

Supplementary Information

Se-Catalyzed Enantioselective Lactamization Enabled by a N-Fluorosulfonyl Group: Total Synthesis of Diaporisoindole A

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1. General information

¹H NMR spectra were recorded on JEOL JNM-ECZ400 or JNM-ECA500 spectrometers. Chemical shifts (δ , ppm) are relative to TMS; reported data include integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, br = broad), and coupling constants (J, Hz).

¹³C NMR spectra were recorded with proton decoupling; chemical shifts are relative to the residual solvent.

¹⁹F NMR spectra were measured with proton decoupling using hexafluorobenzene (−163.0 ppm) as internal standard.

Specific rotations were determined on a JASCO P-2200 or Anton Paar MCP100 polarimeter.

HRMS were obtained on a Bruker MicroTOF-QII (ESI).

HPLC analyses were performed on a Shimadzu SPD-M20A using Daicel chiral columns (IB-3, IC-3, OD-3, OJ-3, OZ-3, AS-3, AZ-3; 4.6 × 25 cm).

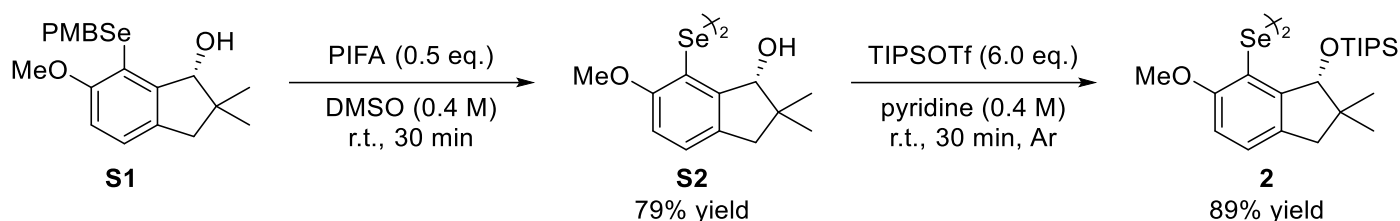
TLC was carried out on Merck silica gel 60 GF254 plates (0.25 mm).

Melting Points (m.p.) were recorded on a Hitachi TG/DTA7220 thermal analysis system.

Commercial reagents were used as received.

Products were purified by Biotage Isolera (CHROMATOREX® 60B, Wakogel® C300 or 60N) or by Japan Analytical Industry LaboACE recycling preparative HPLC (Daicel CHIRALCEL OD-H).

2. Preparation of selenium catalyst 2



(1*R*,1'*R*)-7,7'-diselanylbis(6-methoxy-2,2-dimethyl-2,3-dihydro-1*H*-inden-1-ol) (**S2**)

To a solution of selenide **S1** (1.65 g, 4.2 mmol) in DMSO (10.5 mL), PIFA (907 mg, 2.1 mmol) was added at room temperature. After stirring for 30 min, the reaction was quenched with water and extracted with hexane/EtOAc (1:1). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude material was purified by column chromatography on silica gel (1st: EtOAc/DCM, 0–10%; 2nd: EtOAc/hexane, 8–66%) to give **S2** as a yellow solid in 79% yield (905 mg, 1.7 mmol).

¹H NMR (399 MHz, CDCl₃) δ 7.09 (d, *J* = 8.2 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 4.59 (s, 2H), 3.55 (s, 6H), 3.01 (s, 2H), 2.90 (d, *J* = 15.1 Hz, 2H), 2.48 (d, *J* = 15.1 Hz, 2H), 1.17 (s, 6H), 0.93 (s, 6H)

¹³C NMR (100 MHz, CDCl₃) δ 158.89, 151.11, 136.17, 127.61, 116.78, 110.96, 83.95, 56.22, 44.87, 43.75, 27.16, 22.10

HRMS (ESI) exact mass calculated for C₂₄H₃₀NaO₄Se₂: *m/z* 565.0367 ([M+Na]⁺), found: *m/z* 565.0370 ([M+Na]⁺).

[α]_D²⁵ = +257.0 (*c* = 0.2, CHCl₃).

m.p. = 96 °C

1,2-bis((*R*)-5-methoxy-2,2-dimethyl-3-((triisopropylsilyl)oxy)-2,3-dihydro-1*H*-inden-4-yl)diselane (**2**)

To an argon-purged flask, diselenide **S2** (905 mg, 1.7 mmol), pyridine (4.2 mL), and TIPSOTf (2.7 mL, 10.1 mmol) were added successively. After stirring for 30 min at room temperature, the reaction was quenched with saturated NaHCO₃ and extracted with hexane. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude material was purified by column chromatography on silica gel (DCM/hexane, 8–66%) to give the title compound **2** as a yellow solid in 89% yield (1.27 g, 1.5 mmol).

¹H NMR (399 MHz, CDCl₃) δ 6.98 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 8.2 Hz, 2H), 4.55 (s, 2H), 3.73 (s, 6H), 2.94 (d, *J* = 15.1 Hz, 2H), 2.22 (d, *J* = 15.1 Hz, 2H), 1.17 (sep, *J* = 7.8 Hz, 6H), 1.15 (s, 6H), 1.04 (d, *J* = 7.3 Hz, 18H), 0.87 (d, *J* = 7.3 Hz, 18H), 0.46 (s, 6H)

¹³C NMR (100 MHz, CDCl₃) δ 158.53, 152.18, 136.38, 126.51, 117.17, 110.33, 84.85, 56.43, 45.25, 44.76, 26.14, 23.31, 18.75, 18.54, 14.24

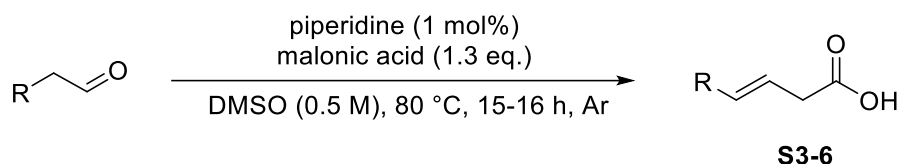
HRMS (ESI) exact mass calculated for C₄₂H₇₀NaO₄Se₂Si₂: *m/z* 877.3035 ([M+Na]⁺), found: *m/z* 877.3036 ([M+Na]⁺).

[α]_D²⁵ = +260.0 (*c* = 0.2, CHCl₃).

m.p. = 142 °C

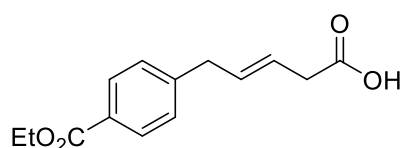
3. Preparation of β,γ -unsaturated carboxylic acids

General Procedure A



To a stirred solution of the aldehyde in DMSO (1 M), malonic acid (1.3 equiv) and piperidine (10 μ L) were added in one portion. The mixture was degassed under reduced pressure and heated at 100 $^{\circ}$ C for 15 h, then poured into water. After extraction with hexane/EtOAc (2:1, repeated several times), the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude material was purified by column chromatography to give the target carboxylic acid.

(*E*)-5-(4-(ethoxycarbonyl)phenyl)pent-3-enoic acid (S3)



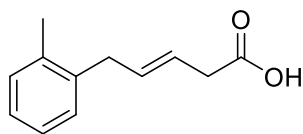
Prepared according to general procedure A with ethyl 4-(3-oxopropyl)benzoate (3.25 mmol, 671 mg) for 15 h. The residue was purified by column chromatography on silica gel (hexane/acetone, 5–40%) to afford the title compound as a white solid in 66% yield (2.13 mmol, 529 mg).

^1H NMR (392 MHz, CDCl_3) δ 7.97 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 5.75 (dt, J = 15.3, 6.7, 1.1 Hz, 1H), 5.64 (dt, J = 15.3, 6.7, 1.1 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 3.44 (d, J = 6.5 Hz, 2H), 3.13 (dd, J = 6.6, 1.0 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 178.0, 166.8, 145.4, 132.9, 129.9, 128.6, 128.6, 123.3, 61.0, 38.9, 37.7, 14.5

HRMS (ESI) exact mass calculated for $\text{C}_{14}\text{H}_{15}\text{O}_4$: m/z 247.0976 ($[\text{M}-\text{H}]^-$), found: m/z 247.0974 ($[\text{M}-\text{H}]^-$).

(*E*)-5-(*o*-tolyl)pent-3-enoic acid (S4)



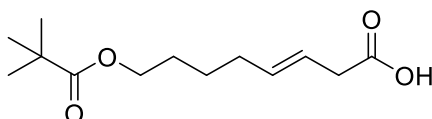
Prepared according to general procedure A with 3-(*o*-tolyl)propanal (3.99 mmol, 591 mg) for 16 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 5–50%) to afford the title compound as a pale yellow oil in 73% yield (2.91 mmol, 554 mg).

^1H NMR (392 MHz, CDCl_3) δ 7.08–7.20 (4H), 5.73 (dt, J = 15.5, 6.5, 1.4 Hz 1H), 5.54 (dt, J = 15.3, 7.0, 1.6 Hz, 1H), 3.37 (dd, J = 6.4, 1.0 Hz, 2H), 3.10 (dq, J = 6.9, 1.1 Hz, 2H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 177.8, 138.1, 136.5, 133.2, 130.3, 129.2, 126.5, 126.2, 122.3, 37.7, 36.6, 19.5.

HRMS (ESI) exact mass calculated for $\text{C}_{12}\text{H}_{13}\text{O}_2$: m/z 189.0921 ($[\text{M}-\text{H}]^-$), found: m/z 189.0921 ($[\text{M}-\text{H}]^-$).

(*E*)-8-(pivaloyloxy)oct-3-enoic acid (S5)



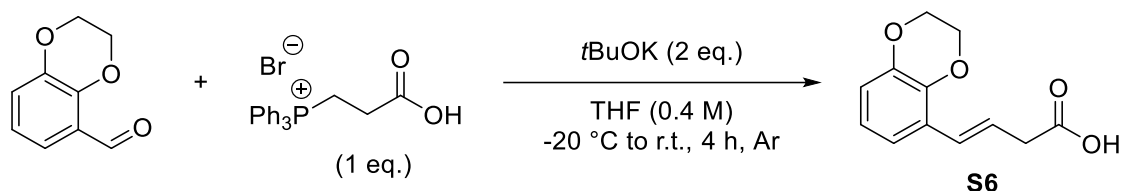
Prepared according to general procedure A with 6-oxohexyl pivalate (2.27 mmol, 455 mg) for 16 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 0–50%) to afford the title compound as a pale yellow solid in 85% yield (1.93 mmol, 468 mg).

¹H NMR (396 MHz, CDCl₃) δ 5.62–5.50 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 3.08 (d, *J* = 5.4 Hz, 2H), 2.11–2.05 (m, 2H), 1.67–1.60 (m, 2H), 1.49–1.39 (m, 2H), 1.20 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 178.8, 178.3, 134.9, 121.4, 64.3, 38.8, 37.8, 32.1, 28.2, 27.3, 25.5.

HRMS (ESI) exact mass calculated for C₁₃H₂₁O₄: *m/z* 241.1445 ([M-H][−]), found: *m/z* 241.1445 ([M-H][−])

(*E*)-4-(2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)but-3-enoic acid (S6)



In a flame-dried two-neck flask, the Wittig reagent (1.1 mmol, 164 mg) in THF (2.5 mL) was sonicated for 10 min. 2,3-Dihydrobenzo[*b*][1,4]dioxine-5-carbaldehyde (1.0 mmol, 200 mg) was added to the resulting homogeneous suspension. *t*BuOK (2.2 mmol, 2.2 mL of 1 M solution in THF) was added at −20 °C to −30 °C over 1 h. After stirring for an additional 2 h at room temperature, the mixture was concentrated in vacuo, poured into water, and filtered through a Celite pad. The mixture was acidified with concentrated HCl, extracted with EtOAc, washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel (hexane/EtOAc, 15–80%) to give the title compound as a white solid in 50% yield (497 μmol, 109.5 mg, *cis:trans* = 6:94).

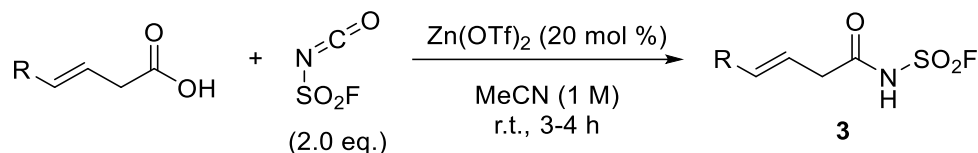
¹H NMR (401 MHz, CDCl₃) δ 7.00 (dd, *J* = 6.5, 2.8 Hz, 1H), 6.70–6.85 (m, 3H), 6.31 (dt, *J* = 16.0, 7.2 Hz, 1H), 4.19–4.41 (m, 4H), 3.31 (dd, *J* = 7.1, 1.4 Hz, 2H)

¹³C NMR (100 MHz, CDCl₃) δ 177.1, 143.8, 141.1, 128.2, 126.0, 122.3, 121.0, 119.3, 116.7, 64.5, 64.2, 38.5

HRMS (ESI) exact mass calculated for C₁₂H₁₁O₄: *m/z* 219.0663 ([M-H][−]), found: *m/z* 219.0663 ([M-H][−])

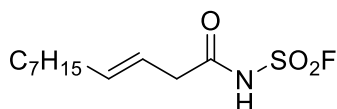
4. Preparation of β,γ -unsaturated N-(fluorosulfonyl)amides 3 and 4

General Procedure B



To a stirred solution of fluorosulfonyl isocyanate (2.0 equiv.) and Zn(OTf)₂ (20 mol%) in CH₃CN (1 M), the corresponding carboxylic acid (1.0 equiv.) was added at room temperature under an argon atmosphere. The progress of the reaction was monitored by TLC. After completion, Na₂CO₃ (3.0 equiv.) was added, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel. The resulting salt was acidified with 1 N HCl, and the organic layer was extracted with CH₂Cl₂, dried over anhydrous Na₂SO₄, and concentrated in vacuo to give the desired N-(fluorosulfonyl)amide.

(*E*)-undec-3-enoylsulfamoyl fluoride (3a)



Prepared according to general procedure B with (*E*)-undec-3-enoic acid (500 μ mol, 92.1 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 10–60%) to give the title compound as a white solid in 72% yield (362 μ mol, 96.0 mg).

¹H NMR (500 MHz, CDCl₃) δ 5.79–5.73 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.49 (dt, *J* = 15.4, 7.1 Hz, 1H), 3.20 (d, *J* = 6.9 Hz, 2H), 2.09 (q, *J* = 7.1 Hz, 2H), 1.44–1.38 (m, 2H), 1.33–1.28 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). The N-H proton was not observed due to broadening..

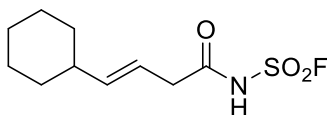
¹³C NMR (126 MHz, CDCl₃) δ 169.3, 139.2, 119.0, 40.3, 32.5, 31.8, 29.1, 29.1, 28.9, 22.6, 14.1.

¹⁹F NMR (471 MHz, CDCl₃) δ 52.4 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₁H₁₉FO₃S: *m/z* 264.1075 ([M-H]⁺), found: *m/z* 264.1076 ([M-H]⁺).

m.p. = 75 °C

(*E*)-(4-cyclohexylbut-3-enoyl)sulfamoyl fluoride (3b)



Prepared according to general procedure B with (*E*)-4-cyclohexylbut-3-enoic acid (500 μ mol, 84.1 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 5–40%) to give the title compound as a white solid in 65% yield (327 μ mol, 82.3 mg).

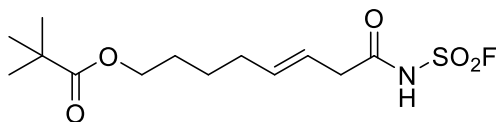
¹H NMR (500 MHz, CDCl₃) δ 7.92–9.13 (1H), 5.71 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.46 (dtd, *J* = 15.5, 6.6, 1.2 Hz, 1H), 3.19 (d, *J* = 6.9 Hz, 2H), 2.05–1.99 (m, 1H), 1.76–1.72 (m, 4H), 1.68–1.65 (m, 1H), 1.32–1.23 (m, 2H), 1.17 (tt, *J* = 12.4, 3.2 Hz, 1H), 1.13–1.05 (m, 2H)

¹³C NMR (126 MHz, CDCl₃) δ 168.4, 145.0, 116.5, 40.6, 40.2, 32.5, 25.9, 25.8.

¹⁹F NMR (471 MHz, CDCl₃) δ 52.7 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₀H₁₅FO₃S: *m/z* 248.0762 ([M-H]⁺), found: *m/z* 248.0762 ([M-H]⁺).

(E)-8-((fluorosulfonyl)amino)-8-oxooct-5-en-1-yl pivalate (3c)



Prepared according to general procedure B with (*E*)-8-(pivaloyloxy)oct-3-enoic acid (1.00 mmol, 242 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–100%) to give the title compound as a pale yellow oil in 62% yield (622 μ mol, 210 mg, 96% purity).

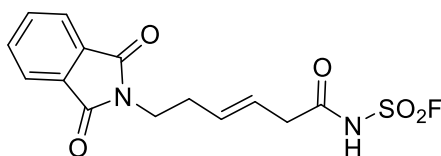
¹H NMR (500 MHz, CDCl₃) δ 5.66 (dt, *J* = 15.3, 6.7 Hz, 1H), 5.53 (dt, *J* = 15.5, 6.9, 1.3 Hz, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 3.19 (dd, *J* = 6.7, 0.7 Hz, 2H), 2.11 (q, *J* = 7.0 Hz, 2H), 1.68–1.62 (m, 2H), 1.49–1.43 (m, 2H), 1.24–1.12 (m, 11H). The N-H proton was not observed due to broadening.

¹³C NMR (126 MHz, CDCl₃) δ 179.8, 169.0, 137.0, 119.8, 64.5, 40.0, 38.8, 31.9, 27.8, 27.1, 25.0.

¹⁹F NMR (471 MHz, CDCl₃) δ 52.2 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₃H₂₁FN₂O₅S: *m/z* 322.1130 ([M-H]⁺), found: *m/z* 322.1130 ([M-H]⁺).

(E)-(6-(1,3-dioxisoindolin-2-yl)hex-3-enoyl)sulfamoyl fluoride (3d)



Prepared according to general procedure B with (*E*)-6-(1,3-dioxisoindolin-2-yl)hex-3-enoic acid (500 μ mol, 130 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 10–60%) to give the title compound as a white solid in 52% yield (260 μ mol, 93.0 mg, 95% purity).

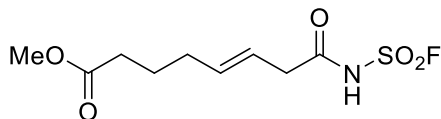
¹H NMR (500 MHz, acetone-d₆) δ 11.16–12.12 (1H), 7.80 (s, 4H), 5.66 (dt, *J* = 15.2, 6.9 Hz, 1H), 5.61–5.55 (m, 1H), 3.68 (t, *J* = 7.0 Hz, 2H), 3.21 (dd, *J* = 6.6, 0.9 Hz, 2H), 2.42 (qd, *J* = 6.9, 0.9 Hz, 2H).

¹³C NMR (126 MHz, acetone-d₆) δ 206.2, 168.7, 134.9, 133.0, 132.9, 123.8, 123.7, 40.2, 37.8, 32.2.

¹⁹F NMR (369 MHz, acetone-d₆) δ 51.9 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₄H₁₂FN₂O₅S: *m/z* 339.0456 ([M-H]⁺), found: *m/z* 339.0461 ([M-H]⁺).

methyl (E)-8-((fluorosulfonyl)amino)-8-oxooct-5-enoate (3e)



Prepared according to general procedure B with (*E*)-8-methoxy-8-oxooct-3-enoic acid (500 μ mol, 93.1 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 20–100%) to give the title compound as a white solid in 62% yield (308 μ mol, 86.6 mg, 95% purity).

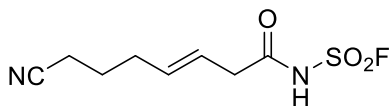
¹H NMR (500 MHz, CDCl₃) δ 9.09–11.18 (1H), 5.65 (dt, *J* = 15.4, 6.8 Hz, 1H), 5.54 (dt, *J* = 15.5, 6.9, 1.3 Hz, 1H), 3.70 (s, 3H), 3.20 (dd, *J* = 6.6, 0.9 Hz, 2H), 2.36 (t, *J* = 7.3 Hz, 2H), 2.12 (q, *J* = 6.9 Hz, 2H), 1.77–1.71 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 175.1, 168.5, 136.9, 120.5, 52.0, 40.1, 33.4, 31.7, 23.8.

¹⁹F NMR (471 MHz, CDCl₃) δ 52.3 (s, 1F).

HRMS (ESI) exact mass calculated for C₉H₁₃FN₂O₅S: *m/z* 266.0504 ([M-H]⁺), found: *m/z* 266.0504 ([M-H]⁺).

(E)-(7-cyanohept-3-enoyl)sulfamoyl fluoride (3f)



Prepared according to general procedure B with (*E*)-7-cyanohept-3-enoic acid (353 μ mol, 54.0 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–100%) to give the title compound as a pale yellow oil in 51% yield (353 μ mol, 43.8 mg, 96% purity).

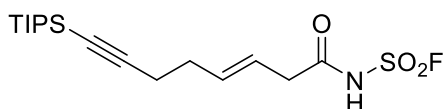
^1H NMR (500 MHz, CDCl_3) δ 8.45–10.69 (1H), 5.68–5.57 (m, 2H), 3.18 (d, J = 5.7 Hz, 2H), 2.41 (t, J = 7.0 Hz, 2H), 2.26 (q, J = 6.7 Hz, 2H), 1.82–1.76 (m, 2H).

^{13}C NMR (99 MHz, CDCl_3) δ 168.2, 135.1, 121.6, 120.0, 39.9, 31.3, 24.1, 16.4.

^{19}F NMR (369 MHz, CDCl_3) δ 52.6 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_8\text{H}_{10}\text{FN}_2\text{O}_3\text{S}$: m/z 233.0402 ($[\text{M}-\text{H}]^-$), found: m/z 233.0402 ($[\text{M}-\text{H}]^-$).

(*E*)-(8-(triisopropylsilyl)oct-3-en-7-ynoyl)sulfamoyl fluoride (3g)



Prepared according to general procedure B with (*E*)-8-(triisopropylsilyl)oct-3-en-7-ynoic acid (500 μ mol, 147 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–75%) to give the title compound as an orange oil in 47% yield (235 μ mol, 91.7 mg, 96% purity).

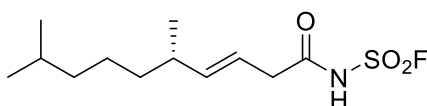
^1H NMR (392 MHz, CDCl_3) δ 5.85–5.78 (m, 1H), 5.59 (dt, J = 15.3, 7.1 Hz, 1H), 3.21 (d, J = 7.0 Hz, 2H), 2.39–2.31 (m, 4H), 1.09–0.98 (m, 21H). The N-H proton was not observed due to broadening.

^{13}C NMR (99 MHz, CDCl_3) δ 168.5, 136.8, 120.3, 107.5, 81.3, 40.0, 31.8, 19.7, 18.5, 11.2.

^{19}F NMR (369 MHz, CDCl_3) δ 52.7 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{17}\text{H}_{29}\text{FNO}_3\text{SSi}$: m/z 374.1627 ($[\text{M}-\text{H}]^-$), found: m/z 374.1631 ($[\text{M}-\text{H}]^-$).

(*S,E*)-(5,9-dimethyldec-3-enoyl)sulfamoyl fluoride (3h)



Prepared according to general procedure B with (*S,E*)-5,9-dimethyldec-3-enoic acid (1.00 mmol, 198 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 12–100%) to give the title compound as a pale yellow oil in 49% yield (493 μ mol, 145 mg, 95% purity).

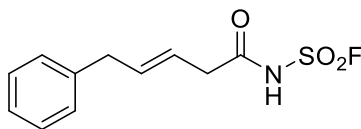
^1H NMR (500 MHz, CDCl_3) δ 5.62 (dd, J = 15.5, 7.7 Hz, 1H), 5.46 (dtd, J = 15.5, 7.7, 0.9 Hz, 1H), 3.19 (d, J = 6.9 Hz, 2H), 2.20–2.15 (m, 1H), 1.55–1.47 (m, 1H), 1.30–1.21 (m, 5H), 1.16–1.12 (m, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.86 (dd, J = 6.6, 0.9 Hz, 7H). The N-H proton was not observed due to broadening.

^{13}C NMR (126 MHz, CDCl_3) δ 168.6, 144.9, 117.1, 40.1, 38.9, 36.8, 27.9, 25.0, 22.6, 22.6, 20.1.

^{19}F NMR (471 MHz, CDCl_3) δ 52.6 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{12}\text{H}_{21}\text{FNO}_3\text{S}$: m/z 278.1232 ($[\text{M}-\text{H}]^-$), found: m/z 278.1232 ($[\text{M}-\text{H}]^-$).

(*E*)-(5-phenylpent-3-enoyl)sulfamoyl fluoride (3j)



Prepared according to general procedure B with (*E*)-5-phenylpent-3-enoic acid (4.00 mmol, 705 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 5–60%) to give the title compound as a white solid in 51% yield (2.04 mmol, 526 mg).

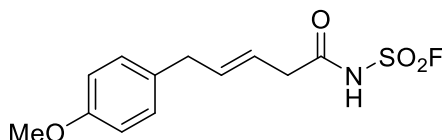
¹H NMR (500 MHz, CDCl₃) δ 8.30–9.48 (1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 5.88 (dt, *J* = 15.2, 6.9 Hz, 1H), 5.57 (dt, *J* = 15.5, 6.9 Hz, 1H), 3.41 (d, *J* = 6.6 Hz, 2H), 3.20 (d, *J* = 6.9 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 168.2, 139.1, 137.5, 128.6, 128.5, 126.4, 120.2, 39.9, 38.8.

¹⁹F NMR (471 MHz, CDCl₃) δ 52.9 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₁H₁₁FNO₃S: *m/z* 256.0449 ([M-H]⁺), found: *m/z* 256.0451 ([M-H]⁺).

(*E*)-(5-(4-methoxyphenyl)pent-3-en-1-yl)sulfamoyl fluoride (3k)



Prepared according to general procedure B with (*E*)-5-(4-methoxyphenyl)pent-3-enoic acid (2.00 mmol, 412 mg). The crude material was purified by column chromatography on silica gel (1st: hexane/acetone, 15–75%; 2nd: DCM/acetone, 5–33%) to give the title compound as a white solid in 47% yield (945 μmol, 280 mg, 97% purity).

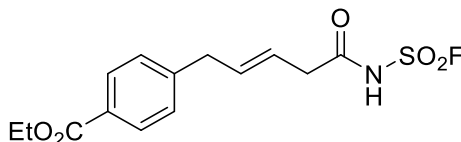
¹H NMR (500 MHz, CDCl₃) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.84 (dt, *J* = 15.2, 6.9 Hz, 1H), 5.54 (dt, *J* = 15.3, 7.0 Hz, 1H), 3.78 (s, 3H), 3.34 (d, *J* = 6.9 Hz, 2H), 3.19 (d, *J* = 6.9 Hz, 2H). The N-H proton was not observed due to broadening.

¹³C NMR (126 MHz, CDCl₃) δ 168.6, 158.1, 137.6, 131.2, 129.4, 119.9, 114.1, 55.3, 39.9, 38.0.

¹⁹F NMR (471 MHz, CDCl₃) δ 52.7 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₂H₁₃FNO₄S: *m/z* 286.0555 ([M-H]⁺), found: *m/z* 286.0558 ([M-H]⁺).

ethyl (*E*)-4-(5-((fluorosulfonyl)amino)-5-oxopent-2-en-1-yl)benzoate (3l)



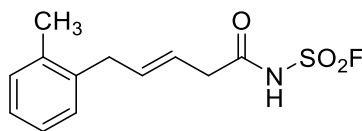
Prepared according to general procedure B with (*E*)-5-(4-(ethoxycarbonyl)phenyl)pent-3-enoic acid (500 μmol, 124 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–75%) to give the title compound as a white solid in 79% yield (395 μmol, 130 mg).

¹H NMR (392 MHz, CDCl₃) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.80 (dt, *J* = 15.1, 6.8 Hz, 1H), 5.62 (dt, *J* = 15.1, 7.0 Hz, 1H), 4.40–4.33 (m, 2H), 3.44 (d, *J* = 6.5 Hz, 2H), 3.25 (d, *J* = 6.7 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). The N-H proton was not observed due to broadening.

¹³C NMR (126 MHz, CDCl₃) δ 168.5, 167.4, 145.1, 135.0, 129.8, 128.6, 128.2, 121.5, 61.4, 39.7, 38.7, 14.2.

¹⁹F NMR (471 MHz, CDCl₃) δ 52.5 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₄H₁₅FNO₅S: *m/z* 328.0660 ([M-H]⁺), found: *m/z* 328.0662 ([M-H]⁺).

(E)-(5-(o-tolyl)pent-3-enoyl)sulfamoyl fluoride (3m)

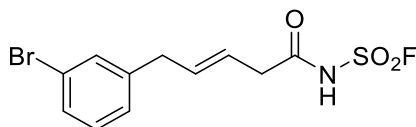
Prepared according to general procedure B with (*E*)-5-(*o*-tolyl)pent-3-enoic acid (500 μ mol, 95.1 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–75%) to give the title compound as a pale yellow oil in 75% yield (372 μ mol, 101 mg).

¹H NMR (396 MHz, CDCl₃) δ 7.16–7.09 (m, 4H), 5.86 (dt, *J* = 15.0, 6.7 Hz, 1H), 5.47 (dt, *J* = 15.9, 7.0, 1.5 Hz, 1H), 3.40 (d, *J* = 6.3 Hz, 2H), 3.19 (d, *J* = 7.0 Hz, 2H), 2.28 (s, 3H). The N-H proton was not observed due to broadening.

¹³C NMR (99 MHz, CDCl₃) δ 171.3, 137.4, 136.2, 135.7, 130.3, 129.0, 126.6, 126.2, 120.8, 40.4, 36.4, 19.2.

¹⁹F NMR (471 MHz, CDCl₃) δ 52.7 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₂H₁₃FNO₃S: *m/z* 270.0606 ([M-H]⁺), found: *m/z* 270.0610 ([M-H]⁺).

(E)-(5-(3-bromophenyl)pent-3-enoyl)sulfamoyl fluoride (3n)

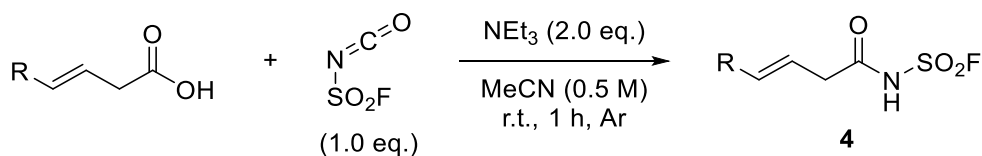
Prepared according to general procedure B with (*E*)-5-(3-bromophenyl)pent-3-enoic acid (500 μ mol, 128 mg). The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–75%) to give the title compound as a white solid in 70% yield (351 μ mol, 118 mg).

¹H NMR (396 MHz, CDCl₃) δ 7.93–9.85 (1H), 7.36–7.31 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 5.84 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.59 (dt, *J* = 15.4, 6.8, 1.4 Hz, 1H), 3.38 (d, *J* = 6.8 Hz, 2H), 3.24 (d, *J* = 6.8 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 170.3, 141.6, 135.4, 131.4, 130.1, 129.4, 127.1, 122.5, 121.3, 39.9, 38.3.

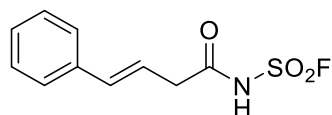
¹⁹F NMR (471 MHz, CDCl₃) δ 52.3 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₁H₁₀BrFNO₃S: *m/z* 333.9554 ([M-H]⁺), found: *m/z* 333.9554 ([M-H]⁺).

General procedure C

To a stirred solution of the corresponding carboxylic acid (1.0 equiv.) and triethylamine (2.0 equiv.) in CH₃CN (0.5 M) was added fluorosulfonyl isocyanate (1.0 equiv.) at room temperature under an argon atmosphere. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was concentrated in vacuo. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) and concentrated in vacuo. The residue was acidified with 1 N HCl, and the organic layer was extracted with TBME, dried over anhydrous Na₂SO₄, and concentrated in vacuo to give the desired N-(fluorosulfonyl)amide.

(E)-(4-phenylbut-3-enoyl)sulfamoyl fluoride (4a)



Prepared according to general procedure C with (*E*)-4-phenylbut-3-enoic acid (1.07 mmol, 173 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 83% yield (884 μ mol, 215 mg).

^1H NMR (399 MHz, CDCl_3) δ 8.03–9.25 (1H), 7.27–7.43 (5H), 6.63 (d, J = 15.6 Hz, 1H), 6.22 (dt, J = 16.0, 7.3 Hz, 1H), 3.42 (dd, J = 7.3, 1.4 Hz, 2H).

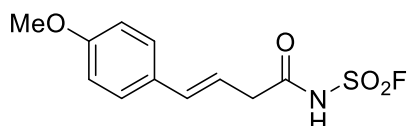
^{13}C NMR (100 MHz, CDCl_3) δ 167.6, 137.3, 135.7, 128.9, 128.7, 126.7, 118.2, 40.5.

^{19}F NMR (376 MHz, CDCl_3) δ 53.2 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{10}\text{H}_9\text{O}_3\text{NFS}$: m/z 242.0293 ($[\text{M}-\text{H}]^-$), found: m/z 242.0293 ($[\text{M}-\text{H}]^-$).

m.p. = 120 $^\circ\text{C}$

(*E*)-(4-(4-methoxyphenyl)but-3-enoyl)sulfamoyl fluoride (4b)



Prepared according to general procedure C with (*E*)-4-(4-methoxyphenyl)but-3-enoic acid (1.01 mmol, 195 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a white solid in 82% yield (830 μ mol, 82 mg).

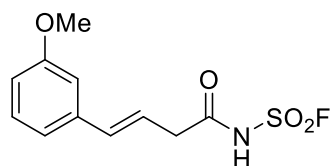
^1H NMR (401 MHz, CDCl_3) δ 7.87–9.17 (s, 1H), 7.33 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.57 (d, J = 15.6 Hz, 1H), 6.06 (dt, J = 15.8, 7.2 Hz, 1H), 3.82 (s, 3H), 3.39 (dd, J = 7.1, 1.1 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 168.0, 160.0, 136.9, 128.5, 128.0, 115.7, 114.3, 55.5, 40.6.

^{19}F NMR (376 MHz, CDCl_3) δ 53.1 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NFS}$: m/z 272.0398 ($[\text{M}-\text{H}]^-$), found: m/z 272.0393 ($[\text{M}-\text{H}]^-$)

(*E*)-(4-(3-methoxyphenyl)but-3-enoyl)sulfamoyl fluoride (4c)



Prepared according to general procedure C with (*E*)-4-(3-methoxyphenyl)but-3-enoic acid (1.81 mmol, 347 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 70% yield (1.27 mmol, 347 mg).

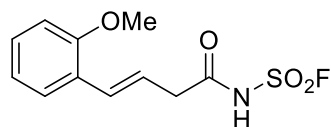
^1H NMR (401 MHz, CDCl_3) δ 7.87–9.07 (s, 1H), 7.27 (t, J = 8.0 Hz, 2H), 6.98 (d, J = 7.4 Hz, 1H), 6.92 (t, J = 2.1 Hz, 1H), 6.86 (dd, J = 8.3, 1.8 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 6.22 (dt, J = 15.7, 7.3 Hz, 1H), 3.83 (s, 3H), 3.43 (dd, J = 7.4, 1.4 Hz, 2H). The N-H proton was not observed due to broadening.

^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 160.0, 137.2, 137.1, 129.9, 119.3, 118.5, 114.3, 112.0, 55.5, 40.4.

^{19}F NMR (376 MHz, CDCl_3) δ 53.2 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NFS}$: m/z 272.0398 ($[\text{M}-\text{H}]^-$), found: m/z 272.0398 ($[\text{M}-\text{H}]^-$)

(*E*)-(4-(2-methoxyphenyl)but-3-enoyl)sulfamoyl fluoride (4d)



Prepared according to general procedure C with (*E*)-4-(2-methoxyphenyl)but-3-enoic acid (931 μ mol, 179 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 91% yield (845 μ mol, 231 mg).

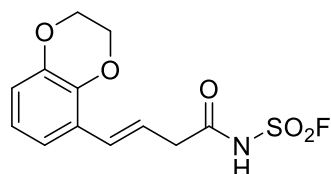
^1H NMR (401 MHz, CDCl_3) δ 8.36–8.80 (s, 1H), 7.39 (dd, J = 7.6, 1.6 Hz, 1H), 7.31–7.27 (m, 1H), 6.98–6.90 (m, 3H), 6.23 (dt, J = 16.1, 7.4 Hz, 1H), 3.87 (s, 3H), 3.42 (dd, J = 7.4, 1.4 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 156.9, 133.1, 129.8, 127.5, 124.7, 121.0, 119.4, 111.1, 55.6, 41.2.

^{19}F NMR (376 MHz, CDCl_3) δ 52.9 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NFS}$: m/z 272.0398 ($[\text{M}-\text{H}]^-$), found: m/z 272.0393 ($[\text{M}-\text{H}]^-$)

(*E*)-(4-(2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)but-3-enoyl)sulfamoyl fluoride (4e)



Prepared according to general procedure C with (*E*)-4-(2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)but-3-enoic acid (2.33 mmol, 514 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 85% yield (1.67 mmol, 594 mg, α,β -isomer of **4e** : **4e** = 4:96). Analytically pure sample was obtained by recrystallizing this material from hexane/DCM.

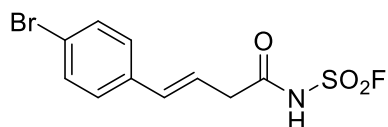
^1H NMR (401 MHz, CDCl_3) δ 8.42 (s, 1H), 6.97–6.93 (m, 1H), 6.86–6.80 (m, 3H), 6.25 (dt, J = 15.9, 7.5 Hz, 1H), 4.30 (dq, J = 20.7, 2.8 Hz, 4H), 3.42 (dd, J = 7.1, 1.1 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 143.9, 141.3, 132.0, 125.0, 121.2, 120.2, 119.7, 117.6, 64.7, 64.2, 41.2.

^{19}F NMR (376 MHz, CDCl_3) δ 52.9 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{12}\text{H}_{11}\text{O}_5\text{NFS}$: m/z 300.0347 ($[\text{M}-\text{H}]^-$), found: m/z 300.0344 ($[\text{M}-\text{H}]^-$)

(*E*)-(4-(4-bromophenyl)but-3-enoyl)sulfamoyl fluoride (4f)



Prepared according to general procedure C with (*E*)-4-(4-bromophenyl)but-3-enoic acid (865 μ mol, 209 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 85% yield (884 μ mol, 238 mg, α,β -isomer of **4f** : **4f** = 5:95).

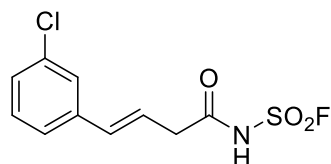
^1H NMR (399 MHz, CDCl_3) δ 7.47 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.7 Hz, 4H), 6.55 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 15.9, 7.1 Hz, 1H), 3.43 (dd, J = 7.3, 1.4 Hz, 2H). The N-H proton was not observed due to broadening.

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 171.9, 136.0, 131.5, 131.4, 128.1, 124.1, 120.3, 40.9.

^{19}F NMR (376 MHz, CDCl_3) δ 53.6 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{10}\text{H}_8\text{O}_3\text{NFBRS}$: m/z 319.9398 ($[\text{M}-\text{H}]^-$), found: m/z 319.9398 ($[\text{M}-\text{H}]^-$)

(*E*)-(4-(3-chlorophenyl)but-3-enoyl)sulfamoyl fluoride (4g)



Prepared according to general procedure C with (*E*)-4-(3-chlorophenyl)but-3-enoic acid (1.04 mmol, 205 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 84% yield (884 μ mol, 244 mg, α,β -isomer of **4g** : **4g** = 11:89).

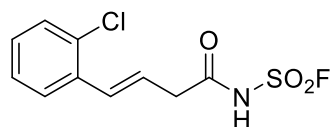
¹H NMR (399 MHz, CDCl₃) δ 8.09-9.49 (s, 1H), 7.37 (s, 1H), 7.23-7.29 (4H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.25 (dt, *J* = 15.6, 7.1 Hz, 1H), 3.44 (dd, *J* = 7.3, 1.4 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 167.7, 137.6, 135.6, 134.9, 130.1, 128.6, 126.6, 124.9, 119.8, 40.2.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.6 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₀H₈O₃NFClS: *m/z* 275.9903 ([M-H]⁺), found: *m/z* 275.9905 ([M-H]⁺)

(*E*)-(4-(2-chlorophenyl)but-3-enoyl)sulfamoyl fluoride (**4h**)



Prepared according to general procedure C with (*E*)-4-(2-chlorophenyl)but-3-enoic acid (1.03 mmol, 203 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 51% yield (522 μ mol, 145 mg, α,β -isomer of **4h** : **4h** = 14:86). Analytically pure sample was obtained by recrystallizing this material from hexane/DCM.

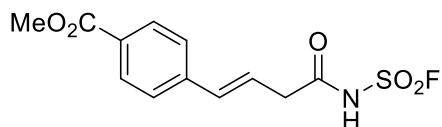
¹H NMR (392 MHz, CDCl₃) δ 8.21-9.30 (s, 1H), 7.54 (dd, *J* = 6.9, 2.3 Hz, 1H), 7.39-7.37 (m, 1H), 7.26-7.23 (m, 2H), 7.01 (d, *J* = 15.6 Hz, 1H), 6.24 (dt, *J* = 15.8, 7.1 Hz, 1H), 3.49 (dd, *J* = 7.4, 1.4 Hz, 2H).

¹³C NMR (100 MHz, DMSO-D₆) δ 173.2, 134.6, 131.5, 129.5, 128.9, 127.9, 127.5, 127.3, 126.9, 41.9.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.4 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₀H₈O₃NFClS: *m/z* 275.9903 ([M-H]⁺), found: *m/z* 275.9905 ([M-H]⁺)

methyl (*E*)-4-(4-((fluorosulfonyl)amino)-4-oxobut-1-en-1-yl)benzoate (**4i**)



Prepared according to general procedure C with (*E*)-4-(4-(methoxycarbonyl)phenyl)but-3-enoic acid (1.41 mmol, 310 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound which contains α,β -isomer of **4i**. Recrystallization from DCM/hexane gave the pure product in 31% yield (481 μ mol, 145 mg, α,β -isomer of **4i** : **4i** = 4:96) as a yellow solid.

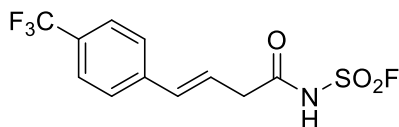
¹H NMR (399 MHz, CDCl₃) δ 8.01 (d, *J* = 8.2 Hz, 3H), 7.44 (d, *J* = 8.2 Hz, 2H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.37 (dt, *J* = 15.9, 7.0 Hz, 1H), 3.92 (s, 5H), 3.47 (dd, *J* = 7.1, 1.1 Hz, 2H). The N-H proton broadens out.

¹³C NMR (100 MHz, DMSO-D₆) δ 172.5, 166.0, 141.6, 131.3, 129.6, 128.1, 127.0, 126.2, 52.1, 41.5.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.5 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₂H₁₁O₅NFS: *m/z* 300.0347 ([M-H]⁺), found: *m/z* 300.0349 ([M-H]⁺)

(*E*)-(4-(4-(trifluoromethyl)phenyl)but-3-enoyl)sulfamoyl fluoride (**4j**)



Prepared according to general procedure C with (*E*)-4-(4-(trifluoromethyl)phenyl)but-3-enoic acid (891 μ mol, 205 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 82% yield (734 μ mol, 229 mg, α,β -isomer of **4j** : **4j** = 12:88).

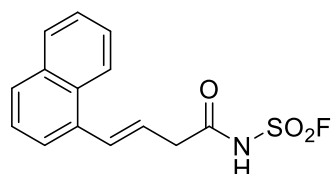
¹H NMR (401 MHz, CDCl₃) δ 8.29 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 16.1 Hz, 1H), 6.35 (dt, *J* = 15.9, 7.1 Hz, 1H), 3.49 (dd, *J* = 7.1, 1.1 Hz, 2H).

¹³C NMR (99 MHz, CDCl₃) δ 166.82, 152.95, 132.01, 132.00, 129.51, 129.30, 123.43, 68.65, 52.36, 27.62, 24.73.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.7 (s, 1F), -63.9 (s, 3F).

HRMS (ESI) exact mass calculated for C₁₁H₈O₃NF₄S: *m/z* 310.0167 ([M-H]⁻), found: *m/z* 310.0167 ([M-H]⁻)

(*E*)-4-(naphthalen-1-yl)but-3-enoyl sulfamoyl fluoride (**4k**)



Prepared according to general procedure C with (*E*)-4-(naphthalen-1-yl)but-3-enoic acid (749 μ mol, 159 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 78% yield (586 μ mol, 172 mg).

¹H NMR (401 MHz, CDCl₃) 8.06 (d, *J* = 7.8 Hz, 1H), 7.88–7.82 (m, 3H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.56–7.50 (m, 3H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 15.6 Hz, 1H), 6.28 (dt, *J* = 15.5, 7.2 Hz, 1H), 3.57 (dd, *J* = 7.1, 1.1 Hz, 2H).

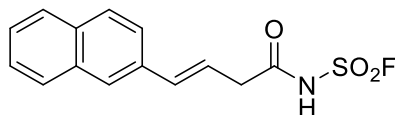
The N-H proton was not observed due to broadening.

¹³C NMR (100 MHz, DMSO-D₆) δ 172.5, 134.2, 133.3, 130.5, 129.3, 128.4, 127.6, 126.4, 126.2, 125.9, 125.8, 123.6, 123.3, 41.5.

¹⁹F NMR (369 MHz, CDCl₃) δ 53.4 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₄H₁₁O₃NFS: *m/z* 292.0449 ([M-H]⁻), found: *m/z* 292.0449 ([M-H]⁻)

(*E*)-4-(naphthalen-2-yl)but-3-enoyl sulfamoyl fluoride (**4l**)



Prepared according to general procedure C with (*E*)-4-(naphthalen-2-yl)but-3-enoic acid (961 μ mol, 204 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 82% yield (788 μ mol, 231 mg, α,β -isomer of **4l** : **4l** = 8:92).

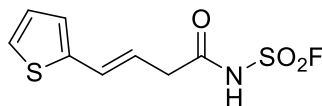
¹H NMR (399 MHz, CDCl₃) δ 7.80–7.84 (m, 3H), 7.73–7.78 (s, 1H), 7.59 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.50–7.47 (m, 2H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.36 (dt, *J* = 15.9, 7.2 Hz, 1H), 3.49 (dd, *J* = 6.9, 1.4 Hz, 2H). The N-H proton broadens out.

¹³C NMR (99 MHz, DMSO-D₆) δ 172.7, 134.4, 133.2, 132.4, 132.3, 128.2, 127.9, 127.6, 126.4, 125.9, 125.6, 124.1, 123.5, 41.5.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.4 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₄H₁₁O₃NFS: *m/z* 292.0449 ([M-H]⁻), found: *m/z* 292.0449 ([M-H]⁻)

(E)-(4-(thiophen-2-yl)but-3-enoyl)sulfamoyl fluoride (4m)



Prepared according to general procedure C with (*E*)-4-(thiophen-2-yl)but-3-enoic acid (1.16 mmol, 195 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 76% yield (880 μ mol, 220 mg).

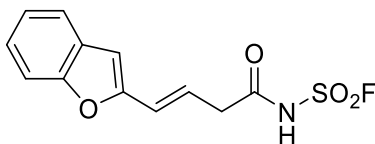
¹H NMR (401 MHz, CDCl₃) δ 8.72 (s, 1H), 7.22 (d, *J* = 4.6 Hz, 1H), 7.01–6.98 (m, 2H), 6.75 (d, *J* = 15.6 Hz, 1H), 6.03 (dt, *J* = 15.6, 7.4 Hz, 1H), 3.39 (dd, *J* = 7.1, 1.1 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 167.5, 140.6, 130.2, 127.7, 127.0, 125.5, 117.4, 40.2.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.2 (s, 1F).

HRMS (ESI) exact mass calculated for C₈H₇O₃NFS₂: *m/z* 247.9857 ([M-H]⁺), found: *m/z* 247.9857 ([M-H]⁺)

(E)-(4-(benzofuran-2-yl)but-3-enoyl)sulfamoyl fluoride (4n)



Prepared according to general procedure C with (*E*)-4-(benzofuran-2-yl)but-3-enoic acid (564 μ mol, 114 mg) for 1 h. The residue was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound with some impurities. Recrystallization from DCM/hexane gave the pure product in 31% yield (180 μ mol, 55 mg) as a brown solid.

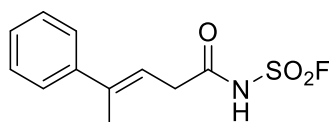
¹H NMR (401 MHz, CDCl₃) δ 8.41 (s, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.30 (td, *J* = 7.7, 1.1 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.65 (s, 1H), 6.57 (d, *J* = 16.1 Hz, 1H), 6.44 (dt, *J* = 15.7, 7.3 Hz, 1H), 3.48 (dd, *J* = 7.1, 1.1 Hz, 2H).

¹³C NMR (100 MHz, DMSO-D₆) δ 172.8, 154.2, 154.0, 128.6, 126.6, 124.5, 123.0, 121.0, 120.7, 110.8, 104.0, 41.4.

¹⁹F NMR (369 MHz, CDCl₃) δ 57.0 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₂H₉O₄NFS: *m/z* 282.0242 ([M-H]⁺), found: *m/z* 282.0242 ([M-H]⁺)

(E)-(4-phenylpent-3-enoyl)sulfamoyl fluoride (4o)



Prepared according to general procedure C with (*E*)-4-phenylbut-3-enoic acid (613 μ mol, 108 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a pale yellow solid in 76% yield (467 μ mol, 120.1 mg). The stereochemistry of the title compound was determined to be the *E*-isomer based on NOE analysis.

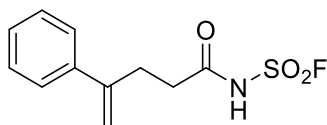
¹H NMR (399 MHz, CDCl₃) δ 7.42–7.40 (m, 2H), 7.34–7.30 (m, 2H), 7.28–7.23 (m, 1H), 5.93 (td, *J* = 7.2, 1.2 Hz, 1H), 3.31 (d, *J* = 7.3 Hz, 2H), 2.08 (s, 3H). The NH proton broadens out.

¹³C NMR (100 MHz, CDCl₃) δ 168.0, 142.6, 142.0, 128.6, 128.1, 126.0, 115.7, 36.5, 16.6.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.0 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₁H₁₁O₃NFS: *m/z* 256.0449 ([M-H]⁻), found: *m/z* 256.0451 ([M-H]⁻)

(4-phenylpent-4-enoyl)sulfamoyl fluoride (18a)



Prepared according to general procedure C with 4-phenylpent-4-enoic acid (1.00 mmol, 176 mg), triethylamine (1.4 mmol, 195 μL, 1.4 equiv.) fluorosulfonyl isocyanate (1.3 mmol, 99.7 μL, 1.3 equiv.) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a white solid in 90% yield (889 μmol, 229 mg).

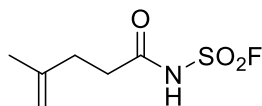
¹H NMR (399 MHz, CDCl₃) δ 7.27-7.45 (m, 5H), 5.36 (s, 1H), 5.14 (s, 1H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.59 (t, *J* = 7.5 Hz, 2H). The N-H proton was not observed due to broadening.

¹³C NMR (100 MHz, CDCl₃) δ 169.6, 145.7, 139.7, 128.9, 128.2, 126.2, 114.5, 35.1, 29.8.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.0 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₁H₁₁O₃NFS: *m/z* 256.0449 ([M-H]⁻), found: *m/z* 256.0449 ([M-H]⁻)

(4-methylpent-4-enoyl)sulfamoyl fluoride (18b)



Prepared according to general procedure C with 4-methylpent-4-enoic acid (1.76 mmol, 200 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a white solid in 58% yield (1.01 mmol, 197 mg).

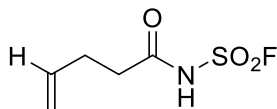
¹H NMR (399 MHz, CDCl₃) δ 4.84 (s, 1H), 4.74 (s, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.77 (s, 3H). The N-H proton was not observed due to broadening.

¹³C NMR (100 MHz, CDCl₃) δ 169.4, 143.0, 111.8, 34.4, 31.6, 22.5.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.1 (s, 1F).

HRMS (ESI) exact mass calculated for C₆H₉O₃NFS: *m/z* 194.0293 ([M-H]⁻), found: *m/z* 194.0293 ([M-H]⁻)

pent-4-enoylsulfamoyl fluoride (18c)



Prepared according to general procedure C with 4-methylpent-4-enoic acid (2.00 mmol, 200 mg) for 1 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 15–80%) to give the title compound as a white solid in 71% yield (1.41 mmol, 255 mg).

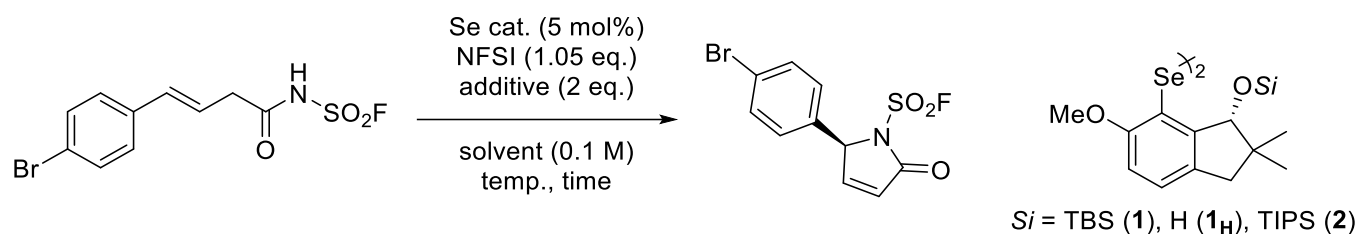
¹H NMR (399 MHz, CDCl₃) δ 5.82 (ddt, *J* = 17.0, 9.9, 6.6 Hz, 1H), 5.15-5.08 (m, 2H), 2.60 (t, *J* = 7.1 Hz, 2H), 2.48-2.42 (m, 2H). The N-H proton was not observed due to broadening.

¹³C NMR (100 MHz, CDCl₃) δ 169.8, 135.3, 117.1, 35.4, 27.9.

¹⁹F NMR (376 MHz, CDCl₃) δ 53.1 (s, 1F).

HRMS (ESI) exact mass calculated for C₅H₇O₃NFS: *m/z* 180.0136 ([M-H]⁻), found: *m/z* 180.0141 ([M-H]⁻)

5. Reaction optimization

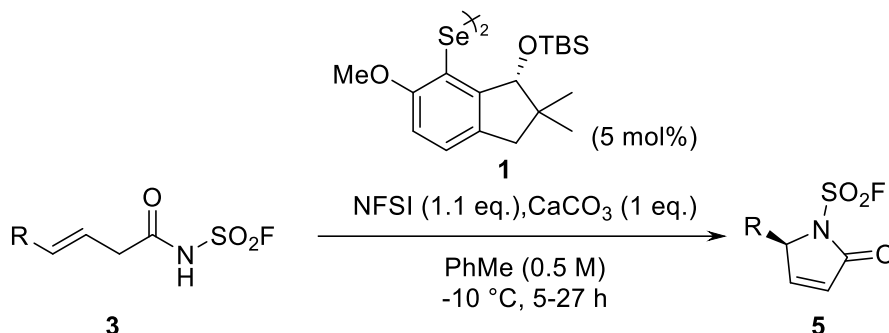


entry	solvent	Se cat.	additive	temp. (°C)	time	%yield	%ee
1	toluene	1	CaCO ₃ (1 eq.)	-10	20 h	11	53
2	toluene	1	CF ₃ OTMS (1.2 eq.)	10	18 h	77	23
3	toluene	1	AcOTMS (2 eq.)	0 to r.t.	20 h	56	39
4	CH ₃ CN	1	AcOTMS (2 eq.)	0	22 h	44	31
5	EtOH	1	AcOTMS (2 eq.)	0	18 h	64	53
6	EtOH	1	w/o AcOTMS	0	24 h	63	-31
7	EtOH	1	AcOTMS (10 eq.)	0	16 h	36	48
8	EtOH	1 _H	AcOTMS (2 eq.)	0	16 h	92	-70
9	DCM	1 _H	AcOTMS (2 eq.)	0	16 h	95	-68
10	toluene	1 _H	AcOTMS (2 eq.)	0	17 h	86	-64
11	CH ₃ CN	1 _H	AcOTMS (2 eq.)	0	17 h	79	-50
12	THF	1 _H	AcOTMS (2 eq.)	0 to r.t.	24 h	61	-40
13	DMF	1 _H	AcOTMS (2 eq.)	0	16 h	68	-38
14	EtOH	1 _H	NaF (4 eq.)	0	22 h	96	-65
15	EtOH	2	AcOTMS (2 eq.)	0 to r.t.	2 d	42	92
16	CH ₃ CN	2	AcOTMS (2 eq.)	0 to r.t.	16 h	80	56
17	2-propanol	2	AcOTMS (2 eq.)	0 to r.t.	3 d	30	74
18	CH ₃ NO ₂	2	AcOTMS (2 eq.)	0	17 h	76	33
19	CH ₃ OH	2	AcOTMS (2 eq.)	0	16 h	64	88
20	MeCN/MeOH 1/1	2	AcOTMS (2 eq.)	0	2 d	80	86
21	MeCN/EtOH 1/1	2	AcOTMS (2 eq.)	0 to r.t.	39 h	83	83
22	toluene/CH ₃ OH 1/1	2	AcOTMS (2 eq.)	0 to r.t.	2 d	41	83
23	DCM/CH ₃ OH 1/1	2	AcOTMS (2 eq.)	0	2 d	67	90
24	CH ₃ NO ₂ /H ₂ O 9/1	2	AcOTMS (2 eq.)	0	24 h	85	55
25	CH ₃ CN/H ₂ O 9/1	2	AcOTMS (2 eq.)	0	2 d	88	83
26	CH ₃ CN and H ₂ O (5 eq.)	2	AcOTMS (2 eq.)	0	2 d	89	49
27	CH ₃ CN/H ₂ O 7/3	2	w/o AcOTMS	0	2 d	71	58
28	CH ₃ CN/H ₂ O 9/1	2	TMS ₂ O (2 eq.) and AcOH (2 eq.)	0	2 d	70	67
29	CH ₃ CN/H ₂ O 9/1	2	NaF (4 eq.)	0	-	n.d.	n.d.
30	CH ₃ CN/H ₂ O 9/1	2	SiO ₂	0	2 d	87	66
31	CH ₃ CN/H ₂ O 9/1	2	AcOTMS (2 eq.)	10	2 d	>99(90) ^a	83(83) ^a
32	CH ₃ CN/H ₂ O 9/1	1	AcOTMS (2 eq.)	10	2 d	>99	38
33	CH ₃ CN/H ₂ O 9/1	2	CF ₃ OTMS (2.0 eq.)	10	18 h	91	90

General reaction conditions: (*E*)-(4-(4-bromophenyl)but-3-en-2-yl)sulfamoyl fluoride (50 μmol), Se cat. (2.5 μmol), NFSI (53 μmol), additive, solvent (500 μL); Yields were isolated yields.; ^a100 μmol scale.

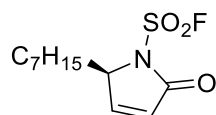
6. Selenium-catalyzed enantioselective lactamization (Figure 2a)

General procedure D



To a stirred solution of the corresponding N-(fluorosulfonyl)amide (0.10 mmol) in toluene (200 μ L) were added selenium catalyst **1** (5.00 μ mol, 3.84 mg),^[2] CaCO₃ (100 μ mol, 10.0 mg), and N-fluorobenzenesulfonimide (0.11 mmol, 34.7 mg) at -10 °C. Progress of the reaction was monitored by TLC. After completion, the reaction was quenched with 1 N HCl aq. The organic layer was extracted with EtOAc, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel.

(*R*)-2-heptyl-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (**5a**)



Prepared according to general procedure D with (*E*)-undec-3-enoylsulfamoyl fluoride **3a** (100 μ mol, 26.5 mg) for 20 h. The crude material was purified by column chromatography on silica gel (hexane/EtOAc, 5–30%) to give the title compound as a pale yellow oil in 64% yield (64.2 μ mol, 16.9 mg) with 94% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.38 (dd, *J* = 6.3, 2.0 Hz, 1H), 6.21 (dd, *J* = 6.3, 1.7 Hz, 1H), 4.87-4.84 (m, 1H), 2.15-2.09 (m, 1H), 1.95-1.88 (m, 1H), 1.34-1.19 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H).

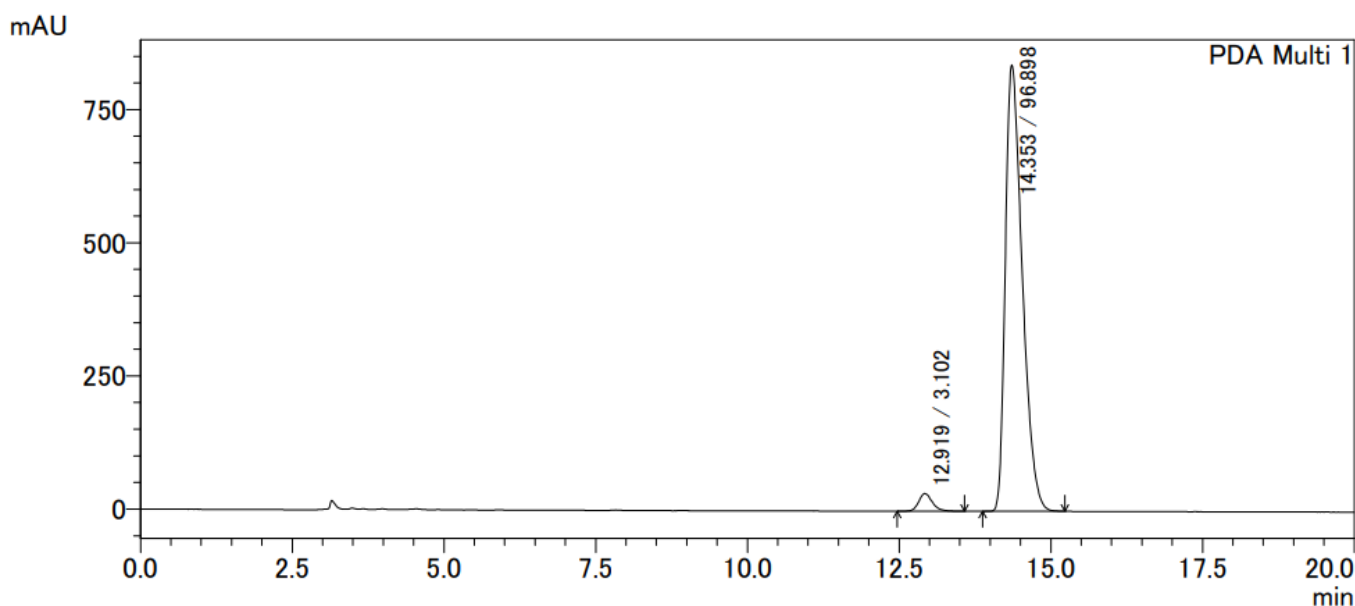
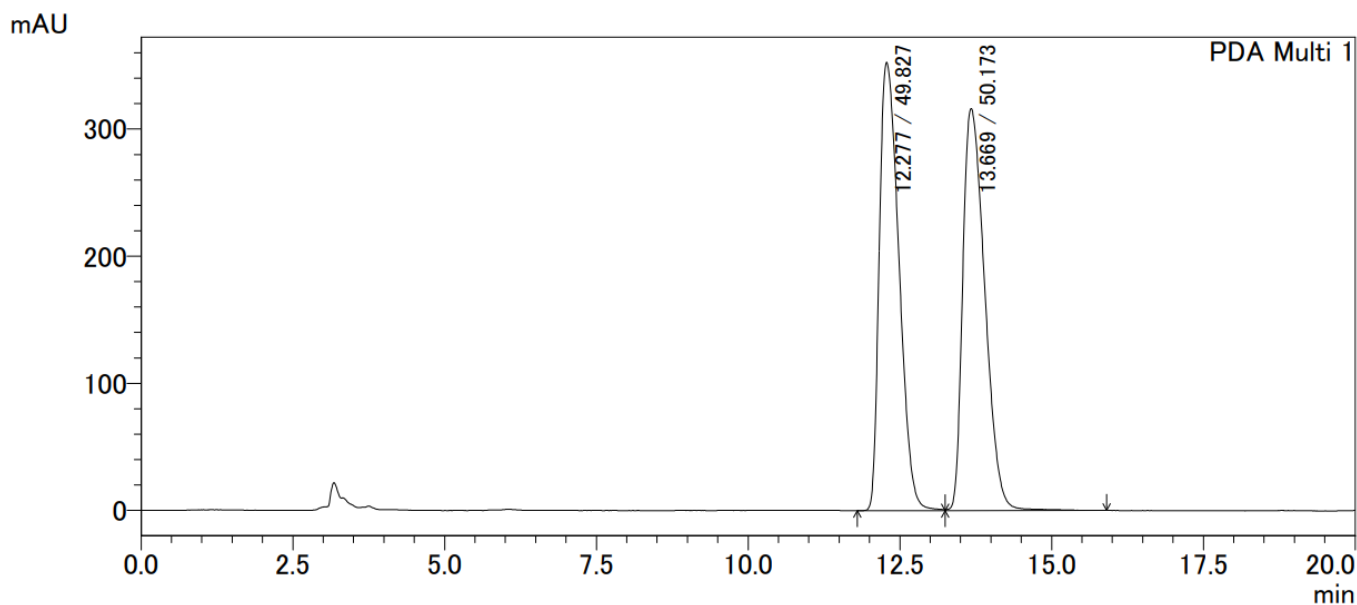
¹³C NMR (126 MHz, CDCl₃) δ 166.6, 153.1, 124.6, 65.7, 31.6, 31.3, 29.2, 28.9, 23.5, 22.5, 14.0.

¹⁹F NMR (471 MHz, CDCl₃) δ 55.0 (s, 1F).

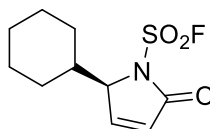
HRMS (ESI) exact mass calculated for C₁₁H₁₈FNO₃SNa: *m/z* 286.0884 ([M+Na]⁺), found: *m/z* 286.0884 ([M+Na]⁺).

$[\alpha]_D^{15}$ = -126.0 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALPAK OZ-3, hexane/*i*PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 12.9 min (minor) and 14.4 min (minor).



(R)-2-cyclohexyl-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5b)



Prepared according to general procedure D with (*E*)-(4-cyclohexylbut-3-en-1-yl)sulfamoyl fluoride **3b** (100 μ mol, 24.9 mg) for 23 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 50–100%) to give the title compound as a white solid in 50% yield (49.7 μ mol, 12.3 mg) with 92% ee.

^1H NMR (392 MHz, CDCl_3) δ 7.37 (dd, J = 6.4, 2.1 Hz, 1H), 6.22 (dd, J = 6.4, 1.5 Hz, 1H), 4.76–4.74 (m, 1H), 2.35–2.26 (m, 1H), 1.89–1.82 (m, 2H), 1.80–1.72 (m, 2H), 1.62 (d, J = 13.0 Hz, 1H), 1.43–1.04 (m, 4H), 0.71 (qd, J = 12.6, 3.4 Hz, 1H).

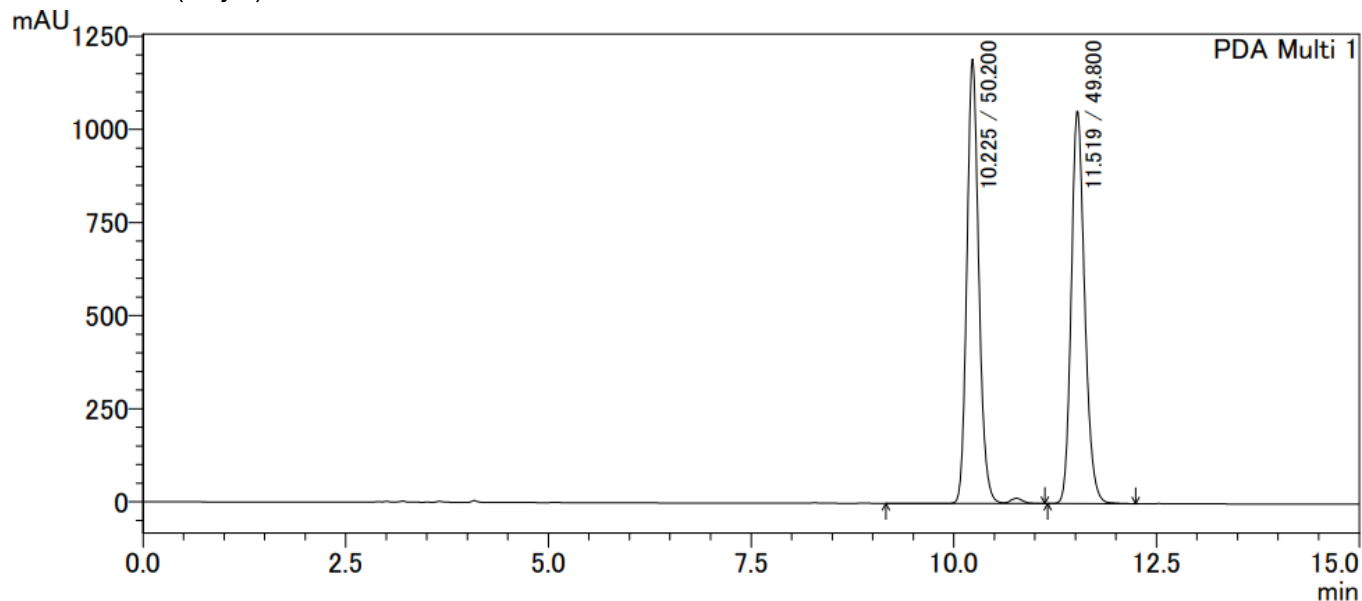
^{13}C NMR (99 MHz, CDCl_3) δ 166.7, 151.4, 125.2, 70.3, 39.2, 30.0, 26.2, 26.1, 25.7, 25.4.

^{19}F NMR (369 MHz, CDCl_3) δ 54.7 (s, 1F).

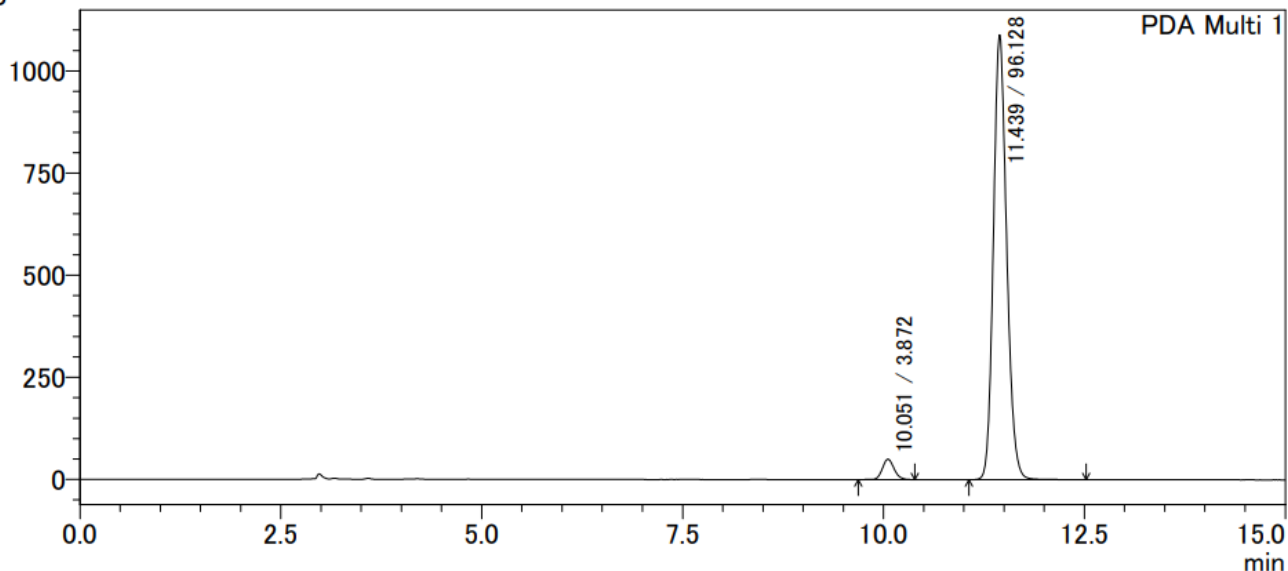
HRMS (ESI) exact mass calculated for $\text{C}_{10}\text{H}_{14}\text{FNO}_3\text{SNa}$: m/z 270.0571 ($[\text{M}+\text{Na}]^+$), found: m/z 270.0571 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_D^{18} = -219.1$ ($c = 0.82$, CHCl_3).

HPLC Daicel CHIRALPAK AD-3, hexane/ i PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 10.1 min (minor) and 11.4 min (major).

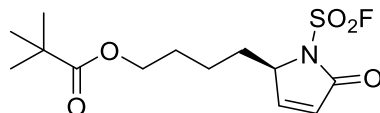


1 PDA Multi 1/208nm 4nm
mAU



1 PDA Multi 1/208nm 4nm

(R)-4-(1-(fluorosulfonyl)-5-oxo-2,5-dihydro-1H-pyrrol-2-yl)butyl pivalate (5c)



Prepared according to general procedure D with (*E*)-8-((fluorosulfonyl)amino)-8-oxooct-5-en-1-yl pivalate **3c** (100 μmol , 33.8 mg, 96% purity) for 16 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 50–100%) to give the title compound as a pale yellow oil in 53% yield (52.9 μmol , 17.0 mg) with 94% ee.

^1H NMR (396 MHz, CDCl_3) δ 7.36 (dd, $J = 6.1, 2.0$ Hz, 1H), 6.23 (dd, $J = 6.2, 1.7$ Hz, 1H), 4.88 (dtd, $J = 7.7, 3.4, 1.8$ Hz, 1H), 4.11–4.02 (m, 2H), 2.19–1.96 (m, 2H), 1.73–1.66 (m, 2H), 1.48–1.24 (m, 2H), 1.19 (s, 9H).

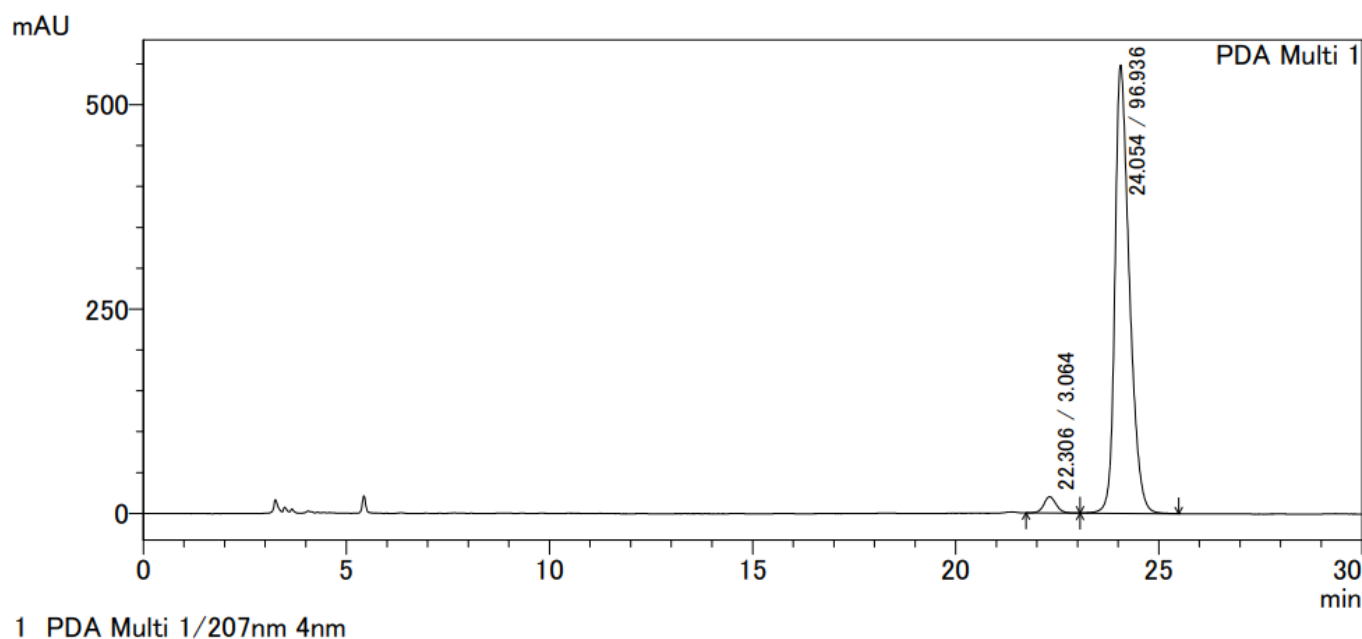
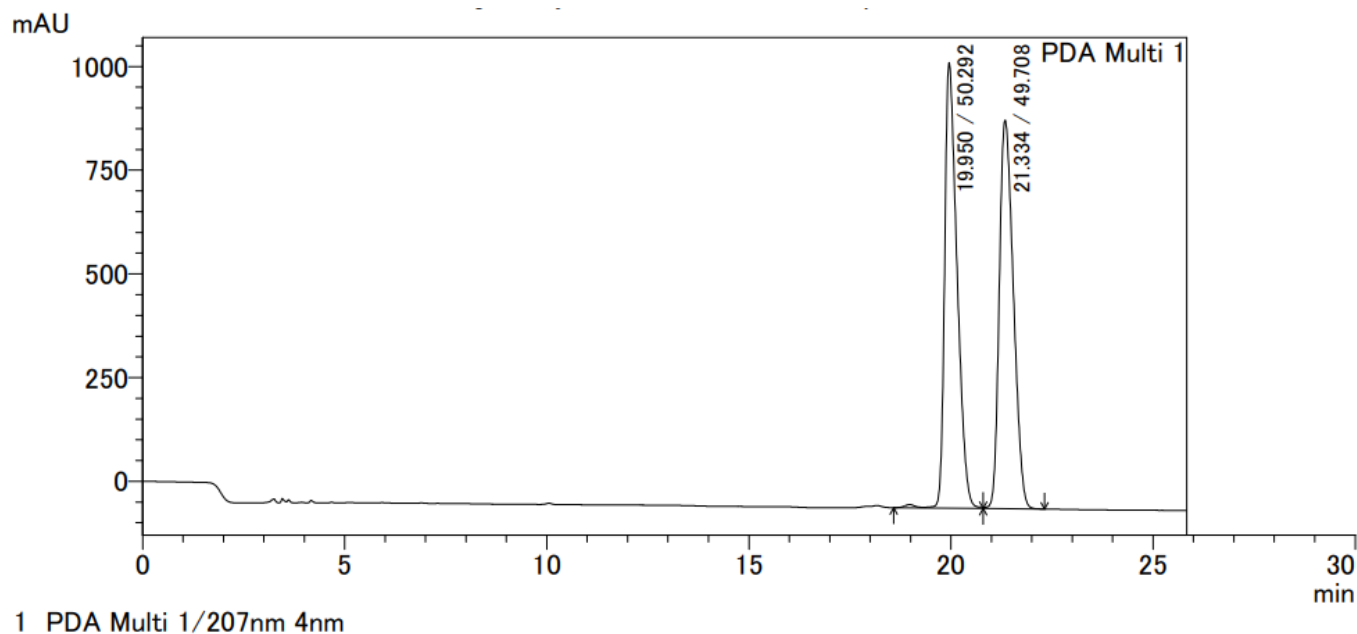
^{13}C NMR (126 MHz, CDCl_3) δ 178.5, 166.4, 152.7, 124.9, 65.3, 63.4, 38.7, 30.7, 28.3, 27.1, 19.9.

^{19}F NMR (471 MHz, CDCl_3) δ 55.0 (s, 1F).

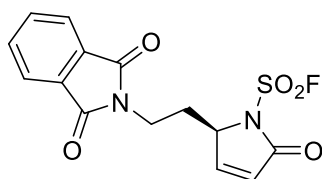
HRMS (ESI) exact mass calculated for $C_{13}H_{20}FNO_5SNa$: m/z 344.0938 ($[M+Na]^+$), found: m/z 344.0938 ($[M+Na]^+$).

$[\alpha]_D^{19} = -122.8$ ($c = 1.0$, $CHCl_3$).

HPLC Daicel CHIRALPAK IB-3, hexane/ i PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 22.3 min (minor) and 24.1 min (major).



(*R*)-2-(2-(1,3-dioxoisindolin-2-yl)ethyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5d)



Prepared according to general procedure D with methyl (*E*)-(6-(1,3-dioxoisindolin-2-yl)hex-3-enoyl)sulfamoyl fluoride **3d** (100 μ mol, 34.0 mg) for 5 h. The crude material was purified by column chromatography on silica gel (hexane/acetone, 10–40%) to give the title compound as a white solid in 51% yield (51.1 μ mol, 17.3 mg) with 89% ee.

¹H NMR (392 MHz, CDCl₃) δ 7.87 (dd, J = 5.4, 3.1 Hz, 2H), 7.76 (q, J = 2.8 Hz, 2H), 7.59 (dd, J = 6.3, 2.0 Hz, 1H), 6.26 (dd, J = 6.3, 1.8 Hz, 1H), 4.88-4.84 (m, 1H), 3.82 (ddd, J = 14.2, 6.7, 5.3 Hz, 1H), 3.75 (ddd, J = 14.4, 8.8, 3.1 Hz, 1H), 2.69-2.61 (m, 1H), 2.29-2.21 (m, 1H).

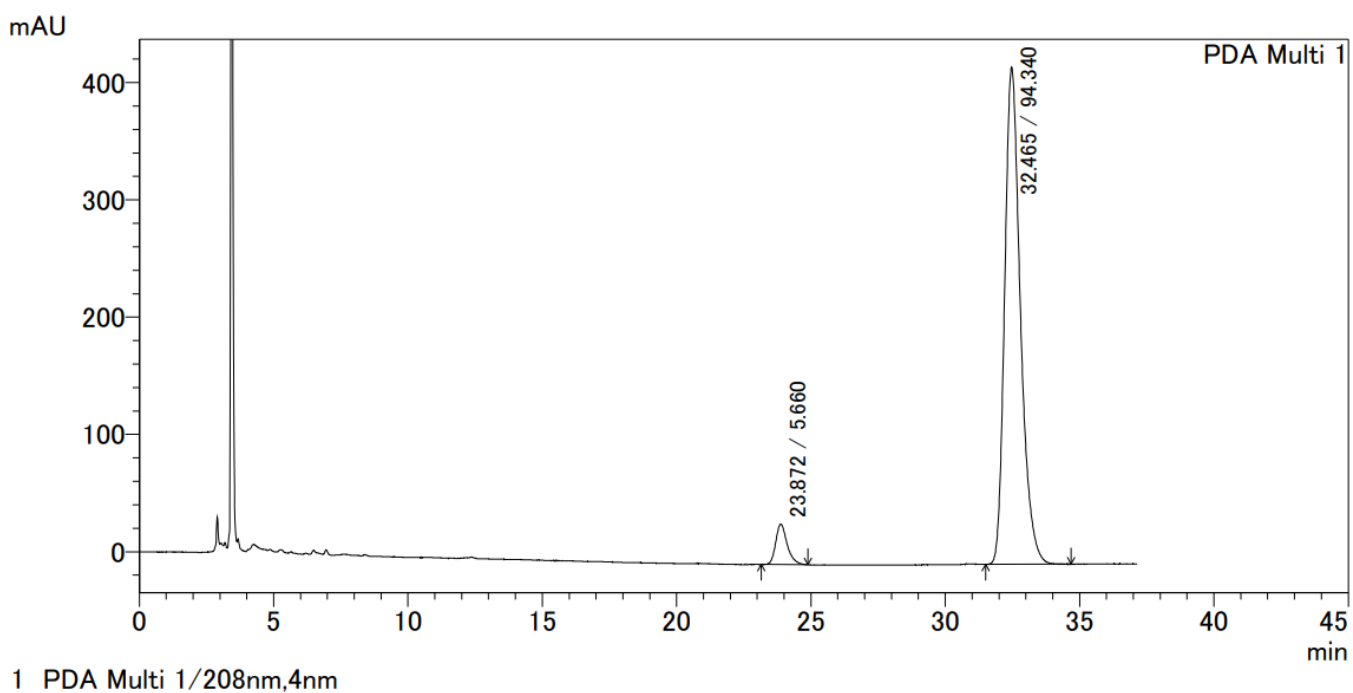
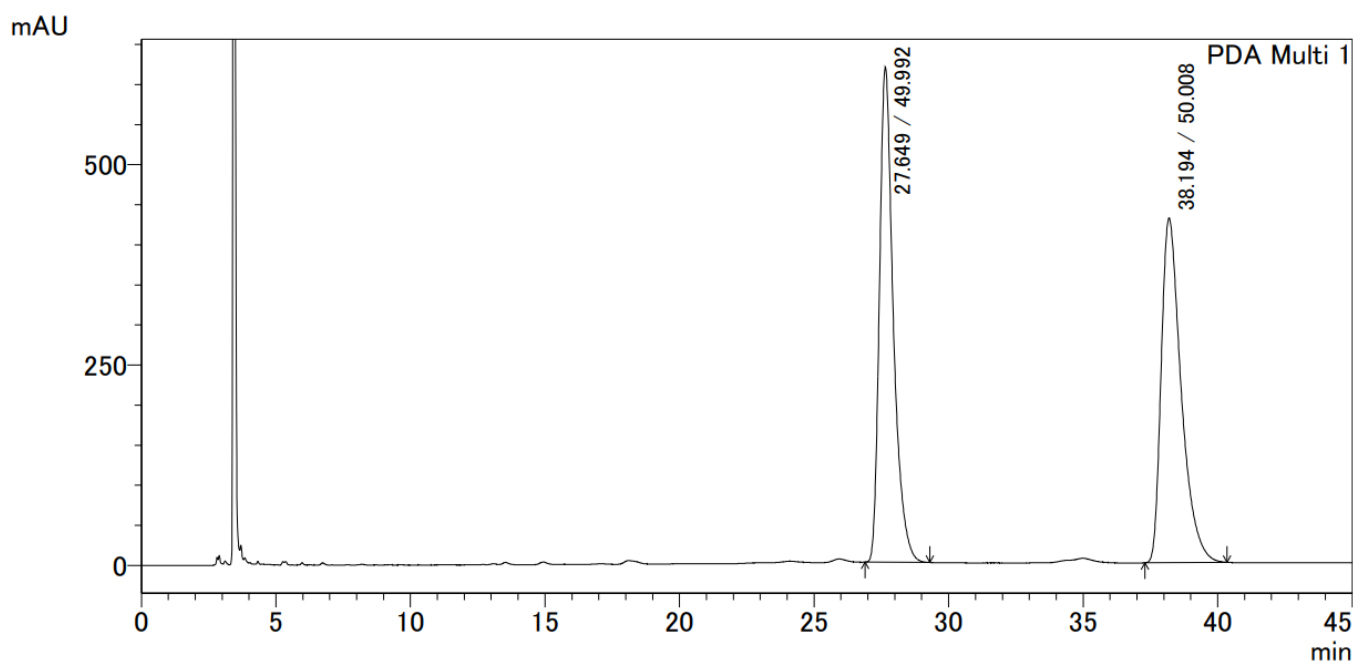
¹³C NMR (126 MHz, CDCl₃) δ 168.0, 166.2, 151.9, 134.4, 131.7, 125.2, 123.6, 63.4 (J_{C-F} = 9.6 Hz), 33.0, 30.8

¹⁹F NMR (369 MHz, CDCl₃) δ 55.2 (s, 1F).

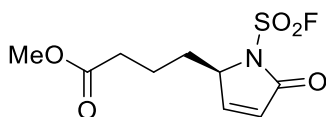
HRMS (ESI) exact mass calculated for C₁₄H₁₁FN₂O₅SNa: *m/z* 361.0265 ([M+Na]⁺), found: *m/z* 361.0265 ([M+Na]⁺).

[α]_D²⁰ = -117.2 (c = 1.0, CHCl₃).

HPLC Daicel CHIRALPAK AD-3, hexane/*i*PrOH = 5:1, flow rate = 1.0 mL/min, retention time; 23.9min (minor) and 32.5 min (major).



methyl (*R*)-4-(1-(fluorosulfonyl)-5-oxo-2,5-dihydro-1H-pyrrol-2-yl)butanoate (5e**)**



Prepared according to general procedure D with methyl (*E*)-8-((fluorosulfonyl)amino)-8-oxooct-5-enoate **3e** (100 μ mol, 28.1 mg, 95% purity) for 27 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 75–100%) to give the title compound as a pale yellow oil in 57% yield (57.3 μ mol, 15.2 mg) with 96% ee.

^1H NMR (392 MHz, CDCl_3) δ 7.40 (dd, J = 6.3, 2.0 Hz, 1H), 6.24 (dd, J = 6.3, 1.8 Hz, 1H), 4.89–4.86 (m, 1H), 3.69 (s, 3H), 2.39 (td, J = 7.1, 1.3 Hz, 2H), 2.20–2.11 (m, 1H), 2.05–1.96 (m, 1H), 1.72–1.52 (m, 2H).

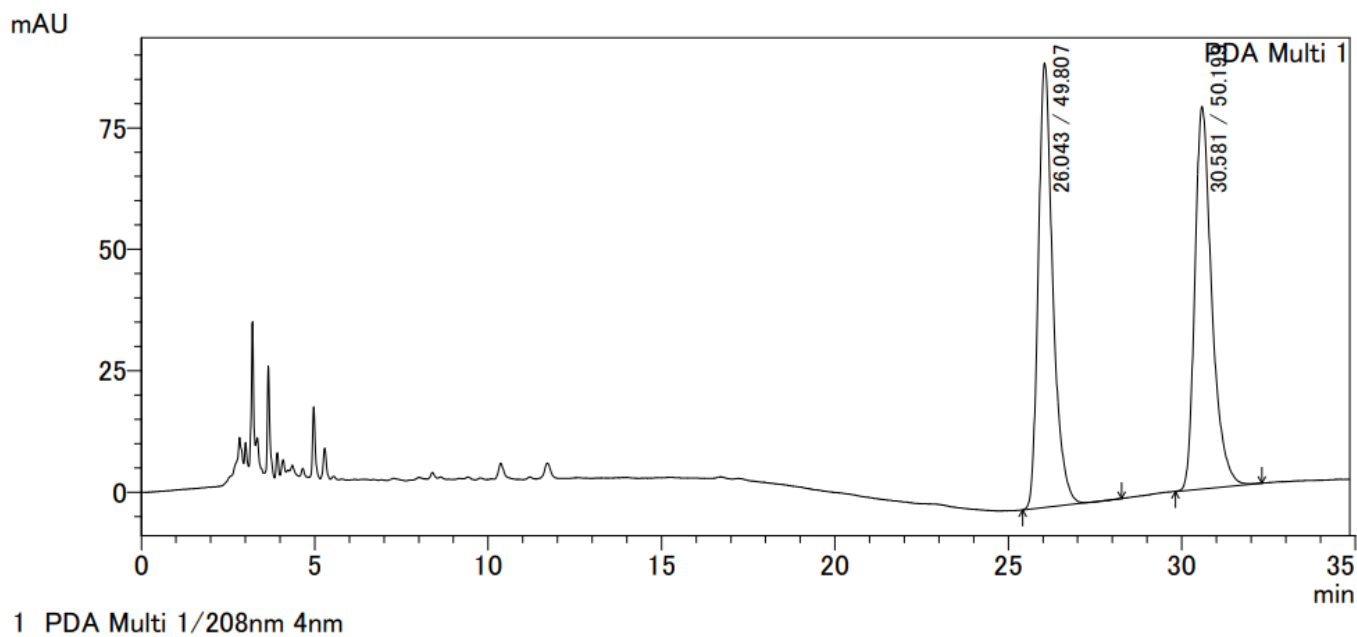
^{13}C NMR (99 MHz, CDCl_3) δ 173.0, 166.5, 152.7, 125.0, 65.1, 51.8, 33.1, 30.5, 18.6.

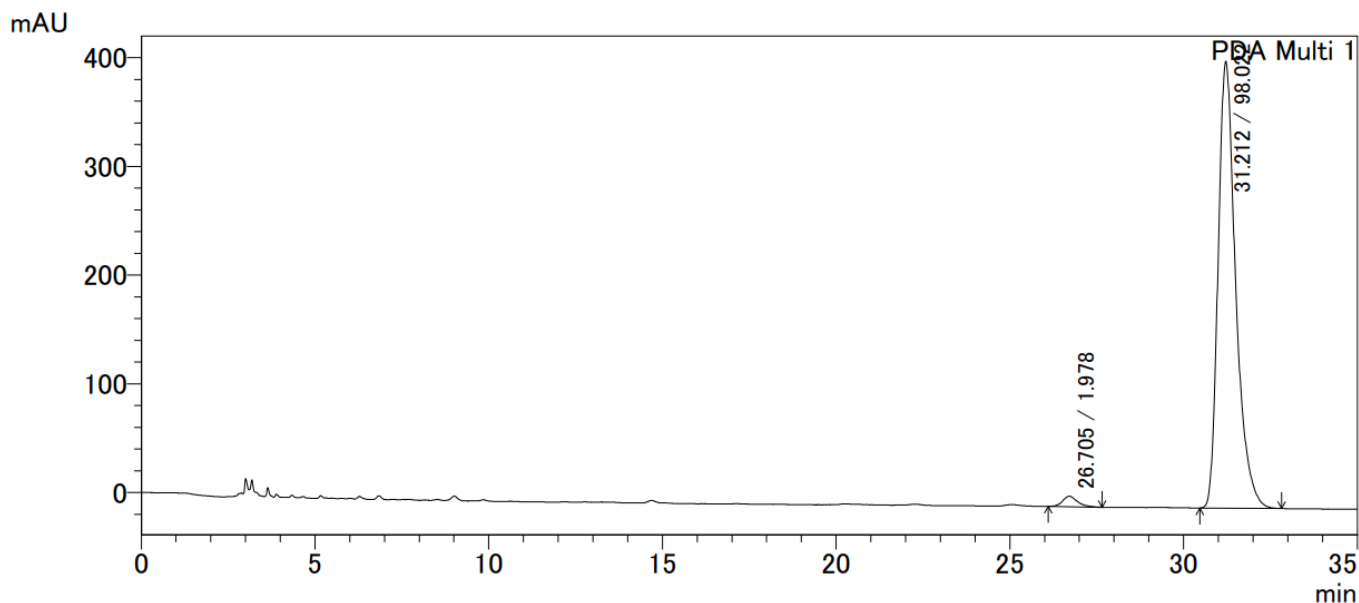
^{19}F NMR (369 MHz, CDCl_3) δ 54.9 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_9\text{H}_{12}\text{FNO}_5\text{SNa}$: m/z 288.0312 ($[\text{M}+\text{Na}]^+$), found: m/z 288.0312 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_{\text{D}}^{20}$ = -137.3 (c = 1.0, CHCl_3).

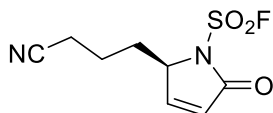
HPLC Daicel CHIRALPAK AD-3, hexane/*i*PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 26.7 min (minor) and 31.2 min (major).





1 PDA Multi 1/208nm 4nm

(R)-2-(3-cyanopropyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5f)



Prepared according to general procedure D with methyl (*E*)-(7-cyanohept-3-enoyl)sulfamoyl fluoride **3f** (100 μ mol, 24.4 mg, 83% purity) for 22 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 15–100%) to give the title compound as a pale yellow oil in 44% yield (65.9 μ mol, 15.3 mg) with 91% ee.

¹H NMR (392 MHz, CDCl₃) δ 7.37 (dd, *J* = 6.3, 2.0 Hz, 1H), 6.28 (dd, *J* = 6.2, 1.7 Hz, 1H), 4.96 (t, *J* = 5.0 Hz, 1H), 2.51–2.37 (m, 2H), 2.25–2.20 (m, 2H), 1.77–1.54 (m, 2H).

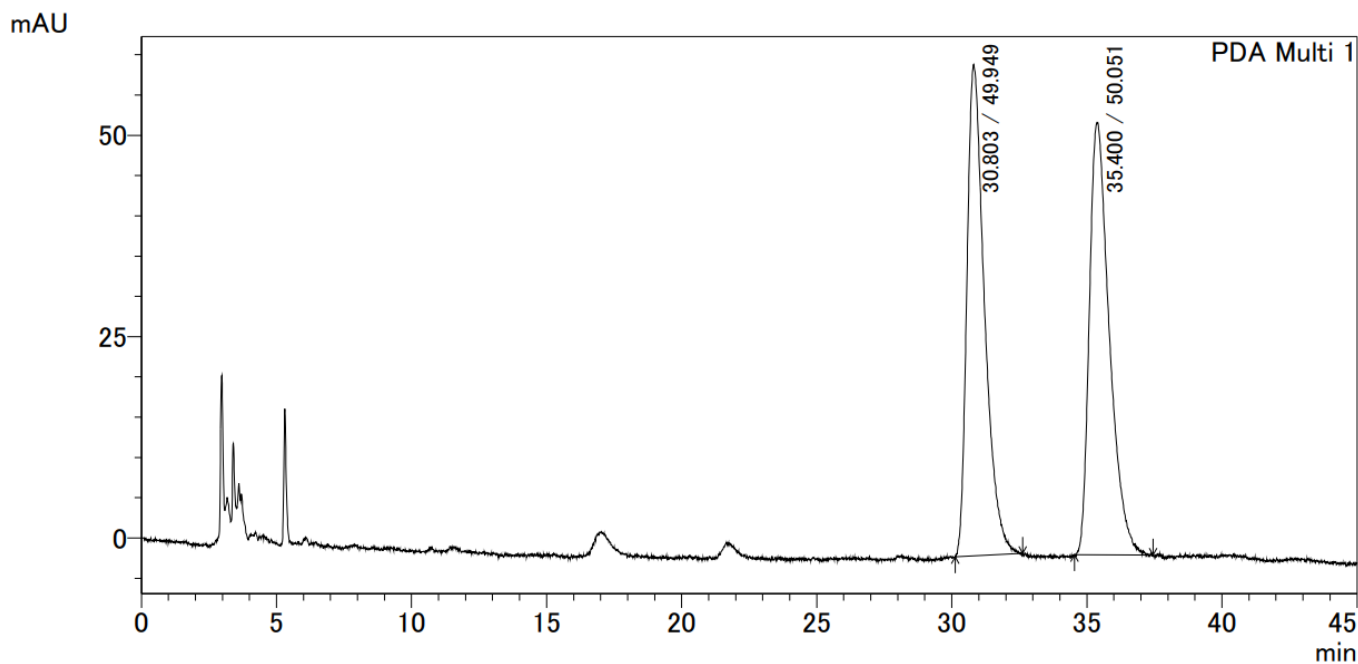
¹³C NMR (99 MHz, CDCl₃) δ 166.2, 152.1, 125.4, 118.5, 64.3, 29.9, 19.3, 17.1.

¹⁹F NMR (369 MHz, CDCl₃) δ 54.8 (s, 1F).

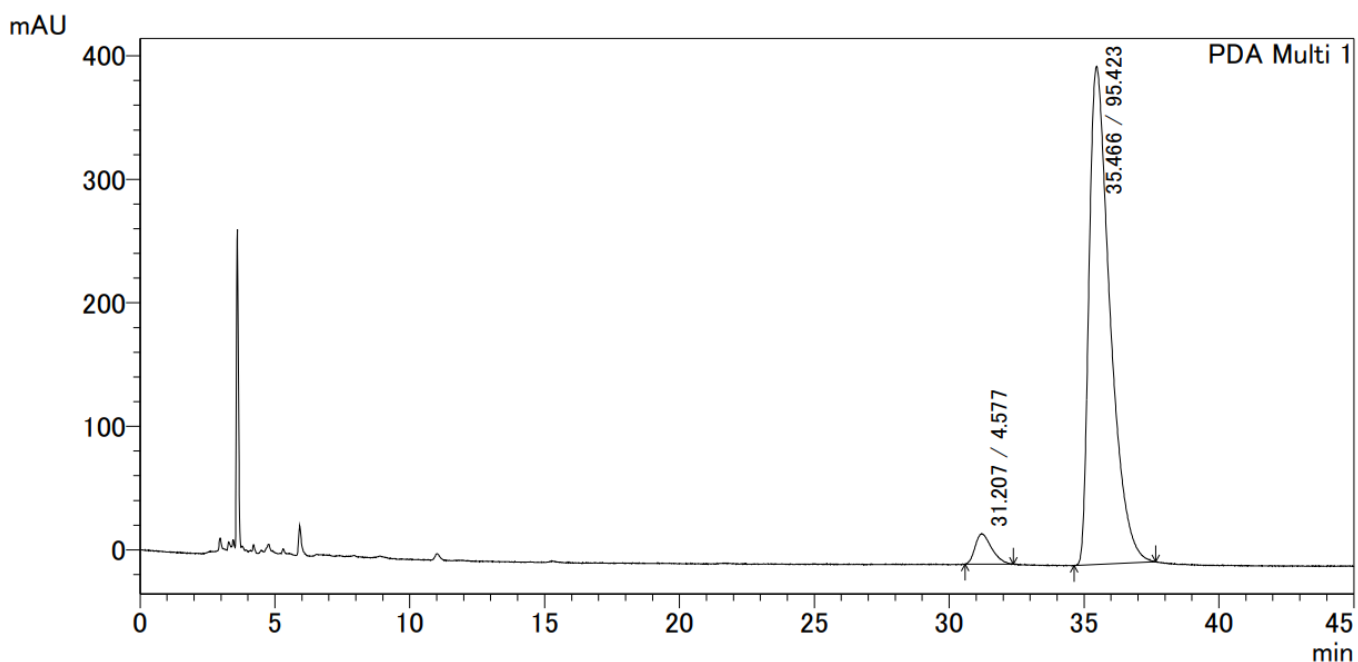
HRMS (ESI) exact mass calculated for C₈H₉FN₂O₃SNa: *m/z* 255.0210 ([M+Na]⁺), found: *m/z* 255.0210 ([M+Na]⁺).

[α]_D¹⁹ = -104.6 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALPAK OD-3, hexane/*i*PrOH = 5:1, flow rate = 1.0 mL/min, retention time; 26.4 min (minor) and 29.8 min (major).

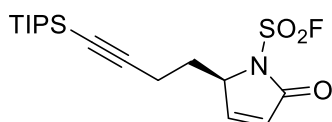


1 PDA Multi 1/204nm,4nm



1 PDA Multi 1/204nm,4nm

(R)-2-oxo-5-(4-(triisopropylsilyl)but-3-yn-1-yl)-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5g)



Prepared according to general procedure D with (*E*)-(8-(triisopropylsilyl)oct-3-en-7-ynoyl)sulfamoyl fluoride **3g** (100 μ mol, 39.1 mg, 96% purity) for 23 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 20–75%) to give the title compound as an orange oil in 60% yield (60.2 μ mol, 22.5 mg) with 94% ee.

^1H NMR (392 MHz, CDCl_3) δ 7.60 (dd, J = 6.2, 2.1 Hz, 1H), 6.21 (dd, J = 6.2, 1.7 Hz, 1H), 5.00–4.96 (m, 1H), 2.53–2.43 (m, 2H), 2.38–2.28 (m, 1H), 2.08–2.00 (m, 1H), 1.11–0.99 (m, 21H).

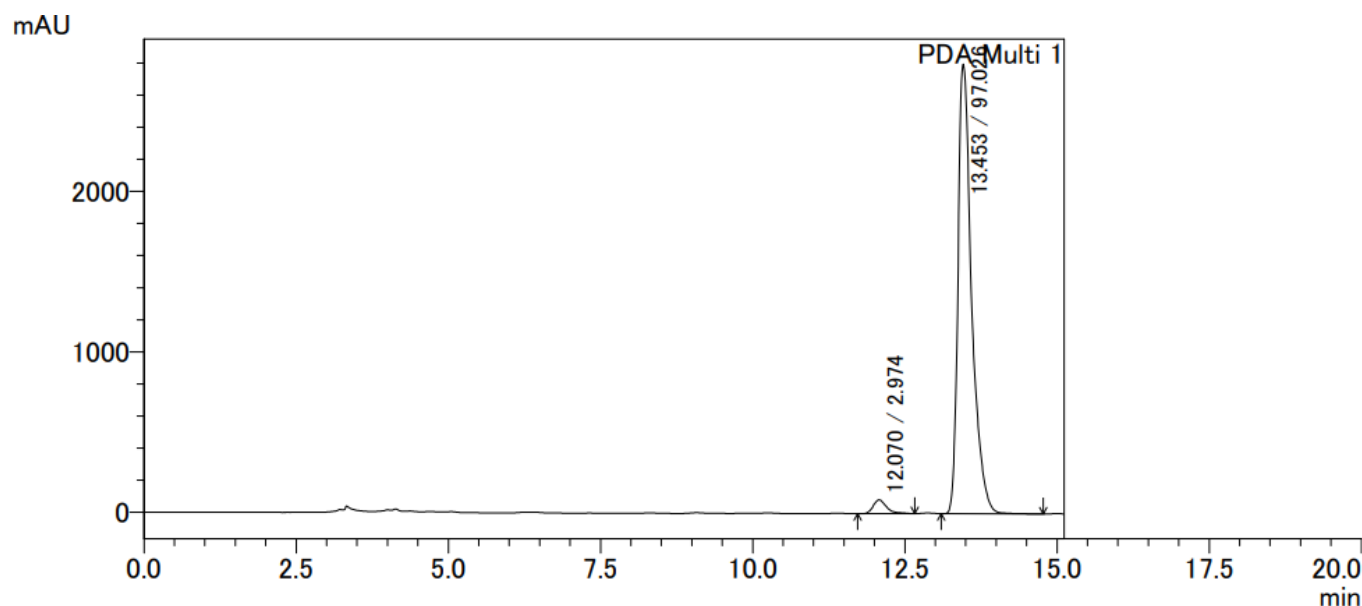
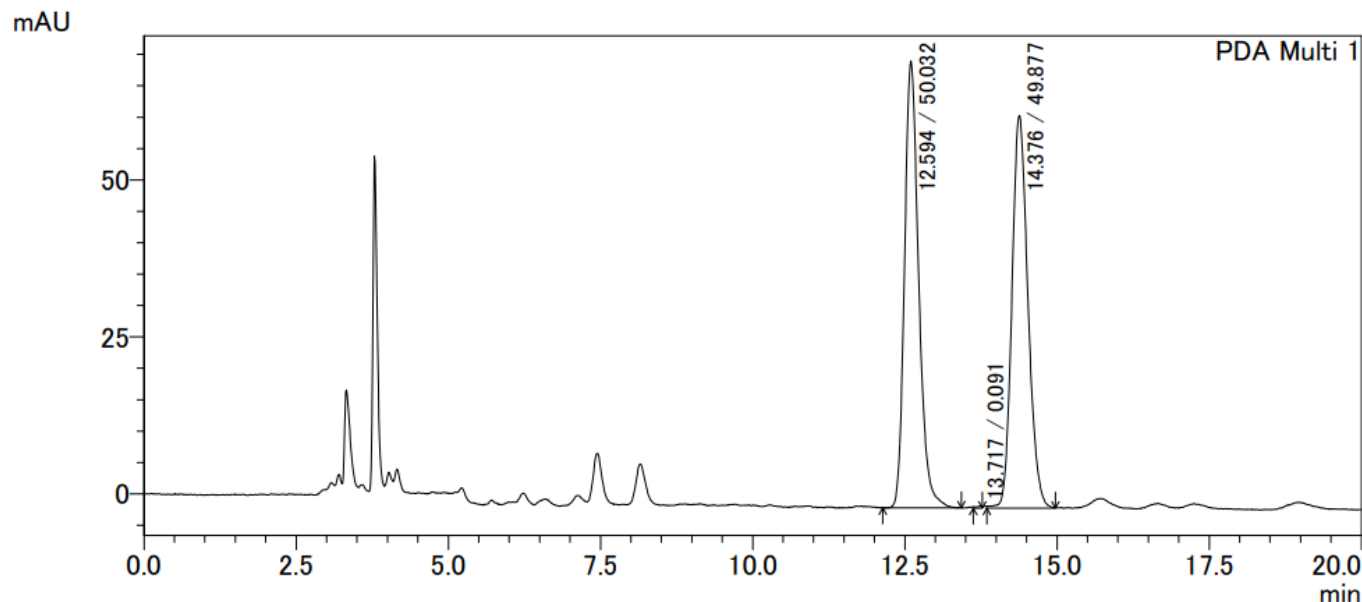
^{13}C NMR (126 MHz, CDCl_3) δ 166.4, 152.6, 124.6, 105.6, 83.6, 64.9, 30.9, 18.5, 15.2, 11.1.

¹⁹F NMR (471 MHz, CDCl₃) δ 55.1 (s, 1F).

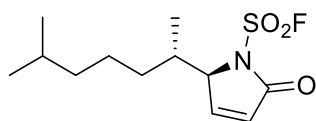
HRMS (ESI) exact mass calculated for C₁₇H₂₈FNO₃SSiNa: *m/z* 396.1435 ([M+Na]⁺), found: *m/z* 396.1435 ([M+Na]⁺).

[α]_D¹⁹ = -112.4 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALPAK IC-3, hexane/*i*PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 12.1min (minor) and 13.5 min (major).



(*R*)-2-((*S*)-6-methylheptan-2-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5h)



Prepared according to general procedure D with (*S,E*)-(5,9-dimethyldec-3-enoyl)sulfamoyl fluoride **3h** (100 μmol, 29.4 mg, 95% purity) for 16 h. The crude material was purified by column chromatography on silica gel

(hexane/DCM, 10–100%) to give the title compound as a pale yellow oil in 52% yield (51.6 μ mol, 14.3 mg) with 85:15 dr.

¹H NMR (500 MHz, CDCl₃) δ 7.35 (dd, J = 6.3, 2.3 Hz, 1H), 6.23 (dd, J = 6.3, 1.7 Hz, 1H), 4.78 (dt, J = 3.4, 1.7 Hz, 1H), 2.51–2.42 (m, 1H), 1.61–1.04 (m, 10H), 0.85 (dd, J = 6.6, 1.4 Hz, 6H).

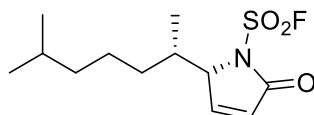
¹³C NMR (126 MHz, CDCl₃) δ 166.8, 150.8, 125.4, 70.7, 38.6, 34.1, 29.4, 27.7, 24.8, 22.5, 22.4, 16.5.

¹⁹F NMR (471 MHz, CDCl₃) δ 54.9 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₂H₂₀FNO₃Na: m/z 300.1040 ([M+Na]⁺), found: m/z 300.1040 ([M+Na]⁺).

$[\alpha]_D^{18}$ = -137.0 (c = 1.0, CHCl₃).

(S)-2-((S)-6-methylheptan-2-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5i)



Prepared according to general procedure D with (*S,E*)-(5,9-dimethyldec-3-enoyl)sulfamoyl fluoride **3h** (100 μ mol, 29.4 mg, 95% purity) for 16 h using **ent-1**. The crude material was purified by column chromatography on silica gel (hexane/DCM, 10–100%) to give the title compound as a pale yellow oil in 56% yield (51.6 μ mol, 14.3 mg) with 93:7 dr.

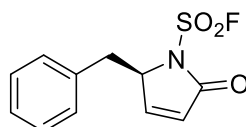
¹H NMR (392 MHz, CDCl₃) δ 7.32 (dd, J = 6.4, 2.1 Hz, 1H), 6.26 (dd, J = 6.4, 1.7 Hz, 1H), 4.85–4.83 (m, 1H), 2.42–2.59 (m, 1H), 1.07–1.69 (m, 7H), 0.90 (s, 3H), 0.88 (s, 3H), 0.75 (d, J = 7.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.9, 150.9, 126.0, 69.8, 38.9, 34.5, 34.3, 28.0, 25.3, 22.7, 22.6, 12.8.

¹⁹F NMR (376 MHz, CDCl₃) δ 54.8 (s, 1F).

$[\alpha]_D^{18}$ = +148.6 (c = 1.0, CHCl₃).

(R)-2-benzyl-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5j)



Prepared according to general procedure D with (*E*)-(5-phenylpent-3-enoyl)sulfamoyl fluoride **3j** (100 μ mol, 25.7 mg). The crude material was purified by column chromatography on silica gel (hexane/DCM, 25–80%) to give the title compound as a pale yellow solid in 76% yield (75.6 μ mol, 19.3 mg) with 95% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.33–7.40 (2H), 7.27–7.32 (1H), 7.24 (dd, J = 6.0, 2.0 Hz, 1H), 7.16–7.21 (2H), 6.12 (dd, J = 6.3, 1.7 Hz, 1H), 4.98 (dtd, J = 9.2, 4.0, 2.0 Hz, 1H), 3.64 (dd, J = 13.7, 4.0 Hz, 1H), 2.93 (dd, J = 13.5, 9.5 Hz, 1H).

¹³C NMR (99 MHz, CDCl₃) δ 166.4, 152.8, 133.6, 129.4, 128.9, 127.7, 124.5, 66.1, 38.4.

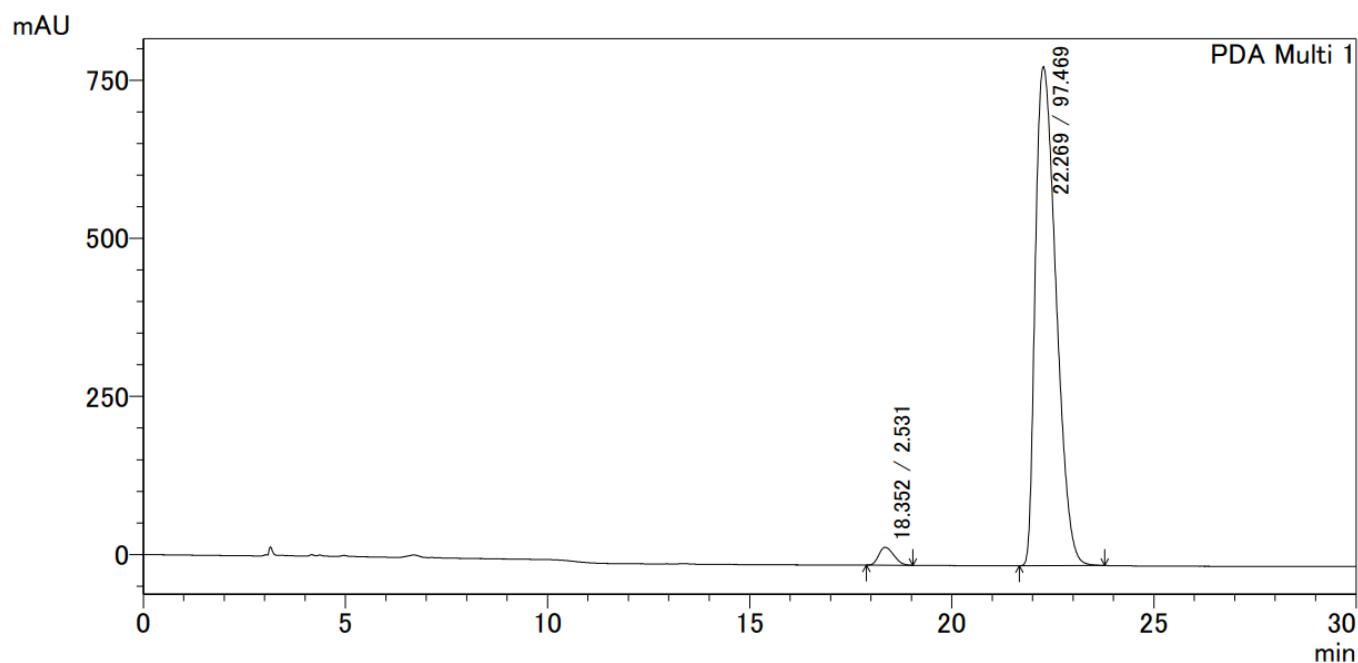
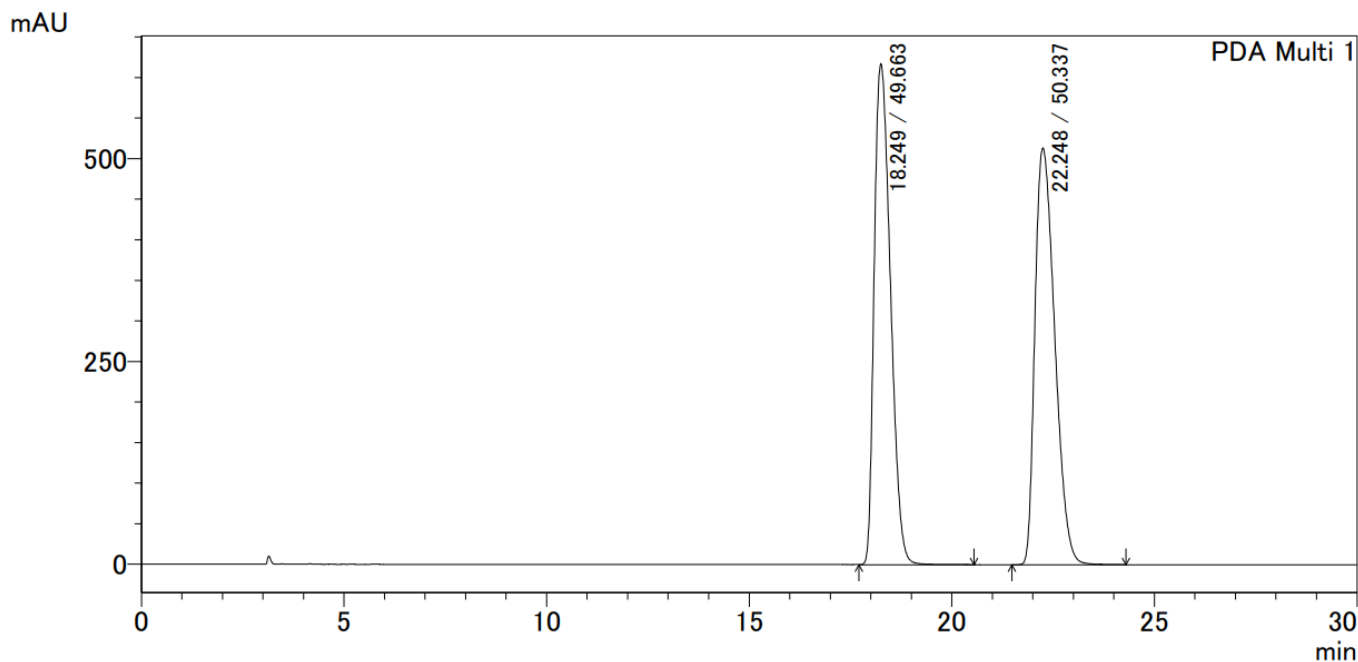
¹⁹F NMR (471 MHz, CDCl₃) δ 55.4 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₁H₁₀FNO₃Na: m/z 278.0258 ([M+Na]⁺), found: m/z 278.0258 ([M+Na]⁺).

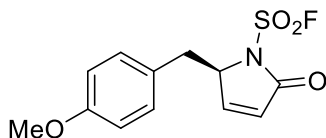
$[\alpha]_D^{18}$ = -199.2 (c = 1.0, CHCl₃).

HPLC Daicel CHIRALPAK OZ-3, hexane/*i*PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 18.4 min (minor) and 22.3 min (major).

CIF File CCDC 2482628 contains supplementary crystallographic data of **5j**.



(R)-2-(4-methoxybenzyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5k)



Prepared according to general procedure D with (*E*)-(5-(4-methoxyphenyl)pent-3-enoyl)sulfamoyl fluoride **3k** (100 μ mol, 29.6 mg, 97.0% purity) for 18 h. The crude material was purified by column chromatography on silica gel (hexane/EtOAc, 5–40%) to give the title compound as an orange oil in 71% yield (70.8 μ mol, 20.2 mg) with 96% ee.

^1H NMR (392 MHz, CDCl_3) δ 7.25 (dd, J = 6.3, 2.0 Hz, 1H), 7.11-7.08 (m, 2H), 6.88-6.85 (m, 2H), 6.12 (dd, J = 6.3, 1.8 Hz, 1H), 4.96-4.92 (m, 1H), 3.80 (s, 3H), 3.56 (dd, J = 13.6, 3.9 Hz, 1H), 2.91 (dd, J = 13.6, 9.3 Hz, 1H).

^{13}C NMR (99 MHz, CDCl_3) δ 166.5, 159.0, 152.9, 130.5, 125.5, 124.6, 114.3, 66.3, 55.3, 37.6.

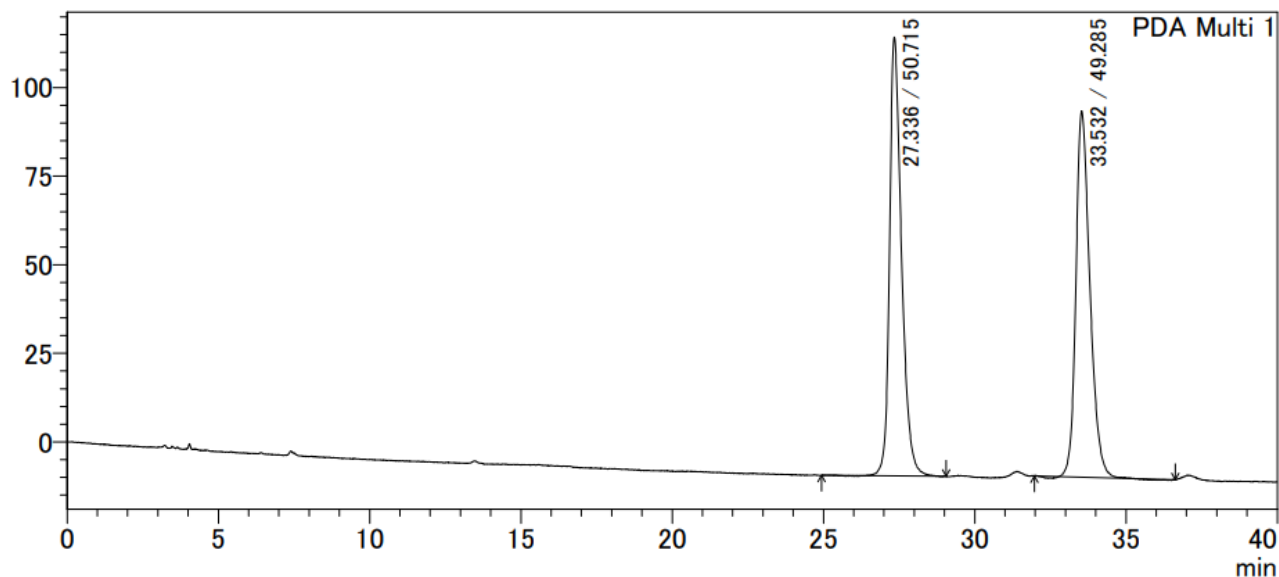
^{19}F NMR (369 MHz, CDCl_3) δ 55.3 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{12}\text{H}_{12}\text{FNO}_4\text{SNa}$: m/z 308.0363 ($[\text{M}+\text{Na}]^+$), found: m/z 308.0363 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_{\text{D}}^{17} = -210.9$ ($c = 1.0$, CHCl_3).

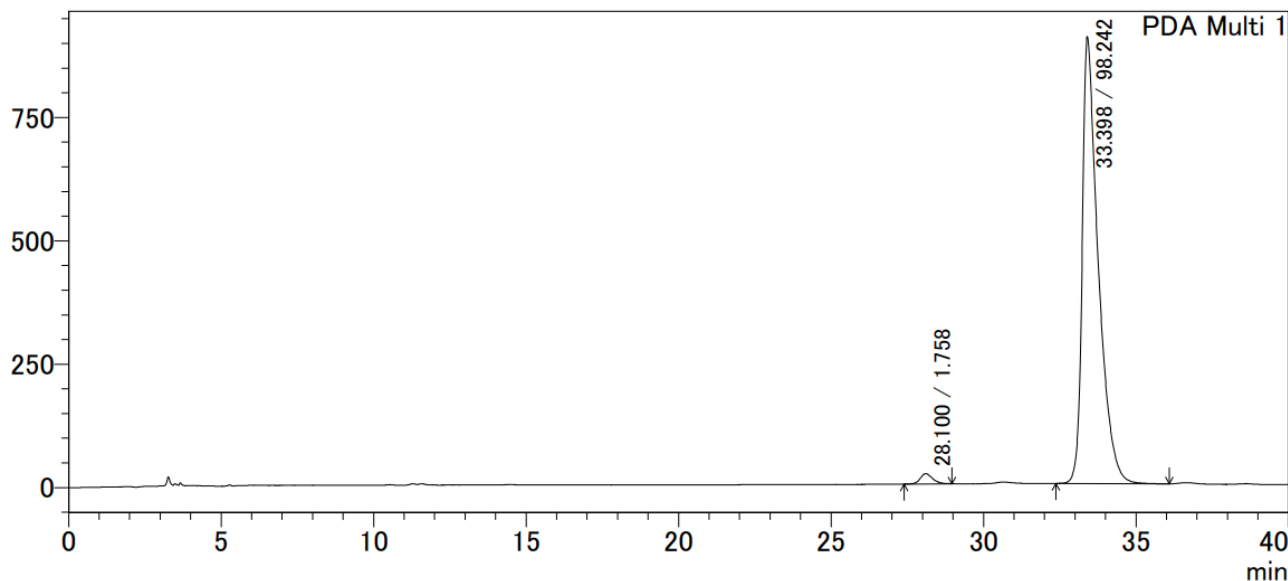
HPLC Daicel CHIRALPAK IB-3, hexane/ i PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 28.1 min (minor) and 33.4 min (major).

mAU



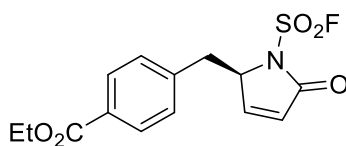
1 PDA Multi 1/205nm 4nm

mAU



1 PDA Multi 1/205nm 4nm

(R)-2-(4-ethoxycarbonylbenzyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5l)



Prepared according to general procedure D with ethyl (*E*)-4-(5-((fluorosulfonyl)amino)-5-oxopent-2-en-1-yl)benzoate **3l** (100 μmol , 32.9 mg) for 23 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 75–100%) to give the title compound as a white solid in 61% yield (61.1 μmol , 20.0 mg) with 93% ee.

¹H NMR (396 MHz, CDCl₃) δ 8.02 (dt, *J* = 8.2, 1.8 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.22 (dd, *J* = 6.1, 2.0 Hz, 1H), 6.14 (dd, *J* = 6.2, 1.7 Hz, 1H), 5.04-5.00 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.65 (dd, *J* = 13.5, 4.0 Hz, 1H), 3.06 (dd, *J* = 13.5, 9.2 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H).

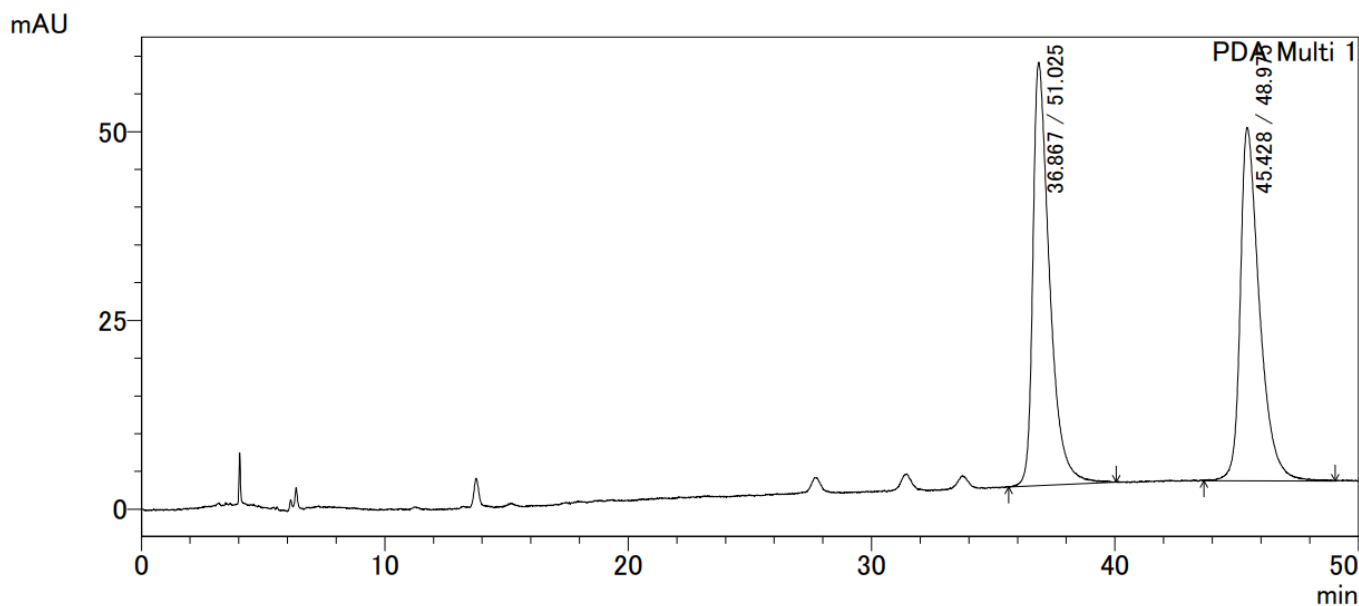
¹³C NMR (99 MHz, CDCl₃) δ 166.2, 166.0, 152.2, 138.6, 130.1, 130.1, 129.5, 124.9, 65.5, 61.1, 38.3, 14.3.

¹⁹F NMR (369 MHz, CDCl₃) δ 55.3 (s, 1F).

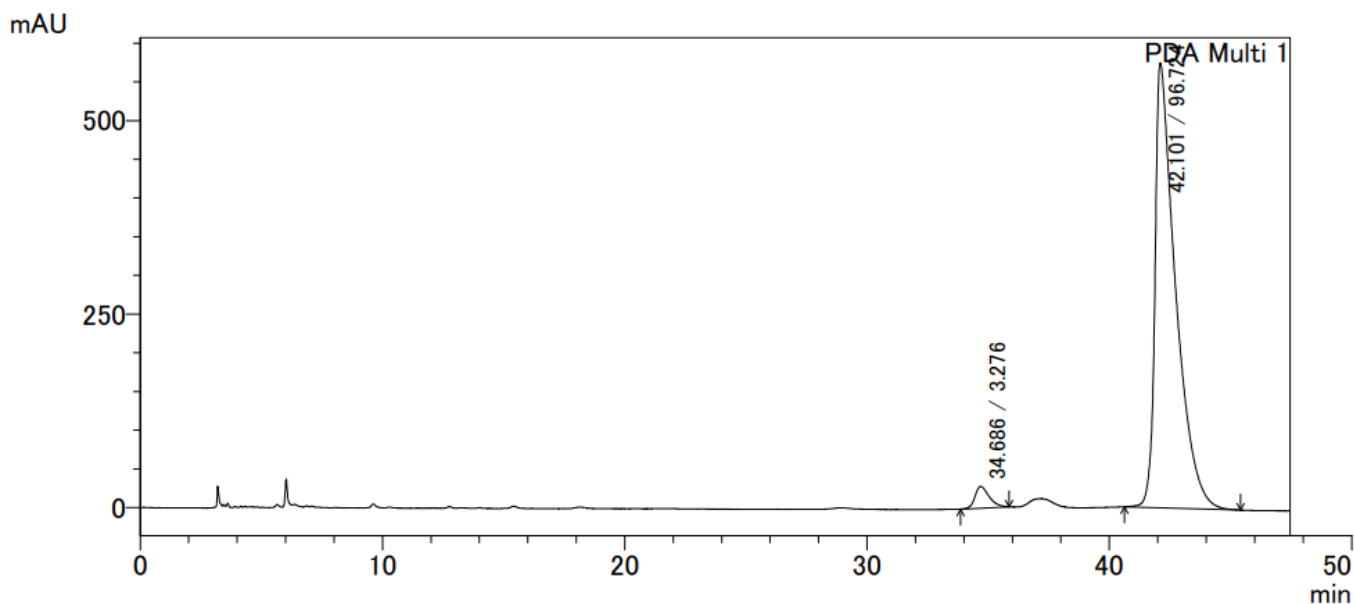
HRMS (ESI) exact mass calculated for C₁₄H₁₄FNO₅SNa: *m/z* 350.0469 ([M+Na]⁺), found: *m/z* 350.0469 ([M+Na]⁺).

[α]_D¹⁸ = -193.4 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALPAK IB-3, hexane/*i*PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 34.7 min (minor) and 42.1 min (major).

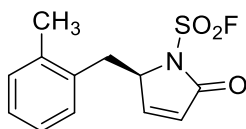


1 PDA Multi 1/205nm 4nm



1 PDA Multi 1/205nm 4nm

(R)-2-(2-methylbenzyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5m)



Prepared according to general procedure D with ethyl (*E*)-(5-(*o*-tolyl)pent-3-enoyl)sulfamoyl fluoride **3m** (100 μ mol, 27.1 mg) for 22 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a white solid in 53% yield (53.1 μ mol, 14.3 mg) with 85% ee.

¹H NMR (396 MHz, CDCl₃) δ 7.24-7.18 (m, 4H), 7.11 (d, *J* = 6.8 Hz, 1H), 6.20 (dd, *J* = 6.3, 1.6 Hz, 1H), 4.92-4.87 (m, 1H), 3.85 (dd, *J* = 13.0, 4.6 Hz, 1H), 2.70 (dd, *J* = 12.9, 11.3 Hz, 1H), 2.38 (s, 3H).

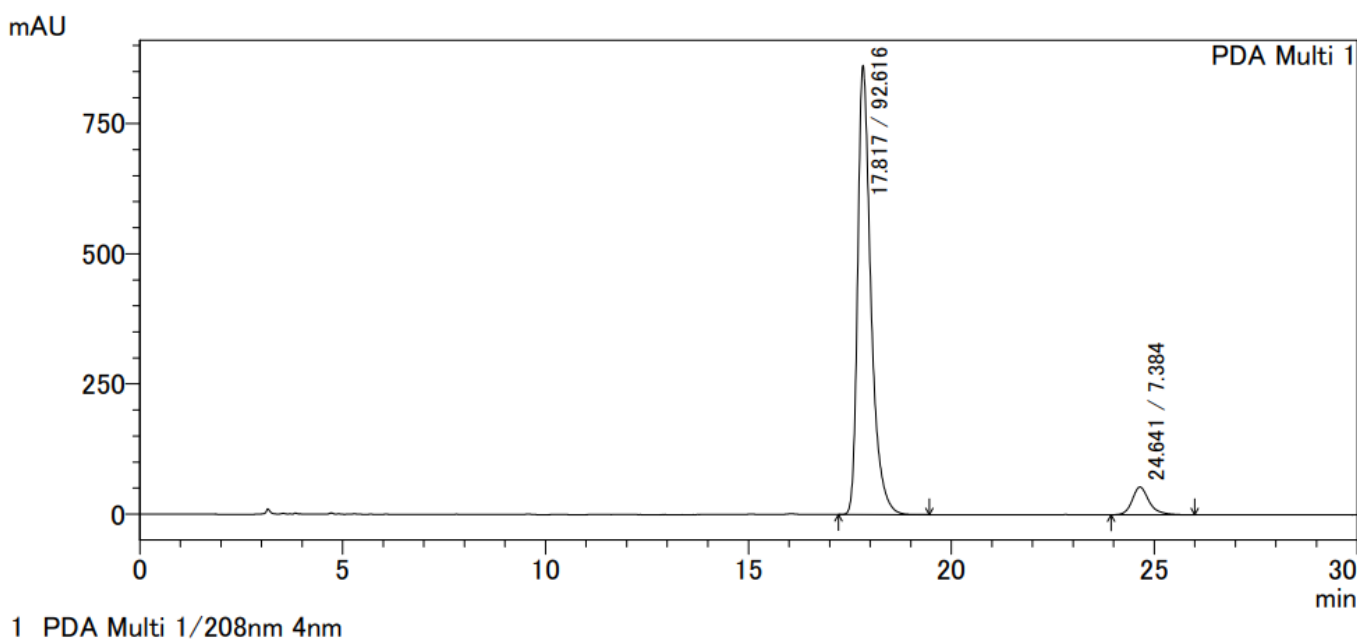
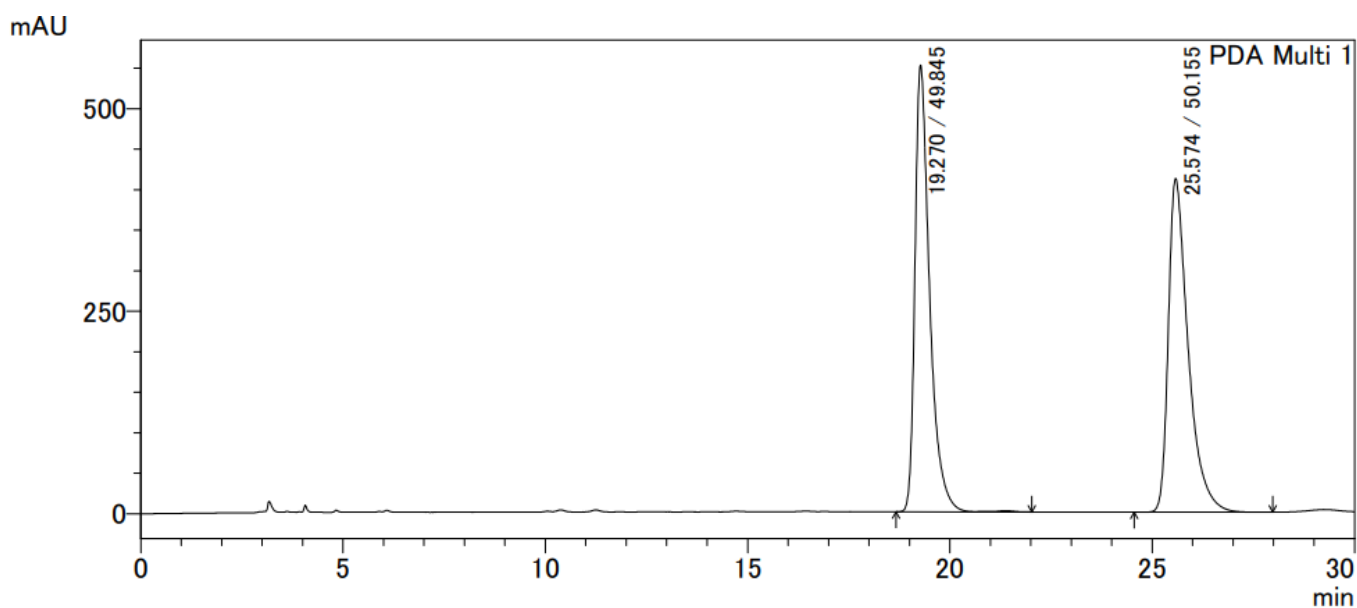
¹³C NMR (126 MHz, CDCl₃) δ 166.3, 153.0, 136.7, 132.4, 131.1, 130.3, 128.0, 126.6, 124.4, 65.2, 36.8, 19.4.

¹⁹F NMR (471 MHz, CDCl₃) δ 55.5 (s, 1F).

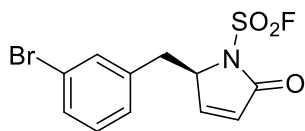
HRMS (ESI) exact mass calculated for C₁₂H₁₂FNO₃SNa: *m/z* 292.0414 ([M+Na]⁺), found: *m/z* 292.0414 ([M+Na]⁺).

[α]_D¹⁷ = -117.9 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALPAK AZ-3, hexane/*i*PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 17.8 min (minor) and 24.6 min (major).



(*R*)-2-(3-bromobenzyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5n)



Prepared according to general procedure D with (*E*)-5-(3-bromophenyl)pent-3-en-2-yl 2-sulfamoylpyrrolidine-1-carboxylate **3n** (100 μ mol, 33.6 mg) for 22 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 50–100%) to give the title compound as a pale yellow oil in 61% yield (61.0 μ mol, 20.4 mg) with 86% ee.

^1H NMR (396 MHz, CDCl_3) δ 7.45 (d, J = 8.2 Hz, 1H), 7.34 (t, J = 1.6 Hz, 1H), 7.26–7.24 (m, 2H), 7.14 (d, J = 7.5 Hz, 1H), 6.17 (dd, J = 6.1, 1.6 Hz, 1H), 4.99–4.95 (m, 1H), 3.60 (dd, J = 13.5, 4.0 Hz, 1H), 2.92 (dd, J = 13.5, 9.4 Hz, 1H).

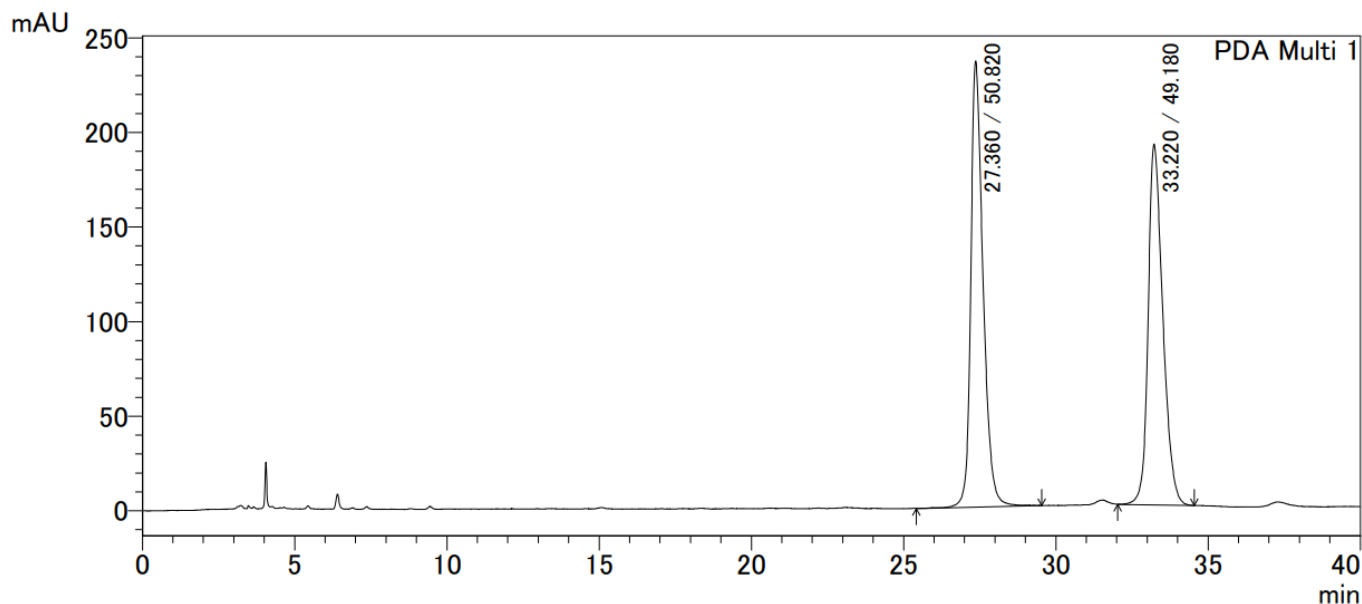
^{13}C NMR (99 MHz, CDCl_3) δ 166.2, 152.2, 135.9, 132.4, 131.0, 130.6, 128.1, 125.0, 122.9, 65.6, 38.0.

^{19}F NMR (369 MHz, CDCl_3) δ 55.3 (s, 1F).

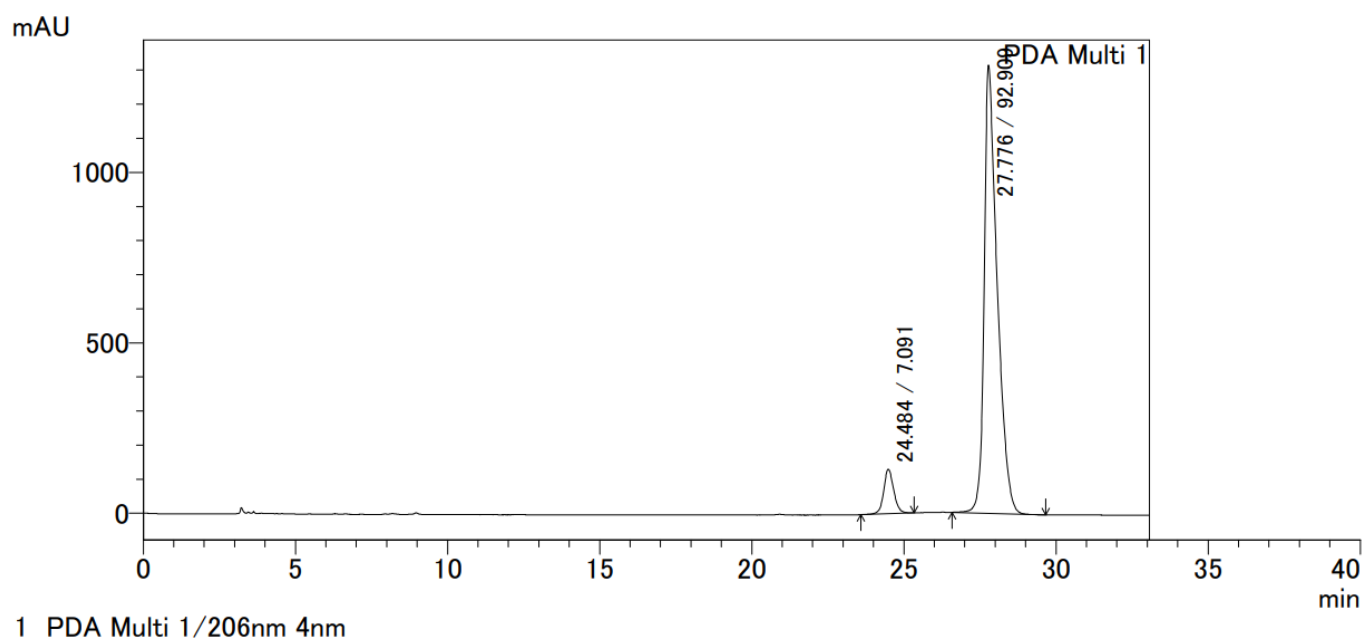
HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_9\text{BrFNaNO}_3\text{S}$: m/z 355.9363 ($[\text{M}+\text{Na}]^+$), found: m/z 355.9363 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_{\text{D}}^{18}$ = -164.7 (c = 1.0, CHCl_3).

HPLC Daicel CHIRALPAK IB-3, hexane/*i*PrOH = 20:1, flow rate = 1.0 mL/min, retention time; 24.5 min (minor) and 27.8 min (major).



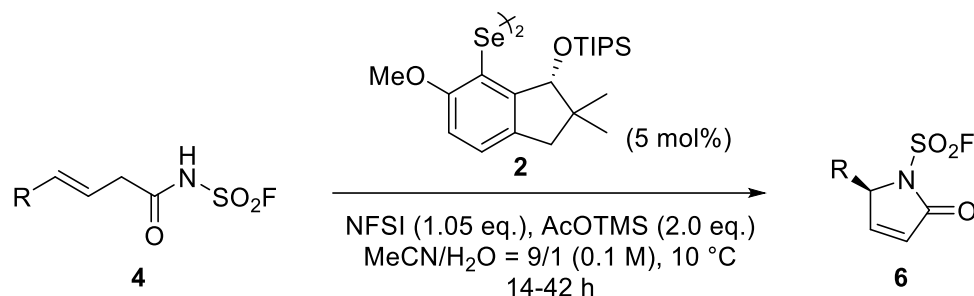
1 PDA Multi 1/206nm 4nm



1 PDA Multi 1/206nm 4nm

7. Selenium-catalyzed enantioselective lactamization (Figure 2b)

General procedure E

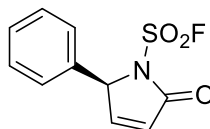


To a stirred solution of the corresponding N-(fluorosulfonyl)amide (100 μ mol), selenium catalyst **2** (5.0 μ mol, 4.3 mg), and AcOTMS (200 μ mol, 30 μ L) in MeCN/H₂O (9:1, 1 mL) was added NFSI (0.105 mmol, 33.1 mg) at 10 °C. After stirring for 12–24 h at the same temperature, the reaction mixture was poured into water and extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on TFA-treated silica gel to give the desired product.

Preparation of TFA-treated C300 silica gel

Trifluoroacetic acid (6 mL) was added to C300 silica gel (100 g) in DCM (300 mL). The resulting suspension was filtered and dried under vacuum.

(S)-2-oxo-5-phenyl-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (**6a**)



Prepared according to general procedure E with ethyl (E)-(4-phenylbut-3-enoyl)sulfamoyl fluoride **4a** (100 μ mol, 24.3 mg) for 16 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 94% yield (93.7 μ mol, 22.6 mg) with 93% ee.

¹H NMR (401 MHz, CDCl₃) δ 7.39–7.46 (m, 3H), 7.31 (dd, *J* = 6.0, 2.3 Hz, 1H), 7.26–7.28 (m, 2H), 6.29 (dd, *J* = 6.4, 1.8 Hz, 1H), (dd, *J* = 2.3, 1.8 Hz, 1H), 5.76 (ddd, *J* = 14.9, 10.1 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 166.8, 152.9, 132.0, 130.0, 129.5, 127.3, 123.4, 68.6.

¹⁹F NMR (376 MHz, CDCl₃) δ 55.6 (s, 1F).

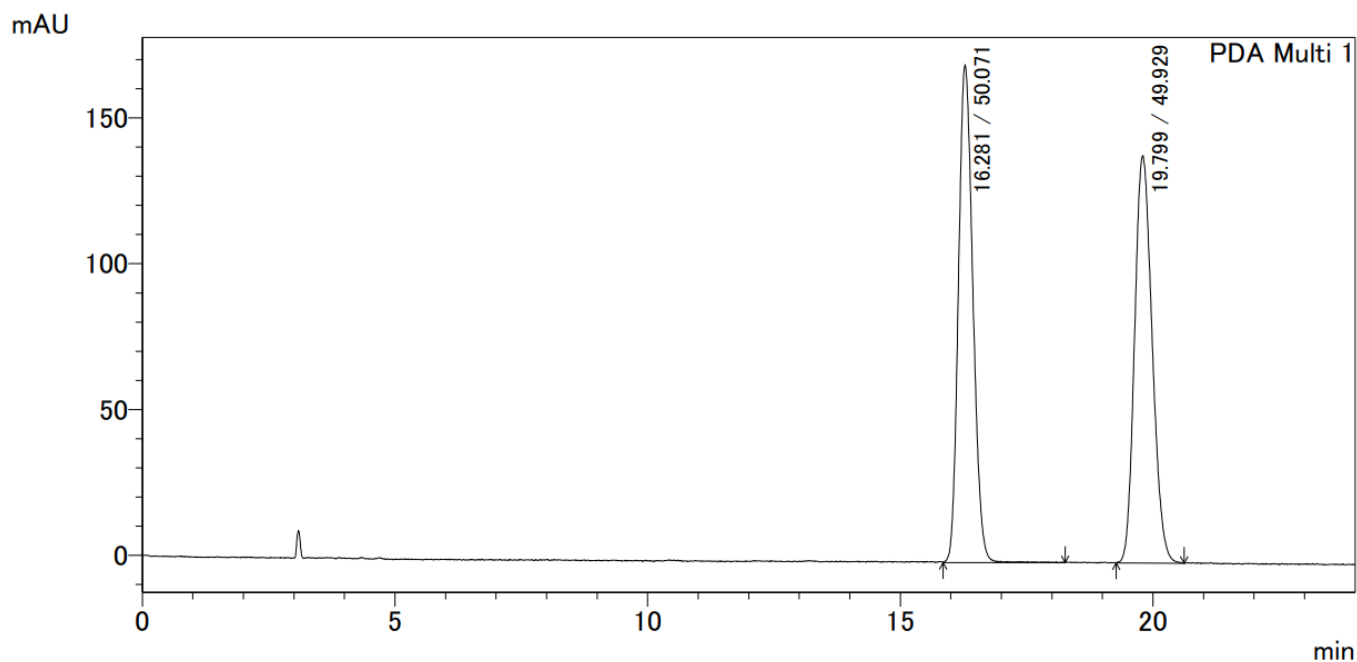
HRMS (ESI) exact mass calculated for C₁₀H₈O₃NFNaS: *m/z* 264.0101 ([M+Na]⁺), found: *m/z* 264.0098 ([M+Na]⁺).

$[\alpha]_D^{20}$ = -258.2 (*c* = 1.0, CHCl₃).

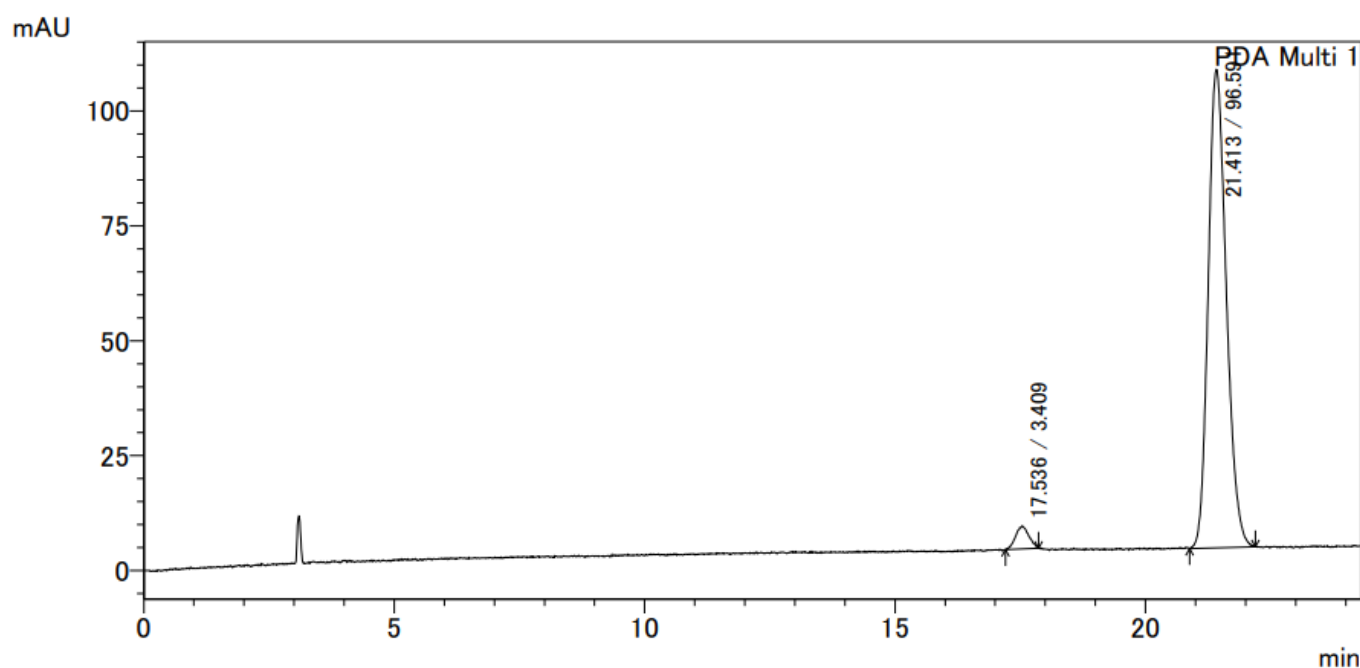
m.p. = 103 °C

HPLC Daicel CHIRALCEL OZ-3, hexane/PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 17.5 min (minor) and 21.4 min (major).

CIF File CCDC 2482629 contains supplementary crystallographic data of **6a**.



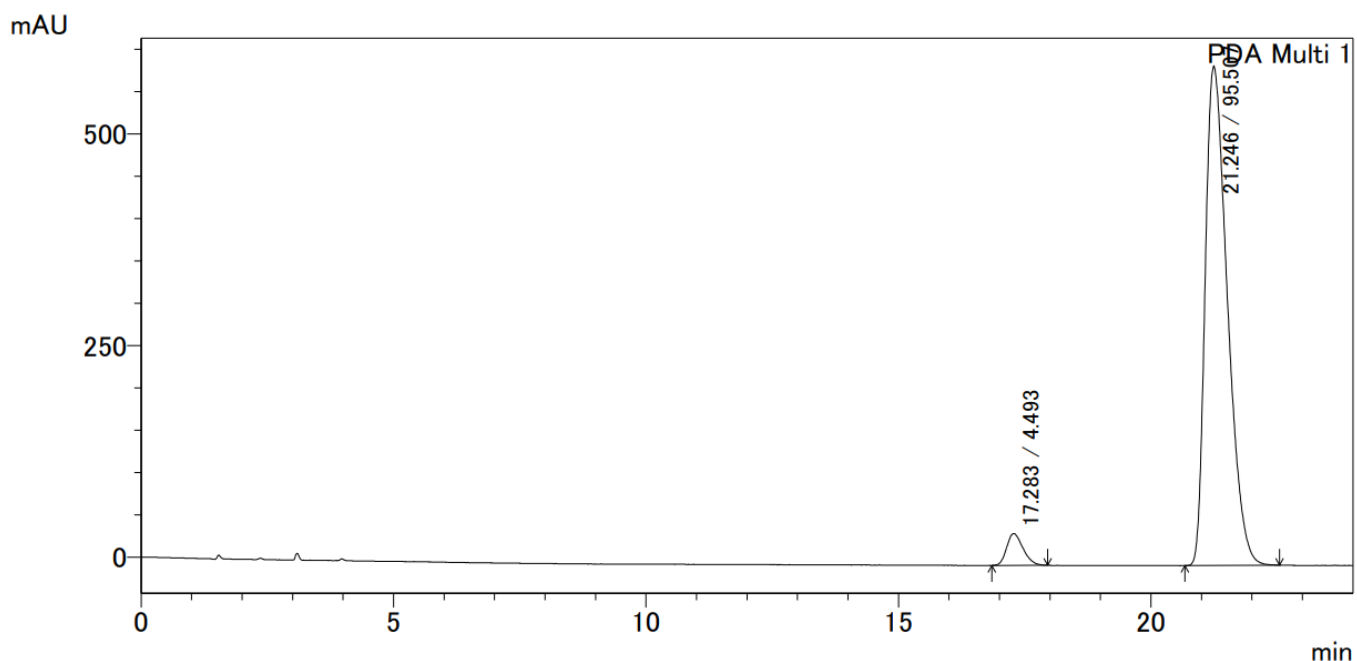
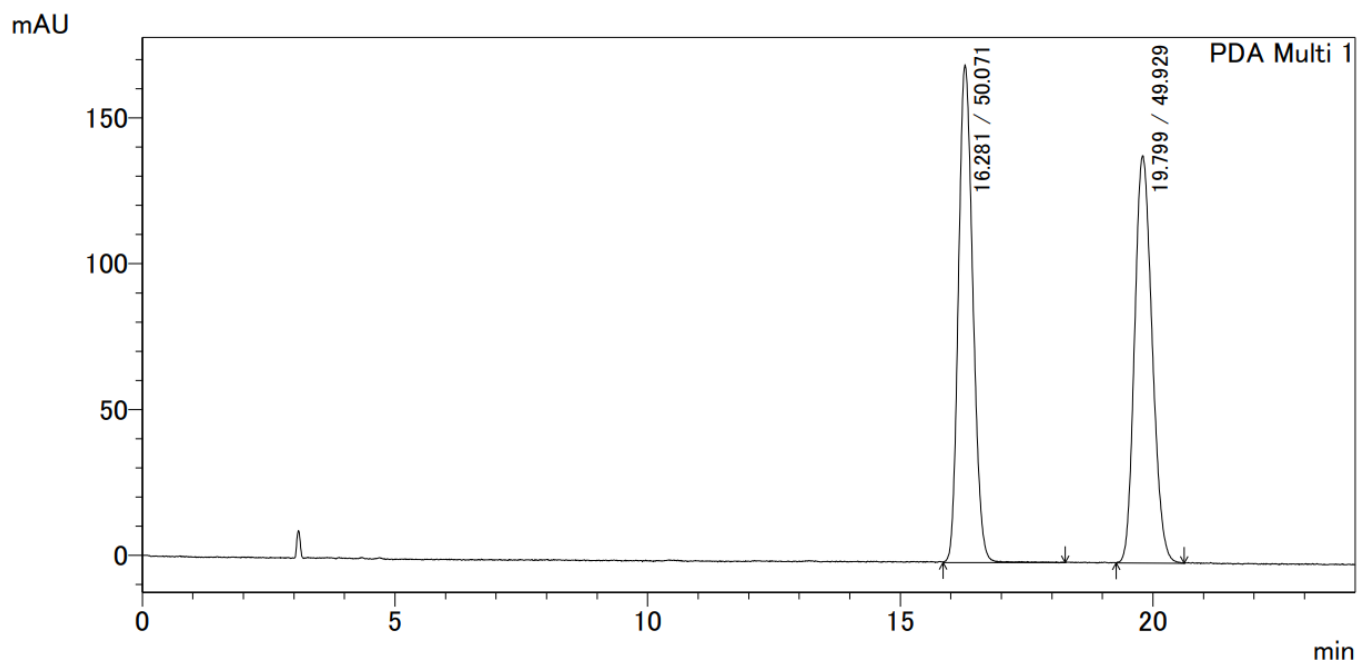
1 PDA Multi 1/205nm,4nm



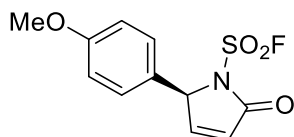
1 PDA Multi 1/205nm,4nm

Scale up experiment (1 mmol): Prepared according to general procedure E with ethyl (*E*)-(4-phenylbut-3-enoyl)sulfamoyl fluoride **4a** (1.00 mmol, 248 mg, 98% purity), selenium catalyst **2** (30.0 μ mol, 25.6 mg), AcOTMS (2.00 mmol, 300 μ L), NFSI (1.05 mmol, 331 mg) in MeCN/H₂O (9:1, 10 mL) at 10 °C for 15 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a white solid in 91% yield (906 μ mol, 219 mg) with 91% ee.

HPLC Daicel CHIRALCEL OZ-3, hexane/PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 17.3 min (minor) and 21.2 min (major).



(S)-2-(4-methoxyphenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6b)



Prepared according to general procedure E with ethyl (*E*)-(4-(4-methoxyphenyl)but-3-enoyl)sulfamoyl fluoride **4b** (100 μ mol, 27.3 mg) for 16 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a white solid in 88% yield (88.1 μ mol, 23.9 mg) with 91% ee.

^1H NMR (401 MHz, CDCl_3) δ 7.28 (dd, J = 6.2, 2.1 Hz, 1H), 7.19 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.28 (dd, J = 6.0, 1.8 Hz, 1H), 5.73 (t, J = 1.8 Hz, 1H), 3.82 (s, 3H).

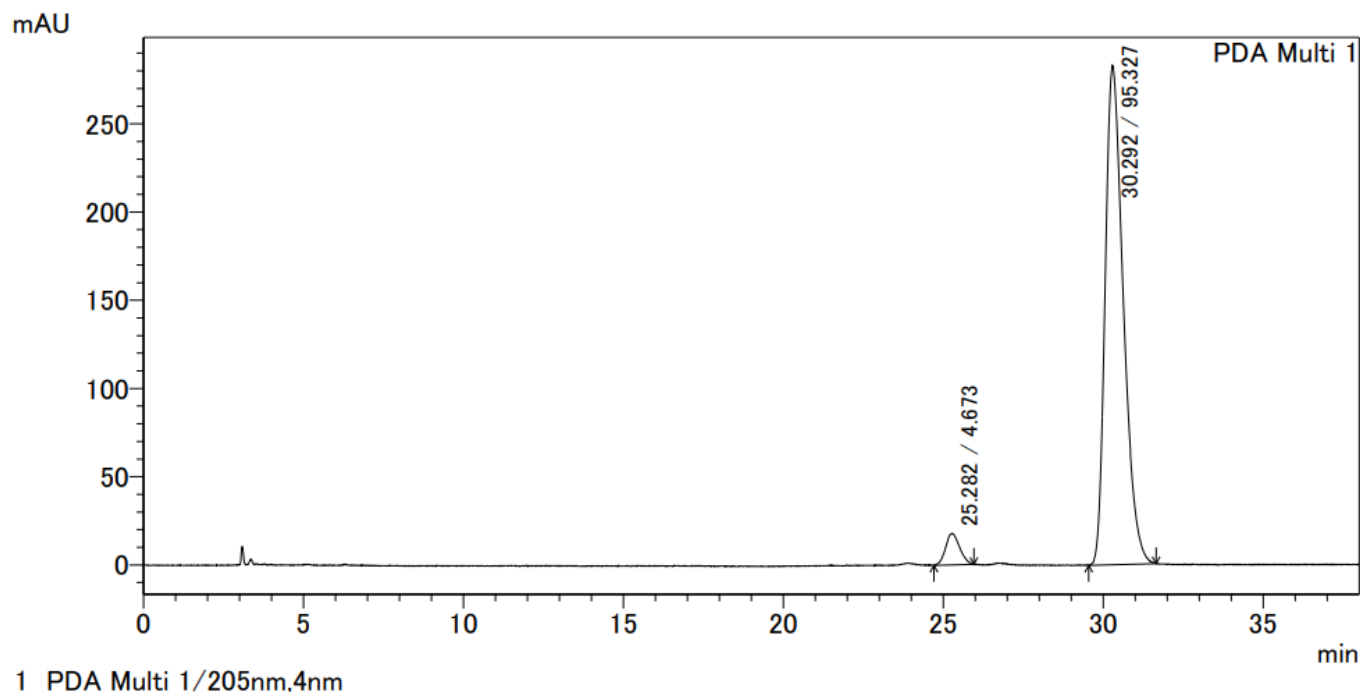
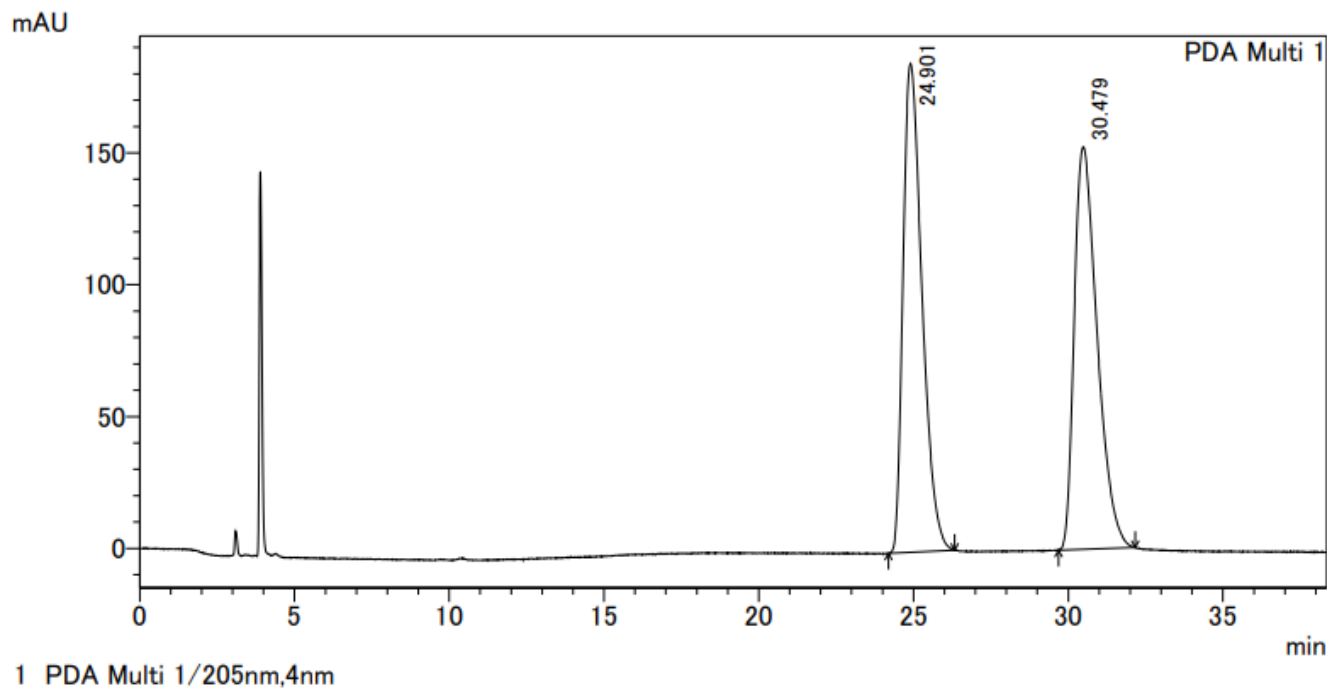
^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 160.8, 153.0, 128.9, 123.5, 123.4, 114.8, 68.3, 55.5.

^{19}F NMR (376 MHz, CDCl_3) δ 55.8 (s, 1F).

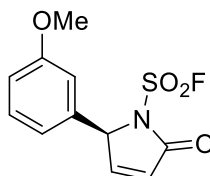
HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{10}\text{FNNaO}_4\text{S}$: m/z 294.0207 ($[\text{M}+\text{Na}]^+$), found: m/z 294.0207 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_{\text{D}}^{20} = -190.5$ ($c = 1.0$, CHCl_3).

HPLC Daicel CHIRALCEL OZ-3, hexane/ $\text{PrOH} = 10/1$, flow rate = 1.0 mL/min, retention time; 10.5 min (minor) and 12.2 min (major).



2-(3-methoxyphenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6c)



Prepared according to general procedure E with ethyl (*E*)-(4-(4-methoxyphenyl)but-3-enoyl)sulfamoyl fluoride **4c** (100 μ mol, 27.9 mg) for 16 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a white solid in 93% yield (92.9 μ mol, 25.2 mg) with 88% ee.

^1H NMR (401 MHz, CDCl_3) δ 7.37 (td, J = 7.9, 1.7 Hz, 1H), 7.31 (q, J = 2.8 Hz, 1H), 7.15 (dd, J = 7.8, 1.8 Hz, 1H), 7.02–6.98 (m, 1H), 6.95 (d, J = 9.2 Hz, 1H), 6.23 (t, J = 2.3 Hz, 1H), 6.21 (dd, J = 6.0, 1.8 Hz, 1H), 3.87 (s, 3H).

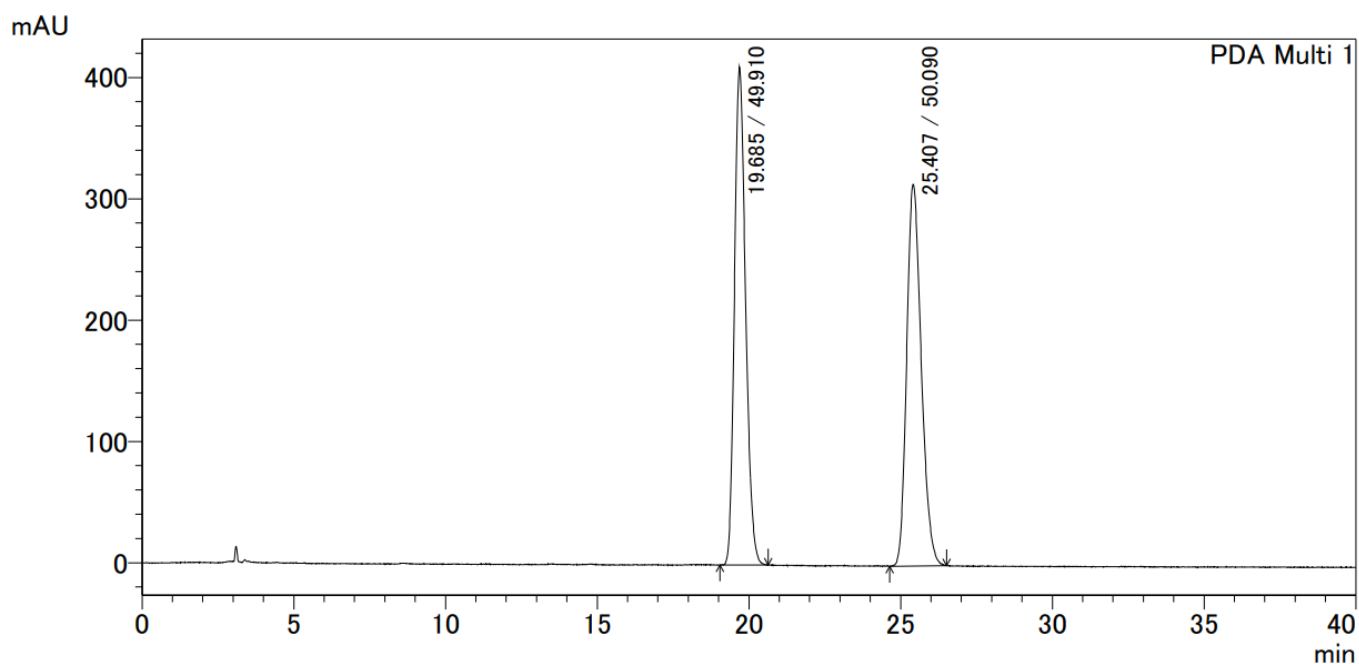
^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 157.0, 153.0, 130.8, 127.0, 123.0, 121.4, 120.1, 111.5, 64.1, 55.8.

^{19}F NMR (376 MHz, CDCl_3) δ 55.7 (s, 1F).

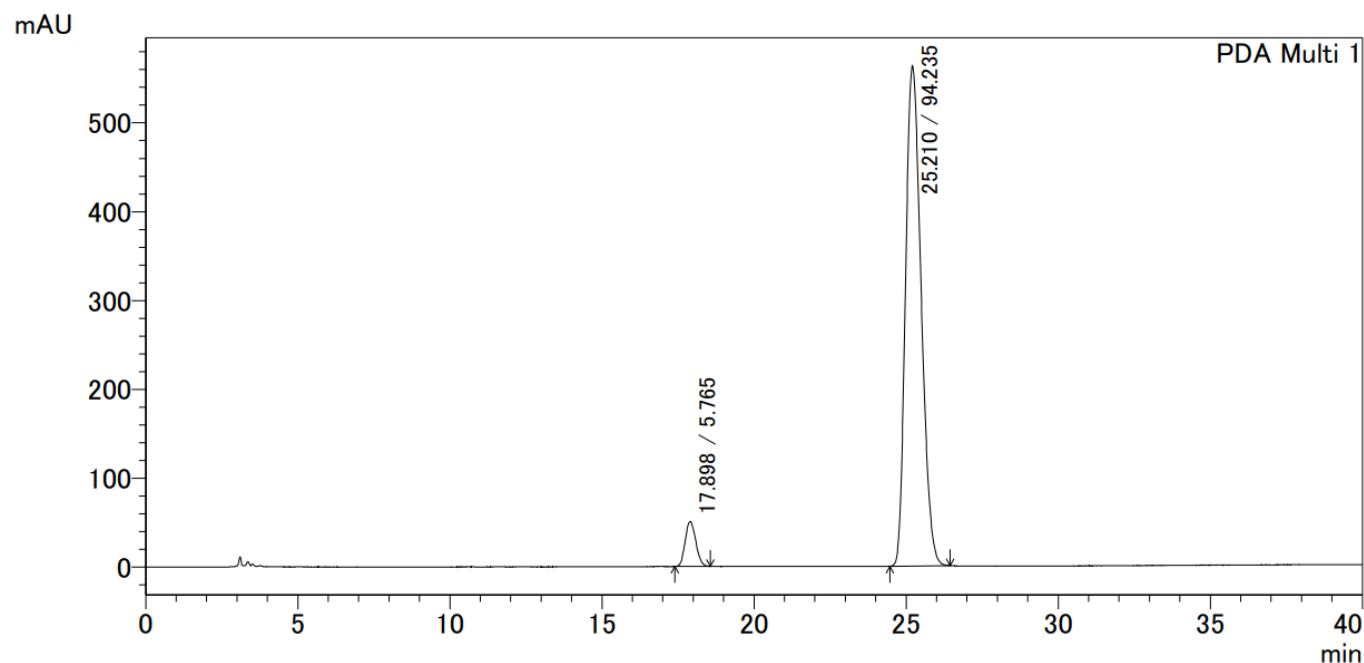
HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{10}\text{FNNaO}_4\text{S}$: m/z 294.0207 ($[\text{M}+\text{Na}]^+$), found: m/z 294.0207 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_{\text{D}}^{20}$ = -236.9 (c = 1.0, CHCl_3).

HPLC Daicel CHIRALCEL OZ-3, hexane/*i*PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 17.9 min (minor) and 25.2 min (major).

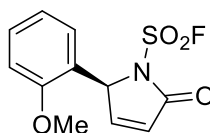


1 PDA Multi 1/205nm,0nm



1 PDA Multi 1/205nm,4nm

(S)-2-(2-methoxyphenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6d)



Prepared according to general procedure E with (*E*)-(4-(2-methoxyphenyl)but-3-enyl)sulfamoyl fluoride **4d** (100 μ mol, 27.3 mg) for 15 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow oil in 88% yield (87.7 μ mol, 23.8 mg) with 93% ee.

^1H NMR (401 MHz, CDCl_3) δ 7.37 (td, J = 7.9, 1.7 Hz, 1H), 7.31 (dd, J = 6.0, 2.3 Hz, 1H), 7.15 (dd, J = 7.8, 1.8 Hz, 1H), 7.00 (td, J = 7.5, 1.1 Hz, 1H), 6.95 (dd, J = 8.3, 0.9 Hz, 1H), 6.23 (t, J = 2.3 Hz, 1H), 6.21 (dd, J = 6.0, 1.8 Hz, 1H), 3.87 (s, 3H).

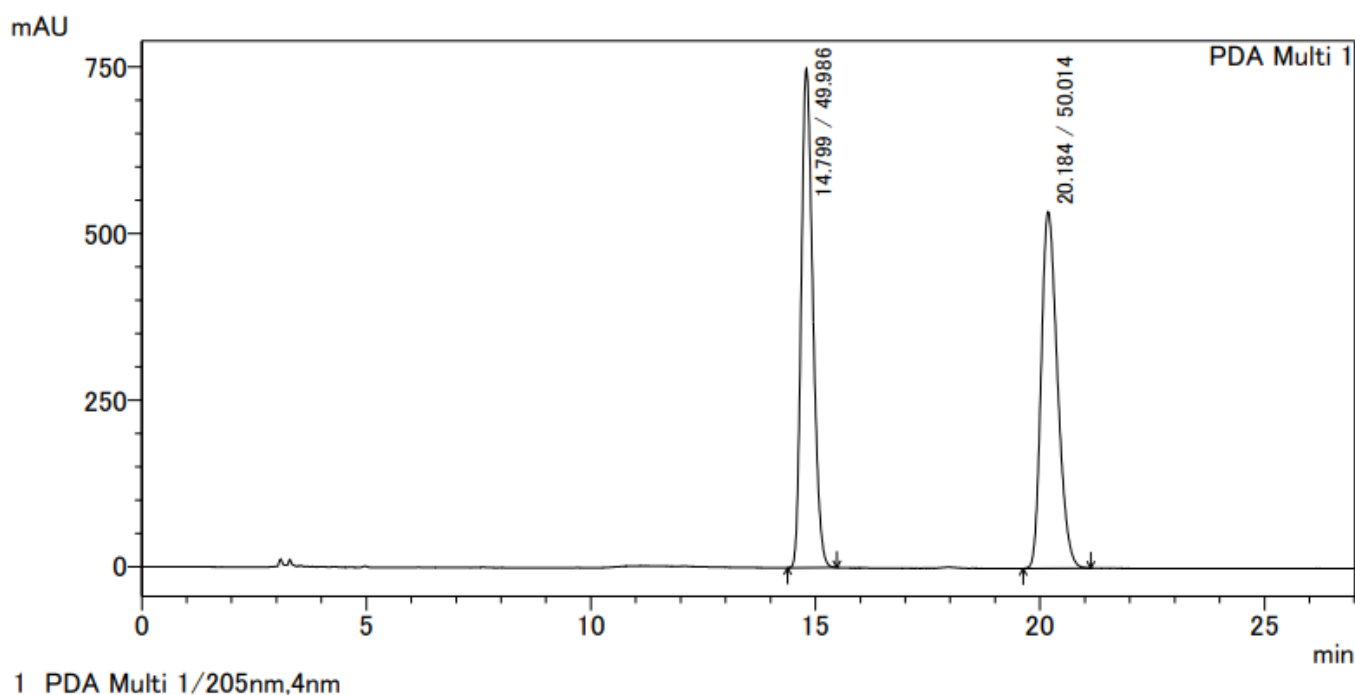
^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 157.0, 153.0, 130.8, 127.0, 123.0, 121.4, 120.1, 111.5, 64.1, 55.8.

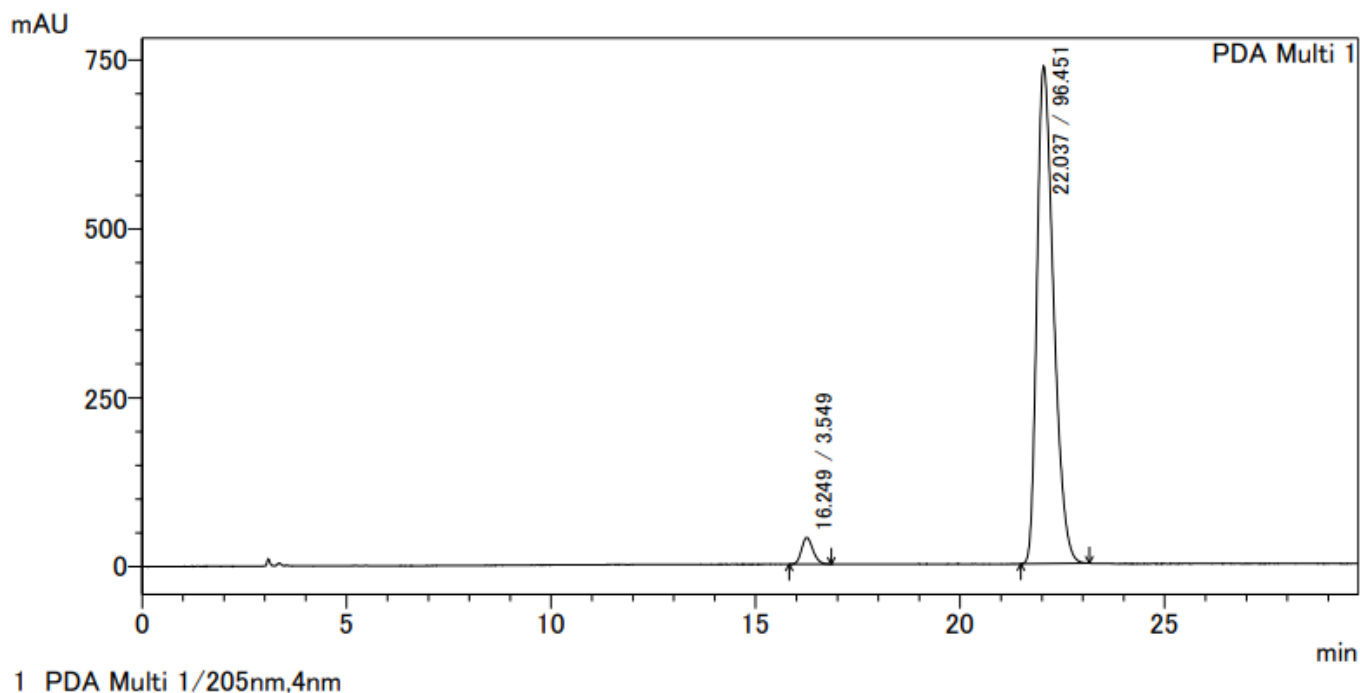
^{19}F NMR (376 MHz, CDCl_3) δ 55.7 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{10}\text{FNNaO}_4\text{S}$: m/z 294.0207 ($[\text{M}+\text{Na}]^+$), found: m/z 294.0210 ($[\text{M}+\text{Na}]^+$).

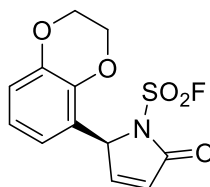
$[\alpha]_{\text{D}}^{20}$ = -294.0 (c = 1.0, CHCl_3).

HPLC Daicel CHIRALCEL OZ-3, hexane/ PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 16.2 min (minor) and 22.0 min (major).





(S)-2-(2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6e)



Prepared according to general procedure E with (*E*)-(4-(2,3-dihydrobenzo[b][1,4]dioxin-5-yl)but-3-en-2-yl)sulfamoyl fluoride **4e** (100 μ mol, 30.4 mg, 99% purity) for 16 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 91% yield (90.6 μ mol, 27.1 mg) with 90% ee.

¹H NMR (399 MHz, CDCl₃) δ 7.31 (q, *J* = 2.7 Hz, 1H), 6.90 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.71 (dd, *J* = 7.3, 1.8 Hz, 1H), 6.23 (dd, *J* = 6.4, 1.8 Hz, 1H), 6.14 (t, *J* = 2.1 Hz, 1H), 4.22–4.37 (4H).

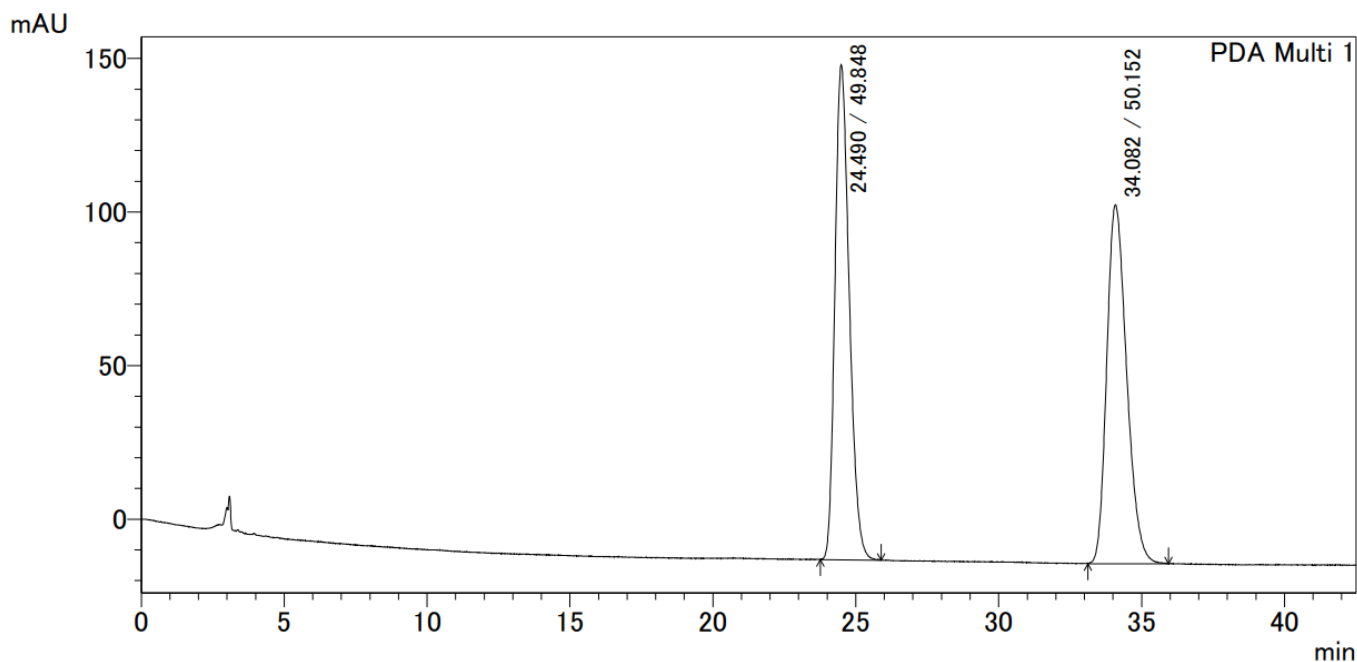
¹³C NMR (100 MHz, CDCl₃) δ 167.3, 152.5, 144.2, 141.7, 123.4, 121.7, 120.3, 119.1, 118.6, 64.6, 64.2, 63.5.

¹⁹F NMR (376 MHz, CDCl₃) δ 54.4 (s, 1F).

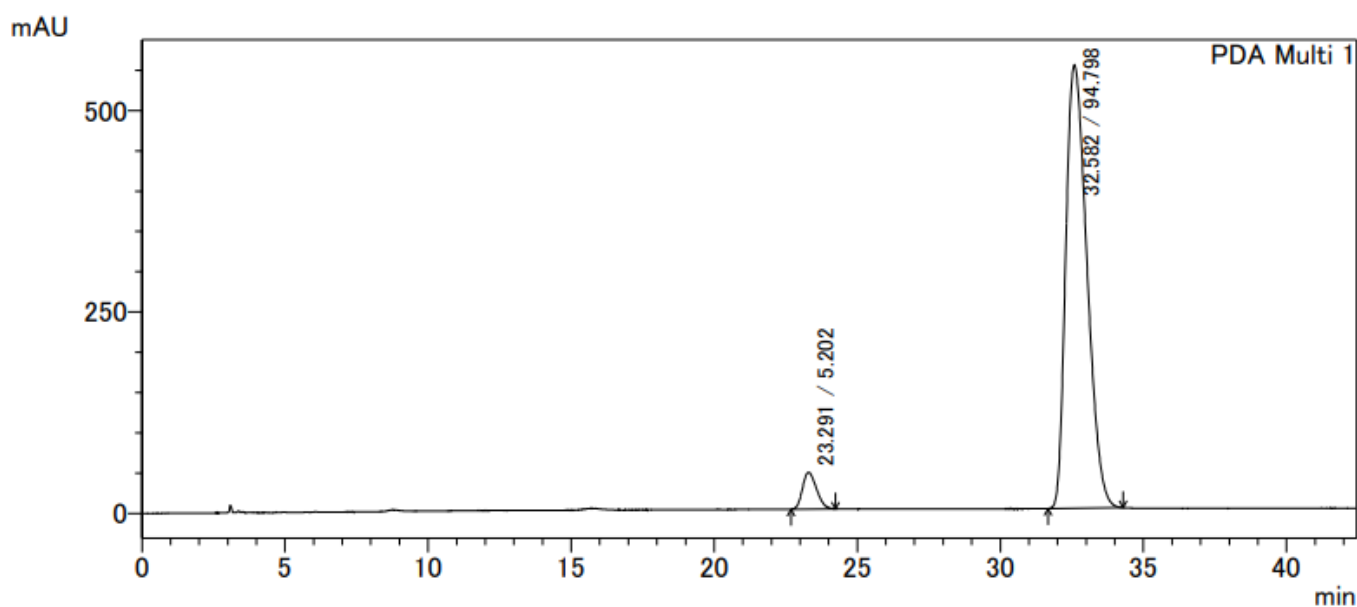
HRMS (ESI) exact mass calculated for C₁₂H₁₀O₅NFNaS: *m/z* 322.0156 ([M+Na]⁺), found: *m/z* 322.0155 ([M+Na]⁺).

[α]_D²⁰ = +25.9 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALCEL OZ-3, hexane/PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 23.3 min (minor) and 32.6 min (major).

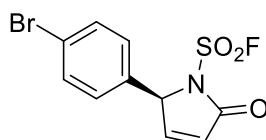


1 PDA Multi 1/207nm,4nm



1 PDA Multi 1 / 207nm,4nm

(S)-2-(4-bromophenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6f)



Prepared according to general procedure E with (*E*)-(4-(4-bromophenyl)but-3-enoyl)sulfamoyl fluoride **4f** (100 μ mol, 35.0 mg, 95% purity) and CF₃CO₂TMS (200 μ mol, 34.1 μ L) instead of AcOTMS for 18 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 90% yield (89.7 μ mol, 28.7 mg) with 90% ee.

¹H NMR (399 MHz, CDCl₃) δ 7.57 (dt, *J* = 8.7, 2.2 Hz, 2H), 7.29 (q, *J* = 2.7 Hz, 1H), 7.16 (dt, *J* = 8.7, 2.2 Hz, 2H), 6.31 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.73 (t, *J* = 1.8 Hz, 1H).

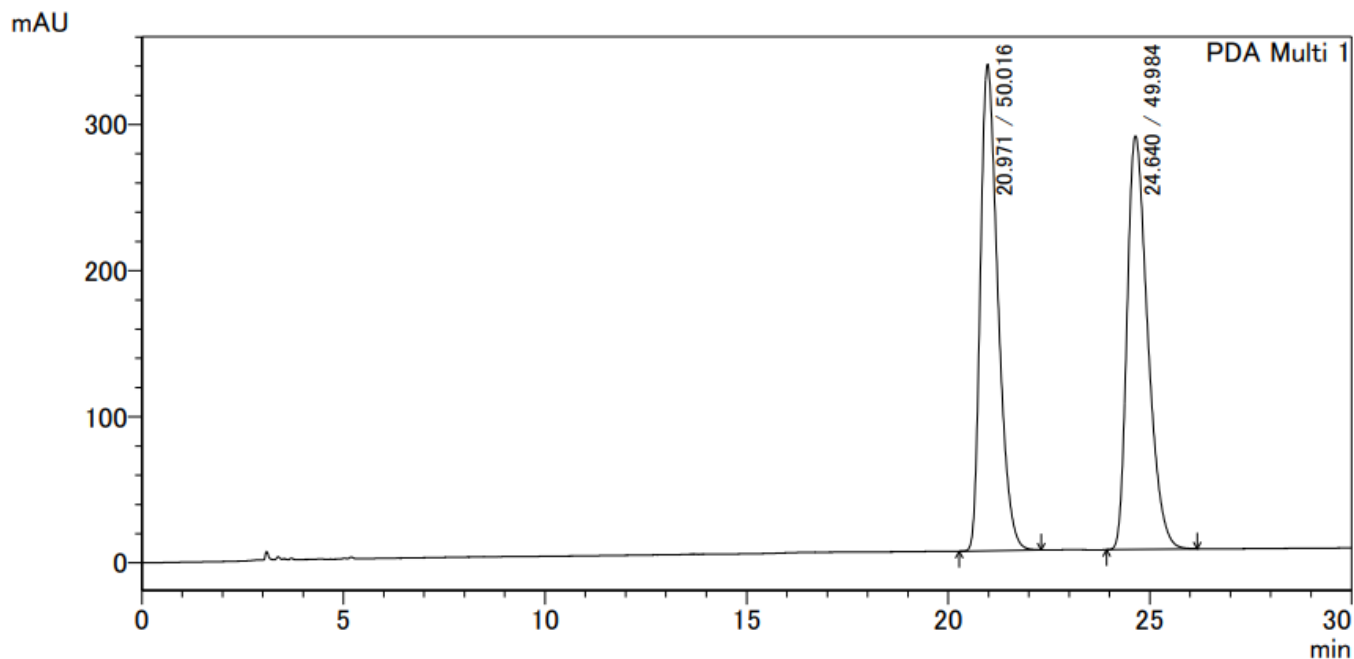
¹³C NMR (100 MHz, CDCl₃) δ 166.4, 152.3, 132.8, 131.1, 129.0, 124.3, 123.9, 67.9.

^{19}F NMR (376 MHz, CDCl_3) δ 57.2 (s, 1F).

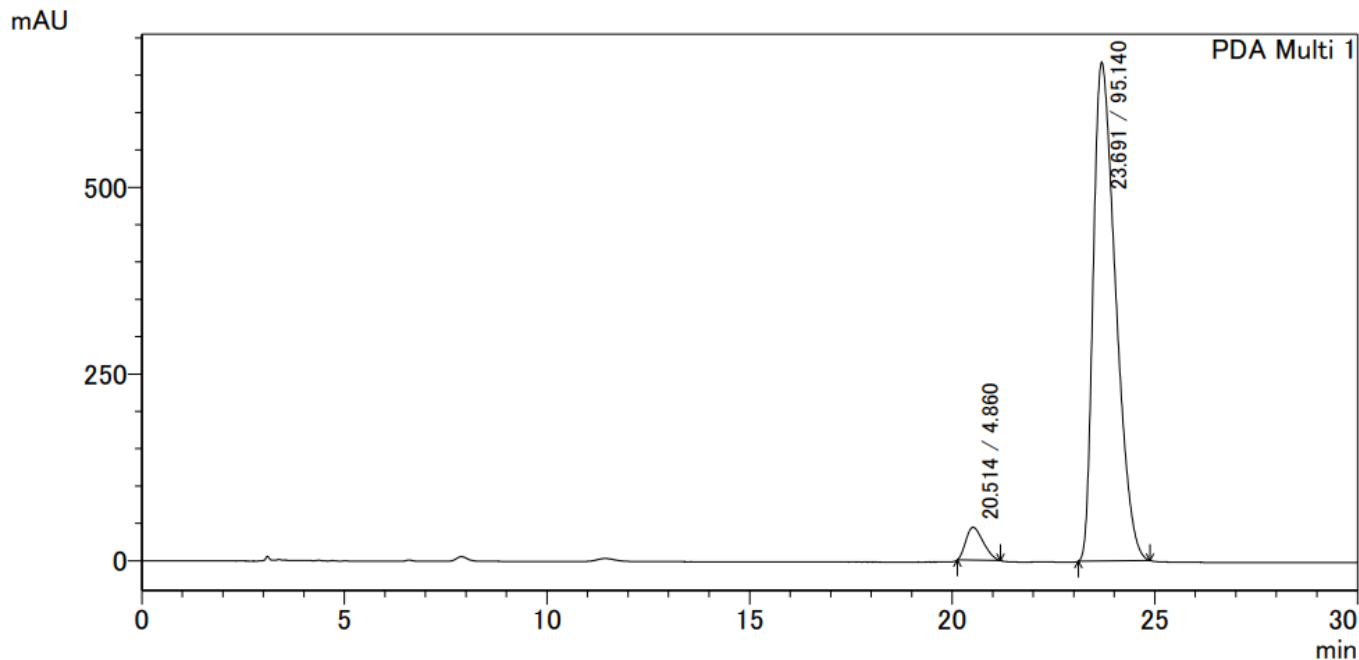
HRMS (ESI) exact mass calculated for $\text{C}_{10}\text{H}_7\text{BrFNNaO}_3\text{S}$: m/z 341.9206 ($[\text{M}+\text{Na}]^+$), found: m/z 341.9200 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_{\text{D}}^{20}$ = -229.9 ($c = 1.0$, CHCl_3).

HPLC Daicel CHIRALCEL OZ-3, hexane/ $\text{PrOH} = 10/1$, flow rate = 1.0 mL/min, retention time; 20.5 min (minor) and 23.7 min (major).

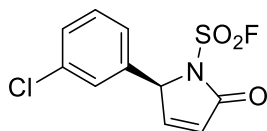


1 PDA Multi 1/211nm,4nm



1 PDA Multi 1/211nm,4nm

(S)-2-(3-chlorophenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6g)



Prepared according to general procedure E with (*E*)-(4-(3-chlorophenyl)but-3-enoyl)sulfamoyl fluoride **4g** (100 μ mol, 30.2 mg, 89% purity) and CF₃CO₂TMS (200 μ mol, 34.1 μ L) instead of AcOTMS for 22 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 91% yield (91.4 μ mol, 25.2 mg) with 88% ee.

¹H NMR (399 MHz, CDCl₃) δ 7.40–7.34 (m, 2H), 7.28 (q, *J* = 2.7 Hz, 1H), 7.24 (t, *J* = 1.6 Hz, 1H), 7.16 (dt, *J* = 7.0, 1.7 Hz, 1H), 6.31 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.72 (t, *J* = 1.8 Hz, 1H).

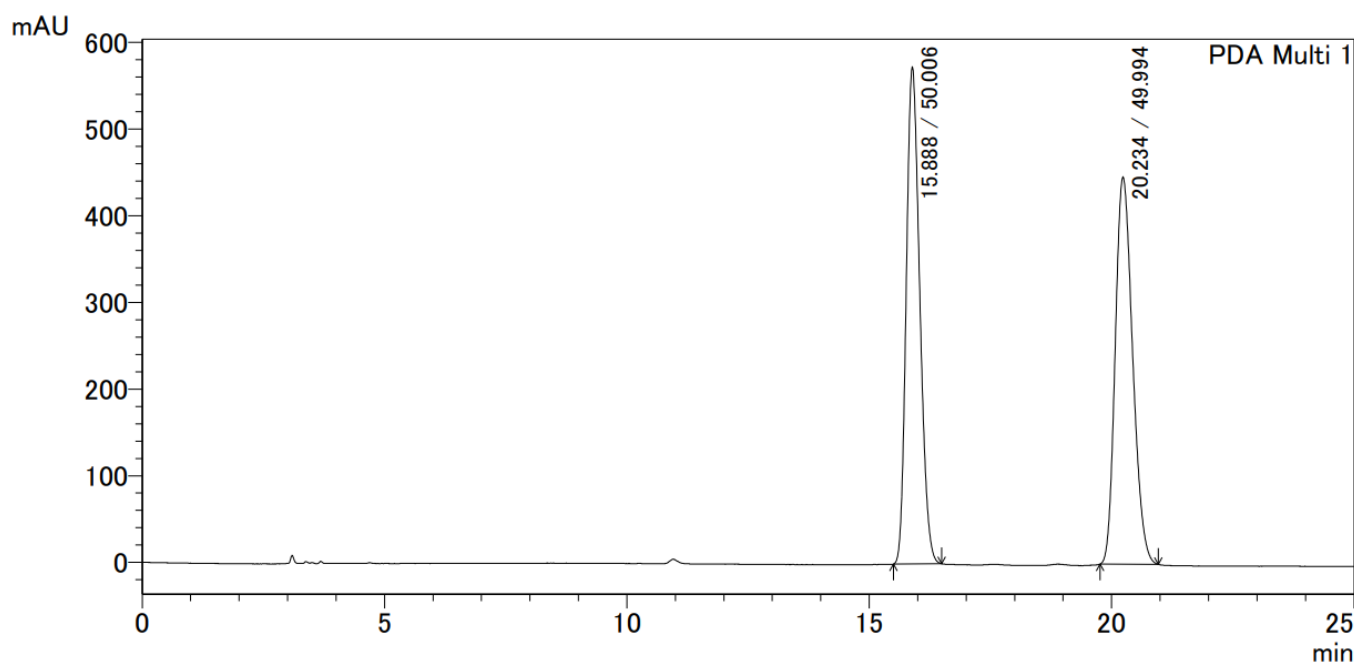
¹³C NMR (100 MHz, CDCl₃) δ 166.5, 152.3, 135.5, 134.1, 130.8, 130.3, 127.4, 125.5, 123.9, 67.8.

¹⁹F NMR (376 MHz, CDCl₃) δ 55.7 (s, 1F).

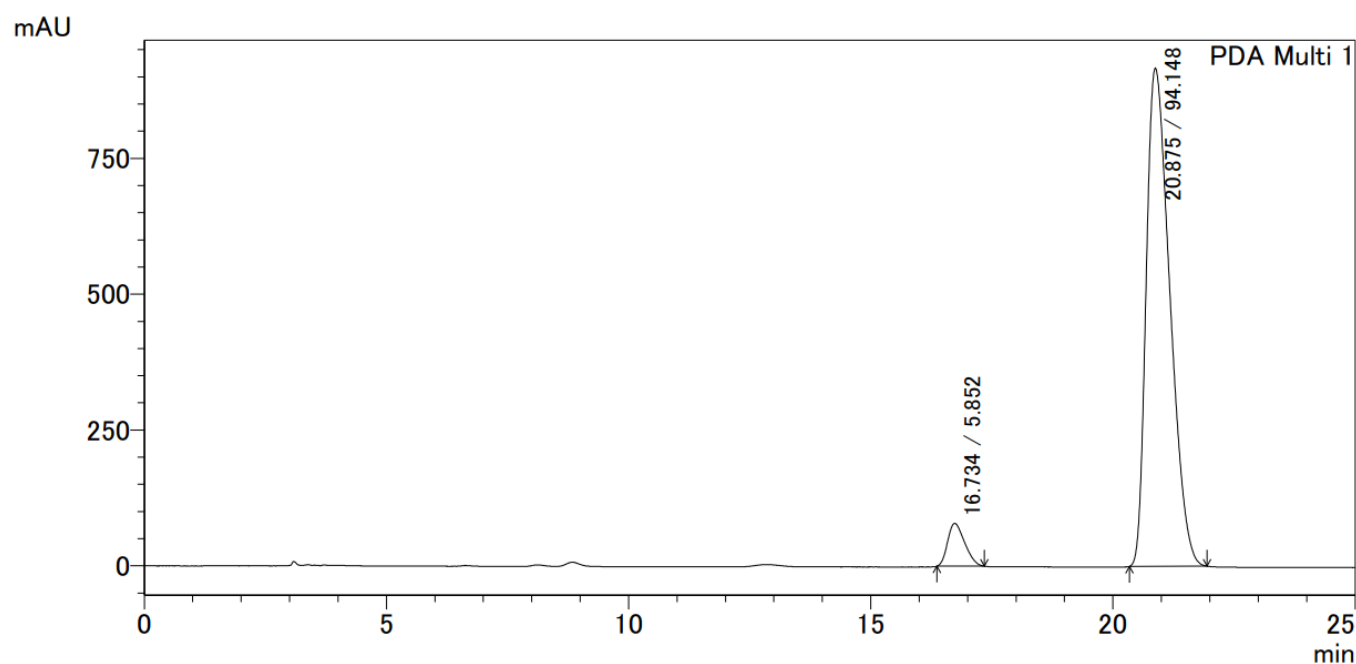
HRMS (ESI) exact mass calculated for C₁₀H₇ClFNNaO₃S: *m/z* 297.9711 ([M+Na]⁺), found: *m/z* 297.9712 ([M+Na]⁺).

[α]_D²⁰ = -223.0 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALCEL OZ-3, hexane/*i*PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 16.7 min (minor) and 20.9 min (major).

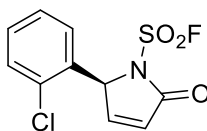


1 PDA Multi 1/207nm,4nm



1 PDA Multi 1/207nm,4nm

(S)-2-(2-chlorophenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6h)



Prepared according to general procedure E with (*E*)-(4-(2-chlorophenyl)but-3-enoyl)sulfamoyl fluoride **4h** (100 μ mol, 30.5 mg, 91% purity) for 23 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 97% yield (97.2 μ mol, 26.8 mg) with 86% ee.

¹H NMR (399 MHz, CDCl₃) δ 7.50–7.44 (m, 1H), 7.38–7.32 (m, 3H), 7.23–7.19 (m, 1H), 6.38 (s, 1H), 6.28 (dd, *J* = 6.1, 1.7 Hz, 1H).

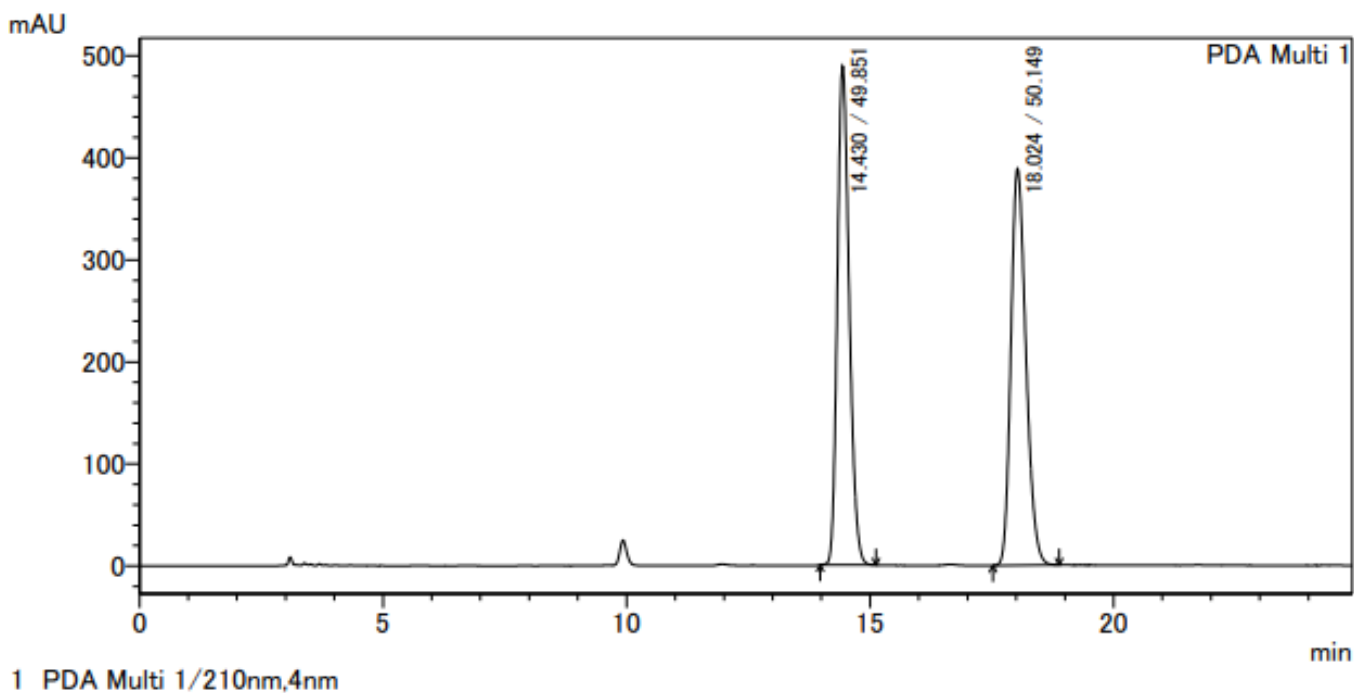
¹³C NMR (100 MHz, CDCl₃) δ 166.9, 152.2, 133.2, 130.8, 130.7, 130.0, 128.1, 126.8, 123.7, 65.2.

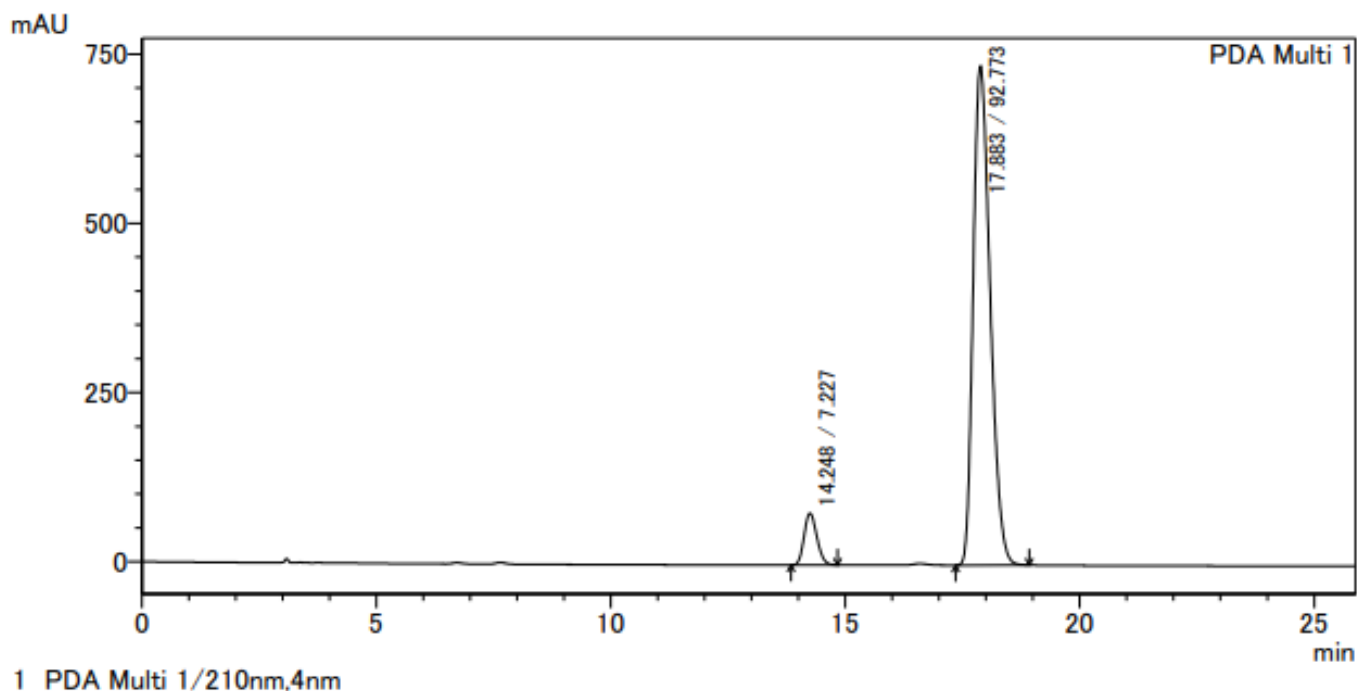
¹⁹F NMR (376 MHz, CDCl₃) δ 55.0 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₀H₇O₃NFCINaS: *m/z* 297.9711 ([M+Na]⁺), found: *m/z* 297.9711 ([M+Na]⁺).

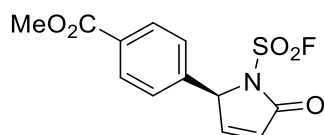
$[\alpha]_D^{20}$ = -253.9 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALCEL OZ-3, hexane/*i*PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 14.2 min (minor) and 17.9 min (major).





(S)-2-(4-methoxycarbonylphenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6i)



Prepared according to general procedure E with methyl (*E*)-4-(4-((fluorosulfonyl)amino)-4-oxobut-1-en-1-yl)benzoate **4i** (100 μ mol, 31.4 mg, 96% purity) for 24 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100% and hexane/TBME, 30–100%) to give the title compound as a pale yellow solid in 76% yield (75.5 μ mol, 22.6 mg) with 85% ee.

¹H NMR (392 MHz, CDCl₃) δ 8.10 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.32 (dd, *J* = 6.2, 2.1 Hz, 1H), 6.34 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.82 (s, 1H), 3.89–4.00 (3H).

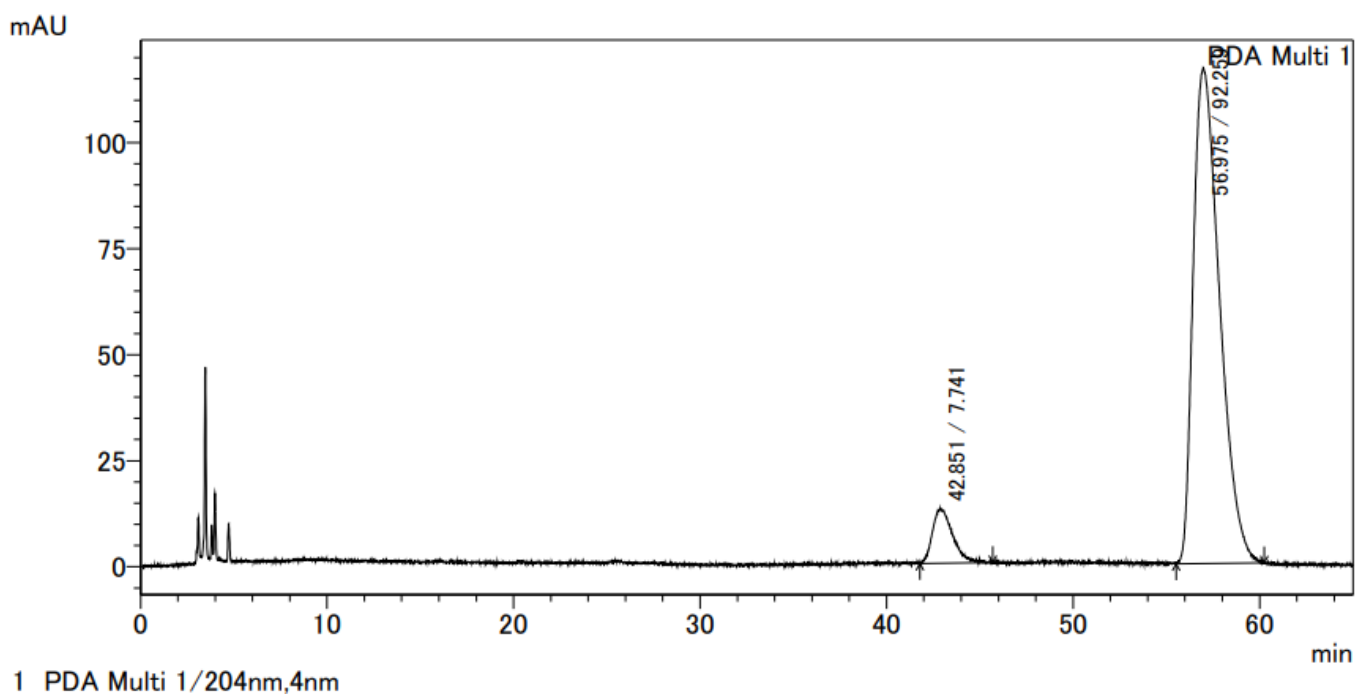
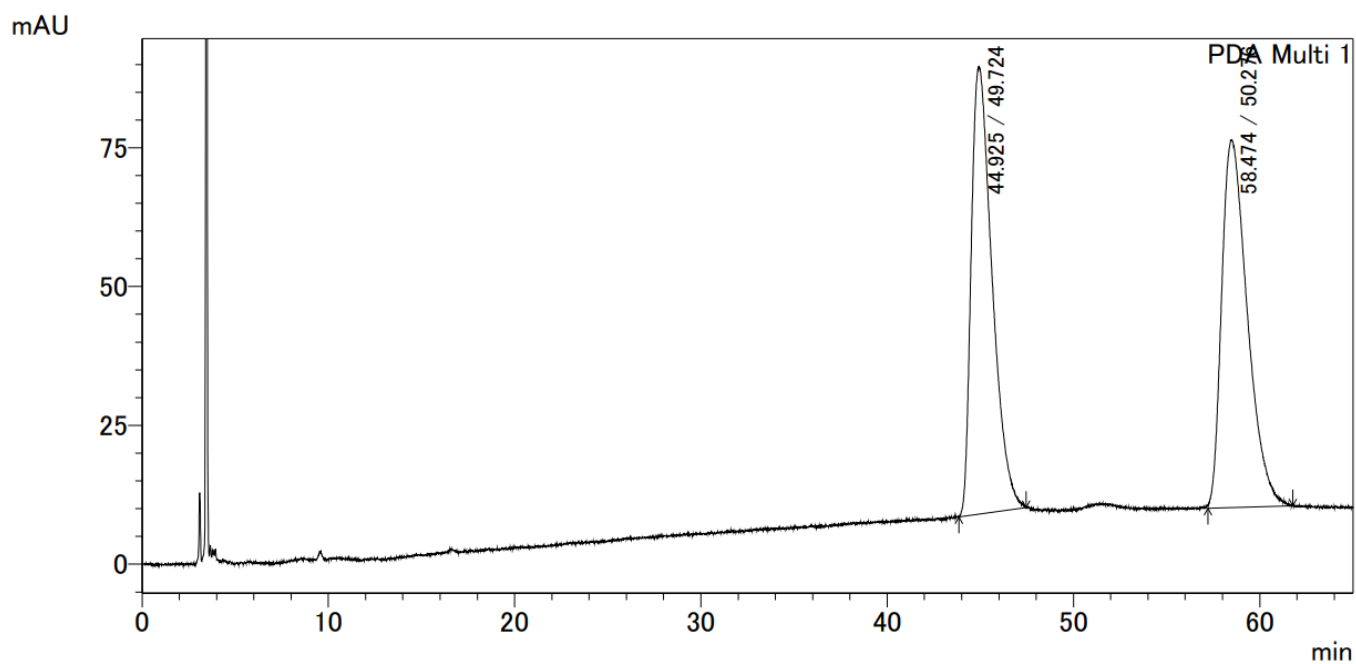
¹³C NMR (100 MHz, CDCl₃) δ 166.5, 166.2, 152.3, 137.0, 131.8, 130.8, 127.3, 124.0, 68.0, 52.5.

¹⁹F NMR (376 MHz, CDCl₃) δ 55.7 (s, 1F).

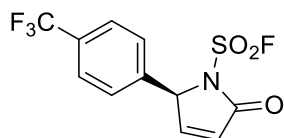
HRMS (ESI) exact mass calculated for C₁₂H₁₀FNNaO₅S: *m/z* 322.0156 ([M+Na]⁺), found: *m/z* 322.0153 ([M+Na]⁺).

[α]_D²⁰ = -243.6 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALCEL OZ-3, hexane/*i*PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 42.9 min (minor) and 57.0 min (major).



(S)-2-oxo-5-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6j)



Prepared according to general procedure E with (*E*)-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yn-1-yl)sulfamoyl fluoride **4j** (100 μ mol, 31.1 mg, 88% purity) and $\text{CF}_3\text{CO}_2\text{TMS}$ (200 μ mol, 34.1 μ L) instead of AcOTMS for 20 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow oil in 68% yield (67.6 μ mol, 20.9 mg) with 82% ee.

¹H NMR (399 MHz, CHLOROFORM-D) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.31 (q, *J* = 2.7 Hz, 1H), 6.35 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.83 (t, *J* = 1.8 Hz, 1H)

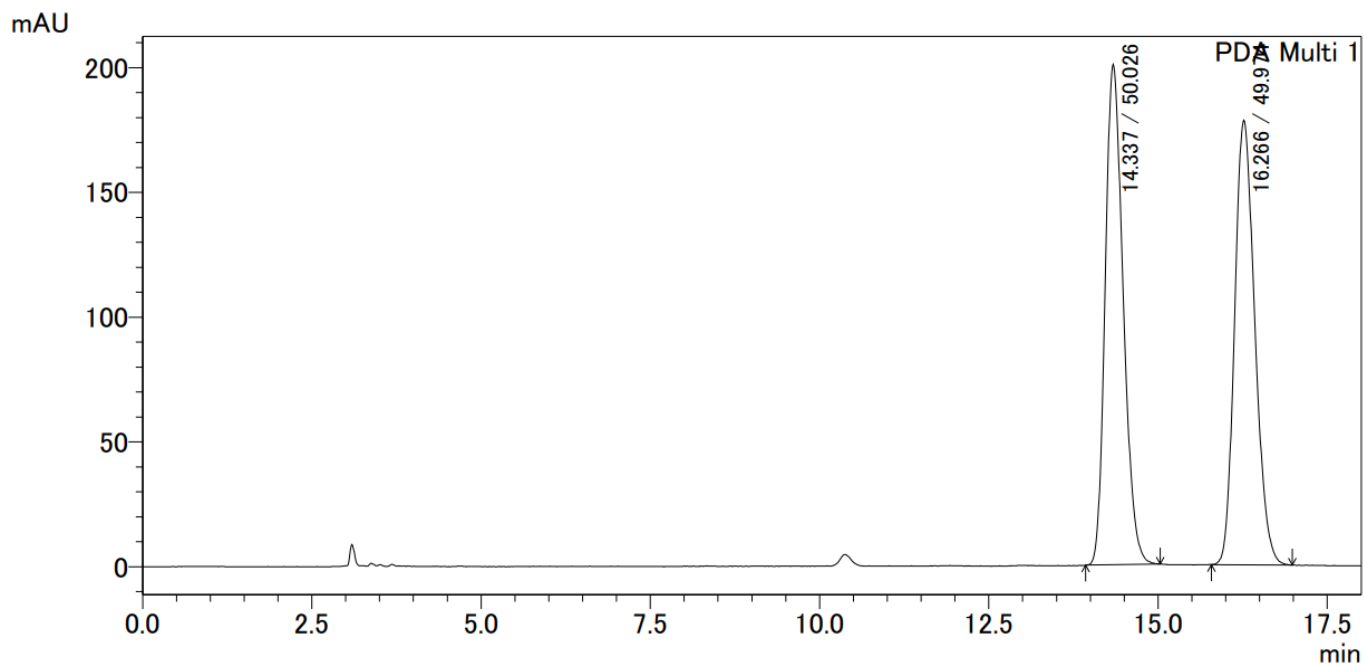
¹³C NMR (100 MHz, CDCl₃) δ 166.4, 152.2, 136.3, 132.3, 127.8, 126.6, 124.2, 123.7, 67.8.

¹⁹F NMR (376 MHz, CDCl₃) δ 55.7 (s, 1F), -64.2 (s, 3F).

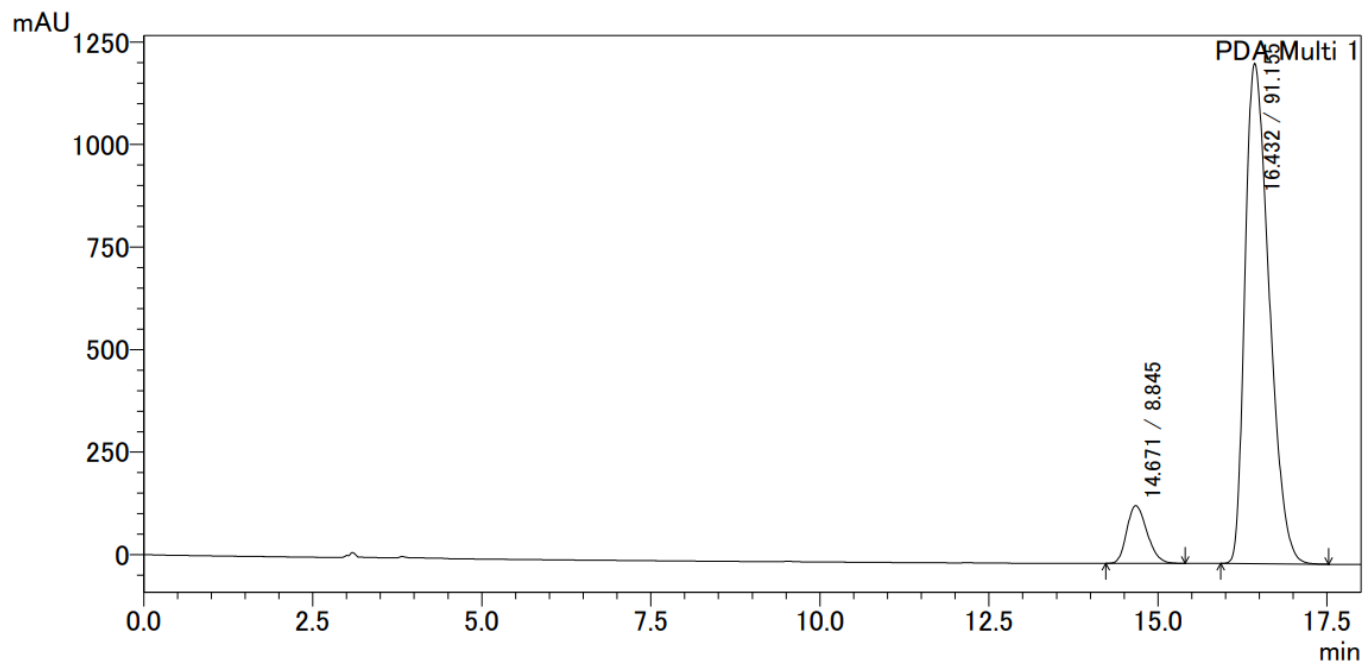
[α]_D²⁵ = -187.5 (*c* = 1.0, CHCl₃).

HRMS (ESI) exact mass calculated for C₁₁H₇F₄NNaO₃S: *m/z* 331.9975 ([M+Na]⁺), found: *m/z* 331.9975 ([M+Na]⁺).

HPLC Daicel CHIRALCEL OZ-3, hexane/*i*PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 14.6 min (minor) and 16.4 min (major).

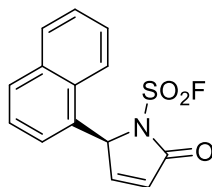


1 PDA Multi 1/207nm,4nm



1 PDA Multi 1/207nm,4nm

(S)-2-(naphthalen-1-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6k)



Prepared according to general procedure E with (*E*)-4-(naphthalen-1-yl)but-3-enoyl sulfamoyl fluoride **4k** (100 μ mol, 31.2 mg, 94% purity) in CH₃CN/H₂O (9:1, 2.0 mL) for 42 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 94% yield (93.7 μ mol, 27.3 mg) with 87% ee.

¹H NMR (399 MHz, CDCl₃) δ 8.03 (s, 1H), 7.95–7.89 (m, 2H), 7.63–7.55 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 6.4, 2.3 Hz, 2H), 6.71 (s, 1H), 6.27 (d, *J* = 3.7 Hz, 1H).

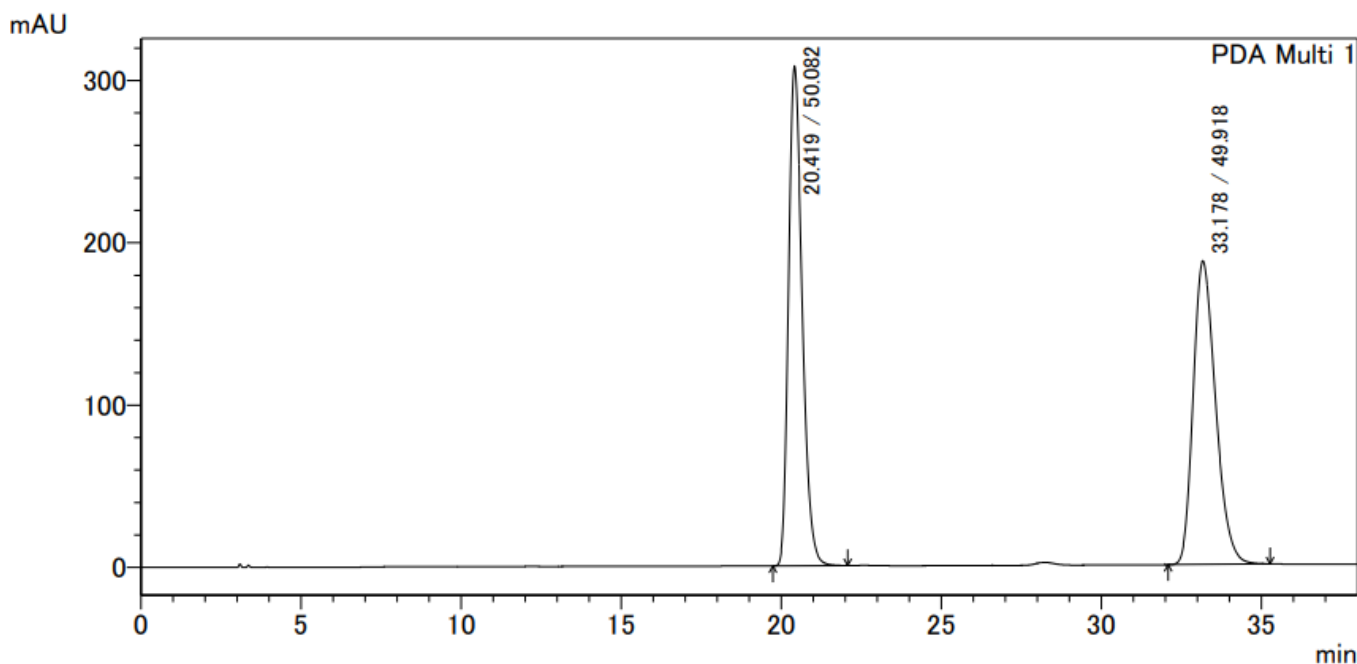
¹³C NMR (100 MHz, CDCl₃) δ 167.3, 153.3, 134.2, 130.3, 129.6, 127.8, 127.4, 126.5, 125.7, 123.0, 121.5, 77.5, 77.1, 76.8, 64.3.

¹⁹F NMR (376 MHz, CDCl₃) δ 55.0 (s, 1F).

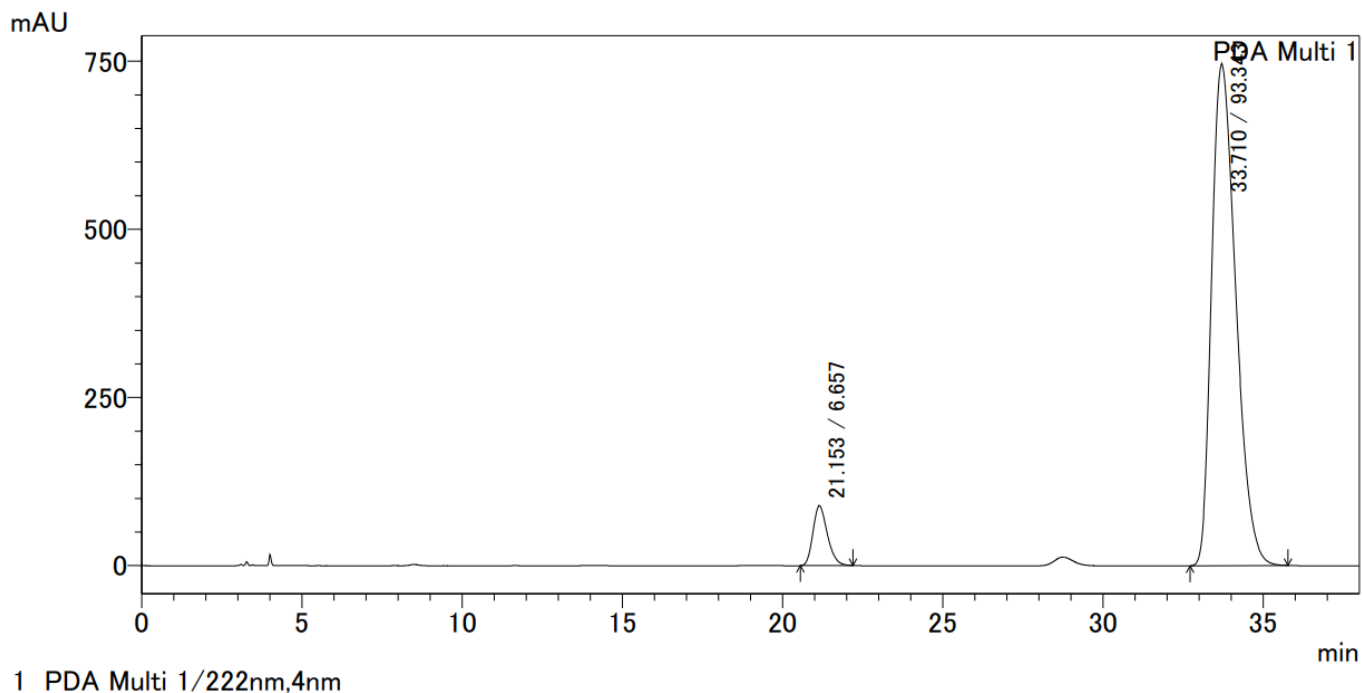
HRMS (ESI) exact mass calculated for C₁₄H₁₀FNNaO₃S: *m/z* 314.0258 ([M+Na]⁺), found: *m/z* 314.0258 ([M+Na]⁺).

[α]_D²⁰ = -327.5 (*c* = 1.0, CHCl₃).

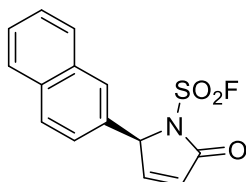
HPLC Daicel CHIRALCEL OZ-3, hexane/*i*PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 21.2 min (minor) and 33.7 min (major).



1 PDA Multi 1/222nm,4nm



(S)-2-(naphthalen-2-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6I)



Prepared according to general procedure E with (*E*)-(4-(naphthalen-2-yl)but-3-en-1-yl)sulfamoyl fluoride **4I** (100 μ mol, 31.9 mg, 92% purity) for 19 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 89% yield (88.6 μ mol, 25.8 mg) with 84% ee.

^1H NMR (399 MHz, CDCl_3) δ 7.89–7.81 (m, 4H), 7.56–7.52 (m, 2H), 7.33 (dd, J = 6.2, 2.1 Hz, 1H), 7.24 (dd, J = 8.7, 1.8 Hz, 1H), 6.32 (dd, J = 6.2, 1.6 Hz, 1H), 5.91 (t, J = 1.8 Hz, 1H).

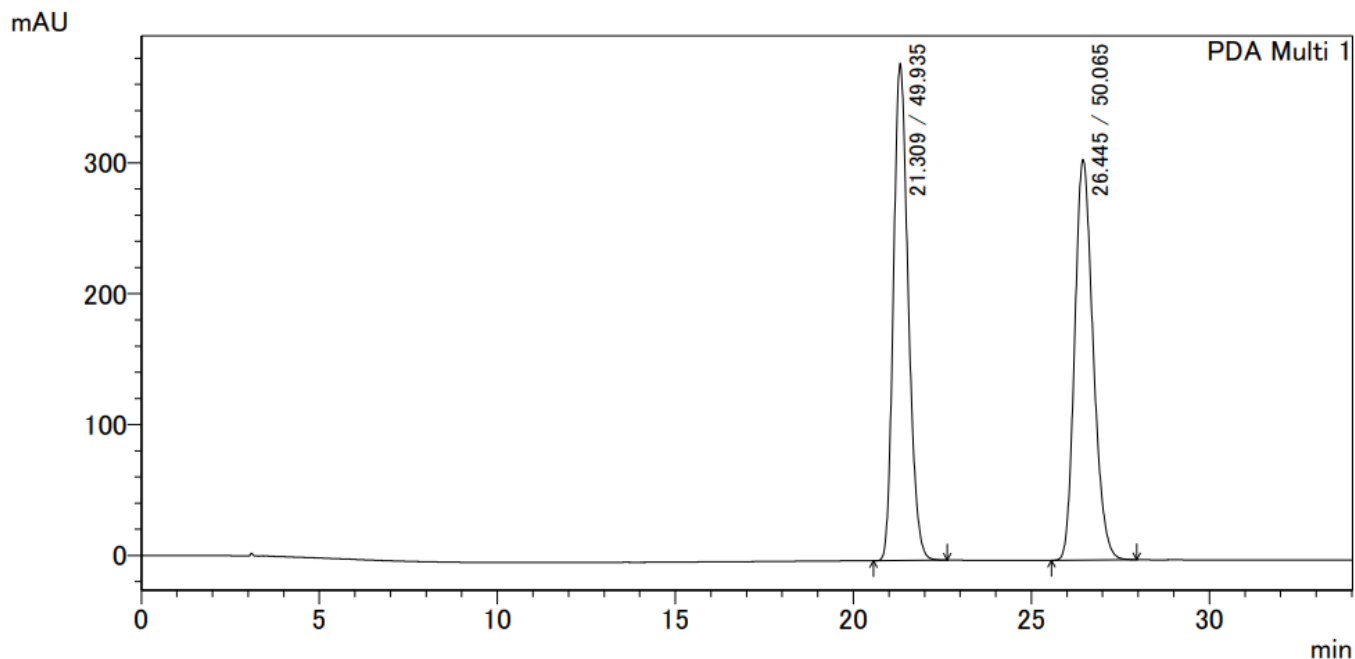
^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 153.0, 133.8, 133.3, 129.7, 129.2, 128.2, 128.0, 127.8, 127.4, 127.1, 123.6, 123.2, 68.8.

^{19}F NMR (376 MHz, CDCl_3) δ 57.2 (s, 1F).

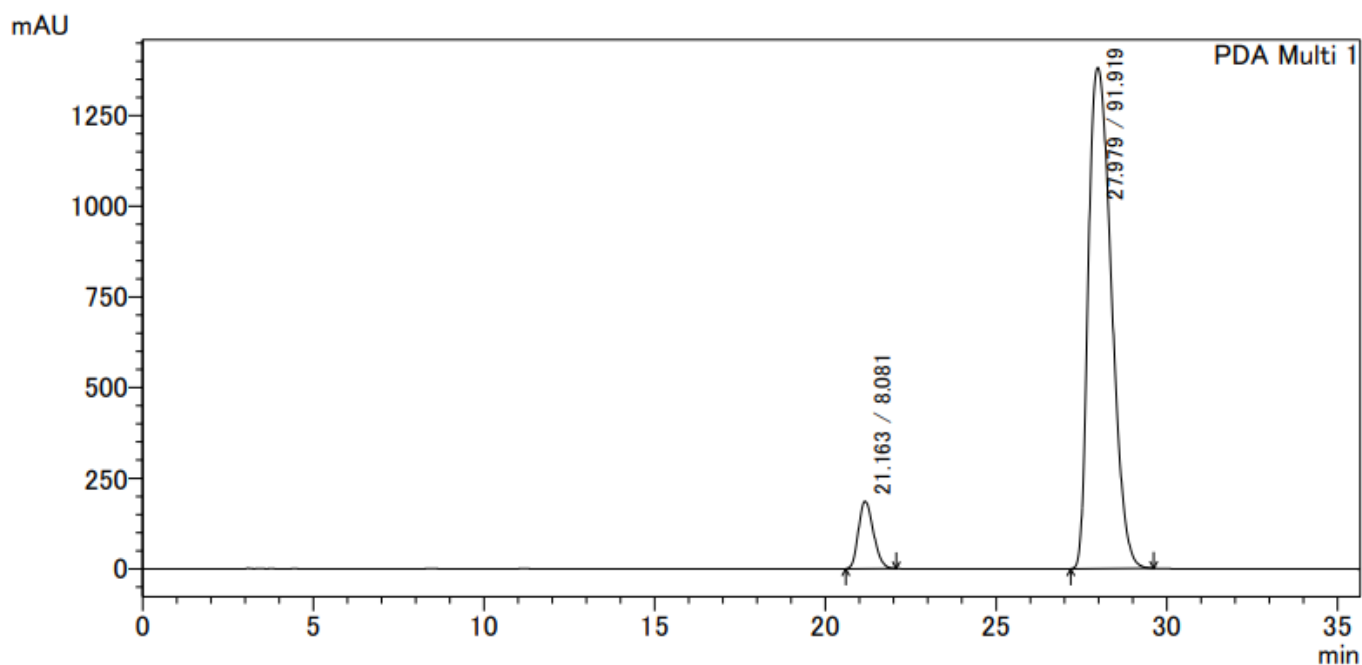
HRMS (ESI) exact mass calculated for $\text{C}_{14}\text{H}_{10}\text{FNNaO}_3\text{S}$: m/z 314.0258 ($[\text{M}+\text{Na}]^+$), found: m/z 314.0261 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_{\text{D}}^{20}$ = -272.3 (c = 1.0, CHCl_3).

HPLC Daicel CHIRALCEL OZ-3, hexane/ i -PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 21.2 min (minor) and 28.0 min (major).

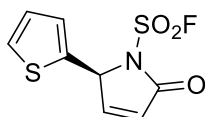


1 PDA Multi 1/222nm,4nm



1 PDA Multi 1/222nm,4nm

(S)-2-oxo-5-(thiophen-2-yl)-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6m)



Prepared according to general procedure E with (*E*)-(4-(thiophen-2-yl)but-3-enoyl)sulfamoyl fluoride **4m** (100 μ mol, 24.9 mg) for 14 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 89% yield (89.0 μ mol, 22.0 mg) with 89% ee.

¹H NMR (399 MHz, CDCl₃) δ 7.42–7.37 (m, 2H), 7.22 (q, *J* = 1.5 Hz, 2H), 7.06 (dd, *J* = 5.0, 3.7 Hz, 2H), 6.32 (dd, *J* = 5.9, 1.8 Hz, 2H), 6.11 (t, *J* = 1.8 Hz, 2H).

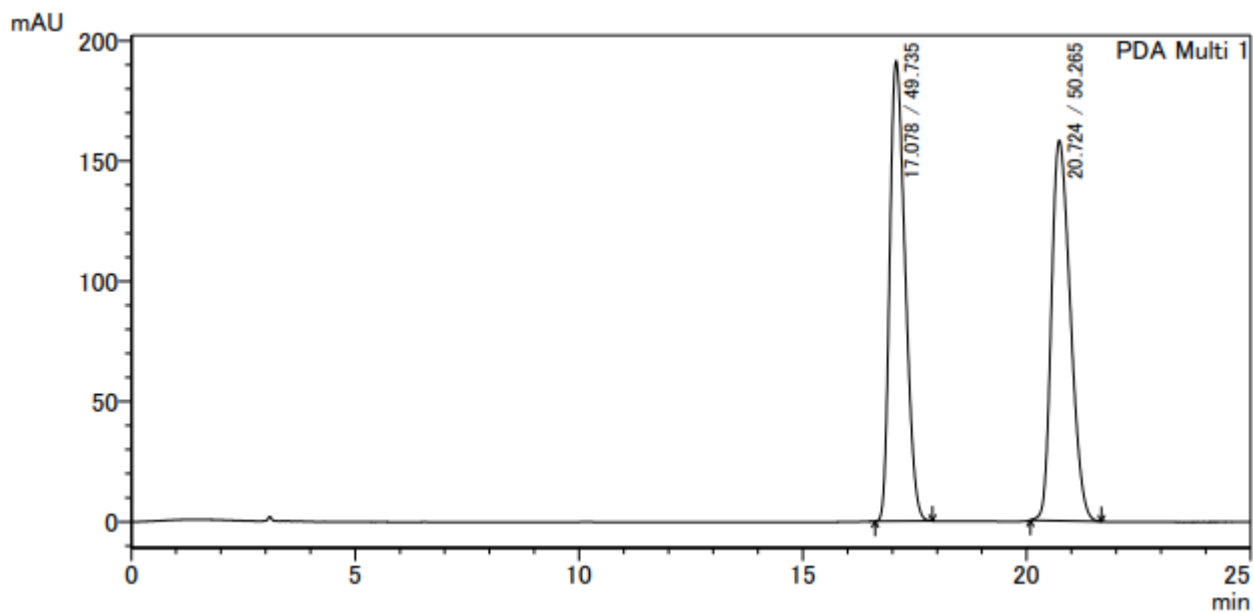
¹³C NMR (100 MHz, CDCl₃) δ 165.9, 151.7, 134.1, 129.6, 128.1, 127.6, 124.1, 63.5.

¹⁹F NMR (376 MHz, CDCl₃) δ 55.9 (s, 1F).

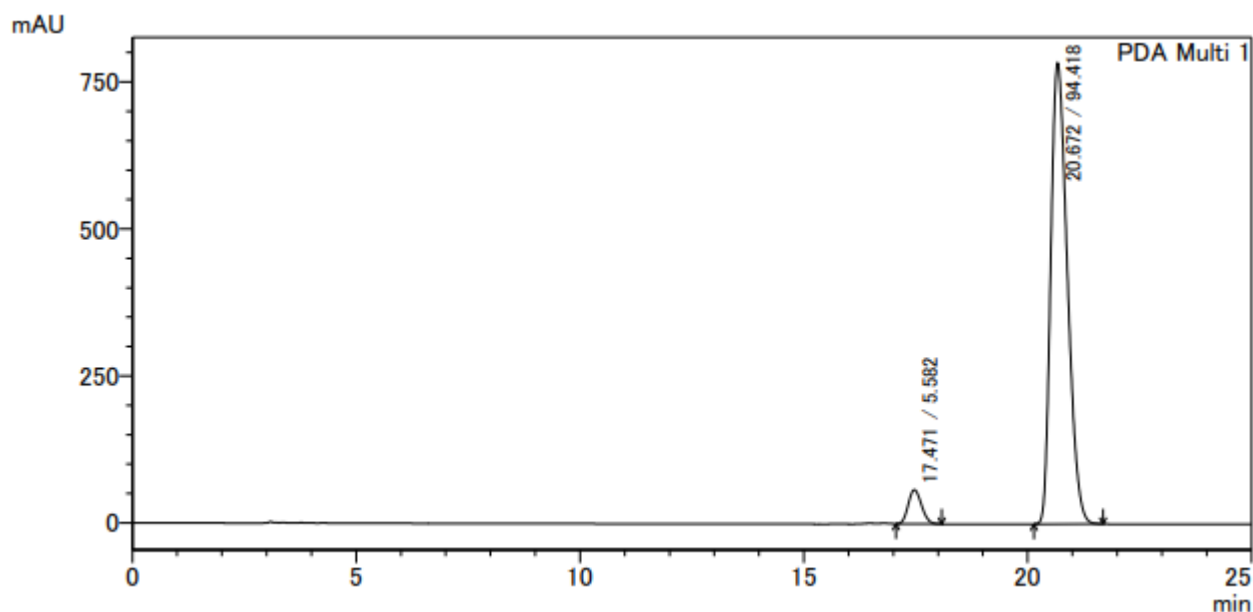
HRMS (ESI) exact mass calculated for $C_8H_6FNNaO_3S_2$: m/z 269.9665 ($[M+Na]^+$), found: m/z 269.9665 ($[M+Na]^+$).

$[\alpha]_D^{20} = -202.3$ ($c = 1.0$, $CHCl_3$).

HPLC Daicel CHIRALCEL OZ-3, hexane/ $PrOH = 10/1$, flow rate = 1.0 mL/min, retention time; 17.5 min (minor) and 20.7 min (major).

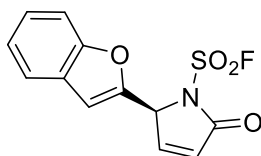


1 PDA Multi 1/225nm,4nm



1 PDA Multi 1/225nm,4nm

(S)-2-(benzofuran-2-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6n)



Prepared according to general procedure E with (*E*)-(4-(benzofuran-2-yl)but-3-enoyl)sulfamoyl fluoride **4n** (100 μ mol, 28.6 mg, 99% purity) for 19 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a red solid in 97% yield (97.0 μ mol, 27.0 mg) with 84% ee.

¹H NMR (401 MHz, CDCl₃) δ 7.61-7.59 (m, 1H), 7.47-7.44 (m, 1H), 7.39 (dd, *J* = 6.4, 2.3 Hz, 1H), 7.37-7.33 (m, 1H), 7.27 (td, *J* = 7.5, 1.1 Hz, 1H), 6.39 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.98 (t, *J* = 2.1 Hz, 1H).

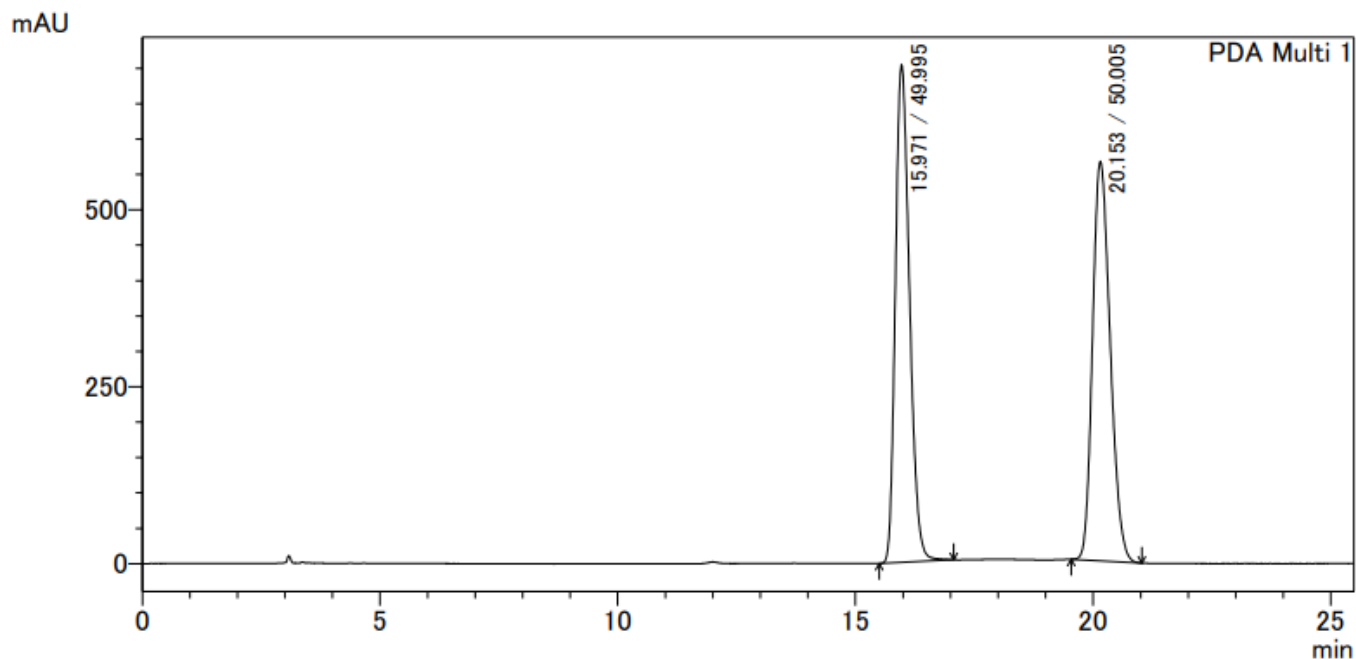
¹³C NMR (100 MHz, CDCl₃) δ 165.9, 155.4, 149.3, 146.7, 127.4, 125.9, 125.4, 123.7, 121.9, 111.7, 108.6, 62.0.

¹⁹F NMR (376 MHz, CDCl₃) δ 55.2 (s, 1F).

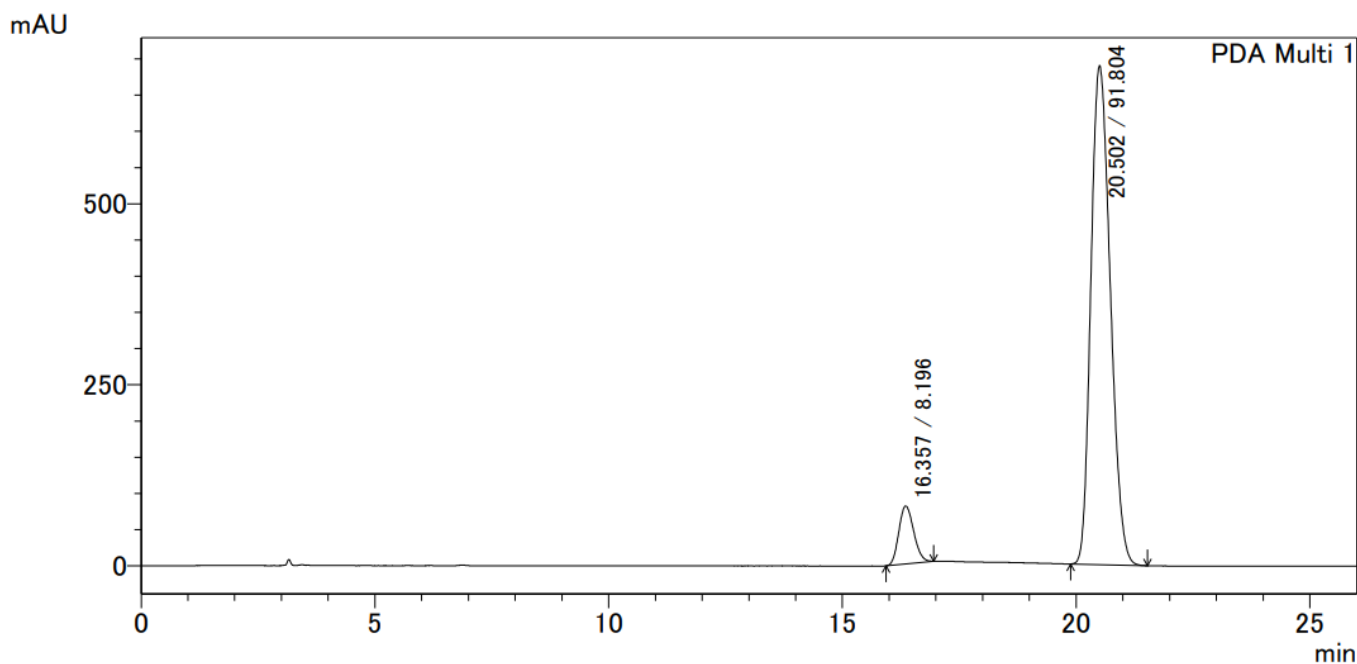
HRMS (ESI) exact mass calculated for C₁₂H₈FNNaO₄S: *m/z* 304.0050 ([M+Na]⁺), found: *m/z* 304.00506 ([M+Na]⁺).

[α]_D²⁰ = -272.1 (*c* = 1.0, CHCl₃).

HPLC Daicel CHIRALCEL OZ-3, hexane/*i*PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 16.4 min (minor) and 20.5 min (major).

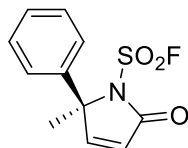


1 PDA Multi 1/207nm,4nm



1 PDA Multi 1/207nm,4nm

(S)-2-methyl-5-oxo-2-phenyl-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6o)



Prepared according to general procedure E with (*E*)-(4-phenylpent-3-enoyl)sulfamoyl fluoride **4o** (100 μ mol, 25.7 mg) for 20 h. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound as a white solid in 83% yield (83.1 μ mol, 21.2 mg) with 75% ee.

^1H NMR (399 MHz, CDCl_3) δ 7.40 (d, J = 6.9 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.23–7.29 (m, 1H), 5.93 (td, J = 7.2, 1.2 Hz, 1H), 3.31 (d, J = 7.3 Hz, 2H), 2.08 (s, 3H).

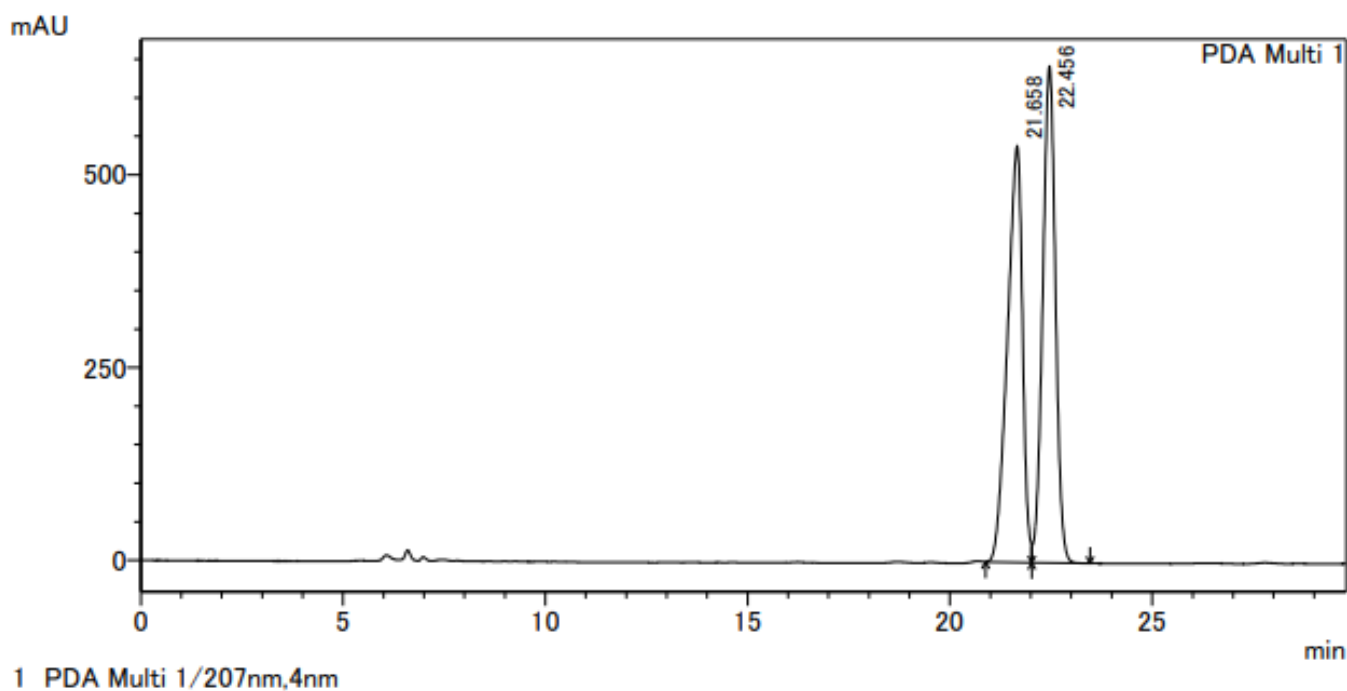
^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 159.6, 134.9, 129.4, 129.3, 126.0, 120.7, 73.3, 21.8.

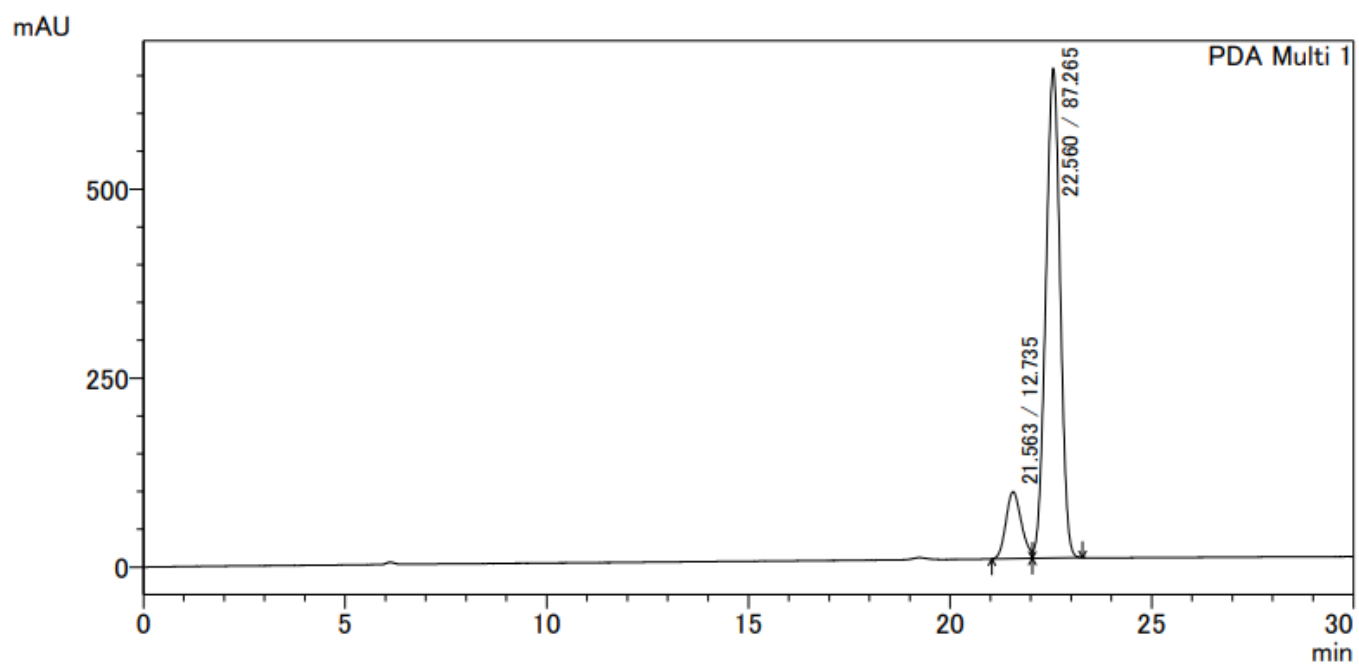
^{19}F NMR (376 MHz, CDCl_3) δ 58.6 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{10}\text{FNNaO}_3\text{S}$: m/z 278.0258 ($[\text{M}+\text{Na}]^+$), found: m/z 278.0264 ($[\text{M}+\text{Na}]^+$).

$[\alpha]_{\text{D}}^{20}$ = -171.4 (c = 1.0, CHCl_3).

HPLC Daicel CHIRALCEL IC-3, hexane/ i PrOH = 4/1, flow rate = 0.5 mL/min, retention time; 21.6 min (minor) and 22.6 min (major).

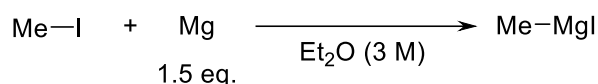




1 PDA Multi 1/207nm,4nm

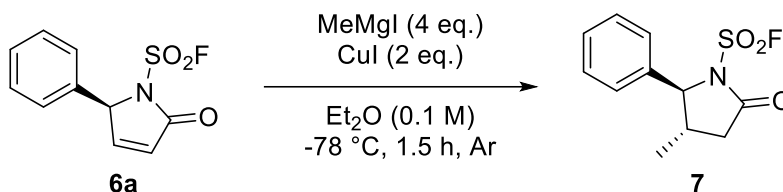
8. Product derivatization (Figure 3a-d)

Preparation of MeMgI



To an argon-purged, two-necked round-bottom flask charged with magnesium turnings (1.5 equiv.) was added Et₂O (1.0–3.0 M), and the mixture was sonicated for 20 min. MeI (1.0 equiv.) was then added dropwise over 30 min at room temperature, and the reaction was stirred for an additional 1 h. The resulting solution was titrated according to a reported literature procedure^[1].

(2S,3S)-3-methyl-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (7)



To a stirred solution of CuI (200 μmol, 38.1 mg) in Et₂O (1 mL) under an argon atmosphere was slowly added freshly prepared MeMgI (2.78 M, 400 μmol, 144 μL) at 0 °C. The mixture was cooled to -78 °C, and **6a** (100 μmol, 24.1 mg) was added. The reaction was stirred for 1.5 h, then 1 M HCl (aq.) was added. The organic layer was extracted with EtOAc, dried over Na₂SO₄, and concentrated under reduced pressure. The crude material was purified by column chromatography (hexane/DCM, 30–100%) to give the title compound as a white solid in 95% yield (94.8 μmol, 24.4 mg) and 91% ee.

¹H NMR (399 MHz, CDCl₃) δ 7.45–7.36 (m, 3H), 7.28 (d, *J* = 6.9 Hz, 2H), 4.82 (d, *J* = 3.7 Hz, 1H), 2.95 (dd, *J* = 17.8, 7.8 Hz, 1H), 2.49–2.39 (m, 1H), 2.34 (dd, *J* = 17.4, 5.5 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 3H).

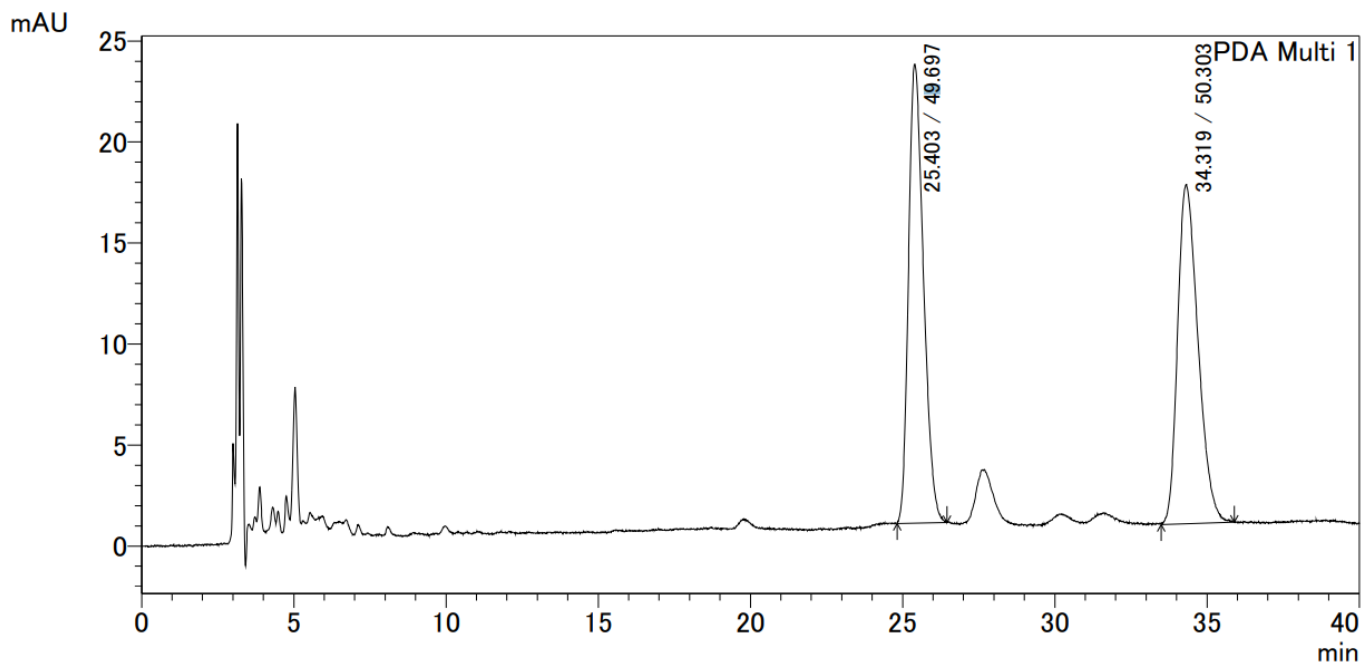
¹³C NMR (100 MHz, CDCl₃) δ 172.0, 138.2, 129.4, 129.0, 125.7, 72.2, 38.1, 37.1, 19.4.

¹⁹F NMR (376 MHz, CDCl₃) δ 54.8 (s, 1F).

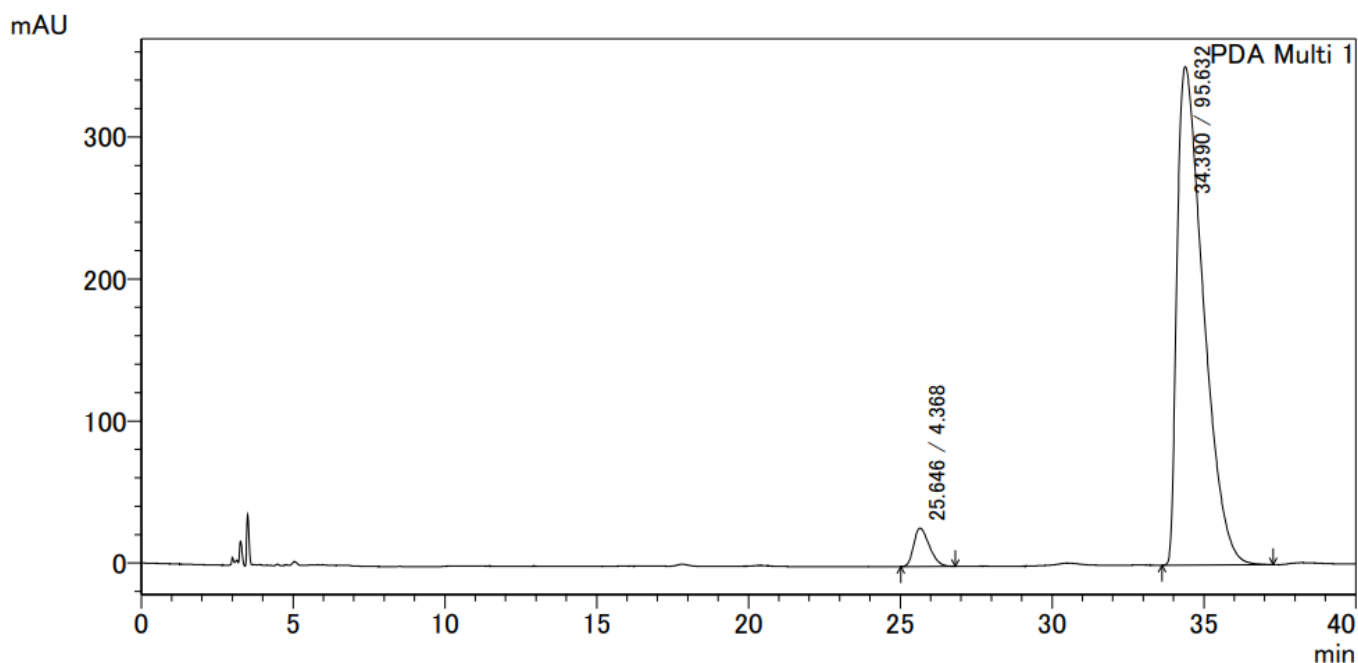
[α]_D²⁰ = -47.2 (*c* = 1.0, CHCl₃).

HRMS (ESI) exact mass calculated for C₁₁H₁₂NO₃SFNa: *m/z* 280.0414 ([M+Na]⁺), found: *m/z* 280.0414 ([M+Na]⁺).

HPLC Daicel CHIRALCEL OZ-3, hexane/PrOH = 40/1, flow rate = 1.0 mL/min, retention time; 25.6 min (minor) and 34.4 min (major).

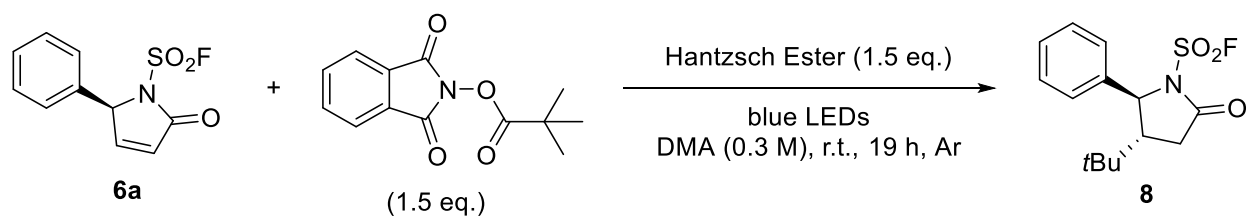


1 PDA Multi 1/209nm,4nm



1 PDA Multi 1/209nm,4nm

(2*S*,3*R*)-3-(*tert*-butyl)-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (8**)**



In a Schlenk tube, **6a** (500 μmol , 120.6 mg), NHPI ester (750 μmol , 185.4 mg), and Hantzsch ester (750 μmol , 193.9 mg) were dissolved in DMA (1.67 mL). The mixture was stirred for 19 h under blue LED irradiation (Kessil A160WE Controllable LED Aquarium Light, 1 cm from the light source) at room temperature. The reaction mixture was poured into water and extracted with EtOAc/hexane (1:1). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography (hexane/DCM,

30–100%) to give the title compound as a colorless oil in 98% yield (146 mg, 488 μ mol) with 89% ee. The relative stereochemistry of the title compound was determined to be trans based on NOE analysis.

^1H NMR (392 MHz, CDCl_3) δ 7.44–7.34 (m, 3H), 7.26 (d, J = 6.9 Hz, 2H), 5.18 (s, 1H), 2.93 (q, J = 9.5 Hz, 1H), 2.60 (dd, J = 18.8, 2.7 Hz, 1H), 2.12 (dt, J = 9.8, 2.3 Hz, 1H), 1.02 (s, 9H).

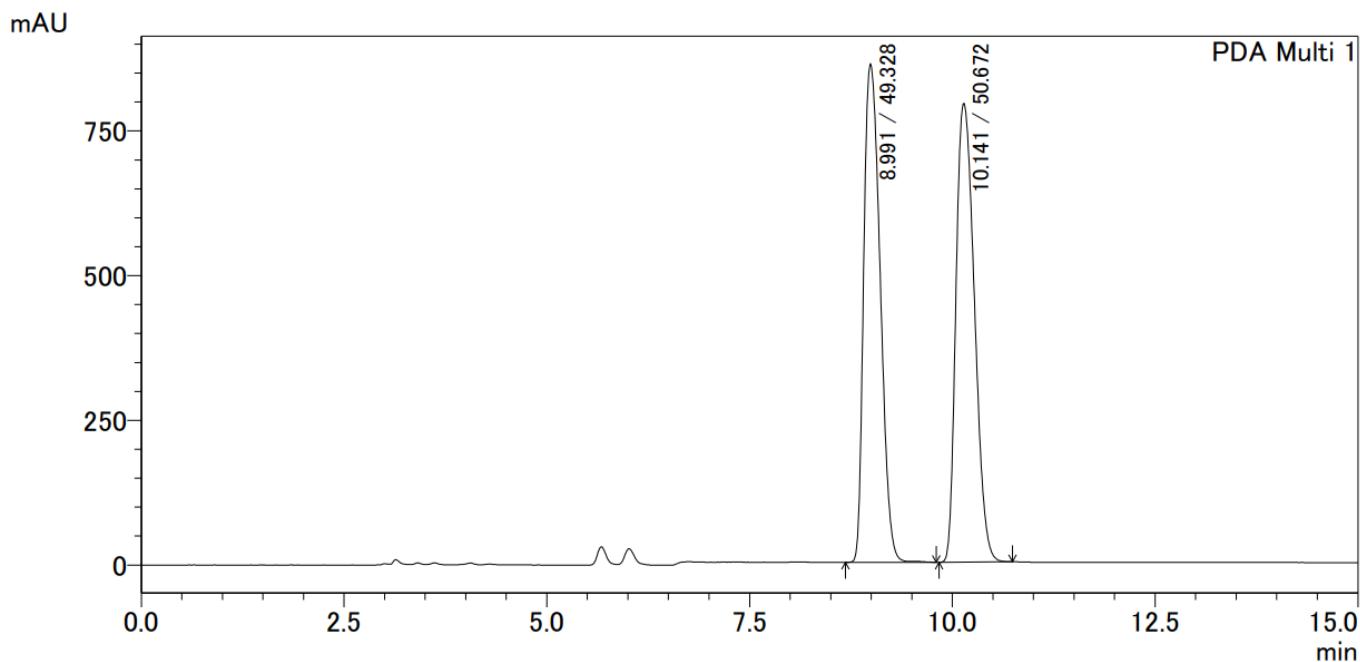
^{13}C NMR (99 MHz, CDCl_3) δ 172.4, 140.1, 129.5, 128.8, 125.3, 66.2, 51.4, 33.7, 32.3, 26.6.

^{19}F NMR (369 MHz, CDCl_3) δ 55.3 (s, 1F).

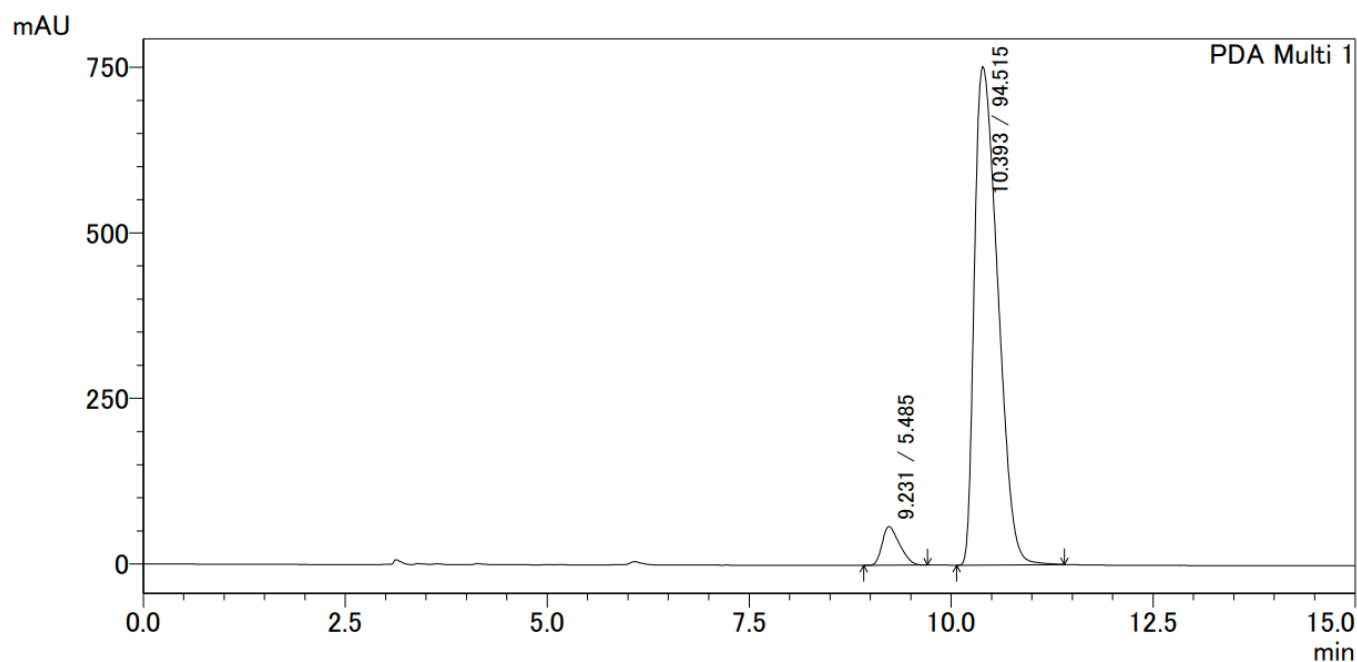
HRMS (ESI) exact mass calculated for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{NFNaS}$: m/z 322.0884 ($[\text{M}+\text{Na}]^+$), found: m/z 322.0884 ($[\text{M}+\text{Na}]^+$).

HPLC Daicel CHIRALCEL OZ-3, hexane/*i*PrOH = 20/1, flow rate = 1.0 mL/min, retention time; 9.2 min (minor) and 10.4 min (major).

$[\alpha]_{\text{D}}^{20}$ = -26.4 (c = 1.0, CHCl_3).

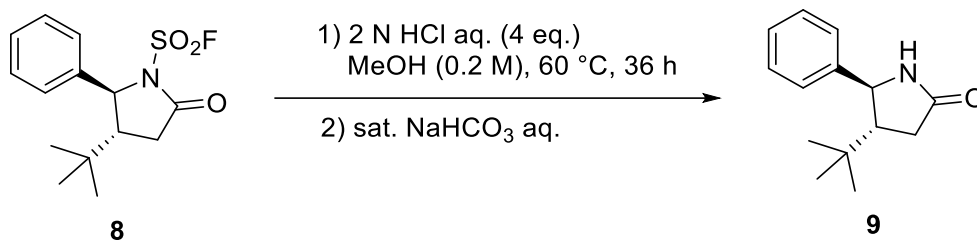


1 PDA Multi 1/209nm,4nm



1 PDA Multi 1/209nm,4nm

(4*R*,5*S*)-4-(tert-butyl)-5-phenylpyrrolidin-2-one (9)



To a stirred solution of **8** (100 μ mol, 29.9 mg) in MeOH (500 μ L) was added 2 M HCl aq. (400 μ mol, 200 μ L). The mixture warmed to 60 $^{\circ}$ C and stirred for 36 h. The reaction mixture was cooled to room temperature and sat. NaHCO₃ aq. was added. After stirring for 1 h, the mixture was extracted with EtOAc, dried over Na₂SO₄, and concentrated under reduced pressure. The crude material was purified by column chromatography (hexane/acetone, 15–70%) to give the title compound as a colorless oil in >99% yield (99.9 μ mol, 21.7 mg) with 89% ee.

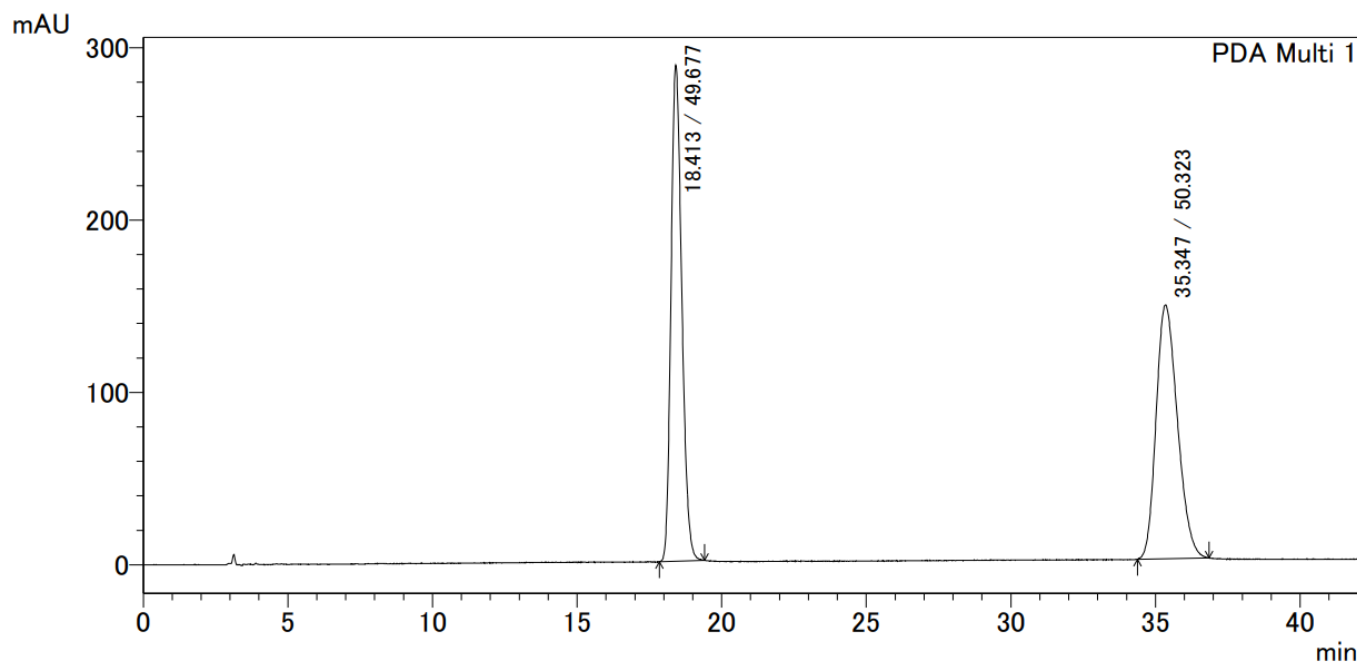
¹H NMR (392 MHz, CDCl₃) δ 7.37-7.34 (m, 2H), 7.29 (d, J = 6.9 Hz, 3H), 6.04 (s, 1H), 4.53 (d, J = 4.6 Hz, 1H), 2.55 (dd, J = 17.4, 9.6 Hz, 1H), 2.32-2.17 (m, 2H), 0.92 (s, 9H).

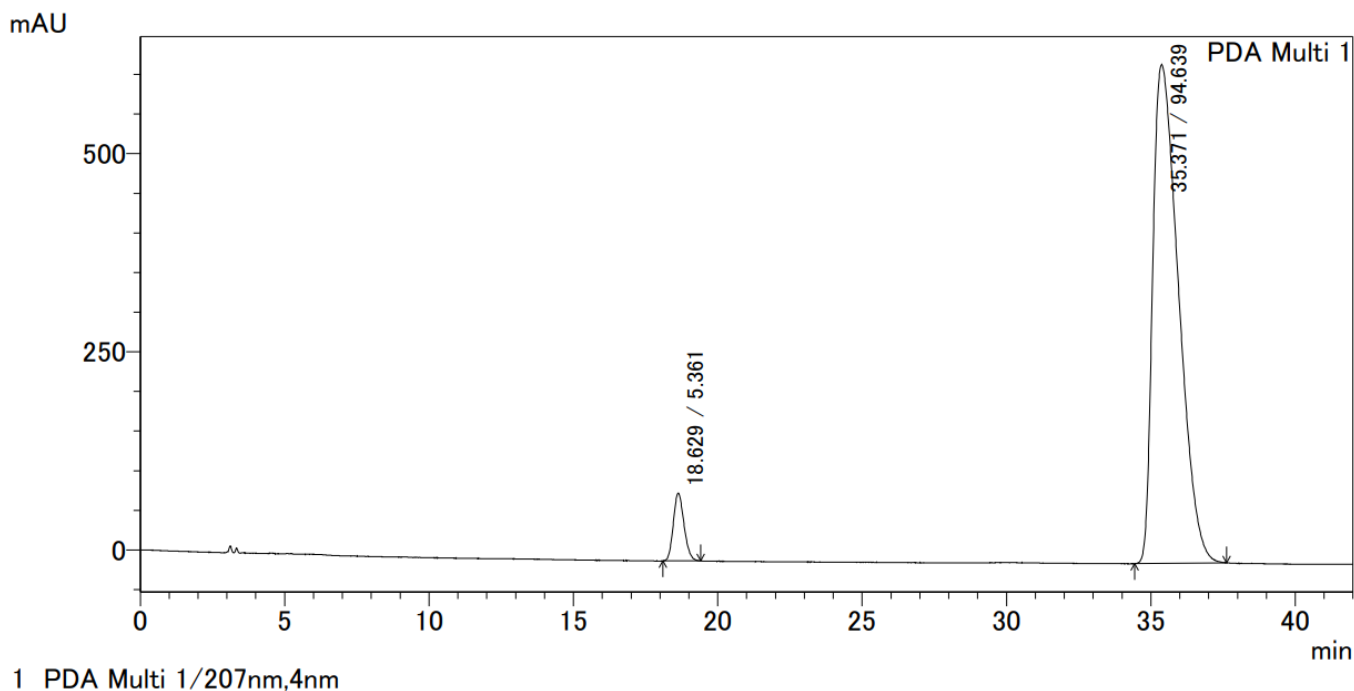
¹³C NMR (99 MHz, CDCl₃) δ 177.5, 143.8, 129.0, 127.9, 126.6, 59.8, 54.2, 33.2, 32.3, 27.2.

HRMS (ESI) exact mass calculated for C₁₄H₁₉NONa: m/z 240.1359 ([M+Na]⁺), found: m/z 240.1359 ([M+Na]⁺).

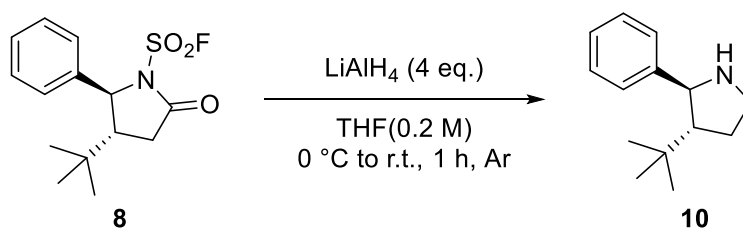
HPLC Daicel CHIRALCEL IC-3, hexane/*i*PrOH = 5/1, flow rate = 1.0 mL/min, retention time; 18.6 min (minor) and 35.4 min (major).

$[\alpha]_D^{20}$ = -19.7 (c = 1.0, CHCl₃).





(2*S*,3*R*)-3-(*tert*-butyl)-2-phenylpyrrolidine (10**)**



To a stirred solution of **8** (100 μ mol, 29.9 mg) in THF (500 μ L) under argon was added LiAlH_4 (12 mmol, 15.2 mL) at 0 $^\circ\text{C}$. The mixture was warmed to room temperature and stirred for 1 h. Saturated Rochelle salt aq. was added, and the mixture was stirred for an additional 1 h. The mixture was extracted with EtOAc, dried over Na_2SO_4 , and concentrated under reduced pressure to give the crude product **10** as a pale yellow oil in >99% yield (103 μ mol, 20.9 mg) with 87% ee. The crude material was further purified by column chromatography (DCM/MeOH, 5%) on triethylamine-treated silica gel to give the title compound as a yellow oil in 92% yield (92 μ mol, 18.7 mg).

Preparation of triethylamine-treated 60N silica gel

Triethylamine (6 mL) was added to 60N silica gel (100 g) in DCM (300 mL). The mixture was filtered, and dried under vacuum.

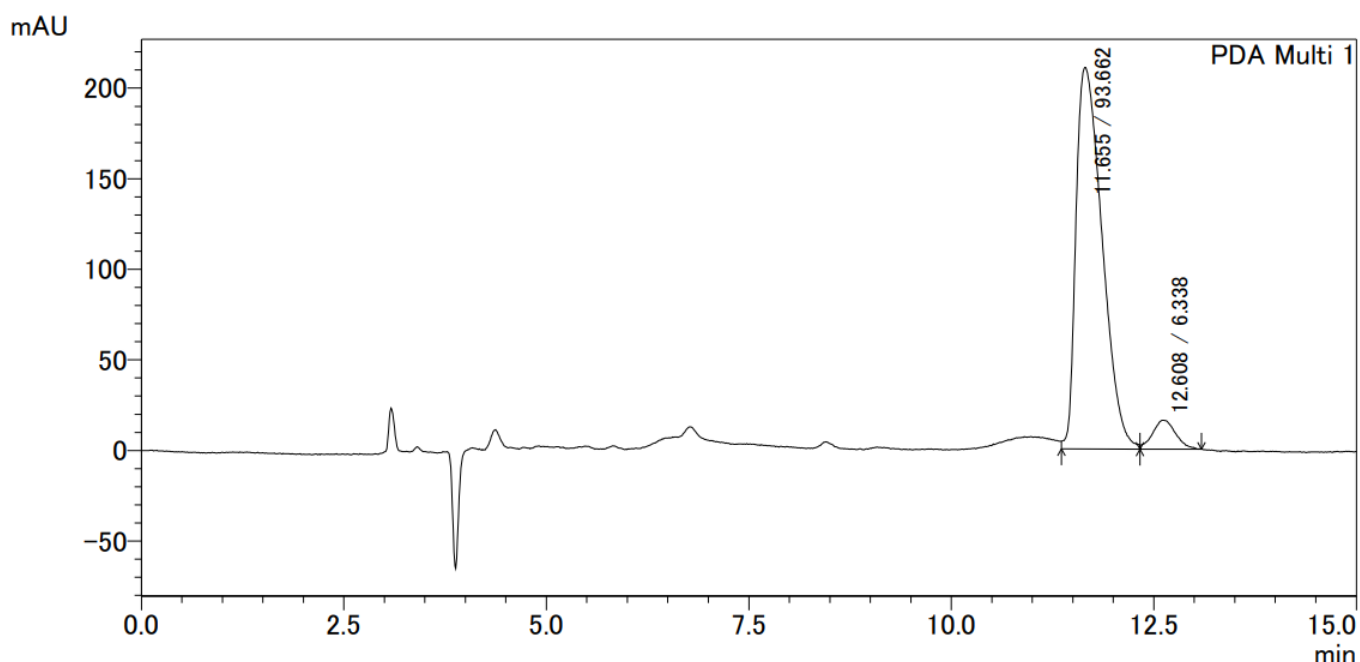
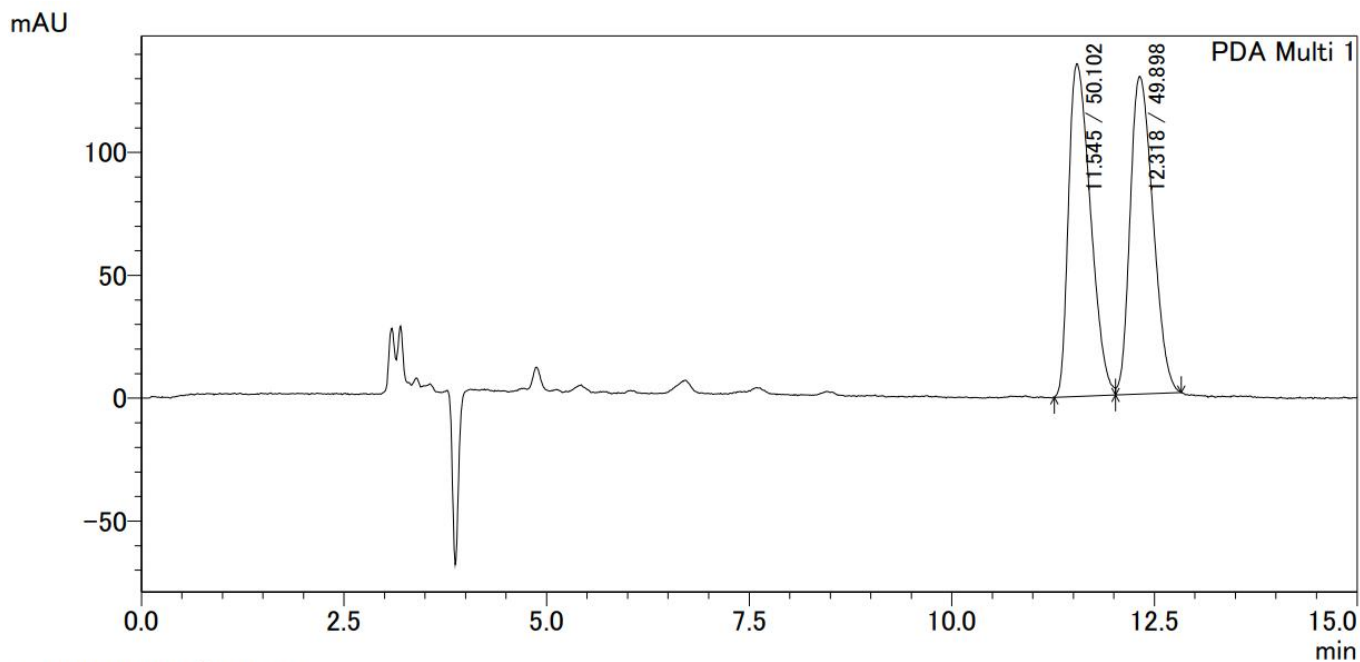
^1H NMR (399 MHz, CDCl_3) δ 7.39 (d, J = 7.3 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.24-7.20 (tt, J = 7.3, 1.4, 1H), 4.31 (d, J = 3.2 Hz, 1H), 3.51 (dt, J = 10.5, 6.0, 1H), 3.20 (ddd, J = 10.5, 7.3, 6.0, 1H), 1.77-1.66 (m, 3H), 0.99 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 147.1, 128.6, 126.8, 126.6, 62.5, 54.3, 54.1, 34.6, 29.0, 28.8.

$[\alpha]_{\text{D}}^{20}$ = -26.4 (c = 1.0, CHCl_3).

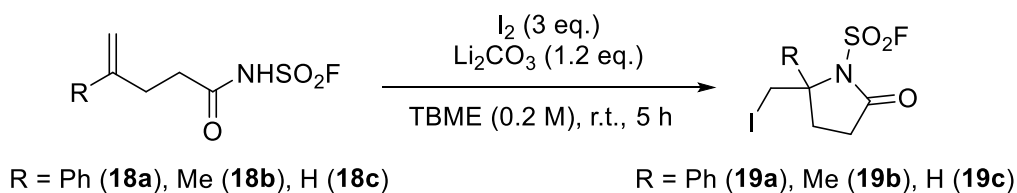
HRMS (ESI) exact mass calculated for $\text{C}_{14}\text{H}_{22}\text{N}$: m/z 204.1747 ($[\text{M}+\text{H}]^+$), found: m/z 204.1741 ($[\text{M}+\text{H}]^+$).

HPLC Daicel CHIRALCEL OZ-3, hexane/ i PrOH = 10/1 0.1% diethylamine, flow rate = 1.0 mL/min, retention time; 11.7 min (major) and 12.6 min (minor).



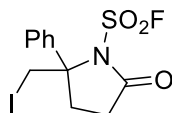
9. Iodo- and hydro-lactamizations (Figure 4)

General procedure F



In a test tube, N-(fluorosulfonyl)amide **18** (100 μmol) and lithium carbonate (120 μmol) were dissolved in TBME (500 μL). After stirring for 10 min, iodine (300 μmol) was added at room temperature. The mixture was stirred for 5 h, then quenched with sat. NaHSO_3 aq. and extracted with EtOAc. The organic layer was concentrated in vacuo, and the residue was purified by column chromatography on TFA-treated silica gel to give the desired product.

2-(iodomethyl)-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (19a)



Prepared according to general procedure F with (4-phenylpent-4-enoyl)sulfamoyl fluoride **18a** (100 μ mol, 25.7 mg). The crude material was purified by column chromatography (hexane/DCM, 30–100%) to give the title compound as a pale yellow solid in 97% yield (96.6 μ mol, 37 mg).

^1H NMR (399 MHz, CDCl_3) δ 7.46–7.45 (m, 3H), 7.33–7.31 (m, 2H), 5.59 (s, 1H), 4.35 (td, J = 4.5, 2.1 Hz, 1H), 3.47 (dd, J = 18.8, 6.4 Hz, 1H), 3.03 (dd, J = 18.8, 2.3 Hz, 1H).

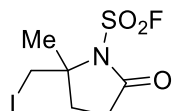
^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 139.8, 129.6, 129.0, 124.9, 73.1, 36.3, 29.6, 15.1.

^{19}F NMR (376 MHz, CDCl_3) δ 58.9 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_{11}\text{H}_{11}\text{O}_3\text{NFNaS}$: m/z 405.9381 ($[\text{M}+\text{Na}]^+$), found: m/z 405.9381 ($[\text{M}+\text{Na}]^+$).

CIF File CCDC 2482632 contains supplementary crystallographic data of **19a**.

2-(iodomethyl)-2-methyl-5-oxopyrrolidine-1-sulfonyl fluoride (19b)



Prepared according to general procedure F with (4-methylpent-4-enoyl)sulfamoyl fluoride **18b** (100 μ mol, 19.5 mg) in 1,4-dioxane (500 μ L) instead of TBME. The crude material was purified by column chromatography (1st: hexane/DCM, 30–100%; 2nd: hexane/TBME, 30–100%) to give the title compound as a white solid in 55% yield (55 μ mol, 17.7 mg).

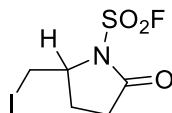
^1H NMR (399 MHz, CDCl_3) δ 3.81 (d, J = 11.0 Hz, 1H), 3.55 (d, J = 11.0 Hz, 1H), 2.78 (ddd, J = 18.3, 10.1, 6.0 Hz, 1H), 2.64 (ddd, J = 18.3, 10.1, 7.8 Hz, 1H), 2.40 (ddd, J = 14.2, 10.5, 7.8 Hz, 1H), 2.10 (ddd, J = 13.2, 10.1, 6.0 Hz, 1H), 1.75–1.92 (3H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.3, 68.5, 33.5, 29.7, 24.8, 14.4.

^{19}F NMR (376 MHz, CDCl_3) δ 58.7 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_6\text{H}_9\text{O}_3\text{NFNaS}$: m/z 343.9224 ($[\text{M}+\text{Na}]^+$), found: m/z 343.9228 ($[\text{M}+\text{Na}]^+$).

2-(iodomethyl)-5-oxopyrrolidine-1-sulfonyl fluoride (19c)



Prepared according to general procedure F with pent-4-enoylsulfamoyl fluoride **18c** (100 μ mol, 18.1 mg). The crude material was purified by column chromatography (hexane/DCM, 30–100%) to give the title compound as a white solid in 82% yield (82.4 μ mol, 25.3 mg).

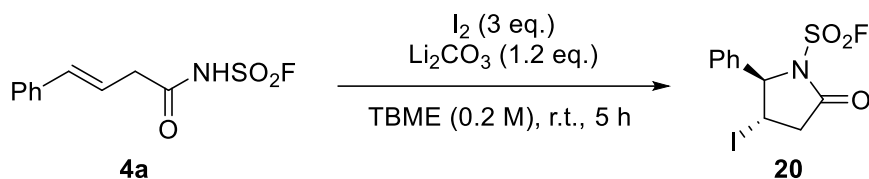
^1H NMR (399 MHz, CDCl_3) δ 4.43–4.38 (m, 1H), 3.58–3.51 (m, 2H), 2.93–2.84 (m, 1H), 2.61 (ddd, J = 18.4, 10.4, 3.5 Hz, 1H), 2.53–2.42 (m, 1H), 2.20–2.12 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 60.6, 30.1, 24.7, 7.8.

^{19}F NMR (376 MHz, CDCl_3) δ 55.7 (s, 1F).

HRMS (ESI) exact mass calculated for $\text{C}_5\text{H}_7\text{O}_3\text{NFNaS}$: m/z 329.9068 ($[\text{M}+\text{Na}]^+$), found: m/z 329.9070 ($[\text{M}+\text{Na}]^+$).

3-iodo-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (**20**)



Prepared according to general procedure F with (*E*)-(4-phenylbut-3-enoyl)sulfamoyl fluoride **4a** (100 μ mol, 24.3 mg) for 5 h. The crude material was purified by column chromatography (hexane/DCM, 30–100%) to give the title compound as a yellow solid in 78% yield (78 μ mol, 28.8 mg).

¹H NMR (399 MHz, CDCl₃) δ 7.46–7.45 (m, 3H), 7.33–7.31 (m, 2H), 5.59 (s, 1H), 4.35 (td, J = 4.5, 2.1 Hz, 1H), 3.47 (dd, J = 18.8, 6.4 Hz, 1H), 3.03 (dd, J = 18.8, 2.3 Hz, 1H).

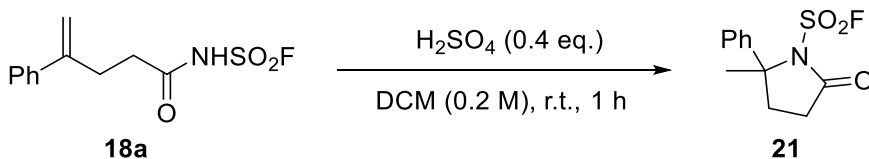
¹³C NMR (100 MHz, CDCl₃) δ 169.3, 135.9, 129.9, 129.8, 125.3, 75.4, 42.4, 16.8.

¹⁹F NMR (376 MHz, CDCl₃) δ 54.5 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₀H₉O₃NFINaS: m/z 391.9224 ([M+Na]⁺), found: m/z 391.9224 ([M+Na]⁺).

CIF File CCDC 2484902 contains supplementary crystallographic data of **20**.

2-methyl-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (**21**)



In a test tube, H₂SO₄ (40 μ mol, 2 μ L) was added to (4-phenylpent-4-enoyl)sulfamoyl fluoride **18a** (100 μ mol, 25.7 mg) in DCM (500 μ L). After stirring for 1 h, the solution was quenched with saturated NaHCO₃ aq., extracted with EtOAc, dried over Na₂SO₄, and concentrated. The crude material was purified by column chromatography (hexane/DCM, 15–80%) to give the desired product as a white solid in 96% yield (96 μ mol, 24.7 mg).

¹H NMR (399 MHz, CDCl₃) δ 7.46–7.45 (m, 3H), 7.33–7.31 (m, 2H), 5.59 (s, 1H), 4.35 (td, J = 4.5, 2.1 Hz, 1H), 3.47 (dd, J = 18.8, 6.4 Hz, 1H), 3.03 (dd, J = 18.8, 2.3 Hz, 1H).

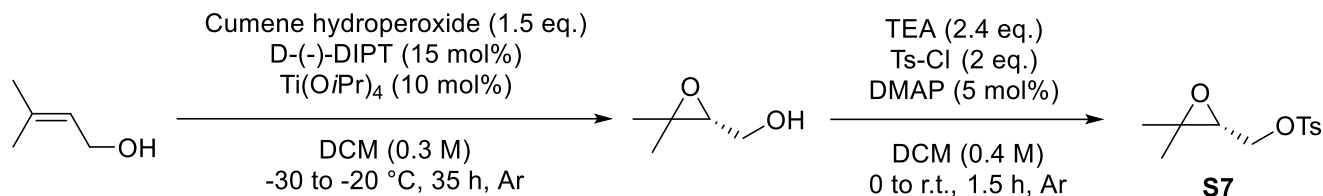
¹³C NMR (100 MHz, CDCl₃) δ 169.3, 135.9, 129.9, 129.8, 125.3, 75.4, 42.4, 16.8.

¹⁹F NMR (376 MHz, CDCl₃) δ 54.5 (s, 1F).

HRMS (ESI) exact mass calculated for C₁₁H₁₂O₃NFNaS: m/z 280.0414 ([M+Na]⁺), found: m/z 280.0414 ([M+Na]⁺).

10. Total Synthesis of diaporisoindole A

(R)-(3,3-dimethyloxiran-2-yl)methyl 4-methylbenzenesulfonate (**S7**)



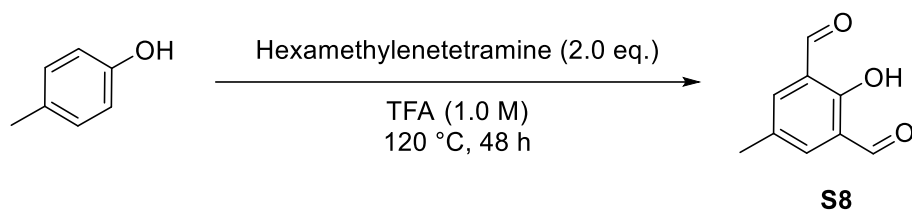
To a flame-dried two-necked flask, D-DIPT (3.0 mmol, 629 μL), $\text{Ti}(\text{O}i\text{Pr})_4$ (2.0 mmol, 595 μL), and powdered 4 Å MS (800 mg) were dissolved in dry DCM (60 mL) at -30 °C. After stirring for 30 min, 3-methylbut-2-en-1-ol (20 mmol, 2 mL) in DCM was added. Cumene hydroperoxide (30.0 mmol, 5.50 mL, 80% purity) was added dropwise over 2 h. The mixture was stirred for 1 h, then warmed to -20 °C. After stirring for 35 h, saturated Na_2SO_4 aq. (2 mL) and Et_2O (20 mL) were added, and the mixture was stirred for 3 h. The reaction was filtered through a pad of Celite and concentrated. The residue was purified by column chromatography (hexane/ EtOAc , 8–66%) to give the epoxy alcohol with moderate purity^[3]. To this epoxy alcohol in dry DCM (50.7 mL), triethylamine (32.4 mmol, 4.52 mL), DMAP (1.01 mmol, 124 mg) and TsCl (28.4 mmol, 5.40 g) were added at 0 °C. The mixture was warmed to room temperature, and additional TsCl and triethylamine were added until the reaction was complete (monitored by TLC). The reaction was quenched with saturated NH_4Cl aq., extracted with DCM, dried over Na_2SO_4 , and concentrated. The crude material was purified by column chromatography (hexane/TBME, 8–66%) to give chiral epoxide **S7** as a colorless oil in 59% yield (11.9 mmol, 3.04 g) and 83% ee. Spectral data matched the literature^[4].

^1H NMR (399 MHz, CDCl_3) δ 7.80 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 4.13 (dd, J = 11.4, 5.5 Hz, 1H), 4.08 (dd, J = 11.2, 5.7 Hz, 1H), 2.96 (t, J = 5.7 Hz, 1H), 2.44 (s, 3H), 1.29 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 132.8, 130.0, 128.1, 68.7, 59.6, 58.7, 24.4, 21.8, 18.8.

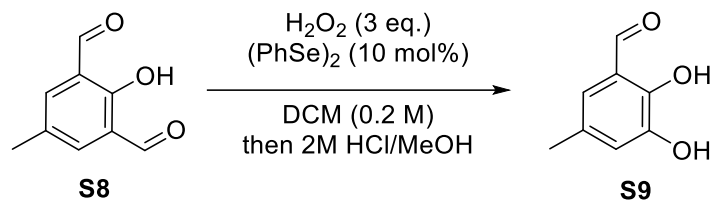
$[\alpha]_{\text{D}}^{20}$ = +18.2 (c = 1.0, CHCl_3). ($[\alpha]_{\text{D}}^{25}$ (lit.) = +20.15 (c = 7.48, CHCl_3)^[4]

2-hydroxy-5-methylisophthalaldehyde (**S8**)



In an oven-dried, pressure-resistant tube, hexamethylenetetramine (11.7 mmol, 1.63 g) was dissolved in TFA (5.83 mL), and p -cresol (5.83 mmol, 612 μL) was added. The tube was sealed and heated at 120 °C for 48 h. After cooling to 40 °C, 1 M HCl aq. was added to the resulting solution, and the mixture was stirred for 1 h at the same temperature. The mixture was extracted with EtOAc , dried over Na_2SO_4 , and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (hexane/DCM, 30–100%) to give the title compound **S8** as a white solid in 61% yield (3.56 mmol, 585 mg). Spectral data matched with the literature^[5].

2,3-dihydroxy-5-methylbenzaldehyde (**S9**)



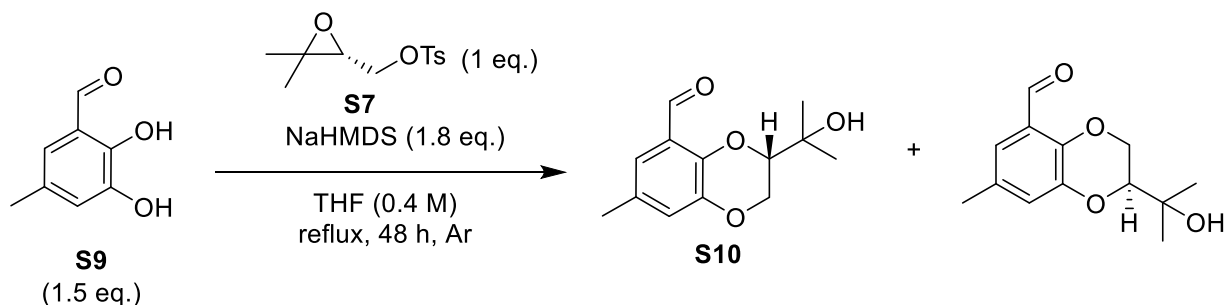
To a stirred solution of 2-hydroxy-5-methylisophthalaldehyde **S8** (3.92 mmol, 643 mg) and diphenyl diselenide (392 μmol , 123 mg) in DCM (19.6 mL), 30% H_2O_2 aq. (11.8 mmol, 1.2 mL) was added at room temperature, and the mixture was stirred at the same temperature until completion. The reaction mixture was poured into water and extracted three times with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The crude material was purified by column chromatography (hexane/acetone, 5–30%). The resulting monoester was treated with 2 M HCl (7.84 mL) in MeOH (10 mL) for 3 h. The reaction mixture was poured into water and extracted three times with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo to give 2,3-dihydroxy-5-methylbenzaldehyde **S9** as a yellow solid in 55% yield (2.14 mmol, 326 mg)^[6].

^1H NMR (399 MHz, CDCl_3) δ 10.88 (s, 1H), 9.84 (s, 1H), 7.02 (s, 1H), 6.93 (s, 1H), 5.57 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 146.3, 144.6, 130.1, 124.2, 122.7, 120.3, 20.7.

HRMS (ESI) exact mass calculated for $\text{C}_8\text{H}_7\text{O}_3$: m/z 151.0401 ($[\text{M}-\text{H}]^-$), found: m/z 151.0402 ($[\text{M}-\text{H}]^-$).

(S)-3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[b][1,4]dioxine-5-carbaldehyde (**S10**)



In a flame-dried Schlenk tube, 2,3-dihydroxy-5-methylbenzaldehyde **S9** (3.05 mmol, 465 mg) was dissolved in dry THF (3.16 mL) under argon. NaHMDS (1.9 M in THF, 3.67 mmol, 1.93 mL) was added at 0 °C. After stirring for 10 min, (*R*)-3-(2-methoxypropan-2-yl)methyl 4-methylbenzenesulfonate **S7** (2.04 mmol, 522 mg) was added, and the mixture was warmed to 70 °C. After stirring for 48 h, the reaction was cooled to room temperature, quenched with 1 M HCl aq., and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated. The crude material was purified by column chromatography on silica gel (hexane/acetone, 5–50%) to give the aldehyde as a mixture of regioisomers (91:9). The undesired regioisomer was removed by recycling preparative HPLC (CHIRALCEL OD, 20×250 mm, hexane/*i*PrOH = 10:1, flow 10.0 mL/min) to afford the pure alcohol **S10** as a yellow oil in 64% yield (1.3 mmol, 308 mg) with 84% ee.

^1H NMR (399 MHz, CDCl_3) δ 10.37 (s, 1H), 7.20 (d, J = 1.1 Hz, 1H), 6.94 (d, J = 2.3 Hz, 1H), 4.49 (dd, J = 11.4, 2.3 Hz, 1H), 4.09 (dd, J = 11.4, 9.1 Hz, 1H), 3.99 (dd, J = 9.1, 1.8 Hz, 1H), 2.28 (s, 3H), 2.03–2.39 (s, 1H), 1.42 (s, 3H), 1.36 (s, 3H).

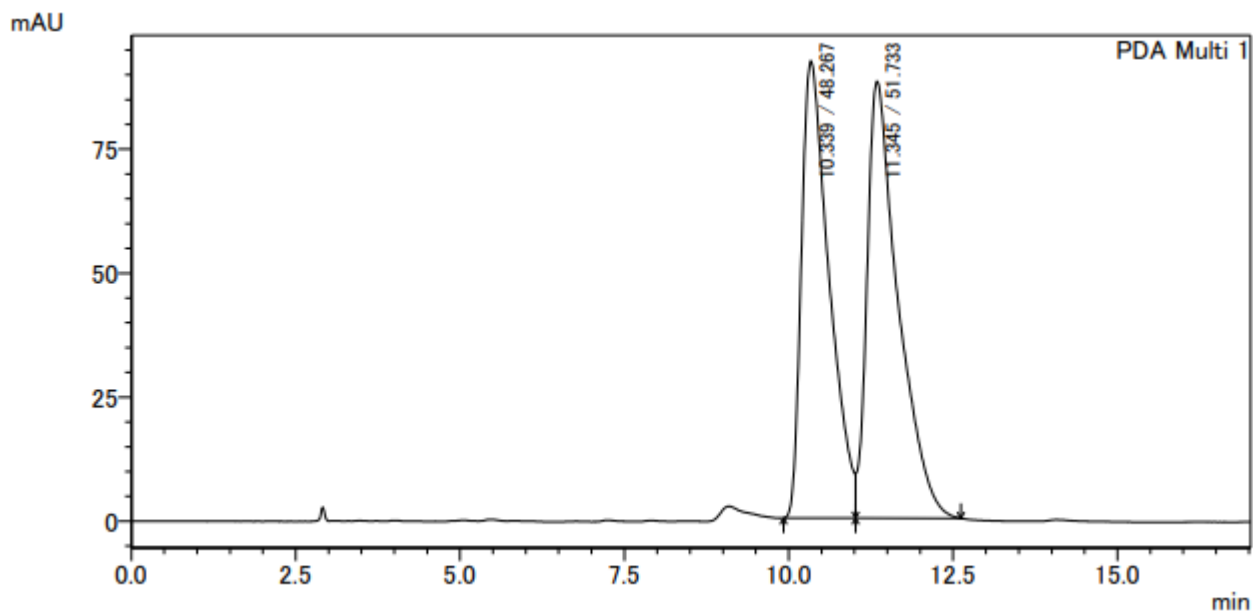
^{13}C NMR (100 MHz, CDCl_3) δ 188.9, 144.4, 143.5, 131.0, 124.6, 123.6, 121.2, 79.3, 70.9, 64.7, 26.2, 25.6, 20.6.

HPLC Daicel CHIRALPAK AS-3, hexane/*i*PrOH = 10/1, flow rate = 1.0 mL/min, retention time; 8.67 min (minor) and 9.36 min (major).

HRMS (ESI) exact mass calculated for $\text{C}_{13}\text{H}_{16}\text{O}_4\text{Na}$: m/z 259.0941 ($[\text{M}+\text{Na}]^+$), found: m/z 259.0940 ($[\text{M}+\text{Na}]^+$).

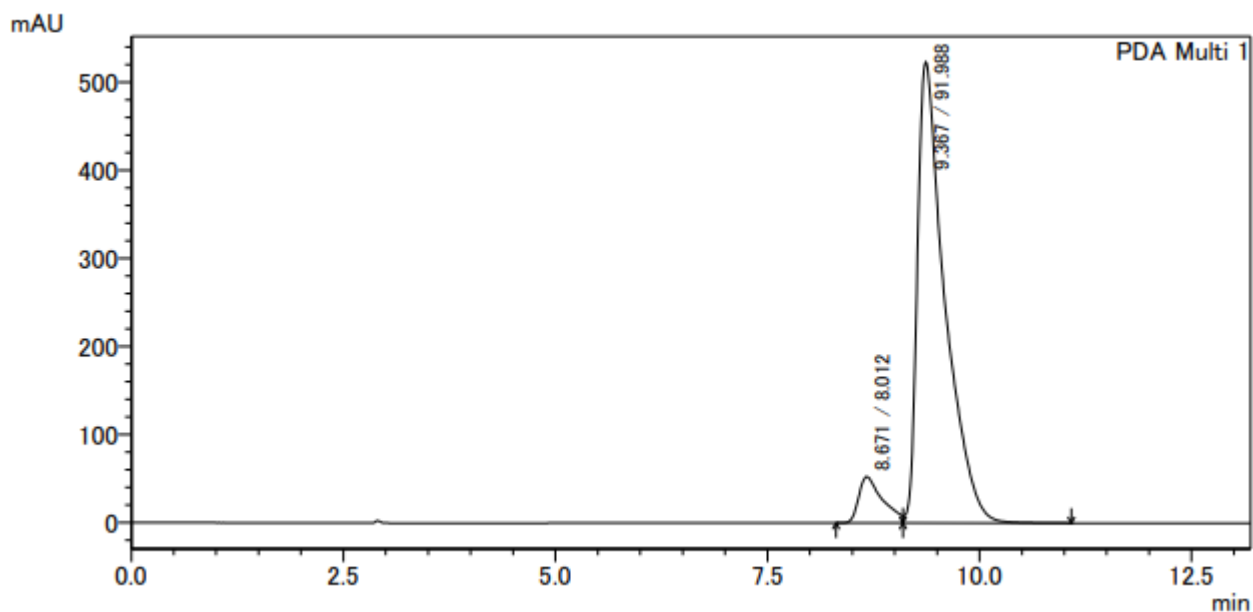
$[\alpha]_{\text{D}}^{25} = +45.5$ ($c = 0.2$, CHCl_3).

HPLC Daicel CHIRALCEL AS-3, hexane/ $\text{PrOH} = 10/1$, flow rate = 1.0 mL/min, retention time; 8.67 min (minor) and 9.36 min (major).



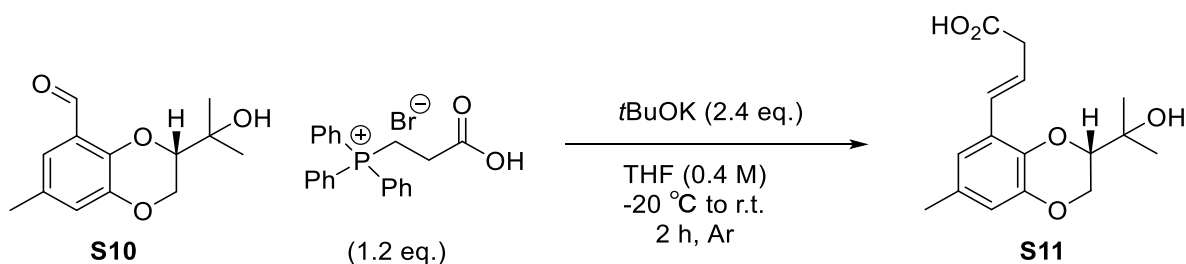
1 PDA Multi 1/220nm,4nm

＜クロマトグラム＞



1 PDA Multi 1/220nm,4nm

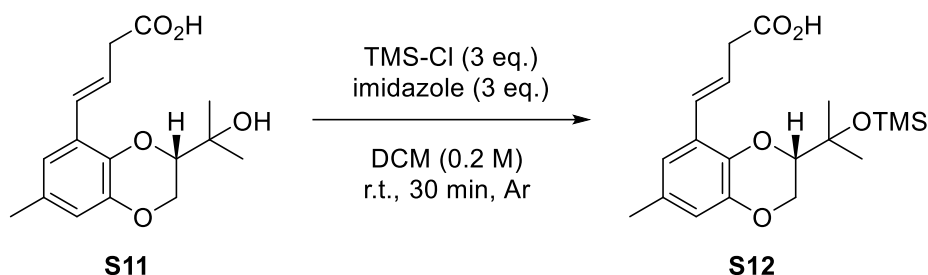
(S,E)-4-(3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[b][1,4]dioxin-5-yl)but-3-enoic acid (S11)



In a flame-dried two-neck flask, the Wittig reagent (1.38 mmol, 574 mg) was dissolved in THF and sonicated for 10 min. Chiral aldehyde **S10** (1.15 mmol, 272 mg) was added, and the solution was cooled to -20°C . Potassium

tert-butoxide (1 M in THF, 2.77 mmol, 2.77 mL) was added dropwise over 1 h via syringe. The solution was then warmed to room temperature and stirred for 30 min. Upon completion, THF was removed under reduced pressure, and water was added to the residue. The suspension was filtered through a pad of Celite and washed with H₂O. The aqueous layer was acidified with 12 M HCl and extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material **S11** was used directly in the next reaction without further purification.

(*S,E*)-4-(7-methyl-3-(2-((trimethylsilyl)oxy)propan-2-yl)-2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)but-3-enoic acid (S12**)**



In a flame-dried two-neck flask, crude β,γ -unsaturated carboxylic acid **S11** was dissolved in anhydrous DCM (5.76 mL, 0.2 M). Imidazole (3.46 mmol, 235 mg) and TMS-Cl (3.46 mmol, 439 μ L) were added, and the mixture was stirred for 30 min. Water was then added, and the solution was extracted with EtOAc/hexane (1:1). The combined organic layers were washed with saturated aqueous citric acid and brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by column chromatography (hexane/TBME, 10–70%) to give the silyl-protected carboxylic acid **S12** as a yellow oil in 76% yield (871 μ mol, 318 mg, two steps).

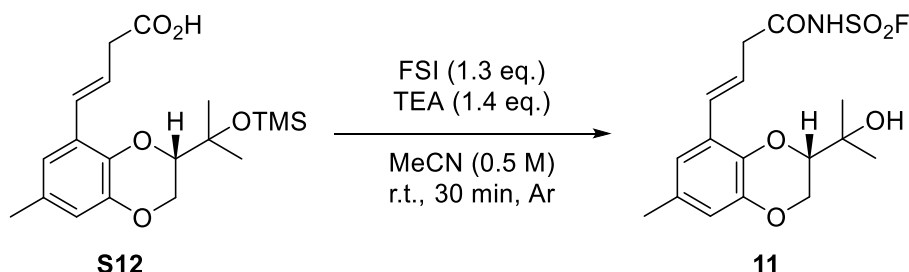
¹H NMR (399 MHz, CDCl₃) δ 6.82 (s, 1H), 6.70 (d, J = 16.0 Hz, 1H), 6.61 (s, 1H), 6.35 (dt, J = 15.9, 7.2 Hz, 1H), 4.43 (dd, J = 11.0, 1.8 Hz, 1H), 3.94 (dd, J = 11.0, 8.7 Hz, 1H), 3.82 (dd, J = 9.1, 1.8 Hz, 1H), 3.31 (d, J = 6.4 Hz, 2H), 2.23 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H), 0.15 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 177.8, 143.3, 139.2, 130.1, 128.3, 125.2, 121.8, 119.7, 116.8, 79.4, 74.0, 64.9, 38.7, 28.4, 24.8, 20.8, 2.6.

$[\alpha]_{\text{D}}^{20}$ = +40.4 (c = 1.0, CHCl₃).

HRMS (ESI) exact mass calculated for C₁₉H₂₈O₅SiNa: m/z 387.1598 ([M+Na]⁺), found: m/z 387.1602 ([M+Na]⁺).

(*S,E*)-(4-(3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)but-3-enoyl)sulfamoyl fluoride (11**)**



In a flame-dried, two-neck flask, silyl-protected β,γ -unsaturated carboxylic acid **S12** (835 μ mol, 305 mg) was dissolved in CH₃CN (1.67 mL, 0.5 M). Triethylamine (1.17 mmol, 163 μ L) and FSI (1.09 mmol, 83.3 μ L) were added at room temperature, and the mixture was stirred for 30 min. TFA (3.34 mmol, 257 μ L) and water were then added, and stirring continued for 10 min. The organic layer was extracted with DCM, concentrated, and the residue was washed with 1 M HCl and extracted with TBME. The combined organic layers were washed with brine, dried

over Na₂SO₄, and concentrated under reduced pressure to afford N-(fluorosulfonyl)amide **11** as an orange amorphous solid in 80% yield (666 μmol, 249 mg) without further purification.

¹H NMR (399 MHz, CDCl₃) δ 6.81 (s, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.60 (s, 1H), 6.33 (dt, *J* = 16.0, 7.3 Hz, 1H), 4.43 (dd, *J* = 11.0, 1.8 Hz, 1H), 3.96-3.91 (m, 1H), 3.81 (dd, *J* = 9.1, 1.8 Hz, 1H), 3.30 (d, *J* = 7.3 Hz, 2H), 2.23 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 0.14 (s, 9H).

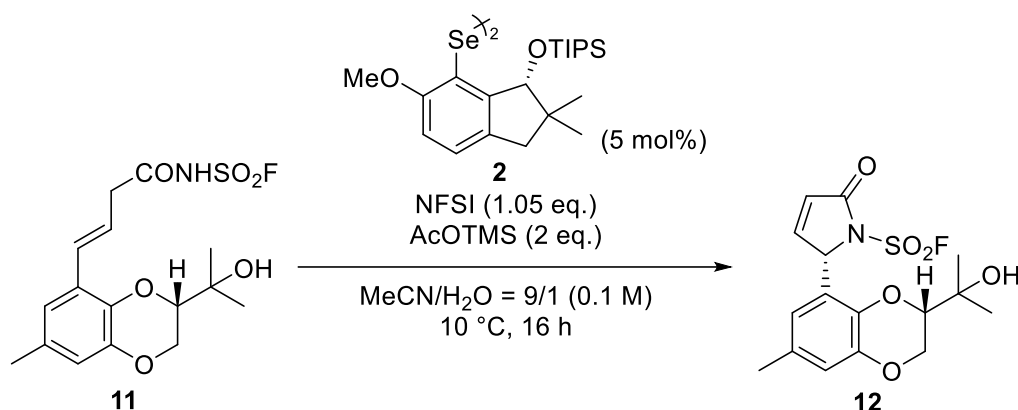
¹³C NMR (100 MHz, CDCl₃) δ 168.9, 143.1, 138.9, 130.9, 130.4, 124.7, 120.4, 120.3, 117.4, 79.1, 71.6, 64.7, 40.9, 26.5, 24.9, 20.8.

¹⁹F NMR (376 MHz, CDCl₃) δ 52.6 (s, 1F).

[α]_D²⁰ = +32.0 (*c* = 1.0, CHCl₃).

HRMS (ESI) exact mass calculated for C₁₆H₁₉O₆SFN: *m/z* 372.0923 ([M-H]⁻), found: *m/z* 372.0923 ([M-H]⁻).

(S)-2-((S)-3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (12)



Prepared according to the general procedure E with **11** (400 μmol, 149 mg) for 16 h. The crude material was purified by column chromatography (1st: hexane/TBME, 30–100%; 2nd: DCM/acetone, 5%) to give the lactamization product **12** as a pale pink amorphous solid in 71% yield (284 μmol, 105 mg, 84:16 dr).

¹H NMR (399 MHz, CDCl₃) δ 7.31 (dd, *J* = 5.9, 2.3 Hz, 1H), 6.74 (d, *J* = 0.9 Hz, 1H), 6.48 (s, 1H), 6.29 (dd, *J* = 5.9, 1.8 Hz, 1H), 6.14 (t, *J* = 2.3 Hz, 1H), 4.46-4.38 (m, 1H), 4.01 (dd, *J* = 19.4, 8.9 Hz, 2H), 2.23 (s, 3H), 1.36 (s, 3H), 1.30 (s, 3H).

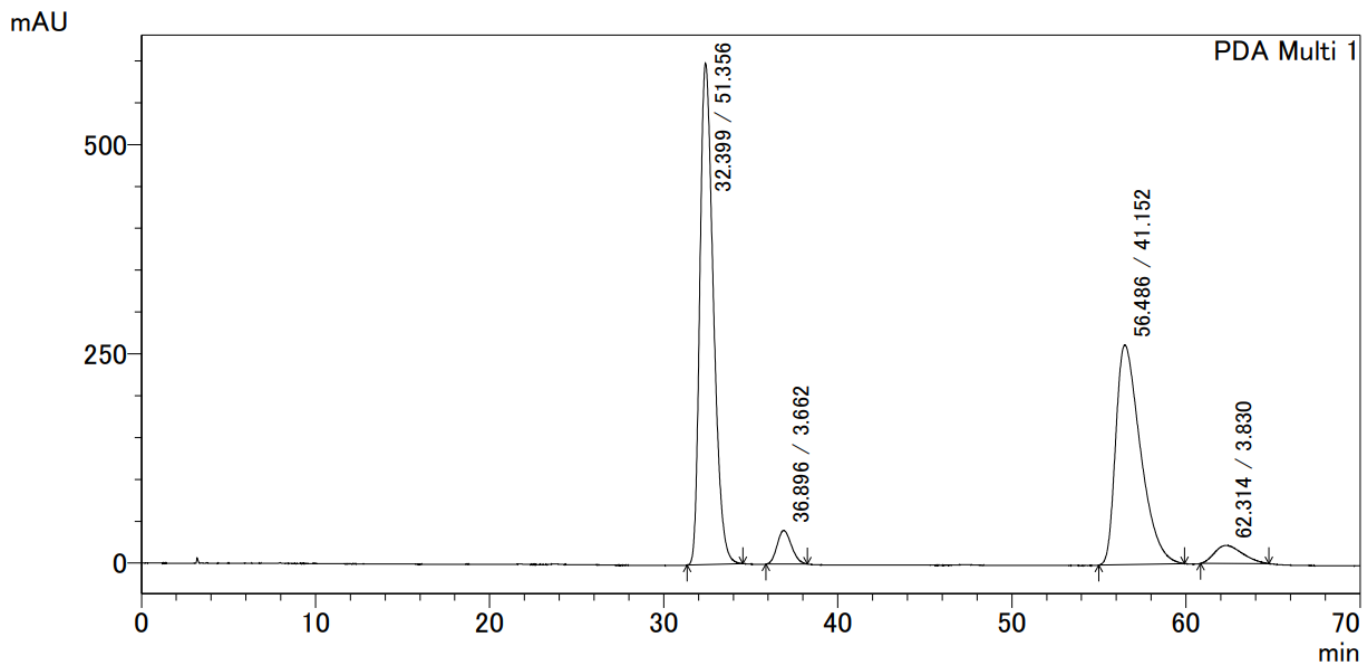
¹³C NMR (100 MHz, CDCl₃) δ 167.2, 152.6, 143.6, 139.8, 131.4, 123.7, 120.3, 119.2, 119.0, 79.7, 70.8, 64.6, 63.0, 26.4, 25.3, 20.8.

¹⁹F NMR (376 MHz, CDCl₃) δ 54.8 (s, 1F).

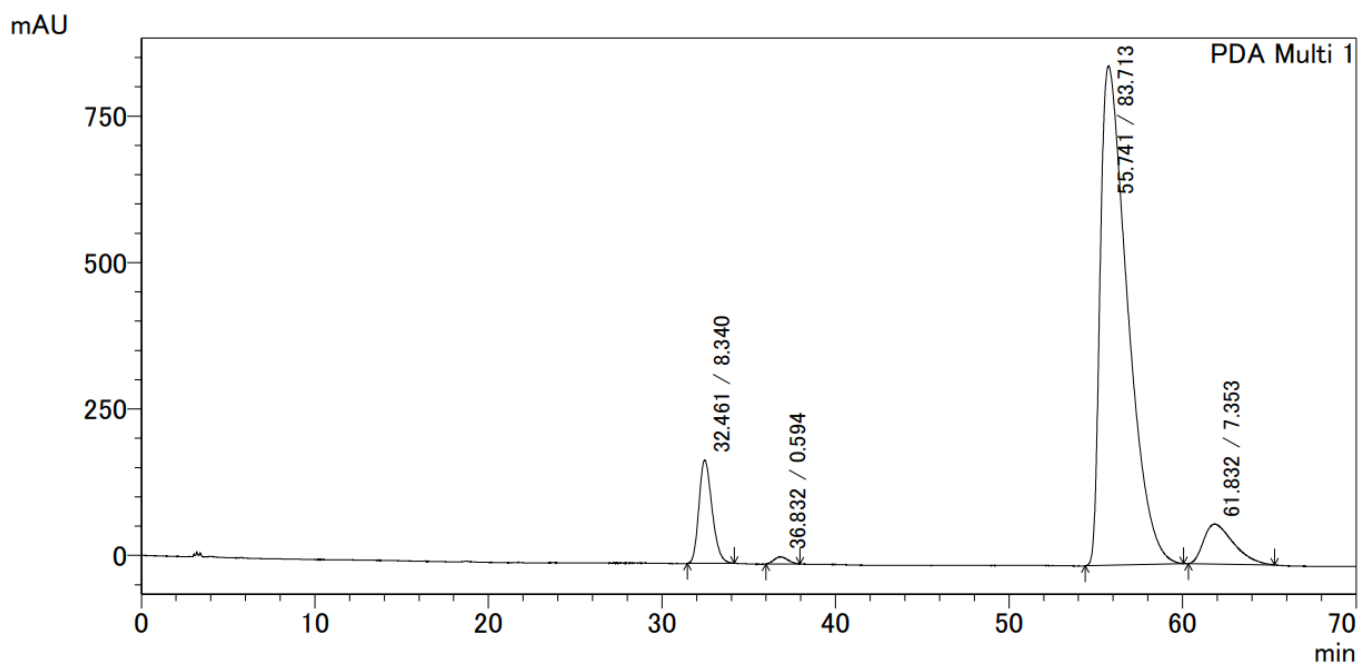
[α]_D²⁰ = -102.4 (*c* = 1.0, CHCl₃).

HRMS (ESI) exact mass calculated for C₁₆H₁₈O₆SFNNa: *m/z* 394.0731 ([M+Na]⁺), found: *m/z* 394.0732 ([M+Na]⁺).

HPLC Daicel CHIRALCEL IC-3, hexane/ⁱPrOH = 10/1, flow rate = 1.0 mL/min, retention time; 32.5 min (major enantiomer of minor diastereomer) 36.8 min (minor enantiomer of major diastereomer), 55.7 min (major enantiomer of major diastereomer) and 61.8 min (minor enantiomer of minor diastereomer).

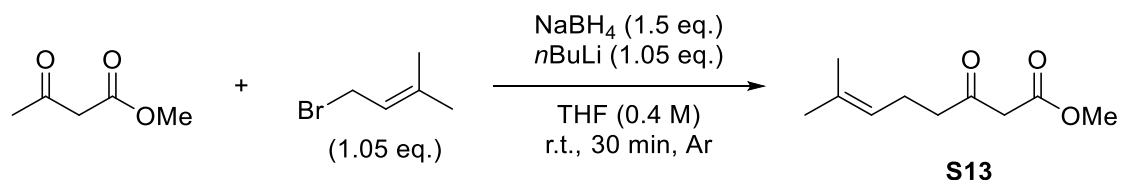


1 PDA Multi 1/207nm,4nm



1 PDA Multi 1/207nm,4nm

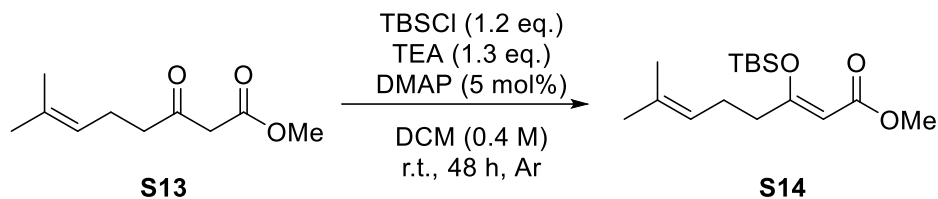
methyl 7-methyl-3-oxooct-6-enoate (S13)



To a stirred suspension of NaBH₄ (571 mg, 14.3 mmol) in THF (25 mL) under argon at 0 °C, methyl 3-oxobutanoate (1.02 mL, 9.5 mmol) was added. After stirring for 10 min, *n*BuLi (2.3 M in cyclohexane, 4.34 mL, 9.98 mmol) was added at 0 °C, and the mixture was stirred for 10 min. 1-Bromo-3-methylbut-2-ene was then added to the mixture at 0 °C. After stirring an additional 10 min, the reaction was quenched with 1 M HCl, extracted with EtOAc, dried over Na₂SO₄, and concentrated. The crude material was purified by column chromatography (hexane/EtOAc, 8–

66%) to give the title compound **S13** as an orange liquid in >99% yield (9.5 mmol, 1.75 g). The spectral data matched those reported in the literature.^[7]

methyl (Z)-3-((tert-butyldimethylsilyl)oxy)-7-methylocta-2,6-dienoate (S14**)**



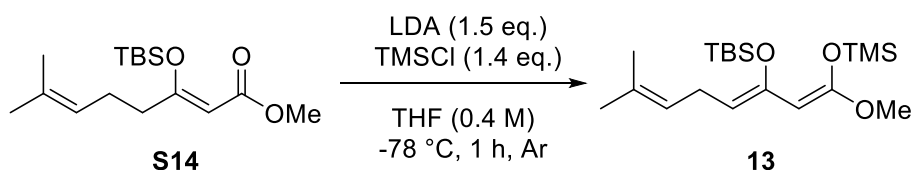
In a flame-dried, two-necked flask, triethylamine (11.0 mmol, 1.53 mL), DMAP (42.0 mg, 344 μ mol), and TBSCl (1.56 g, 10.3 mmol) were added to β -keto ester **S13** (1.27 g, 6.88 mmol) in DCM at 0 °C. The mixture was stirred for 48 h, then quenched with 1 M HCl aq. and extracted with DCM. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified by column chromatography (hexane/DCM, 8–66%) to afford silyl enol ether **S14** as a colorless oil in 85% yield (9.36 mmol, 1.75 g).

¹H NMR (399 MHz, CDCl₃) δ 5.15 (tt, J = 7.2, 1.3 Hz, 1H), 5.07 (s, 1H), 3.66 (s, 3H), 2.73 (dd, J = 8.5, 7.1 Hz, 2H), 2.23 (q, J = 7.6 Hz, 2H), 1.67 (s, 3H), 1.61 (s, 3H), 0.95 (s, 9H), 0.23 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 173.5, 168.1, 132.2, 123.4, 98.5, 50.7, 33.6, 25.8, 25.8, 25.5, 18.1, 17.7, -4.67.

HRMS (ESI) exact mass calculated for C₁₆H₃₀O₃NaSi: m/z 321.1857 ([M+Na]⁺), found: m/z 321.1856 ([M+Na]⁺).

(4Z,6Z)-4-methoxy-2,2,8,8,9,9-hexamethyl-6-(4-methylpent-3-en-1-ylidene)-3,7-dioxa-2,8-disiladec-4-ene (13**)**



To a stirred solution of LDA (1.26 mmol), which was freshly prepared from diisopropylamine (1.34 mmol, 190 μ L) and *n*BuLi (1.6 M in hexane, 1.26 mmol, 788 μ L) in THF (2.1 mL) under an argon atmosphere, silyl enol ether **S14** (251 mg, 840 μ mol) was added at –78 °C. After stirring for 45 min, TMSCl (1.18 mmol, 149 μ L) was added at –78 °C. After stirring for another 15 min, the mixture was concentrated in vacuo. Hexane was added to the residue, and the mixture was filtered through a Celite pad and concentrated in vacuo. The desired product **13** was obtained as an orange oil in >99% yield (869 μ mol, 322 mg, containing a small amount of by-products) without further purification and used directly in the next reaction. The geometry of the title compound was determined to be (1Z,3Z) based on NOE analysis.

¹H NMR (399 MHz, CDCl₃) δ 5.13 (tt, J = 7.1, 1.4 Hz, 1H), 4.83 (t, J = 7.1 Hz, 1H), 3.89 (s, 1H), 3.52 (s, 3H), 2.78 (t, J = 7.3 Hz, 2H), 1.67 (s, 3H), 1.62 (s, 3H), 0.96 (s, 9H), 0.22 (s, 9H), 0.13 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 157.4, 144.4, 130.9, 124.3, 107.2, 78.1, 54.9, 26.1, 25.8, 24.8, 18.4, 17.8, 0.5, -3.8.

HRMS (ESI) exact mass calculated for C₁₉H₃₈NaO₃Si₂: m/z 393.2252 ([M+Na]⁺), found: m/z 393.2251 ([M+Na]⁺).

(3S)-3-((S)-3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-7-methoxy-4-(3-methylbut-2-en-1-yl)-2,3,3a,7a-tetrahydro-1H-isoindole-1,5(4H)-dione (15**)**

in vacuo. The crude material was purified by column chromatography (DCM/MeOH, 5%) to give the unsaturated ketone **16** as a white powder in 89% yield (99.4 μ mol, 42.3 mg).

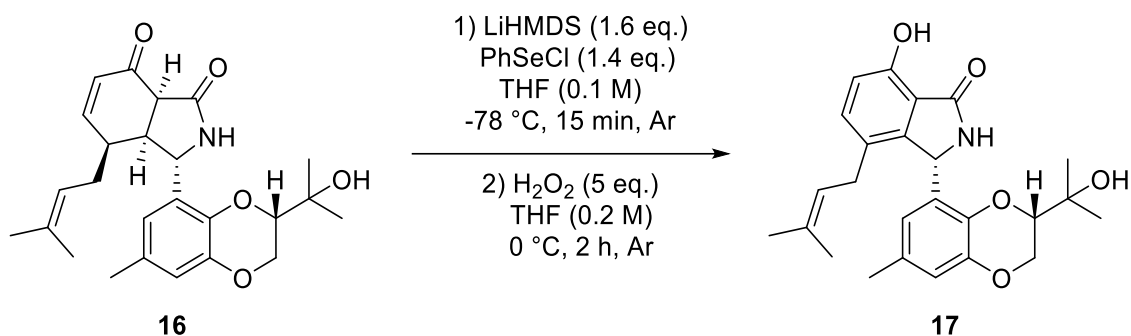
¹H NMR (399 MHz, CDCl₃) δ 6.84 (d, J = 10.5 Hz, 1H), 6.71 (d, J = 2.1 Hz, 1H), 6.64 (d, J = 1.4 Hz, 1H), 6.54 (s, 1H), 6.27 (dd, J = 10.3, 2.5 Hz, 1H), 5.01 (d, J = 7.8 Hz, 1H), 4.79 (t, J = 6.9 Hz, 1H), 4.41 (dd, J = 11.4, 1.8 Hz, 1H), 4.01 (dd, J = 11.4, 9.1 Hz, 1H), 3.86 (dd, J = 9.1, 2.3 Hz, 1H), 3.31 (td, J = 13.0, 7.2 Hz, 2H), 2.77-2.71 (m, 1H), 2.23 (s, 3H), 2.09-2.00 (m, 1H), 1.88-1.81 (m, 1H), 1.61 (s, 3H), 1.46 (s, 3H), 1.37 (s, 3H), 1.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 189.7, 171.2, 153.0, 143.2, 139.2, 134.7, 131.2, 131.0, 128.0, 121.0, 120.6, 117.6, 79.2, 70.7, 64.7, 54.1, 51.8, 45.7, 36.7, 29.8, 26.4, 25.8, 25.7, 20.9, 18.1.

$[\alpha]_{\text{D}}^{20} = -6.7$ (c = 1.0, CHCl₃)

HRMS (ESI) exact mass calculated for C₂₅H₃₁O₅NNa: m/z 448.2094 ([M+Na]⁺), found: m/z 448.2094 ([M+Na]⁺).

Diaporisoindole A (**17**)



To a stirred solution of unsaturated ketone **16** (31.0 μ mol, 13.2 mg) in THF (310 μ L) under argon atmosphere, LiHMDS (1 M in THF, 49.6 μ mol, 49.6 μ L) was added at 0 °C. The solution was then cooled to -78 °C, and PhSeCl (43.4 μ mol, 8.3 mg) in THF was added rapidly. The resulting solution was quenched with 0.1 M HCl and extracted with TBME. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was dissolved in THF (310 μ L), and 30% H₂O₂ was added at 0 °C. After 2 h, the solution was quenched with 0.1 M HCl and extracted with TBME. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by flash column chromatography (hexane/acetone, 30–100%) to give diaporisoindole A **17** as a pale pink amorphous solid in 66% yield (21 μ mol, 8.7 mg).^[8]

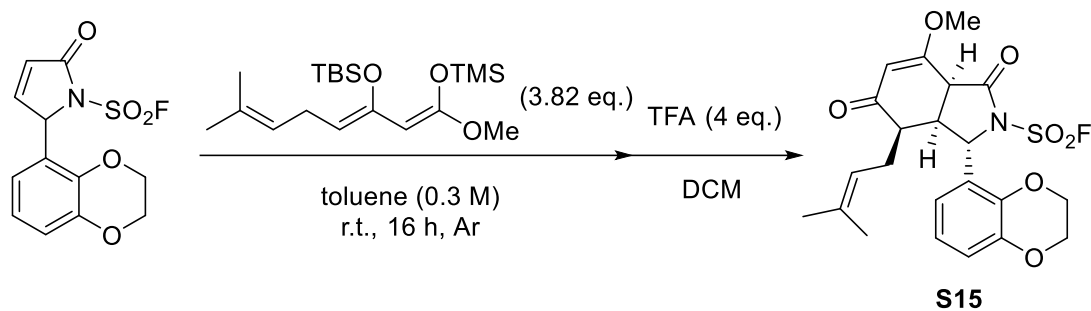
¹H NMR (399 MHz, CDCl₃) δ 8.61 (s, 1H), 7.27 (d, J = 7.8 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.65 (d, J = 1.8 Hz, 1H), 6.08 (s, 1H), 5.84 (s, 1H), 5.05 (d, J = 14.2 Hz, 1H), 4.43 (s, 1H), 4.13-4.09 (m, 1H), 3.95 (d, J = 7.8 Hz, 1H), 3.10 (q, J = 7.9 Hz, 1H), 2.96 (dd, J = 15.8, 6.2 Hz, 1H), 2.09 (s, 3H), 1.65 (s, 3H), 1.48 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 172.5, 153.9, 144.1, 143.0, 140.0, 134.8, 133.1, 130.8, 128.6, 124.6, 121.7, 120.2, 117.8, 117.4, 117.1, 79.1, 70.8, 64.7, 55.0, 30.7, 27.3, 25.8, 24.6, 20.8, 17.5.

$[\alpha]_{\text{D}}^{25} = +58.0$ (c = 0.05, MeOH). ($[\alpha]_{\text{D}}^{25} = +29.4$ (c = 0.05, MeOH) in the reported literature.^[8])

HRMS (ESI) exact mass calculated for C₂₅H₂₉O₅NNa: m/z 446.1938 ([M+Na]⁺), found: m/z 446.1938 ([M+Na]⁺).

Model Diels-Alder reaction (S15)



In a flame-dried Schlenk tube, (*rac*)-2-(2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (300 μ mol, 89.8 mg) and diene **13** (1.15 mmol, 424.8 mg) were dissolved in dry toluene (775 μ L). The solution was freeze-degassed at -78 $^{\circ}$ C, then allowed to warm to room temperature and stirred for 14 h. The resulting solution was concentrated in vacuo. The residue was dissolved in DCM (1 mL). TFA (1.2 mmol, 92.4 μ L) was added to the resulting solution. After stirring for 30 minutes, the solution was concentrated in vacuo. The crude material was purified by column chromatography (hexane/acetone, 30–100%) to give the unsaturated ketone **S15** as amorphous solid in >99% yield (305 μ mol, 142 mg, **S15:unidentified isomer** = 86:14). The minor regioisomer was removed by recycling preparative HPLC (COSMOSIL (R) 5SL- II, 20×250 mm, hexane/EtOAc = 2:3, flow 10.0 mL/min) to afford the single isomer **S15**. The stereochemistry of the title compound was determined to be endo isomer based on X-ray crystallographic analysis.

^1H NMR (399 MHz, CDCl_3) δ 6.86–6.98 (m, 2H), 6.78 (dd, J = 7.1, 2.1 Hz, 1H), 5.54 (s, 1H), 5.39 (d, J = 3.2 Hz, 1H), 5.04 (t, J = 6.9 Hz, 1H), 4.19–4.38 (m, 4H), 3.80 (s, 3H), 3.71 (d, J = 6.9 Hz, 1H), 2.95 (ddd, (dd, J = 8.7, 6.9 Hz, 3.2 Hz, 1H), 2.48–2.66 (m, 2H), 2.42–2.38 (m, 1H), 1.67 (s, 3H), 1.65 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 196.5, 167.6, 167.0, 144.3, 140.8, 134.6, 124.4, 121.6, 120.8, 118.6, 118.6, 104.1, 64.6, 64.2, 63.3, 56.9, 45.9, 44.8, 43.6, 27.1, 25.9, 18.2.

^{19}F NMR (376 MHz, CDCl_3) δ 54.5 (s, 1F)

HRMS (ESI) exact mass calculated for $\text{C}_{22}\text{H}_{24}\text{FNO}_7\text{SNa}^+$: m/z 488.1150 ($[\text{M}+\text{Na}]^+$), found: m/z 488.1151 ($[\text{M}+\text{Na}]^+$).

CIF File CCDC 2482630 contains supplementary crystallographic data of **S15**.

11. Computational details (Figure 1e)

All calculations were performed using Gaussian 16 (Revision C.02).^[9] Geometry optimizations and frequency calculations were carried out at the M06-2X/def2-TZVPP level of theory. Solvent effects (acetonitrile) were included using the SMD solvation model. Frequency calculations confirmed that all optimized structures are minima (no imaginary frequencies). Gibbs free energies were obtained by adding thermal free energy corrections (computed in solution at 298.15 K and 1 atm) to the electronic energies. All reported energies in the energy diagrams refer to these corrected Gibbs free energies.

Condensed Fukui functions were calculated using Multiwfn (version 3.8)^[10] based on the electron density results from Gaussian.

Solvent accessible surface areas were calculated using MORFEUS, Version v0.7.2. downloaded from <https://github.com/digital-chemistry-laboratory/morfeus>.

Calculation of the pK_a values

The free energy change for the proton transfer reaction between the target acid (HA) and the reference molecule (HB) was calculated as:

$$\Delta G = (G_{A^-} + G_{HB}) - [G_{HA} + G_{B^-}]$$

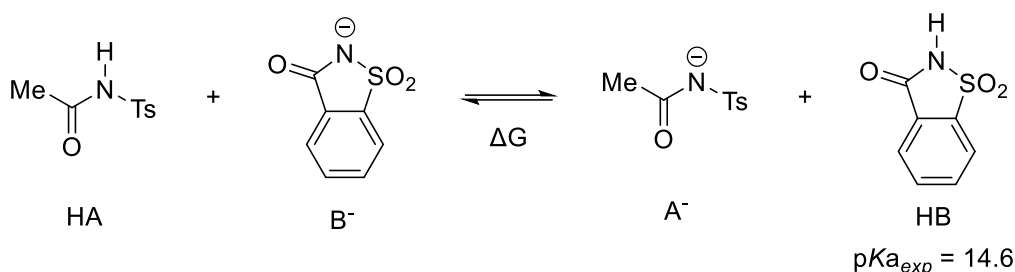
The pK_a of the target acid (HA) was then calculated by:

$$\Delta pK_a = \frac{\Delta G}{RT \ln 10}$$

$$pK_{a,HA} = pK_{a,HB} + \Delta pK_a$$

where $RT \ln 10$ equals 1.364 kcal/mol at 298.15 K.

The pK_a value of TsNHAc was calculated as follows using saccharin as the reference.



$$\Delta G = [(-948.299844 + -1027.598546) \times 627.5] - [(-1028.055877 + -947.852865) \times 627.5]$$

$$\Delta pK_a = \frac{6.496}{1.364}$$

$$pK_{a,HA} = 14.6 + 4.8$$

The pK_a value of FSO₂NHAc was determined by following the same steps as 11.2.

This method was benchmarked by calculating the pK_a value of TsNH₂ (25.6), which has a known experimental pK_a of 26.6.^[11]

EE + G _{corr} (Hartree)	-1028.055877	-1027.598546	-857.067772	-856.628274

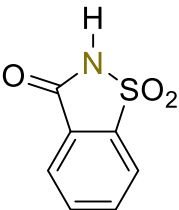
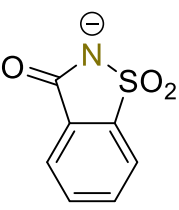
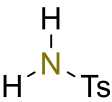
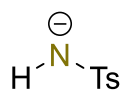
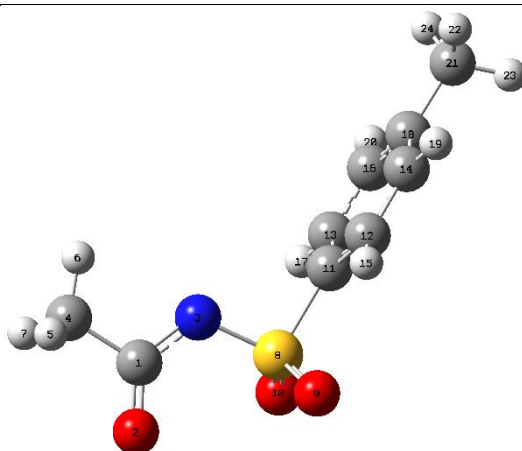
				
EE + G _{corr} (Hartree)	-948.299844	-947.852865	-836.145137	-835.67434

Table S1. Calculated Gibbs free energy.

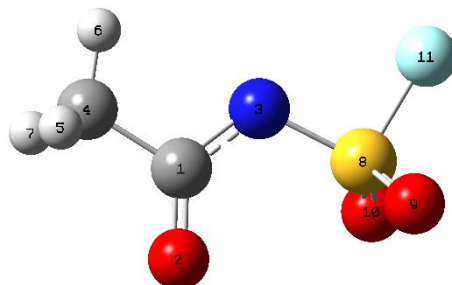
Calculation of Condensed Fukui Indices

Single-point energy calculations were performed on the optimized geometry of the neutral species and on its corresponding anionic and cationic states (i.e., with N , $N+1$, and $N-1$ electrons, respectively) at the M06-2X/def2-TZVPP level of theory with a tight SCF convergence criterion (SCF=conver=7) using the SMD solvation model (acetonitrile). The resulting wavefunction files were used as input for Multiwfn to evaluate the condensed Fukui indices.^[11]



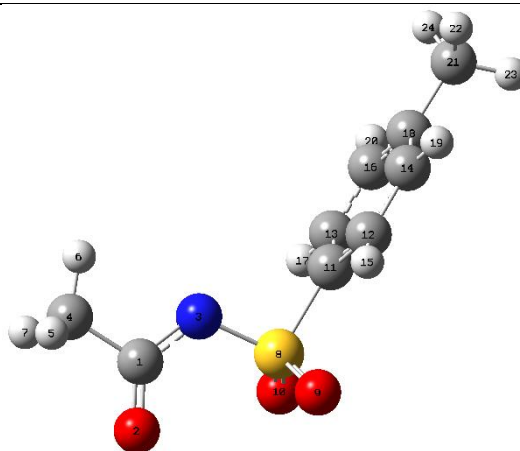
Atom	q(N)	q(N+1)	q(N-1)	f ⁻	f ⁺	f ₀	CDD
1(C)	0.1237	0.1166	0.1972	0.0735	0.0071	0.0403	-0.0663
2(O)	-0.4009	-0.4099	-0.2106	0.1903	0.009	0.0996	-0.1812
3(N)	-0.3246	-0.3329	-0.0479	0.2766	0.0083	0.1425	-0.2683
4(C)	-0.1096	-0.1127	-0.0804	0.0292	0.0031	0.0161	-0.0261
5(H)	0.0357	0.033	0.0603	0.0246	0.0027	0.0136	-0.0218
6(H)	0.0263	0.0243	0.0517	0.0255	0.002	0.0137	-0.0234
7(H)	0.0404	0.0379	0.0654	0.025	0.0025	0.0138	-0.0225
8(S)	0.4057	0.3915	0.4596	0.0539	0.0142	0.034	-0.0397
9(O)	-0.3946	-0.4101	-0.3023	0.0923	0.0155	0.0539	-0.0769
10(O)	-0.4047	-0.4202	-0.308	0.0967	0.0155	0.0561	-0.0812
11(C)	-0.0506	-0.0927	-0.0479	0.0027	0.0421	0.0224	0.0394
12(C)	-0.0476	-0.1659	-0.0337	0.0139	0.1183	0.0661	0.1044
13(C)	-0.0478	-0.1797	-0.0358	0.012	0.132	0.072	0.12
14(C)	-0.0499	-0.1778	-0.0386	0.0113	0.1279	0.0696	0.1167
15(H)	0.0427	-0.0096	0.0521	0.0095	0.0522	0.0309	0.0428
16(C)	-0.0469	-0.183	-0.0354	0.0114	0.1362	0.0738	0.1247
17(H)	0.0454	-0.0132	0.0553	0.0099	0.0585	0.0342	0.0486
18(C)	0.0063	-0.0491	0.0196	0.0133	0.0554	0.0344	0.0421

19(H)	0.0506	-0.0095	0.0577	0.0071	0.0601	0.0336	0.053
20(H)	0.0525	-0.01	0.0594	0.007	0.0625	0.0347	0.0555
21(C)	-0.0824	-0.1054	-0.0782	0.0041	0.023	0.0136	0.0189
22(H)	0.0425	0.0255	0.0454	0.0029	0.017	0.0099	0.0141
23(H)	0.0438	0.0265	0.0477	0.0038	0.0174	0.0106	0.0135
24(H)	0.0439	0.0265	0.0475	0.0036	0.0174	0.0105	0.0138



Atom	q(N)	q(N+1)	q(N-1)	f-	f+	f0	CDD
1(C)	0.1386	-0.0879	0.2127	0.0741	0.2265	0.1503	0.1524
2(O)	-0.3839	-0.5702	-0.185	0.1989	0.1863	0.1926	-0.0126
3(N)	-0.3168	-0.4157	-0.0268	0.29	0.0989	0.1945	-0.1911
4(C)	-0.1022	-0.1785	-0.0724	0.0298	0.0762	0.053	0.0464
5(H)	0.0441	-0.0358	0.0696	0.0255	0.0799	0.0527	0.0544
6(H)	0.0316	-0.0101	0.0575	0.0259	0.0417	0.0338	0.0159
7(H)	0.0441	-0.0359	0.0697	0.0255	0.08	0.0528	0.0545
8(S)	0.4611	0.3864	0.5371	0.076	0.0747	0.0754	-0.0013
9(O)	-0.3732	-0.4233	-0.2702	0.103	0.0501	0.0765	-0.0529
10(O)	-0.3732	-0.4233	-0.2702	0.103	0.0501	0.0765	-0.0529
11(F)	-0.1702	-0.2057	-0.122	0.0482	0.0355	0.0419	-0.0127

Calculation of Solvent Accessible Surface Area (SASA)



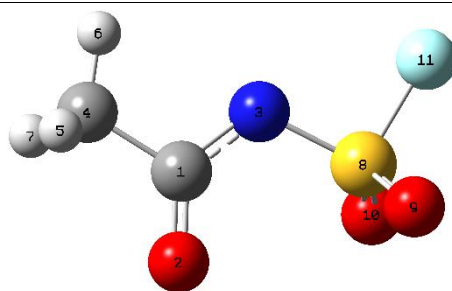
Probe radius (Å): 1.4

Solvent accessible surface area (Å²): 402.6

Volume inside solvent accessible surface (Å³): 599.6

Atom	Area (Å ²)
1(C)	6
2(O)	36.4
3(N)	8.3

4(C)	18.7
5(H)	20.9
6(H)	19.4
7(H)	21.8
8(S)	0.2
9(O)	33.9
10(O)	35.9
11(C)	2.6
12(C)	13.3
13(C)	10.8
14(C)	15
15(H)	13.5
16(C)	13.8
17(H)	14.8
18(C)	5
19(H)	17.8
20(H)	18.7
21(C)	17.1
22(H)	17.4
23(H)	20.7
24(H)	20.7



Probe radius (Å): 1.4

Solvent accessible surface area (Å²): 270.1

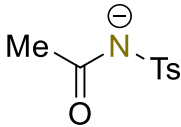
Volume inside solvent accessible surface (Å³): 364.6

Atom	Area (Å²)
1(C)	6.1
2(O)	36.7
3(N)	13.7
4(C)	18.9
5(H)	21.4
6(H)	19.2
7(H)	21.4
8(S)	0.4
9(O)	43.9
10(O)	43.8
11(F)	44.4

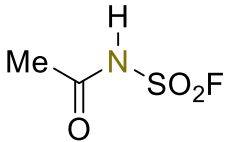
Cartesian Coordinates

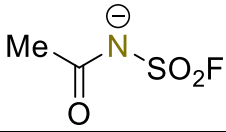
C	3.040634	0.792723	0.00035
O	3.7865	-0.15832	-0.00553
N	1.665599	0.630809	0.002081
C	3.482589	2.226529	0.004943

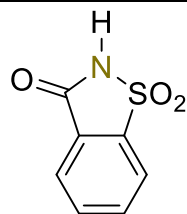
H	4.567432	2.266195	0.007583
H	3.092639	2.735216	-0.87712
H	3.088177	2.731979	0.88683
S	0.933028	-0.86801	-0.00014
O	1.241922	-1.53059	-1.23324
O	1.240168	-1.53498	1.231098
C	-0.75164	-0.37656	-0.00017
C	-1.40079	-0.17987	-1.21216
C	-1.40279	-0.18565	1.211772
C	-2.72921	0.211413	-1.20179
H	-0.87617	-0.33624	-2.14509
C	-2.73111	0.205741	1.20108
H	-0.87967	-0.34651	2.144782
C	-3.41168	0.407023	-0.00047
H	-3.24686	0.366934	-2.13986
H	-3.25028	0.356896	2.139036
C	-4.8598	0.797048	-0.00038
H	-5.11206	1.371262	-0.89062
H	-5.48774	-0.09681	0.006625
H	-5.10879	1.382319	0.883623
H	1.059663	1.442044	0.014176

			
C	3.018857	0.69858	-0.2656
O	3.816551	-0.18751	0.042265
N	1.66679	0.624475	-0.24964
C	3.550735	2.050641	-0.69857
H	4.368699	1.908015	-1.40397
H	2.781274	2.677139	-1.14223
H	3.956266	2.558323	0.178974
S	0.988728	-0.73787	0.240298
O	1.207597	-1.85305	-0.66267
O	1.216847	-1.0155	1.647378
C	-0.72955	-0.30221	0.092938
C	-1.49302	-0.82656	-0.93514
C	-1.3014	0.555341	1.027394
C	-2.83923	-0.48812	-1.03184
H	-1.03885	-1.4978	-1.65132
C	-2.64047	0.886237	0.920529

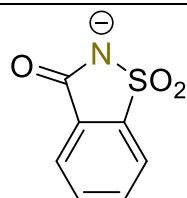
H	-0.6995	0.955873	1.833004
C	-3.43057	0.370059	-0.11112
H	-3.43698	-0.90015	-1.8357
H	-3.0874	1.553725	1.64788
C	-4.88276	0.740229	-0.20839
H	-5.3567	0.25621	-1.06063
H	-5.41788	0.446727	0.696266
H	-4.99957	1.819841	-0.3166

			
C	1.624476	-0.12796	-0.00527
O	1.548055	-1.33072	0.003128
N	0.461824	0.645661	-0.03067
H	0.49796	1.657357	0.032082
C	2.883801	0.67584	0.003036
H	2.919439	1.307673	-0.88498
H	2.897224	1.324752	0.879377
H	3.736288	0.004473	0.020395
S	-1.00112	-0.07414	0.005178
O	-1.26989	-0.77166	-1.19425
O	-1.27641	-0.66598	1.259585
F	-1.81439	1.247986	-0.04993

			
C	1.568823	-0.06756	-8.4E-05
O	1.604113	-1.29486	0.000187
N	0.447417	0.703821	-0.00017
C	2.855735	0.724611	0.000006
H	3.437826	0.44697	-0.87935
H	2.682997	1.797142	-0.00058
H	3.437111	0.447861	0.880122
S	-0.92931	-0.0545	-5E-06
O	-1.27712	-0.7138	-1.22279
O	-1.27705	-0.71336	1.223036
F	-1.86309	1.23189	-0.00021

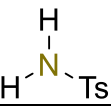


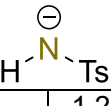
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C	-0.31626	-0.58416	0.000232
C	-1.13386	-1.69538	0.000134
C	-2.50573	-1.46325	-0.000011
C	-3.01642	-0.16759	-0.000082
C	-2.17174	0.936474	0.000022
H	-0.73282	-2.69977	0.000183
H	-3.18438	-2.30527	-0.00009
H	-4.08759	-0.01949	-0.00022
H	-2.56092	1.945482	-0.000011
C	0.26988	1.737916	0.000248
O	0.131366	2.933223	-0.000184
S	1.442161	-0.57125	-0.000043
O	1.982855	-1.08208	1.223679
O	1.982077	-1.08096	-1.224605
N	1.491081	1.089301	0.000785
H	2.374482	1.588648	-0.000214



C	-0.77776	0.700843	-0.000051
C	-0.30346	-0.59466	-0.000037
C	-1.13725	-1.69544	-0.00011
C	-2.50773	-1.45058	-0.000198
C	-3.00189	-0.1472	-0.000208
C	-2.13992	0.945222	-0.000135
H	-0.74792	-2.70507	-0.000099
H	-3.19847	-2.28342	-0.000257
H	-4.07185	0.014	-0.000274
H	-2.51719	1.959425	-0.000142
C	0.356312	1.703396	0.00004
O	0.149366	2.910888	0.000019
S	1.467732	-0.48764	0.000103
O	1.995184	-1.06337	1.218808
O	1.995398	-1.06338	-1.218504

N	1.571755	1.110687	0.000106
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C	-2.33356	-1.2397	-0.01432
C	-3.06067	-0.05372	0.042234
C	-2.40791	1.17019	0.058405
C	-1.01931	1.219676	0.017982
C	-0.30914	0.031139	-0.03695
C	-0.95013	-1.20294	-0.05384
H	-2.84642	-2.19181	-0.02721
H	-4.14168	-0.08795	0.07404
H	-2.97543	2.089831	0.101953
H	-0.49515	2.164873	0.027873
H	-0.3731	-2.11768	-0.09521
S	1.455522	0.070925	-0.11657
O	1.89954	-0.81332	-1.15991
O	1.855809	1.450783	-0.15842
N	1.898687	-0.63775	1.285995
H	2.748238	-1.18323	1.179562
H	1.94596	0.00785	2.067748

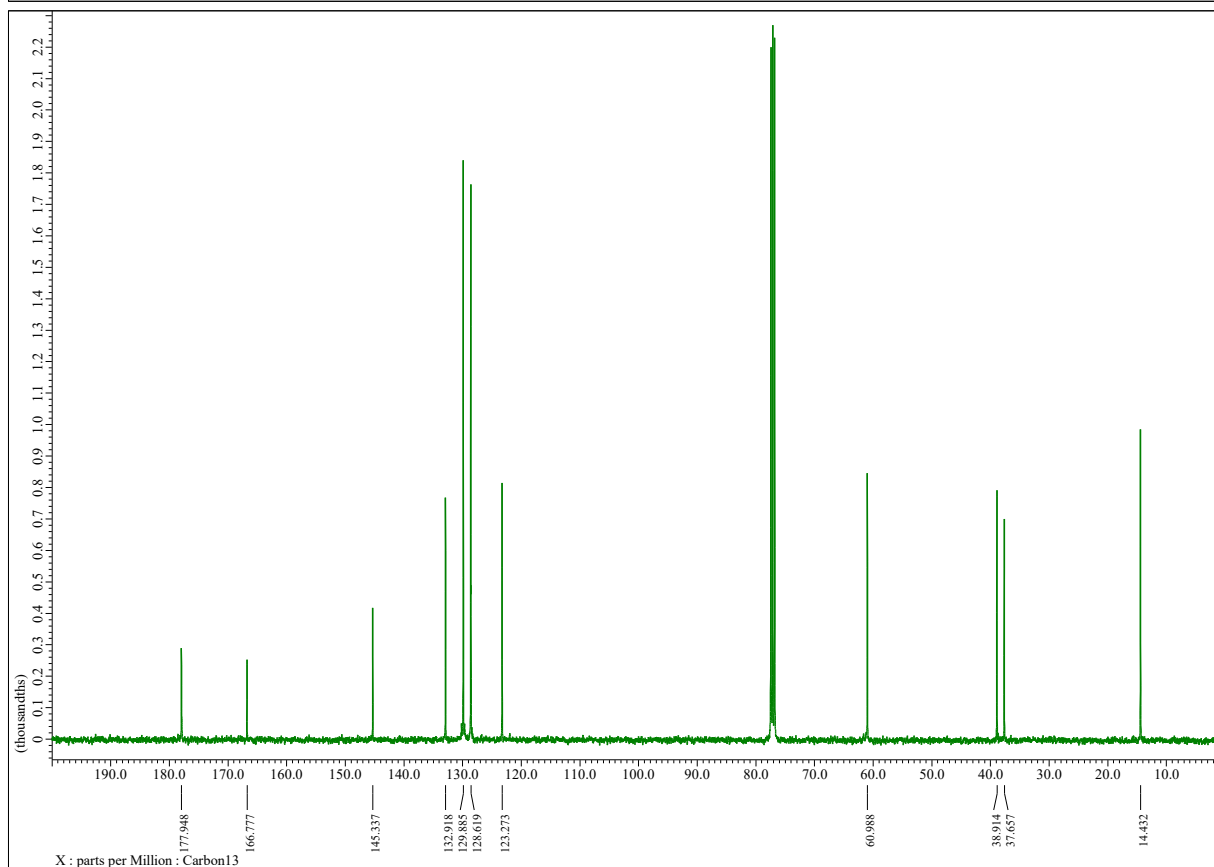
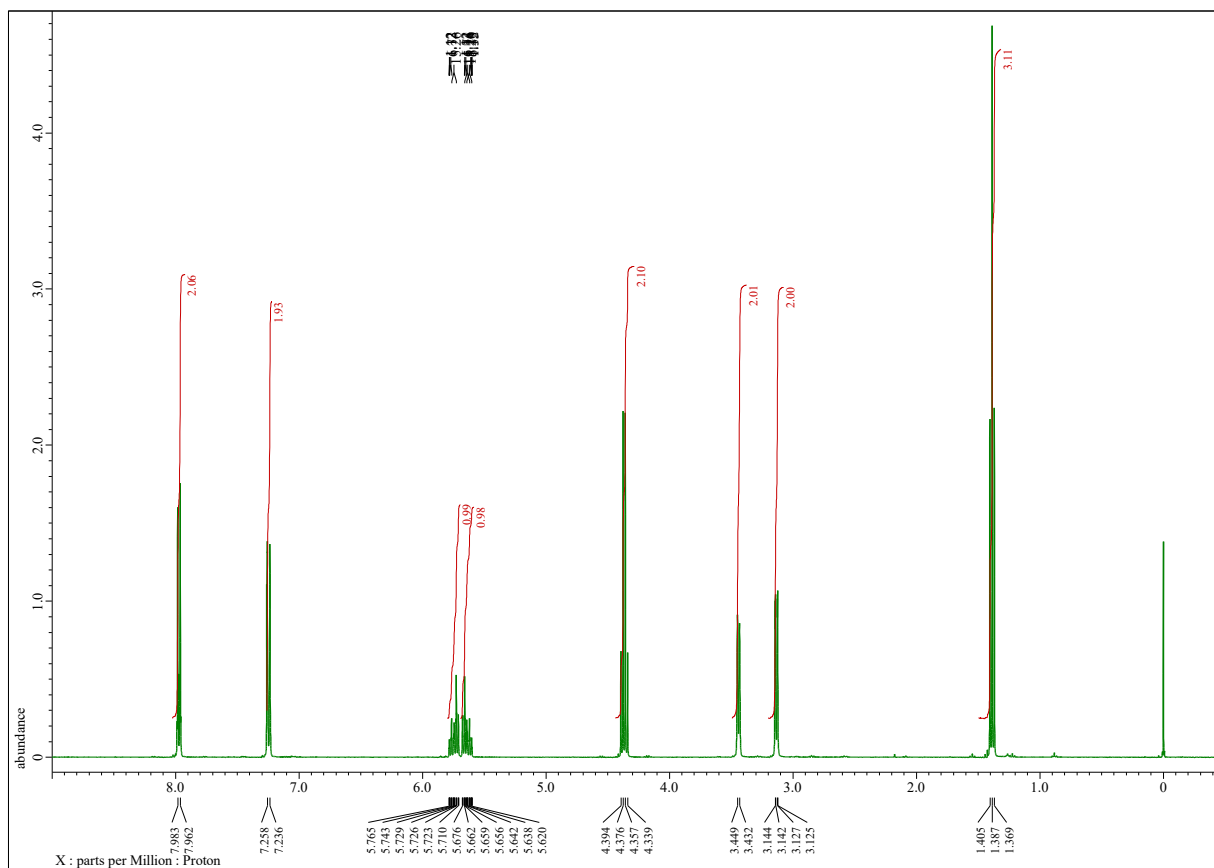
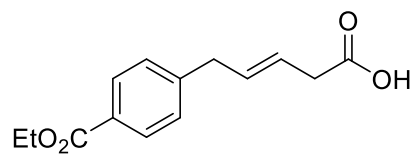
			
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C	3.050772	-0.02751	0.019393
C	2.376224	1.184687	0.024586
C	0.984297	1.21058	0.009251
C	0.272126	0.020652	-0.00756
C	0.946981	-1.19711	-0.00971
H	2.856126	-2.16806	-0.00139
H	4.132809	-0.04704	0.031604
H	2.930706	2.114191	0.04045
H	0.447655	2.149328	0.012338
H	0.383181	-2.12172	-0.01409
S	-1.5276	0.014545	-0.02879
O	-1.88616	1.426611	0.068645
O	-1.86635	-0.61955	-1.29584
N	-2.02305	-0.87089	1.14039
H	-1.90711	-0.34415	2.003608

12. References

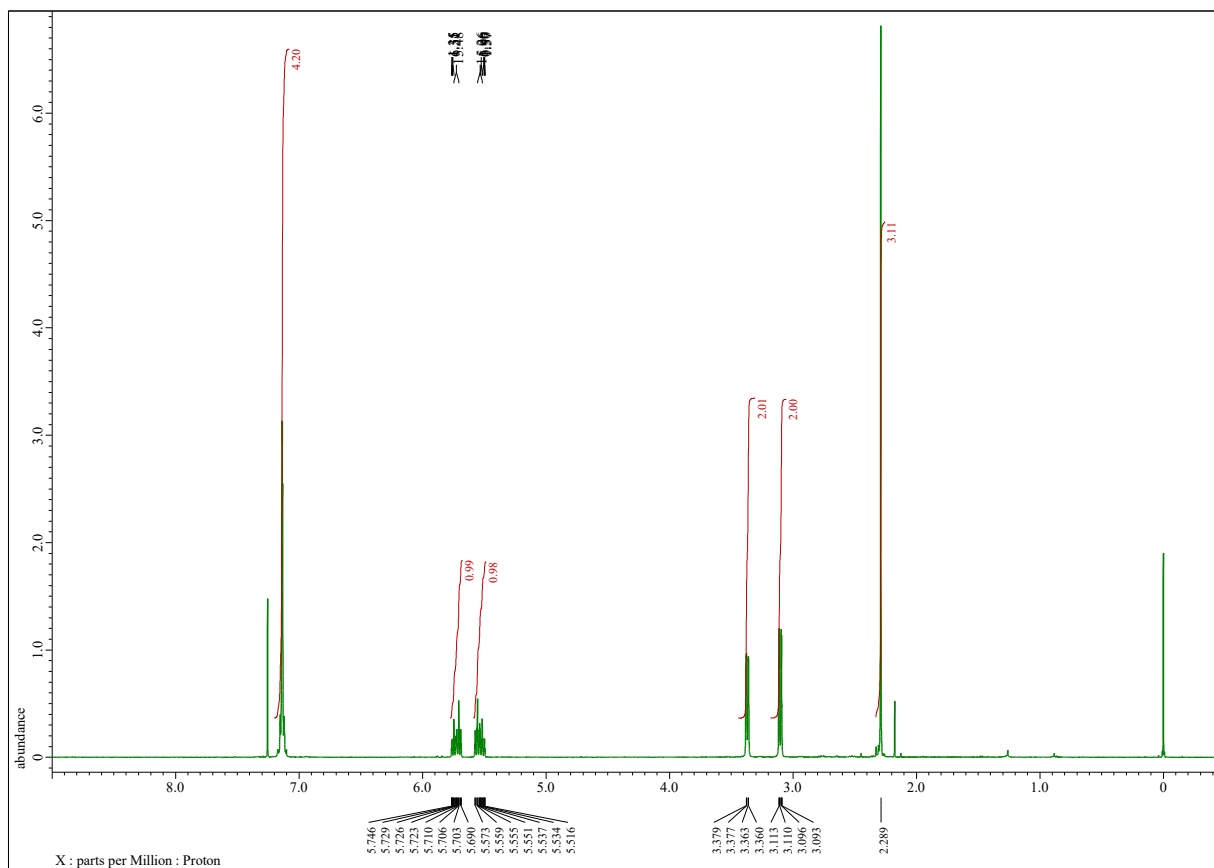
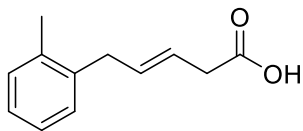
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13. Copies of NMR charts

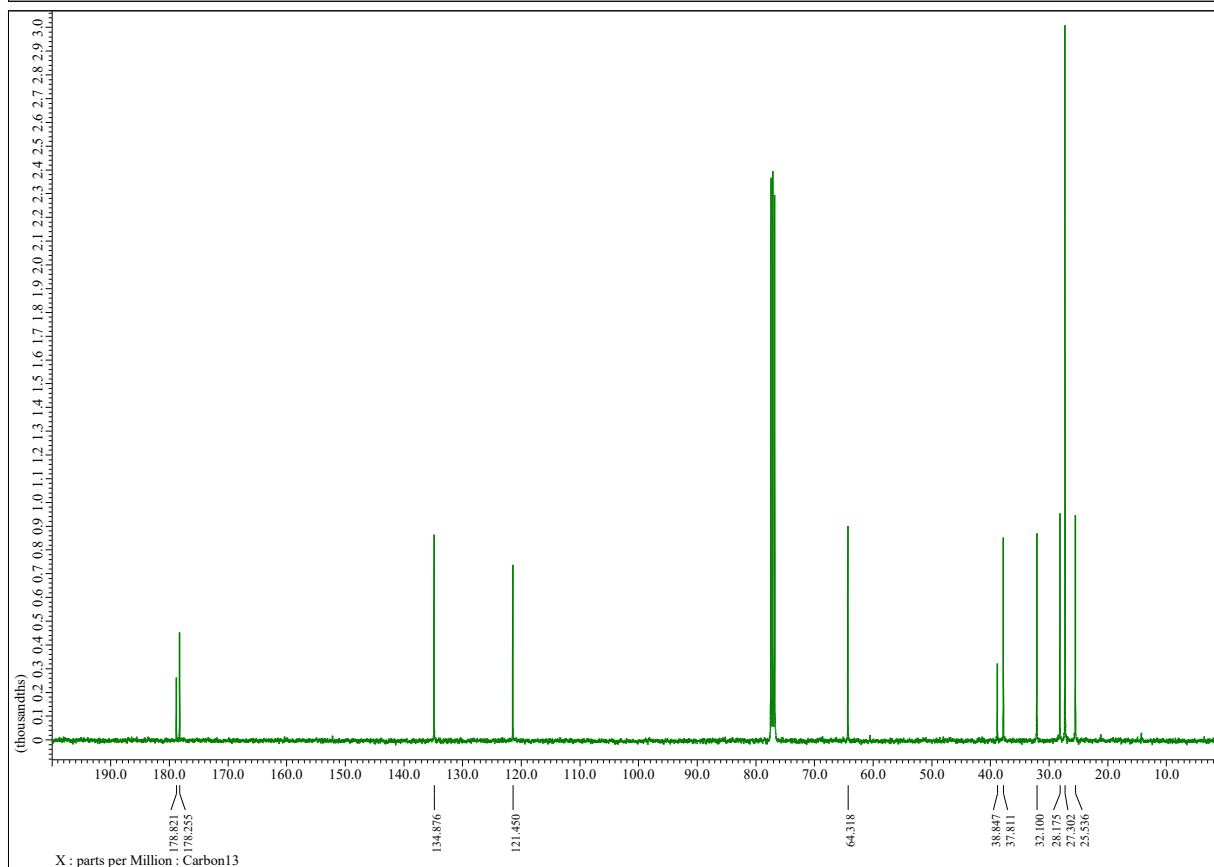
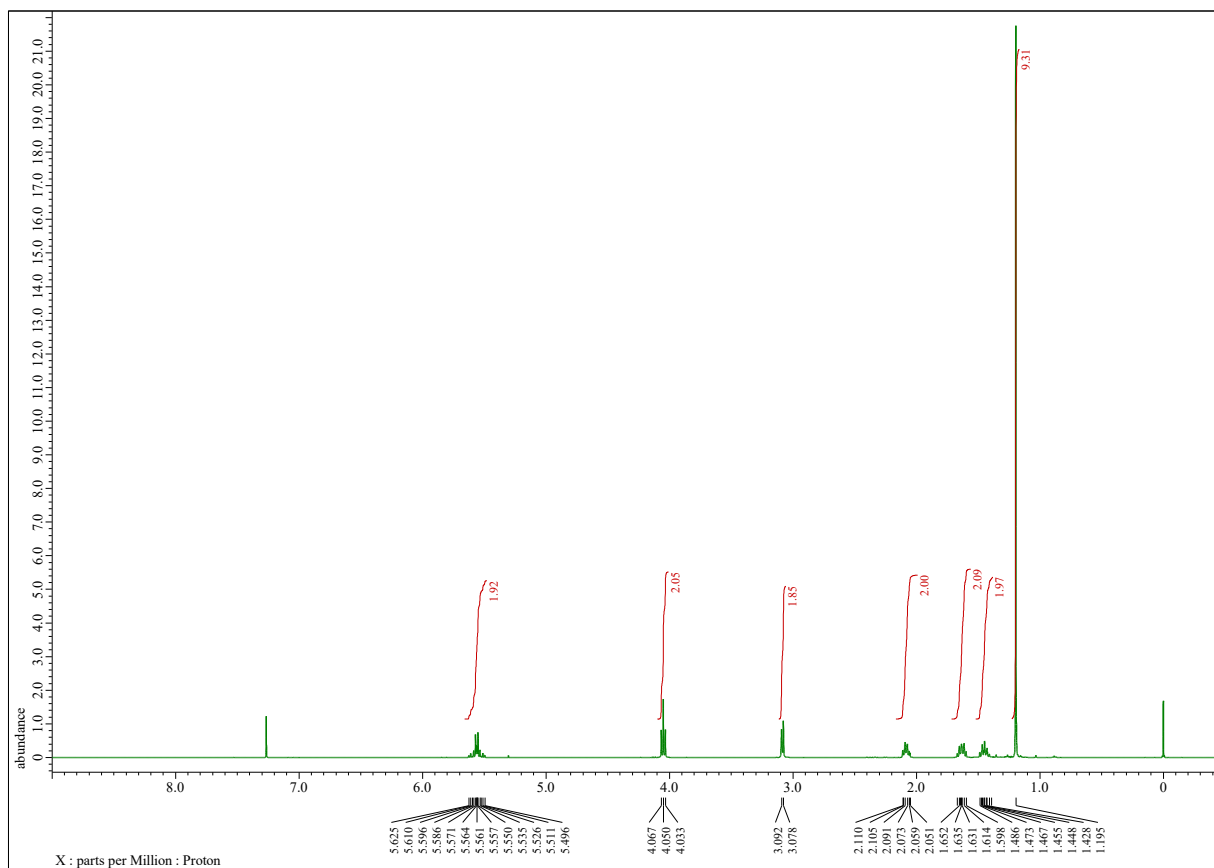
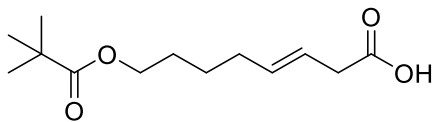
(E)-5-(4-(ethoxycarbonyl)phenyl)pent-3-enoic acid (S1)



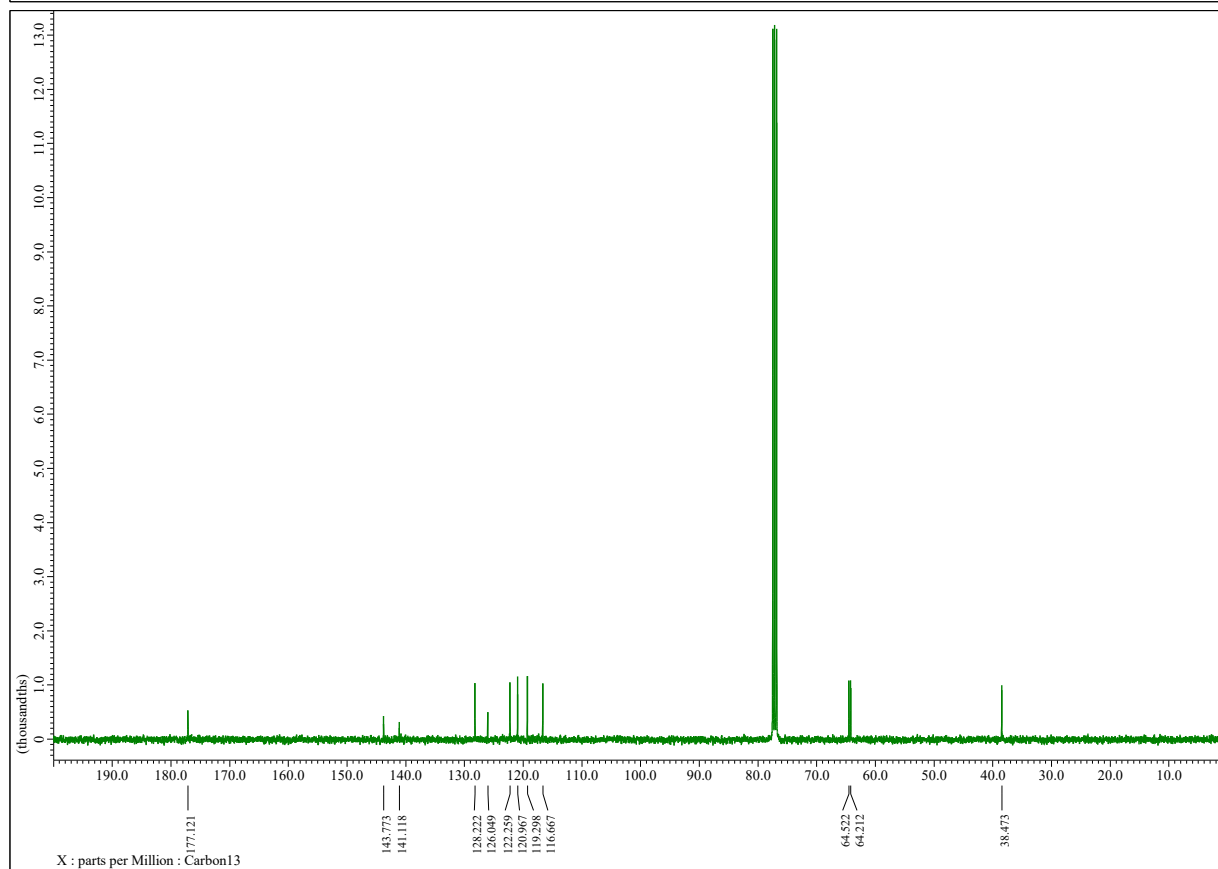
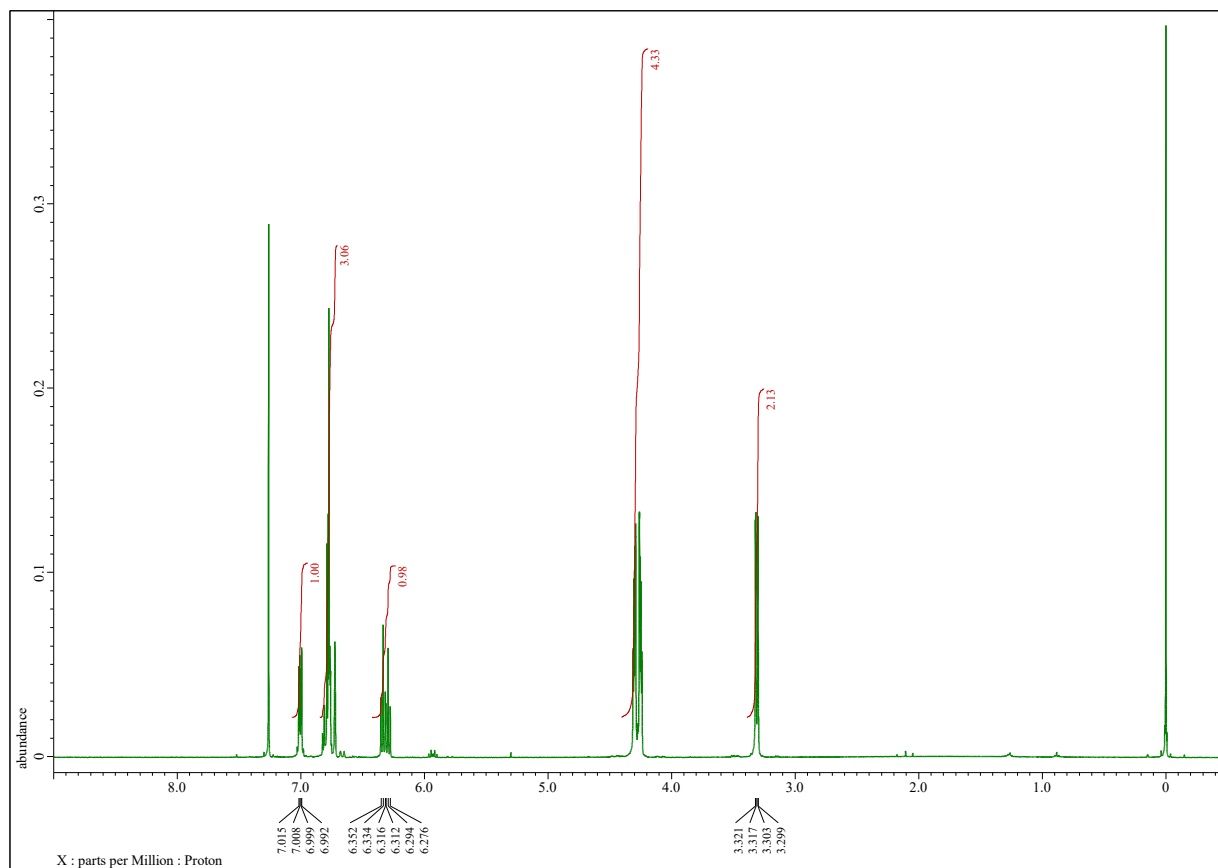
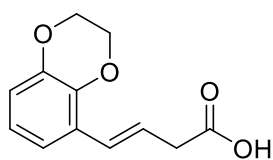
(E)-5-(o-tolyl)pent-3-enoic acid (S2)



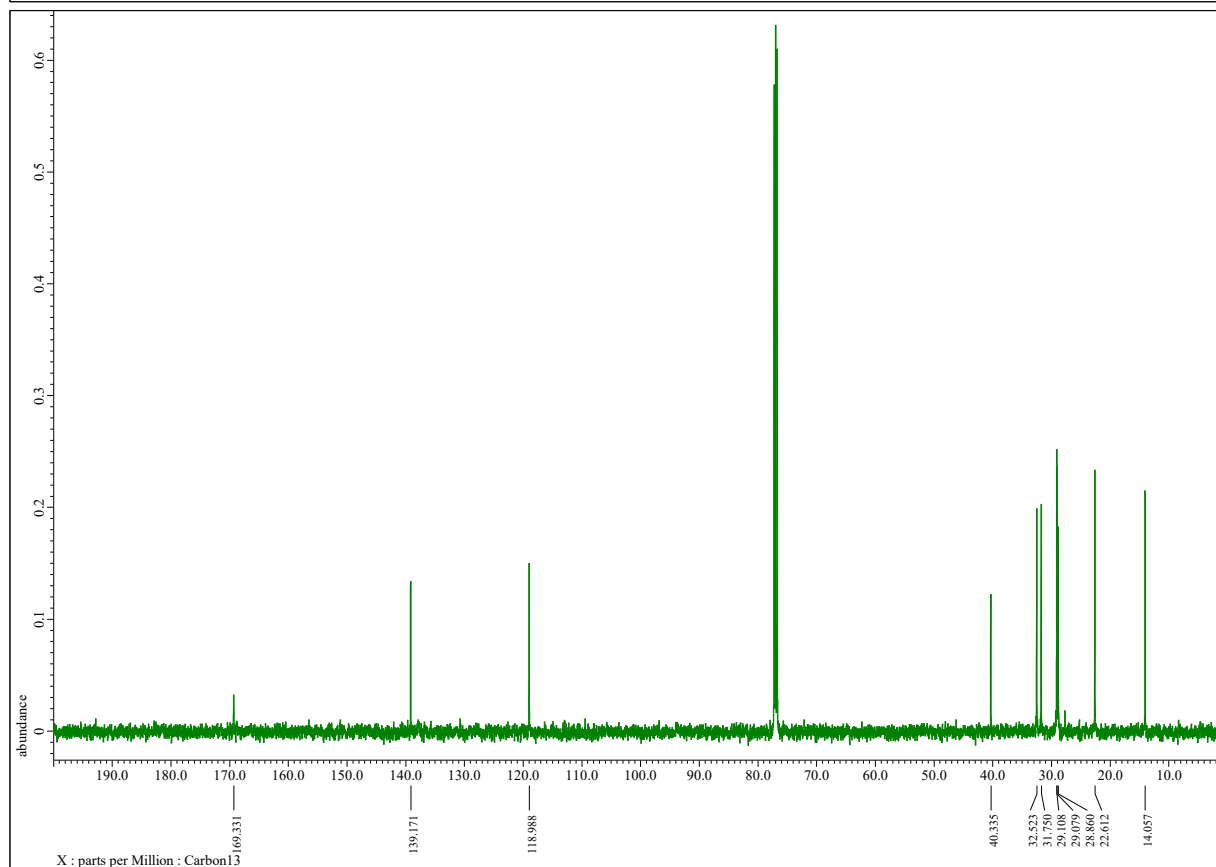
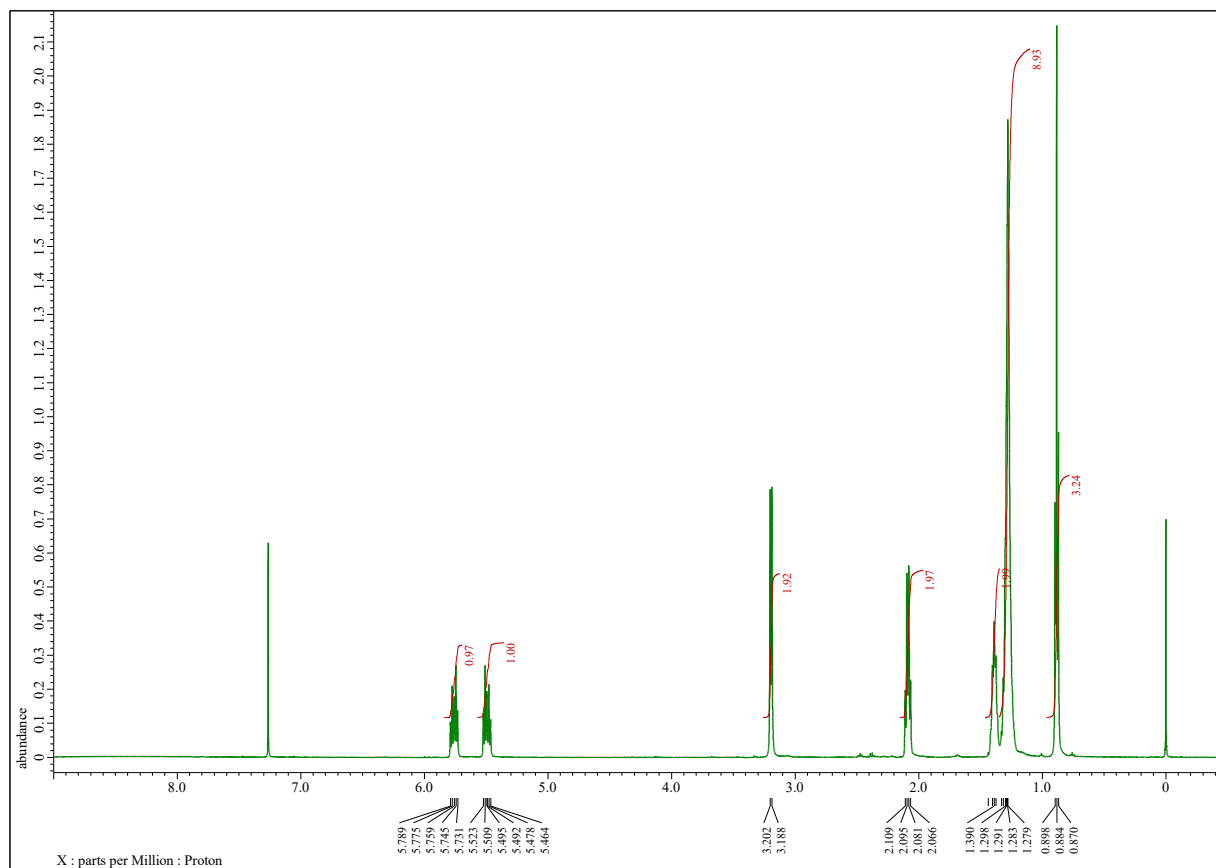
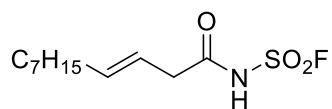
(E)-8-(pivaloyloxy)oct-3-enoic acid (S3)

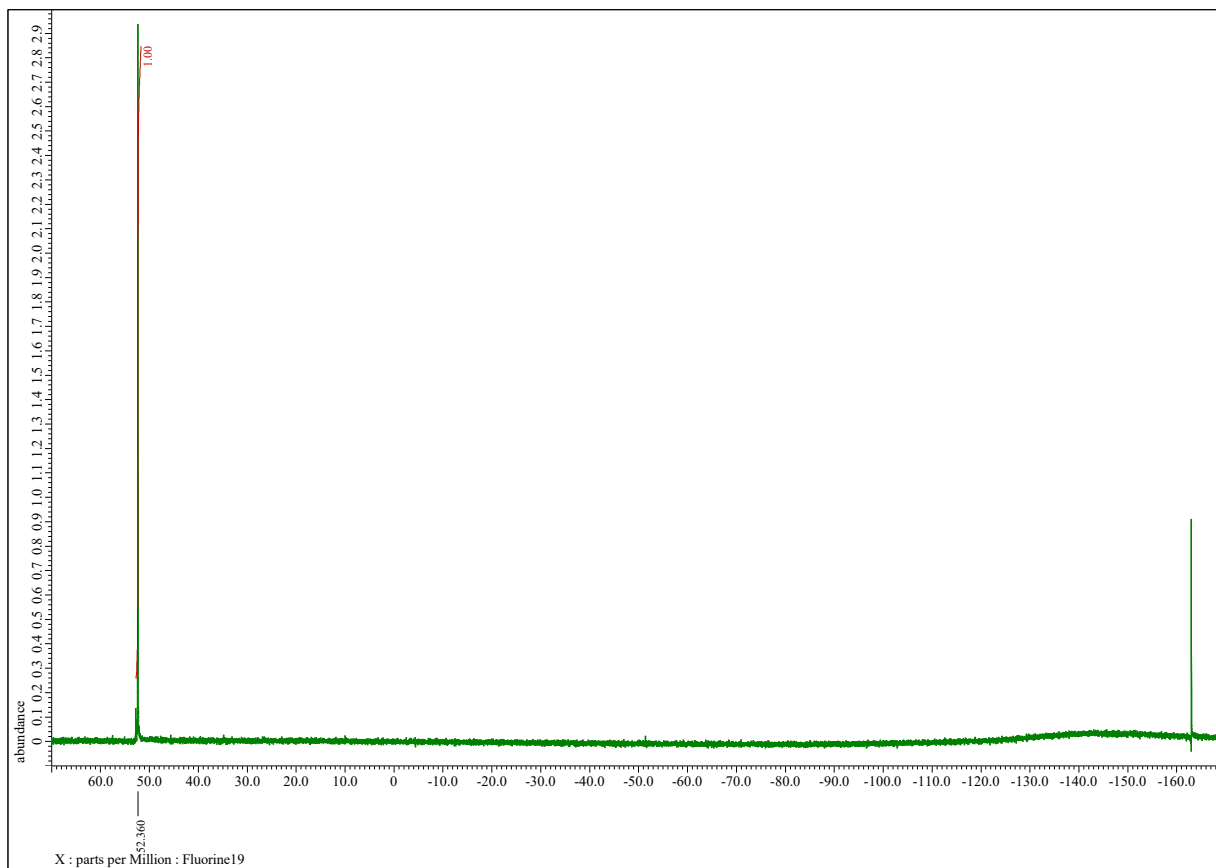


(E)-4-(2,3-dihydrobenzo[b][1,4]dioxin-5-yl)but-3-enoic acid (S4)

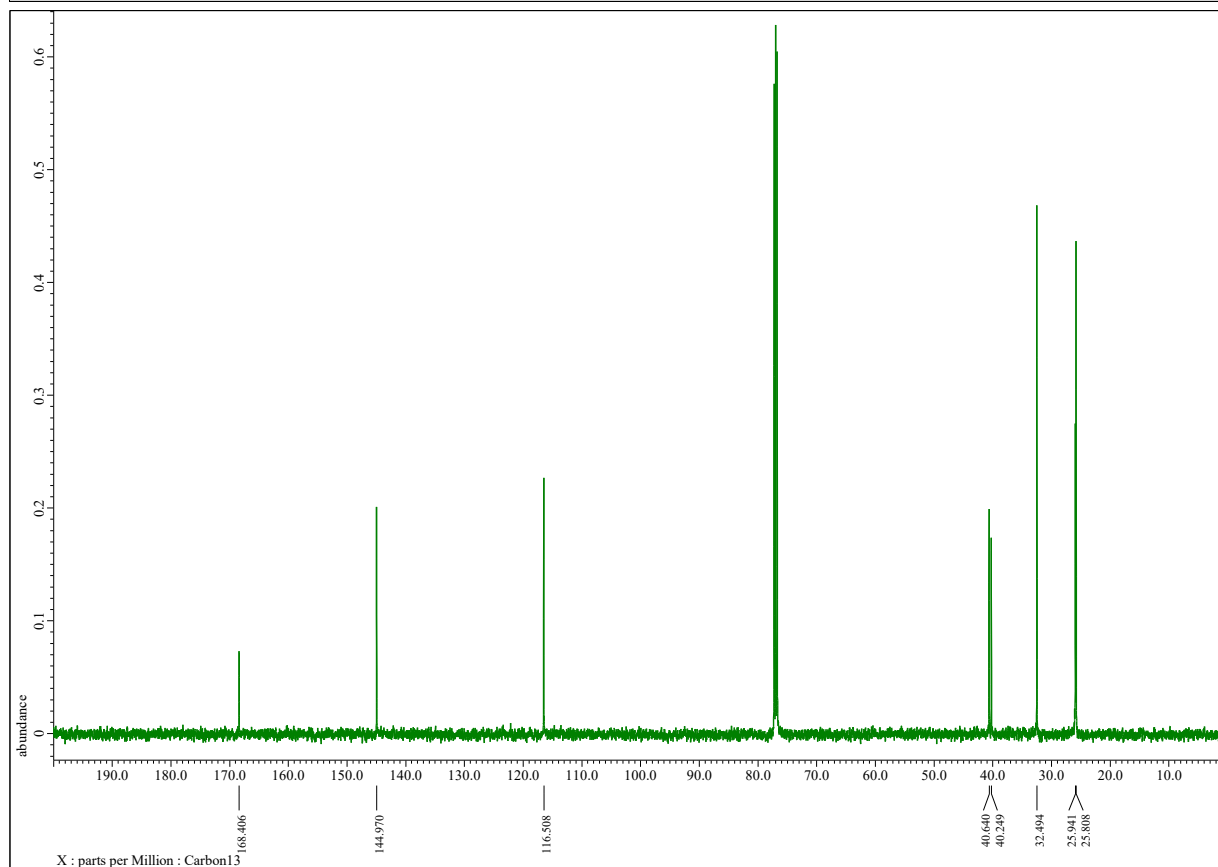
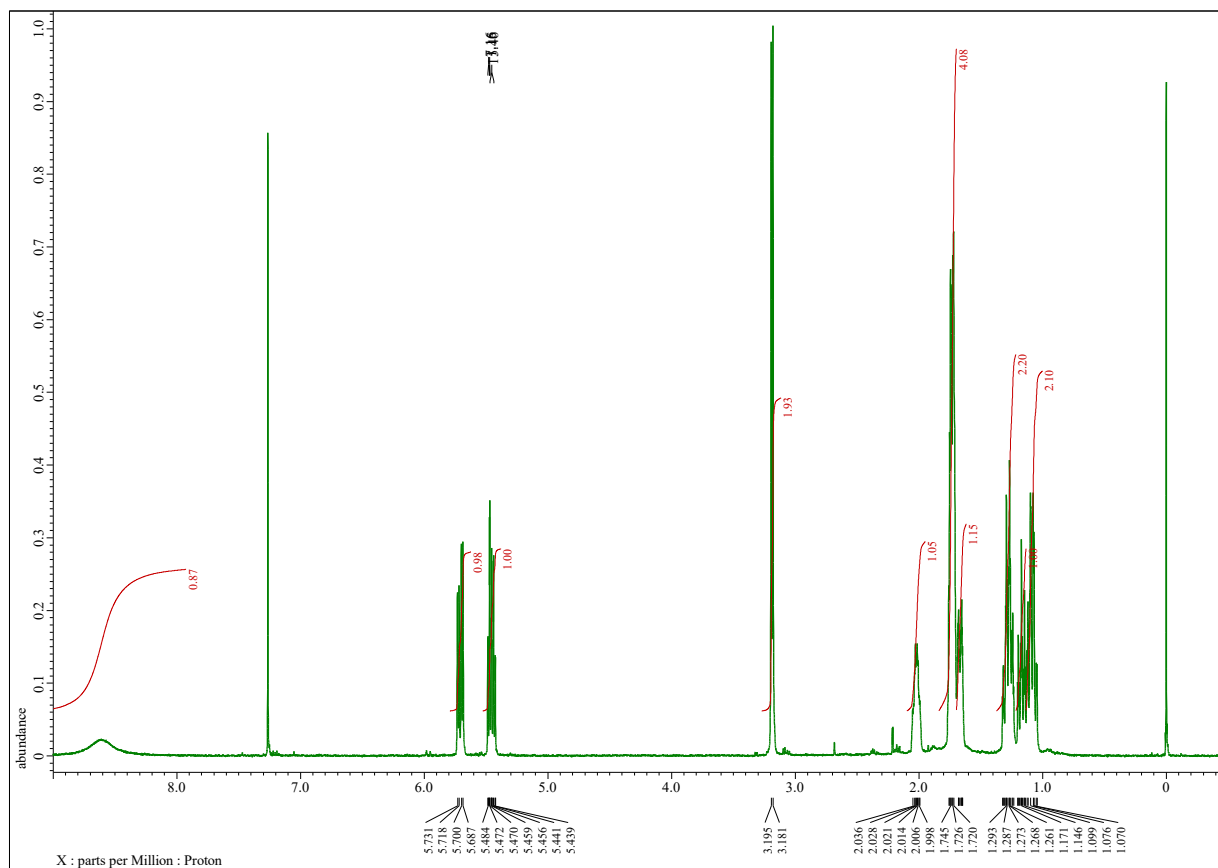
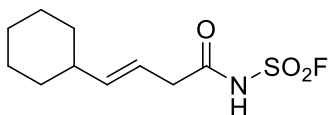


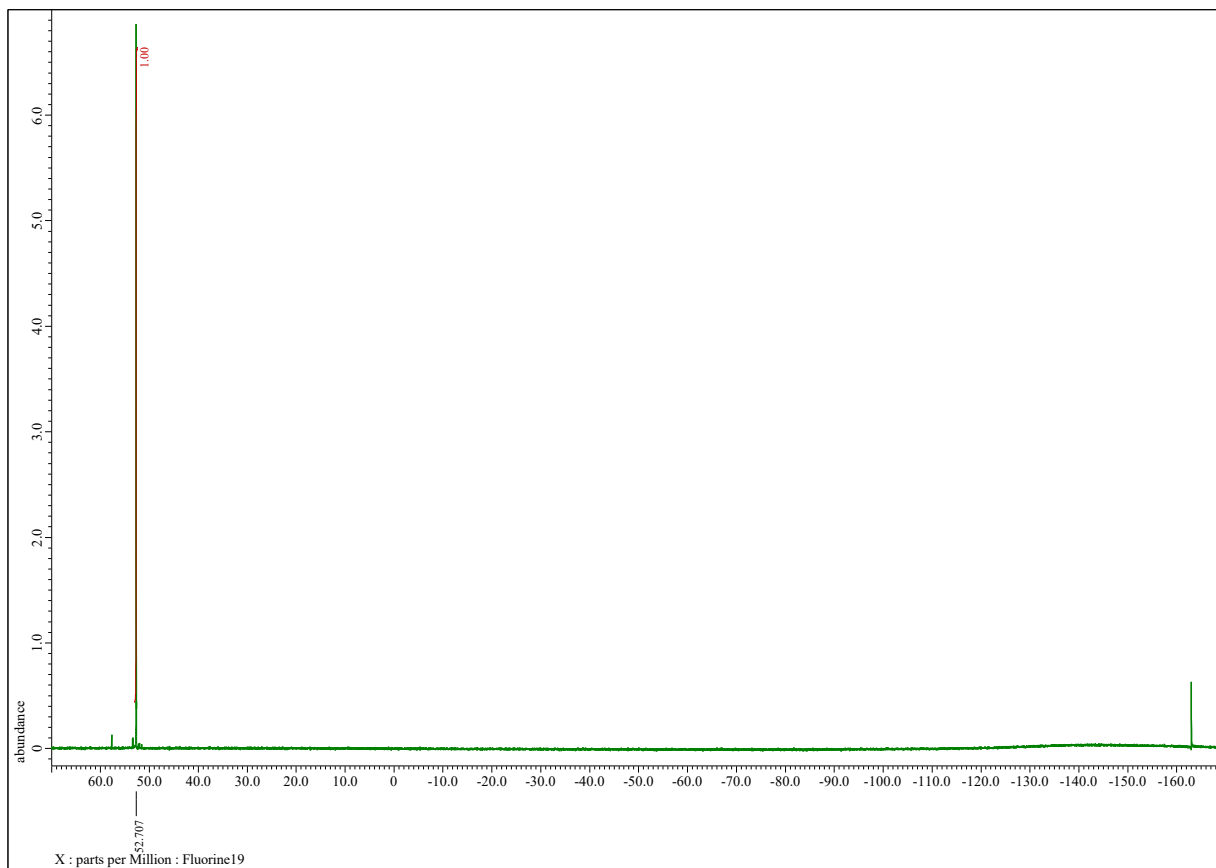
(E)-undec-3-enoylsulfamoyl fluoride (3a)



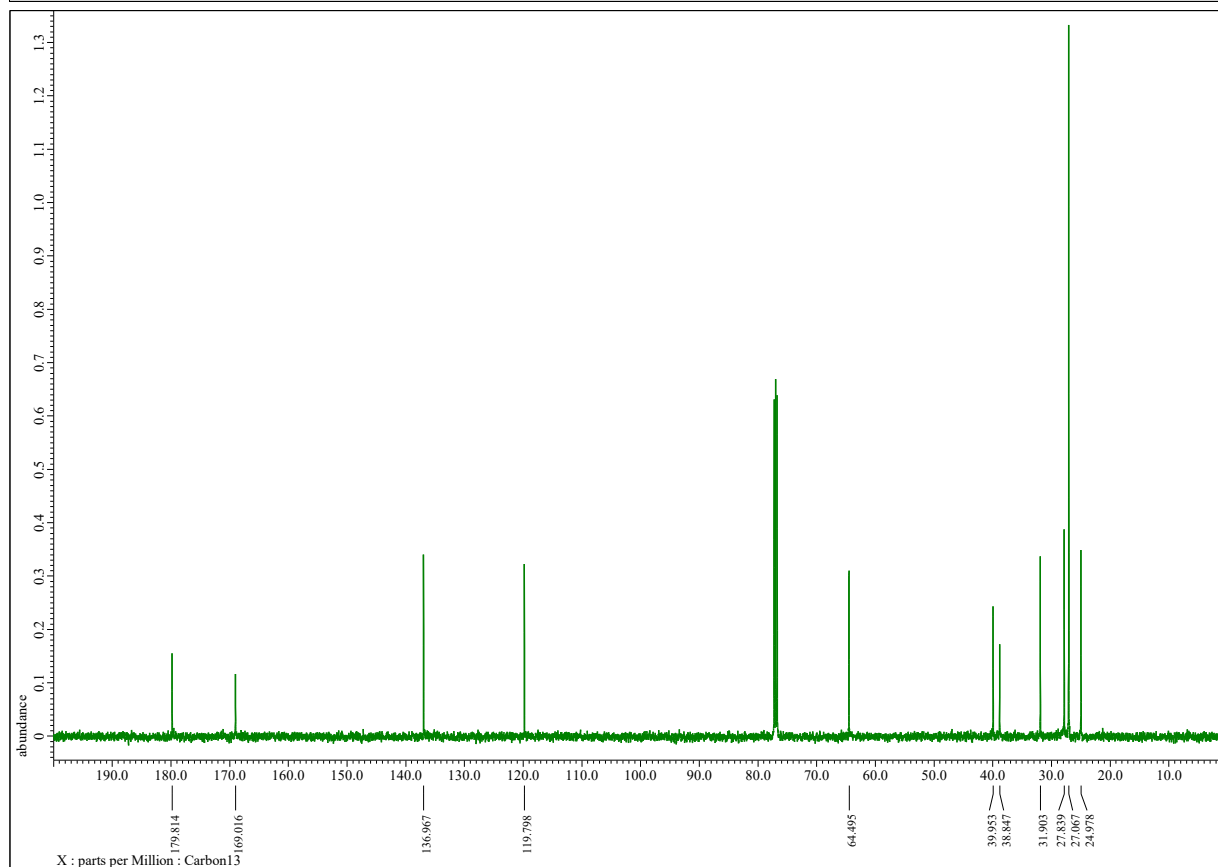
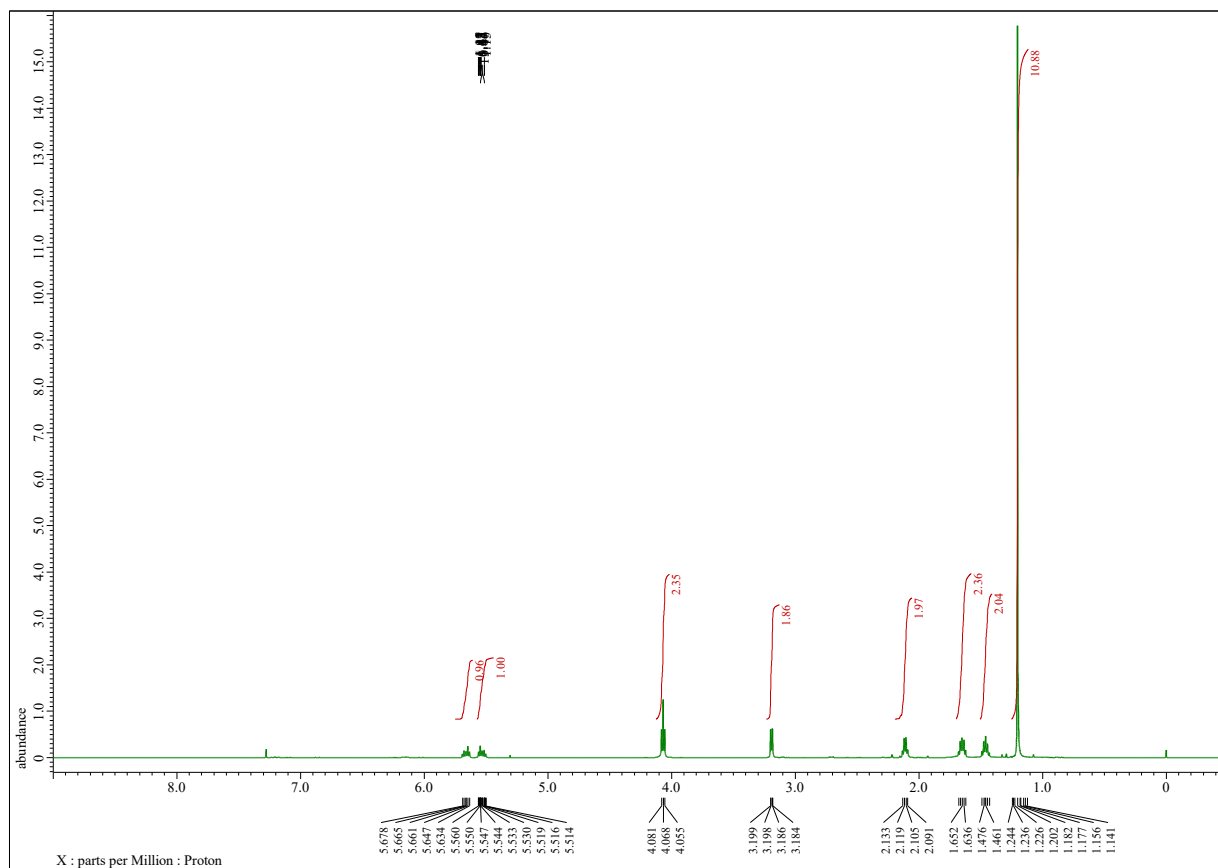
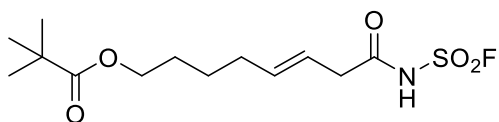


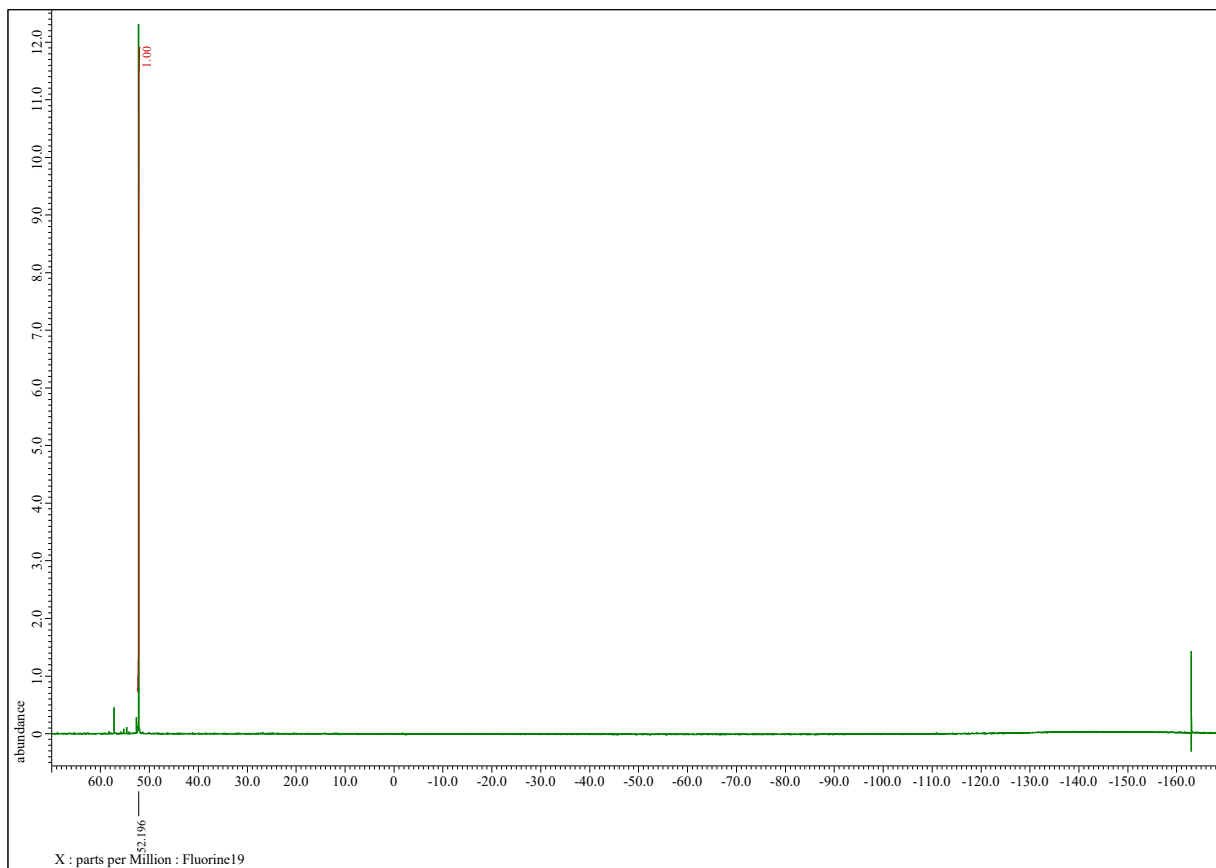
(E)-(4-cyclohexylbut-3-enoyl)sulfamoyl fluoride (3b)



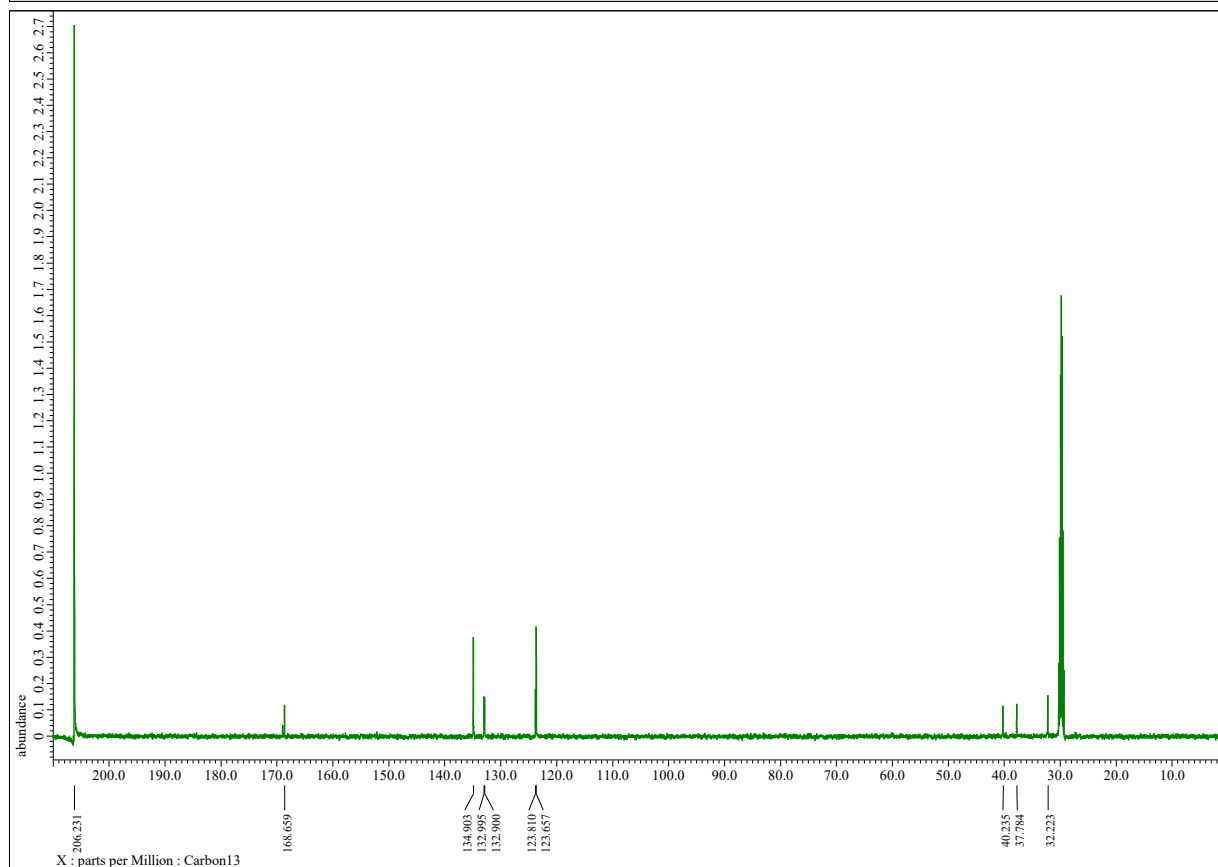
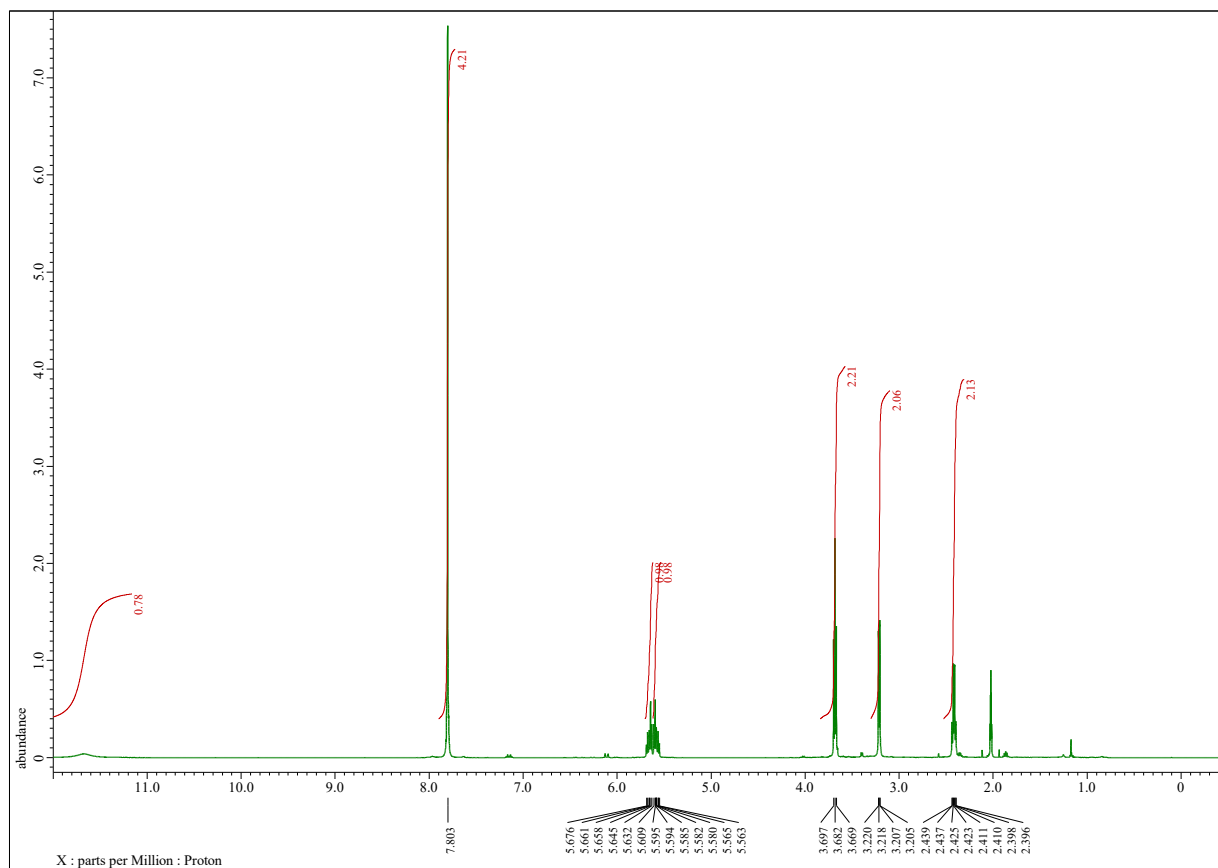
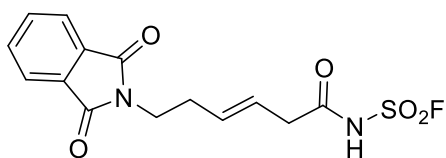


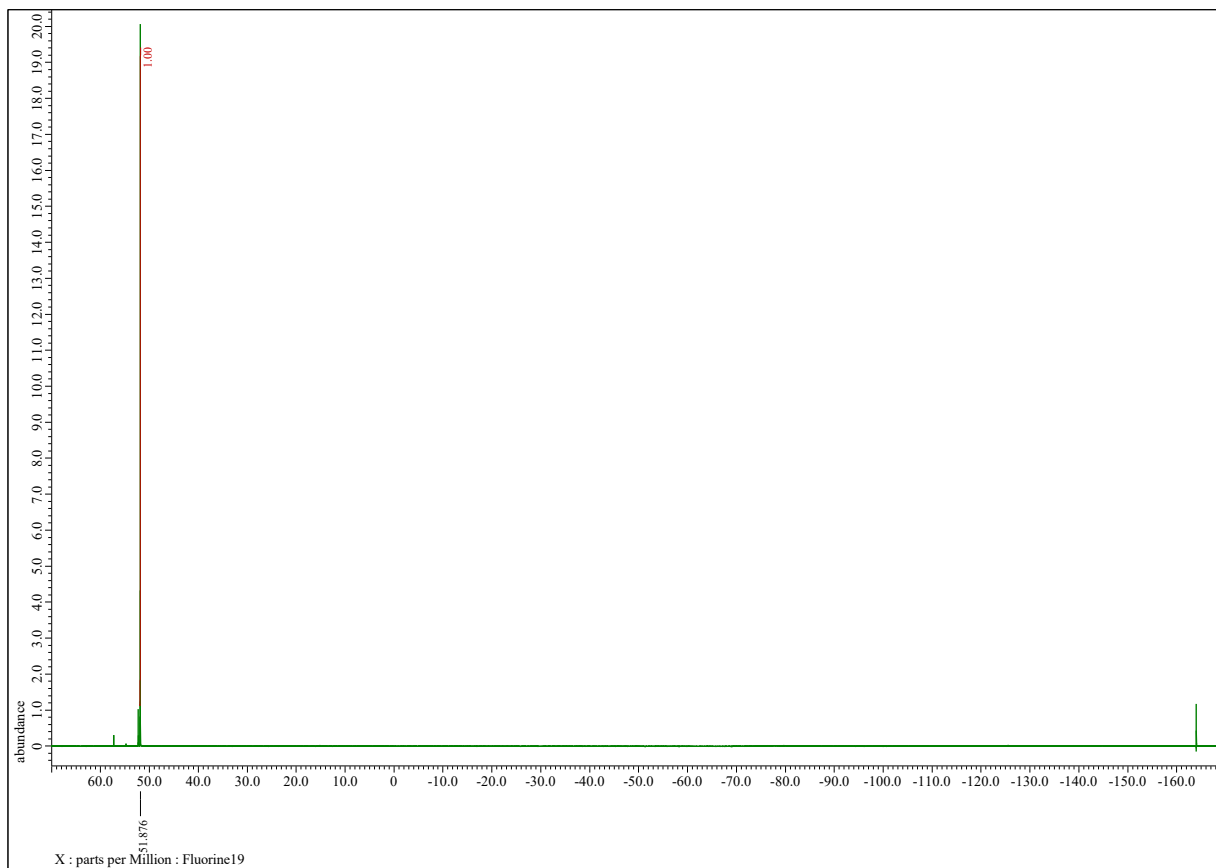
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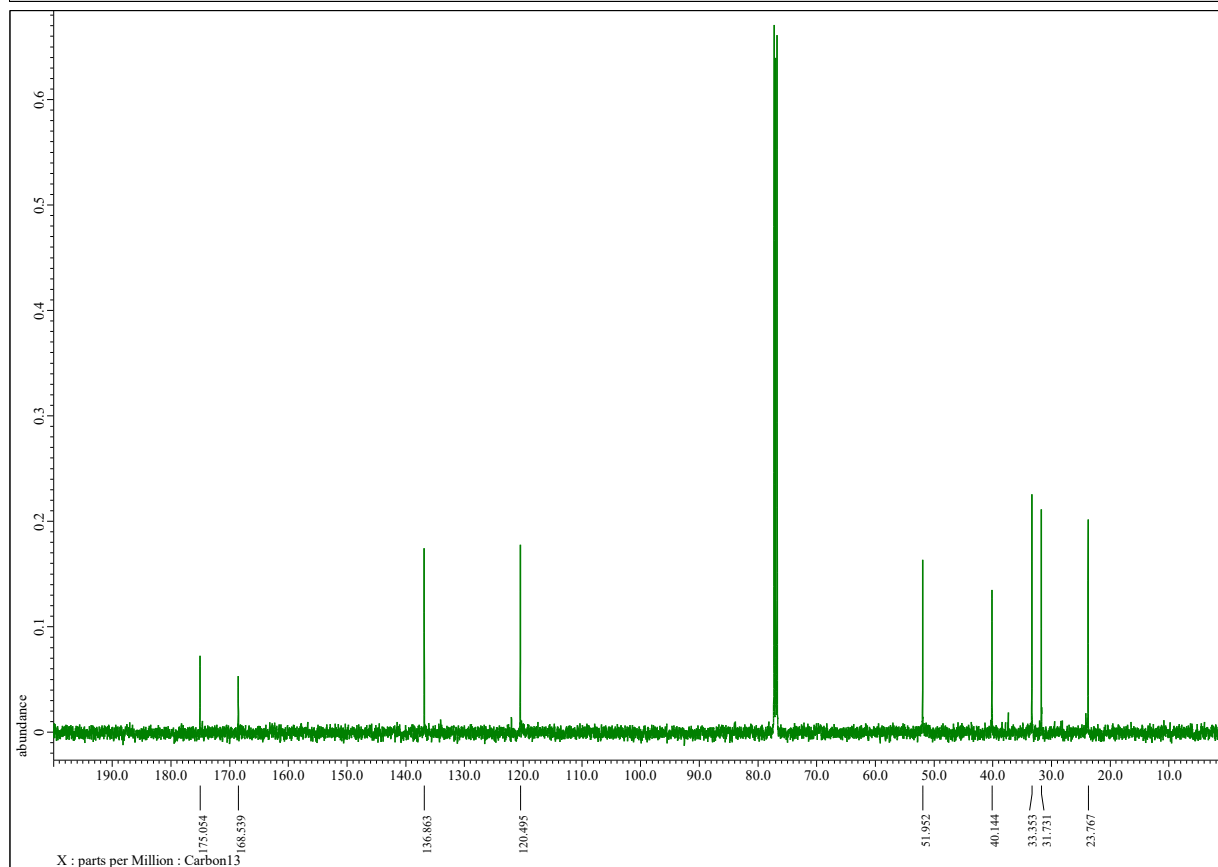
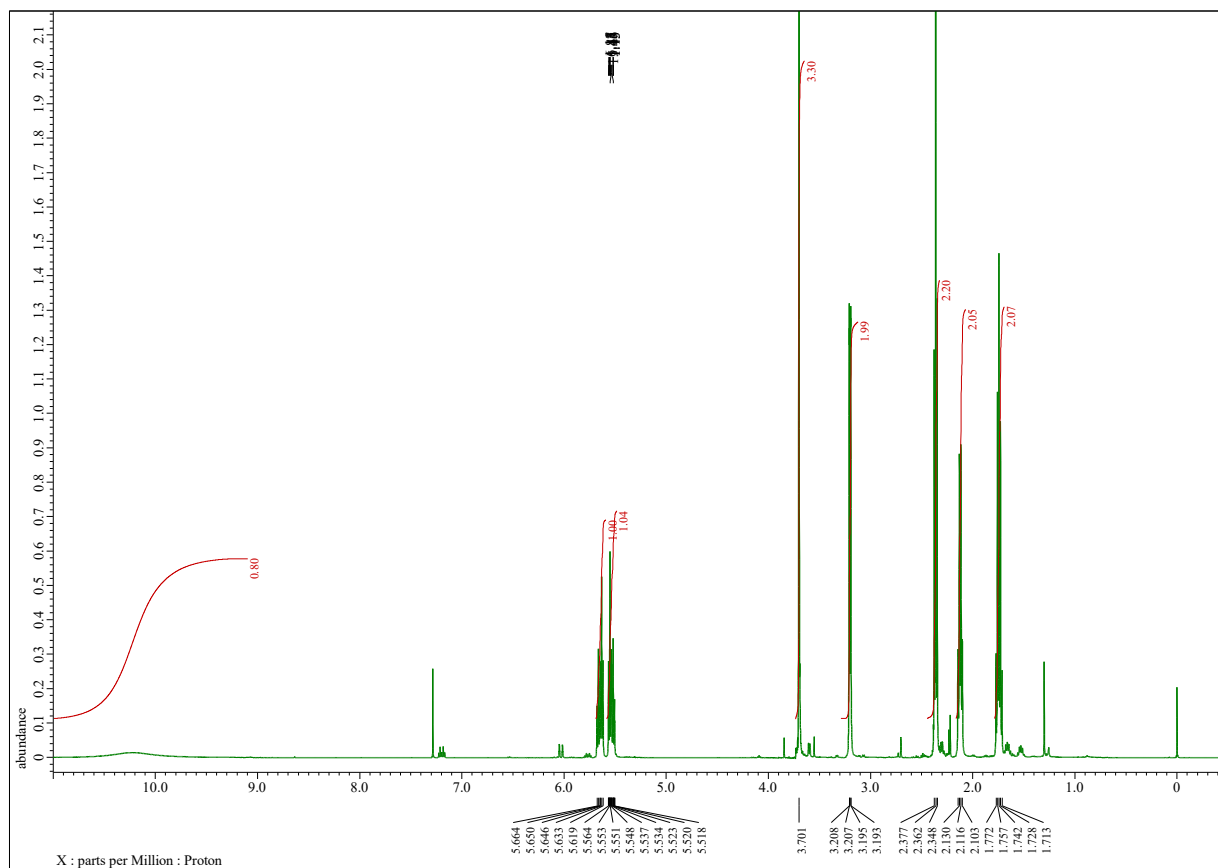
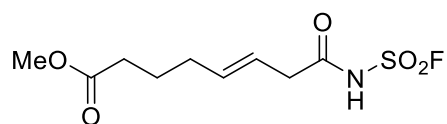


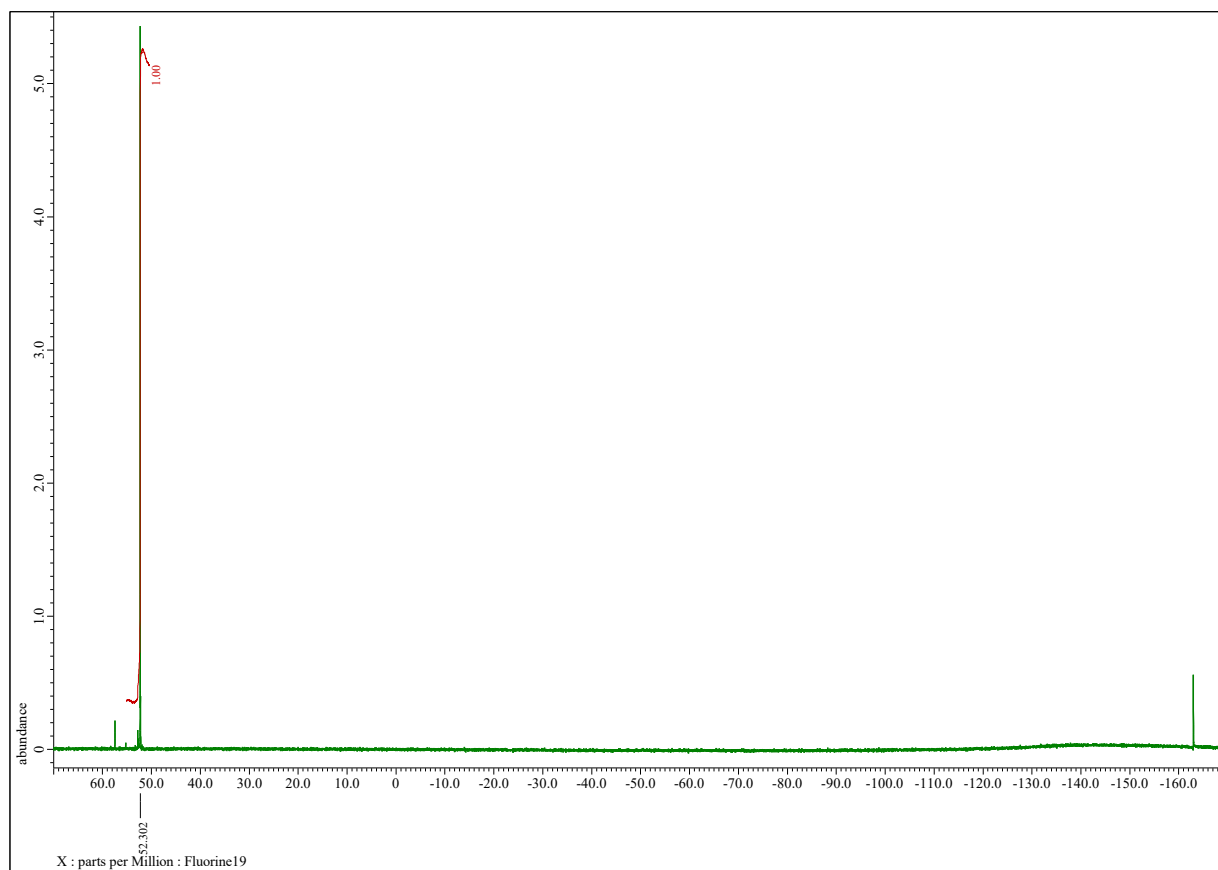
(E)-(6-(1,3-dioxisoindolin-2-yl)hex-3-enyl)sulfamoyl fluoride (3d)



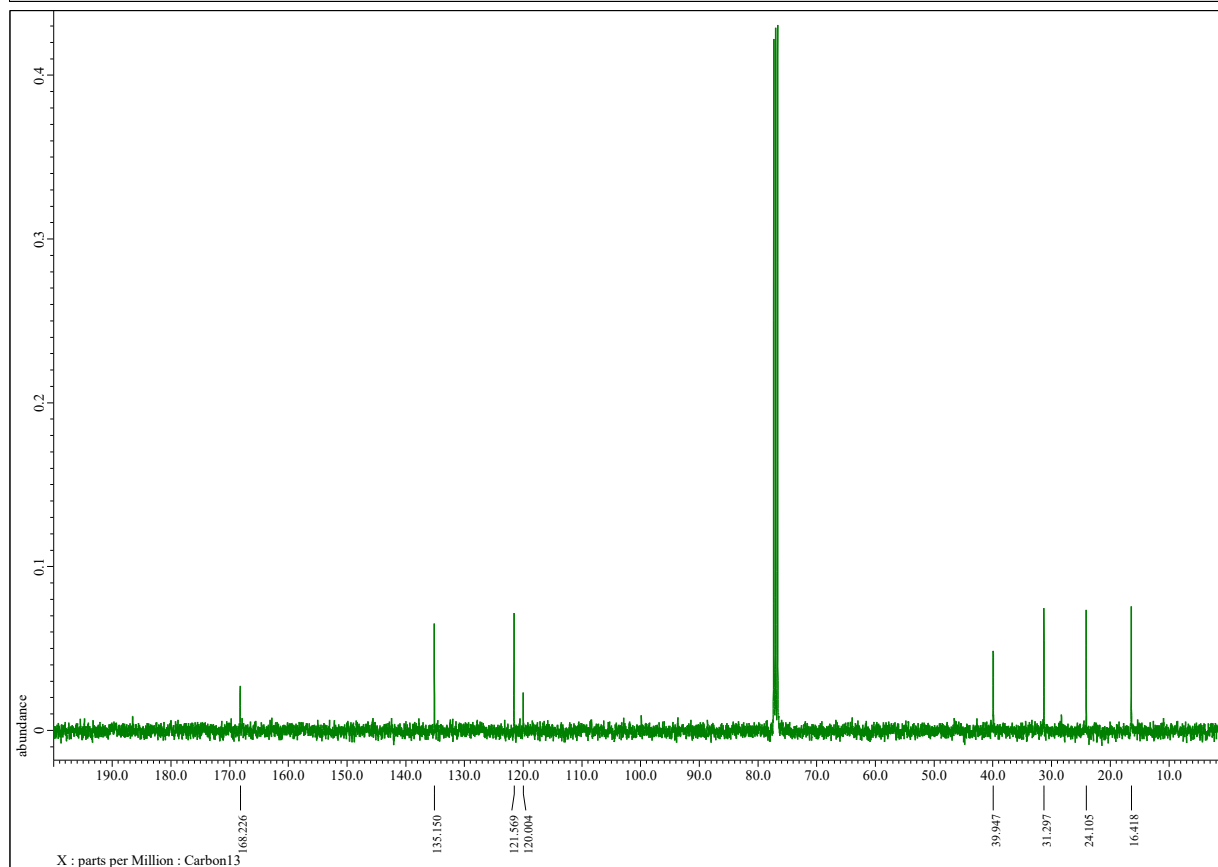
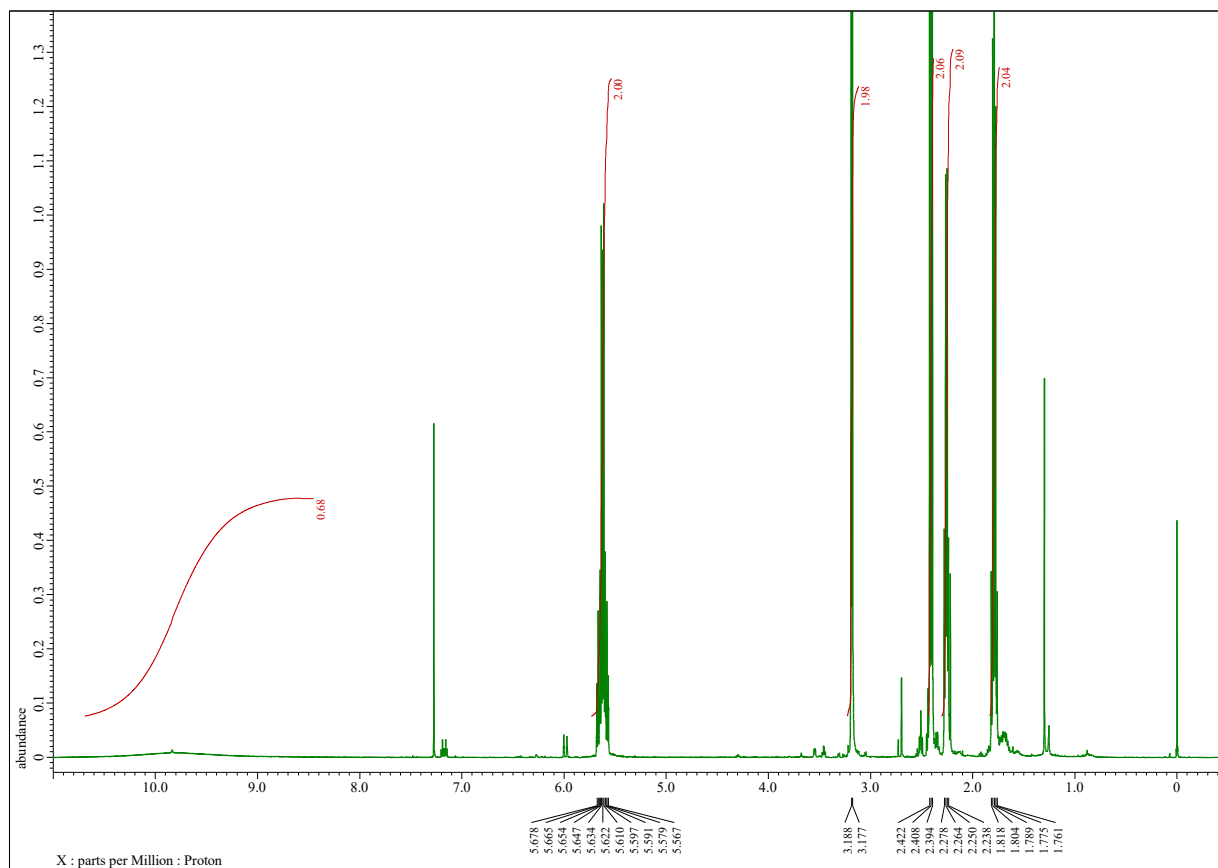
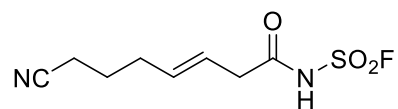


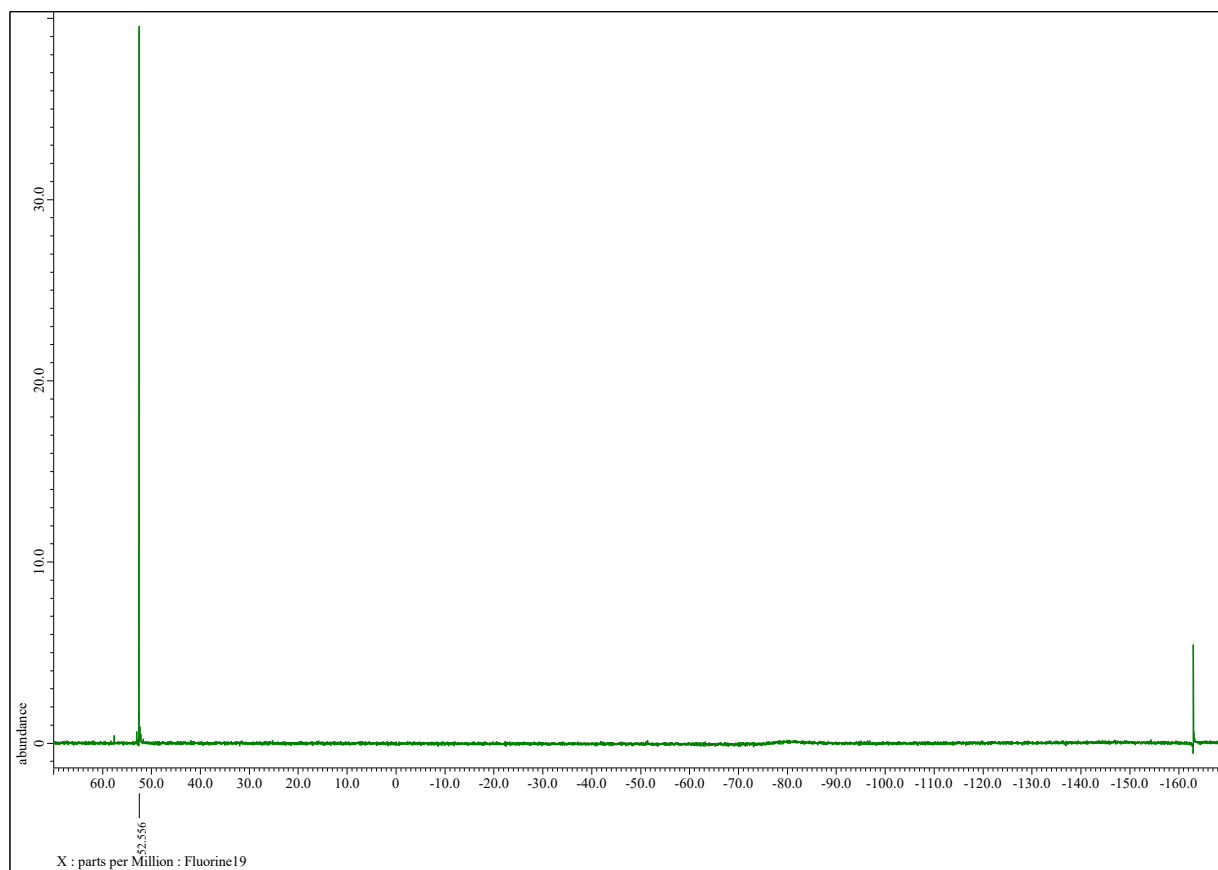
(E)-8-((fluorosulfonyl)amino)-8-oxooct-5-en-1-yl pivalate (3e)



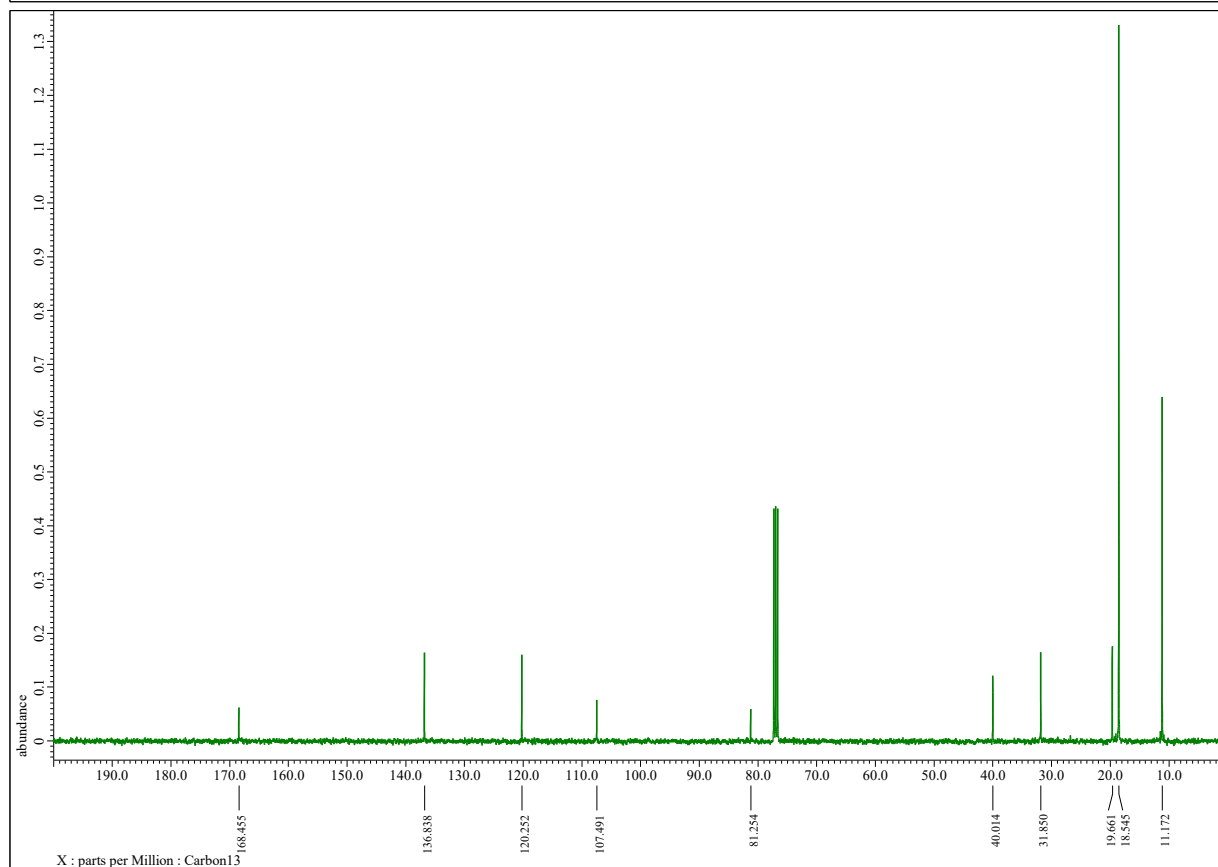
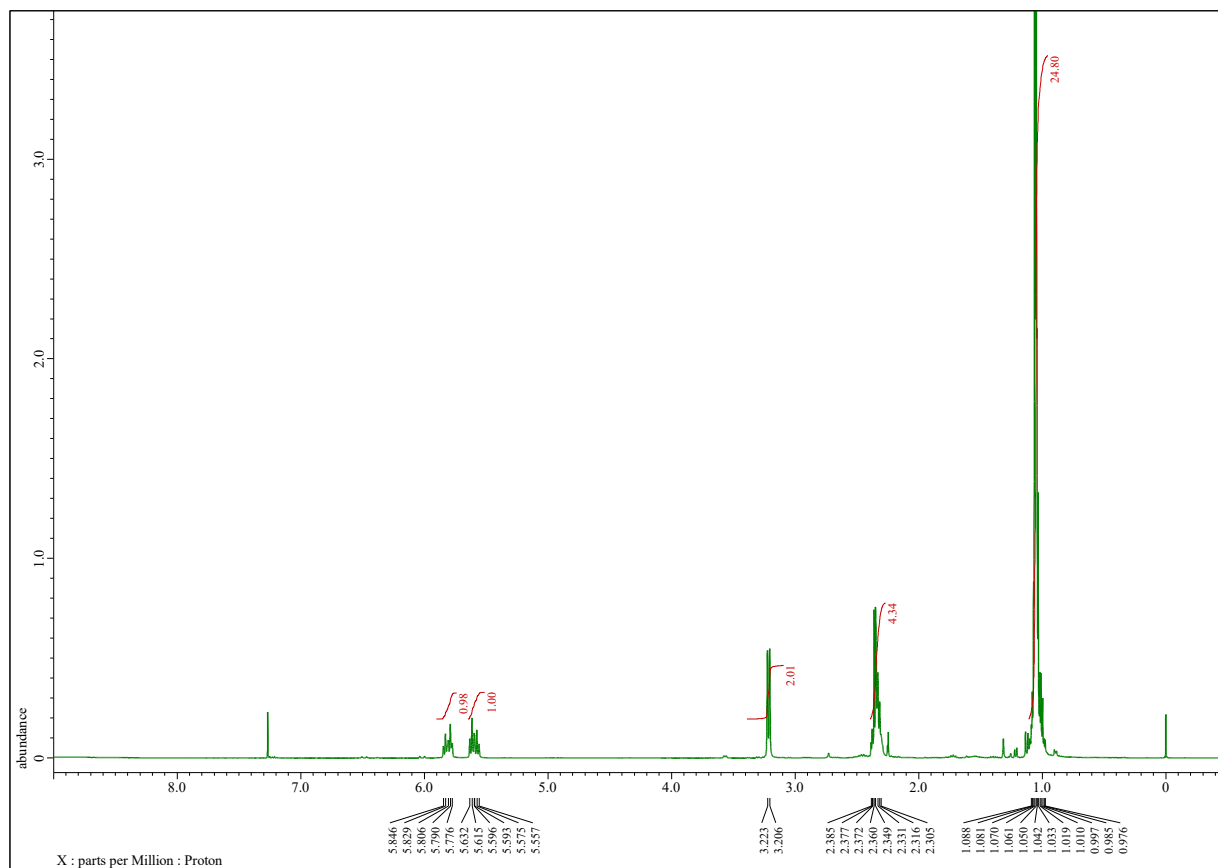
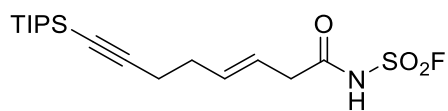


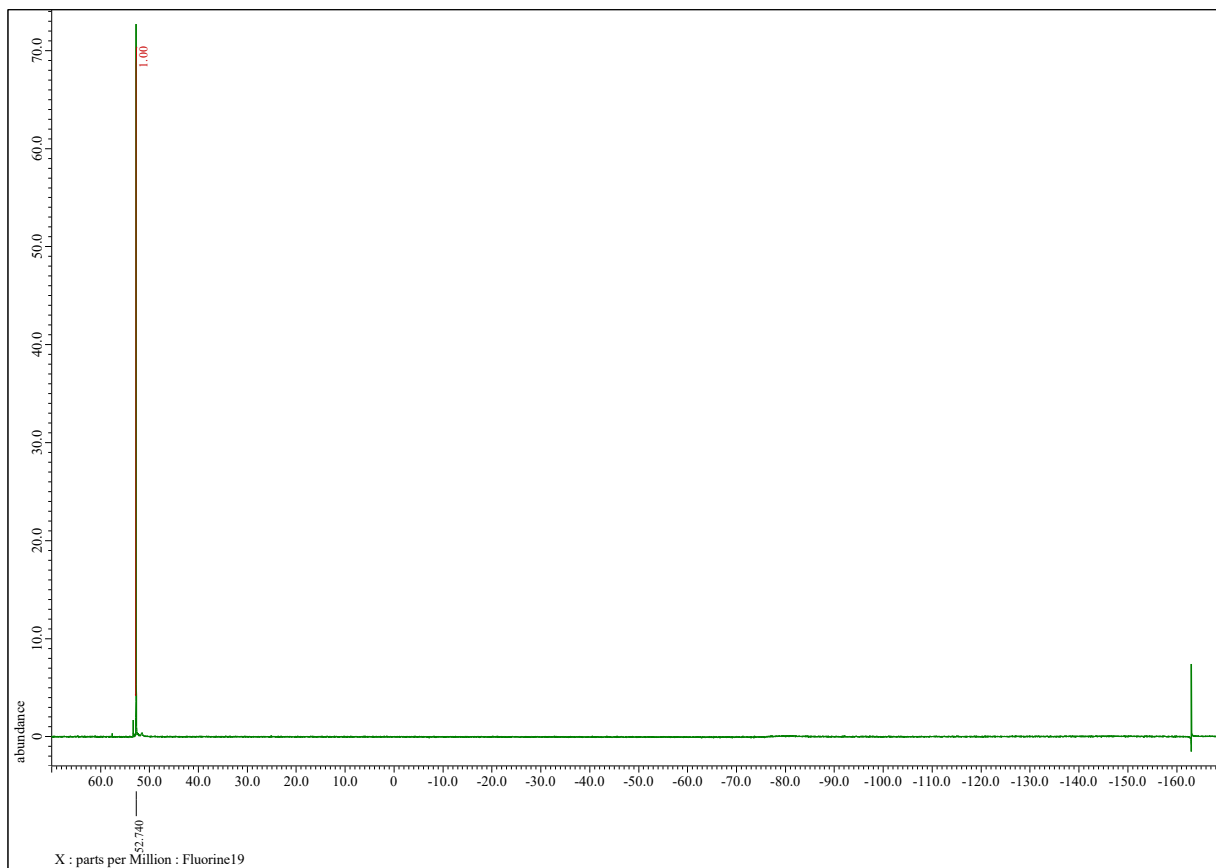
(E)-(7-cyanohept-3-enoyl)sulfamoyl fluoride (3f)



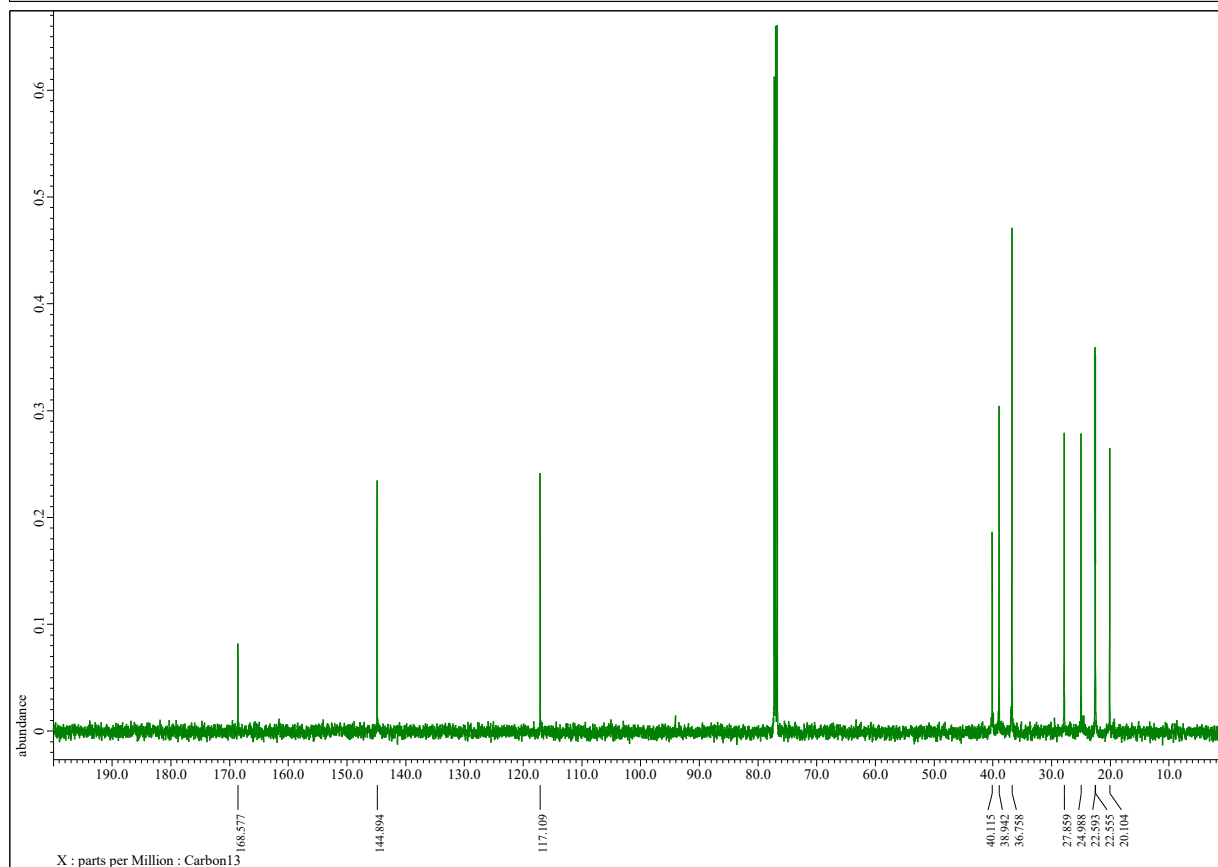
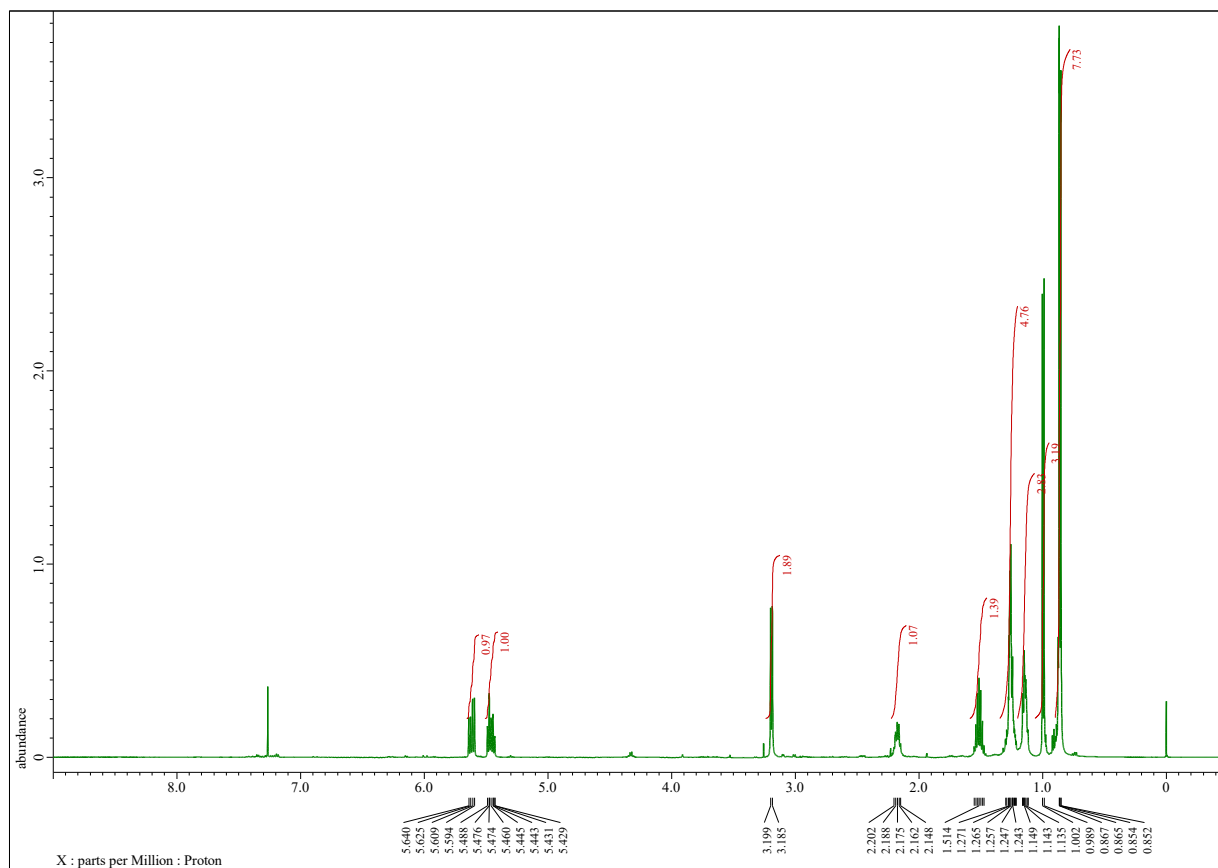
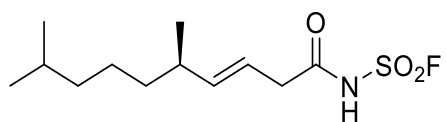


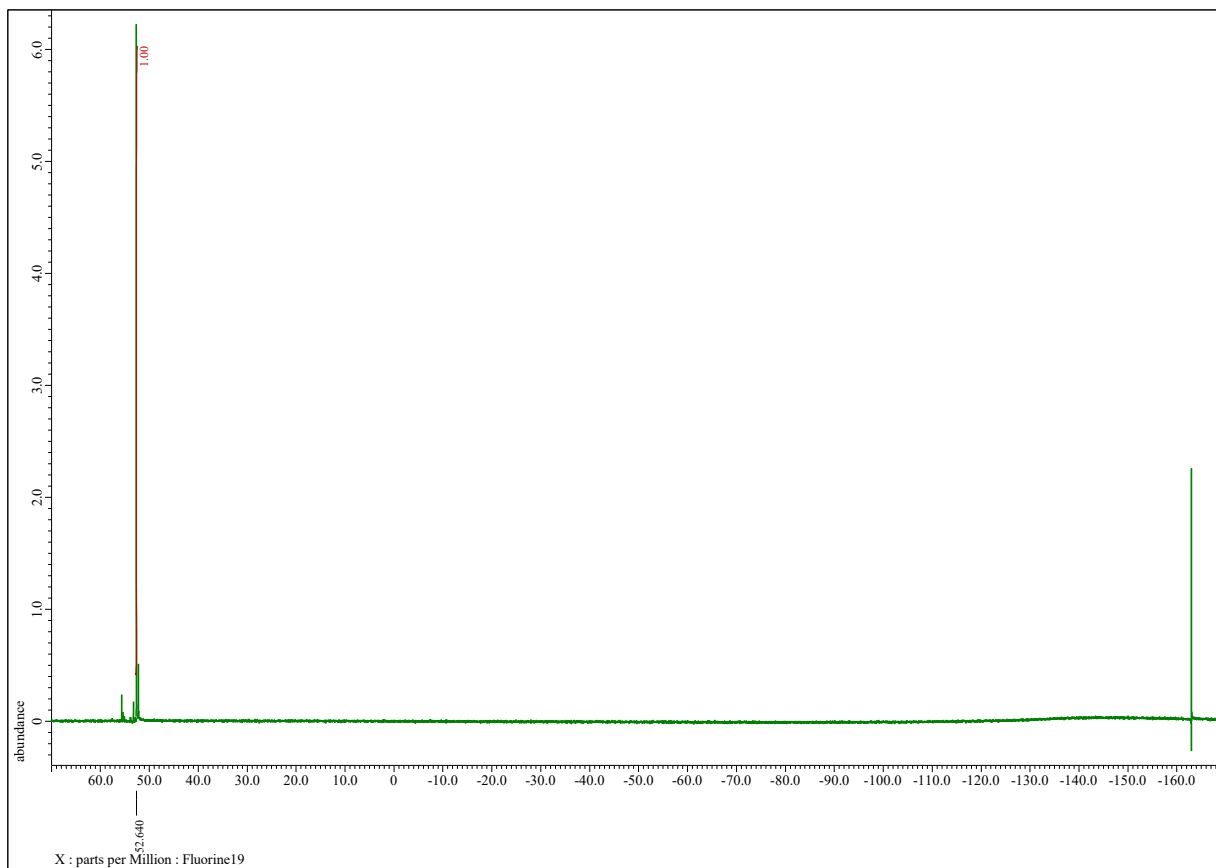
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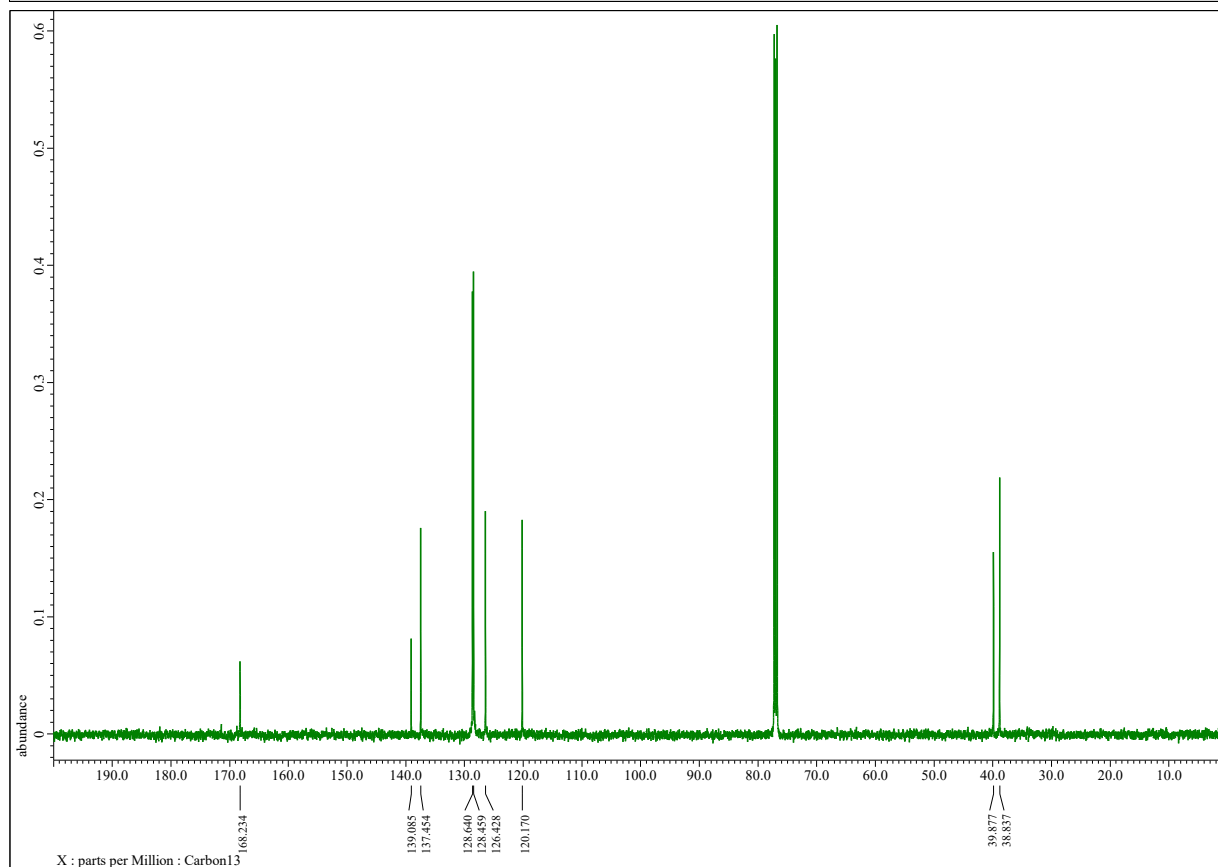
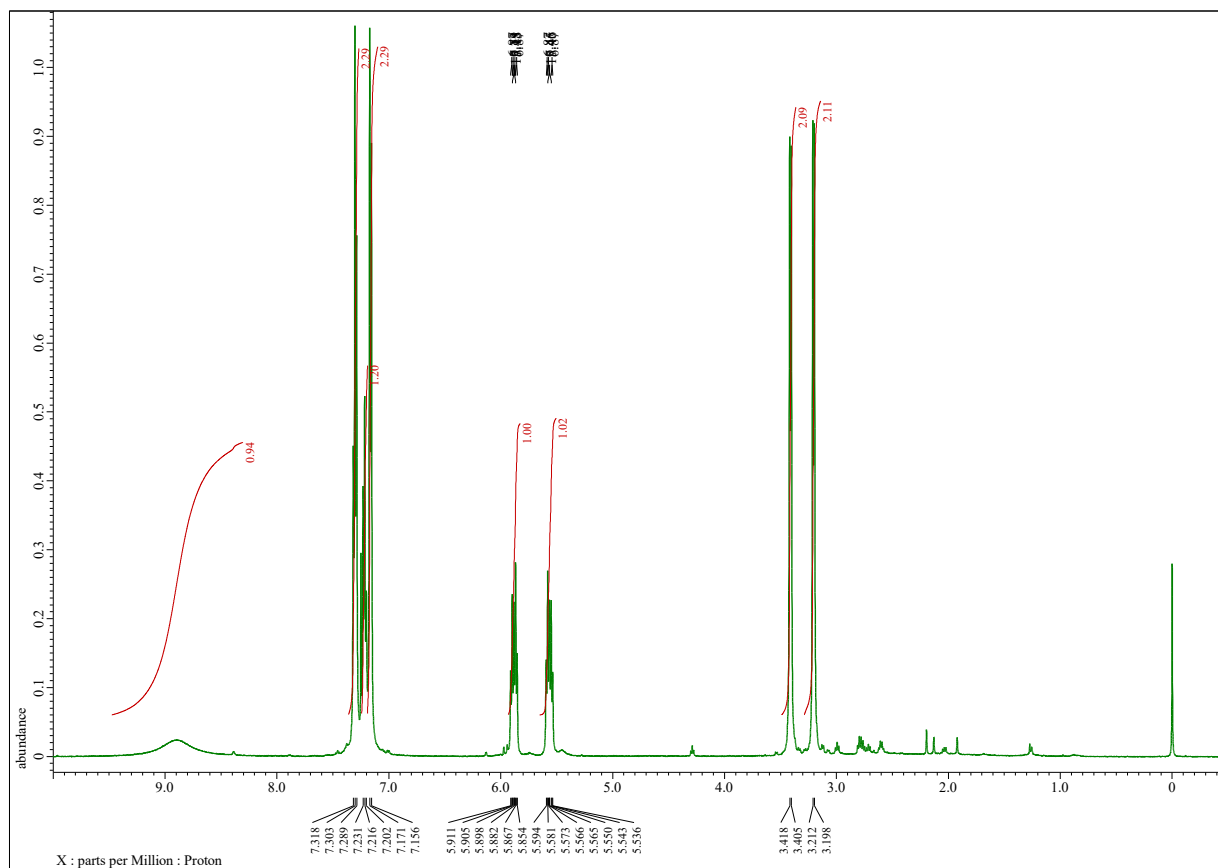
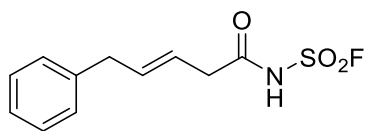


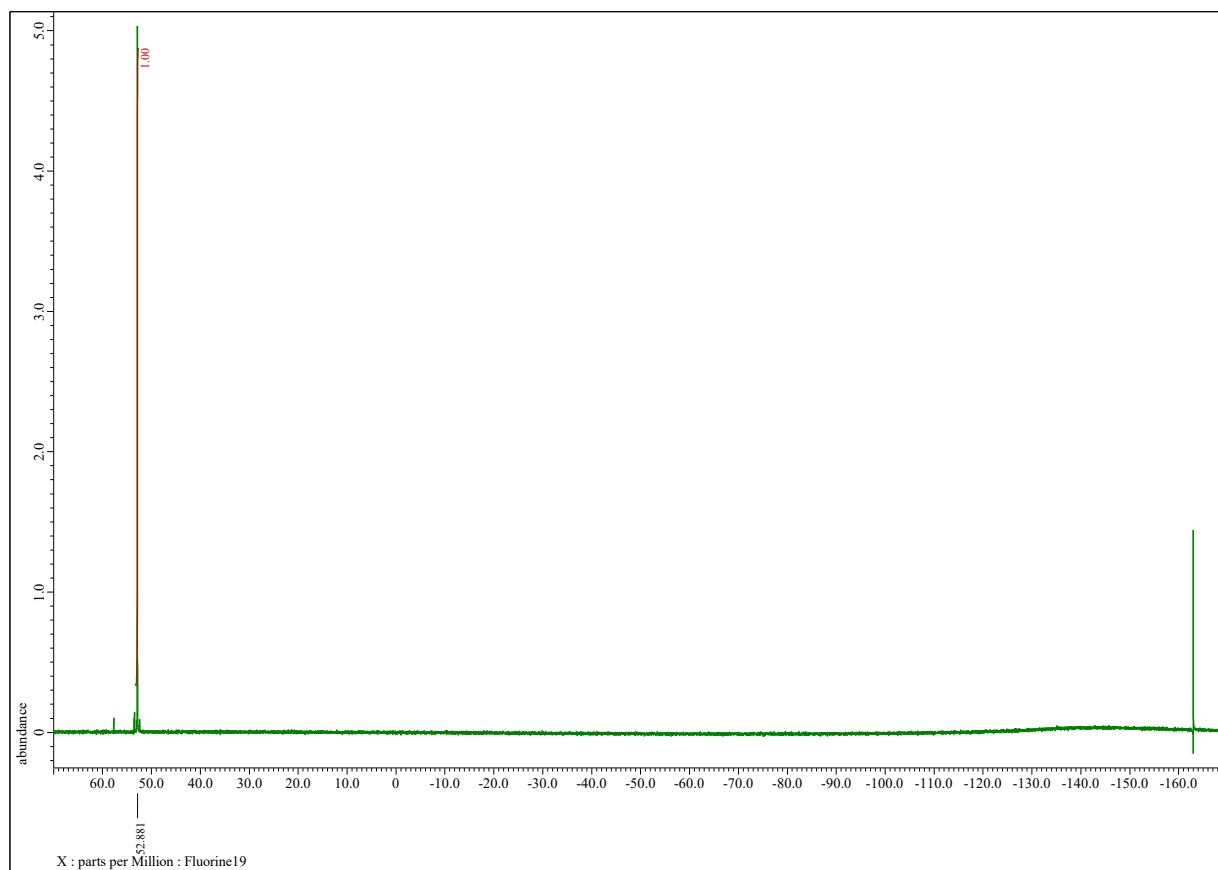
(*S,E*)-(5,9-dimethyldec-3-enoyl)sulfamoyl fluoride (3h)



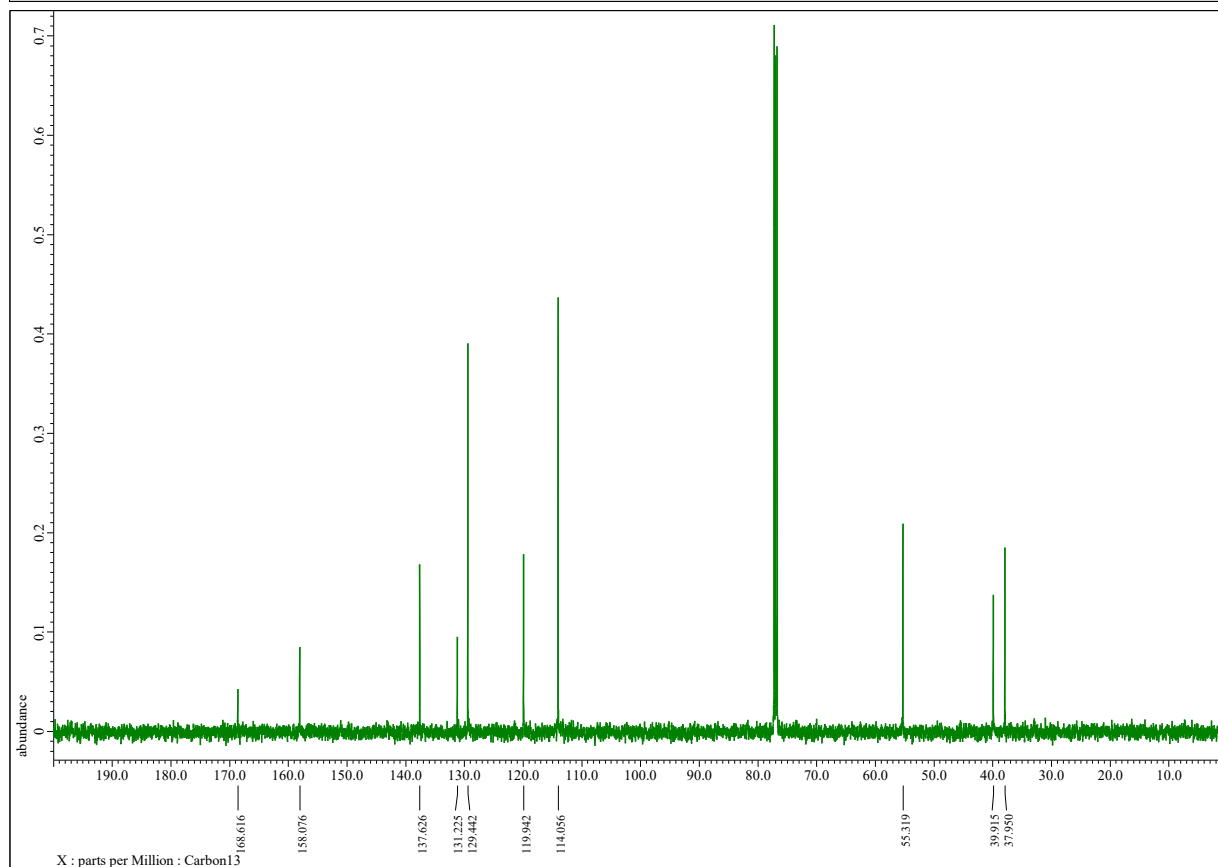
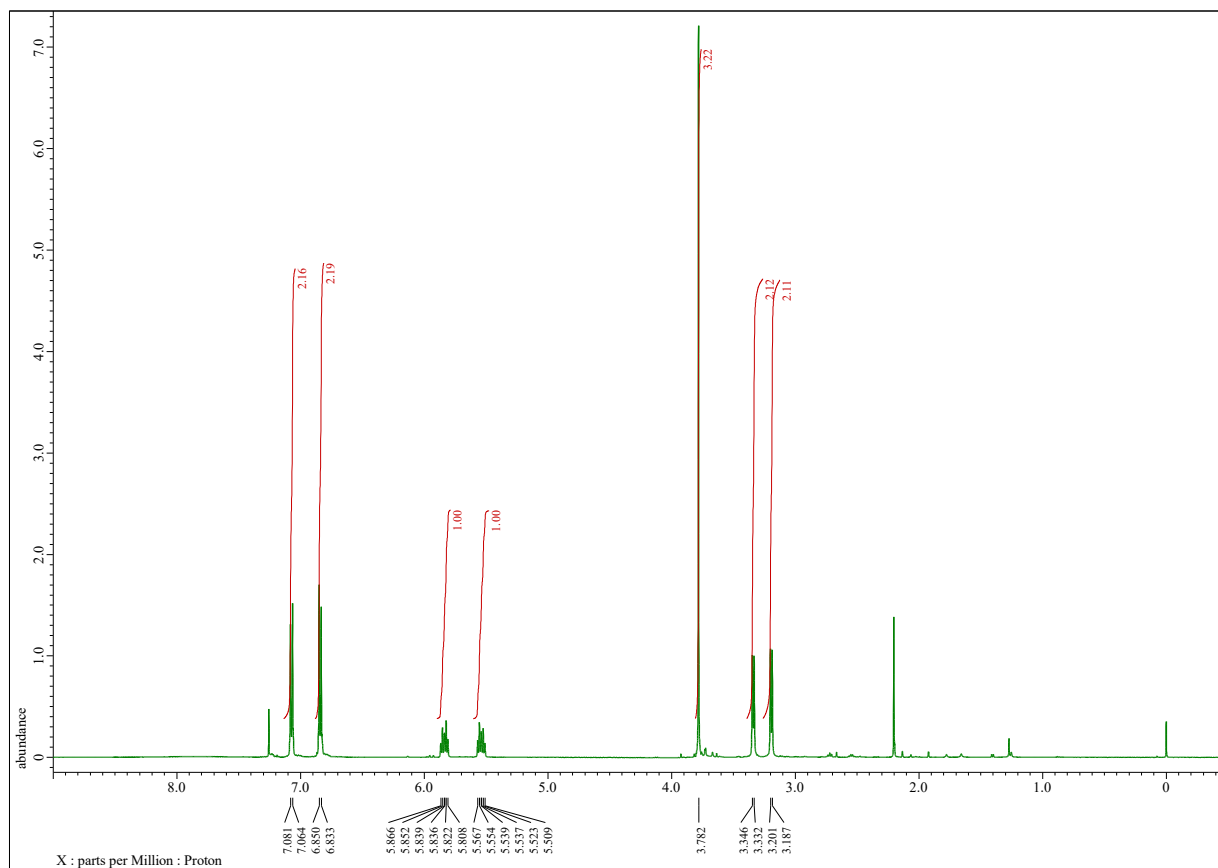
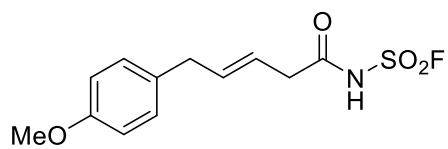


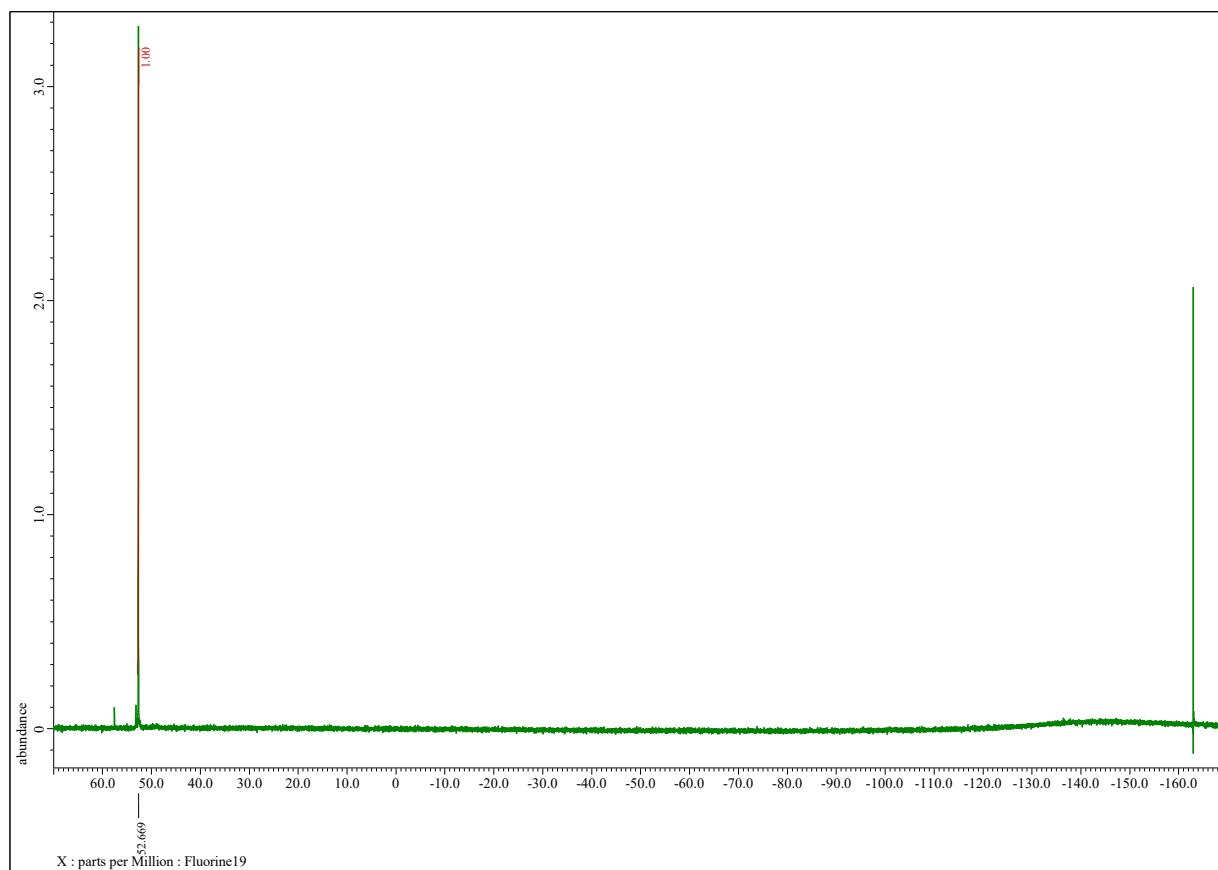
(E)-(5-phenylpent-3-enoyl)sulfamoyl fluoride (3j)



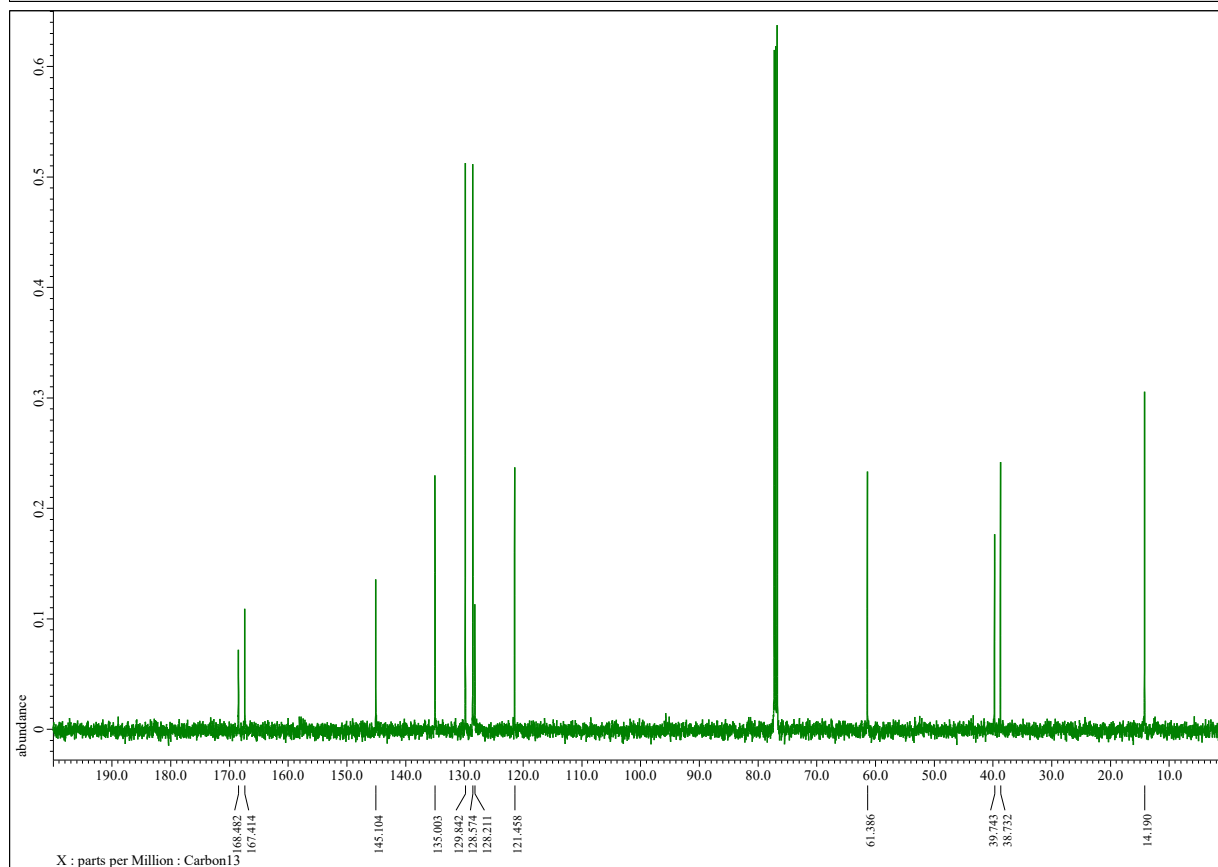
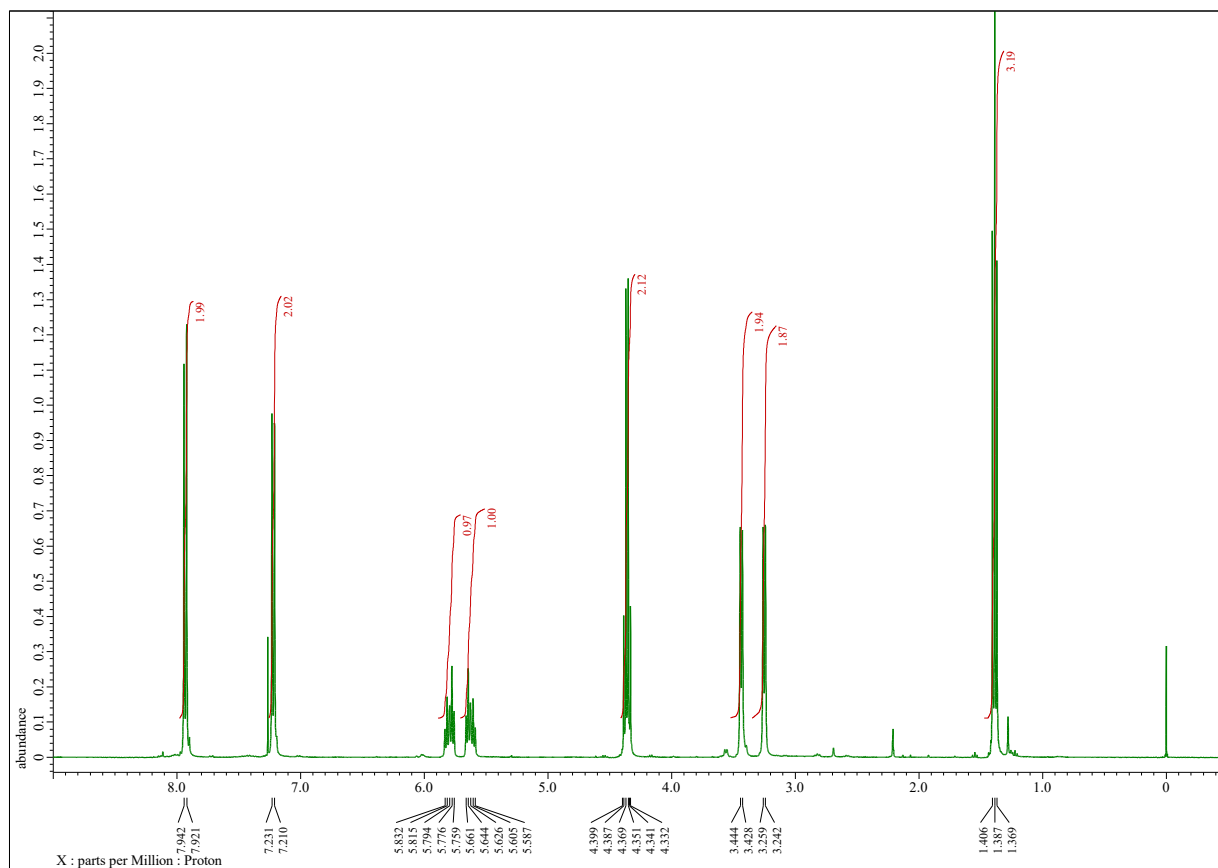
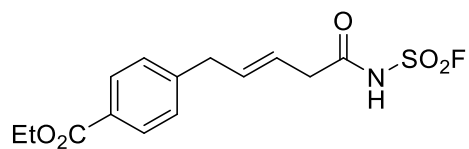


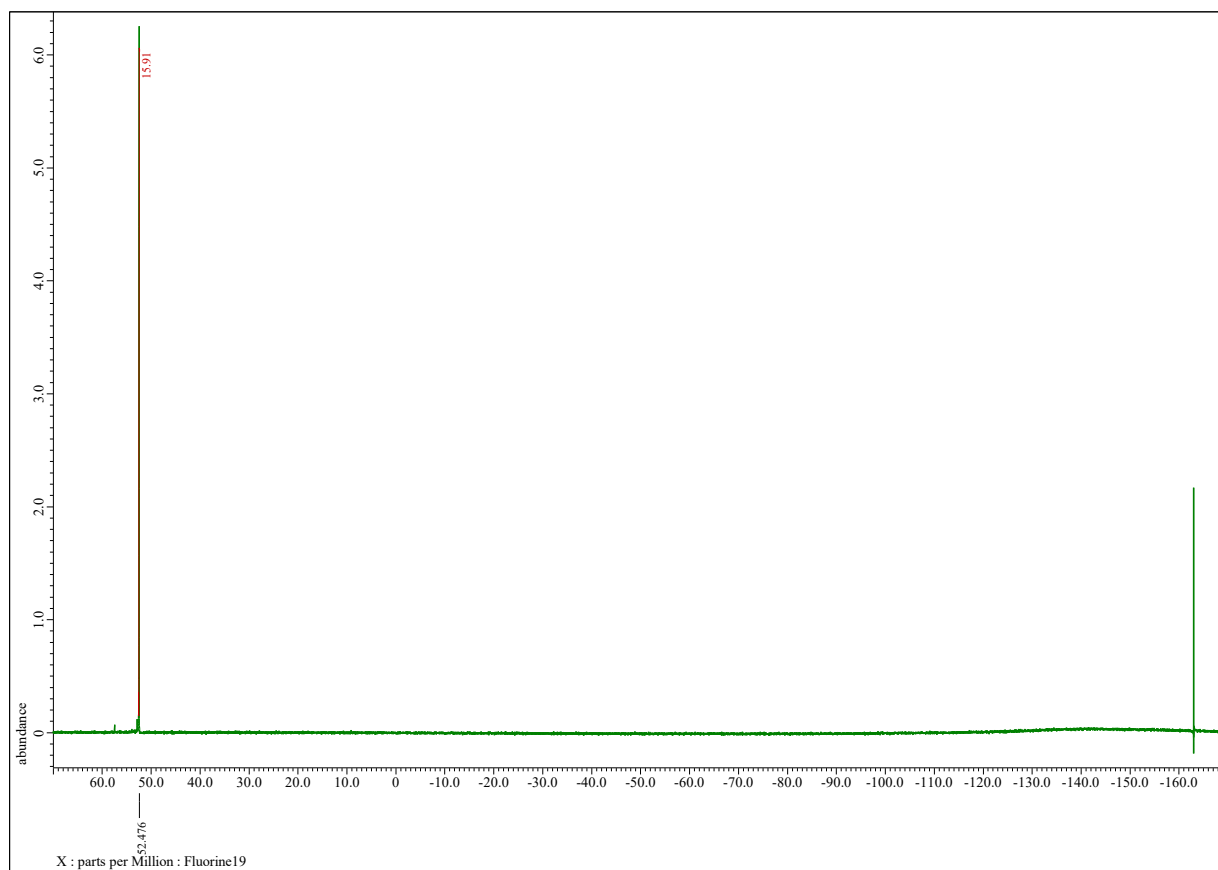
(E)-(5-(4-methoxyphenyl)pent-3-enoyl)sulfamoyl fluoride (3k)



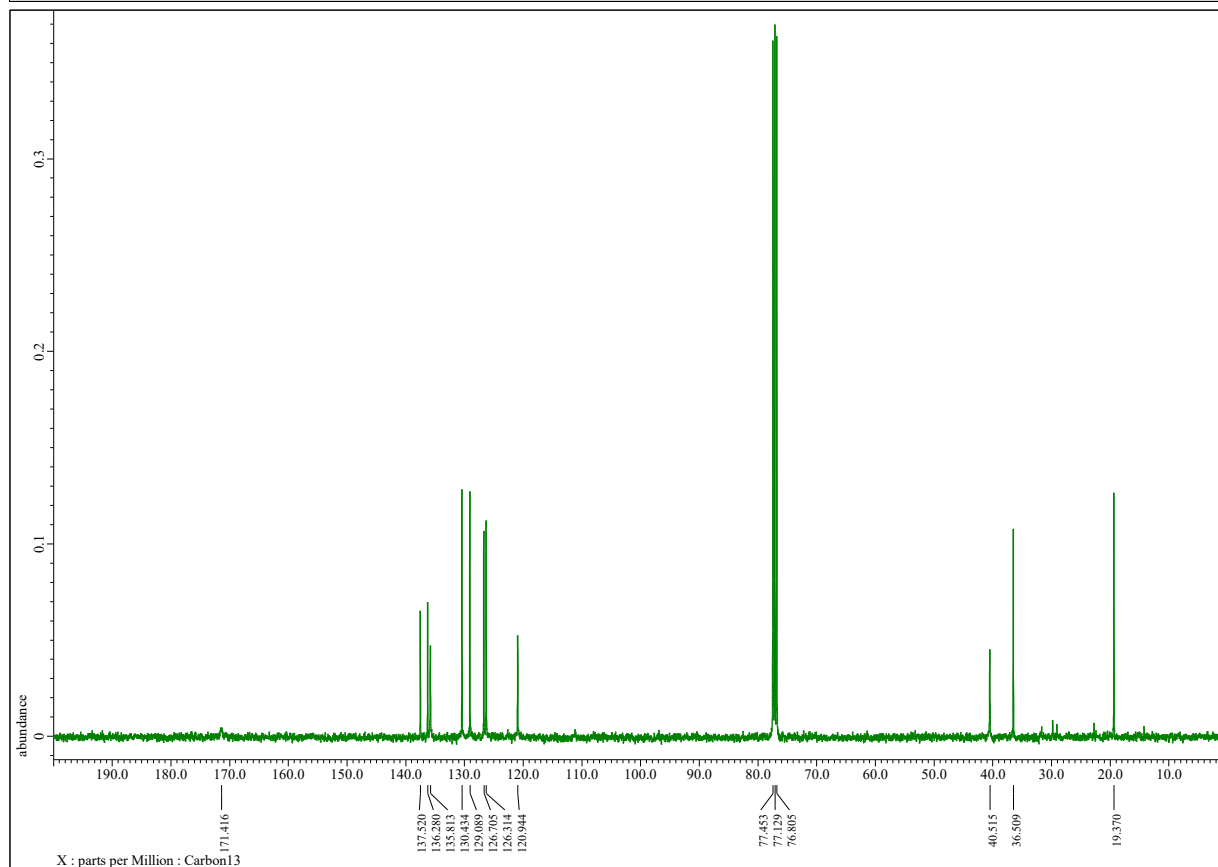
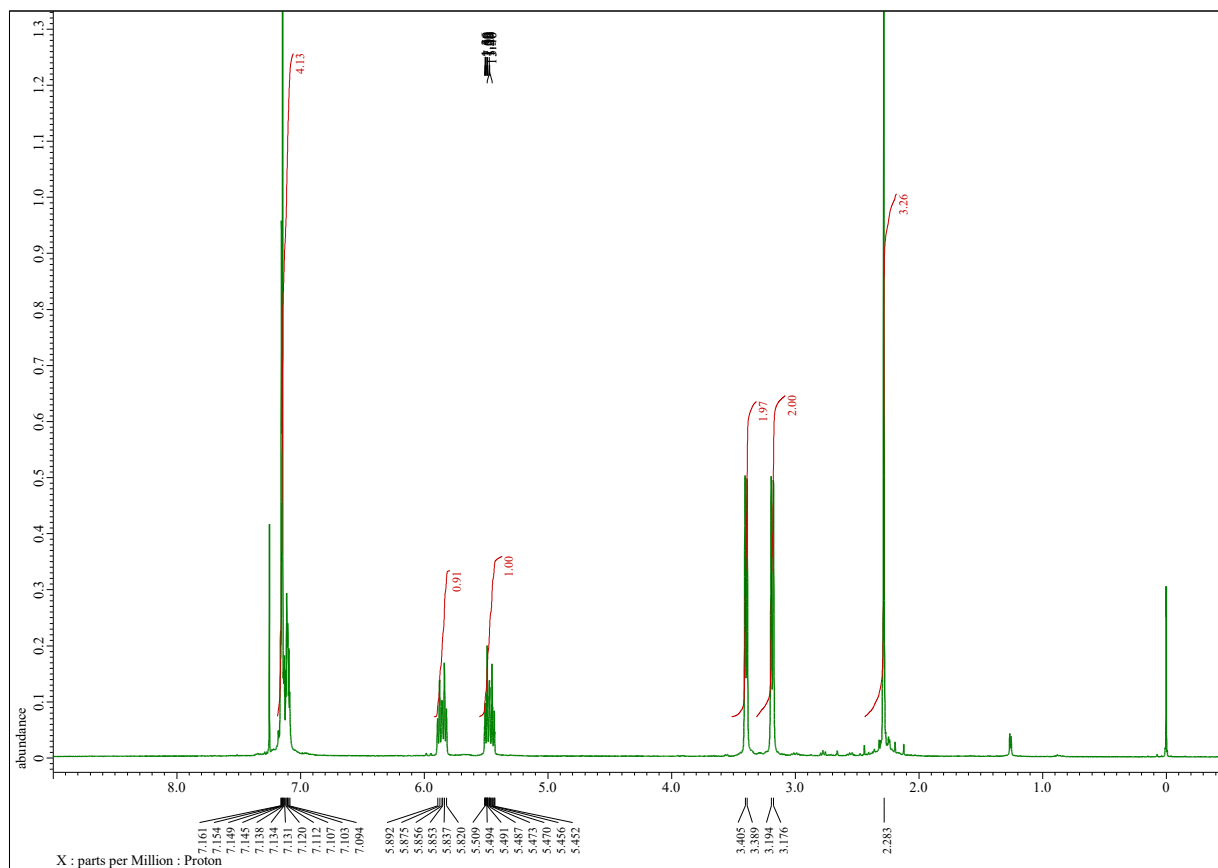
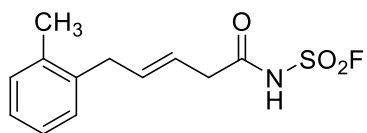


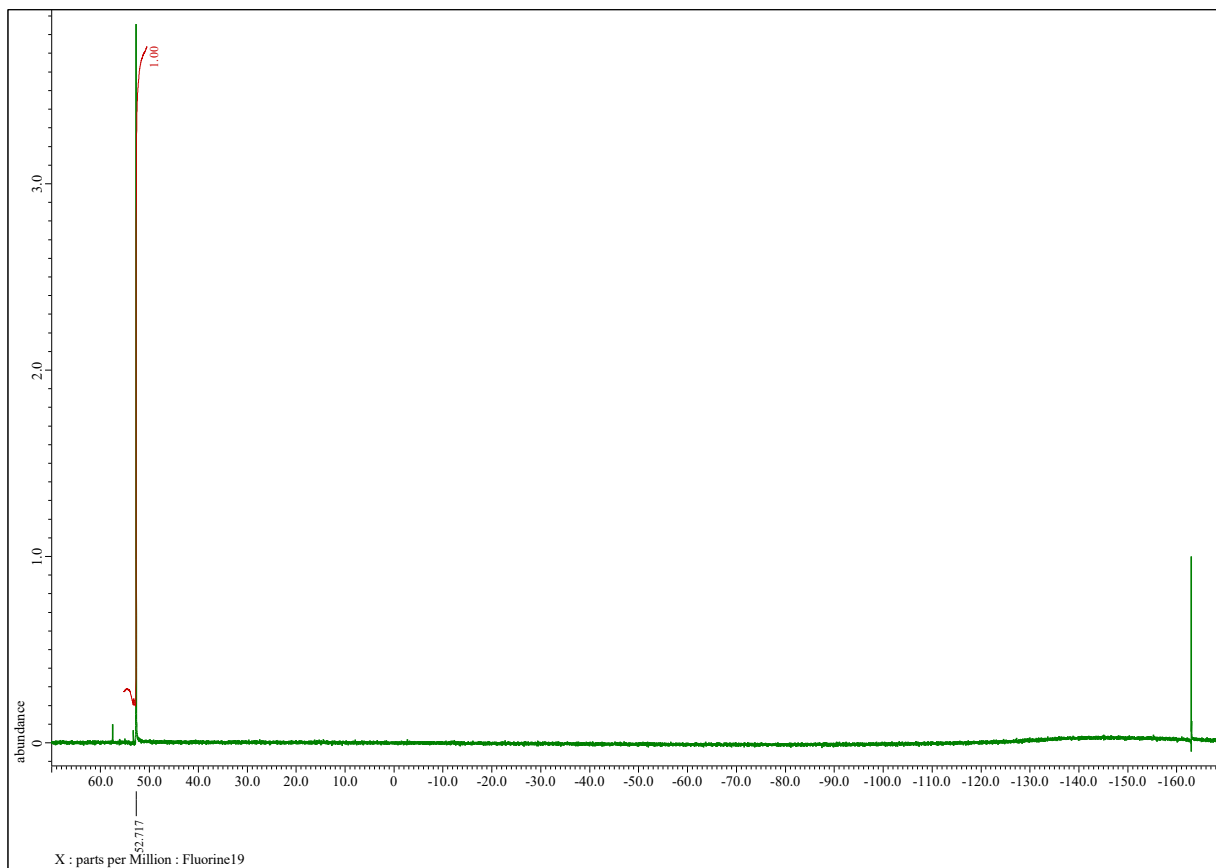
ethyl (E)-4-(5-((fluorosulfonyl)amino)-5-oxopent-2-en-1-yl)benzoate (3I)



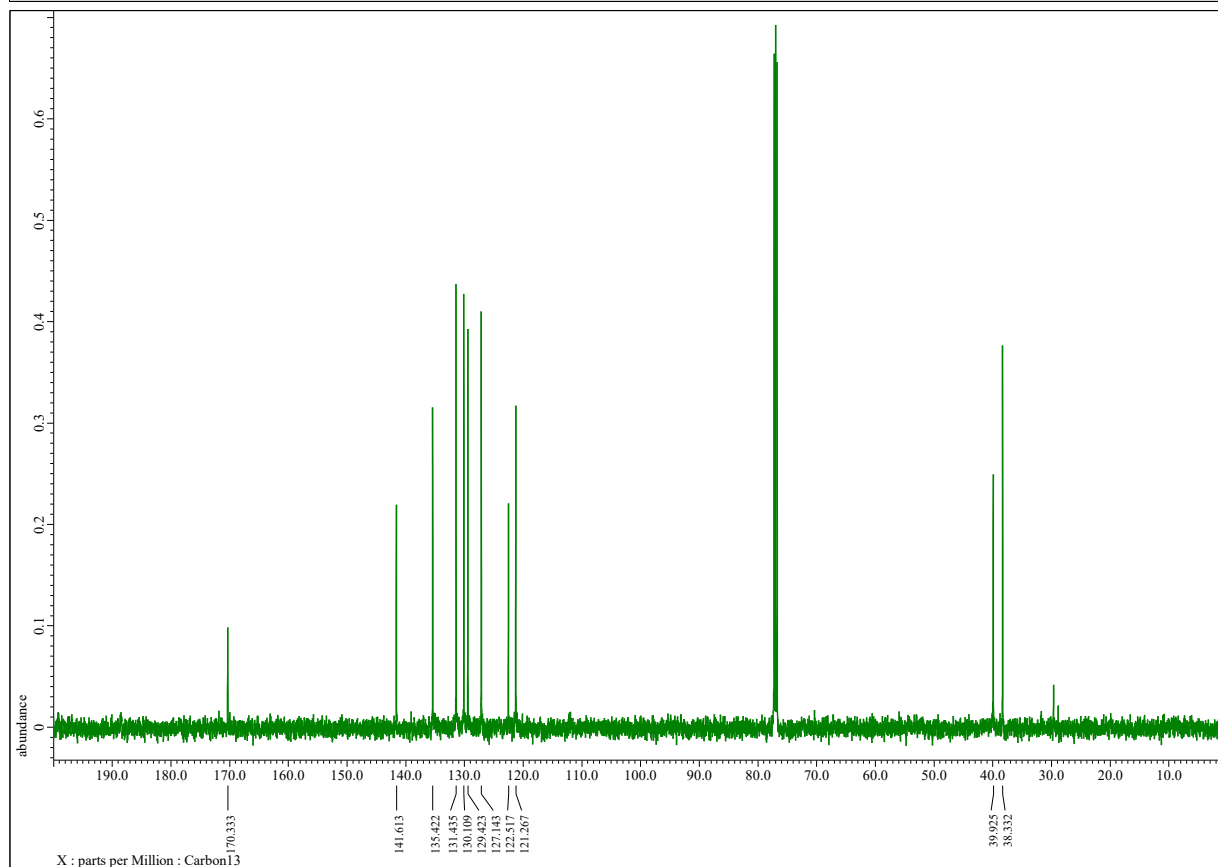
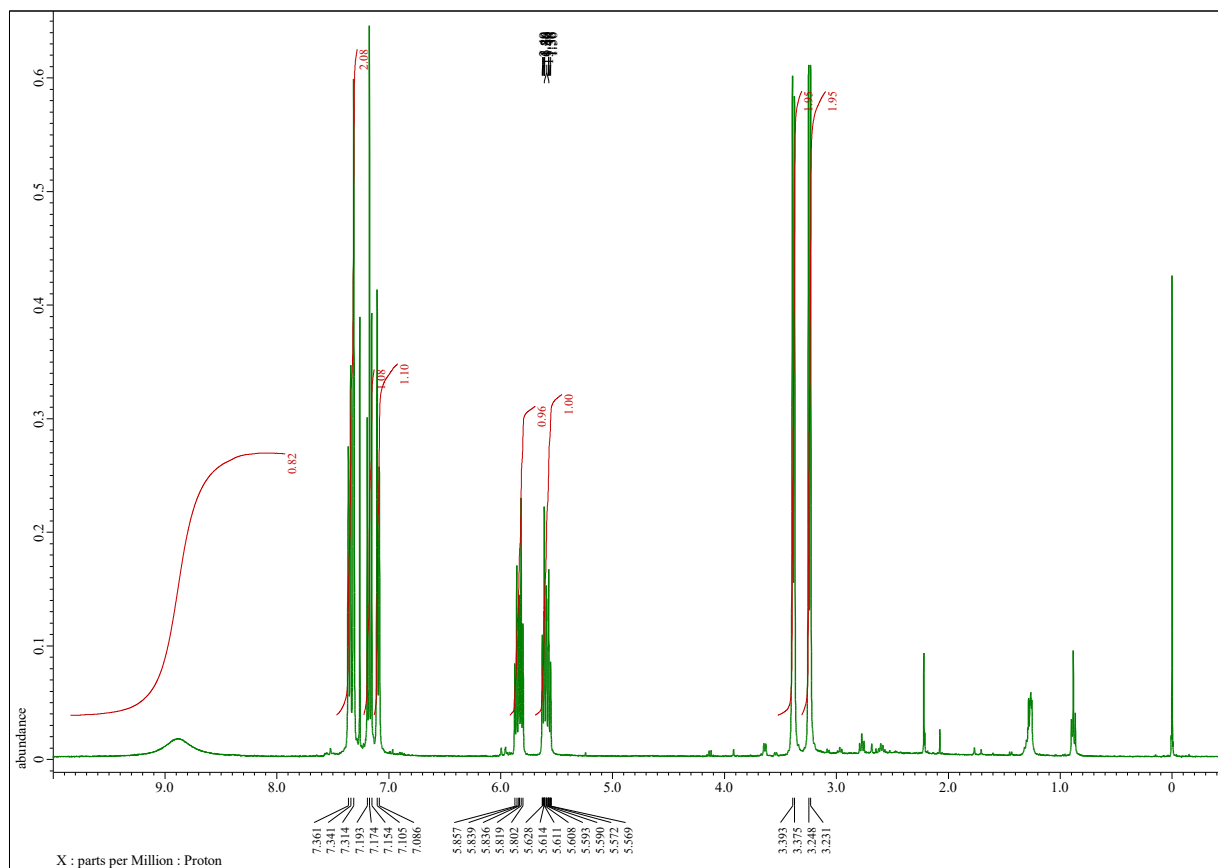
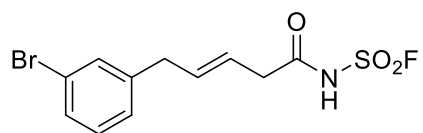


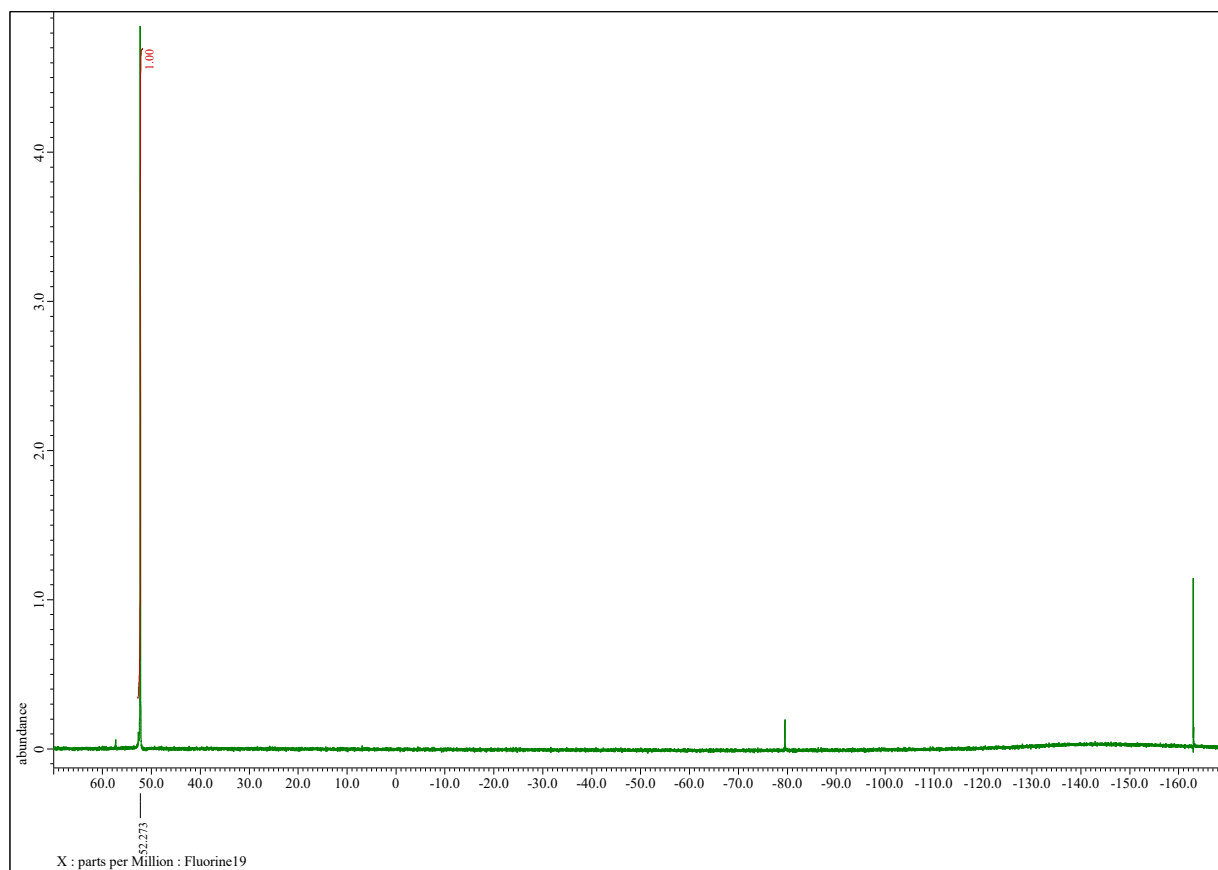
(E)-(5-(o-tolyl)pent-3-enoyl)sulfamoyl fluoride (3m)



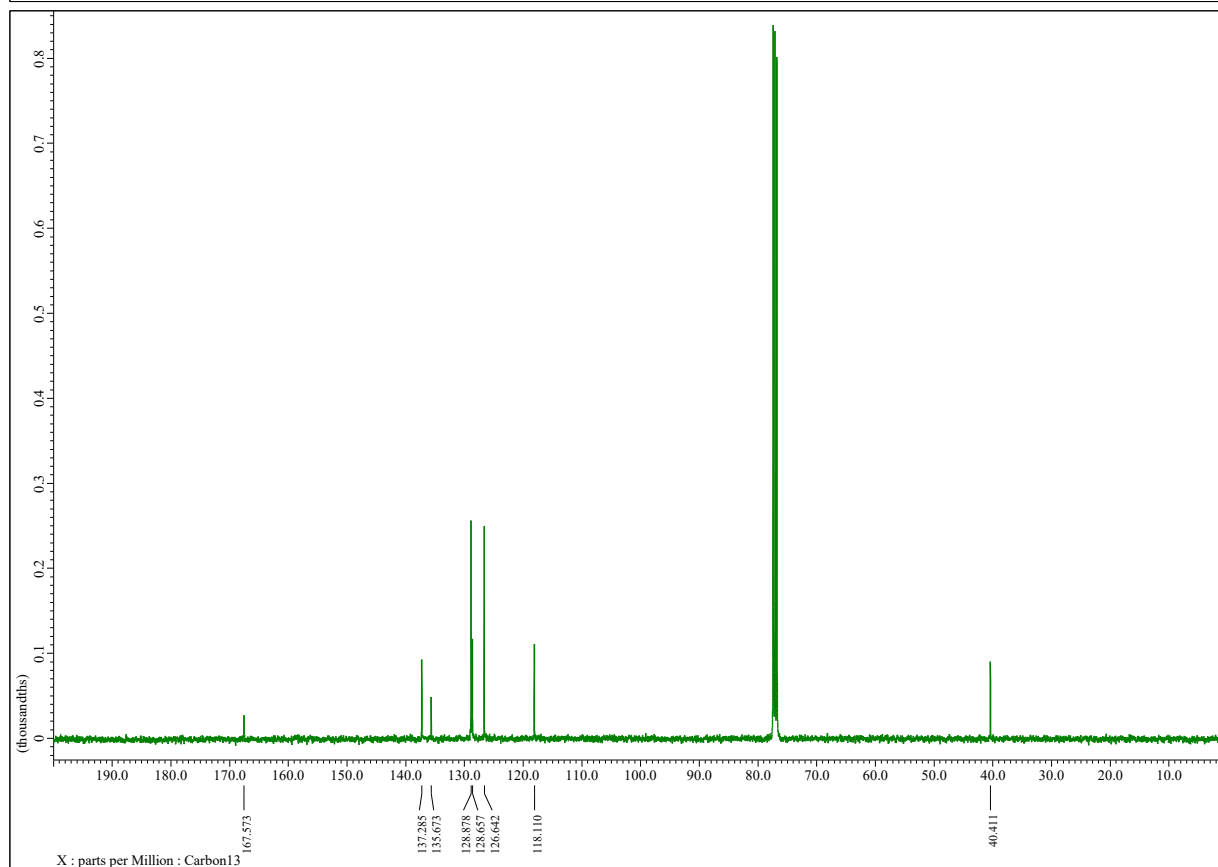
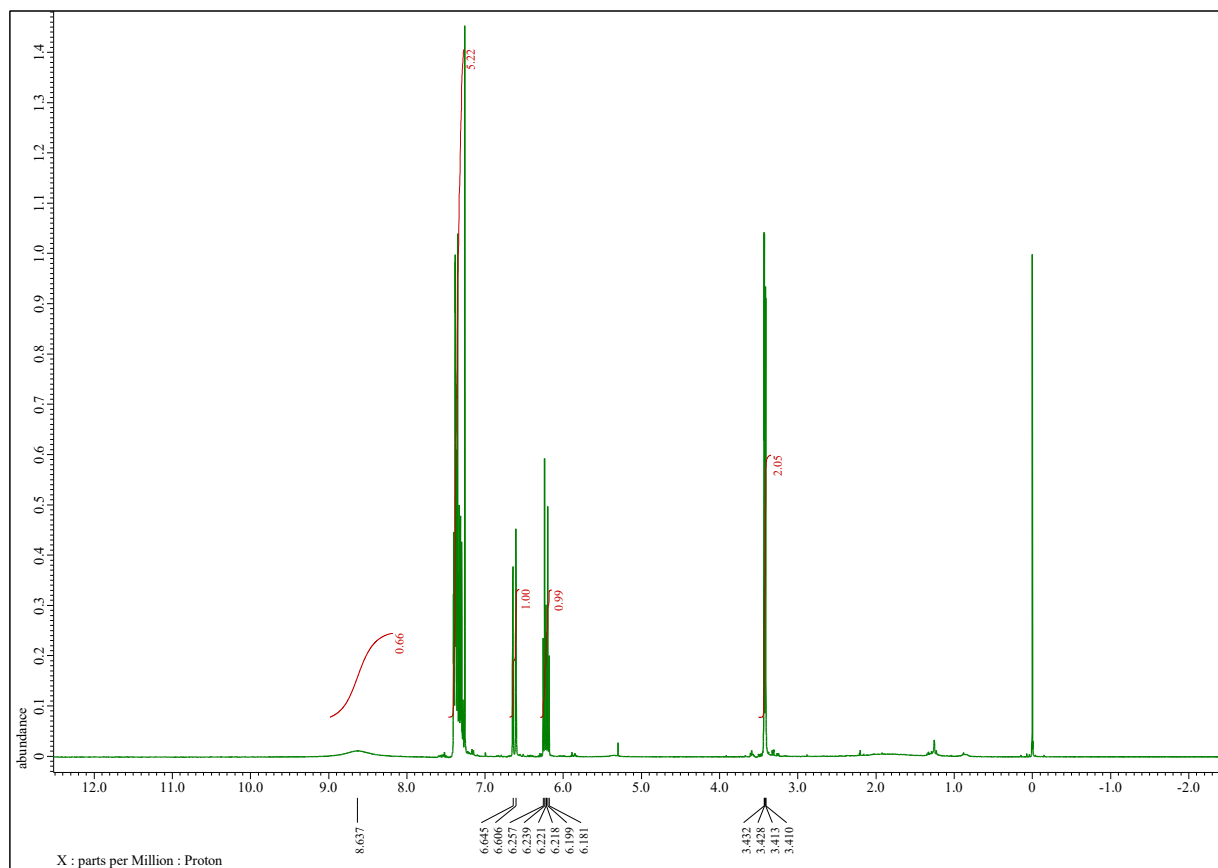
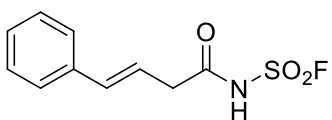


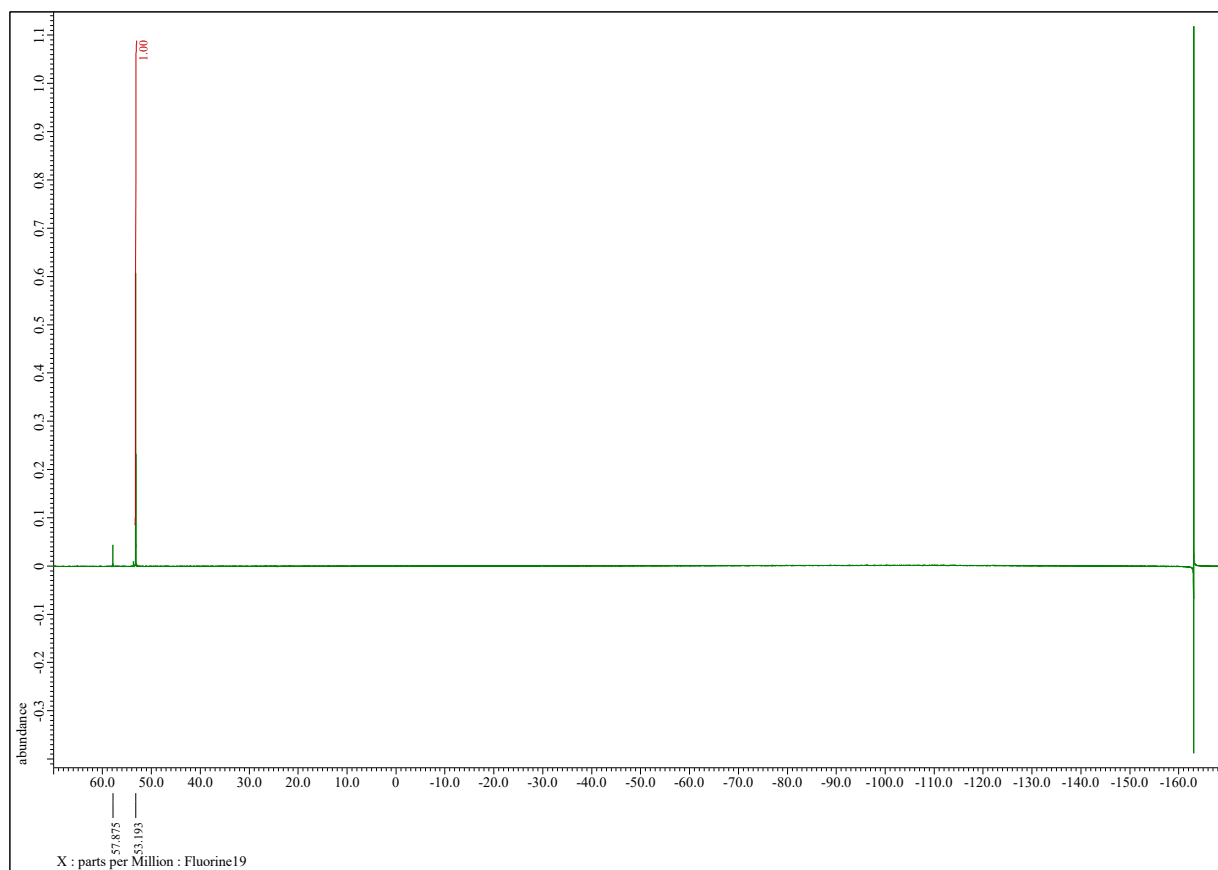
(E)-(5-(3-bromophenyl)pent-3-enoyl)sulfamoyl fluoride (3n)



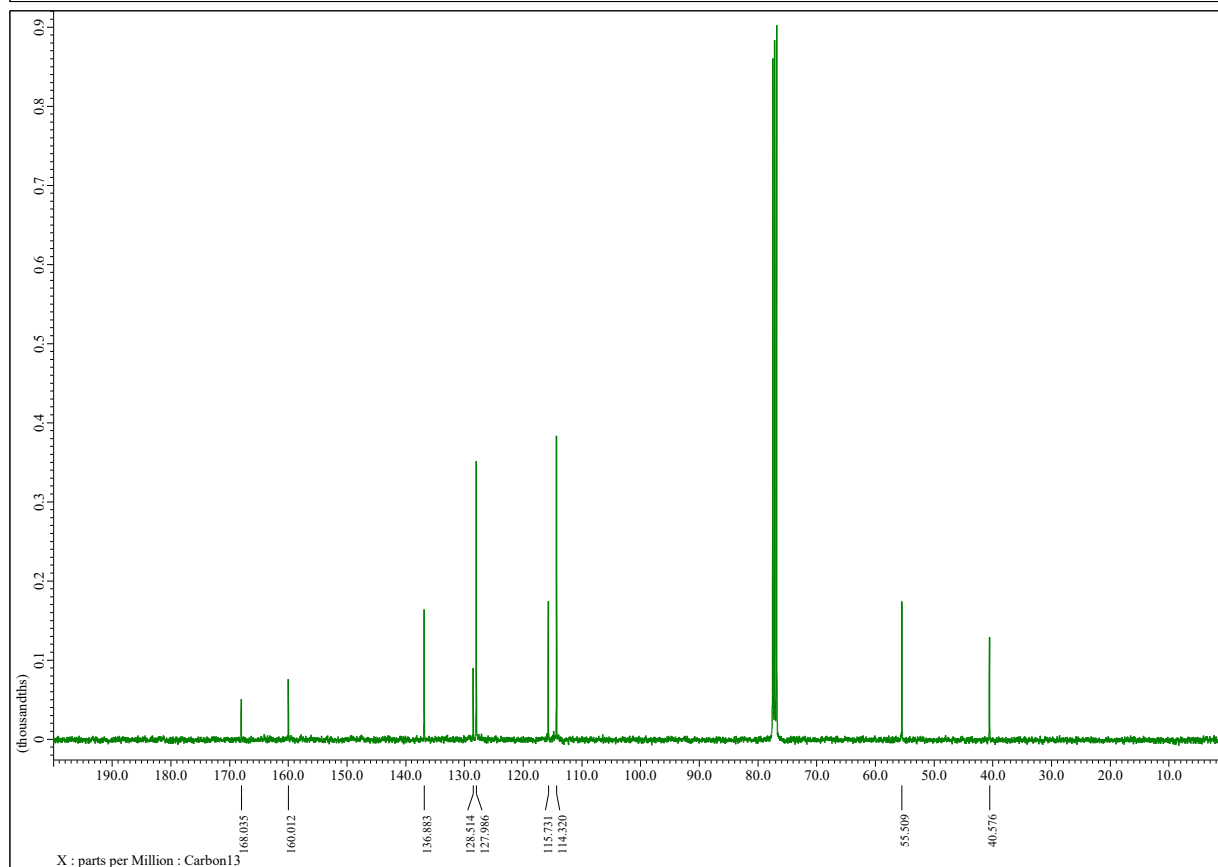
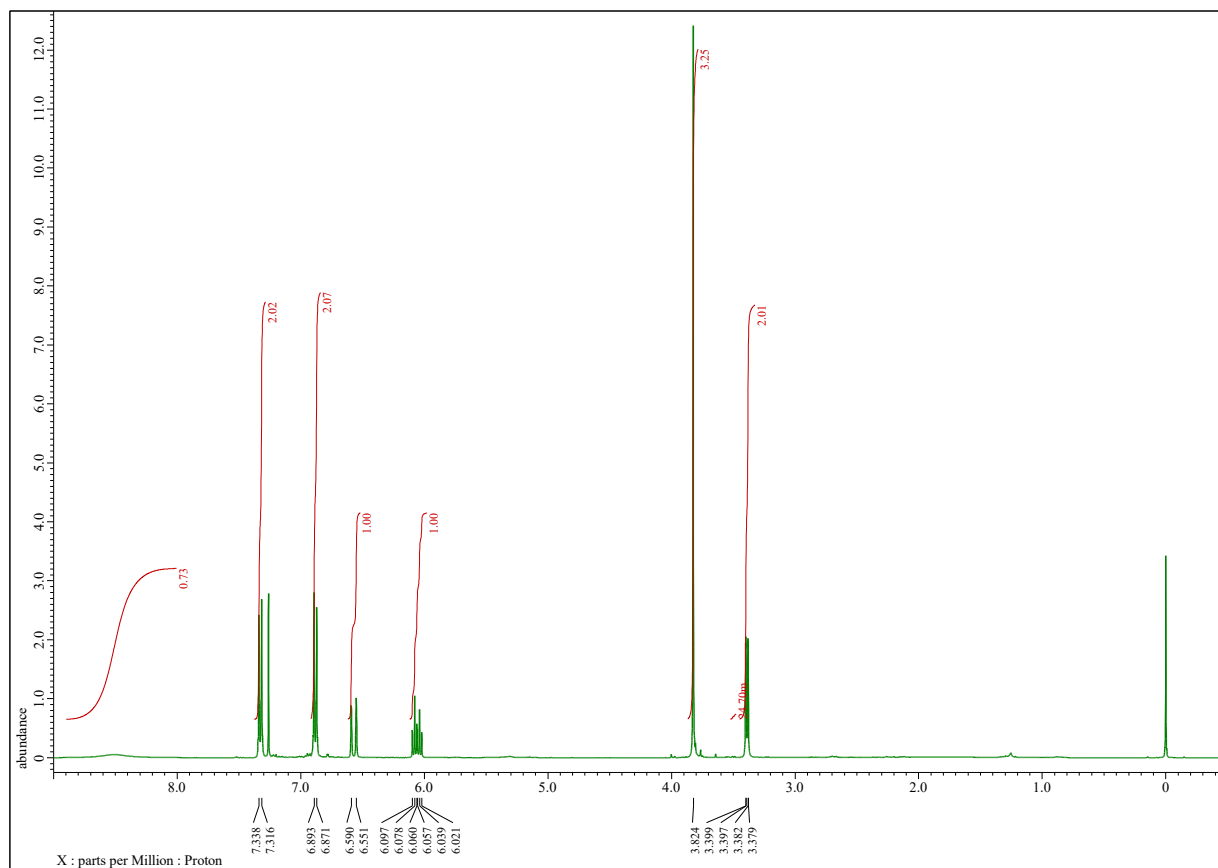
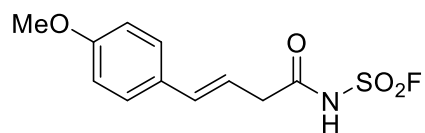


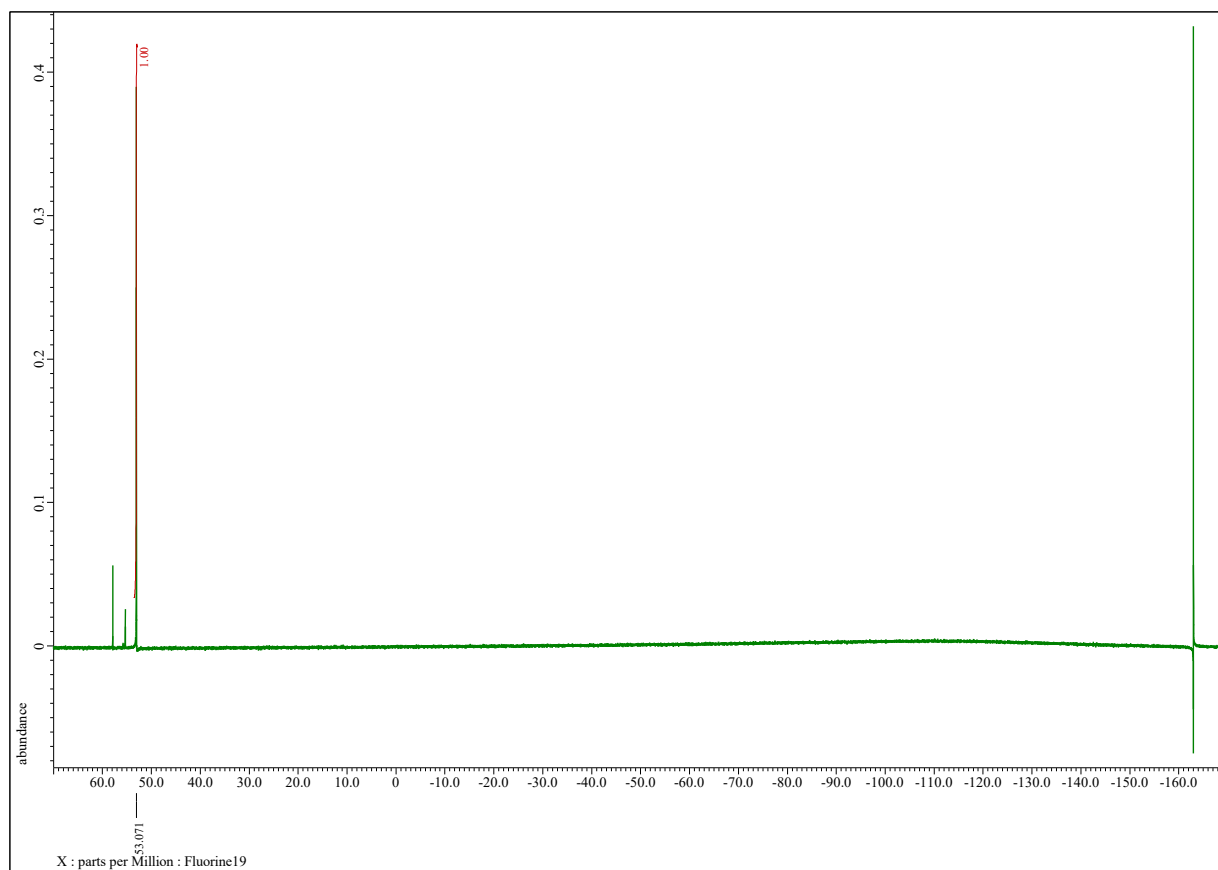
(E)-(4-phenylbut-3-enoyl)sulfamoyl fluoride (4a)



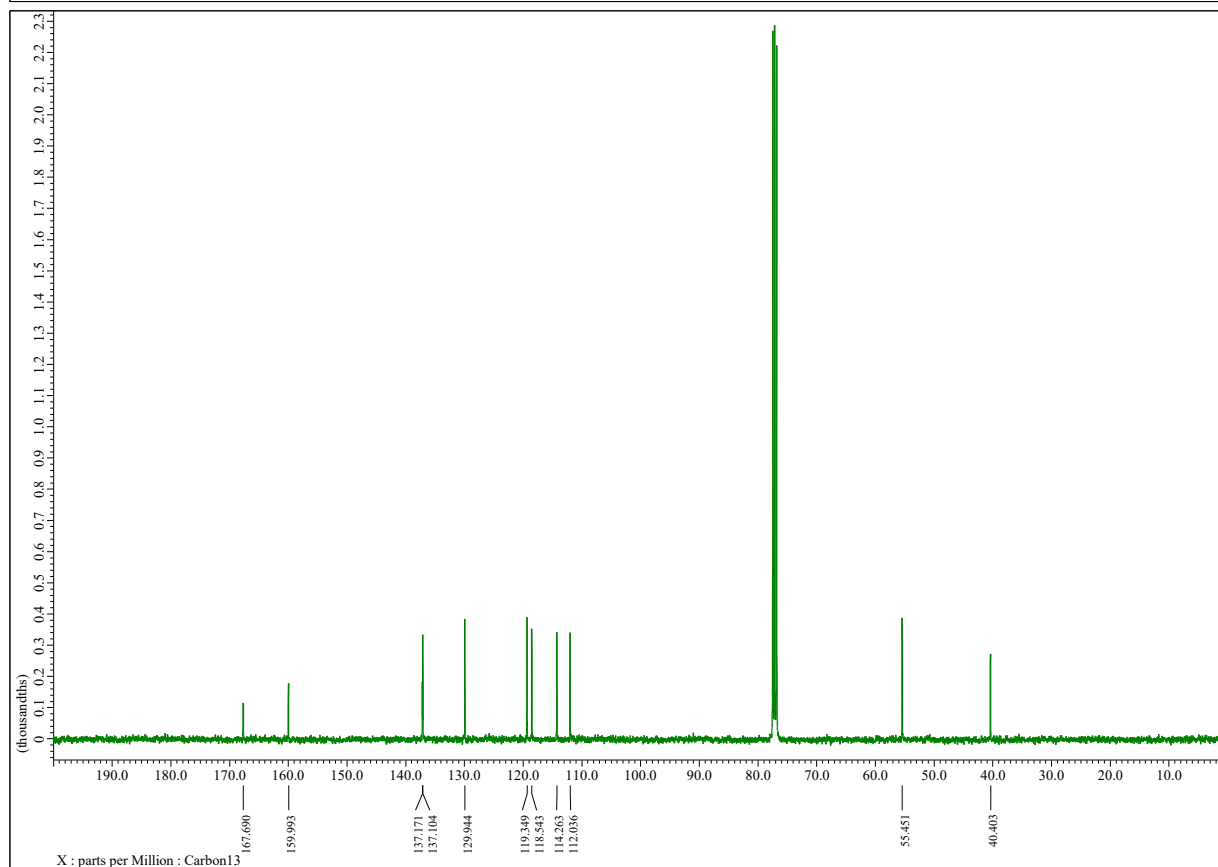
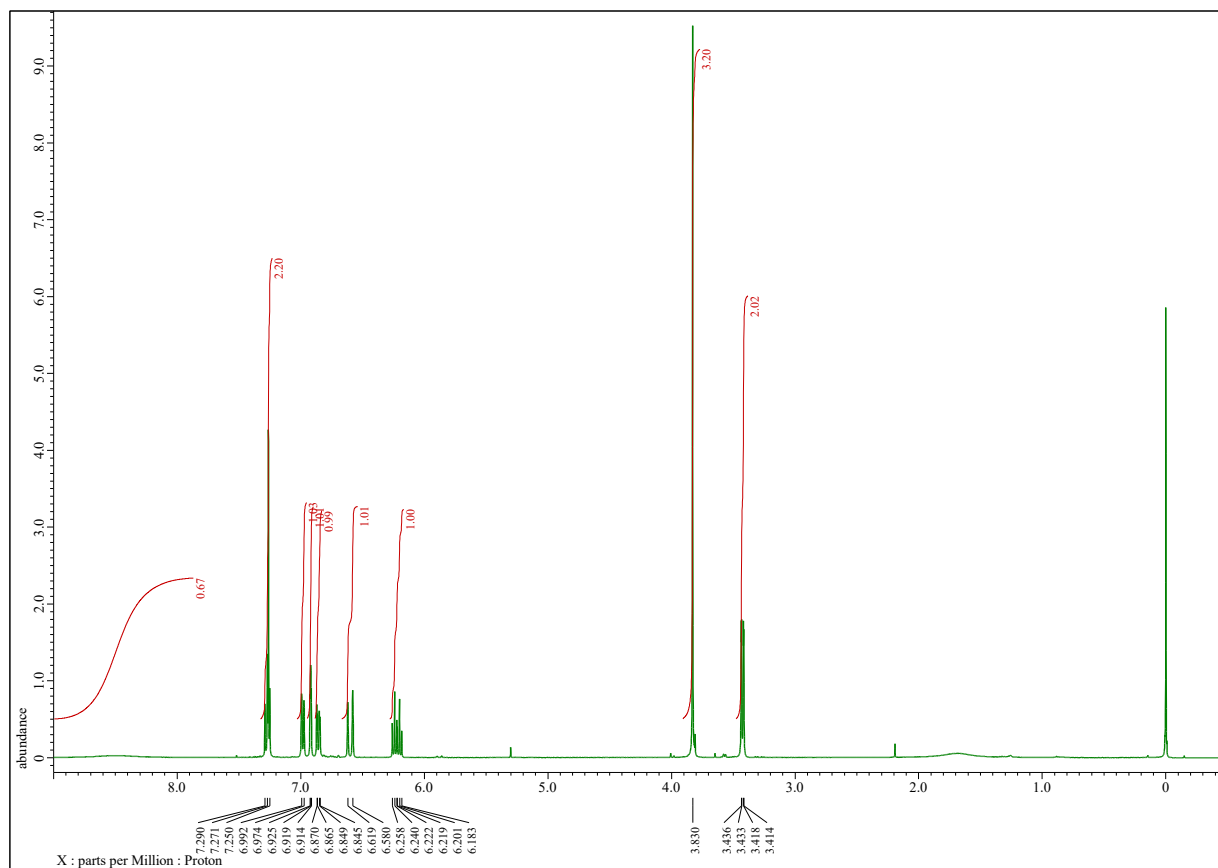
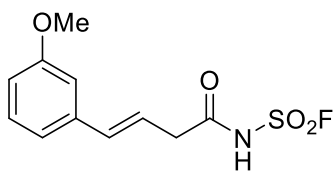


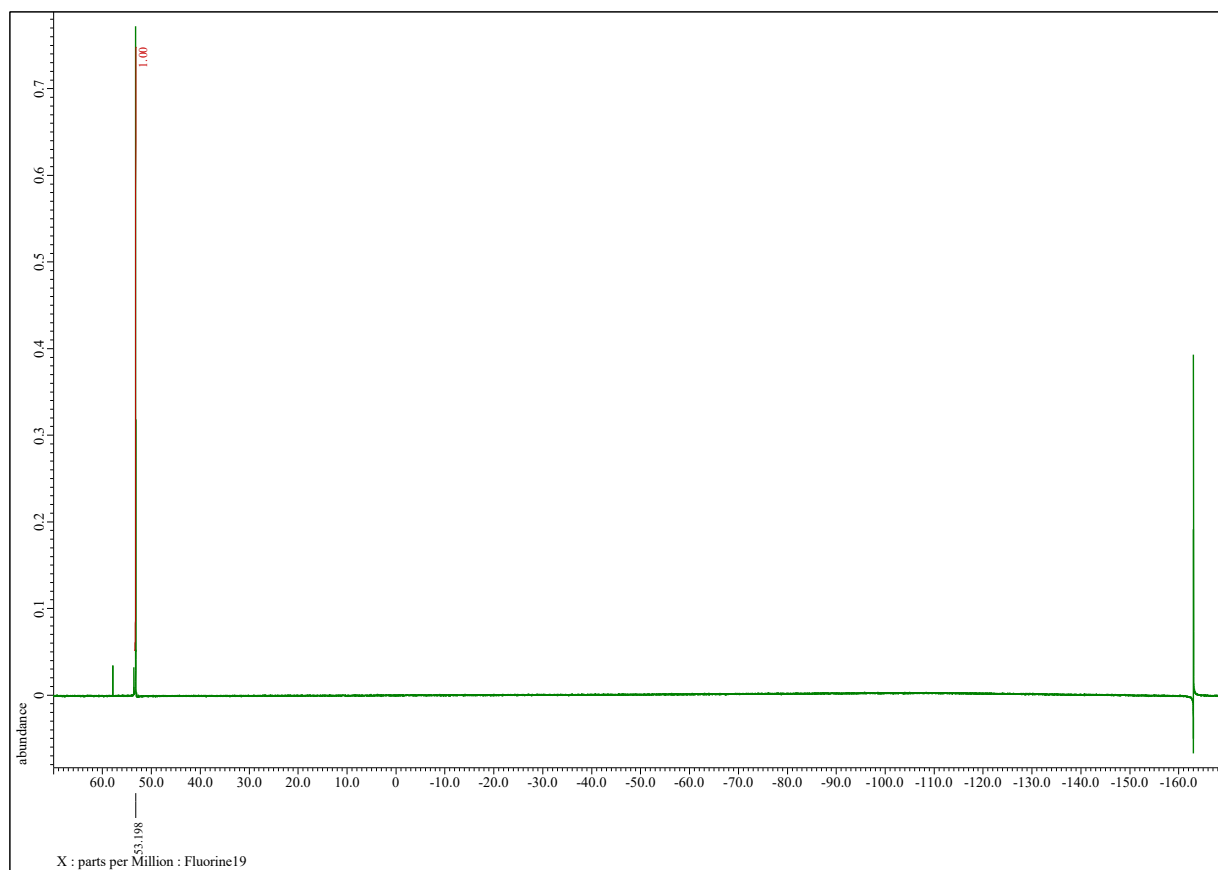
(E)-(4-(4-methoxyphenyl)but-3-enoyl)sulfamoyl fluoride (4b)



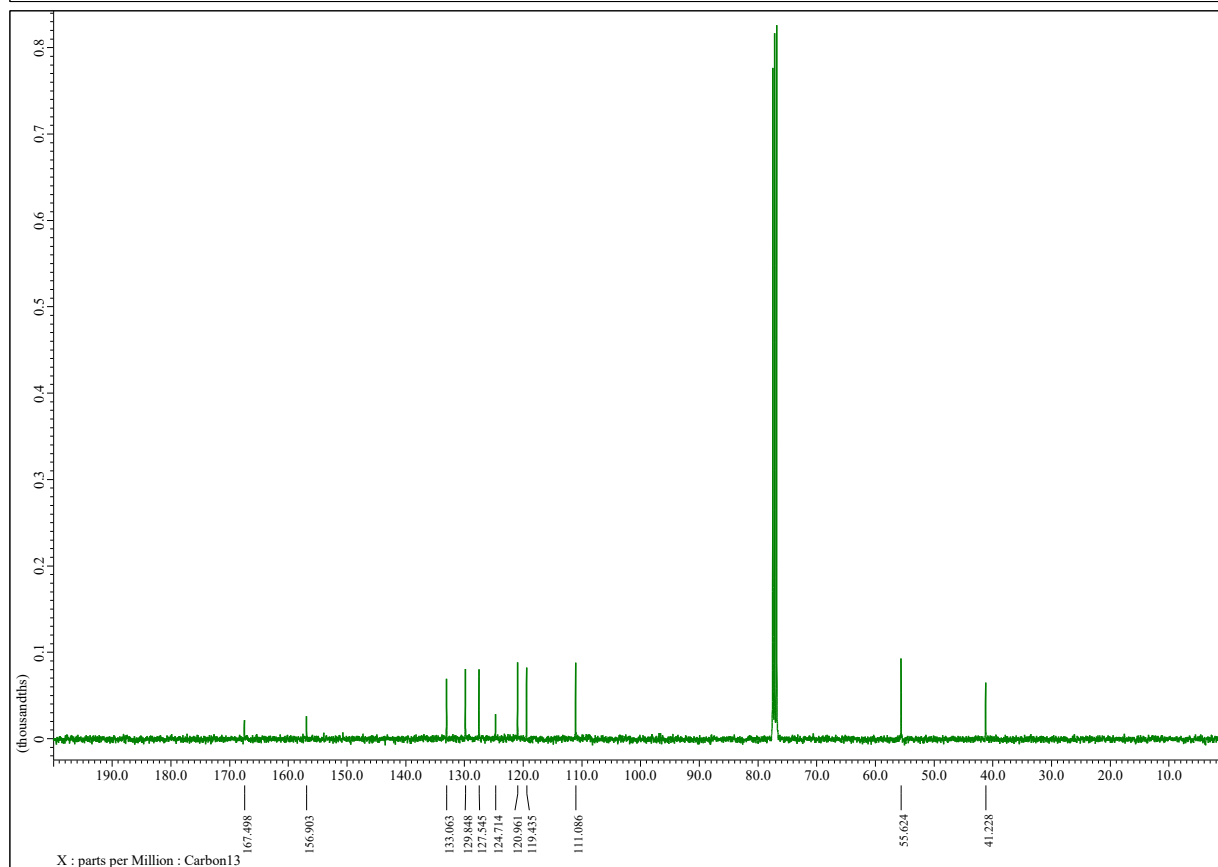
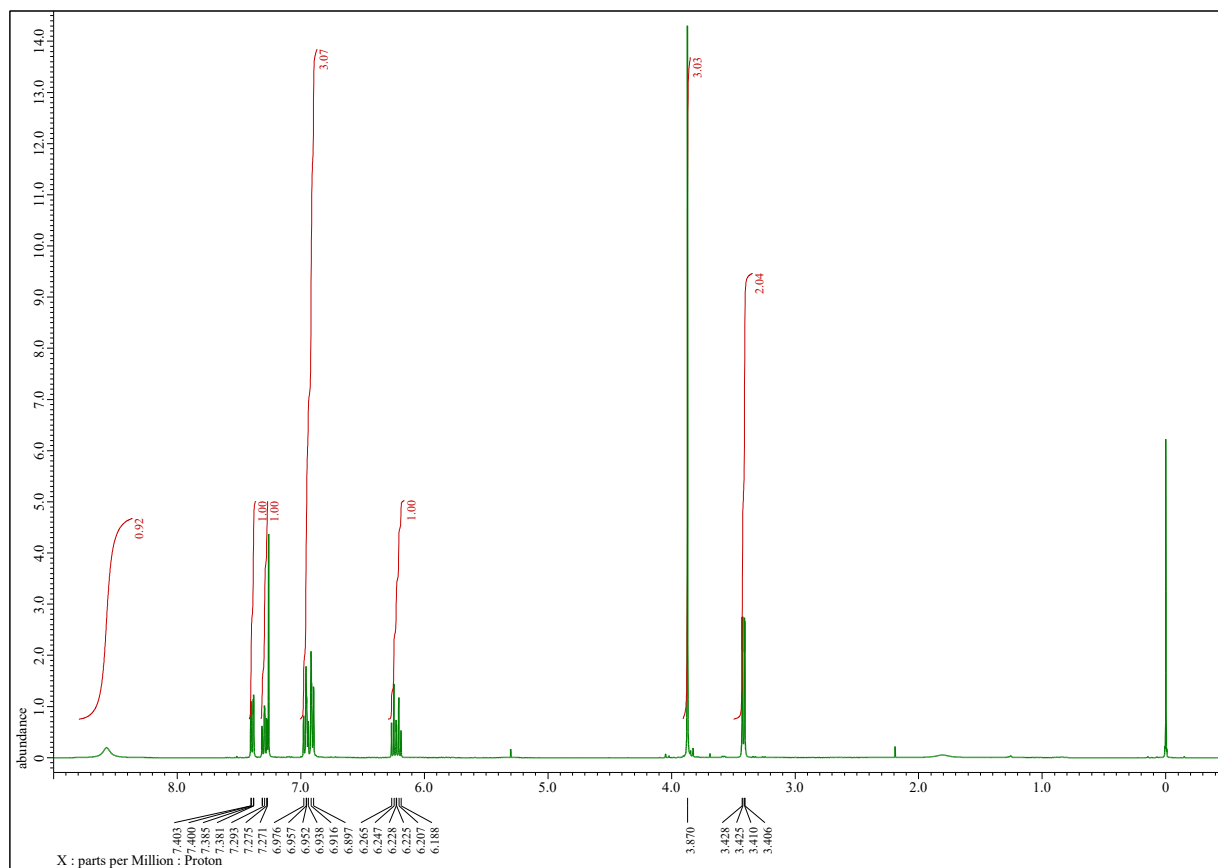
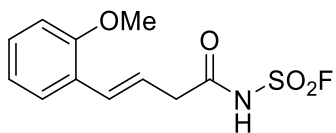


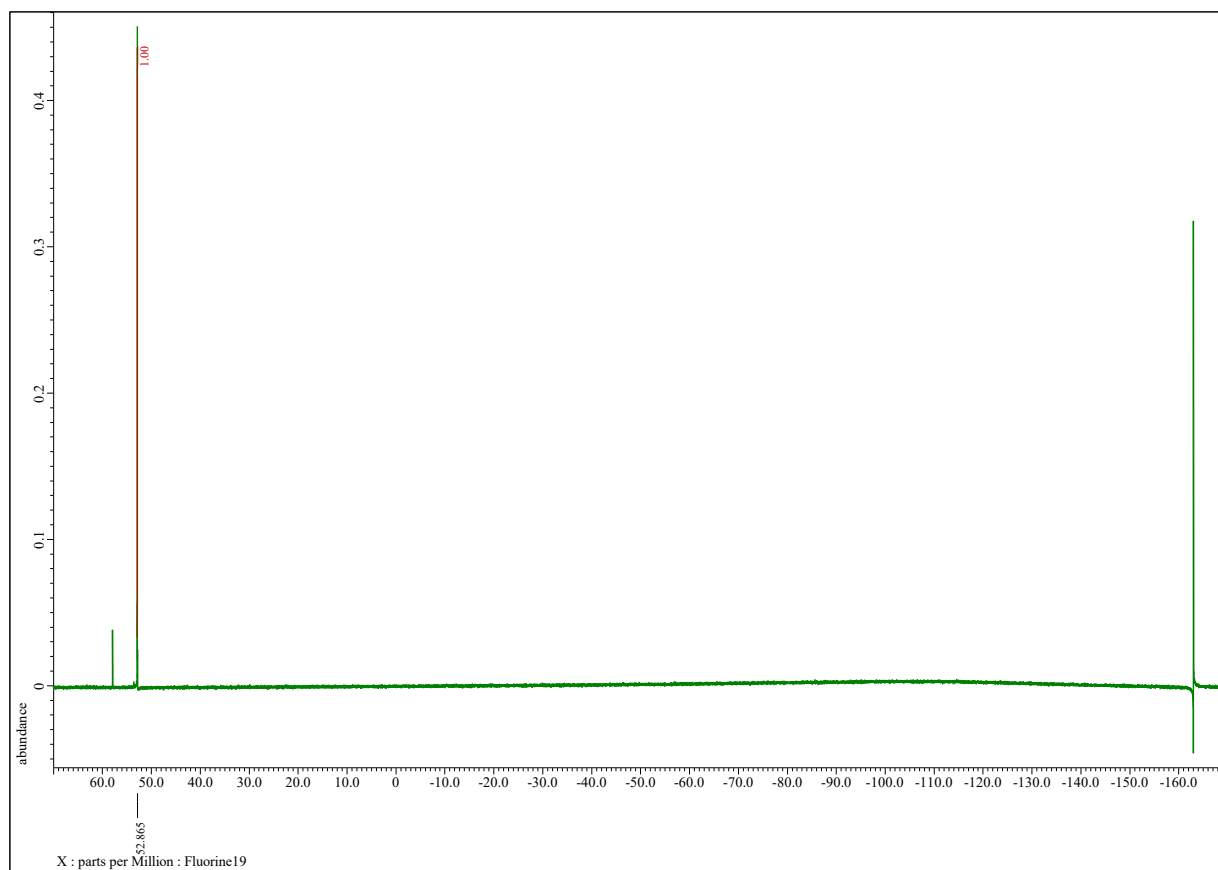
(E)-(4-(3-methoxyphenyl)but-3-enyl)sulfamoyl fluoride (4c)



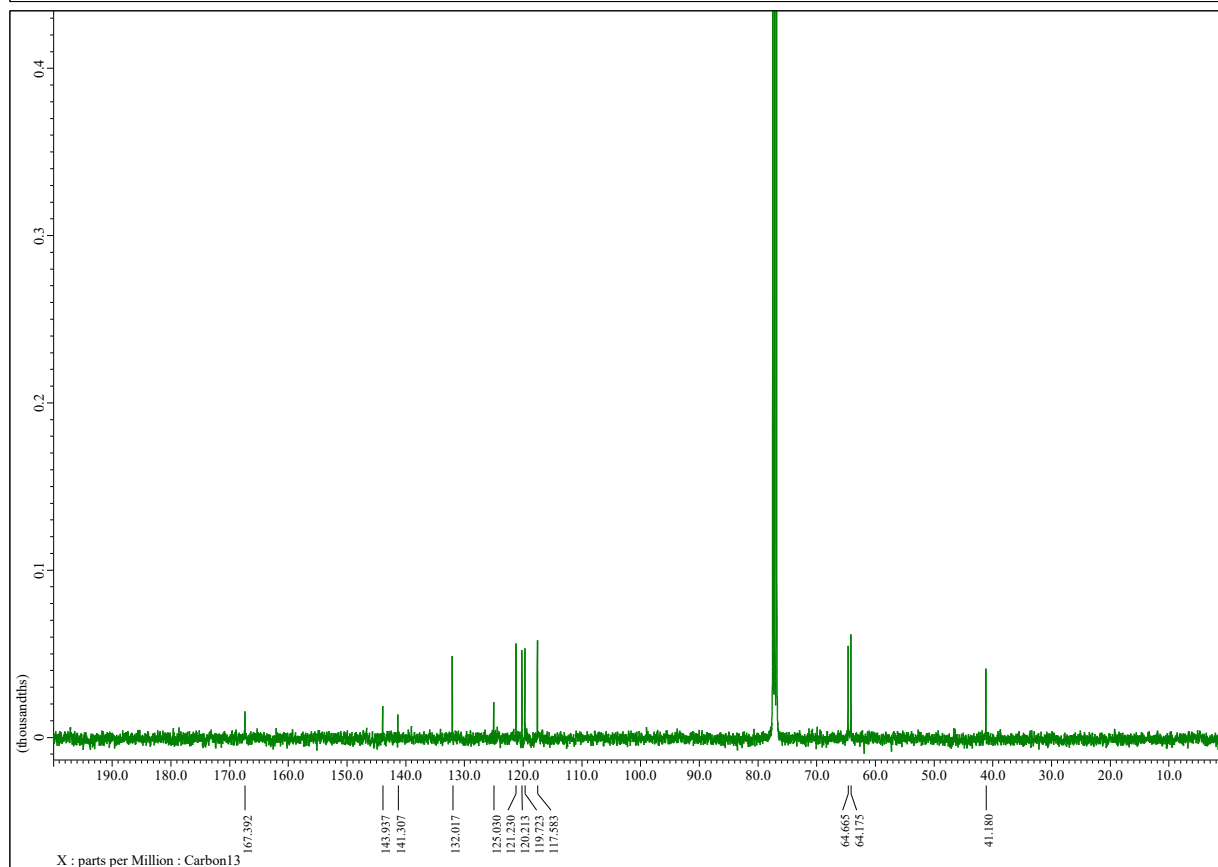
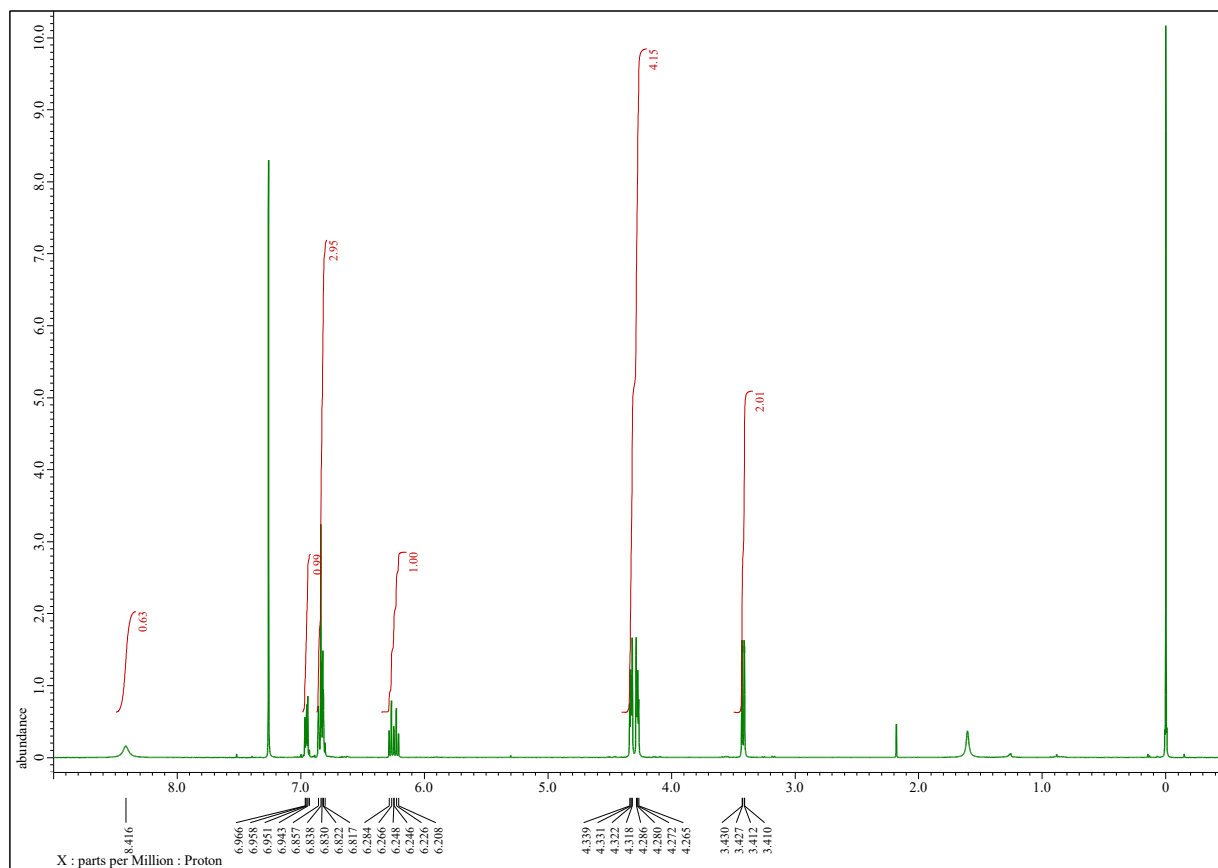
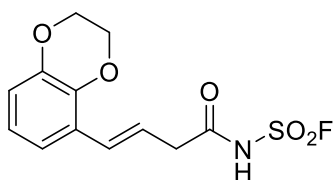


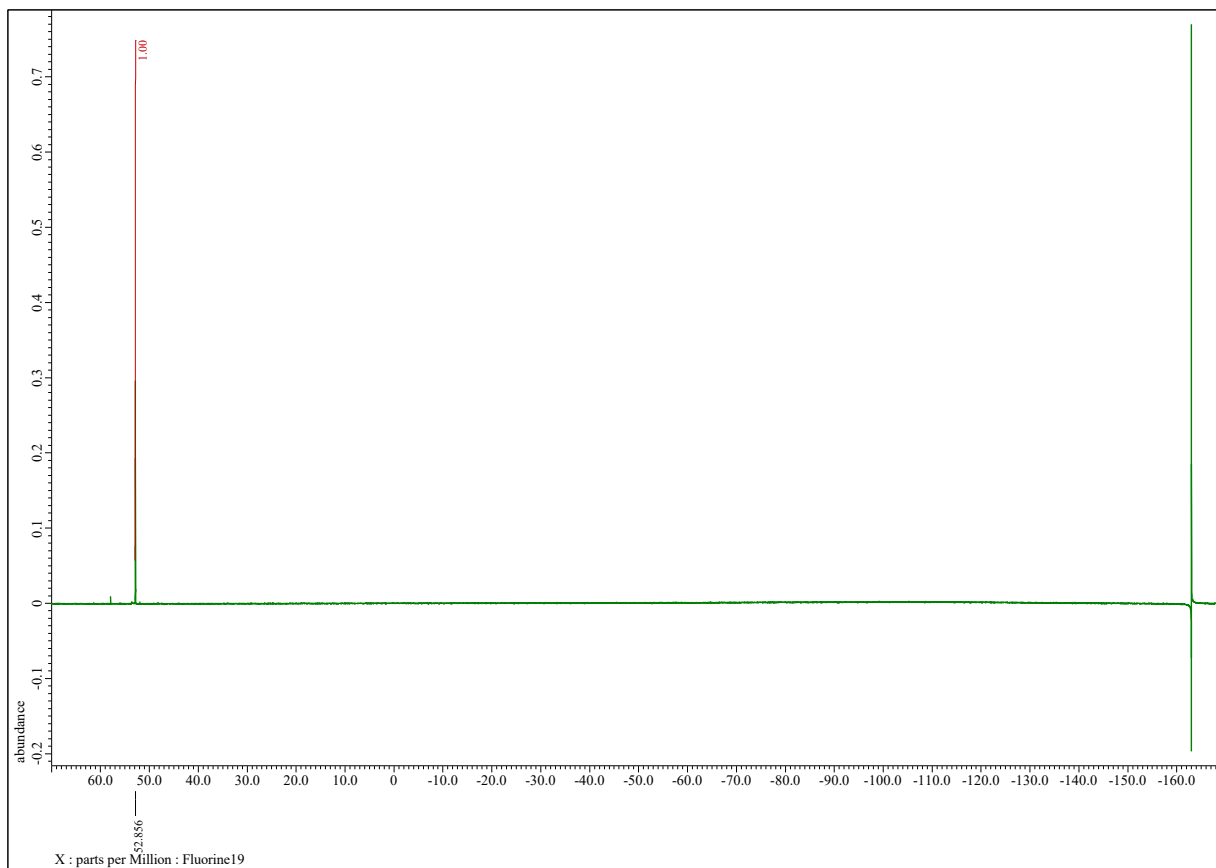
(E)-(4-(2-methoxyphenyl)but-3-enyl)sulfamoyl fluoride (4d)



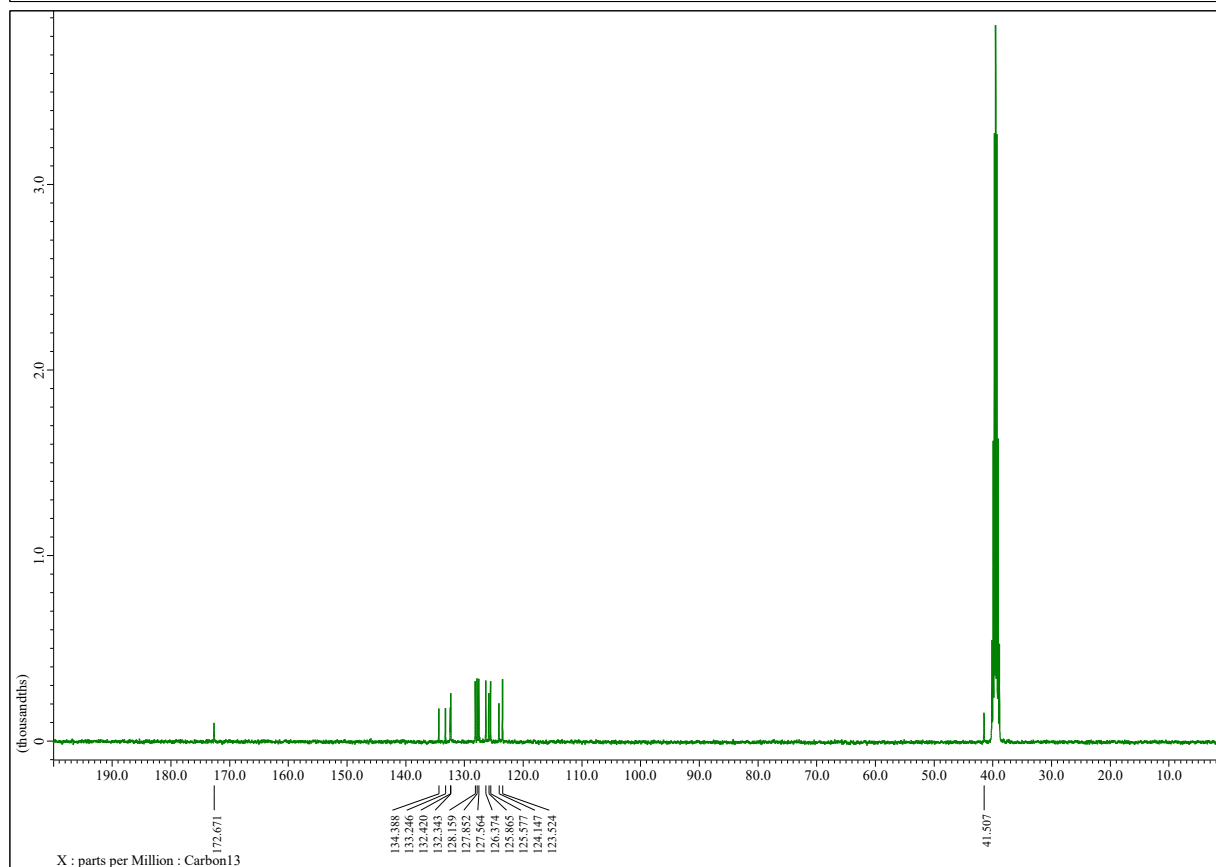
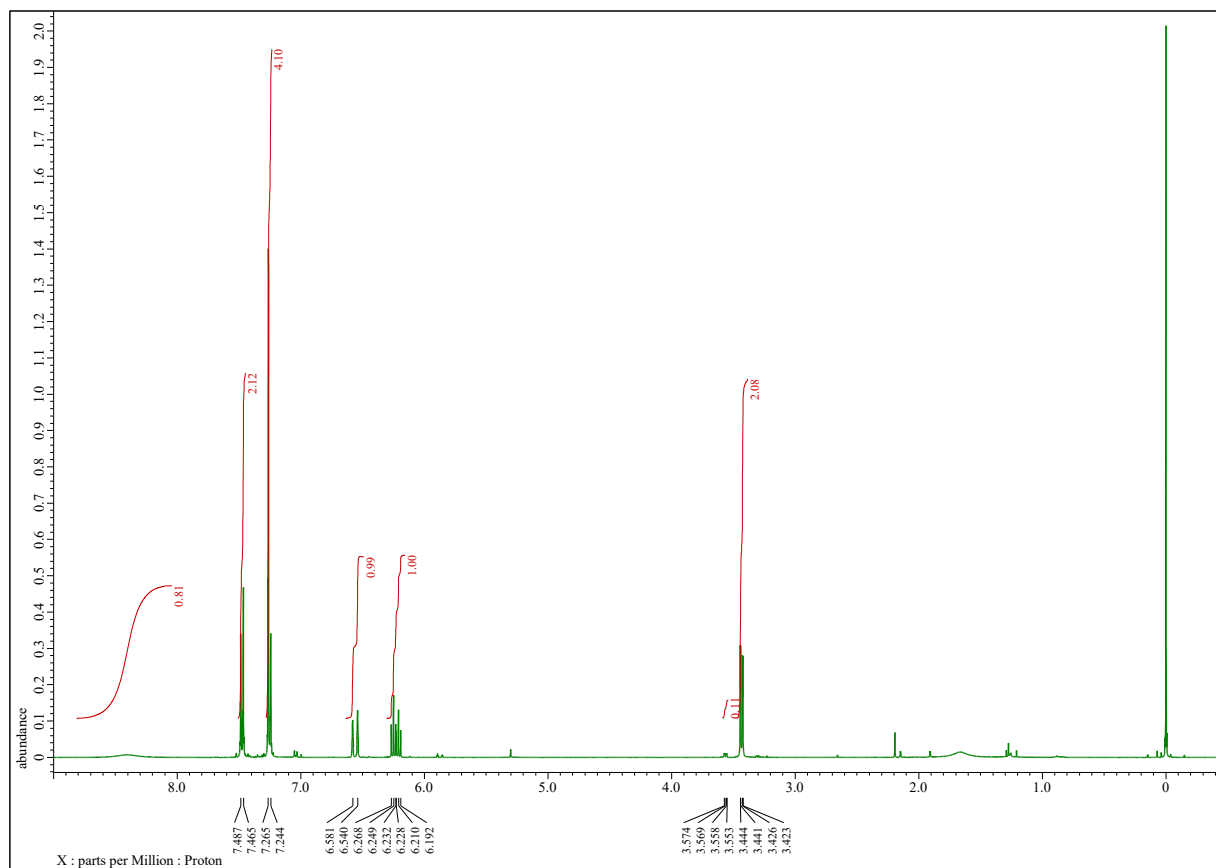
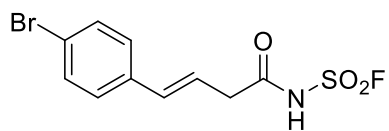


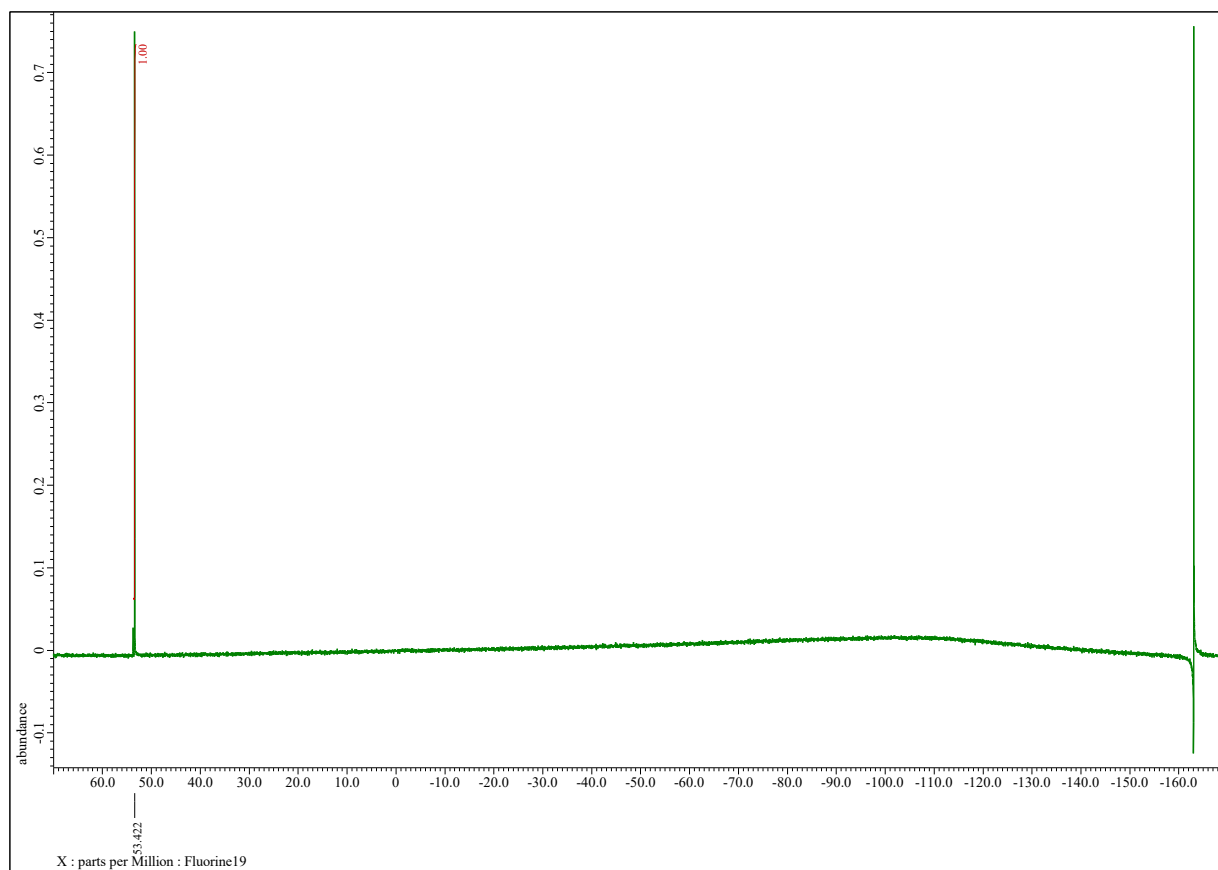
(E)-(4-(2,3-dihydrobenzo[b][1,4]dioxin-5-yl)but-3-enoyl)sulfamoyl fluoride (4e)



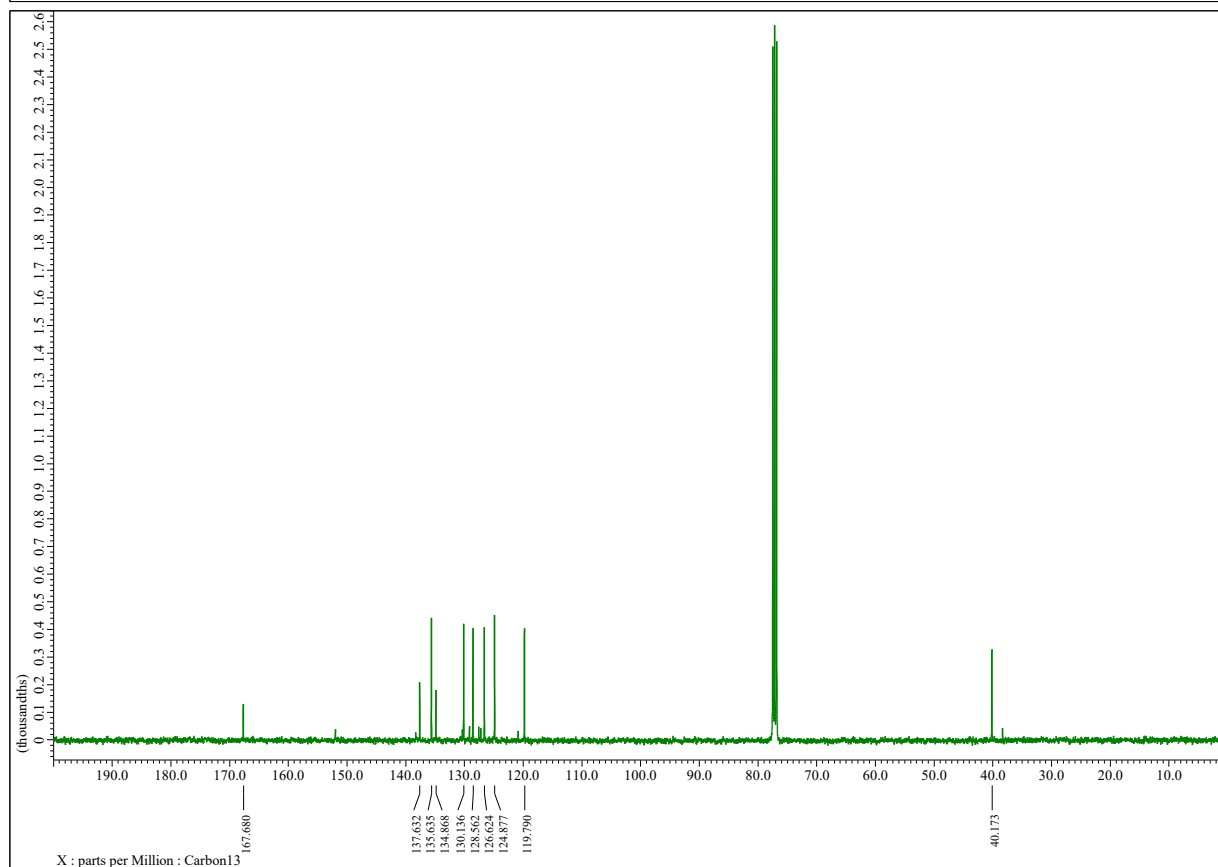
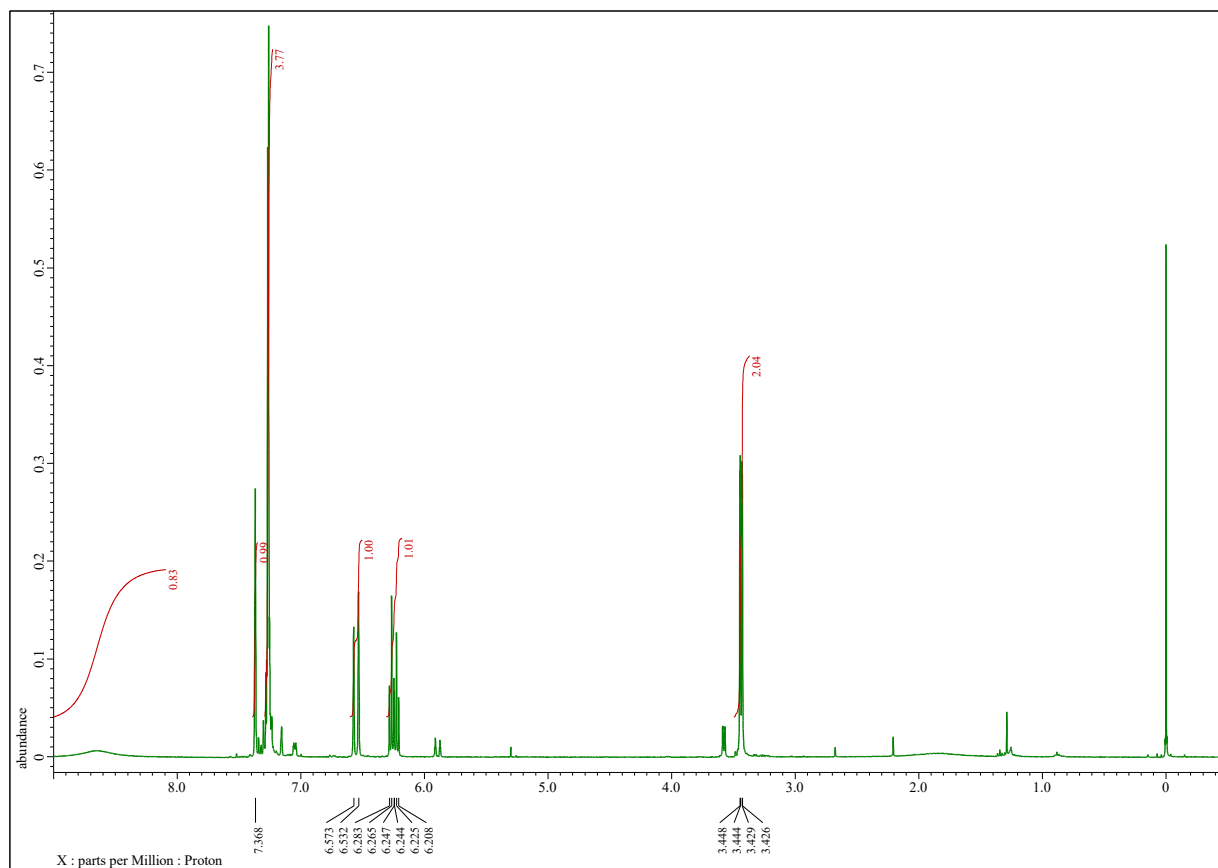
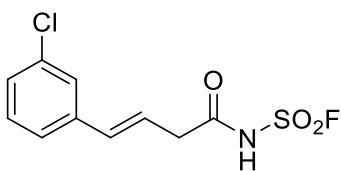


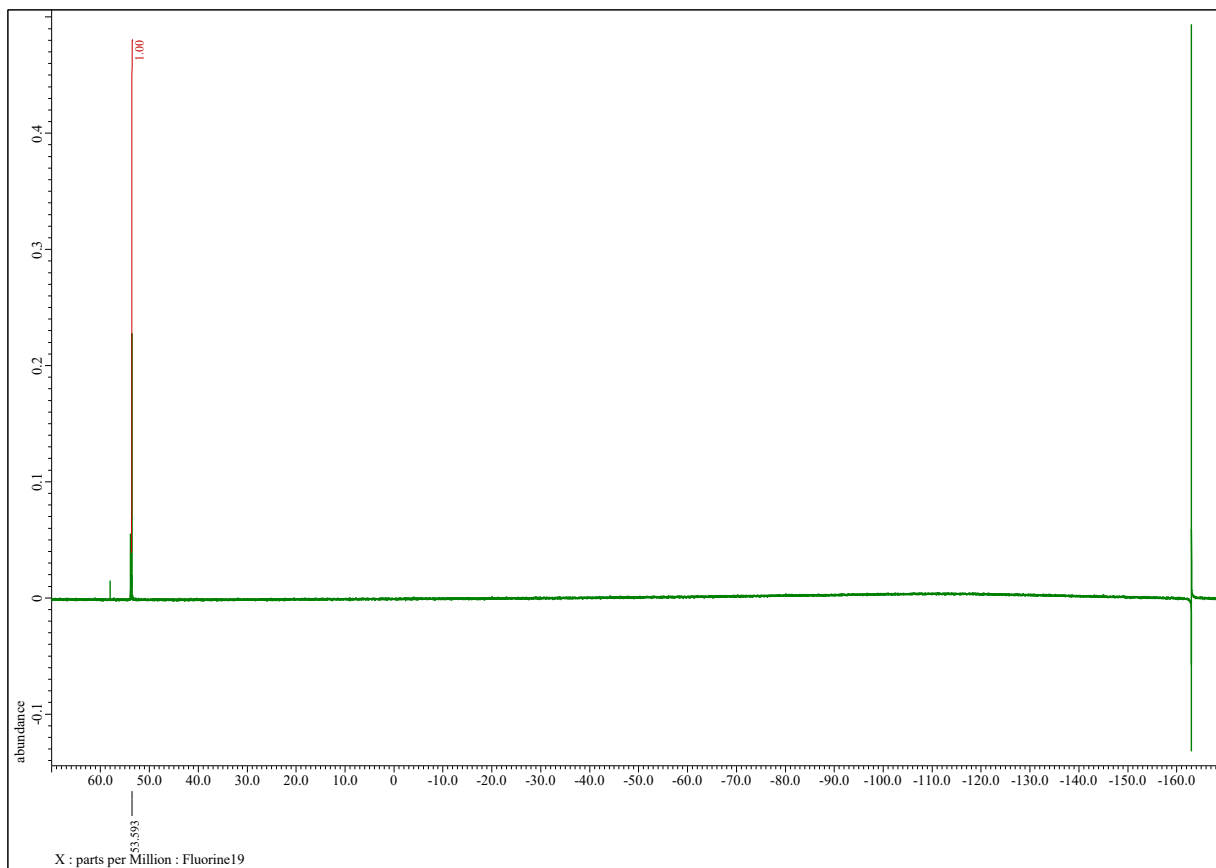
(E)-(4-(4-bromophenyl)but-3-enoyl)sulfamoyl fluoride (4f)



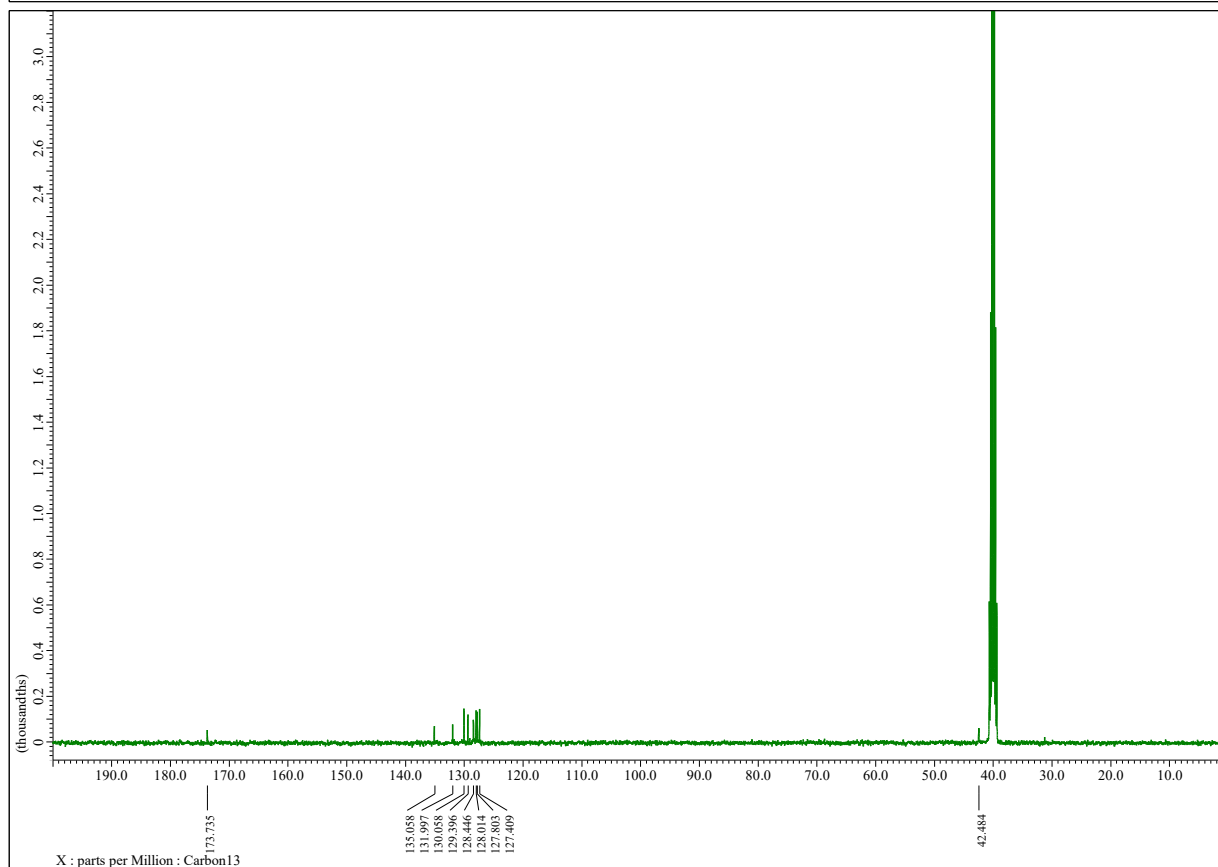
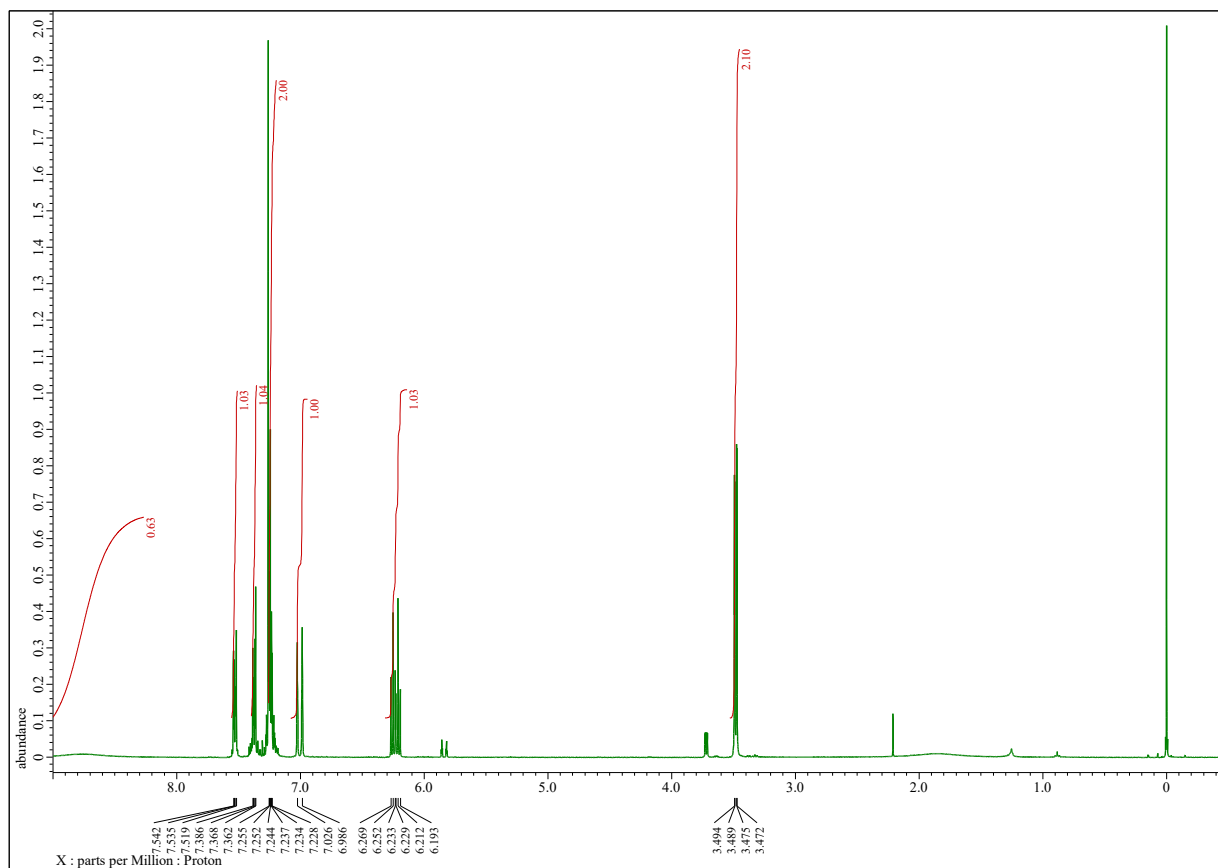
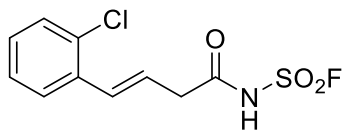


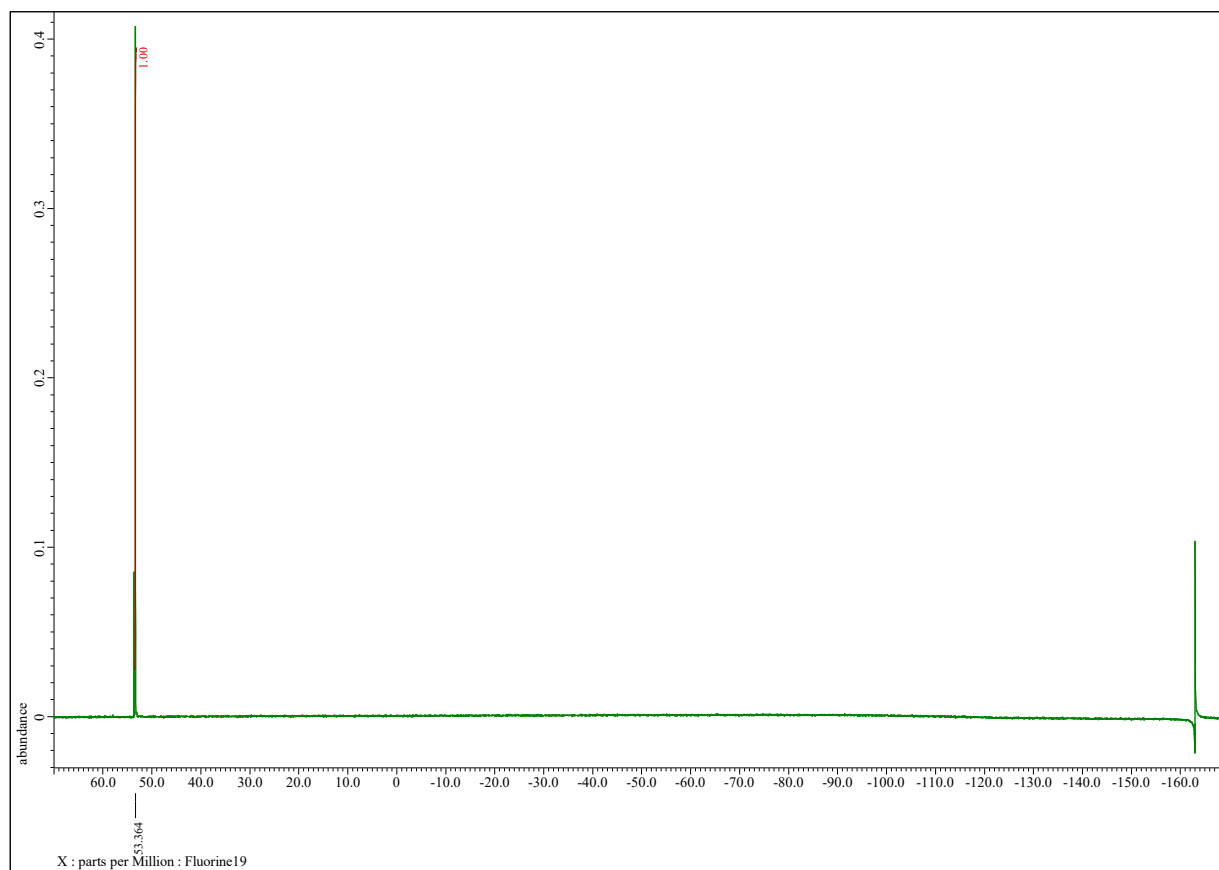
(E)-(4-(3-chlorophenyl)but-3-enyl)sulfamoyl fluoride (4g)



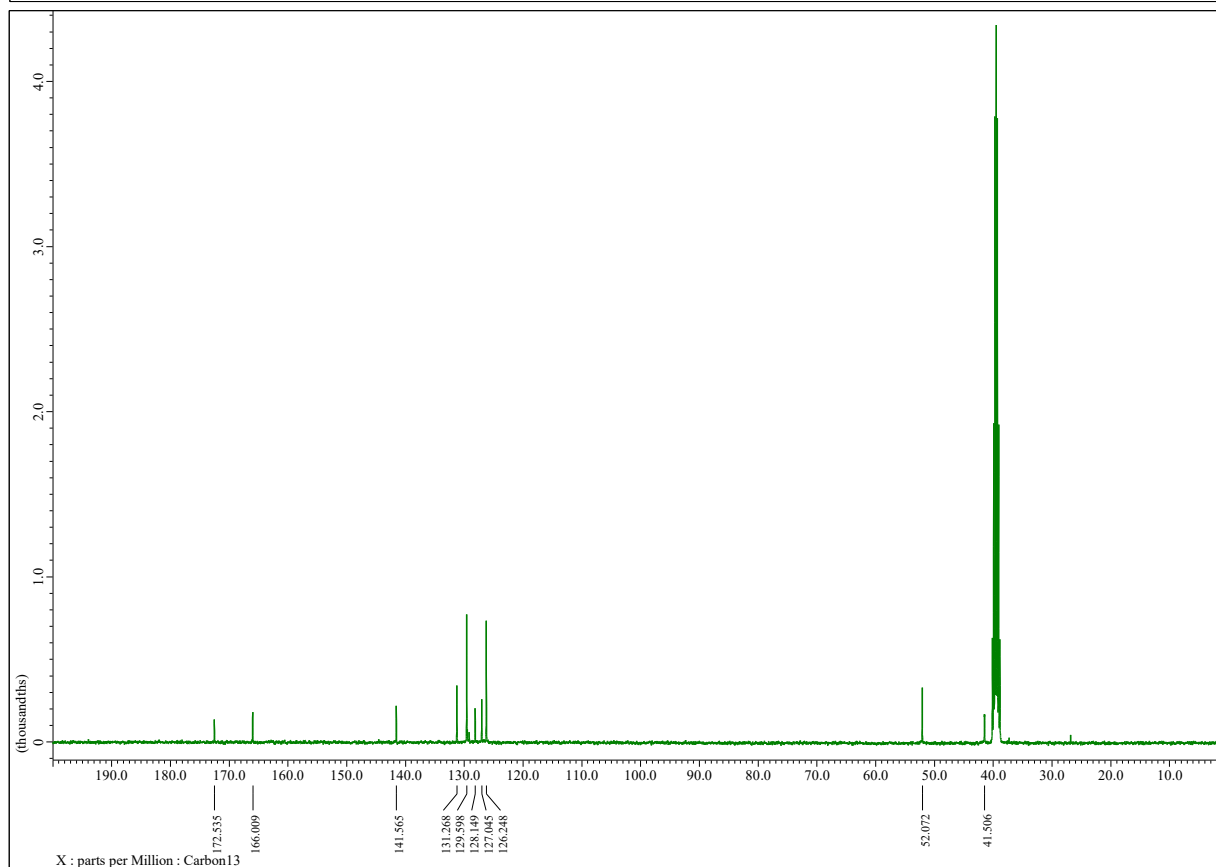
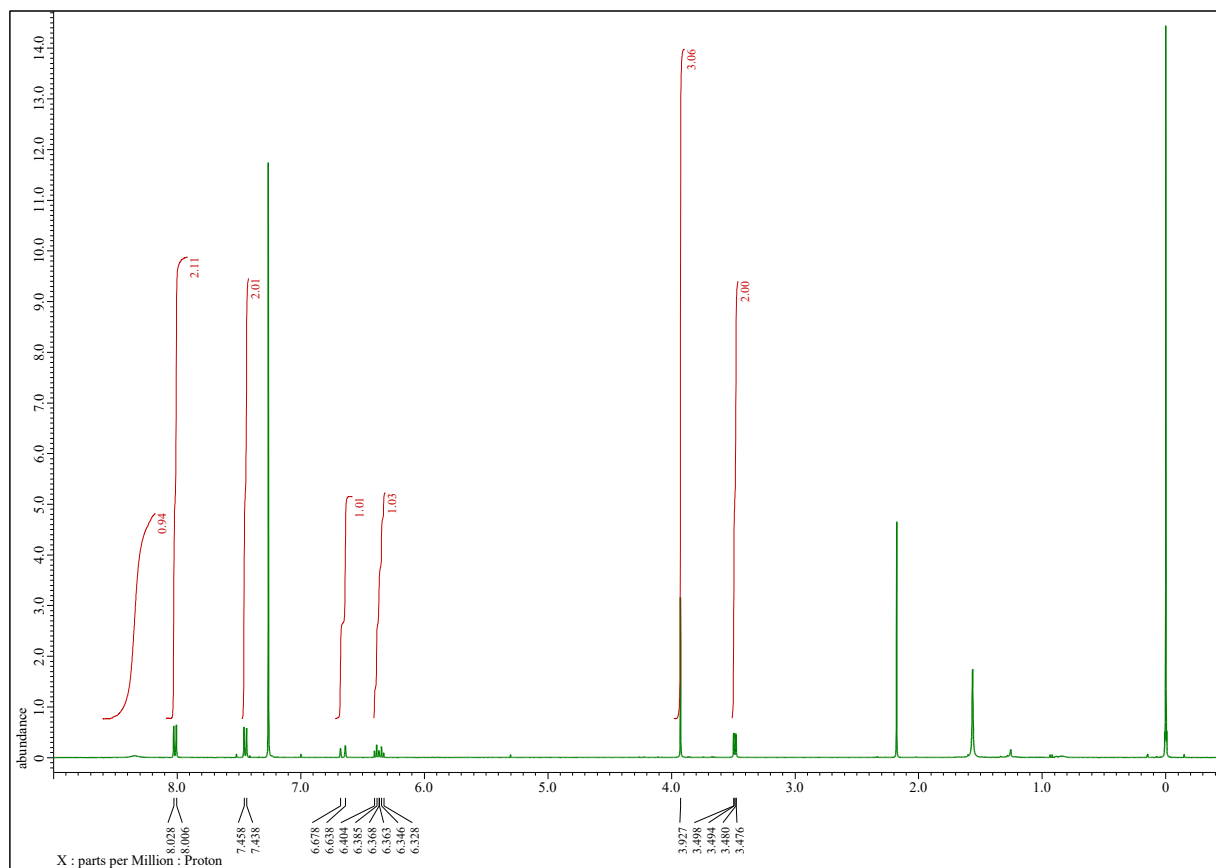
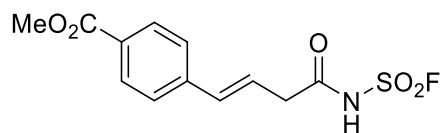


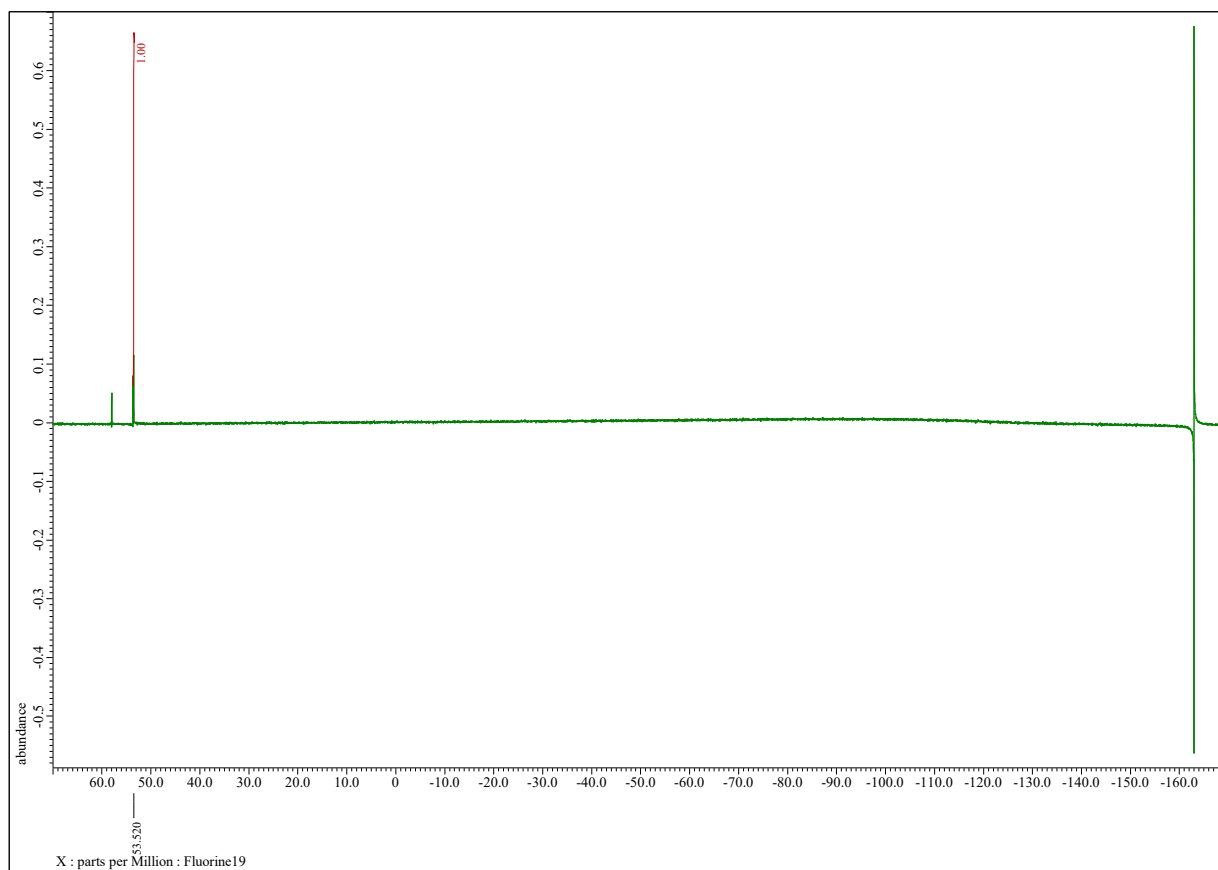
(E)-(4-(2-chlorophenyl)but-3-enyl)sulfamoyl fluoride (4h)



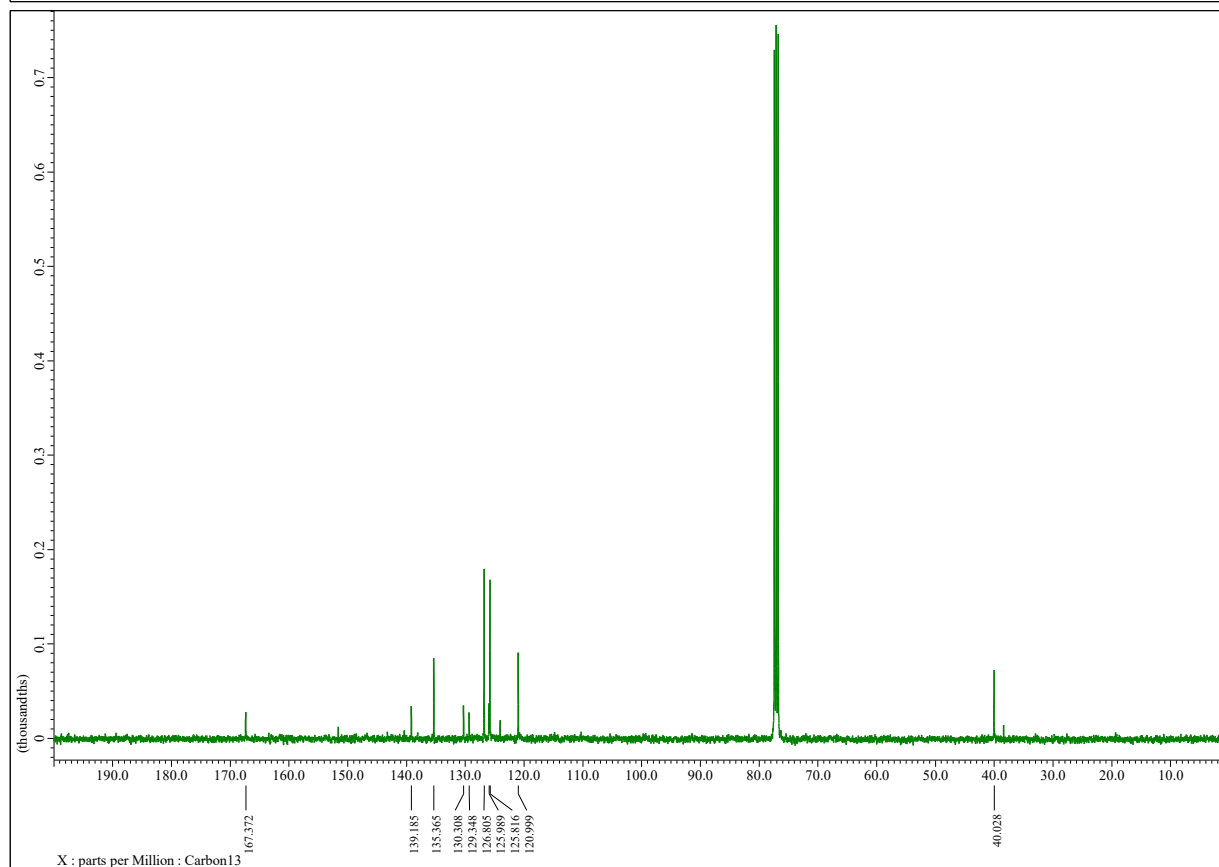
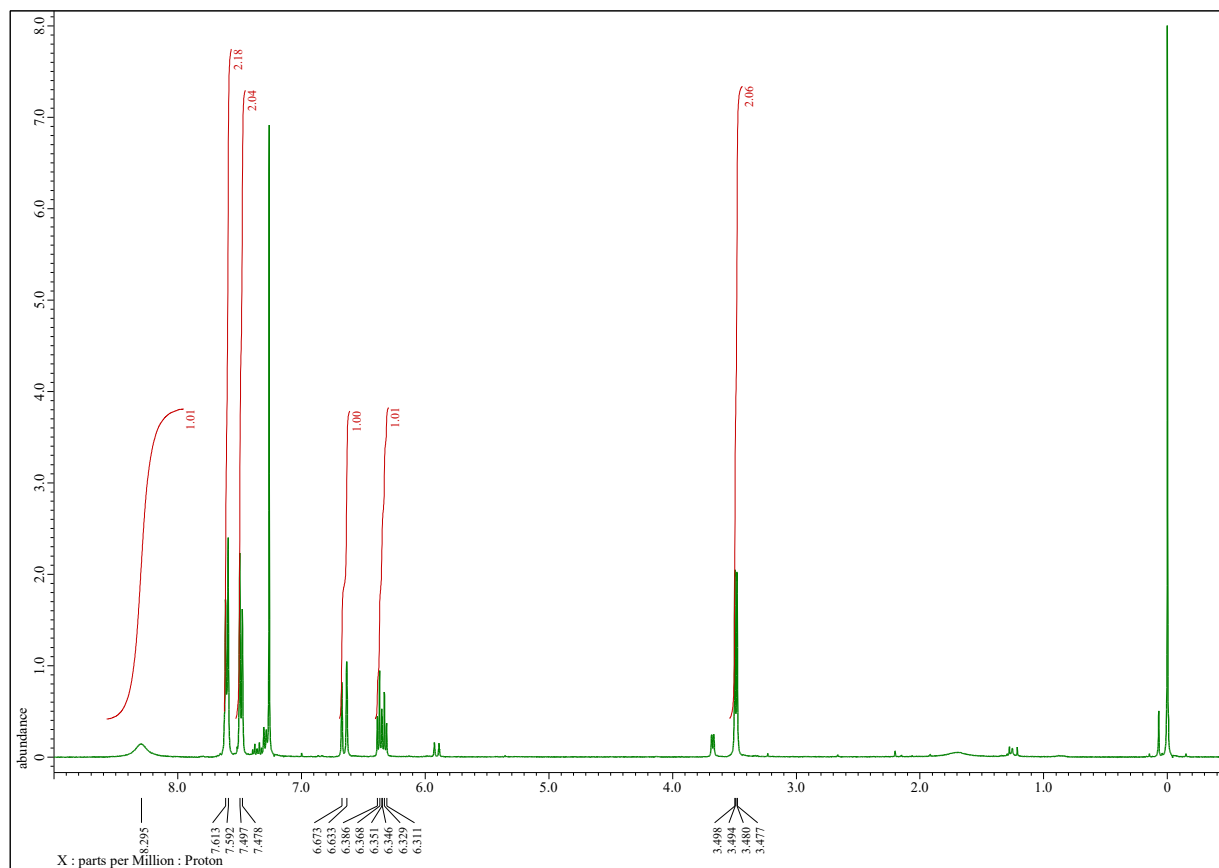
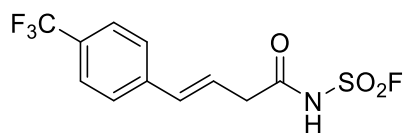


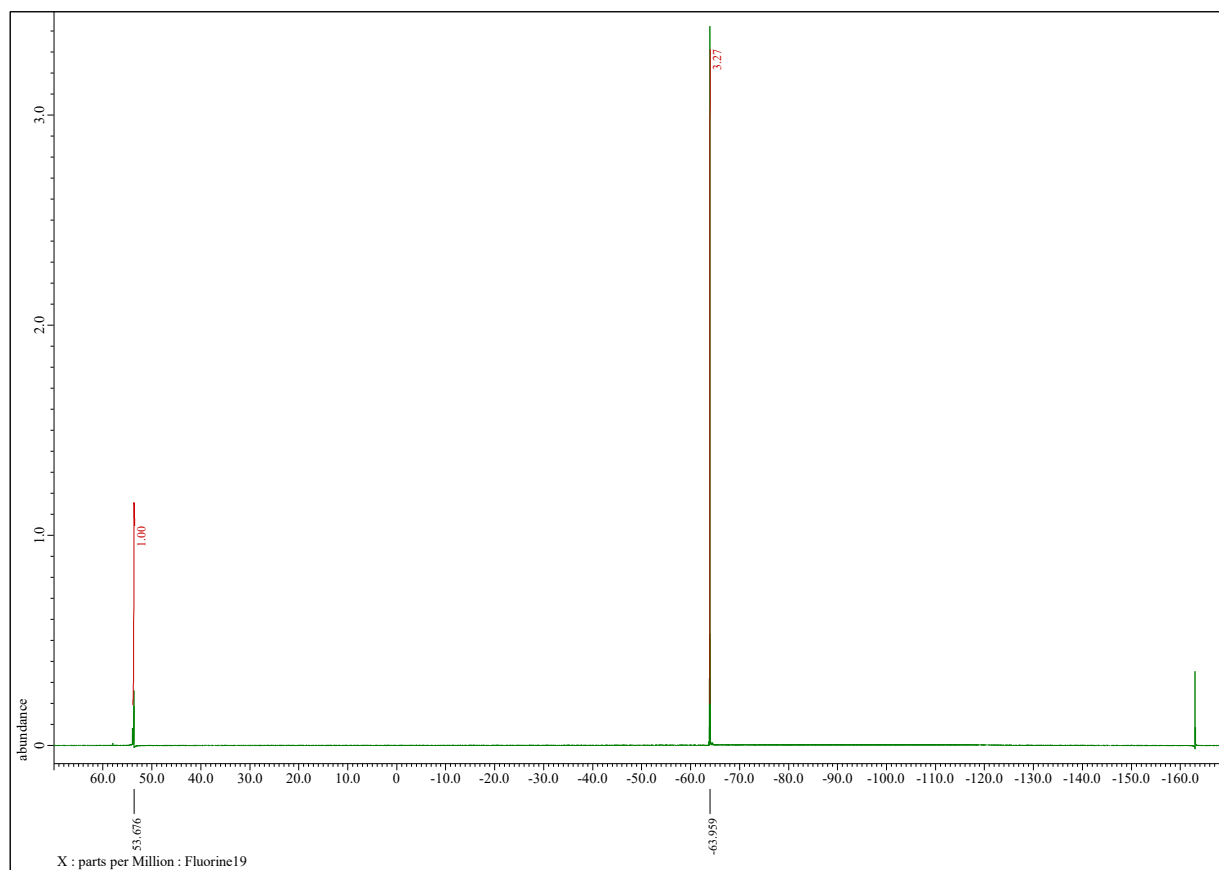
methyl (E)-4-(4-((fluorosulfonyl)amino)-4-oxobut-1-en-1-yl)benzoate (4i)



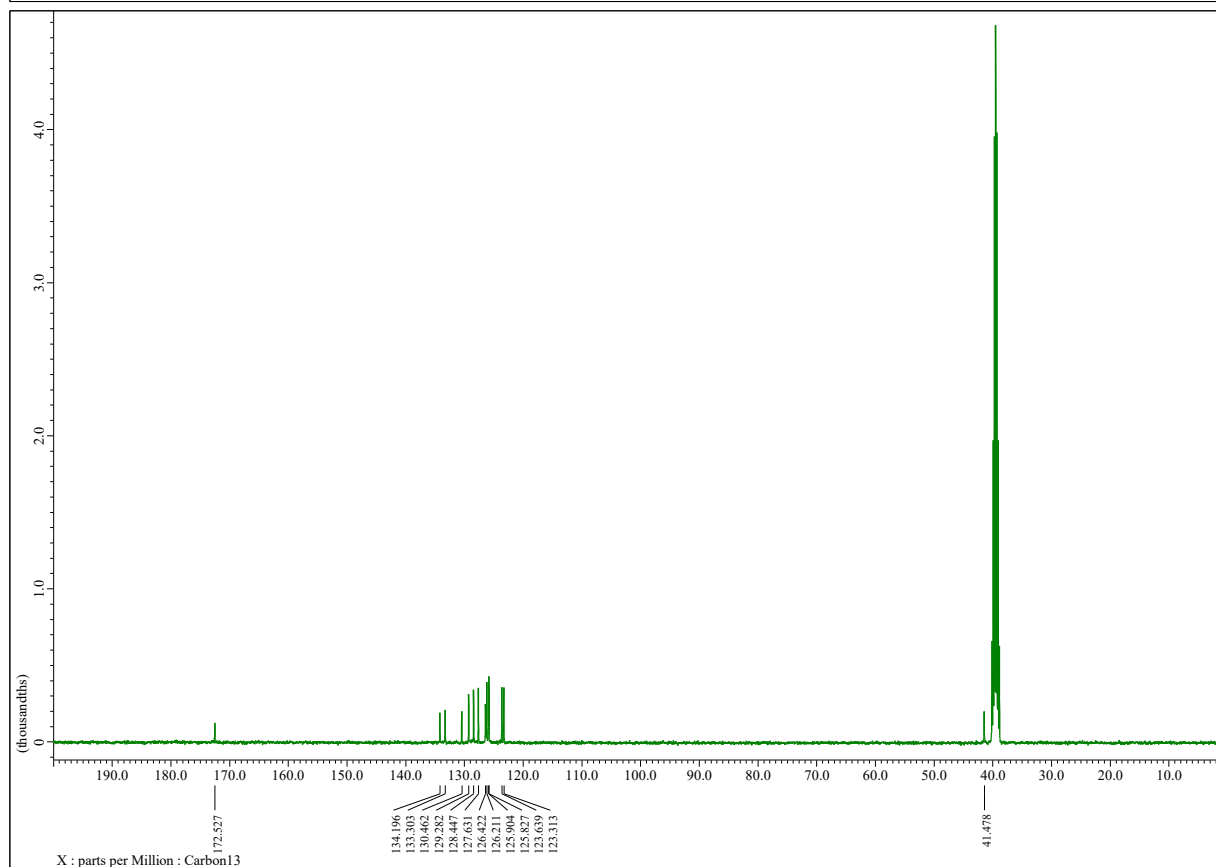
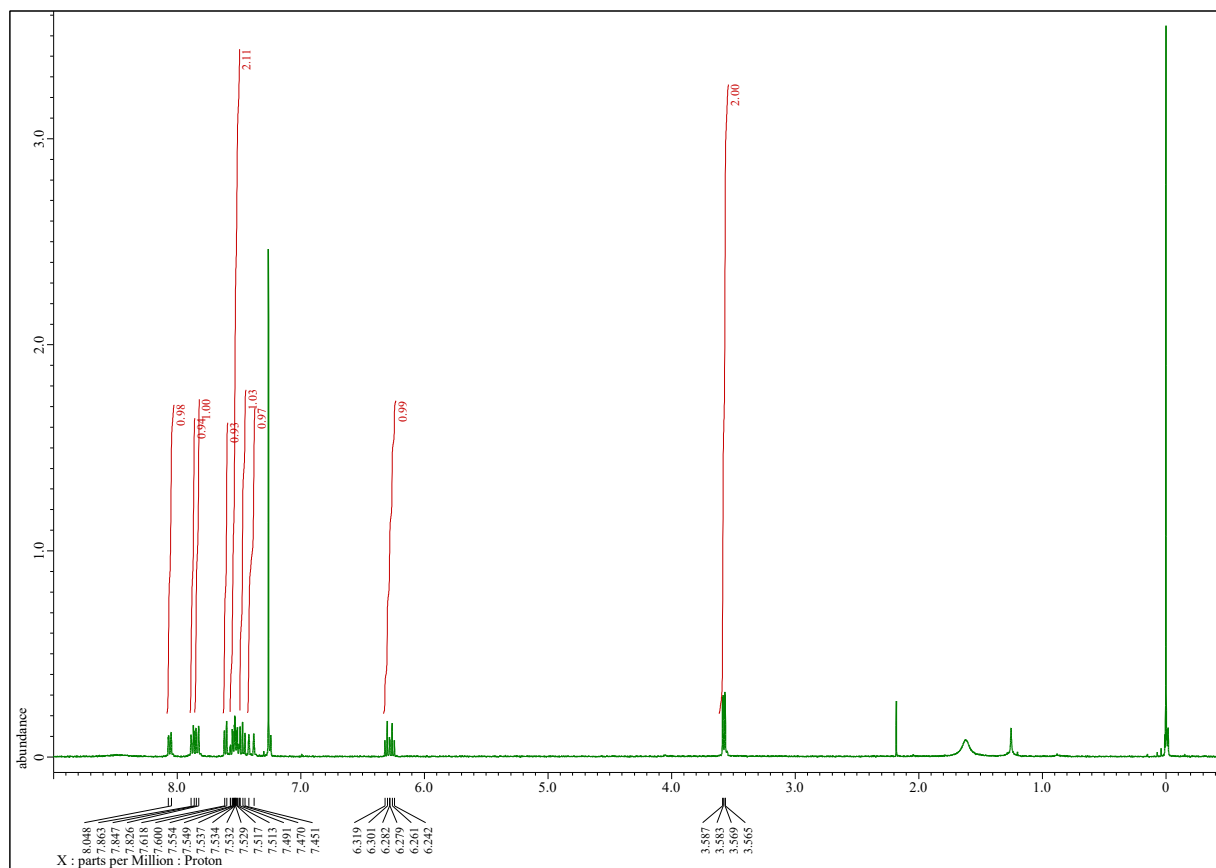
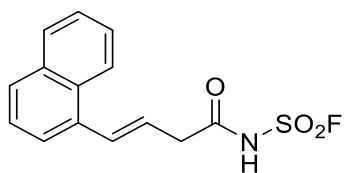


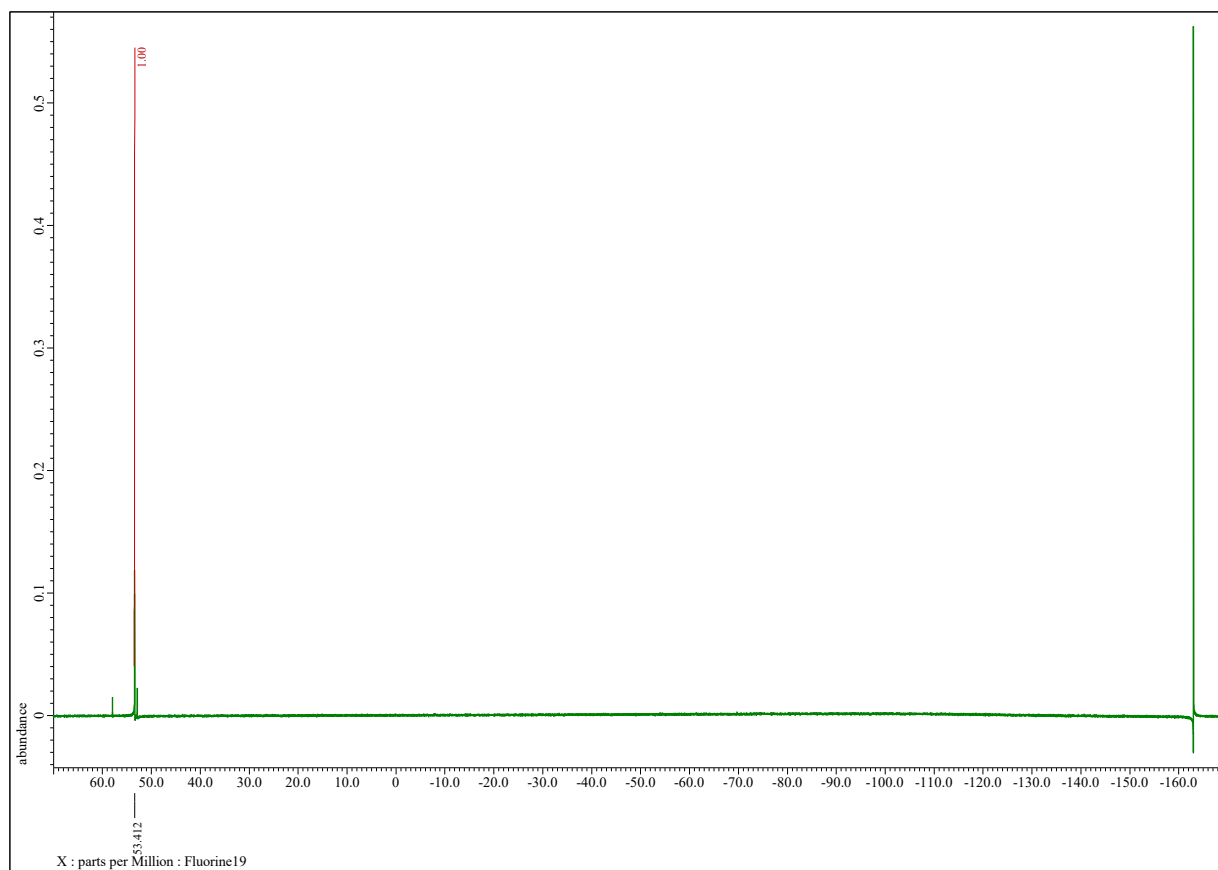
(E)-(4-(4-(trifluoromethyl)phenyl)but-3-enyl)sulfamoyl fluoride (4j)



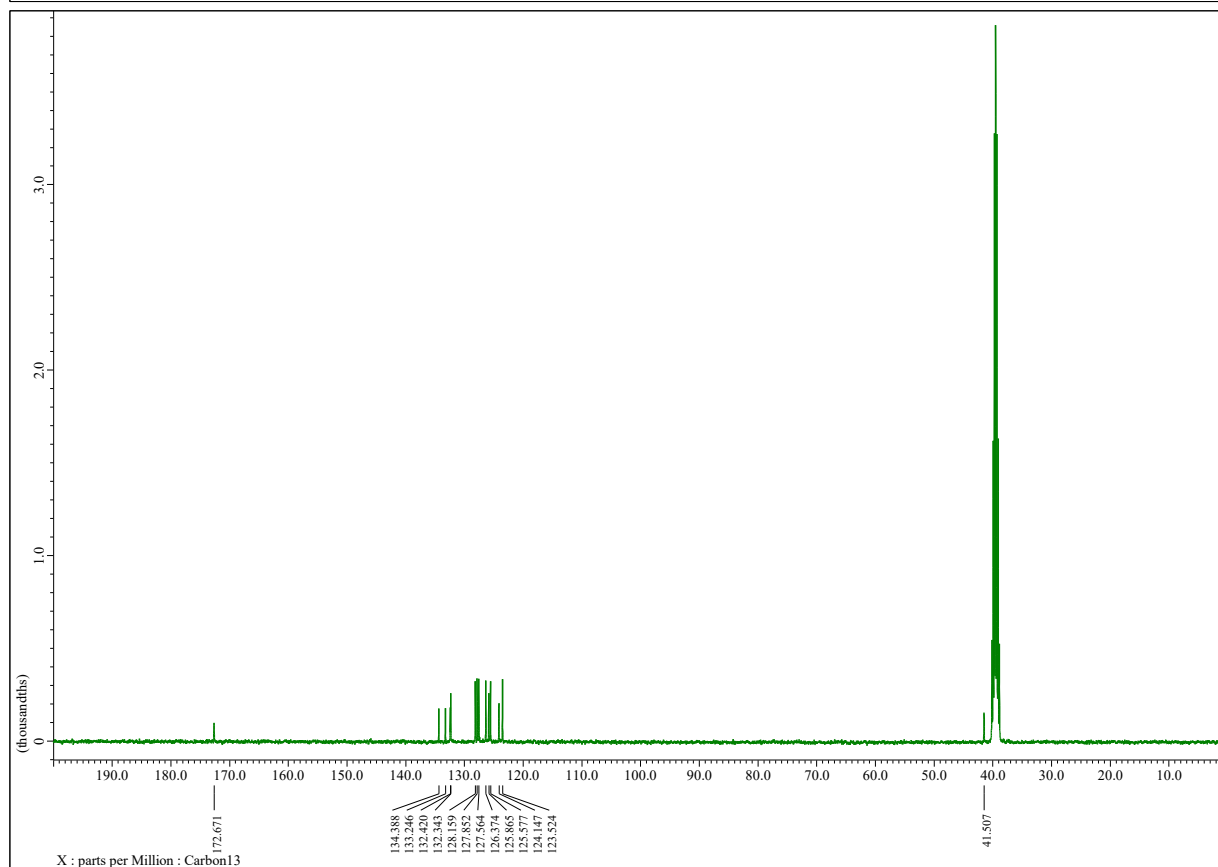
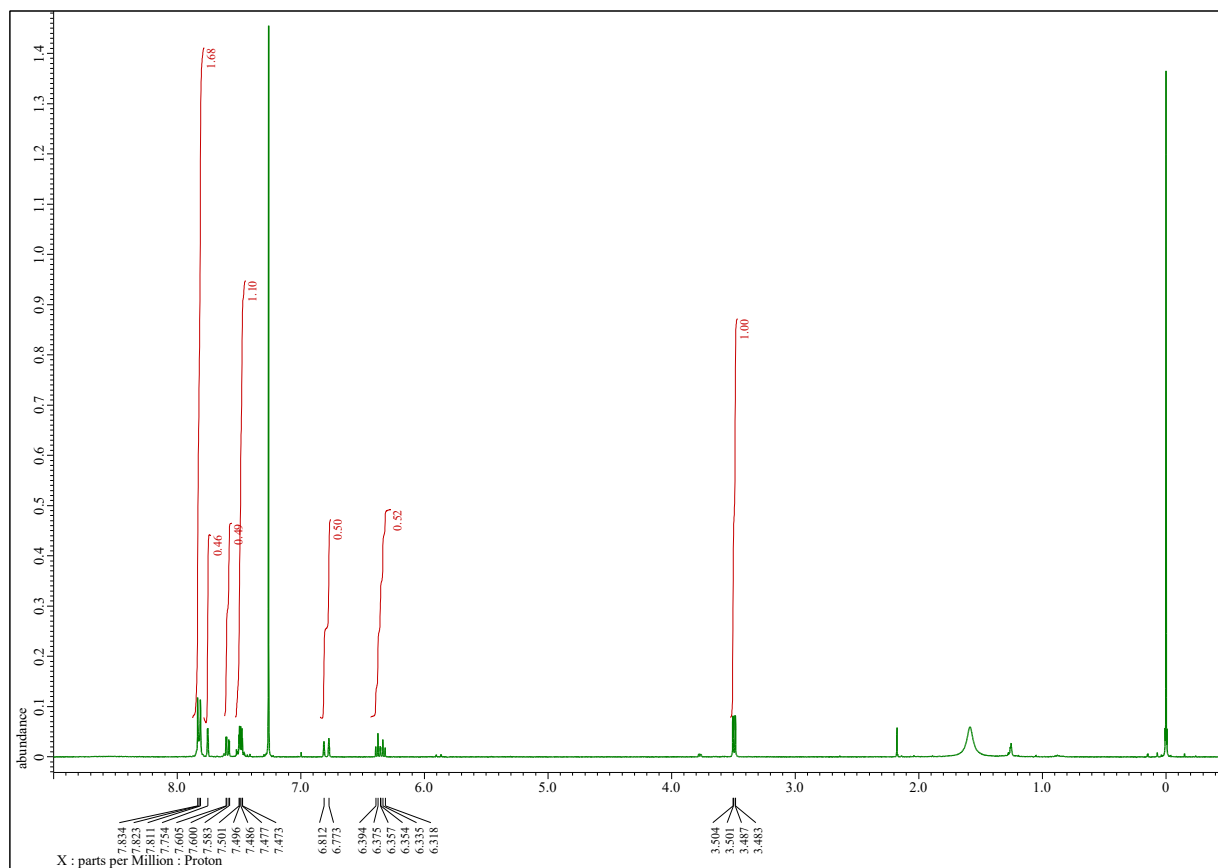
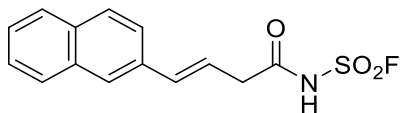


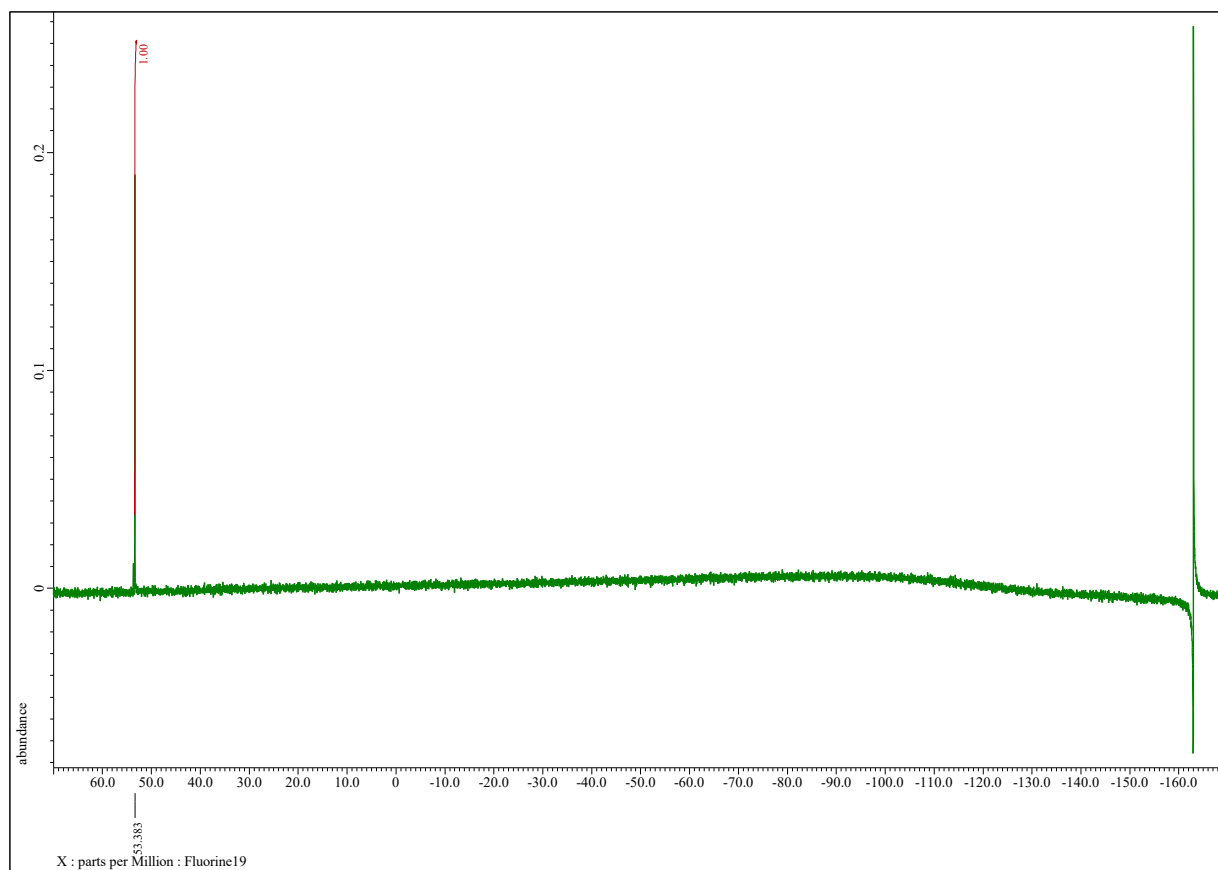
(E)-(4-(naphthalen-1-yl)but-3-enoyl)sulfamoyl fluoride (4k)



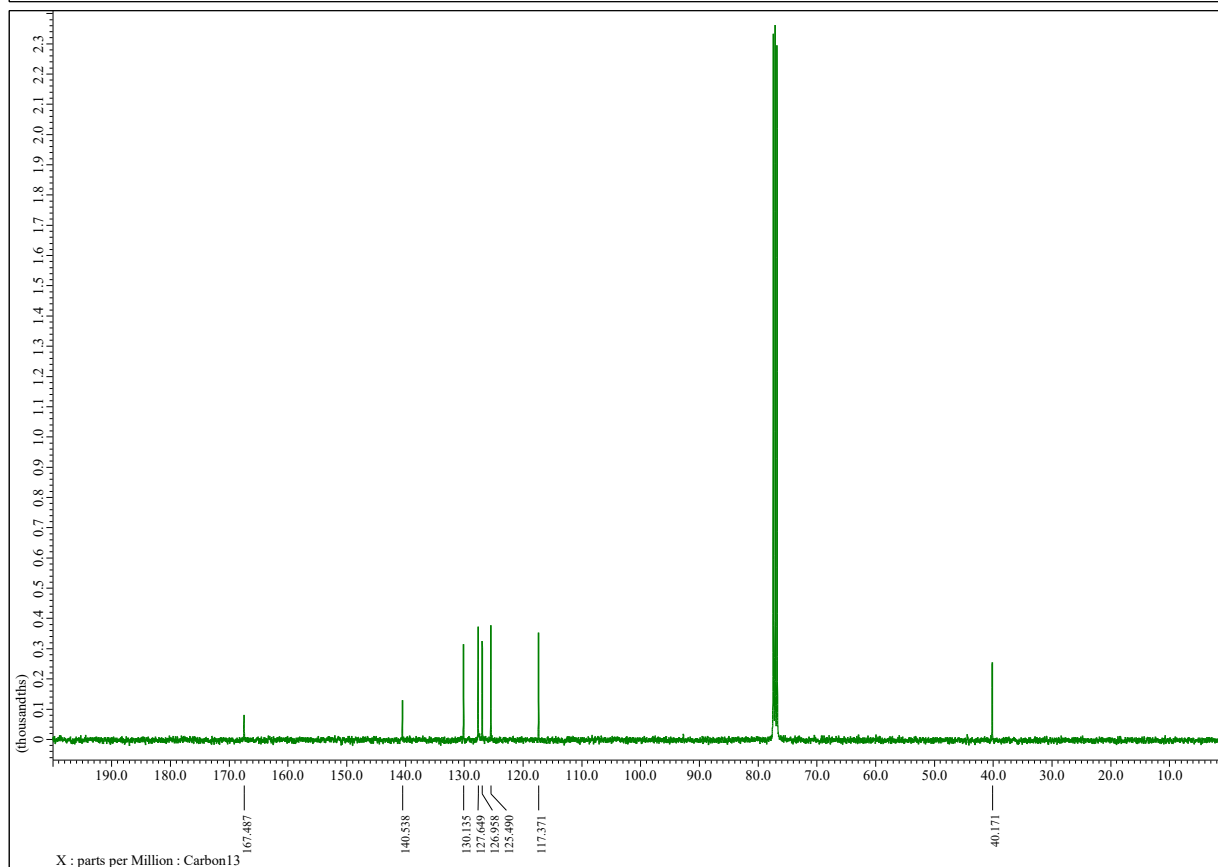
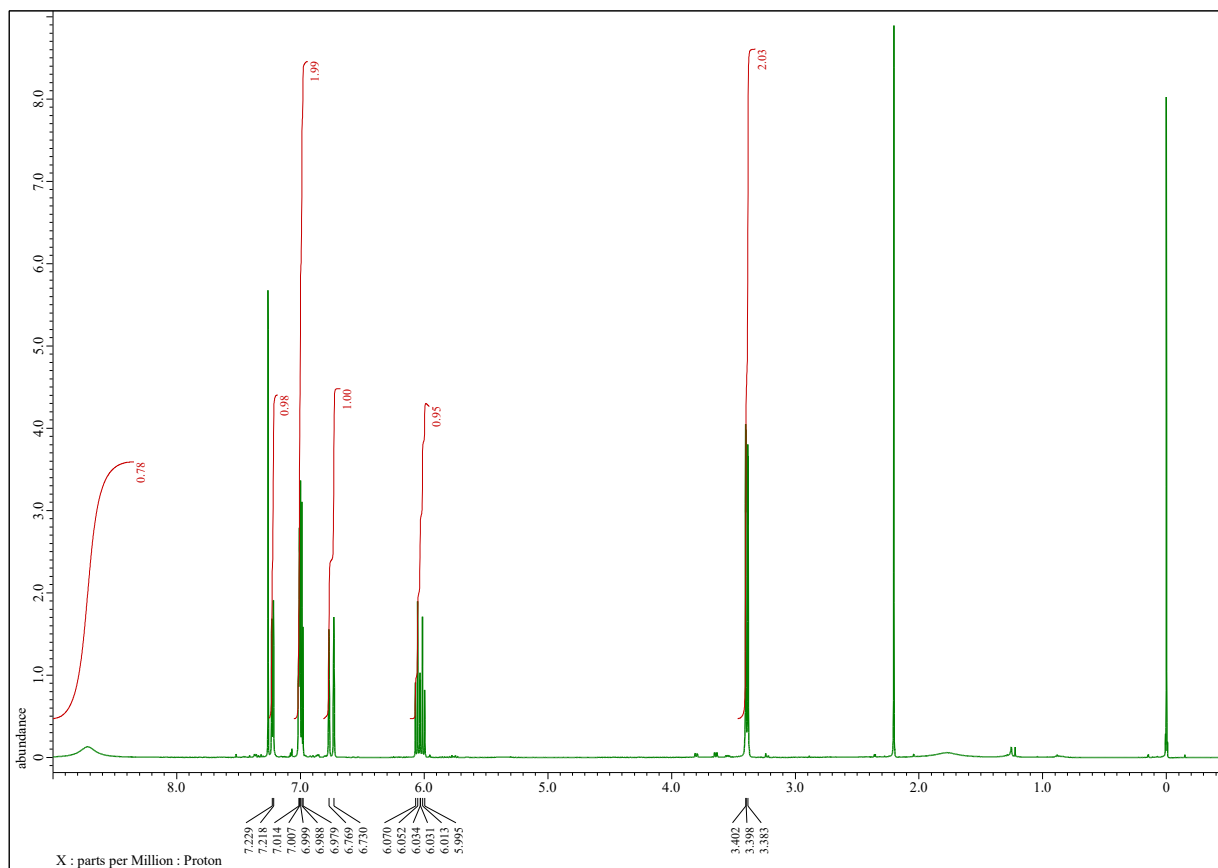
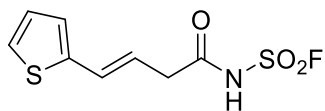


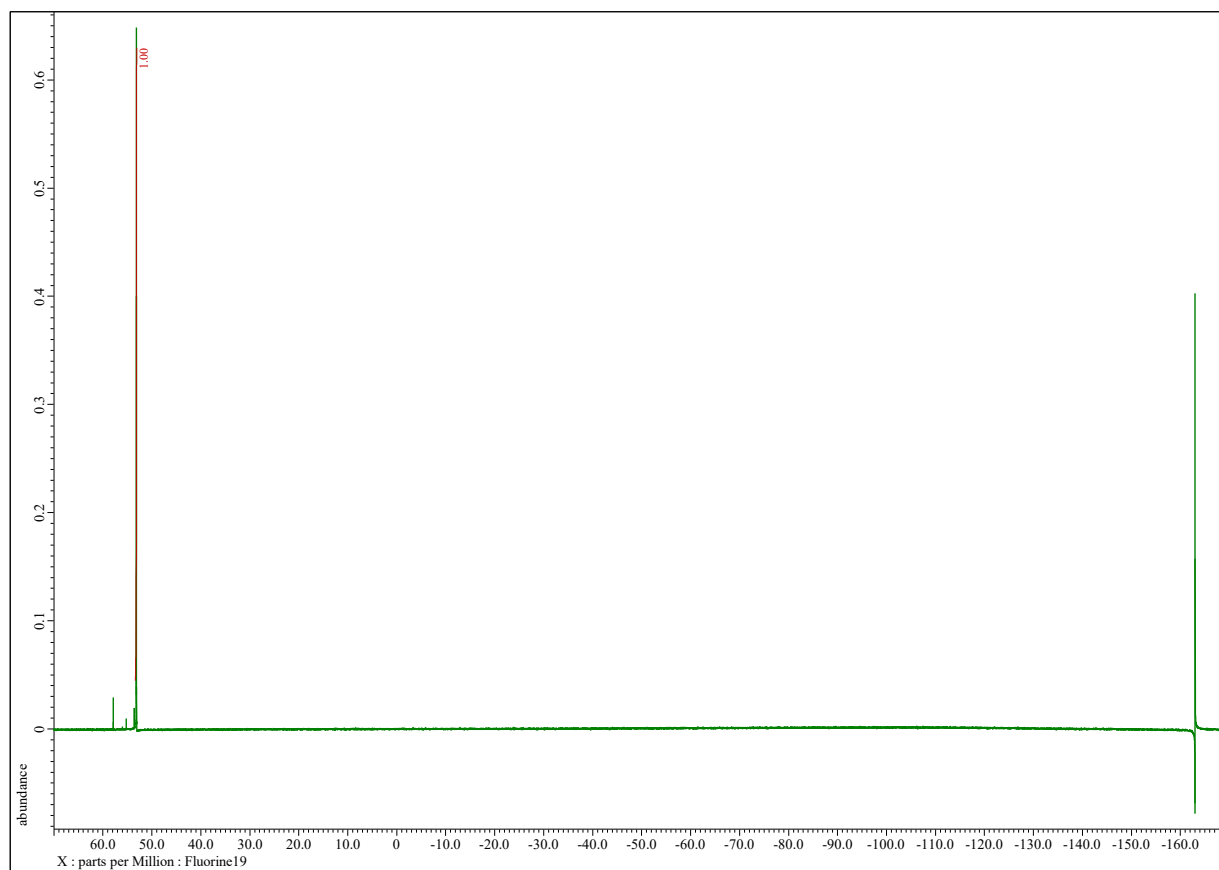
(E)-(4-(naphthalen-2-yl)but-3-enoyl)sulfamoyl fluoride (4l)



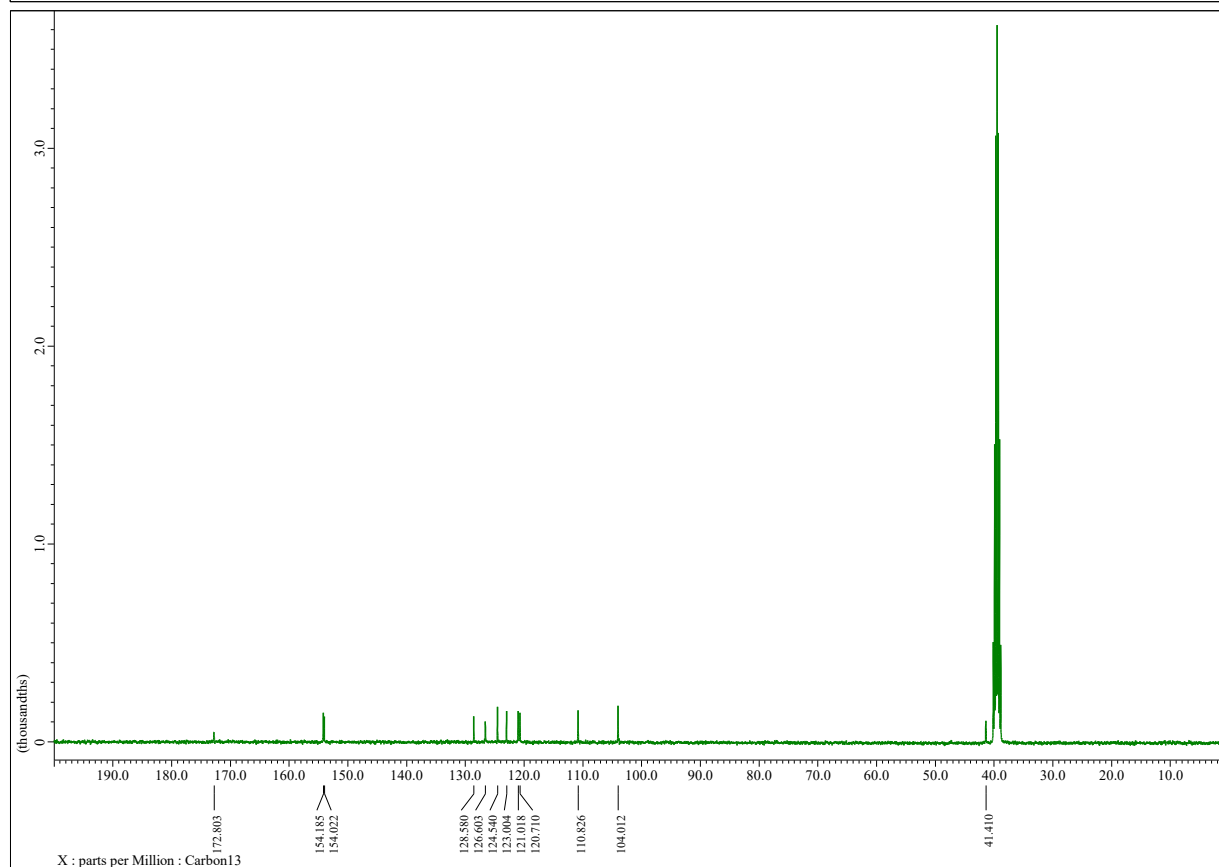
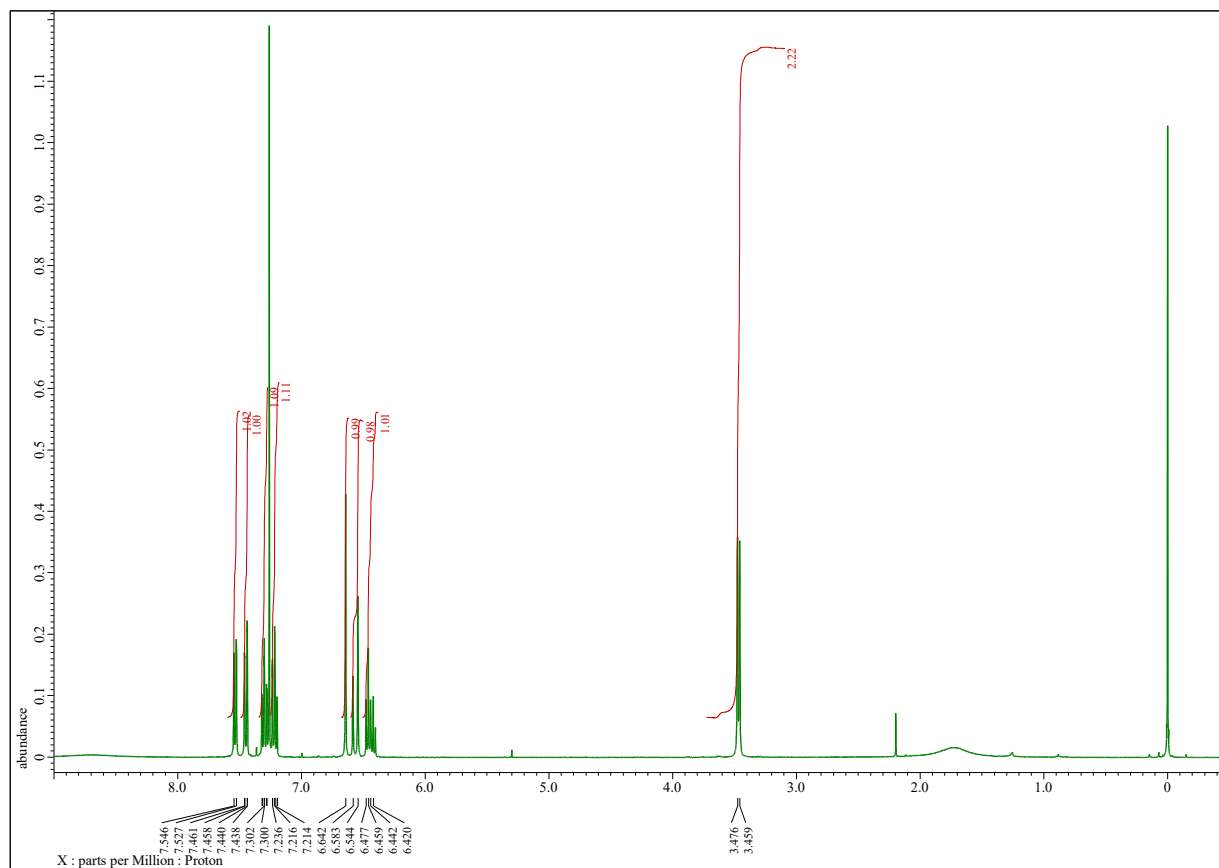
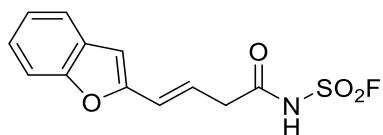


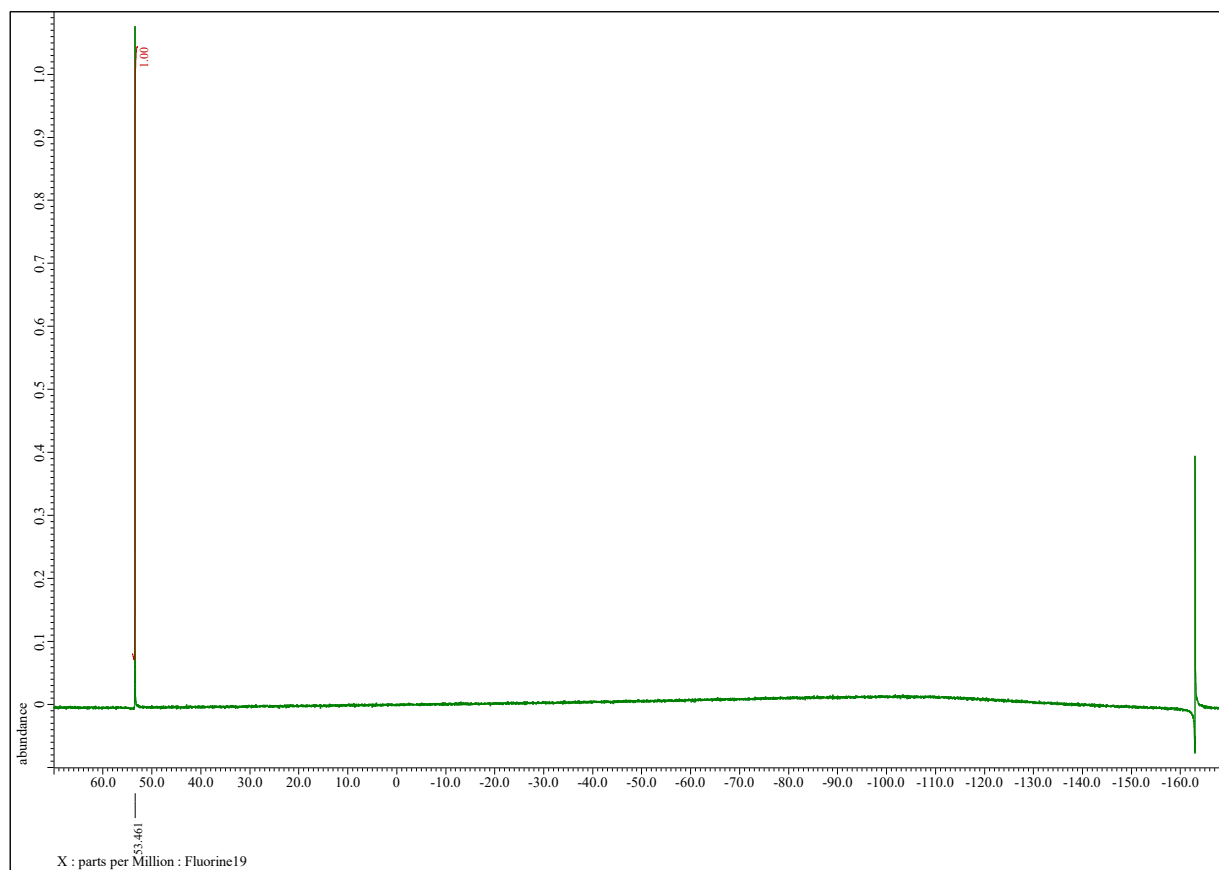
(E)-(4-(thiophen-2-yl)but-3-enyl)sulfamoyl fluoride (4m)



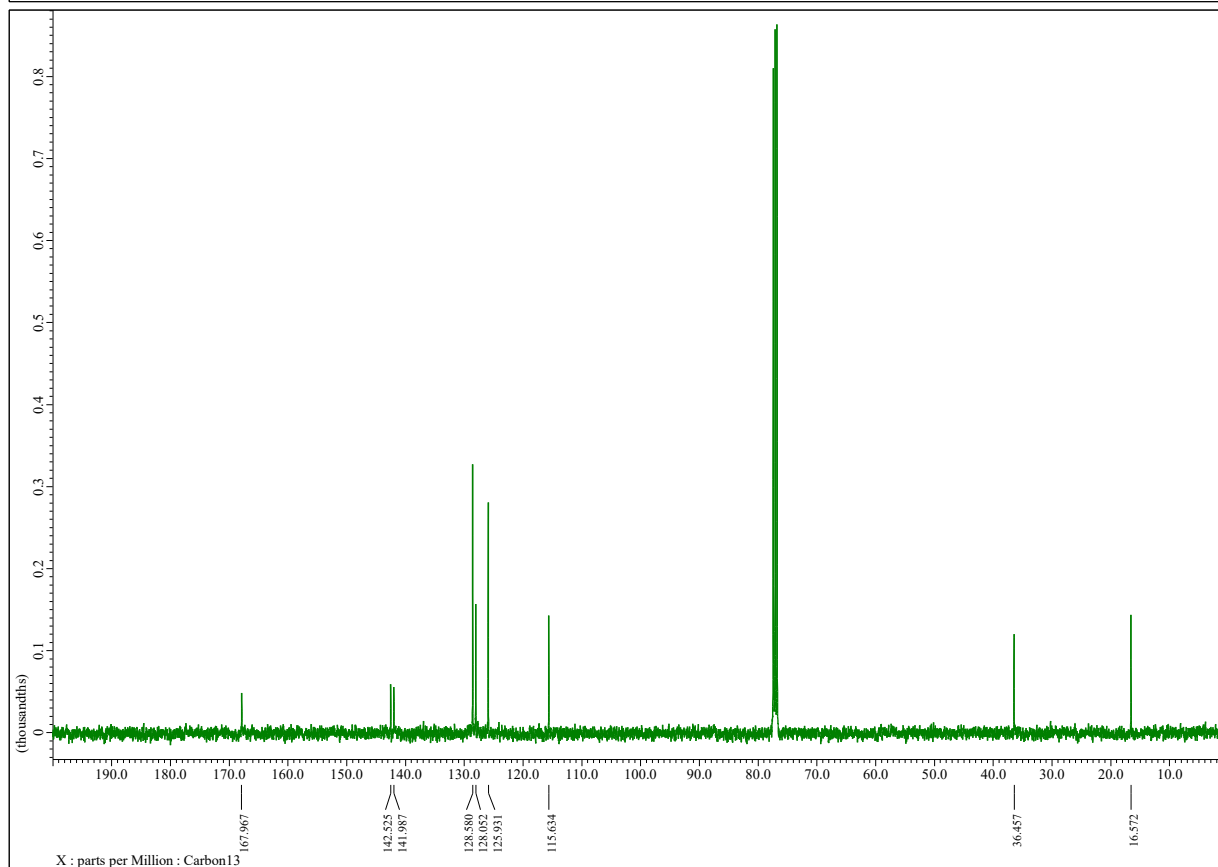
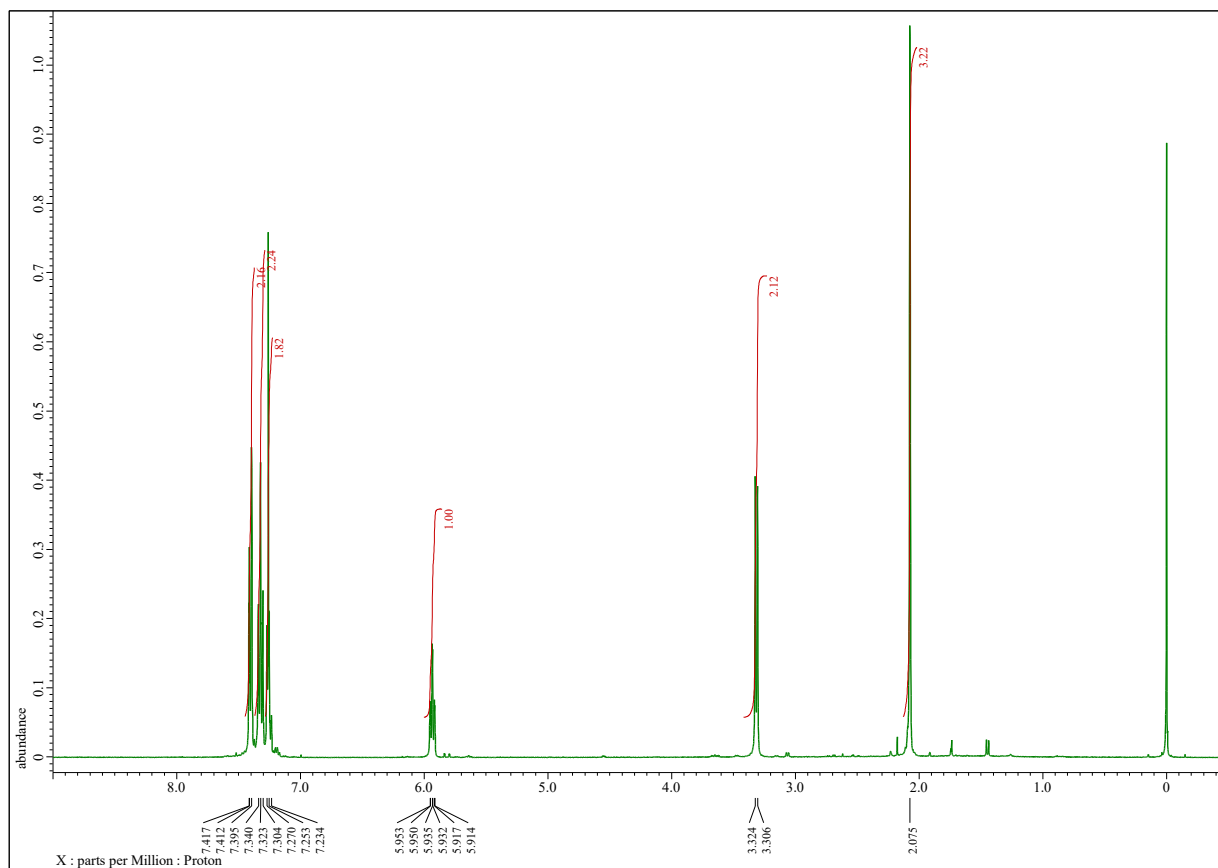
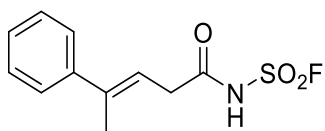


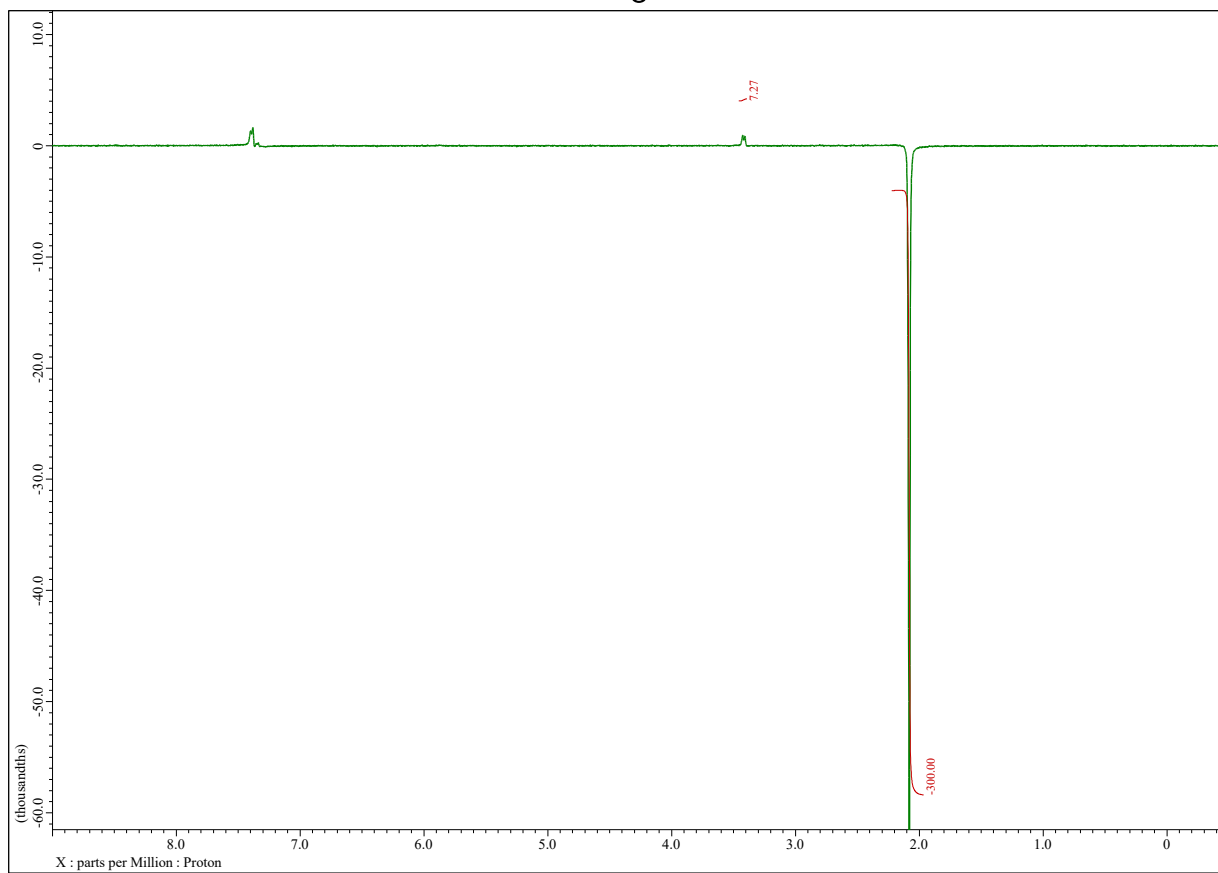
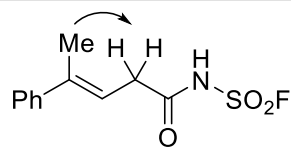
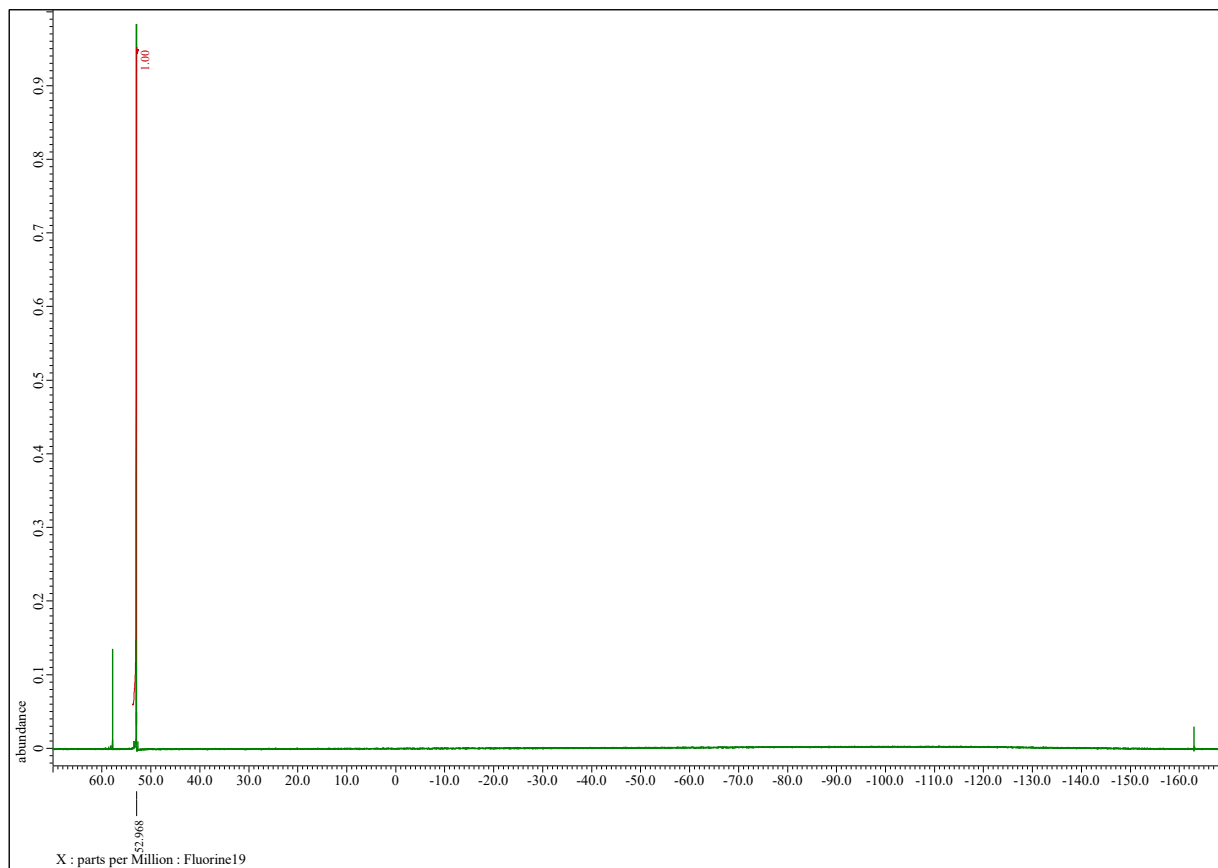
(E)-(4-(benzofuran-2-yl)but-3-enyl)sulfamoyl fluoride (4n)



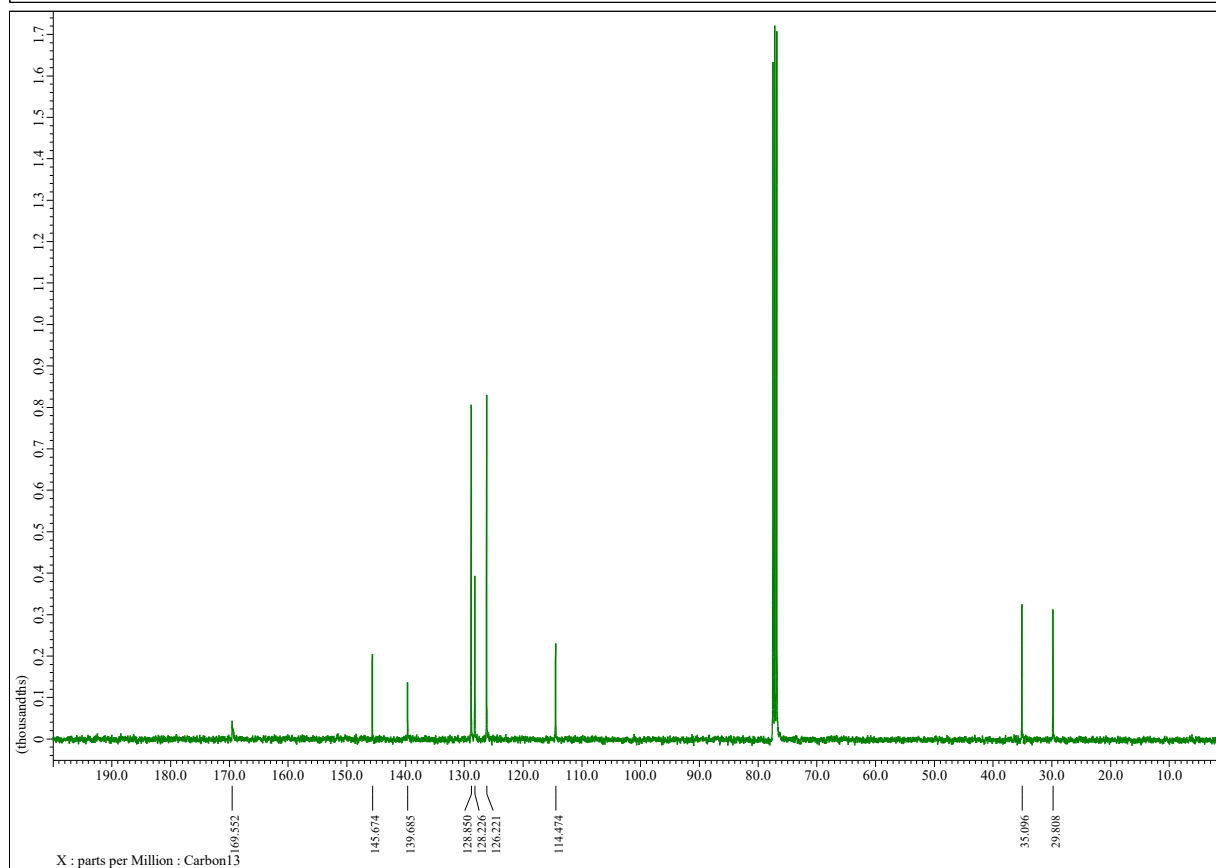
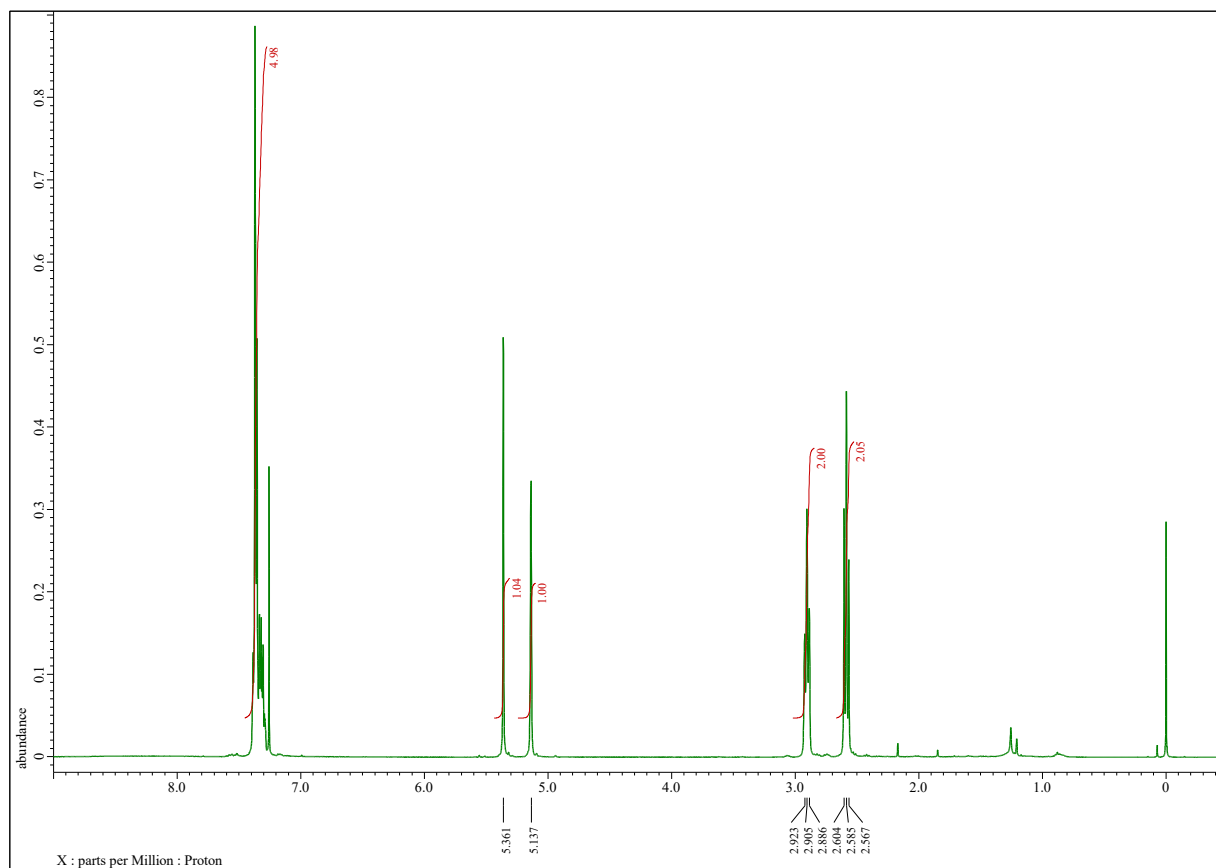
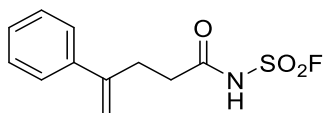


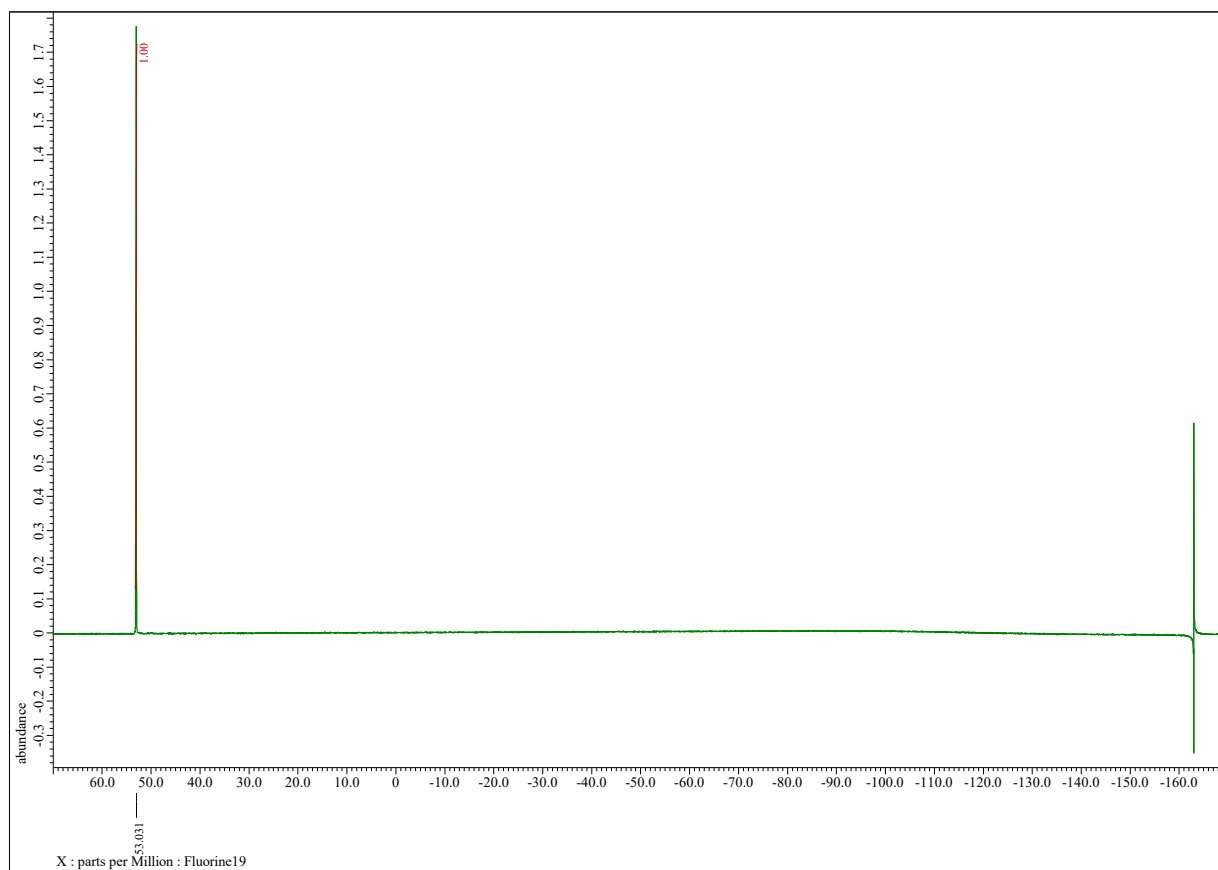
(E)-(4-phenylpent-3-enoyl)sulfamoyl fluoride (4o)



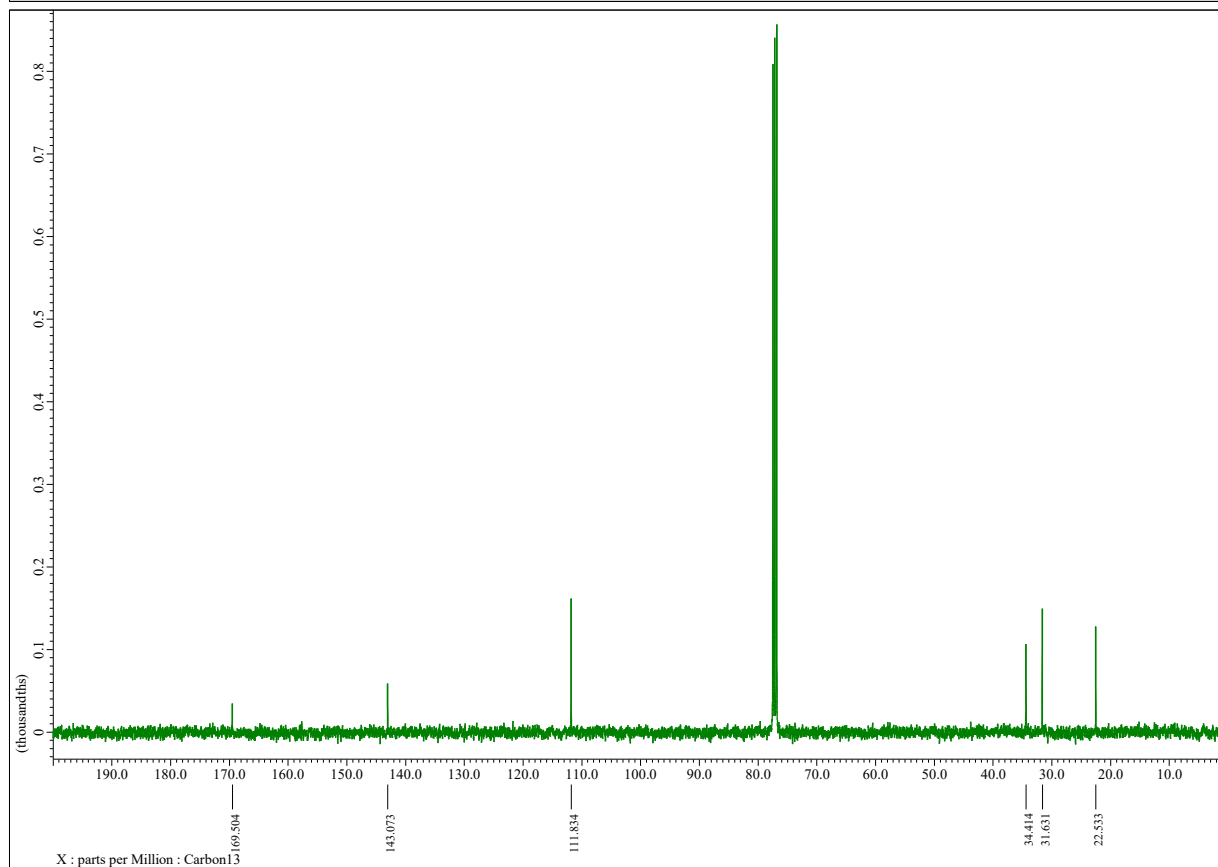
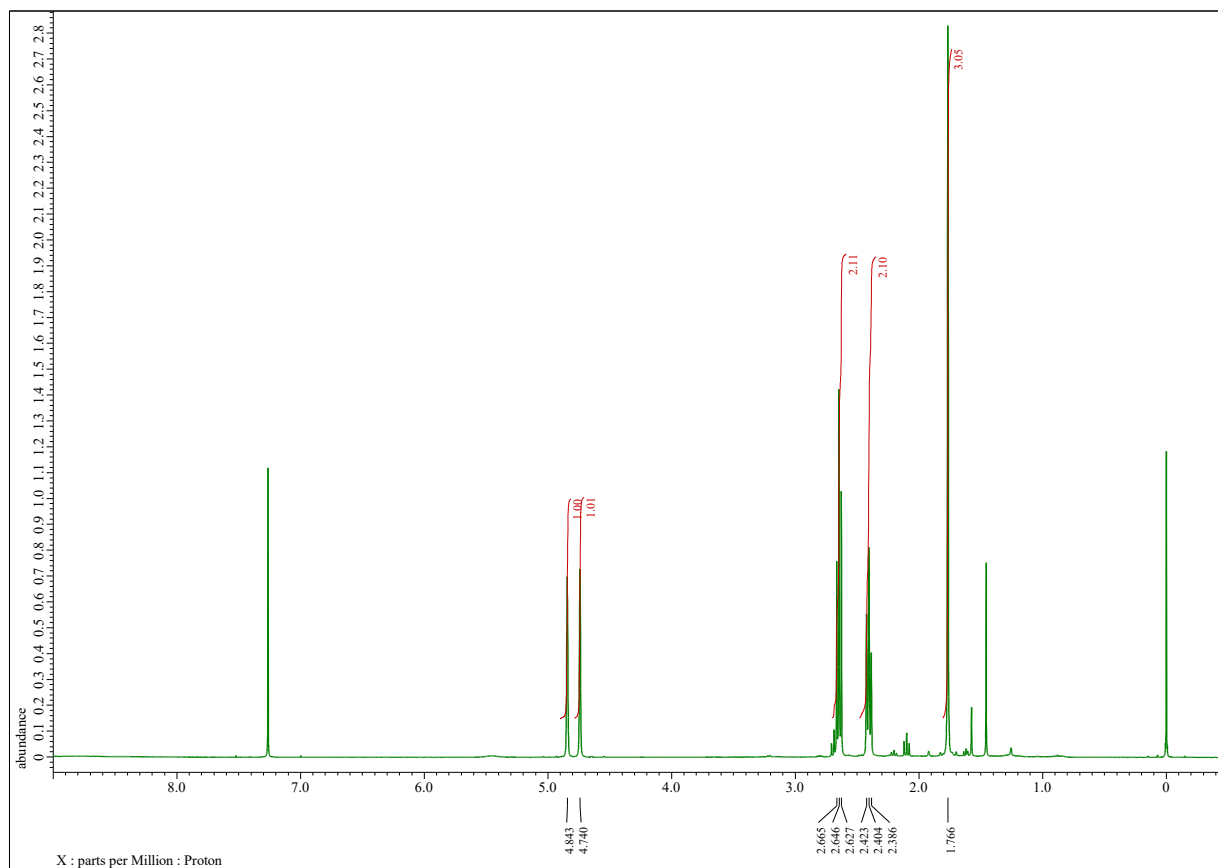
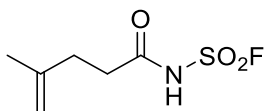


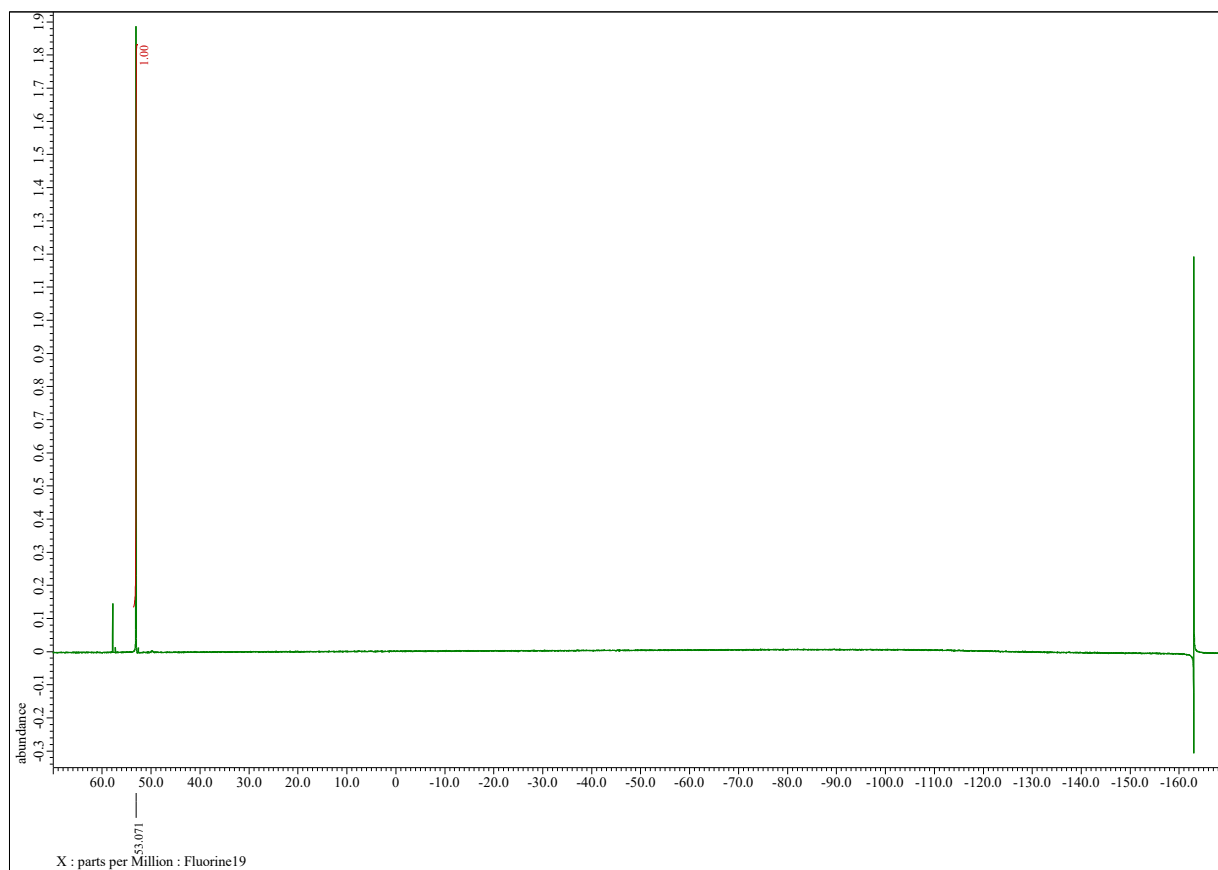
(4-phenylpent-4-enyl)sulfamoyl fluoride (18a)



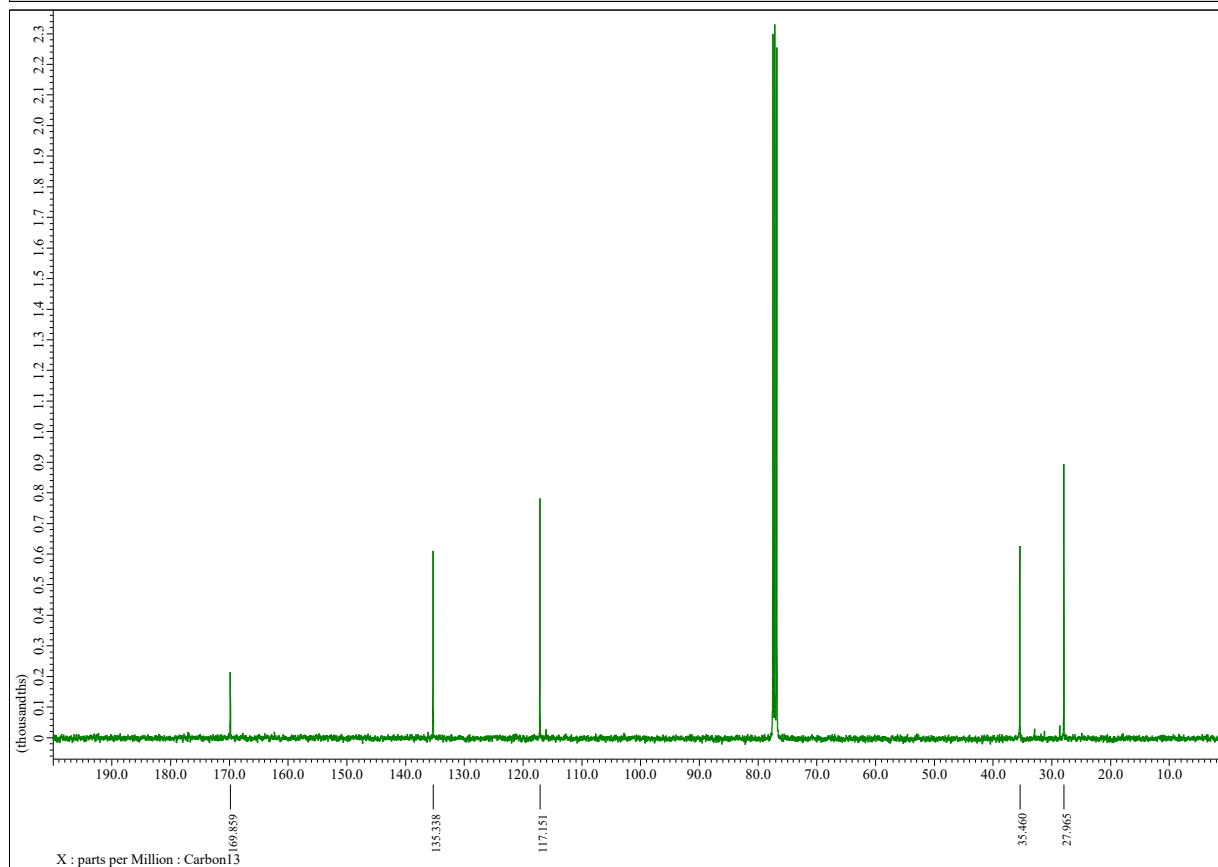
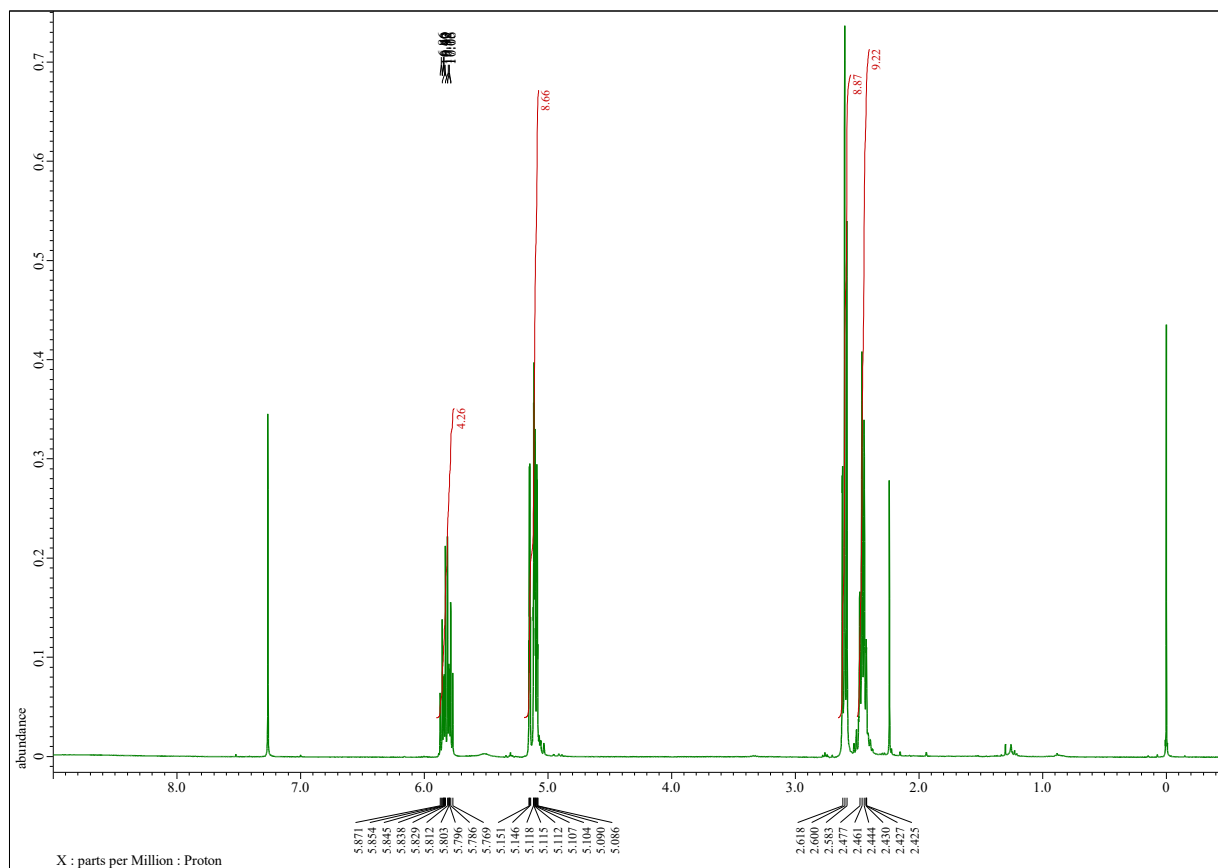
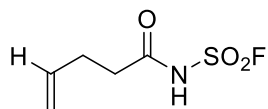


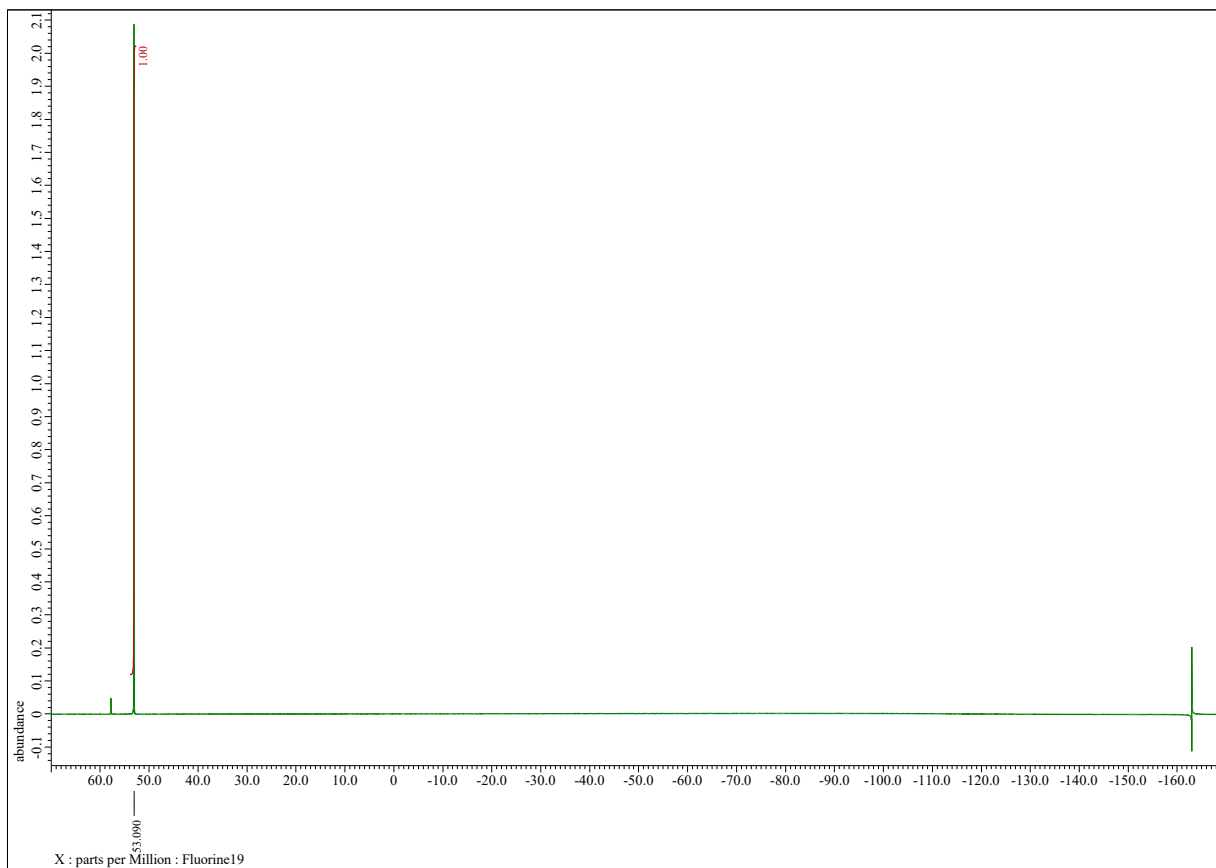
(4-methylpent-4-enoyl)sulfamoyl fluoride (18b)



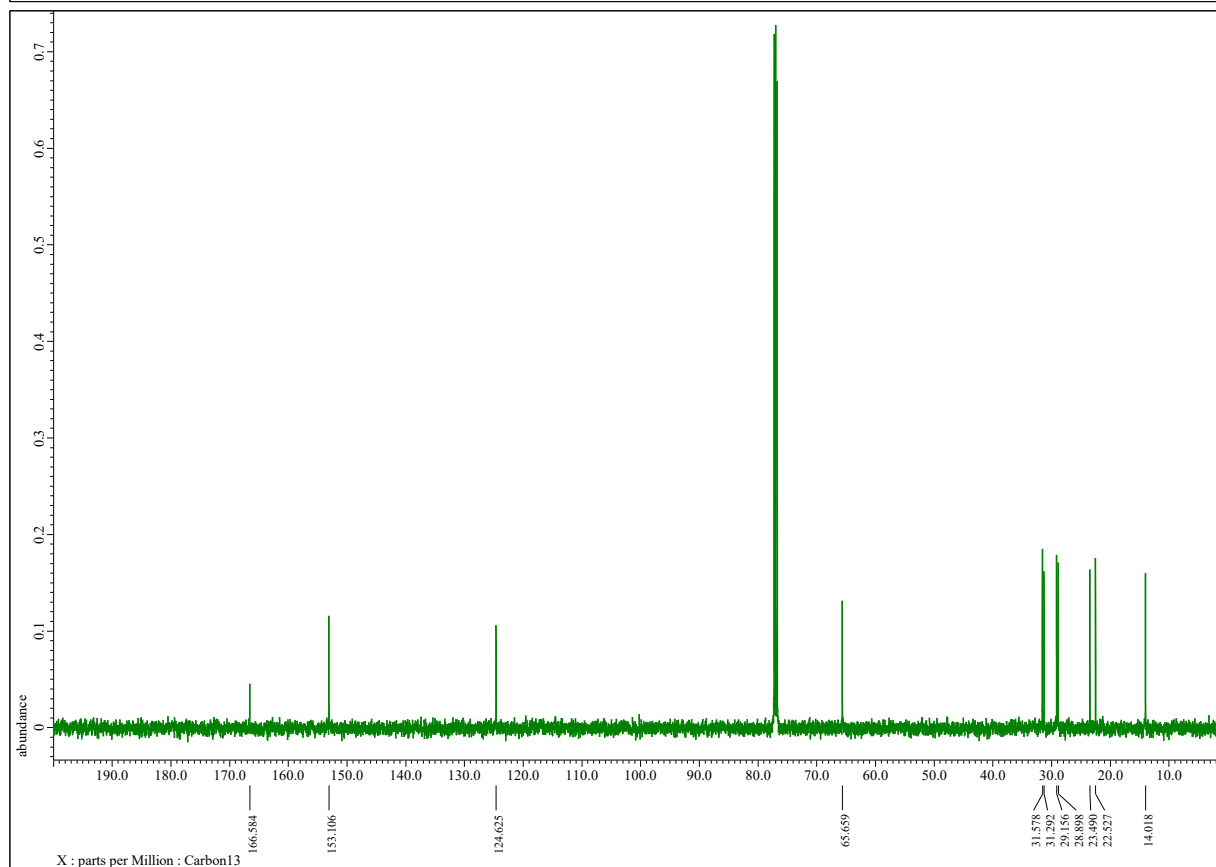
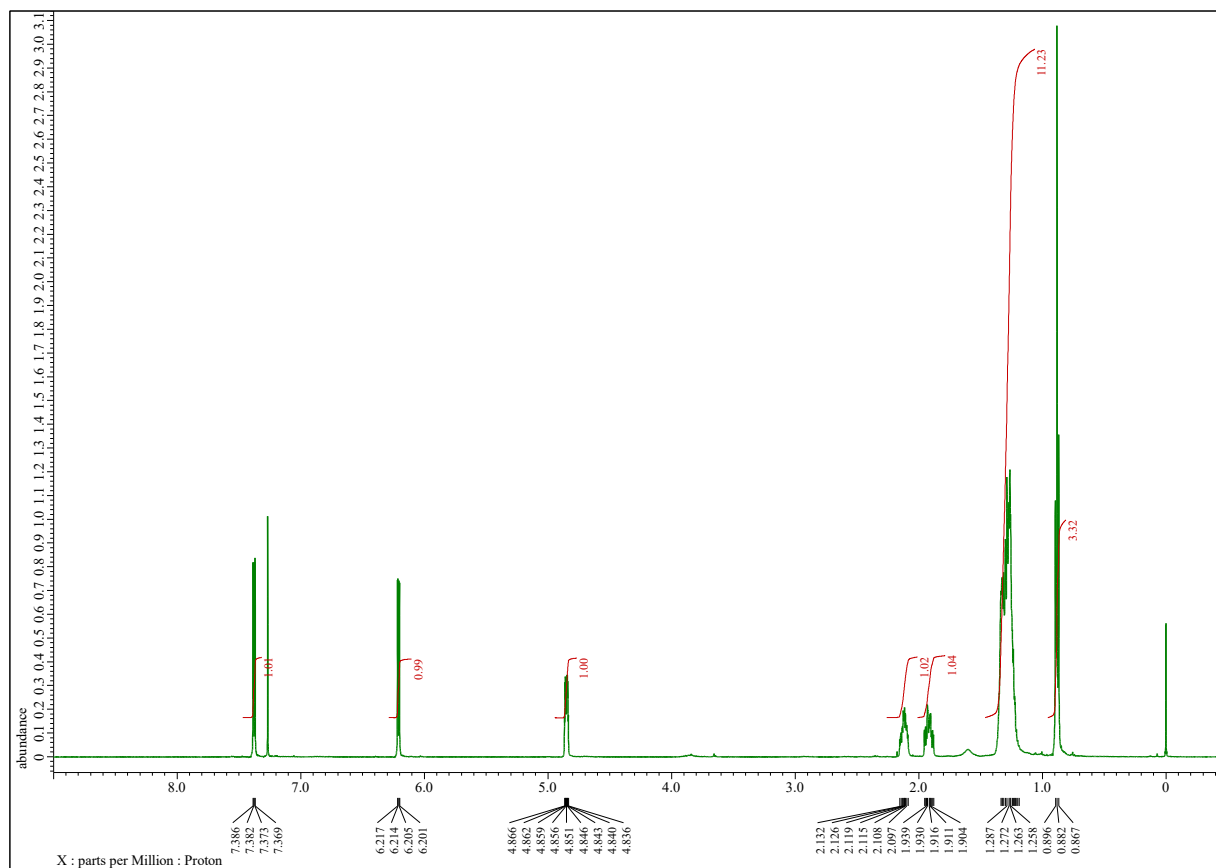
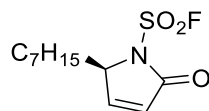


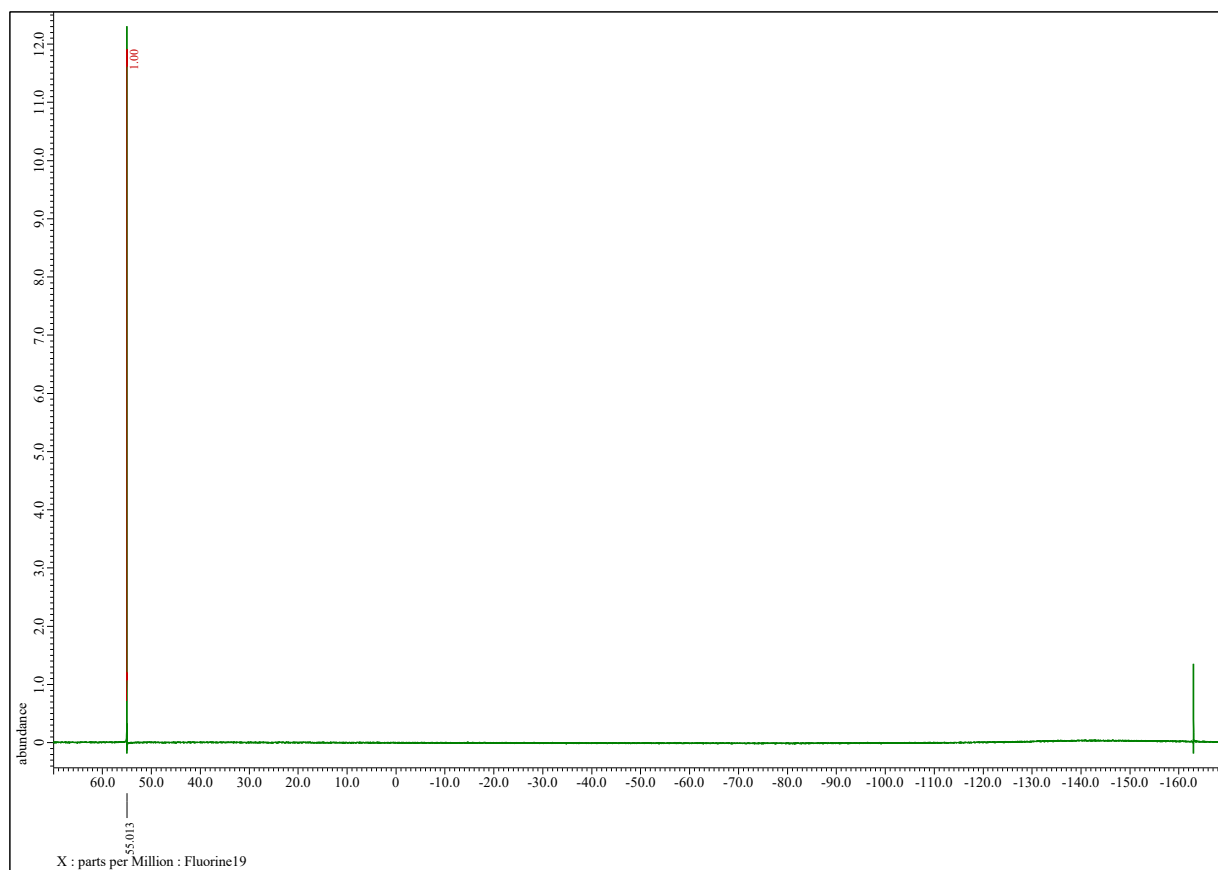
pent-4-enoylsulfamoyl fluoride (18c)



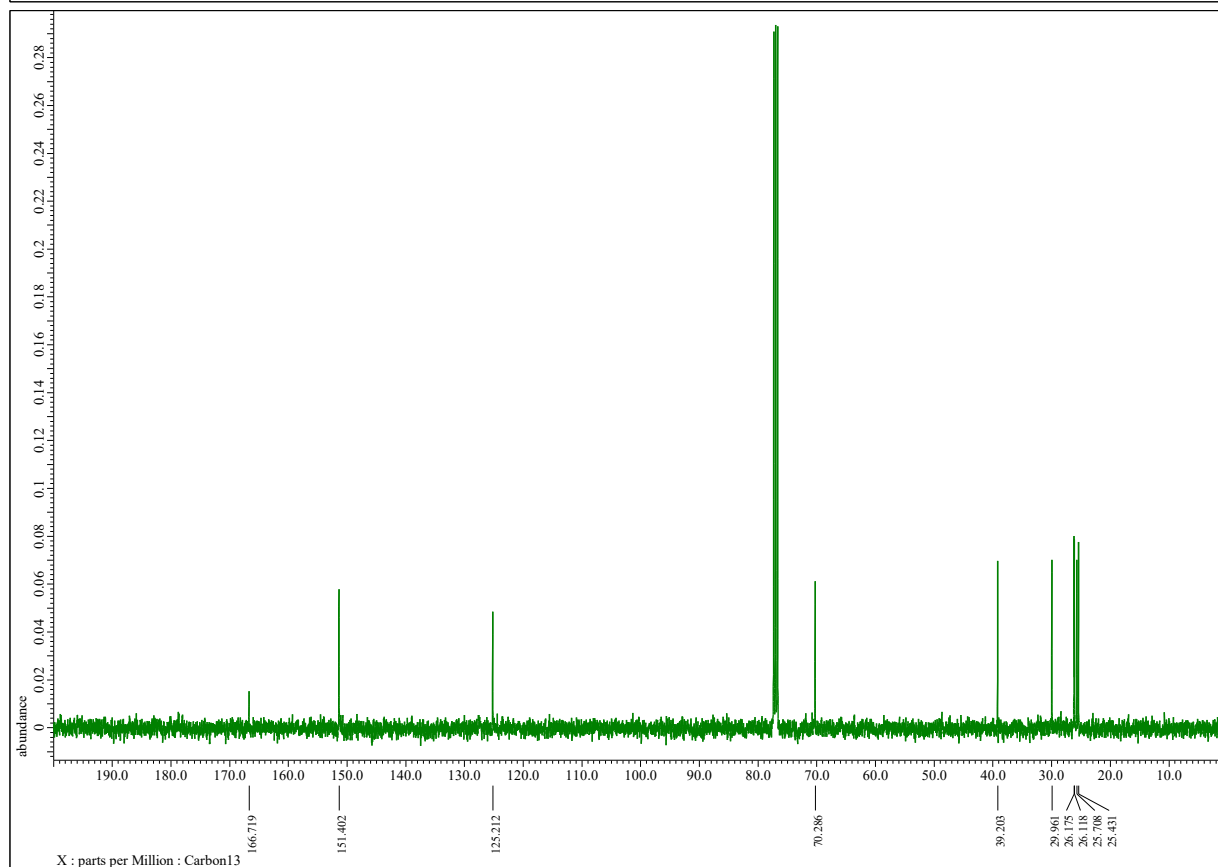
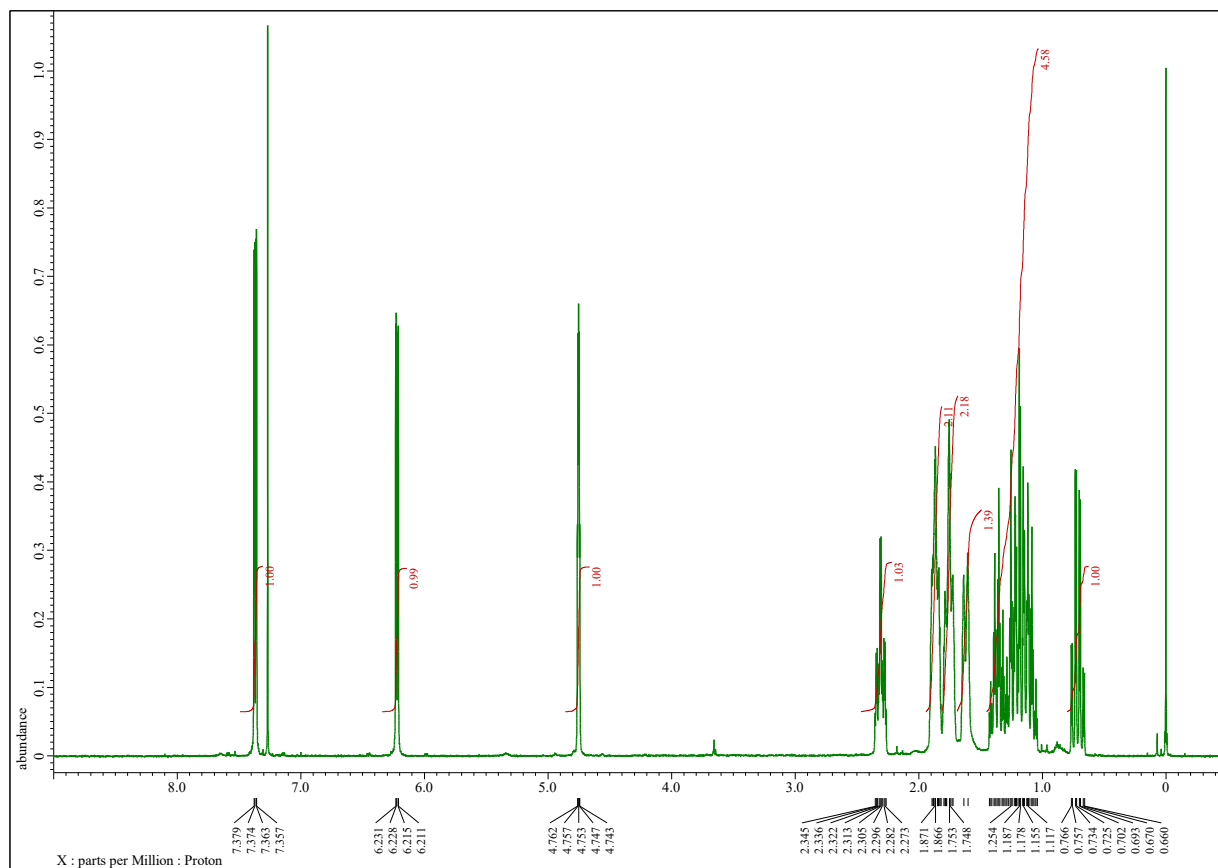
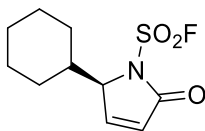


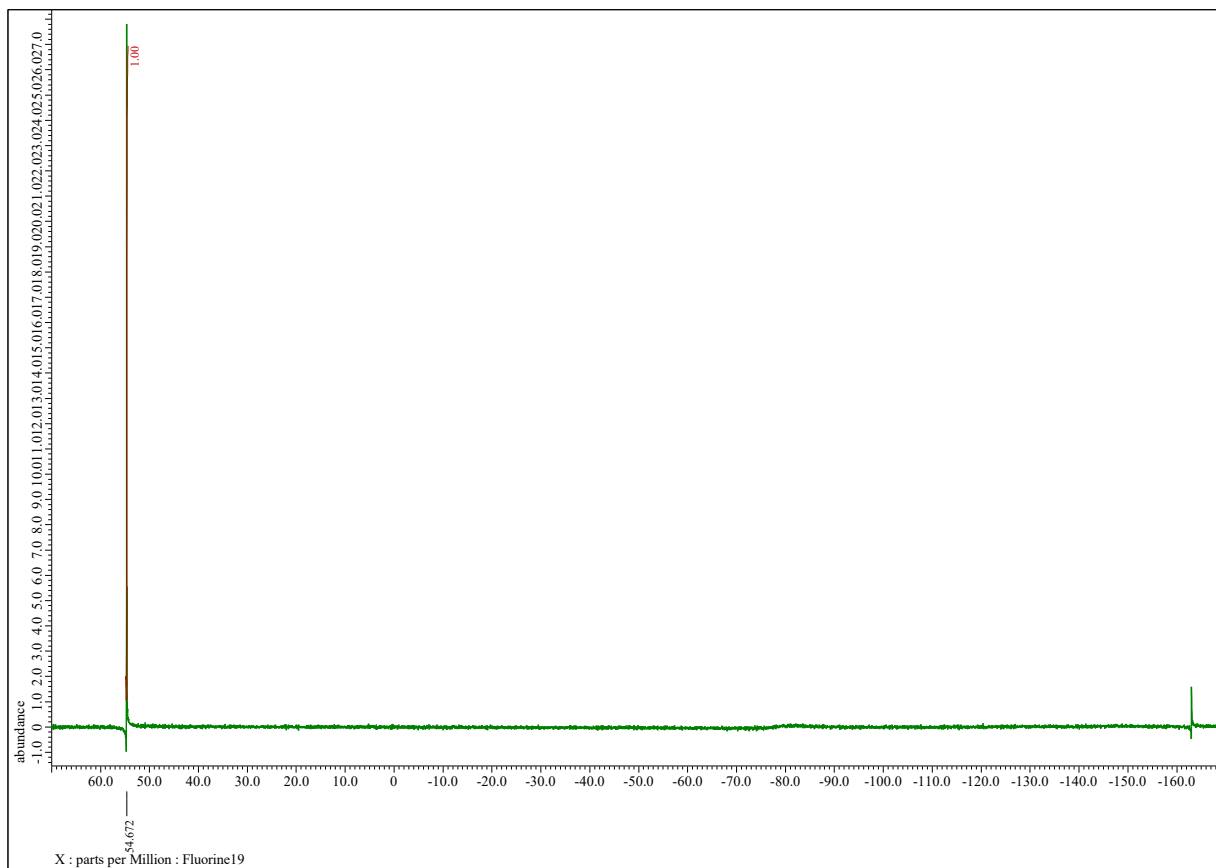
(R)-2-heptyl-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5a)



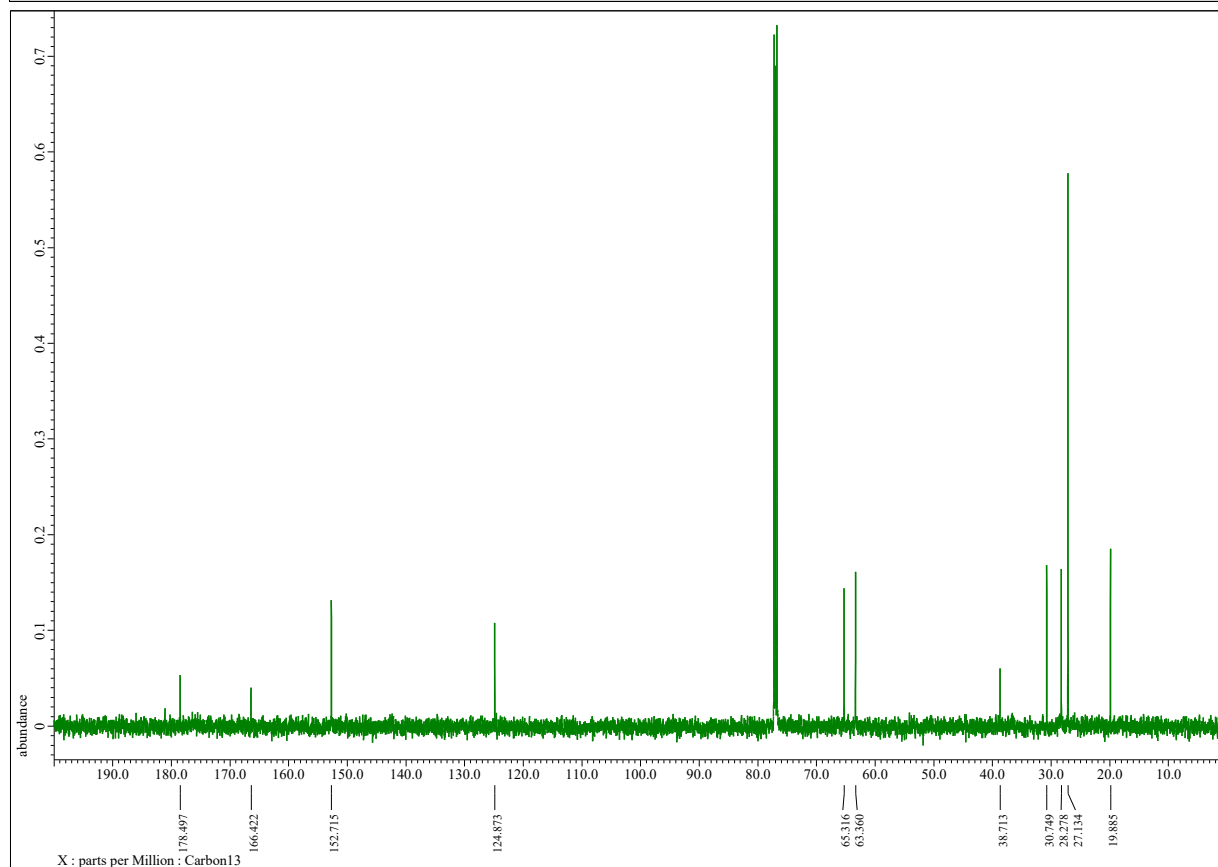
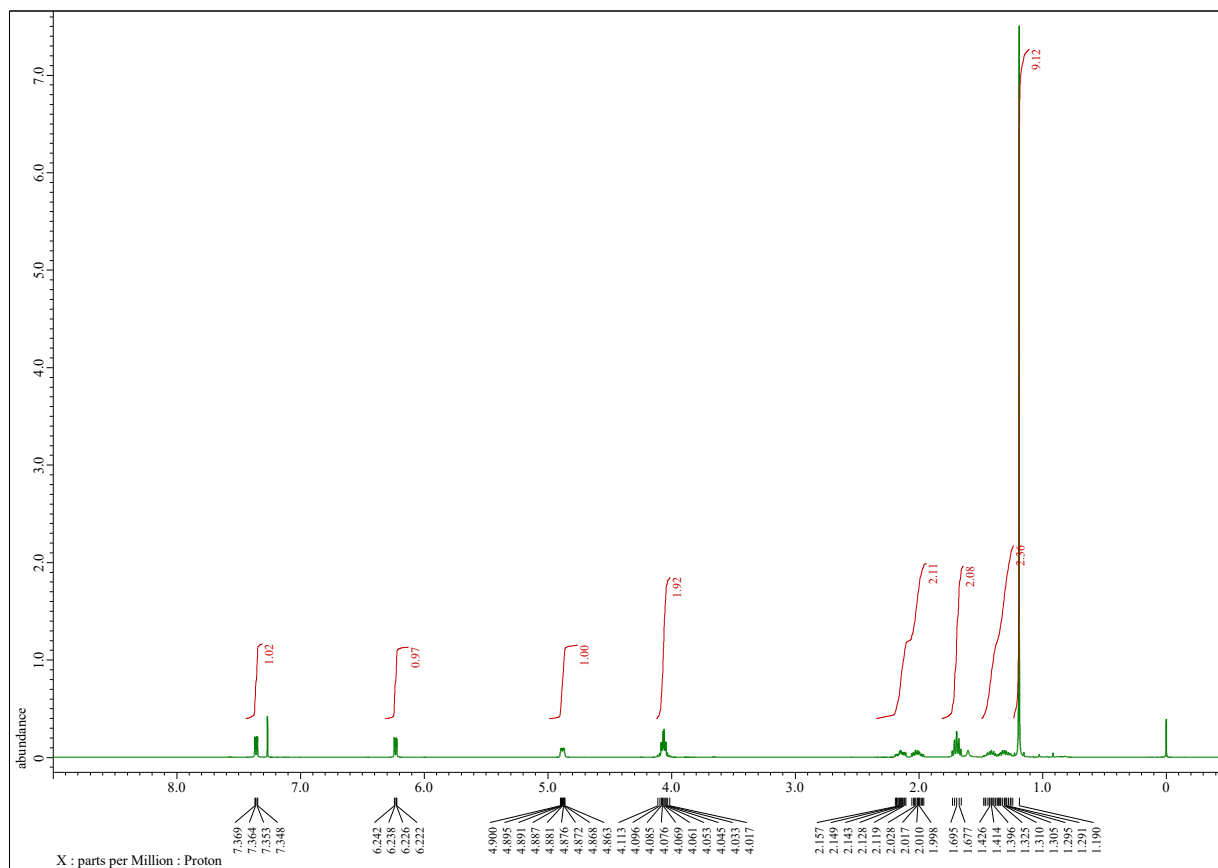
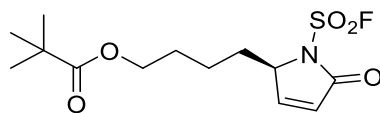


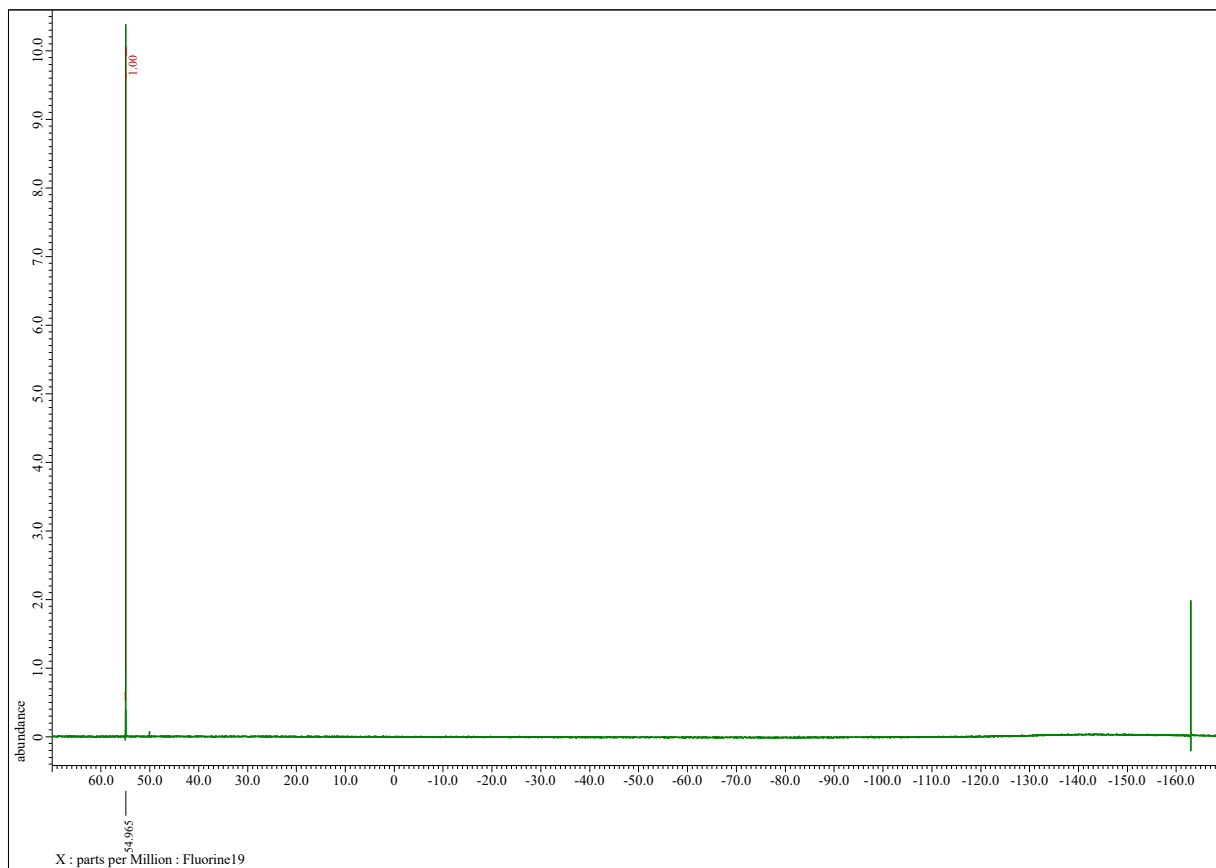
(R)-2-cyclohexyl-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5b)



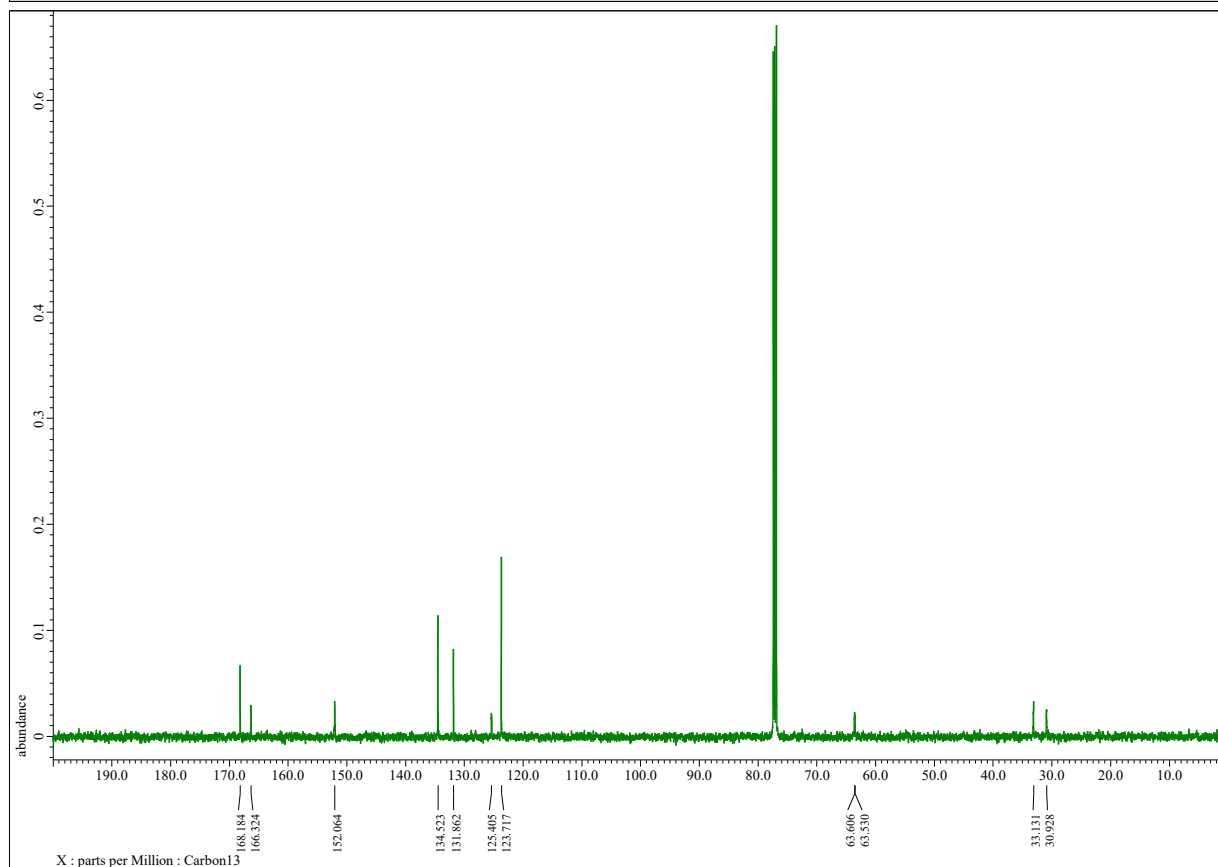
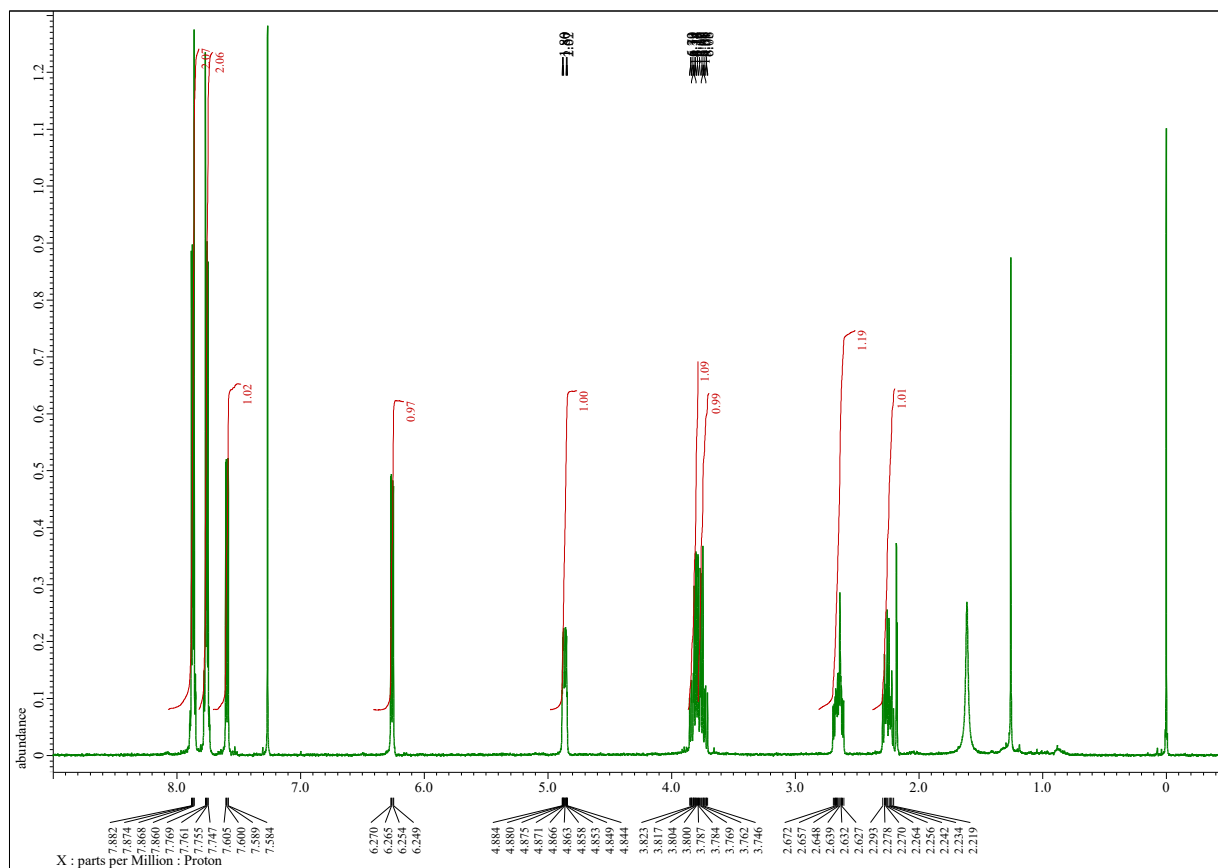
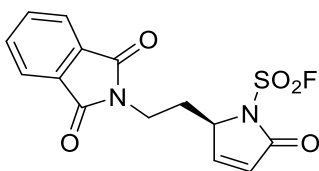


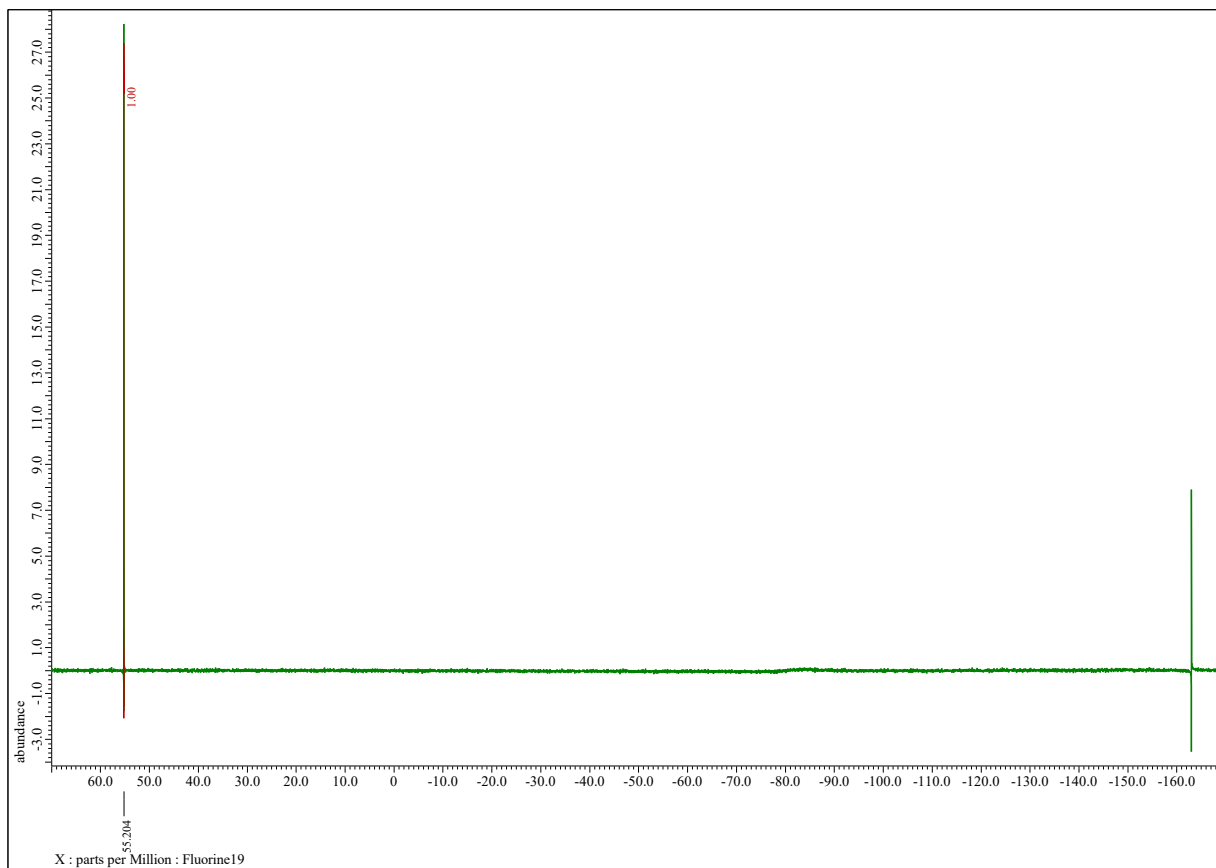
(R)-4-(1-(fluorosulfonyl)-5-oxo-2,5-dihydro-1H-pyrrol-2-yl)butyl pivalate (5c)



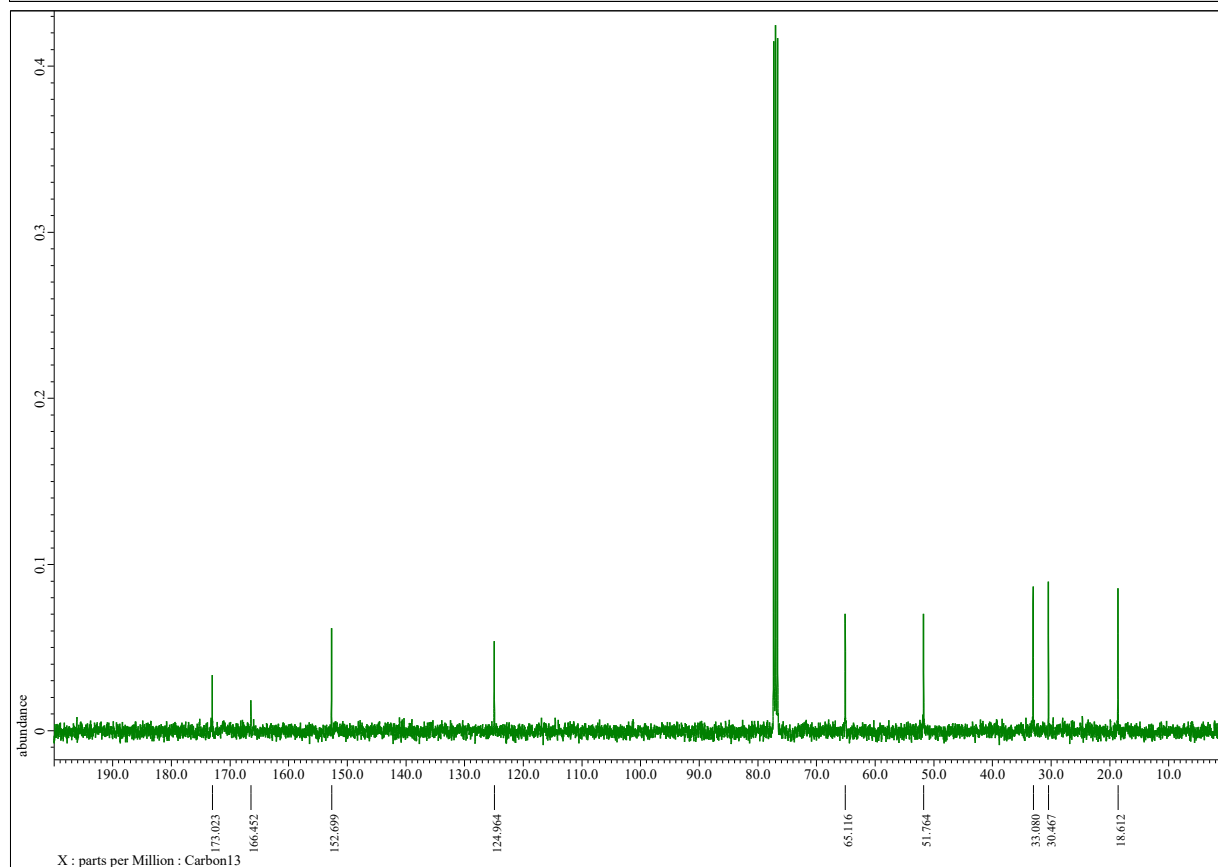
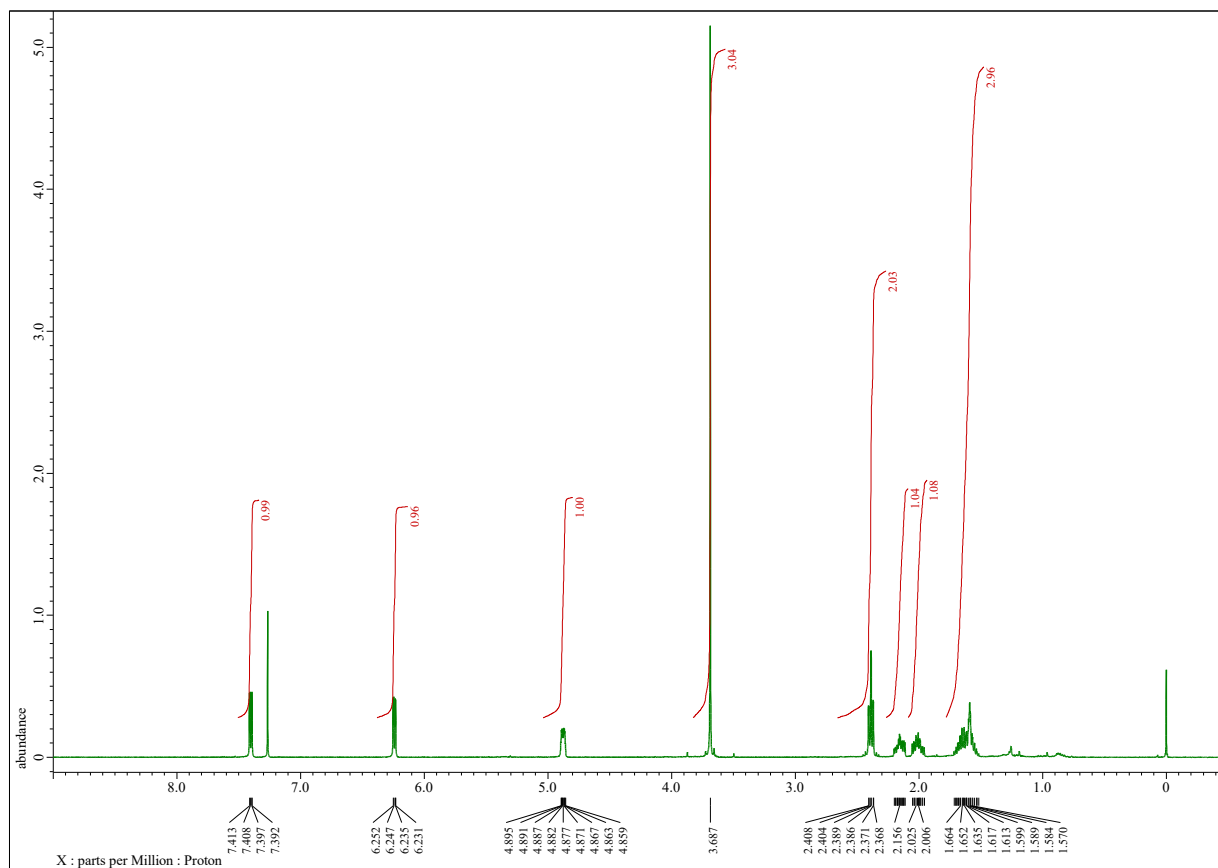
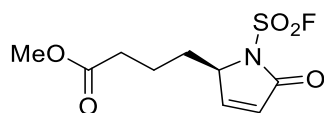


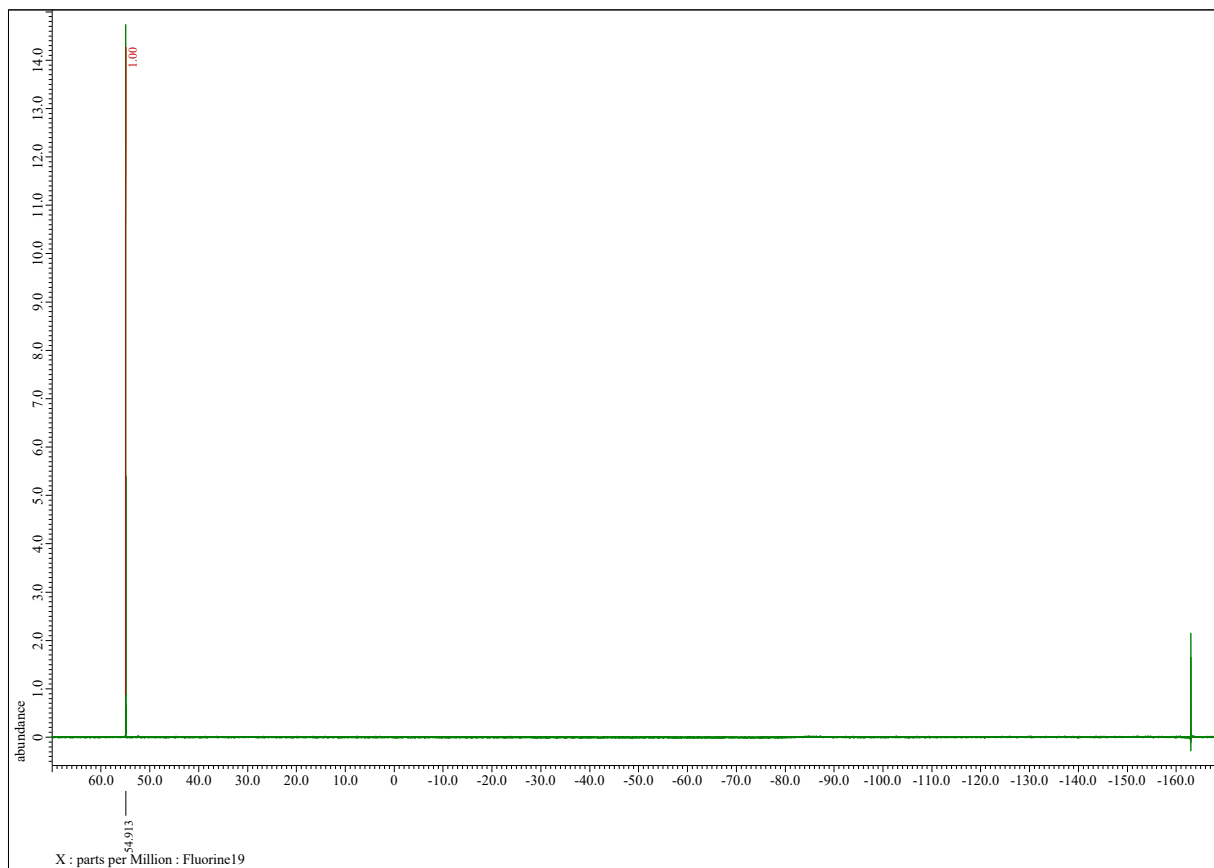
(R)-2-(2-(1,3-dioxisoindolin-2-yl)ethyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5d)



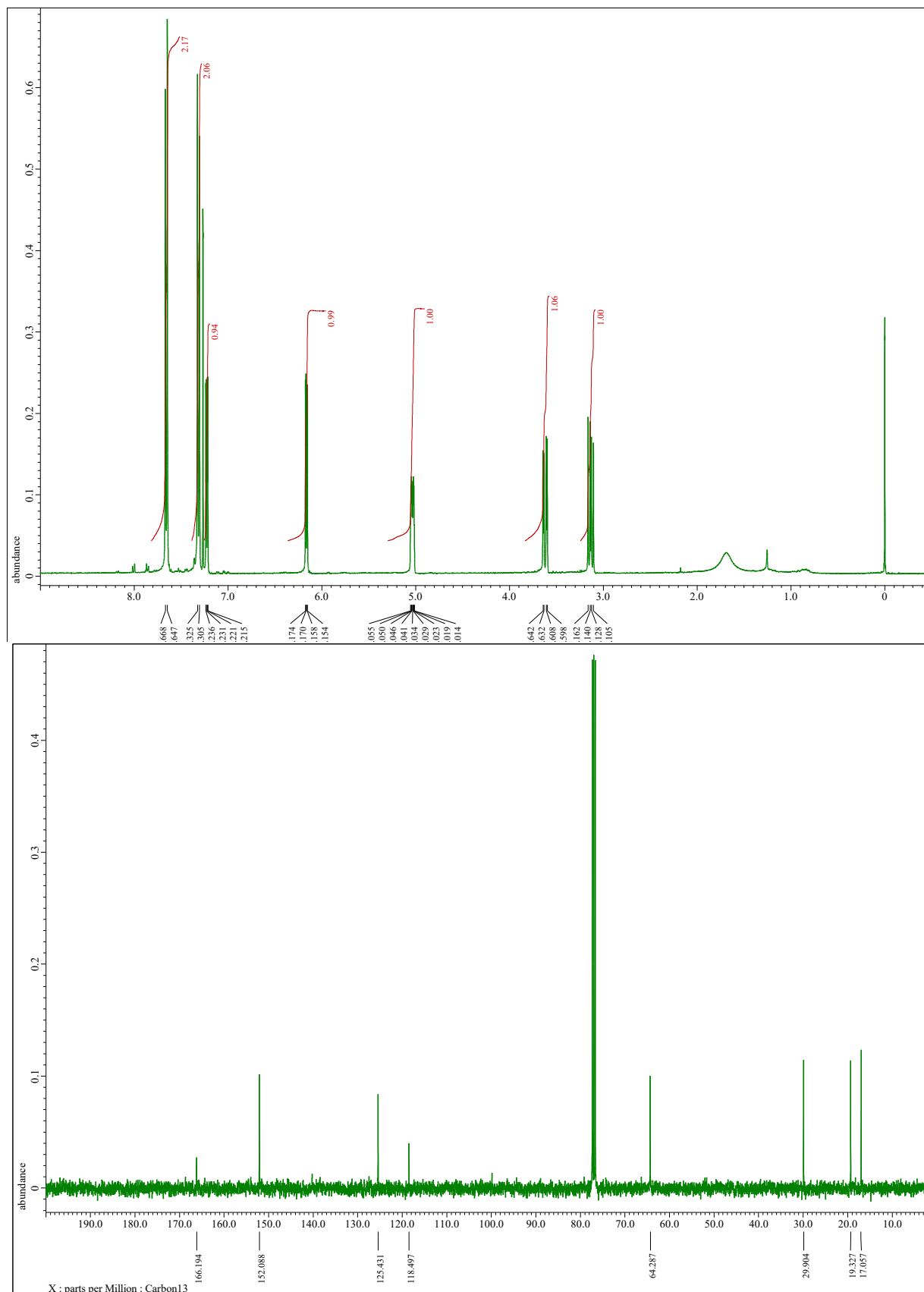
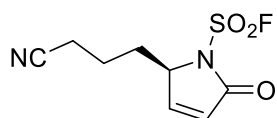


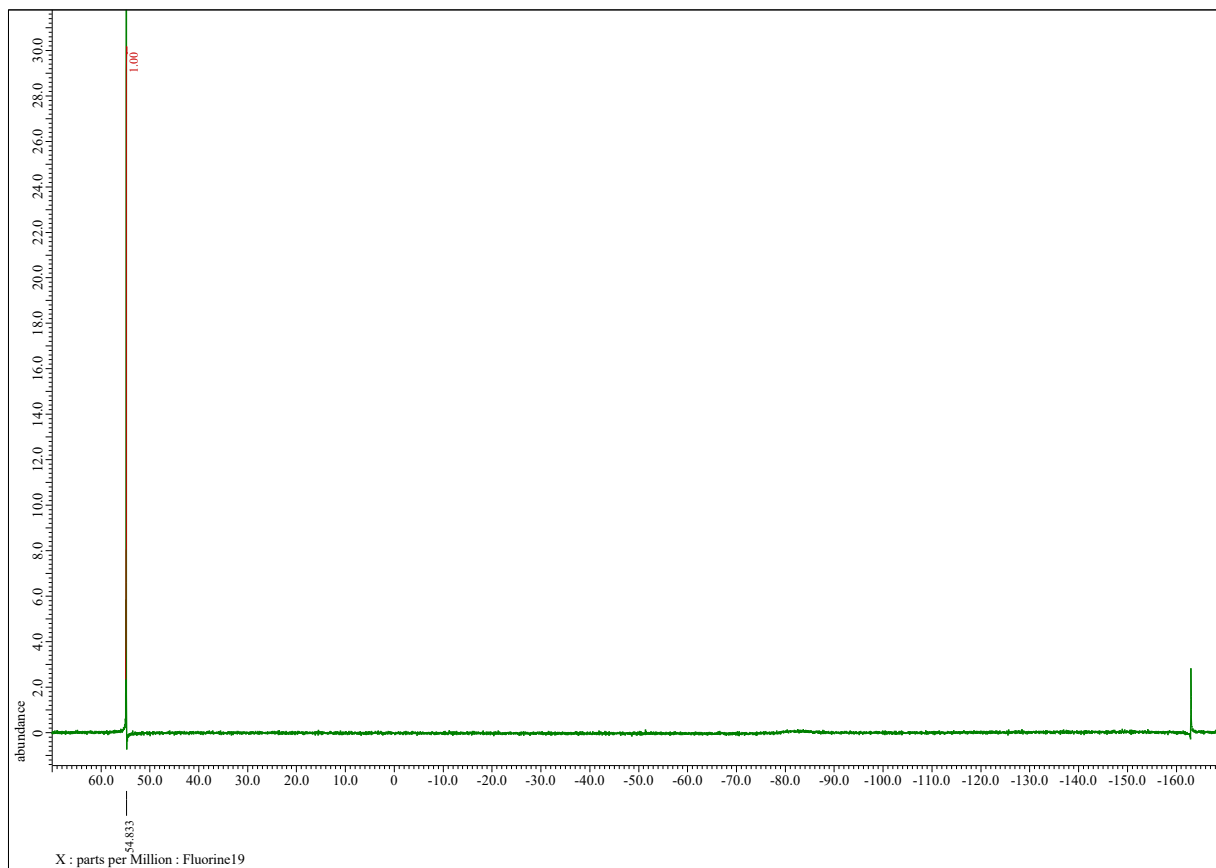
methyl (*R*)-4-(1-(fluorosulfonyl)-5-oxo-2,5-dihydro-1H-pyrrol-2-yl)butanoate (5e)



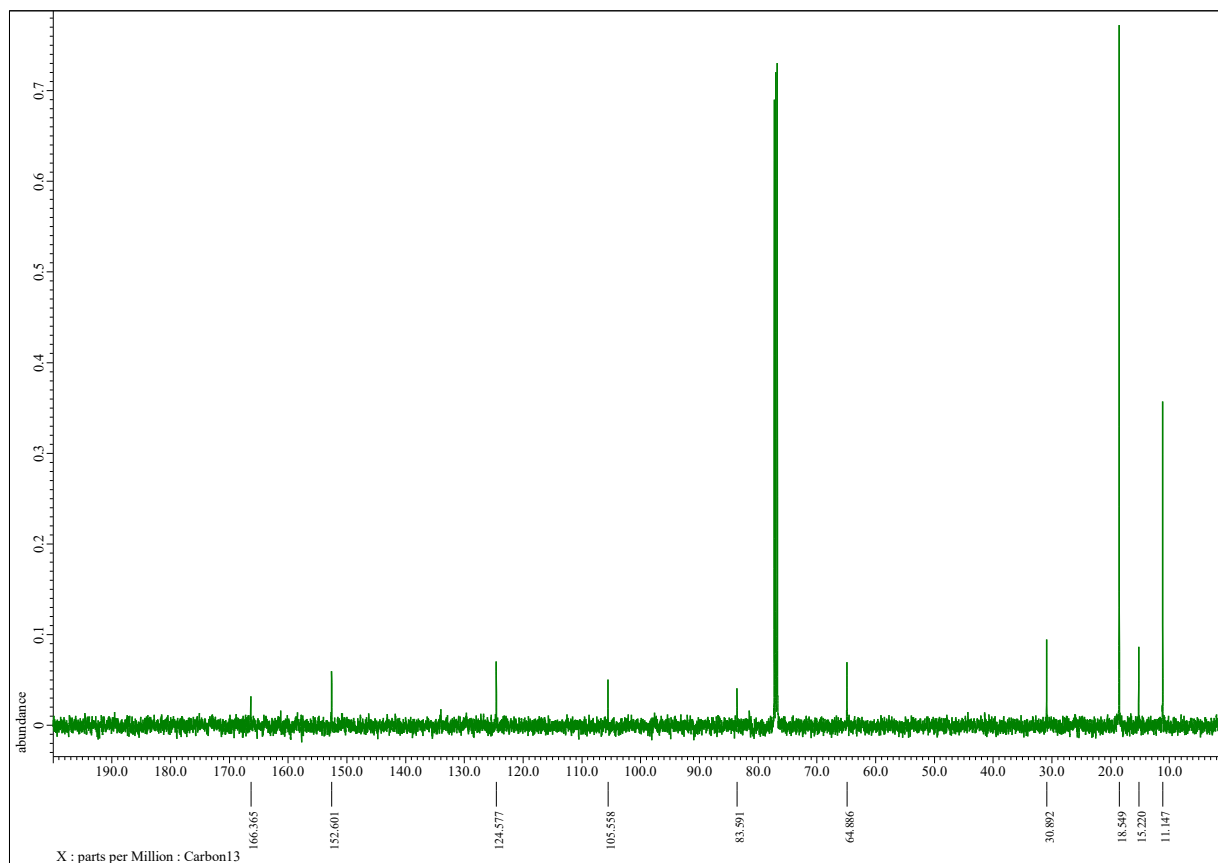
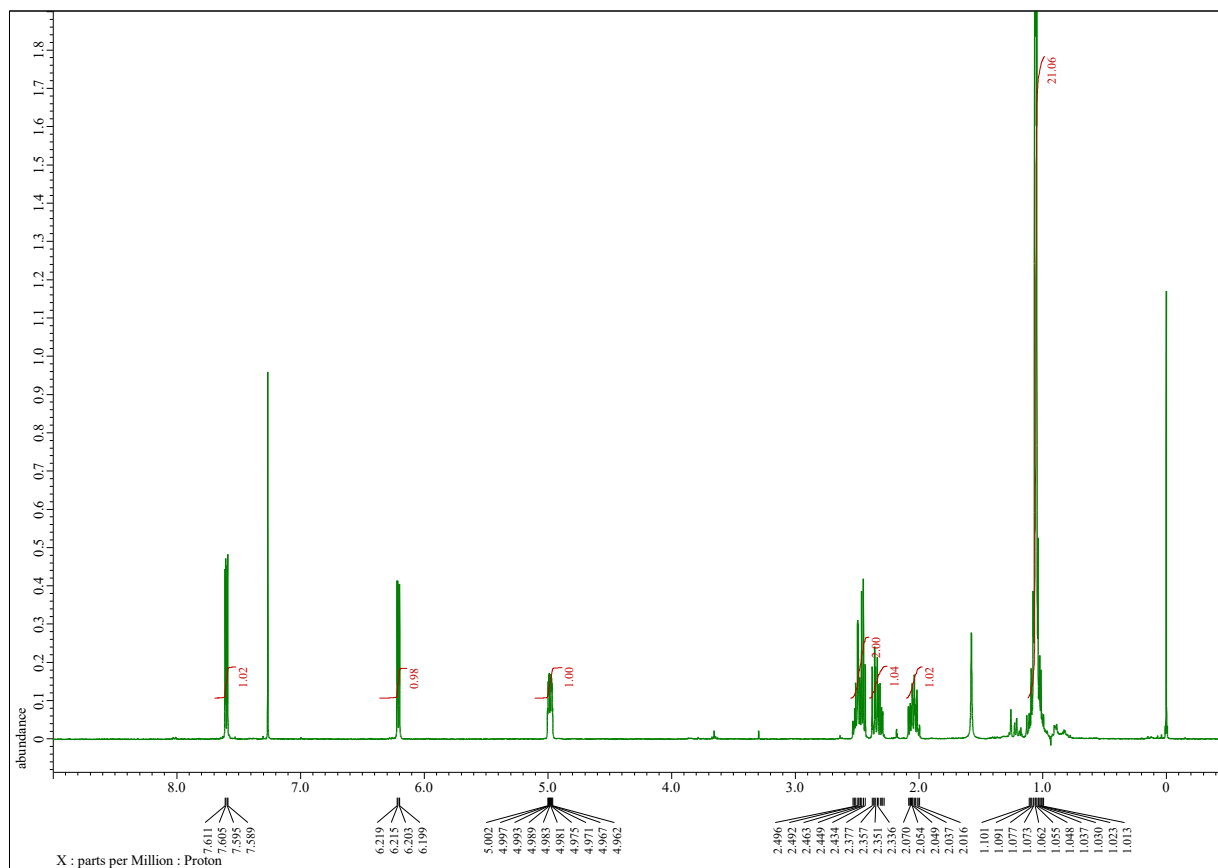
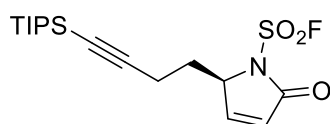


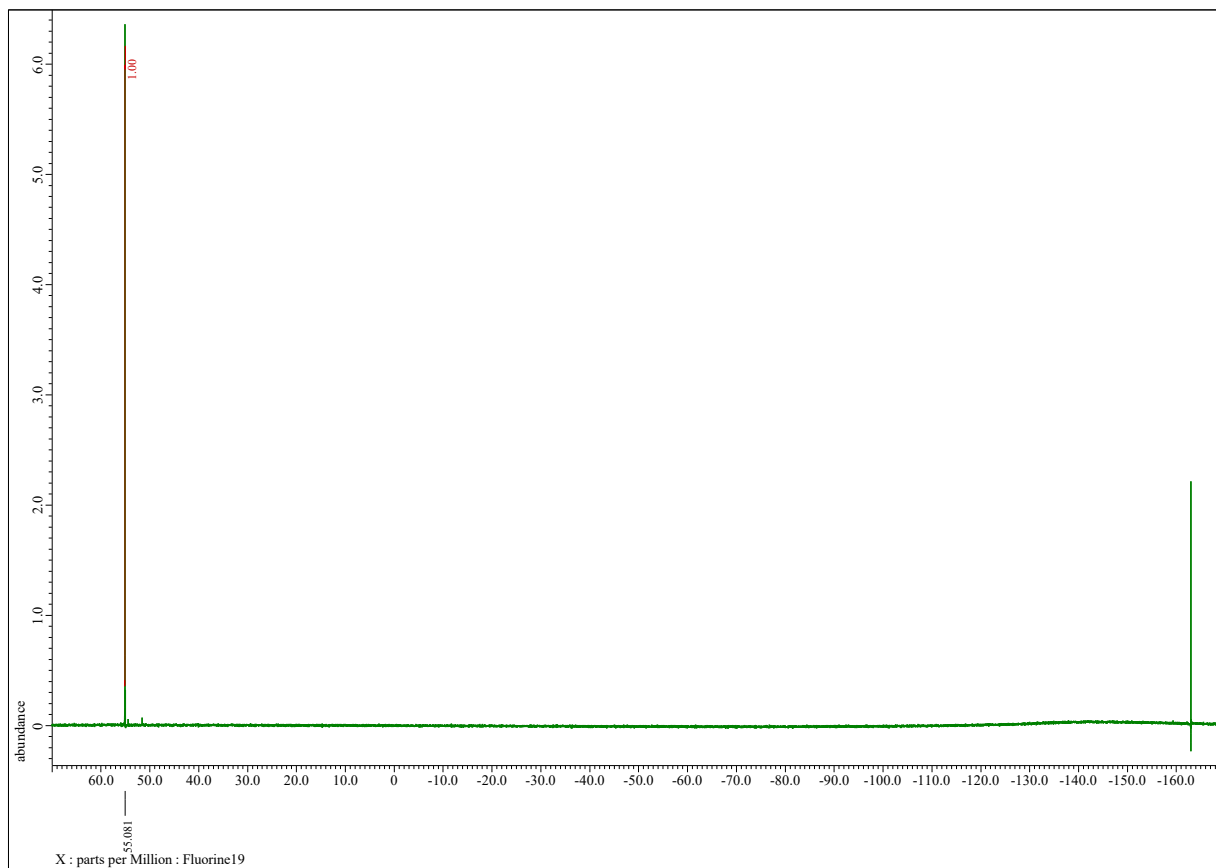
(R)-2-(3-cyanopropyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5f)



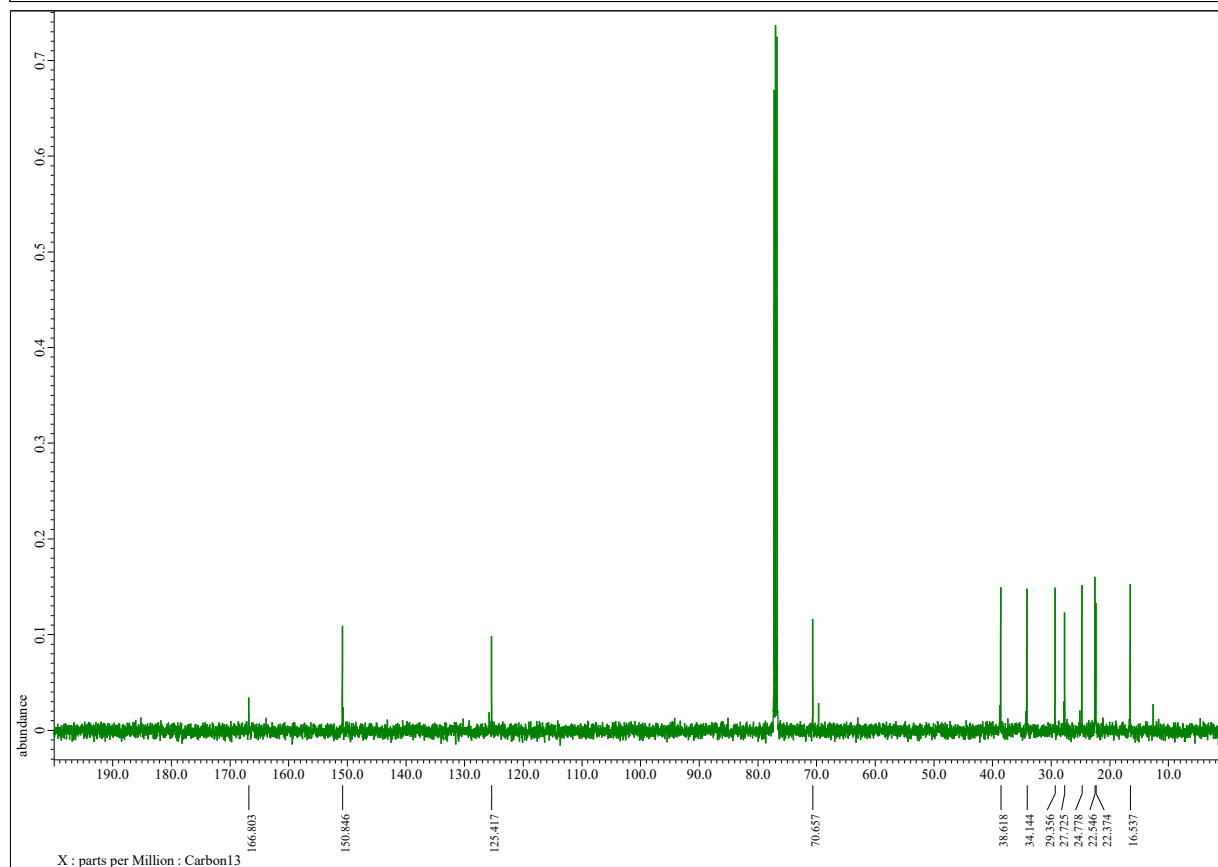
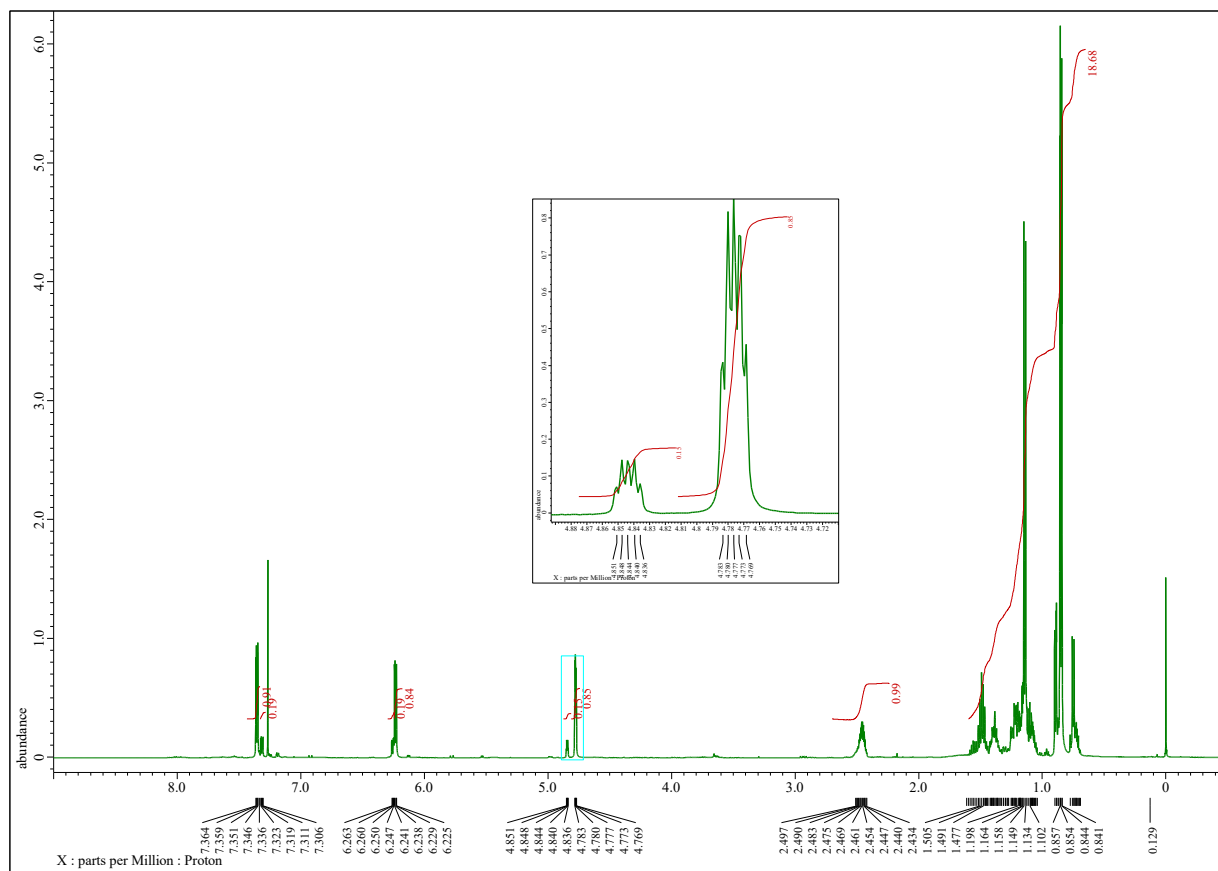
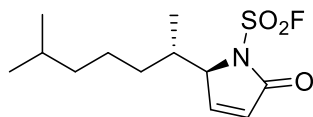


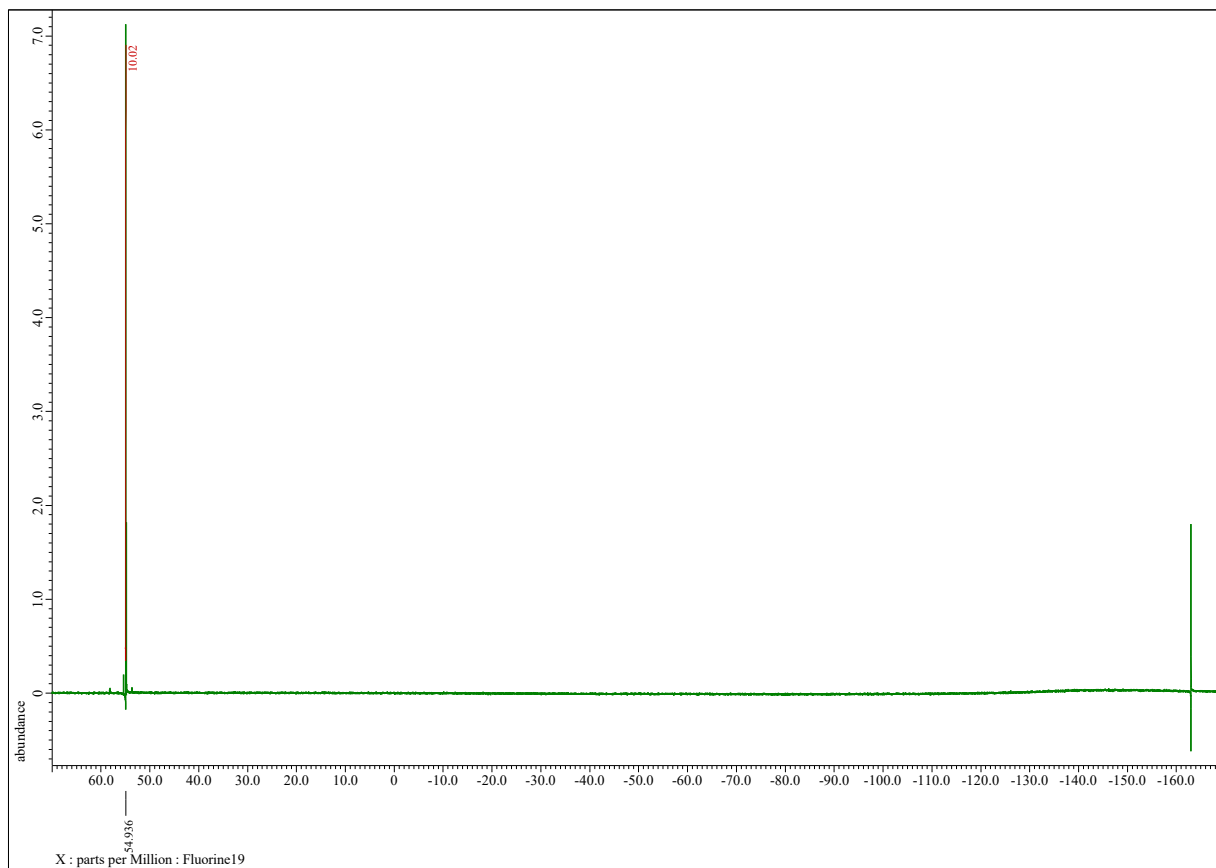
(R)-2-oxo-5-(4-(triisopropylsilyl)but-3-yn-1-yl)-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5g)



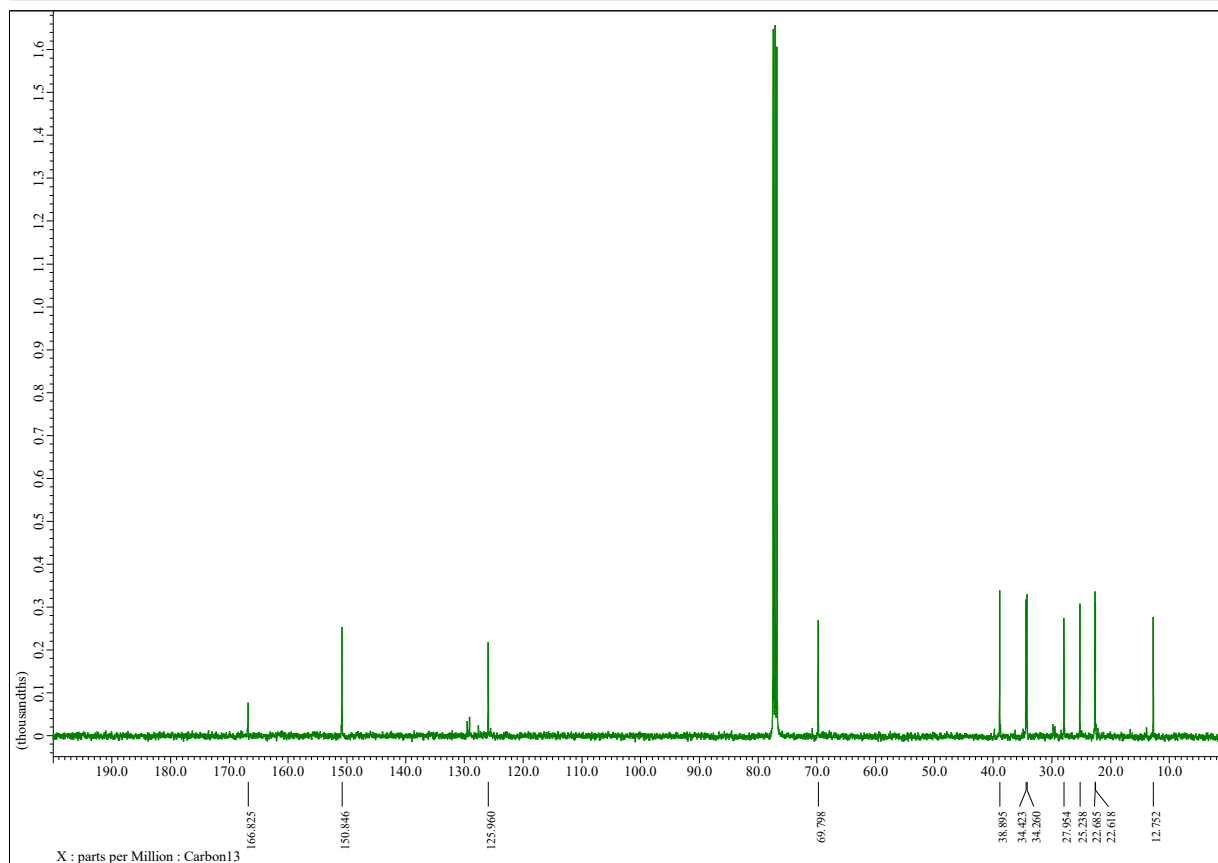
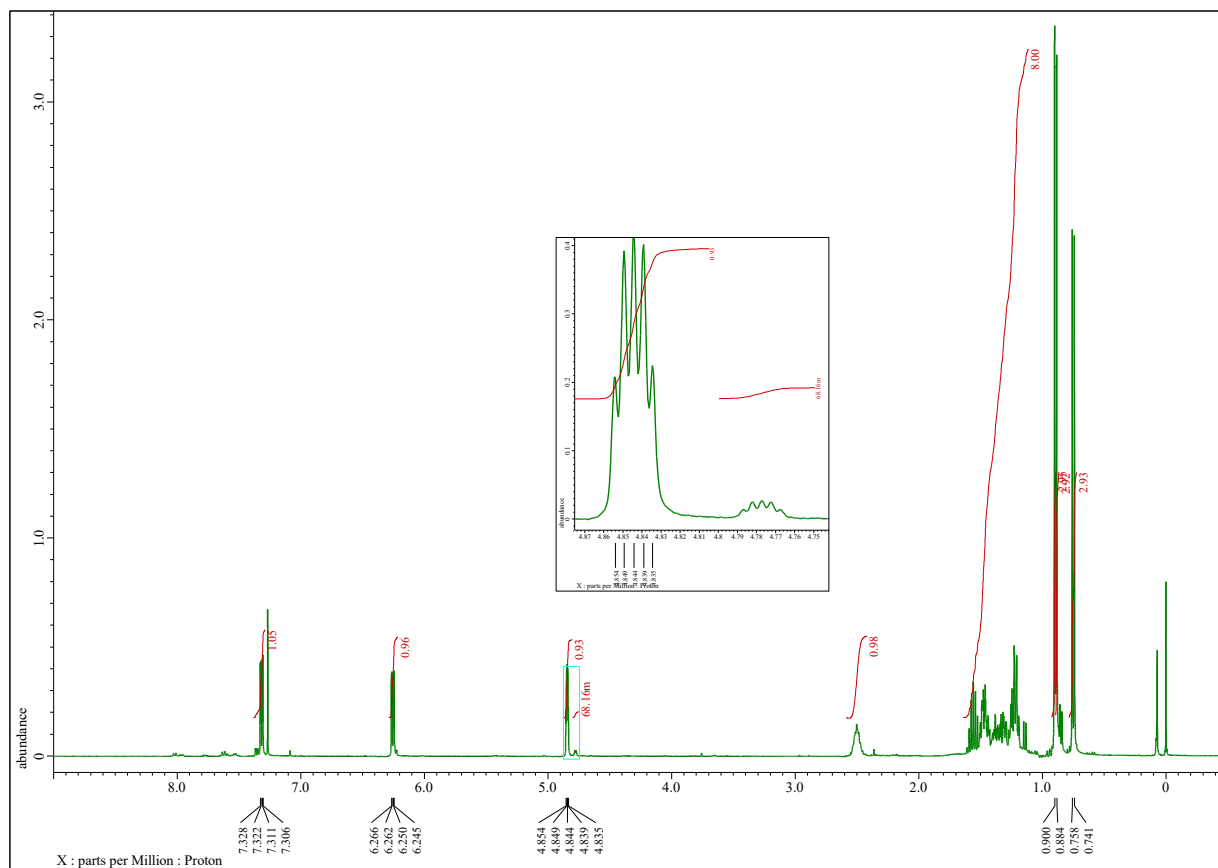
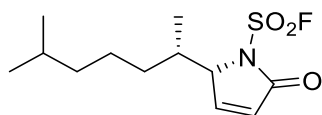


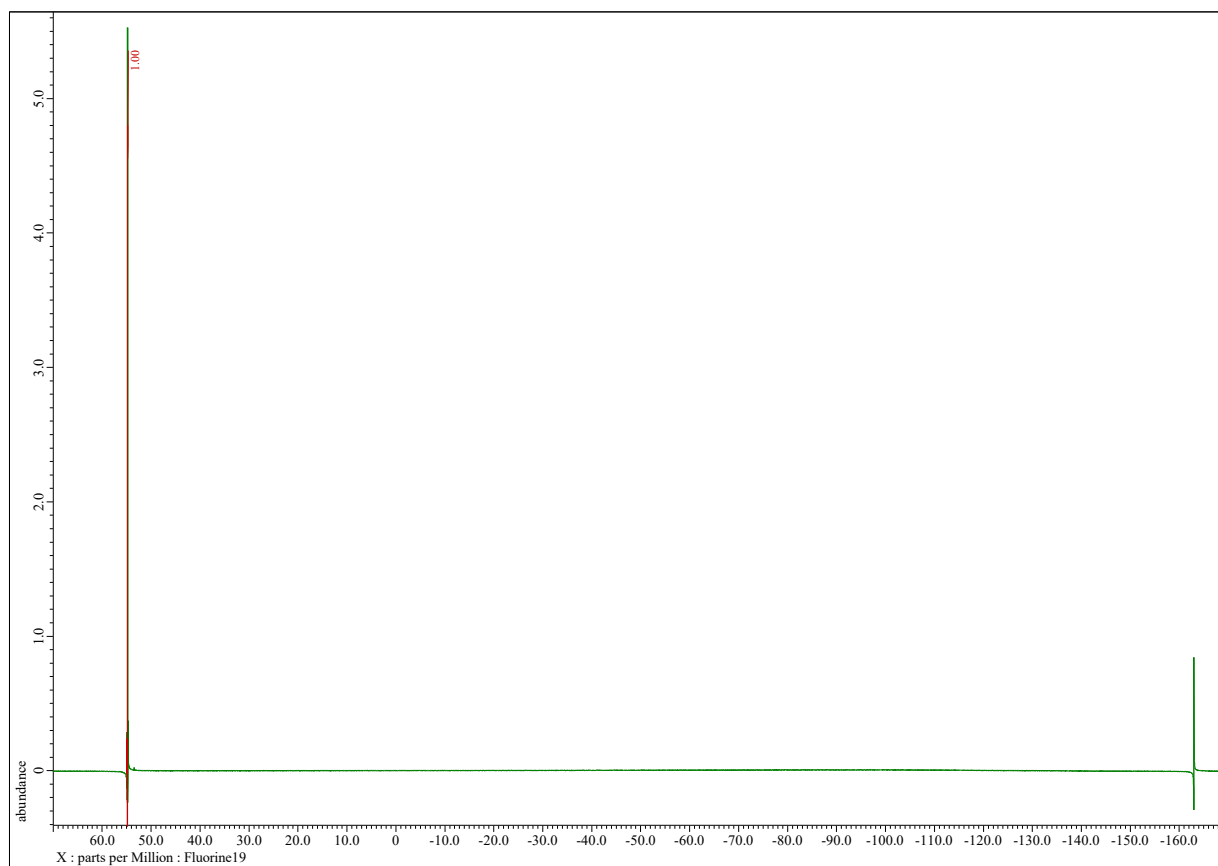
(R)-2-((S)-6-methylheptan-2-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5h)



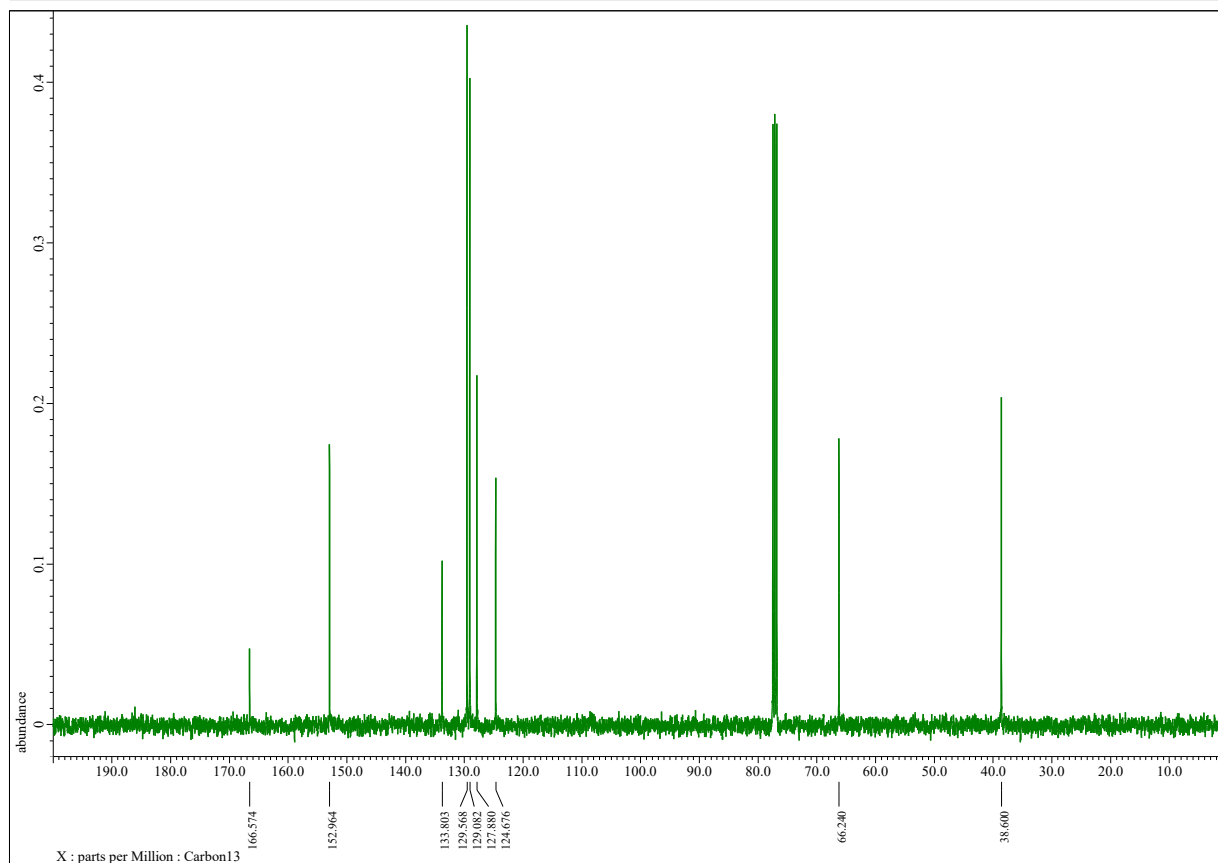
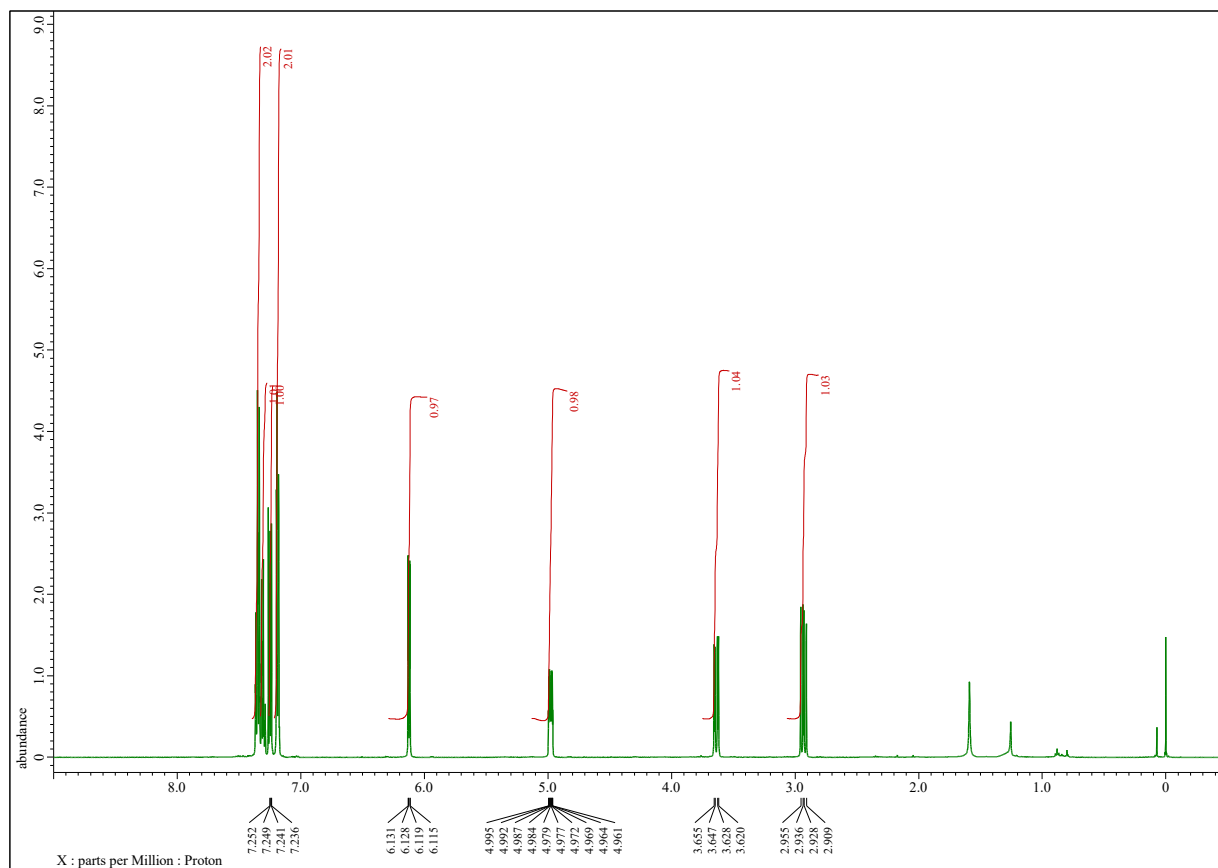
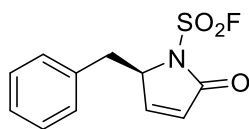


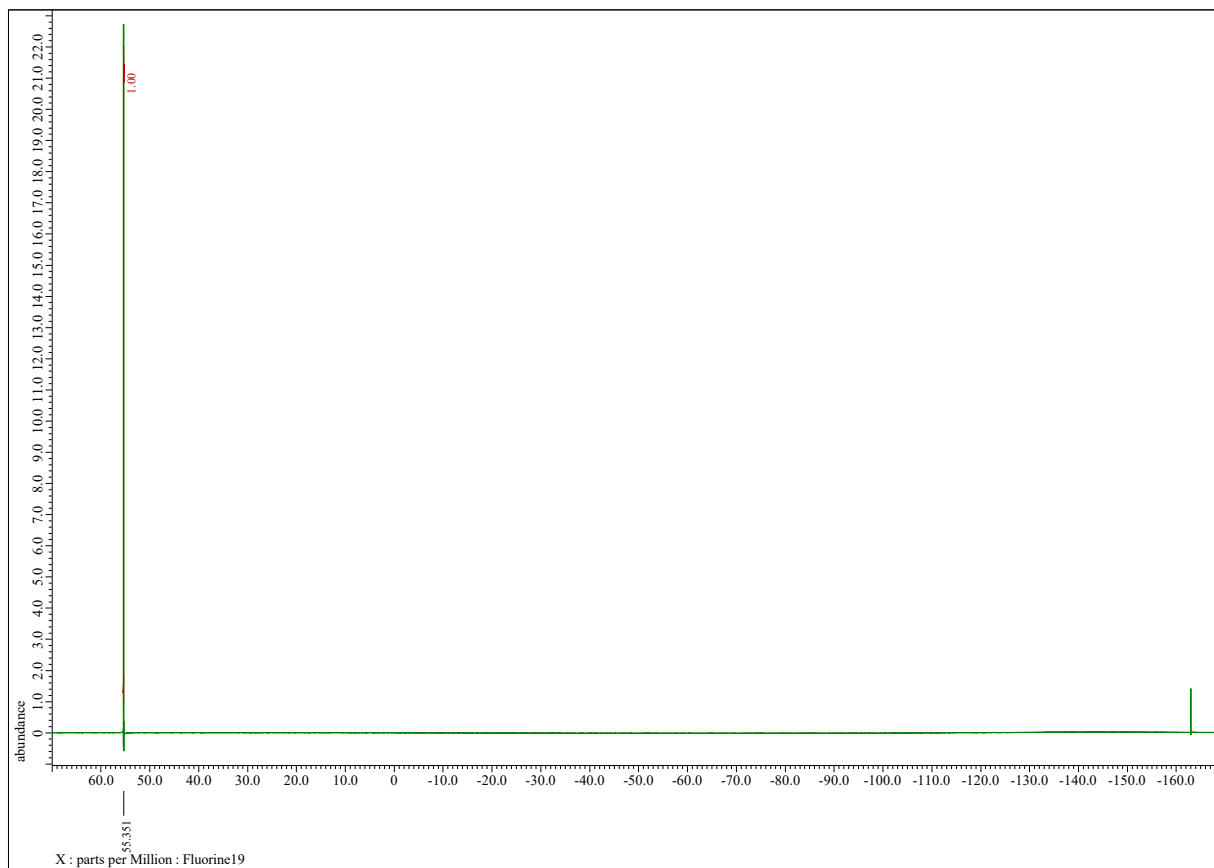
(S)-2-((S)-6-methylheptan-2-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5i)



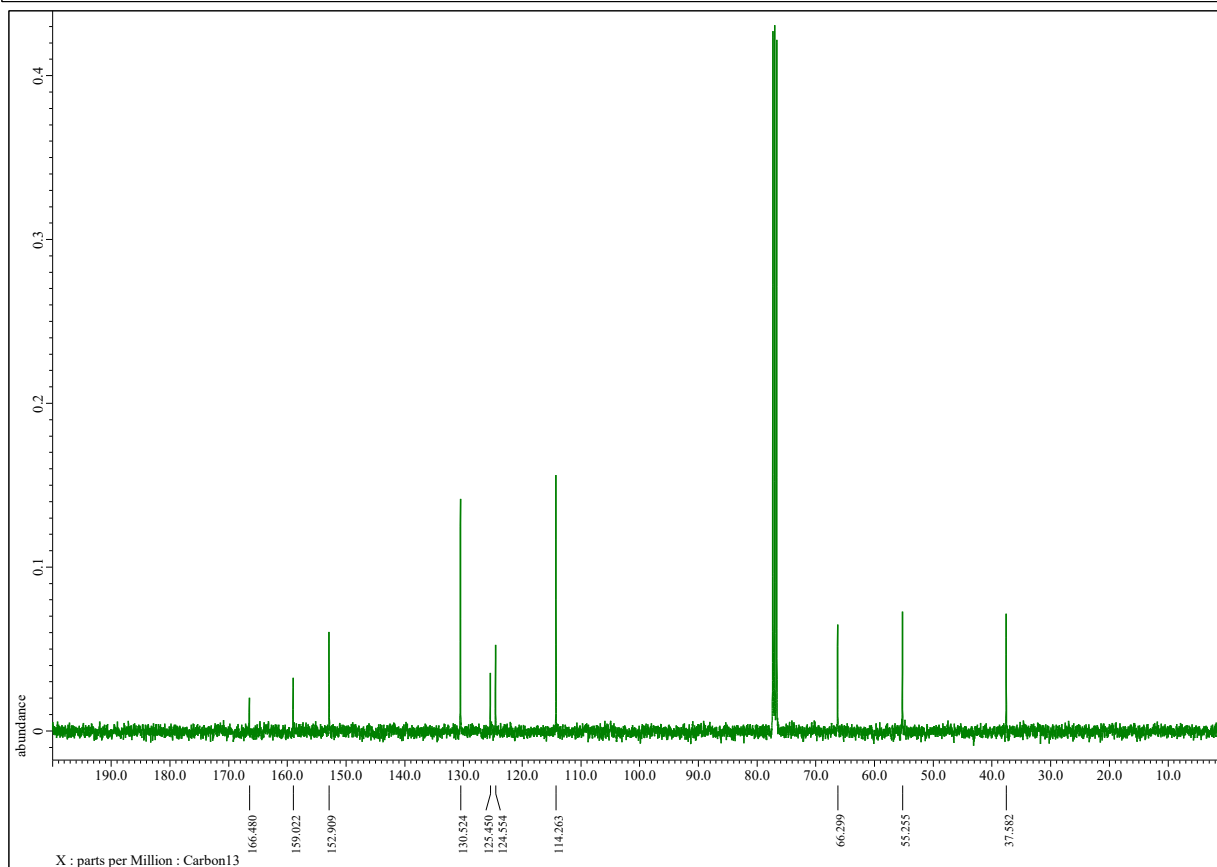
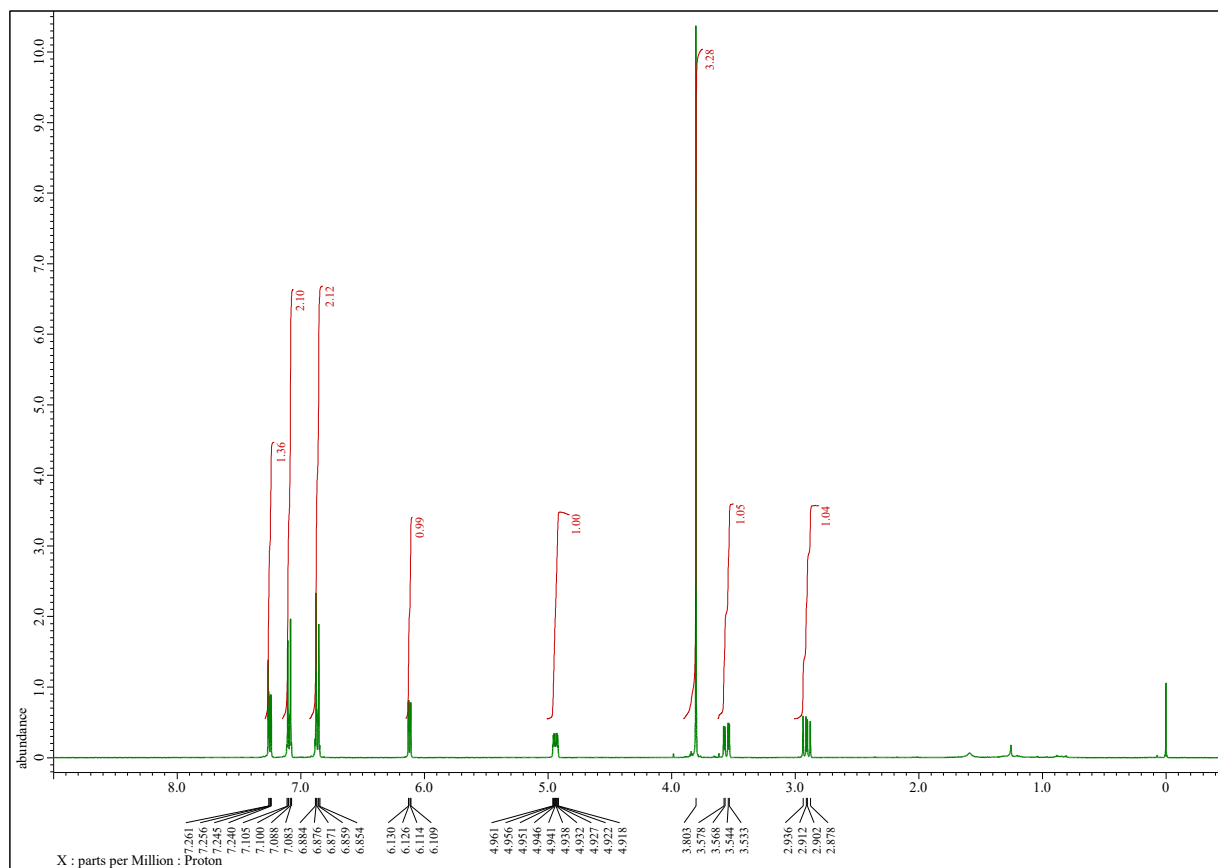
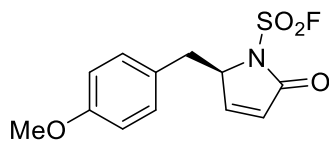


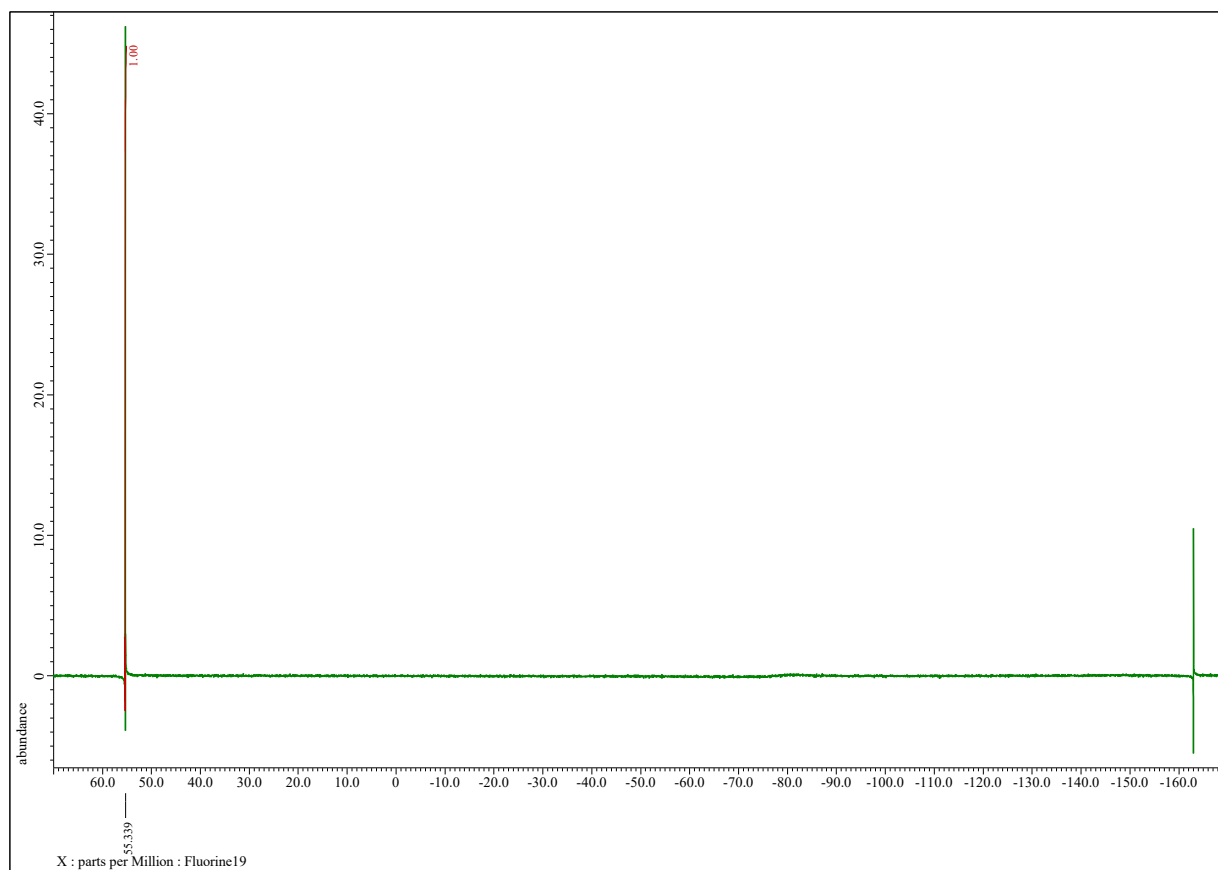
(R)-2-benzyl-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5j)



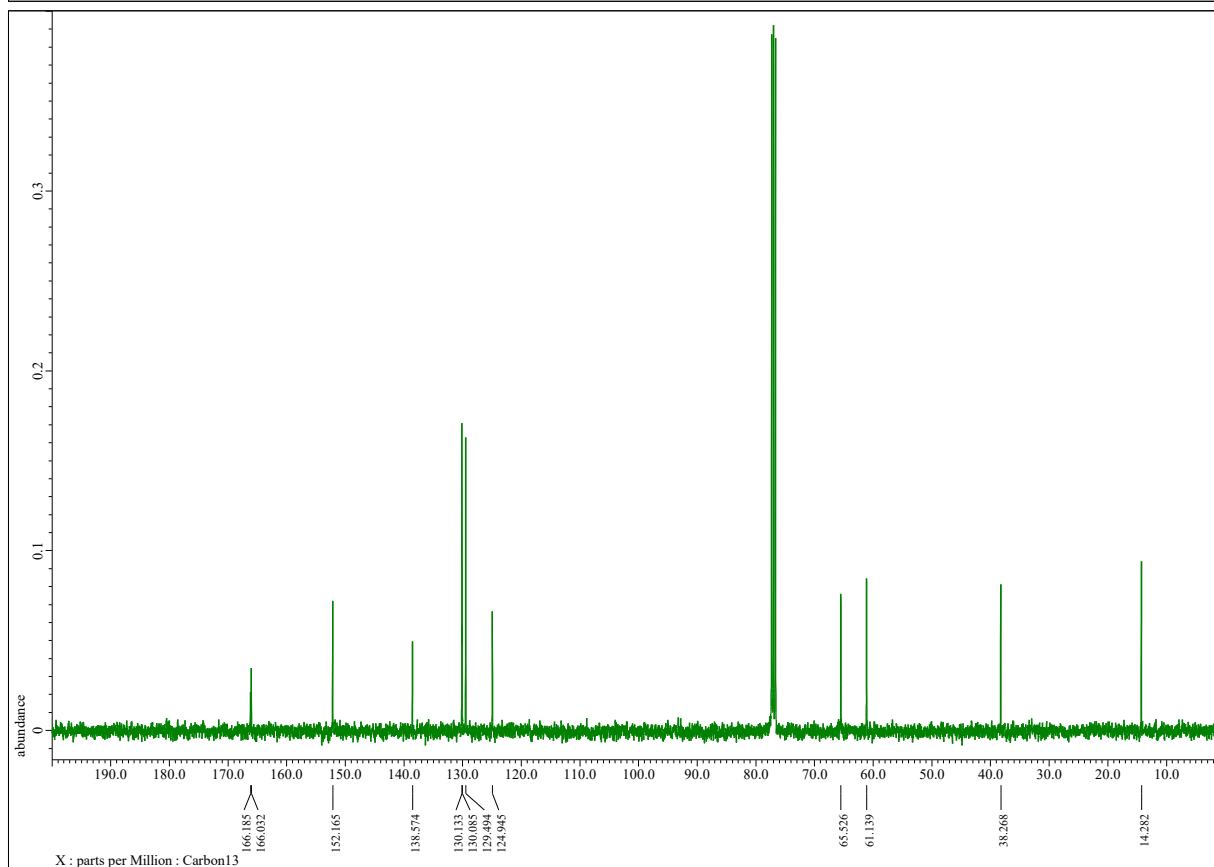
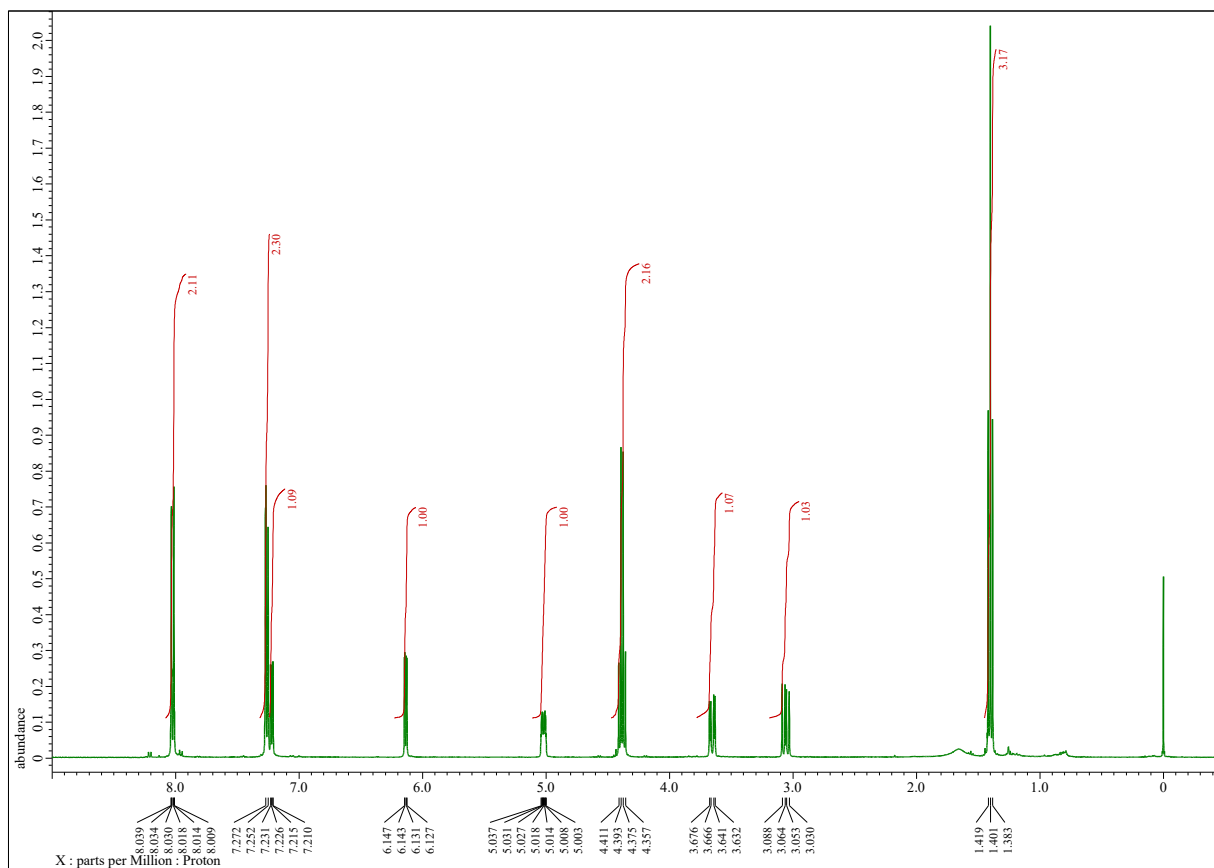
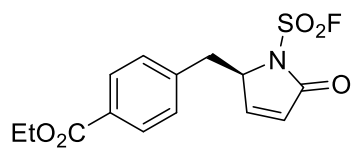


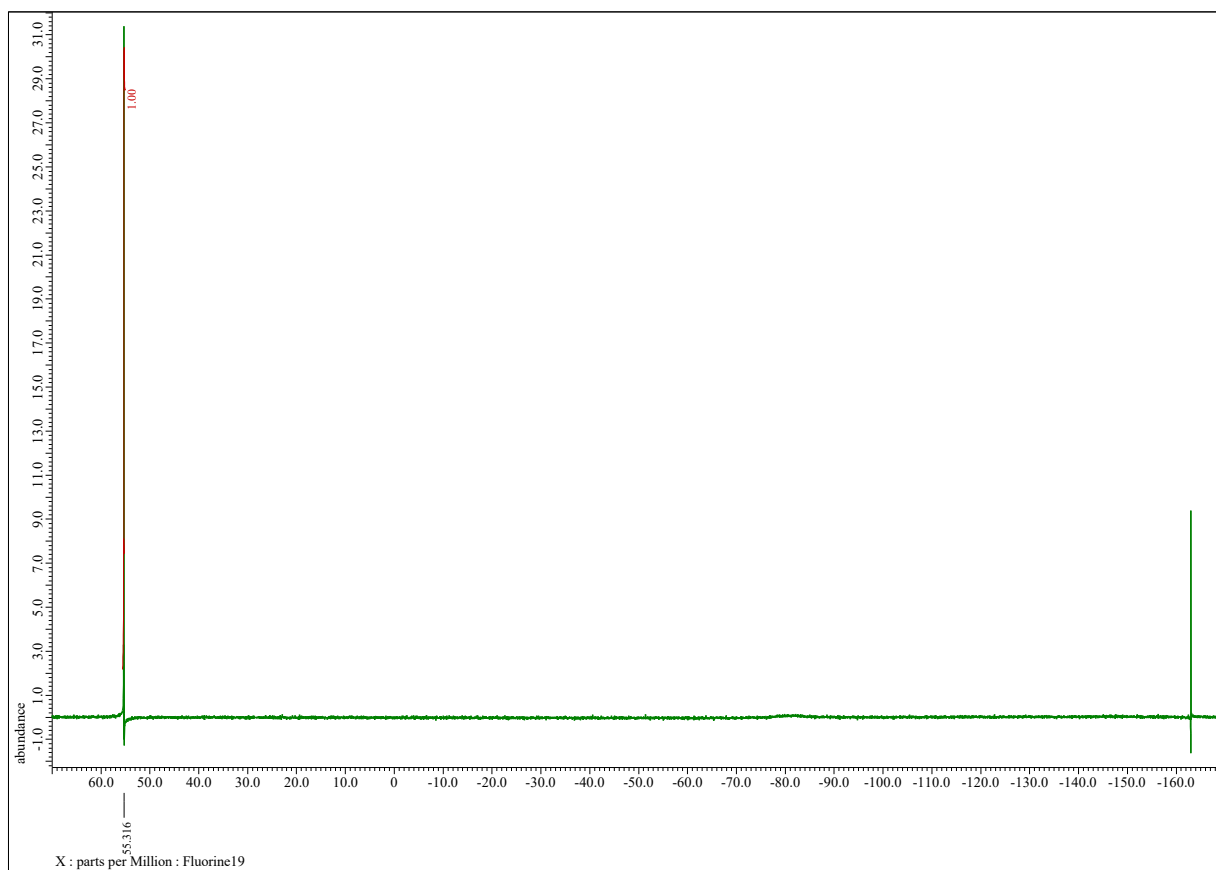
(R)-2-(4-methoxybenzyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5k)



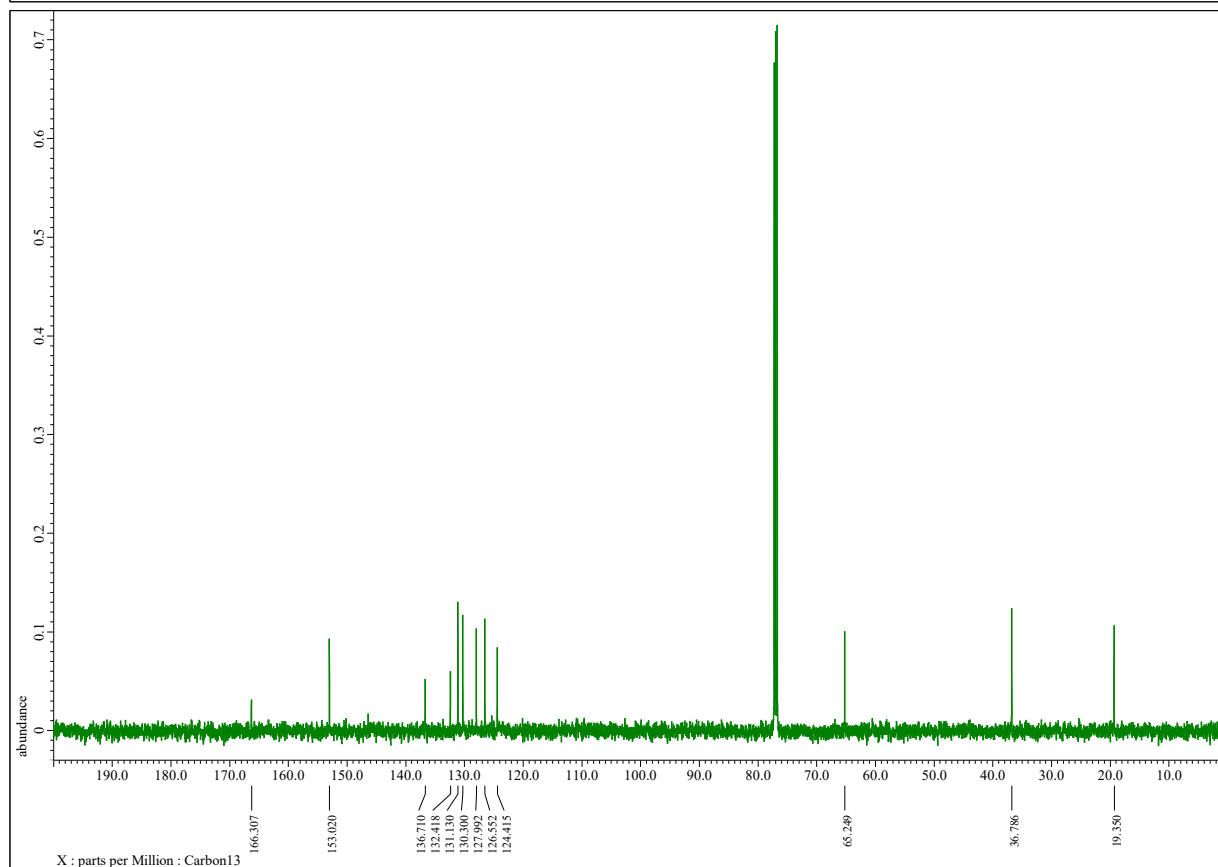
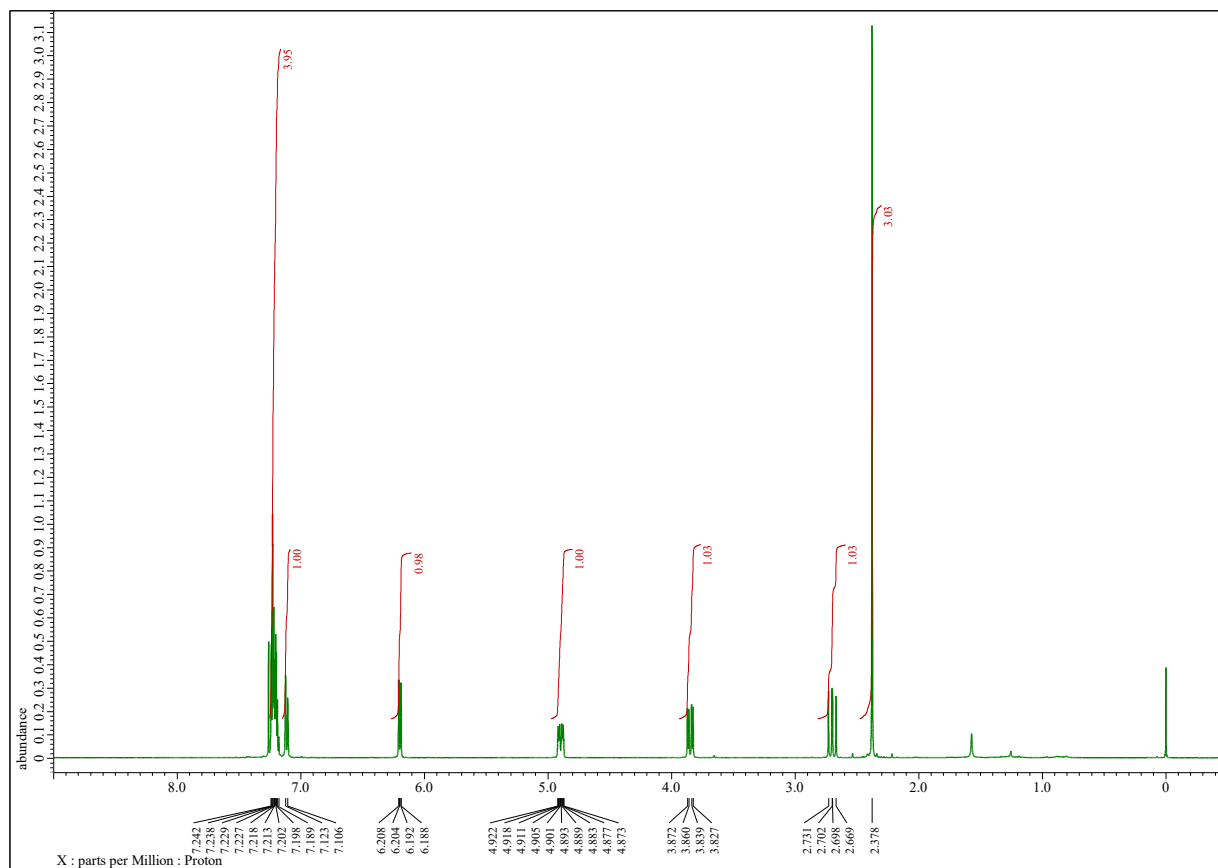
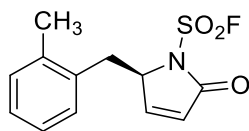


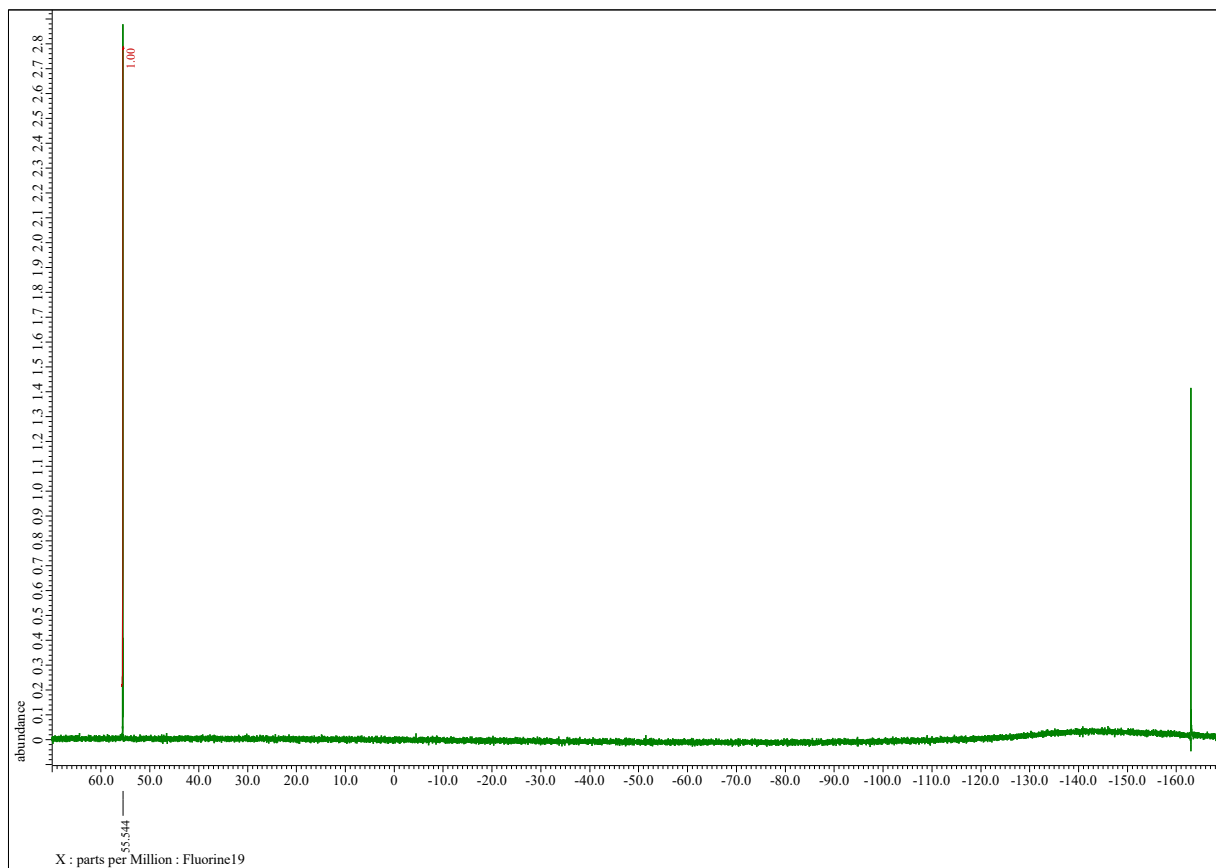
(R)-2-(4-ethoxycarbonylbenzyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5l)



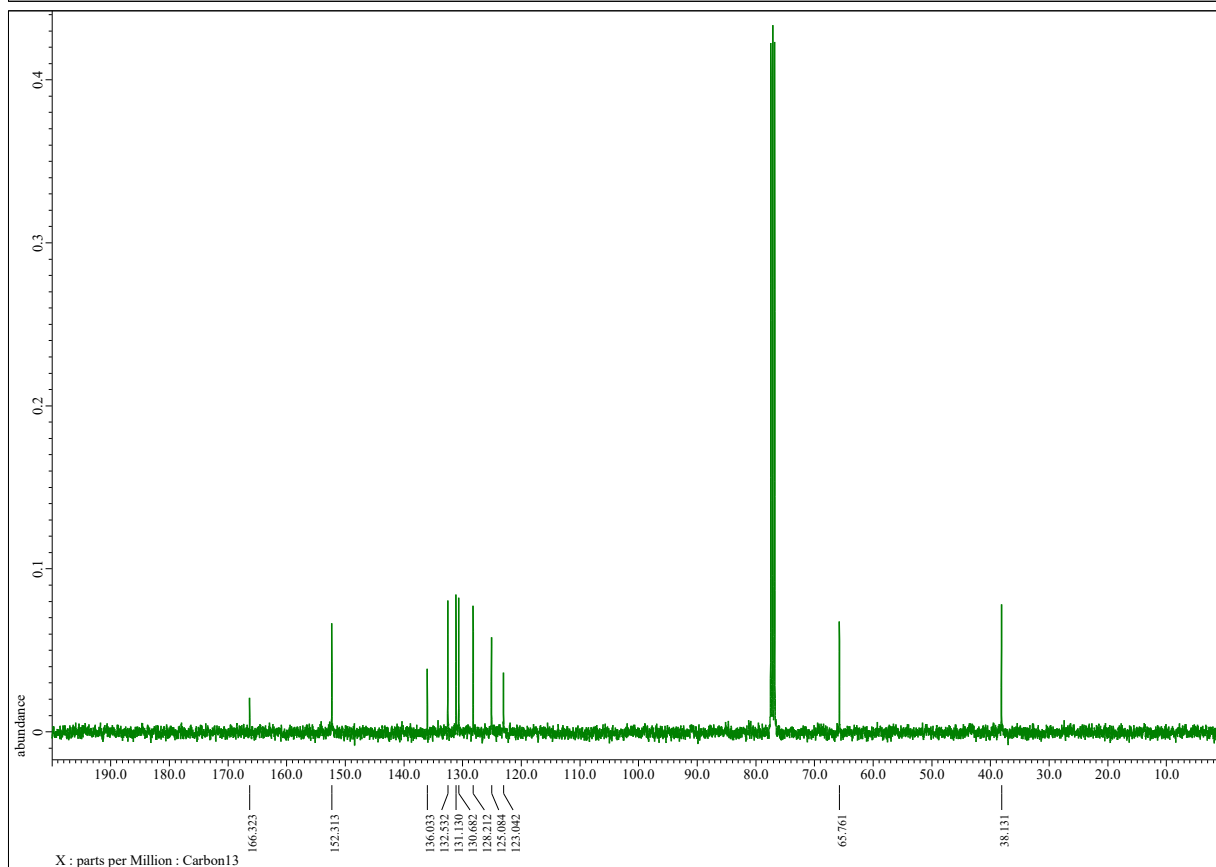
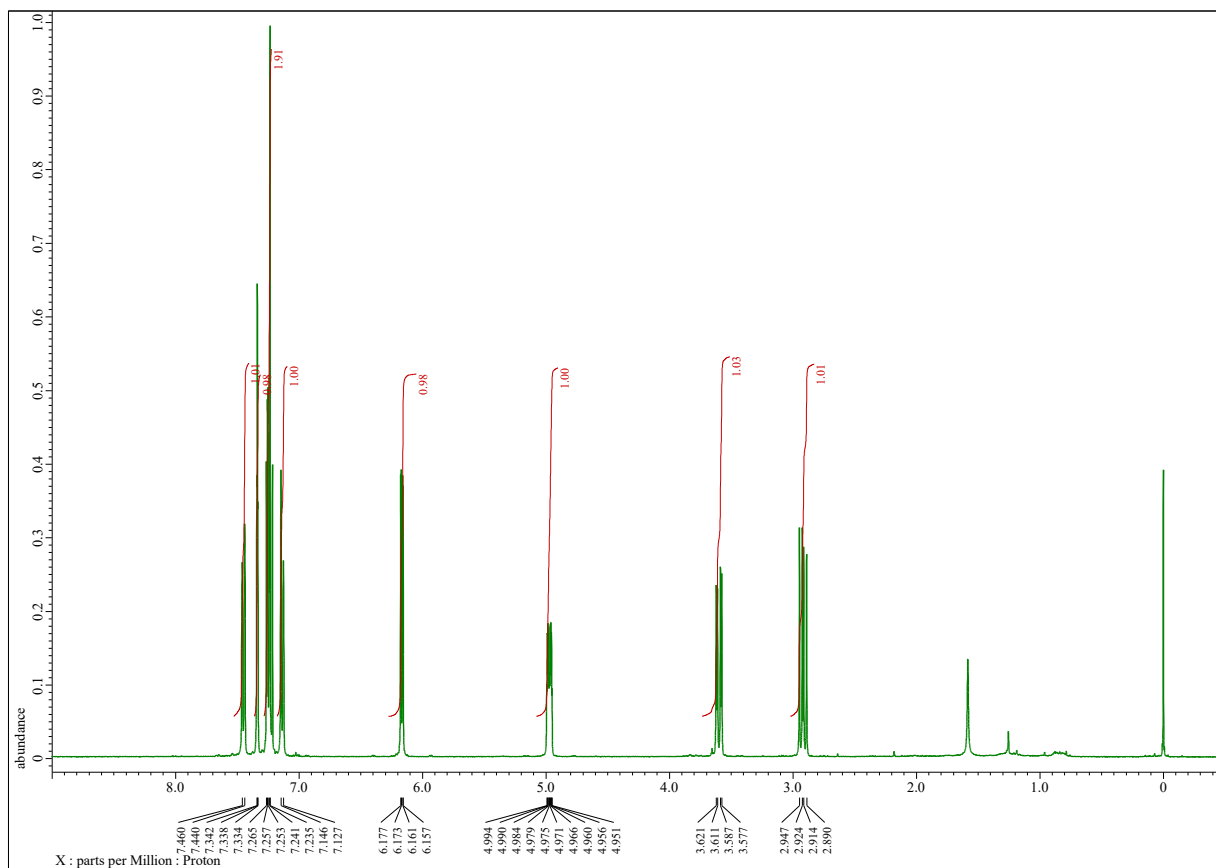
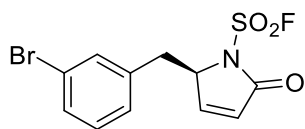


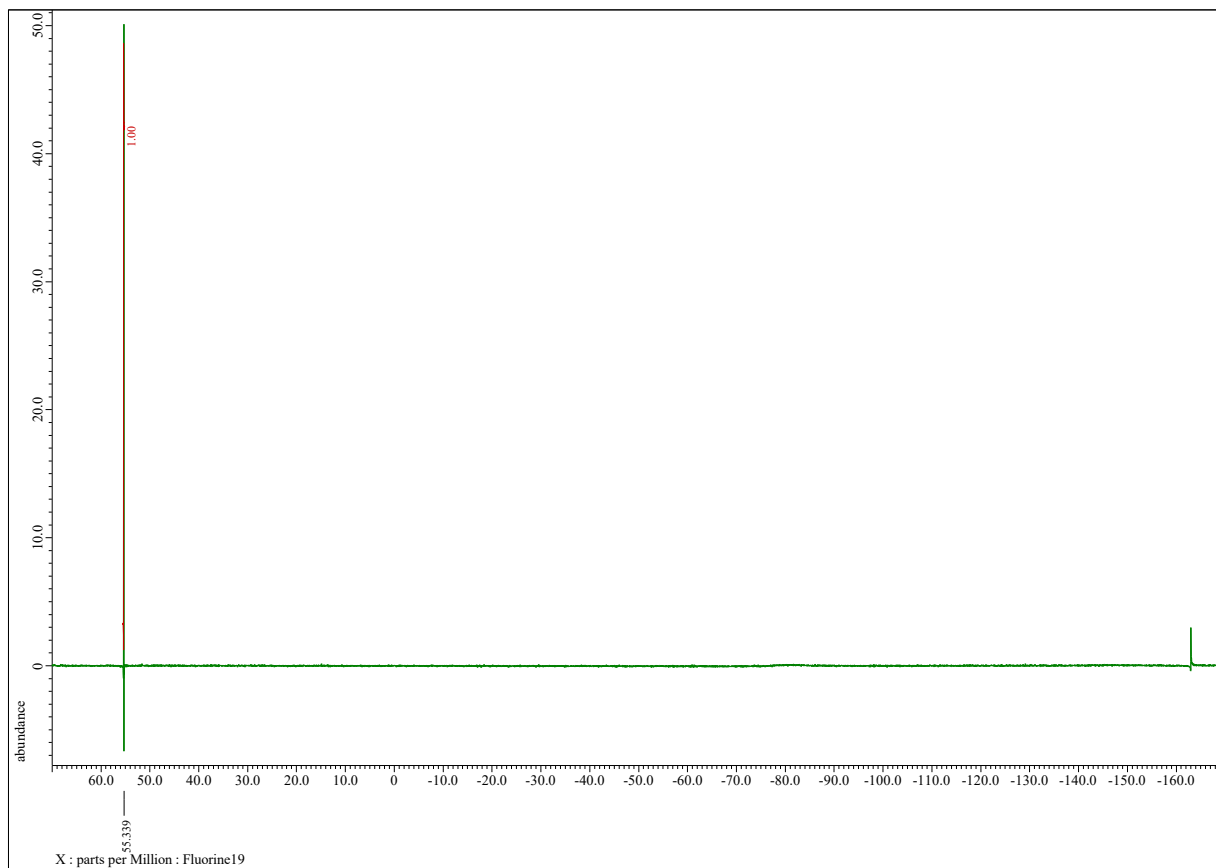
(R)-2-(2-methylbenzyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5m)



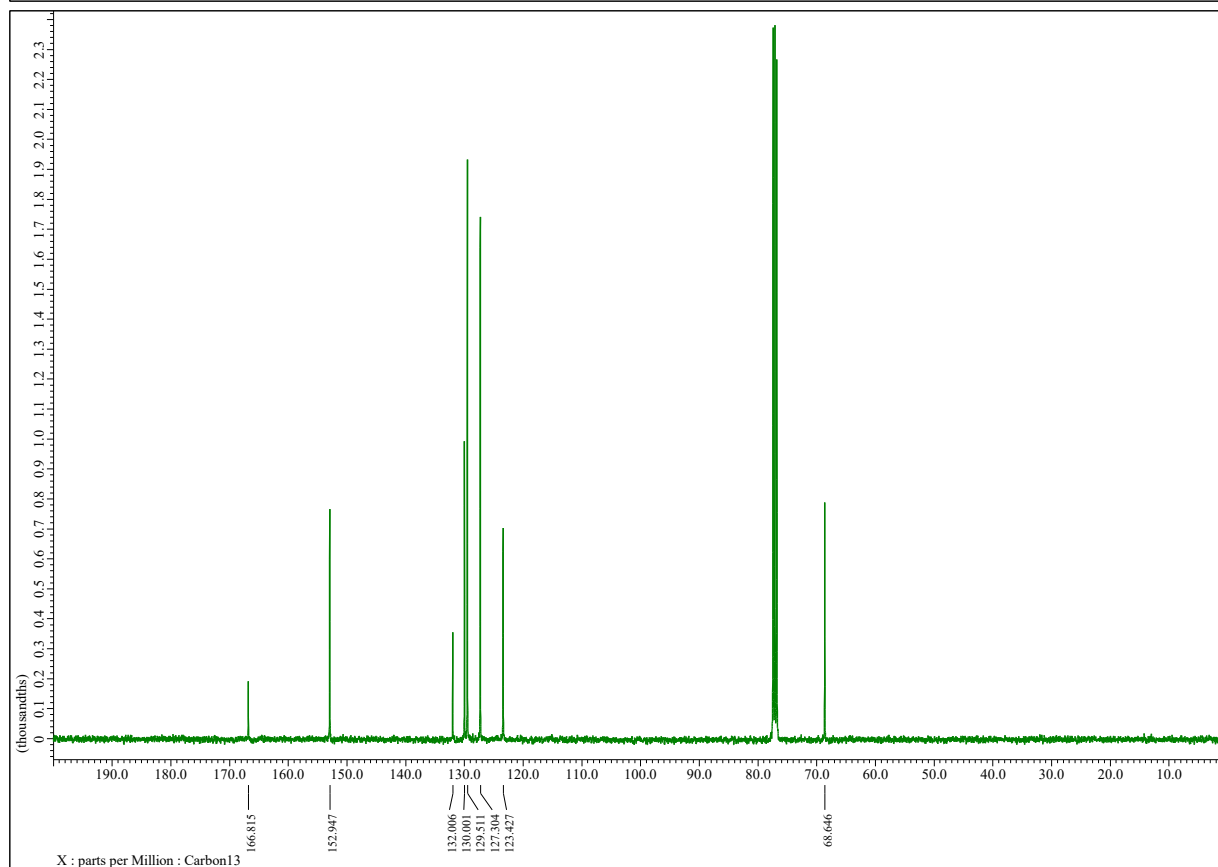
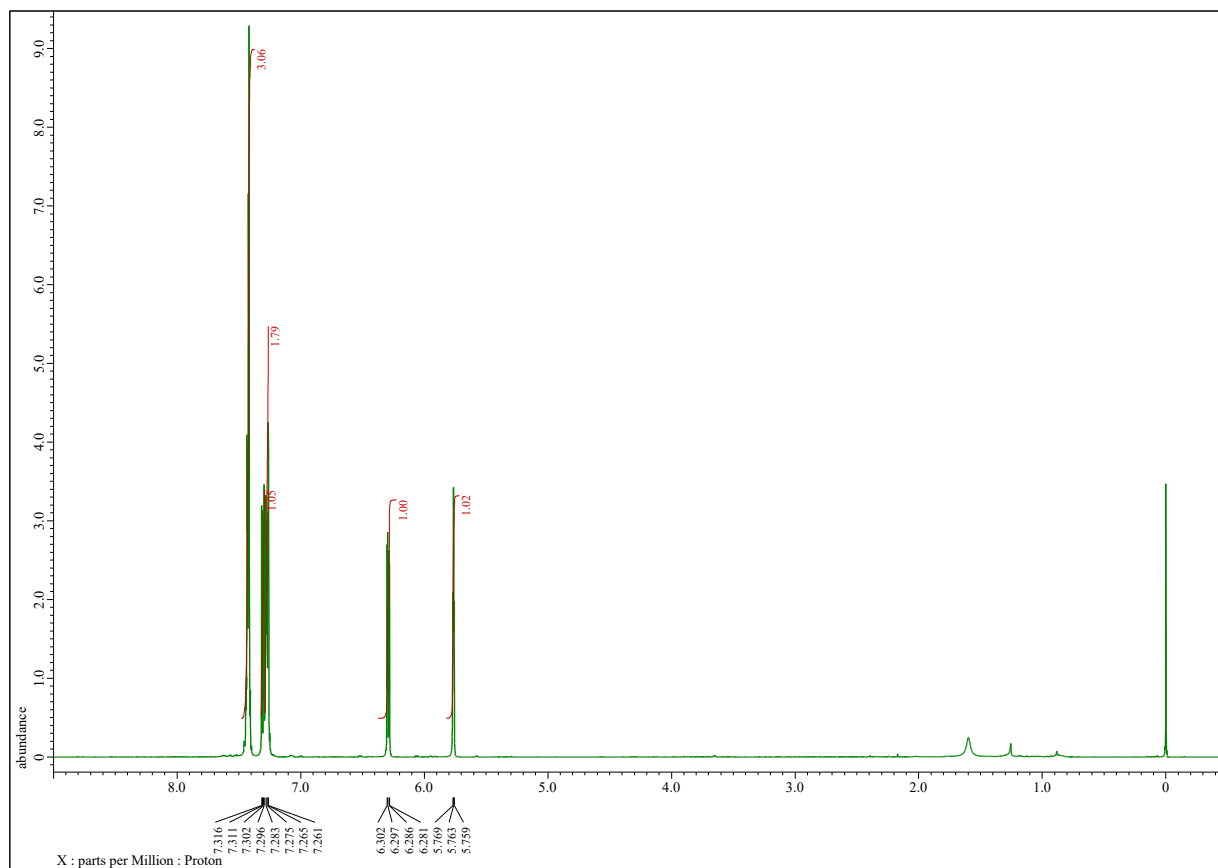
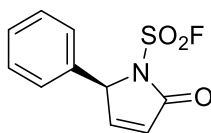


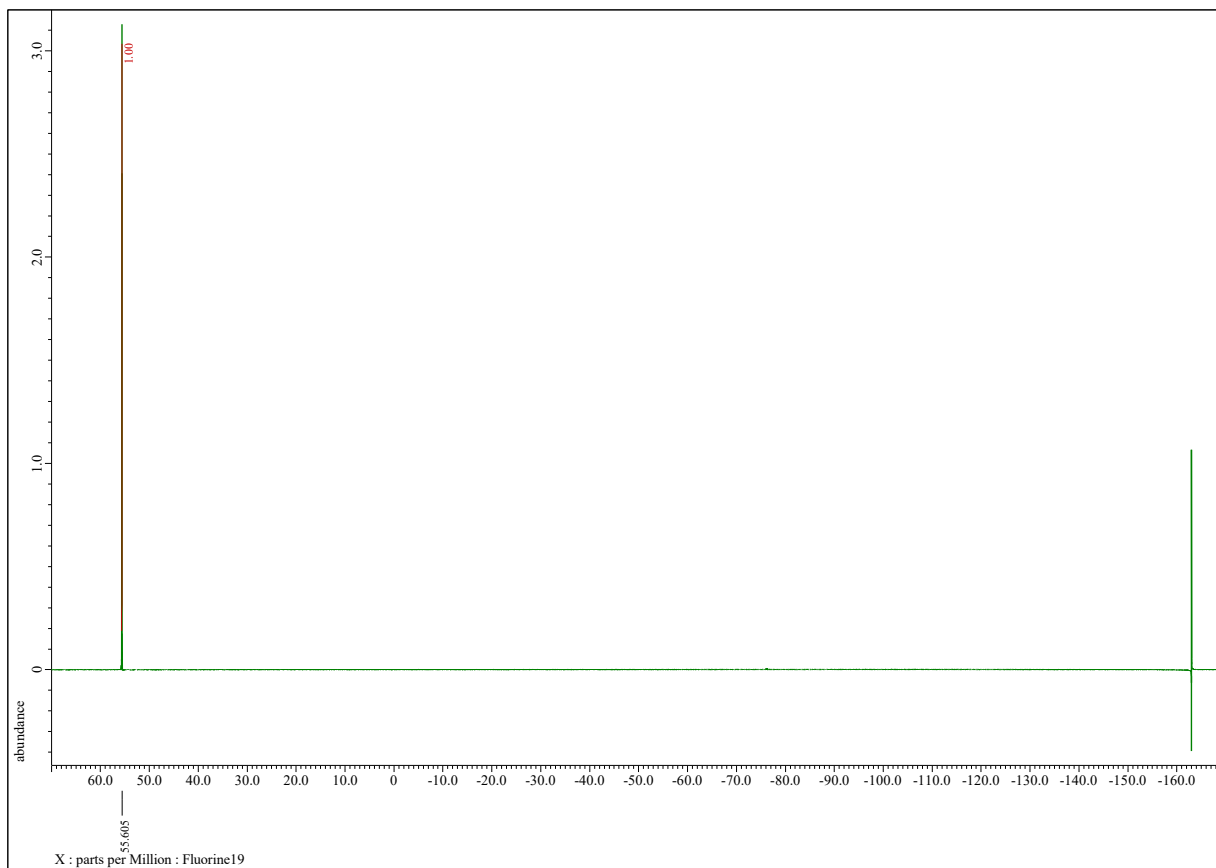
(R)-2-(3-bromobenzyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (5n)



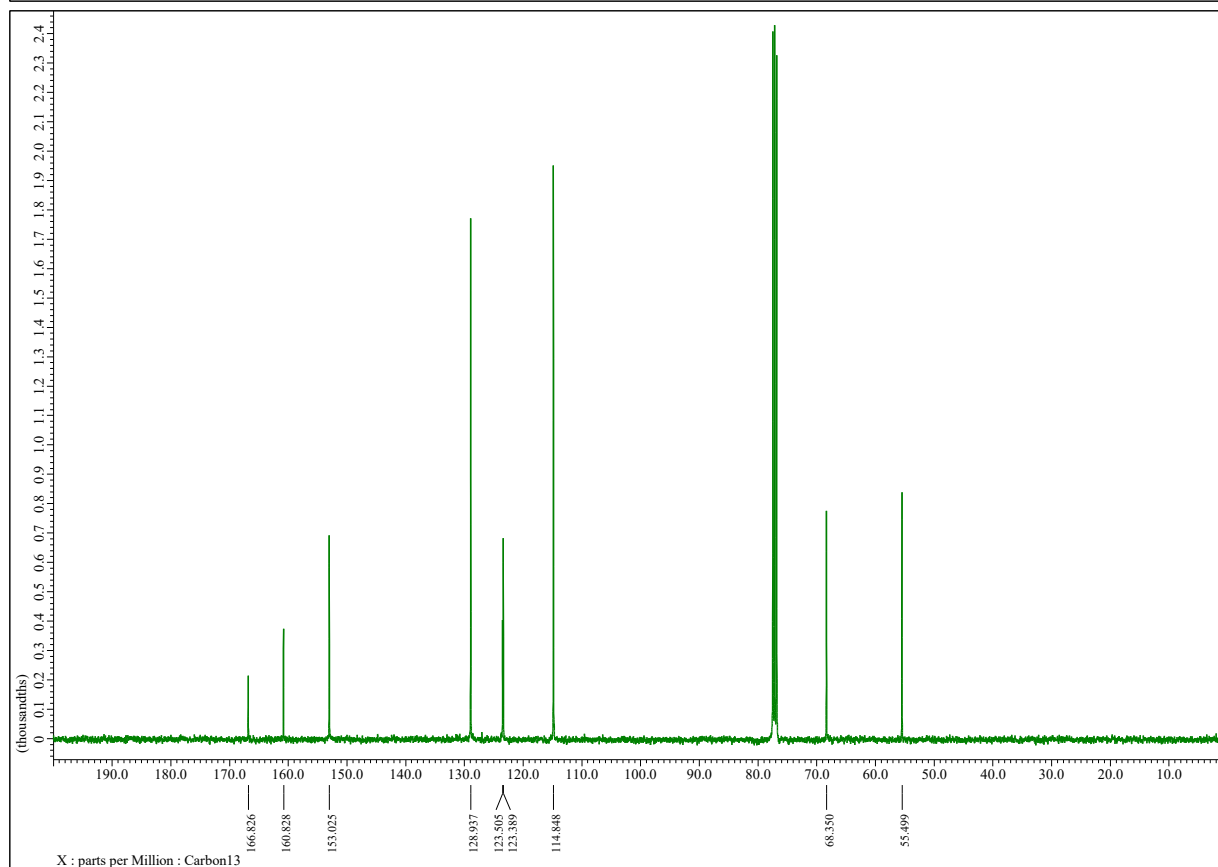
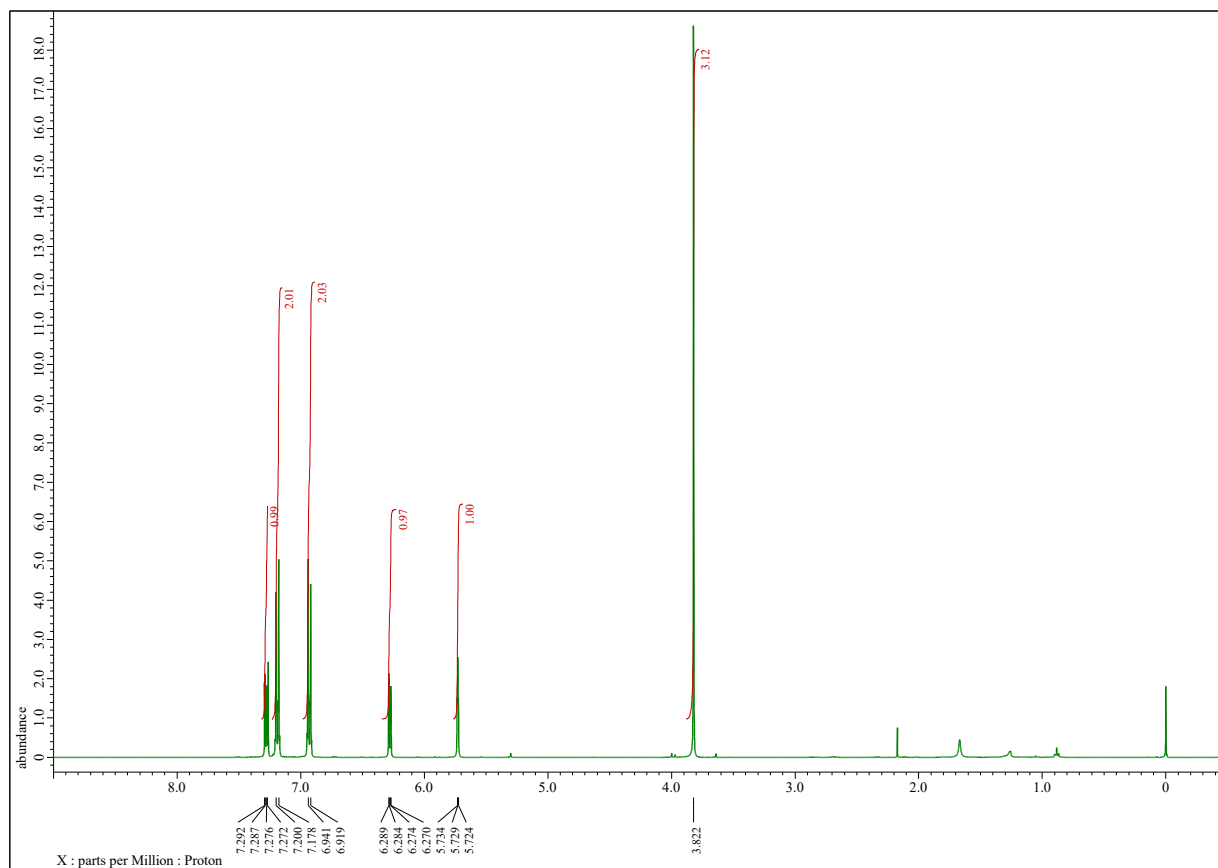
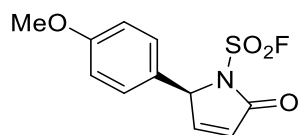


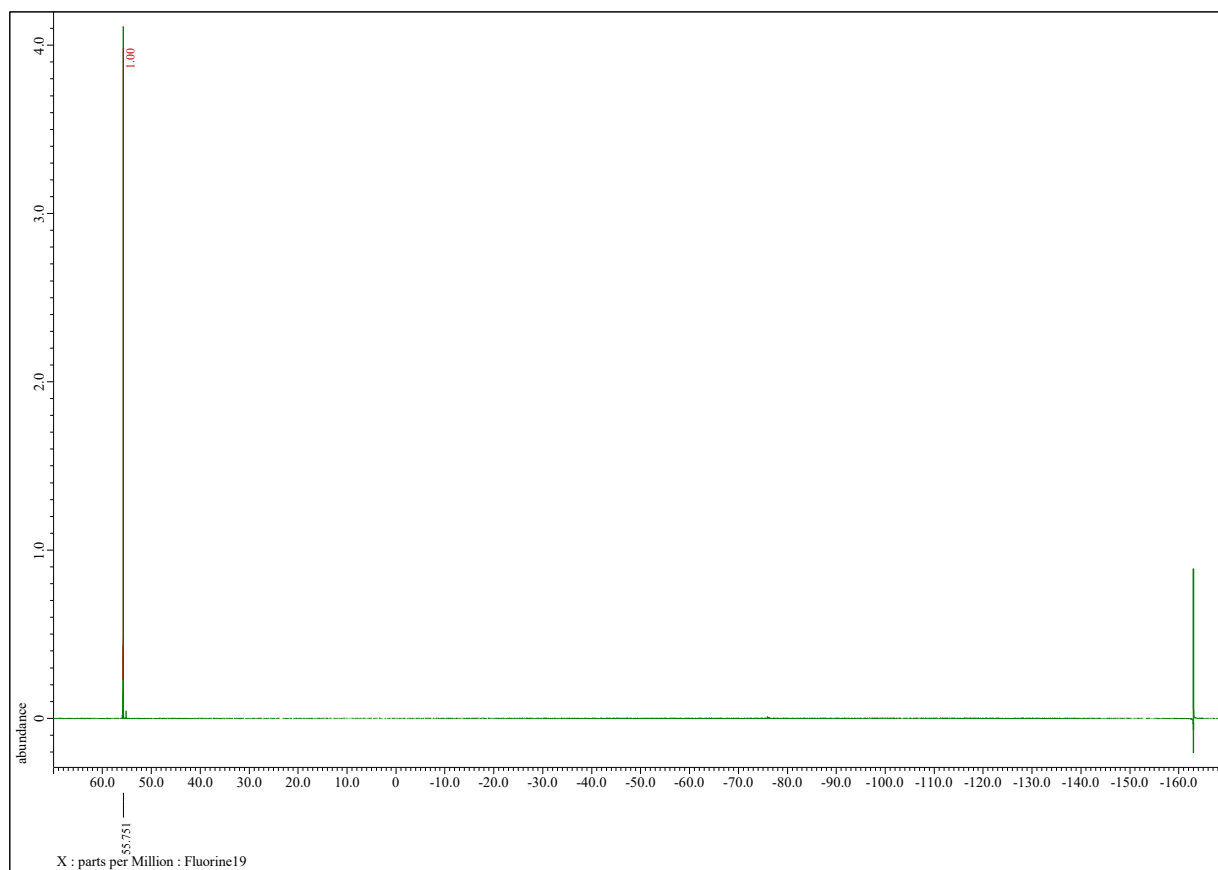
(S)-2-oxo-5-phenyl-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6a)



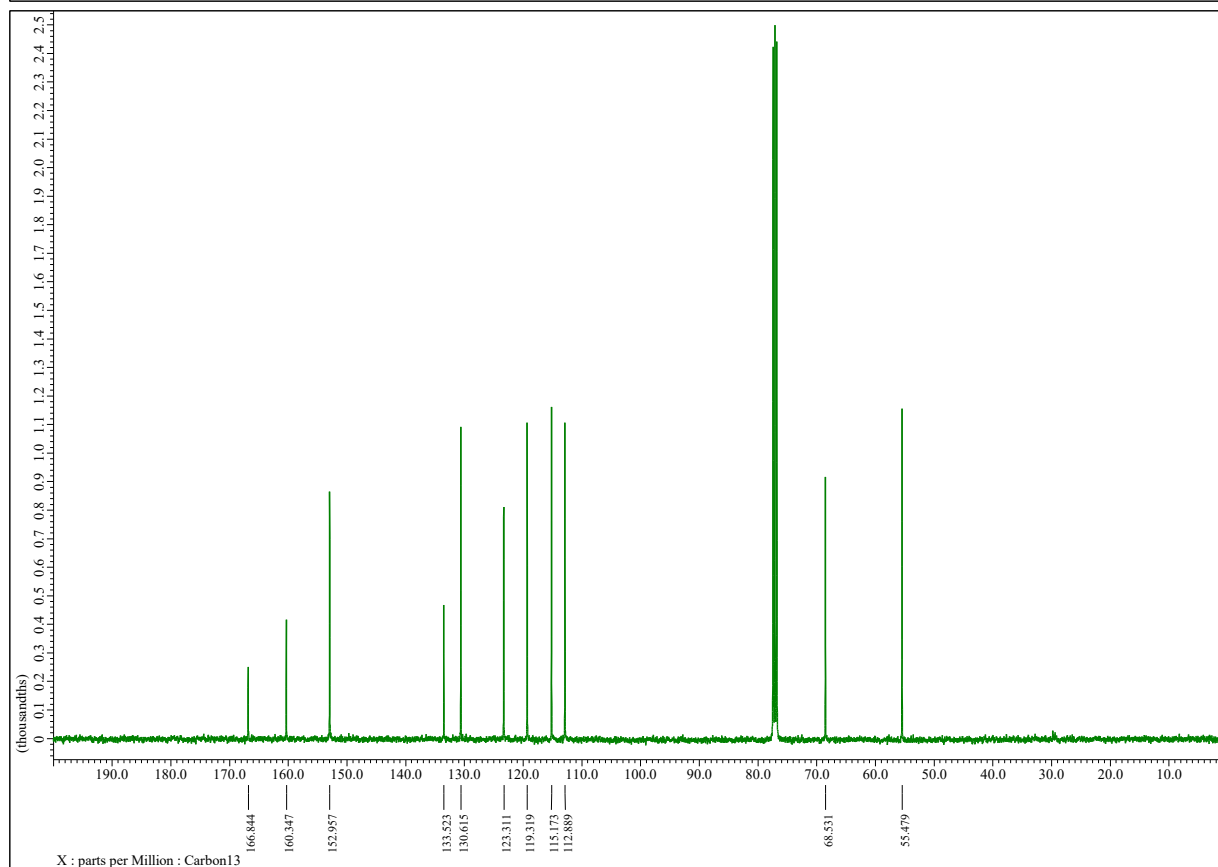
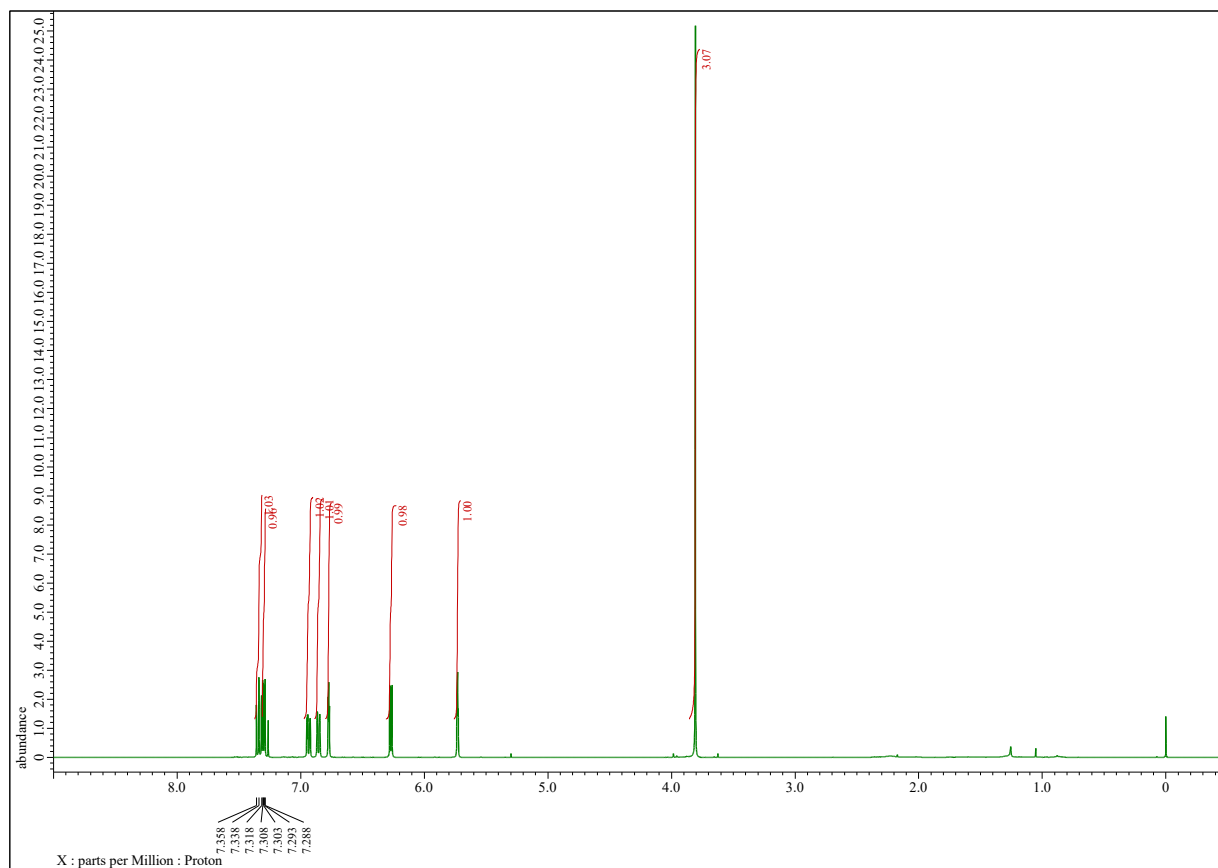
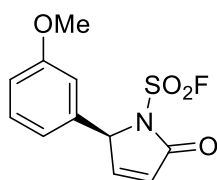


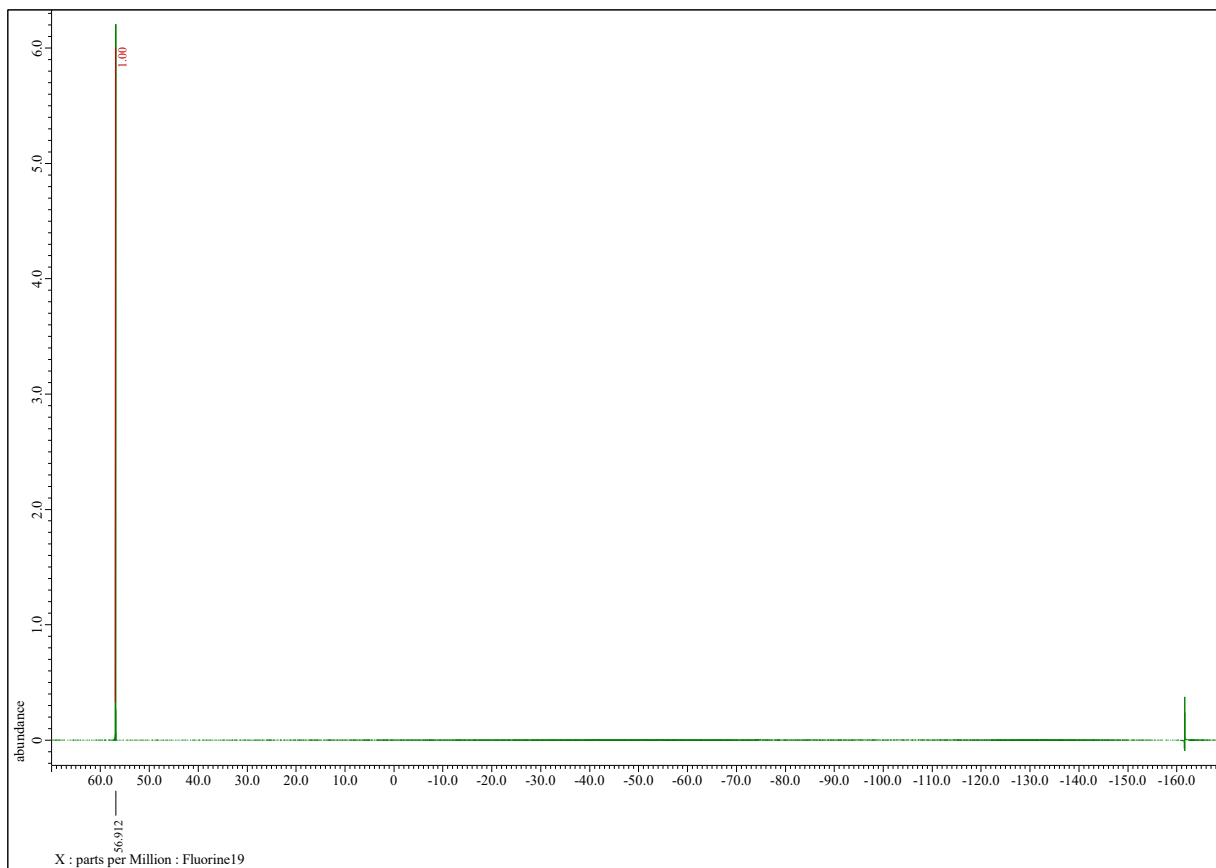
(S)-2-(4-methoxyphenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6b)



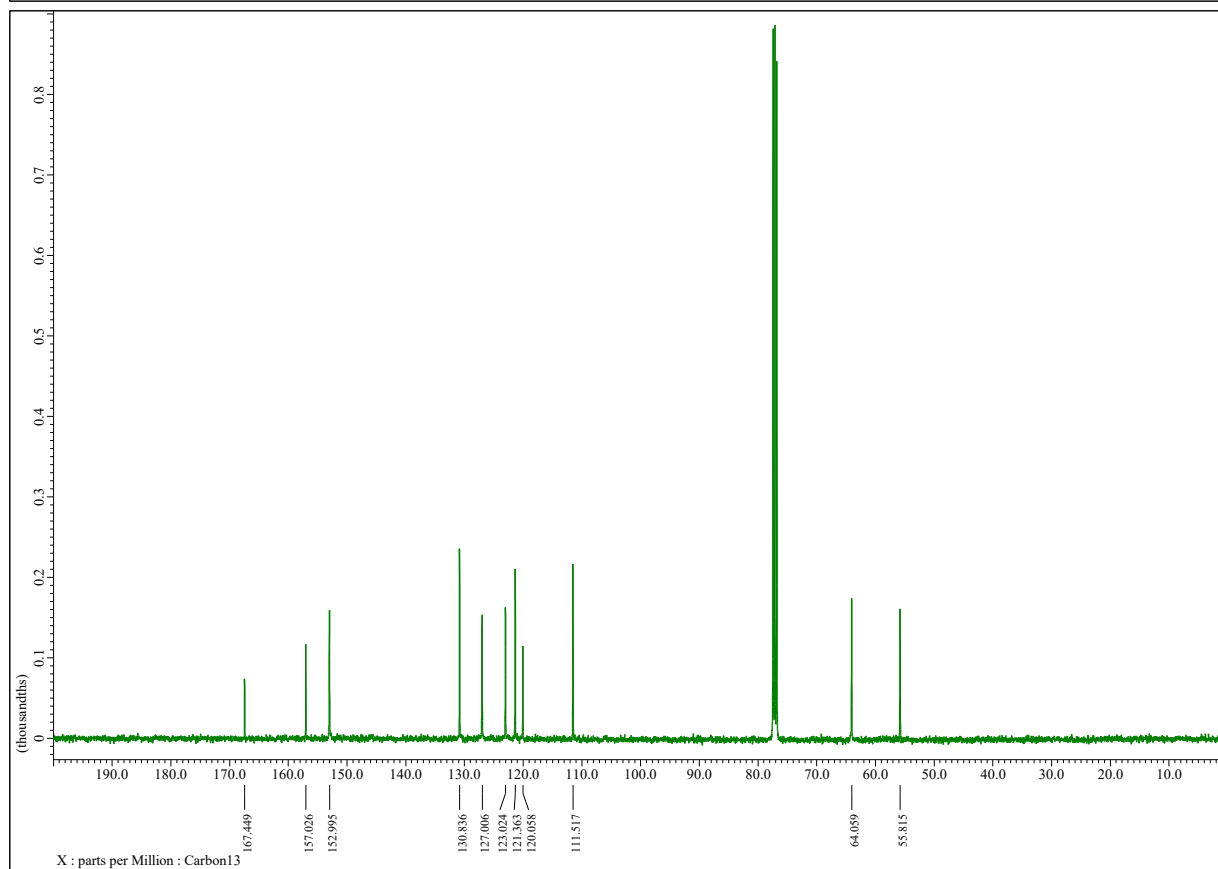
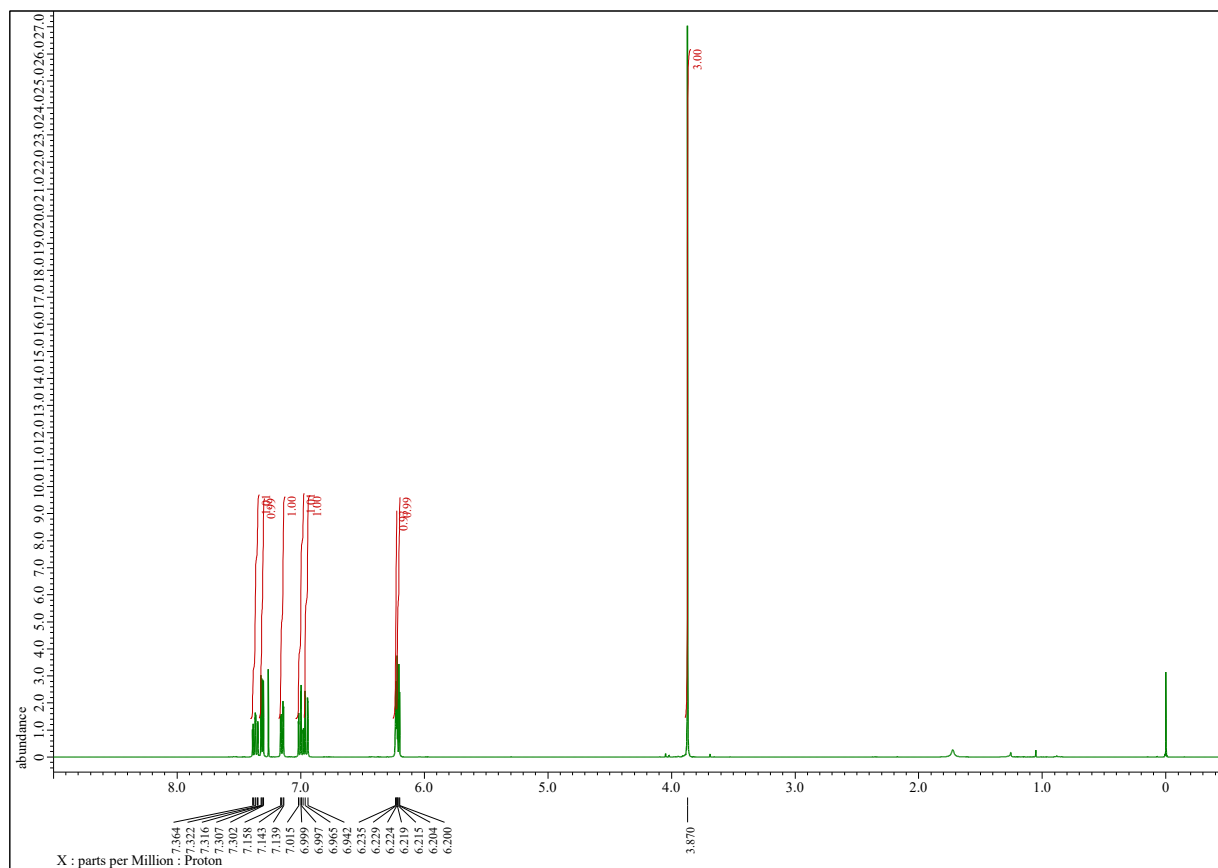
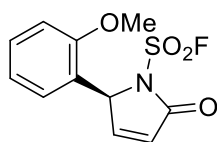


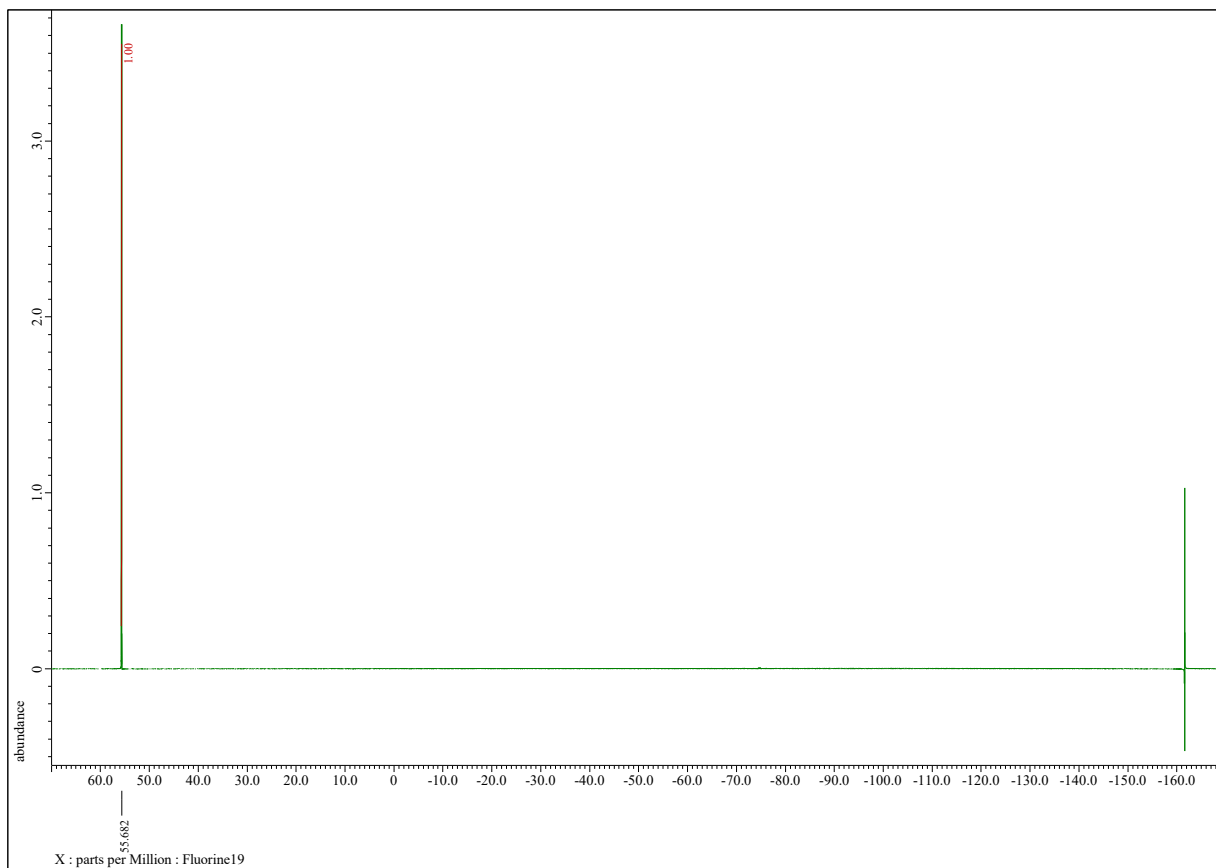
(S)-2-(3-methoxyphenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6c)



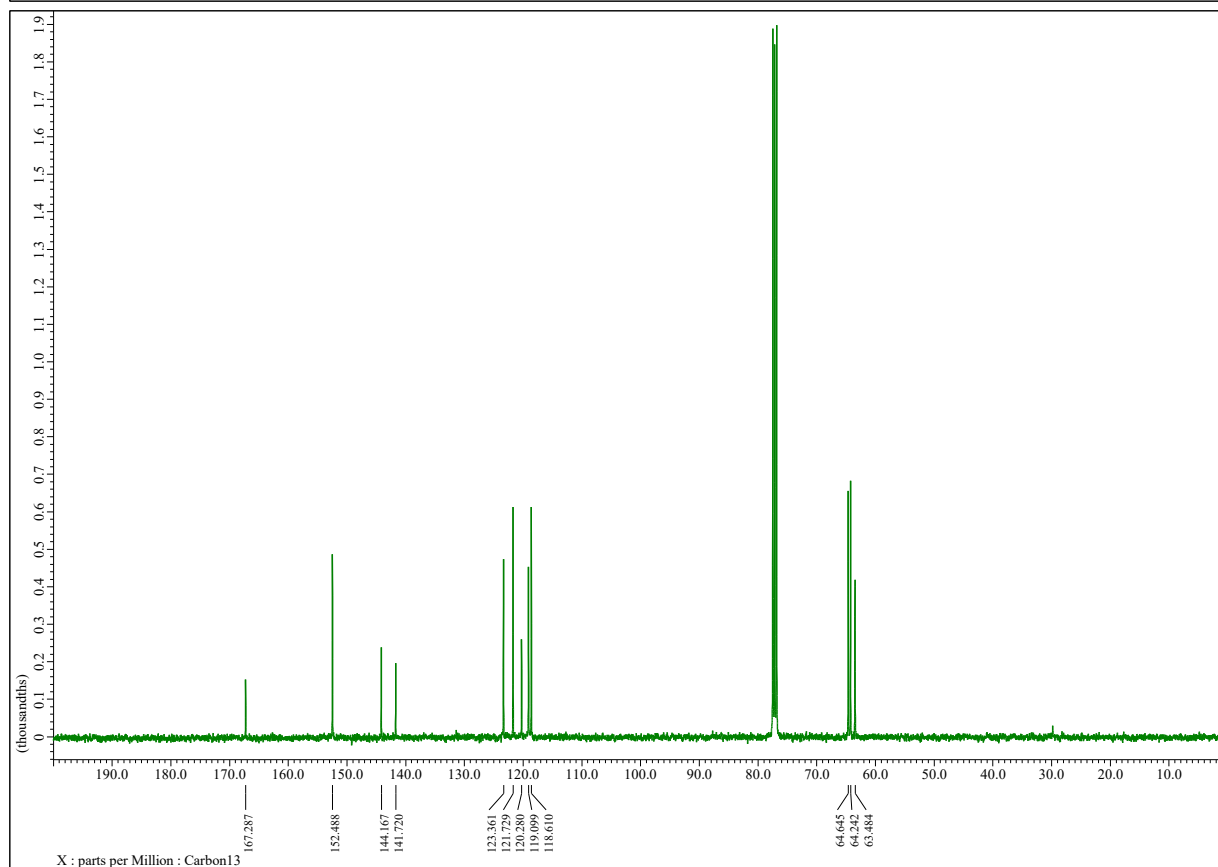
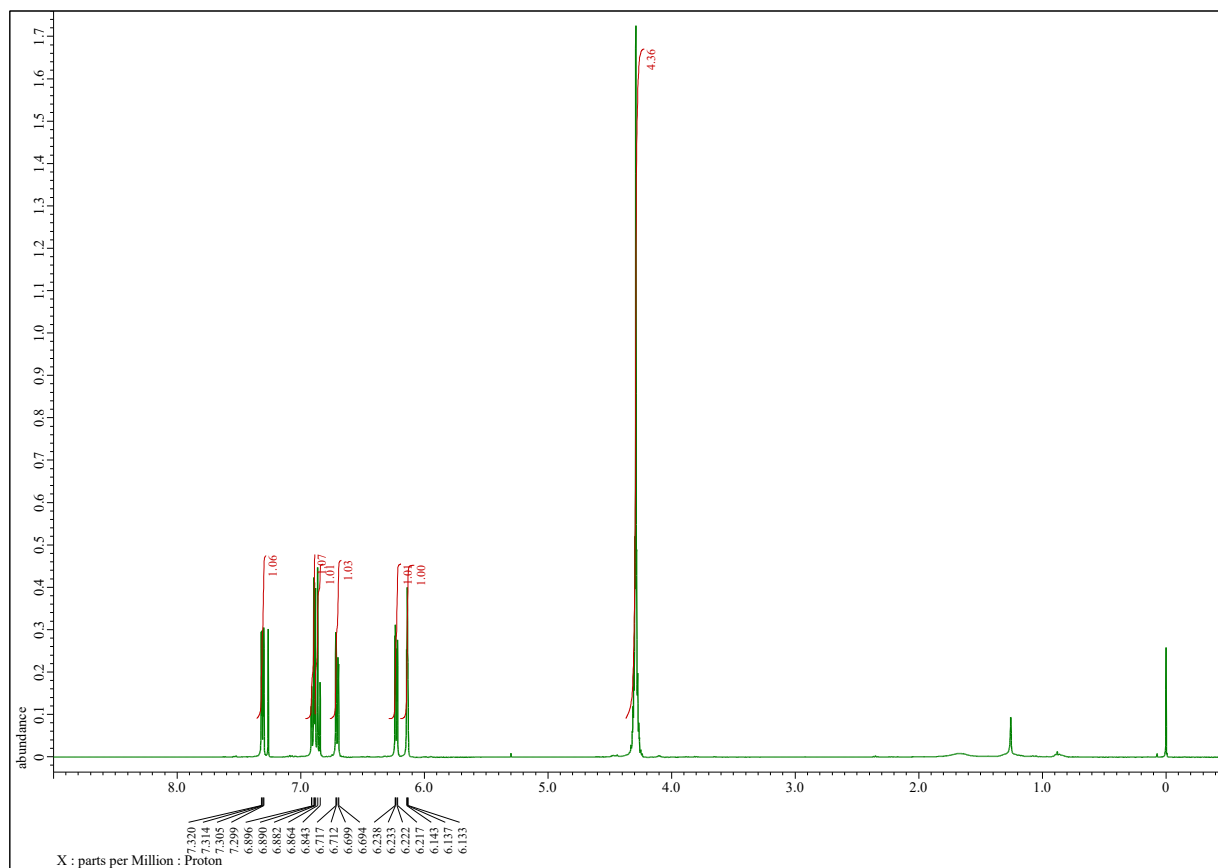
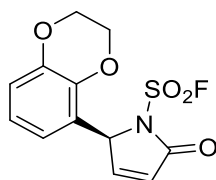


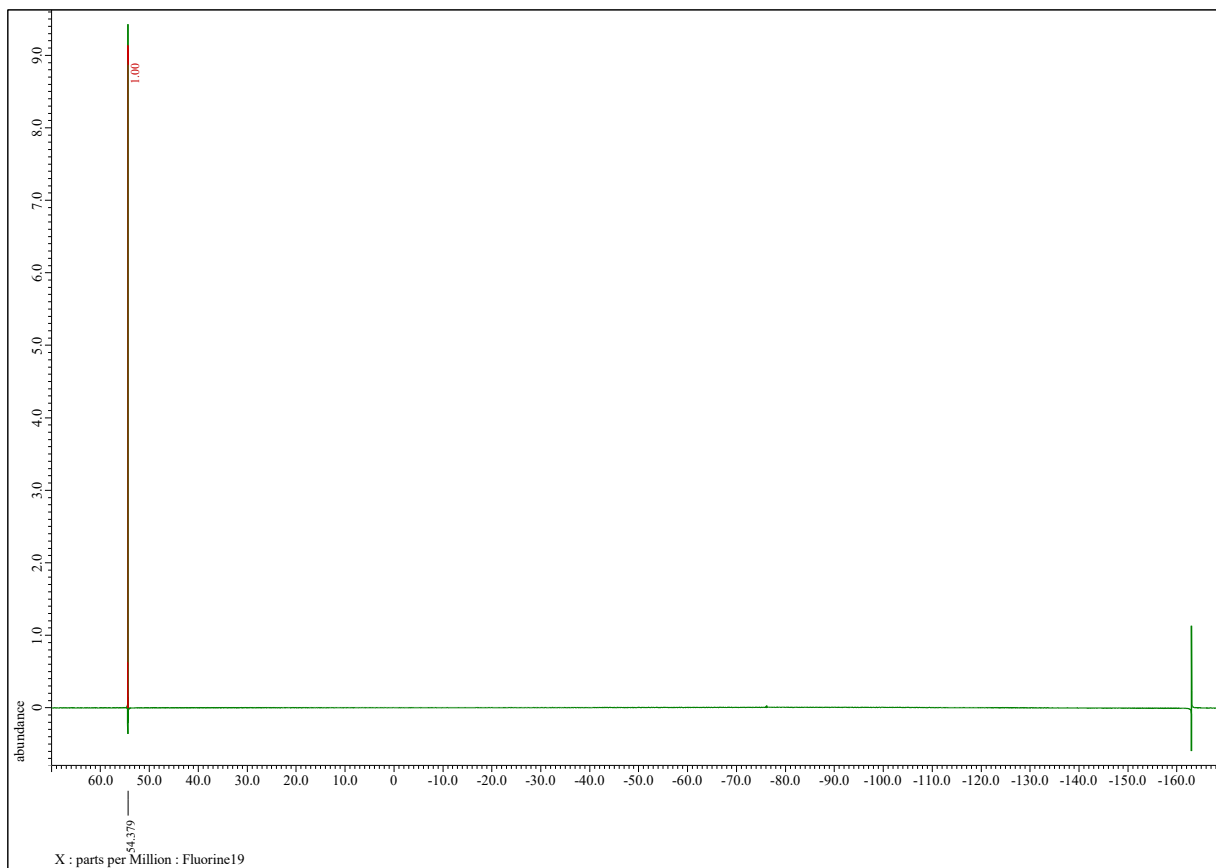
(S)-2-(2-methoxyphenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6d)



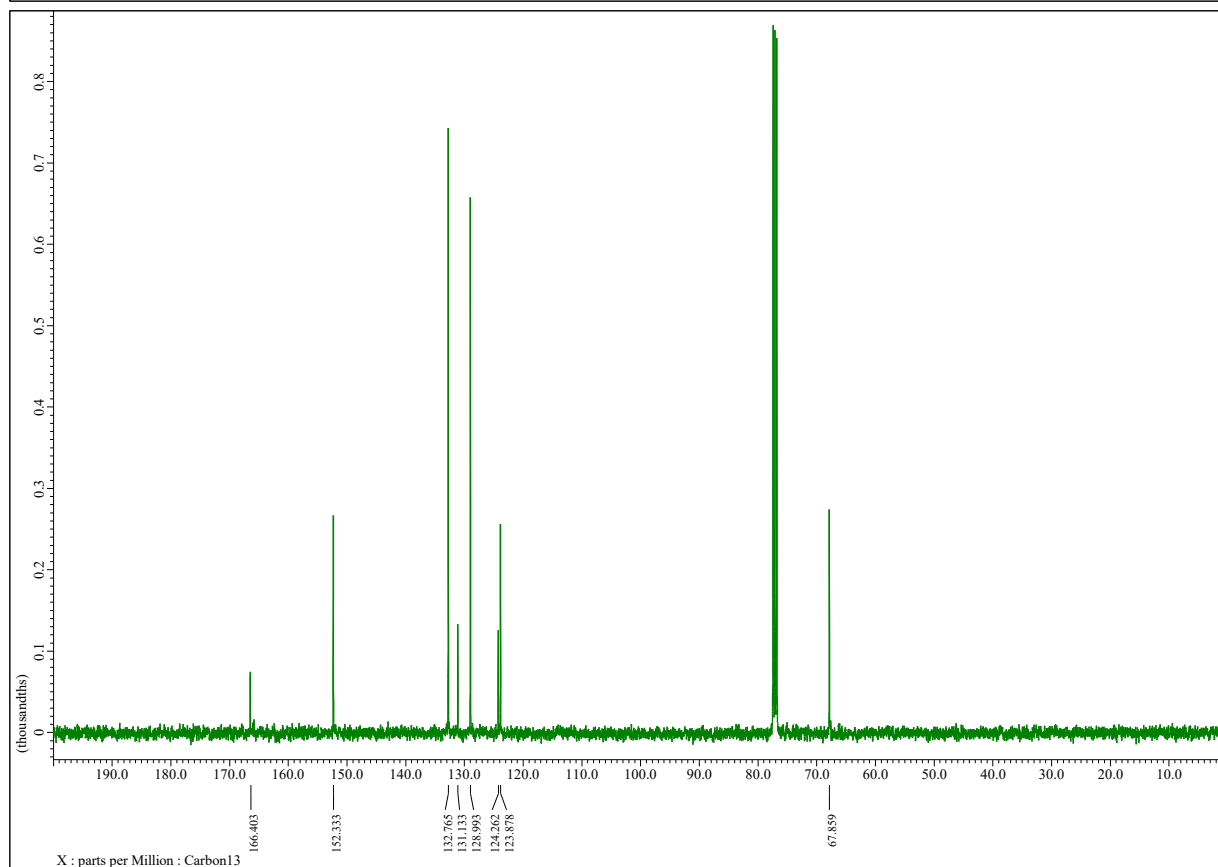
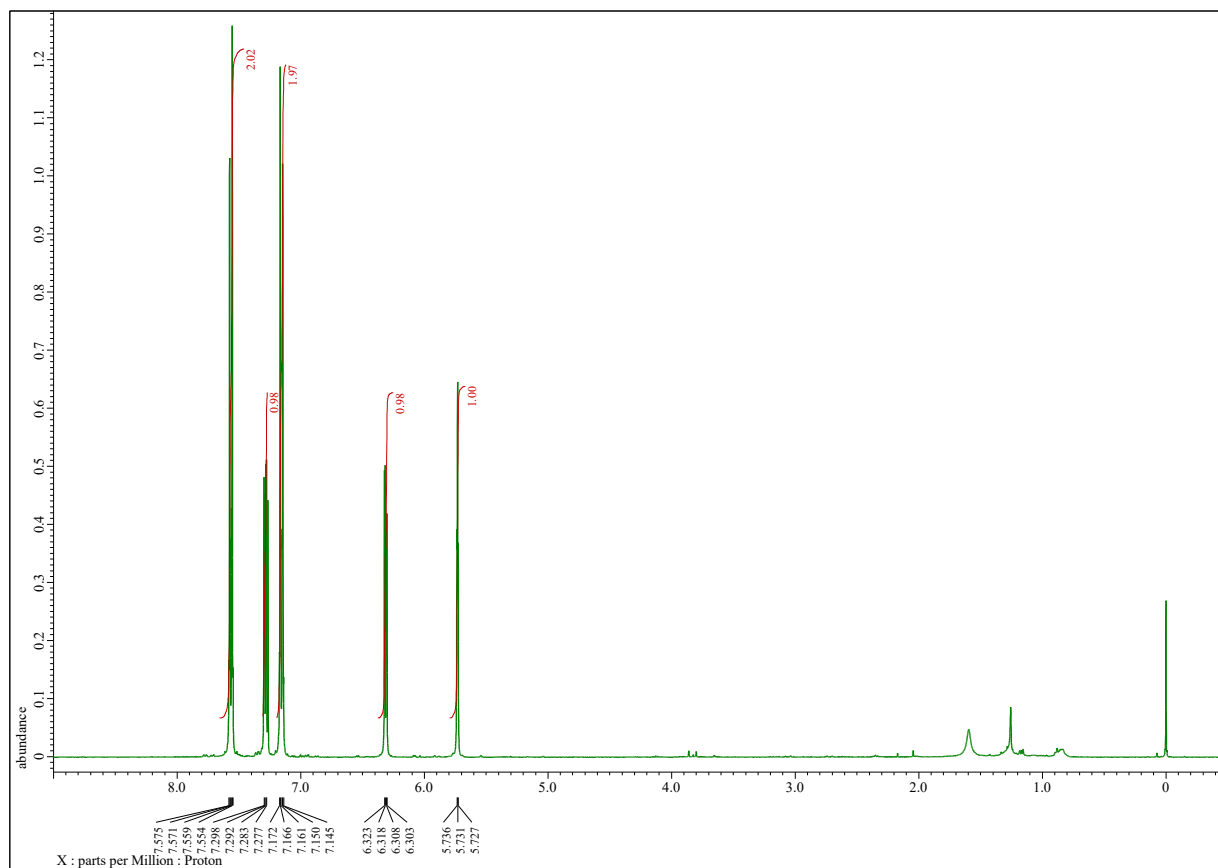
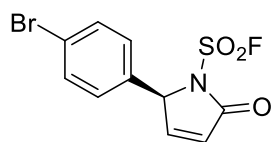


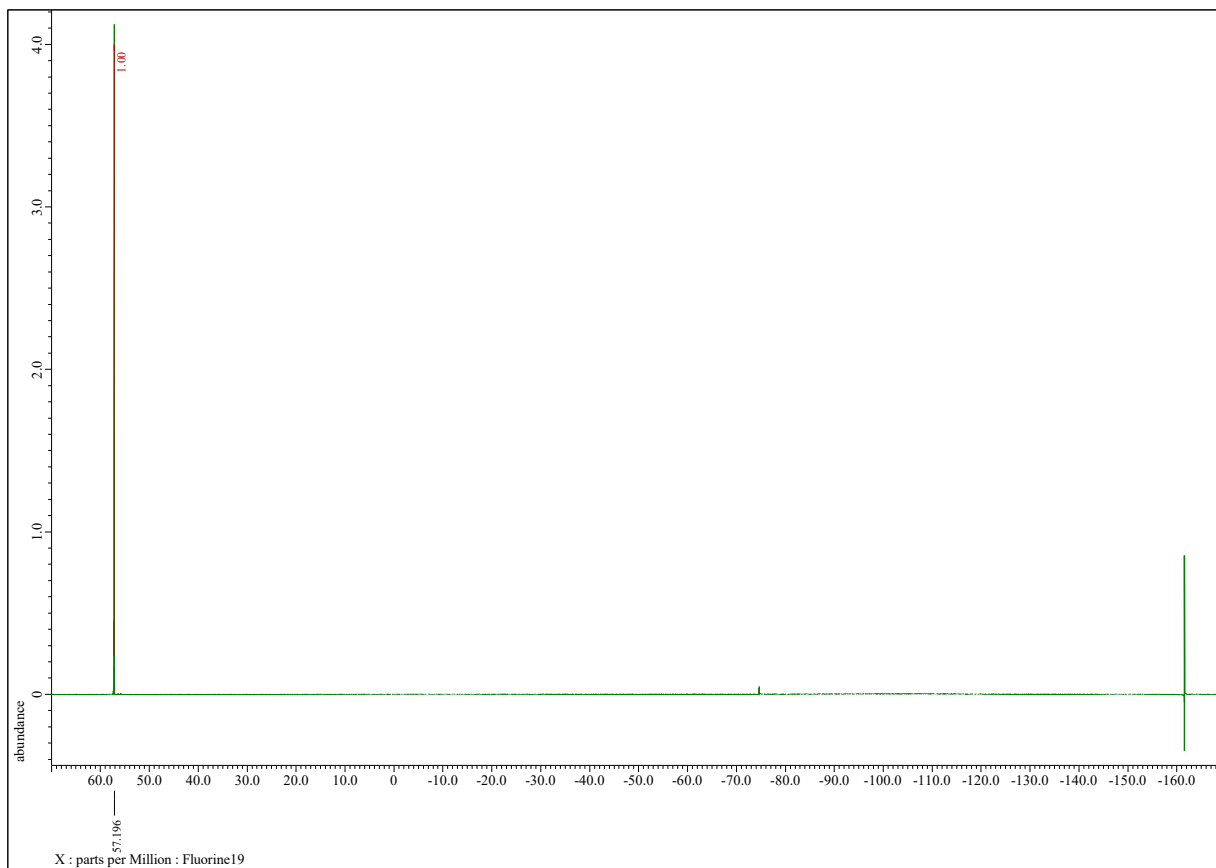
(S)-2-(2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6e)



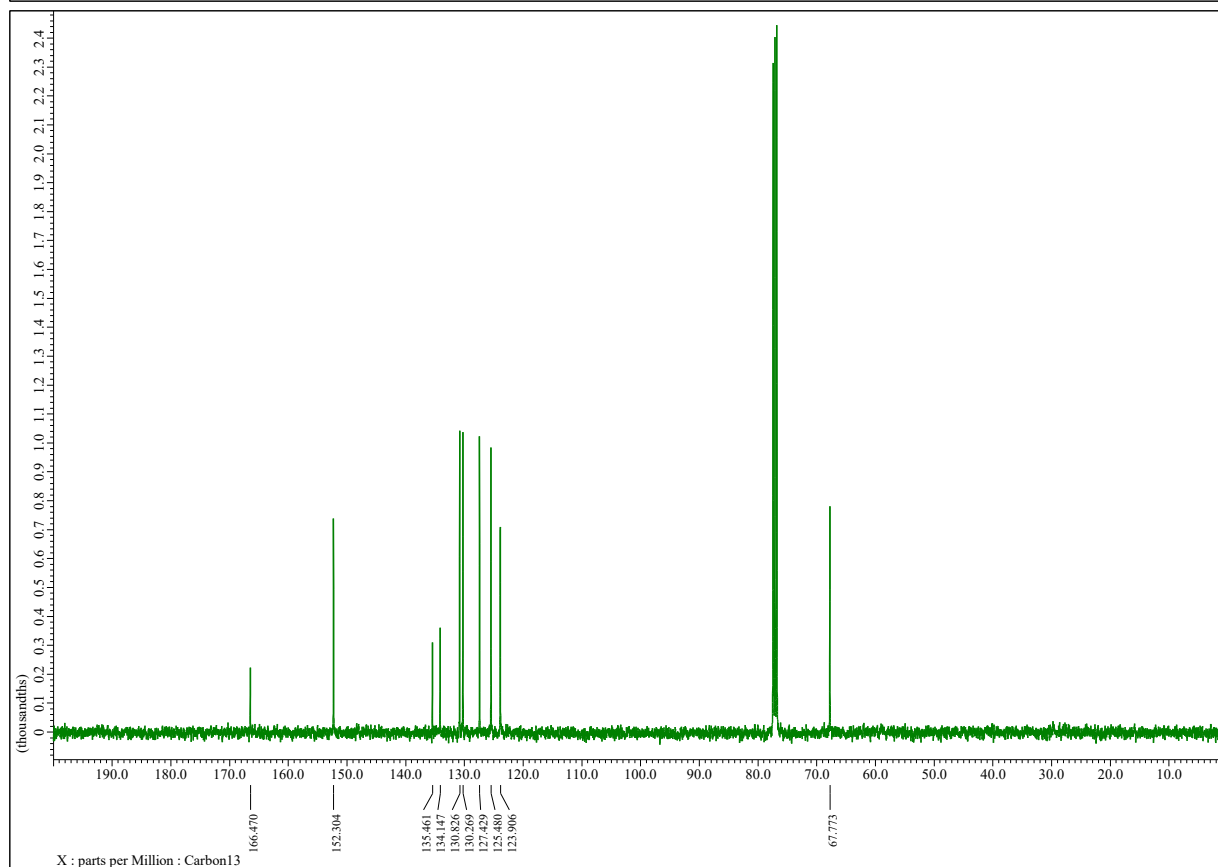
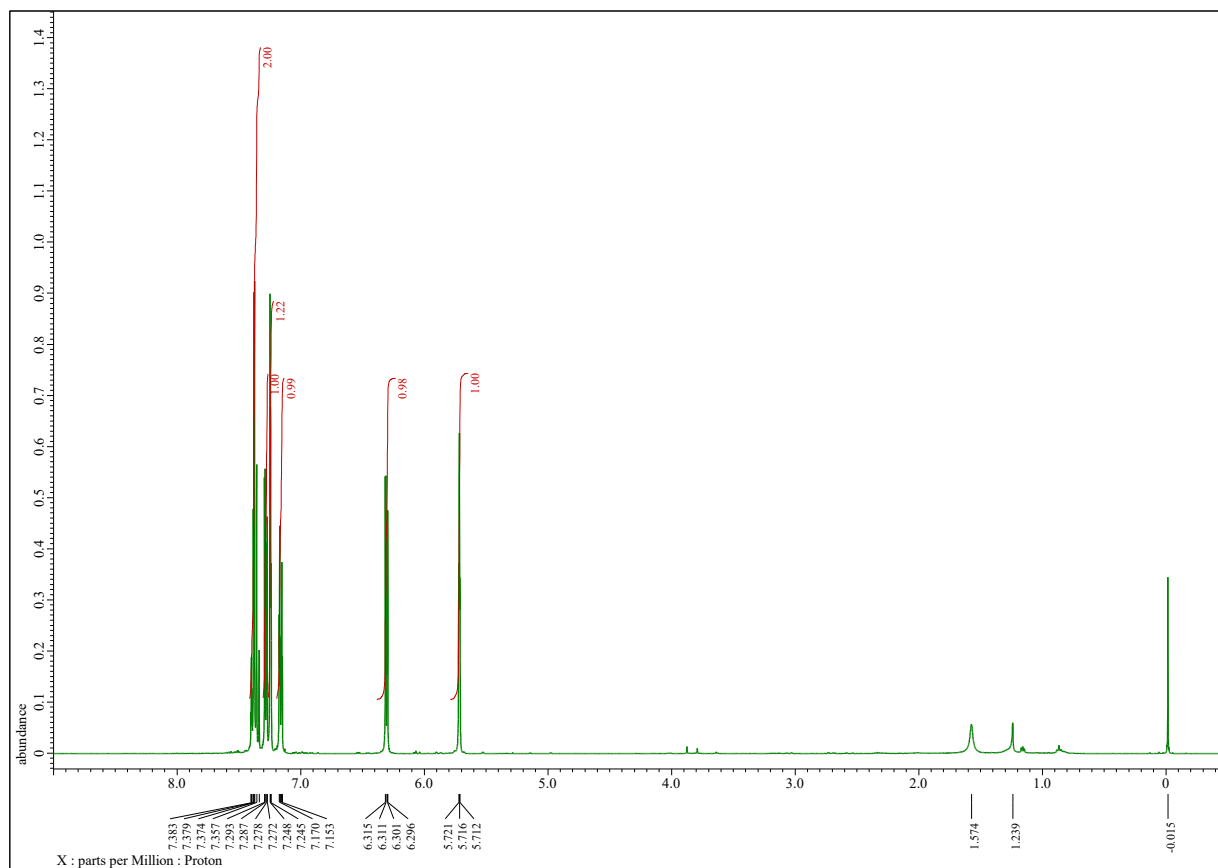
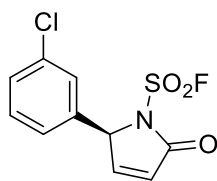


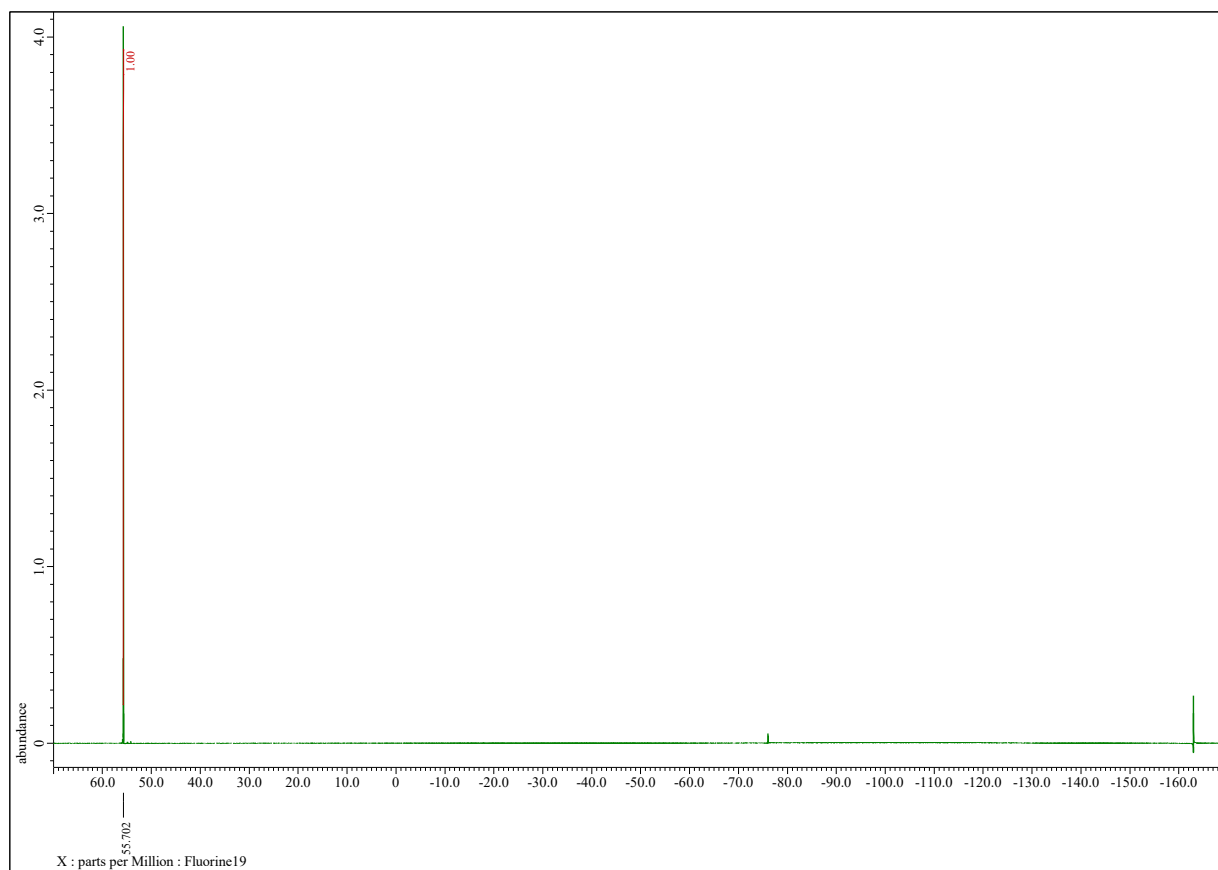
(S)-2-(4-bromophenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6f)



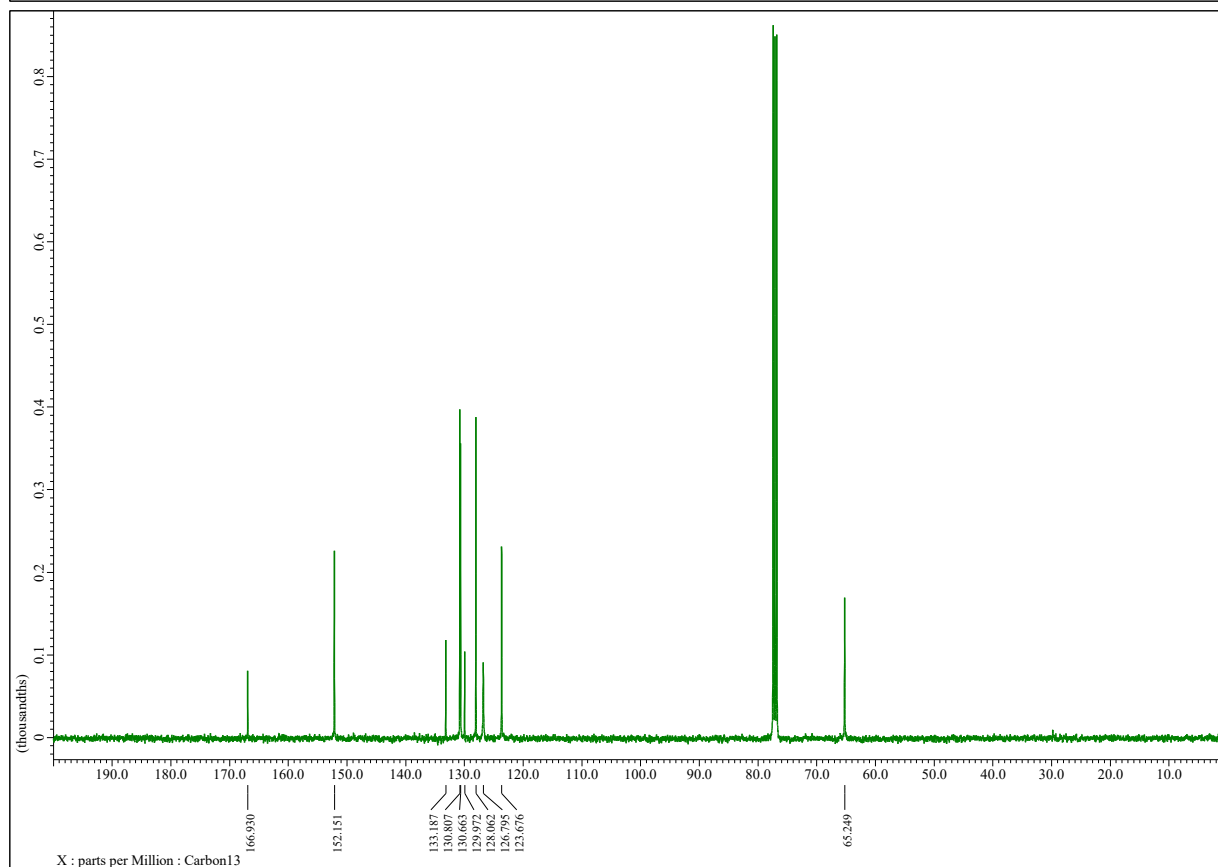
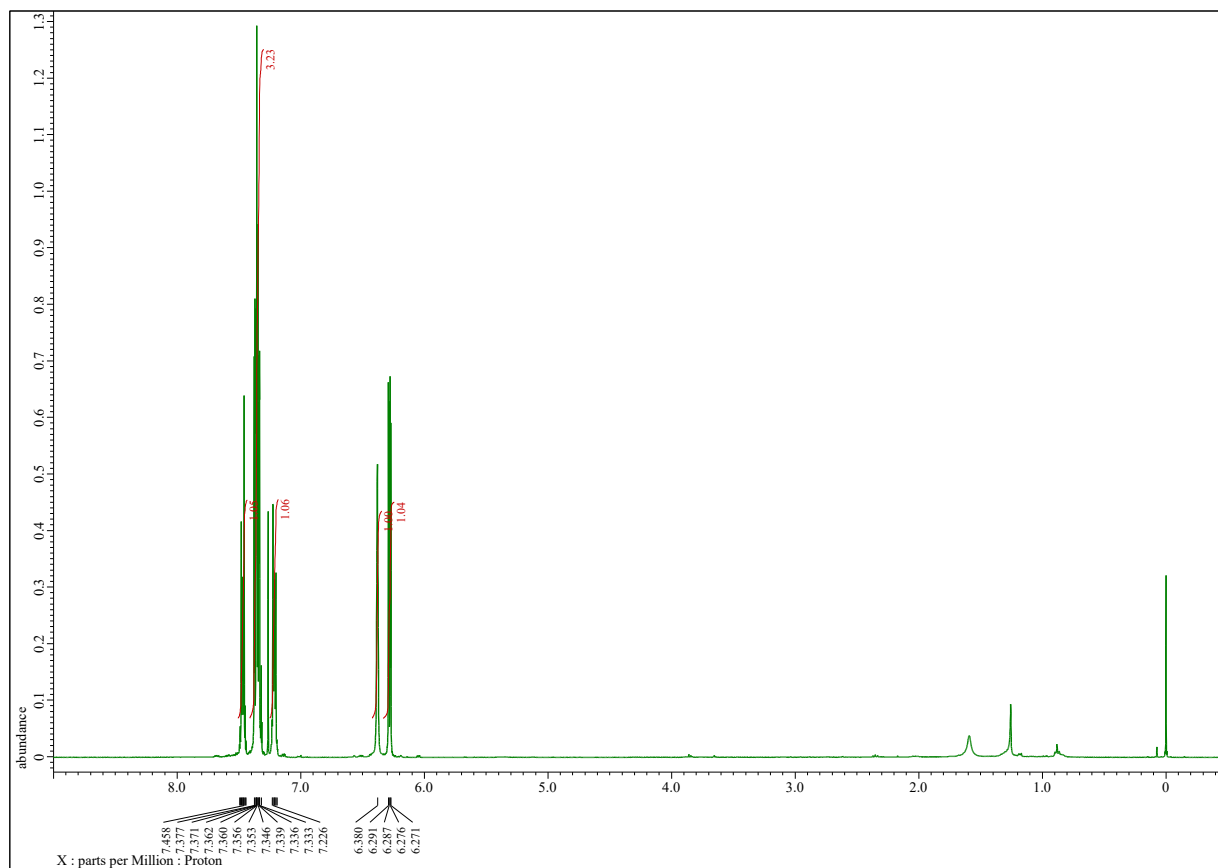
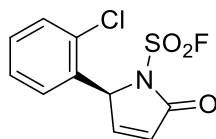


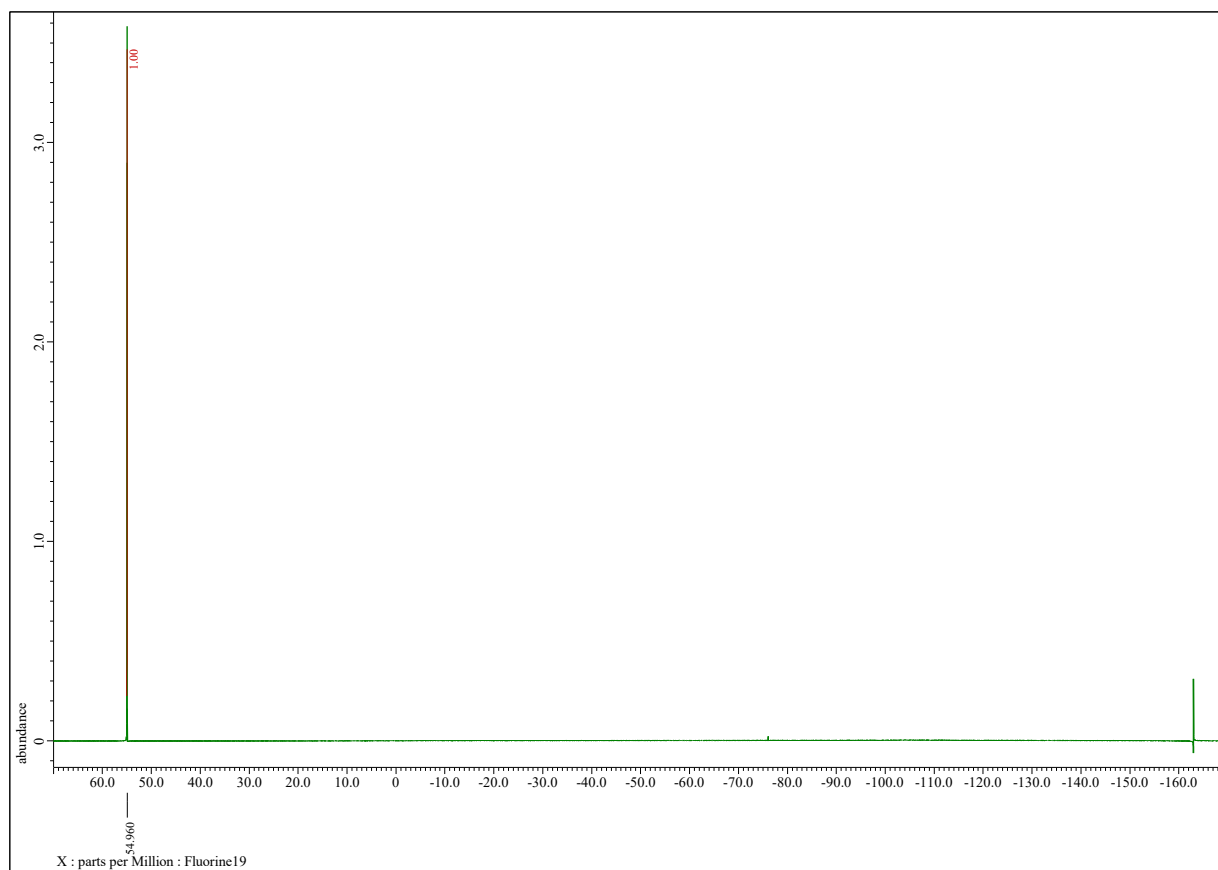
(S)-2-(3-chlorophenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6g)



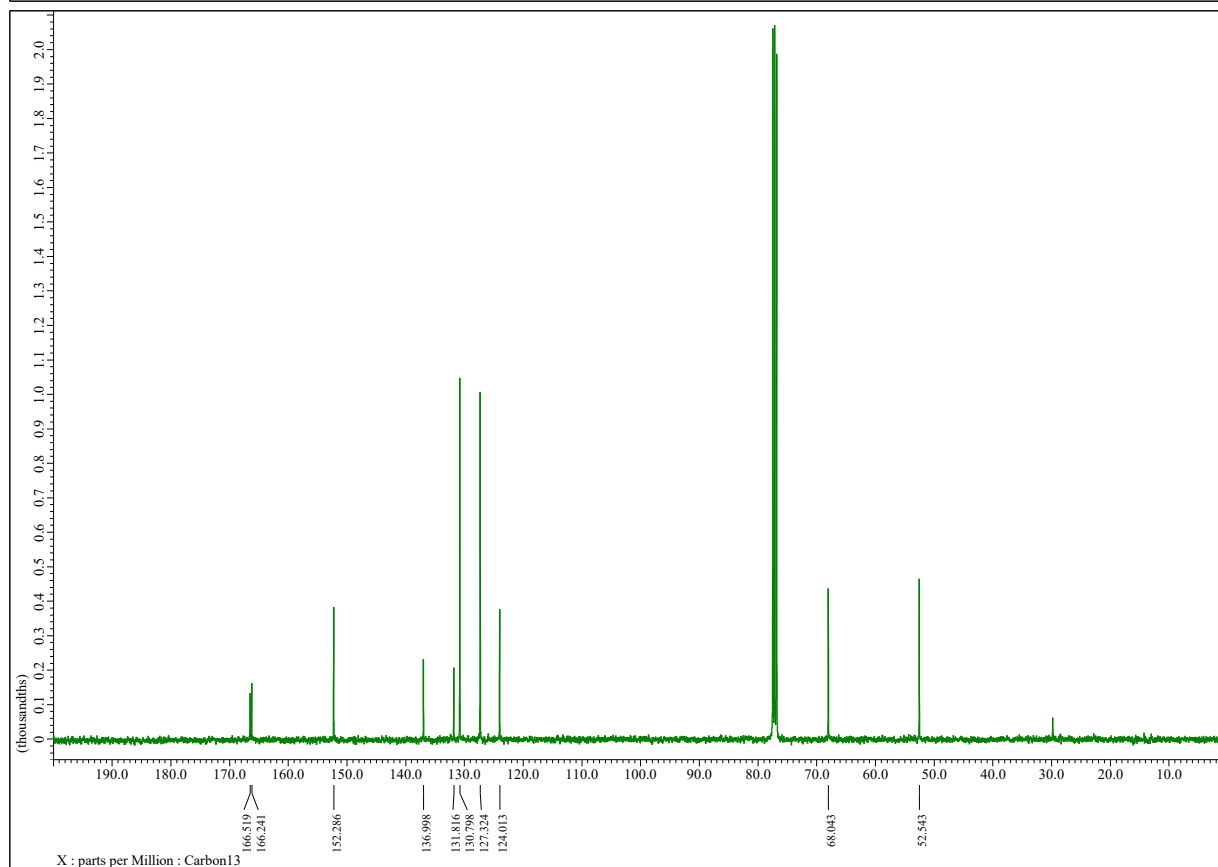
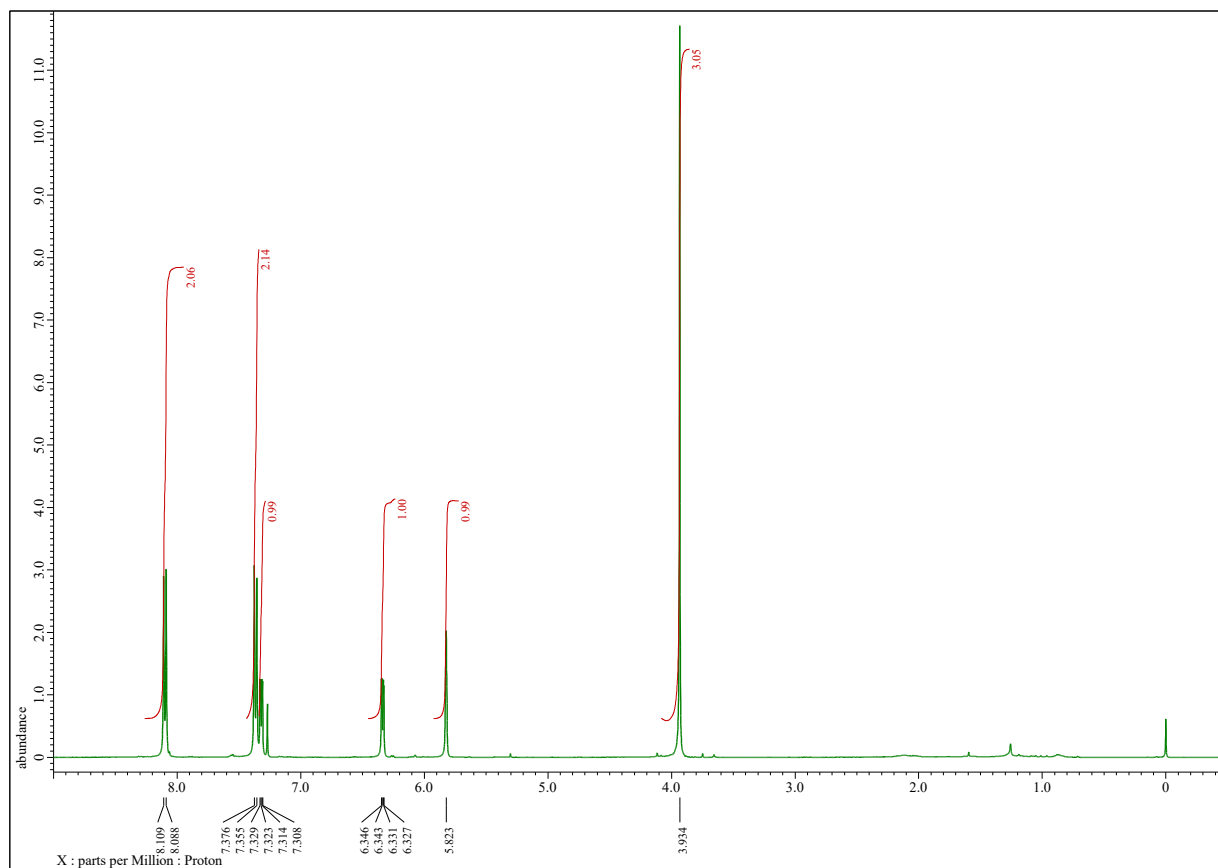
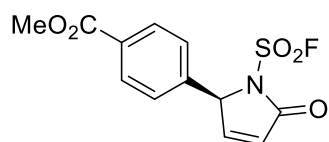


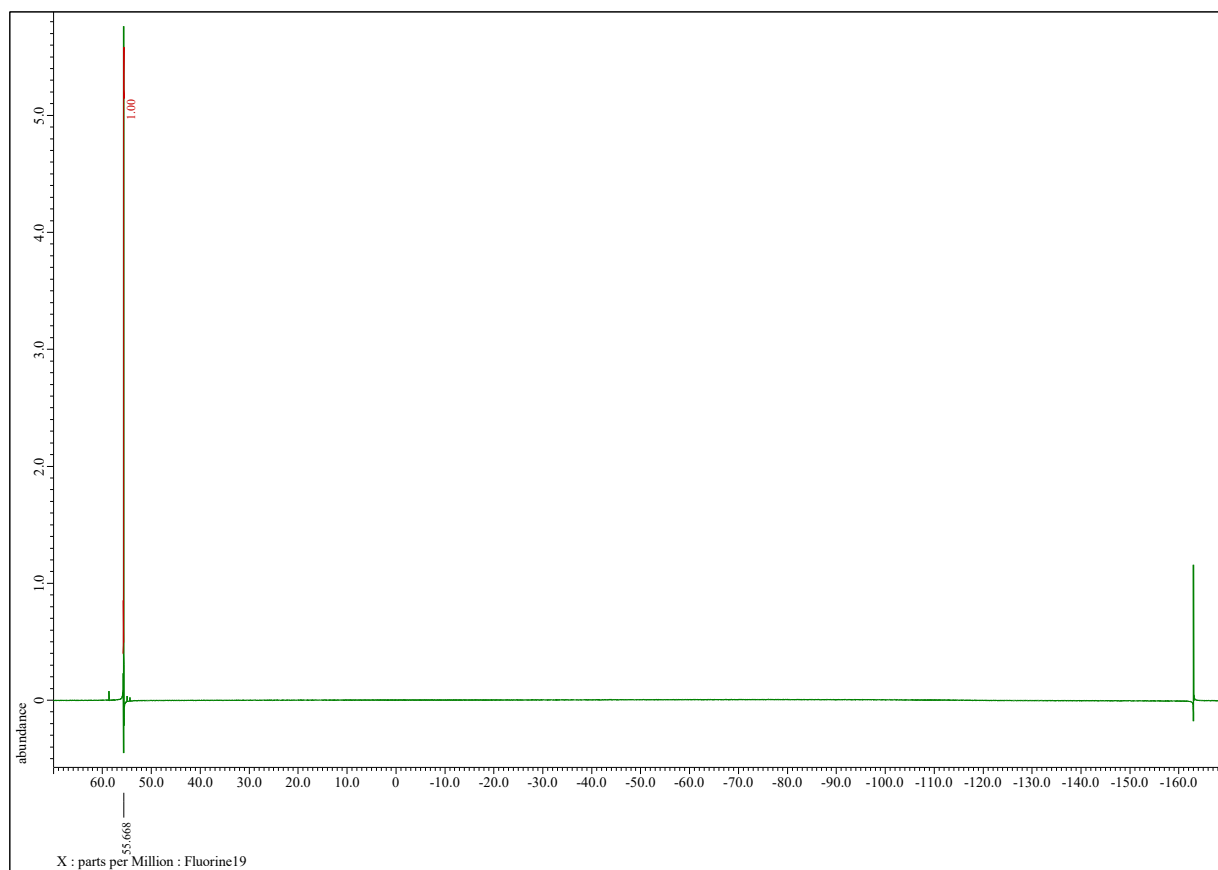
(S)-2-(2-chlorophenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6h)



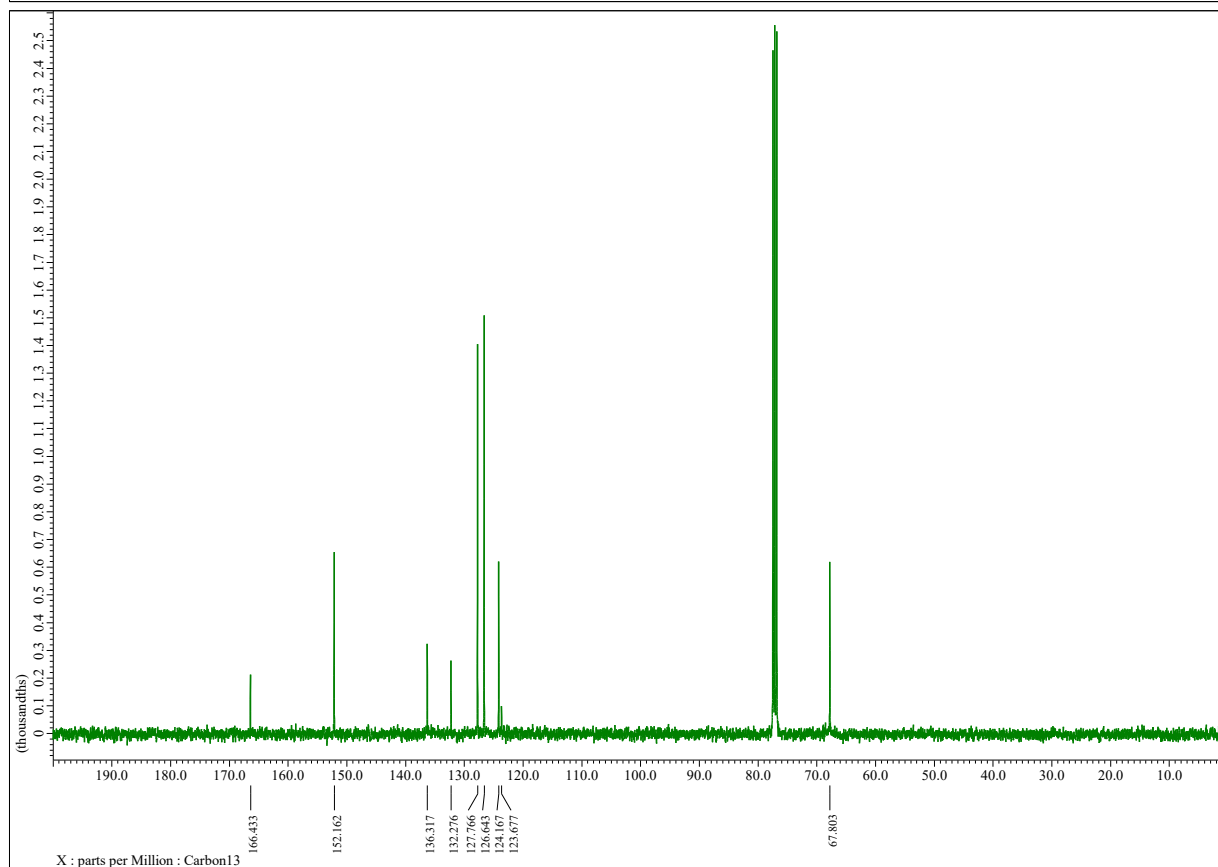
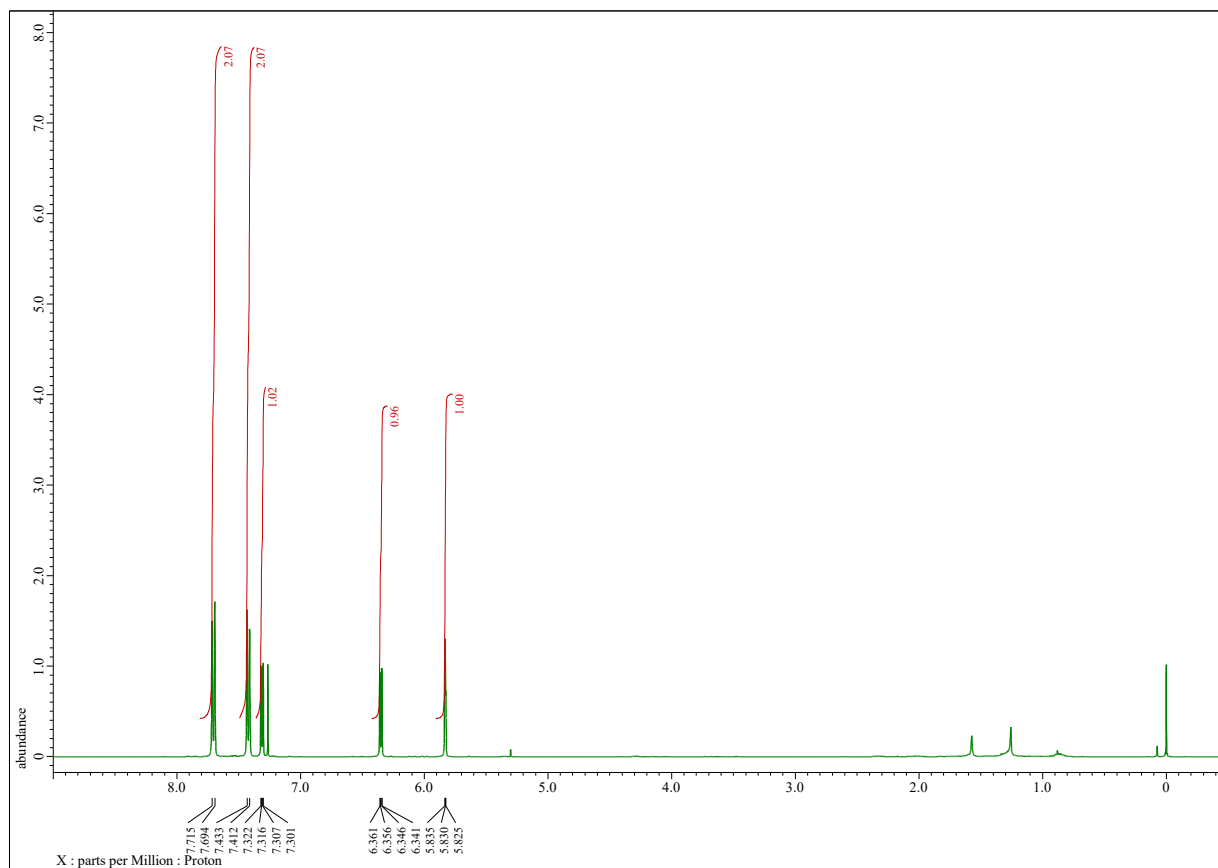
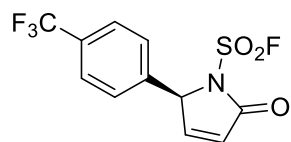


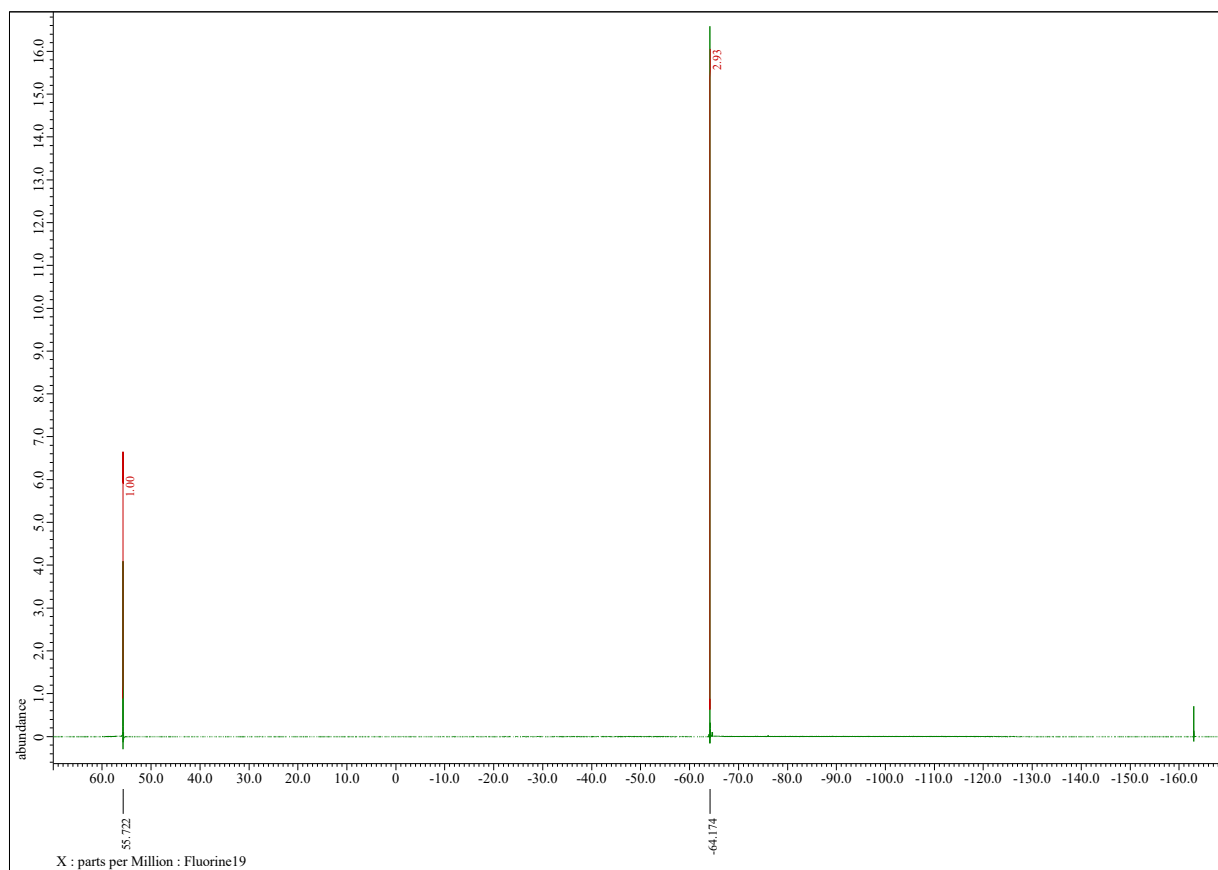
(S)-2-(4-methoxycarbonylphenyl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6i)



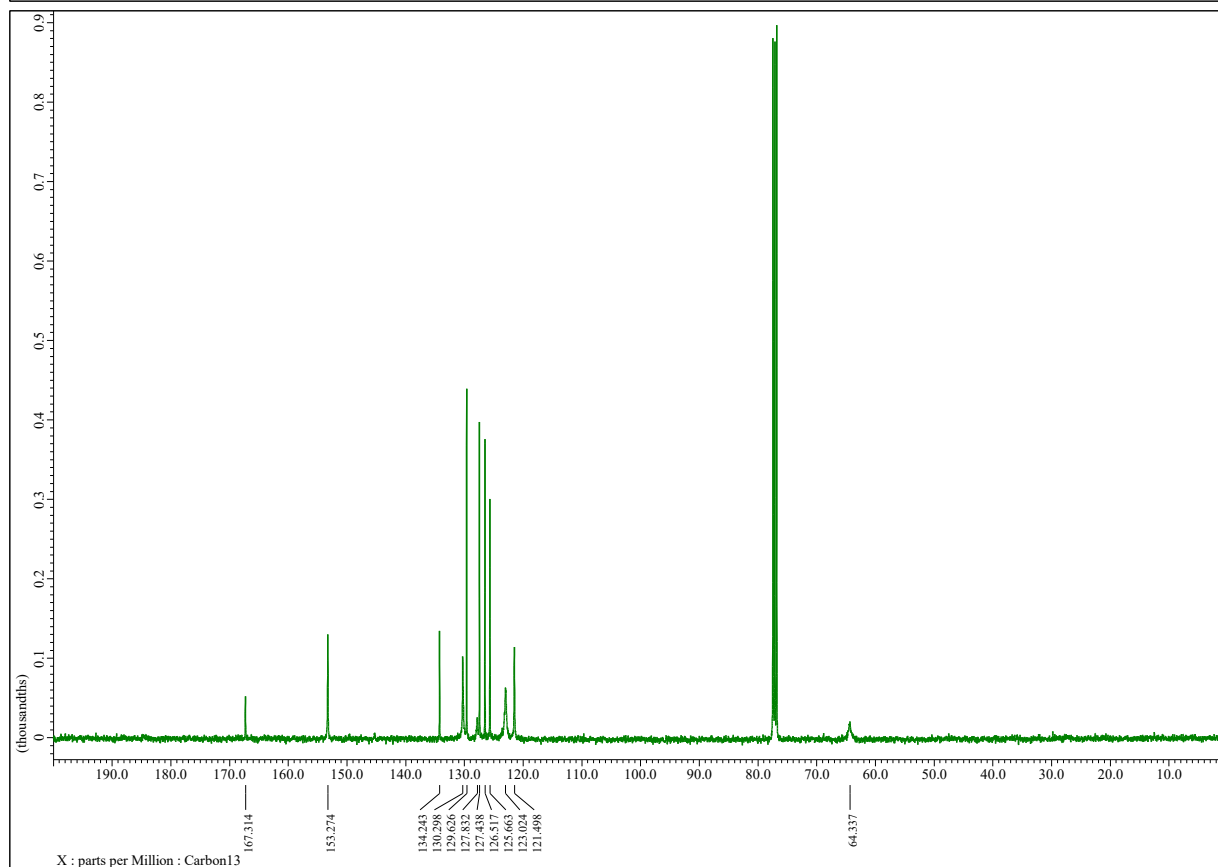
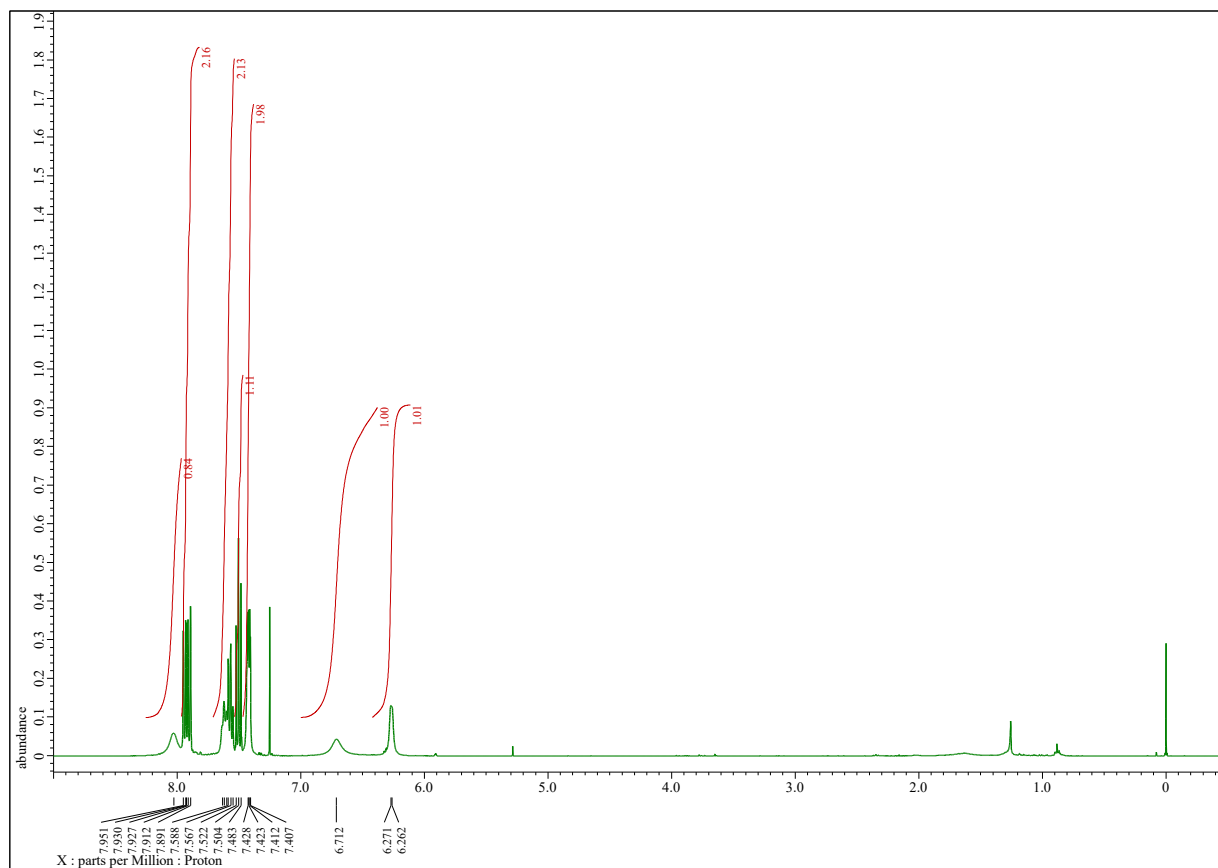
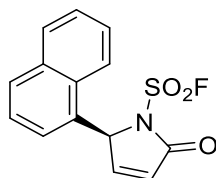


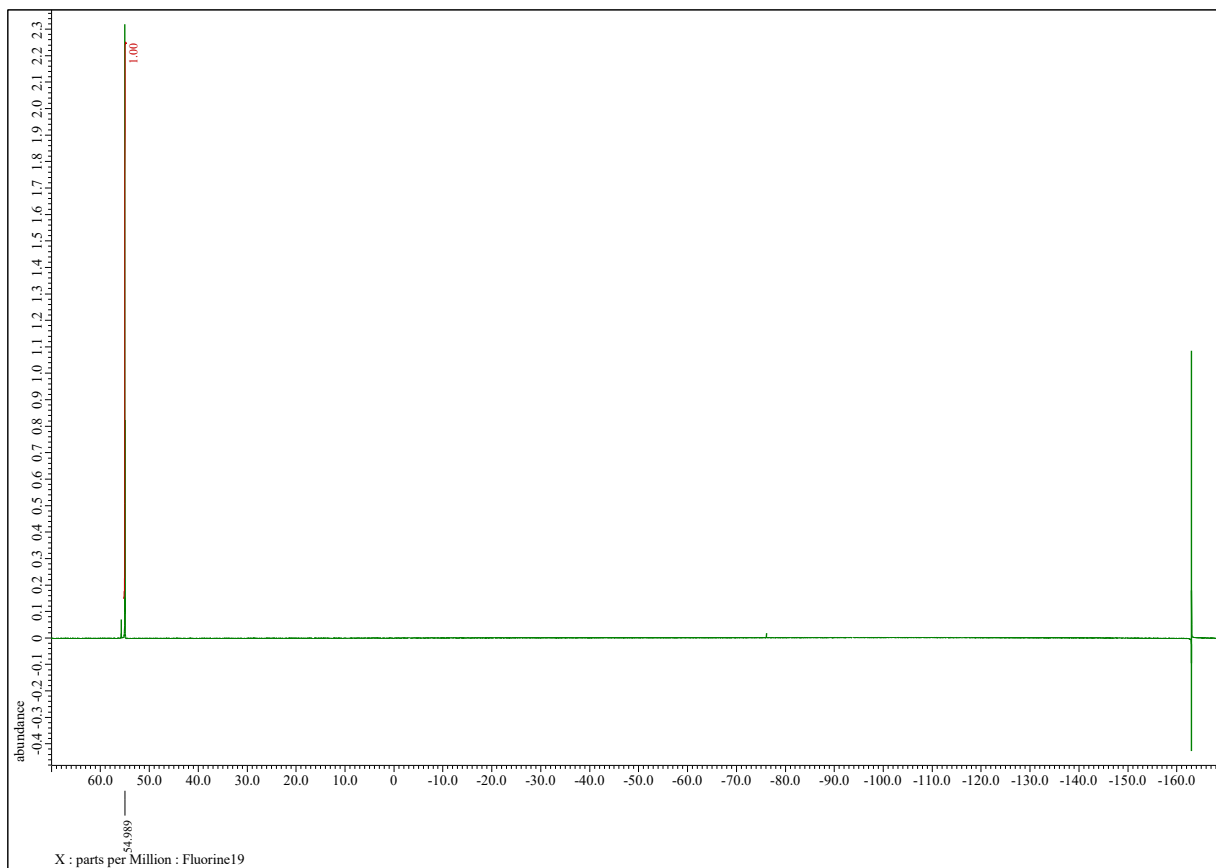
(S)-2-oxo-5-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6j)



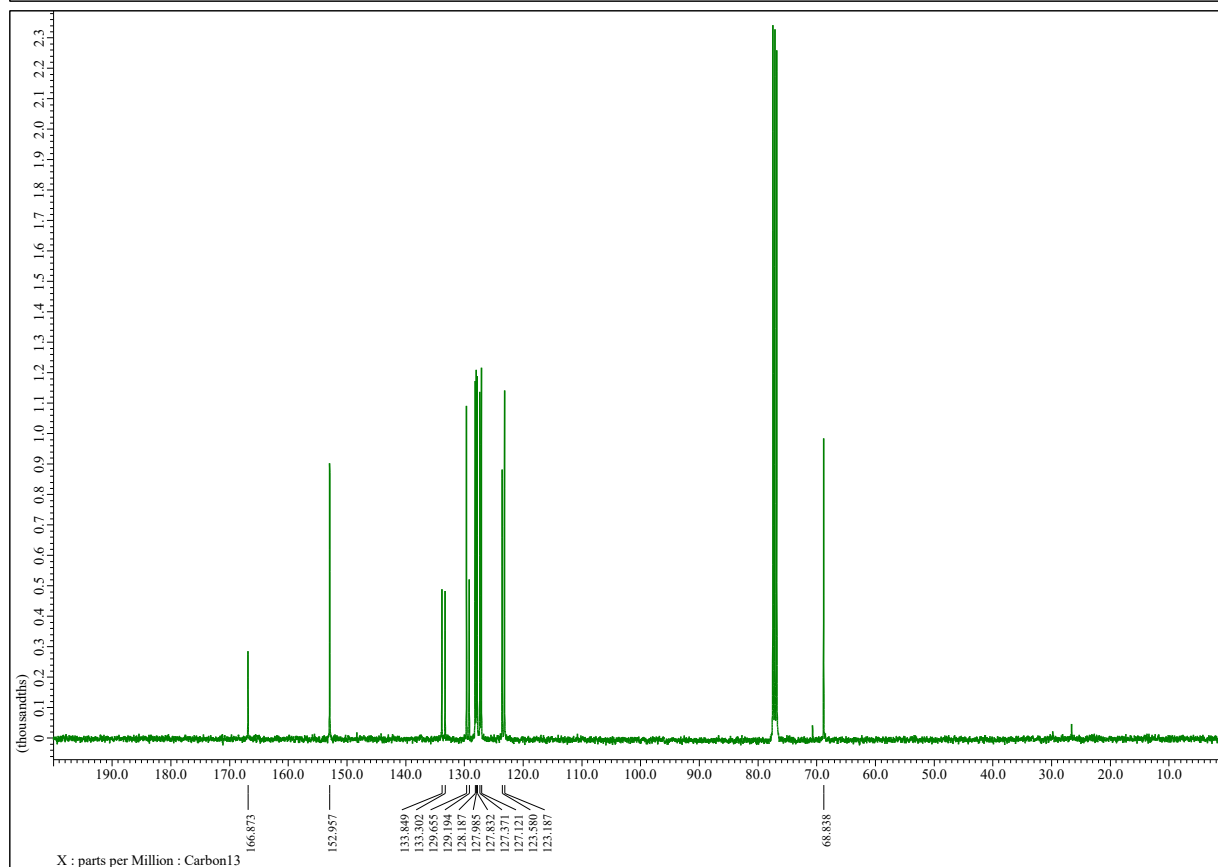
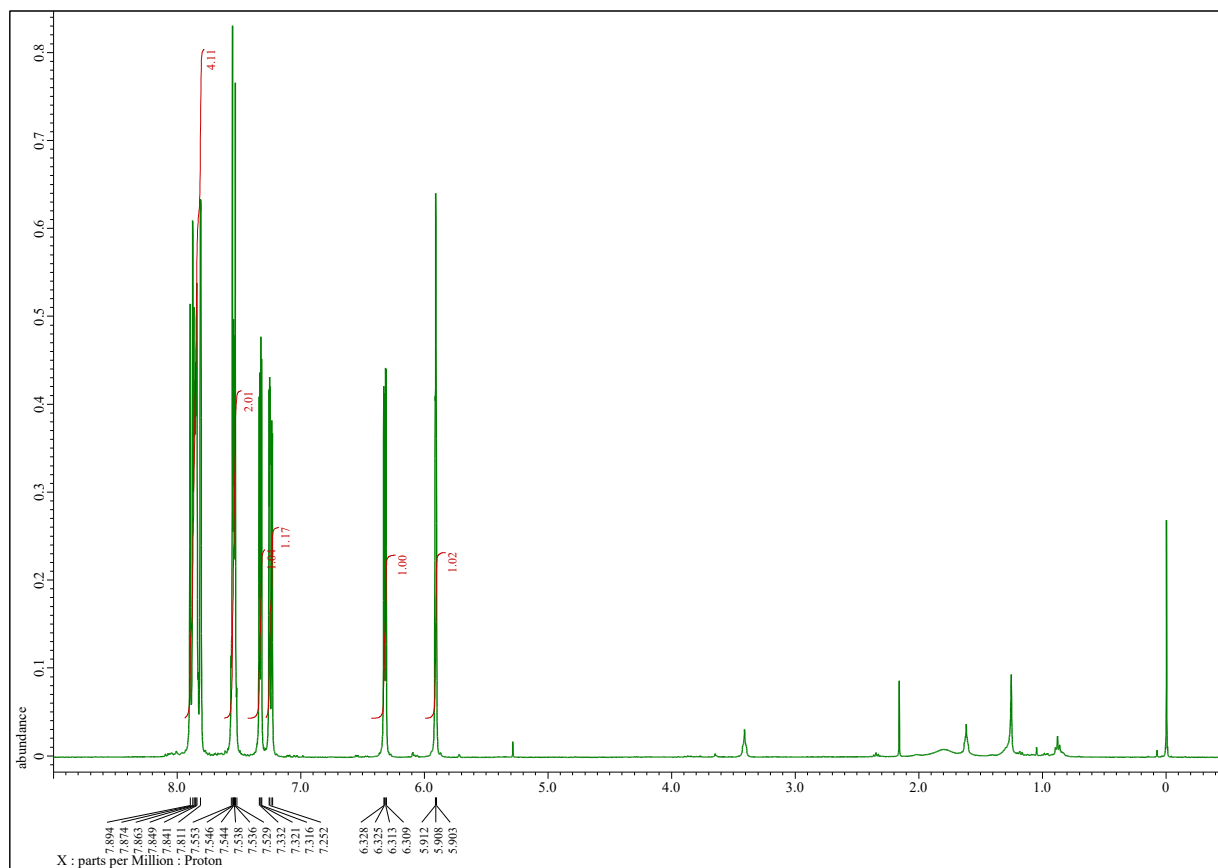
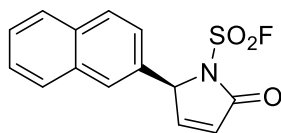


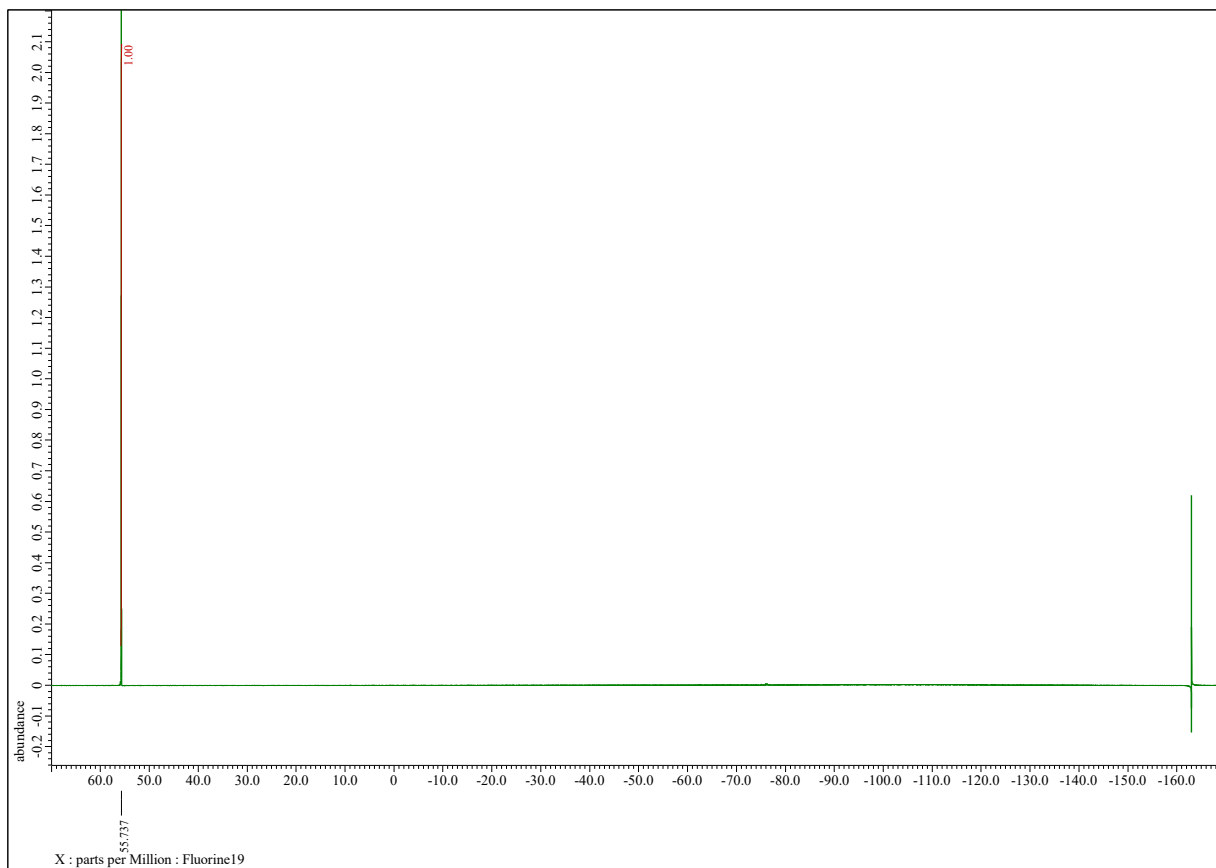
(S)-2-(naphthalen-1-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6k)



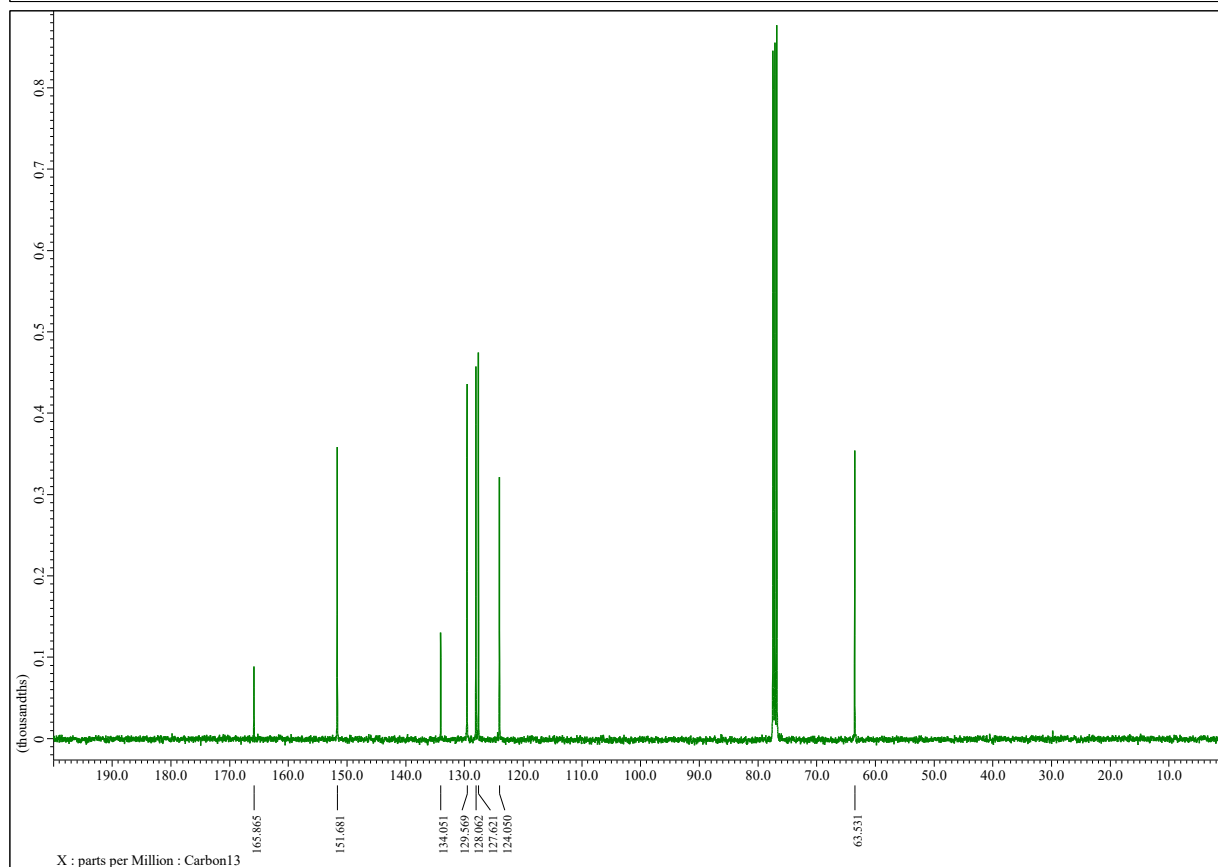
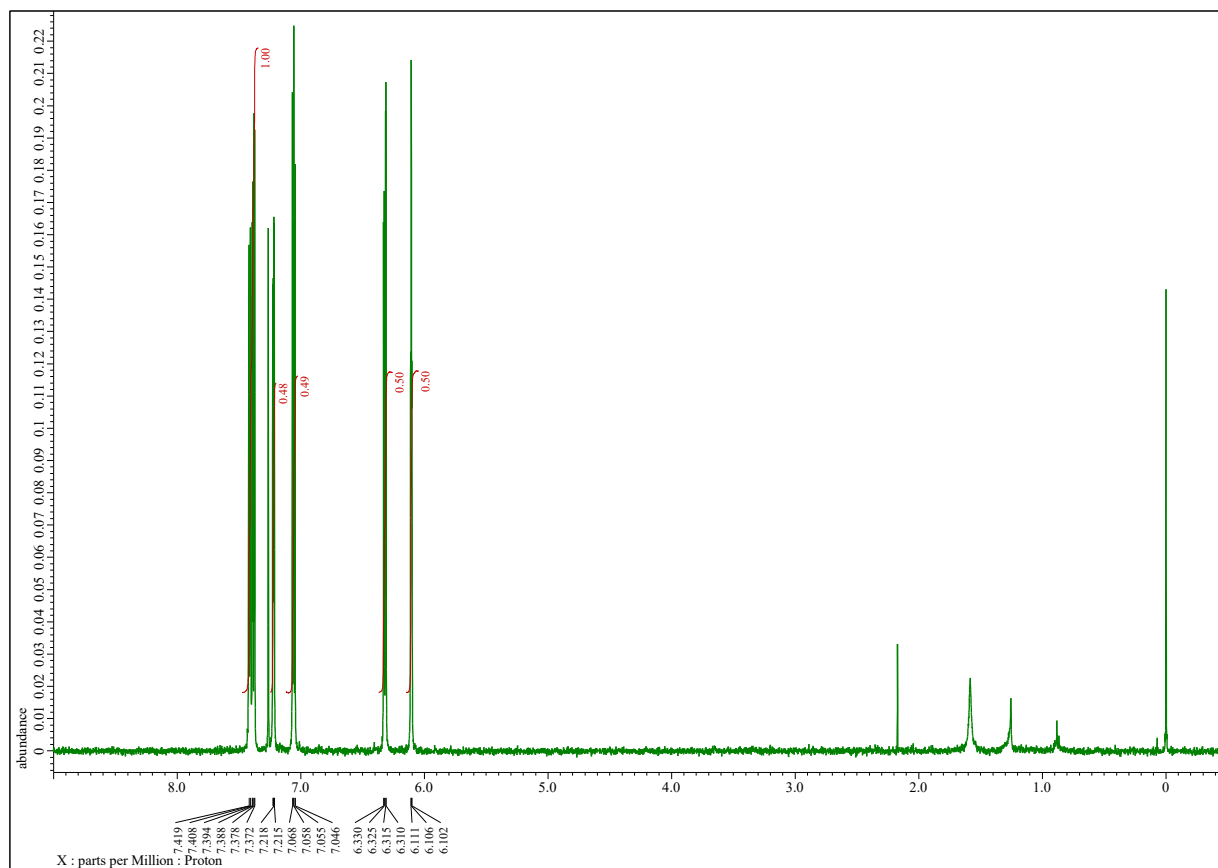
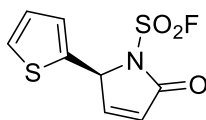


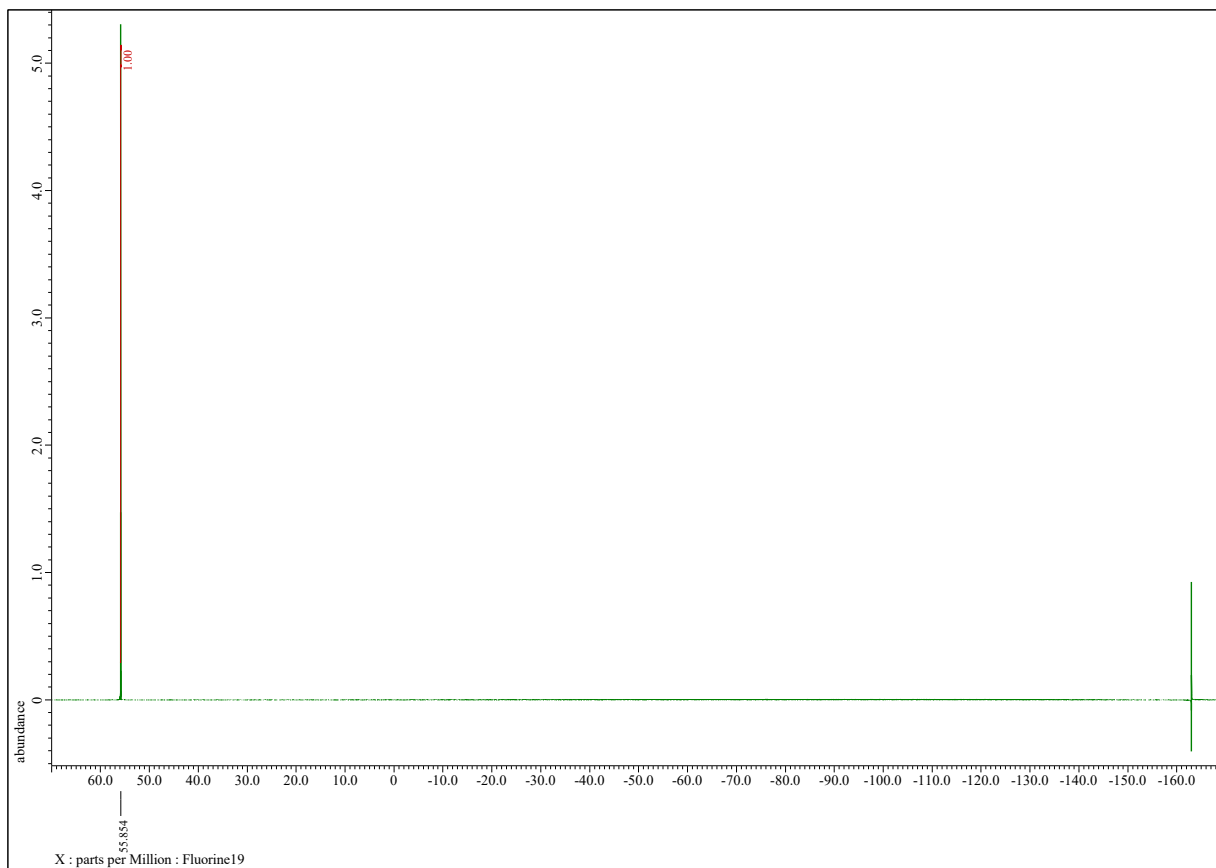
(S)-2-(naphthalen-2-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6I)



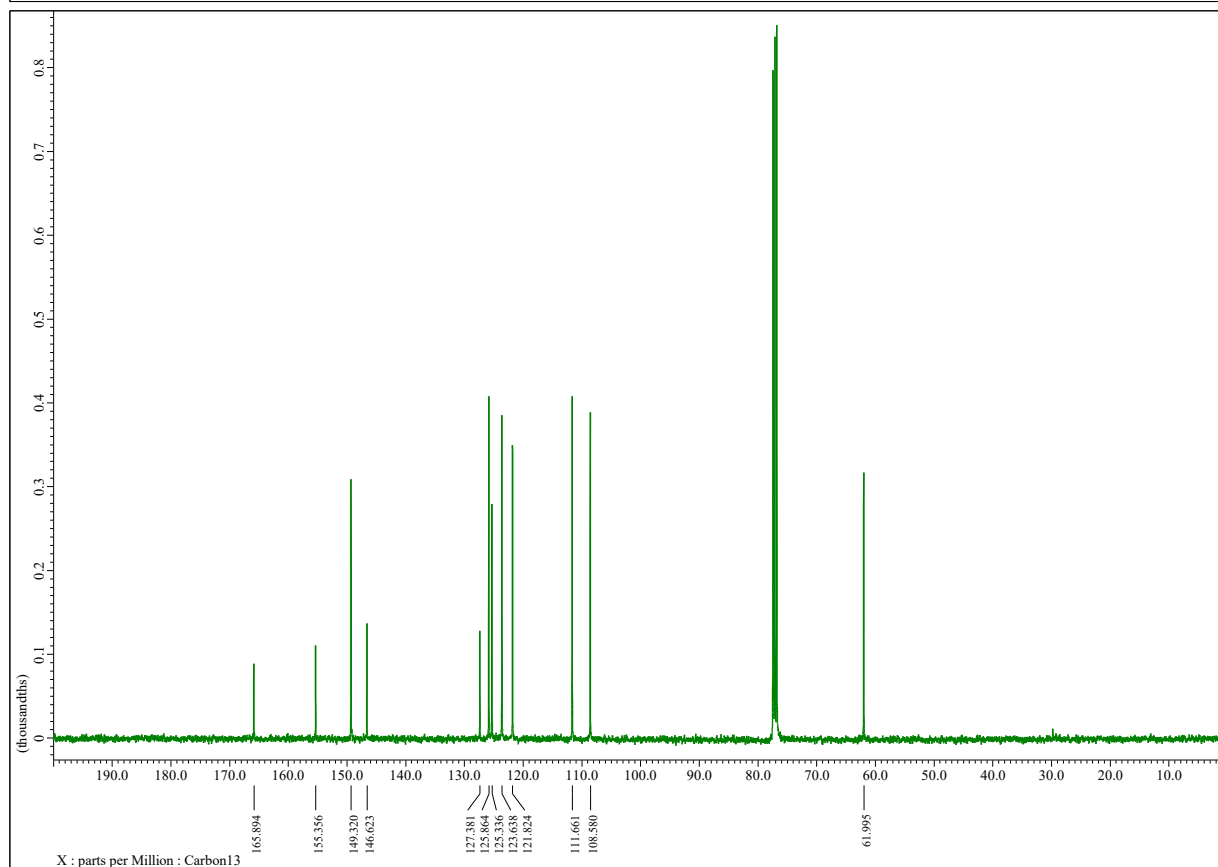
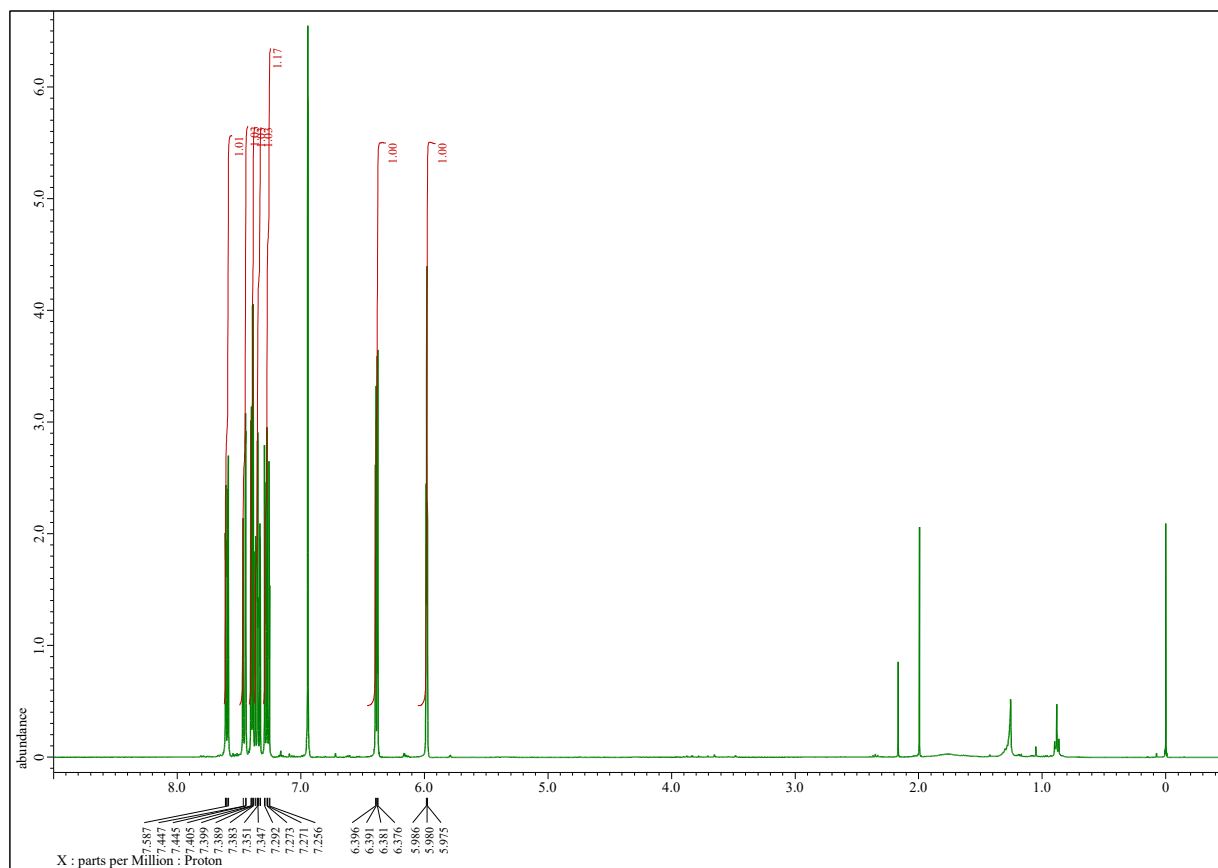
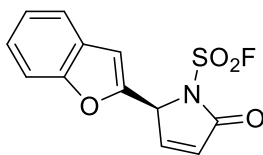


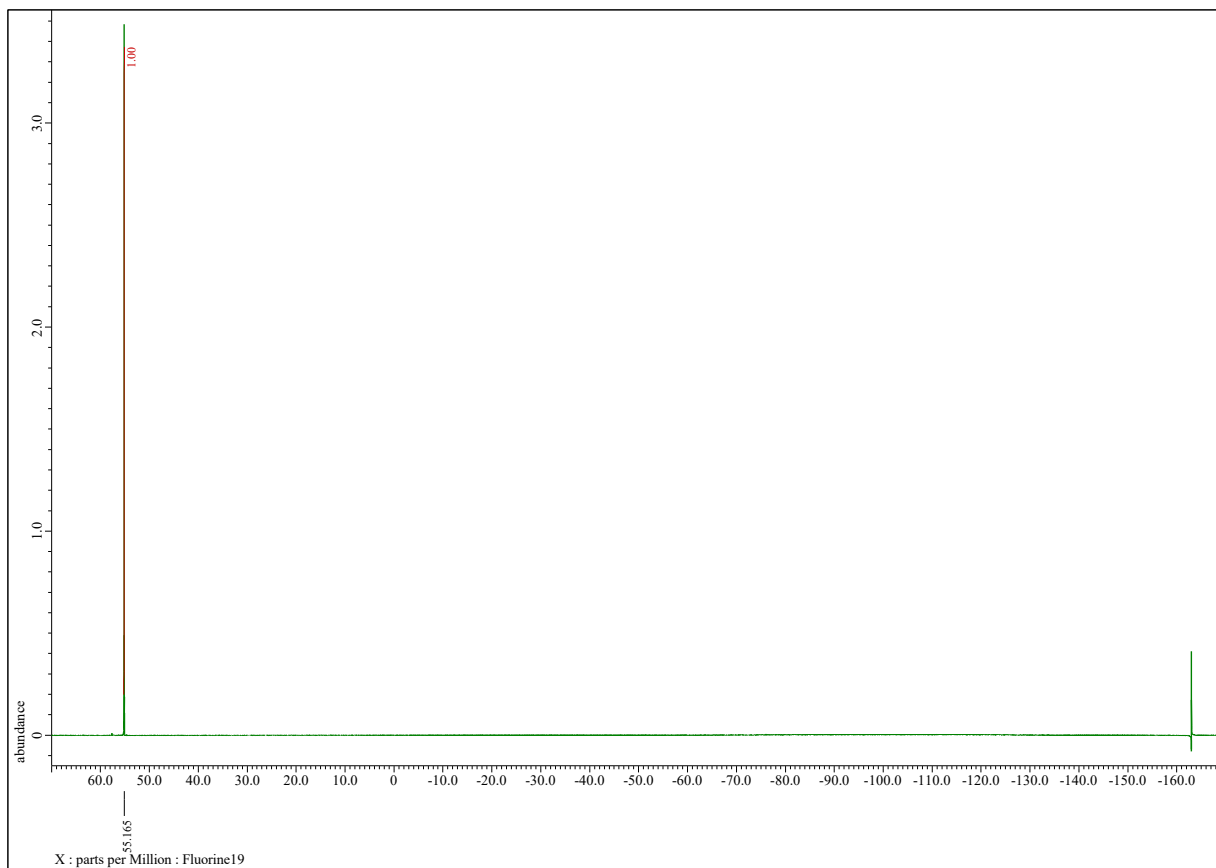
(S)-2-oxo-5-(thiophen-2-yl)-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6m)



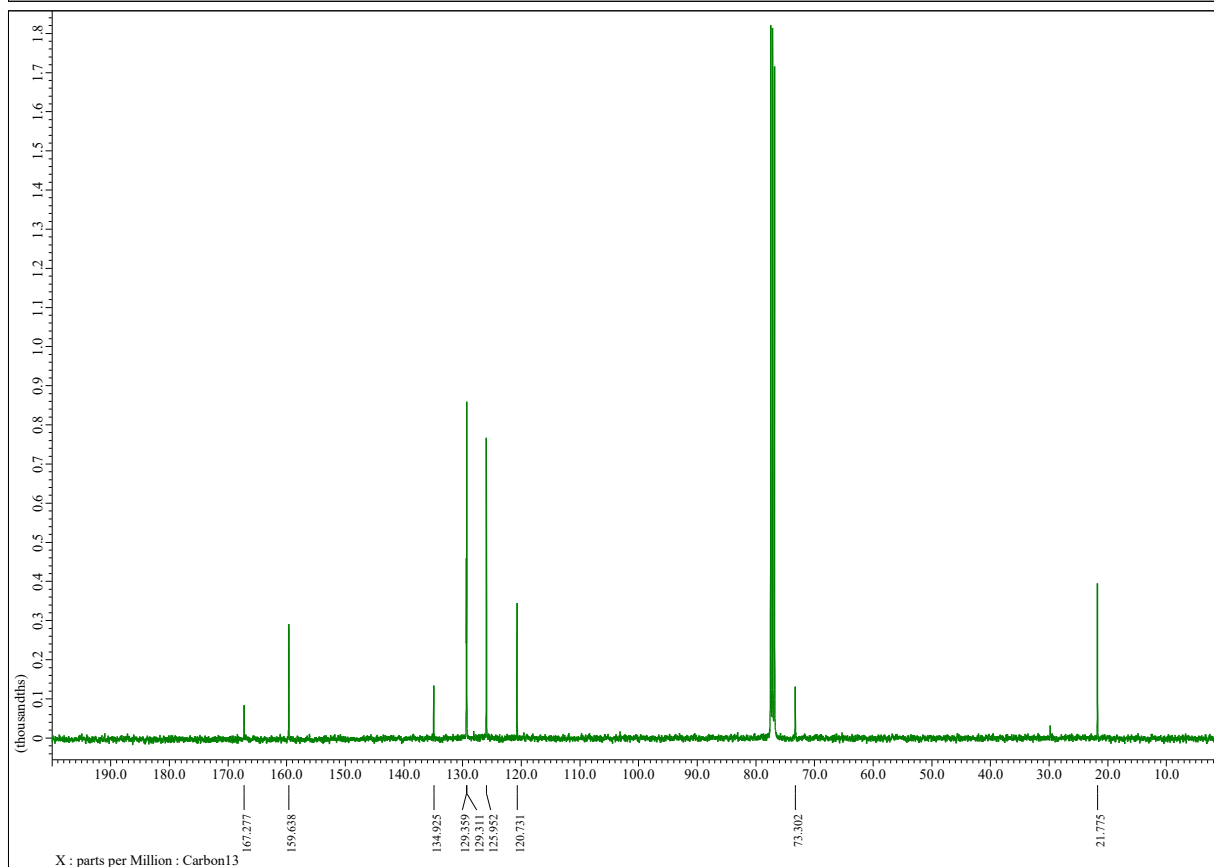
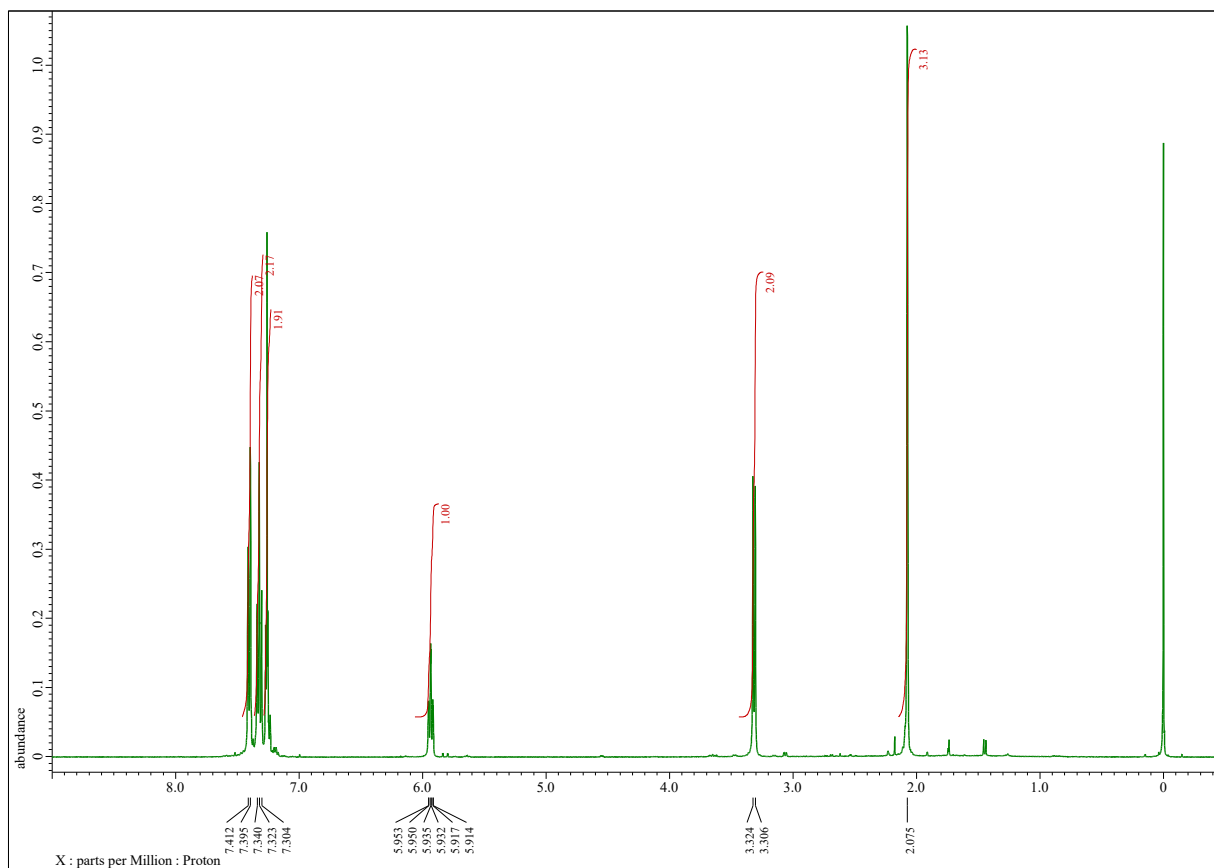
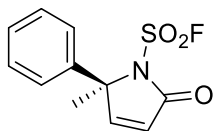


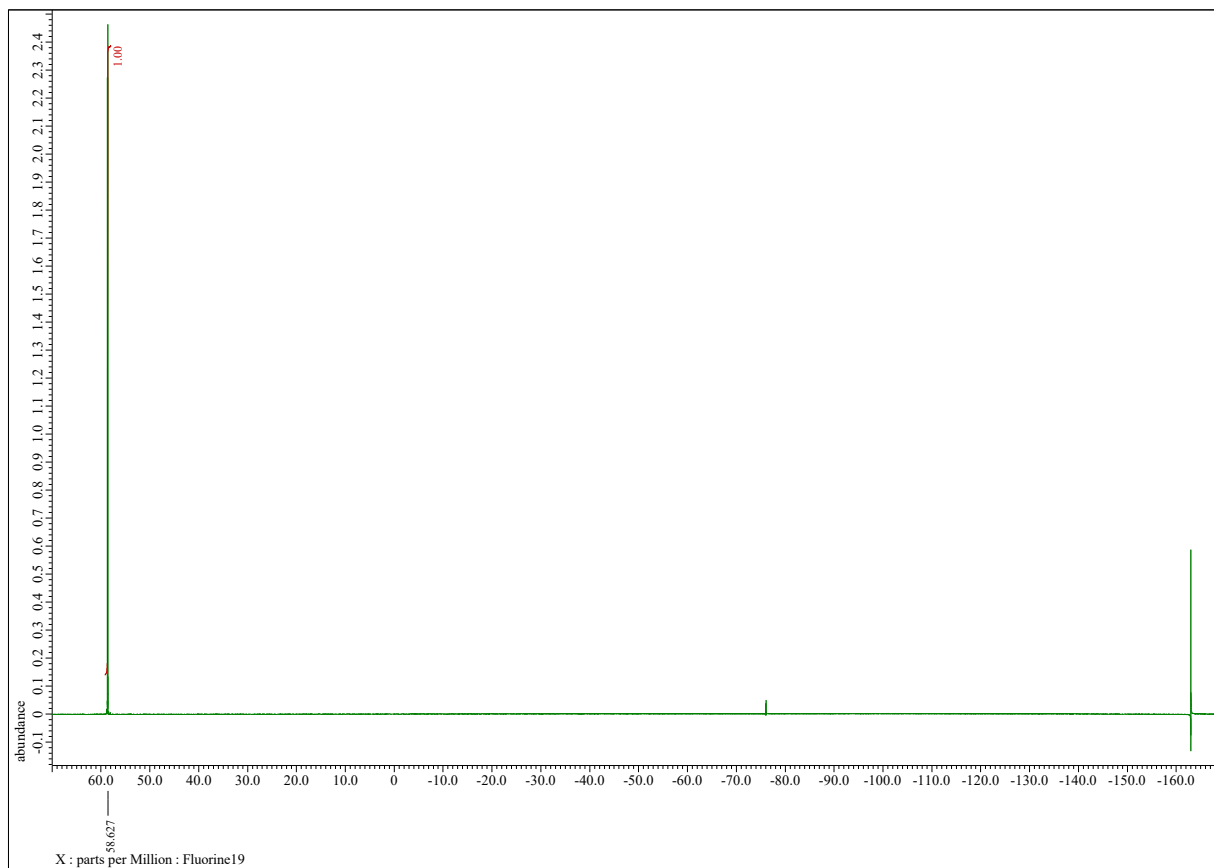
(S)-2-(benzofuran-2-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6n)



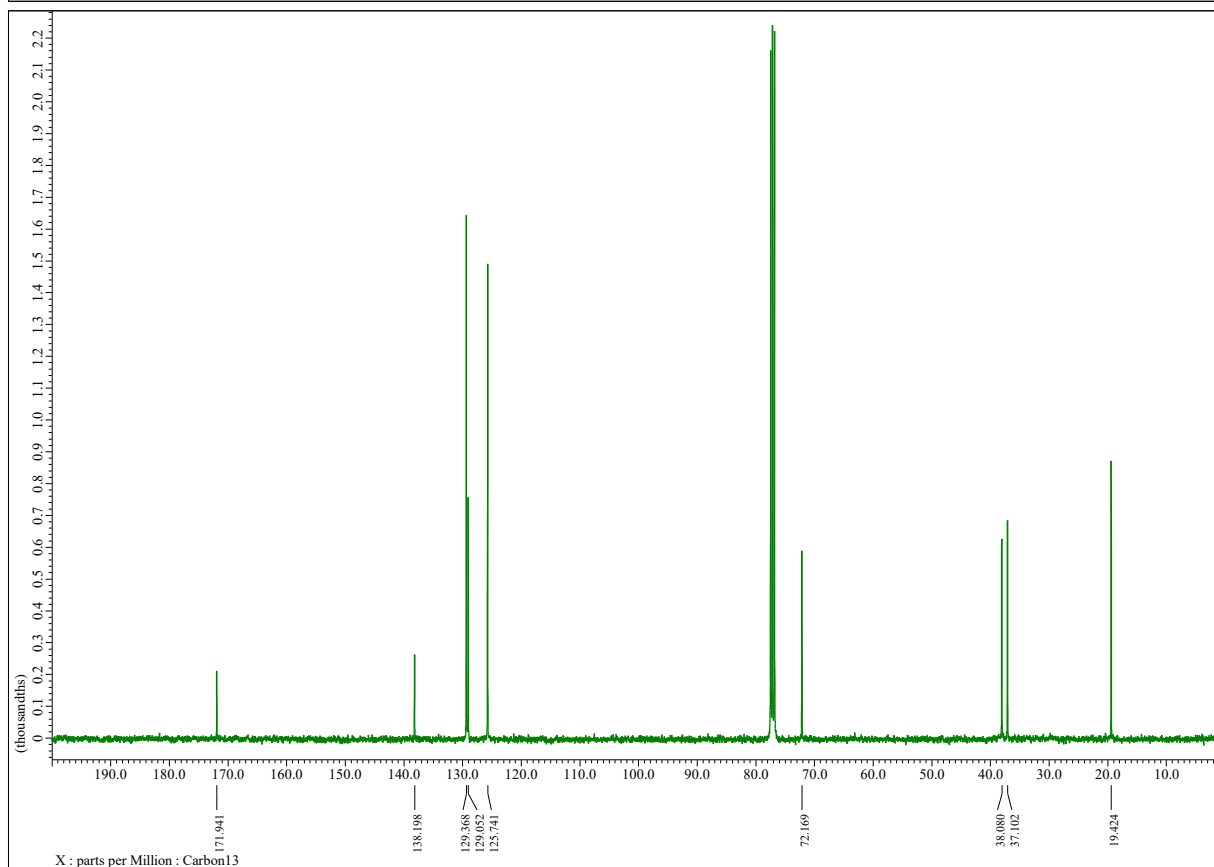
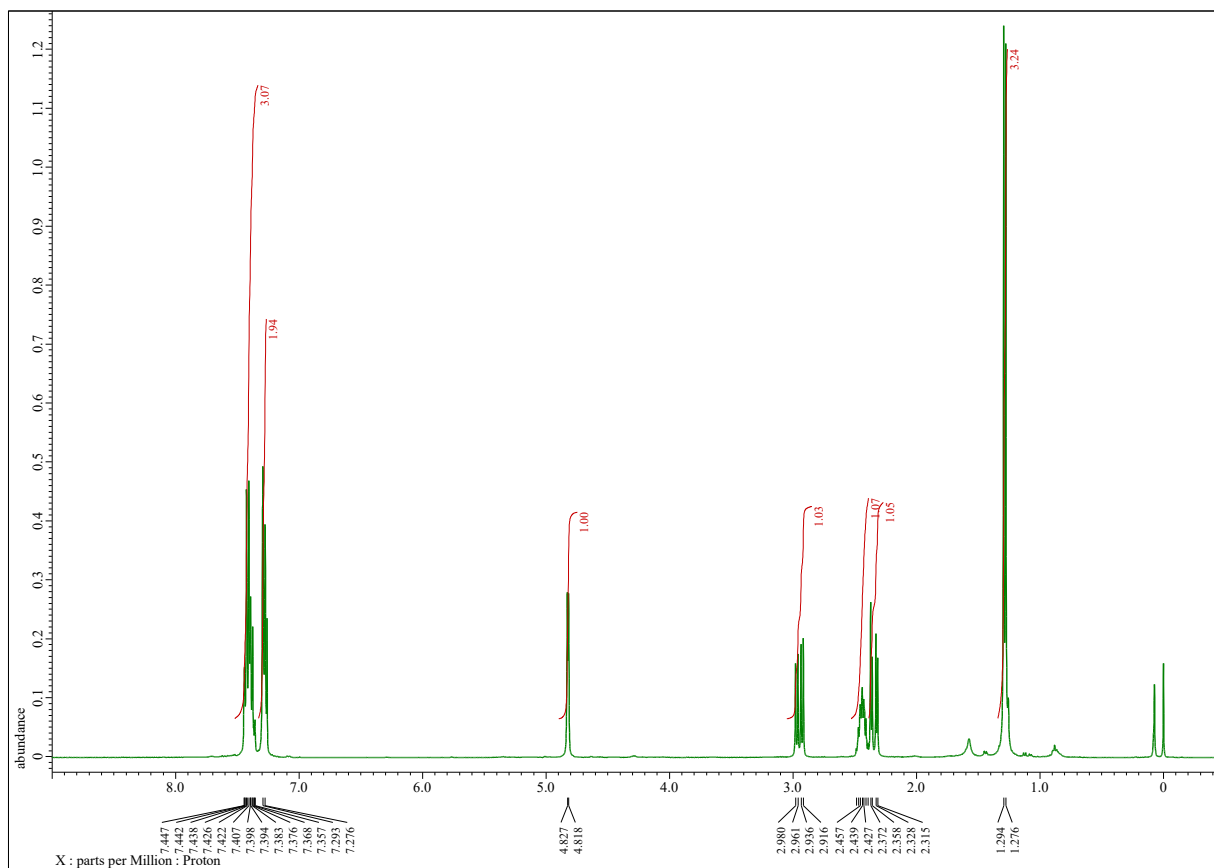
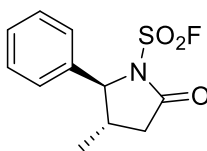


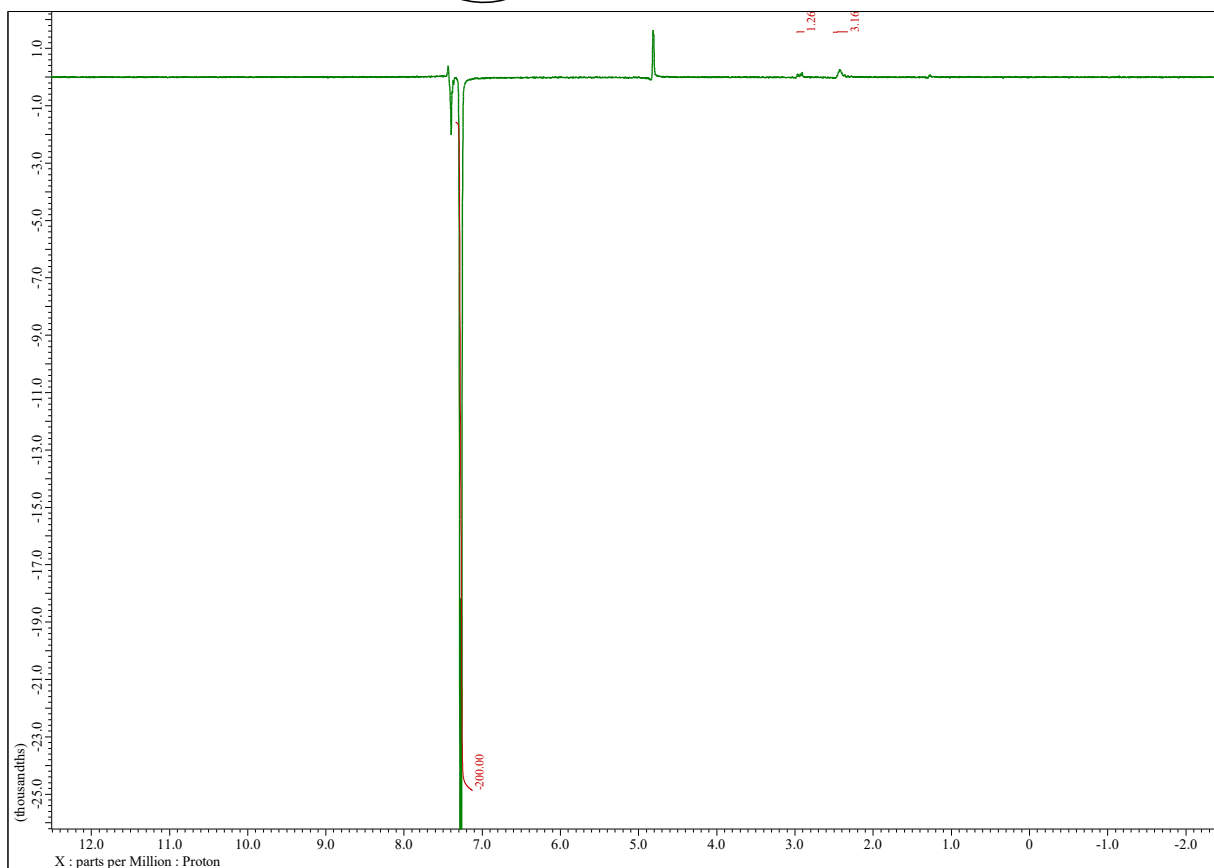
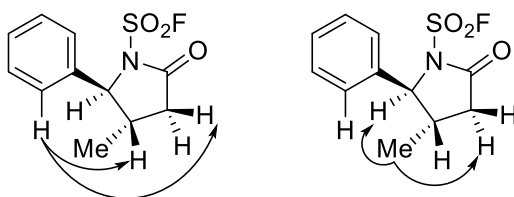
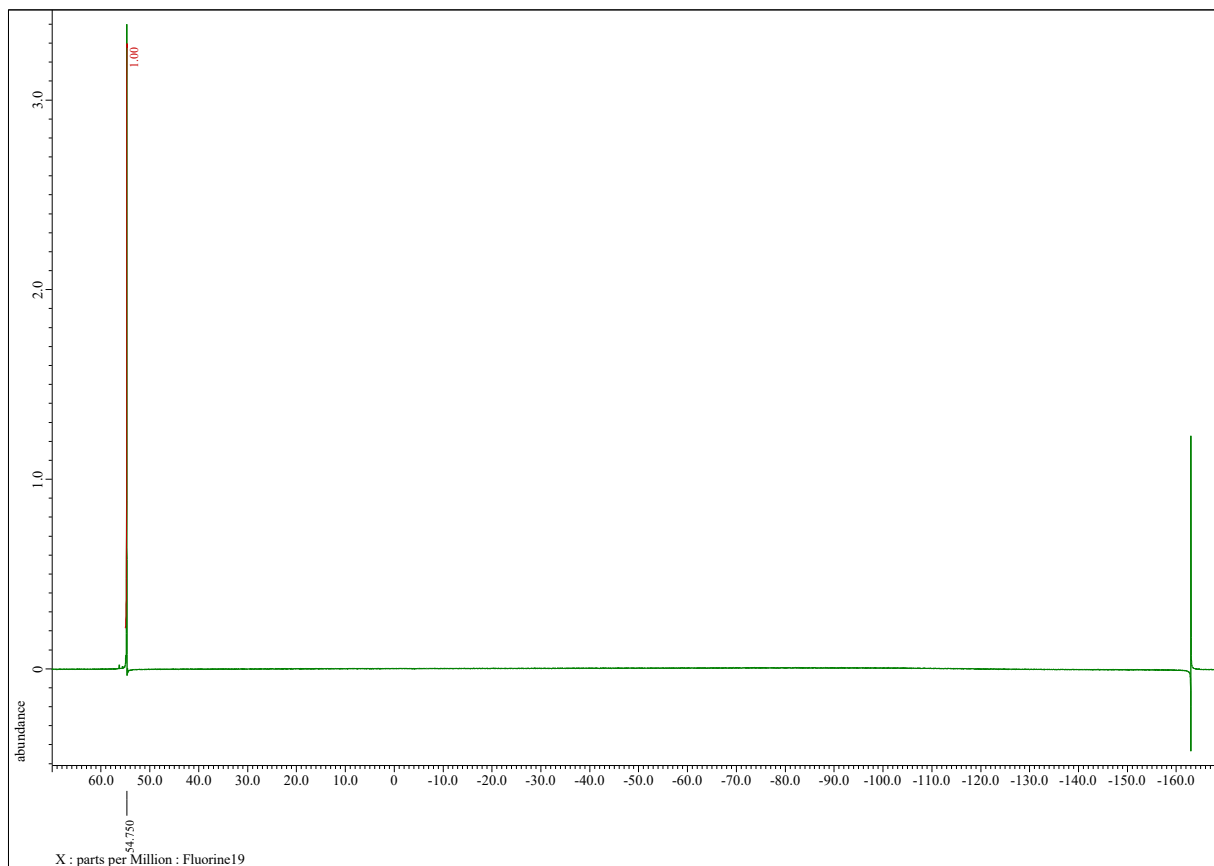
(S)-2-methyl-5-oxo-2-phenyl-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (6o)

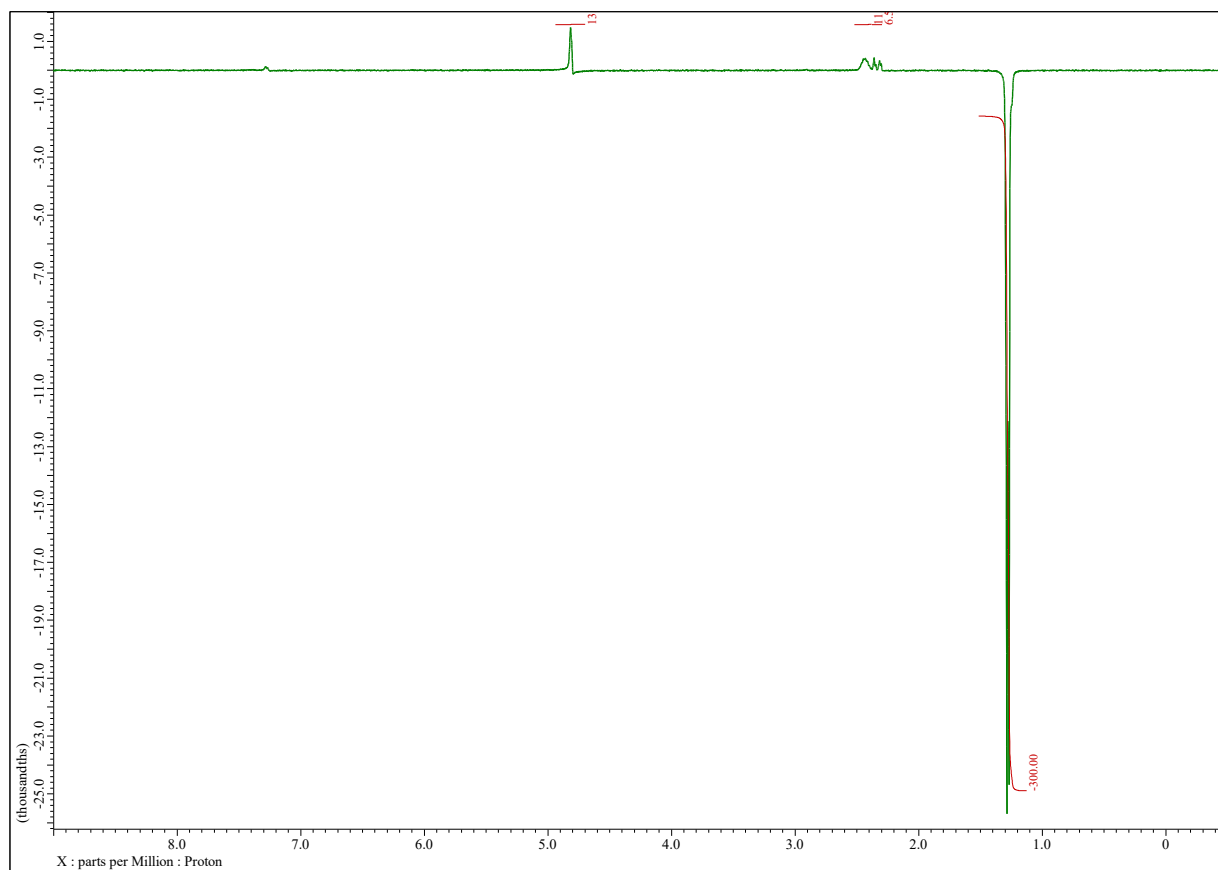




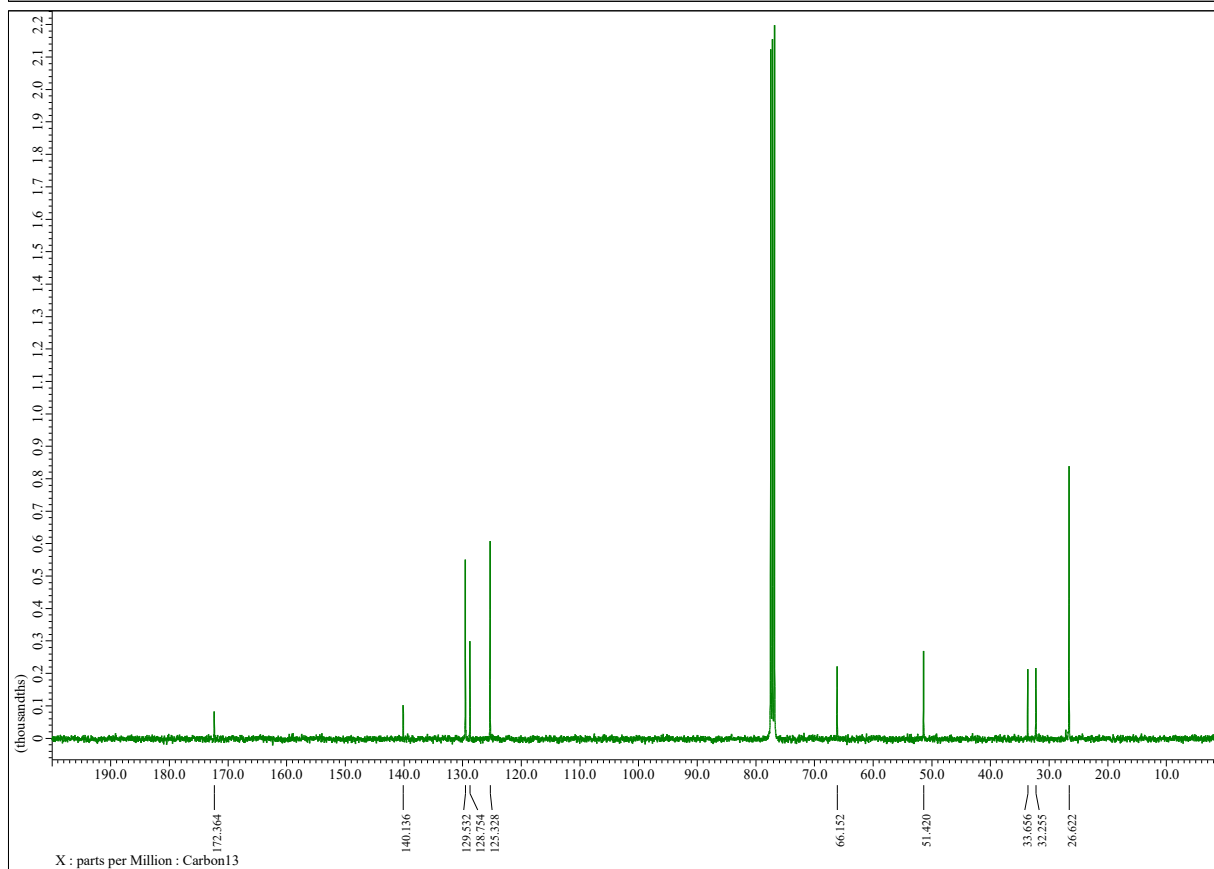
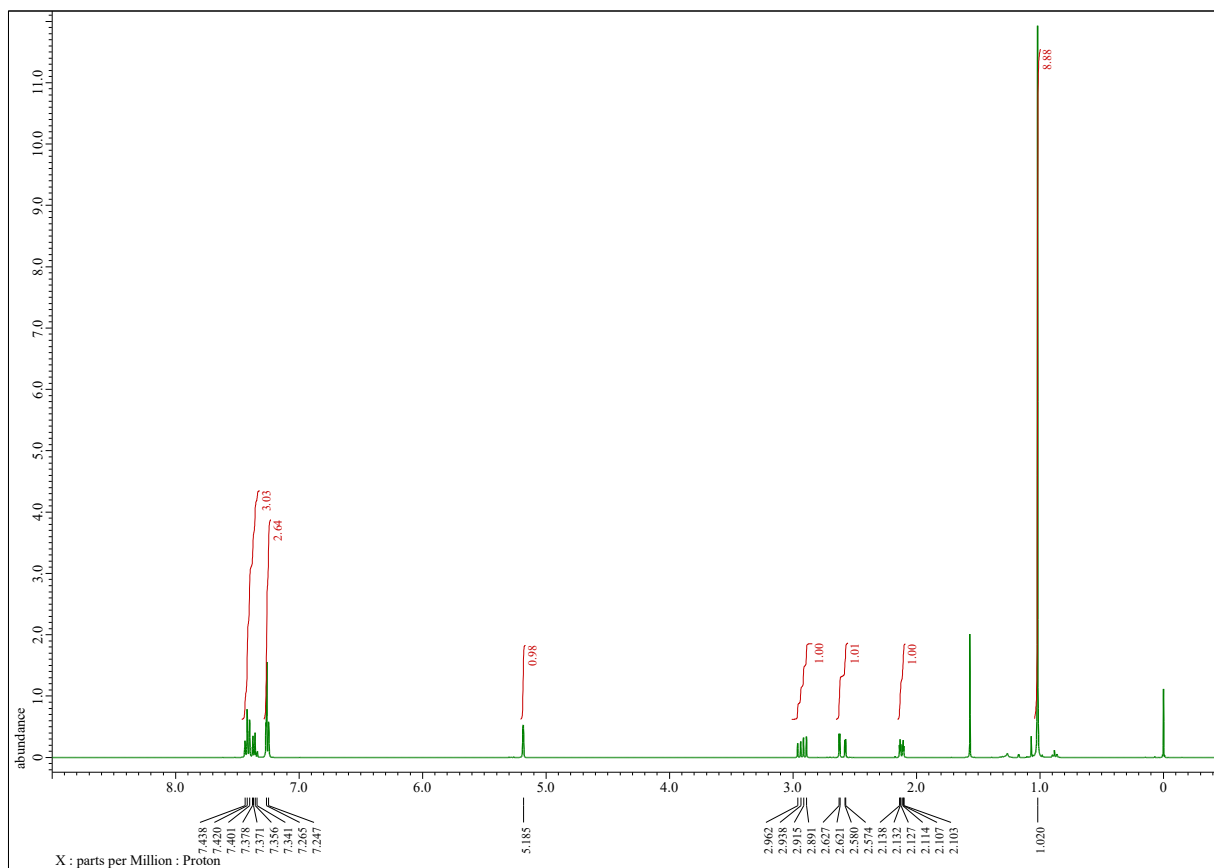
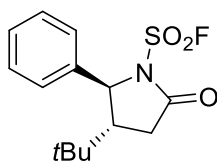
(2S,3S)-3-methyl-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (7)

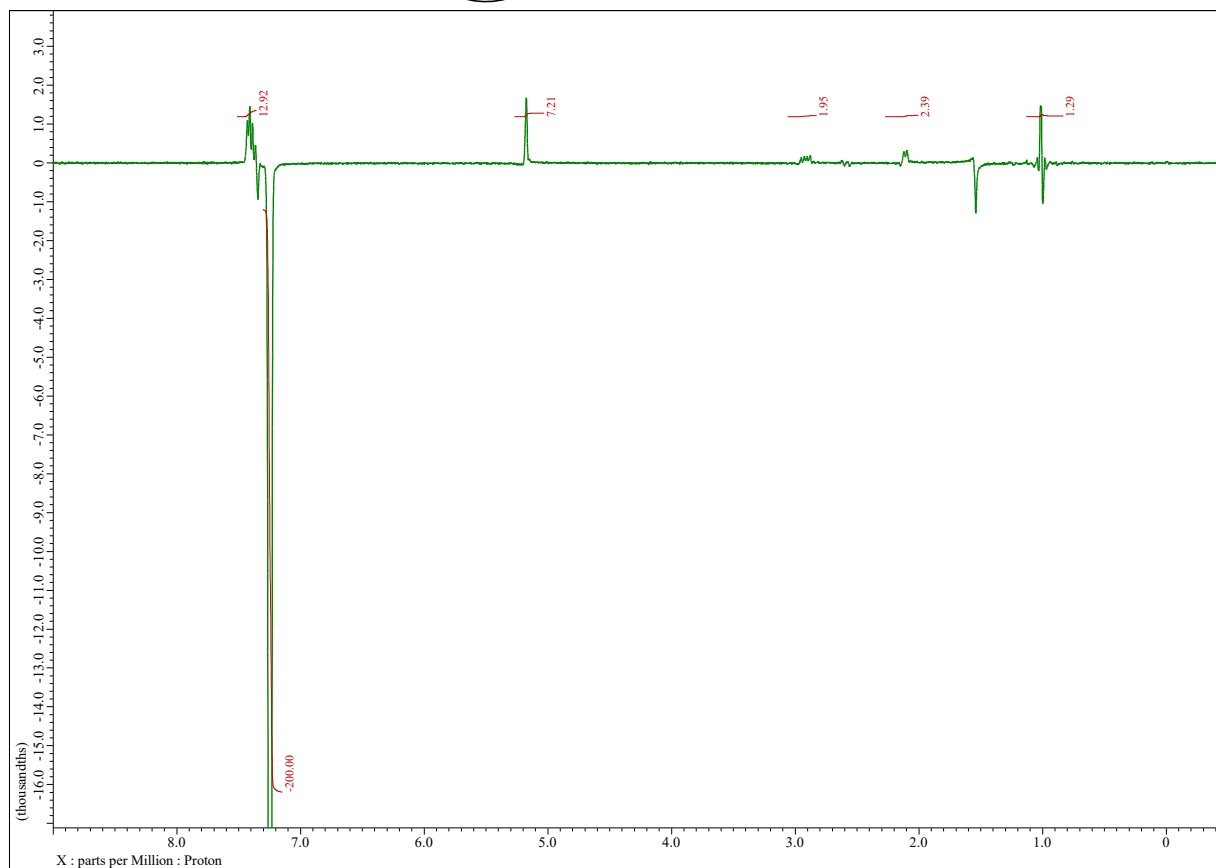
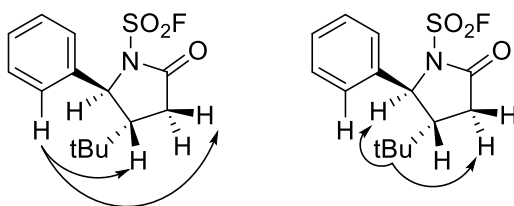
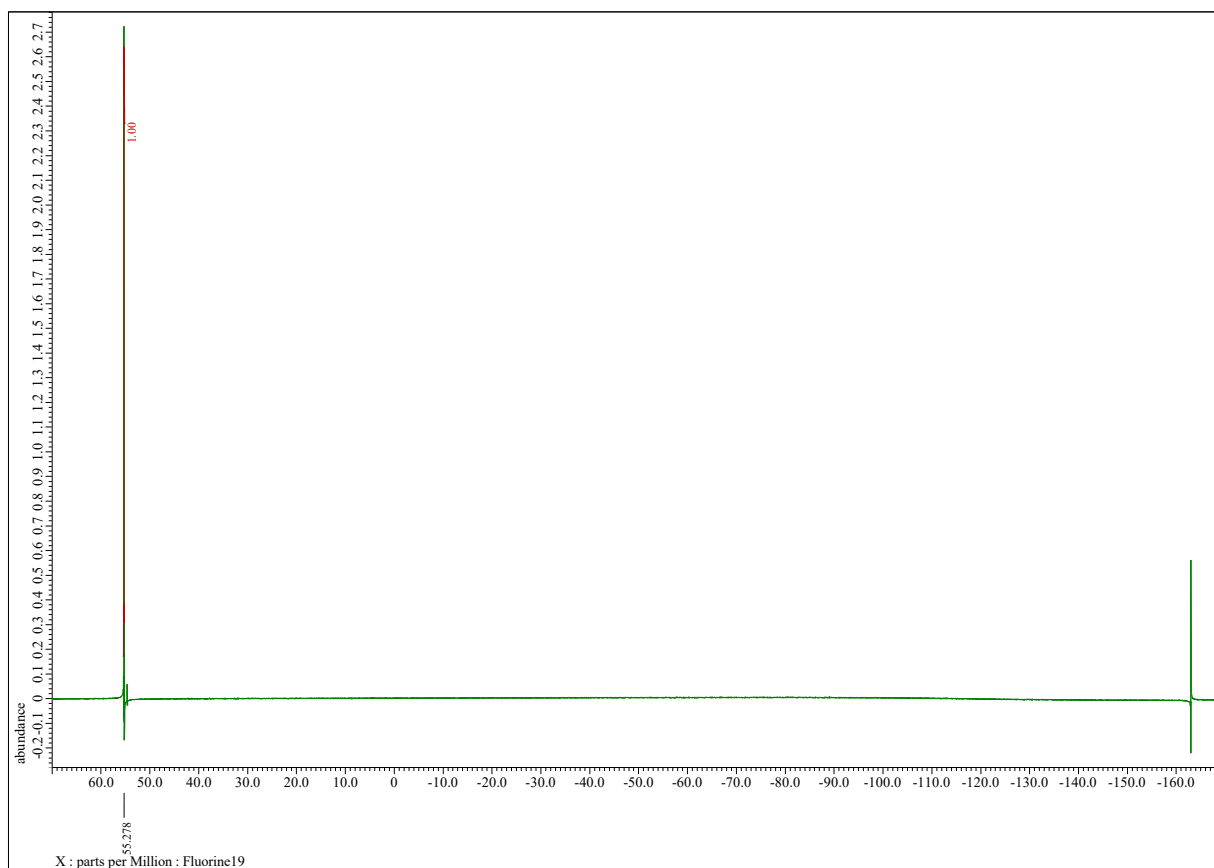


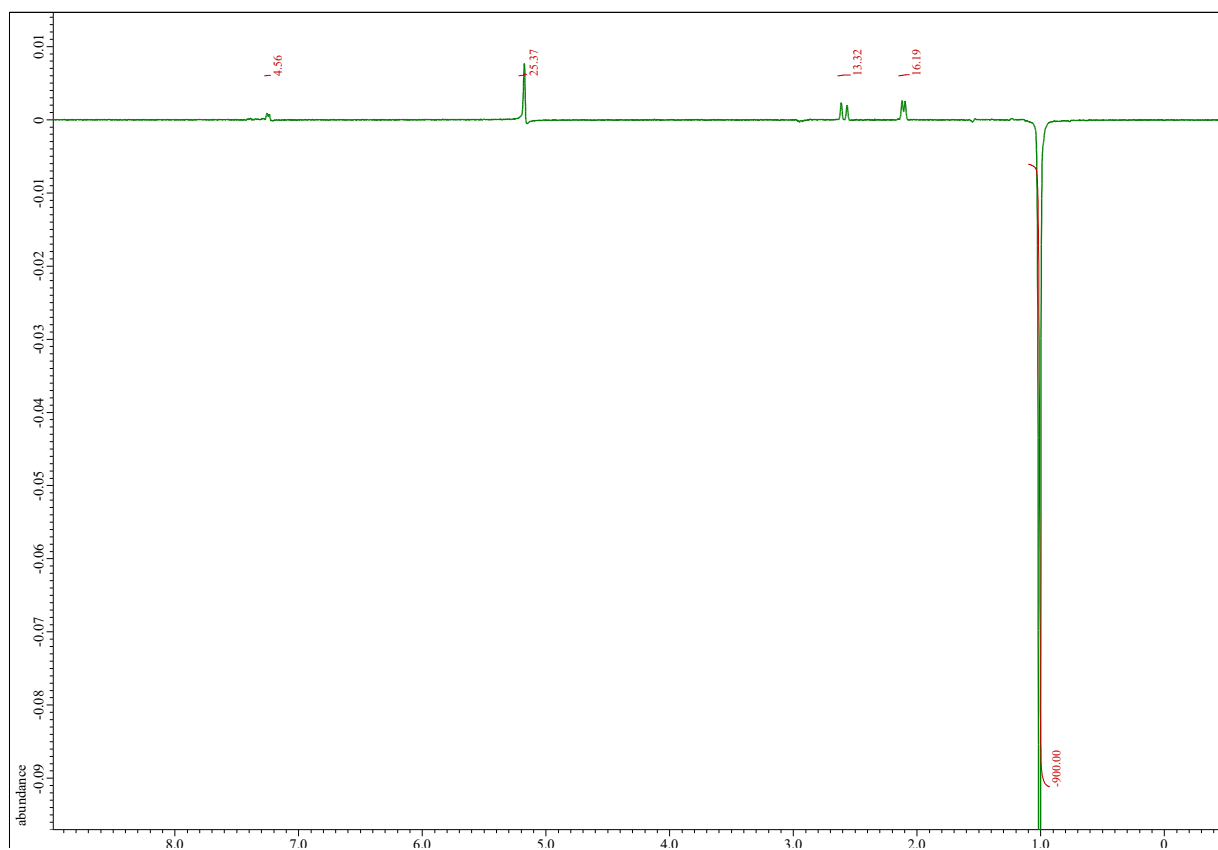




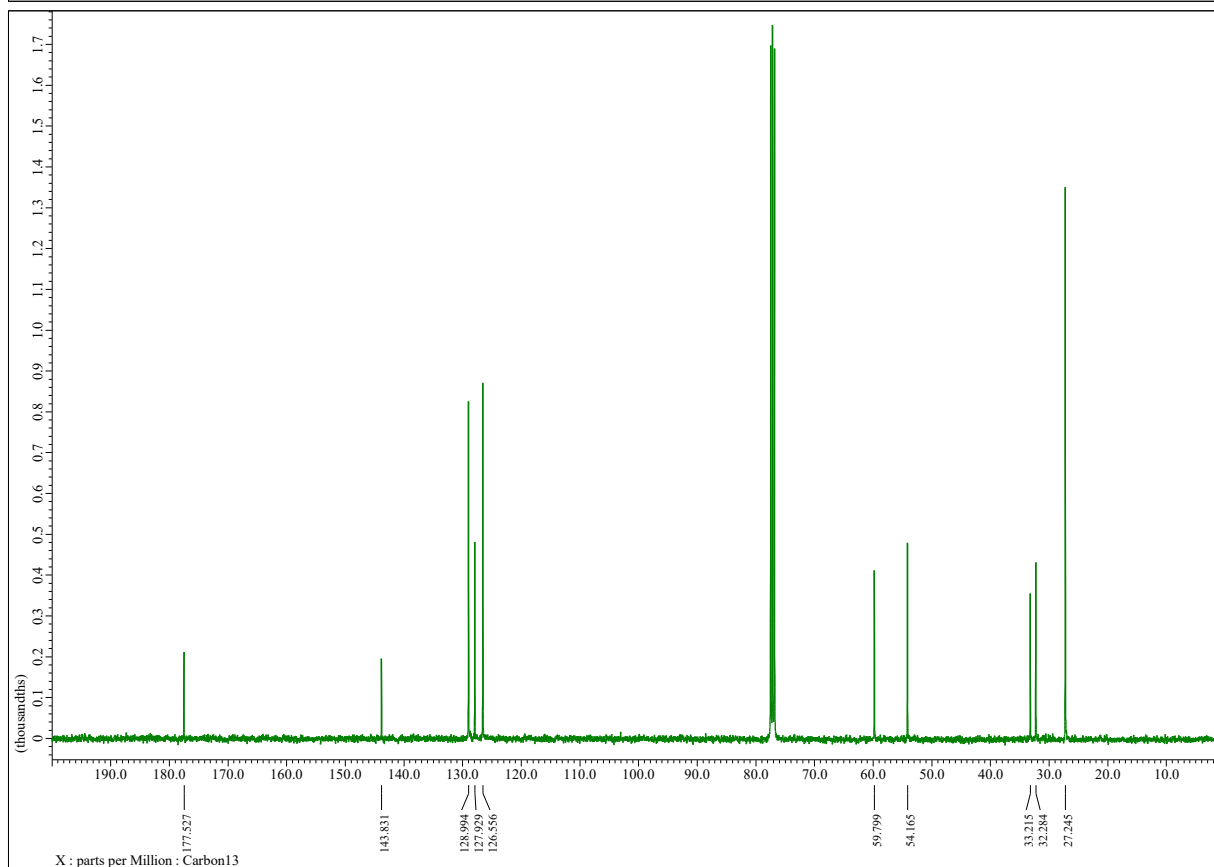
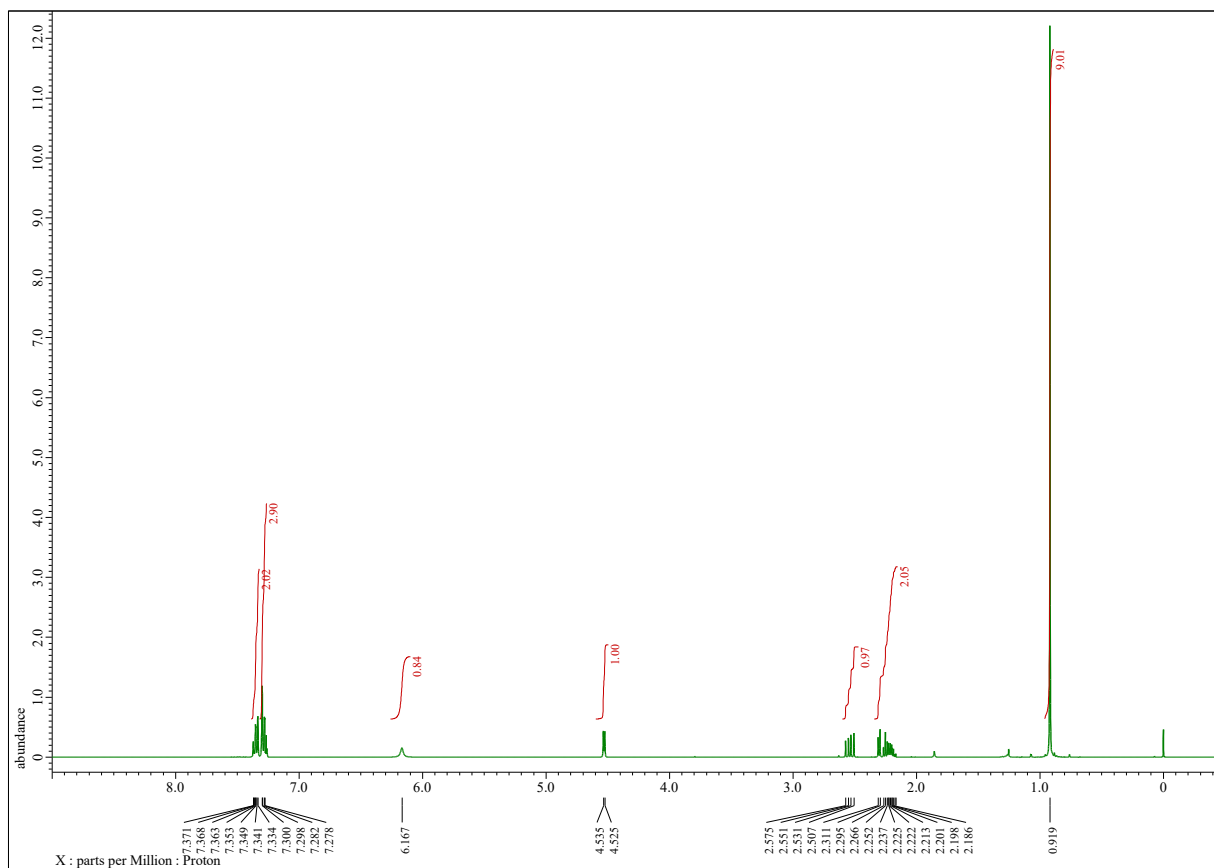
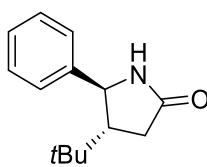
(2*S*,3*R*)-3-(*tert*-butyl)-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (8)



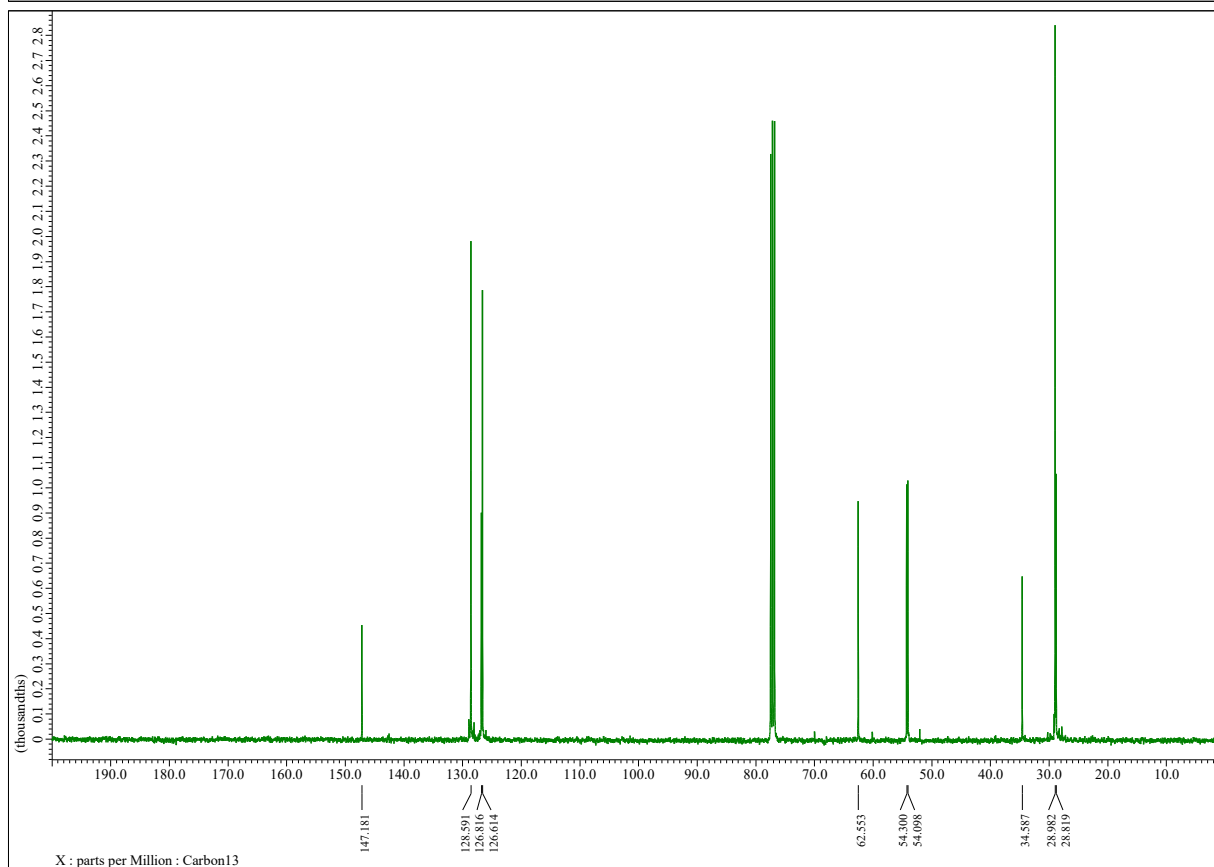
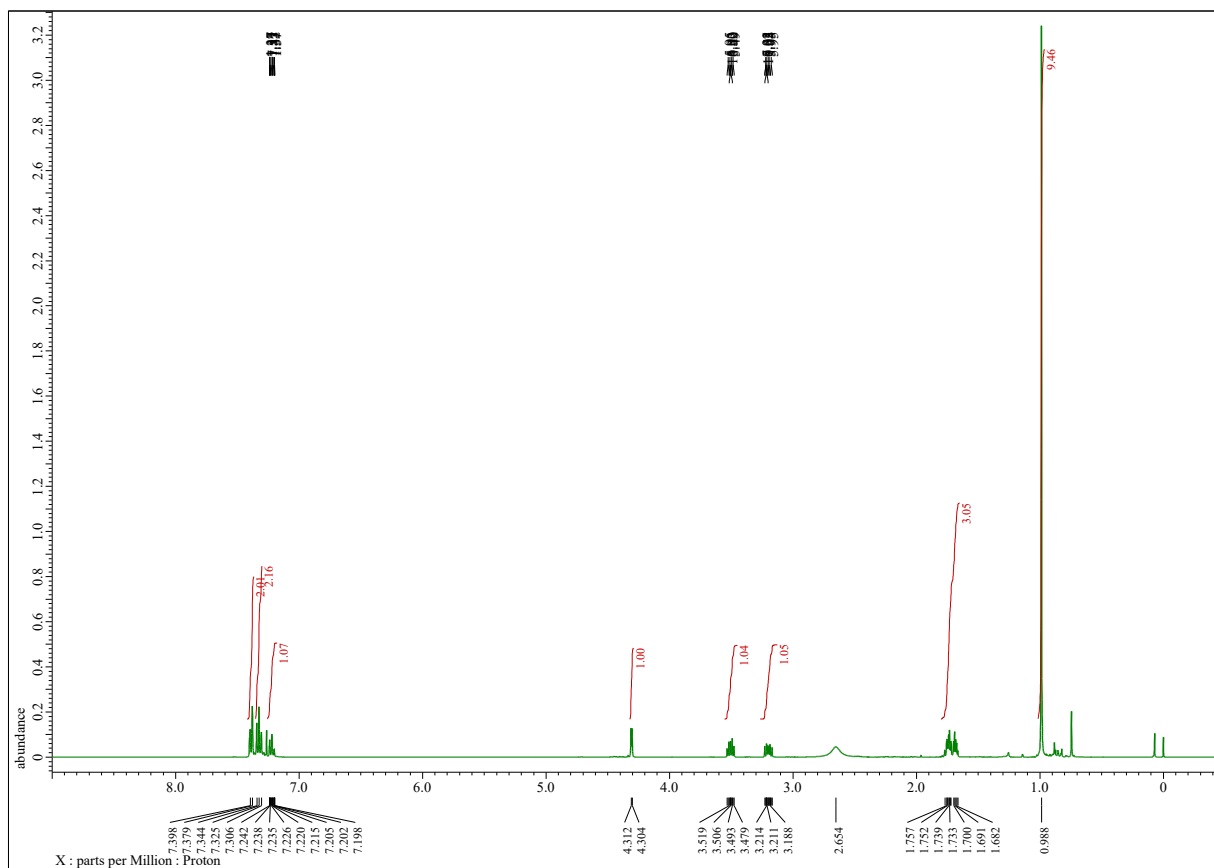
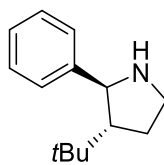




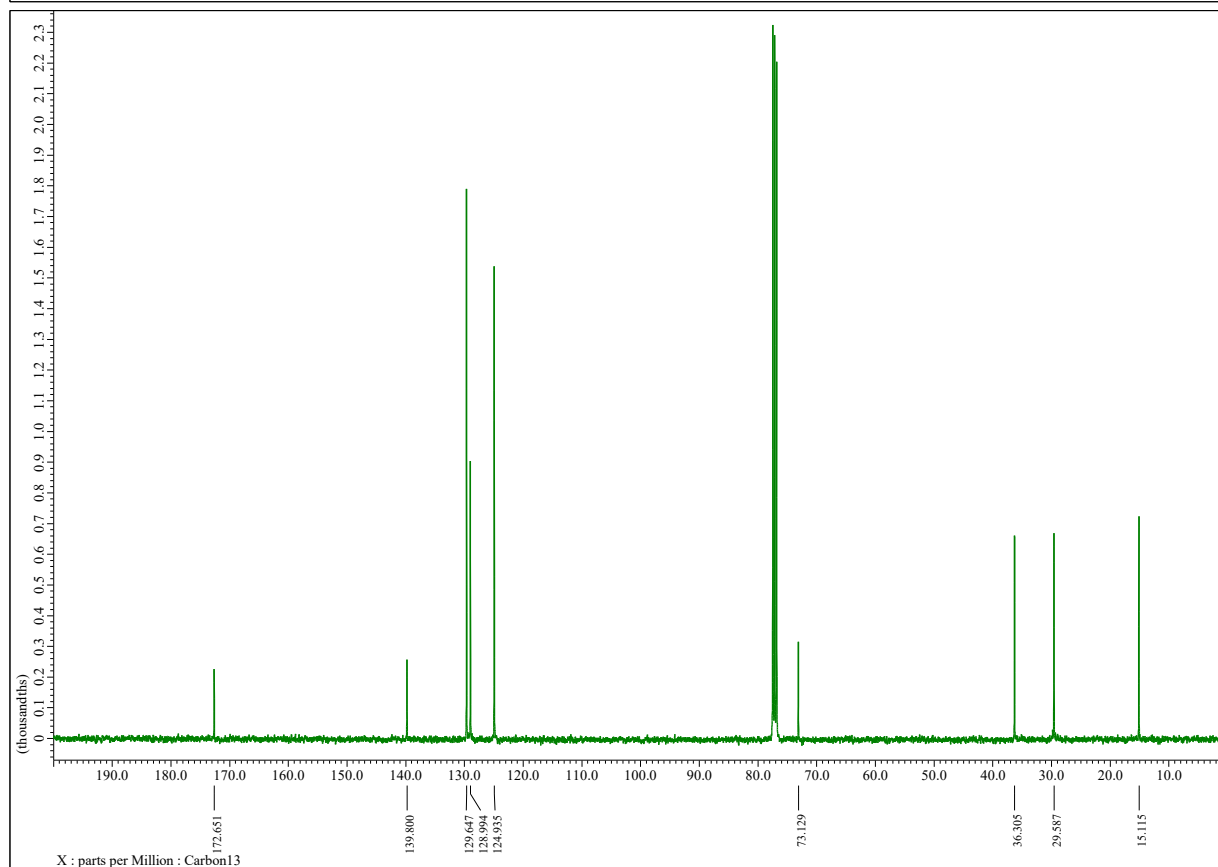
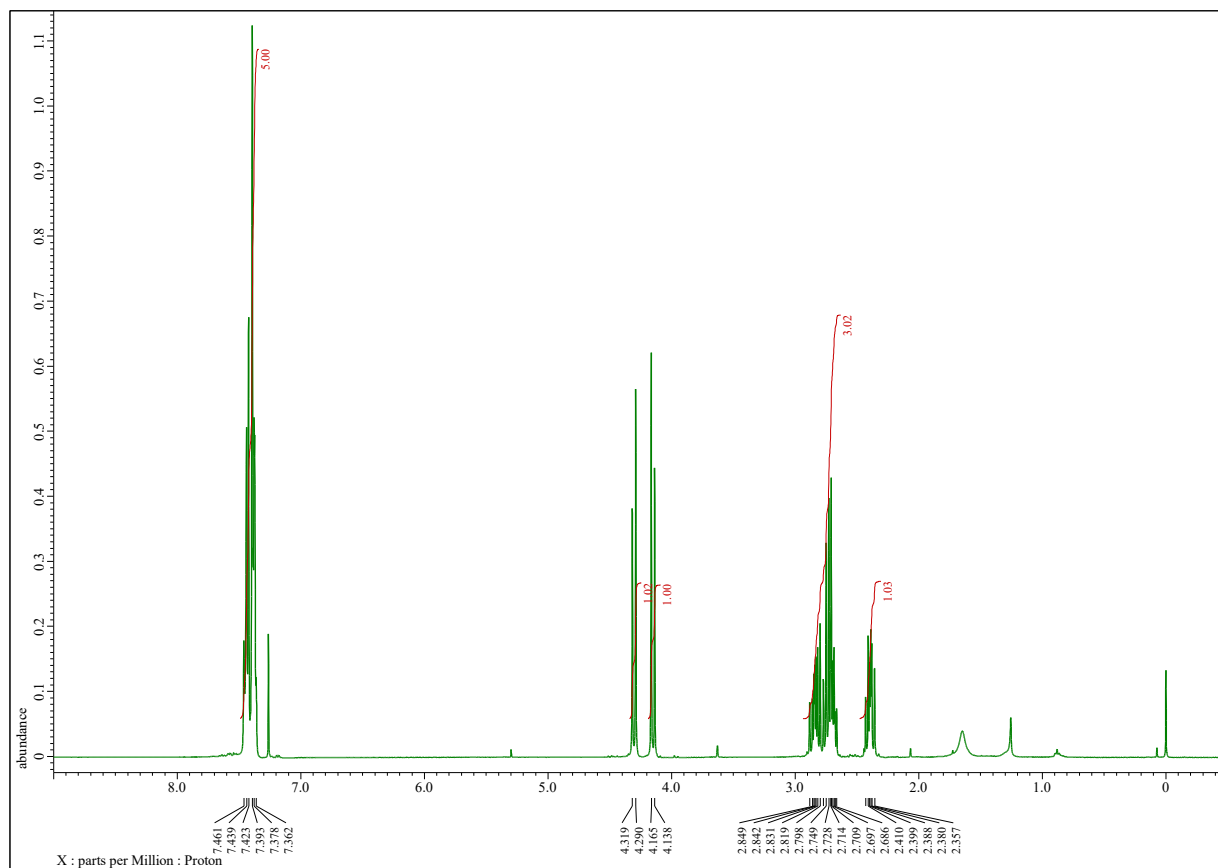
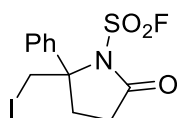
(4*R*,5*S*)-4-(*tert*-butyl)-5-phenylpyrrolidin-2-one (9)

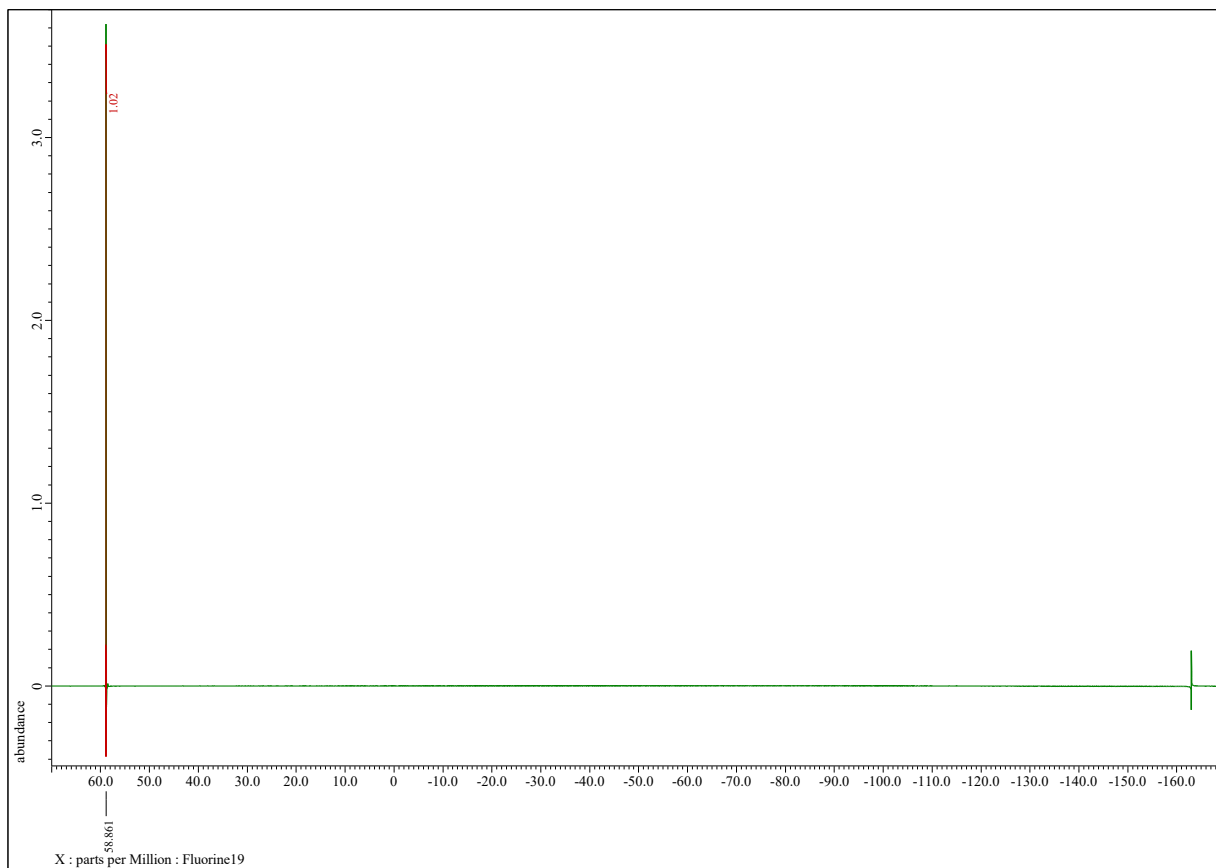


(2*S*,3*R*)-3-(*tert*-butyl)-2-phenylpyrrolidine (10)

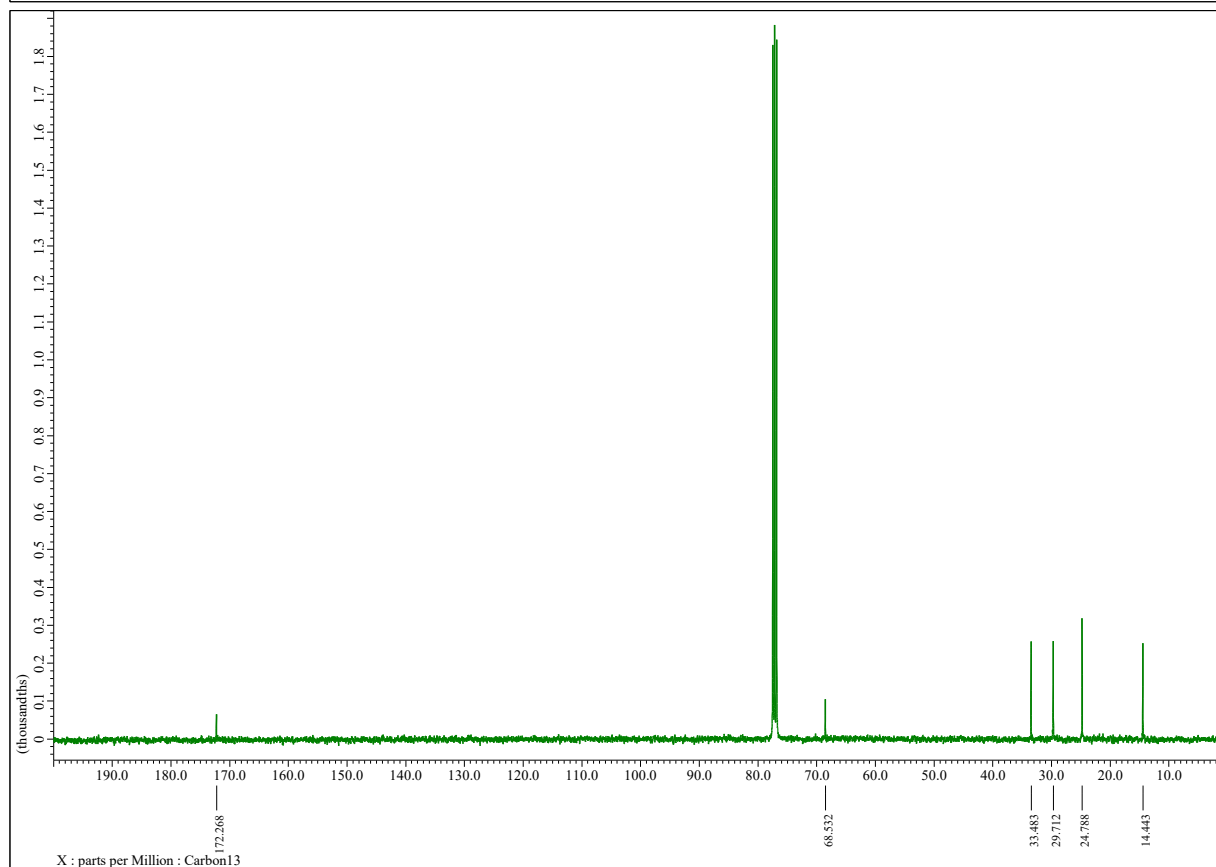
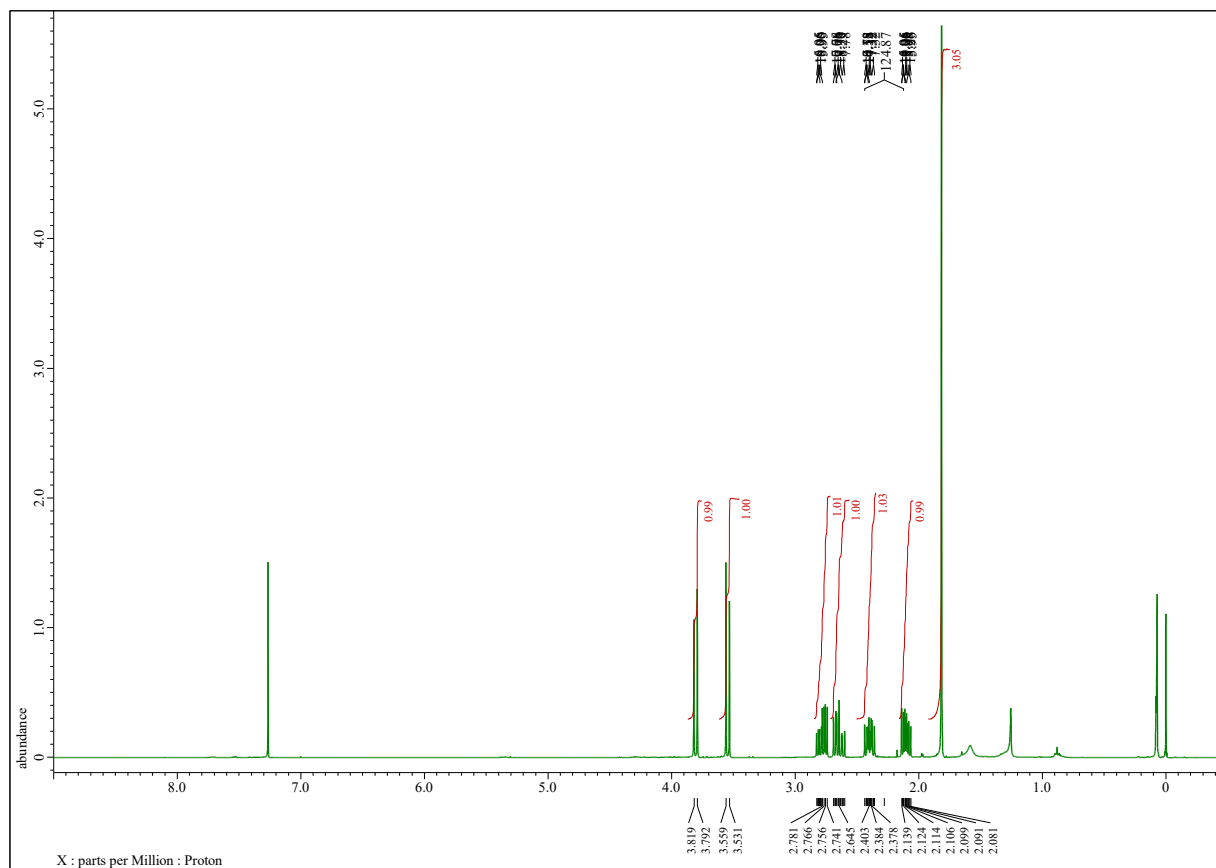
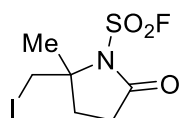


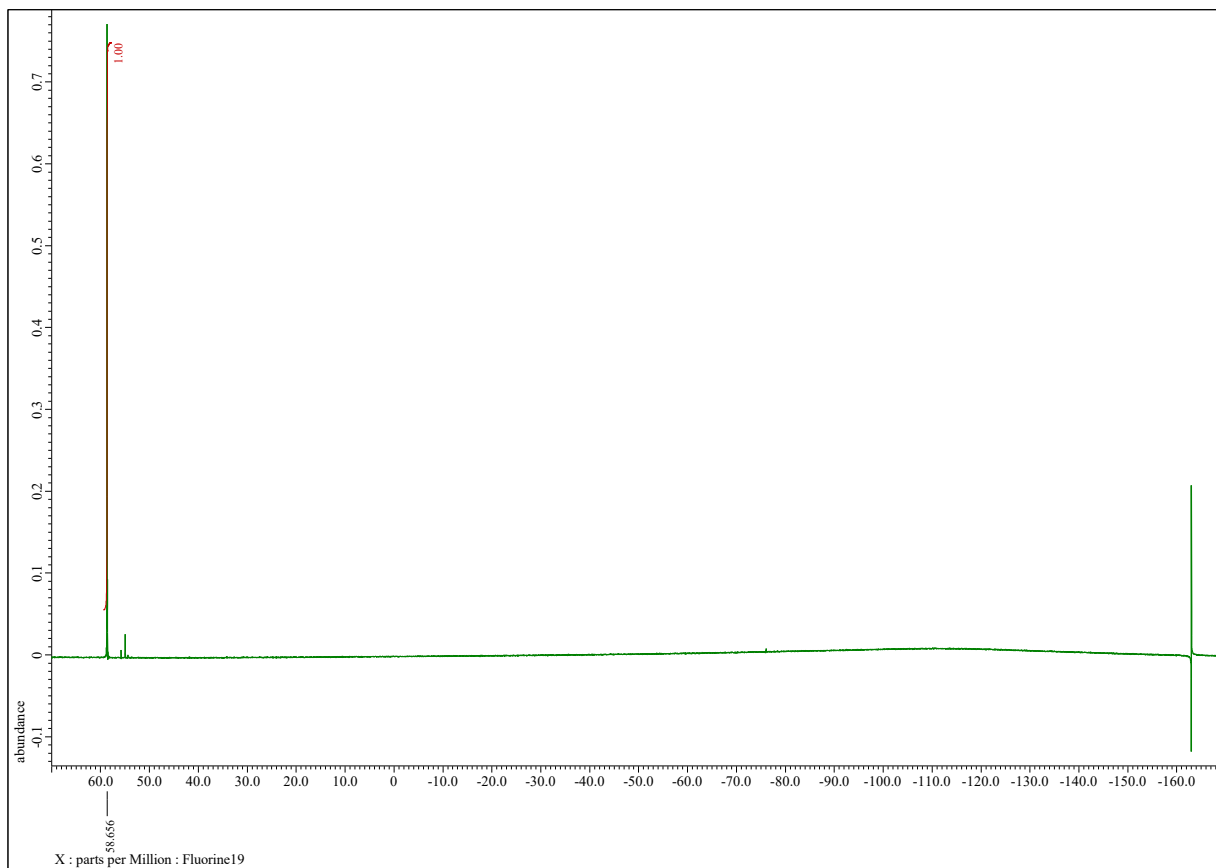
2-(iodomethyl)-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (19a)



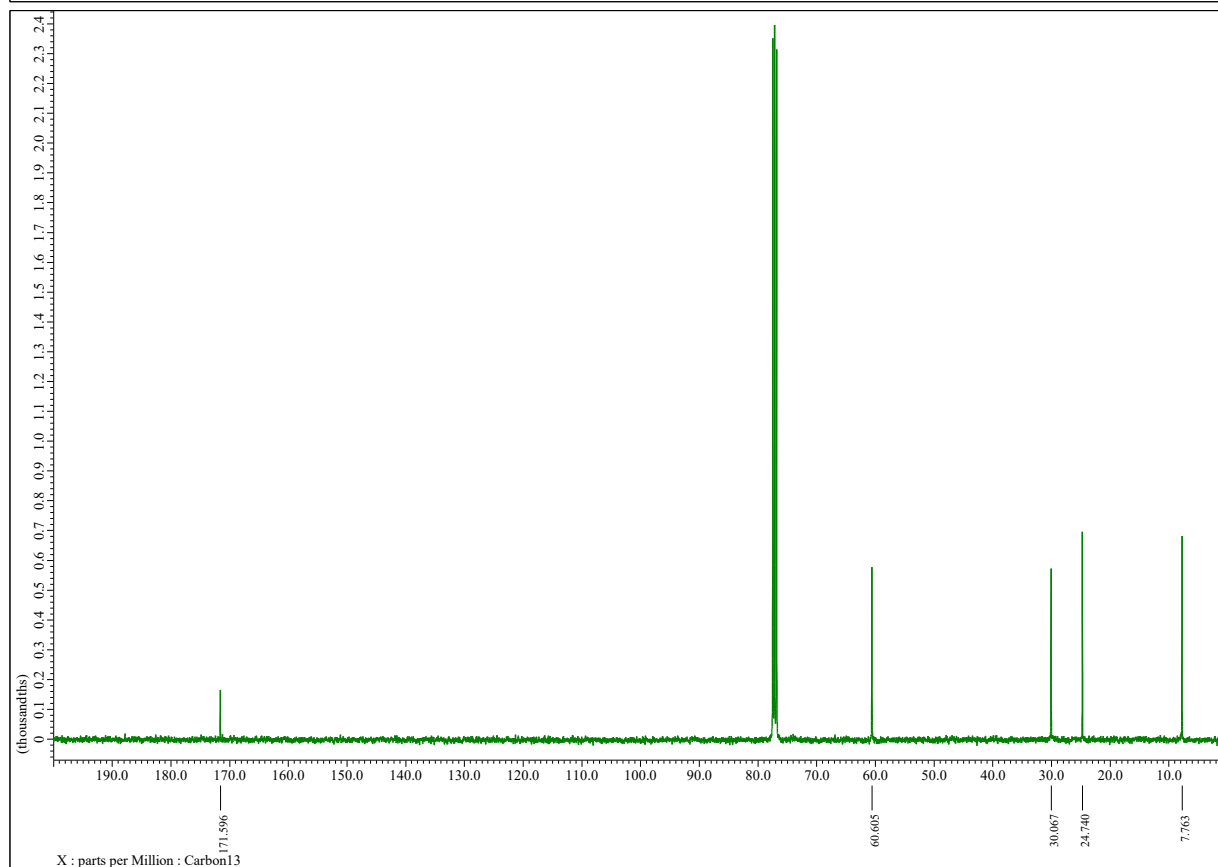
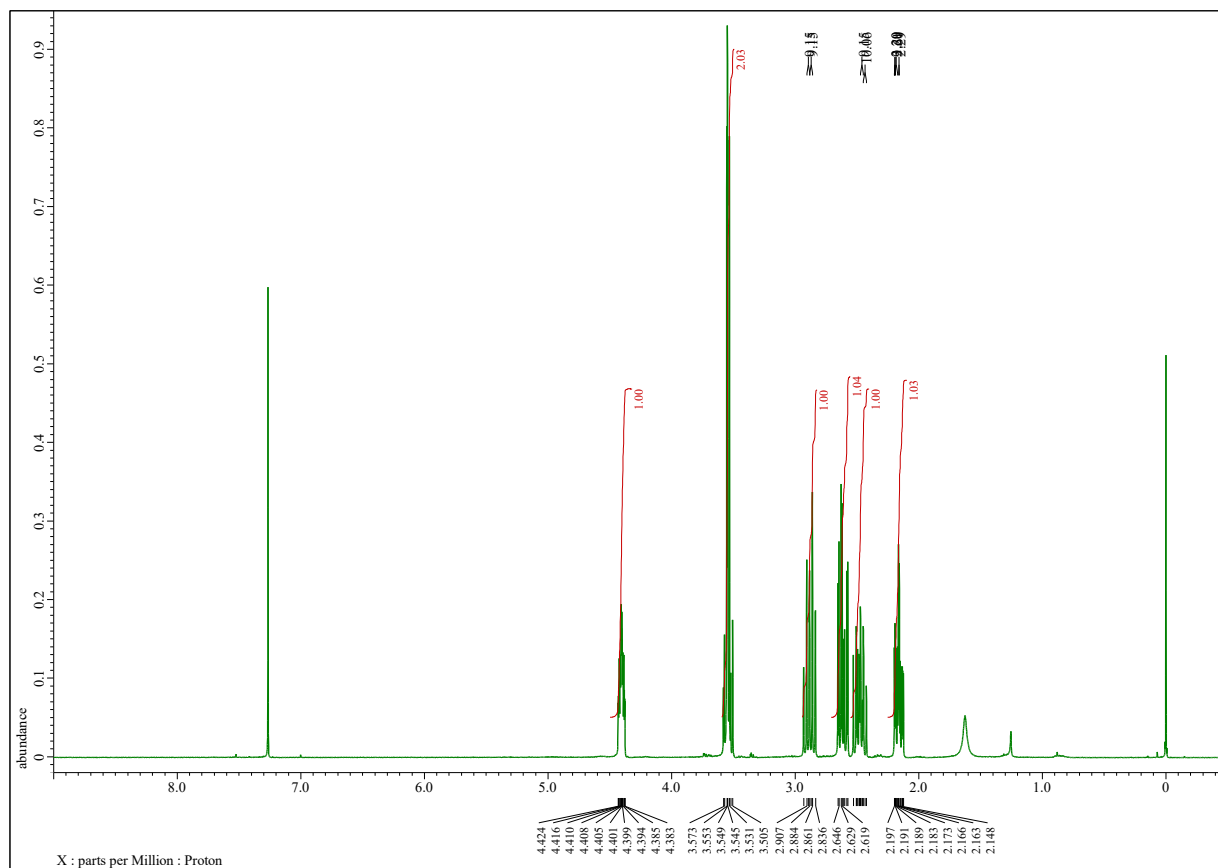
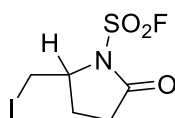


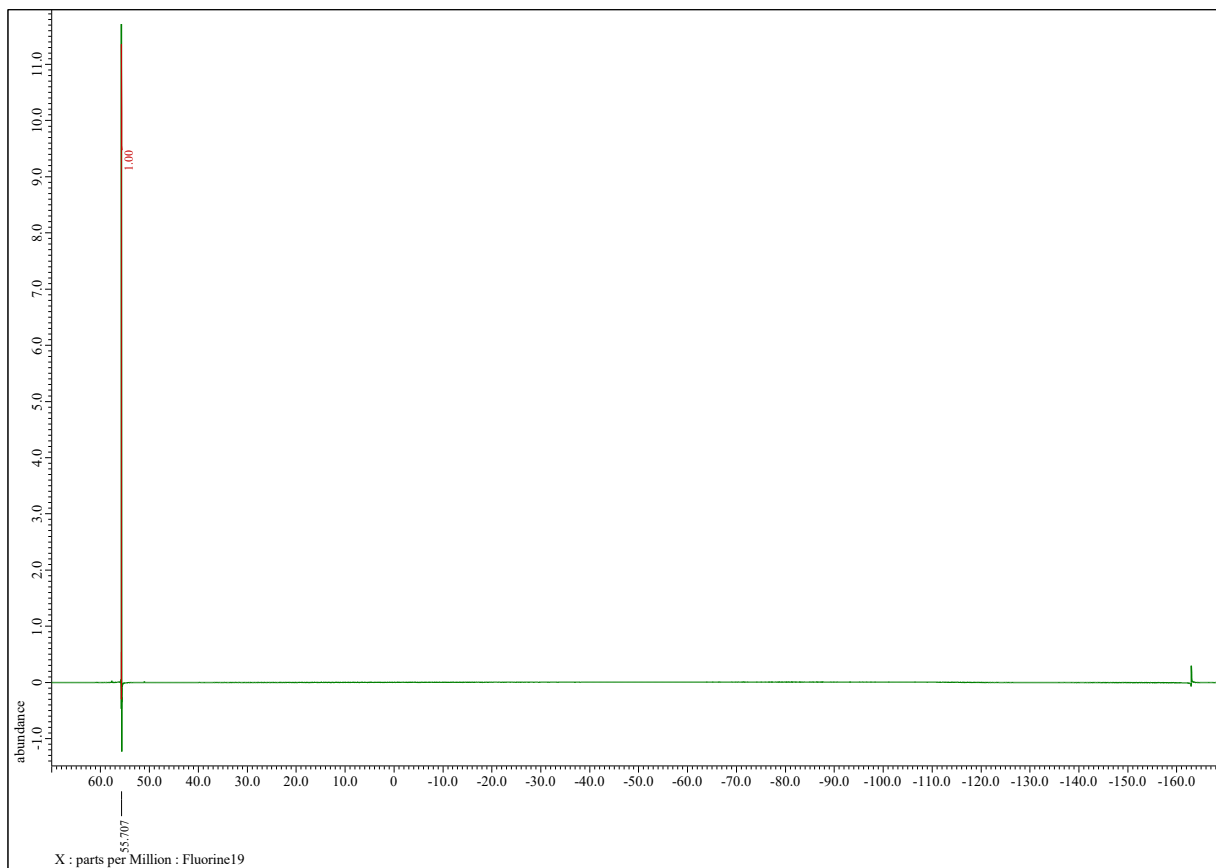
2-(iodomethyl)-2-methyl-5-oxopyrrolidine-1-sulfonyl fluoride (19b)



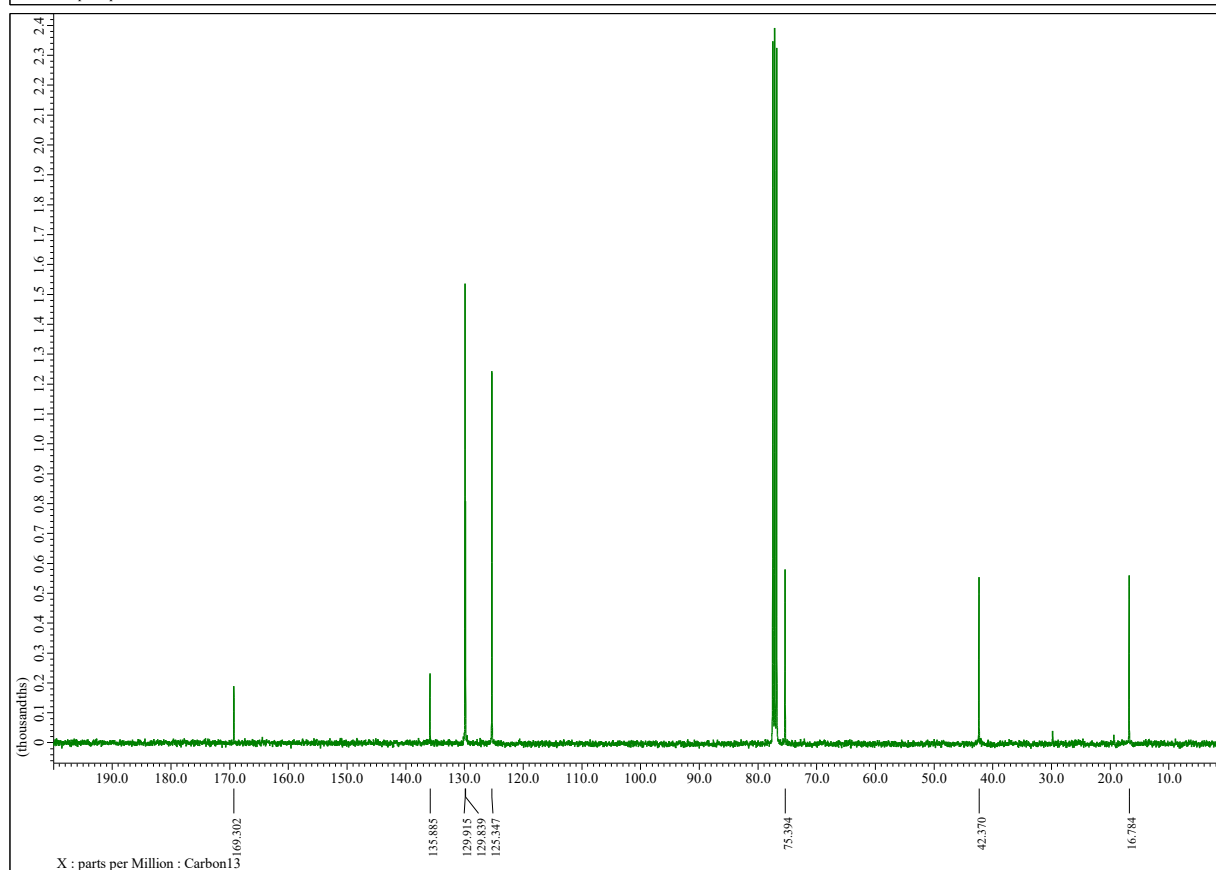
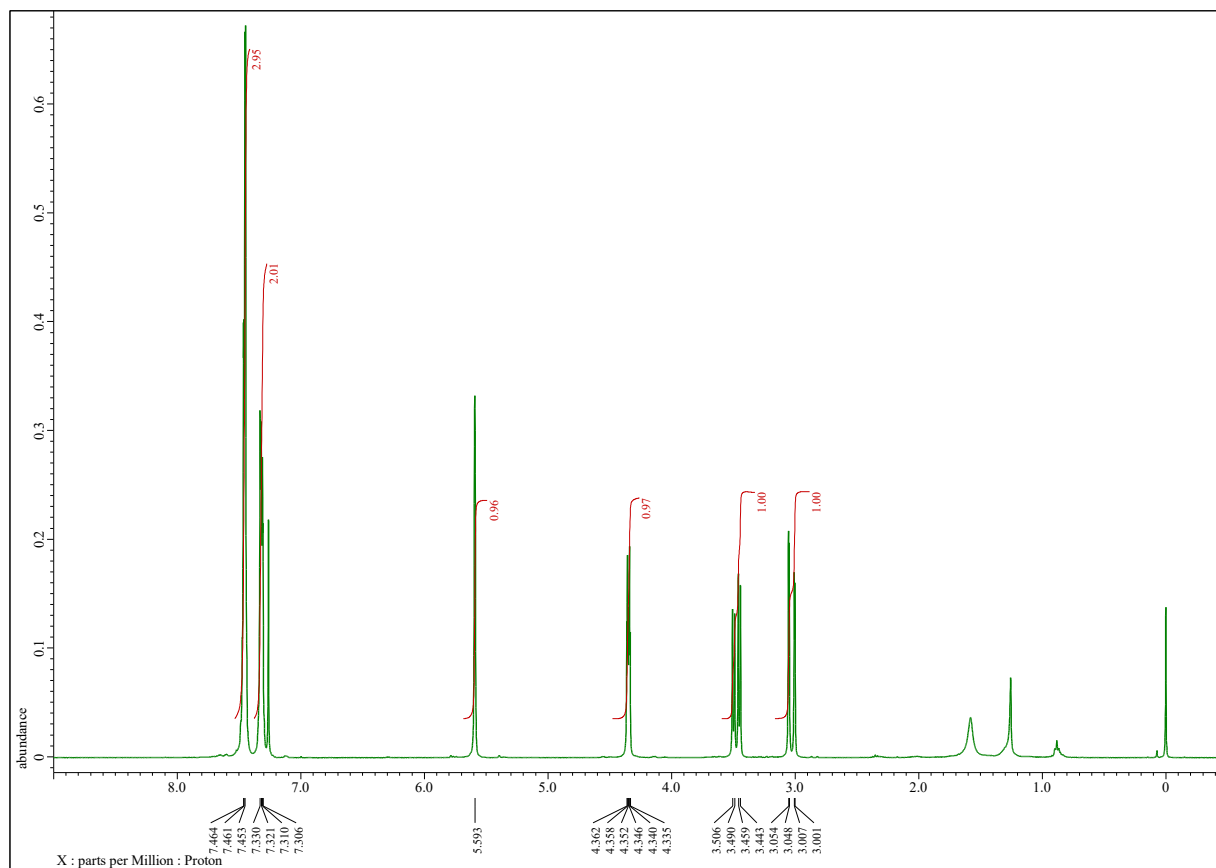
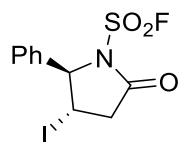


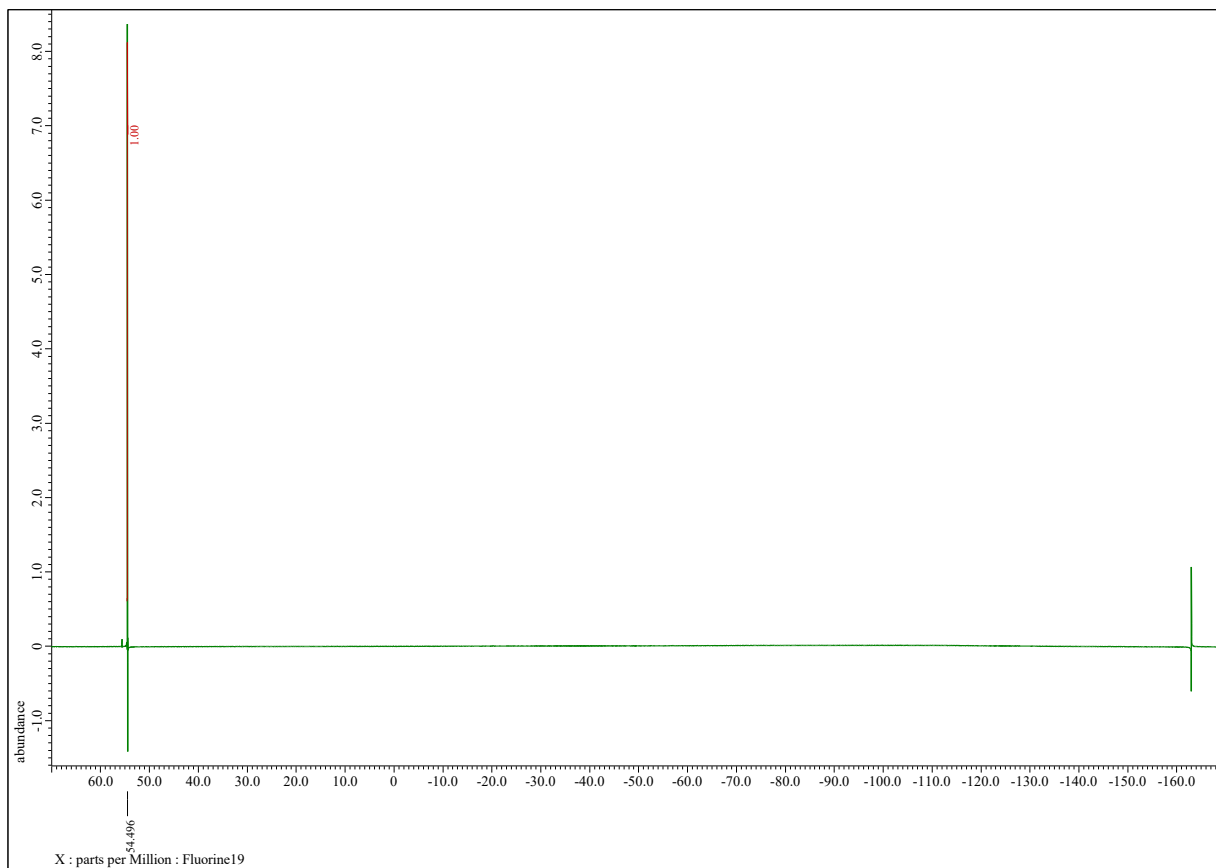
2-(iodomethyl)-5-oxopyrrolidine-1-sulfonyl fluoride (19c)



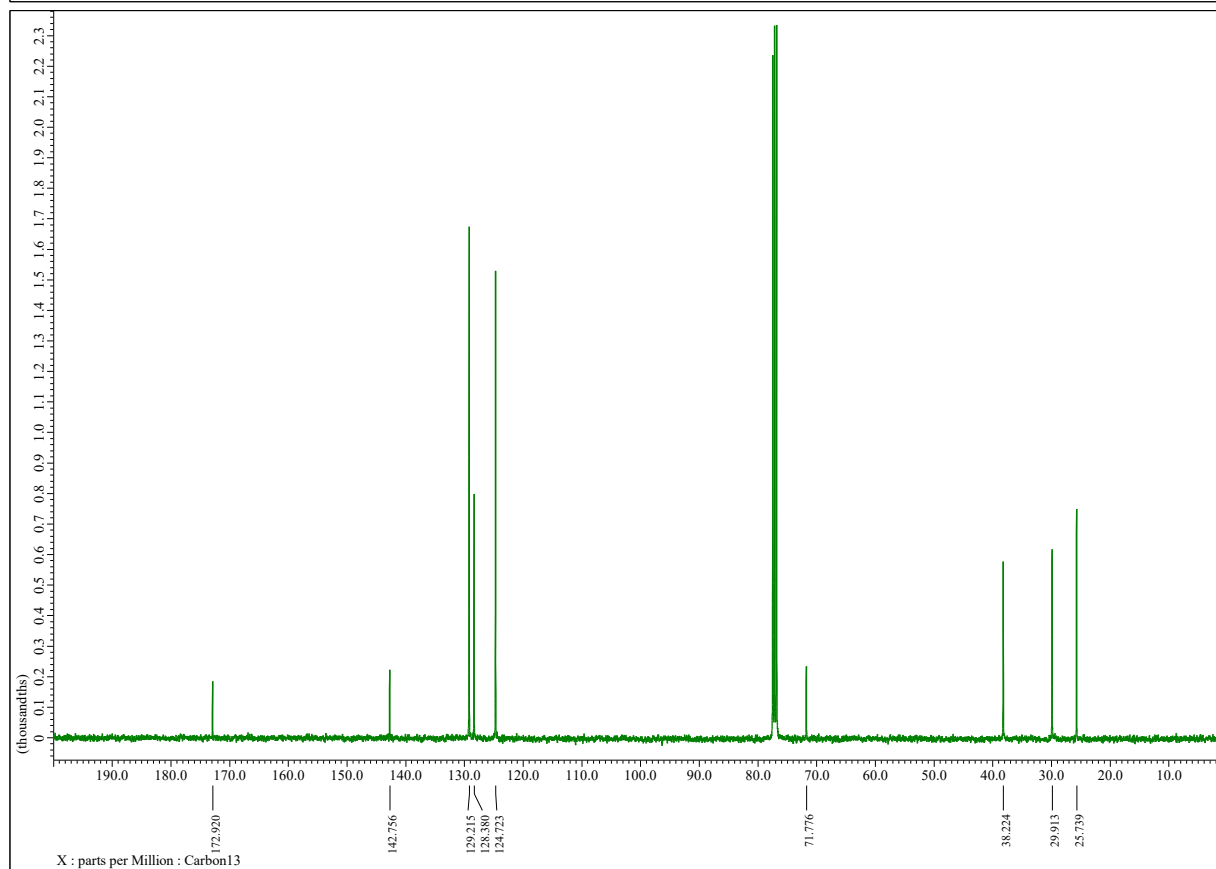
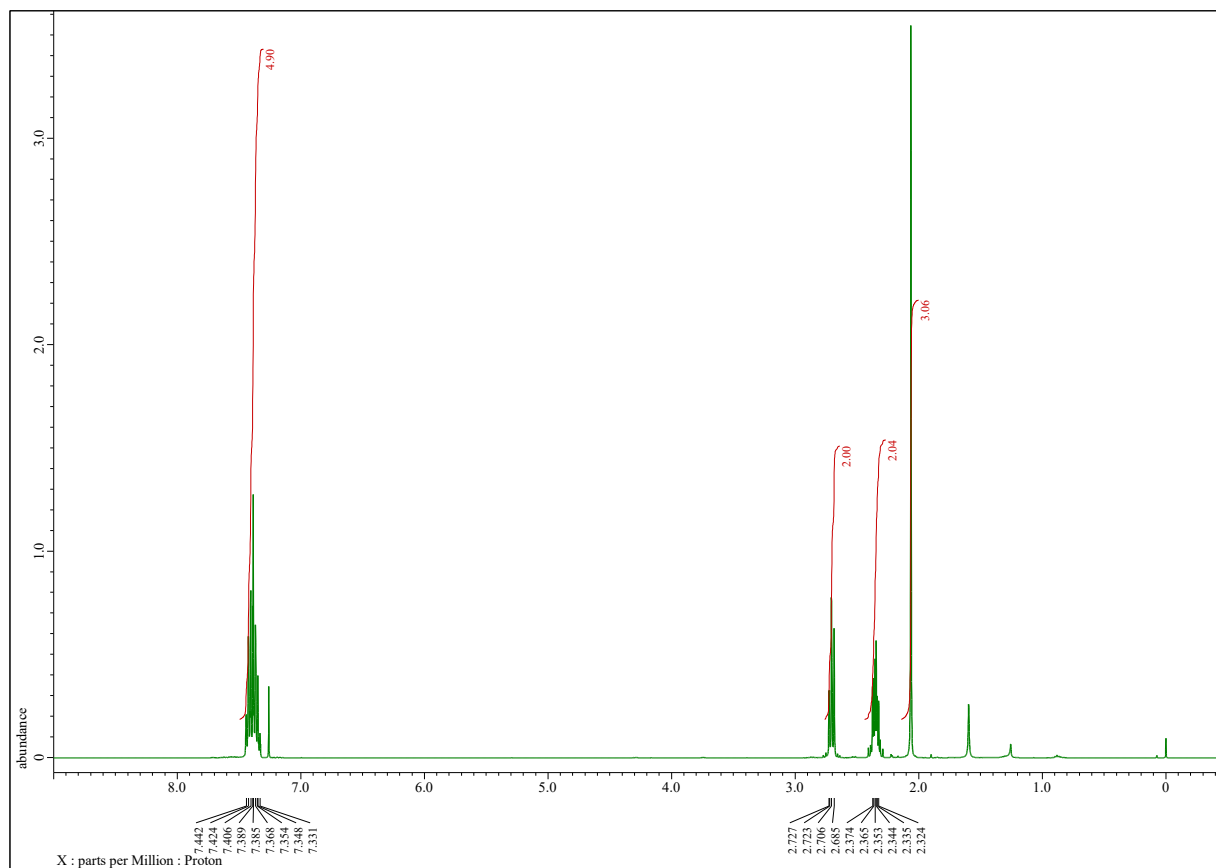
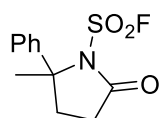


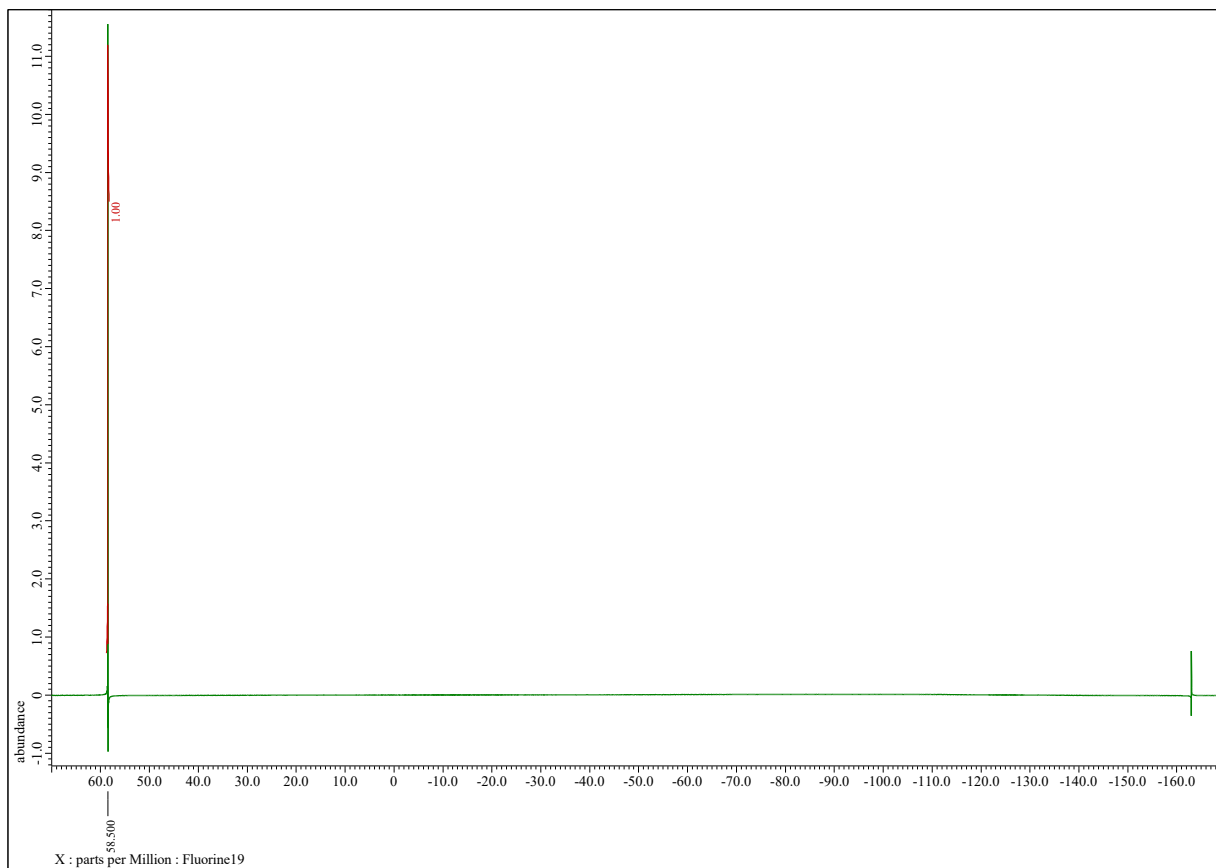
3-iodo-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (20)



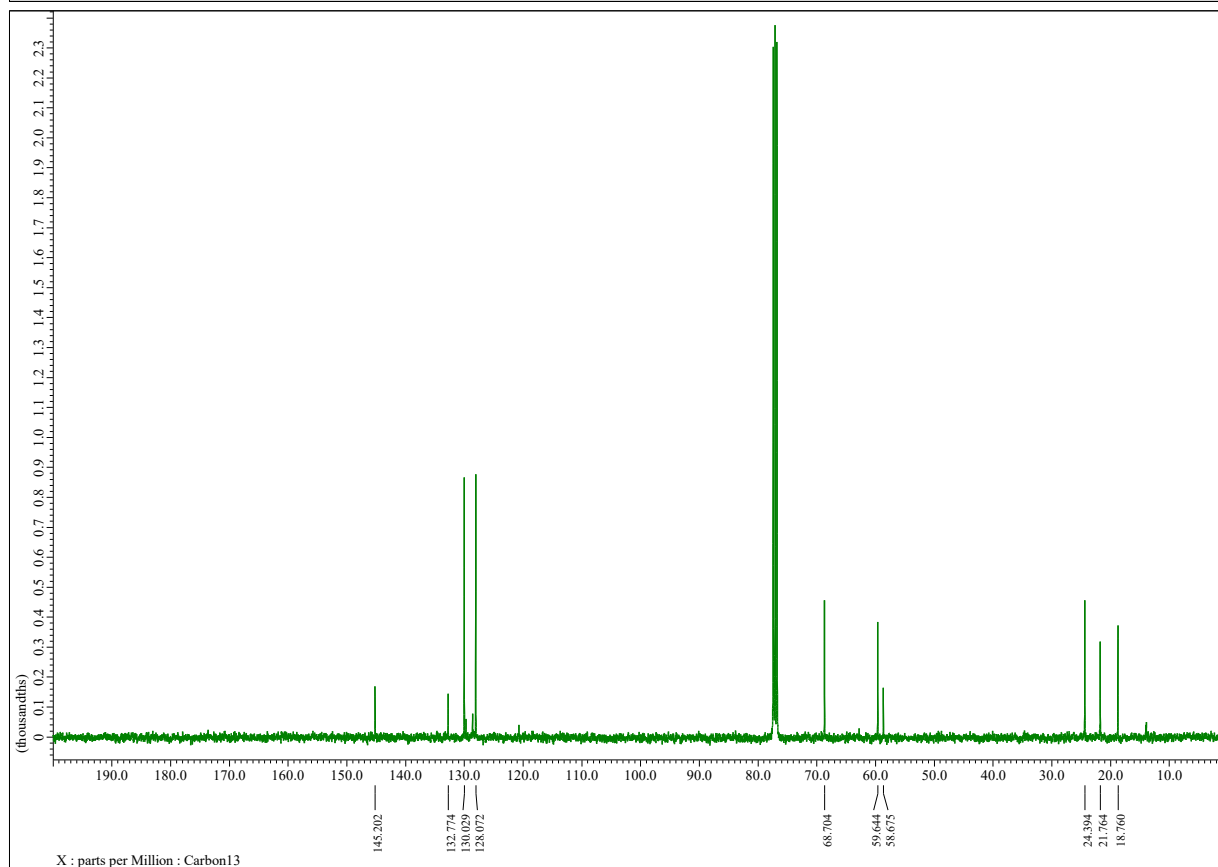
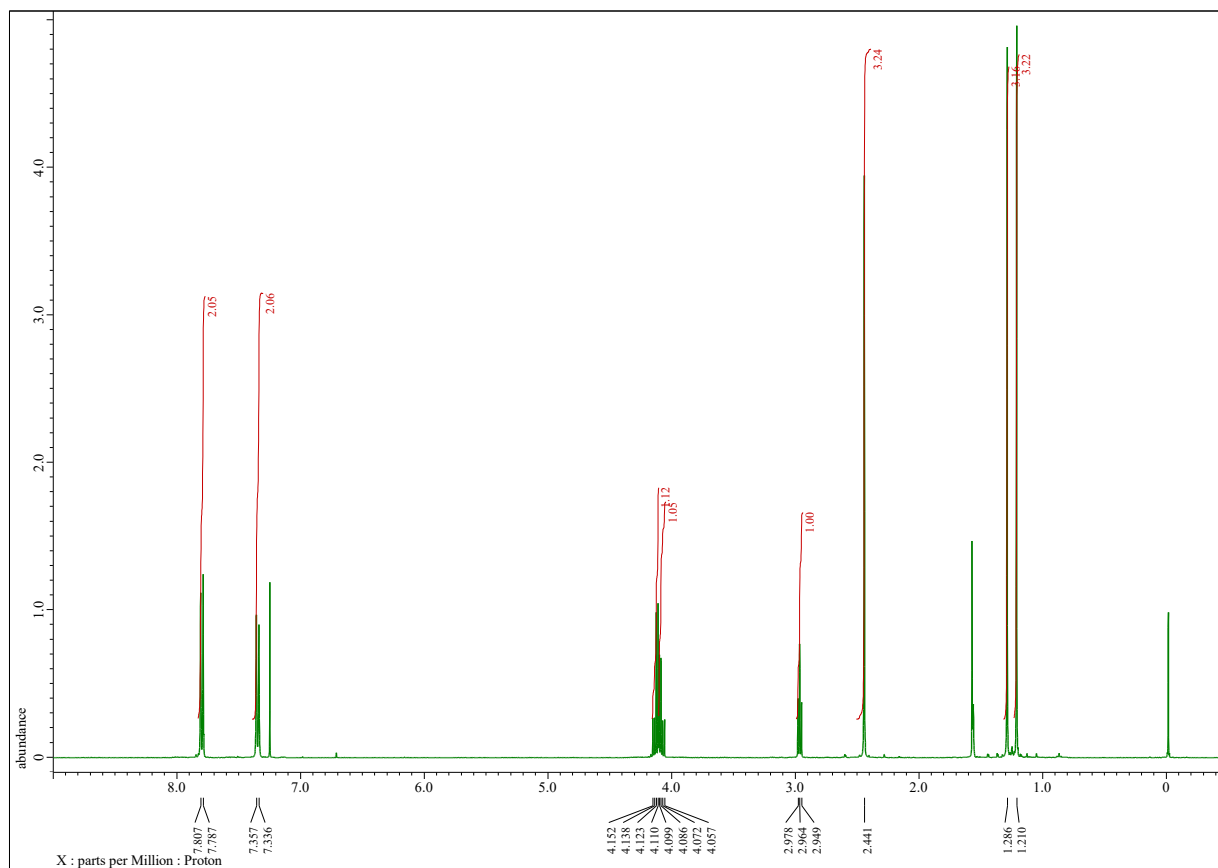
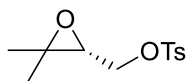


2-methyl-5-oxo-2-phenylpyrrolidine-1-sulfonyl fluoride (21)

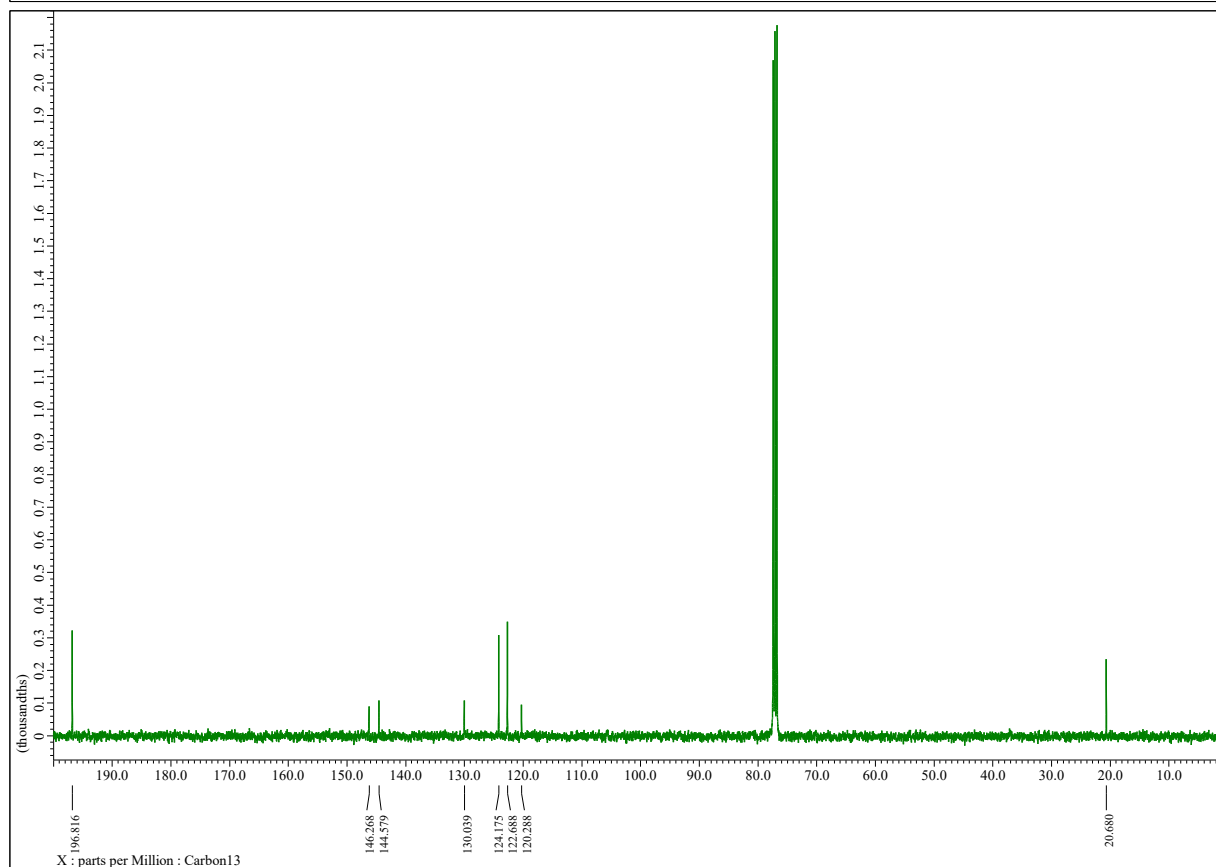
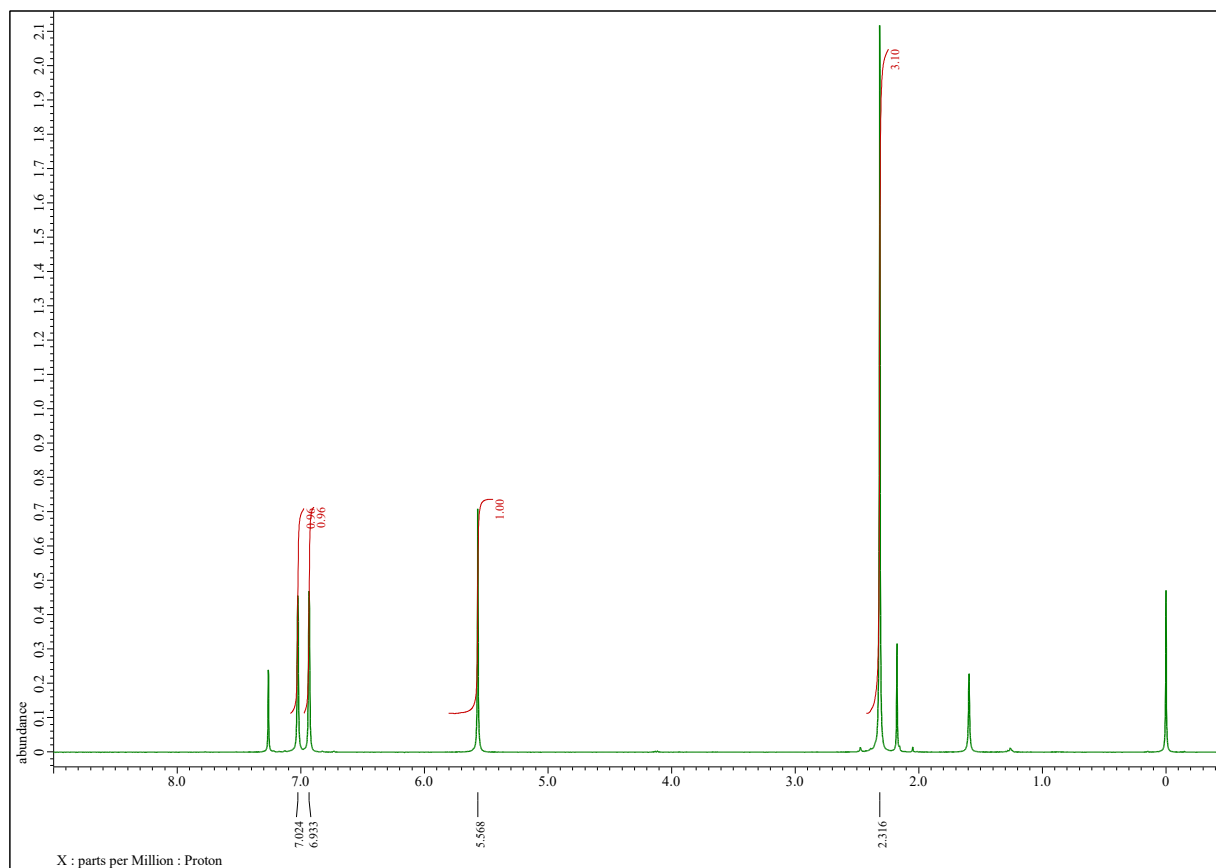
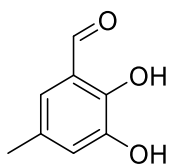




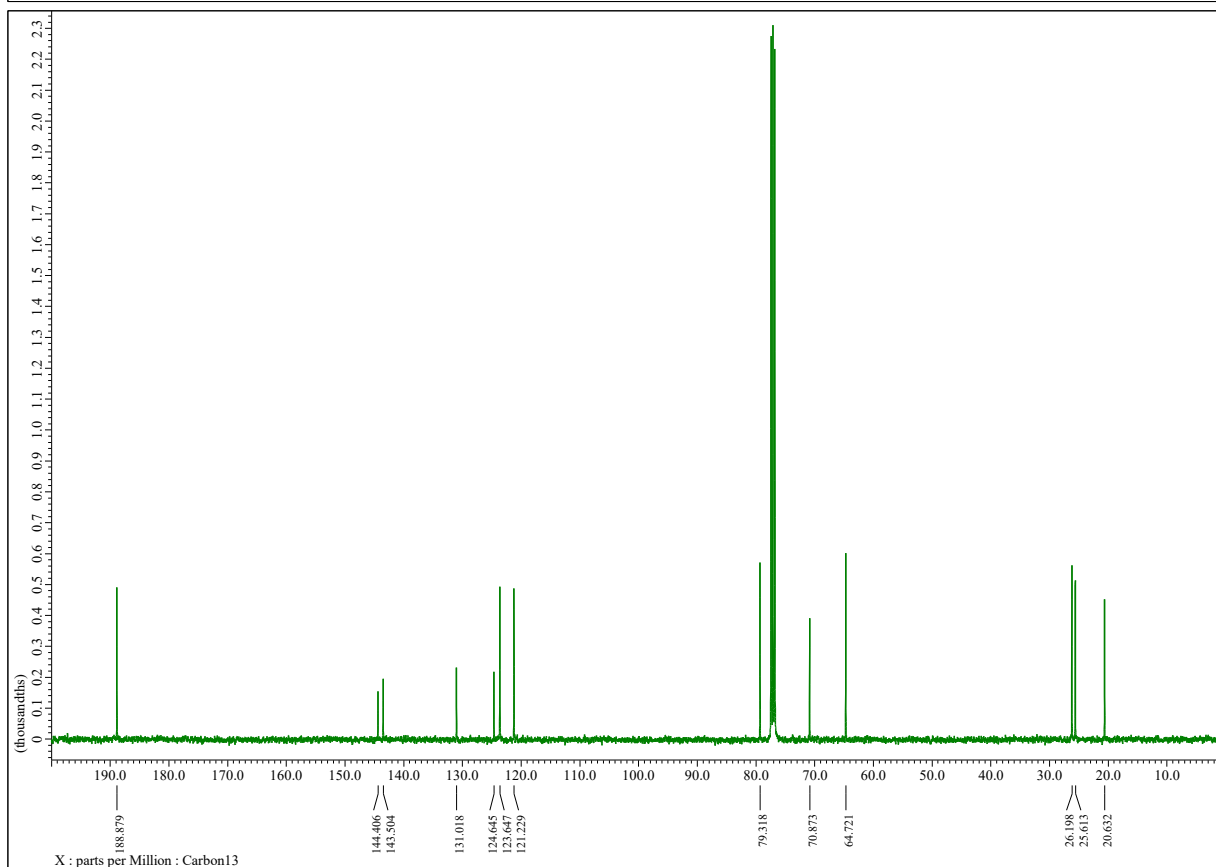
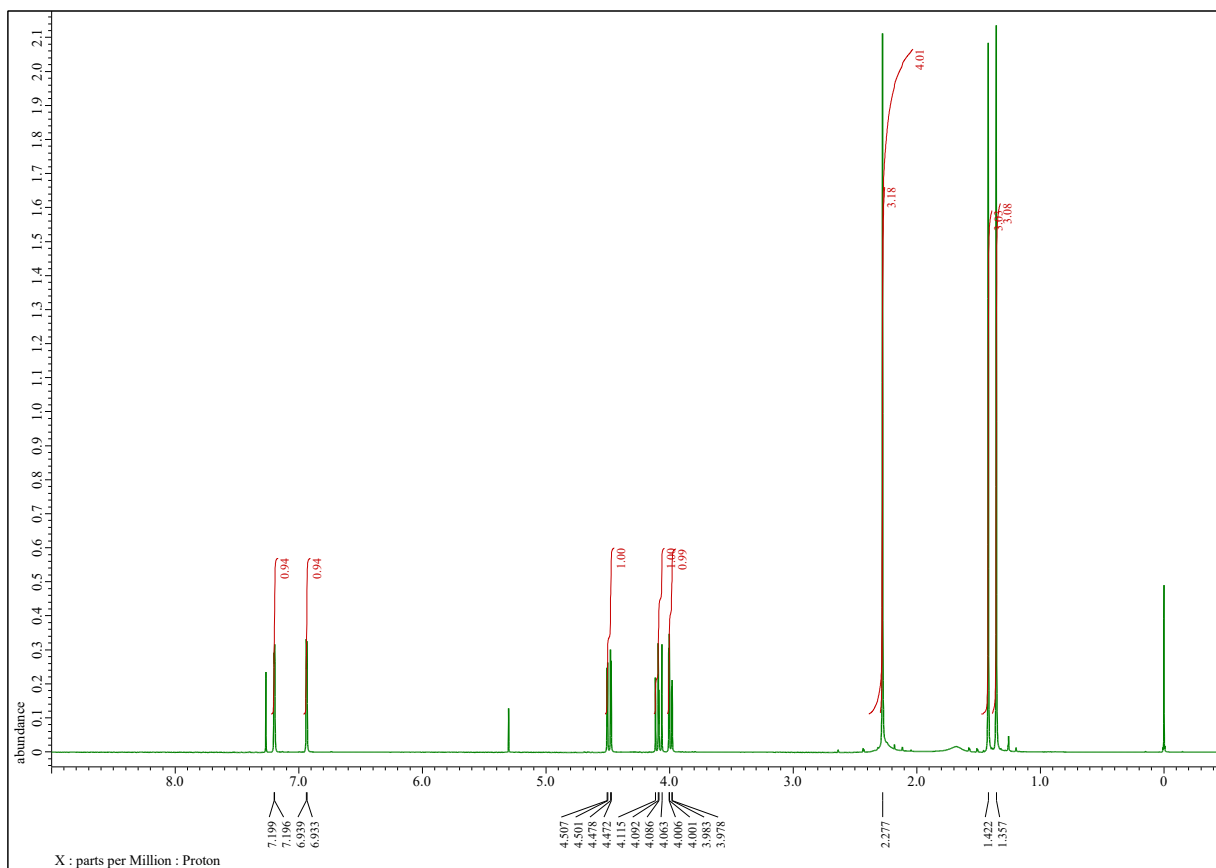
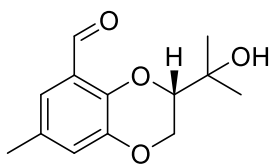
(R)-(3,3-dimethyloxiran-2-yl)methyl 4-methylbenzenesulfonate (S5)



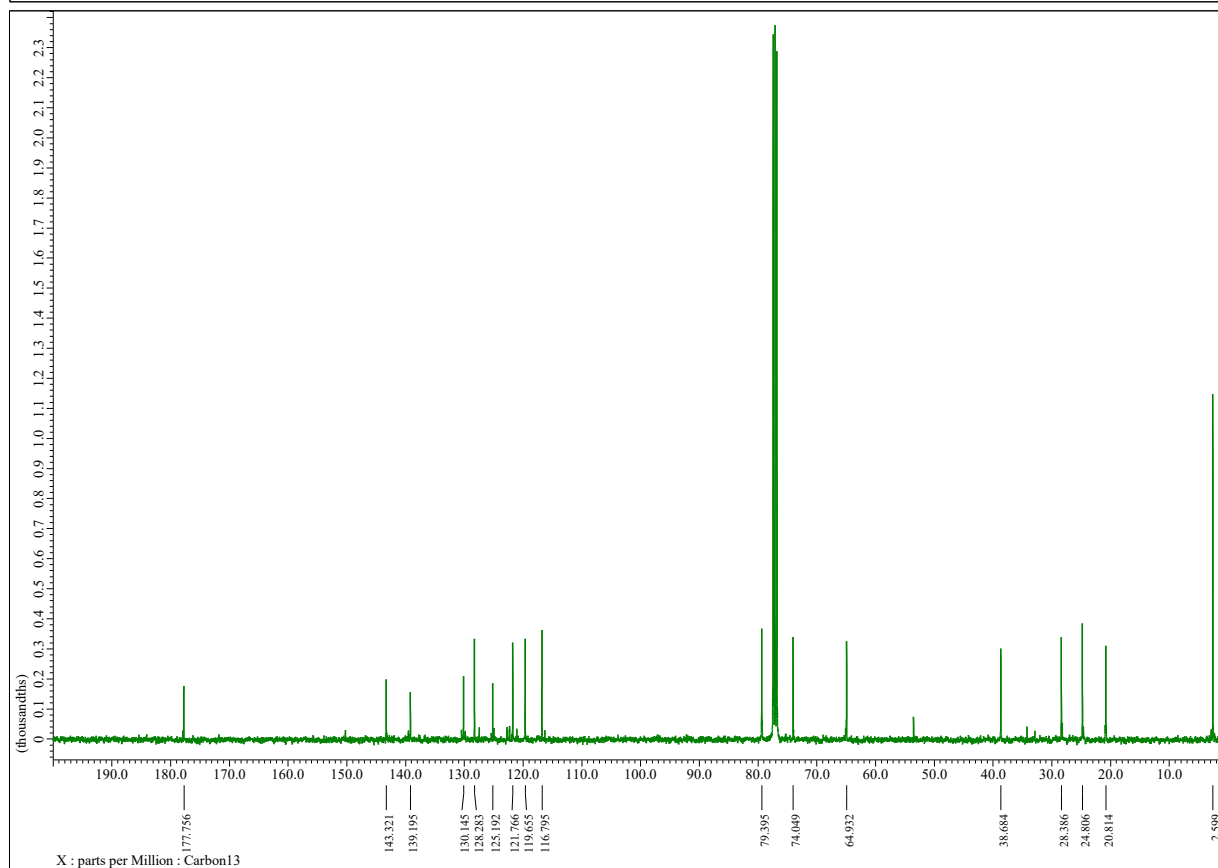
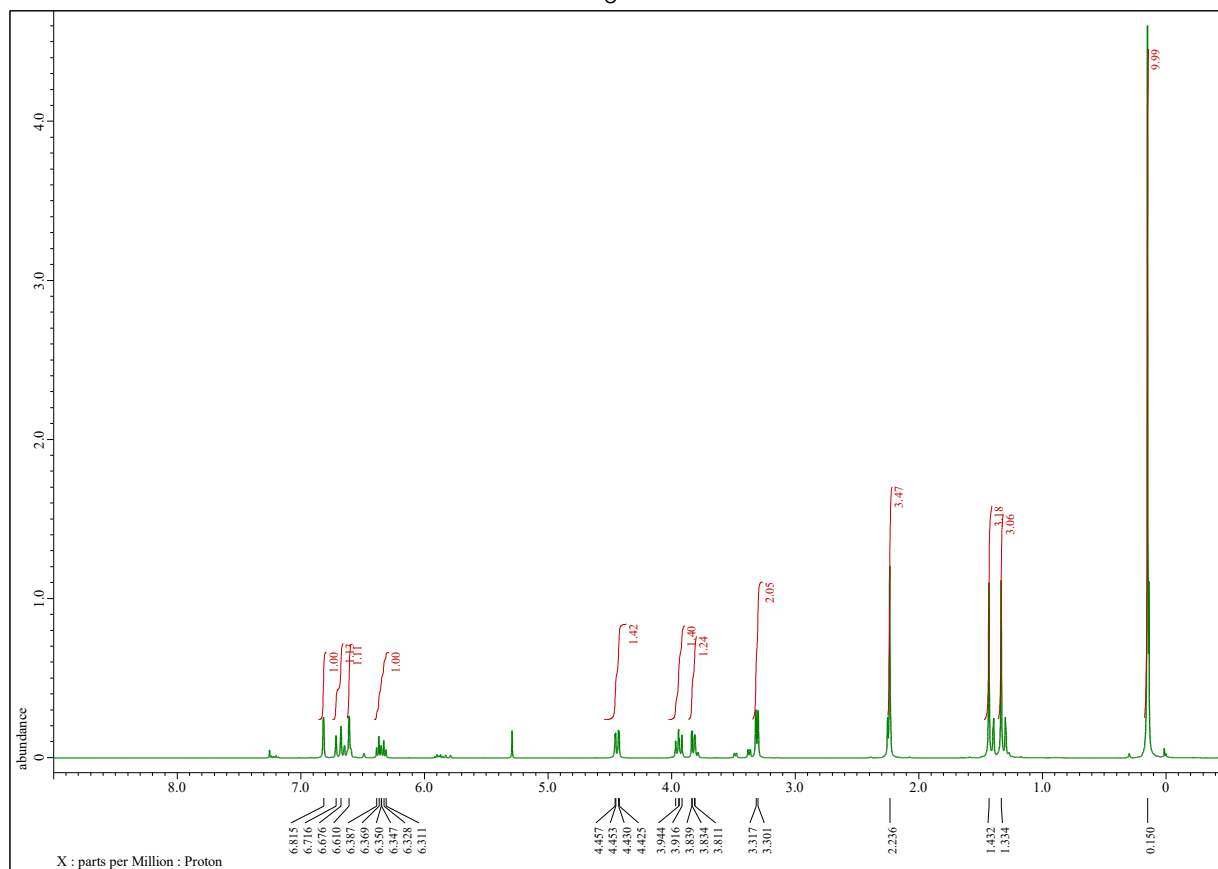
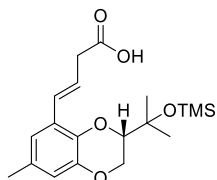
2,3-dihydroxy-5-methylbenzaldehyde (S7)



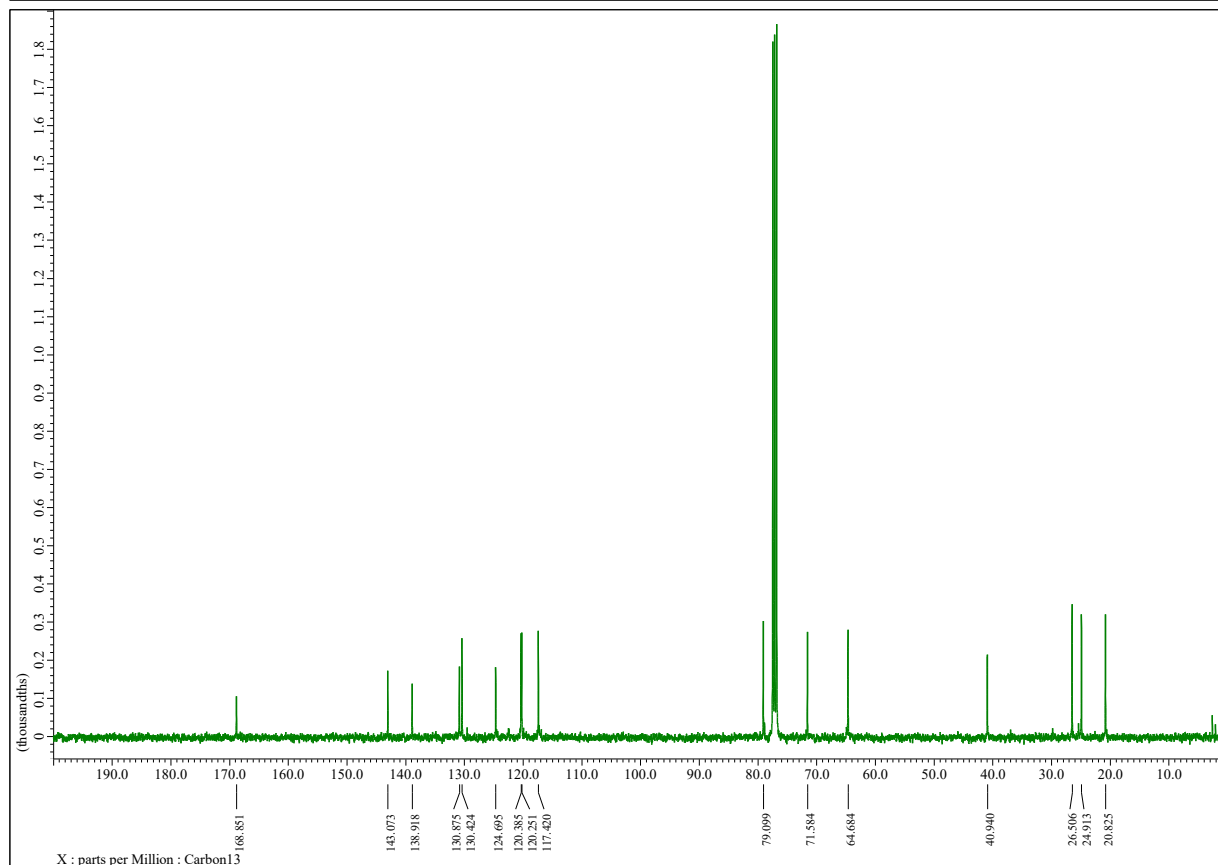
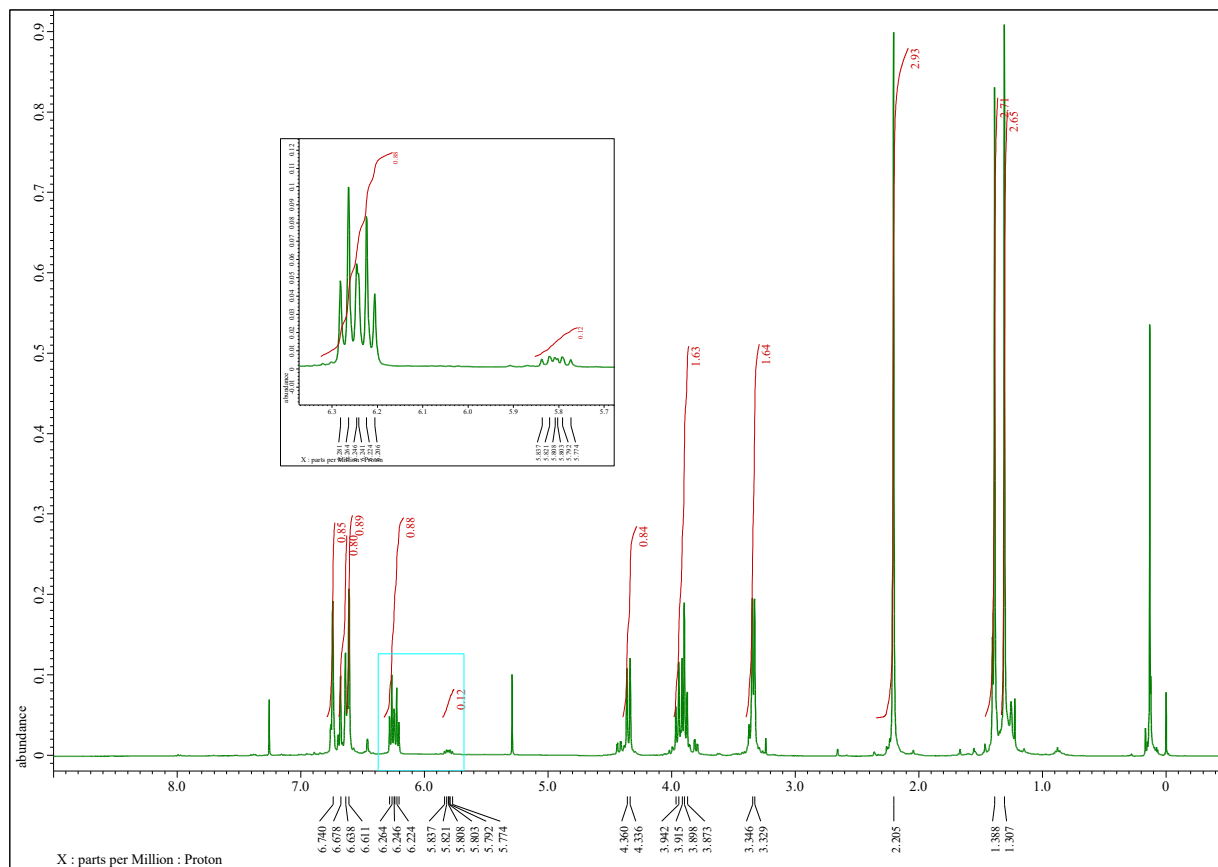
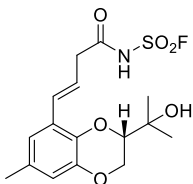
3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[b][1,4]dioxine-5-carbaldehyde (S8)

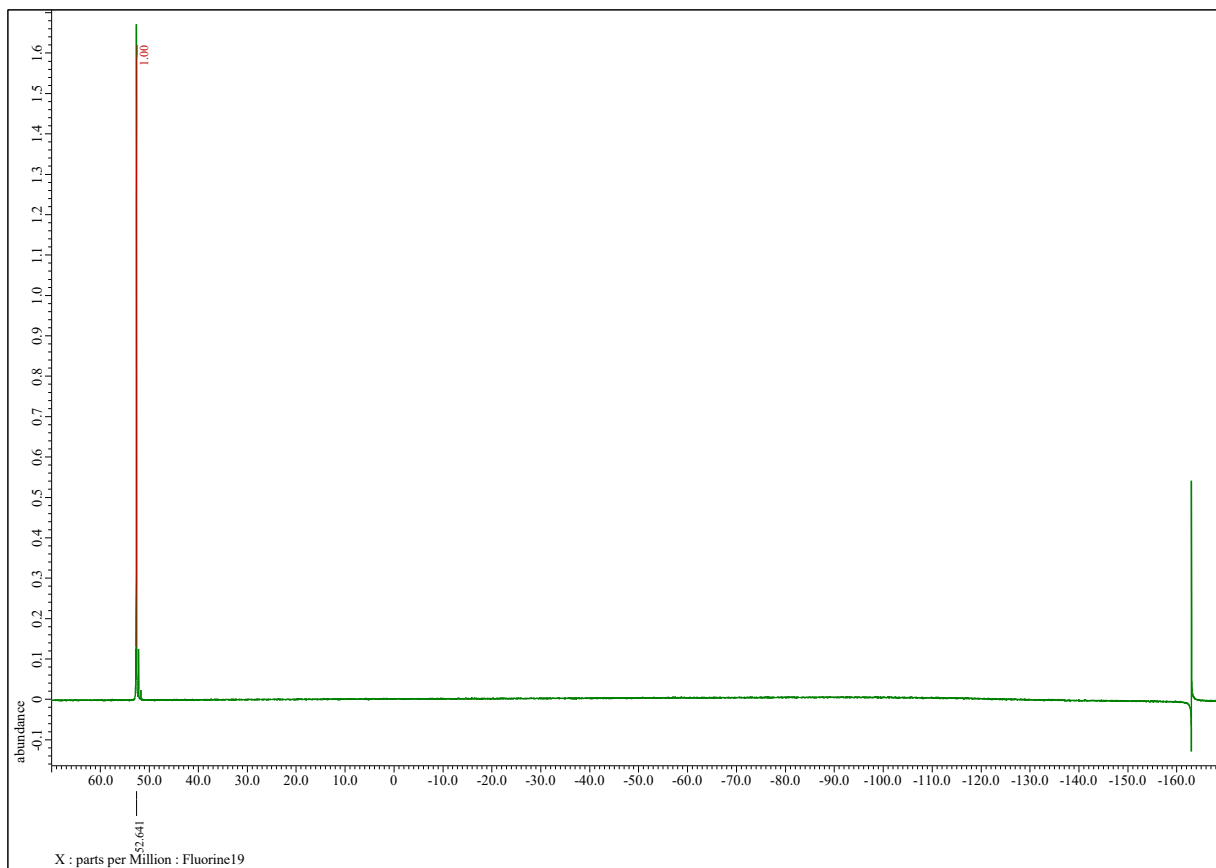


(*S,E*)-4-(7-methyl-3-(2-((trimethylsilyl)oxy)propan-2-yl)-2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)but-3-enoic acid (*S10*)

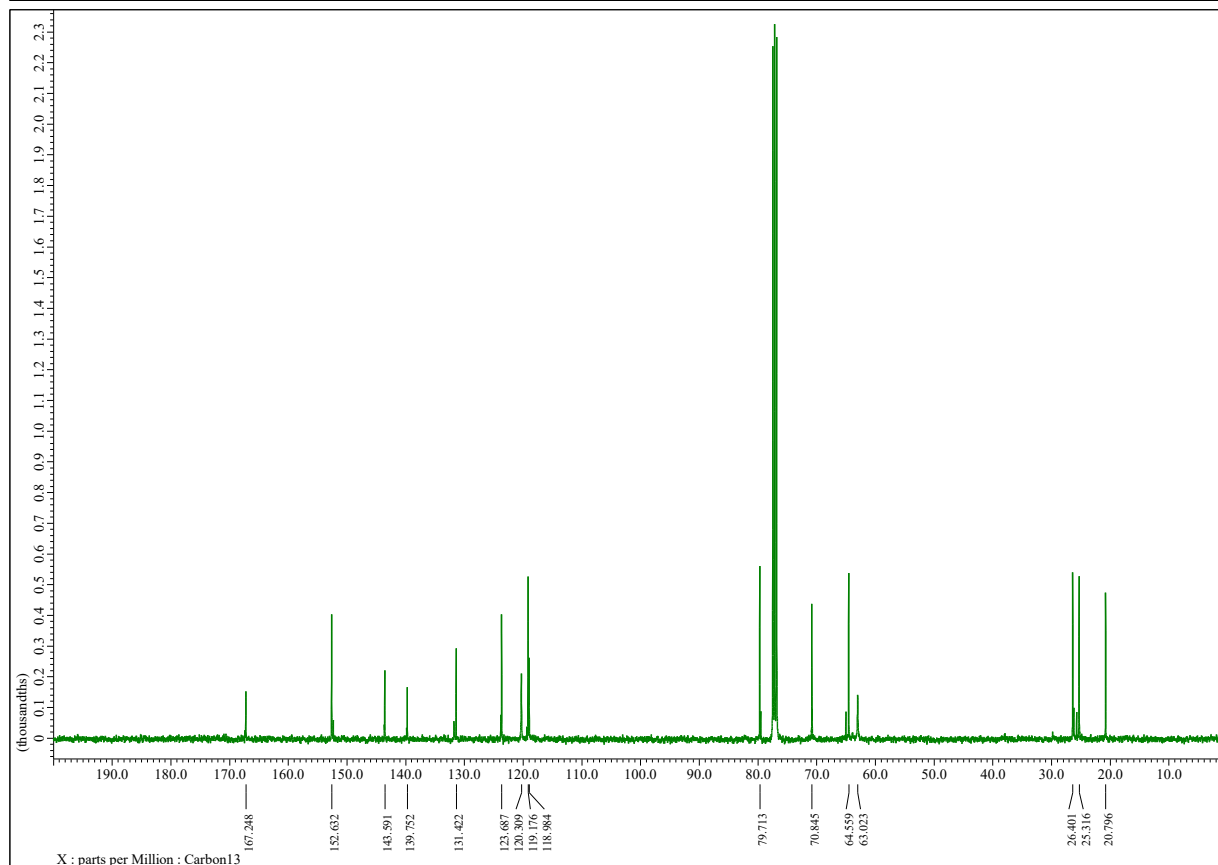
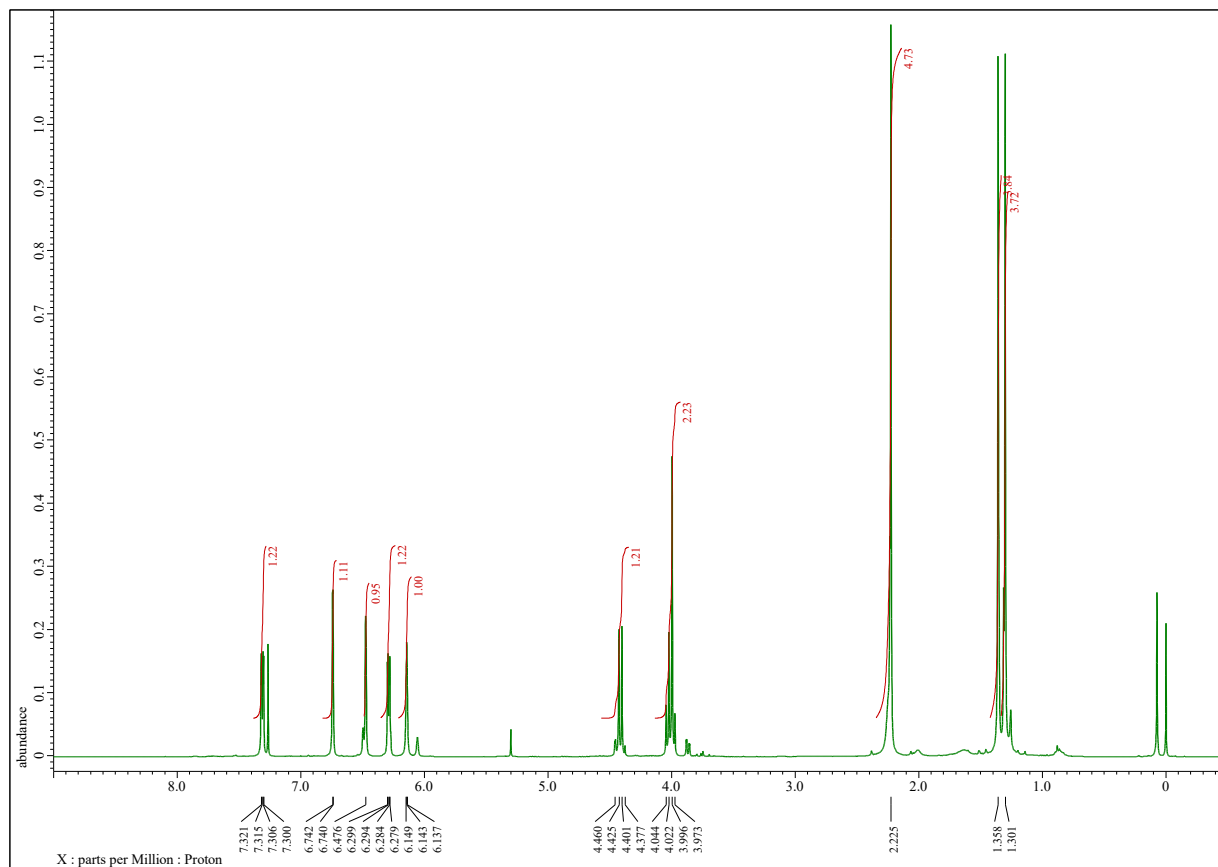
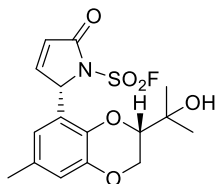


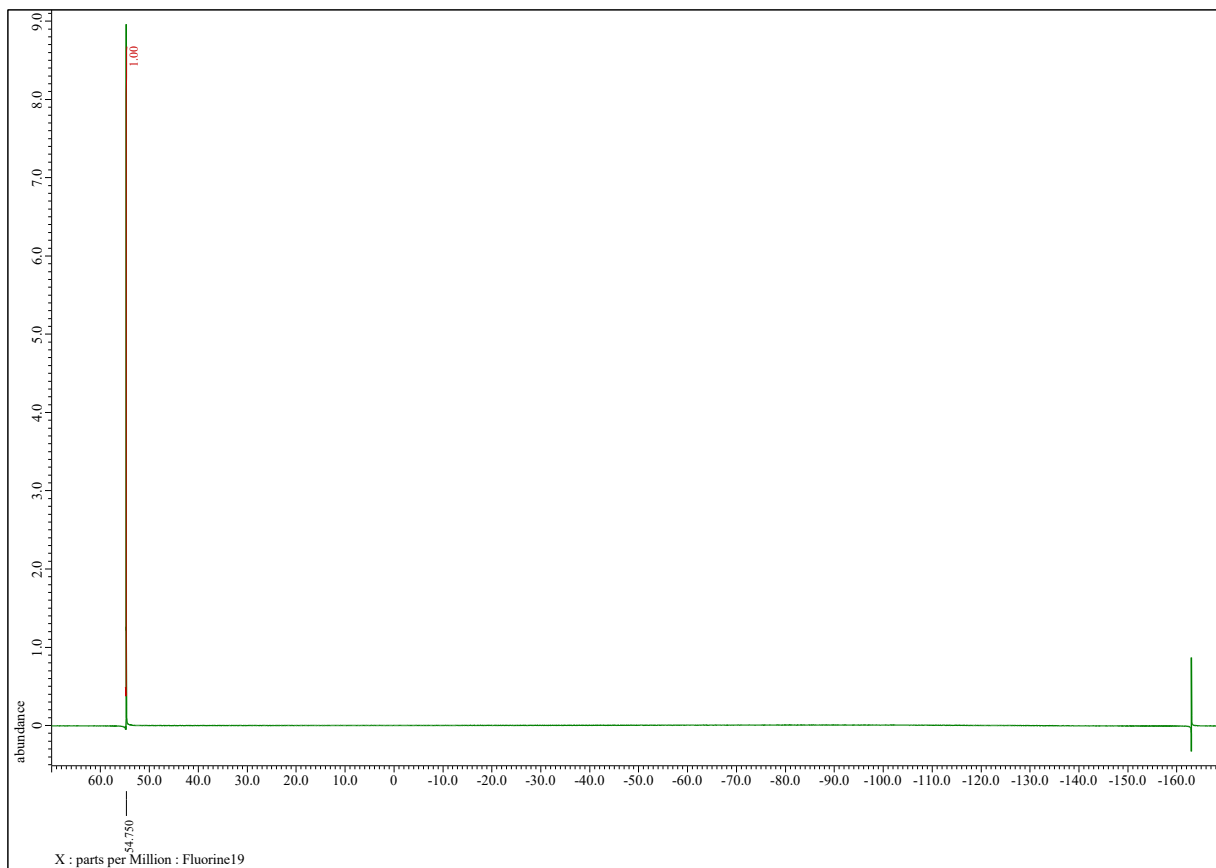
(*S,E*)-(4-(3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)but-3-enoyl)sulfamoyl fluoride (11)



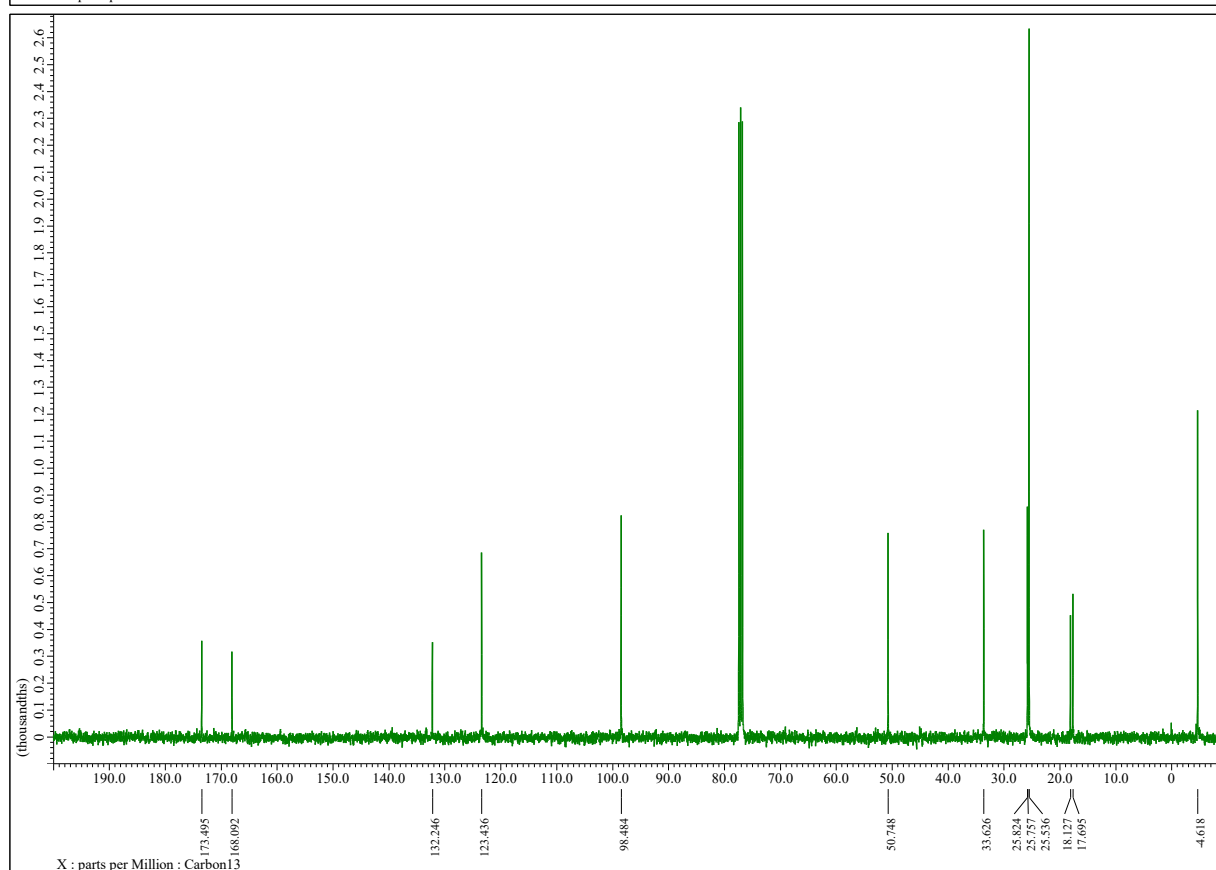
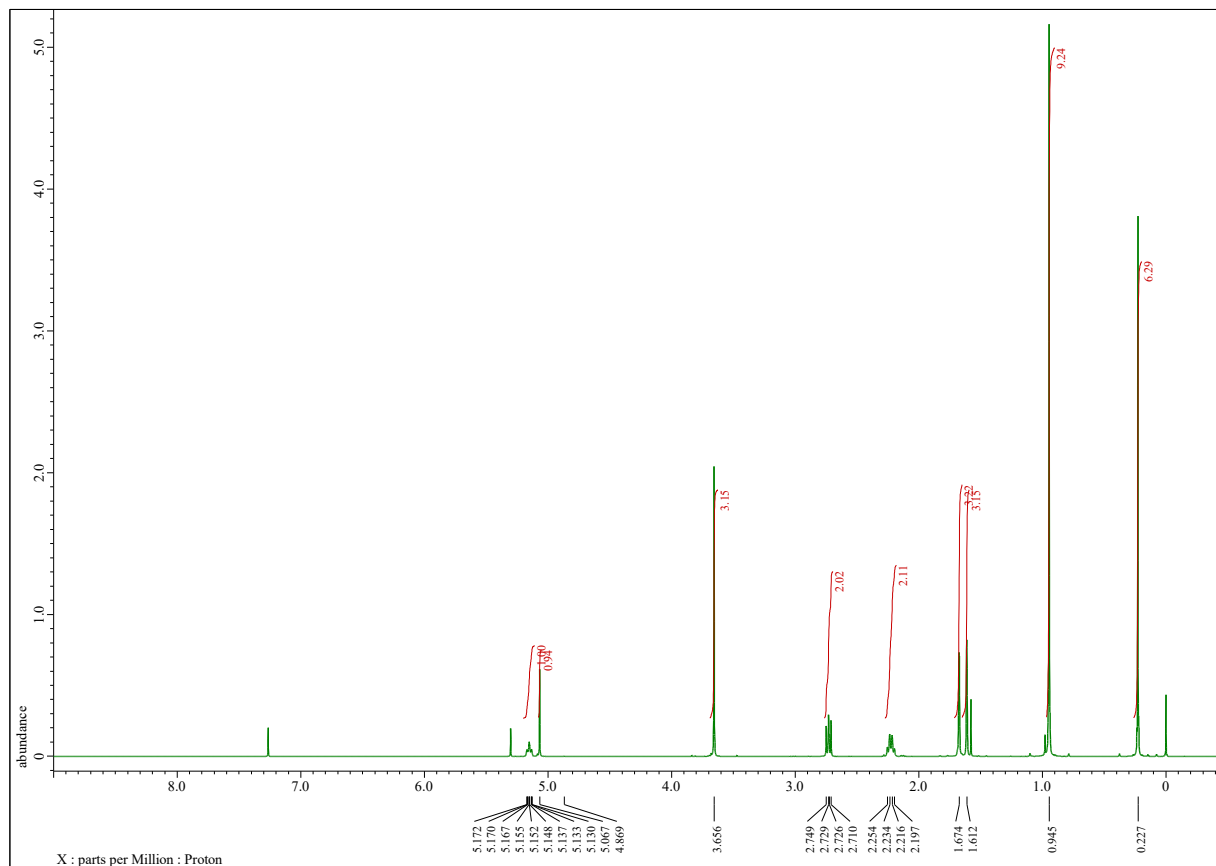
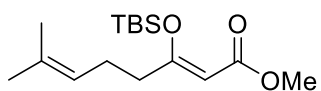


(S)-2-((S)-3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-5-oxo-2,5-dihydro-1H-pyrrole-1-sulfonyl fluoride (12)

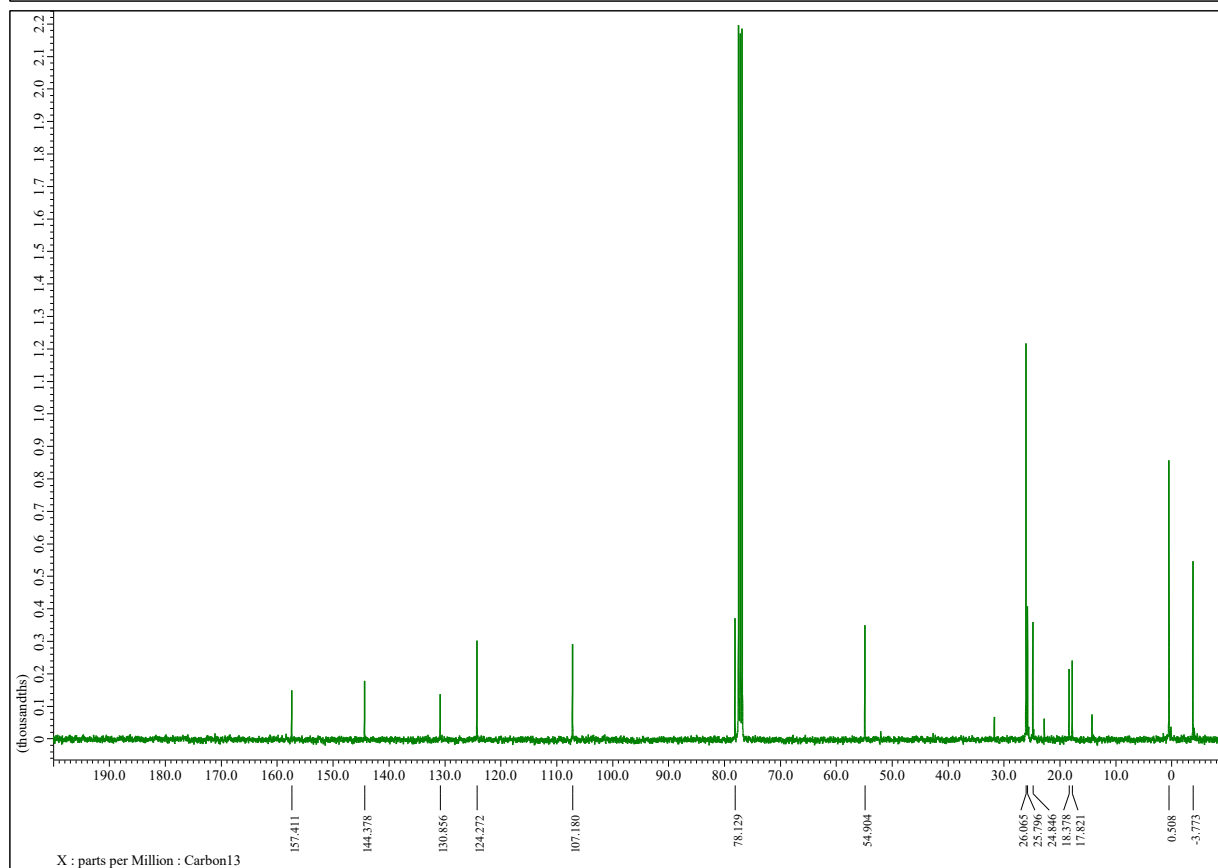
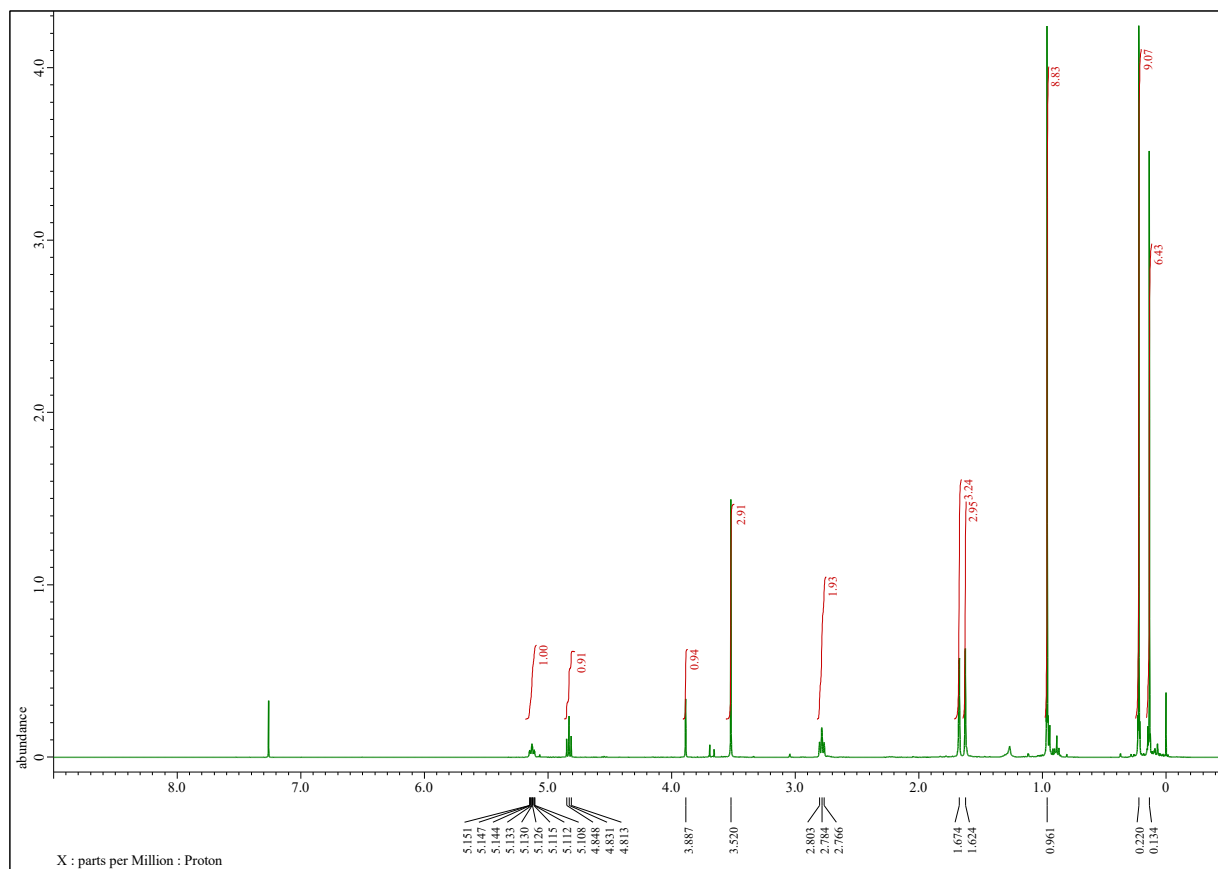
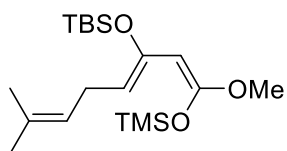


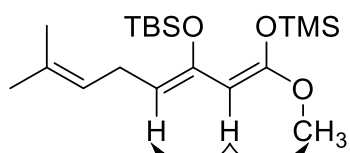


methyl (Z)-3-((tert-butyldimethylsilyl)oxy)-7-methylocta-2,6-dienoate (S12)

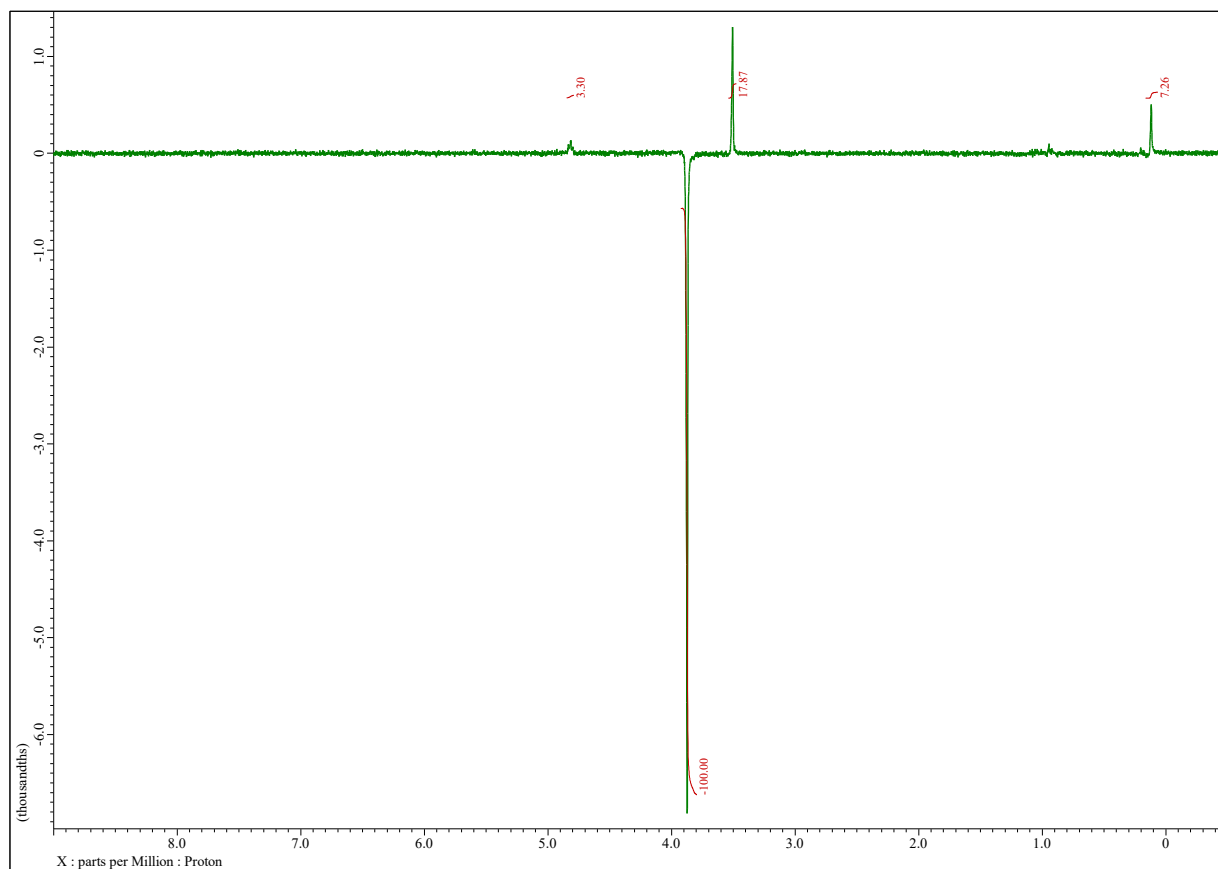


**(4Z,6Z)-4-methoxy-2,2,8,8,9,9-hexamethyl-6-(4-methylpent-3-en-1-ylidene)-3,7-dioxa-2,8-disiladec-4-ene
(13)**

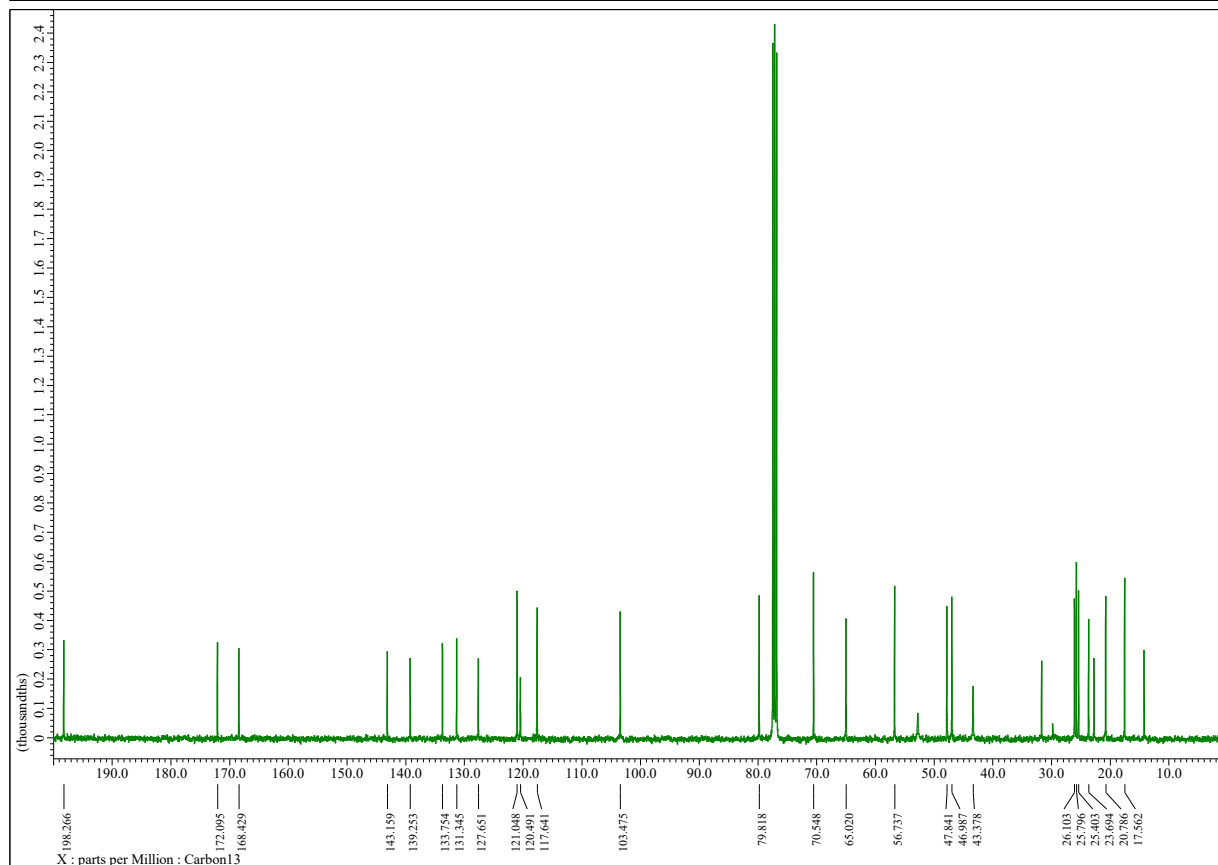
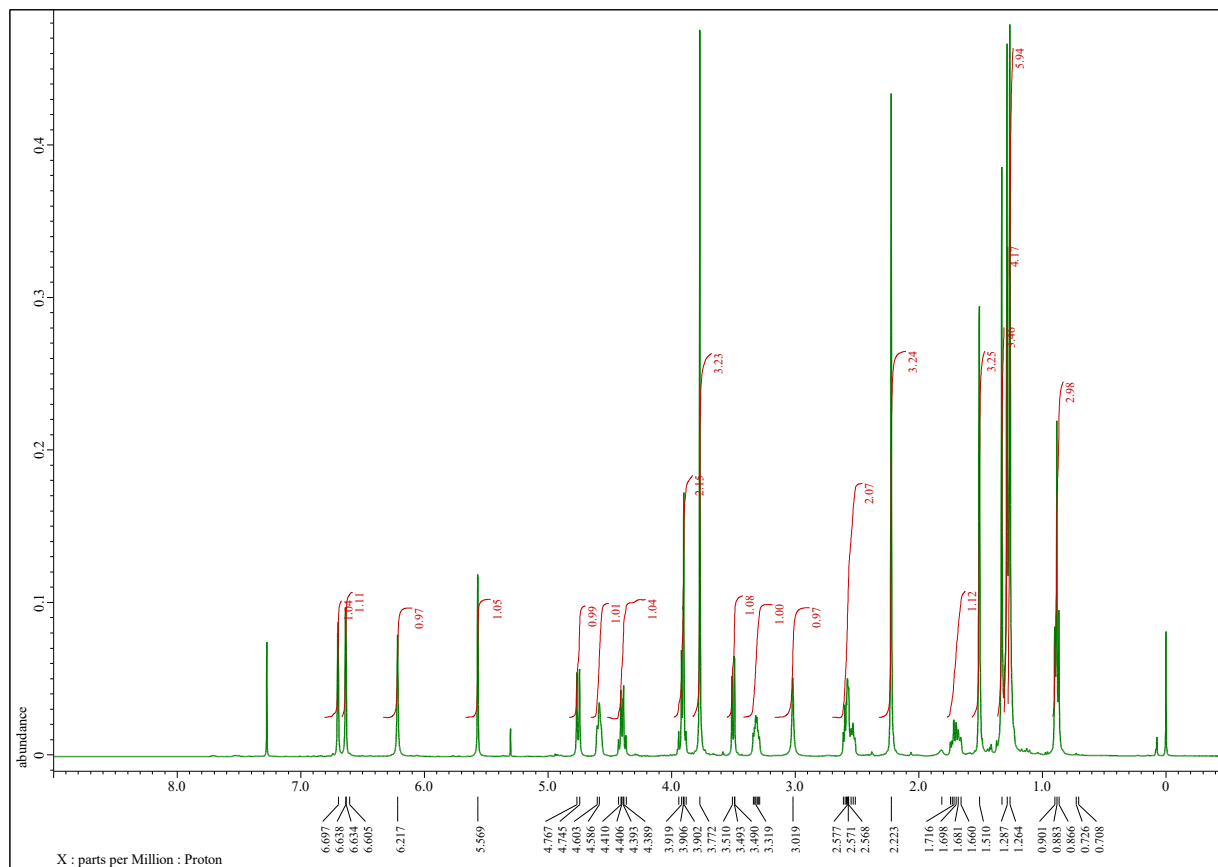
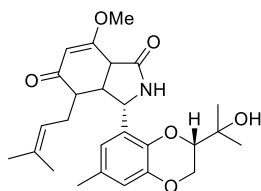




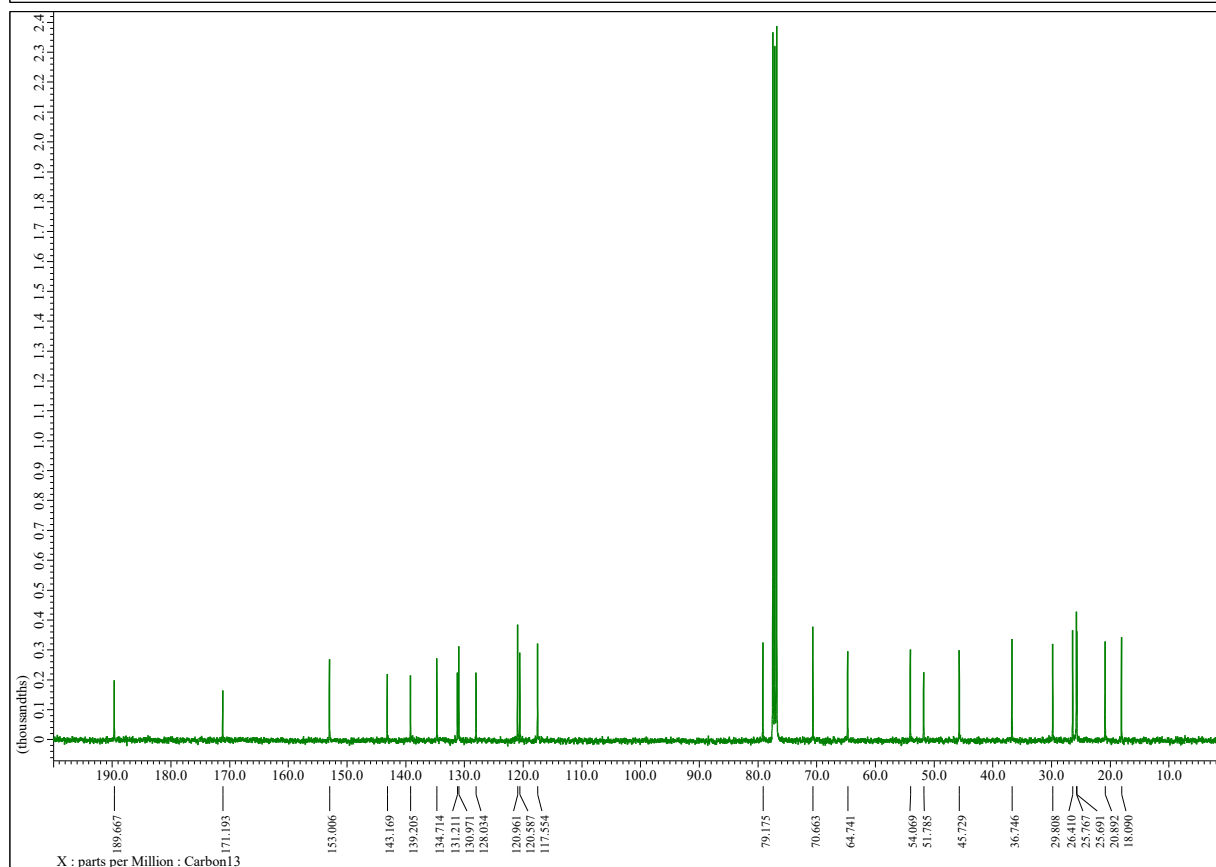
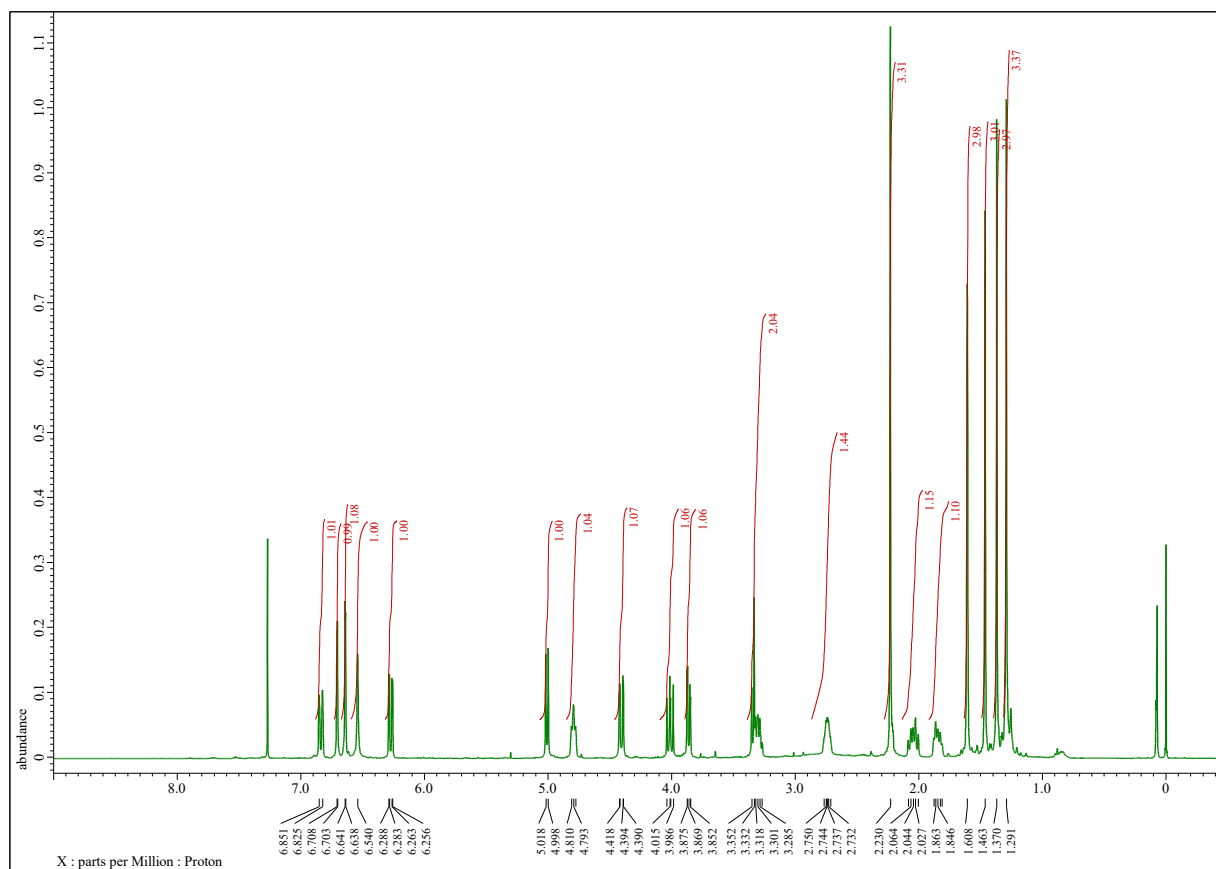
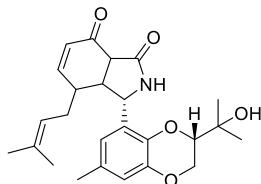
3.3% NOE 6.0% NOE



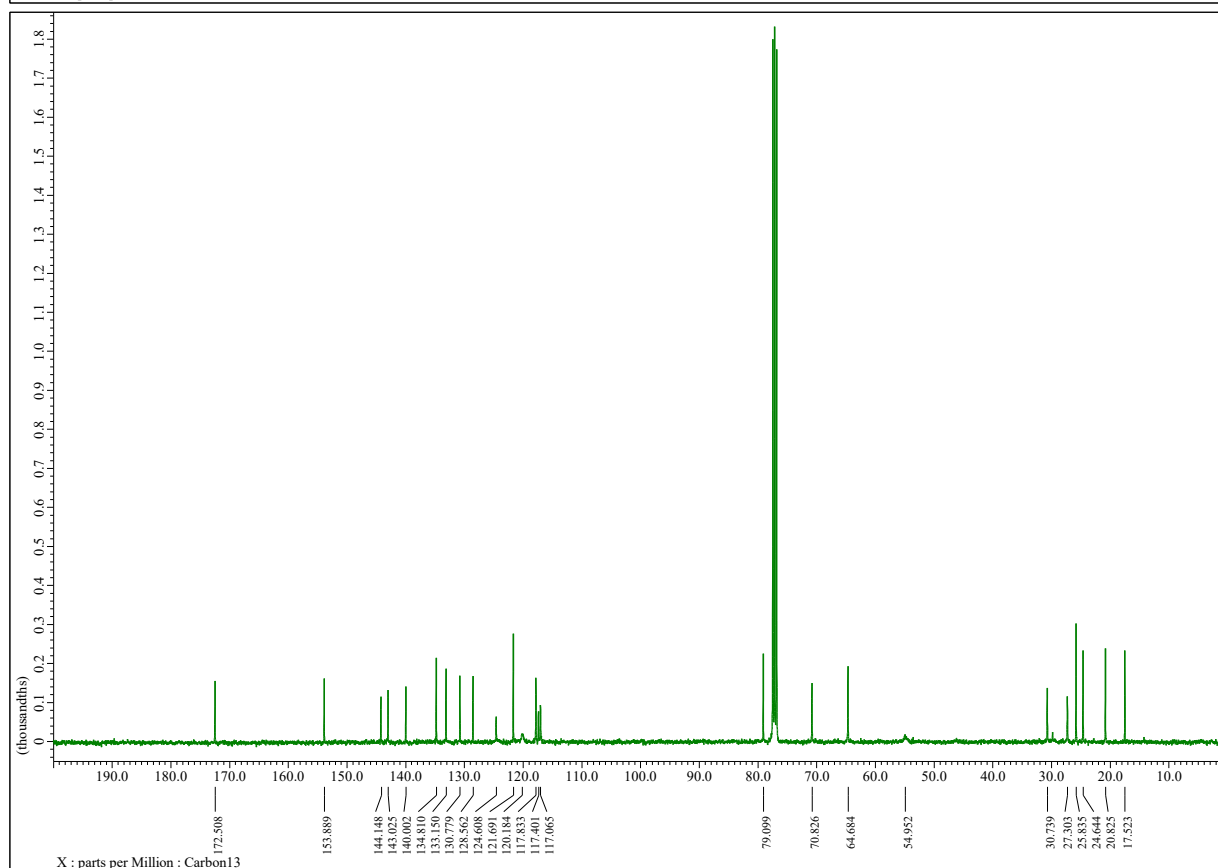
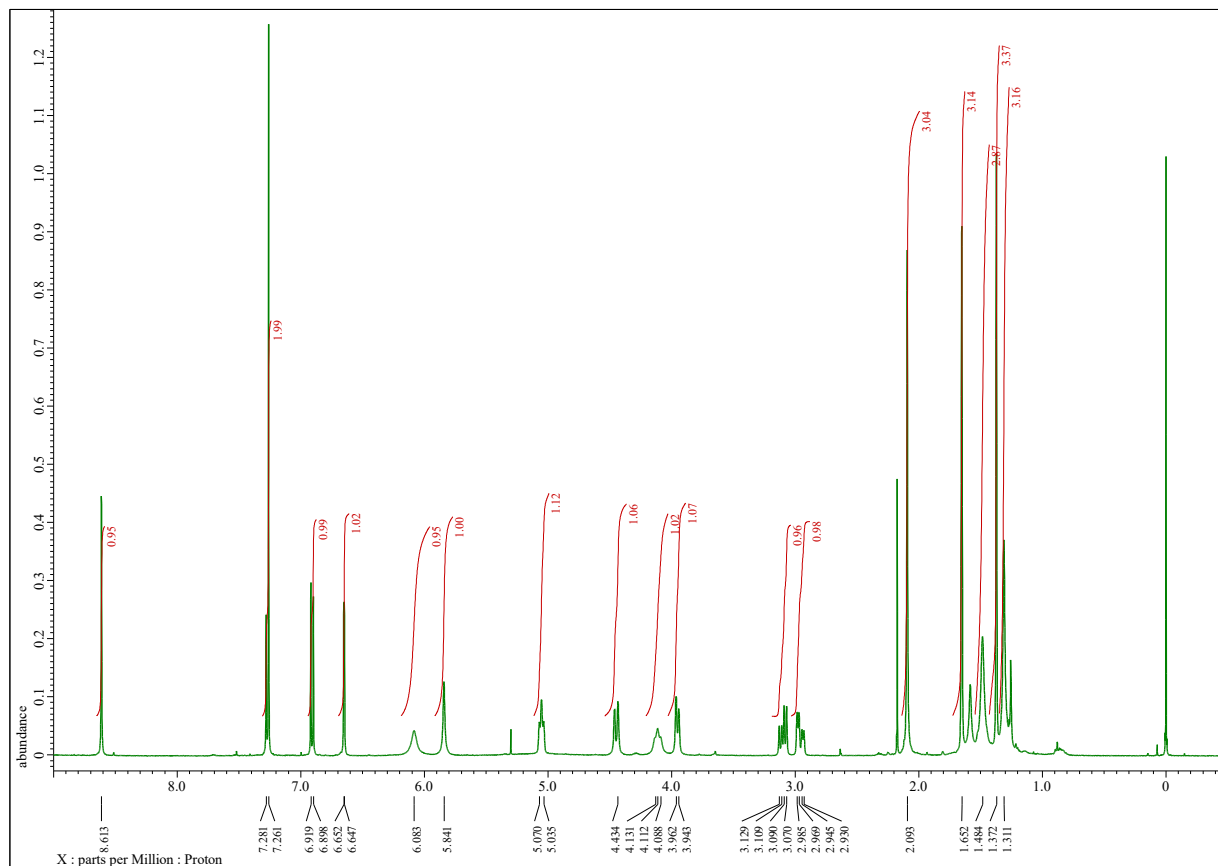
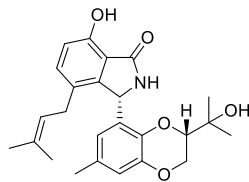
(3S)-3-((S)-3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-7-methoxy-4-(3-methylbut-2-en-1-yl)-2,3,3a,7a-tetrahydro-1H-isoindole-1,5(4H)-dione (15)



(3S)-3-((S)-3-(2-hydroxypropan-2-yl)-7-methyl-2,3-dihydrobenzo[b][1,4]dioxin-5-yl)-4-(3-methylbut-2-en-1-yl)-2,3,3a,7a-tetrahydro-1H-isoindole-1,7(4H)-dione (16)



diaporisoindole A (17)



Model substrate (S15)

