Supporting Information

Nickel-Catalyzed Selective C-5 Fluorination of 8-Aminoquinolines with NFSI

Junshuai Ding, Yingchao Zhang, Jizhen Li *

Department of Organic Chemistry, College of Chemistry, Jilin University, 2519 Jiefang Road, Changchun, 130023, China

Corresponding author E-mail: ljz@jlu.edu.cn

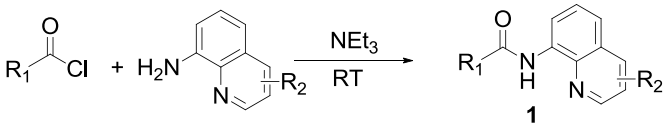
Contents

1. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. All the solvents were dried and newly distilled. NMR spectra were obtained on a Bruker AMX 400 system using chloroform-d as deuterated solvents. The ^{1}H-NMR spectra were recorded at 400 MHz in $CDCl_3$, the ^{13}C-NMR spectra were recorded at 100 MHz in $CDCl_3$, and the ^{19}F-NMR spectra were recorded at 376 MHz in $CDCl_3$ with TMS as internal standard. All shifts were given in ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Single crystal X-ray diffraction data were collected using a Bruker-AXS SMART APEX2 CCD diffracometer (Mo Kα, $\lambda = 0.71073$ Å). Column chromatography was performed on silica gel 100-200 mesh or 200-300 mesh. Ethyl acetate and petroleum ether were used for column chromatography.

2. Preparation of substrated amides 1a-1q.[1]

Preparation of amides **1a-1q**: A solution of 8-aminoquinoline (1.44 g, 10.0 mmol) and NEt_3 (1.01g, 11.0 mmol) in dichloromethane (10 mL) was added dropwise to a stirring solution of an acid chloride (11.0 mmol) in dichloromethane (40 mL). The resulting mixture was stirred at 25℃ for 3 hours. Then, the mixture was quenched with saturated aq. $NaHCO_3$ (50mL), and was extracted with dichloromethane for three times (3 x 50 mL). The organic layer was dried over Na_2SO_4. After filtration and evaporation, the amides were purified by column chromatography on silica gel.



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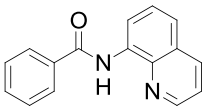

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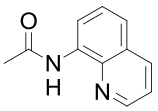

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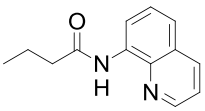

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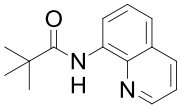

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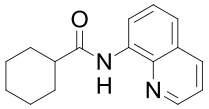

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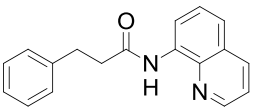

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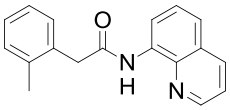

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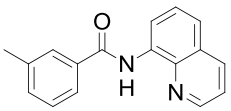

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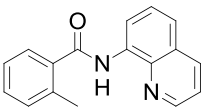

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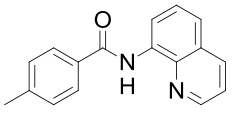

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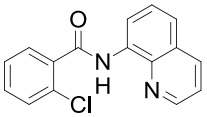

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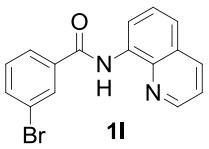

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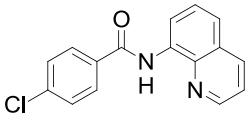

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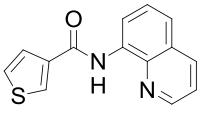

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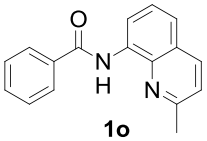

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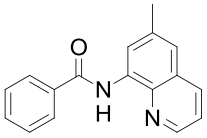

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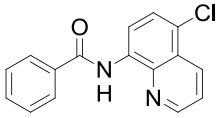
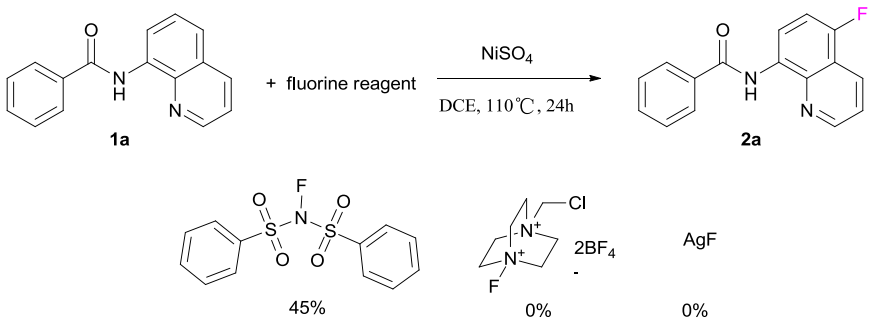


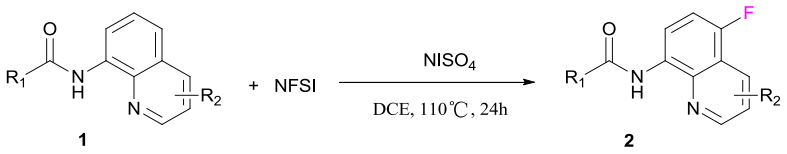
1q

3. Screening of fluorine reagents



N-(8-quinolinyl) benzamide **1a** (0.2 mmol, 1.0 equiv), fluorine reagent (0.4 mmol, 2.0 equiv), $NiSO_4$ (0.04 mmol, 0.2 equiv) were mixed in DCE (1.0 mL) and stirred for 24 h in a sealed tube at 110 ℃. The resulting organic solution was concentrated under reduced pressure and further purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate gradient), yielding the target product **2a**.

4. General procedure for preparation of regioselective C-5 fluorinated N-(8-quinolinyl) amides



N-(8-quinolinyl) amide **1** (0.2 mmol, 1.0 equiv), NFSI (0.4 mmol, 2.0 equiv), $NiSO_4$ (0.04 mmol, 0.2 equiv) were mixed in DCE (1.0 mL) and stirred for 24 h in a sealed tube at 110 ℃. The resulting organic solution was concentrated under reduced pressure and further purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate gradient), yielding the target product **2** and yields in parentheses were determined by ^{19}F NMR spectroscopy with with fluorobenzene as an internal standard.

5. The single crystal X-ray diffraction study of N-(5-fluoro-quinolin-8-yl) benzamide 2a.

Single-crystal X-ray structure of **2a**

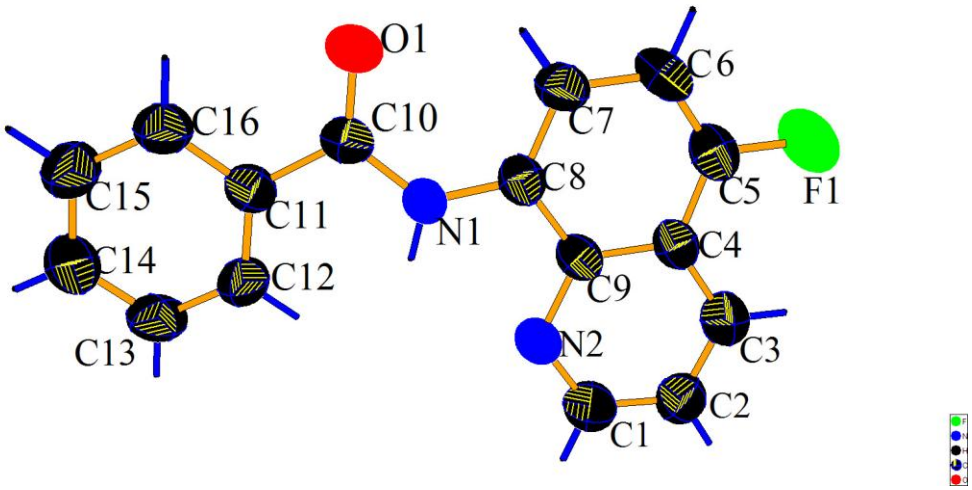


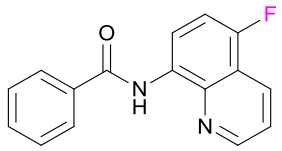
Table 1. Crystal data and structure refinement for **2a**.

Identification code	**2a**
Empirical formula	C_{16} H_{11} F N_2 O
Formula weight	266.27
Temperature	273(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 21.229(10) A alpha = 90 deg.
	b = 3.9190(19) A beta = 105.861(11) deg.
	c = 15.628(8) A gamma = 90 deg.
Volume	1250.7(10) A^3
Z, Calculated density	4, 1.414 Mg/m^3
Absorption coefficient	0.100 mm^-1

F(000)	552
Crystal size	0.220 x 0.200 x 0.180 mm
Theta range for data collection	0.997 to 25.654 deg.
Limiting indices	-25<=h<=25, -4<=k<=4, -19<=l<=14
Reflections collected / unique	7250 / 2342 [R(int) = 0.0644]
Completeness to theta = 25.242	99.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2342 / 0 / 181
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0737, wR2 = 0.2007
R indices (all data)	R1 = 0.1172, wR2 = 0.2307
Extinction coefficient	n/a
Largest diff. peak and hole	0.212 and -0.184 e.A^-3

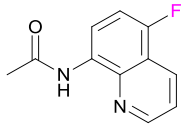
6. Characterization data of the products

2a:



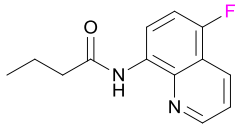
White solid, isolated yield: 45%; ^{19}F NMR yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.57 (s, 1H), 8.96-8.90 (m, 2H), 8.50 (dd, *J* = 8.6 Hz, 5.5 Hz, 1H), 8.10 (d, *J* = 7.0 Hz, 2H), 7.67-7.55 (m, 4H), 7.32 (t, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.34 (s), 153.01 (d, *J* = 251.2 Hz), 149.14 (s), 138.97 (d, J = 3.0 Hz), 134.99 (s), 131.91 (s), 131.12 (d, *J* = 4.0 Hz), 129.86 (d, *J* = 3.6 Hz), 128.83 (s), 127.24 (s), 121.77 (d, *J* = 2.6 Hz), 118.82 (d, *J* = 18.3 Hz), 116.04 (d, *J* = 7.7 Hz), 110.52 (d, *J* = 19.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.00 (s).

2b:



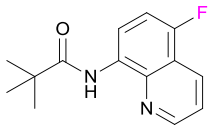
White solid, isolated yield: 40%; ^{19}F NMR yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.62 (s, 1H), 8.88 (d, *J* = 4.1 Hz, 1H), 8.74 (dd, *J* = 8.6, 5.5 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.25 (t, *J* = 9.2 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.61 (s), 152.80 (d, *J* = 250.8 Hz), 148.94 (s), 138.44 (d, *J* = 2.1 Hz), 131.04 (d, *J* = 4.1 Hz), 129.82 (d, *J* = 3.7 Hz), 121.64 (d, *J* = 2.5 Hz), 118.71 (d, *J* = 18.1 Hz), 115.94 (d, *J* = 7.6 Hz), 110.42 (d, *J* = 19.6 Hz), 25.03 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.40 (s).

2c:



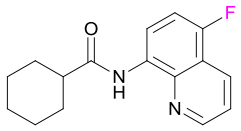
White solid, isolated yield: 44%; ^{19}F NMR yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.65 (s, 1H), 8.88 (d, *J* = 4.2 Hz, 1H), 8.77 (dd, *J* = 8.4, 5.6 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.25 (t, *J* = 9.2 Hz, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.94-1.82 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.58 (s), 152.74 (d, *J* = 250.6 Hz), 148.93 (s), 138.54 (d, *J* = 2.9 Hz), 131.10 (d, *J* = 3.9 Hz), 129.78 (d, *J* = 3.6 Hz), 121.60 (d, *J* = 2.6 Hz), 118.72 (d, *J* = 18.0 Hz), 115.86 (d, *J* = 7.6 Hz), 110.43 (d, *J* = 19.6 Hz), 40.09 (s), 19.13 (s), 13.82 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.55 (s).

2d:



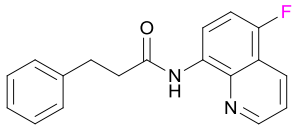
White solid, isolated yield: 46%; ^{19}F NMR yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.09 (s, 1H), 8.89 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.77 (dd, *J* = 8.6, 5.5 Hz, 1H), 8.46 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.55 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.23 (t, *J* = 9.2 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.10 (s), 152.71 (d, *J* = 250.5 Hz), 149.04 (s), 138.94 (d, *J* = 3.0 Hz), 131.22 (d, *J* = 4.1 Hz), 129.76 (d, *J* = 3.6 Hz), 121.59 (d, *J* = 2.5 Hz), 118.72 (d, *J* = 18.1 Hz), 115.65 (d, *J* = 7.6 Hz), 110.42 (d, *J* = 19.4 Hz), 40.27 (s), 27.73 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.81 (s).

2e:



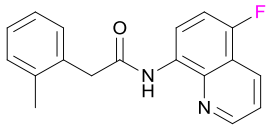
White solid, isolated yield: 46%; ^{19}F NMR yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 8.90 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.79 (dd, *J* = 8.7, 5.5 Hz, 1H), 8.50 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.58 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.25 (t, *J* = 9.2 Hz, 1H), 2.55-2.46 (m, 1H), 2.21-2.03 (m, 2H), 1.99-1.83 (m, 2H), 1.81-1.59 (m, 3H), 1.49-1.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.71 (s), 152.68 (d, *J* = 250.7 Hz), 148.89 (s), 138.61 (d, *J* = 2.6 Hz), 131.16 (d, *J* = 4.0 Hz), 129.81 (d, *J* = 3.7 Hz), 121.58 (d, *J* = 2.5 Hz), 118.71 (d, *J* = 18.0 Hz), 115.90 (d, *J* = 7.6 Hz), 110.45 (d, *J* = 19.5 Hz), 46.82 (s), 29.75 (s), 25.77 (s), 25.75 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.73 (s).

2f:



White solid, isolated yield: 41%; ^{19}F NMR yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.61 (s, 1H), 8.85 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.76 (dd, *J* = 8.6, 5.4 Hz, 1H), 8.45 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.54 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.36-7.30 (m, 4H), 7.27-7.19 (m, 2H), 3.22-3.12 (t, *J* = 7.8 Hz, 2H), 2.95-2.85 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 170.57 (s), 152.82 (d, *J* = 250.9 Hz), 148.92 (s), 140.71 (s), 138.51 (d, *J* = 3.0 Hz), 130.96 (d, *J* = 4.1 Hz), 129.78 (d, *J* = 3.7 Hz), 128.57 (s), 128.39 (s), 126.27 (s), 121.63 (d, *J* = 2.5 Hz), 118.71 (d, *J* = 18.1 Hz), 115.96 (d, *J* = 7.7 Hz), 110.43 (d, *J* = 19.6 Hz), 39.66 (s), 31.48 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.34 (s).

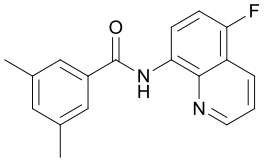
2g:



White solid, isolated yield: 39%; ^{19}F NMR yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.67 (s, 1H), 8.76-8.68 (m, 2H), 8.40 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.48 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.41-.29 (m, 5H), 7.20

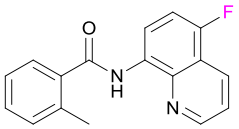
(t, *J* = 9.2 Hz, 1H), 3.92 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.21 (s), 152.90 (d, *J* = 250.9 Hz), 149.00 (s), 138.71 (d, *J* = 2.7 Hz), 137.25 (s), 133.09 (s), 130.91 (d, *J* = 4.0 Hz), 130.81 (s), 130.59 (s), 129.59 (d, *J* = 3.6 Hz), 127.83 (s), 126.64 (s), 121.54 (d, *J* = 2.6 Hz), 118.62 (d, *J* = 18.2 Hz), 115.75 (d, *J* = 7.8 Hz), 110.32 (d, *J* = 19.6 Hz), 43.21 (s), 19.71 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.20 (s).

2h:



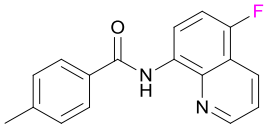
White solid, isolated yield: 43%; ^{19}F NMR yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.49 (s, 1H), 8.98 – 8.89 (m, 2H), 8.49 (d, *J* = 8.4 Hz, 1H), 7.68 (s, 2H), 7.58 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.30 (t, *J* = 9.2 Hz, 1H), 7.24 (s, 1H), 2.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.80 (s), 152.94 (d, *J* = 251.0 Hz), 149.11 (s), 138.99 (d, *J* = 3.1 Hz), 138.51 (s), 135.05 (s), 133.53 (s), 131.25 (d, *J* = 4.2 Hz), 129.82 (d, *J* = 3.7 Hz), 124.98 (s), 121.70 (d, *J* = 2.6 Hz), 118.81 (d, *J* = 18.2 Hz), 116.04 (d, *J* = 7.7 Hz), 110.52 (d, *J* = 19.6 Hz), 21.39 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.26 (s).

2i:



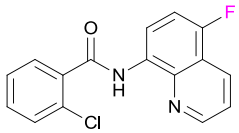
White solid, isolated yield: 44%; ^{19}F NMR yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.06 (s, 1H), 8.93 (dd, *J* = 8.5, 5.5 Hz, 1H), 8.86 (d, *J* = 4.1 Hz, 1H), 8.50 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.57 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.48-7.29 (m, 4H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.06 (s), 153.05 (d, *J* = 251.3 Hz), 149.12 (s), 138.82 (d, *J* = 3.1 Hz), 136.71 (s), 136.46 (s), 131.42 (s), 131.26 (d, *J* = 4.0 Hz), 130.41 (s), 129.81 (d, *J* = 3.6 Hz), 127.23 (s), 126.05 (s), 121.75 (d, *J* = 2.5 Hz), 118.80 (d, *J* = 18.1 Hz), 116.01 (d, *J* = 7.7 Hz), 110.46 (d, *J* = 19.6 Hz), 20.24 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -128.93 (s).

2j:



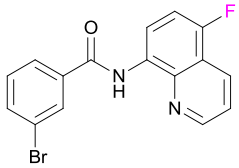
White solid, isolated yield: 45%; ^{19}F NMR yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.54 (s, 1H), 8.99-8.88 (m, 2H), 8.49 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.58 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 9.2 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.32 (s), 152.92 (d, *J* = 251.1 Hz), 149.08 (s), 142.40 (s), 138.97 (d, *J* = 2.8 Hz), 132.19 (s), 131.24 (d, *J* = 4.0 Hz), 129.83 (d, *J* = 3.8 Hz), 129.48 (s), 127.25 (s), 121.71 (d, *J* = 2.4 Hz), 118.82 (d, *J* = 18.1 Hz), 115.94 (d, *J* = 7.6 Hz), 110.53 (d, *J* = 19.6 Hz), 21.56 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.27 (s).

2k:



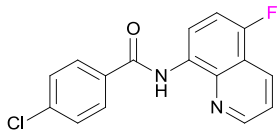
White solid, isolated yield: 43%; ^{19}F NMR yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.35 (s, 1H), 8.94 (dd, *J* = 8.6, 5.4 Hz, 1H), 8.88 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.49 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.85 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.60-7.51 (m, 2H), 7.51-7.41 (m, 2H), 7.30 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.72 (s), 153.26 (d, *J* = 251.7 Hz), 149.23 (s), 138.92 (d, *J* = 3.2 Hz), 135.63 (s), 131.60 (s), 131.15 (s), 130.97 (d, *J* = 4.2 Hz), 130.55 (s), 130.14 (s), 129.79 (d, *J* = 3.7 Hz), 127.19 (s), 121.79 (d, *J* = 2.7 Hz), 118.81 (d, *J* = 18.1 Hz), 116.47 (d, *J* = 7.8 Hz), 110.46 (d, *J* = 19.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -128.40 (s)

2l:



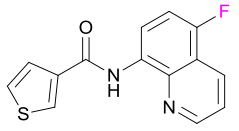
White solid, isolated yield: 41%; ^{19}F NMR yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.51 (s, 1H), 8.95 (d, *J* = 4.2 Hz, 1H), 8.89 (dd, *J* = 8.6, 5.4 Hz, 1H), 8.51 (d, *J* = 8.5 Hz, 1H), 8.23 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.60 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.49-7.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.76 (s), 153.21 (d, *J* = 251.8 Hz), 149.26 (s), 138.95 (s), 136.99 (s), 134.85 (s), 130.78 (d, *J* = 4.0 Hz), 130.57 (s), 130.34 (s), 129.92 (d, *J* = 3.6 Hz), 125.66 (s), 123.08 (s), 121.85 (d, *J* = 2.5 Hz), 118.84 (d, *J* = 18.3 Hz), 116.27 (d, *J* = 7.8 Hz), 110.50 (d, *J* = 19.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -128.39 (s).

2m:



White solid, isolated yield: 33%; ^{19}F NMR yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.53 (s, 1H), 8.94 (d, *J* = 4.1 Hz, 1H), 8.89 (dd, *J* = 8.6, 5.5 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.64-7.52 (m, 3H), 7.30 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.20 (s), 153.14 (d, *J* = 251.6 Hz), 149.20 (s), 138.93 (d, *J* = 3.1 Hz), 138.19 (s), 133.38 (s), 130.88 (d, *J* = 4.0 Hz), 129.94 (d, *J* = 3.6 Hz), 129.10 (s), 128.67 (s), 121.83 (d, *J* = 2.5 Hz), 118.85 (d, *J* = 18.3 Hz), 116.15 (d, *J* = 7.7 Hz), 110.53 (d, *J* = 19.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -128.57 (s).

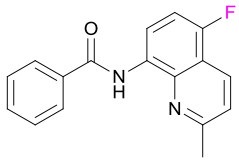
2n:



White solid, isolated yield: 32%; ^{19}F NMR yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.36 (s, 1H),

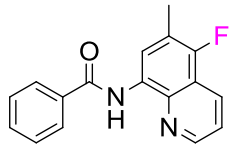
8.92 (d, *J* = 4.2 Hz, 1H), 8.86 (dd, *J* = 8.6, 5.4 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.22-8.15 (m, 1H), 7.70 (d, *J* = 5.0 Hz, 1H), 7.58 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.47 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.30 (t, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.90 (s), 152.96 (d, *J* = 251.2 Hz), 149.11 (s), 138.79 (d, *J* = 3.0 Hz), 138.19 (s), 131.02 (d, *J* = 4.0 Hz), 129.85 (d, *J* = 3.6 Hz), 128.93 (s), 126.78 (s), 126.27 (s), 121.74 (d, *J* = 2.5 Hz), 118.82 (d, *J* = 18.2 Hz), 115.99 (d, *J* = 7.6 Hz), 110.53 (d, *J* = 19.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.10 (s).

2o:



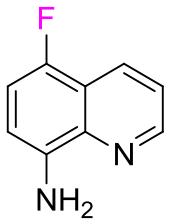
White solid, isolated yield: 42%; ^{19}F NMR yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.62 (s, 1H), 8.88 (dd, *J* = 8.6, 5.5 Hz, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 6.9 Hz, 2H), 7.65-7.56 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.21 (t, *J* = 9.2 Hz, 1H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.17 (s), 158.32 (s), 153.28 (d, *J* = 250.7 Hz), 138.52 (s), 135.19 (s), 131.79 (s), 130.46 (d, *J* = 4.2 Hz), 129.88 (d, *J* = 3.4 Hz), 128.83 (s), 127.19 (s), 122.55 (d, *J* = 2.4 Hz), 116.87 (d, *J* = 18.2 Hz), 116.03 (d, *J* = 7.8 Hz), 109.52 (d, *J* = 19.7 Hz), 25.50 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -129.19 (s).

2p:



White solid, isolated yield: 45%; ^{19}F NMR yield: 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.85 (m, 2H), 8.44 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.10 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.76-7.40 (m, 4H), 2.53 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.30 (s), 150.44 (d, *J* = 248.1 Hz), 148.09 (s), 137.79 (d, *J* = 2.8 Hz), 135.05 (s), 131.86 (s), 130.46 (d, *J* = 4.1 Hz), 129.31 (d, *J* = 4.2 Hz), 128.83 (s), 127.23 (s), 121.72 (d, *J* = 2.6 Hz), 118.82 (d, *J* = 18.2 Hz), 115.99 (d, *J* = 7.6 Hz), 110.53 (d, *J* = 19.7 Hz). 14.82 (d, *J* = 3.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -133.73 (s).

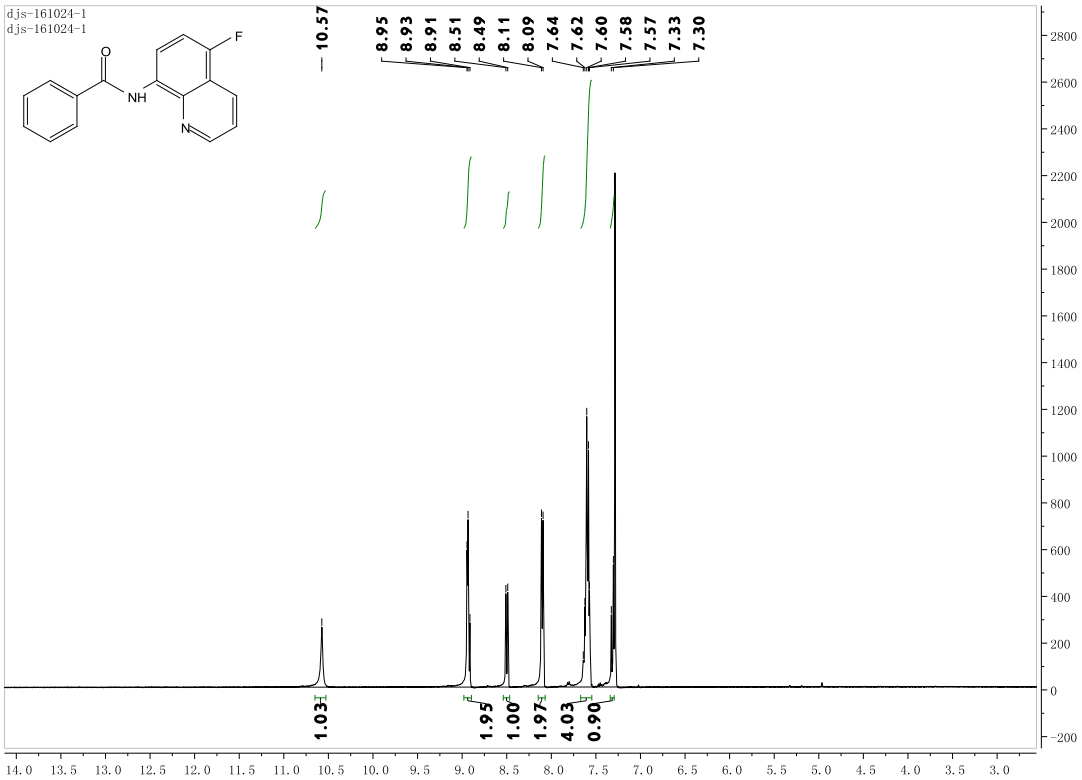
9:

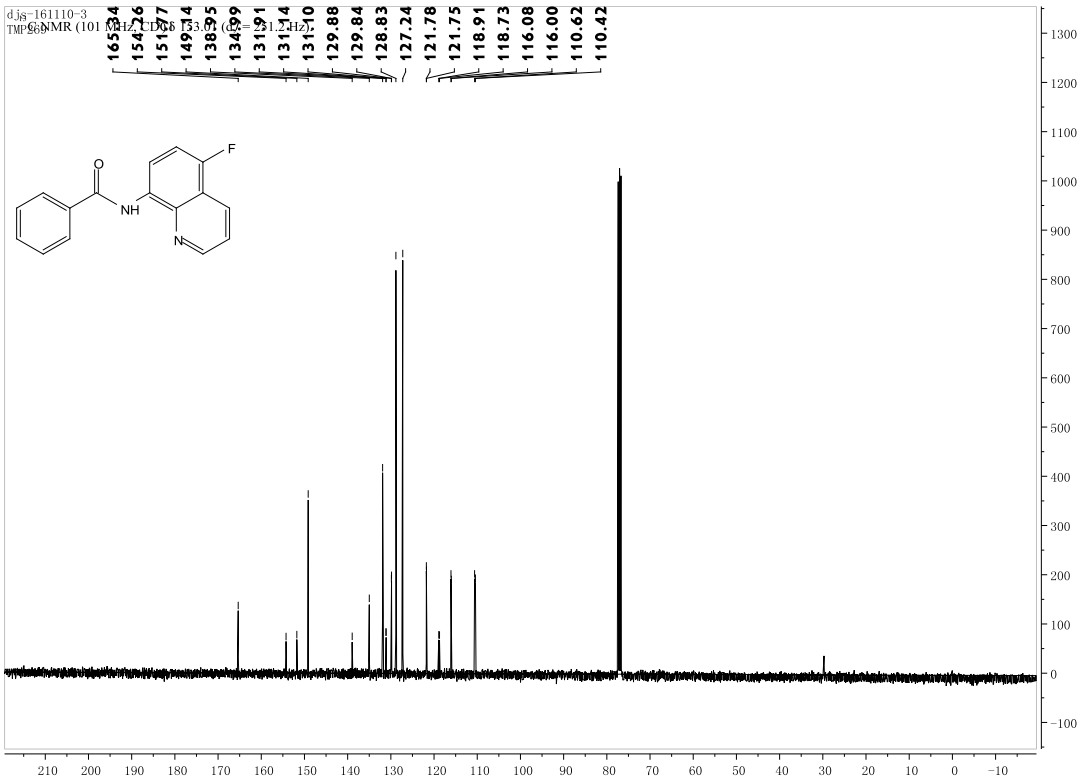


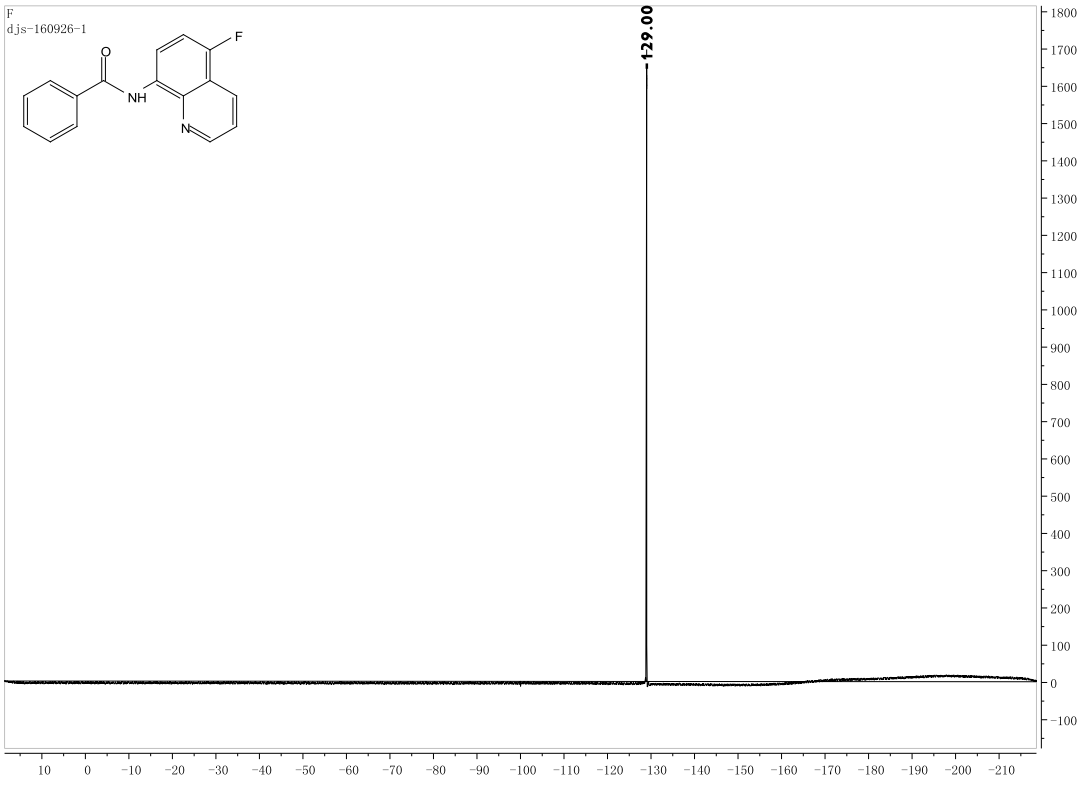
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.37 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.47 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.06 (dd, *J* = 9.9, 8.3 Hz, 1H), 6.84 (dd, *J* = 8.3, 4.9 Hz, 1H), 4.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.97 (d, *J* = 243.4 Hz), 148.17 (s), 140.25 (d, *J* = 3.2 Hz), 137.99 (d, *J* = 2.6 Hz), 129.38 (d, *J* = 3.7 Hz), 121.31 (d, *J* = 2.7 Hz), 119.27 (d, *J* = 17.7 Hz), 110.57 (d, *J* = 20.1 Hz), 108.50 (d, *J* = 7.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.37 (s).

7. Spectra for the Products

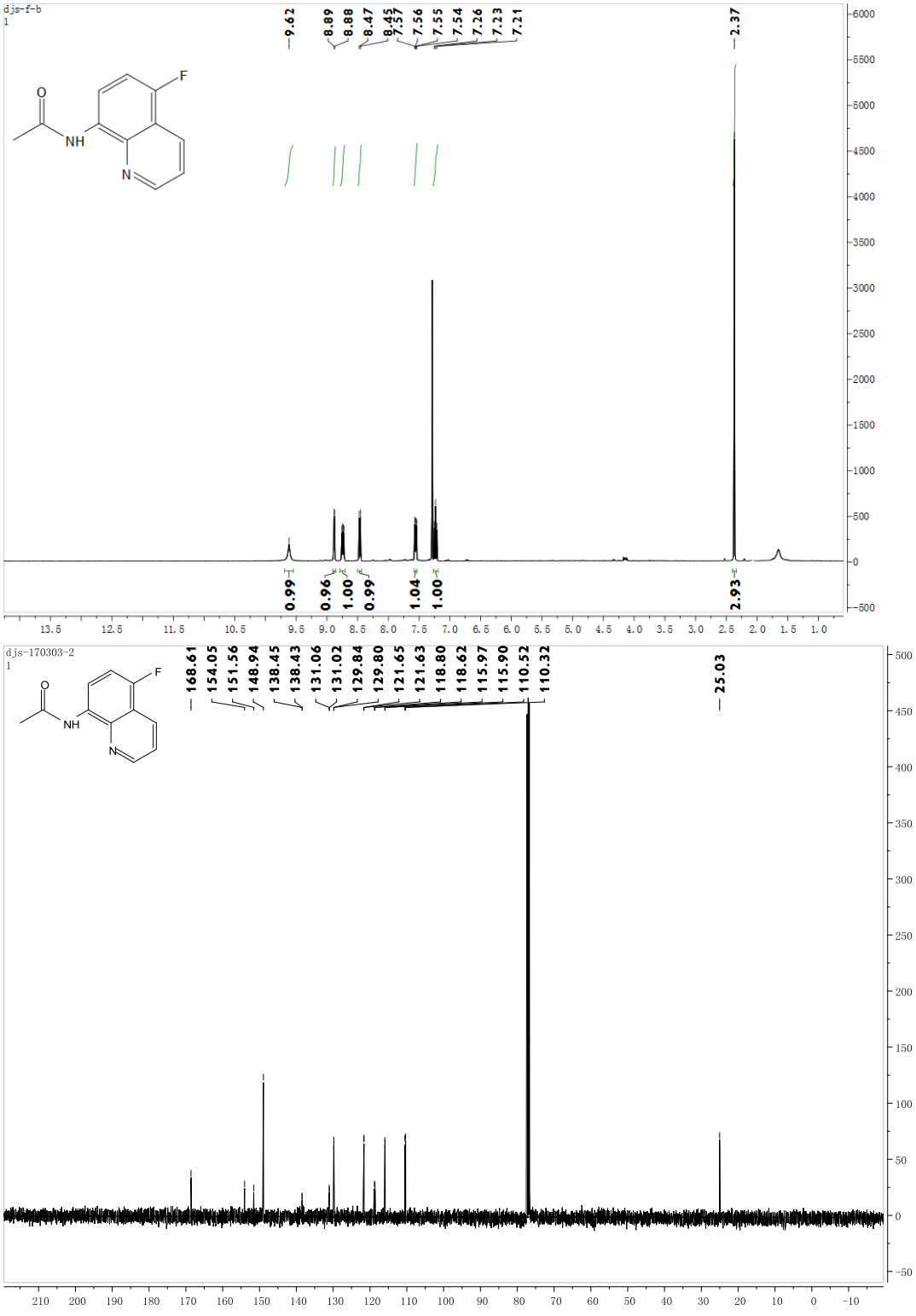
2a:






F
djs-160926-1
O
NH
F
N
-129.00
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

2b:


djs-f-b
1
9.62
8.89
8.88
8.47
8.45
7.57
7.56
7.55
7.54
7.26
7.23
7.21
2.37
0.99
0.96
1.00
0.99
1.04
1.00
2.93
djs-170303-2
1
168.61
154.05
151.56
148.94
138.45
138.43
131.06
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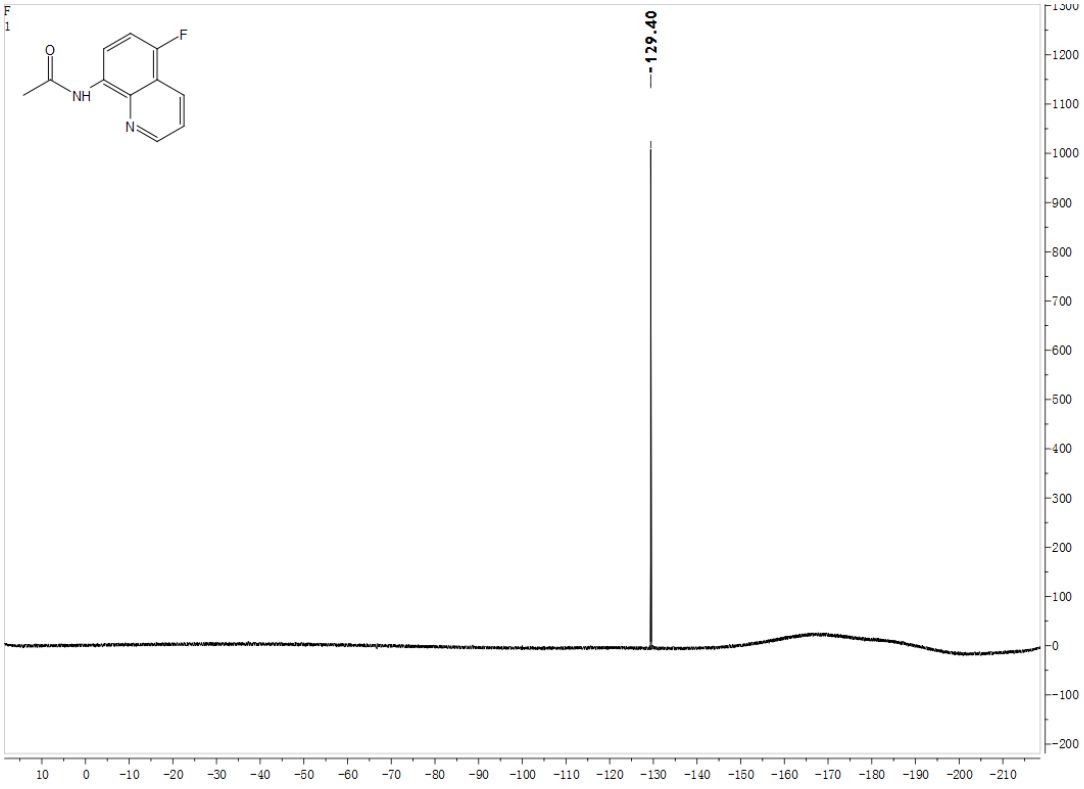
118.62
115.97
115.90
110.52
110.32
25.03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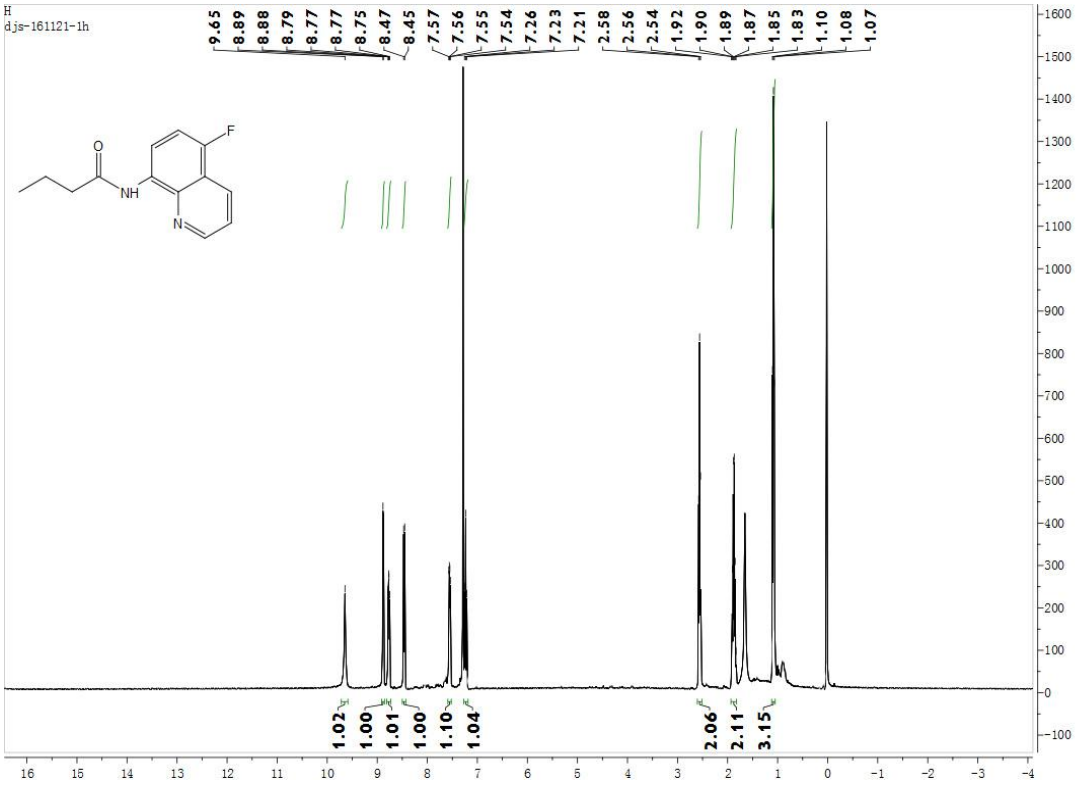
1
O
NH
N
F
-129.40

2c: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8.88
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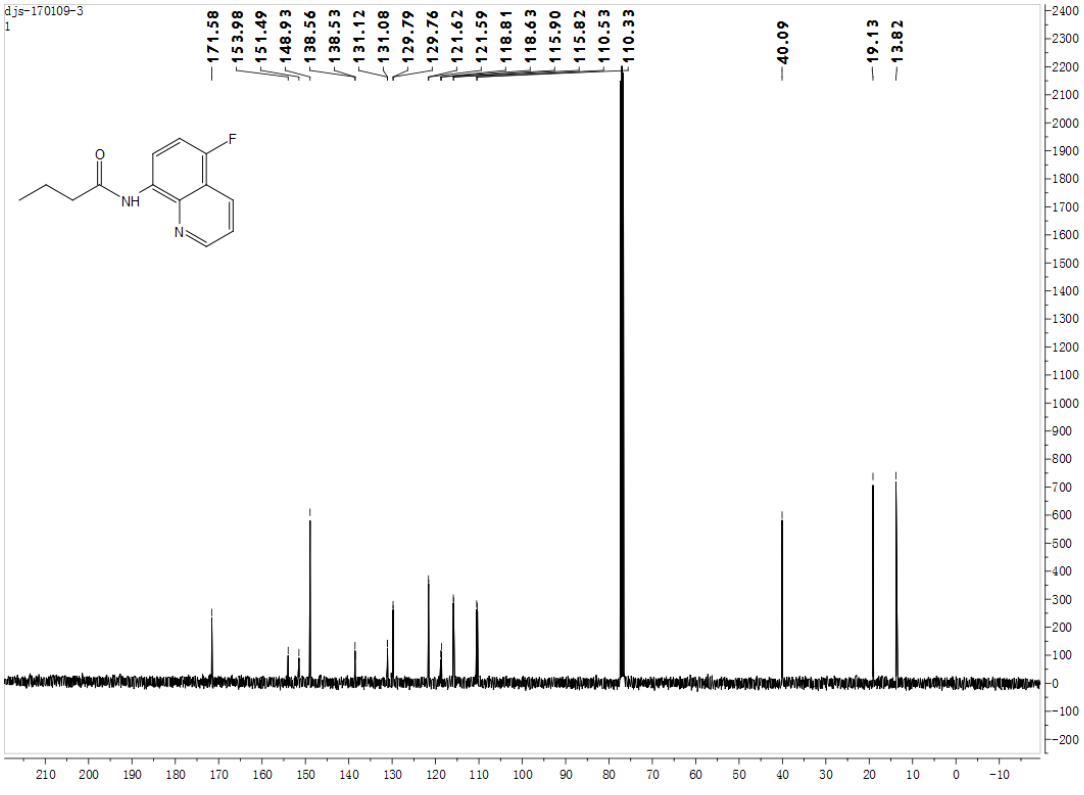
8.77
8.75
8.47
8.45
7.57
7.56
7.55
7.54
7.26
7.23
7.21
2.58
2.56
2.54
1.92
1.90
1.89
1.87
1.85
1.83
1.10
1.08
1.07
O
NH
N
F
1.02
1.00
1.01
1.00
1.10
1.04
2.06
2.11
3.15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151.49
148.93
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138.53
131.12
131.08
129.79
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121.62
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110.53
110.33
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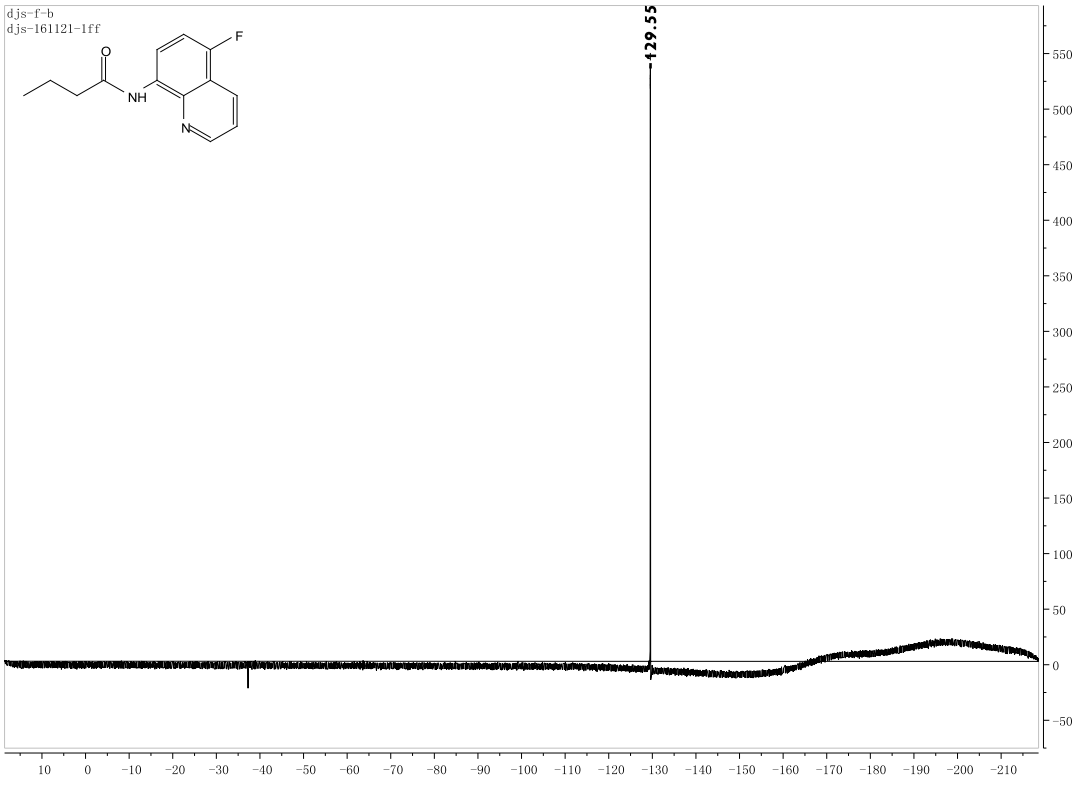
19.13
13.82
O
NH
F
N


djs-f-b
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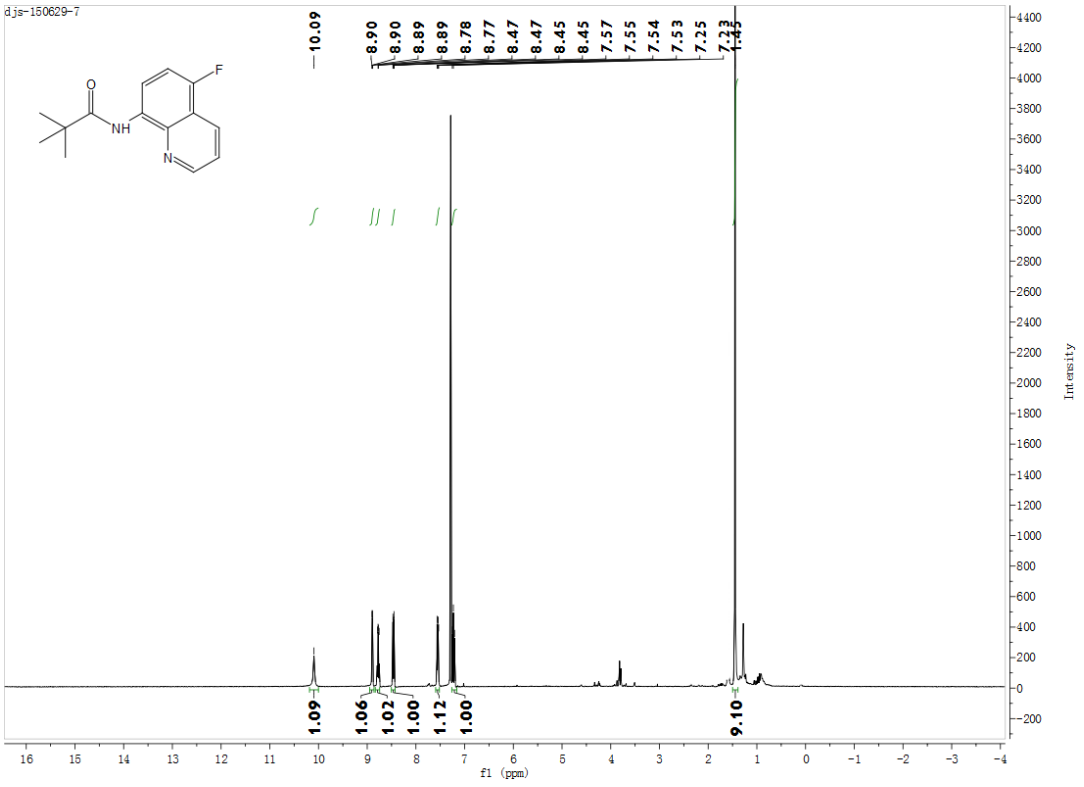
O
NH
F
N

2d: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8.90
8.89
8.89
8.78
8.77
8.47
8.47
8.45
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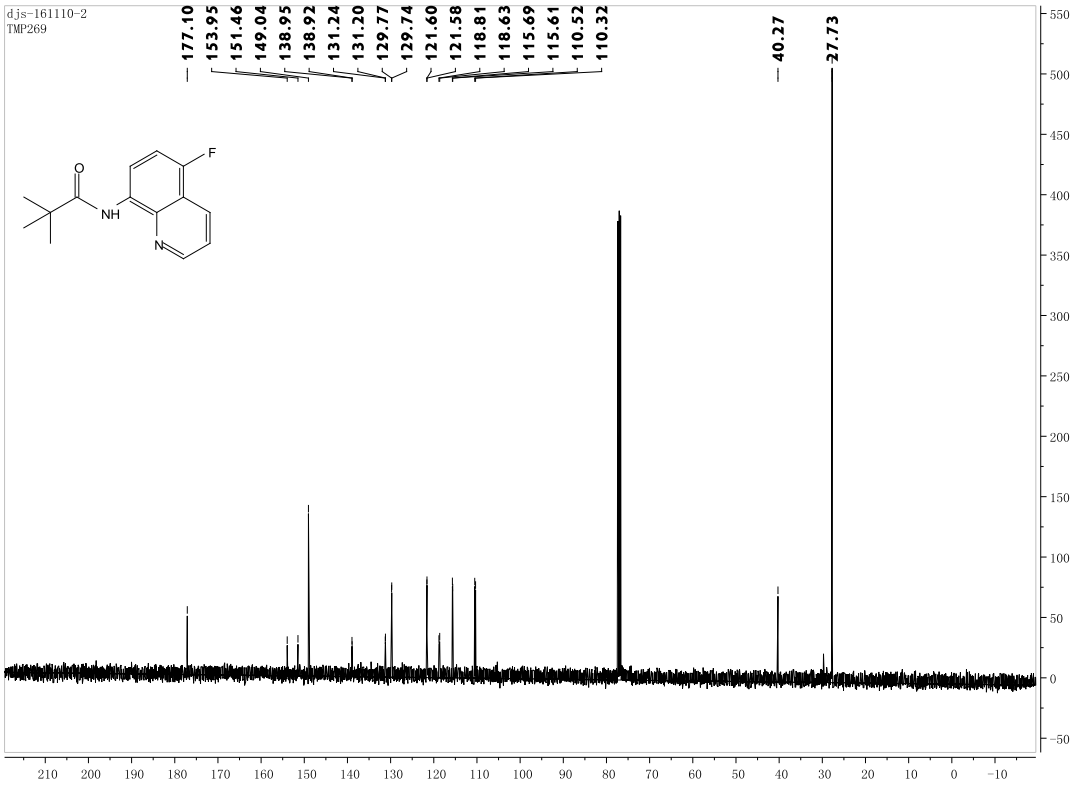
7.55
7.54
7.53
7.25
7.23
7.23
1.09
1.06
1.02
1.00
1.12
1.00
9.10
f1 (ppm)
Intensity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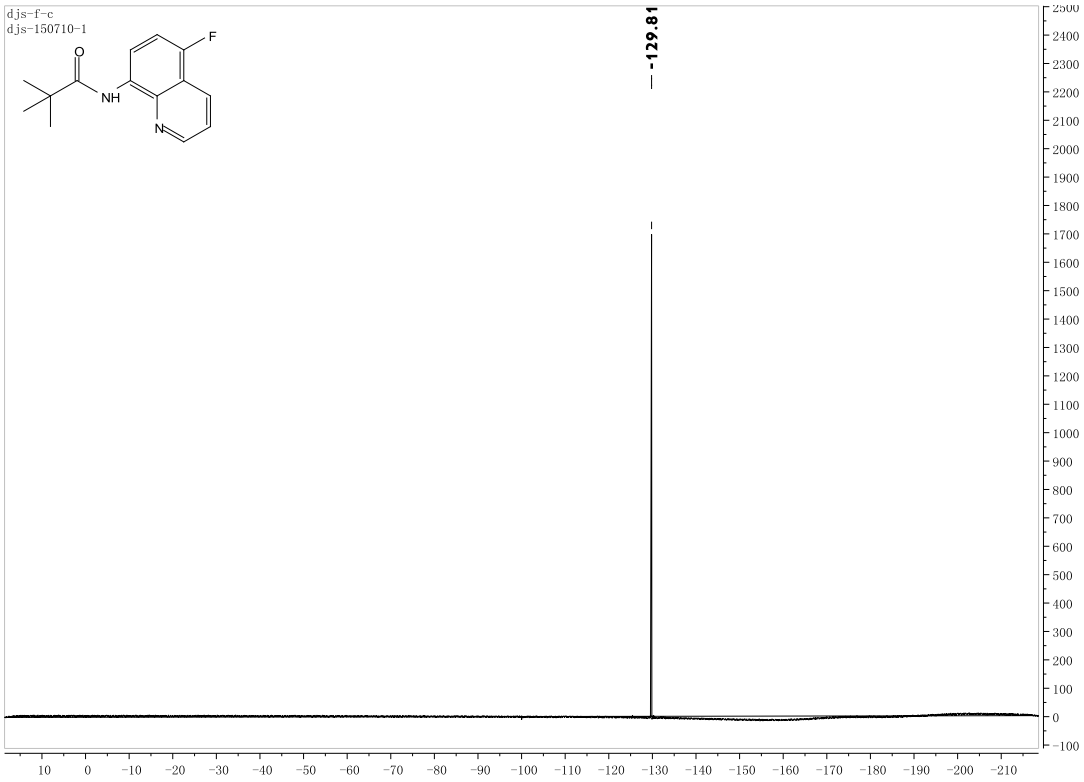
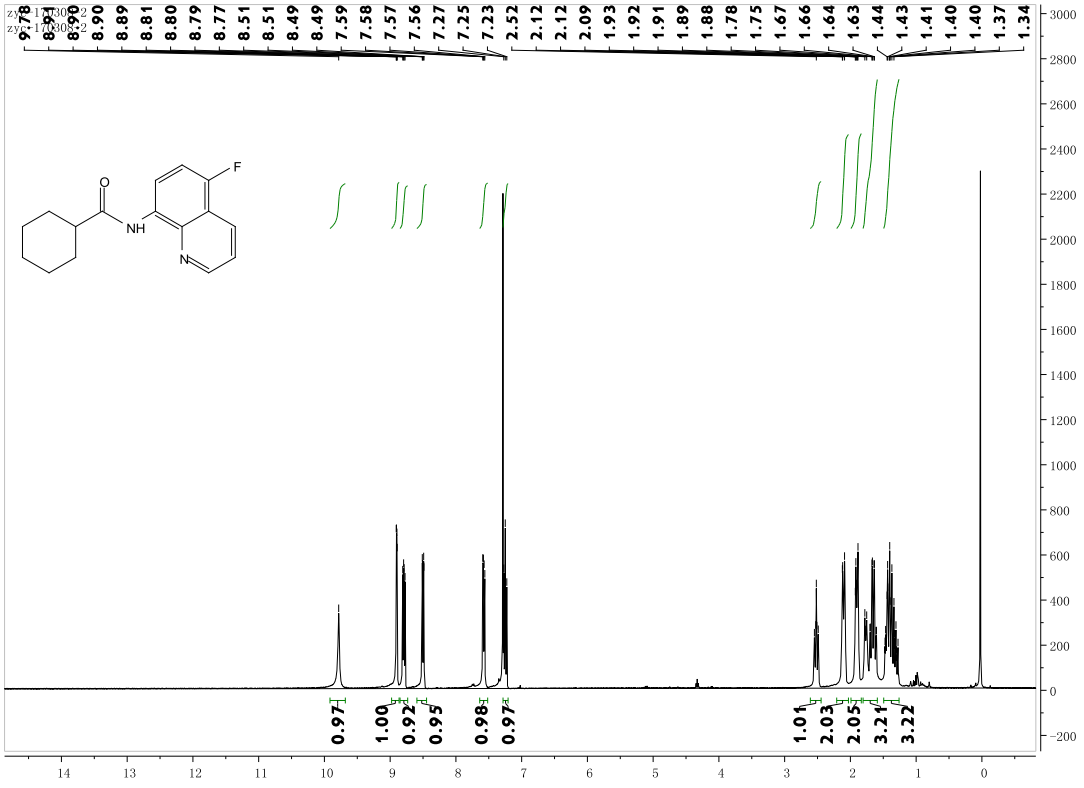
151.46
149.04
138.95
138.92
131.24
131.20
129.77
129.74
121.60
121.58
118.81
118.63
115.69
115.61
110.52
110.32
40.27
27.73


djs-f-c
djs-150710-1
-129.81

2e: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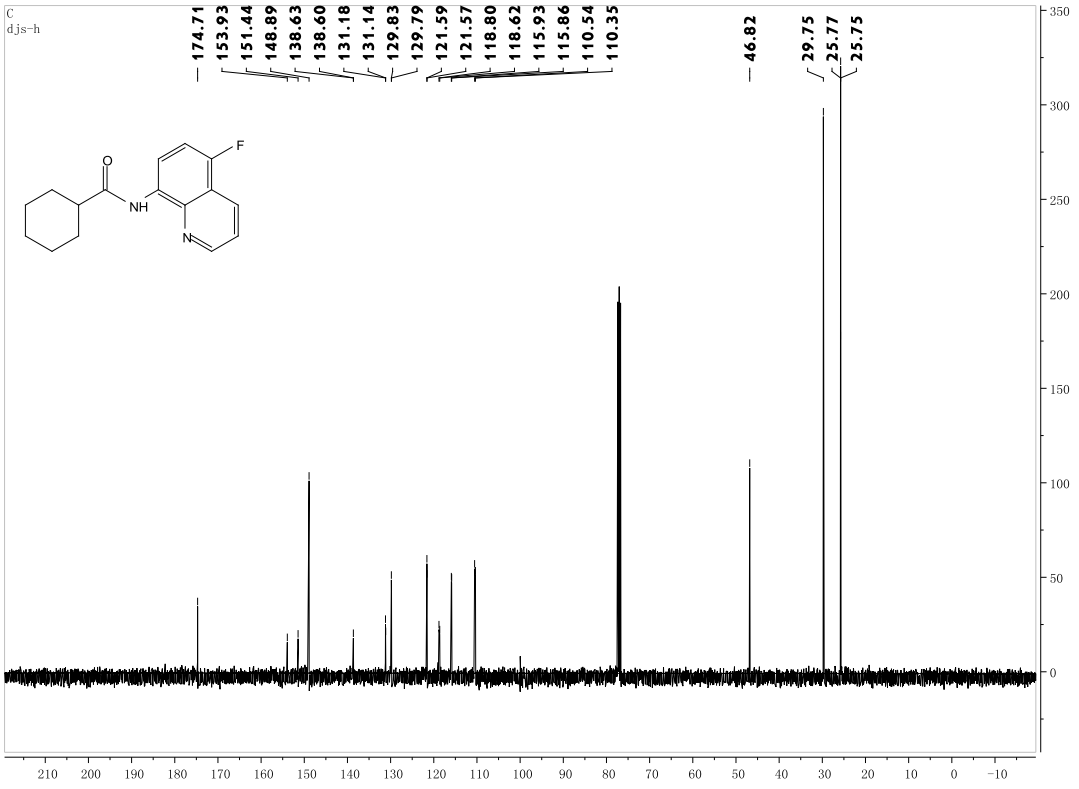
0.95
0.98
0.97
1.01
2.03
2.05
3.24
3.22


C
djs-h
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153.93
151.44
148.89
138.63
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131.14
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121.57
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25.77
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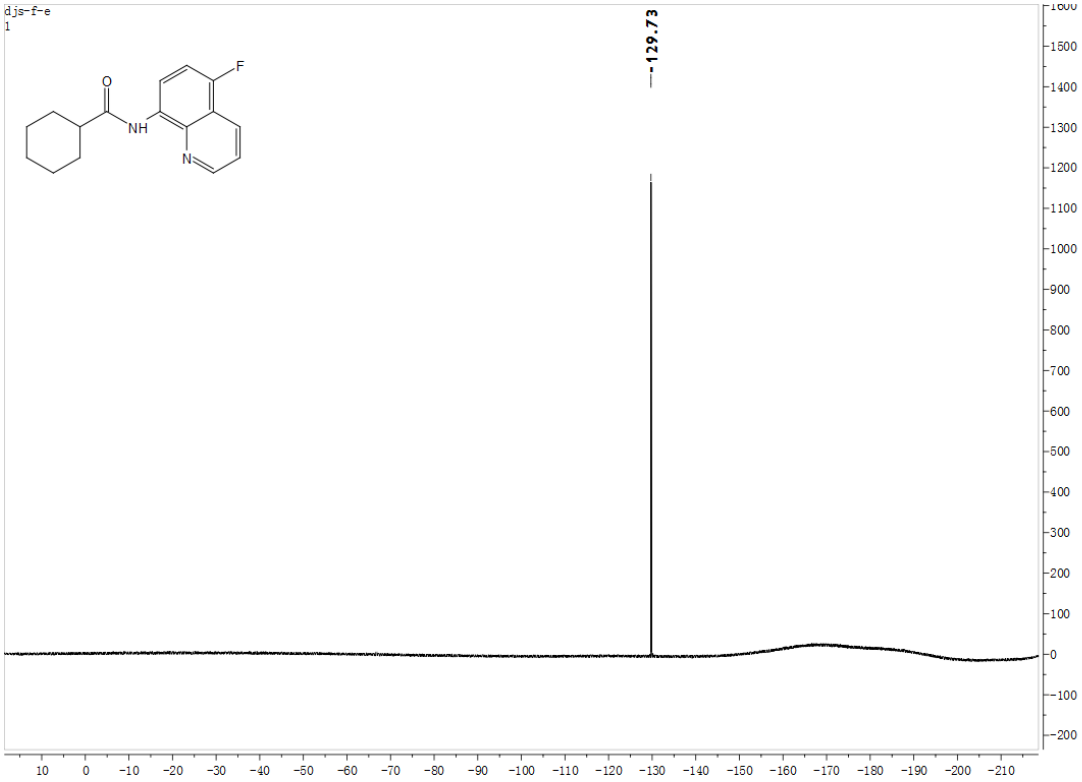
O
NH
F
N


djs-f-e
1
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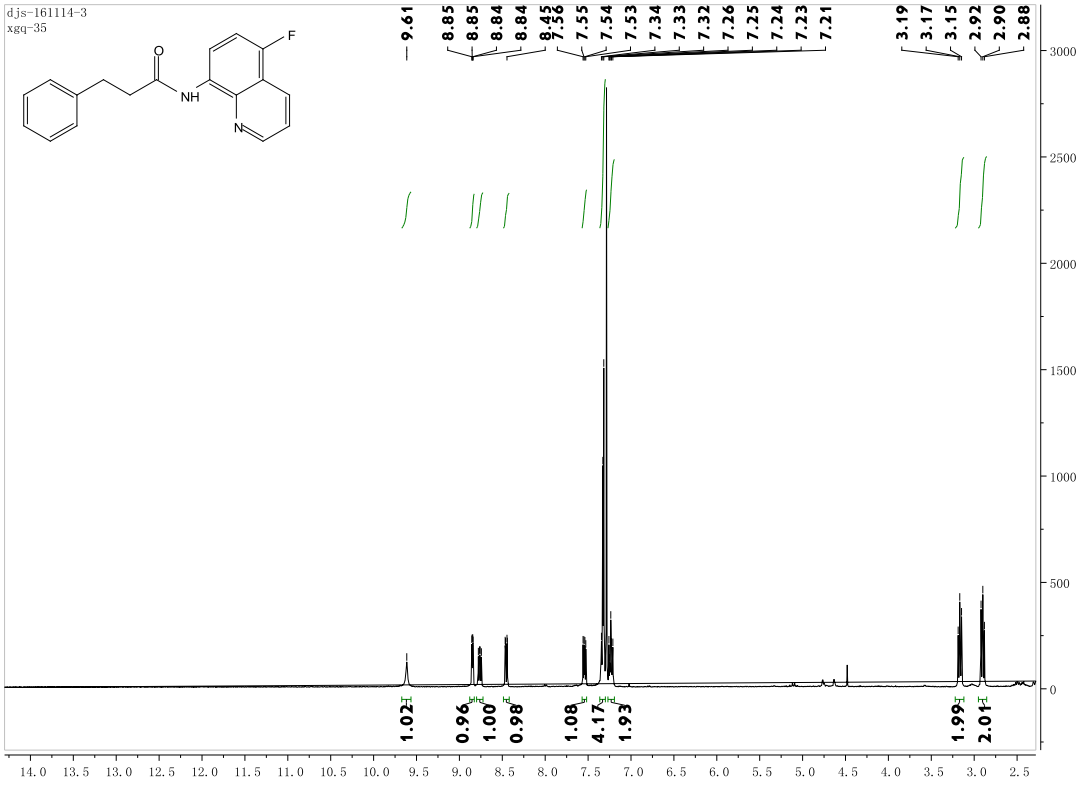
O
NH
F
N

2f: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8.84
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7.25
7.24
7.23
7.21
3.19
3.17
3.15
2.92
2.90
2.88
1.02
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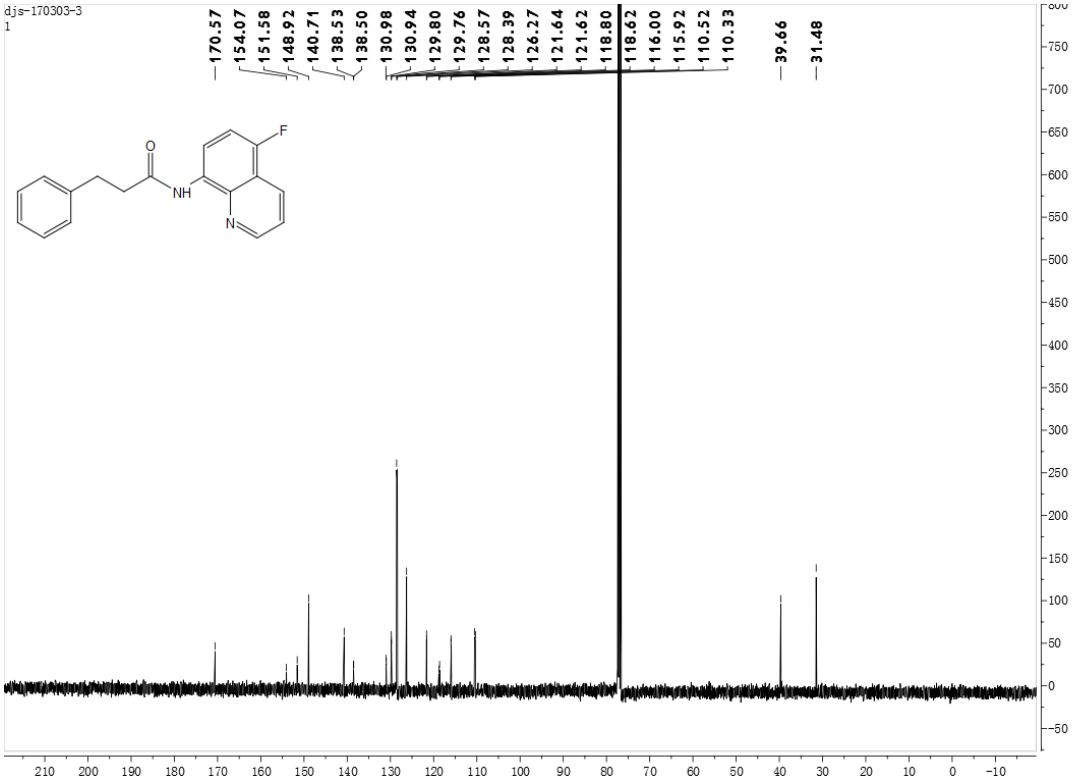
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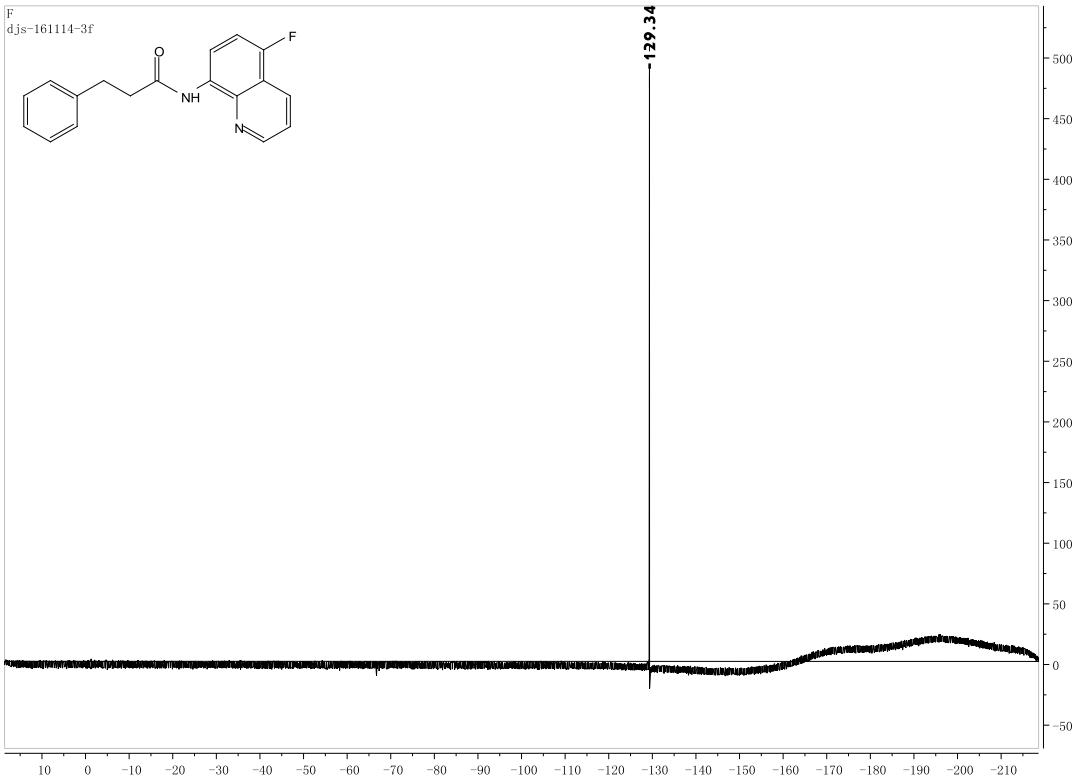
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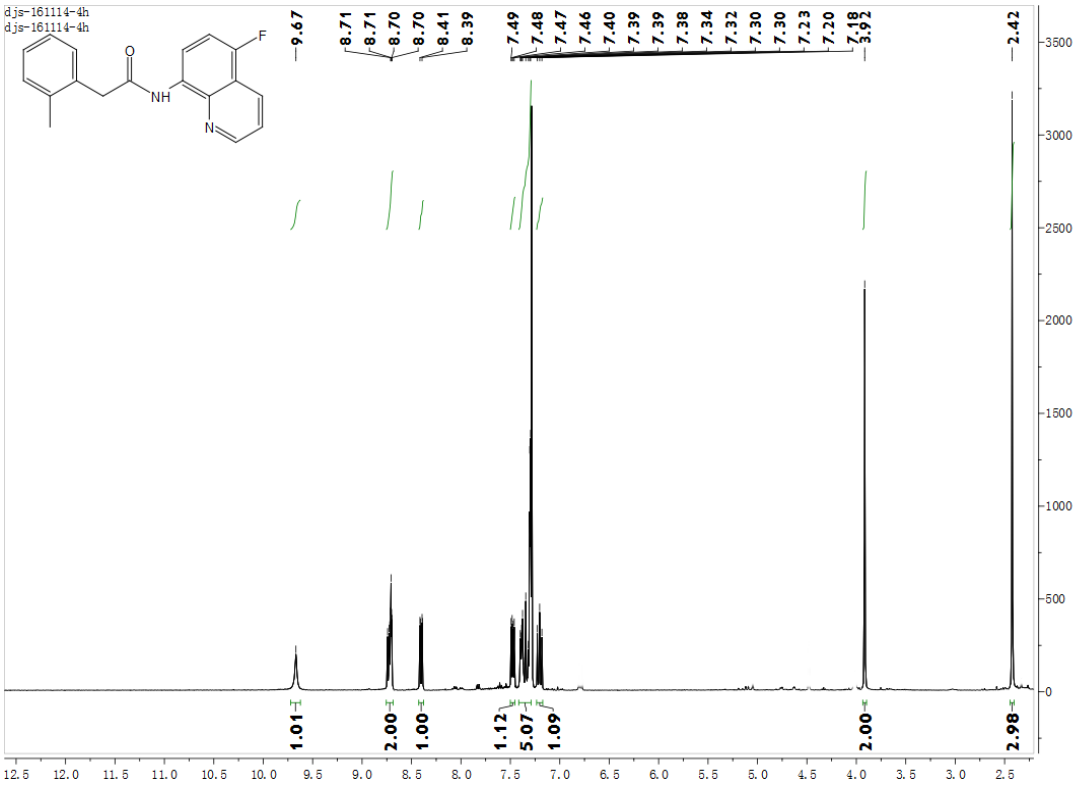
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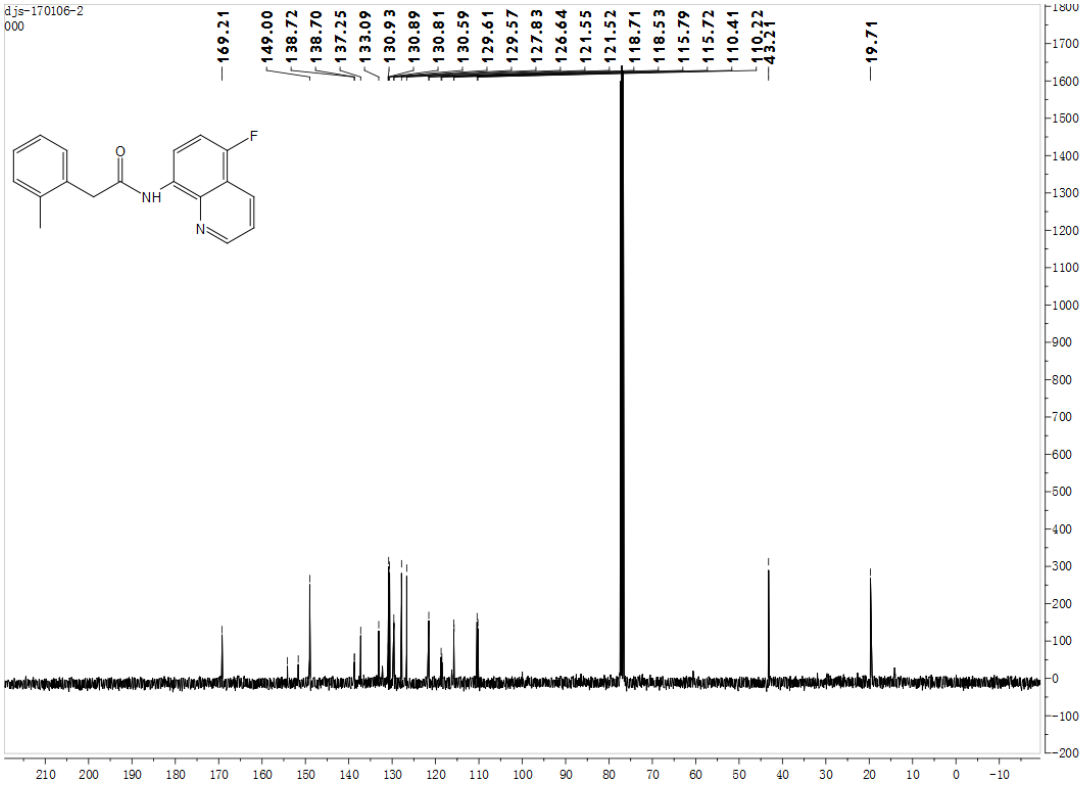
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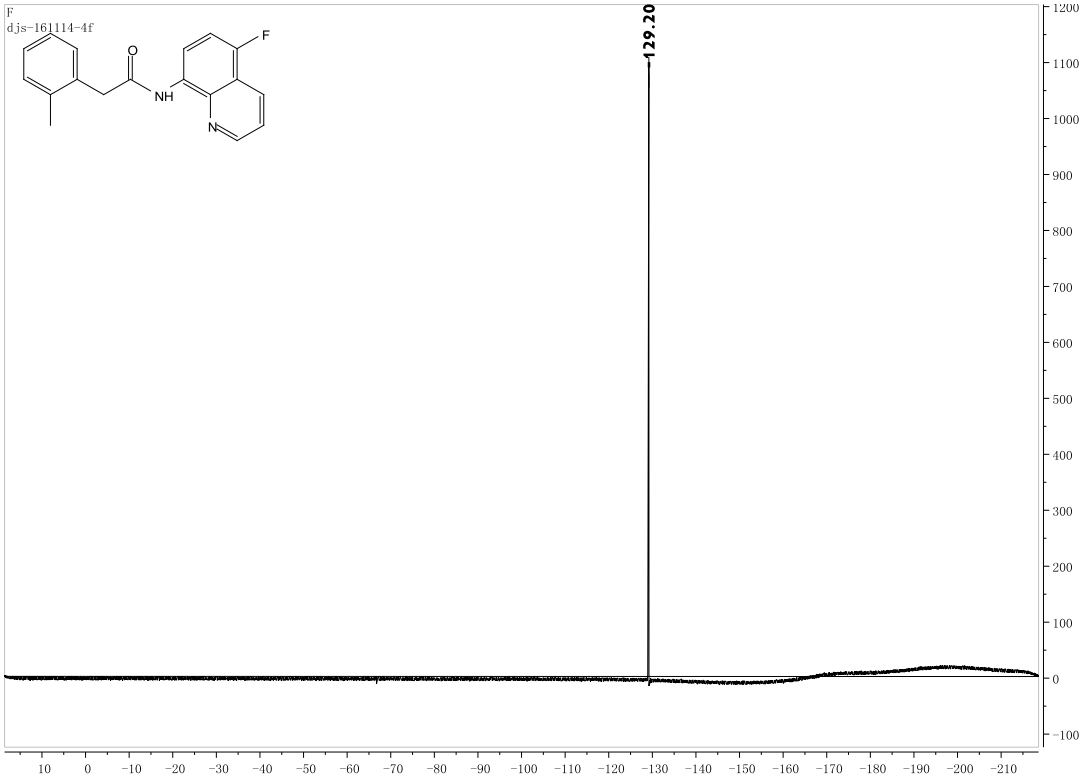
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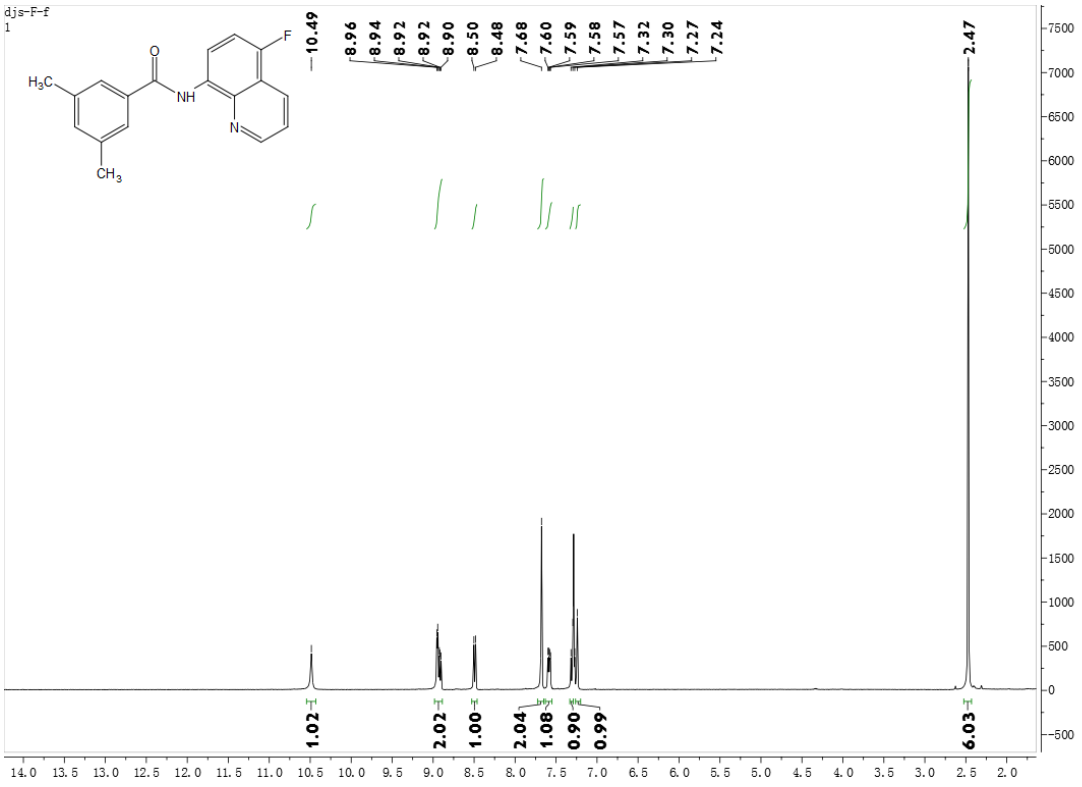
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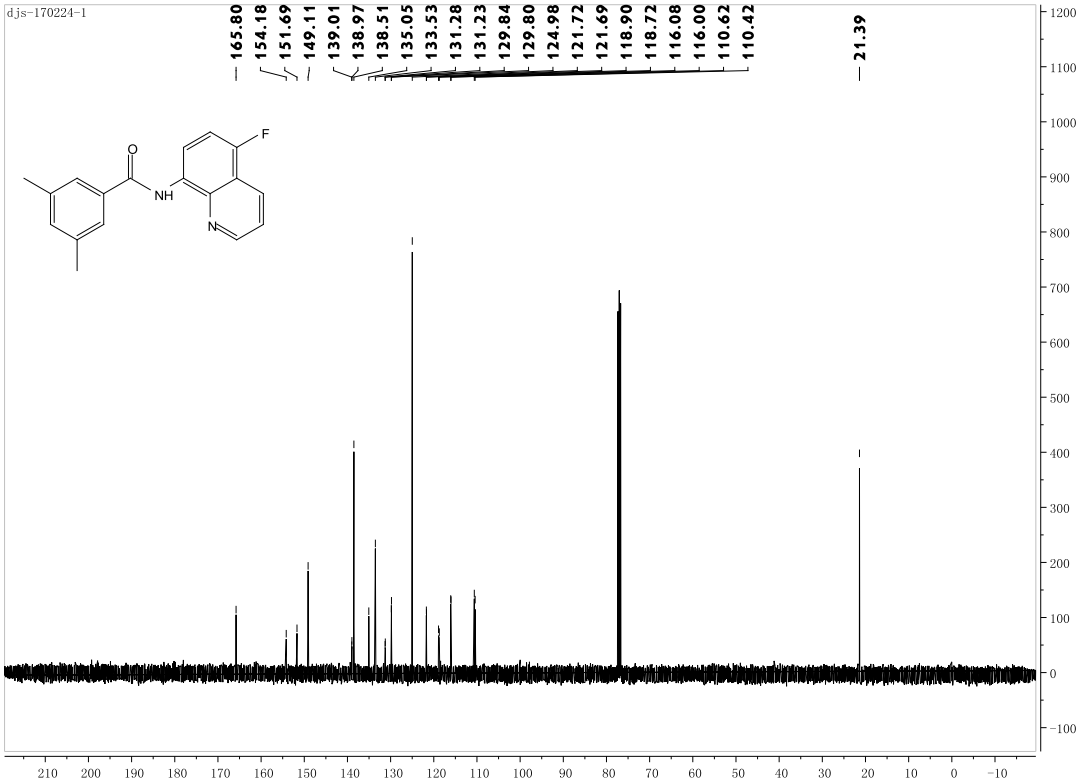
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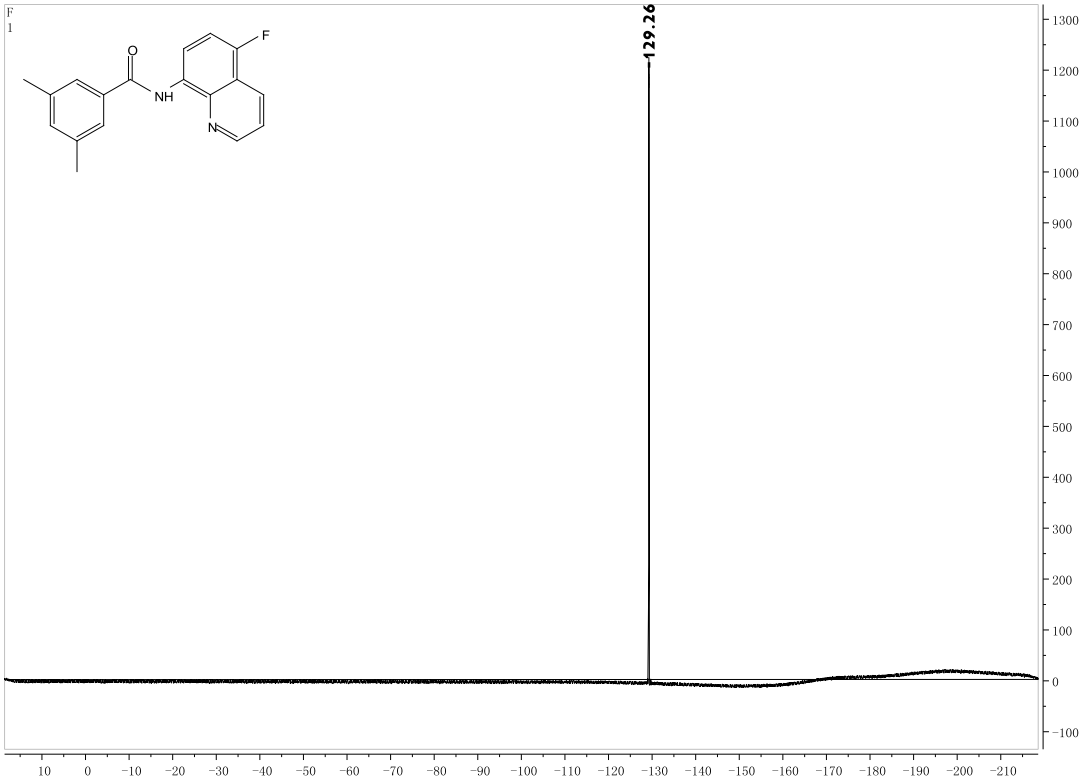
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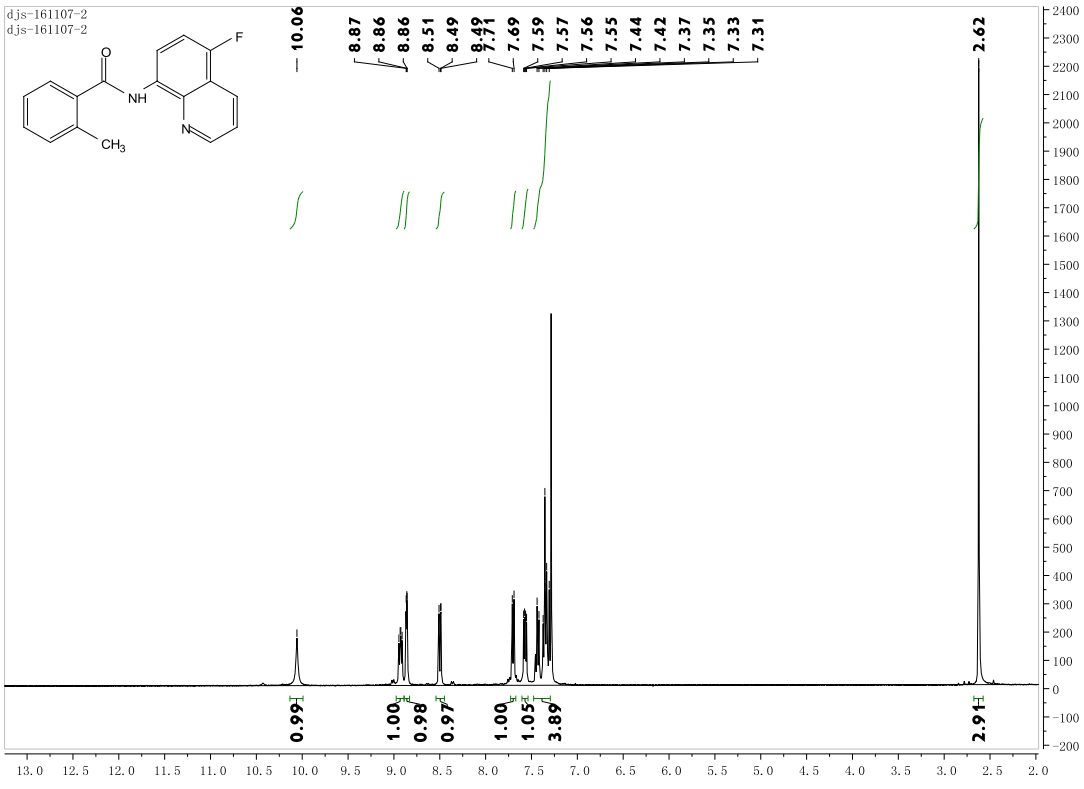
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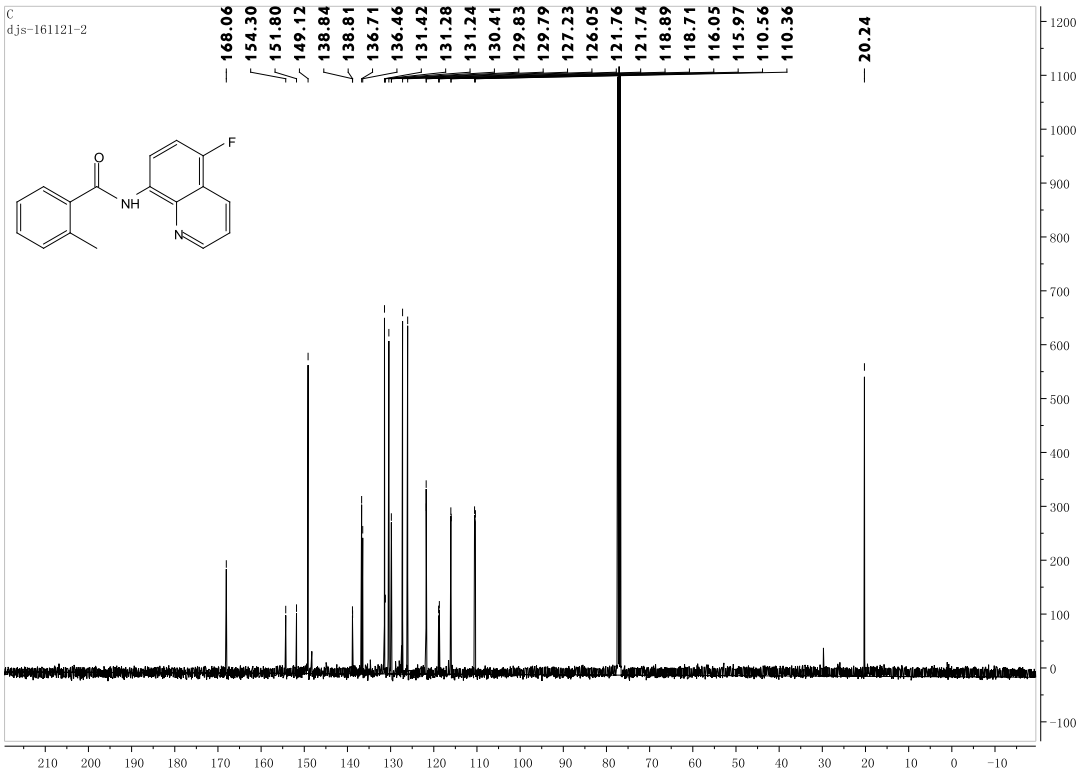
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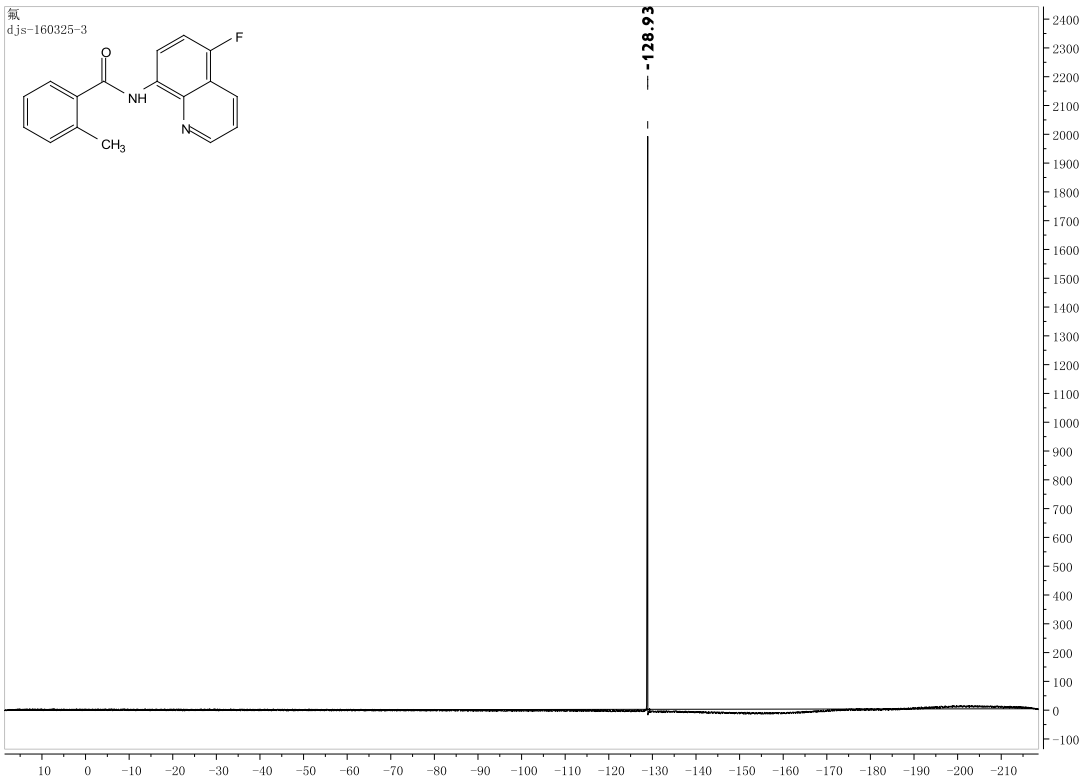
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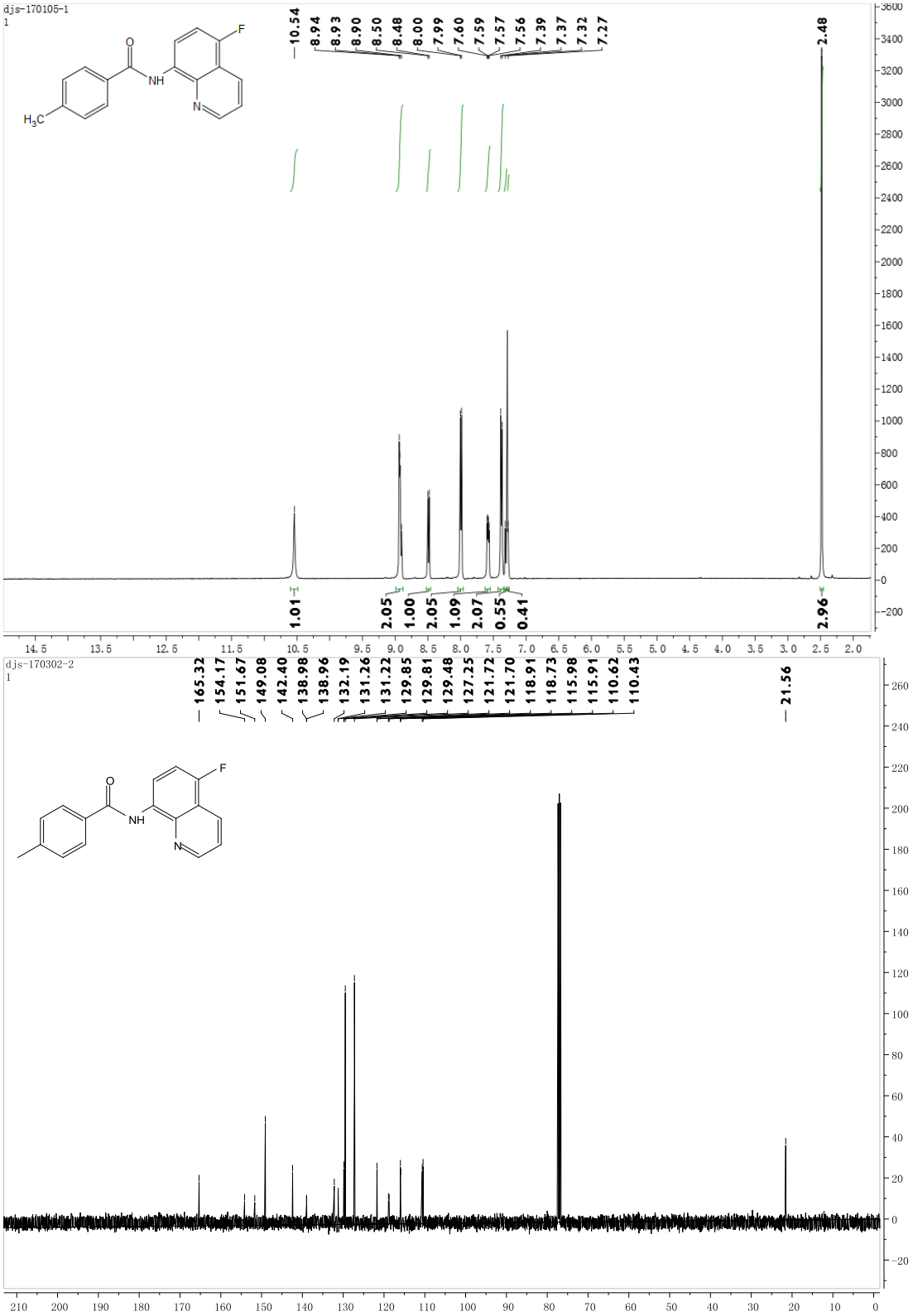
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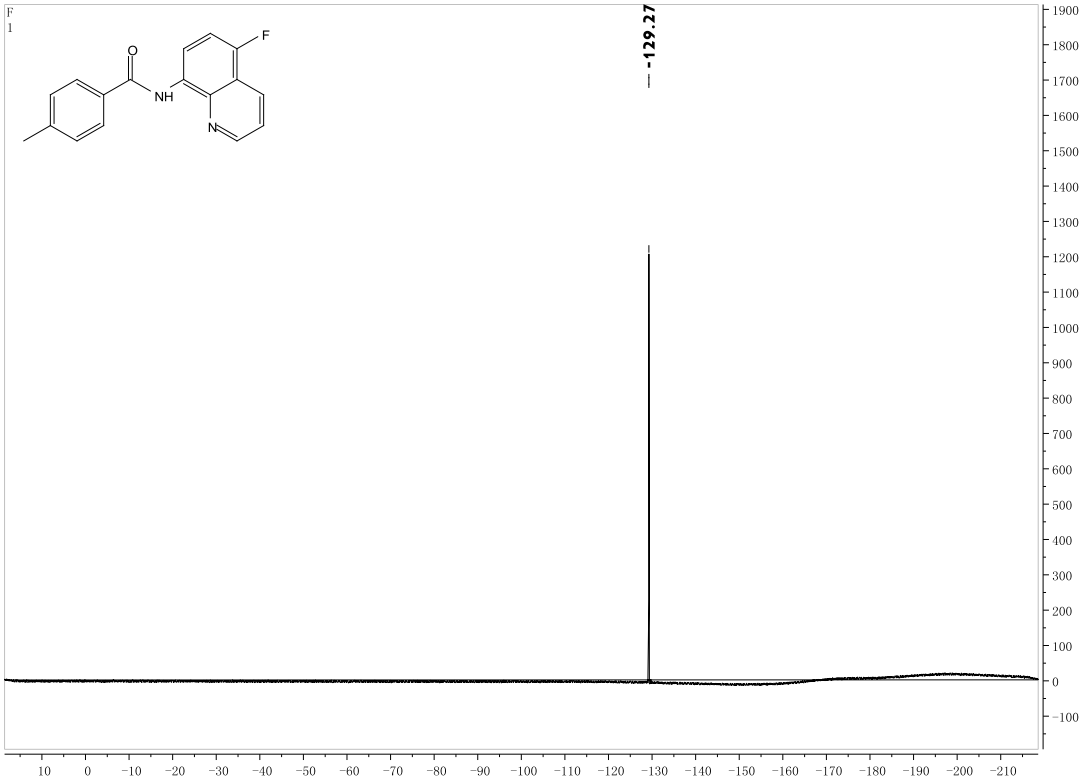
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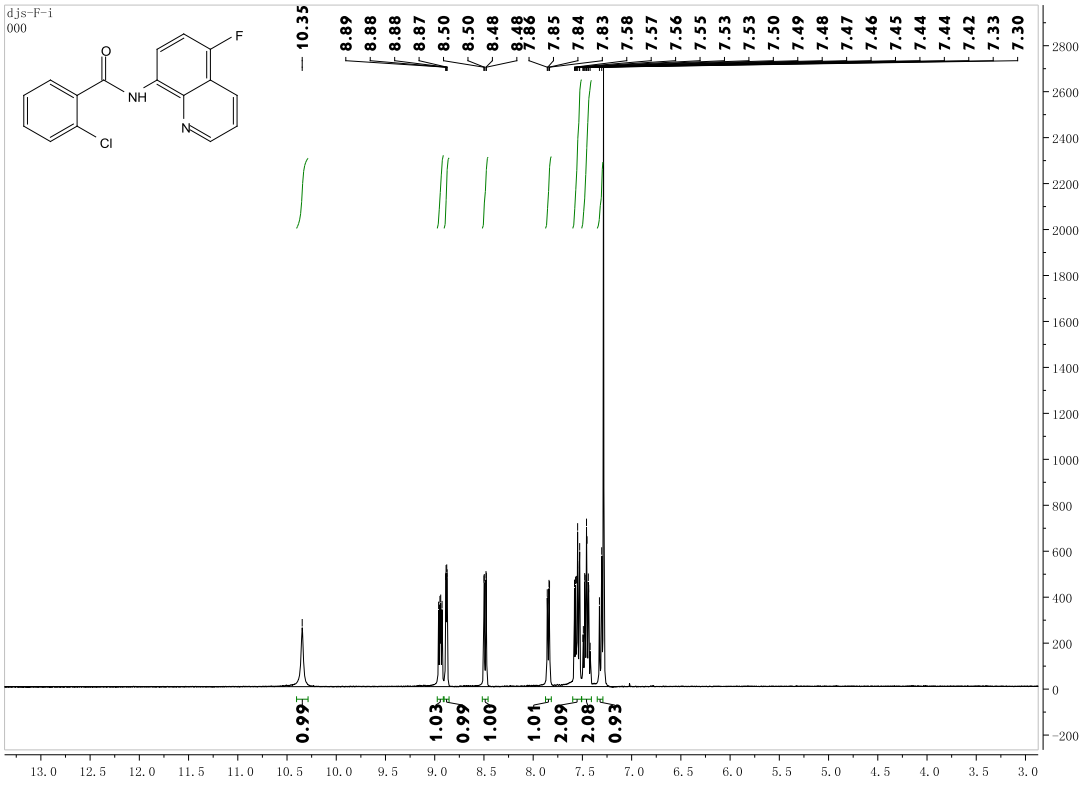
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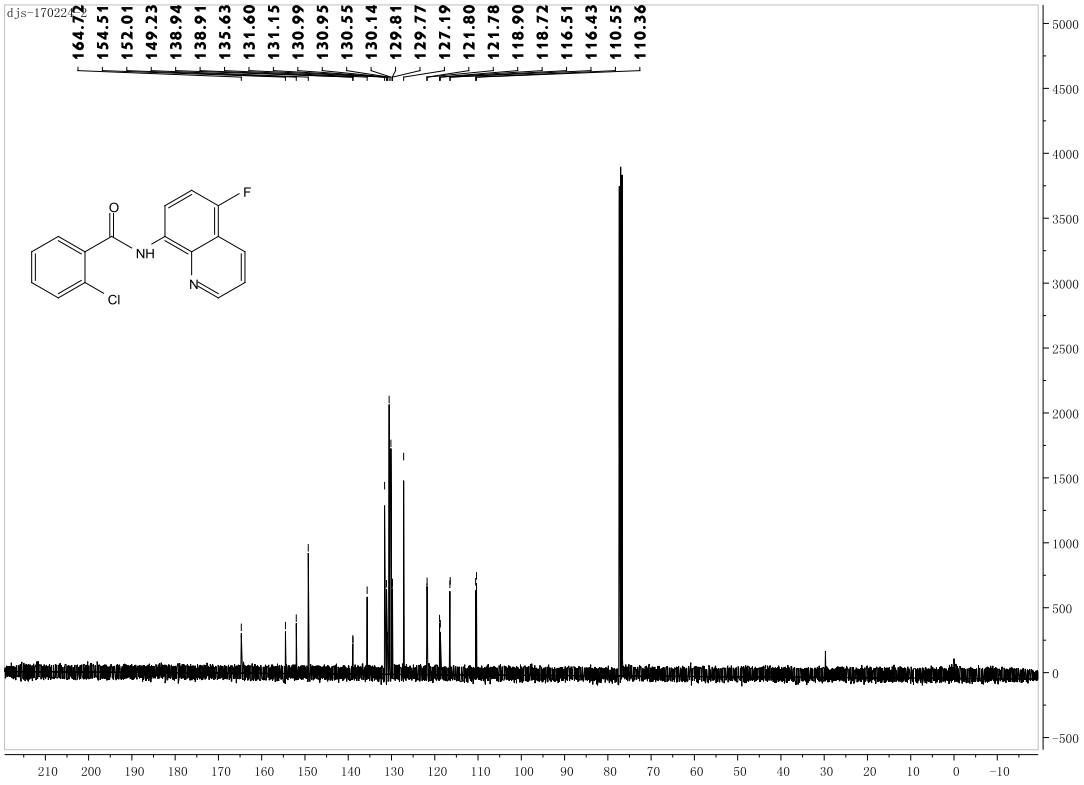
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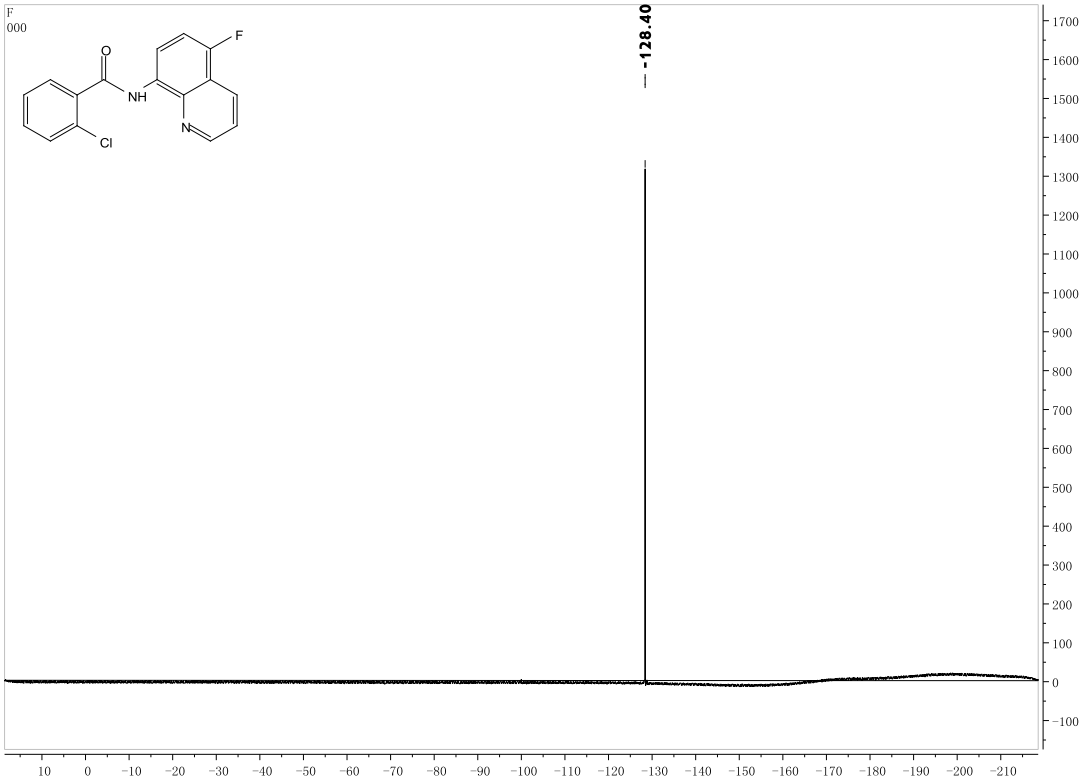
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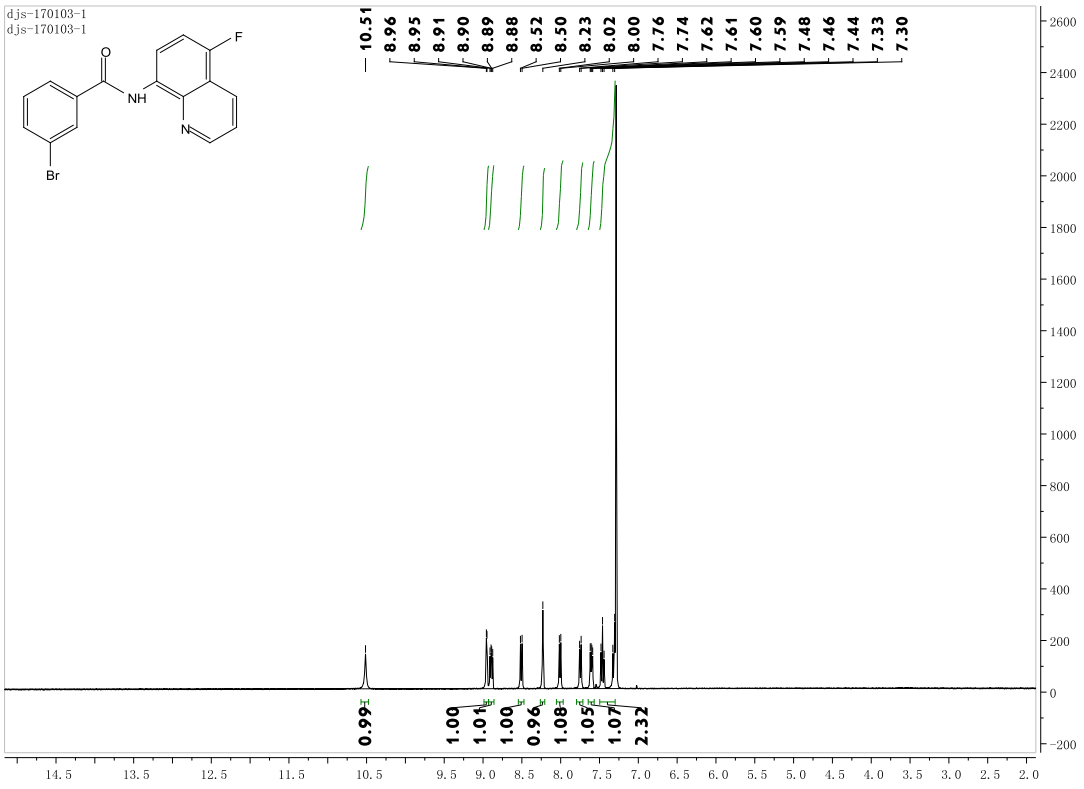
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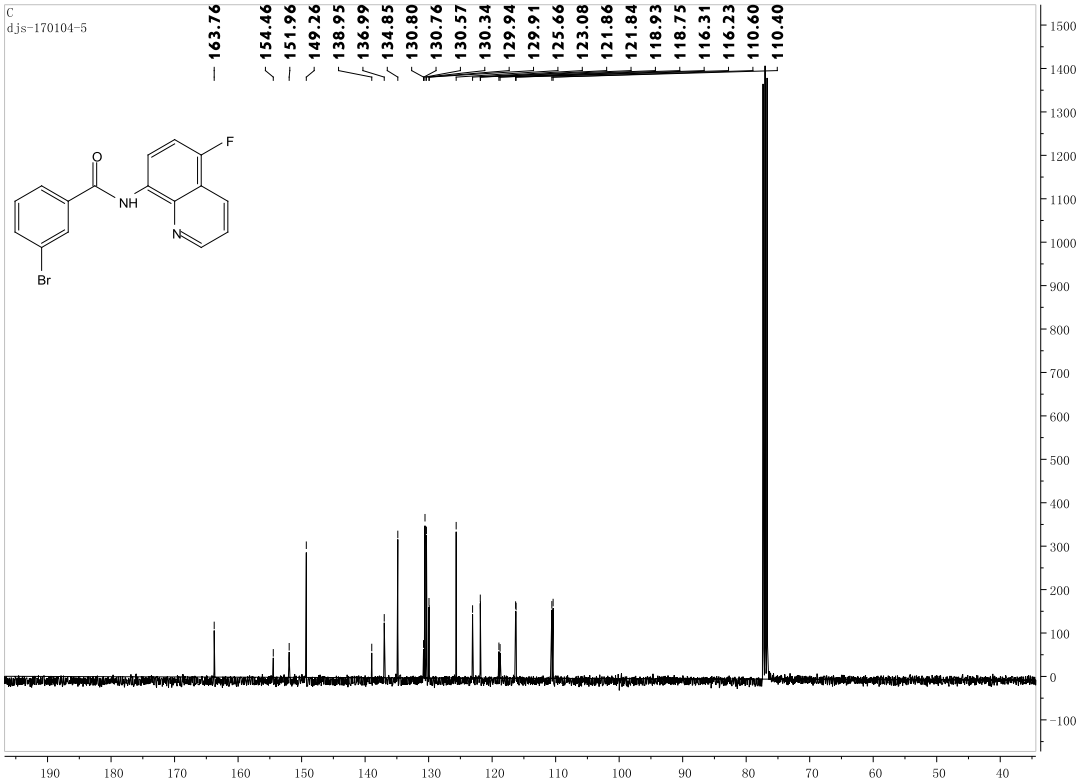
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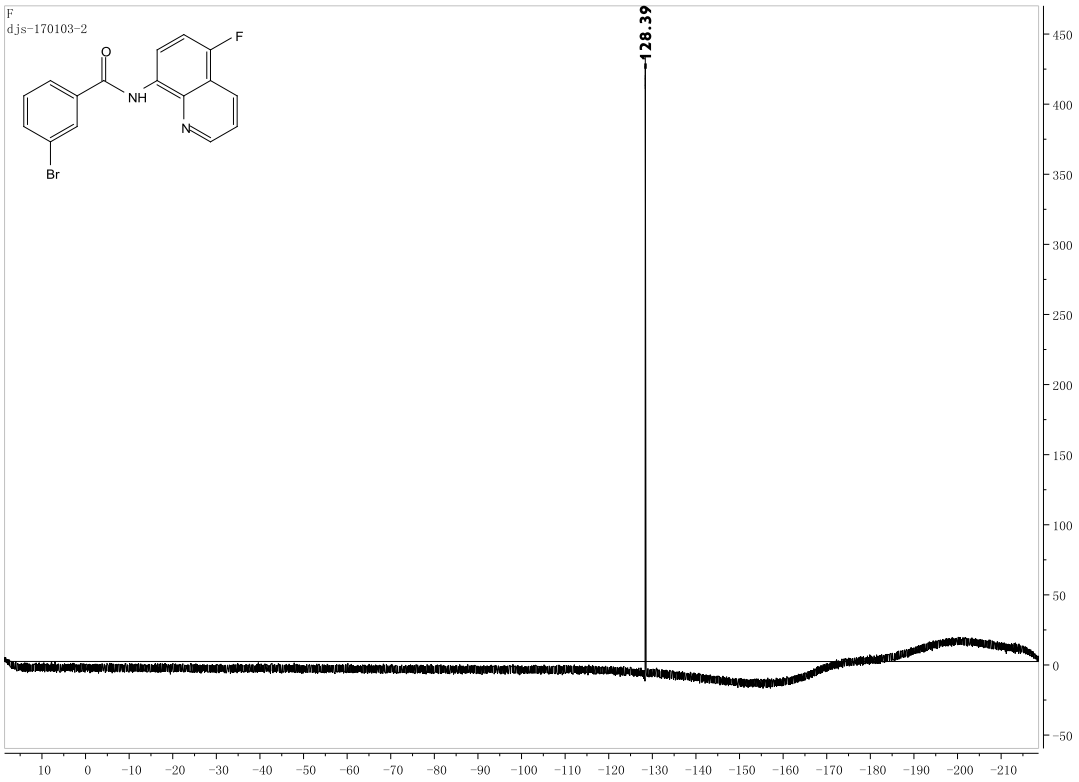
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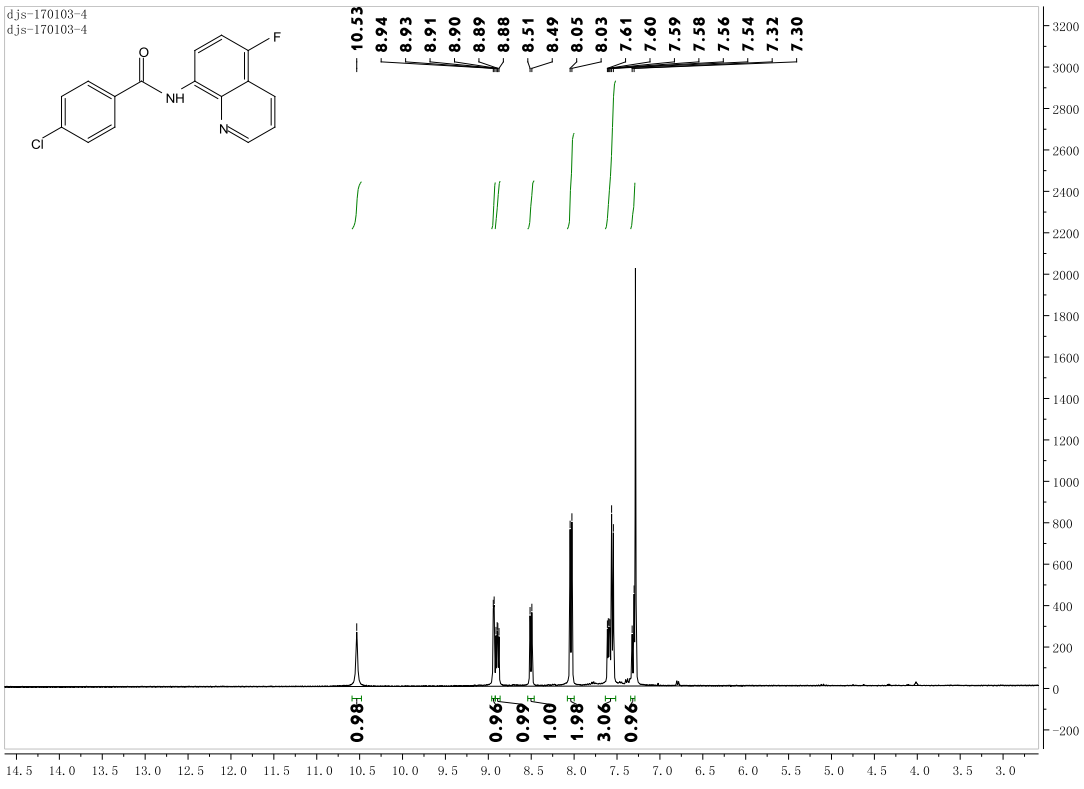
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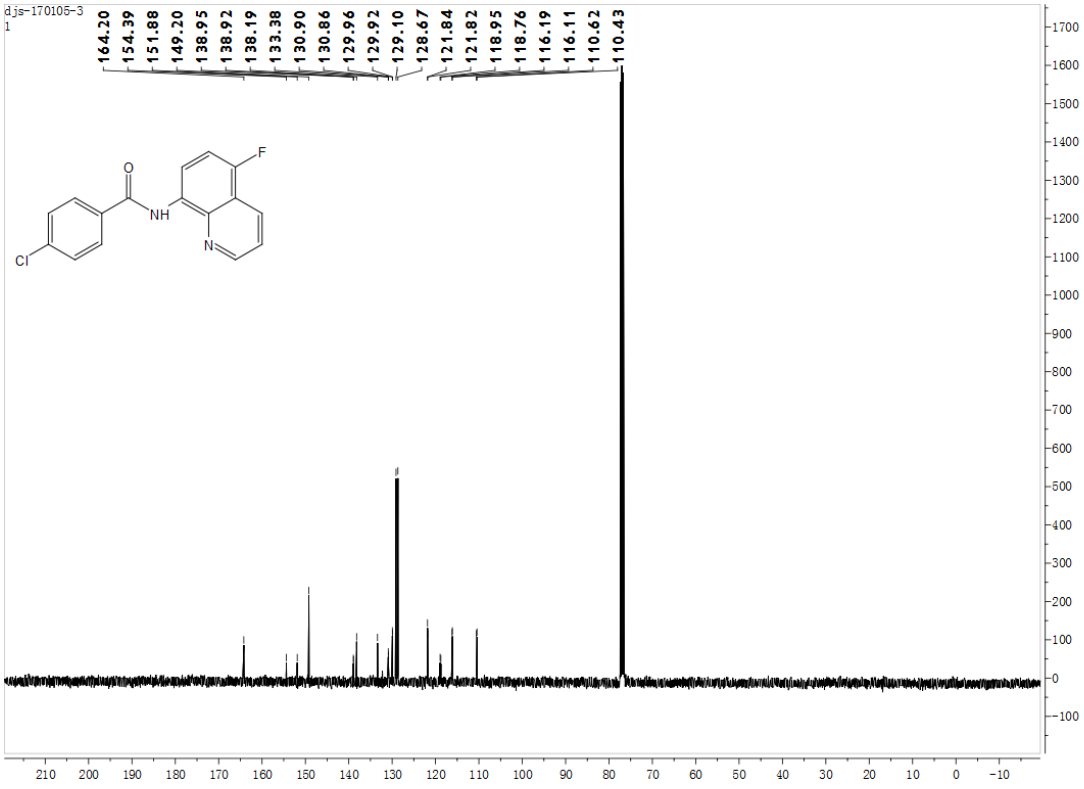
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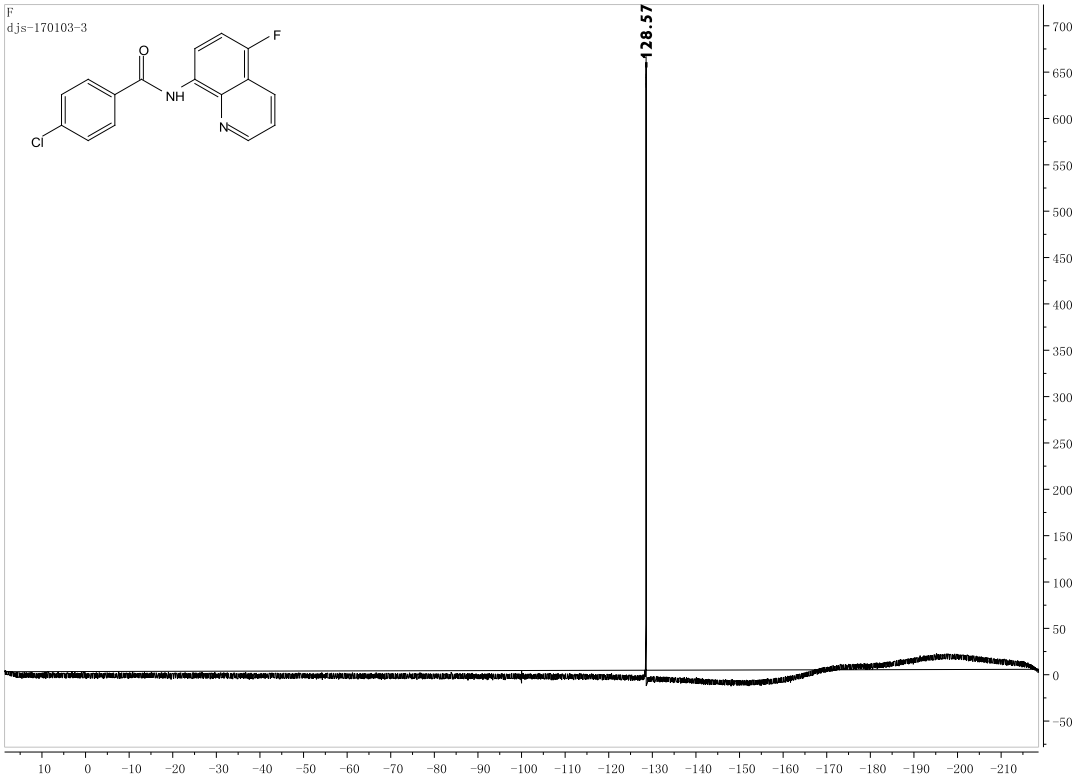
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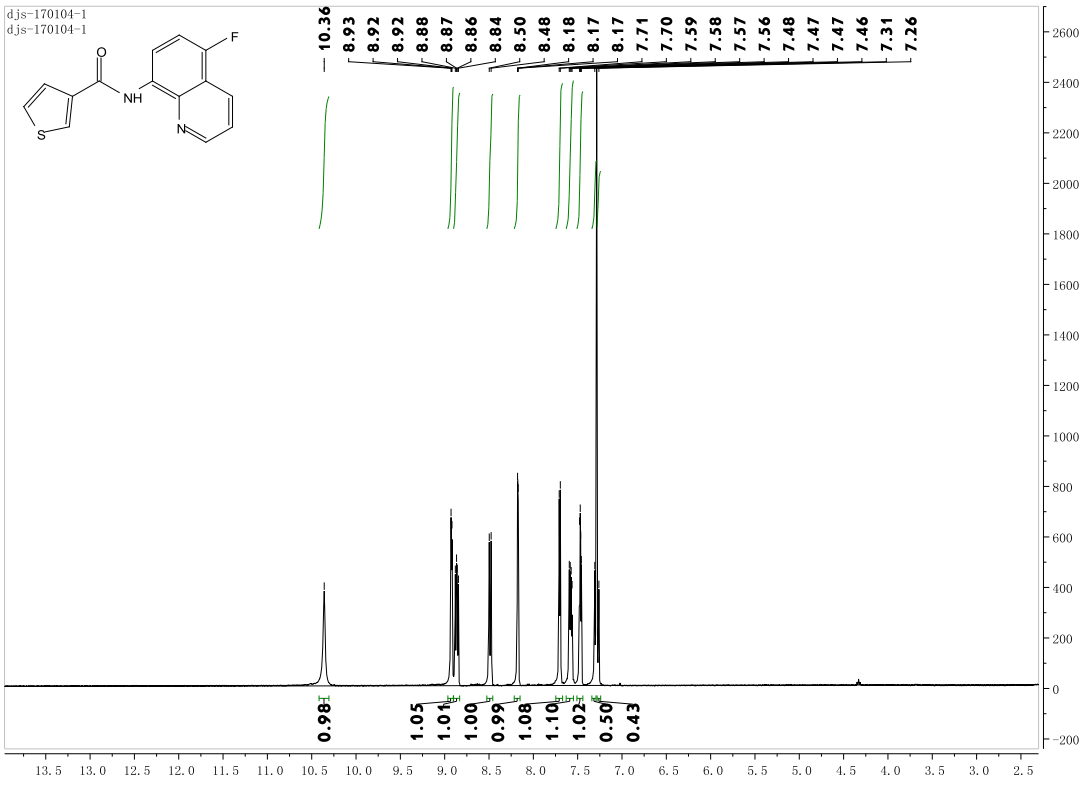
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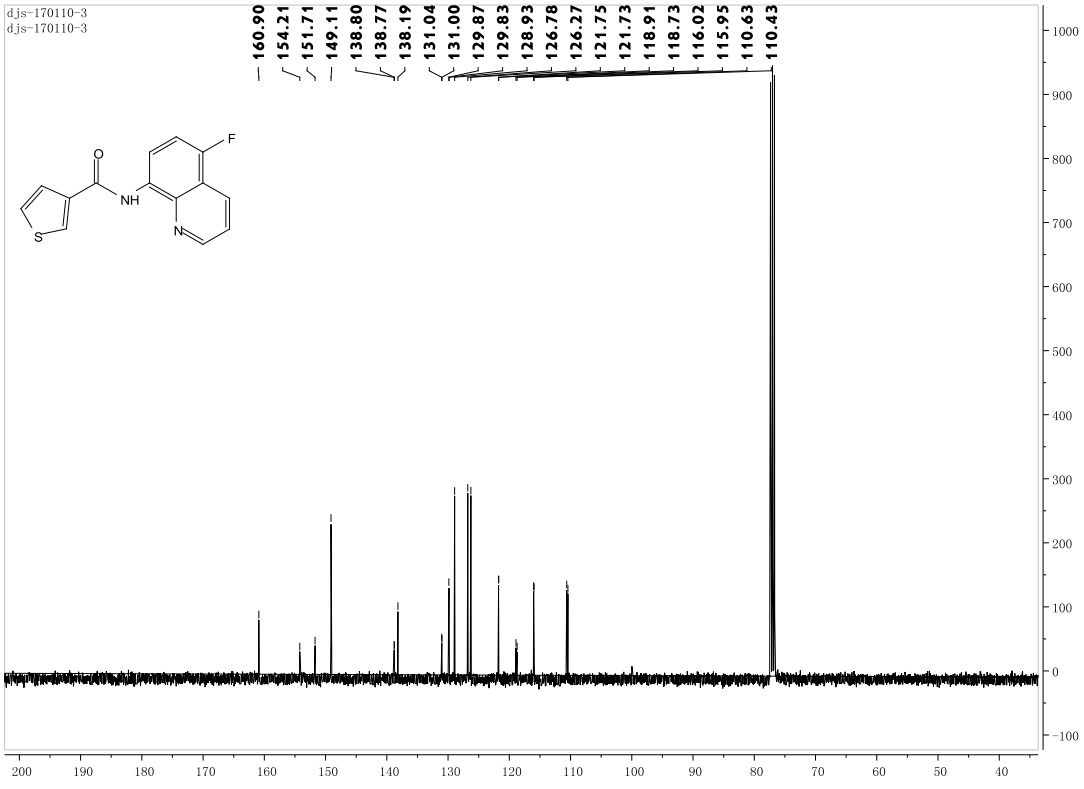
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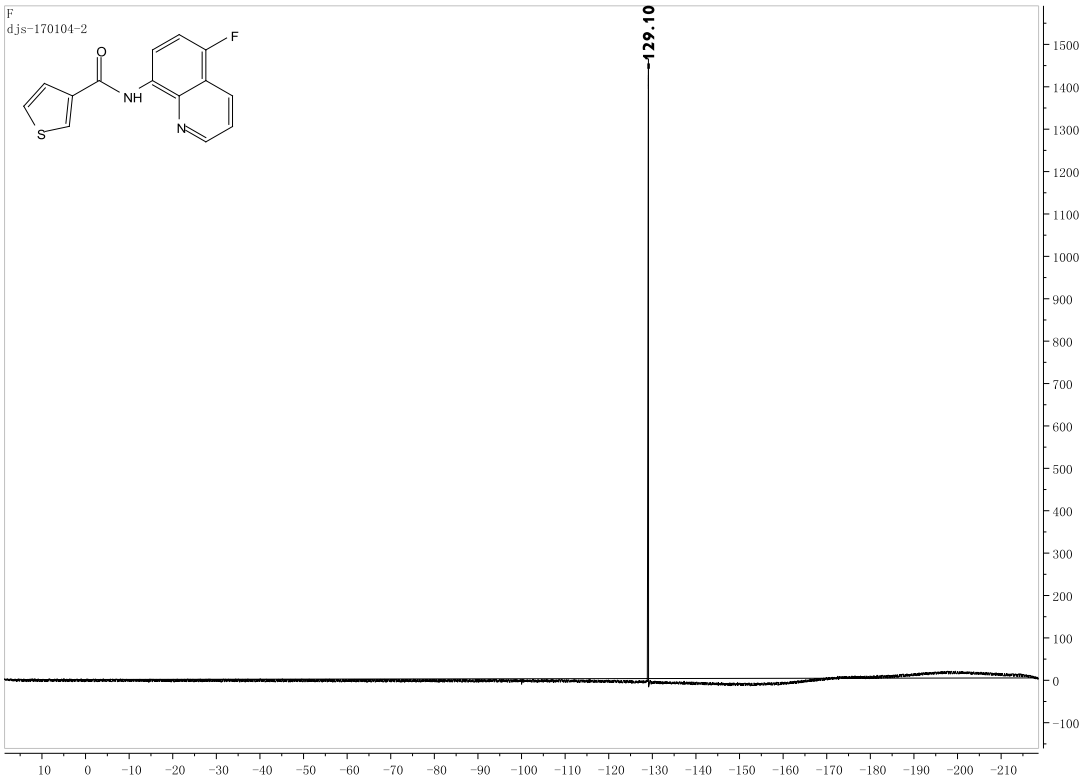
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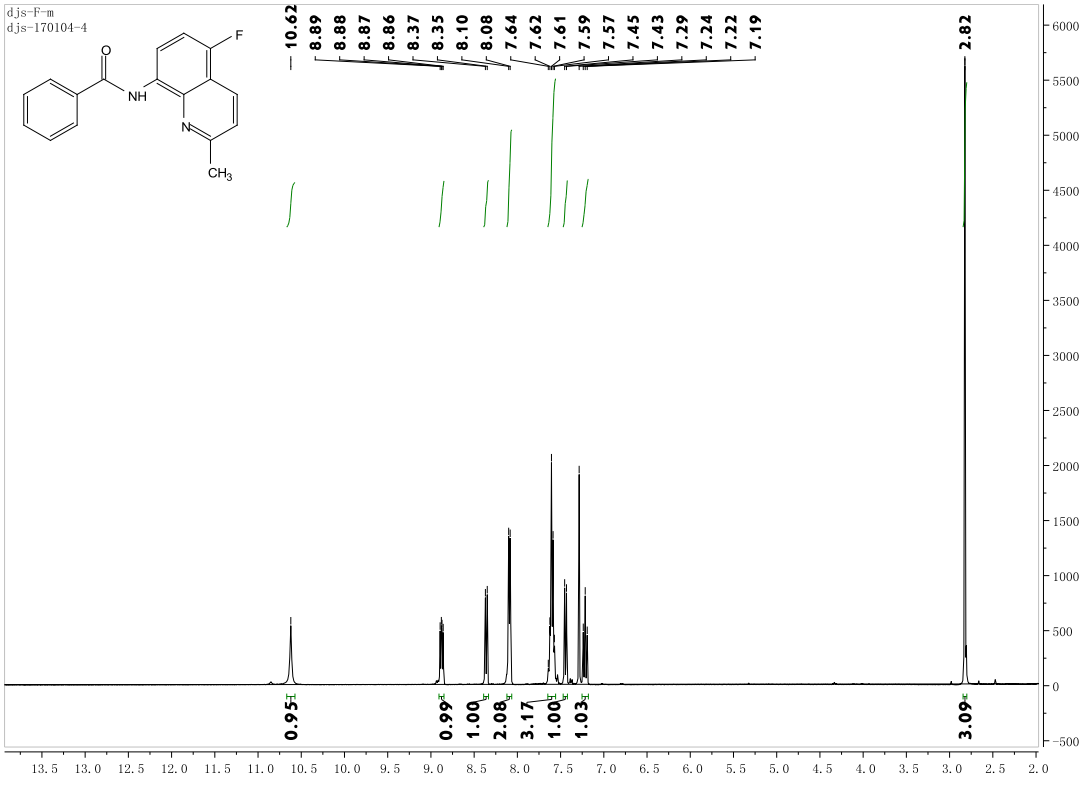
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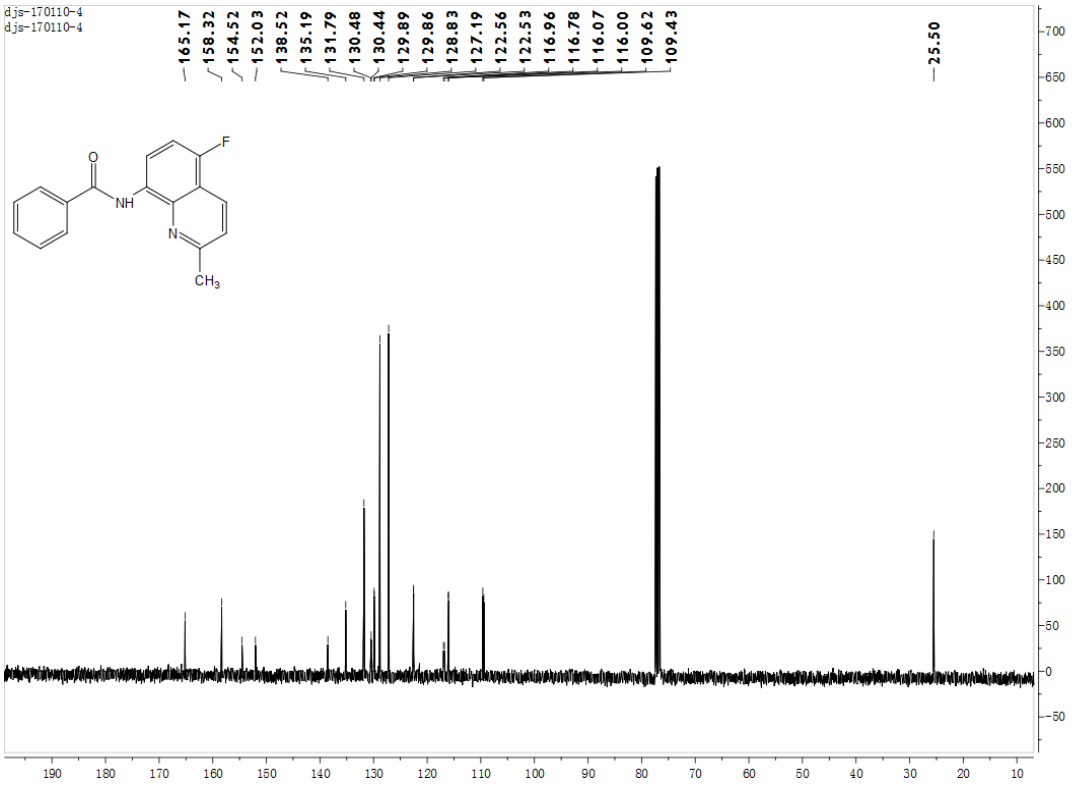
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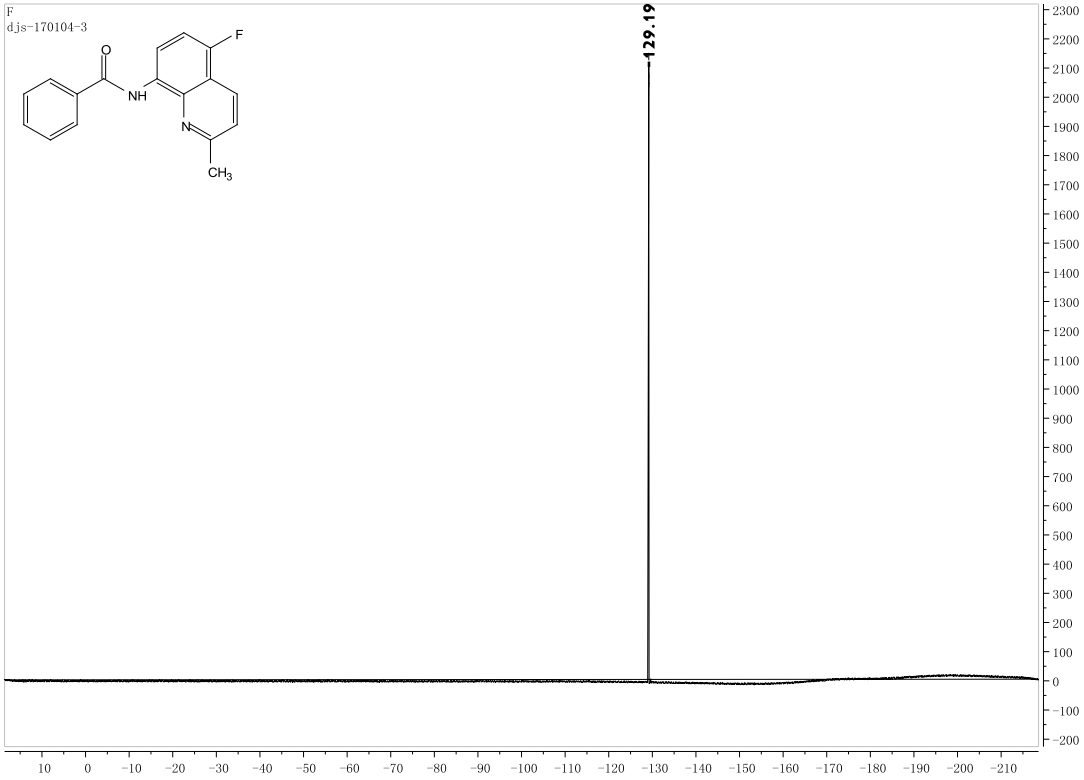
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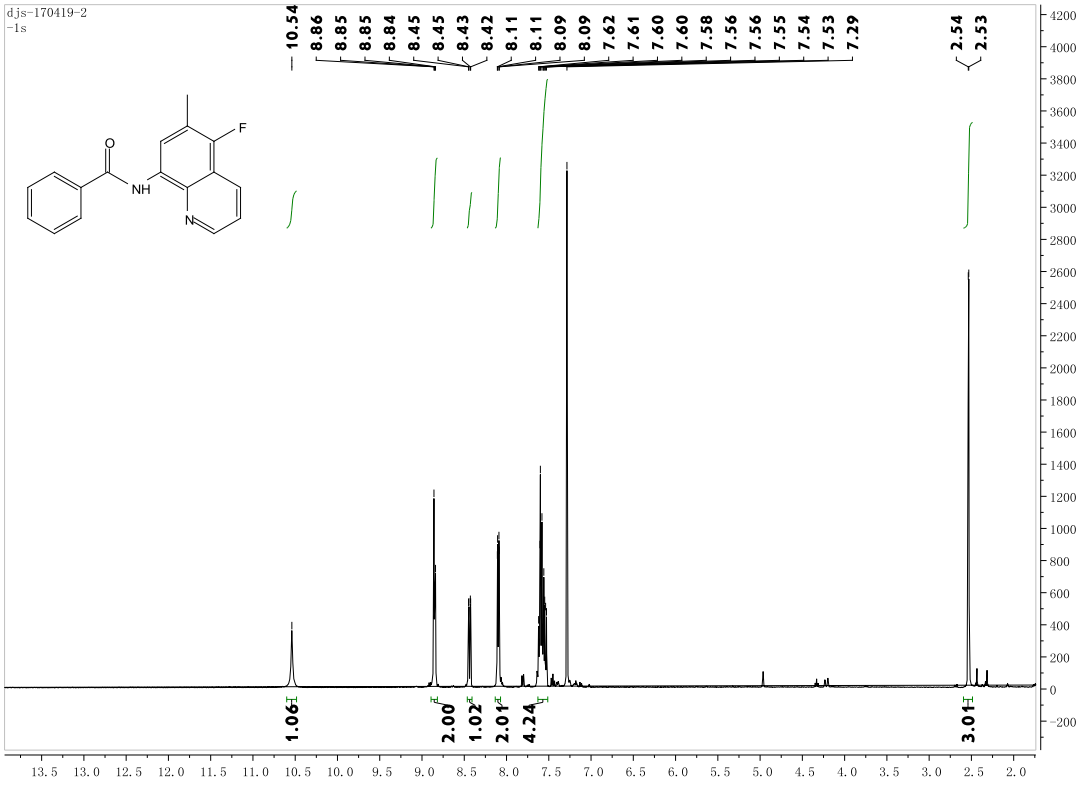
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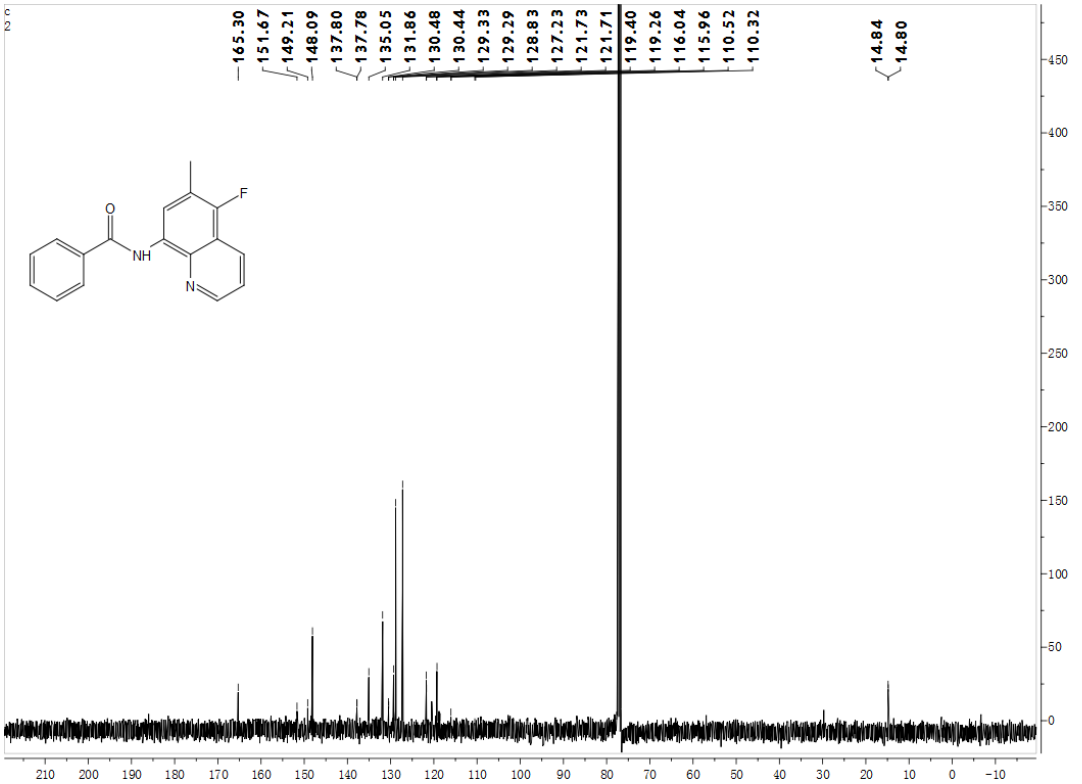
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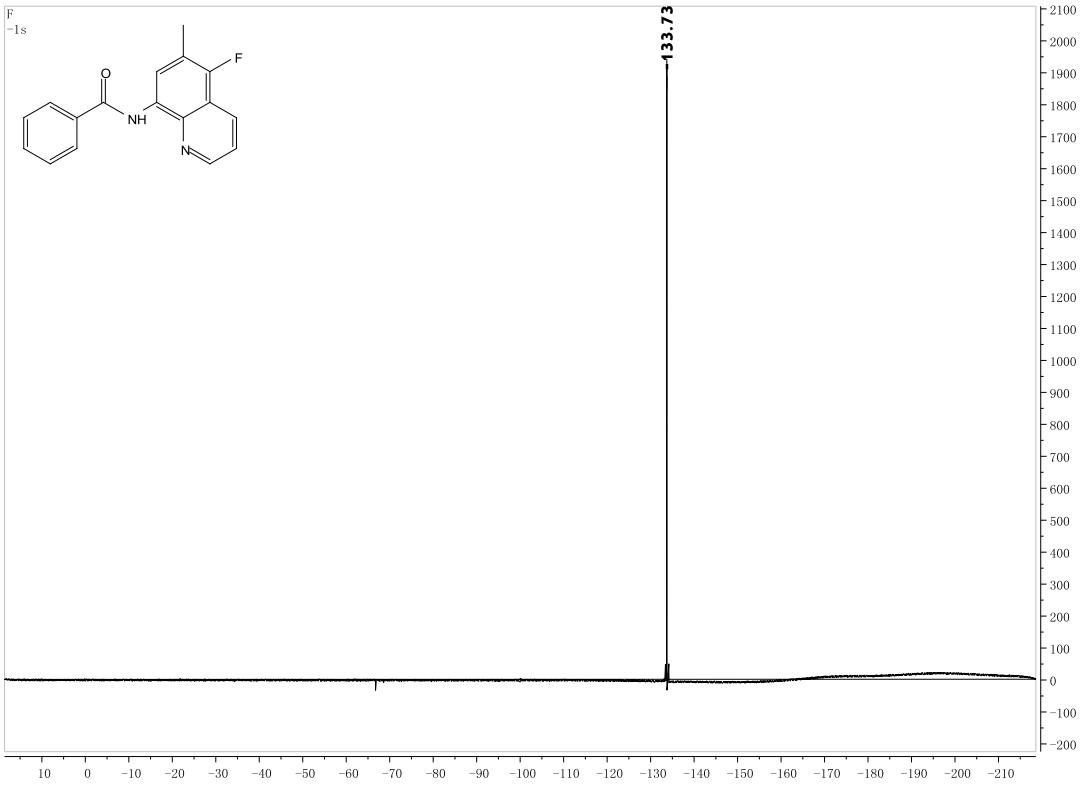
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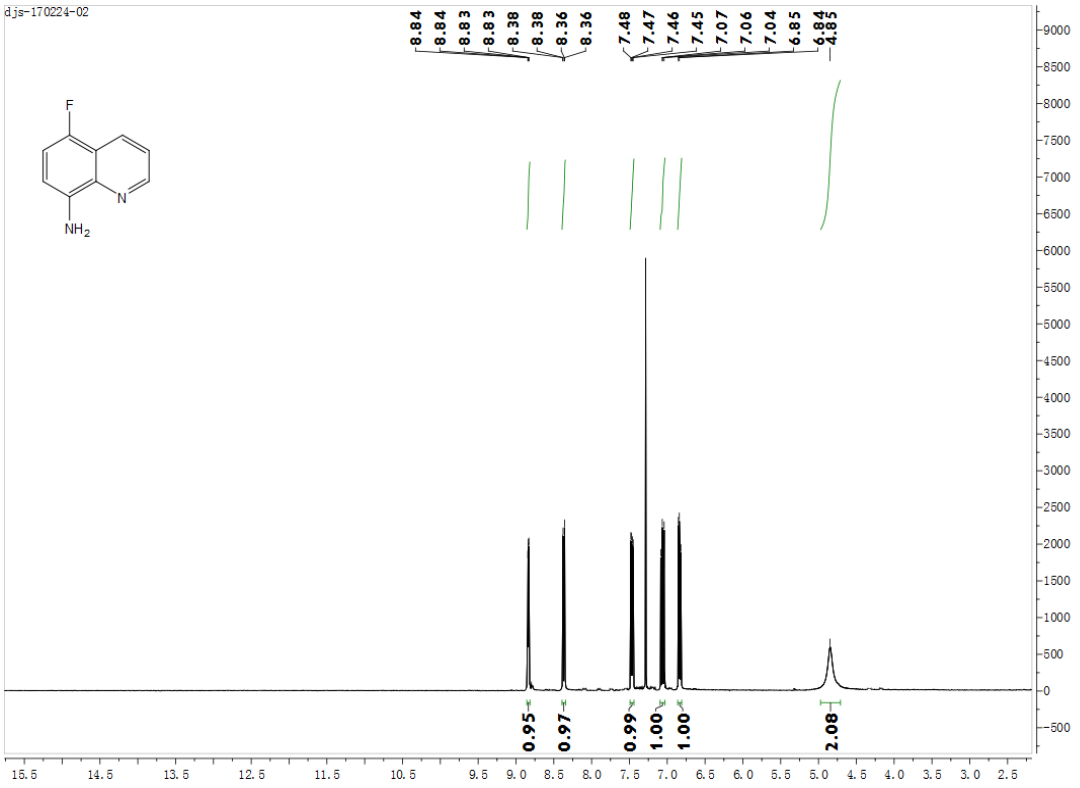
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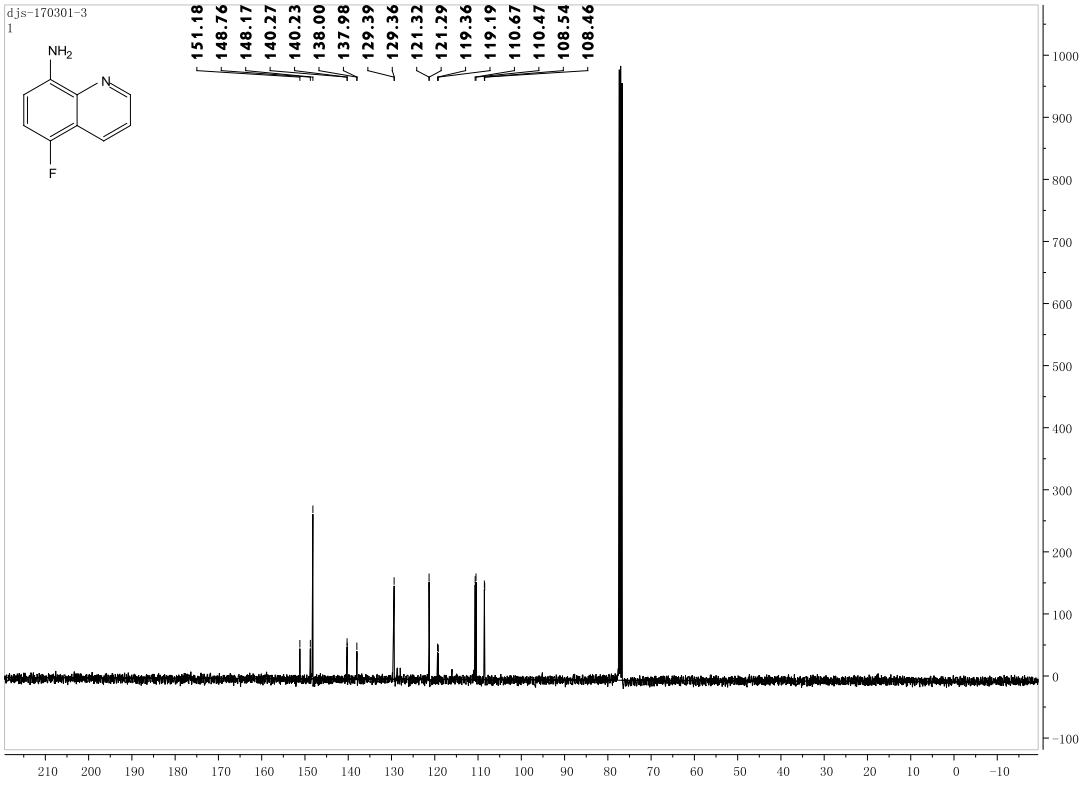
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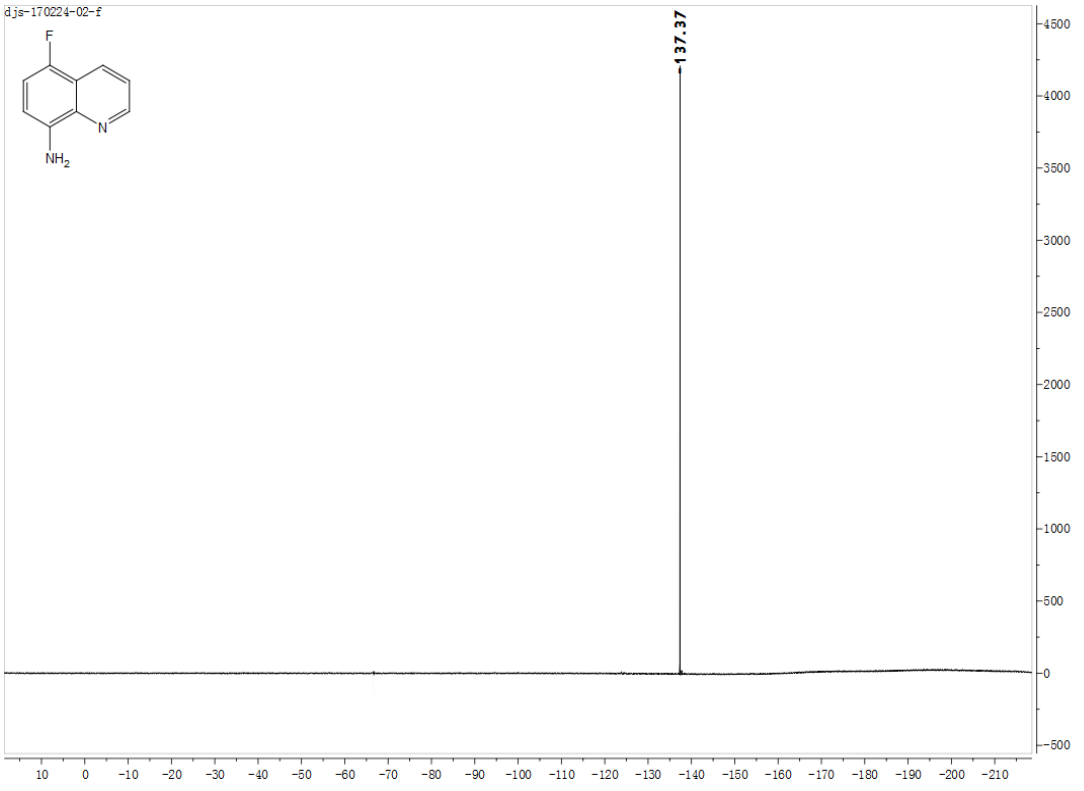
140.23
138.00
137.98
129.39
129.36
121.32
121.29
119.36
119.19
110.67
110.47
108.54
108.46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F
N
NH2
137.37

8. Reference

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