

Supporting Information

2-Iodoxybenzoic acid ditriflate: the most powerful hypervalent iodine(V) oxidant

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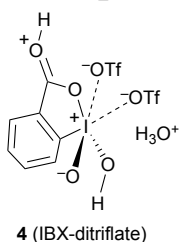
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1. General experimental remarks

All precursors, and other reagents and solvents were from commercial sources and used without further purification from freshly opened containers. Dichloromethane and acetonitrile were distilled from CaH₂ immediately prior to use. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. NMR spectra were recorded at the 300, 400 MHz, and 500 MHz spectrometers. Chemical shifts (δ) are reported in parts per million.

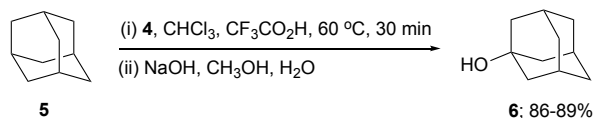
2. Preparation of 2-iodoxybenzoic acid triflate



To a suspension of 2-iodoxybenzoic acid **1** (1.4 g, 5 mmol) in dichloromethane (20 mL), trifluoromethanesulfonic acid (1 mL, 11.3 mmol) was added dropwise at 0 °C resulting in formation of a pale-yellow semisolid substance. Then trifluoroacetic acid (0.3 mL, 1.8 mmol) was added under stirring. Stirring was continued for 4 hours until the pale-yellow semisolid substance turned into a white precipitate. The precipitate was filtered and washed with dry dichloromethane (3x10 mL). The product was dried in vacuum to give IBX-ditriflate **4**, 2.4-2.8 g (80-94%) as a white, moderately hygroscopic solid: mp 110-112 °C; ¹H NMR (400 MHz, CD₃CN): δ 10.37 (broad s), 8.44 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 7.6 Hz, 1H), 8.28 (t, J = 8.0 Hz, 1H), 8.03 (t, J = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CD₃CN): δ 172.9, 146.7, 138.2, 136.1, 133.3, 126.5, 125.4, 121.1 (q, J = 317 Hz, CF₃SO₃⁻); ¹⁹F NMR (376 MHz, CD₃CN): δ -79.58; HRMS (ESI-TOF-positive mode): calcd for C₇H₆IO₄ ([M-HOTf-OTf])⁺: 280.9305, found: 280.9304. Anal. Calcd for C₉H₁₁F₆IO₁₂S₂ (4 x H₂O): C, 17.54; H, 1.80; I, 20.60; S, 10.41. Found: C, 17.59; H, 1.78; I, 20.50; S, 10.32.

Single crystals of product **4** suitable for X-ray crystallographic analysis were obtained by slow crystallization from solution in CH₂Cl₂/CF₃CO₂H. X-ray diffraction data for **4** were collected on Rigaku RAPID II Image Plate system using graphite-monochromated CuK α radiation ($\lambda = 1.54187 \text{ \AA}$) at 123 K. The structure was solved by the Patterson method (SHELXS 86) and refined by full-matrix least-squares refinement on F² using Crystals for Windows program. Crystal data for **4** C₉H₉F₆I₁O₁₁S₂: M 598.19, monoclinic, space group P21/n, a = 15.4493(5), b = 5.7324(2), c = 20.1514(14) \AA , $\beta = 97.086(7)^\circ$, V = 1771.01(12) \AA^3 , Z = 4, $\mu = 17.569 \text{ mm}^{-1}$, 8356 reflections measured, 2811 unique; final R₁ = 0.0953, R_w = 0.2256. CCDC 1908422.

3. Oxidation of adamantane

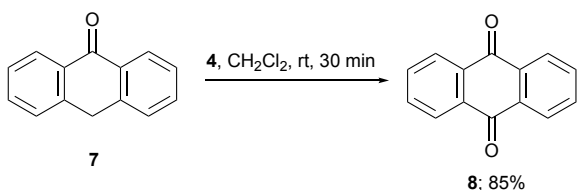


Method A. A mixture of adamantane **5** (136 mg, 1 mmol), IBX-ditriflate **4** (657 mg, 1.1 mmol), chloroform (3 mL) and trifluoroacetic acid (0.5 mL, 3 mmol) was heated at 60 °C for 30 min until full conversion of adamantane **5** (according to GC-MS). Then sodium hydroxide (0.4 g, 10 mmol) and methanol (5 mL) were added and the resulting mixture was stirred for 1 hour. Water (5 mL) was added to the reaction mixture and the organic product was extracted with dichloromethane (3x5 mL). Organic layer was dried over Na₂SO₄, solvent was removed under reduced pressure. The product was dried in vacuum to give 1-adamantanol **6** as a white solid (131 mg, 86%), mp 249-251 °C (sublm) (lit.¹ mp >220 °C (sublm)); ¹H NMR (300 MHz, CDCl₃) δ 2.13 (s, 3H), 1.70-1.54 (m, 13H). ¹³C NMR (100 MHz, CDCl₃) δ 68.4, 45.5, 36.2, 30.8.

Method B (with IBX-ditriflate **4** generated *in situ*). A mixture of adamantane **5** (136 mg, 1 mmol), IBX **1** (308 mg, 1.1 mmol), triflic acid (0.1 mL, 1.1 mmol), chloroform (3 mL),

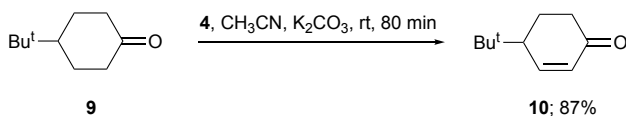
trifluoroacetic acid (0.5 mL) was heated at 60 °C for 30 min. 1-Adamantanol **6** was isolated according to method **A** as a white solid (136 mg, 89%).

4. Oxidation of anthracen-9(10H)-one



Reagent IBX-ditriflate **4** (194 mg, 0.32 mmol) was added to the solution of anthracen-9(10H)-one **7** (49 mg, 0.25 mmol) in CH₂Cl₂ (5 mL) and stirred for 30 minutes at room temperature. Reaction was monitored by TLC (eluent hexane:EtOAc 9:1). Reaction mixture was diluted with water and extracted with dichloromethane (3x15 mL). Organic layer was washed with an aqueous solution of NaHCO₃ and dried over Na₂SO₄. Solvent was removed under reduced pressure. The product was dried under reduced pressure to give anthraquinone **8** as a grey solid (44 mg, 85%), mp 289-290 °C (lit.² mp 287-288 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24-8.21 (m, 4H), 7.99-7.91 (m, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 182.6, 134.7, 133.1, 126.8.

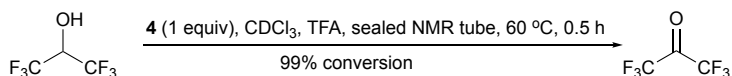
5. Oxidation of 4-(tert-butyl)-cyclohexan-1-one³



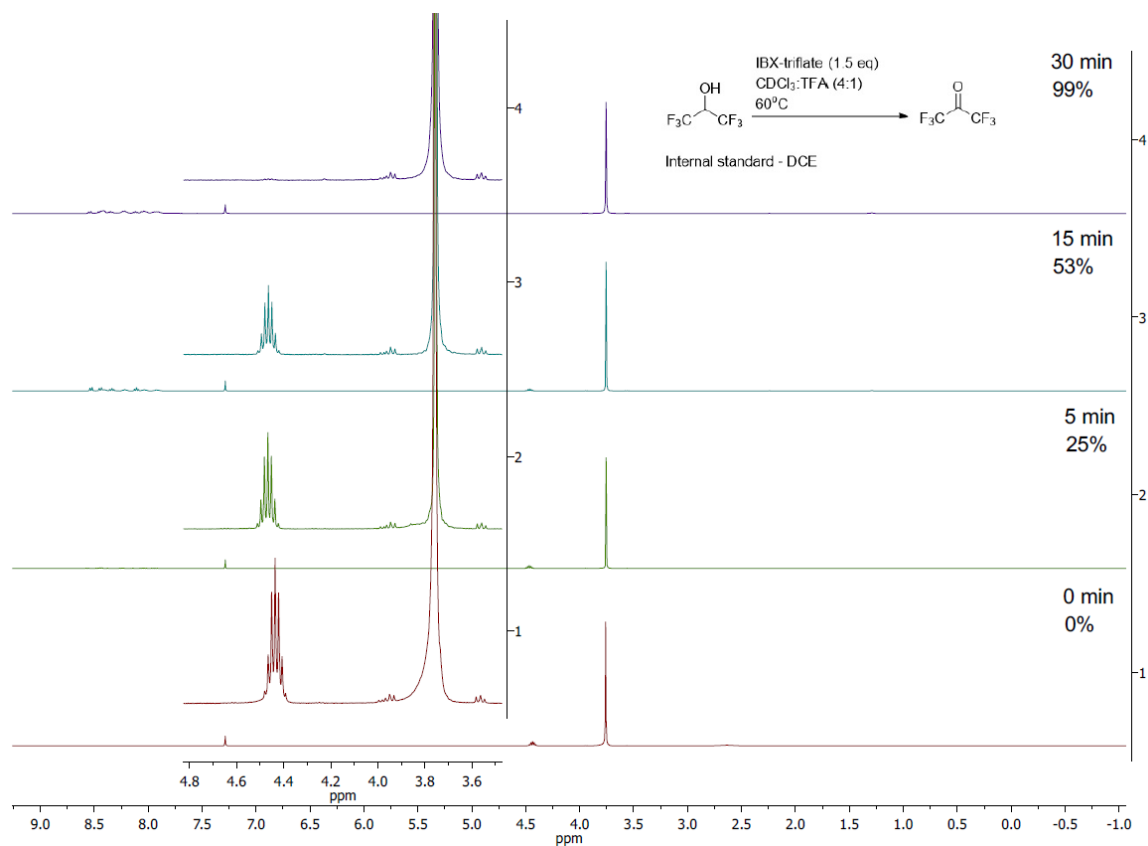
Reagent IBX-ditriflate **4** (194 mg, 0.32 mmol) was added to a stirred mixture of 4-(tert-butyl)-cyclohexan-1-on **9** (38 mg, 0.25 mmol), K₂CO₃ (45 mg, 0.33 mmol), acetonitrile (1.5 mL). Reaction mixture was stirred for 80 min at room temperature. Reaction was monitored by TLC (eluent hexane: EtOAc 9:1, 2,4-dinitrophenylhydrazine

stain). Reaction mixture was diluted with water and extracted with dichloromethane (3x15 mL). Organic layer was washed with an aqueous solution of NaHCO₃ and dried over Na₂SO₄. The solvent was removed under reduced pressure. The product was purified by column chromatography on Silicagel (eluent hexane: EtOAc 9:1) to give the 4-(*tert*-butyl)-cyclohex-2-en-1-one **10** as a colorless oil³ (33 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, *J* = 10.4 Hz, 1H), 6.03 (d, *J* = 10.4, 1H), 2.51 (d, *J* = 16.4 Hz, 1H), 2.37-2.28 (m, 1H), 2.19 (d, *J* = 11.2 Hz, 1H), 2.10-2.08 (m, 1H), 1.84-1.66 (m, 1H), 0.97 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 200.4, 153.3, 130.0, 47.0, 37.9, 33.0, 27.5, 24.5.

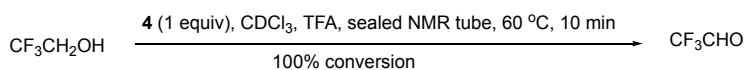
6. Oxidation of 1,1,1,3,3,3-hexafluoroisopropanol in NMR tube



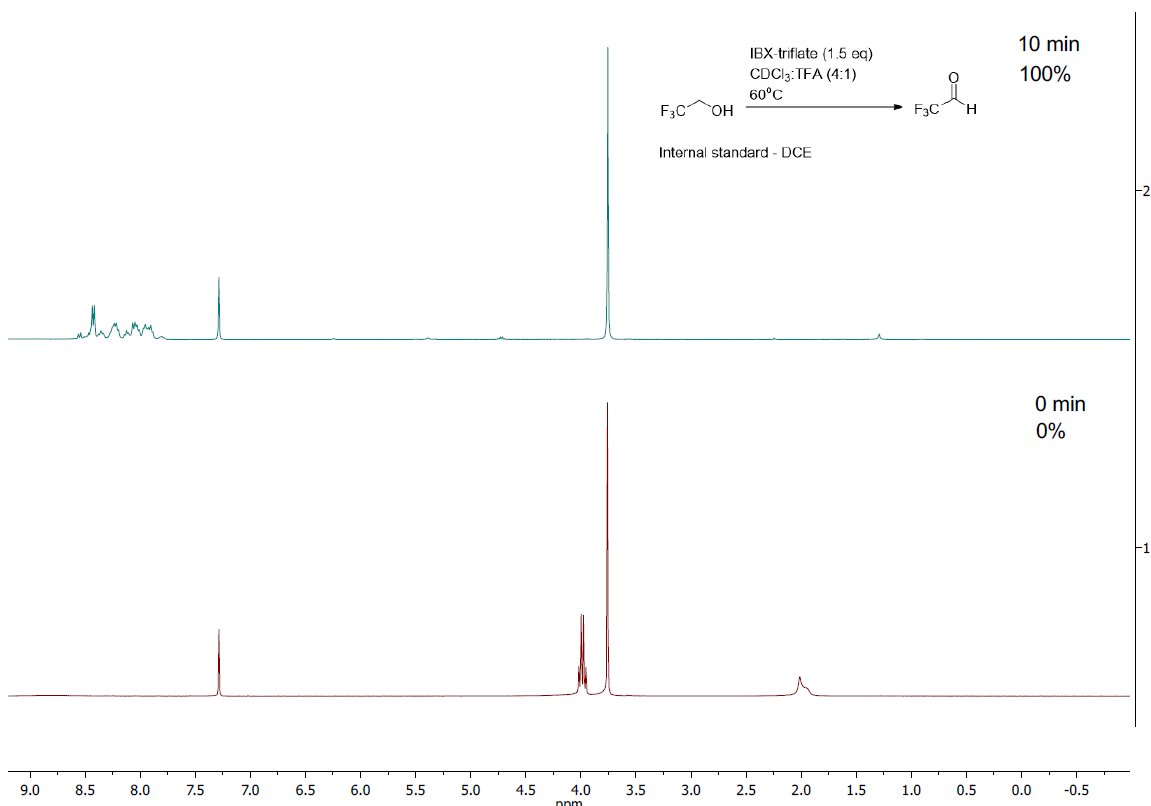
To a mixture of 2-iodoxybenzoic acid ditriflate **4** (24 mg, 0.040 mmol) in CDCl₃ (0.3 mL) in sealed NMR tube was added 0.26 M solution of hexafluoroisopropanol in CDCl₃ (0.1 mL, 0.026 mmol) and DCE as internal standard. After measuring initial ¹H NMR spectrum (0 min) trifluoroacetic acid (0.1 mL) was added to the reaction mixture in order to partially dissolve IBX-ditriflate **4** and initiate the reaction, and the reaction was heated at 60 °C. The progress of oxidation and conversion was monitored by ¹H NMR.



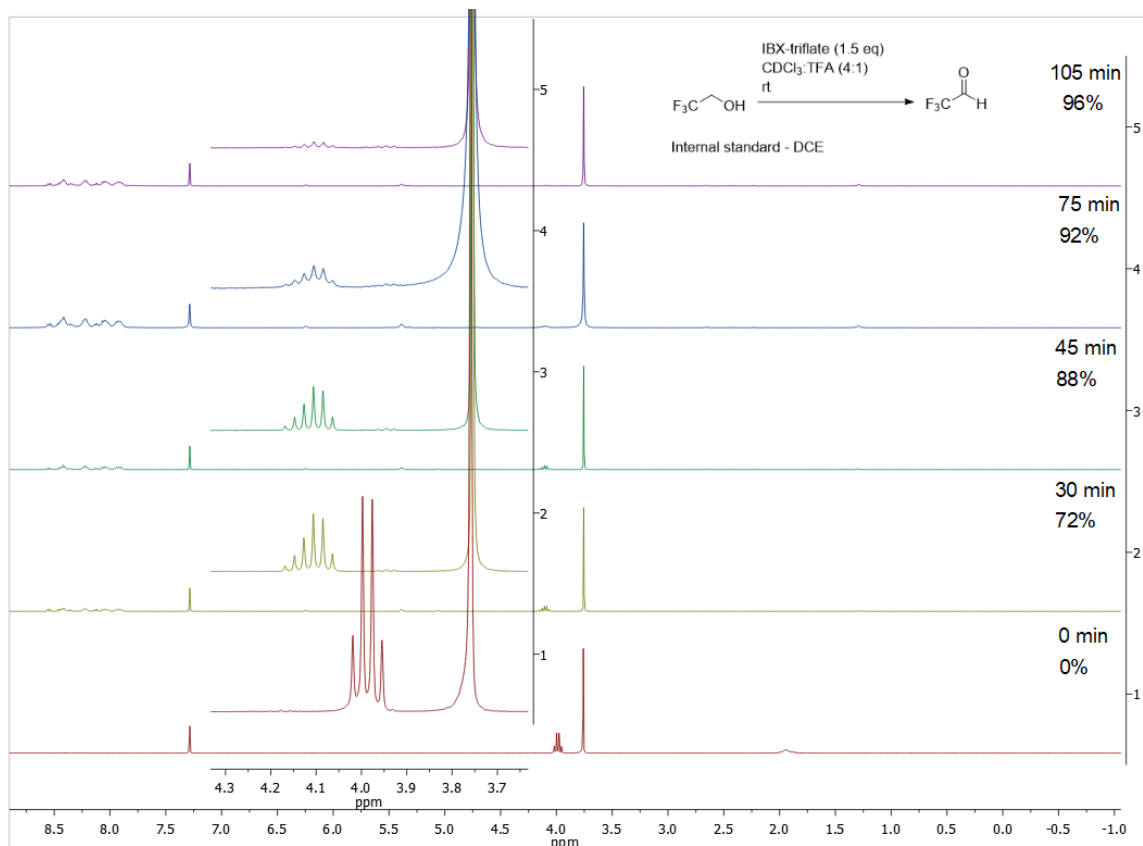
7. Oxidation of 2,2,2-trifluoroethanol in NMR tube



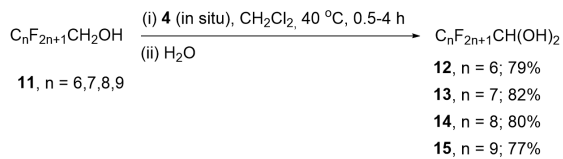
7.1. Oxidation at 60 °C. To a mixture of 2-iodoxybenzoic acid ditriflate **4** (24 mg, 0.040 mmol) in CDCl_3 (0.3 mL) in sealed NMR tube was added 0.26 M solution of trifluoroethanol in CDCl_3 (0.1 mL, 0.026 mmol) and DCE as internal standard. After measuring initial ^1H NMR spectrum (0 min), trifluoroacetic acid (0.1 mL) was added to reaction mixture in order to partially dissolve IBX-ditriflate **4** and initiate the reaction. According to ^1H NMR full conversion of starting material at 60 °C was reached in 10 min.



7.2. Oxidation at room temperature. To a mixture of 2-iodoxybenzoic acid ditriflate **4** (24 mg, 0.040 mmol) in CDCl_3 (0.3 mL) in sealed NMR tube was added 0.26 M solution of trifluoroethanol in CDCl_3 (0.1 mL, 0.026 mmol) and DCE as internal standard. After measuring initial ^1H NMR spectrum (0 min), trifluoroacetic acid (0.1 mL) was added to the reaction mixture in order to partially dissolve IBX-ditriflate **4** and initiate the reaction. The progress of oxidation and conversion was monitored by ^1H NMR. A 96% conversion of starting material at room temperature was reached in 105 min.



8. Oxidation of polyfluorinated alcohols with IBX ditriflate generated *in situ*



Cooled trifluoromethanesulfonic acid (88 μL , 1 mmol) was added to the mixture of fluorinated alcohol **11** (0.25 mmol) and IBX **1** (140 mg, 0.5 mmol) in dichloromethane at 0 $^\circ\text{C}$. Reaction mixture was refluxed from 30 min to 4 h and monitored by TLC (eluent hexane:EtOAc 3:1, KMnO_4 stain). After completion of reaction, the mixture was cooled to room temperature and mixed with ether (10 mL) and saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$

(0.2 mL). The obtained white precipitate was filtered and 100 mg of Na₂CO₃ was added to mother liquor. The organic solution was filtered and dried over Na₂SO₄. Solvent was removed under reduced pressure. Products were purified by column chromatography on Silicagel (eluent hexane:Et₂O 5:1) to give the corresponding polyfluorinated aldehydes in the form of polyfluoroalkane-1,1-diols **12-15**, which were identified by comparison with the available literature data.⁶⁻¹⁰

2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptane-1,1-diol^{6,7}

The reaction of 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-ol (88 mg, 0.25 mmol), IBX (140mg, 0.5 mmol), TfOH (88 μ L, 1 mmol) according to the general procedure afforded 72 mg (79%) of 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptane-1,1-diol⁶ **12** as a white, semicrystalline solid; ¹H NMR (500 MHz, acetone-*d*₆) δ 6.38 (d, *J* = 8.0 Hz, 2H), 5.52-5.35 (m, 1H). ¹⁹F NMR (471 MHz, acetone-*d*₆) δ -81.70 (s, 3F), -122.65 (s, 2F), -123.04 (s, 2F), -123.37 (s, 2F), -126.76 (s, 2F), -128.49 (s, 2F).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1,1-diol^{8,9}

The reaction of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1-ol (100 mg, 0.25 mmol), IBX (140 mg, 0.5 mmol), TfOH (88 μ L, 1 mmol) according to the general procedure afforded 85 mg (82%) of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8--pentadecafluorooctan-1,1-diol^{8,9} **13** as a white semicrystalline, solid; ¹H NMR (400 MHz, acetone-*d*₆) δ 6.43 (d, *J* = 7.2 Hz, 2H), 5.43 (m, *J* = 8.0 Hz, 1H). ¹⁹F NMR (376 MHz, acetone-*d*₆) δ -81.67 (s, 3F), -122.51 (s, 4F), -122.99 (s, 2F), -123.28 (s, 2F), -126.72 (s, 2F), -128.47 (s, 2F).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluorononane-1,1-diol⁷

The reaction of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluorononan-1-ol (113 mg, 0.25

mmol), IBX **1** (140mg, 0.5 mmol), TfOH (88 μ L, 1 mmol) according to the general procedure afforded 83 mg (80%) of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8--pentadecafluorooctan-1-ol **14** as a white, semicrystalline solid; ^1H NMR (300 MHz, Acetone- d_6) δ 6.44 (d, J = 7.2 Hz, 1H), 5.48-5.38 (m, 1H). ^{19}F NMR (376 MHz, Acetone- d_6) δ -81.66 (s, 3F), -122.48 (s, 6F), -123.03 (s, 2F), -123.29 (s, 2F), -126.76 (s, 2F), -128.52 (s, 2F).

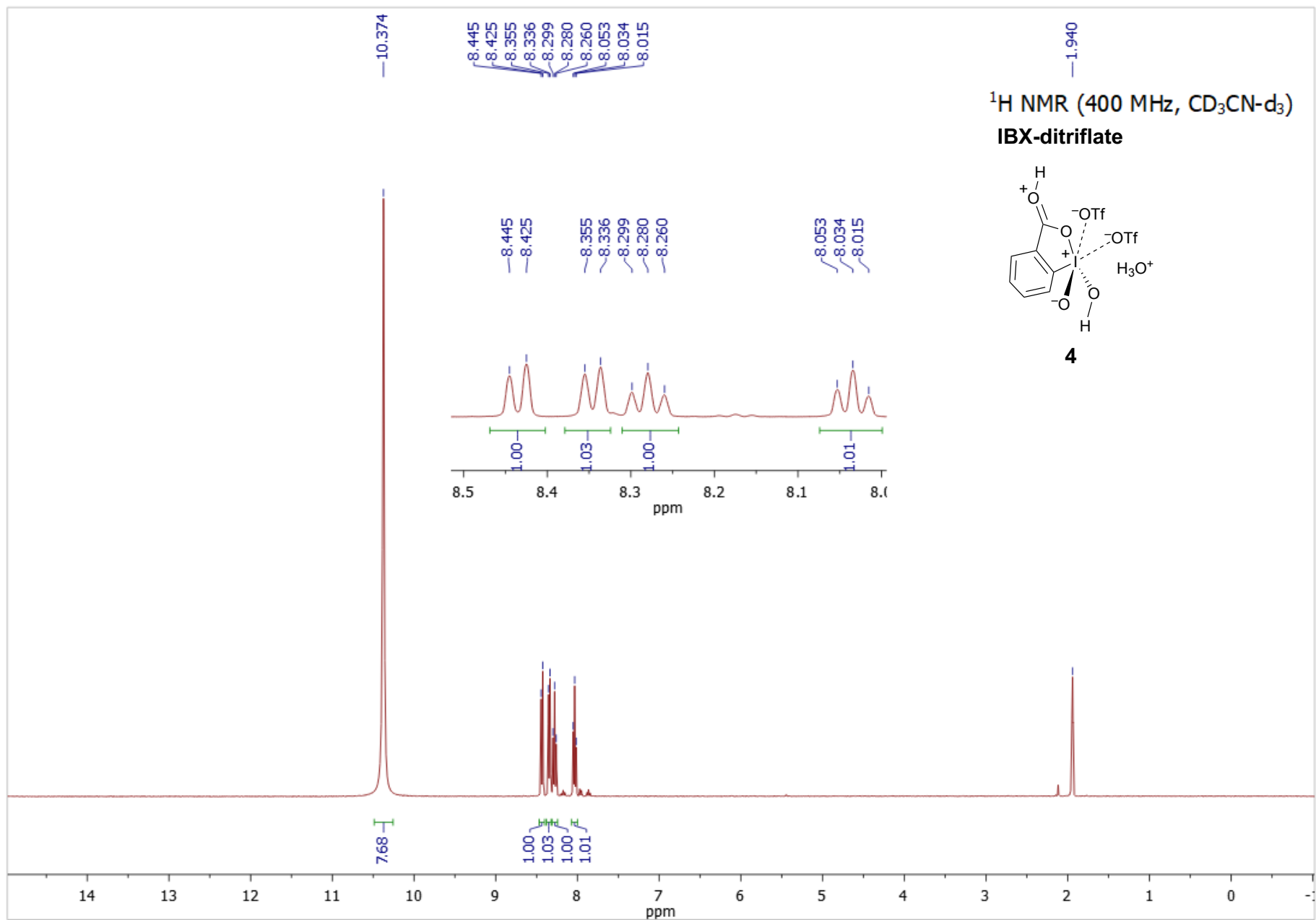
2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluorodecane-1,1-diol¹⁰

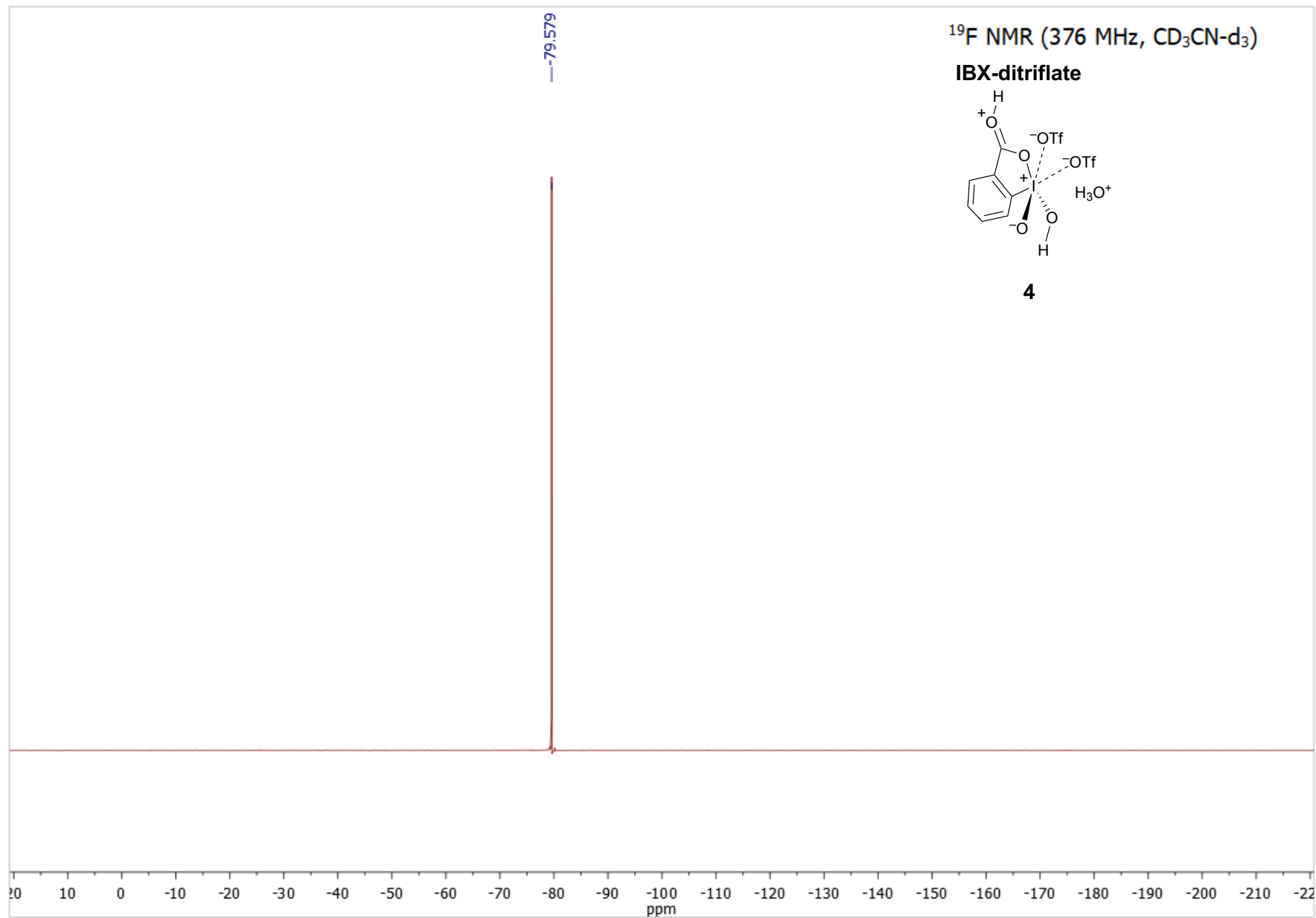
The reaction of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluorodecan-1-ol (125 mg, 0.25 mmol), IBX (140mg, 0.5 mmol), TfOH (88 μ L, 1 mmol) according to the general procedure afforded 99 mg (77%) of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nona-decafluorodecane-1,1-diol¹⁰ **15** as a white, semicrystalline solid; ^1H NMR (300 MHz, acetone- d_6) δ 6.46 (d, J = 7.2 Hz, 2H), 5.43 (m, J = 7.5 Hz 1H). ^{19}F NMR (471 MHz, acetone- d_6) δ -81.63 (s, 3F), -122.41 (s, 8F), -123.03 (s, 2F), -123.27 (s, 2F), -126.75 (s, 2F), -128.52 (s, 2F).

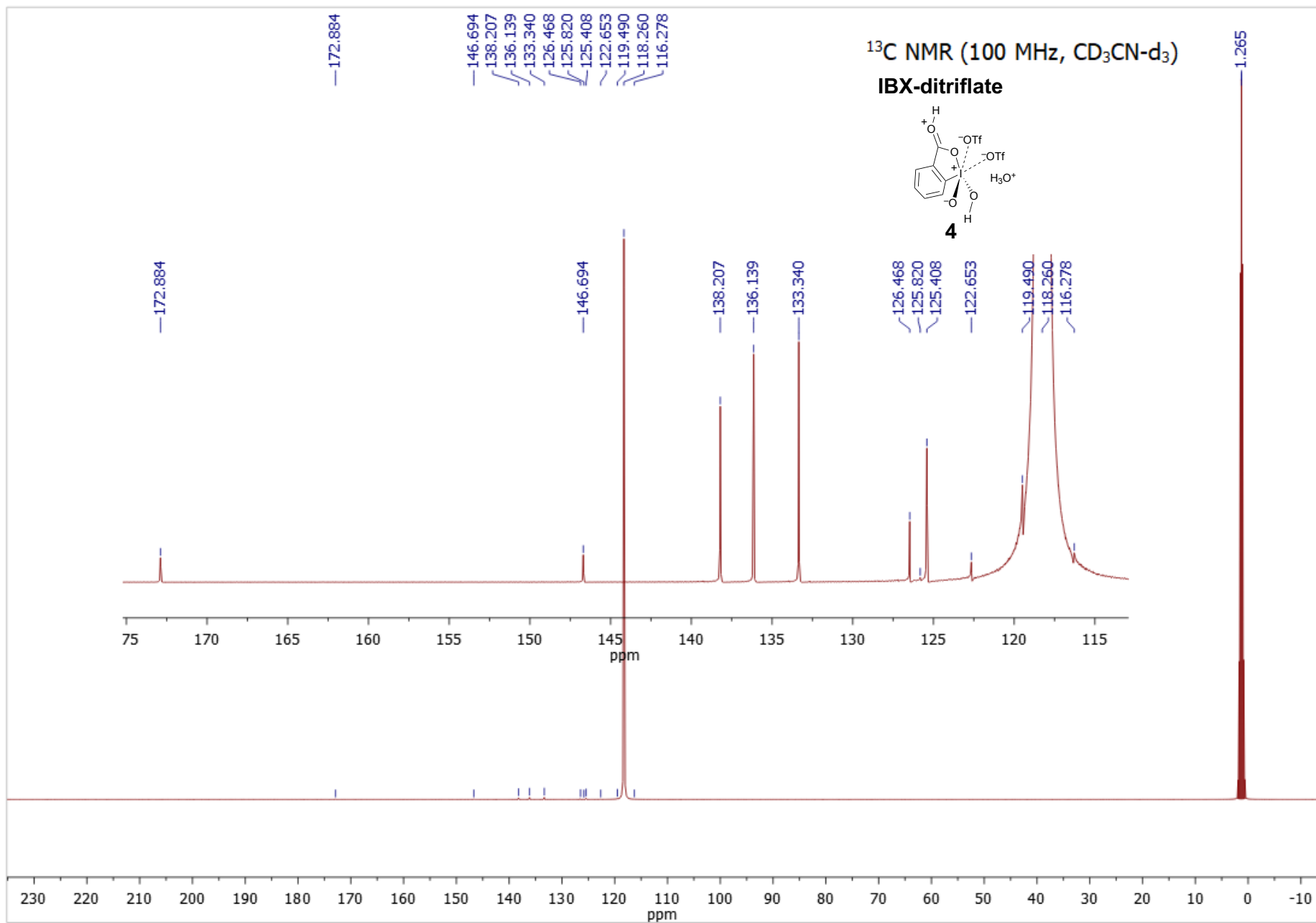
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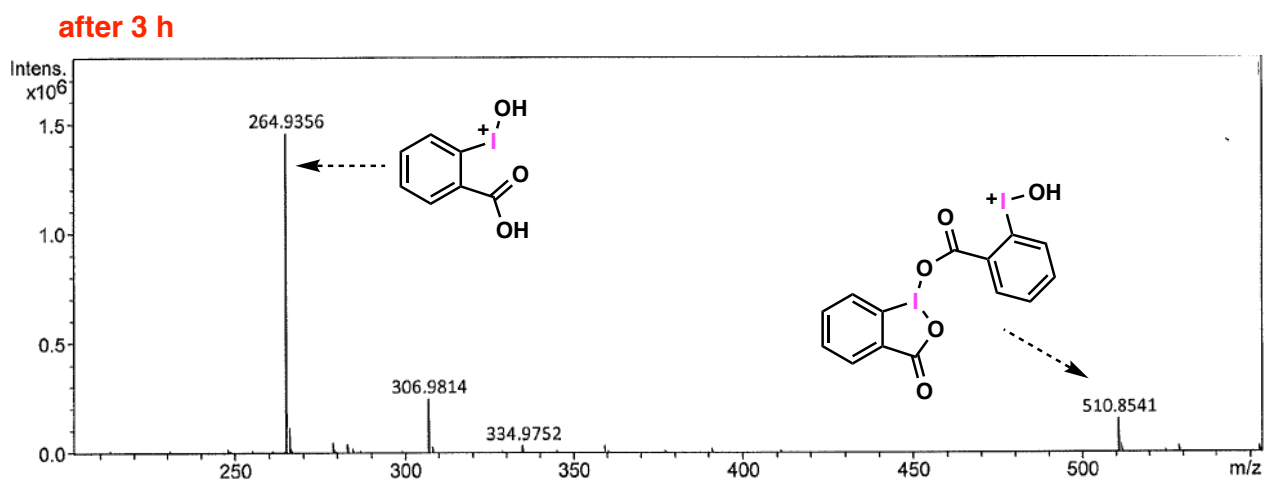
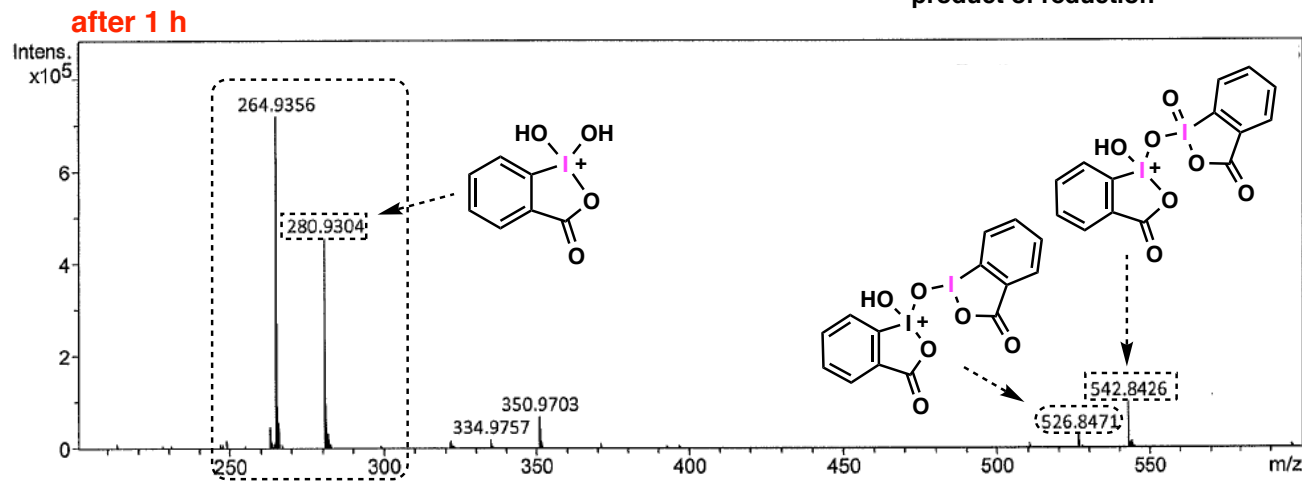
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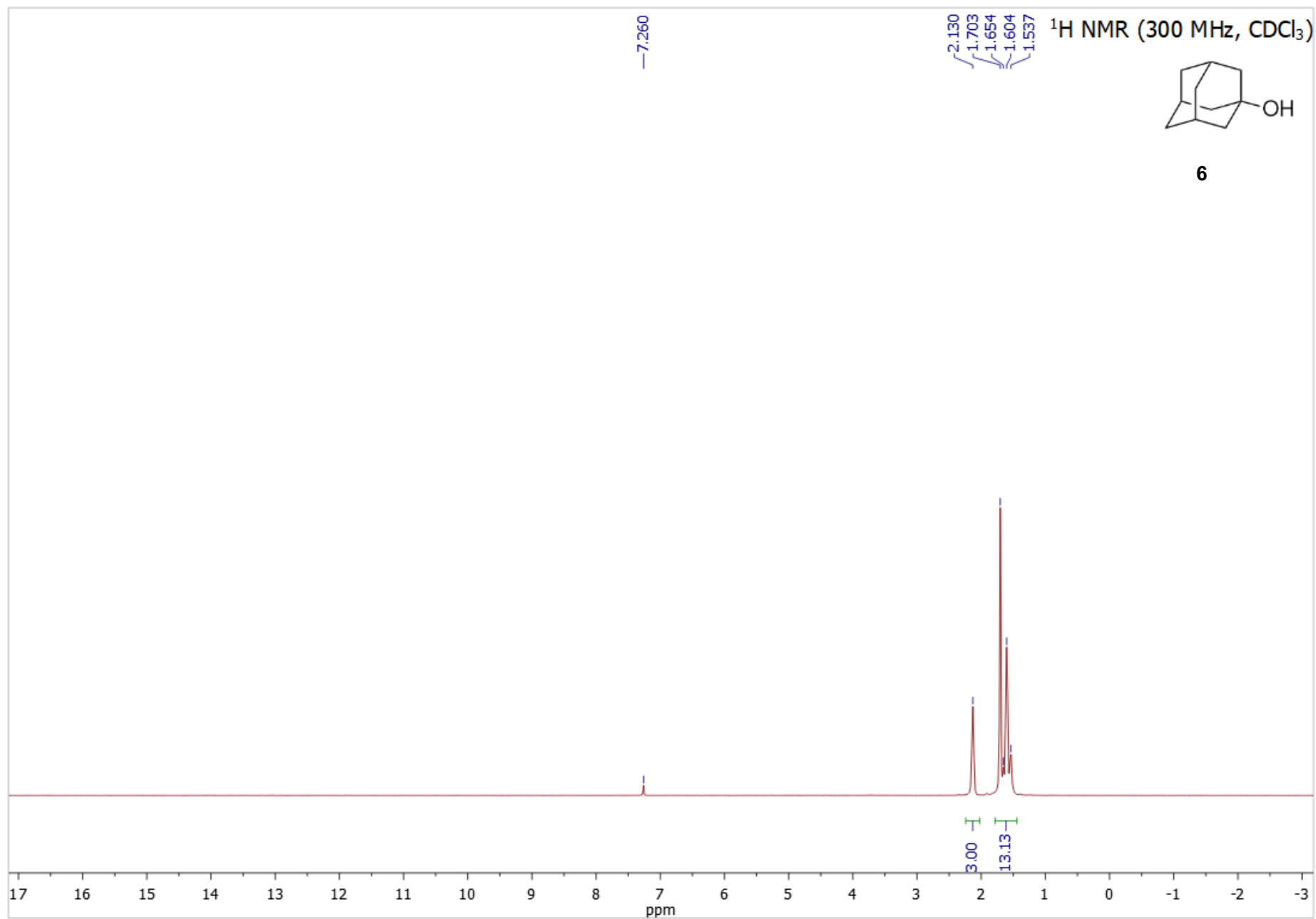


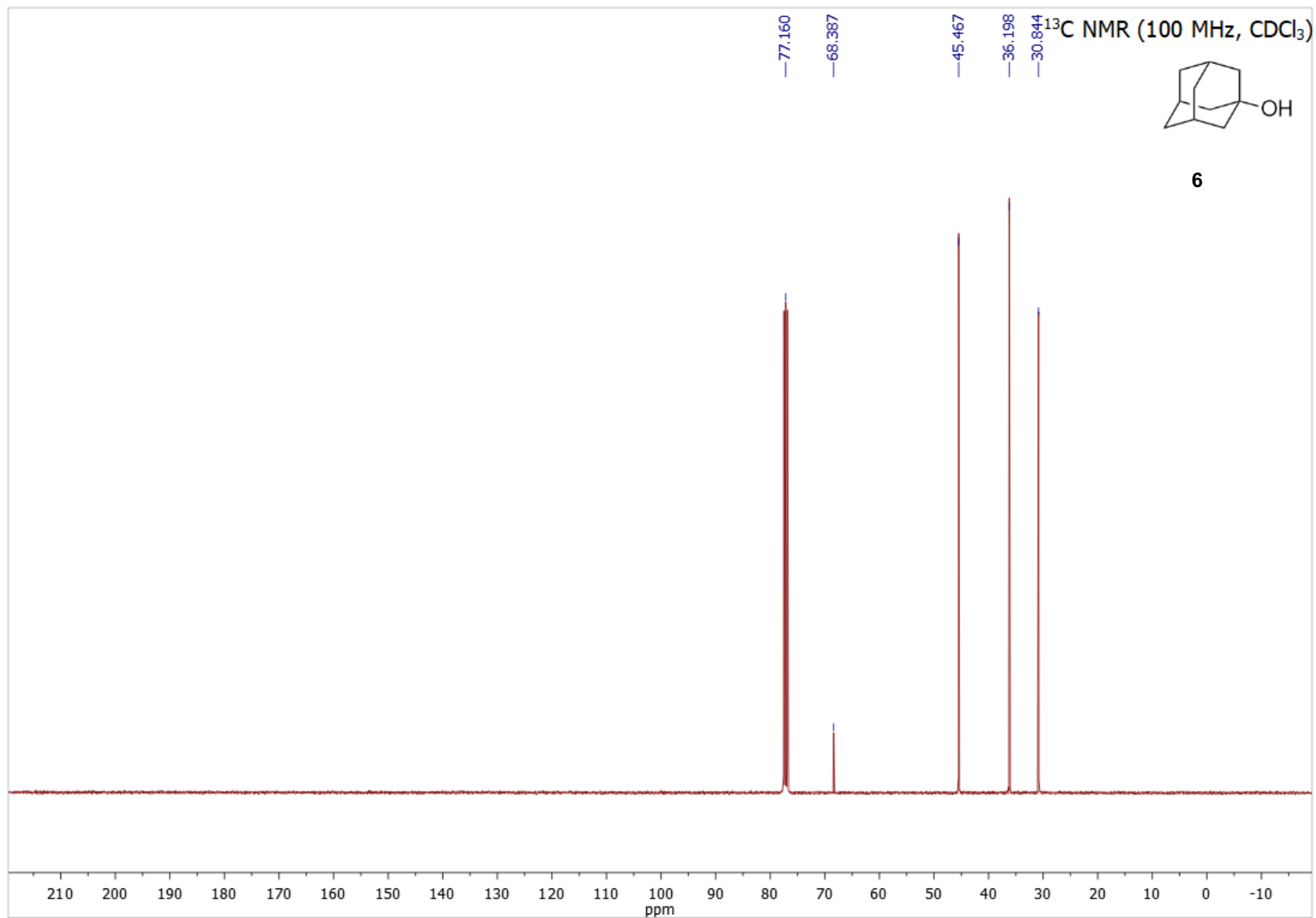




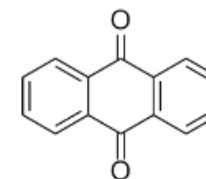
ESI Mass Spectrometry Study of stability of IBX-ditriflate **4** in acetonitrile solution:



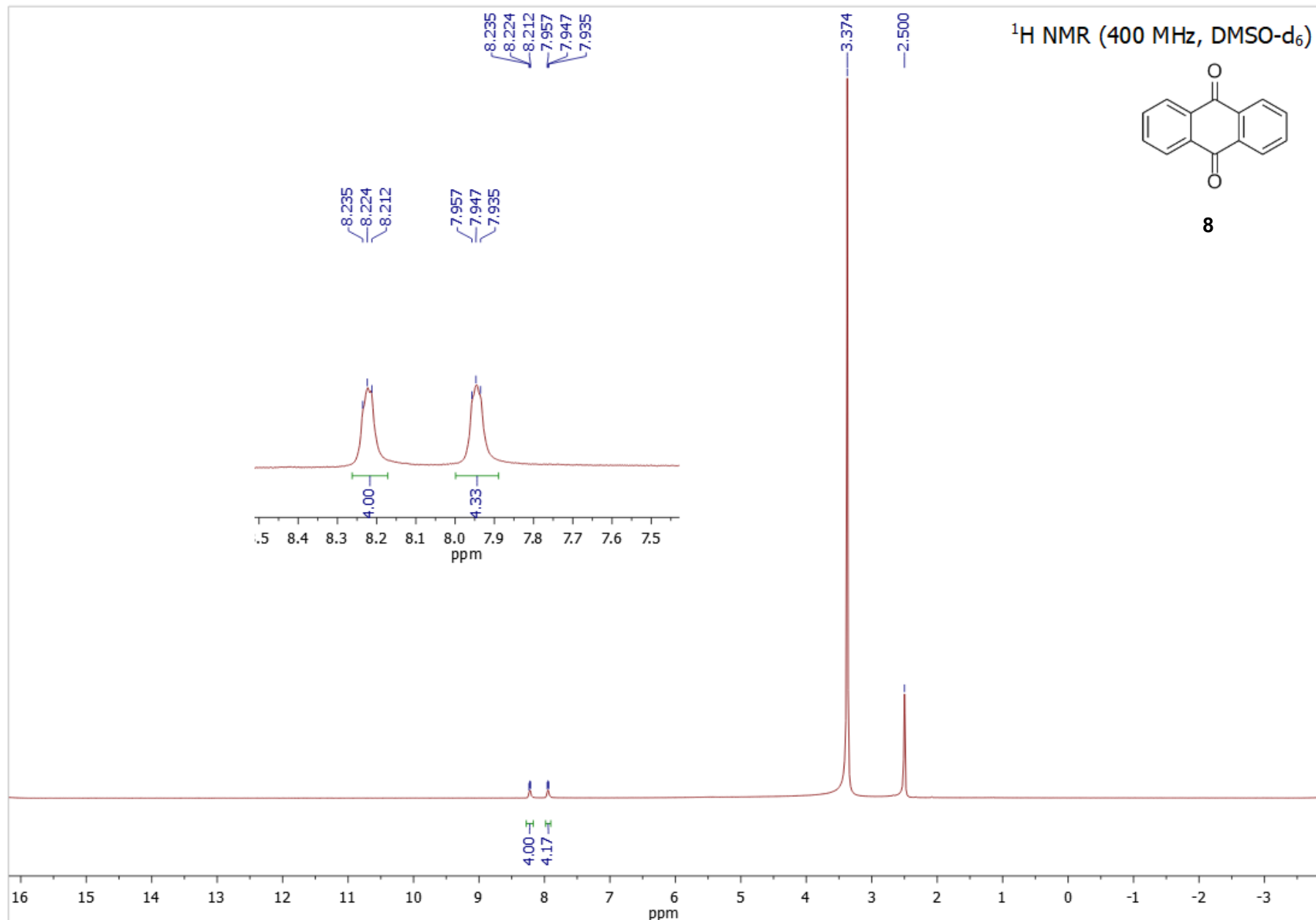


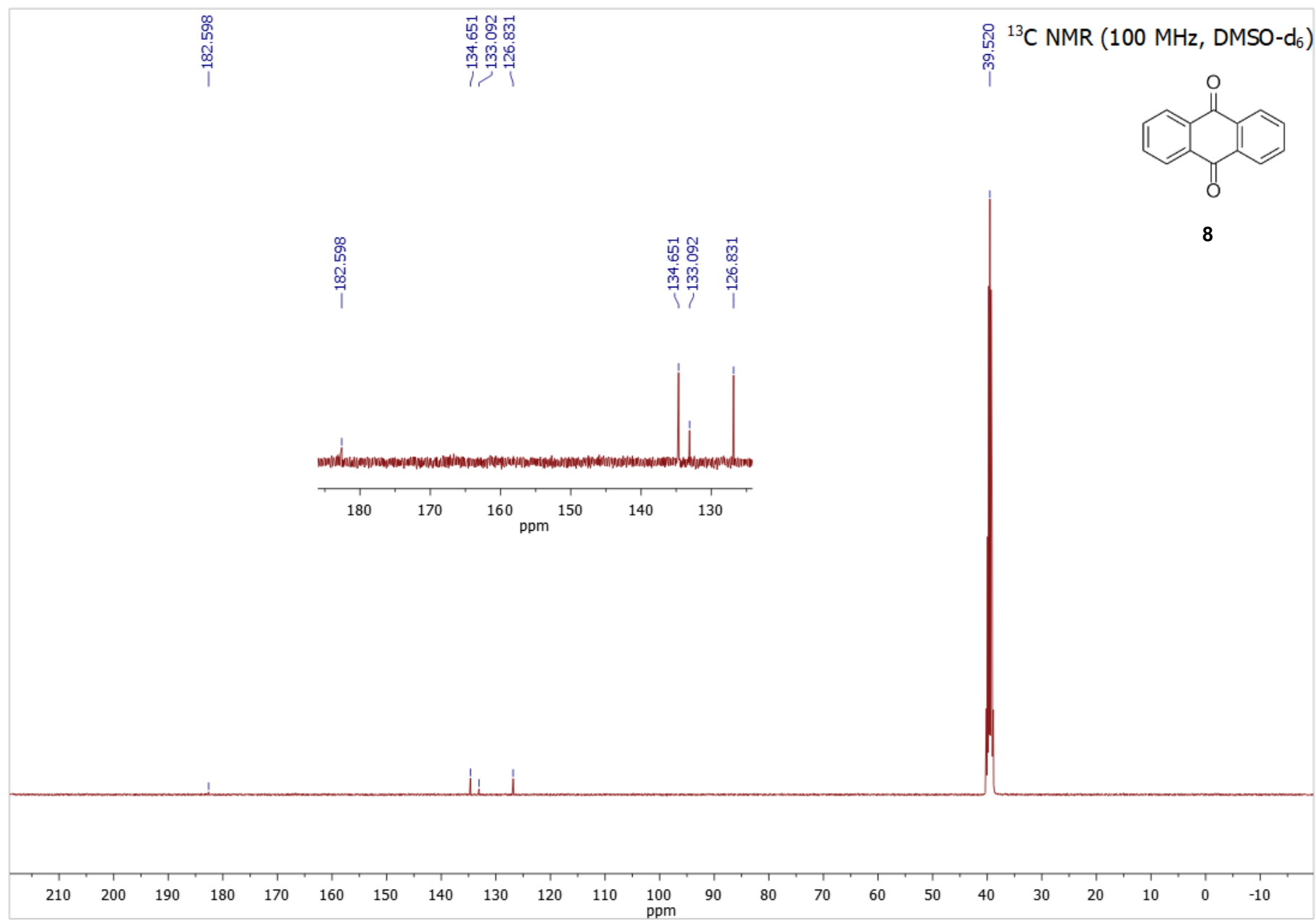


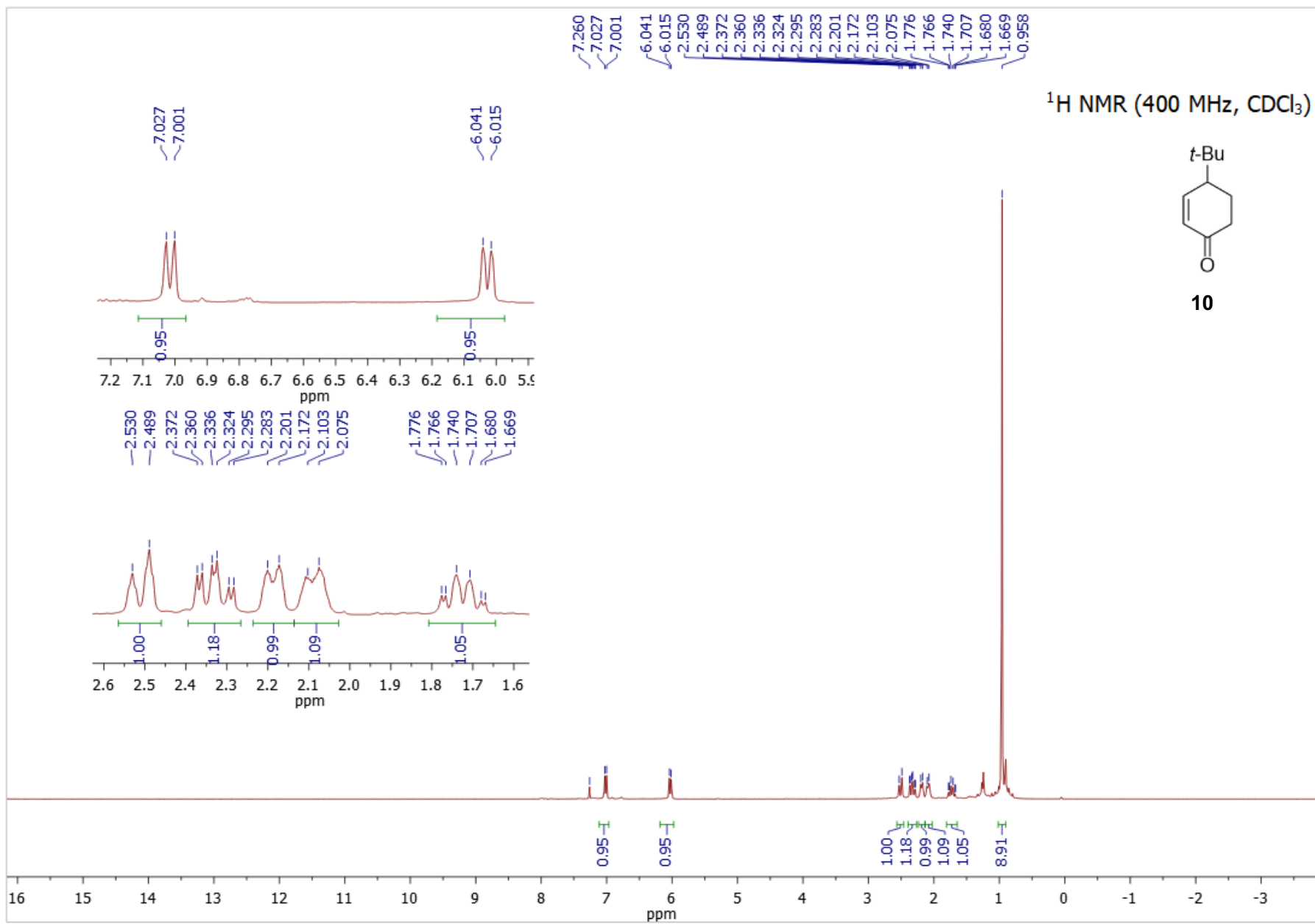
¹H NMR (400 MHz, DMSO-d₆)

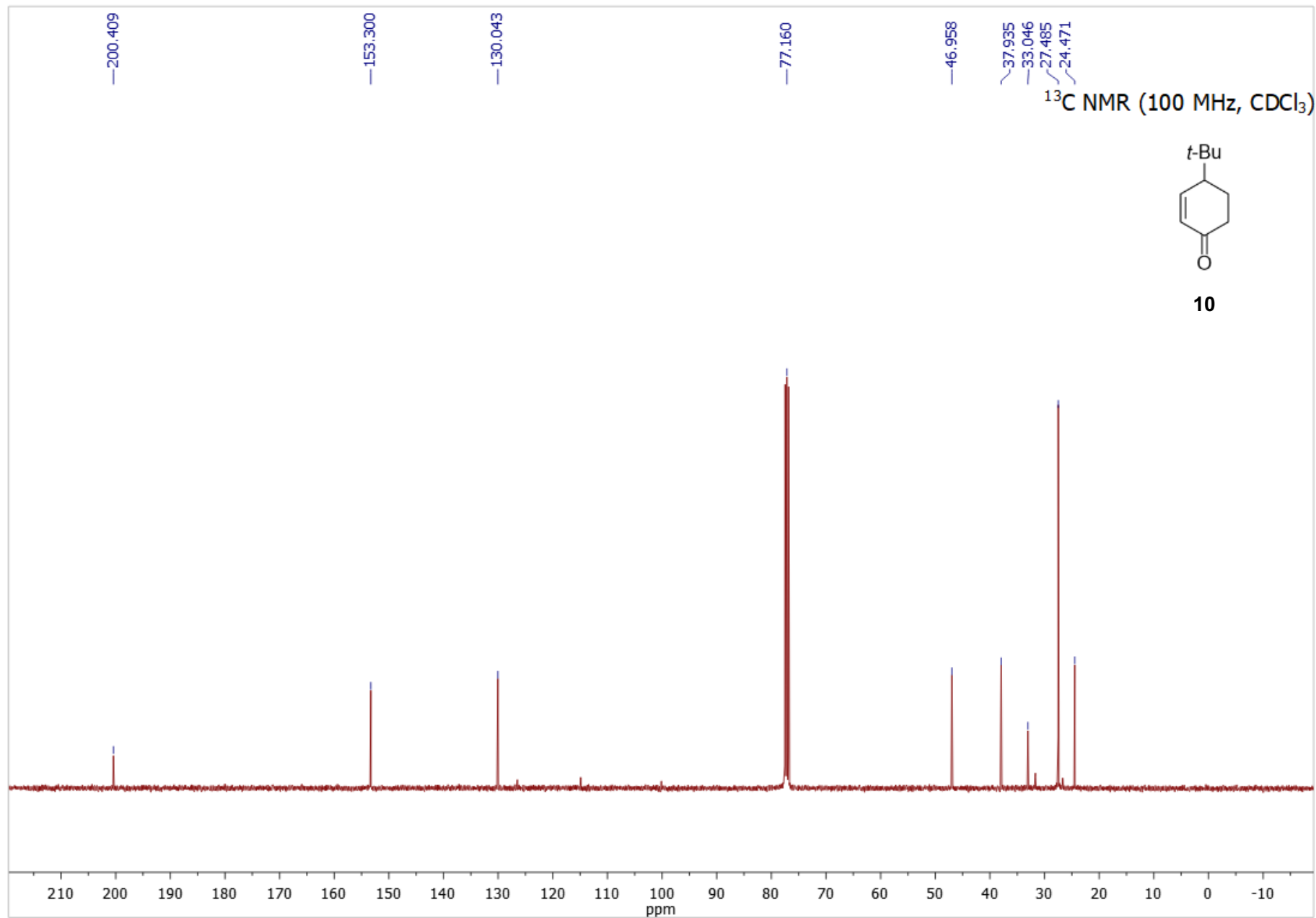


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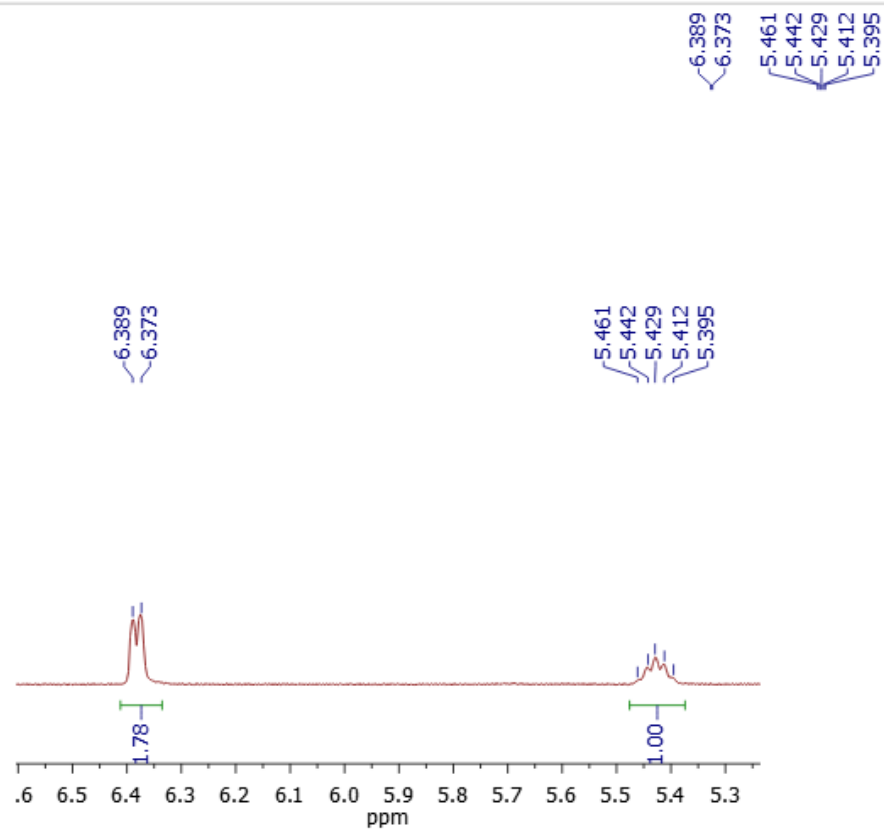




¹H NMR (500 MHz, Acetone-d₆)



12



2.795

2.050

ppm

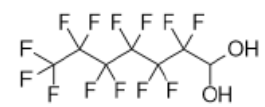
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

ppm

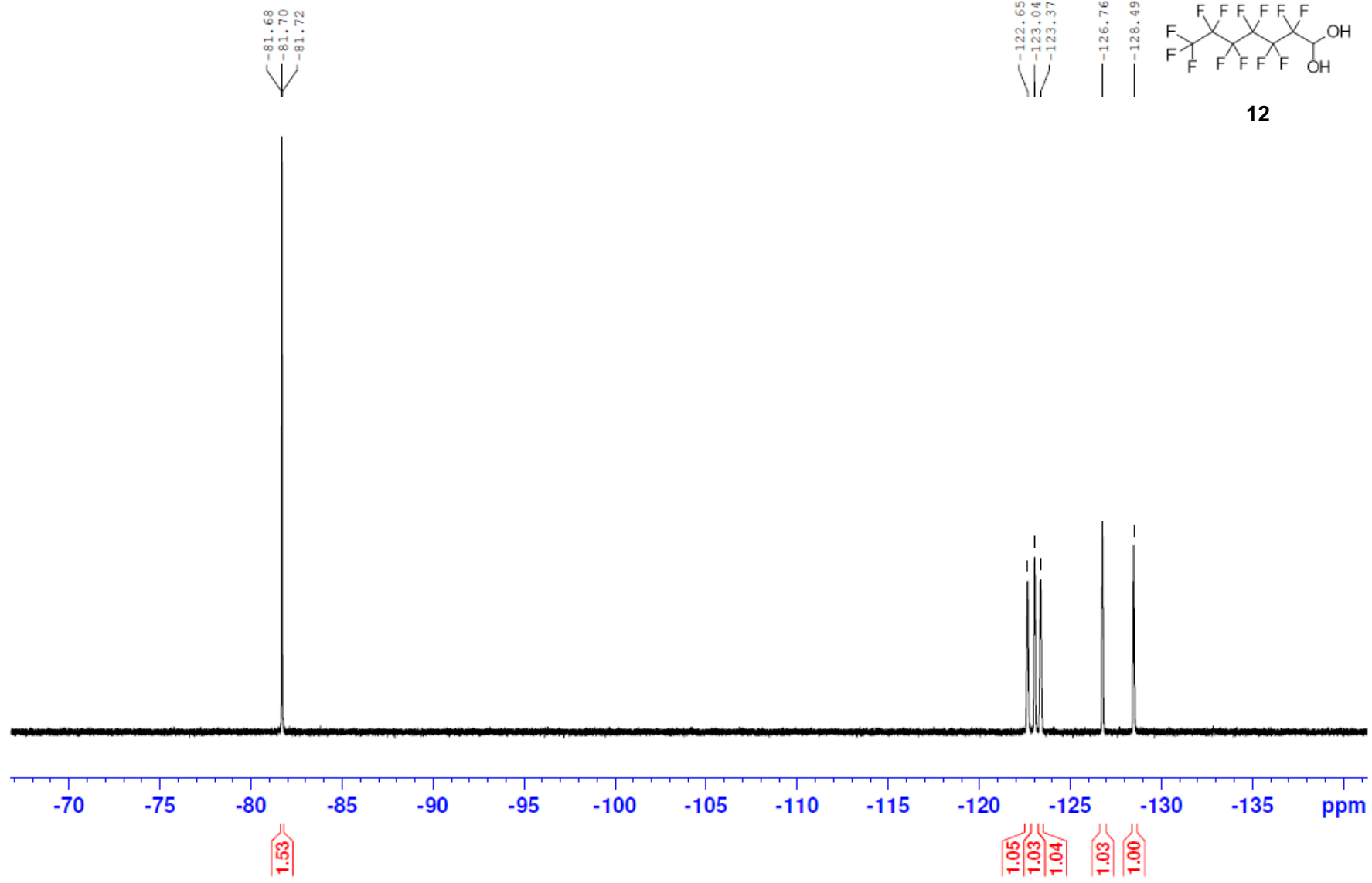
¹⁹F NMR (471 MHz, Acetone-d₆)

-122.65
-123.04
-123.37

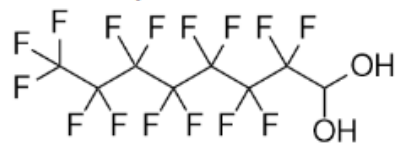
-126.76
-128.49



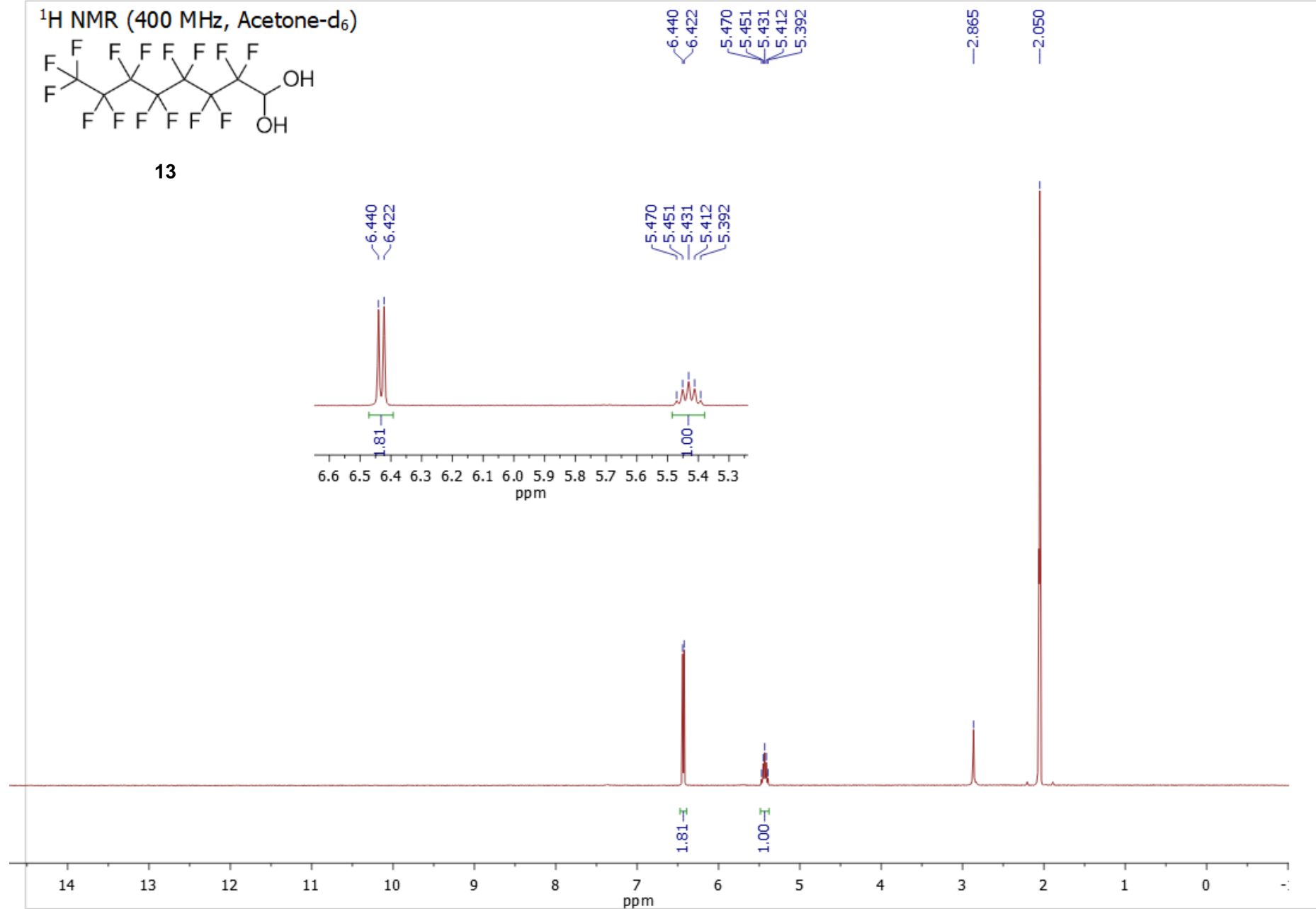
12

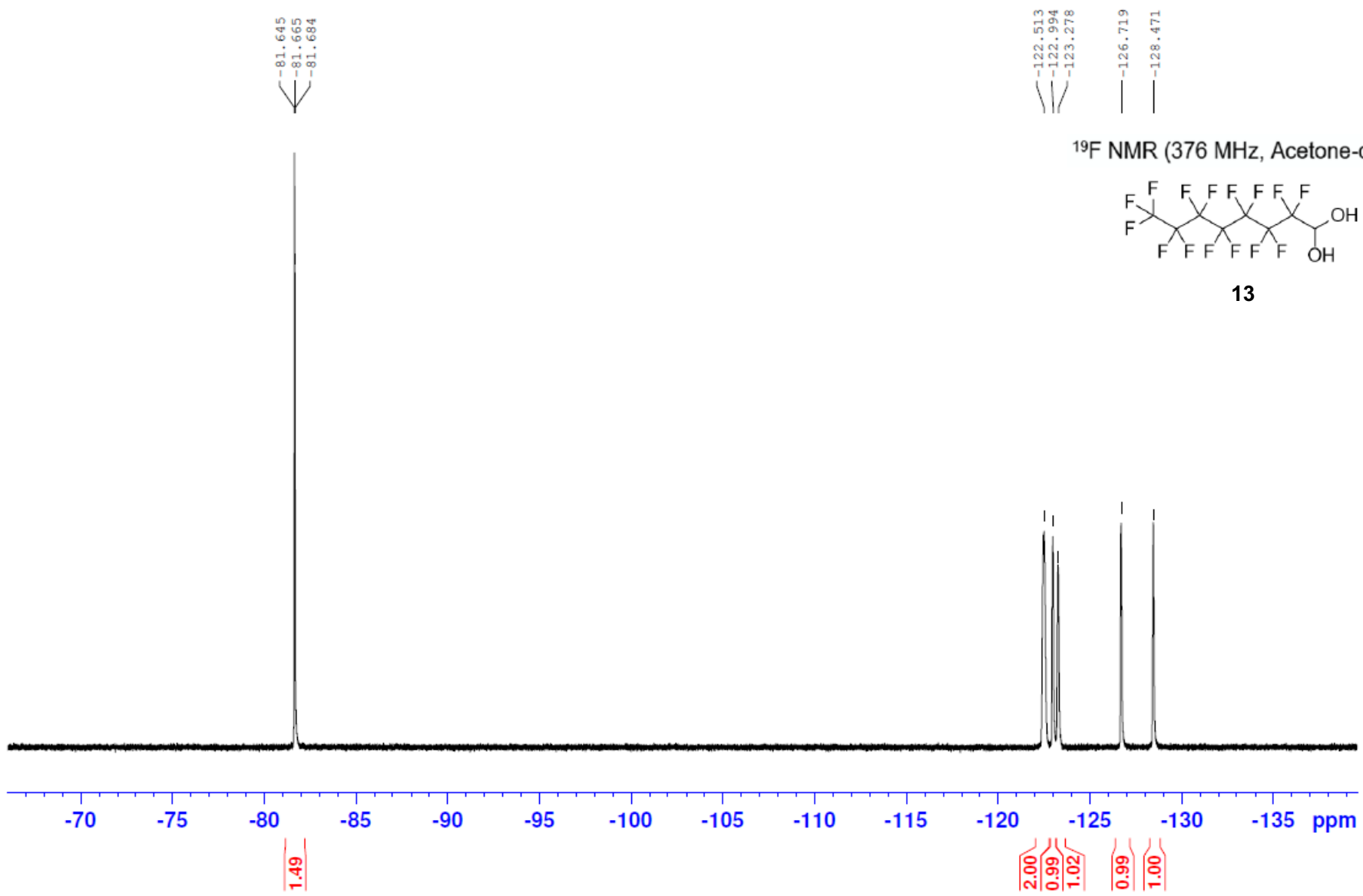


^1H NMR (400 MHz, Acetone- d_6)



13





¹H NMR (300 MHz, Acetone-d₆)



14

