

Supporting Information for

Synthesis of Heteroaromatic Trifluoromethyl Ethers with Trifluoromethyl Triflate as the Source of the Trifluoromethoxy Group

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General information

Nuclear magnetic resonance (^1H NMR, ^{19}F NMR, ^{13}C NMR) spectra were acquired on commercial instruments (DRX500, AV600, AV700 MHz) at the University of California, Berkeley NMR facility. ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 100 M, 151 MHz and 176MHz on the DRX500, AV600, AV700 instruments. ^{19}F nuclear magnetic resonance spectra were acquired at 376 MHz on the AVQ400 instrument. The ^1H NMR signal for residual non-deuterated solvent (δ 7.27 for CHCl_3 , 2.50 for DMSO, 2.05 for acetone, 3.31 for methanol) was used as an internal reference for ^1H NMR spectra. The ^{13}C NMR signal for CDCl_3 (δ 77.0), d_6 -DMSO (δ 39.5), d_4 -methanol (δ 49.0) or d_6 -acetone (δ 29.8) was used as an internal reference for ^{13}C NMR spectra. Coupling constants are reported in Hz. High-resolution mass spectra of the products **2** and **3** (EI) were recorded on a commercial GC-HRMS spectrometer at the Micro Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. High-resolution mass spectra of the starting materials **1** were recorded on a commercial LC-HRMS spectrometer(PerkinElmer) in the LBNL catalysis facility.

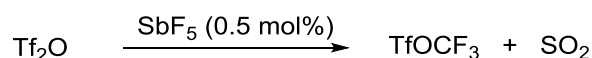
Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. TLC plates were visualized with UV light. Products were generally purified by column chromatography performed on a Teledyne Isco Combiflash® Rf system with RediSep Gold™ columns.

Substrates **1d** (ref. 1), **1g** and **1r** (ref. 2) were synthesized according to literature procedures. All other substrates were synthesized by oxidation of the corresponding N-heterocycles with *m*-CPBA (ref. 3). $\text{C}_2\text{F}_5\text{SO}_2(\text{OC}_2\text{F}_5)$ and $\text{C}_4\text{F}_9\text{SO}_2(\text{OC}_4\text{F}_9)$ were synthesized according to ref. 4

Tetrahydrofuran (THF), was purged with nitrogen and dried with an Innovative Pure-Solv solvent purification system. Dry DME and all other solvents were purchased and used without further purification.

General procedures

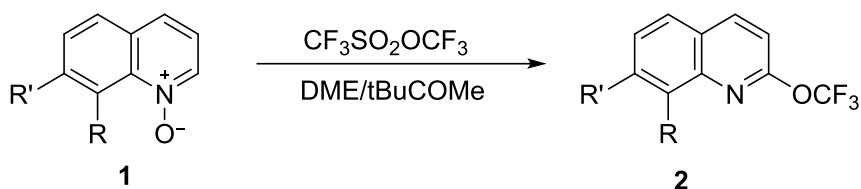
Preparation of TFMT



TFMT was synthesized according to slightly modified literature procedure⁵ with Tf₂O (100 mL, 0.60 mol) and SbF₅ (0.65 g, 3 mmol). Tf₂O was added by a syringe pump in three hours to a flask containing SbF₅ equipped with a distillation apparatus. The flask was kept warm at 25 °C and the receiver was cooled to -78 °C. After addition of Tf₂O, the reaction flask was heated to 60 °C and stirred for additional 15 min. The receiver was warmed to -15 °C, 3 M KOH (15 mL) solution was added to destroy unreacted Tf₂O. The TFMT layer was separated, dried with P₂O₅ and distilled to afford pure TFMT (110 g, 84%). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -52.4 (q, *J* = 3.9 Hz), -73.0 (q, *J* = 3.9 Hz). Lit.⁵ (-53.3, -74.0, *J* = 3.3 Hz)

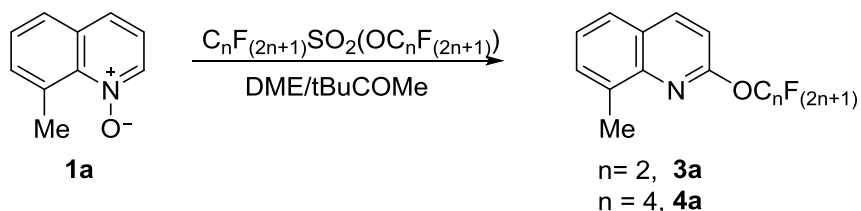
Procedure 1: the reaction of quinoline N-oxides (1a-1i, 1p-1t)

Procedure 1a



Quinoline oxides **1a-1i**, **1p-1t**, (1 mmol) were dissolved in a mixture containing DME (16 mL) and *t*-BuC(O)Me (1 mL). TFMT (0.5 M, 3 mL) was then added at room temperature, and the mixture was stirred until the starting material was consumed (3-8 h), as indicated by TLC. Et₃N (0.2 mL) and water (30 mL) were added, and the system was extracted with ether (30 mL x 2). The combined organic phase was sequentially washed with water (20 mL) and brine (20 mL), dried over MgSO₄, and filtered. The filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel with a mixture of ethyl acetate (EtOAc) or DCM with hexane as eluent. The same procedure was adopted for other reaction scale under the same concentration (0.05 M).

Procedure 1b

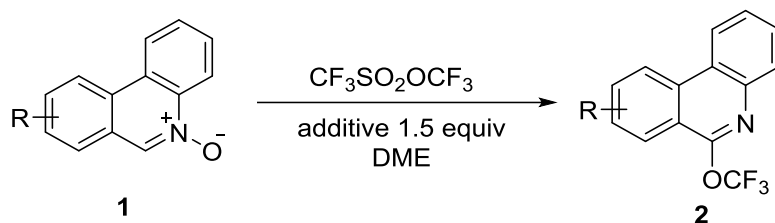


8-Methyl-quinoline N-oxides **1a** (1 mmol) were dissolved in a mixture containing DME (19 mL) and *t*-BuC(O)Me (1 mL). C_nF_(2n+1)SO₂(OC_nF_(2n+1)) (1.5 equiv, 1.5 mmol) was then added at room temperature for 4 h, as indicated by TLC. Et₃N (0.2 mL) and water (30 mL) were added, and the system was extracted with ether (30 mL x 2). The combined organic phase was sequentially washed with water (20 mL) and brine (20 mL), dried over MgSO₄, and filtered. The filtrate was concentrated under vacuum. The residue was purified by flash

chromatography on silica gel with a mixture of ethyl acetate (EtOAc) or DCM with hexane as eluent.

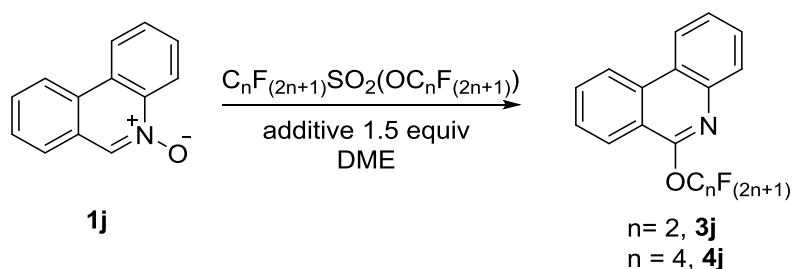
Procedure 2: the reaction of other heterocyclic N-oxides (1j-1o)

Procedure 2a



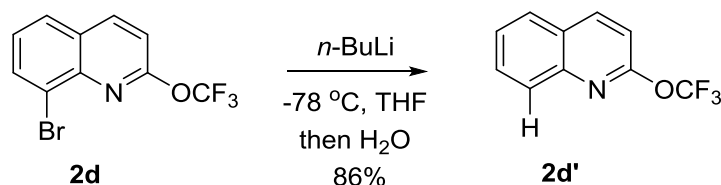
Tricyclic oxides **1j-1o** (1 mmol) and 2,6-dichloropyridine N-Oxide (1.5 equiv) were dissolved in DME (97 mL), and 4 Å molecular sieves (1.0 g) were added. TFMT (0.5 M, 3 mL) was then added at room temperature, and the mixture was stirred for 8 h. Et₃N (0.2 mL) was then added to the system. The mixture was filtered, and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel with a mixture of ethyl acetate and hexane as eluent. The same procedure was adopted for other reaction scale under the same concentration (0.01 M).

Procedure 2b



Phenanthridine N-oxides **1j** (1 mmol) and 2,6-dichloropyridine N-Oxide (1.5 equiv) were dissolved in DME (100 mL), and 4 Å molecular sieves (1.0 g) were added. C_nF_(2n+1)SO₂(OC_nF_(2n+1)) (1.5 equiv, 1.5 mmol) was then added at room temperature, and the mixture was stirred for 4 h. Et₃N (0.2 mL) was then added to the system. The mixture was filtered, and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel with a mixture of ethyl acetate and hexane as eluent.

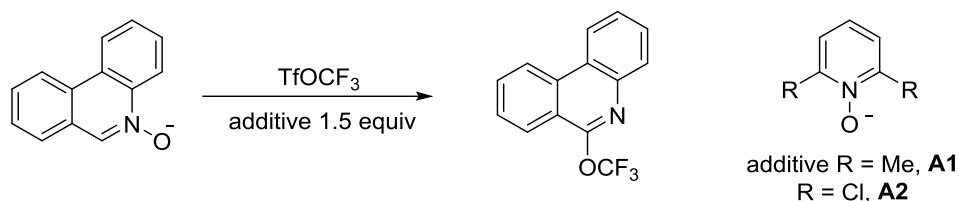
Reduction of 2d



Substrate **2d** (0.10 mmol, 29.2 mg) was dissolved in dry THF (1 mL) under argon. The solution was cooled to -78 °C in a dry ice/acetone bath. *n*-BuLi (0.12 mmol, 2.5 M, 48 μL) was added slowly to the stirring solution at -78 °C. After stirring for an additional 5 min, water (5 mL) was added. The mixture was warmed to room temperature, at which point *n*-hexane (10 mL) was added. The organic phase was separated, dried over MgSO₄, and filtered. The filtrate was concentrated and purified by preparative TLC. Compound **2d'** was obtained as a colorless oil (18.3 mg, 86%). ¹H NMR (700 MHz, CDCl₃) δ 8.24 (d, *J* = 8.8

Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.75 (t, $J = 7.8$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.12 (dd, $J = 8.9, 2.1$ Hz, 1H). ^{13}C NMR (176 MHz, CDCl_3) δ 154.8, 145.8, 140.7, 130.6, 128.6, 127.5, 126.6, 126.5, 120.3 (q, $J = 260$ Hz), 112.2. ^{19}F NMR (376 MHz, CDCl_3) δ -55.5. **HRMS** (ESI) calcd for $\text{C}_{10}\text{H}_6\text{F}_3\text{NO}^+$ $[\text{M}]^+$ 213.0396, Found: 213.0398.

TABLE S1. Evaluation of reaction parameters for the trifluoromethyl etherification of phenanthridine *N*-oxide.^a



Entry ^a	Additive	Sol.	Temp.	Concentration	yield ^b		
1	15-crown-5	DME	r.t.	0.05 M	38%		
2	18-crown-6				47%		
3	A1				17%		
4	A2				56%		
5					35 °C	54%	
6					40 °C	42%	
7	A2 + 4A molecular sieve		DCM	r.t.	0.05 M	68%	
8						0.01 M	78%
9						0.05 M	58%
10						Tol.	12%
11						MeCN	<5%
12						DME	0.01 M (1 mmol)

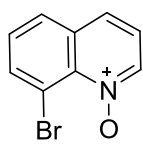
^a substrate (0.1 mmol) in solvent (2 mL), additive (1.5 equiv) and TFMT (1.5 equiv).

^b ^{19}F NMR yield using trifluorotoluene as internal standard. ^c Isolated yield.

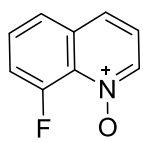
References:

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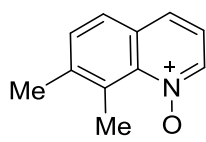
Spectroscopic data of key compounds



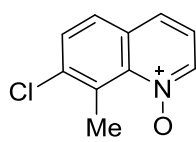
8-bromoquinoline 1-oxide (1d). The product was synthesized from 3.10 g quinoline N-oxide ($x\text{H}_2\text{O}$) according to ref. 1 to give 697 mg of **1d** (24% yield over two steps). ^1H NMR (600 MHz, CDCl_3) δ 8.46 (d, $J = 5.8$ Hz, 1H), 7.96 (d, $J = 7.4$ Hz, 1H), 7.77 (d, $J = 7.9$ Hz, 1H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.35 (t, $J = 7.7$ Hz, 1H), 7.28 – 7.22 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 138.9, 137.8, 137.7, 133.2, 128.5, 128.5, 125.8, 121.5, 112.8.



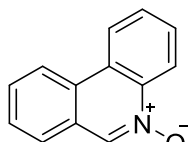
8-fluoroquinoline 1-oxide (1e). Synthesized from 1.47 g of starting material according to ref. 3 to give 245 mg of **1e** (15% yield). ^1H NMR (700 MHz, CDCl_3) δ 8.44 (dd, $J = 6.1, 1.0$ Hz, 1H), 7.67 (dt, $J = 8.4, 1.2$ Hz, 1H), 7.63 (dt, $J = 8.1, 1.3$ Hz, 1H), 7.52 (td, $J = 8.0, 4.0$ Hz, 1H), 7.35 (ddd, $J = 12.9, 7.8, 1.3$ Hz, 1H), 7.30 – 7.25 (m, 1H). ^{13}C NMR (176 MHz, CDCl_3) δ 154.7 (d, $J = 265$ Hz), 138.0, 133.4, 132.4, 128.7 (d, $J = 8.3$ Hz), 125.0 (d, $J = 3.3$ Hz), 124.3 (d, $J = 5.8$ Hz), 121.8, 116.4 (d, $J = 21.8$ Hz). ^{19}F NMR (376 MHz, DMSO) δ -114.6.



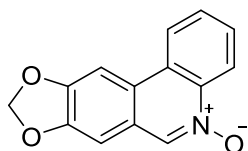
7,8-dimethylquinoline 1-oxide (1h). Synthesized from 1.00 g starting material according to ref. 3 to give 223 mg of **1h** (21% yield). ^1H NMR (700 MHz, CDCl_3) δ 8.42 (d, $J = 6.0$ Hz, 1H), 7.61 (d, $J = 8.3$ Hz, 1H), 7.55 (d, $J = 8.3$ Hz, 1H), 7.39 (d, $J = 8.3$ Hz, 1H), 7.13 (dd, $J = 8.3, 6.0$ Hz, 1H), 3.12 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (176 MHz, CDCl_3) δ 141.4, 140.1, 137.9, 131.4, 131.0, 126.7, 125.5, 119.7, 21.8, 18.4. (1 C overlapped) HRMS (ESI) calcd for $\text{C}_{13}\text{H}_9\text{FNO}^+$ $[\text{M}+\text{H}]^+$ 174.0913, Found: 174.0906.



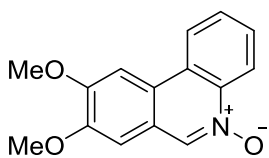
7-chloro-8-methylquinoline 1-oxide (1i). Synthesized from 1.00 g starting material according to ref. 3 to give 180 mg of **1i** (17% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.44 (dd, $J = 6.1, 1.2$ Hz, 1H), 7.61 (dd, $J = 8.3, 1.2$ Hz, 1H), 7.59 (d, $J = 8.9$ Hz, 1H), 7.57 (d, $J = 8.9$ Hz, 1H), 7.21 (dd, $J = 8.3, 6.1$ Hz, 1H), 3.28 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 142.1, 138.4, 137.6, 131.3, 131.1, 130.2, 126.8, 126.1, 121.0, 19.5. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_9\text{ClNO}^+$ $[\text{M}+\text{H}]^+$ 194.0367, Found: 194.0368.



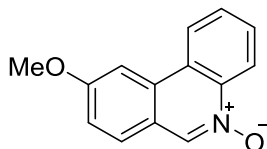
phenanthridine 5-oxide (1j). Synthesized from 900 mg starting material according to ref. 3 to give 829 mg of **1j** (85% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.93 (dd, $J = 7.8, 1.9$ Hz, 1H), 8.91 (s, 1H), 8.57 (d, $J = 7.9$ Hz, 1H), 8.50 (d, $J = 8.3$ Hz, 1H), 7.82 (td, $J = 7.0, 1.7$ Hz, 2H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 139.2, 134.7, 129.6, 129.5, 129.3, 128.8, 126.8, 126.6, 126.6, 126.1, 122.7, 122.0, 120.6.



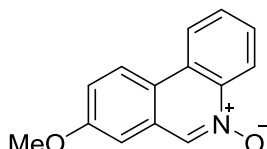
[1,3]dioxolo[4,5-j]phenanthridine 5-oxide (1k). Synthesized from 249 mg starting material according to ref. 3 to give 124 mg of **1k** (50% yield). $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 8.53 – 8.49 (m, 1H), 8.50 (s, 1H), 8.19 – 8.08 (m, 1H), 7.60 (s, 1H), 7.51 – 7.43 (m, 2H), 6.87 (s, 1H), 5.89 (s, 2H). $^{13}\text{C NMR}$ (176 MHz, $\text{CDCl}_3/\text{DMSO-}d_6$) δ 149.9, 148.6, 137.5, 133.4, 128.2, 128.0, 125.5, 123.0, 122.2, 122.1, 119.5, 102.4, 101.6, 99.8. **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_{10}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$ 240.0655, Found: 240.0639.



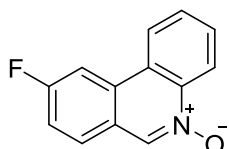
8,9-dimethoxyphenanthridine 5-oxide (1l). Synthesized from 941 mg starting material according to ref. 3 to give 654 mg of **1l** (65% yield). $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 8.78 (dd, $J = 8.2, 1.6$ Hz, 1H), 8.64 (s, 1H), 8.23 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.64 (dddd, $J = 17.7, 8.5, 6.9, 1.4$ Hz, 2H), 7.57 (s, 1H), 6.92 (s, 1H), 4.02 (s, 3H), 3.96 (s, 3H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 151.4, 150.6, 138.0, 133.6, 128.5, 128.3, 125.7, 122.0, 121.7, 121.4, 120.4, 105.1, 102.0, 56.0, 56.0. **HRMS** (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$ 256.0968., Found: 256.0969.



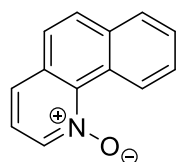
9-methoxyphenanthridine 5-oxide (1m). Synthesized from 643 mg starting material according to ref. 3 to give 426 mg of **1m** (62% yield). $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 8.93 (dd, $J = 8.5, 1.3$ Hz, 1H), 8.83 (s, 1H), 8.50 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.86 – 7.81 (m, 2H), 7.81 – 7.76 (m, 1H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.31 – 7.27 (m, 1H), 4.03 (s, 3H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 160.8, 139.2, 134.4, 129.7, 128.8, 128.6, 127.9, 126.0, 122.7, 121.1, 120.8, 119.0, 103.6, 55.7. **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_{12}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$ 226.0863, Found: 226.0853.



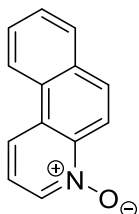
8-methoxyphenanthridine 5-oxide (1n). Synthesized from 341 mg starting material according to ref. 3 to give 124 mg of **1n** (35% yield). $^1\text{H NMR}$ (700 MHz, Methanol- d_4) δ 8.82 (s, 1H), 8.61 (d, $J = 8.5$ Hz, 1H), 8.49 (d, $J = 8.1$ Hz, 1H), 7.79 (t, $J = 7.7$ Hz, 1H), 7.76-7.69 (m, 3H), 7.17 (dd, $J = 8.7, 2.3$ Hz, 1H), 3.94 (s, 3H). $^{13}\text{C NMR}$ (176 MHz, Methanol- d_4) δ 163.5, 138.8, 137.8, 131.3, 131.2, 130.3, 130.2, 127.2, 124.5, 121.3, 120.6, 120.5, 104.4, 56.4. **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_{12}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$ 226.0863, Found: 226.0855.



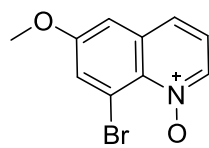
9-fluorophenanthridine 5-oxide (1o). Synthesized from 332 mg starting material according to ref. 3 to give 203 mg of **1o** (56% yield). $^1\text{H NMR}$ (700 MHz, Methanol- d_4) δ 9.10 (s, 1H), 8.75 (d, $J = 8.6$ Hz, 1H), 8.69 (d, $J = 8.1$ Hz, 1H), 8.39 (dd, $J = 10.3, 2.4$ Hz, 1H), 8.07 (dd, $J = 8.8, 5.5$ Hz, 1H), 7.93 (t, $J = 7.7$ Hz, 1H), 7.89 (t, $J = 7.5$ Hz, 1H), 7.54 (td, $J = 8.5, 2.2$ Hz, 1H). $^{13}\text{C NMR}$ (176 MHz, Methanol- d_4) δ 165.0 (d, $J = 253$ Hz), 139.4, 137.4, 131.9, 131.4 (d, $J = 9.8$ Hz), 131.3 (d, $J = 8.8$ Hz), 119.5 (d, $J = 25.0$ Hz), 131.1, 127.4, 125.0, 124.2, 120.8, 109.2 (d, $J = 24.0$ Hz). **HRMS** (ESI) calcd for $\text{C}_{13}\text{H}_9\text{FNO}^+$ $[\text{M}+\text{H}]^+$ 214.0663., Found: 214.0670.



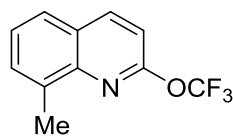
benzo[h]quinoline 1-oxide (1p). Synthesized from 1.27 g starting material according to ref. 3 to give 950 mg of **1p** (69% yield). ^1H NMR (700 MHz, CDCl_3) δ 10.86 (d, $J = 8.3$ Hz, 1H), 8.65 (d, $J = 6.3$ Hz, 1H), 7.93 – 7.89 (m, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.78 (q, $J = 8.2, 7.6$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.40 – 7.35 (m, 1H). ^{13}C NMR (176 MHz, CDCl_3) δ 139.2, 138.4, 134.0, 131.2, 130.5, 129.0, 128.2, 128.0, 127.7, 126.0, 125.7, 124.9, 121.2.



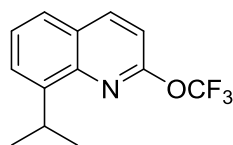
benzo[f]quinoline 4-oxide (1q). Synthesized from 538 mg starting material according to ref. 3 to give 208 mg of **1q** (39% yield). ^1H NMR (600 MHz, CDCl_3) δ 10.86 (dd, $J = 8.0, 1.7$ Hz, 1H), 8.66 (dd, $J = 6.2, 1.3$ Hz, 1H), 7.92 (dd, $J = 6.9, 2.4$ Hz, 1H), 7.84 (d, $J = 8.8$ Hz, 1H), 7.82 – 7.71 (m, 3H), 7.64 (d, $J = 8.8$ Hz, 1H), 7.39 (dd, $J = 8.0, 6.2$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 139.3, 138.5, 134.0, 131.2, 130.5, 129.0, 128.2, 128.0, 127.7, 126.0, 125.7, 125.0, 121.2.



8-bromo-6-methoxyquinoline 1-oxide (1t). Synthesized from 175 mg starting material according to ref. 2 to give 86 mg of **1t** (34% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.78 (d, $J = 9.6$ Hz, 1H), 8.44 (d, $J = 5.9$ Hz, 1H), 8.09 (d, $J = 8.8$ Hz, 1H), 7.49 (d, $J = 9.6$ Hz, 1H), 7.36 (dd, $J = 8.9, 5.9$ Hz, 1H), 4.08 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.8, 137.6, 133.9, 131.2, 124.7, 122.2, 120.9, 116.4, 108.0, 57.1. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_9\text{BrNO}_2^+$ $[\text{M}+\text{H}]^+$ 253.9811, Found: 253.9804.

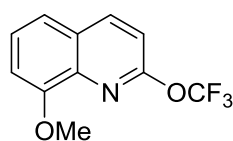


8-methyl-2-(trifluoromethoxy)quinoline (2a). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 47% yield of the product by ^{19}F NMR spectroscopy using PhCF_3 as internal standard. For isolation, the reaction was run according to the same general procedure on a 1 mmol scale. The product was isolated (94.9 mg, 42% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (500 MHz, CDCl_3) δ 8.19 (d, $J = 8.7$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.60 (d, $J = 7.0$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 8.7$ Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 153.8, 144.7, 140.9, 136.7, 130.6, 126.5, 126.1, 120.2 (q, $J = 263$ Hz), 125.2, 111.5 (q, $J = 1.4$ Hz), 17.4. ^{19}F NMR (376 MHz, CDCl_3) δ -55.7. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_8\text{F}_3\text{NO}$ $[\text{M}]^+$ 227.0552, Found: 227.0561.

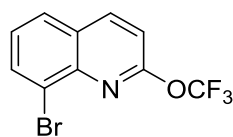


8-isopropyl-2-(trifluoromethoxy)quinoline (2b). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 48% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. For isolation, the reaction was run according to the same general procedure on a 1 mmol scale. The product was isolated (145.3 mg, 57% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (600 MHz, CDCl_3) δ 8.20 (d, $J = 8.8$ Hz, 1H), 7.66 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.63 (s, 1H), 7.51 (d, $J = 1.7$ Hz, 1H), 7.06 (d, $J = 8.7$ Hz, 1H), 4.09 (heptet, $J = 4.2$ Hz, 1H), 1.42-1.35 (m, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 153.7, 146.7,

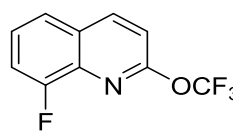
143.6, 141.0, 126.6, 126.5, 126.3, 125.1, 120.3 (q, $J = 263$ Hz), 111.4, 28.1, 23.0. ^{19}F NMR (376 MHz, CDCl_3) δ -55.8. **HRMS** (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{NO}$ $[\text{M}]^+$ 255.0866, Found: 255.0869.



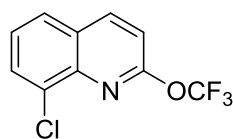
8-methoxy-2-(trifluoromethoxy)quinoline (2c). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 55% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. For isolation, the reaction was run according to the same general procedure on a 1 mmol scale. The product was isolated (126.4 mg, 52% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, $J = 8.8$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.42 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.20 (d, $J = 8.7$ Hz, 1H), 7.12 (dd, $J = 7.8, 1.2$ Hz, 1H), 4.07 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.0, 153.7 (q, $J = 1.8$ Hz), 140.8, 137.6, 128.0, 126.9, 120.2 (q, $J = 261$ Hz), 119.2, 112.8 (q, $J = 1.8$ Hz), 109.72, 56.38. ^{19}F NMR (376 MHz, CDCl_3) δ -55.3. **HRMS** (ESI) calcd for $\text{C}_{11}\text{H}_8\text{F}_3\text{NO}_2$ $[\text{M}]^+$ 243.0502, Found: 243.0508.



8-bromo-2-(trifluoromethoxy)quinoline (2d). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 66% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. For isolation, the reaction was run according to the same general procedure on a 1 mmol scale. The product was isolated (179.6 mg, 62% yield) by flash chromatography on silica gel using hexane/DCM as eluent. ^1H NMR (700 MHz, CDCl_3) δ 8.21 (d, $J = 8.7$ Hz, 1H), 8.04 (dd, $J = 7.5, 1.3$ Hz, 1H), 7.77 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 7.12 (d, $J = 8.7$ Hz, 1H). ^{13}C NMR (176 MHz, CDCl_3) δ 155.2, 143.1, 141.3, 134.2, 127.6, 127.2, 126.9, 123.4, 120.1 (q, $J = 262$ Hz), 112.8. ^{19}F NMR (376 MHz, CDCl_3) δ -56.7. **HRMS** (ESI) calcd for $\text{C}_{10}\text{H}_5\text{BrF}_3\text{NO}$ $[\text{M}]^+$ 290.9501, Found: 290.9508.

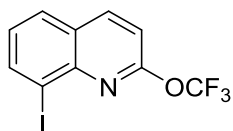


8-fluoro-2-(trifluoromethoxy)quinoline (2e). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 49% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. ^1H NMR (700 MHz, CDCl_3) δ 8.24 (dd, $J = 8.9, 3.1$ Hz, 1H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.49 – 7.45 (m, 1H), 7.45 – 7.40 (m, 1H), 7.15 (d, $J = 9.0$ Hz, 1H). ^{13}C NMR (176 MHz, CDCl_3) δ 157.1 (d, $J = 257$ Hz), 154.8, 140.6 (d, $J = 2.8$ Hz), 135.6 (d, $J = 12.1$ Hz), 128.2, 126.4 (d, $J = 7.6$ Hz), 123.0 (d, $J = 4.8$ Hz), 120.0 (d, $J = 264$ Hz), 115.0 (d, $J = 18.5$ Hz), 113.18. ^{19}F NMR (376 MHz, CDCl_3) δ -56.3, -124.4. **HRMS** (ESI) calcd for $\text{C}_{10}\text{H}_5\text{F}_4\text{NO}$ $[\text{M}]^+$ 231.0302, Found: 231.0307.

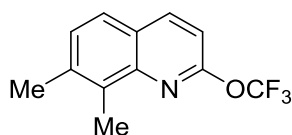


8-chloro-2-(trifluoromethoxy)quinoline (2f). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 50% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. For isolation, the reaction was run according to the same general procedure on a 0.46 mmol scale. The

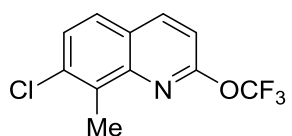
product was isolated (55.5 mg, 49% yield) by flash chromatography on silica gel using hexane/DCM as eluent. ^1H NMR (700 MHz, CDCl_3) δ 8.23 (d, $J = 8.7$ Hz, 1H), 7.83 (dd, $J = 7.5, 1.3$ Hz, 1H), 7.73 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 1H), 7.14 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR (176 MHz, CDCl_3) δ 155.0, 142.2, 141.2, 132.6, 130.7, 127.7, 126.4, 126.4, 120.1 (q, $J = 262$ Hz), 112.8 (q, $J = 1.3$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -56.4. **HRMS** (ESI) calcd for $\text{C}_{10}\text{H}_5\text{ClF}_3\text{NO}$ $[\text{M}]^+$ 247.0006, Found: 247.0017.



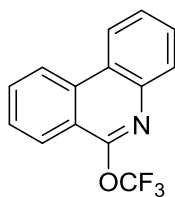
8-iodo-2-(trifluoromethoxy)quinoline (2g). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 31% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. ^1H NMR (600 MHz, CDCl_3) δ 8.34 (dd, $J = 7.5, 1.3$ Hz, 1H), 8.18 (d, $J = 8.7$ Hz, 1H), 7.82 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.28 (dd, $J = 8.1, 7.4$ Hz, 1H), 7.11 (d, $J = 8.7$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.5, 145.3, 141.5, 141.0, 128.1, 127.6, 126.9, 120.1 (q, $J = 263$ Hz), 112.8, 101.1. ^{19}F NMR (376 MHz, CDCl_3) δ -56.4. **HRMS** (ESI) calcd for $\text{C}_{10}\text{H}_5\text{F}_3\text{INO}$ $[\text{M}]^+$ 338.9362, Found: 338.9368.



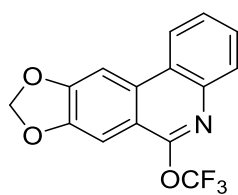
7,8-dimethyl-2-(trifluoromethoxy)quinoline (2h). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 43% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. For isolation, the reaction was run according to the same general procedure on a 0.5 mmol scale. The product was isolated (58.7 mg, 49% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.14 (d, $J = 8.6$ Hz, 1H), 7.57 (d, $J = 8.2$ Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 1H), 7.00 (d, $J = 8.7$ Hz, 1H), 2.68 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 153.9, 144.7, 140.7, 138.7, 134.1, 129.1, 124.9, 124.3, 120.3 (q, $J = 261$ Hz), 110.4 (q, $J = 1.4$ Hz), 20.6, 13.0. ^{19}F NMR (376 MHz, CDCl_3) δ -56.2. **HRMS** (ESI) calcd for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{NO}$ $[\text{M}]^+$ 241.0709, Found: 241.0713.



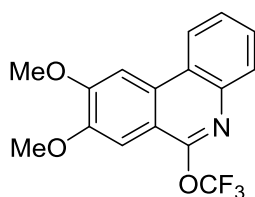
7-chloro-8-methyl-2-(trifluoromethoxy)quinoline (2i). To obtain a yield by NMR spectroscopy, the reaction was run according to general procedure 1a on a 0.10 mmol scale to give 54% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. For isolation, the reaction was run according to the same general procedure on a 0.5 mmol scale. The product was isolated (69.2 mg, 53% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.17 (d, $J = 8.7$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.52 (d, $J = 8.7$ Hz, 1H), 7.06 (d, $J = 8.7$ Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 154.5, 145.2, 140.8, 136.2, 134.5, 127.7, 125.5, 125.0, 120.2 (q, $J = 262$ Hz), 111.5 (q, $J = 1.3$ Hz), 14.2. ^{19}F NMR (376 MHz, CDCl_3) δ -56.3. **HRMS** (ESI) calcd for $\text{C}_{11}\text{H}_7\text{ClF}_3\text{NO}$ $[\text{M}]^+$ 261.0163, Found: 261.0172.



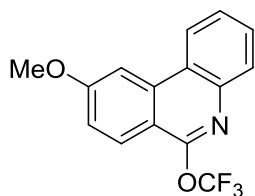
6-(trifluoromethoxy)phenanthridine (2j). The reaction was run according to the general procedure 2a on a 1.0 mmol scale. The product was isolated (215.7 mg, 82% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (600 MHz, CDCl_3) δ 8.51 (d, $J = 8.3$ Hz, 1H), 8.44 (dd, $J = 8.2, 1.4$ Hz, 1H), 8.26 (dd, $J = 8.2, 1.3$ Hz, 1H), 8.02 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.86 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.74 – 7.66 (m, 2H), 7.63 (ddd, $J = 8.3, 7.1, 1.4$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 151.9, 141.4, 135.4, 131.7, 129.2, 129.2, 127.8, 126.7, 124.3, 123.6, 122.1, 122.0, 120.4 (q, $J = 263$ Hz), 118.3. ^{19}F NMR (376 MHz, CDCl_3) δ -55.0. **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}$ $[\text{M}]^+$ 263.0552, Found: 263.0561.



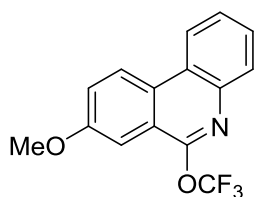
6-(trifluoromethoxy)-[1,3]dioxolo[4,5-j]phenanthridine (2k). The reaction was run according to the general procedure 2a on a 0.10 mmol scale. The product was isolated (15.4 mg, 50% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (400 MHz, CDCl_3) δ 8.29 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.99 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.87 (s, 1H), 7.67 (ddd, $J = 8.3, 7.0, 1.5$ Hz, 1H), 7.60 (ddd, $J = 8.3, 7.0, 1.4$ Hz, 1H), 7.57 (s, 1H), 6.19 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.1, 151.5, 148.6, 141.2, 133.4, 129.2, 128.6, 126.4, 123.7, 121.8, 120.4 (q, $J = 263$ Hz), 114.3, 102.2, 101.8, 100.4. ^{19}F NMR (376 MHz, CDCl_3) δ -54.9. **HRMS** (ESI) calcd for $\text{C}_{15}\text{H}_8\text{F}_3\text{NO}_3$ $[\text{M}]^+$ 307.0451, Found: 307.0454.



8,9-dimethoxy-6-(trifluoromethoxy)phenanthridine (2l). The reaction was run according to the general procedure 2a on a 0.1 mmol scale. The product was isolated (8.7 mg, 27% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (600 MHz, CDCl_3) δ 8.39 (d, $J = 8.2$ Hz, 1H), 8.03 – 7.98 (m, 1H), 7.88 (s, 1H), 7.71 – 7.65 (m, 1H), 7.65 – 7.59 (m, 1H), 7.56 (s, 1H), 4.16 (s, 3H), 4.09 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 153.5, 151.3, 150.2, 146.9, 141.2, 131.5, 129.3, 128.4, 126.3, 123.4, 121.6, 120.4 (q, $J = 262$ Hz), 103.8, 102.4, 56.2, 56.2. ^{19}F NMR (376 MHz, CDCl_3) δ -54.7. **HRMS** (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{NO}_3$ $[\text{M}]^+$ 323.0764, Found: 323.0773.

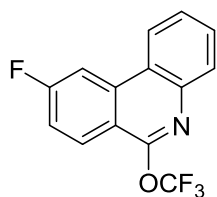


9-methoxy-6-(trifluoromethoxy)phenanthridine (2m). The reaction was run according to the general procedure 2a on a 0.10 mmol scale. The product was isolated (12.0 mg, 41% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (600 MHz, CDCl_3) δ 8.34 (d, $J = 8.2$ Hz, 1H), 8.14 (d, $J = 8.9$ Hz, 1H), 7.98 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.79 (d, $J = 2.4$ Hz, 1H), 7.69 (t, $J = 7.2$ Hz, 1H), 7.58 (7.2, 1H), 7.24 (dd, $J = 9.0, 2.4$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.3, 152.0, 142.0, 137.7, 129.3, 129.2, 126.2, 126.2, 123.4, 122.0, 120.4 (q, $J = 263$ Hz), 117.8, 112.7, 103.2, 55.5. ^{19}F NMR (376 MHz, CDCl_3) δ -54.8. **HRMS** (ESI) calcd for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NO}_2$ $[\text{M}]^+$ 293.0658, Found: 293.0668.



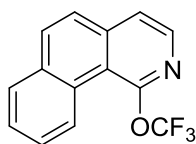
8-methoxy-6-(trifluoromethoxy)phenanthridine (2n).

The reaction was run according to the general procedure 2a on a 0.10 mmol scale. The product was isolated (24.9 mg, 85% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (600 MHz, CDCl_3) δ 8.45 (d, $J = 9.0$ Hz, 1H), 8.39 (dd, $J = 8.1, 1.4$ Hz, 1H), 8.00 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.66 (ddd, $J = 8.2, 7.0, 1.5$ Hz, 1H), 7.61 (ddd, $J = 8.3, 7.0, 1.4$ Hz, 1H), 7.56 (d, $J = 2.7$ Hz, 1H), 7.49 (dd, $J = 9.0, 2.7$ Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.2, 151.4, 140.5, 129.9, 129.1, 128.2, 126.7, 123.9, 123.8, 122.7, 121.5, 120.4 (q, $J = 261$ Hz), 119.6, 104.0, 55.6. ^{19}F NMR (376 MHz, CDCl_3) δ -55.0. **HRMS** (ESI) calcd for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NO}_2$ $[\text{M}]^+$ 293.0658, Found: 293.0661.



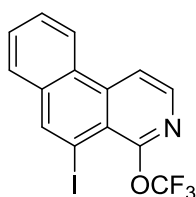
9-fluoro-6-(trifluoromethoxy)phenanthridine (2o).

The reaction was run according to the general procedure 2a on a 0.10 mmol scale. The product was isolated (15.7 mg, 56% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (600 MHz, CDCl_3) δ 8.39 (d, $J = 8.0$ Hz, 1H), 8.34 (dd, $J = 9.0, 5.7$ Hz, 1H), 8.20 (dd, $J = 10.1, 2.4$ Hz, 1H), 8.03 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.76 (ddd, $J = 8.3, 7.1, 1.4$ Hz, 1H), 7.67 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.46 (ddd, $J = 9.0, 8.0, 2.4$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 164.7 (d, $J = 254$ Hz), 151.5, 141.9, 138.0 (d, $J = 9.1$ Hz), 130.0, 129.3, 127.5 (d, $J = 9.1$ Hz), 126.8, 123.1 (d, $J = 3.0$ Hz), 122.3, 120.3 (q, $J = 263$ Hz), 117.0 (d, $J = 24$ Hz), 115.2, 107.7 (d, $J = 23$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -55.1, -103.8. **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_7\text{F}_4\text{NO}$ $[\text{M}]^+$ 281.0458, Found: 281.0465.



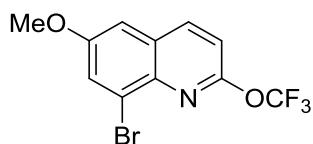
1-(trifluoromethoxy)benzo[h]isoquinoline (2p).

The reaction was run according to the general procedure 2a on a 0.10 mmol scale to give 21% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. ^1H NMR (700 MHz, CDCl_3) δ 9.17 (d, $J = 7.9$ Hz, 1H), 8.26 (dd, $J = 8.5, 1.4$ Hz, 1H), 7.97 – 7.91 (m, 1H), 7.84 (d, $J = 8.7$ Hz, 1H), 7.80 – 7.69 (m, 3H), 7.21 (dd, $J = 8.5, 1.4$ Hz, 1H). ^{13}C NMR (176 MHz, CDCl_3) δ 154.6, 144.4, 140.3, 133.9, 130.6, 128.7, 127.7, 127.5, 127.2, 124.7, 124.4, 124.4, 120.3 (q, $J = 262$ Hz), 111.6. ^{19}F NMR (376 MHz, CDCl_3) δ -55.6. **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}$ $[\text{M}]^+$ 263.0552, Found: 263.0561.



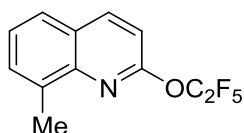
5-iodo-4-(trifluoromethoxy)benzo[f]isoquinoline (2r).

The reaction was run according to the general procedure 2a on a 0.10 mmol scale to give 19% yield of the product by ^{19}F NMR yield using PhCF_3 as internal standard. ^1H NMR (700 MHz, CDCl_3) δ 8.98 (d, $J = 8.8$ Hz, 1H), 8.72 (s, 1H), 8.53 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.75 (t, $J = 7.7$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (176 MHz, CDCl_3) δ 155.4, 144.6, 142.4, 135.9, 132.7, 129.3, 128.0, 128.0, 127.8, 123.5, 122.5, 120.7 (q, $J = 262$ Hz), 112.0, 99.6. ^{19}F NMR (376 MHz, CDCl_3) δ -55.8. **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_7\text{F}_3\text{INO}$ $[\text{M}]^+$ 388.9524, Found: 388.9528.



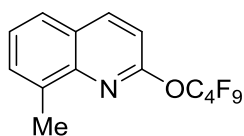
8-bromo-6-methoxy-2-(trifluoromethoxy)quinoline (2t).

The reaction was run according to the general procedure 1a on a 0.10 mmol scale. The product was isolated (16.2 mg, 19% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ¹H NMR (600 MHz, CDCl₃) δ 8.60 (dd, *J* = 9.1, 0.8 Hz, 1H), 7.98 (dd, *J* = 9.2, 0.8 Hz, 1H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.17 (d, *J* = 9.1 Hz, 1H), 4.06 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 154.1, 153.8, 141.4, 139.5, 129.2, 127.2, 120.1 (q, *J* = 263 Hz), 117.2, 113.7, 107.6, 57.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -55.6. **HRMS** (ESI) calcd for C₁₁H₇BrF₃NO₂ [M]⁺ 320.9607, Found: 320.9616.



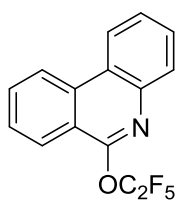
8-methyl-2-(perfluoroethoxy)quinoline (3a).

The reaction was run according to the general procedure 1b on a 1.0 mmol scale. The product was isolated (154.2 mg, 56% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ¹H NMR (600 MHz, CDCl₃) δ 8.19 (d, *J* = 8.7 Hz, 1H), 7.67 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.45 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 2.75 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 153.9, 144.8, 140.9, 136.8, 130.7, 126.7, 126.2, 125.2, 112.0, 17.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -85.6 (CF₃), -89.2 (OCF₂). **HRMS** (ESI) calcd for C₁₂H₈F₅NO [M]⁺ 277.0521, Found: 277.0526.



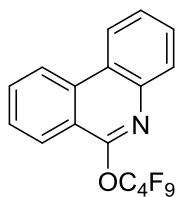
8-methyl-2-(perfluorobutoxy)quinoline (4a).

The reaction was run according to the general procedure 1b on a 1.0 mmol scale. The product was isolated (181.0 mg, 48% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ¹H NMR (600 MHz, CDCl₃) δ 8.18 (td, *J* = 8.5, 4.1 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.45 (td, *J* = 7.8, 2.2 Hz, 1H), 7.07 (dd, *J* = 8.6, 3.4 Hz, 1H), 2.75 (d, *J* = 2.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 153.8, 144.8, 140.9, 136.9, 130.7, 126.7, 126.3, 125.2, 112.0, 17.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.2 (CF₃), -84.2 (OCF₂), -125.5 (2CF₂). **HRMS** (ESI) calcd for C₁₄H₈F₉NO [M]⁺ 377.0457, Found: 377.0462.

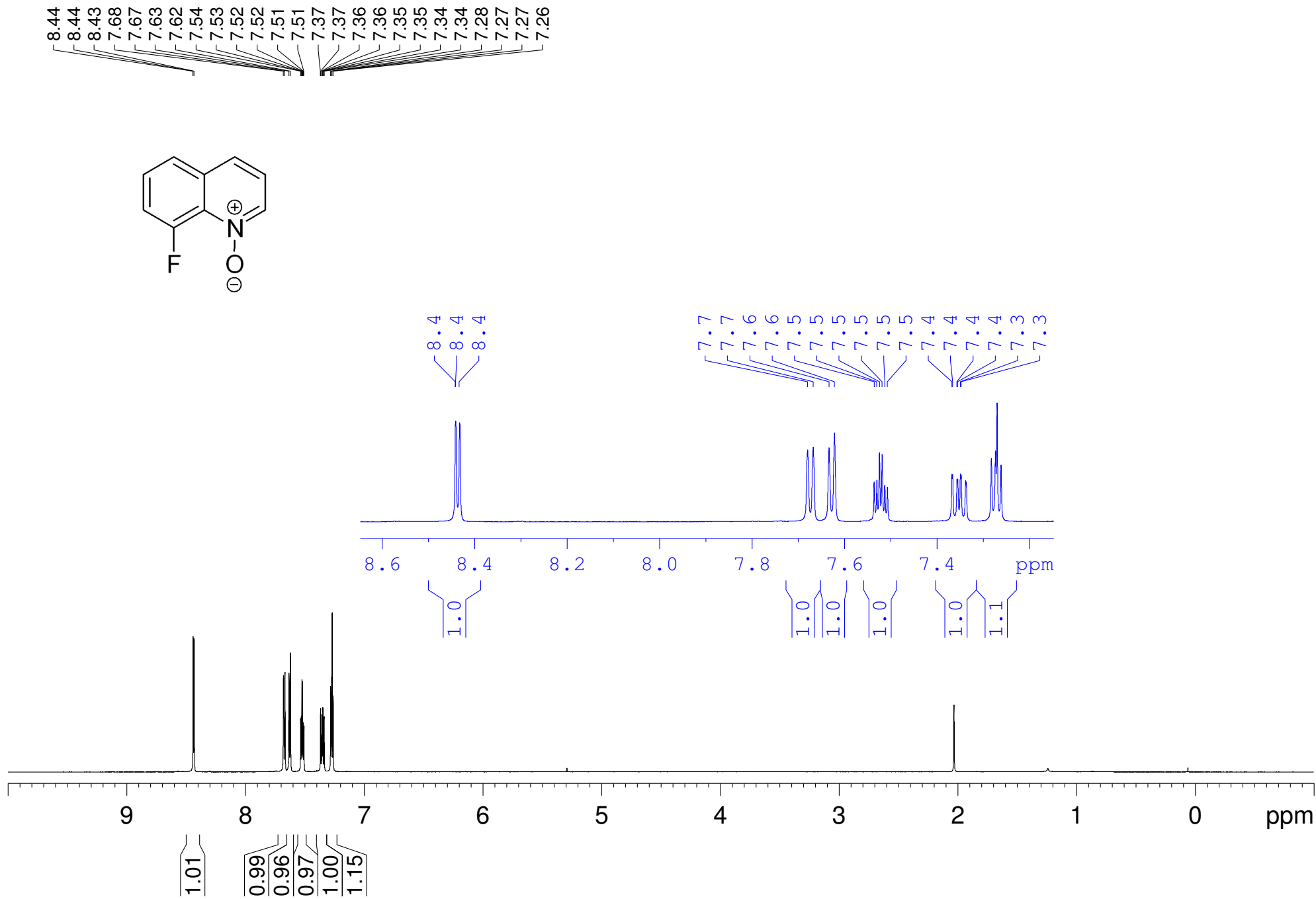


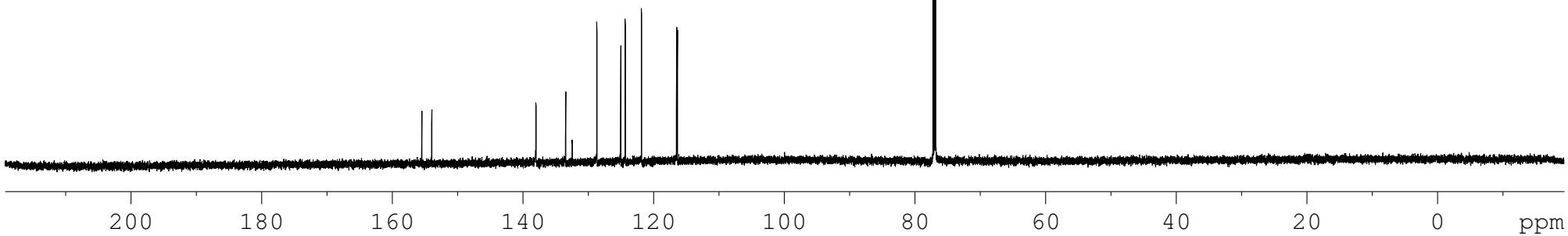
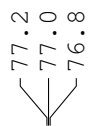
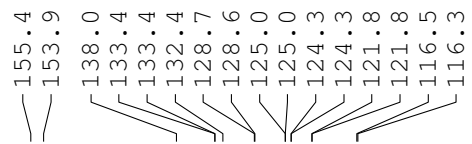
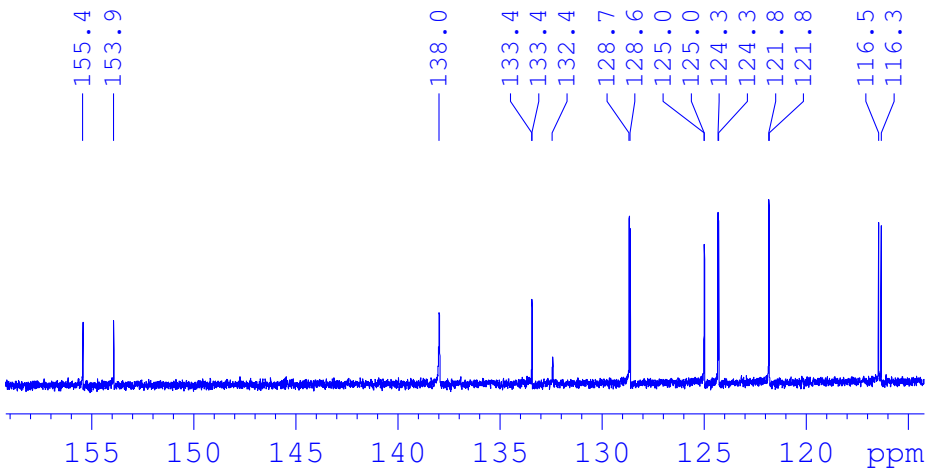
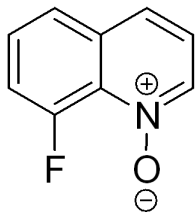
6-(perfluoroethoxy)phenanthridine (3j).

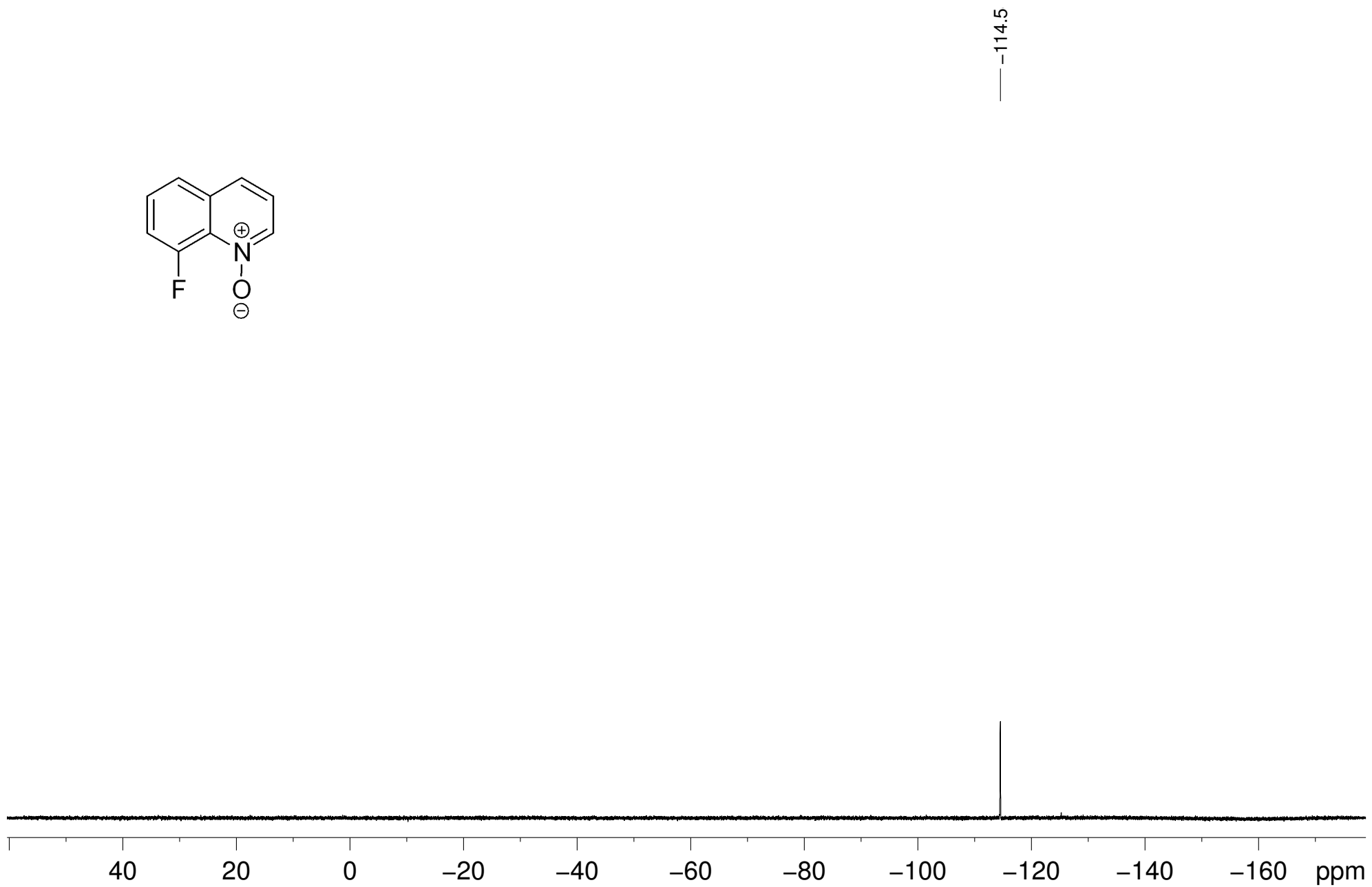
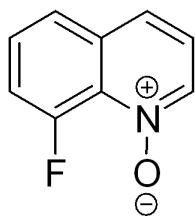
The reaction was run according to the general procedure 1b on a 1.0 mmol scale. The product was isolated (248.1 mg, 79% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ¹H NMR (600 MHz, CDCl₃) δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.53 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.26 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.06 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.93 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.75 (td, *J* = 8.2, 1.2 Hz, 2H), 7.68 (td, *J* = 7.7, 7.0, 1.4 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 152.1, 141.5, 135.7, 131.9, 129.4, 129.3, 128.0, 126.9, 124.4, 123.8, 122.3, 122.2, 118.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -86.0 (CF₃), -89.4 (OCF₂). **HRMS** (ESI) calcd for C₁₅H₈F₅NO [M]⁺ 313.0521, Found: 313.0531.

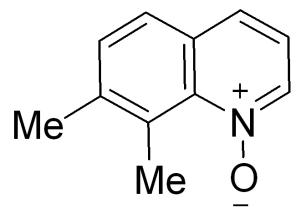


6-(perfluorobutoxy)phenanthridine (4j). The reaction was run according to the general procedure 1b on a 1.0 mmol scale. The product was isolated (305.4 mg, 81% yield) by flash chromatography on silica gel using hexane/EtOAc as eluent. ^1H NMR (600 MHz, CDCl_3) δ 8.56 (d, $J = 8.3$ Hz, 1H), 8.48 (dd, $J = 8.1, 1.3$ Hz, 1H), 8.20 (dd, $J = 8.3, 1.2$ Hz, 1H), 8.04 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.89 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.72 (dddd, $J = 8.2, 7.2, 5.8, 1.2$ Hz, 2H), 7.65 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 152.0, 141.4, 135.7, 131.8, 129.3, 129.3, 128.0, 126.9, 124.1, 123.7, 122.2, 122.1, 118.6. ^{19}F NMR (376 MHz, CDCl_3) δ -80.1 (CF_3), -84.0 (OCF_2), -125.4 (2CF_2). **HRMS** (ESI) calcd for $\text{C}_{17}\text{H}_8\text{F}_9\text{NO}$ $[\text{M}]^+$ 413.0457, Found: 413.0468.





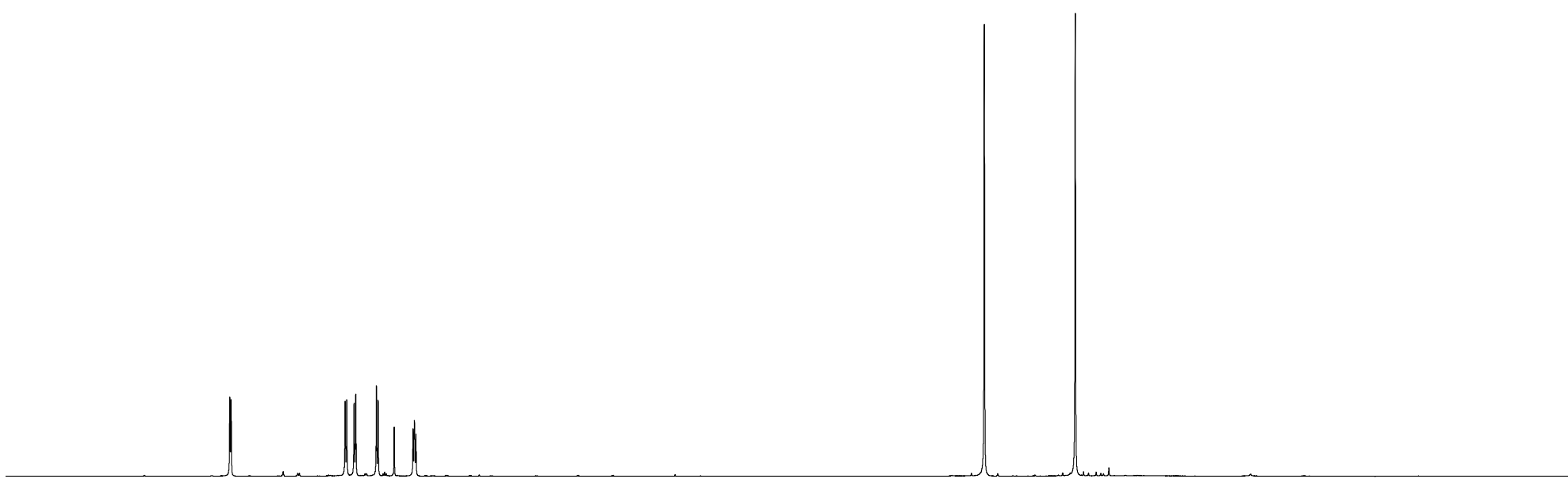




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3.12

2.48



9

8

7

6

5

4

3

2

1

0

ppm

1.05

1.04

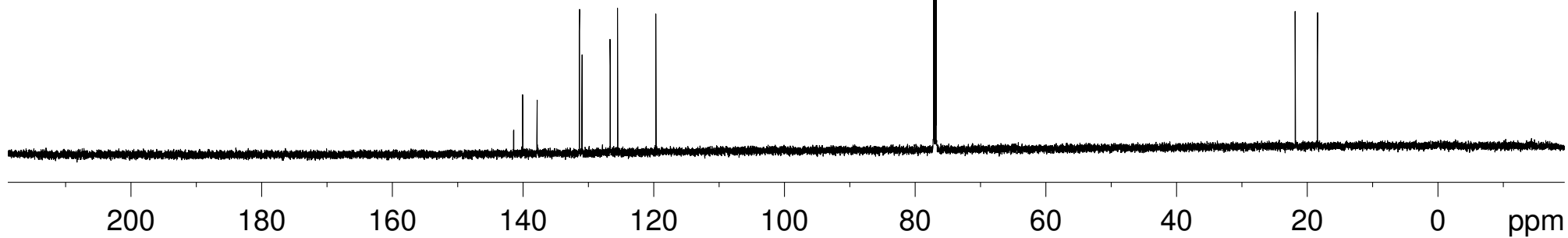
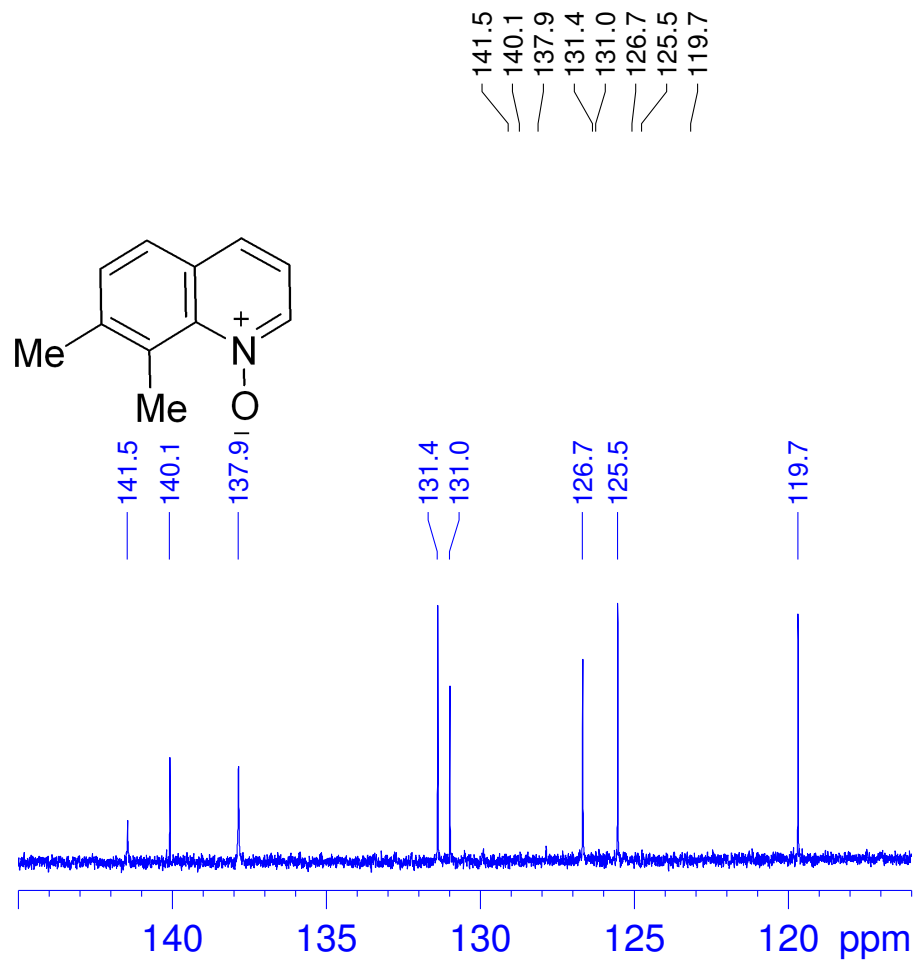
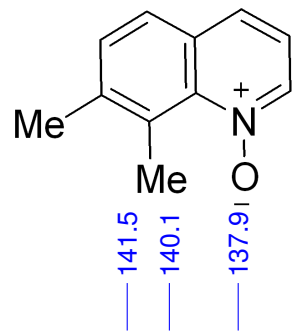
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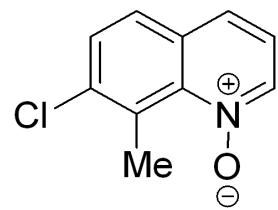
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1.01

3.00

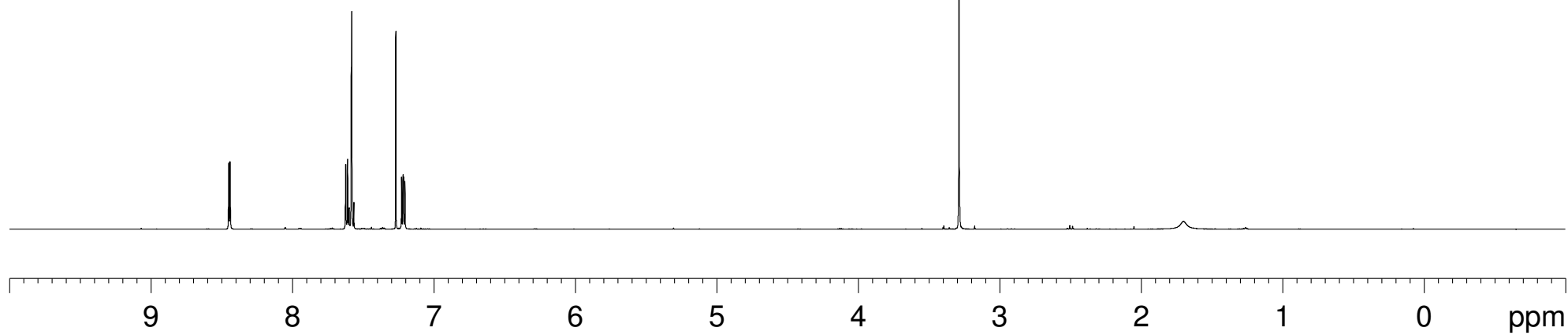
3.09





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7.21

3.29

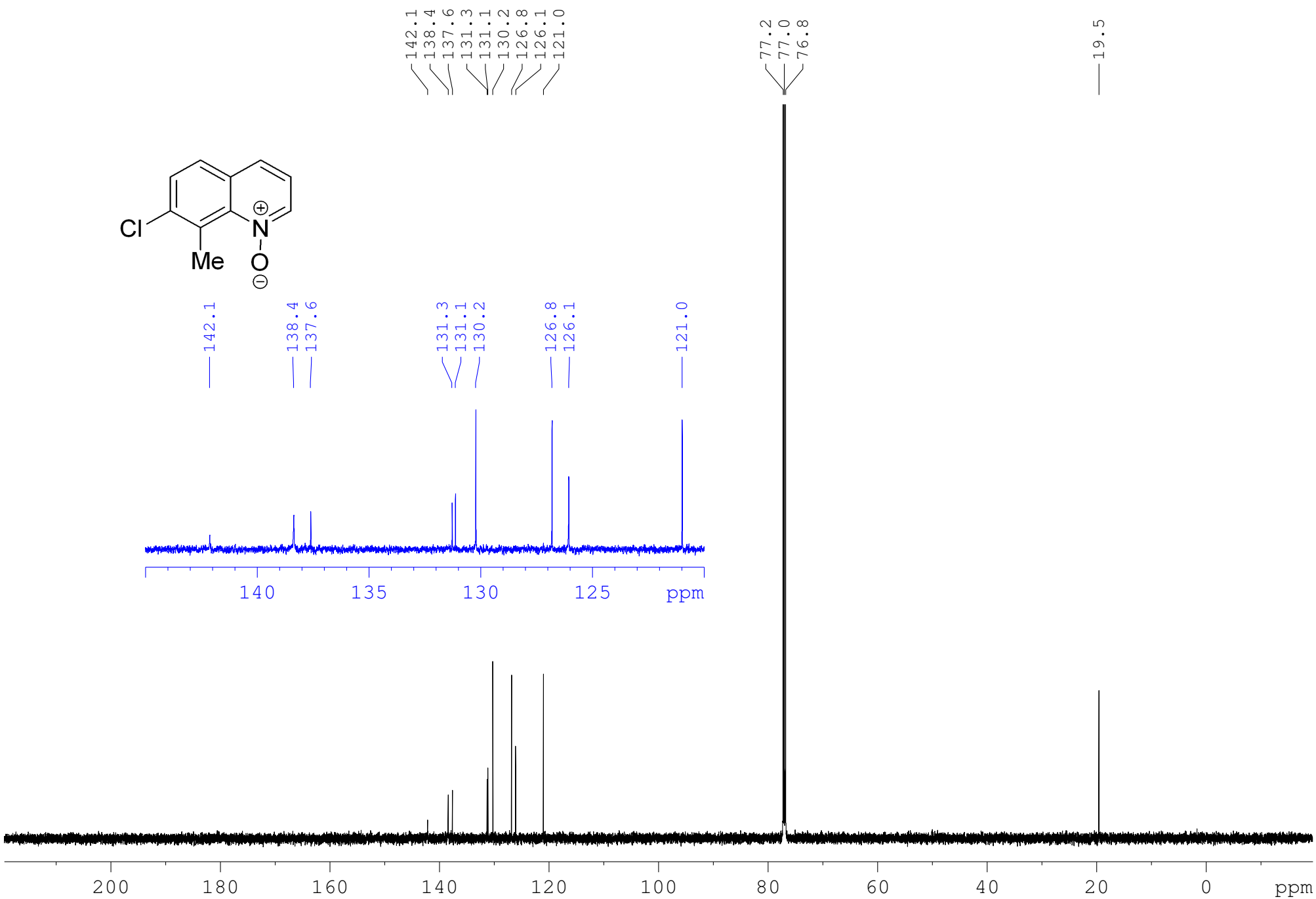
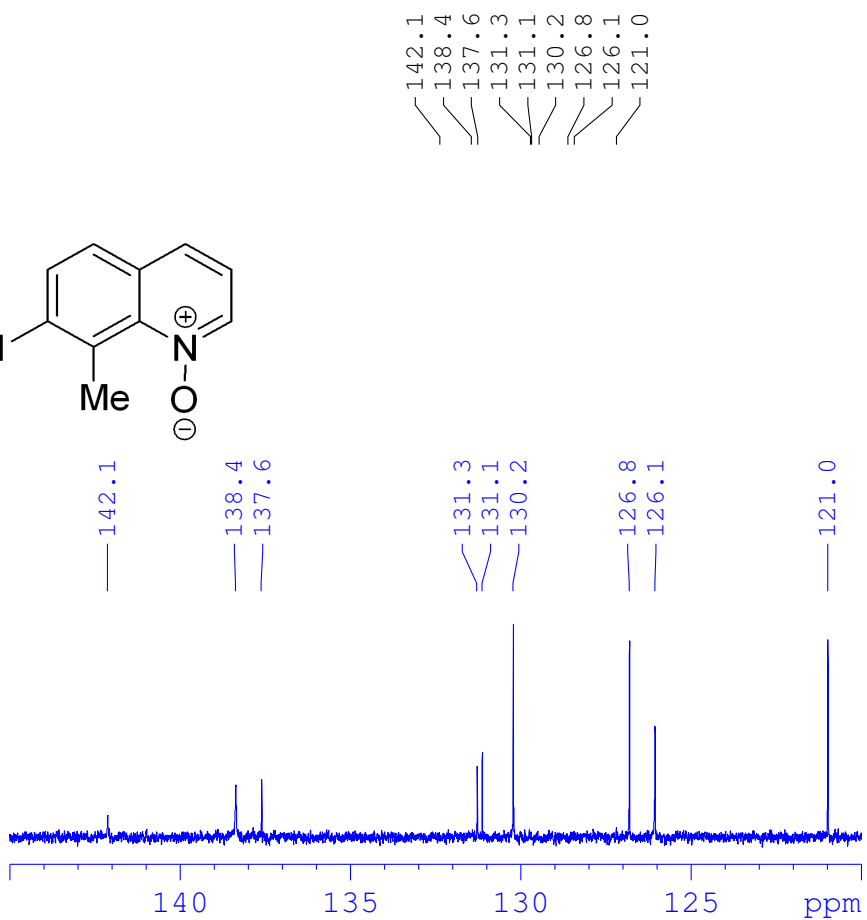
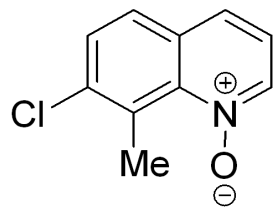


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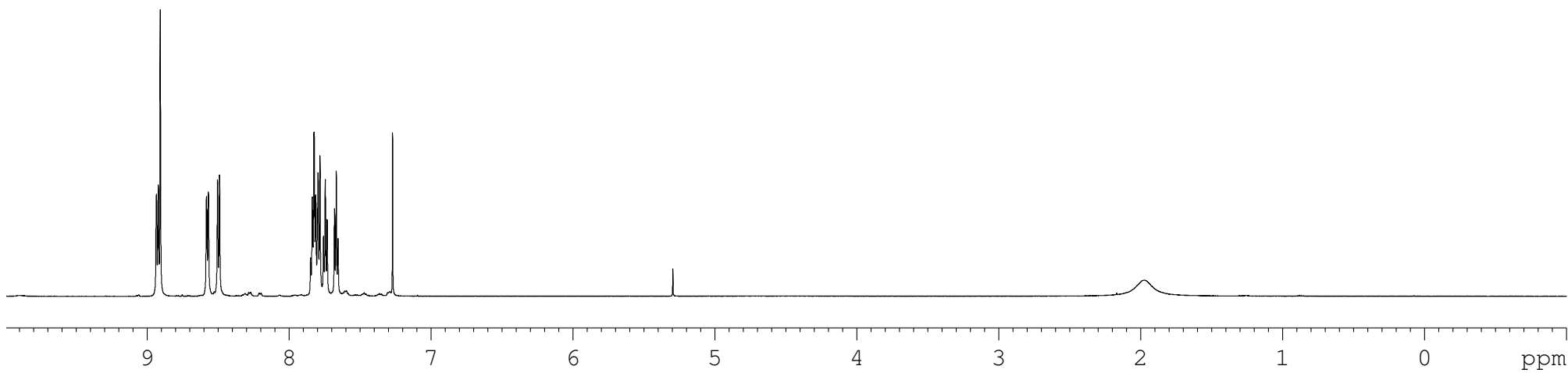
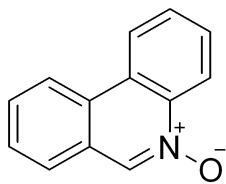
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2.07

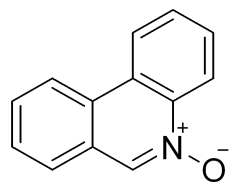
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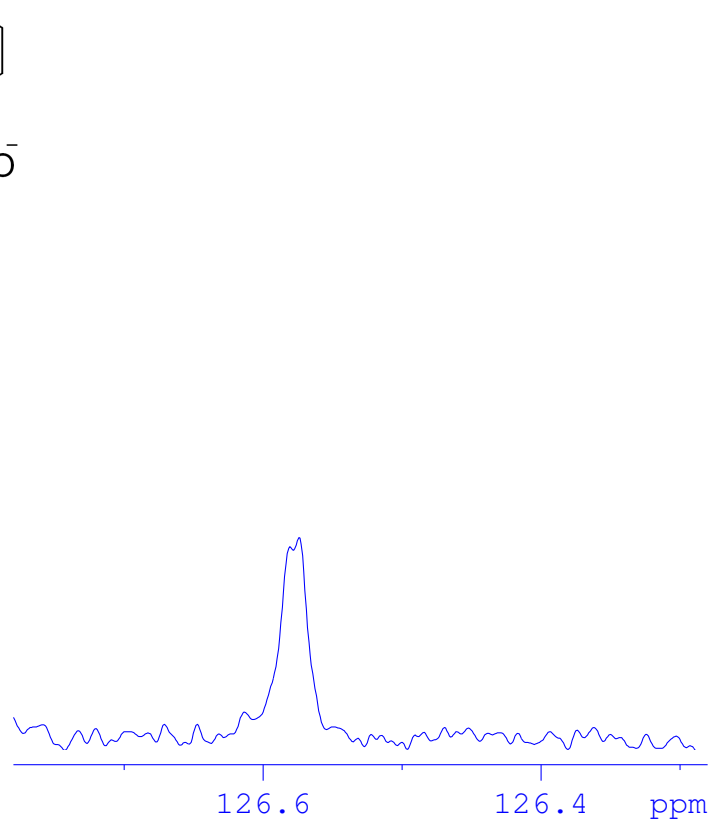
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7.667
7.654
7.270



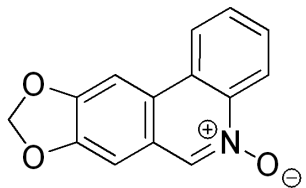
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1.875
1.262
1.116
1.087



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129.3
128.8
126.8
126.6
126.2
122.7
122.1
120.7

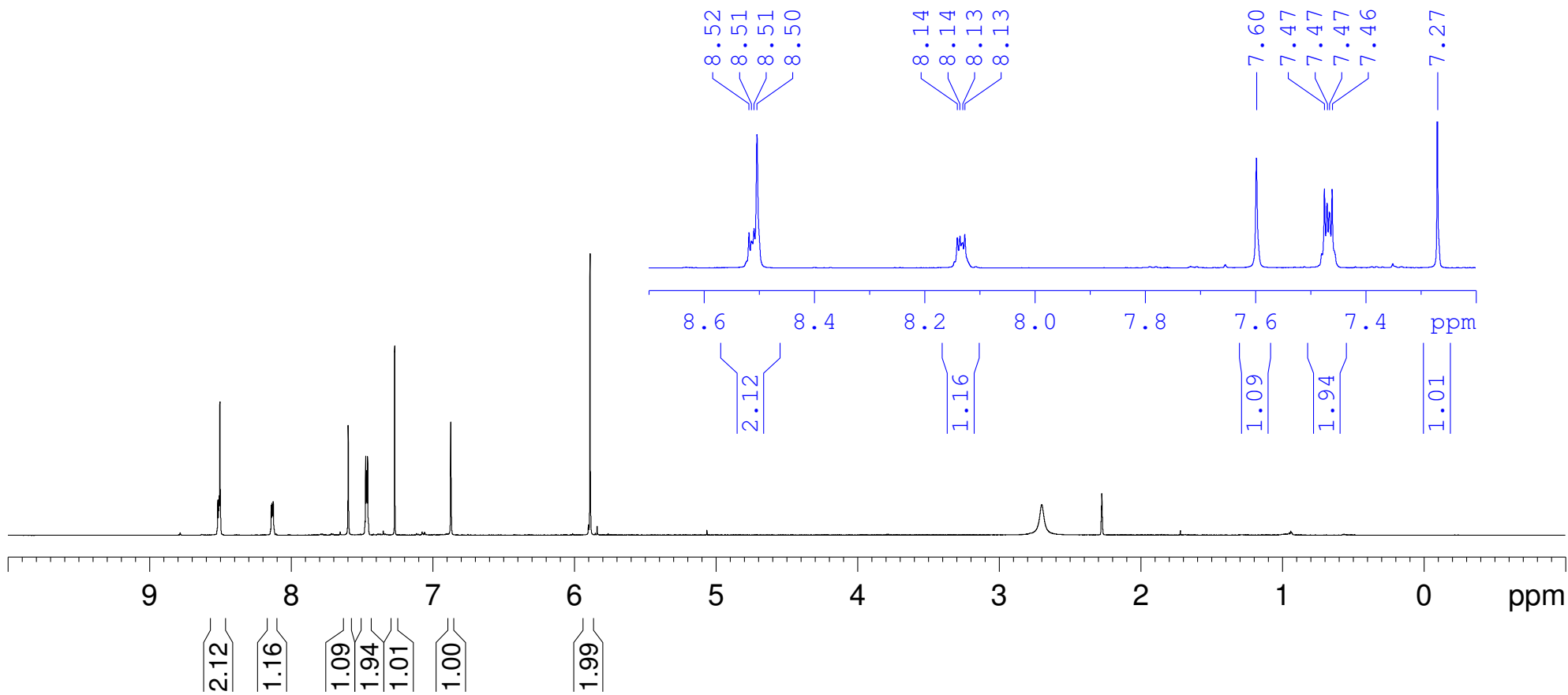


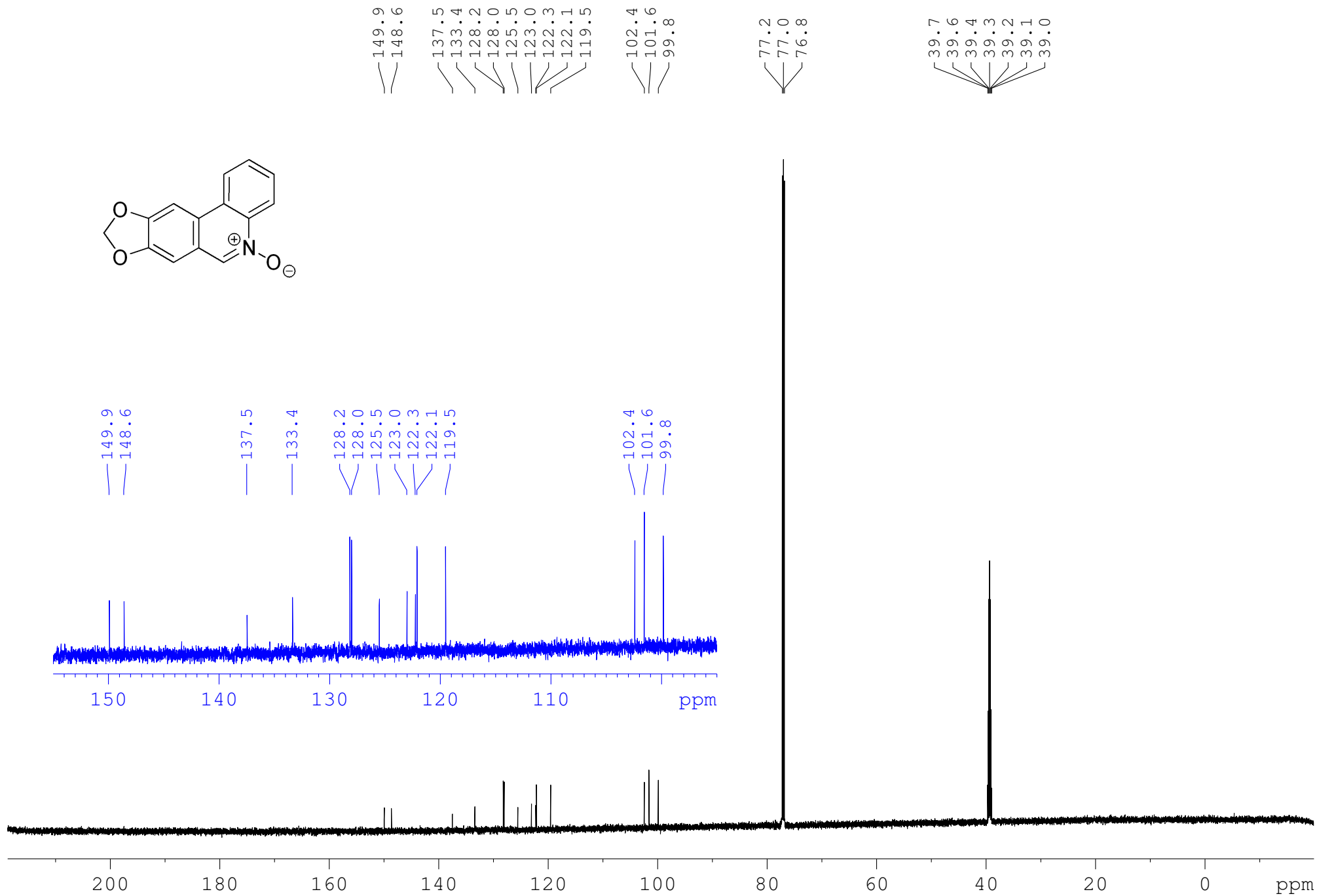
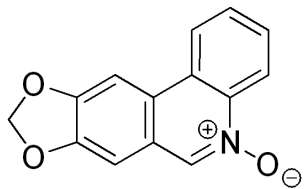
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7.47
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7.27
6.87

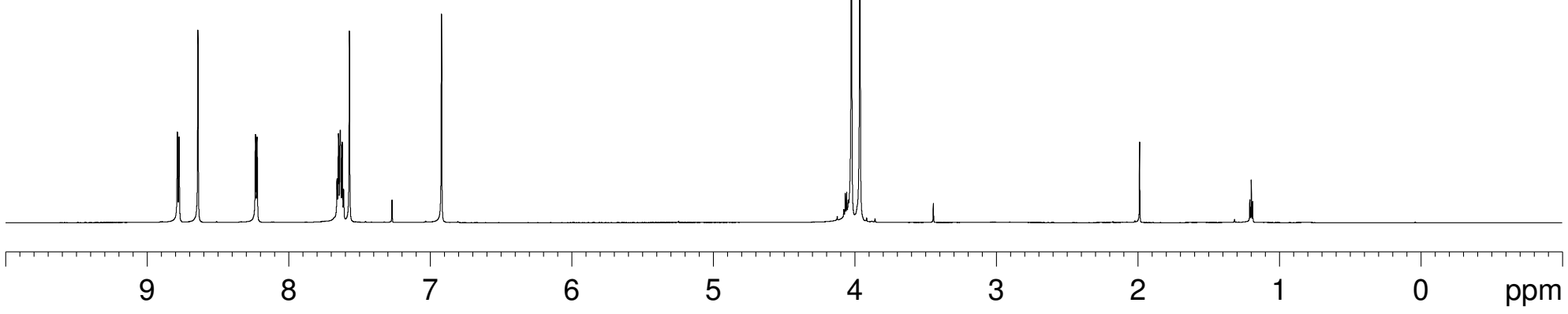
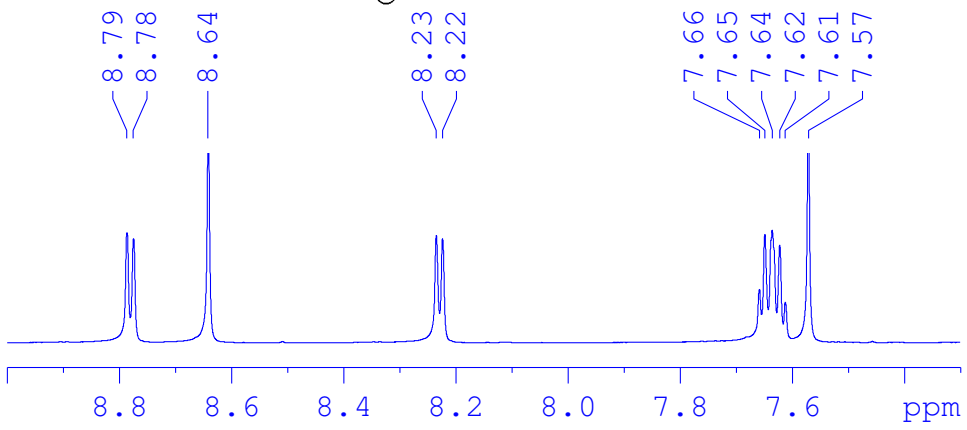
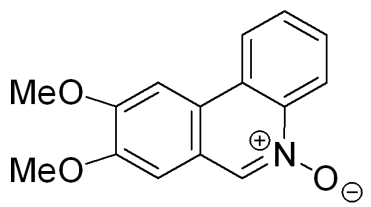
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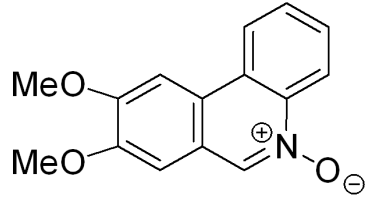




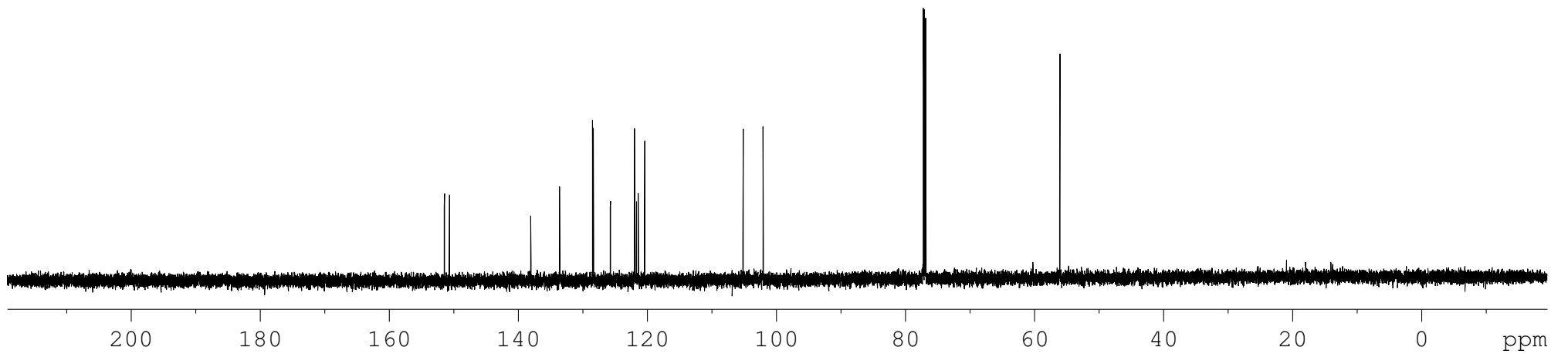
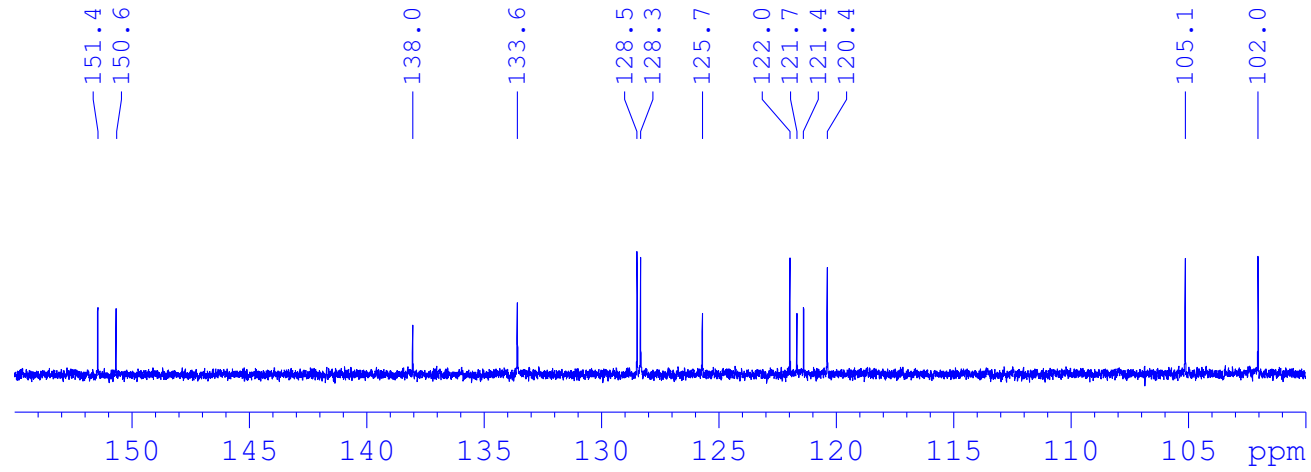
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7.64
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7.27
6.92

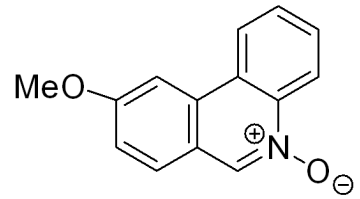
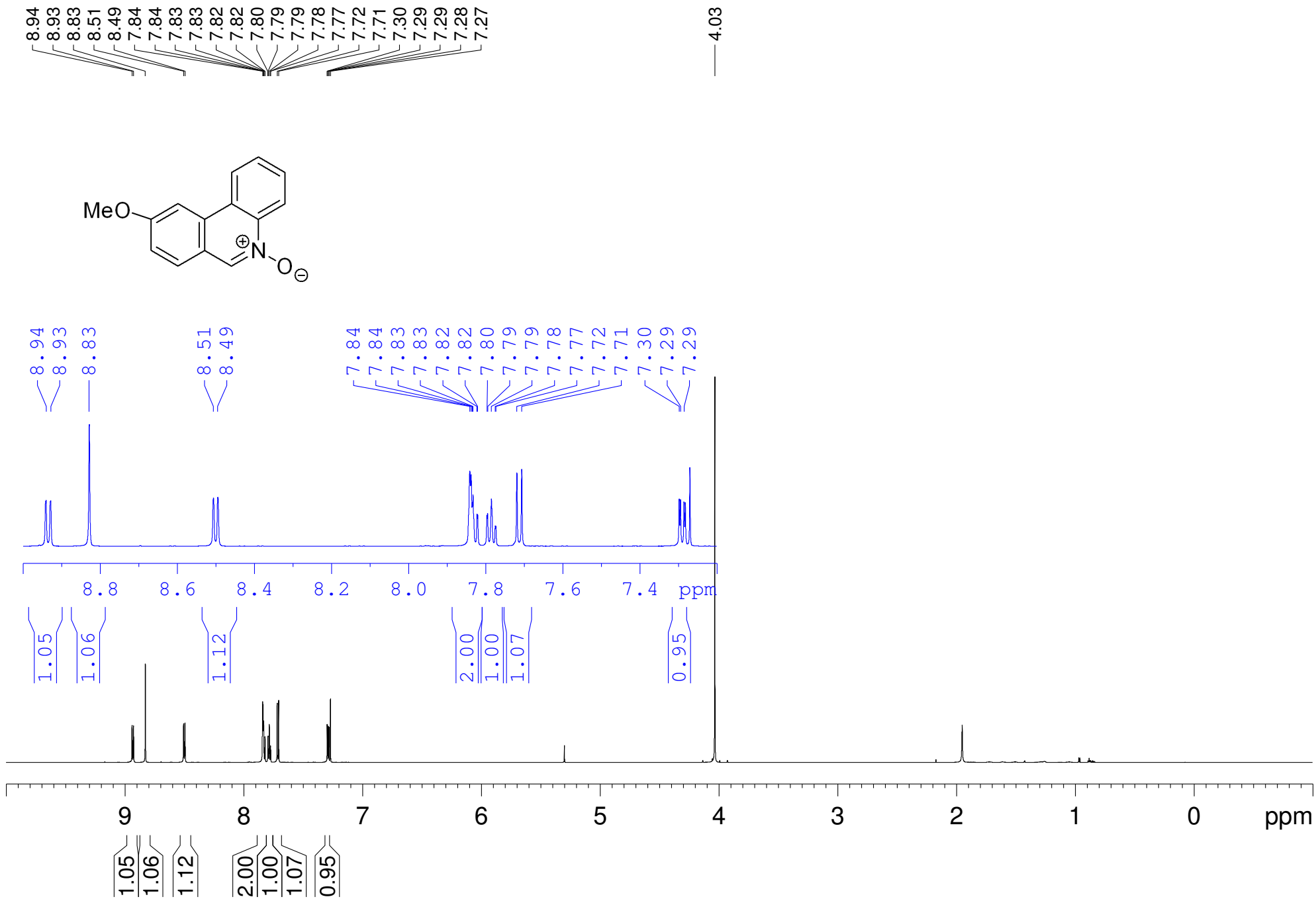
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3.96

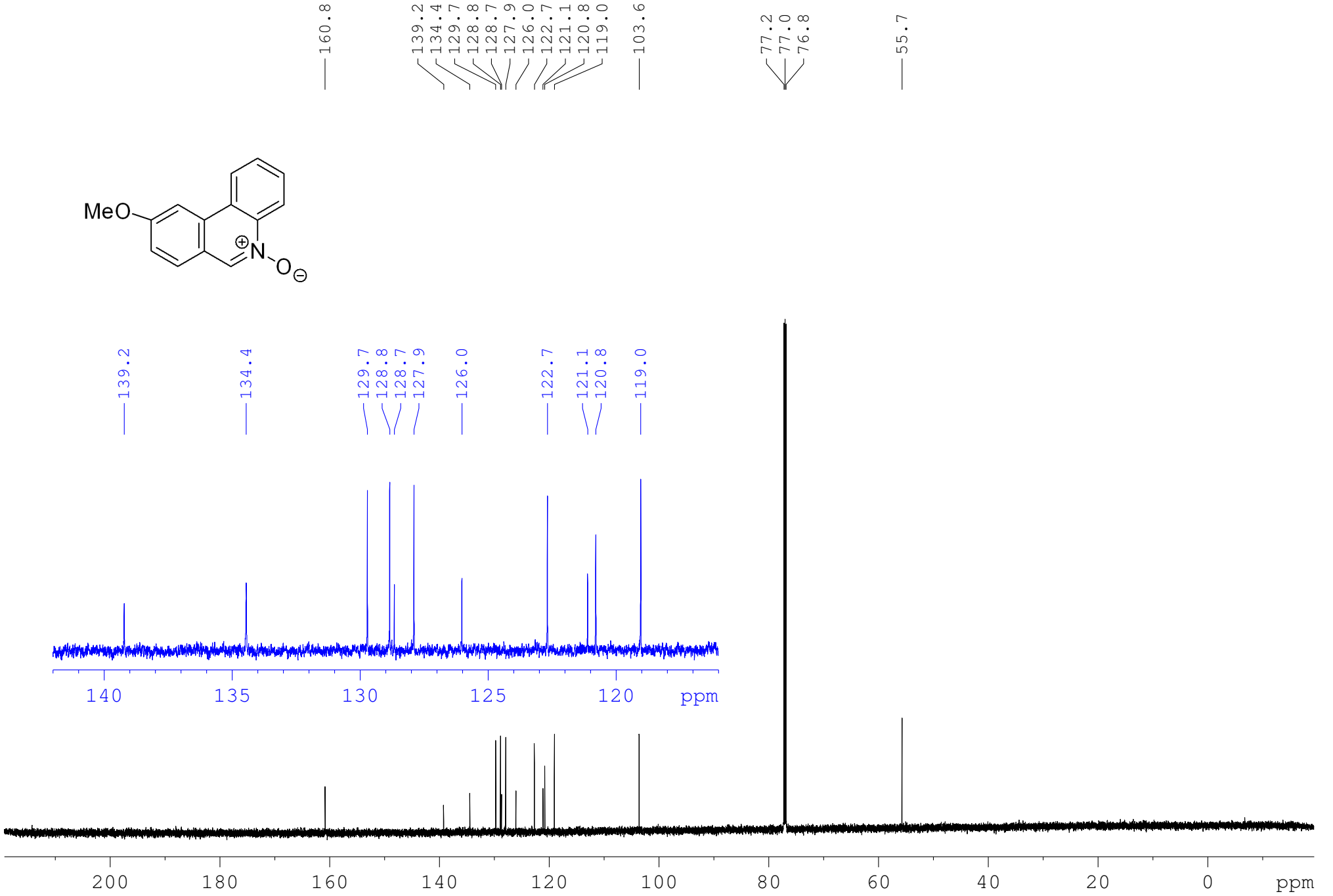
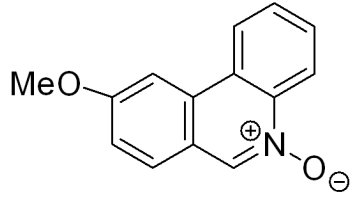


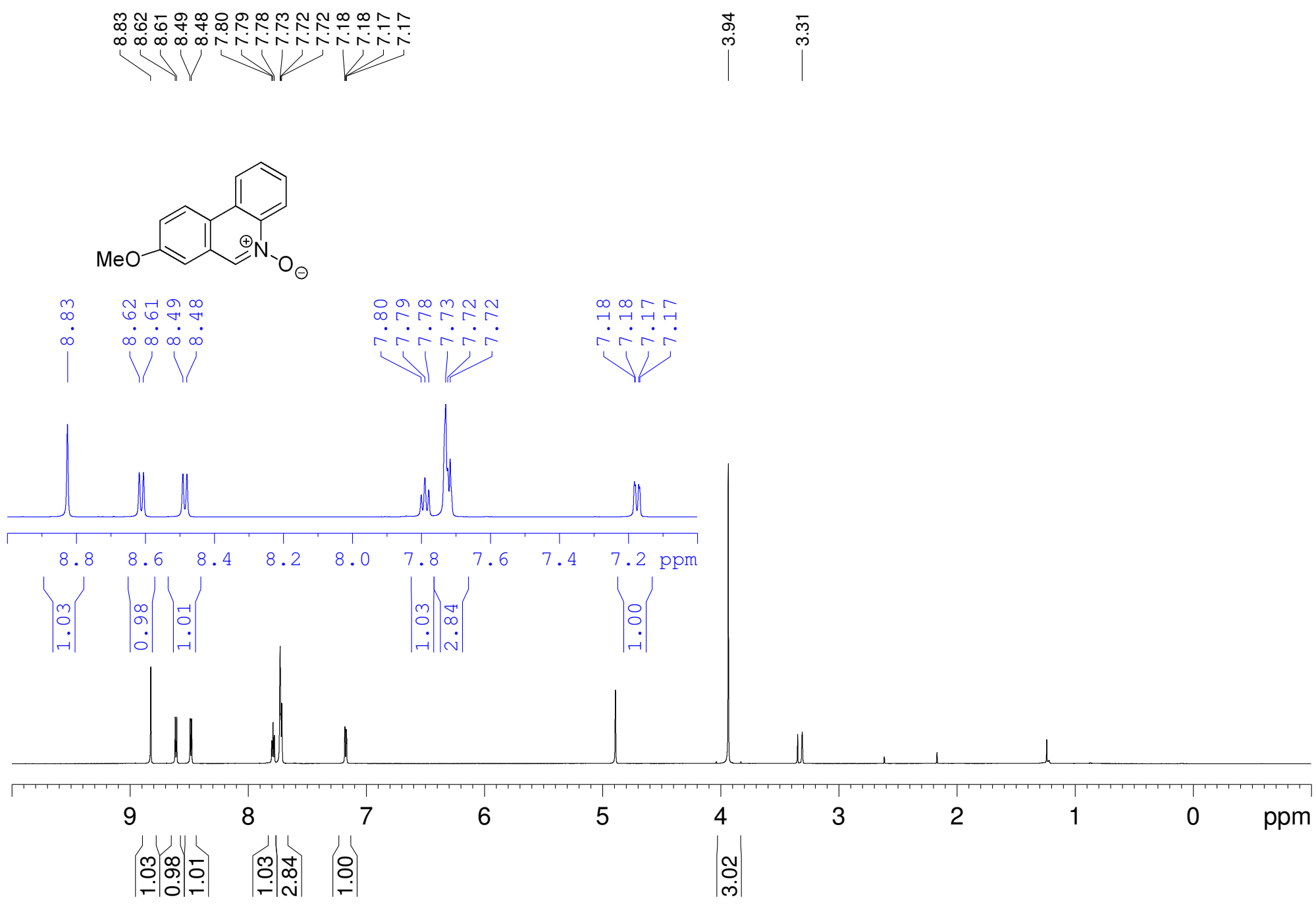
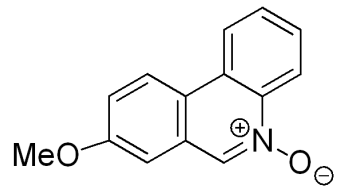


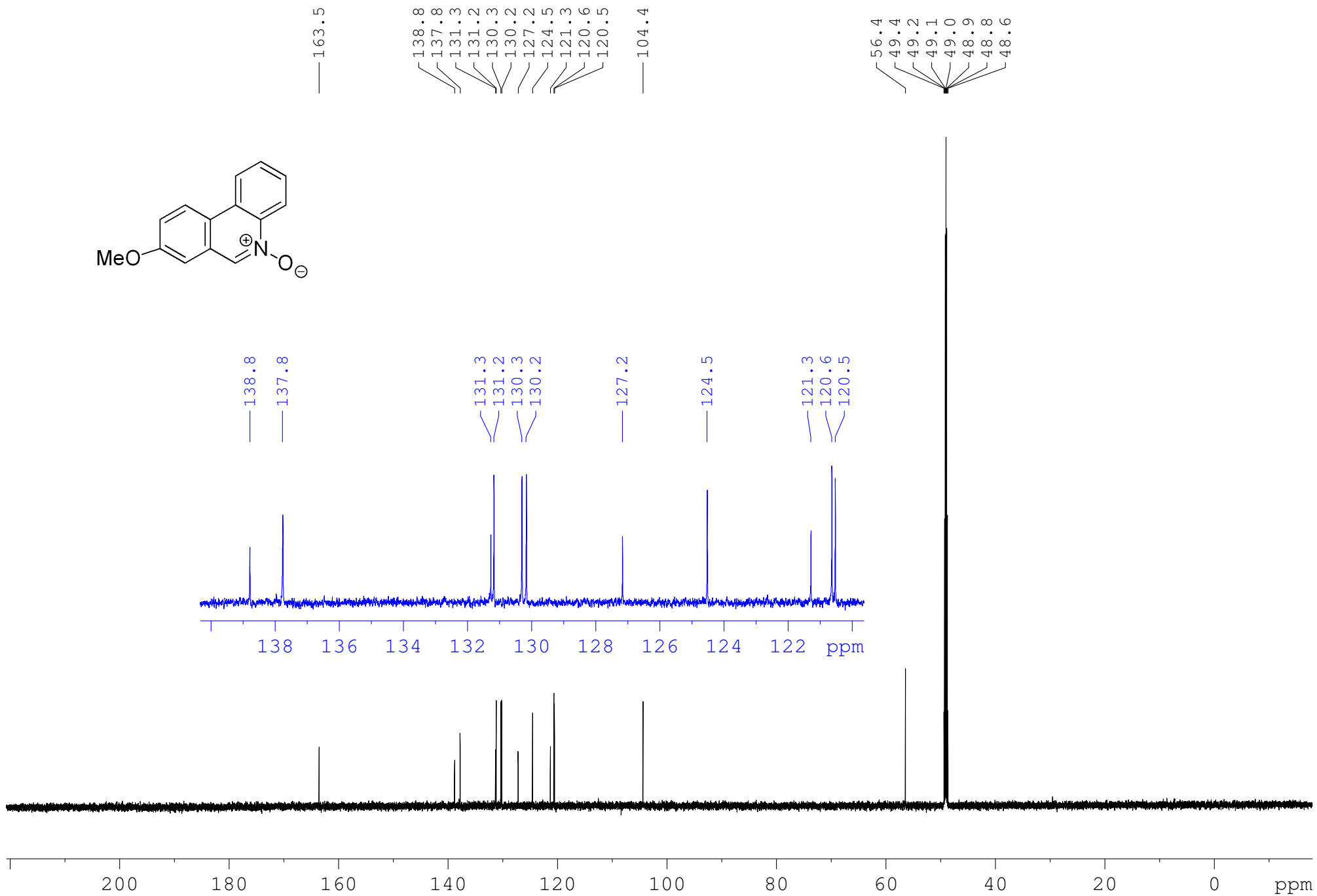
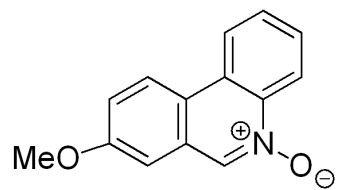
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128.3
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121.4
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105.1
102.0
77.2
77.0
76.8
56.0
56.0





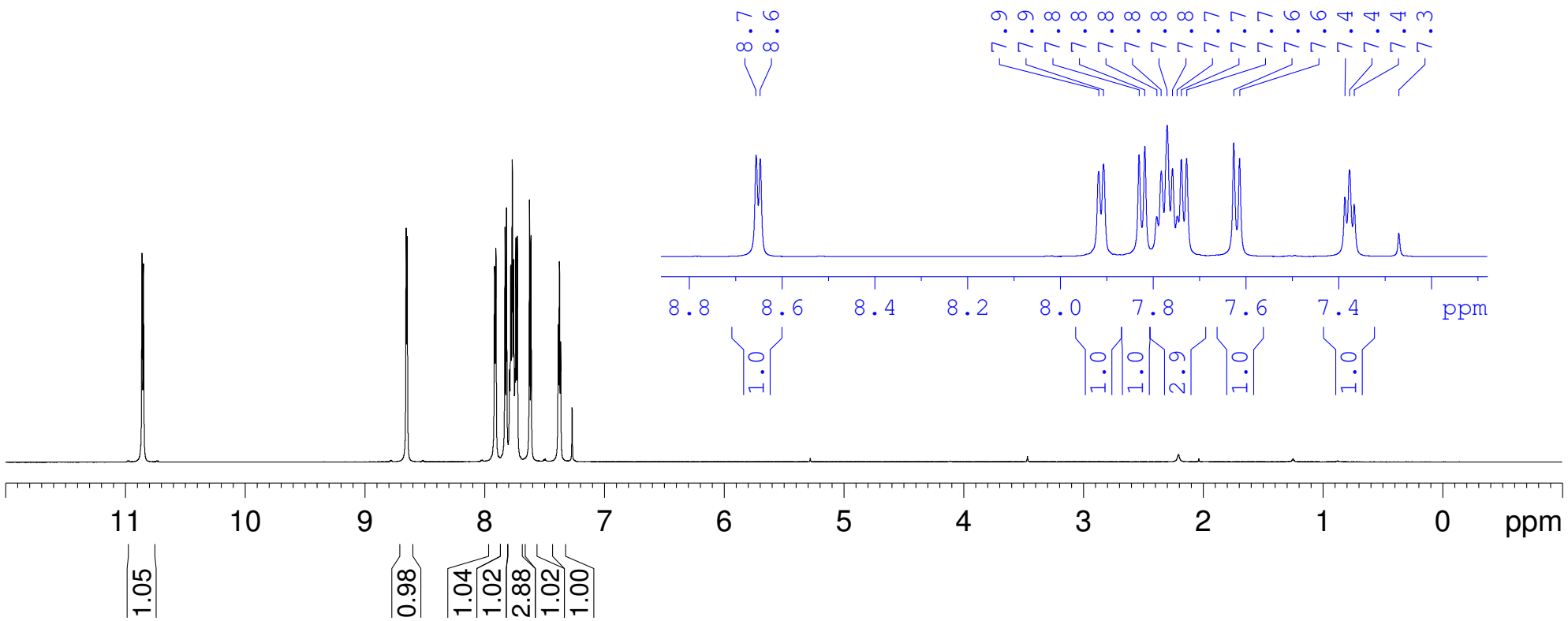
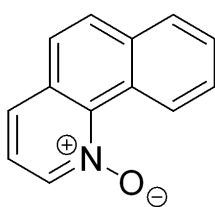


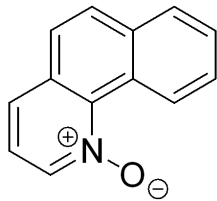




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7.75
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7.73
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7.38
7.37
7.27





— 139.2
— 138.4

— 134.0

— 131.2
— 130.5

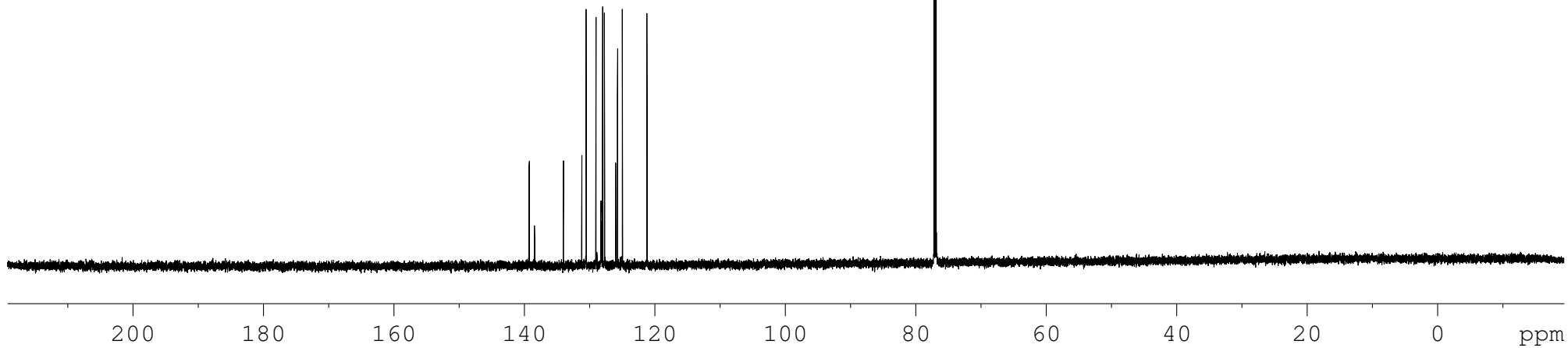
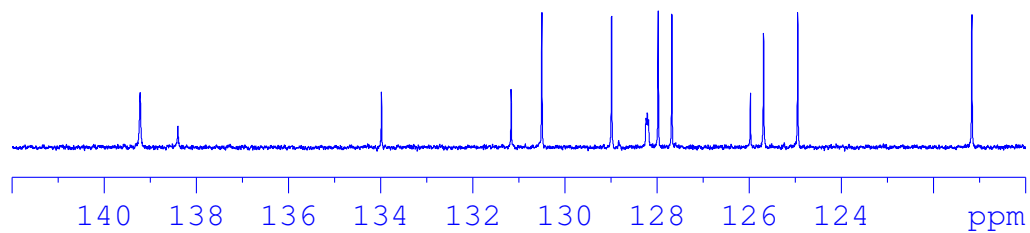
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— 128.2
— 128.0
— 127.7

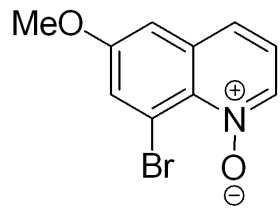
— 126.0
— 125.7
— 124.9

— 121.2

139.2
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124.9
121.2

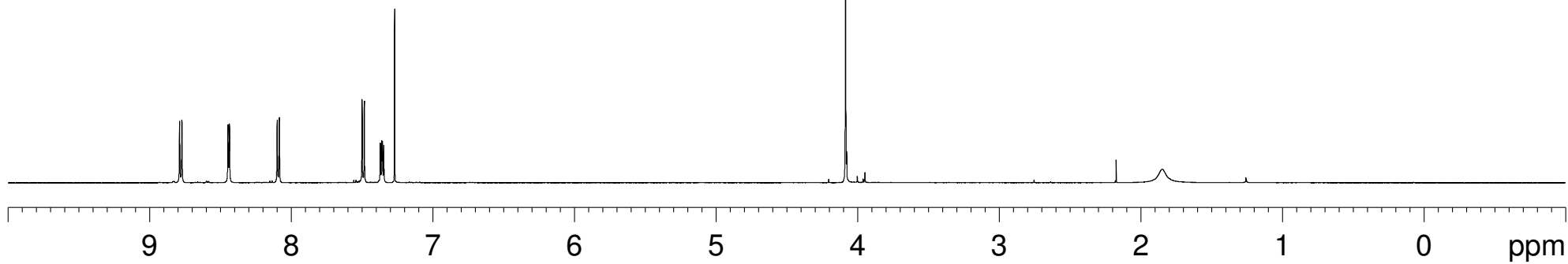
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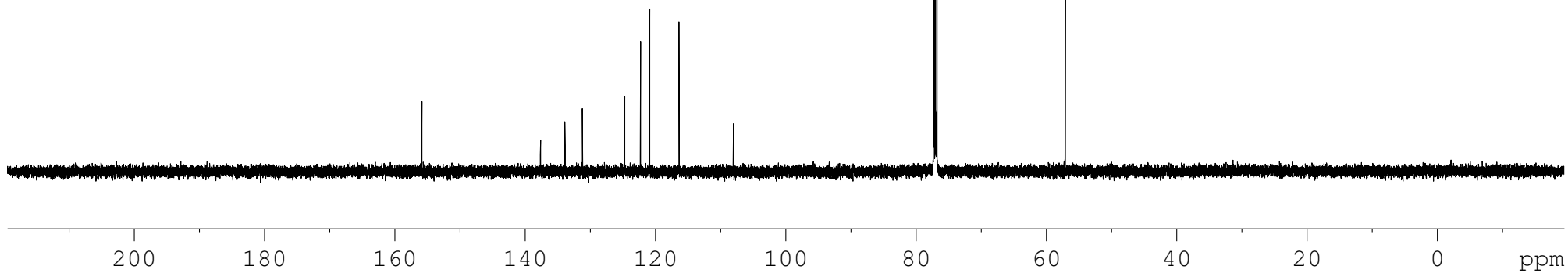
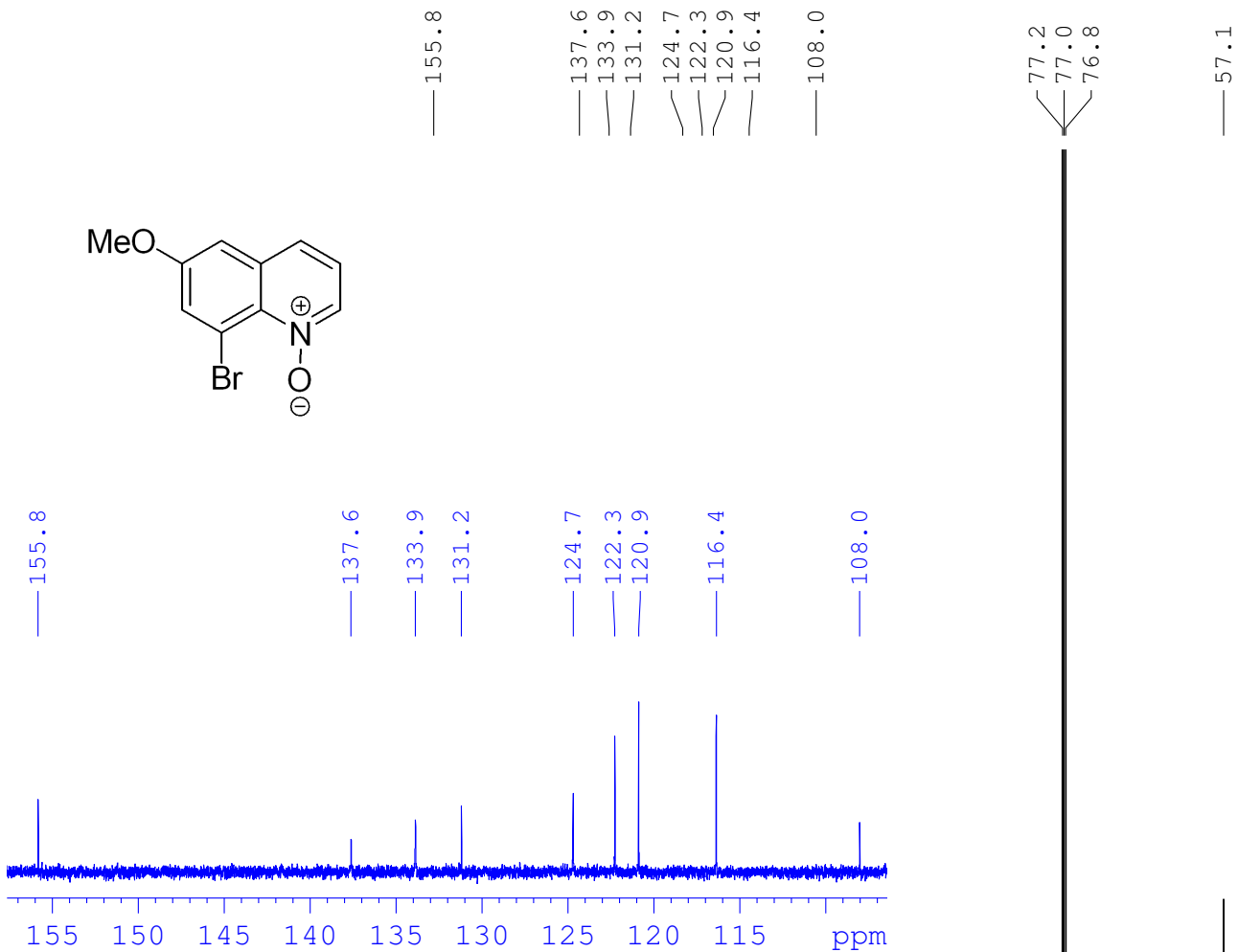
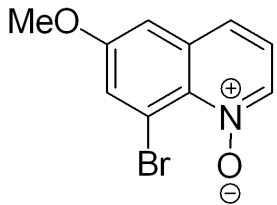
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7.35
7.27

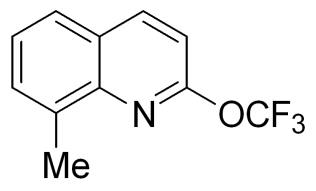
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1.03

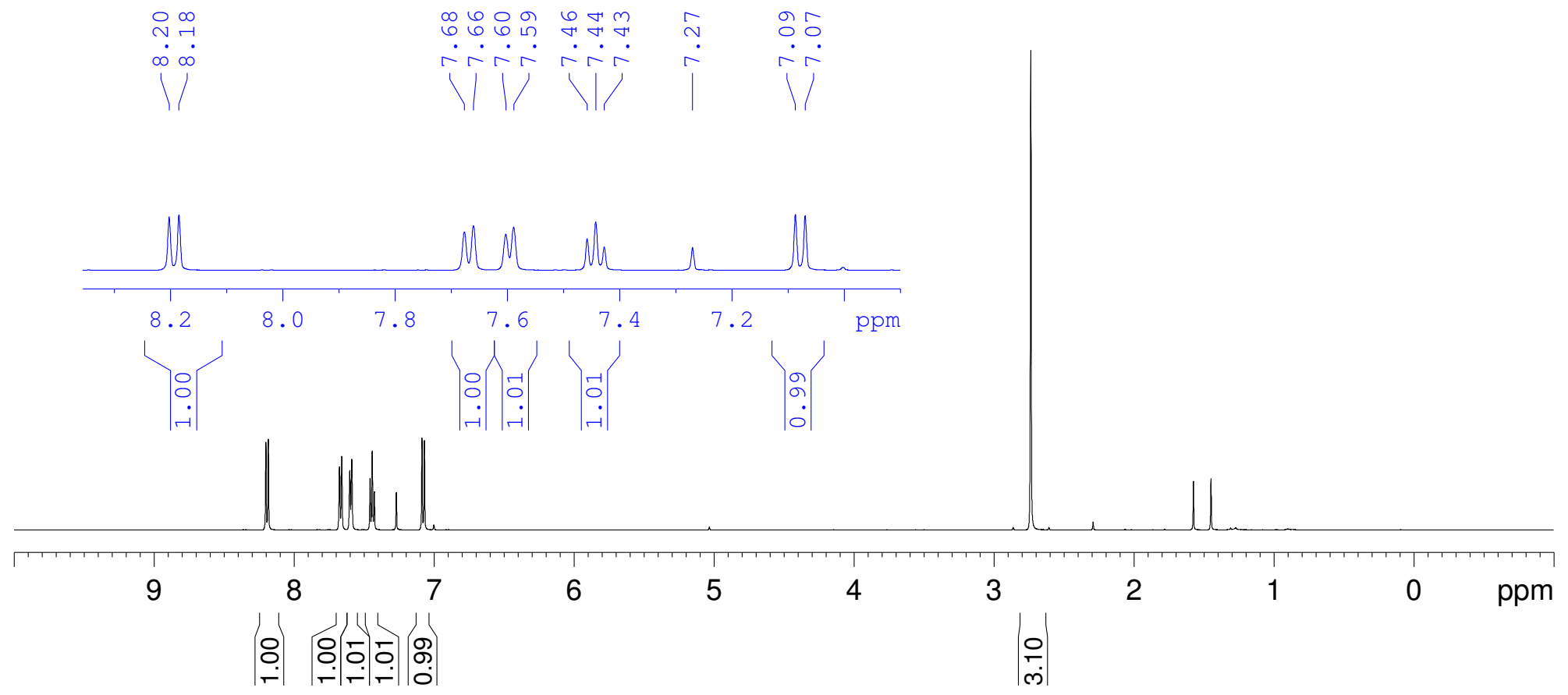
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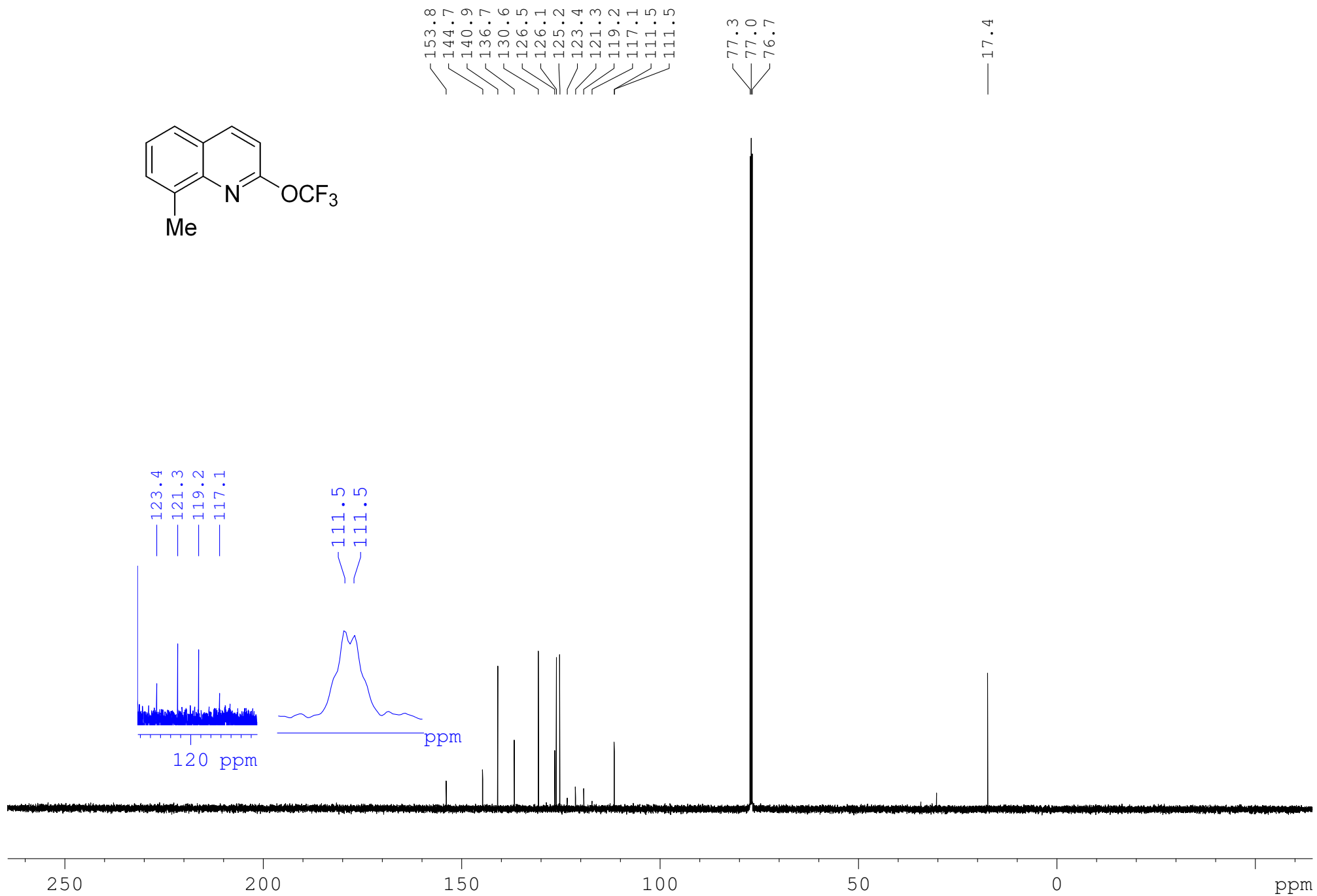
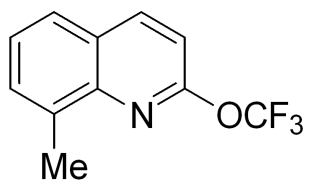


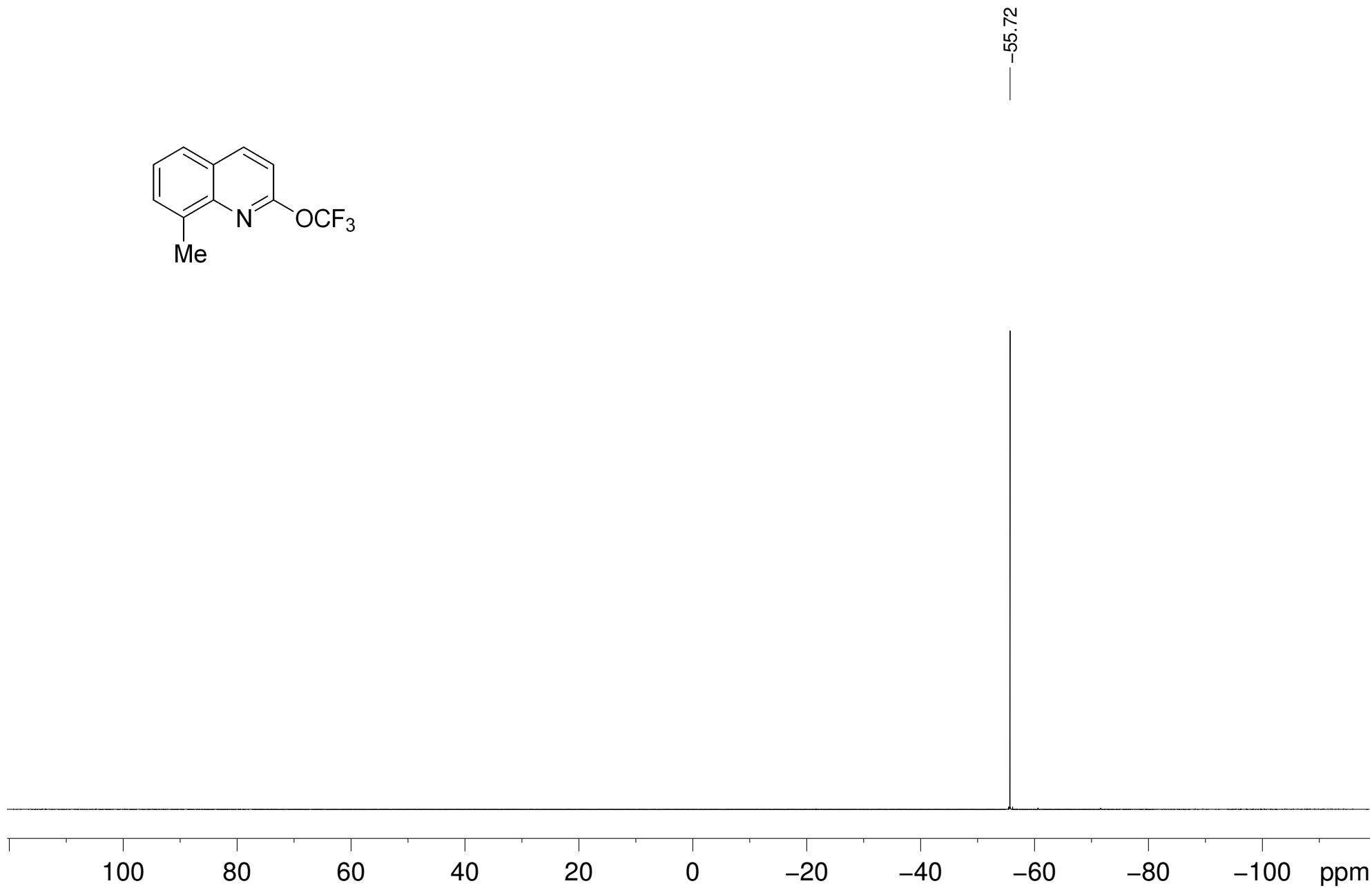
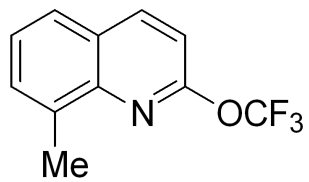


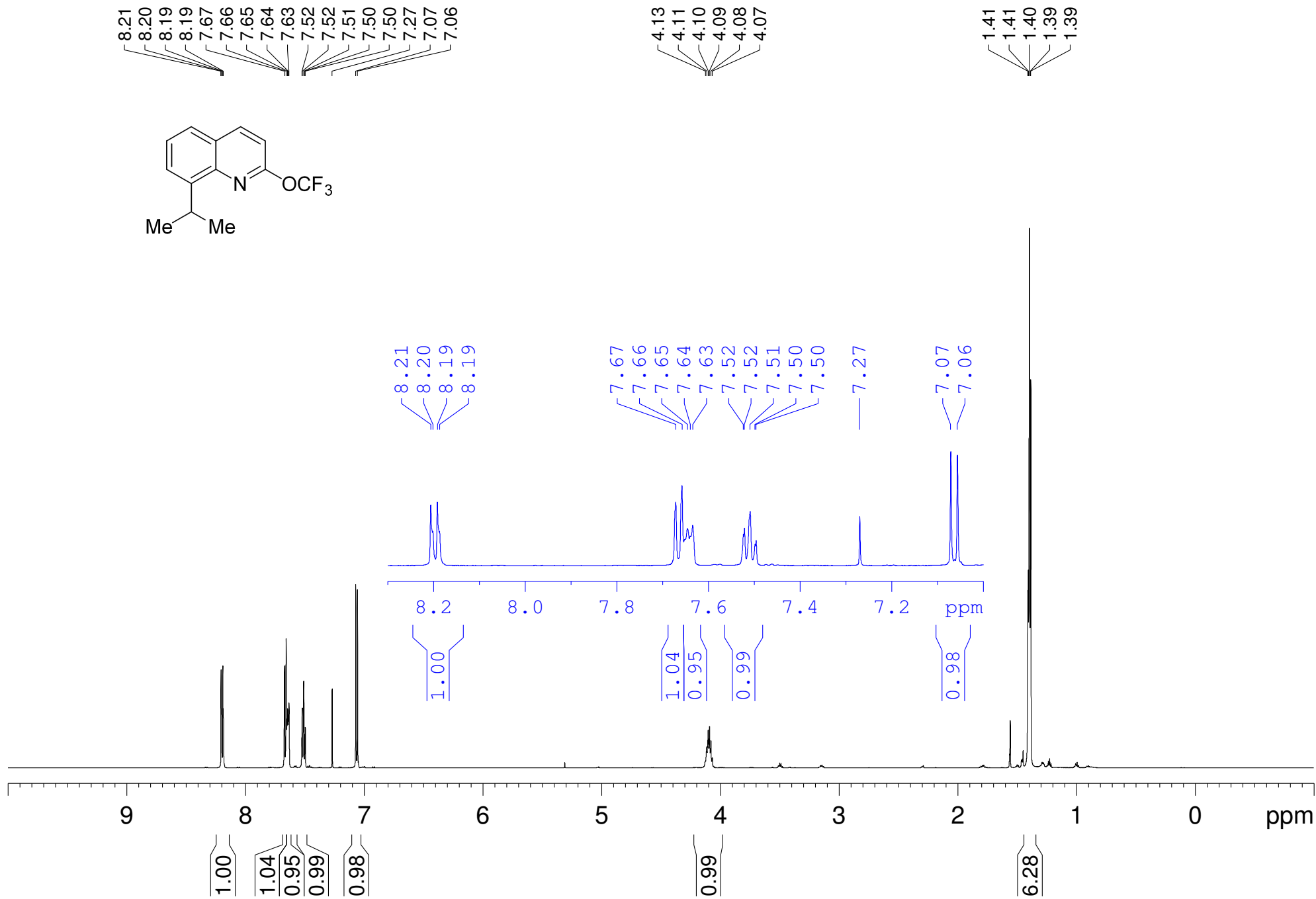
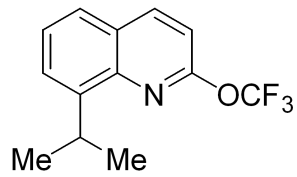
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7.07

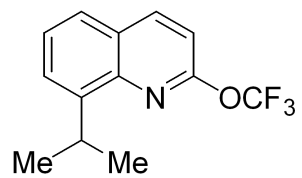
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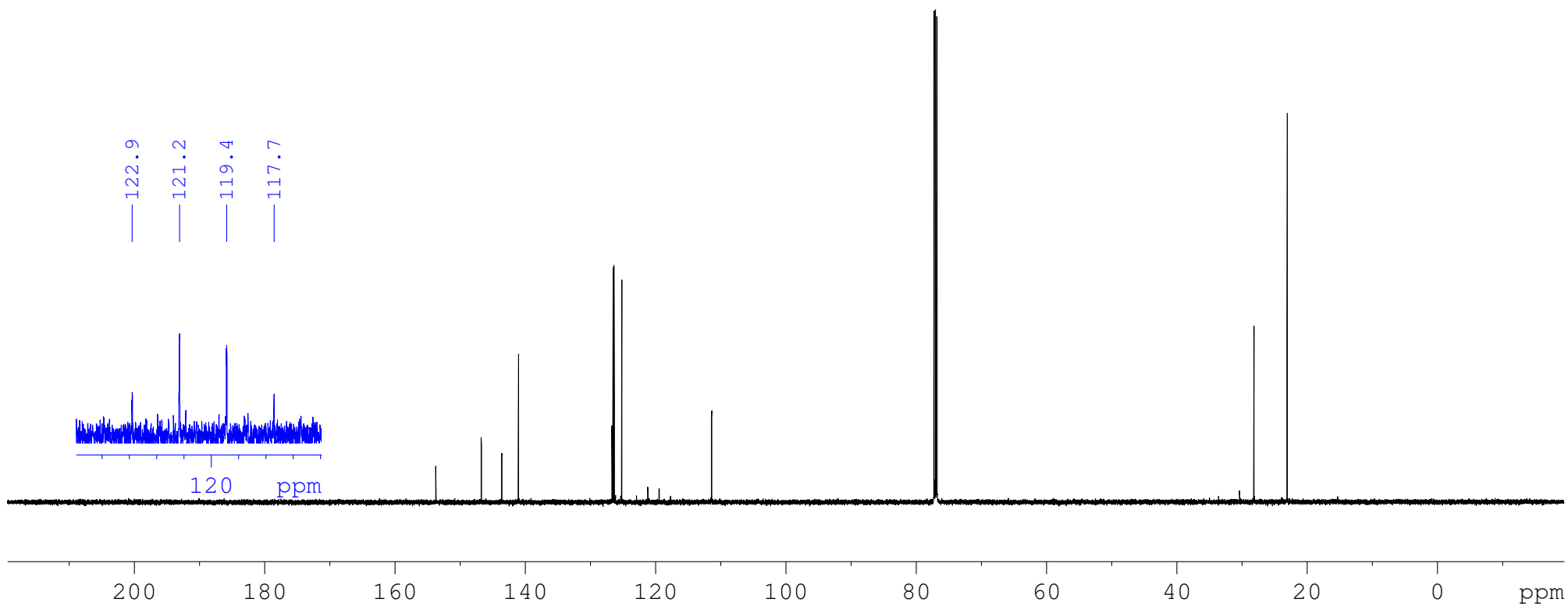
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126.1
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125.1
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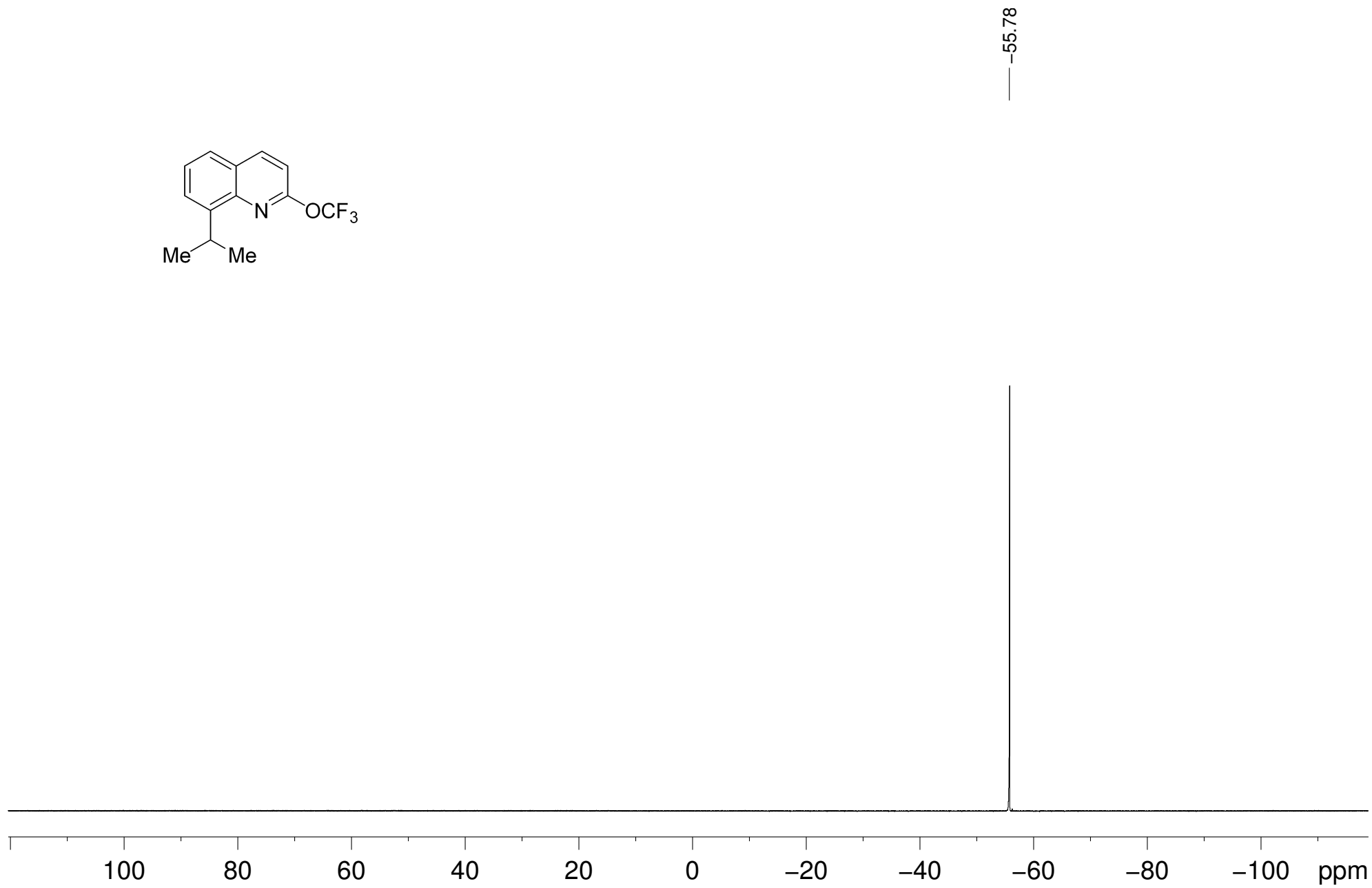
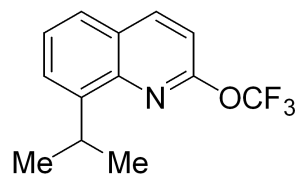
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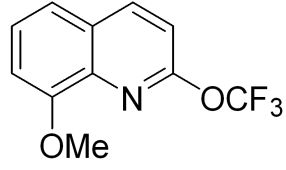
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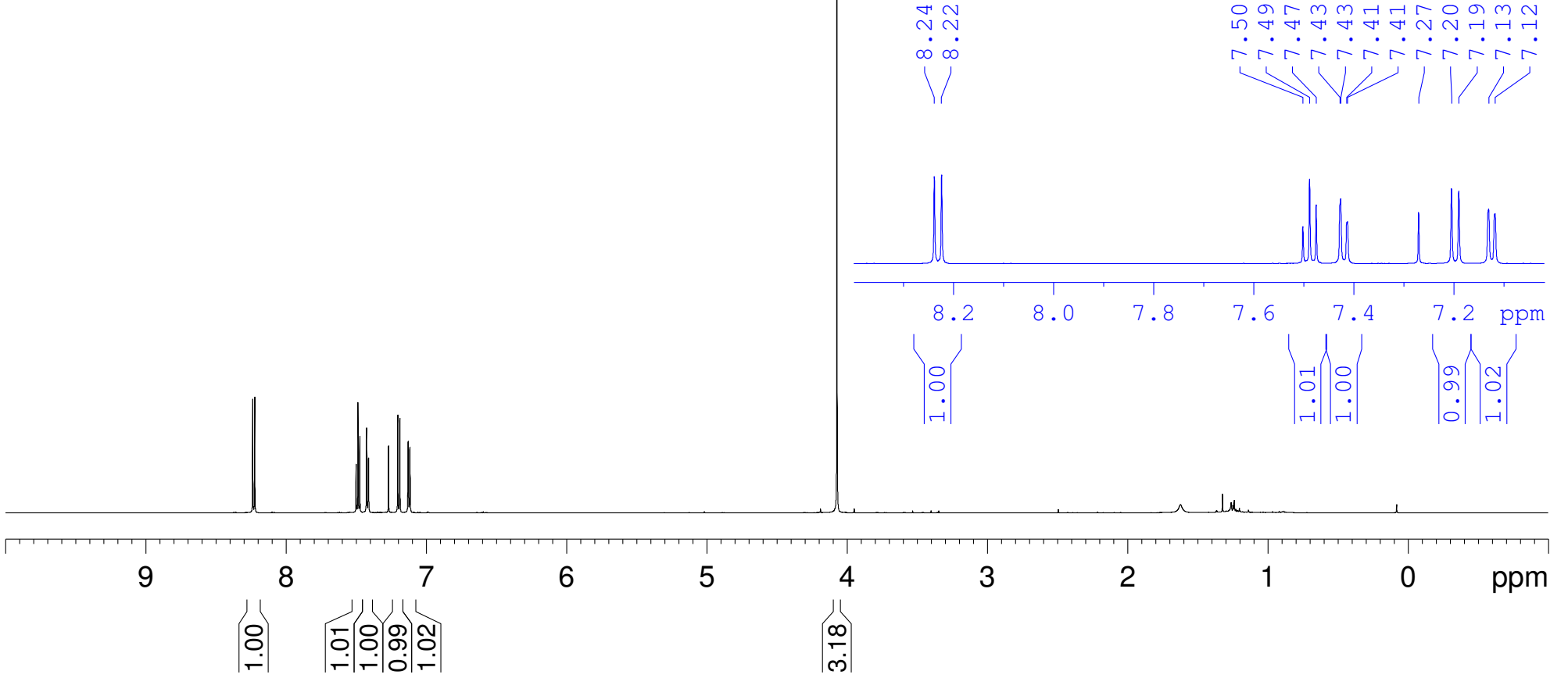


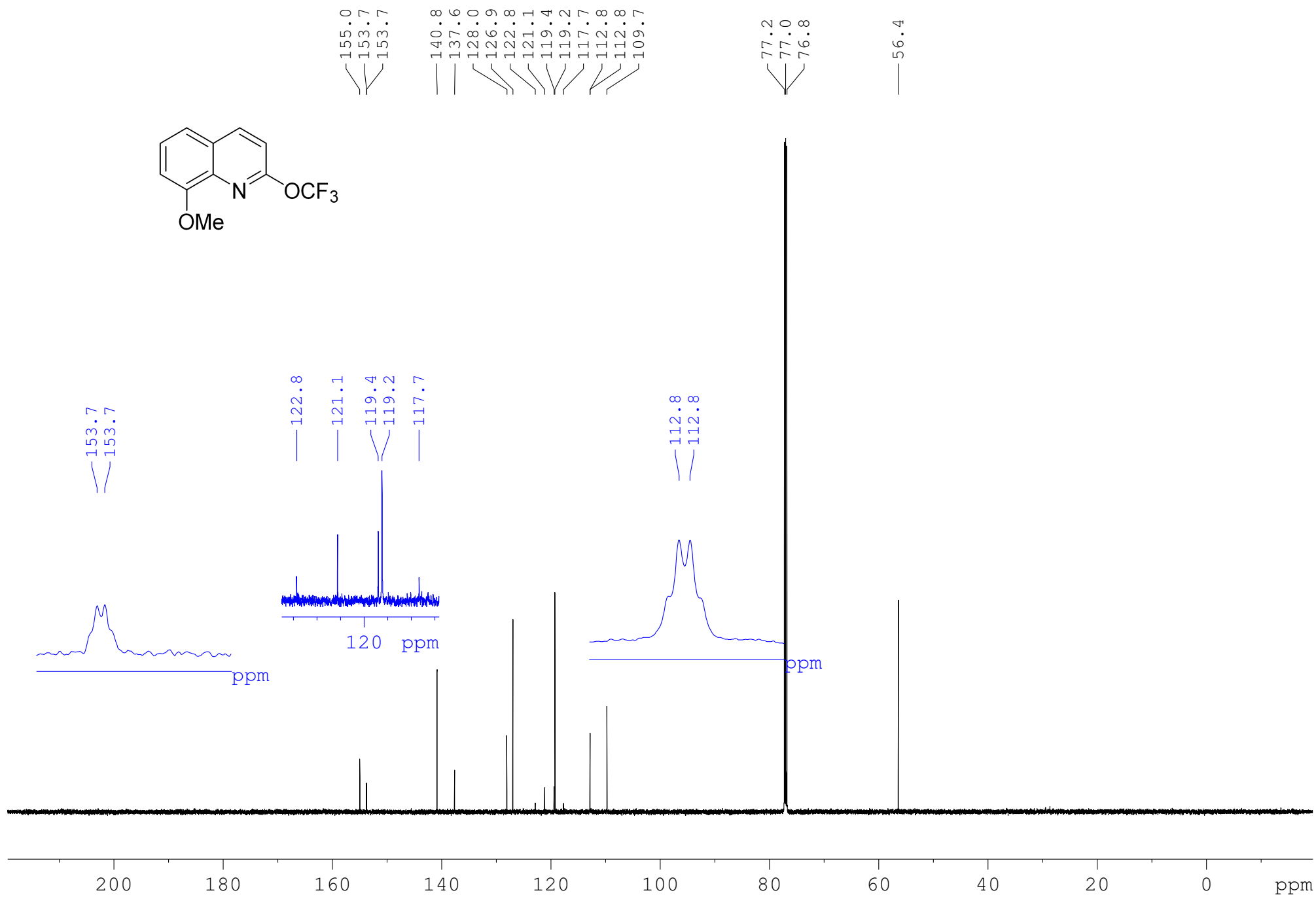
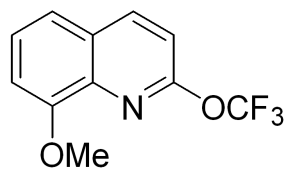


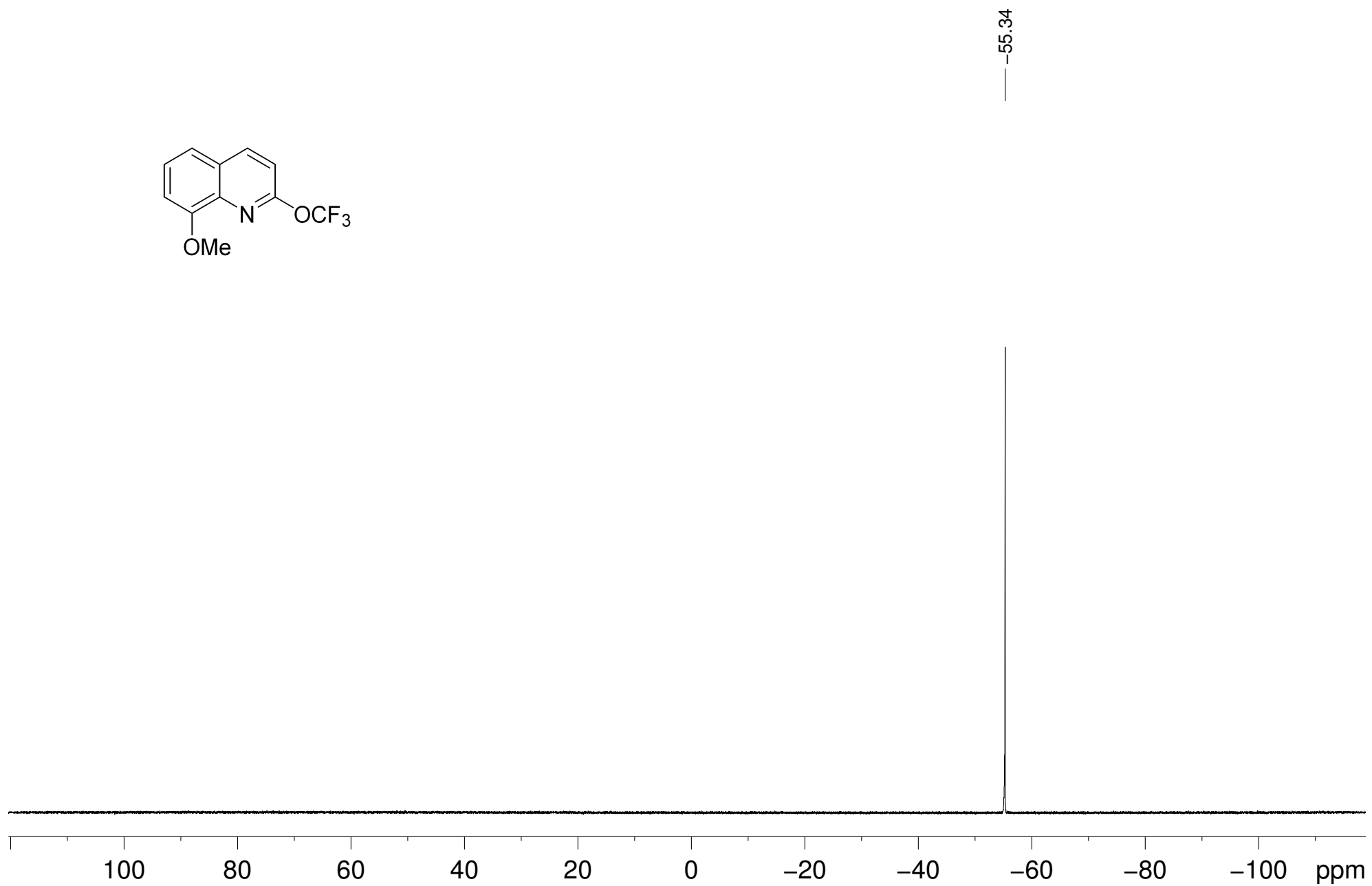
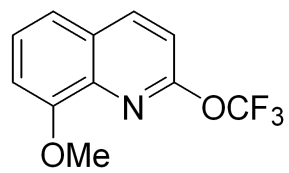


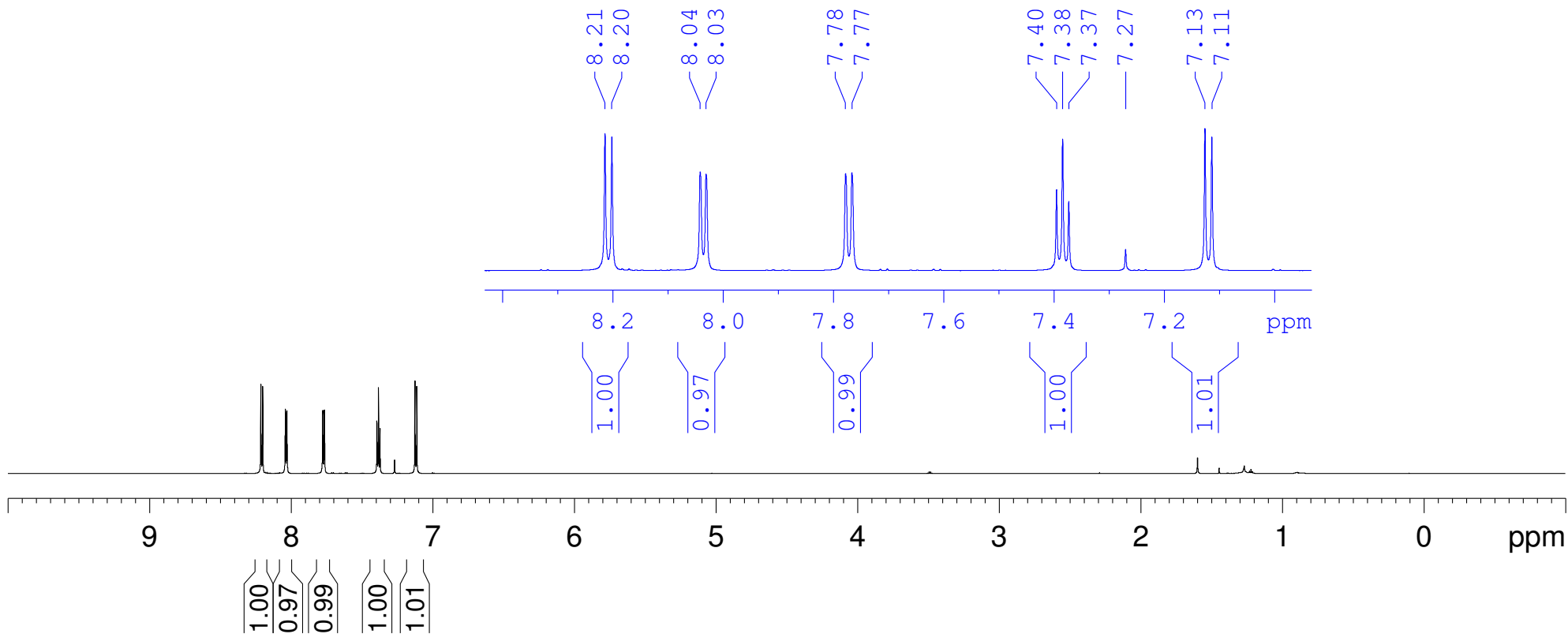
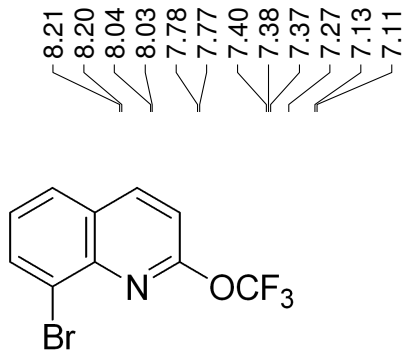
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7.13
7.12

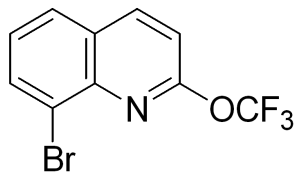
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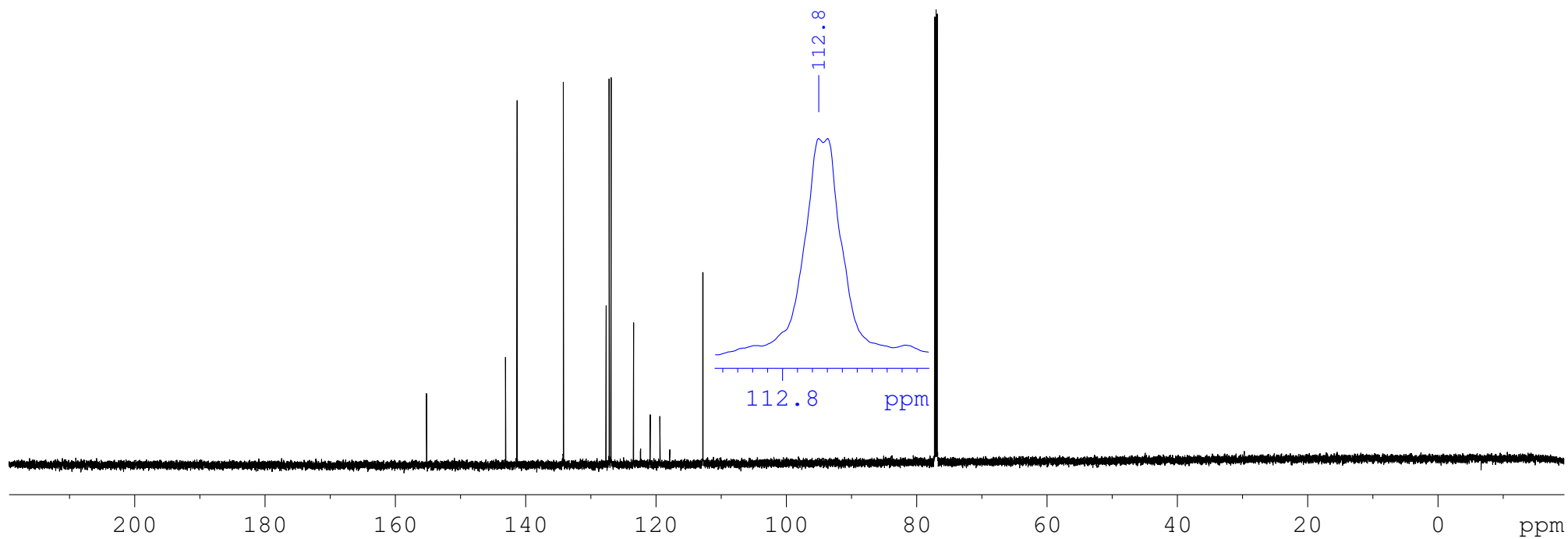


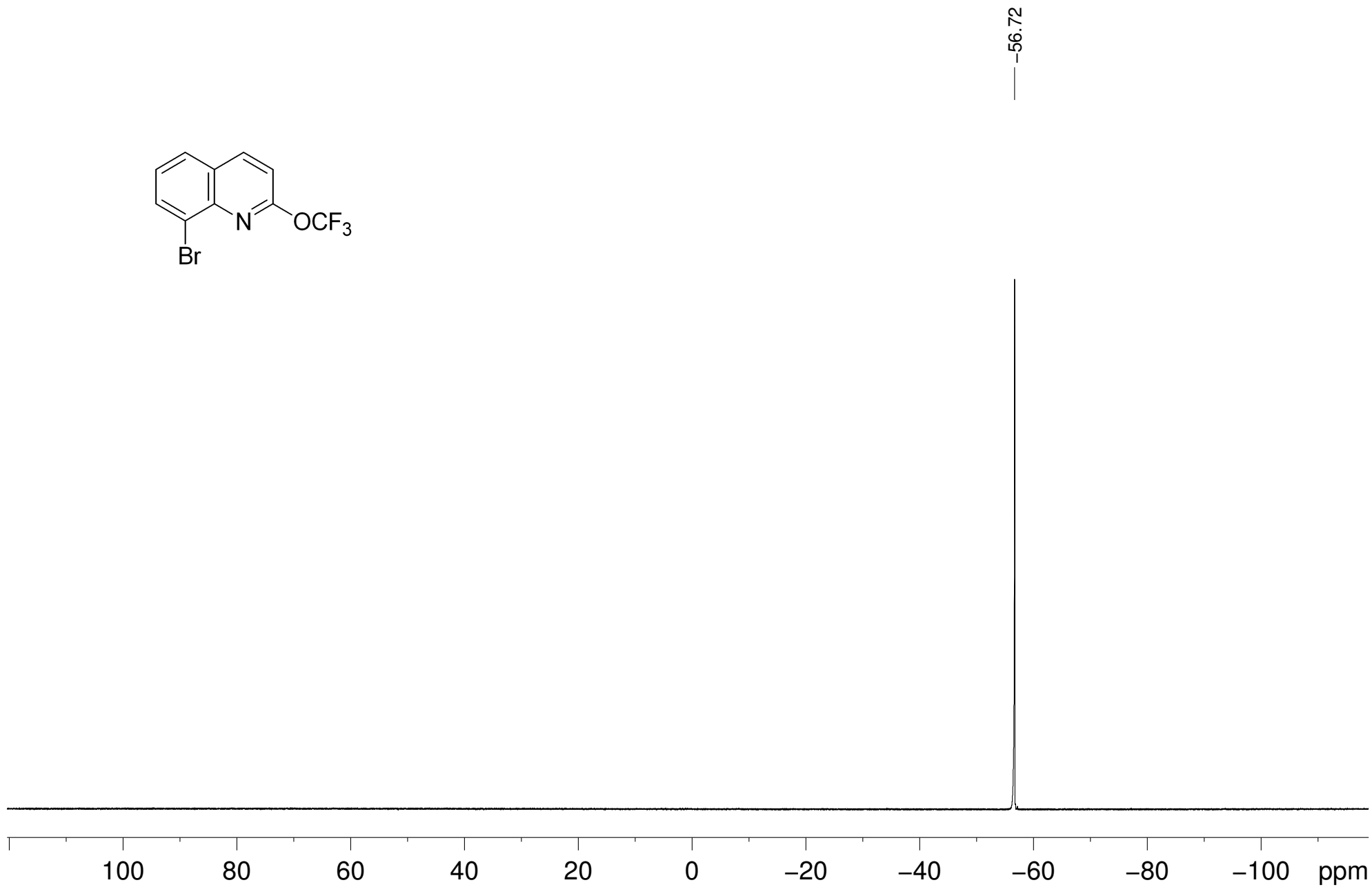
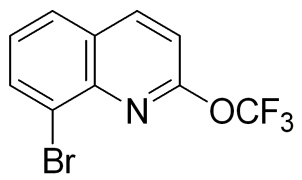




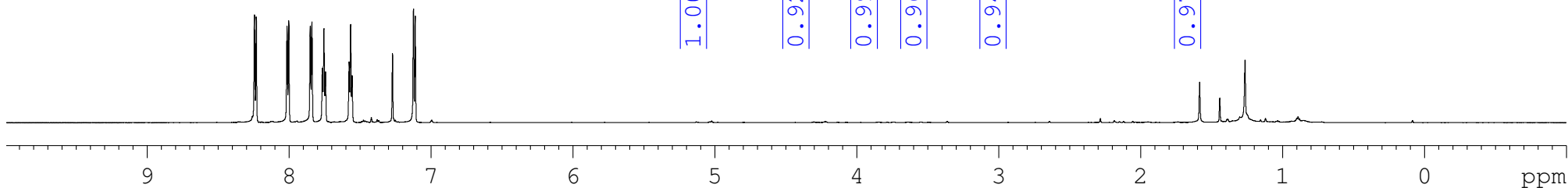
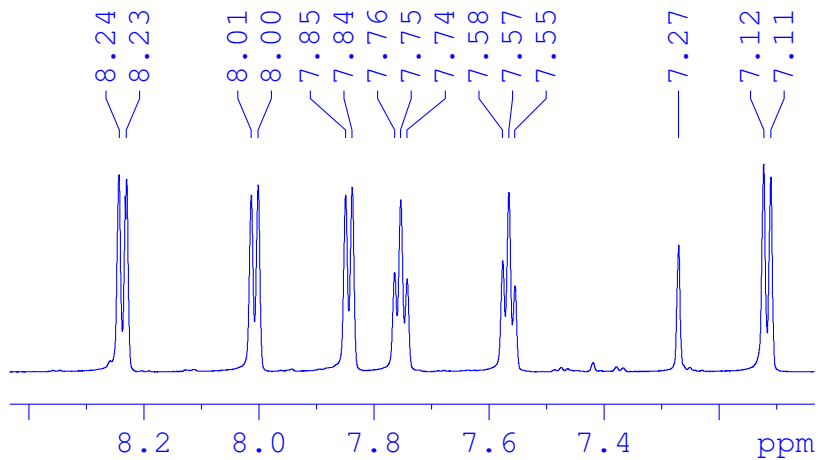
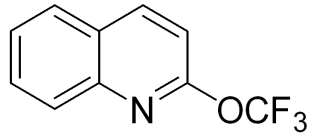


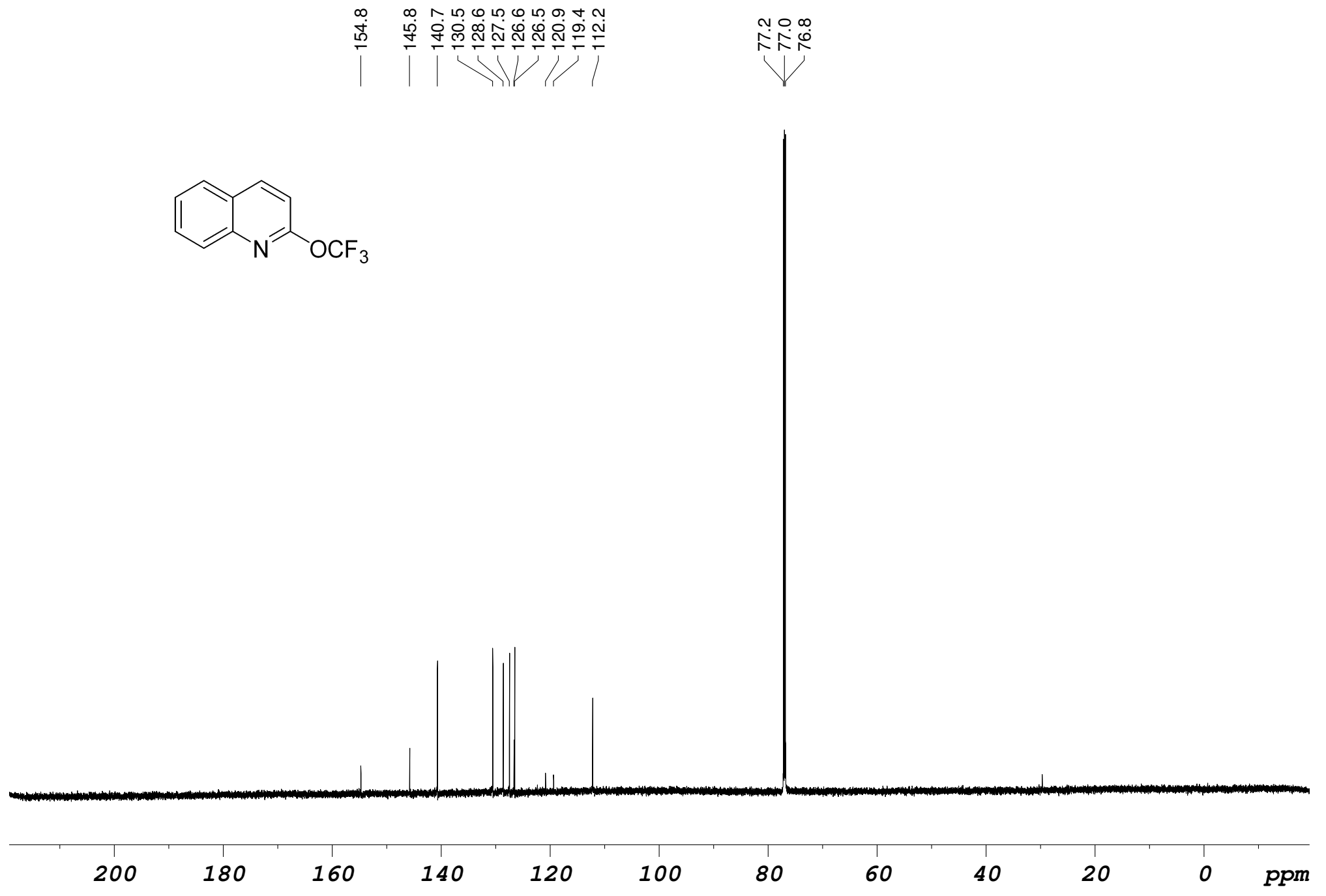
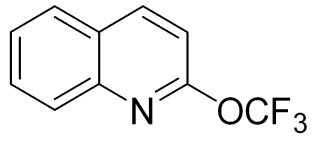
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112.8
77.2
77.0
76.8

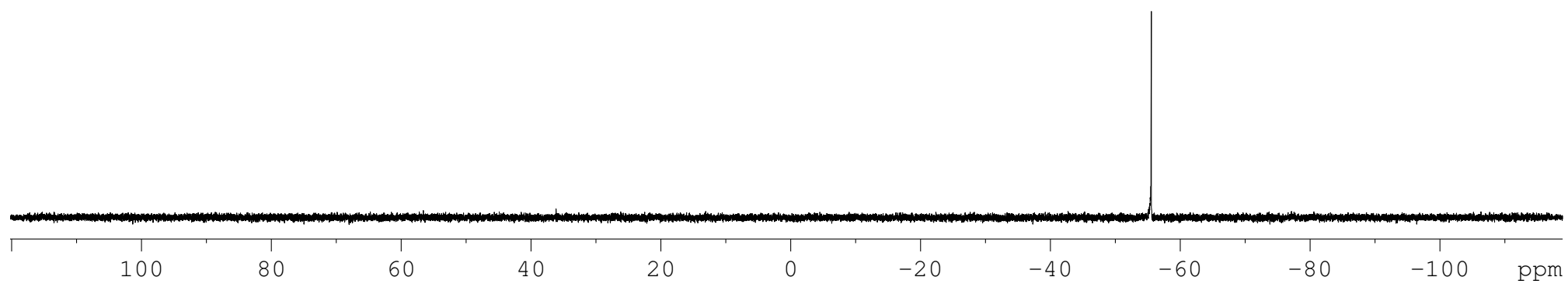
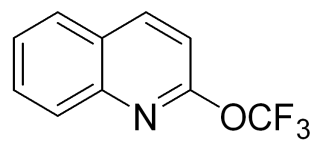


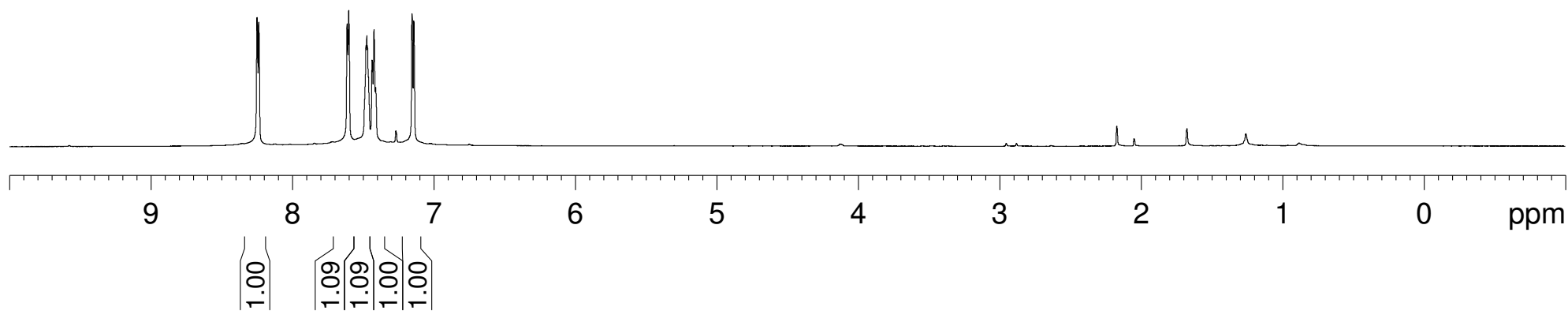
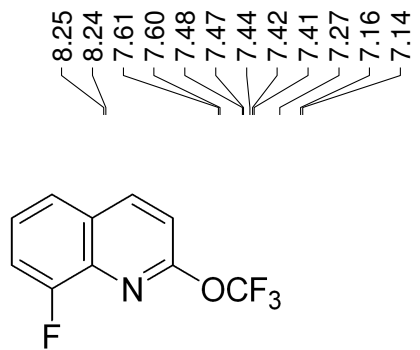


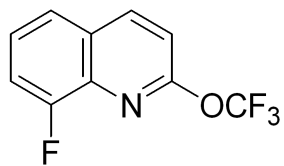
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7.55
7.27
7.12
7.11











157.9
156.4
154.8
140.6
140.6
135.7
135.6
128.2
126.4
126.3
123.1
123.0
122.3
120.8
119.3
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114.9
113.2

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77.0
76.8

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154.8

140.6
140.6

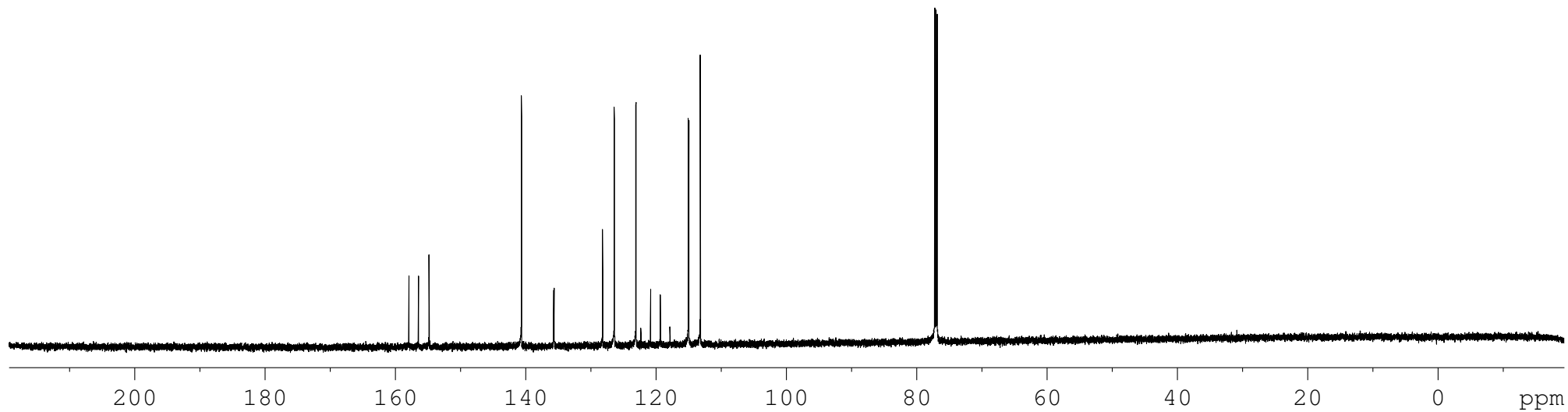
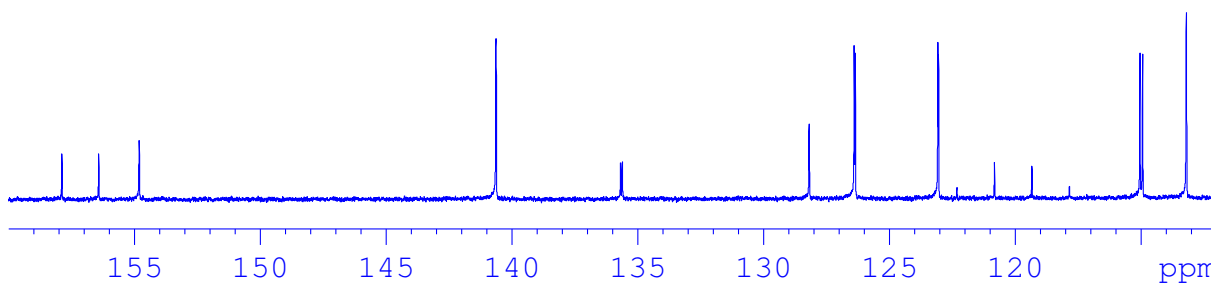
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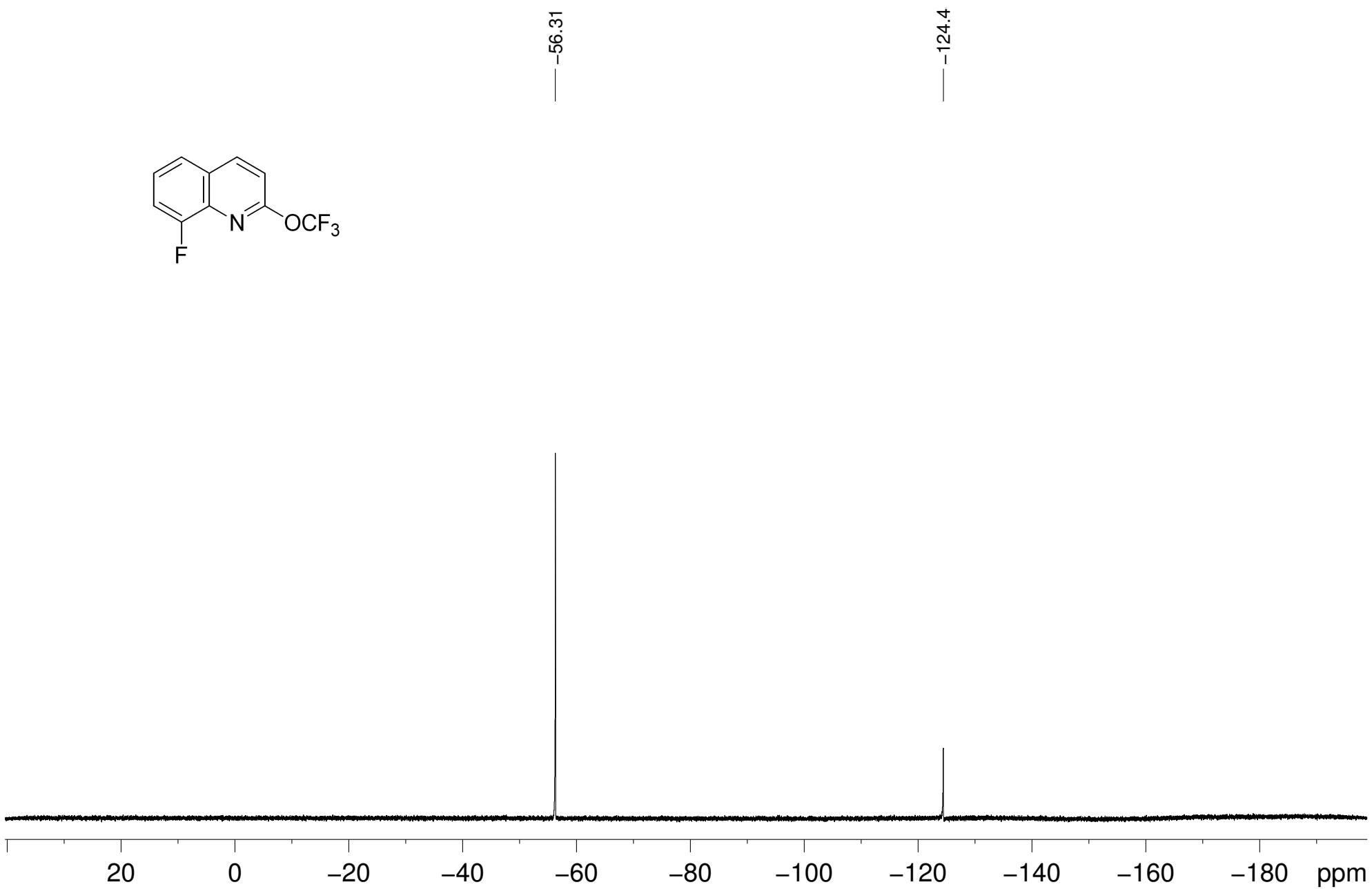
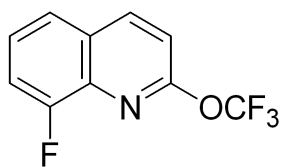
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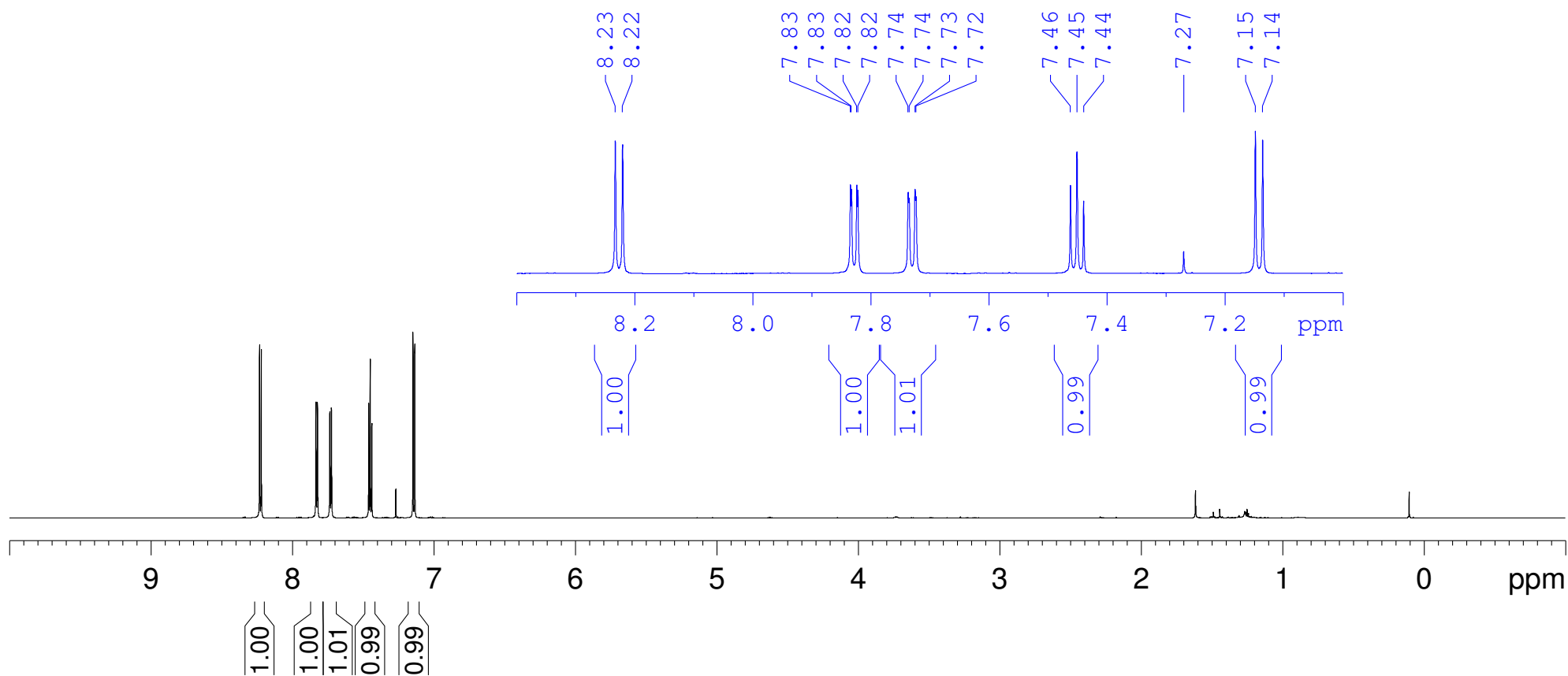
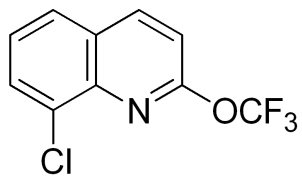
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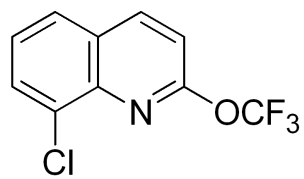
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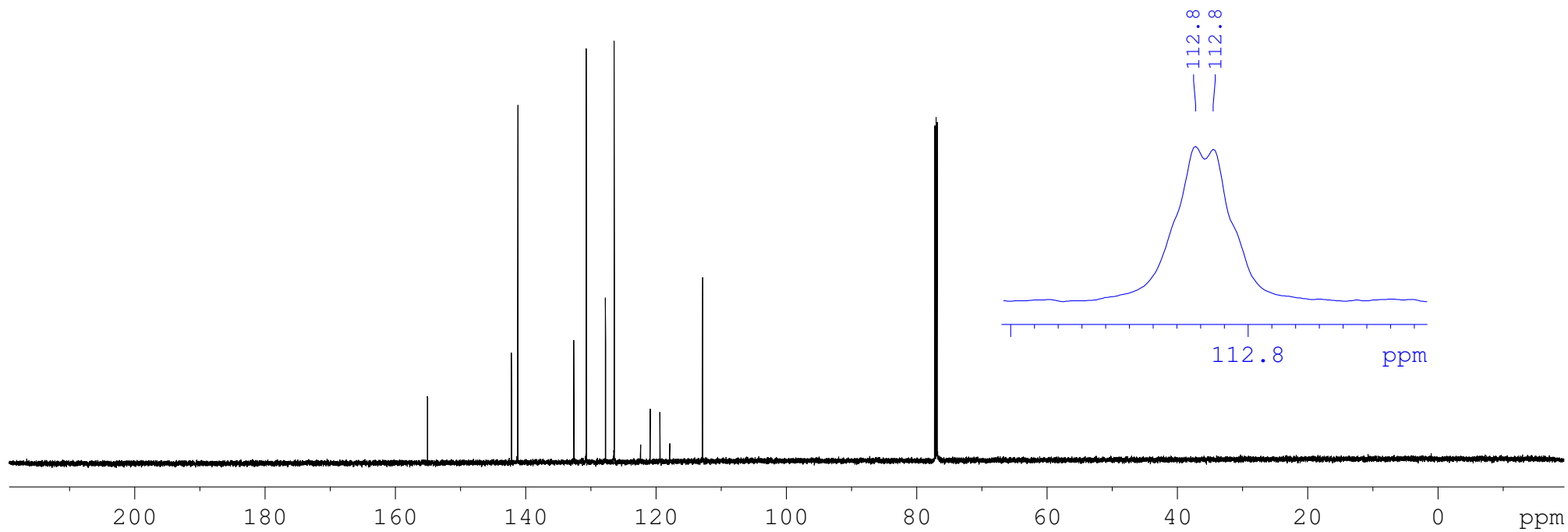
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7.14

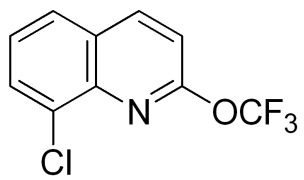




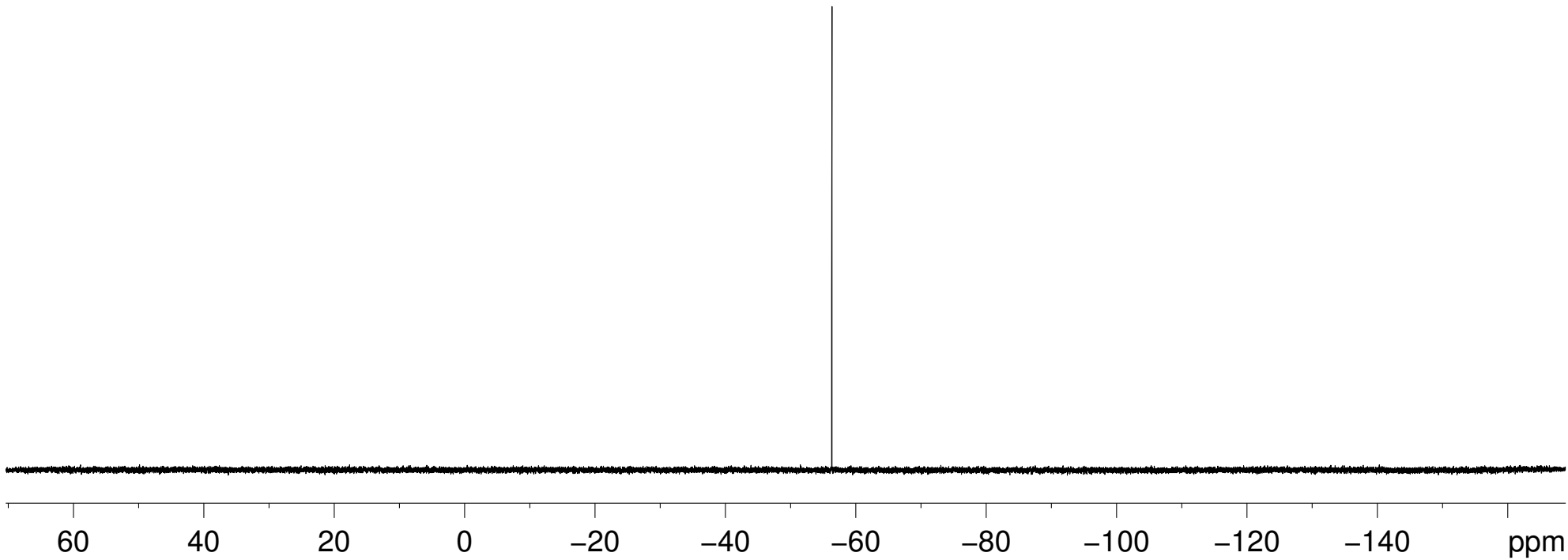
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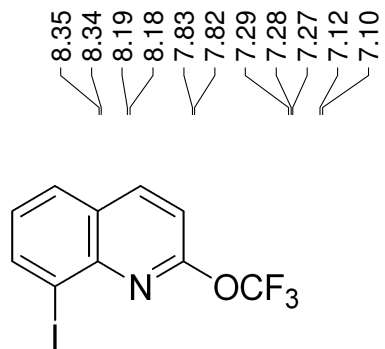
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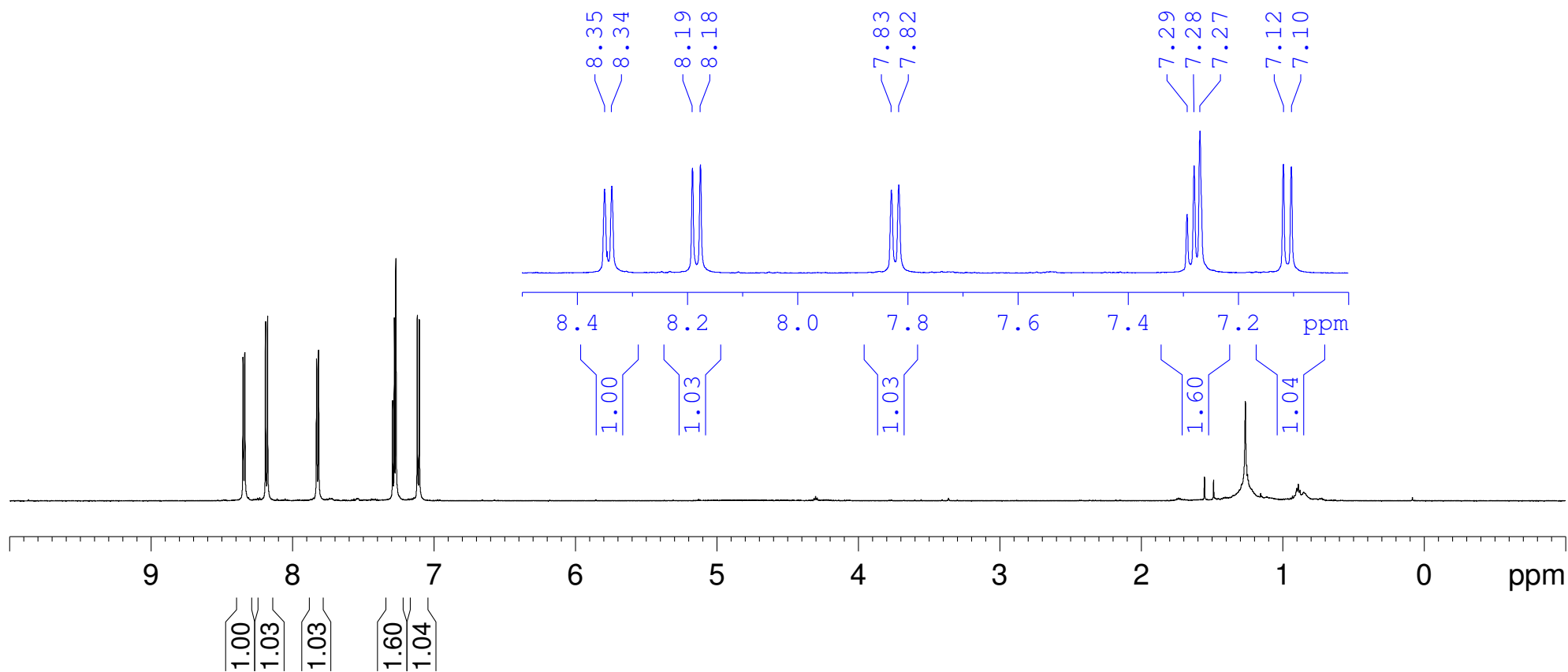


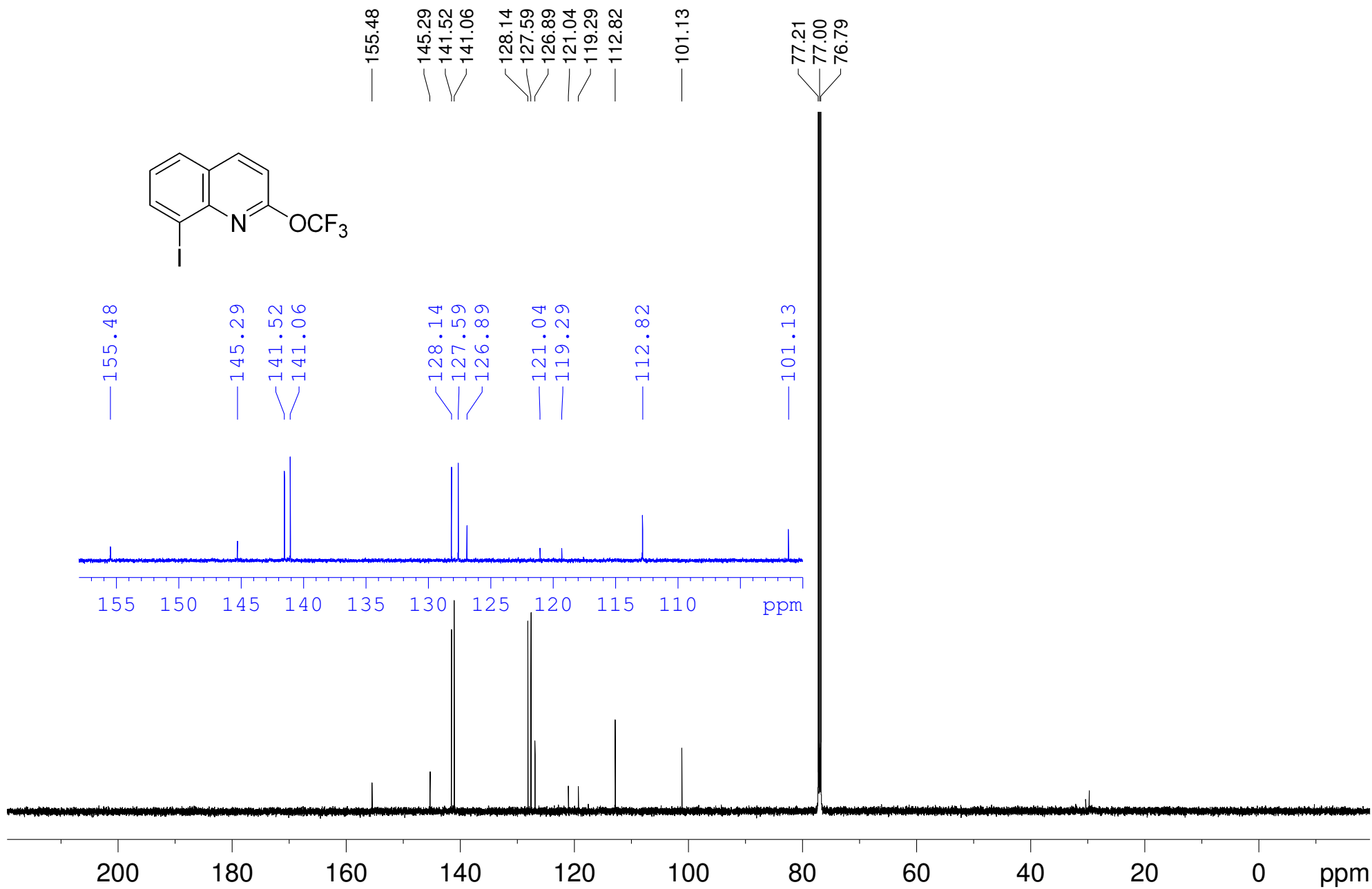
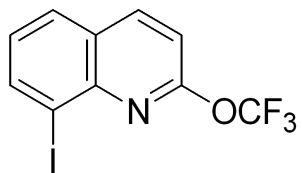
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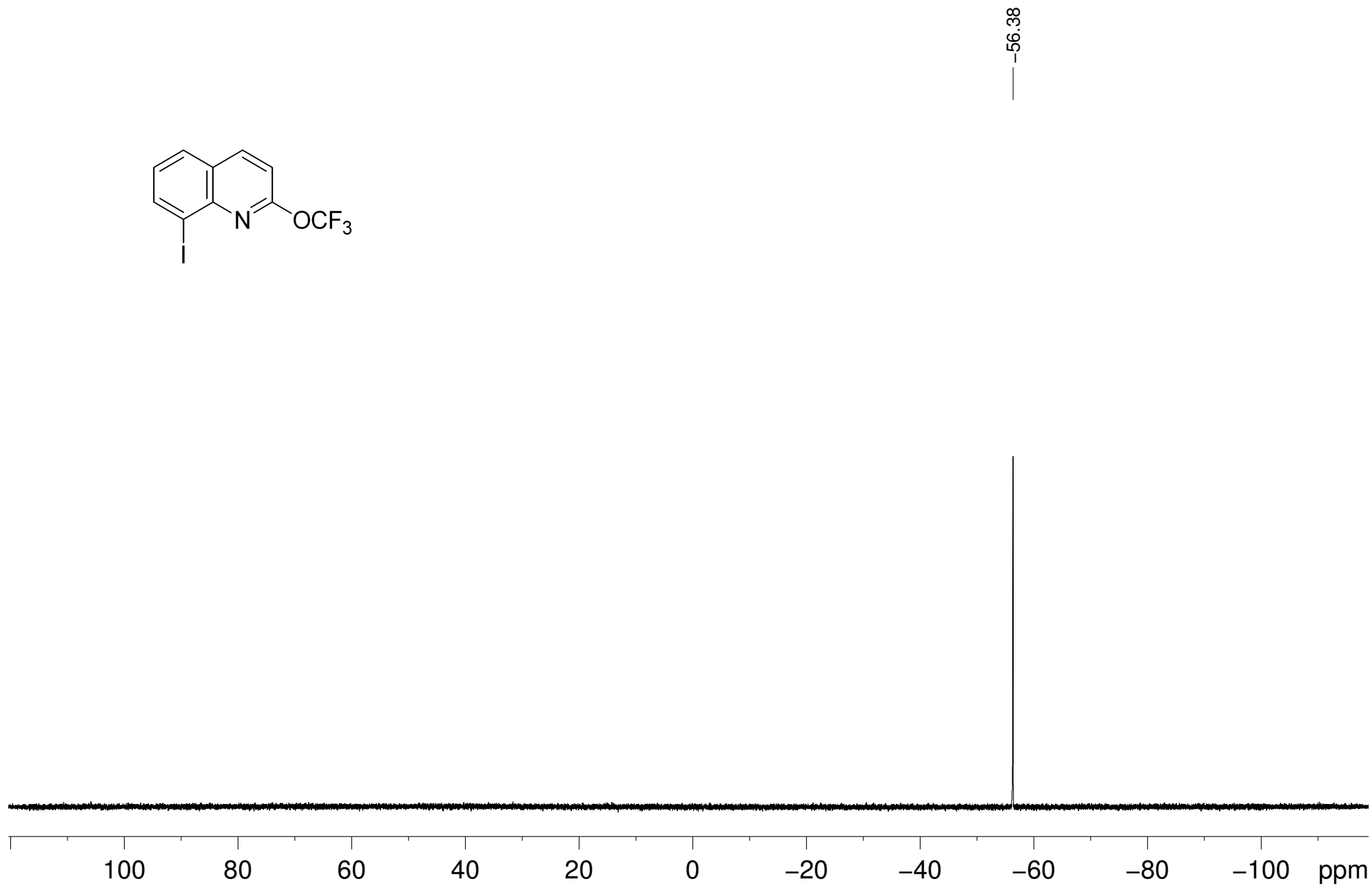
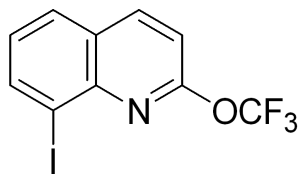


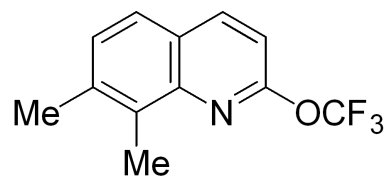


8.35
8.34
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8.18
7.83
7.82
7.29
7.28
7.27
7.12
7.10









8.15
8.14
7.58
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7.37
7.36
7.27
7.01
7.00

2.68
2.51

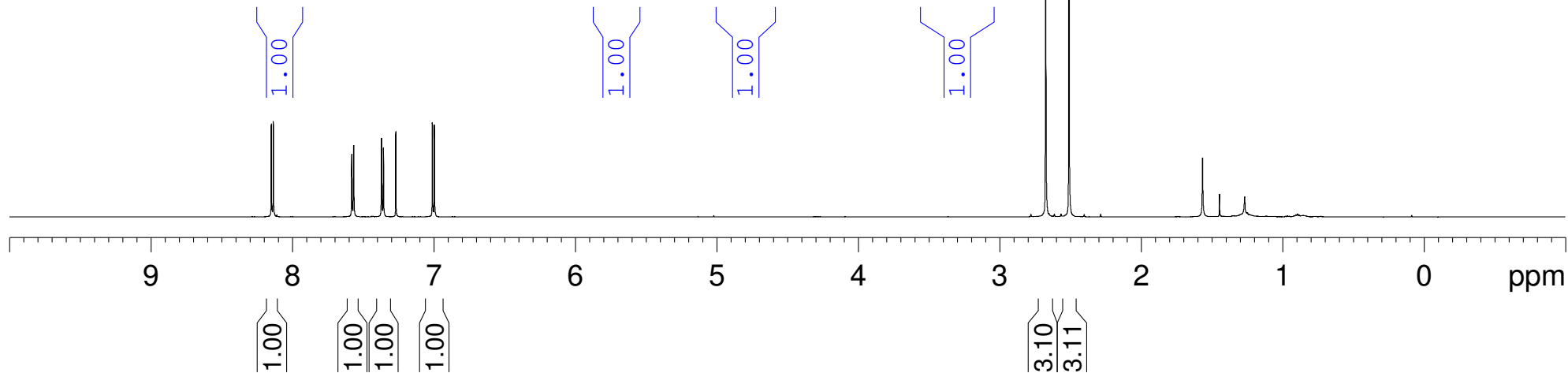
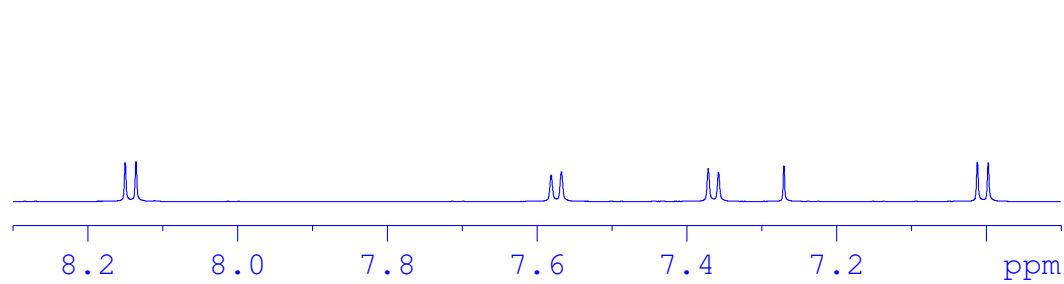
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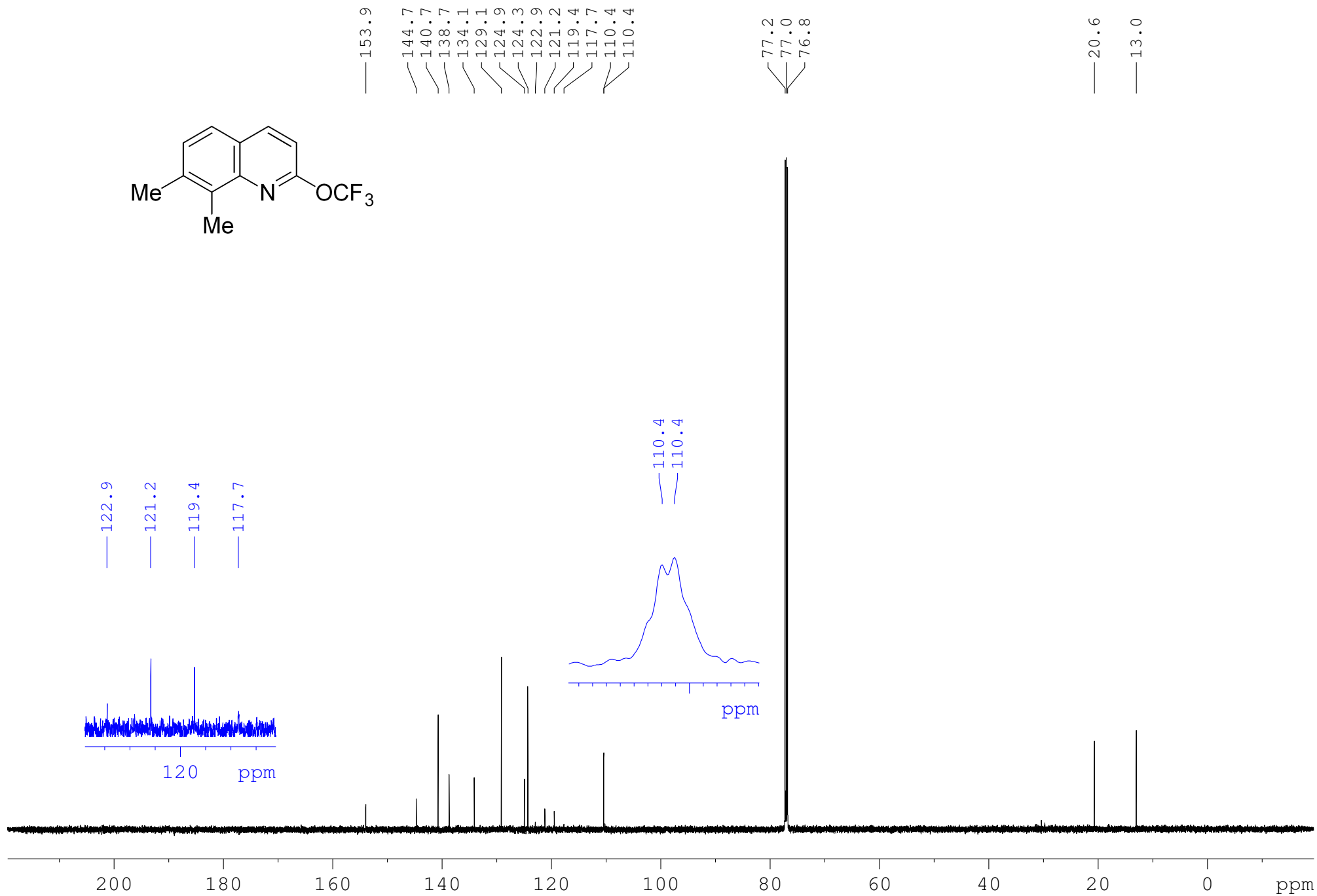
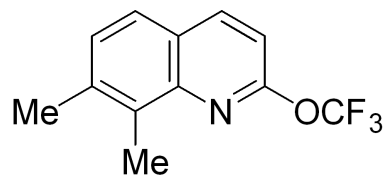
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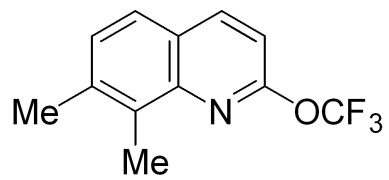
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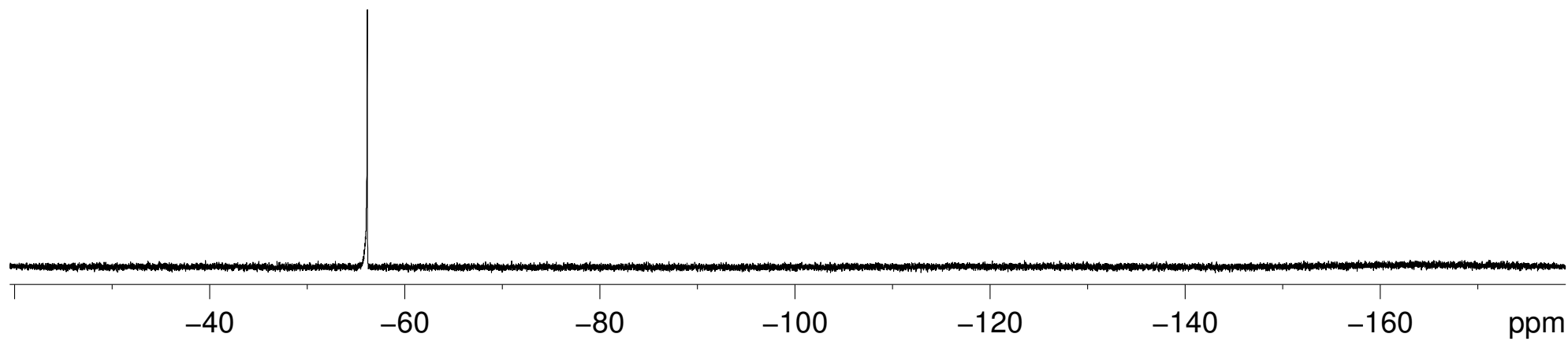
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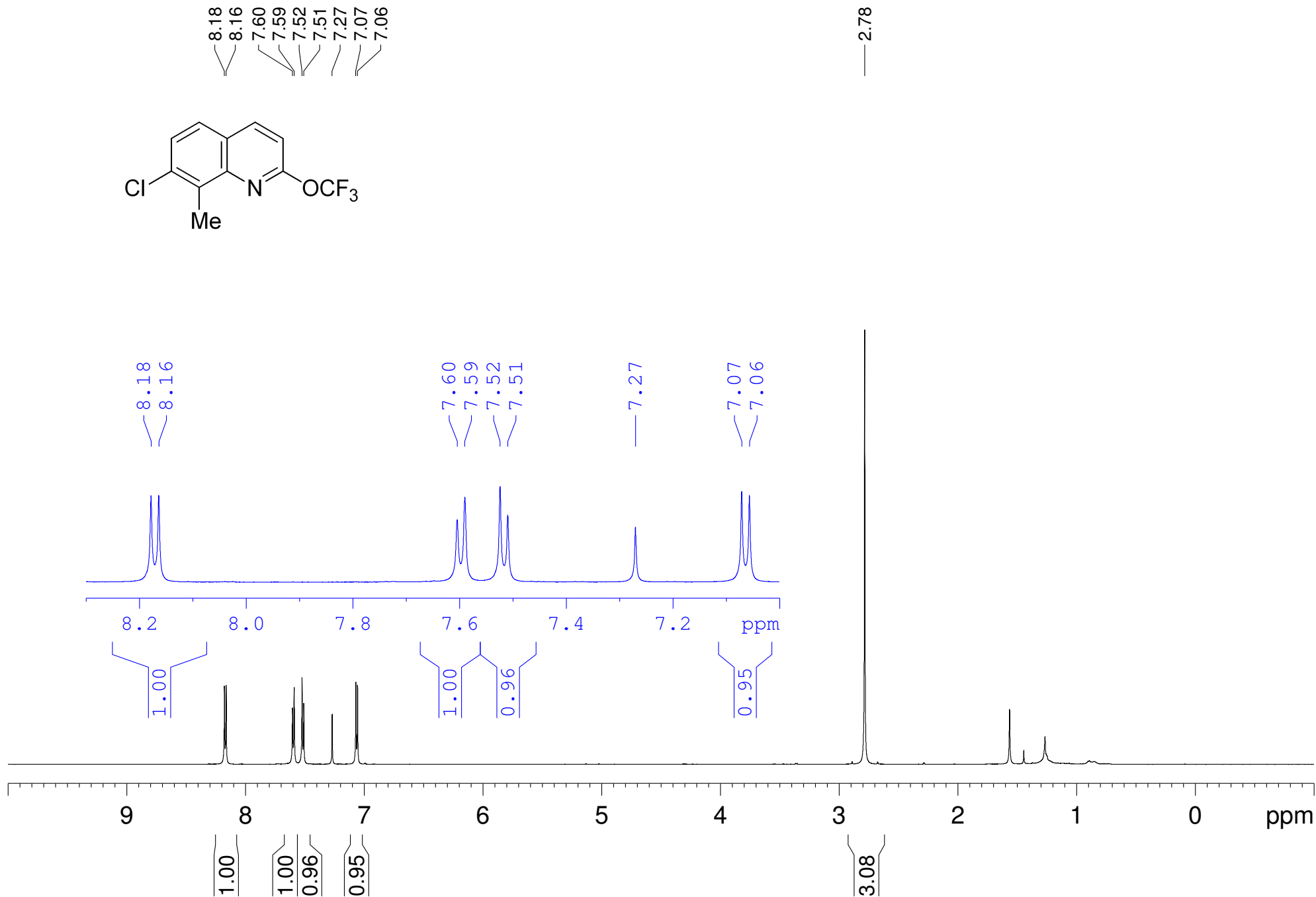
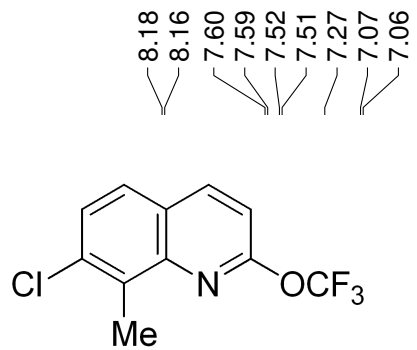


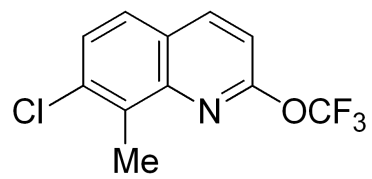




—56.16



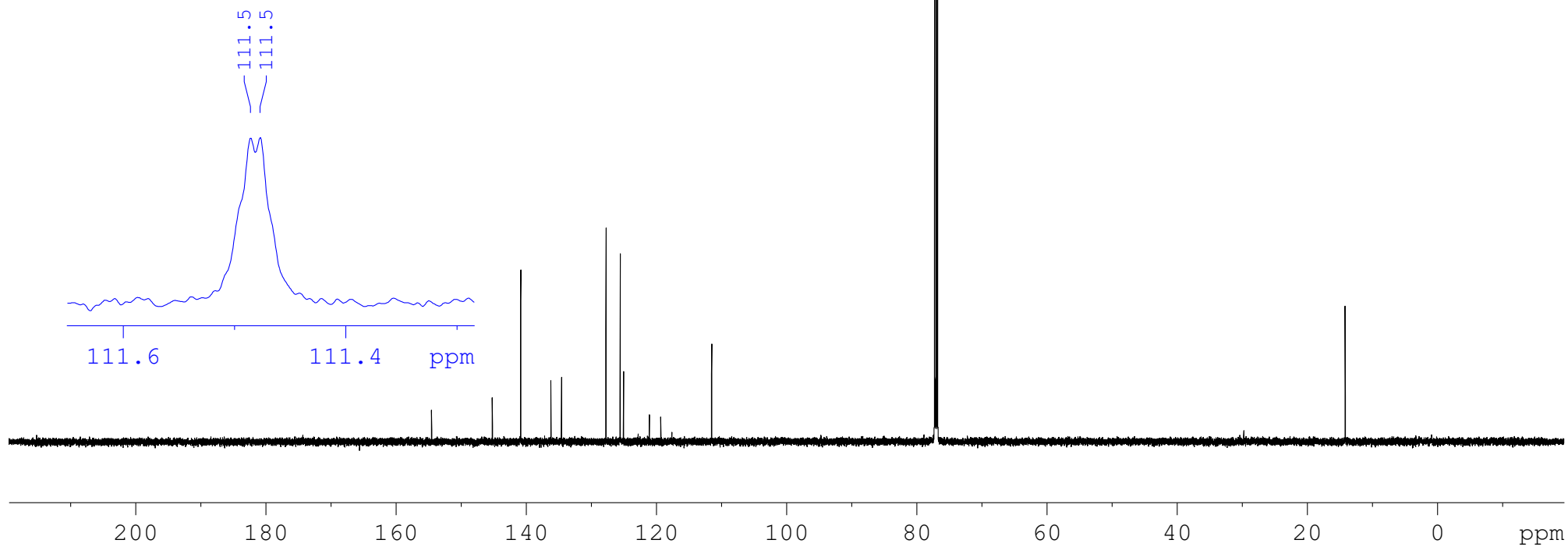


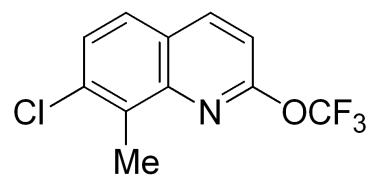


154.5
145.2
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125.0
122.8
121.1
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111.5
111.5

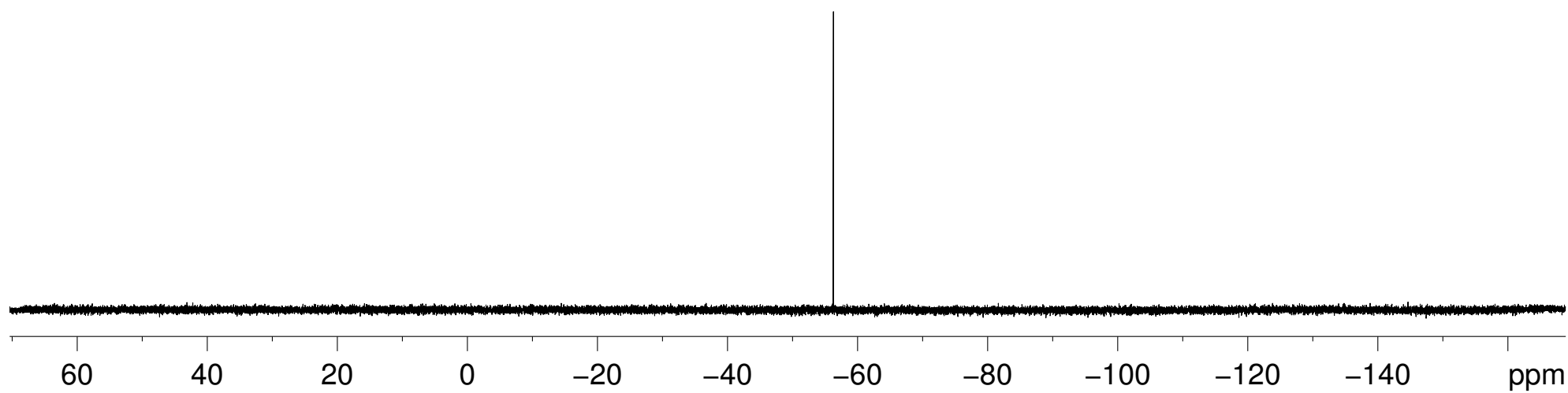
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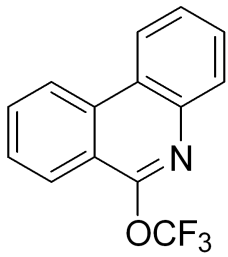
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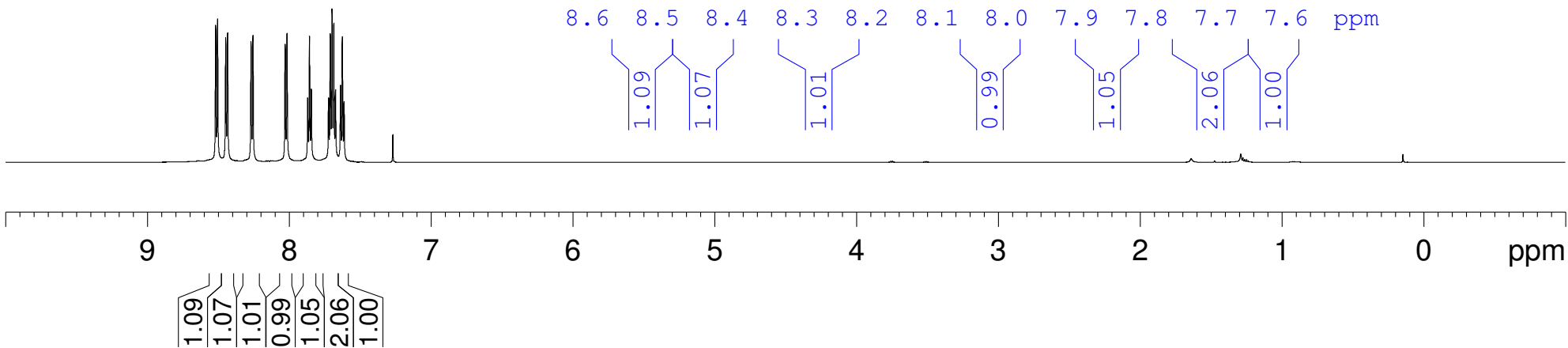
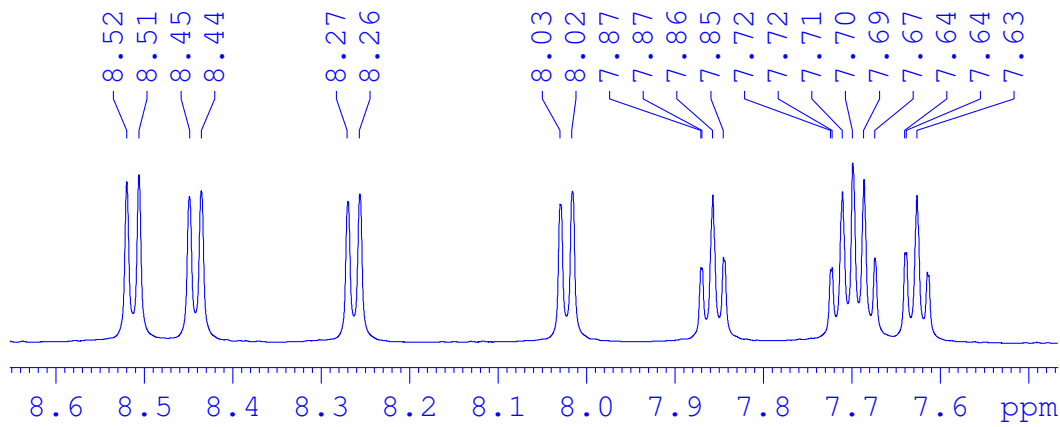


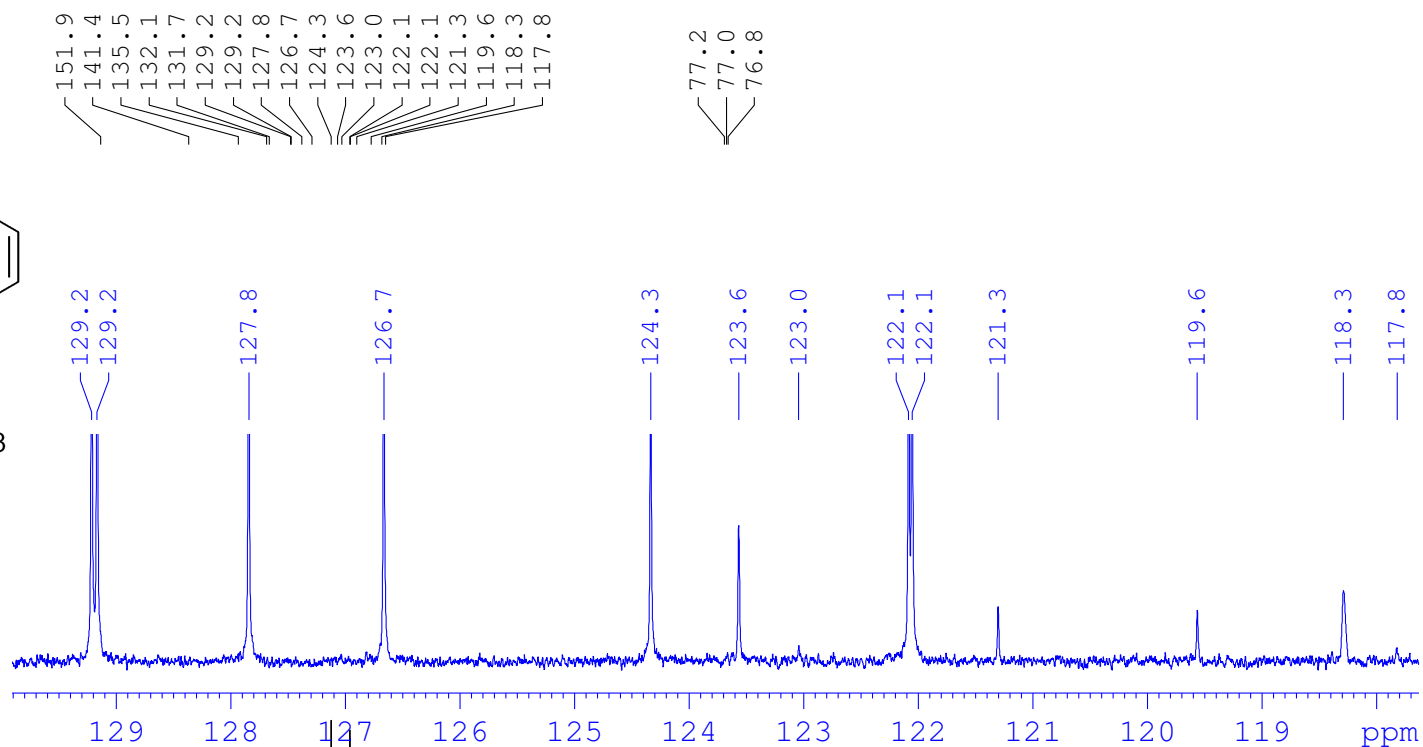
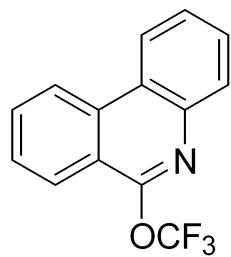
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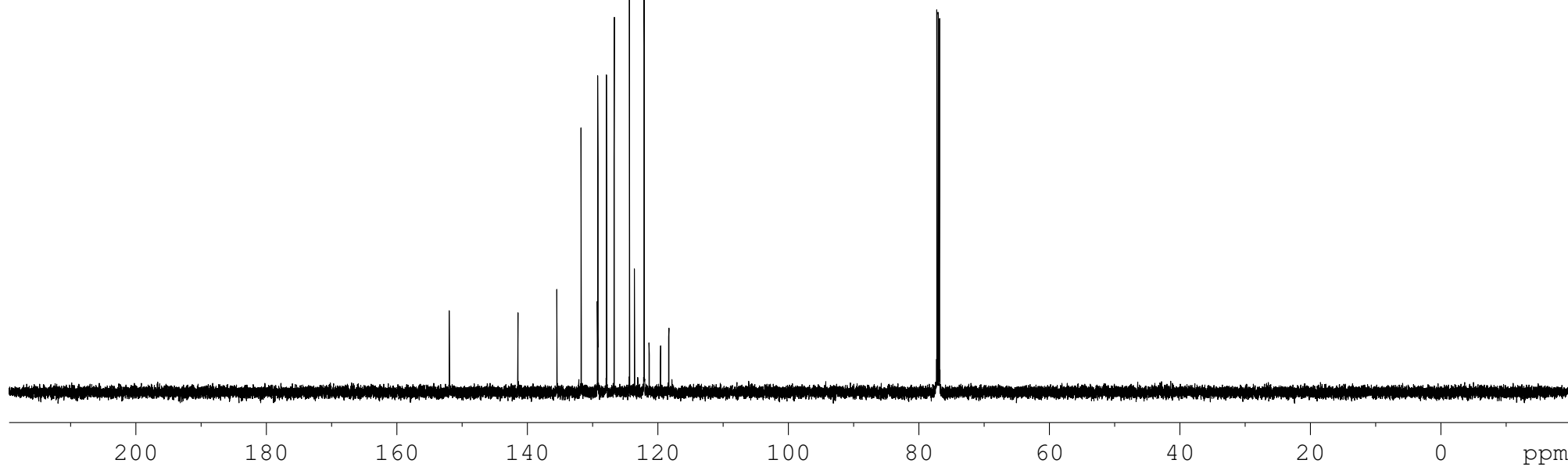
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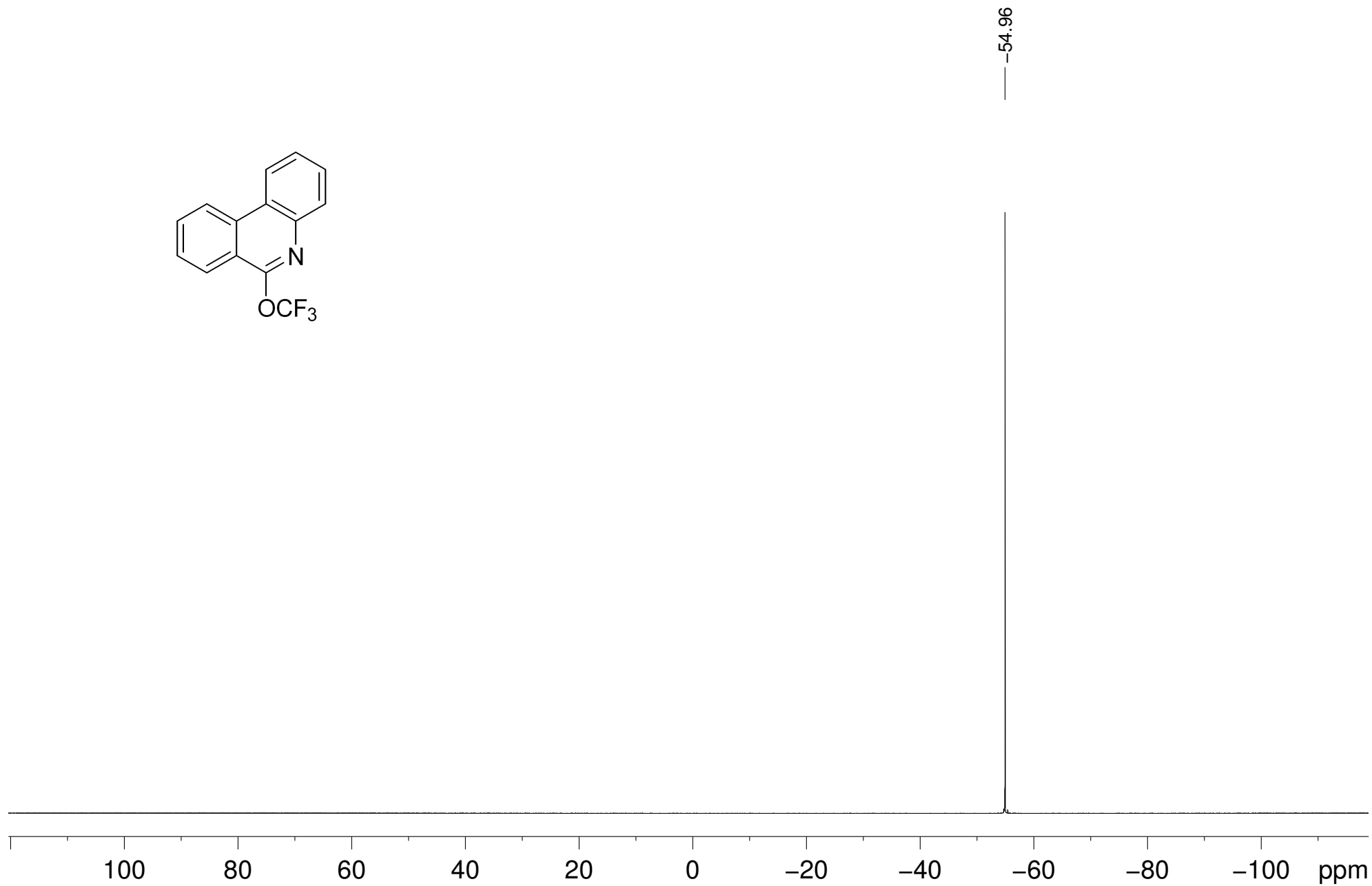
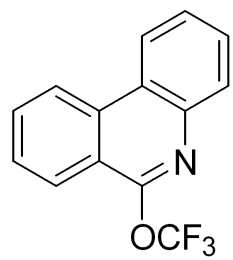




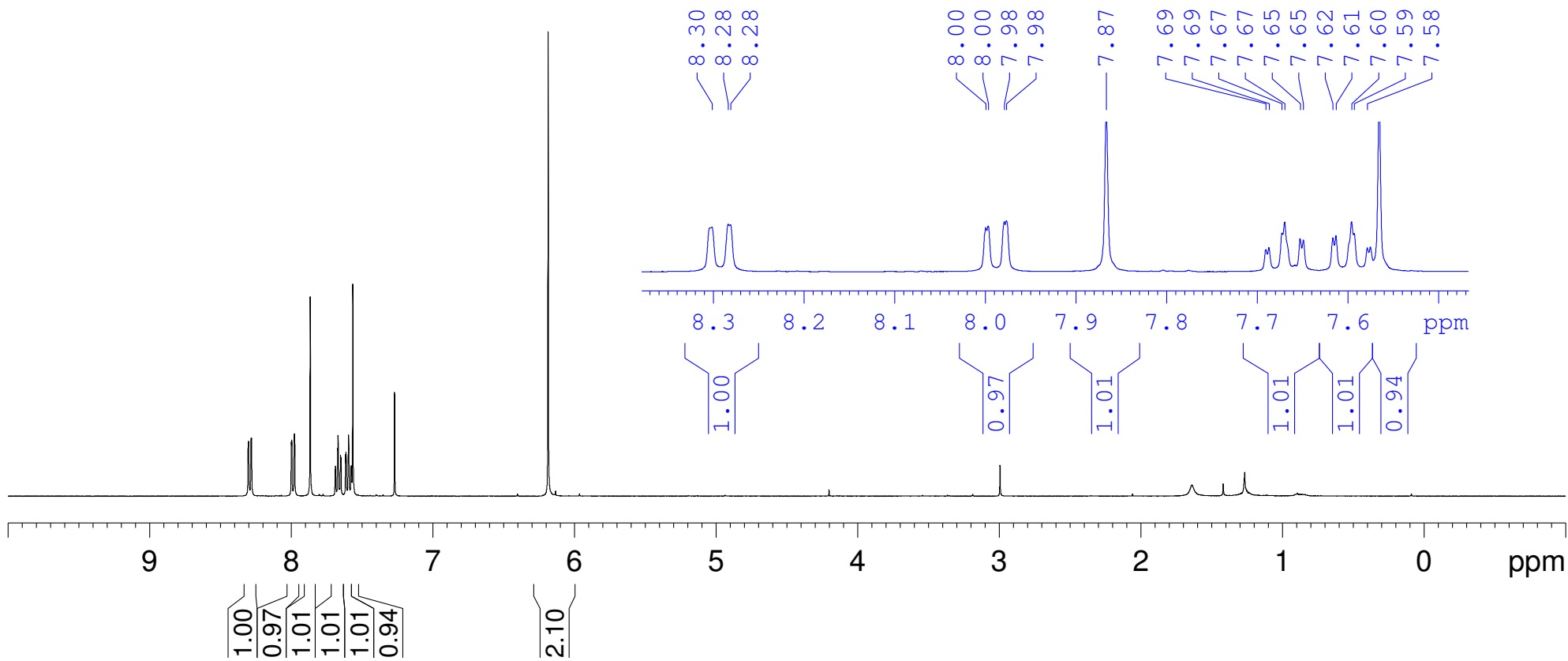
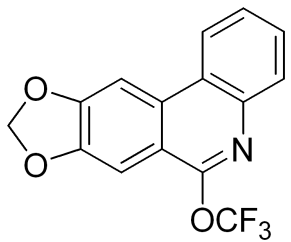
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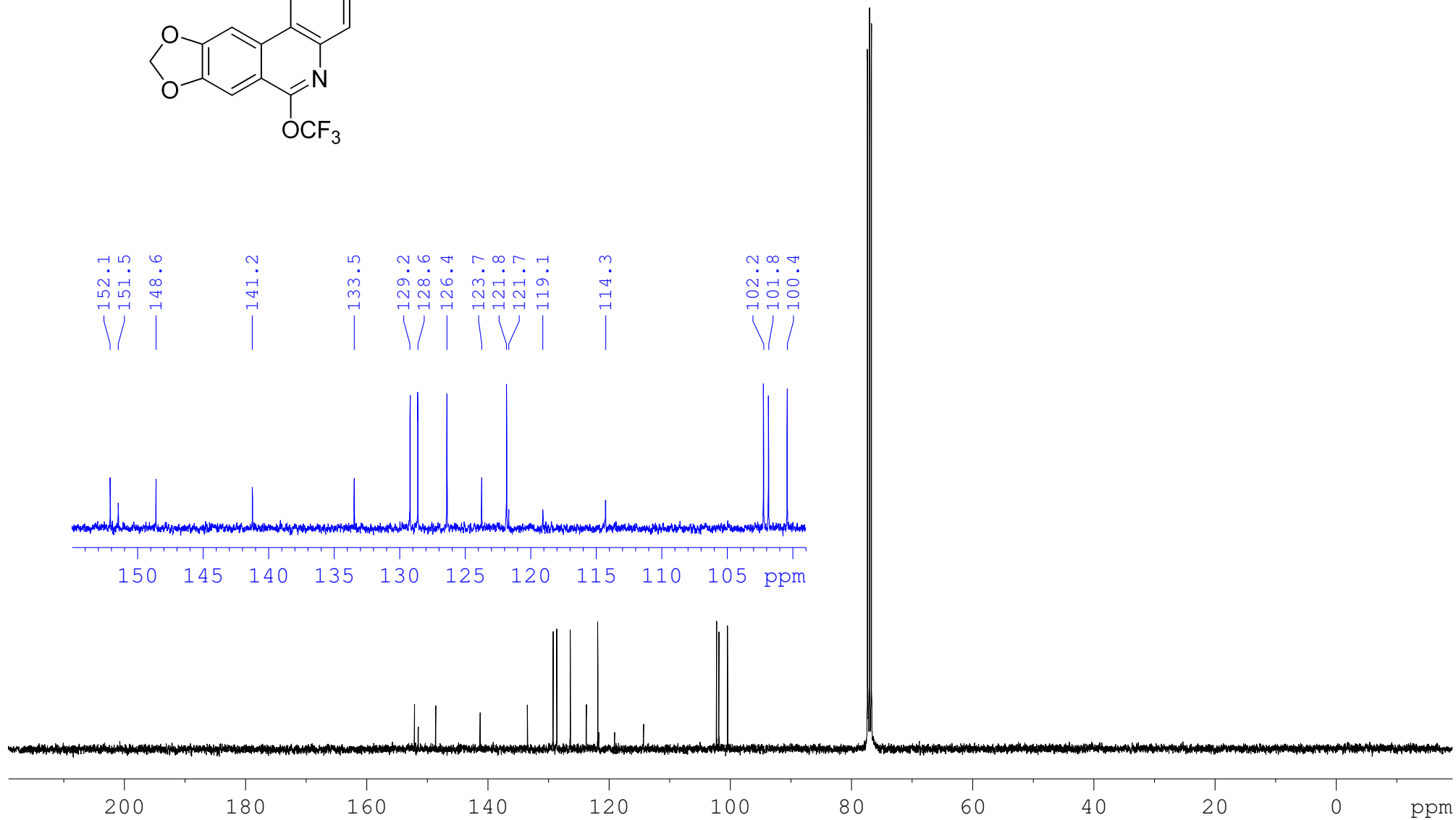
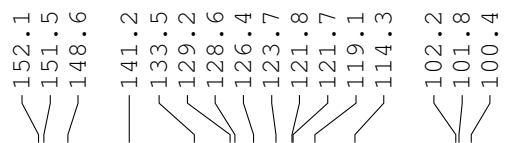
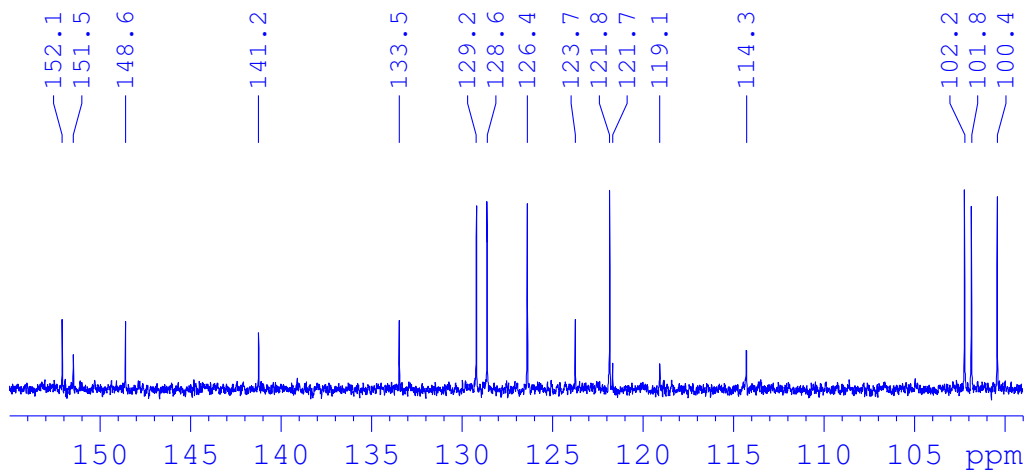
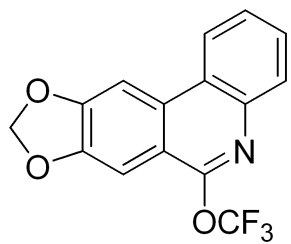
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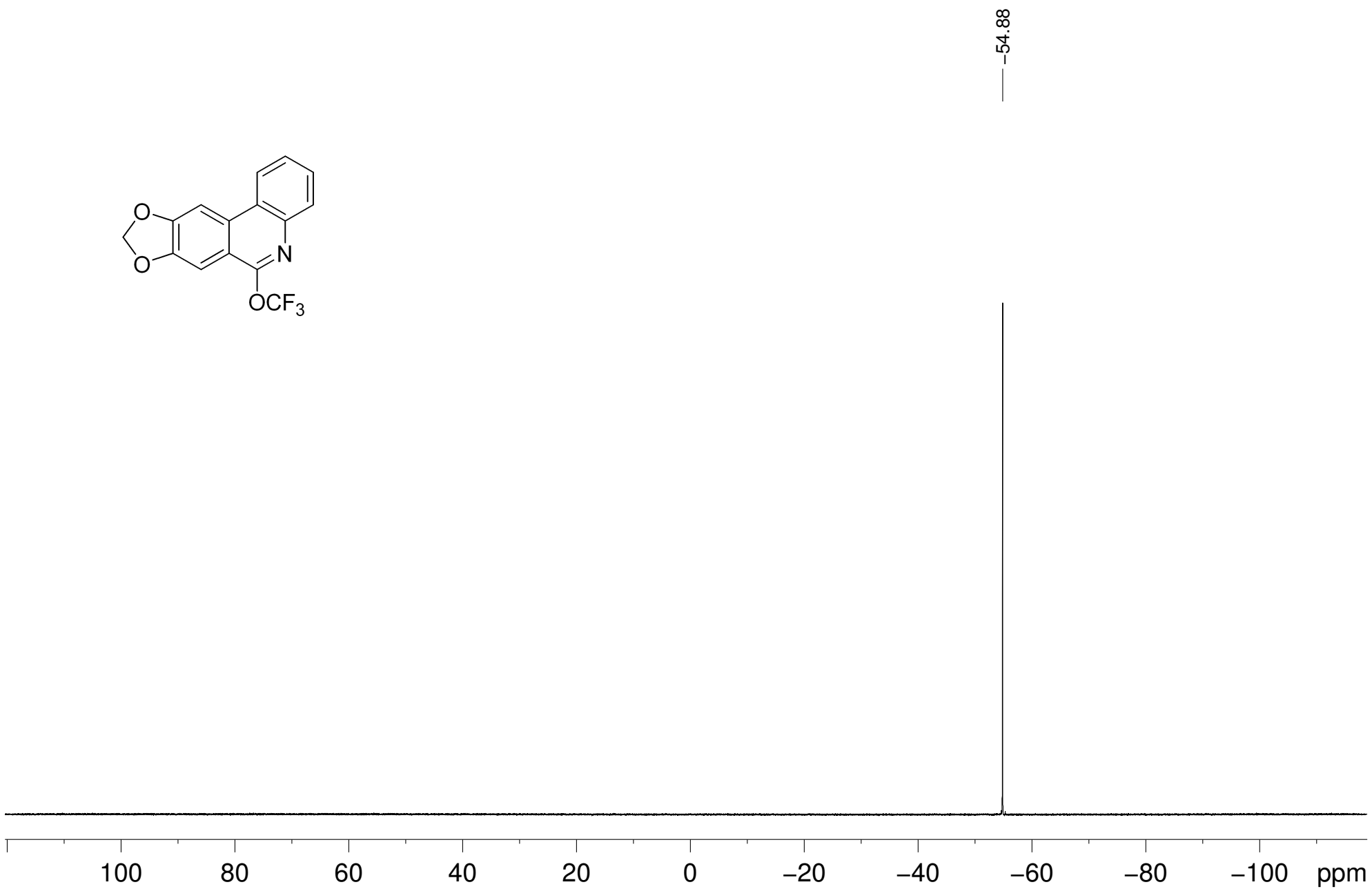
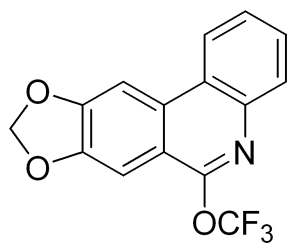


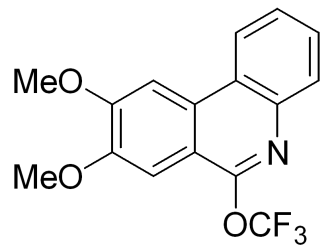


8.30
8.28
8.28
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6.19



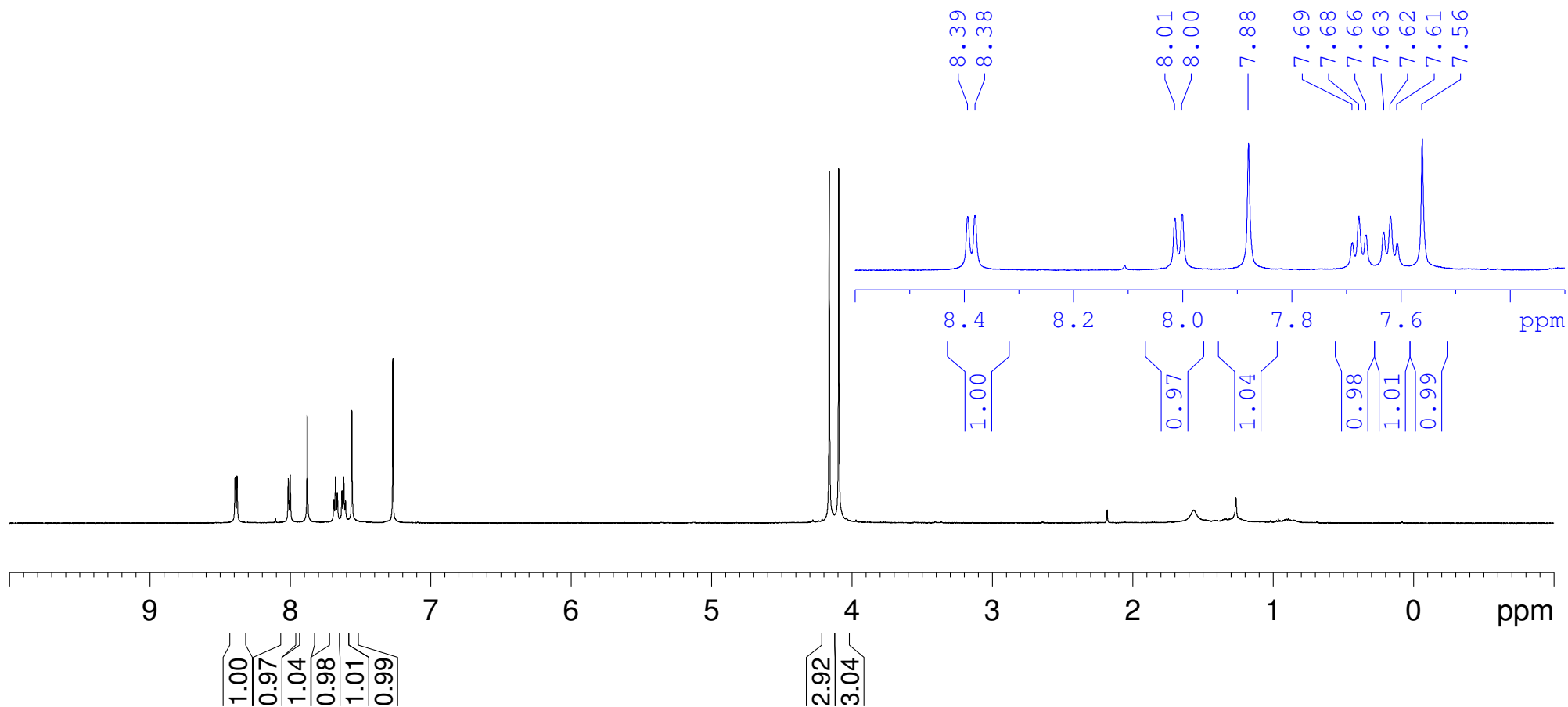


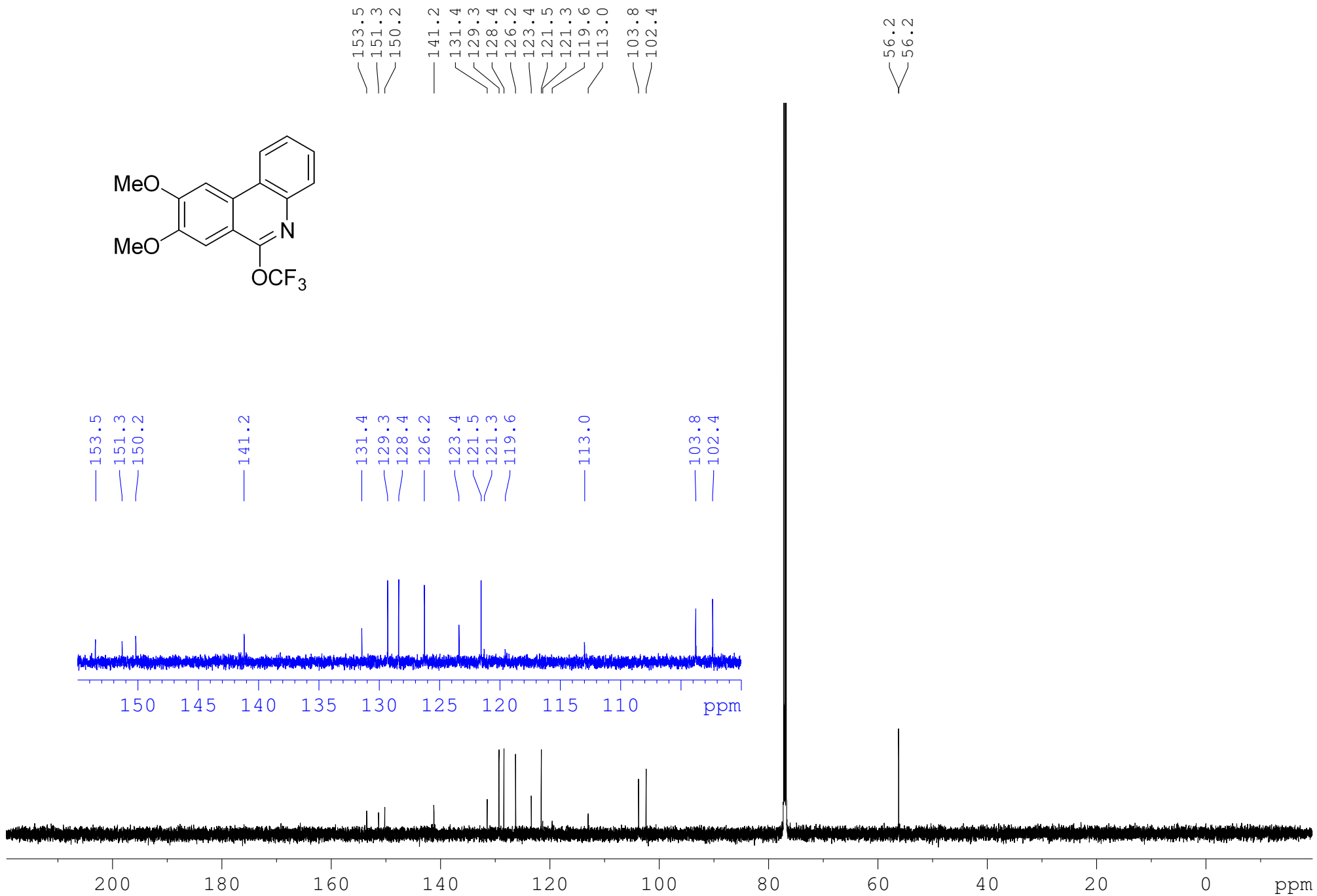
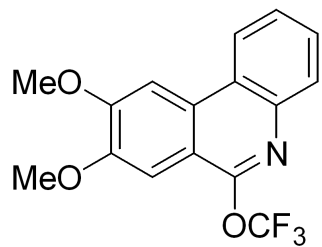


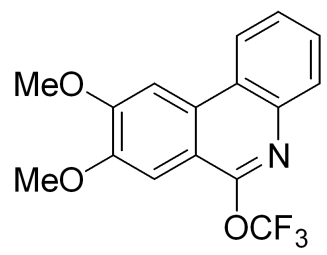


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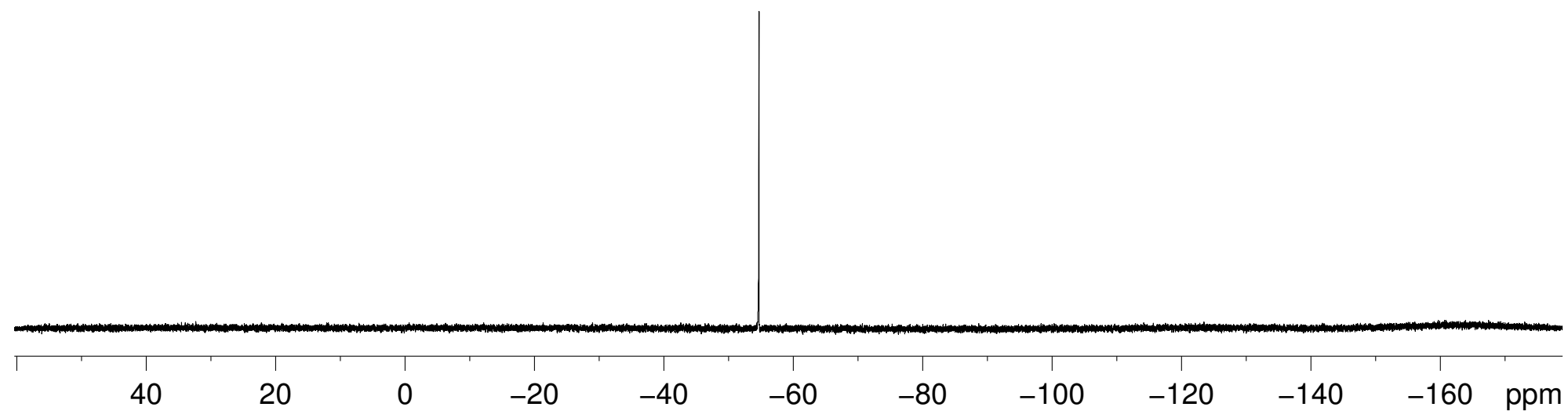
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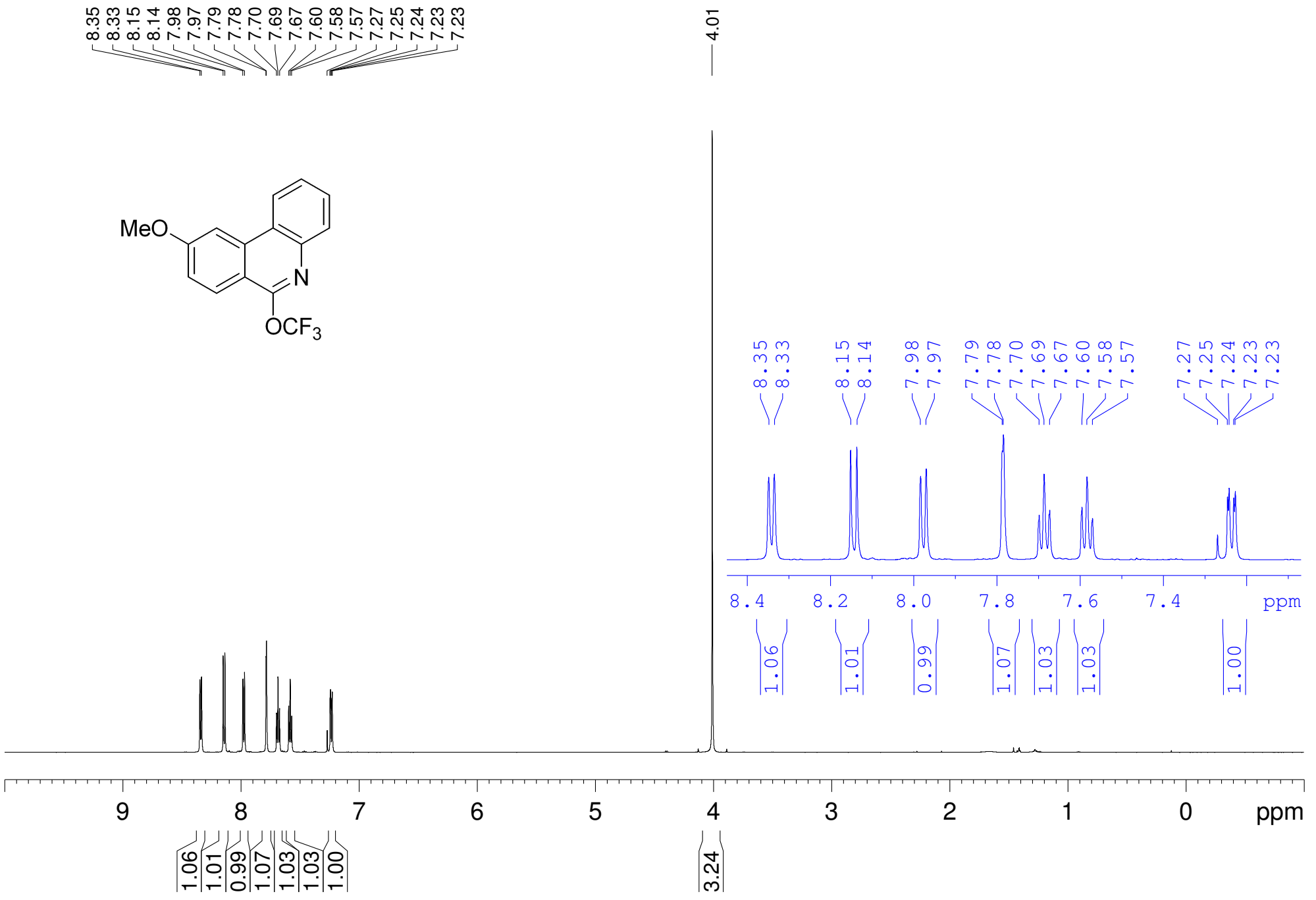
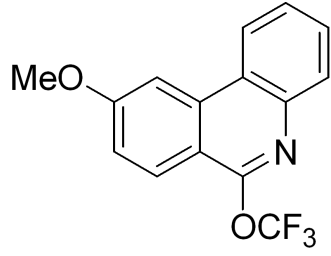


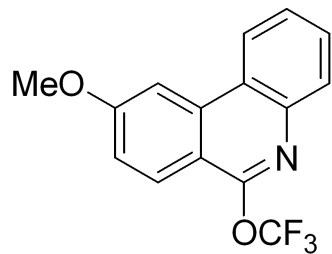




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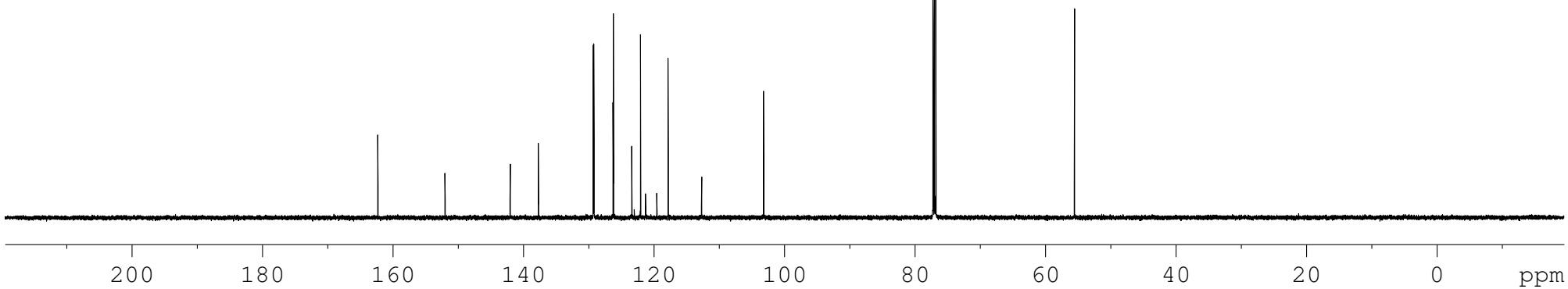
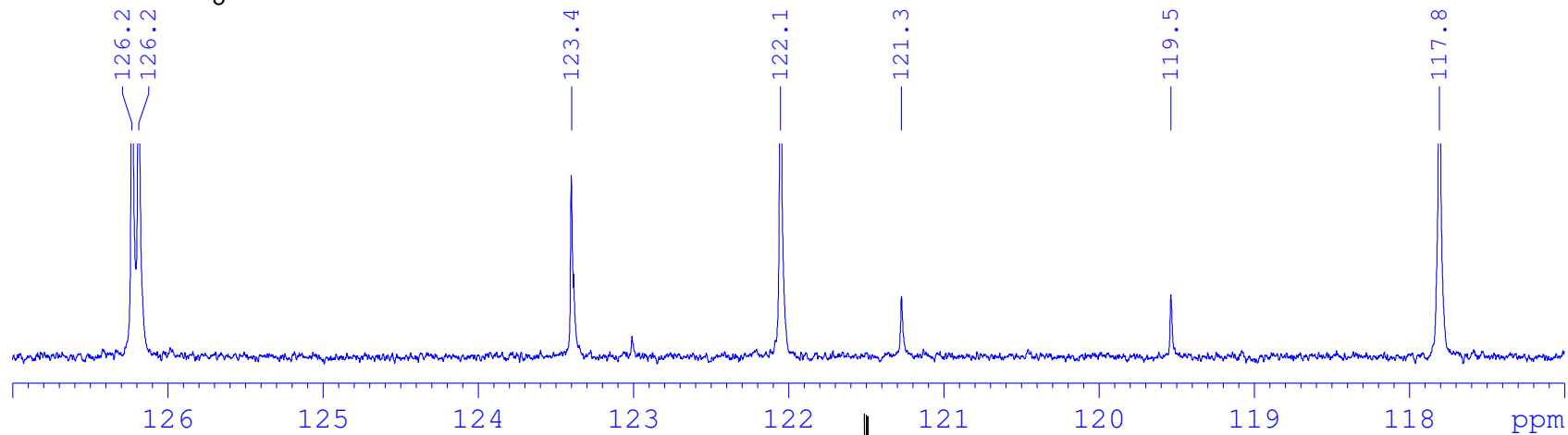


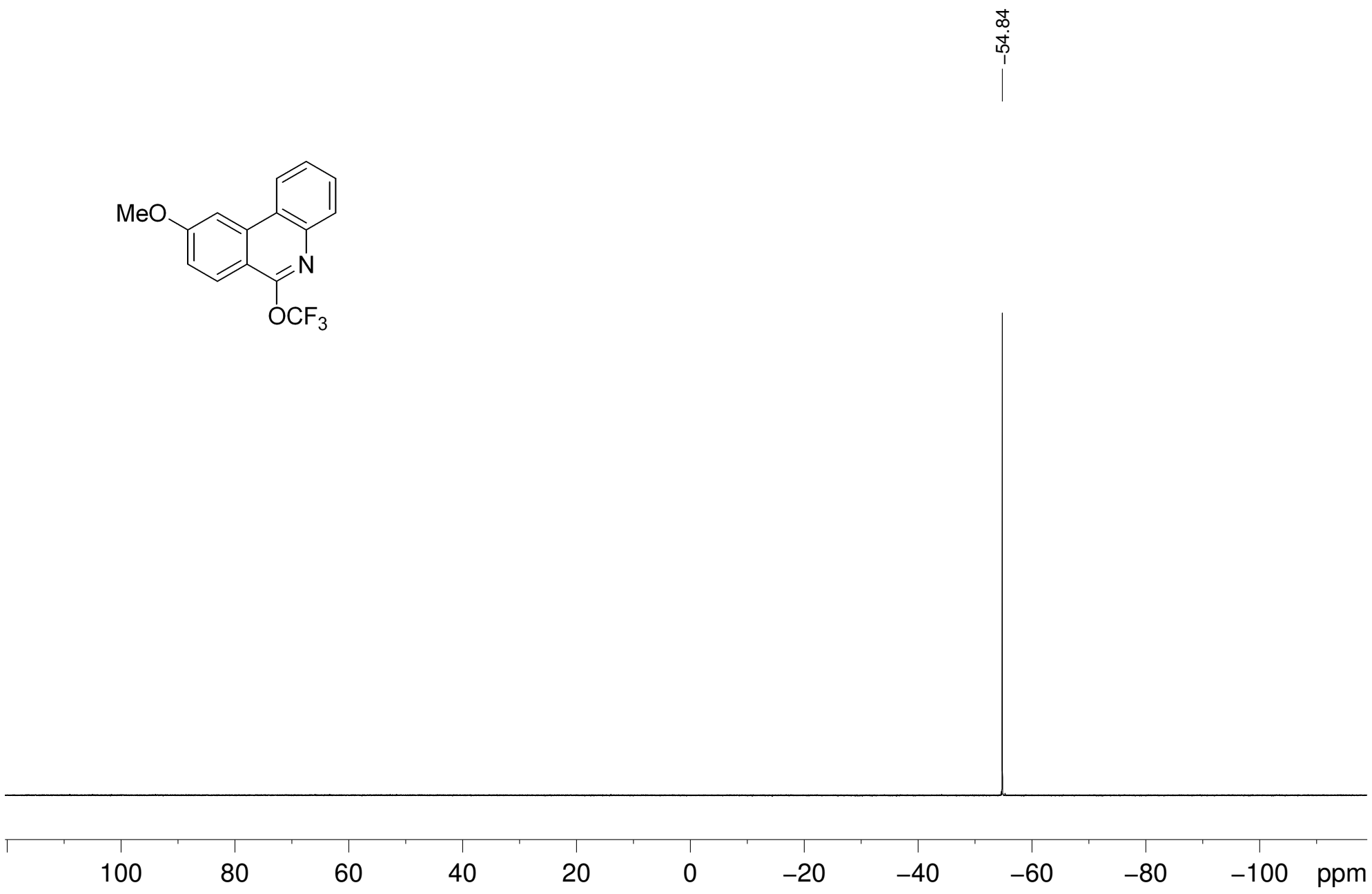
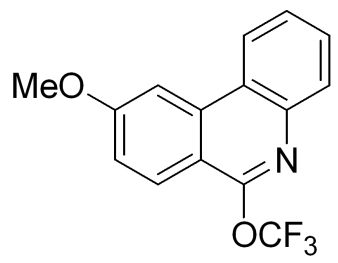


— 162.3
— 152.0
— 142.0
— 137.7
— 129.3
— 129.2
— 126.2
— 126.2
— 123.4
— 122.1
— 121.3
— 119.5
— 117.8
— 112.7
— 103.2

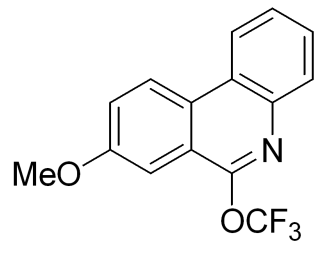
— 77.2
— 77.0
— 76.8

— 55.5





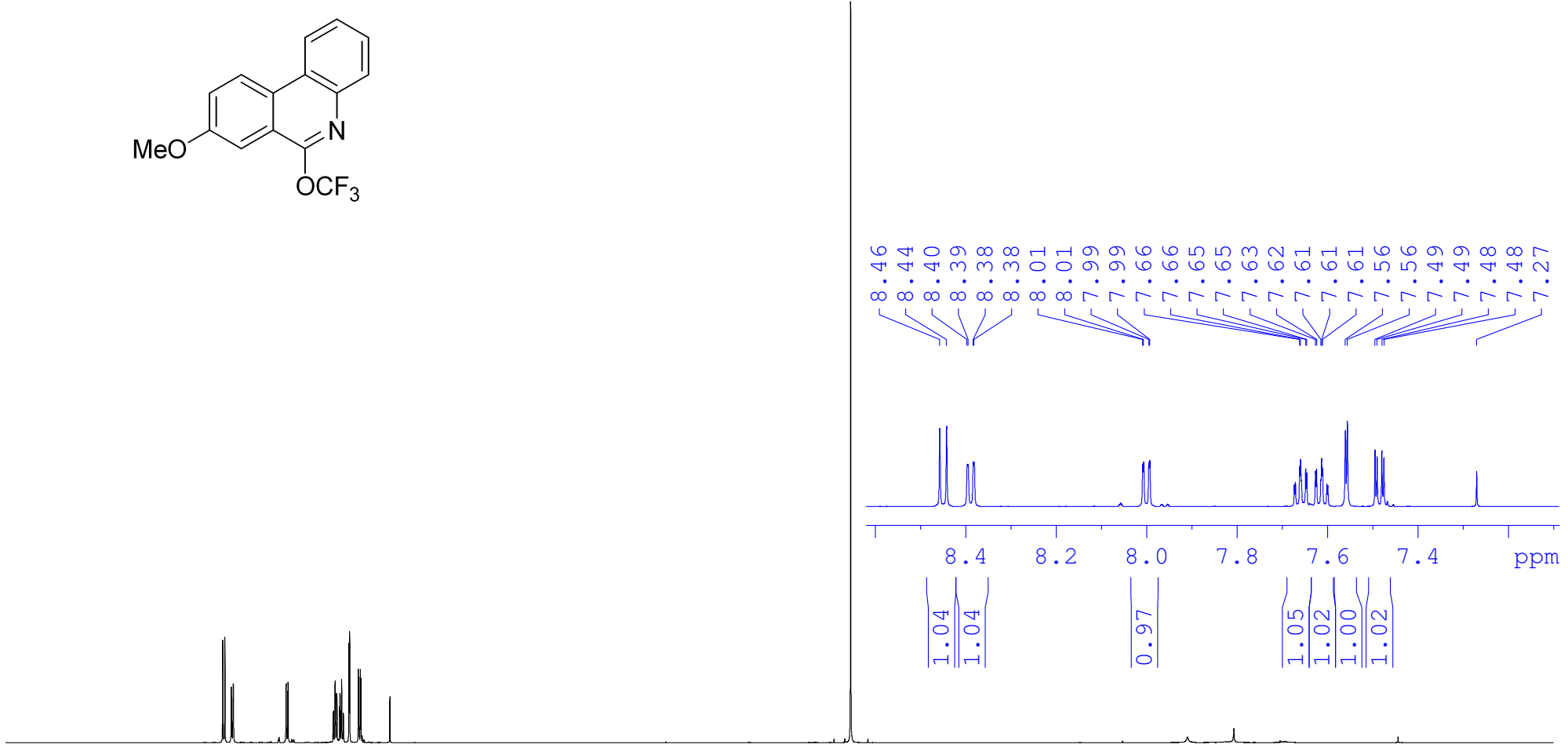
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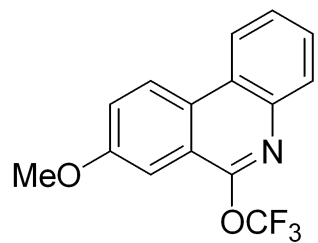


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1.05
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1.02
3.16
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1.05
1.02
1.00
1.02

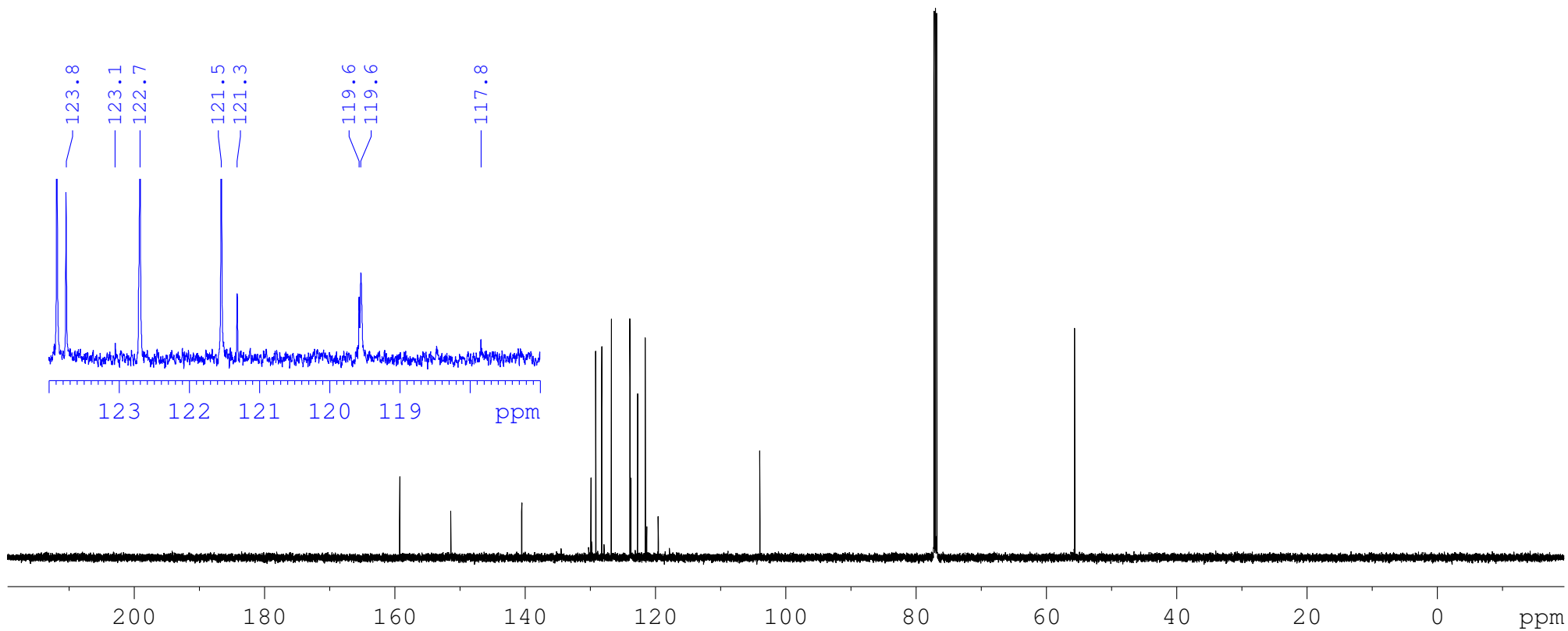
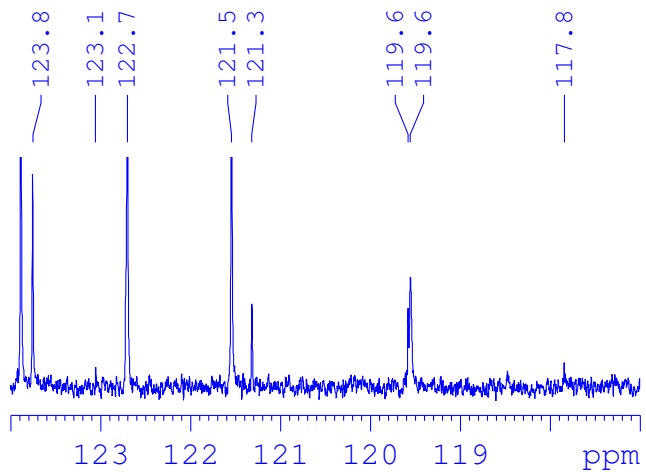
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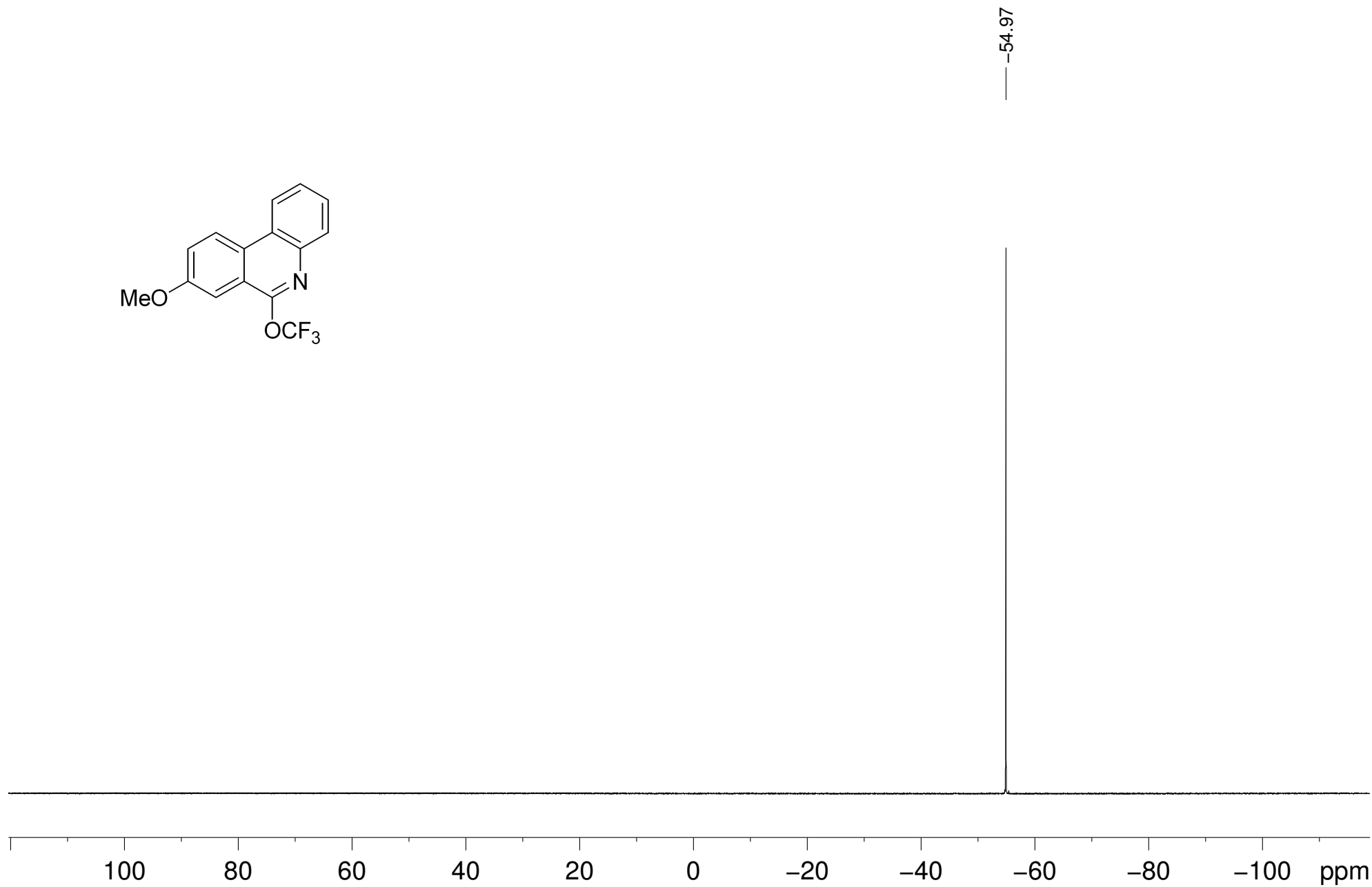
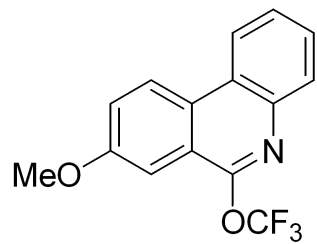
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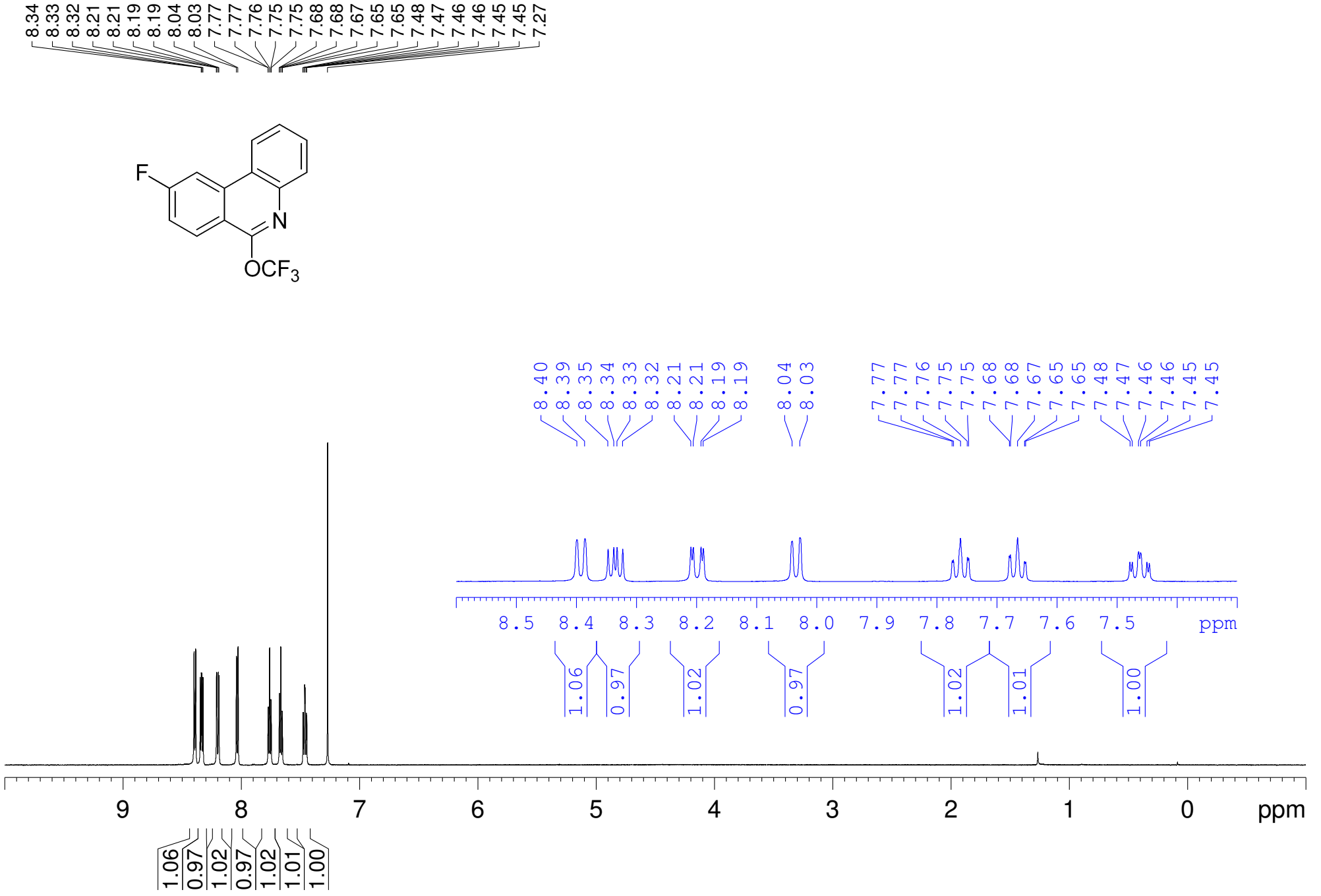
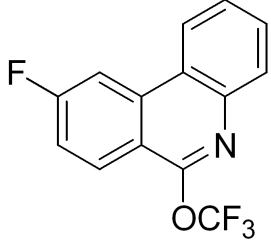


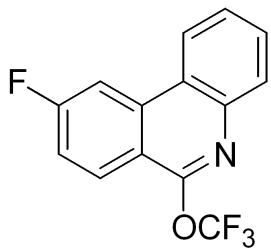


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119.6
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77.2
77.0
76.8
55.6



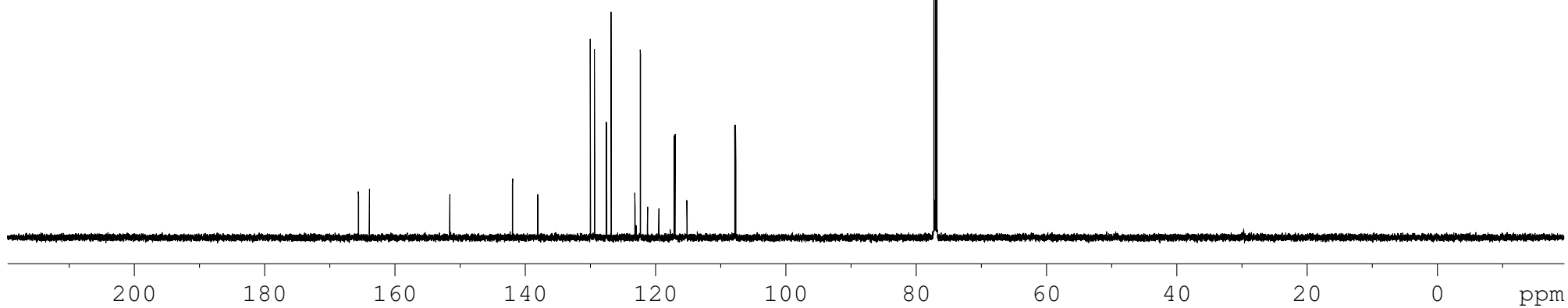
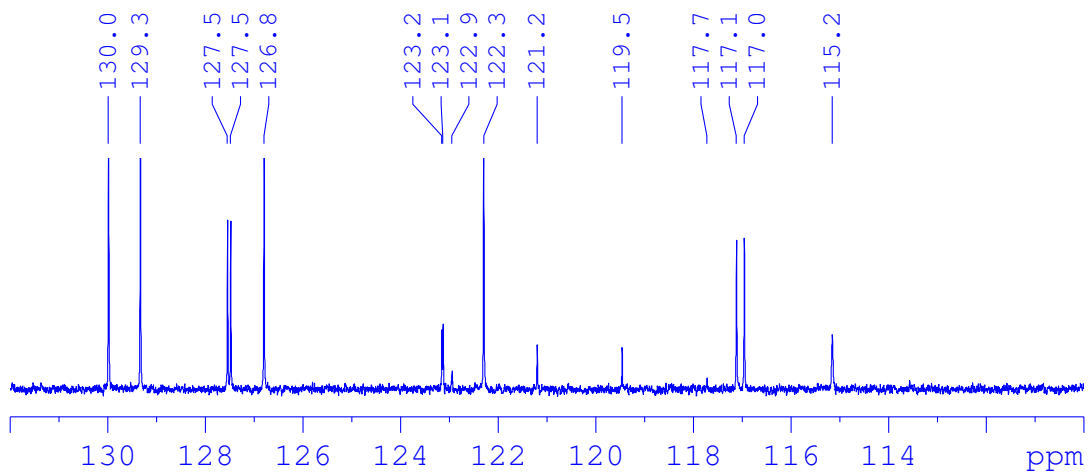


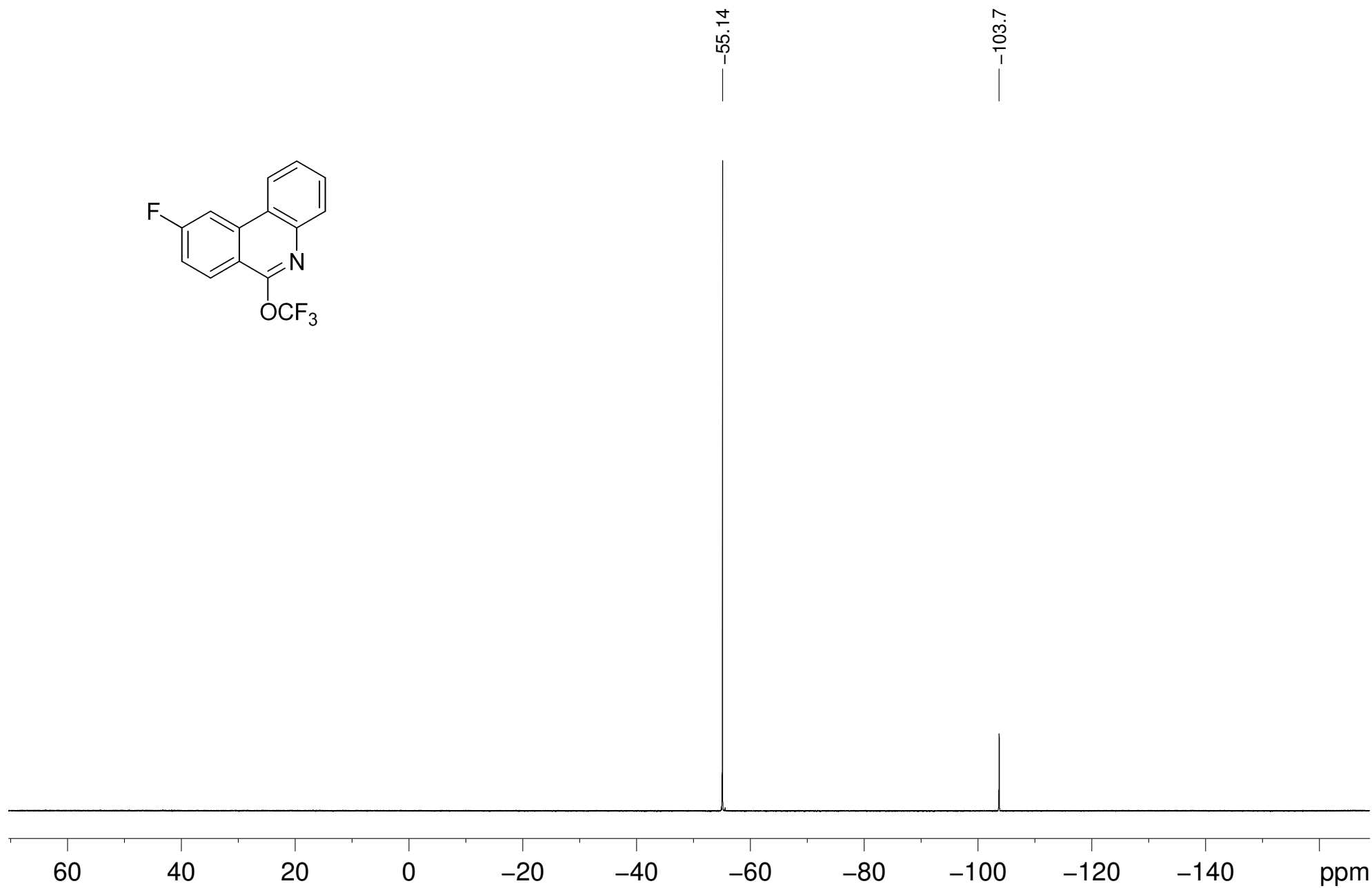
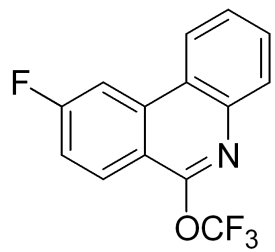




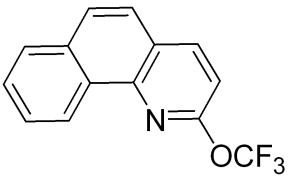
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122.9
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121.2
119.5
117.7
117.1
117.0
115.2
107.8
107.7

77.2
77.0
76.8





9.17
9.16
8.27
8.26
7.93
7.92
7.85
7.83
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7.20

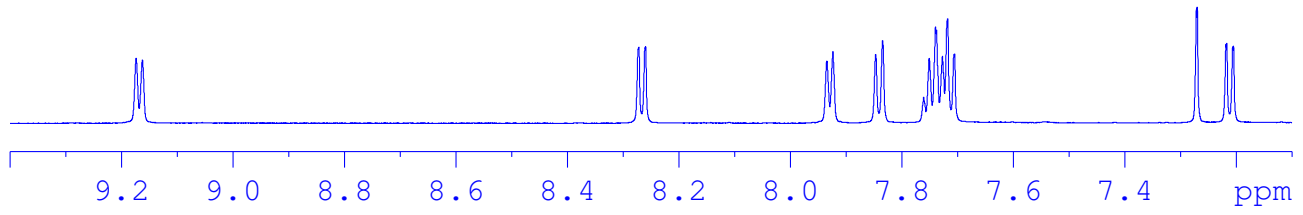


9.17
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7.27
7.27
7.22
7.22



0.98

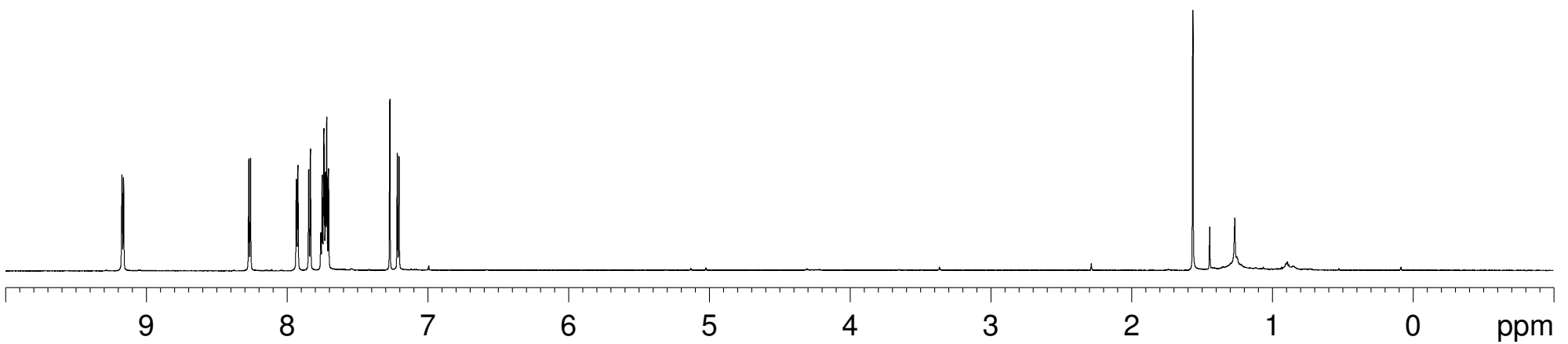
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1.05

2.81

1.09



0.98

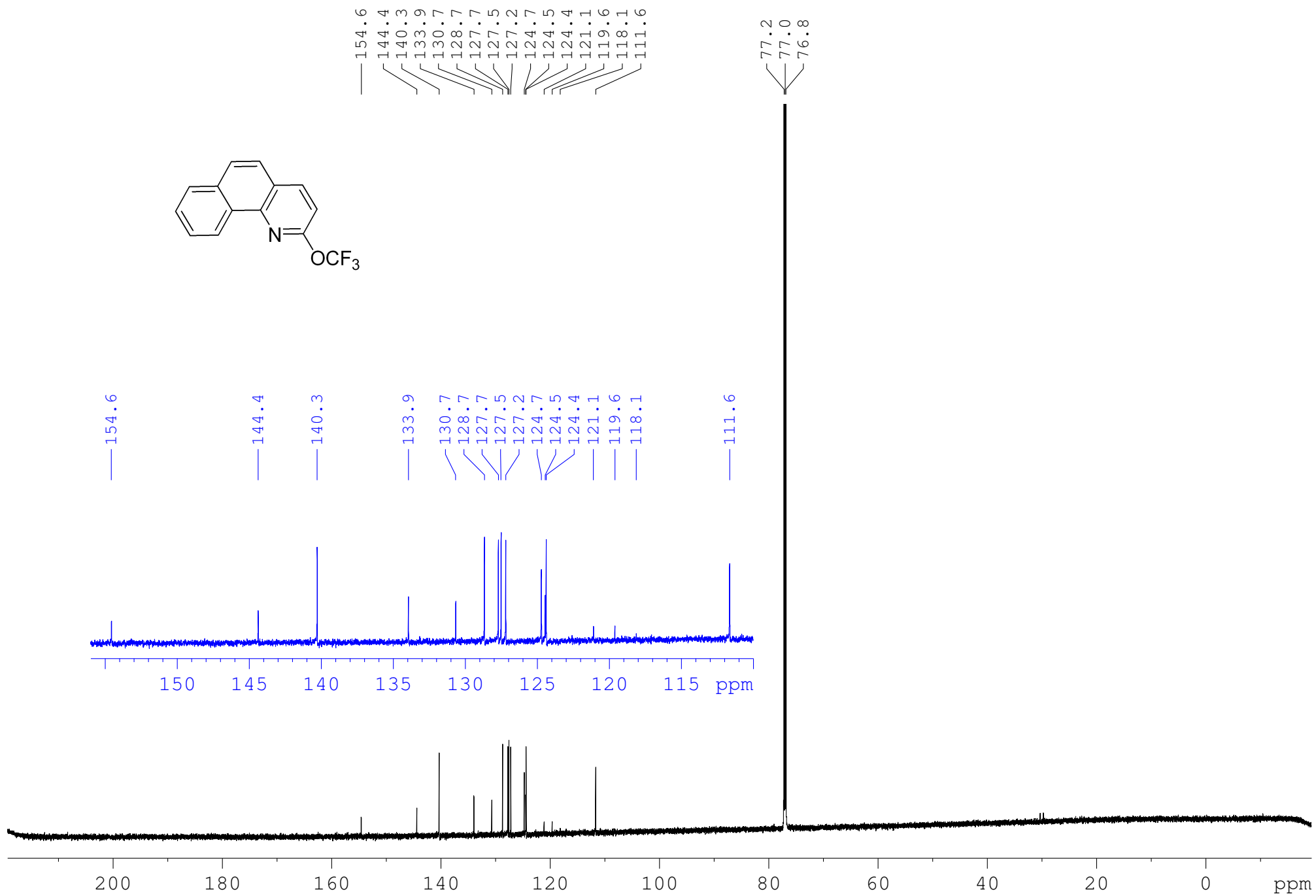
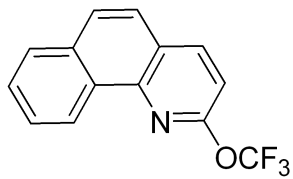
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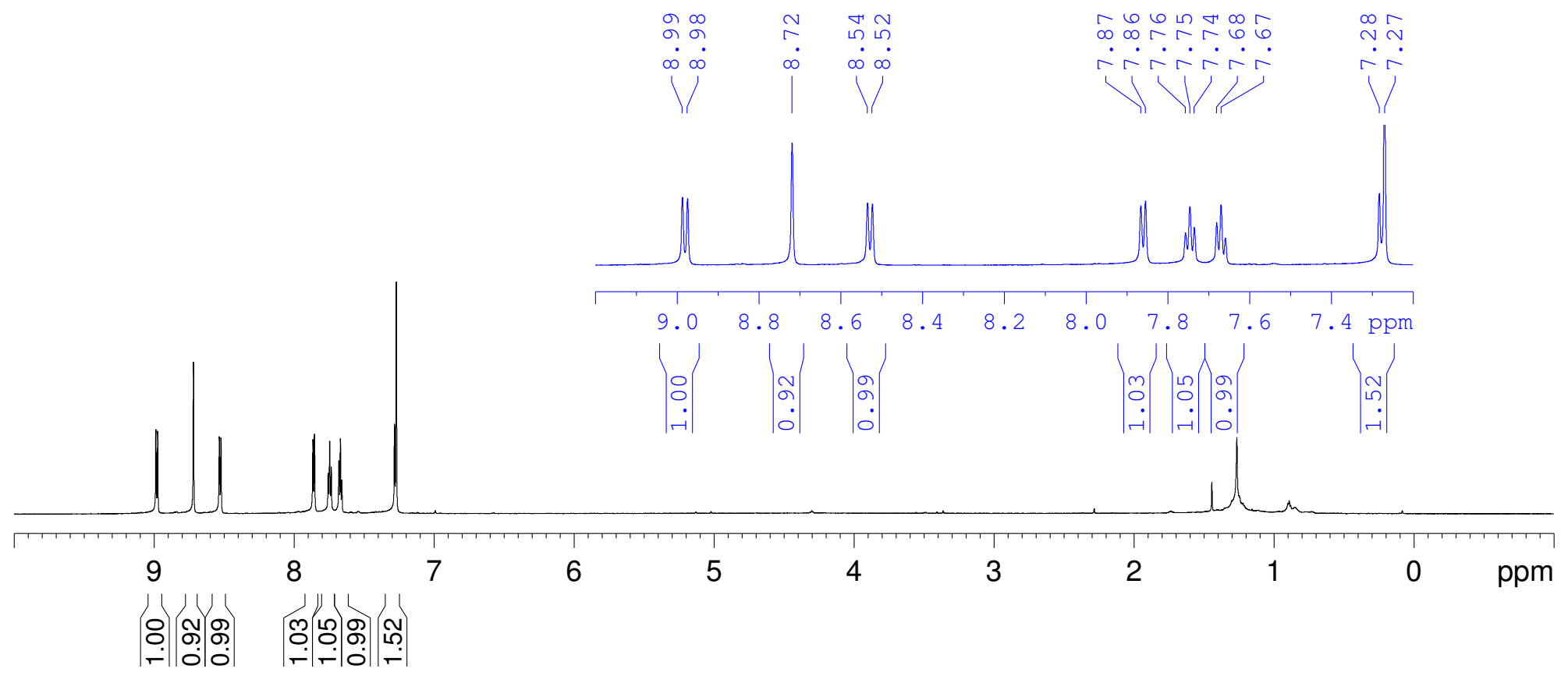
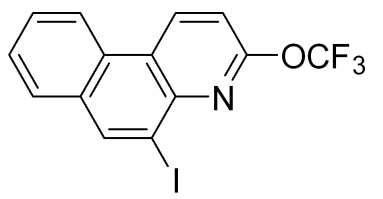
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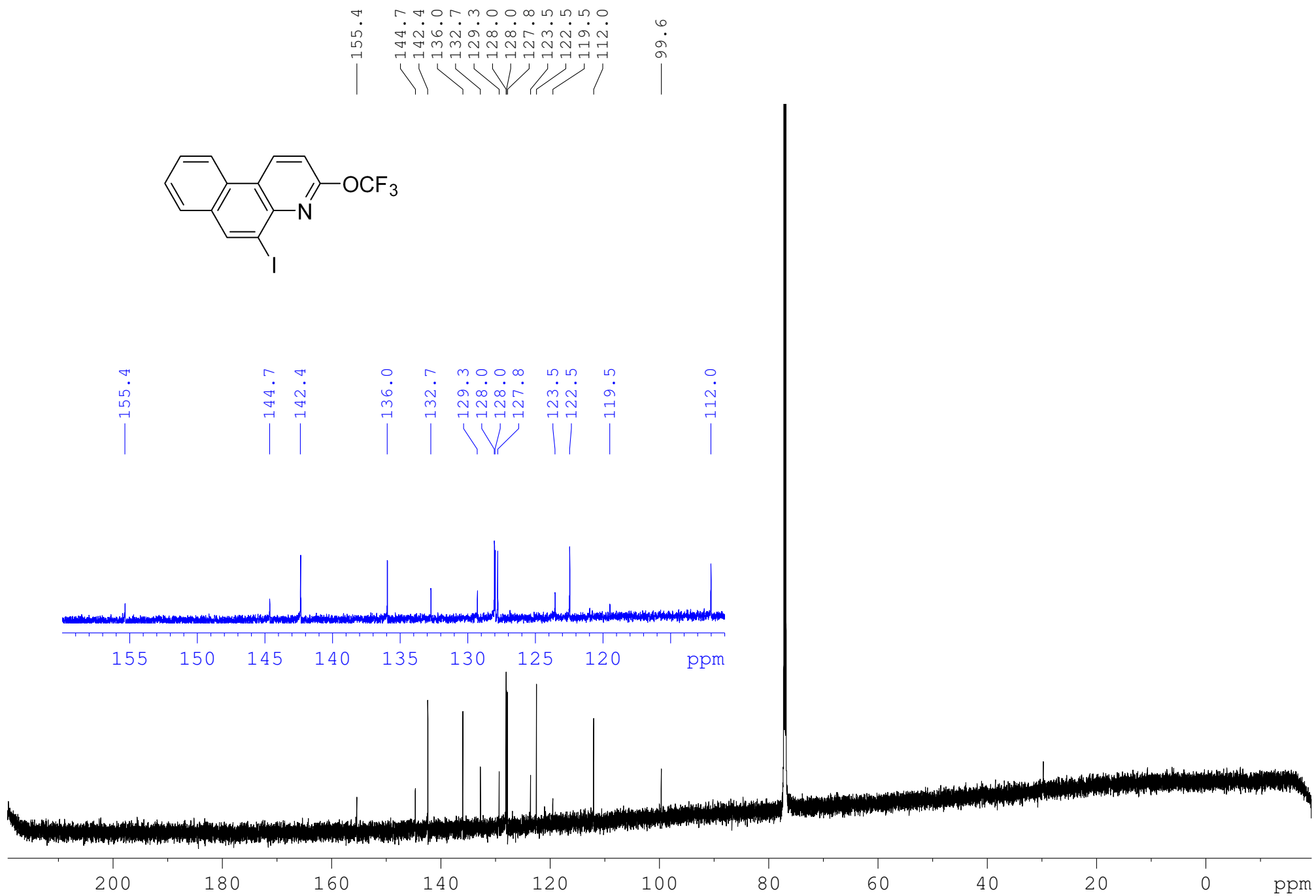
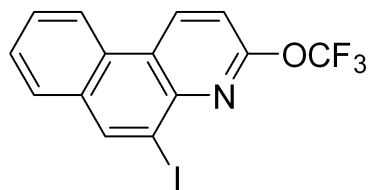
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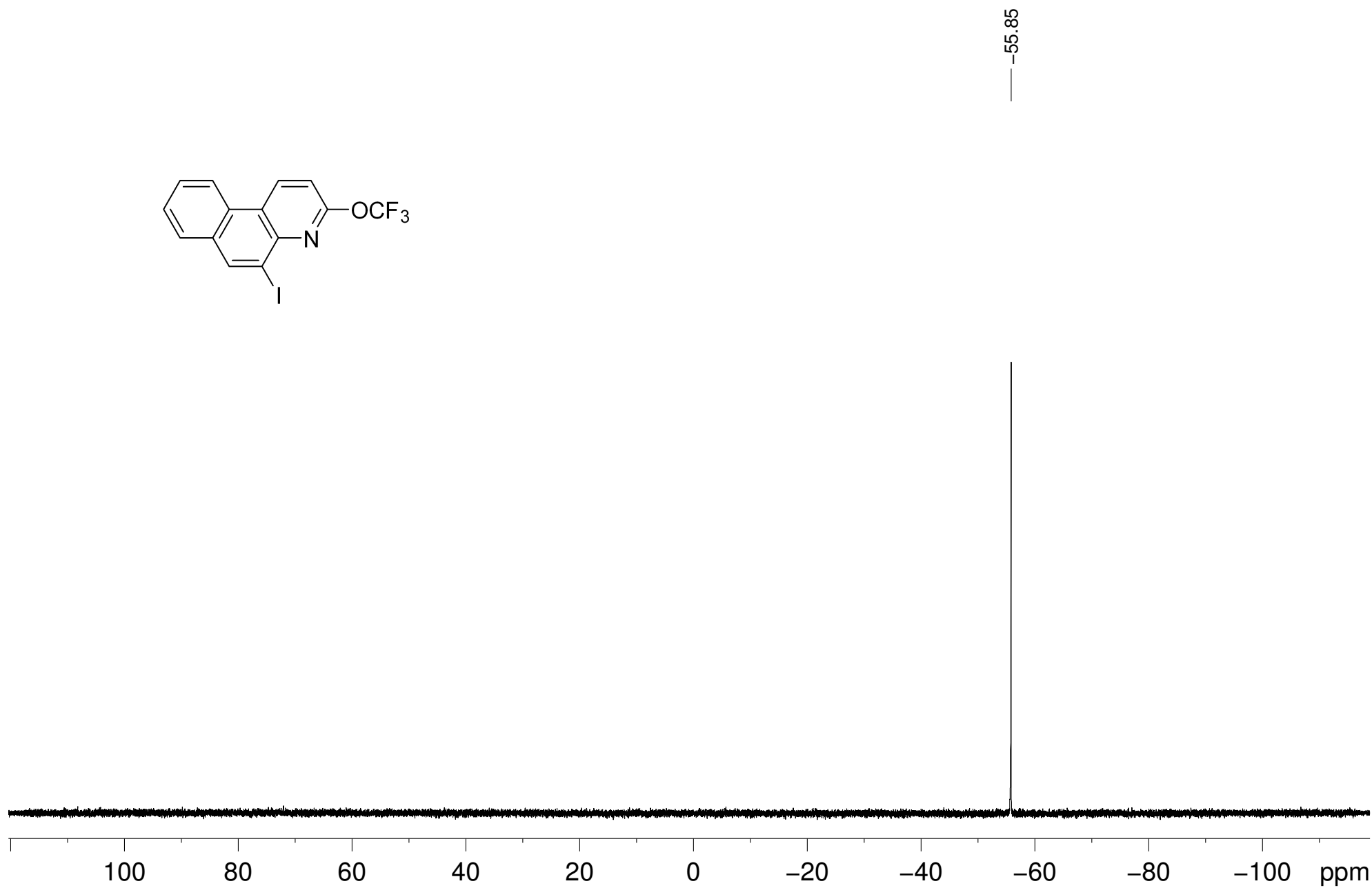
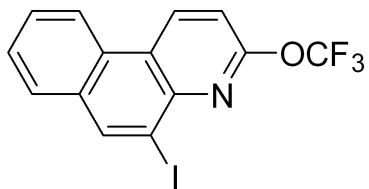
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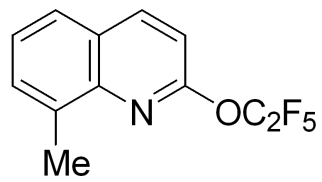


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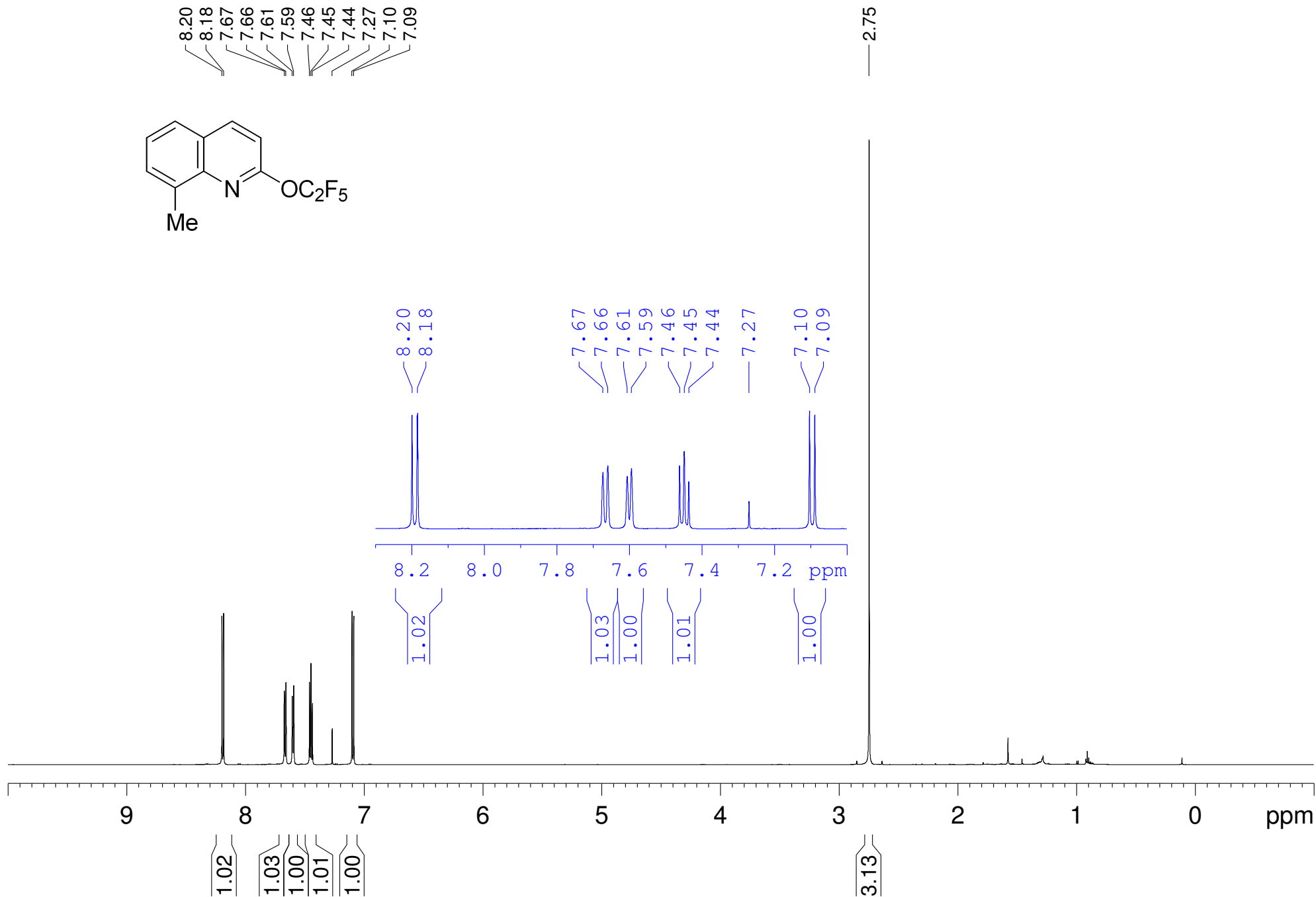


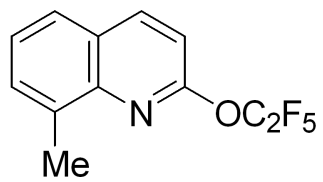






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7.09

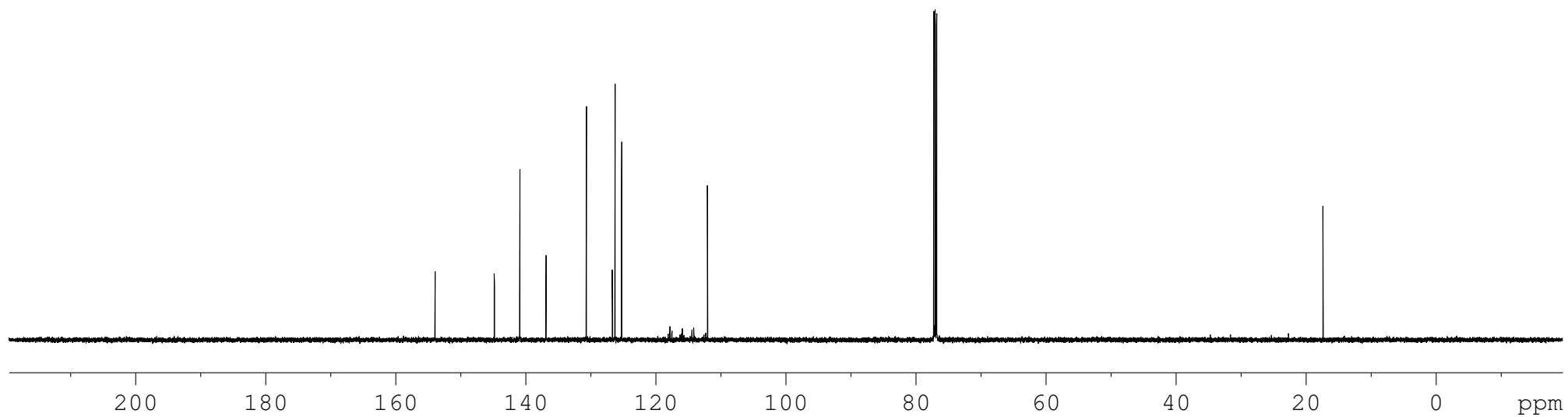
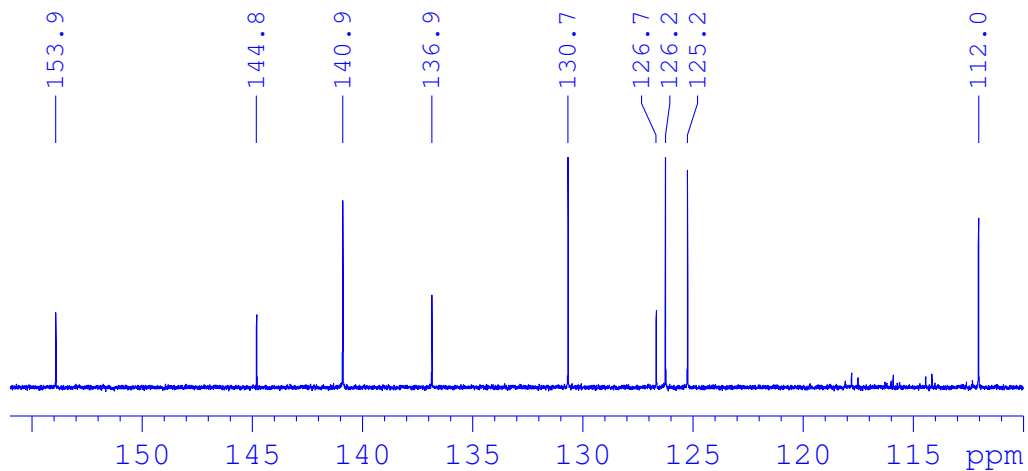


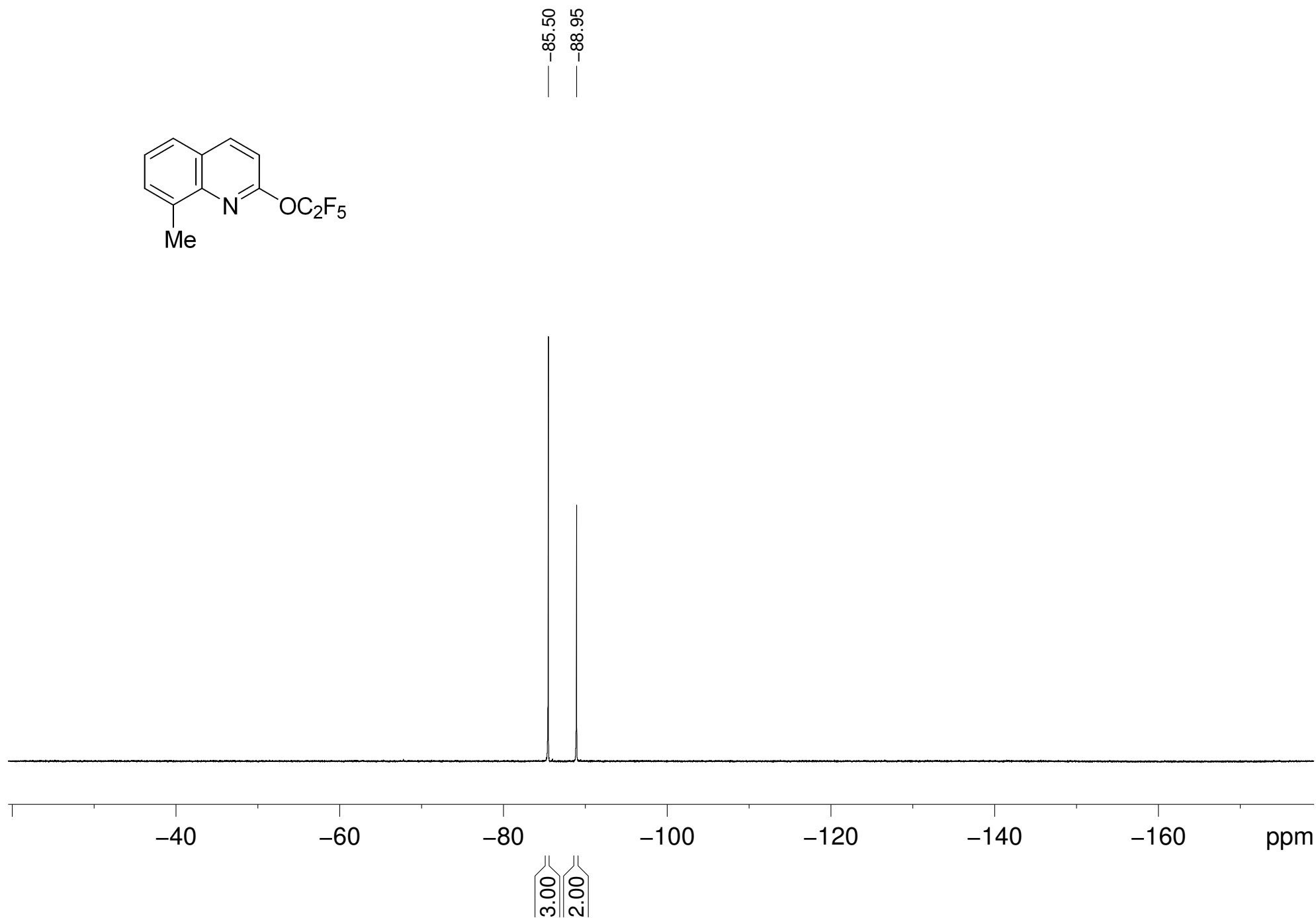
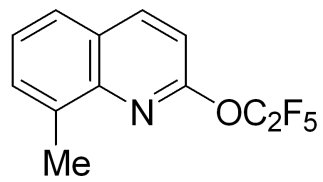


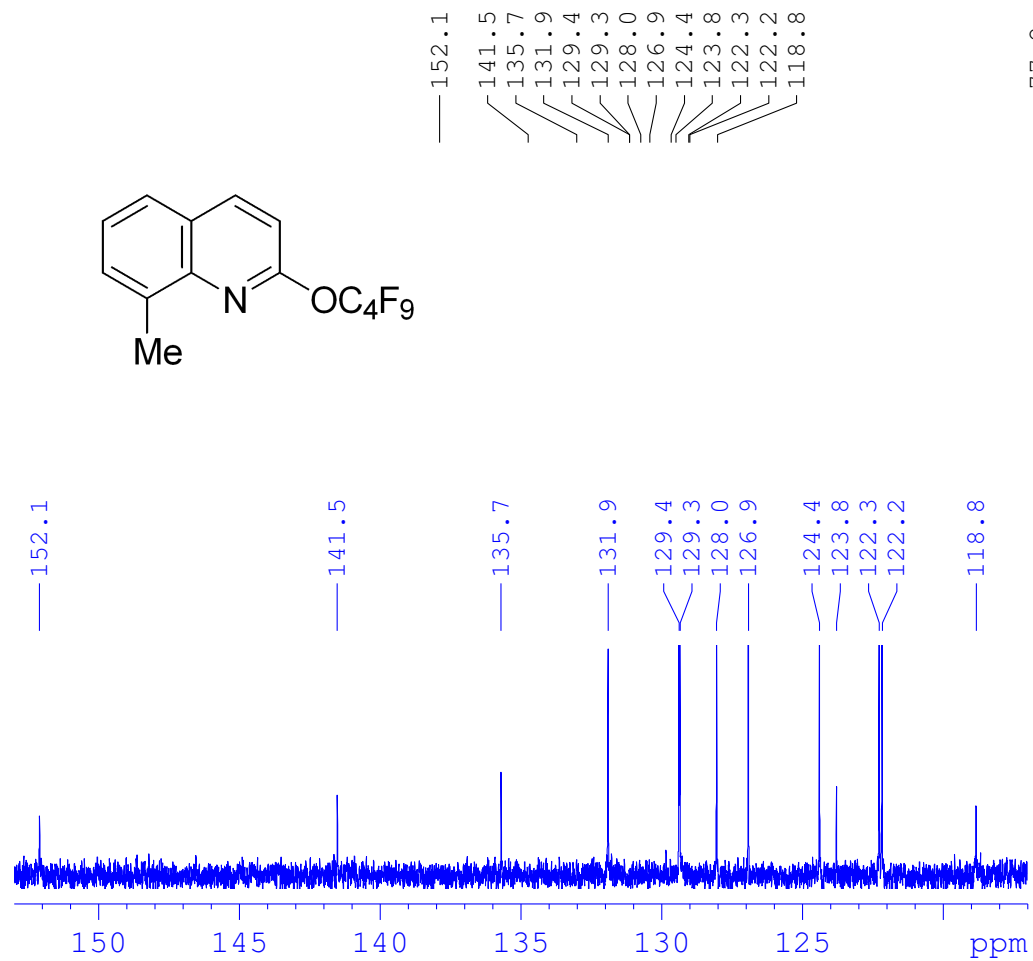
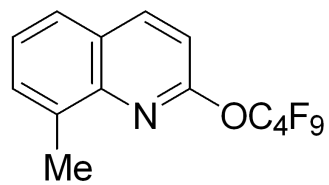
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— 144.8
— 140.9
— 136.9
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— 126.7
— 126.2
— 125.2
— 112.0

— 77.2
— 77.0
— 76.8

— 17.4

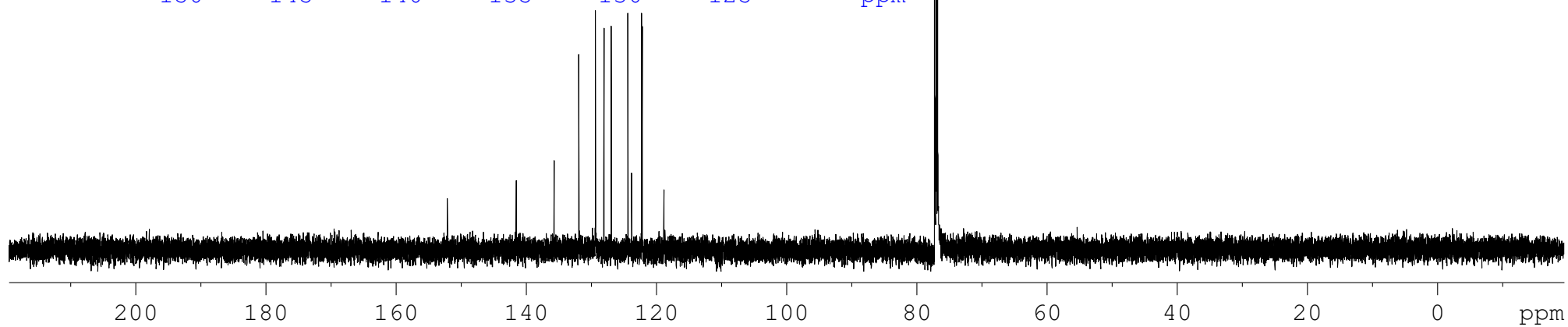


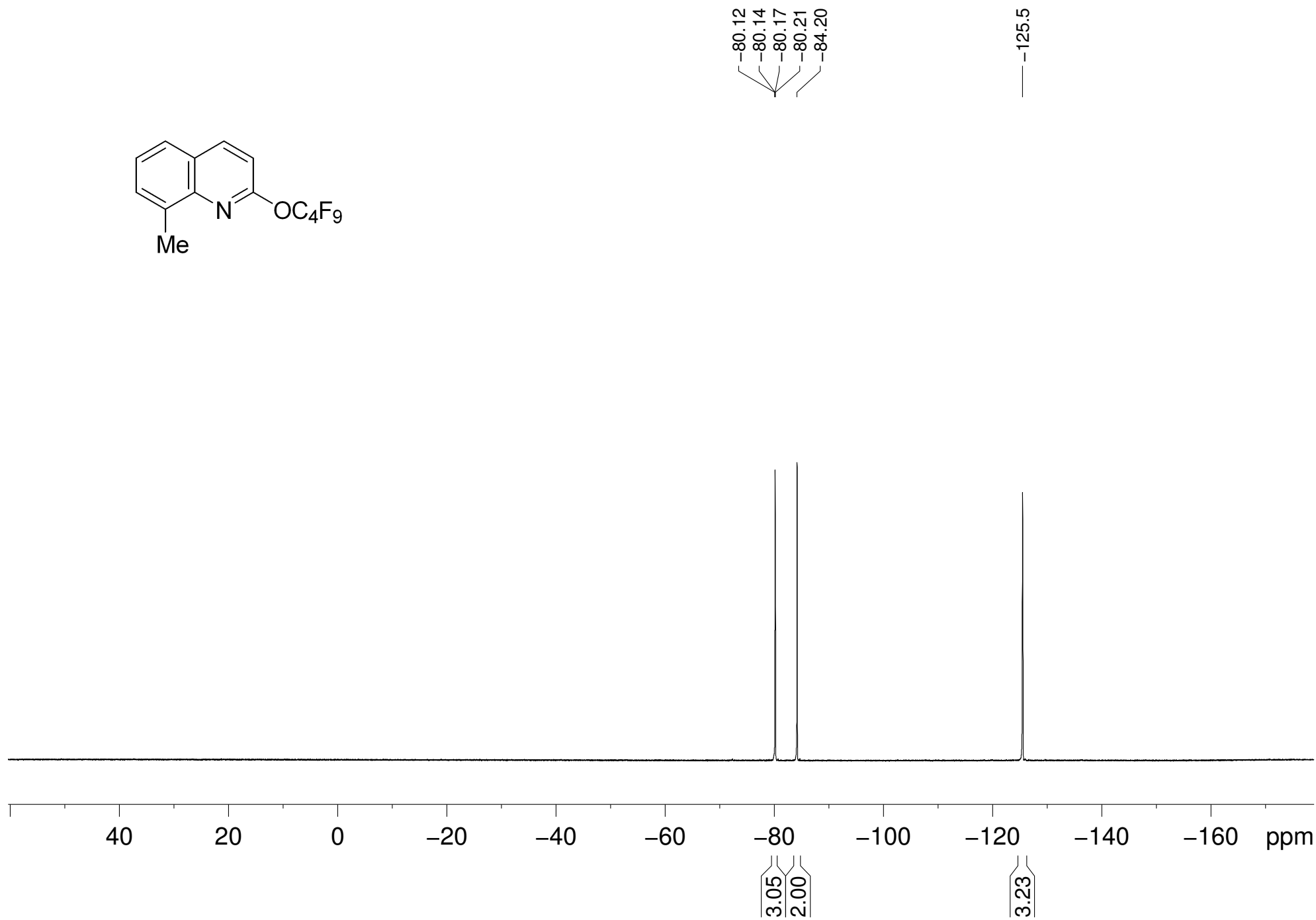
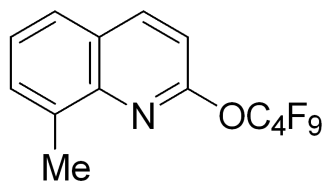


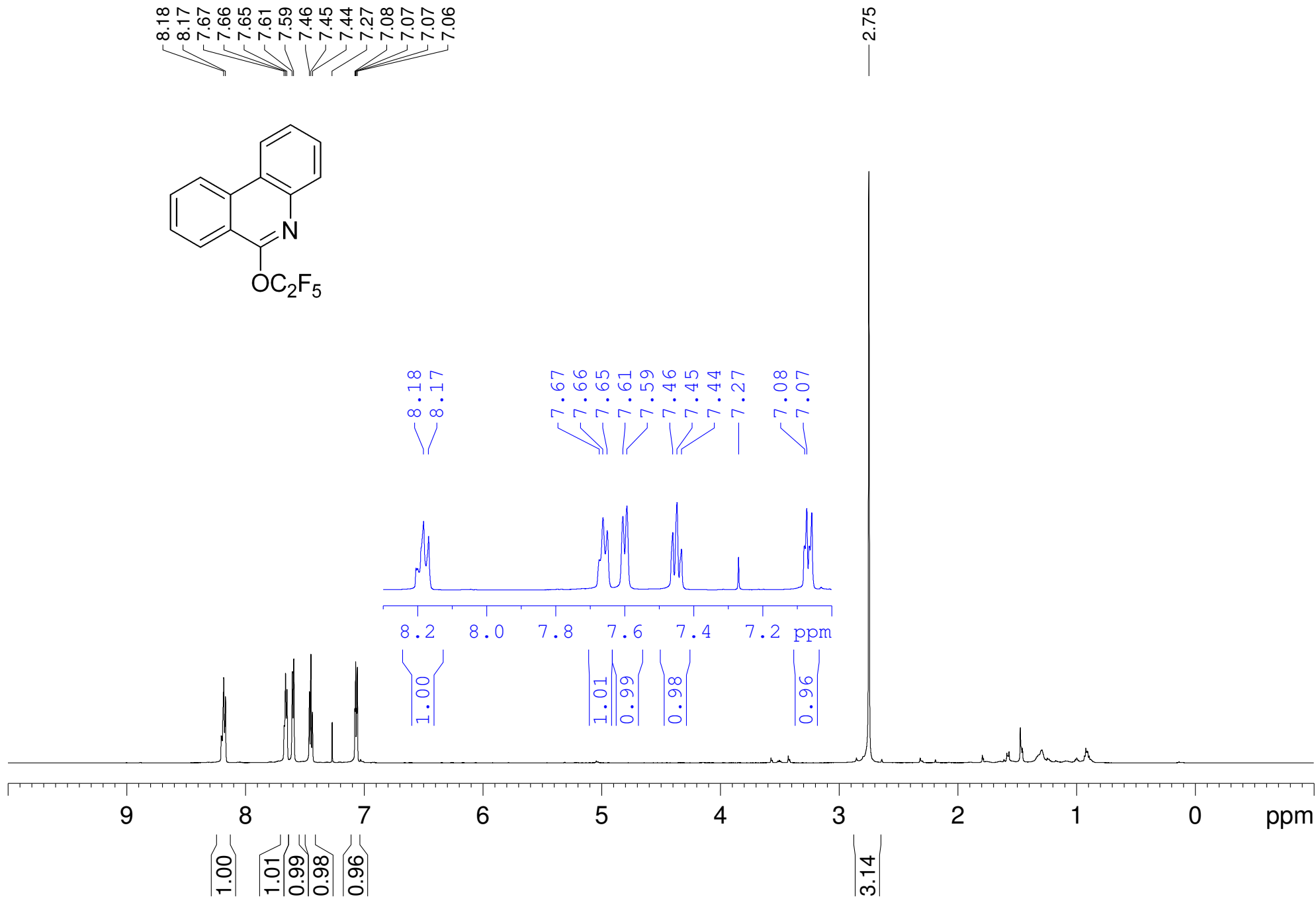
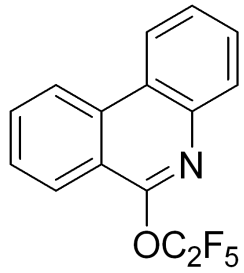


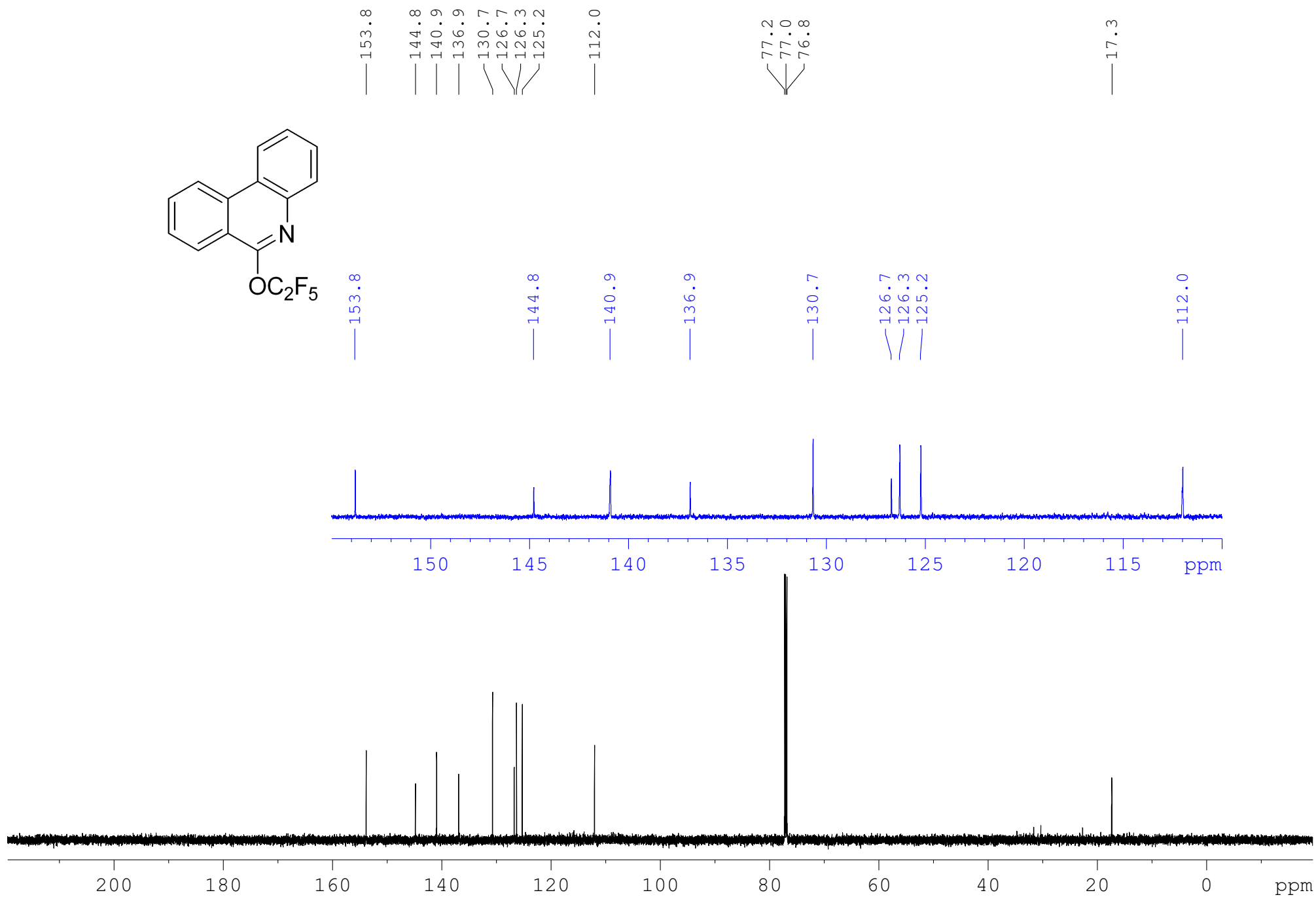
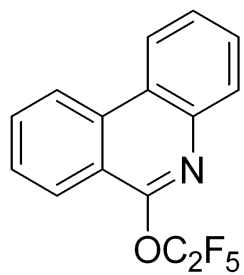
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122.2
118.8

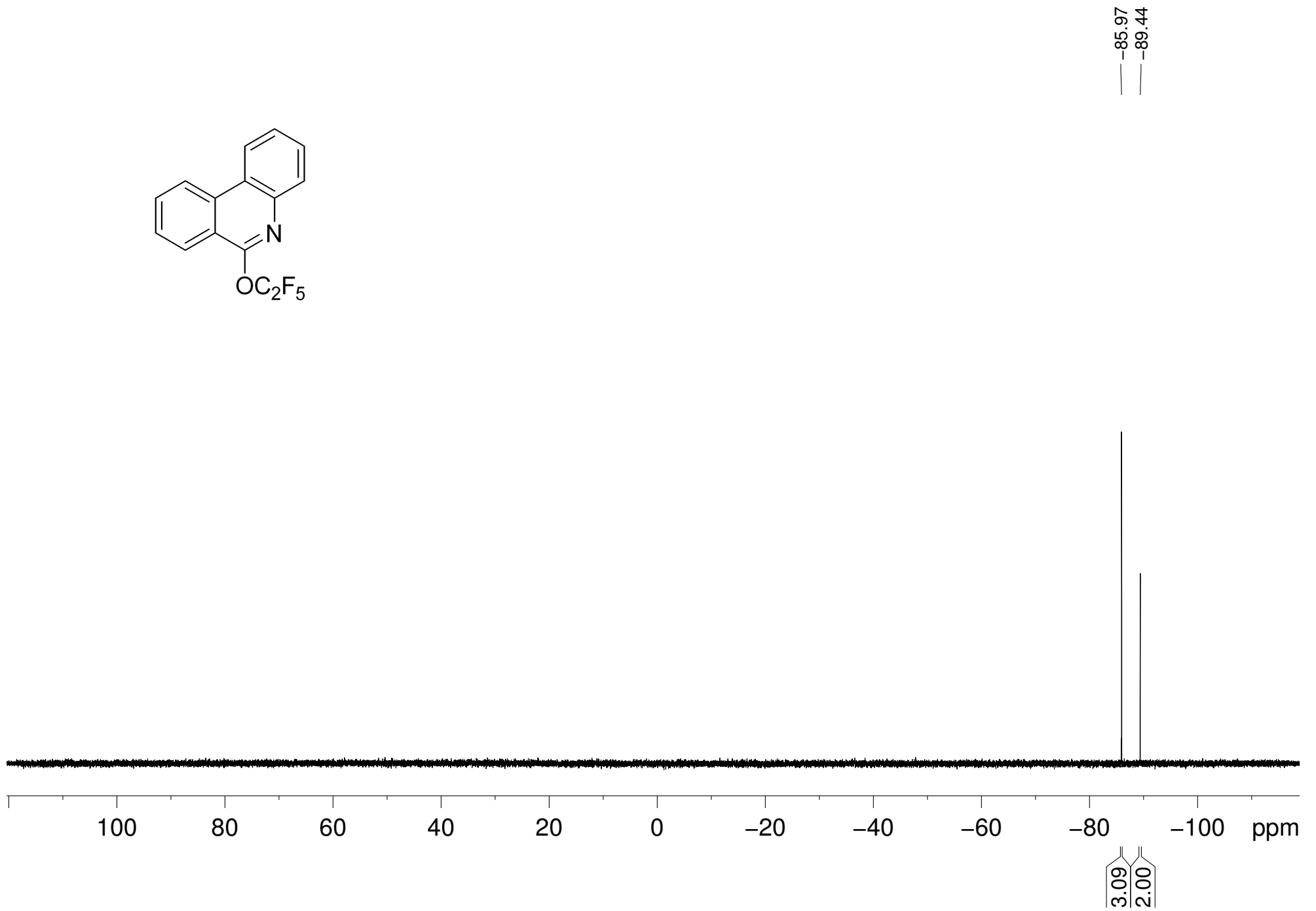
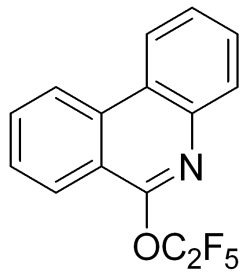
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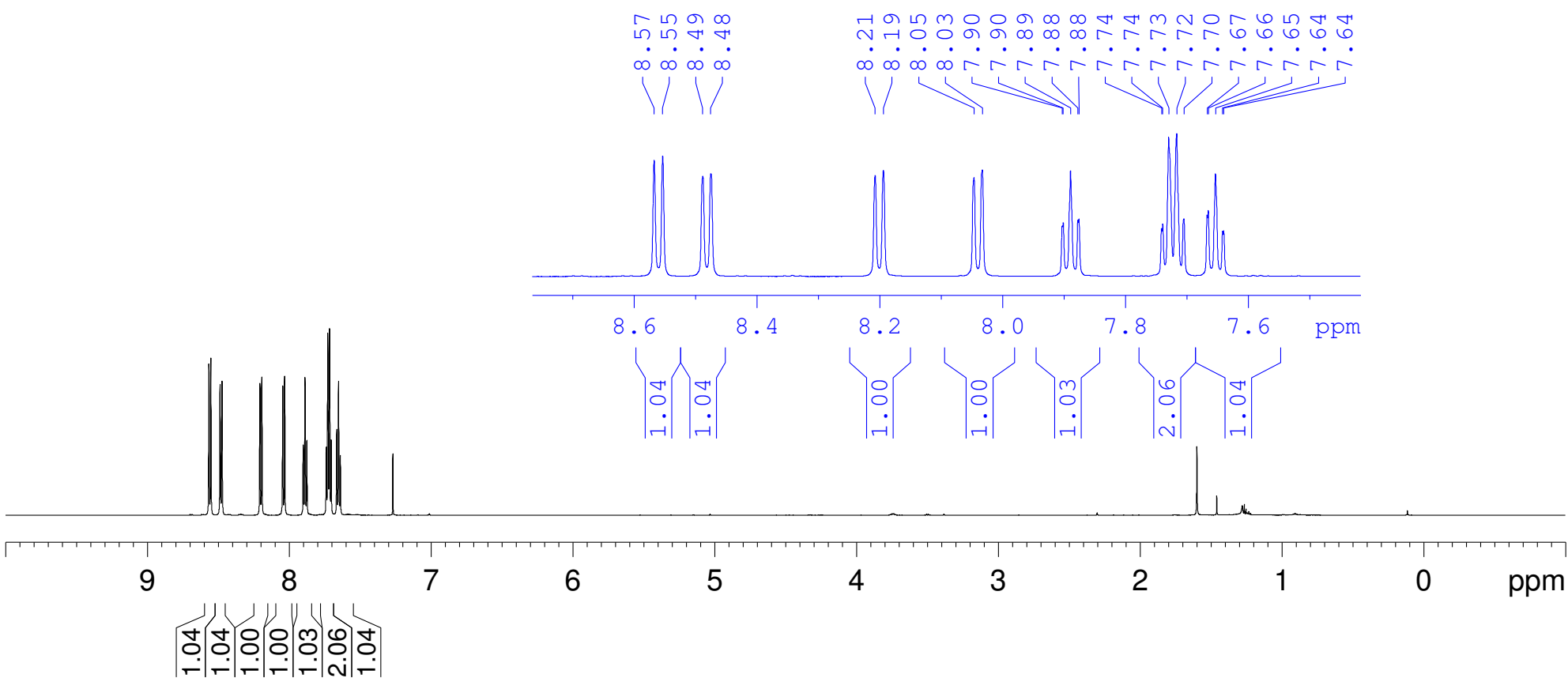
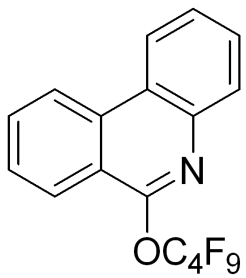


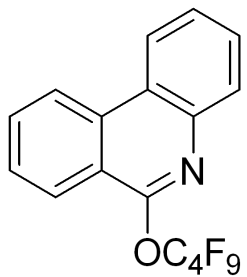






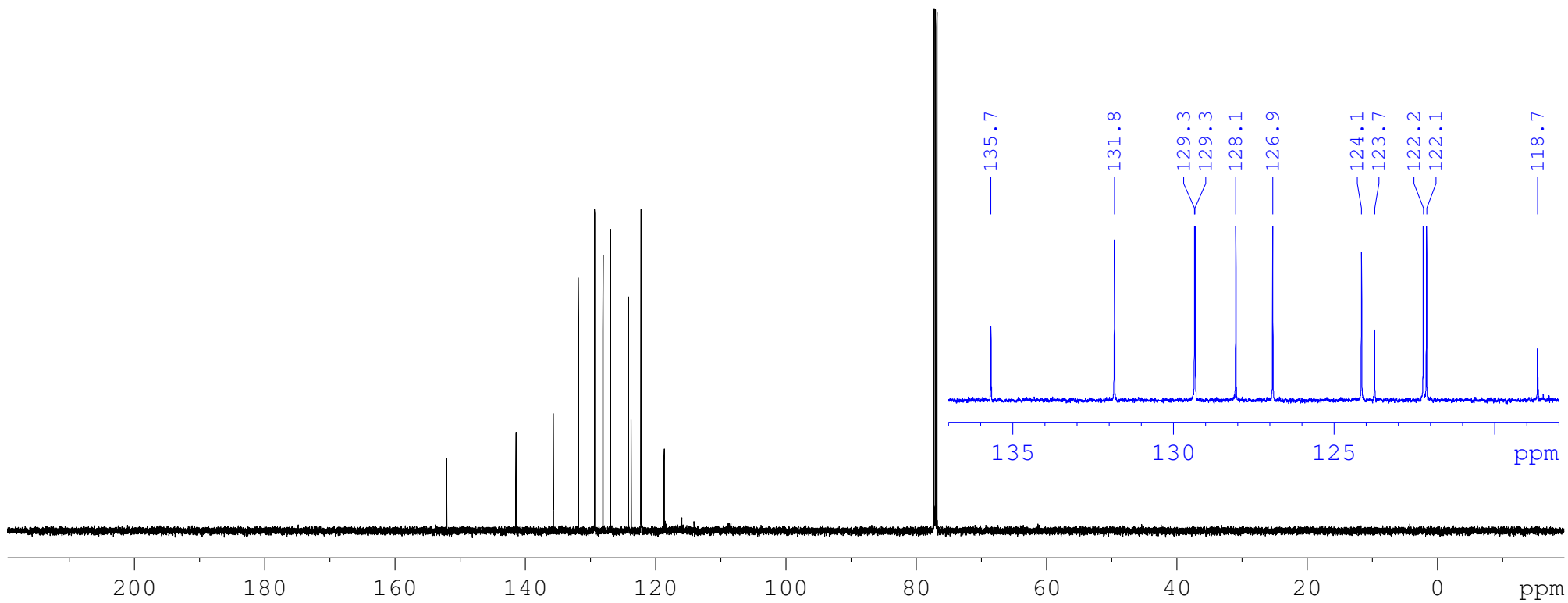
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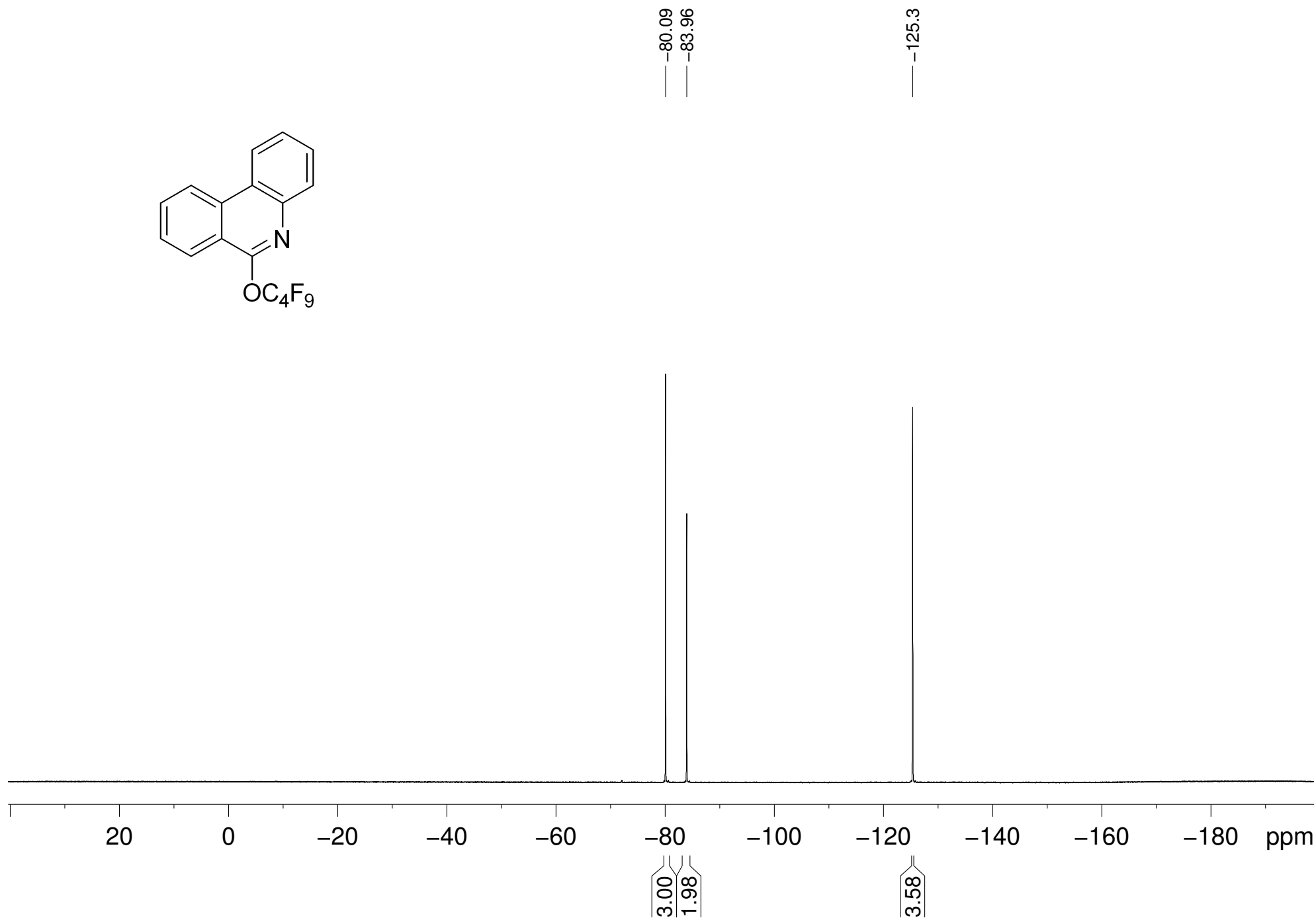
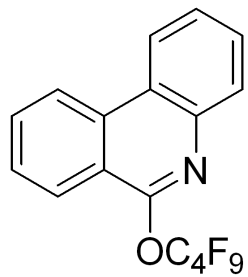


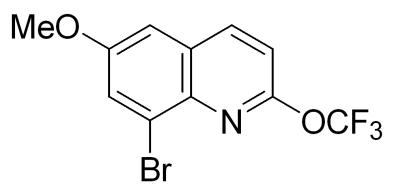


152.1
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118.7

77.2
77.0
76.8

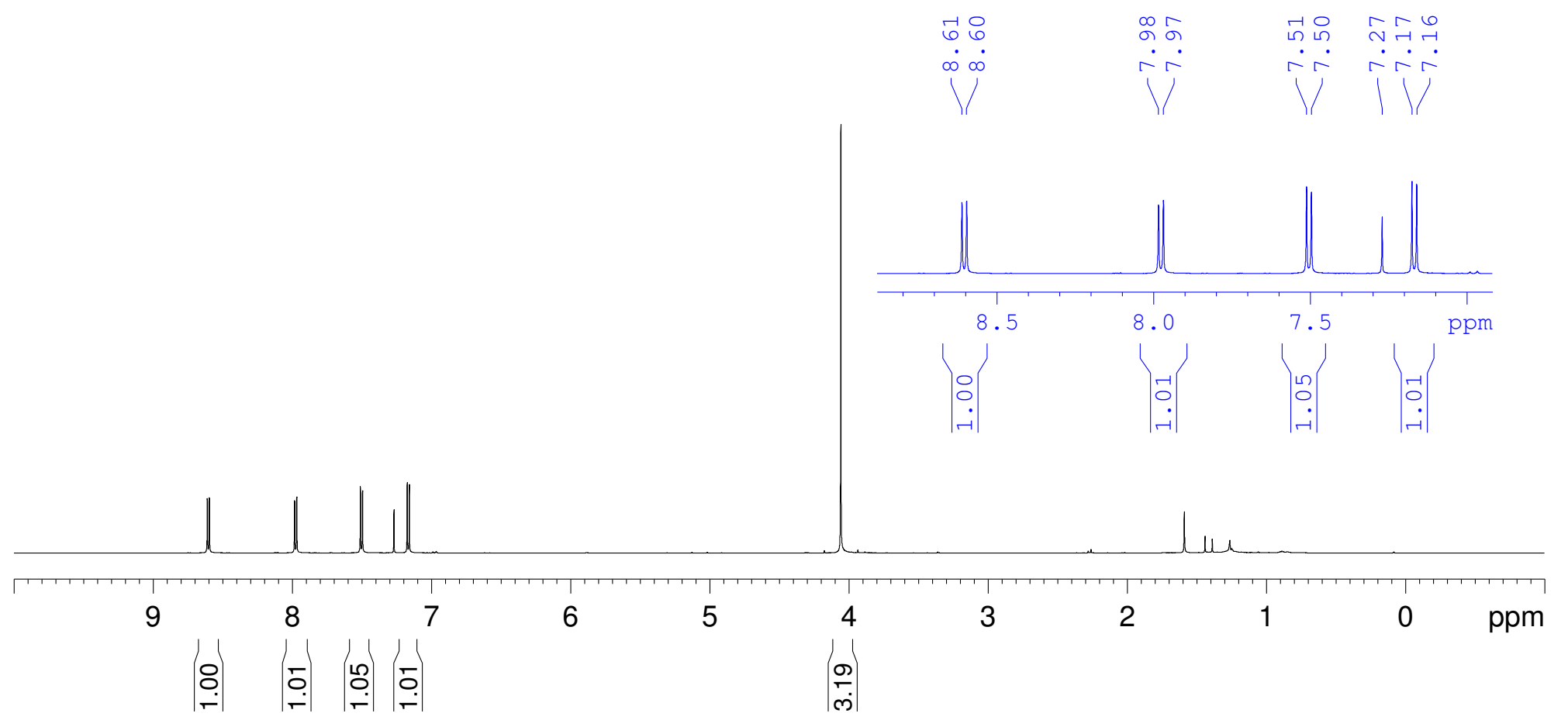


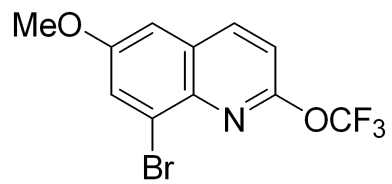




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4.06

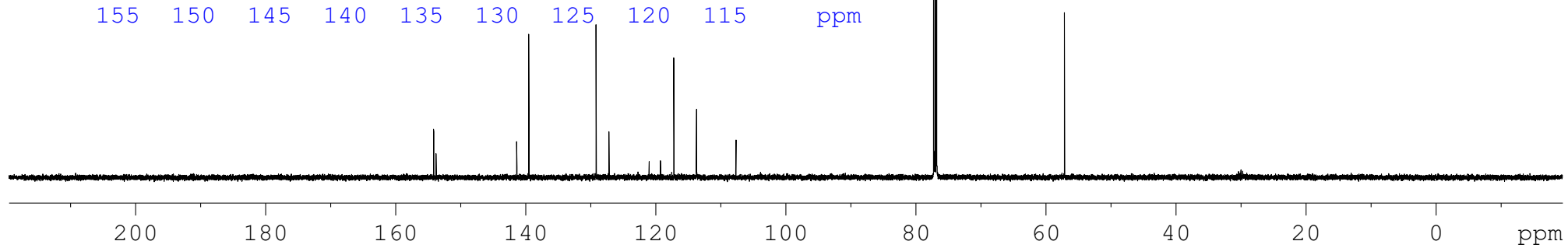
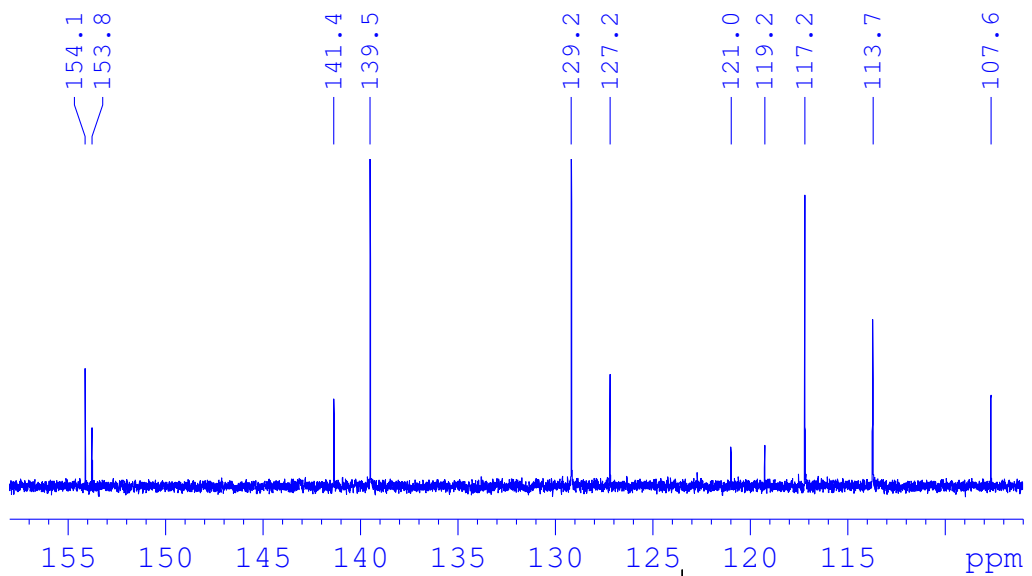


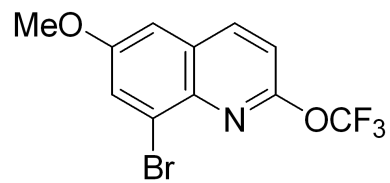


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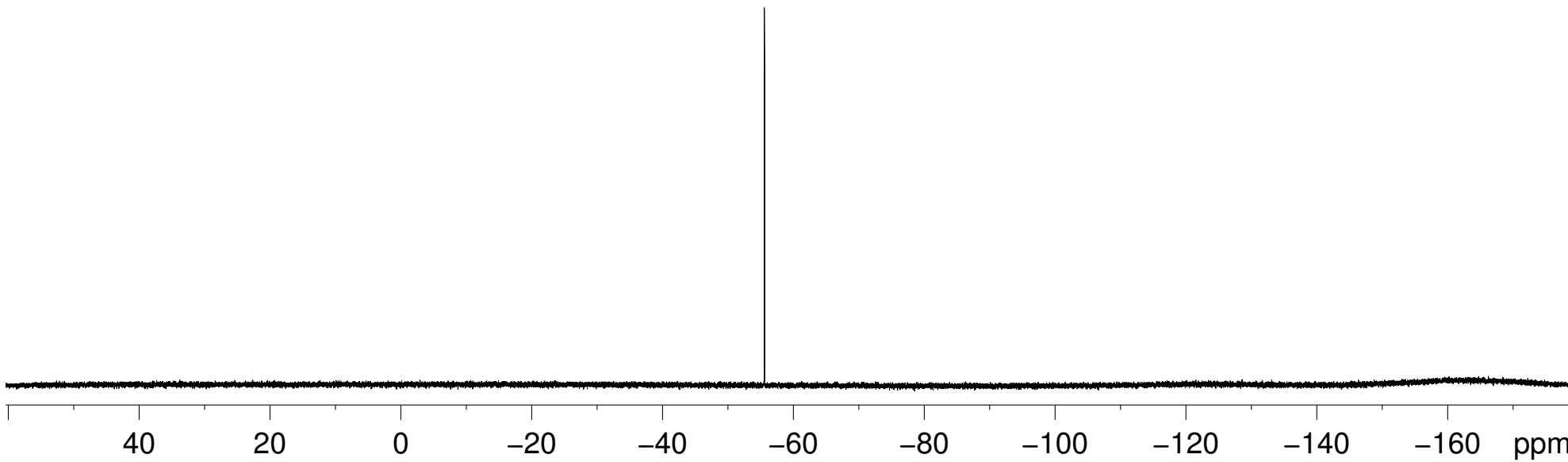
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76.8

57.1

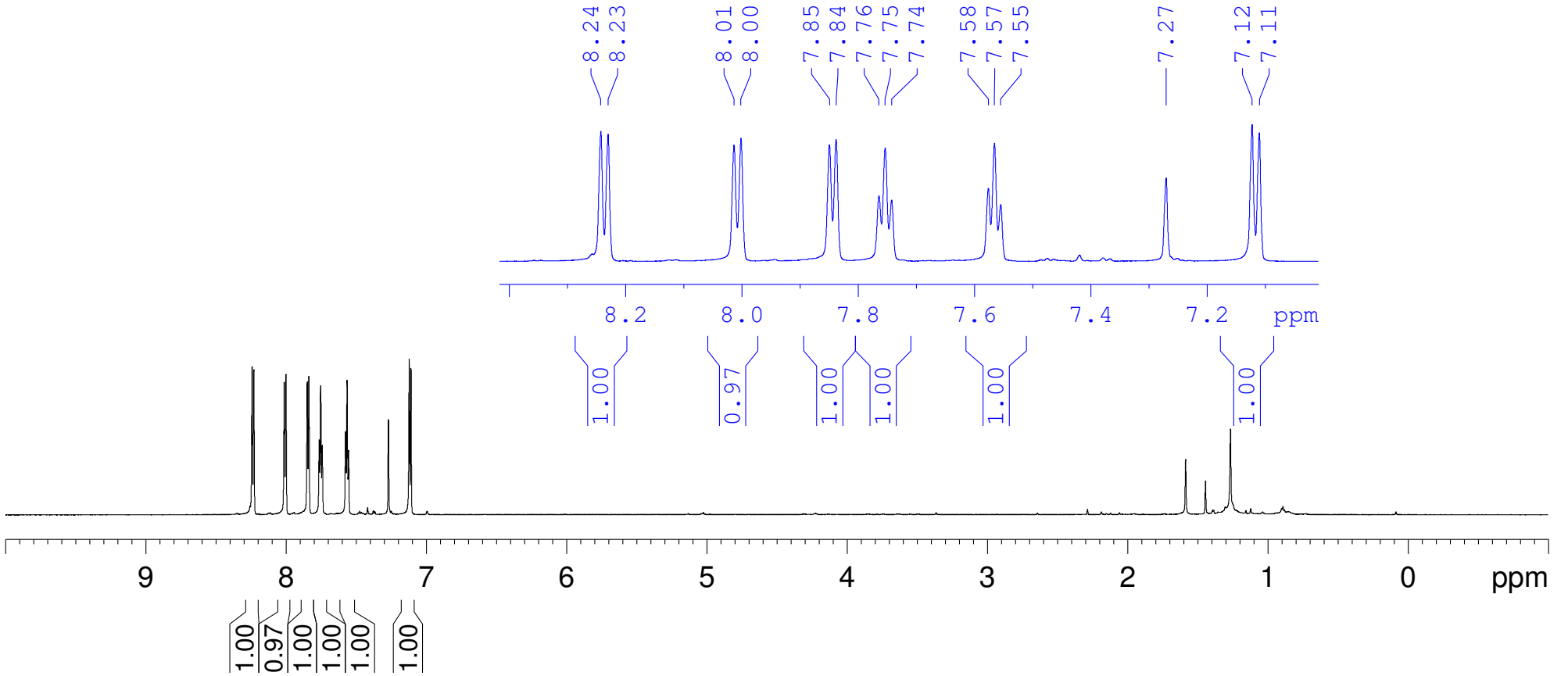
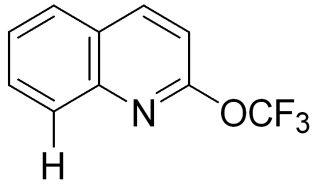


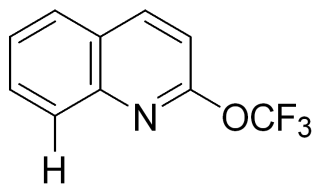


-55.60



8.24
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154.8
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77.2
77.0
76.8

