

Supporting Information

**PCl₃ or PCl₃/SnCl₄-Promoted Fluoroalkylthiolation
of Arenes with Fluoroalkanesulfinyl Chlorides**

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Experimental Section

General information

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Solvents were freshly distilled by standard procedure prior to use. Melting points were measured on a RY-I apparatus and uncorrected. ^1H NMR spectra were recorded in CDCl_3 on a Bruker AM 400 spectrometer (400 MHz) with TMS as internal standard. ^{19}F NMR spectra were taken on a Bruker AM 400 (376 MHz) spectrometer with CFCl_3 as external standard. ^{13}C NMR spectra were recorded in CDCl_3 on a Varian AM-400 spectrometer (100 MHz) or Agilent AM-400 (100 MHz) spectrometer with TMS as internal standard. For compounds **2k-m**, **2o-q**, the peaks for fluorine-possessing carbon atoms in perfluoroalkyl groups are difficult to find out in ^{13}C NMR spectra because of their multiplicity. High Resolution Mass Spectra (HRMS) were recorded on Waters Micromass GCT (EI), Thermo Scientific Q Exactive HF Orbitrap-FTMS (ESI), Thermo Fisher Scientific LTQ (DART) or IonSpec FT-ICR mass spectrometer (FI) spectrometers.

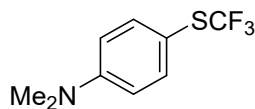
Typical procedure for the PCl_3 -promoted reaction

To a sealed tube containing a solution of **1a** (1.0 mmol, 2.0 equiv) in MeCN (0.2 mL) was slowly added PCl_3 (0.5 mmol, 1.0 equiv) and CF_3SOCl (0.5 mmol, 1.0 equiv). The mixture was stirred at room temperature for 3 hours. After the completion of reaction, water was added to quench the reaction. The aqueous layer was extracted with ethyl acetate (15 mL \times 3) and the combined organic layer was dried over anhydrous Na_2SO_4 . After removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (PE) to give product **2a**.

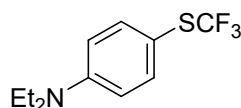
Typical procedure for the $\text{PCl}_3/\text{SnCl}_4$ -promoted reaction

To a sealed tube containing a solution of **1n** (0.5 mmol, 1.0 equiv) in DCM (0.2 mL) was slowly added SnCl₄ (0.5 mmol, 1.0 equiv), PCl₃ (1.0 mmol, 2.0 equiv) and CF₃SOCl (1.0 mmol, 2.0 equiv). The mixture was stirred at 100 °C for 3 hours. After the completion of reaction, water was added to quench the reaction. The aqueous layer was extracted with ethyl acetate (15 mL ×3) and the combined organic layer was dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (PE) to give product **2n**.

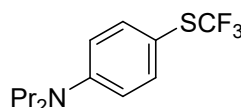
Compound characterization



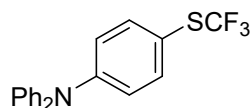
Compound **2a**: Colorless liquid, 85% yield, 93.9 mg. This is a known compound.^[1] ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 3.02 (s, 6H). ¹⁹F NMR (376 MHz, CDCl₃) δ -44.67 (s).



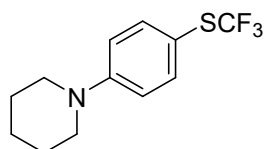
Compound **2b**: Yellow oil, 82% yield, 102.1 mg. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 3.39 (q, *J* = 7.1 Hz, 4H), 1.20 (t, *J* = 7.1 Hz, 6H). ¹⁹F NMR (376 MHz, CDCl₃) δ -44.94 (s). ¹³C NMR (101 MHz, CDCl₃) δ 149.48, 138.24, 129.87 (q, *J* = 310.1 Hz), 111.81, 107.11, 44.44, 12.39. MS (FI) *m/z* (%): 249 (100) [M]⁺. HRMS (FI) calcd for C₁₁H₁₄F₃NS [M]⁺ requires 249.0791, found 249.0794.



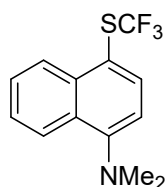
Compound **2c**: Colorless oil, 87% yield, 120.5 mg (*ortho/para* = 1:41). This is a known compound.^[2] *para*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 3.27 (t, *J* = 8.0 Hz, 2H), 1.68-1.59 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -44.87 (s).



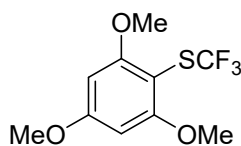
Compound **2d**: Colorless liquid, 57% yield, 98.3 mg. This is a known compound.^[3] ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 4H), 7.17-7.11 (m, 6H), 7.02 (d, *J* = 8.6 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.74 (s).



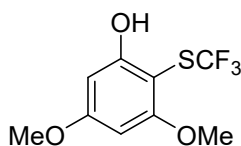
Compound **2e**: Colorless oil, 62% yield, 80.9 mg. ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 3.27 (t, $J = 5.3$ Hz, 4H), 1.72-1.59 (m, 6H). ^{19}F NMR (376 MHz, CDCl_3) δ -44.35 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 153.32, 137.89, 129.79 (q, $J = 308.4$ Hz), 115.53, 110.61, 49.07, 25.46, 24.26. MS (EI) m/z (%): 261 (75) $[\text{M}]^+$, 260 (32), 192 (100), 136 (30). HRMS (EI) calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{NS}$ $[\text{M}]^+$ requires 261.0794, found 261.0790.



Compound **2f**: Brown oil, 57% yield, 77.3 mg. ^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, $J = 8.4$ Hz, 1H), 8.25 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.62 (t, $J = 6.9$ Hz, 1H), 7.55 (t, $J = 7.0$ Hz, 1H), 7.03 (d, $J = 7.9$ Hz, 1H), 2.96 (s, 6H). ^{19}F NMR (376 MHz, CDCl_3) δ -43.05 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 154.76, 138.45, 136.62, 129.77 (q, $J = 311.1$ Hz), 129.20, 127.29, 126.41, 125.54, 124.98, 114.01, 113.39, 44.85. MS (FI) m/z (%): 271 (100) $[\text{M}]^+$. HRMS (FI) calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{NS}$ $[\text{M}]^+$ requires 271.0637, found 271.0632.

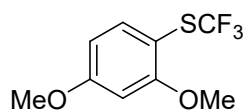


Compound **2g**: Colorless oil, 67% yield, 89.8 mg. This is a known compound.^[4] ^1H NMR (400 MHz, CDCl_3) δ 6.15 (s, 2H), 3.86 (s, 6H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -43.56 (s).

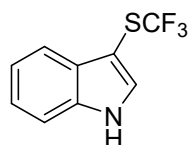


Compound **2h**: Yellow solid, 64% yield, 81.3 mg. This is a known compound.^[5] ^1H

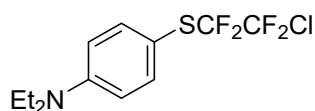
NMR (400 MHz, CDCl₃) δ 6.62 (s, 1H), 6.24 (s, 1H), 6.09 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.75 (s).



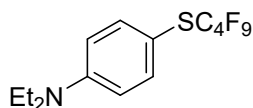
Compound **2i**: Colorless oil, 72% yield, 85.7 mg. This is a known compound.^[4] ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.4 Hz, 1H), 6.53-6.51 (m, 2H), 3.88 (s, 3H), 3.84 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.71 (s).



Compound **2j**: Colorless oil, 54% yield, 58.6 mg. This is a known compound.^[6] ¹H NMR (400 MHz, CDCl₃) δ 8.46 (s, 1H), 7.86-7.84 (m, 1H), 7.52-7.51 (m, 1H), 7.43-7.41 (m, 1H), 7.35-7.30 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -44.56 (s, 3F).

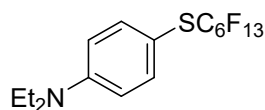


Compound **2k**: Yellow oil, 55% yield, 86.6 mg. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 3.37 (q, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H). ¹⁹F NMR (376 MHz, CDCl₃) δ -67.53 (t, *J* = 6.8 Hz, 2F), -88.99 (t, *J* = 6.8 Hz, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 149.55, 138.93, 111.70, 105.63, 44.40, 12.41. MS (FI) *m/z* (%): 315 (100) [M]⁺. HRMS (FI) calcd for C₁₂H₁₄ClF₄NS [M]⁺ requires 315.0466, found 315.0465.

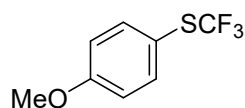


Compound **2l**: Brown oil, 71% yield, 141.7 mg. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.40 (q, *J* = 7.1 Hz, 4H), 1.21 (t, *J* = 7.1 Hz, 6H). ¹⁹F NMR (376 MHz, CDCl₃) δ -81.16 (t, *J* = 9.8 Hz, 3F), -88.92 (t, *J* = 13.3 Hz, 2F), -120.33~-120.45 (m, 2F), -125.61~-125.72 (m, 2F). ¹³C NMR (101 MHz, CDCl₃)

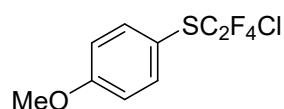
δ 149.66, 139.07, 111.72, 104.62, 44.38, 12.29. MS (FI) m/z (%): 399 (100) $[M]^+$. HRMS (FI) calcd for $C_{14}H_{14}F_9NS$ $[M]^+$ requires 399.0698, found 399.0695.



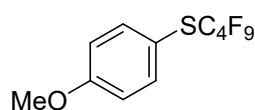
Compound **2m**: Brown oil, 79% yield, 197.1 mg. 1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, $J = 8.9$ Hz, 2H), 6.65 (d, $J = 8.9$ Hz, 2H), 3.39 (q, $J = 7.1$ Hz, 4H), 1.20 (t, $J = 7.1$ Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.05 (t, $J = 10.0$ Hz, 3F), -88.72 (t, $J = 13.8$ Hz, 2F), -119.48~-119.60 (m, 2F), -121.54 (s, 2F), -122.92 (s, 2F), -126.22~-126.39 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.64, 138.12, 111.70, 104.94, 42.86, 11.39. MS (FI) m/z (%): 499 (100) $[M]^+$. HRMS (FI) calcd for $C_{16}H_{14}F_{13}NS$ $[M]^+$ requires 499.0634, found 499.0629.



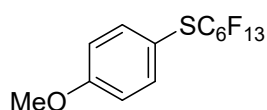
Compound **2n**: Colorless oil, 95% yield, 98.8 mg. This is a known compound.^[4] 1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 2H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.01 (s).



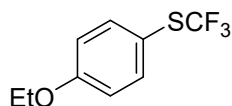
Compound **2o**: Yellow liquid, 66% yield, 90.4 mg. 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, $J = 8.9$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.66 (t, $J = 6.6$ Hz, 2F), -88.26 (t, $J = 6.6$ Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.98, 139.00, 114.94, 113.65 (t, $J = 2.9$ Hz), 55.36. MS (EI) m/z (%): 276 (21), 274 (71) $[M]^+$, 139 (100), 124 (18), 96 (17). HRMS (EI) calcd for $C_9H_7ClF_4OS$ $[M]^+$ requires 273.9839, found 273.9836.



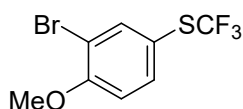
Compound **2p**: Colorless liquid, 81% yield, 145.0 mg (*ortho/para* = 1:18). *para*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -81.02 (t, J = 9.6 Hz, 3F), -88.13 (t, J = 15.0 Hz, 2F), -120.18~-120.30 (m, 2F), -125.56~-125.72 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 162.04, 139.13, 114.98, 112.98, 55.41. MS (EI) m/z (%): 358 (49) $[\text{M}]^+$, 139 (100), 124 (15), 96 (12). HRMS (EI) calcd for $\text{C}_{11}\text{H}_7\text{F}_9\text{OS}$ $[\text{M}]^+$ requires 358.0068, found 358.0071.



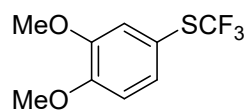
Compound **2q**: Colorless oil, 92% yield, 210.7 mg (*ortho/para* = 1:36). *para*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -80.89 (t, J = 10.1 Hz, 3F), -87.93 (t, J = 13.6 Hz, 2F), -119.34~-119.46 (m, 2F), -121.56 (s, 2F), -122.91 (s, 2F), -126.18~-126.36 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 162.04, 139.13, 114.97, 113.03, 55.38. MS (EI) m/z (%): 458 (95) $[\text{M}]^+$, 439 (30), 139 (100), 124 (34), 96 (32). HRMS (EI) calcd for $\text{C}_{13}\text{H}_7\text{F}_{13}\text{OS}$ $[\text{M}]^+$ requires 458.0005, found 458.0009.



Compound **2r**: Colorless liquid, 95% yield, 105.5 mg (*ortho/para* = 1:27). This is a known compound. ^[7] *para*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.04 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -44.03 (s).



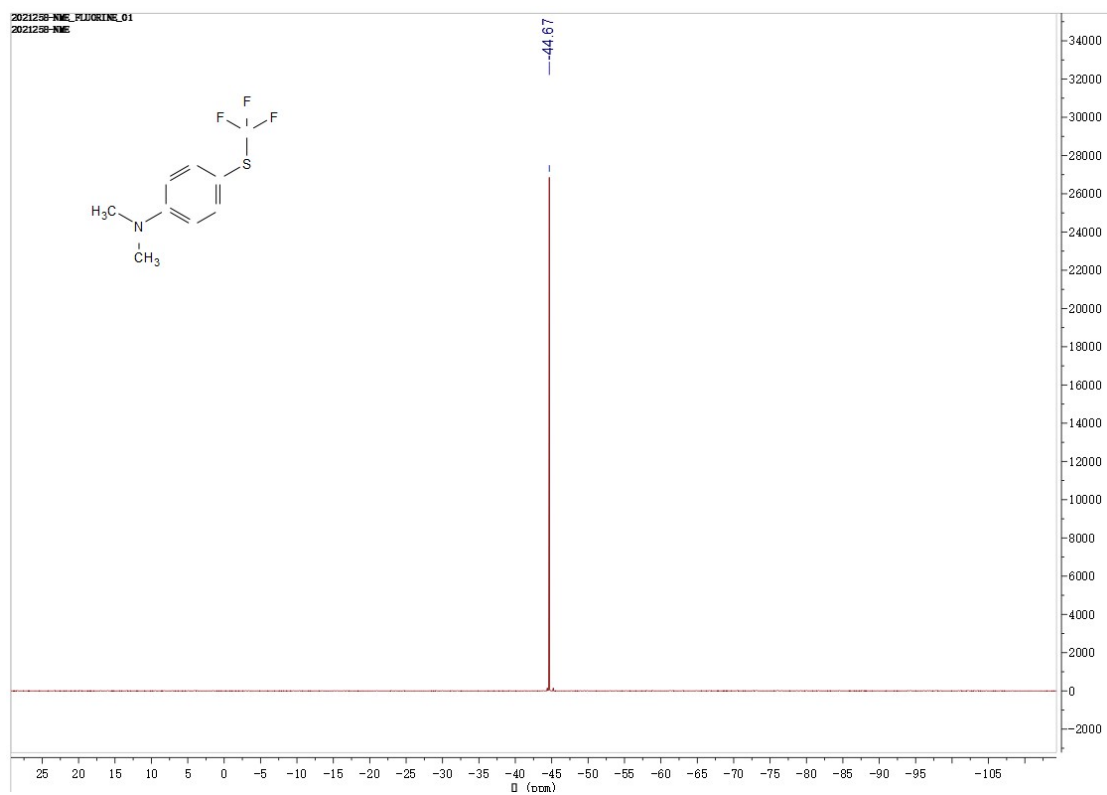
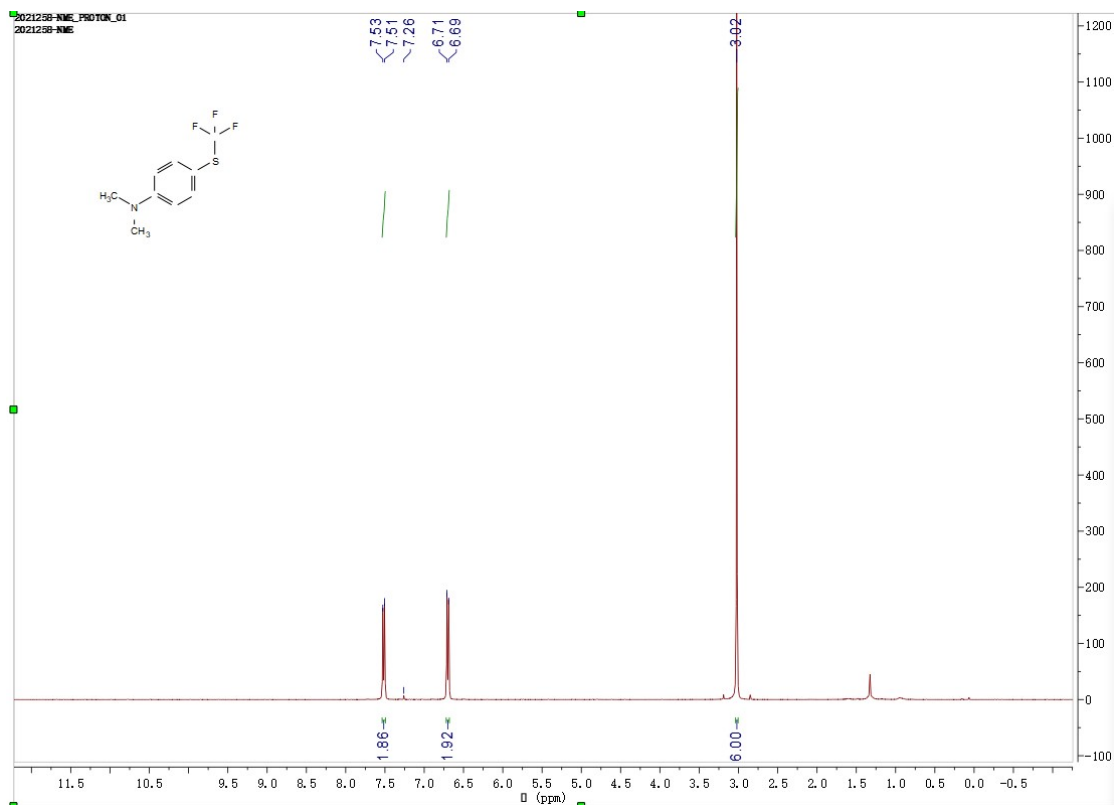
Compound **2s**: Yellow liquid, 43% yield, 51.2 mg (*ortho/para* = 1:33). This is a known compound. ^[4] *para*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, J = 8.4 Hz, 1H), 7.10 (s, 1H), 6.86 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -43.76 (s).



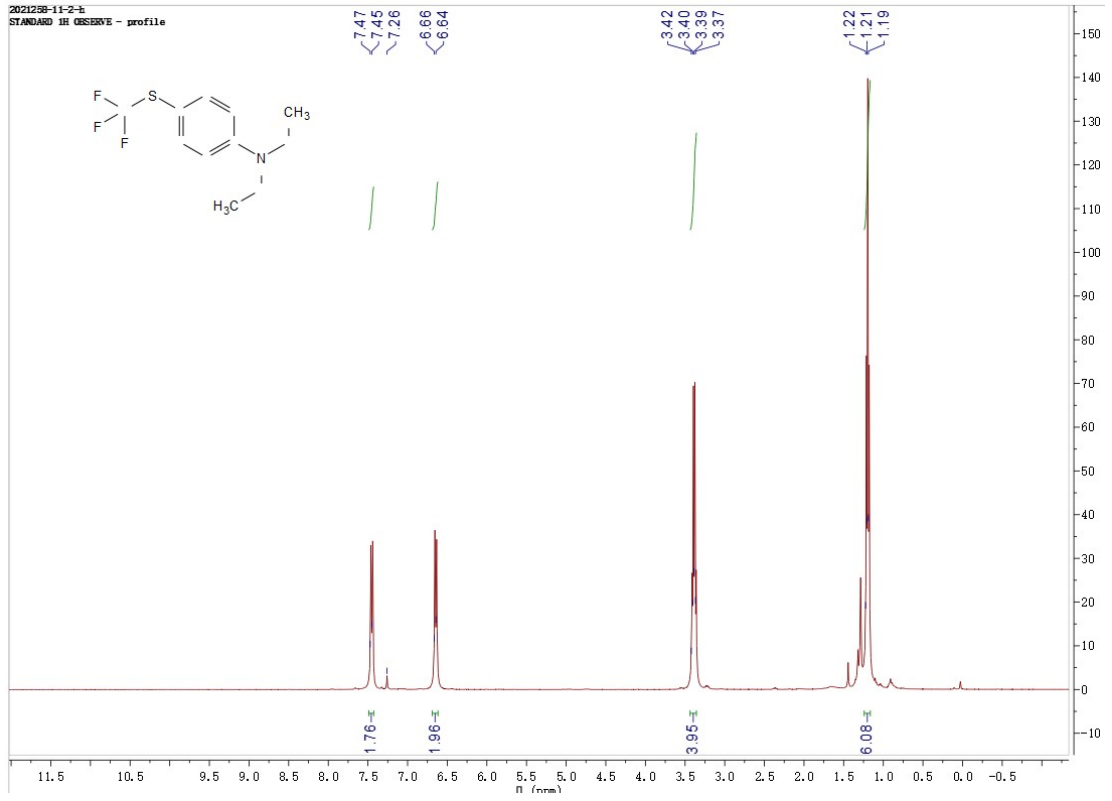
Compound **2t**: Colorless oil, 64% yield, 91.5 mg. This is a known compound. ^[4] ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 2.2 Hz, 1H), 7.58 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.94 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.98 (s).

References

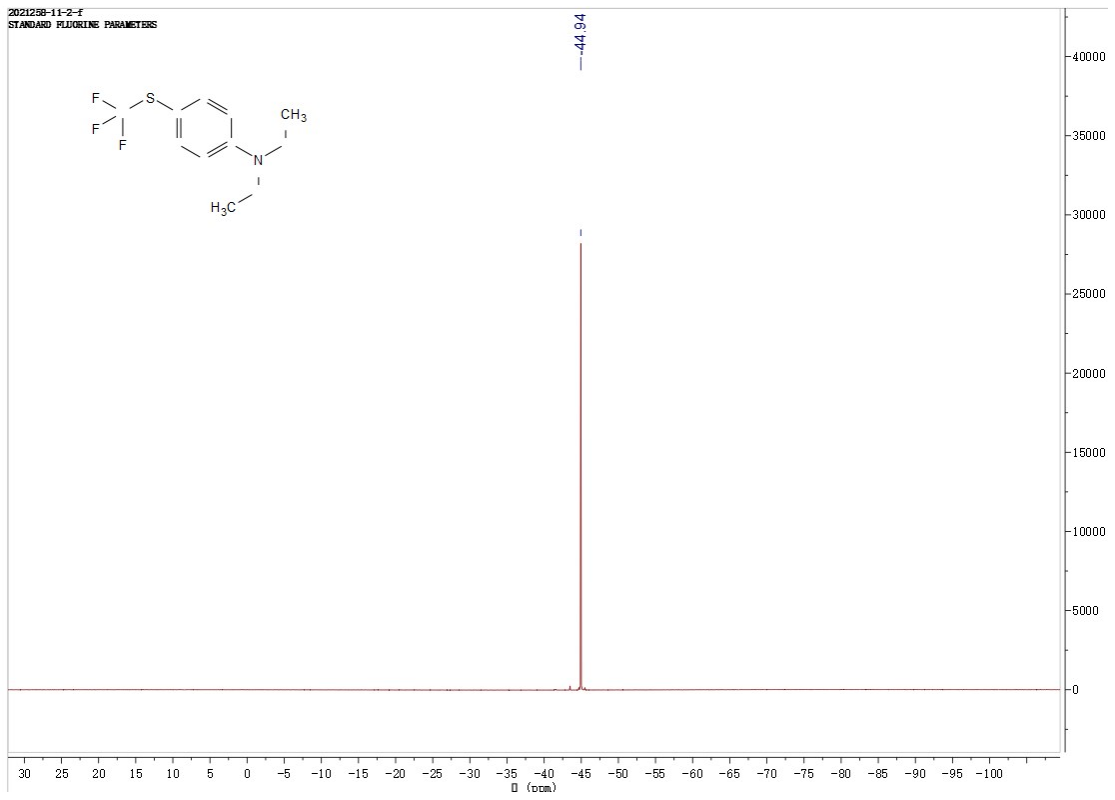
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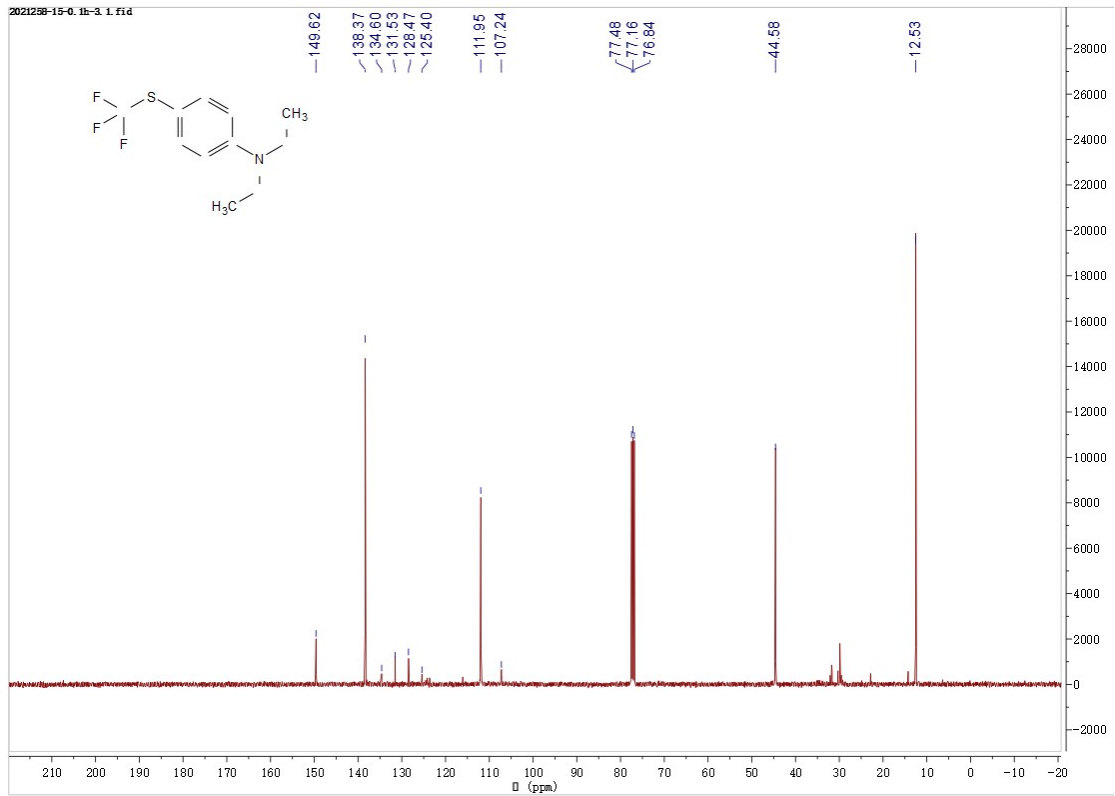
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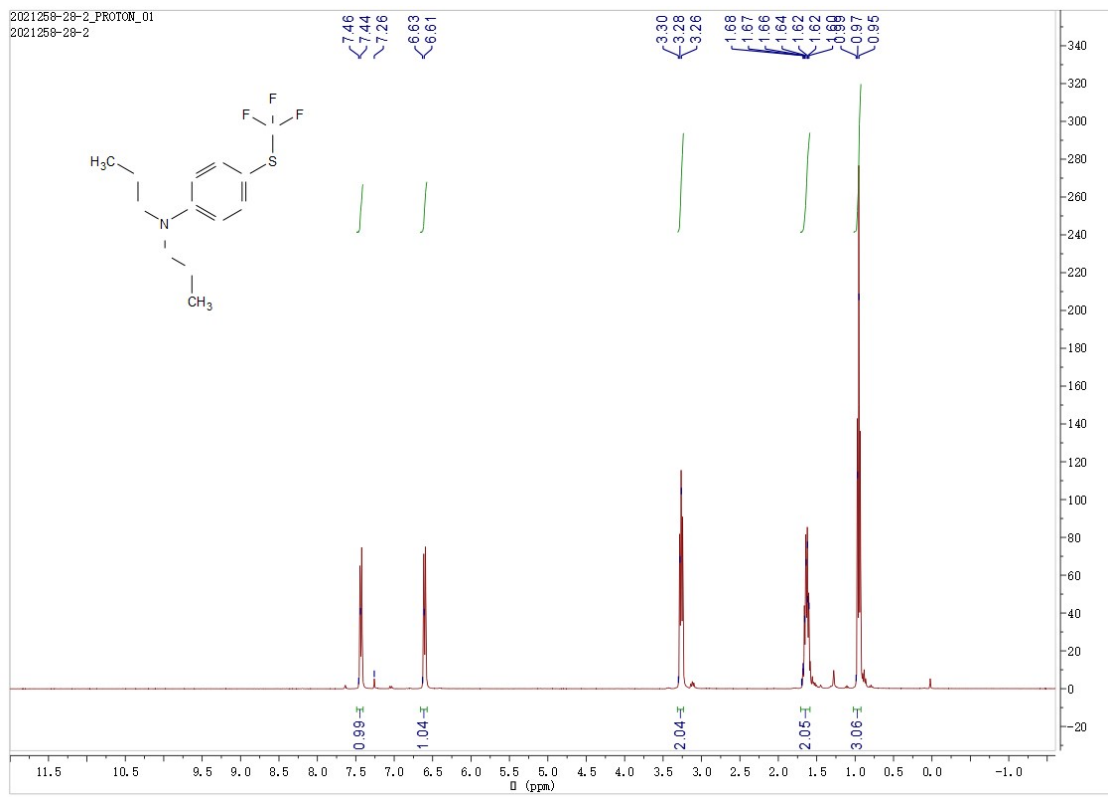
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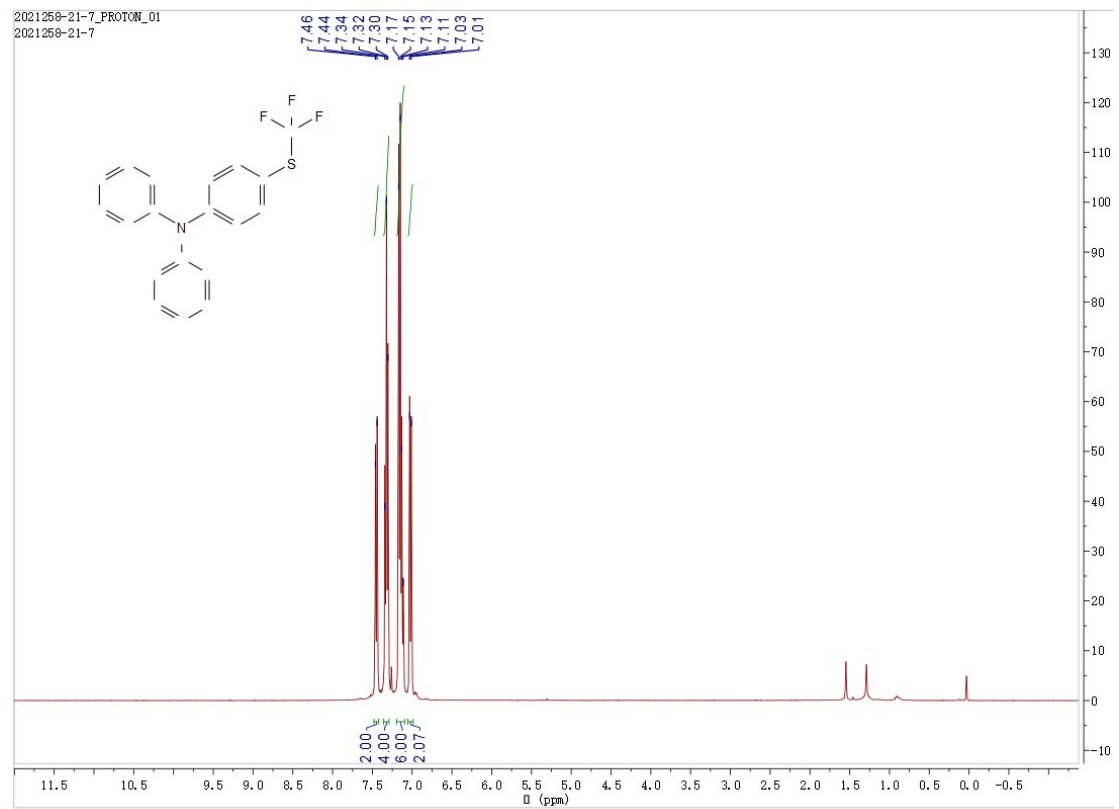
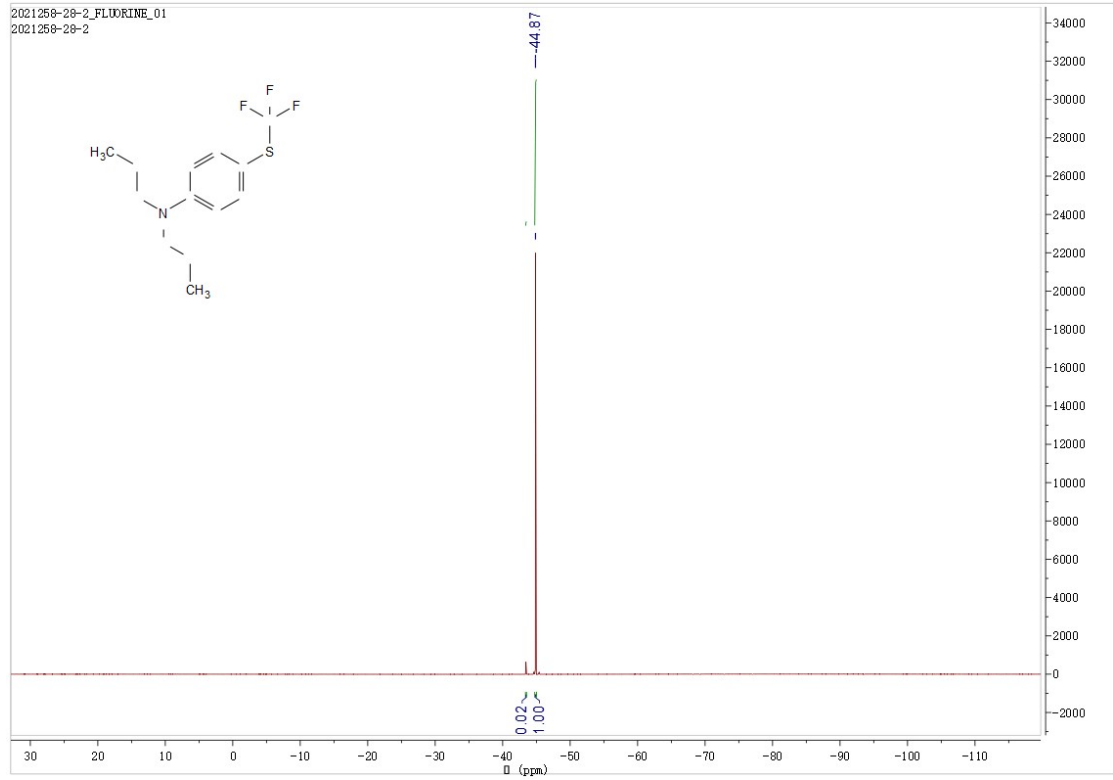


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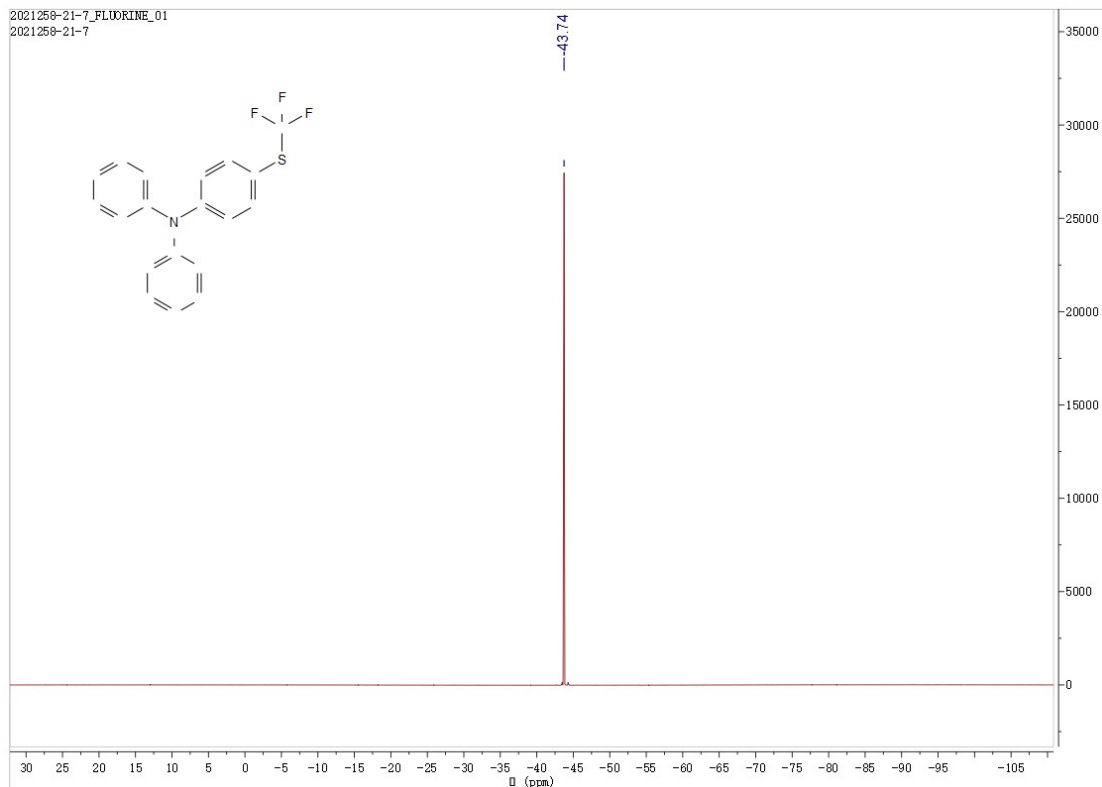


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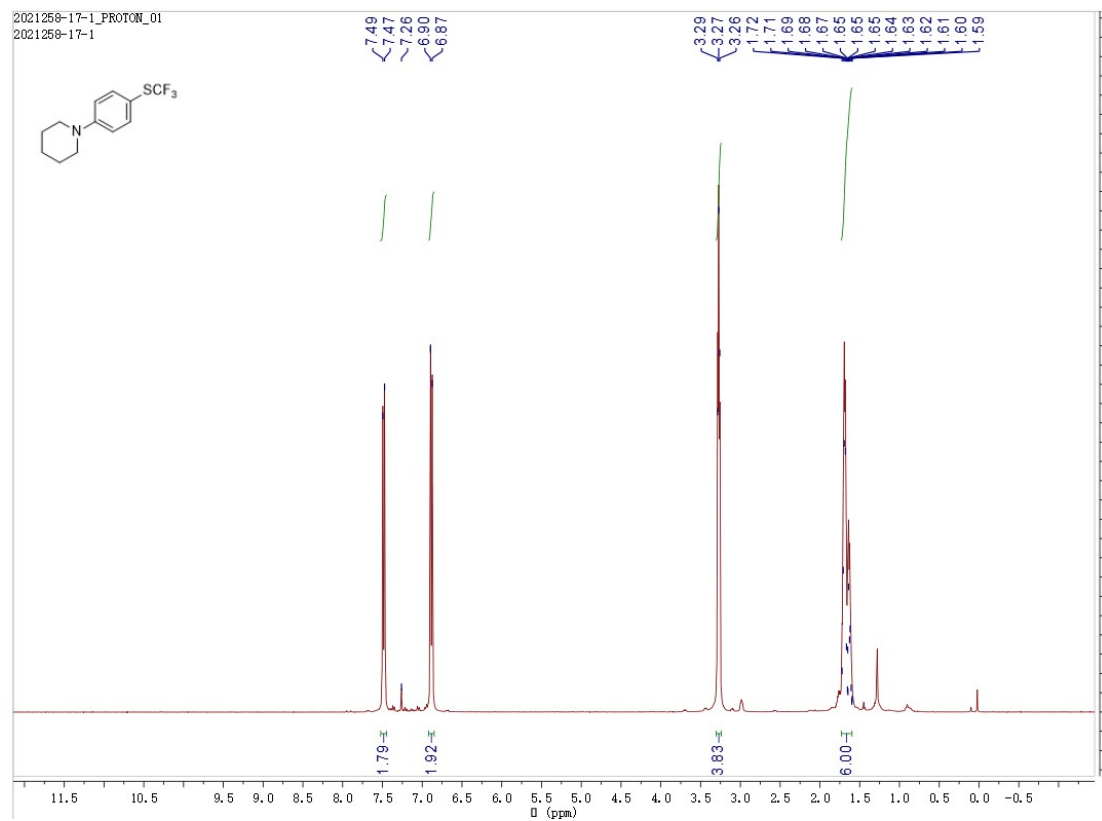




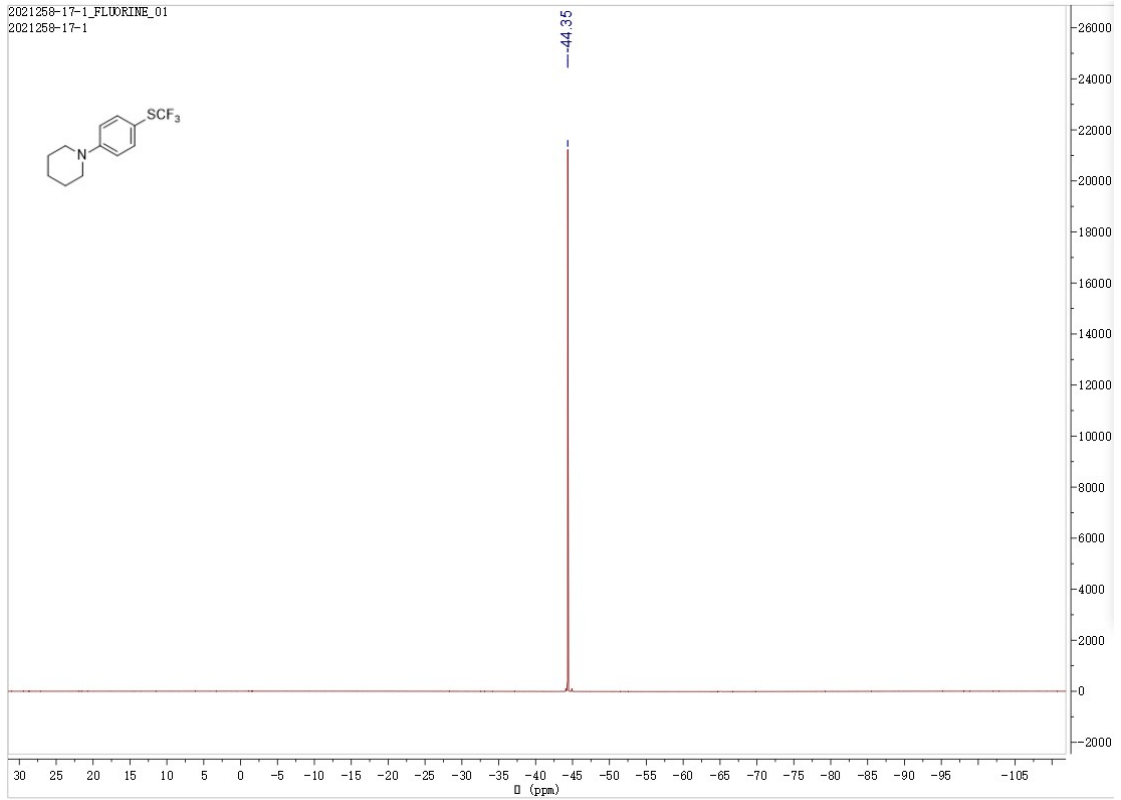
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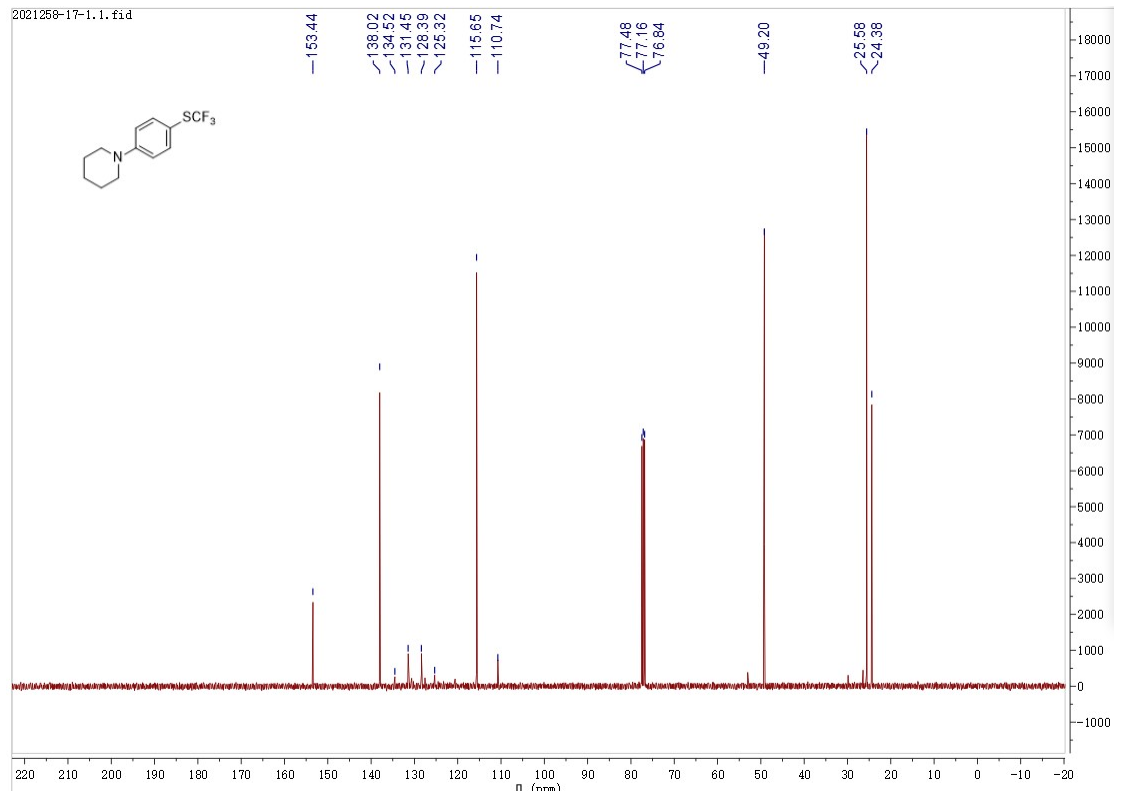
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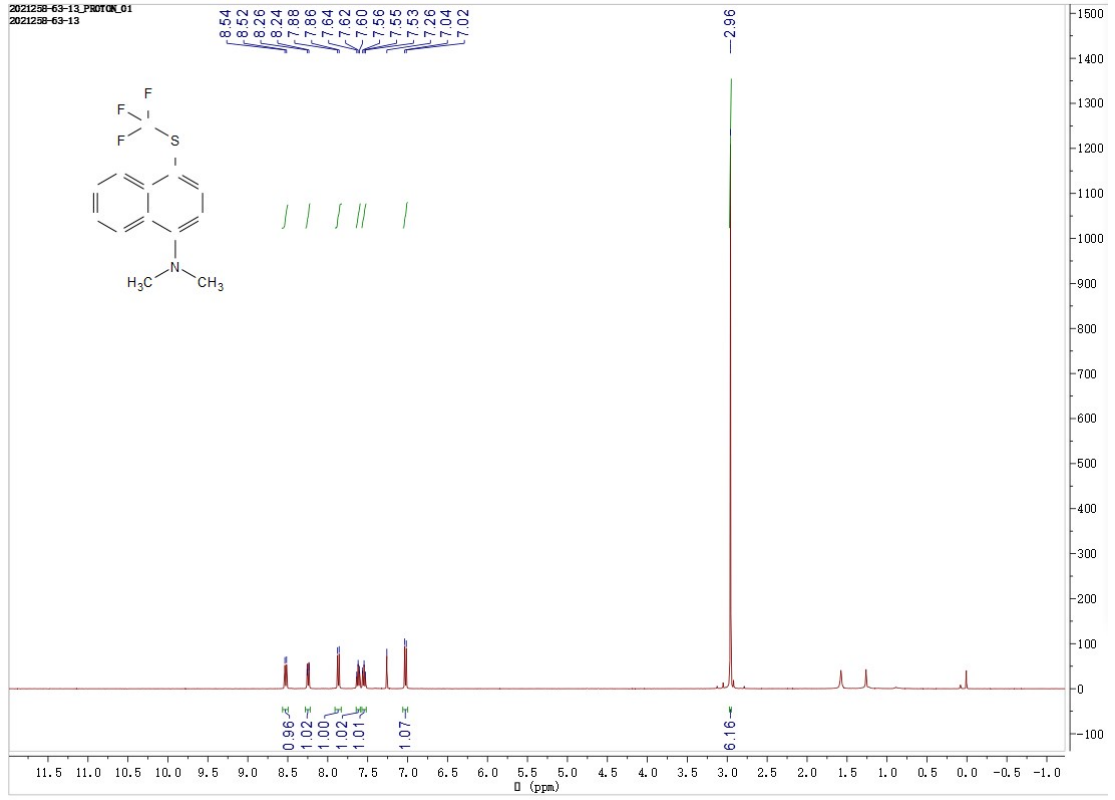
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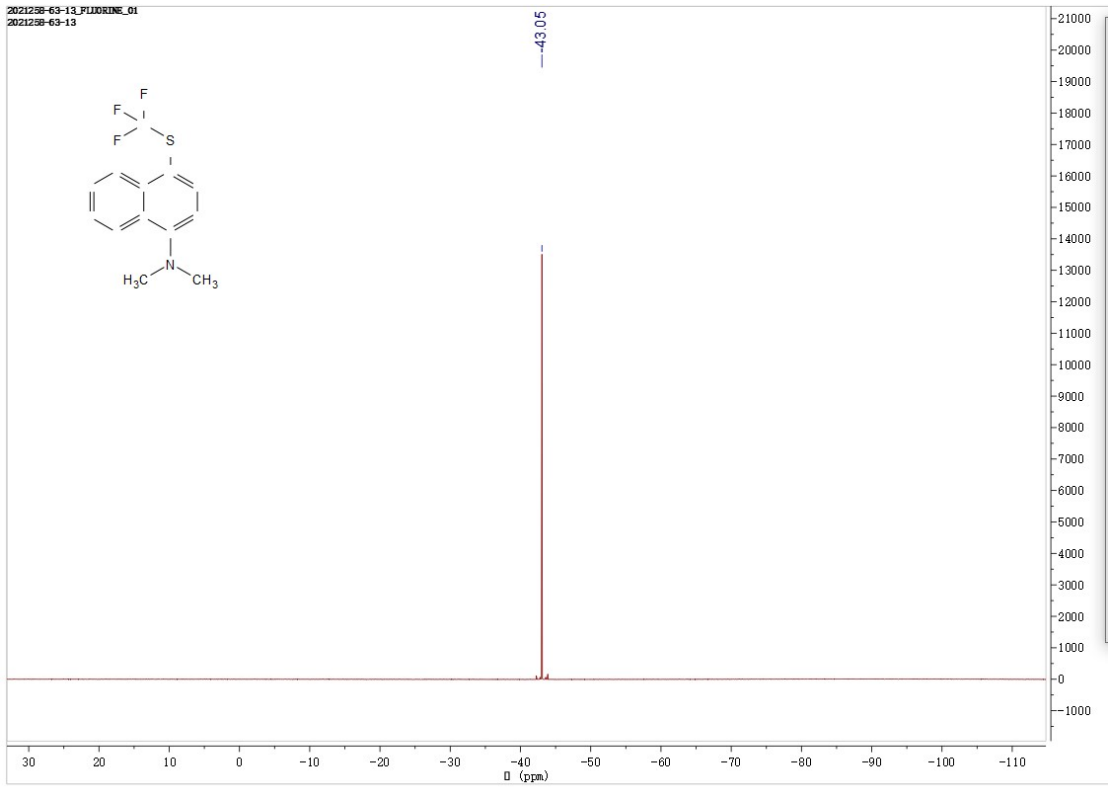
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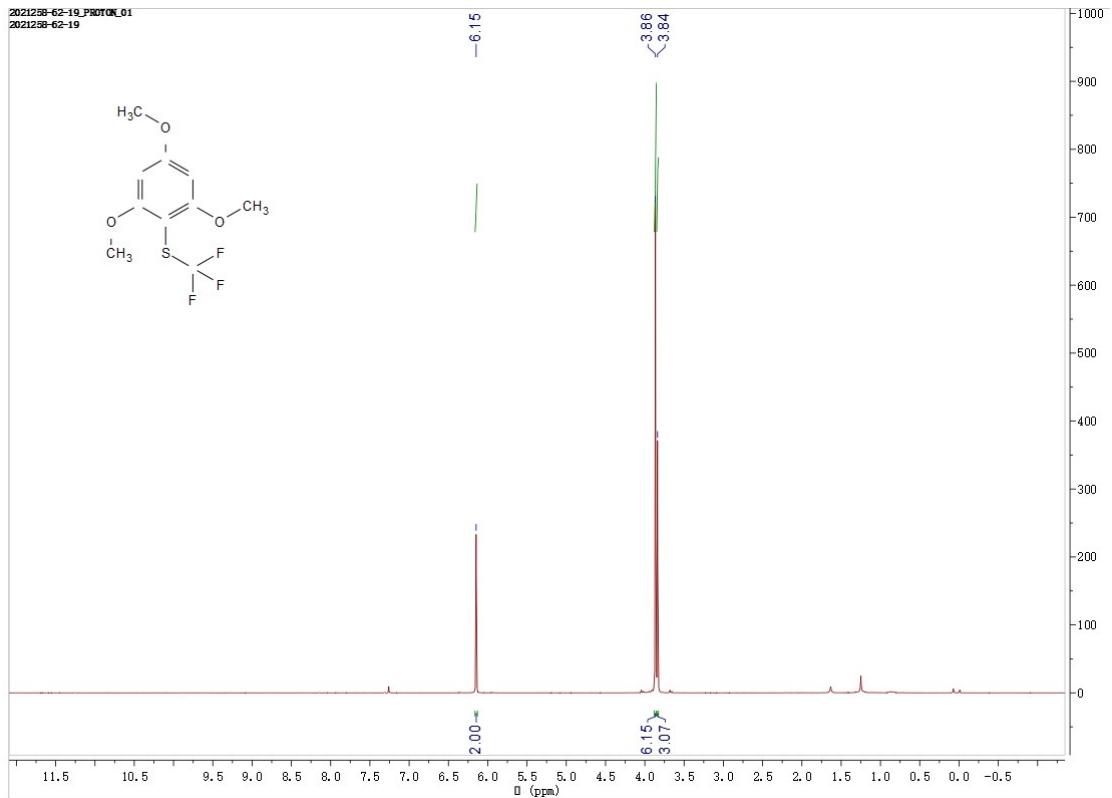
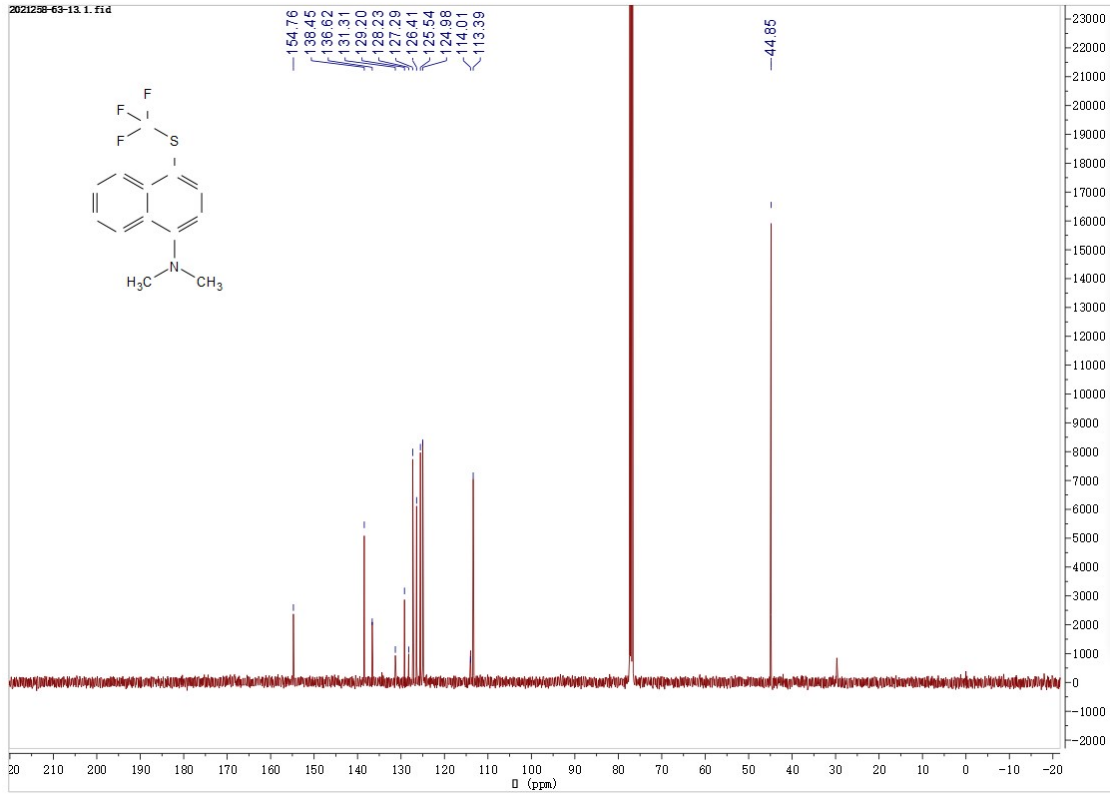


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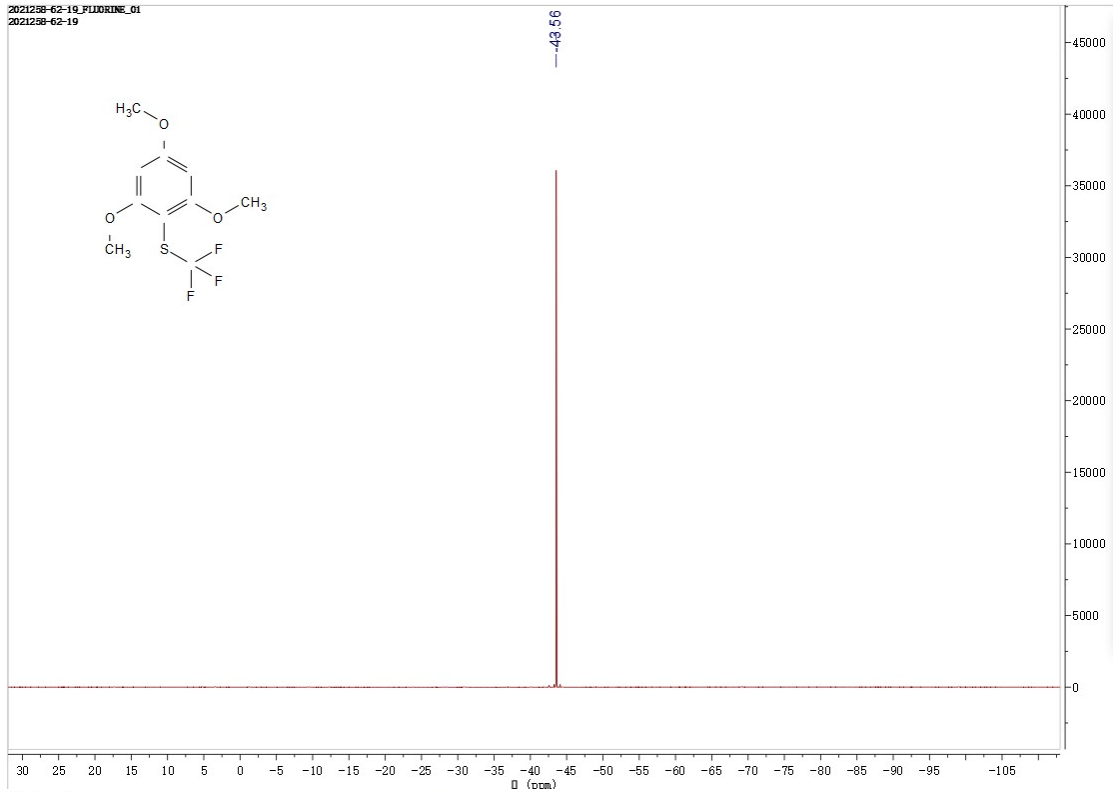


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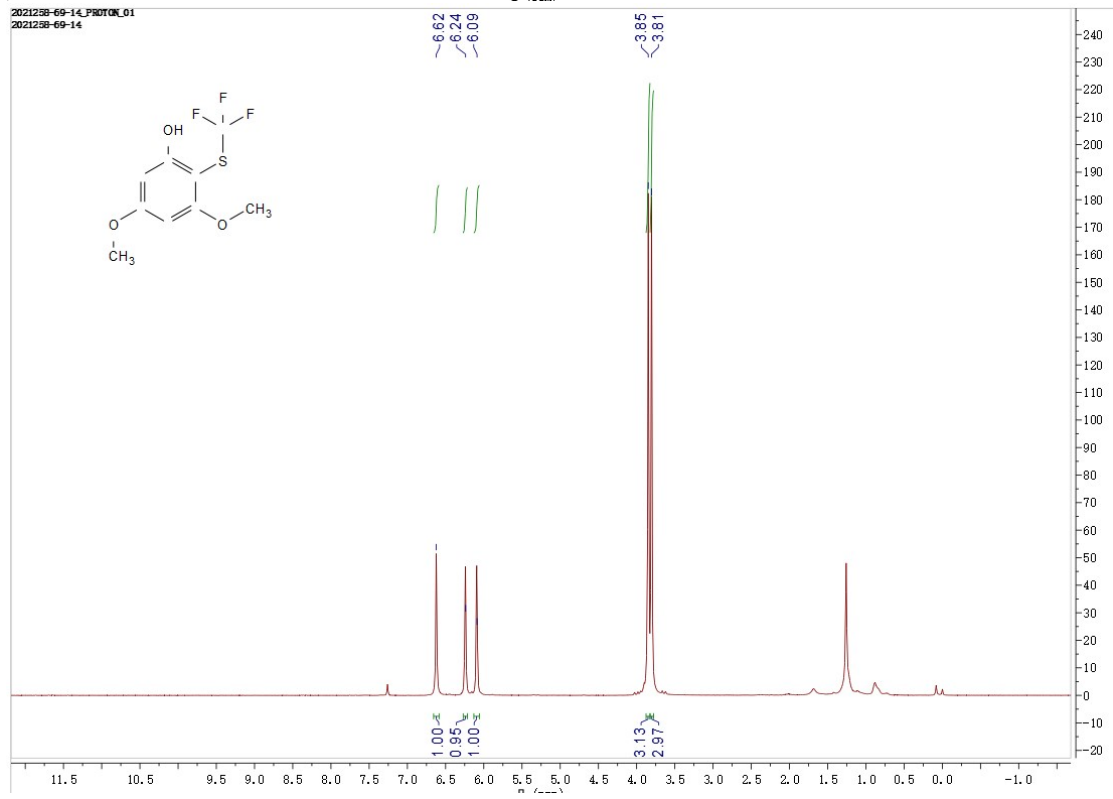




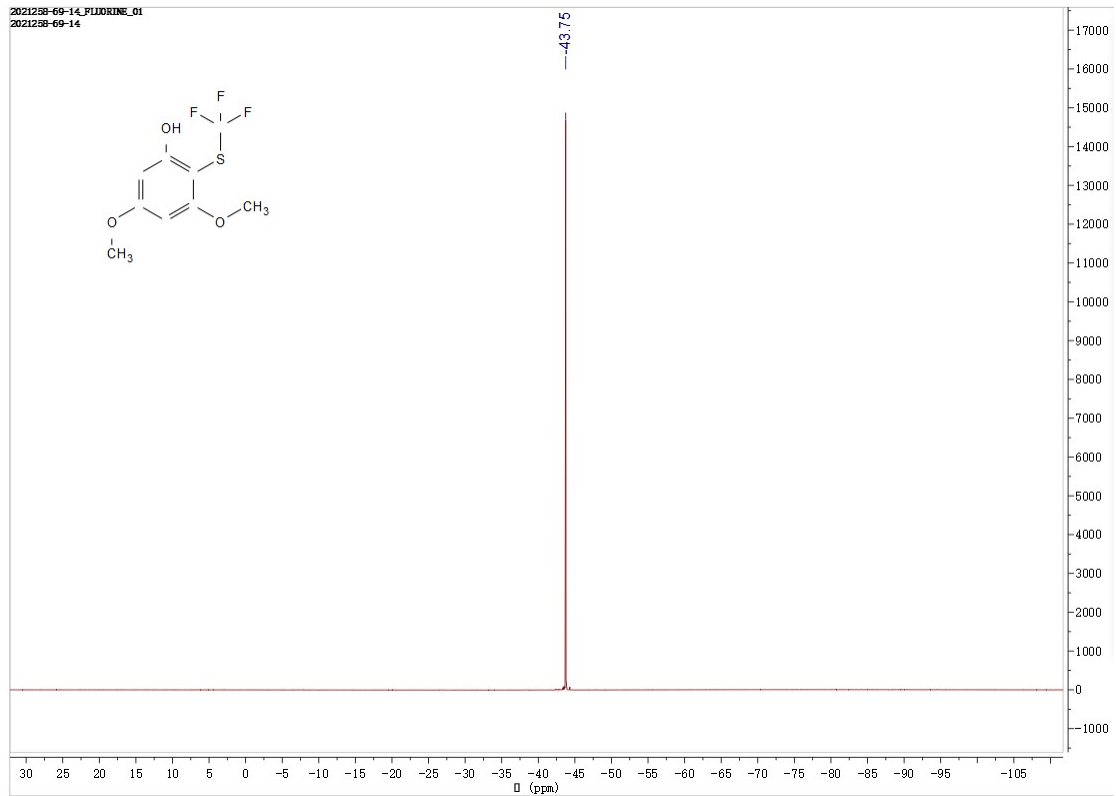
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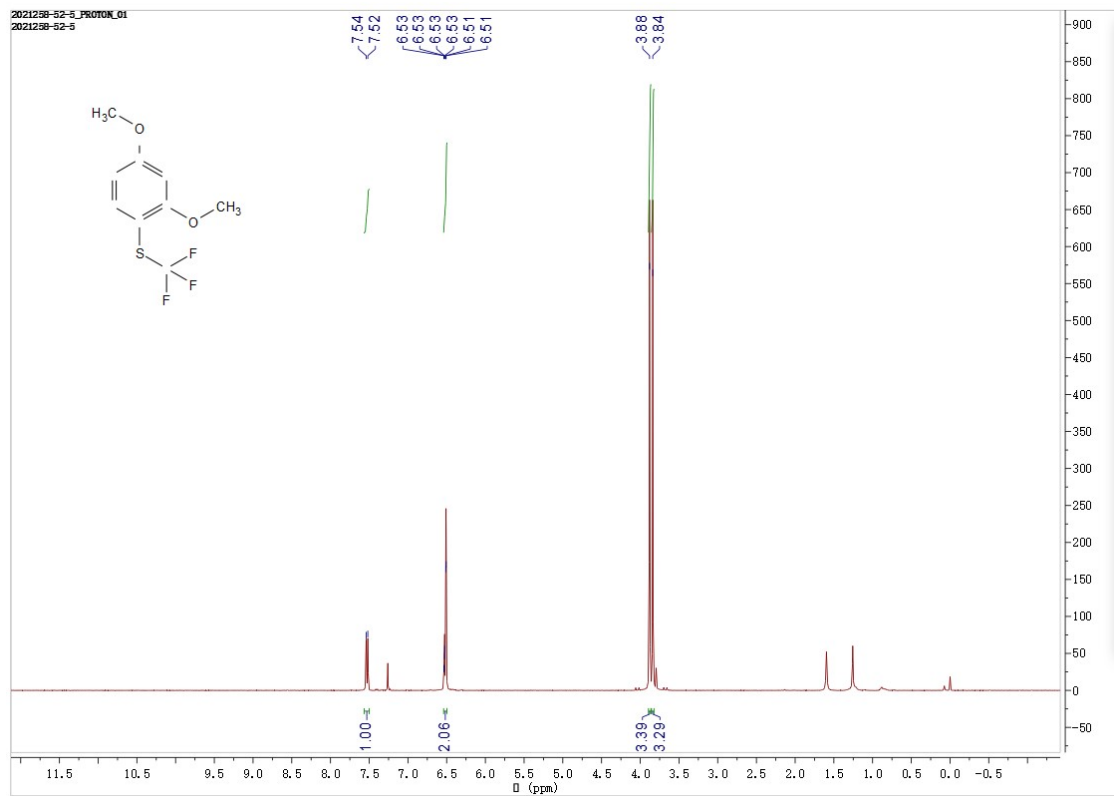
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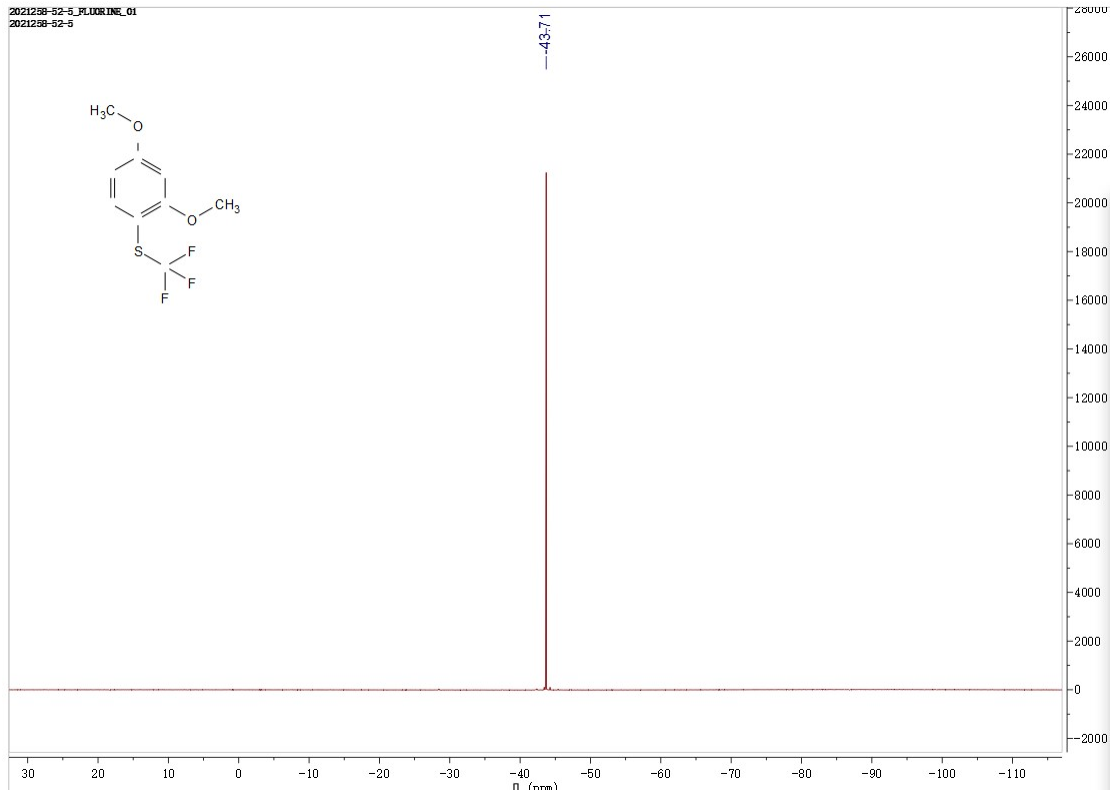
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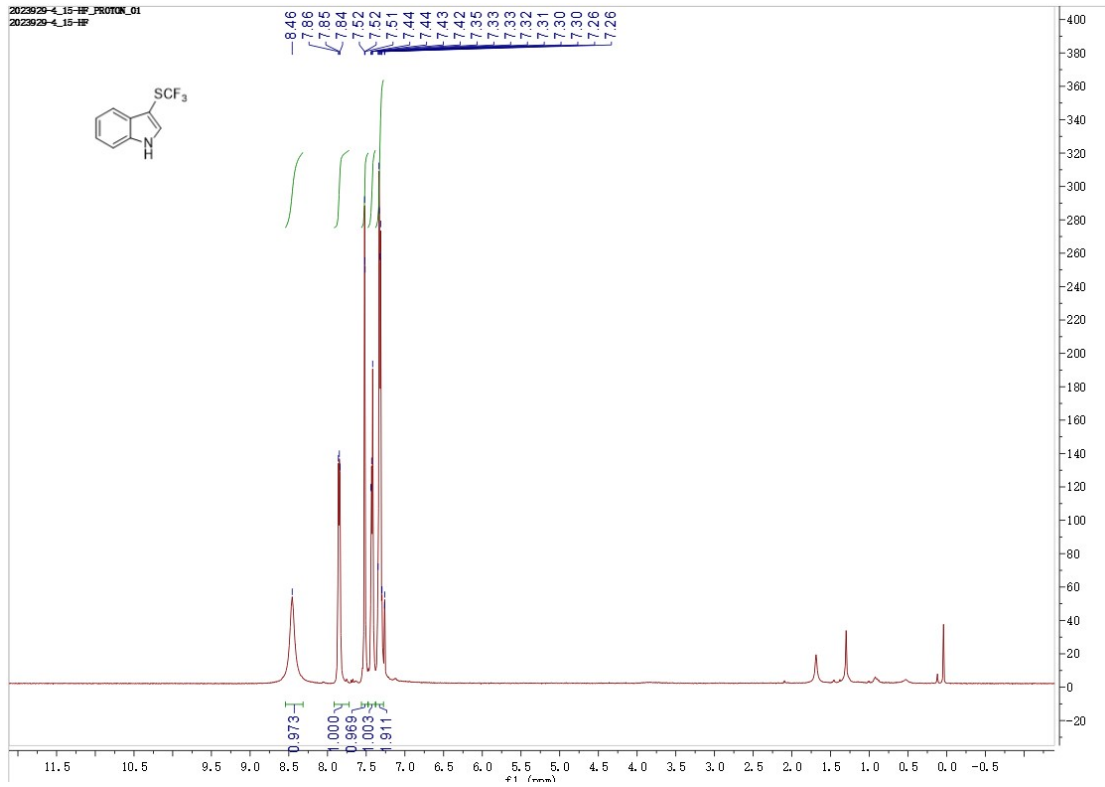
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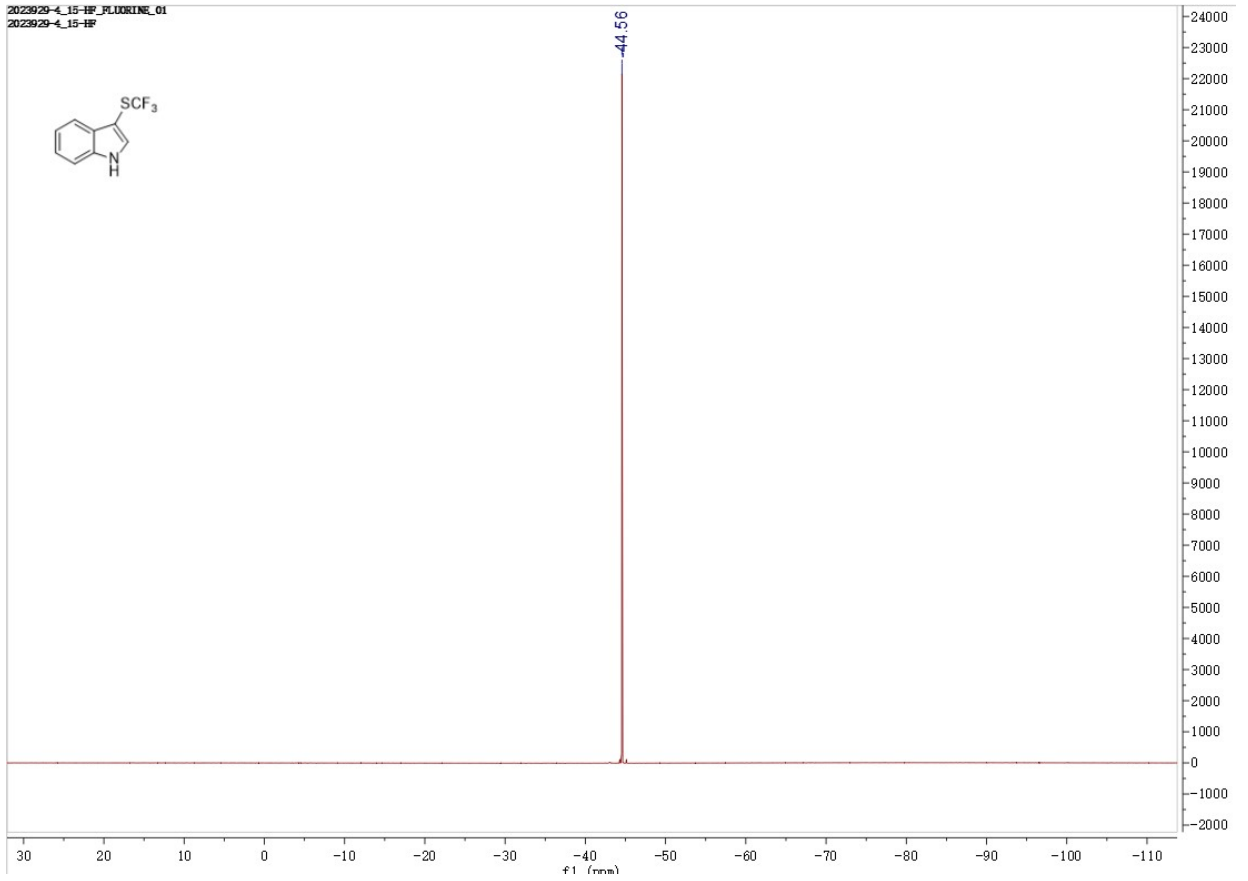
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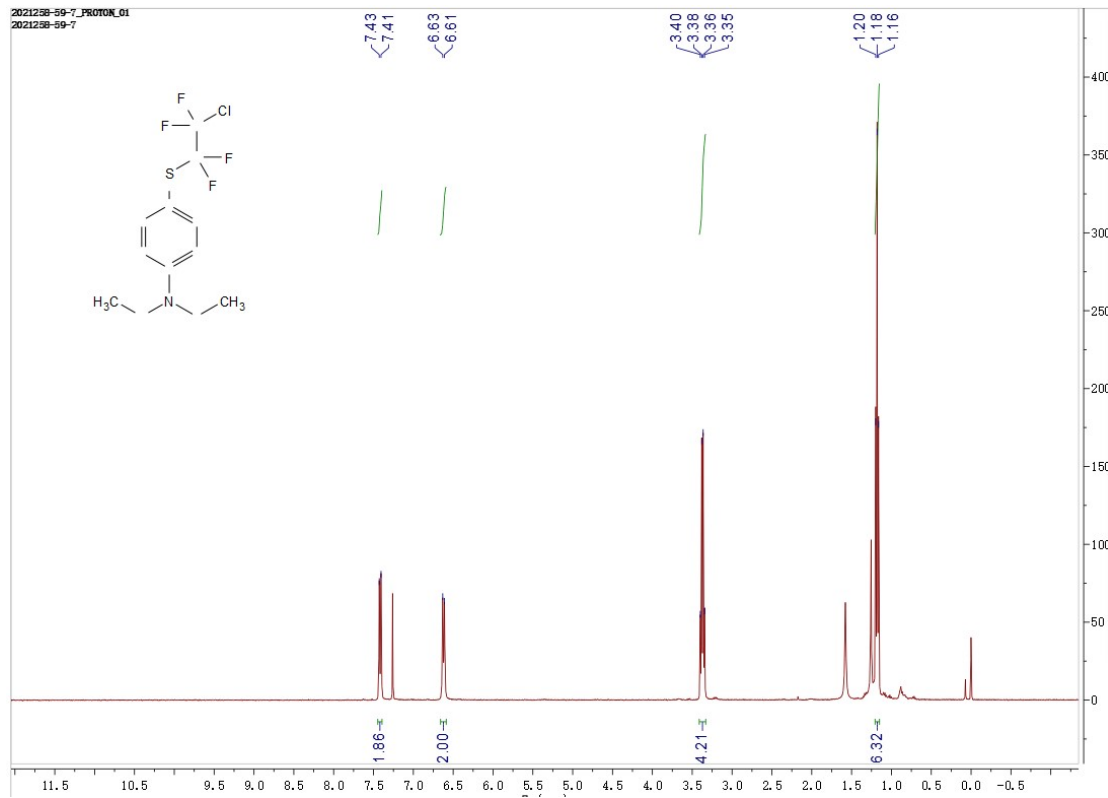
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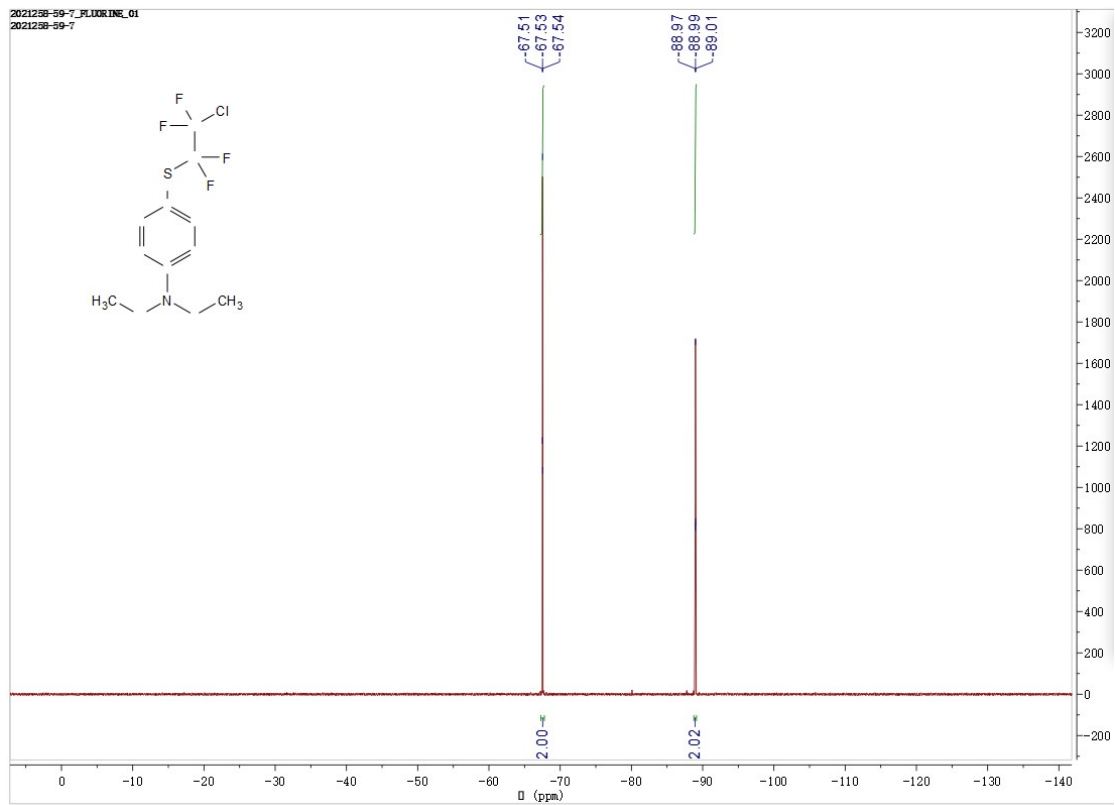
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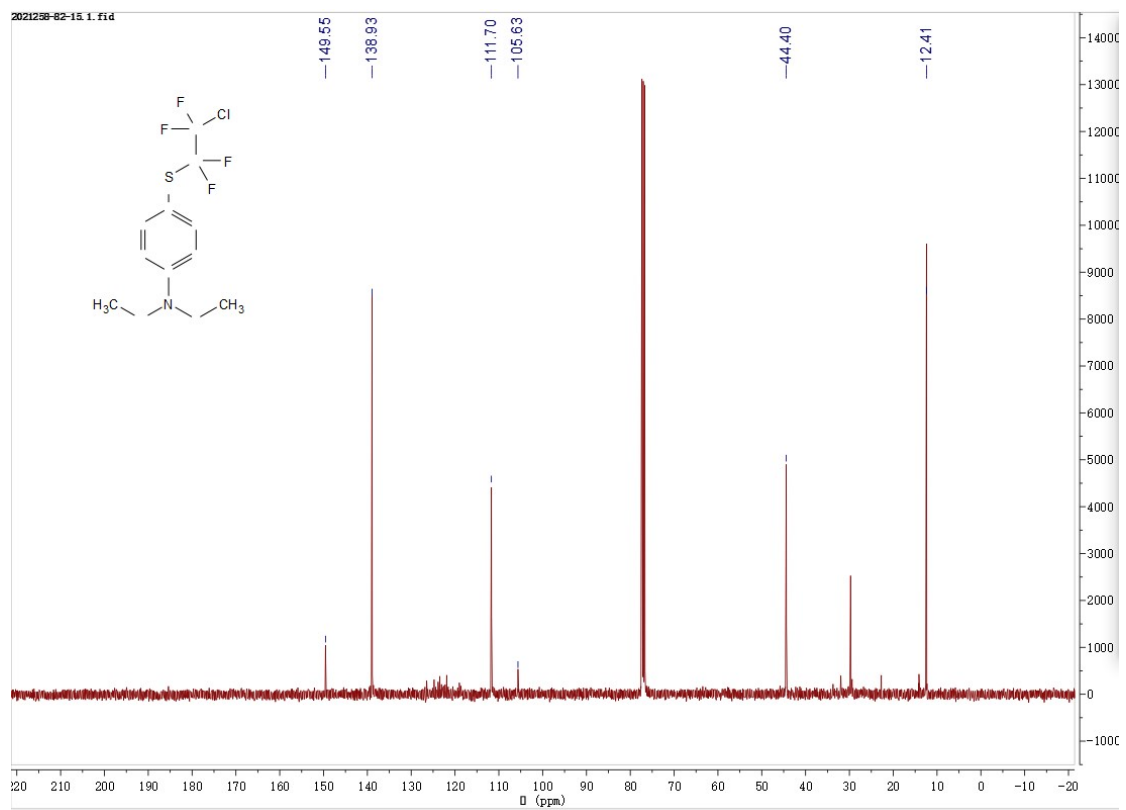
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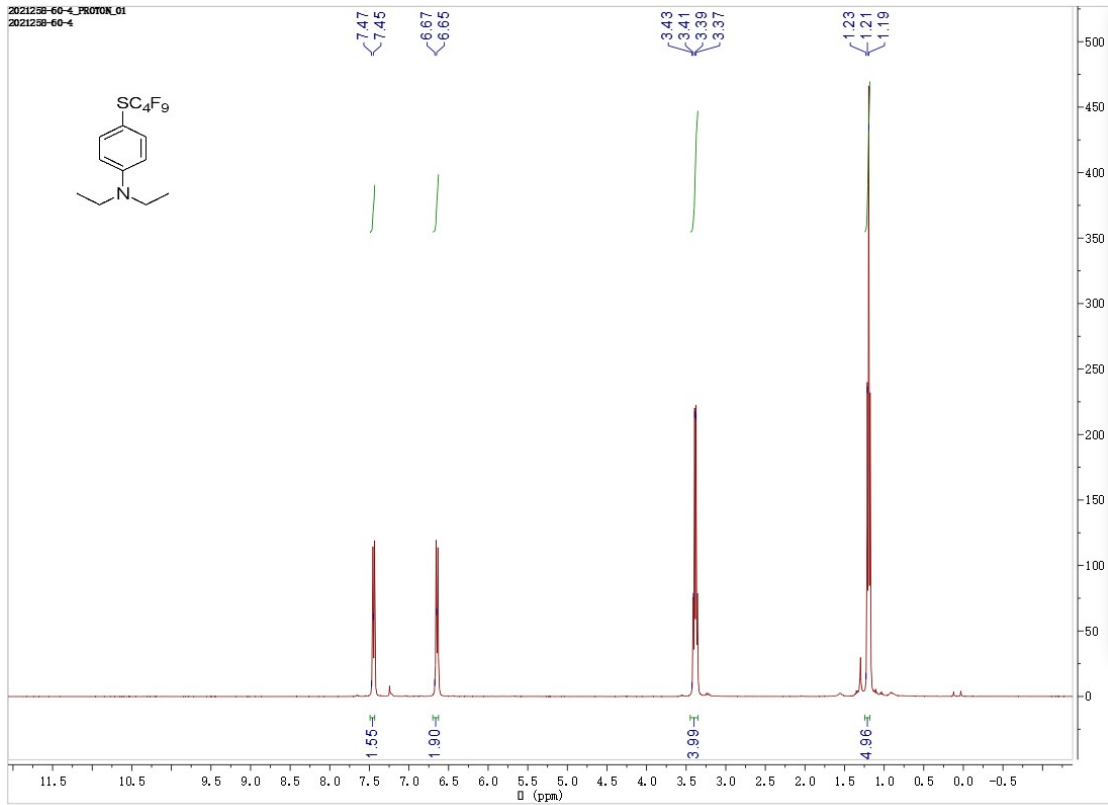
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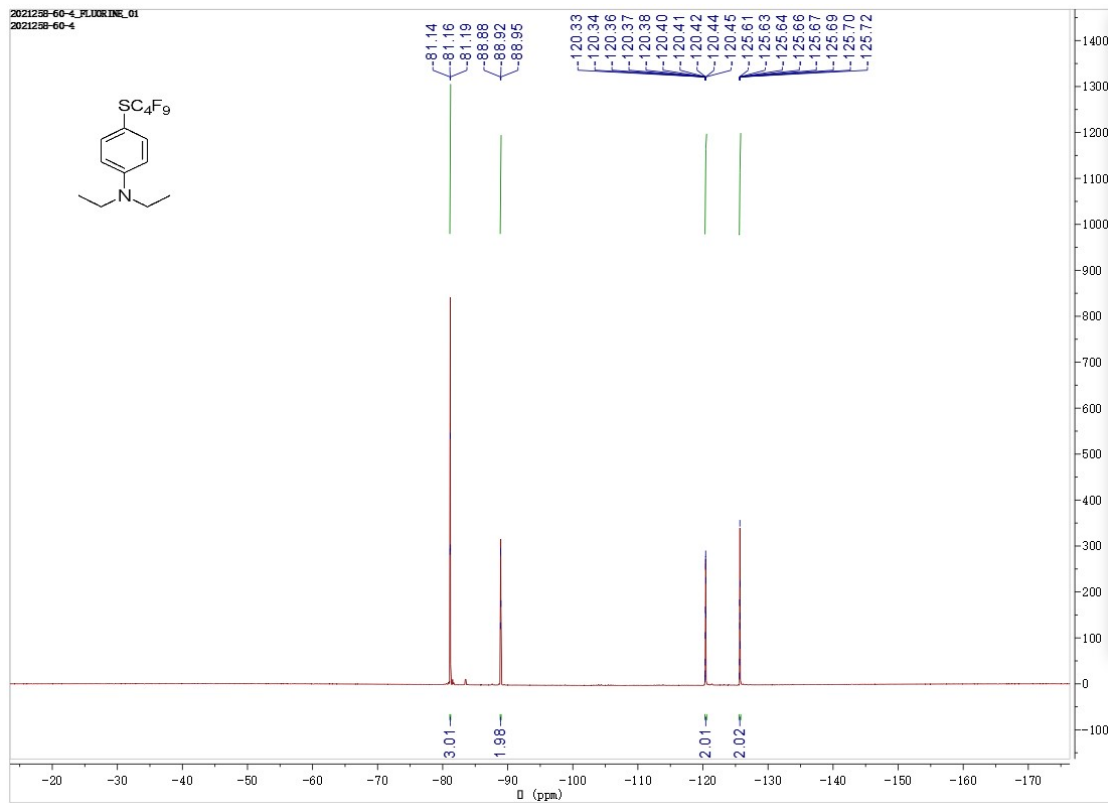
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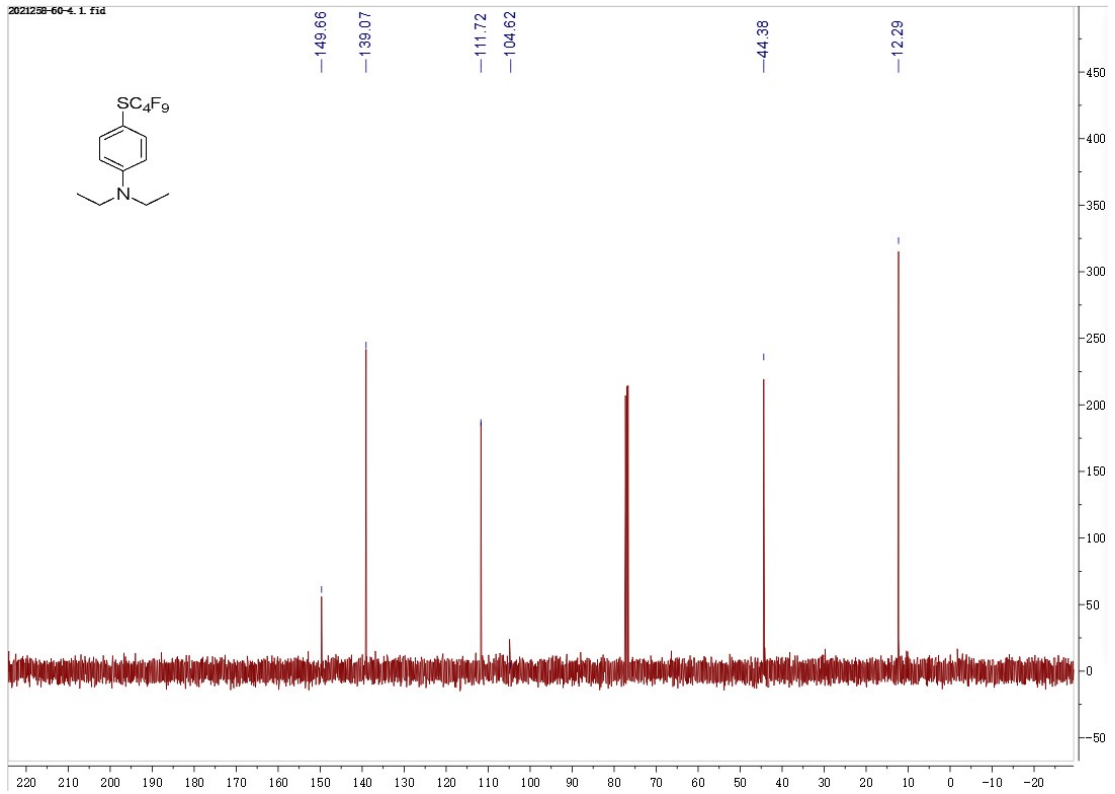
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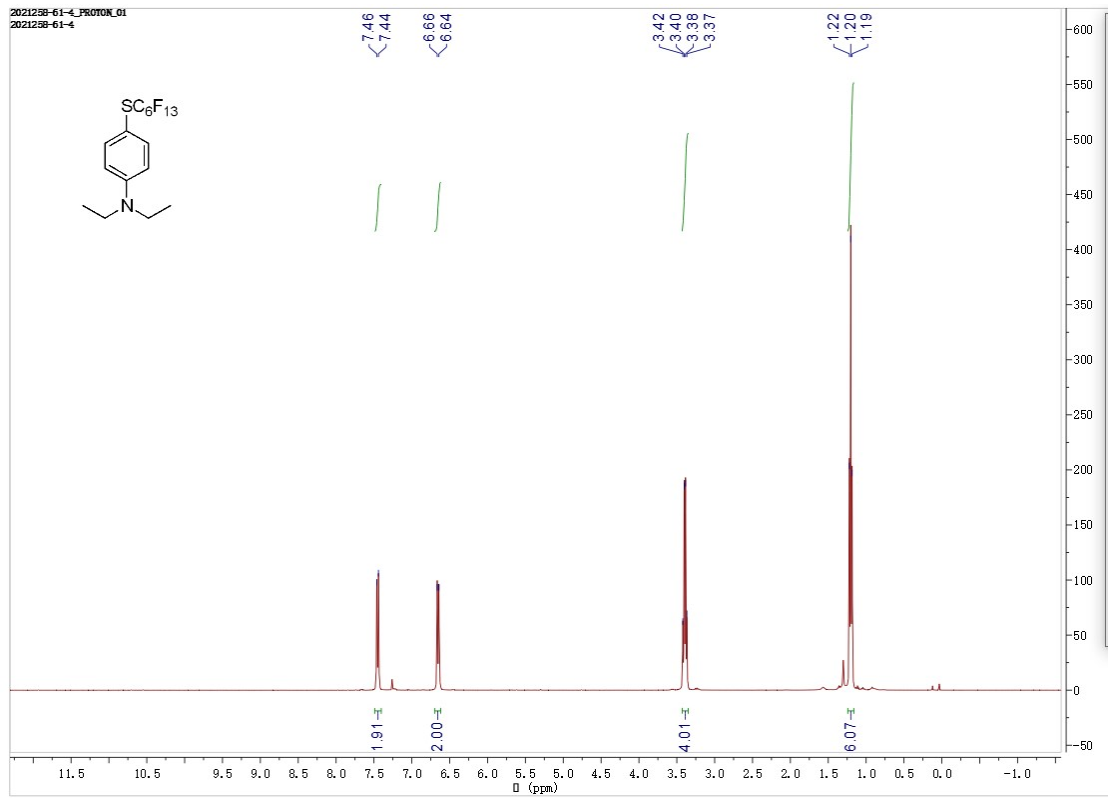
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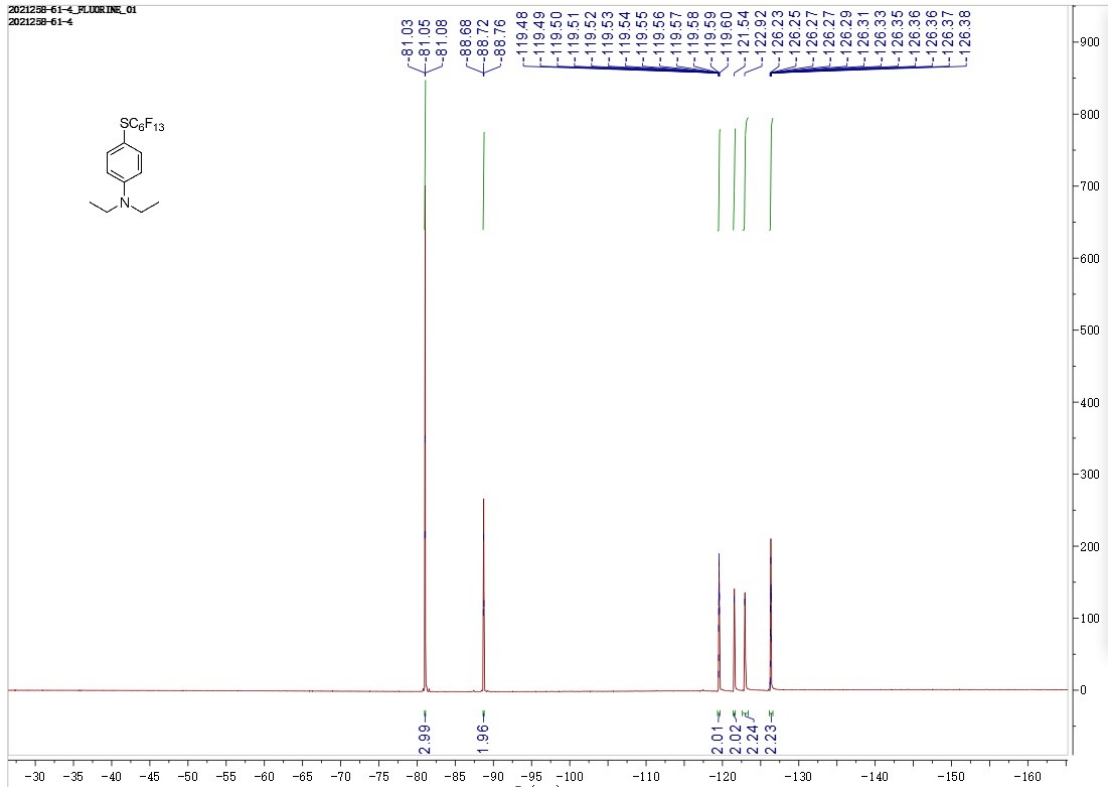
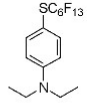
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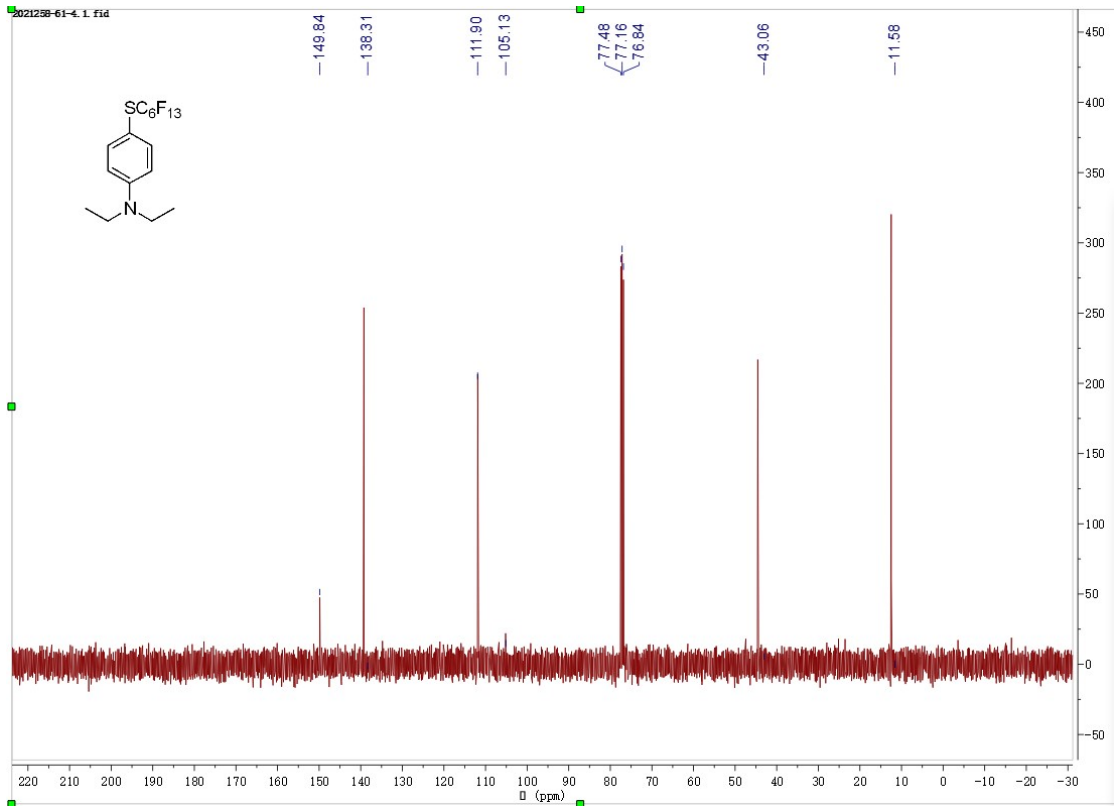
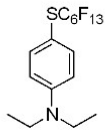
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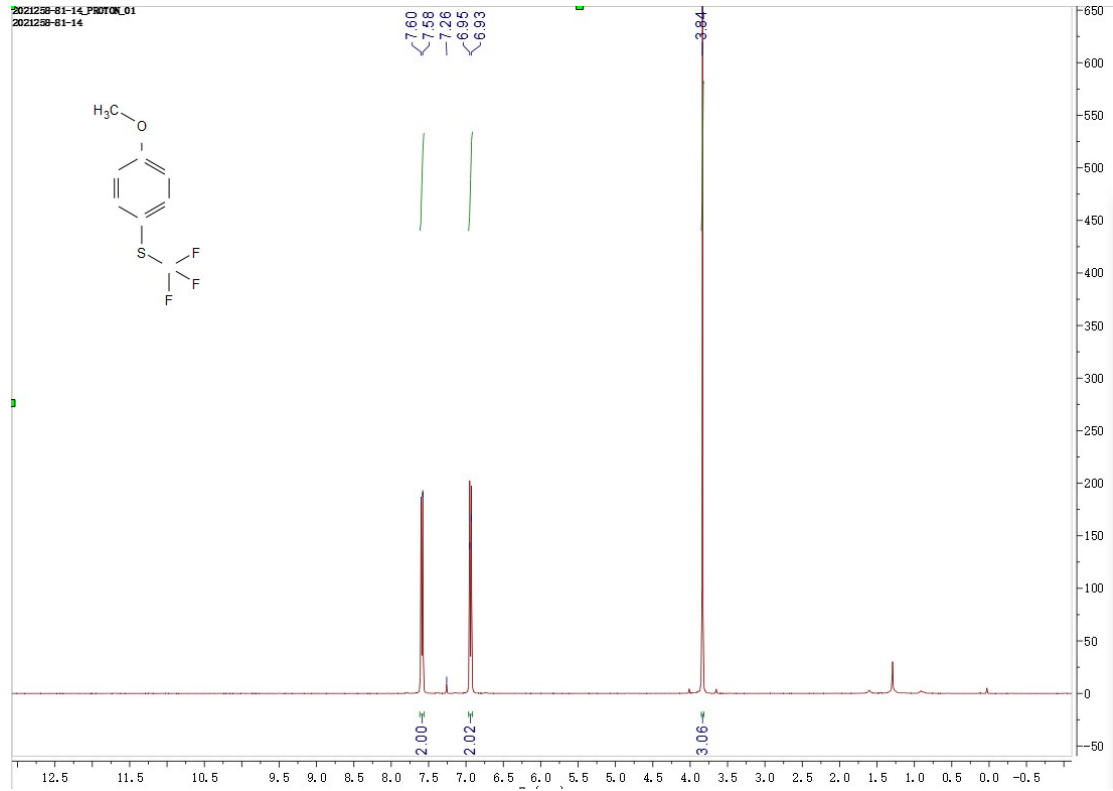
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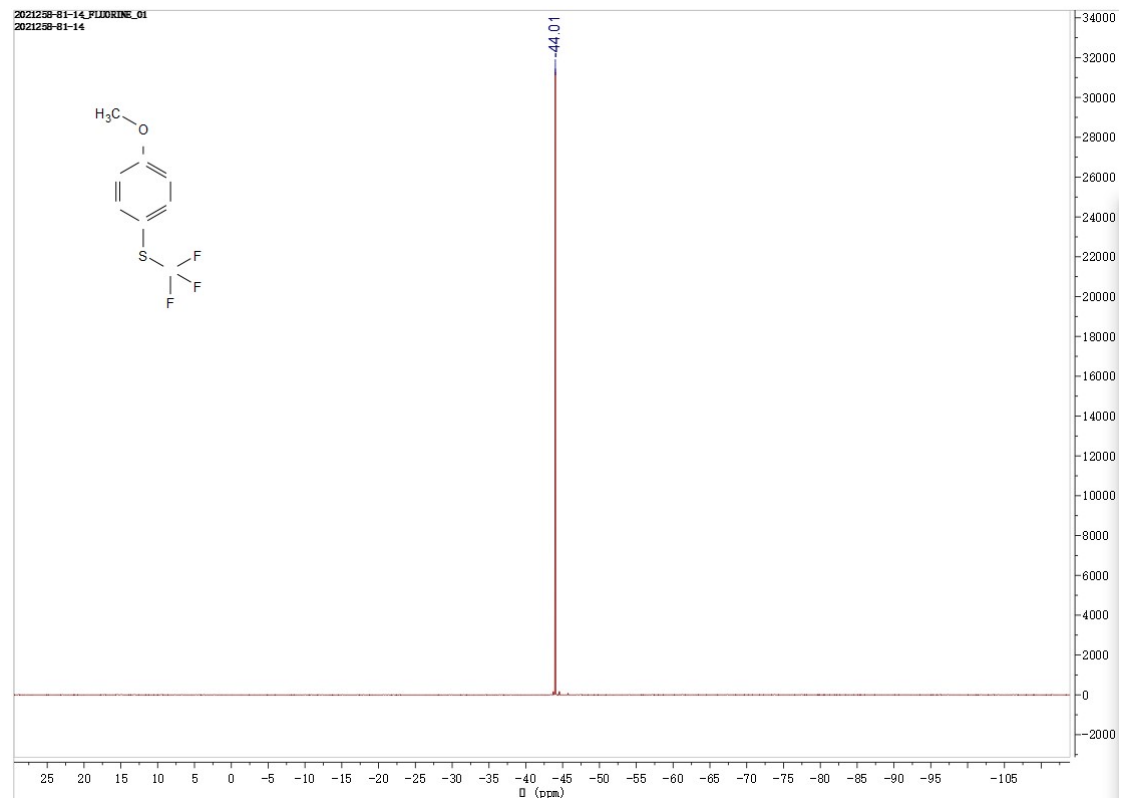
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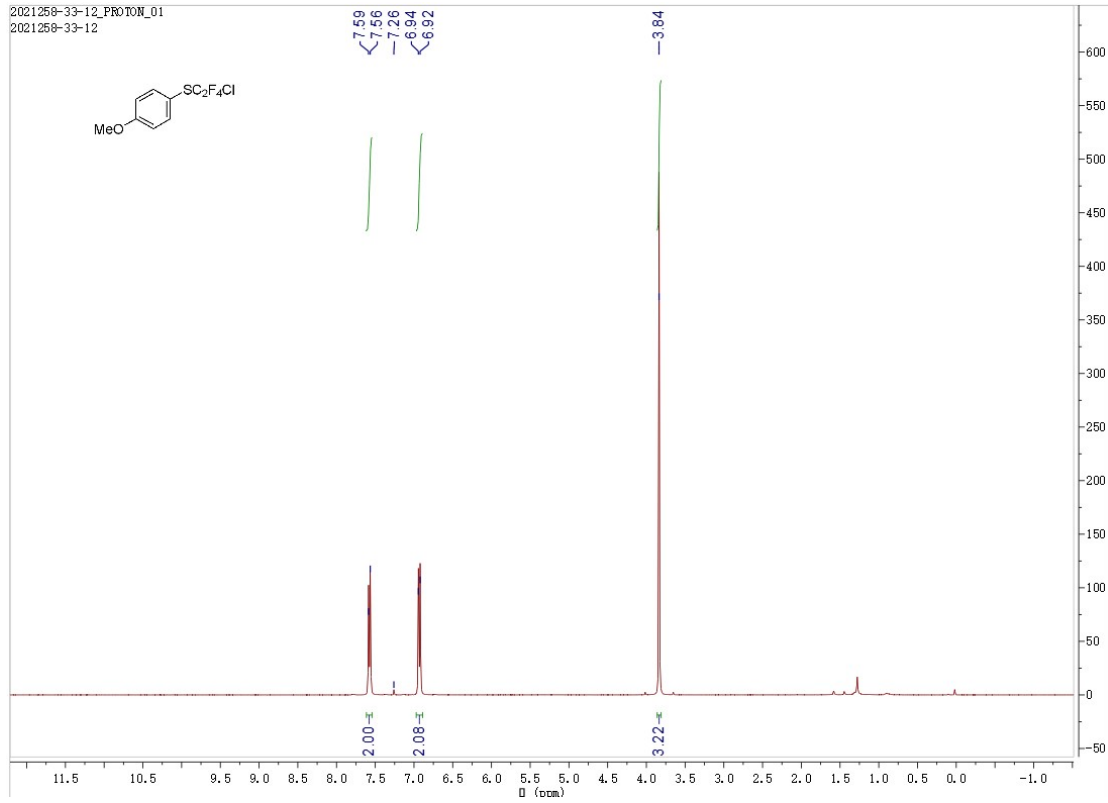
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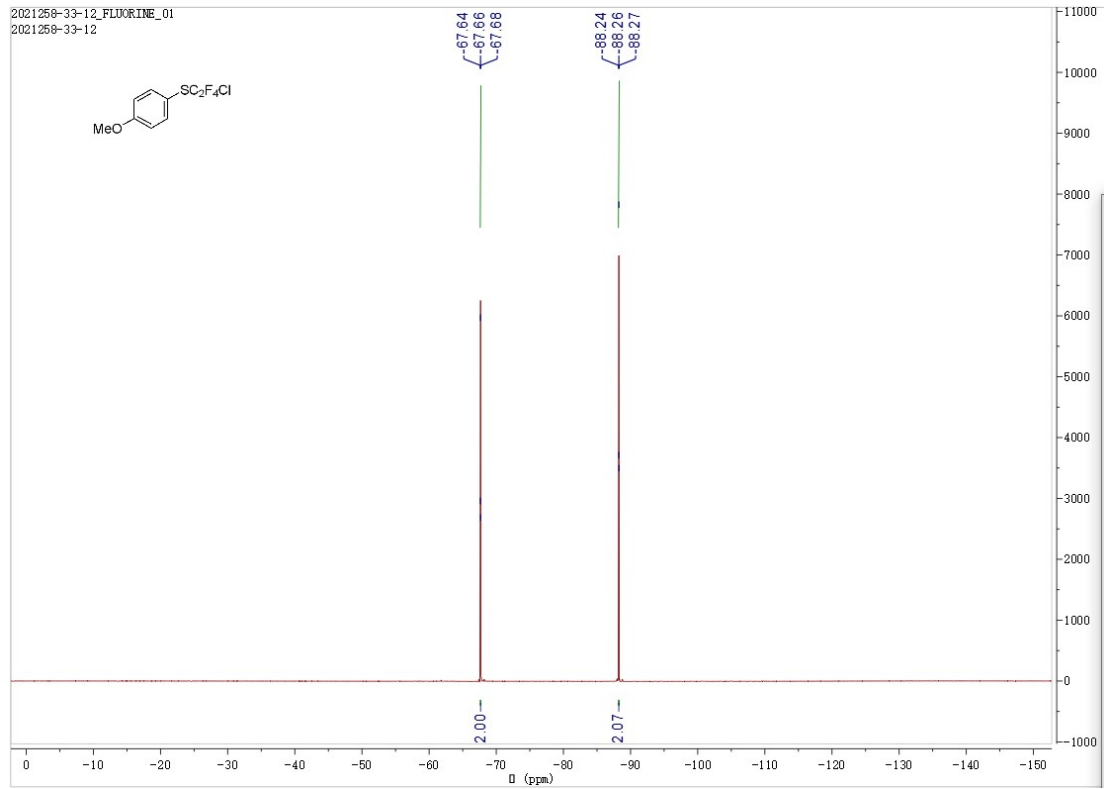
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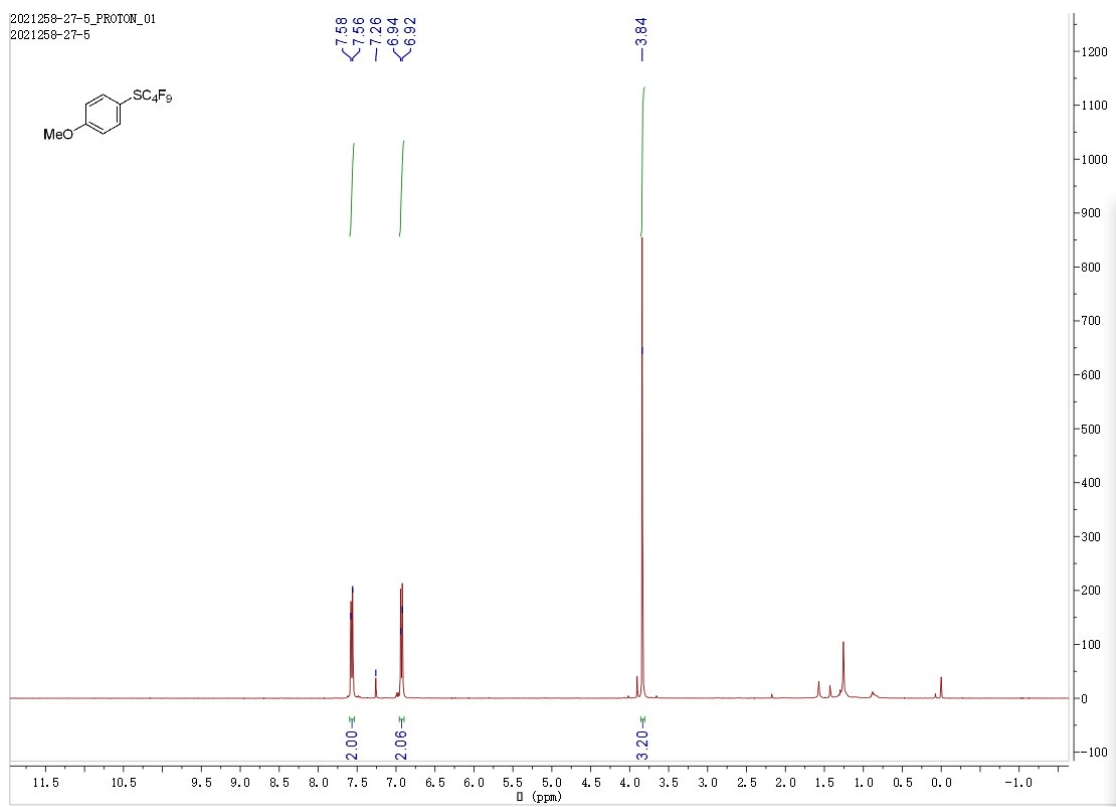
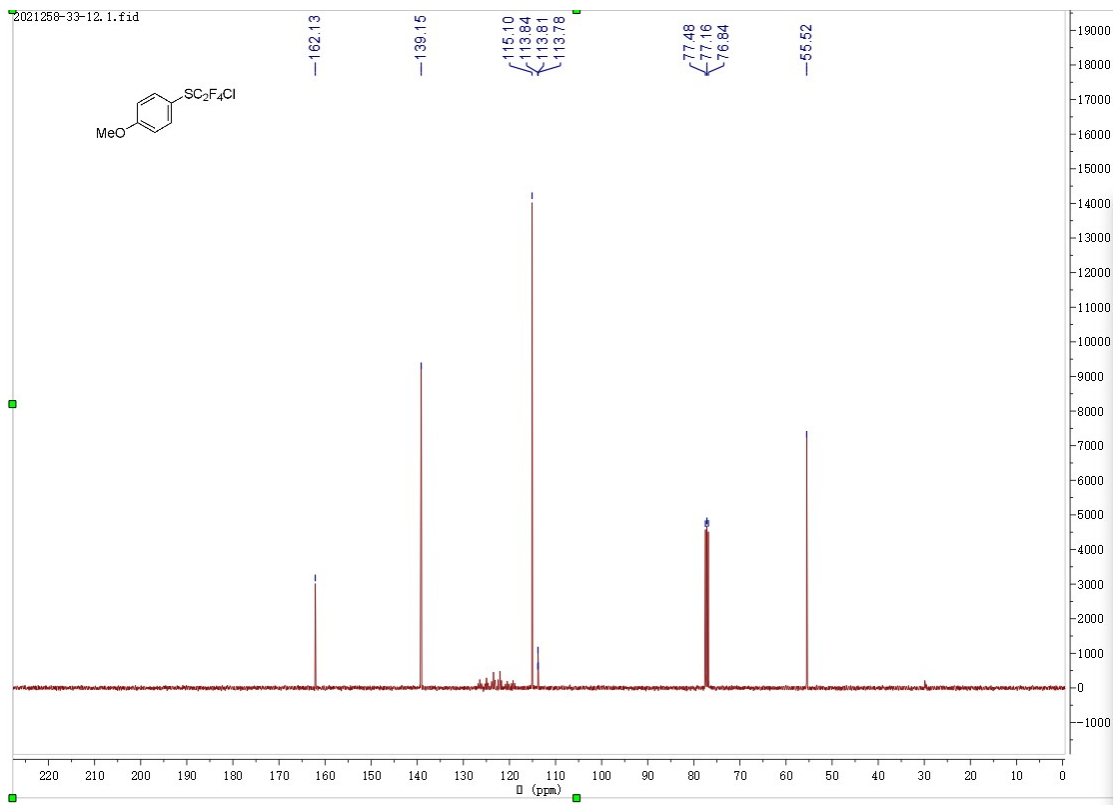


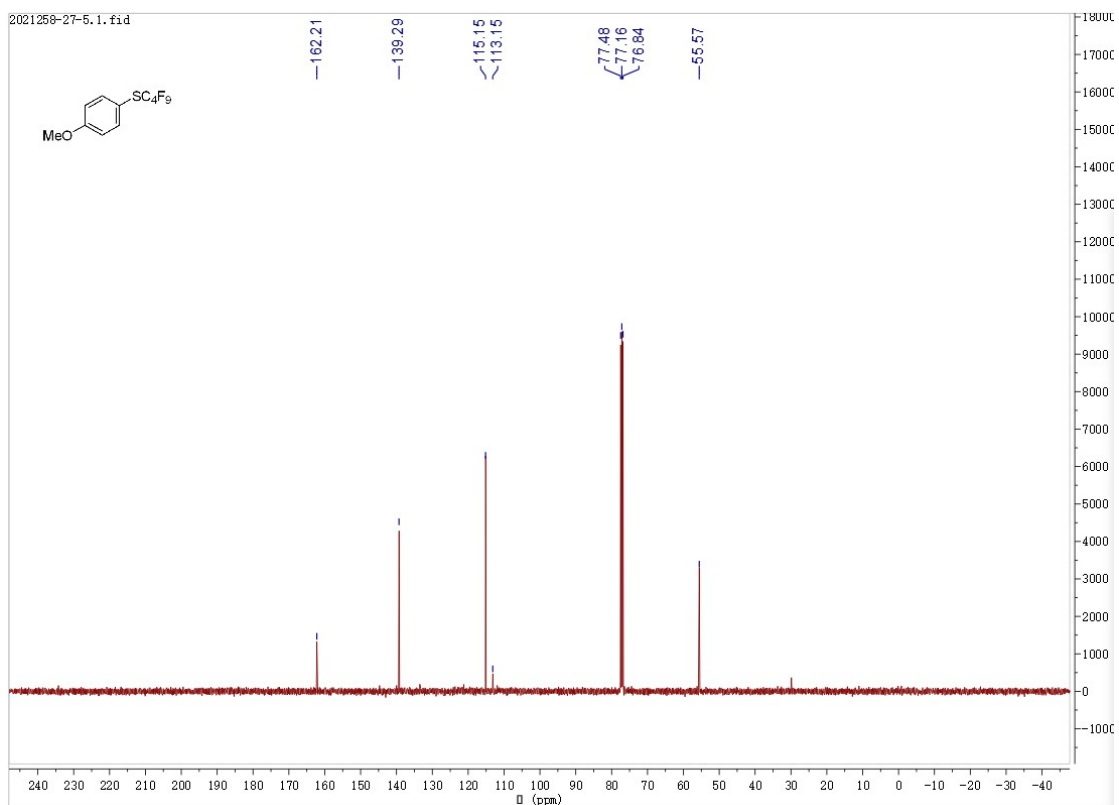
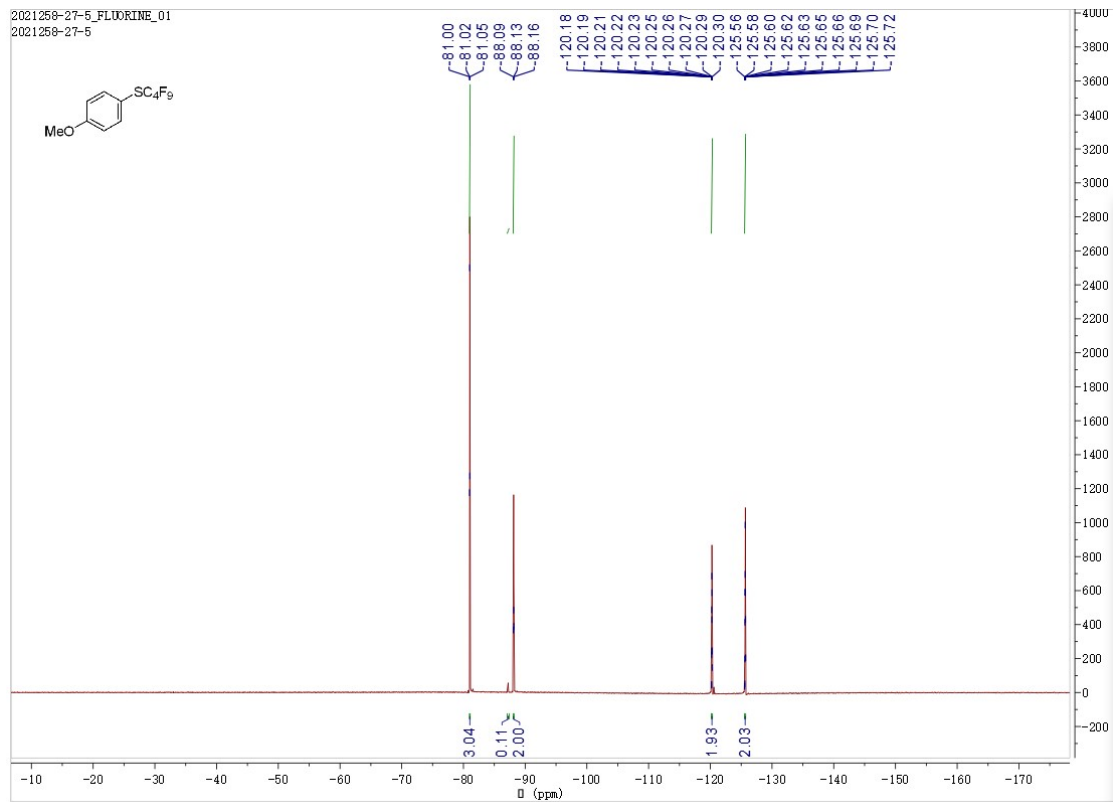
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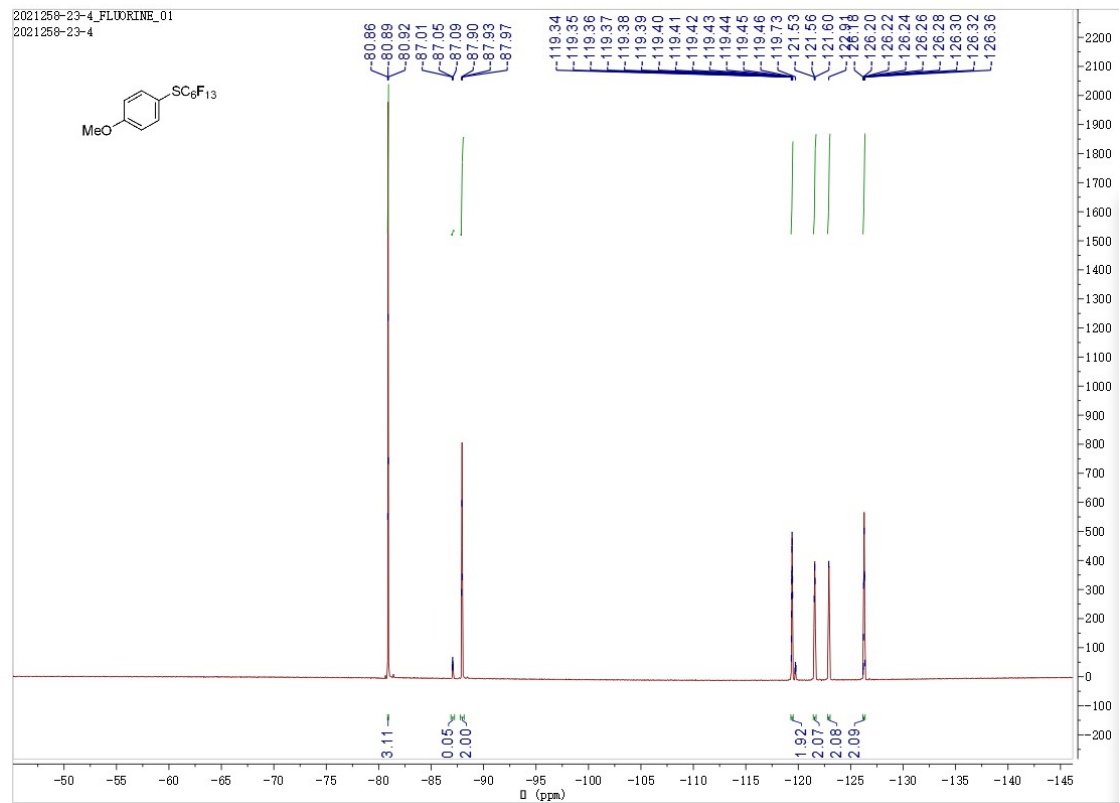
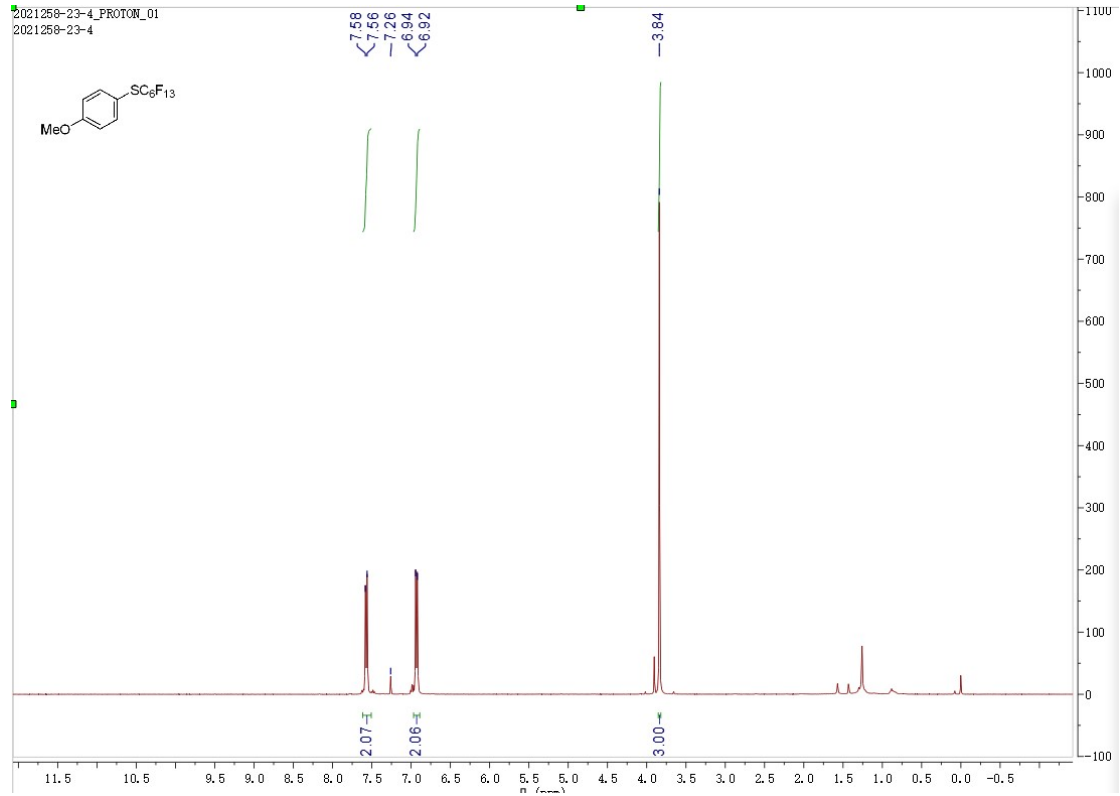


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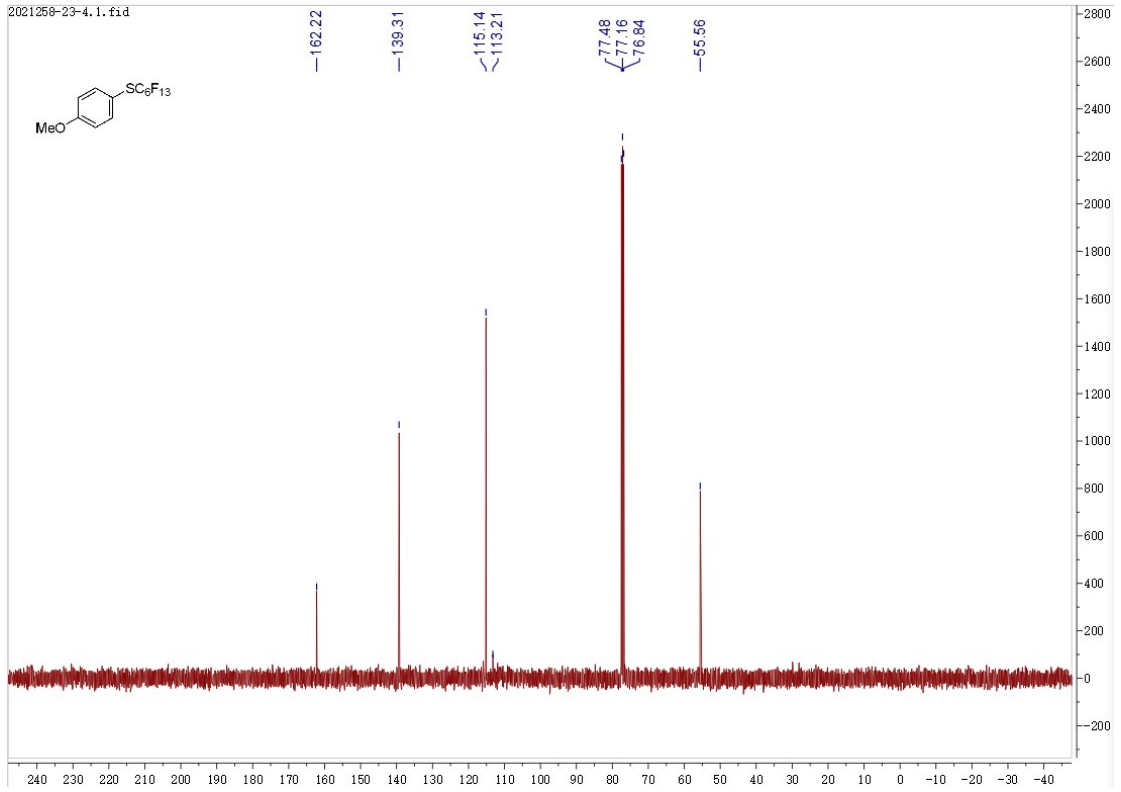




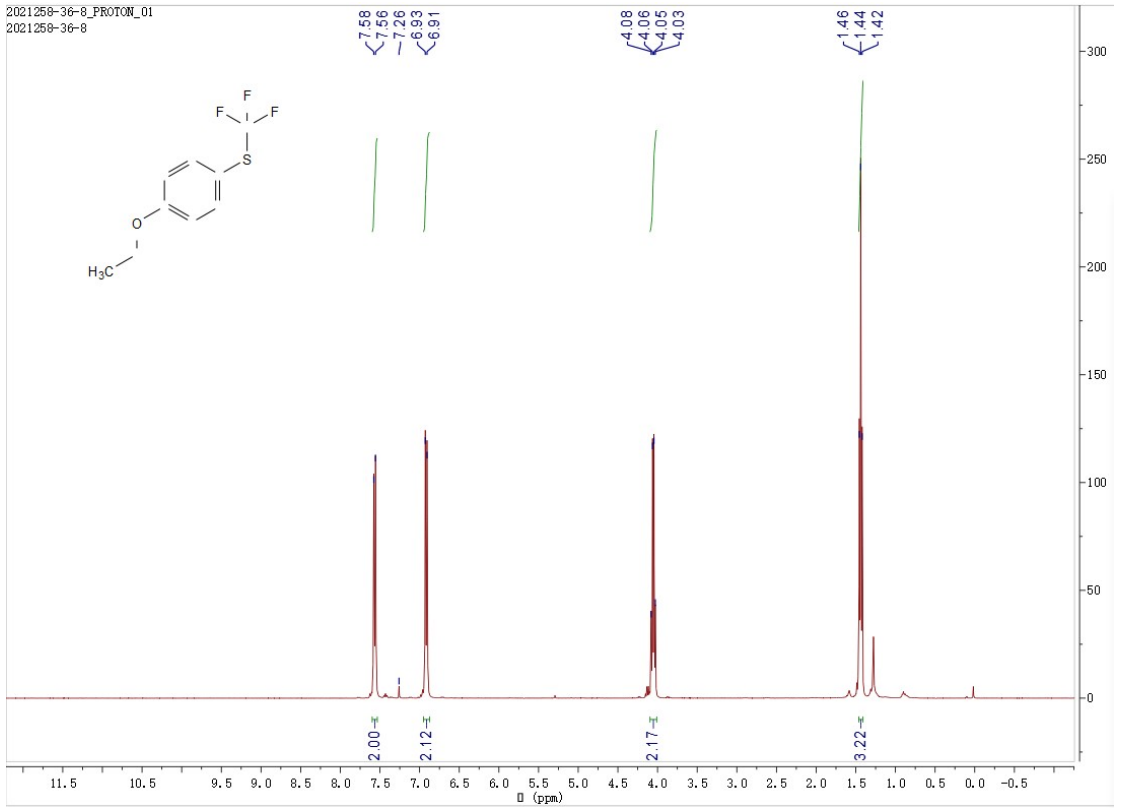




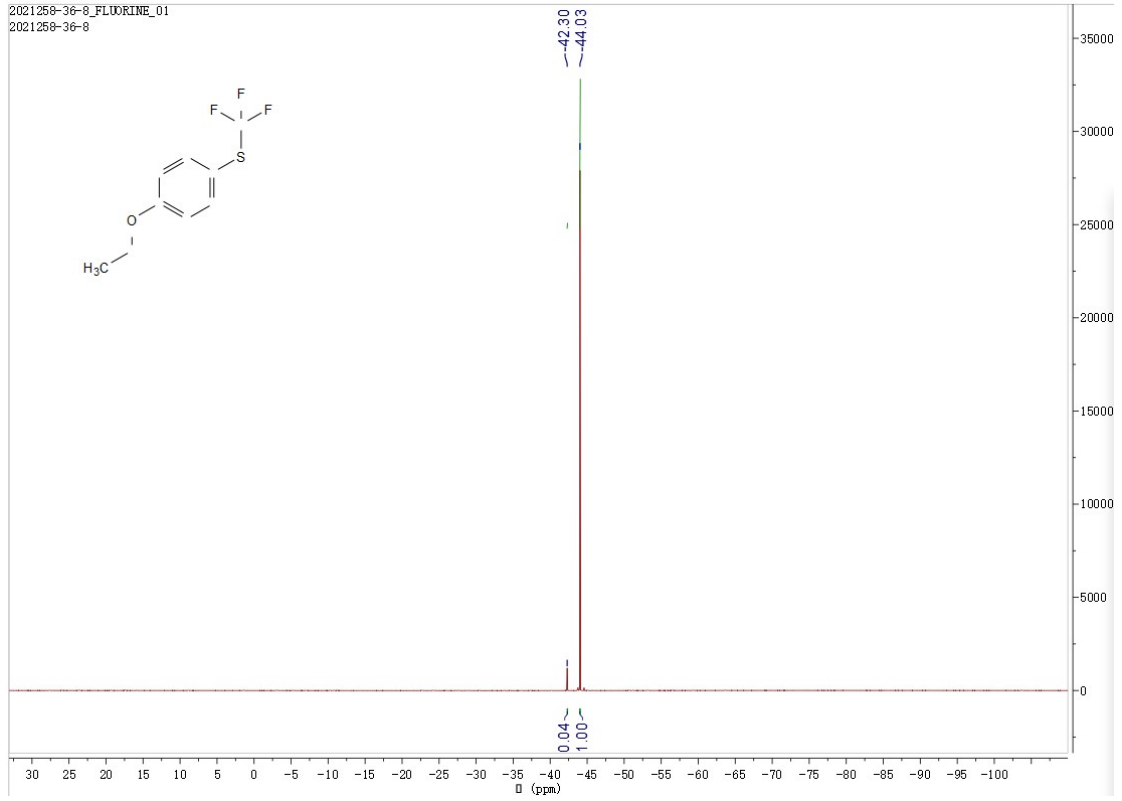
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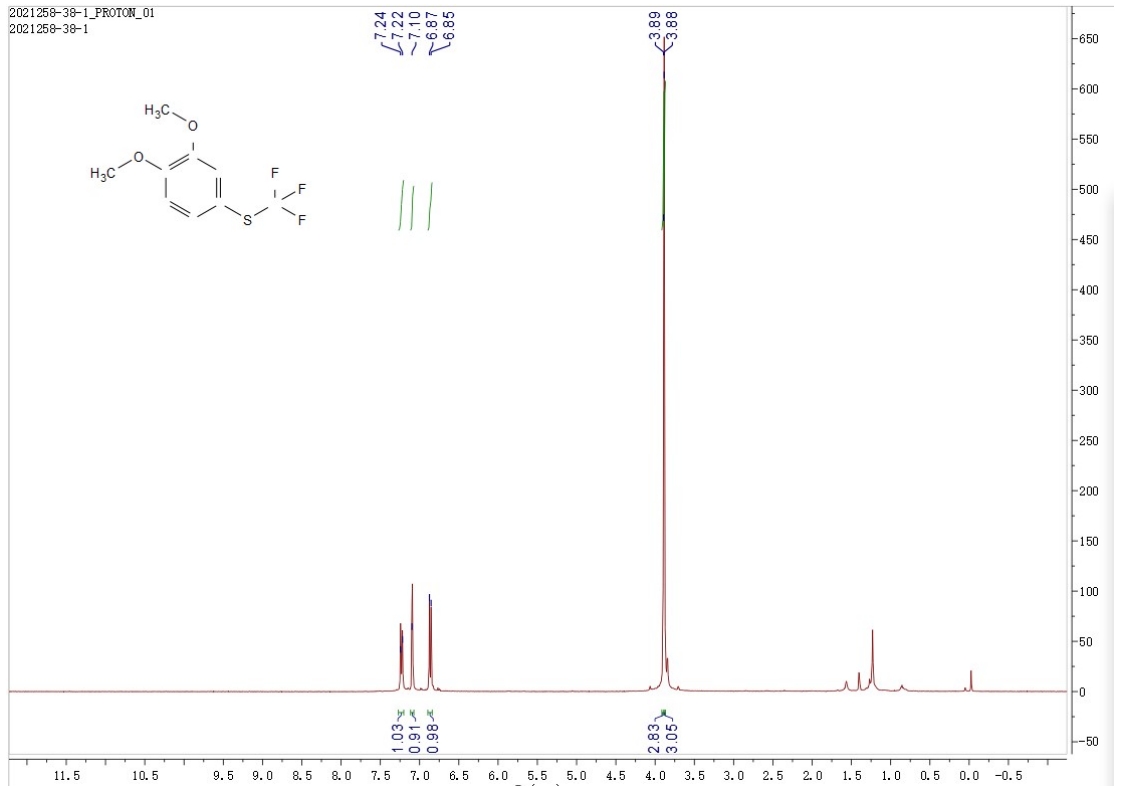
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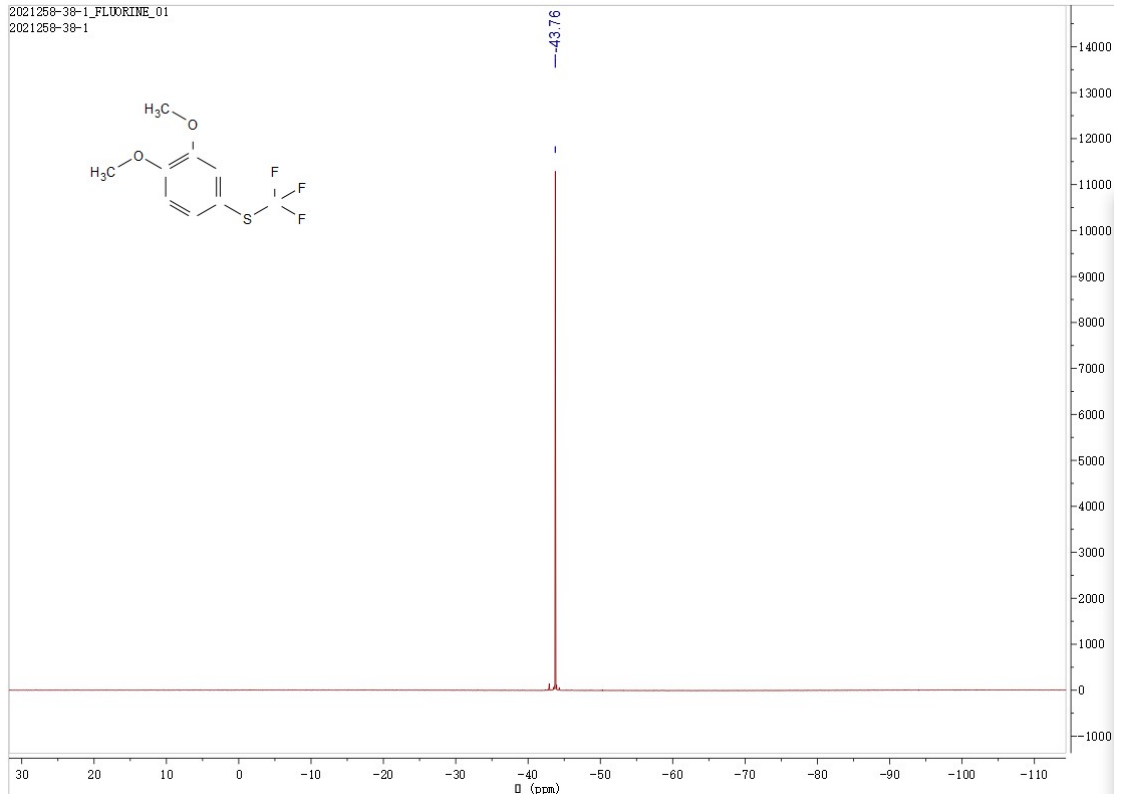
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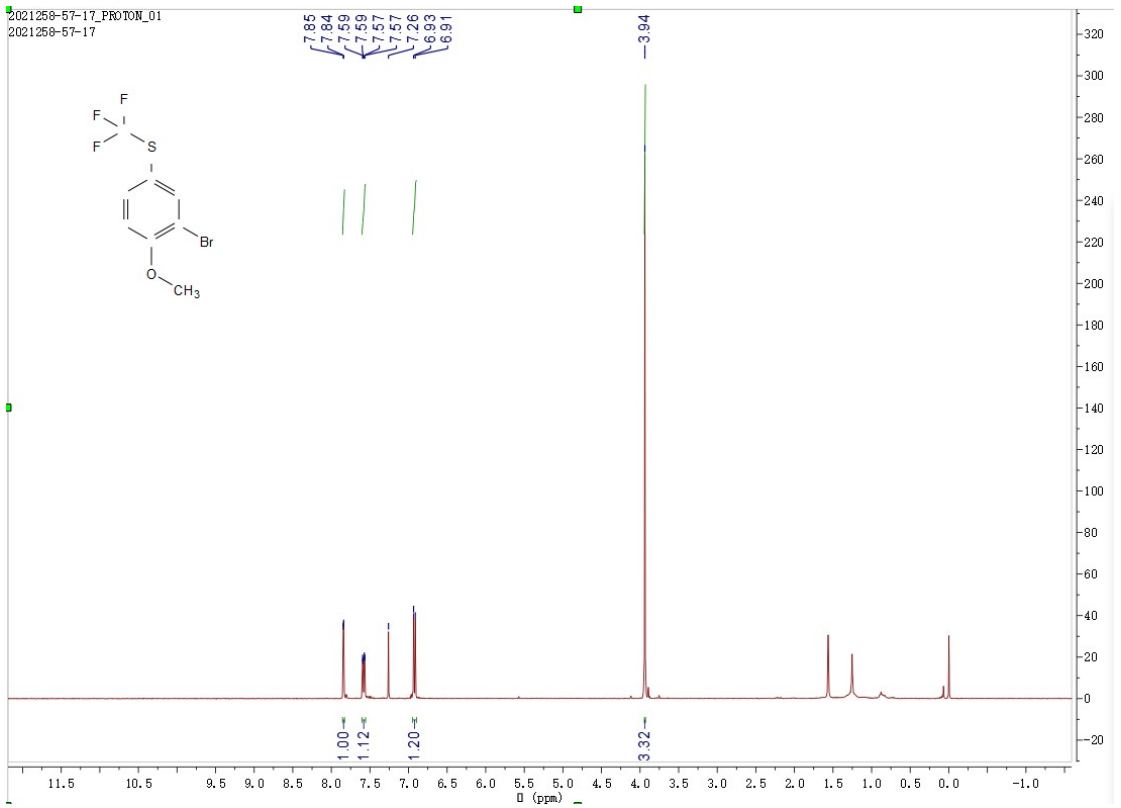
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2021259-57-17_PROTON_01
2021259-57-17



2021258-57-19_FLUORINE_01
2021258-57-19

