Electronic Supplementary Information

Ring Strain-Dictated Divergent Fluorinating Prins Cyclization or Semipinacol Rearrangement

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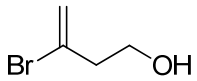
1. General Information

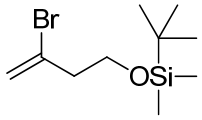
All reactions that required anhydrous conditions were carried out by standard procedures under nitrogen atmosphere unless otherwise stated. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Infrared spectra were recorded on a Varian 3100 FTIR spectrophotometer and reported in wave numbers (cm^{-1}). Melting points were determined on a Stuart SMP3 melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300 MHz), Bruker DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^{1}H NMR and to chloroform (δ 77.0) for the ^{13}C NMR measurements. Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode. High resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

2. Experimental Procedures and physical data



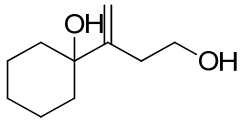
3-bromobut-3-en-1-ol (3)[1]

2,3-dibromopropene **2** (30 mmol, 6.0 g), paraformaldehyde (900 mg, 30 mmol) and tin powder (60 mmol, 7.08 g) were added to a 100 mL round-bottom flask in mixed solvent (H_2O/Et_2O; 30ml/30ml). Then, 48% HBr aqueous solution (0.5 mL) was added. Under nitrogen protection, the resultant mixture was stirred for 24 h at 25 ^oC. The reaction was diluted with Et_2O (100 mL) and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography eluted with hexane/EtOAc (5:1) to yield **3** in 48% yield. Colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 5.72 (1H), 5.55 (d, *J* = 1 Hz, 1H), 3.83 (t, *J* = 6.5 Hz, 2H), 2.68 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 130.48, 119.33, 60.06, 44.42.



((3-bromobut-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (4)[1]

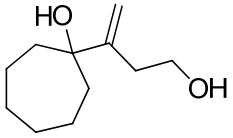
3-Bromobut-3-en-1-ol (**3**) (2.2 g, 14.6 mmol) was added to a 50 mL round-bottom flask containing anhydrous dichloromethane (30 mL). The mixture was cooled to 0 ^oC and imidazole (1.49 g, 21.6 mmol) was added. Then, a solution of *tert*-butyldimethylsilyl chloride (3.26 g, 21.6 mmol) dissolved in anhydrous dichloromethane (15 mL) was added dropwise to the reaction mixture over 30 minutes. The resultant was allowed to rise to 25 ^oC and further stirred for 15 hours. The reaction was quenched by water (50 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified purified by silica gel chromatography eluted with hexane/EtOAc (20:1) to yield **4** in 95% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 5.67 (d, *J* = 1.5 Hz, 1H), 5.49 (d, *J* = 1.5 Hz, 1H), 3.83 (t, *J* = 6.3 Hz, 2H), 2.66 (t, *J* = 6.3 Hz, 2H), 0.93 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.76, 118.31, 60.76, 44.71, 25.79, 18.21, -5.42.



1-(4-hydroxybut-1-en-2-yl)cyclohexanol (1a)

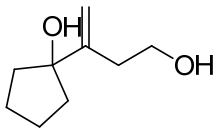
((3-bromobut-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane **4** (1.06 g, 4.0 mmol) was added to a 50 mL schlenk flask containing tetrahydrofuran (15 mL) at -78 ^oC. *n*-butyl lithium (4.8 mmol, 3 ml, 1.6 M in hexane) was added dropwise over 30 minutes. The resultant mixture was stirred for additional 30 minutes at the same temperature. Then, a solution of cyclohexanone (490 mg, 5 mmol) in THF (10 mL) was added dropwise over 30 minutes. The reaction was allowed to warm to 25 ^oC and stirred for 10 hours. Water (10 mL) was added to quench the reaction and most of THF was removed under reduced pressure. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was dissolved in THF (10 mL) and transferred to a 25 mL round-bottom flask. A

solution of TBAF (1 M in THF, 5 ml, 5 mmol) was added at 0 °C. The resultant mixture was stirred at 25 °C for 3 hours. The solvent was then removed under reduced pressure and the residue was diluted with water (20 mL). The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified purified by silica gel chromatography eluted with hexane/EtOAc (2:1) to yield **1a** (500 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.15 (1H), 4.93 (1H), 3.77 (t, *J* = 6.2 Hz, 2H), 2.42 (t, *J* = 6.1 Hz, 2H), 1.70 – 1.55 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.34, 110.99, 73.19, 63.24, 36.53, 34.74, 25.62, 22.07. HRMS (ESI): $C_{10}H_{18}O_2$, calculated for [M+Na]: $C_{10}H_{18}O_2Na$, 193.1199, found 193.1195.



1-(4-hydroxybut-1-en-2-yl)cycloheptanol (1b)

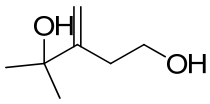
((3-bromobut-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane **4** (1.06 g, 4.0 mmol) was added to a 50 mL schlenk flask containing tetrahydrofuran (15 mL) at -78 °C. *n*-butyl lithium (4.8 mmol, 3 ml, 1.6 M in hexane) was added dropwise over 30 minutes. The resultant mixture was stirred for additional 30 minutes at the same temperature. Then, a solution of cycloheptanone (560 mg, 5 mmol) in THF (10 ml) was added dropwise over 30 minutes. The reaction was allowed to warm to 25 °C and stirred for 10 hours. Water (10 mL) was added to quench the reaction and most of THF was removed under reduced pressure. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was dissolved in THF (10 mL) and transferred to a 25 mL round-bottom flask. A solution of TBAF (1 M in THF, 5 ml, 5 mmol) was added at 0 °C. The resultant mixture was stirred at 25 °C for 3 hours. Then, most of THF was removed under reduced pressure and water (20 mL) was added. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography eluted with hexane/EtOAc (2:1) to yield **1b** (530 mg, 72%) Colorless oil. IR (cm^{-1}): 3348, 2926, 2858, 1634, 1456, 1194, 1037. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.89 (d, *J* = 1.0 Hz, 1H), 4.66 (d, *J* = 1.0 Hz, 1H), 3.54 (t, *J* = 6.0 Hz, 2H), 2.19 (t, *J* = 6.0, 2H), 1.67 (m, 2H), 1.59 – 1.15 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.91, 110.17, 77.19, 63.25, 40.29, 34.78, 29.34, 22.35.



1-(4-hydroxybut-1-en-2-yl)cyclopentanol (1c)

((3-bromobut-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane **4** (1.06 g, 4.0 mmol) was added to a 50 mL schlenk flask containing tetrahydrofuran (15 mL) at -78 °C. *n*-butyl lithium (4.8 mmol, 3 ml, 1.6 M in hexane) was added dropwise over 30 minutes. The resultant mixture was stirred for additional 30 minutes at the same temperature. Then, a solution of cyclopentanone (420 mg, 5 mmol) in THF (10 mL) was added dropwise over 30 minutes. The reaction was allowed to warm to 25 °C and stirred for 10 hours. Water (10 mL) was added to quench the reaction and most of THF was removed under reduced pressure. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered, and concentrated under

reduced pressure. The residue was dissolved in THF (10 mL) and transferred to a 25 mL round-bottom flask. A solution of TBAF (1 M in THF, 5 ml, 5 mmol) was added at 0 ^{o}C. The resultant mixture was stirred at 25 ^{o}C for 3 hours. Then, most of THF was removed under reduced pressure and water (20 mL) was added. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography eluted with hexane/EtOAc (2:1) to yield **1c** (424 mg, 68%) Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.18 (1H), 4.91 (1H), 3.79 (t, *J* = 6 Hz, 2H), 2.44 (t, *J* = 6 Hz, 2H), 1.91 – 1.69 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.28, 110.76, 83.94, 63.03, 38.73, 36.14, 23.30. HRMS (ESI): $C_9H_{16}O_2$, calculated for [M+Na]: $C_9H_{16}O_2Na$, 179.1043, found: 179.1039.

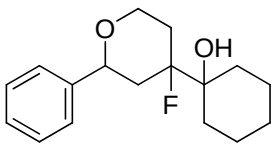


4-methyl-3-methylenepentane-1,4-diol (1d)[1]

((3-bromobut-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane **4** (1.06 g, 4.0 mmol) was added to a 50 mL schlenk flask containing tetrahydrofuran (15 mL) at -78 ^{o}C. *n*-butyl lithium (4.8 mmol, 3 ml, 1.6 M in hexane) was added dropwise over 30 minutes. The resultant mixture was stirred for additional 30 minutes at the same temperature. Then, a solution of anhydrous acetone (290 mg, 5 mmol) in THF (10 mL) was added dropwise over 30 minutes. The reaction was allowed to warm to 25 ^{o}C and stirred for 10 hours. Water (10 mL) was added to quench the reaction and most of THF was removed under reduced pressure. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was dissolved in THF (10 mL) and transferred to a 25 mL round-bottom flask. A solution of TBAF (1 M in THF, 5 ml, 5 mmol) was added at 0 ^{o}C. The resultant mixture was stirred at 25 ^{o}C for 3 hours. Then, most of THF was removed under reduced pressure and water (20 mL) was added. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography eluted with hexane/EtOAc (2:1) to yield **1d** (234 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (1H), 4.86 (1H), 3.78 (t, *J* = 6.5 Hz, 2H), 2.42 (t, *J* = 6.5 Hz, 2H), 1.38 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.29, 110.06, 72.69, 63.05, 34.71, 29.47. HRMS (ESI): $C_7H_{14}O_2$, calculated for [M+Na]: $C_7H_{14}O_2Na$, 153.0886, found: 153.0883.

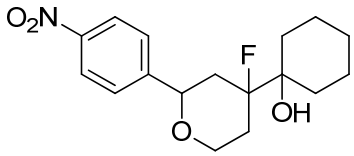
Representative procedure for the fluorinating Prins cyclization or semi-pinacol rearrangement

To a solution of **1a** (34 mg, 0.2 mmol) and benzaldehyde **6a** (25 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) in a 25 ml Schlenk flask at -20 ^{o}C was added 3 equivalent of BF_3•Et_2O (0.6 mmol, 85 mg) slowly under N_2 protection. The resultant mixture was stirred at -20 ^{o}C for 6 hours. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel eluted with hexane/EtOAc (2:1) to give **7aa** in 73% yield.



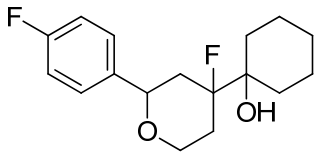
1-(4-fluoro-2-phenyltetrahydro-2H-pyran-4-yl)cyclohexanol (7aa)

Yield: 73%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 – 7.28 (m, 5H), 4.74 – 4.69 (1H), 4.14 – 4.12 (1H), 3.97 – 3.96 (1H), 2.12 – 1.37 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.28, 128.35, 127.51, 125.72, 99.97, 97.66, 77.39, 76.96, 76.54, 75.17, 74.22, 73.94, 63.83, 37.65, 37.36, 30.71, 30.66, 30.63, 30.58, 29.23, 28.93, 25.59, 21.13. HRMS (ESI): $C_{17}H_{23}FO_2$, calculated for [M-H] 277.1609, found 277.1602.



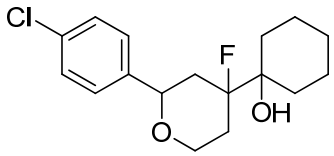
1-(4-fluoro-2-(4-nitrophenyl)tetrahydro-2H-pyran-4-yl)cyclohexanol (7ab)

Yield: 69%. White solid. Melting point: 114 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 9 Hz, 2H), 7.56 (d, *J* = 9 Hz, 2H), 4.82 – 4.78 (dd, *J* = 3.5 Hz, 11.4 Hz, 1H), 4.19 – 4.14 (m, 1H), 3.97 – 3.95 (m, 1H), 2.23 – 1.23 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.79, 147.14, 126.34, 123.57, 99.54, 97.22, 63.77, 37.59, 37.30, 30.62, 30.58, 29.13, 28.84, 25.51, 21.07. HRMS (ESI): $C_{17}H_{22}FNO_4$, calculated for [M-H]: 322.1460, found: 322.1462.



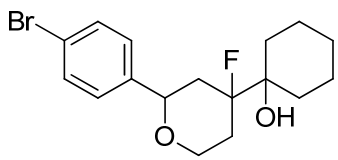
1-(4-fluoro-2-(4-fluorophenyl)tetrahydro-2H-pyran-4-yl)cyclohexanol (7ac)

Yield: 75%. White solid. Melting point: 79 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 – 7.34 (m, 2H), 7.09 – 7.03 (m, 2H), 4.71 – 4.66 (dd, *J* = 2.1 Hz, 11.4 Hz, 1H), 4.12 – 4.09 (m, 1H), 3.95 – 3.94 (m, 1H), 1.97 – 1.39 (m, 14H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 163,72, 160.47, 138.11, 138.07, 127.48, 127.37, 115.27, 114.99, 99.86, 97.55, 74.54, 74.16, 73.88, 63.83, 37.59, 37.31, 30.65, 30.61, 30.57, 29.18, 28.89, 25.56, 21.11. HRMS (ESI): $C_{17}H_{21}F_2O_2$, calculated for [M-H]: 295.1515, found: 295.1514.



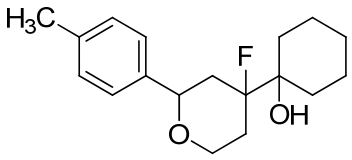
1-(2-(4-chlorophenyl)-4-fluorotetrahydro-2H-pyran-4-yl)cyclohexanol (7ad)

Yield: 77%. White solid. Melting point: 96 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 4H), 4.68 – 4.65 (dd, *J* = 2 Hz, 11.5 Hz, 1H), 4.12 – 4.10 (m, 1H), 3.96 – 3.93 (m, 1H), 2.15 – 1.38 (m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.96, 133.21, 128.51, 127.16, 99.41, 98.03, 74.54, 74.19, 74.02, 63.89, 37.62, 37.44, 30.76, 30.73, 30.69, 29.22, 29.05, 25.65, 21.02. HRMS (ESI): $C_{17}H_{22}ClFO_2$, calculated for [M-H]: 311.1220, found: 311.1229.



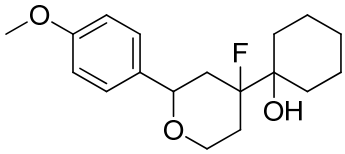
1-(2-(4-bromophenyl)-4-fluorotetrahydro-2H-pyran-4-yl)cyclohexanol (7ae)

Yield: 72%. White solid. Melting point: 102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.48 (m, 2H), 7.30 – 7.26 (m, 2H), 4.69 – 4.64 (dd, *J* = 2.4 Hz, 11.7 Hz, 1H), 4.13 – 4.10 (m, 1H), 3.95 – 3.94 (m, 1H), 1.99 – 1.39 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.39, 131.41, 127.42, 121.22, 99.79, 97.48, 74.48, 74.17, 73.89, 63.80, 37.57, 37.28, 30.68, 30.63, 30.59, 29.18, 28.89, 25.56, 21.11. HRMS (ESI): $C_{17}H_{22}BrFO_2$, calculated for [M-H]: 355.0714, found: 355.0702.



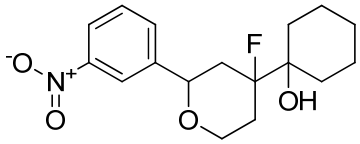
1-(4-fluoro-2-(p-tolyl)tetrahydro-2H-pyran-4-yl)cyclohexanol (7af)

Yield: 68%. White solid. Melting point: 103 – 105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.18 (m, 4H), 4.71 – 4.67 (m, 1H), 4.16 – 4.11 (m, 1H), 4.01 – 3.92 (m, 1H), 2.39 – 1.13 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.33, 137.14, 129.01, 125.71, 100.03, 97.73, 75.06, 74.21, 73.92, 63.84, 37.64, 37.35, 30.71, 30.66, 30.62, 30.57, 29.22, 28.93, 25.63, 21.15, 21.06. HRMS (ESI): $C_{18}H_{25}FO_2$, calculated for [M-H]: 291.1766, found: 291.1777.



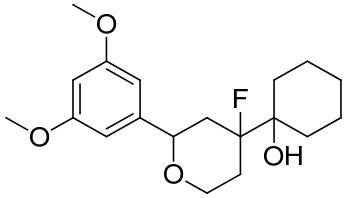
1-(4-fluoro-2-(4-methoxyphenyl)tetrahydro-2H-pyran-4-yl)cyclohexanol (7ag)

Yield: 69%. White solid. Melting point: 70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.30 (m, 2H), 6.92 – 6.89 (m, 2H), 4.67 – 4.63 (dd, *J* = 1.8 Hz, 11.4 Hz, 1H), 4.11 – 4.08 (m, 1H), 3.99 – 3.94 (m, 1H), 3.82 (s, 3H), 2.14 – 1.15 (m, 14 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.98, 134.43, 127.09, 113.72, 100.02, 97.72, 74.83, 74.19, 73.92, 63.83, 55.19, 37.44, 37.16, 30.67, 30.59, 30.55, 29.20, 28.91, 25.61, 21.14. HRMS (ESI): $C_{18}H_{25}FO_3$, calculated for [M-1]: 307.1715, found: 307.1722.



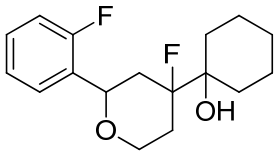
1-(4-fluoro-2-(3-nitrophenyl)tetrahydro-2H-pyran-4-yl)cyclohexanol (7ah)

Yield: 71%. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 – 8.21 (m, 2H), 7.53 – 7.49 (m, 2H), 4.65 – 4.62 (1H), 4.10 – 4.09(m, 1H), 3.86 – 3.83 (m, 1H), 3.86 – 0.86 (m, 14H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.37, 144.69, 131.89, 129.31, 122.44, 120.83, 99.19, 97.80, 74.17, 74.10, 73.99, 63.89, 37.53, 37.36, 30.71, 30.69, 30.66, 29.16, 28.99, 25.60, 21.16. HRMS (ESI): $C_{17}H_{22}FNO_4$, calculated for [M-H]: 322.1460, found: 322.1469.



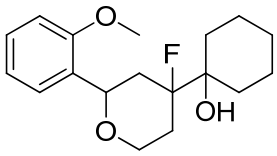
1-(2-(3,5-dimethoxyphenyl)-4-fluorotetrahydro-2H-pyran-4-yl)cyclohexanol (7ai)

Yield: 56%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.56-6.55 (d, *J* = 2.4 Hz, 2H), 6.41 – 6.40 (d, *J* = 2.4 Hz, 1H), 4.66 – 4.61 (dd, *J* = 2.1 Hz, 11.4 Hz, 1H), 4.15 – 4.09 (m, 1H), 3.97 – 3.88 (m, 1H), 3.82 (s, 6H), 2.17 – 1.15 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.77, 144.78, 103.55, 99.97, 99.63, 97.66, 75.19, 74.19, 73.91, 63.78, 55.27, 37.69, 37.41, 30.69, 30.64, 30.59, 30.55, 29.17, 28.88, 25.59, 21.12. HRMS (ESI): $C_{19}H_{27}FO_4$, calculated for [M-1]: 337.1821, found: 337.1829.



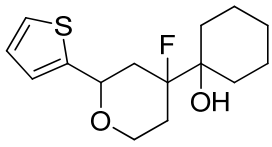
1-(4-fluoro-2-(2-fluorophenyl)tetrahydro-2H-pyran-4-yl)cyclohexanol (7aj)

Yield: 71%. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 – 7.02 (m, 4H), 5.03 – 5.00 (dd, *J* = 1.5 Hz, 11 Hz, 1H), 4.13 – 4.11 (m, 1H), 3.98 – 3.96 (m, 1H), 2.30 – 1.39 (m, 14H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.40, 158.44, 129.58, 129.48, 128.93, 128.86, 127.29, 127.26, 124.31, 124.28, 115.31, 115.14, 99.31, 97.92, 74.22, 74.04, 69.38, 64.03, 36.42, 36.25, 30.77, 30.74, 30.71, 30.68, 29.30, 29.12, 25.68, 21.22, 21.20. HRMS (ESI): $C_{17}H_{22}F_2O_2$, calculated for [M-H]:295.1515, found: 295.1524.



1-(4-fluoro-2-(2-methoxyphenyl)tetrahydro-2H-pyran-4-yl)cyclohexanol (7ak)

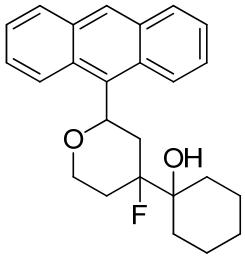
Yield: 59%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 – 7.49 (m, 1H), 7.30 – 7.24 (m, 1H), 7.04 – 6.88 (m, 2H), 5.12 – 5.08 (dd, *J* = 1.5 Hz, 11.1 Hz, 1H), 4.13 – 3.97 (m, 2H), 3.87 (s, 3H), 2.26 – 1.16 (m, 14 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.60, 130.79, 128.17, 126.17, 120.68, 110.15, 100.09, 97.78, 74.29, 74.01, 69.56, 63.91, 55.28, 36.16, 35.88, 30.75, 30.70, 30.64, 30.59, 29.43, 29.14, 25.65, 21.18, 21.15. HRMS (ESI): $C_{18}H_{25}FO_3$, calculated for [M-H]: 307.1715, found: 307.1722.



1-(4-fluoro-2-(thiophen-2-yl)tetrahydro-2H-pyran-4-yl)cyclohexanol (7al)

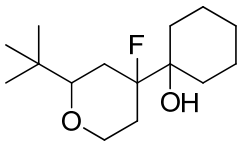
Yield: 67%. White solid. Melting point: 98 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.26 (m, 1H), 7.01 – 6.97 (m, 2H),

4.97 – 4.93 (m, 1H), 4.09 – 3.94 (m, 2H), 2.40 – 1.15 (m, 14H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.50, 126.49, 124.65, 123.61, 99.41, 98.02, 74.21, 74.04, 71.40, 64.03, 37.49, 37.32, 30.72, 29.20, 29.03, 25.67, 21.22. HRMS (ESI): $C_{15}H_{21}FO_2S$, calculated for [M-H]: 283.1174, found: 283.1179.



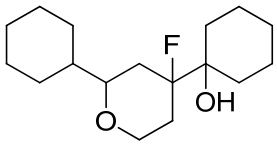
1-(2-(anthracen-9-yl)-4-fluorotetrahydro-2H-pyran-4-yl)cyclohexanol (7am)

Yield: 68%. Light yellow color. Melting point: 140 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 – 8.60 (2H), 8.46 (1H), 8.06 – 8.02 (2H), 7.58 – 7.49 (m, 4H), 6.30 – 6.25 (dd, *J* = 2.4 Hz, 12 Hz, 1H), 4.50 – 4.40 (m, 2H), 2.24 – 1.43 (m, 14H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.16, 131.64, 129.28, 129.12, 128.23, 125.66, 124.67, 100.30, 97.99, 74.30, 74.02, 72.99, 64.66, 35.40, 35.11, 30.72, 30.67, 30.59, 30.55, 29.46, 29.17, 25.55, 21.16, 21.09. HRMS (ESI): $C_{25}H_{27}FO_2$, calculated for [M-H]: 377.1922, found: 377.1918.



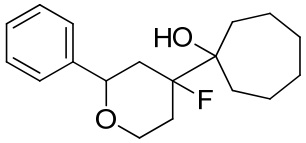
1-(2-(tert-butyl)-4-fluorotetrahydro-2H-pyran-4-yl)cyclohexanol (7an)

Yield: 61%. White solid. Melting point: 63 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$):δ 3.97-3.94 (dd, *J* = 5.5 Hz, 12 Hz, 1H), 3.73 – 3.68 (m, 1H), 3.26 – 3.23 (m, 1H), 1.94 – 1.14 (m, 14H), 0.91 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 100.09, 98.71, 80.52, 74.47, 74.29, 63.72, 63.68, 33.83, 30.81, 30.78, 29.72, 29.54, 29.42, 29.24, 26.02, 25.92, 25.72, 21.27. HRMS (ESI): $C_{15}H_{27}FO_2$, calculated for [M-H]: 257.1922, found: 257.1926.



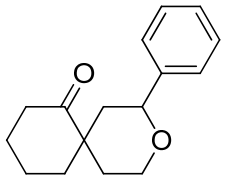
1-(2-cyclohexyl-4-fluorotetrahydro-2H-pyran-4-yl)cyclohexanol (7ao)

Yield: 63%. White solid. Melting point: 64 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.00 – 3.90 (1H), 3.70 – 3.69 (1H), 3.50 -3.40 (1H), 1.92 – 1.01 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 99.72, 98.34, 74.37, 74.19, 63.55, 43.00, 32.18, 32.00, 30.76, 30.74, 29.77, 29.59, 28.82, 28.64, 26.56, 26.21, 26.15. HRMS (ESI): $C_{17}H_{29}FO_2$, calculated for [M-H]: 283.2632, found: 283.2636.



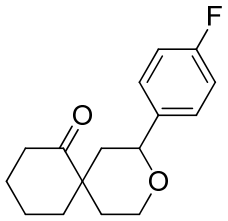
1-(4-fluoro-2-phenyltetrahydro-2H-pyran-4-yl)cycloheptanol (7ba)

Yield: 47%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.32 (m, 5H), 4.73 – 4.68 (dd, *J* = 2.4 Hz, 11.4 Hz, 1H), 4.14 – 3.95 (m, 2H), 2.18 – 1.54 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.27, 128.37, 127.52, 125.71, 100.90, 98.59, 75.18, 63.85, 37.95, 37.67, 35.21, 35.16, 35.10, 35.05, 29.70, 29.68, 29.63, 29.34, 22.60. HRMS (ESI): $C_{18}H_{25}FO_2$, calculated for [M-H]: 291.1766, found: 291.1777.



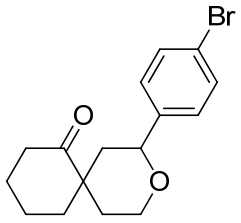
2-phenyl-3-oxaspiro[5.5]undecan-7-one (8ca)

Yield: 43%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 5H), 4.59 – 4.54 (dd, *J* = 1.8 Hz, 11.7 Hz, 1H), 4.07 – 4.02 (m, 1H), 3.79 – 3.75 (m, 1H), 2.55 – 1.38 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.65, 142.83, 128.28, 127.37, 125.60, 76.28, 65.32, 48.27, 43.35, 42.60, 38.90, 34.47, 28.63, 20.20. HRMS (ESI): $C_{16}H_{20}O_2$, calculated for [M+Na]: $C_{16}H_{20}O_2Na$, 267.1356, found 267.1352.



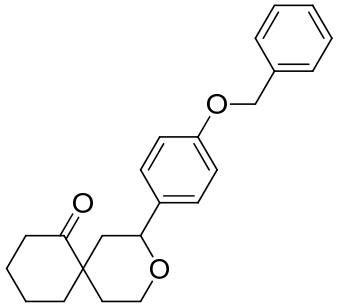
2-(4-fluorophenyl)-3-oxaspiro[5.5]undecan-7-one (8cc)

Yield: 49%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 – 7.02 (m, 4H), 4.61 – 4.57 (1H), 4.10 – 4.00 (1H), 3.80 -3.65 (1H), 2.55 – 1.30 (m, 12H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.53, 163.74, 160.33, 138.65, 127.42, 127.32, 115.18, 114.89, 75.63, 65.28, 48.23, 43.32, 42.58, 38.89, 34.45, 28.60, 20.21. HRMS (ESI): $C_{16}H_{19}FO_2$, calculated for [M+Na]: $C_{16}H_{20}FO_2Na$, 285.1261, found 285.1260.



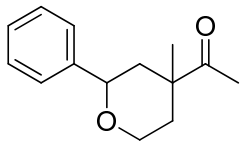
2-(4-bromophenyl)-3-oxaspiro[5.5]undecan-7-one (8ce)

Yield: 47%. White solid. Melting point: 117 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 – 7.22 (m, 4H), 4.56 – 4.53 (dd, *J* = 1.2 Hz, 6.9 Hz, 1H), 4.00 – 3.65 (m, 2H), 2.52 – 1.25 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.48, 141.98, 131.31, 127.40, 121.03, 75.58, 65.19, 48.17, 43.27, 42.53, 38.88, 34.42, 28.57, 20.19. HRMS (ESI) $C_{16}H_{20}BrO_2$, calculated for [M+Na]: $C_{16}H_{20}BrO_2Na$, 345.0461, found 345.0458.



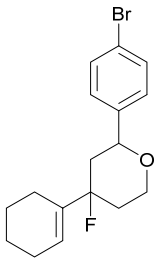
2-(4-(benzyloxy)phenyl)-3-oxaspiro[5.5]undecan-7-one (8cr)

Yield: 39%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 – 6.97 (m, 9H), 5.10 (s, 2H), 4.50 – 4.49 (1H), 4.10 – 4.00 (m, 1H), 3.80 – 3.70 (m, 1H), 2.55 – 0.90 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.66, 158.10, 136.99, 135.32, 128.47, 127.82, 127.36, 127.05, 114.66, 75.88, 69.94, 65.36, 48.31, 43.38, 42.44, 38.91, 34.48, 28.64, 20.21. HRMS (ESI) $C_{23}H_{26}O_3$, calculated for [M+Na]: $C_{23}H_{26}O_3Na$, 373.1774, found 373.1779.



1-(4-methyl-2-phenyltetrahydro-2H-pyran-4-yl)ethanone (8da)

Yield: 42%. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 – 7.30 (m, 5H), 4.61 – 4.56 (dd, *J* = 3.6 Hz, 10.2 Hz, 1H), 4.17 – 4.12 (m, 1H), 3.91 – 3.82 (m, 1H), 2.19 (s, 3H), 2.08 – 1.59 (m, 4H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.33, 142.35, 128.34, 127.55, 125.77, 74.94, 63.74, 45.79, 40.63, 32.10, 24.20, 19.23.

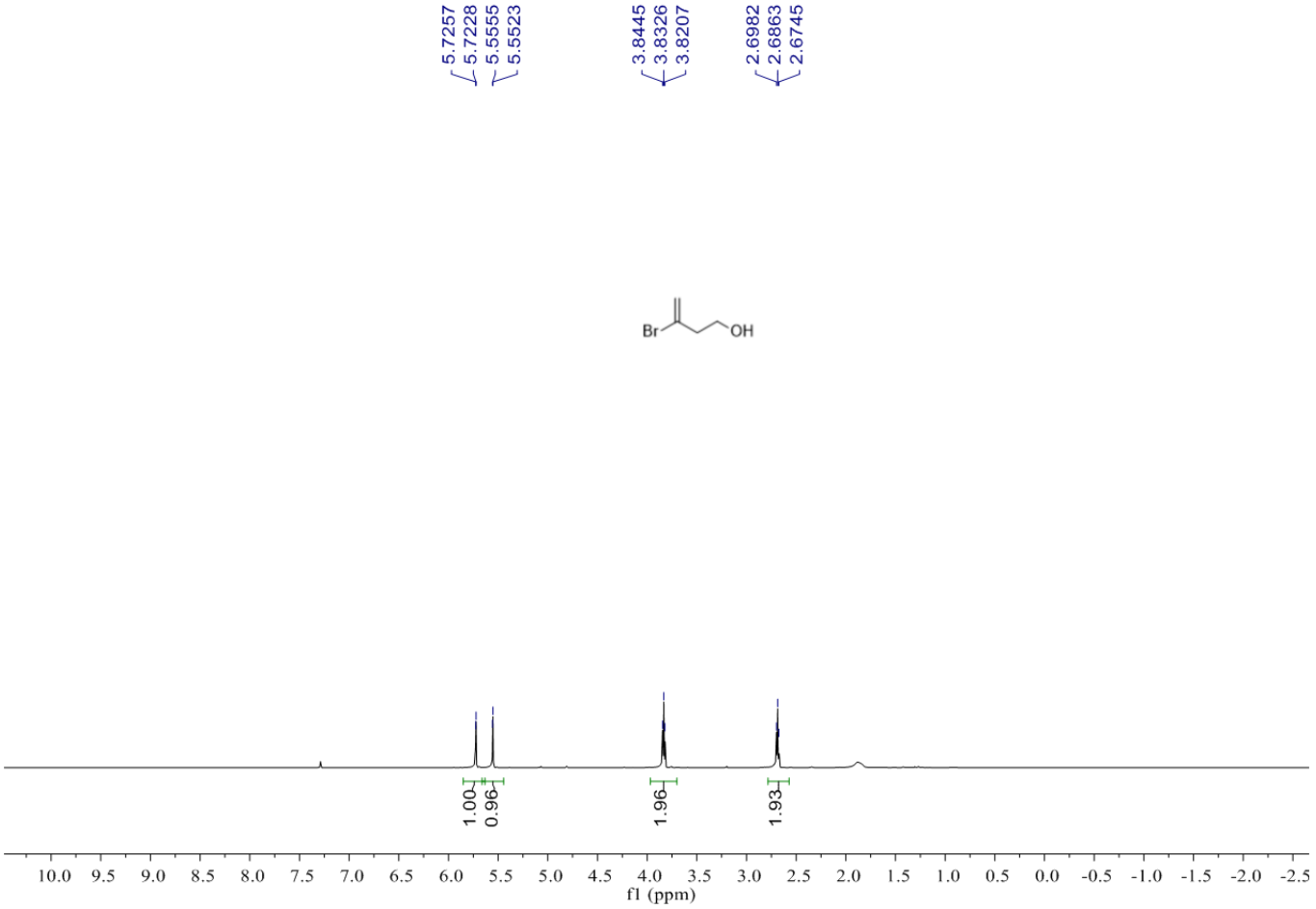


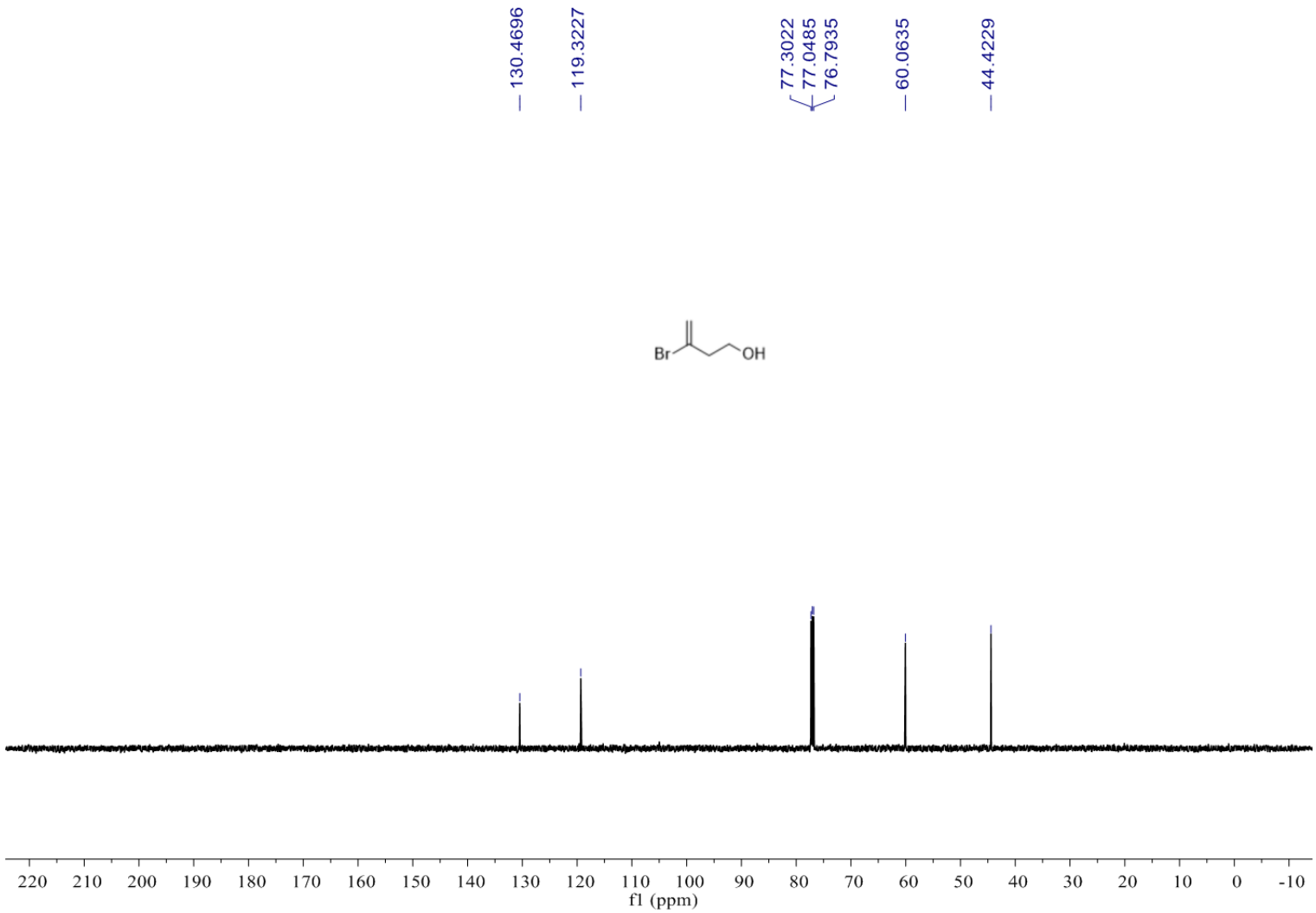
2-(4-bromophenyl)-4-(cyclohex-1-en-1-yl)tetrahydro-2H-pyran (9)

Yield: 95%. White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 – 7.37 (m, 2H), 7.18 – 7.14 (m, 2H), 5.71 – 5.68 (m, 1H), 4.61 (dd, *J* = 11.5 Hz, 2.3 Hz, 1H), 4.02 – 3.85 (m, 2H), 2.01 – 1.46 (m, 12H), ^{13}C NMR (75 MHz, $CDCl_3$): 141.41, 139.04, 138.78, 131.38, 127.40, 122.21, 122.08, 121.15, 95.59, 93.33, 74.46, 63.87, 42.20, 41.90, 33.81, 33.51, 24.84, 23.40, 23.34, 22.53, 21.99.

3. ^{1}H and ^{13}C NMR spectra

Compound **3**

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77.0485
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Br
OH
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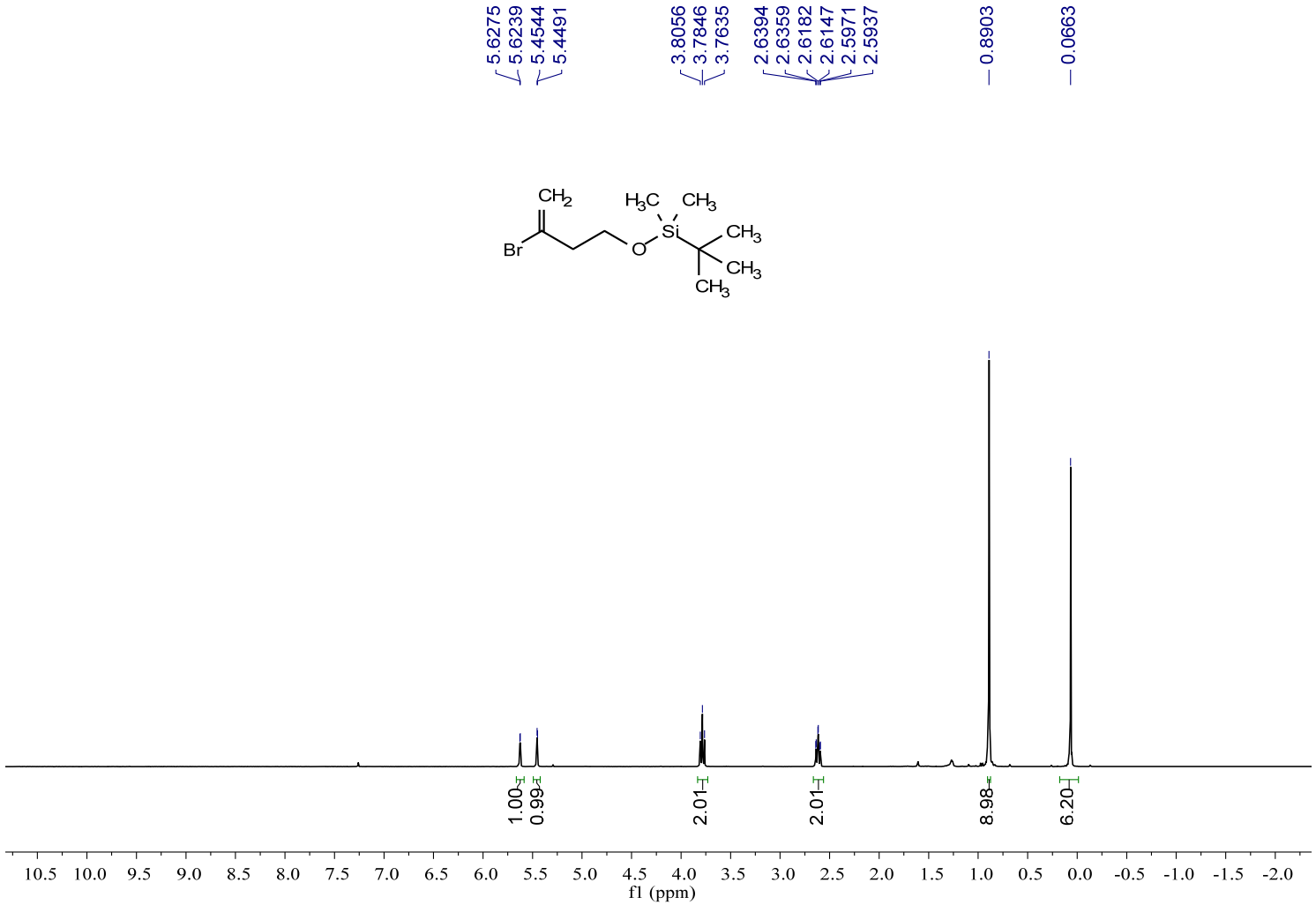
f1 (ppm)

Compound **4**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3.8056
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3.7635
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2.6359
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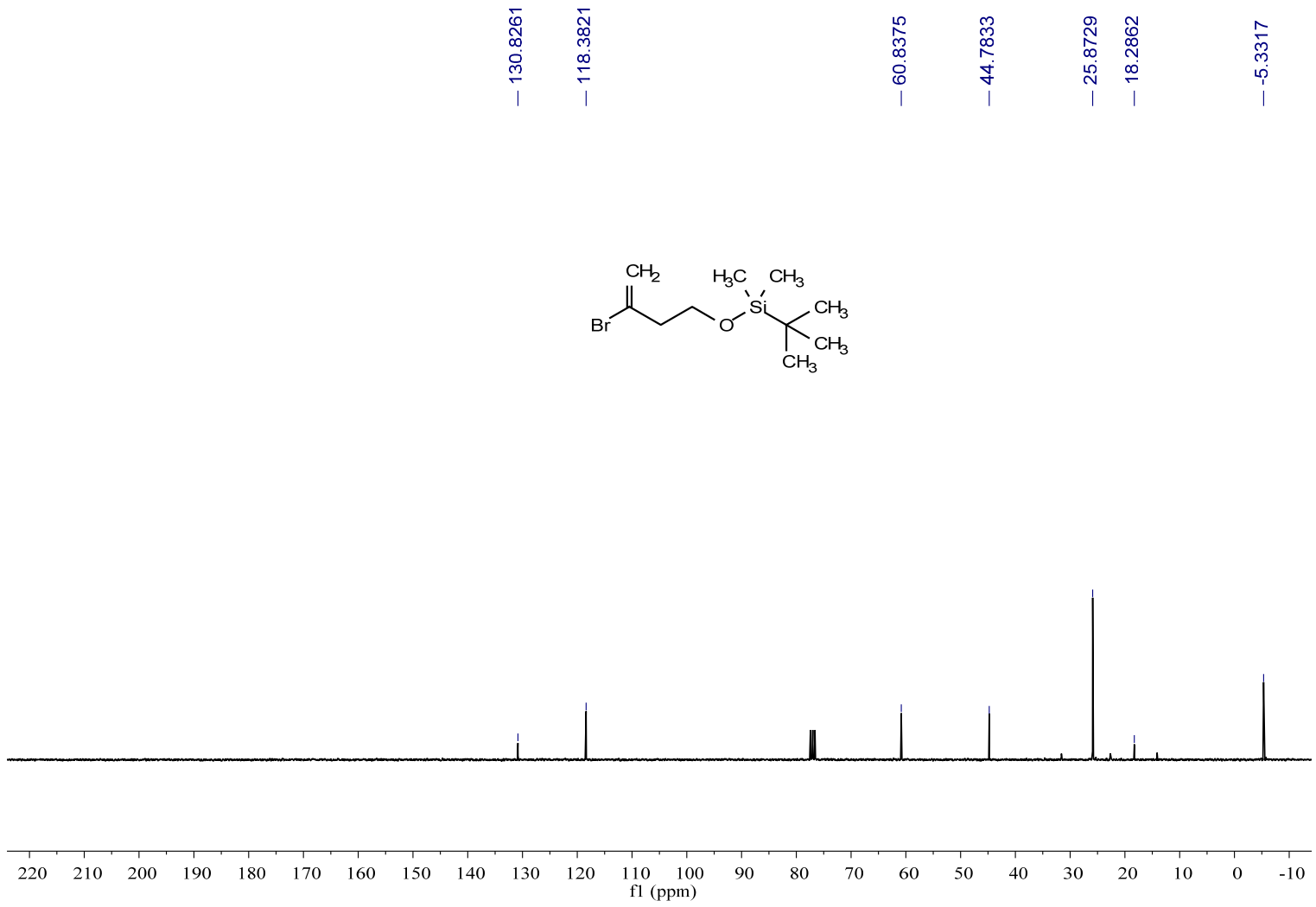
2.6147
2.5971
2.5937
0.8903
0.0663
CH2
H3C
CH3
Si
CH3
CH3
CH3
Br
O
1.00
0.99
2.01
2.01
8.98
6.20
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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44.7833
25.8729
18.2862
-5.3317
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H3C
CH3
Si
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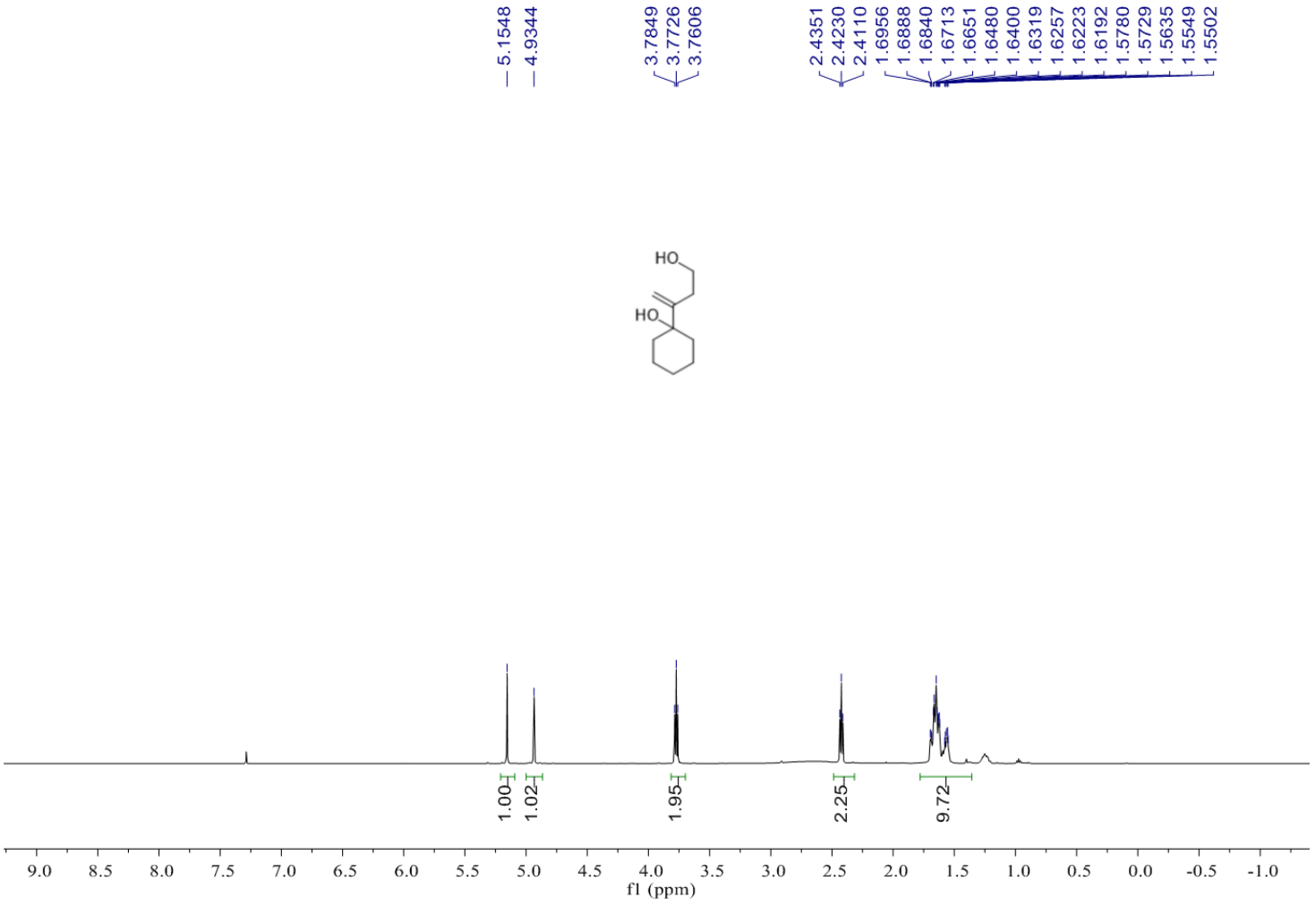
CH3
CH3
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound **1a**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1.6713
1.6651
1.6480
1.6400
1.6319
1.6257
1.6223
1.6192
1.5780
1.5729
1.5635
1.5549
1.5502
HO
HO
1.00
1.02
1.95
2.25
9.72
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
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0.0
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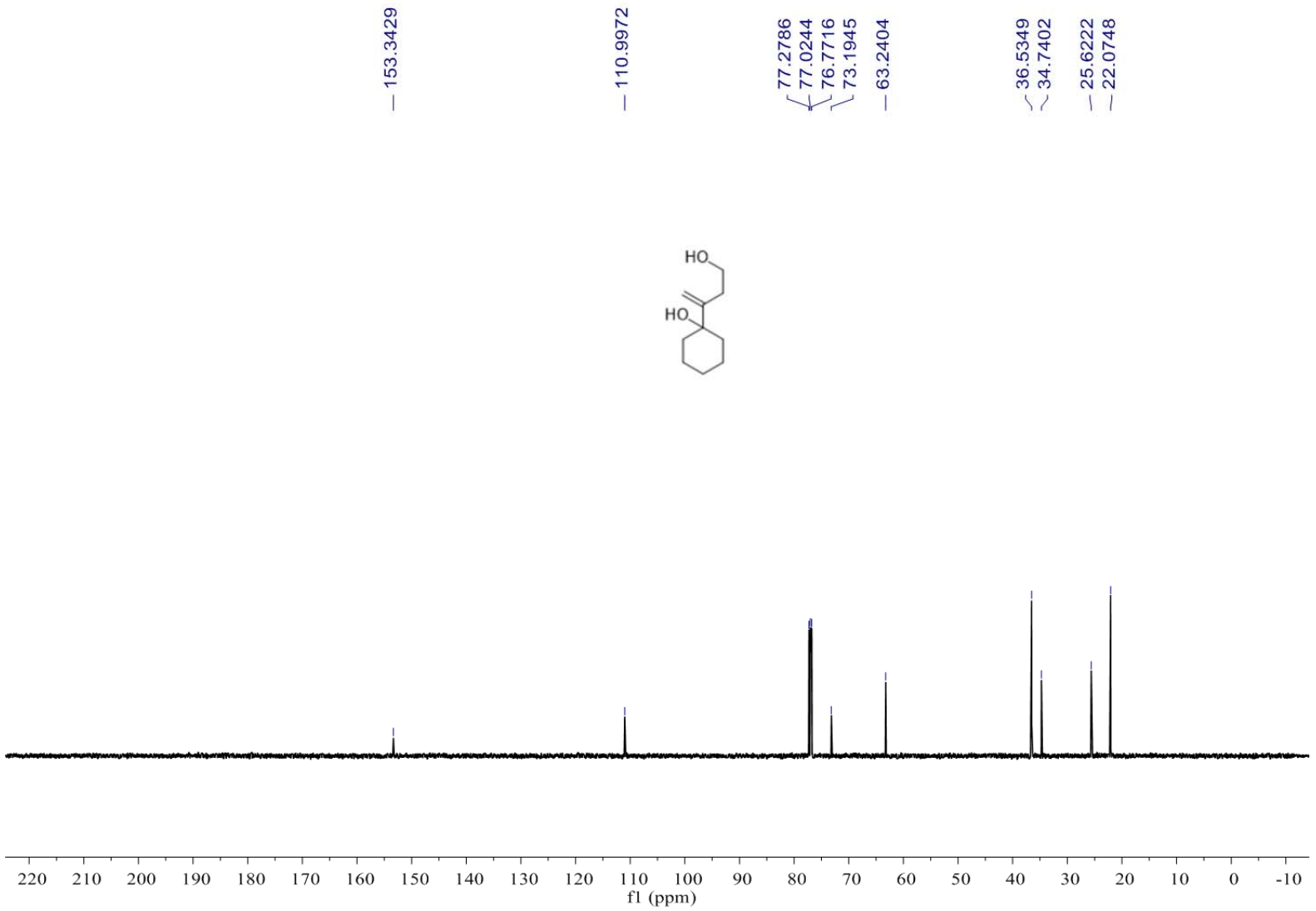
-1.0
f1 (ppm)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110.9972
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77.0244
76.7716
73.1945
63.2404
36.5349
34.7402
25.6222
22.0748
HO
HO
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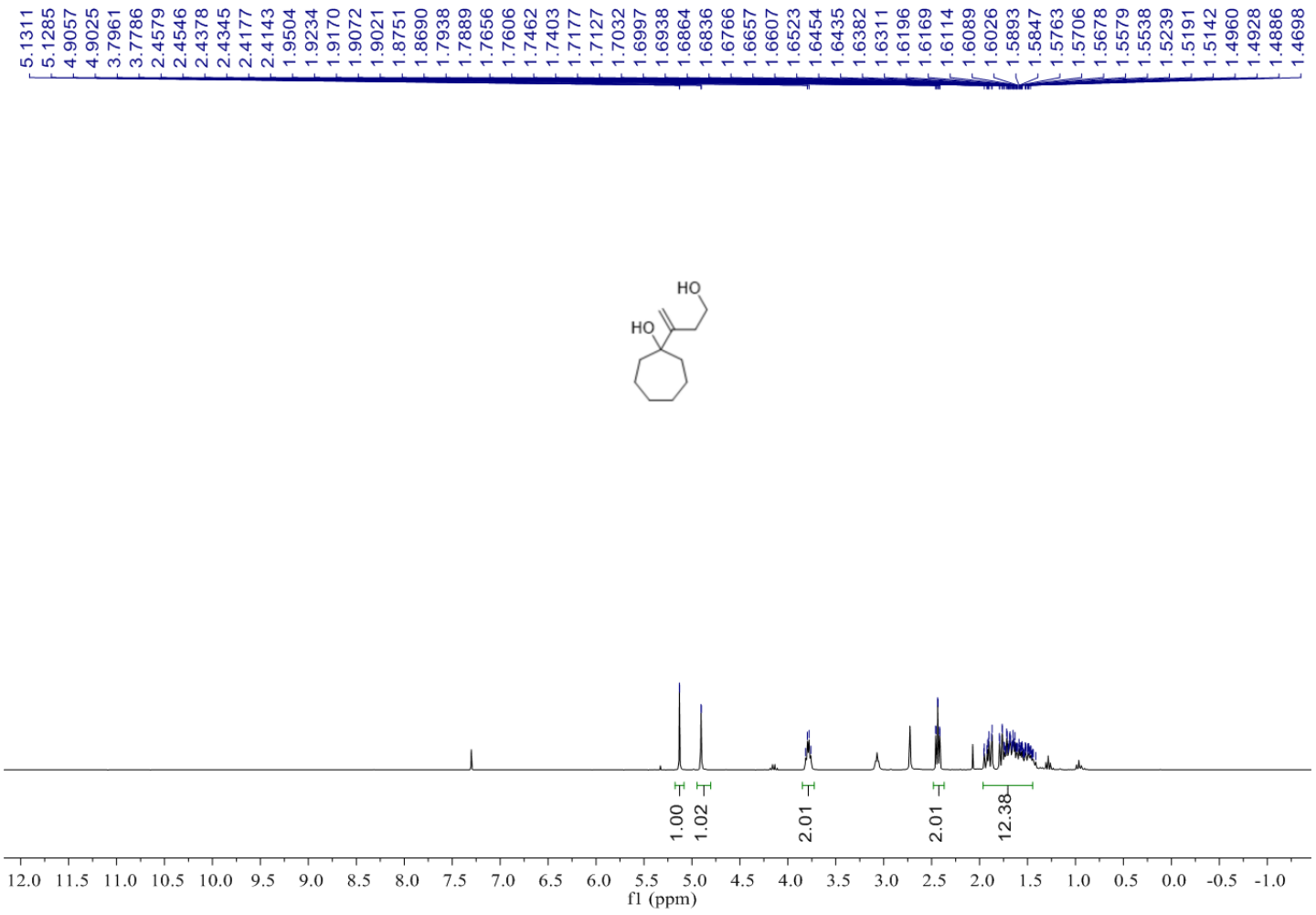
f1 (ppm)

Compound **1b**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4.9057
4.9025
3.7961
3.7786
2.4579
2.4546
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2.4345
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2.01
2.01
12.38
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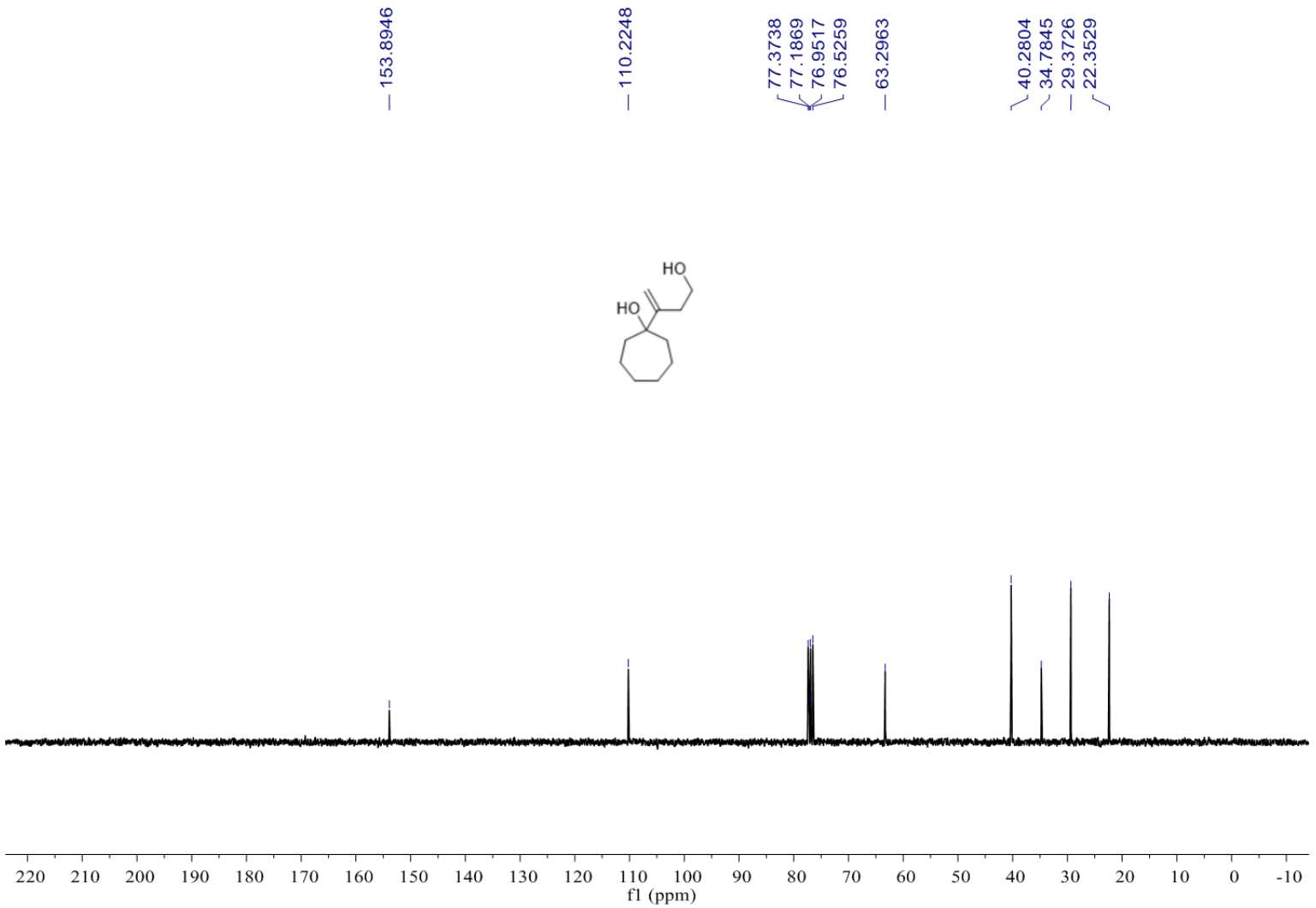
f1 (ppm)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77.1869
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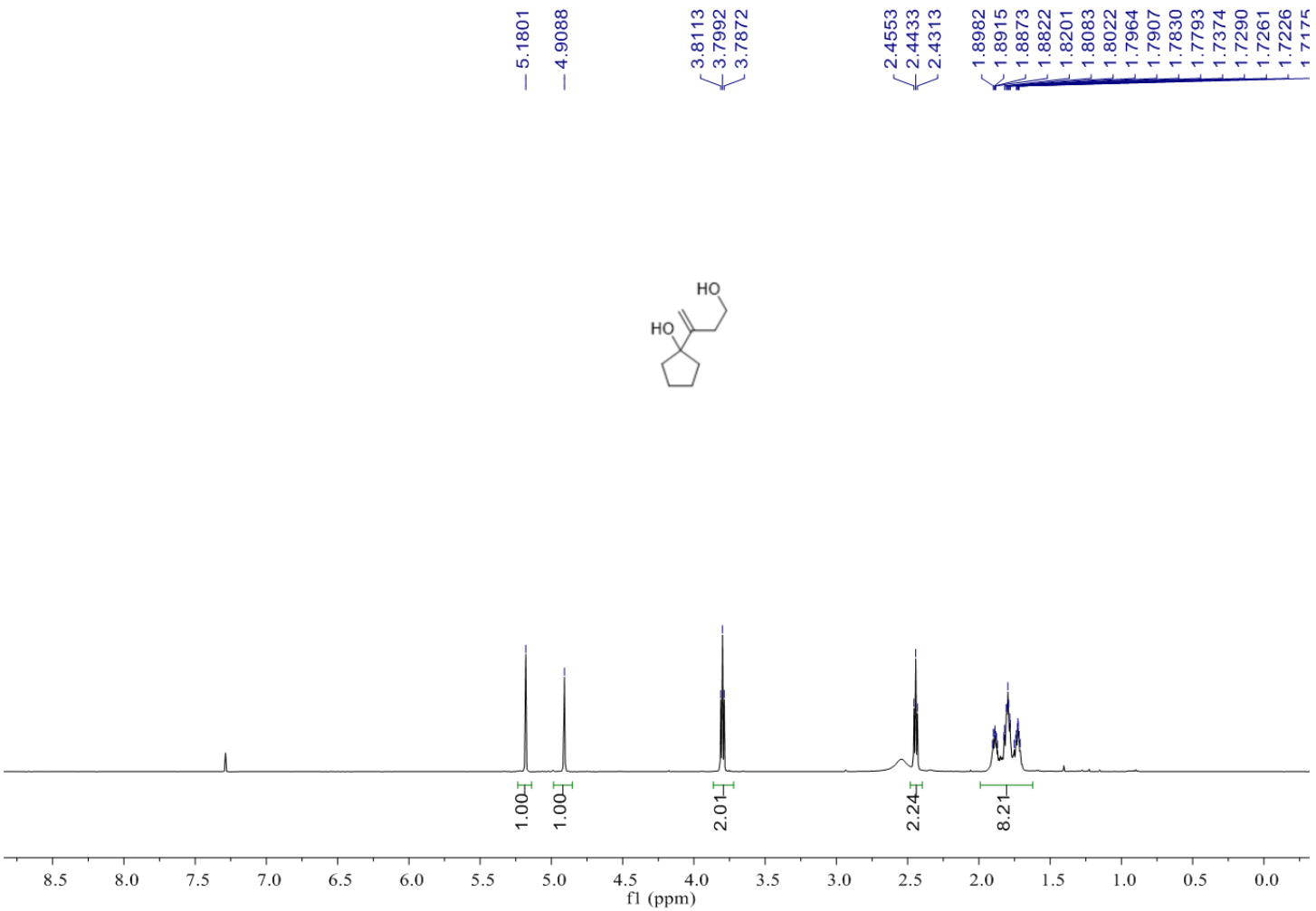
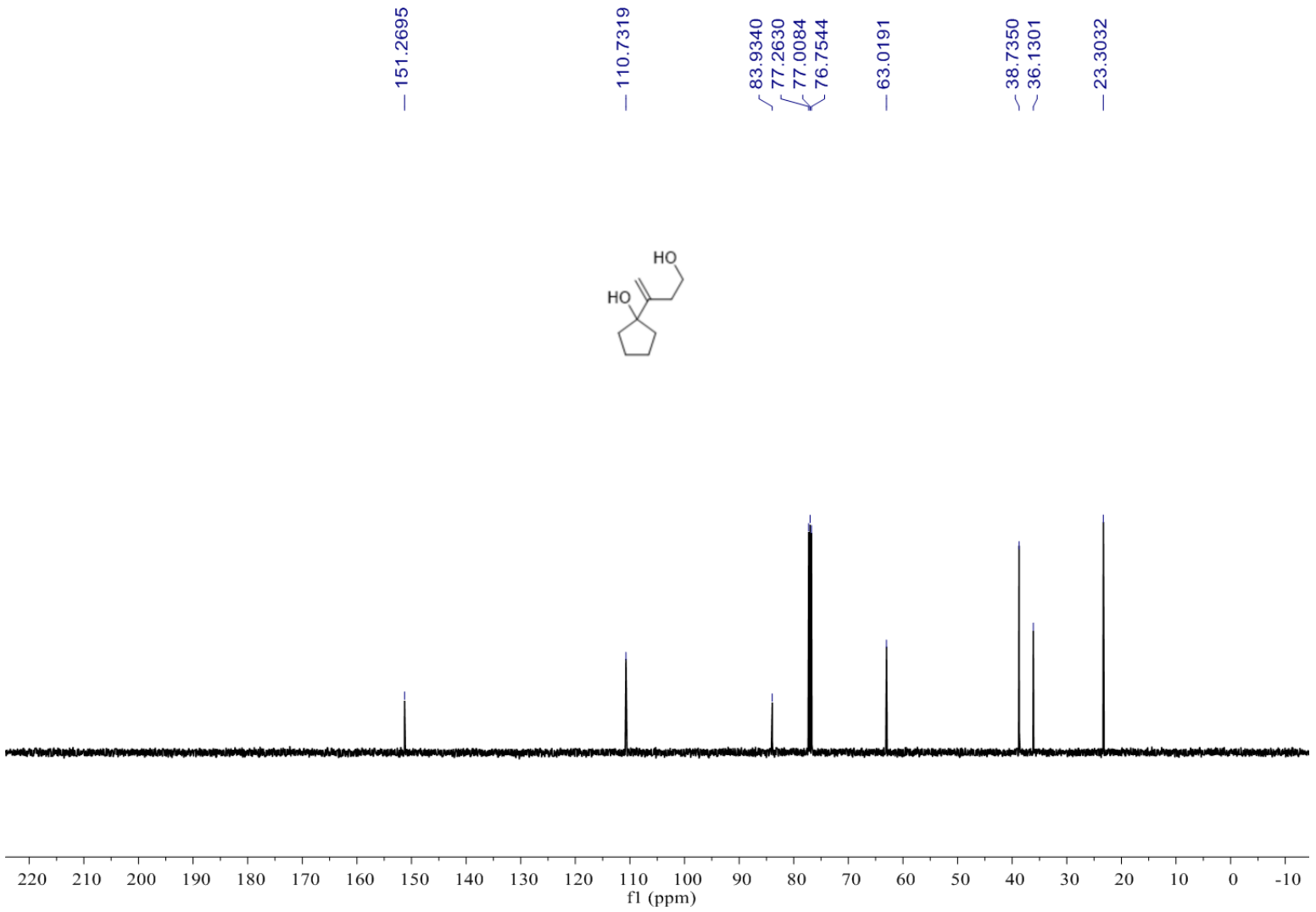
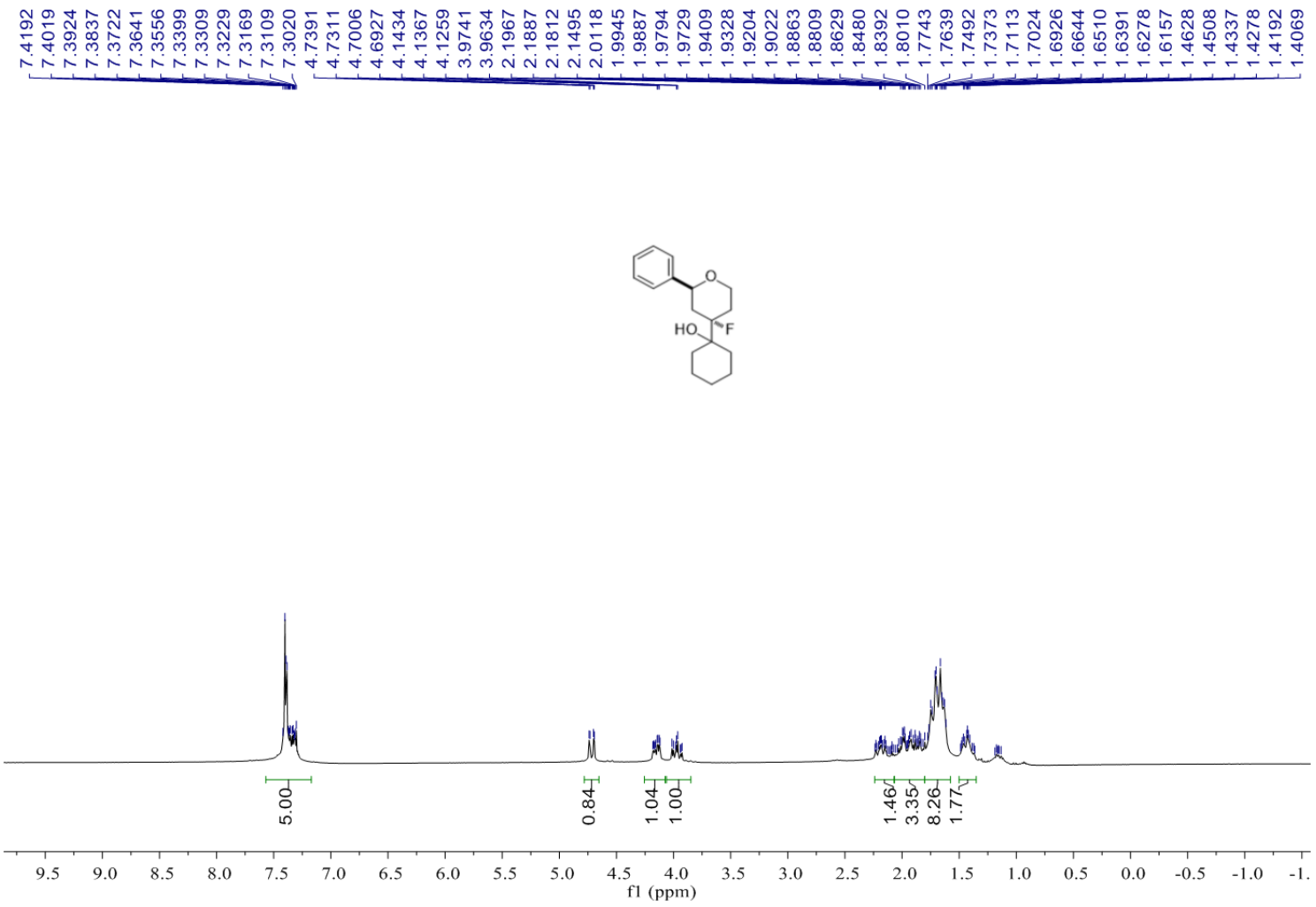
76.5259
63.2963
40.2804
34.7845
29.3726
22.3529
HO
HO
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

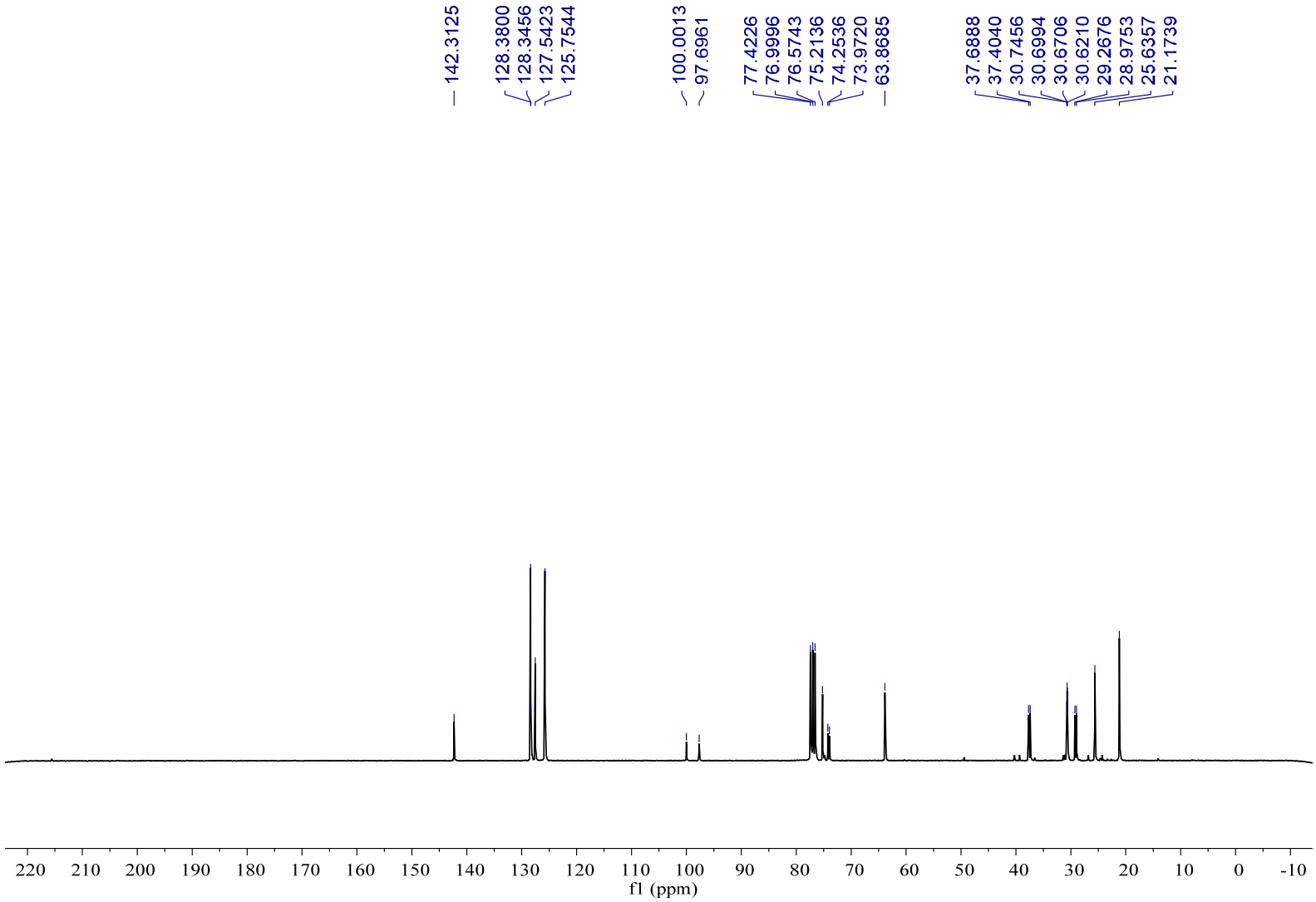
Compound **1c**


5.1801
4.9088
3.8113
3.7992
3.7872
2.4553
2.4433
2.4313
1.8982
1.8915
1.8873
1.8822
1.8201
1.8083
1.8022
1.7964
1.7907
1.7830
1.7793
1.7374
1.7290
1.7261
1.7226
HO
HO
1.00
1.00
2.01
2.24
8.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

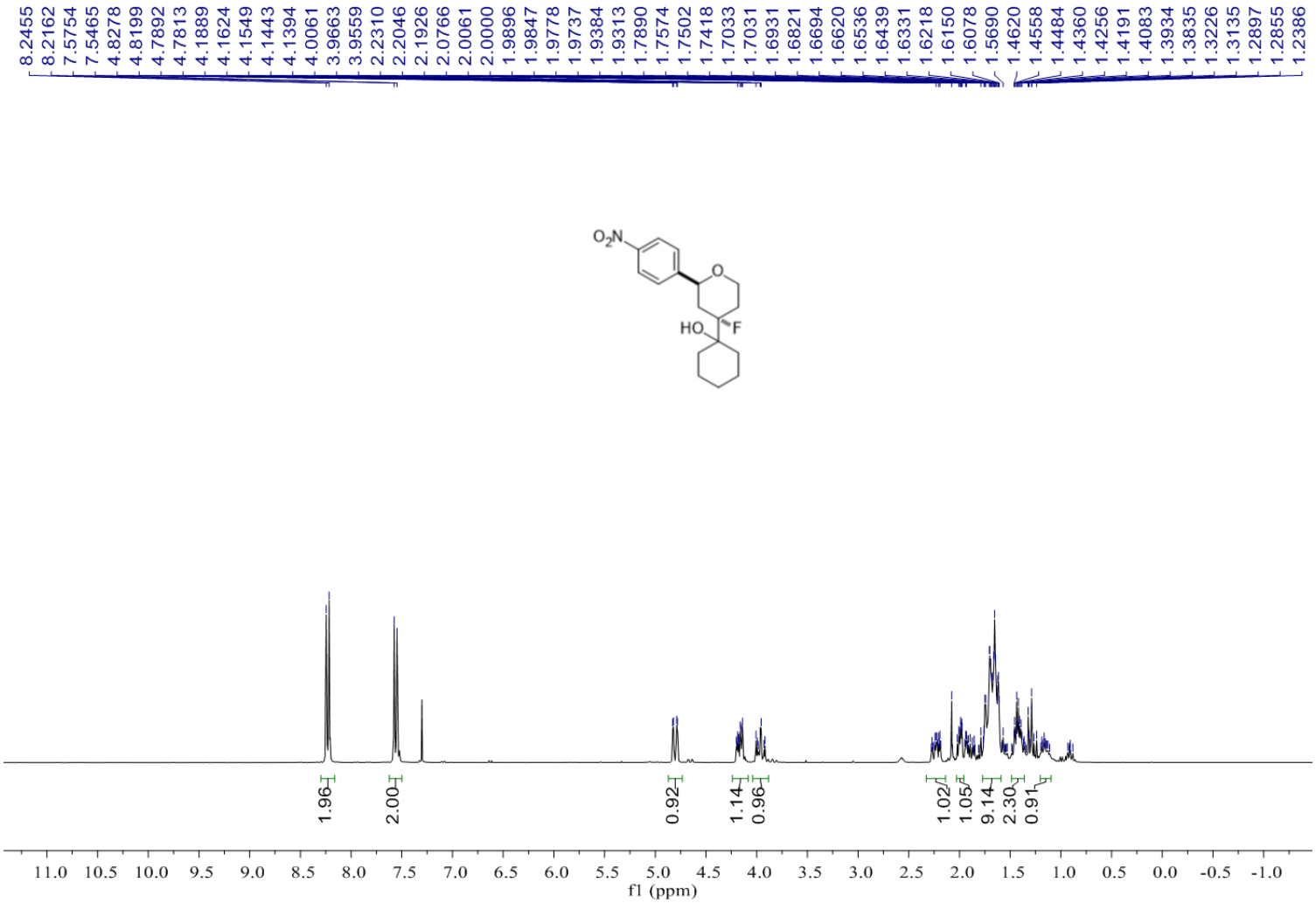

151.2695
110.7319
83.9340
77.2630
77.0084
76.7544
63.0191
38.7350
36.1301
23.3032
HO
HO
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

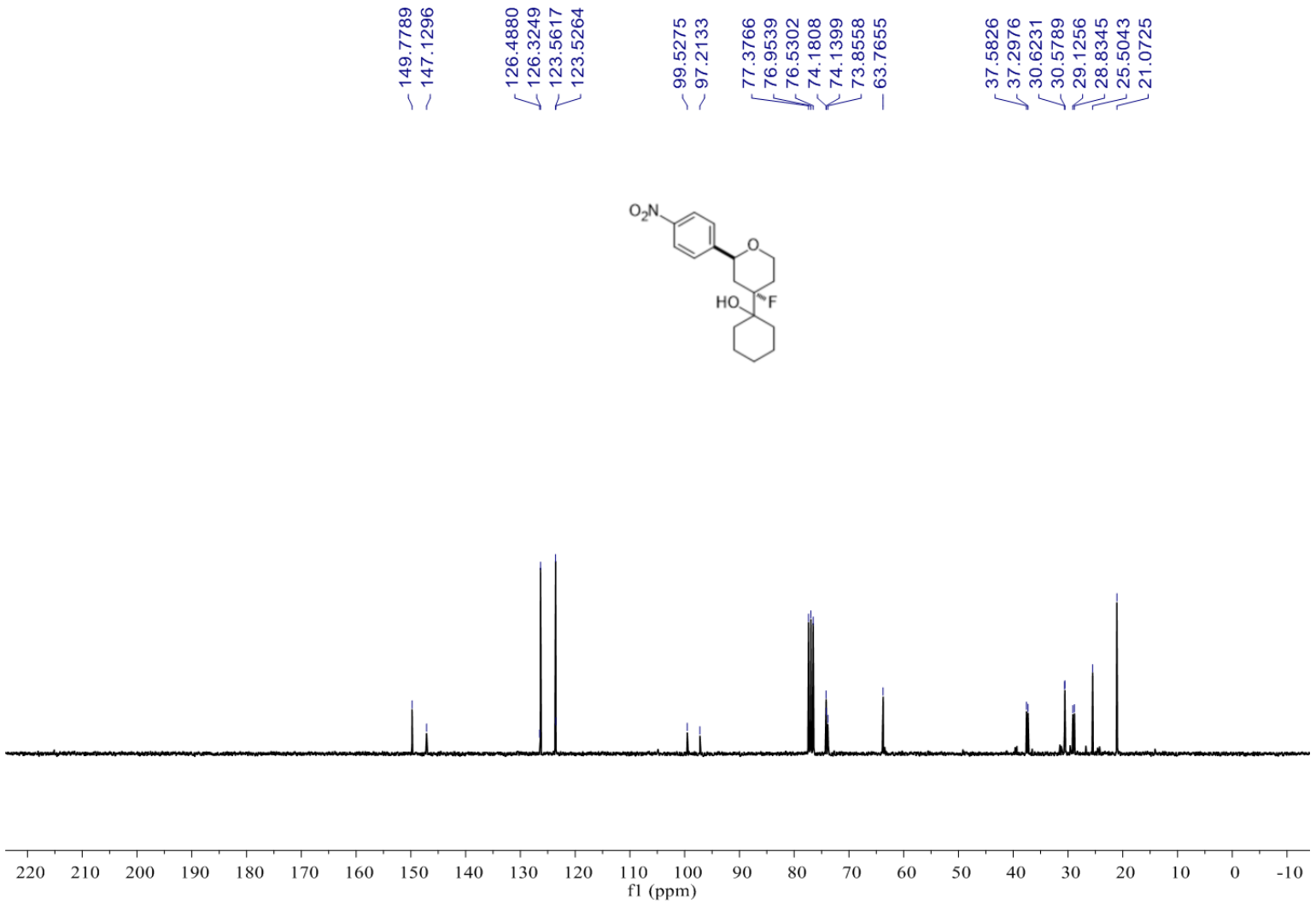
Compound **7aa**



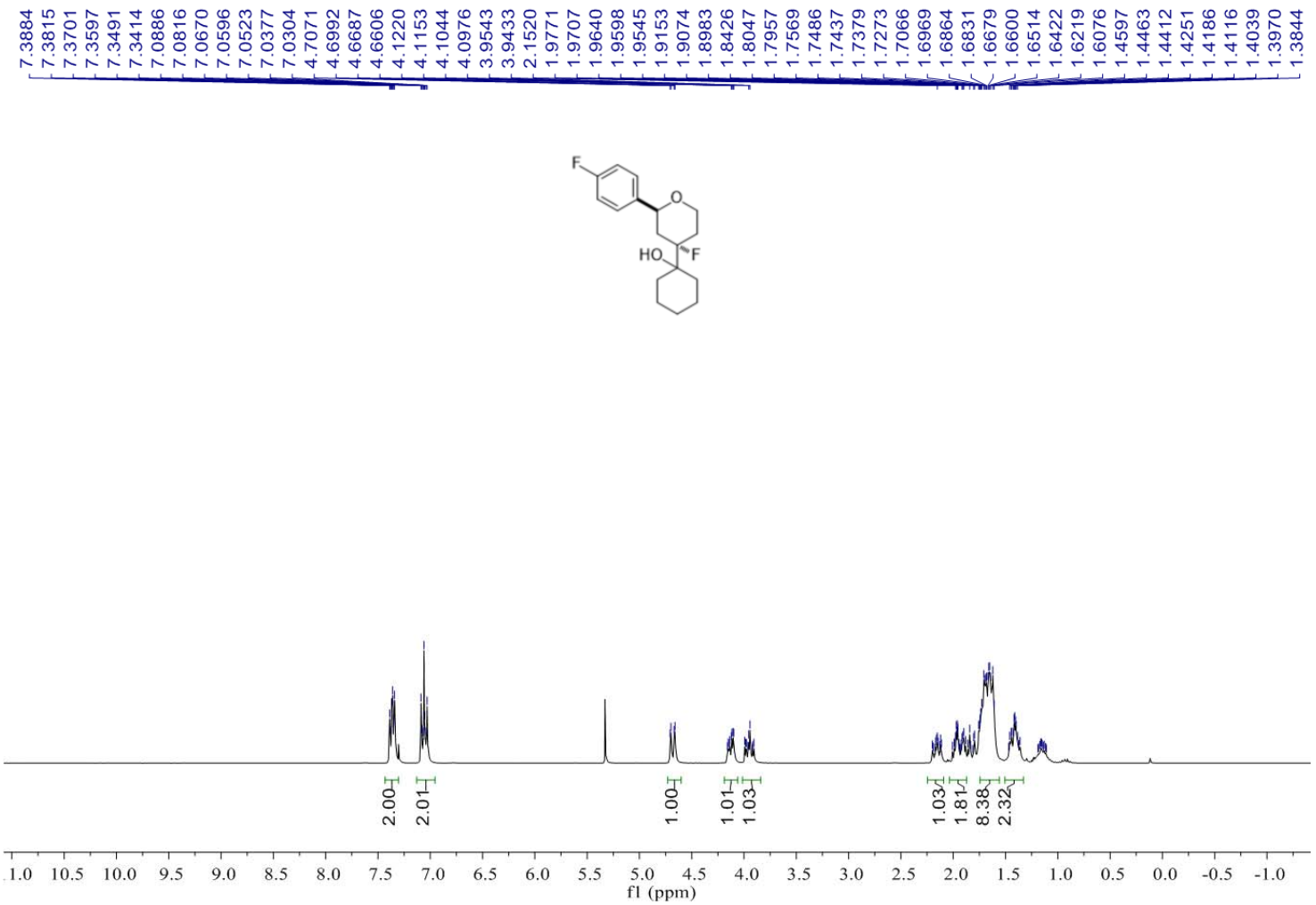

142.3125
128.3800
128.3456
127.5423
125.7544
100.0013
97.6961
77.4226
76.9996
76.5743
75.2136
74.2536
73.9720
63.8685
37.6888
37.4040
30.7456
30.6994
30.6706
30.6210
29.2676
28.9753
25.6357
21.1739
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

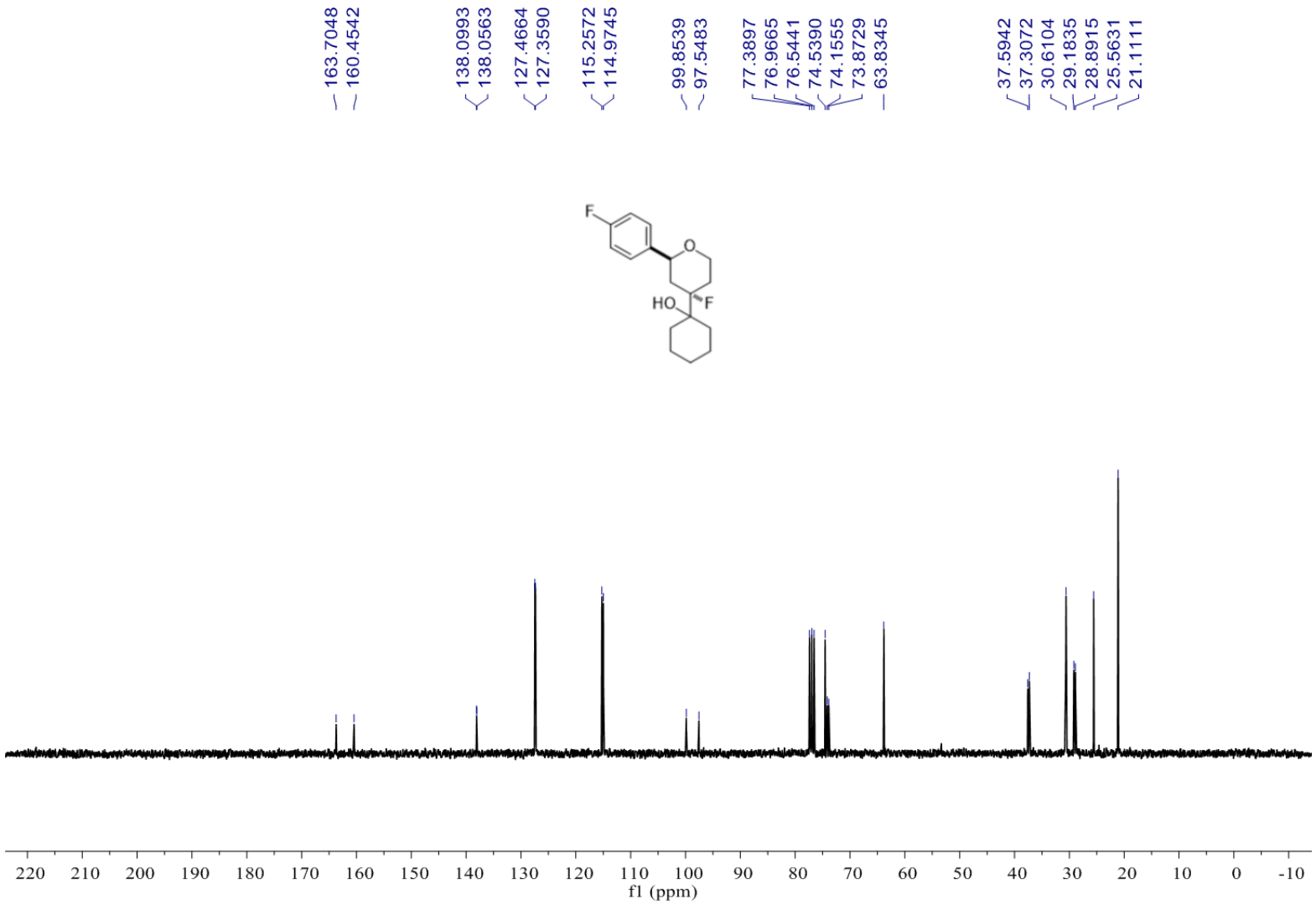
Compound **7ab**



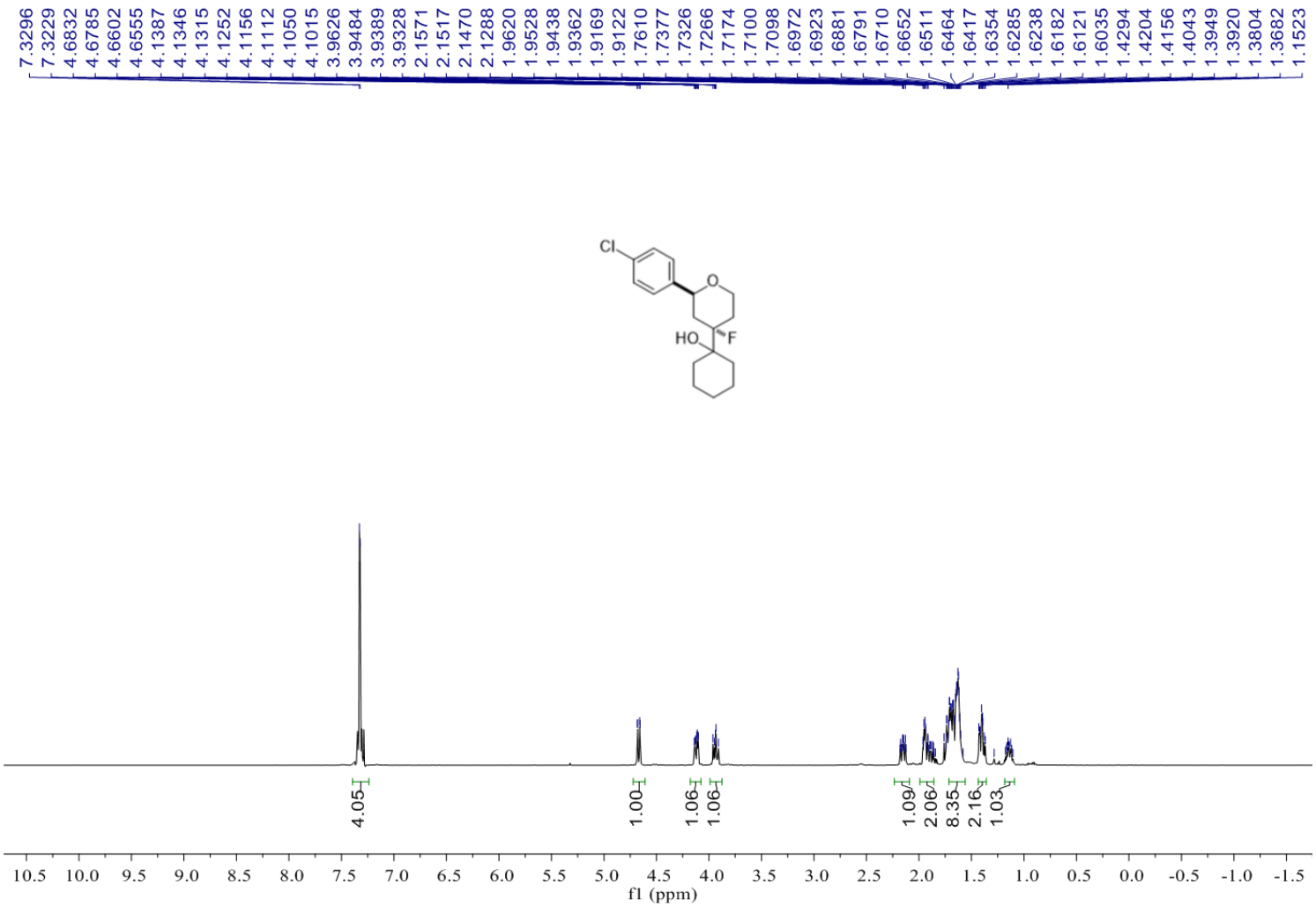

149.7789
147.1296
126.4880
126.3249
123.5617
123.5264
99.5275
97.2133
77.3766
76.9539
76.5302
74.1808
74.1399
73.8558
63.7655
37.5826
37.2976
30.6231
30.5789
29.1256
28.8345
25.5043
21.0725
O2N
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

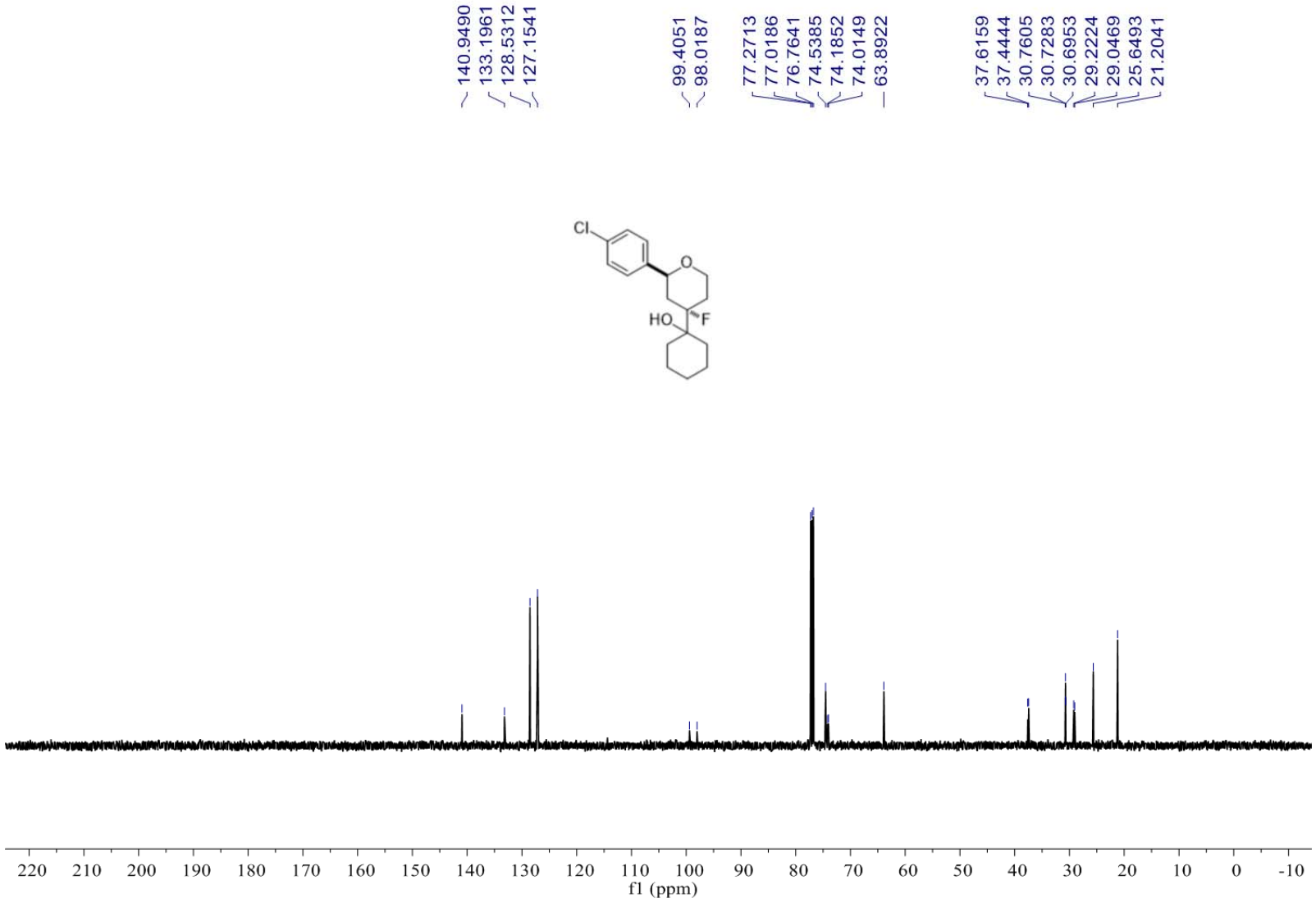
Compound **7ac**



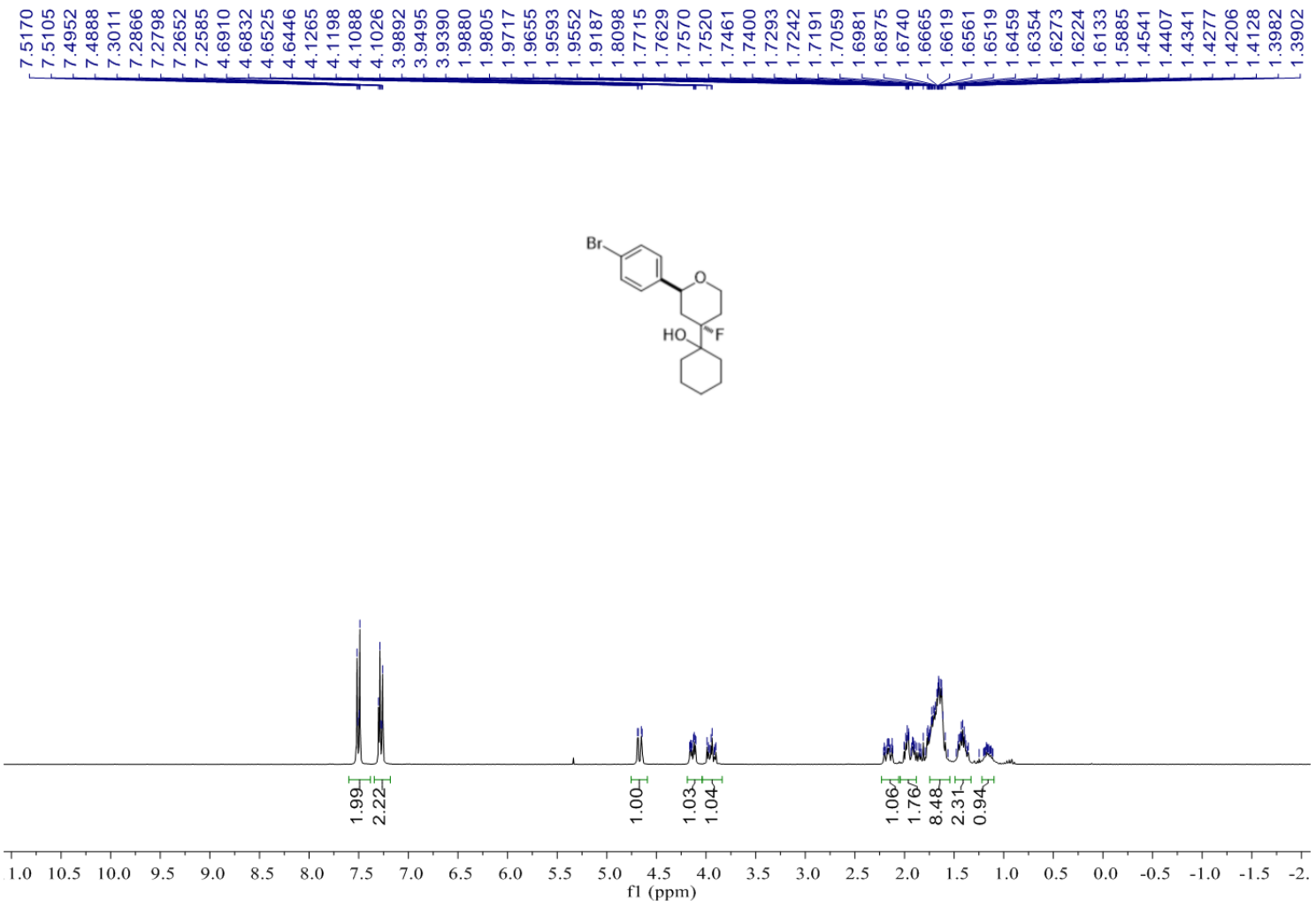

163.7048
160.4542
138.0993
138.0563
127.4664
127.3590
115.2572
114.9745
99.8539
97.5483
77.3897
76.9665
76.5441
74.5390
74.1555
73.8729
63.8345
37.5942
37.3072
30.6104
29.1835
28.8915
25.5631
21.1111
F
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

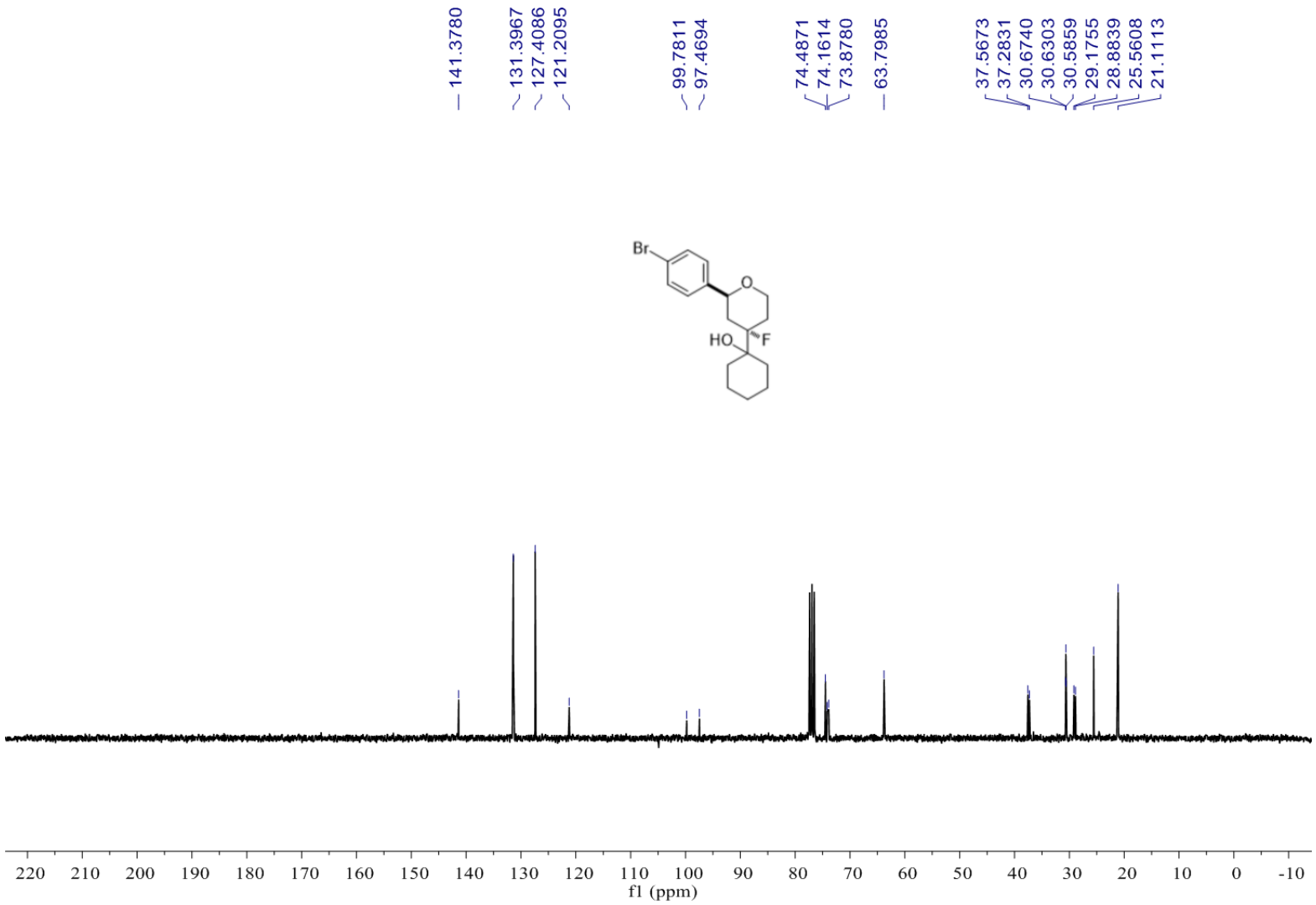
Compound **7ad**



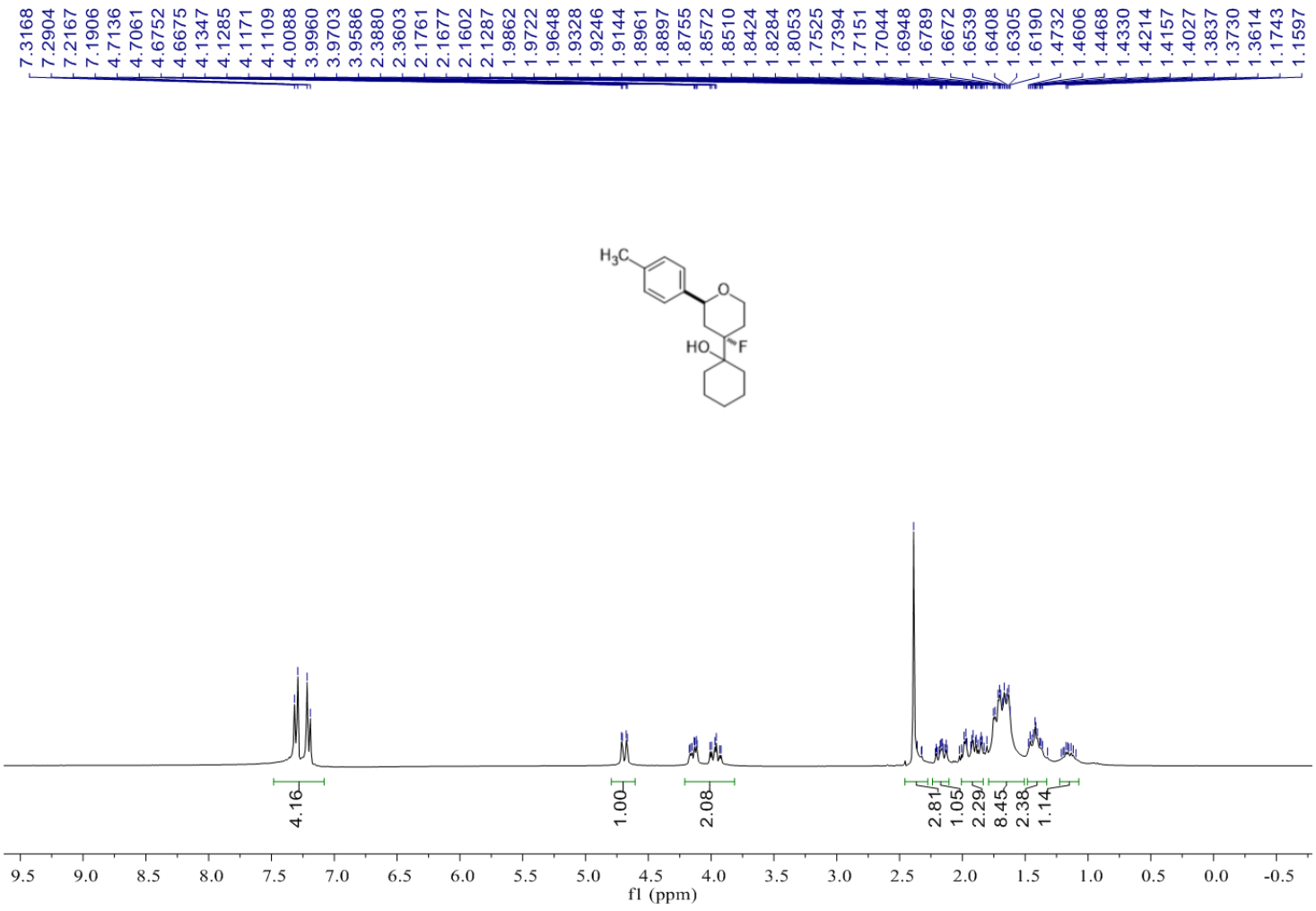

140.9490
133.1961
128.5312
127.1541
99.4051
98.0187
77.2713
77.0186
76.7641
74.5385
74.1852
74.0149
63.8922
37.6159
37.4444
30.7605
30.7283
30.6953
29.2224
29.0469
25.6493
21.2041
Cl
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

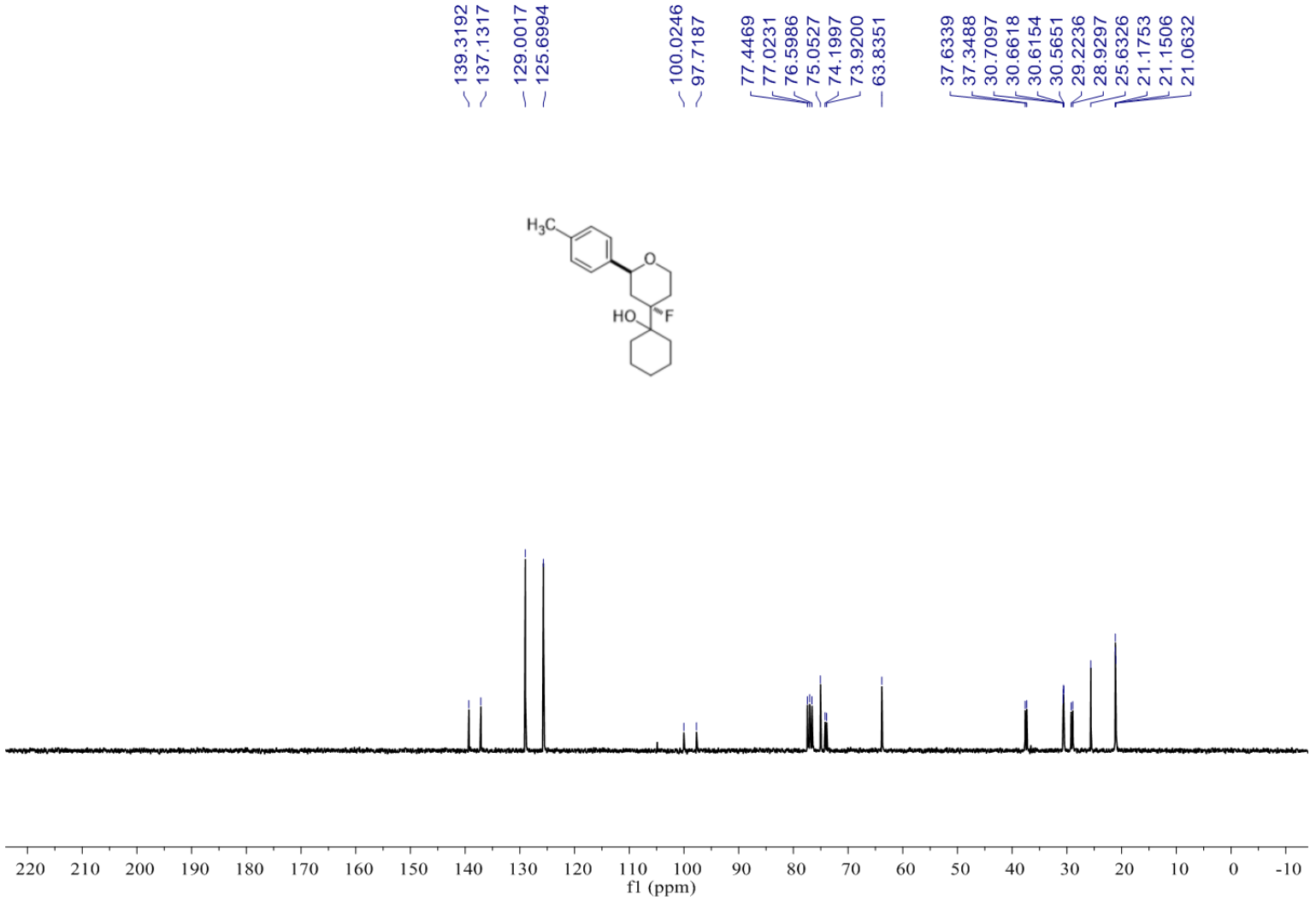
Compound **7ae**



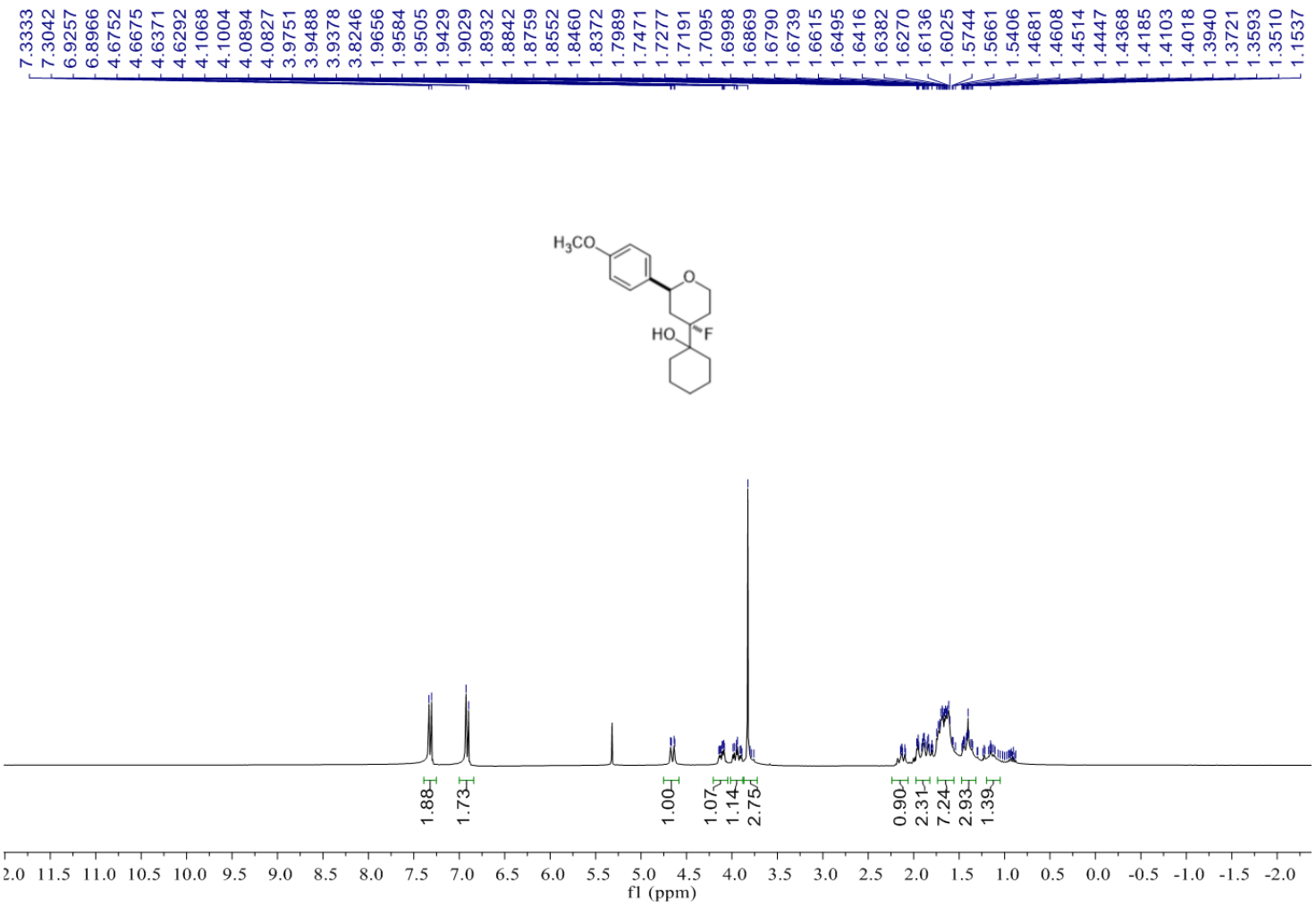

141.3780
131.3967
127.4086
121.2095
99.7811
97.4694
74.4871
74.1614
73.8780
63.7985
37.5673
37.2831
30.6740
30.6303
30.5859
29.1755
28.8839
25.5608
21.1113
Br
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

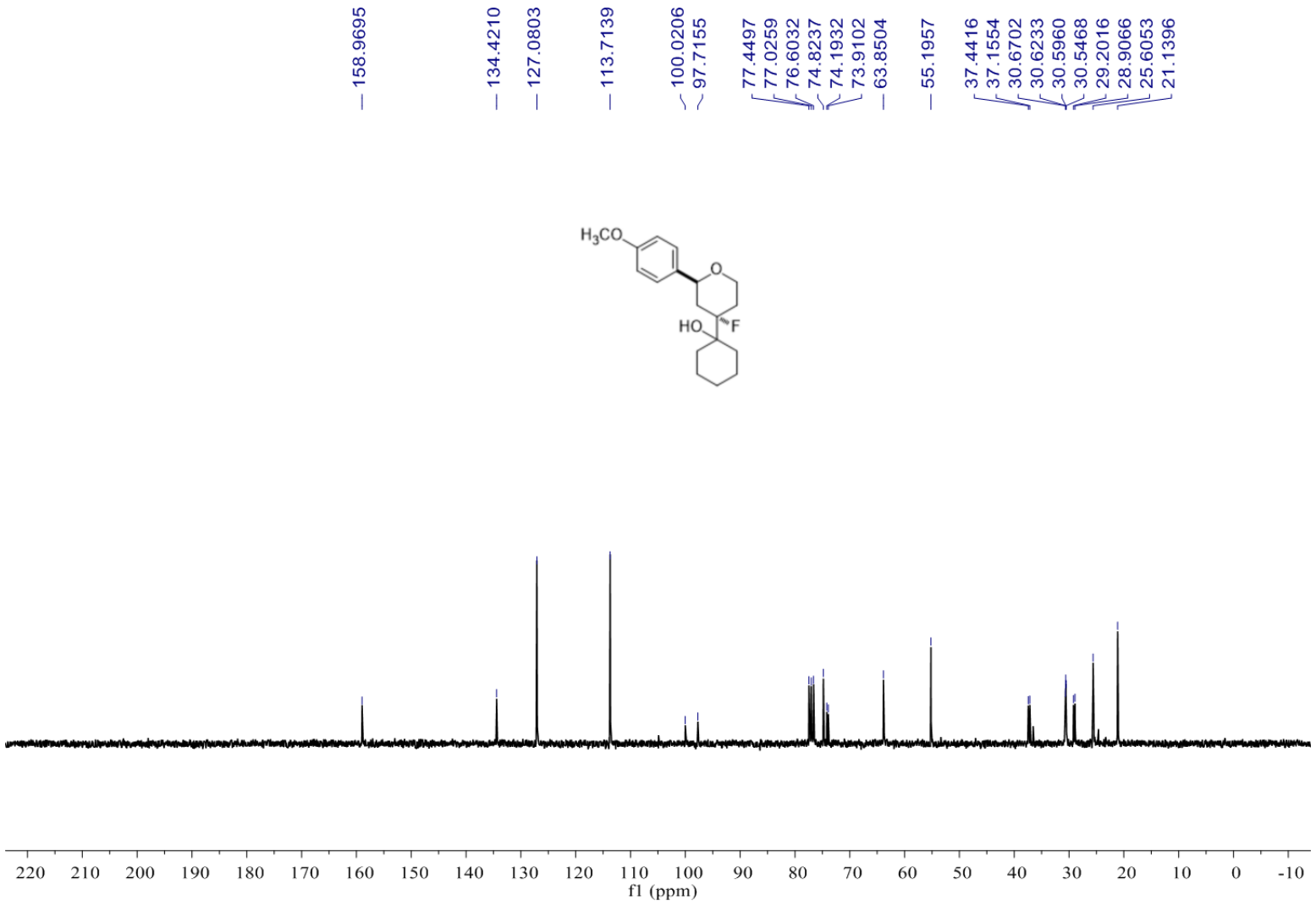
Compound **7af**



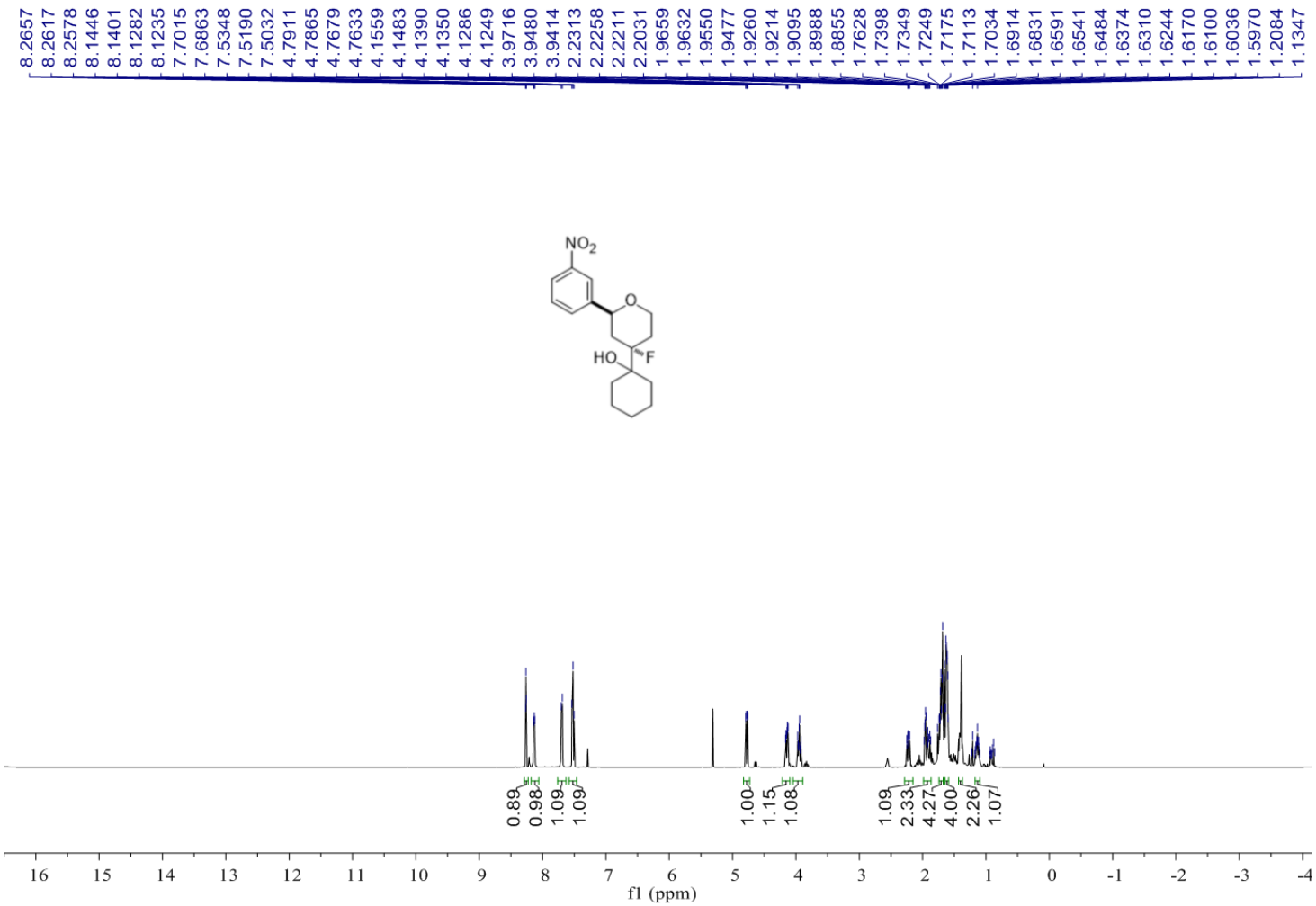

139.3192
137.1317
129.0017
125.6994
100.0246
97.7187
77.4469
77.0231
76.5986
75.0527
74.1997
73.9200
63.8351
37.6339
37.3488
30.7097
30.6618
30.6154
30.5651
29.2236
28.9297
25.6326
21.1753
21.1506
21.0632
H3C
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

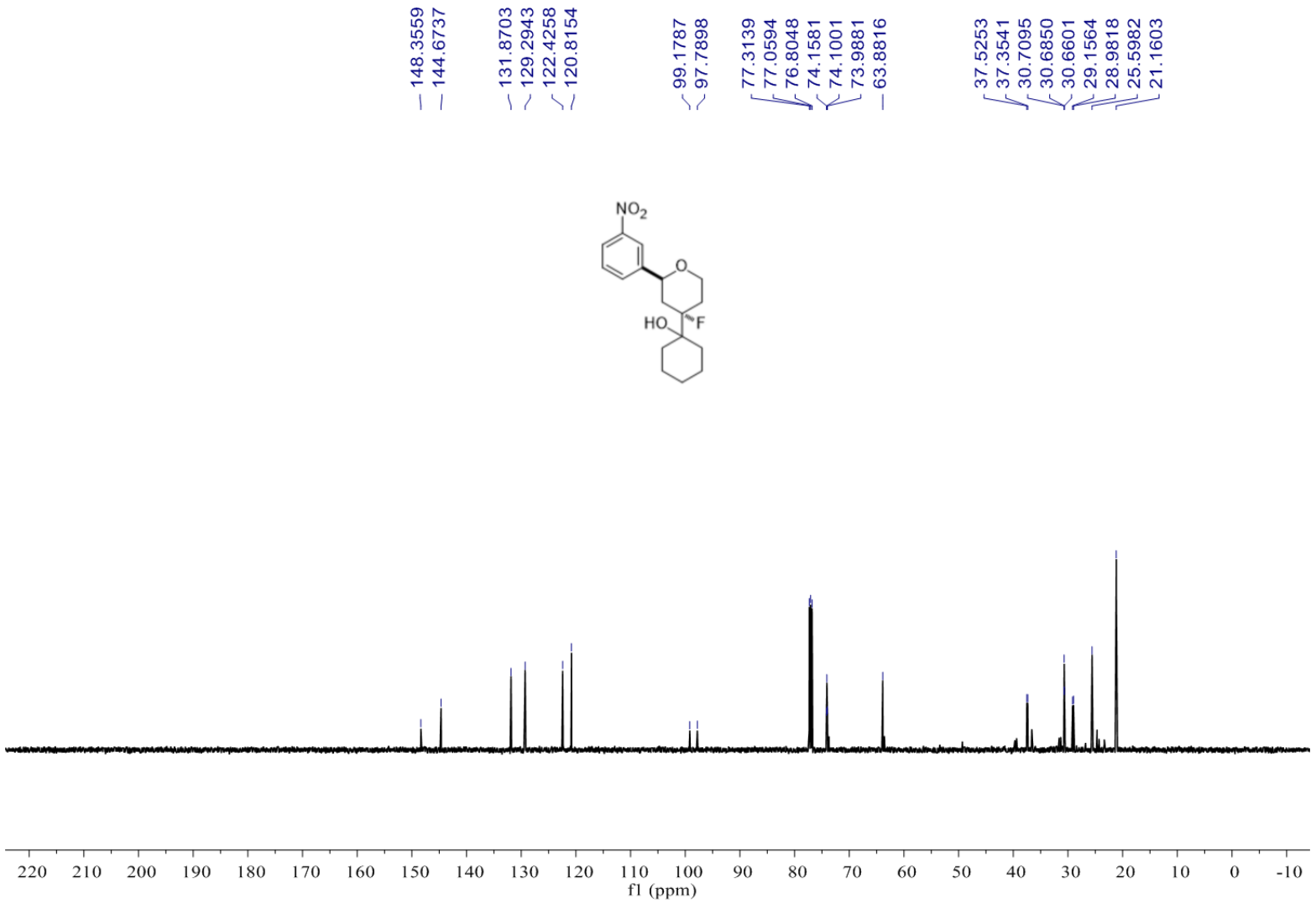
Compound **7ag**



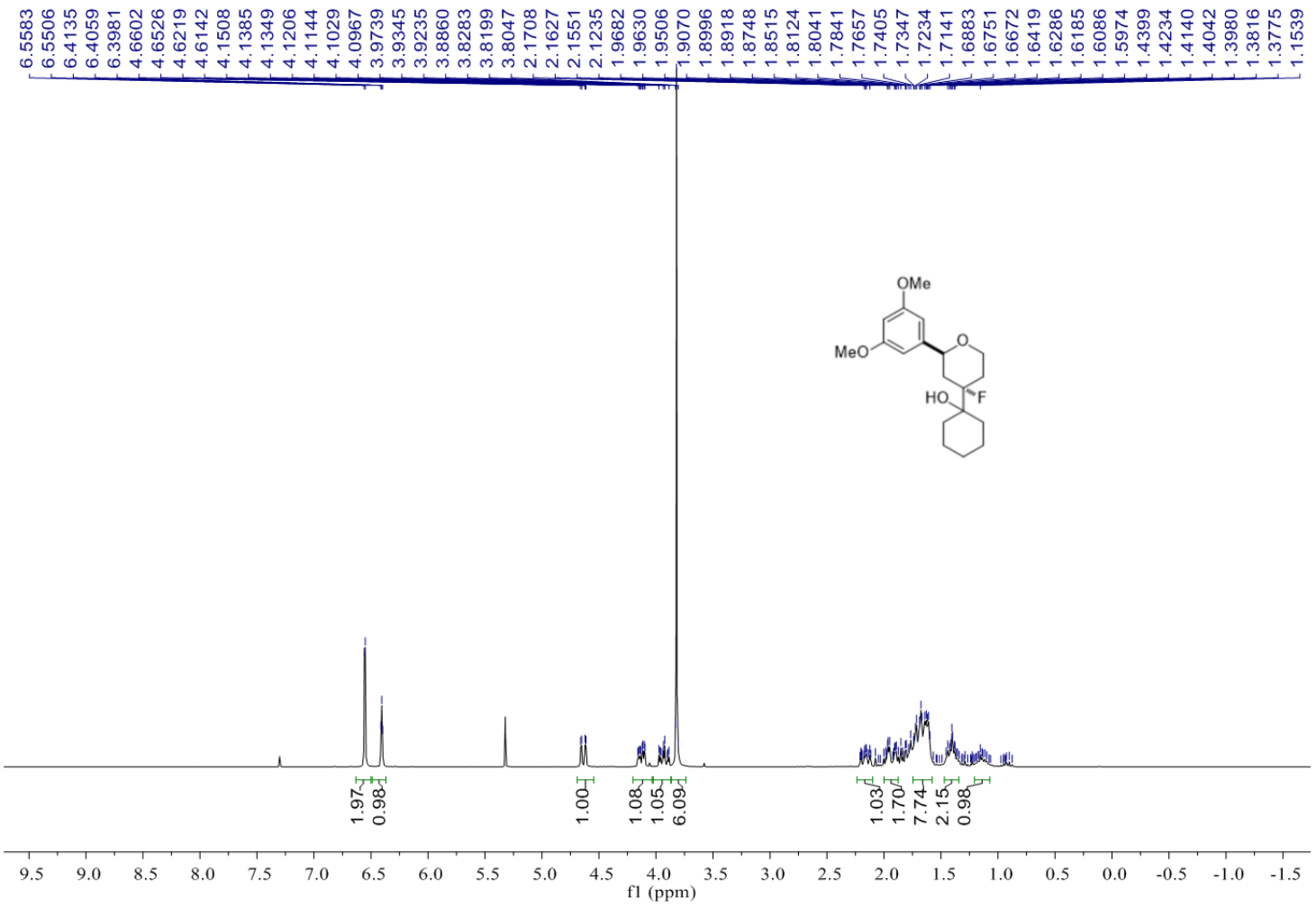

158.9695
134.4210
127.0803
113.7139
100.0206
97.7155
77.4497
77.0259
76.6032
74.8237
74.1932
73.9102
63.8504
55.1957
37.4416
37.1554
30.6702
30.6233
30.5960
30.5468
29.2016
28.9066
25.6053
21.1396
H3CO
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

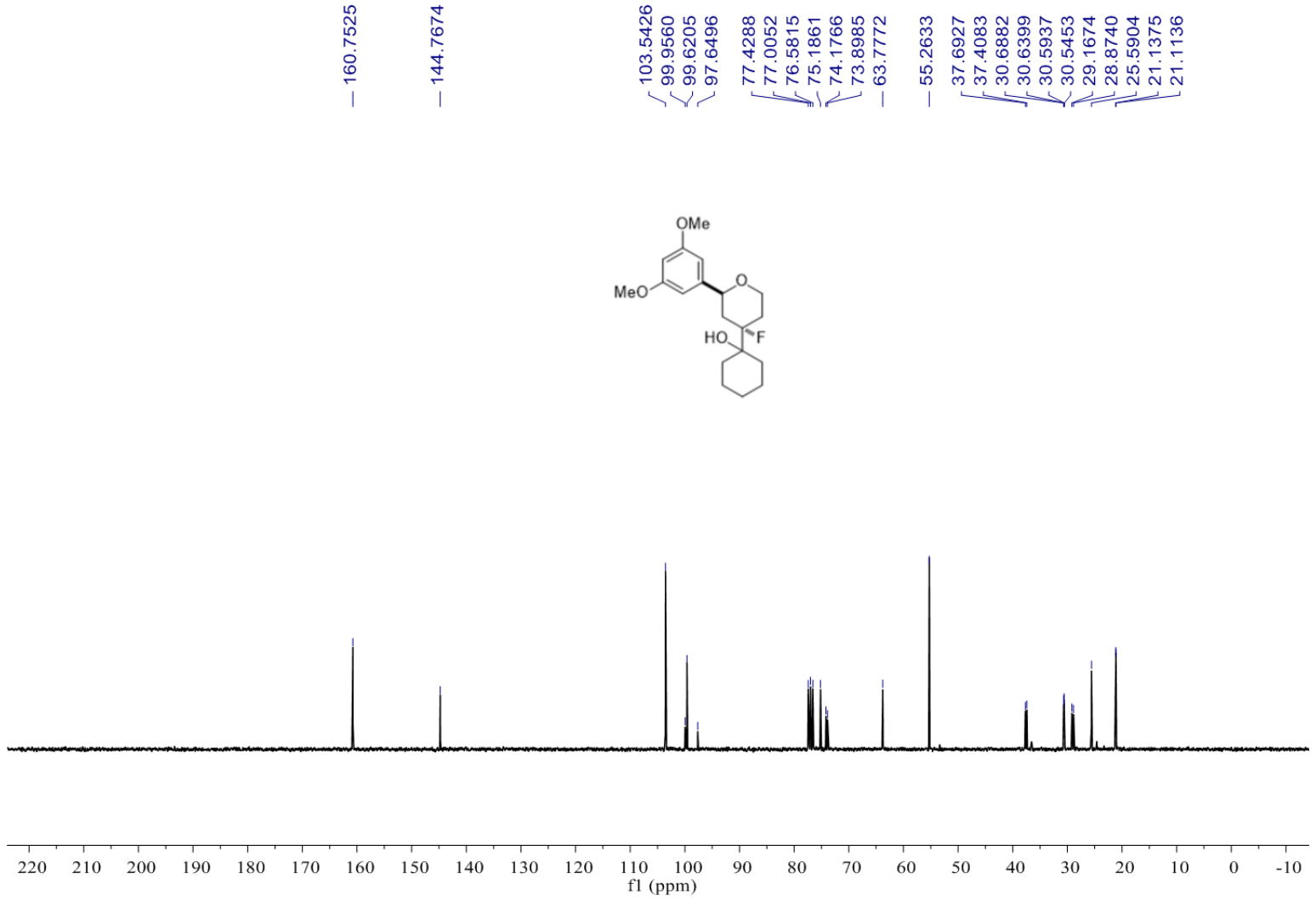
Compound **7ah**



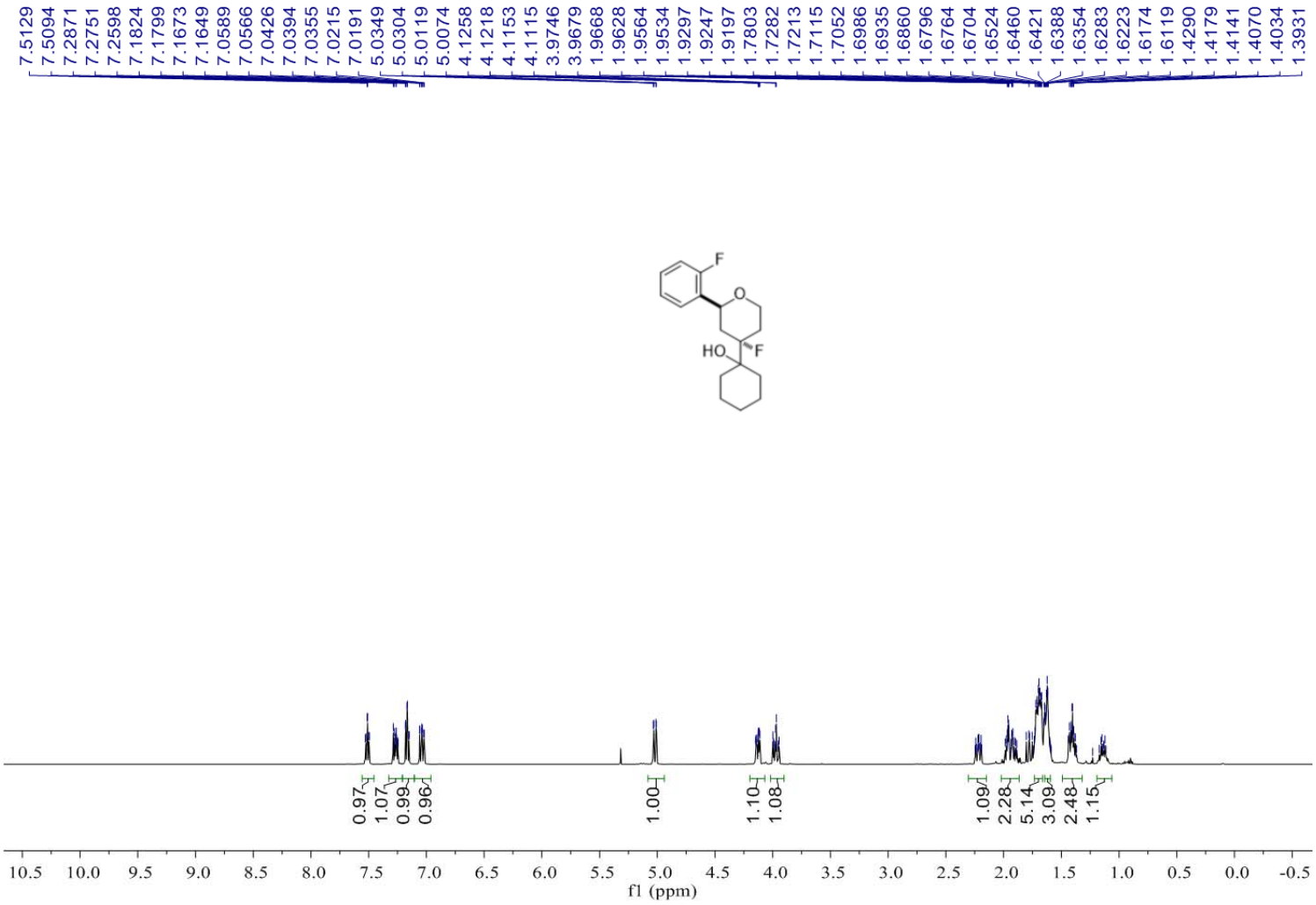

148.3559
144.6737
131.8703
129.2943
122.4258
120.8154
99.1787
97.7898
77.3139
77.0594
76.8048
74.1581
74.1001
73.9881
63.8816
37.5253
37.3541
30.7095
30.6850
30.6601
29.1564
28.9818
25.5982
21.1603
NO2
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

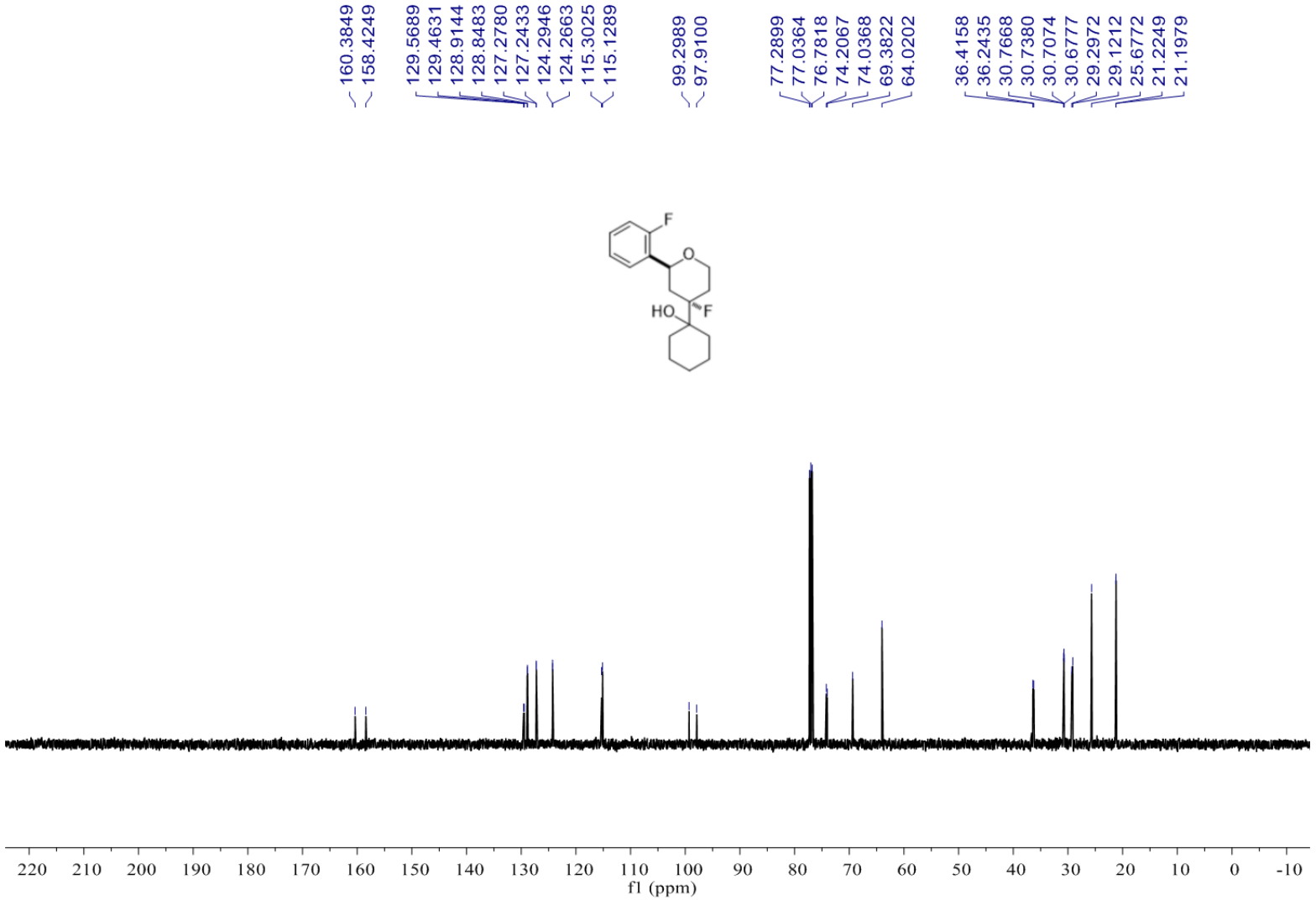
Compound **7ai**



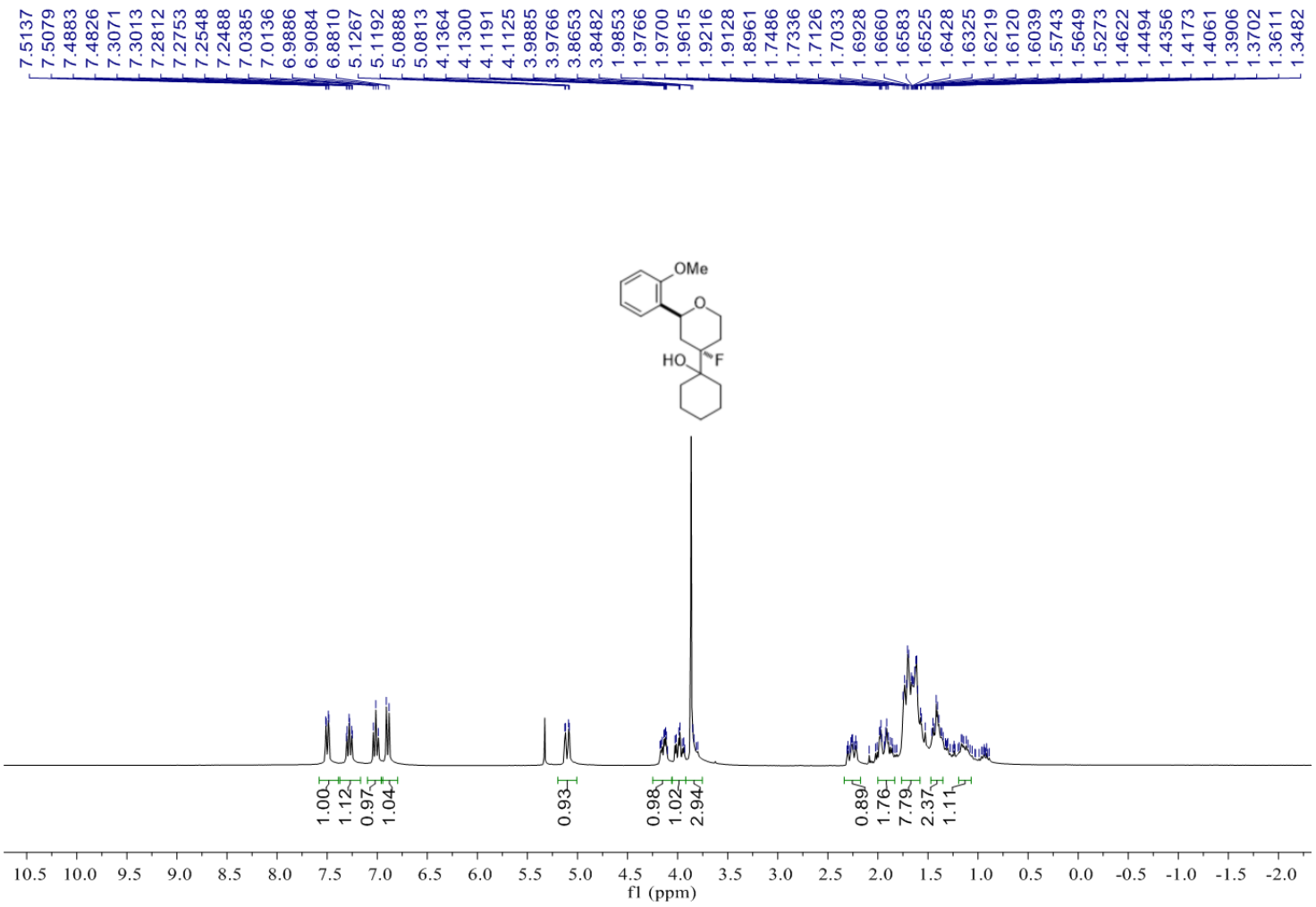

160.7525
144.7674
103.5426
99.9560
99.6205
97.6496
77.4288
77.0052
76.5815
75.1861
74.1766
73.8985
63.7772
55.2633
37.6927
37.4083
30.6882
30.6399
30.5937
30.5453
29.1674
28.8740
25.5904
21.1375
21.1136
OMe
MeO
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

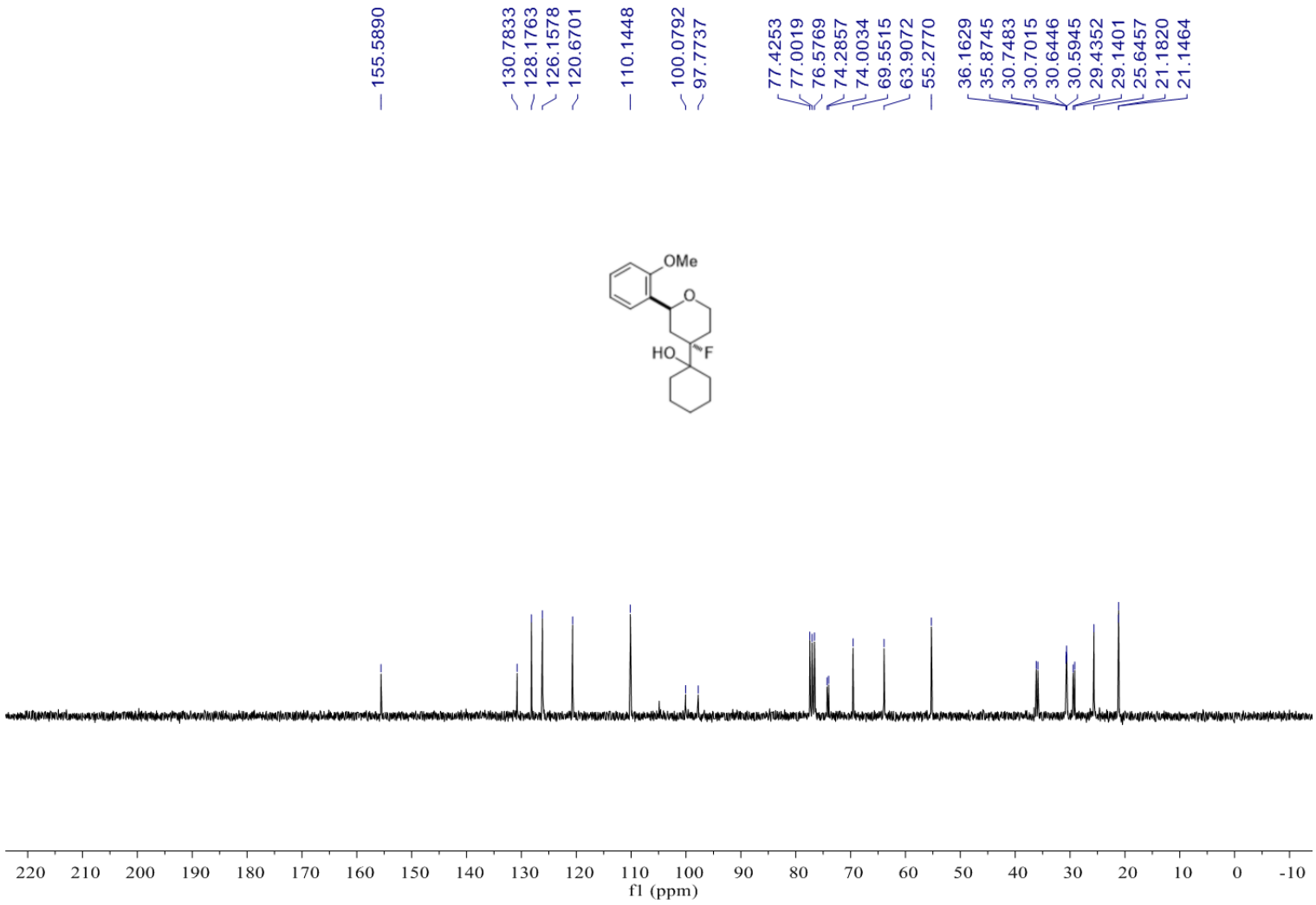
Compound **7aj**



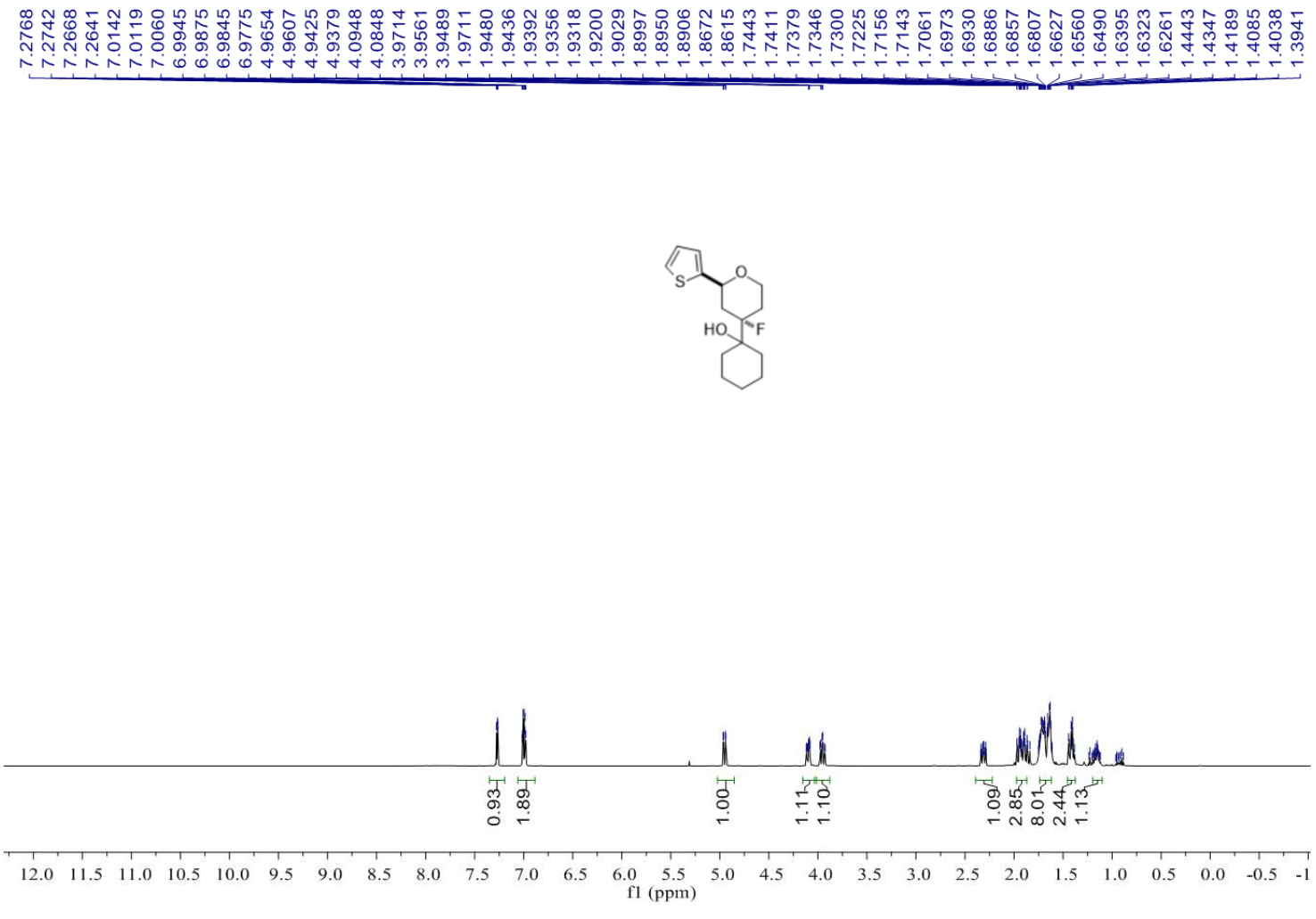

160.3849
158.4249
129.5689
129.4631
128.9144
128.8483
127.2780
127.2433
124.2946
124.2663
115.3025
115.1289
99.2989
97.9100
77.2899
77.0364
76.7818
74.2067
74.0368
69.3822
64.0202
36.4158
36.2435
30.7668
30.7380
30.7074
30.6777
29.2972
29.1212
25.6772
21.2249
21.1979
F
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

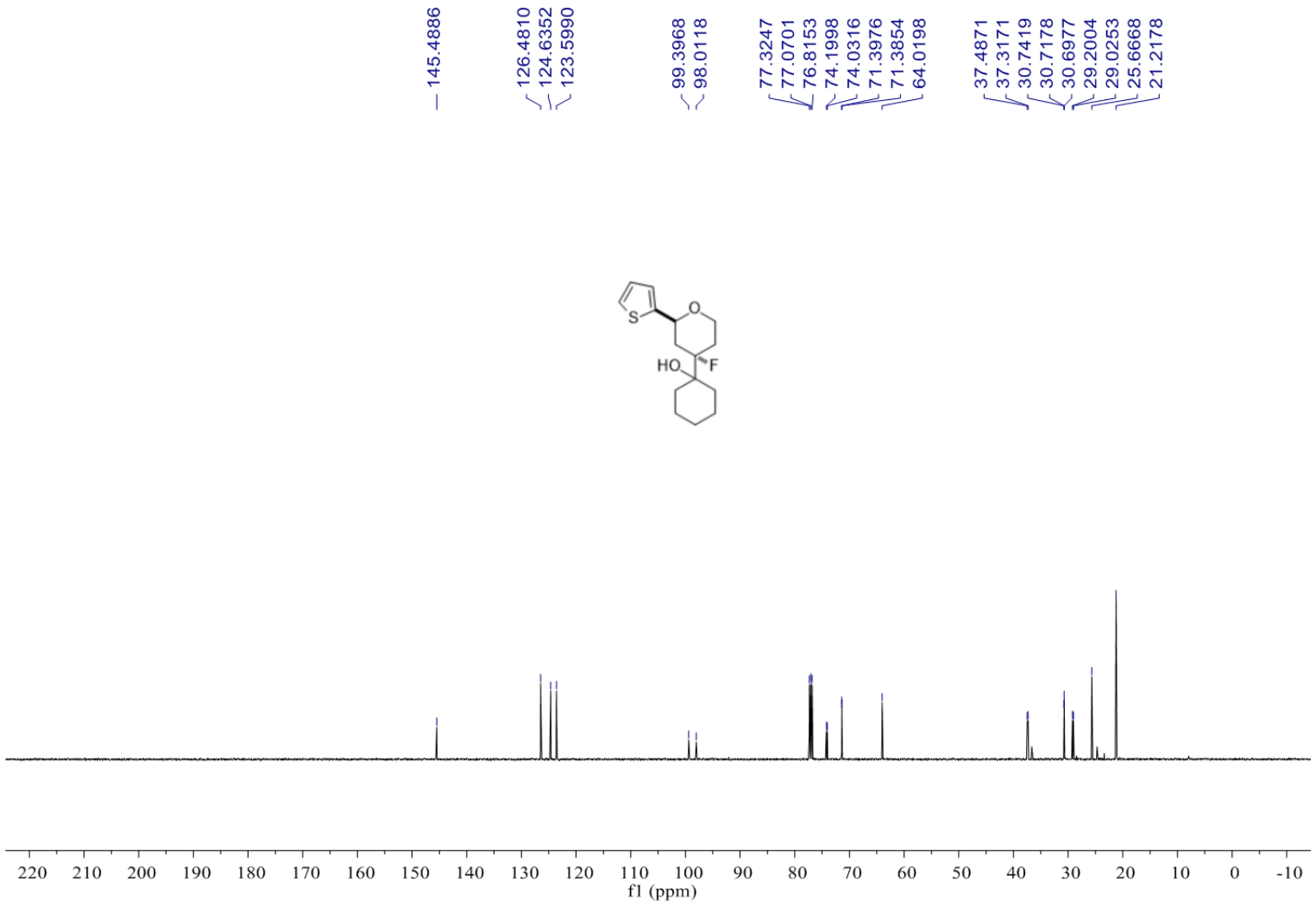
Compound **7ak**



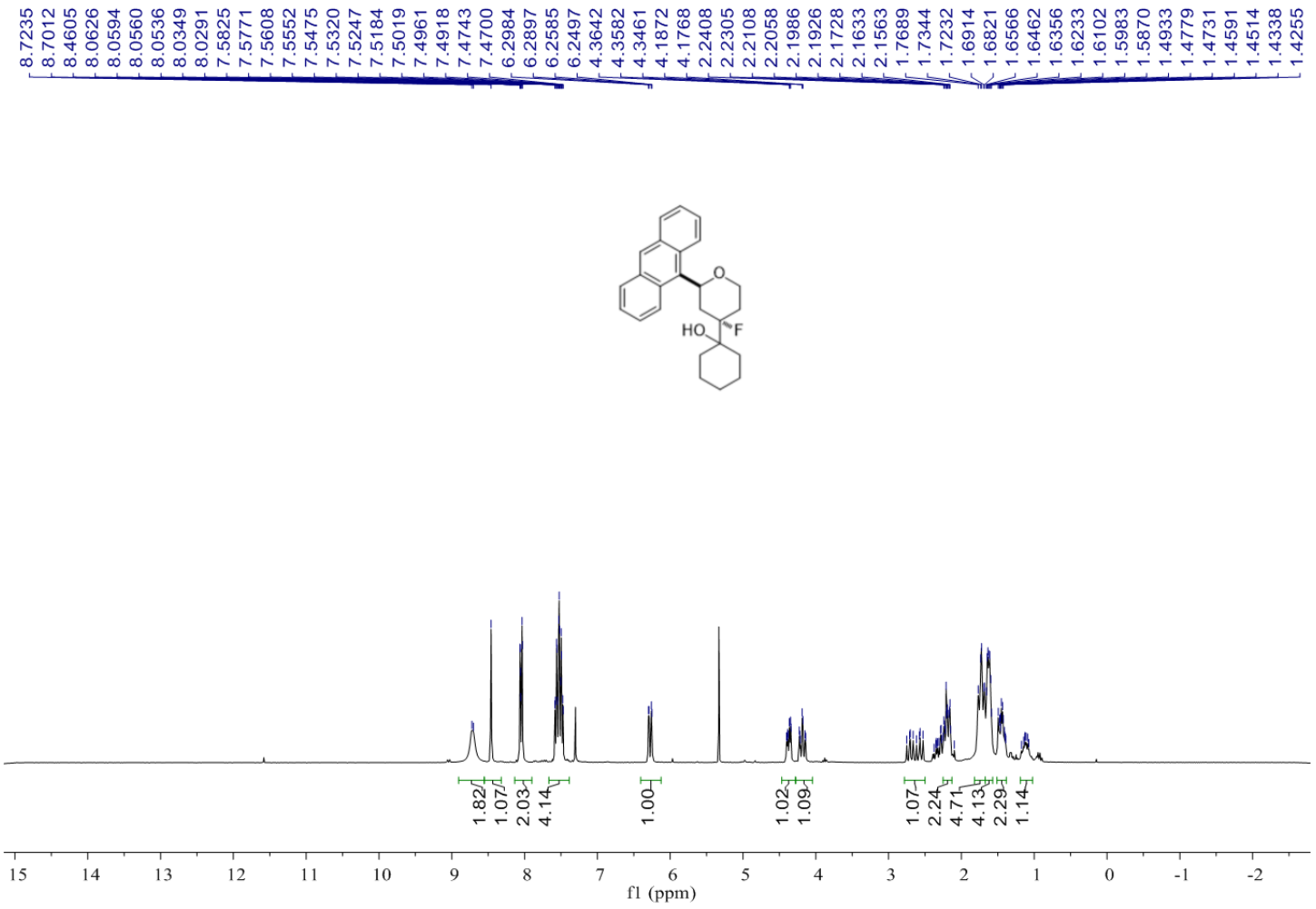

155.5890
130.7833
128.1763
126.1578
120.6701
110.1448
100.0792
97.7737
77.4253
77.0019
76.5769
74.2857
74.0034
69.5515
63.9072
55.2770
36.1629
35.8745
30.7483
30.7015
30.6446
30.5945
29.4352
29.1401
25.6457
21.1820
21.1464
OMe
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

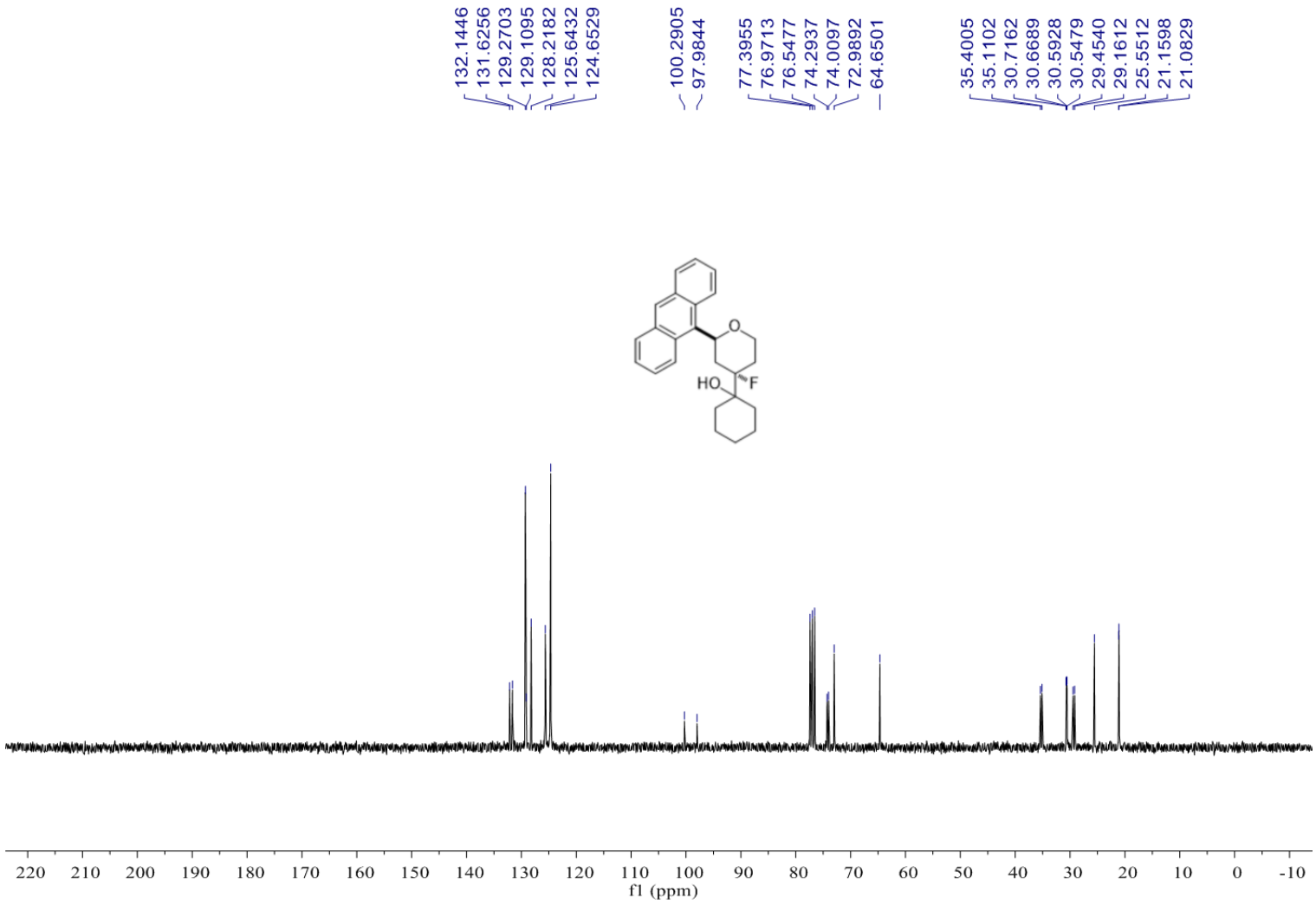
Compound **7al**



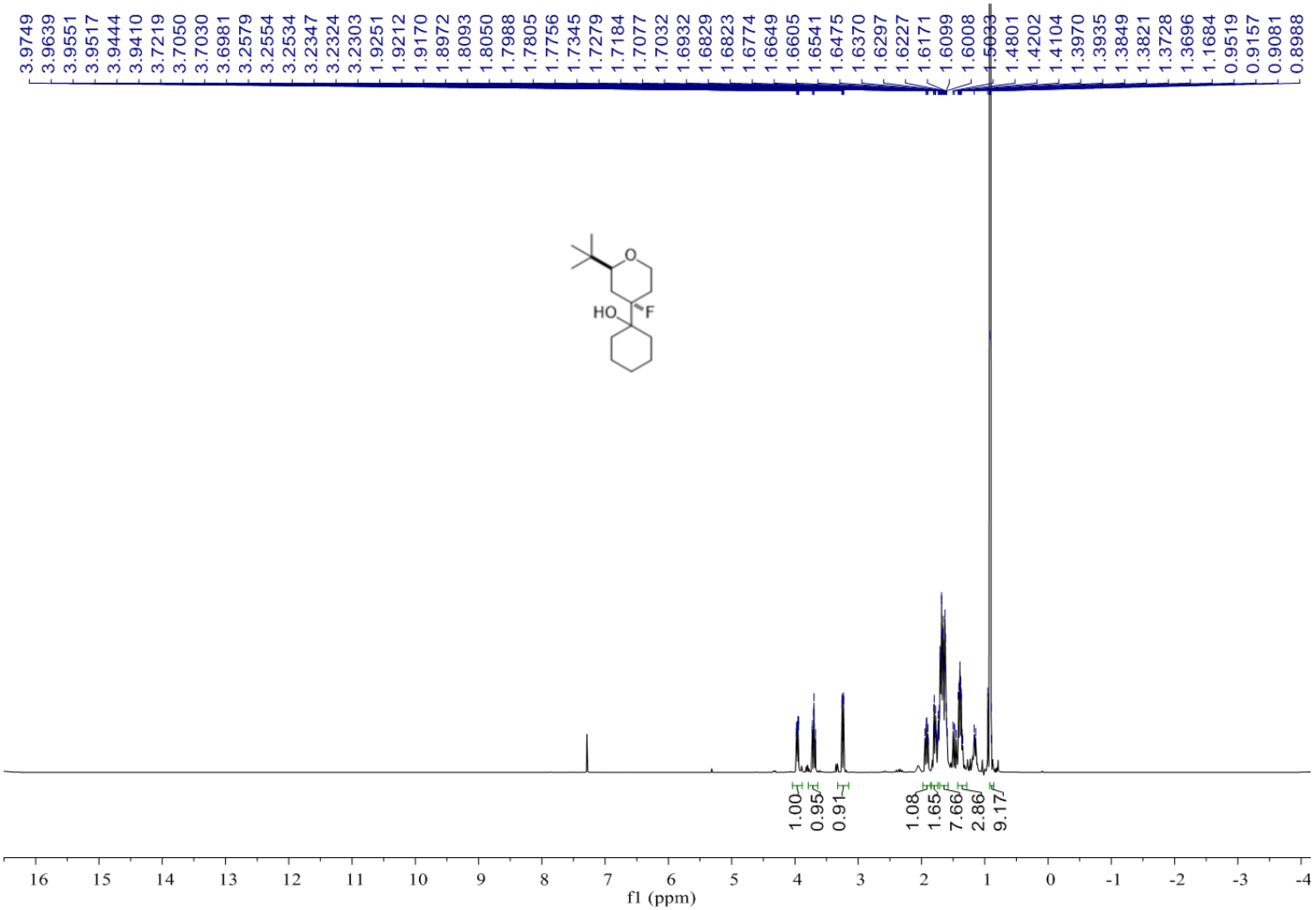

145.4886
126.4810
124.6352
123.5990
99.3968
98.0118
77.3247
77.0701
76.8153
74.1998
74.0316
71.3976
71.3854
64.0198
37.4871
37.3171
30.7419
30.7178
30.6977
29.2004
29.0253
25.6668
21.2178
S
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

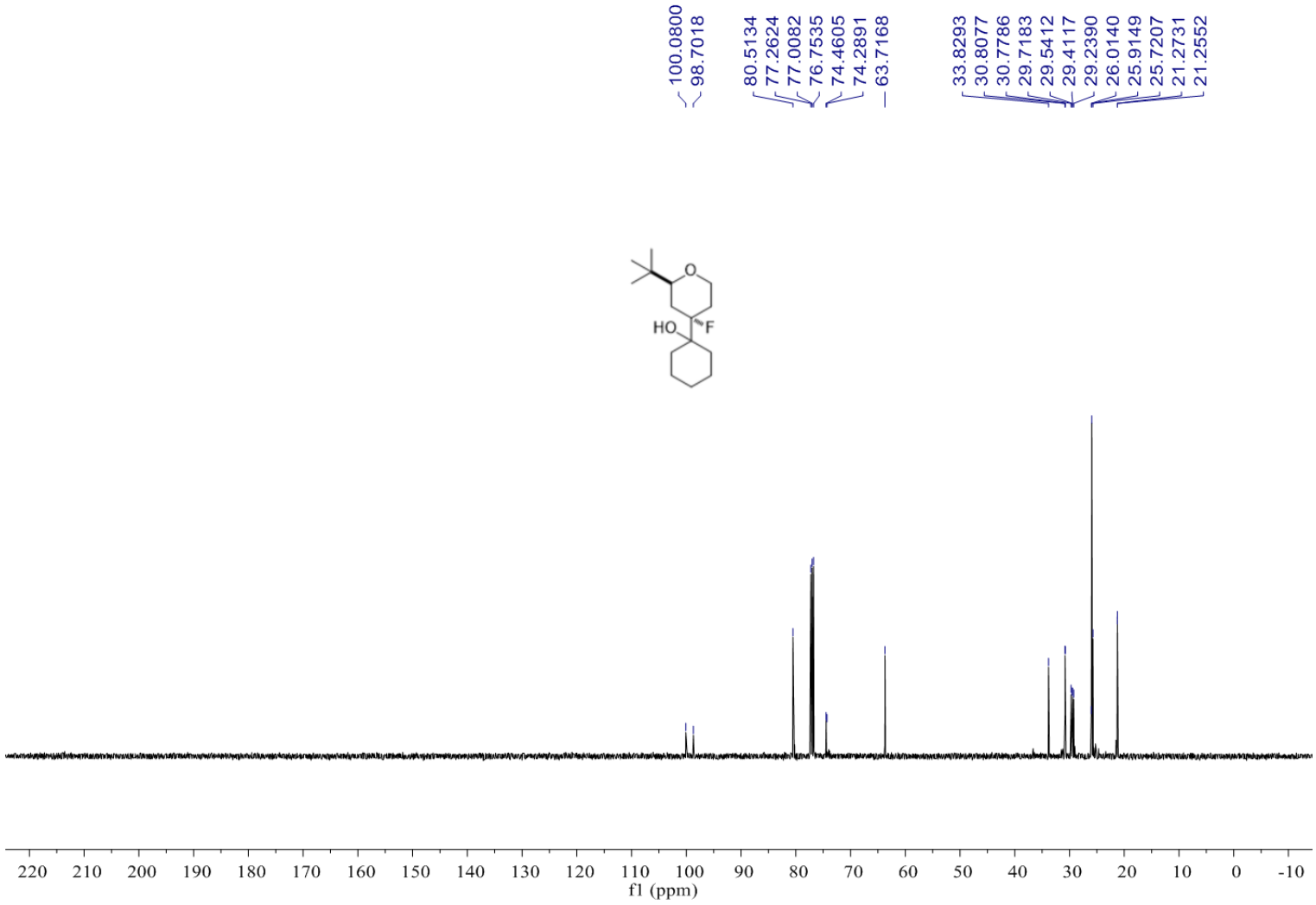
Compound **7am**



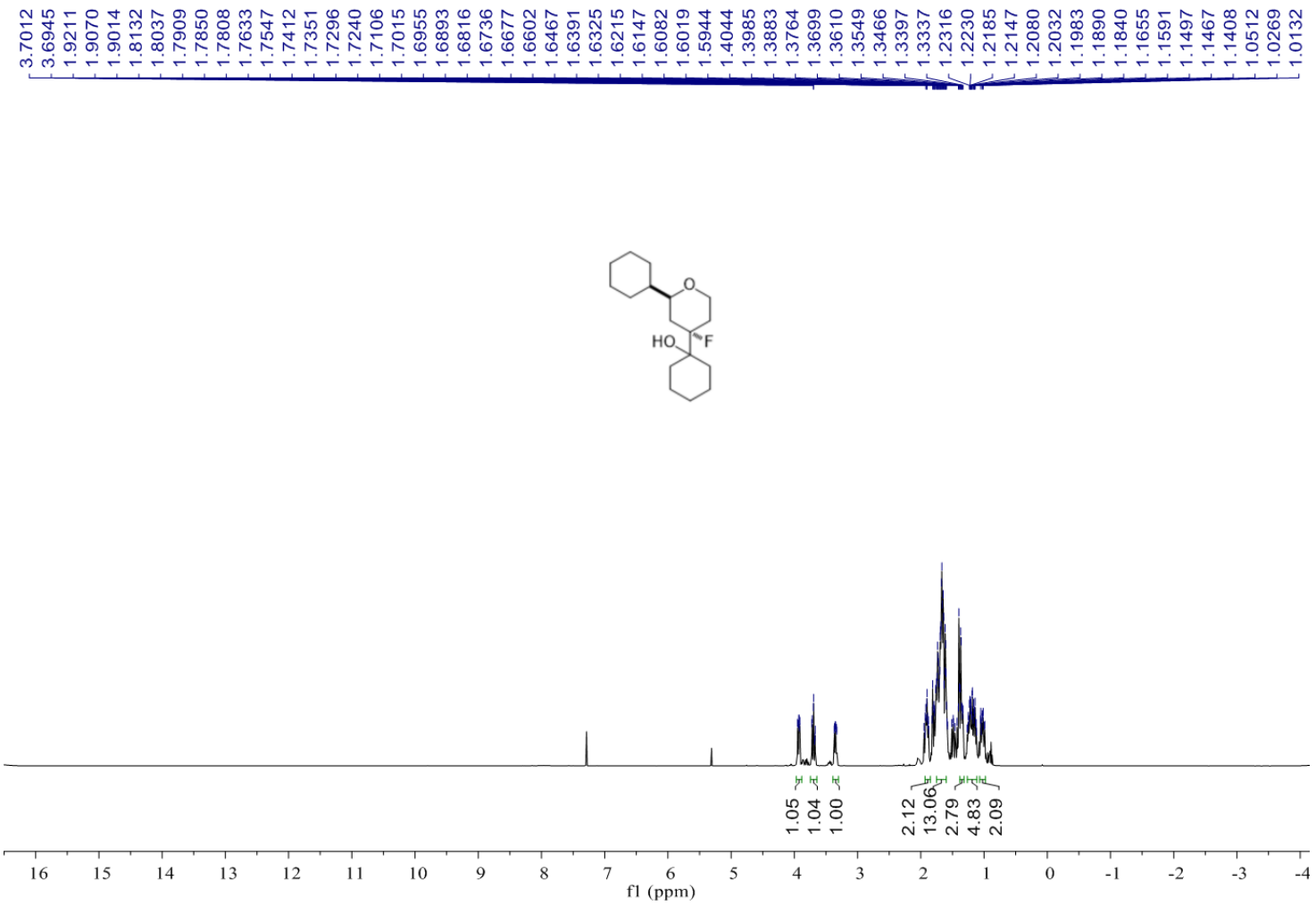

132.1446
131.6256
129.2703
129.1095
128.2182
125.6432
124.6529
100.2905
97.9844
77.3955
76.9713
76.5477
74.2937
74.0097
72.9892
64.6501
35.4005
35.1102
30.7162
30.6689
30.5928
30.5479
29.4540
29.1612
25.5512
21.1598
21.0829
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

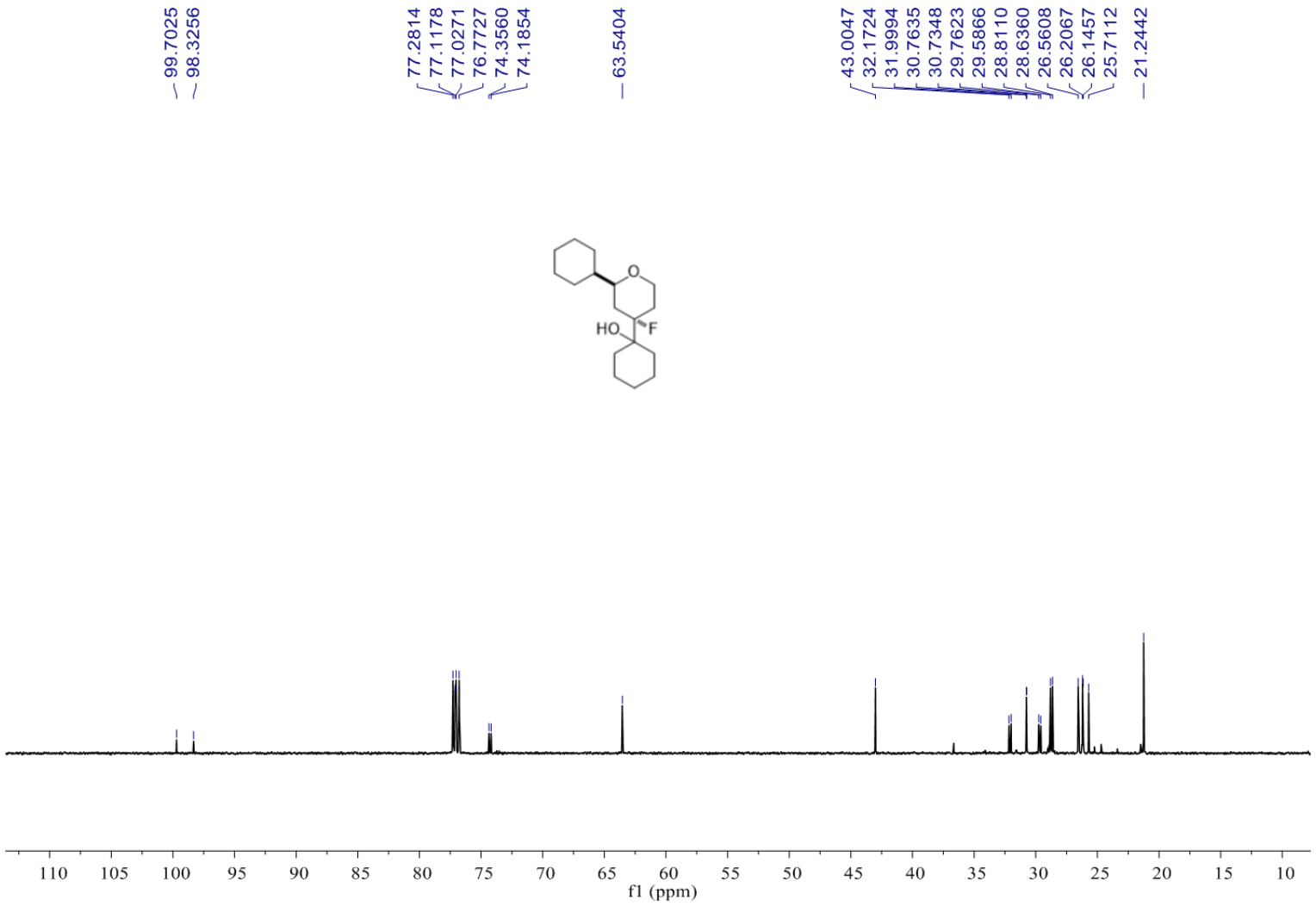
Compound **7an**



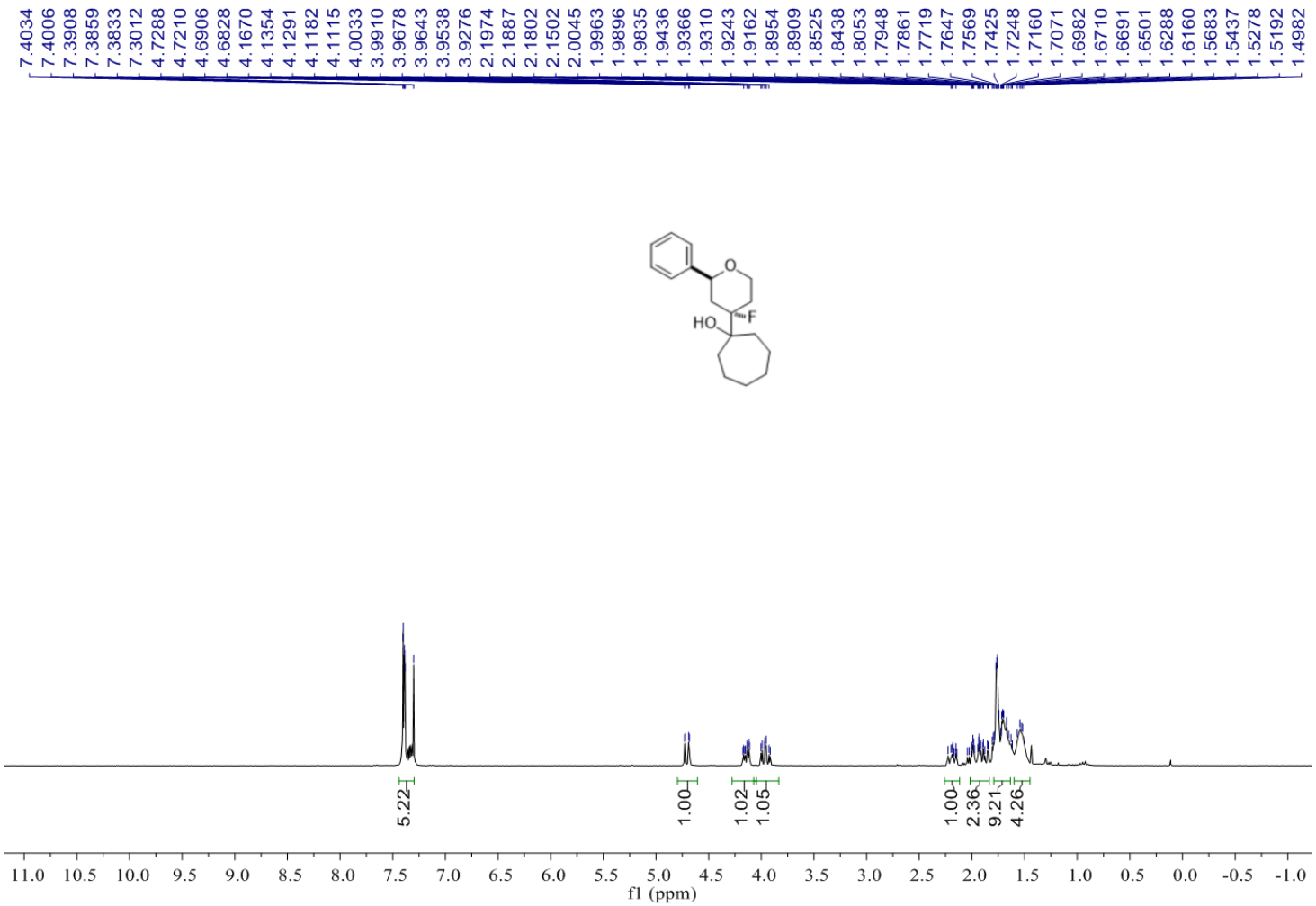

100.0800
98.7018
80.5134
77.2624
77.0082
76.7535
74.4605
74.2891
63.7168
33.8293
30.8077
30.7786
29.7183
29.5412
29.4117
29.2390
26.0140
25.9149
25.7207
21.2731
21.2552
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

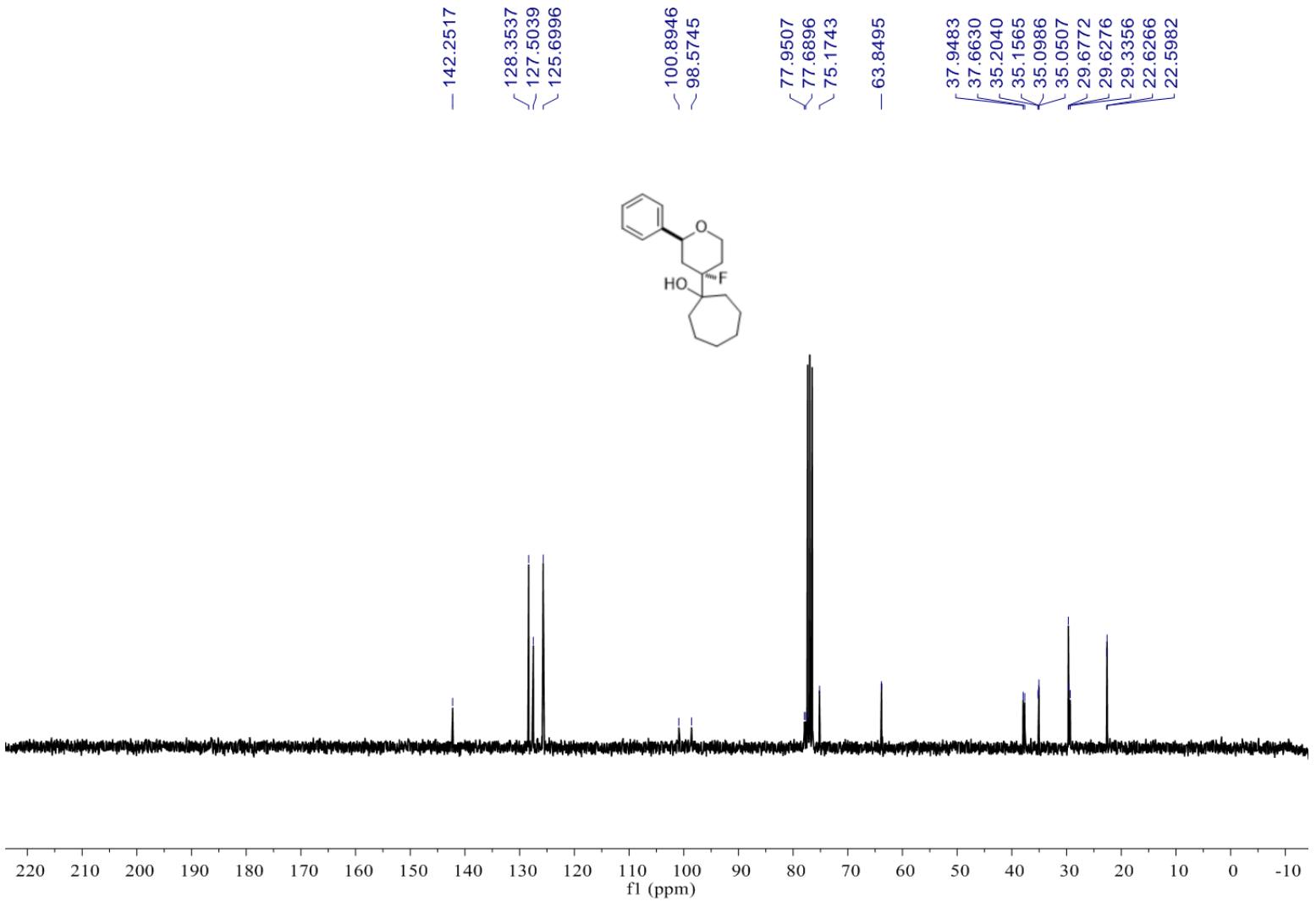
Compound **7ao**



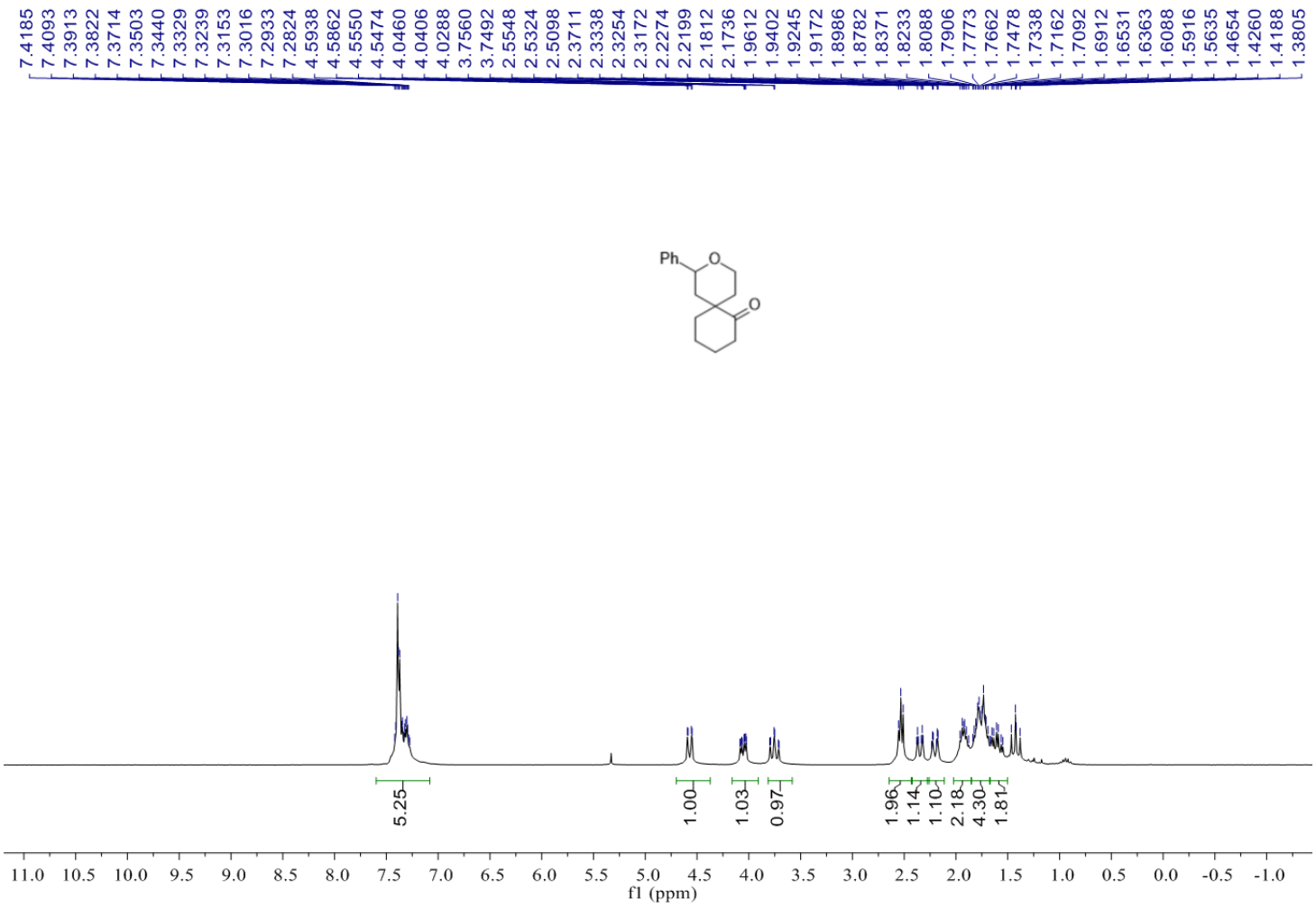

99.7025
98.3256
77.2814
77.1178
77.0271
76.7727
74.3560
74.1854
63.5404
43.0047
32.1724
31.9994
30.7635
30.7348
29.7623
29.5866
28.8110
28.6360
26.5608
26.2067
26.1457
25.7112
21.2442
HO
F
O
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

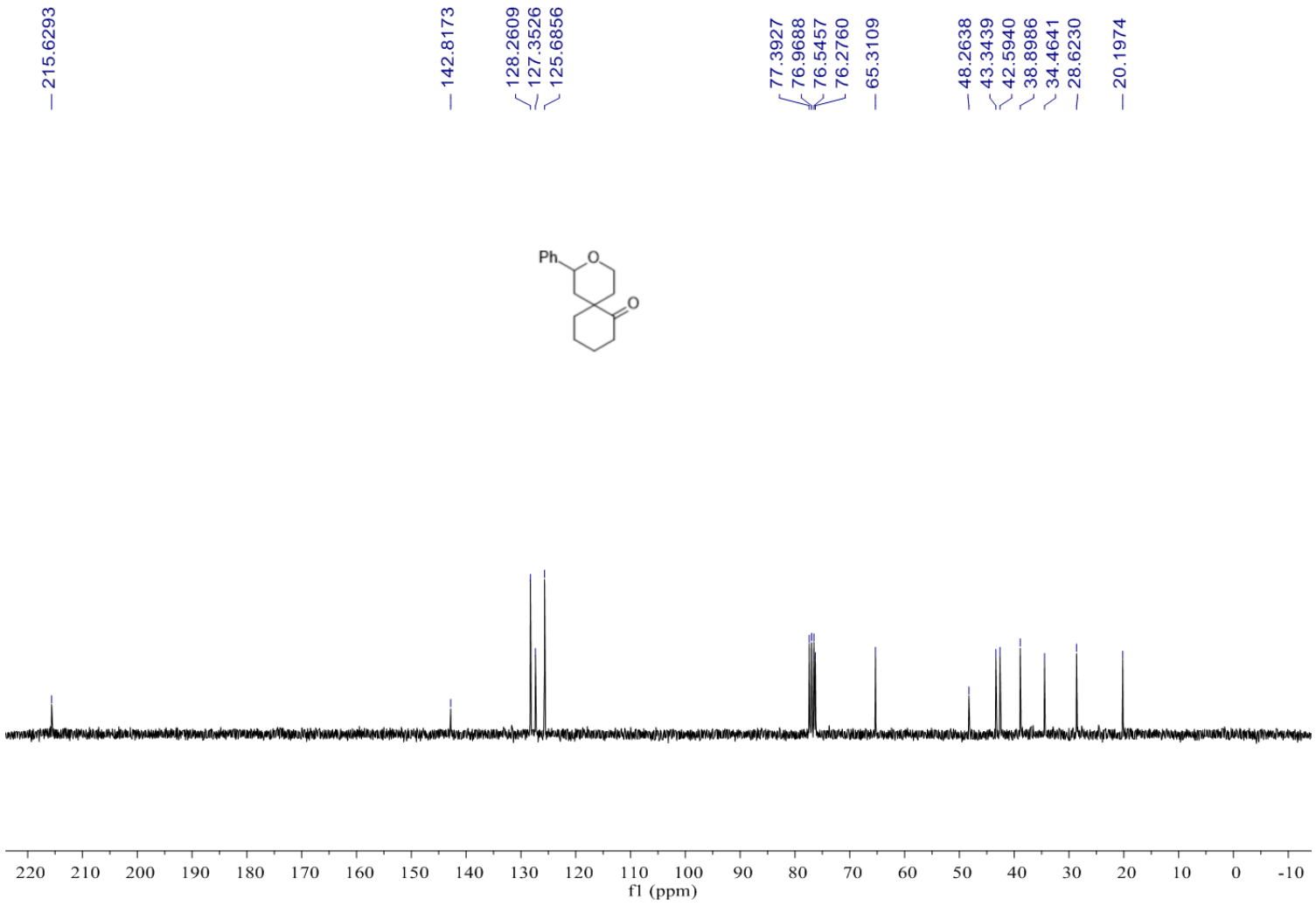
Compound **7ba**



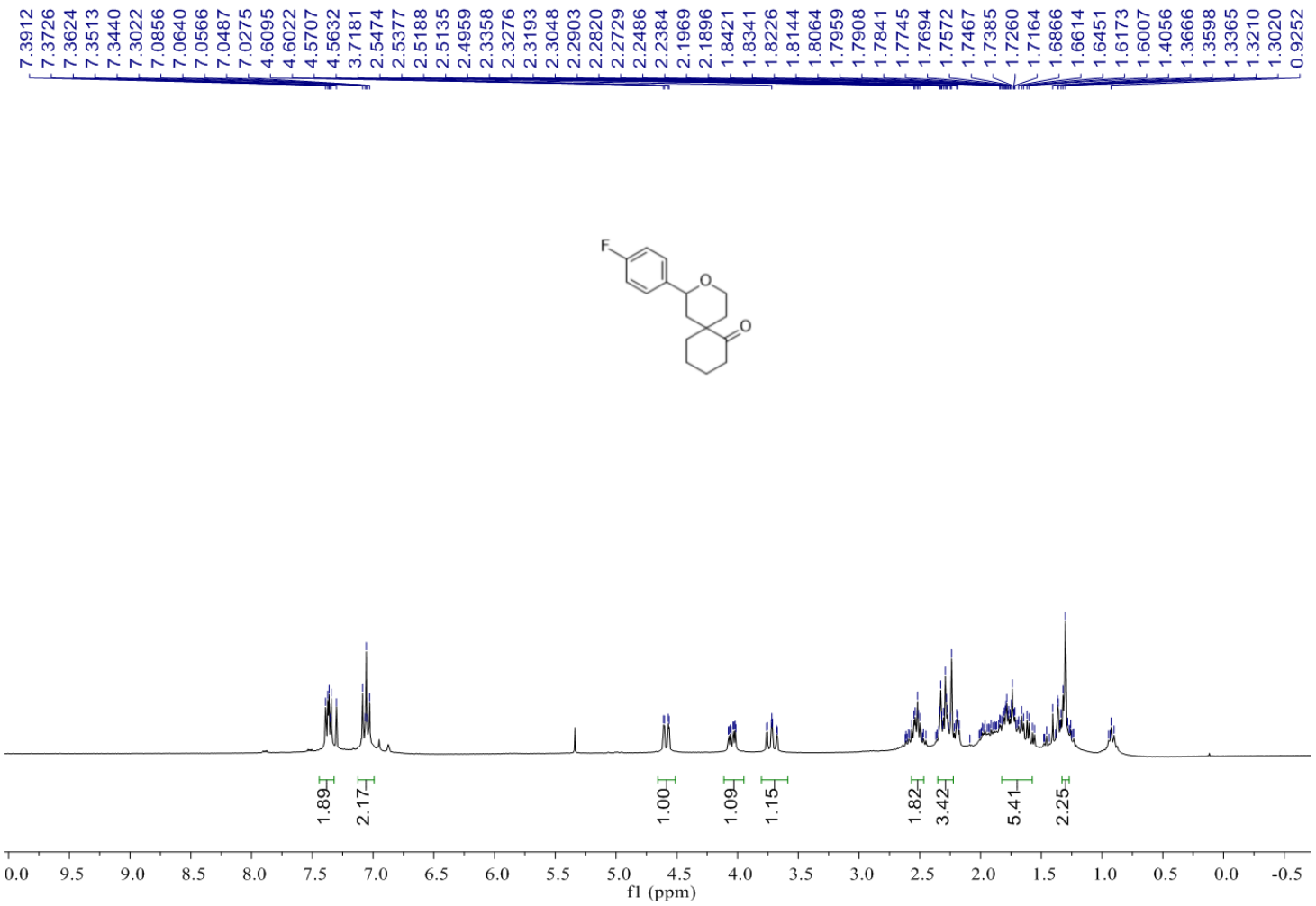

142.2517
128.3537
127.5039
125.6996
100.8946
98.5745
77.9507
77.6896
75.1743
63.8495
37.9483
37.6630
35.2040
35.1565
35.0986
35.0507
29.6772
29.6276
29.3356
22.6266
22.5982
O
HO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

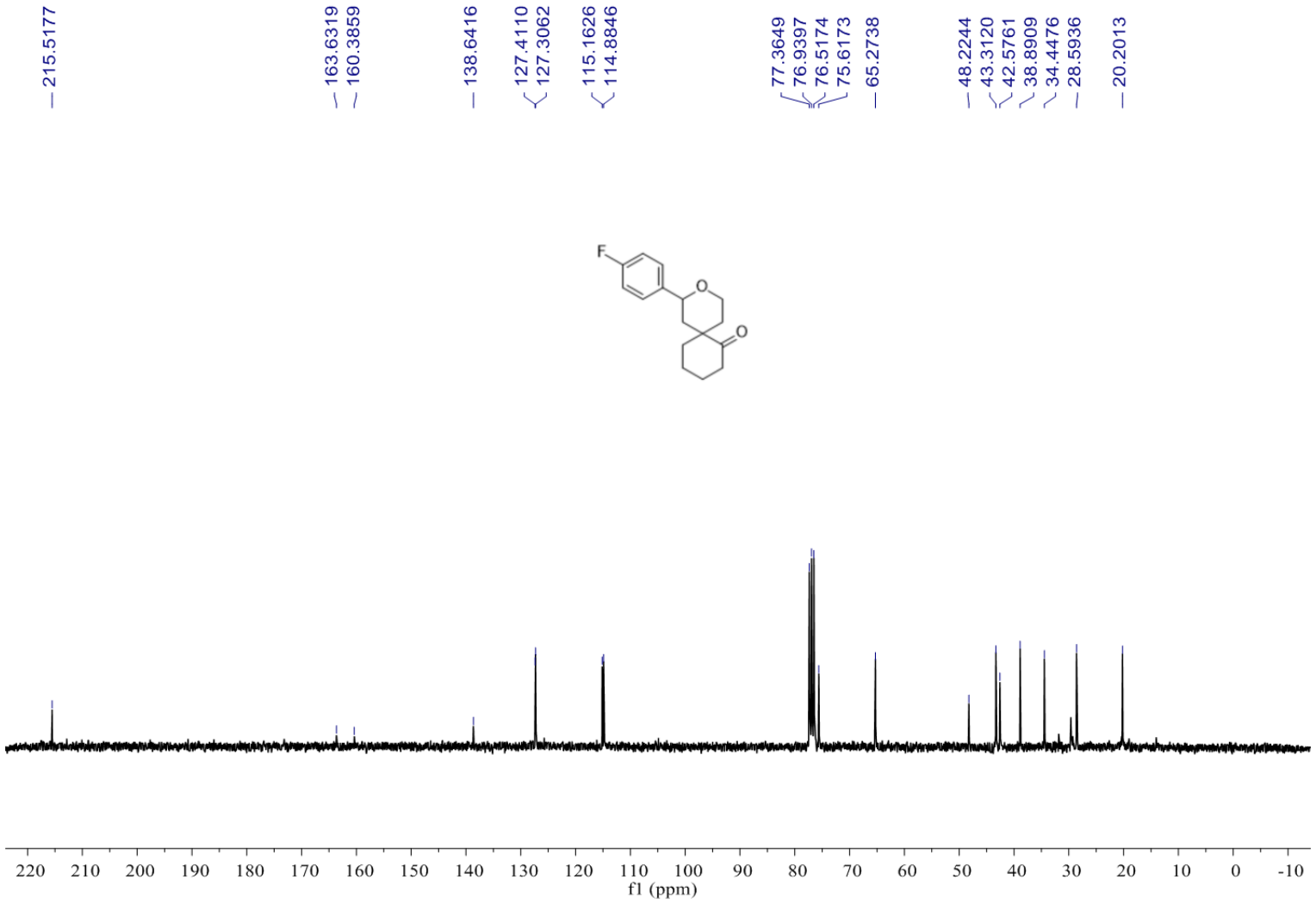
Compound **8ca**



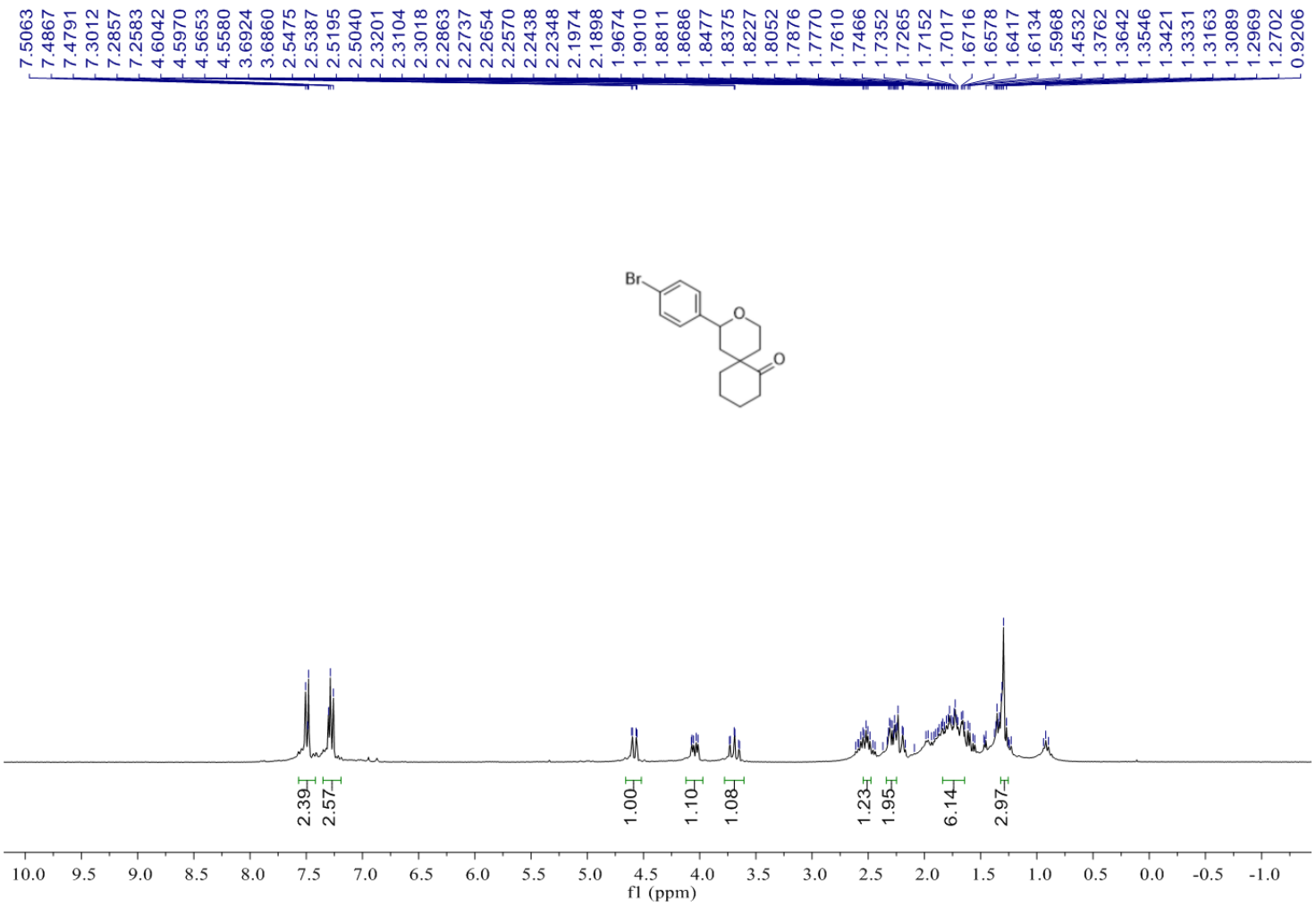

215.6293
142.8173
128.2609
127.3526
125.6856
77.3927
76.9688
76.5457
76.2760
65.3109
48.2638
43.3439
42.5940
38.8986
34.4641
28.6230
20.1974
Ph
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

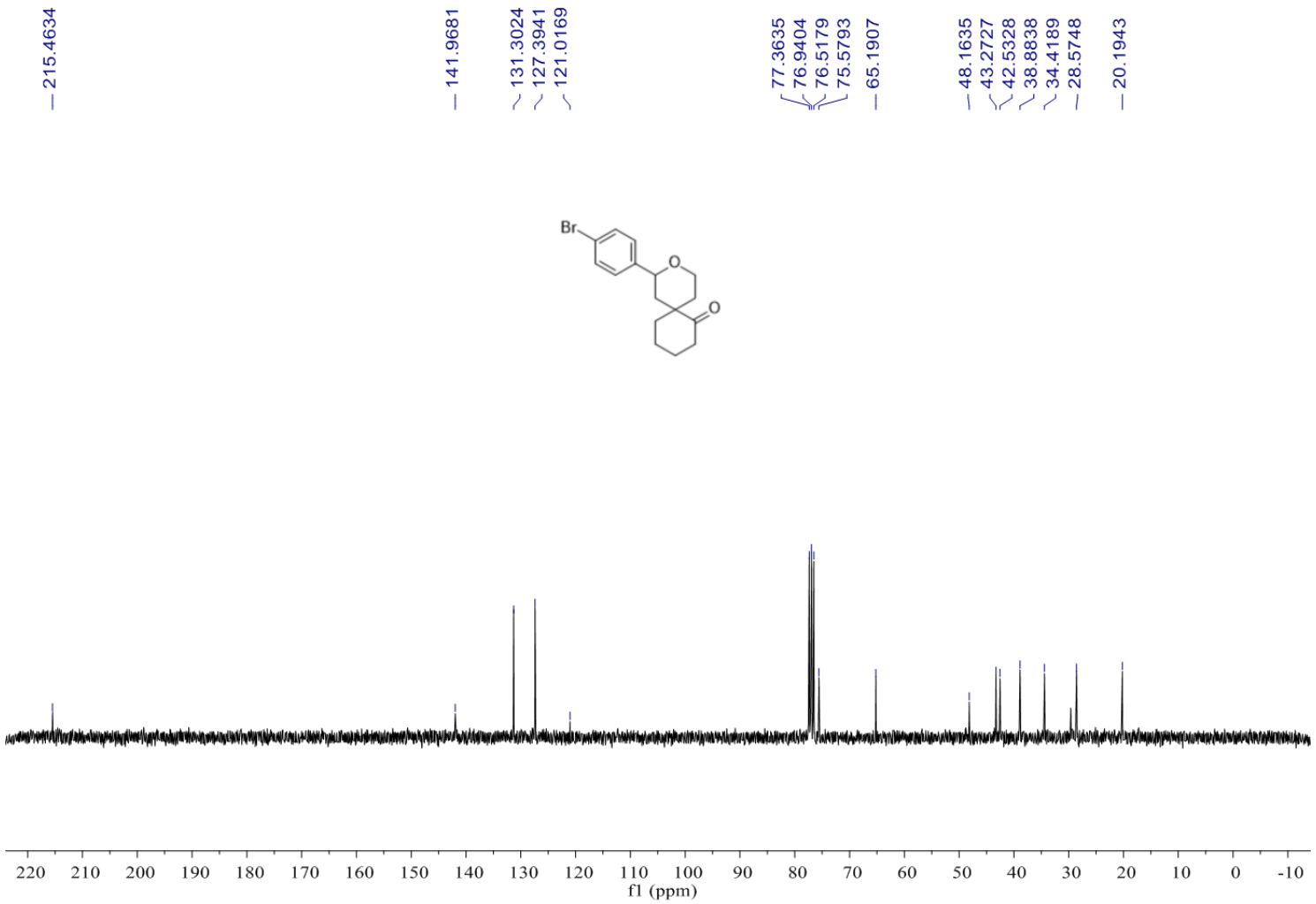
Compound **8cc**



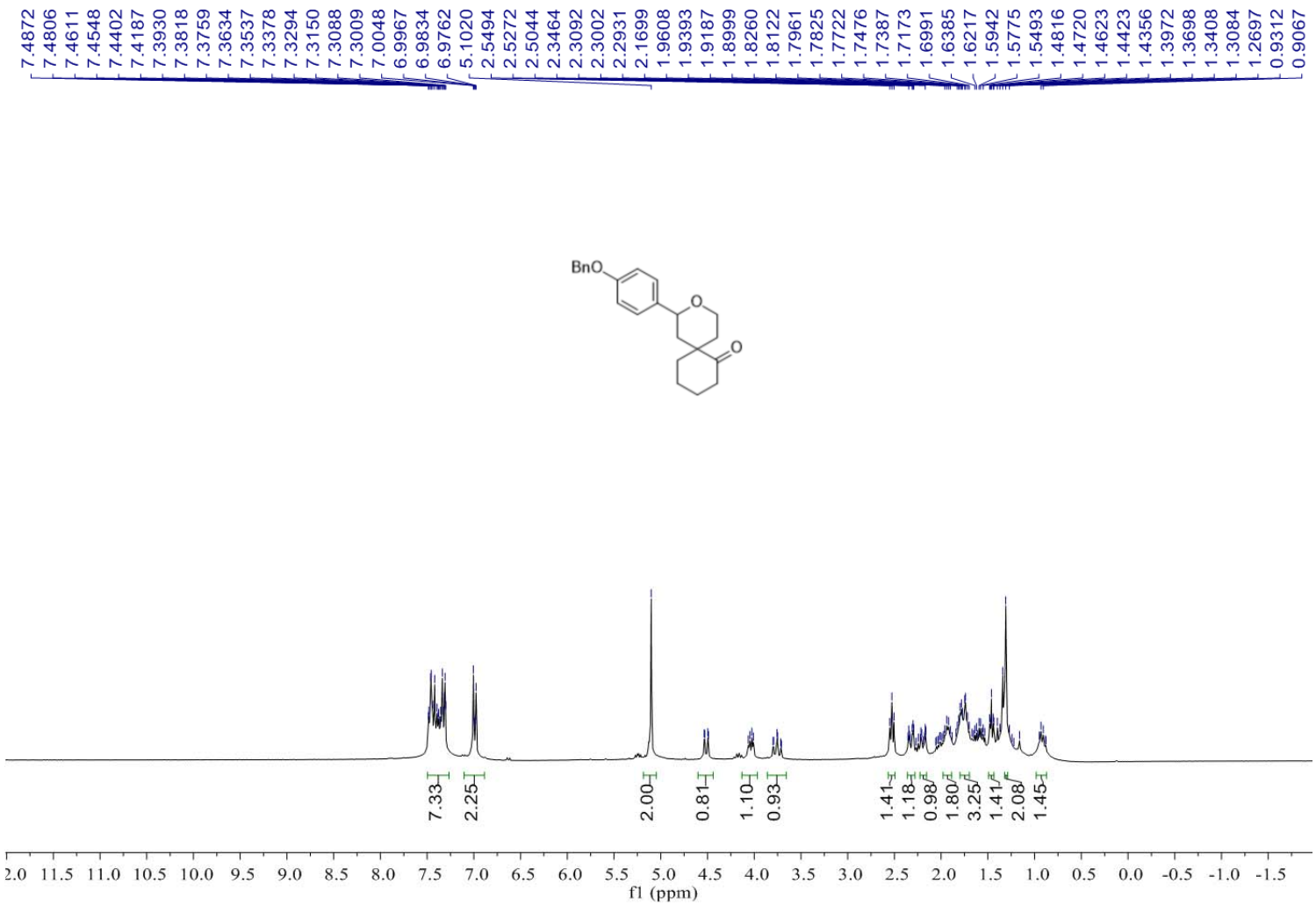

215.5177
163.6319
160.3859
138.6416
127.4110
127.3062
115.1626
114.8846
77.3649
76.9397
76.5174
75.6173
65.2738
48.2244
43.3120
42.5761
38.8909
34.4476
28.5936
20.2013
F
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

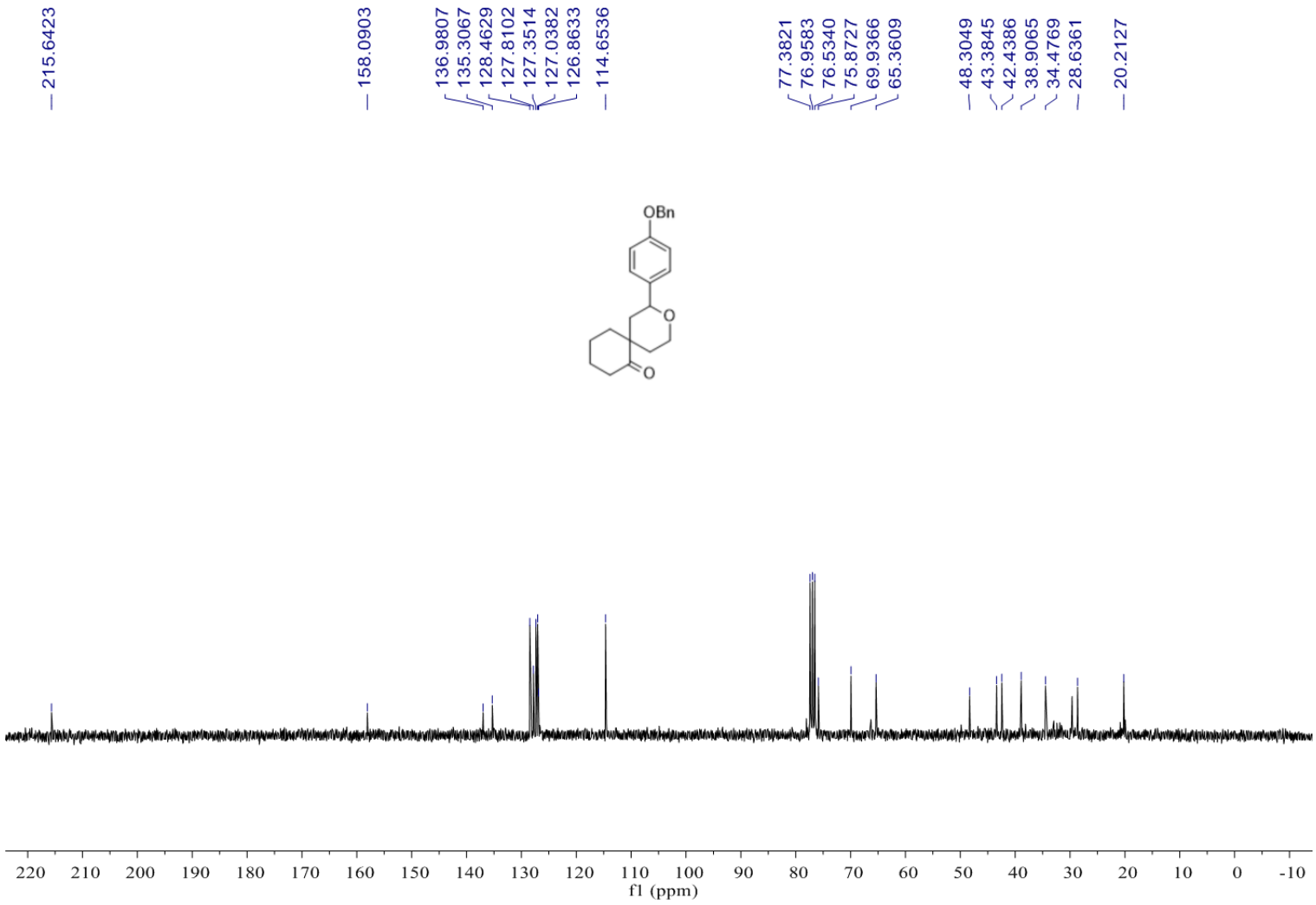
Compound **8ce**




215.4634
141.9681
131.3024
127.3941
121.0169
77.3635
76.9404
76.5179
75.5793
65.1907
48.1635
43.2727
42.5328
38.8838
34.4189
28.5748
20.1943
Br
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound **8cr**

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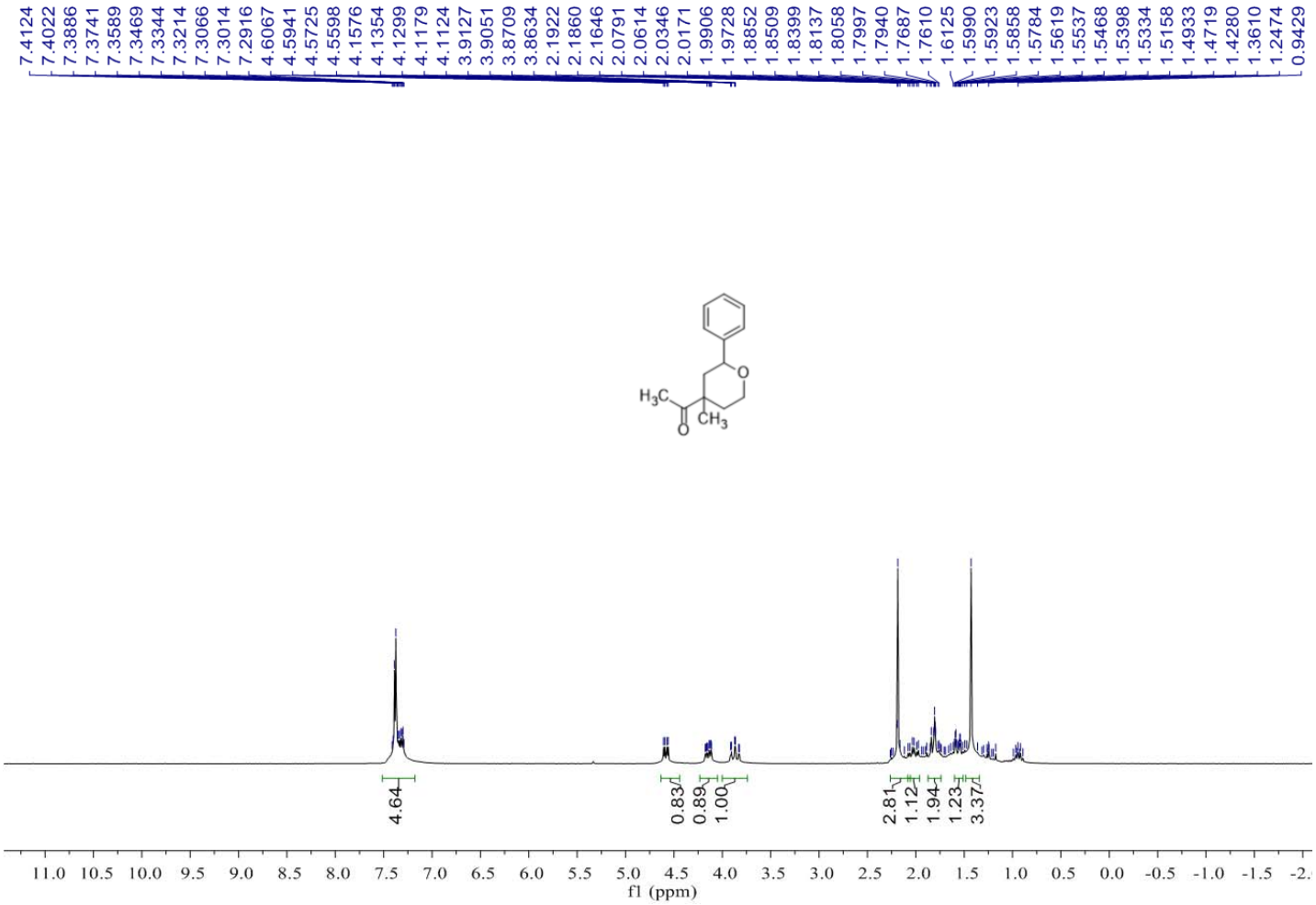
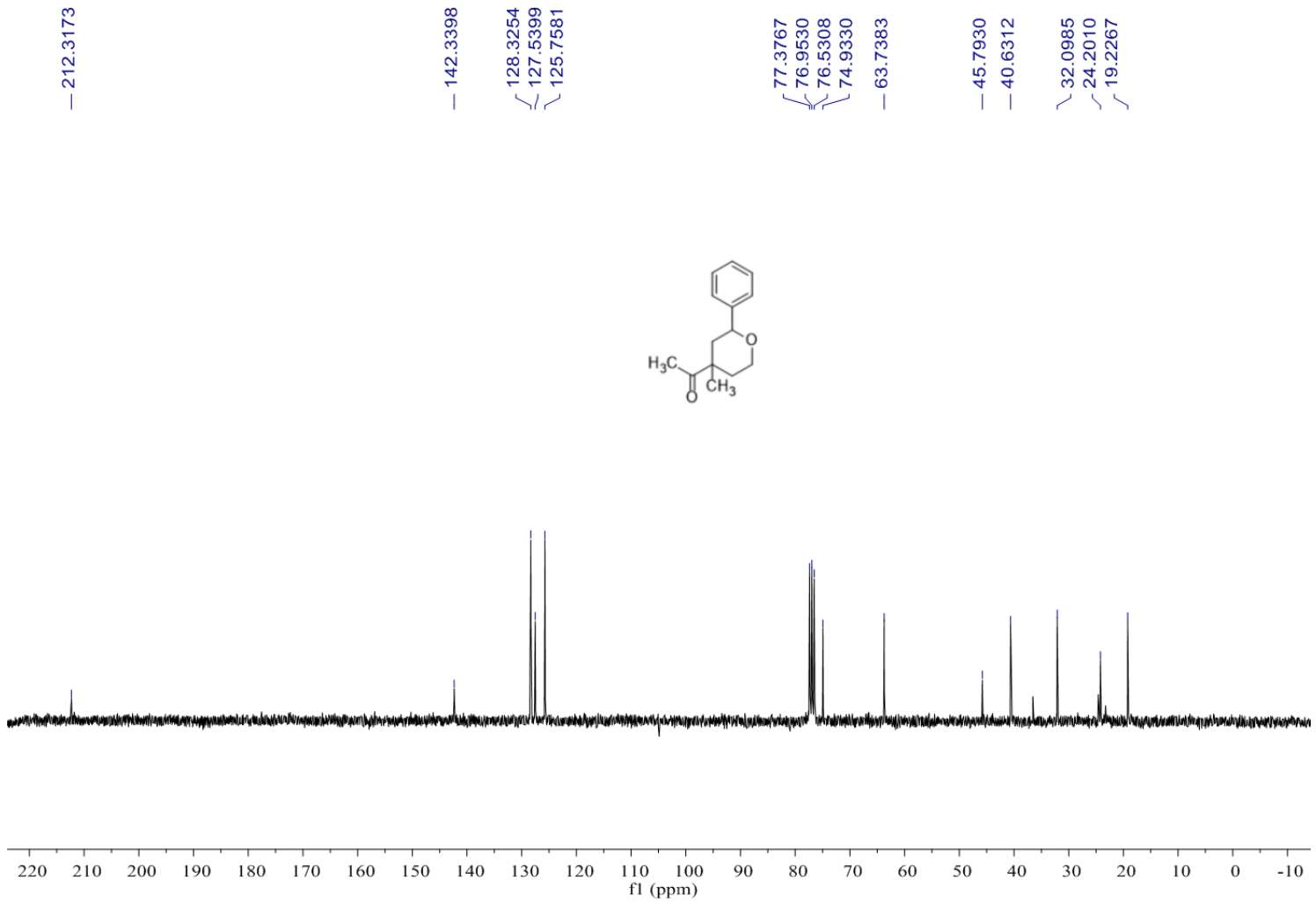
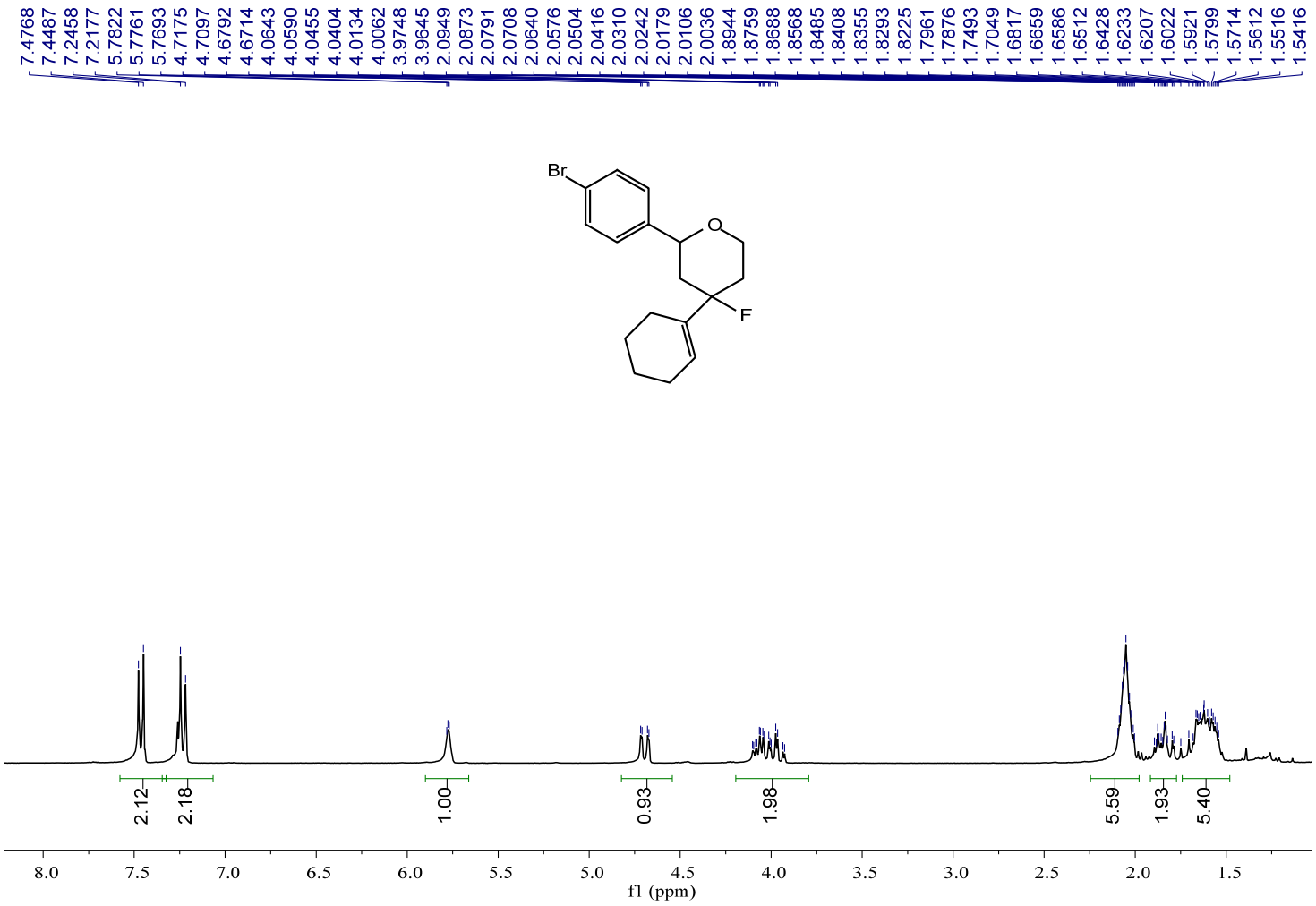
158.0903
136.9807
135.3067
128.4629
127.8102
127.3514
127.0382
126.8633
114.6536
77.3821
76.9583
76.5340
75.8727
69.9366
65.3609
48.3049
43.3845
42.4386
38.9065
34.4769
28.6361
20.2127
OBn
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

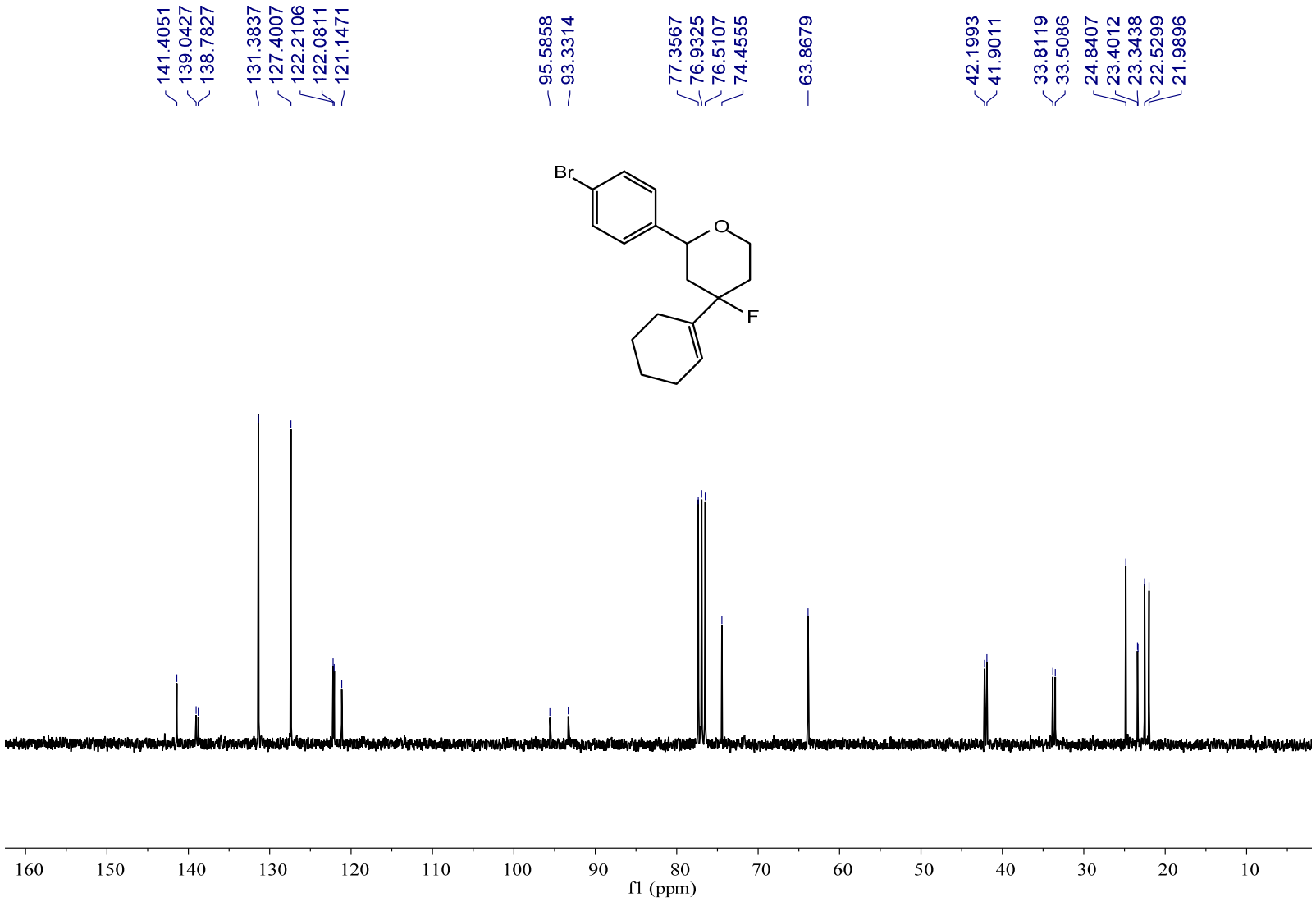
Compound **8da**



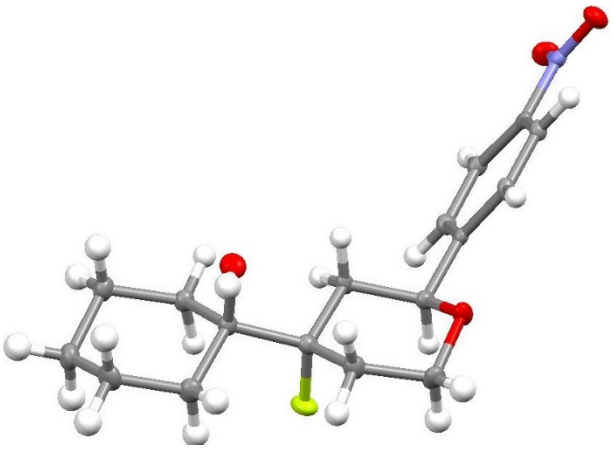

212.3173
142.3398
128.3254
127.5399
125.7581
77.3767
76.9530
76.5308
74.9330
63.7383
45.7930
40.6312
32.0985
24.2010
19.2267
H3C
CH3
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound **9**


7.4768
7.4487
7.2458
7.2177
5.7822
5.7761
5.7693
4.7175
4.7097
4.6792
4.6714
4.0643
4.0590
4.0455
4.0404
4.0134
4.0062
3.9748
3.9645
2.0949
2.0873
2.0791
2.0708
2.0640
2.0576
2.0504
2.0416
2.0310
2.0242
2.0179
2.0106
2.0036
1.8944
1.8759
1.8688
1.8568
1.8485
1.8408
1.8355
1.8293
1.8225
1.7961
1.7876
1.7493
1.7049
1.6817
1.6659
1.6586
1.6512
1.6428
1.6233
1.6207
1.6022
1.5921
1.5799
1.5714
1.5612
1.5516
1.5416
Br
O
F
2.12
2.18
1.00
0.93
1.98
5.59
1.93
5.40
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


141.4051
139.0427
138.7827
131.3837
127.4007
122.2106
122.0811
121.1471
95.5858
93.3314
77.3567
76.9325
76.5107
74.4555
63.8679
42.1993
41.9011
33.8119
33.5086
24.8407
23.4012
23.3438
22.5299
21.9896
Br
O
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

4. X-ray crystallographic data



X-ray crystal structure of Product **7ab**

Table 1. Crystal data and structure refinement for f415.

Identification code	f415	
Empirical formula	C17 H23 F N O4.50	
Formula weight	332.36	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.6999(3) Å	a= 99.119(2)°.
	b = 11.1232(5) Å	b= 96.526(2)°.
	c = 18.8431(9) Å	g = 94.243(2)°.
Volume	1576.16(12) $Å^3$	
Z	4	
Density (calculated)	1.401 Mg/m^3	
Absorption coefficient	0.108 mm^{-1}	
F(000)	708	
Crystal size	0.386 x 0.352 x 0.074 mm^3	
Theta range for data collection	2.207 to 28.281°.	
Index ranges	-10<=h<=9, -14<=k<=14, -25<=l<=25	
Reflections collected	36644	
Independent reflections	7841 [R(int) = 0.0510]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.7037	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7841 / 4 / 454	

Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0765, wR2 = 0.2009
R indices (all data)	R1 = 0.1141, wR2 = 0.2250
Extinction coefficient	n/a
Largest diff. peak and hole	0.871 and -0.848 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for f415. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	5650(2)	6403(1)	8188(1)	22(1)
F(2)	4864(2)	1543(1)	8303(1)	22(1)
O(1)	2411(3)	6543(2)	8598(1)	25(1)
O(2)	5908(2)	7313(2)	6546(1)	18(1)
O(3)	902(3)	4523(2)	3419(1)	26(1)
O(4)	147(2)	2973(2)	3910(1)	22(1)
O(5)	2104(3)	3981(2)	8038(1)	22(1)
O(6)	5826(2)	2250(2)	6621(1)	18(1)
O(7)	1078(2)	-473(2)	3417(1)	22(1)
O(8)	366(2)	-2067(2)	3883(1)	22(1)
N(1)	912(3)	3992(2)	3939(1)	17(1)
N(2)	1073(3)	-1025(2)	3928(1)	15(1)
C(1)	3410(3)	7644(2)	8520(1)	16(1)
C(2)	2113(3)	8547(2)	8313(1)	17(1)
C(3)	950(3)	8871(2)	8915(1)	20(1)
C(4)	2061(4)	9358(3)	9638(1)	22(1)
C(5)	3356(4)	8471(3)	9842(1)	23(1)
C(6)	4514(4)	8159(3)	9247(1)	22(1)
C(7)	6976(3)	7866(3)	7205(1)	20(1)
C(8)	5863(4)	8326(2)	7796(1)	19(1)
C(9)	4588(3)	7298(2)	7922(1)	14(1)
C(10)	3569(3)	6651(2)	7202(1)	14(1)
C(11)	4820(3)	6283(2)	6651(1)	14(1)
C(12)	3799(3)	5696(2)	5933(1)	12(1)
C(13)	3732(3)	6279(2)	5331(1)	13(1)
C(14)	2780(3)	5736(2)	4674(1)	14(1)
C(15)	1902(3)	4590(2)	4632(1)	13(1)

C(16)	1920(3)	3987(2)	5222(1)	15(1)
C(17)	2879(3)	4544(2)	5871(1)	15(1)
C(18)	2772(3)	3045(2)	8404(1)	14(1)
C(19)	3685(4)	3621(3)	9164(1)	21(1)
C(20)	2399(4)	4111(3)	9678(1)	23(1)
C(21)	975(4)	3115(3)	9734(2)	23(1)
C(22)	-2(3)	2606(3)	8986(1)	21(1)
C(23)	1252(3)	2110(2)	8462(1)	16(1)
C(24)	6812(3)	2767(3)	7308(1)	22(1)
C(25)	5630(3)	3343(2)	7836(1)	18(1)
C(26)	4119(3)	2441(2)	7930(1)	15(1)
C(27)	3248(3)	1760(2)	7196(1)	14(1)
C(28)	4590(3)	1287(2)	6709(1)	14(1)
C(29)	3682(3)	689(2)	5973(1)	13(1)
C(30)	3706(3)	1277(2)	5374(1)	14(1)
C(31)	2850(3)	733(2)	4699(1)	14(1)
C(32)	1970(3)	-419(2)	4638(1)	12(1)
C(33)	1894(3)	-1023(2)	5225(1)	14(1)
C(34)	2759(3)	-462(2)	5892(1)	15(1)
O(1W)	9131(4)	5379(3)	8348(2)	68(1)

Table 3.

Bond lengths [Å] and angles [°] for f415.

F(1)-C(9)	1.448(3)
F(2)-C(26)	1.427(3)
O(1)-C(1)	1.434(3)
O(1)-H(1O)	0.850(10)
O(2)-C(11)	1.422(3)
O(2)-C(7)	1.431(3)
O(3)-N(1)	1.221(3)
O(4)-N(1)	1.228(3)
O(5)-C(18)	1.432(3)
O(5)-H(5O)	0.839(10)
O(6)-C(28)	1.422(3)
O(6)-C(24)	1.434(3)
O(7)-N(2)	1.220(3)
O(8)-N(2)	1.230(3)
N(1)-C(15)	1.468(3)

N(2)-C(32)	1.469(3)
C(1)-C(6)	1.530(4)
C(1)-C(2)	1.531(3)
C(1)-C(9)	1.545(3)
C(2)-C(3)	1.539(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.520(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.515(4)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.524(4)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.529(4)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.517(3)
C(8)-H(8A)	1.00(3)
C(8)-H(8B)	0.87(3)
C(9)-C(10)	1.529(3)
C(10)-C(11)	1.524(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.509(3)
C(11)-H(11)	1.0000
C(12)-C(13)	1.391(3)
C(12)-C(17)	1.398(3)
C(13)-C(14)	1.388(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.384(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.385(3)
C(16)-C(17)	1.383(3)

C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(23)	1.532(3)
C(18)-C(19)	1.540(3)
C(18)-C(26)	1.565(3)
C(19)-C(20)	1.531(4)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.524(4)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.522(4)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.527(3)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-H(23A)	0.98(3)
C(23)-H(23B)	0.95(3)
C(24)-C(25)	1.524(4)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26)	1.524(3)
C(25)-H(25A)	0.99(3)
C(25)-H(25B)	0.87(3)
C(26)-C(27)	1.522(3)
C(27)-C(28)	1.526(3)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-C(29)	1.509(3)
C(28)-H(28)	1.0000
C(29)-C(30)	1.393(3)
C(29)-C(34)	1.395(3)
C(30)-C(31)	1.387(3)
C(30)-H(30)	0.9500
C(31)-C(32)	1.386(3)
C(31)-H(31)	0.9500
C(32)-C(33)	1.387(3)

C(33)-C(34)	1.383(3)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
O(1W)-H(1W)	0.868(10)
O(1W)-H(2W)	0.872(10)

C(1)-O(1)-H(1O)	109(2)
C(11)-O(2)-C(7)	111.19(18)
C(18)-O(5)-H(5O)	104(2)
C(28)-O(6)-C(24)	109.89(18)
O(3)-N(1)-O(4)	123.2(2)
O(3)-N(1)-C(15)	118.6(2)
O(4)-N(1)-C(15)	118.1(2)
O(7)-N(2)-O(8)	123.8(2)
O(7)-N(2)-C(32)	118.5(2)
O(8)-N(2)-C(32)	117.7(2)
O(1)-C(1)-C(6)	108.2(2)
O(1)-C(1)-C(2)	107.7(2)
C(6)-C(1)-C(2)	110.4(2)
O(1)-C(1)-C(9)	107.23(19)
C(6)-C(1)-C(9)	111.2(2)
C(2)-C(1)-C(9)	111.8(2)
C(1)-C(2)-C(3)	110.8(2)
C(1)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	108.1
C(4)-C(3)-C(2)	111.0(2)
C(4)-C(3)-H(3A)	109.4
C(2)-C(3)-H(3A)	109.4
C(4)-C(3)-H(3B)	109.4
C(2)-C(3)-H(3B)	109.4
H(3A)-C(3)-H(3B)	108.0
C(5)-C(4)-C(3)	111.8(2)
C(5)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4A)	109.3
C(5)-C(4)-H(4B)	109.3

C(3)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	107.9
C(4)-C(5)-C(6)	110.9(2)
C(4)-C(5)-H(5A)	109.5
C(6)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
C(6)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	108.0
C(5)-C(6)-C(1)	111.3(2)
C(5)-C(6)-H(6A)	109.4
C(1)-C(6)-H(6A)	109.4
C(5)-C(6)-H(6B)	109.4
C(1)-C(6)-H(6B)	109.4
H(6A)-C(6)-H(6B)	108.0
O(2)-C(7)-C(8)	111.7(2)
O(2)-C(7)-H(7A)	109.3
C(8)-C(7)-H(7A)	109.3
O(2)-C(7)-H(7B)	109.3
C(8)-C(7)-H(7B)	109.3
H(7A)-C(7)-H(7B)	107.9
C(9)-C(8)-C(7)	110.6(2)
C(9)-C(8)-H(8A)	108.4(17)
C(7)-C(8)-H(8A)	107.5(18)
C(9)-C(8)-H(8B)	104(2)
C(7)-C(8)-H(8B)	115(2)
H(8A)-C(8)-H(8B)	111(3)
F(1)-C(9)-C(8)	106.2(2)
F(1)-C(9)-C(10)	105.84(19)
C(8)-C(9)-C(10)	110.3(2)
F(1)-C(9)-C(1)	104.38(18)
C(8)-C(9)-C(1)	115.5(2)
C(10)-C(9)-C(1)	113.7(2)
C(11)-C(10)-C(9)	110.7(2)
C(11)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1

O(2)-C(11)-C(12)	108.93(18)
O(2)-C(11)-C(10)	111.19(19)
C(12)-C(11)-C(10)	110.33(19)
O(2)-C(11)-H(11)	108.8
C(12)-C(11)-H(11)	108.8
C(10)-C(11)-H(11)	108.8
C(13)-C(12)-C(17)	119.0(2)
C(13)-C(12)-C(11)	121.6(2)
C(17)-C(12)-C(11)	119.4(2)
C(14)-C(13)-C(12)	121.2(2)
C(14)-C(13)-H(13)	119.4
C(12)-C(13)-H(13)	119.4
C(15)-C(14)-C(13)	118.0(2)
C(15)-C(14)-H(14)	121.0
C(13)-C(14)-H(14)	121.0
C(14)-C(15)-C(16)	122.4(2)
C(14)-C(15)-N(1)	118.9(2)
C(16)-C(15)-N(1)	118.7(2)
C(17)-C(16)-C(15)	118.5(2)
C(17)-C(16)-H(16)	120.7
C(15)-C(16)-H(16)	120.7
C(16)-C(17)-C(12)	120.7(2)
C(16)-C(17)-H(17)	119.6
C(12)-C(17)-H(17)	119.6
O(5)-C(18)-C(23)	109.3(2)
O(5)-C(18)-C(19)	109.6(2)
C(23)-C(18)-C(19)	110.2(2)
O(5)-C(18)-C(26)	106.04(18)
C(23)-C(18)-C(26)	111.0(2)
C(19)-C(18)-C(26)	110.7(2)
C(20)-C(19)-C(18)	113.0(2)
C(20)-C(19)-H(19A)	109.0
C(18)-C(19)-H(19A)	109.0
C(20)-C(19)-H(19B)	109.0
C(18)-C(19)-H(19B)	109.0
H(19A)-C(19)-H(19B)	107.8
C(21)-C(20)-C(19)	111.1(2)
C(21)-C(20)-H(20A)	109.4

C(19)-C(20)-H(20A)	109.4
C(21)-C(20)-H(20B)	109.4
C(19)-C(20)-H(20B)	109.4
H(20A)-C(20)-H(20B)	108.0
C(22)-C(21)-C(20)	110.0(2)
C(22)-C(21)-H(21A)	109.7
C(20)-C(21)-H(21A)	109.7
C(22)-C(21)-H(21B)	109.7
C(20)-C(21)-H(21B)	109.7
H(21A)-C(21)-H(21B)	108.2
C(21)-C(22)-C(23)	111.3(2)
C(21)-C(22)-H(22A)	109.4
C(23)-C(22)-H(22A)	109.4
C(21)-C(22)-H(22B)	109.4
C(23)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0
C(22)-C(23)-C(18)	113.6(2)
C(22)-C(23)-H(23A)	113.1(17)
C(18)-C(23)-H(23A)	97.7(17)
C(22)-C(23)-H(23B)	108.9(18)
C(18)-C(23)-H(23B)	108.0(18)
H(23A)-C(23)-H(23B)	115(2)
O(6)-C(24)-C(25)	111.3(2)
O(6)-C(24)-H(24A)	109.4
C(25)-C(24)-H(24A)	109.4
O(6)-C(24)-H(24B)	109.4
C(25)-C(24)-H(24B)	109.4
H(24A)-C(24)-H(24B)	108.0
C(24)-C(25)-C(26)	112.0(2)
C(24)-C(25)-H(25A)	107.4(18)
C(26)-C(25)-H(25A)	110.6(18)
C(24)-C(25)-H(25B)	116(2)
C(26)-C(25)-H(25B)	102(2)
H(25A)-C(25)-H(25B)	108(3)
F(2)-C(26)-C(27)	106.29(19)
F(2)-C(26)-C(25)	107.0(2)
C(27)-C(26)-C(25)	110.5(2)
F(2)-C(26)-C(18)	106.98(18)

C(27)-C(26)-C(18)	112.6(2)
C(25)-C(26)-C(18)	113.0(2)
C(26)-C(27)-C(28)	112.08(19)
C(26)-C(27)-H(27A)	109.2
C(28)-C(27)-H(27A)	109.2
C(26)-C(27)-H(27B)	109.2
C(28)-C(27)-H(27B)	109.2
H(27A)-C(27)-H(27B)	107.9
O(6)-C(28)-C(29)	108.80(19)
O(6)-C(28)-C(27)	111.3(2)
C(29)-C(28)-C(27)	110.38(19)
O(6)-C(28)-H(28)	108.8
C(29)-C(28)-H(28)	108.8
C(27)-C(28)-H(28)	108.8
C(30)-C(29)-C(34)	119.2(2)
C(30)-C(29)-C(28)	121.3(2)
C(34)-C(29)-C(28)	119.5(2)
C(31)-C(30)-C(29)	121.2(2)
C(31)-C(30)-H(30)	119.4
C(29)-C(30)-H(30)	119.4
C(32)-C(31)-C(30)	117.9(2)
C(32)-C(31)-H(31)	121.1
C(30)-C(31)-H(31)	121.1
C(31)-C(32)-C(33)	122.5(2)
C(31)-C(32)-N(2)	119.1(2)
C(33)-C(32)-N(2)	118.4(2)
C(34)-C(33)-C(32)	118.6(2)
C(34)-C(33)-H(33)	120.7
C(32)-C(33)-H(33)	120.7
C(33)-C(34)-C(29)	120.7(2)
C(33)-C(34)-H(34)	119.7
C(29)-C(34)-H(34)	119.7
H(1W)-O(1W)-H(2W)	121(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for f415. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	26(1)	21(1)	21(1)	7(1)	2(1)	7(1)
F(2)	27(1)	21(1)	18(1)	6(1)	-2(1)	7(1)
O(1)	30(1)	18(1)	31(1)	6(1)	14(1)	-2(1)
O(2)	16(1)	20(1)	18(1)	3(1)	4(1)	-5(1)
O(3)	27(1)	33(1)	17(1)	8(1)	-1(1)	1(1)
O(4)	16(1)	24(1)	24(1)	-1(1)	0(1)	-5(1)
O(5)	28(1)	14(1)	24(1)	4(1)	3(1)	4(1)
O(6)	14(1)	21(1)	16(1)	1(1)	3(1)	-6(1)
O(7)	24(1)	26(1)	14(1)	5(1)	0(1)	-2(1)
O(8)	21(1)	17(1)	24(1)	-2(1)	-3(1)	-5(1)
N(1)	9(1)	25(1)	16(1)	2(1)	2(1)	3(1)
N(2)	10(1)	19(1)	17(1)	0(1)	2(1)	3(1)
C(1)	17(1)	14(1)	18(1)	3(1)	6(1)	-1(1)
C(2)	13(1)	17(1)	20(1)	0(1)	-1(1)	2(1)
C(3)	18(1)	20(1)	24(1)	4(1)	5(1)	6(1)
C(4)	24(1)	24(1)	20(1)	3(1)	6(1)	4(1)
C(5)	24(1)	29(2)	17(1)	4(1)	4(1)	6(1)
C(6)	22(1)	28(1)	17(1)	5(1)	3(1)	5(1)
C(7)	14(1)	23(1)	20(1)	1(1)	1(1)	-5(1)
C(8)	22(1)	18(1)	16(1)	1(1)	4(1)	-7(1)
C(9)	15(1)	13(1)	16(1)	4(1)	3(1)	2(1)
C(10)	14(1)	16(1)	12(1)	2(1)	4(1)	-2(1)
C(11)	13(1)	15(1)	14(1)	4(1)	3(1)	0(1)
C(12)	9(1)	14(1)	14(1)	2(1)	4(1)	3(1)
C(13)	15(1)	10(1)	17(1)	3(1)	8(1)	1(1)
C(14)	16(1)	16(1)	14(1)	5(1)	6(1)	4(1)
C(15)	9(1)	17(1)	13(1)	0(1)	2(1)	3(1)
C(16)	11(1)	15(1)	21(1)	4(1)	4(1)	-1(1)
C(17)	14(1)	14(1)	16(1)	6(1)	4(1)	1(1)
C(18)	14(1)	14(1)	15(1)	2(1)	2(1)	-1(1)
C(19)	19(1)	22(1)	21(1)	-2(1)	1(1)	-2(1)
C(20)	25(1)	25(1)	17(1)	-5(1)	2(1)	-3(1)
C(21)	22(1)	26(1)	22(1)	2(1)	9(1)	3(1)
C(22)	17(1)	25(1)	23(1)	3(1)	6(1)	1(1)
C(23)	14(1)	16(1)	17(1)	1(1)	3(1)	-1(1)

C(24)	13(1)	29(2)	21(1)	-1(1)	0(1)	-3(1)
C(25)	17(1)	17(1)	19(1)	0(1)	2(1)	-5(1)
C(26)	16(1)	15(1)	15(1)	4(1)	2(1)	-1(1)
C(27)	12(1)	16(1)	13(1)	2(1)	2(1)	-4(1)
C(28)	13(1)	16(1)	15(1)	4(1)	1(1)	-1(1)
C(29)	10(1)	14(1)	14(1)	2(1)	4(1)	2(1)
C(30)	16(1)	10(1)	16(1)	2(1)	6(1)	-2(1)
C(31)	15(1)	14(1)	14(1)	4(1)	4(1)	1(1)
C(32)	8(1)	15(1)	13(1)	-1(1)	2(1)	2(1)
C(33)	12(1)	12(1)	20(1)	4(1)	3(1)	-1(1)
C(34)	16(1)	13(1)	16(1)	5(1)	3(1)	0(1)
O(1W)	42(2)	87(3)	79(2)	19(2)	7(2)	18(2)

Table 5.

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

for f415.

	x	y	z	U(eq)
H(1O)	1325(17)	6650(30)	8530(18)	30
H(5O)	2670(40)	4625(18)	8266(15)	26
H(2A)	1363	8182	7857	21
H(2B)	2769	9302	8230	21
H(3A)	177	9496	8785	24
H(3B)	195	8134	8960	24
H(4A)	2710	10147	9609	27
H(4B)	1283	9509	10020	27
H(5A)	2709	7713	9924	27
H(5B)	4102	8839	10299	27
H(6A)	5309	7550	9383	26
H(6B)	5246	8904	9198	26
H(7A)	7747	8561	7111	24
H(7B)	7734	7262	7376	24
H(8A)	6680(40)	8610(30)	8253(17)	23
H(8B)	5190(40)	8890(30)	7697(17)	23
H(10A)	2868	5913	7282	17
H(10B)	2750	7202	7011	17
H(11)	5581	5679	6834	17

H(13)	4349	7063	5371	16
H(14)	2732	6139	4265	17
H(16)	1288	3207	5181	18
H(17)	2914	4140	6280	18
H(19A)	4334	2999	9376	26
H(19B)	4551	4300	9120	26
H(20A)	3047	4422	10165	28
H(20B)	1848	4800	9499	28
H(21A)	1513	2449	9946	28
H(21B)	140	3458	10057	28
H(22A)	-617	3259	8793	25
H(22B)	-897	1941	9025	25
H(23A)	1960(40)	1490(30)	8641(16)	19
H(23B)	610(40)	1860(30)	7992(17)	19
H(24A)	7723	3397	7236	26
H(24B)	7410	2120	7514	26
H(25A)	6370(40)	3640(30)	8305(17)	22
H(25B)	5080(40)	3950(30)	7712(17)	22
H(27A)	2530	2315	6953	17
H(27B)	2453	1062	7269	17
H(28)	5233	667	6936	17
H(30)	4321	2065	5428	17
H(31)	2867	1136	4291	17
H(33)	1262	-1806	5169	17
H(34)	2724	-865	6299	18
H(1W)	8200(40)	5770(40)	8300(30)	82
H(2W)	9580(70)	5050(40)	7969(18)	82

Table 6.

Torsion angles [°] for f415.

O(1)-C(1)-C(2)-C(3)	62.1(3)
C(6)-C(1)-C(2)-C(3)	-55.9(3)
C(9)-C(1)-C(2)-C(3)	179.7(2)
C(1)-C(2)-C(3)-C(4)	55.4(3)
C(2)-C(3)-C(4)-C(5)	-55.4(3)
C(3)-C(4)-C(5)-C(6)	55.8(3)
C(4)-C(5)-C(6)-C(1)	-56.4(3)
O(1)-C(1)-C(6)-C(5)	-61.1(3)

C(2)-C(1)-C(6)-C(5)	56.7(3)
C(9)-C(1)-C(6)-C(5)	-178.6(2)
C(11)-O(2)-C(7)-C(8)	-61.0(3)
O(2)-C(7)-C(8)-C(9)	55.6(3)
C(7)-C(8)-C(9)-F(1)	63.7(3)
C(7)-C(8)-C(9)-C(10)	-50.5(3)
C(7)-C(8)-C(9)-C(1)	178.8(2)
O(1)-C(1)-C(9)-F(1)	-59.2(2)
C(6)-C(1)-C(9)-F(1)	58.9(2)
C(2)-C(1)-C(9)-F(1)	-177.10(19)
O(1)-C(1)-C(9)-C(8)	-175.4(2)
C(6)-C(1)-C(9)-C(8)	-57.2(3)
C(2)-C(1)-C(9)-C(8)	66.7(3)
O(1)-C(1)-C(9)-C(10)	55.6(3)
C(6)-C(1)-C(9)-C(10)	173.8(2)
C(2)-C(1)-C(9)-C(10)	-62.3(3)
F(1)-C(9)-C(10)-C(11)	-63.3(2)
C(8)-C(9)-C(10)-C(11)	51.2(3)
C(1)-C(9)-C(10)-C(11)	-177.23(19)
C(7)-O(2)-C(11)-C(12)	-176.92(19)
C(7)-O(2)-C(11)-C(10)	61.3(3)
C(9)-C(10)-C(11)-O(2)	-56.5(3)
C(9)-C(10)-C(11)-C(12)	-177.47(19)
O(2)-C(11)-C(12)-C(13)	-12.3(3)
C(10)-C(11)-C(12)-C(13)	110.0(2)
O(2)-C(11)-C(12)-C(17)	168.5(2)
C(10)-C(11)-C(12)-C(17)	-69.2(3)
C(17)-C(12)-C(13)-C(14)	-0.3(3)
C(11)-C(12)-C(13)-C(14)	-179.5(2)
C(12)-C(13)-C(14)-C(15)	-0.3(3)
C(13)-C(14)-C(15)-C(16)	1.1(4)
C(13)-C(14)-C(15)-N(1)	-179.0(2)
O(3)-N(1)-C(15)-C(14)	0.3(3)
O(4)-N(1)-C(15)-C(14)	179.7(2)
O(3)-N(1)-C(15)-C(16)	-179.7(2)
O(4)-N(1)-C(15)-C(16)	-0.4(3)
C(14)-C(15)-C(16)-C(17)	-1.2(4)
N(1)-C(15)-C(16)-C(17)	178.9(2)

C(15)-C(16)-C(17)-C(12)	0.5(4)
C(13)-C(12)-C(17)-C(16)	0.2(4)
C(11)-C(12)-C(17)-C(16)	179.5(2)
O(5)-C(18)-C(19)-C(20)	69.3(3)
C(23)-C(18)-C(19)-C(20)	-50.9(3)
C(26)-C(18)-C(19)-C(20)	-174.1(2)
C(18)-C(19)-C(20)-C(21)	55.6(3)
C(19)-C(20)-C(21)-C(22)	-57.7(3)
C(20)-C(21)-C(22)-C(23)	57.2(3)
C(21)-C(22)-C(23)-C(18)	-54.9(3)
O(5)-C(18)-C(23)-C(22)	-69.8(3)
C(19)-C(18)-C(23)-C(22)	50.7(3)
C(26)-C(18)-C(23)-C(22)	173.6(2)
C(28)-O(6)-C(24)-C(25)	-62.9(3)
O(6)-C(24)-C(25)-C(26)	55.1(3)
C(24)-C(25)-C(26)-F(2)	68.7(3)
C(24)-C(25)-C(26)-C(27)	-46.6(3)
C(24)-C(25)-C(26)-C(18)	-173.8(2)
O(5)-C(18)-C(26)-F(2)	177.25(18)
C(23)-C(18)-C(26)-F(2)	-64.2(2)
C(19)-C(18)-C(26)-F(2)	58.5(2)
O(5)-C(18)-C(26)-C(27)	-66.3(2)
C(23)-C(18)-C(26)-C(27)	52.2(3)
C(19)-C(18)-C(26)-C(27)	174.9(2)
O(5)-C(18)-C(26)-C(25)	59.8(3)
C(23)-C(18)-C(26)-C(25)	178.3(2)
C(19)-C(18)-C(26)-C(25)	-59.0(3)
F(2)-C(26)-C(27)-C(28)	-69.1(2)
C(25)-C(26)-C(27)-C(28)	46.7(3)
C(18)-C(26)-C(27)-C(28)	174.12(19)
C(24)-O(6)-C(28)-C(29)	-175.17(19)
C(24)-O(6)-C(28)-C(27)	63.0(2)
C(26)-C(27)-C(28)-O(6)	-55.6(3)
C(26)-C(27)-C(28)-C(29)	-176.48(19)
O(6)-C(28)-C(29)-C(30)	-18.3(3)
C(27)-C(28)-C(29)-C(30)	104.0(3)
O(6)-C(28)-C(29)-C(34)	163.4(2)
C(27)-C(28)-C(29)-C(34)	-74.2(3)

C(34)-C(29)-C(30)-C(31)	-0.8(4)
C(28)-C(29)-C(30)-C(31)	-179.1(2)
C(29)-C(30)-C(31)-C(32)	-0.1(4)
C(30)-C(31)-C(32)-C(33)	1.1(4)
C(30)-C(31)-C(32)-N(2)	-179.1(2)
O(7)-N(2)-C(32)-C(31)	-2.7(3)
O(8)-N(2)-C(32)-C(31)	176.9(2)
O(7)-N(2)-C(32)-C(33)	177.1(2)
O(8)-N(2)-C(32)-C(33)	-3.3(3)
C(31)-C(32)-C(33)-C(34)	-1.2(4)
N(2)-C(32)-C(33)-C(34)	179.1(2)
C(32)-C(33)-C(34)-C(29)	0.2(4)
C(30)-C(29)-C(34)-C(33)	0.8(4)
C(28)-C(29)-C(34)-C(33)	179.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for f415 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...O(1W)#1	0.850(10)	2.08(3)	2.708(4)	130(3)
O(5)-H(5O)...O(1)	0.839(10)	2.16(2)	2.861(3)	141(3)
O(1W)-H(1W)...F(1)	0.868(10)	2.134(14)	2.991(3)	169(5)
O(1W)-H(2W)...O(5)#2	0.872(10)	2.35(5)	2.923(4)	123(4)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 x+1,y,z

5. Reference

(1) Y. Liu and Y.-Y. Yeung, *Org. Lett.*, 2017, **19**, 1422-1425.