

Supporting Information

GENERATION OF MONOARYL- λ^3 -IODANES FROM ARYL BORON COMPOUNDS THROUGH IPSO-SUBSTITUTION

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General information

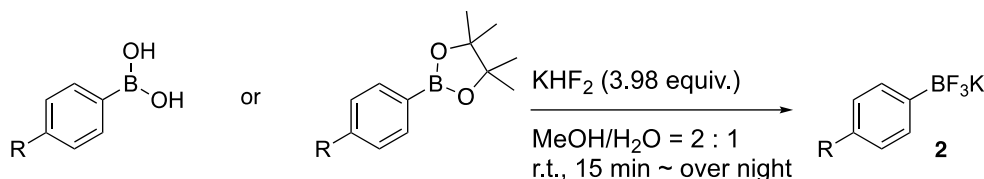
General: NMR spectra were recorded on JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for ¹H NMR and 98.52 MHz for ¹³C NMR, JOEL JNM-ECX400 spectrometers, operating at 395.88 MHz for ¹H NMR and 99.55 MHz for ¹³C NMR, and JNM-ECA500 spectrometers, operating at 500.16 MHz for ¹H NMR and 125.77 MHz for ¹³C NMR and 470.54 MHz for ¹⁹F NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ¹H NMR), CHCl₃ (7.26 ppm for ¹H NMR), (CH₃)₂SO (2.50 ppm for ¹H NMR), (CH₃)₂CO (2.05 ppm for ¹H NMR), CDCl₃ (77.0 ppm for ¹³C NMR), (CD₃)₂SO (39.52 ppm for ¹³C NMR), (CD₃)₂CO (29.84 ppm for ¹³C NMR), C₆F₆ (−164.9 ppm for ¹⁹F NMR), C₆H₅CF₃ (−63.7 ppm for ¹⁹F NMR) as an internal reference, respectively. ESI mass spectra were measured on JEOL JMS-T100LCP spectrometer. Silica gel column chromatography was performed with Kanto Silica gel 60 N (40-50 mesh). TLC analysis was carried out on Silicagel 70 F₂₅₄ TLC Plate-*Wako* with visualization by UV light, anisaldehyde stain solution, phosphomolybdic acid stain solution, or ceric ammonium molybdate stain solution. All non-aqueous reactions were carried out in a flame-dried glassware under argon atmosphere unless otherwise noted.

Materials: Propionitrile was distilled from P₂O₅ and then CaH₂, and stored over activated molecular sieves 4A under argon atmosphere before use. Dichloromethane (DCM), tetrahydrofuran (THF) was purified by Glass Contour solvent purification system. Commercially available *N,N*-dimethylformamide (DMF, KANTO Chemical Co., Inc., dehydrated grade), *N,N*-dimethylacetamide (DMA, KANTO Chemical Co., Inc., dehydrated grade), and 1,4-dioxane (Wako Ltd., Super dehydrated) were used without further manipulation unless otherwise stated. [I(OCOCF₃)₃]₂(OCOCF₃)NO^[1] was synthesized according to the literature. Meldrum's acid **3** was

synthesized according to the literature.^[2] Potassium aryltrifluoroborate derivatives **1**^[3], pinacol boronic ester **4a**^[4], neopentylglycol boronic ester **5a**^[5], MIDA boronate ester **7a**^[6], triol borate **8a**^[7] were synthesized according to the reported procedures. All other reagents were commercially available and used as received.

Preparation of substrates

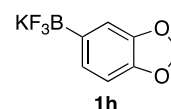
General procedure for synthesis of potassium aryltrifluoroborate derivatives **1** (GP1):^[3]



To a solution of a boronic acid or an aryl boronpinacol ester in MeOH (0.5 M) was added a solution of KHF₂ (3.98 equiv.) in H₂O (1.0 M) dropwise. The mixture was vigorously stirred at room temperature for 15 min to 12 hours. The solvent was removed, and the resulting white solids were dried completely under high vacuum at 50 °C. The residual solids were extracted with boiling acetone three times, and the combined extracts were concentrated. The residue was again dissolved in acetone or boiling acetone, and then treated with Et₂O to form white precipitates. The precipitates were filtered and dried under high vacuum at 50 °C to give the corresponding potassium aryltrifluoroborate.

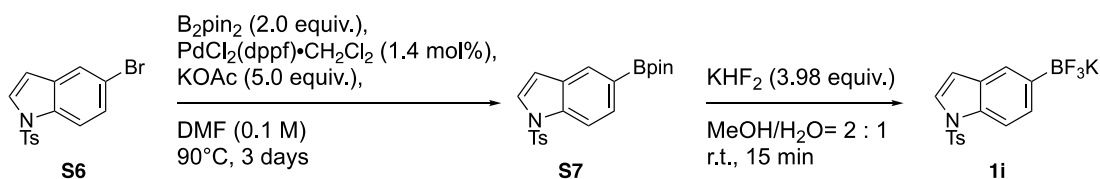
benzo[d][1,3]dioxol-5-yltrifluoro- λ^4 -borane, potassium salt (**1h**)

Prepared according to **GP1** from (3,4-methylenedioxyphenyl)boronic acid (332 mg, 2.0 mmol). Purification of the crude product by recrystallization from Et₂O/acetone afforded **1h** as a colorless solid (458 mg, quant).



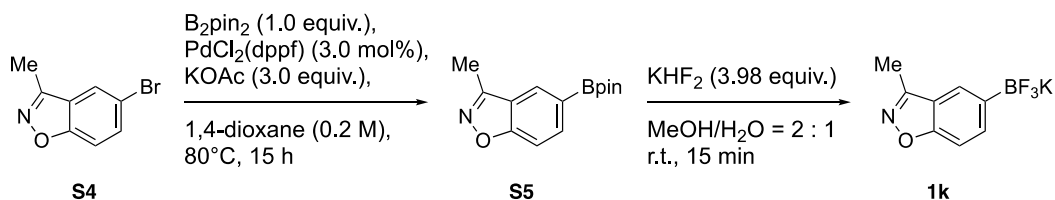
¹H NMR (500 MHz, DMSO-*d*₆) δ 6.80 (d, *J* = 7.5 Hz, 1H), 6.79 (s, 1H), 6.65 (d, *J* = 7.4 Hz, 1H) 5.82 (s, 2H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 145.7, 144.6, 123.9 (q, ³*J*_{C-F} = 1.9 Hz), 111.2 (q, ³*J*_{C-F} = 1.6 Hz), 106.9, 99.1; ¹⁹F NMR (400 MHz, DMSO-*d*₆) δ -140.9 (br s). HRMS (ESI): *m/z* (M-K⁺) calcd for C₇H₅O₂BF₃: 188.03765; found: 188.03742. IR (KBr): 3079, 2935, 1508, 1488, 1423, 1267, 1239, 1208, 1131, 1103, 980, 866, 813 cm⁻¹. Mp: over 200 °C.

1-tosyl-5-(trifluoro- λ^4 -boraneyl)-1*H*-indole, potassium salt (**1i**)



The transformation was performed based on the literature procedure.^[8] A 30 mL dry round-bottomed flask was charged with 5-bromo-1-tosyl-1*H*-indole **S6**^[9] (350 mg, 1.0 mmol), bis(pinacolato)diborane (508 mg, 2.0 mmol), PdCl₂(dppf)•CH₂Cl₂ (11.4 mg, 14 μmol) and potassium acetate (491 mg, 5.0 mmol). The reaction vessel was purged with Ar gas three times. To the vessel was added DMF (10.0 mL), and the mixture was stirred at 90 °C for 3 days. After cooling to room temperature, the mixture was diluted with EtOAc, washed with water and brine, and then dried over Na₂SO₄. Filtration and concentration *in vacuo* furnished the crude product, which was filtered through a silica gel column (*n*-hexane/EtOAc = 8:1) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF₂ according to **GP1**. Purification of the crude product by recrystallization from Et₂O/acetone afforded **1i** as a colorless solid (223 mg, 59% yield, 2 steps). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.80-7.70 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 3.4 Hz, 1H), 7.46 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 1H), 6.68 (d, *J* = 3.4 Hz, 1H), 2.29 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 145.0, 134.3, 133.0, 130.0, 129.5, 128.6 (q, ³*J*_{C-F} = 1.5 Hz), 126.5, 125.2, 123.8 (q, ³*J*_{C-F} = 1.7 Hz), 111.0, 110.1, 21.0; ¹⁹F NMR (400 MHz, DMSO-*d*₆) δ -140.9 (br s). HRMS (ESI): *m/z* (M-K⁺) calcd for C₁₅H₁₂O₂NBF₃S: 337.06757; found: 337.06823. IR (KBr): 3142, 1599, 1363, 1260, 1174, 1146, 1130, 996, 887, 818, 717, 671, 588 cm⁻¹. Mp: 191.2 °C (decomp.)

3-methyl-5-(trifluoro-λ⁴-boraneyl)benzo[*d*]isoxazole, potassium salt (**1k**)

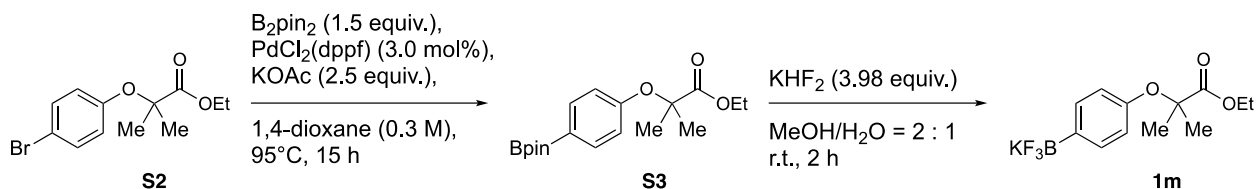


The transformation was performed based on the literature procedure.^[10] A 30 mL dry round-bottomed flask was charged with 5-bromo-3-methylbenzo[*d*]isoxazole **S4**^[10] (304 mg, 1.4 mmol), bis(pinacolato)diborane (726 mg, 2.9 mmol), PdCl₂(dppf) (31.4 mg, 43 μmol) and potassium acetate (422 mg, 4.3 mmol). The reaction vessel was purged with Ar gas three times. To the vessel was added 1,4-dioxane (7.2 mL), and the mixture was stirred at 80 °C for 15 hours. After cooling to room temperature, the mixture was diluted with CH₂Cl₂, washed with water and brine, and then dried over Na₂SO₄. Filtration and concentration *in vacuo* furnished the crude product, which was filtered through a silica gel column (*n*-hexane/EtOAc = 20:1 to 10:1) to remove inorganic compounds. The solvent was evaporated under reduced pressure and the residue was treated with KHF₂ according to **GP1**. Purification of the crude product by recrystallization from Et₂O/acetone afforded **1k** as a colorless solid (134.1 mg, 37% yield, 2 steps).

¹H NMR (400 MHz, acetone-*d*₆) δ 7.75 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 2.50 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 161.3, 154.6, 133.9 (q, ³*J*_{C-F} = 1.4 Hz), 123.2 (q, ³*J*_{C-}

$F = 1.8$ Hz), 120.7, 106.9, 9.6; ^{19}F NMR (400 MHz, $\text{DMSO-}d_6$) δ -140.8 (br s). HRMS (ESI): m/z (M-K^+) calcd for $\text{C}_8\text{H}_6\text{ONBF}_3$: 199.05363; found: 199.05372. IR (KBr): 3047, 1614, 1446, 1303, 1203, 1078, 970, 897, 823, 776, 739, 588 cm^{-1} . Mp: over 200 $^\circ\text{C}$.

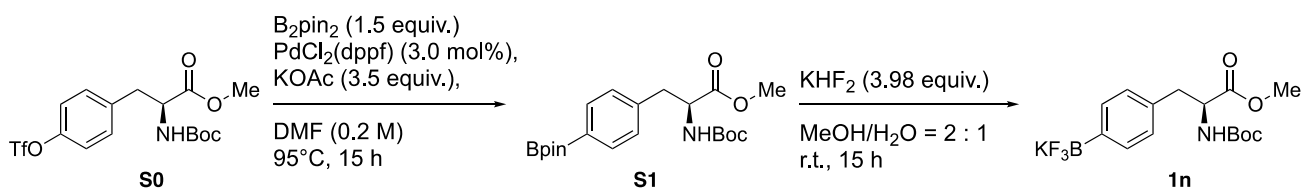
ethyl 2-methyl-2-(4-(trifluoro- λ^4 -boraneyl)phenoxy)propanoate, potassium salt (**1m**)



The transformation was performed based on the literature procedure.^[11] A 30 mL dry round-bottomed flask was charged with ethyl 2-(4-bromophenoxy)-2-methylpropanoate **S2**^[12] (504 mg, 1.8 mmol), bis(pinacolato)diborane (668 mg, 2.6 mmol), $\text{PdCl}_2(\text{dppf})$ (38.4 mg, 52 μmol) and potassium acetate (429 mg, 4.4 mmol). The reaction vessel was purged with Ar gas three times. To the vessel was added 1,4-dioxane (6.0 mL), and the mixture was stirred at 95°C for 15 hours. After cooling to room temperature, the mixture was diluted with EtOAc, washed with water and brine, and then dried over Na_2SO_4 . Filtration and concentration *in vacuo* furnished the crude product, which was filtered through a silica gel column (*n*-hexane/EtOAc = 1:1) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF_2 according to **GP1**. Purification of the crude product by recrystallization from Et_2O /acetone afforded **1m** as a colorless solid (320 mg, 67% yield, 2 steps).

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.17 (d, $J = 8.3$ Hz, 2H), 6.54 (d, $J = 7.9$ Hz, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 1.45 (s, 6H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 173.7, 152.7, 132.0 (q, $^3J_{\text{C-F}} = 1.6$ Hz), 117.5, 78.1, 60.7, 25.1, 13.9; ^{19}F NMR (400 MHz, $\text{DMSO-}d_6$) δ -140.9 (br s). HRMS (ESI): m/z (M-2F+2(OMe)-K^+) calcd for $\text{C}_{14}\text{H}_{21}\text{BFO}_5$: 299.14716; found: 299.14715. IR(KBr): 2994, 1732, 1599, 1274, 1205, 1151, 960, 832 cm^{-1} . Mp: 101.9-103.0 $^\circ\text{C}$

methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(trifluoro- λ^4 -boraneyl)phenyl)propanoate, potassium salt (**1n**)

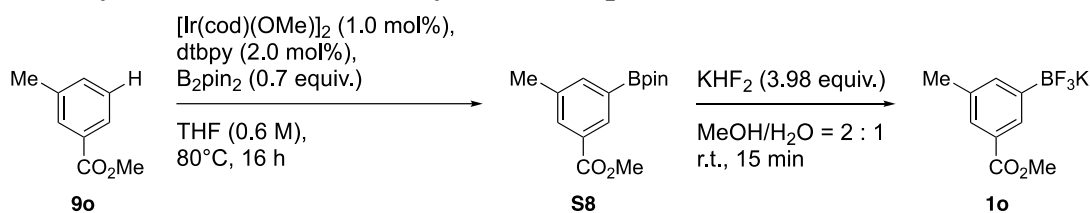


The transformation was performed based on the literature procedure.^[13] A 50 mL dry round-bottomed flask was charged with methyl *N*-(tert-butoxycarbonyl)-*O*-[(trifluoromethyl)sulfonyl]-*L*-tyrosinate

S0^[14] (1.17 g, 2.7 mmol), bis(pinacolato)diborane (1.05 g, 4.1 mmol), PdCl₂(dppf) (60.1 mg, 82 μmol) and potassium acetate (1.31 g, 13 mmol). The reaction vessel was purged with Ar gas three times. To the vessel was added DMF (14.0 mL), and the mixture was stirred at 95 °C for 16 hours. After cooling to room temperature, the mixture was diluted with EtOAc, washed with water and brine, and then dried over Na₂SO₄. Filtration and concentration *in vacuo* furnished the crude product, which was filtered through a silica gel column (*n*-hexane/EtOAc = 1:1) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF₂ according to **GP1**. Purification of the crude product by recrystallization from Et₂O/acetone afforded **1n** as a colorless solid (728 mg, 69% yield, 2 steps).

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.23 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 2H) 4.14-4.07 (m, 1H), 3.60 (s, 3H), 2.87 (dd, *J* = 13.7, 5.3 Hz, 1H) 2.77 (dd, *J* = 13.7, 9.6 Hz, 1H), 1.34 (s, 9H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 172.9, 155.3, 133.5, 131.3 (q, ³*J*_{C-F} = 1.7 Hz), 126.9, 78.2, 55.5, 51.6, 36.5, 28.1; ¹⁹F NMR (400 MHz, DMSO-*d*₆) δ -141.2 (br s). HRMS (ESI): *m/z* (M-K⁺) calcd for C₁₅H₂₀O₄NBF₃: 345.14793; found: 345.14837. IR (KBr): 3398, 2978, 1748, 1668, 1508, 1229, 1194, 1167, 1003, 975, 814 cm⁻¹. Mp: 167.8-168.2 °C.

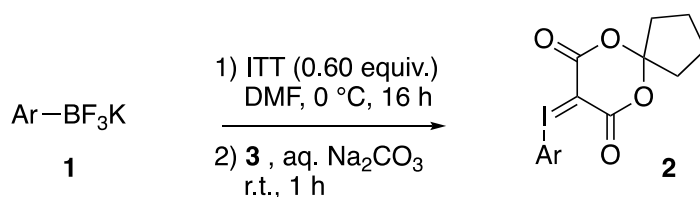
methyl 3-methyl-5-(trifluoro-λ⁴-boranonyl)benzoate, potassium salt (**1o**)



The transformation was performed based on the literature procedure.^[15] In a glovebox, a sealed tube was charged with methyl 3-methylbenzoate **9o** (300 mg, 2.0 mmol), [Ir(cod)(OMe)₂] (1.33 mg, 2.0 μmol), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (1.1 mg, 4.1 μmol), bis(pinacolato)diborane (356 mg, 1.4 mmol) and THF (3.0 ml). The mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the crude product was filtered through silica gel column (EtOAc) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF₂ according to **GP1**. Purification of the crude product by recrystallization from Et₂O/acetone afforded **1o** as a colorless solid (243.7 mg, 48% yield, 2 steps).

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.79 (s, 1H), 7.48 (s, 1H), 7.40 (s, 1H), 3.80 (s, 3H), 2.28 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 167.6, 137.4 (q, ³*J*_{C-F} = 1.6 Hz), 135.1, 129.7 (q, ³*J*_{C-F} = 1.7 Hz), 127.5, 126.5, 51.5, 21.0; ¹⁹F NMR (400 MHz, DMSO-*d*₆) δ -141.9 (br s). HRMS (ESI): *m/z* (M-K⁺) calcd for C₉H₉O₂BF₃: 216.06895; found: 216.06919. IR(KBr): 3142, 1727, 1317, 1216, 965, 763 cm⁻¹. Mp: over 200 °C.

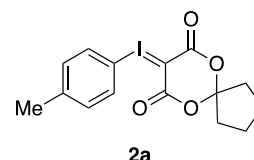
General procedure for synthesis of iodonium ylide (GP2):



To a solution of [I(OCOCF₃)₃]₂(OCOCF₃)NO (193.5 mg, 0.18 mmol) in DMF (1.5 mL) was added potassium aryltrifluoroborate **1** (0.30 mmol) in DMF (1.5 mL) at -20 °C. The reaction mixture was stirred at 0 °C for 16 h. After the mixture was cooled to -10 °C [when the reaction temperature was different, the temperature was set to the reaction temperature - 10 °C], a solution of 6,10-dioxaspiro[4.5]decane-7,9-dione **3** (102 mg, 0.60 mmol) in Na₂CO₃ aq. (15% w/v, 3.0 mL) was added. The pH of the reaction mixture was tested and adjusted with Na₂CO₃ until the pH > 10. [We confirmed that the use of excess aqueous Na₂CO₃ solution did not show any deleterious effects.] The reaction mixture was then stirred at room temperature for 1 h. The reaction mixture was diluted with EtOAc and the organic layer was successively washed with sat. NaHCO₃ aq., water (three times), and brine, and then dried over anhydrous Na₂SO₄. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1), or recrystallization from CH₂Cl₂/hexane to afford the corresponding iodonium ylide **2**.

8-(p-tolyl-λ³-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2a**)

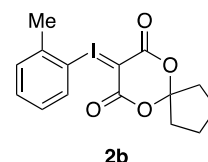
Prepared according to **GP2** from potassium (4-methylphenyl)trifluoroborate **1a**.^[3c] Purification of the crude product by recrystallization from CH₂Cl₂/hexane afforded **2a** as a colorless solid (85.7 mg, 74% yield).



¹H NMR (400 MHz, DMSO-*d*₆) δ 7.69-7.63 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H), 2.01-1.93 (m, 4H), 1.71-1.62 (m, 4H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.5, 140.7, 132.5, 131.5, 112.7, 112.1, 58.6, 36.7, 22.7, 20.7. HRMS (ESI): *m/z* (M+Na⁺) calcd for C₁₅H₁₅IO₄Na: 408.99072; found: 408.99135. IR (KBr): 2962, 1689, 1641, 1609, 1338, 1284, 1104, 758 cm⁻¹. Mp: 92.5 °C (decomp.).

8-(o-tolyl-λ³-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2b**)

Prepared according to **GP2** from potassium (2-methylphenyl)trifluoroborate **1b**.^[3c] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2b** as a colorless solid (66.0 mg, 57% yield).

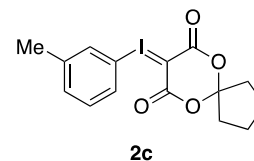


¹H NMR (400 MHz, CDCl₃) δ 7.88 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.47 (td, *J* = 7.4, 1.1 Hz, 1H), 7.38 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.22 (td, *J* = 7.7, 1.2 Hz, 1H), 2.67 (s, 3H), 2.23-2.07 (m, 4H), 1.87-1.73 (m, 4H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 163.5, 139.9, 136.1, 131.6, 130.5, 128.3, 122.3, 112.0, 59.0, 36.7,

24.9, 22.7. HRMS (ESI): m/z ($M+Na^+$) calcd for $C_{15}H_{15}IO_4Na$: 408.99072; found: 408.99138. IR (KBr): 2956, 2866, 1685, 1647, 1461, 1343, 1274, 1205, 1098, 763 cm^{-1} . Mp: 90.3 °C (decomp.).

8-(*m*-tolyl- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2c**)

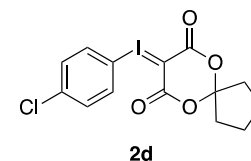
Prepared according to **GP2** from potassium (3-methylphenyl)trifluoroborate **1c**.^[16] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2c** as a colorless solid (82.3 mg, 71% yield).



1H NMR (400 MHz, $DMSO-d_6$) δ 7.66-7.51 (m, 2H), 7.41-7.29 (m, 2H), 2.32 (s, 3H), 2.04-1.90 (m, 4H), 1.74-1.62 (m, 4H); ^{13}C NMR (125 MHz, $DMSO-d_6$) δ 163.5, 140.7, 132.5, 131.3, 130.7, 129.5, 116.2, 112.1, 58.4, 36.8, 22.7, 20.8. HRMS (ESI): m/z ($M+Na^+$) calcd for $C_{15}H_{15}IO_4Na$: 408.99072; found: 408.99162. IR (KBr): 2967, 1748, 1685, 1588, 1471, 1338, 1280, 1195, 1098, 763, 683 cm^{-1} . Mp: 83.5 °C (decomp.).

8-((4-chlorophenyl)- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2d**)

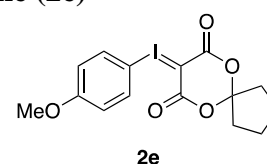
Prepared according to **GP2** from potassium (4-chlorophenyl)trifluoroborate **1d**.^[17] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2d** as a pale brown solid (80.5 mg, 66% yield).



1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.78 (m, 2H), 7.44-7.34 (m, 2H), 2.20-2.06 (m, 4H), 1.85-1.73 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 139.4, 134.9, 132.3, 114.4, 111.0, 57.4, 37.5, 23.5. The 1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

8-((4-methoxyphenyl)- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2e**)

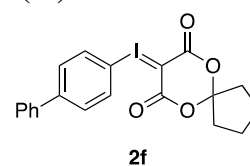
Prepared according to **GP2** from potassium (4-methoxyphenyl)trifluoroborate **1e**.^[16] Purification of the crude product by recrystallization CH_2Cl_2 /hexane afforded **2e** as a colorless solid (62.7 mg, 52% yield).



1H NMR (500 MHz, $CDCl_3$) δ 7.91-7.82 (m, 2H), 6.95-6.88 (m, 2H), 3.84 (s, 3H), 2.19-2.08 (m, 4H), 1.84-1.73 (m, 4H); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 163.5, 161.1, 134.6, 116.6, 112.0, 105.6, 59.2, 55.5, 36.7, 22.7. The 1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

8-([1,1'-biphenyl]-4-yl- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2f**)

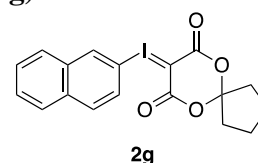
Prepared according to **GP2** [$-20\text{ }^\circ\text{C}$ instead of $0\text{ }^\circ\text{C}$] from potassium (4-biphenyl)trifluoroborate **1f**.^[16] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2f** as a colorless solid (99.5 mg, 74% yield).



^1H NMR (400 MHz, CDCl_3) δ 7.98-7.92 (m, 2H), 7.64-7.59 (m, 2H), 7.57-7.52 (m, 2H), 7.51-7.45 (m, 2H), 7.45-7.40 (m, 1H), 2.21-2.14 (m, 4H), 1.83-1.77 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.4, 145.8, 138.9, 134.2, 130.7, 129.3, 128.9, 127.4, 114.3, 112.2, 57.2, 37.6, 23.5. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

8-(naphthalen-2-yl- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2g**)

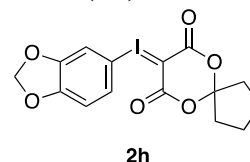
Prepared according to **GP2** from Potassium 2-naphthyltrifluoroborate **1g**.^[16] Purification of the crude product by recrystallization from CH_2Cl_2 /hexane afforded **2g** as a pale orange solid (72.2 mg, 57% yield).



^1H NMR (400 MHz, CDCl_3) δ 8.42 (s, 1H), 7.94-7.79 (m, 4H), 7.69-7.57 (m, 2H), 2.20-2.12 (m, 4H), 1.86-1.72 (m, 4H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 163.6, 133.6, 133.1, 132.8, 130.6, 128.5, 128.1, 127.9, 127.9, 127.5, 113.5, 112.2, 58.9, 36.8, 22.7. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

8-(benzo[d][1,3]dioxol-5-yl- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2h**)

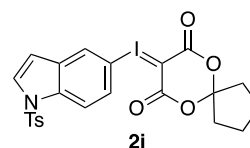
Prepared according to **GP2** [ITT (0.53 equiv.)] from potassium (3,4-methylenedioxyphenyl)trifluoroborate **1h**.^[16] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2h** as a colorless solid (68.7 mg, 55% yield).



^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 8.2, 2.1$ Hz, 1H), 7.39 (d, $J = 2.1$ Hz, 1H), 6.83 (d, $J = 8.2$ Hz, 1H), 6.08 (s, 2H), 2.19-2.11 (m, 4H), 1.82-1.76 (m, 4H); ^{13}C NMR (125 MHz, acetone- d_6) δ 164.4, 151.7, 150.3, 129.1, 114.2, 113.4, 111.4, 105.1, 103.6, 58.6, 37.9, 23.9. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

8-((1-tosyl-1H-indol-5-yl)- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2i**)

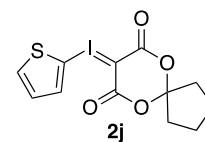
Prepared according to **GP2** [$-10\text{ }^\circ\text{C}$ instead of $0\text{ }^\circ\text{C}$] from potassium [1-[(4-methylphenyl)sulfonyl]-indol-5-yl]trifluoroborate **1i**. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2i** as a pale brown solid (103.5 mg, 61% yield).



^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.08 (d, $J = 1.8$ Hz, 1H), 8.02 (d, $J = 9.1$ Hz, 1H), 7.99-7.82 (m, 3H), 7.72 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 2H), 6.96 (d, $J = 3.6$ Hz, 1H), 2.31 (s, 3H), 1.98-1.91 (m, 4H), 1.73-1.59 (m, 4H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 163.6, 146.1, 134.7, 133.8, 132.2, 130.5, 128.8, 128.4, 126.9, 126.6, 115.5, 112.3, 110.4, 109.0, 59.2, 36.8, 22.8, 21.1. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[19]

8-(thiophen-2-yl- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2j**)

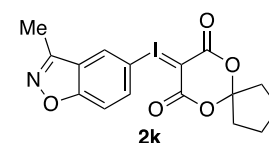
Prepared according to **GP2** [– 40°C instead of 0 °C, **ITT (0.53 equiv.)**] from potassium (thiophen-2-yl)trifluoroborate **1j**.^[3c] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2j** as a colorless solid (52.2 mg, 46% yield).



^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.84 (dd, $J = 5.3, 1.1$ Hz, 1H), 7.59 (dd, $J = 3.7, 1.1$ Hz, 1H), 7.08 (dd, $J = 5.3, 3.7$ Hz, 1H), 1.97-1.90 (m, 4H), 1.70-1.63 (m, 4H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 163.2, 136.7, 134.3, 128.6, 112.1, 101.7, 62.2, 36.8, 22.7. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[19]

8-((3-methylbenzo[d]isoxazol-5-yl)- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2k**)

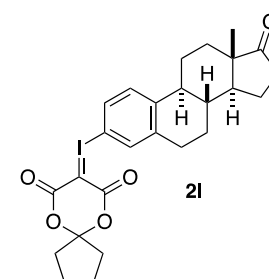
Prepared according to **GP2** [– 20°C instead of 0 °C] from potassium (3-methyl-1,2-benzoxazol-5-yl)trifluoroborate **1k**. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2k** as a colorless solid (87.1 mg, 68% yield).



^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 1.3$ Hz, 1H), 8.10 (dd, $J = 9.0, 1.6$ Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 1H), 2.63 (s, 3H), 2.19-2.11 (m, 4H), 1.83-1.77 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.4, 164.1, 155.1, 134.8, 129.2, 125.5, 114.5, 113.7, 106.7, 58.4, 37.5, 23.5, 10.2. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

8-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2l**)

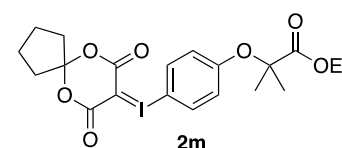
Prepared according to **GP2** from (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(trifluoro- λ^4 -boraneyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one, potassium salt **1l**.^[20] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2l** as a colorless solid (126.7 mg, 77% yield).



^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 8.7, 2.4$ Hz, 1H), 7.60-7.57 (m, 1H), 7.25 (d, $J = 8.5$ Hz, 1H), 3.03-2.89 (m, 2H), 2.58-2.46 (m, 1H), 2.41-2.29 (m, 2H), 2.19-1.94 (m, 8H), 1.84-1.74 (m, 4H), 1.71-1.39 (m, 6H), 0.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 220.2, 164.4, 144.7, 141.5, 133.4, 130.7, 129.0, 114.0, 111.1, 56.9, 50.4, 47.8, 44.3, 37.5, 37.4, 35.8, 31.4, 29.4, 25.9, 25.5, 23.4, 21.6, 13.8$. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

ethyl 2-(4-((7,9-dioxo-6,10-dioxaspiro[4.5]decan-8-ylidene)- λ^3 -iodanyl)phenoxy)-2-methylpropanoate (2m)

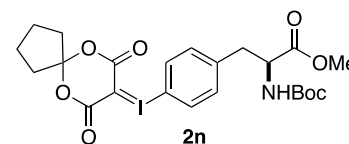
Prepared according to **GP2** from potassium (4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)trifluoroborate **1m**. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2m** as a colorless solid (111.5 mg, 74% yield).



^1H NMR (400 MHz, CDCl_3) δ 7.83-7.76 (m, 2H), 6.84-6.78 (m, 2H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.18-2.11 (m, 4H), 1.82-1.76 (m, 4H), 1.63 (s, 6H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 172.6, 163.5, 157.1, 134.2, 120.4, 112.1, 106.8, 79.1, 61.3, 59.0, 36.7, 24.9, 22.7, 13.8. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-((7,9-dioxo-6,10-dioxaspiro[4.5]decan-8-ylidene)- λ^3 -iodanyl)phenyl)propanoate (2n)

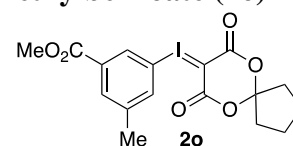
Prepared according to **GP2** from potassium (S)-4-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl)trifluoroborate **1n**. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2n** as a colorless solid (111.8 mg, 65% yield).



^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 5.05 (d, $J = 7.4$ Hz, 1H), 4.56 (d, $J = 5.7$ Hz, 1H), 3.71 (s, 3H), 3.18 (dd, $J = 14.0, 5.2$ Hz, 1H), 3.04 (dd, $J = 14.0, 5.7$ Hz, 1H), 2.17-2.09 (m, 4H), 1.81-1.74 (m, 4H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 172.2, 163.5, 155.3, 140.7, 132.3, 131.7, 113.9, 112.1, 78.4, 58.4, 54.7, 51.8, 36.8, 35.9, 28.1, 22.7. The ^1H and ^{13}C NMR spectra were in agreement with those reported in the literature.^[18]

methyl 3-((7,9-dioxo-6,10-dioxaspiro[4.5]decan-8-ylidene)- λ^3 -iodanyl)-5-methylbenzoate (2o)

Prepared according to **GP2** from potassium (3-methoxycarbonyl-5-methylphenyl)trifluoroborate **1o**. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded **2o** as a colorless solid (66.6 mg, 50% yield).

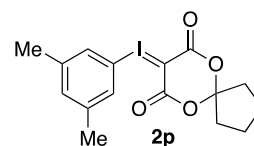


^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.14 (s, 1H), 7.91 (s, 1H), 7.87 (s, 1H), 3.86 (s, 3H), 2.40 (s, 3H), 2.06-1.97 (m, 4H), 1.74-1.66 (m, 4H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 164.7, 163.5, 141.4, 136.7, 131.7, 131.6, 129.6, 116.0, 112.3, 58.7, 52.6, 36.8, 22.8, 20.6. HRMS (ESI): m/z ($\text{M}+\text{Na}^+$) calcd for $\text{C}_{17}\text{H}_{17}\text{INaO}_6$: 466.9962; found: 466.99696. IR (KBr): 2956, 1721, 1641, 1434, 1349, 1280, 1200, 1093, 758 cm^{-1} . Mp: 191.2 $^\circ\text{C}$ (decomp.).

8-((3,5-dimethylphenyl)- λ^3 -iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (**2p**)

The transformation was performed based on the literature procedure.^[21] In a glovebox, a sealed tube was charged with *m*-xylene **9p** (618 μL , 5.0 mmol), $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (16.6 mg, 25 μmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (13.4 mg, 50 μmol), bis(pinacolato)diborane (889 mg, 3.5 mmol) and THF (7.5 ml). The mixture was stirred at 80 $^\circ\text{C}$ for 16 h. After cooling to room temperature, the crude product was filtered through silica gel column (EtOAc) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF_2 according to **GP1**. Purification of the crude product by recrystallization from Et_2O /acetone afforded potassium (3,5-dimethylphenyl)trifluoroborate **1p** as a colorless solid (414 mg, 39% yield, 2 steps).

Prepared **2p** according to **GP2** from **1p**. Purification of the crude product by silica gel column chromatography ($\text{AcOEt}/\text{MeOH} = 100 : 0$ to $99 : 1$) afforded **2p** as a colorless solid (82.8 mg, 69% yield). ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.41 (s, 2H), 7.18 (s, 1H), 2.28 (s, 6H), 2.01-1.95 (m, 4H), 1.71-1.66 (m, 4H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 163.5, 140.4, 132.1, 129.7, 116.1, 112.1, 58.3, 36.7, 22.7, 20.7. HRMS (ESI): m/z ($\text{M}+\text{Na}^+$) calcd for $\text{C}_{16}\text{H}_{17}\text{INaO}_4$: 423.00637; found: 423.00731. IR (KBr): 2952, 1685, 1631, 1343, 1284, 1104, 758 cm^{-1} . Mp: 126.0 $^\circ\text{C}$ (decomp.).

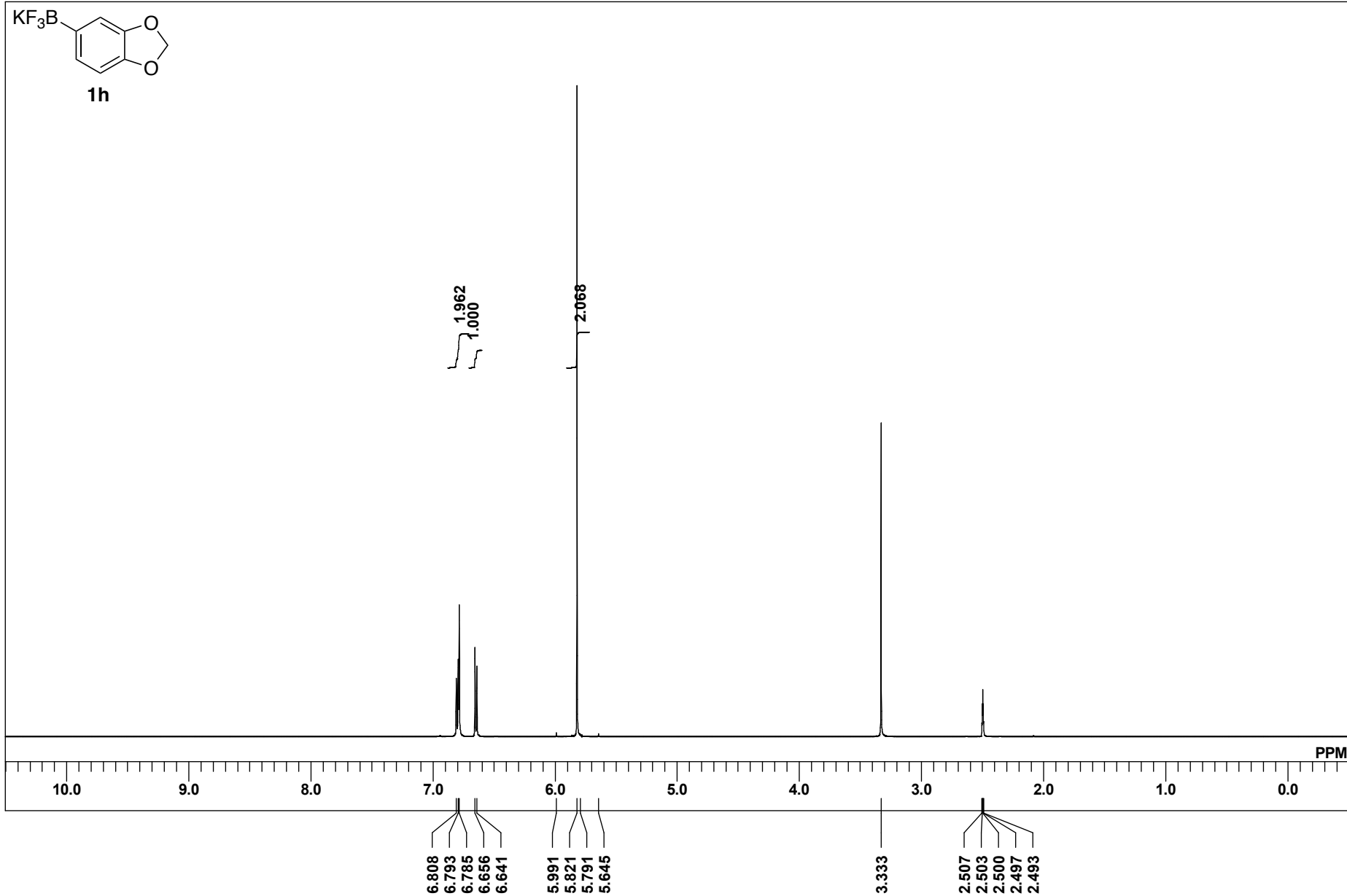


Supplementary references

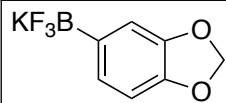
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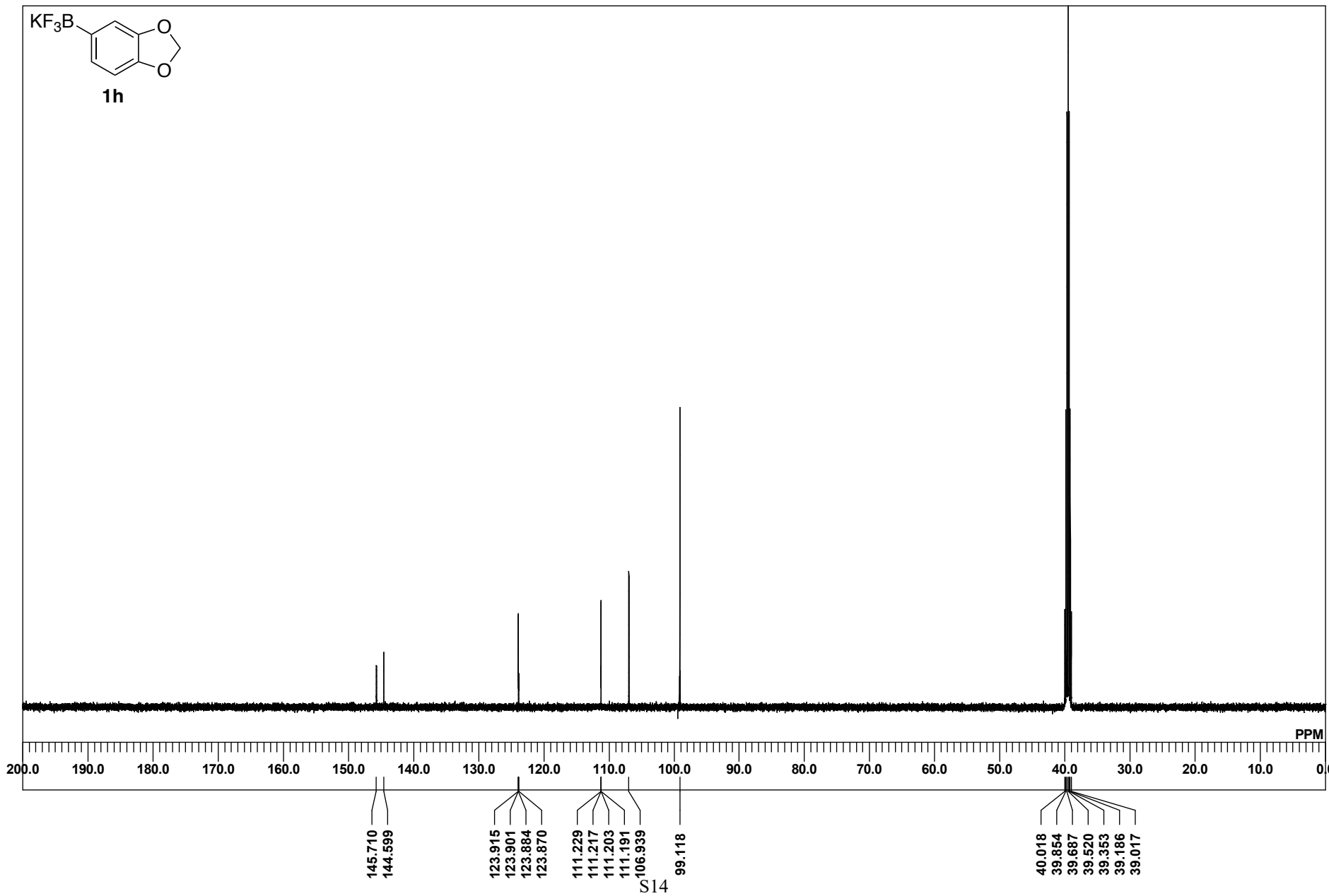
^1H NMR spectrum of **1h**



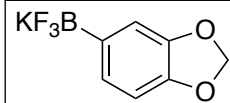
^{13}C NMR spectrum of **1h**



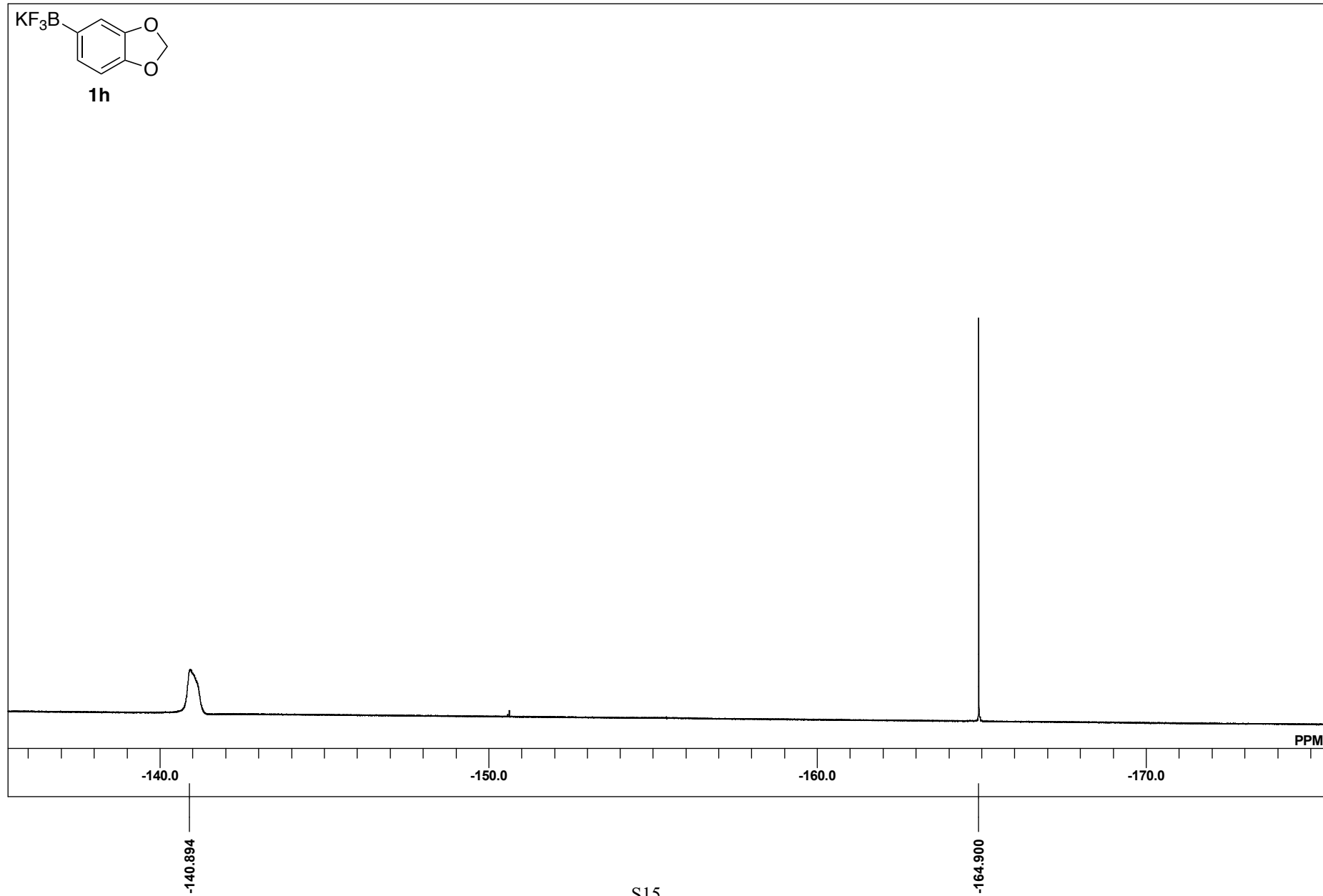
1h



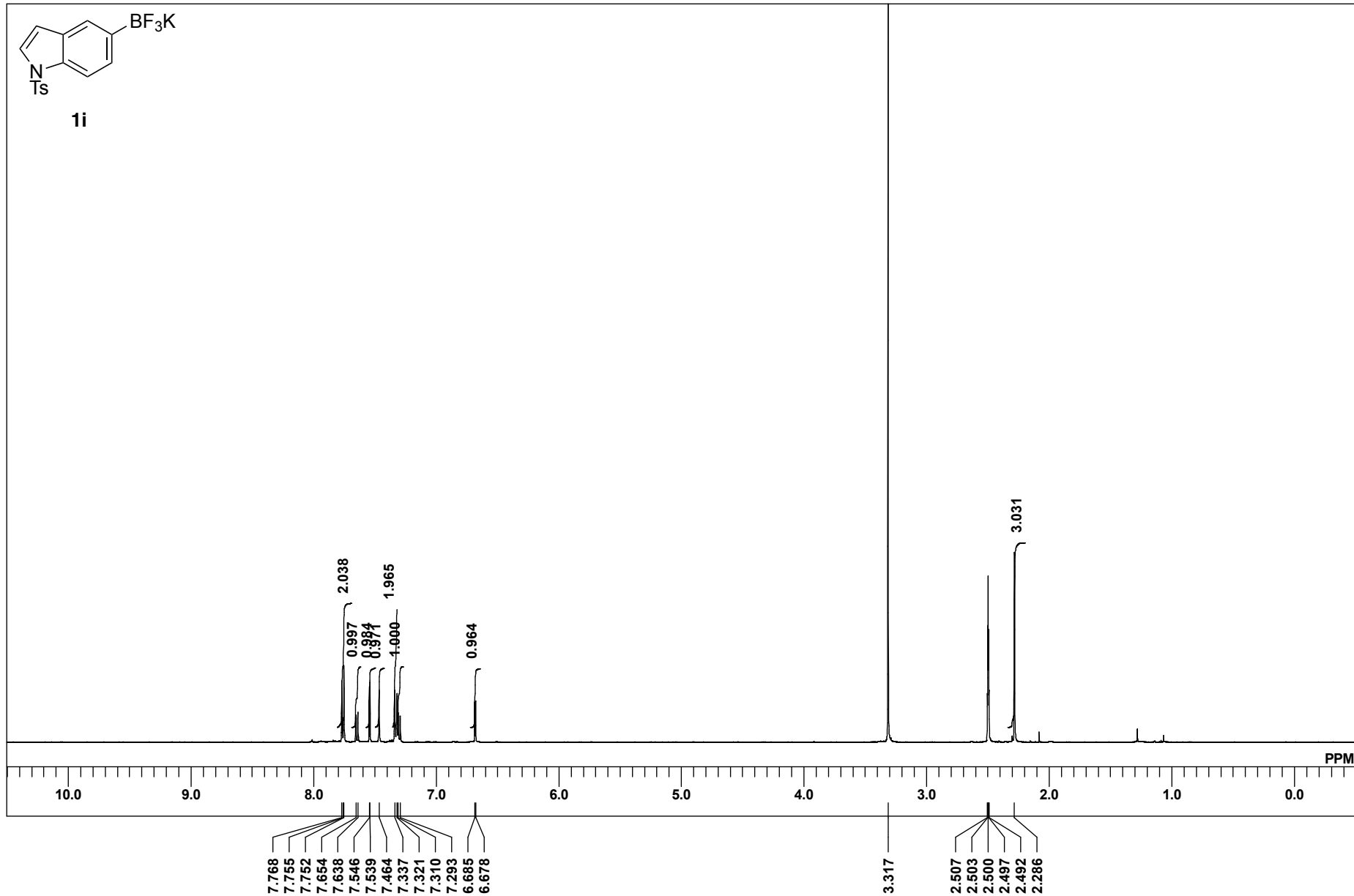
^{19}F NMR spectrum of **1h**



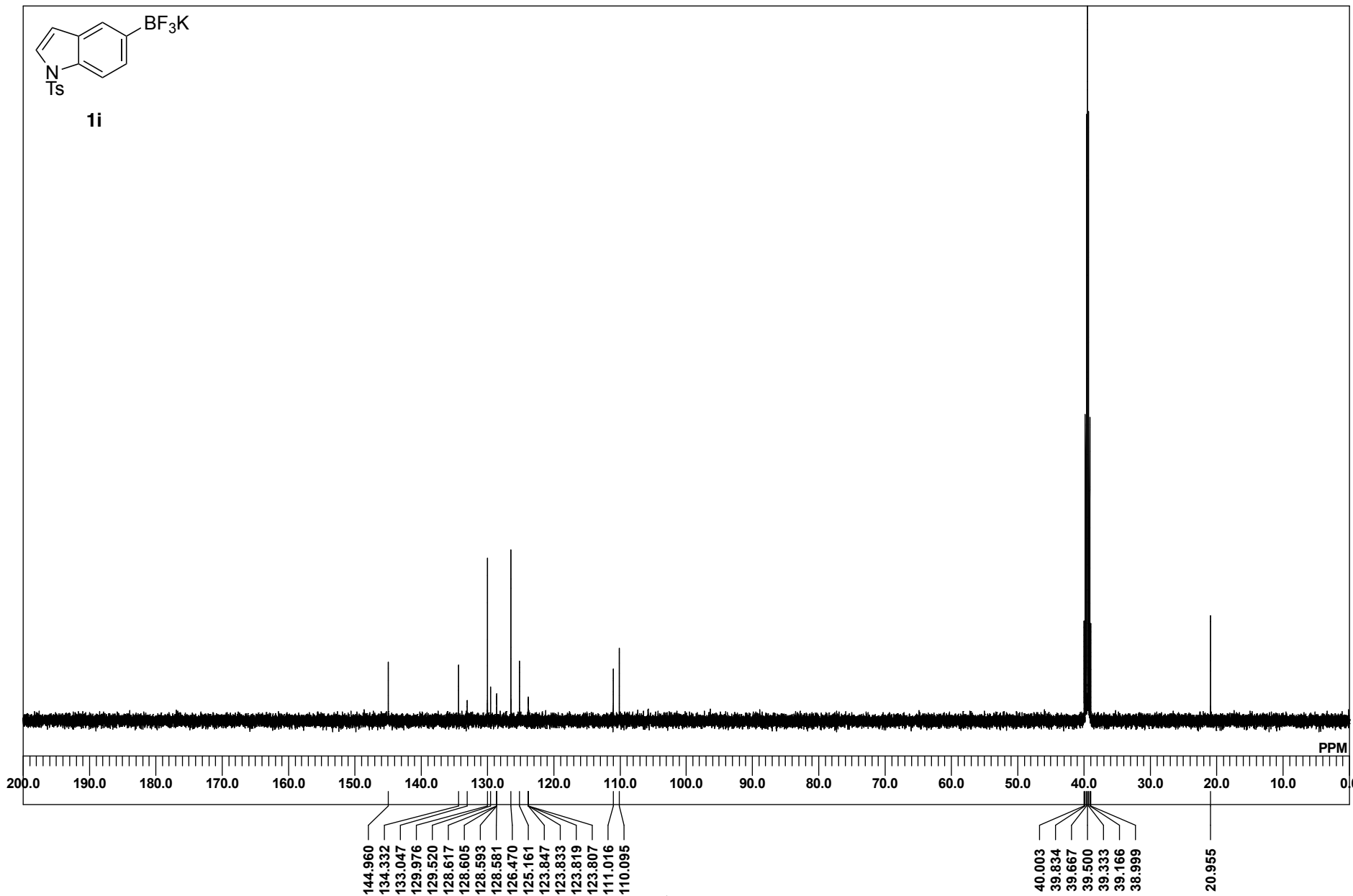
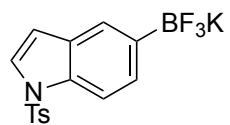
1h



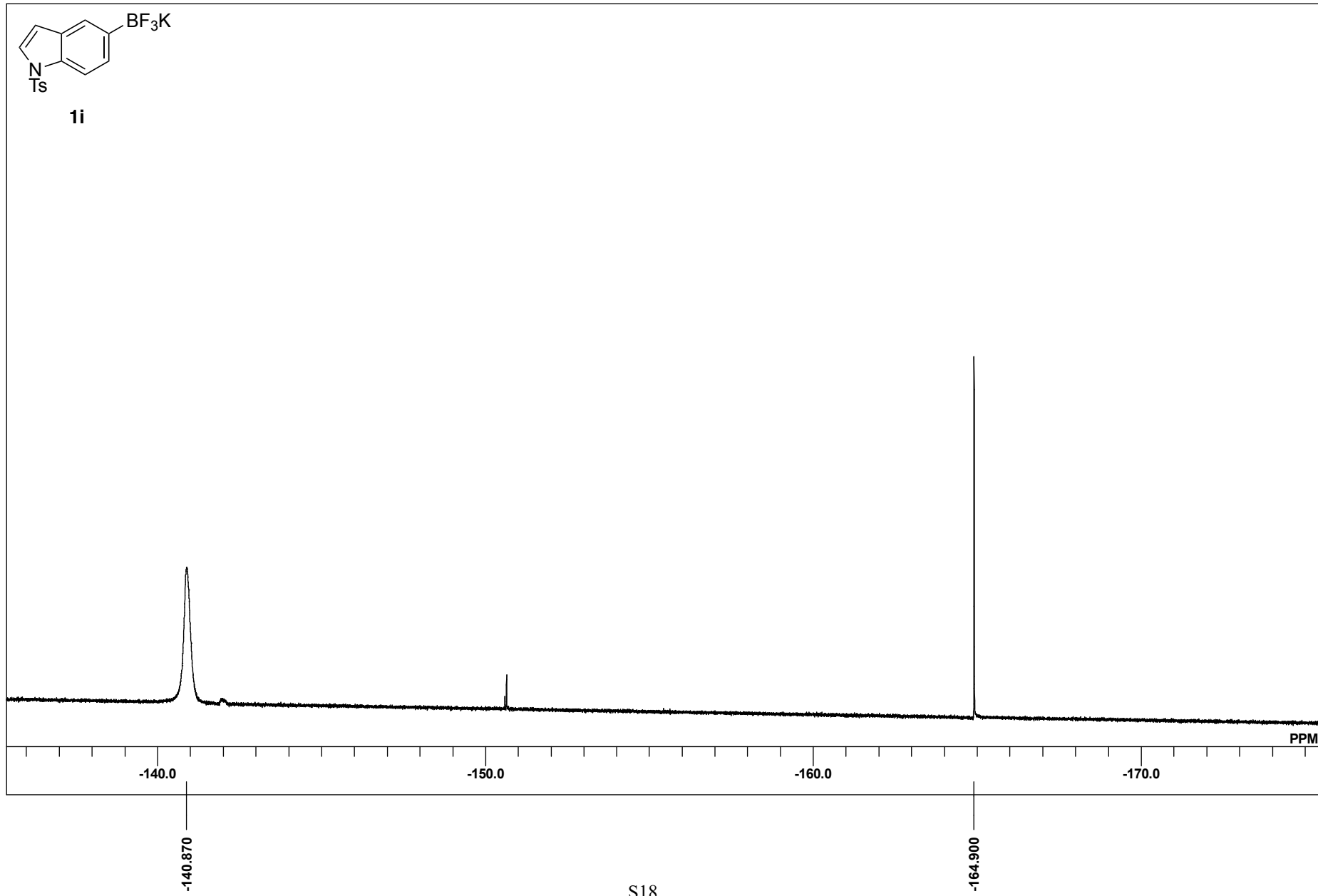
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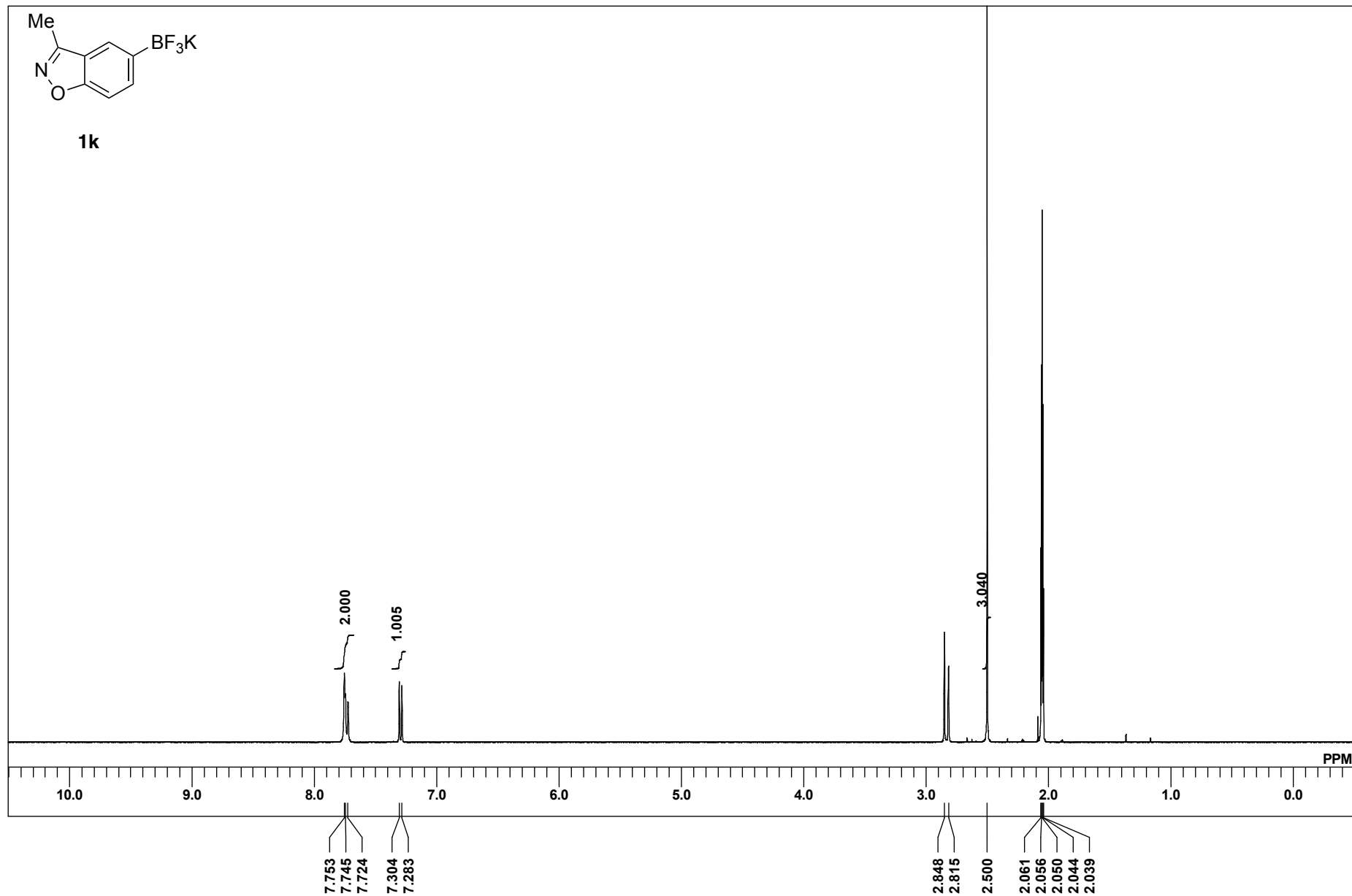
^{13}C NMR spectrum of **1i**



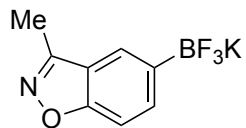
^{19}F NMR spectrum of **1i**



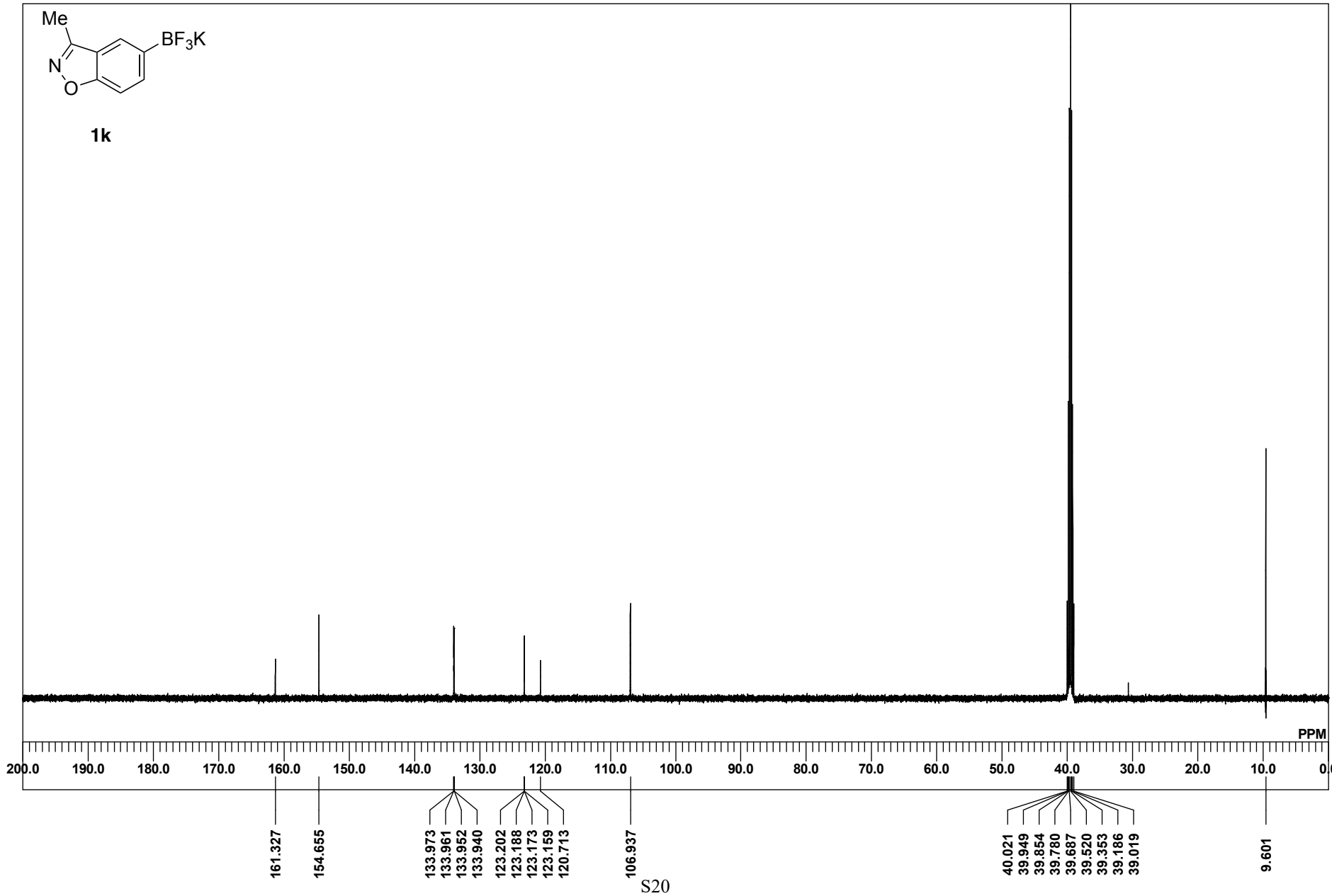
^1H NMR spectrum of **1k**



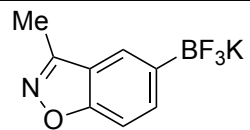
^{13}C NMR spectrum of **1k**



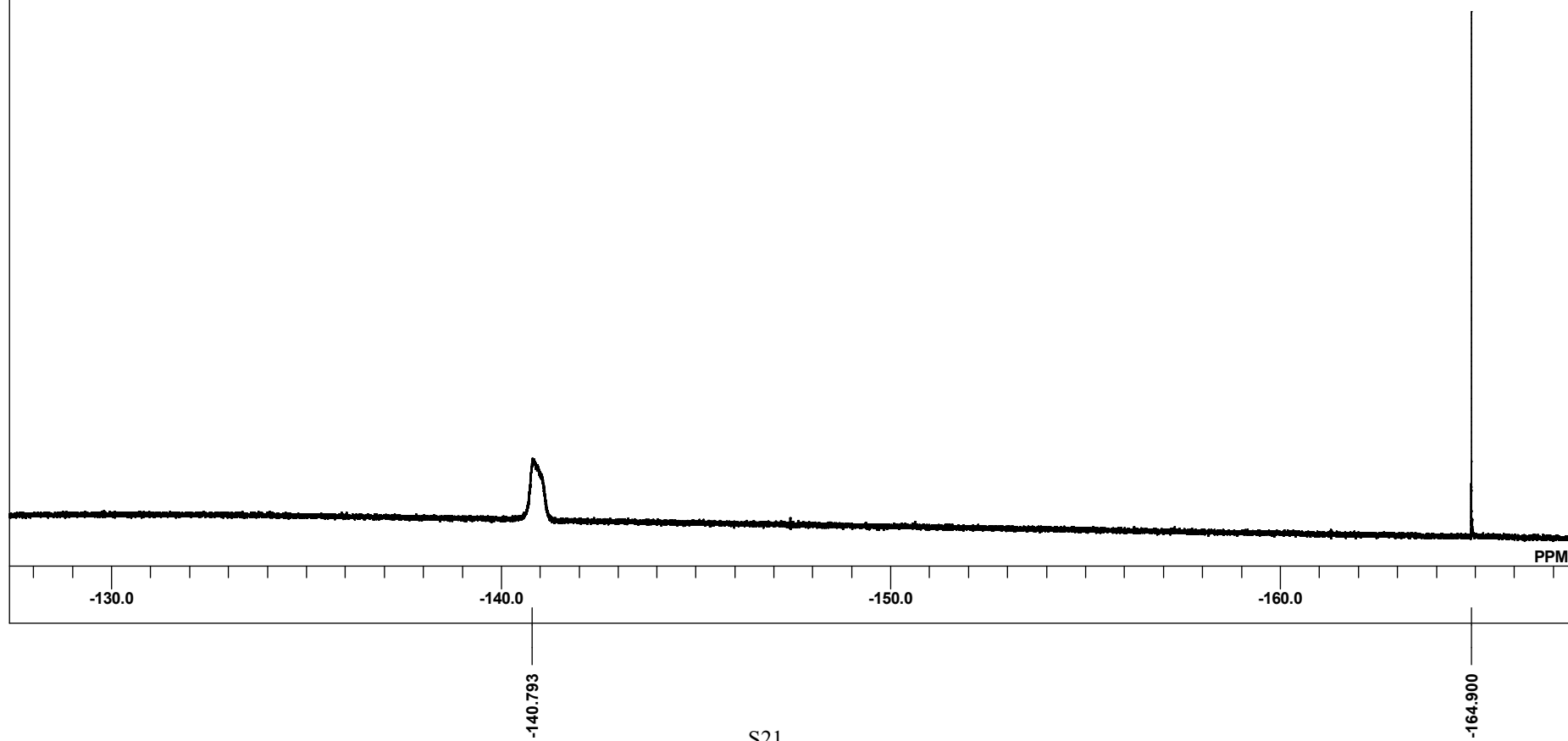
1k



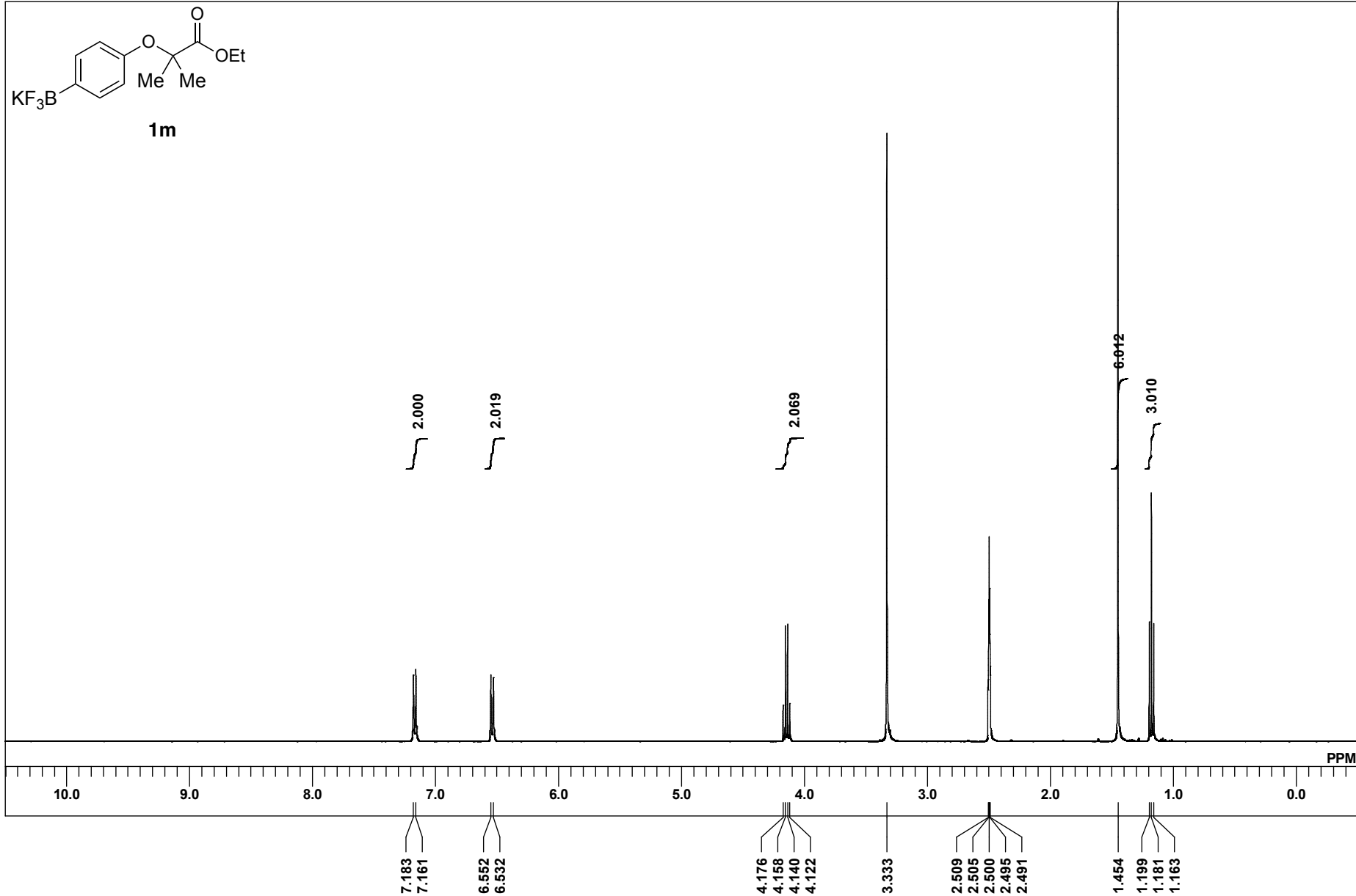
^{19}F NMR spectrum of **1k**



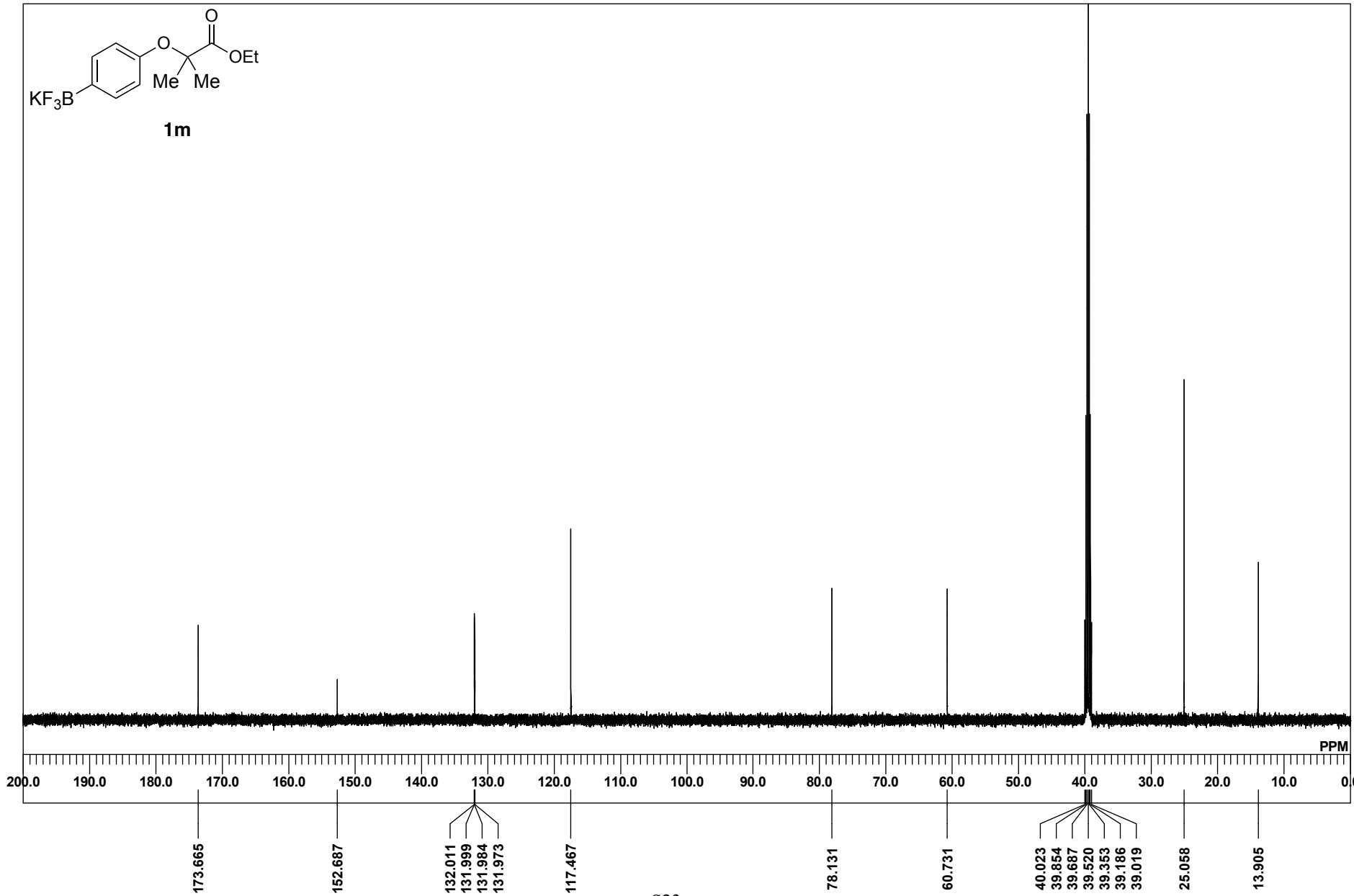
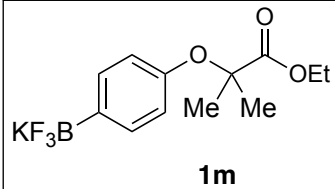
1k



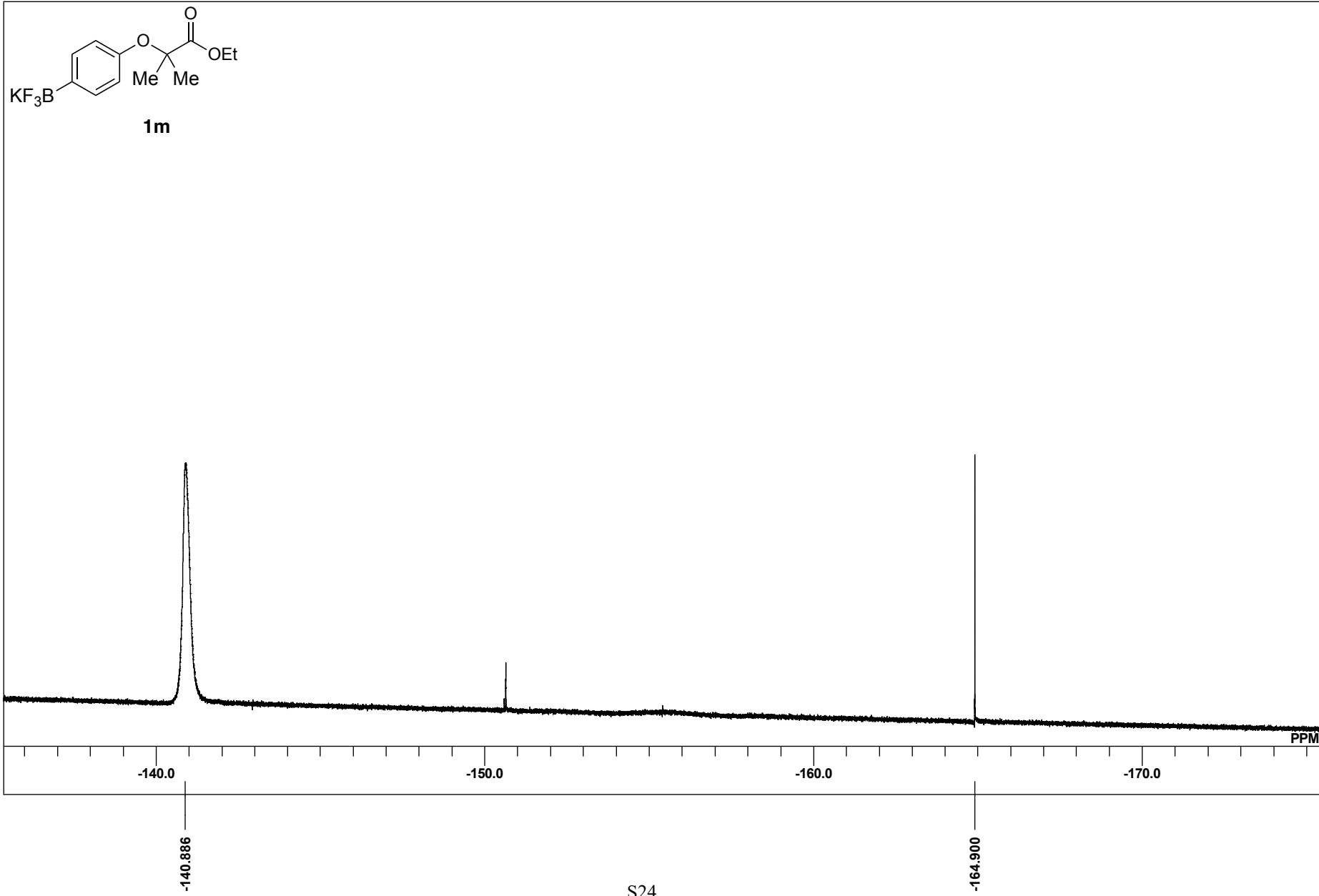
^1H NMR spectrum of **1m**



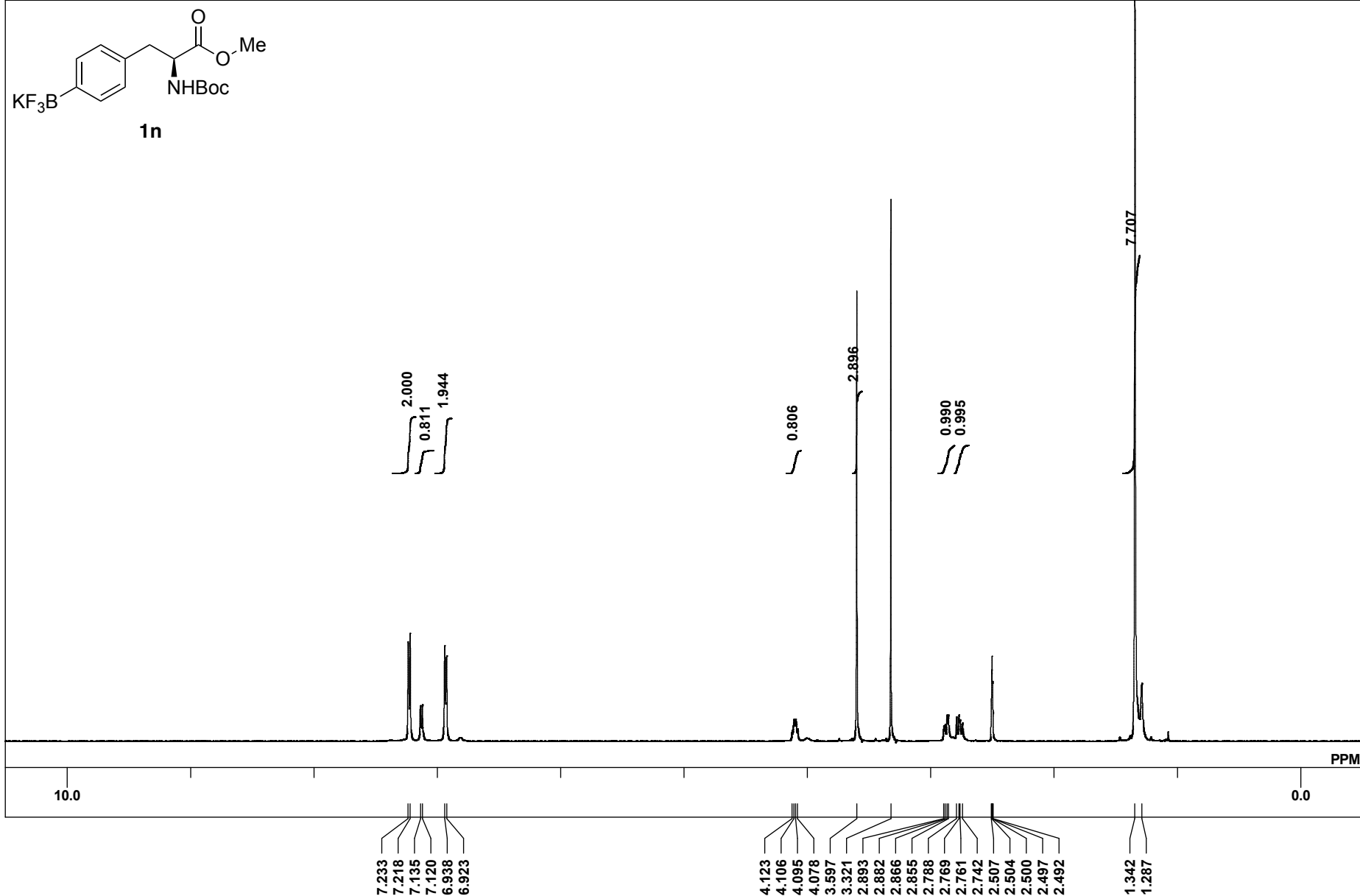
^{13}C NMR spectrum of **1m**



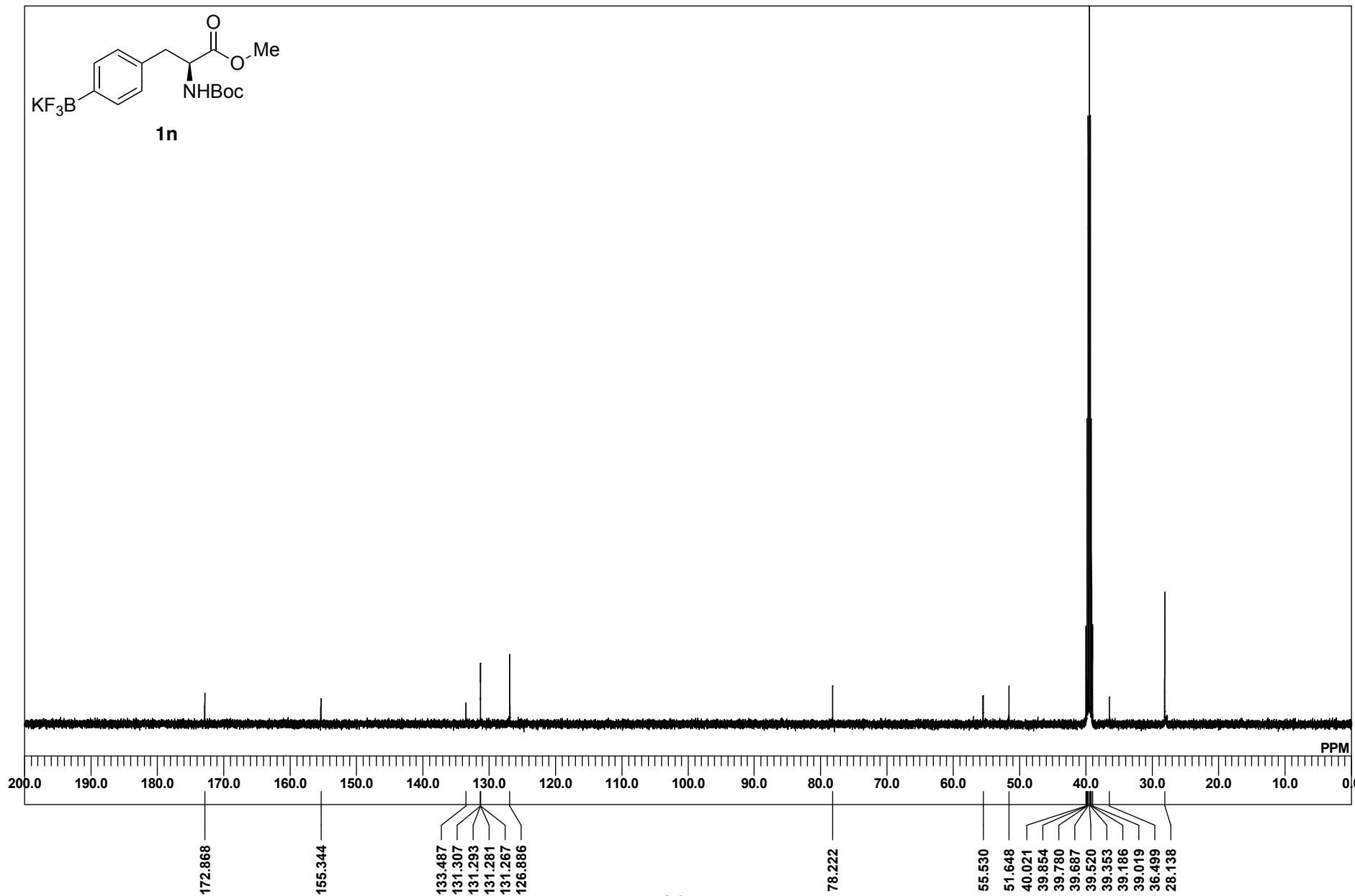
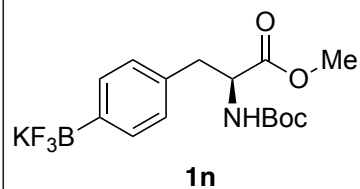
^{19}F NMR spectrum of **1m**



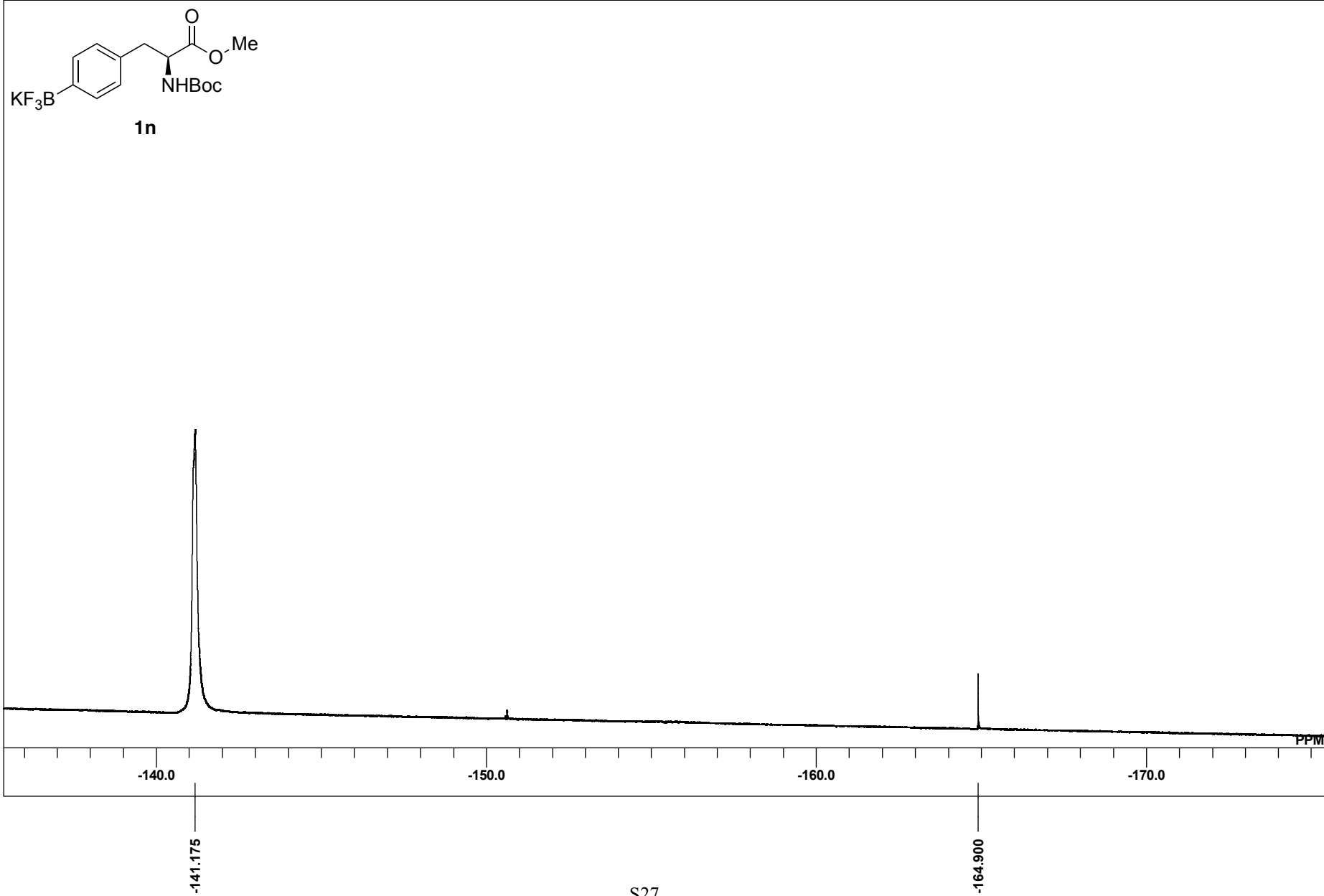
^1H NMR spectrum of **1n**



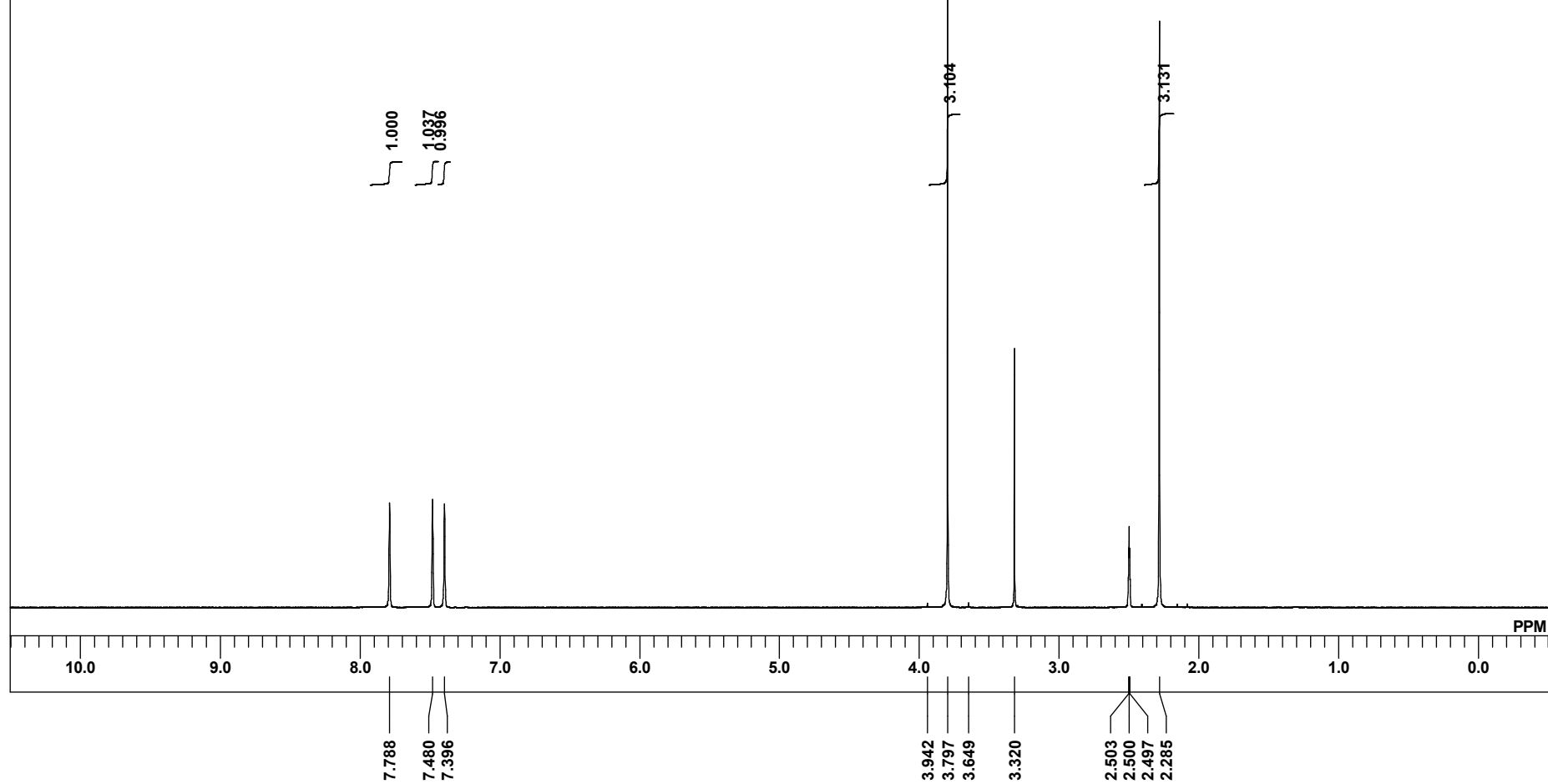
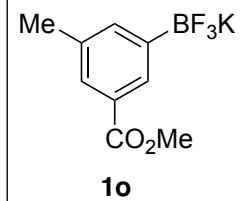
^{13}C NMR spectrum of **1n**



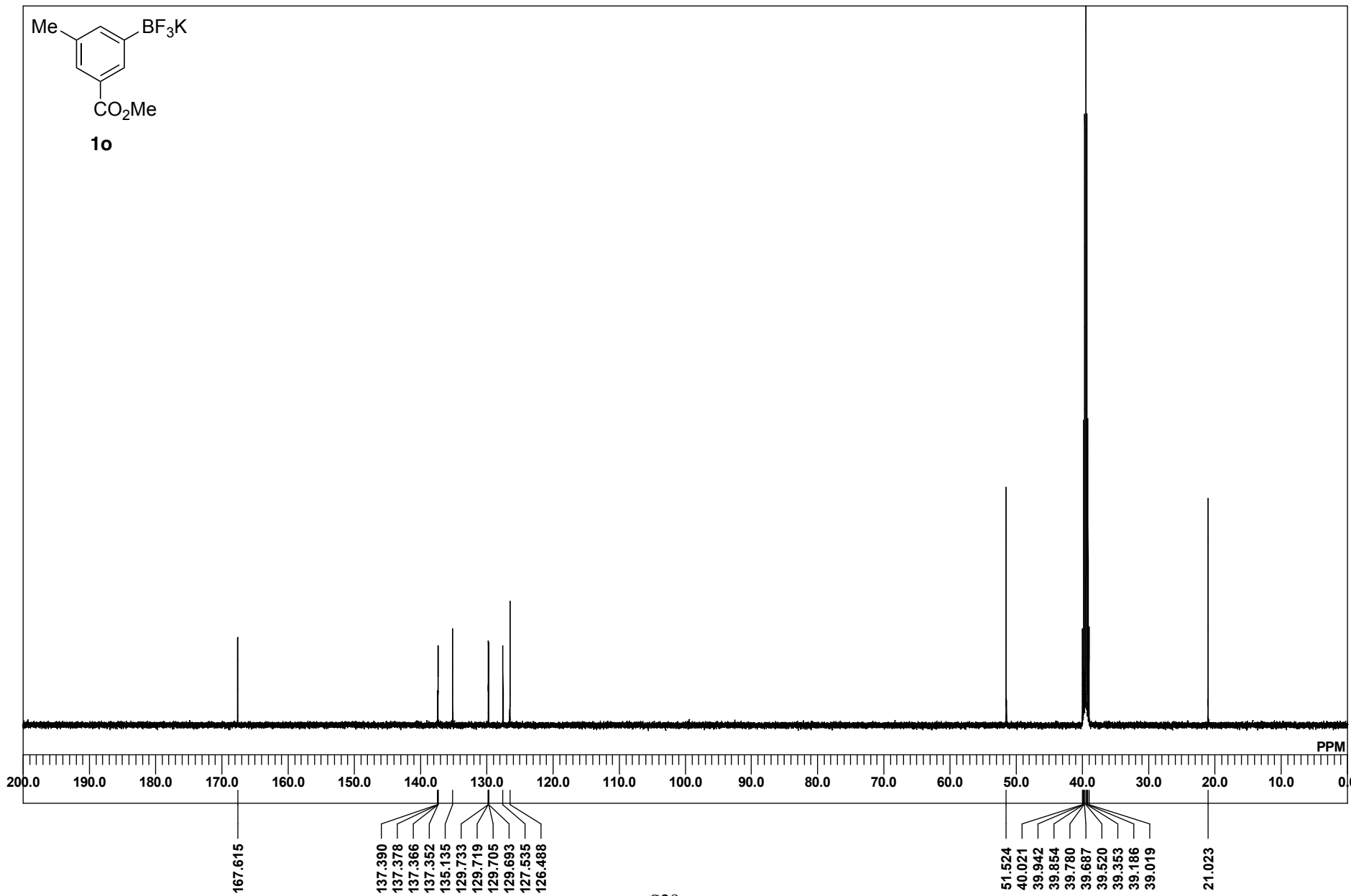
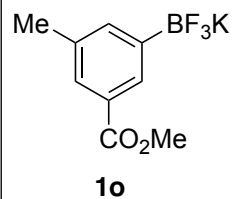
^{19}F NMR spectrum of **1n**



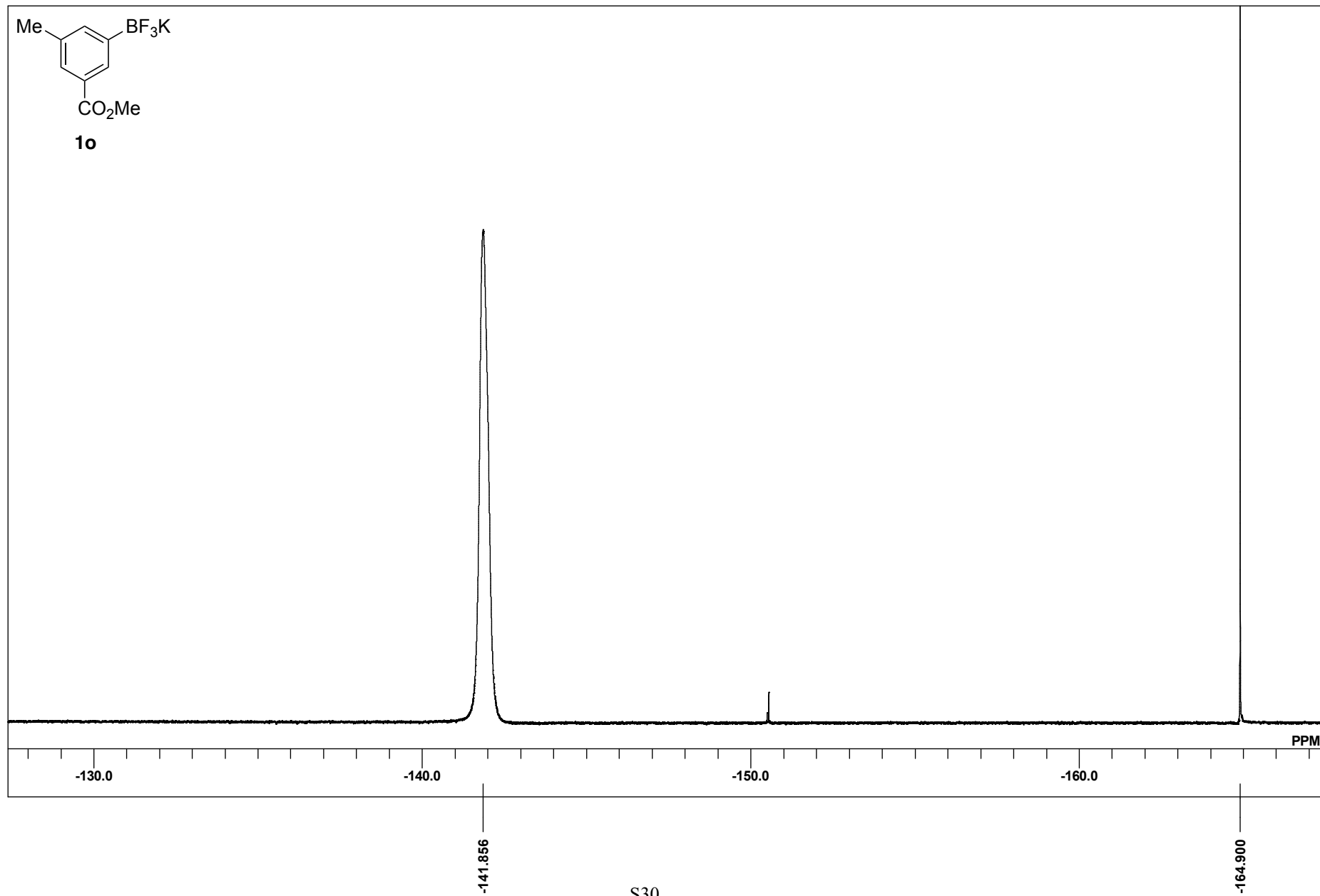
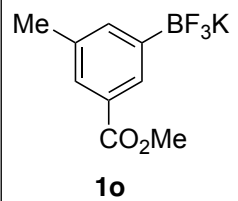
^1H NMR spectrum of **1o**



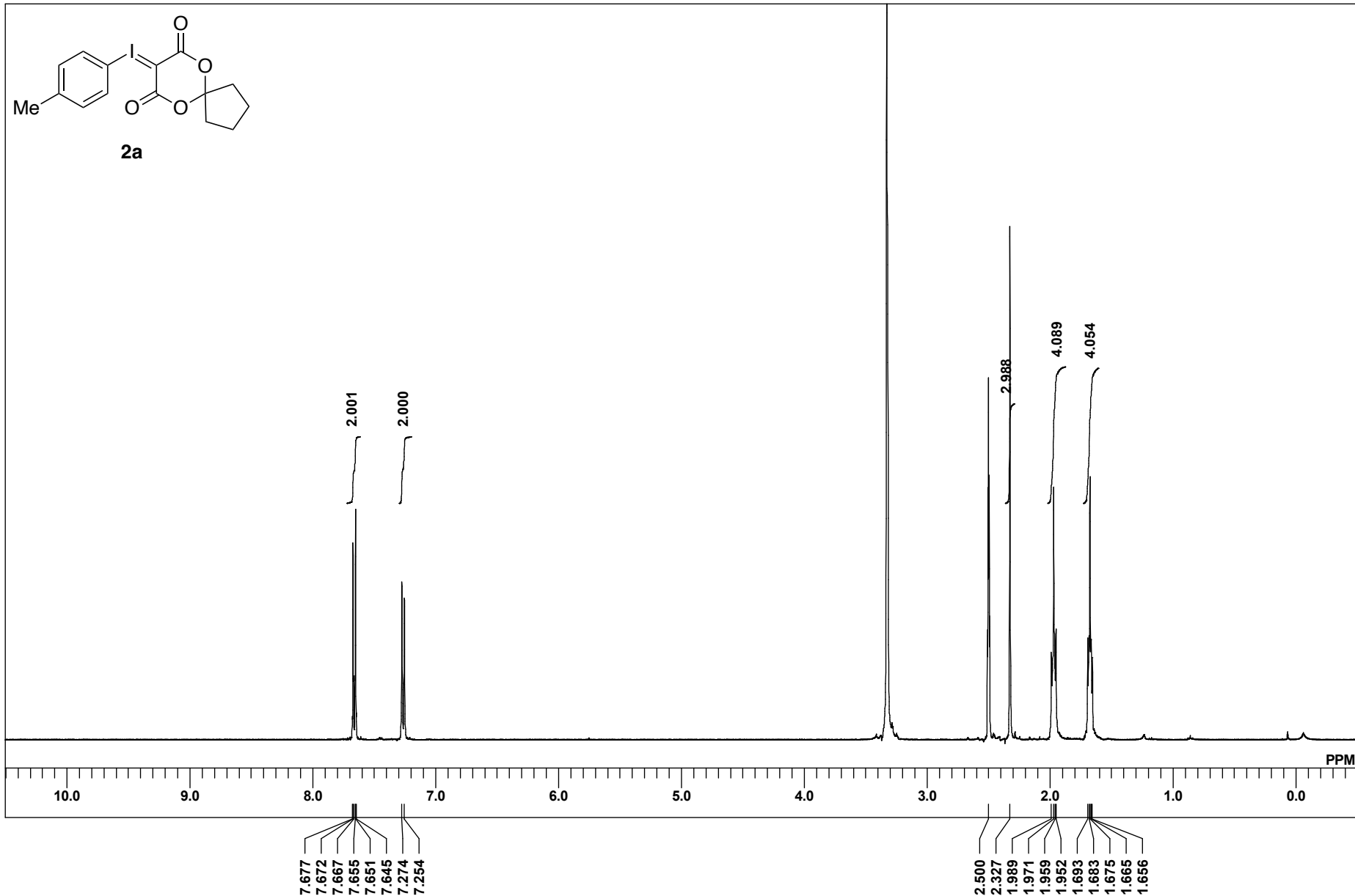
^{13}C NMR spectrum of **1o**



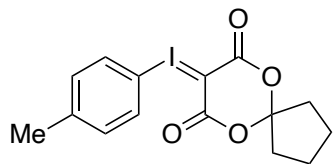
^{19}F NMR spectrum of **1o**



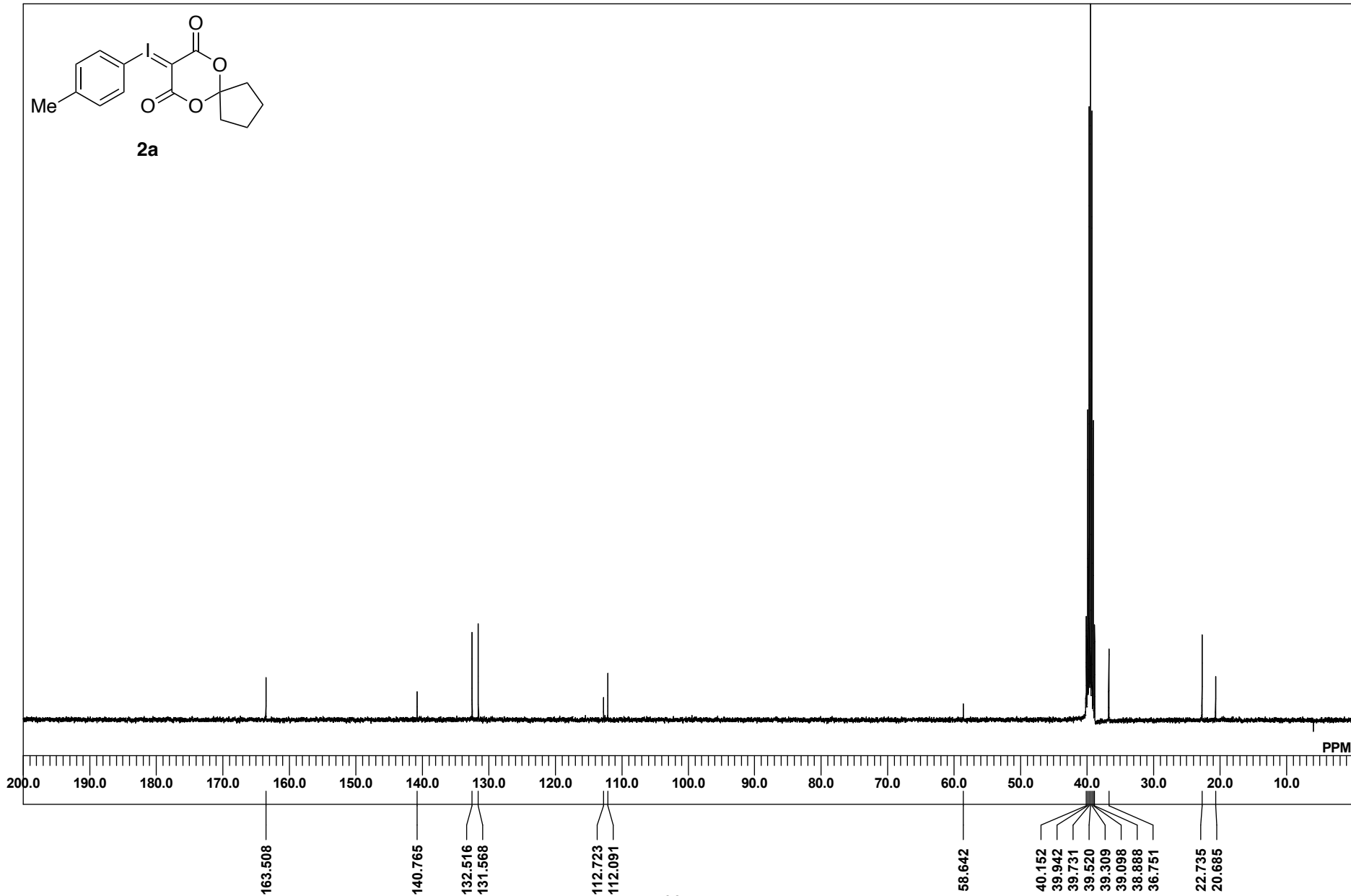
¹H NMR spectrum of 2a



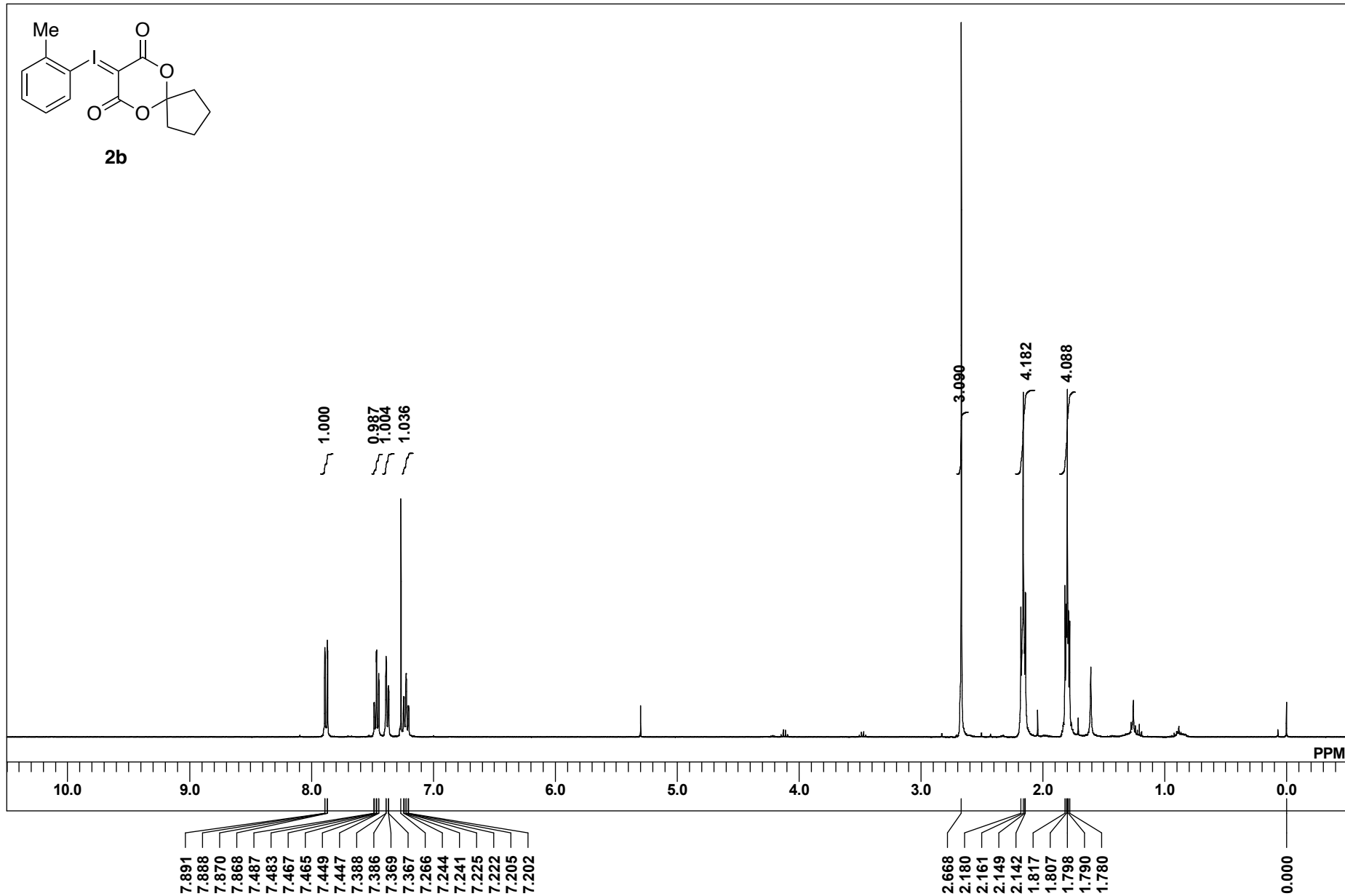
^{13}C NMR spectrum of **2a**



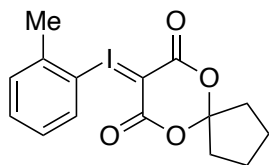
2a



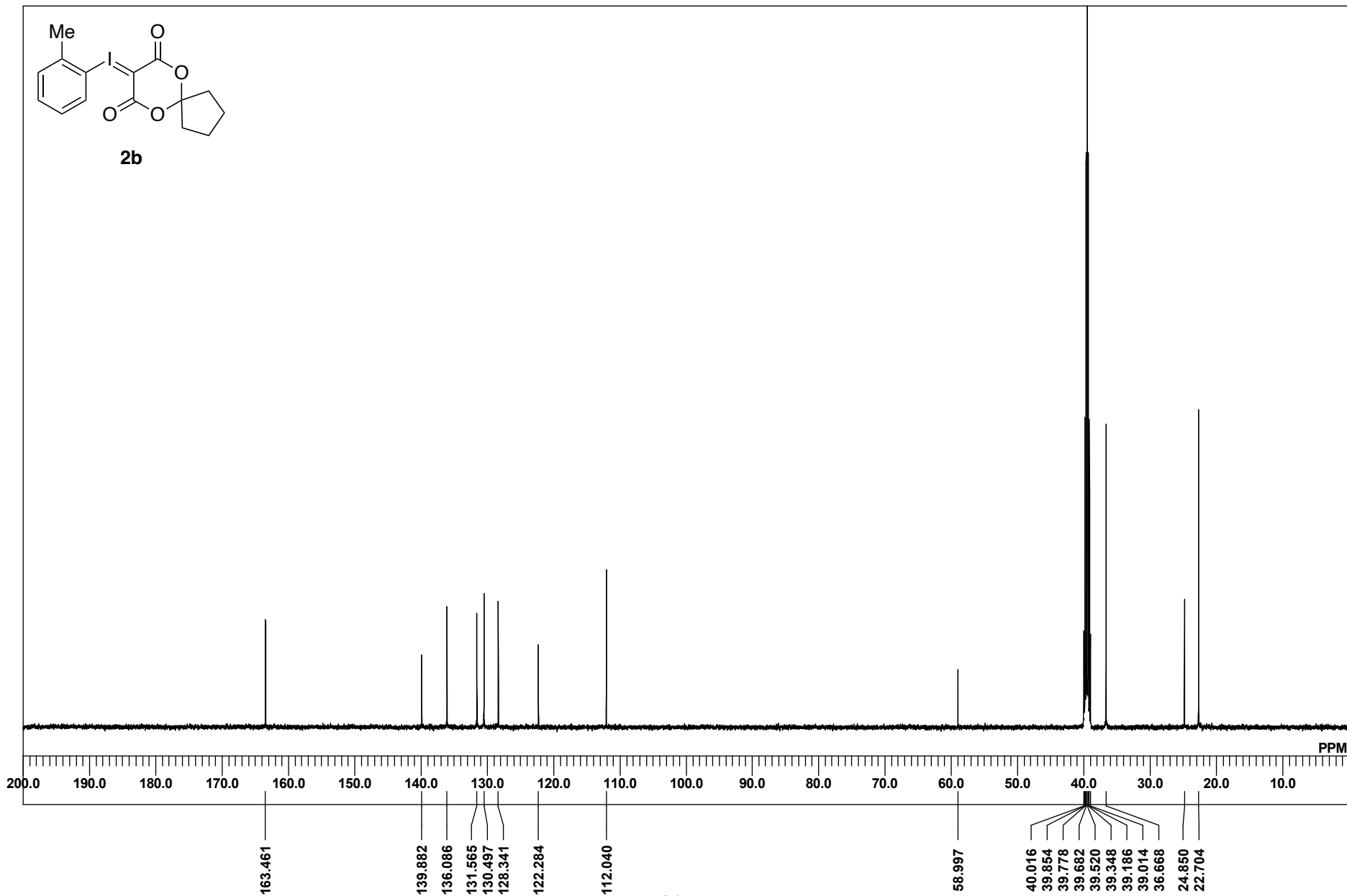
¹H NMR spectrum of **2b**



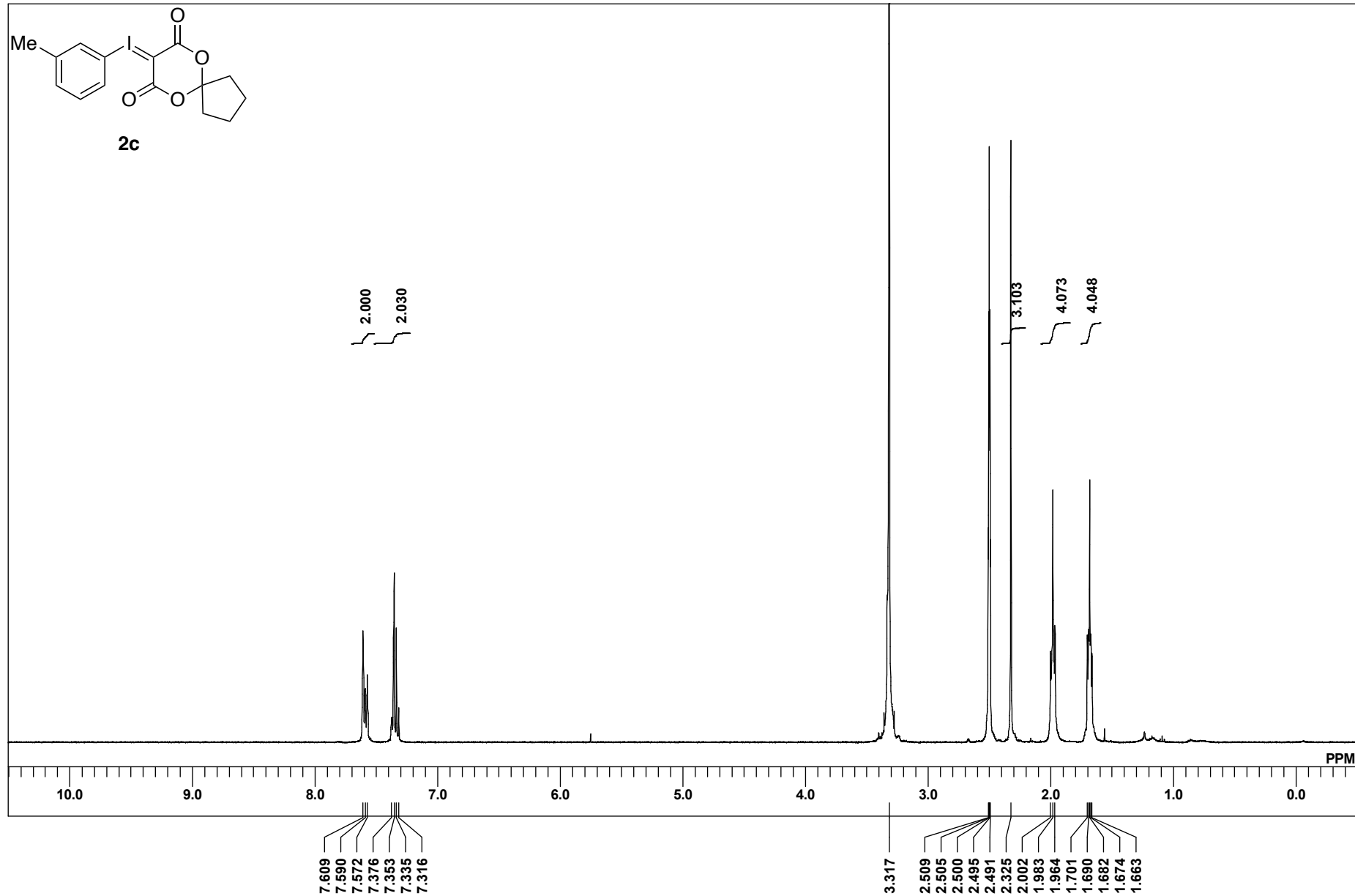
¹³C NMR spectrum of **2b**



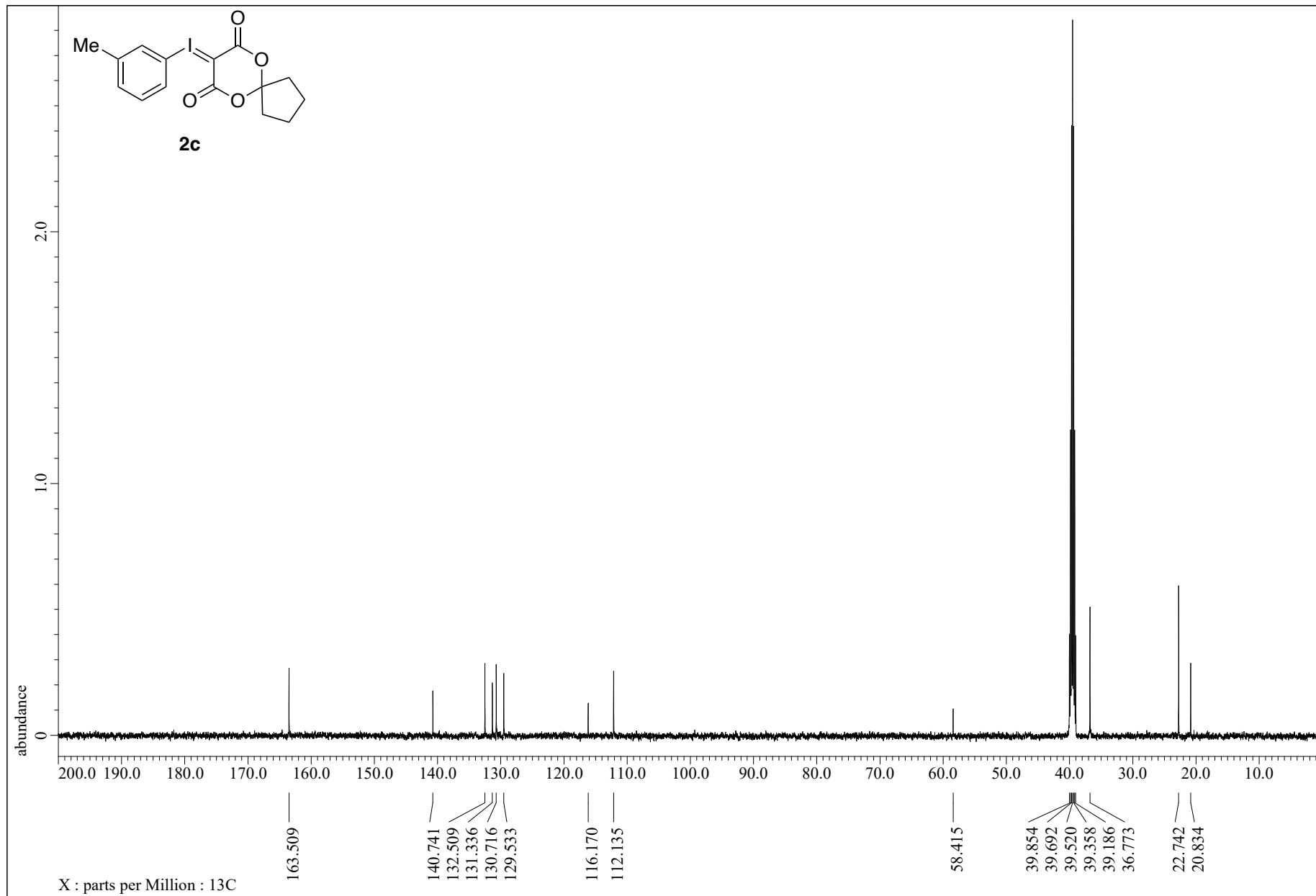
2b



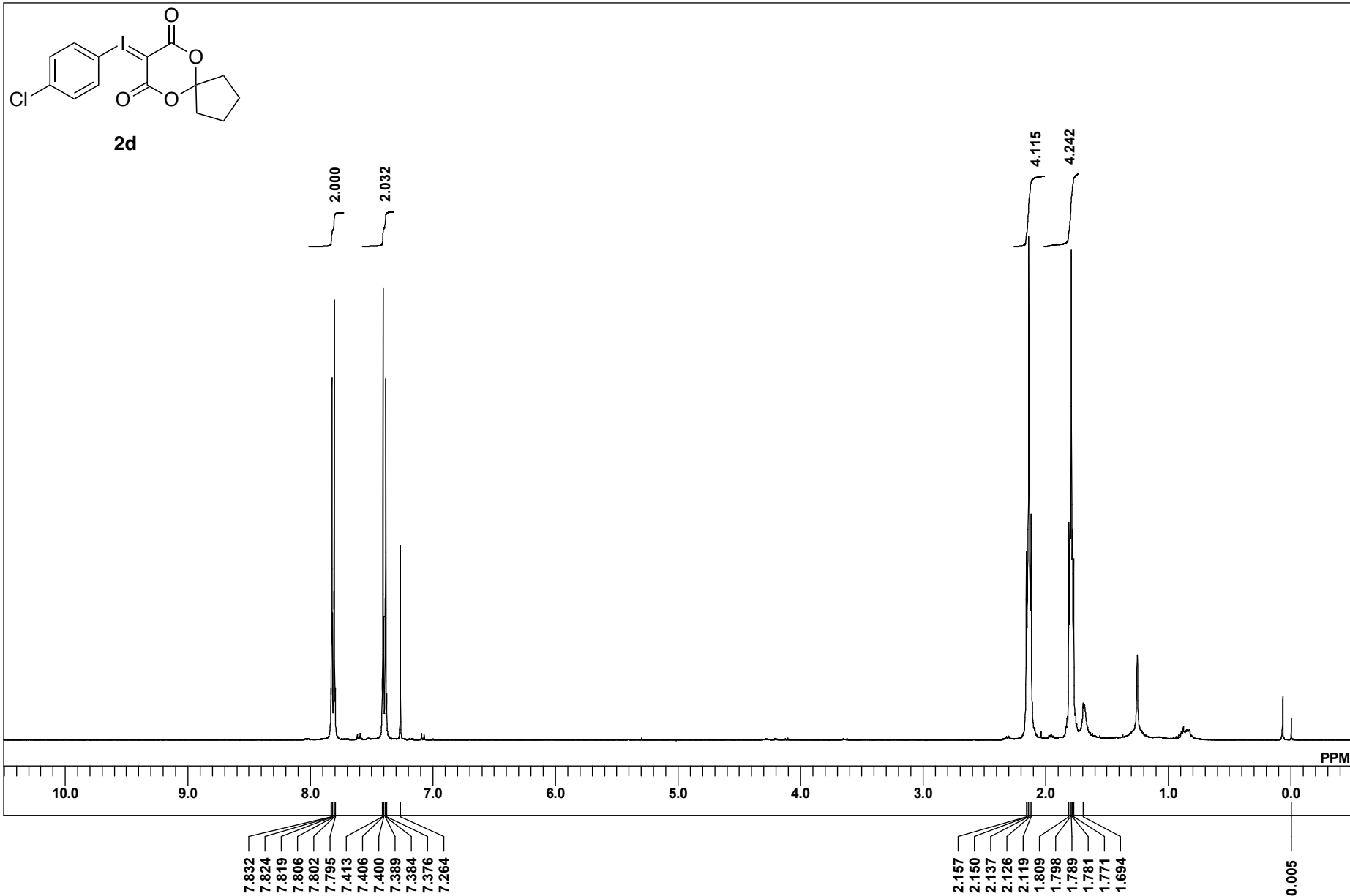
¹H NMR spectrum of 2c



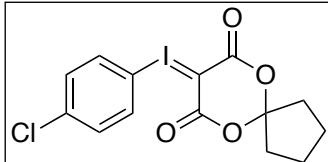
^{13}C NMR spectrum of **2c**



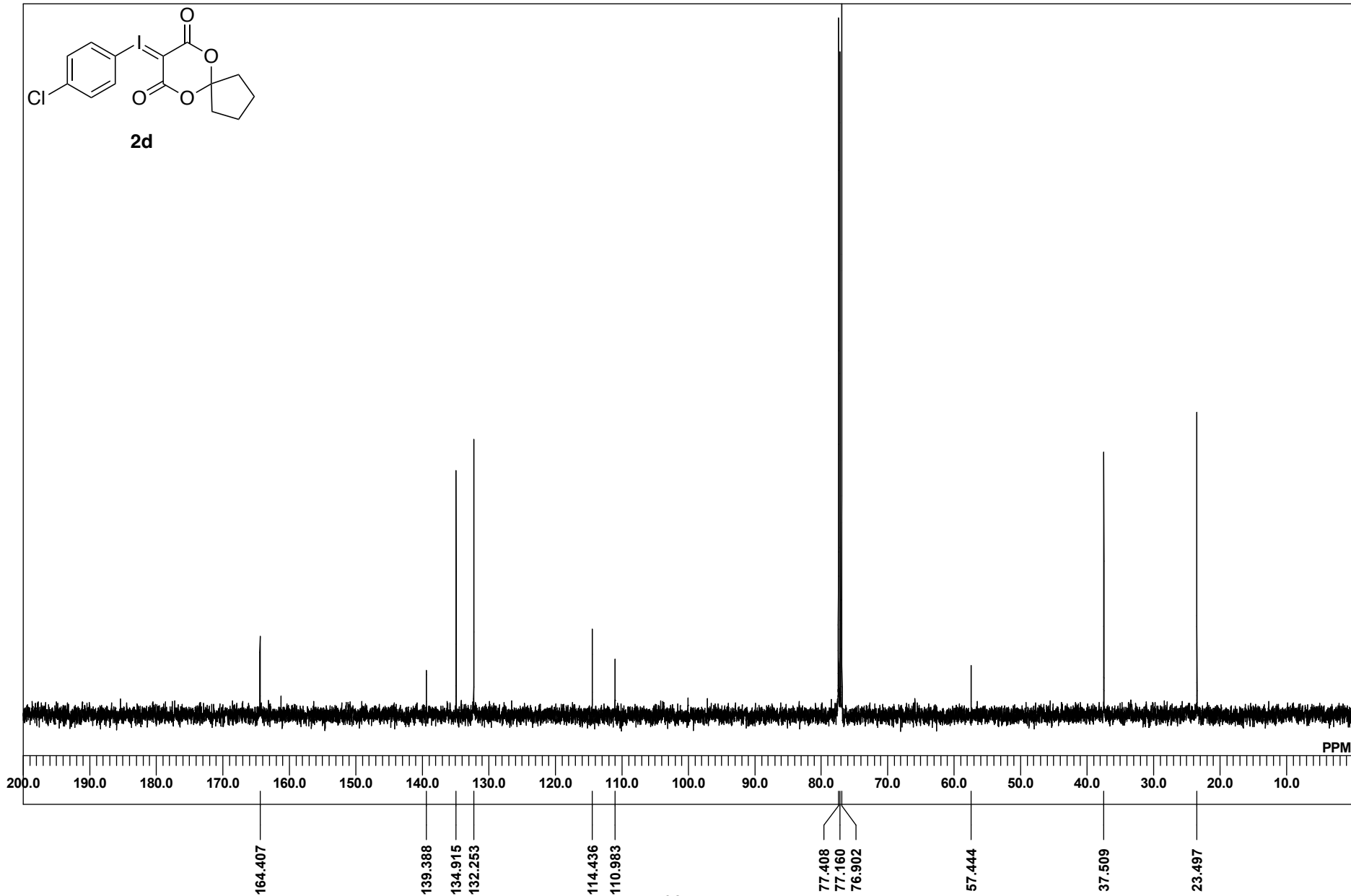
¹H NMR spectrum of 2d



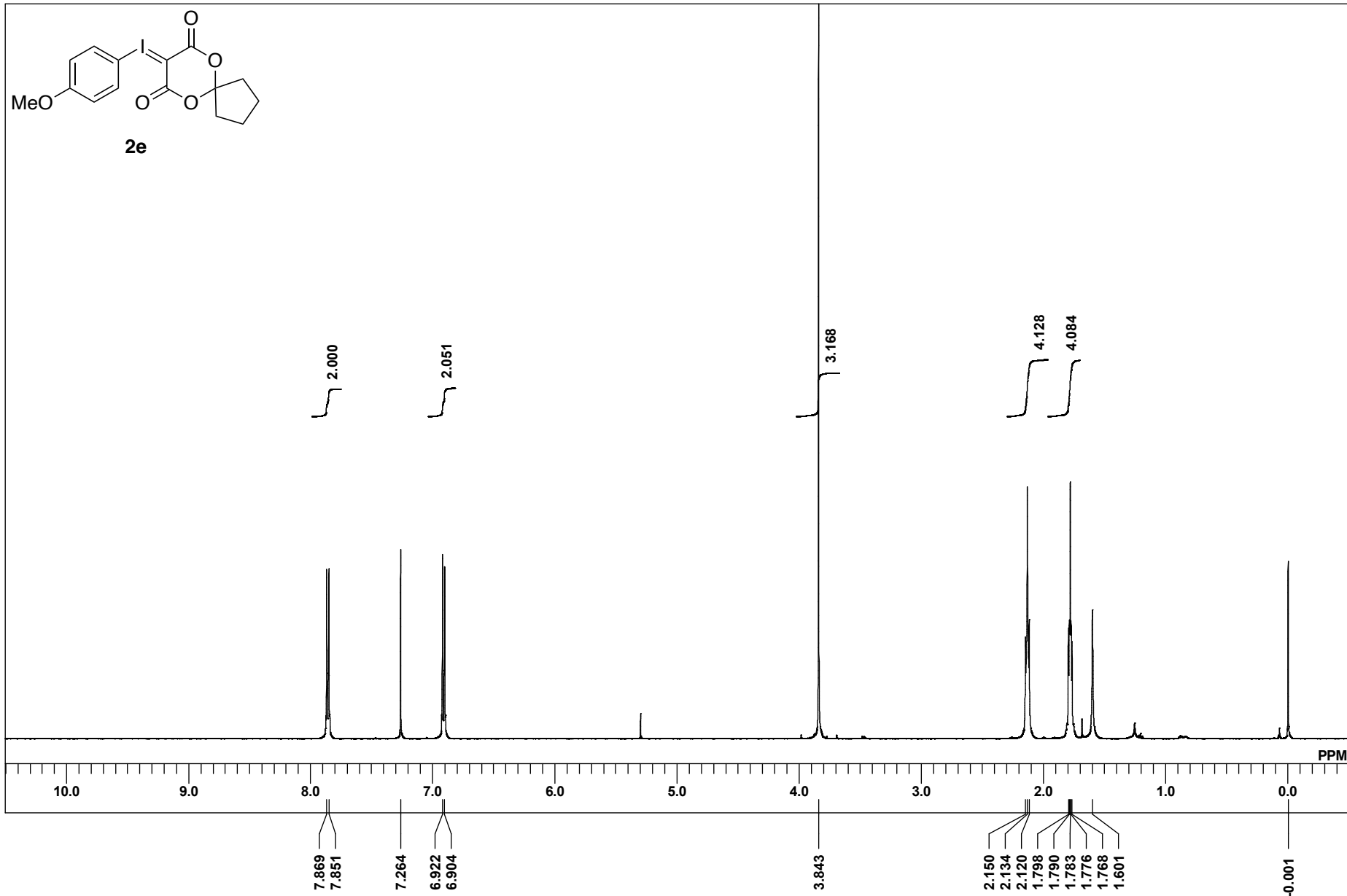
¹³C NMR spectrum of **2d**



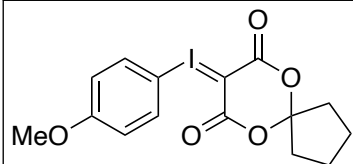
2d



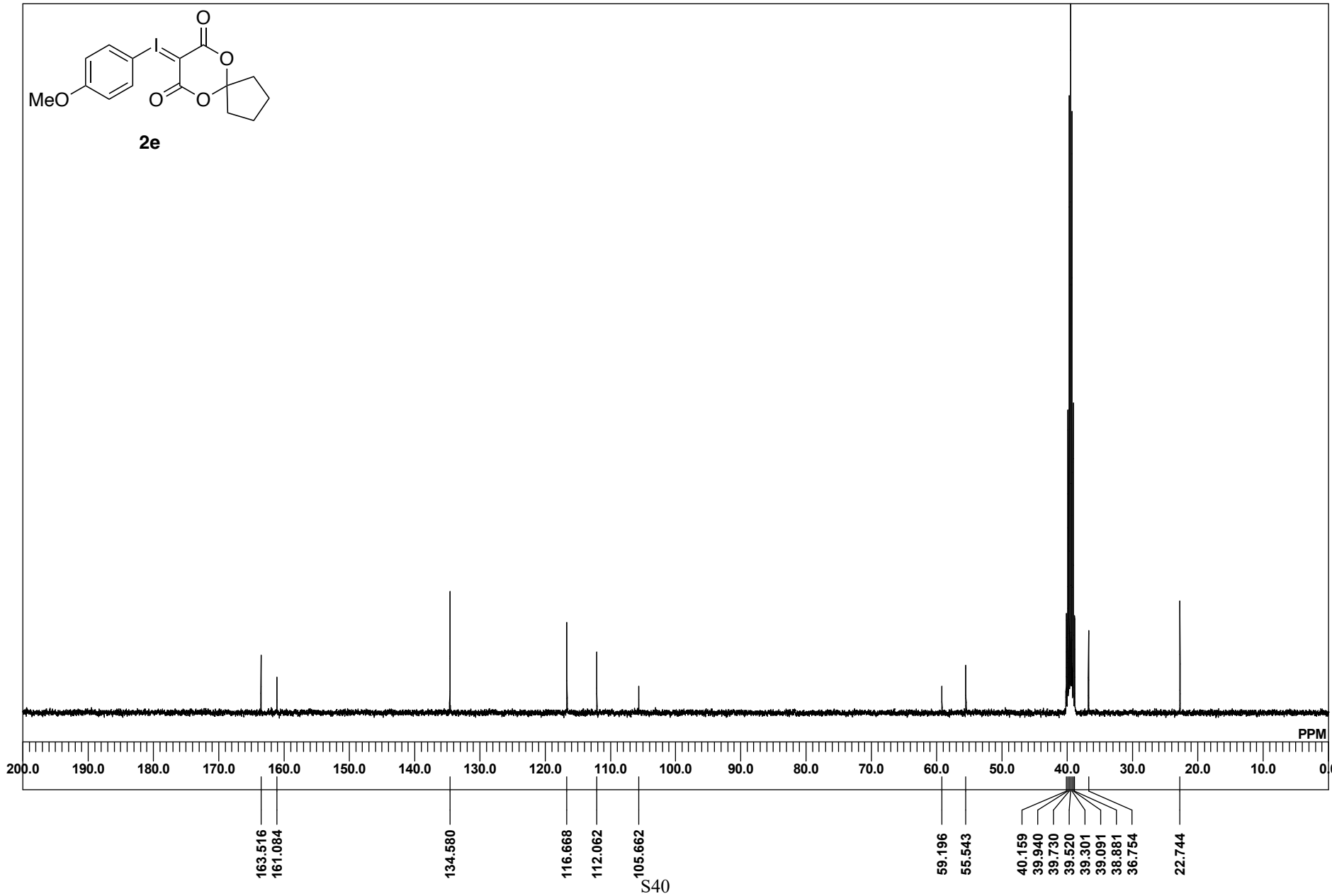
^1H NMR spectrum of **2e**



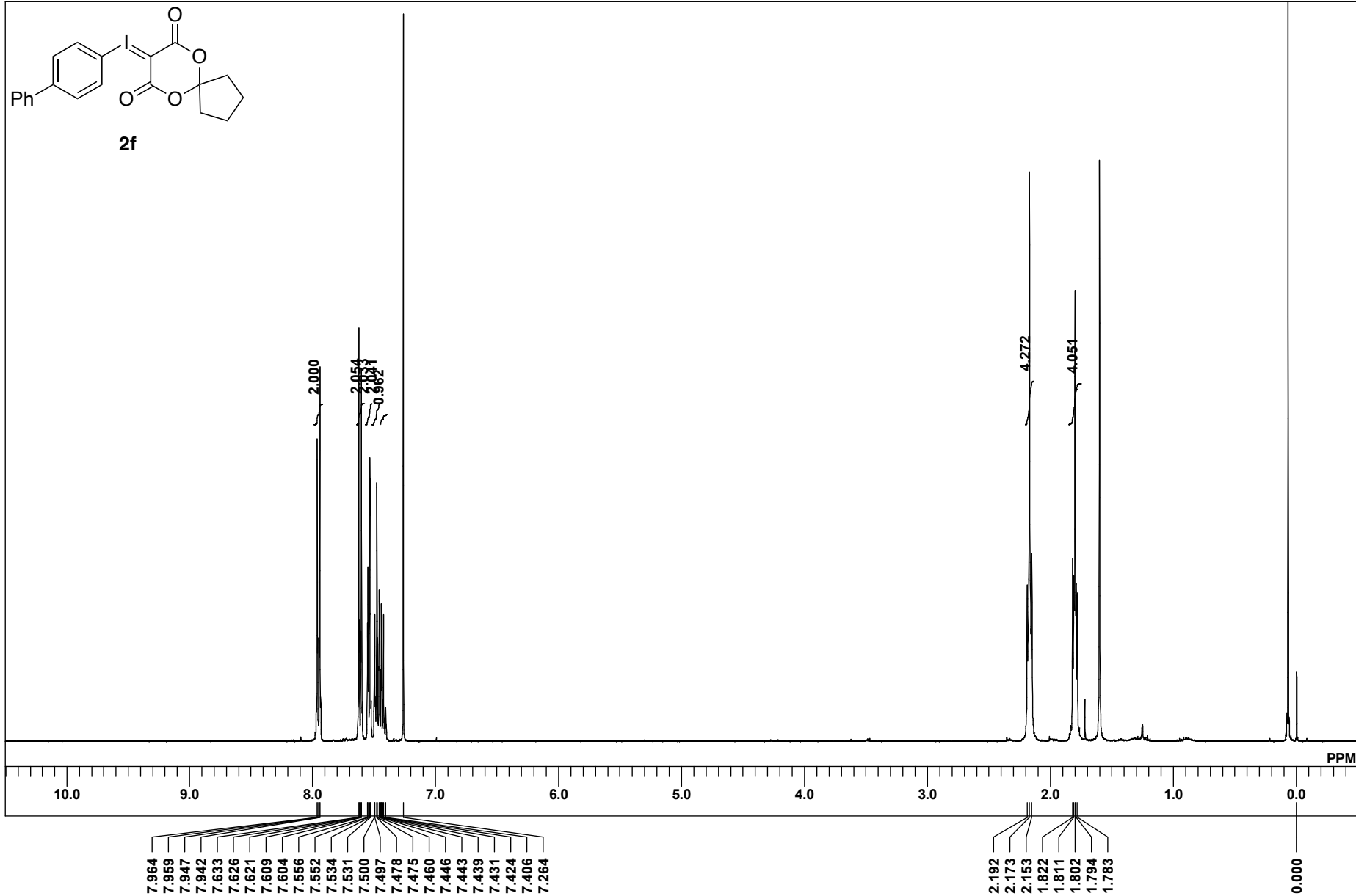
^{13}C NMR spectrum of **2e**



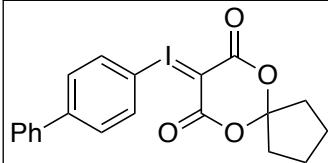
2e



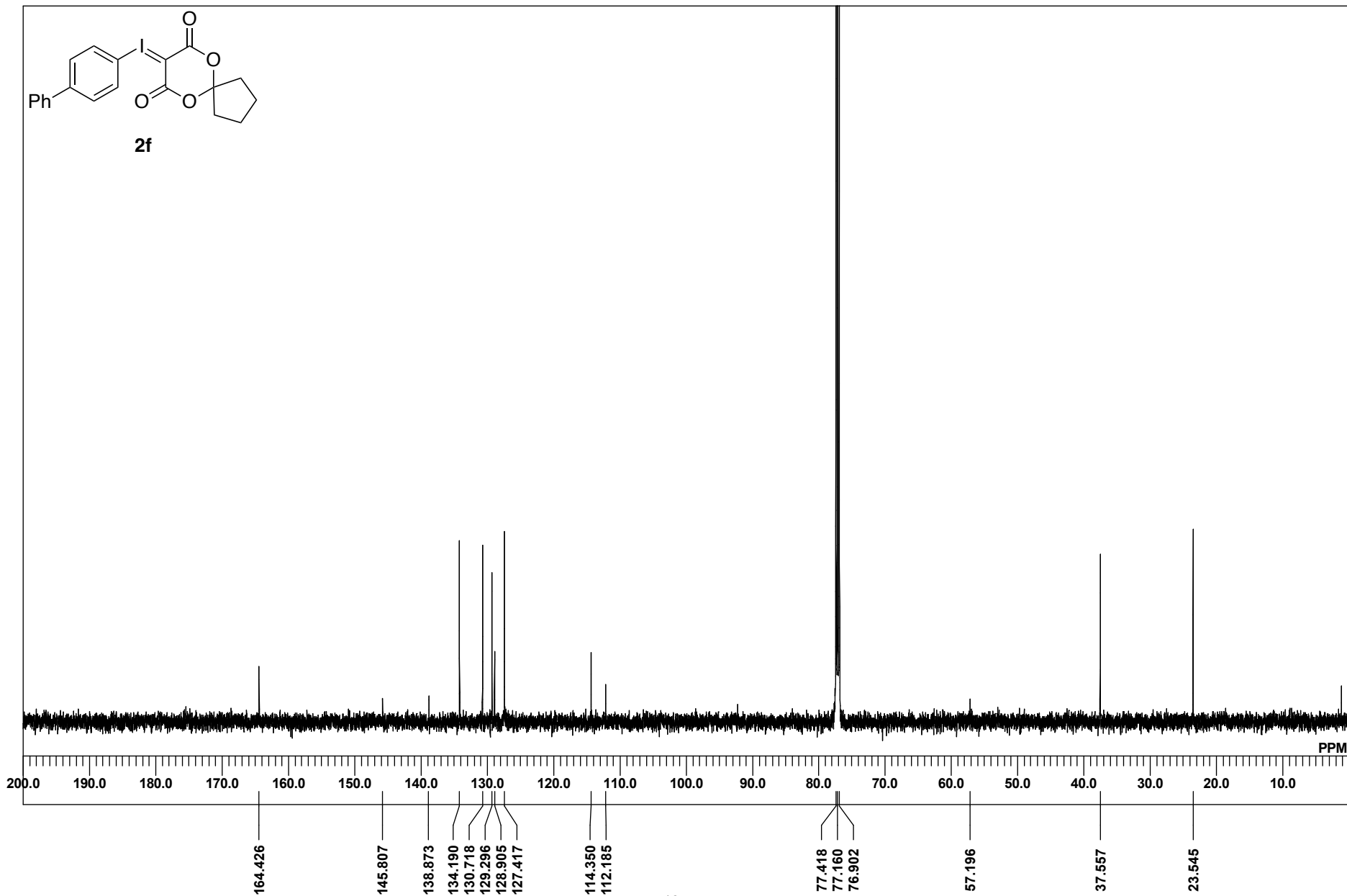
^1H NMR spectrum of **2f**



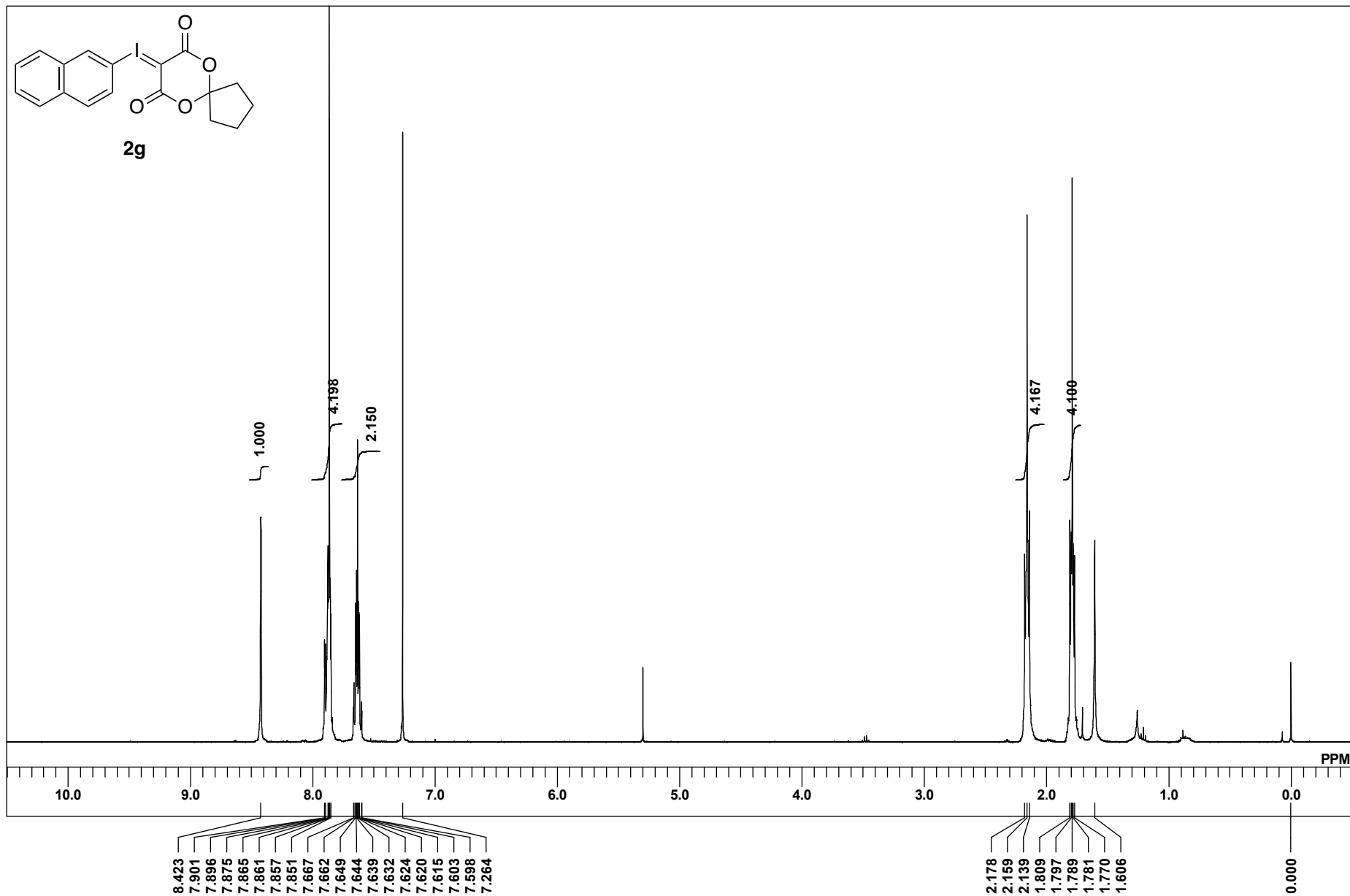
^{13}C NMR spectrum of **2f**



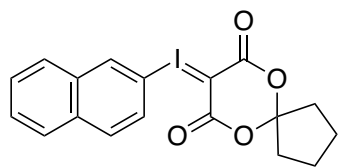
2f



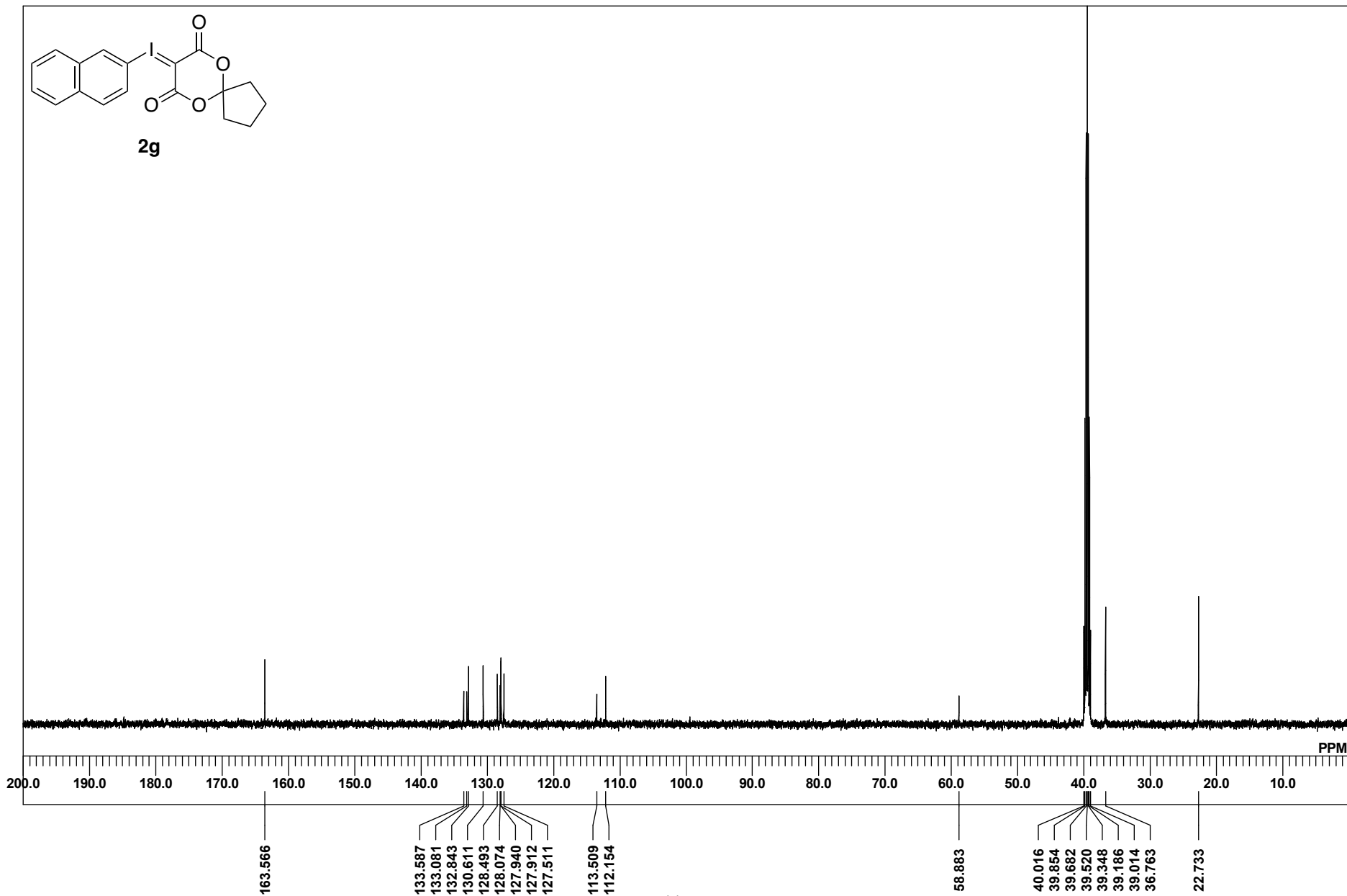
^1H NMR spectrum of **2g**



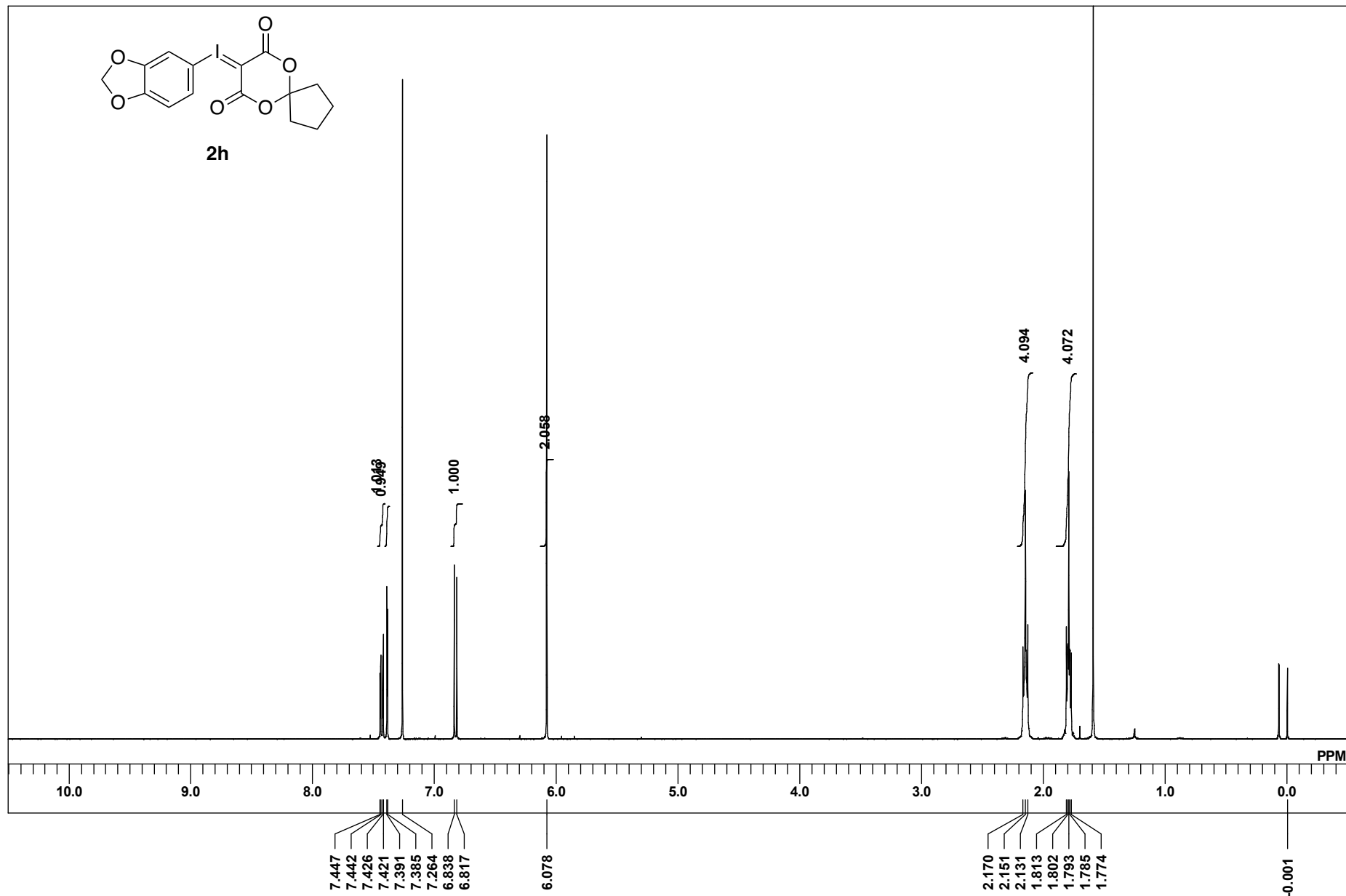
¹³C NMR spectrum of **2g**



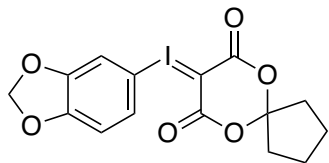
2g



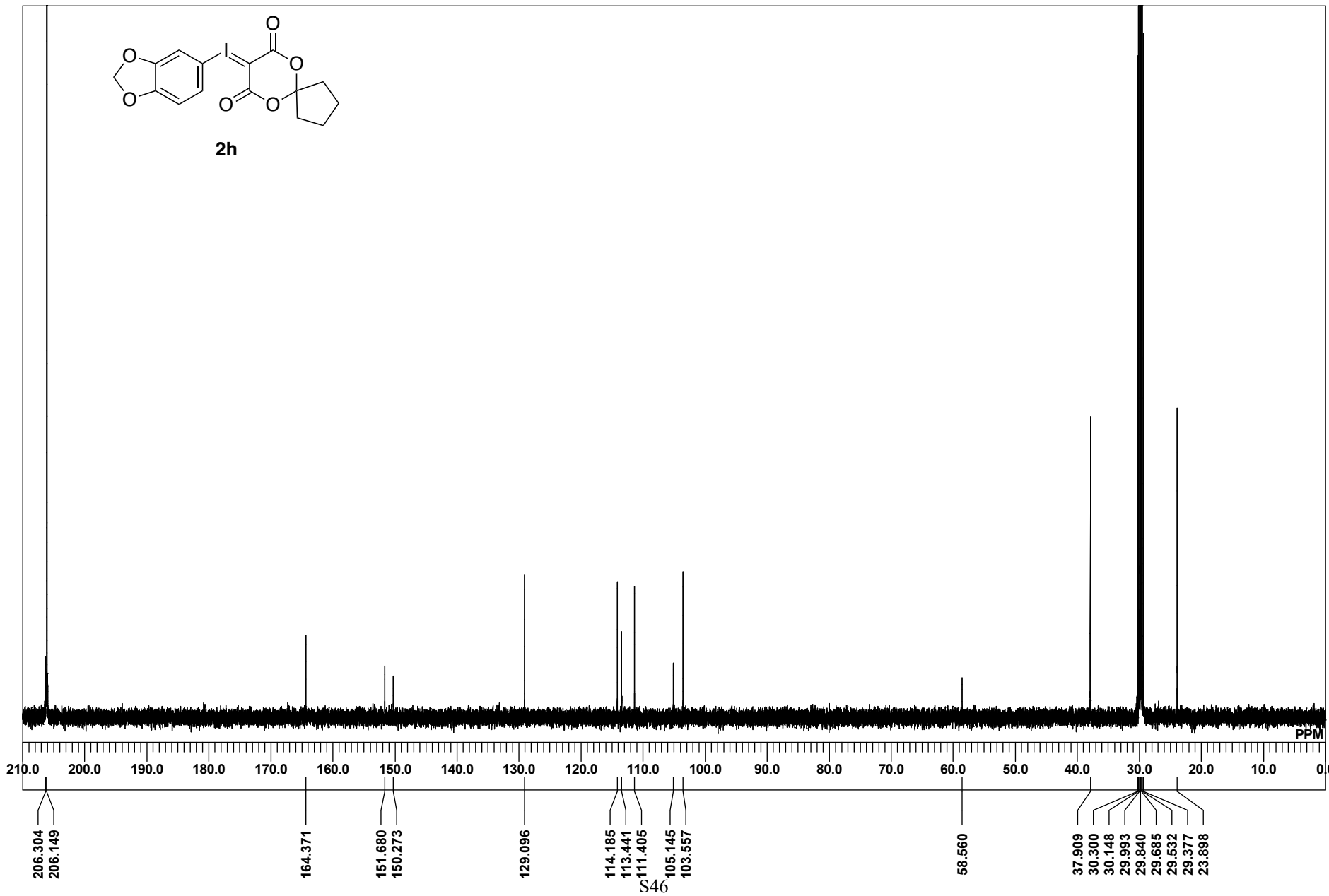
¹H NMR spectrum of **2h**



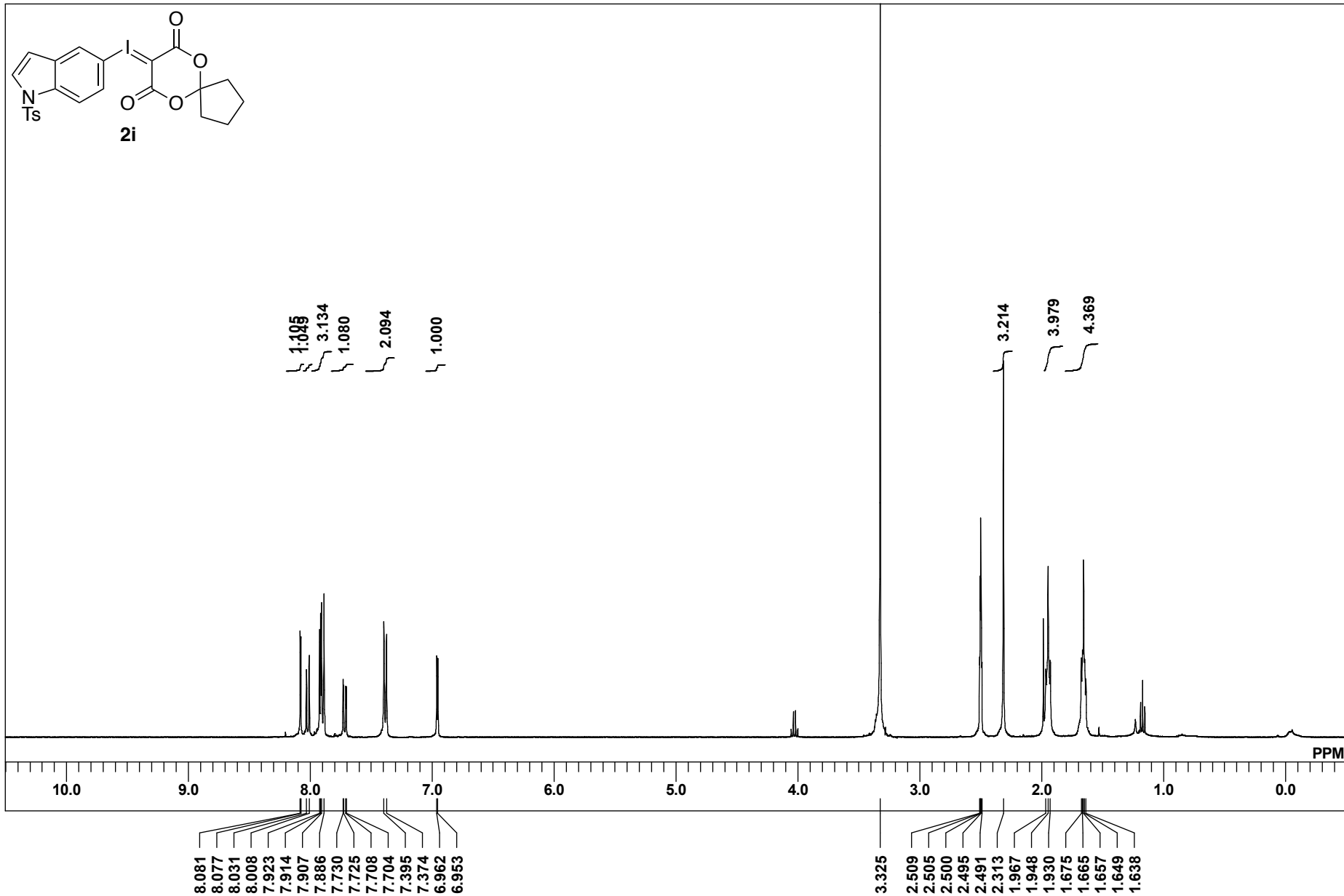
¹³C NMR spectrum of **2h**



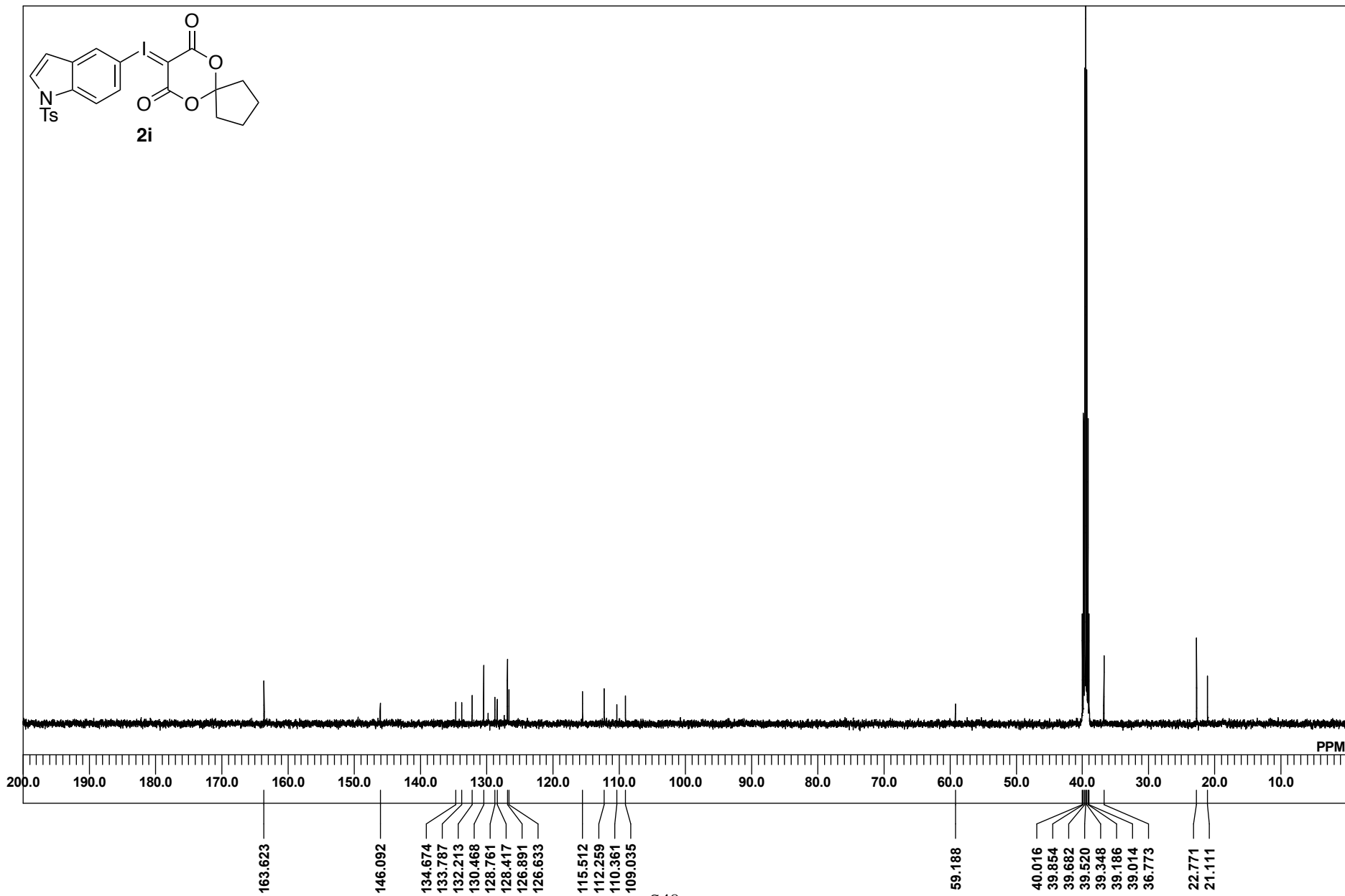
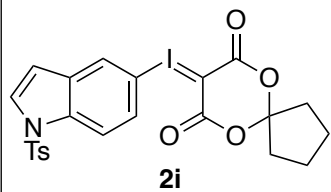
2h



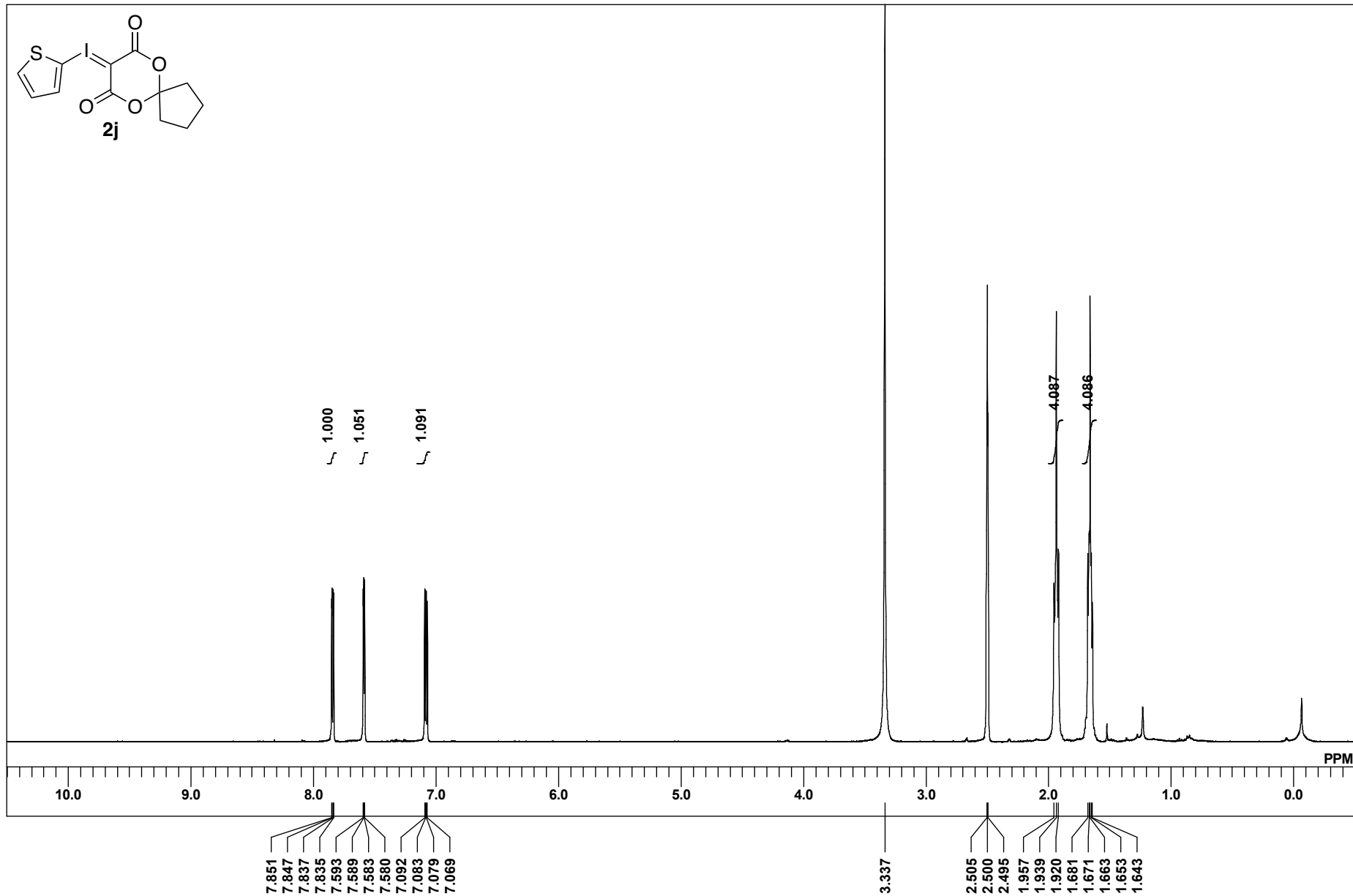
¹H NMR spectrum of **2i**



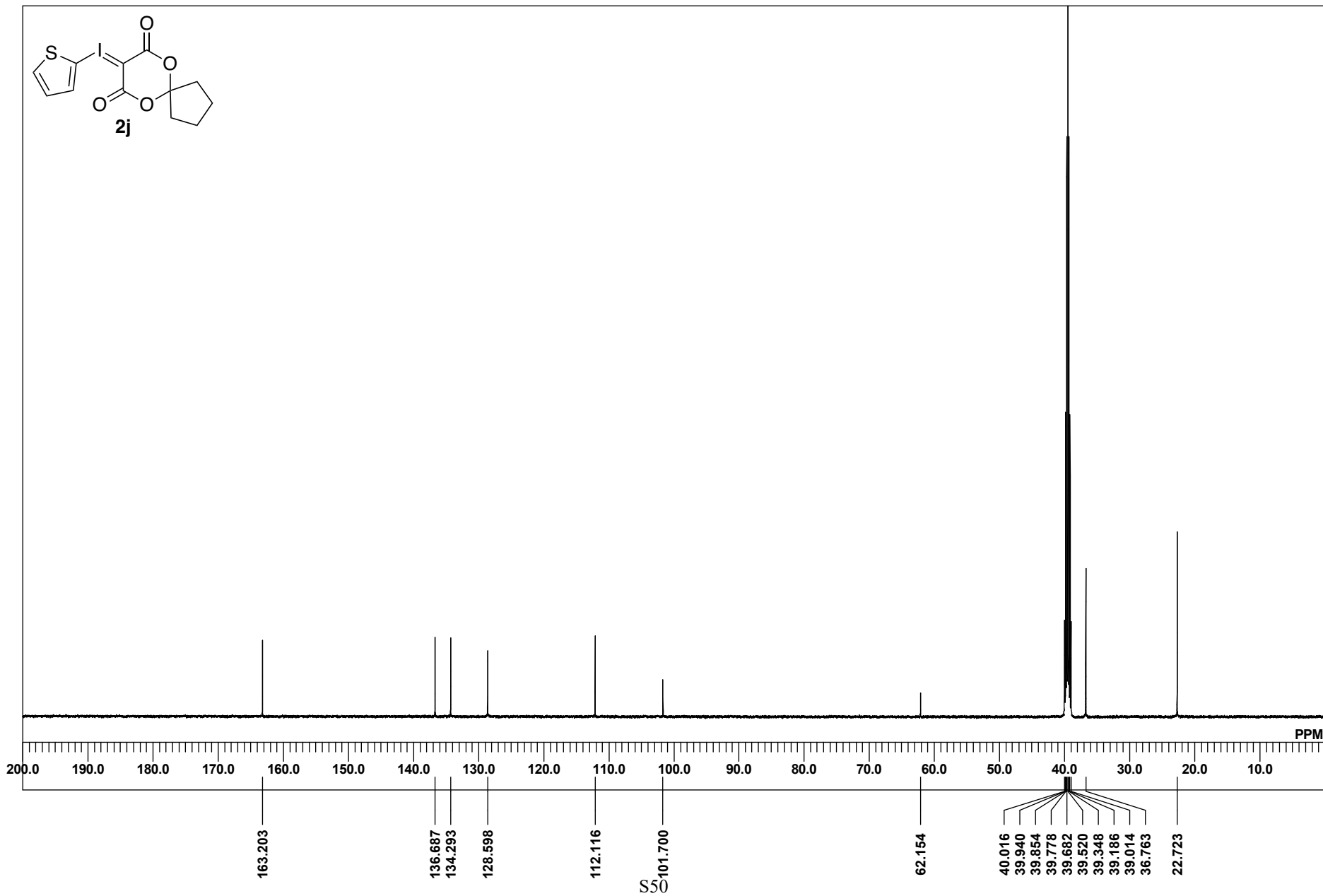
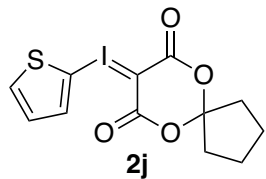
^{13}C NMR spectrum of **2i**



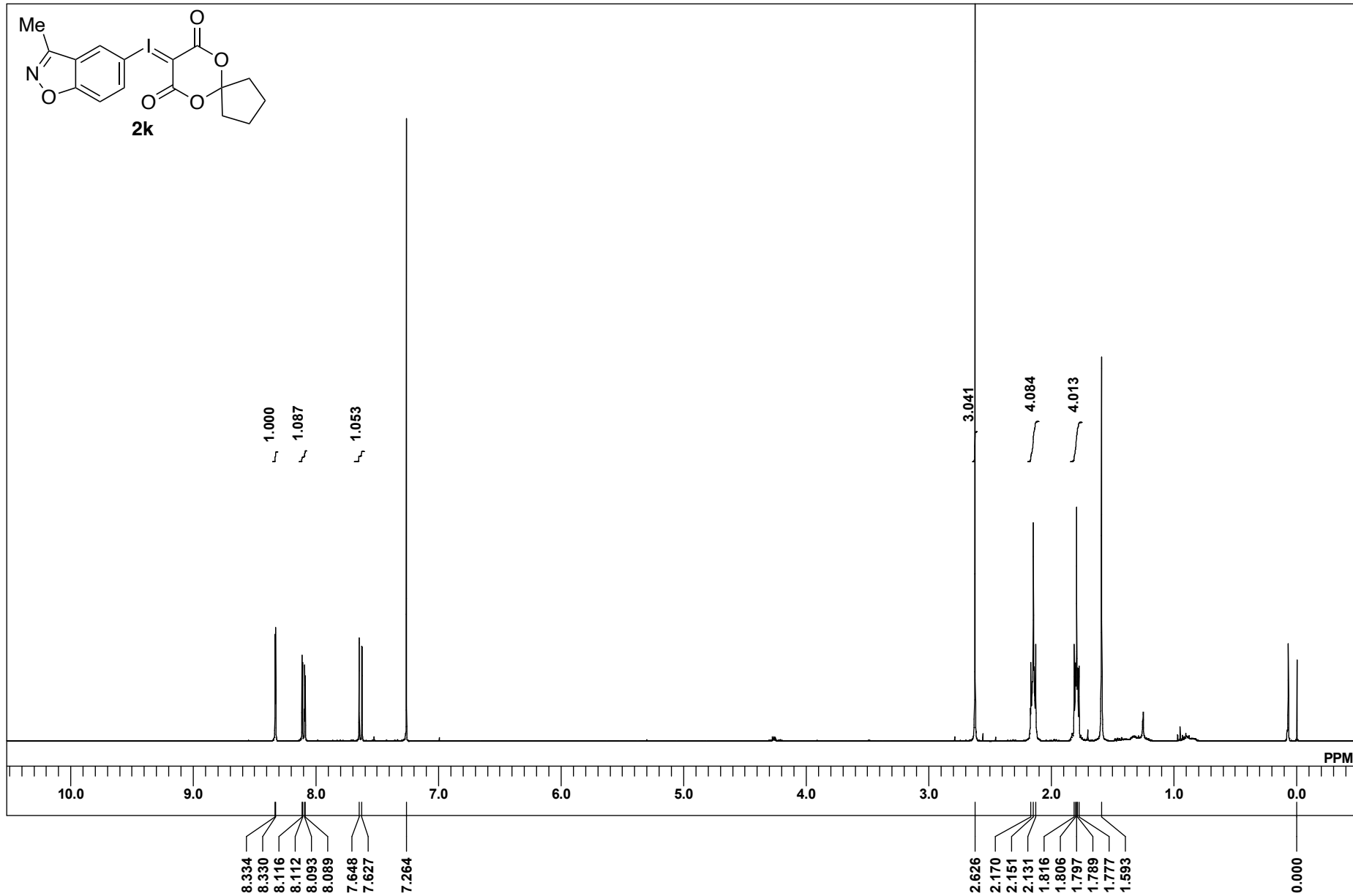
^1H NMR spectrum of **2j**



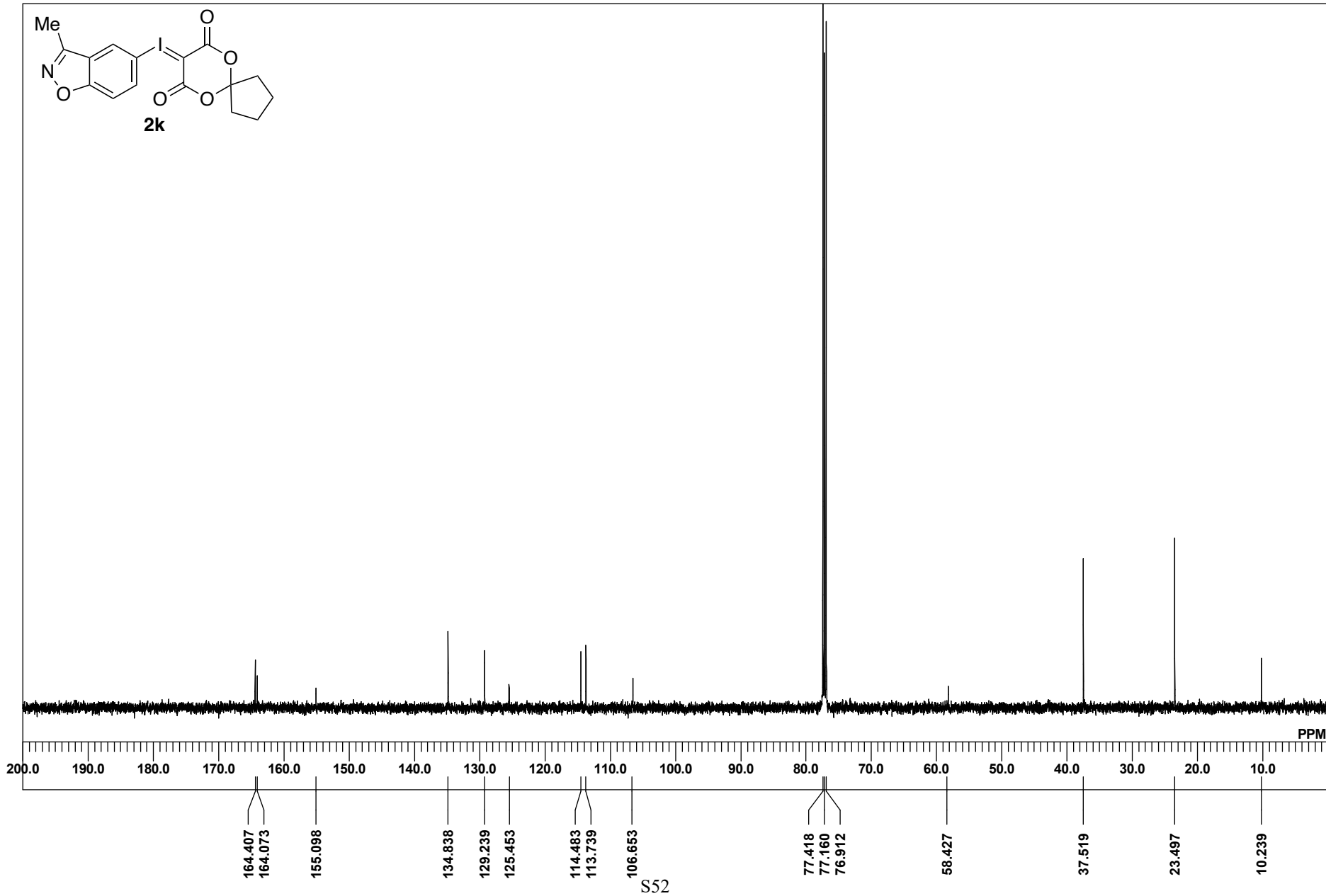
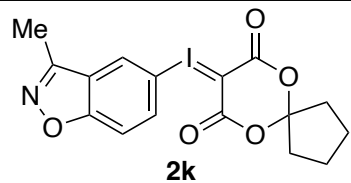
^{13}C NMR spectrum of **2j**



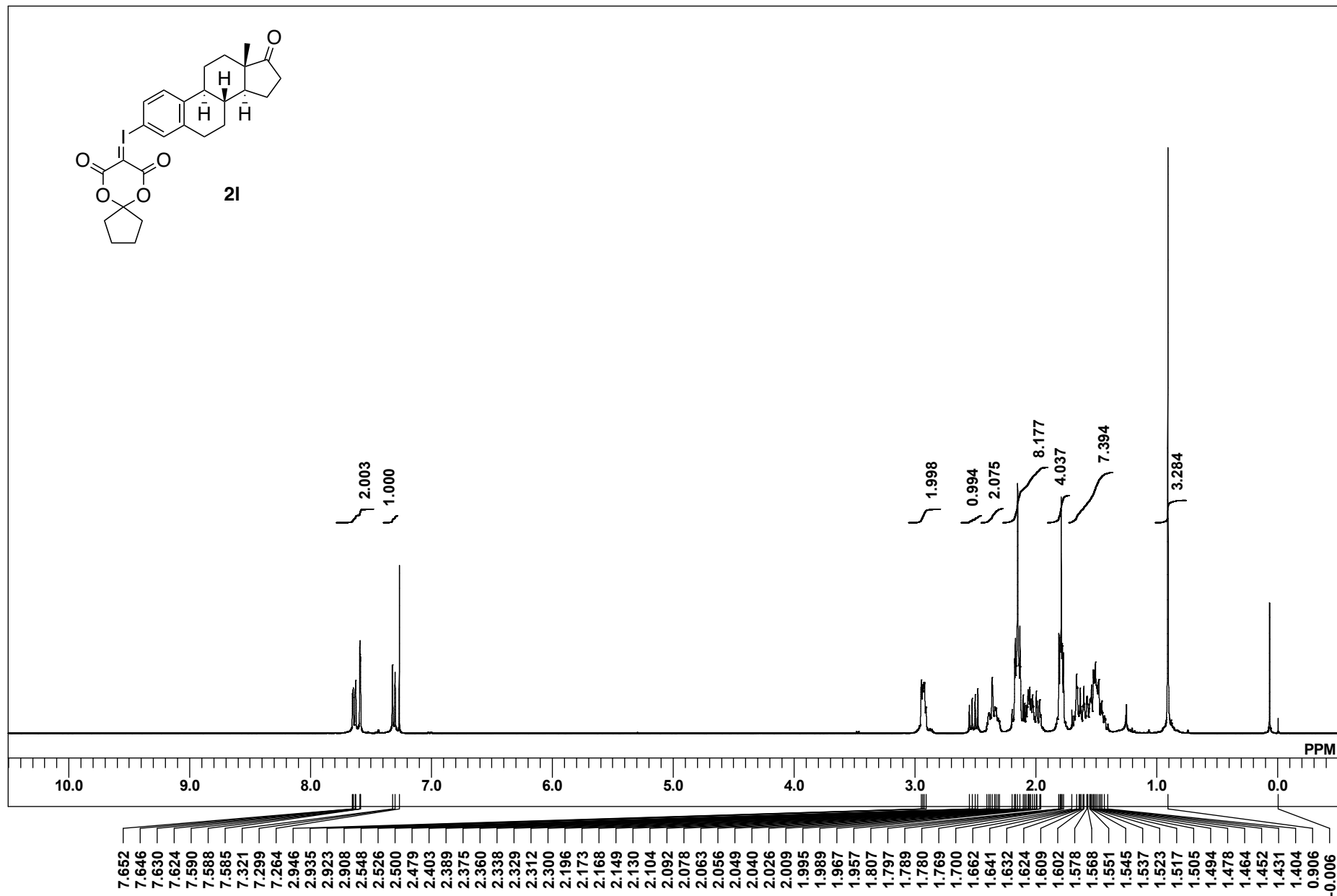
¹H NMR spectrum of **2k**



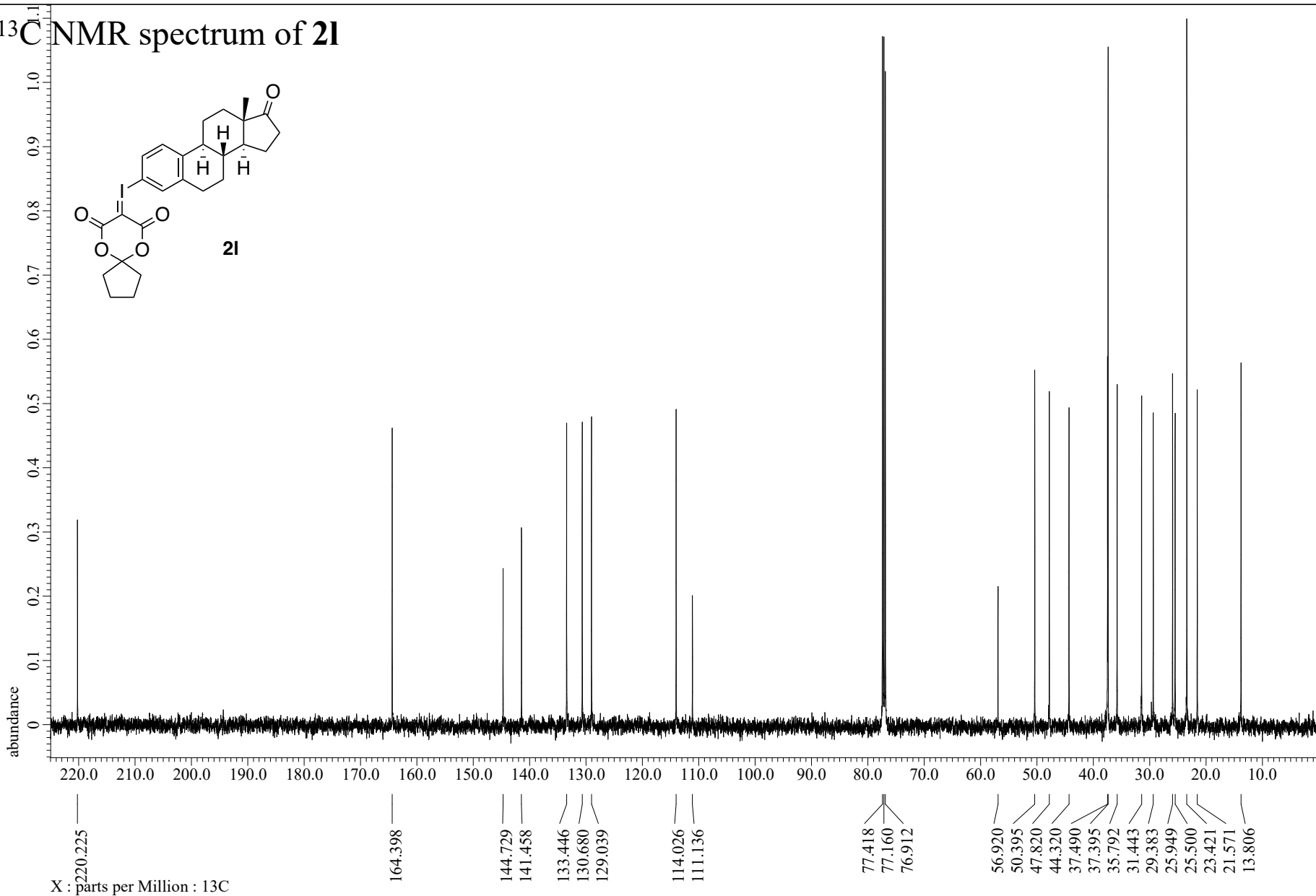
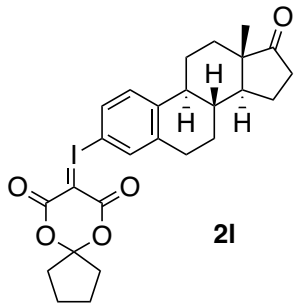
^{13}C NMR spectrum of **2k**



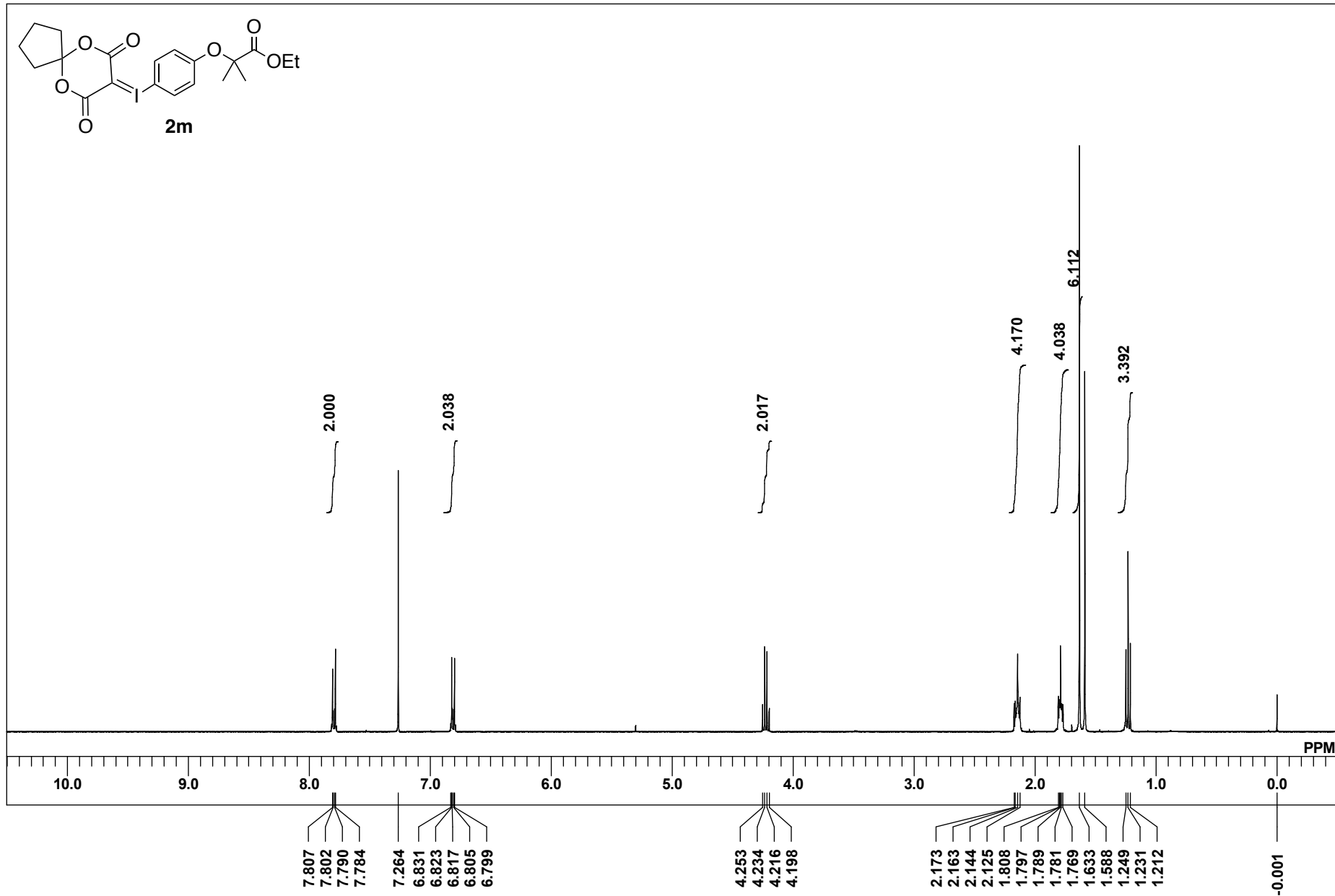
^1H NMR spectrum of **21**



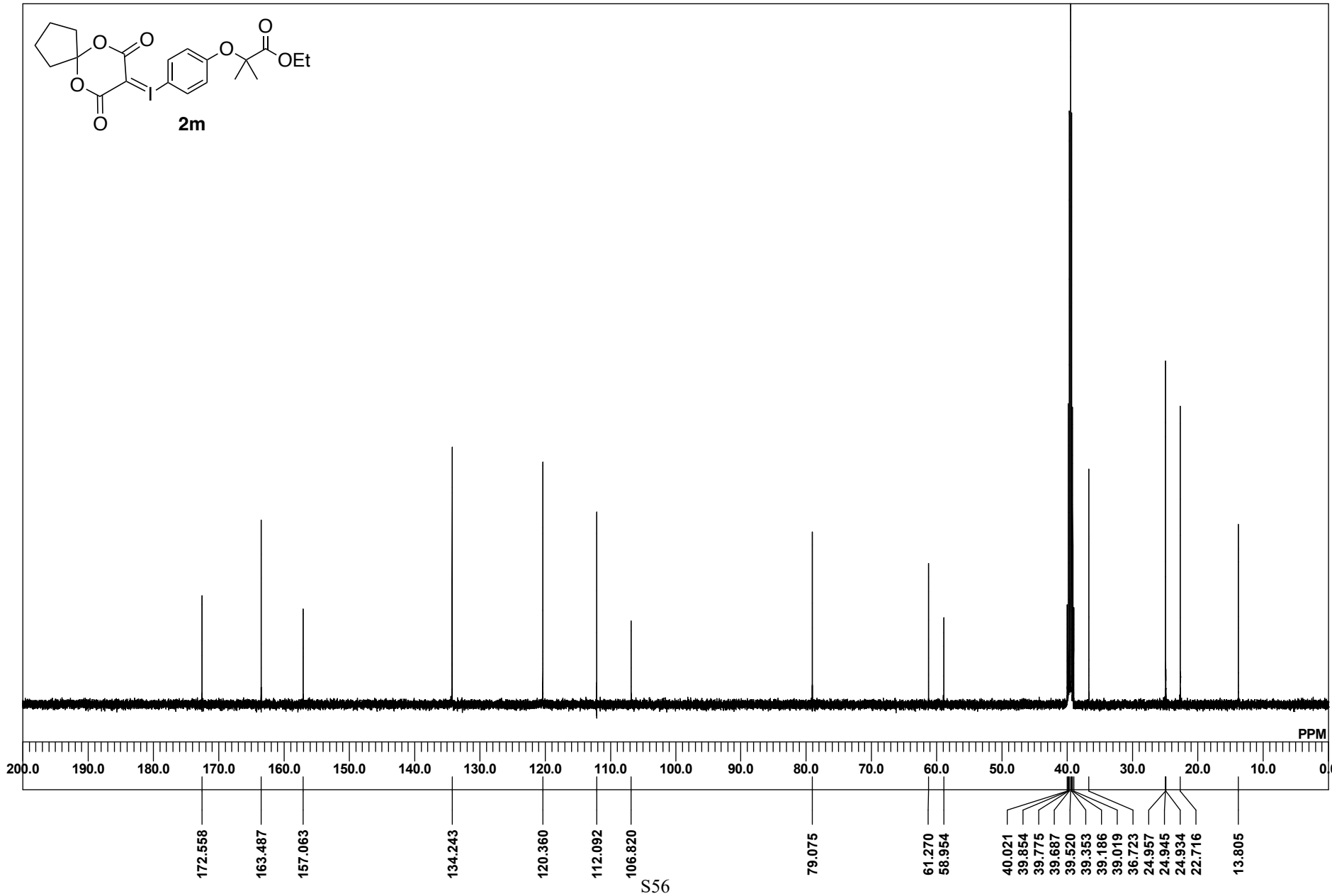
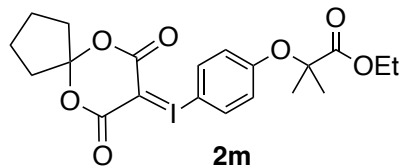
¹³C NMR spectrum of 21



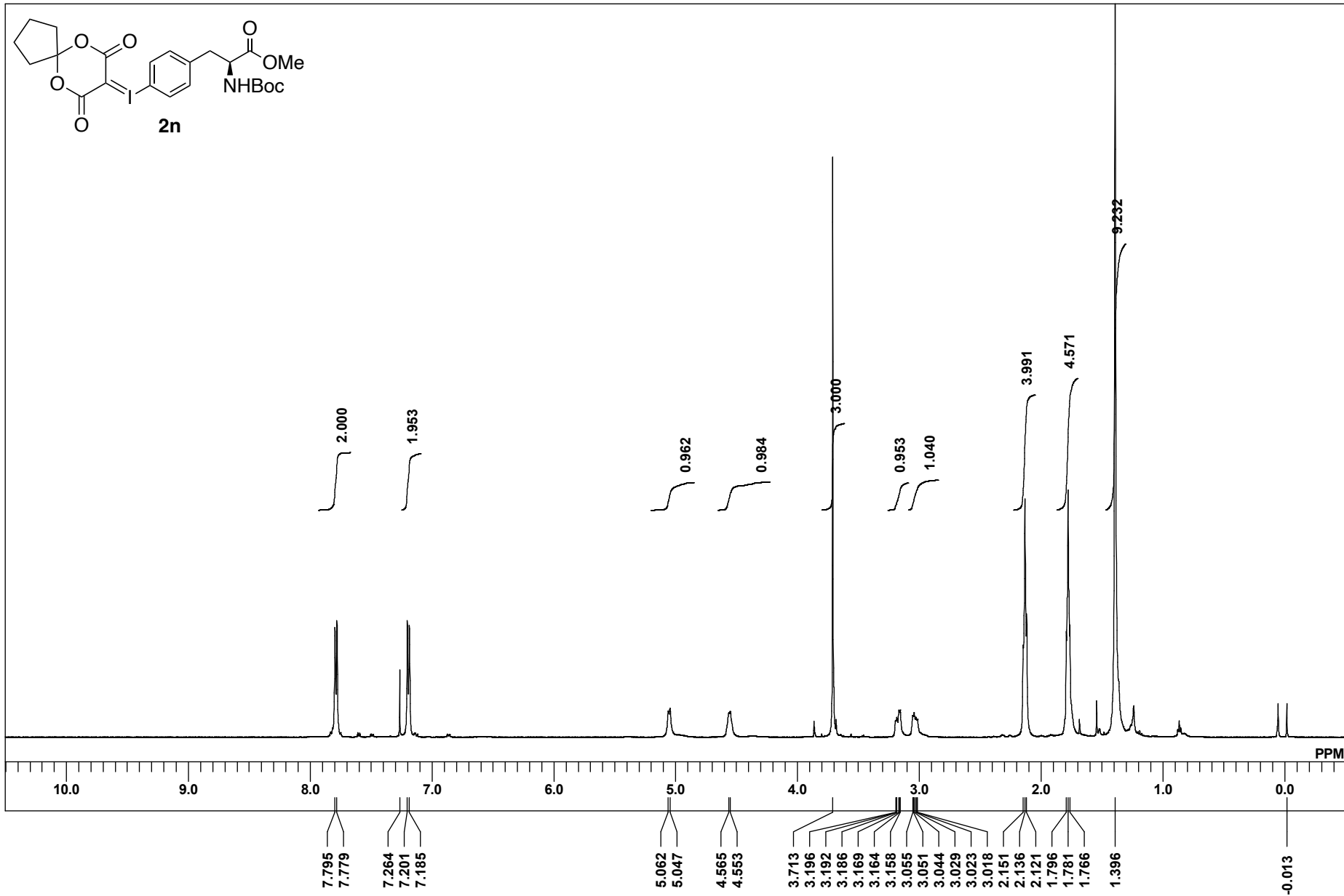
¹H NMR spectrum of **2m**



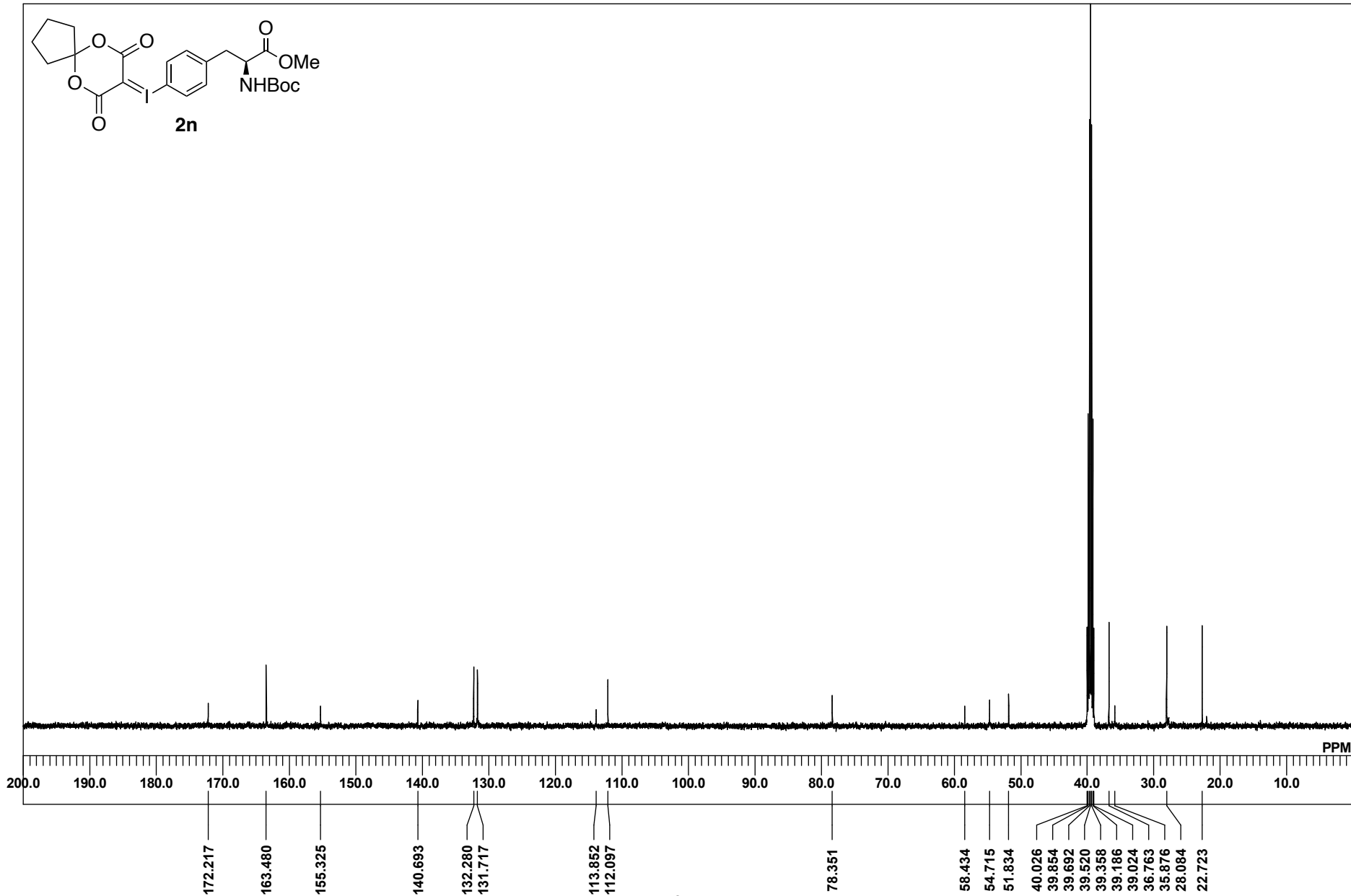
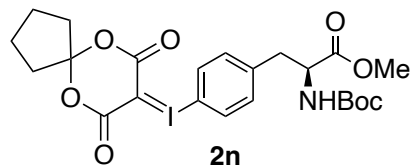
¹³C NMR spectrum of 2m



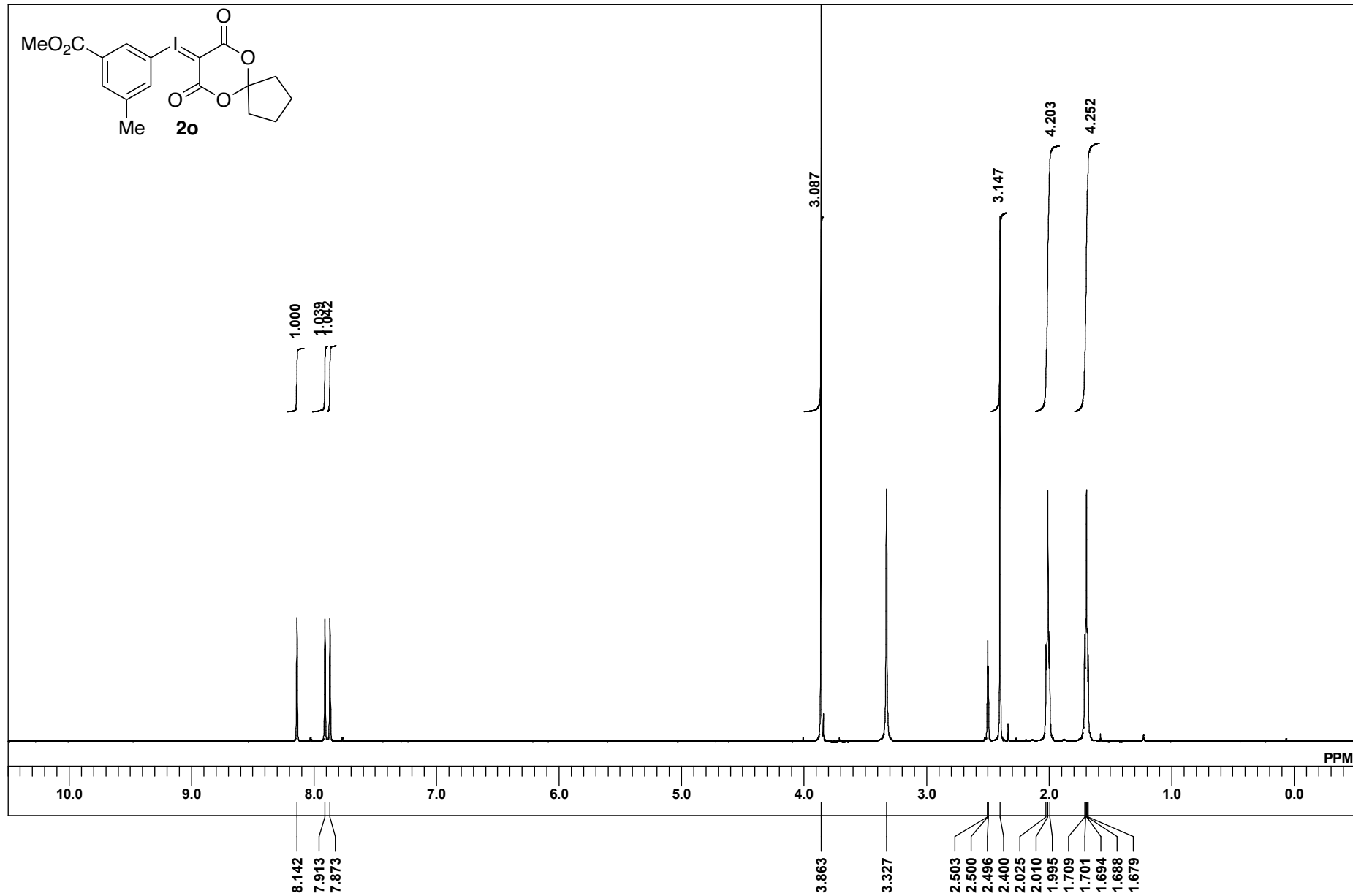
^1H NMR spectrum of **2n**



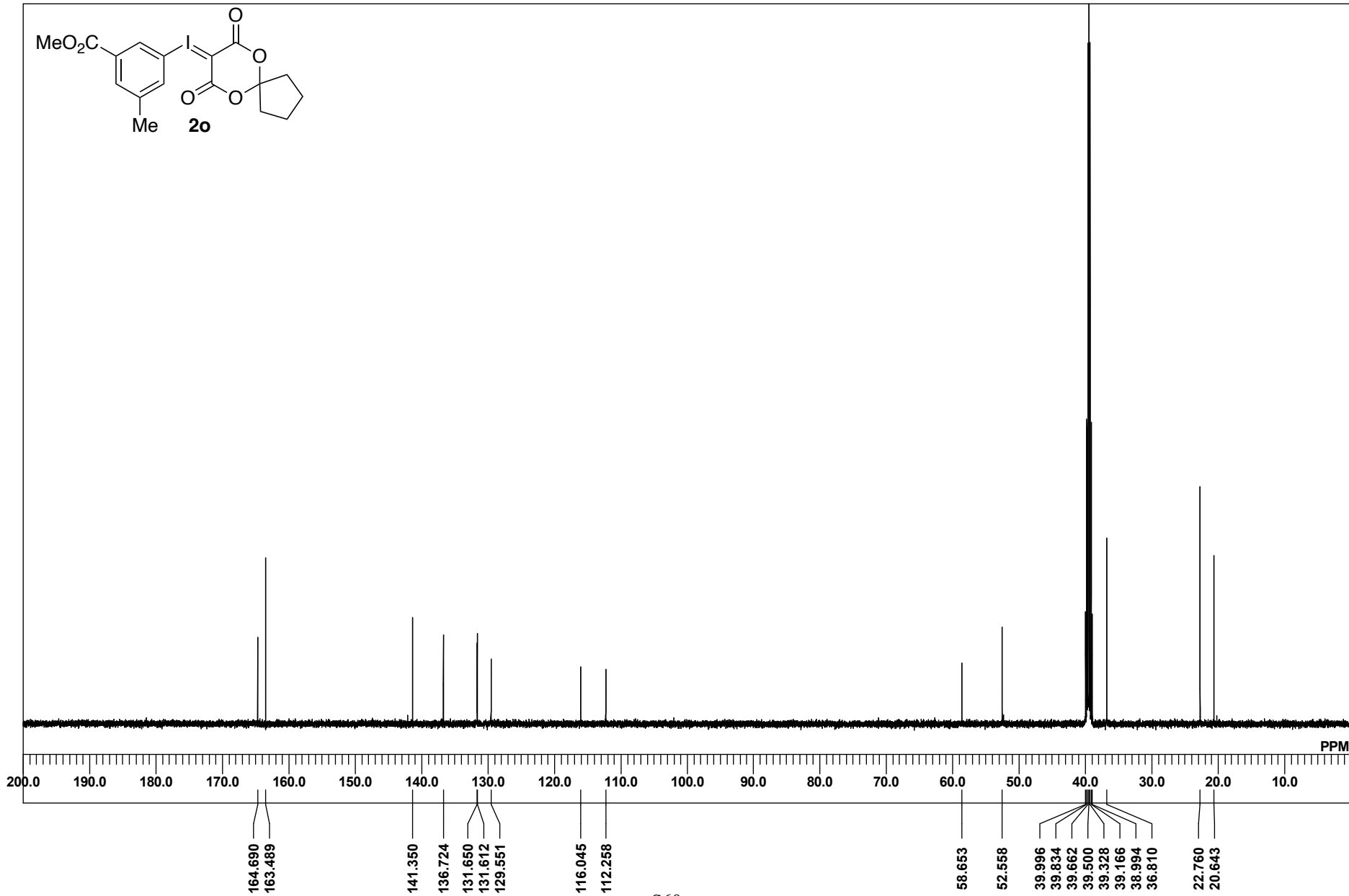
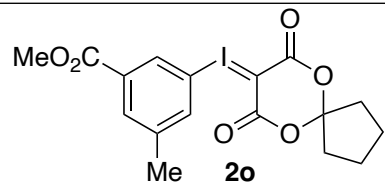
¹³C NMR spectrum of **2n**



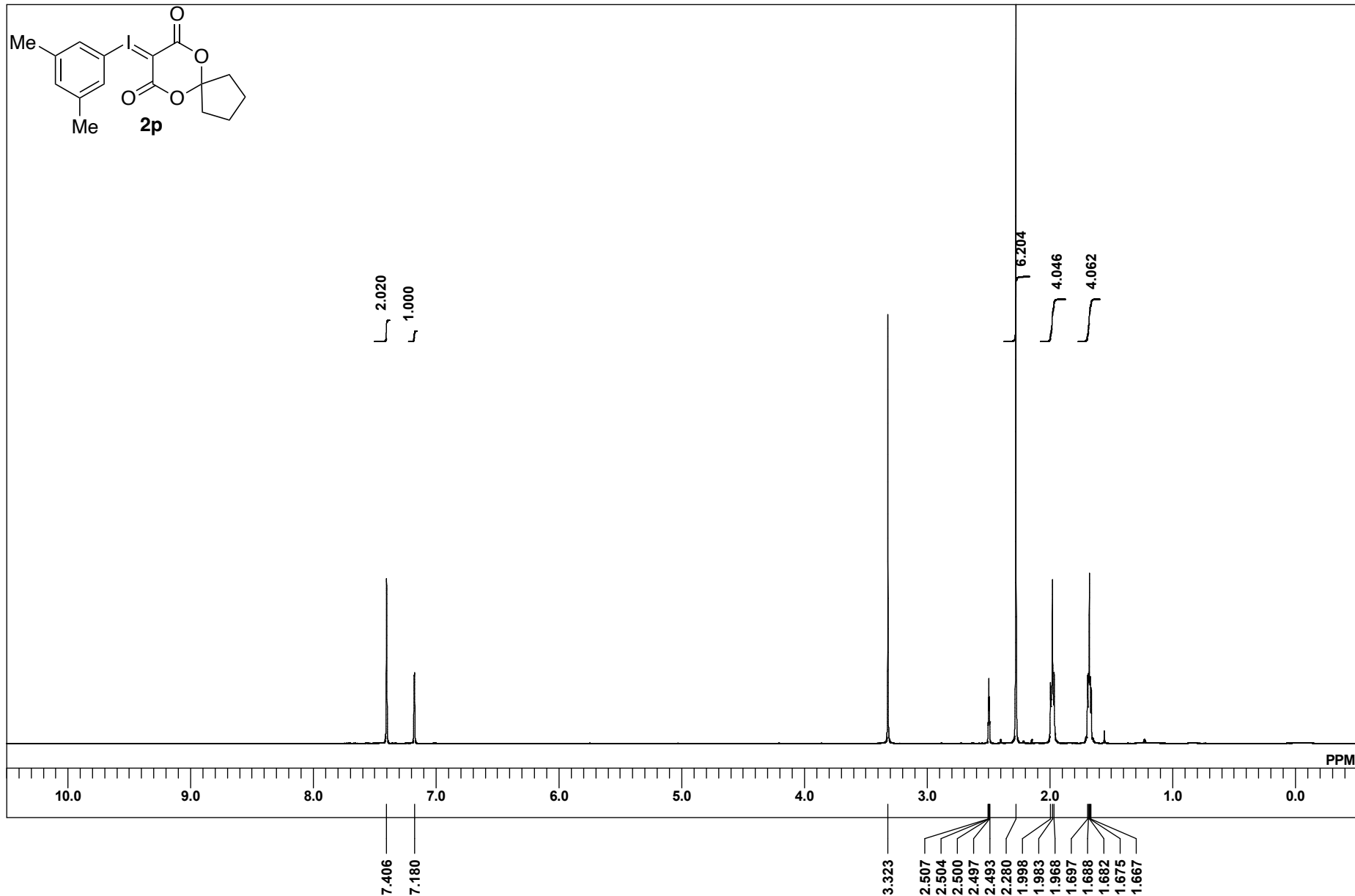
¹H NMR spectrum of **2o**



^{13}C NMR spectrum of **2o**



^1H NMR spectrum of **2p**



^{13}C NMR spectrum of **2p**

