

Supplementary material

Efficient Catalytic α -Trifluoromethylthiolation of Aldehydes

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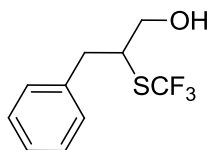
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1. General Information

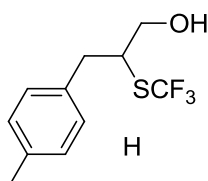
Unless otherwise stated, all commercial reagents were used as received. Reactions were conducted in dry glassware using anhydrous solvents (pass through activated alumina columns). Reaction temperatures were controlled using IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately, 24 °C). Thin-layer chromatography (TLC) was conducted on plates (GF254) supplied by Yantai Chemicals (China) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining. Silica gel (200-300 mesh) supplied by Tsingdao Haiyang Chemicals (China) was used for flash column chromatography. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker spectrometers (400 MHz). Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.16) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra were obtained from the Tsinghua University Mass Spectrometry Facility.

2. Experimental Procedure

The aldehyde (0.2 mmol), trifluoromethylthiolation reagent (0.21 mmol) and catalyst (0.02 mmol) were placed in an oven-dried Schlenk tube equipped with a magnetic stir bar. The tube was closed with a septum, evacuated and refilled with argon. Dry DCM (2.0 mL) was added. After the consumption of the starting materials (monitored by TLC or GC-MS), the reaction mixture was cooled to 0 °C, MeOH (0.1 mL) and NaBH₄ (2 mmol) were added into sequentially. The resulting mixture was stirred at room temperature for 30 min and then filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography eluted with hexane/EtOAc = 5:1 to afford the corresponding desired product **3a** as colorless oil (40 mg, 84% yield).

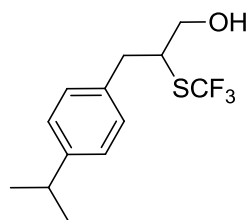


3-Phenyl-2-((trifluoromethyl)thio)propan-1-ol (3a): 40 mg, 84% yield; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.34 – 7.22 (m, 5H), 3.80 – 3.69 (m, 2H), 3.56 – 3.50 (m, 1H), 3.12 – 3.01 (m, 2H), 1.87 (t, *J* = 5.2Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 137.4, 131.0 (q, *J* = 306.0Hz), 129.42, 128.81, 127.20, 63.39, 49.80, 37.96; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): – 39.13; HRMS (ESI) exact mass calculated for [M+H]⁺ (C₁₀H₁₂F₃OS) requires *m/z* 237.0561, found *m/z* 237.0562.

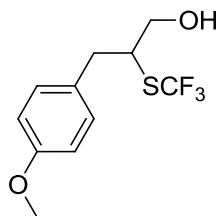


3-(*p*-Tolyl)-2-((trifluoromethyl)thio)propan-1-ol (3b): 43 mg, 86% yield; yellow oil; ¹H NMR (400

MHz, CDCl₃) δ (ppm): 7.15 – 7.10 (m, 4H), 3.80 – 3.69 (m, 2H), 3.54 – 3.48 (m, 1H), 3.07 – 2.98 (m, 2H), 2.34 (s, 3H), 1.85 (t, $J = 6.0\text{Hz}$, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 136.82, 134.29, 131.0 (q, $J = 304.7\text{Hz}$), 129.48, 129.28, 63.38, 49.67, 37.52, 21.21; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): –39.07; HRMS (ESI) exact mass calculated for [M+H]⁺ (C₁₁H₁₄F₃OS) requires m/z 251.0717, found m/z 251.0719.

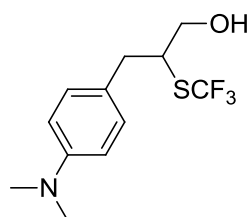


3-(4-Isopropylphenyl)-2-((trifluoromethyl)thio)propan-1-ol (3c): 43 mg, 78% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.20 – 7.14 (m, 4H), 3.78 (dd, $J_1 = 11.6$, $J_2 = 4.8\text{Hz}$, 1H), 3.72 (dd, $J_1 = 11.6$ Hz, $J_2 = 4.8\text{Hz}$, 1H), 3.56 – 3.50 (m, 1H), 3.04 (d, $J = 7.6\text{Hz}$, 2H), 2.96 – 2.85 (m, 1H), 1.97 (brs, 1H), 1.25 (d, $J = 6.8\text{Hz}$, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 147.70, 134.55, 130.90 (q, $J = 304.5\text{Hz}$), 129.20, 126.71, 63.17, 49.50, 37.44, 33.76, 23.98; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): –39.07; HRMS (ESI) exact mass calculated for [M+H]⁺ (C₁₃H₁₈F₃OS) requires m/z 279.1030, found m/z 279.1031.

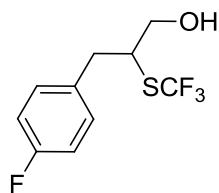


3-(4-Methoxyphenyl)-2-((trifluoromethyl)thio)propan-1-ol (3d): 41 mg, 75% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.18 – 7.13 (m, 2H), 6.88 – 6.84 (m, 2H), 3.80 (s, 3H), 3.77 – 3.71 (m, 2H), 3.51 – 3.45 (m, 1H), 3.05 – 2.96 (m, 2H), 1.90 (t, $J = 6.0\text{Hz}$, 1H); ¹³C NMR (100 MHz, CDCl₃)

δ (ppm): 158.73, 131.01 (q, $J = 304.6\text{Hz}$), 130.44, 114.15, 77.48, 77.16, 77.16, 76.84, 63.31, 55.38, 49.74, 37.01; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -39.08 ; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{11}\text{H}_{14}\text{F}_3\text{O}_2\text{S}$) requires m/z 267.0667, found m/z 267.0669.

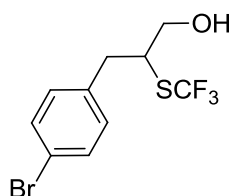


3-(4-(Dimethylamino)phenyl)-2-((trifluoromethyl)thio)propan-1-ol (3e): 37 mg, 66% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.10 (d, $J = 8.4\text{Hz}$, 2H), 6.72 (d, $J = 8.4\text{Hz}$, 2H), 3.79 – 3.69 (m, 2H), 3.52 – 3.46 (m, 1H), 3.13 (d, $J = 7.6\text{Hz}$, 2H), 2.94 (s, 6H), 2.02 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 149.66, 131.11 (q, $J = 304.7\text{Hz}$), 130.11, 113.05, 63.31, 49.89, 40.89, 37.01; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -38.99 ; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{12}\text{H}_{17}\text{F}_3\text{NOS}$) requires m/z 280.0983, found m/z 280.0985.

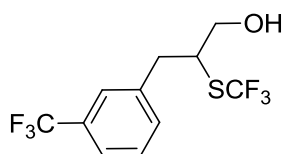


3-(4-Fluorophenyl)-2-((trifluoromethyl)thio)propan-1-ol (3f): 43 mg, 85% yield; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.22 – 7.17 (m, 2H), 7.04 – 6.98 (m, 2H), 3.78 – 3.72 (m, 2H), 3.49 – 3.47 (m, 1H), 3.08 (dd, $J_1 = 14.0\text{ Hz}$, $J_2 = 7.6\text{ Hz}$, 1H), 3.00 (dd, $J_1 = 14\text{ Hz}$, $J_2 = 6.8\text{ Hz}$, 1H), 1.93 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 162.06 (d, $J = 244.0\text{ Hz}$), 133.08 (d, $J = 2.3\text{ Hz}$), 130.90 (q, $J = 304.7\text{ Hz}$), 128.77 (d, $J = 81.0\text{ Hz}$), 115.63 (d, $J = 22\text{ Hz}$), 63.36, 49.56, 37.00; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -38.18 , -115.63 ; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{10}\text{H}_{11}\text{F}_4\text{OS}$)

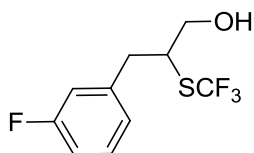
requires m/z 255.0467, found m/z 255.0469.



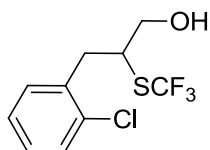
3-(4-Bromophenyl)-2-((trifluoromethyl)thio)propan-1-ol (3g): 41 mg, 65% yield; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.45 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 3.74 (s, 2H), 3.51 – 3.45 (m, 1H), 3.07 (dd, $J_1=14.0$ Hz, $J_2 = 8.0$ Hz, 1H), 2.97 (dd, $J_1 = 14.4$ Hz, $J_2 = 6.8$ Hz, 1H), 1.96 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 136.37, 131.89, 131.19, 130.87 (q, $J = 305.0$ Hz), 63.32, 49.22, 37.22; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): – 39.16; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{10}\text{H}_{11}\text{BrF}_3\text{OS}$) requires m/z 314.9666, found m/z 314.9670.



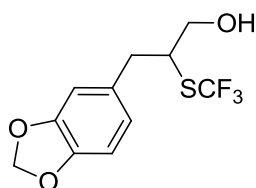
3-(3-(Trifluoromethyl)phenyl)-2-((trifluoromethyl)thio)propan-1-ol (3h): 46 mg, 75% yield; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.54 – 7.42 (m, 4H), 3.81 – 3.73 (m, 2H), 3.55 – 3.49 (m, 1H), 3.19 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.6$ Hz, 1H), 3.06 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.2$ Hz, 1H), 2.03 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 138.38, 131.16 (q, $J = 31.9$ Hz), 130.82 (q, $J = 304.8$ Hz), 129.24, 127.62, 124.17 (q, $J = 270.7$ Hz), 126.16 (q, $J = 3.7$ Hz), 124.13, 124.11 (q, $J = 3.8$ Hz), 63.15, 49.15, 37.55; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): – 62.68, – 39.26; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{11}\text{H}_{11}\text{F}_6\text{OS}$) requires m/z 305.0435, found m/z 305.0439.



3-(3-Fluorophenyl)-2-((trifluoromethyl)thio)propan-1-ol (3i): 42 mg, 82% yield; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.32 – 7.26 (m, 1H), 7.02 – 6.94 (m, 3H), 3.78 – 3.73 (m, 2H), 3.54 – 3.48 (m, 1H), 3.11(q, $J = 14.0$ Hz, 1H), 3.02 (q, $J_1 = 14.0$ Hz, $J_2 = 6.8$ Hz), 1.91 (t, $J = 5.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 163.03 (d, $J = 245$ Hz), 139.86 (t, $J = 7.1$ Hz), 130.88 (q, $J = 305$ Hz), 130.28 (d, $J = 8.3$ Hz), 125.13 (d, $J = 2.9$ Hz), 116.38 (d, $J = 21.1$ Hz), 114.18 (d, $J = 20.9$ Hz), 63.41, 49.22, 37.56; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): – 39.20, – 112.91; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{10}\text{H}_{11}\text{F}_4\text{OS}$) requires m/z 255.0467, found m/z 255.0471.

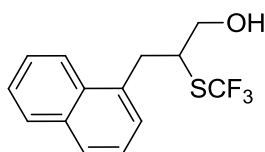


3-(2-Chlorophenyl)-2-((trifluoromethyl)thio)propan-1-ol (3j): 46 mg, 84% yield; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.40 – 7.36 (m, 1H), 7.28 – 7.21 (m, 3H), 3.83 – 3.72 (m, 2H), 3.71 – 3.65 (m, 1H), 3.24 (dd, $J_1=14.0$ Hz, $J_2 = 8.4$ Hz, 1H), 3.12 (dd, $J_1 = 14.4$ Hz, $J_2 = 7.2$ Hz, 1H), 2.14 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 135.29, 134.35, 132.00, 130.90 (q, $J = 305.0$ Hz), 129.91, 128.77, 127.08, 63.75, 48.11, 36.00; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): – 39.16; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{10}\text{H}_{11}\text{ClF}_3\text{OS}$) requires m/z 271.0171, found m/z 271.0172.

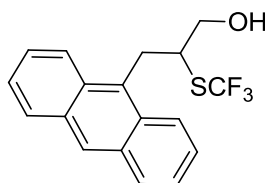


3-(Benzo[d][1,3]dioxol-5-yl)-2-((trifluoromethyl)thio)propan-1-ol (3k): 47 mg, 78% yield; yellow

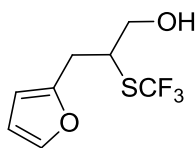
oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.77 – 6.66 (m, 3H), 5.95(s, 2H), 3.78 – 3.71 (m, 2H), 3.49 – 3.43 (m, 1H), 3.03 – 2.93 (m, 2H), 1.95 (t, $J = 6.4\text{Hz}$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 147.95, 131.06, 130.98 (q, $J = 304.7\text{Hz}$), 63.27, 49.65, 37.60; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): –39.11; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{11}\text{H}_{12}\text{F}_3\text{O}_3\text{S}$) requires m/z 281.0459, found m/z 281.0460.



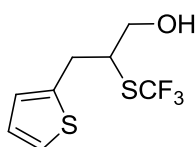
3-(Naphthalen-1-yl)-2-((trifluoromethyl)thio)propan-1-ol (3l): 52 mg, 90% yield; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.04 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 4.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.58 – 7.54 (m, 2H), 7.44 – 7.40 (m, 2H), 3.77 – 3.71 (m, 3H), 3.59 – 3.48 (m, 2H), 1.98 (t, $J = 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 134.16, 133.65, 131.85, 131.06 (q, $J = 304.8$ Hz), 129.20, 128.15 (d, $J = 3.0$ Hz), 126.63, 126.43, 125.94, 125.51, 123.33, 63.40, 48.83, 35.29; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): – 39.91; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{14}\text{H}_{14}\text{F}_3\text{OS}$) requires m/z 287.0717, found m/z 287.0717.



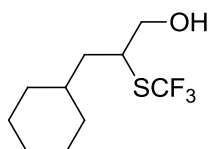
3-(Anthracen-9-yl)-2-((trifluoromethyl)thio)propan-1-ol (3m): 65 mg, 96% yield; yellow solid; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.42 (s, 1H), 8.30 (d, $J = 9.2$ Hz, 2H), 8.03 (d, $J = 8.0$ Hz, 2H), 7.58 (t, $J = 6.8$ Hz, 2H), 7.50 (t, $J = 8.0$ Hz, 2H), 4.23 (dd, $J_1 = 14.8$ Hz, $J_2 = 10.8$ Hz, 1H), 3.94 (dd, $J_1 = 14.4$ Hz, $J_2 = 4.8$ Hz, 1H), 3.90 – 3.84 (m, 1H), 3.70 – 3.66 (m, 1H), 3.59 – 3.55 (m, 1H), 2.04(s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 131.64, 131.21 (q, $J = 304.9$ Hz), 130.50, 129.79, 129.57, 127.58, 126.51, 125.16, 124.03, 62.97, 49.52, 30.08; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): – 38.85; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{18}\text{H}_{16}\text{F}_3\text{OS}$) requires m/z 337.0874, found m/z 337.0876;



1-Acetyl-4-(3-bromophenyl)azet-2(1H)-one (3n): 30 mg, 67% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.35 (dd, $J_1 = 2.0$ Hz, $J_2 = 0.8$ Hz, 1H), 6.32 (dd, $J_1 = 3.2$ Hz, $J_2 = 2.0$ Hz, 1H), 6.16 (dd, $J_1 = 3.2$ Hz, $J_2 = 0.4$ Hz, 1H), 3.82 – 3.74 (m, 2H), 3.64 – 3.58 (m, 1H), 3.17 – 3.05 (m, 2H), 2.4 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 151.14, 142.13, 130.97 (q, $J = 304.0$ Hz), 110.58, 108.16, 63.97, 47.00, 30.57; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): – 38.85; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_8\text{H}_{10}\text{F}_3\text{O}_2\text{S}$) requires m/z 227.0354, found m/z 227.0355.

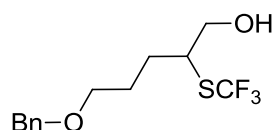


3-(Thiophen-2-yl)-2-((trifluoromethyl)thio)propan-1-ol (3o): 36 mg, 74% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.21 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.2$ Hz, 1H), 6.97 (dd, $J_1 = 5.2$ Hz, $J_2 = 3.6$ Hz, 1H), 6.91 (dd, $J_1 = 3.2$ Hz, $J_2 = 0.4$ Hz, 1H), 3.80 (t, $J = 4.0$ Hz, 2H), 3.56 – 3.50 (m, 1H), 3.37 – 3.25 (m, 2H), 2.03 (q, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 139.11, 130.92 (q, $J = 304.0$ Hz), 127.19, 126.94, 124.81, 63.40, 49.21, 31.97; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): – 39.19; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_8\text{H}_{10}\text{F}_3\text{OS}_2$) requires m/z 243.0125, found m/z 243.0126.

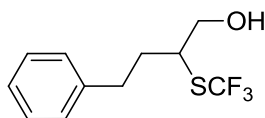


3-Cyclohexyl-2-((trifluoromethyl)thio)propan-1-ol (3p): 39 mg, 80% yield; yellow oil; ^1H NMR

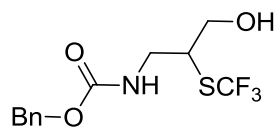
(400 MHz, CDCl₃) δ (ppm): 3.82 – 3.69 (m, 2H), 3.40 – 3.33 (m, 1H), 1.95 (t, $J = 6.4$ Hz, 1H), 1.79 – 1.64 (m, 5H), 1.60 – 1.45 (m, 3H), 1.31 – 1.13 (m, 2H), 1.01 – 0.84 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 131.03(q, $J = 304.6$ Hz), 65.33, 46.50, 38.96, 34.75, 33.58, 32.70, 26.58, 26.26, 26.16; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): – 38.76; HRMS (ESI) exact mass calculated for [M+H]⁺ (C₁₀H₁₈F₃OS) requires m/z 243.1030, found m/z 243.1028.



5-(Benzyloxy)-2-((trifluoromethyl)thio)pentan-1-ol (3q): 40 mg, 68% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.38 – 7.26 (m, 5H), 4.51 (s, 2H), 3.75 (t, $J = 5.6$ Hz, 1H), 3.52 (t, $J = 6.0$ Hz, 2H), 3.80 – 3.24 (m, 1H), 2.36 (t, $J = 6.4$ Hz, 1H), 1.96 – 1.81 (m, 2H), 1.76 – 1.70 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 138.15, 130.90 (q, $J = 304.4$ Hz), 128.41, 127.70, 73.04, 69.54, 64.68, 48.40, 28.23, 26.72; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): – 38.99; HRMS (ESI) exact mass calculated for [M+H]⁺ (C₁₃H₁₈F₃O₂S) requires m/z 295.0980, found m/z 295.0981.

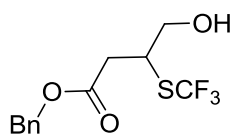


4-Phenyl-2-((trifluoromethyl)thio)butan-1-ol (3r): 43 mg, 86% yield; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.30 (t, $J = 8$ Hz, 2H), 7.21 (t, $J = 6.4$ Hz, 3H), 3.78 (t, $J = 4.4$ Hz, 2H), 3.28 – 3.22 (m, 1H), 2.92 – 2.86 (m, 1H), 2.77 – 2.71 (m, 1H), 2.10 – 2.08 (m, 1H), 1.97 – 1.88 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 140.71, 130.94 (q, $J = 304.6$ Hz), 128.71, 128.54, 126.42, 65.10, 48.24, 33.08, 32.88; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): – 38.66; HRMS (ESI) exact mass calculated for [M+H]⁺ (C₁₁H₁₄F₃OS) requires m/z 251.0717, found m/z 251.0720.



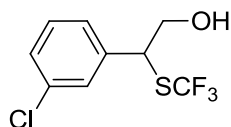
Benzyl (3-hydroxy-2-((trifluoromethyl)thio)propyl)carbamate (3s): 37 mg, 59% yield; yellow oil;

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.35 (m, 5H), 5.32 (s, 1H), 5.13 (s, 2H), 3.85 – 3.61 (m, 4H), 3.54 – 3.48 (m, 1H), 3.36 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 158.02, 135.96, 130.97 (q, $J = 305.0$ Hz), 128.74, 128.55, 128.27, 67.66, 61.83, 47.36, 41.70; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): –39.43; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{12}\text{H}_{15}\text{F}_3\text{NO}_3\text{S}$) requires m/z 310.0725, found m/z 310.0726.



Benzyl-5-hydroxy-4-((trifluoromethyl)thio)pentanoate (3t): 27 mg, 45% yield; yellow oil; ^1H NMR

(400 MHz, CDCl_3) δ (ppm): 7.38 – 7.34 (m, 5H), 5.16 (s, 2H), 3.93 – 3.87 (m, 1H), 3.84 – 3.78 (m, 1H), 3.73 – 3.67 (m, 1H), 2.95 (dd, $J_1 = 16.8$ Hz, $J_2 = 6.8$ Hz, 1H), 2.82 (dd, $J_1 = 16.8$ Hz, $J_2 = 6.0$ Hz, 1H), 2.21 (dd, $J_1 = 12.4$ Hz, $J_2 = 6.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.63, 135.44, 130.78 (q, $J = 304.8$ Hz), 67.18, 64.60, 43.43, 36.97; ^{19}F NMR (376 MHz, CDCl_3) δ (ppm): –39.67; HRMS (ESI) exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{12}\text{H}_{14}\text{F}_3\text{O}_3\text{S}$) requires m/z 295.0616, found m/z 295.0618.



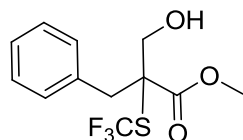
2-(3-Chlorophenyl)-2-((trifluoromethyl)thio)ethanol (3u): 39 mg, 74% yield; colorless oil; ^1H NMR

(400 MHz, CDCl₃) δ (ppm): 7.37 – 7.28 (m, 4H), 4.42 (t, $J = 6.4$ Hz, 1H), 4.00 (s, 2H), 1.97 (s, 1H);

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.76, 130.41, 130.37 (q, $J = 305.5$ Hz), 128.84, 128.18,

126.23; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): – 39.68; HRMS (ESI) exact mass calculated for [M+H]⁺

(C₉H₉ClF₃OS) requires m/z 257.0015, found m/z 257.0020.



1-Acetyl-3,4-dihydronaphtho[1,2-b]azet-2(1H)-one (3v): 12 mg, 21% yield; yellow oil; ¹H NMR

(400 MHz, CDCl₃) δ (ppm): 7.37 – 7.26 (m, 5H), 4.06 (q, $J_1 = 12.4$ Hz, $J_2 = 6.8$ Hz, 1H), 3.85 – 3.80

(m, 4H), 3.42 (d, $J = 13.6$ Hz, 1H), 3.22 (d, $J = 13.6$ Hz, 1H), 2.47 (t, $J = 7.2$ Hz, 1H); ¹³C NMR (100

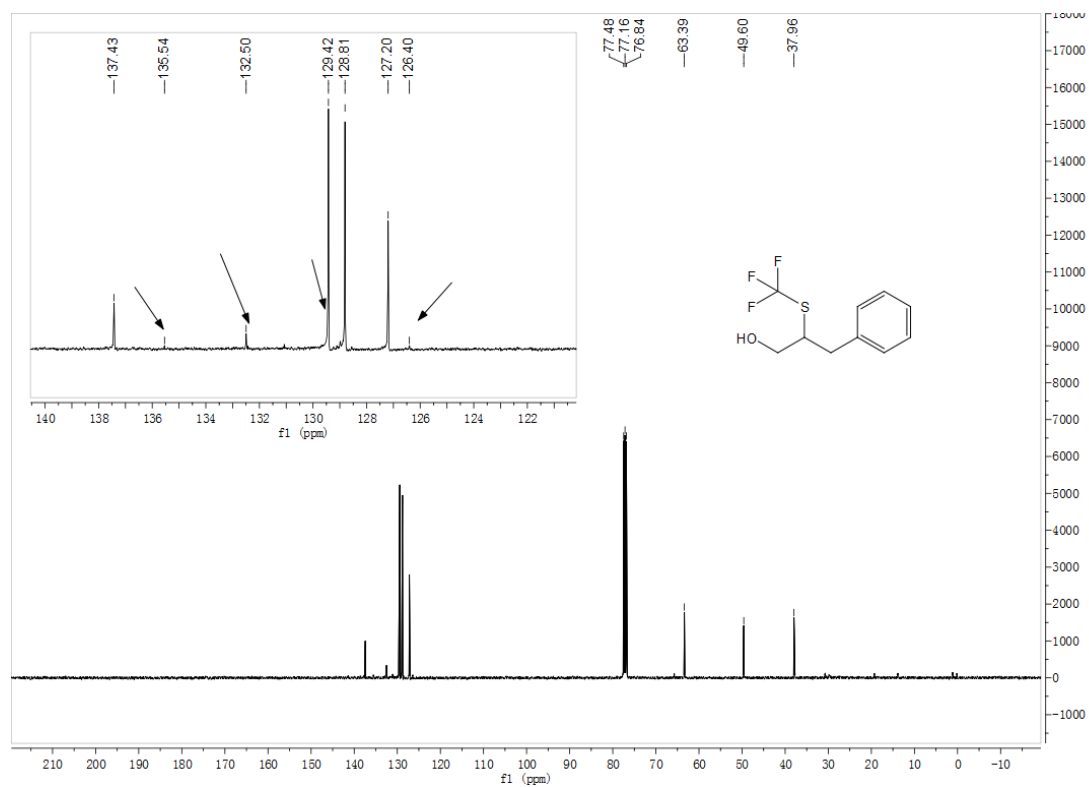
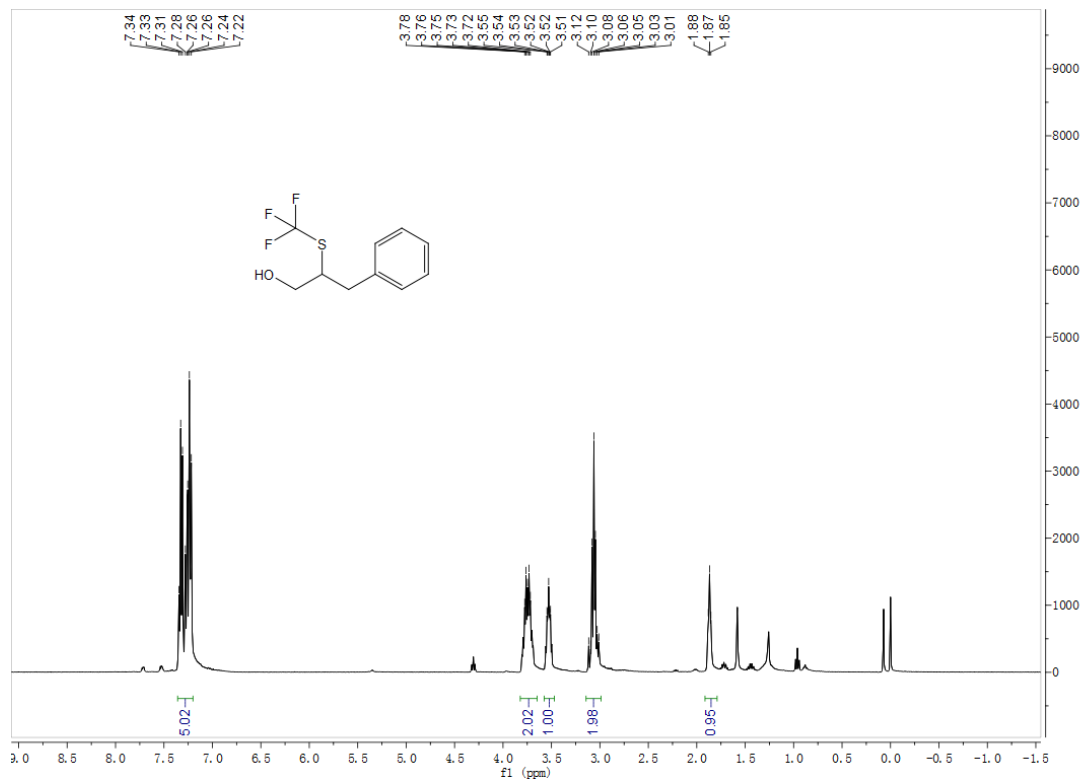
MHz, CDCl₃) δ (ppm): 171.47, 130.70, 129.82 (d, $J = 307$ Hz), 128.67, 127.93, 62.58, 60.65, 53.24,

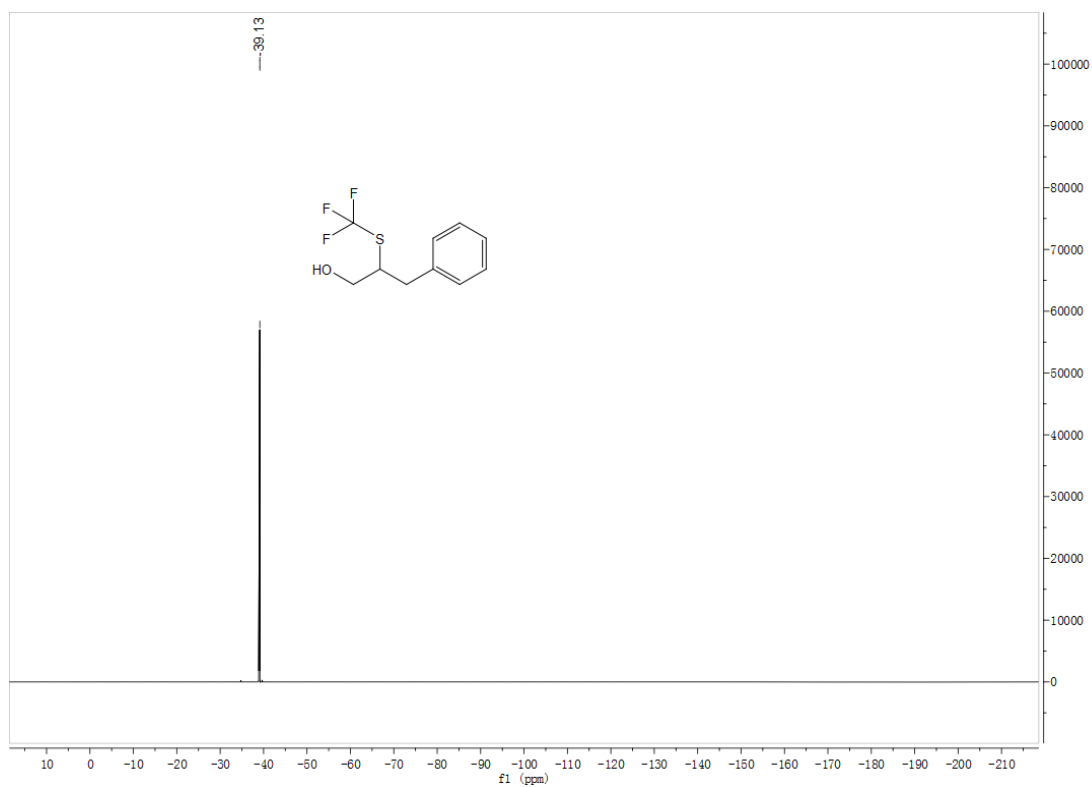
38.41, 29.85; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): – 36.18; HRMS (ESI) exact mass calculated for

[M+H]⁺ (C₁₂H₁₄F₃O₃S) requires m/z 295.0616, found m/z 295.0619.

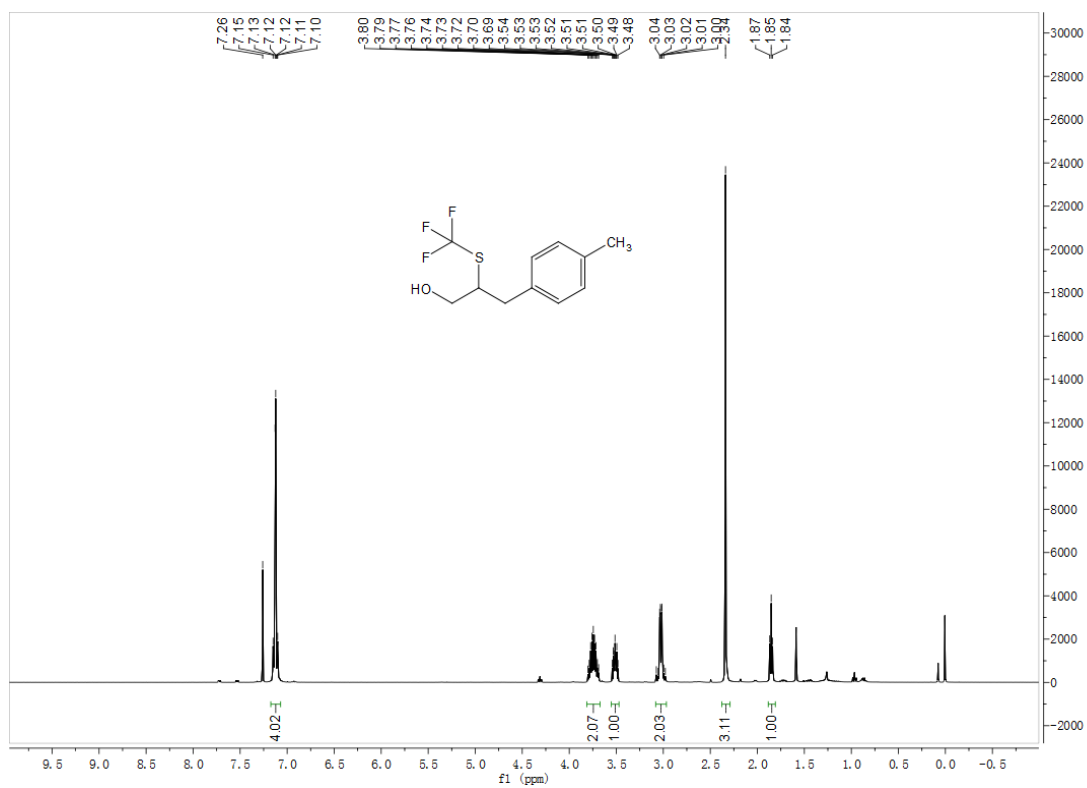
3. NMR Spectra:

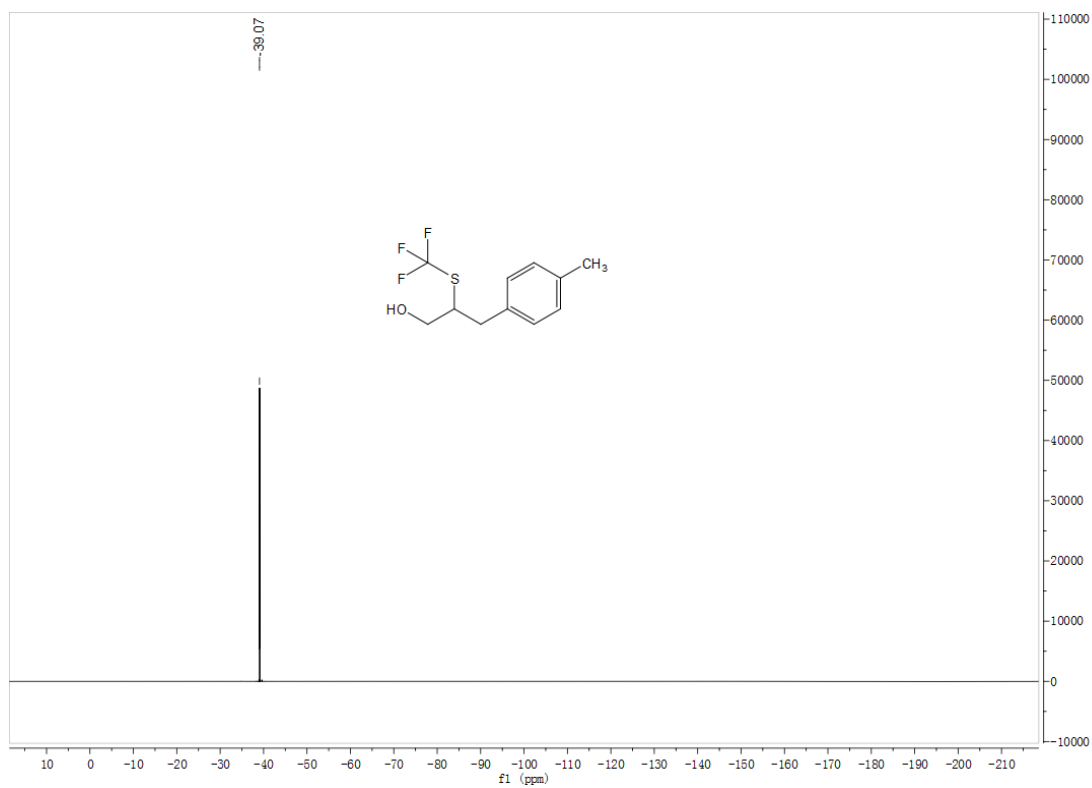
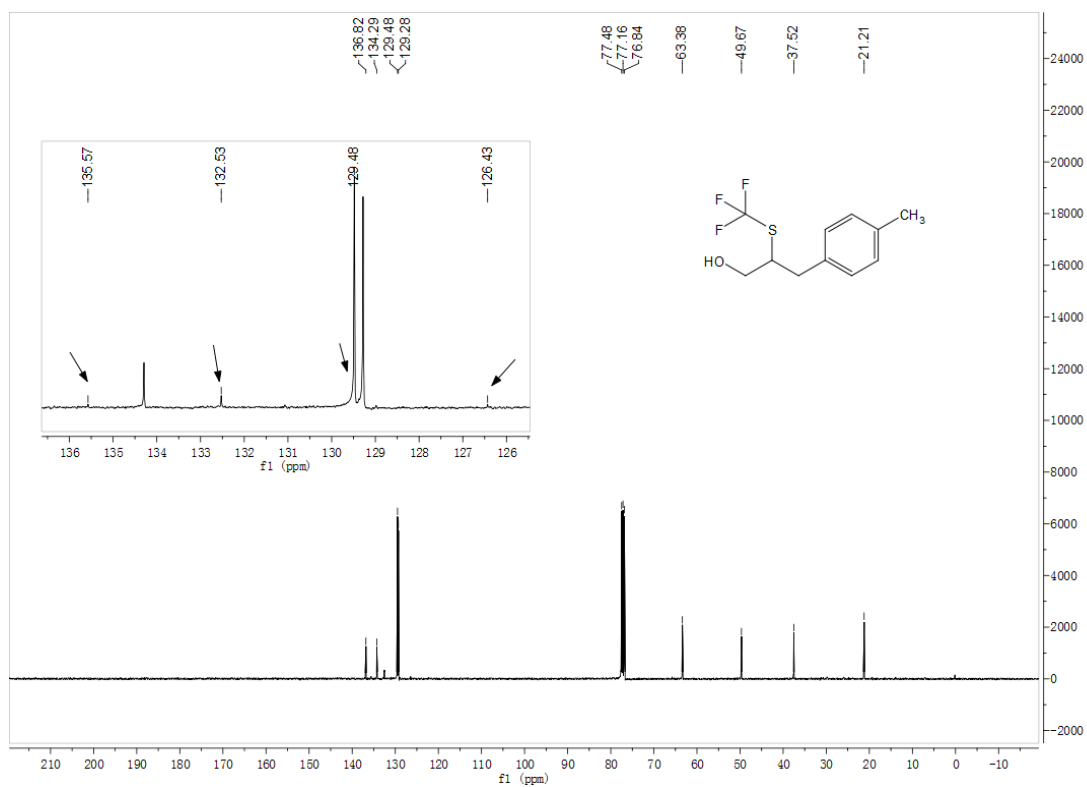
3-Phenyl-2-((trifluoromethyl)thio)propan-1-ol (3a):



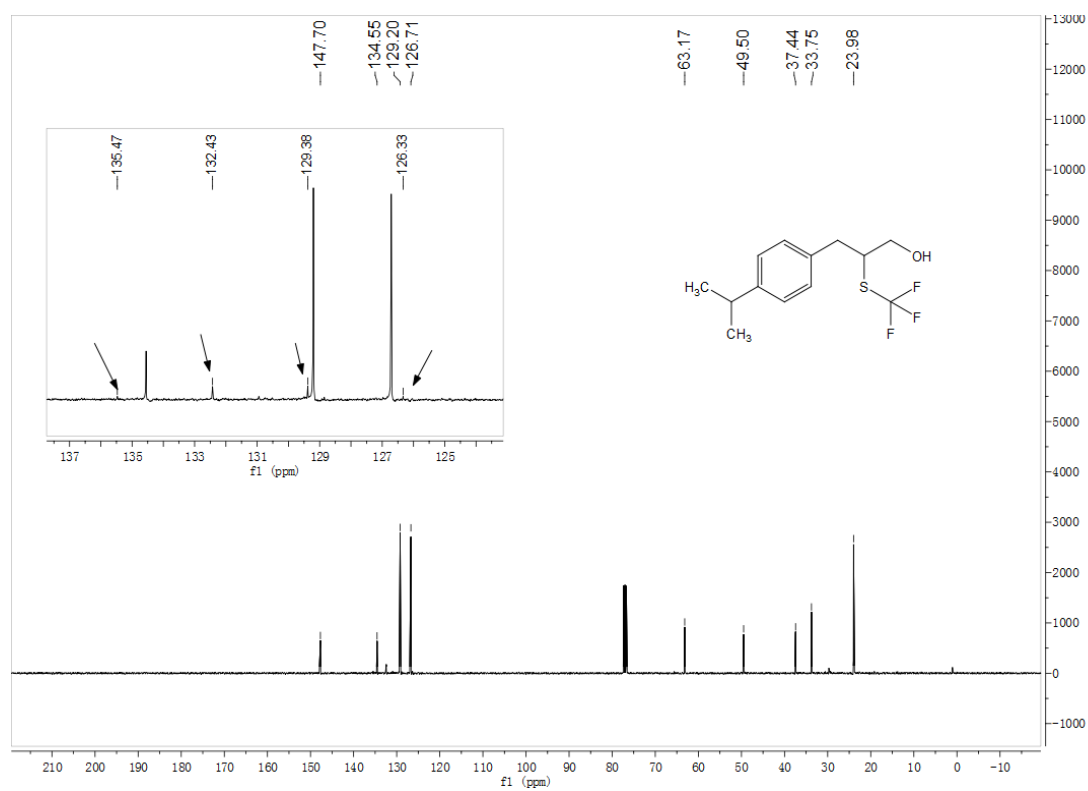
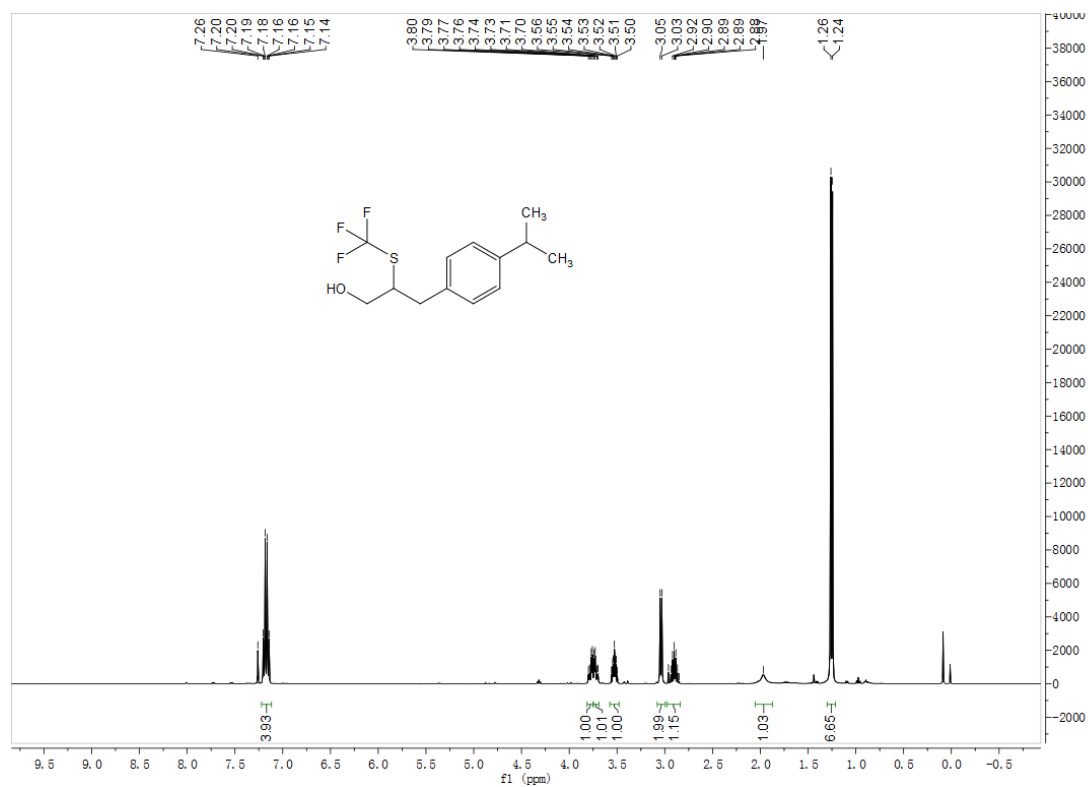


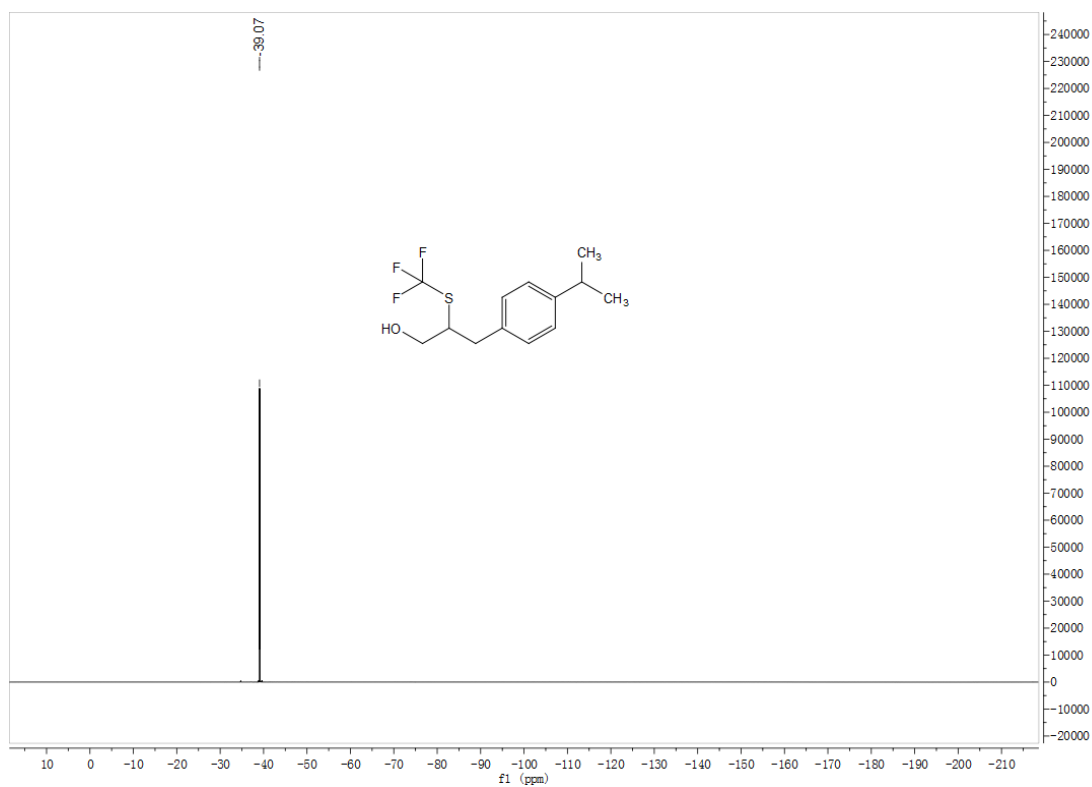
3-(*p*-Tolyl)-2-((trifluoromethyl)thio)propan-1-ol (3b):



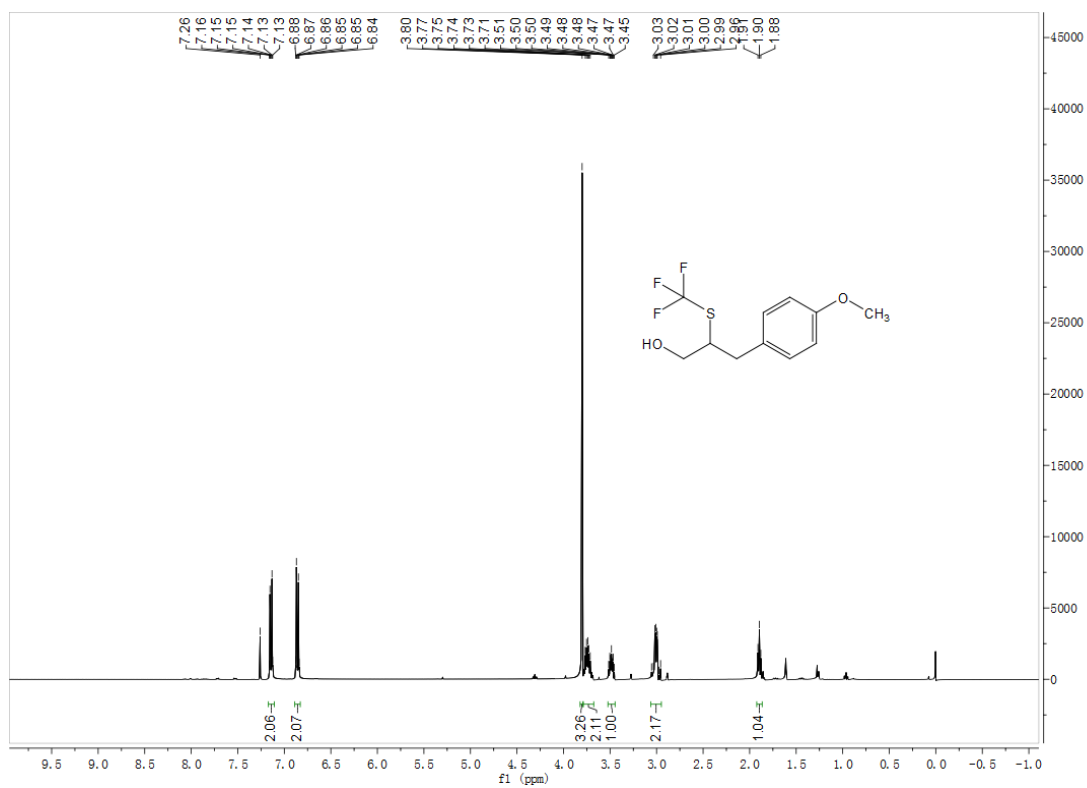


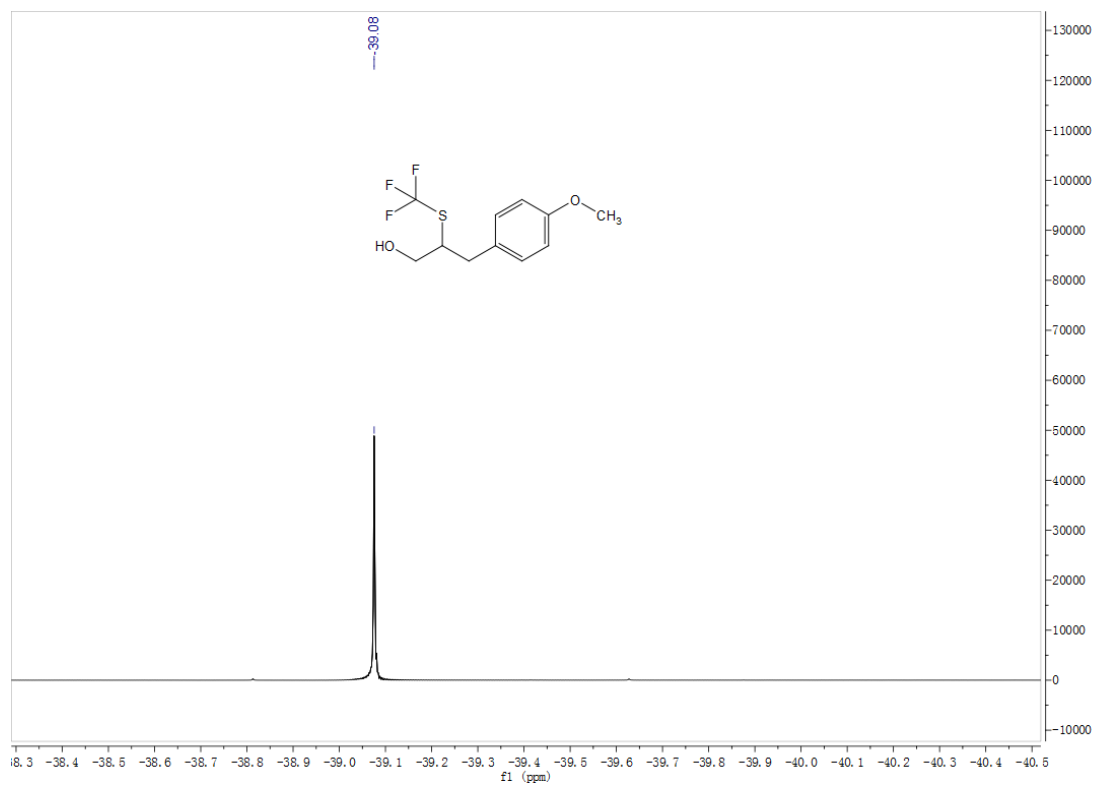
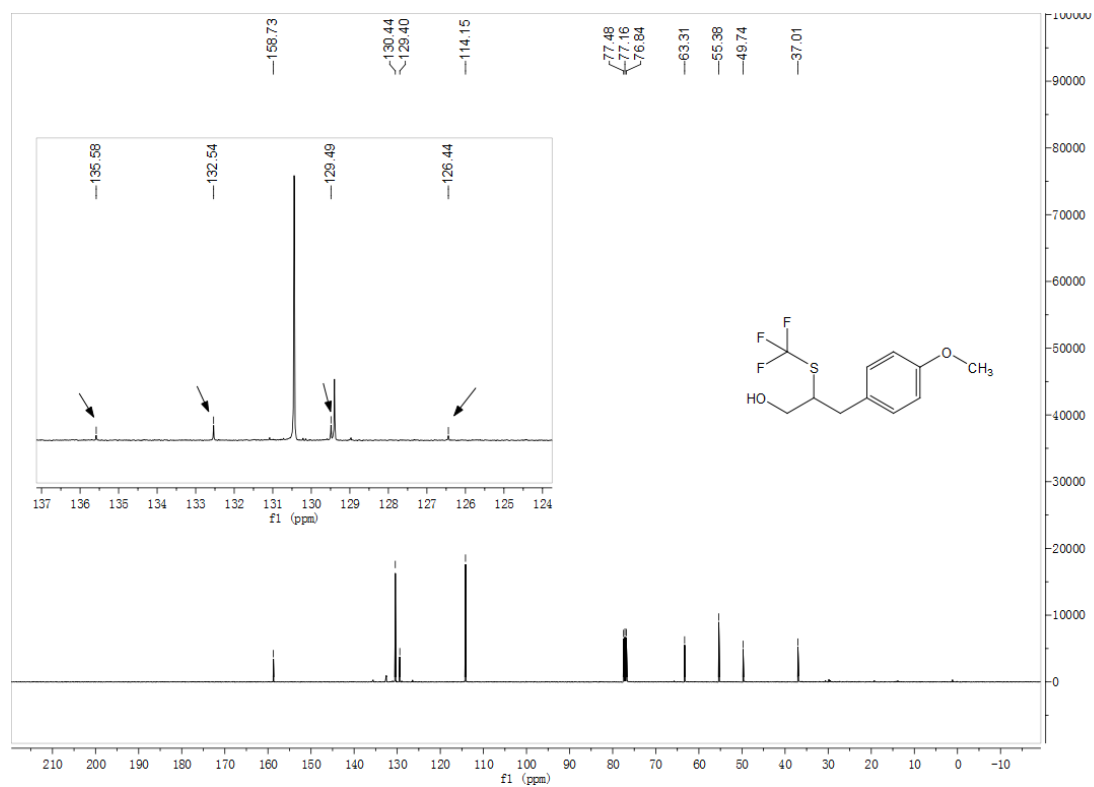
3-(4-Isopropylphenyl)-2-((trifluoromethyl)thio)propan-1-ol (3c):



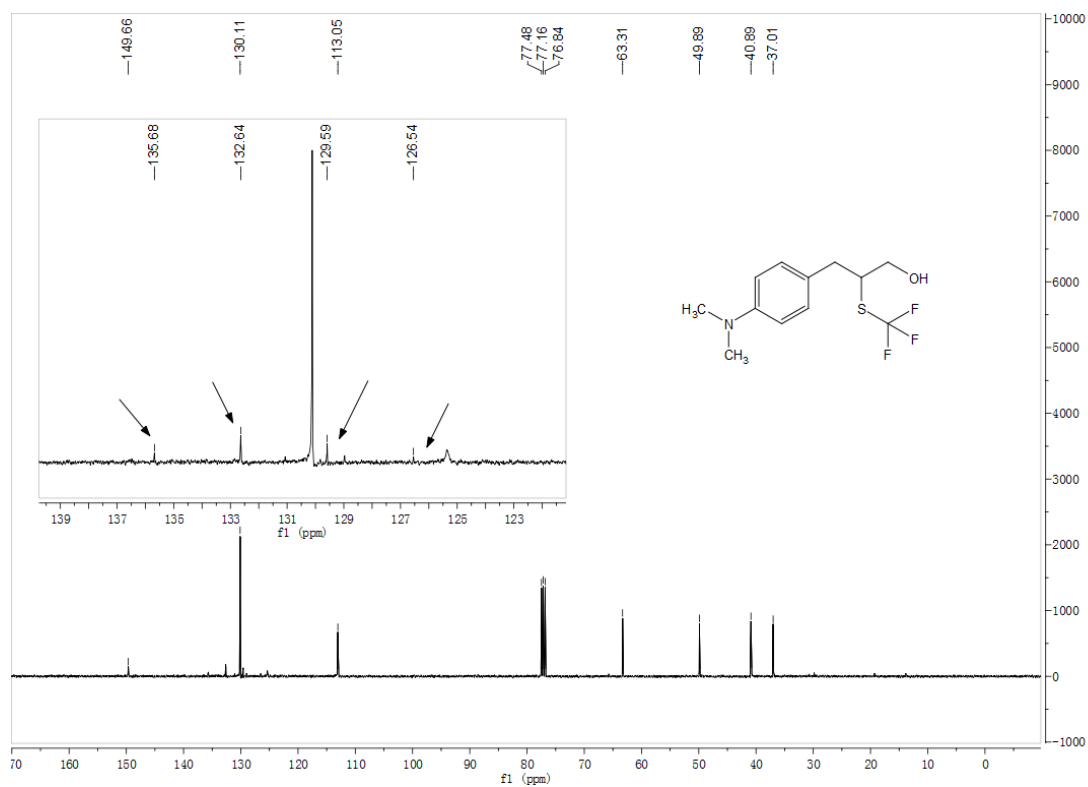
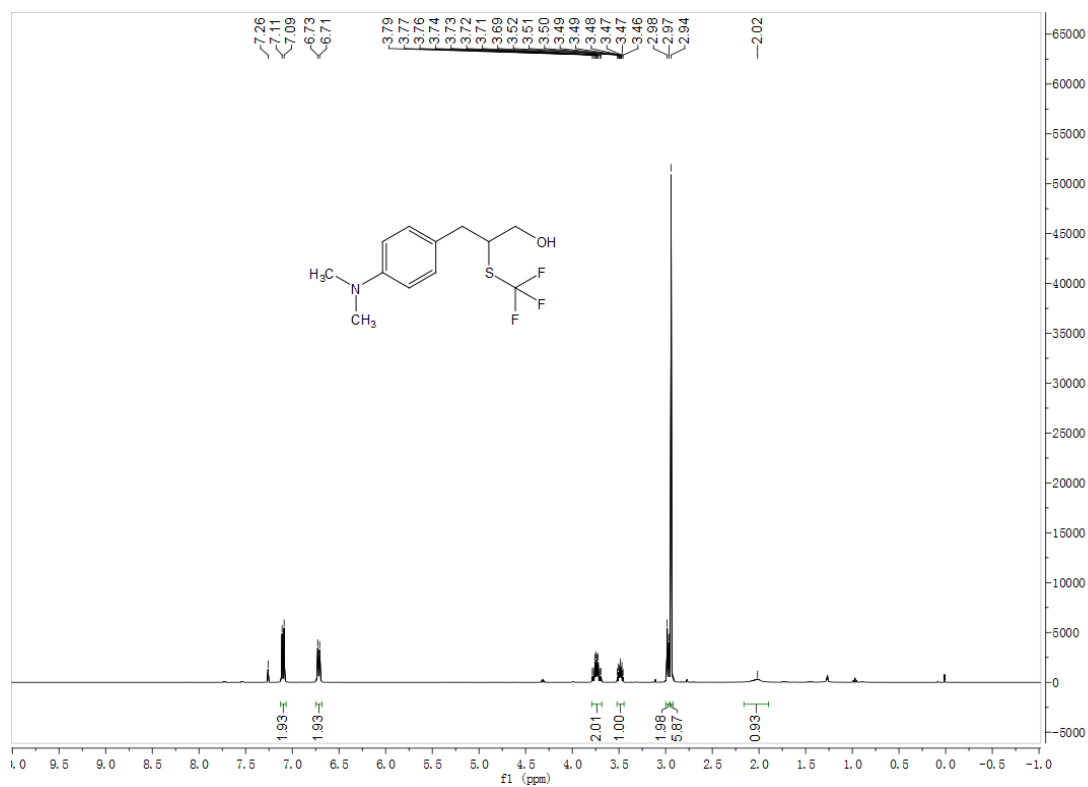


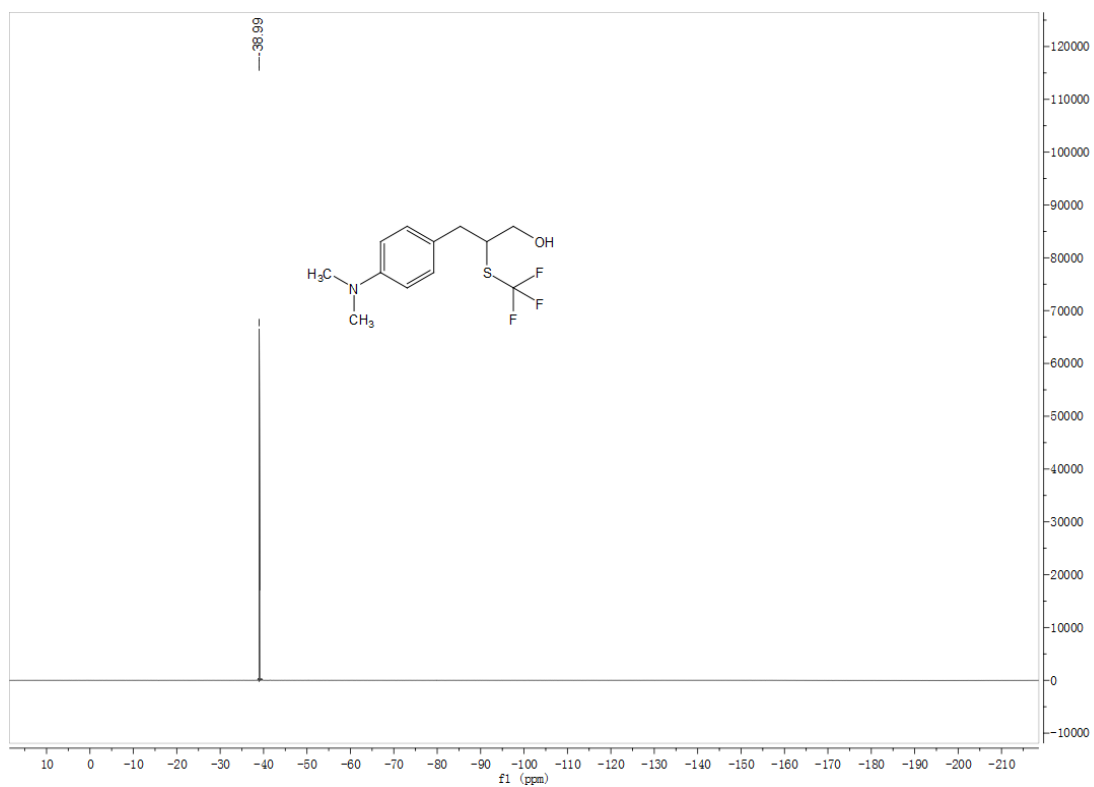
3-(4-Methoxyphenyl)-2-(trifluoromethyl)thio-1-propanol (3d):



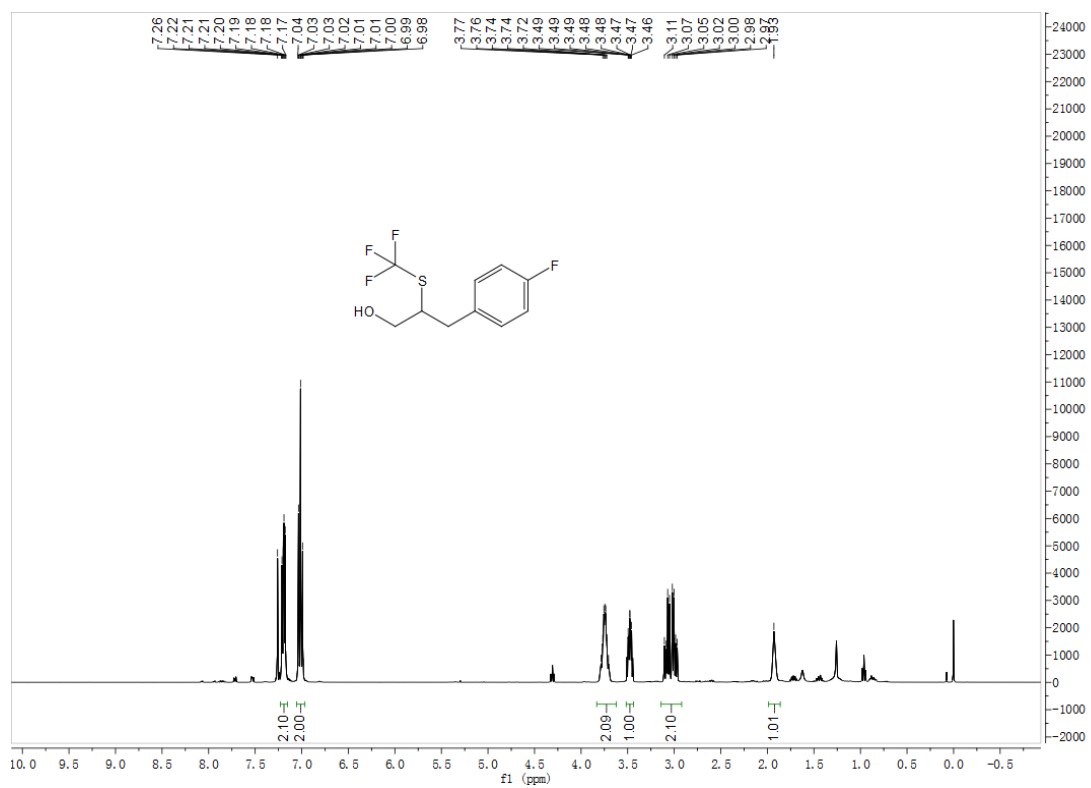


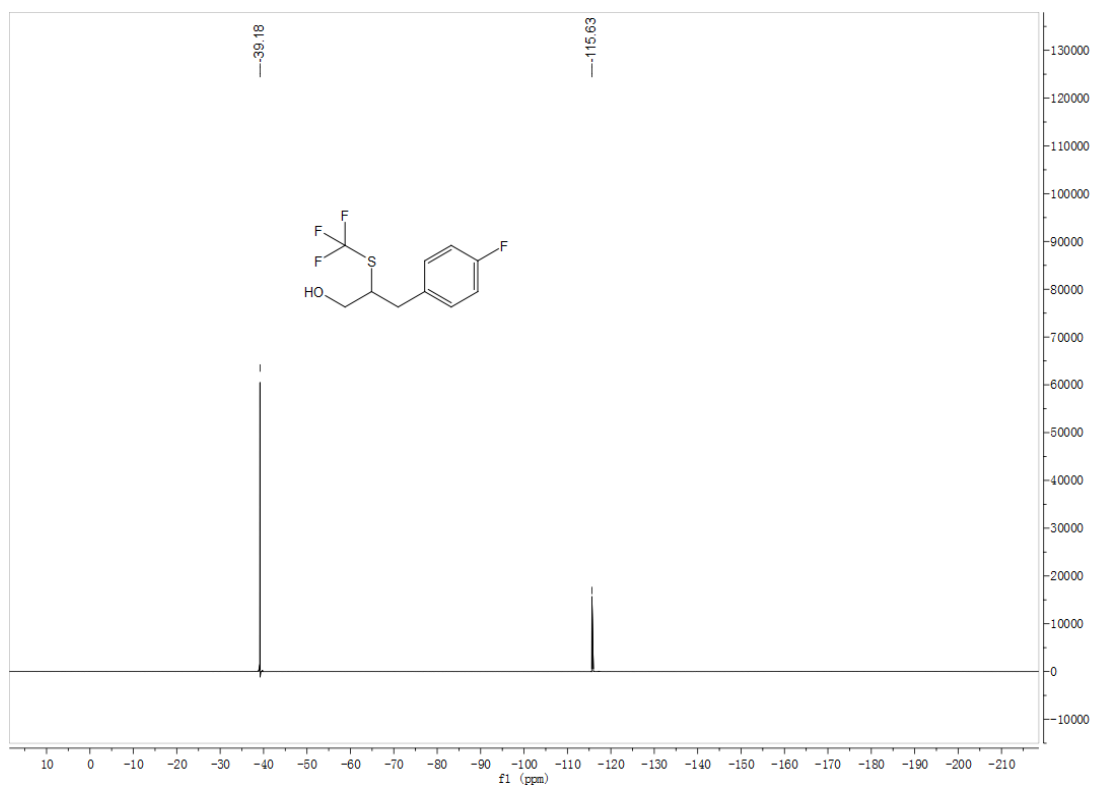
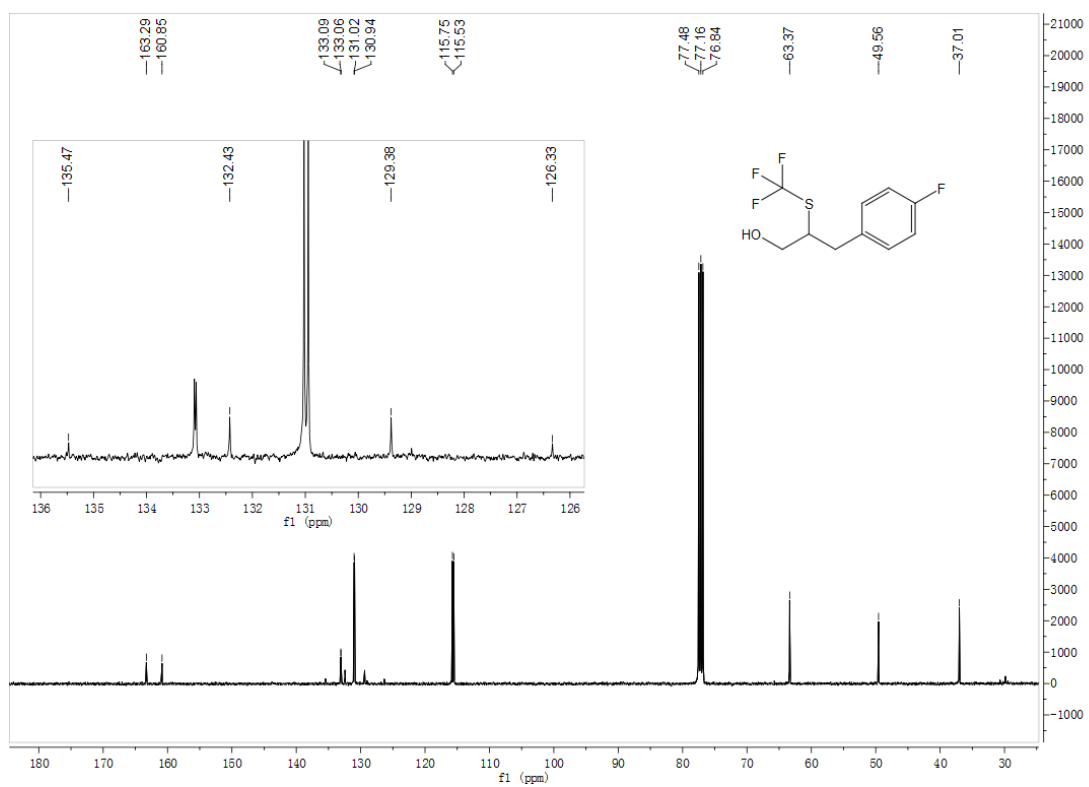
3-(4-(Dimethylamino)phenyl)-2-((trifluoromethyl)thio)propan-1-ol (3e):



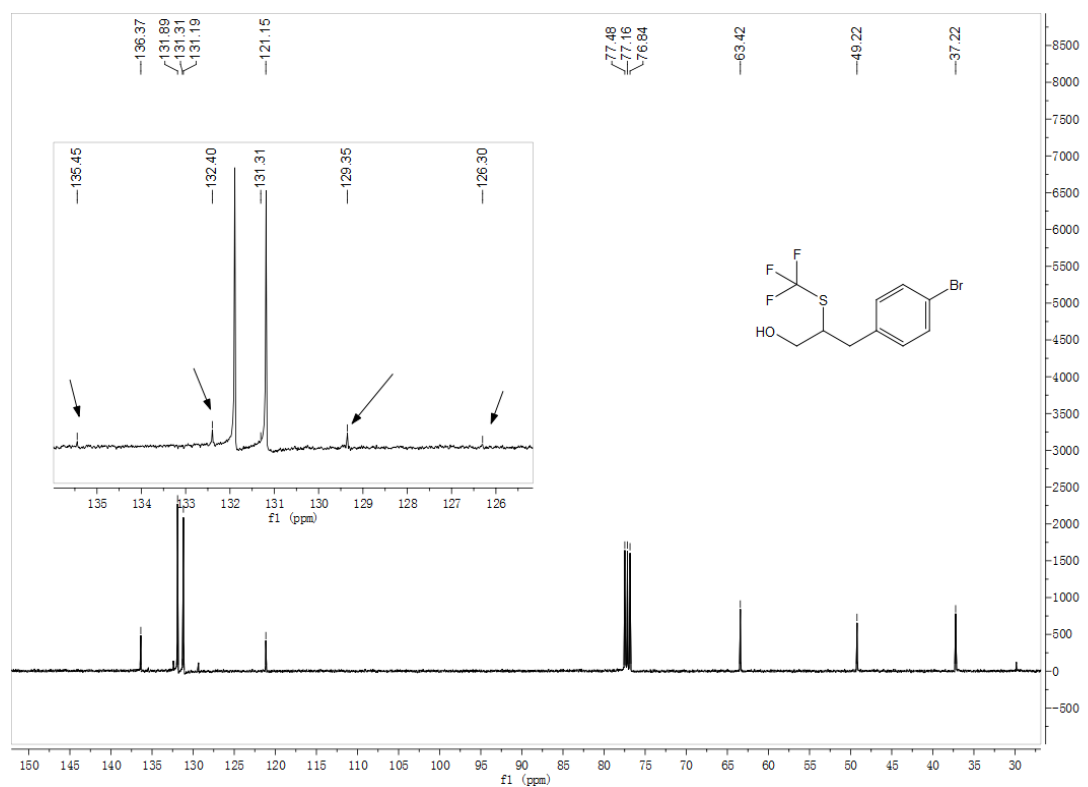
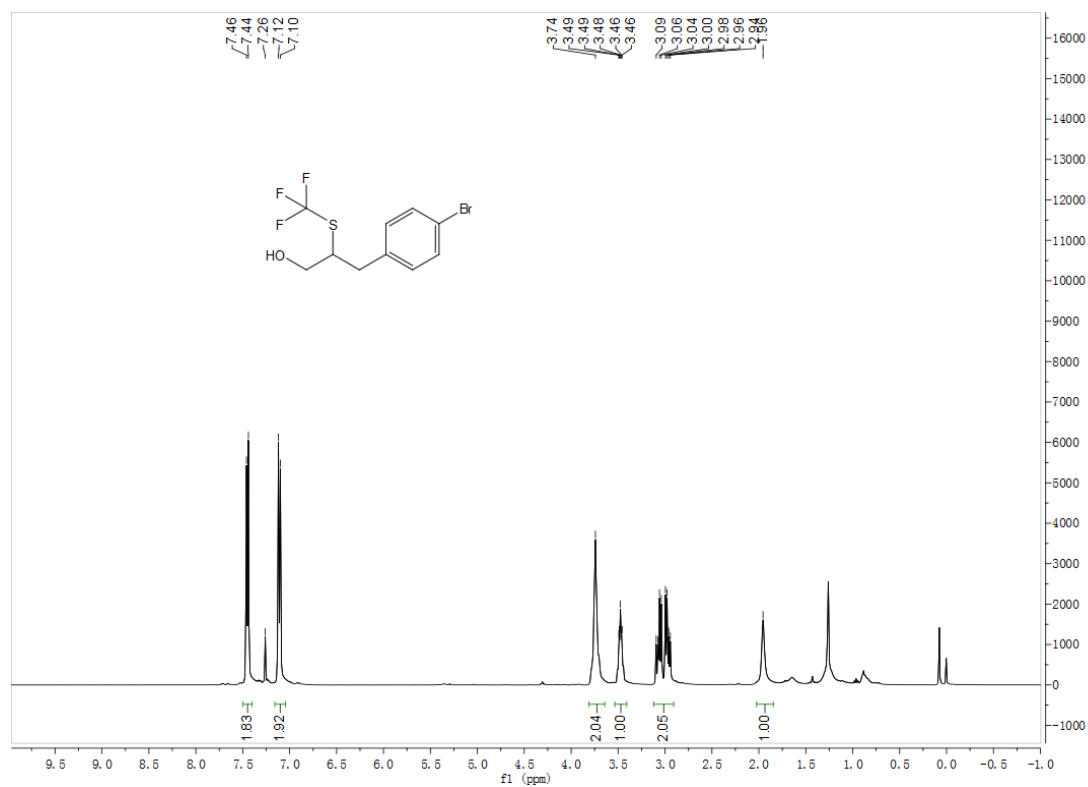


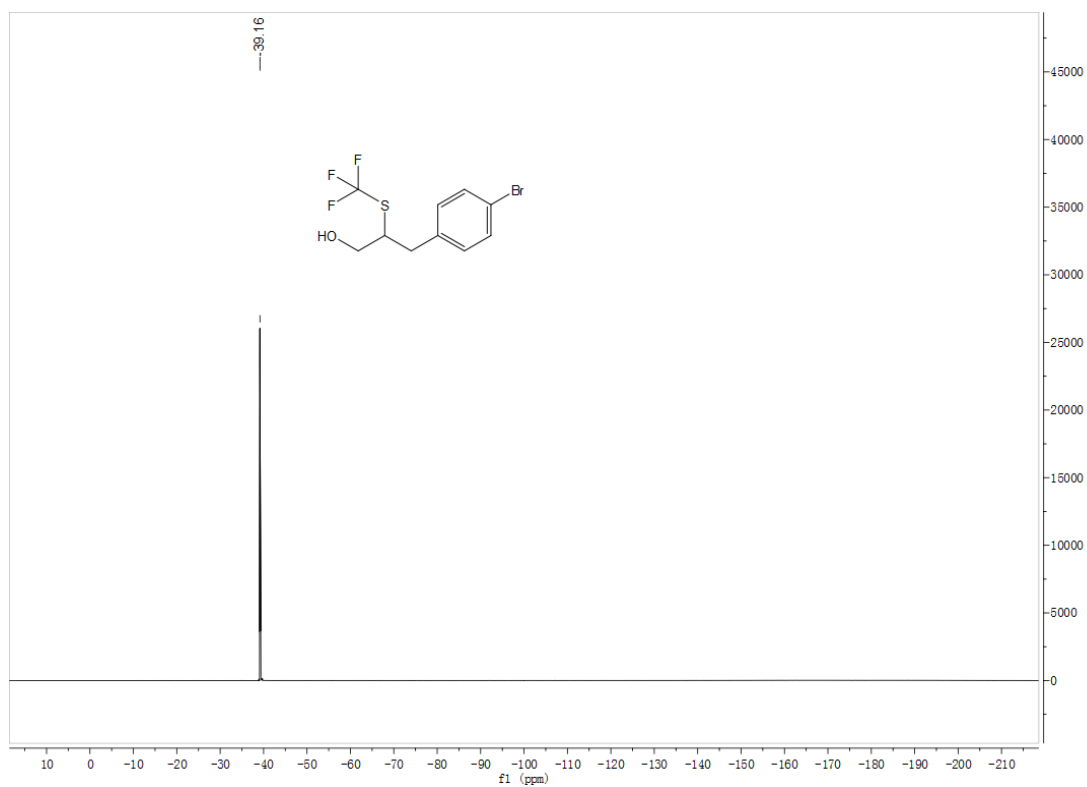
3-(4-Fluorophenyl)-2-((trifluoromethyl)thio)propan-1-ol (3f):



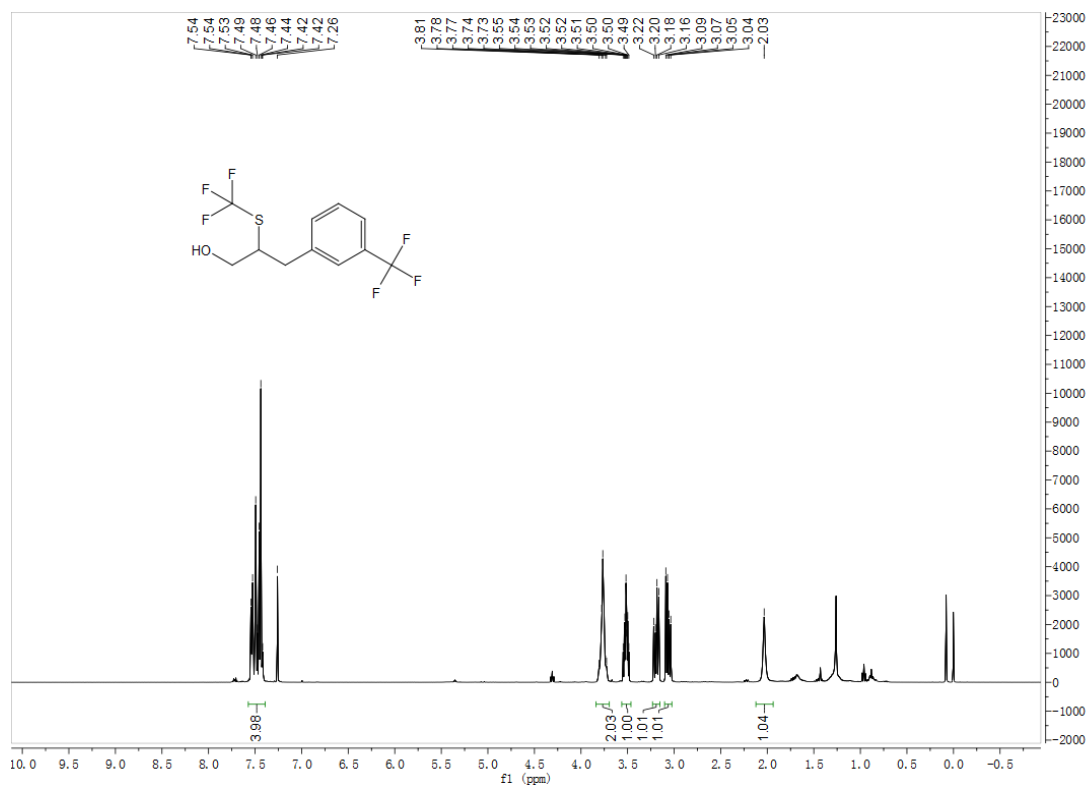


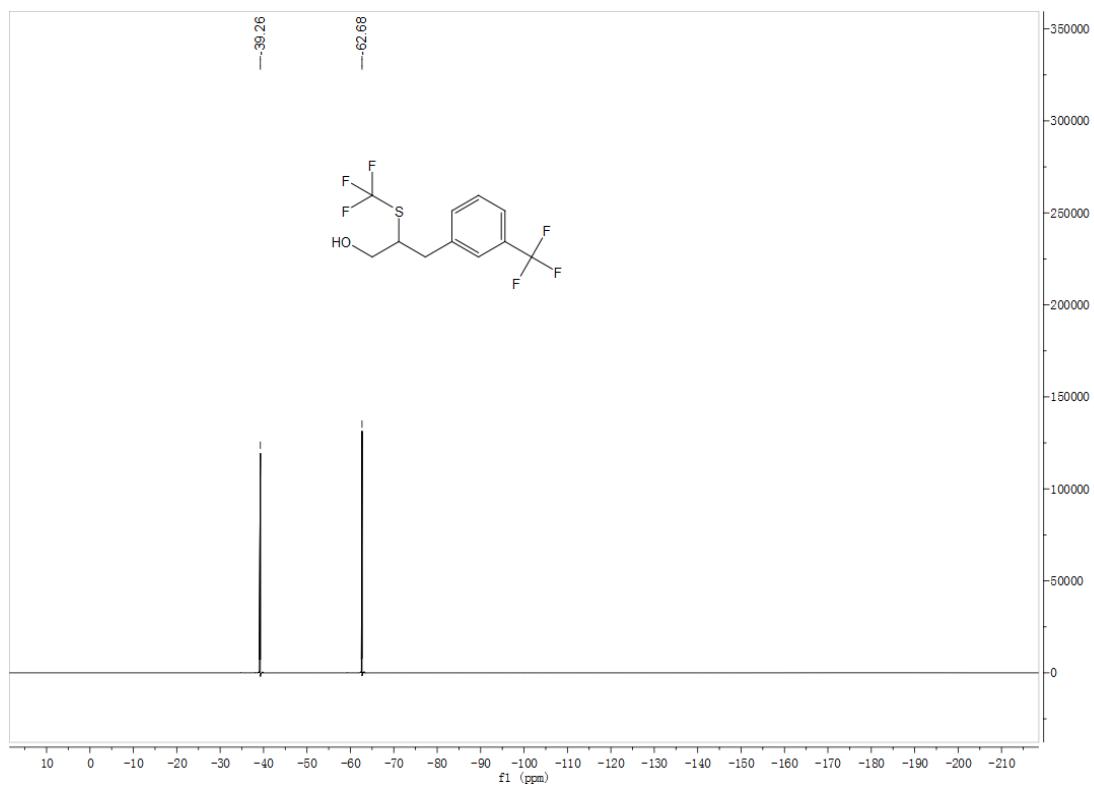
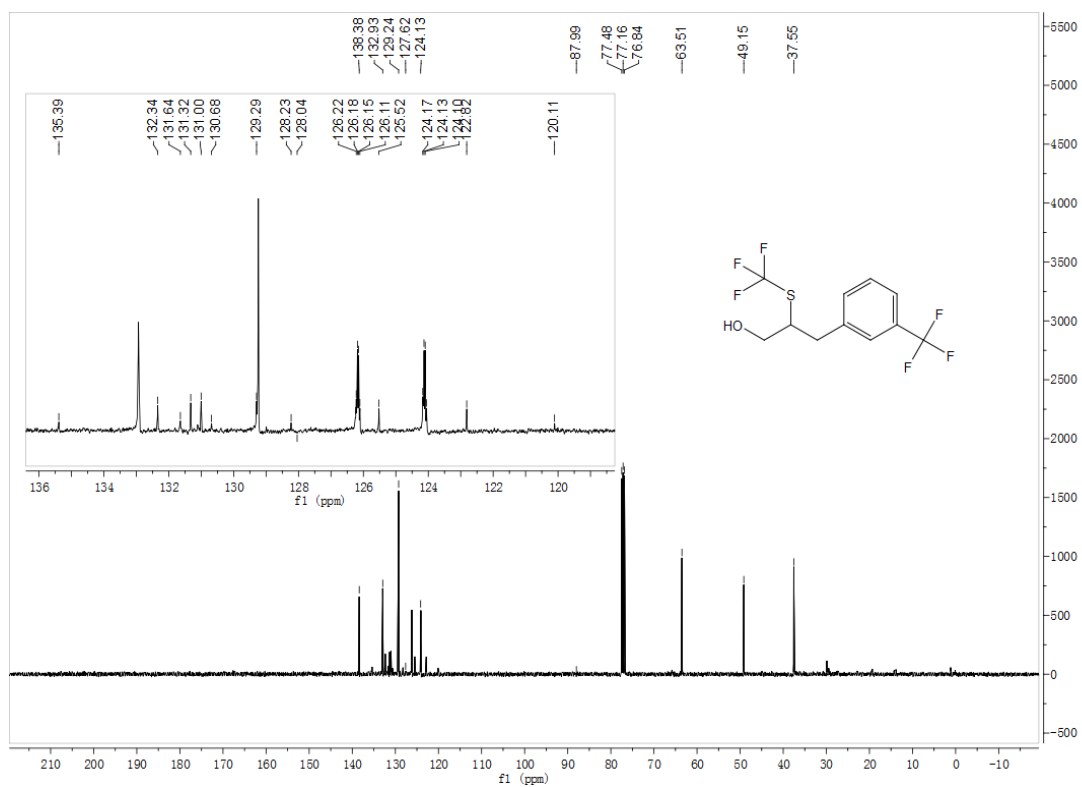
3-(4-Bromophenyl)-2-((trifluoromethyl)thio)propan-1-ol (3g):



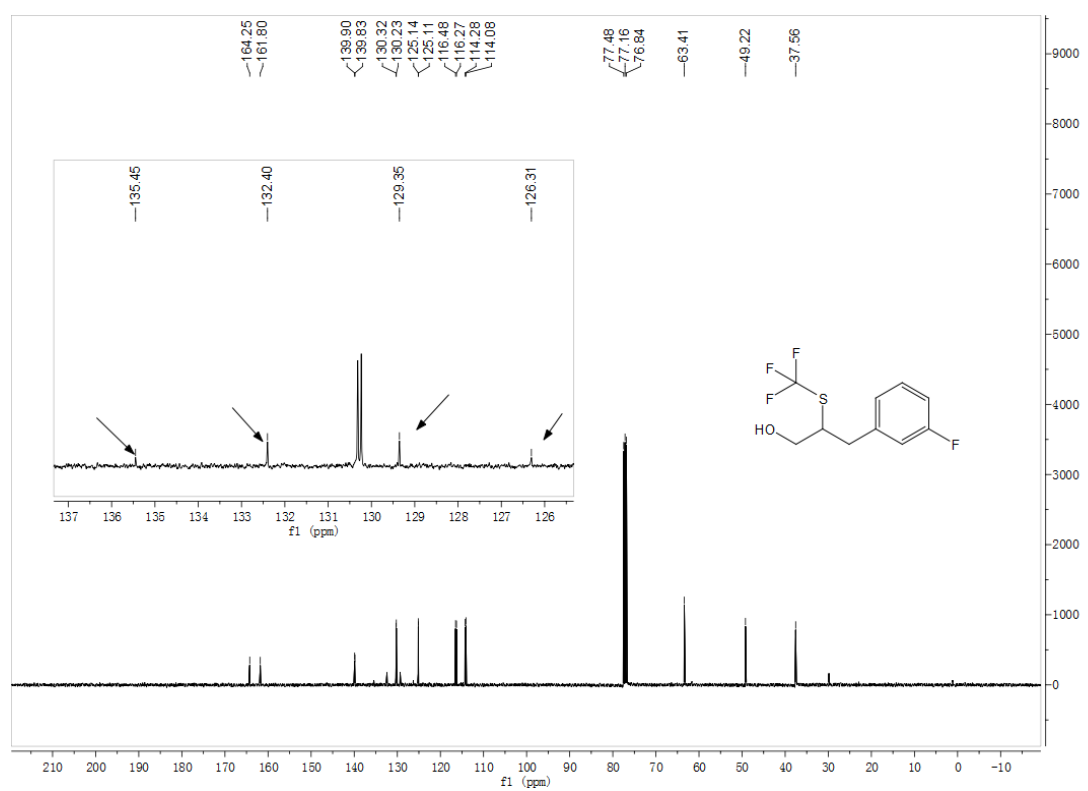
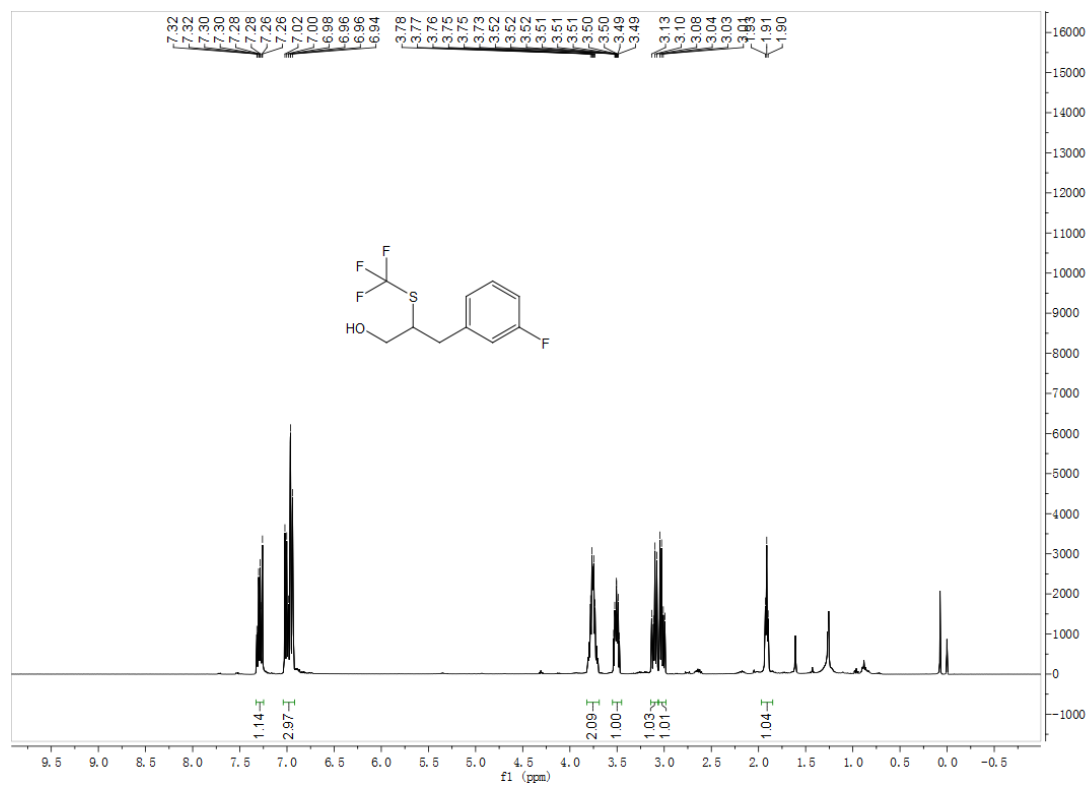


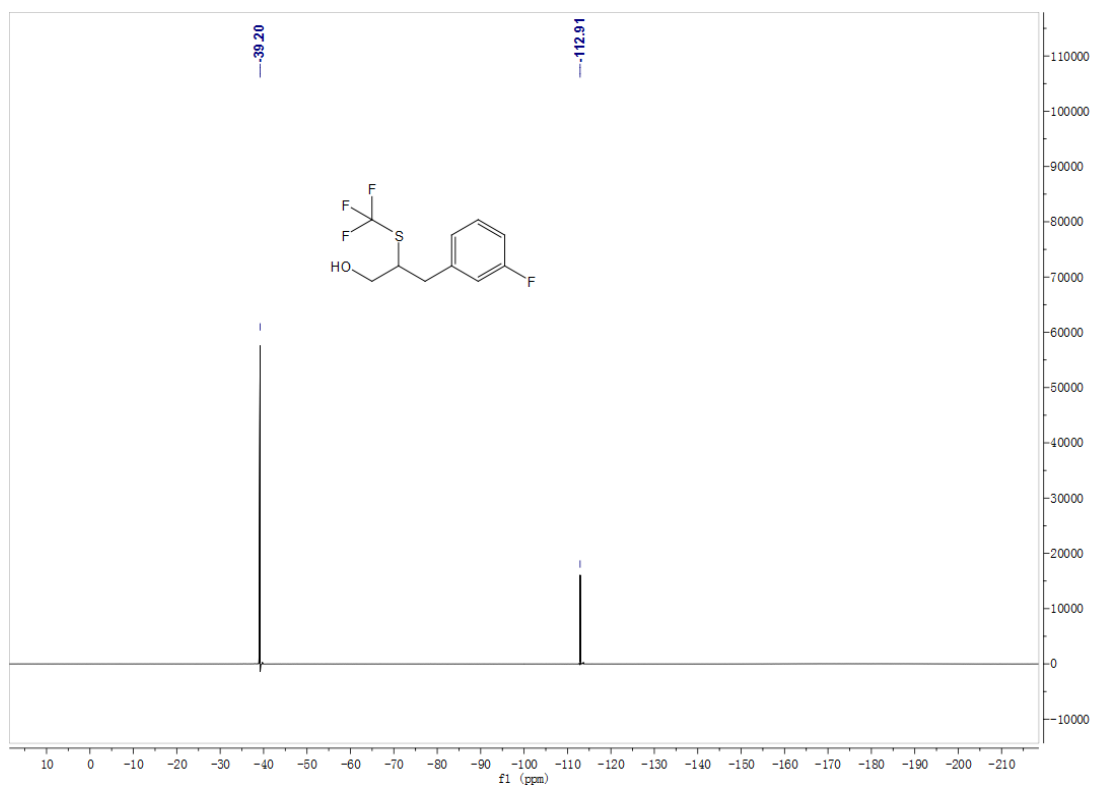
3-(3-(Trifluoromethyl)phenyl)-2-((trifluoromethyl)thio)propan-1-ol (3h)



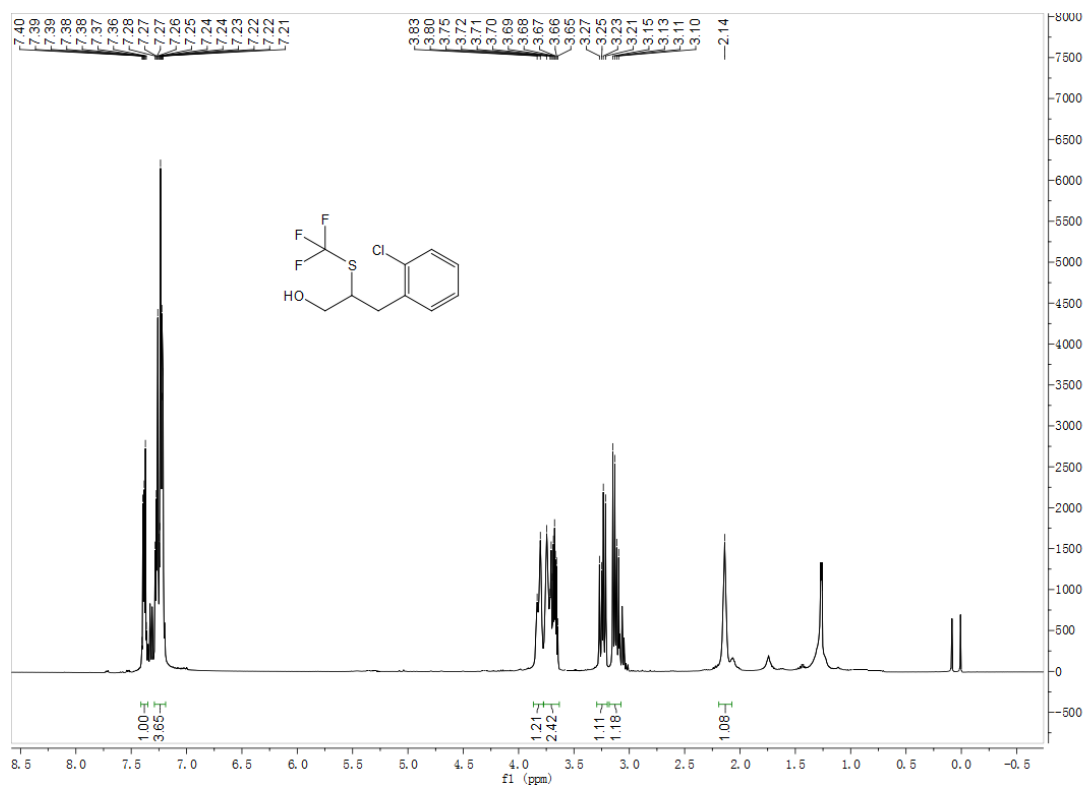


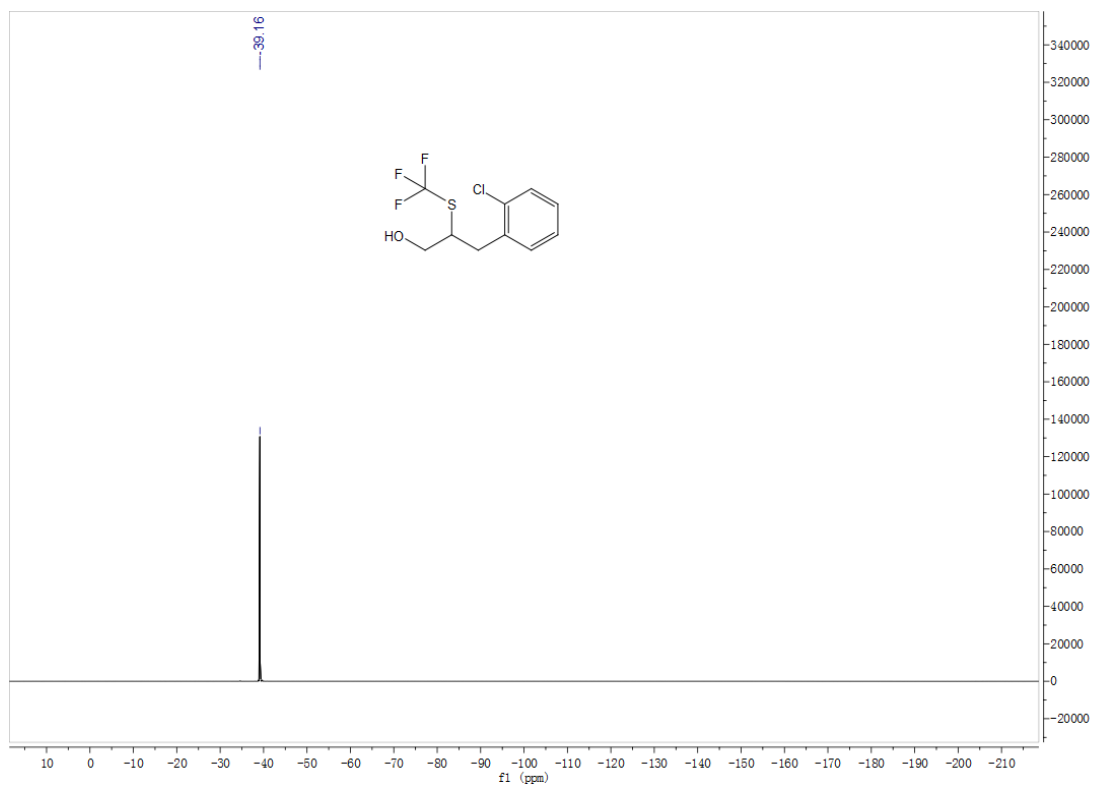
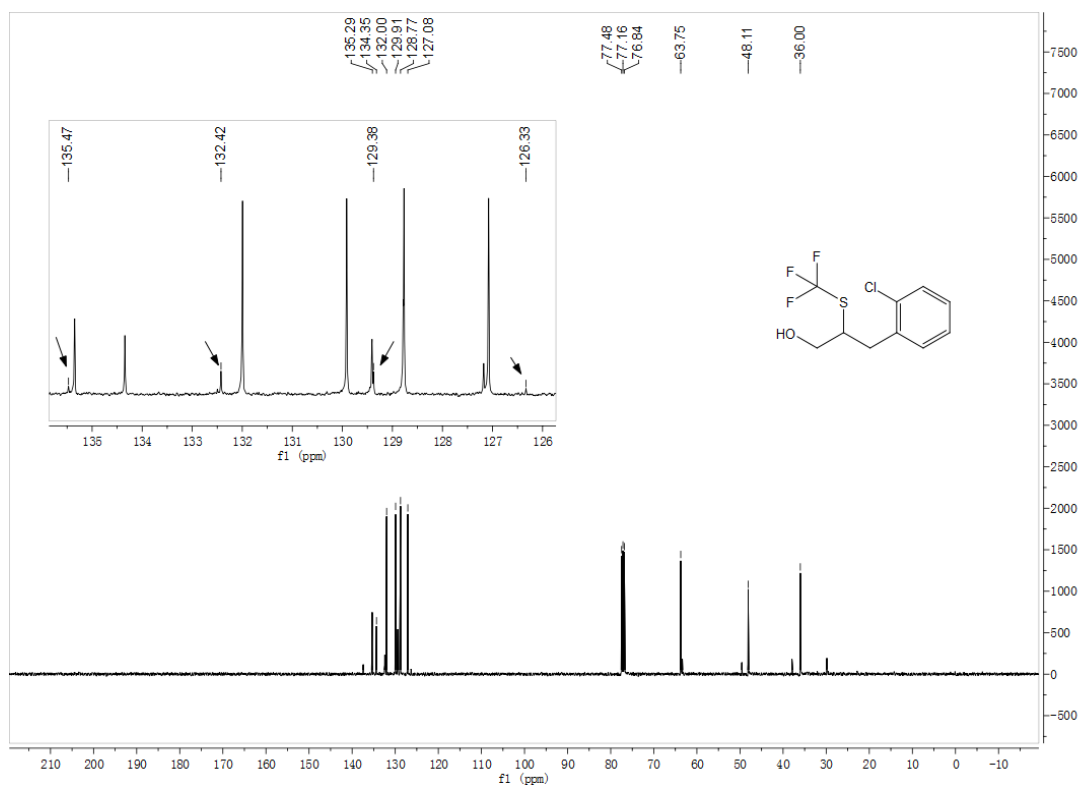
3-(3-Fluorophenyl)-2-((trifluoromethyl)thio)propan-1-ol (3i):



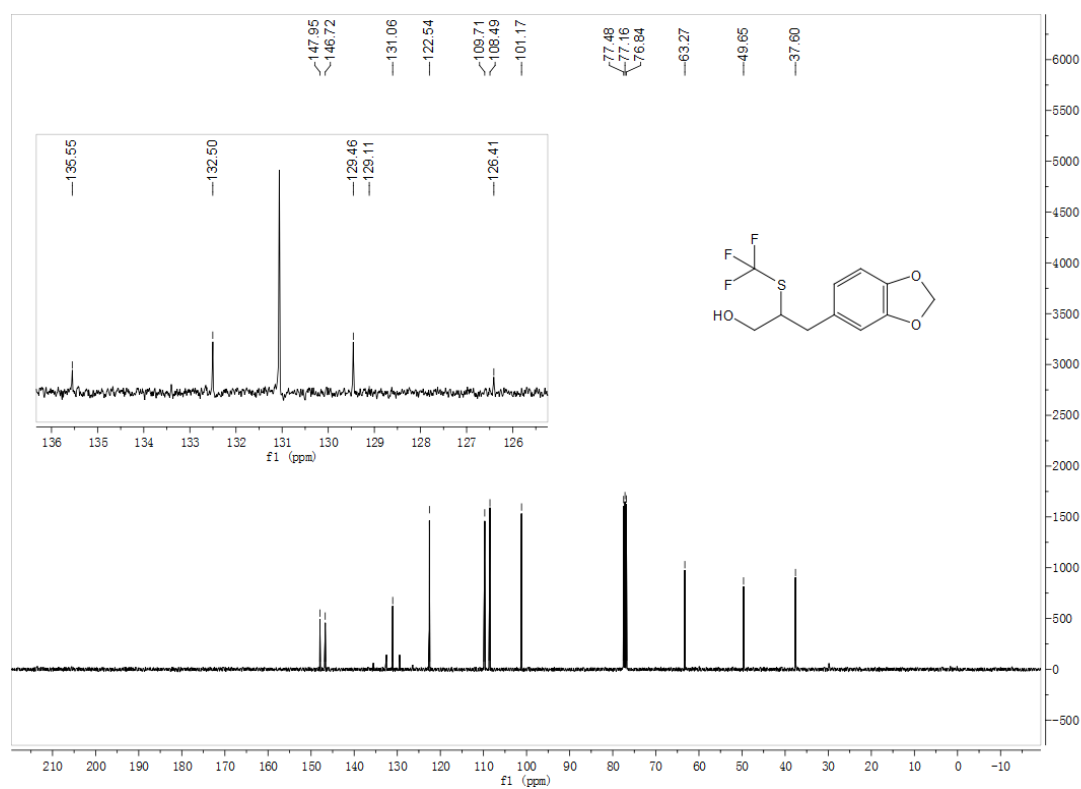
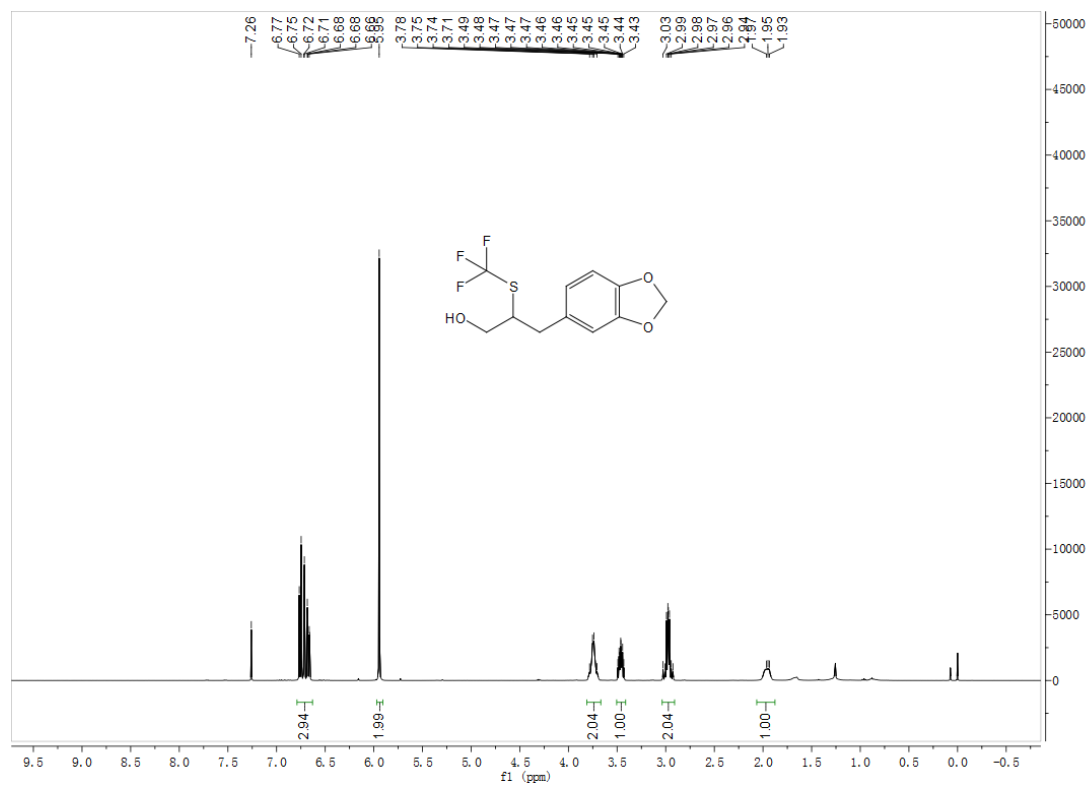


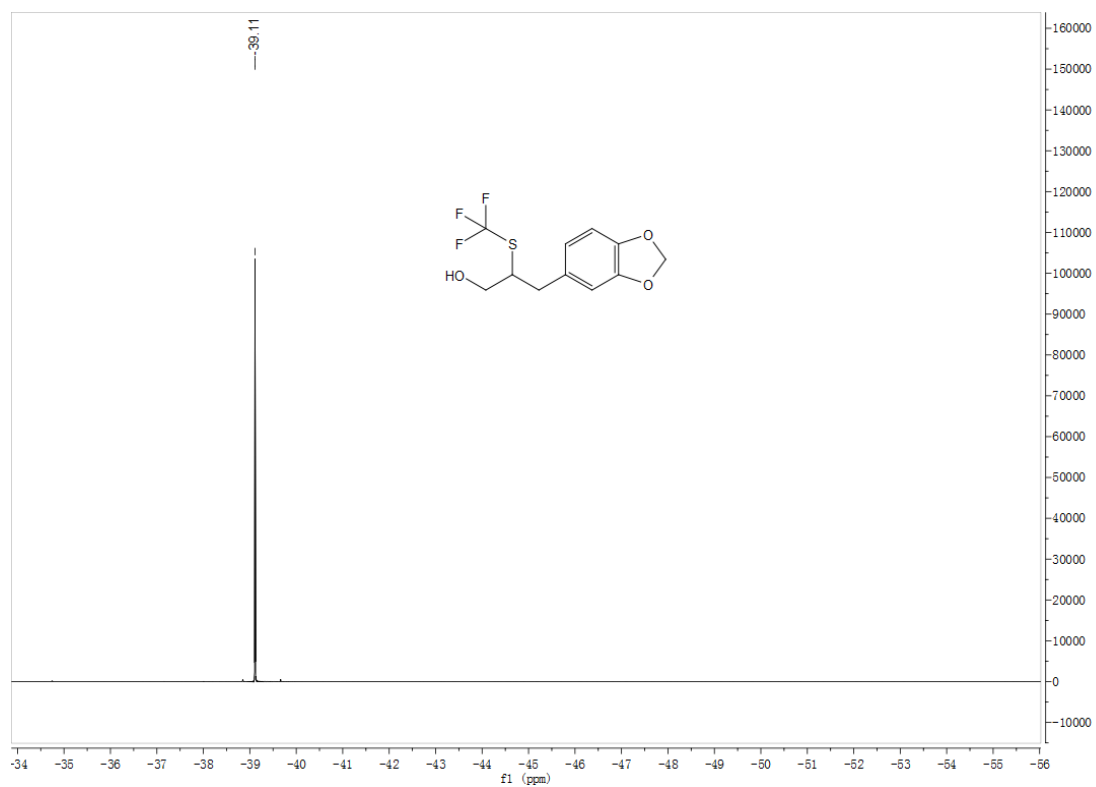
3-(2-Chlorophenyl)-2-(trifluoromethylthio)propan-1-ol (3j):



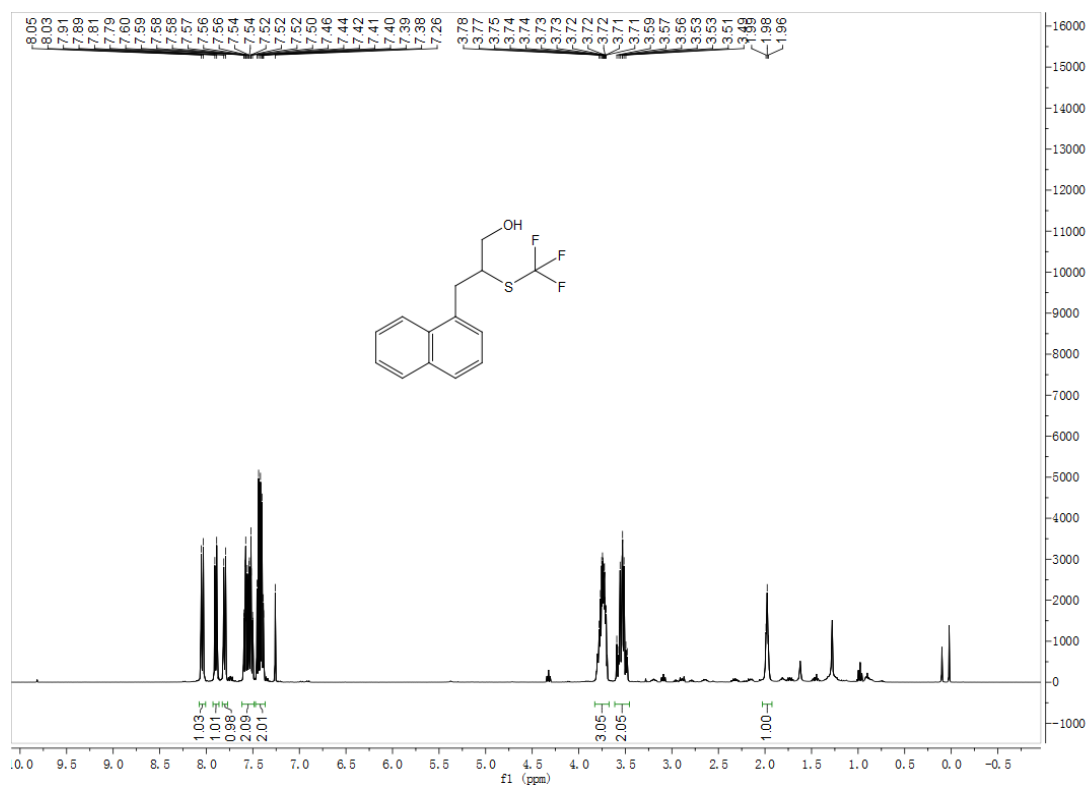


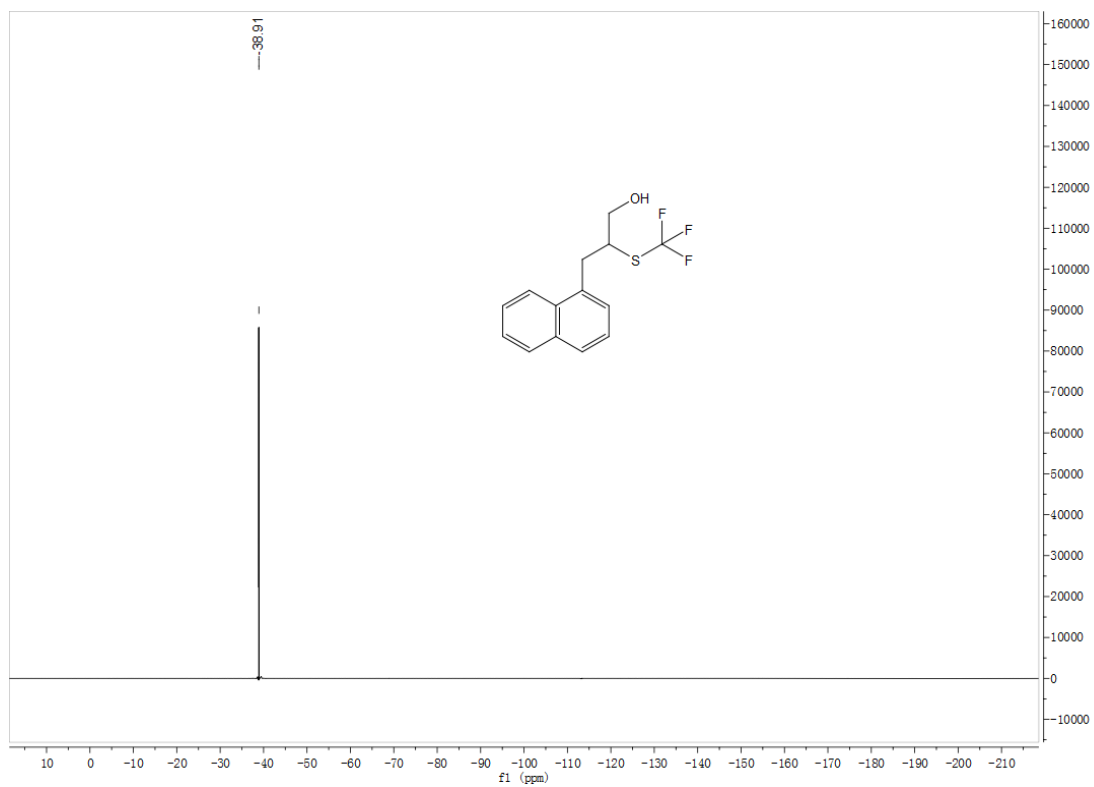
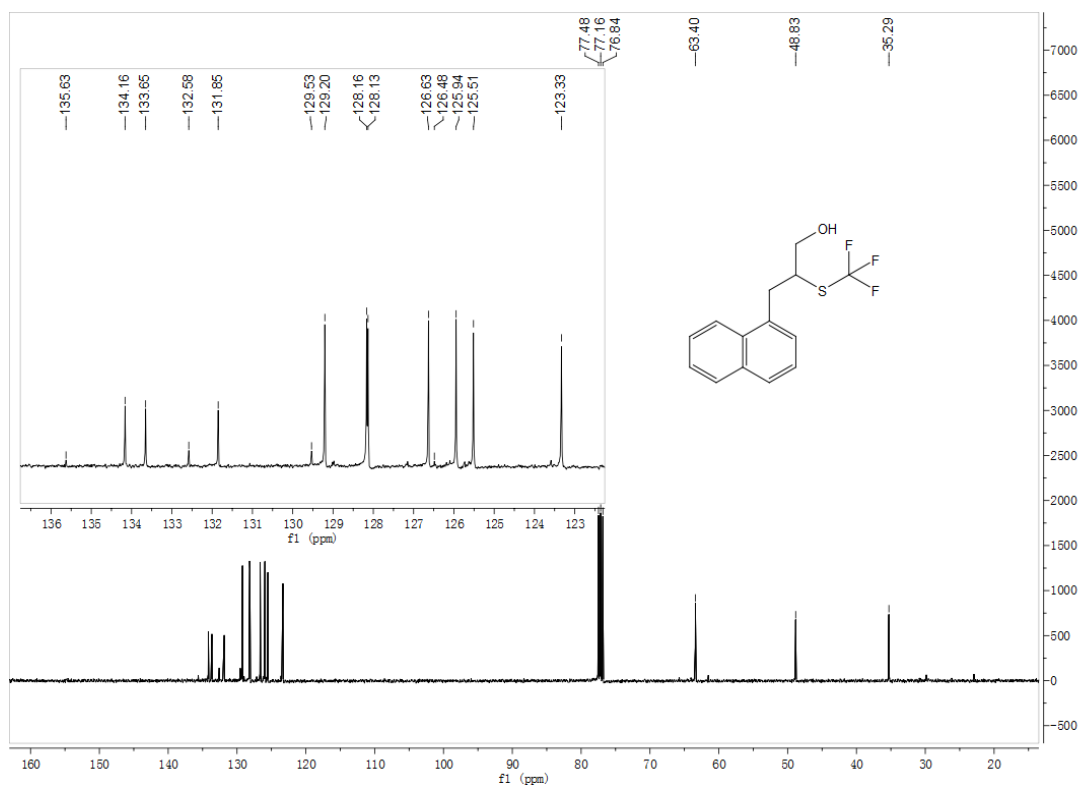
3-(Benzo[d][1,3]dioxol-5-yl)-2-((trifluoromethyl)thio)propan-1-ol (3k):



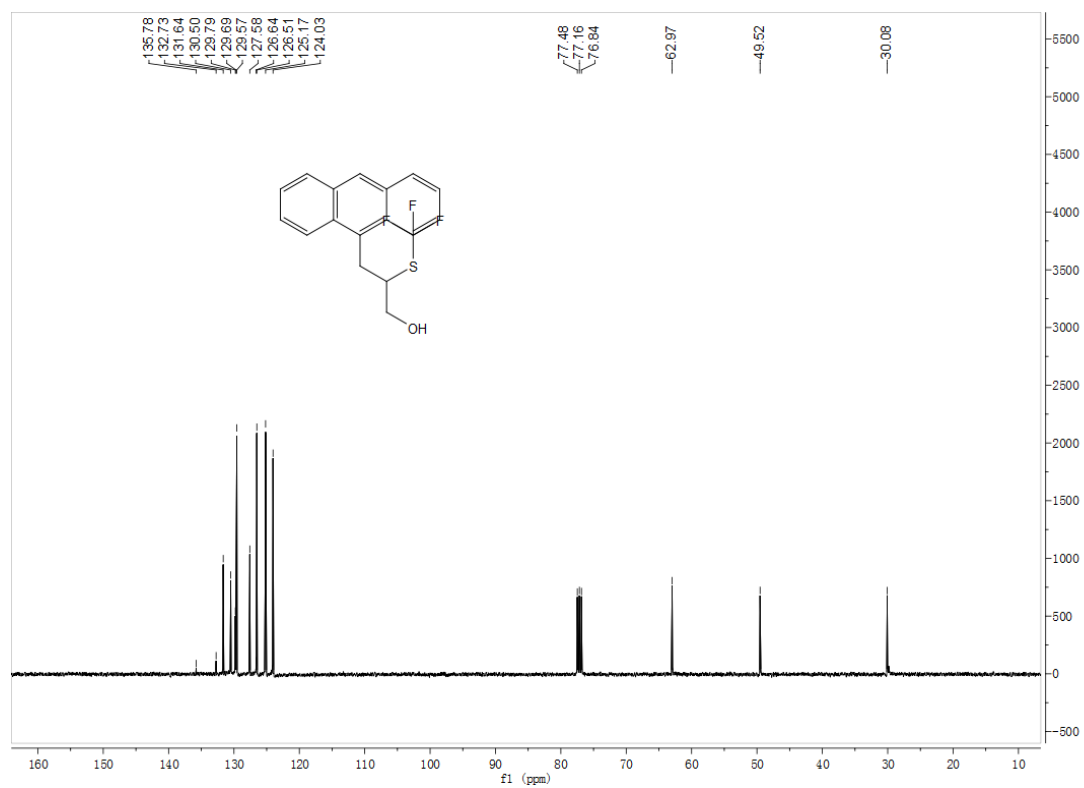
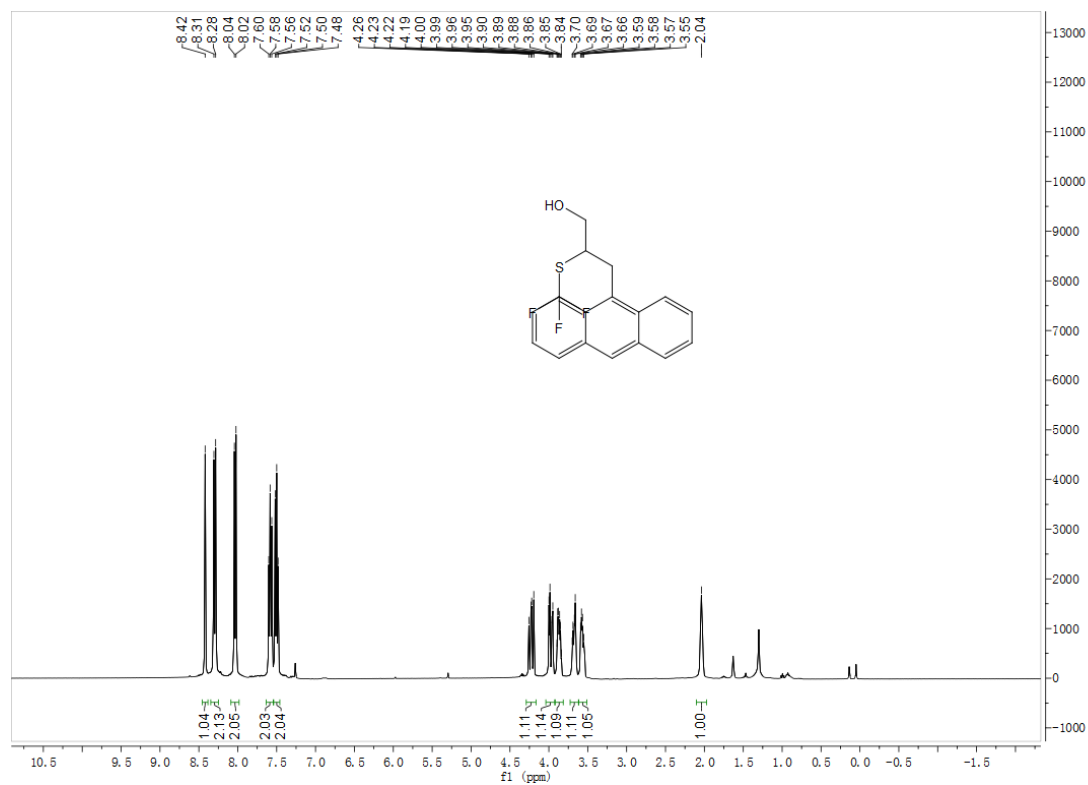


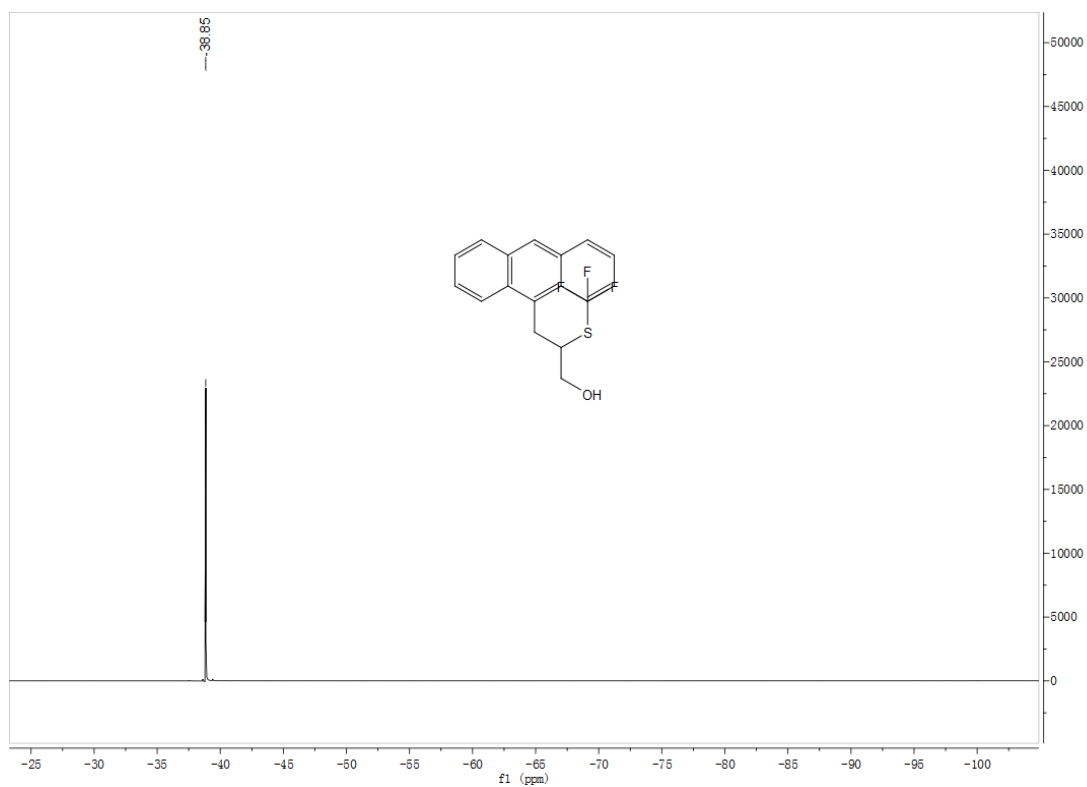
3-(Naphthalen-1-yl)-2-((trifluoromethyl)thio)propan-1-ol (3l)



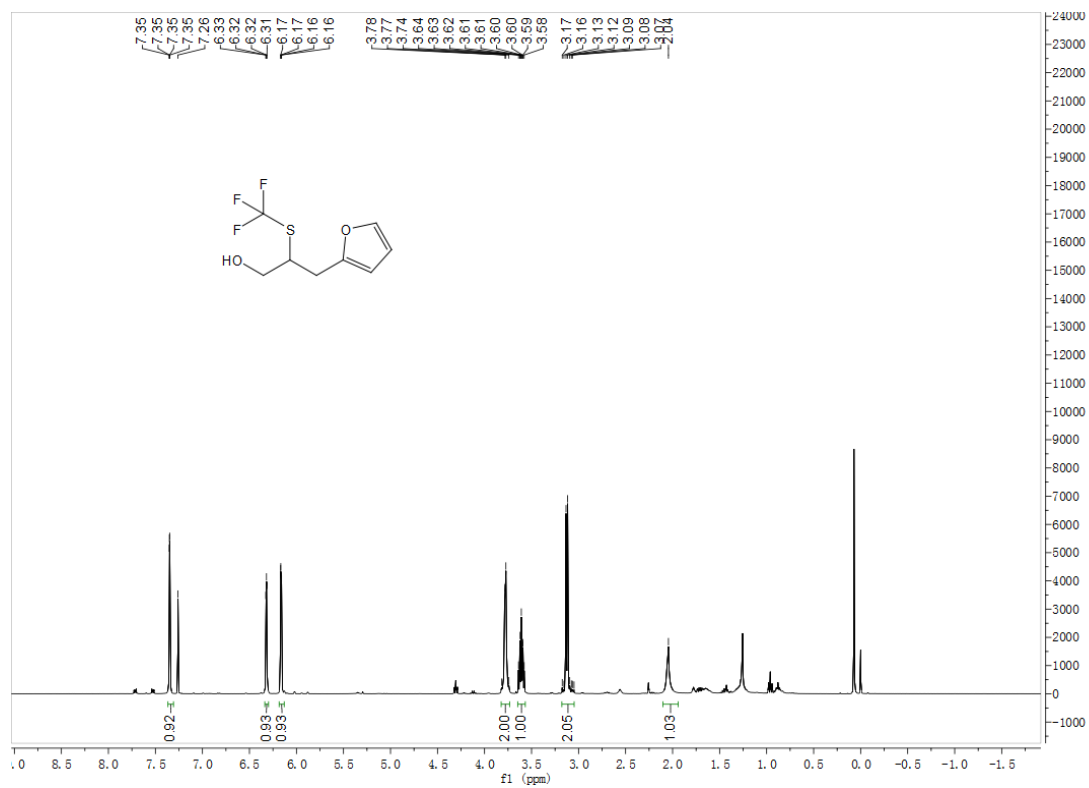


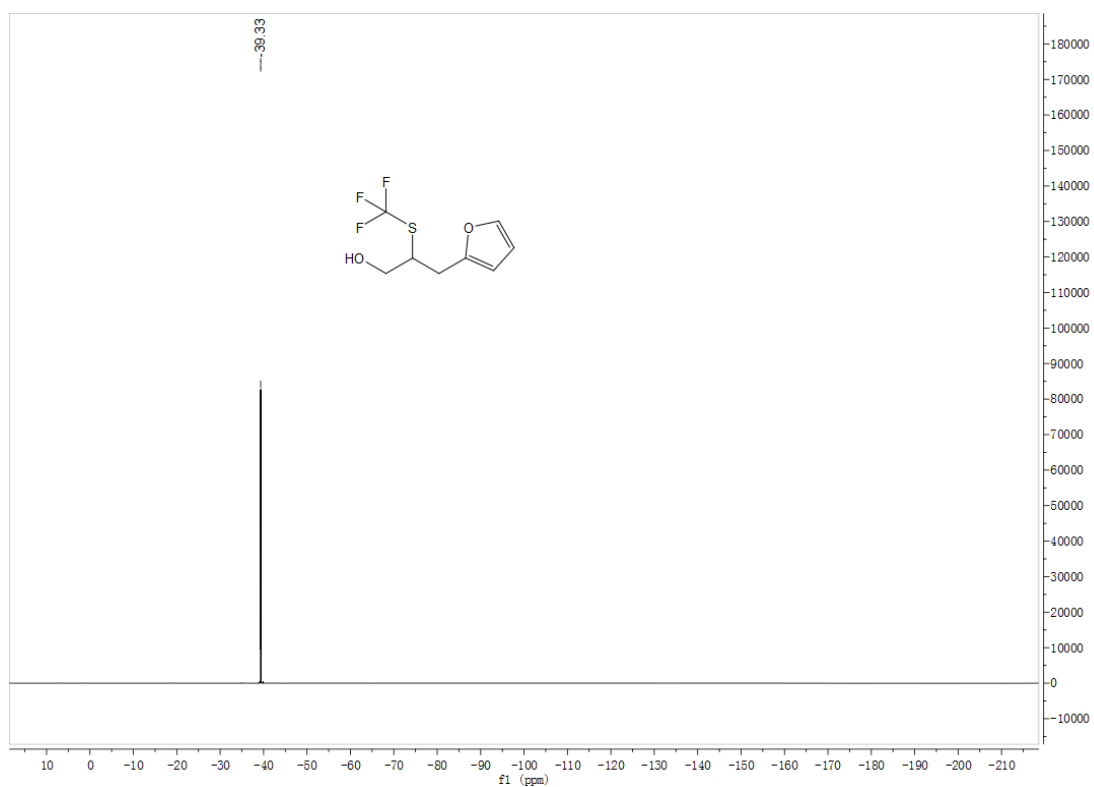
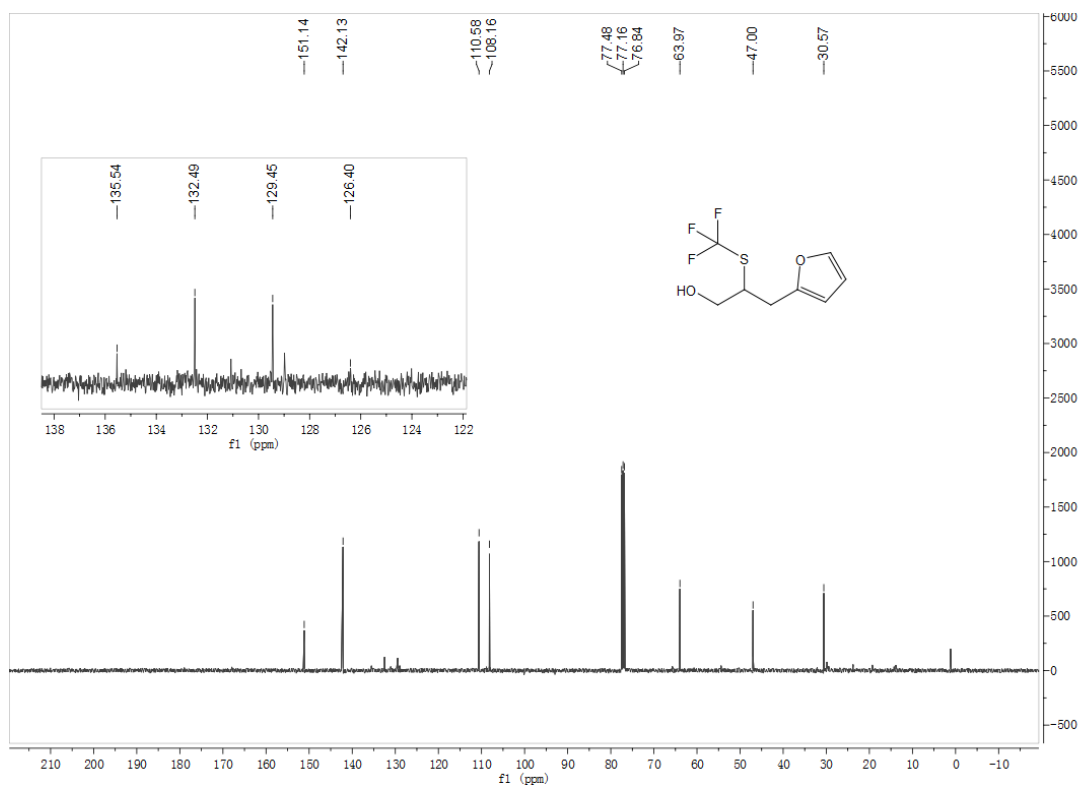
3-(Anthracen-9-yl)-2-((trifluoromethyl)thio)propan-1-ol (3m):



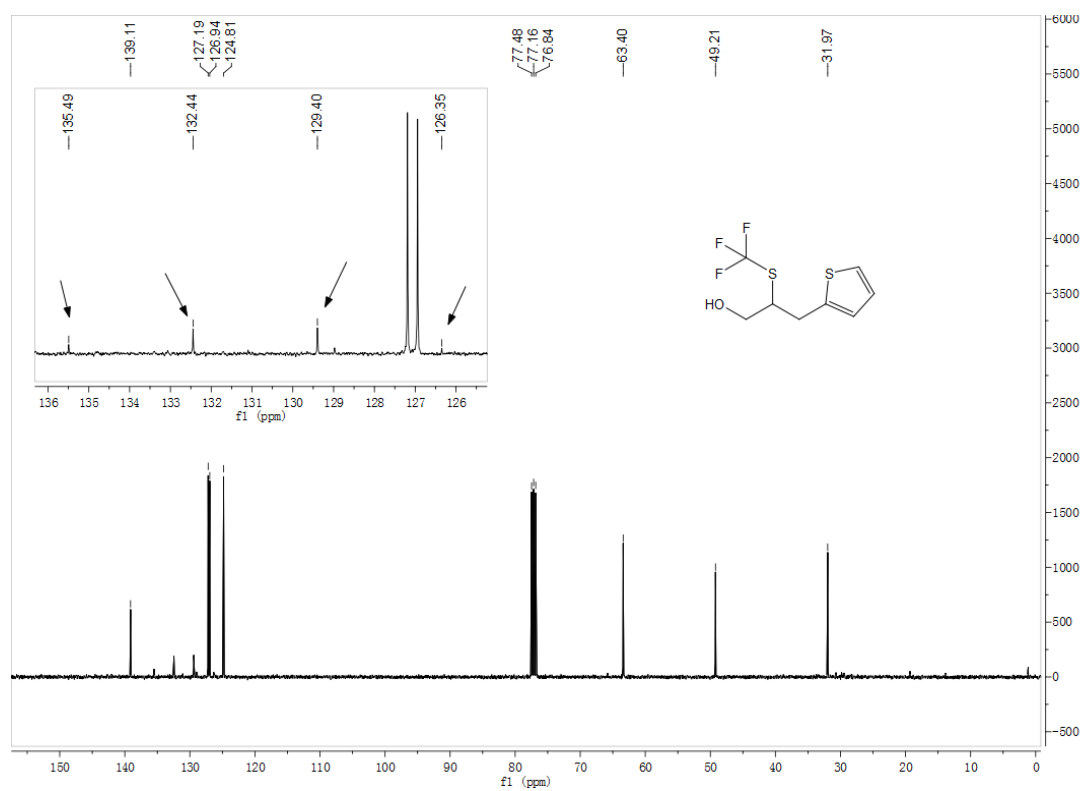
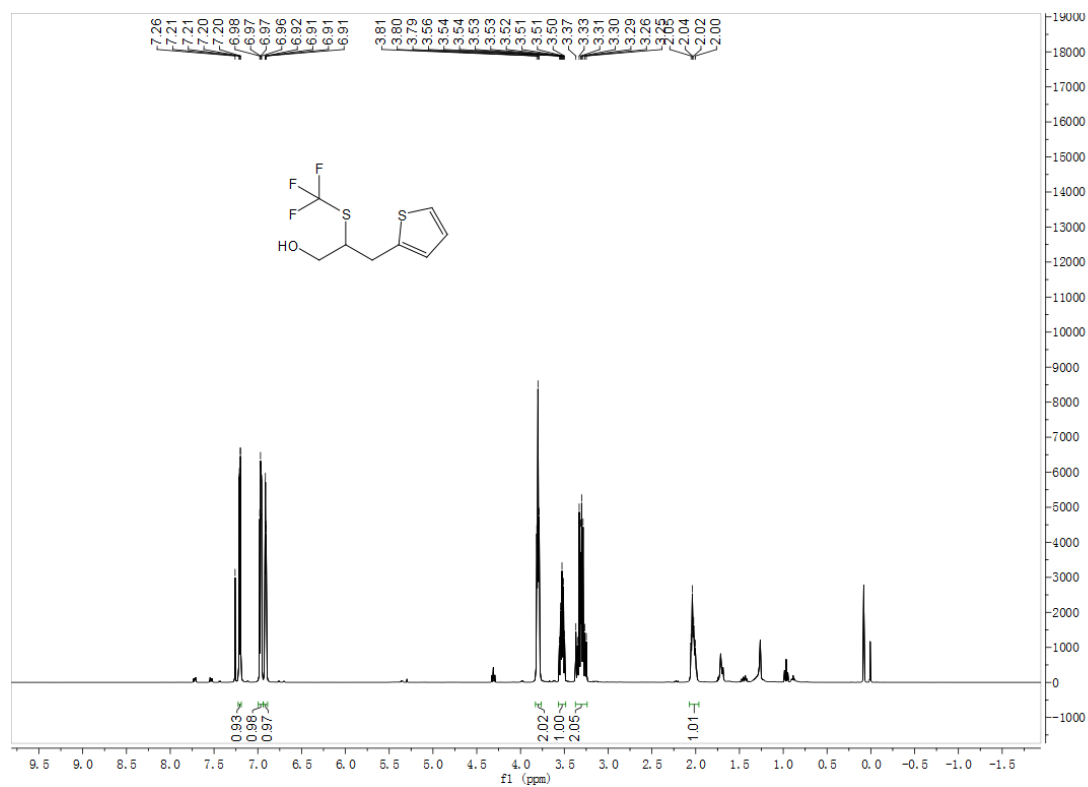


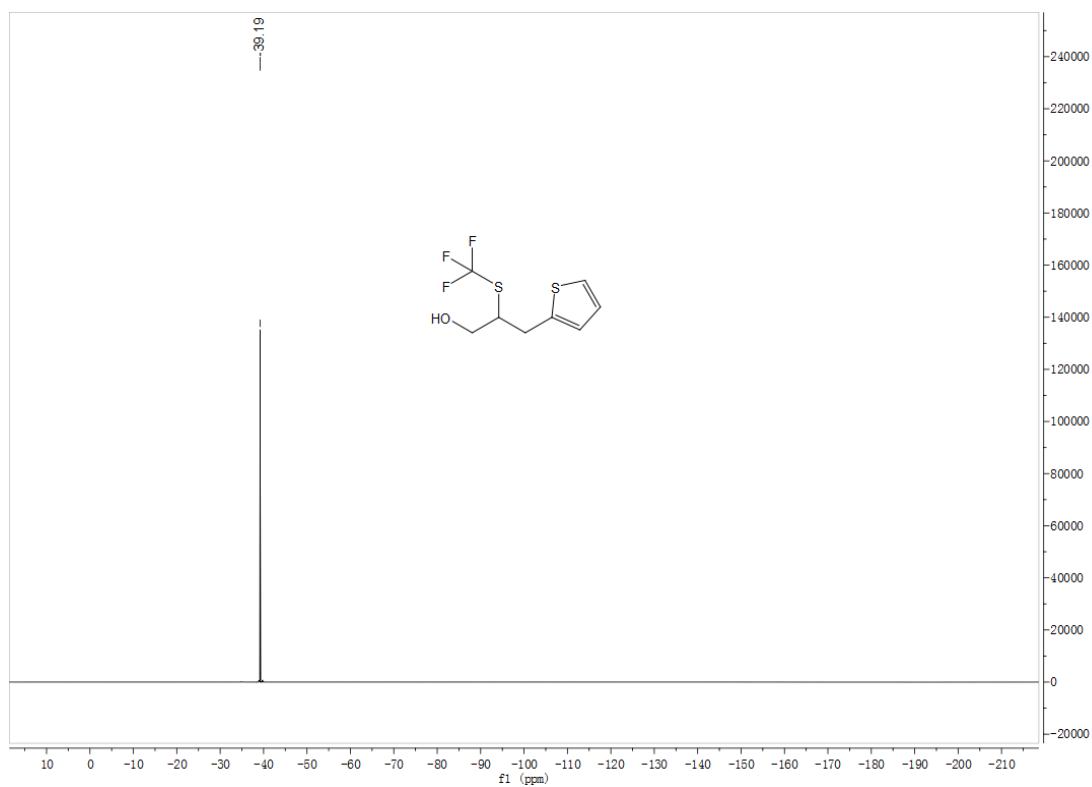
3-(Furan-2-yl)-2-((trifluoromethyl)thio)propan-1-ol (3n):



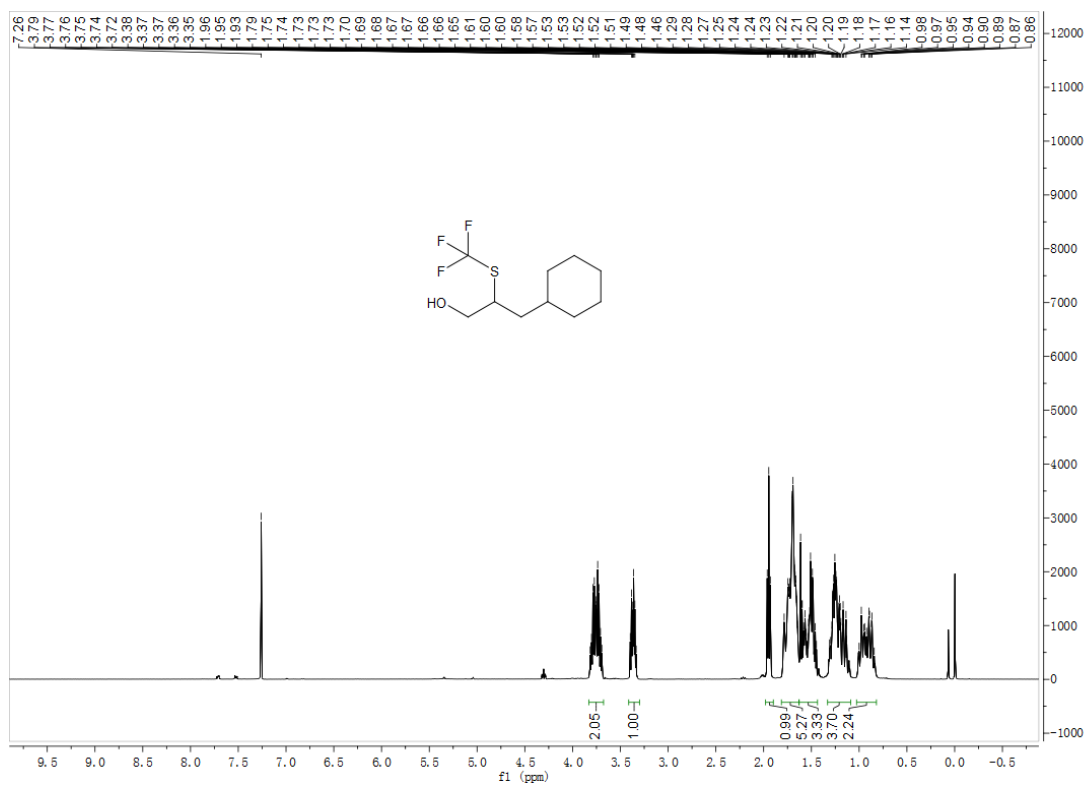


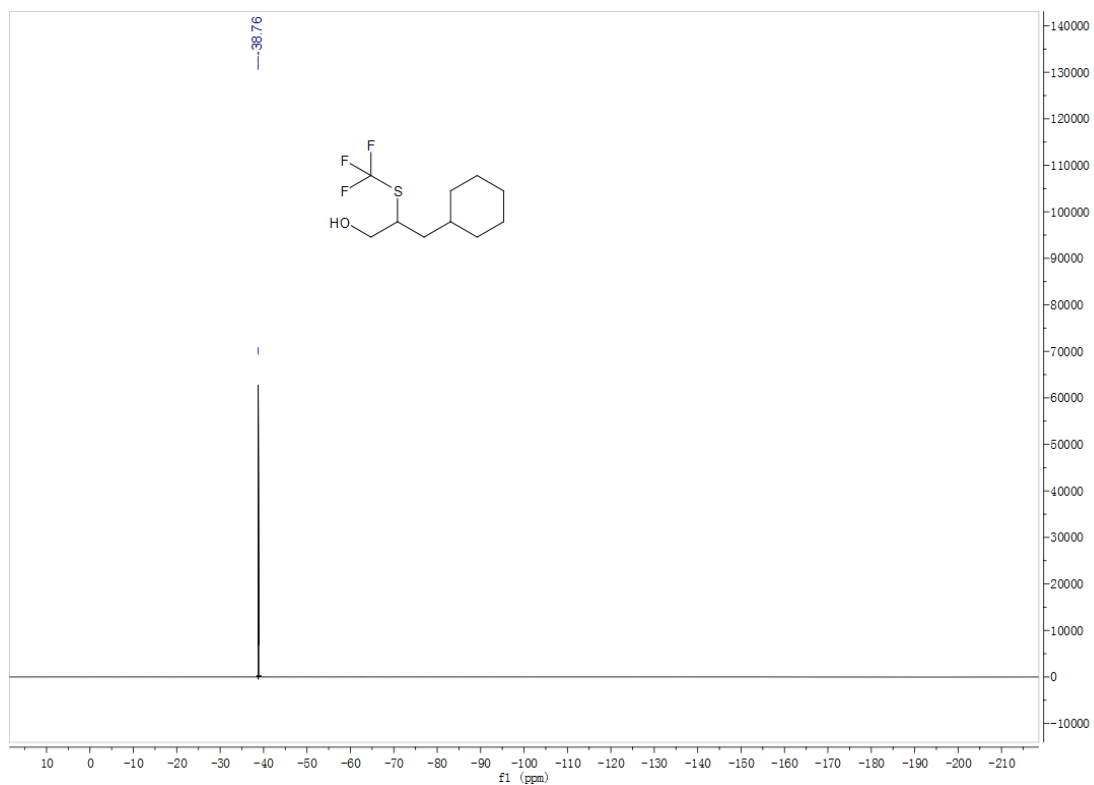
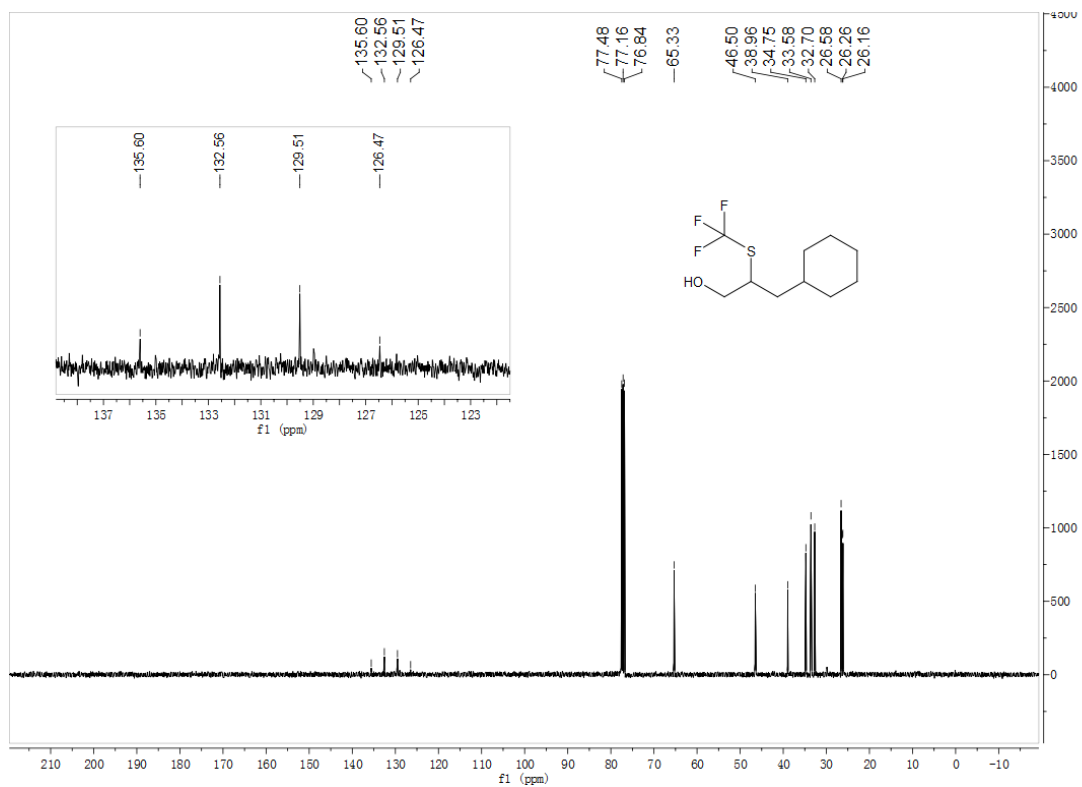
3-(Thiophen-2-yl)-2-((trifluoromethyl)thio)propan-1-ol (3o):



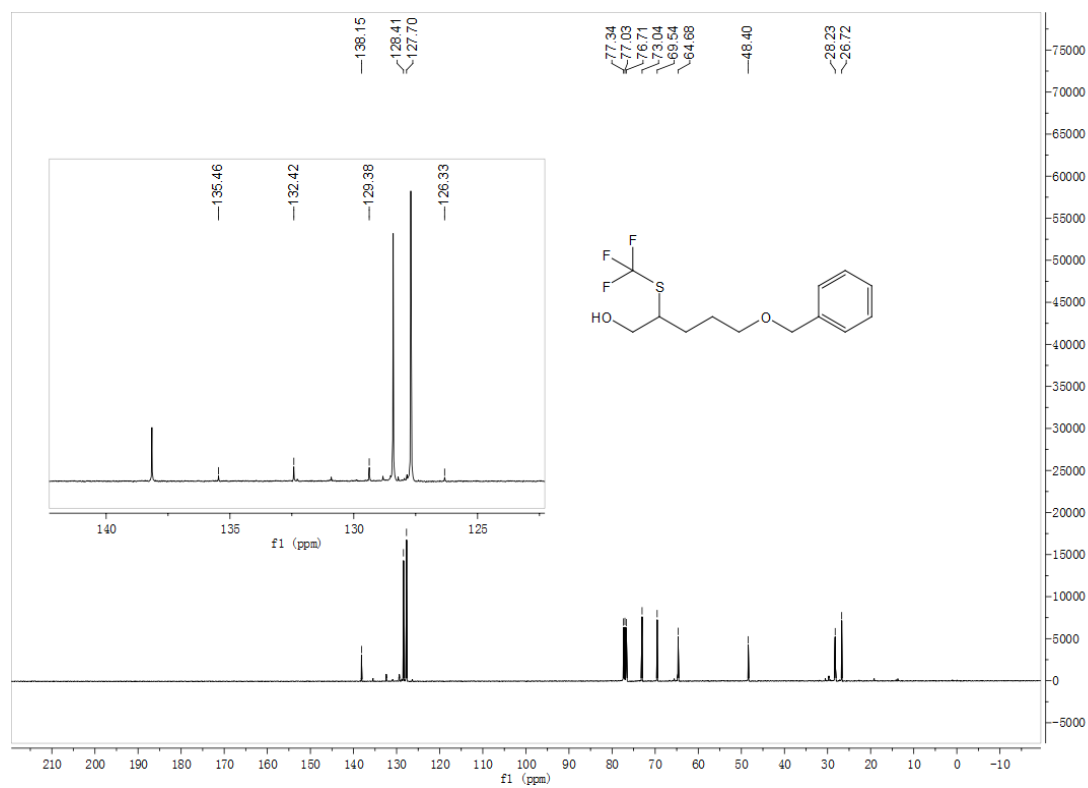
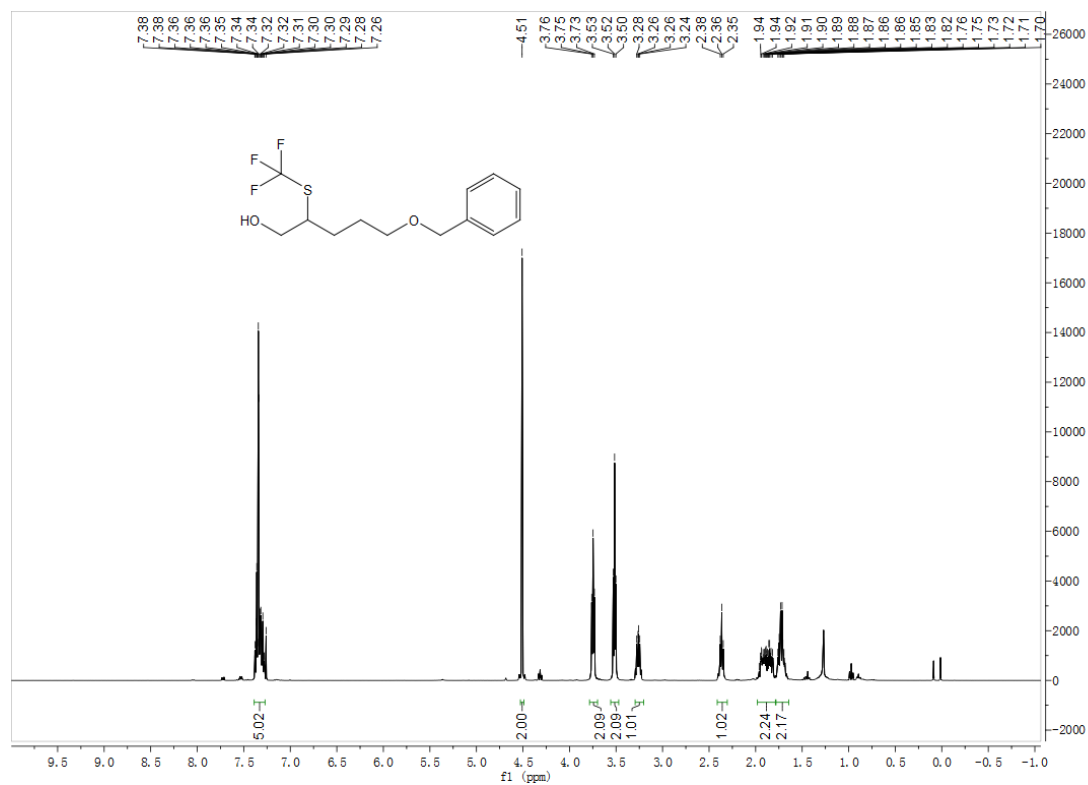


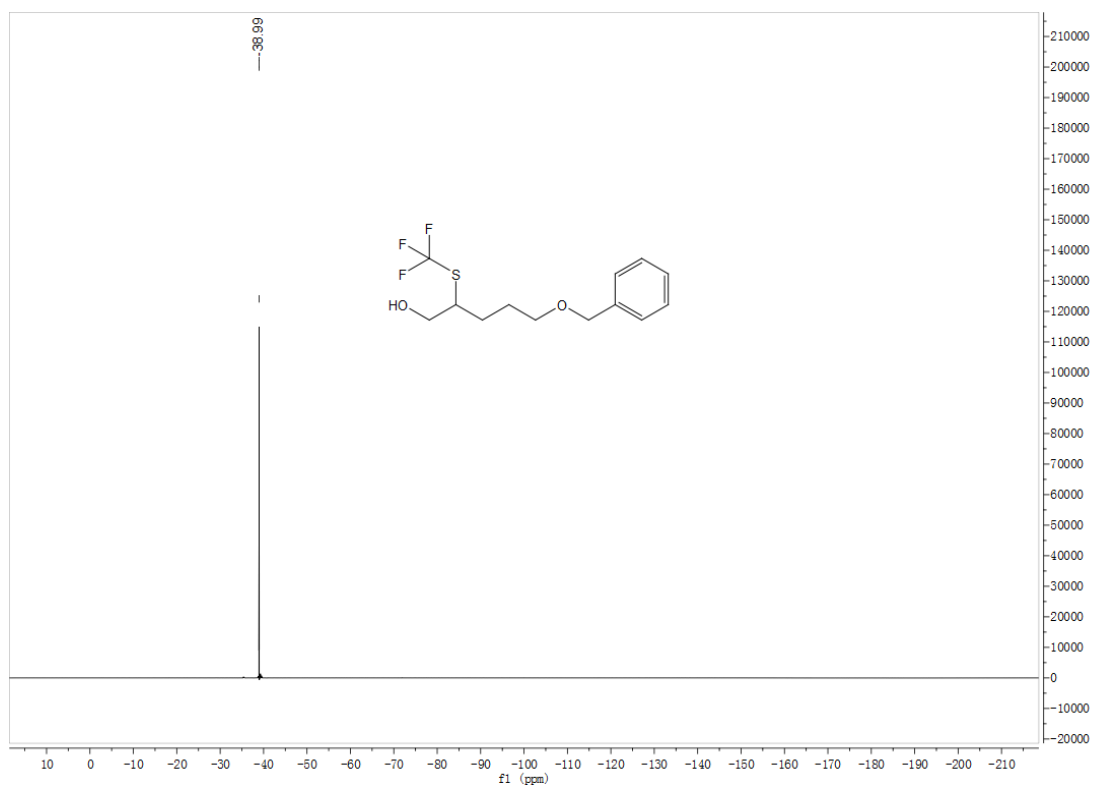
3-Cyclohexyl-2-((trifluoromethyl)thio)propan-1-ol (3p):



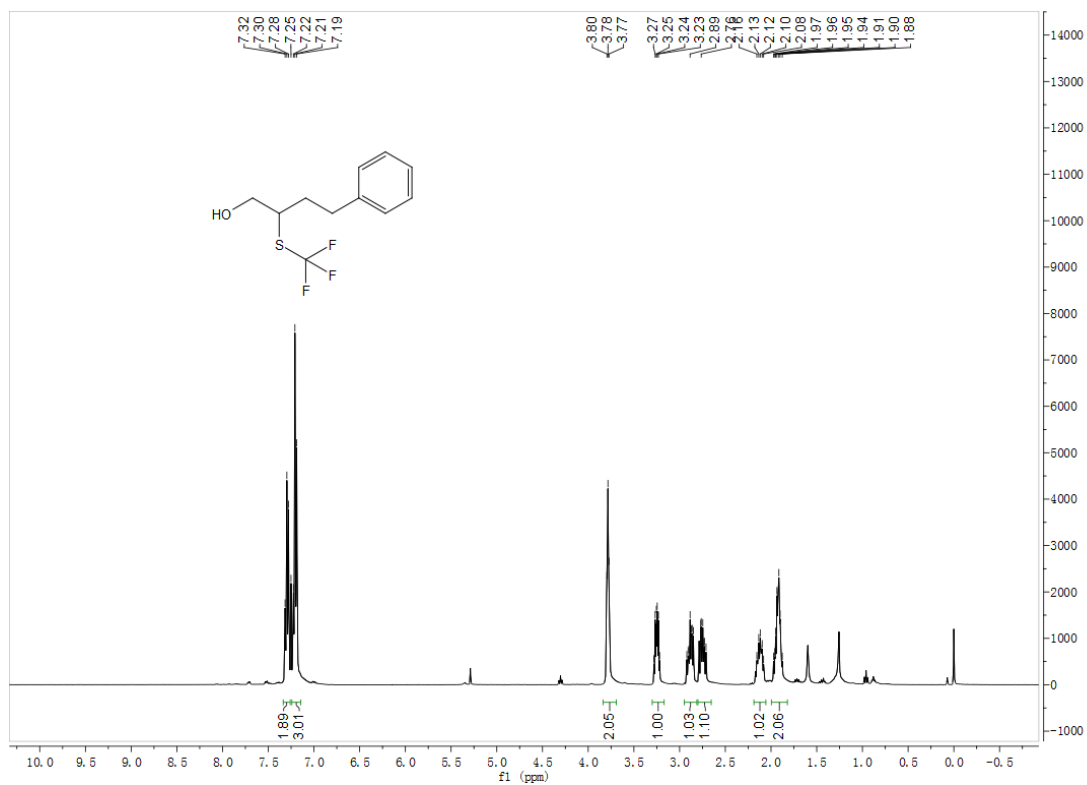


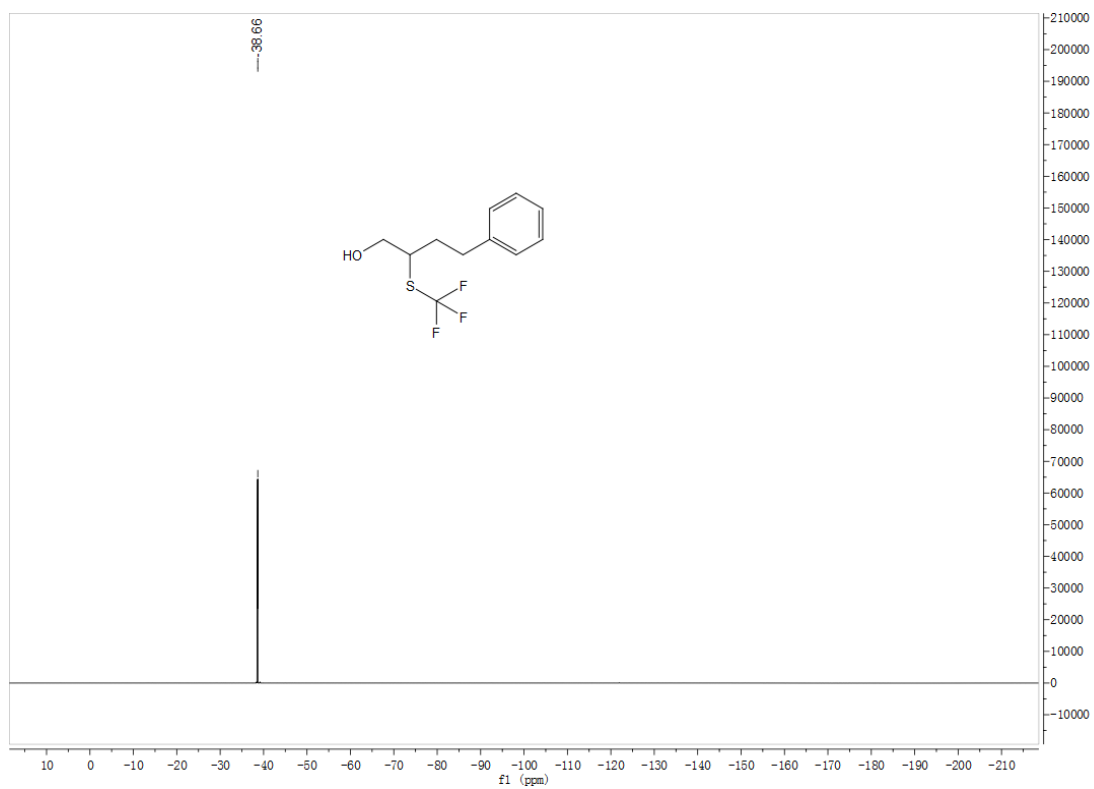
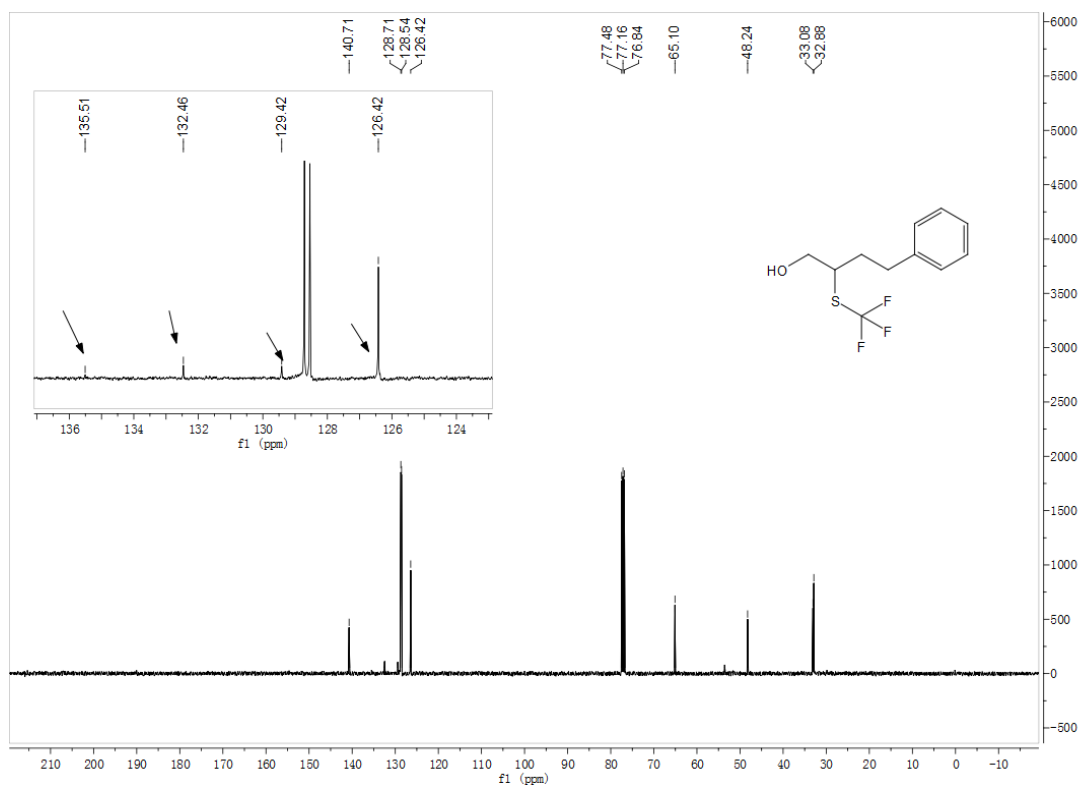
5-(Benzyloxy)-2-((trifluoromethyl)thio)pentan-1-ol (3q)



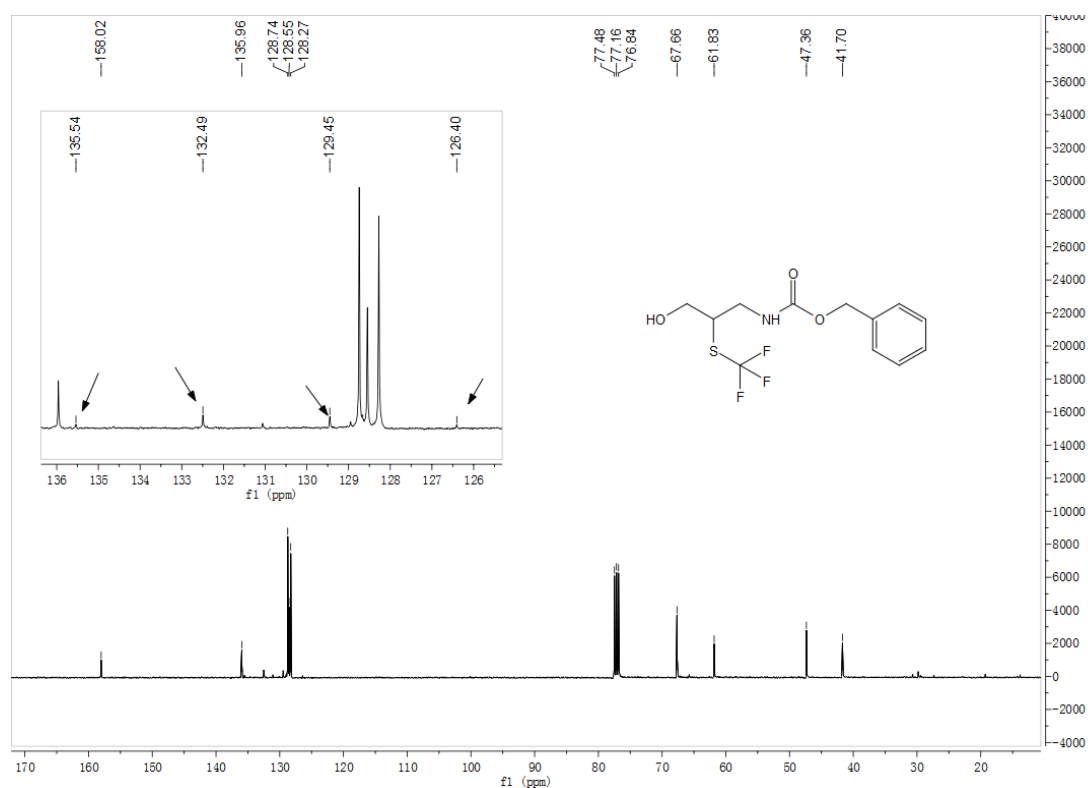
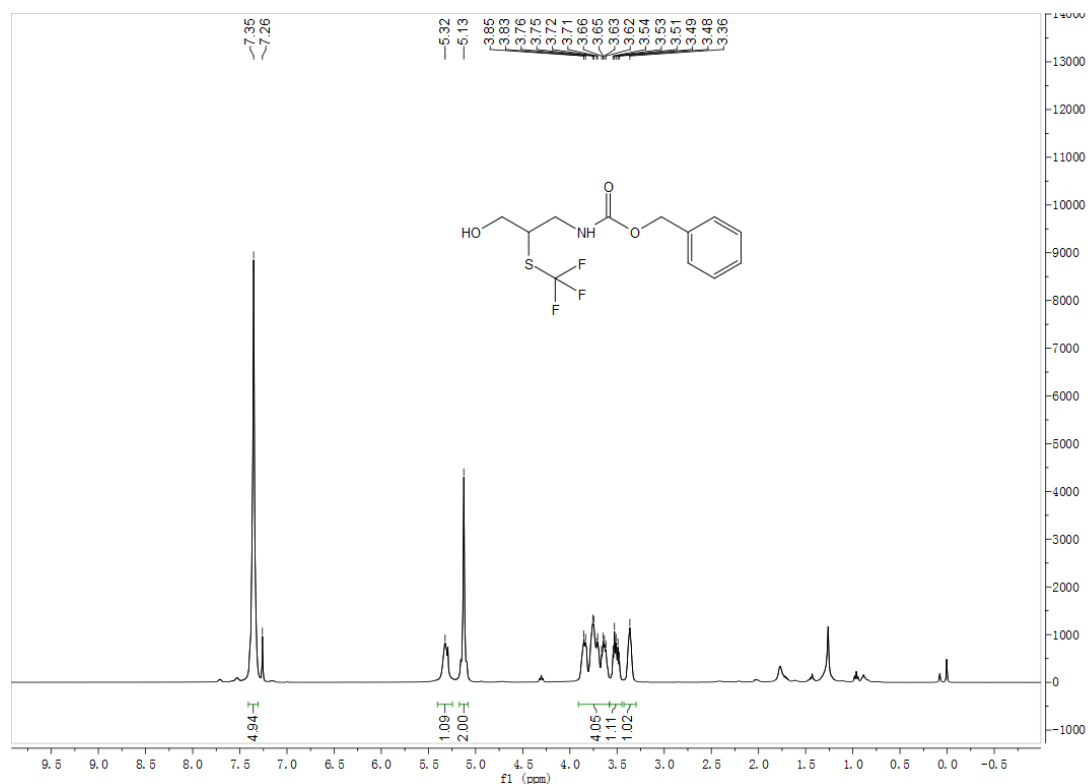


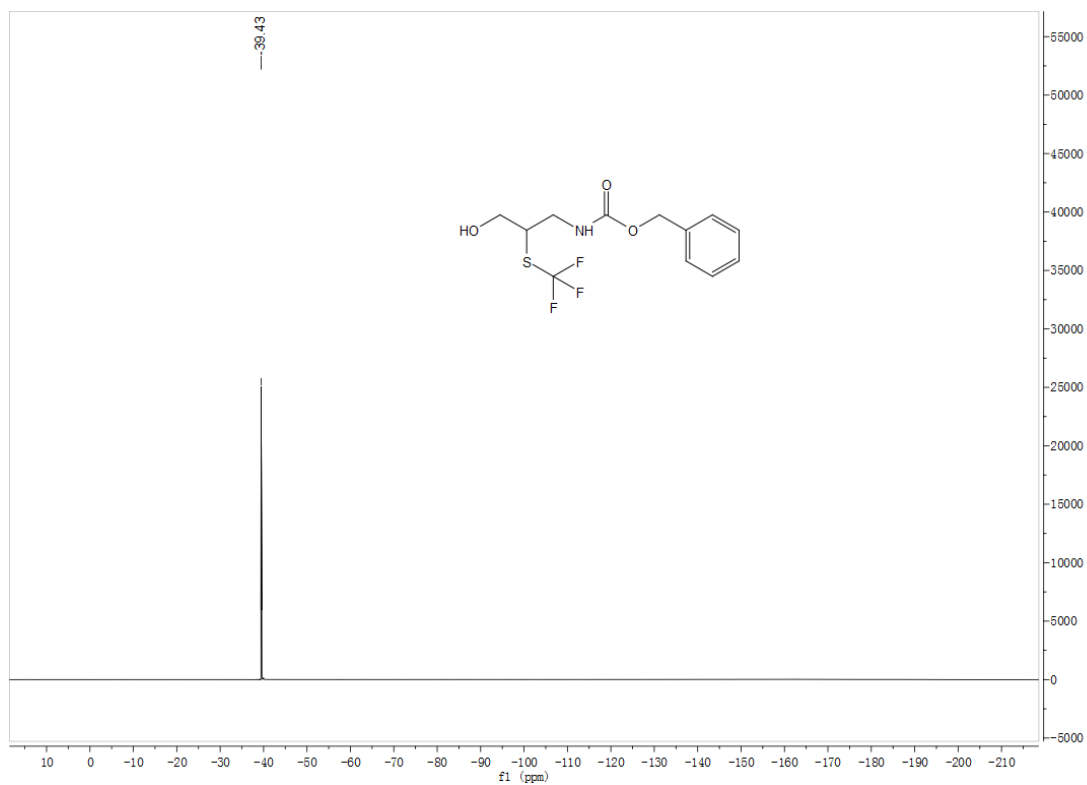
4-Phenyl-2-(trifluoromethylthio)butan-1-ol (3r)



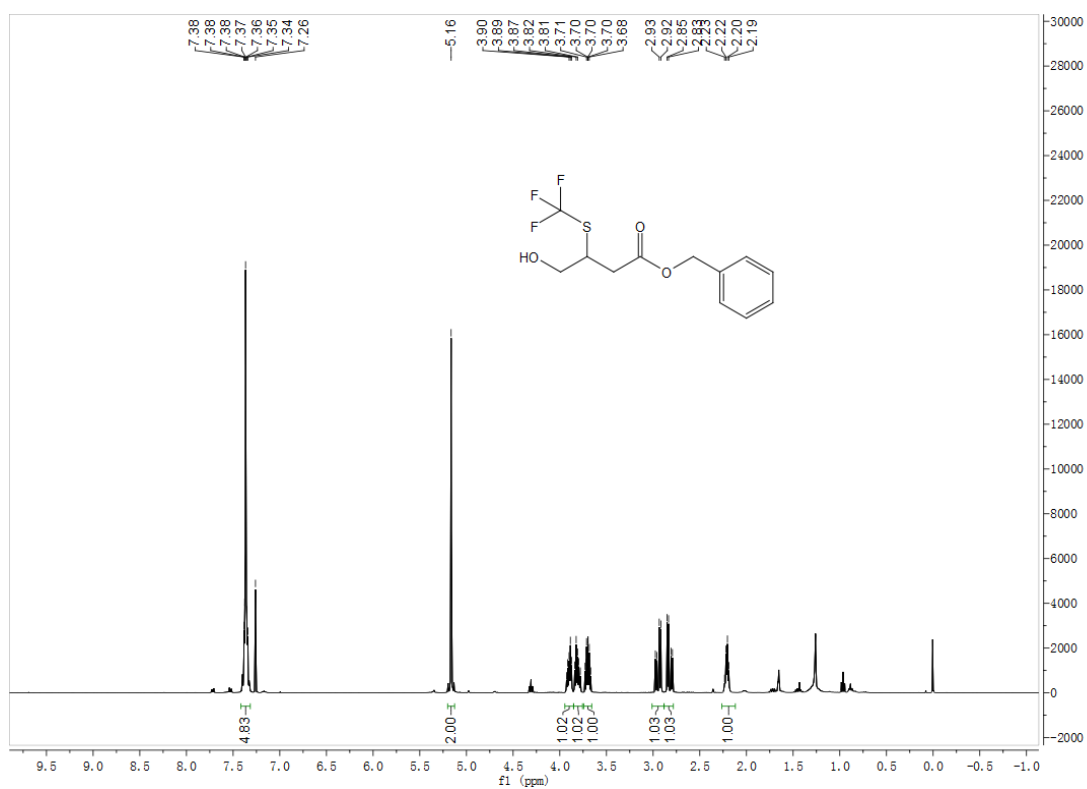


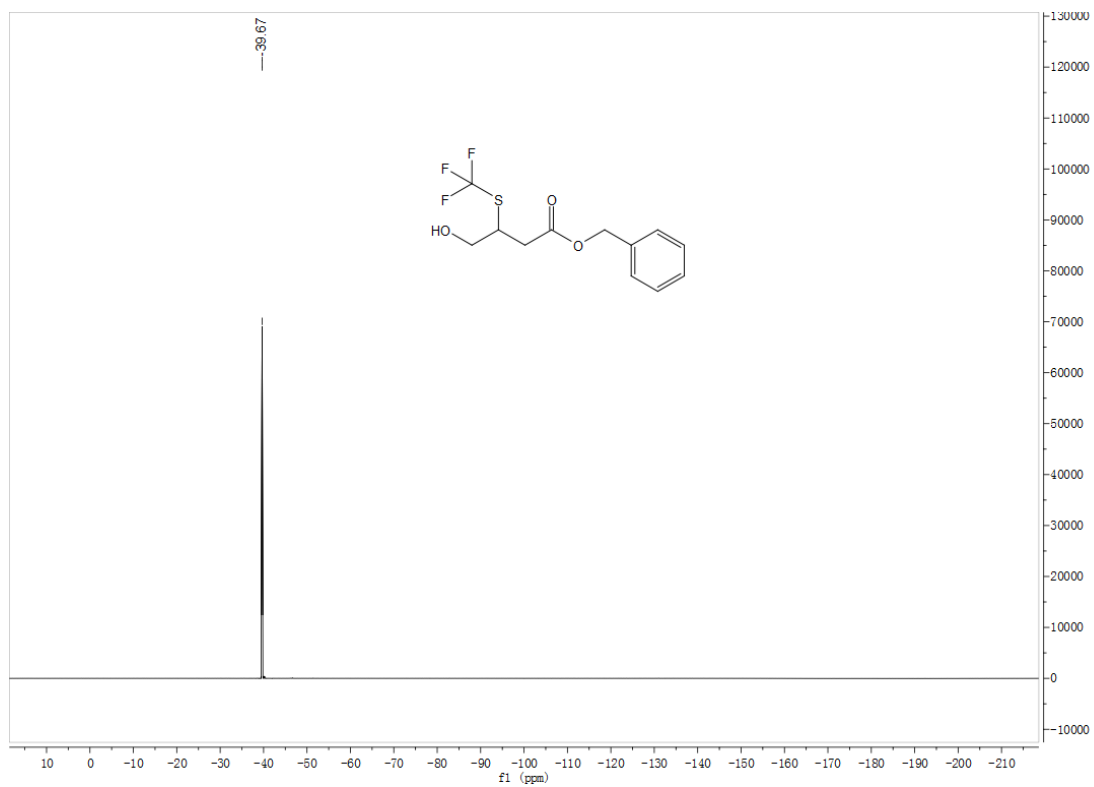
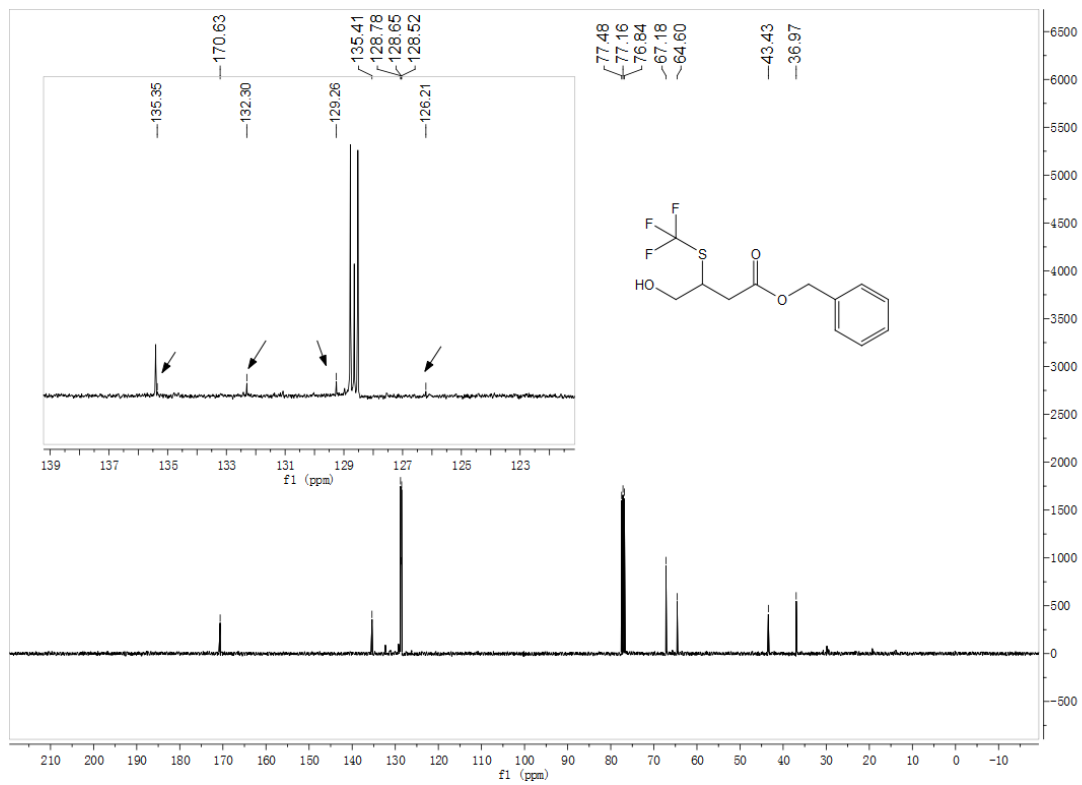
Benzyl (3-hydroxy-2-((trifluoromethyl)thio)propyl)carbamate (3s):



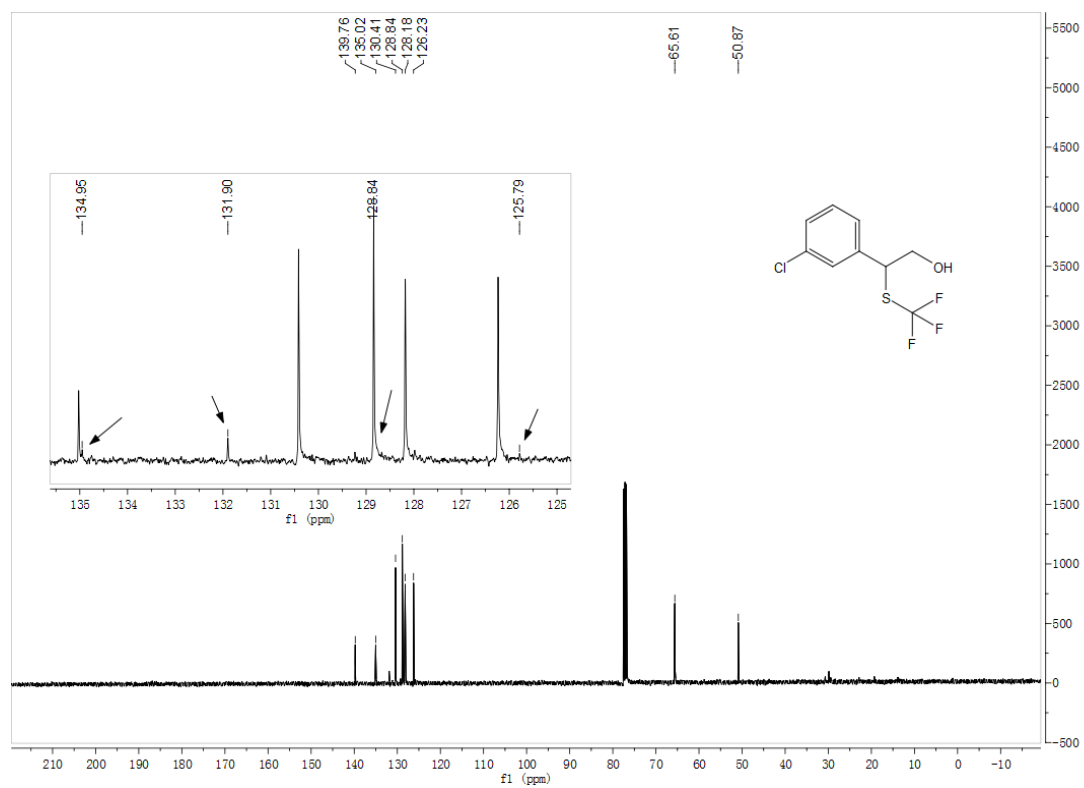
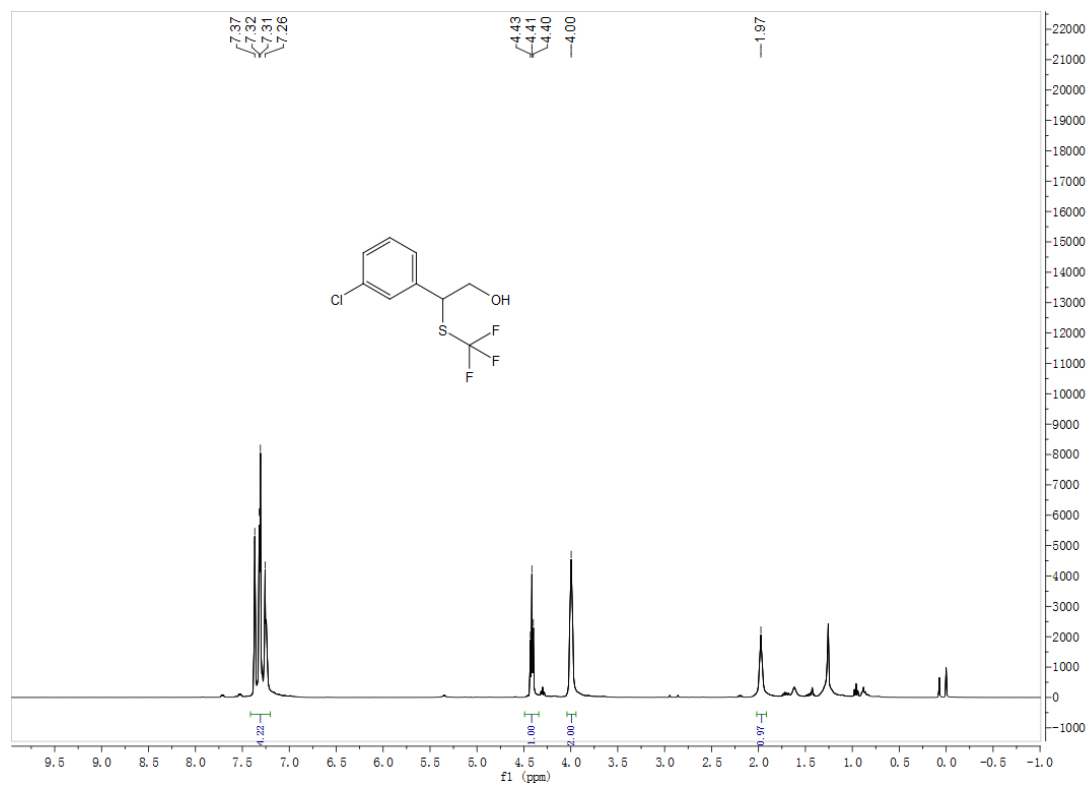


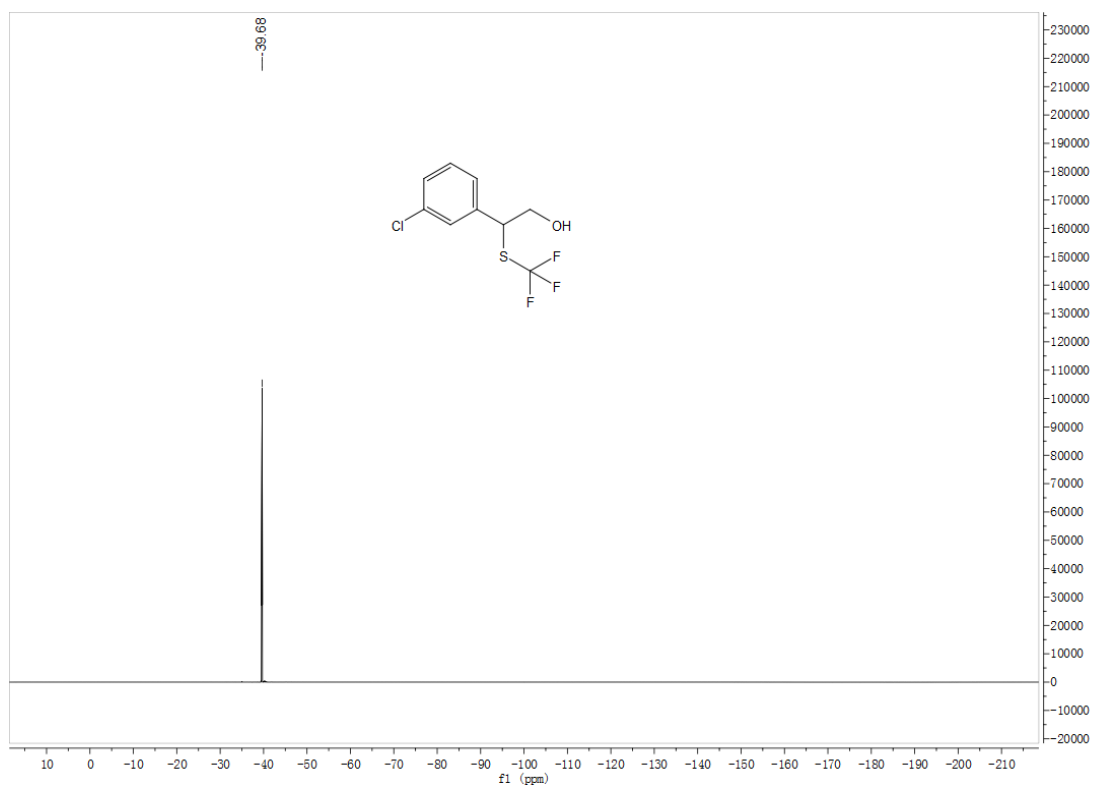
Benzyl-5-hydroxy-4-((trifluoromethyl)thio)pentanoate (3t):





2-(3-Chlorophenyl)-2-((trifluoromethyl)thio)ethanol (3u)





Methyl 2-benzyl-3-hydroxy-2-((trifluoromethyl)thio)propanoate (3v):

