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Electronic Supplementary Information

Direct (Het)Arylation of Tetrahydroisoquinoline via a Metal and Oxidant Free C(sp^3)-H Functionalization Enabled Three Component Reaction

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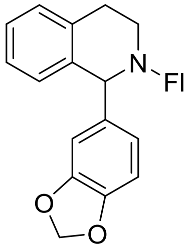
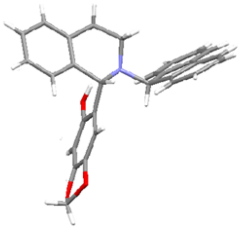
Experimental section:

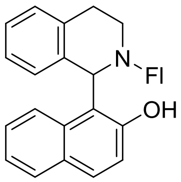
General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. THF and diethylether (Et_2O) were freshly distilled from Sodium under argon. Dichloromethane (CH_2Cl_2) was freshly distilled from phosphorus(V)oxide (P_2O_5).Triethylamine (Et_3N) was distilled from CaH_2 and stored under argon. Commercial grade xylene, benzene and toluene were distilled before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. ^{1}H, ^{13}C NMR spectroscopy: *Varian Mercury plus 400 MHz* (at 298 K). Chemical shifts, δ (in ppm), are reported relative to TMS δ(^{1}H)0.0 ppm, δ(^{13}C)0.0 ppm) which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ(^{1}H) 7.26 ppm, δ(^{13}C) 77.0 ppm; CD_3OD, (^{1}H) 3.31 ppm, δ(^{13}C) 49.0 ppm) were used for calibration. Column chromatography: Merck or Spectrochem silica gel 60-120 under gravity. IR: spectra were spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on a Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in *m/z* (% of basis peak). X–ray crystallographic data were collected using a Bruker SMART APEX–II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo−Kα radiation (l = 0.71073 Å) at 296(2) K, with increasing w (width of 0.3° per frame) at a scan speed of 3 s/frame. Structures were solved by direct methods using SHELXS–97 and refined with full matrix least squares on F^2 using SHELXL–97. Using Olex2, structure was solved with the Super flip structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss–Newton minimization. All the non–hydrogen atoms were refined anisotropically.

Crystal Structures:

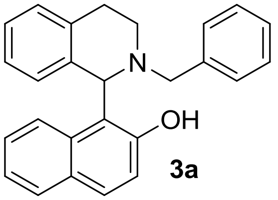
Crystal data and structure refinement for **4g (**CCDC 1868392).

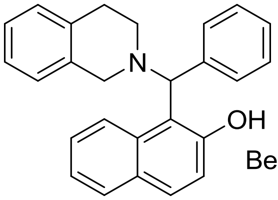
	
Crystal data and structure refinement for **4g**	
Empirical formula	C29 H23 N O3
Formula weight	433.48
Crystal habit, colour	needle / colorless
Crystal size, mm^3	0.24* 0.17* 0.15
Temperature, *T*	293(2) K
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*' P21/n'*
Unit cell dimensions	*a* = 15.1652(8)Å
	*b= 15.1364(13)*Å
	c = 19.9955(13)Å
	α = 90.00°, γ = 90.00 °, β = 106.480(6)°
Volume, *V*(Å^3)	4401.3(5)
Z	8
Calculated density, Mg·m^{-3}	1.308
Absorption coefficient, μ(mm^{-1})	0.085
F(000)	1824

θ range for data collection	3.00 ° to 25.00°
Limiting indices	$-18 \leq h \leq 18$, $-16 \leq k \leq 18$, $-23 \leq l \leq 23$
Reflection collected / unique	16211 /3089 [R(int) = 0.1058]
Completeness to θ	98.7% (θ = 25.00°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	7645 / 0 / 597
Goodness–of–fit on F^2	0.885
Final R indices [I>2sigma(I)]	$R1 = 0.0840$, $wR2 = 0.1888$
R indices (all data)	$R1 = 0.3467$, $wR2 = 0.2036$
Largest diff. peak and hole	0.574 and -0.650 Å^{-3}

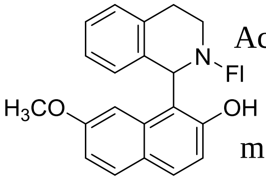


1-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-2-ol (3): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 2- naphthol (0.25 mmol, 1.0 equiv, 36 mg) were reacted for 48h. Then the reaction mixture was dissolved in methanol and the solid product was precipitated from reaction mixture. The solid was filtered and washed with (3×5 mL) methanol to obtain the desired product **3** (70 mg) as light brown solid. Next, mother liquor was evaporated under reduced pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:20) to give an additional amount (20 mg) of the product. The combined yield is 90 mg (82%). FTIR (KBr): ʋ̆ = 3056, 3033, 2838, 1619, 1462, 1448, 1268, 1227, 811, 741, 531 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.77 (s, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.83 – 7.79 (m, 3H), 7.7 – 7.65 (m, 2H), 7.63- 7.61 (m, 1H), 7.42 – 7.38 (m, 1H), 7.38 – 7.33 (m, 3H), 7.27 – 7.20 (m, 2H), 7.1 – 7.03 (m, 2H), 6.94 – 6.90 (m, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.65 (s, 1H), 4.98 (s, 1H), 3.13 – 3.02 (m, 1H), 2.64 – 2.51 (m, 2H), 2.48 – 2.44 (m,1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.8, 144.0, 142.1, 141.4, 141.2, 136.6, 134.4, 134.3, 130.3, 129.5, 129.0, 128.7, 128.66, 128.56, 128.2, 127.9, 127.7, 127.1, 126.8, 126.6, 126.4, 125.9, 123.0, 121.5, 120.5, 120.1, 119.6, 118.0, 65.2, 60.7, 43.2, 29.9 ppm. HRMS (ESI) exact mass calculated for $C_{32}H_{26}N_5O^+$([M+H]$^+$): 440.2009, found: 440.2001.

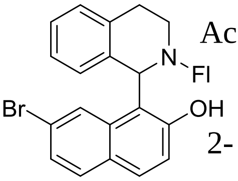

3a


Betti-product

1-(2-benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-2-ol (3a) and 1-((3,4-dihydroisoquinolin-2(1H)-yl)(phenyl)methyl)naphthalen-2-ol : According to general procedure I, benzaldehyde (0.24 mmol, 1.2 equiv, 25 μL), 1,2,3,4-tetrahydroisoquinoline (0.6 mmol, 3 equiv, 76 μL) and 2-naphthol (0.20 mmol, 1 equiv, 29 mg), in neat condition were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (ethyl acetate: hexane; 1:50) to obtain the oxazine corresponding to Betti product as light yellow solid (26 mg, 36%) and with (ethyl acetate: hexane; 1:40) to obtain an inseparable mixture of corresponding Betti and α-arylated product as yellow gum with 2:1 regioisomeric ratio (17 mg, 23%). Characteristic NMR-signals of **3a** and Betti product: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.27 (s, 2H) (Betti product), 11.75 (s, 1H) (**3a**), 5.54 (s, 1H) (**3a**), 5.22 (s, 2H) (Betti product), 4.05 (d, *J* = 13.2 Hz, 1H) (**3a**), 3.21 (d, *J* = 13.2 Hz, 1H) (**3a**). HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO^+$ ($[M+H]^+$): 366.1852, found 366.1851.

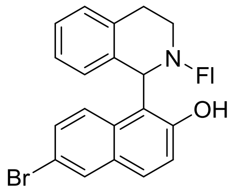


1-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-7-methoxynaphthalen-2-ol (4a): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 μL) and 7-methoxy 2- naphthol (0.25 mmol, 1.0 equiv, 43.5 mg), in neat condition were reacted for 48 h. Then the reaction mixture was dissolved in methanol and the solid product was precipitated from reaction mixture. The solid was filtered and washed with (3×5 mL) methanol to obtain the desired product **4a** (65 mg) as light brown solid. Next, mother liquor was evaporated under reduced pressure and residue was purified by column SiO_2 chromatography (Ethyl acetate: hexane; 1:20) to give an additional amount (23 mg) of the product. The combined yield is 88 mg (75%). FTIR (KBr): ῠ = 3412, 3023, 2962, 2809, 1446, 1262, 742 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 11.67 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.67 – 7.66 (m, 2H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.23 – 7.21 (m, 1H), 7.11 – 7.05 (m, 4H), 6.97 – 6.94 (m,1H), 6.87 – 6.85 (m, 1H), 6.57 (s, 1H), 5.00 (s, 1H), 4.05 (s, 3H), 3.09 – 3.00 (m, 1H), 2.64 – 2.61 (m, 1H), 2.57 – 2.43(m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.5, 156.4, 144.0, 142.1, 141.5, 141.1, 136.7, 135.6, 134.3, 131.0, 130.1, 128.7, 128.67, 128.61, 128.3, 127.8, 126.9, 126.8, 126.6, 126.3, 125.9, 124.4, 120.64, 119.6, 117.6, 117.3, 115.1, 100.9, 65.2, 60.9, 55.6, 43.2, 29.9 ppm. HRMS (ESI) exact mass calculated for $C_{33}H_{28}NO_2^+$ ($[M+H]^+$): 470.2115, found 470.2118.



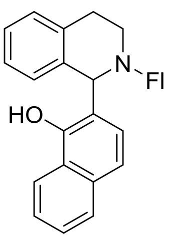
1-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-7-bromonaphthalen-2-ol (4b): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 7-bromo 2- naphthol (0.25 mmol, 1.0 equiv, 56 mg), in neat condition were reacted for 48 h. Then the reaction mixture was dissolved in methanol and the solid product was precipitated from reaction mixture. The solid was filtered and washed with (3×5 mL) methanol to obtain the desired product **4b** (74 mg) as light brownish solid. Next, mother liquor was evaporated under reduced pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:20) to give an additional amount (27 mg) of the product. The combined yield is (78%, 101 mg). FTIR (KBr): ῠ = 3431, 2842, 1589, 1449, 1260, 925, 742 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 11.88 (s, 1H), 8.52 (s, 1H), 7.78 – 7.71 (m, 4H), 7.65 – 7.60 (m, 2H), 7.48 – 7.47 (m, 1H), 7.38 – 7.30 (m, 4H), 7.23 – 7.20 (m, 1H), 7.10 – 7.05 (m, 2H), 6.97 – 6.94 (m, 1H), 6.77 – 6.75 (m, 1H), 6.51 (s, 1H), 4.92 (s, 1H), 3.10 – 3.00 (m, 1H), 2.67 – 2.59 (m, 1H), 2.54 – 2.50 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.7, 143.7, 142.0, 141.2, 141.1, 136.1, 135.6, 134.3, 131.0, 130.3, 128.8, 128.76, 128.7, 128.2, 127.8, 127.34, 127.29, 127.0, 126.7, 126.4, 126.3, 125.8, 123.9, 122.3, 120.6, 119.7, 117.4, 65.2, 60.7, 43.2, 29.8 ppm. (Total count of ^{13}C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{32}H_{25}BrN^+$ ($[M+H]^+$): 518.1114, found, 518.1120.

1-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-6-bromonaphthalen-2-ol (4c): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 6- bromo 2- naphthol (0.25 mmol, 1.0 equiv, 56 mg) were reacted for 48 h. Then, the reaction mixture was dissolved in methanol and the solid product was precipitated from reaction mixture. The solid was filtered and washed with (3×5 mL) methanol to obtain the desired product **4c** (68 mg) as light brown solid. Next, mother liquor was evaporated under reduced pressure and residue was purified by SiO_2 column chromatography



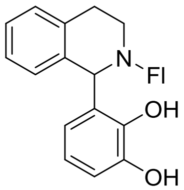
(Ethyl acetate: hexane; 1:20) to give an additional amount (29 mg) of the product. The combined yield is 97 mg (75%). FTIR (KBr): ῠ = 3057, 2842, 1612, 1589, 1507, 1448, 1260, 925, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.87 (s, 1H), 8.26 – 8.23 (m,1H), 8.01 (s, 1H), 7.83 – 7.81 (m,1H), 7.79 – 7.70 (m, 4H), 7.67 – 7.68 (m, 1H), 7.42 – 7.35 (m, 3H), 7.30 – 7.28 (m, 1H), 7.23 – 7.21 (m,1H), 7.12 – 7.05 (m, 2H), 6.96 – 6.92 (m, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.59 (s, 1H), 4.97 (s, 1H), 3.11 – 3.02 (m, 1H), 2.63 – 2.61 (m, 1H), 2.56 – 2.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.1, 143.7, 142.0, 141.2, 141.1, 136.1, 134.3, 132.9, 131.3, 130.8, 130.2, 129.4, 128.83, 128.77, 128.7, 128.3, 127.7, 127.2, 127.0, 126.6, 126.2, 125.9, 123.3, 121.3, 120.7, 119.7, 118.3, 116.5, 65.2, 60.7, 43.2, 29.9 ppm. HRMS (ESI) exact mass calculated for $C_{32}H_{25}BrN_5^+$ ($[M+H]^+$): 518.1114, found, 518.1107.

2-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-1-ol (4d): According to



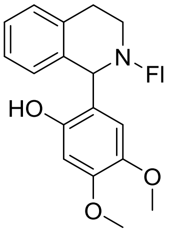
general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 1- naphthol (0.25 mmol, 1.0 equiv, 36 mg) were reacted for 48 h. Then, the reaction mixture was dissolved in methanol and the solid product was precipitated from reaction mixture. The solid was filtered and washed with (3×5 mL) methanol to obtain the desired product **4d** (48 mg) as light brown solid. Next, mother liquor was evaporated under reduced pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:20) to give an additional amount (12 mg) of the product. The combined yield is 60 mg (55%). FTIR (KBr): ῠ = 3956, 2838, 1619, 1462, 1448, 1258, 811, 741 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 11.32 (s, 1H), 8.31 – 8.30 (m, 1H), 7.81 (d, *J* = 7.2 Hz, 3H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.40 – 7.34 (m, 3H), 7.29 – 7.27 (m, 1H), 7.10 – 7.04 (m, 2H), 7.00 – 7.04 (m, 1H), 6.96 – 6.95 (m, 1H), 5.90 (s, 1H), 5.15 (s, 1H), 3.10 – 3.04 (m, 1H), 2.61 – 2.59 (m, 1H), 2.51 – 2.44 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.8, 144.0, 142.1, 142.0, 141.2, 136.8, 134.5, 134.2, 128.6, 128.3, 127.6, 127.5, 126.7, 126.5, 126.4, 125.9, 125.8, 125.3, 125.1, 122.6, 122.7, 120.7, 120.5, 119.7, 119.7, 119.6, 119.1, 119.0, 67.3, 65.2, 42.9, 30.0 ppm. HRMS (ESI) exact mass calculated for $C_{32}H_{26}NO^+$ ($[M+H]^+$): 440.2009, found, 440.2020.

3-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)benzene-1,2-diol (4e):



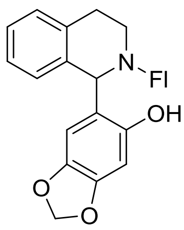
According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and pyro-catechol (0.25 mmol, 1.0 equiv, 27.5 mg) were reacted for 36 h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:10) to obtain **4e** as brown solid 56 mg (53%). FTIR (KBr): ʋ = 3501, 2923, 1602, 1479, 1450, 1259, 1180, 745, 737 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 10.85 (s, 1H), 7.74 – 7.72 (m, 2H), 7.68 – 7.67 (m, 2H), 7.41 – 7.38 (m, 2H), 7.36 – 7.33 (m, 1H), 7.29 – 7.24 (m, 1H), 7.13 – 7.11 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.06 – 7.04 (m, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.96 – 6.94 (m, 1H), 6.92 – 6.89 (m, 1H), 5.75 (s, 1H), 5.60 (s, 1H), 5.09 (s, 1H), 3.01 – 2.95 (m, 1H), 2.59 – 2.56 (m, 1H), 2.43 – 2.41 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 145.8, 143.8, 143.4, 142.0, 141.8, 141.3, 136.0, 134.1, 128.83, 128.77, 128.6, 128.2, 127.1, 126.9, 126.7, 126.5, 125.5, 122.0, 120.6, 120.2, 119.8, 115.1, 66.9, 65.1, 42.7, 29.9 ppm. (Total count of ^{13}C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{24}H_{28}N_5^+$ ($[M+H]^+$): 406.1802, found: 406.1803.

2-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4,5-dimethoxyphenol (4f):



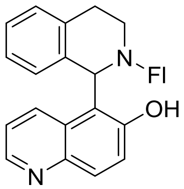
According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 3,4 dimethoxy phenol (0.25 mmol, 1.0 equiv, 38 mg) were reacted for 24h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:10) to obtain **4f** as brown solid 82 mg (73%). FTIR (KBr): ʋ = 2922, 2845, 1504, 1449, 1191, 1113, 740 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 10.07 (s, 1H), 7.76 – 7.74 (s, 3H), 7.69 – 7.65 (m, 1H), 7.42 – 7.31 (m, 3H), 7.29 – 7.24 (m, 1H), 7.13 – 7.05 (m, 3H), 7.03 (s, 1H), 6.98 (s, 1H), 6.54 (s, 1H), 5.64 (s, 1H), 5.18 (s, 1H), 3.96 (s, 3H), 3.84 (s, 3H), 3.01 – 2.91 (m, 1H), 2.58 – 2.52 (m, 1H), 2.48 – 2.35 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.2, 150.4, 144.1, 142.3, 142.2, 142.0, 141.1, 136.7, 134.2, 128.7, 128.64, 128.62, 128.2, 128.0, 127.0, 126.8, 126.4, 126.3, 125.7, 120.6, 119.7, 117.2, 115.0, 102.4, 67.0, 65.0, 57.5, 56.0, 43.0, 29.9.ppm. HRMS (ESI) exact mass calculated for $C_{30}H_{28}NO_3^+$ ($[M+H]^+$): 450.2064, found, 450.2062.

6-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)benzo[d][1,3]dioxol-5-ol (4g):



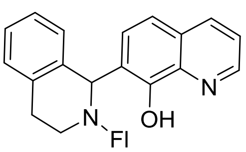
According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 μL) and sesamol (0.25 mmol, 1.0 equiv, 34.5 mg) were reacted for 18 h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane: 1:10) to obtain **4g** as brown solid 73 mg (67%). FTIR (KBr): ῠ = 2890, 2830, 1479, 1450, 1181, 1033, 743 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.30 (s, 1H), 7.73 – 7.70 (m, 3H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.38 (m, 2H), 7.36 – 7.33 (m, 1H), 7.27 – 7.24 (m, 1H), 7.12 – 7.07 (m, 2H), 7.02 – 7.01 (m, 3H), 6.51 (s, 1H), 5.95 (d, *J* = 1.2 Hz, 1H), 5.90 (d, *J* = 1.2 Hz, 1H), 5.61 (s, 1H), 5.17 (s, 1H), 2.98 – 2.92 (m, 1H), 2.55 – 2.52 (m, 1H), 2.43 – 2.36 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.1, 148.5, 144.0, 142.0, 141.1, 140.7, 136.5, 134.3, 128.7, 128.6, 128.2, 127.9, 127.1, 126.8, 126.4, 126.3, 125.7, 120.6, 119.7, 117.9, 110.17, 101.3, 100.1, 67.1, 64.9, 42.9, 29.9 ppm. (Total count of ^{13}C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{29}H_{24}NO_3^+$ ([M+H]$^+$): 434.1751, found, 434.1759.

5-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)quinolin-6-ol (4h): According to

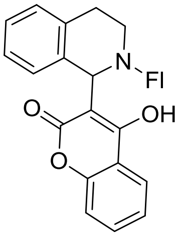


general procedure I 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 μL) and 6-hydroxyquinol (0.25 mmol, 1.0 equiv, 36 mg) were reacted for 24 h. After, the completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane) to obtain **4h** as brown solid 62 mg (56%). FTIR (KBr): ῠ = 2915, 2841, 1610, 1447, 1249, 1128, 828, 742, 728 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.83 (s, 1H), 8.85 (d, *J* = 3.8 Hz, 1H), 8.68 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 6.8 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.45 – 7.42 (m, 1H), 7.40 – 7.37 (m, 3H), 7.29 – 7.27 (m, 1H), 7.14 – 7.06 (m, 2H), 6.96 – 6.92 (m, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 4.98 (s, 1H), 3.14 – 3.02 (m, 1H), 2.70 – 2.62 (m, 1H), 2.60 – 2.45 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.0, 147.3, 144.2, 143.6, 142.1, 141.3, 141.1, 136.1, 134.4, 131.7, 129.6, 129.2, 128.9, 128.8, 128.7, 128.4, 127.7, 127.2, 127.1, 126.7, 126.0, 125.9, 123.7, 122.3, 120.7, 119.7, 117.6, 65.3, 60.3, 43.3, 29.9 ppm. HRMS (ESI) exact mass calculated for $C_{31}H_{25}N_2O^+$ ($[M+H]^+$): 441.1961, found, 441.1962.

7-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)quinolin-8-ol (4i): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 8-hydroxyquinol (0.25 mmol, 1.0 equiv, 36 mg) were reacted for 24 h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:6) to obtain **4i** as brown solid 58 mg (53%). FTIR (KBr): ῠ = 2923, 1629, 1449, 1375, 1090, 742 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.59 (s, 1H), 8.83 (d, *J* = 3.0 Hz, 1H), 8.13 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.42 – 7.39 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 7.09 – 7.06 (m, 2H), 7.01 – 6.98 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.40 (s, 1H), 4.94 (s, 1H), 3.08 – 3.01 (m, 1H), 2.56 – 2.54 (m, 2H), 2.39 – 2.36 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.7, 148.5, 145.4, 143.6, 141.7, 140.9, 139.0, 138.4, 136.1, 135.4, 129.2, 128.7, 128.69, 128.4, 128.3, 128.2, 127.7, 127.0, 126.8, 126.2, 126.0, 125.5, 125.41, 121.9, 120.3, 119.4, 118.5, 65.3, 61.4, 43.0, 30.5 ppm. HRMS (ESI) exact mass calculated for $C_{31}H_{25}N_2O^+$ ($[M+H]^+$): 441.1961, found, 441.1961.

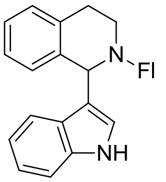


3-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-hydroxy-2H-chromen-2-one (4j): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 4-hydroxy coumarin (0.25 mmol, 1.0 equiv, 36 mg) were reacted for 48 h. Then, the reaction mixture was dissolved in methanol and the solid product was precipitated from reaction mixture. The solid was filtered and washed with (3×5 mL) methanol to obtain the desired product **4j** (70 mg) as light yellow solid. Next, mother liquor was evaporated under reduced pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:20) to give an additional amount (10 mg) of the product. The combined yield is 80 mg (70%). FTIR (KBr): ῠ = 2925, 1671, 1604, 1130, 748, 615 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.51 – 7.51 (m, 2H), 7.46 – 7.36 (m, 3H), 7.34 – 7.24 (m, 3H), 7.19 – 7.10 (m,

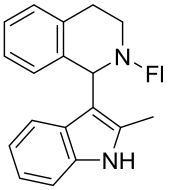


2H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.40 (s, 1H), 5.27 (s, 1H), 3.15 – 3.07 (m, 1H), 2.63 – 2.58 (m, 2H), 2.54 – 2.46 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.5, 154.4, 142.1, 141.6, 139.5, 136.6, 134.8, 134.7, 132.1, 131.7, 130.3, 130.1, 129.2, 128.8, 128.4, 127.9, 127.8, 127.5, 127.4, 127.4, 125.6, 124.4, 124.20, 123.6, 120.4, 120.2, 116.9, 64.1, 61.6, 42.3, 28.1 ppm. HRMS (ESI) exact mass calculated for $C_{31}H_{24}NO_3^+$ ([M+H]$^+$): 458.1751, found, 458.1766.

2-(9H-fluoren-9-yl)-1-(1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5a): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and indole (0.25 mmol, 1.0 equiv, 29 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:15) to obtain **5a** as brown solid 67 mg (65%). FTIR (KBr): ʊ̆ = 3328, 2955, 1687, 1274, 117, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.47 (m, 1H), 7.41 – 7.39 (m, 2H), 7.35 – 7.26 (m, 3H), 7.26 – 7.19 (m, 2H), 7.18 – 7.13 (m, 2H), 7.08 – 7.05 (m, 2H), 6.94 – 6.93 (m, 2H), 5.92 (s, 1H), 5.07 (s, 1H), 3.13 – 3.02 (m, 1H), 2.60 – 2.51 (m, 2H), 2.40 – 2.32 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 146.5, 144.8, 141.7, 140.6, 139.4, 137.4, 135.8, 128.6, 128.2, 127.8, 127.8, 127.5, 126.5, 126.5, 126.2, 125.9, 125.8, 125.8, 124.9, 122.5, 121.67, 120.3, 119.6, 119.2, 118.4, 111.3, 65.2, 60.9, 43.8, 30.8 ppm. HRMS (ESI) exact mass calculated for $C_{30}H_{25}N_2^+$ ([M+H]$^+$): 413.2012, found, 413.2017.

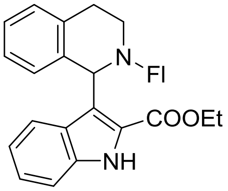


2-(9H-fluoren-9-yl)-1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5b): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 2-methylindole (0.25 mmol, 1.0 equiv, 33 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:15) to obtain **5b** as brown solid 64 mg (60 %). FTIR (KBr): ʊ̆ = 3409, 1601, 1449, 1286, 1217, 742 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 7. 2Hz, 1H), 7.80 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.32 (m, 1H), 7.29 – 7.22 (m, 3H), 7.19 – 7.16 (m, 1H), 7.09 – 7.07 (m, 1H), 7.05



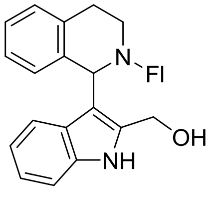
– 7.03 (m, 3H), 6.95 – 6.92 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.00 (s, 1H), 5.03 (s, 1H), 3.11 – 3.05 (m, 1H), 2.63 – 2.61 (m, 1H), 2.60 (s, 3H), 2.58 – 2.55 (m, 1H), 2.33 – 2.31 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 146.7, 144.9, 141.7, 140.5, 139.6, 135.8, 135.4, 133.9, 128.5, 128.1, 127.79, 127.77, 127.5, 126.6, 126.0, 125.9, 125.9, 125.8, 121.4, 120.4, 119.5, 119.2, 113.9, 110.3, 65.4, 59.3, 44.1, 30.9, 12.7 ppm. (Total count of 13C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{31}H_{27}N_2^+$ ([M+H]$^+$): 427.2169, found, 427.2166.

Ethyl3-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-indole-2-carboxylate (5c):



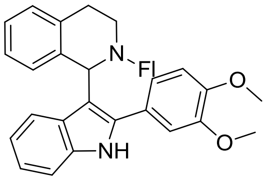
According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and ethyl 1H-indole-2-carboxylate (0.25 mmol, 1.0 equiv, 47 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:20) to obtain **5c** as brown solid 72 mg (60%). FTIR (KBr): ῠ = 3339, 3036, 2971, 2804, 1675, 1541, 1251, 1190, 1092, 748, 735 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.87 (s, 1H), 8.08 – 8.03 (m, 2H), 7.70 – 7.69 (m, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.28 – 7.25 (m, 3H), 7.17 – 7.15 (m, 1H), 7.10 – 7.08 (m, 2H), 7.06 – 7.04 (m, 1H), 6.97 – 6.94 (m, 1H), 6.91 – 6.90 (m, 2H), 4.86 (s, 1H), 4.60 – 4.51 (m, 2H), 3.19 – 3.13 (m, 1H), 2.63 – 2.57 (m, 2H), 2.35 – 2.70 (m, 1H), 1.50 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz,) δ = 162.5, 146.3, 144.3, 141.7, 140.7, 138.5, 136.8, 135.1, 128.7, 128.1, 127.9, 127.4, 126.6, 126.57, 126.1, 126.07, 126.01, 125.9, 124.7, 120.2, 119.2, 111.8, 65.9, 61.5, 58.8, 43.4, 30.9, 14.7 ppm. (Total count of 13C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{33}H_{29}N_2O_2^+$ ([M+H]$^+$): 485.2224, found, 485.2230.

(3-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-indol-2-yl)methanol (5d):

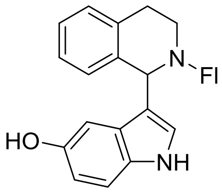


According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and (1H-indol-2-yl)methanol (0.25 mmol, 1.0 equiv, 37 mg) were reacted for 44h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:1) to obtain **5d** as yellow solid 80 mg (72%). FTIR (KBr): ῠ = 3178, 3108, 1448, 1286, 1042, 744, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.94 – 7.92 (m, 1H), 7.70 – 7.68 (m, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 7.10 – 7.04 (m, 2H), 6.98 – 6.94 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.25 (s, 1H), 5.10 (s, 1H), 4.68 (d, *J* = 13.6 Hz, 1H) 4.68 (d, *J* = 14.0 Hz, 1H), 3.15 – 3.07 (m, 1H), 2.65 – 2.61 (m, 1H), 2.58 – 2.53 (m, 1H), 2.41 – 2.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.0, 143.3, 141.9, 140.9, 138.8, 137.3, 135.1, 134.9, 134.9, 129.3, 128.53, 128.35, 128.3, 127.9, 126.9, 126.4, 126.3, 126.1, 125.7, 124.5, 122.2, 120.42, 120.39, 119.4, 115.1, 111.4, 65.4, 58.4, 58.2, 44.0, 30.1 ppm. HRMS (ESI) exact mass calculated for $C_{31}H_{27}N_2O^+$ ([M+H]$^+$): 443.2118, found, 443.2128.

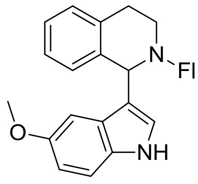
1-(2-(3,4-dimethoxyphenyl)-1H-indol-3-yl)-2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinoline



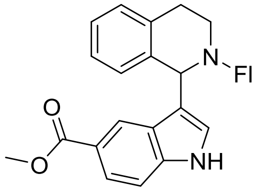
(5e): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 2-(3,4-dimethoxyphenyl)-1H-indole (0.25 mmol, 1.0 equiv, 63 mg) were reacted for 48h. Then, the reaction mixture was dissolved in methanol and the solid product was precipitated from reaction mixture. The solid was filtered and washed with (3×5 mL) methanol to obtain the desired product **5e** (60 mg) as light yellow solid. Next, mother liquor was evaporated under reduced pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:3) to give an additional amount (10 mg) of the product. The combined yield is 70 mg (51%). FTIR (KBr): ῠ = 3421, 3349, 1510, 1450, 1260, 1242, 1136, 1023, 746 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.24 – 7.22 (m, 3H), 7.20 – 7.18 (m, 2H), 7.16 – 7.14 (m, 2H), 7.11 – 7.10 (m, 4H), 7.04 – 7.00 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 5.99 (s, 1H), 4.83 (s, 1H), 3.95 (s, 3H), 3.70 (s, 3H), 3.12 – 3.00 (m, 1H), 2.57 – 2.53 (m, 1H), 2.46 – 2.4 (m, 1H), 2.25 – 2.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.7, 149.5, 146.6, 144.1, 141.5, 140.6, 139.7, 138.2, 136.5, 135.7, 128.8, 127.8, 127.7, 127.5, 127.4, 126.3, 126.2, 126.1, 126.0, 125.9, 125.88, 122.6, 121.8, 120.0, 119.9, 119.1, 114.2, 112.6, 111.7, 110.8, 65.2, 59.7, 56.3, 56.2, 44.0, 30.7 ppm. HRMS (ESI) exact mass calculated for $C_{38}H_{33}N_2O_2^+$ ([M+H]$^+$): 549.2537 found, 549.2569.



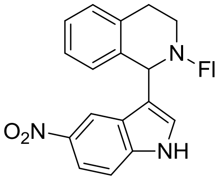
3-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-indol-5-ol (5f): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 5-hydroxyindole (0.25 mmol, 1.0 equiv, 33 mg) condition were reacted for 44h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:4) to obtain **5f** as brown solid 103 mg (96%). FTIR (KBr): ῠ = 3328, 2923, 1687, 1615, 1247, 1237, 739 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 7.2Hz, 1H), 7.35 – 7.33 (m, 1H), 7.30 – 7.27 (m, 1H), 7.24 – 7.17 (m, 3H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 2H), 6.97 – 6.95 (m, 2H), 6.74 – 6.73 (m, 1H), 5.86 (s, 1H), 5.07 (s, 1H), 3.09 – 3.03 (m, 1H), 2.56 – 2.53 (m, 2H), 2.36 – 2.34 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.2, 146.4, 144.7, 141.6, 140.5, 139.2, 135.3, 132.6, 128.5, 128.0, 127.74, 127.72, 127.5, 127.2, 127.0, 126.4, 126.1, 125.9, 125.88, 125.7, 120.2, 119.2, 117.5, 112.3, 111.8, 106.0, 65.1, 60.8, 43.7, 30.7 ppm. HRMS (ESI) exact mass calculated for $C_{30}H_{25}N_2O^+$ ($[M+H]^+$): 429.1961 found, 429.1962.



2-(9H-fluoren-9-yl)-1-(5-methoxy-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5g): According to the general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 5-methoxyindole (0.25 mmol, 1.0 equiv, 36 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:5) to obtain **5g** as brown solid 83 mg (75%). FTIR (KBr): ῠ = 3421, 2924, 1581, 1448, 1201, 741 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.06 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.45 (s, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.30 – 7.27 (m, 1H), 7.23 – 7.21 (m, 3H), 7.20 – 7.17 (m, 1H), 7.06 (s, 2H), 6.96 – 6.95 (m, 2H), 6.83 – 6.82 (m, 1H), 5.89 (s, 1H), 5.10 (s, 1H), 3.78 (s, 3H), 3.09 – 3.03 (m, 1H), 2.57 – 2.54 (m, 2H), 2.37 – 2.35 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.7, 146.5, 144.8, 141.6, 140.7, 139.2, 135.4, 132.6, 128.5, 128.2, 127.8, 127.8, 127.4, 127.0 126.5, 126.2, 125.9, 125.8, 125.76, 125.6, 120.3, 119.3, 118.1, 112.5, 111.9, 103.6, 65.2, 60.8, 56.0, 43.8, 30.9 ppm. HRMS (ESI) exact mass calculated for $C_{31}H_{27}N_2O^+$ ($[M+H]^+$): 443.2118, found, 443.2126.

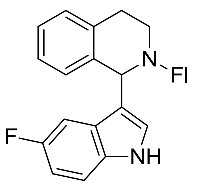


Methyl 3-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-indole-5-carboxylate (5h): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and methyl 1H-indole-5-carboxylate (0.25 mmol, 1.0 equiv, 44 mg) were reacted for 44h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:4) to obtain **5h** as brown solid 104 mg (88%). FTIR (KBr): ʋ̆ = 339, 3058, 2911, 1713, 1445, 1211, 1090, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.66 (s, 1H), 8.44 (s, 1H), 7.87 – 7.85 (m, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.34 – 7.29 (m, 3H), 7.22 – 7.18 (m, 2H), 7.07 – 7.05 (m, 2H), 6.96 – 6.90 (m, 2H), 5.94 (s, 1H), 5.02 (s, 1H), 3.92 (s, 3H) 3.17 – 3.09 (m, 1H), 2.60 – 2.54 (m, 2H), 2.43 – 2.39 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.4, 146.1, 144.6, 141.6, 140.6, 140.0, 138.9, 135.4, 128.9, 127.9, 127.6, 126.6, 126.14, 126.12, 126.07, 125.9, 125.74, 125.72, 125.26, 124.7, 124.0, 121.8, 120.3, 120.2, 119.9, 119.3, 111.1, 65.4, 60.6, 52.1, 43.9, 30.7 ppm. HRMS (ESI) exact mass calculated for $C_{32}H_{27}N_2O_2^+$ ($[M+H]^+$): 471.2067, found, 471.2060.



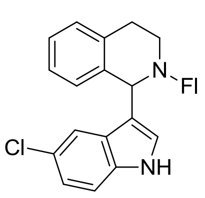
2-(9H-fluoren-9-yl)-1-(5-nitro-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5i): According to general procedure II: 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 5-nitroindole (0.25 mmol, 1.0 equiv, 40 mg), in neat condition were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:2) to obtain **5i** as yellow solid 95 mg (83%). FTIR (KBr): ῠ = 3429, 2923, 1610, 1584, 1489, 1450, 1360, 1258, 1235, 1211, 1149 743, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.79 (s, 1H), 8.45 (s, 1H), 8.10 – 8.07 (m, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H), 7.24 – 7.19 (m, 2H), 7.14 – 7.08 (m, 2H), 6.99 – 6.95 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 1H), 4.98 (s, 1H), 3.25 – 3.17 (m, 1H), 2.68 – 2.61 (m, 2H), 2.52 – 2.48 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.6, 144.3, 141.7, 141.6, 140.6, 140.3, 138.1, 135.4, 129.1, 128.1, 128.0, 127.8, 127.7, 127.5, 126.6, 126.4, 126.0, 125.8, 125.6, 125.5, 121.2, 120.4, 119.5, 119.1, 118.4, 111.4, 65.6, 60.4, 44.1, 30.7 ppm. HRMS (ESI) exact mass calculated for $C_{30}H_{24}N_3O_2^+$ ($[M+H]^+$): 458.1863, found, 458.1879.

2-(9H-fluoren-9-yl)-1-(5-fluoro-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5j): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 μL) and 5-fluoroindole (0.25 mmol, 1.0 equiv, 34 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:5) to obtain **5j** as yellow solid 80 mg (74%). FTIR (KBr): ῠ = 3432, 2922, 1484, 1448, 1581, 1168, 746, 738 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.51 – 7.50 (m, 1H), 7.40 – 7.39 (m, 2H), 7.35 – 7.33 (m, 1H), 7.31 – 7.28 (m, 1H), 7.24 – 7.20 (m, 3H), 7.09 – 7.07 (m, 2H), 6.98 (m, 1H), 6.91 – 6.87 (m, 2H), 5.87 (s, 1H), 5.02 (s, 1H), 3.12 – 3.05 (m, 1H), 2.57 – 2.54 (m, 2H), 2.38 – 2.35 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.3, 156.8, 146.2, 144.6, 141.7, 140.6, 138.8, 135.4, 133.9, 128.7, 128.0, 127.9, 127.6, 126.6, 126.5, 126.14, 126.08, 125.8, 125.7, 120.4, 119.3, 118.4, 111.9, 111.86, 111.1, 110.9, 106.5, 106.4, 65.2, 60.8, 43.8, 30.7 ppm. HRMS (ESI) exact mass calculated for $C_{30}H_{24}FN_2^+$ ($[M+H]^+$): 431.1918, found, 431.1920.

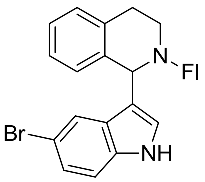


1-(5-chloro-1H-indol-3-yl)-2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinoline (5k): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 μL) and 5-chloroindole (0.25 mmol, 1.0 equiv, 38 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by

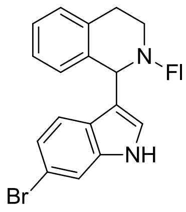
SiO_2 column chromatography (Ethyl acetate: hexane; 1:5) to obtain **5k** as brown solid 79 mg (71%). FTIR (KBr): ʊ̆ = 3441, 2924, 17112, 1609, 1446, 1297, 1261, 1095, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.17 (s, 1H), 7.75 – 7.74 (m, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.46 (m, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.34 (m, 2H), 7.25 – 7.19 (m, 3H), 7.10 – 7.06 (m, 3H), 7.00 – 6.93 (m, 1H), 6.90 – 6.88 (m, 1H), 5.85 (s, 1H), 4.99 (s, 1H), 3.12 – 3.04 (m, 1H), 2.57 – 2.52 (m, 2H), 2.40 – 2.36 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.1, 144.6, 141.6, 140.7, 138.8, 135.8, 135.4, 128.8, 127.93, 127.91, 127.7, 127.4, 126.6, 126.14, 126.12, 125.8, 125.7, 125.2, 122.9, 121.1, 120.3, 119.3, 118.2, 112.3, 65.3, 60.7, 43.9, 30.7 ppm. (Total count of 13C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{30}H_{24}ClN_2^+$ ($[M+H]^+$): 447.1623, found, 447.1620.



1-(5-bromo-1H-indol-3-yl)-2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinoline (5l): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 µL) and 5-bromoindole (0.25 mmol, 1.0 equiv, 48.5 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:5) to obtain **5l** as yellow brown solid 113 mg (92%). FTIR (KBr): ʊ̆ = 3442, 3027, 3058, 2911, 1713, 1445, 1090, 1041, 881, 822, 796, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.08 (s, 1H), 7.95 – 7.94 (m, 1H), 7.73 – 7.68 (m, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.27 – 7.25 (m, 1H), 7.24 – 7.22 (m, 2H), 7.20 –7.17 (m, 1H), 7.09 – 7.08 (m, 2H), 6.98 – 6.94 (m, 1H), 6.91 – 6.89 (m, 1H), 5.87 (s, 1H), 4.99 (s, 1H), 3.13 – 3.05 (m, 1H), 2.58 – 2.51 (m, 2H), 2.41 – 2.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.1, 144.5, 141.6, 140.7, 138.7, 136.0, 135.3, 128.8, 128.0, 127.94, 127.91, 127.7, 126.6, 126.2, 126.1, 125.9, 125.8, 125.8, 125.7, 125.5, 124.3, 120.3, 119.4, 118.2, 112.9, 112.8, 65.3, 60.7, 43.9, 30.7 ppm. HRMS (ESI) exact mass calculated for $C_{30}H_{24}BrN_2^+$($[M+H]^+$): 493.1097, found, 493.1129.

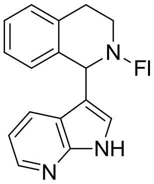


1-(5-bromo-1H-indol-3-yl)-2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinoline (5m):



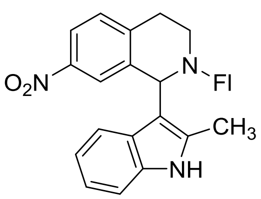
According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 μL) and 6-bromoindole (0.25 mmol, 1.0 equiv, 48.5 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:5) to obtain **5m** as yellow brown solid 112 mg (91%). FTIR (KBr): ʋ = 3442, 2951, 1713, 1445, 1417, 1211, 1041, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.15 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.51 – 7.49 (s, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.29 (m, 1H), 7.25 – 7.19 (m, 2H), 7.17 – 7.14 (m, 1H), 7.08 – 7.07 (m, 2H), 6.98 – 6.94 (m, 1H), 6.90 – 6.88 (m, 1H), 5.89 (s, 1H), 5.02 (s, 1H), 3.11 – 3.03 (m, 1H), 2.59 – 2.50 (m, 2H), 2.38 – 2.34 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 146.2, 144.6, 141.7, 140.6, 138.9, 138.3, 135.4, 128.7, 128.0, 127.92, 127.91, 127.6, 126.6, 126.12, 126.10, 125.8, 125.7, 125.4, 125.2, 123.0, 122.9, 120.4, 119.3, 118.7, 116.2, 114.3, 65.2, 60.7, 43.8, 30.8 ppm. HRMS (ESI) exact mass calculated for $C_{30}H_{24}BrN_2^+$ ($[M+H]^+$): 491.1117, found, 491.1121.

2-(9H-fluoren-9-yl)-1-(1H-pyrrolo[2,3-b]pyridin-3-yl)-1,2,3,4-tetrahydroisoquinoline (5n):



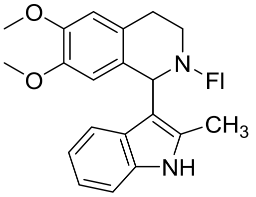
According to general procedure II: 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 μL) and 7-azaindole (0.25 mmol, 1.0 equiv, 29.5 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:2) to obtain **5n** as yellow solid 90 mg (82%). FTIR (KBr): ʋ = 2895, 2814, 1582, 1446, 1418, 1120, 773, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.20 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.39 – 7.21 (m, 3H), 7.19 (s, 1H), 7.13 – 7.11 (m, 2H), 7.02 – 7.01(m, 2H), 6.97 – 6.94 (m, 1H), 6.92 – 6.87 (m, 1H), 6.85 – 6.83 (m, 1H), 5.81 (s, 1H), 4.97 (s, 1H), 3.05 – 2.96 (m, 1H), 2.56 – 2.49 (m, 2H), 2.35 – 2.31 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.0, 146.1, 144.6, 143.4, 141.6, 140.7, 138.8, 135.4, 130.2, 128.7, 128.2, 128.0, 127.9, 127.5, 126.6, 126.2, 126.1, 125.8, 125.5, 125.3, 120.4, 119.4, 119.0, 117.1, 116.0, 65.3, 61.0, 43.9, 30.8 ppm. HRMS (ESI) exact mass calculated for $C_{29}H_{24}N_5^+$ ($[M+H]^+$): 414.1965, found, 414.1964.

2-(9H-fluoren-9-yl)-1-(2-methyl-1H-indol-3-yl)-7-nitro-1,2,3,4-tetrahydroisoquinoline (5o):

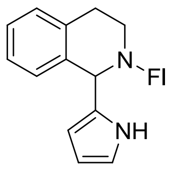


According to general procedure I, 9-fluorenone imine (0.18 mmol, 1.2 equiv, 32 mg), 7-nitro-1,2,3,4-tetrahydroisoquinoline (0.23 mmol, 1.5 equiv,32 mg) and 2-methylindole (0.15 mmol, 1.0 equiv, 20 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:15) to obtain **5b** as brown solid (71 %, 51 mg). FTIR (KBr): ῠ = 3411, 2957, 2924, 2853, 1518, 1304, 740 cm^{-1}. FTIR (KBr): ῠ = 3411, 2957, 2924, 2853, 1518, 1304, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.90 (s, 1H), 7.82 – 7.79 (m, 1H), 7.71 – 7.69 (m, 1H), 7.63 – 7.61 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.22 – 7.15 (m, 3H), 7.12 – 7.08 (m, 2H), 7.04 – 7.02 (m, 1H), 6.97 – 6.93 (m, 1H), 5.88 (s, 1H), 4.93 (s, 1H), 3.07 – 3.01 (m, 1H), 2.59 (s, 3H), 2.54 – 2.47 (m, 2H), 2.31– 2.27 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.6, 146.0, 144.3, 143.5, 141.7, 141.5, 140.6, 136.1, 134.4, 129.6, 128.1, 128.0, 127.6, 126.7, 126.0, 125.8, 123.5, 121.9, 121.0, 120.5, 119.7, 119.4, 112.4, 110.7, 65.2, 59.5, 43.4, 31.2, 12.7 ppm. (Total count of 13C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{31}H_{26}N_3O_2^+$ ($[M+H]^+$): 472.2020, found, 472.2034.

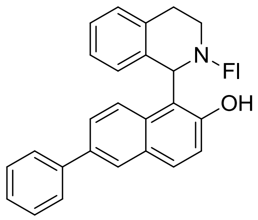
2-(9H-fluoren-9-yl)-6,7-dimethoxy-1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline



(5p): According to general procedure I, 9-fluorenone imine (0.18 mmol, 1.2 equiv, 32 mg), 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (0.23 mmol, 1.5 equiv, 43 mg) and 2-methylindole (0.15 mmol, 1.0 equiv, 20 mg) were reacted for 48h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:5) to obtain **5b** as light yellow solid (73 %, 53 mg). FTIR (KBr): ῠ = 3348, 3296, 2923, 2851, 2807, 1506, 1460, 1445, 1253, 1133, 1025, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.20 – 7.18 (m, 2H), 7.17 – 7.15 (m, 1H), 7.12 – 7.10 (m, 1H), 7.03 – 6.96 (m, 2H), 6.48 (s, 1H), 6.27 (s, 1H), 5.88 (s, 1H), 4.93 (s, 1H), 3.74 (s, 3H), 3.47 (s, 3H), 2.99 – 2.89 (m, 1H), 2.53 (s, 3H), 2.49 – 2.48 (m, 1H), 2.41 – 2.37 (m, 1H), 2.24 – 2.21 (m, 1H). ^{13}C ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.4, 147.3, 146.7, 144.9, 141.7, 140.5, 135.9, 133.8, 131.6, 127.8, 127.8, 127.7, 127.5, 126.5, 126.0, 125.9, 121.4, 120.3, 119.5, 119.2, 113.9, 111.3, 111.1, 110.3, 65.5, 58.9, 56.1, 56.0, 44.2, 30.5, 12.7 ppm (Total count of 13C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{33}H_{31}N_2O_2^+$ ([M+H]$^+$): 487.2380, found, 487.2386.

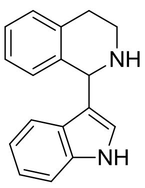


2-(9H-fluoren-9-yl)-1-(1H-pyrrol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5q): According to general procedure I, 9-fluorenone imine (0.3 mmol, 1.2 equiv, 54 mg), 1,2,3,4-tetrahydroisoquinoline (0.75 mmol, 3 equiv, 96 μL) and pyrrole (0.25 mmol, 1.0 equiv, 18 μL), in neat condition were reacted for 24h. After completion of the reaction, the reaction mixture was dissolved in methanol and solution mixture was evaporated under reduce pressure and residue was purified by SiO_2 column chromatography (Ethyl acetate: hexane; 1:20) to obtain **5o** as yellow solid 48 mg (53%). FTIR (KBr): ʊ̆ = 3398, 3060, 1713, 1428, 1287, 1110, 772, 748 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1H), 7.77 – 7.70 (m, 2H), 7.69 – 7.65(m, 1H), 7.46 – 7.44 (m, 1H), 7.35 – 7.33 (m, 2H), 7.29 – 7.28 (m, 1H), 7.24 – 7.23 (m, 1H), 7.13 – 7.03 (m, 3H), 6.98 – 6.96 (m, 1H), 6.80 (s, 1H), 6.56 (s, 1H), 6.18 (s, 1H), 5.75 (s, 1H), 4.96 (s, 1H), 2.94 – 2.85 (m, 1H), 2.51 – 2.45 (m, 2H), 2.32 – 2.28 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.8, 144.2, 141.6, 140.9, 137.9, 135.2, 132.4, 128.8, 128.4, 128.1, 128.0, 127.5, 126.8, 126.5, 126.4, 126.0, 125.0, 120.4, 119.6, 118.6, 110.5, 107.7, 65.3, 61.2, 43.3, 30.3 ppm. HRMS (ESI) exact mass calculated for $C_{26}H_{23}N_2^+$ ([M+H]$^+$): 363.1856, found, 363.1857.

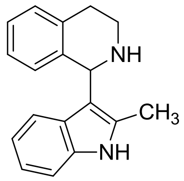


1-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-6-phenylnaphthalen-2-ol (9): Phenyl boronic acid (0.26 mmol, 1.5 equiv, 31 mg), $Ba(OH)_{2.}8H_2O$ (0.23 mmol, 1.2 equiv, 40mg) $Pd(PPh_3)_4$ (0.01 mmol, 0.019 equiv, 11 mg), 1,4 dioxane (1.3 mL), H_2O (0.4 mL) and 1-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-6-bromonaphthalen-2-ol, **4c** (0.193 mmol, 1equiv, 100 mg) were refluxed for 24 h under inert atmosphere. After completion of the reaction 1,4 dioxane was evaporated under reduce pressure. The resulting mass was diluted with DCM (30 mL) and the mixture was washed with 1M HCl (3×20 mL) and then with brine (2×20 mL). Combined organic layers were dried over sodium sulfate and concentrated under vacuum to give crude product which was further was purified by SiO_2 column chromatography (ethyl acetate: hexane; 1:2) to afford desired product **9** as light yellow solid 82 mg (82%). FTIR (KBr): ῠ = 2959, 2924, 1493, 1448, 1261, 1079, 812, 739 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$) δ = 11.78 (s, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 1.2 Hz, 1H), 7.97 – 7.95 (m, 1H), 7.86 – 7.83 (m, 3H), 7.77 – 7.76 (m, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 6.6 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.40 – 7.35 (m, 4H), 7.29 – 7.27 (m, 1H), 7.23 (s, 1H), 7.11 – 7.09 (m, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.95 – 6.94 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.68 (s, 1H), 5.03 (s, 1H), 3.10 – 3.05 (m, 1H), 2.65 – 2.62 (m, 1H), 2.59 – 2.55 (m, 1H), 2.49 – 2.47 (m, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ = 155.9, 143.9, 142.1, 141.5, 141.1, 141.0, 136.5, 135.7, 134.3, 133.6, 130.6, 129.3, 129.1, 128.8, 128.7, 128.6, 128.3, 127.9, 127.37, 127.36, 127.29, 127.27, 127.18, 126.9, 126.6, 126.4, 125.9, 122.1, 120.60, 120.59, 119.7, 118.0, 65.3, 60.8, 43.2, 29.9 ppm. HRMS (ESI) exact mass calculated for $C_{38}H_{30}NO^+$ ([M+H]$^+$): 516.2322, found, 516.2322.

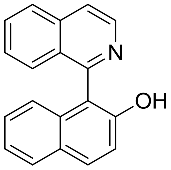
1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (10): 2-(9H-fluoren-9-yl)-1-(1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline, (**5a)** (0.18 mmol, 1 equiv, 75 mg) was dissolved in ethyl acetate and methanol (3:1, v/v). Palladium (10%) on charcoal (0.18 mmol, 1 equiv, 20 mg) was added to it. Then the flask was evacuated and re-filled with hydrogen. The process was repeated three times. Then, the reaction mixture was kept on shaking at 25 PSI of hydrogen for 48 h. After the completion of the reaction, the reaction mixture was filtered through a pad of celite, and the celite pad was washed successively with methanol (3×5 mL) and of ethyl acetate (3×5 mL). The filtrate was concentrated and the crude product was purified (preparative TLC, ethyl acetate: hexane; 2:1) to afford desired product **10** as brown gum 25 mg (55%). FTIR (KBr): ῠ = 2923, 2855, 1622, 1452, 1263, 1099, 742 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$) δ = 8.19 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.07 – 7.05 (m, 1H), 7.04 – 7.01 (m, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.93 – 6.92 (m, 1H), 5.51 (s, 1H), 3.29 – 3.25 (m, 1H), 3.12 – 3.08 (m, 1H), 3.03 – 2.98 (m, 1H), 2.92 – 2.88 (m, 1H).^{13}C NMR (151 MHz, CDCl$_3$) δ = 138.1, 136.7, 135.1, 129.1, 128.1, 126.5, 125.9, 124.3, 122.3, 119.9, 119.6, 119.2, 111.5, 53.9, 41.8, 29.7 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{17}N_2^+$ ([M+H]$^+$): 249.1386, found, 249.1387.



1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (11): 2-(9H-fluoren-9-yl)-1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (**5b**) (0.23 mmol, 1 equiv, 100 mg) was dissolved in ethyl acetate and methanol (3:1, v/v). Palladium (10%) on charcoal (0.23 mmol, 1 equiv, 25 mg) was added to it.

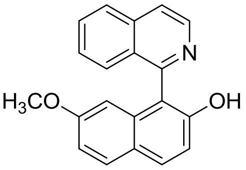


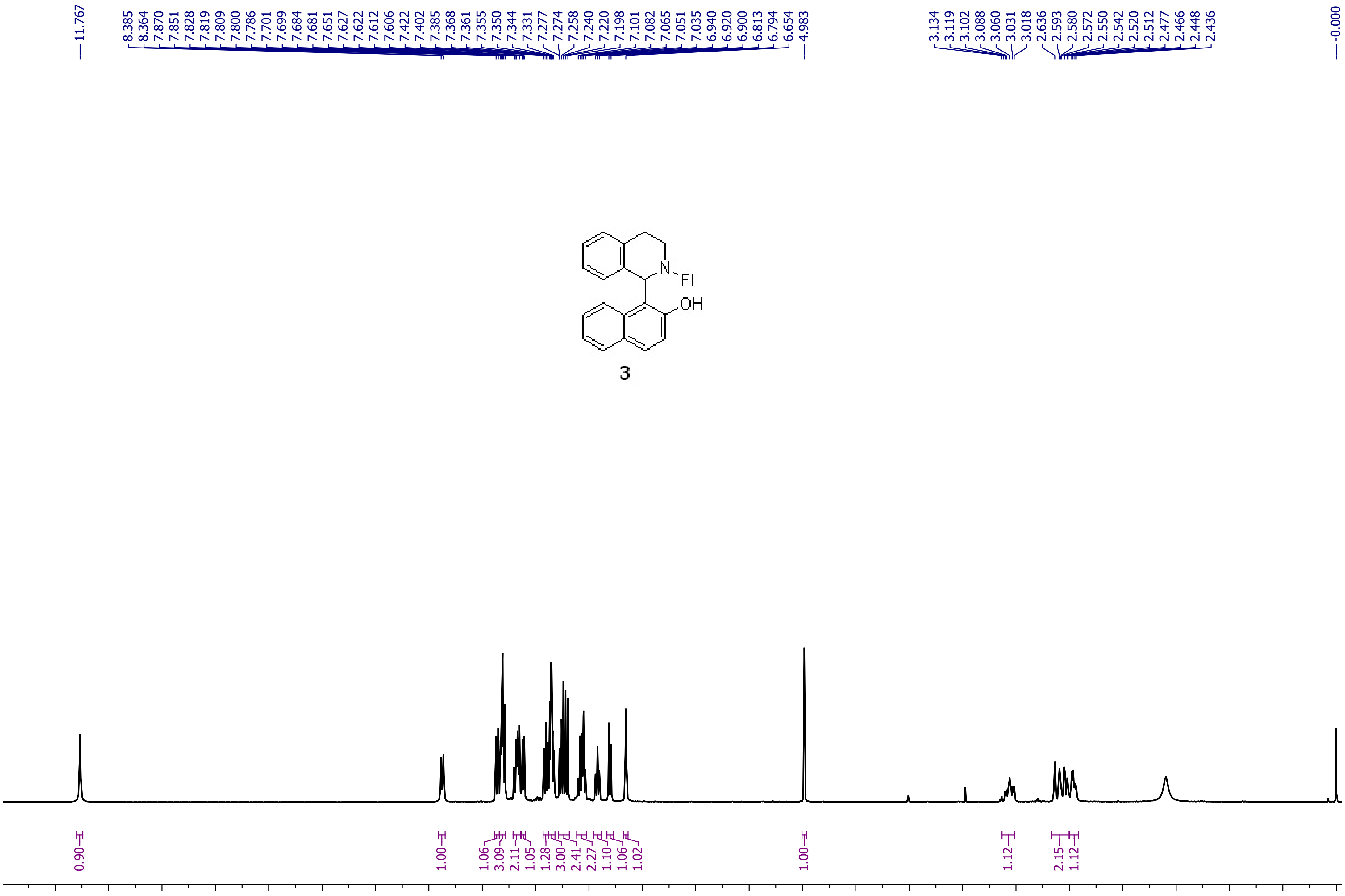
Then the flask was evacuated and re-filled with hydrogen. The process was repeated three times. Then, the reaction mixture was kept on shaking at 25 PSI of hydrogen for 48 hours. After the completion of the reaction, the reaction mixture was filtered through a pad of celite, and the celite pad was washed successively with methanol (3×5 mL) and of ethyl acetate (3×5 mL). The filtrate was concentrated and the crude product was purified (preparative TLC, ethyl acetate: hexane; 2:1) to afford desired product **11** as brown gum 35 mg (57%). FTIR (KBr): ʊ̆ = 3604, 3298, 3228, 2922, 1622, 1460, 1428, 1261, 738 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$) δ = 7.97 (s, 1H), 7.25 – 7.23 (m, 1H), 7.17 – 7.16 (m, 1H), 7.13 – 7.09 (m, 2H), 7.06 – 7.03 (m, 1H), 6.99 – 6.96 (m, 1H), 6.93 – 6.89 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.42 (s, 1H), 3.40 – 3.37 (m, 1H), 3.20 – 3.11 (m, 2H), 2.88 – 2.85 (m, 1H), 2.34 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ = 139.0, 135.5, 135.3, 133.2, 129.0, 127.6, 126.2, 126.1, 121.1, 119.5, 119.2, 114.4, 110.4, 53.9, 43.8, 30.3, 12.3 ppm (Total count of ^{13}C is less than expected due to the merging of signals in the aromatic region). HRMS (ESI) exact mass calculated for $C_{18}H_{19}N_2^+$ ([M+H]$^+$): 263.1543, found, 263.1543.



1-(isoquinolin-1-yl)naphthalen-2-ol(12): 1-(2-(9H-fluoren-9-yl)-1,2,3,4 tetrahydroisoquinolin-1-yl)naphthalen-2-ol, (**3**) (0.17 mmol, 1 equiv, 75 mg) was dissolved in 3 mL mesitylene. Palladium (10%) on charcoal (0.34 mmol, 2 equiv, 36 mg) was added to it. Then, the reaction mixture was placed and refluxed for 24 h. After the completion of the reaction, the reaction mixture was filtered through a pad of celite, and the celite pad was washed successively with methanol (3×5 mL) and of ethyl acetate (3×5 mL). The filtrate was concentrated and the crude product was purified SiO$_2$ column chromatography (ethyl acetate: hexane; 1:2) to afford desired product **12** as brown solid 44 mg (96%). FTIR (KBr): ʊ̆ = 3050, 1620, 1582, 1558, 1434, 1350, 1276, 823, 747 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.59 (d, *J* = 5.6 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.78 – 7.76 (m, 2H), 7.71 – 7.69 (m,1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.33 – 7.29 (m, 1H), 7.21 – 7.18 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ = 157.6, 153.6, 141.8, 137.3, 133.3, 131.2, 131.0, 129.0, 128.4, 128.4, 128.0, 127.7, 127.3, 126.6, 125.1, 123.4, 121.1, 119.4, 117.5 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{14}NO^+$ ([M+H]$^+$): 272.1070, found, 272.1097.

1-(isoquinolin-1-yl)-7-methoxynaphthalen-2-ol (13): 1-(2-(9H-fluoren-9-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-7-methoxynaphthalen-2-ol, (**4a**) (0.16 mmol, 1 equiv, 75 mg) was dissolved in 3 mL mesitylene. Palladium (10%) on charcoal (0.32 mmol, 2 equiv, 34 mg) was added to it. Then, the reaction mixture was placed and refluxed for 24 h. After the completion of the reaction, the reaction mixture was filtered through a pad of celite, and the celite pad was washed successively with methanol (3×5 mL) and of ethyl acetate (3×5 mL). The filtrate was concentrated and the crude product was purified SiO_2 column chromatography (ethyl acetate: hexane; 1:2) to afford desired product **13** as brown solid 41 mg (84%). FTIR (KBr): ῠ = 2952, 1623, 1588, 1348, 1223, 827 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.67 (d, *J* = 6.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.77 (m, 2H), 7.74 – 7.70 (m, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.17 (d, *J* = 9.0 Hz, 1H), 6.98 (dd, *J* = 9.0, 3.6 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 3.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.3, 157.7, 154.4, 141.9, 137.3, 134.4, 131.0, 131.0, 129.9, 128.6, 128.0, 127.5, 127.3, 124.4, 121.0, 116.8, 116.7, 115.5, 104.6, 55.1 ppm. HRMS (ESI) exact mass calculated for $C_{20}H_{16}NO_2^+$ ($[M+H]^+$): 302.1176, found, 302.1179.

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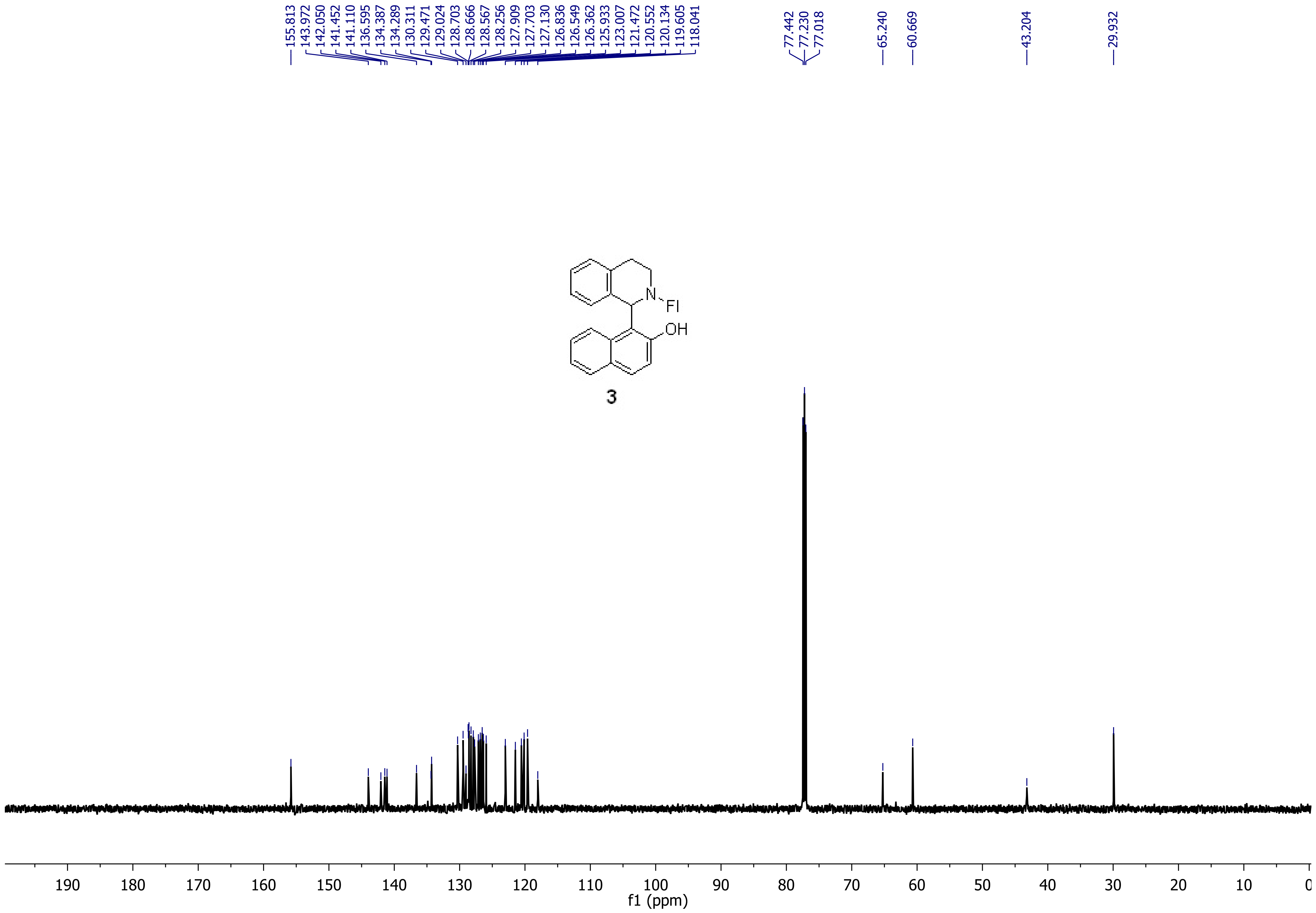
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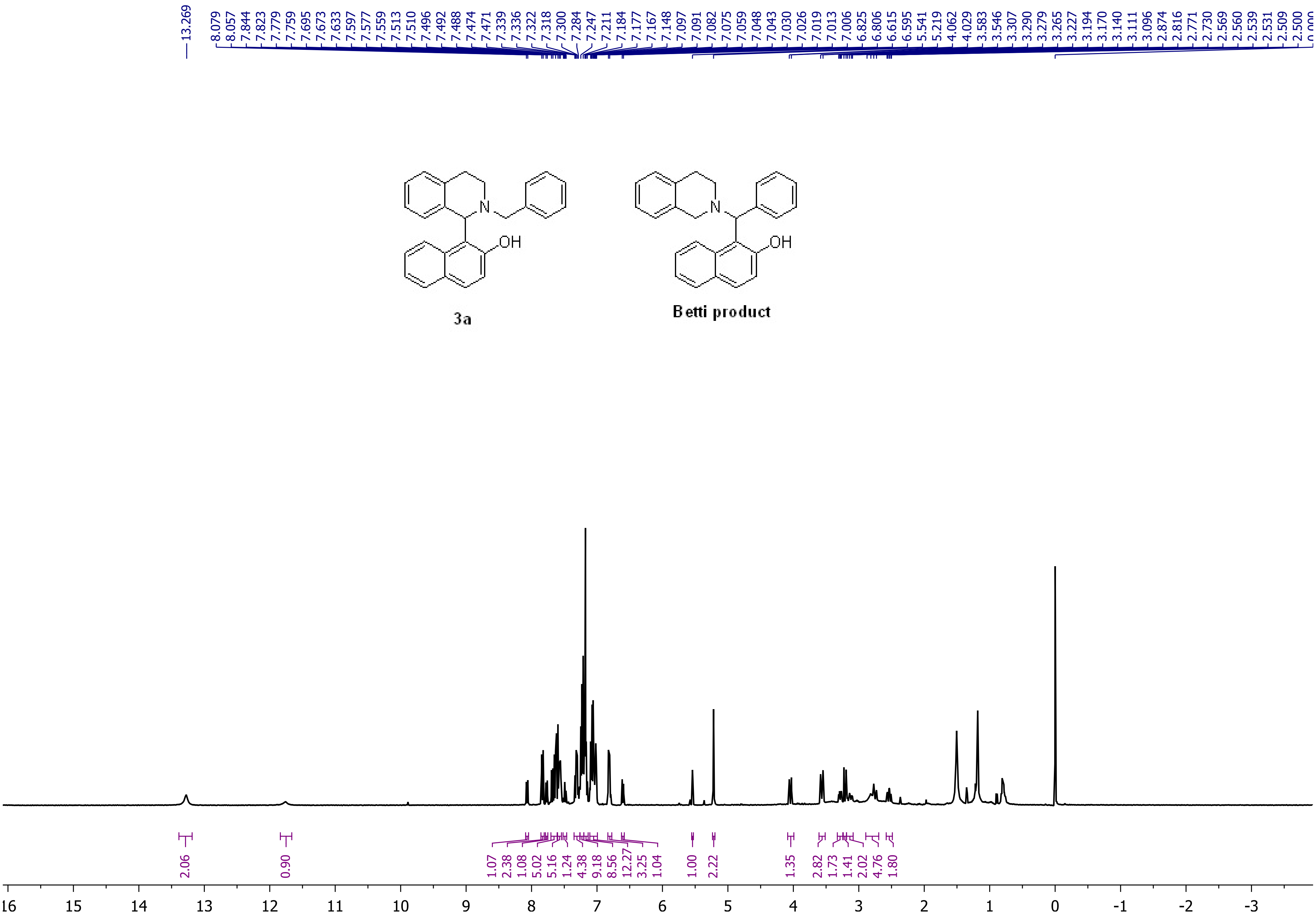
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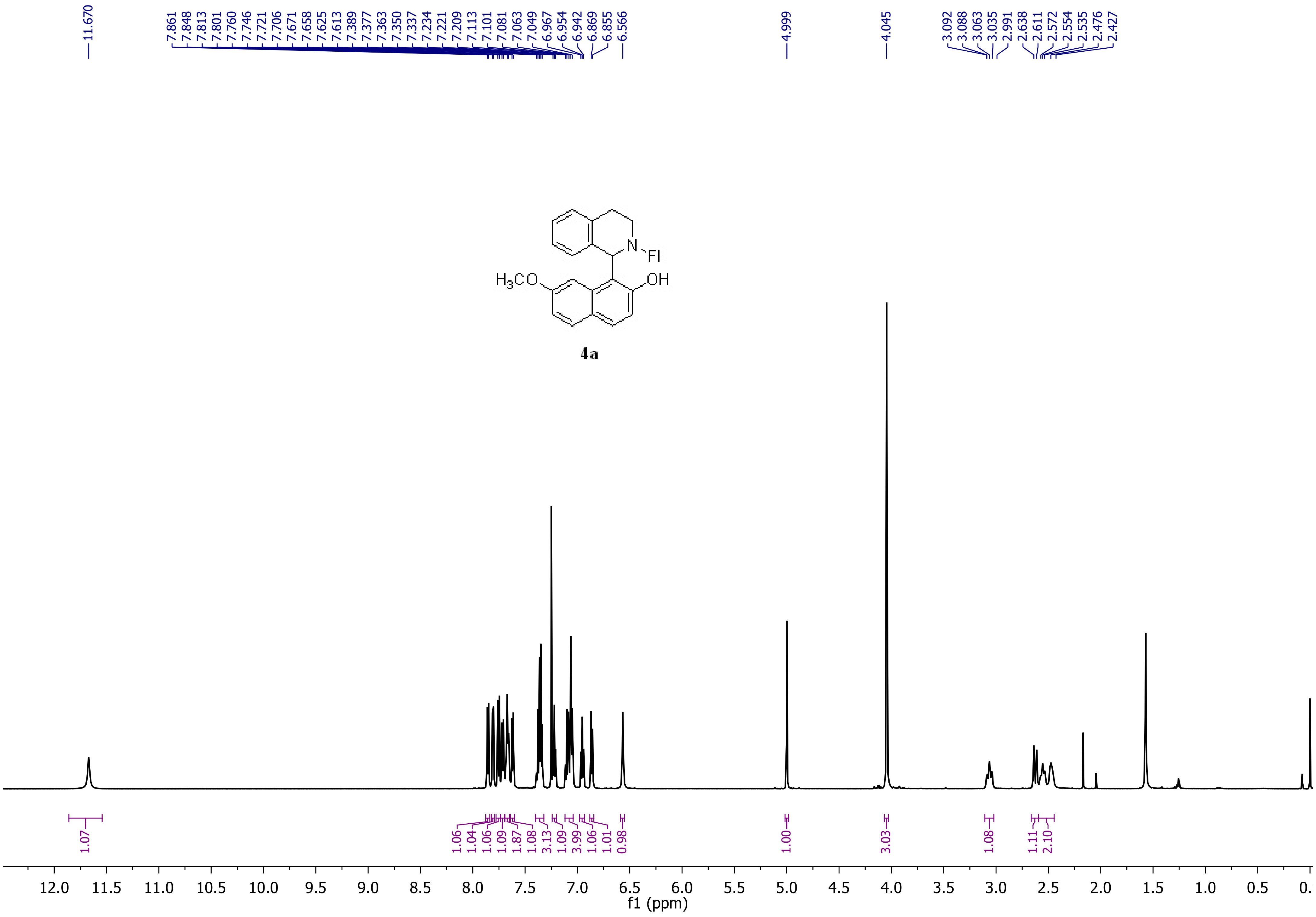

4a

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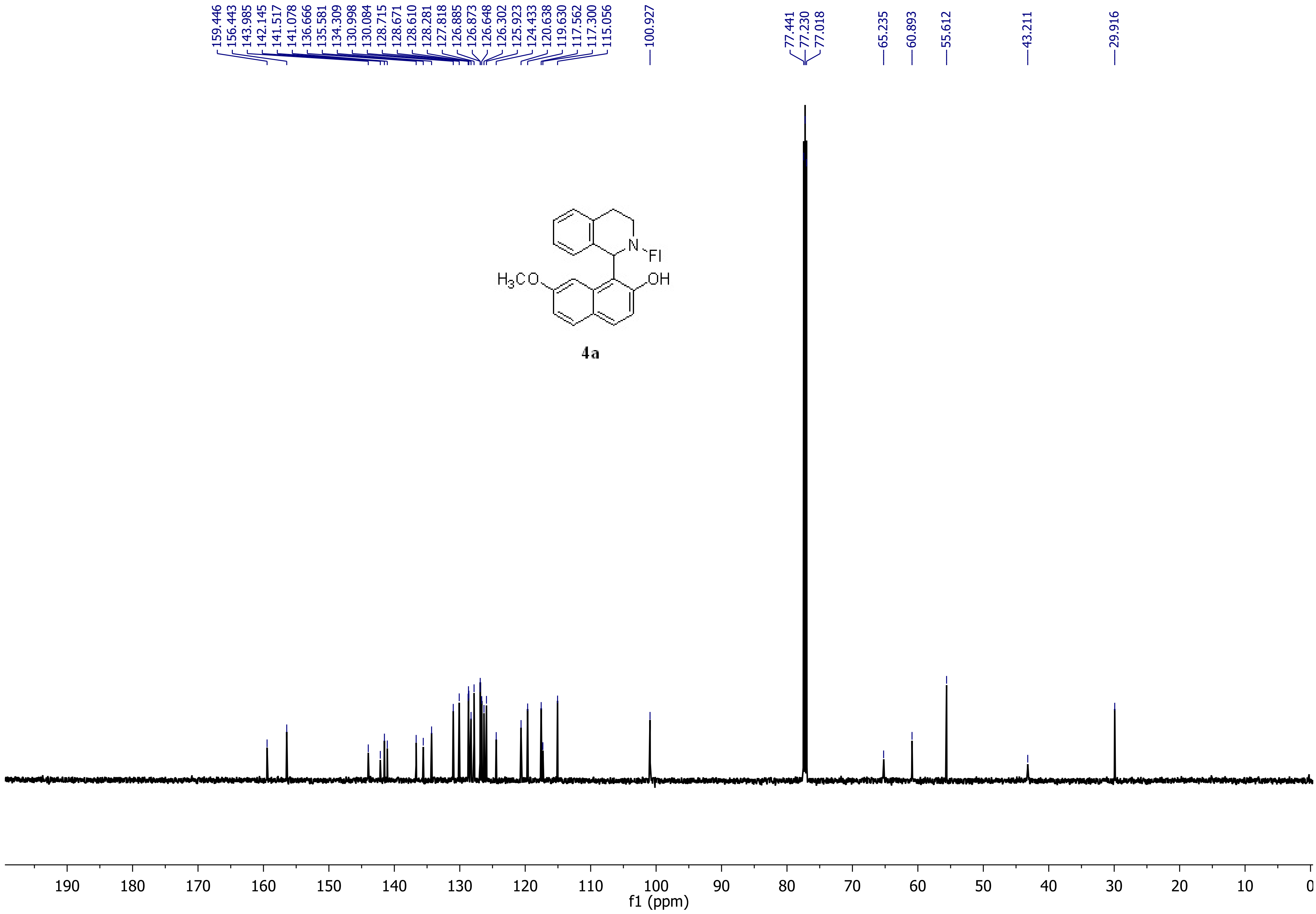
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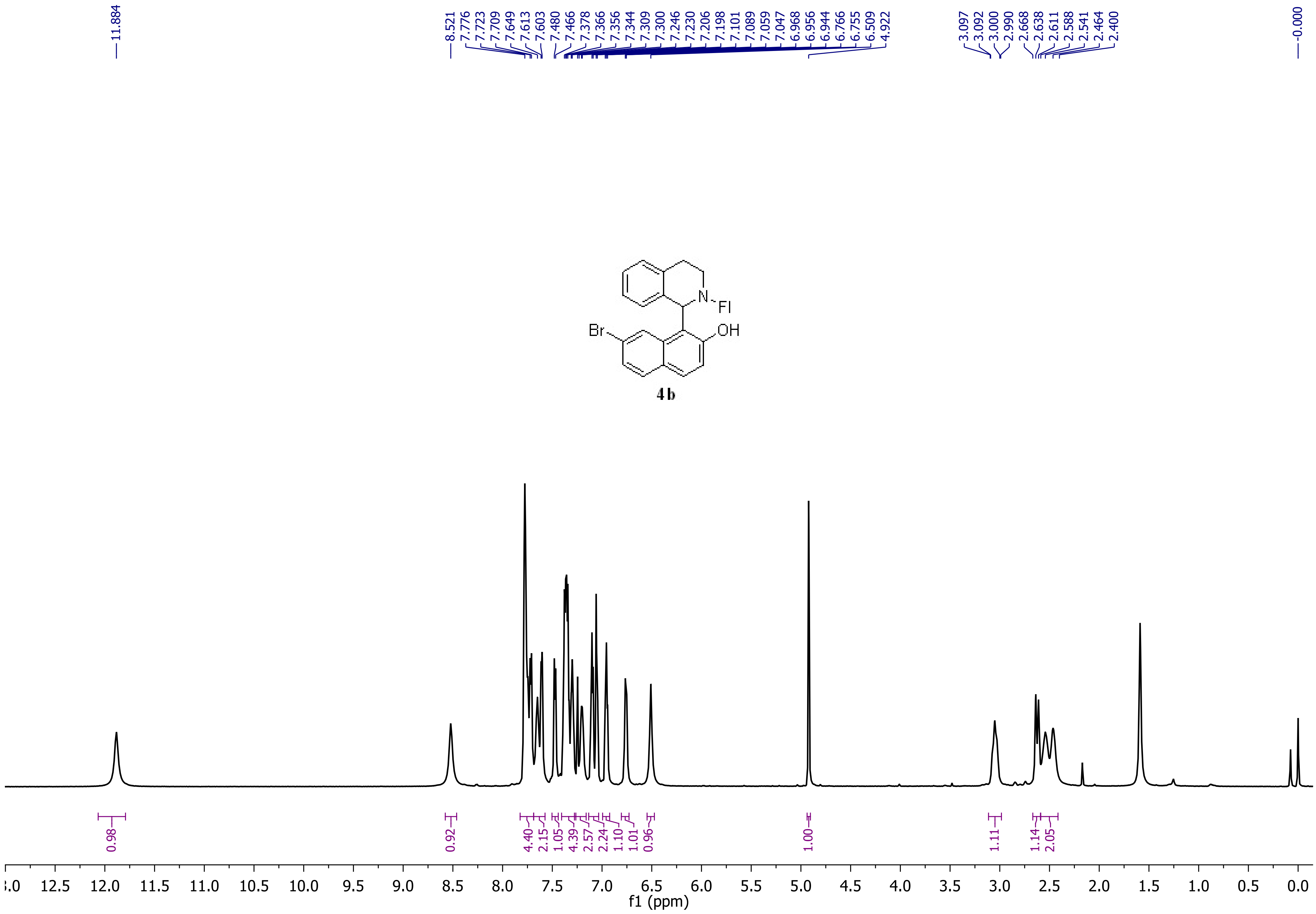
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Br
N
Fl
OH
0.98
0.92
4.40
2.15
1.05
4.39
2.57
2.24
1.10
1.01
0.96
1.00
1.11
1.14
2.05
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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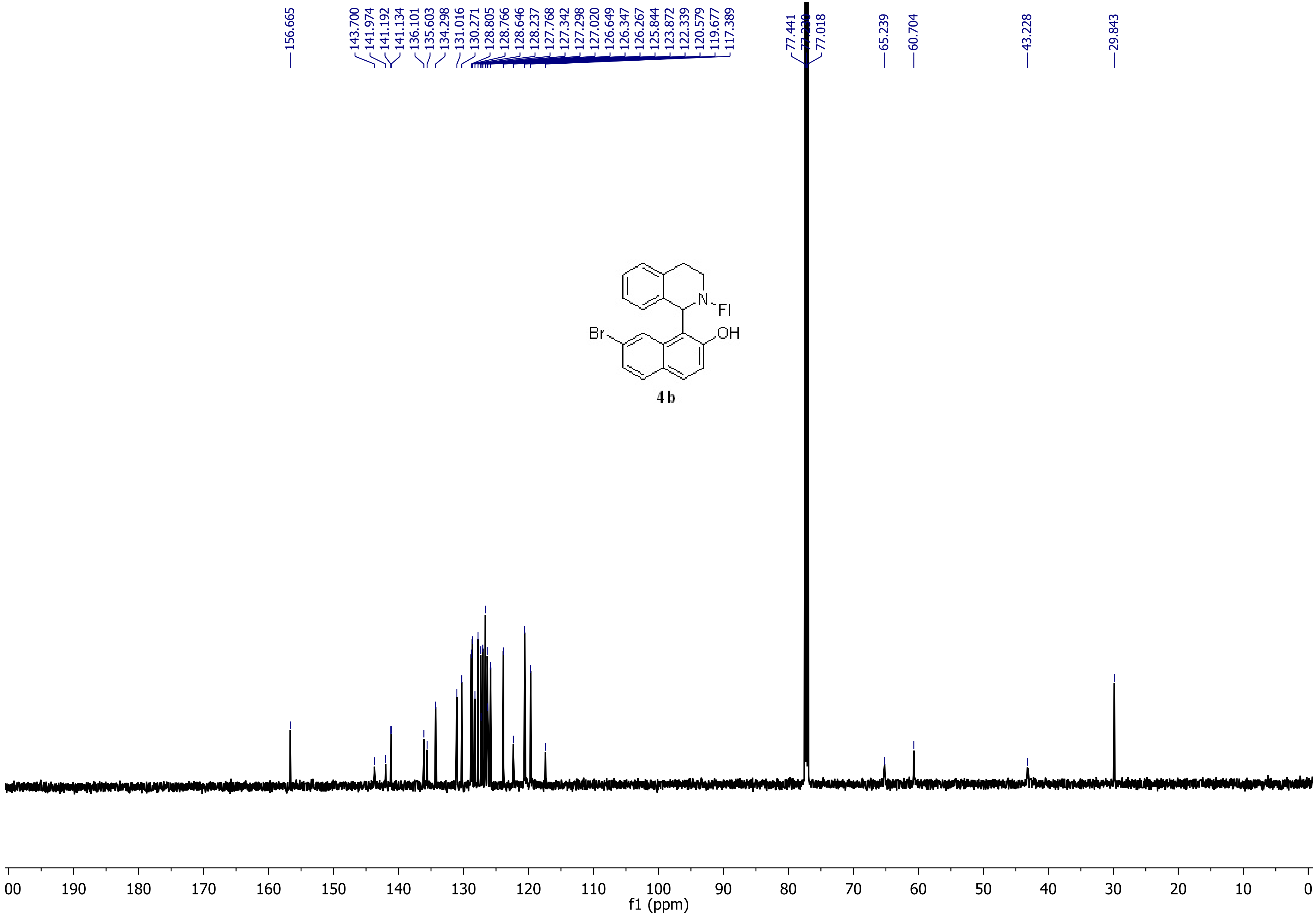
0.5
0.0
f1 (ppm)

4b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141.192
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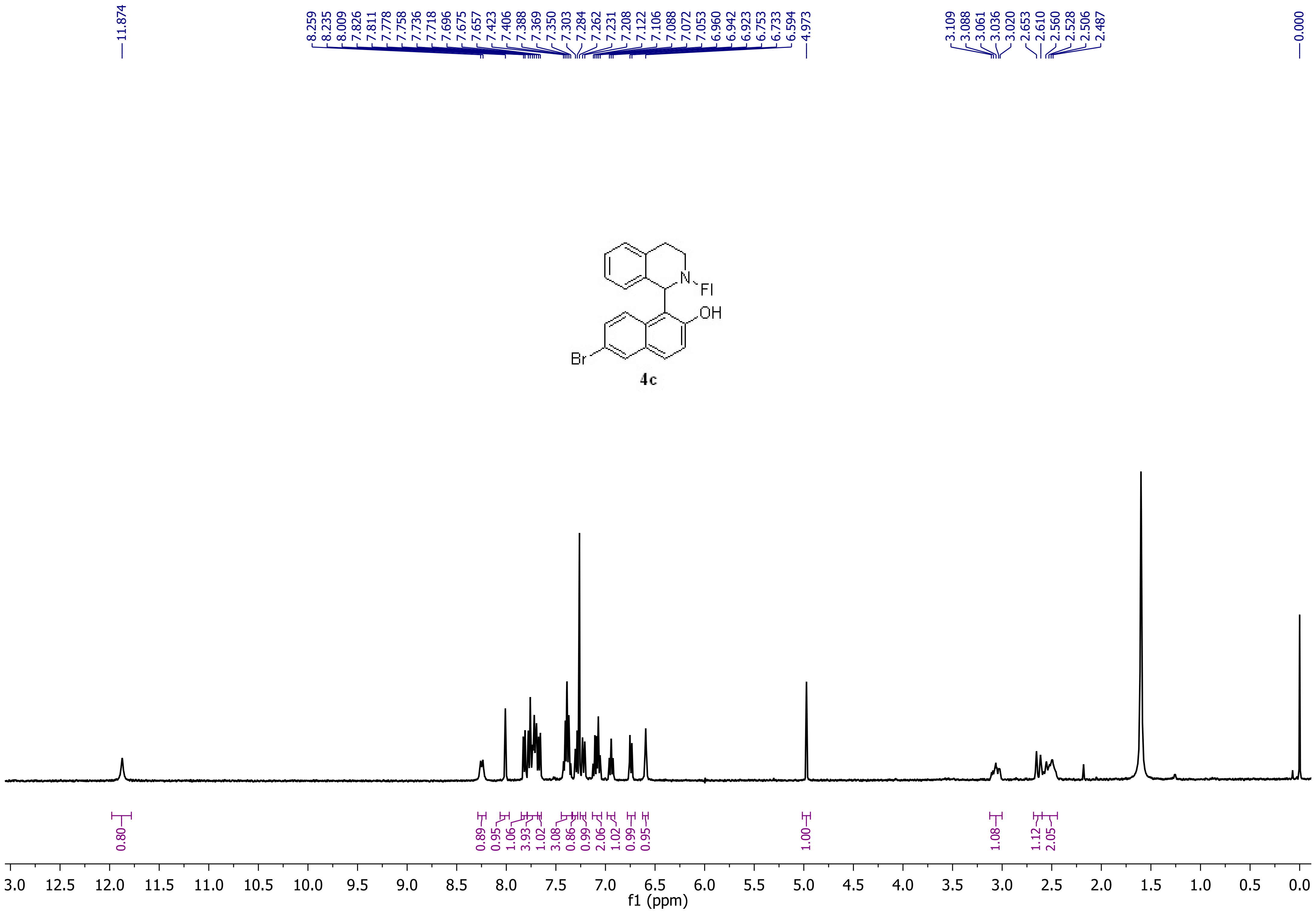
134.298
131.016
130.271
128.805
128.766
128.646
128.237
127.768
127.342
127.298
127.020
126.649
126.347
126.267
125.844
123.872
122.339
120.579
119.677
117.389
77.441
77.230
77.018
65.239
60.704
43.228
29.843
N
Fl
Br
OH
4b
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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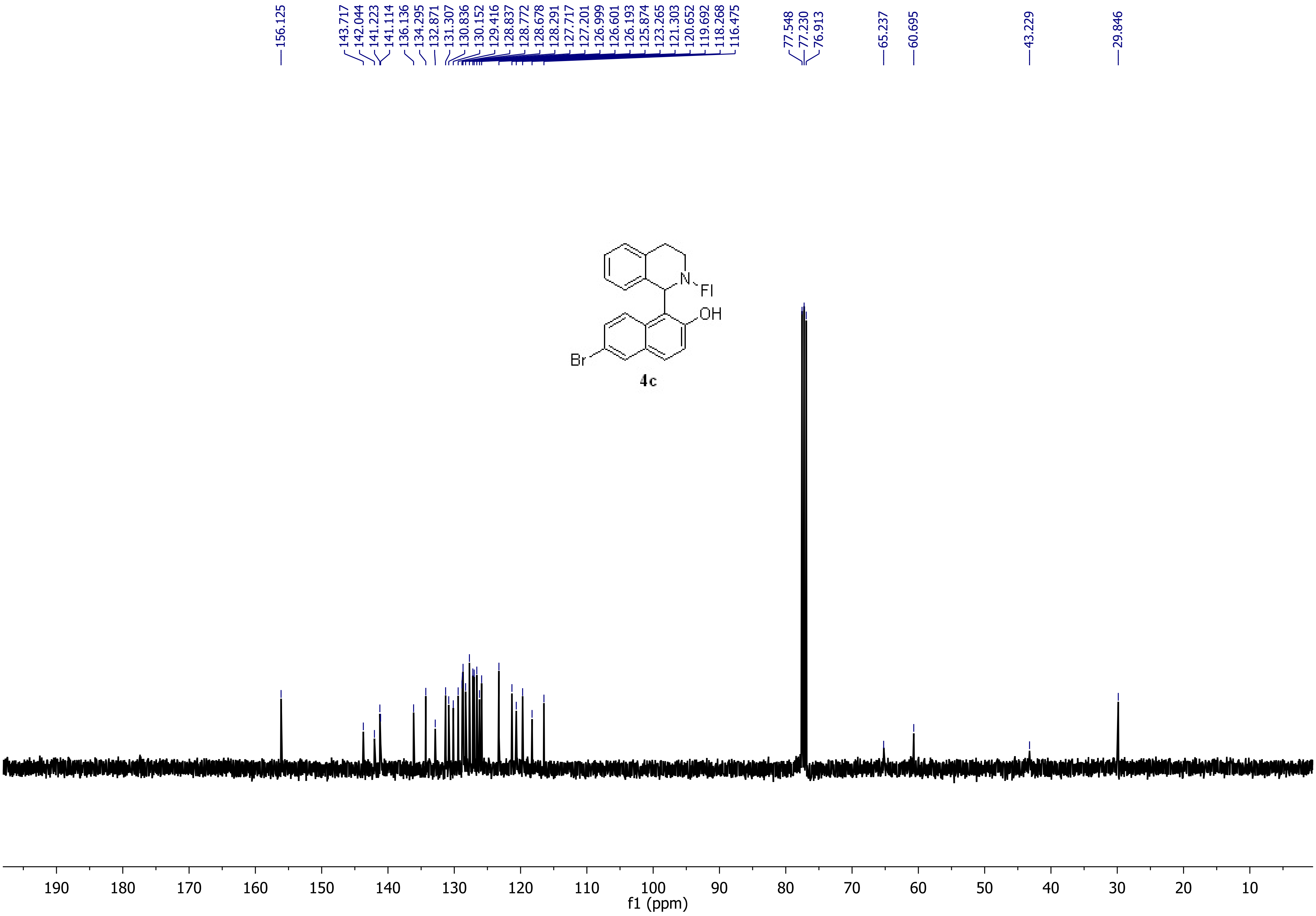
8.259
8.235
8.009
7.826
7.811
7.778
7.758
7.736
7.718
7.696
7.675
7.657
7.423
7.406
7.388
7.369
7.350
7.303
7.284
7.262
7.231
7.208
7.122
7.106
7.088
7.072
7.053
6.960
6.942
6.923
6.753
6.733
6.594
4.973
3.109
3.088
3.061
3.036
3.020
2.653
2.610
2.560
2.528
2.506
2.487
0.000
N
Fl
OH
Br
4c
0.80
0.89
0.95
1.06
3.93
1.02
3.08
0.86
0.99
2.06
1.02
0.99
0.95
1.00
1.08
1.12
2.05
3.0
12.5
12.0
11.5
11.0
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
f1 (ppm)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142.044
141.223
141.114
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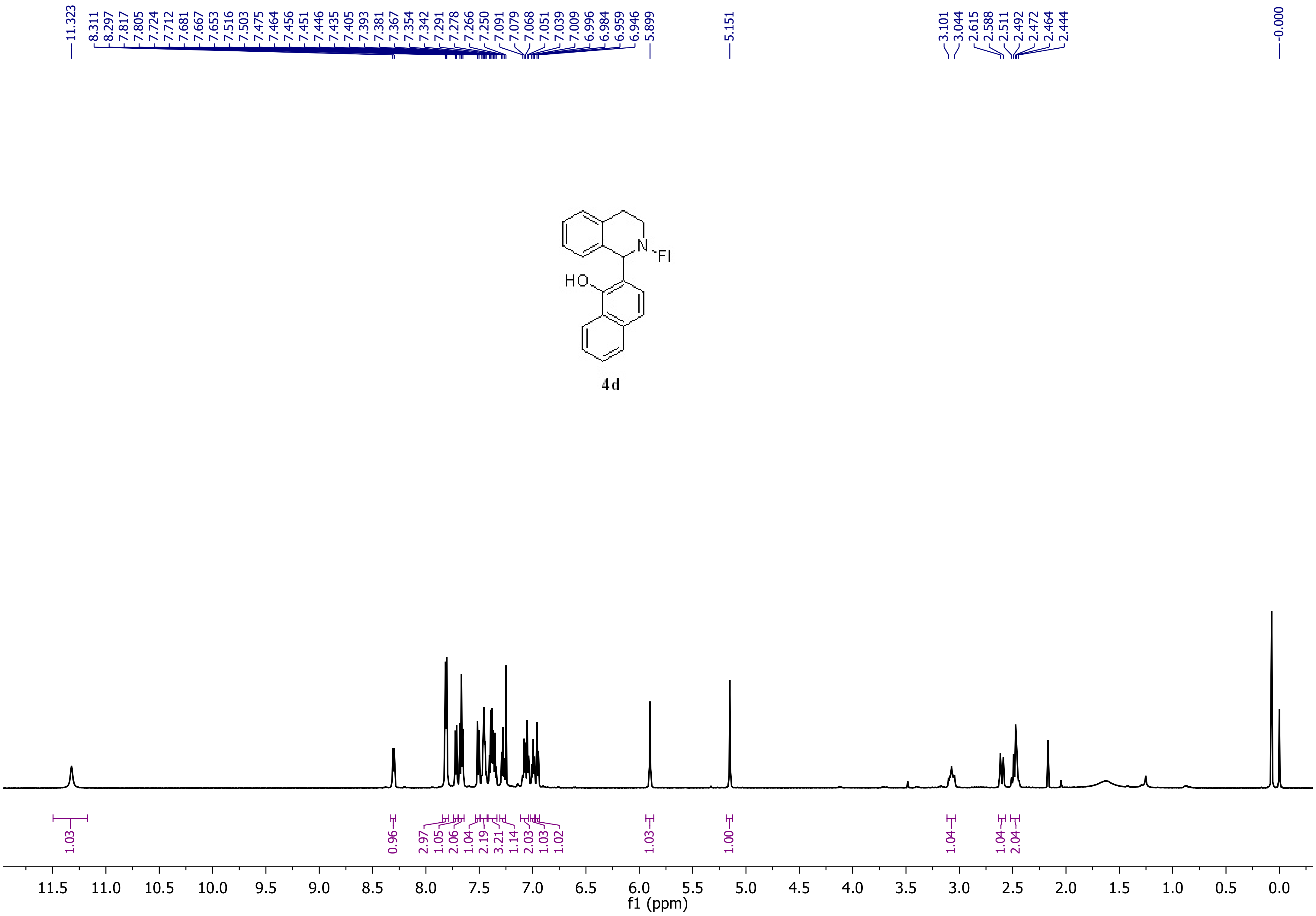
134.295
132.871
131.307
130.836
130.152
129.416
128.837
128.772
128.678
128.291
127.717
127.201
126.999
126.601
126.193
125.874
123.265
121.303
120.652
119.692
118.268
116.475
77.548
77.230
76.913
65.237
60.695
43.229
29.846
N
Fl
OH
Br
4c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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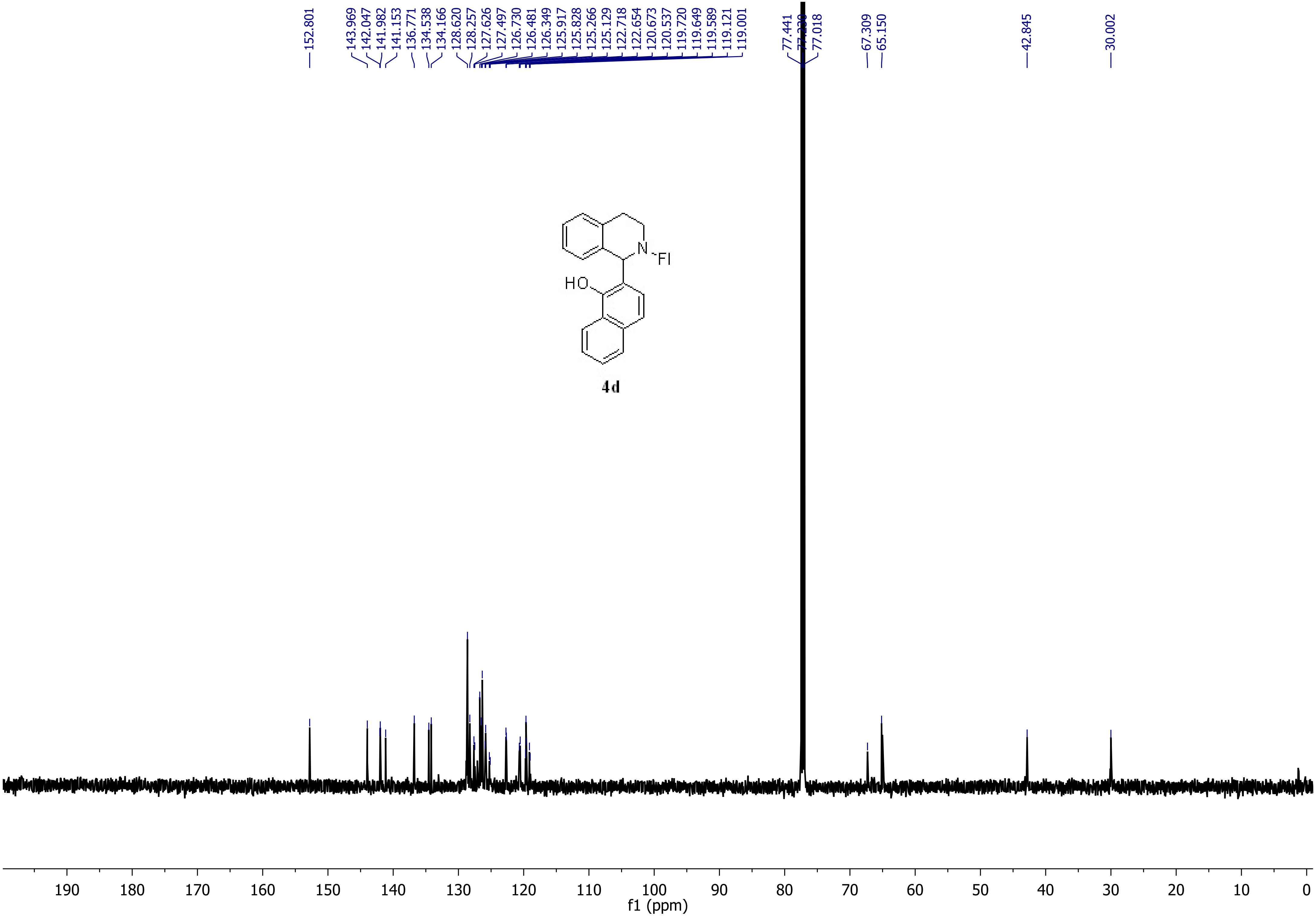
8.297
7.817
7.805
7.724
7.712
7.681
7.667
7.653
7.516
7.503
7.475
7.464
7.456
7.451
7.446
7.435
7.405
7.393
7.381
7.367
7.354
7.342
7.291
7.278
7.266
7.250
7.091
7.079
7.068
7.051
7.039
7.009
6.996
6.984
6.959
6.946
5.899
5.151
3.101
3.044
2.615
2.588
2.511
2.492
2.472
2.464
2.444
-0.000
HO
N
Fl
4d
1.03
0.96
2.97
1.05
2.06
1.04
2.19
3.21
1.14
2.03
1.03
1.02
1.03
1.00
1.04
1.04
2.04
11.5
11.0
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
f1 (ppm)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143.969
142.047
141.982
141.153
136.771
134.538
134.166
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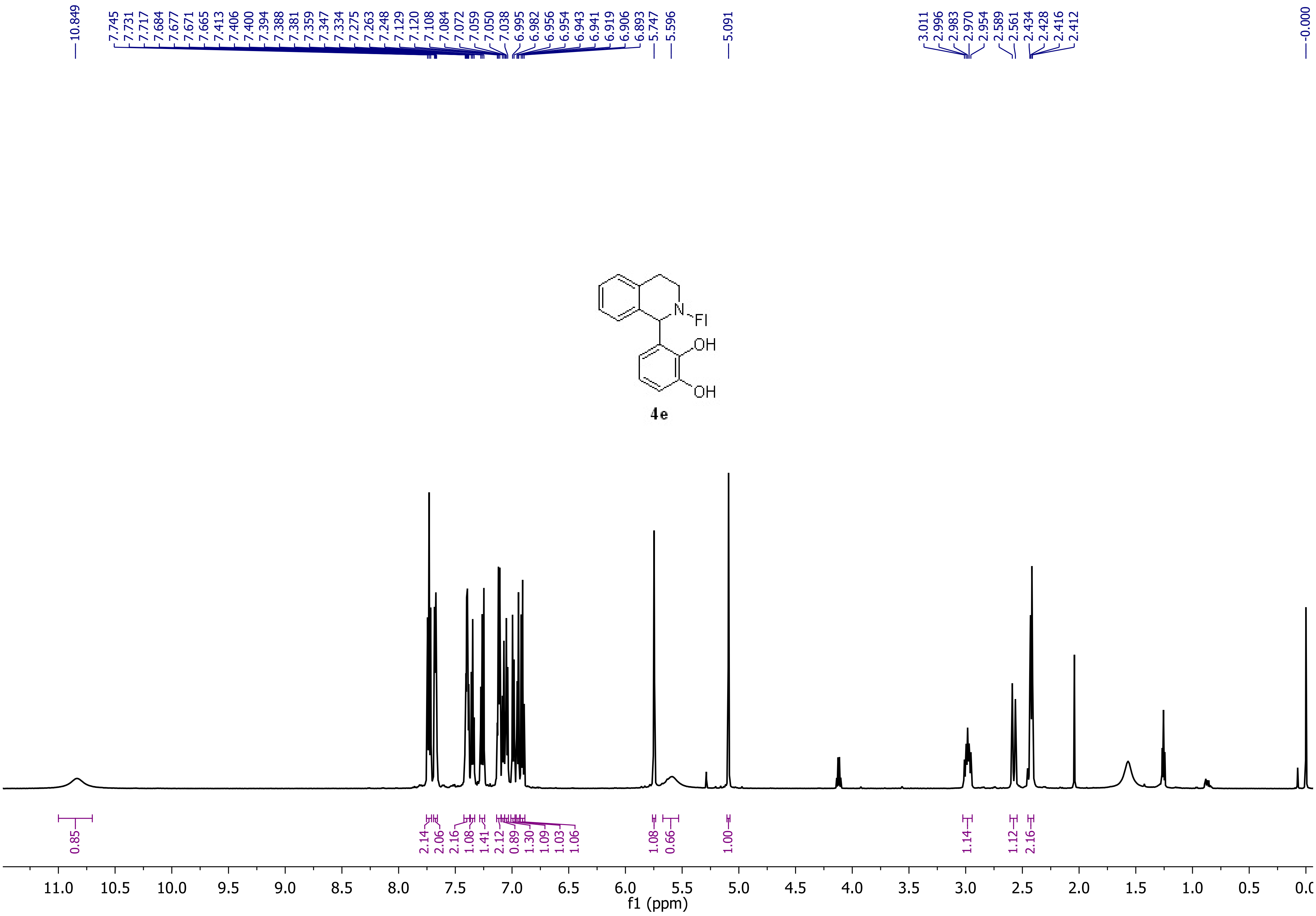
128.257
127.626
127.497
126.730
126.481
126.349
125.917
125.828
125.266
125.129
122.718
122.654
120.673
120.537
119.720
119.649
119.589
119.121
119.001
77.441
77.230
77.018
67.309
65.150
42.845
30.002
HO
N
Fl
4d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.731
7.717
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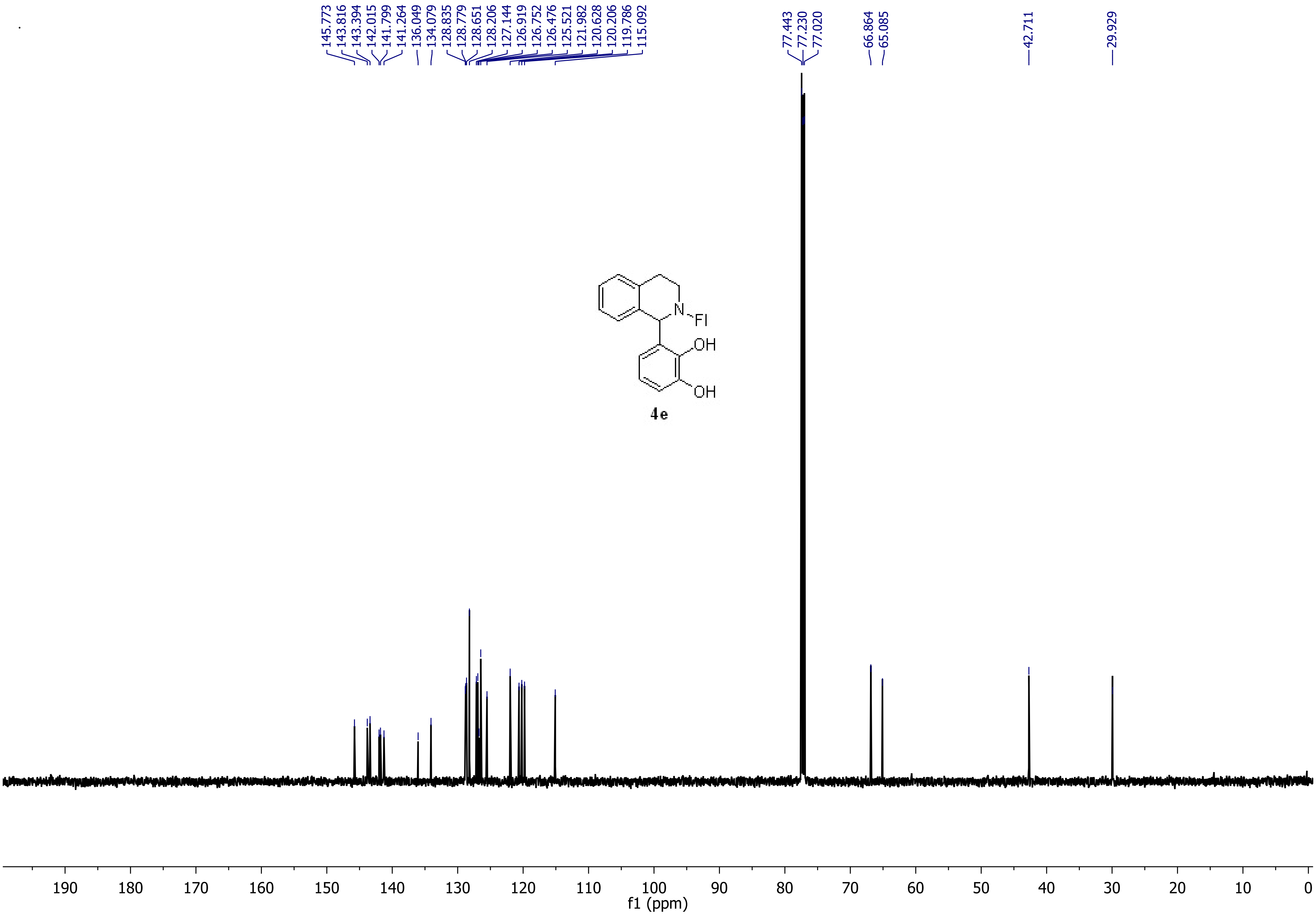
7.677
7.671
7.665
7.413
7.406
7.400
7.394
7.388
7.381
7.359
7.347
7.334
7.275
7.263
7.248
7.129
7.120
7.108
7.084
7.072
7.059
7.050
7.038
6.995
6.982
6.956
6.954
6.943
6.941
6.919
6.906
6.893
5.747
5.596
5.091
3.011
2.996
2.983
2.970
2.954
2.589
2.561
2.434
2.428
2.416
2.412
-0.000
N
Fl
OH
OH
0.85
2.14
2.06
2.16
1.08
1.41
2.12
0.89
1.30
1.09
1.03
1.06
1.08
0.66
1.00
1.14
1.12
2.16
11.0
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
f1 (ppm)

4e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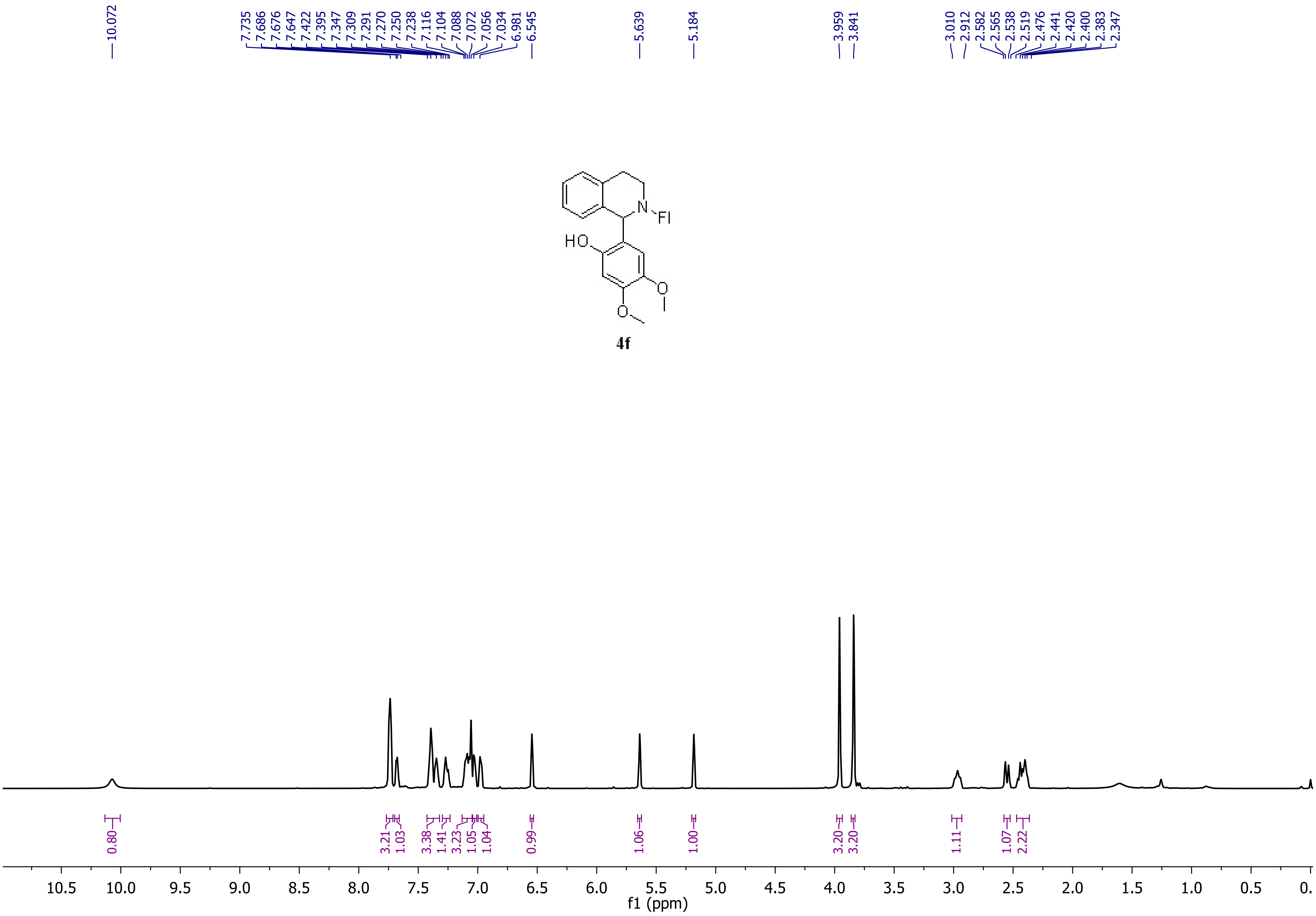
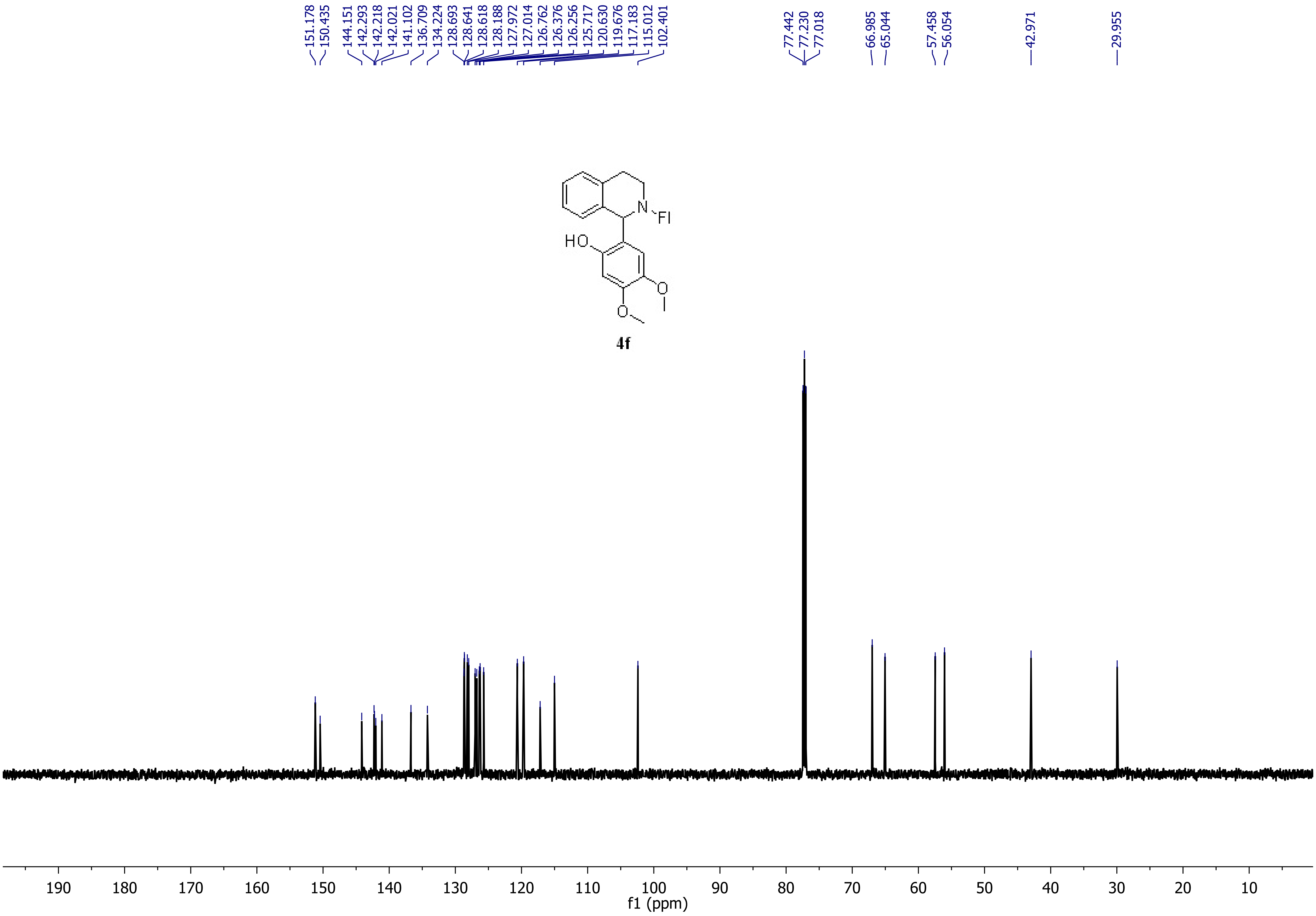
143.394
142.015
141.799
141.264
136.049
134.079
128.835
128.779
128.651
128.206
127.144
126.919
126.752
126.476
125.521
121.982
120.628
120.206
119.786
115.092
77.443
77.230
77.020
66.864
65.085
42.711
29.929
N
Fl
OH
OH
4e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.072
7.735
7.686
7.676
7.647
7.422
7.395
7.347
7.309
7.291
7.270
7.250
7.238
7.116
7.104
7.088
7.072
7.056
7.034
6.981
6.545
5.639
5.184
3.959
3.841
3.010
2.912
2.582
2.565
2.538
2.519
2.476
2.441
2.420
2.400
2.383
2.347
HO
N
Fl
O
O
0.80
3.21
1.03
3.38
1.41
3.23
1.05
1.04
0.99
1.06
1.00
3.20
3.20
1.11
1.07
2.22
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.
f1 (ppm)

4f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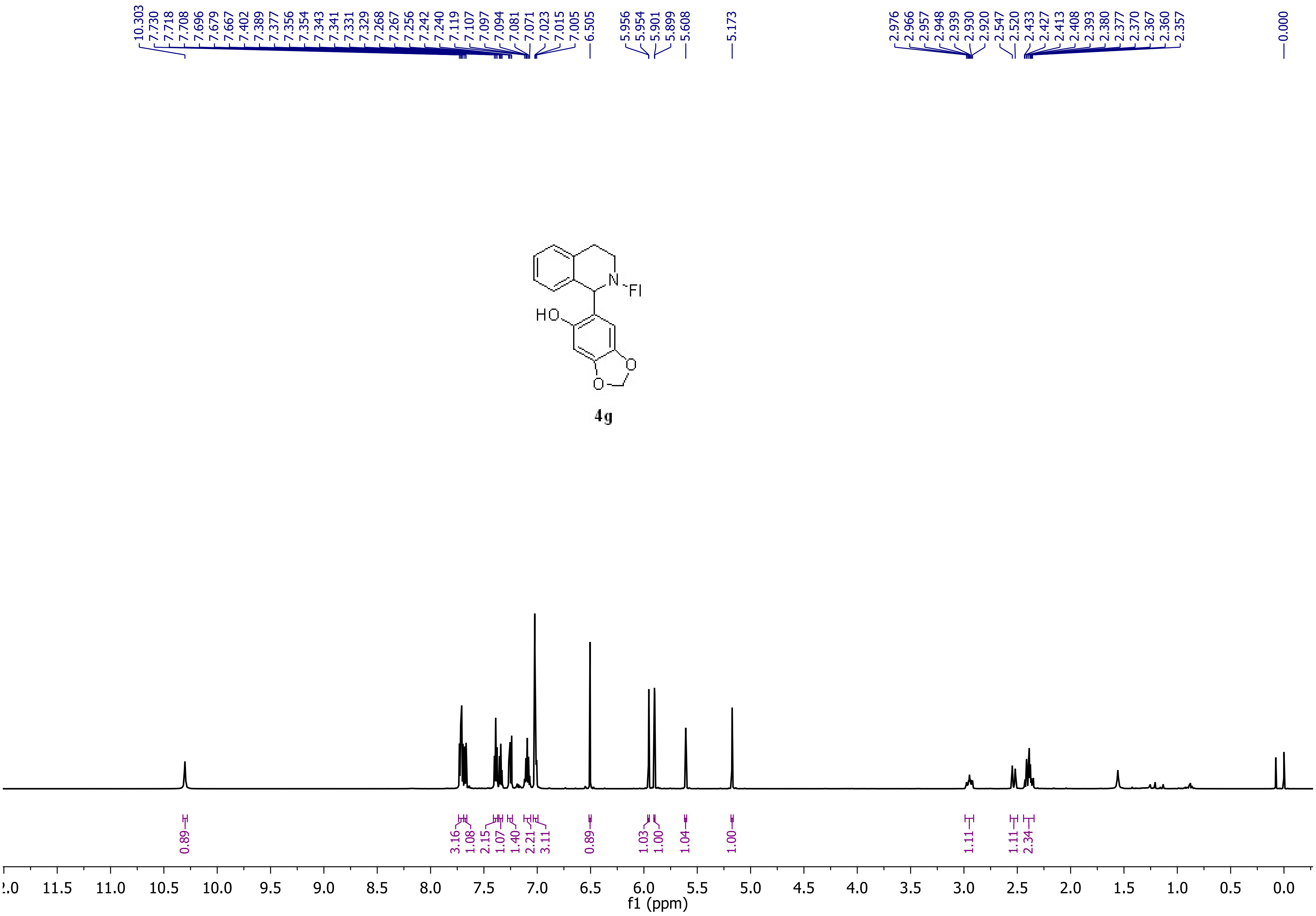
150.435
144.151
142.293
142.218
142.021
141.102
136.709
134.224
128.693
128.641
128.618
128.188
127.972
127.014
126.762
126.376
126.256
125.717
120.630
119.676
117.183
115.012
102.401
77.442
77.230
77.018
66.985
65.044
57.458
56.054
42.971
29.955
HO
N
Fl
O
O
4f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


10.303
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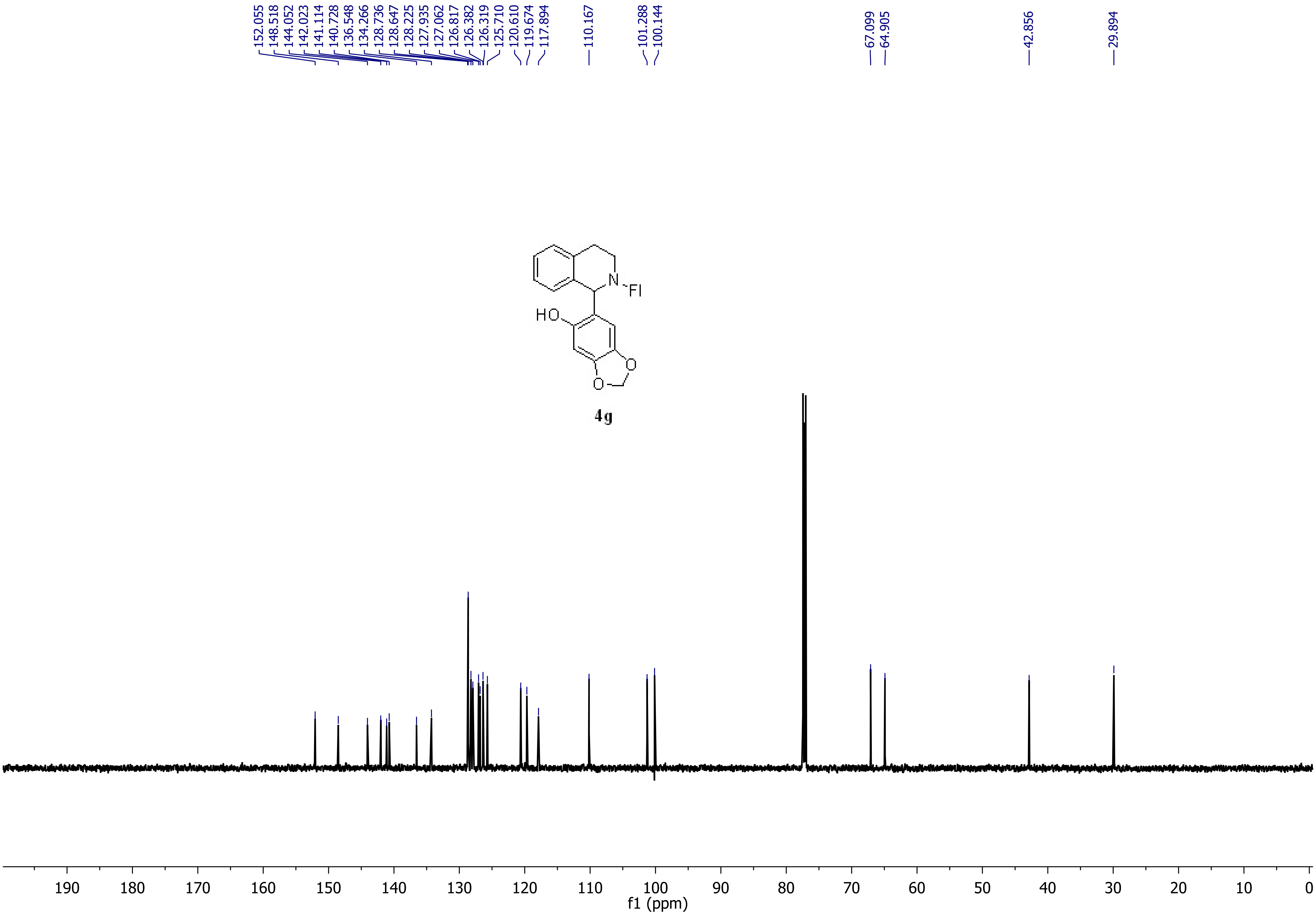
7.718
7.708
7.696
7.679
7.667
7.402
7.389
7.377
7.356
7.354
7.343
7.341
7.331
7.329
7.268
7.267
7.256
7.242
7.240
7.119
7.107
7.097
7.094
7.081
7.071
7.023
7.015
7.005
6.505
5.956
5.954
5.901
5.899
5.608
5.173
2.976
2.966
2.957
2.948
2.939
2.930
2.920
2.547
2.520
2.433
2.427
2.413
2.408
2.393
2.380
2.377
2.370
2.367
2.360
2.357
0.000
N
Fl
HO
O
O
4g
0.89
3.16
1.08
2.15
1.07
1.40
2.21
3.11
0.89
1.03
1.00
1.04
1.00
1.11
1.11
2.34
.0
11.5
11.0
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
f1 (ppm)


4g
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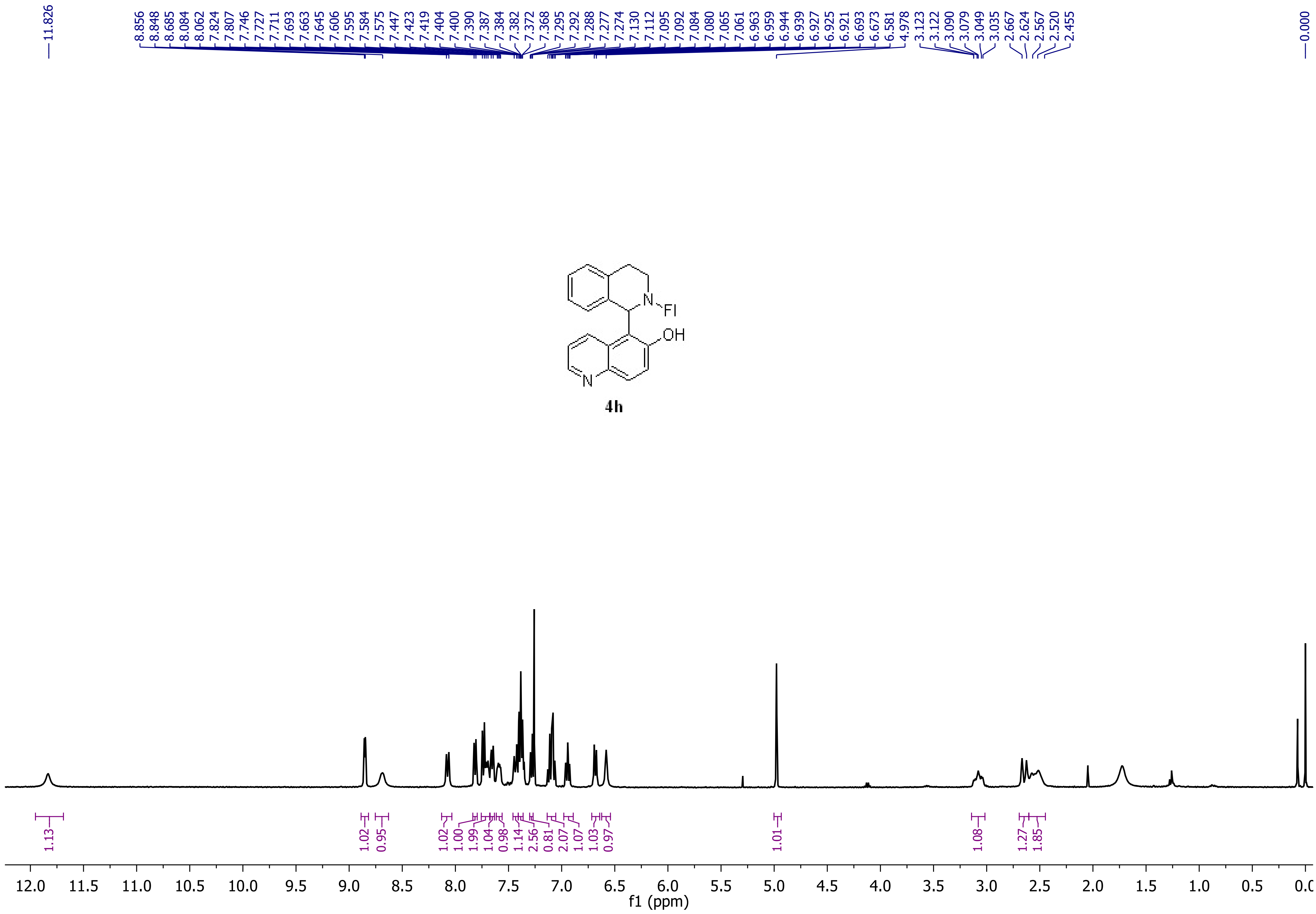
144.052
142.023
141.114
140.728
136.548
134.266
128.736
128.647
128.225
127.935
127.062
126.817
126.382
126.319
125.710
120.610
119.674
117.894
110.167
101.288
100.144
67.099
64.905
42.856
29.894
N
Fl
HO
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.807
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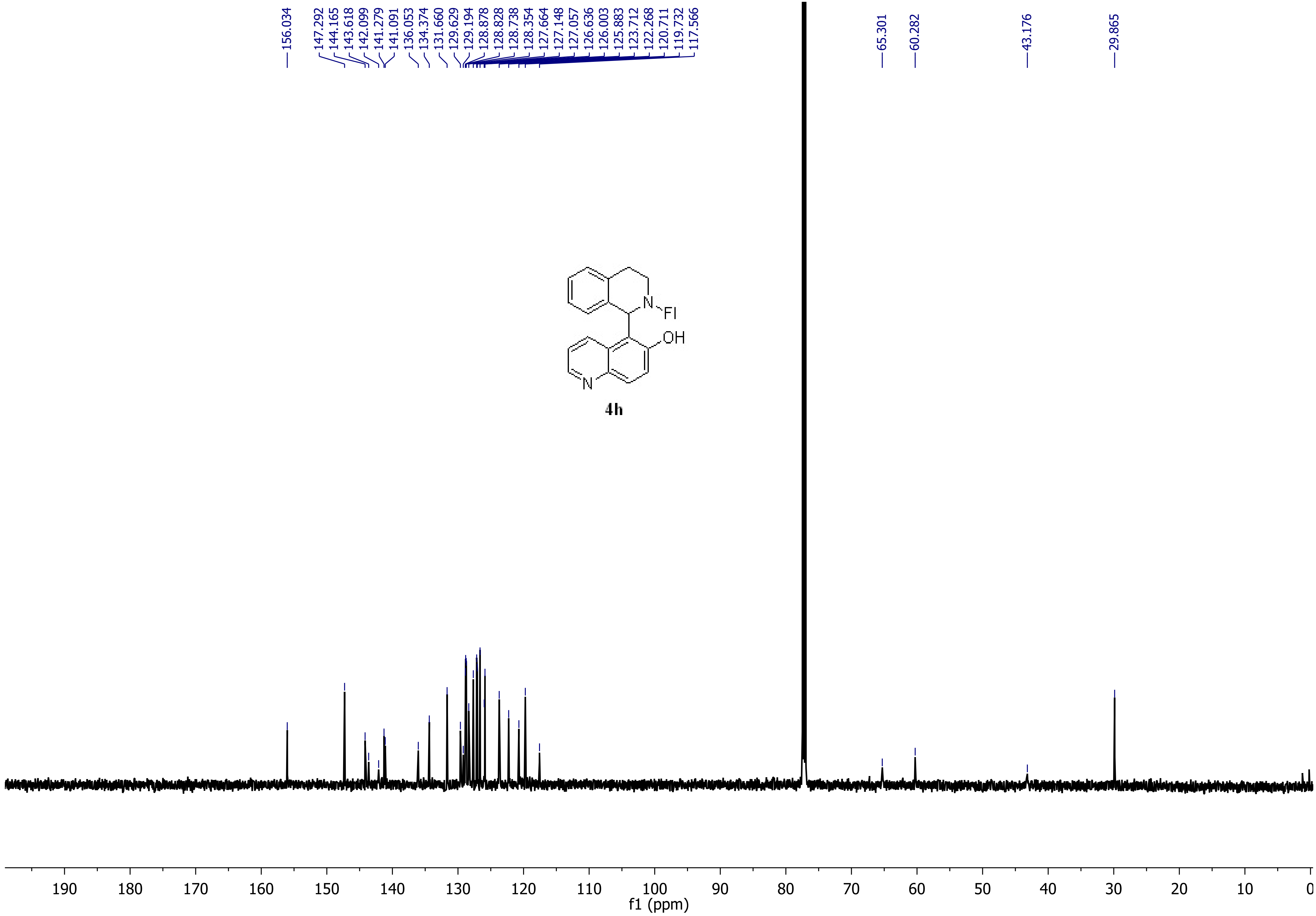
7.727
7.711
7.693
7.663
7.645
7.606
7.595
7.584
7.575
7.447
7.423
7.419
7.404
7.400
7.390
7.387
7.384
7.382
7.372
7.368
7.295
7.292
7.288
7.277
7.274
7.130
7.112
7.095
7.092
7.084
7.080
7.065
7.061
6.963
6.959
6.944
6.939
6.927
6.925
6.921
6.693
6.673
6.581
4.978
3.123
3.122
3.090
3.079
3.049
3.035
2.667
2.624
2.567
2.520
2.455
0.000
N
Fl
OH
N
4h
1.13
1.02
0.95
1.02
1.00
1.99
1.04
0.98
1.14
2.56
0.81
2.07
1.07
1.03
0.97
1.01
1.08
1.27
1.85
12.0
11.5
11.0
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
f1 (ppm)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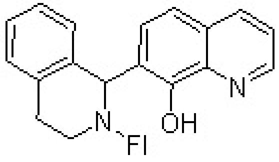
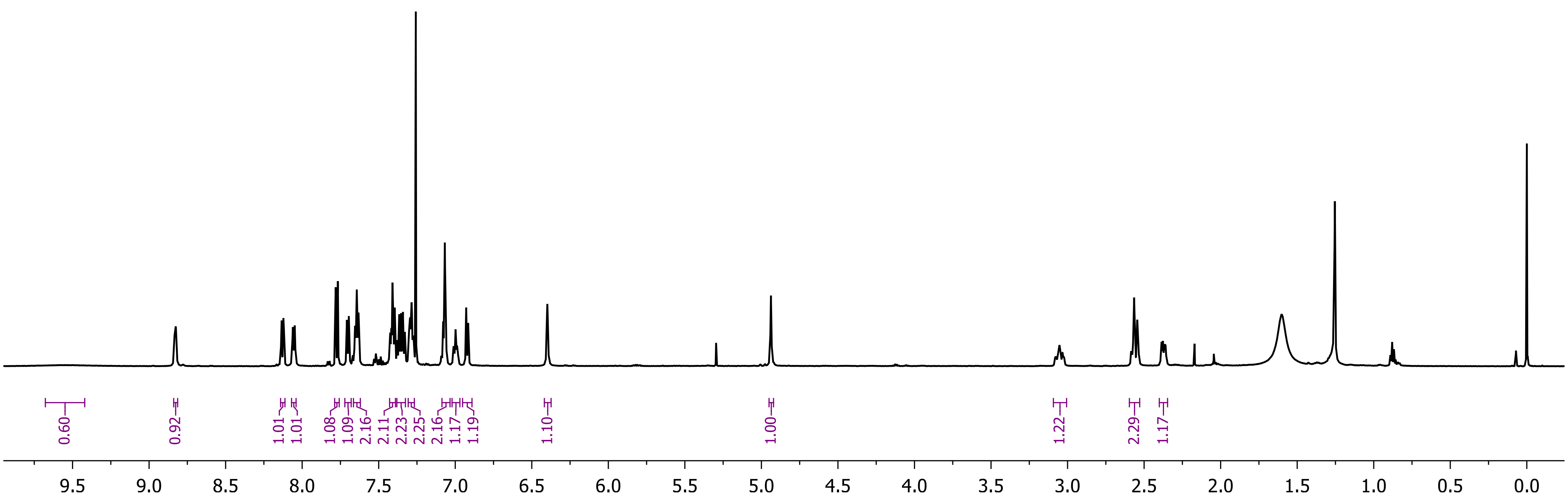
142.099
141.279
141.091
136.053
134.374
131.660
129.629
129.194
128.878
128.828
128.738
128.354
127.664
127.148
127.057
126.636
126.003
125.883
123.712
122.268
120.711
119.732
117.566
65.301
60.282
43.176
29.865
N
Fl
OH
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4h


N
Fl
OH
N

4i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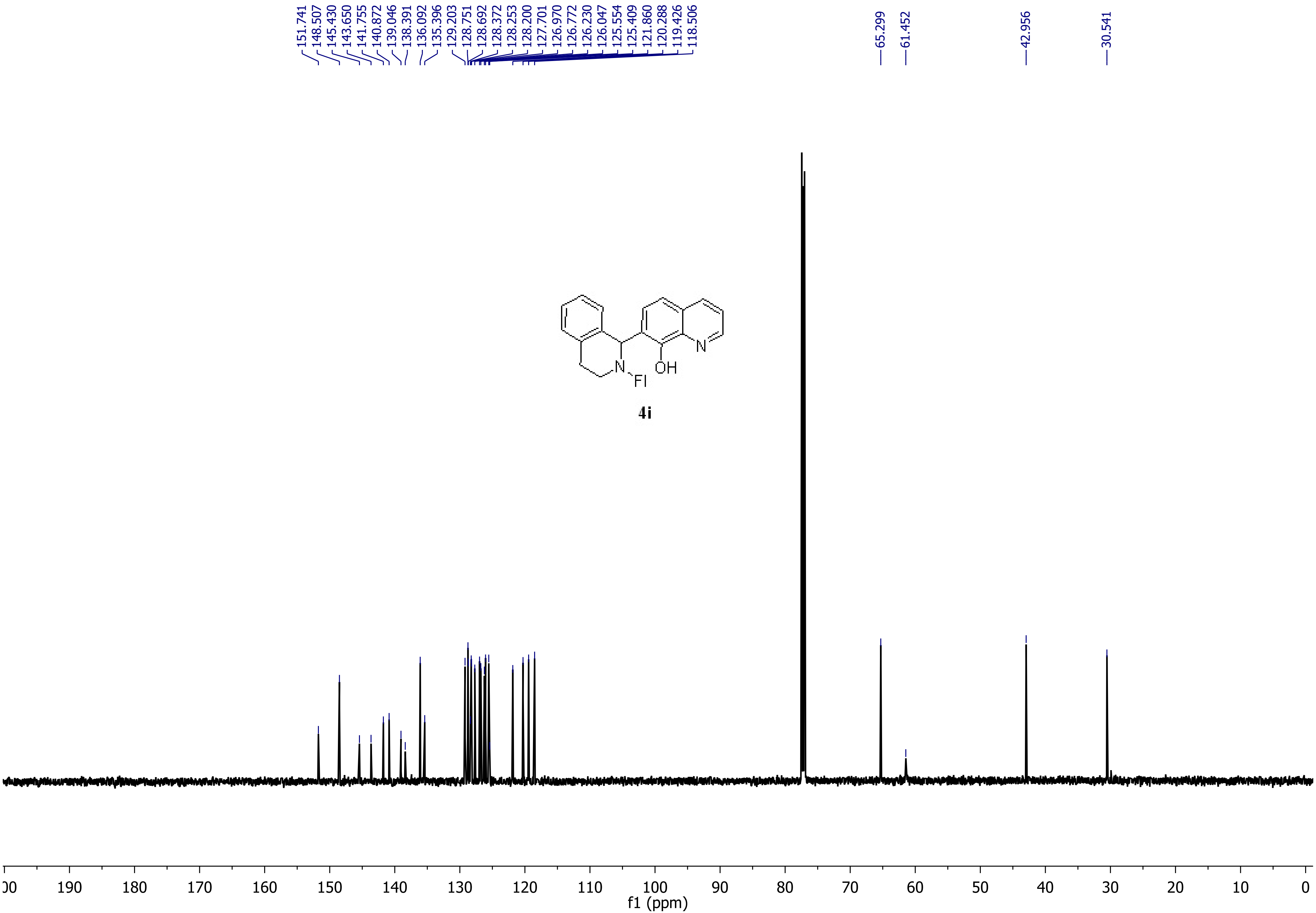
8.120
8.061
8.048
7.781
7.767
7.708
7.695
7.669
7.655
7.643
7.632
7.425
7.418
7.410
7.405
7.396
7.379
7.366
7.354
7.342
7.329
7.306
7.298
7.285
7.273
7.086
7.079
7.068
7.059
7.011
7.006
6.998
6.988
6.984
6.929
6.915
6.398
4.938
3.081
3.053
3.033
3.026
2.585
2.580
2.565
2.545
2.541
2.386
2.378
2.367
2.360
-0.000
0.60
0.92
1.01
1.01
1.08
1.09
2.16
2.11
2.23
2.25
2.16
1.17
1.19
1.10
1.00
1.22
2.29
1.17
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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145.430
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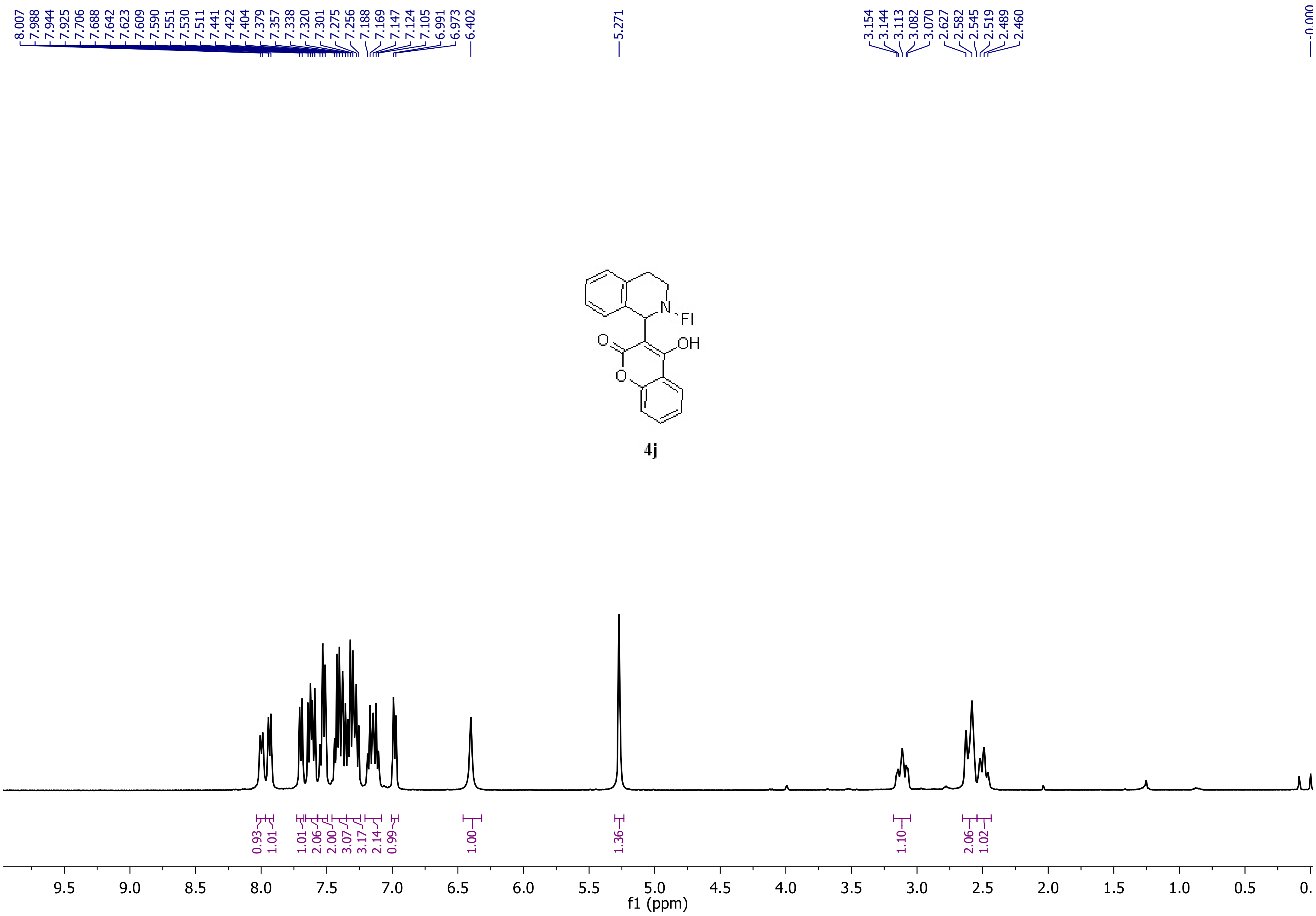
140.872
139.046
138.391
136.092
135.396
129.203
128.751
128.692
128.372
128.253
128.200
127.701
126.970
126.772
126.230
126.047
125.554
125.409
121.860
120.288
119.426
118.506
65.299
61.452
42.956
30.541
N
Fl
OH
N
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4i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7.688
7.642
7.623
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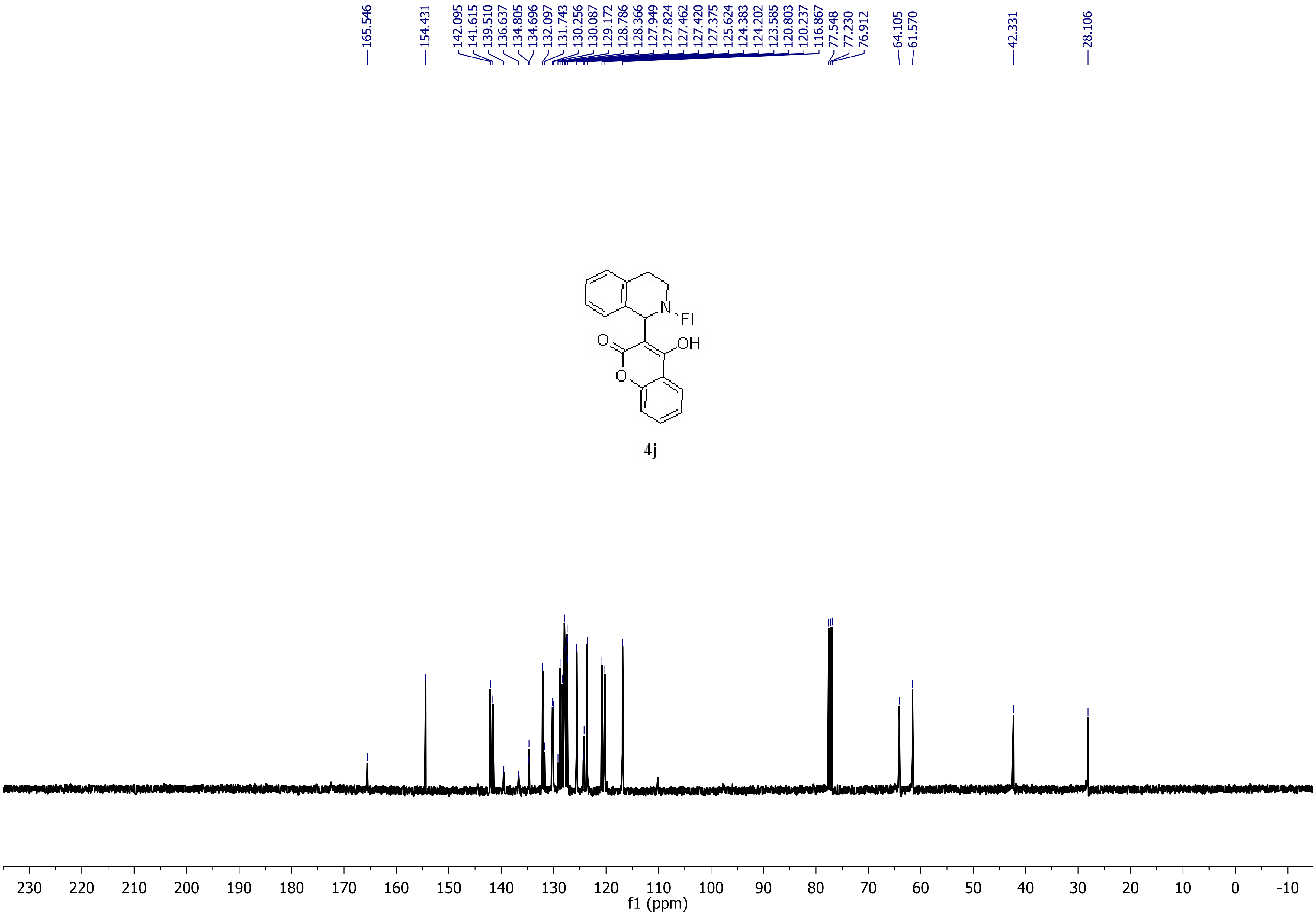
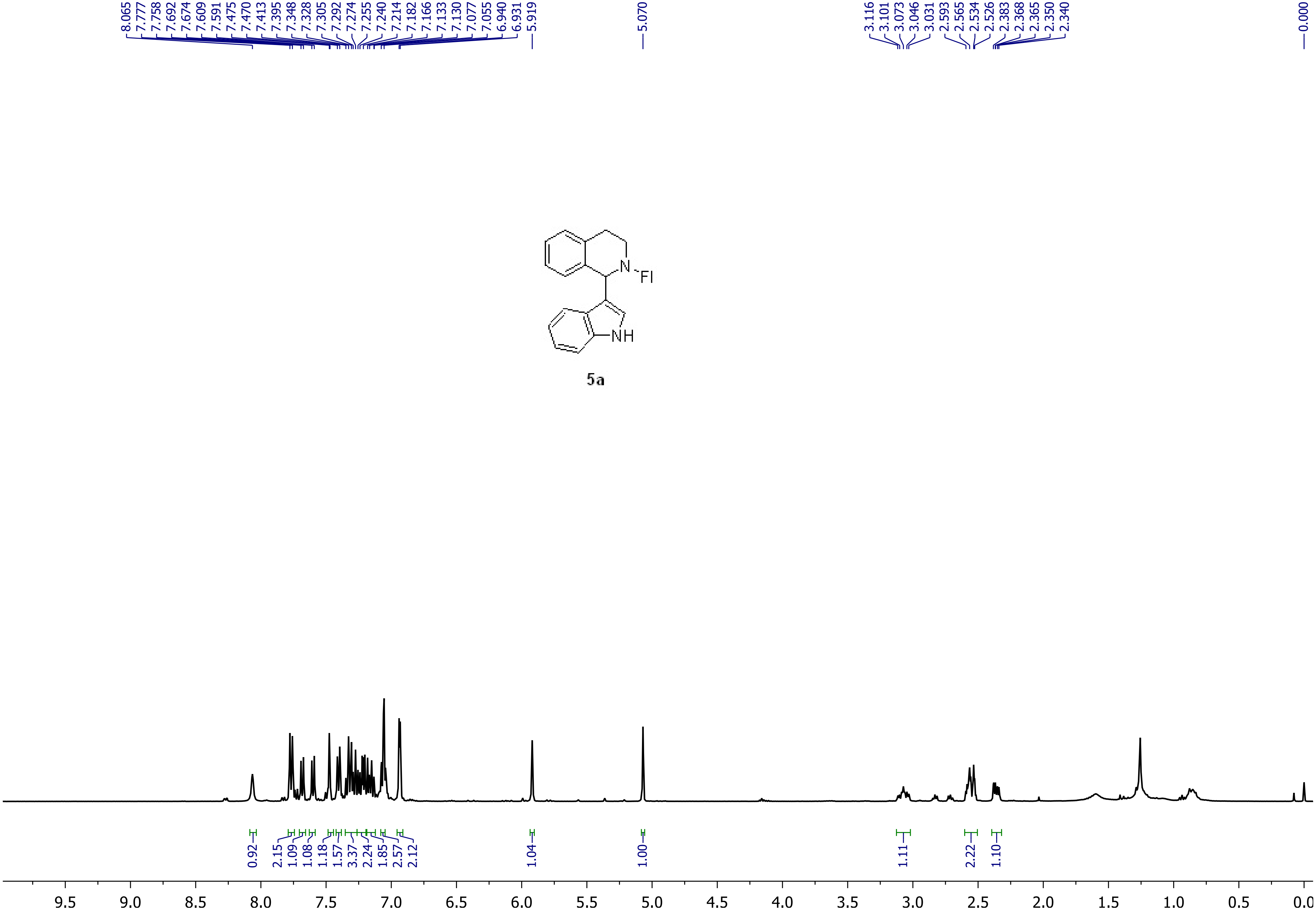
7.590
7.551
7.530
7.511
7.441
7.422
7.404
7.379
7.357
7.338
7.320
7.301
7.275
7.256
7.188
7.169
7.147
7.124
7.105
6.991
6.973
6.402
5.271
3.154
3.144
3.113
3.082
3.070
2.627
2.582
2.545
2.519
2.489
2.460
-0.000
N
Fl
O
OH
O
4j
0.93
1.01
1.01
2.06
2.00
3.07
3.17
2.14
0.99
1.00
1.36
1.10
2.06
1.02
9.5
9.0
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.
f1 (ppm)


165.546
154.431
142.095
141.615
139.510
136.637
134.805
134.696
132.097
131.743
130.256
130.087
129.172
128.786
128.366
127.949
127.824
127.462
127.420
127.375
125.624
124.383
124.202
123.585
120.803
120.237
116.867
77.548
77.230
76.912
64.105
61.570
42.331
28.106
N
Fl
O
OH
O
230
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)

4j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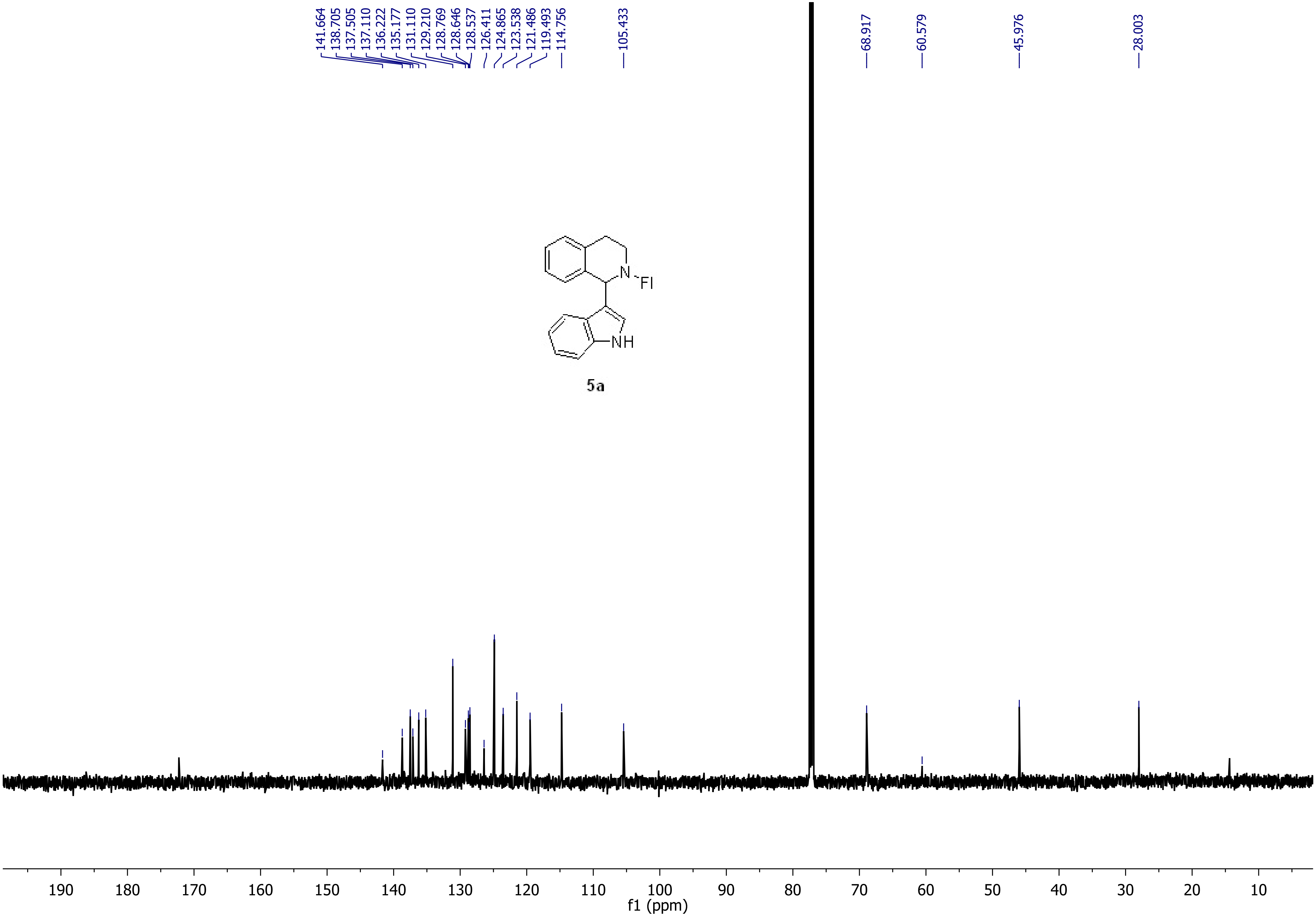
7.758
7.692
7.674
7.609
7.591
7.475
7.470
7.413
7.395
7.348
7.328
7.305
7.292
7.274
7.255
7.240
7.214
7.182
7.166
7.133
7.130
7.077
7.055
6.940
6.931
5.919
5.070
3.116
3.101
3.073
3.046
3.031
2.593
2.565
2.534
2.526
2.383
2.368
2.365
2.350
2.340
0.000
N
Fl
NH
5a
0.92
2.15
1.09
1.08
1.18
1.57
3.37
2.24
1.85
2.57
2.12
1.04
1.00
1.11
2.22
1.10
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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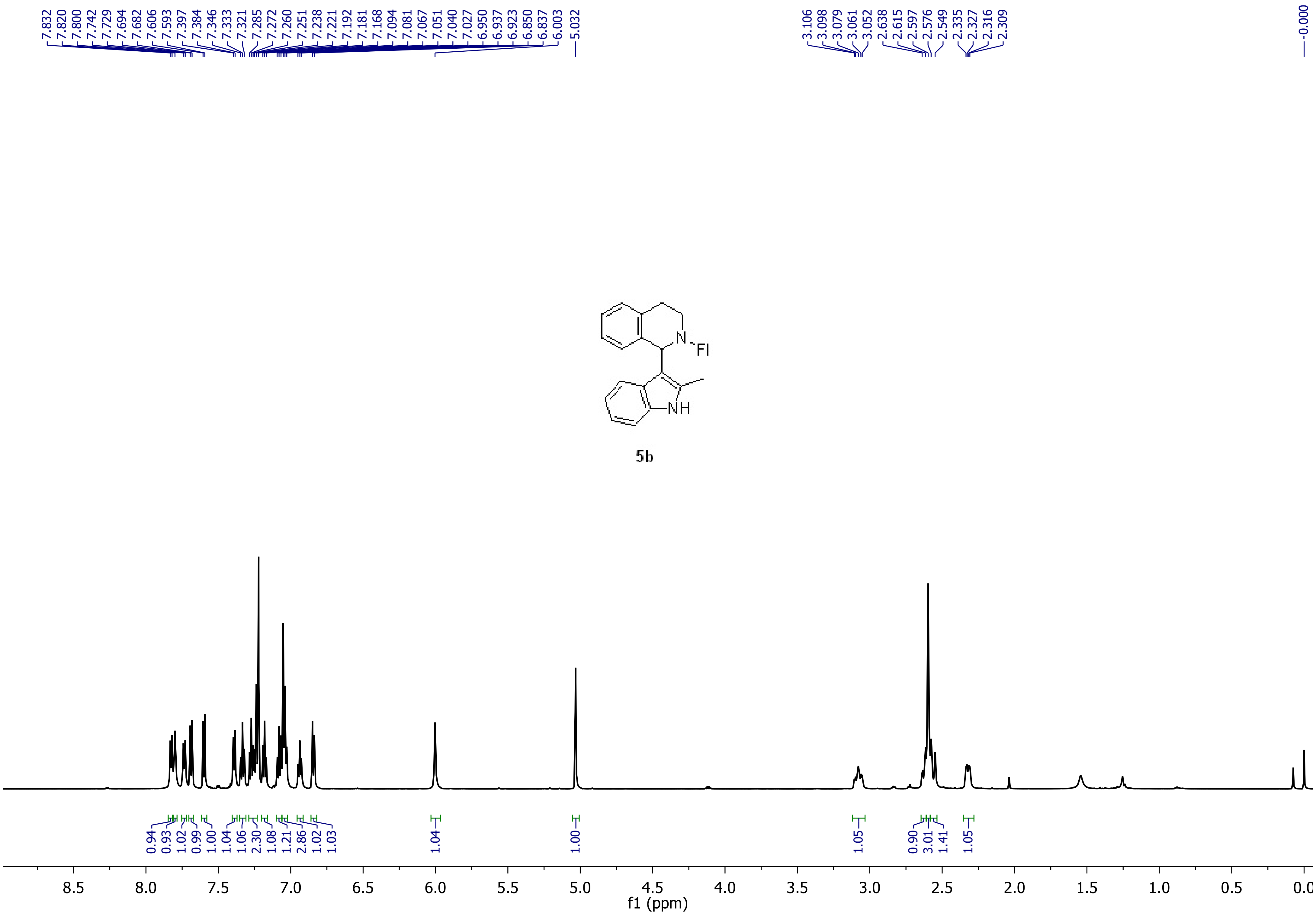
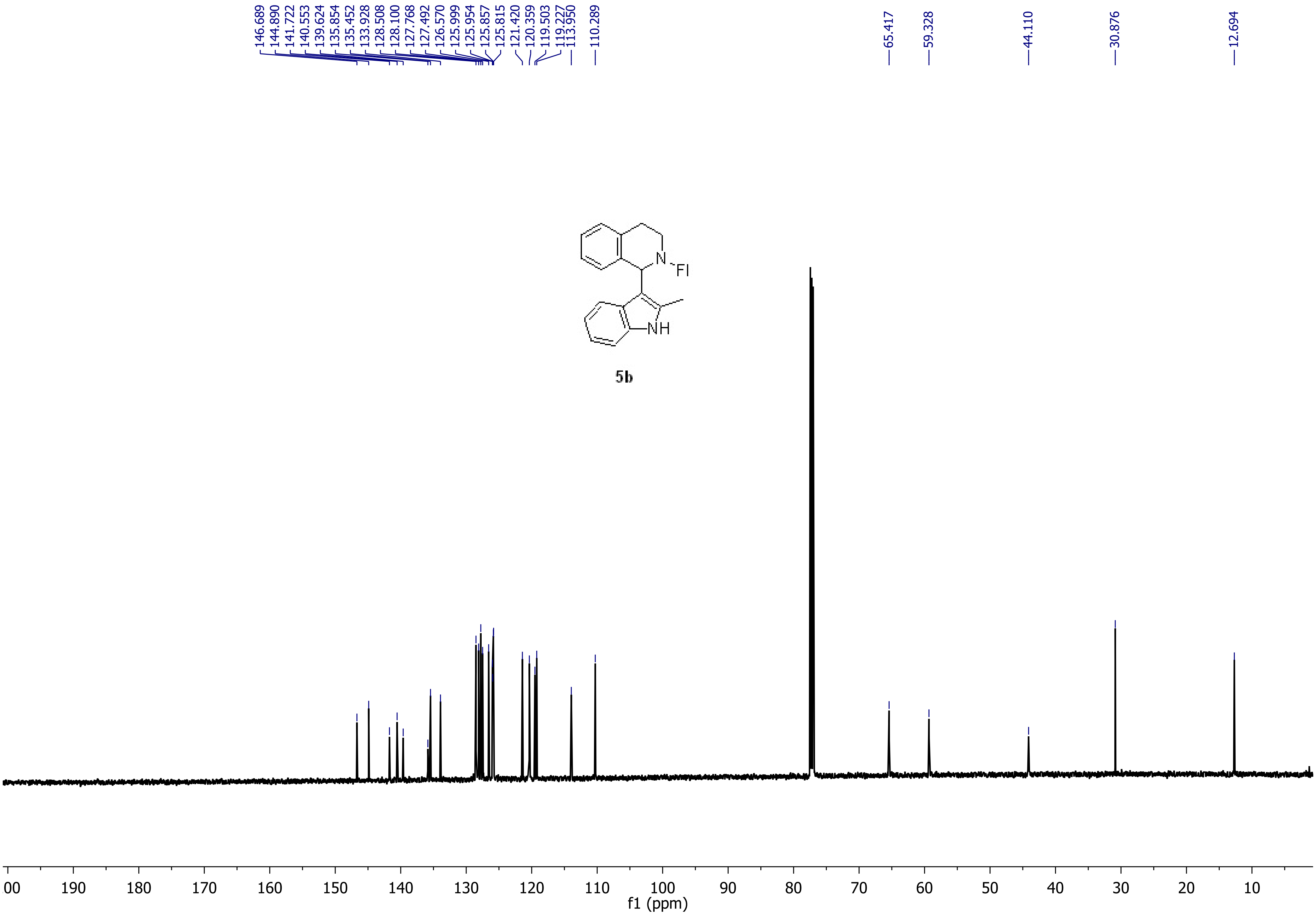
138.705
137.505
137.110
136.222
135.177
131.110
129.210
128.769
128.646
128.537
126.411
124.865
123.538
121.486
119.493
114.756
105.433
68.917
60.579
45.976
28.003
N
Fl
NH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

5a



5b

7.832
7.820
7.800
7.742
7.729
7.694
7.682
7.606
7.593
7.397
7.384
7.346
7.333
7.321
7.285
7.272
7.260
7.251
7.238
7.221
7.192
7.181
7.168
7.094
7.081
7.067
7.051
7.040
7.027
6.950
6.937
6.923
6.850
6.837
6.003
5.032
3.106
3.098
3.079
3.061
3.052
2.638
2.615
2.597
2.576
2.549
2.335
2.327
2.316
2.309
-0.000
N
Fl
NH
0.94
0.93
1.02
0.99
1.00
1.04
1.06
2.30
1.08
1.21
2.86
1.02
1.03
1.04
1.00
1.05
0.90
3.01
1.41
1.05
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)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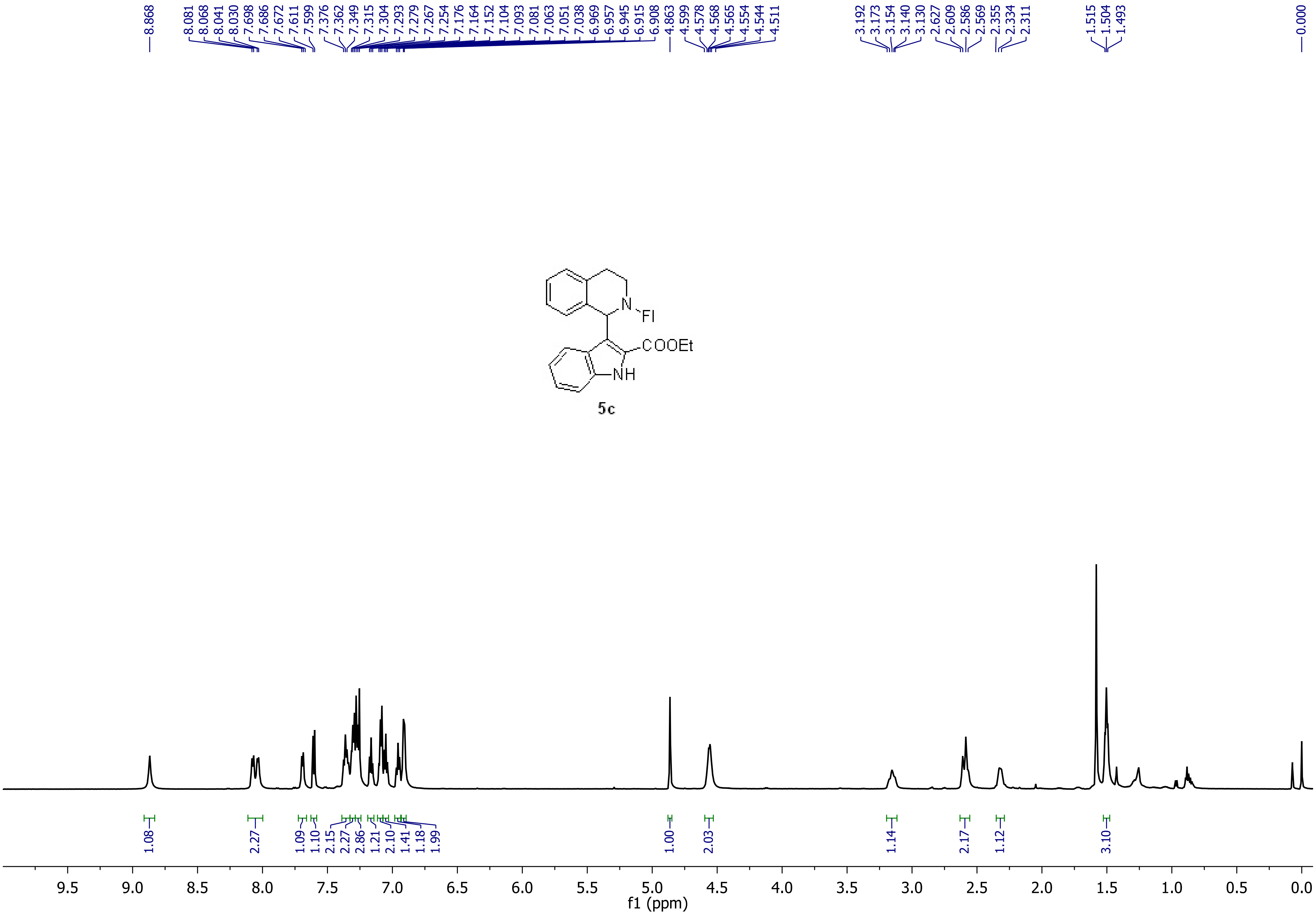
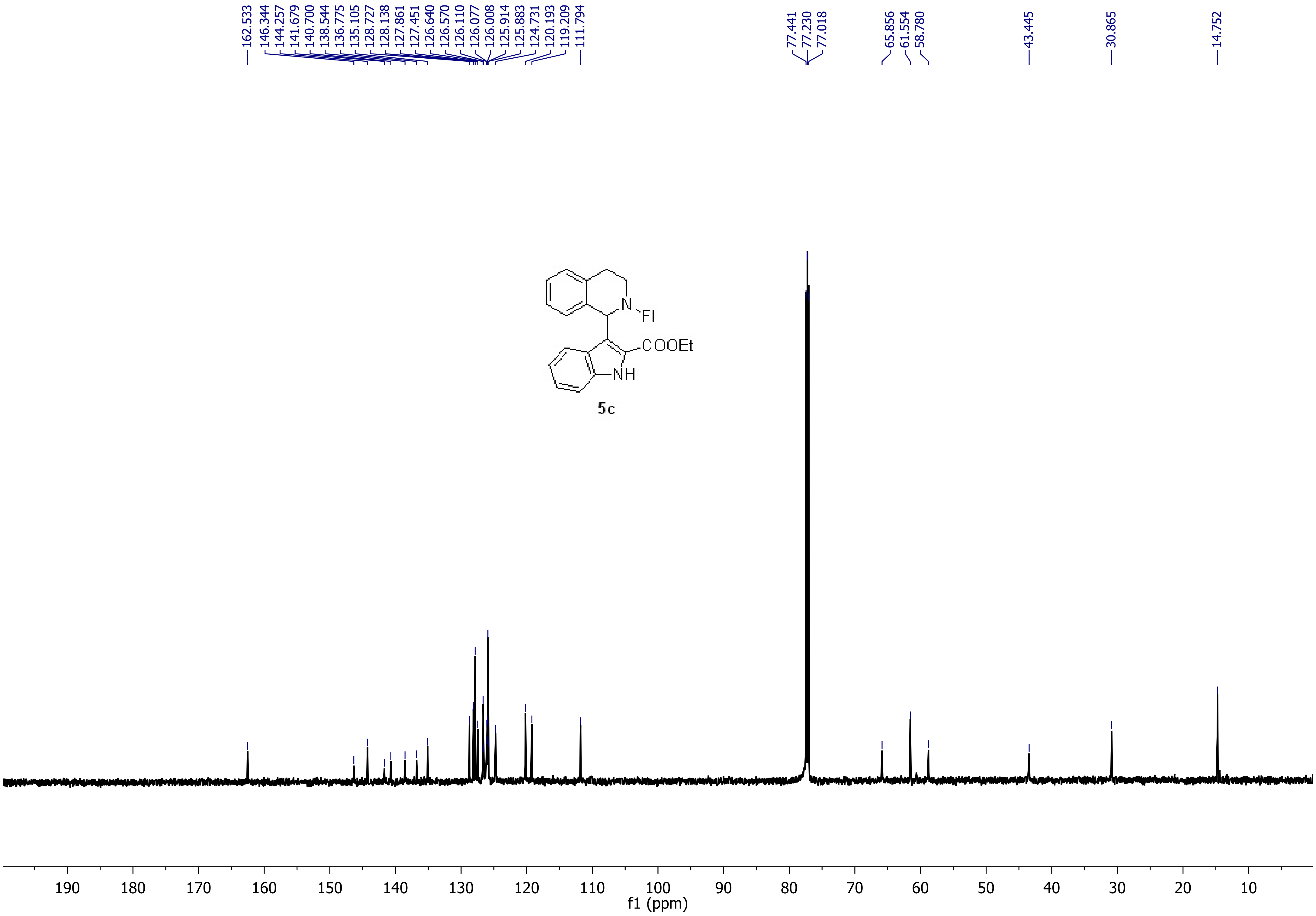
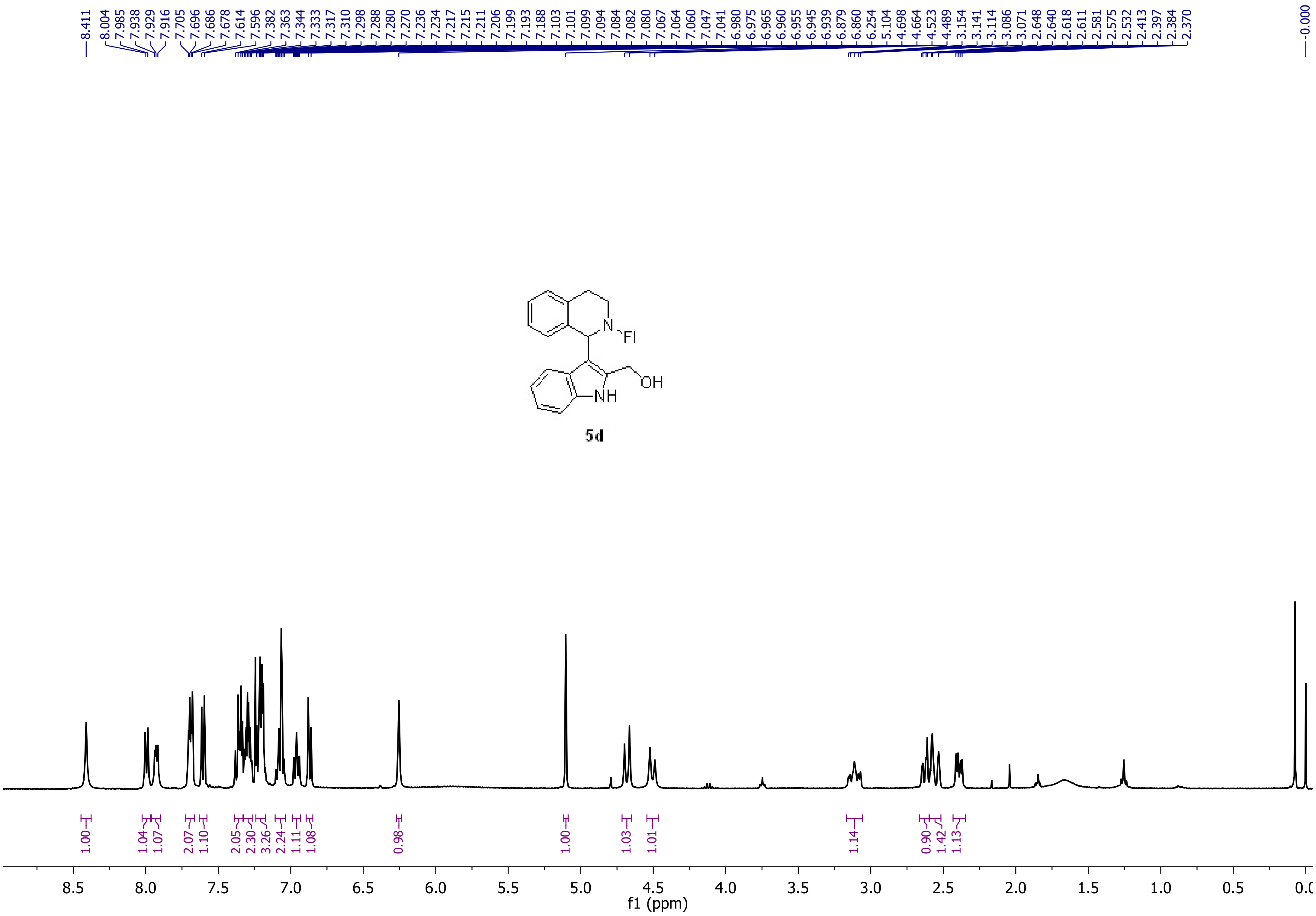
144.890
141.722
140.553
139.624
135.854
135.452
133.928
128.508
128.100
127.768
127.492
126.570
125.999
125.954
125.857
125.815
121.420
120.359
119.503
119.227
113.950
110.289
65.417
59.328
44.110
30.876
12.694
N
Fl
NH
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

5b


8.868
8.081
8.068
8.041
8.030
7.698
7.686
7.672
7.611
7.599
7.376
7.362
7.349
7.315
7.304
7.293
7.279
7.267
7.254
7.176
7.164
7.152
7.104
7.093
7.081
7.063
7.051
7.038
6.969
6.957
6.945
6.915
6.908
4.863
4.599
4.578
4.568
4.565
4.554
4.544
4.511
3.192
3.173
3.154
3.140
3.130
2.627
2.609
2.586
2.569
2.355
2.334
2.311
1.515
1.504
1.493
0.000
N
Fl
COOEt
NH
1.08
2.27
1.09
1.10
2.15
2.27
2.86
1.21
2.10
1.41
1.18
1.99
1.00
2.03
1.14
2.17
1.12
3.10
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
f1 (ppm)

5c


162.533
146.344
144.257
141.679
140.700
138.544
136.775
135.105
128.727
128.138
127.861
127.451
126.640
126.570
126.110
126.077
126.008
125.914
125.883
124.731
120.193
119.209
111.794
77.441
77.230
77.018
65.856
61.554
58.780
43.445
30.865
14.752
N
Fl
COOEt
NH
5c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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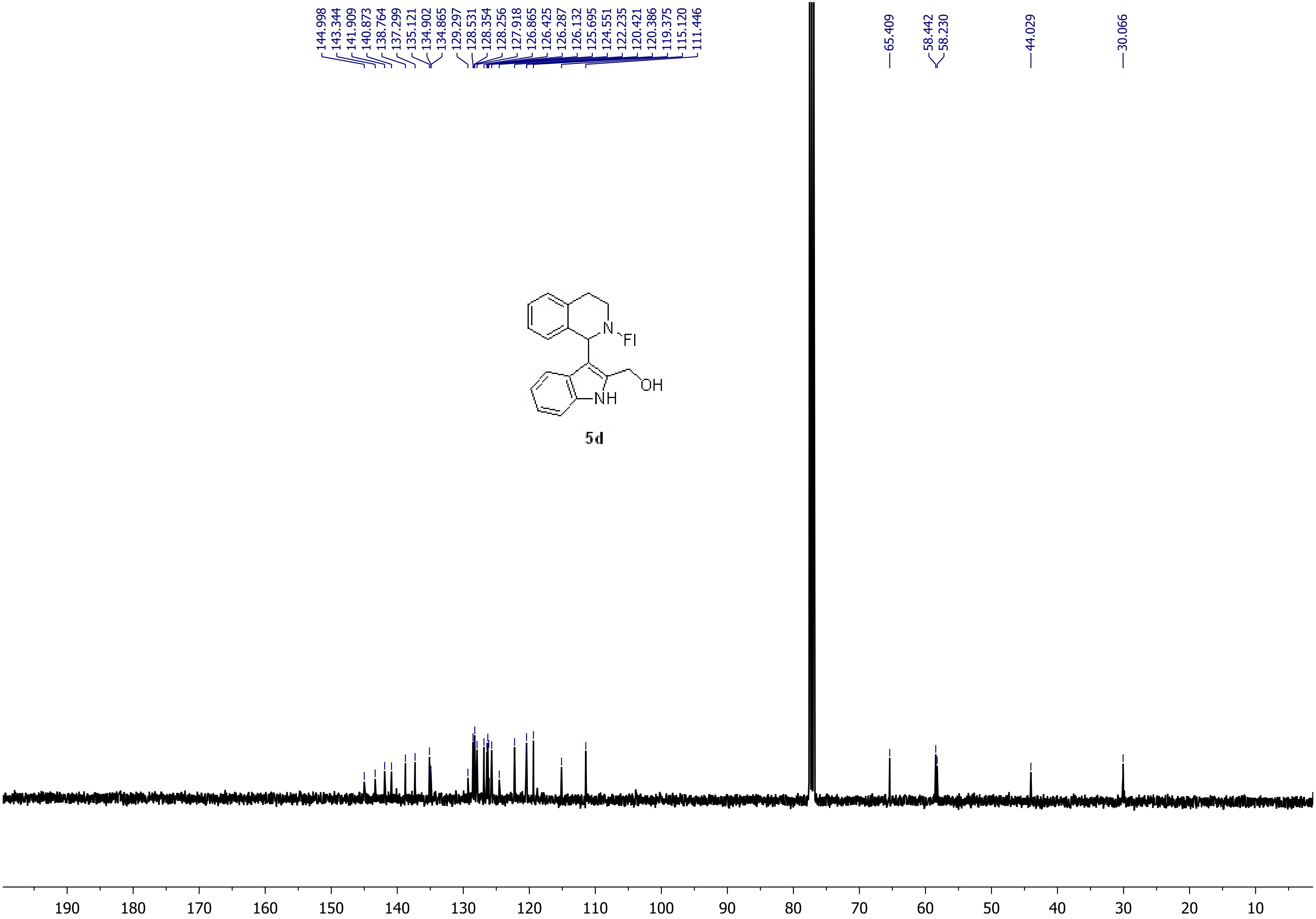
7.985
7.938
7.929
7.916
7.705
7.696
7.686
7.678
7.614
7.596
7.382
7.363
7.344
7.333
7.317
7.310
7.298
7.288
7.280
7.270
7.236
7.234
7.217
7.215
7.211
7.206
7.199
7.193
7.188
7.103
7.101
7.099
7.094
7.084
7.082
7.080
7.067
7.064
7.060
7.047
7.041
6.980
6.975
6.965
6.960
6.955
6.945
6.939
6.879
6.860
6.254
5.104
4.698
4.664
4.523
4.489
3.154
3.141
3.114
3.086
3.071
2.648
2.640
2.618
2.611
2.581
2.575
2.532
2.413
2.397
2.384
2.370
-0.000
N
Fl
OH
NH
1.00
1.04
1.07
2.07
1.10
2.05
2.30
3.26
2.24
1.11
1.08
0.98
1.00
1.03
1.01
1.14
0.90
1.42
1.13
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.
f1 (ppm)

5d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143.344
141.909
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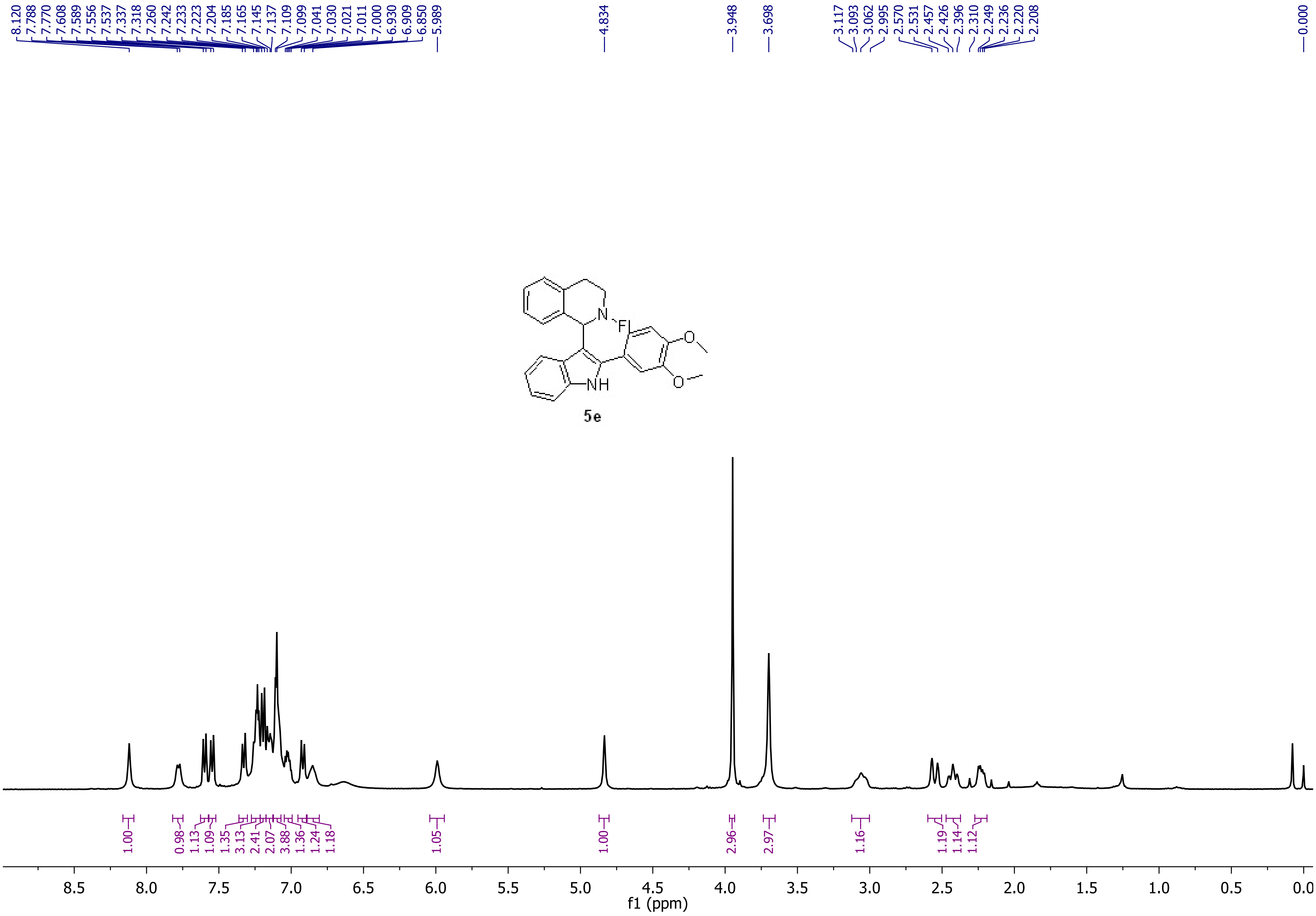
138.764
137.299
135.121
134.902
134.865
129.297
128.531
128.354
128.256
127.918
126.865
126.425
126.287
126.132
125.695
124.551
122.235
120.421
120.386
119.375
115.120
111.446
65.409
58.442
58.230
44.029
30.066
N
Fl
OH
NH
5d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.120
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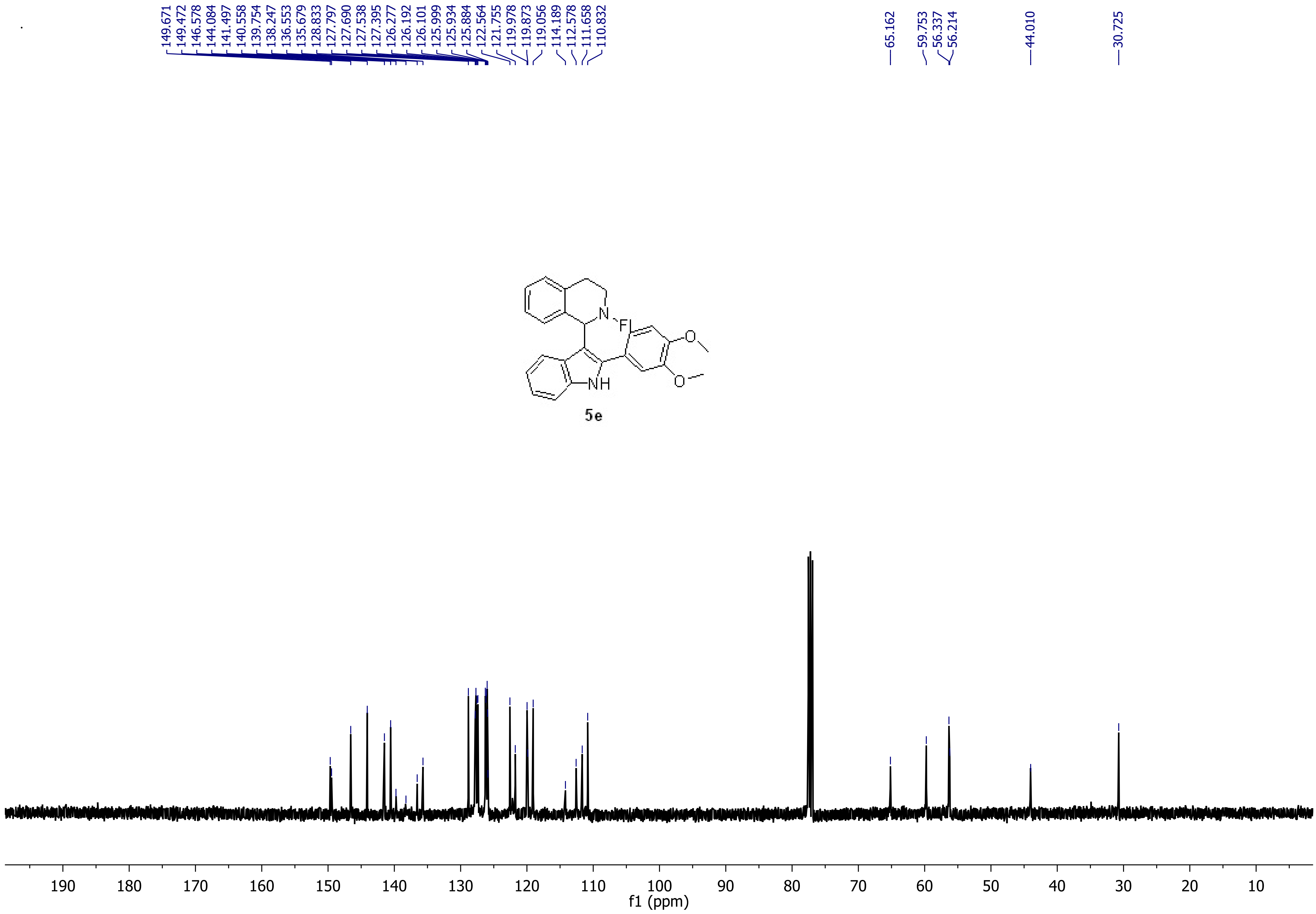
7.770
7.608
7.589
7.556
7.537
7.337
7.318
7.260
7.242
7.233
7.223
7.204
7.185
7.165
7.145
7.137
7.109
7.099
7.041
7.030
7.021
7.011
7.000
6.930
6.909
6.850
5.989
4.834
3.948
3.698
3.117
3.093
3.062
2.995
2.570
2.531
2.457
2.426
2.396
2.310
2.249
2.236
2.220
2.208
0.000
N
F
O
O
NH
5e
1.00
0.98
1.13
1.09
1.35
3.13
2.41
2.07
3.88
1.36
1.24
1.18
1.05
1.00
2.96
2.97
1.16
1.19
1.14
1.12
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)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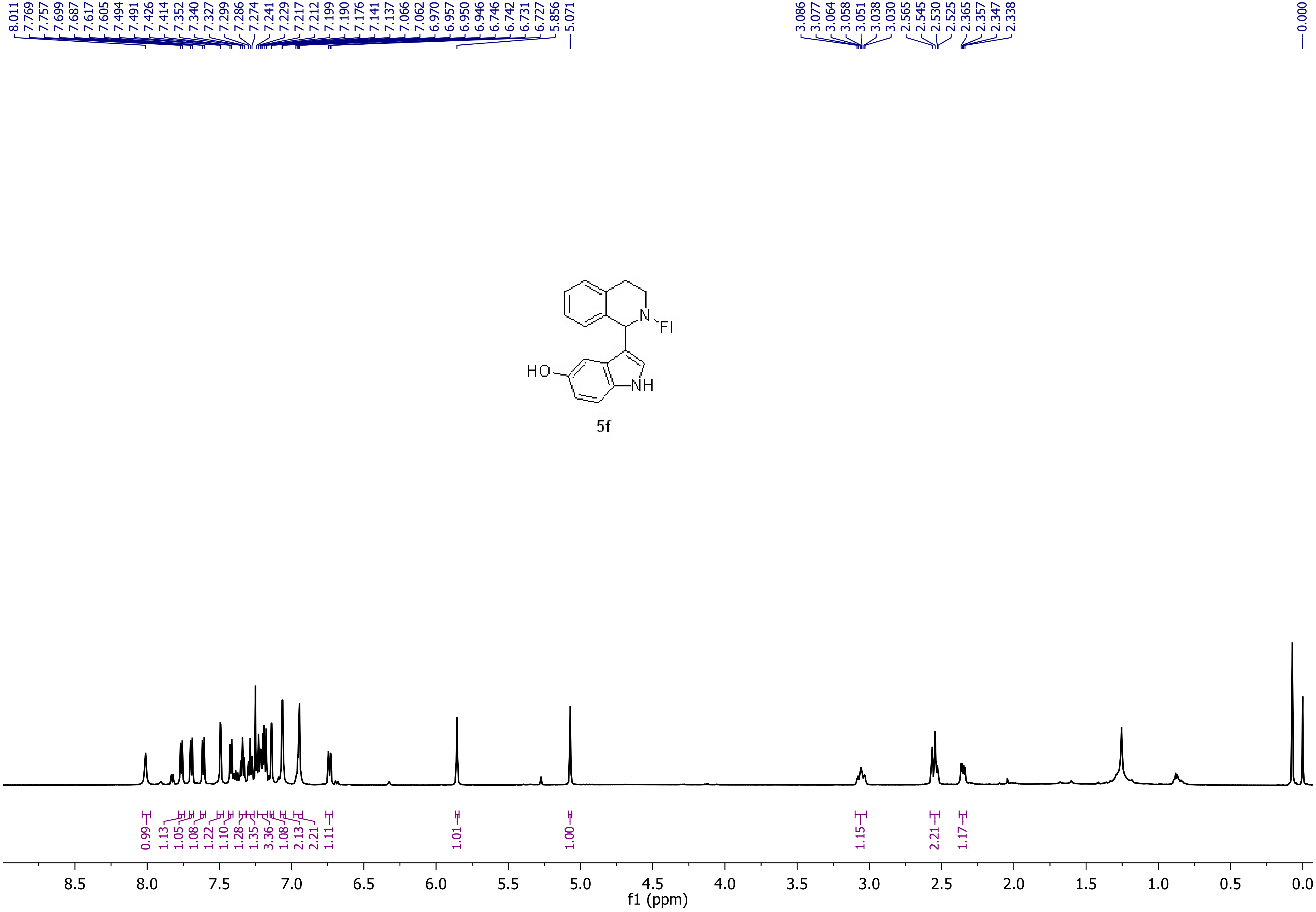
149.472
146.578
144.084
141.497
140.558
139.754
138.247
136.553
135.679
128.833
127.797
127.690
127.538
127.395
126.277
126.192
126.101
125.999
125.934
125.884
122.564
121.755
119.978
119.873
119.056
114.189
112.578
111.658
110.832
65.162
59.753
56.337
56.214
44.010
30.725
N
F
O
O
NH
5e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.011
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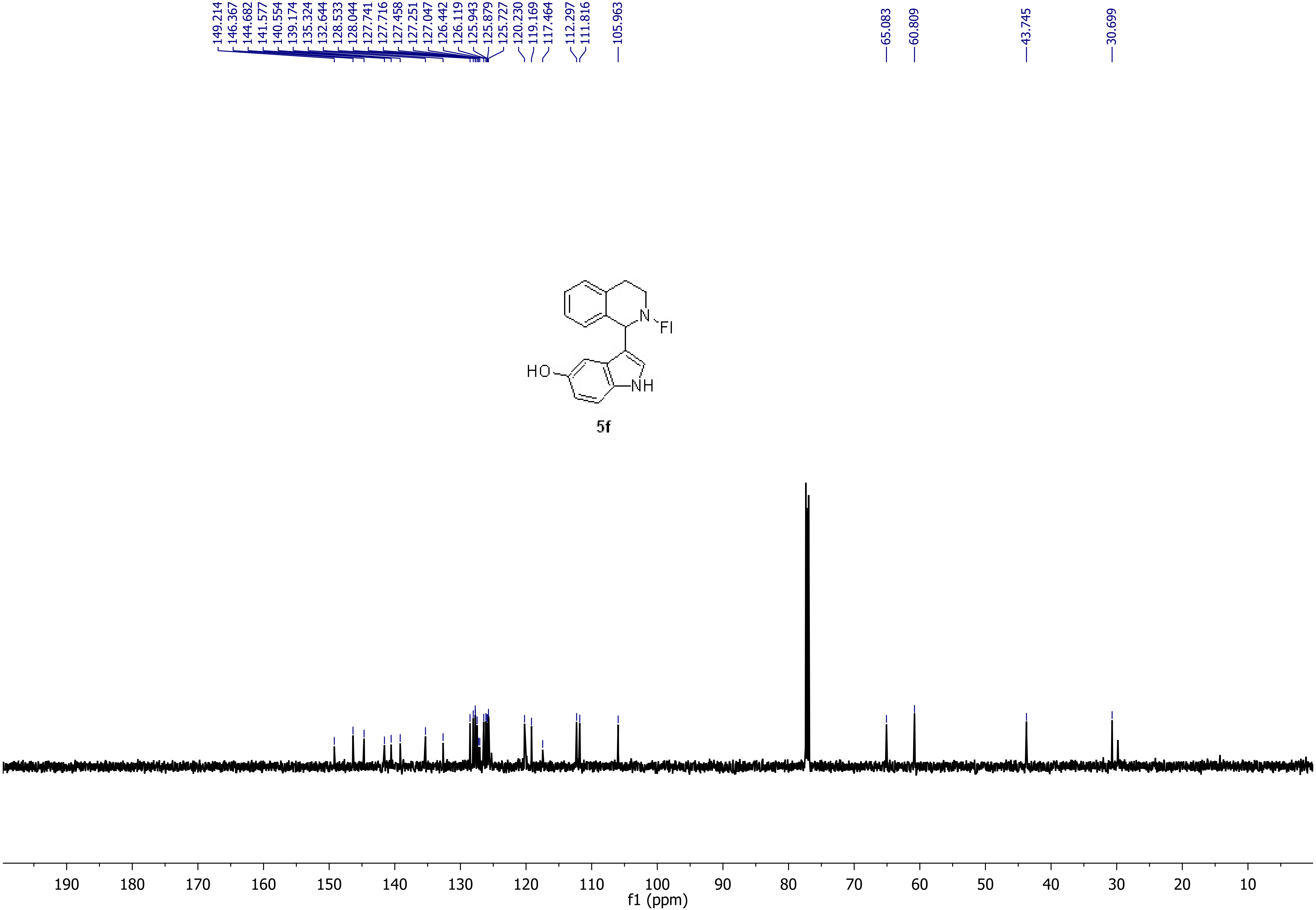
7.757
7.699
7.687
7.617
7.605
7.494
7.491
7.426
7.414
7.352
7.340
7.327
7.299
7.286
7.274
7.241
7.229
7.217
7.212
7.199
7.190
7.176
7.141
7.137
7.066
7.062
6.970
6.957
6.950
6.946
6.746
6.742
6.731
6.727
5.856
5.071
3.086
3.077
3.064
3.058
3.051
3.038
3.030
2.565
2.545
2.530
2.525
2.365
2.357
2.347
2.338
0.000
N
Fl
HO
NH
0.99
1.13
1.05
1.08
1.22
1.10
1.28
1.35
3.36
1.08
2.13
2.21
1.11
1.01
1.00
1.15
2.21
1.17
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)

5f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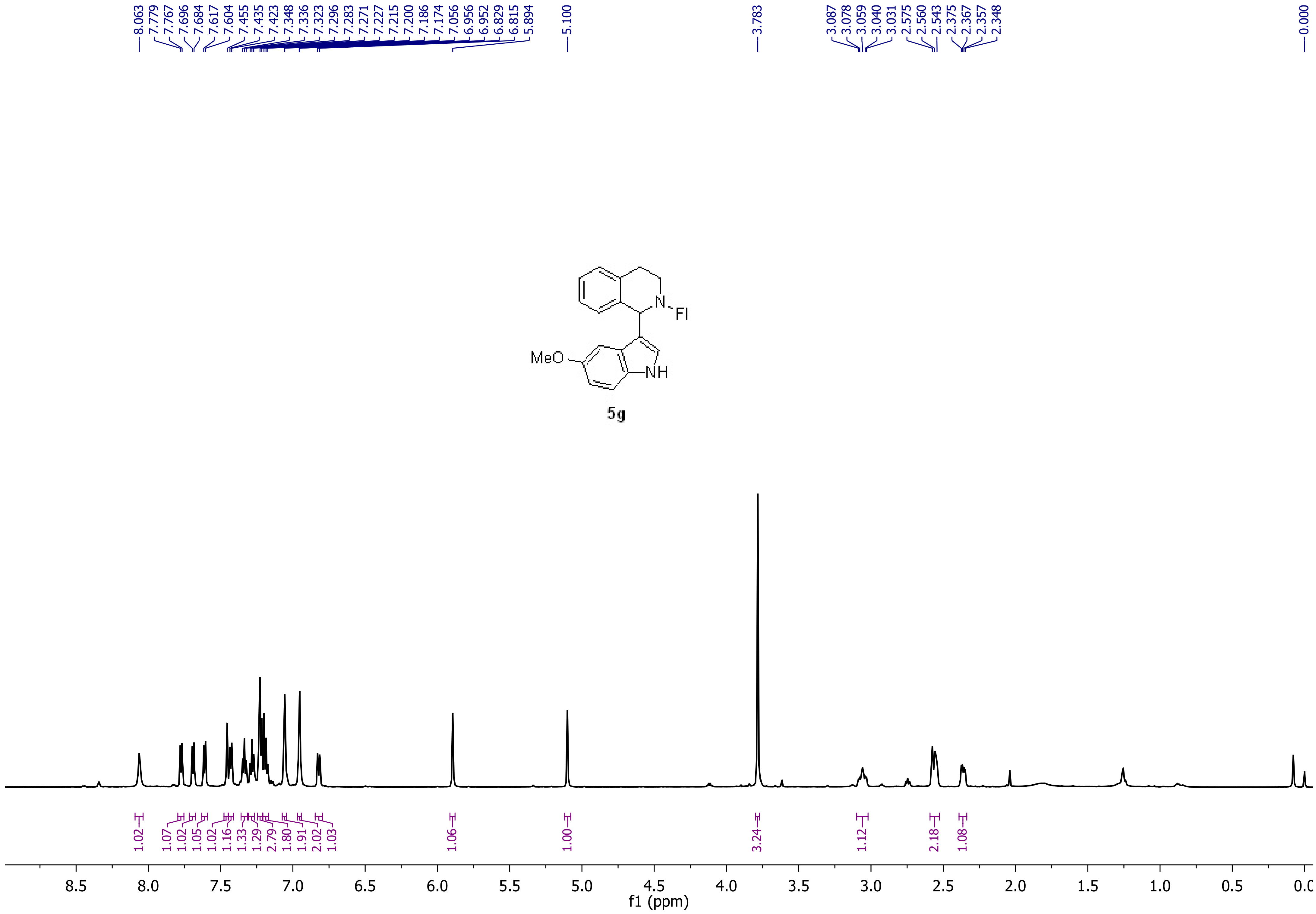
141.577
140.554
139.174
135.324
132.644
128.533
128.044
127.741
127.716
127.458
127.251
127.047
126.442
126.119
125.943
125.879
125.727
120.230
119.169
117.464
112.297
111.816
105.963
65.083
60.809
43.745
30.699
N
Fl
HO
NH
5f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


5g
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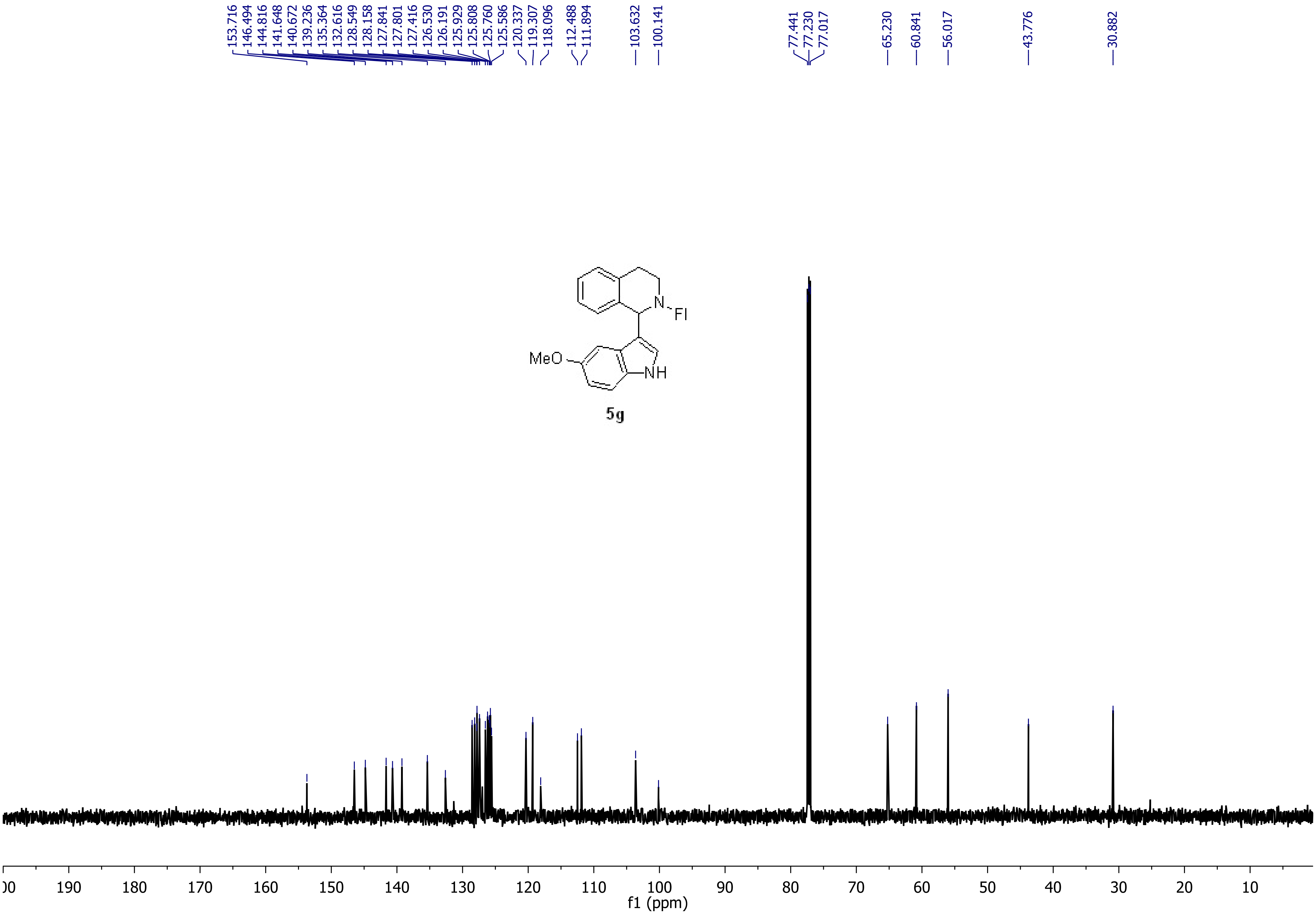
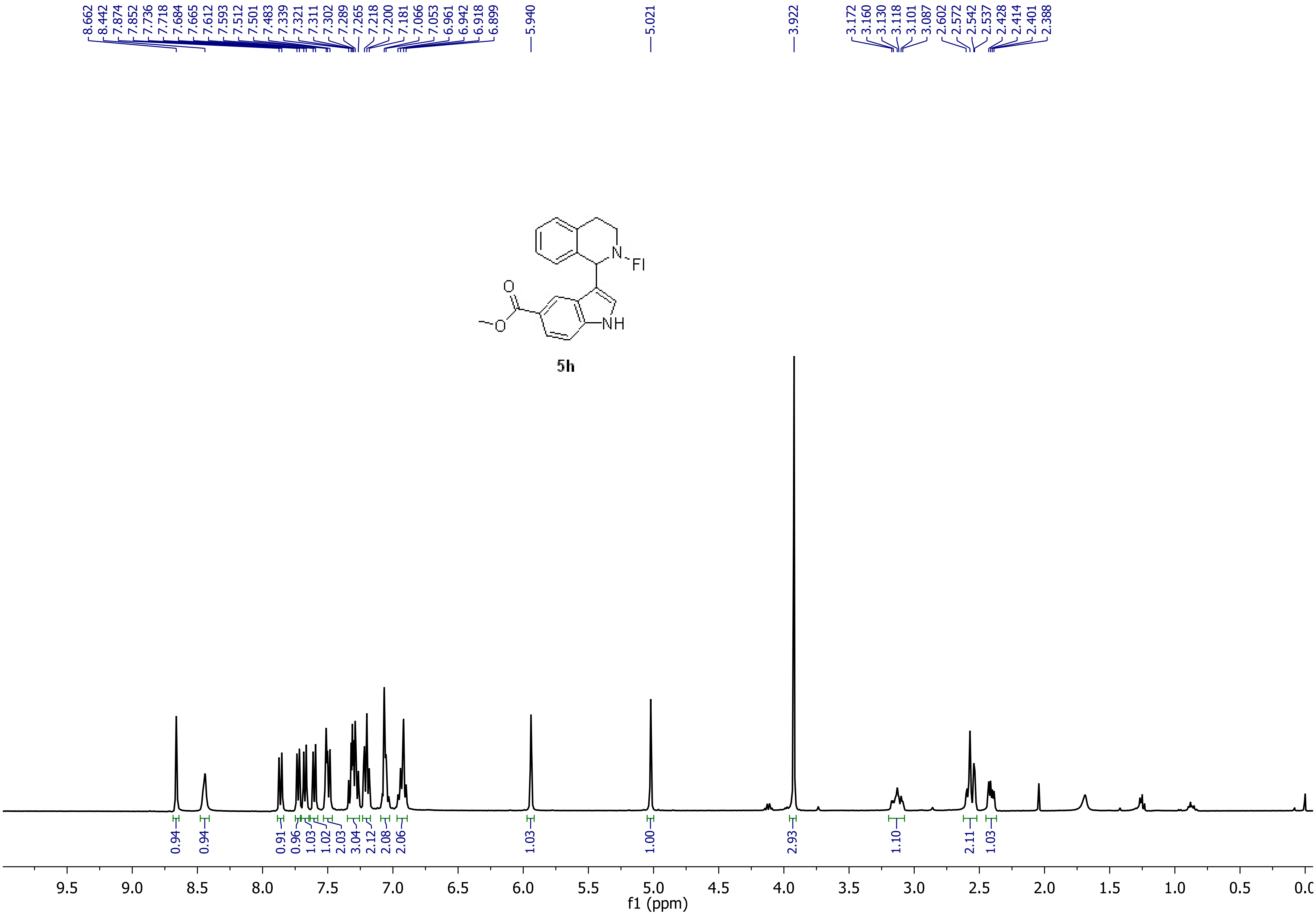
7.767
7.696
7.684
7.617
7.604
7.455
7.435
7.423
7.348
7.336
7.323
7.296
7.283
7.271
7.227
7.215
7.200
7.186
7.174
7.056
6.956
6.952
6.829
6.815
5.894
5.100
3.783
3.087
3.078
3.059
3.040
3.031
2.575
2.560
2.543
2.375
2.367
2.357
2.348
0.000
MeO
N
Fl
NH
1.02
1.07
1.02
1.05
1.02
1.16
1.33
1.29
2.79
1.80
1.91
2.02
1.03
1.06
1.00
3.24
1.12
2.18
1.08
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)


153.716
146.494
144.816
141.648
140.672
139.236
135.364
132.616
128.549
128.158
127.841
127.801
127.416
126.530
126.191
125.929
125.808
125.760
125.586
120.337
119.307
118.096
112.488
111.894
103.632
100.141
77.441
77.230
77.017
65.230
60.841
56.017
43.776
30.882
N
Fl
MeO
NH
5g
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

8.662
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7.874
7.852
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7.684
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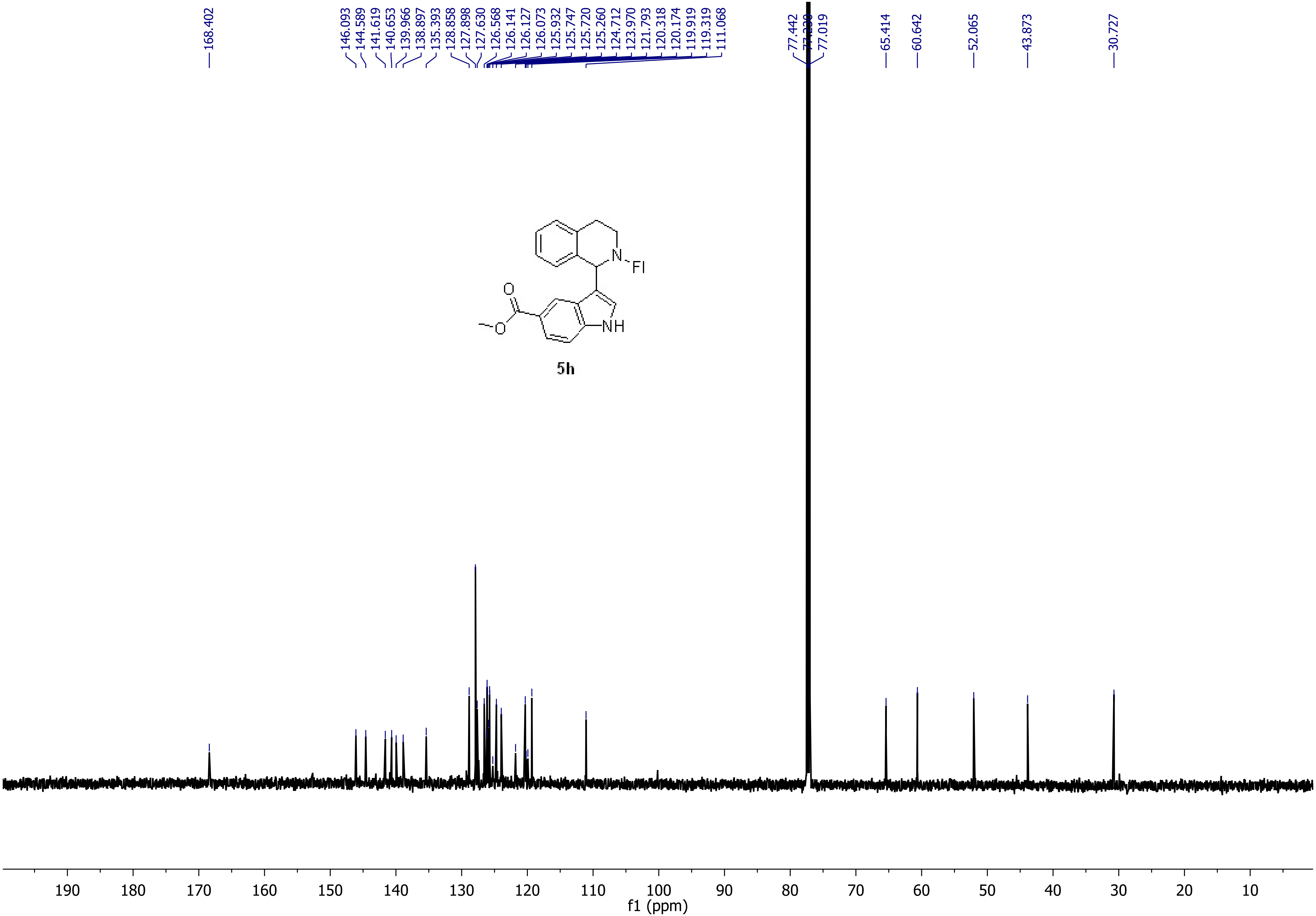
7.512
7.501
7.483
7.339
7.321
7.311
7.302
7.289
7.265
7.218
7.200
7.181
7.066
7.053
6.961
6.942
6.918
6.899
5.940
5.021
3.922
3.172
3.160
3.130
3.118
3.101
3.087
2.602
2.572
2.542
2.537
2.428
2.414
2.401
2.388
O
O
N
Fl
NH
5h
0.94
0.94
0.91
0.96
1.03
1.02
2.03
3.04
2.12
2.08
2.06
1.03
1.00
2.93
1.10
2.11
1.03
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
f1 (ppm)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140.653
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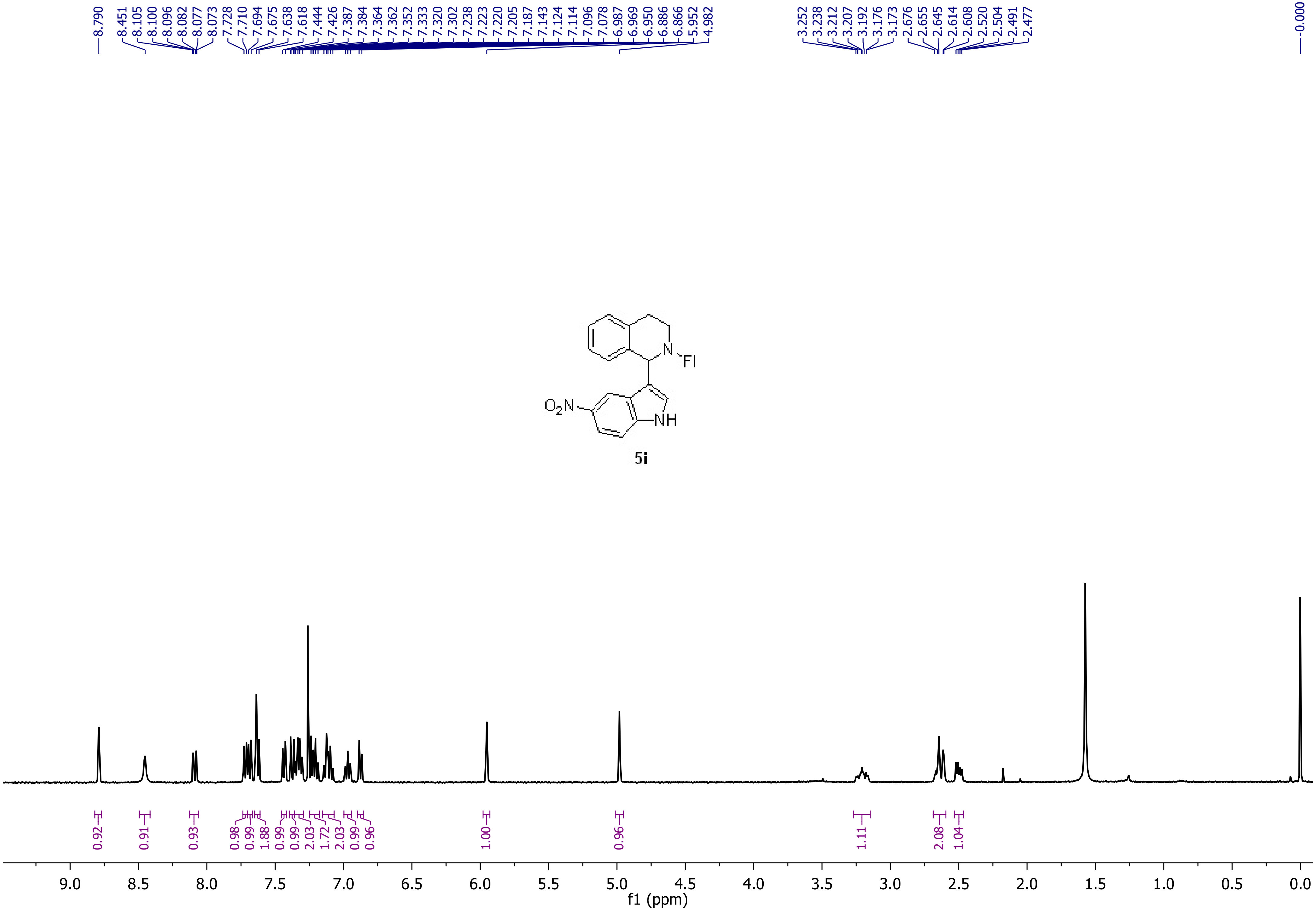
135.393
128.858
127.898
127.630
126.568
126.141
126.127
126.073
125.932
125.747
125.720
125.260
124.712
123.970
121.793
120.318
120.174
119.919
119.319
111.068
77.442
77.230
77.019
65.414
60.642
52.065
43.873
30.727
N
Fl
O
O
NH
5h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.790
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8.105
8.100
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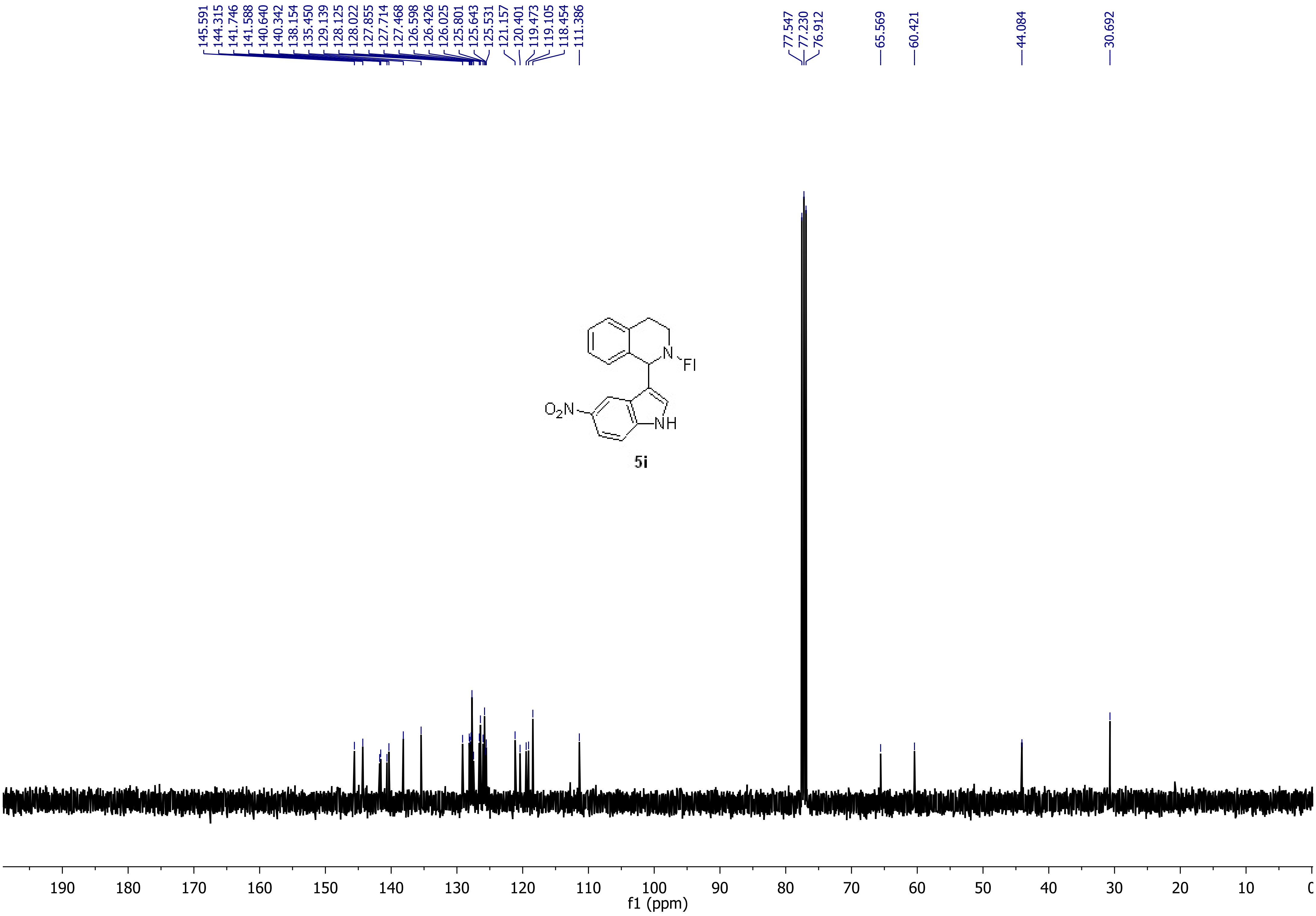
8.082
8.077
8.073
7.728
7.710
7.694
7.675
7.638
7.618
7.444
7.426
7.387
7.384
7.364
7.362
7.352
7.333
7.320
7.302
7.238
7.223
7.220
7.205
7.187
7.143
7.124
7.114
7.096
7.078
6.987
6.969
6.950
6.886
6.866
5.952
4.982
3.252
3.238
3.212
3.207
3.192
3.176
3.173
2.676
2.655
2.645
2.614
2.608
2.520
2.504
2.491
2.477
-0.000
N
Fl
O2N
NH
0.92
0.91
0.93
0.98
0.99
1.88
0.99
0.99
2.03
1.72
2.03
0.99
0.96
1.00
0.96
1.11
2.08
1.04
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
f1 (ppm)

5i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144.315
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141.588
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140.342
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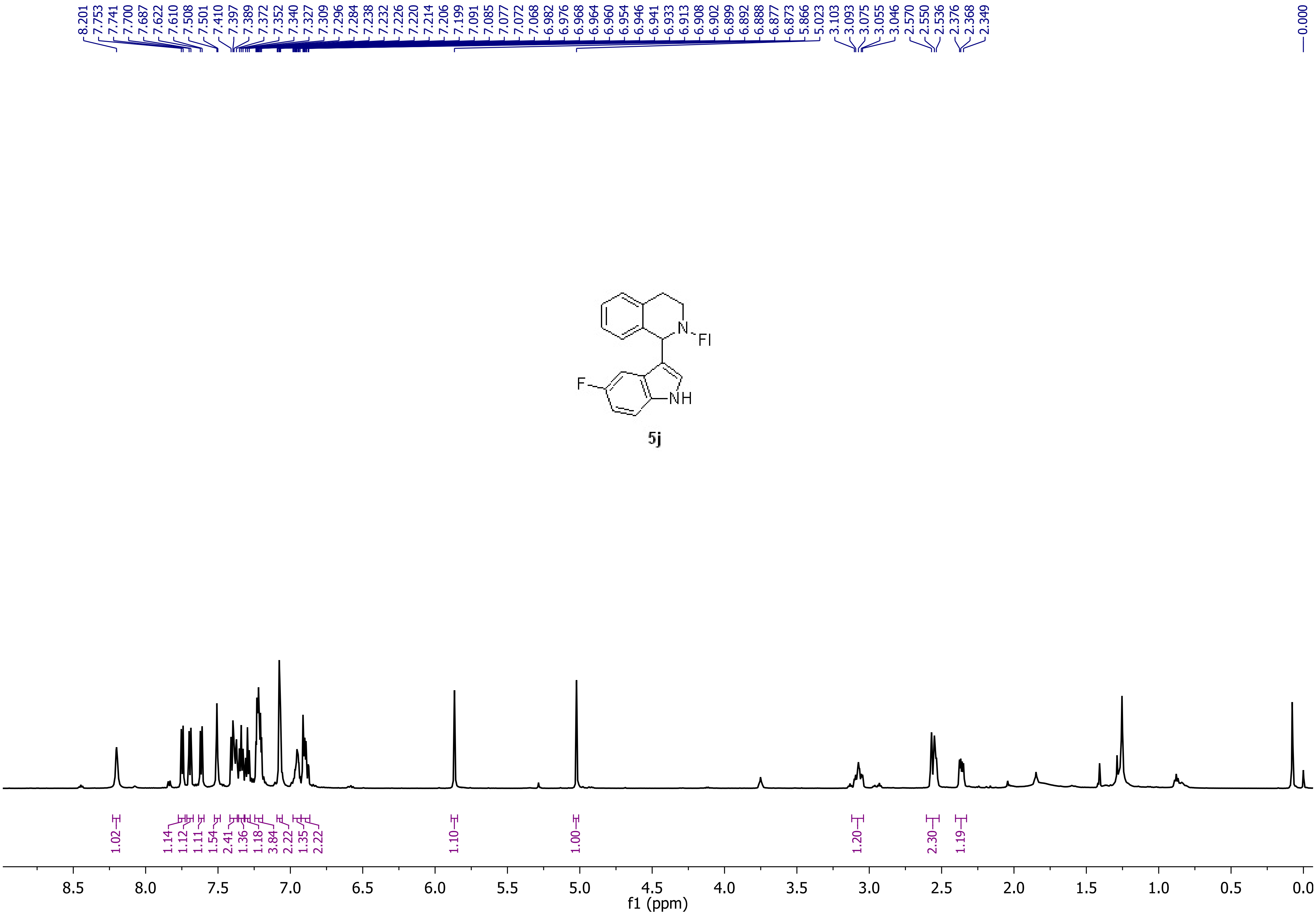
f1 (ppm)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Fl
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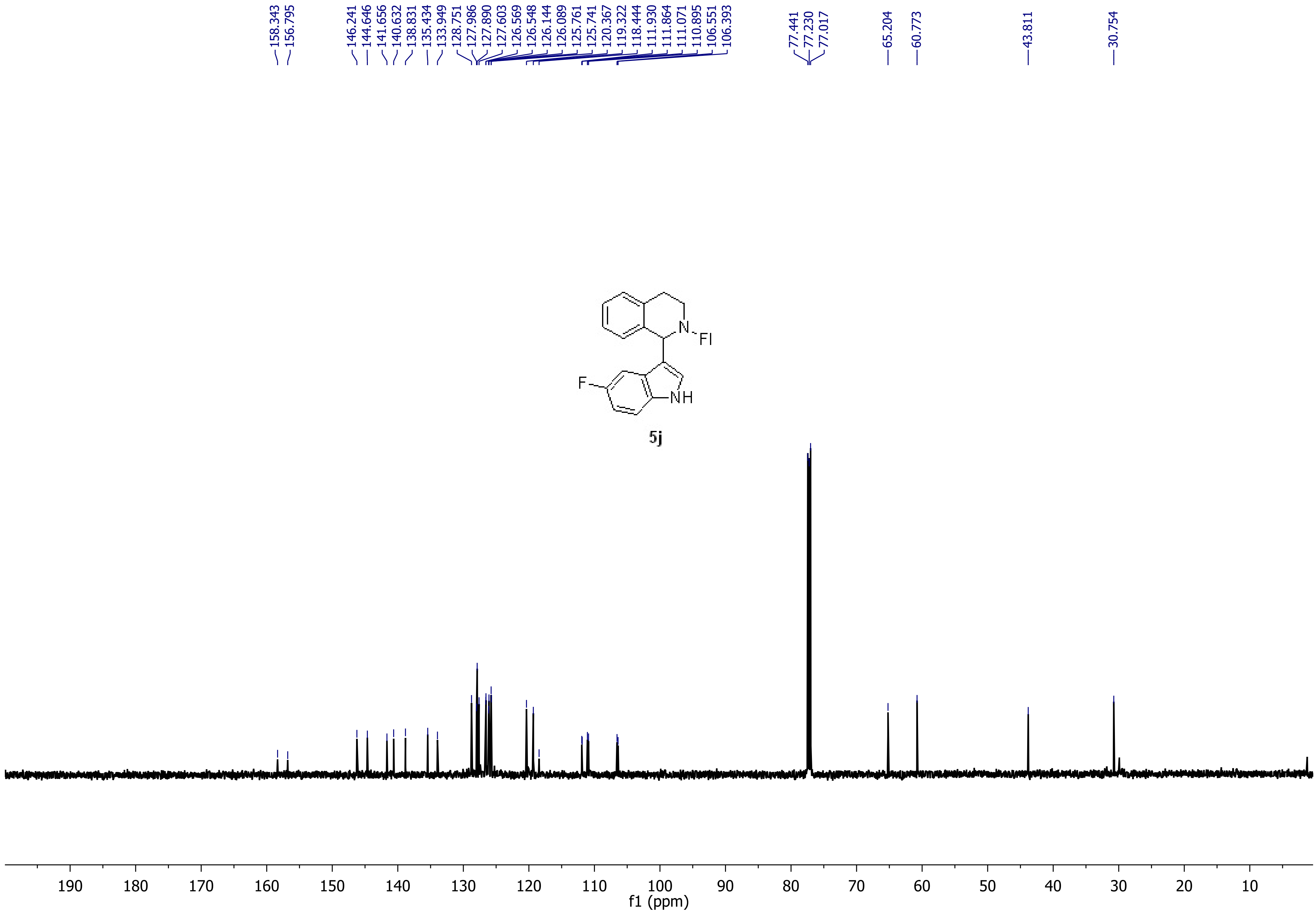
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N
Fl
F
NH
5j
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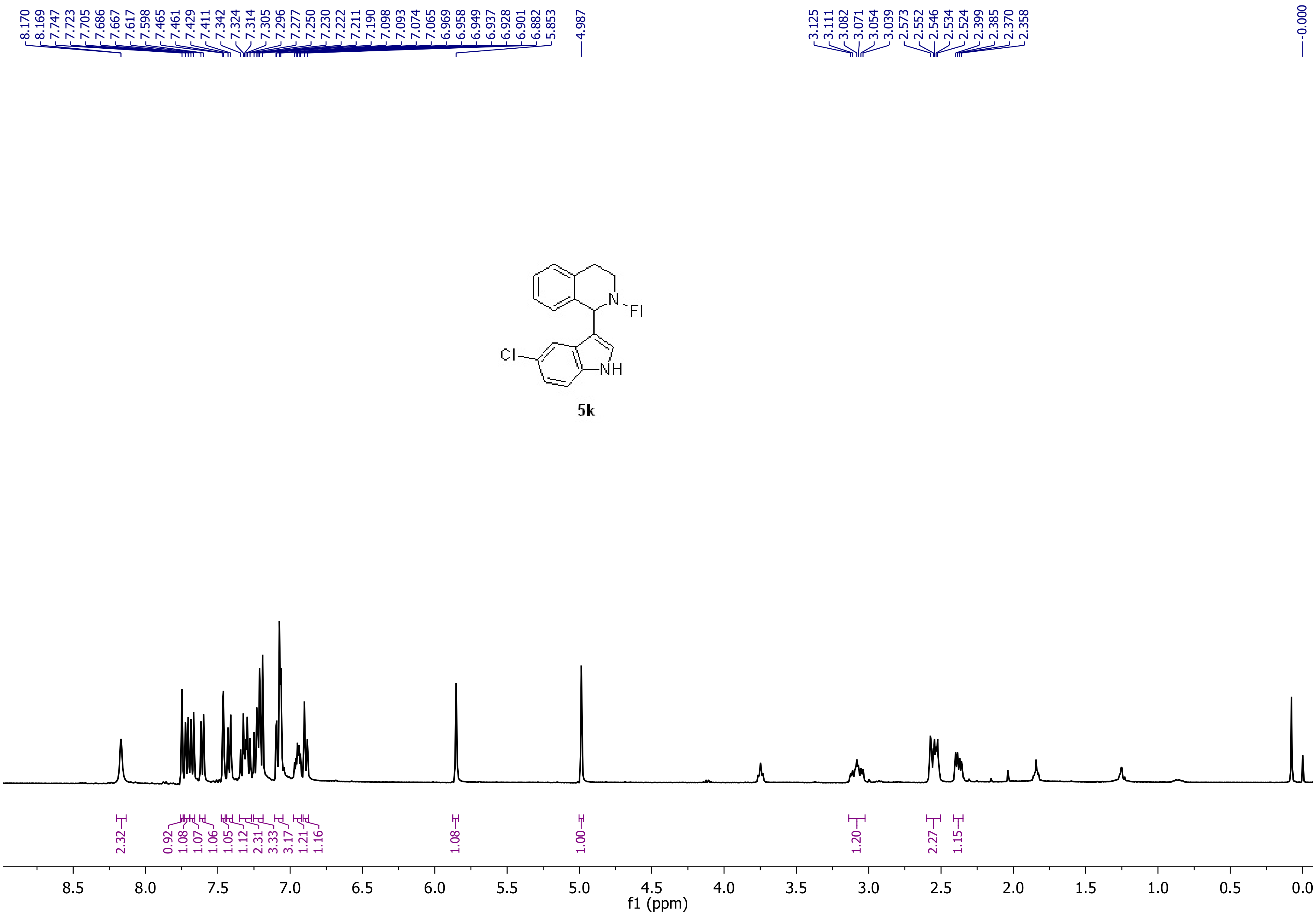
f1 (ppm)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7.296
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7.230
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6.928
6.901
6.882
5.853
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3.111
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3.071
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Cl
N
Fl
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5k
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1.16
1.08
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6.0
5.5
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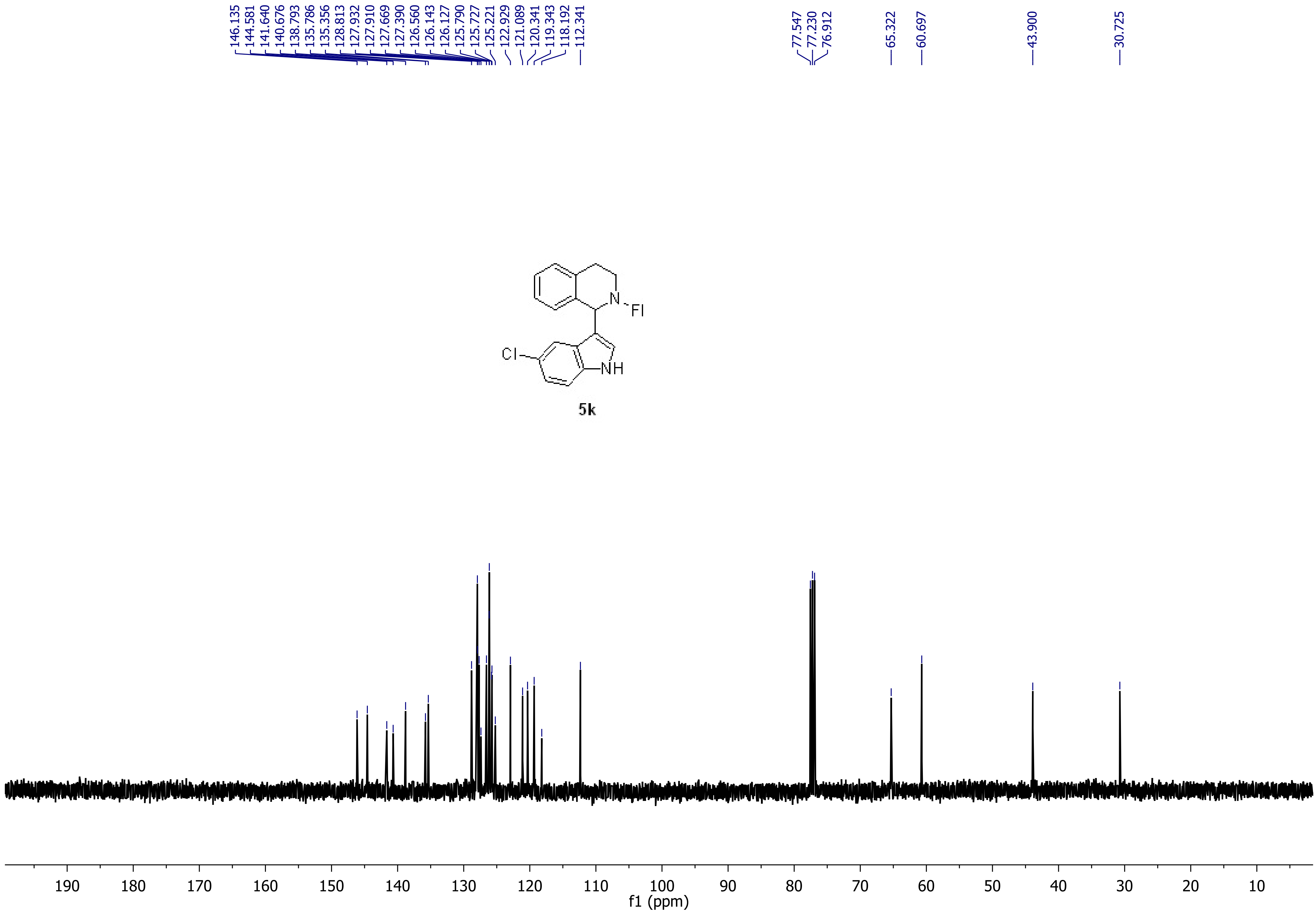
f1 (ppm)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Fl
Cl
NH
190
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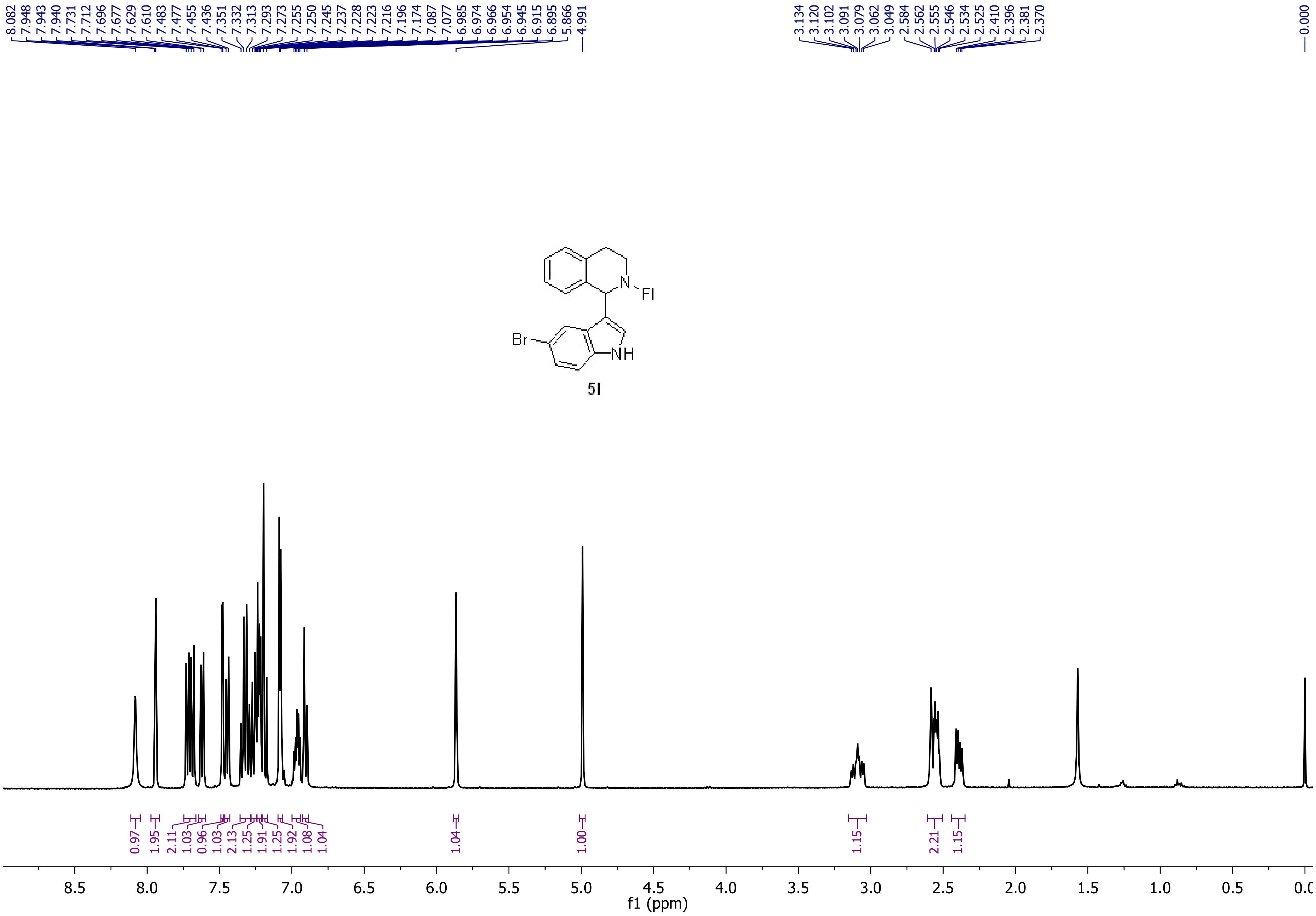
f1 (ppm)

5k



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7.313
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7.245
7.237
7.228
7.223
7.216
7.196
7.174
7.087
7.077
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6.974
6.966
6.954
6.945
6.915
6.895
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3.091
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2.546
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Fl
Br
NH
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2.13
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1.08
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1.04
1.00
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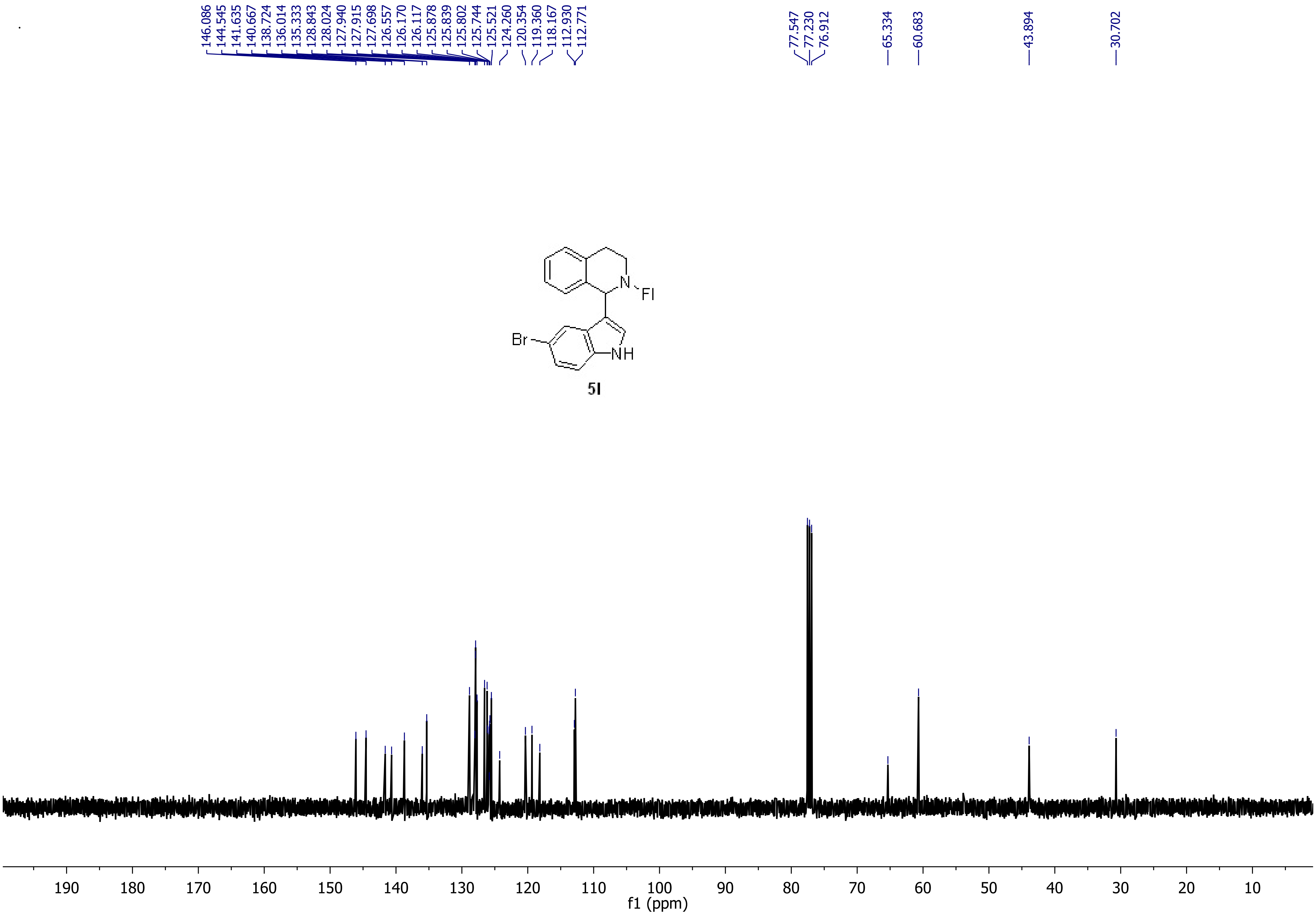
f1 (ppm)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Fl
Br
NH
190
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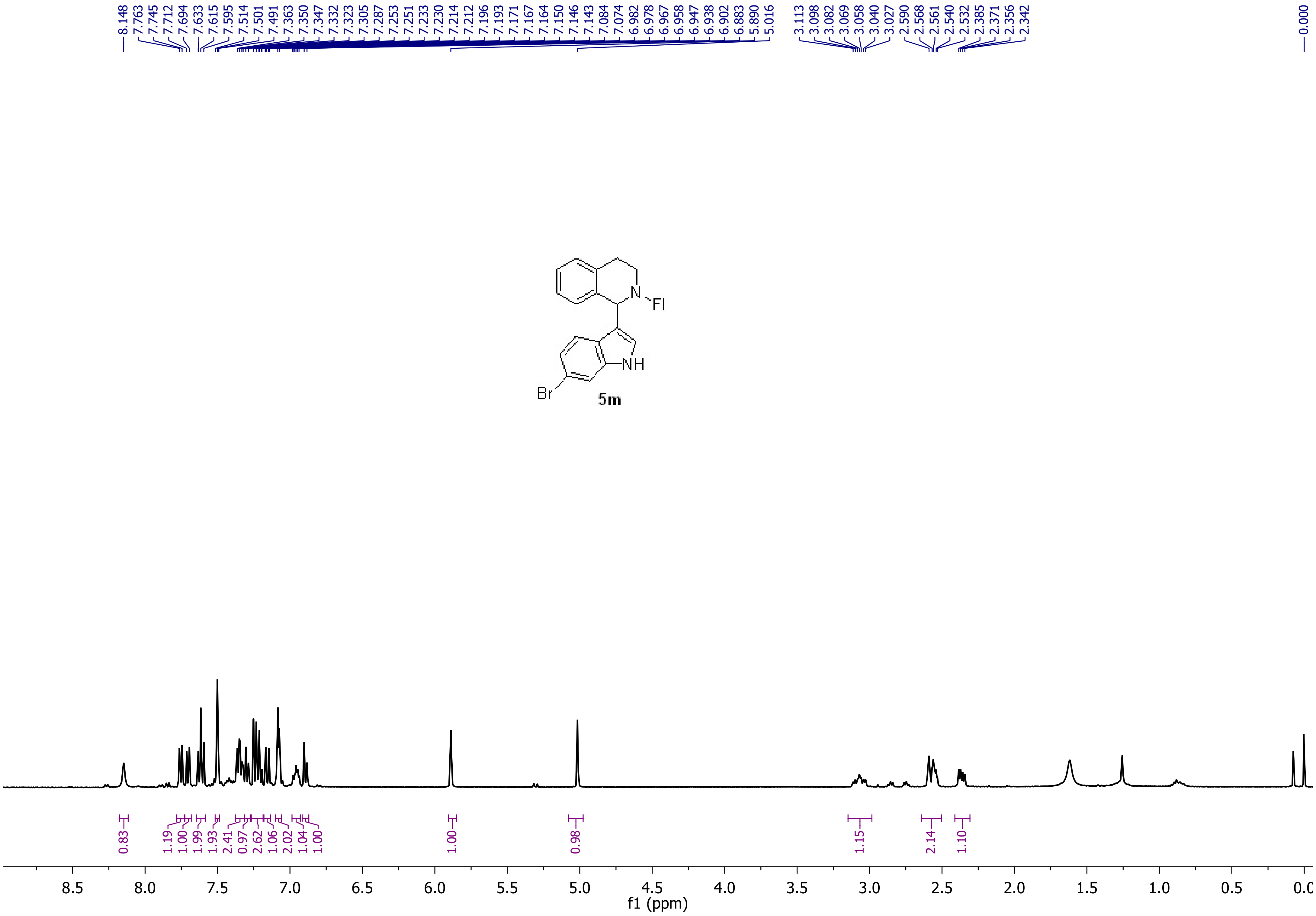
f1 (ppm)

5l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6.938
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Fl
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Br
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1.00
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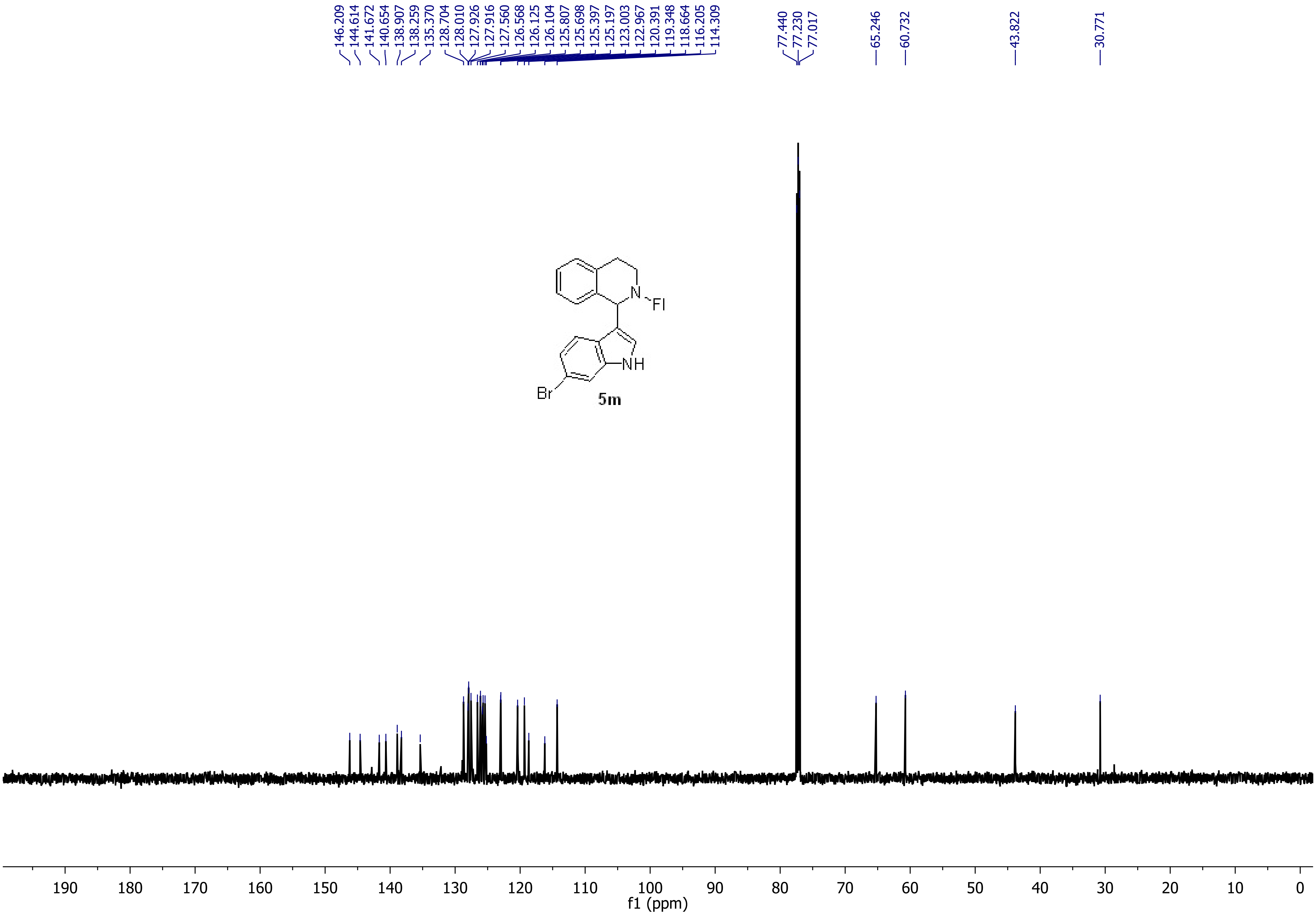
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77.440
77.230
77.017
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60.732
43.822
30.771
N
Fl
NH
Br
5m
190
180
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120
110
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90
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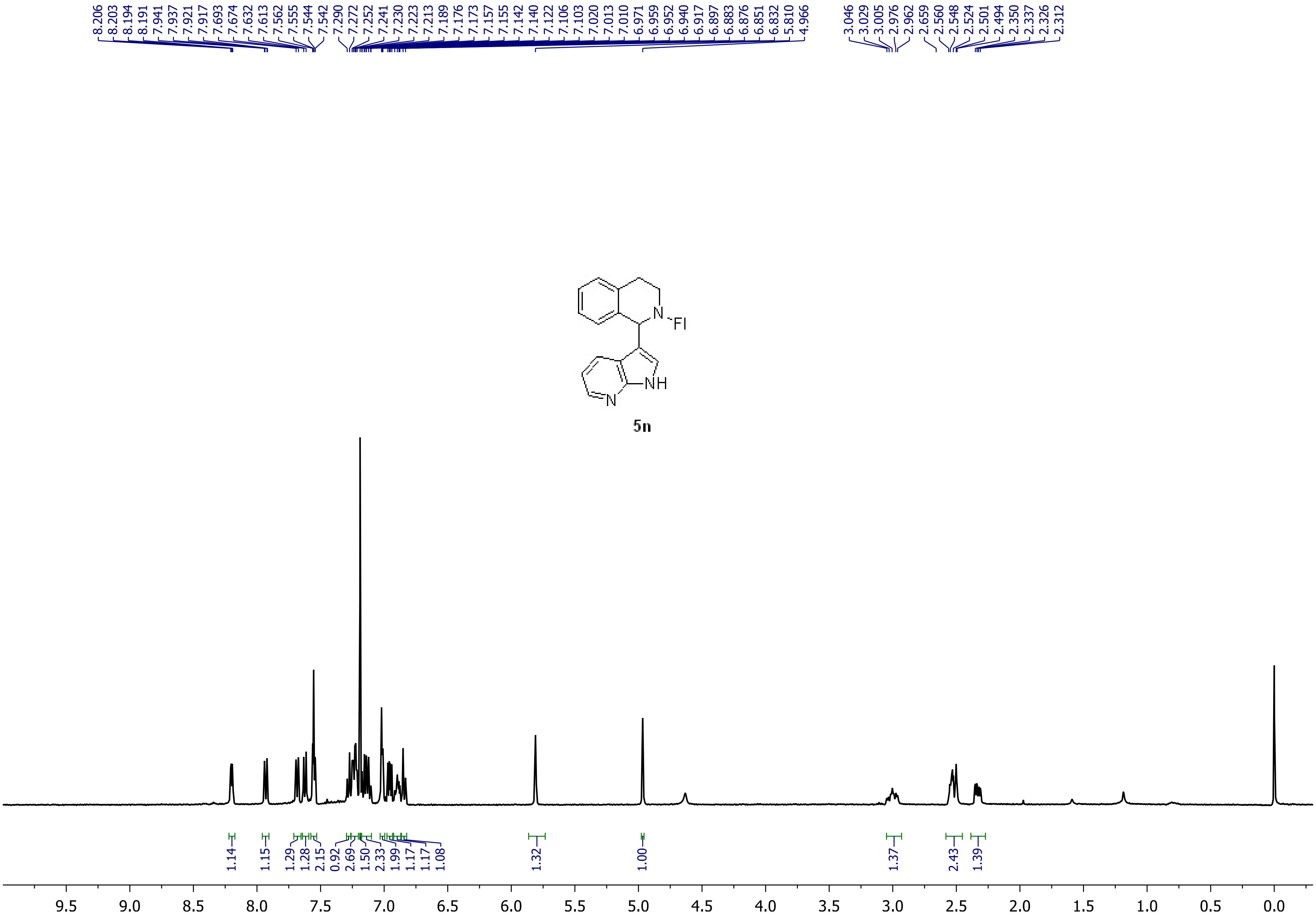
f1 (ppm)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6.0
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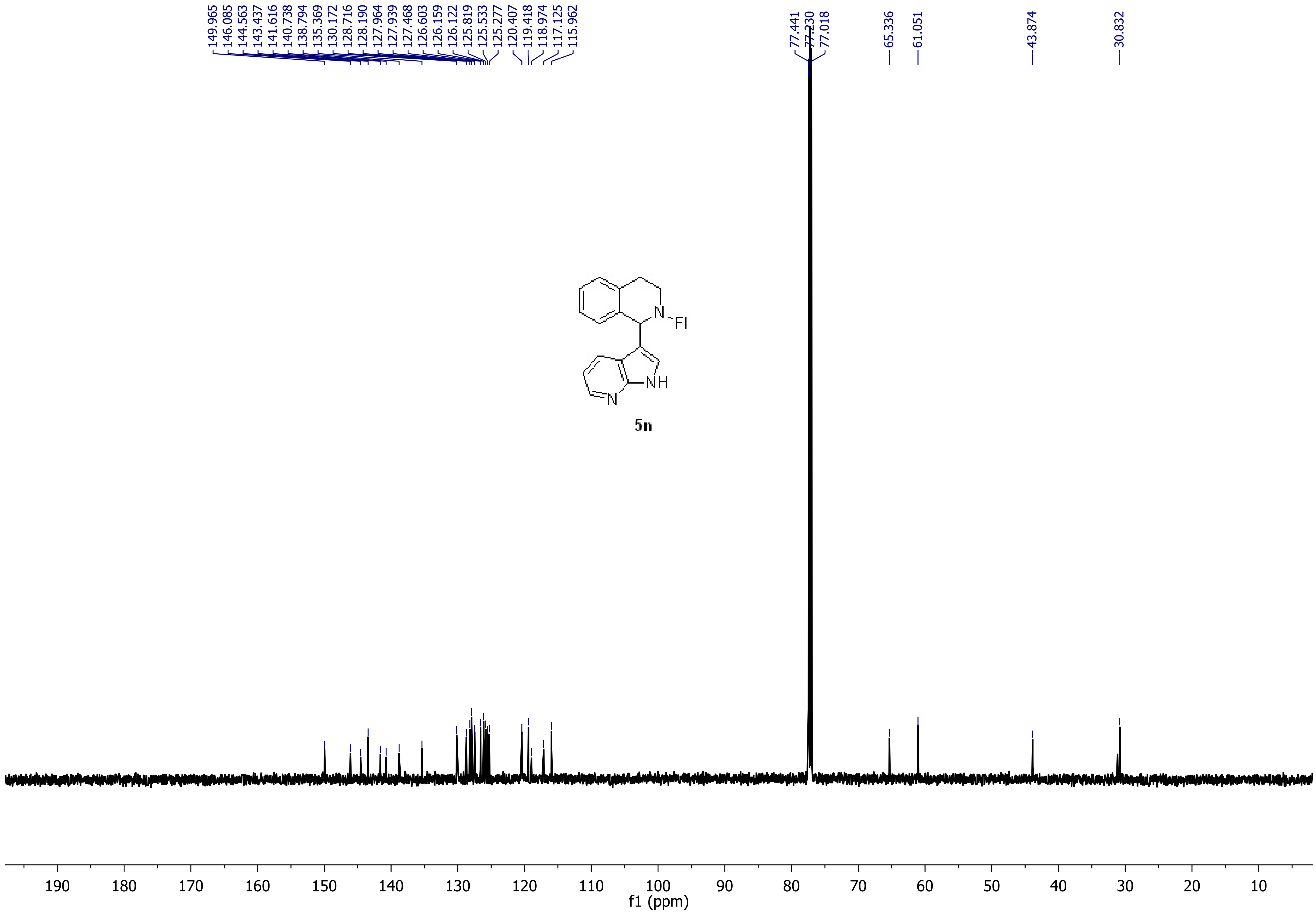
5n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Fl
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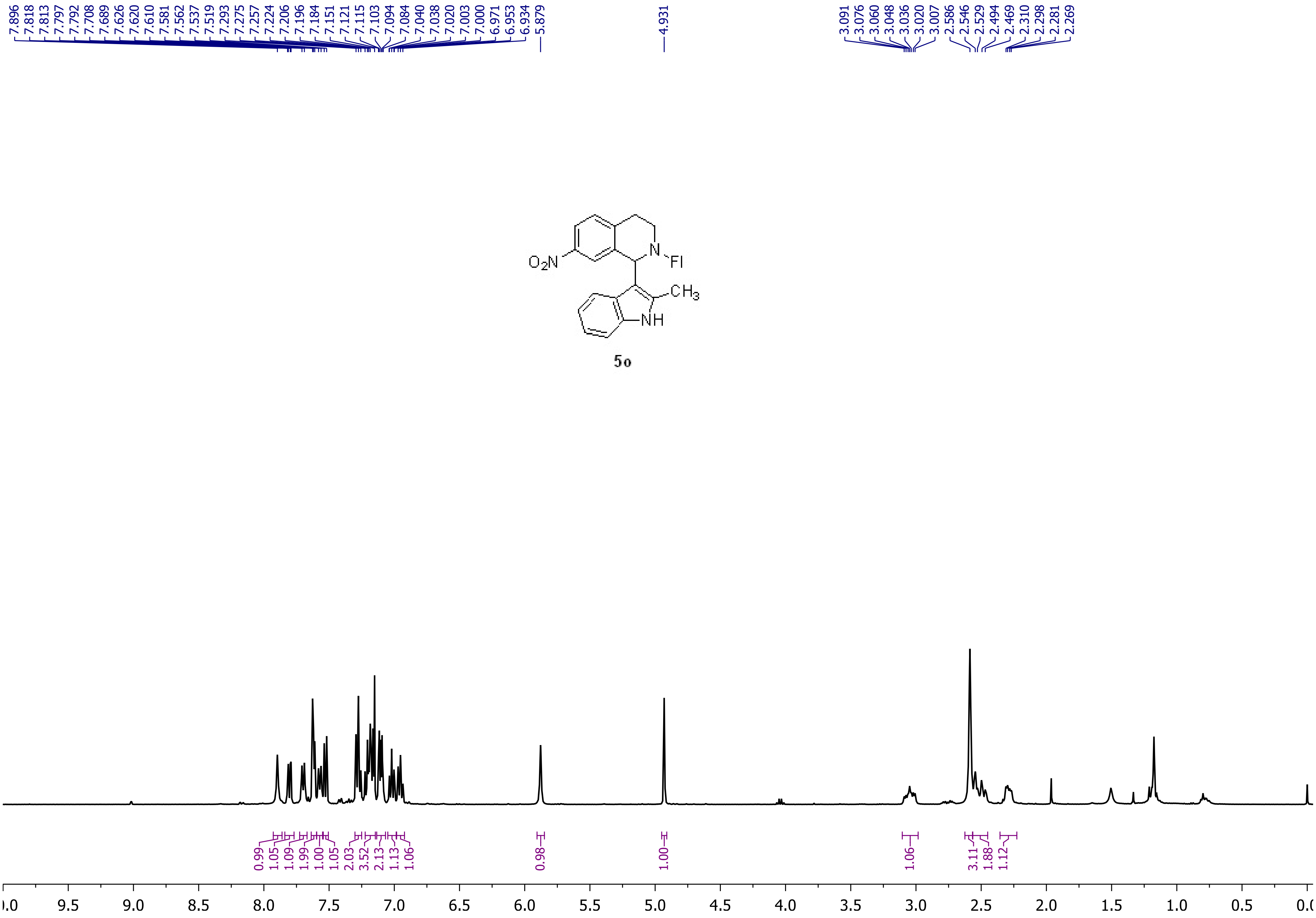
f1 (ppm)

5n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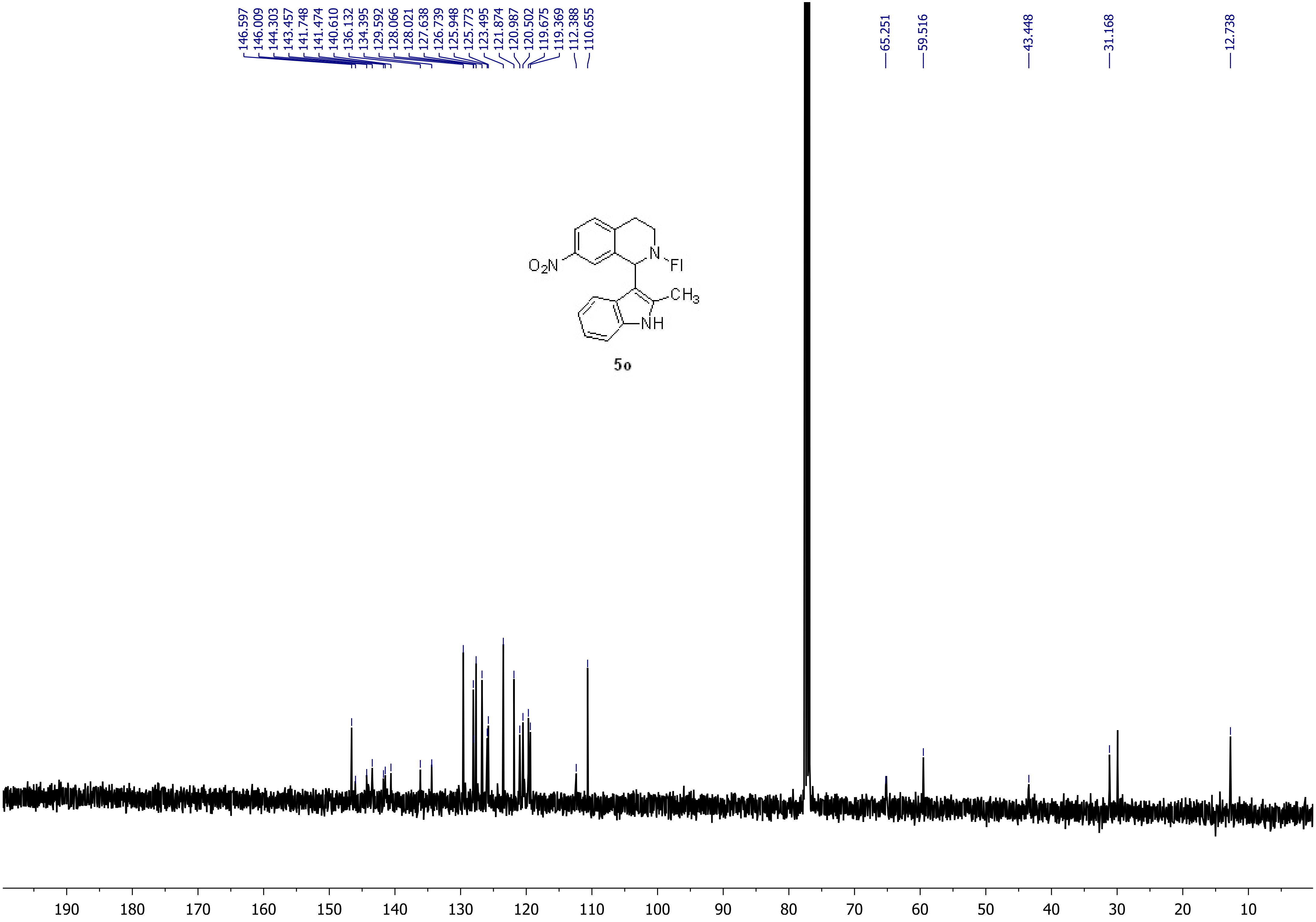
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N
Fl
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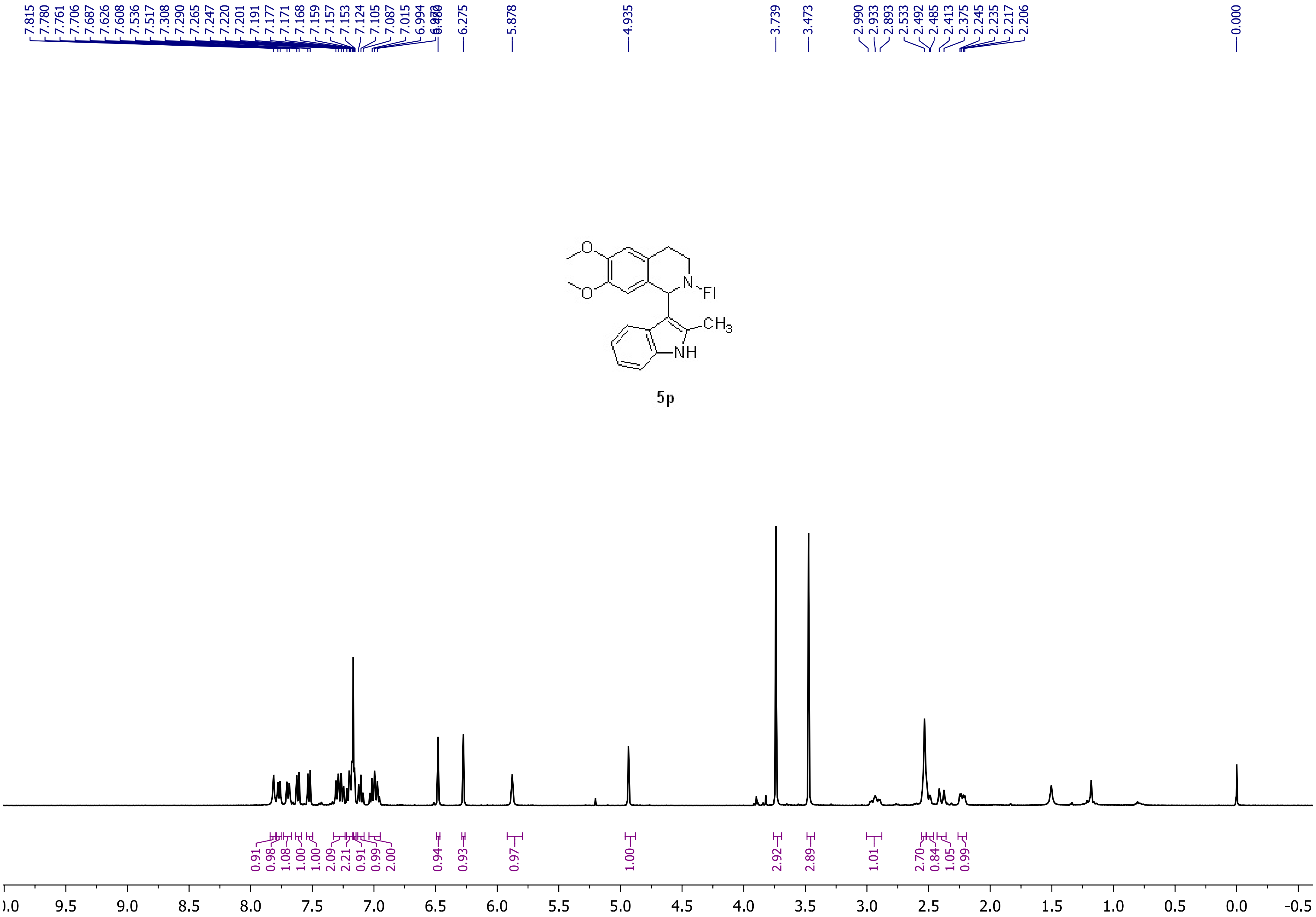
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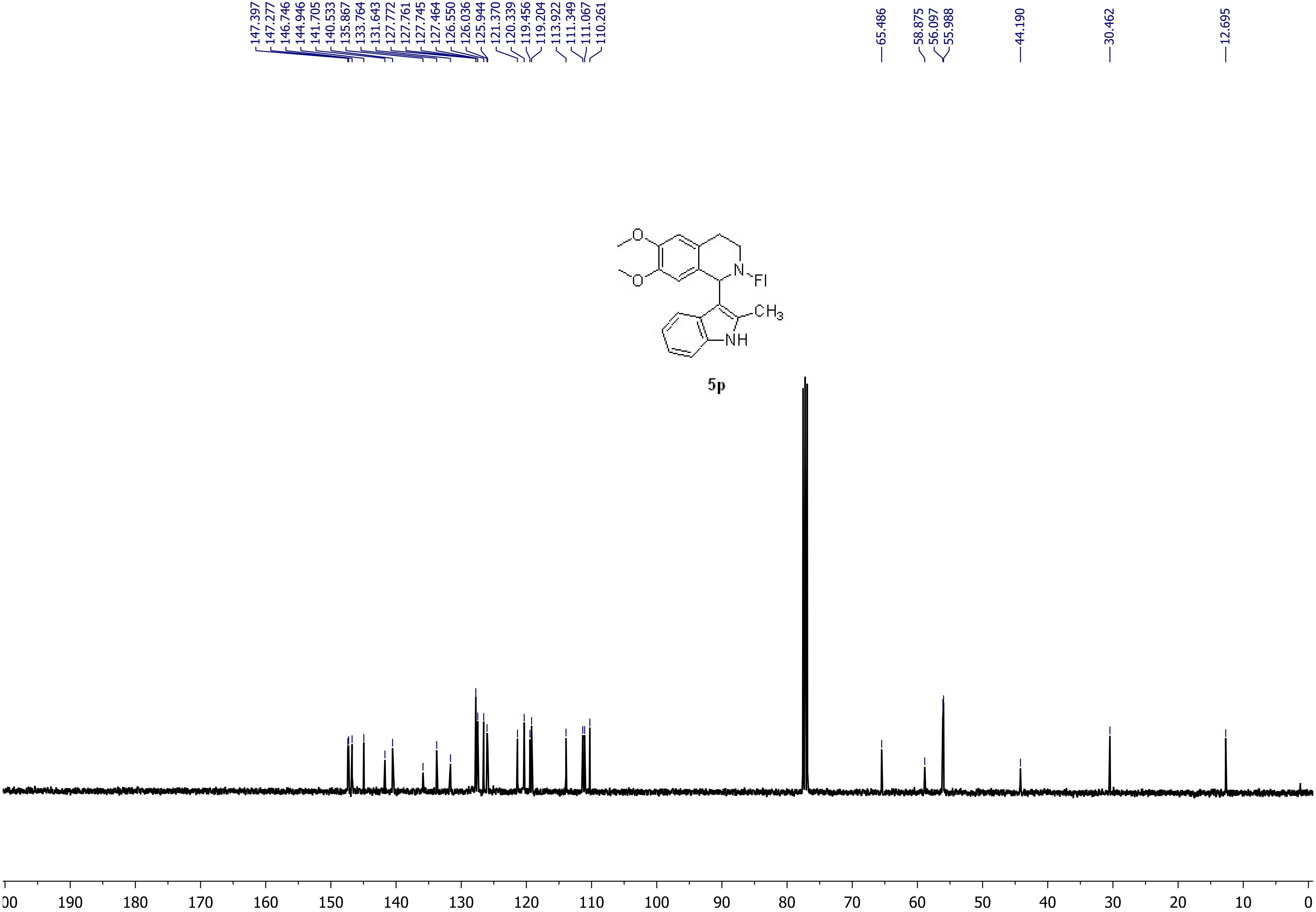
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111.349
111.067
110.261
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44.190
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12.695
O
O
N
Fl
CH3
NH
00
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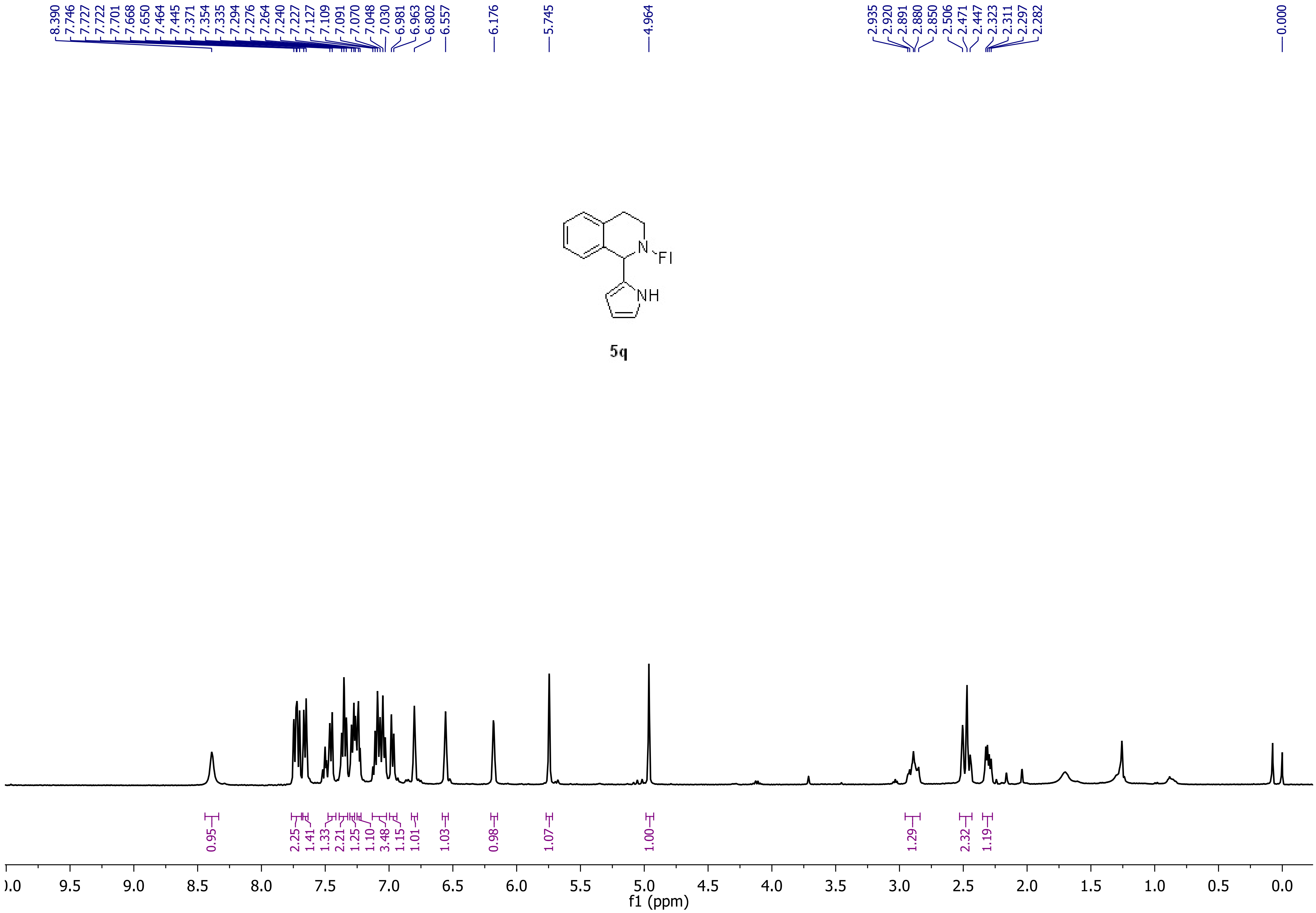
5p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Fl
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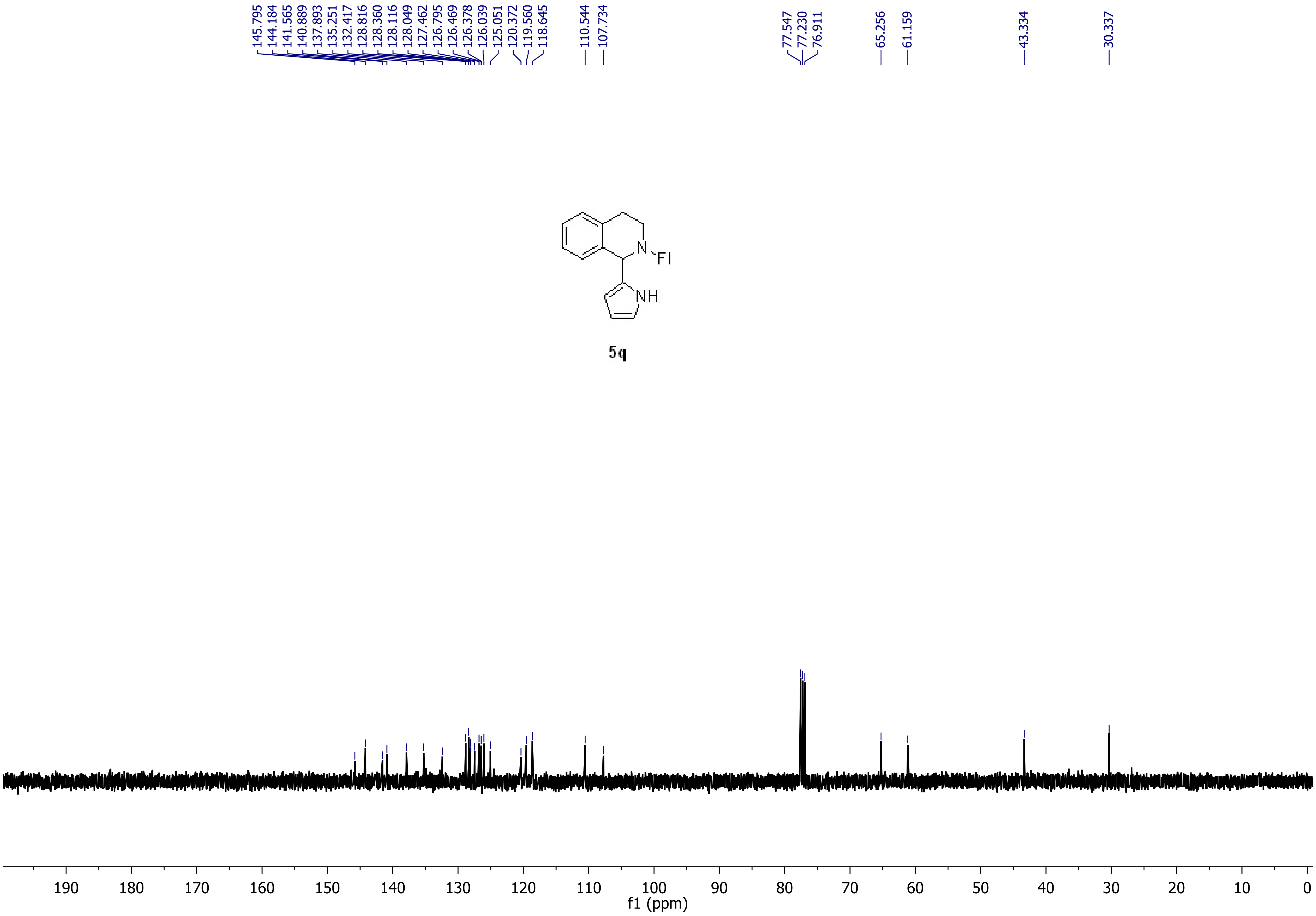
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76.911
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Fl
NH
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180
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30
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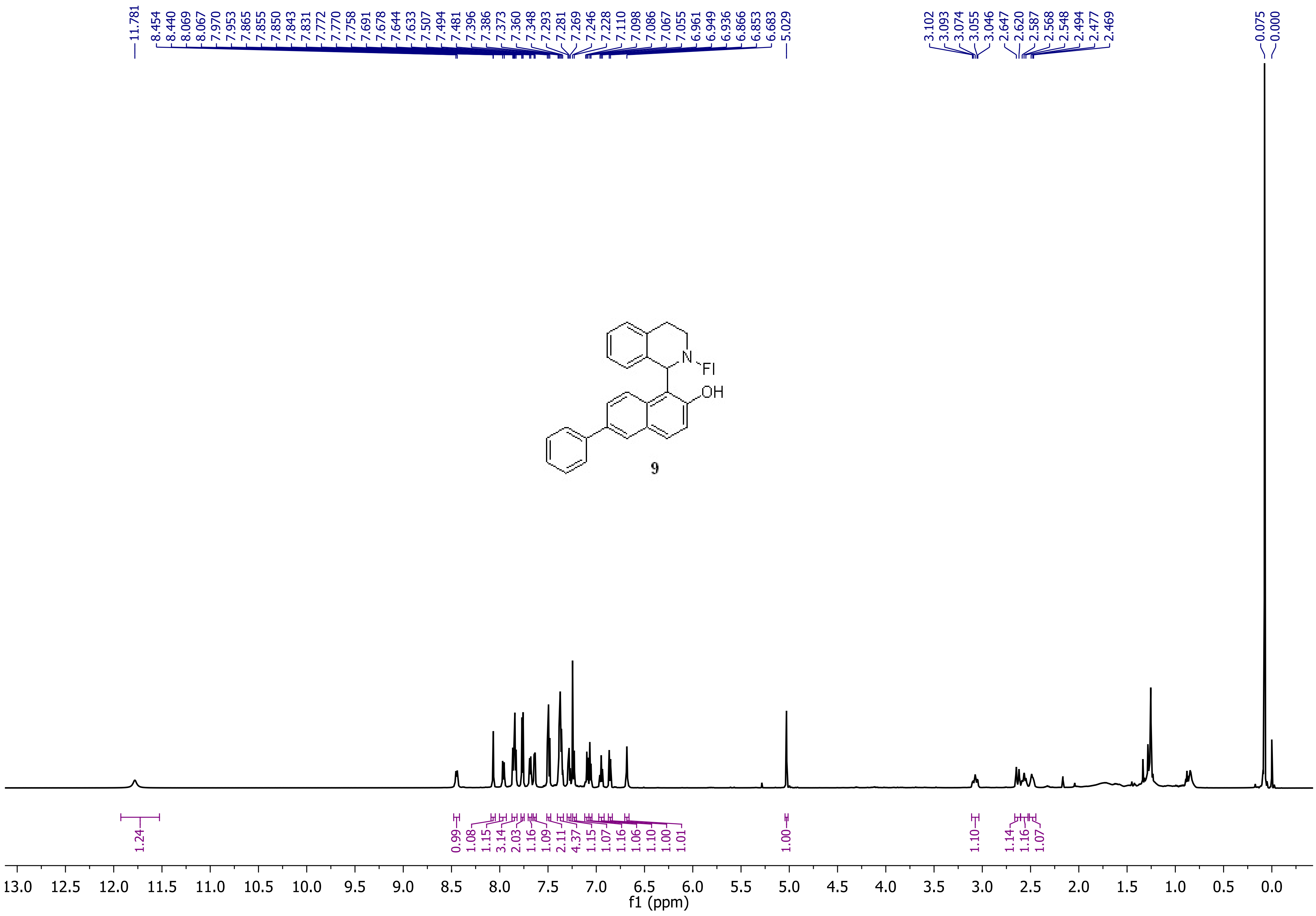
f1 (ppm)

5q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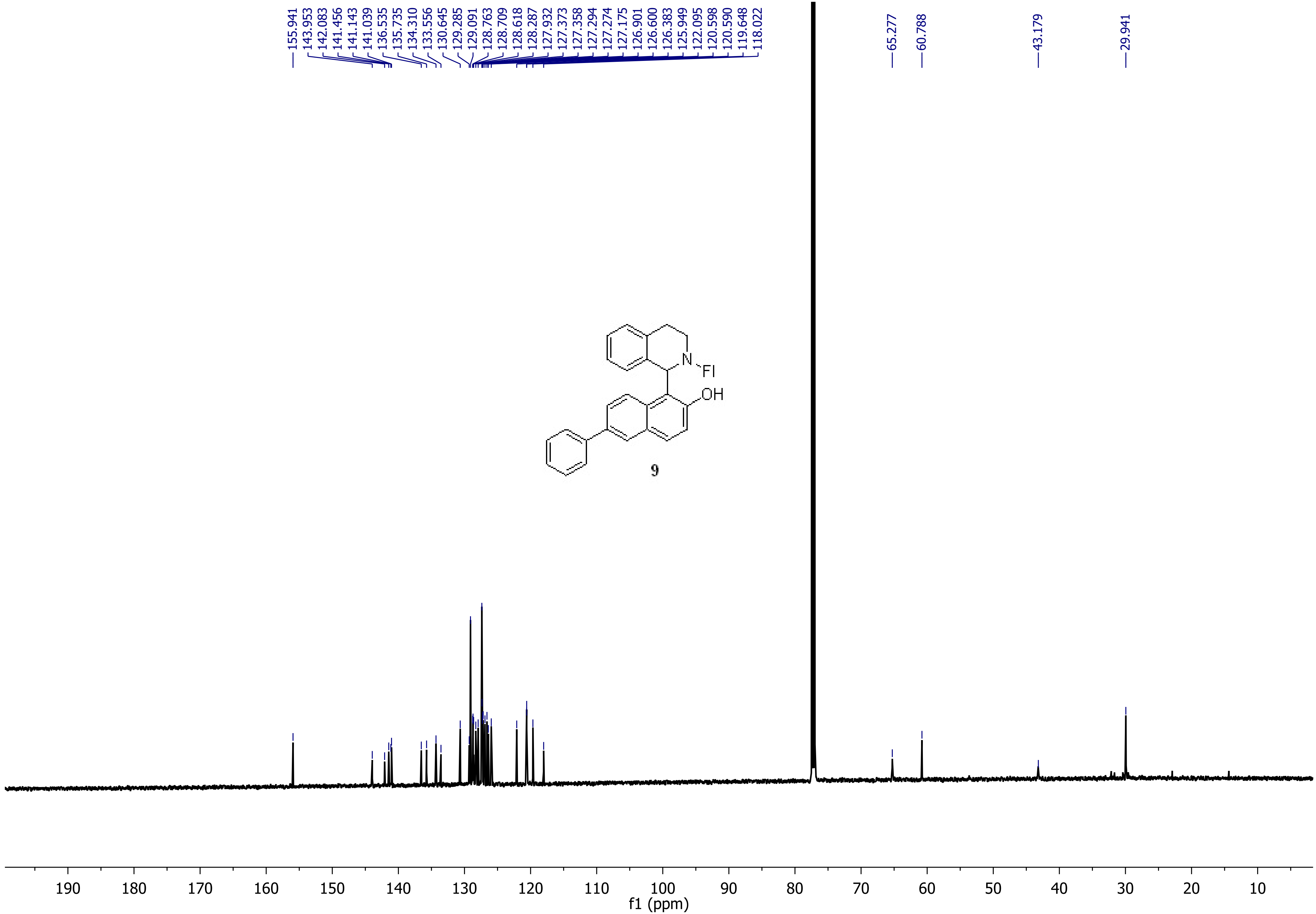
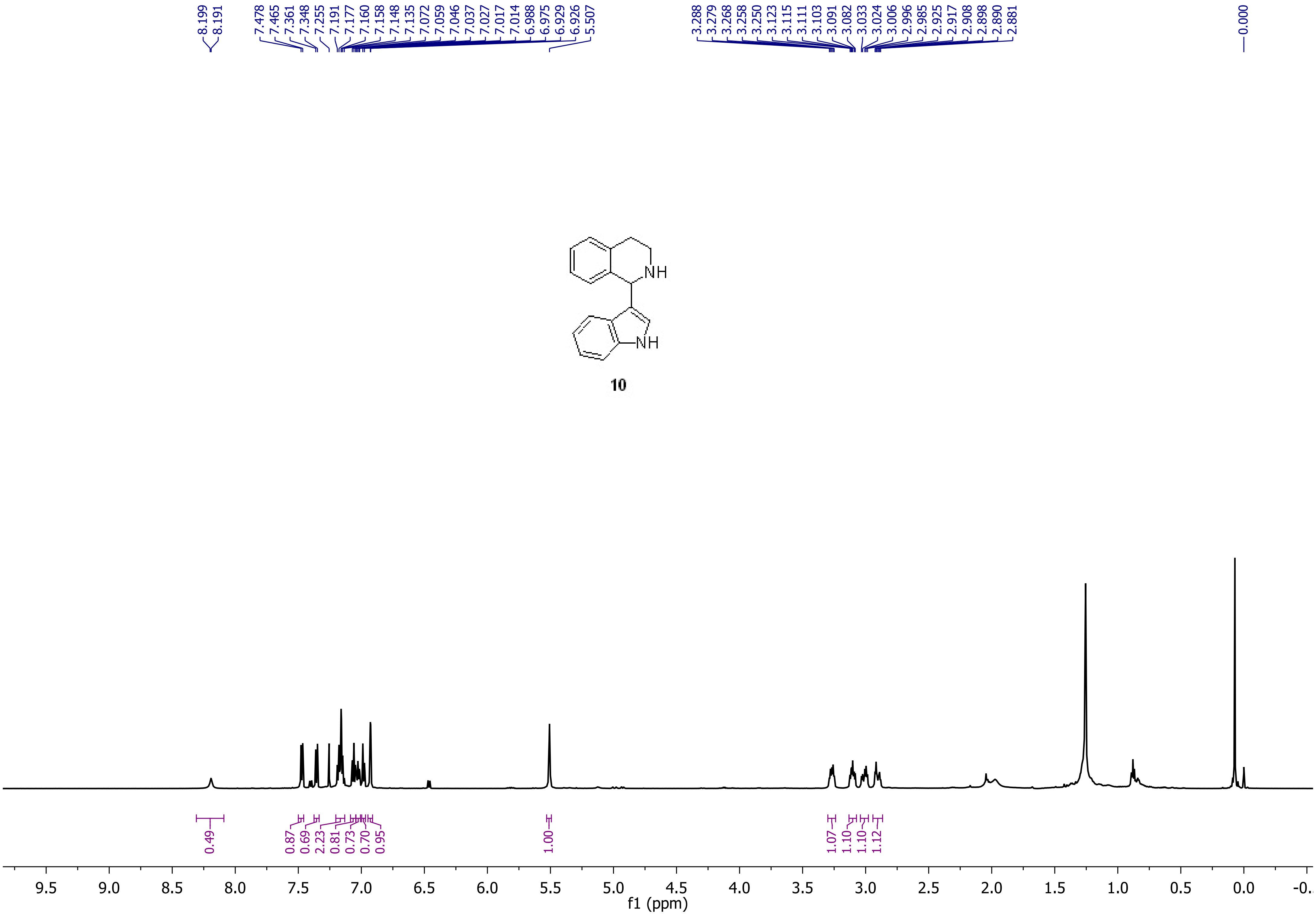
0.000
N
Fl
OH
9
1.24
0.99
1.08
1.15
3.14
2.03
1.16
1.09
2.11
4.37
1.15
1.07
1.16
1.06
1.10
1.00
1.01
1.00
1.10
1.14
1.16
1.07
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



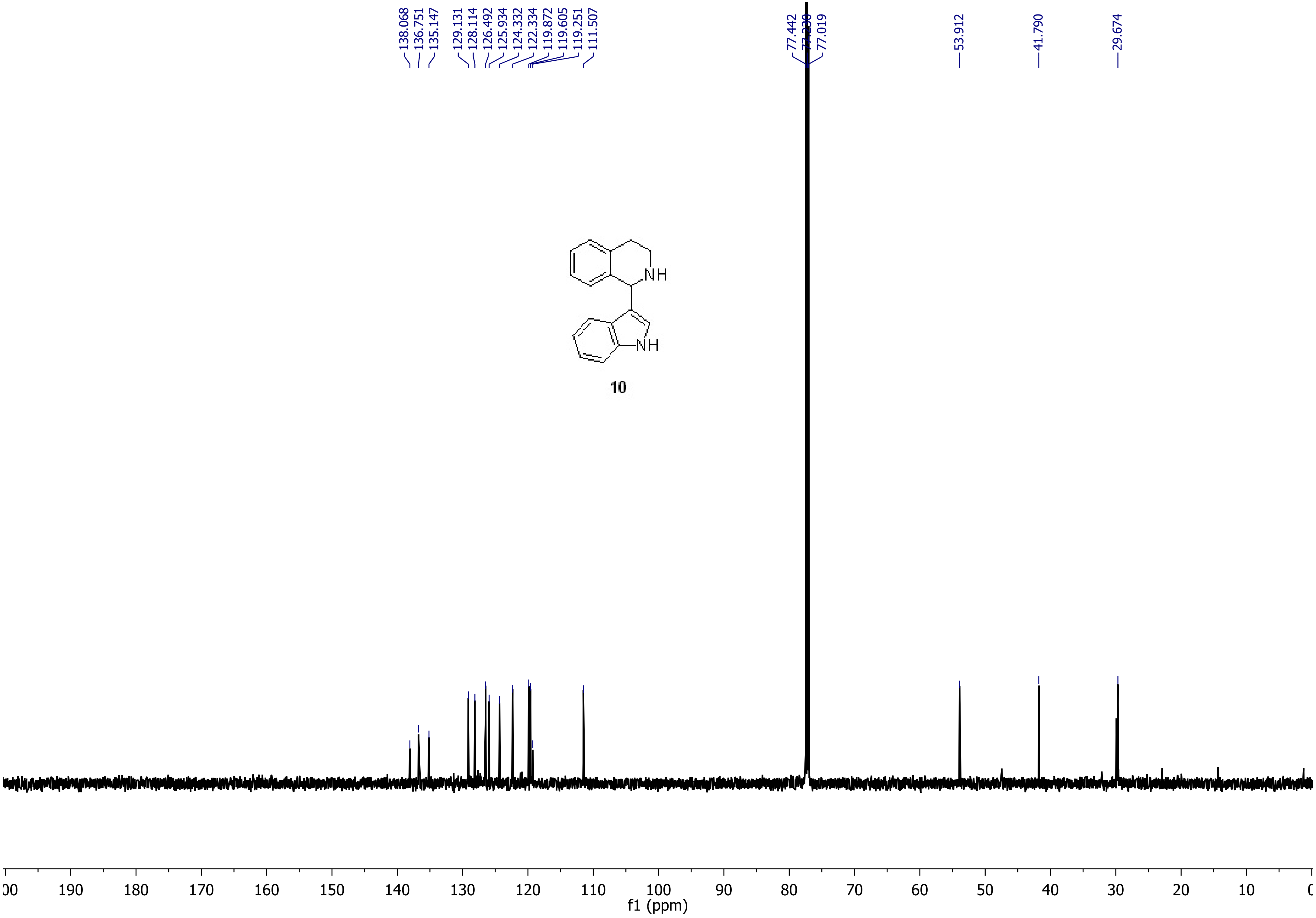
9

155.941
143.953
142.083
141.456
141.143
141.039
136.535
135.735
134.310
133.556
130.645
129.285
129.091
128.763
128.709
128.618
128.287
127.932
127.373
127.358
127.294
127.274
127.175
126.901
126.600
126.383
125.949
122.095
120.598
120.590
119.648
118.022
65.277
60.788
43.179
29.941
N
Fl
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



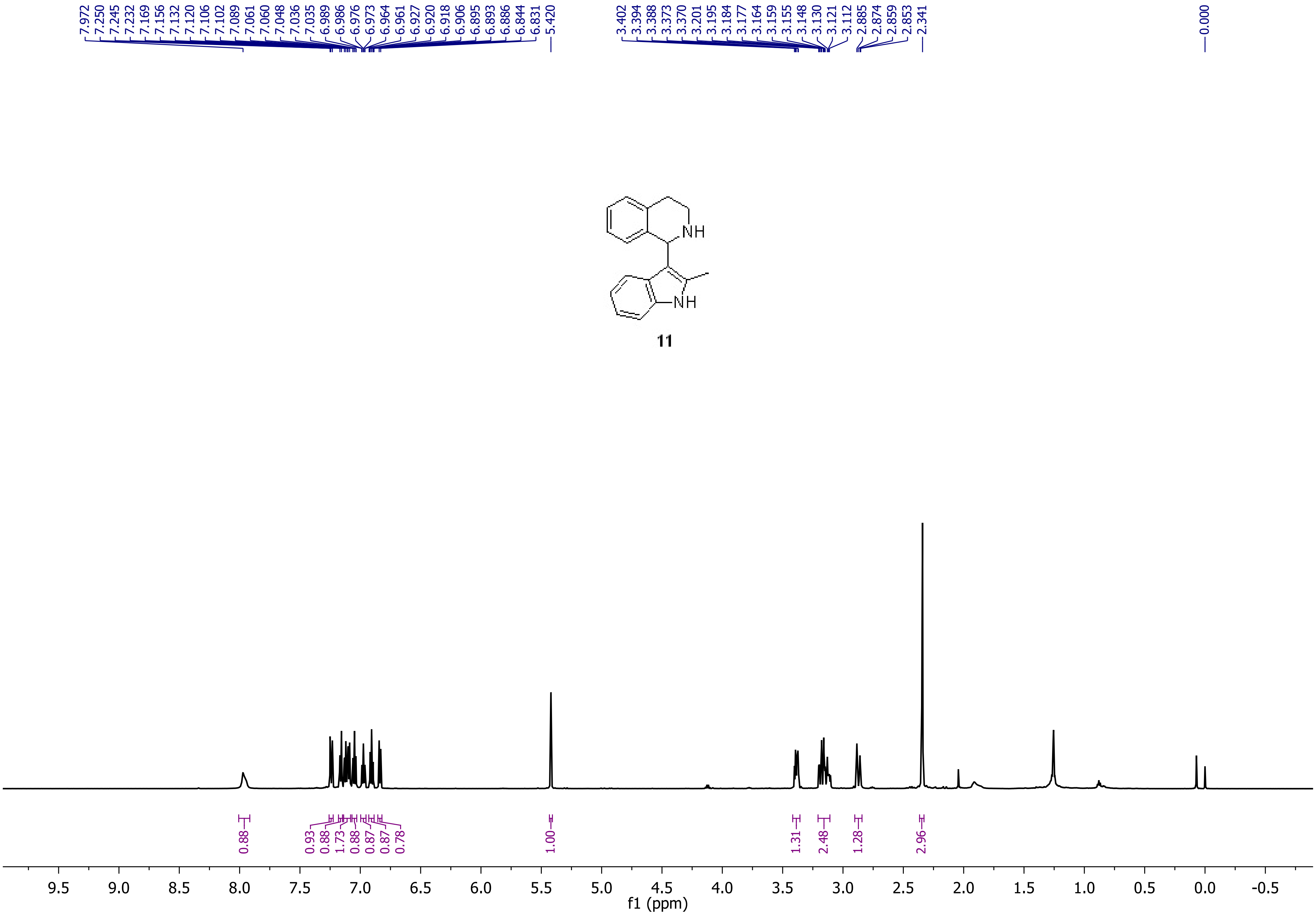
8.199
8.191
7.478
7.465
7.361
7.348
7.255
7.191
7.177
7.160
7.158
7.148
7.135
7.072
7.059
7.046
7.037
7.027
7.017
7.014
6.988
6.975
6.929
6.926
5.507
3.288
3.279
3.268
3.258
3.250
3.123
3.115
3.111
3.103
3.091
3.082
3.033
3.024
3.006
2.996
2.985
2.925
2.917
2.908
2.898
2.890
2.881
0.000
NH
NH
0.49
0.87
0.69
2.23
0.81
0.73
0.70
0.95
1.00
1.07
1.10
1.10
1.12
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.
f1 (ppm)

10

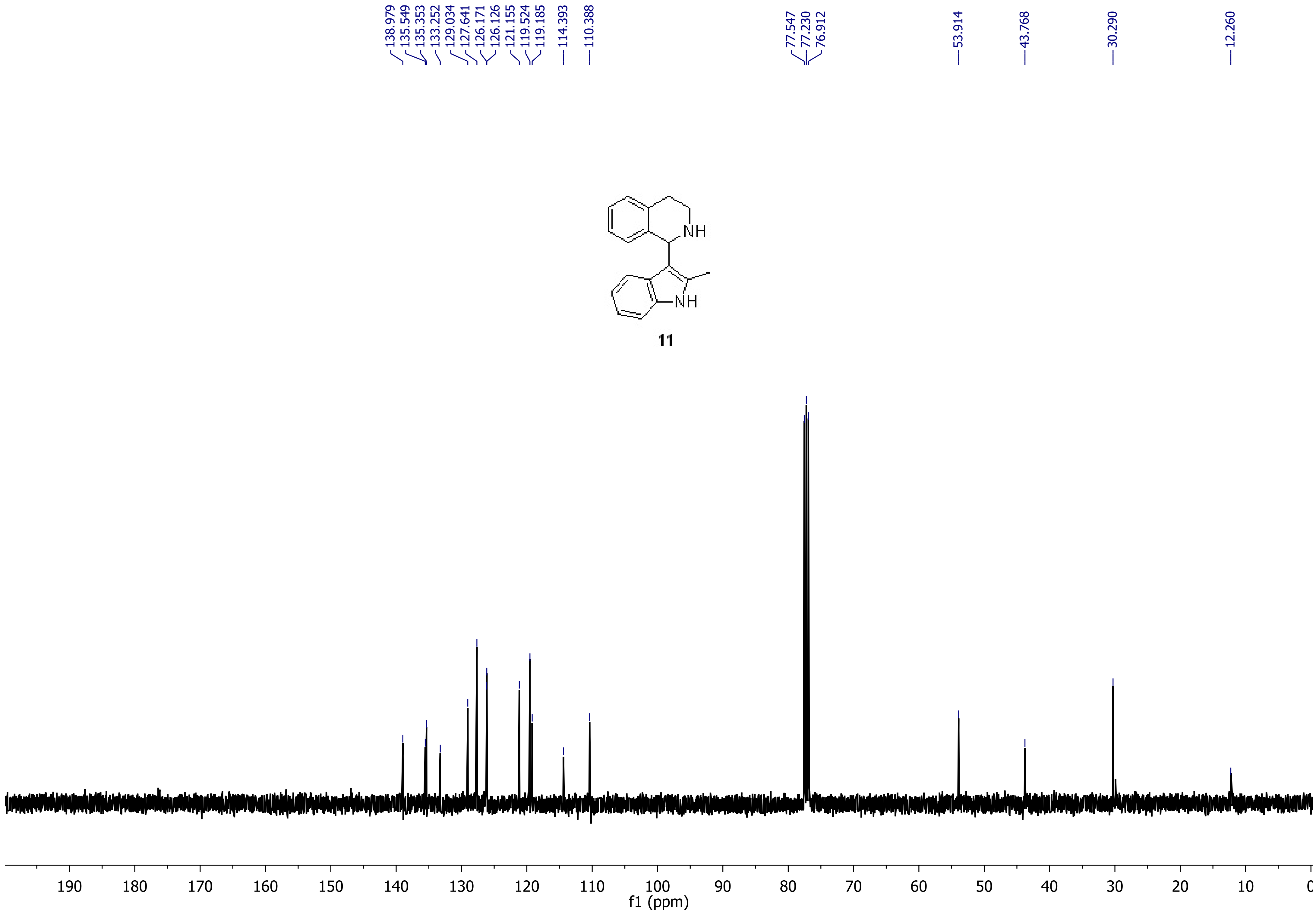


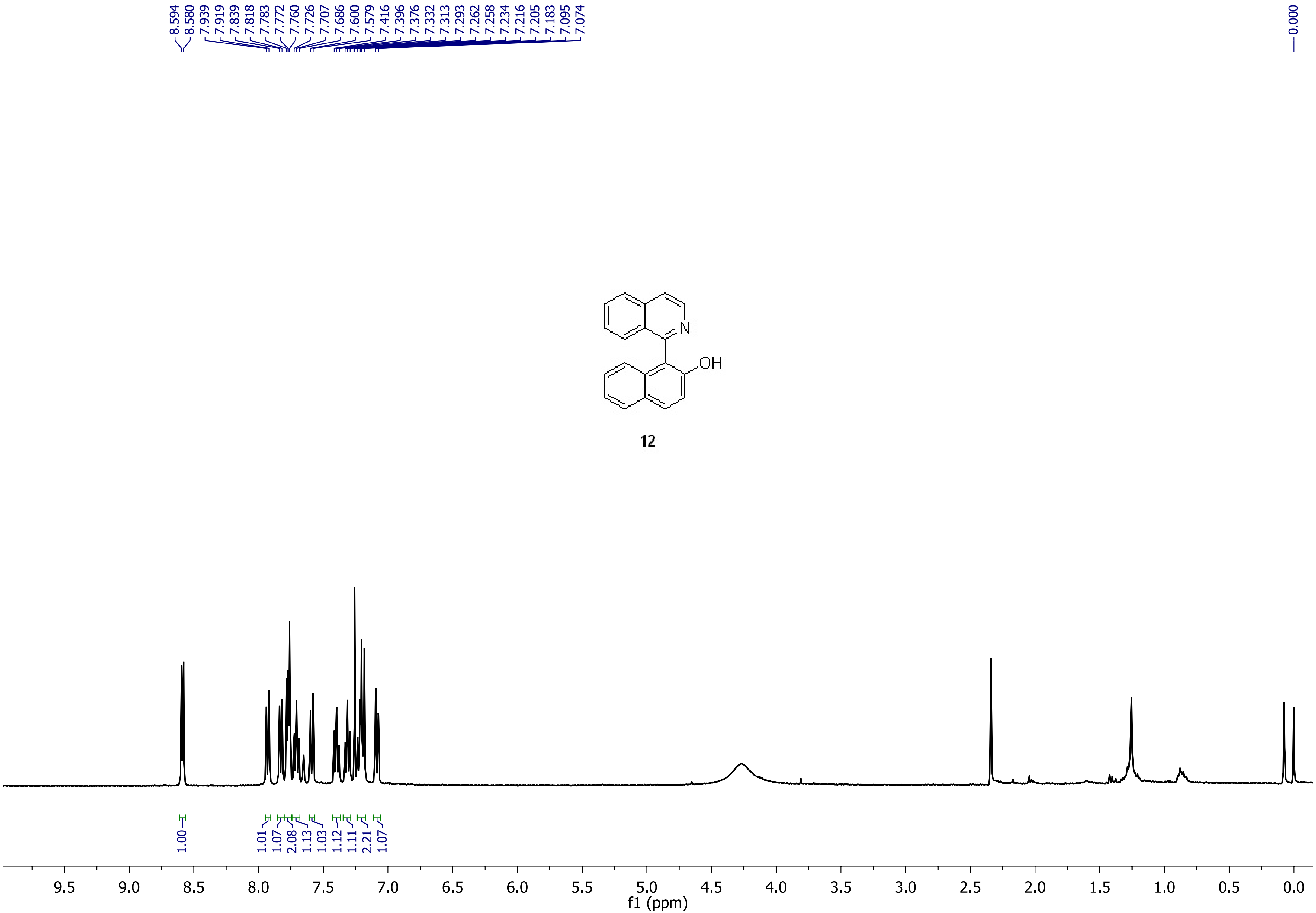
10

138.068
136.751
135.147
129.131
128.114
126.492
125.934
124.332
122.334
119.872
119.605
119.251
111.507
77.442
77.230
77.019
53.912
41.790
29.674
NH
NH
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

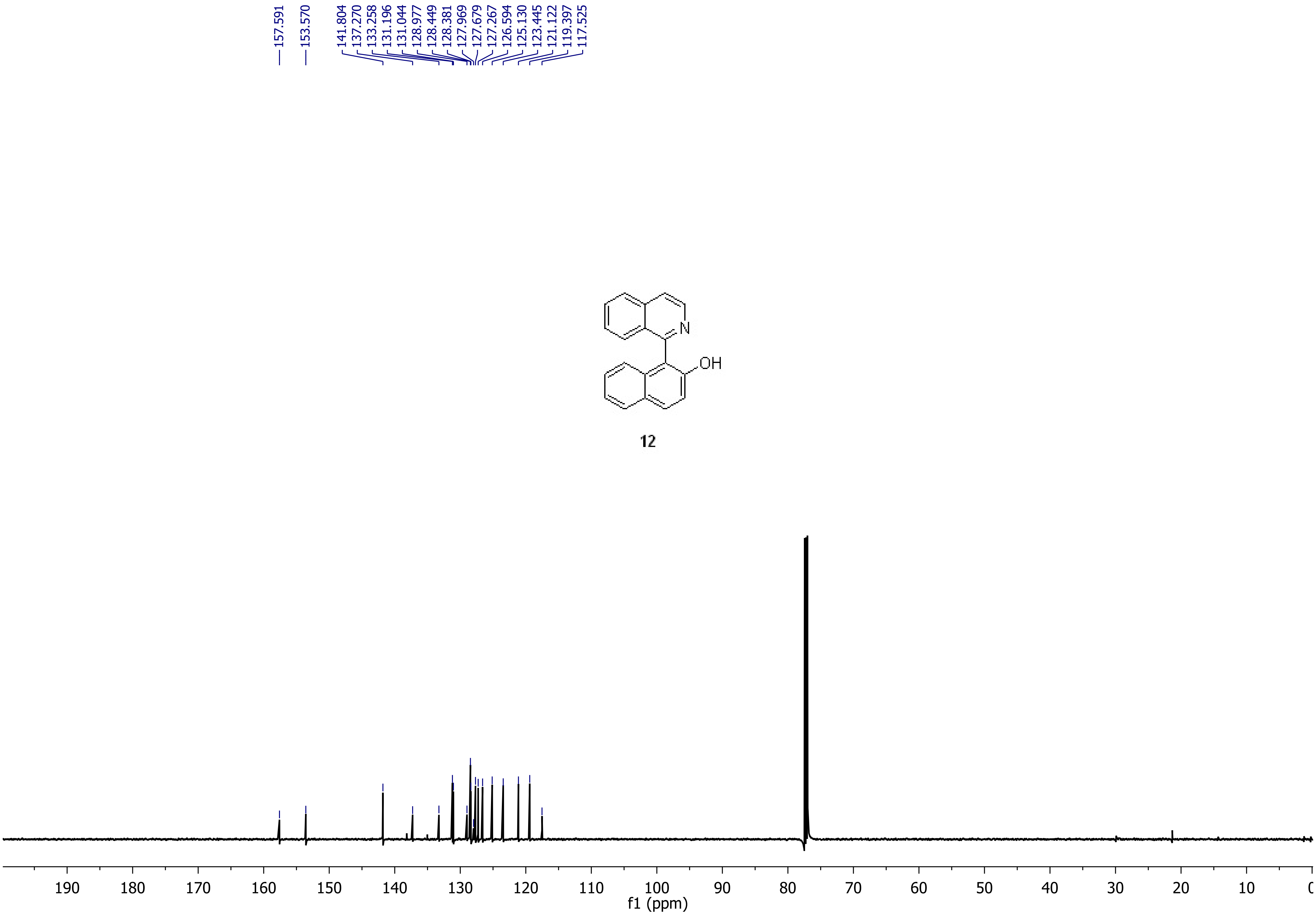

7.972
7.250
7.245
7.232
7.169
7.156
7.132
7.120
7.106
7.102
7.089
7.061
7.060
7.048
7.036
7.035
6.989
6.986
6.976
6.973
6.964
6.961
6.927
6.920
6.918
6.906
6.895
6.893
6.886
6.844
6.831
5.420
3.402
3.394
3.388
3.373
3.370
3.201
3.195
3.184
3.177
3.164
3.159
3.155
3.148
3.130
3.121
3.112
2.885
2.874
2.859
2.853
2.341
0.000
NH
NH
0.88
0.93
0.88
1.73
0.88
0.87
0.87
0.78
1.00
1.31
2.48
1.28
2.96
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
f1 (ppm)

11

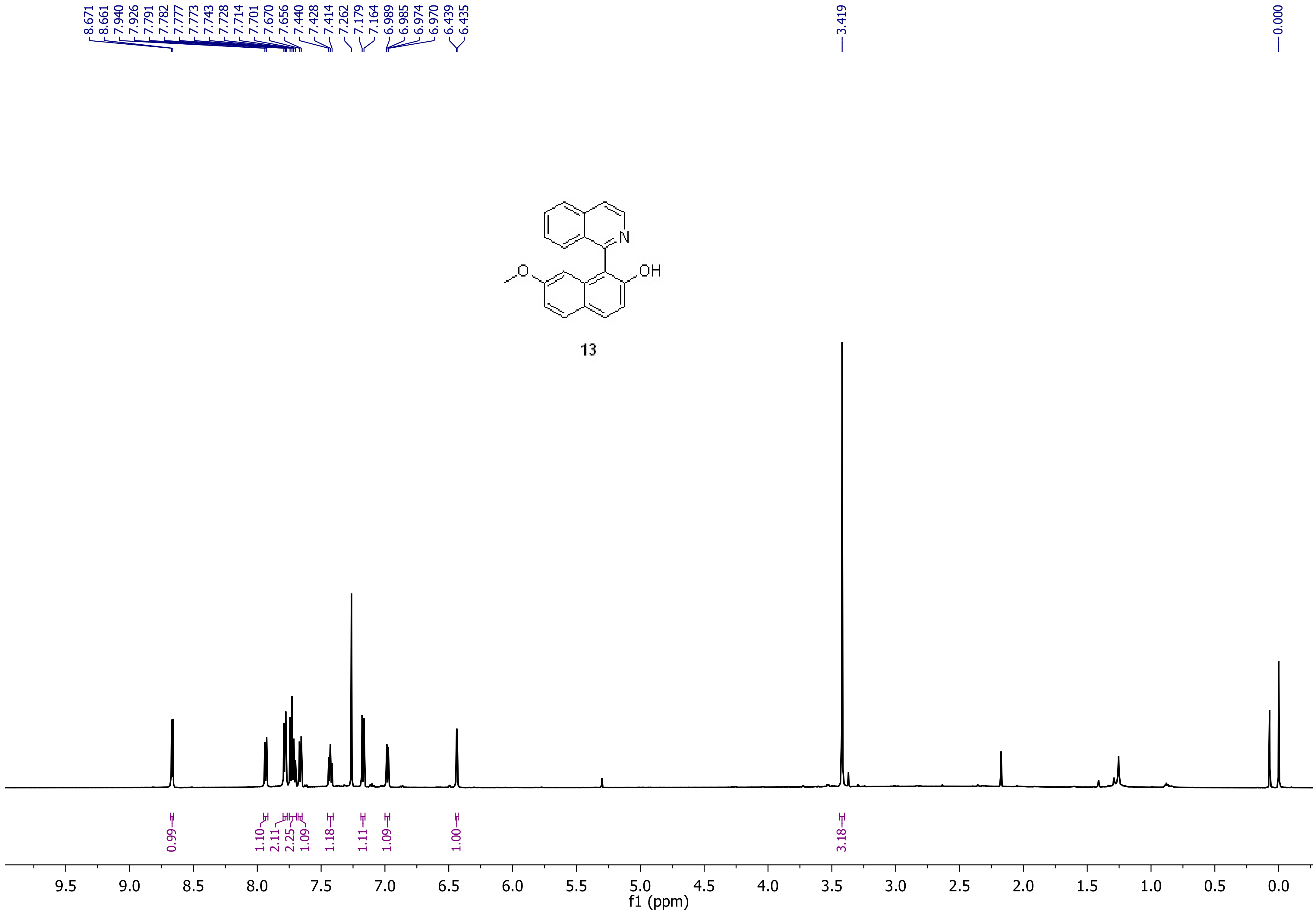

138.979
135.549
135.353
133.252
129.034
127.641
126.171
126.126
121.155
119.524
119.185
114.393
110.388
77.547
77.230
76.912
53.914
43.768
30.290
12.260
NH
NH
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

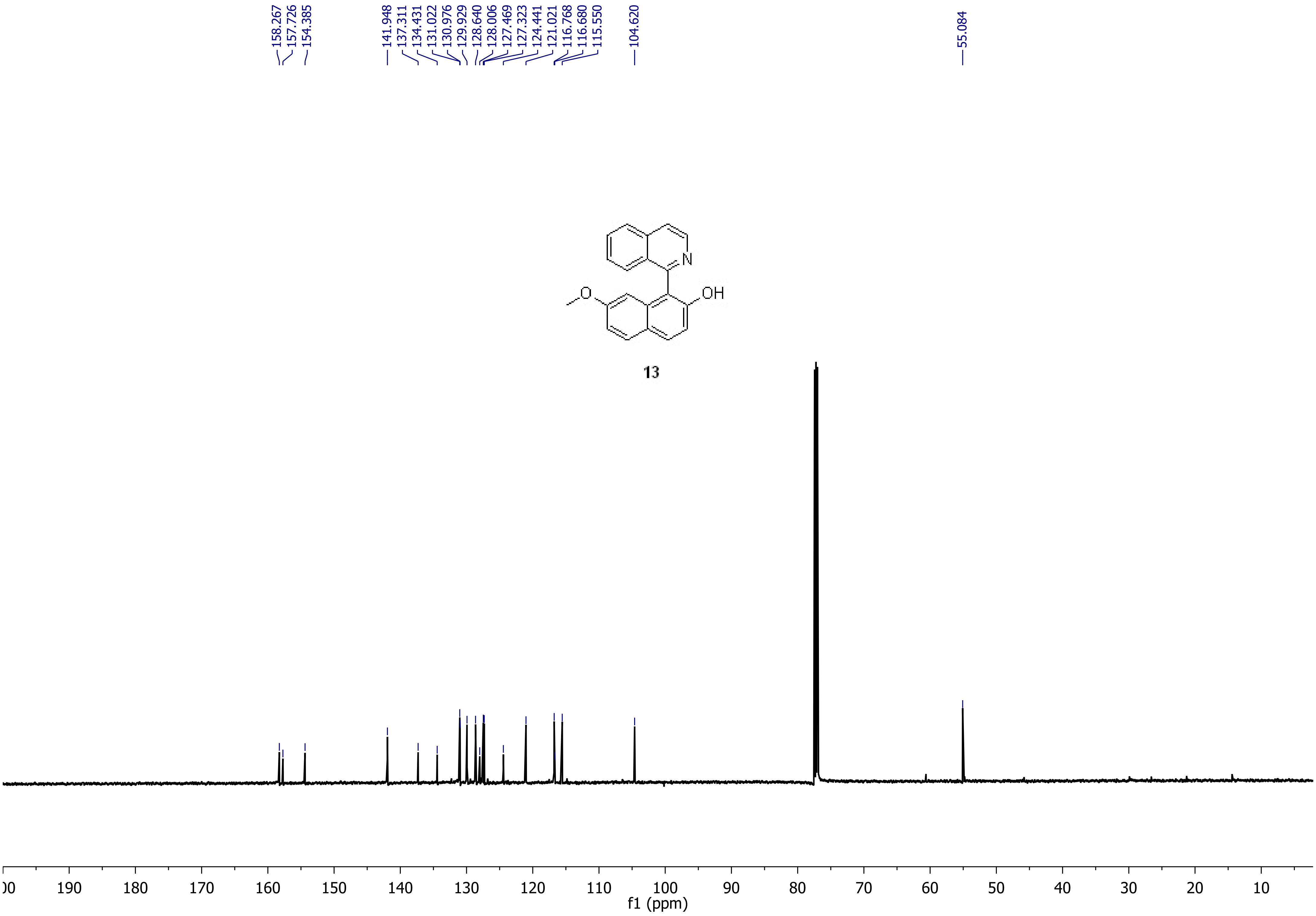

8.594
8.580
7.939
7.919
7.839
7.818
7.783
7.772
7.760
7.726
7.707
7.686
7.600
7.579
7.416
7.396
7.376
7.332
7.313
7.293
7.262
7.258
7.234
7.216
7.205
7.183
7.095
7.074
0.000
N
OH
1.00
1.01
1.07
2.08
1.13
1.03
1.12
1.11
2.21
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

12


157.591
153.570
141.804
137.270
133.258
131.196
131.044
128.977
128.449
128.381
127.969
127.679
127.267
126.594
125.130
123.445
121.122
119.397
117.525
N
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

12


8.671
8.661
7.940
7.926
7.791
7.782
7.777
7.773
7.743
7.728
7.714
7.701
7.670
7.656
7.440
7.428
7.414
7.262
7.179
7.164
6.989
6.985
6.974
6.970
6.439
6.435
3.419
0.000
N
O
OH
13
0.99
1.10
2.11
2.25
1.09
1.18
1.11
1.09
1.00
3.18
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
f1 (ppm)



13

158.267
157.726
154.385
141.948
137.311
134.431
131.022
130.976
129.929
128.640
128.006
127.469
127.323
124.441
121.021
116.768
116.680
115.550
104.620
55.084
N
OH
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)