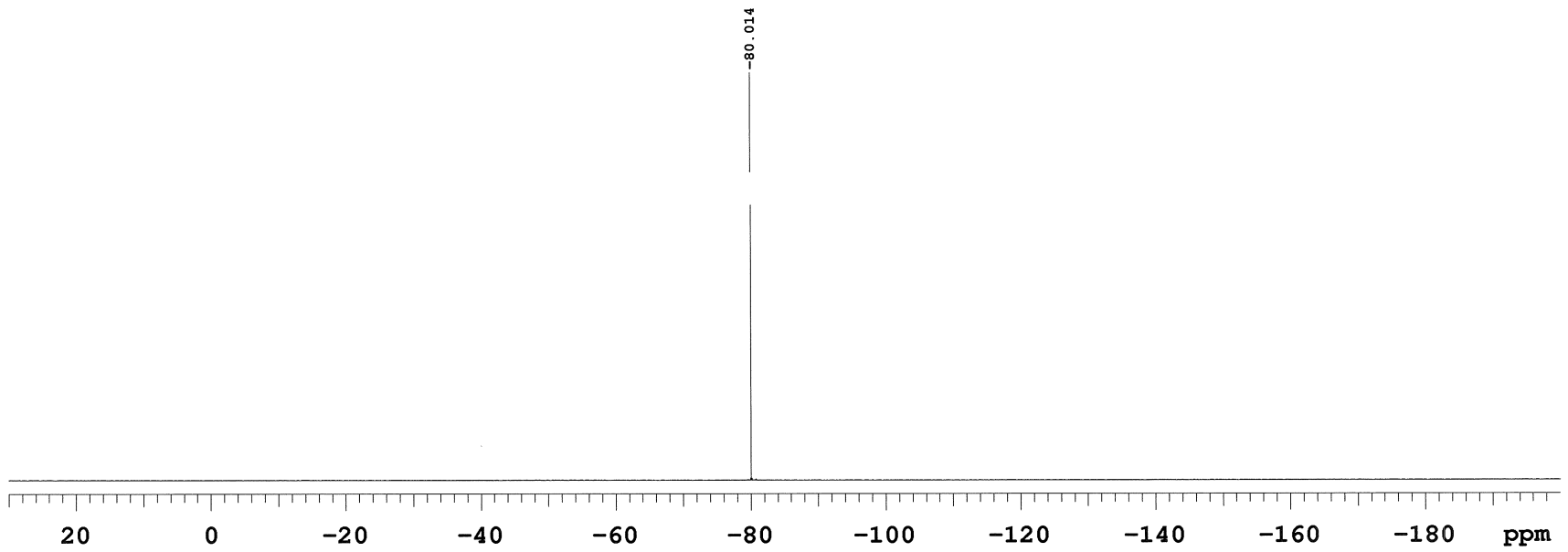


^{13}C NMR (75 MHz, CD_3OD)

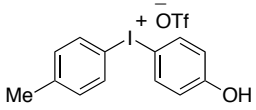


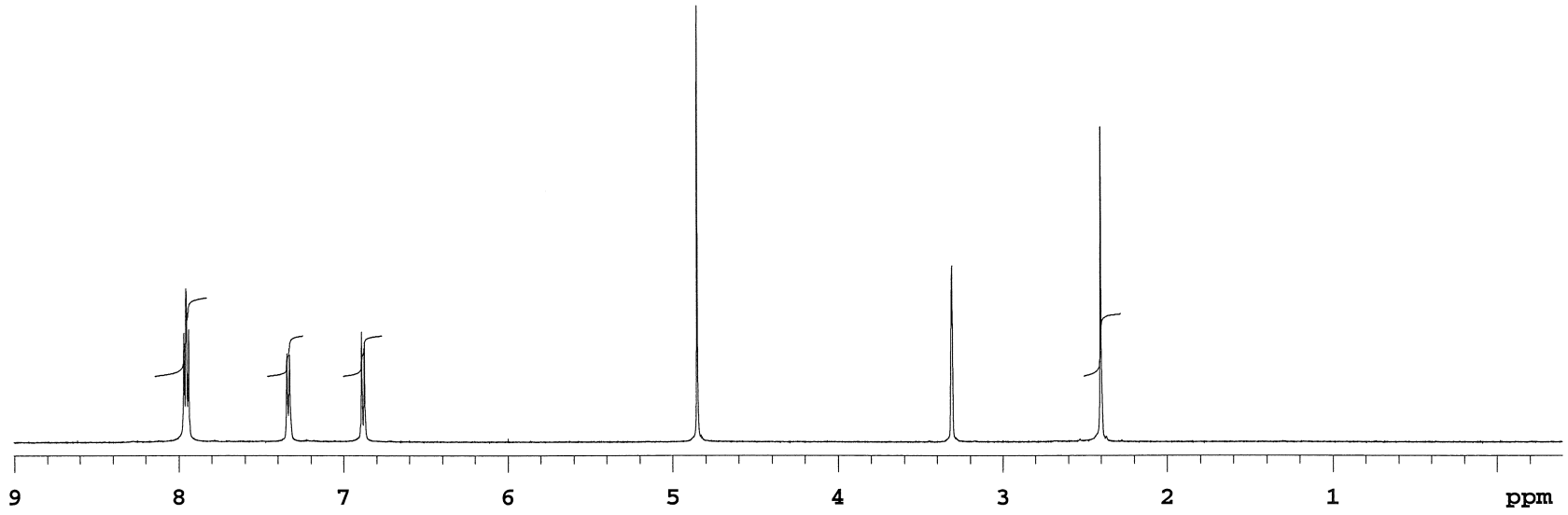
^{19}F NMR (282 MHz, CD_3OD)



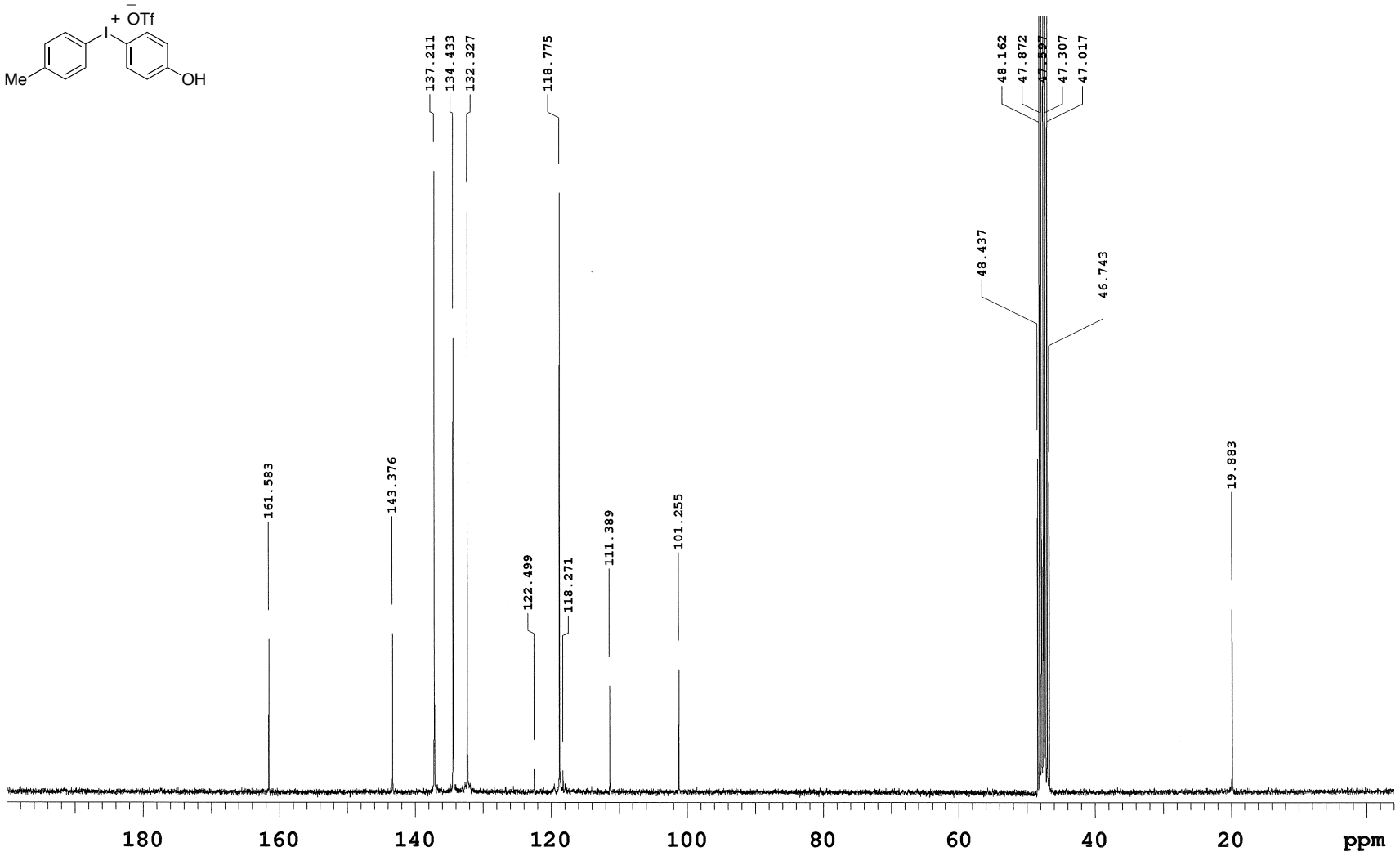


^{1}H NMR (500 MHz, CD_3OD)

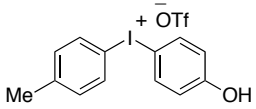


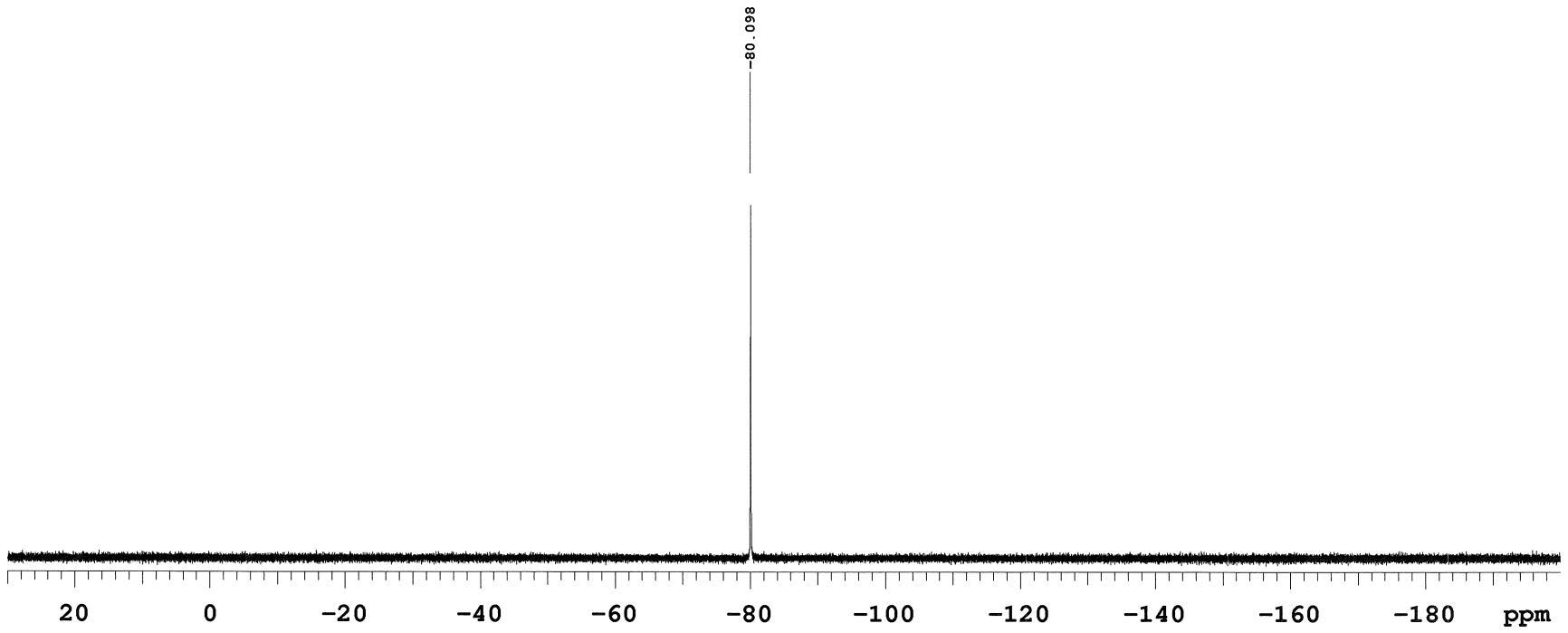


^{13}C NMR (75 MHz, CD_3OD)

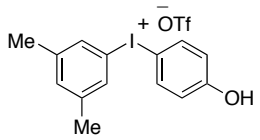


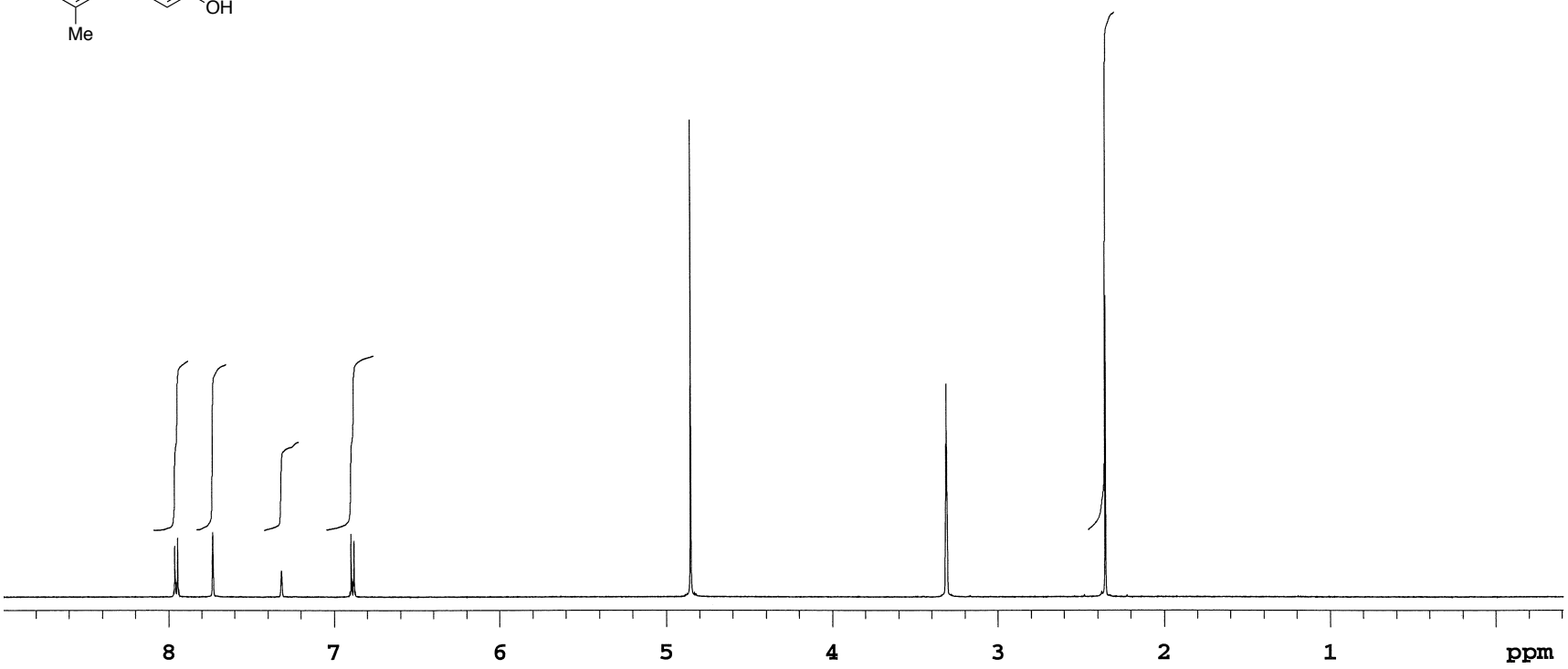
^{19}F NMR (282 MHz, CD_3OD)



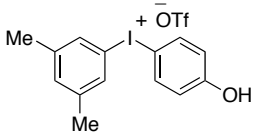


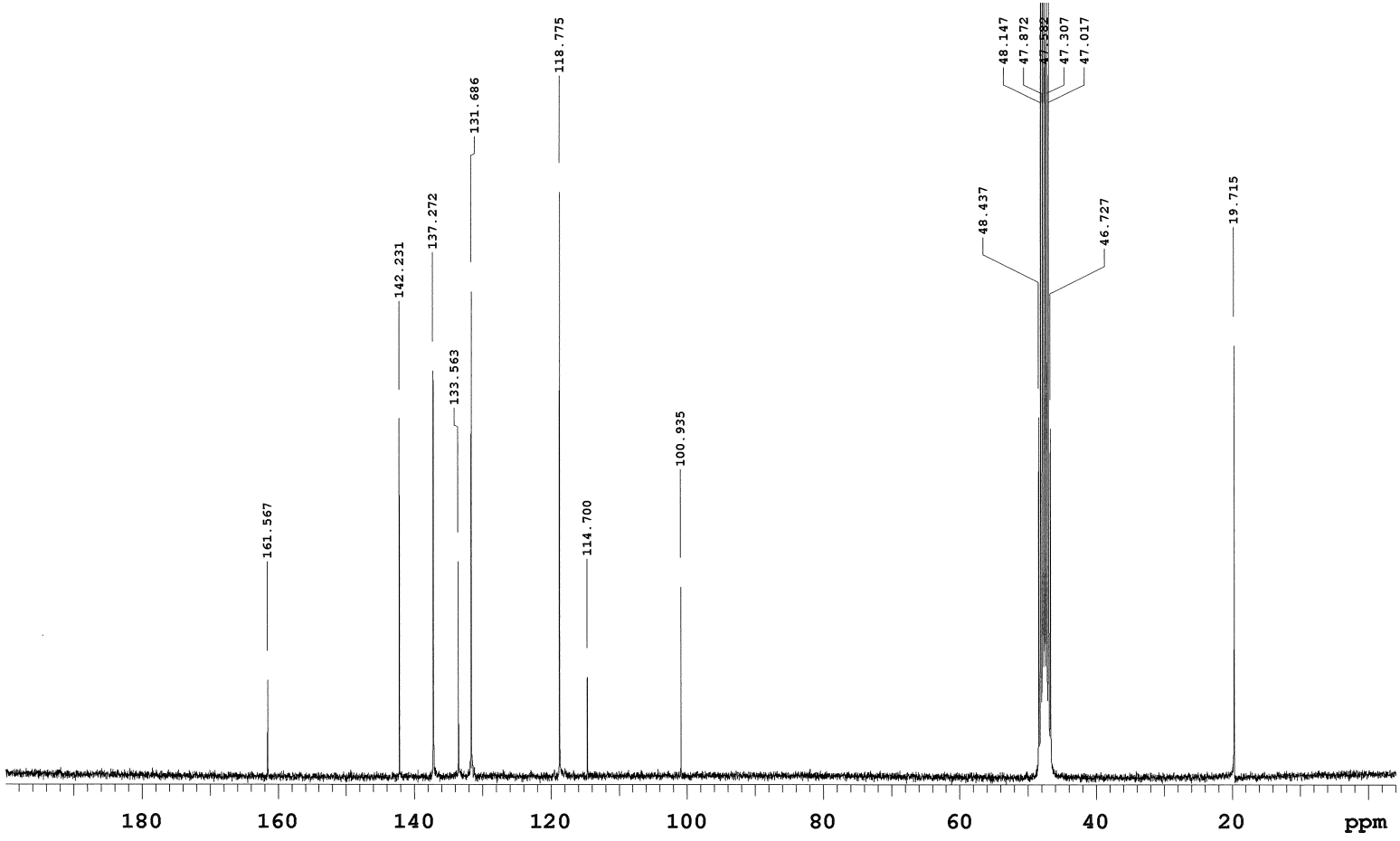
^{1}H NMR (500 MHz, CD_3OD)



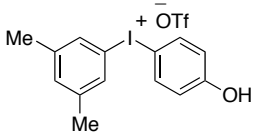


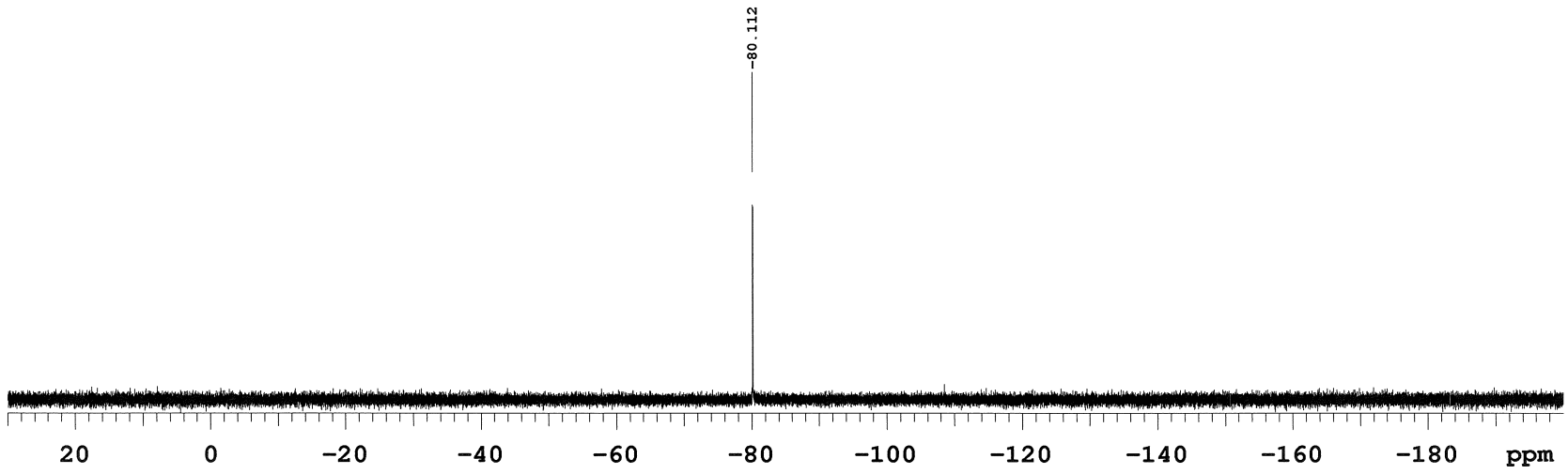
^{13}C NMR (75 MHz, CD_3OD)



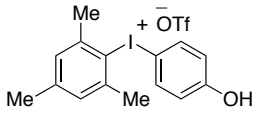


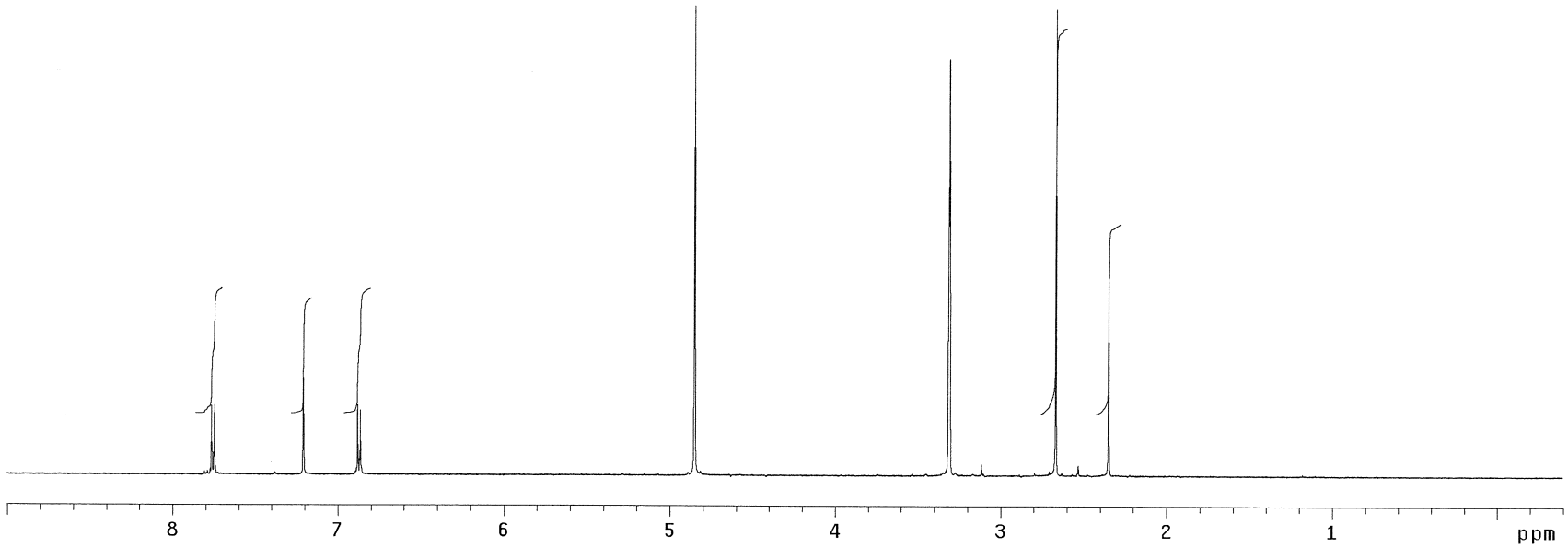
^{19}F NMR (282 MHz, CD_3OD)



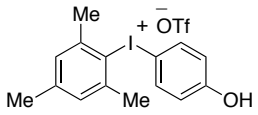


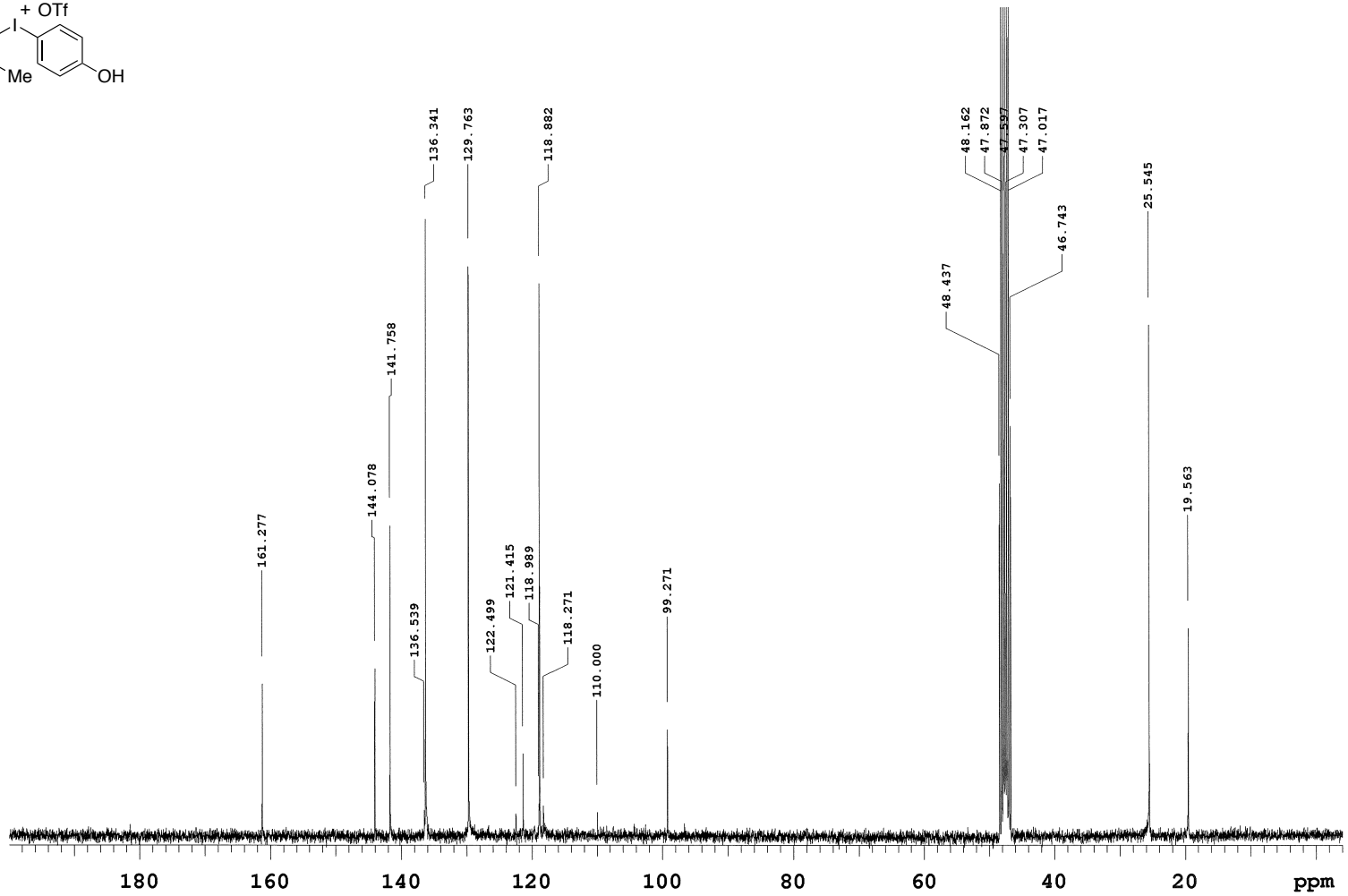
^{1}H NMR (500 MHz, CD_3OD)



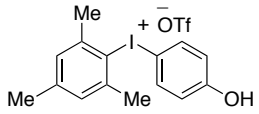


^{13}C NMR (75 MHz, CD_3OD)

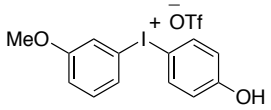


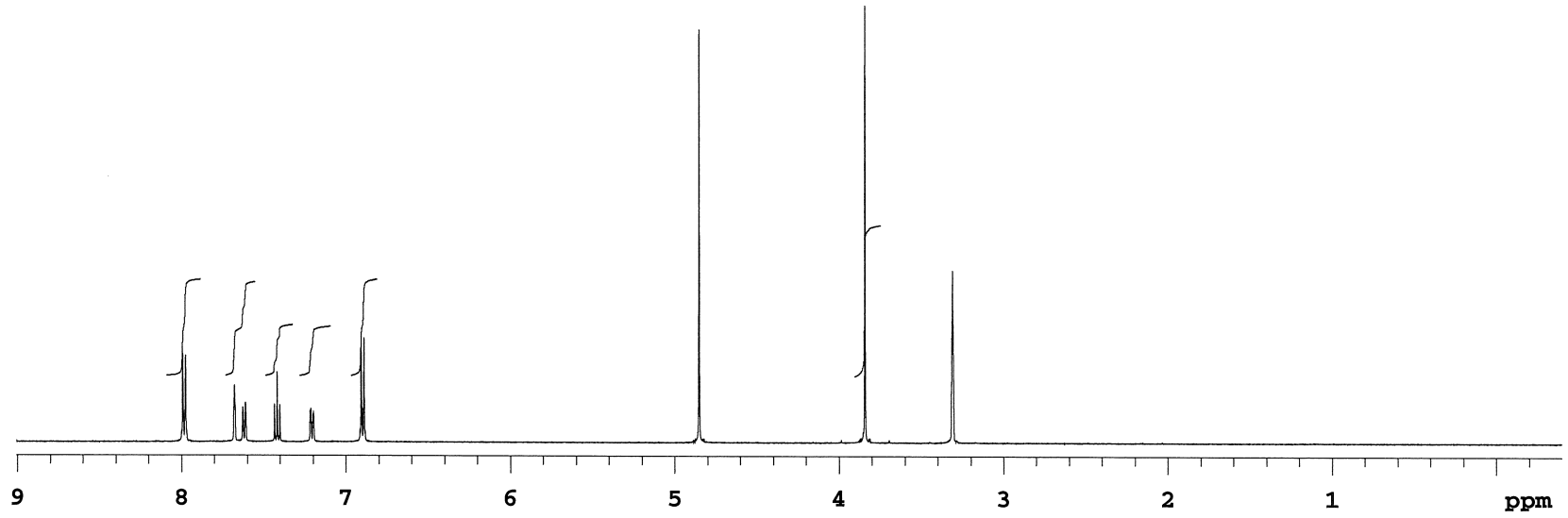


^{19}F NMR (282 MHz, CD_3OD)

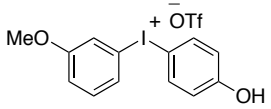


^{1}H NMR (500 MHz, CD_3OD)

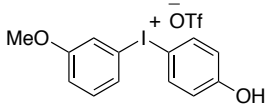


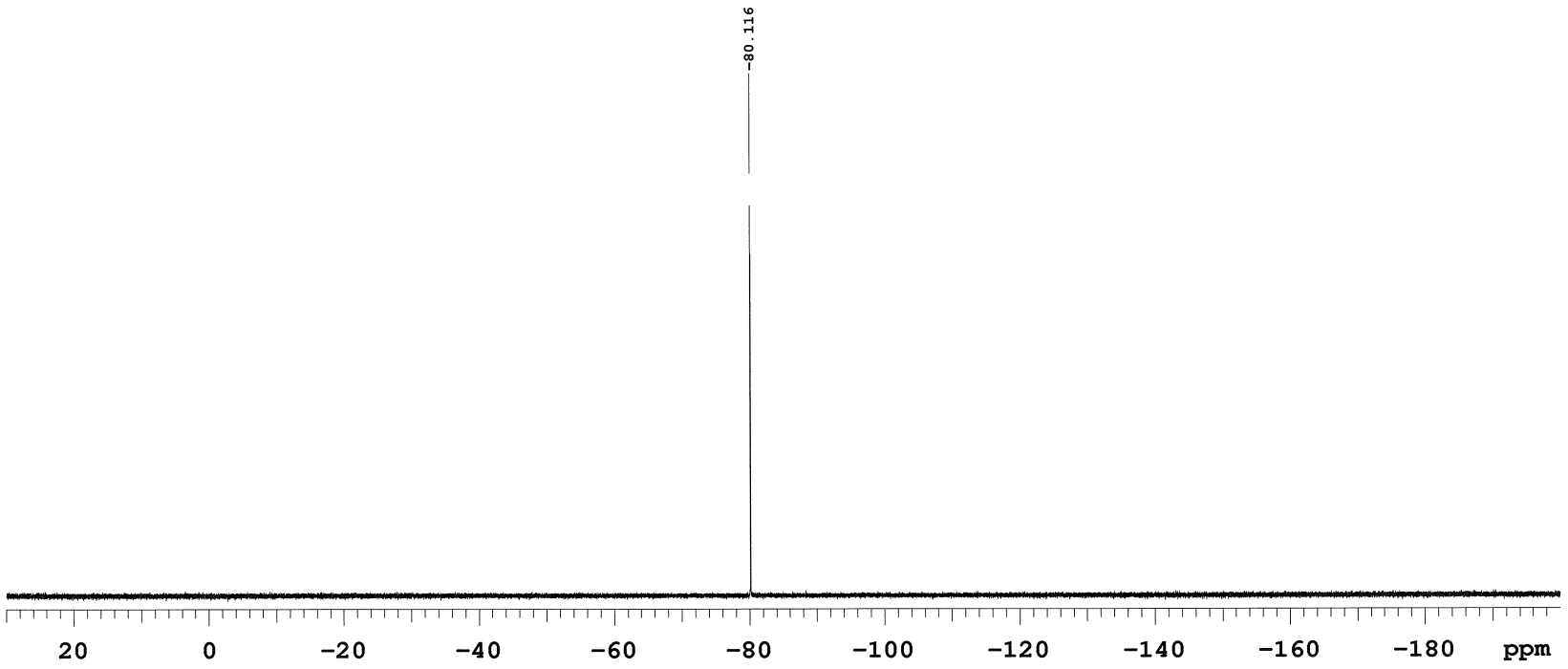


^{13}C NMR (75 MHz, CD_3OD)

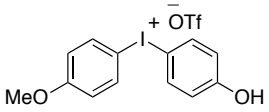


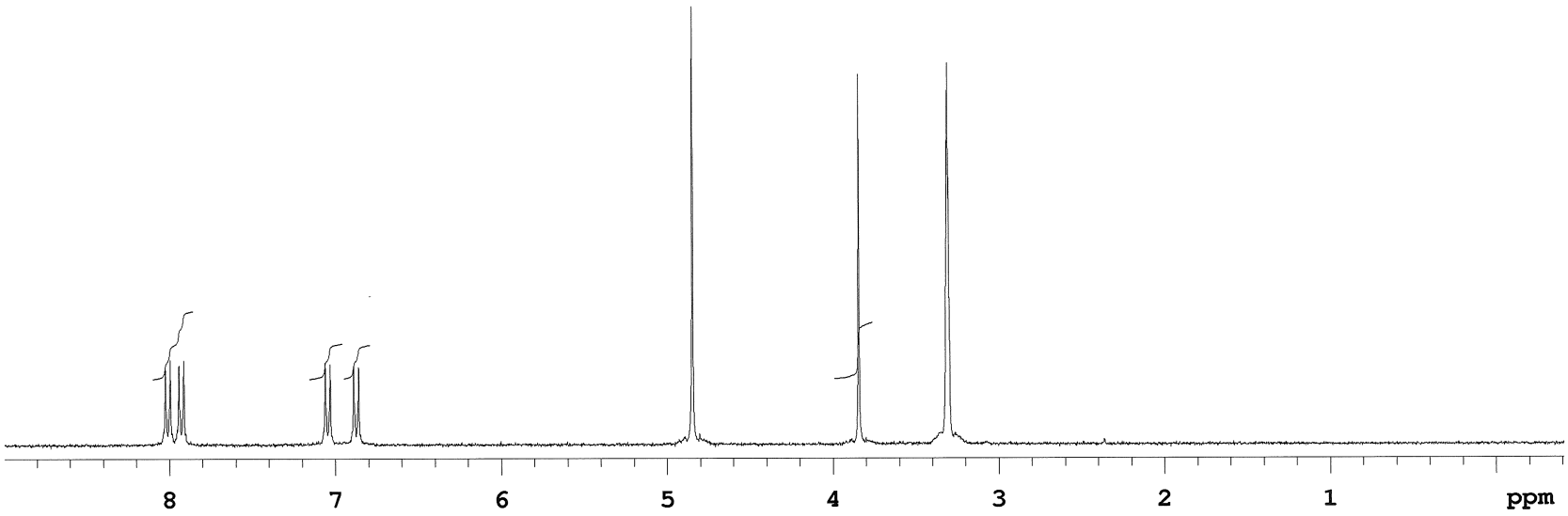
^{19}F NMR (282 MHz, CD_3OD)



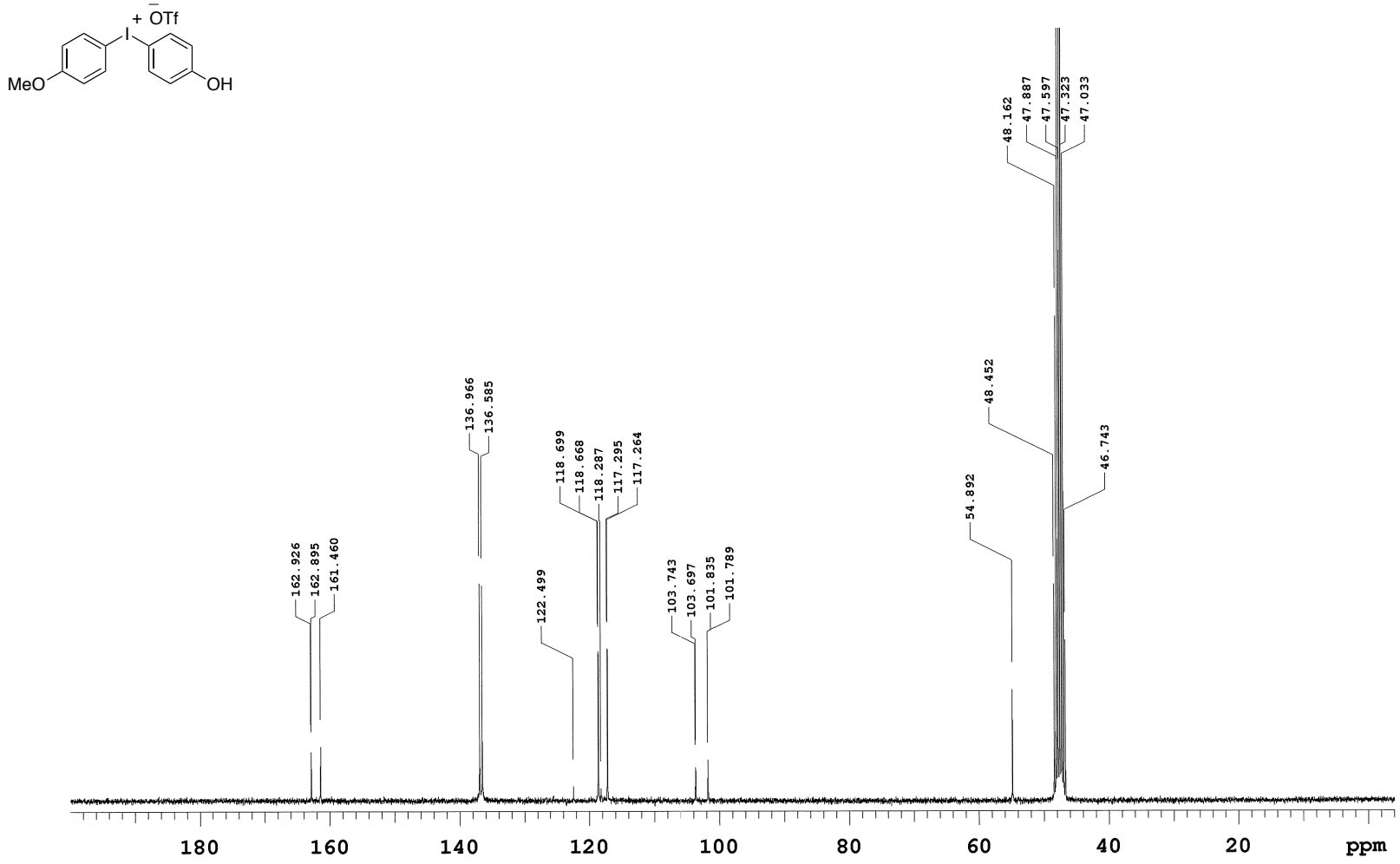


^{1}H NMR (300 MHz, CD_3OD)

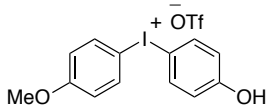


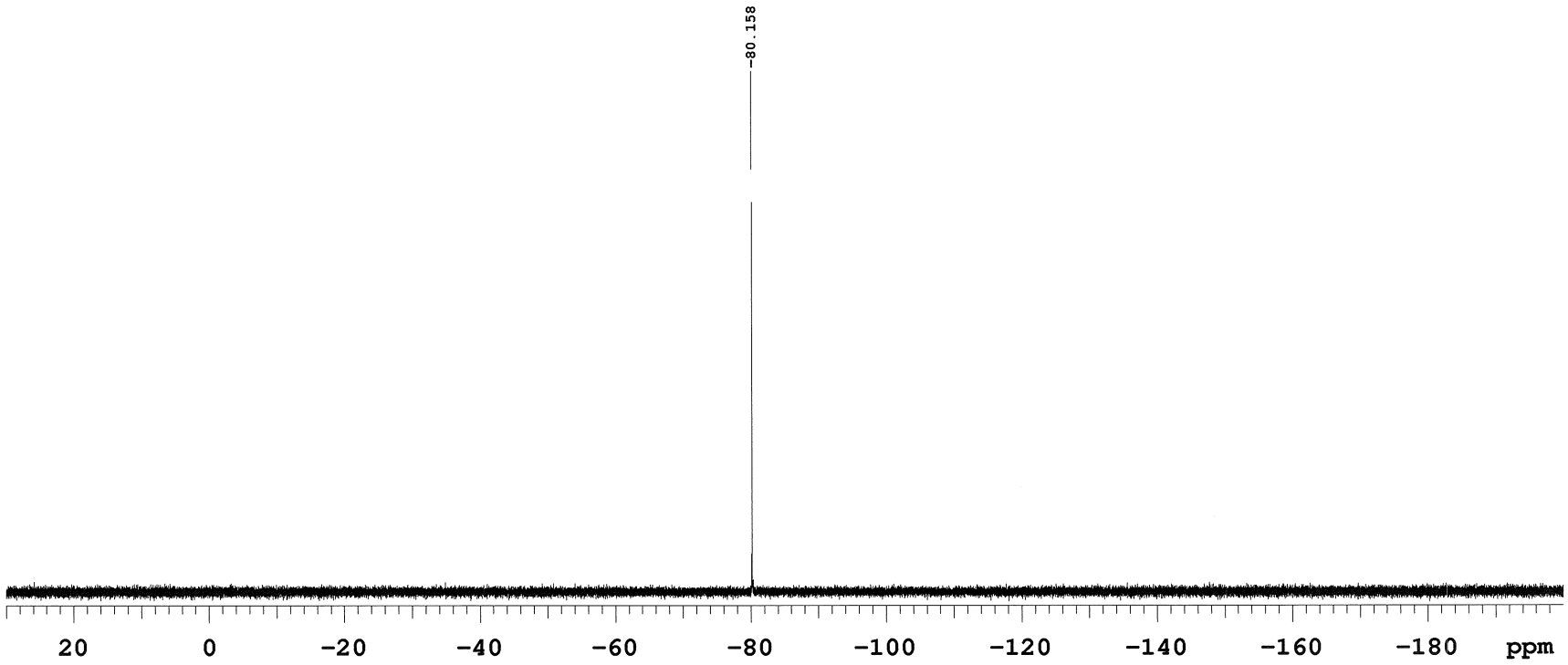


^{13}C NMR (75 MHz, CD_3OD)

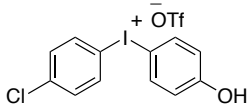


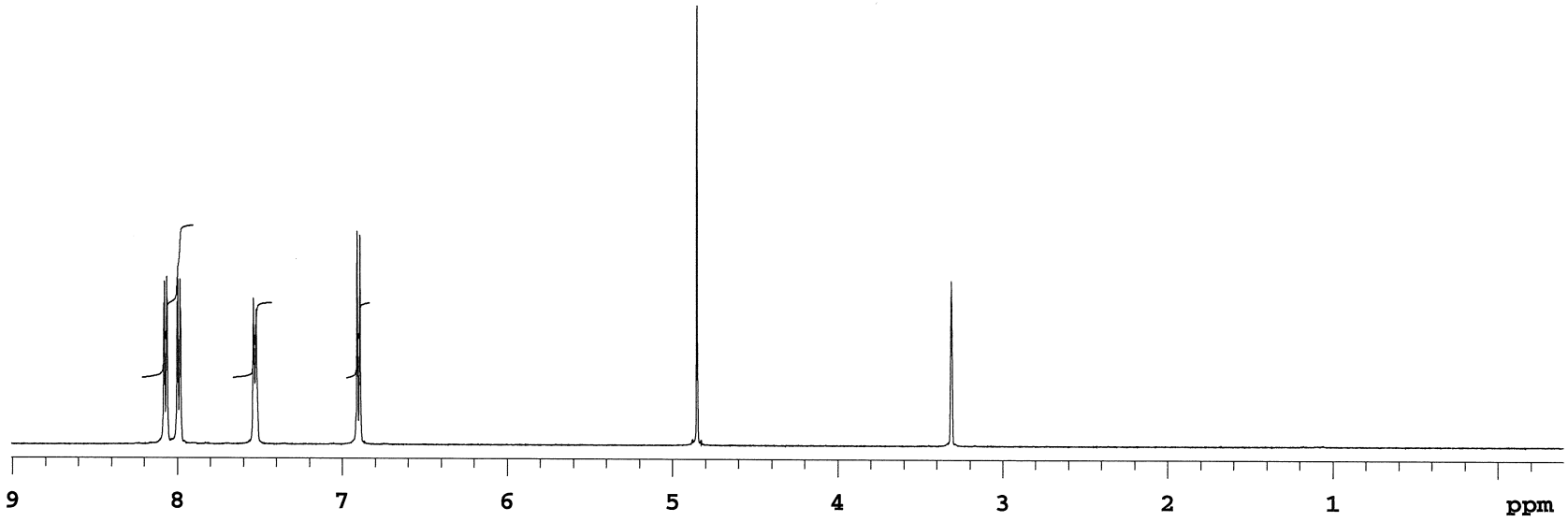
^{19}F NMR (282 MHz, CD_3OD)



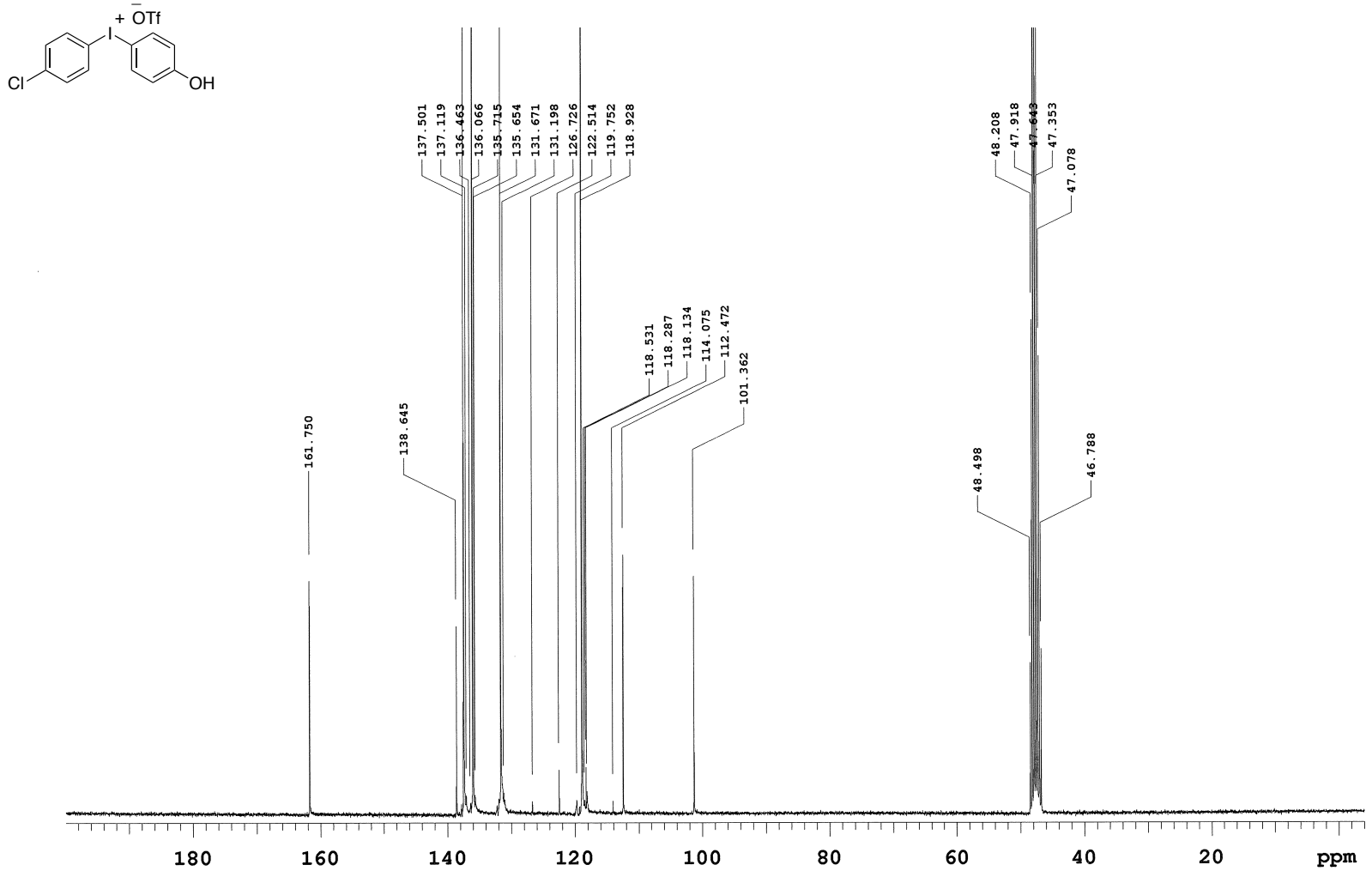


^{1}H NMR (500 MHz, CD_3OD)

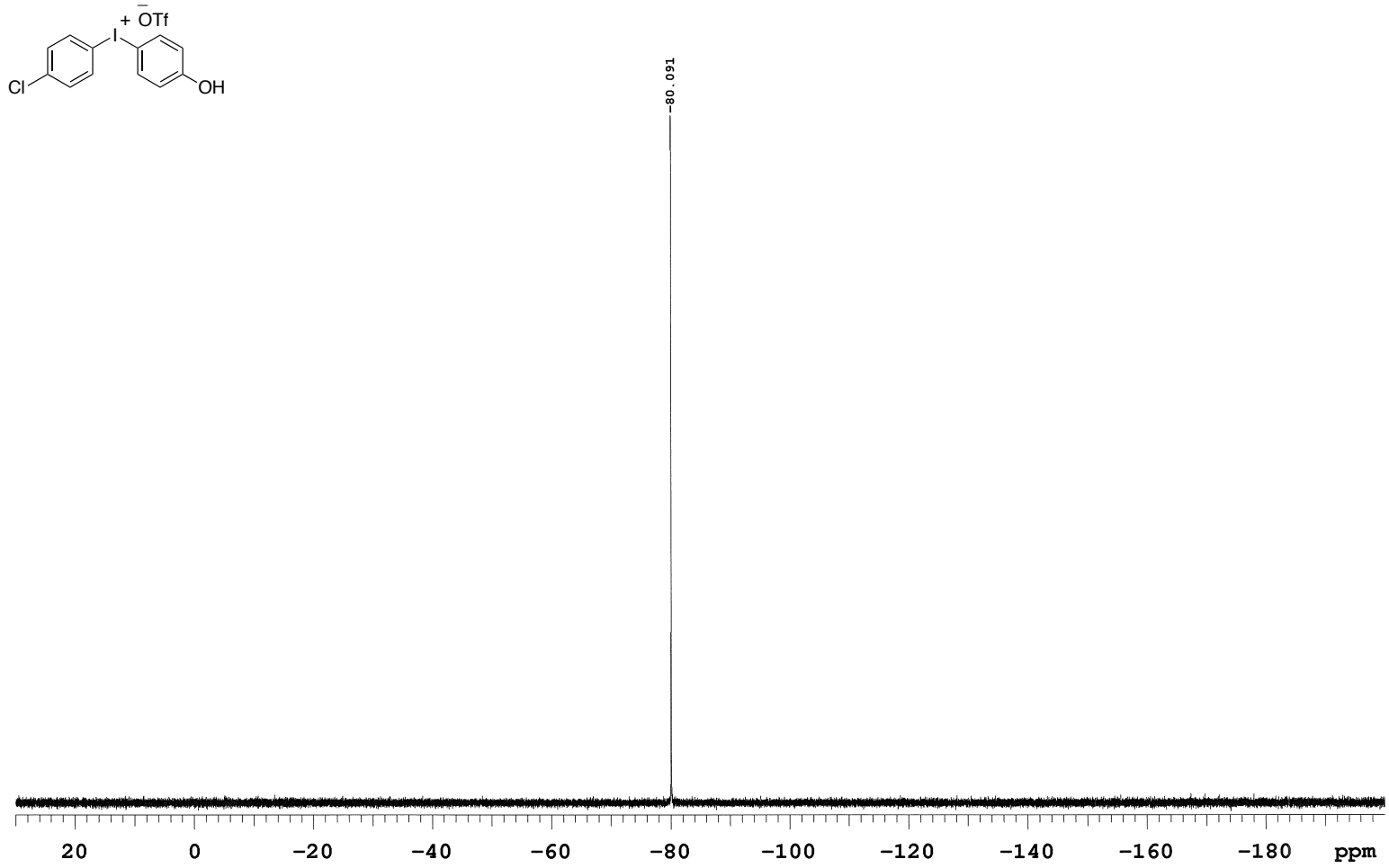




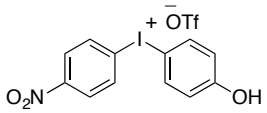
^{13}C NMR (75 MHz, CD_3OD)

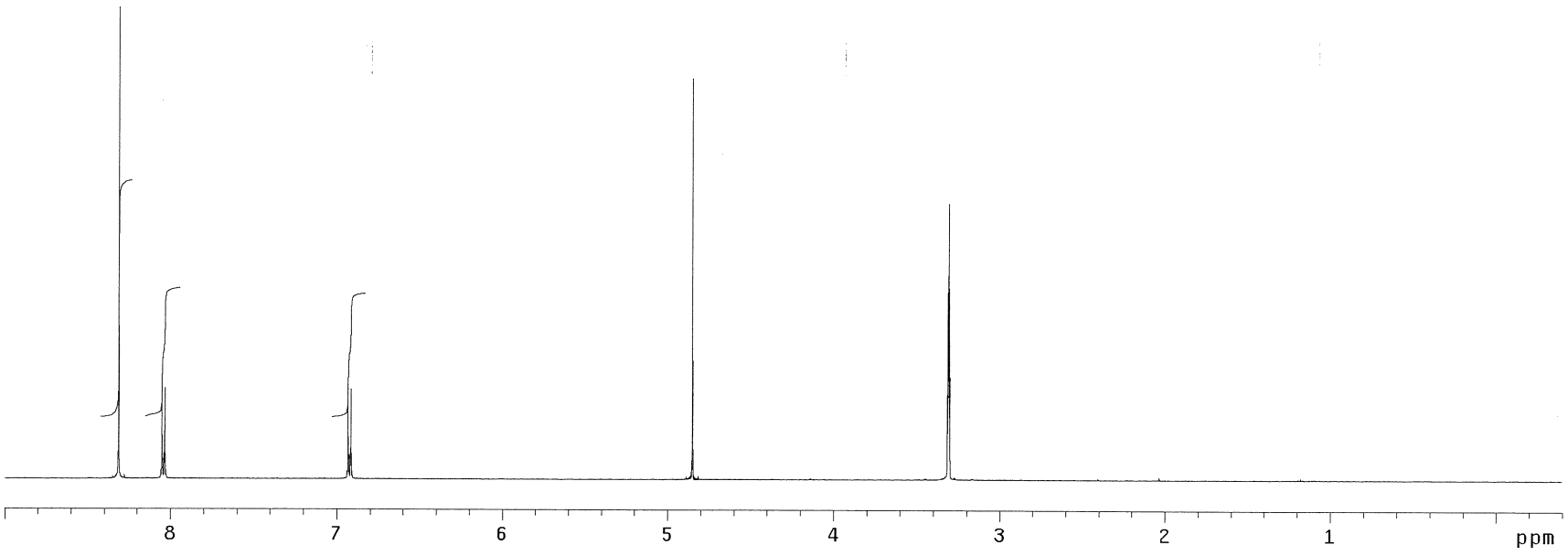


^{19}F NMR (282 MHz, CD_3OD)

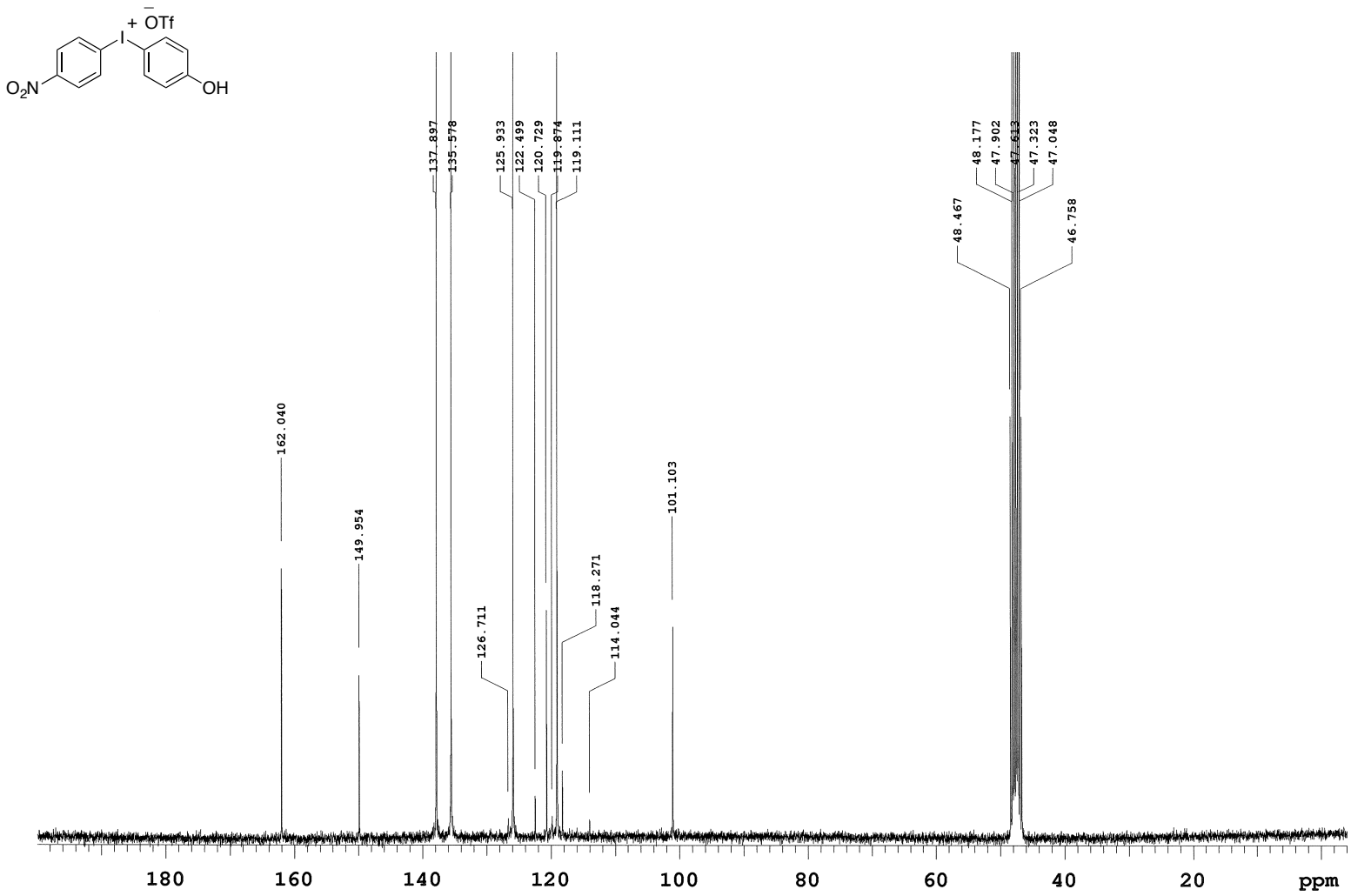


^{1}H NMR (500 MHz, CD_3OD)

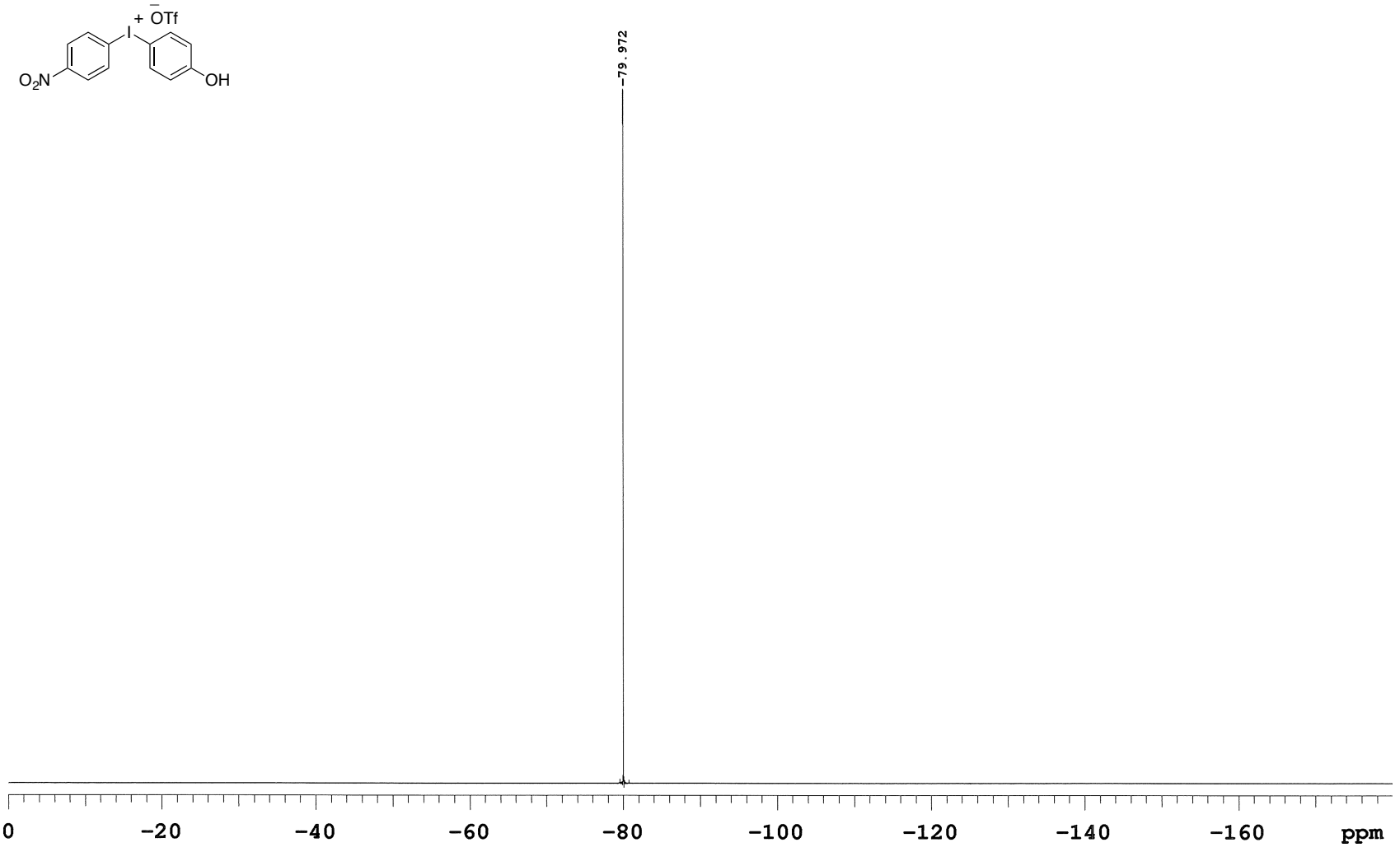




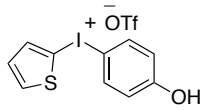
^{13}C NMR (75 MHz, CD_3OD)

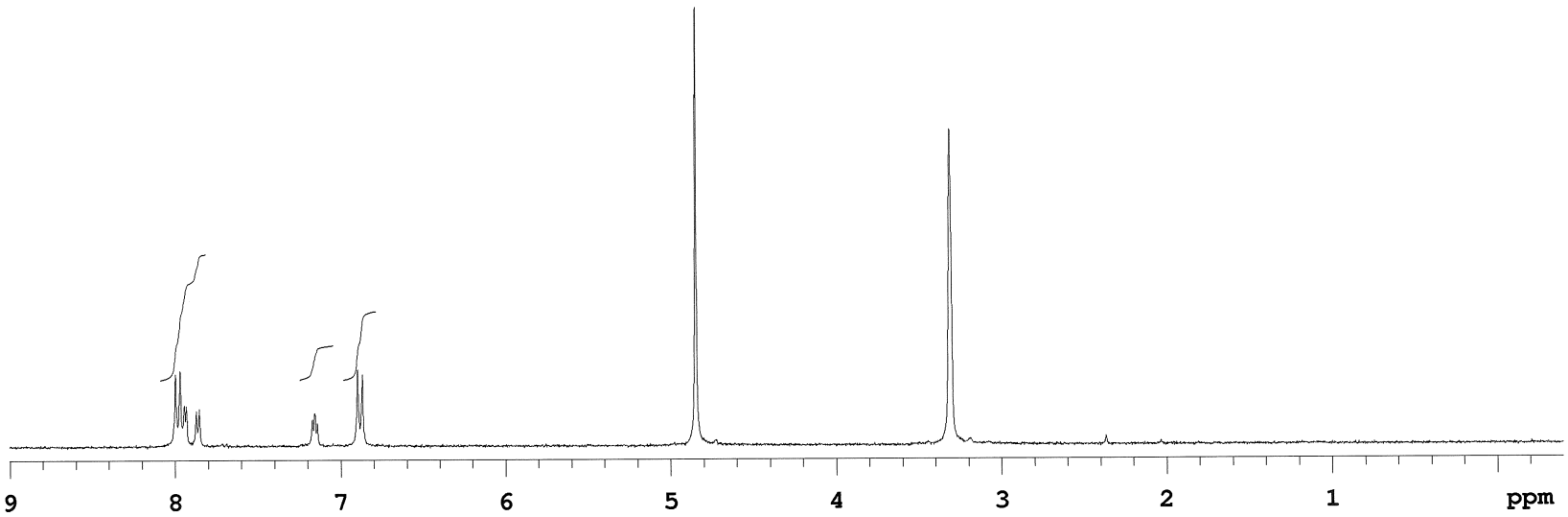


^{19}F NMR (282 MHz, CD_3OD)

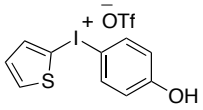


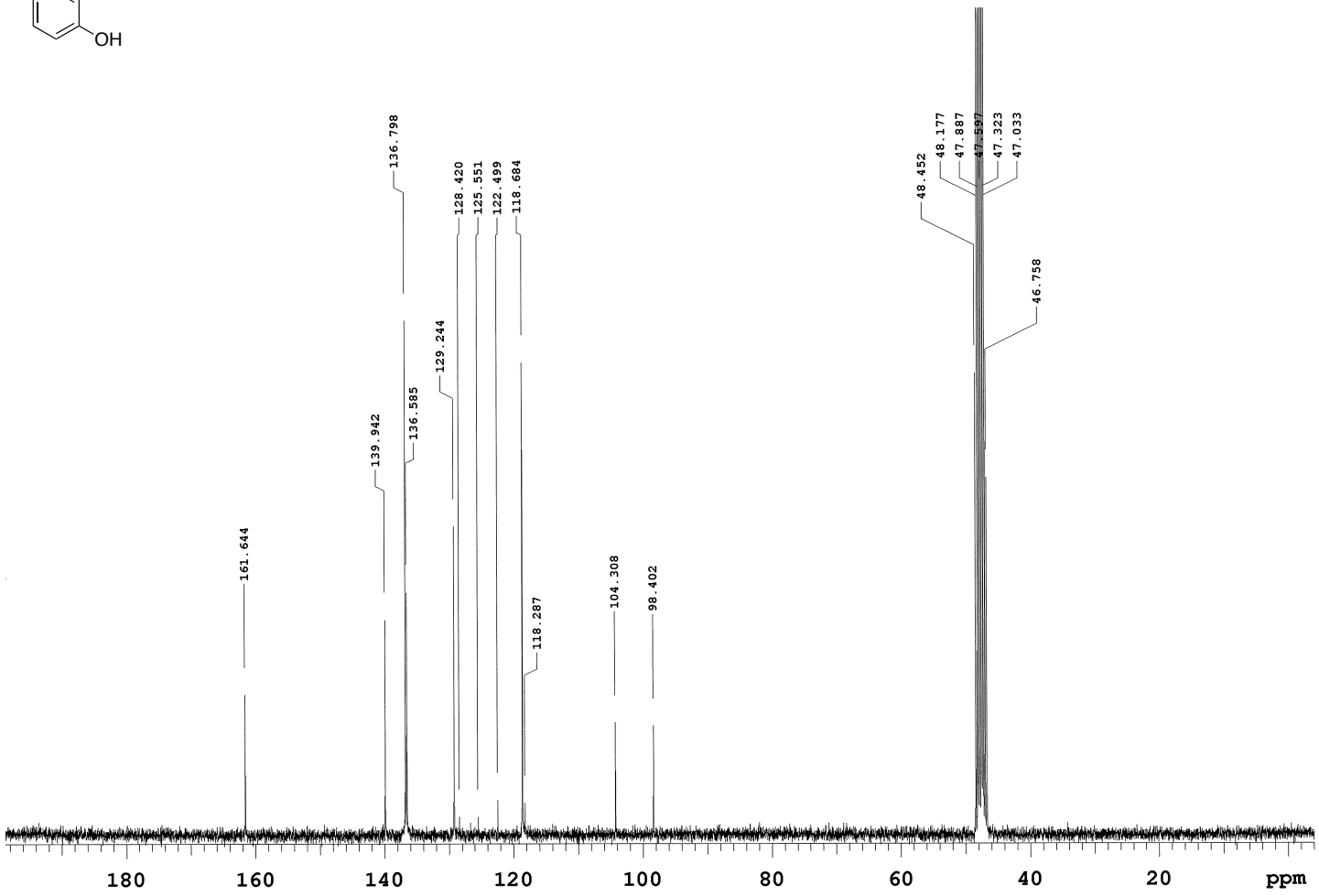
^{1}H NMR (300 MHz, CD_3OD)



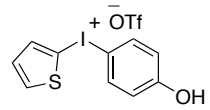


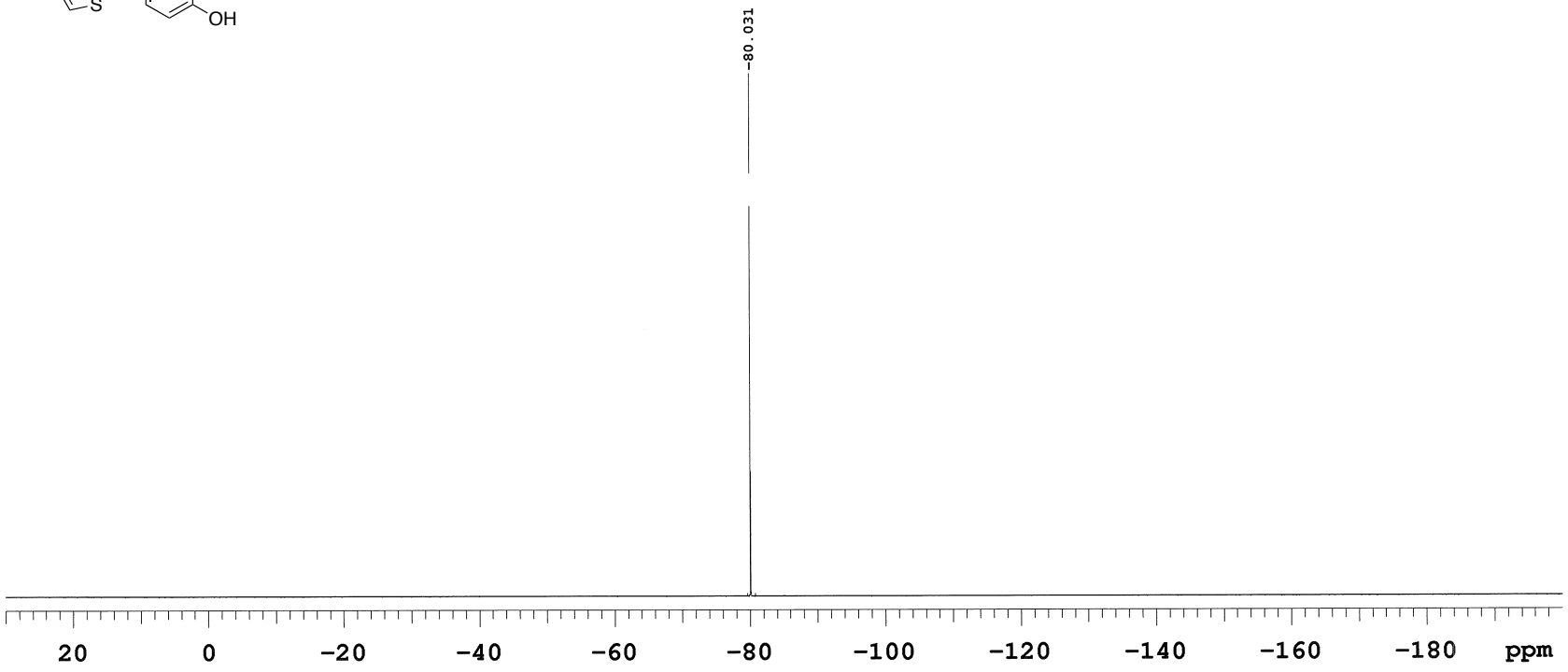
^{13}C NMR (75 MHz, CD_3OD)



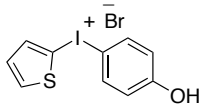


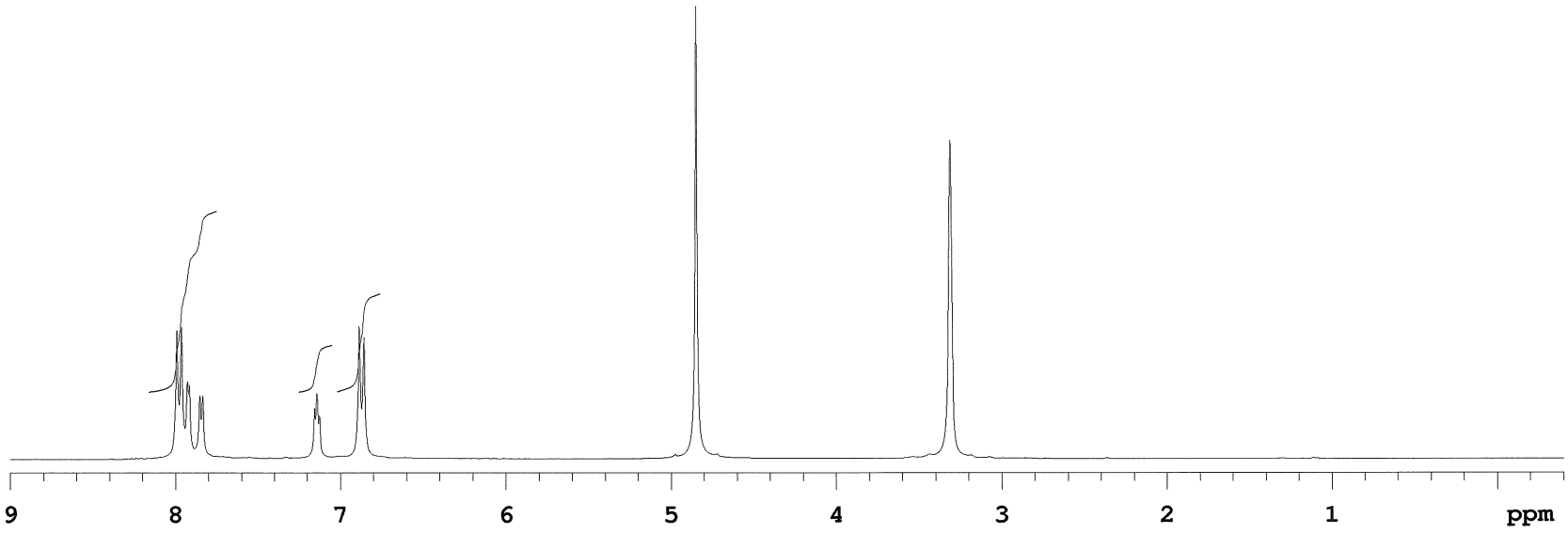
^{19}F NMR (282 MHz, CD_3OD)



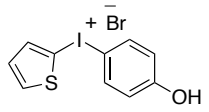


^{1}H NMR (500 MHz, CD_3OD)

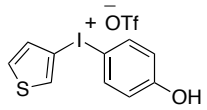


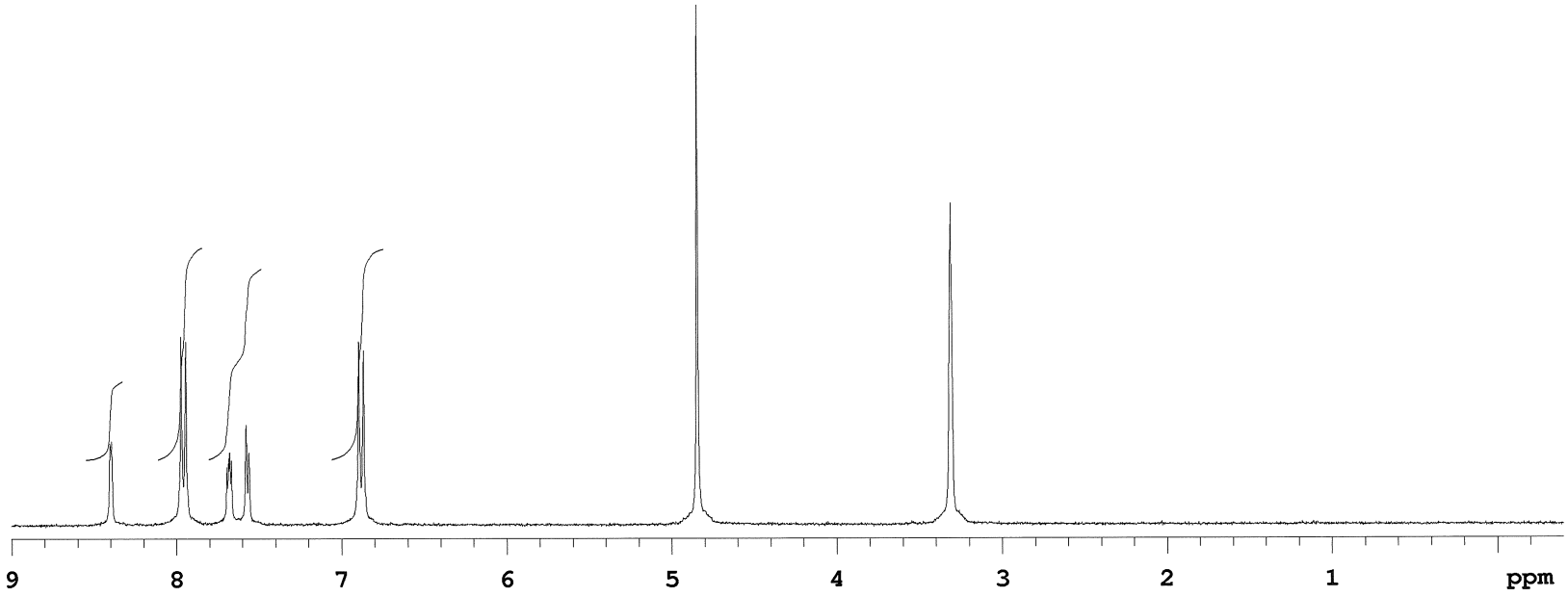


^{13}C NMR (75 MHz, CD_3OD)

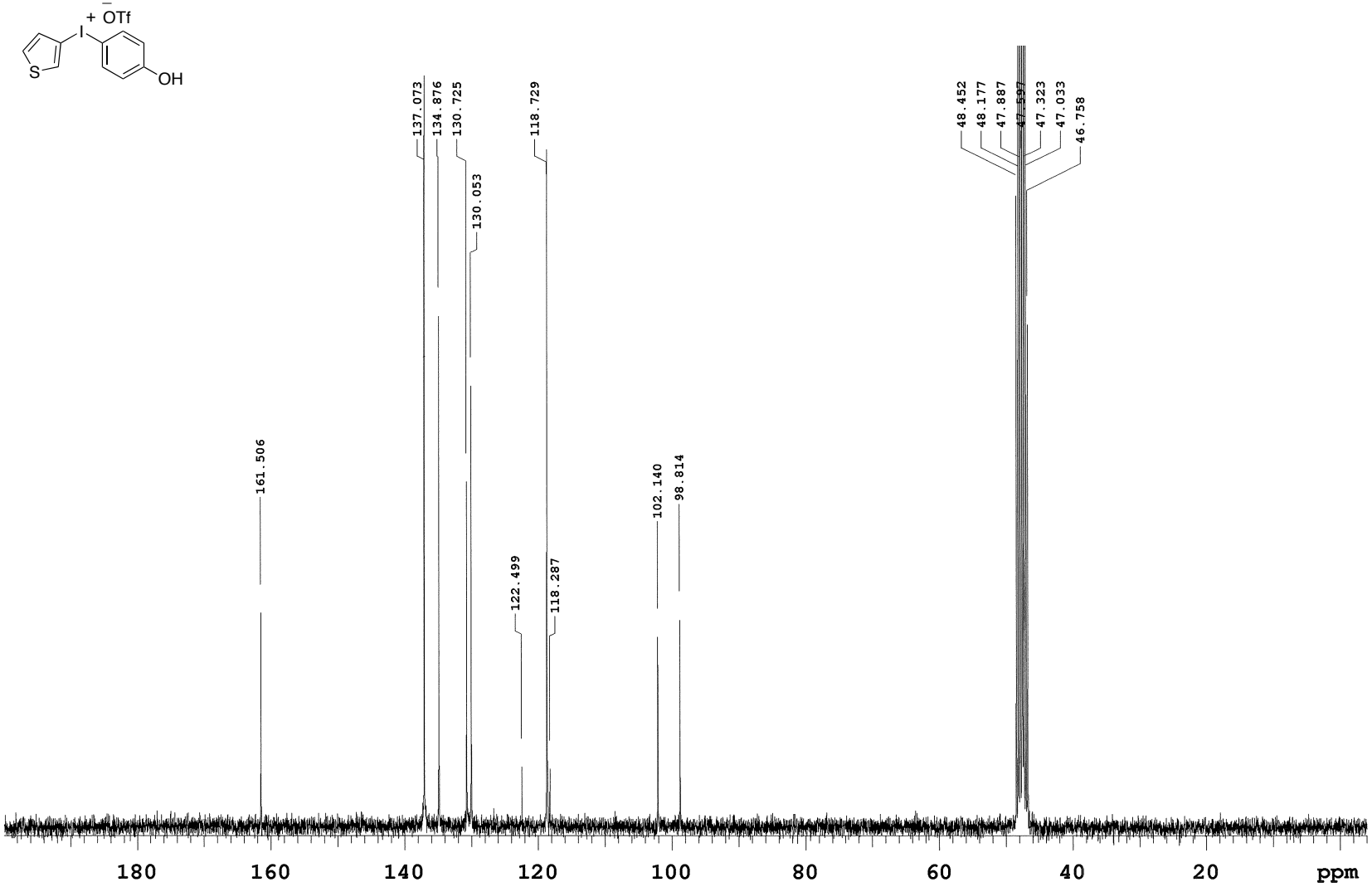


^{1}H NMR (300 MHz, CD_3OD)

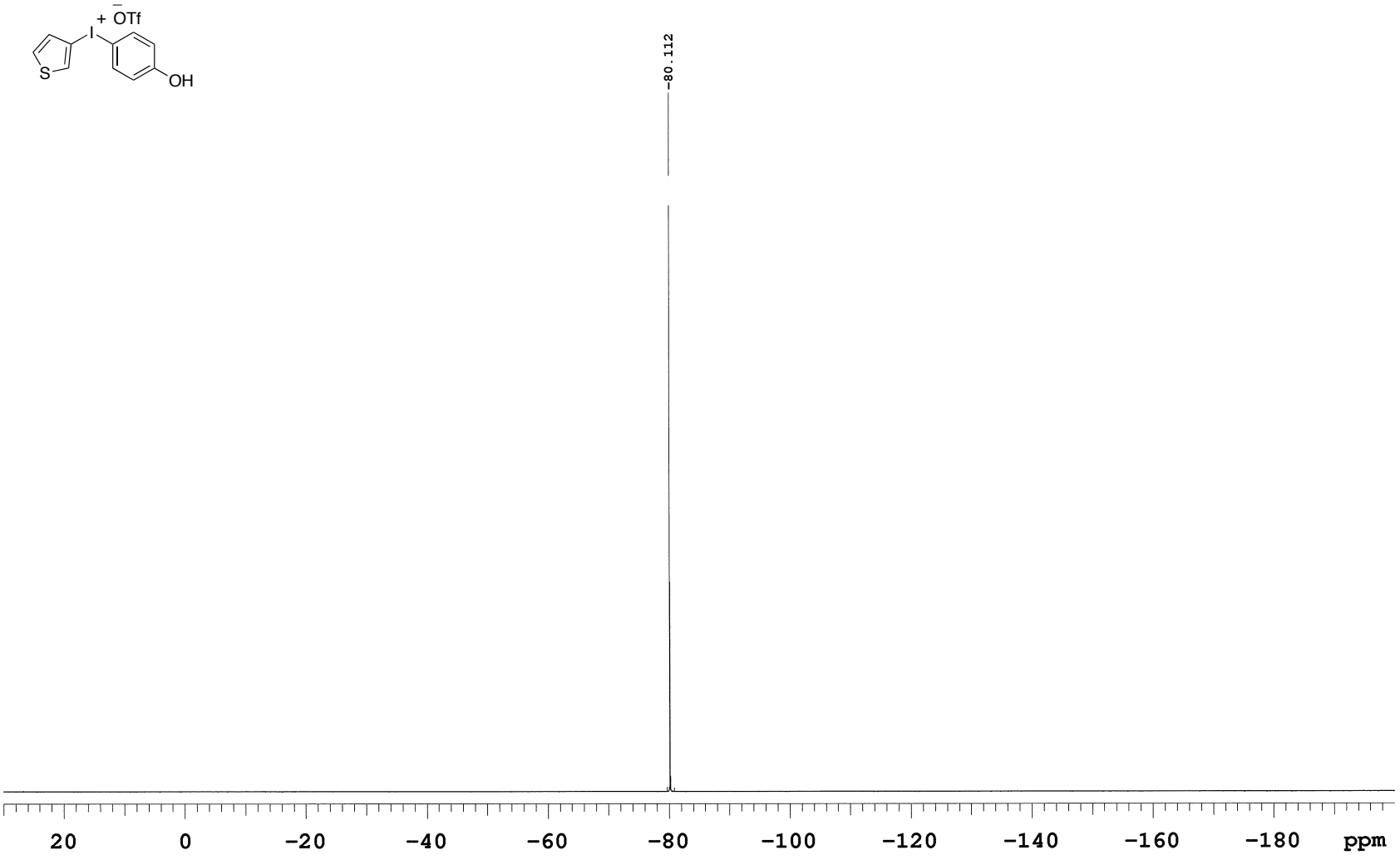




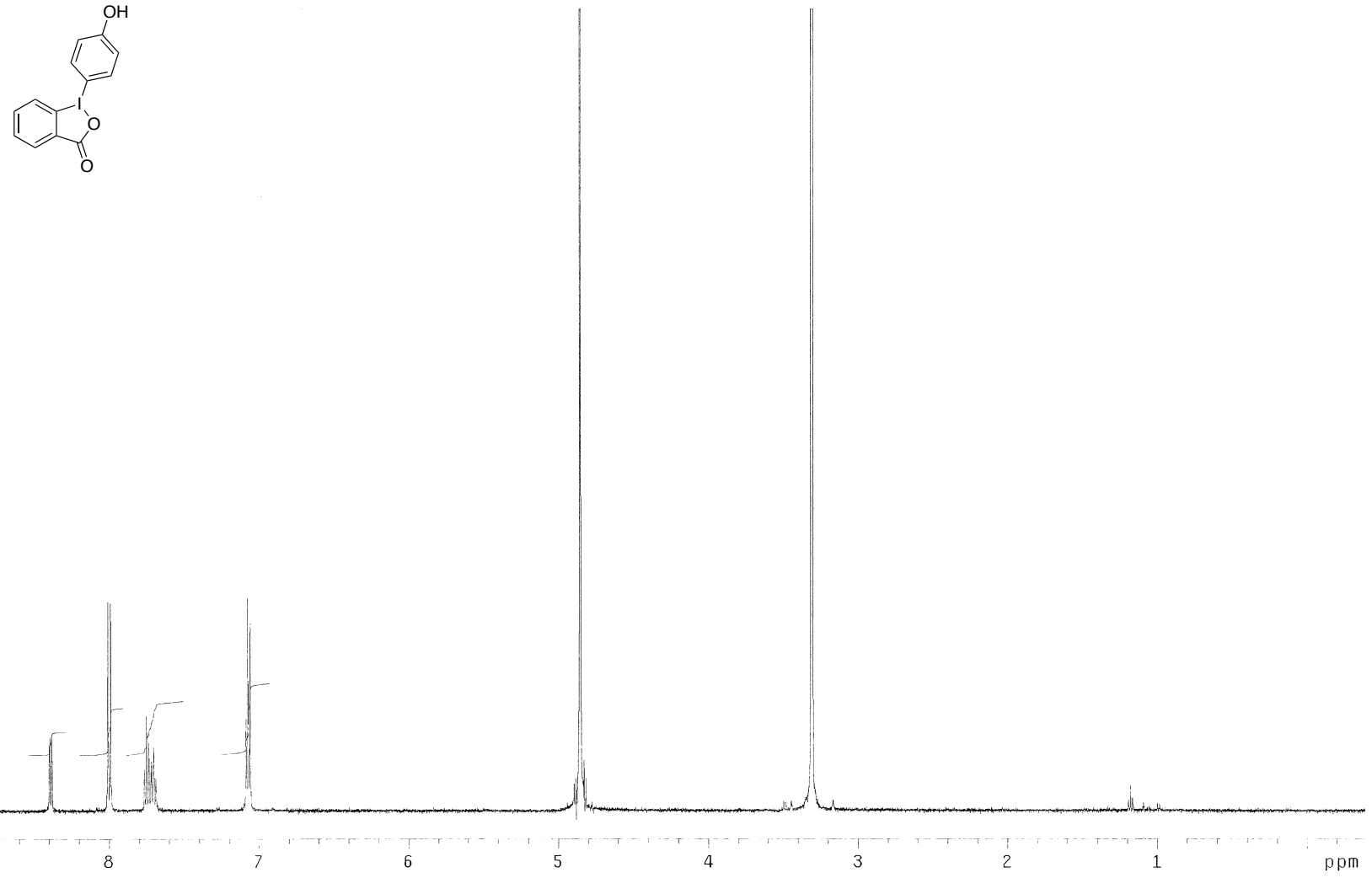
^{13}C NMR (75 MHz, CD_3OD)



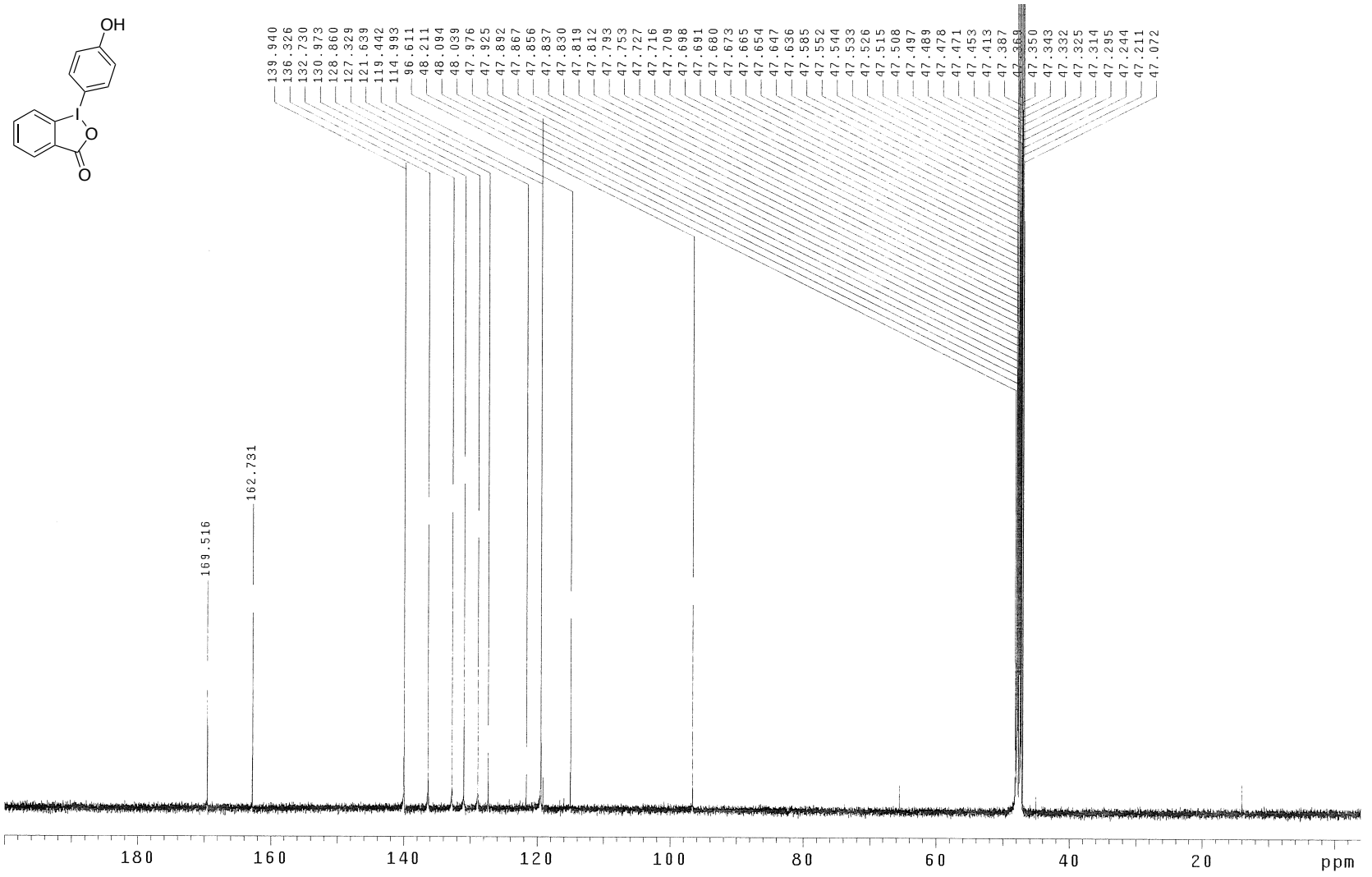
^{19}F NMR (282 MHz, CD_3OD)



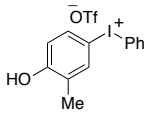
^{1}H NMR (500 MHz, CD_3OD)

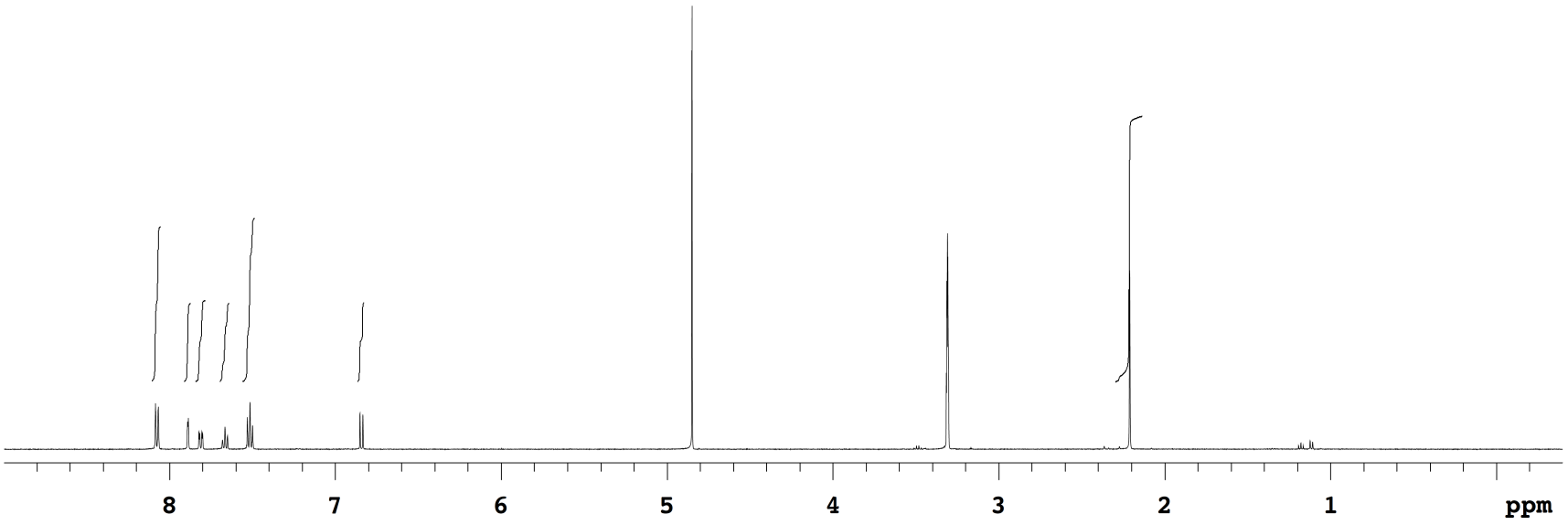


^{13}C NMR (75 MHz, CD_3OD)

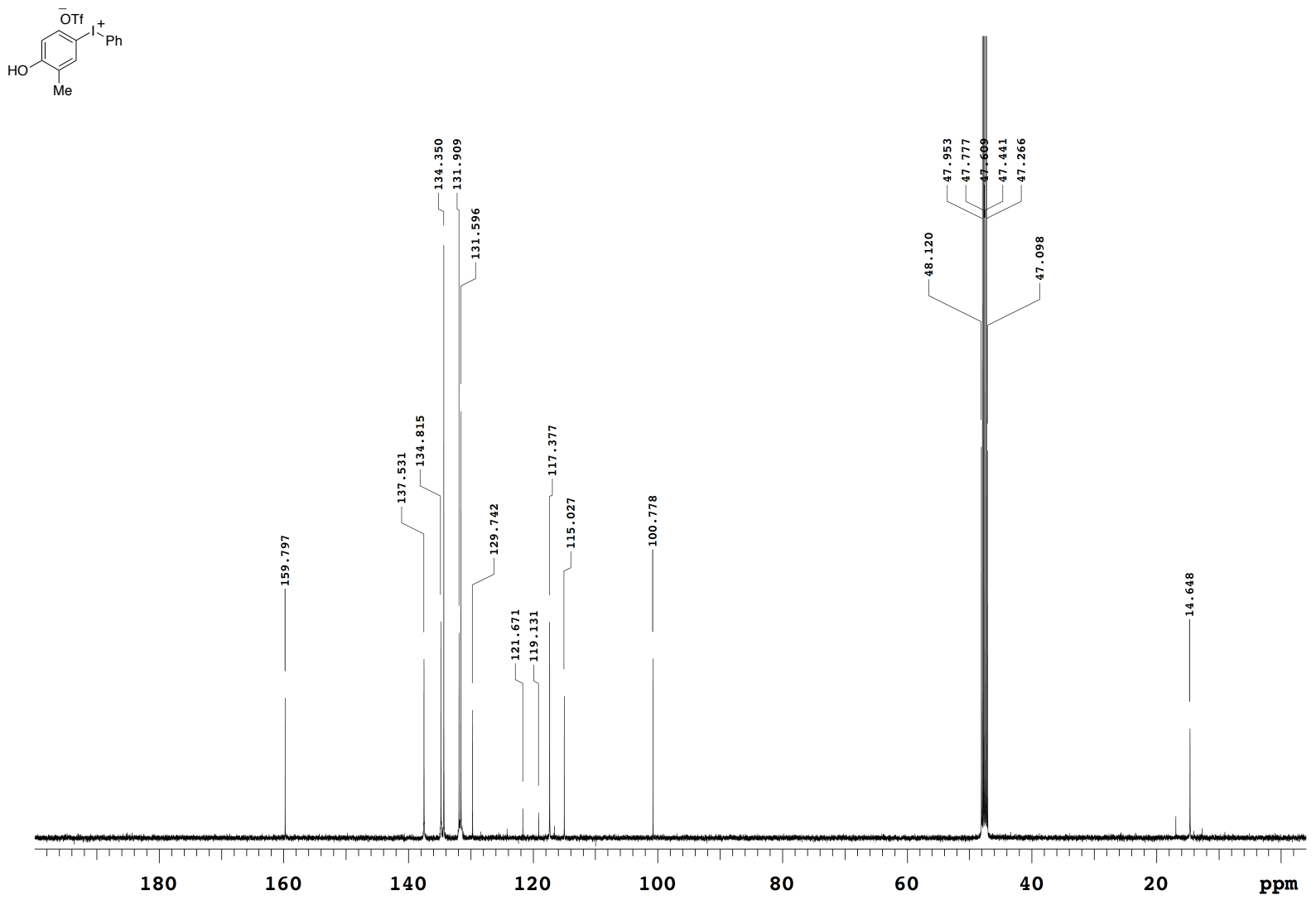


^{1}H NMR (500 MHz, CD_3OD)

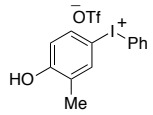


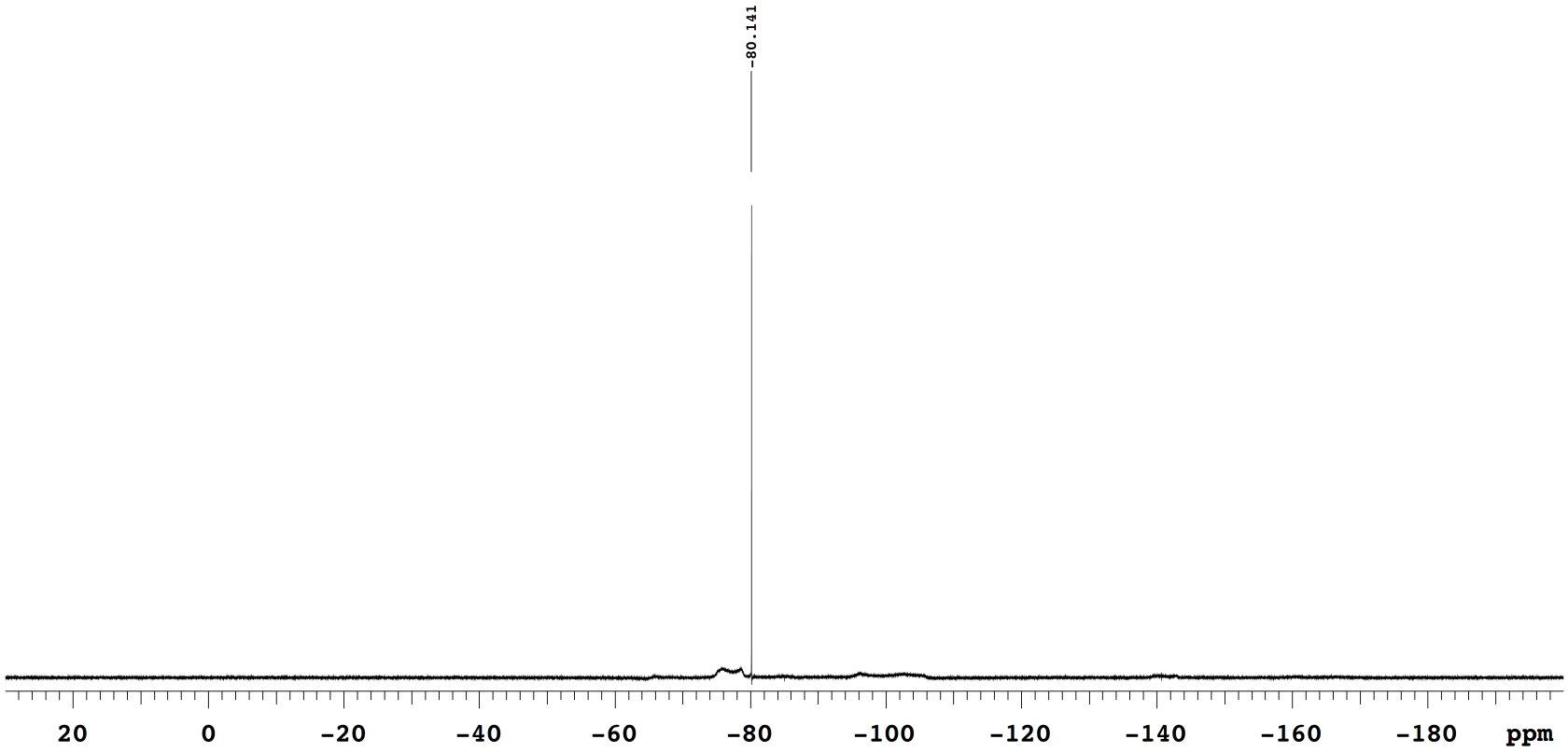


^{13}C NMR (125 MHz, CD_3OD)

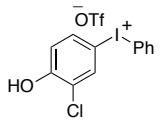


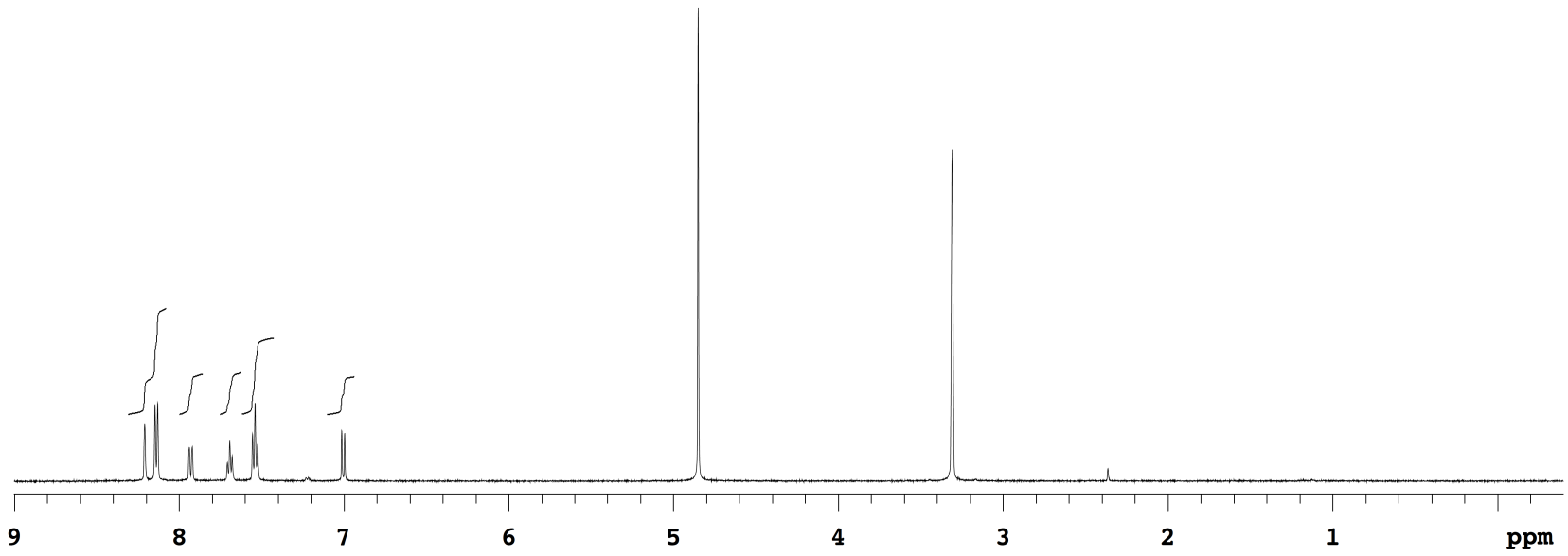
^{19}F NMR (470 MHz, CD_3OD)



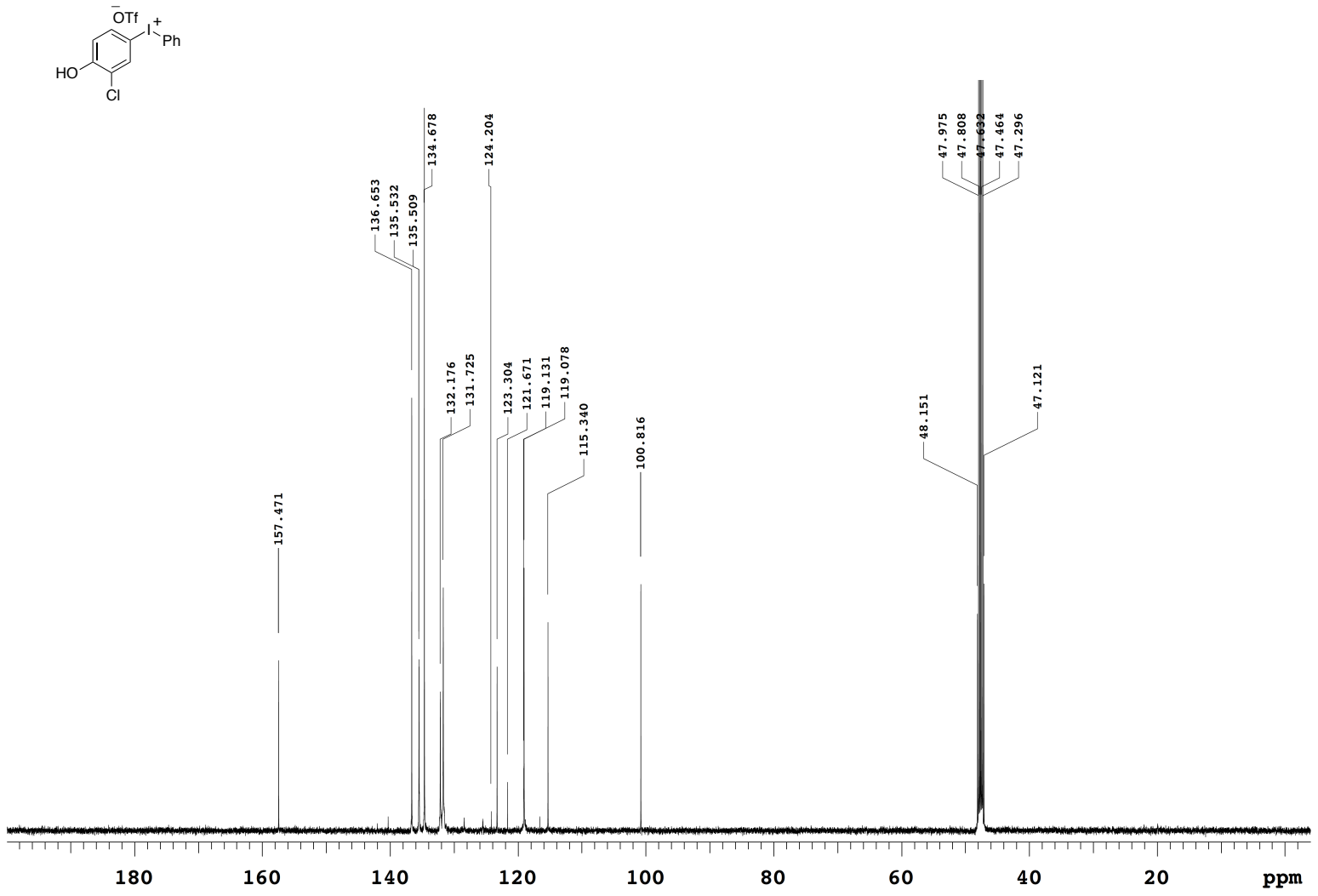


^{1}H NMR (500 MHz, CD_3OD)

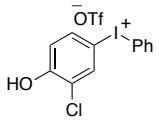


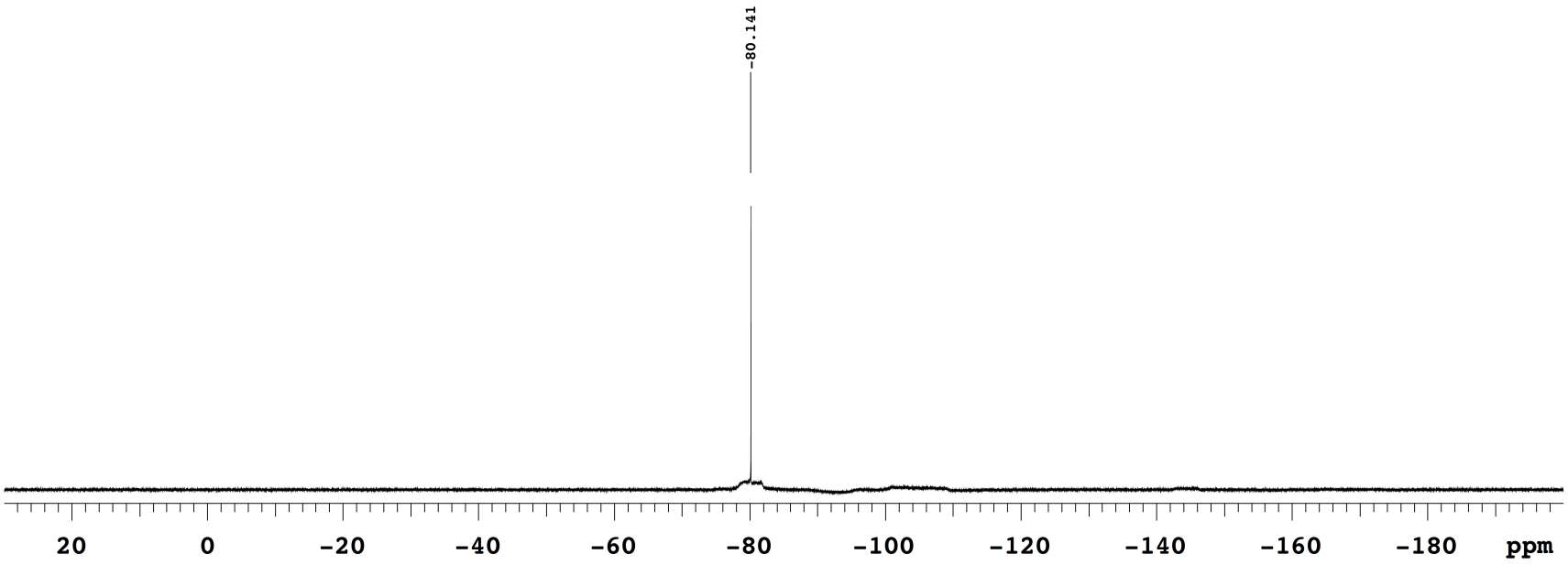


^{13}C NMR (125 MHz, CD_3OD)

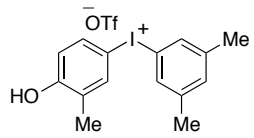


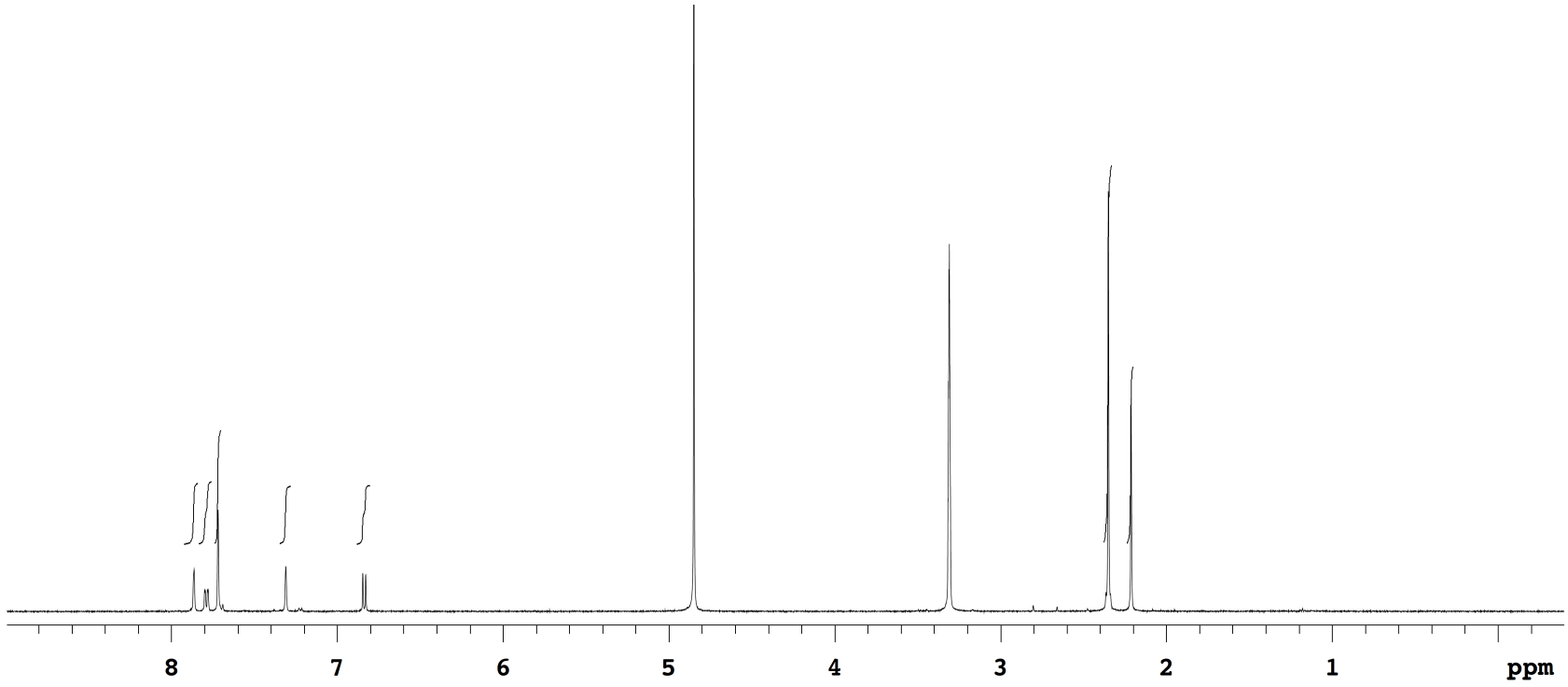
^{19}F NMR (470 MHz, CD_3OD)



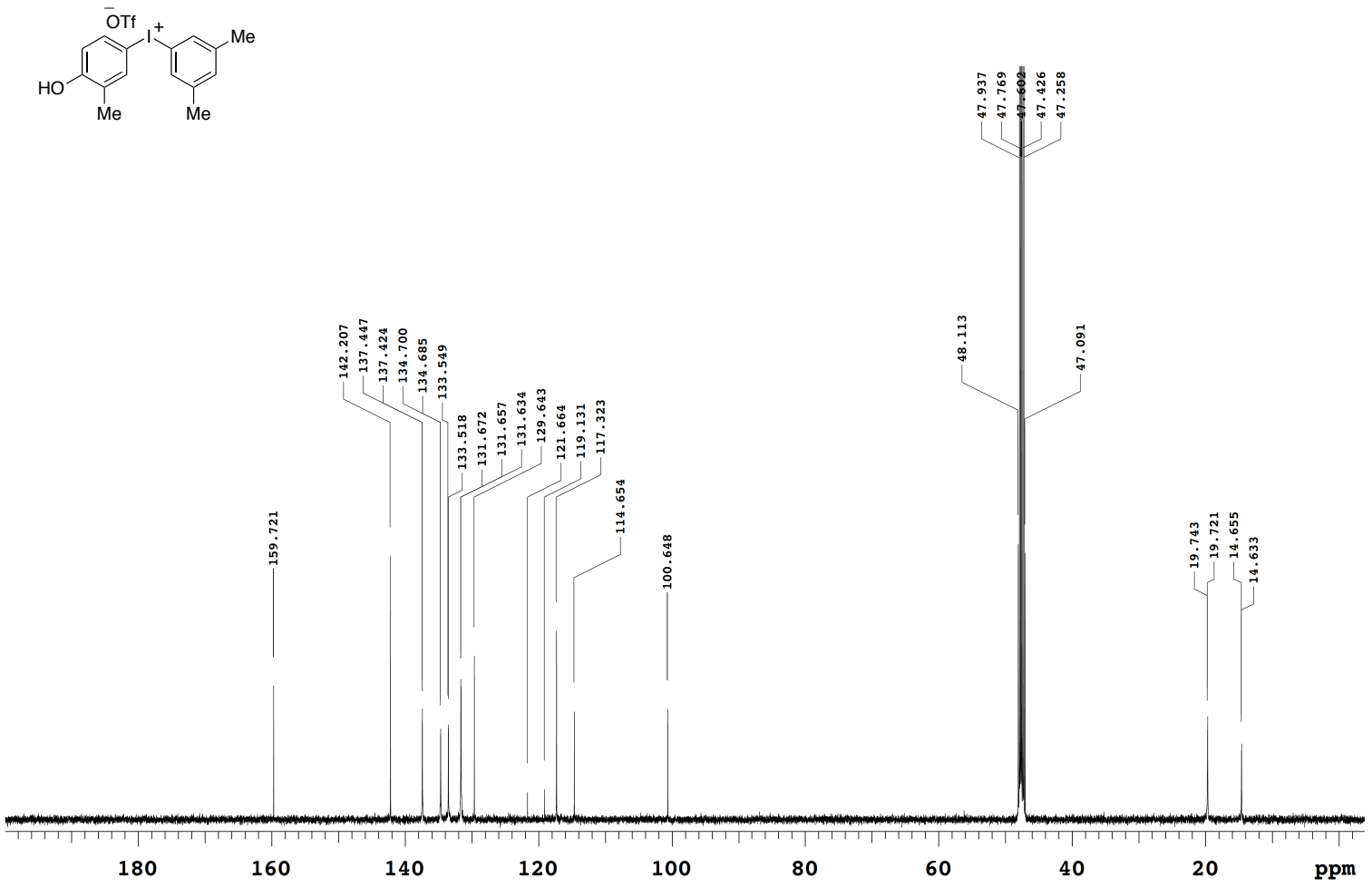


^{1}H NMR (500 MHz, CD_3OD)

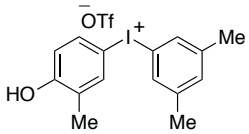


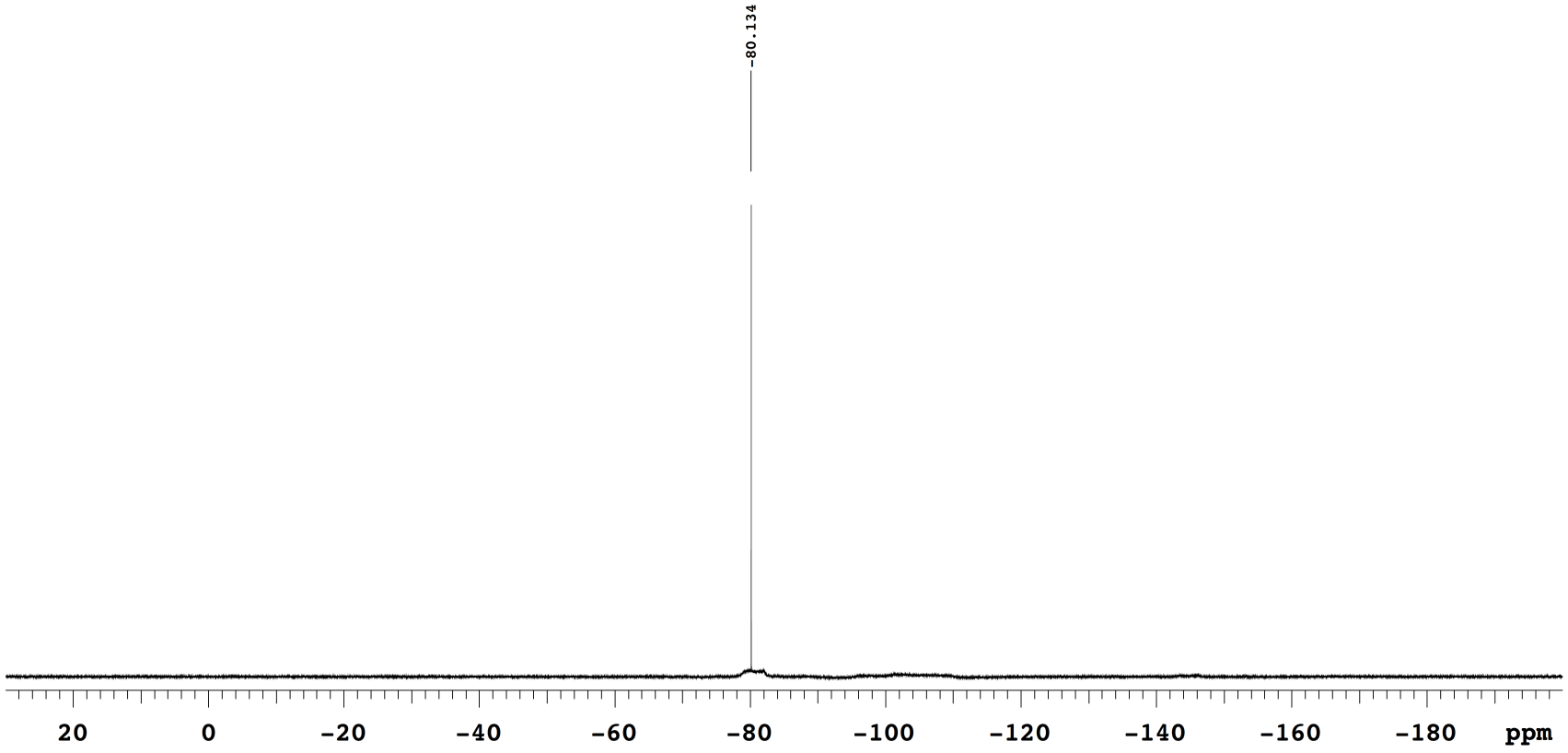


^{13}C NMR (125 MHz, CD_3OD)

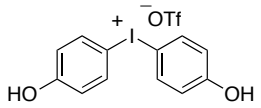


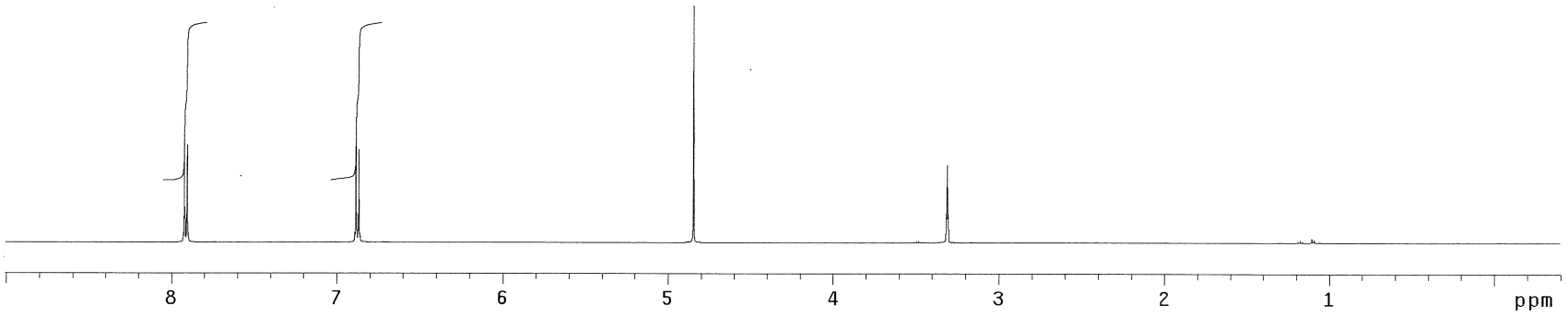
^{19}F NMR (470 MHz, CD_3OD)



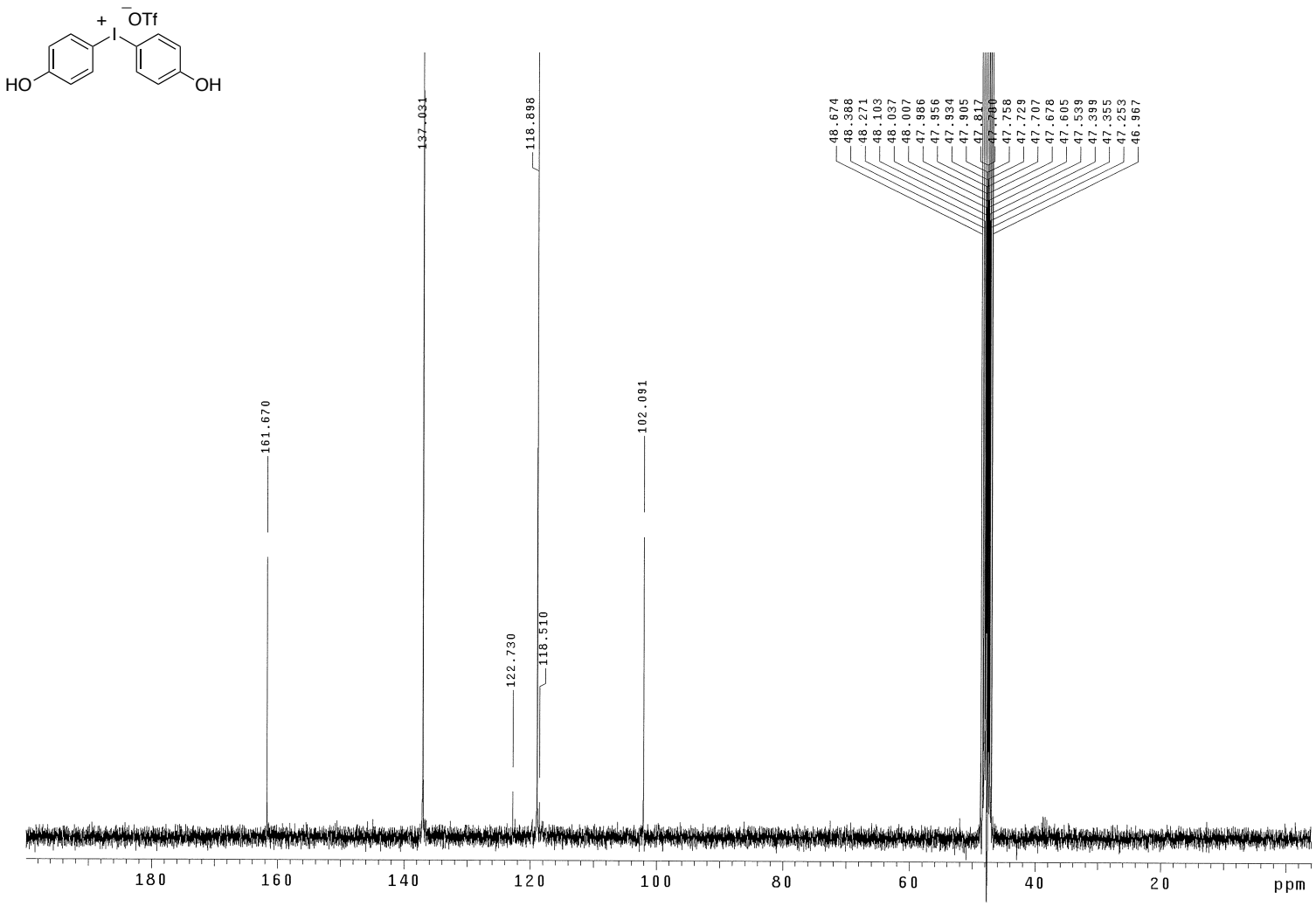


^{1}H NMR (500 MHz, CD_3OD)

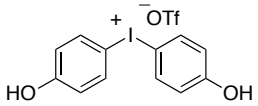


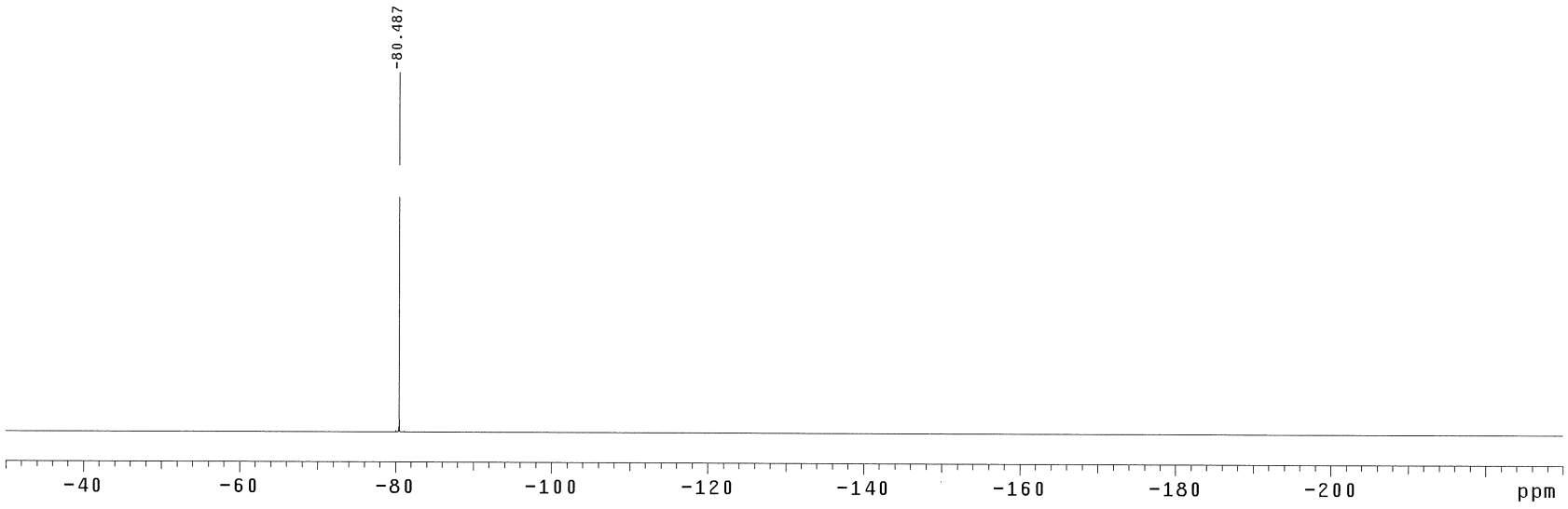


^{13}C NMR (75 MHz, CD_3OD)

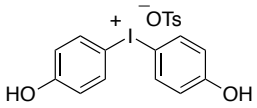


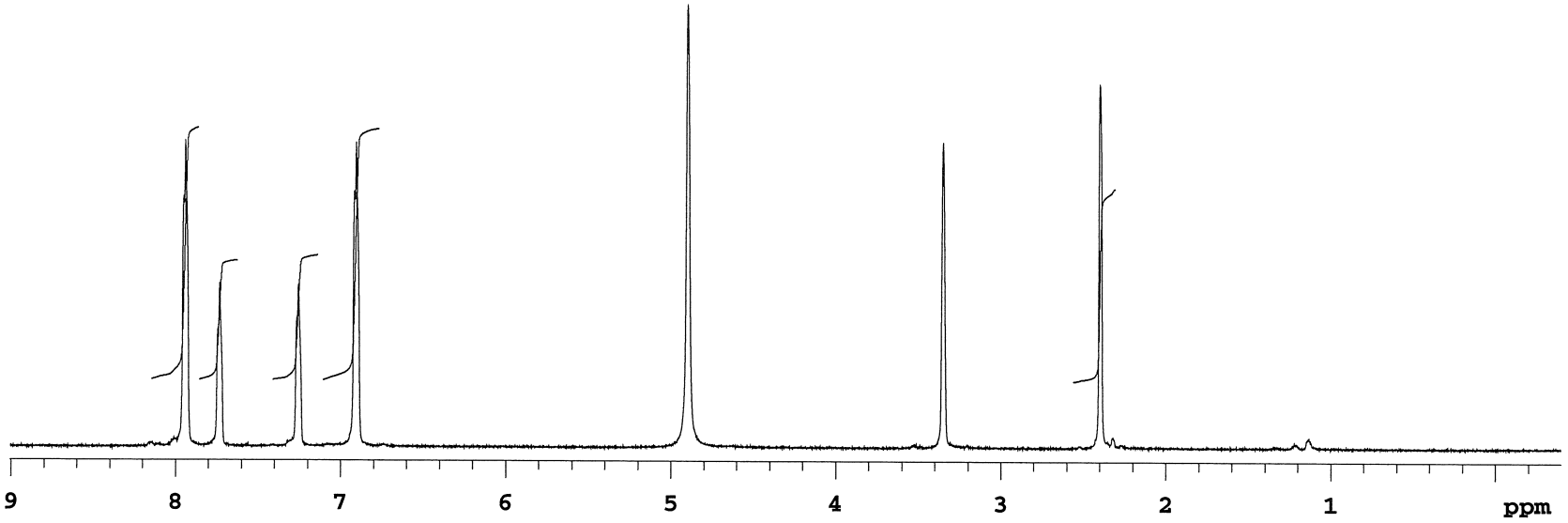
^{19}F NMR (282 MHz, CD_3OD)



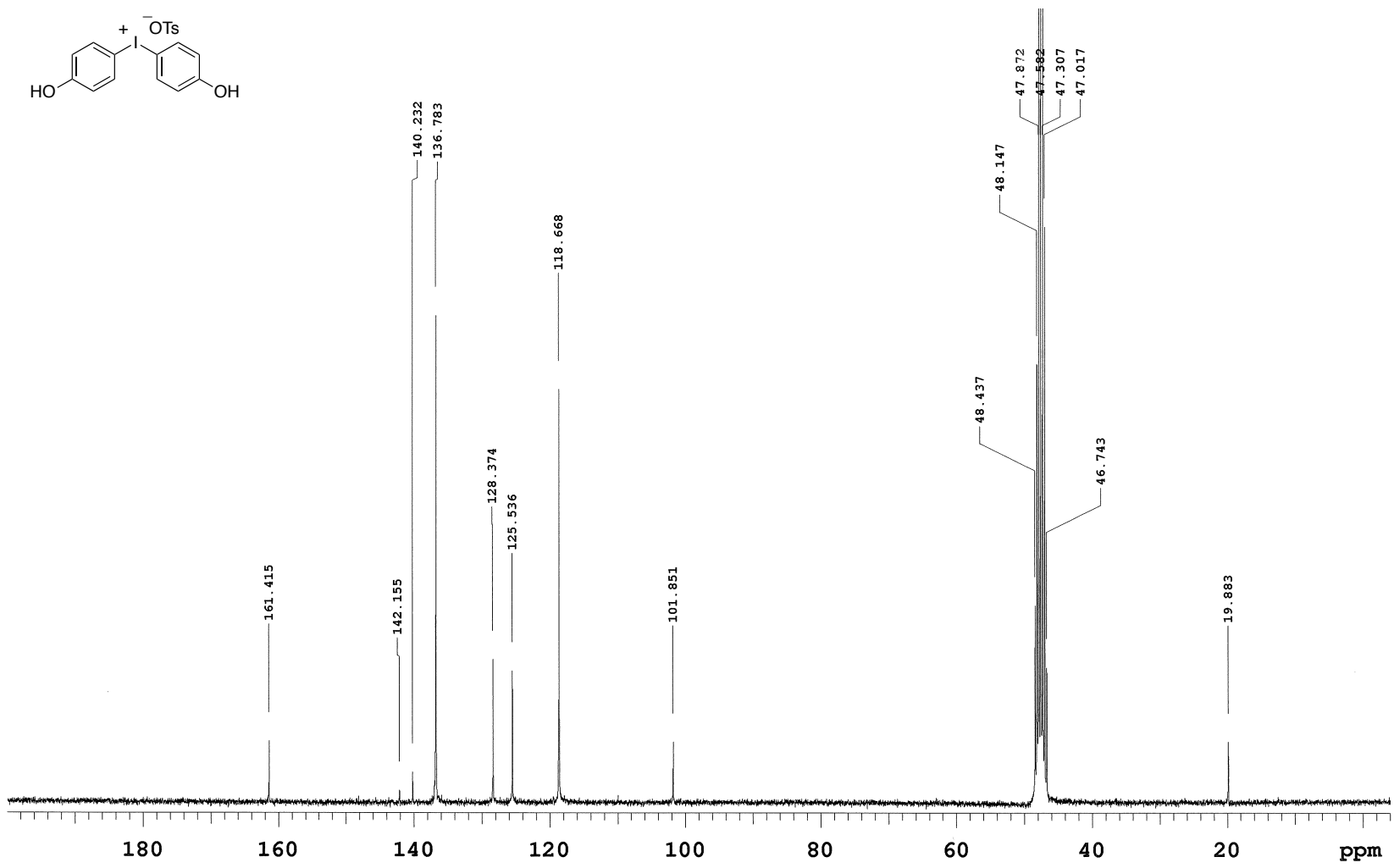


^{1}H NMR (500 MHz, CD_3OD)

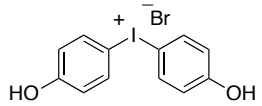




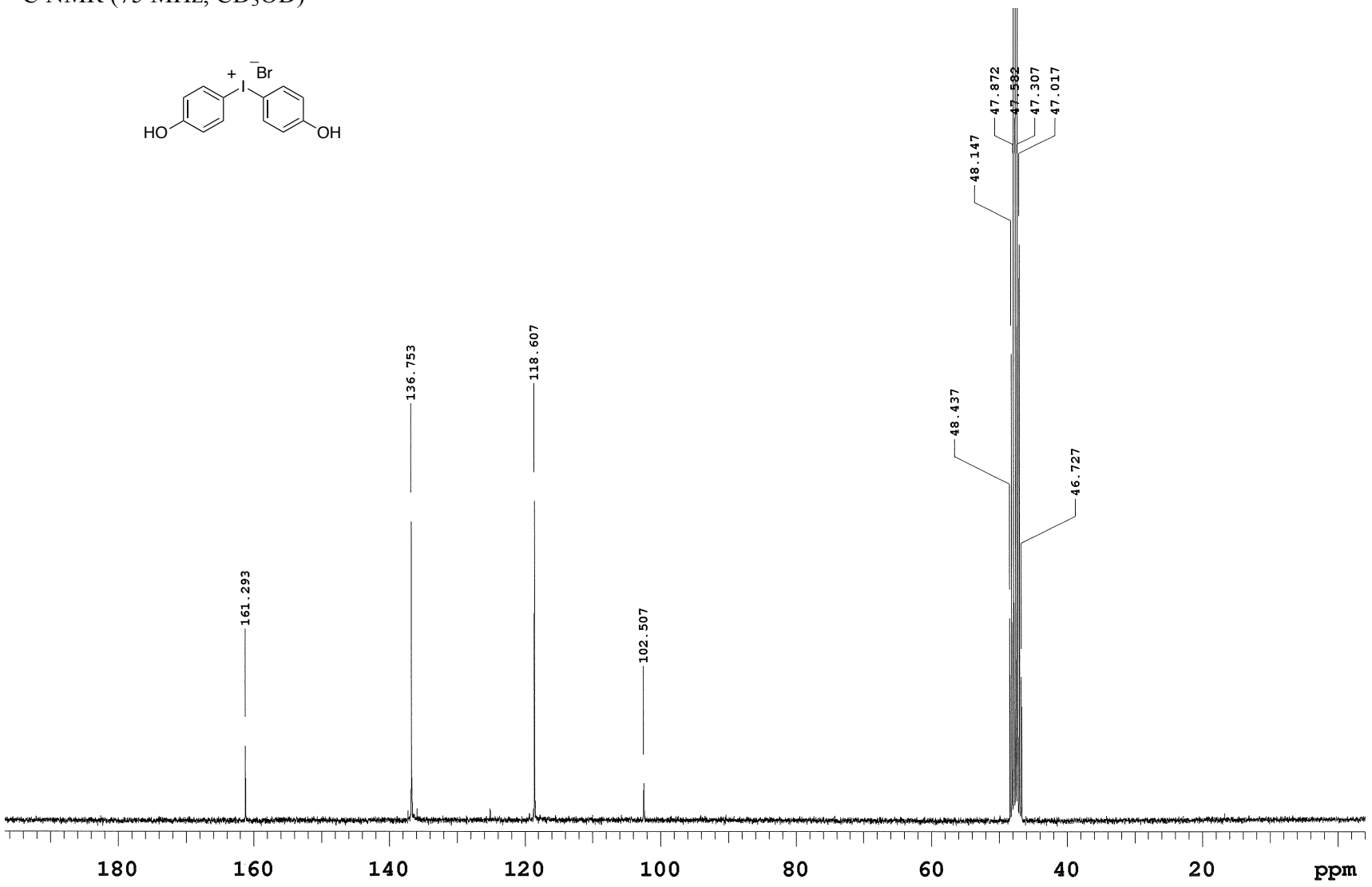
^{13}C NMR (75 MHz, CD_3OD)



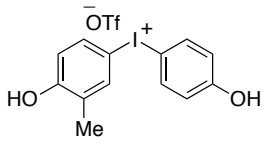
^{1}H NMR (500 MHz, CD_3OD)

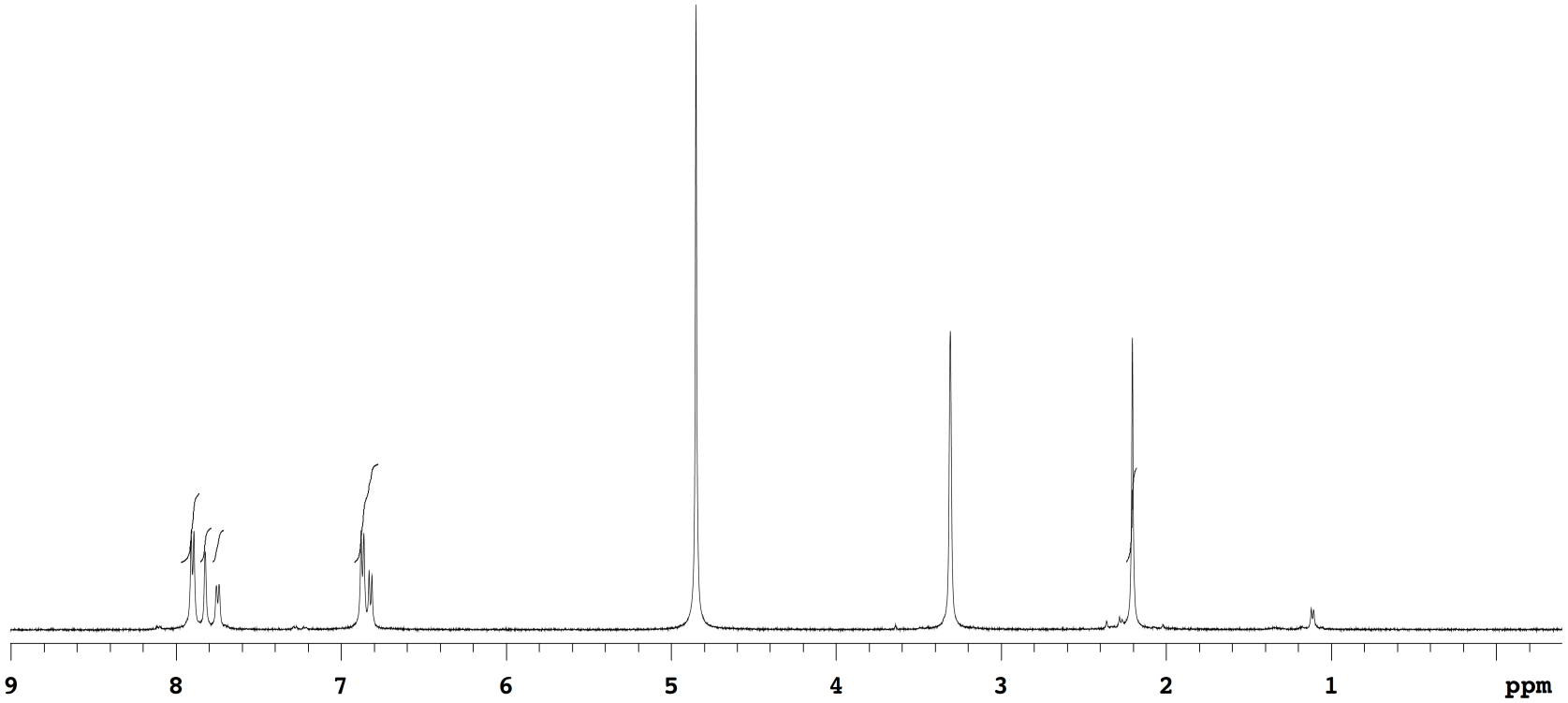


^{13}C NMR (75 MHz, CD_3OD)

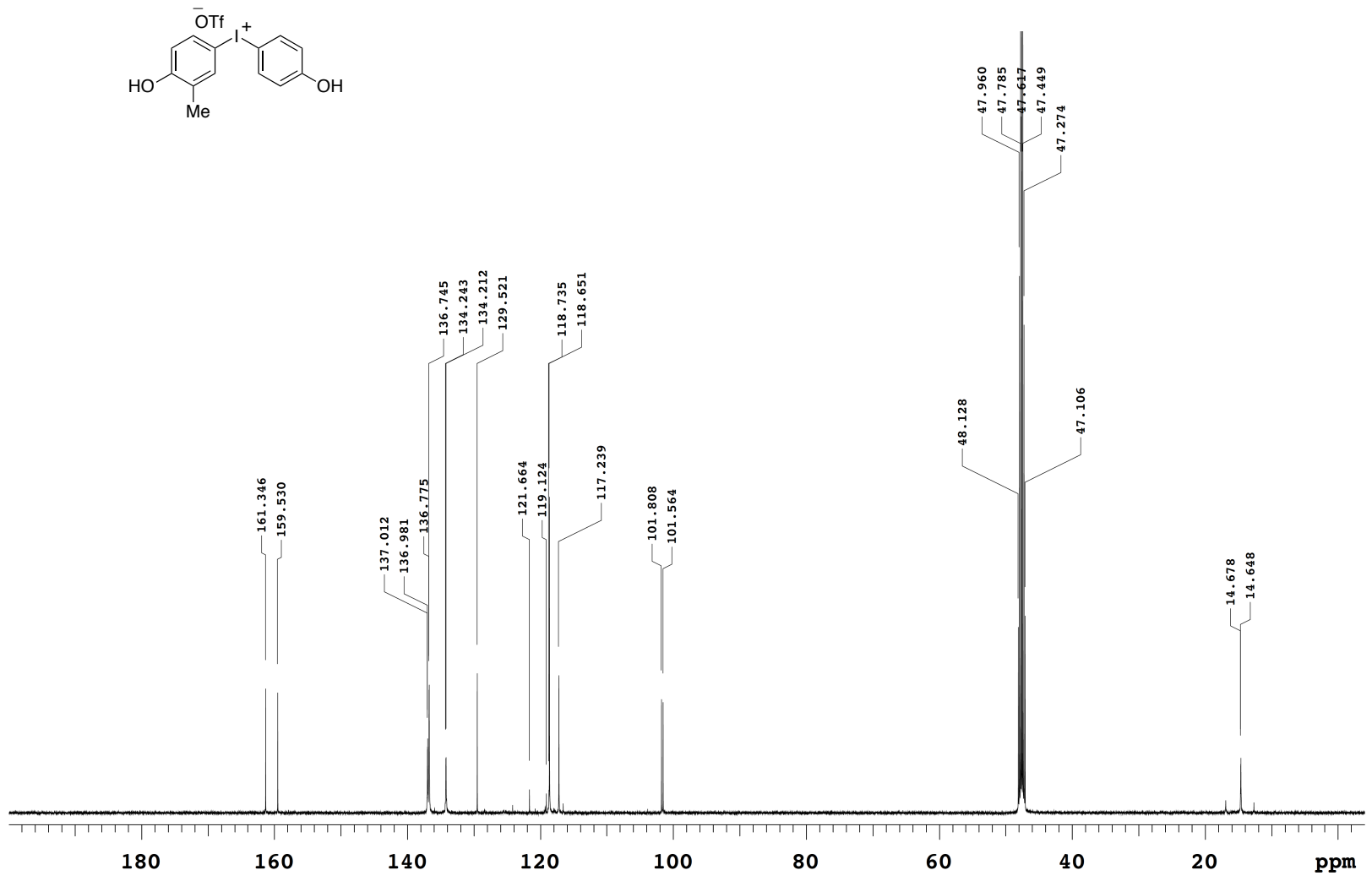


^{1}H NMR (500 MHz, CD_3OD)

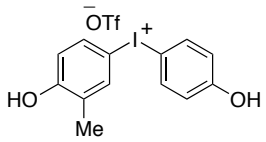


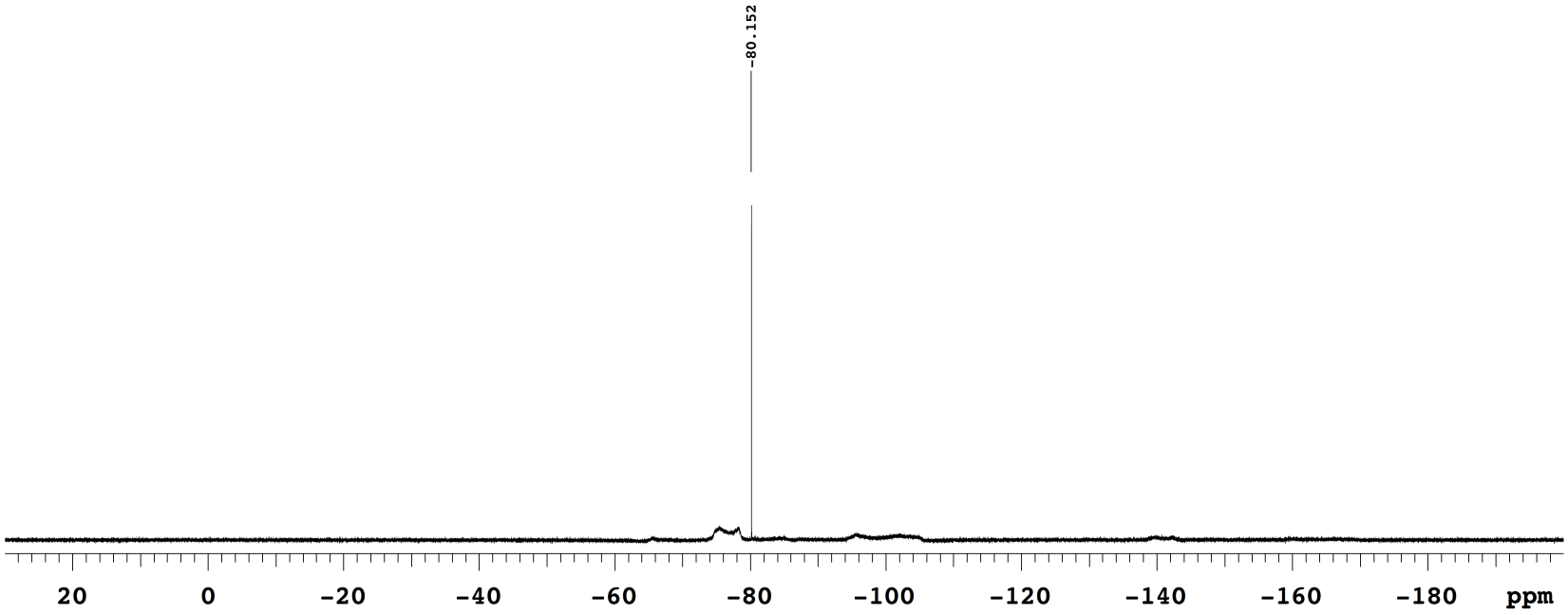


^{13}C NMR (125 MHz, CD_3OD)

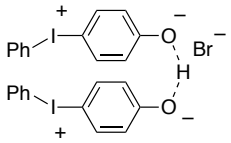


^{19}F NMR (470 MHz, CD_3OD)

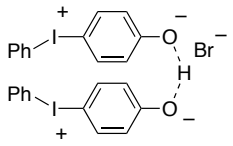


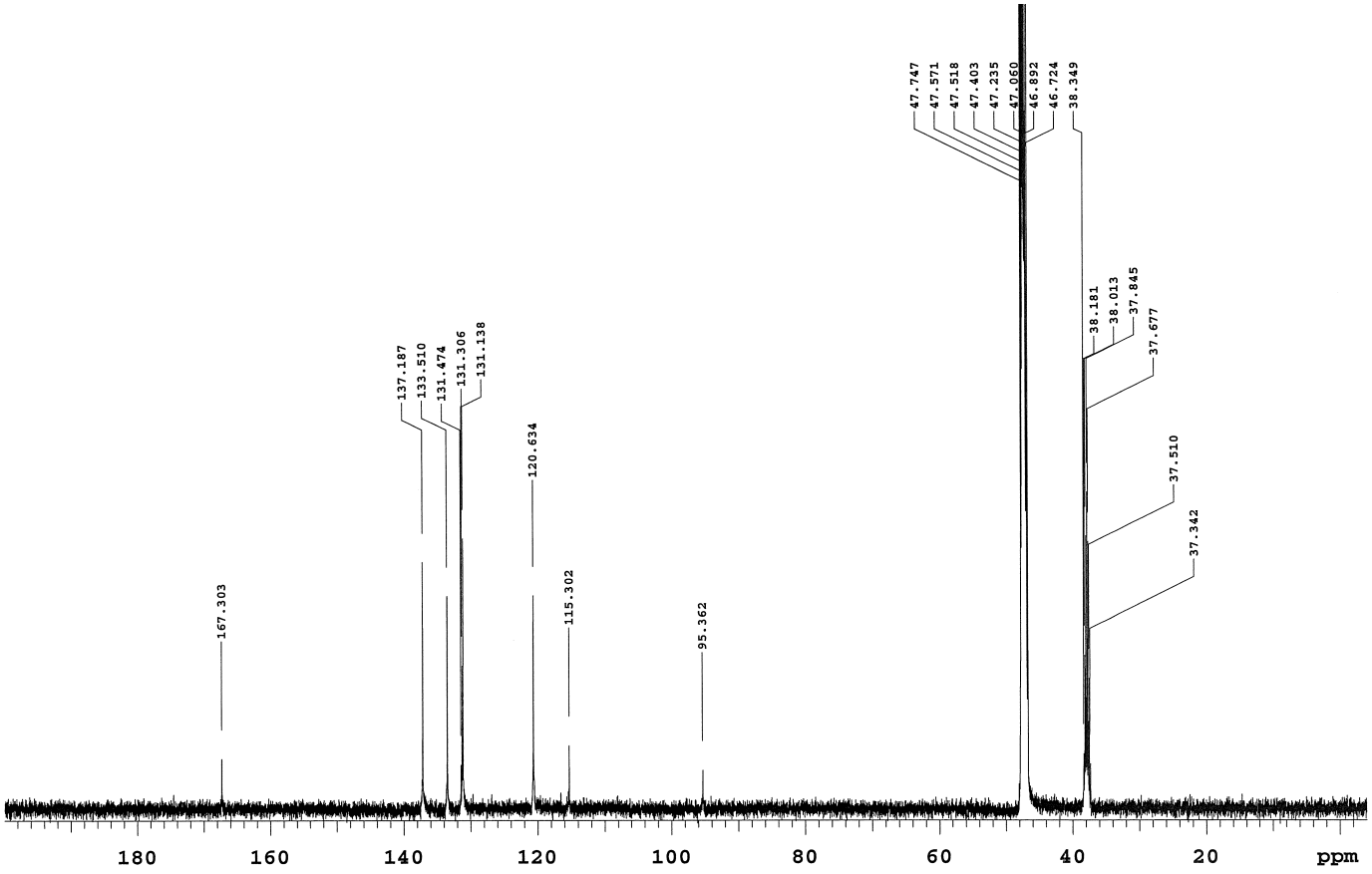


^{1}H NMR (500 MHz, CD_3OD)

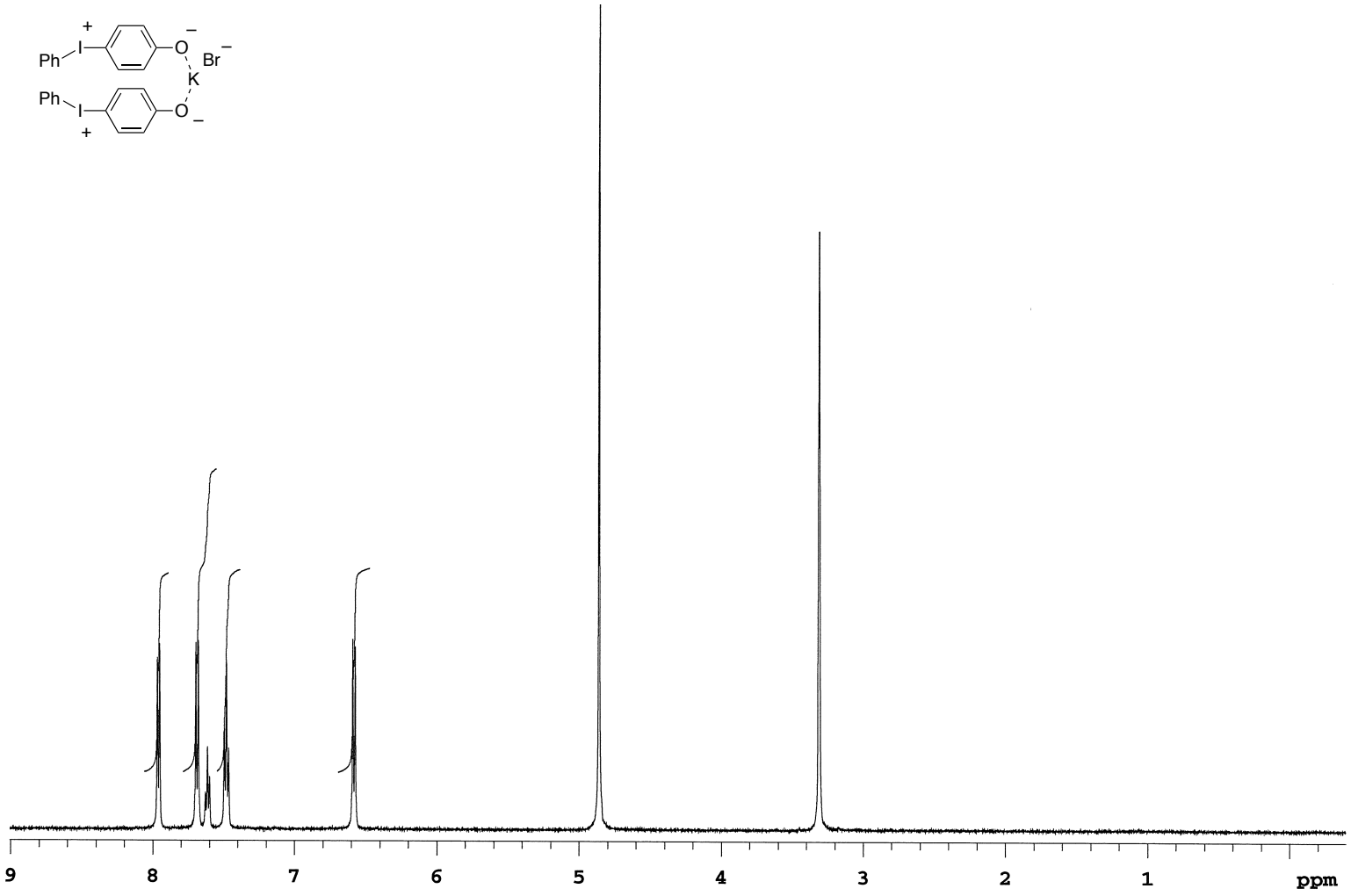


^{13}C NMR (125 MHz, CD_3OD-DMSO = 20:1)

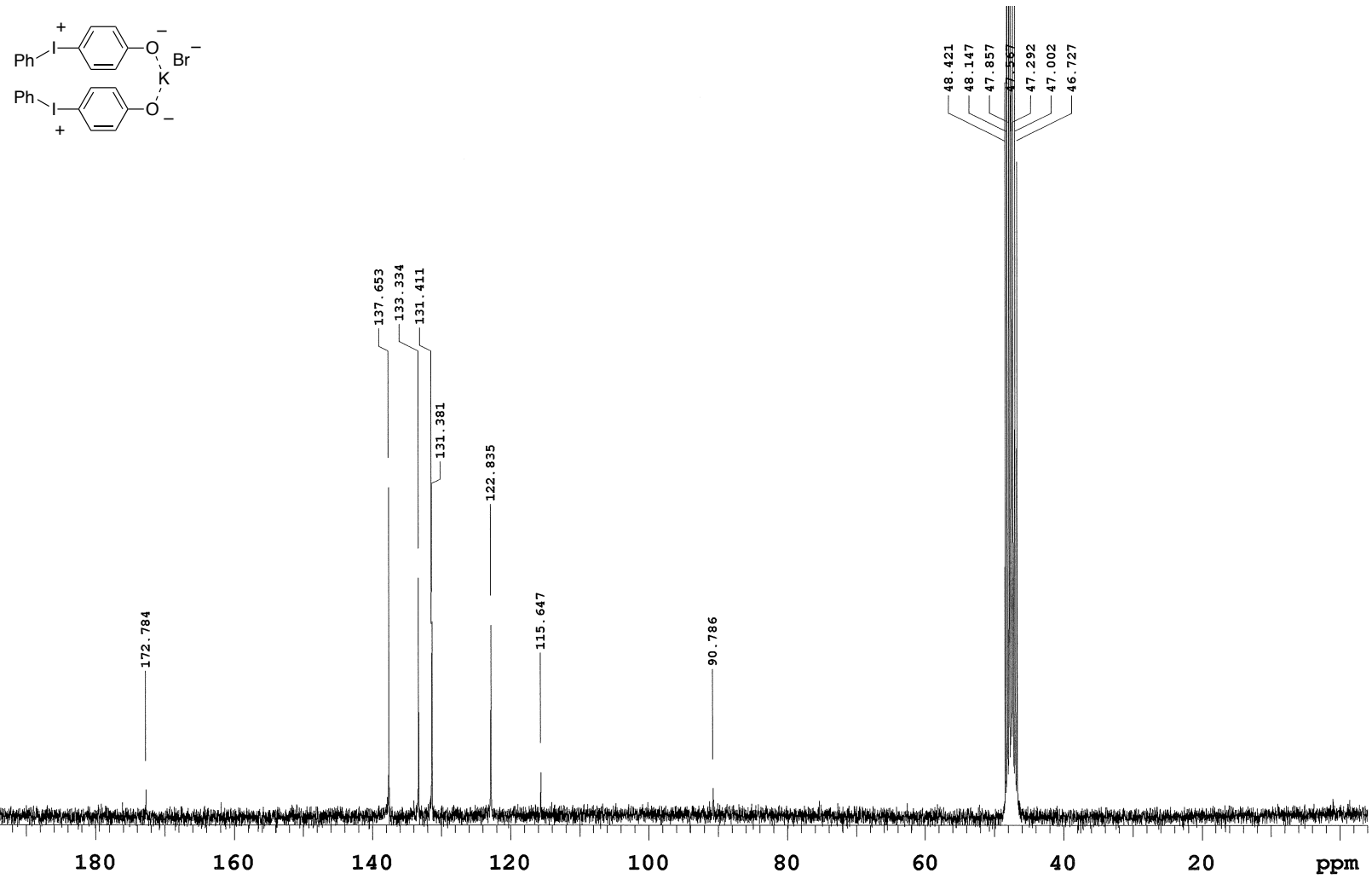




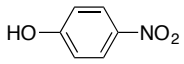
^{1}H NMR (500 MHz, CD_3OD)

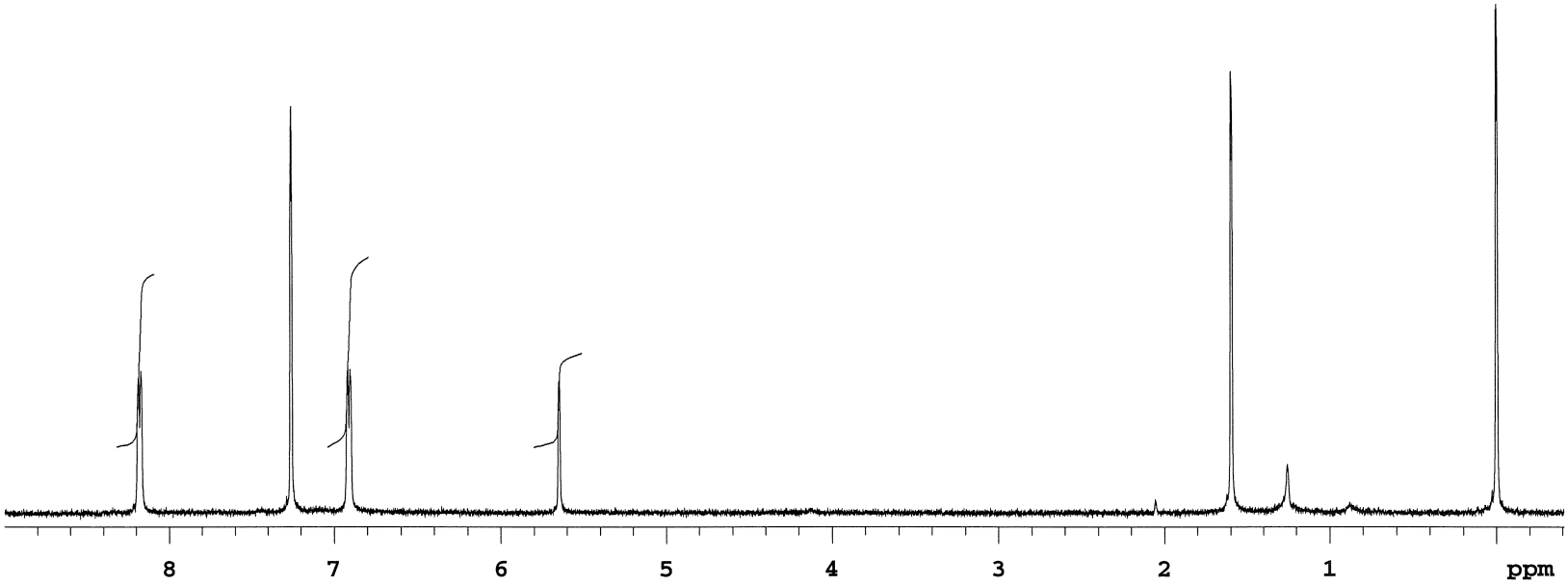


^{13}C NMR (75 MHz, CD_3OD)

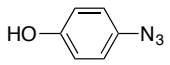


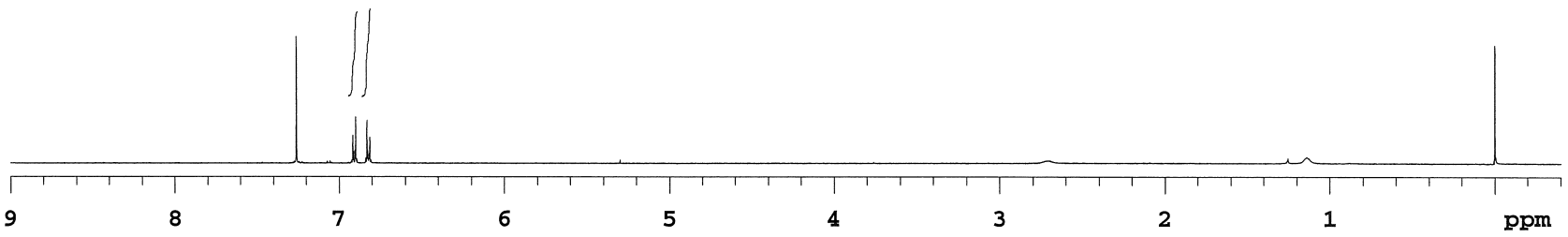
^{1}H NMR (500 MHz, $CDCl_3$)



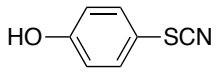


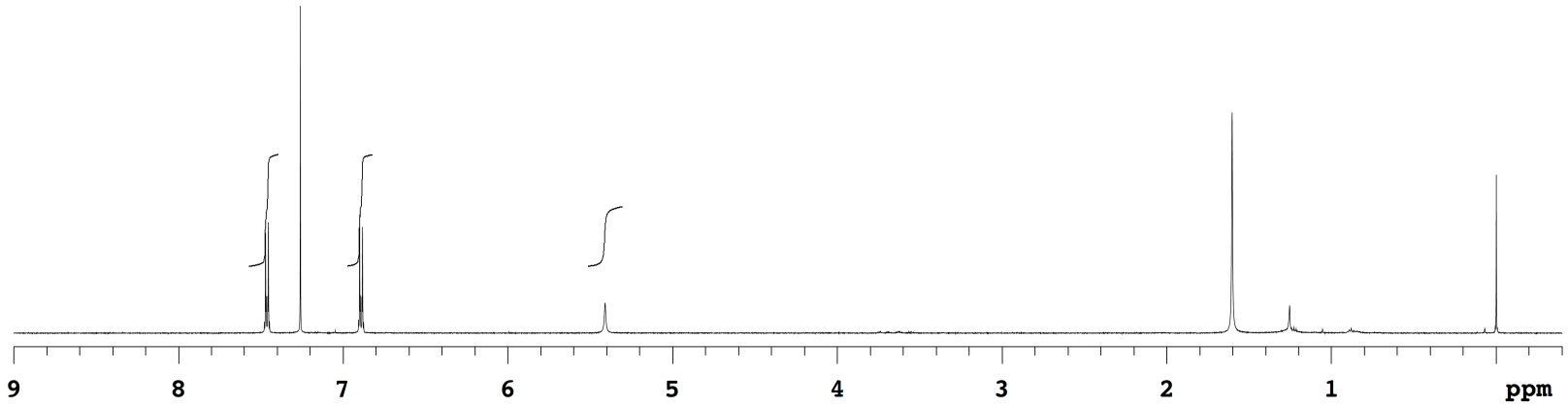
^{1}H NMR (500 MHz, $CDCl_3$)



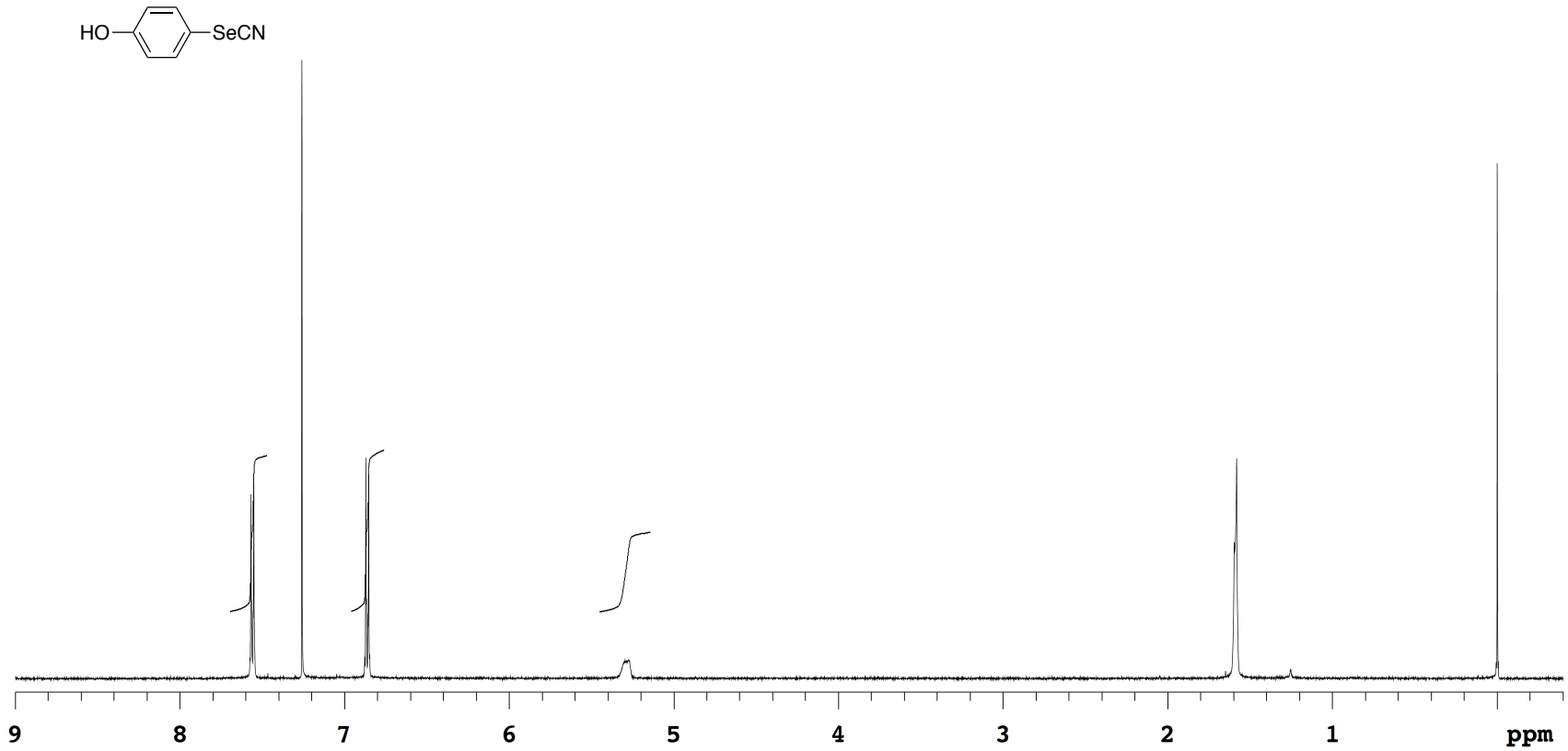


^{1}H NMR (500 MHz, $CDCl_3$)





^{1}H NMR (500 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)