Supplementary Information

Stereoselective Migratory Heteroaryltrifluoromethylation of Allylic Amine via Electrosynthesis

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Table of Contents

1. General Information

Commercial reagents were purchased from TCI, J&K, 3A Chemicals, Accela, Macklin or Adamas and used without further purification. The solvents used in the experiments were all purchased anhydrous solvents and used directly. All reactions were carried out with oven-dried glassware. Analytical thin layer chromatography was performed on 0.20 mm silica gel HSGF-254 plates (Huanghai, China), and visualized under 254 nm UV light. Column chromatography was performed on 200-300 mesh silica gel or 300-400 mesh silica gel (General-Reagent, China).

^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on an Bruker Ascend 400MHz or 500MHz spectrometer and Bruker Ultrashield 300MHz, at ambient temperature unless otherwise stated. Chemical shifts were recorded in parts per million (ppm, δ) relative to chloroform (for 1H NMR, δ = 7.26 ppm; for 13C NMR, δ = 77.16 ppm) and dimethyl sulfoxide (1H NMR, δ = 2.50 ppm; for 13C NMR, δ = 39.52 ppm). 1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br).

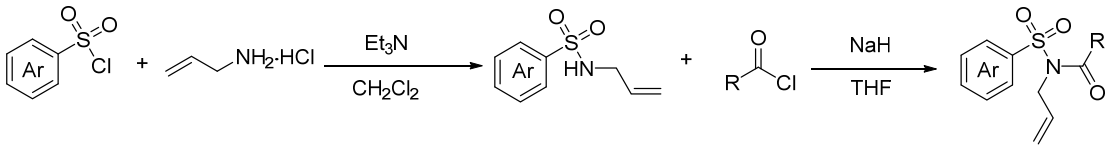
High resolution mass spectra of new compounds were recorded on LTQ Orbitrap Elite LC/MS (ESI or APCI) or MAT 95XP (Thermo, EI). Infrared (IR) spectra were recorded on PerkinElmer Frontier spectrometer and reported in wave numbers (cm^{-1}). X-ray diffraction data was collected on Rigakuoxford diffraction SuperNova using the CuKα radiation at 150 K. Optical rotations were recorded on an Anton Paar MCD-200 polarimeter. The determination of Diastereoisomer ratio and enantiomeric excesses were performed via Waters Acquity UltraPerformance Convergence Chromatography (UPCC) and determined by SFC (supercritical fluid CO_2 chromatography)-MS. The cyclic voltammetry was carried out with a Metrohm Autolab M204 workstation. The detection of sulfates was performed via Metrohm 882 ionic chromatography.

2. General procedure for the preparation of substrates

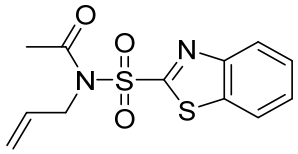
1). sulfonyl chlorides were prepared according to previous procedure.[1, 2]

2). 3-methylbut-2-en-1-amine,[3] (S)-but-3-en-2-amine,[4] (S)-1-phenylbut-3-en-2-amine[4] and (S)-1-phenylprop-2-en-1-amine[5] were prepared according to previous procedure.

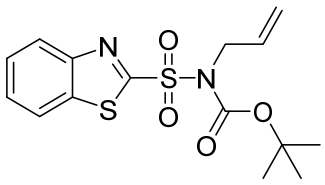
3). general procedure for substrates **1a-1e**, **1g-1m**, **3o-3u**.[6]



To a solution of Allylamine hydrochloride (1.5 equiv.) and Et_3N (3.0 equiv.) in dry DCM was added aryl sulfonyl chloride (1.0 equiv.) in small portions over five minutes in 0 ºC. The reaction mixture was stirred for overnight at room temperature. The reaction mixture was washed with 1N HCl (2 x 25 mL), water (25 mL) and brine. The organic phase was dried over Na_2SO_4, filtered and evaporated in *vacuo* to get the *N*-allyl arylsulfonamide. The compound was used without purification. To a solution of NaH (1.2 equiv.) in THF at 0 ºC was added *N*-allyl arylsulfonamide and stirred for 40 min. the mixture was treated with acyl chloride (1.5 equiv.) and stirred at room temperature for 3 h. the reaction was quenched with water and the aqueous layer was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography.

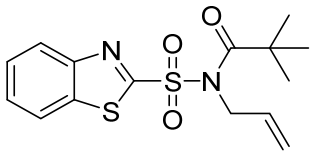


***N*-allyl-*N*-(benzo[d]thiazol-2-ylsulfonyl)acetamide (1a)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), white solid; 300 mg, yield = 48% over 2 steps;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.64 (dt, *J* = 16.0, 7.2 Hz, 2H), 5.92 (ddt, *J* = 16.2, 10.6, 5.8 Hz, 1H), 5.34 (d, *J* = 18.0 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 4.55 (d, *J* = 5.7 Hz, 2H), 2.62 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 170.3, 164.4, 151.9, 136.6, 132.1, 128.3, 127.8, 125.5, 122.2, 118.7, 49.5, 25.3. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{12}N_2O_3S_2Na^+$ 319.0182, found: 319.0180. IR ν_{max} (film, cm $^{-1}$): 2920, 1712, 1369, 1227, 1172, 964, 762, 619.

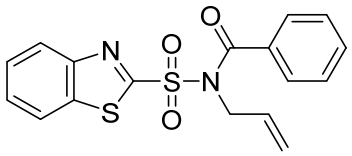


tert-butyl allyl(benzo[d]thiazol-2-ylsulfonyl)carbamate (1b): Silica gel column chromatography (petroleum ether/ethyl acetate = 8:1), colorless oil; 382 mg, yield = 52% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.62 (dt, *J* = 16.0, 7.2 Hz, 2H), 6.09 (ddt, *J* = 16.2, 11.1, 5.8 Hz, 1H), 5.43 (d, *J* = 17.1 Hz, 1H), 5.31 (d, *J* = 10.3 Hz, 1H), 4.59 (d, *J* = 5.6 Hz, 2H), 1.37 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.1, 151.8, 150.2, 136.7, 132.8, 127.9, 127.5, 125.4, 122.1, 118.2, 85.6, 50.1, 27.8. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for

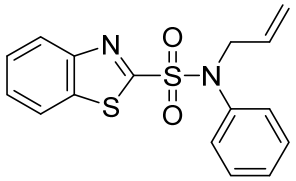
$C_{15}H_{18}N_2O_4S_2Na^+$ 377.0600, found: 377.0596. IR ν_{max} (film, cm $^{-1}$): 2930, 1733, 1450, 1366, 1140, 1085, 760, 624.



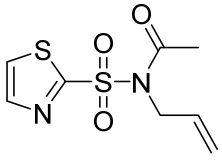
***N*-allyl-*N*-(benzo[d]thiazol-2-ylsulfonyl)pivalamide (1c)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), white solid; 311 mg, yield = 46% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.57 (p, *J* = 7.2 Hz, 2H), 6.05 (ddt, *J* = 15.8, 10.3, 5.1 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.6 Hz, 1H), 4.72 (d, *J* = 4.8 Hz, 2H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 180.8, 165.6, 151.8, 137.0, 133.2, 127.8, 127.3, 125.3, 122.2, 118.6, 50.7, 42.2, 27.8. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_3S_2^+$ 339.0832, found: 339.0829. IR ν_{max} (film, cm $^{-1}$): 2930, 1687, 1475, 1360, 1168, 1083, 8353 761, 619.



***N*-allyl-*N*-(benzo[d]thiazol-2-ylsulfonyl)benzamide (1d)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), yellow oil; 372 mg, yield = 52% over 2 steps. ^{1}H NMR (400 MHz, CDCl3) δ 8.20 (d, *J* = 8.1 Hz, 1H), 8.01 – 7.95 (m, 1H), 7.60 (h, *J* = 7.1, 6.7 Hz, 4H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 6.04 (ddt, *J* = 16.4, 11.3, 5.8 Hz, 1H), 5.25 – 5.22 (m, 1H), 5.20 (d, *J* = 10.7 Hz, 1H), 4.62 (d, *J* = 5.8 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 171.4, 164.9, 151.9, 137.0, 133.9, 132.5, 132.4, 128.4, 128.4, 128.1, 127.6, 125.5, 122.3, 119.3, 51.9. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}N_2O_3S_2Na^+$ 319.0182, found: 319.0180. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}N_2O_3S_2^+$ 359.0519, found: 359.0515. IR ν_{max} (film, cm $^{-1}$): 2926, 1691, 1412, 1369, 1170, 1023, 727, 620.

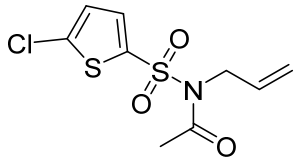


***N*-allyl-*N*-phenylbenzo[d]thiazole-2-sulfonamide** : Silica gel column chromatography (petroleum ether/ethyl acetate = 8:1), yellow solid; 396 mg, yield = 60% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.62 – 7.53 (m, 1H), 7.33 (m, 3H), 7.28 – 7.20 (m, 2H), 5.89 (m, 1H), 5.25 – 5.10 (m, 2H), 4.56 (d, *J* = 6.4 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 152.5, 138.2, 136.5, 132.4, 129.3, 129.1, 128.6, 127.6, 127.4, 125.3, 122.2, 119.5, 55.5. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_2S_2^+$ 331.0570, found: 331.0564. IR ν_{max} (film, cm $^{-1}$): 2930, 1471, 1363, 1169, 1066, 870, 762, 622.

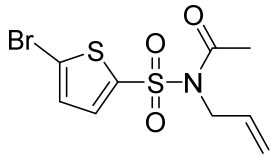


***N*-allyl-*N*-(thiazol-2-ylsulfonyl)acetamide (1f)**: Silica gel column chromatography (petroleum

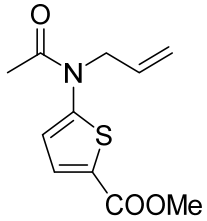
ether/ethyl acetate = 2:1), yellow oil; 271 mg, yield = 55% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 3.0 Hz, 1H), 7.72 (d, *J* = 3.1 Hz, 1H), 5.89 – 5.78 (m, 1H), 5.29 – 5.23 (m, 1H), 5.19 – 5.13 (m, 1H), 4.47 (d, *J* = 5.7 Hz, 2H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.5, 164.3, 144.6, 132.1, 126.1, 118.6, 49.5, 25.3. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{10}N_2O_3S_2^+$ 247.0206, found: 247.0202. IR ν_{max} (film, cm $^{-1}$): 2944, 1707, 1413, 1363, 1178, 963, 863, 730.



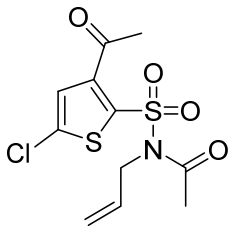
***N*-allyl-*N*-((5-chlorothiophen-2-yl)sulfonyl)acetamide (1g)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 10:1), colorless oil; 296 mg, yield = 54% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 4.0 Hz, 1H), 6.97 (d, *J* = 4.0 Hz, 1H), 5.88 (ddt, *J* = 15.9, 10.6, 5.4 Hz, 1H), 5.41 – 5.20 (m, 2H), 4.45 (d, *J* = 5.3 Hz, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 170.1, 139.5, 137.3, 134.1, 132.1, 126.5, 118.6, 49.3, 24.6. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{11}ClNO_3S_2^+$ 279.9863, found: 279.9862. IR ν_{max} (film, cm $^{-1}$): 2923, 1703, 1405, 1359, 1163, 992, 728, 604.



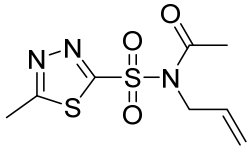
***N*-allyl-*N*-((5-bromothiophen-2-yl)sulfonyl)acetamide (1h)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 10:1), colorless oil; 329 mg, yield = 51% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 4.0 Hz, 1H), 7.08 (d, *J* = 4.1 Hz, 1H), 5.91 – 5.80 (m, 1H), 5.30 – 5.22 (m, 2H), 4.42 (d, *J* = 5.5 Hz, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.1, 140.4, 134.8, 132.2, 130.2, 122.4, 118.8, 49.4, 24.7. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{11}BrNO_3S_2^+$ 323.9358, found: 323.9355. IR ν_{max} (film, cm $^{-1}$): 2955, 1701, 1398, 1357, 1152, 967, 836, 670.



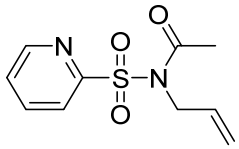
methyl 5-(*N*-acetyl-*N*-allylsulfamoyl)thiophene-2-carboxylate (1i): Silica gel column chromatography (petroleum ether/ethyl acetate = 8:1), white solid; 345 mg, yield = 57% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 5.2 Hz, 1H), 7.52 (d, *J* = 5.3 Hz, 1H), 5.90 (ddt, *J* = 15.8, 10.2, 5.1 Hz, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.50 (d, *J* = 4.7 Hz, 2H), 3.87 (s, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.6, 159.4, 142.5, 133.4, 133.0, 132.8, 129.5, 117.4, 53.1, 49.9, 24.5. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}NO_5S_2^+$ 304.0308, found: 304.0303. IR ν_{max} (film, cm $^{-1}$): 2962, 1730, 1703, 1436, 1363, 1181, 1076, 841, 600.



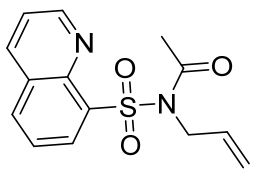
***N*-((3-acetyl-5-chlorothiophen-2-yl)sulfonyl)-*N*-allylacetamide (1j)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), yellow solid; 315 mg, yield = 49% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 5.90 (dq, *J* = 16.0, 4.9 Hz, 1H), 5.27 (dd, *J* = 25.4, 13.8 Hz, 2H), 4.60 – 4.41 (m, 2H), 2.52 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.2, 170.8, 141.5, 138.1, 132.9, 128.1, 117.7, 50.3, 30.0, 24.7. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{12}ClNO_4S_2Na^+$ 343.9789, found: 343.9786. IR ν_{max} (film, cm $^{-1}$): 2933, 1698, 1646, 1353, 1226, 1161, 1019, 839，631.



***N*-allyl-*N*-((5-methyl-1,3,4-thiadiazol-2-yl)sulfonyl)acetamide (1k)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), yellow oil; 288 mg, yield = 60% over 2 steps. ^{1}H NMR (400 MHz, CDCl3) δ 5.89 (ddt, *J* = 16.3, 11.1, 5.7 Hz, 1H), 5.31 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.51 (d, *J* = 5.6 Hz, 2H), 2.88 (s, 3H), 2.47 (s, 3H). $^{13C\{1H\}}$ NMR (101 MHz, CDCl3) δ 170.8, 170.4, 167.3, 131.9, 119.1, 49.9, 25.0, 16.2. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_8H_{11}N_3O_3S_2Na^+$ 284.0134, found: 284.0130. IR ν_{max} (film, cm $^{-1}$): 2947, 1710, 1421, 1366, 1171, 1087, 840, 631.

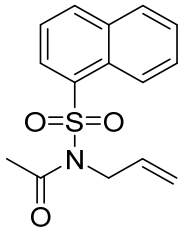


***N*-allyl-*N*-(pyridin-2-ylsulfonyl)acetamide (1m)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), yellow oil; 288 mg, yield = 60% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.6 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.95 (td, *J* = 7.8, 1.5 Hz, 1H), 7.54 (dd, *J* = 7.6, 4.7 Hz, 1H), 5.87 (ddt, *J* = 16.1, 10.8, 5.6 Hz, 1H), 5.27 (d, *J* = 17.3 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 4.45 (d, *J* = 5.6 Hz, 2H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.1, 157.0, 150.3, 138.3, 132.8, 127.6, 123.2, 118.0, 49.4, 25.0. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{12}N_2O_3S_2Na^+$ 263.0461, found: 263.0458. IR ν_{max} (film, cm $^{-1}$): 2962, 1701, 1405, 1349, 1177, 1115, 750, 586.

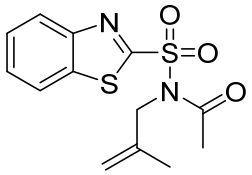


***N*-allyl-*N*-(quinolin-8-ylsulfonyl)acetamide (1n)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), white solid; 232 mg, yield = 40% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$)

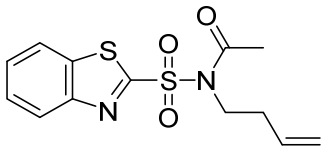
δ 8.96 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.55 (d, *J* = 7.4 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.88 (ddt, *J* = 15.8, 10.5, 5.4 Hz, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.3 Hz, 1H), 4.57 (d, *J* = 5.3 Hz, 2H), 2.44 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 151.4, 143.6, 136.6, 136.2, 134.6, 133.3, 133.3, 128.9, 125.4, 122.4, 117.2, 49.4, 25.3. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}N_2O_3S^+$ 291.0798, found: 291.0795. IR ν_{max} (film, cm^{-1}): 2927, 1702, 1509, 1340, 1163, 830, 769, 591.



***N*-allyl-*N*-(naphthalen-1-ylsulfonyl)acetamide (1o)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 10:1), white solid; 347 mg, yield = 60% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 1H), 8.31 – 8.25 (m, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.66 (m, 1H), 7.65 – 7.54 (m, 2H), 5.91 (ddt, *J* = 15.8, 10.6, 5.5 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 10.3 Hz, 1H), 4.56 (d, *J* = 5.5 Hz, 2H), 2.29 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.2, 135.4, 134.5, 134.3, 132.4, 130.6, 129.3, 128.8, 128.2, 127.2, 124.1, 123.8, 118.4, 48.9, 25.0. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}NO_3S^+$ 290.0845, found: 290.0843. IR ν_{max} (film, cm^{-1}): 2937, 1702, 1509, 1340, 1162, 830, 769, 583.

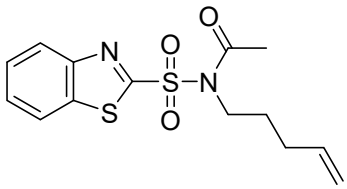


***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(2-methylallyl)acetamide (1p):** Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), white solid; 285 mg, yield = 46% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.61 (dt, *J* = 15.5, 7.0 Hz, 2H), 4.95 (d, *J* = 10.2 Hz, 2H), 4.48 (s, 2H), 2.56 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 164.4, 151.9, 139.5, 136.7, 128.2, 127.7, 125.5, 122.2, 112.4, 52.2, 25.0, 20.2. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2O_3S_2^+$ 311.0519, found: 311.0513. IR ν_{max} (film, cm^{-1}): 2930, 1714, 1471, 1366, 1168, 867, 761, 620.

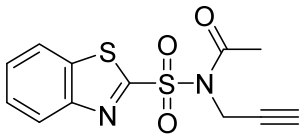


***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(but-3-en-1-yl)acetamide (1q)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), white solid; 298 mg, yield = 48% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 9.3 Hz, 1H), 7.69 – 7.58 (m, 2H), 5.77 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.14 – 5.06 (m, 1H), 5.04 (d, *J* = 10.2 Hz, 1H), 3.94 (dd, *J* = 8.5, 6.7 Hz, 2H), 2.60 (s, 3H), 2.49 (q, *J* = 7.2 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4, 164.2, 152.0, 136.6, 134.0, 128.3, 127.8, 125.6, 122.2, 117.7, 46.9, 33.9, 25.5. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{14}N_2O_3S_2Na^+$ 333.0338, found: 333.0333. IR ν_{max} (film, cm^{-1}): 2933,

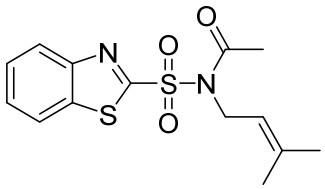
1708, 1470, 1365, 1167, 912, 760, 620.



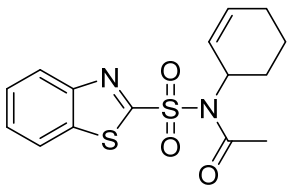
***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(pent-4-en-1-yl)acetamide**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 324 mg, yield = 50% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.13 (m, 1H), 8.04 – 7.96 (m, 1H), 7.71 – 7.50 (m, 2H), 5.80 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.04 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.99 (dq, *J* = 10.2, 1.2 Hz, 1H), 3.93 – 3.78 (m, 2H), 2.59 (s, 3H), 2.11 (q, *J* = 7.4 Hz, 2H), 1.94 – 1.70 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.4, 164.3, 152.0, 137.2, 136.6, 128.3, 127.8, 125.6, 122.2, 115.4, 47.4, 30.8, 28.5, 25.5. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{16}N_2O_3S_2Na^+$ 347.0495, found: 347.0487. IR ν_{max} (film, cm $^{-1}$): 2937, 1713, 1473, 1369, 1170, 939, 762, 622.



***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(prop-2-yn-1-yl)acetamide (1r)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), white solid; 235 mg, yield = 40% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.57 (m, 2H), 4.69 (d, *J* = 2.4 Hz, 2H), 2.69 (s, 3H), 2.10 (t, *J* = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 163.8, 152.0, 136.7, 128.4, 127.9, 125.6, 122.2, 77.3, 72.6, 36.2, 25.2. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}N_2O_3S_2Na^+$ 319.0182, found: 319.0180. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{10}N_2O_3S_2Na^+$ 317.0025, found: 317.0019. IR ν_{max} (film, cm $^{-1}$): 3290, 2933, 2111, 1717, 1470, 1369, 1170, 1095, 856, 621.



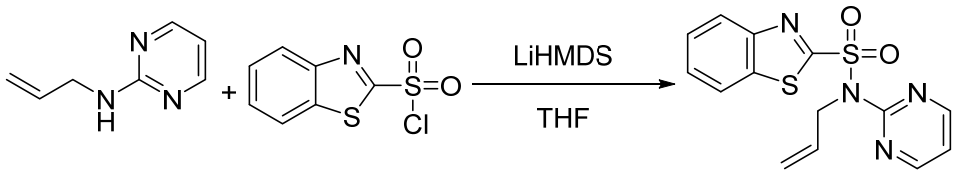
***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(3-methylbut-2-en-1-yl)acetamide (1t)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 305 mg, yield = 47% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.3 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.55 (m, 2H), 5.20 (ddt, *J* = 6.8, 4.2, 1.3 Hz, 1H), 4.52 (d, *J* = 6.9 Hz, 2H), 2.61 (s, 3H), 1.72 (s, 3H), 1.61 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.6, 164.8, 152.0, 137.2, 136.6, 128.2, 127.7, 125.5, 122.1, 119.0, 45.7, 25.6, 25.5, 18.0. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{16}N_2O_3S_2Na^+$ 347.0495, found: 347.0487. IR ν_{max} (film, cm $^{-1}$): 2923, 1711, 1477, 1367, 1167, 950, 762, 623.



***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(cyclohex-2-en-1-yl)acetamide (1u)**: Silica gel column

chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 168 mg, yield = 25% over 4 steps. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 – 8.08 (m, 1H), 8.07 – 7.85 (m, 1H), 7.73 – 7.47 (m, 2H), 5.85 – 5.71 (m, 1H), 5.57 (d, *J* = 10.1 Hz, 1H), 5.25 – 5.09 (m, 1H), 2.55 (s, 3H), 2.31 – 2.16 (m, 1H), 2.14 – 1.96 (m, 3H), 1.96 – 1.83 (m, 1H), 1.69 (qdd, *J* = 13.8, 5.5, 3.2 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 165.1, 151.9, 136.7, 129.3, 128.2, 127.7, 127.5, 125.5, 122.2, 58.4, 28.2, 26.7, 24.0, 22.6. (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{16}N_2O_3S_2^+$ 359.0495, found: 359.0488. IR ν_{max} (film, cm $^{-1}$): 2935, 1712, 1471, 1365, 1170, 970, 761, 647.

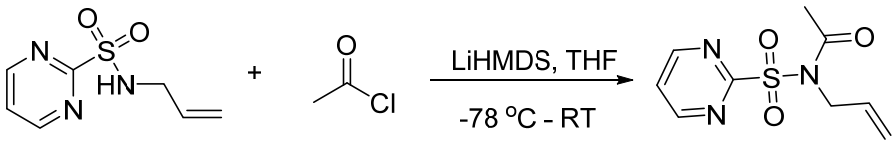
procedure for substrates 1e



N-allylpyrimidin-2-amine was prepared according to previous reports. To a solution of *N*-allylpyrimidin-2-amine (1 equiv.) in THF was added LiHMDS (1.0 M in THF, 1.2 equiv.) in -78 ºC. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was cooled to –78 ºC and a solution of benzo[d]thiazole-2-sulfonyl chloride (1.5 equiv.) in THF was added. The reaction mixture was allowed to warm to room temperature and stirred for 3 h and quenched with saturated NH_4Cl and extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography.

N-allyl-N-(pyrimidin-2-yl)benzo[d]thiazole-2-sulfonamide (1e): Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 266 mg, yield = 40% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 2H), 8.20 – 8.09 (m, 1H), 8.05 – 7.89 (m, 1H), 7.66 – 7.46 (m, 2H), 6.94 (t, *J* = 4.8 Hz, 1H), 6.20 (ddt, *J* = 15.8, 10.7, 5.5 Hz, 1H), 5.49 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.29 (dd, *J* = 10.3, 1.2 Hz, 1H), 5.04 (d, *J* = 5.5 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.5, 157.8, 157.7, 151.7, 137.1, 133.1, 127.6, 127.1, 125.3, 122.0, 118.1, 116.4, 50. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}N_4O_2S_2^+$ 333.0474, found: 333.0466. IR ν_{max} (film, cm $^{-1}$): 2937, 1566, 1402, 1358, 1169, 866, 759, 619.

Procedure for substrates 1l

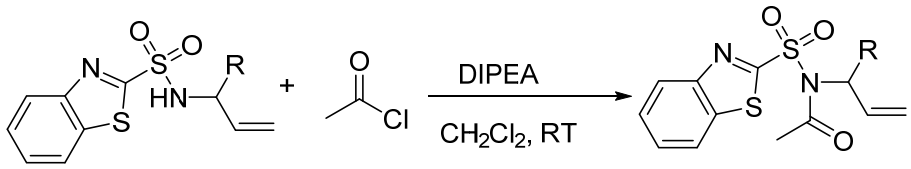


LiHMDS in THF (1.0 M, 1.2 equiv.) was added to a mixture of *N*-allylpyrimidine-2-sulfonamide (1.0 equiv.) in THF carefully at -78 ºC. The mixture was stirred at -78 ºC for 40 min, treated with acetyl chloride (1.5 equiv.) and them warmed to room temperature. The mixture was stirred for 4 hours and quenched with saturated NH_4Cl and extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography.

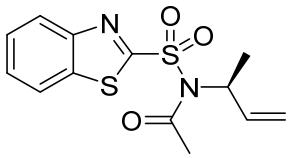
N-allyl-*N*-(pyrimidin-2-ylsulfonyl)acetamide (1l): Silica gel column chromatography (petroleum ether/ethyl acetate = 2:1), yellow oil; 217 mg, yield = 45% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 4.9 Hz, 2H), 7.56 (t, *J* = 4.9 Hz, 1H), 5.90 (ddt, *J* = 16.1, 10.4, 5.8 Hz, 1H), 5.34 – 5.26 (m, 1H), 5.20 – 5.12 (m, 1H), 4.48 (d, *J* = 5.8 Hz, 2H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.2, 165.3, 159.0, 132.5, 123.9, 118.5, 49.5, 25.1. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_9H_{11}N_3O_3SNa^+$ 264.0413, found: 264.0410. IR ν_{max} (film, cm $^{-1}$): 2930, 1704, 1567, 1361, 1138,

868, 767, 601.

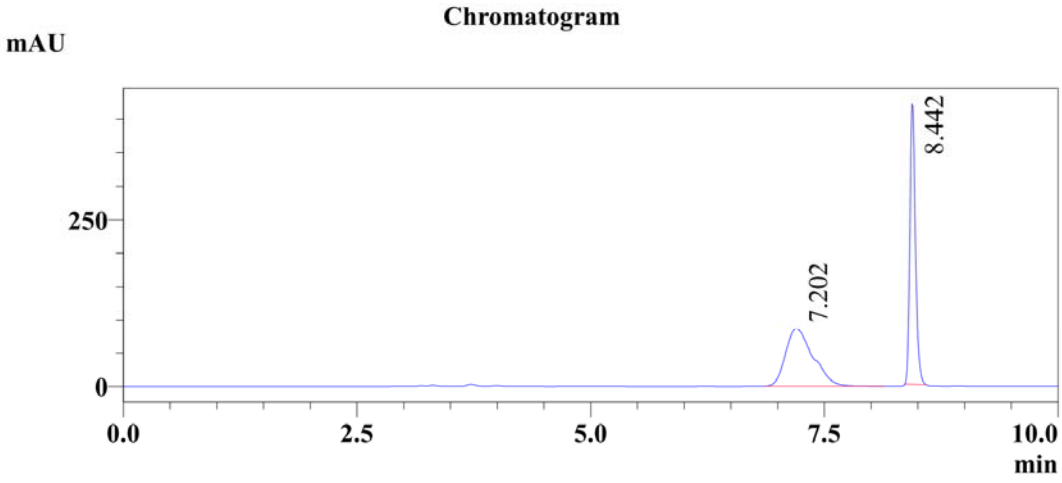
Procedure for substrates 1u-1w.[7]



To a solution of *N*-(1-phenylallyl)benzo[d]thiazole-2-sulfonamide (1 equiv.) in dry CH_2Cl_2 was added diisopropylethylamine (1.2 equiv) at room temperature. After 40 min, acetyl chloride (1.2 equiv) was added dropwise at 0 °C. The mixture was stirred overnight. The resulting mixture was quenched with water. The organic layer was dried Na_2SO_4, filtered and evaporated in *vacuo*. The residue was purified by column chromatography.



(S)-*N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(but-3-en-2-yl)acetamide (1v): Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 310 mg, yield = 50% over 2 steps, 88:12 er. $[\alpha]_D^{20.0}$ = 4.00 (*c* = 0.3 in acetone, λ = 589 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.62 (dt, *J* = 15.9, 7.3 Hz, 2H), 6.11 (ddd, *J* = 17.1, 10.1, 5.9 Hz, 1H), 5.27 – 5.12 (m, 2H), 5.09 (d, *J* = 10.2 Hz, 1H), 2.59 (s, 3H), 1.58 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.6, 164.9, 151.9, 137.5, 136.5, 128.2, 127.8, 125.5, 122.2, 117.0, 58.6, 26.8, 18.8. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{14}N_2O_3S_2Na^+$ 333.0338, found: 333.0331. IR ν_{max} (film, cm $^{-1}$): 2951, 1710, 1474, 1362, 1167, 947, 760, 618. The enantioselectivity was determined by HPLC (AD-H, n-hexane/i-PrOH = 97:3, flow rate: 1.0 mL/min, λ = 254 nm), t_R (major) = 8.4 min, t_R(minor) = 7.1 min.

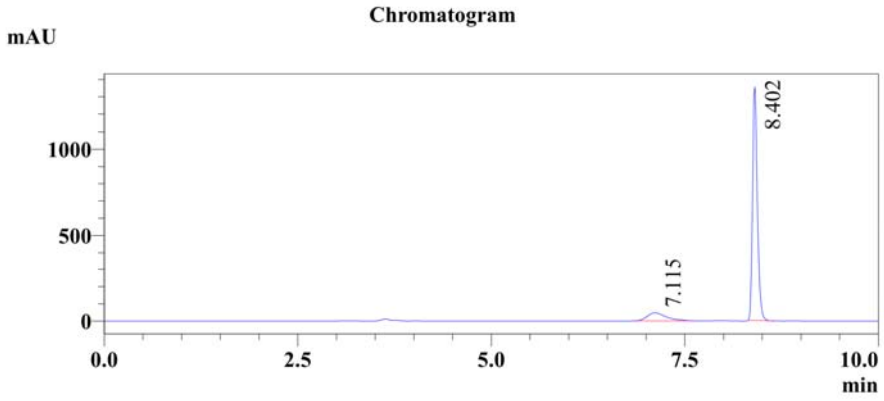


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Height%	Area%
1	7.202	85957	1742645	17.002	50.101
2	8.442	419627	1735590	82.998	49.899
Total		505584	3478235	100.000	100.000

Figure S1. Chromatograms of Racemic **1v**

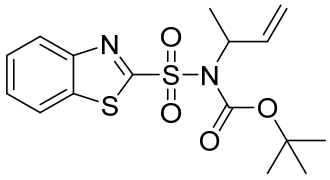


Peak Table

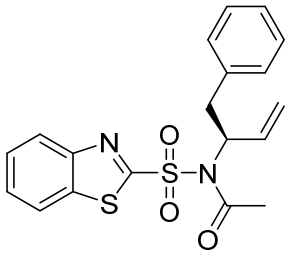
PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Height%	Area%
1	7.115	46810	810261	3.344	12.236
2	8.402	1352848	5811760	96.656	87.764
Total		1399658	6622021	100.000	100.000

Figure S2. Chromatograms of Product **1v**

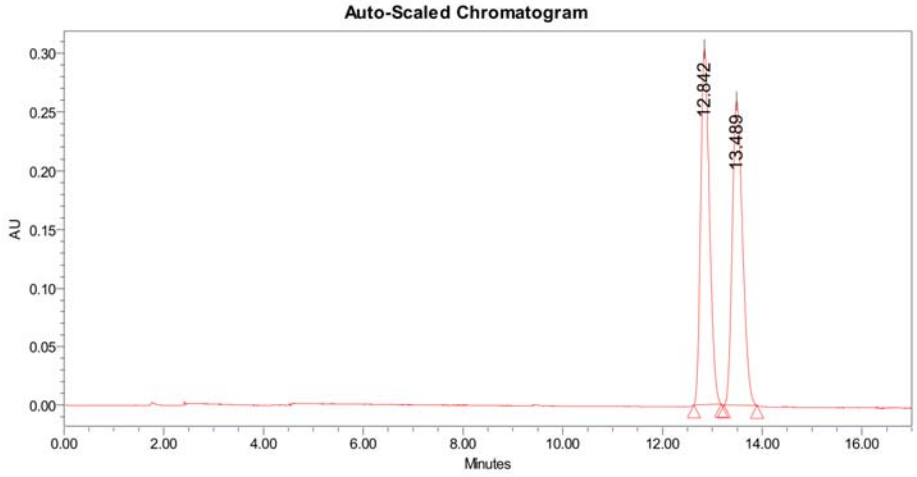


***tert*-butyl (benzo[d]thiazol-2-ylsulfonyl)(but-3-en-2-yl)carbamate (1v')**: Using Di-tert-butyl decarbonate insead of Acetyl chloride. Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 120 mg, yield = 23% over 5 steps. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.13 (m, 1H), 8.03 – 7.92 (m, 1H), 7.65 – 7.52 (m, 2H), 6.21 (ddd, *J* = 17.3, 10.4, 5.5 Hz, 1H), 5.36 – 5.29 (m, 1H), 5.29 – 5.18 (m, 2H), 1.68 (d, *J* = 6.9 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.6, 151.8, 150.0, 138.1, 136.7, 127.8, 127.4, 125.3, 122.1, 116.5, 85.5, 57.7, 27.9, 18.9. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{20}N_2O_4S_2Na^+$ 391.0757, found:391.0750. IR ν_{max} (film, cm $^{-1}$): 2934, 1736, 1457, 1364, 1145, 1023, 761, 632.



(S)-*N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(1-phenylbut-3-en-2-yl)acetamide (1w): Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 386 mg, yield = 50% over 2 steps, 90:10 er. $[\alpha]_D^{20.0}$ = -12.00 (*c* = 0.3 in acetone, λ = 589 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.06 (m, 1H), 7.99 – 7.85 (m, 1H), 7.73 – 7.51 (m, 2H), 7.14 – 7.01 (m, 4H), 7.01 – 6.87 (m, 1H), 6.23 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.27 – 4.99 (m, 3H), 3.34 (dd, *J* = 13.6, 7.6 Hz, 1H), 3.21 (dd, *J* = 13.6, 7.8 Hz, 1H), 2.65 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.0, 164.4, 152.1, 137.6, 136.6, 135.6, 129.3, 128.3, 128.2, 127.7, 126.5, 125.6, 122.1, 118.8, 65.1, 39.1, 27.0. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2O_3S_2^+$ 387.0832, found: 387.0821. IR ν_{max} (film, cm

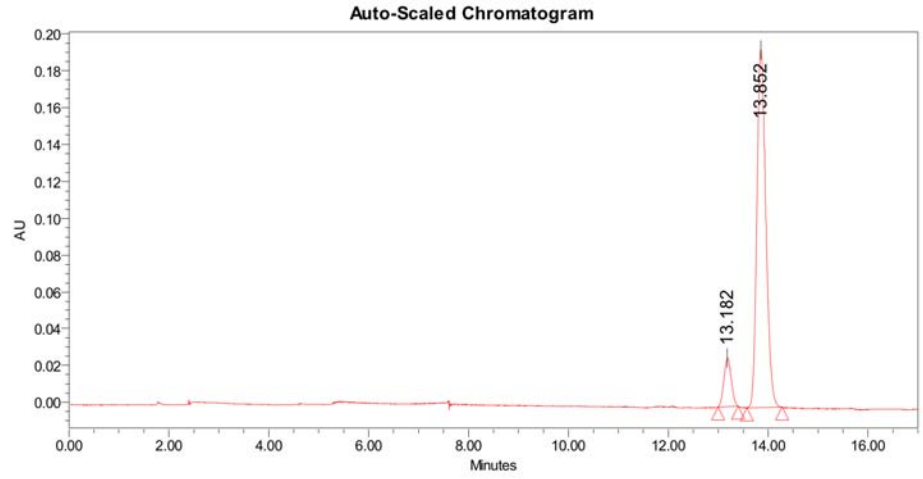
$^{-1}$): 2927, 1709, 1474, 1366, 1165, 918, 760, 623. The enantioselectivity was determined by UPCC (Chiralpak AD-3, gradient 100% CO_2 to CO_2/MeOH = 90:10 in 0-15th min, flow rate: 0.5 mL/min, λ = 254 nm), t_R (major) = 13.9 min, t_R(minor) = 13.2 min.



Peak Results

	RT	Area	Height	% Area	% Height
1	12.842	3759117	303344	50.02	53.90
2	13.489	3756442	259466	49.98	46.10

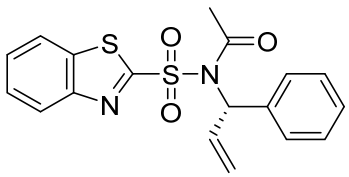
Figure S3. Chromatograms of Racemic **1w**



Peak Results

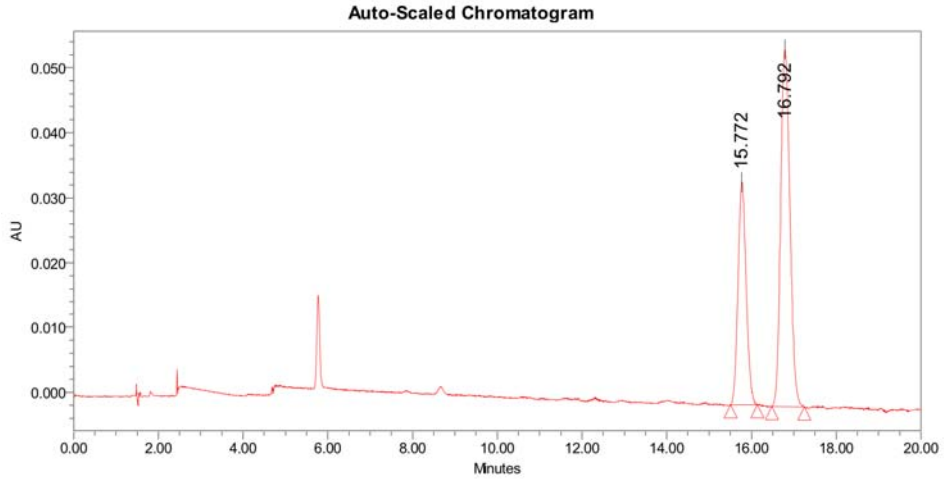
	RT	Area	Height	% Area	% Height
1	13.182	273009	26359	10.08	11.95
2	13.852	2434094	194175	89.92	88.05

Figure S4. Chromatograms of Product **1w**



(S)-*N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(1-phenylallyl)acetamide (1x): Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 120 mg, yield = 23% over 5 steps, 98:2 er. $[\alpha]_D^{20.0}$ = -50.67 (*c* = 0.3 in acetone, λ = 589 nm). ^{1}H NMR (400 MHz, CDCl3) δ 8.21

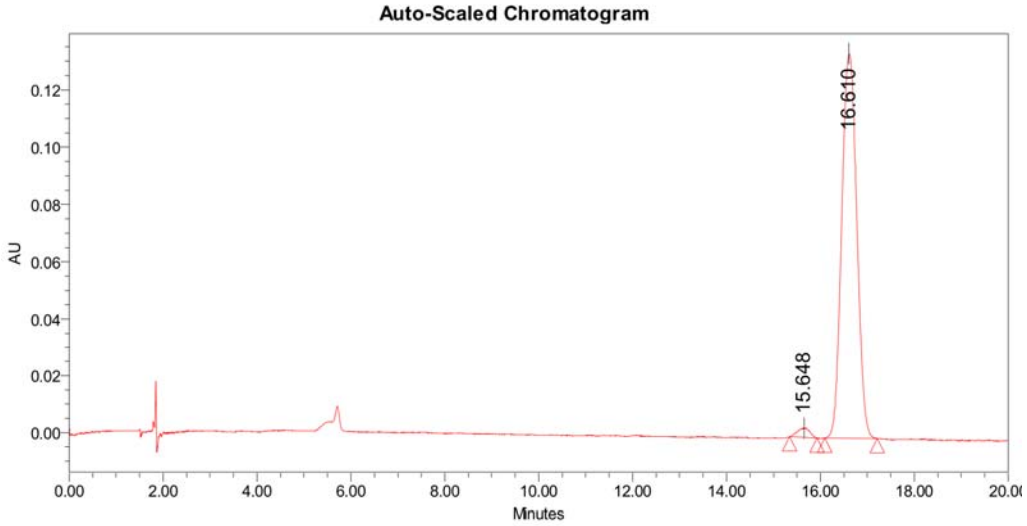
(d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.64 (dt, *J* = 20.3, 7.3 Hz, 2H), 7.38 (d, *J* = 6.7 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 3H), 6.54 (dt, *J* = 17.3, 8.9 Hz, 1H), 6.34 (d, *J* = 7.4 Hz, 1H), 5.44 – 5.32 (m, 2H), 2.62 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl3) δ 170.8, 165.2, 152.0, 138.3, 136.8, 134.2, 128.4, 128.3, 127.8, 127.7, 127.5, 125.6, 122.3, 120.7, 64.5, 26.7. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}N_2O_3S_2Na^+$ 319.0182, found: 319.0180. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}N_2O_3S_2Na^+$ 395.0495, found: 395.0489. IR ν_{max} (film, cm^{-1}): 2937, 1706, 1474, 1365, 1167, 929, 760, 632. The enantioselectivity was determined by UPCC (Chiralpak AD-3, gradient 100% CO_2 to CO_2/MeOH = 90:10 in 0-20th min, flow rate: 0.5 mL/min, λ = 254 nm), t_R (major) = 13.9 min, t_R(minor) = 13.2 min.



Peak Results

	RT	Area	Height	% Area	% Height
1	15.772	461864	34334	35.75	38.43
2	16.792	830101	55010	64.25	61.57

Figure S5. Chromatograms of Racemic **1x**

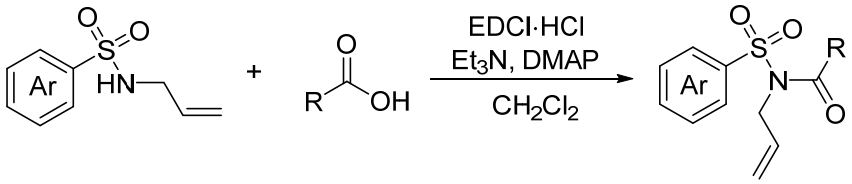


Peak Results

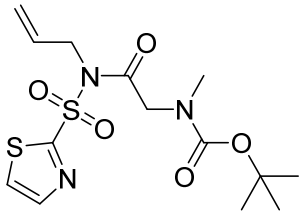
	RT	Area	Height	% Area	% Height
1	15.648	60761	3315	1.98	2.40
2	16.610	3006197	134642	98.02	97.60

Figure S6. Chromatograms of Product **1x**

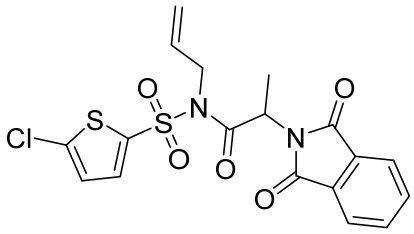
General procedure for substrates 3x to 3z5.[8]



N-allyl arylsulfonamide was prepared according to above procedure. To a solution of *N*-allyl arylsulfonamide (1.0 equiv.) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.5 equiv), Et_3N (2.0 equiv.) and DMAP (1.2 equiv.) in dry CH_2Cl_2. The corresponding acid (1.2 equiv.) was added at 0 ºC. The mixture was stirred for overnight at room temperature. The resulting mixture was washed by 1N HCl (2 x 20 mL), 1N NaOH (2 x 20 mL), and water (1 x 20 mL). The organic layer was dried Na_2SO_4, filtered and evaporated in *vacuo*. The residue was purified by column chromatography.

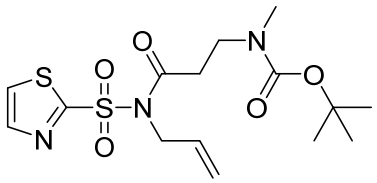


tert-butyl (2-(*N*-allylthiazole-2-sulfonamido)-2-oxoethyl)(methyl)carbamate (1y): Silica gel column chromatography (petroleum ether/ethyl acetate = 3:1), white solid; 330 mg, yield = 44% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.9 Hz, 0.4H), 8.00 (d, *J* = 3.0 Hz, 0.6H), 7.76 (d, *J* = 3.0 Hz, 0.6H), 7.74 (d, *J* = 3.0 Hz, 0.4H), 5.80 (ddq, *J* = 16.2, 10.7, 5.6 Hz, 1H), 5.26 (d, *J* = 17.1 Hz, 1H), 5.16 (dd, *J* = 10.2, 3.9 Hz, 1H), 4.64 (d, *J* = 23.9 Hz, 2H), 4.46 (d, *J* = 5.8 Hz, 2H), 2.91 (s, 1.8H), 2.89 (s, 1.2H), 1.46 (s, 3.6H), 1.35 (s, 5.4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 169.6, 163.9, 163.8, 156.2, 155.7, 144.8, 144.7, 131.6, 131.5, 126.2, 126.1, 119.0, 118.9, 80.1, 80.0, 54.3, 53.5, 49.5, 49.3, 35.6, 28.3, 28.2. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{21}N_3O_5S_2Na^+$ 398.0815, found: 398.0811. IR ν_{max} (film, cm $^{-1}$): 2983, 1717, 1695, 1478, 1366, 1145, 1059, 761, 602.

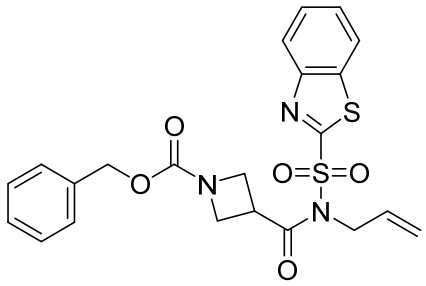


***N*-allyl-*N*-((5-chlorothiophen-2-yl)sulfonyl)-2-(1,3-dioxoisoindolin-2-yl)propanamide (1z)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 6:1), white solid; 385 mg, yield = 44% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.76 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.67 (d, *J* = 4.1 Hz, 1H), 6.92 (d, *J* = 4.1 Hz, 1H), 5.80 (ddt, *J* = 15.9, 10.5, 5.4 Hz, 1H), 5.46 (q, *J* = 7.1 Hz, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 4.37 (t, *J* = 4.8 Hz, 2H), 1.76 (d, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.4, 167.3, 139.7, 136.5, 134.6, 134.3, 131.8, 131.7, 126.7, 123.6, 118.7, 49.9, 49.5, 15.9. HR-MS (ESI) m/z: $[M+H]^+$ Calcd

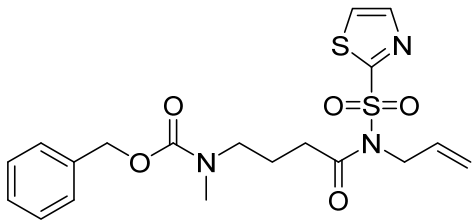
for $C_{18}H_{16}ClN_2O_5S_2^+$ 439.0184, found: 439.0179. IR ν_{max} (film, cm $^{-1}$): 2961, 1780, 1713, 1405, 1365, 1167, 994, 882, 717, 602.



tert-butyl (3-(*N*-allylthiazole-2-sulfonamido)-3-oxopropyl)(methyl)carbamate (1z1): Silica gel column chromatography (petroleum ether/ethyl acetate = 3:1), colorless oil; 335 mg, yield = 43% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 3.0 Hz, 1H), 7.71 (d, *J* = 3.0 Hz, 1H), 5.84 (s, 1H), 5.26 (d, *J* = 17.1 Hz, 1H), 5.18 (d, *J* = 10.3 Hz, 1H), 4.51 – 4.45 (m, 2H), 3.51 (t, *J* = 6.9 Hz, 2H), 3.14 (s, 2H), 2.83 (s, 3H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.8, 164.3, 155.6, 144.6, 132.1, 126.1, 118.7, 79.8, 49.4, 45.0, 35.7, 35.2, 28.5. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{23}N_3O_5S_2Na^+$ 412.0971, found: 412.0964. IR ν_{max} (film, cm $^{-1}$): 2947, 1738, 1728, 1435, 1365, 1143, 762, 603.

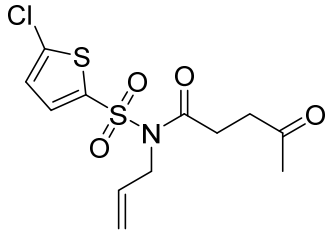


benzyl 3-(allyl(benzo[d]thiazol-2-ylsulfonyl)carbamoyl)azetidine-1-carboxylate (1z2): Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil; 415 mg, yield = 44% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.64 (p, *J* = 7.2 Hz, 2H), 7.48 – 7.29 (m, 5H), 5.82 (ddt, *J* = 16.4, 11.5, 5.9 Hz, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 5.10 (s, 2H), 4.47 (d, *J* = 5.9 Hz, 2H), 4.41 (ddd, *J* = 14.3, 8.7, 5.8 Hz, 1H), 4.36 – 4.29 (m, 2H), 4.23 (t, *J* = 8.7 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.8, 163.9, 156.2, 151.9, 136.6, 136.5, 131.4, 128.5, 128.1, 128.0, 125.6, 122.3, 119.4, 66.8, 51.7, 49.6, 35.1. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}N_3O_5S_2^+$ 472.0995, found: 472.0989. IR ν_{max} (film, cm $^{-1}$): 2902, 1702, 1420, 1346, 1125, 1026, 760, 621.

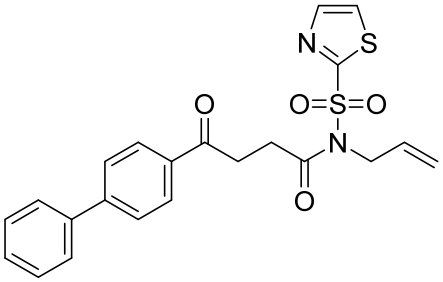


benzyl (4-(*N*-allylthiazole-2-sulfonamido)-4-oxobutyl)(methyl)carbamate (1z3): Silica gel column chromatography (petroleum ether/ethyl acetate = 3:1), colorless oil; 376 mg, yield = 43% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 3.1 Hz, 1H), 7.67 (s, 1H), 7.37 – 7.29 (m, 5H), 5.83 (s, 1H), 5.29 – 5.14 (m, 2H), 5.09 (s, 2H), 4.43 (d, *J* = 29.2 Hz, 2H), 3.31 (t, *J* = 7.0 Hz, 2H), 2.89 (s, 5H), 1.88 (q, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 164.3, 156.3, 144.5, 136.9, 132.2, 128.5, 128.0, 127.8, 125.9, 118.5, 67.1, 49.3, 48.1, 47.6, 33.5, 22.8. HR-MS

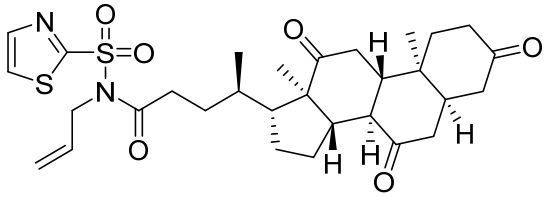
(ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}N_3O_5S_2^+$ 438.1152, found: 438.1147. IR ν_{max} (film, cm^{-1}): 2947, 1740, 1695, 1408, 1365, 1183, 1027, 886, 743.



***N*-allyl-*N*-((5-chlorothiophen-2-yl)sulfonyl)-4-oxopentanamide (1z4)**: Silica gel column chromatography (petroleum ether/ethyl acetate = 10:1), colorless oil; 302 mg, yield = 45% over 2 steps. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 4.1 Hz, 1H), 6.94 (d, *J* = 4.1 Hz, 1H), 5.86 (ddt, *J* = 15.8, 10.5, 5.4 Hz, 1H), 5.34 – 5.17 (m, 2H), 4.45 (d, *J* = 5.3 Hz, 2H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.78 (t, *J* = 6.1 Hz, 2H), 2.18 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 206.5, 172.0, 139.5, 138.3, 137.3, 134.0, 132.1, 126.5, 118.5, 49.0, 37.5, 30.2, 29.8. HR-MS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{14}ClNO_4S_2Na^+$ 357.9945, found: 357.9941. IR ν_{max} (film, cm^{-1}): 2923, 1743, 1702, 1405, 1360, 1164, 993, 800, 614.



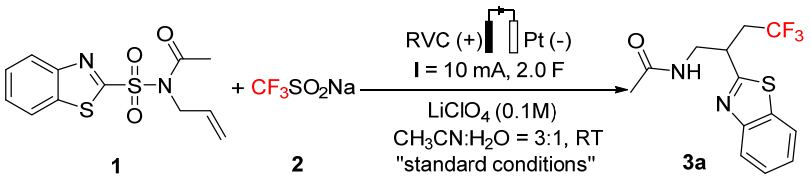
4-([1,1'-biphenyl]-4-yl)-*N*-allyl-4-oxo-*N*-(thiazol-2-ylsulfonyl)butanamide (1z5): Silica gel column chromatography (petroleum ether/ethyl acetate = 3:1), red solid; 414 mg, yield = 47% over 2 steps. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.7, 2.5 Hz, 3H), 7.72 (d, *J* = 3.1 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 5.92 (ddt, *J* = 16.0, 10.8, 5.6 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.57 (d, *J* = 5.6 Hz, 2H), 3.35 (q, *J* = 3.1 Hz, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.3, 172.5, 145.9, 144.5, 139.9, 135.2, 132.2, 129.0, 128.6, 128.3, 127.3, 127.2, 126.0, 118.5, 49.6, 33.2, 30.9. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}N_2O_4S_2^+$ 441.0937, found: 441.0931. IR ν_{max} (film, cm^{-1}): 2930, 1710, 1680, 1503, 1361, 1181, 988, 843, 762, 599.



(R)-*N*-allyl-4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)-*N*-(thiazol-2-ylsulfonyl)pentanamide (1z6): Silica gel column chromatography (petroleum ether/ethyl acetate = 3:1), white solid; 470 mg, yield = 40% over 2 steps. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.9 Hz, 1H), 7.71 (d, *J* = 2.9 Hz, 1H), 5.85 (ddt, *J* = 15.9, 10.6, 5.5 Hz, 1H), 5.25 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 4.47 (d, *J* = 5.2 Hz, 2H), 2.94 – 2.82 (m, 3H), 2.77 (dd, *J* = 22.5, 10.6 Hz, 2H), 2.34 – 2.08 (m, 8H), 2.02 – 1.90 (m, 4H), 1.80 (q, *J* = 11.2 Hz, 3H), 1.62 (d, *J* = 4.5 Hz, 1H), 1.36 (s, 3H), 1.32 – 1.20 (m, 3H), 1.02 (s, 3H),

0.77 (d, J = 6.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 211.9, 209.0, 208.7, 173.5, 164.4, 144.4, 132.4, 126.0, 118.3, 56.9, 51.7, 49.3, 49.0, 46.8, 45.7, 45.5, 45.0, 42.8, 38.6, 36.5, 36.0, 35.2, 33.7, 30.1, 27.5, 25.1, 21.9, 18.8, 11.8. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{41}N_2O_6S_2^+$ 589.2328, found: 589.2392. IR ν_{max} (film, cm^{-1}): 2942, 1735, 1705, 1444, 1369, 1243, 1140, 1045, 861, 604, 571.

3. Table S1. Optimization of reaction conditions[a]

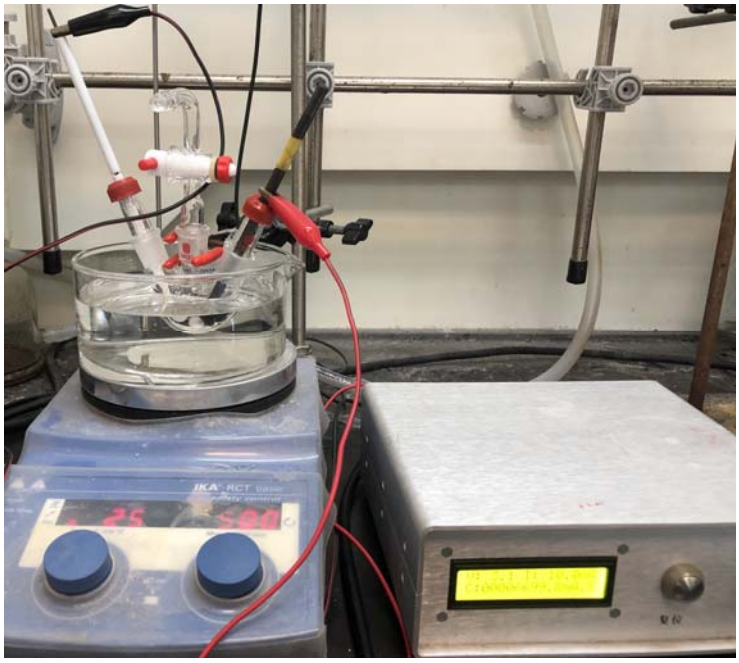


entry	changed from the standard conditions	yield[b] (%)
1	None	86 (82)
2	$^{n}Bu_4NBF_4$ as the electrolyte	66
3	$NaClO_4$ as the electrolyte	80
4	$LiBF_4$ as the electrolyte	74
5	No H_2O	32
6	CH_3CN/H_2O (5:1) as solvent	63
7	CH_3CN/H_2O (1:1) as solvent	78
8	THF instead of CH_3CN	0
9	Acetone instead of CH_3CN	75
10	5 mA	71
11	15 mA	63
12	Graphite rods as anode	20
13	Carbon felt as anode	Trace
14	Pt as anode	15
15	RVC as cathode	77
16	Under N_2	84
17	No electricity	0

[a] reaction conditions: RVC anode (100 PPI, 0.8 cm×0.8 cm×1.0 cm), Pt cathode (1.0 cm×1.0 cm), **1** (0.2 mmol), **2** (0.4 mmol), 0.1 M $LiClO_4$ in CH_3CN: H_2O (6 mL, v/v = 3:1) under air at room temperature, 10 mA (j_{anode}≈0.25 mA cm^{-2}), 2.0 F/mol, undivided cell. [b] Yield determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard. isolated yields in parentheses.

4. General procedure of the electrolysis

To the 10 mL three-necked round bottom flask with a magnetic stir bar was added the *N*-allylsulfonamide (0.2 mmol), CF_3SO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv.), $LiClO_4$ (63.6 mg, 0.1 M.) and CH_3CN : H_2O (3:1 v/v, 6.0 mL). The flask was equipped with a reticulated vitreous carbon (100 PPI) anode (0.8 cm x 0.8 cm x 1 cm) and a platinum plate (1 cm x 1cm) cathode. The electrolysis was carried out at rt using a constant current of 10 mA. The reaction mixture was stirred and electrolyzed for 1.08 h (2.0 F per mol of sulfonamide). When the reaction was finished, the reaction was quenched with saturated NaCl aqueous solution and extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The crude mixture was purified via silica gel column chromatography or preparative TLC (25 % acetone/ petroleum ether) to afford the desired product.



Procedure for gram-scale experiment

To the 50 mL three-necked round bottom flask with a magnetic stir bar was added the *N*-allyl-N-(benzo[d]thiazol-2-ylsulfonyl)acetamide (2 mmol, 592 mg), CF_3SO_2Na (624 mg, 4 mmol, 2.0 equiv.), $LiClO_4$ (318 mg, 0.1 M.) and CH_3CN:H_2O (3:1 v/v, 30 mL). The flask was equipped with a reticulated vitreous carbon (100 PPI) anode (0.8 cm x 0.8 cm x 1 cm) and a platinum plate (1 cm x 1cm) cathode. The electrolysis was carried out at rt using a constant current of 10 mA. The reaction mixture was stirred and electrolyzed for 11 h (2.0 F per mol of sulfonamide). When the reaction was finished, the reaction was quenched with saturated NaCl aqueous solution and extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The crude mixture was purified via silica gel column chromatography or preparative TLC (25 % acetone/ petroleum ether) to afford the desired product. Colorless oil was obtained in 70% isolated yield for *N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)acetamide.

The detection of sulfates was performed via Metrohm 882 ionic chromatography.
Column: Metrosep A supp 4 250/4.05.2;
Eluent: 1.8 mmol/L Na_2CO_3 + 1.7 mmol/L $NaHCO_3$;
Flow rate: 1.0 mL/min;

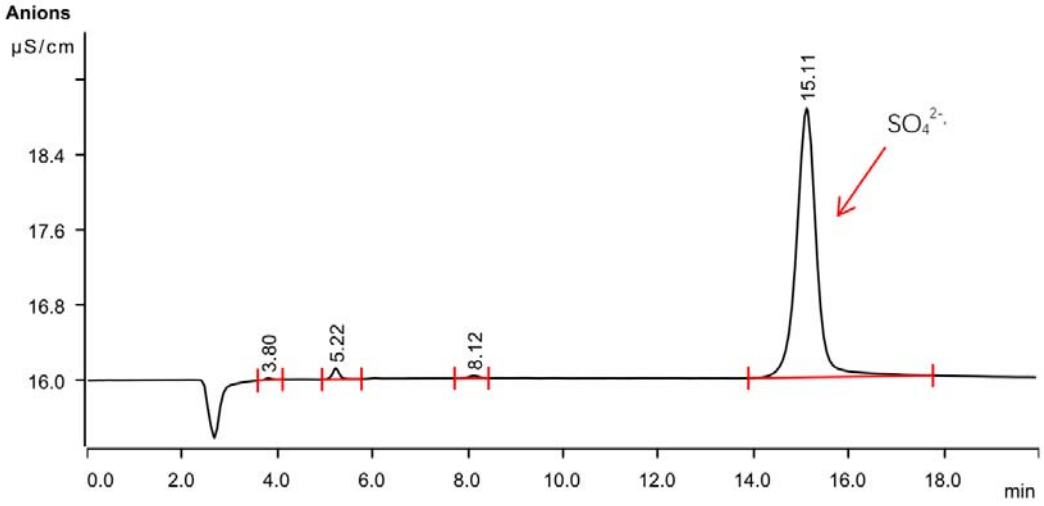


Figure S7. Standard sulfate solution

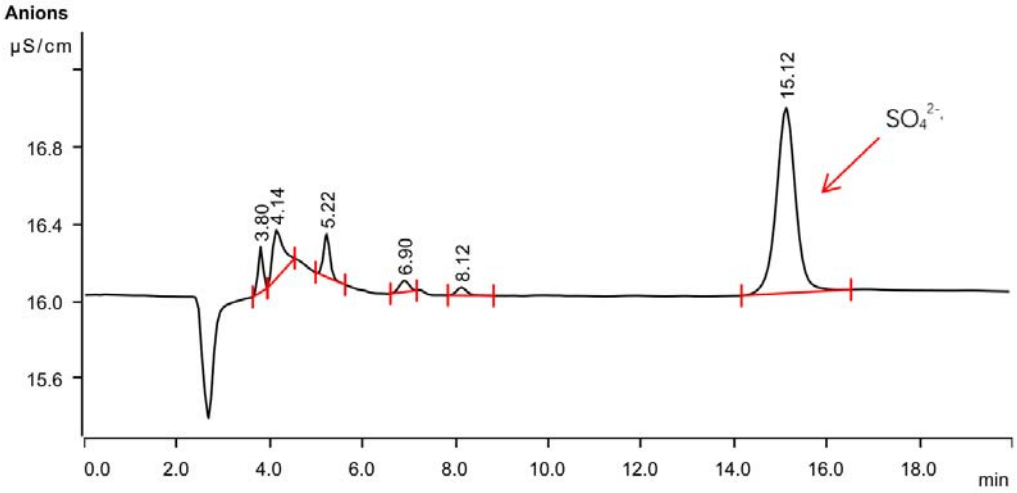
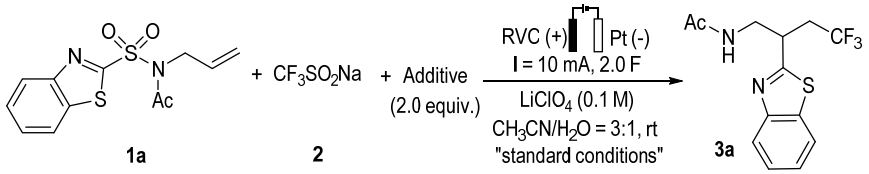
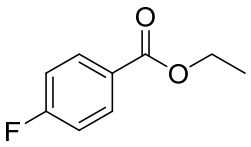
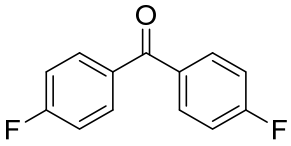
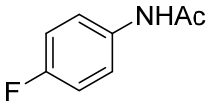
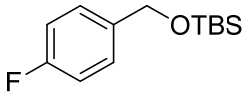
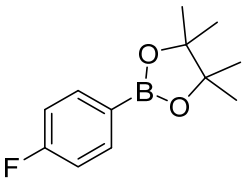
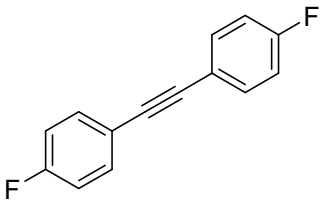
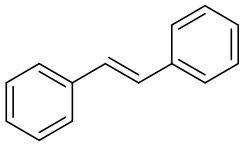


Figure S8. reaction mixture

5. Table S2. Functional group compatibility

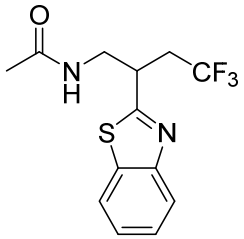


Entry	Additive	Product yield	Additive	SM remaining

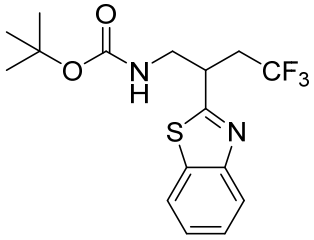
		(%)[a]	remaining (%)[a]	(%)[b]
1		86	98	<5
2		86	98	<5
3		83	95	<5
4		84	44	<5
5		86	84	<5
6		76	64	18
7		30	12[c]	63

[a] Yield determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard. [b] Yield determined by ^{19}F NMR spectroscopy using 4-Fluoroacetophenone as an internal standard. [c]determined by GC-MS.

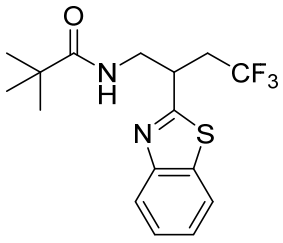
6. Characterization data of electrolysis products



***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)acetamide (3a)**: Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 300 mg, yield = 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 6.25 (s, 1H), 3.72 (m, 2H), 2.89 (m, 1H), 2.75 – 2.45 (m, 1H), 1.94 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.6, 170.5, 153.0, 134.7, 126.4, 126.1 (q. *J* =275 Hz), 125.4, 123.0, 121.8, 43.4, 38.2 (q, *J* = 2.6 Hz), 36.7 (q, *J* = 29.0 Hz), 23.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.08. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_3N_2OS^+$ 303.0773, found: 303.0771. IR ν_{max} (film, cm $^{-1}$): 3230, 2931, 1653, 1548, 1405, 1255, 1126, 758, 600.

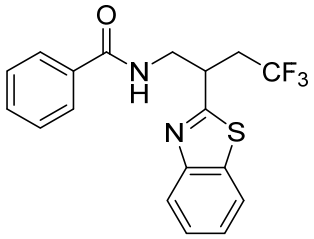


tert-butyl (2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)carbamate (3b): Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 43.9 mg, yield = 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.45 – 7.36 (m, 1H), 4.96 (s, 1H), 3.75 (m, 1H), 3.63 (m, 2H), 2.91 (m, 1H), 2.64 (m, 1H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.5, 155.9, 153.1, 134.8, 126.3, 126.2 (q, *J* = 275 Hz), 125.3, 123.0, 121.7, 79.9, 44.7, 38.7, 36.5 (q, *J* = 29.1 Hz), 28.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.11. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}F_3N_2O_2S^+$ 361.1192, found: 361.1186. IR ν_{max} (film, cm $^{-1}$): 3340, 2985, 1693, 1511, 1367, 1251, 1127, 758, 708.

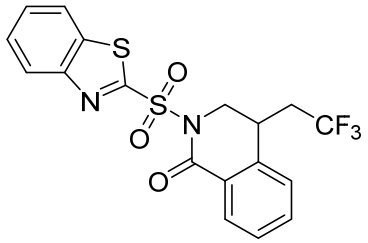


***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)pivalamide (3c)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), colorless oil; 27.5 mg, yield = 40%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 3.82 – 3.73 (m, 3H), 3.68 (m, 2H), 2.99 – 2.80 (m, 1H), 2.60 (m, 1H), 1.16 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 178.9, 170.6, 153.0, 134.5, 126.4, 126.1 (q, *J* = 275Hz), 125.4, 122.9, 121.8, 43.3, 38.8, 37.9 (d, *J* = 2.8 Hz), 36.8 (q, *J* = 29.1 Hz), 27.5. ^{19}F NMR

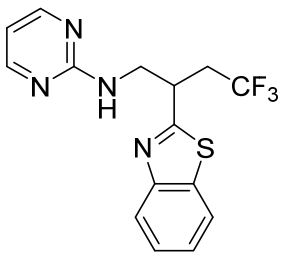
(377 MHz, $CDCl_3$) δ -64.18. (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}F_3N_2OS^+$ 345.1243, found: 345.1242. IR ν_{max} (film, cm $^{-1}$): 3353, 2965, 1639, 1516, 1436, 1264, 1126, 1043, 758, 651.



***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)benzamide (3d)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), white solid; 35.7 mg, yield = 49%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.55 – 7.46 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 3H), 7.10 (s, 1H), 4.02 (dt, *J* = 14.7, 7.4 Hz, 1H), 3.89 (m, 2H), 3.05 – 2.85 (m, 1H), 2.70 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.6, 167.8, 153.0, 134.6, 134.0, 131.7, 128.6, 127.0, 126.4, 126.1 (q, *J* = 276 Hz), 125.5, 123.0, 121.8, 43.6, 38.1 (q, *J* = 2.5 Hz), 36.9 (q, *J* = 29.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.06. (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}F_3N_2OS^+$ 365.0930, found: 365.0928. IR ν_{max} (film, cm $^{-1}$): 3303, 2956, 1637, 1534, 1446, 1284, 1136, 760, 693.

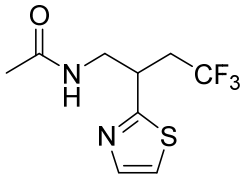


2-(benzo[d]thiazol-2-ylsulfonyl)-4-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinolin-1(2H)-one (3d'): Silica gel column chromatography (petroleum ether/acetone = 5:1), white solid; 8.0 mg, yield = 9%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.08 (m, 1H), 8.03 (dd, *J* = 7.4, 4.2 Hz, 2H), 7.66 – 7.54 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 4.86 (d, *J* = 13.1 Hz, 1H), 4.26 (d, *J* = 12.9 Hz, 1H), 3.54 (s, 1H), 3.20 – 2.85 (m, 1H), 2.52 (dqd, *J* = 15.6, 11.1, 5.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.38, 163.07, 151.89, 141.16, 137.09, 134.65, 129.75, 128.64, 128.07, 127.61, 127.55, 126.74, 126.1 (q, *J* = 276 Hz), 125.35, 122.25, 49.44, 37.2 (q, *J* = 28.3 Hz), 33.10 (q, *J* = 2.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.82. (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}F_3N_2O_3S_2^+$ 327.0392, found: 327.0389. IR ν_{max} (film, cm $^{-1}$): 2920, 1697, 1471, 1370, 1259, 1176, 1063, 760, 630.

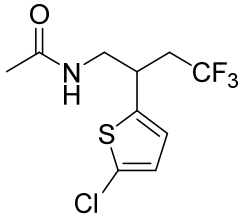


N-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)pyrimidin-2-amine (3e): Silica gel column chromatography (petroleum ether/acetone = 5:1), white solid; 45.3 mg, yield = 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 4.6 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.57 –

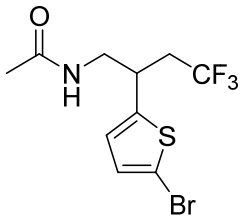
7.45 (m, 1H), 7.45 – 7.33 (m, 1H), 6.52 (t, *J* = 4.8 Hz, 1H), 6.08 (s, 1H), 4.02 – 3.78 (m, 3H), 3.01 (m, 1H), 2.80 – 2.59 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.7, 162.1, 158.0, 153.1, 134.8, 126.3 (q, *J* = 276 Hz), 126.2, 125.2, 123.0, 121.6, 111.1, 45.8, 38.3 (q, *J* = 2.6 Hz), 36.6 (q, *J* = 28.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.00. (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}F_3N_4S^+$ 339.0886, found: 339.0881. IR ν_{max} (film, cm^{-1}): 3267, 2977, 1585, 1538, 1436, 1254, 1125, 801, 729.



***N*-(4,4,4-trifluoro-2-(thiazol-2-yl)butyl)acetamide (3f)**: Silica gel column chromatography (petroleum ether/acetone = 4:1), light yellow oil; 41.8 mg, yield = 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 3.3 Hz, 1H), 7.29 (d, *J* = 3.3 Hz, 1H), 6.45 (s, 1H), 3.67 (m, 3H), 2.84 – 2.67 (m, 1H), 2.65 – 2.45 (m, 1H), 1.96 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.7, 170.0, 142.7, 126.1 (q, *J* = 277.1 Hz), 119.0, 43.6, 37.1 (q, *J* = 2.7 Hz), 37.0 (d, *J* = 28.8 Hz), 23.13. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.14. (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{12}F_3N_2OS^+$ 253.0617, found: 253.0615. IR ν_{max} (film, cm^{-1}): 3291, 2942, 1655, 1547, 1372, 1256, 1129, 1090, 728, 592.

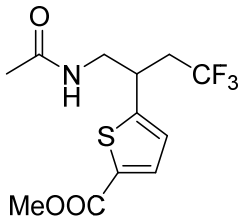


***N*-(2-(5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)acetamide (3g)**: Silica gel column chromatography (petroleum ether/acetone = 10:1), yellow oil; 42.8 mg, yield = 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, *J* = 3.5 Hz, 1H), 6.68 (d, *J* = 3.4 Hz, 1H), 5.65 (s, 1H), 3.73 (dt, *J* = 13.1, 6.4 Hz, 1H), 3.41 (m, 1H), 3.23 (dt, *J* = 13.5, 6.7 Hz, 1H), 2.52 – 2.36 (m, 2H), 1.97 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4, 142.4, 128.8, 126.1, 125.9 (q, *J* = 277 Hz), 124.8, 45.0, 38.4 (q, *J* = 28.5 Hz), 36.1 (q, *J* = 2.5 Hz), 23.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.82. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}ClF_3NOS^+$ 286.0275, found: 286.0274. IR ν_{max} (film, cm^{-1}): 3305, 2950, 1637, 1534, 1436, 1254, 1136, 758, 693.

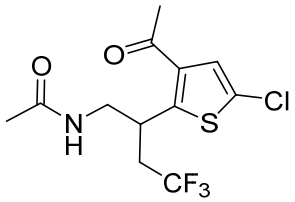


***N*-(2-(5-bromothiophen-2-yl)-4,4,4-trifluorobutyl)acetamide (3h)**: Silica gel column chromatography (petroleum ether/acetone = 10:1), yellow oil; 47.4 mg, yield = 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 3.3 Hz, 1H), 6.66 (d, *J* = 3.1 Hz, 1H), 5.72 (s, 1H), 3.71 (dt, *J* = 13.1, 6.3 Hz, 1H), 3.43 (m, 1H), 3.22 (m, 1H), 2.68 – 2.25 (m, 2H), 1.95 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4, 145.3, 129.9, 126.0 (q, J = 275 Hz), 125.9, 110.9, 45.0, 38.4 (q, *J* = 28.4 Hz), 36.1 (q, *J* = 2.8 Hz), 23.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.78. (ESI) m/z: $[M+H]^+$ Calcd for

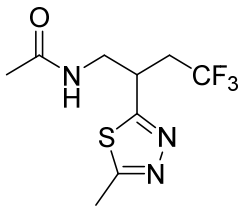
$C_{10}H_{12}BrF_3NOS^+$ 329.9770, found: 329.9768. IR ν_{max} (film, cm $^{-1}$): 3291, 2946, 1653, 1551, 1437, 1251, 1128, 1046, 795, 599.



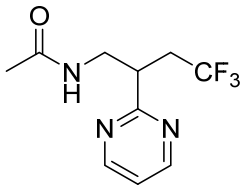
ethyl 5-(1-acetamido-4,4,4-trifluorobutan-2-yl)thiophene-2-carboxylate (3i): Silica gel column chromatography (petroleum ether/acetone = 8:1), yellow solid; 43.2 mg, yield = 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 5.1 Hz, 1H), 7.05 (d, *J* = 5.1 Hz, 1H), 5.89 (s, 1H), 4.37 – 4.25 (m, 1H), 3.87 (s, 3H), 3.60 (dt, *J* = 12.4, 5.9 Hz, 1H), 3.45 (dt, *J* = 13.9, 7.2 Hz, 1H), 2.58 – 2.47 (m, 2H), 1.87 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.2, 163.2, 148.5, 131.5, 127.9, 127.7, 126.3 (q, *J* = 276 Hz), 52.2, 44.0, 36.8 (q, *J* = 28.3 Hz), 33.2 (q, *J* =2.7 Hz), 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.98. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}F_3NO_3S^+$ 310.0719, found: 310.0716. IR ν_{max} (film, cm $^{-1}$): 3285, 2953, 1709, 1657, 1536, 1438, 1246, 1143, 778, 680.



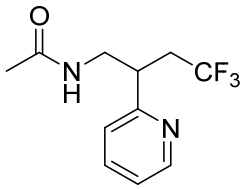
***N*-(2-(3-acetyl-5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)acetamide (3j)**: Silica gel column chromatography (petroleum ether/acetone = 8:1), yellow solid; 40.0 mg, yield = 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.32 (s, 1H), 4.35 – 4.22 (m, 1H), 3.59 (dt, *J* = 11.8, 5.0 Hz, 1H), 3.45 (dt, *J* = 13.4, 6.4 Hz, 1H), 2.57 – 2.49 (m, 2H), 2.48 (s, 3H), 1.92 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.4, 170.8, 150.7, 136.7, 128.5, 127.4, 126.0 (q, *J* = 275 Hz), 45.0, 38.0 (q, *J* = 28.7 Hz), 34.2 (q, *J* = 2.8 Hz), 30.1, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.98. (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}F_3N_1O_2SCl^+$ 328.03380, found: 329.0379. IR ν_{max} (film, cm $^{-1}$): 3297, 3068, 1655, 1524, 1444, 1363, 1255, 1134, 1060, 873, 596.



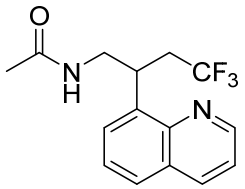
***N*-(4,4,4-trifluoro-2-(5-methyl-1,3,4-thiadiazol-2-yl)butyl)acetamide (3k)**: Silica gel column chromatography (petroleum ether/acetone = 4:1), yellow oil; 40.0 mg, yield = 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (s, 1H), 3.78 (dt, *J* = 8.1, 5.6 Hz, 1H), 3.66 (t, *J* = 6.2 Hz, 2H), 2.73 (m, 4H), 2.60 (m, 1H), 1.95 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.8, 167.0, 165.7, 125.9 (q, *J* = 277 Hz), 43.23, 36.9 (q, *J* = 29.1 Hz), 35.0 (q, *J* = 2.5 Hz), 23.1, 15.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.01. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{13}F_3N_3OS^+$ 268.0726, found: 268.0725. IR ν_{max} (film, cm $^{-1}$): 3276, 2921, 1654, 1546, 1433, 1255, 1136, 1059, 632.



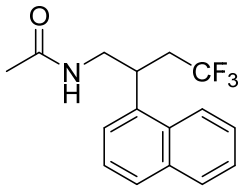
***N*-(4,4,4-trifluoro-2-(pyrimidin-2-yl)butyl)acetamide (3l)**: Silica gel column chromatography (petroleum ether/acetone = 4:1), white solid; 23.7 mg, yield = 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.9 Hz, 2H), 7.22 (t, *J* = 4.9 Hz, 1H), 6.33 (s, 1H), 3.78 – 3.59 (m, 2H), 3.52 (ddd, *J* = 12.7, 8.2, 5.0 Hz, 1H), 3.04 – 2.76 (m, 1H), 2.48 (m, 1H), 1.92 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.5, 169.6, 157.3, 126.6 (q, *J* = 277.0 Hz), 119.6, 42.7, 42.4 (q, *J* = 2.4 Hz), 35.4 (q, *J* = 28.7 Hz), 23.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.20. (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{13}F_3N_3O^+$ 248.1005 found: 2248.1005. IR ν_{max} (film, cm $^{-1}$): 3291, 2942, 1652, 1565, 1427, 1259, 1145, 1080, 805, 637.



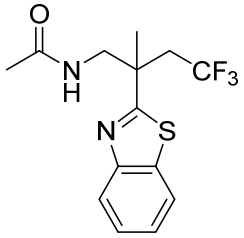
***N*-(4,4,4-trifluoro-2-(pyridin-2-yl)butyl)acetamide (3m)**: Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 12.3 mg, yield = 25%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.2 Hz, 1H), 7.77 – 7.57 (m, 1H), 7.21 (t, *J* = 8.3 Hz, 2H), 6.33 (s, 1H), 3.67 (dt, *J* = 13.7, 6.9 Hz, 1H), 3.54 (dt, *J* = 13.4, 4.9 Hz, 1H), 3.45 – 3.29 (m, 1H), 2.74 (m, 1H), 2.56 – 2.36 (m, 1H), 1.94 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.6, 160.4, 149.5, 137.2, 126.5 (q, J = 275 Hz), 123.8, 122.5, 43.6, 40.3 (d, *J* = 2.4 Hz), 36.4 (q, *J* = 28.3 Hz), 23.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.03. (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}F_3N_2O^+$ 247.1053, found: 247.1053. IR ν_{max} (film, cm $^{-1}$): 3294, 2933, 1651, 1550, 1437, 160, 1141, 750, 594.



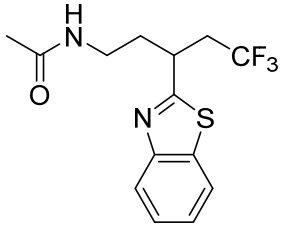
***N*-(4,4,4-trifluoro-2-(quinolin-8-yl)butyl)acetamide (3n)**: Silica gel column chromatography (petroleum ether/acetone = 6:1), yellow solid; 23.7 mg, yield = 40%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 – 8.82 (m, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 6.7 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.24 (s, 1H), 4.35 – 4.19 (m, 1H), 3.79 (qt, *J* = 13.3, 6.7 Hz, 2H), 3.03 (m, 1H), 2.73 (m, 1H), 1.80 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.2, 149.3, 146.4, 138.8, 136.9, 129.1, 128.8, 127.7, 126.8 (q, *J* = 276 Hz), 126.5, 121.2, 44.6, 36.6, (q, *J* = 27.8 Hz), 36.3, 23.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.96. (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}F_3N_2O^+$ 297.1209, found: 297.1208. IR ν_{max} (film, cm $^{-1}$): 3288, 2936, 1646, 1551, 1268, 1258, 1141, 1037, 795, 595.



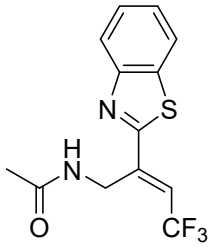
***N*-(4,4,4-trifluoro-2-(naphthalen-1-yl)butyl)acetamide (3o)**: Silica gel column chromatography (petroleum ether/acetone = 8:1), white solid; 20.6 mg, yield = 35%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.53 (m, 3H), 7.39 (d, *J* = 7.2 Hz, 1H), 5.47 (s, 1H), 4.17 (m, 1H), 4.00 – 3.82 (m, 1H), 3.47 (m, 1H), 2.64 (m, 2H), 1.81 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.4, 136.7, 134.1, 131.8, 129.16, 128.02, 126.67, 126.5 (q, *J* = 275 Hz), 125.97, 125.41, 123.52, 122.48, 44.38, 37.74 (q, *J* = 28.2 Hz), 32.7, 23.10. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.67. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}F_3NO^+$ 296.1257, found: 296.1256. IR ν_{max} (film, cm $^{-1}$): 3285, 2930, 1650, 1550, 1370, 1261, 1137, 778, 662.



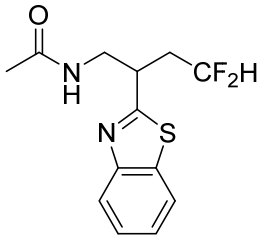
***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluoro-2-methylbutyl)acetamide (3p)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), colorless oil; 48.0 mg, yield = 76%; ^{1}H NMR (400 MHz, CDCl3) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.37 (s, 1H), 3.85 (dd, *J* = 13.6, 6.9 Hz, 1H), 3.53 (dd, *J* = 13.6, 5.4 Hz, 1H), 3.01(m, 1H), 2.74 – 2.44 (m, 1H), 2.00 (s, 3H), 1.67 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.9, 170.4, 152.8, 134.6, 126.3, 126.1 (q, *J* = 277 Hz), 125.4, 123.1, 121.7, 48.6, 42.5, 42.2 (d, *J* = 27.7 Hz), 23.4, 23.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.57. (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}F_3N_2OS^+$ 317.0930, found: 317.0927. IR ν_{max} (film, cm $^{-1}$): 3285, 2942, 1656, 1551, 1436, 1259, 1107, 759, 600.



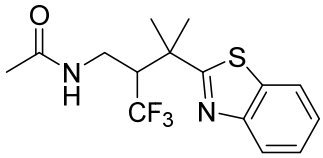
***N*-(3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentyl)acetamide (3q)**: Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 31.6 mg, yield = 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.44 (m, 1H), 7.42 – 7.34 (m, 1H), 6.01 (s, 1H), 3.60 (tt, *J* = 9.7, 5.3 Hz, 1H), 3.30 (dq, *J* = 13.0, 6.2 Hz, 1H), 3.12 (dq, *J* = 13.6, 7.1 Hz, 1H), 2.94 – 2.74 (m, 1H), 2.57 (m, 1H), 2.22 – 2.00 (m, 2H), 1.86 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 170.5, 152.8, 134.6, 126.4, 126.0 (q, *J* = 276 Hz), 125.4, 122.9, 121.8, 39.1 (q, *J* = 28.6 Hz), 37.0, 36.6 (q, *J* = 2.7 Hz), 35.3, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.01. (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}F_3N_2OS^+$ 317.0930, found: 317.0930. IR ν_{max} (film, cm $^{-1}$): 3282, 2942, 1647, 1553, 1437, 1251, 1124, 1050, 759, 647.



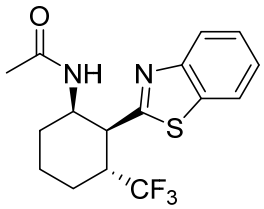
(E)-N-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobut-2-en-1-yl)acetamide (3r): Silica gel column chromatography (petroleum ether/acetone = 4:1), white solid; 22.8 mg, yield = 38%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 6.62 (q, *J* = 8.2 Hz, 1H), 6.48 (s, 1H), 4.70 (d, *J* = 5.7 Hz, 2H), 1.97 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.0, 165.4, 153.3, 141.7 (q, *J* = 5.3 Hz), 134.8, 126.9, 126.7, 123.9, 122.8 (q, *J* = 35.7 Hz), 122.4 (q, *J* = 270 Hz), 121.8, 37.6, 23.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.84. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}F_3N_2OS^+$ 301.0617, found: 301.0616. IR ν_{max} (film, cm $^{-1}$): 3279, 2988, 1654, 1559, 1281, 1270, 1123, 1056, 879, 760.



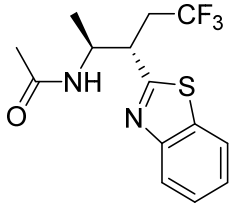
***N*-(2-(benzo[d]thiazol-2-yl)-4,4-difluorobutyl)acetamide (3s)**: Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 22.2 mg, yield = 39%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 6.33 (s, 1H), 5.95 (tt, *J* = 56.4, 4.7 Hz, 1H), 3.70 (m, 3H), 2.50 (m, 1H), 2.32 (m, 1H), 1.96 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.3, 170.8, 152.9, 134.6, 126.4, 125.5, 123.0, 121.8, 115.7 (t, *J* = 239.6 Hz), 43.0, 38.7 (t, *J* = 5.4 Hz), 36.9 (t, *J* = 22.2 Hz), 23.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.29 (dd, *J* = 417.4 Hz, *J* = 285.7 Hz). (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}F_2N_2OS^+$ 285.0868, found: 285.0866. IR ν_{max} (film, cm $^{-1}$): 3288, 2933, 1654, 1549, 1437, 1286, 1121, 1013, 760, 709.



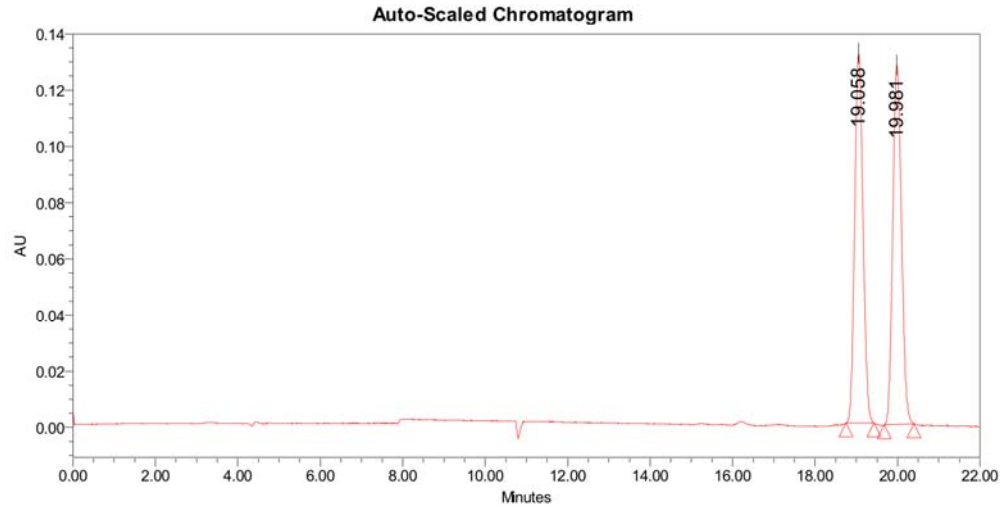
***N*-(3-(benzo[d]thiazol-2-yl)-3-methyl-2-(trifluoromethyl)butyl)acetamide (3t)**: Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 29.0 mg, yield = 44%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.47 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1H), 5.98 (s, 1H), 3.75 – 3.68 (m, 1H), 3.52 (ddd, *J* = 14.6, 7.1, 5.3 Hz, 1H), 3.29 (m, 1H), 1.83 (s, 3H), 1.64 (s, 3H), 1.63 – 1.61 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 179.1, 169.8, 152.8, 134.6, 127.5 (q, *J* = 282 Hz), 126.2, 125.1, 122.8, 121.7, 51.5 (q, *J* = 22.8 Hz), 42.2, 36.4 (q, *J* = 3.0 Hz), 27.5 (q, *J* = 2.5 Hz), 26.0, 23.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.05. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}F_3N_2OS^+$ 331.1087, found: 331.1084. IR ν_{max} (film, cm $^{-1}$): 3297, 2985, 1653, 1554, 1437, 1245, 1152, 758, 602.



***N*-((1R,2S,3R)-2-(benzo[d]thiazol-2-yl)-3-(trifluoromethyl)cyclohexyl)acetamide (3u):** Silica gel column chromatography (petroleum ether/acetone = 5:1), white oil; 29.4 mg, yield = 43%, > 20:1 dr; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 5.1 Hz, 1H), 4.40 (m, 1H), 3.69 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.04 (m, 1H), 2.29 – 2.17 (m, 2H), 1.91 (s, 3H) 1.77 (m, 1H), 1.73 – 1.65 (m, 2H), 1.62 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.1, 169.3, 152.9, 134.4, 127.3 (q, *J* = 279 Hz), 126.3, 125.4, 122.8, 121.7, 48.1, 42.5 (q, *J* = 25.5 Hz), 42.3, 28.4, 23.5, 22.8, 19.3. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -68.34. (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}F_3N_2OS^+$ 343.1087, found: 343,1081. IR ν_{max} (film, cm $^{-1}$): 3285, 2945, 1645, 1545, 1437, 1343, 1148, 907, 759, 502.



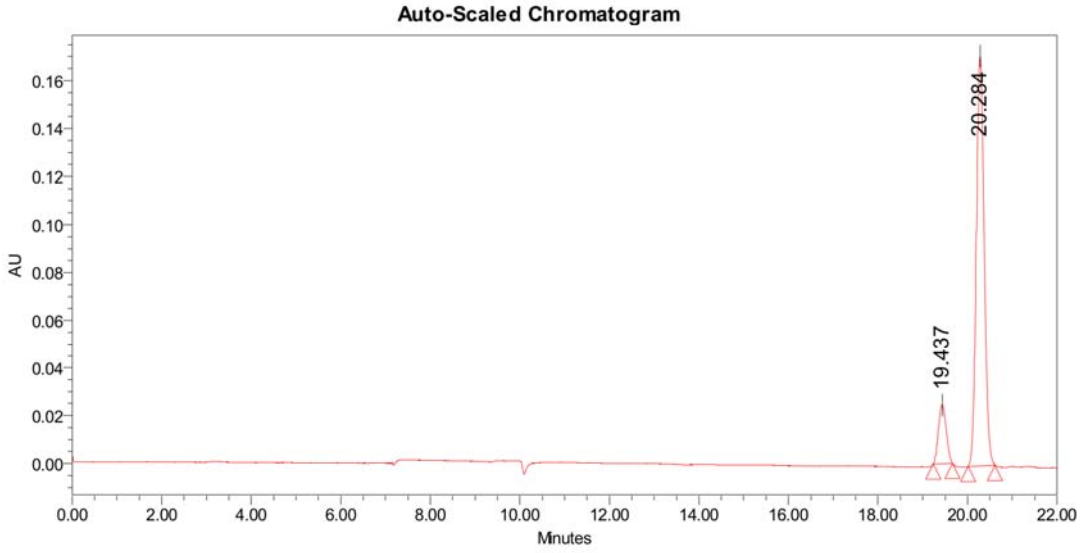
***N*-((2S,3S)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentan-2-yl)acetamide (3v)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), colorless oil; 36.5 mg, yield = 58%, 88:12 er. $[\alpha]_D^{20.0}$ = -22.67 (*c* = 0.3 in acetone, λ = 589 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.54 (m, 1H), 3.54 (d, *J* = 9.1 Hz, 1H), 2.92 (dq, *J* = 20.4, 10.3 Hz, 1H), 2.64 (p, *J* = 12.5, 11.8 Hz, 1H), 2.08 (s, 3H), 1.08 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.9, 169.4, 153.2, 134.4, 126.4, 126.3 (q, *J* = 276 Hz), 125.5, 123.0, 121.7, 48.1, 42.0 (q, *J* = 2.5 Hz), 37.7 (q, *J* = 28.7 Hz), 23.6, 19.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.39. (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}F_3N_2OS^+$ 317.0930, found: 317.0924. IR ν_{max} (film, cm $^{-1}$): 3250, 2986, 1651, 1515, 1438, 1257, 1128, 759, 649. The enantioselectivity was determined by UPCC (Trefoil AMY1, gradient 100% CO_2 to CO_2/MeOH = 90:10 in 0-22th min, flow rate: 0.2 mL/min, λ = 254 nm), t_R (major) = 20.3 min, t_R(minor) = 19.4 min.



Peak Results

	RT	Area	Height	% Area	% Height
1	19.058	1809211	131590	49.48	50.69
2	19.981	1847008	127985	50.52	49.31

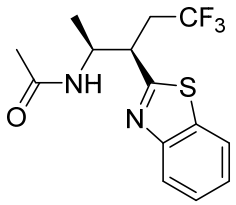
Figure S9. Chromatograms of Racemic **3v**



Peak Results

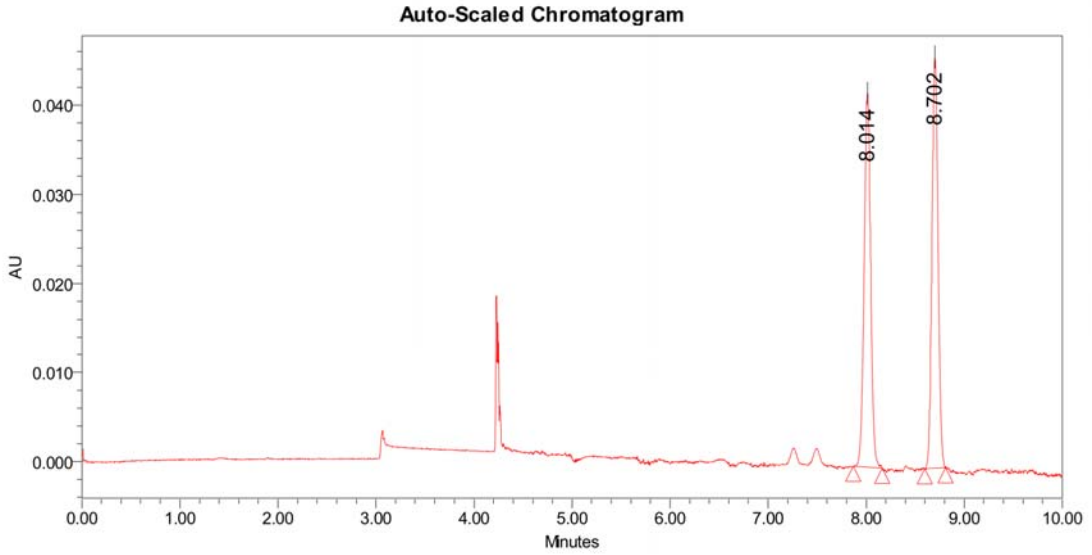
	RT	Area	Height	% Area	% Height
1	19.437	294147	24479	12.27	12.51
2	20.284	2103952	171183	87.73	87.49

Figure S10. Chromatograms of Product**3v**



***N*-((2S,3R)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentan-2-yl)acetamide (3v2)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), colorless oil; 5.2 mg, yield = 8%, 88:12

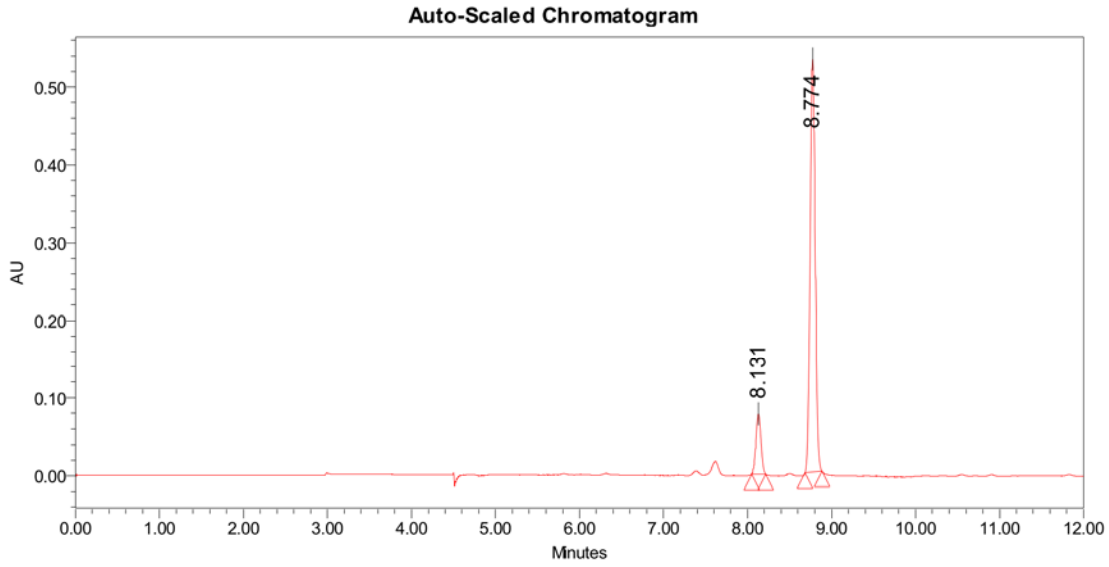
er. $[\alpha]_D^{20.0}$ = -5.33 (*c* = 0.3 in acetone, λ = 589 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 5.62 (d, *J* = 7.8 Hz, 1H), 4.43 (dq, *J* = 13.6, 6.8 Hz, 1H), 3.72 (ddd, *J* = 9.7, 6.3, 3.7 Hz, 1H), 3.03 (m, 1H), 2.60 (m, 1H), 2.02 (s, 3H), 1.13 (d, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.7, 168.7, 153.0, 134.7, 126.3, 126.2 (q, *J* = 275 Hz), 125.4, 123.2, 121.6, 48.3, 42.9 (q, *J* = 2.5 Hz), 36.4 (q, *J* = 29.1 Hz), 23.5, 16.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.37. (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}F_3N_2OS^+$ 317.0930, found: 317.0925. IR ν_{max} (film, cm $^{-1}$): 3280, 2923, 1654, 1545, 1438, 1263, 1127, 759, 647. The enantioselectivity was determined by UPCC (Chiralcel OD-3, gradient 100% CO_2 to CO_2/MeOH = 80:20 in 0-10th min, flow rate: 0.5 mL/min, λ = 254 nm), t_R (major) = 8.7 min, t_R(minor) = 8.1 min.



Peak Results

	RT	Area	Height	% Area	% Height
1	8.014	196204	41921	49.97	47.60
2	8.702	196430	46141	50.03	52.40

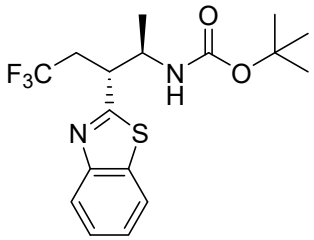
Figure S11. Chromatograms of racemic **3v2**



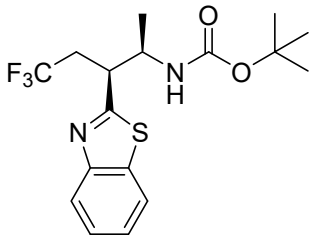
Peak Results

	RT	Area	Height	% Area	% Height
1	8.131	318522	77051	12.25	12.66
2	8.774	2280933	531682	87.75	87.34

Figure S12. Chromatograms of product **3v2**

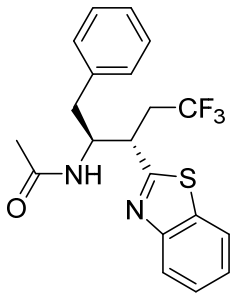


***tert*-butyl ((2R,3R)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentan-2-yl)carbamate (3v')**: Silica gel column chromatography (petroleum ether/acetone = 15:1), colorless oil; 12 mg, yield = 32%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.46 (m, 1H), 7.45 – 7.36 (m, 1H), 5.61 (d, *J* = 8.9 Hz, 1H), 4.20 (m, 1H), 3.74 – 3.44 (m, 2H), 3.18 – 2.87 (m, 1H), 2.87 – 2.53 (m, 1H), 1.48 (s, 9H), 1.09 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 155.6, 153.2, 134.5, 126.5 (q, *J* = 275 Hz), 126.3, 125.4, 123.1, 121.6, 79.7, 49.7, 42.4, 37.0 (q, J = 28.4 Hz), 28.4, 19.5. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -64.45. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}F_3N_2O_2S^+$ 375.1349, found: 375.1342. IR ν_{max} (film, cm $^{-1}$): 3355, 2978, 1705, 1504, 1366, 1248, 1159, 759, 709.

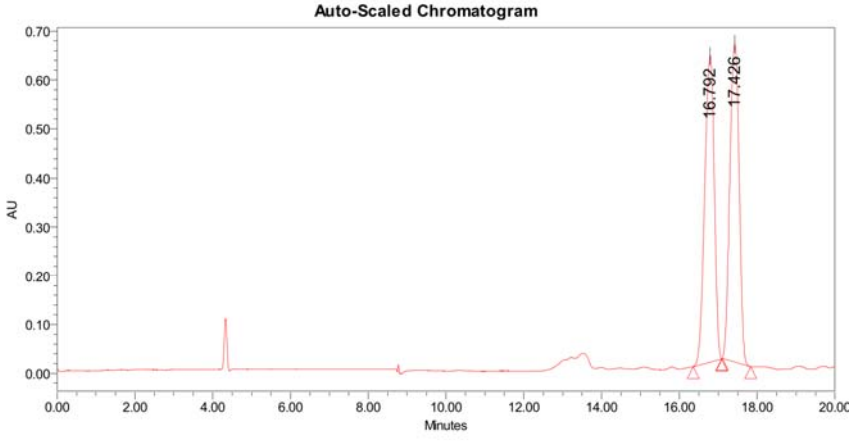


***tert*-butyl ((2R,3S)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentan-2-yl)carbamate (3v'2)**: Silica gel column chromatography (petroleum ether/acetone = 15:1), colorless oil; 1.5 mg, yield = 4%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.49

(t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 4.56 (s, 1H), 4.09 (s, 1H), 3.71 (s, 1H), 3.16 – 2.94 (m, 1H), 2.70 – 2.50 (m, 1H), 1.47 (s, 9H), 1.12 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.0, 155.1, 153.0, 134.9, 126.4 (q, *J* = 275 Hz), 126.2, 125.3, 123.1, 121.6, 80.0, 49.8, 43.4, 36.2 (q, *J* = 28.2 Hz), 28.4, 17.2. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -64.33. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}F_3N_2O_2S^+$ 375.1349, found: 375.1342. IR ν_{max} (film, cm $^{-1}$): 3332, 2979, 1691, 1504, 1366, 1250, 1126, 758, 645.



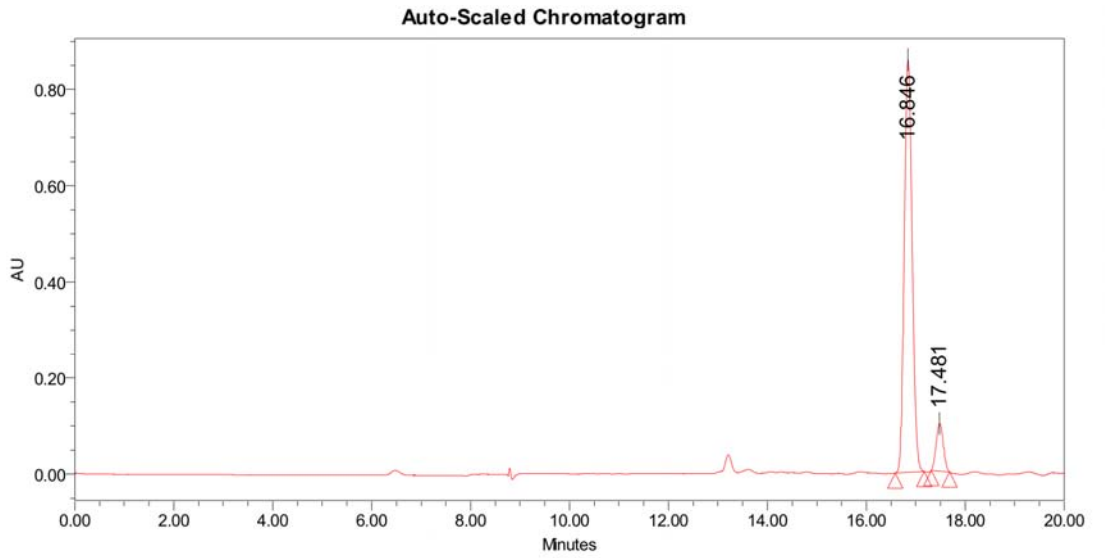
***N*-((2S,3S)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoro-1-phenylpentan-2-yl)acetamide (3w)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), colorless oil; 43.1 mg, yield = 55%, 90:10 er. $[\alpha]_D^{20.0}$ = -16.00 (*c* = 0.3 in acetone, λ = 589 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.54 (m, 1H), 7.53 – 7.45 (m, 1H), 7.39 – 7.31 (m, 3H), 7.30 – 7.18 (m, 3H), 4.75 (tdd, *J* = 9.3, 6.2, 3.2 Hz, 1H), 3.00 – 2.87 (m, 1H), 2.82 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.71 – 2.59 (m, 1H), 2.55 (dd, *J* = 14.0, 9.0 Hz, 1H), 2.12 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.0, 169.4, 153.1, 137.1, 134.4, 129.1, 128.7, 126.9, 126.5, 126.1 (*J* = 276 Hz), 125.7, 123.1, 121.8, 54.0, 39.7, 38.6 (q, *J* = 2.5 Hz), 38.1 (q, *J* = 28.5 Hz), 23.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.20. (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}F_3N_2OS^+$ 393.1243, found: 393.1238. IR ν_{max} (film, cm $^{-1}$): 3279, 2930, 1653, 1516, 1436, 1257, 1143, 1056, 760, 700. The enantioselectivity was determined by UPCC (Chiralcel OX-3, gradient 100% CO_2 to CO_2/MeOH = 70:30 in 0-20th min, flow rate: 0.2 mL/min, λ = 254 nm), t_R (major) = 16.8 min, t_R(minor) = 17.5 min.



Peak Results

	RT	Area	Height	% Area	% Height
1	16.792	10732234	625745	50.03	49.06
2	17.426	10719955	649774	49.97	50.94

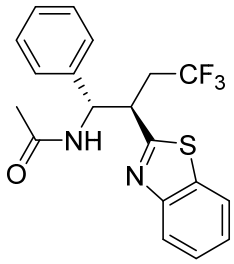
Figure S13. Chromatograms of Racemic **3w**



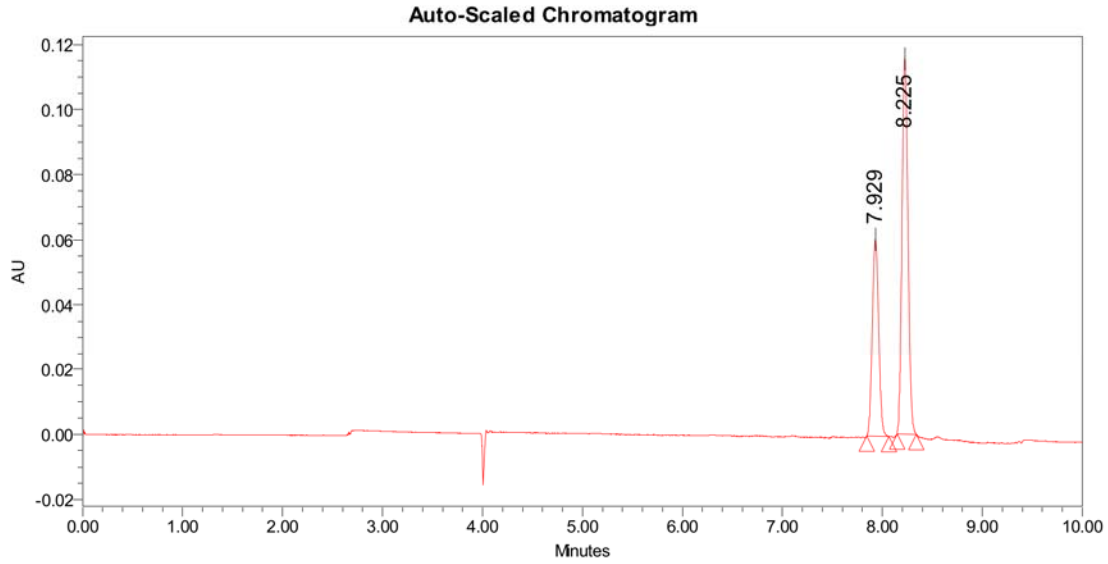
Peak Results

	RT	Area	Height	% Area	% Height
1	16.846	9319324	858235	90.27	89.67
2	17.481	1004069	98914	9.73	10.33

Figure S14. Chromatograms of product **3w**



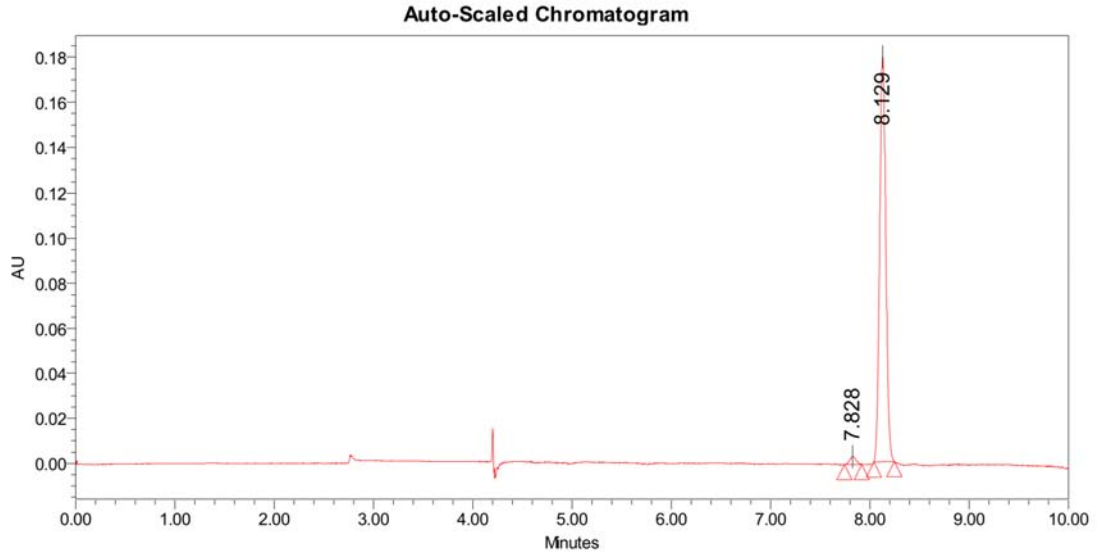
***N*-((1S,2R)-2-(benzo[d]thiazol-2-yl)-4,4,4-trifluoro-1-phenylbutyl)acetamide (3x)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), white solid; 30.2 mg, yield = 40%, 98:2 er, $[\alpha]_D^{20.0}$ = -22.67 (*c* = 0.3 in acetone, λ = 589 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.57 – 7.44 (m, 1H), 7.44 – 7.33 (m, 1H), 7.18 (qd, *J* = 4.3, 1.6 Hz, 3H), 7.05 – 6.95 (m, 2H), 5.57 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.83 (dt, *J* = 8.8, 4.1 Hz, 1H), 3.05 (m, 1H), 2.77 (m, 1H), 2.14 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.8, 169.2, 152.8, 139.4, 134.4, 128.6, 127.7, 126.3, 126.1 (q, *J* = 275 Hz), 125.5, 124.8, 122.9, 121.7, 56.1, 43.2 (q, *J* = 2.5 Hz), 38.0 (q, *J* = 28.8 Hz), 23.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.37. (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}F_3N_2OS^+$ 379.1087, found: 379.1084. IR ν_{max} (film, cm $^{-1}$): 3299, 2922, 1651, 1511, 1436, 1256, 1125, 759, 701. The enantioselectivity was determined by UPCC (Trefoil CEL1, gradient 100% CO_2 to CO_2/MeOH = 80:20 in 0-10th min, flow rate: 0.5 mL/min, λ = 254 nm), t_R (major) = 8.1 min, t_R(minor) = 7.8 min.



Peak Results

	RT	Area	Height	% Area	% Height
1	7.929	264332	60832	35.81	34.45
2	8.225	473810	115752	64.19	65.55

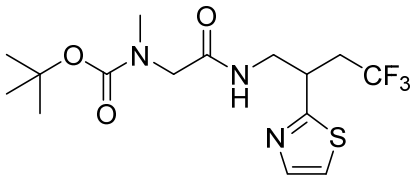
Figure S15. Chromatograms of Racemic **3x**



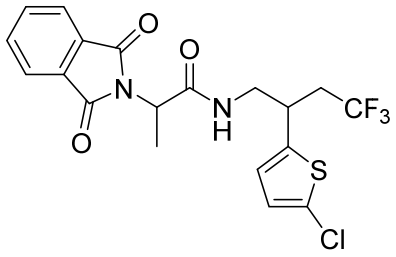
Peak Results

	RT	Area	Height	% Area	% Height
1	7.828	14450	3454	1.80	1.89
2	8.129	788206	179433	98.20	98.11

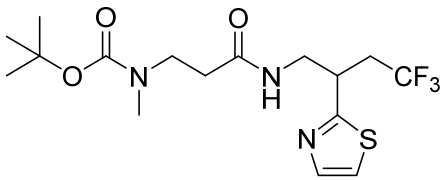
Figure S16. Chromatograms of product **3x**



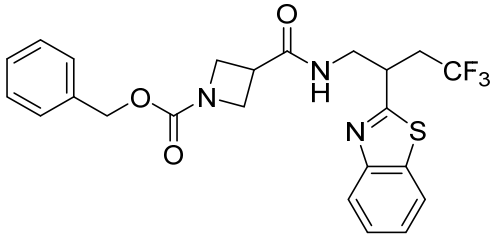
tert-butyl methyl(2-oxo-2-((4,4,4-trifluoro-2-(thiazol-2-yl)butyl)amino)ethyl)carbamate (3y): Silica gel column chromatography (petroleum ether/acetone = 4:1), light yellow solid; 54.9 mg, yield = 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 3.2 Hz, 1H), 7.28 (d, *J* = 3.3 Hz, 1H), 6.98 (s, 1H), 4.12 – 3.68 (m, 4H), 3.61 (dd, *J* = 8.4, 5.0 Hz, 1H), 2.87 (s, 3H), 2.82 – 2.66 (m, 1H), 2.55 (ddt, *J* = 15.1, 10.5, 5.2 Hz, 1H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.9, 169.5, 155.5, 142.8, 126.0 (q, *J* = 277.0 Hz), 119.0, 80.7, 53.0, 43.1, 37.1, 36.8, 35.8, 28.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.13. (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}F_3N_3O_3S^+$ 382.1407, found: 382.1402. IR ν_{max} (film, cm $^{-1}$): 3312, 2971, 1667, 1649, 1535, 1290, 1251, 1145, 1056, 879, 726.



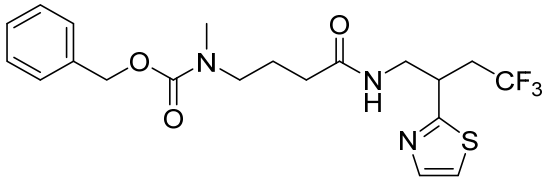
***N*-(2-(5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)-2-(1,3-dioxoisoindolin-2-yl)propanamide (3z)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), white solid; 53.3 mg, yield = 60%, 7:3 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.75 (m, 2H), 6.61 (d, *J* = 3.7 Hz, 1H), 6.55 (dd, *J* = 6.0, 3.8 Hz, 1H), 6.31–6.05 (m, 1H), 4.85 (p, *J* = 7.2 Hz, 1H), 3.71 (m, 0.7H), 3.58 (m, 0.3H), 3.40 (m, 1.3H), 3.25 (m, 0.7H), 2.58 – 2.28 (m, 2H), 1.63 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 169.5, 167.8, 167.7, 142.1, 142.0, 134.5, 134.4, 131.7, 128.7, 125.9 (q, *J* = 276 Hz), 125.9, 125.9, 125.0, 123.6, 123.6, 49.5, 49.3, 45.1, 44.91, 38.2 (q, *J* = 28.5 Hz), 38.0 (q, *J* = 28.6 Hz), 36.0 (q, *J* = 2.6 Hz), 35.9 (q. *J* = 2.5 Hz), 15.11, 14.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.83. (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}ClF_3N_2O_3S^+$ 445.0595, found: 445.0592. IR ν_{max} (film, cm $^{-1}$): 3314, 2928, 1715, 1661, 1538, 1386, 1255, 1140, 798, 720.



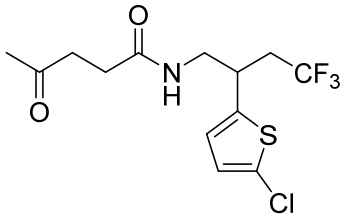
tert-butyl methyl(3-oxo-3-((4,4,4-trifluoro-2-(thiazol-2-yl)butyl)amino)propyl)carbamate (3z1): Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 59.3 mg, yield = 75%; ^{1}H NMR (400 MHz, CDCl3) δ 7.80 – 7.74 (m, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 6.97 (s, 1H), 3.85 – 3.57 (m, 3H), 3.55 – 3.32 (m, 2H), 2.85 (s, 3H), 2.76 (m, 1H), 2.57 (m, 1H), 2.44 (s, 2H), 1.44 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 171.4, 169.5, 156.5, 142.8, 126.1 (q, *J* = 277.3 Hz), 119.0, 79.9, 45.3, 43.6, 37.1 (q, J = 2.6 Hz), 36.6 (d, *J* = 29.0 Hz), 35.3, 34.8, 28.4. ^{19}F NMR (376 MHz, CDCl3) δ -64.14. (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{25}F_3N_3O_3S^+$ 396.1563, found: 396.1558. IR ν_{max} (film, cm $^{-1}$): 3291, 2971, 1654, 1552, 1366, 1255, 1130, 725, 596.



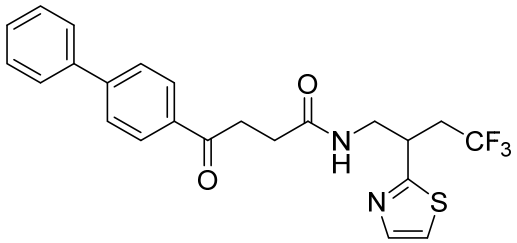
benzyl 3-((2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)carbamoyl)azetidine-1-carboxylate (3z2): Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 68.7 mg, yield = 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.44 – 7.38 (t, J = 7.7 Hz, 1H), 7.34 (m, 5H), 6.60 (s, 1H), 5.06 (s, 2H), 4.14 (s, 2H), 4.05 (m, 2H), 3.78 (m, 3H), 3.16 (p, *J* = 8.5 Hz, 1H), 2.90 (m, 1H), 2.63 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.0, 170.3, 156.3, 152.9, 136.4, 134.6, 128.5, 128.1, 127.9, 126.5, 126.0 (q, *J* = 275 Hz), 125.6, 122.9, 121.8, 66.8, 51.8, 43.4, 38.0 (q, *J* = 2.7 Hz), 36.8 (q, *J* = 29.1 Hz), 33.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.02. (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{23}F_3N_3O_3S^+$ 478.1407, found: 478.1403. IR ν_{max} (film, cm $^{-1}$): 3300, 2987, 1683, 1655, 1546, 1435, 1256, 1128, 759, 701.



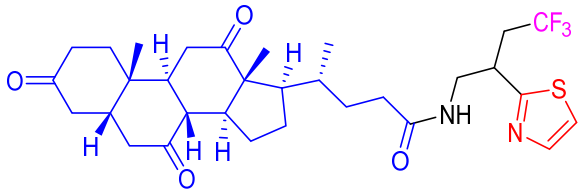
benzyl methyl(4-oxo-4-((4,4,4-trifluoro-2-(thiazol-2-yl)butyl)amino)butyl)carbamate (3z3): Silica gel column chromatography (petroleum ether/acetone = 4:1), colorless oil; 61.1 mg, yield = 69%; ^{1}H NMR (400 MHz, CDCl3) δ 7.76 (d, *J* = 3.1 Hz, 1H), 7.35 (m, 5H), 7.27 (d, J = 3.1 Hz, 1H), 6.93 (s, 0.64H), 6.17 (s, 0.36H), 5.10 (s, 2H), 3.69 (m, 3H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.90 (s, 3H), 2.78 (m, 1H), 2.61 (m, 1H), 2.13 (m, 2H), 1.83 (p, *J* = 6.9 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.1, 172.5, 169.8, 156.9, 156.2, 142.7, 136.8, 130.2, 128.5, 128.0, 127.9, 127.8, 126.2 (q, *J* = 274 Hz), 119.0, 67.1, 48.0, 43.7, 43.6, 37.3, 36.7 (q, *J* = 28.2 Hz), 34.6, 33.9, 33.1, 23.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.07. (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}F_3N_3O_3S^+$ 444.1563, found: 444.1558. IR ν_{max} (film, cm $^{-1}$): 3288, 2956, 1679, 1534, 1653, 1404, 1256, 1129, 1055, 767, 697.



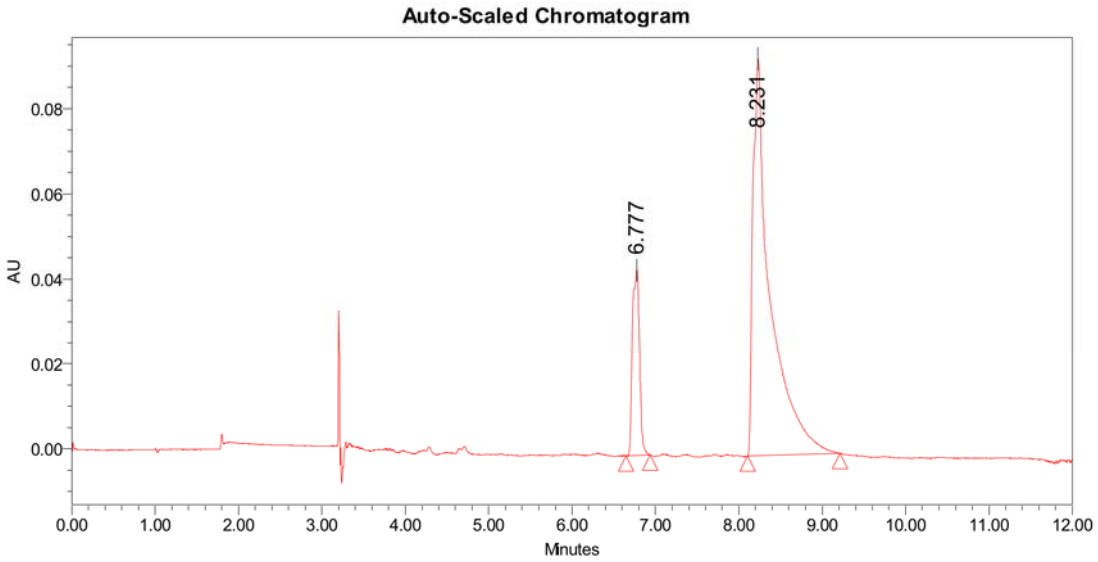
***N*-(2-(5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)-4-oxopentanamide (3z4)**: Silica gel column chromatography (petroleum ether/acetone = 10:1), yellow oil; 43.0 mg, yield = 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 3.8 Hz, 1H), 6.69 (d, *J* = 3.7 Hz, 1H), 5.92 (s, 1H), 3.63 (dt, *J* = 13.0, 6.3 Hz, 1H), 3.39 (ddd, *J* = 13.6, 8.1, 5.6 Hz, 2H), 3.26 (m, 1H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.53 – 2.40 (m, 2H), 2.36 (t, *J* = 6.4 Hz, 2H), 2.16 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 207.8, 172.3, 142.3, 128.7, 126.0, 126.0 (q, *J* = 277 Hz), 124.9, 44.9, 38.5, 38.2 (q, *J* = 28.4 Hz), 36.0 (q, *J* = 2.7 Hz), 29.9, 29.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.84. (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}ClF_3N_1O_2S^+$ 342.0537, found: 342.0536. IR ν_{max} (film, cm $^{-1}$): 3312, 2972, 1705, 1665, 1550, 1406, 1251, 1056, 892, 797.



4-([1,1'-biphenyl]-4-yl)-4-oxo-N-(4,4,4-trifluoro-2-(thiazol-2-yl)butyl)butanamide (3z5): Silica gel column chromatography (petroleum ether/acetone = 4:1), yellow solid; 60.7 mg, yield = 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 3.3 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 3.1 Hz, 1H), 6.62 (t, *J* = 5.5 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.78 – 3.63 (m, 2H), 3.39 (t, *J* = 6.5 Hz, 2H), 2.89 – 2.75 (m, 1H), 2.71 – 2.57 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.4, 172.7, 170.2, 146.0, 142.7, 139.8, 135.2, 129.0, 128.8, 128.7, 128.3, 127.3, 126.1 (q, *J* = 275 Hz), 119.1, 43.7, 37.3 (q, *J* = 2.5 Hz), 37.0 (q, *J* = 28.8 Hz), 34.0, 30.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.04. (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}F_3N_2O_2S^+$ 447.1347, found: 447.1346. IR ν_{max} (film, cm $^{-1}$): 3297, 2974, 1673, 1603, 1535, 1252, 1127, 1065, 762, 695.



(4R)-4-((5S,8R,9R,10S,13R,14S,17R)-13-methyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-N-(4,4,4-trifluoro-2-(thiazol-2-yl)butyl)pentanamide (3z6): Silica gel column chromatography (petroleum ether/acetone = 4:1), white solid; 83.2 mg, yield = 70%, 84:16 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.7 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 6.33 (s, 1H), 3.77 – 3.67 (m, 1H), 3.67 – 3.53 (m, 2H), 2.98 – 2.65 (m, 4H), 2.53 (m, 1H), 2.39 – 2.03 (m, 11H), 2.03 – 1.89 (m, 4H), 1.84 – 1.72 (m, 2H), 1.58 (m, 1H), 1.36 (s, 3H), 1.27 (m, 3H), 1.02 (s, 3H), 0.78 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.1, 209.2, 208.8, 173.9, 170.1, 142.7, 126.1 (q, *J* = 277.2 Hz), 119.1, 56.9, 51.8, 49.0, 46.8, 45.6, 45.5, 45.0, 43.6, 42.8, 38.6, 37.3 (d, *J* = 2.6 Hz), 37.0 (d, *J* = 28.6 Hz), 36.4, 36.0, 35.4, 35.2, 33.4, 31.0, 27.6, 25.1, 21.9, 18.7, 11.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.07. (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{42}F_3N_2O_4S^+$ 595.2812, found: 595.2809. IR ν_{max} (film, cm $^{-1}$): 3310, 2970, 1706, 1654, 1540, 1382, 1256, 1129, 1052, 892, 768, 532. the diastereo ratio (dr) was determined by UPCC (viridis® BEH 2-ethylpyridine 1.7 μm, CO_2/MeOH = 90:10, flow rate: 0.5 mL/min, λ = 254 nm), t_R (major) = 8.2 min, t_R(minor) = 6.8 min;

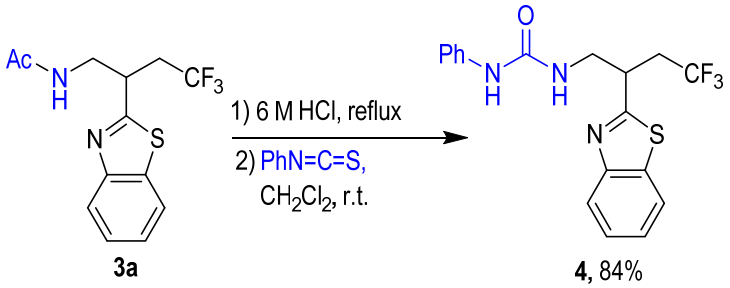


Peak Results

	RT	Area	Height	% Area	% Height
1	6.777	256565	43703	15.99	31.89
2	8.231	1348230	93350	84.01	68.11

Figure S17. Chromatograms of **3z6**

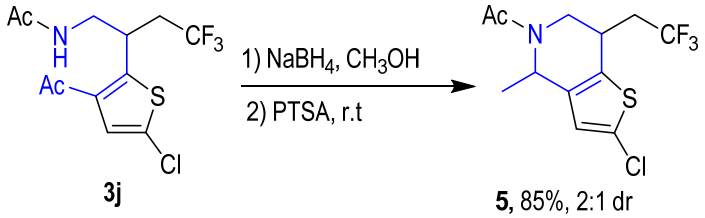
7. Product transformation



3a **4**, 84%

6M HCl (1.5 mL) was added to a solution of *N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)acetamide (**3a**, 30.2 mg, 0.1 mmol) in ethanol (0.5 mL) and the reaction mixture was stirred reflux until the starting material was disappeared (reaction monitored by TLC). The reaction mixture was cooled to room temperature, the solution was basified to 14 with 15% NaOH and then extracted with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The corresponding amine was dissolved in anhydrous CH_2Cl_2 (2 mL), phenyl isocyanate (17.9 mg, 0.15 mmol) was added and the solution was stirred at room temperature overnight. The organic layers concentrated in *vacuo*. The crude mixture was purified via silica gel column chromatography to afford the desired product **1-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)-3-phenylthiourea (4)**: Silica gel column chromatography (petroleum ether/acetone = 5:1), yellow oil; 33.2 mg, yield = 84% over two steps; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.92 – 7.86 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.46 – 7.40 (m, 1H), 7.29 – 7.22 (m, 3H), 7.07 – 7.01 (m, 2H), 6.99 (t, *J* = 5.4 Hz, 1H), 4.29 – 4.13 (m, 2H), 3.98 (tt, *J* = 7.9, 4.7 Hz,

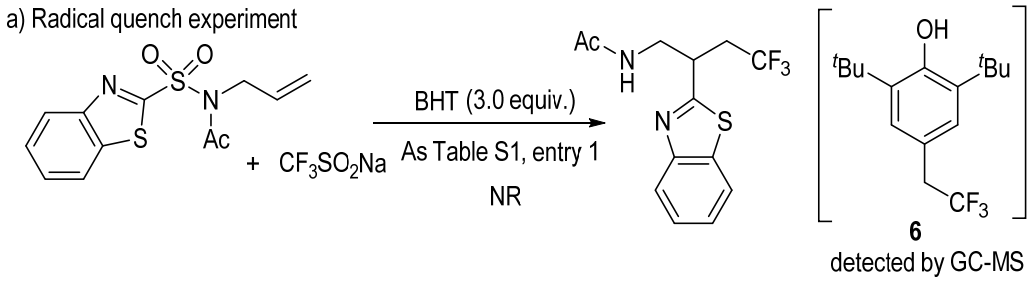
1H), 2.85 (m, 1H), 2.73 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 181.0, 170.6, 126.0 (q, J = 275 Hz), 152.8, 135.6, 134.5, 130.1, 127.5, 126.3, 125.5, 125.4, 122.9, 121.7, 48.5, 37.4 (q, J = 2.3 Hz), 37.1 (q, J = 29.1 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.93. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}F_3N_3S_2^+$ 396.0810, found: 396.0811. IR ν_{max} (film, cm $^{-1}$): 3211, 2970, 1534, 1497, 1251, 1076, 760.



3j **5**, 85%, 2:1 dr

$NaBH_4$ (15.2 mg, 0.4 mmol) was added portionwise to a solution of *N*-(2-(3-acetyl-5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)acetamide (**3j**, 65.4 mg, 0.2 mmol) in methanol (1.0 mL). The solution was stirred 1 h at room temperature. Then the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and water (2 mL) was added dropwise. The solution was extracted with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The corresponding compound was dissolved in CH_2Cl_2 and p-Toluenesulfonic acid (34 mg, 0.2 mmol) was added. The solution was stirred at room temperature until the starting material disappeared. The organic layers concentrated in *vacuo*. The crude mixture was purified via silica gel column chromatography to afford the desired product **1-(2-chloro-4-methyl-7-(2,2,2-trifluoroethyl)-6,7-dihydrothieno[3,2-c]pyridin-5(4H)-yl)ethan-1-one (5)**: Silica gel column chromatography (petroleum ether/acetone = 10:1), yellow oil; 52.9 mg, yield = 85% over two steps; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (s, 1H), 5.48 (q, J = 6.6 Hz, 0.66H), 5.05 (dd, J = 13.0, 5.1 Hz, 0.34H), 4.78 (q, J = 6.5 Hz, 0.34H), 4.11 (dd, J = 13.6, 4.4 Hz, 0.66H), 3.40 – 3.18 (m, 1H), 3.14 (dd, J = 13.5, 11.0 Hz, 0.66H), 2.74 – 2.43 (m, 1.35H), 2.28 (m, 1H), 2.14 (s, 3H), 1.44 (d, J = 6.7 Hz, 1H), 1.34 (d, J = 6.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 168.9, 168.7, 138.8, 137.3, 135.6, 133.3, 129.3, 129.1, 125.9 (q, J = 276 Hz), 125.8 (q, J = 276 Hz), 124.9, 124.2, 50.9, 46.7, 45.1, 39.7, 38.4 (q, J = 29 Hz), 38.2 (q, J = 29 Hz), 31.9 (q, J = 2.3 Hz), 30.8 (q, J = 2.4 Hz), 21.7, 21.4, 20.7, 19.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.31, -63.42. HR-MS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}ClF_3NOS^+$ 312.0431, found: 312.0429. IR ν_{max} (film, cm $^{-1}$): 2973, 1648, 1422, 1250, 1141, 1057, 827, 639.

8. Mechanistic Experiments



To the 10 mL three-necked round bottom flask with a magnetic stir bar was added the *N*-allylsulfonamide (0.2 mmol), CF_3SO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv.), $LiClO_4$ (63.6 mg, 0.1 M.), Butylated hydroxytoluene (132 mg, 3.0 equiv.) and CH_3CN : H_2O (3:1 v/v, 6.0 mL). The flask was equipped with a reticulated vitreous carbon (100 PPI) anode (0.8 cm x 0.8 cm x 1 cm) and a platinum plate (1 cm x 1cm) cathode. The electrolysis was carried out at rt using a constant current of 10 mA. The reaction mixture was stirred and electrolyzed for 1.08 h (2.0 F per mol of sulfonamide). After the electrolysis, no desired product was obtained (detected by TLC) and we detected 1,3-di-tert-butyl-5-methyl-2-(trifluoromethoxy)benzene **6** by GC-MS.

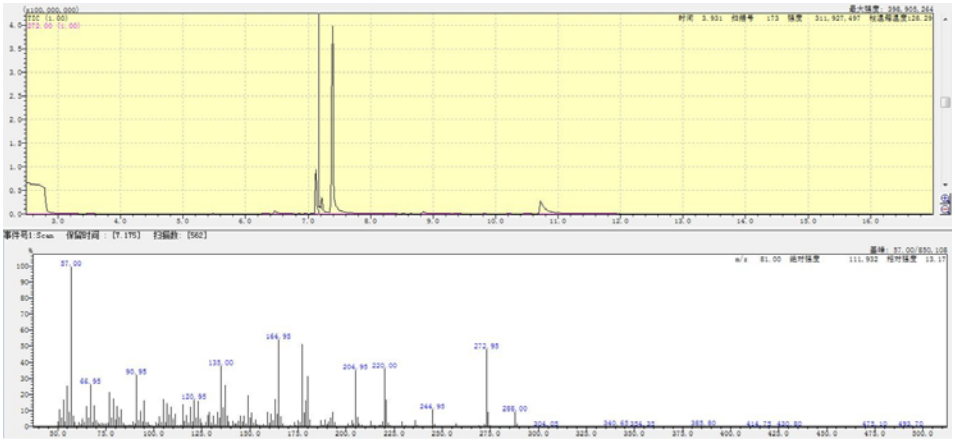
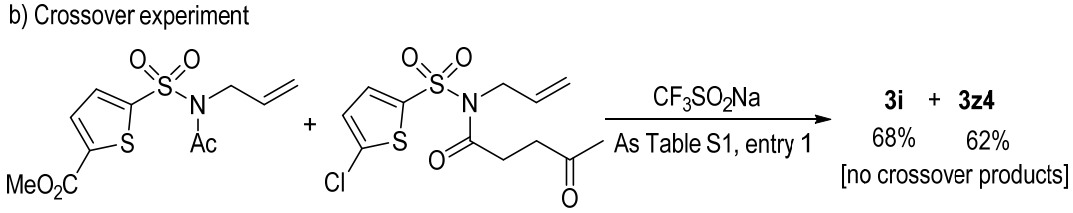


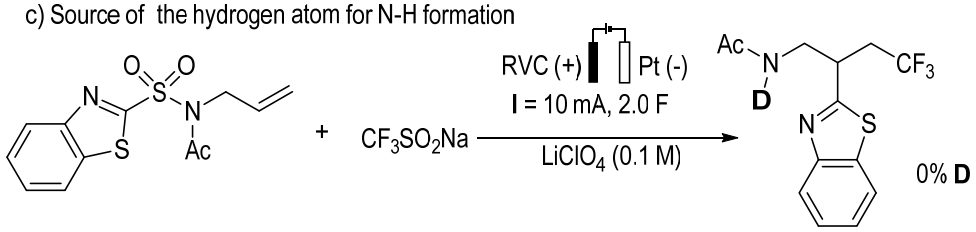
Figure S18. GC-MS spectrum of the BHT adducts



To the 10 mL three-necked round bottom flask with a magnetic stir bar was added the methyl 5-(N-acetyl-N-allylsulfamoyl)thiophene-2-carboxylate (0.1 mmol), *N*-allyl-*N*-((5-chlorothiophen-2-yl)sulfonyl)-4-oxopentanamide (0.1 mmol), CF_3SO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv.), $LiClO_4$ (63.6 mg, 0.1 M.) and CH_3CN:H_2O (3:1 v/v, 6.0 mL). The flask was equipped with a reticulated vitreous carbon (100 PPI) anode (0.8 cm x 0.8 cm x 1 cm) and a platinum plate (1 cm x 1cm) cathode. The electrolysis was carried out at rt using a constant current of 10 mA. The reaction mixture was stirred and electrolyzed for 1.08 h (2.0 F per mol of sulfonamide). When the reaction was finished, the reaction was quenched with saturated NaCl aqueous solution and extracted three times with

ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The crude mixture was purified via silica gel column chromatography (10 % acetone/ petroleum ether) to afford the products **9** (21 mg, 68 %) and product **28** (21 mg, 62%). No crossover products were detected.

c) Source of the hydrogen atom for N-H formation



To the 10 mL three-necked round bottom flask with a magnetic stir bar was added the *N*-allylsulfonamide (0.2 mmol, 59.2 mg), CF_3SO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv.), $LiClO_4$ (63.6 mg, 0.1 M.) and CD_3CN (6.0 mL). The flask was equipped with a reticulated vitreous carbon (100 PPI) anode (0.8 cm x 0.8 cm x 1 cm) and a platinum plate (1 cm x 1cm) cathode. The electrolysis was carried out at rt using a constant current of 10 mA. The reaction mixture was stirred and electrolyzed for 1.08 h (2.0 F per mol of sulfonamide). After the electrolysis, The mixture was concentrated in *vacuo* and check by ^{1}H-NMR in DMSO-d_6.

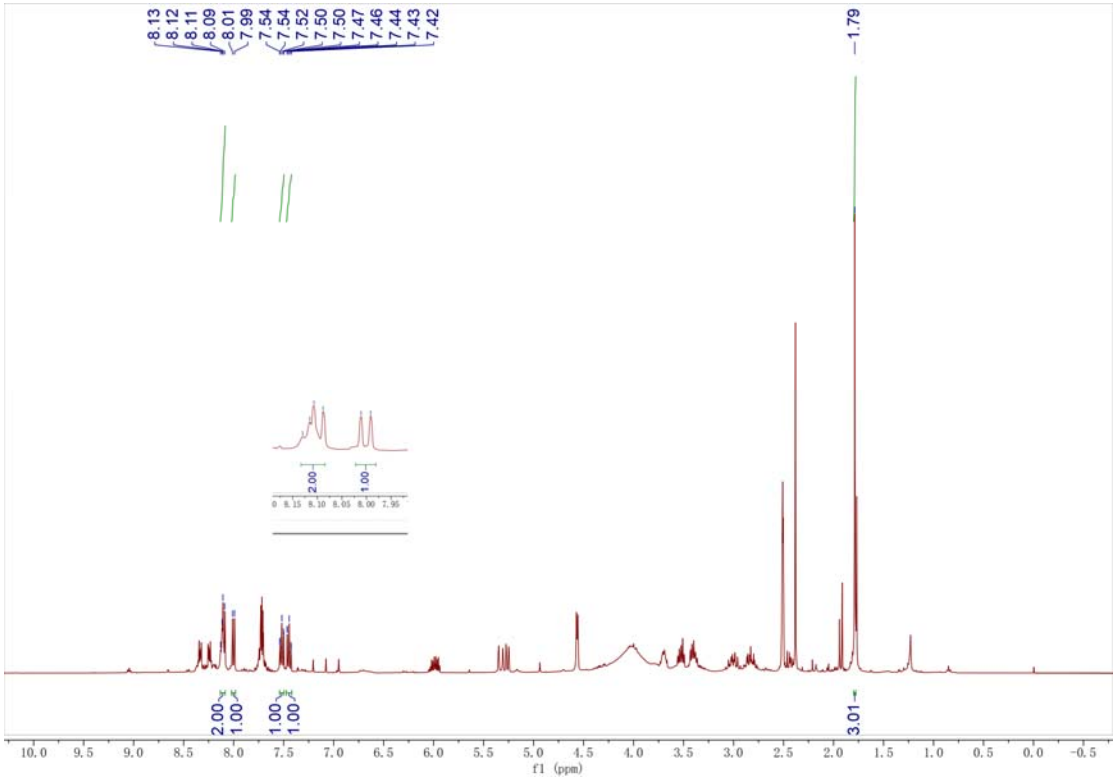


Figure S19 ^{1}H-NMR of reaction mixture

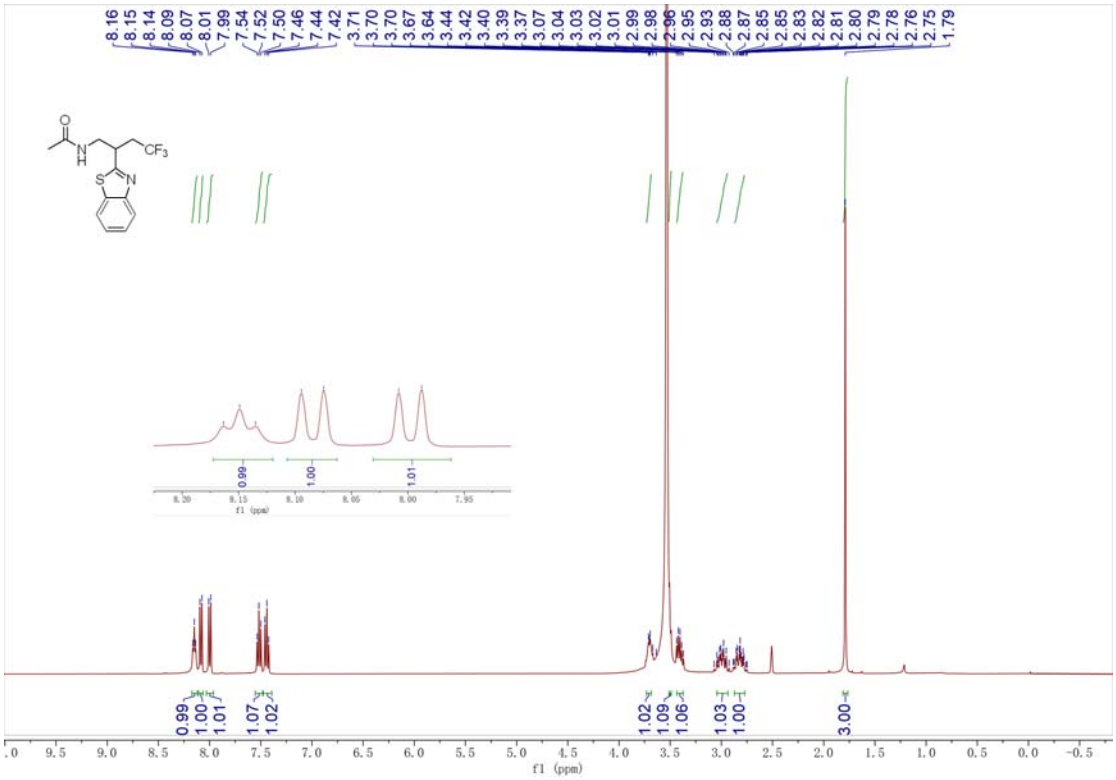
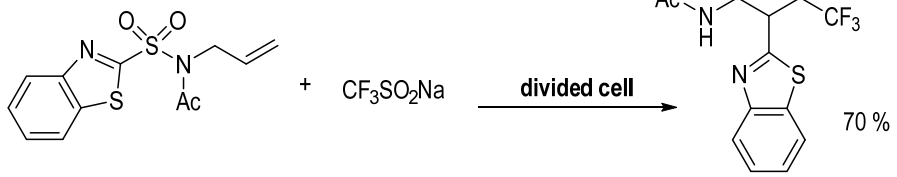


Figure S20 ^{1}H-NMR of **3a**

d) Divided-cell experiment



To the anodic cell with a magnetic stir bar was added the *N*-allyl-*N*-(benzo[d]thiazol-2-ylsulfonyl)acetamide (0.2 mmol), CF_3SO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv.), $LiClO_4$ (127.2 mg, 0.1 M.) and CH_3CN:H_2O (3:1 v/v, 12.0 mL). The cell was equipped with a reticulated vitreous carbon (100 PPI) anode (0.8 cm x 0.8 cm x 1 cm). To the cathodic cell with a magnetic stir bar was added $LiClO_4$ (127.2 mg, 0.1 M.) and CH_3CN: H_2O (3:1 v/v, 12.0 mL). The cell was equipped with a platinum plate (1 cm x 1cm) cathode. The membrance was used Aquivion membrane E98-05S. The electrolysis was carried out at rt using a constant current of 10 mA. The reaction mixture was stirred and electrolyzed for 1.08 h (2.0 F per mol of sulfonamide). When the reaction was finished, the reaction was quenched with saturated NaCl aqueous solution and extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The crude mixture was purified via silica gel column chromatography (25 % acetone/ petroleum ether) to afford product **1**(21 mg, 79%).

(e) On-off experiments

To the 10 mL three-necked round bottom flask with a magnetic stir bar was added the *N*-allylsulfonamide (0.2 mmol), CF_3SO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv.), $LiClO_4$ (63.6 mg, 0.1 M.) and CH_3CN: H_2O (3:1 v/v, 6.0 mL). The flask was equipped with a reticulated vitreous carbon (100

PPI) anode (0.8 cm x 0.8 cm x 1 cm) and a platinum plate (1 cm x 1cm) cathode. The electrolysis was carried out at rt using a constant current of 10 mA. The reaction mixture was stirred and electrolyzed for 0, 10, 20, 30, 40, 50, 60, 70, 80 min respectively. the reaction was quenched with saturated NaCl aqueous solution and extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The yield of product was determined by ^{19}F NMR using Trifluoromethoxybenzene as an internal standard.

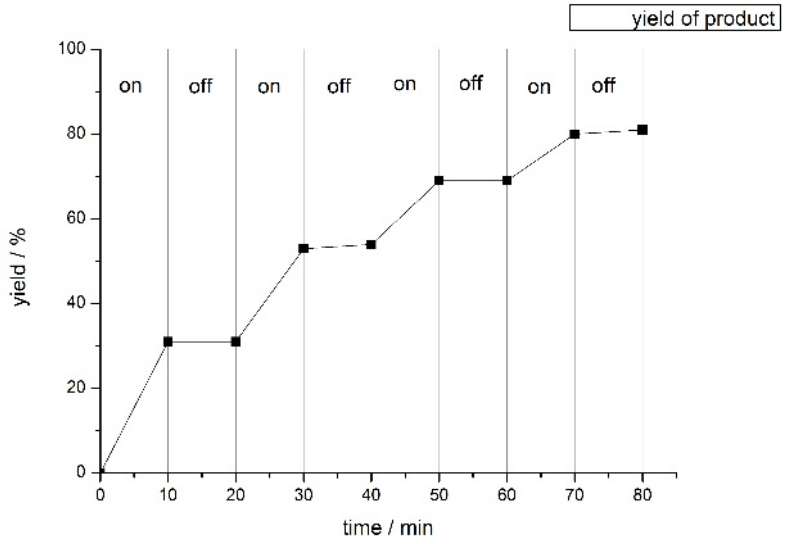


Figure S21. Electro on-off experiments

Cyclic Voltammetry Studies

The cyclic voltammograms were recorded on a Metrohm Autolab M204 workstation using Pt wire as working electrode and counter electrode, Ag/AgCl (saturated aq. KCl) as reference electrode and a scan rate of 100 mV/s. Cyclic voltammograms of 0.1 M $LiClO_4$ solution in CH_3CN at room temperature.

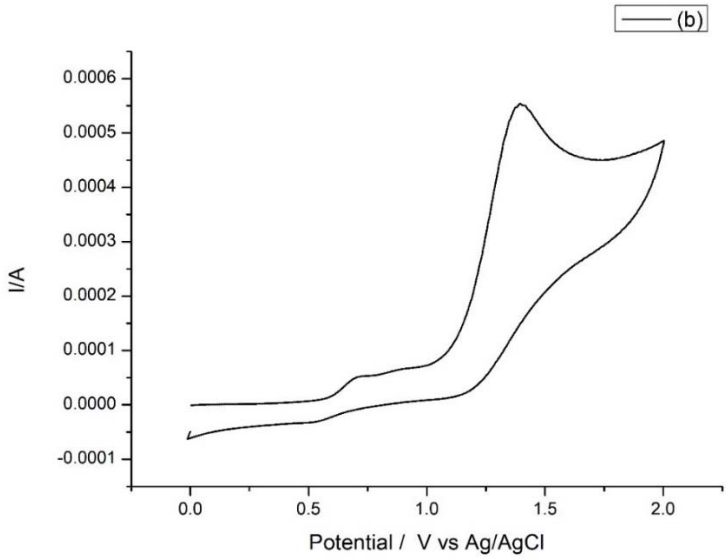


Figure S22. Cyclic voltammogram of **CF_3SO_2Na** (0.02 M), E_p = 1.37 V.

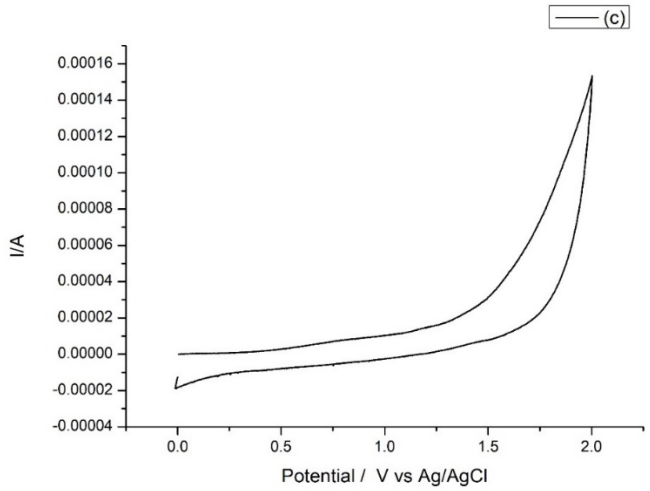


Figure S23. Cyclic voltammogram of **1a** (0.02 M), no oxidant peak in 0 - 2V.

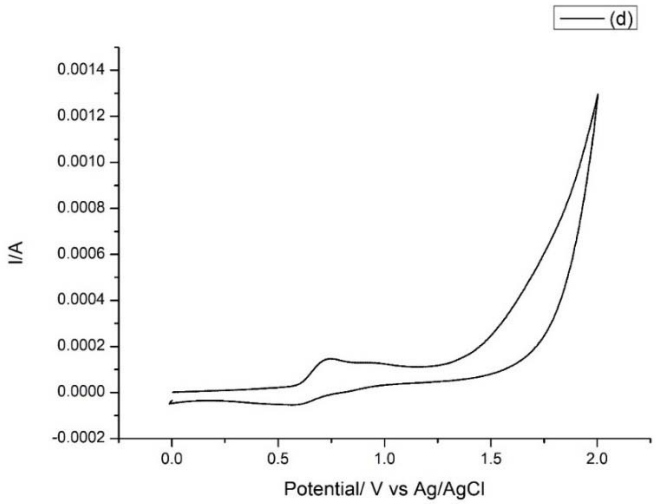


Figure S24. Cyclic voltammogram of **3a** in the presence of $^{n}Bu_4NOH$ (0.02 M), E_p = 0.70 V

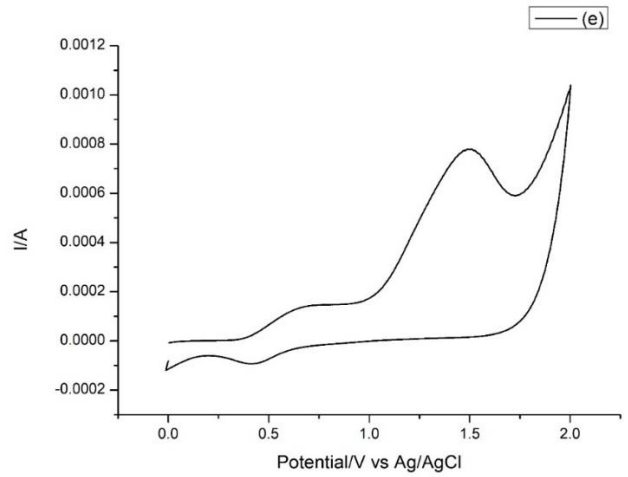


Figure S25. Cyclic voltammogram of **H_2SO_3** (0.04 M), E_p = 0.60 V, 1.41 V.

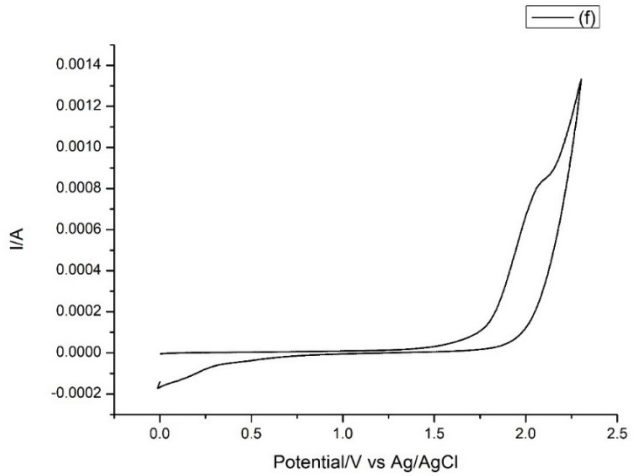
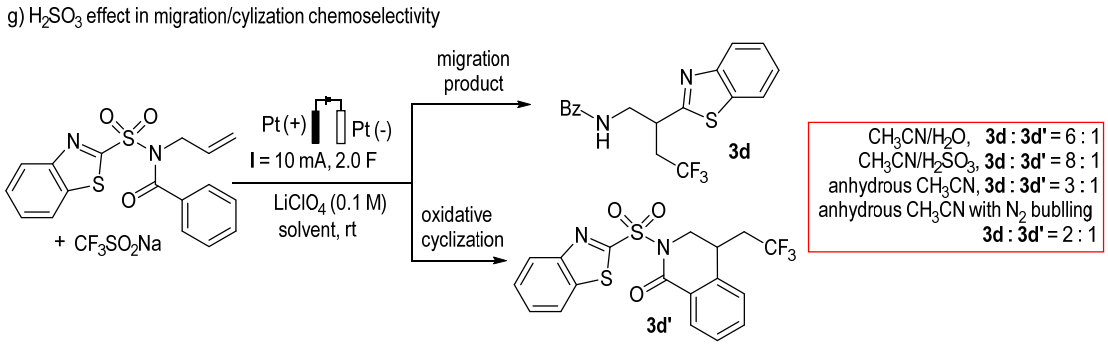


Figure S26. Cyclic voltammogram of **3a**, E_p = 2.0 V.



The electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. To the 10 mL vial with a magnetic stir bar was added the substituted *N*-allyl-*N*-(benzo[*d*]thiazol-2-ylsulfonyl)benzamide (35.8 mg, 0.1 mmol), CF_3SO_2Na (31.2 mg, 0.2 mmol, 2.0 equiv.), $LiClO_4$ (63.6 mg, 0.6 mmol),solvent (6 mL). The vial was attached to the vial cap equipped with Pt anode and Pt cathode. The electrolysis was carried out at rt using a constant current of 10 mA. The reaction mixture was stirred and electrolyzed for 0.54 h (2.0 F per mol of amide). When the reaction was finished, the reaction was quenched with saturated NaCl aqueous solution and extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The ratio of **3d** to **3d'** was determined by ^{19}F NMR spectroscopy.

9. X-Ray Crystallographic Data

Absolute configurations of products 3 were assigned based on the crystal X-ray structures of **3x**.

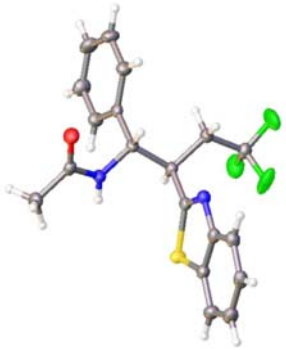


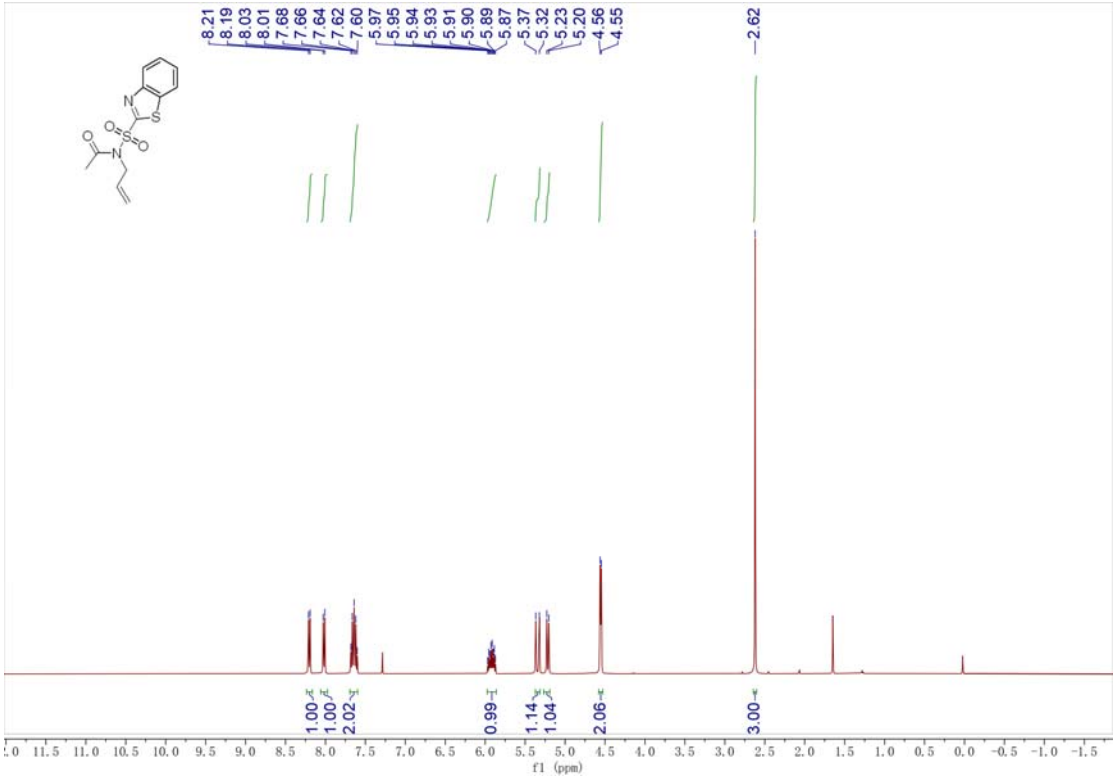
Figure S27. The crystal sturture of **3x**

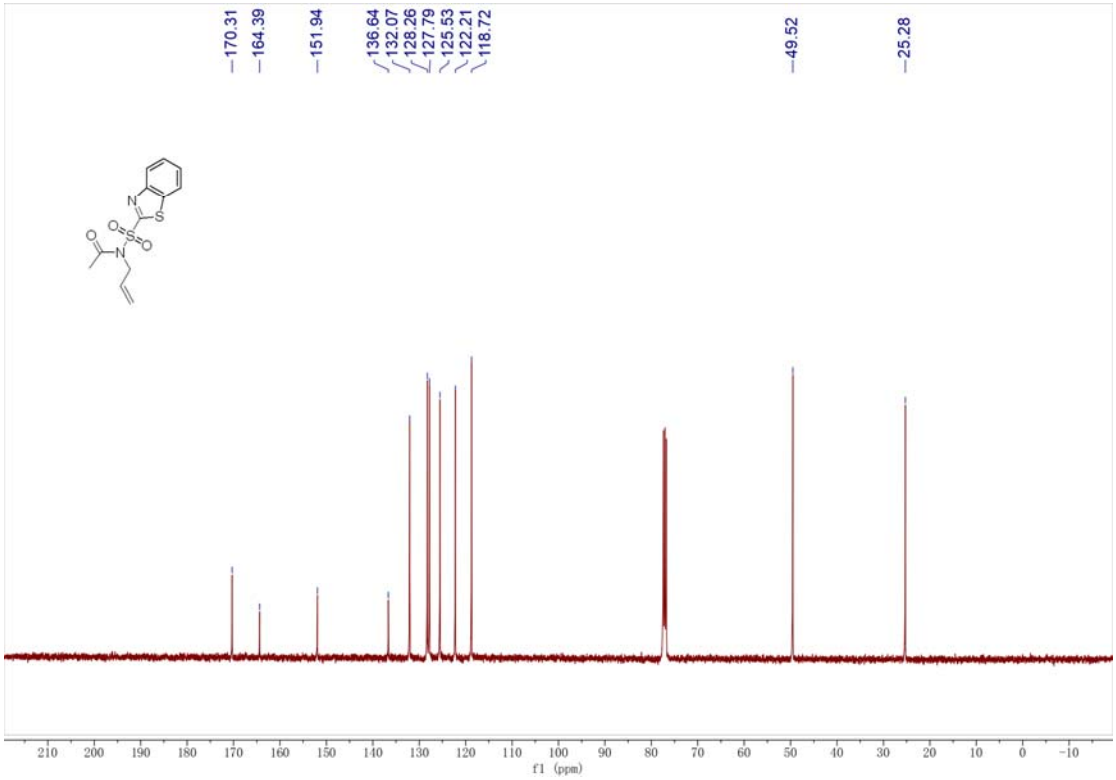
Table S3 Crystal data and structure refinement

Empirical formula	$C_{19}H_{17}F_3N_2OS$
Formula weight	378.40
Space group	P 1 21/n 1
a (Å)	8.79170(18)
b (Å)	10.2470(2)
c (Å)	19.1126(4)
α (deg)	90
β (deg)	98.050(2)
γ (deg)	90
V (Å ^{3})	1704.86(6)
Z	4
T (K)	150K
$\rho_{calculated}$ (g/cm^3)	1.474
μ (mm^{-1})	2.072
F(000)	784.0
Nref	3320
Theta (max)	72.942
wR2 (reflections)	0.1072 (3320)

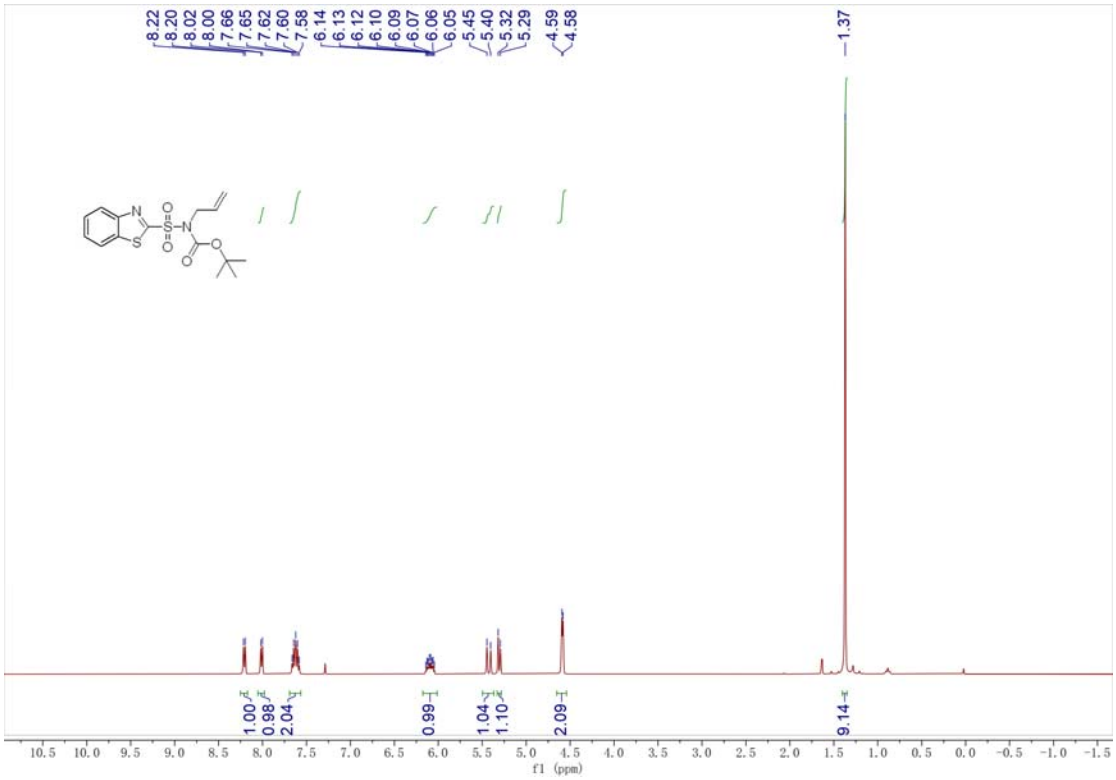
10. NMR Spectra for new compounds

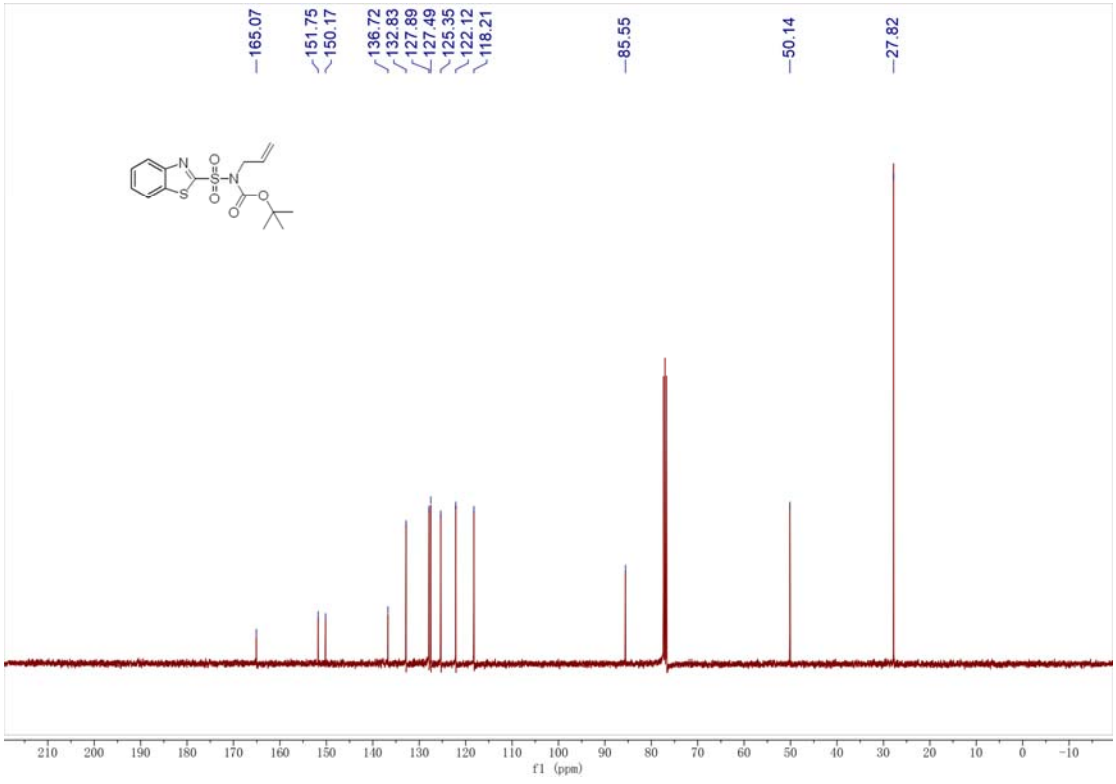
***N*-allyl-*N*-(benzo[d]thiazol-2-ylsulfonyl)acetamide (1a)**



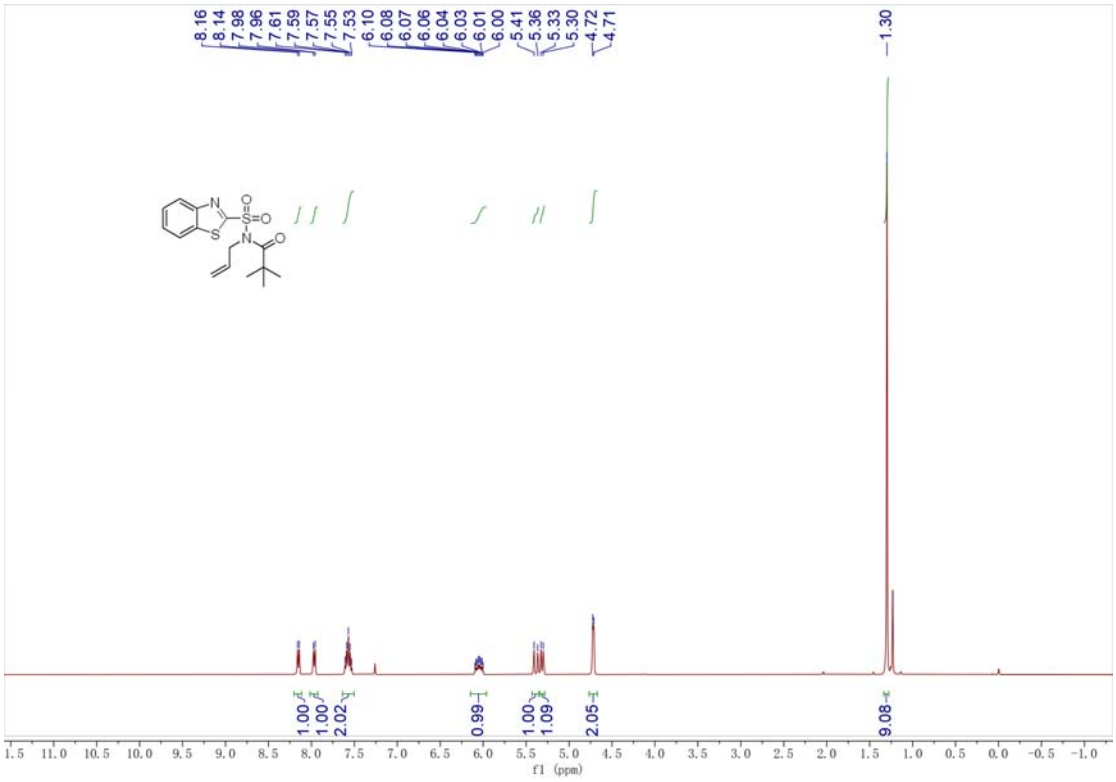


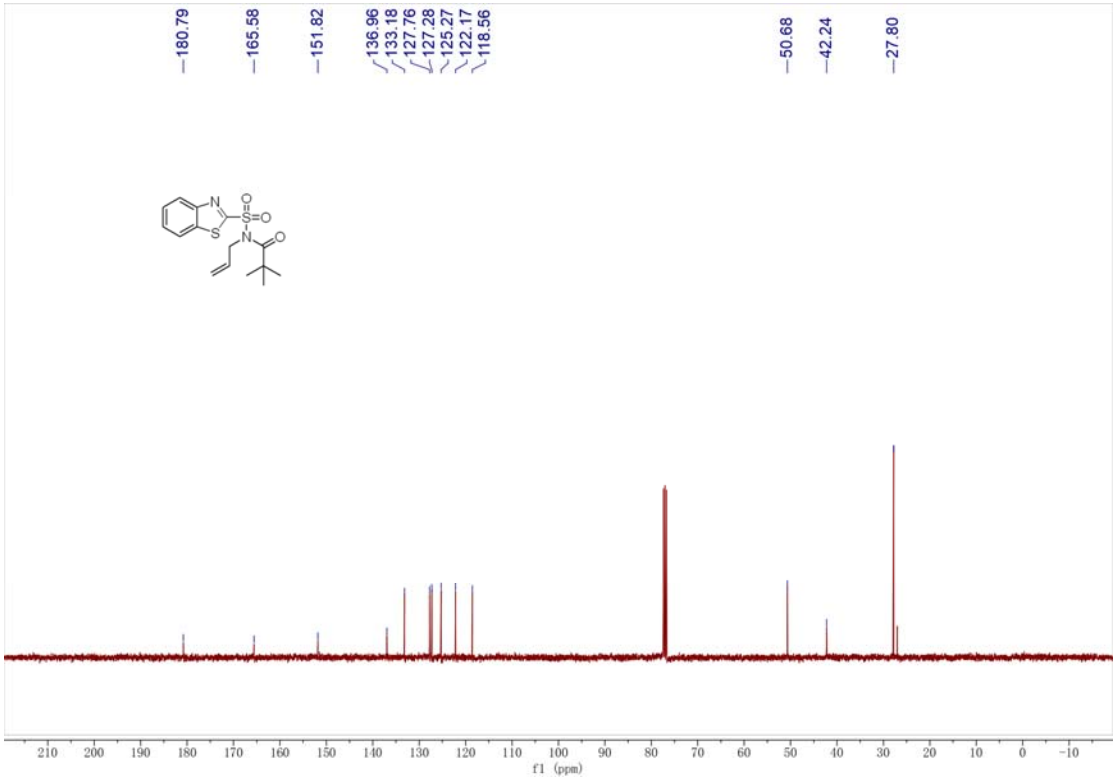
tert-butyl allyl(benzo[d]thiazol-2-ylsulfonyl)carbamate (1b)


8.22
8.20
8.02
8.00
7.66
7.65
7.62
7.60
7.58
6.14
6.13
6.12
6.10
6.09
6.07
6.06
6.05
5.45
5.40
5.32
5.29
4.59
4.58
1.37
1.00
0.98
2.04
0.99
1.04
1.10
2.09
9.14
f1 (ppm)

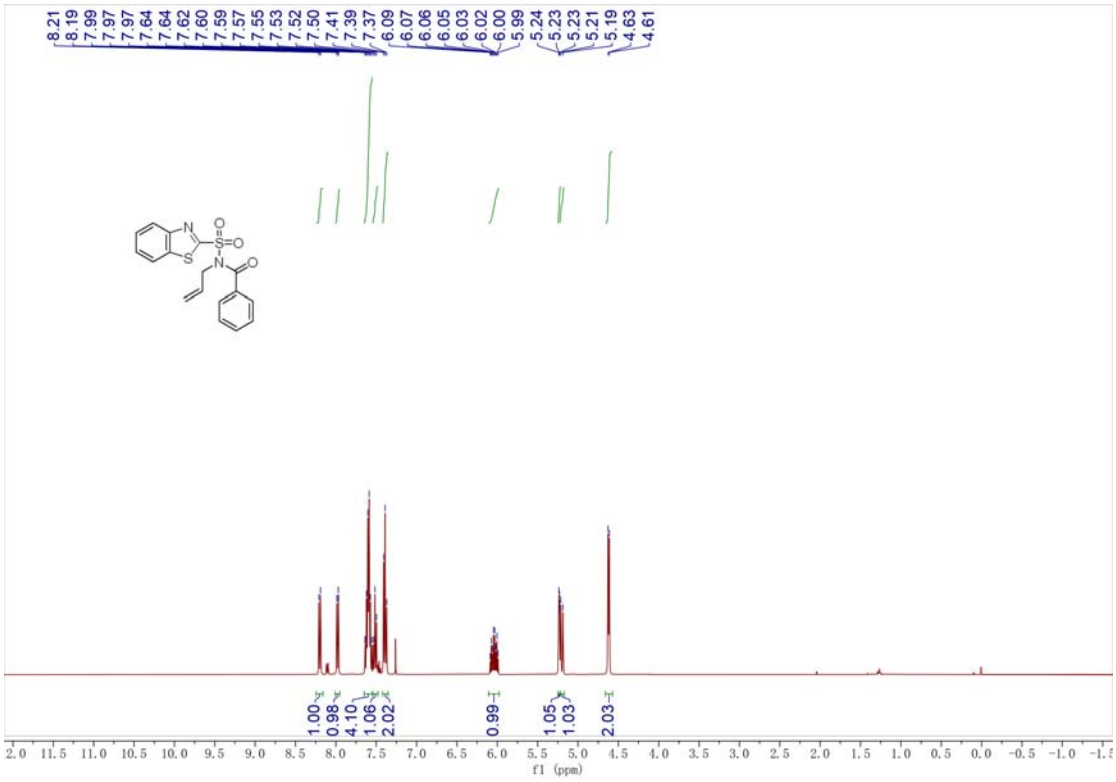

165.07
151.75
150.17
136.72
132.83
127.89
127.49
125.35
122.12
118.21
85.55
50.14
27.82
f1 (ppm)

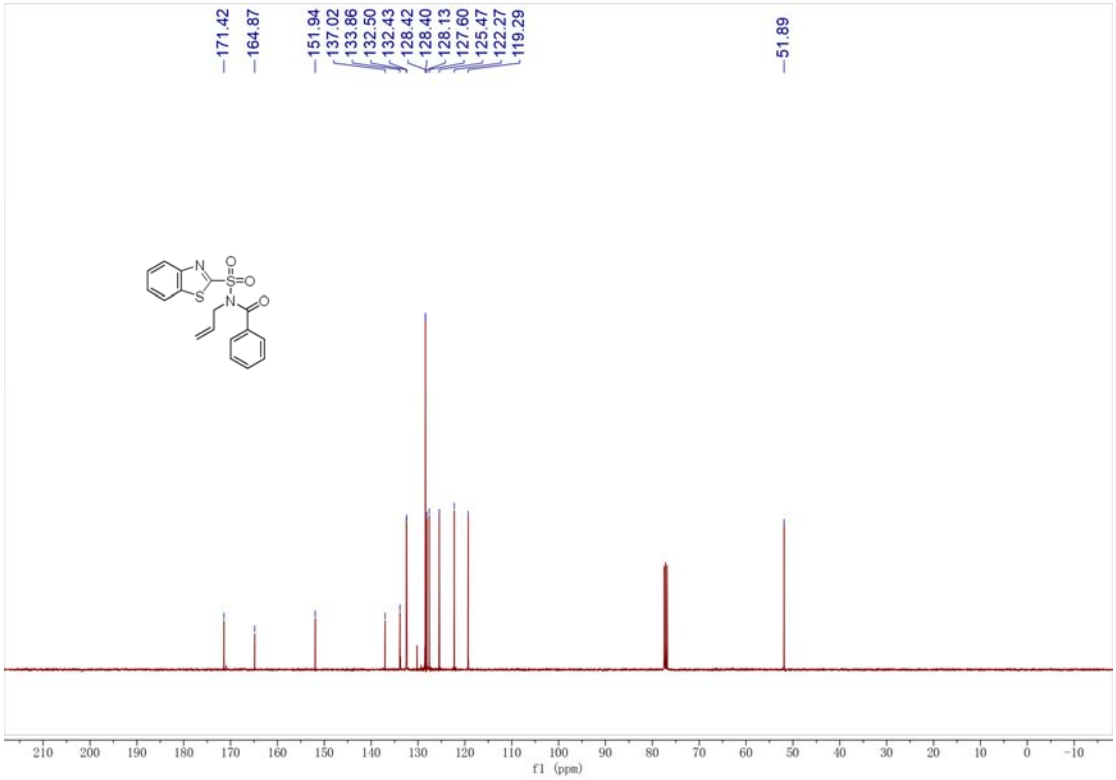
***N*-allyl-*N*-(benzo[d]thiazol-2-ylsulfonyl)pivalamide (1c)**



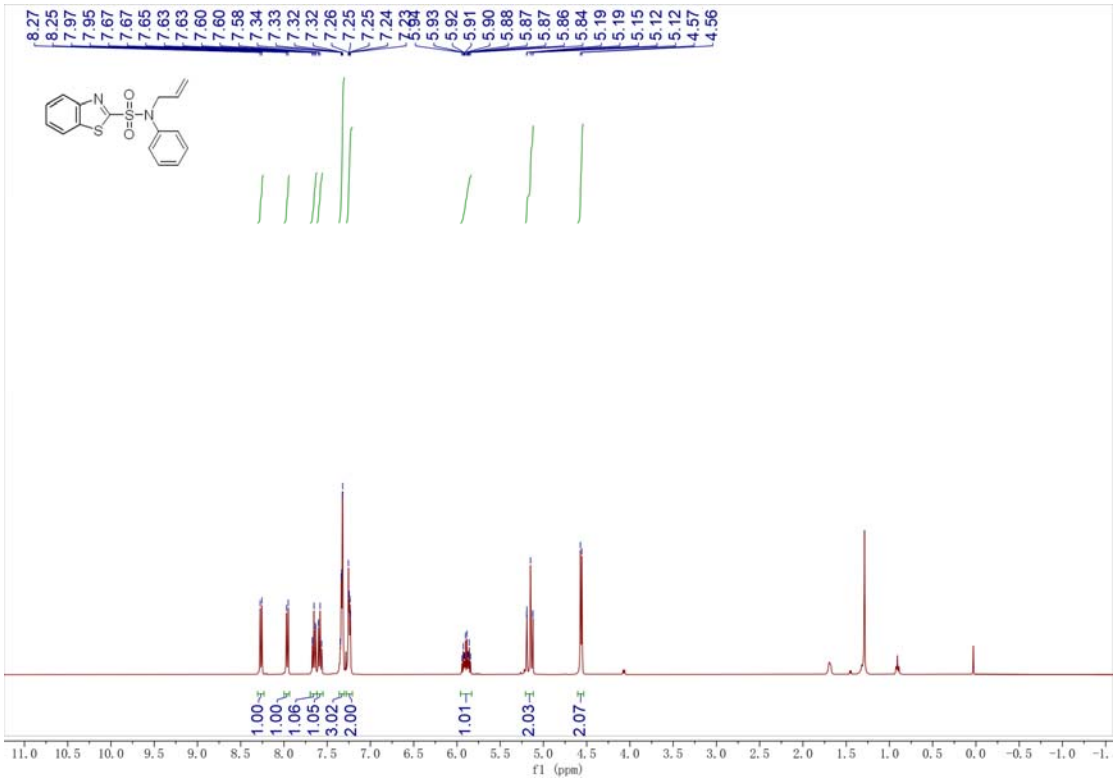


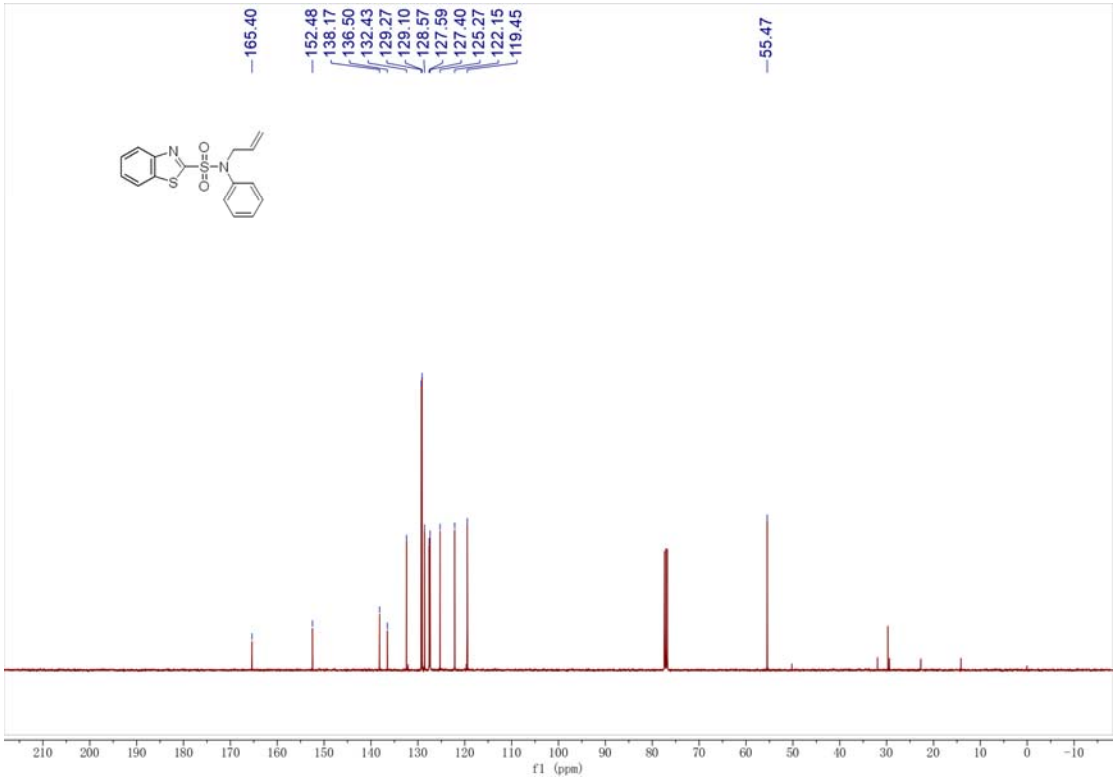
***N*-allyl-*N*-(benzo[d]thiazol-2-ylsulfonyl)benzamide (1d)**



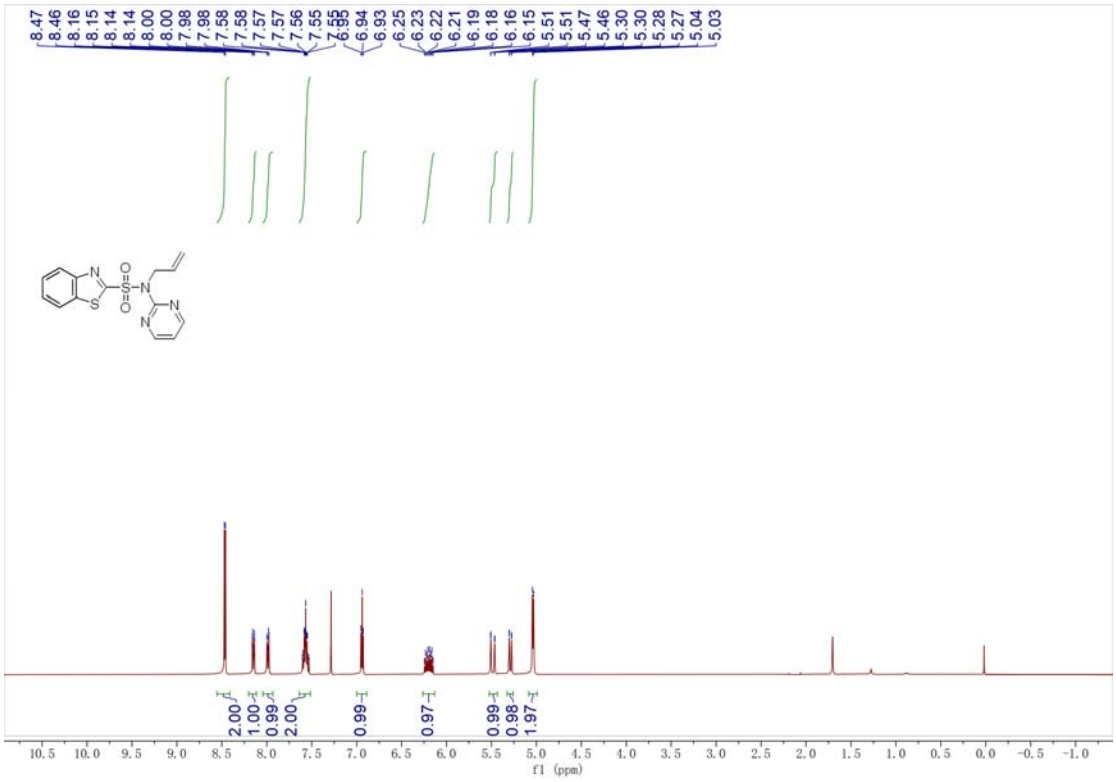


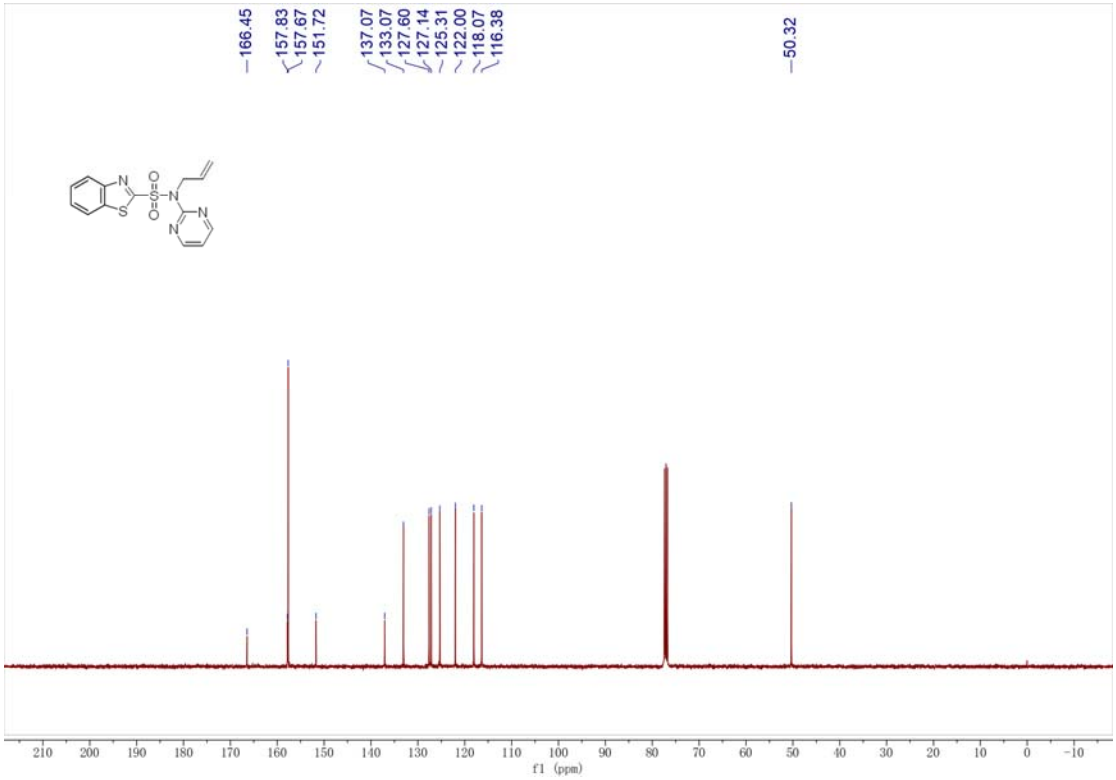
***N*-allyl-*N*-phenylbenzo[d]thiazole-2-sulfonamide**



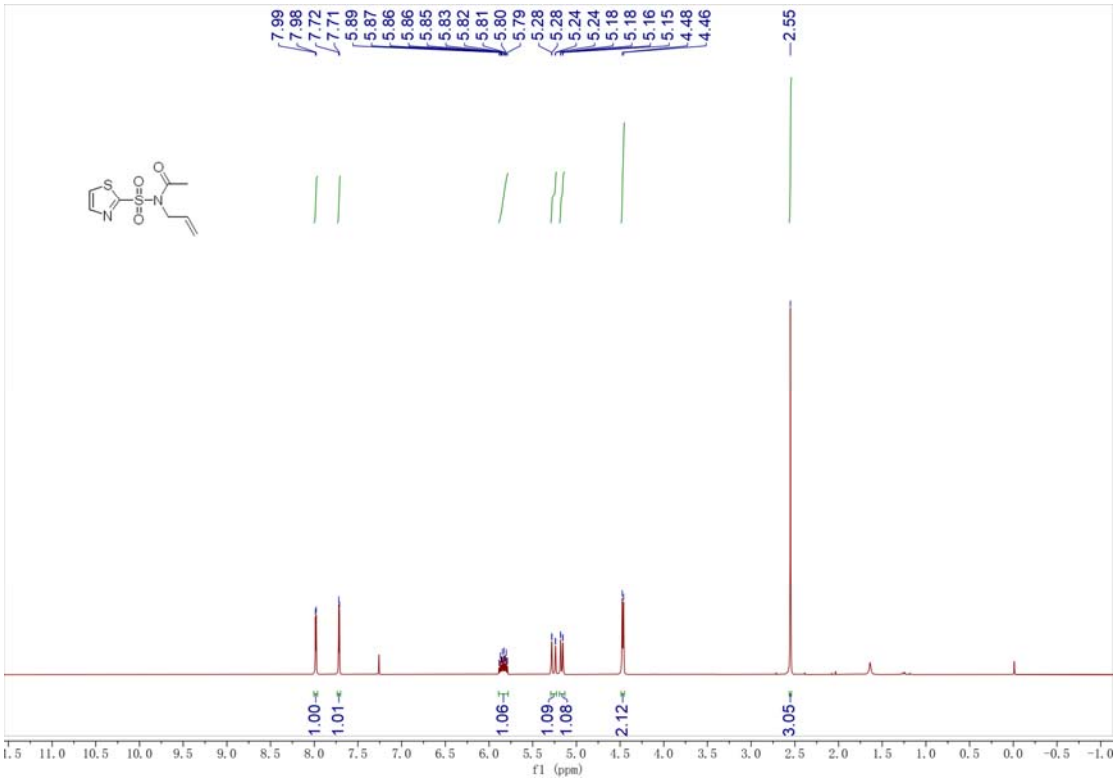


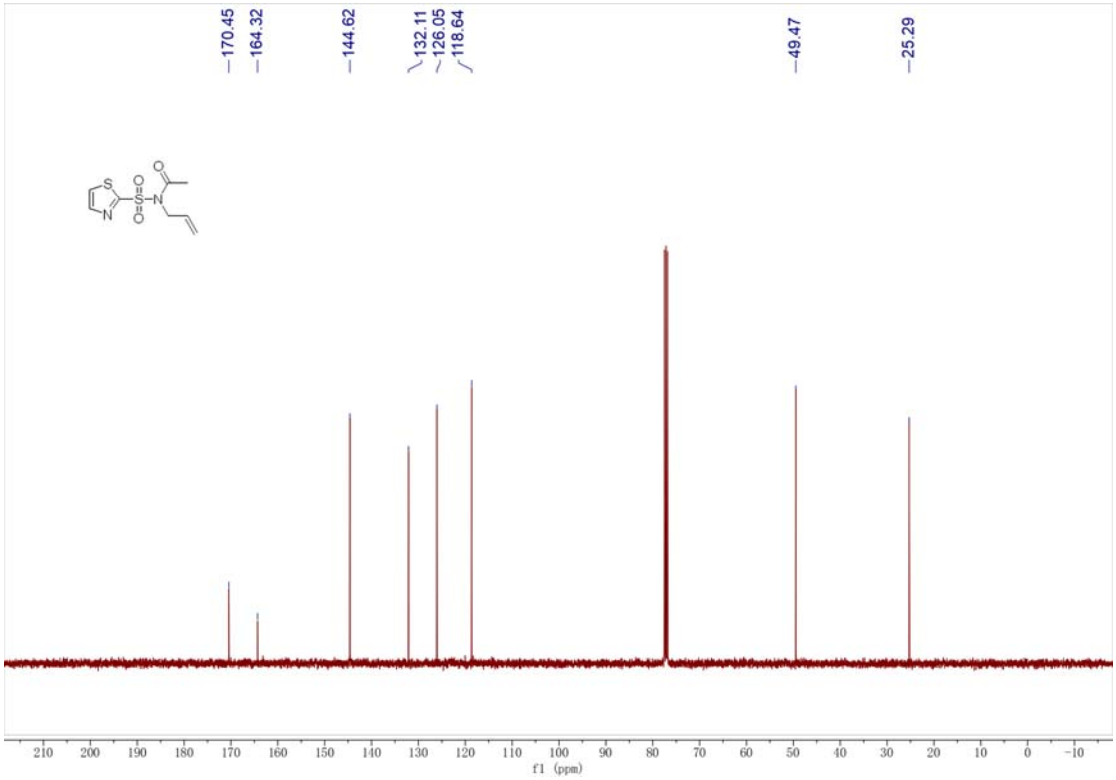
***N*-allyl-*N*-(pyrimidin-2-yl)benzo[d]thiazole-2-sulfonamide (1e)**



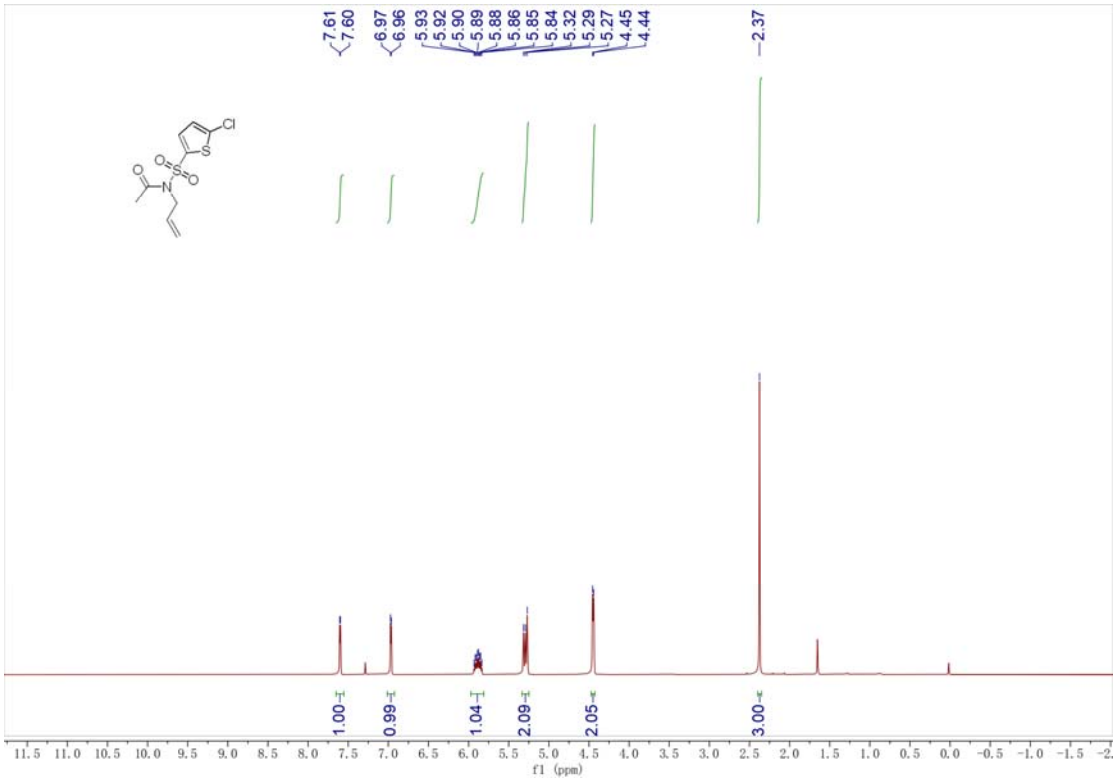


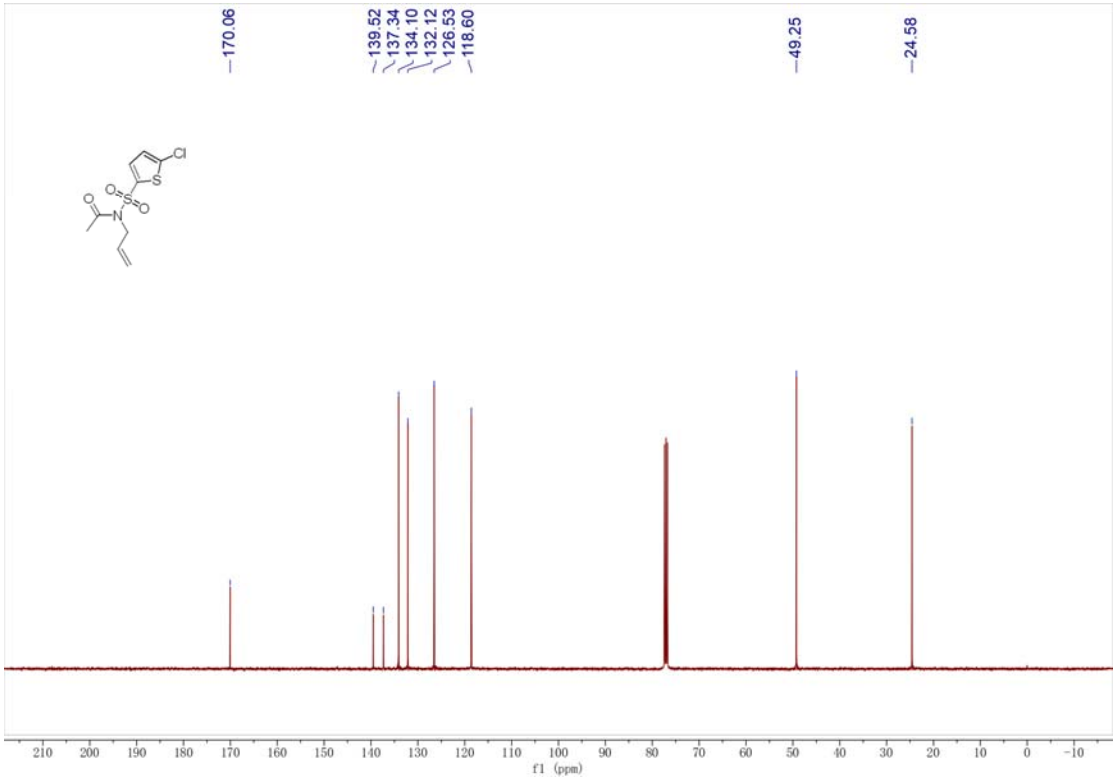
***N*-allyl-*N*-(thiazol-2-ylsulfonyl)acetamide (1f)**



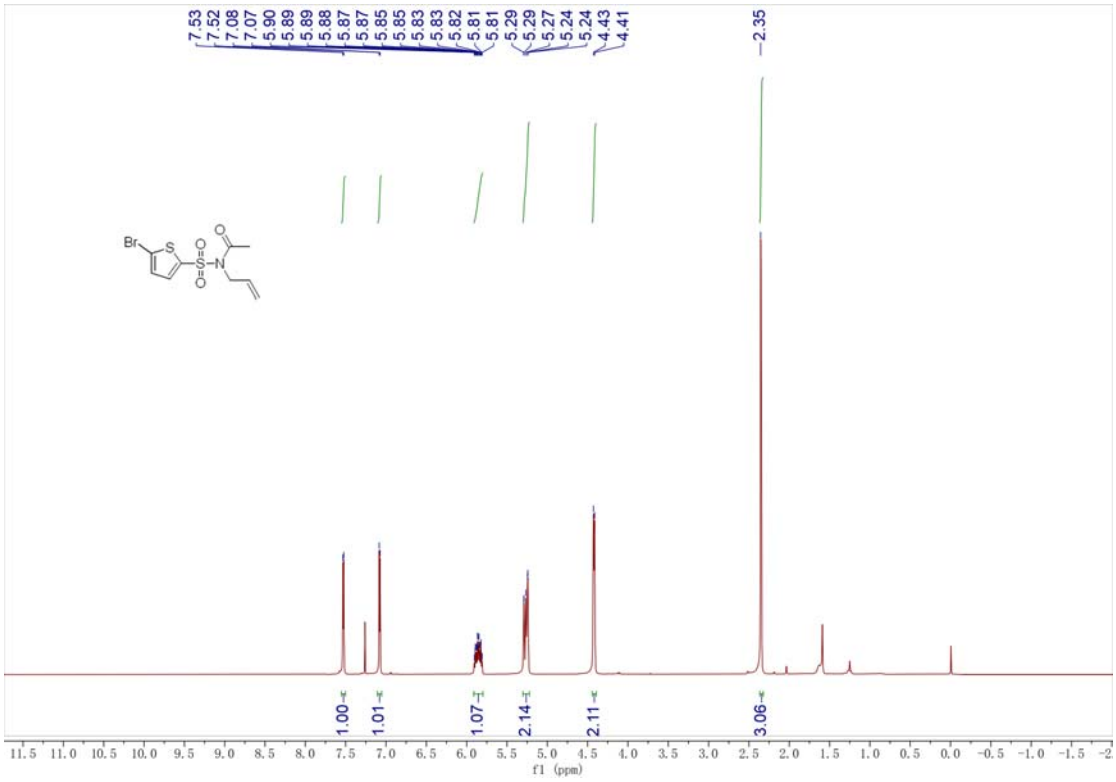


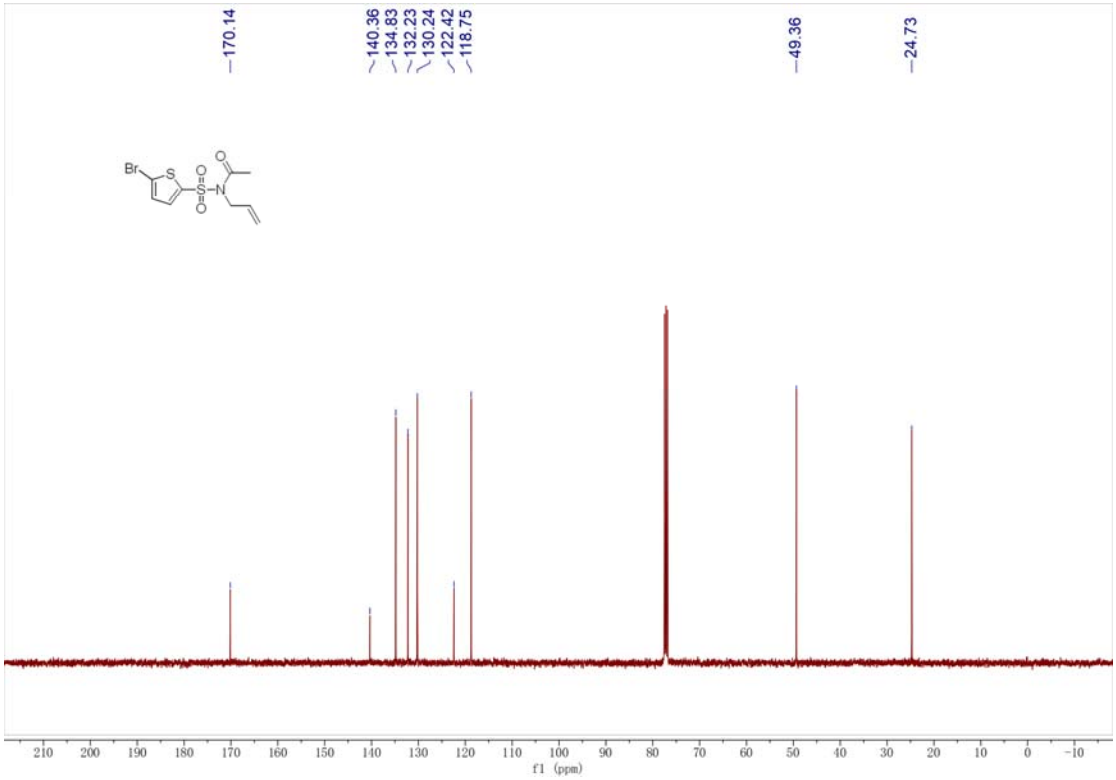
***N*-allyl-*N*-((5-chlorothiophen-2-yl)sulfonyl)acetamide (1g)**



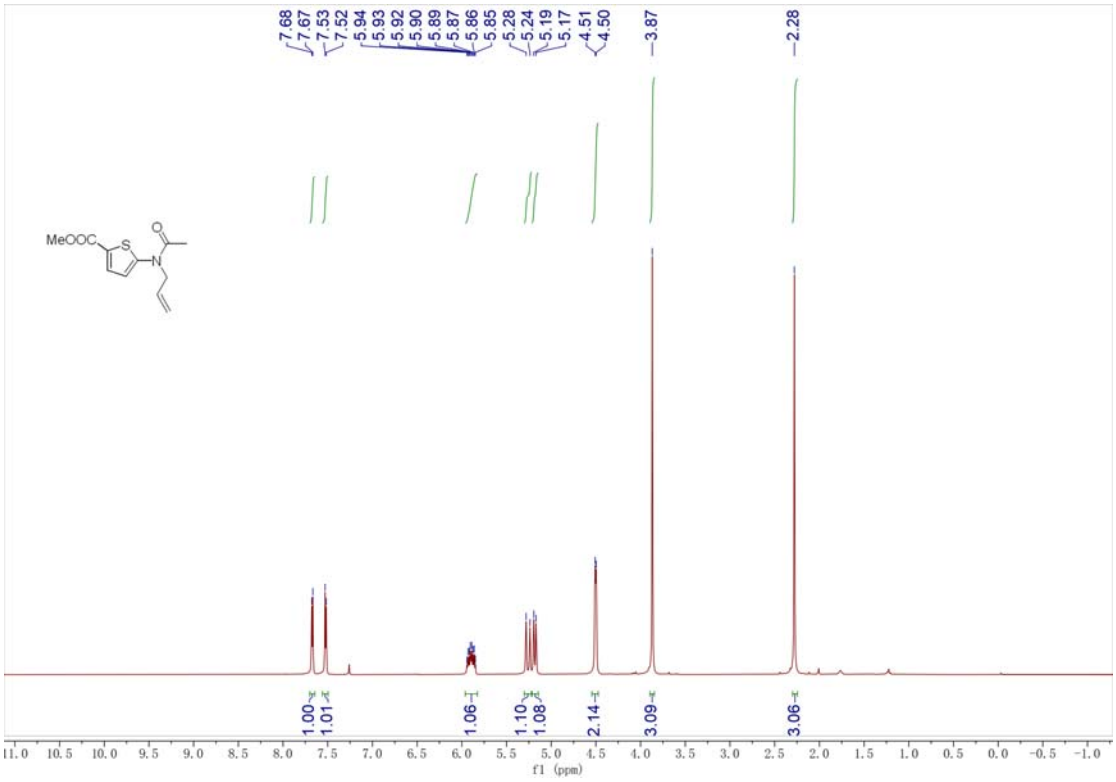


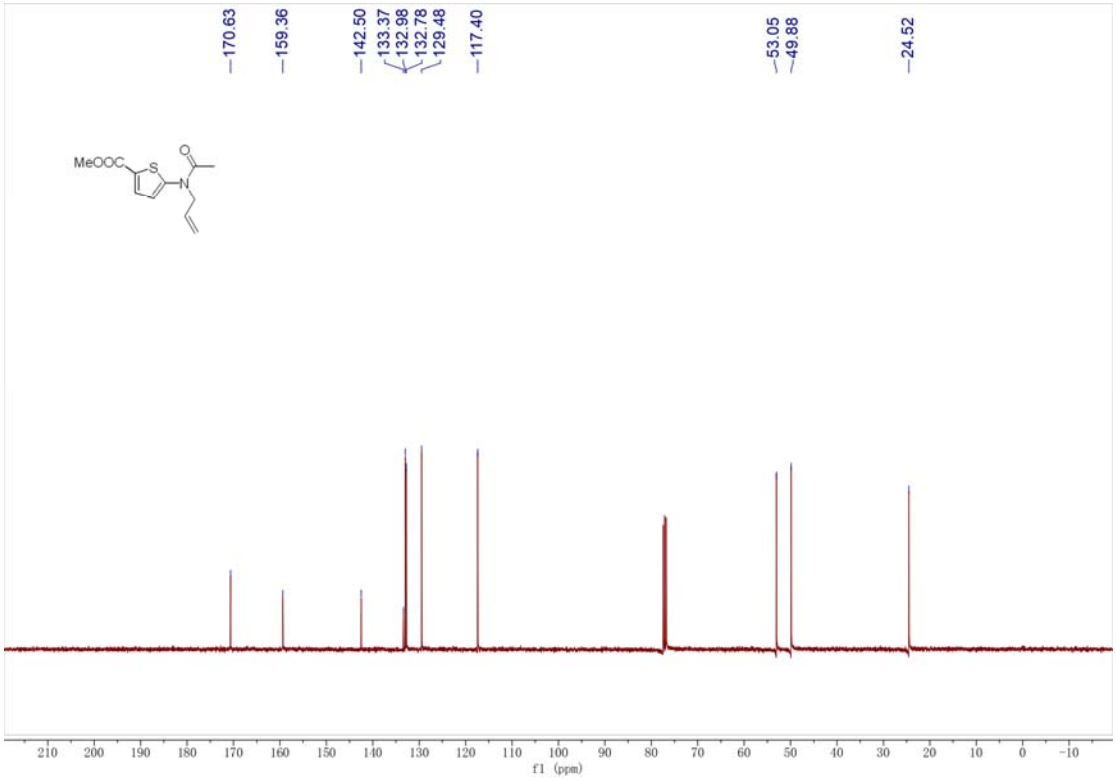
***N*-allyl-*N*-((5-bromothiophen-2-yl)sulfonyl)acetamide (1h)**



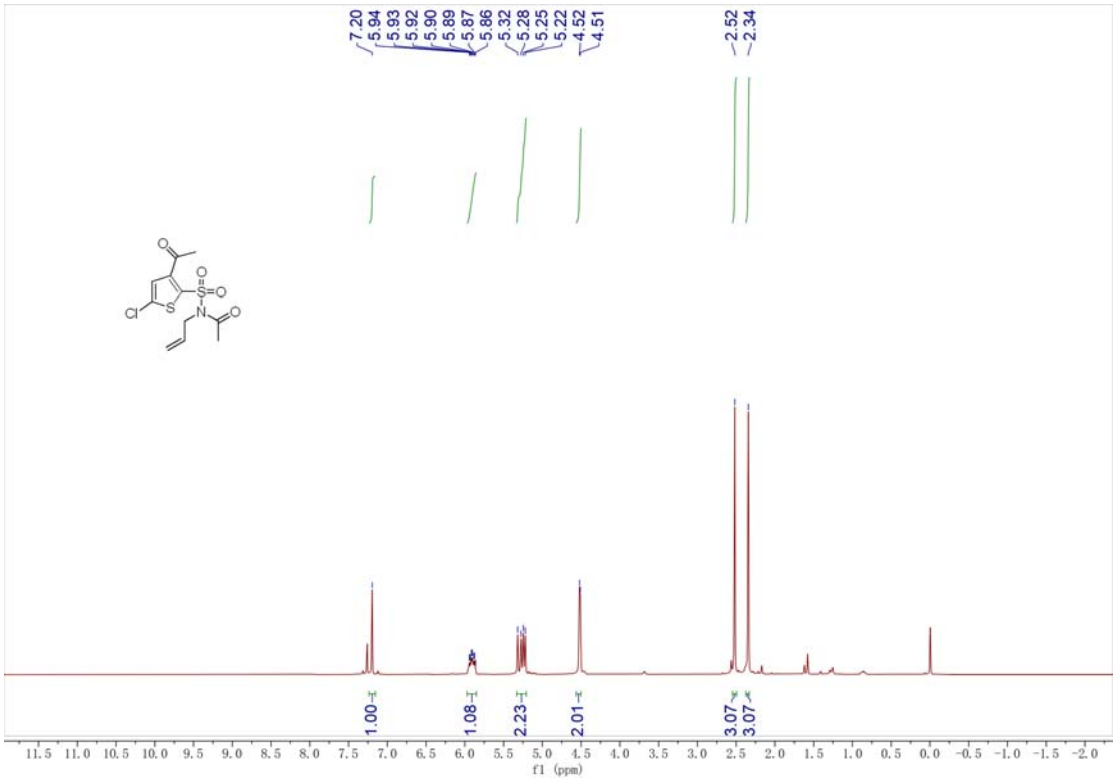


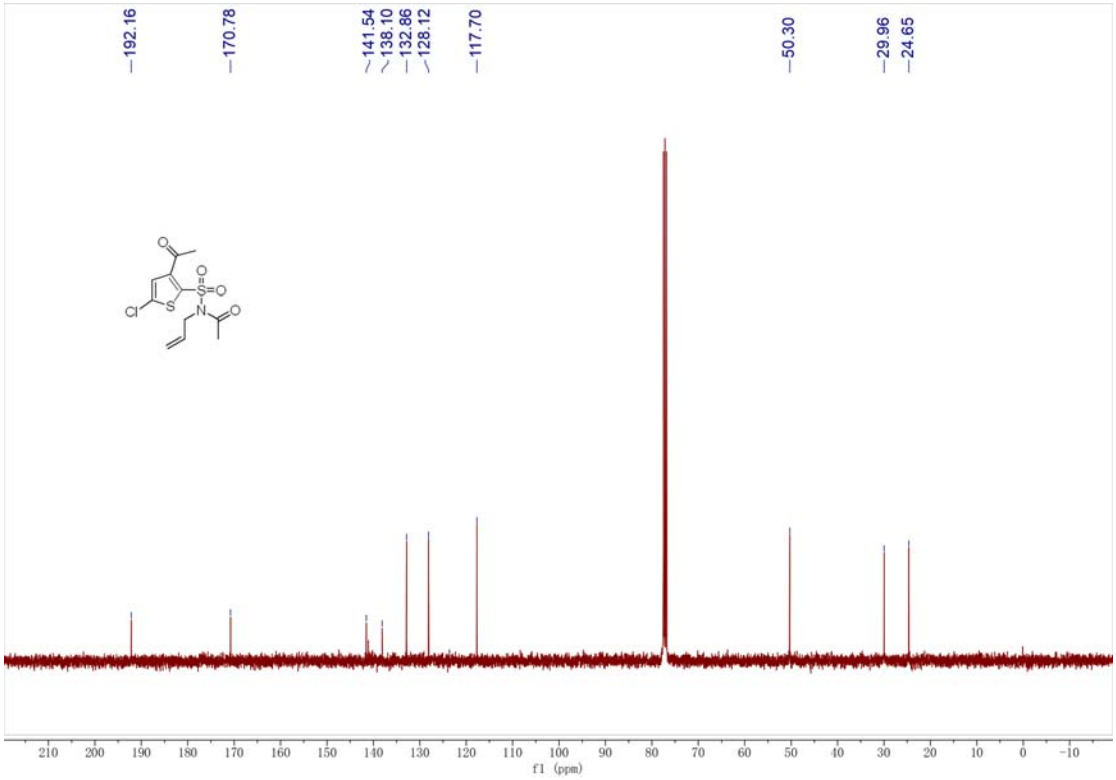
methyl 5-(*N*-acetyl-*N*-allylsulfamoyl)thiophene-2-carboxylate (1i)



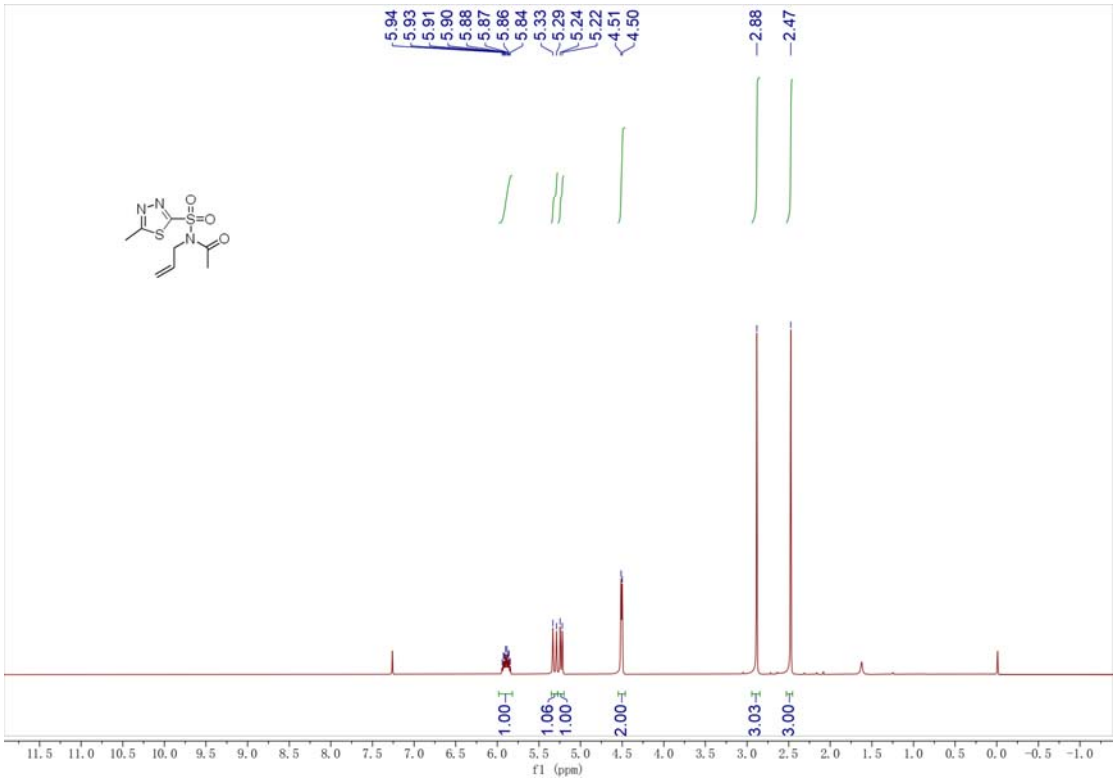


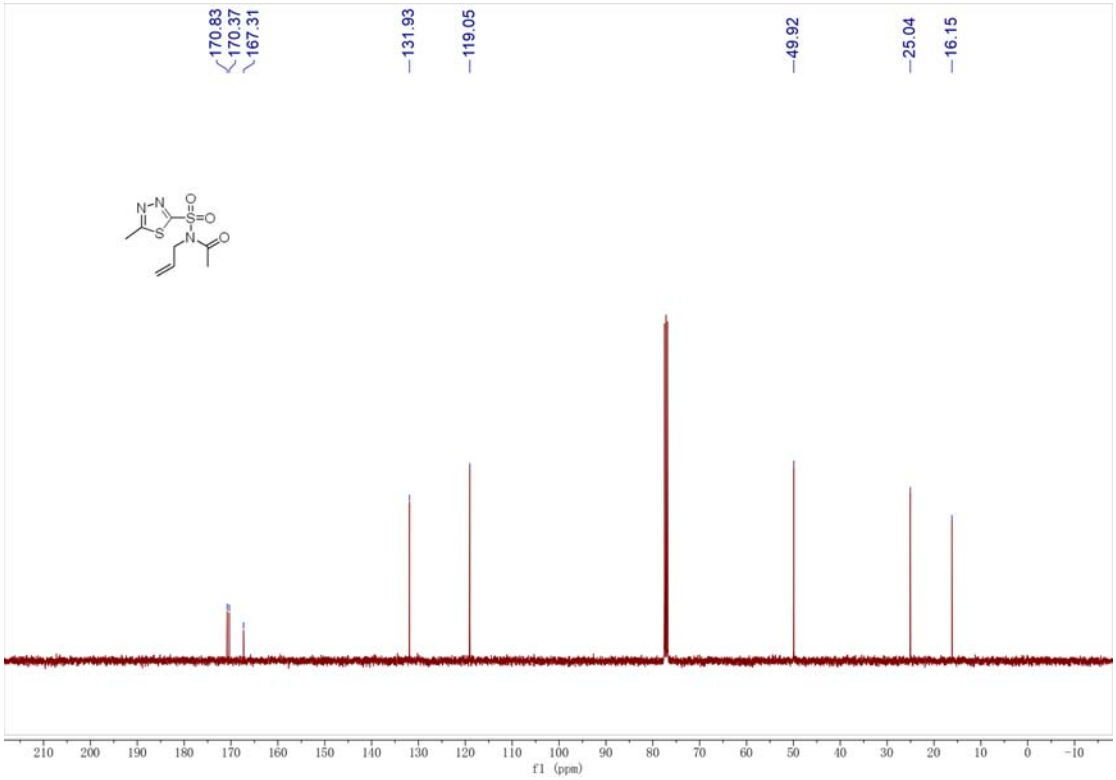
***N*-((3-acetyl-5-chlorothiophen-2-yl)sulfonyl)-*N*-allylacetamide (1j)**



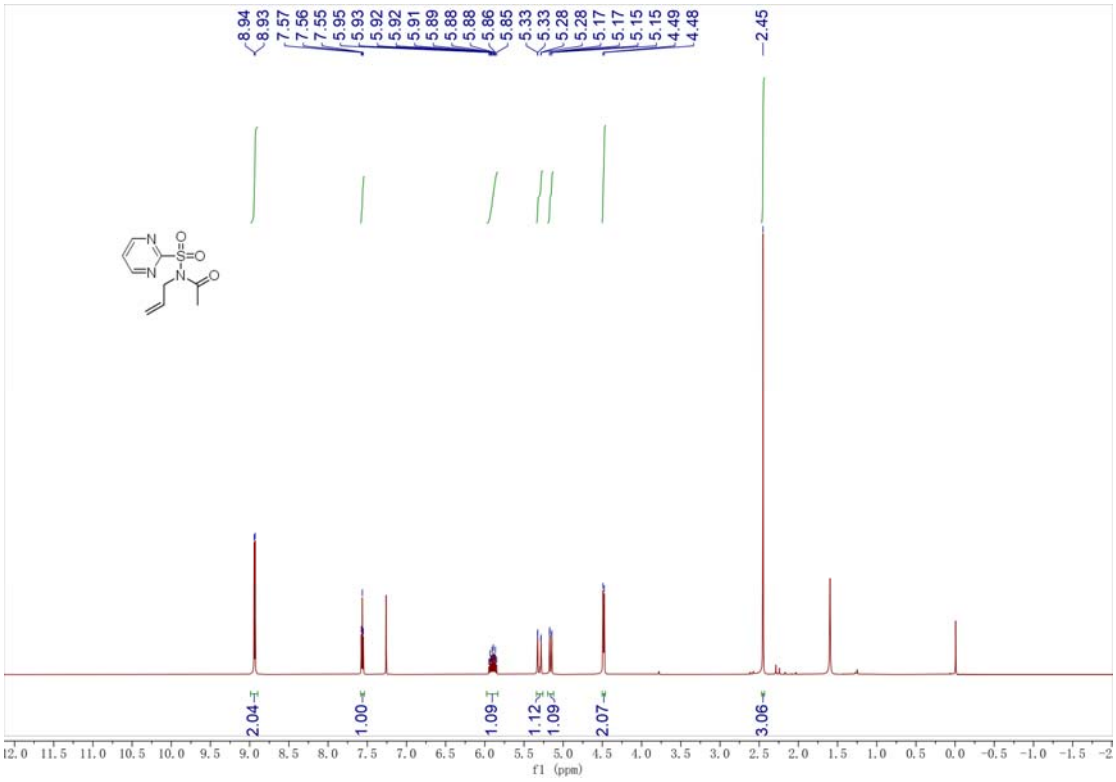


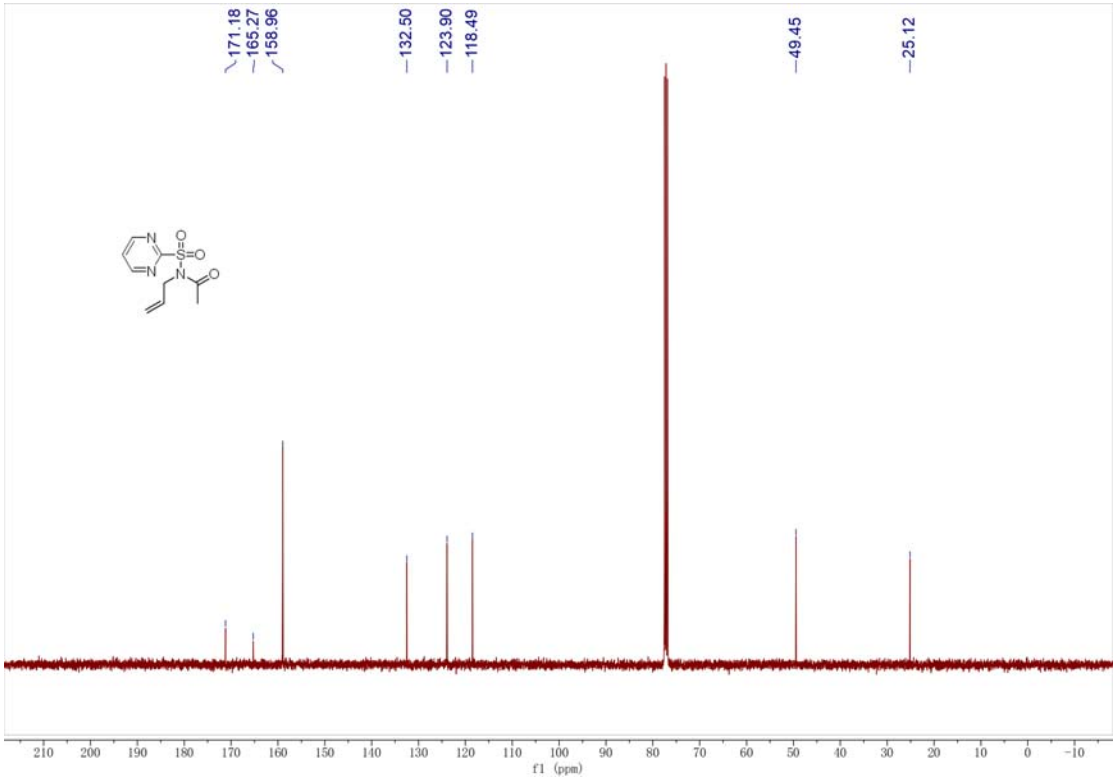
***N*-allyl-*N*-((5-methyl-1,3,4-thiadiazol-2-yl)sulfonyl)acetamide (1k)**



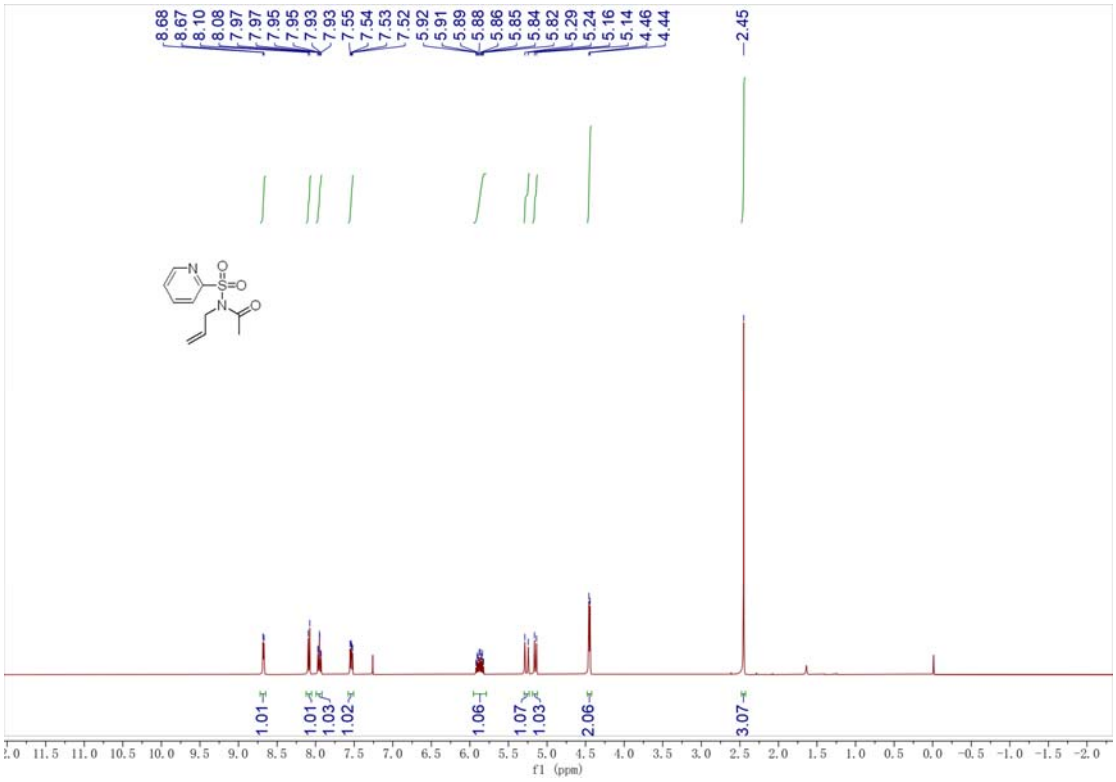


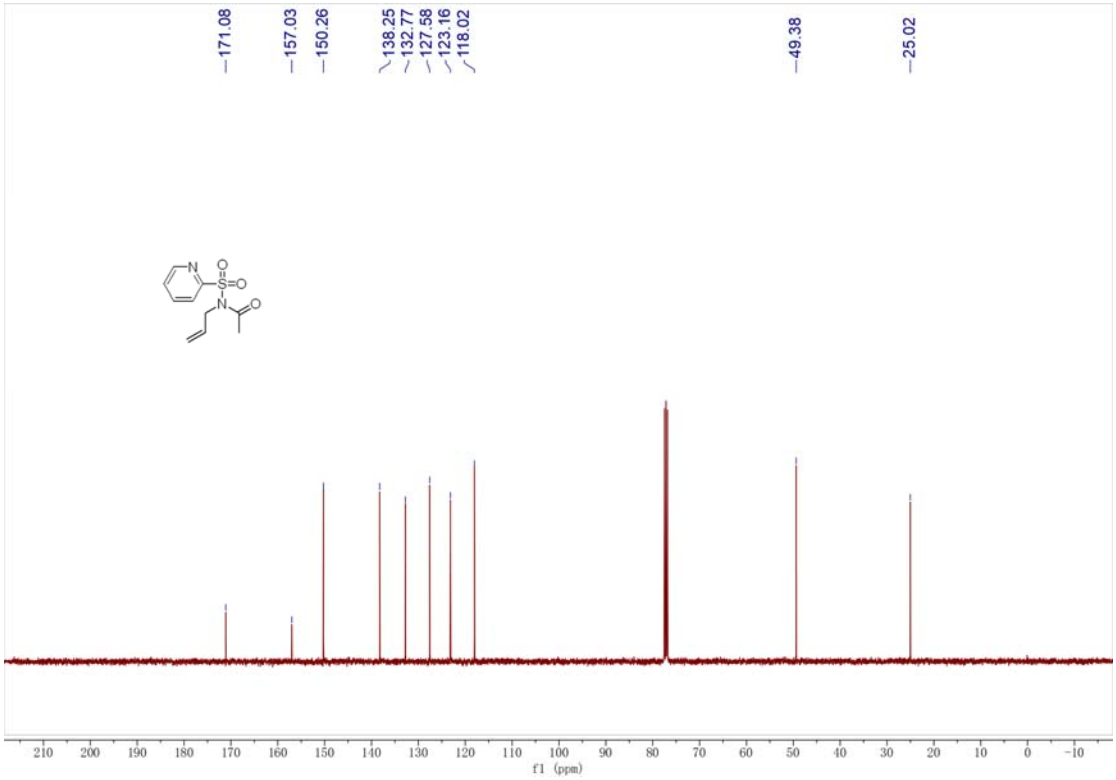
***N*-allyl-*N*-(pyrimidin-2-ylsulfonyl)acetamide (1l)**



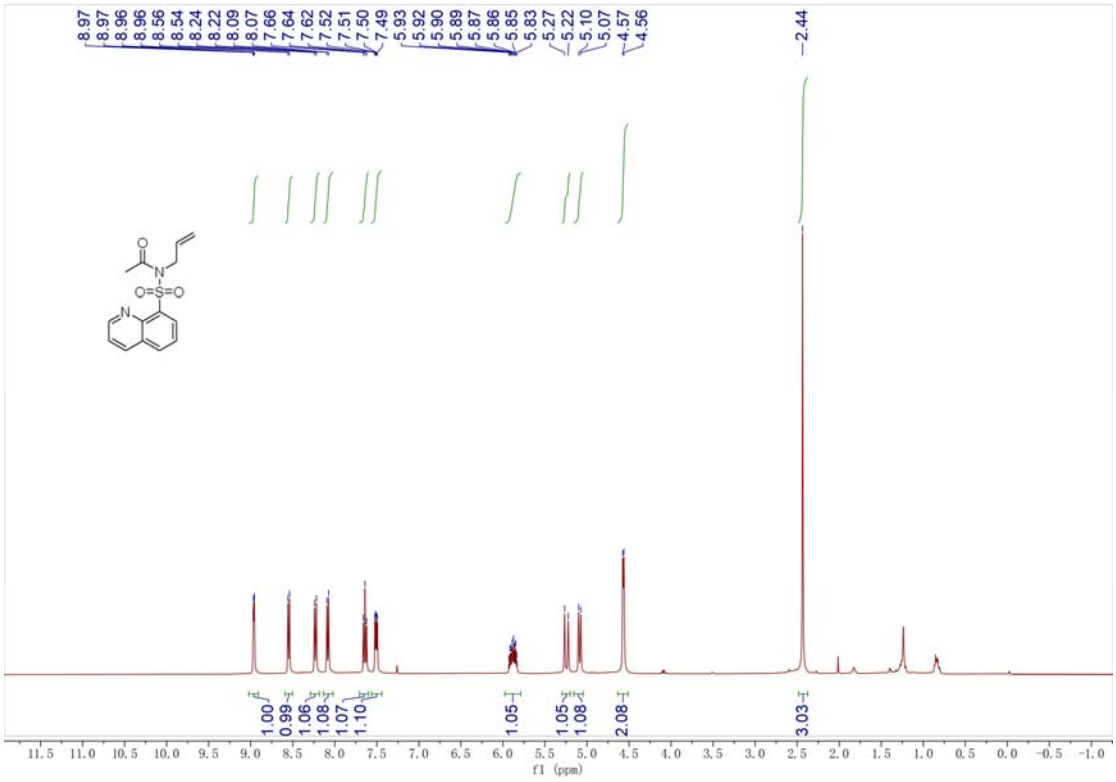


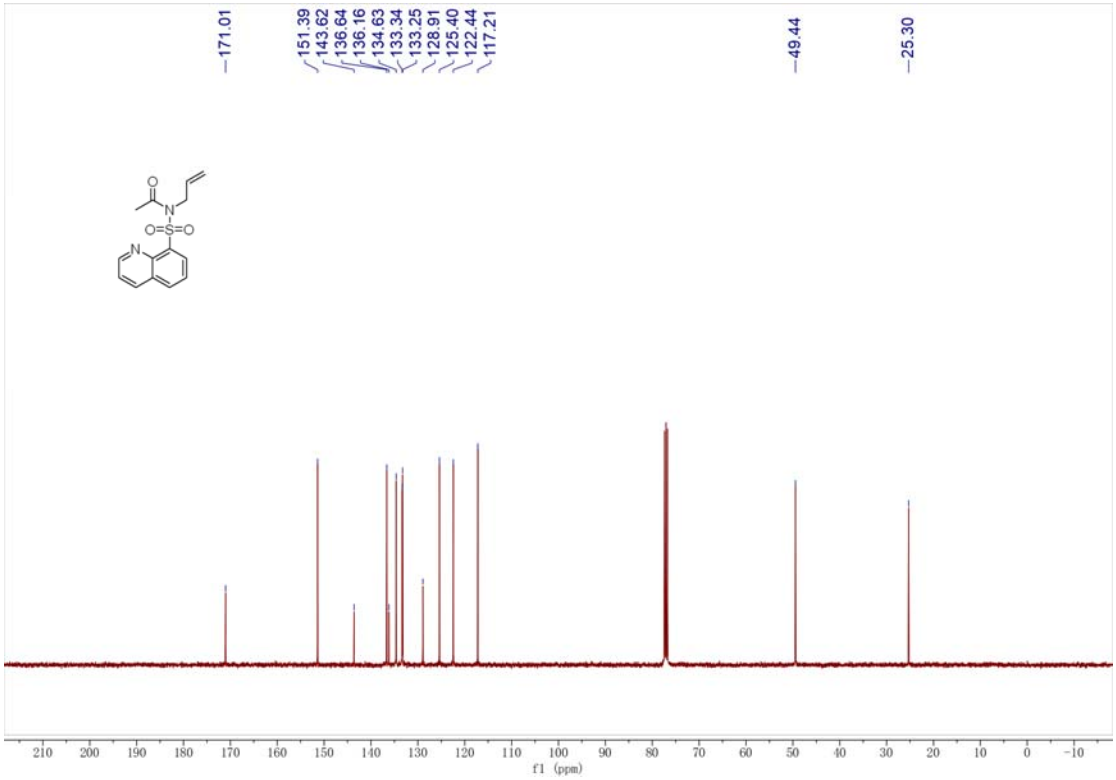
***N*-allyl-*N*-(pyridin-2-ylsulfonyl)acetamide (1m)**



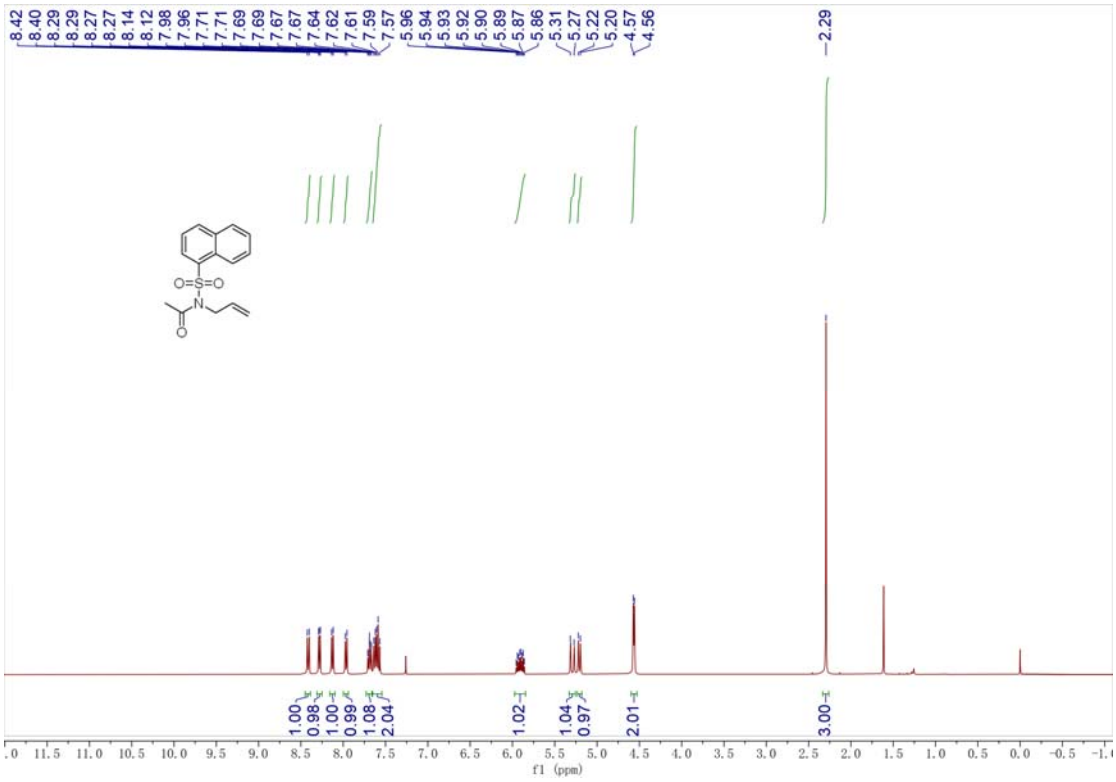


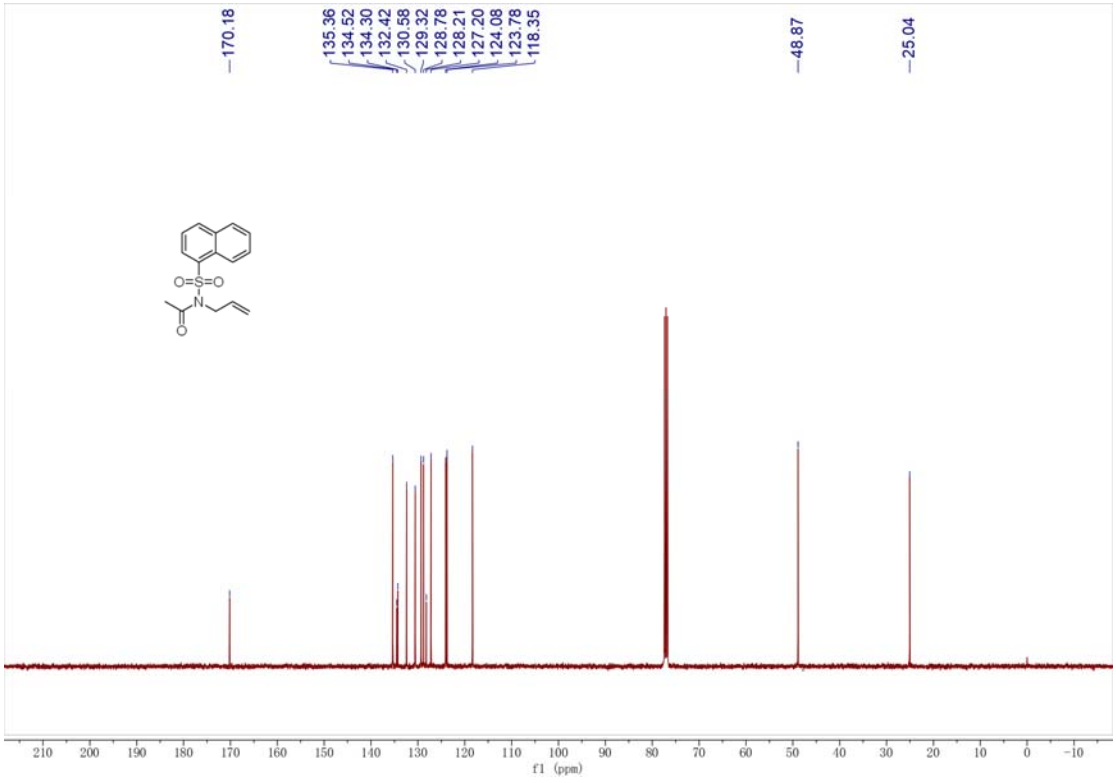
***N*-allyl-*N*-(quinolin-8-ylsulfonyl)acetamide (1n)**



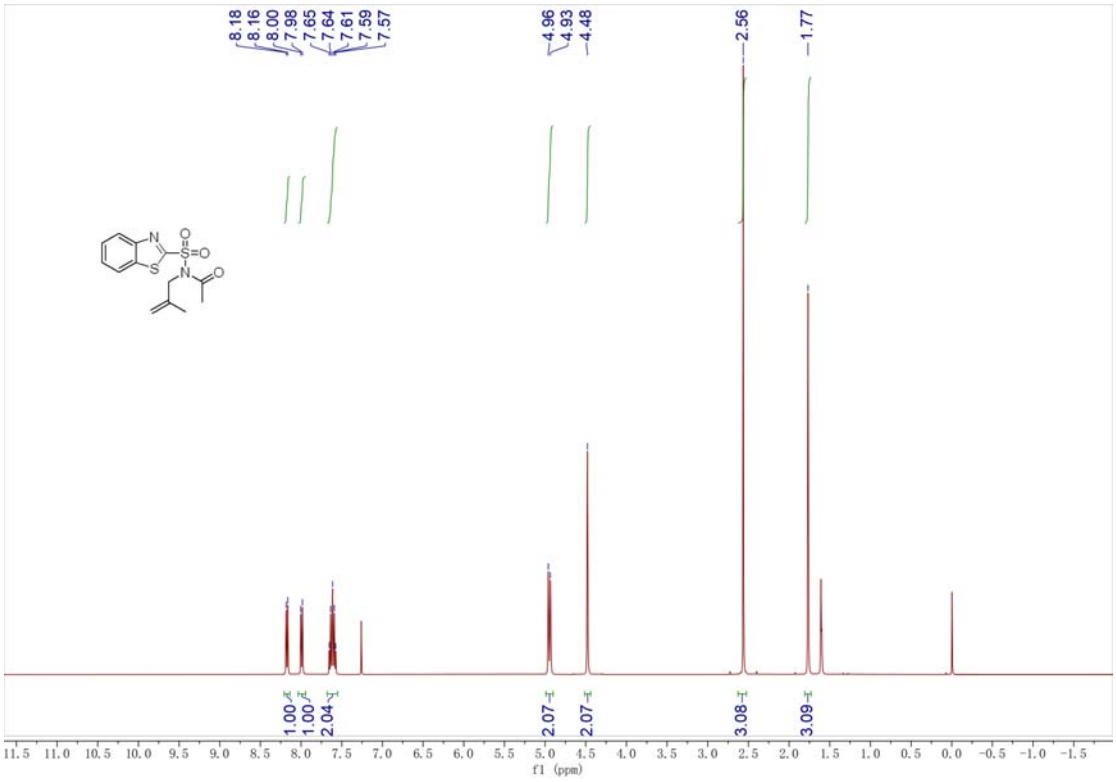


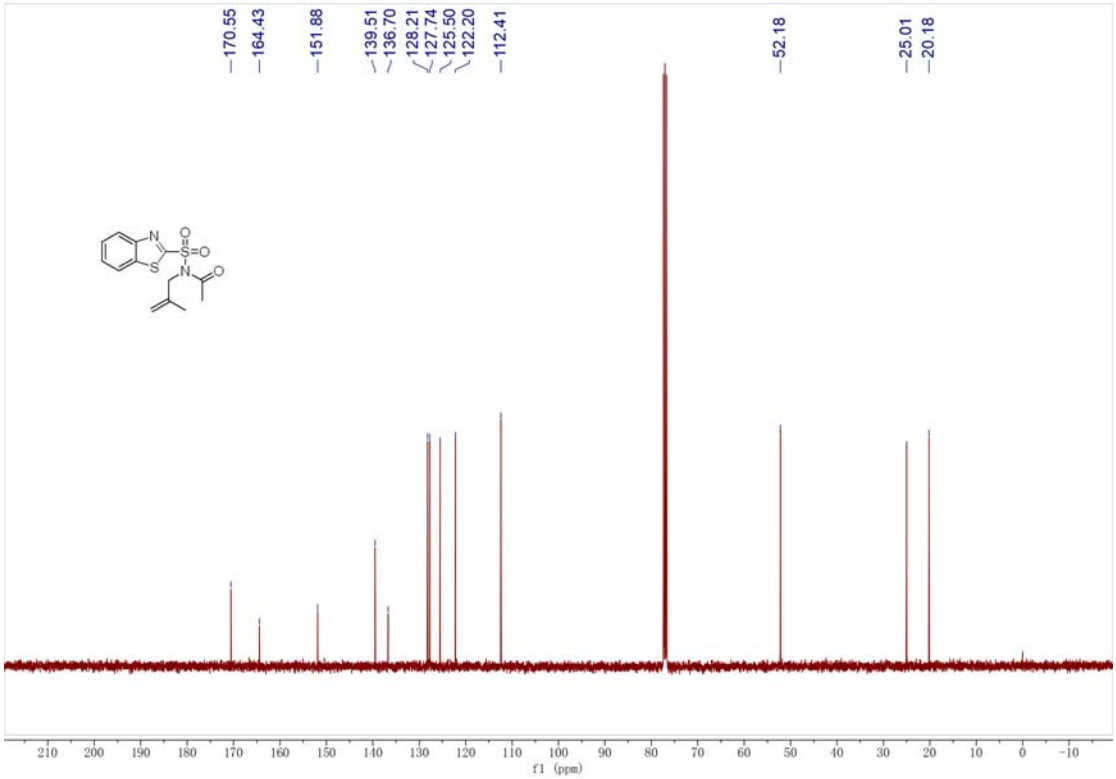
***N*-allyl-*N*-(naphthalen-1-ylsulfonyl)acetamide (1o)**



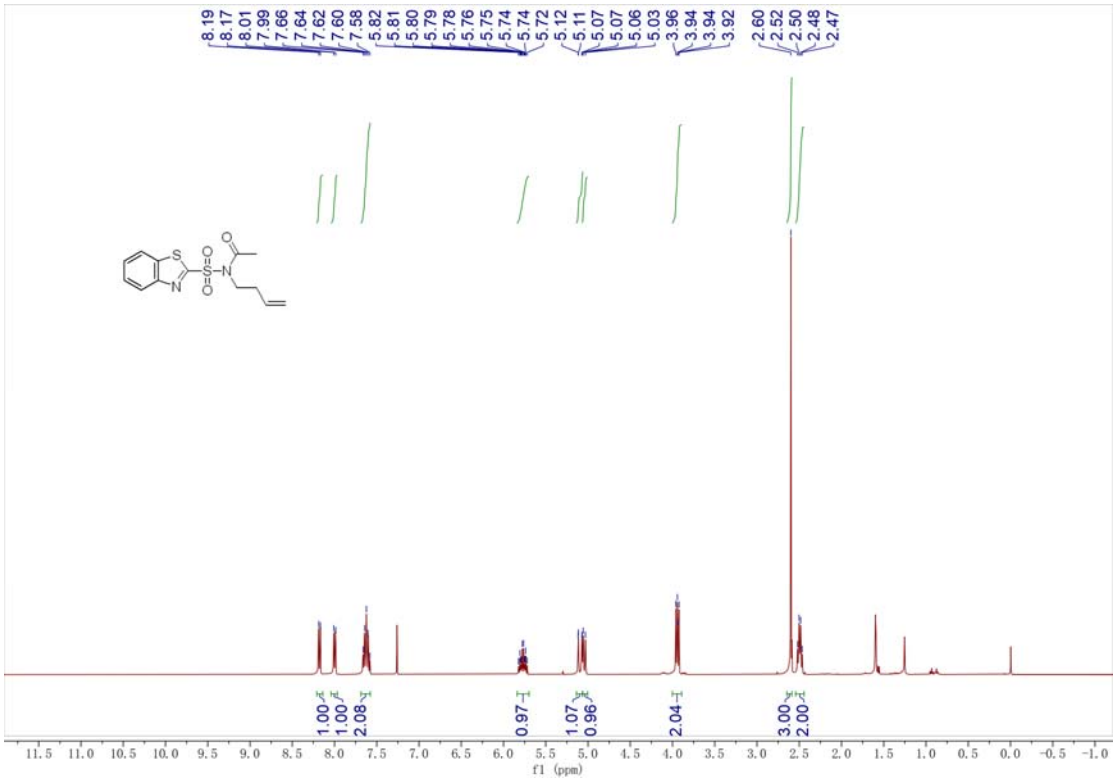


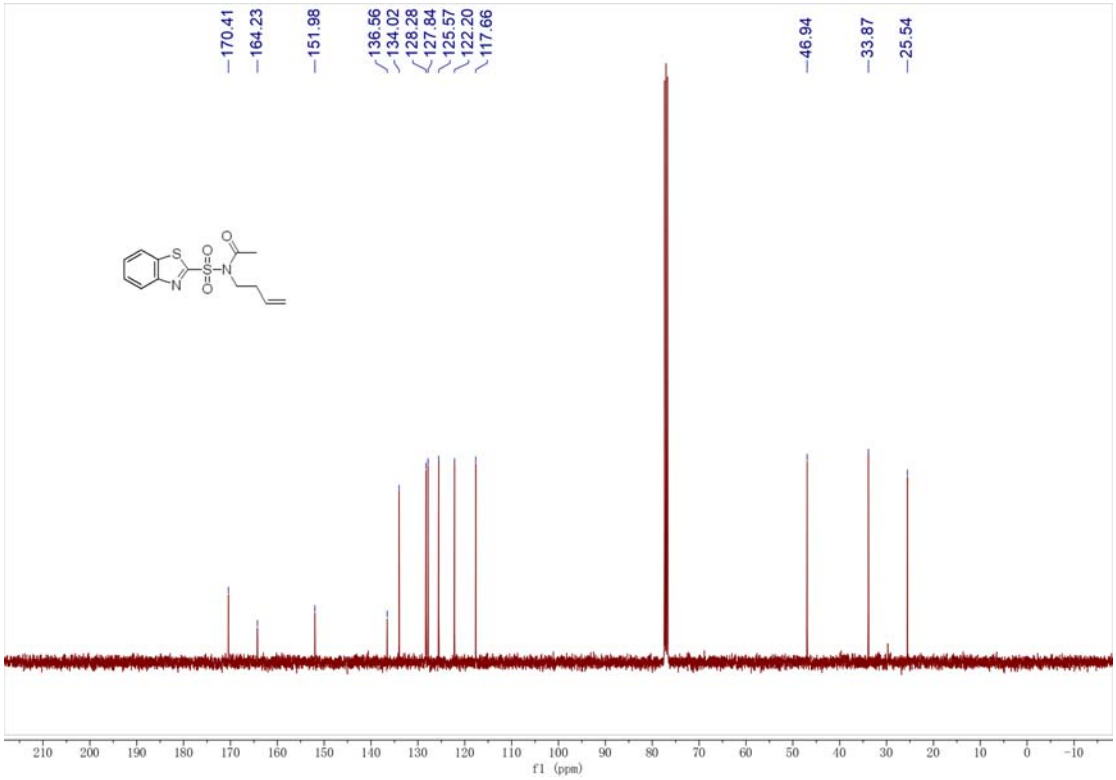
***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(2-methylallyl)acetamide (1p)**



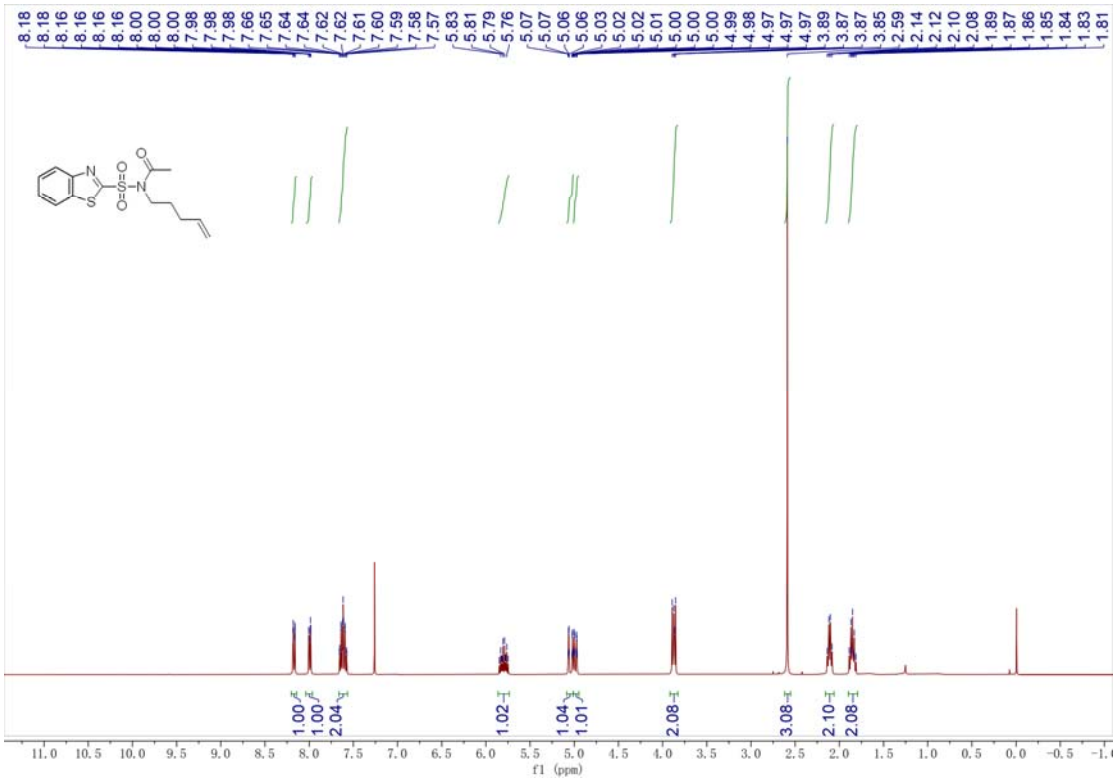


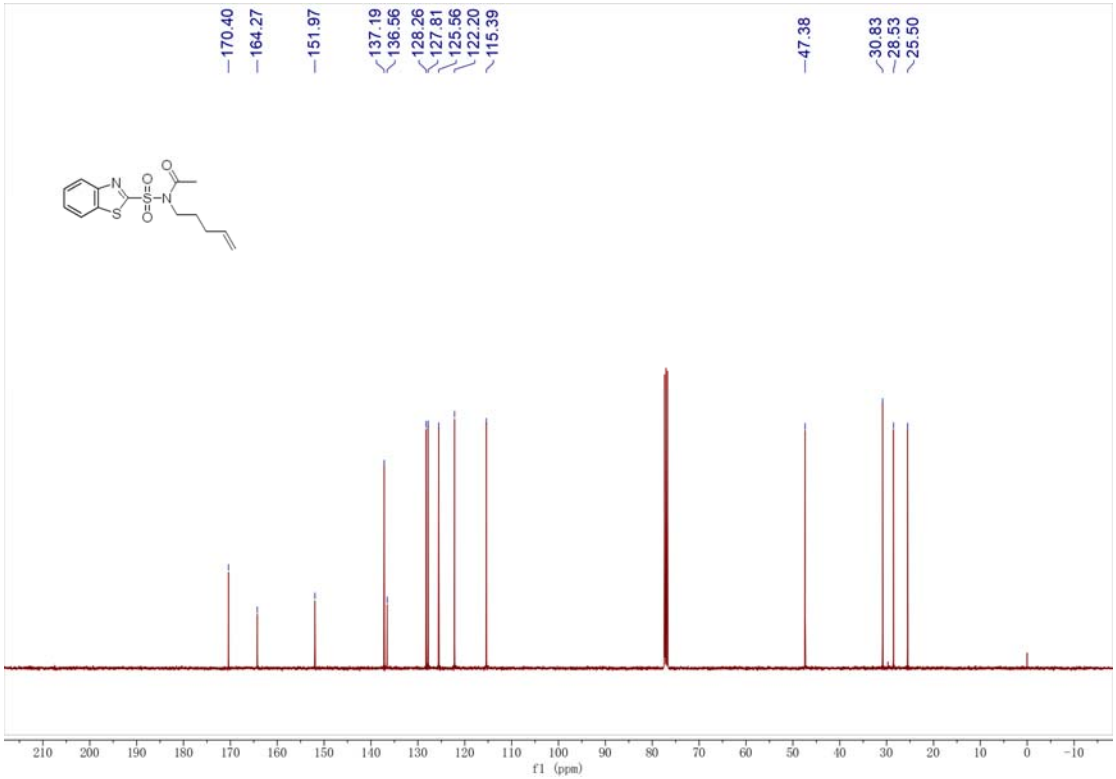
***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(but-3-en-1-yl)acetamide (1q)**



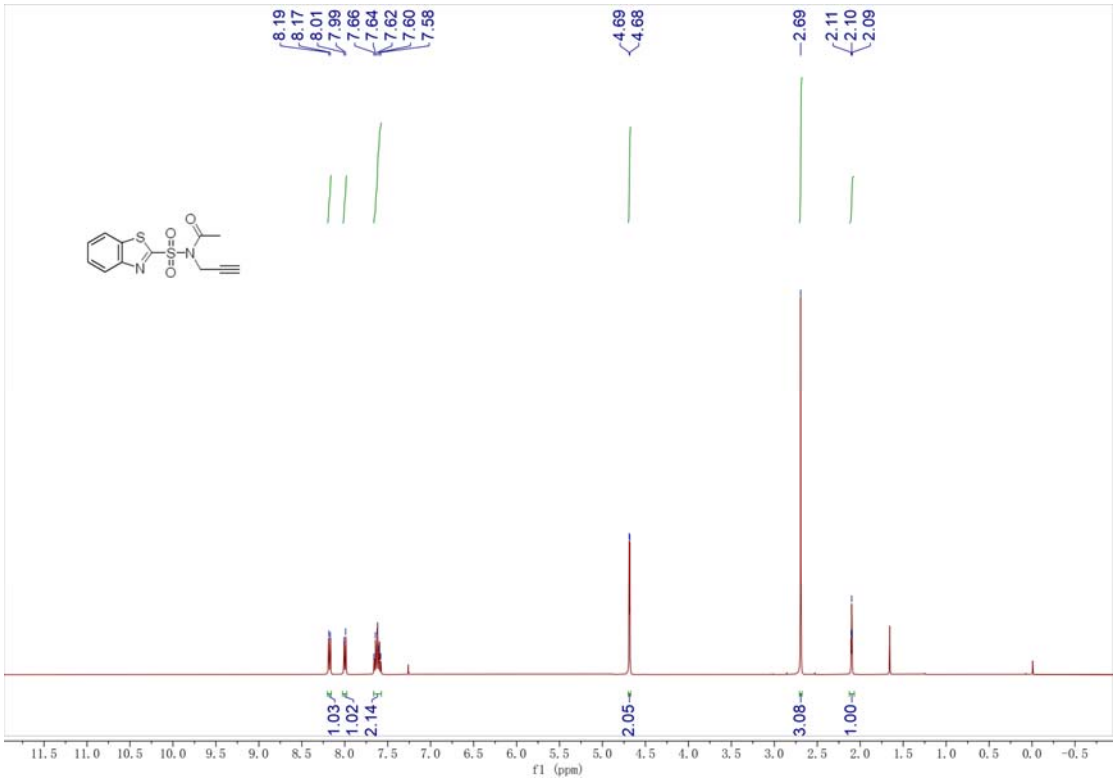


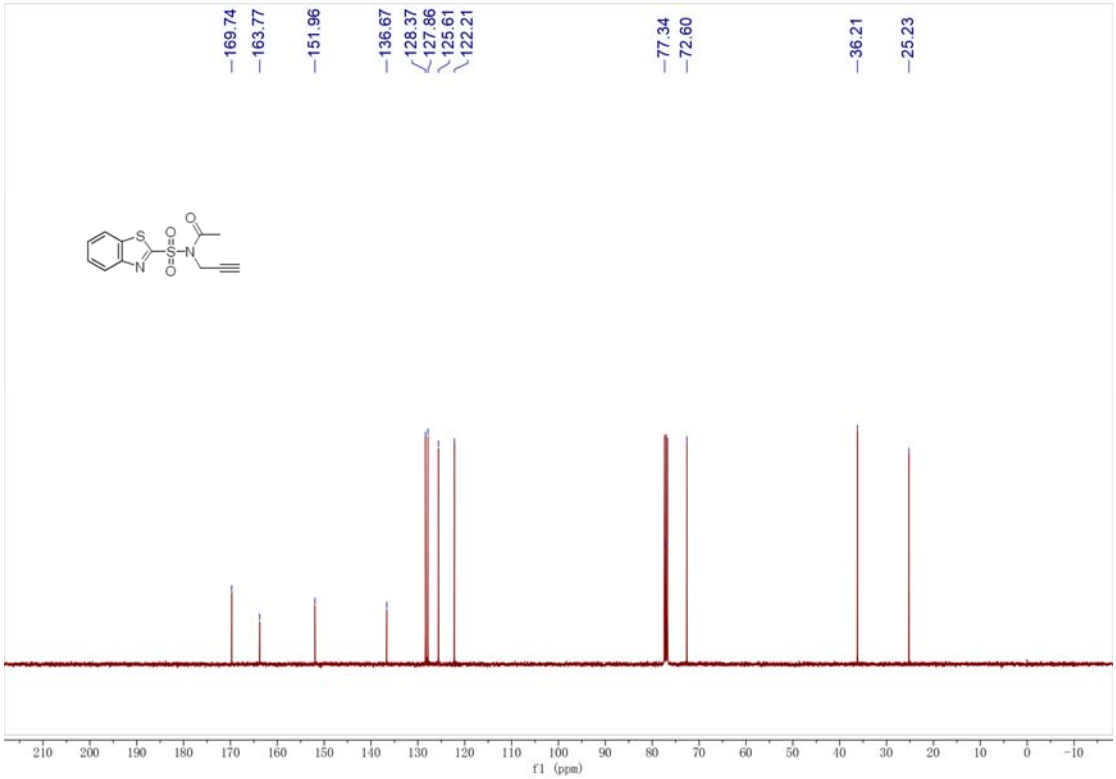
***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(pent-4-en-1-yl)acetamide**



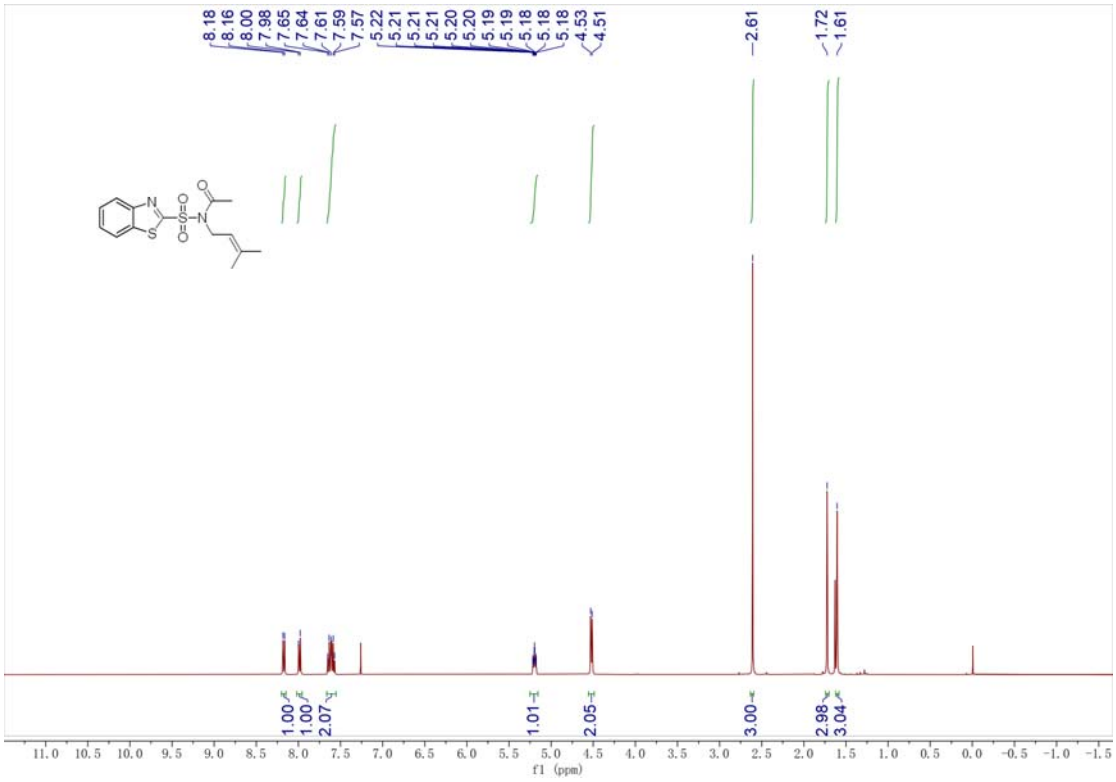


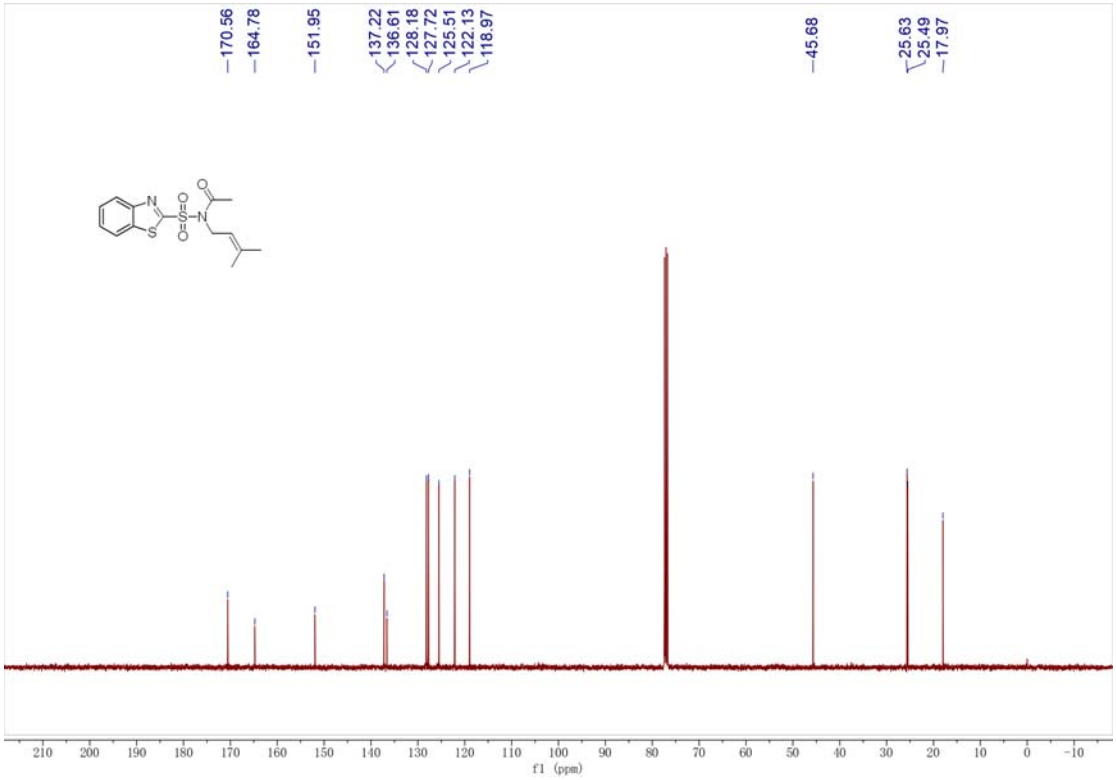
***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(prop-2-yn-1-yl)acetamide (1r)**



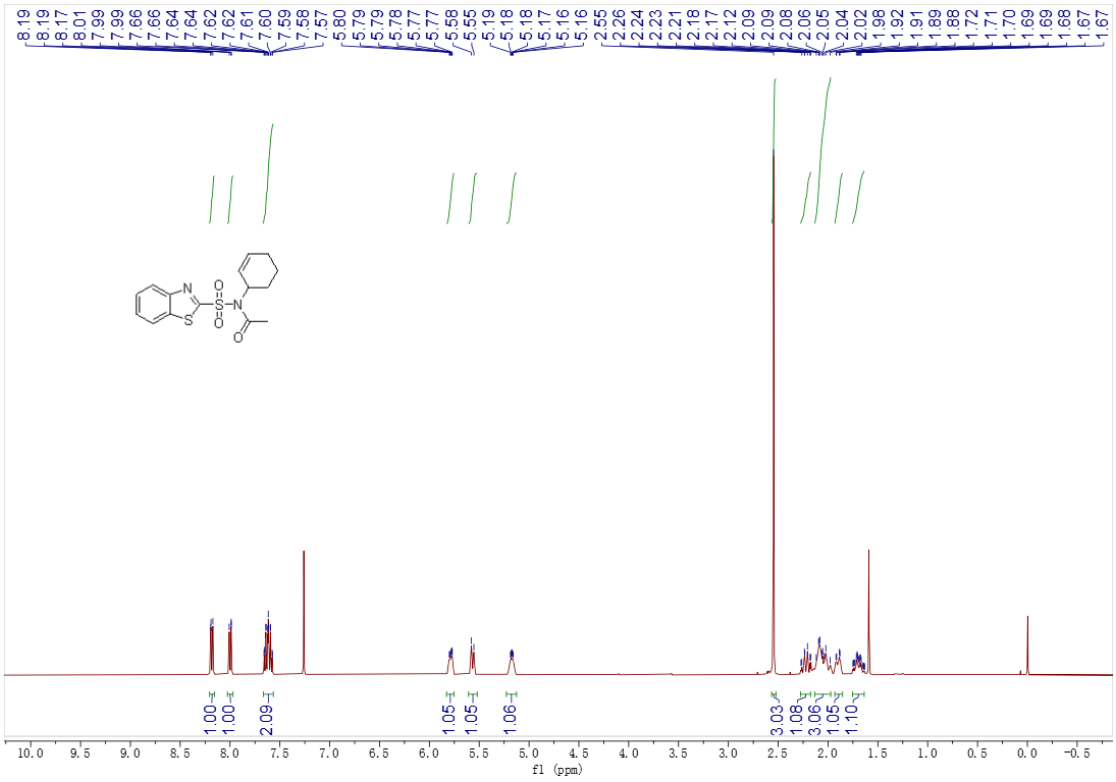


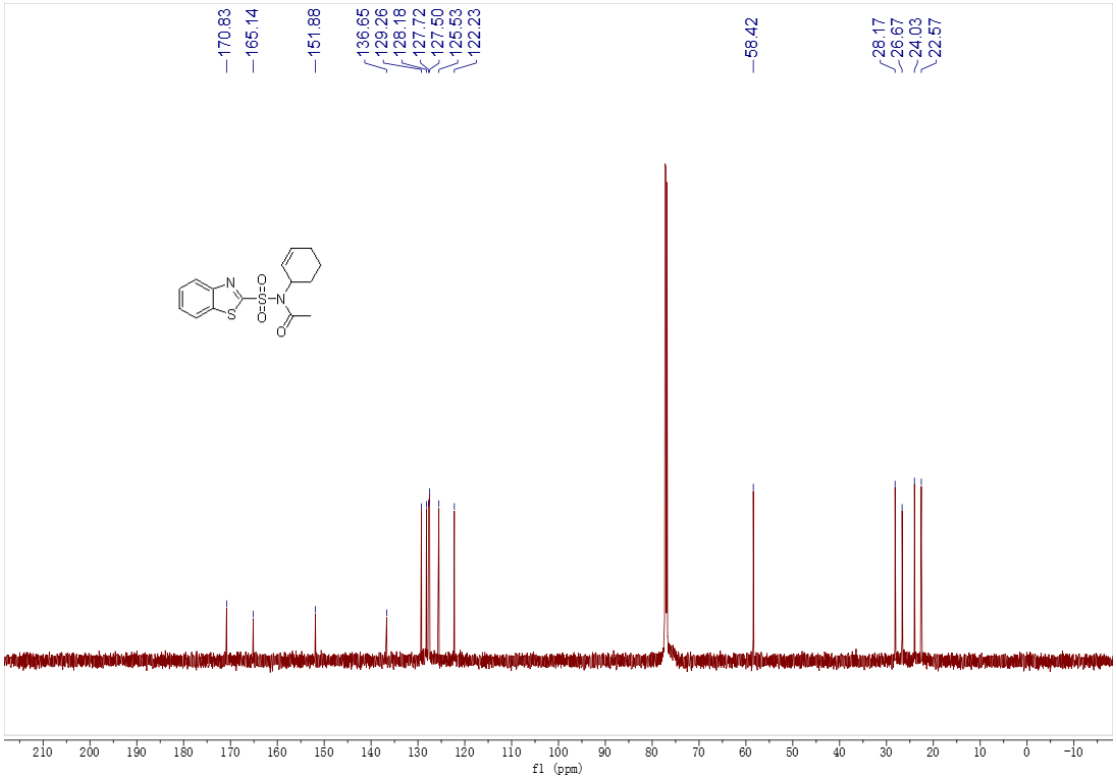
***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(3-methylbut-2-en-1-yl)acetamide (1t)**



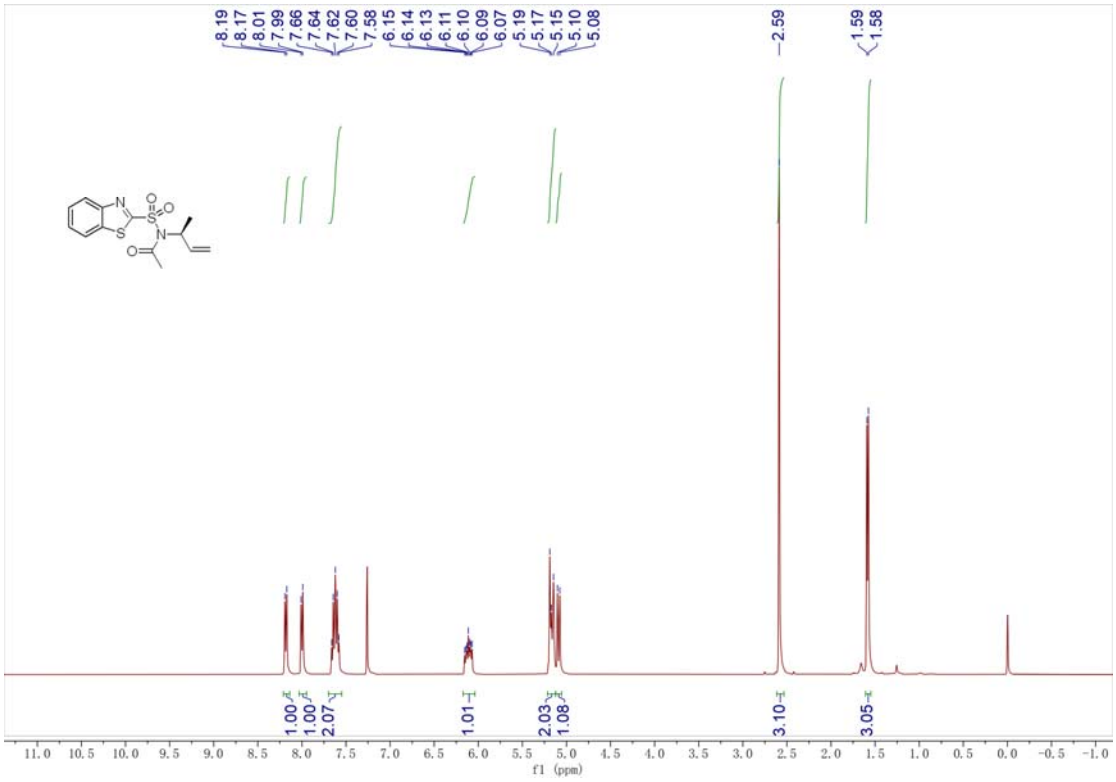


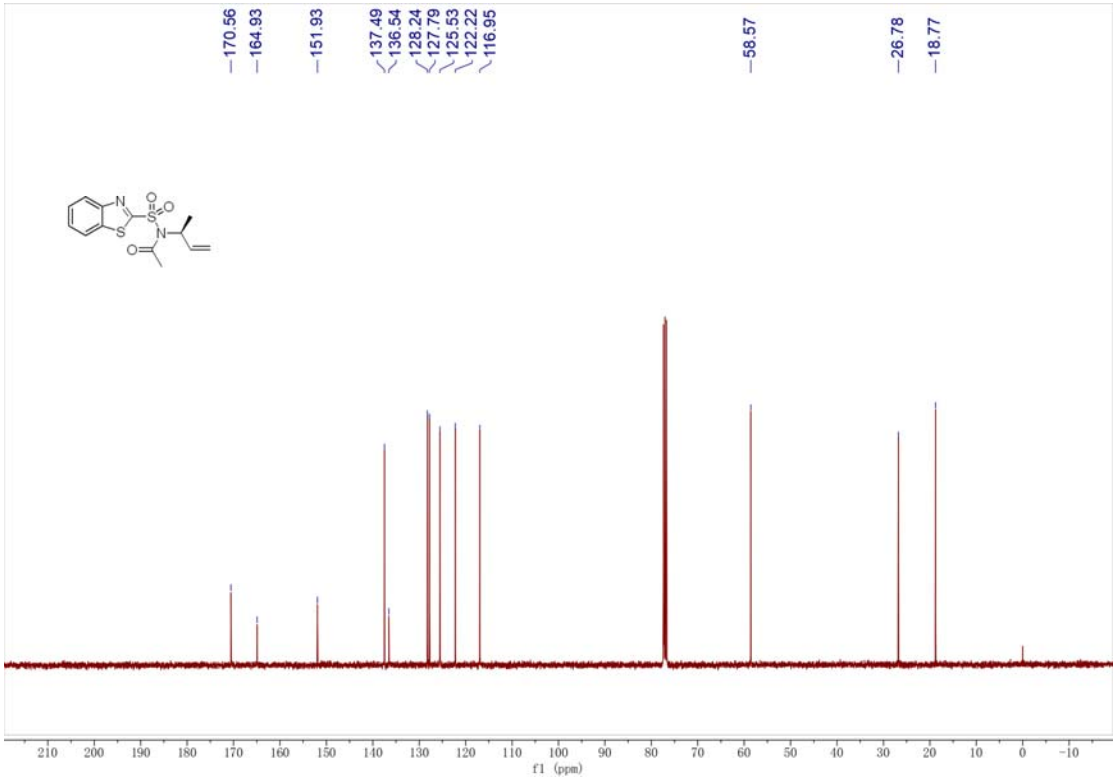
***N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(cyclohex-2-en-1-yl)acetamide (1u)**:



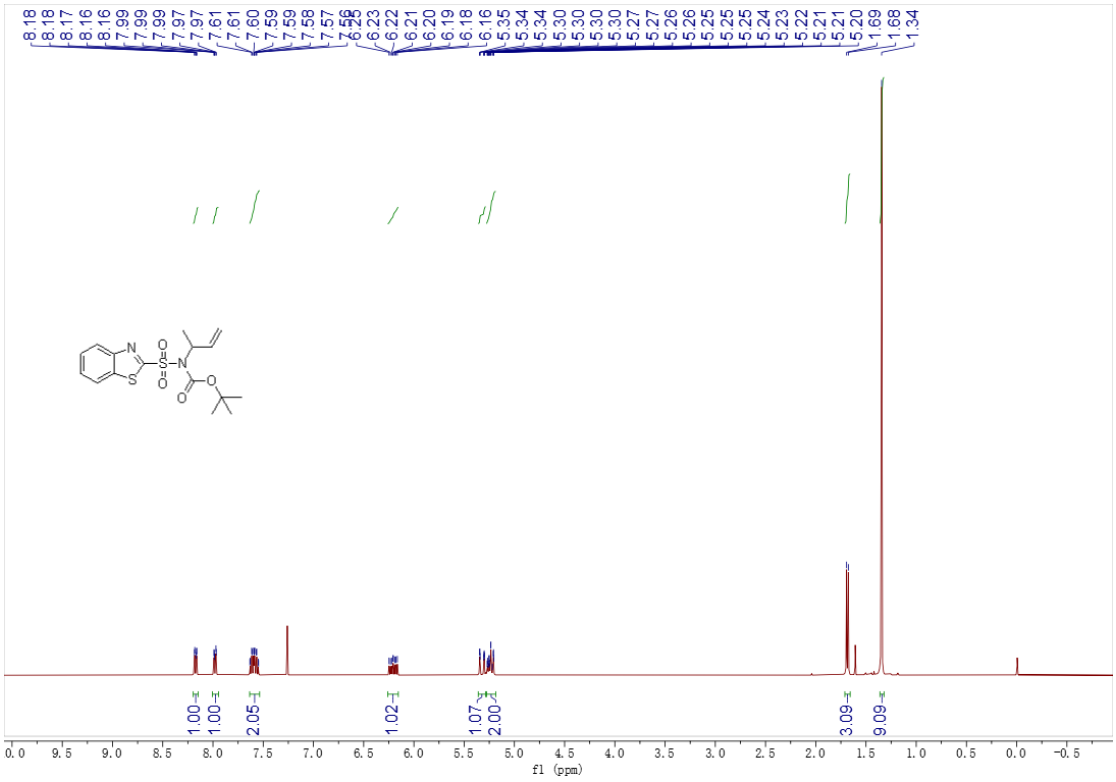


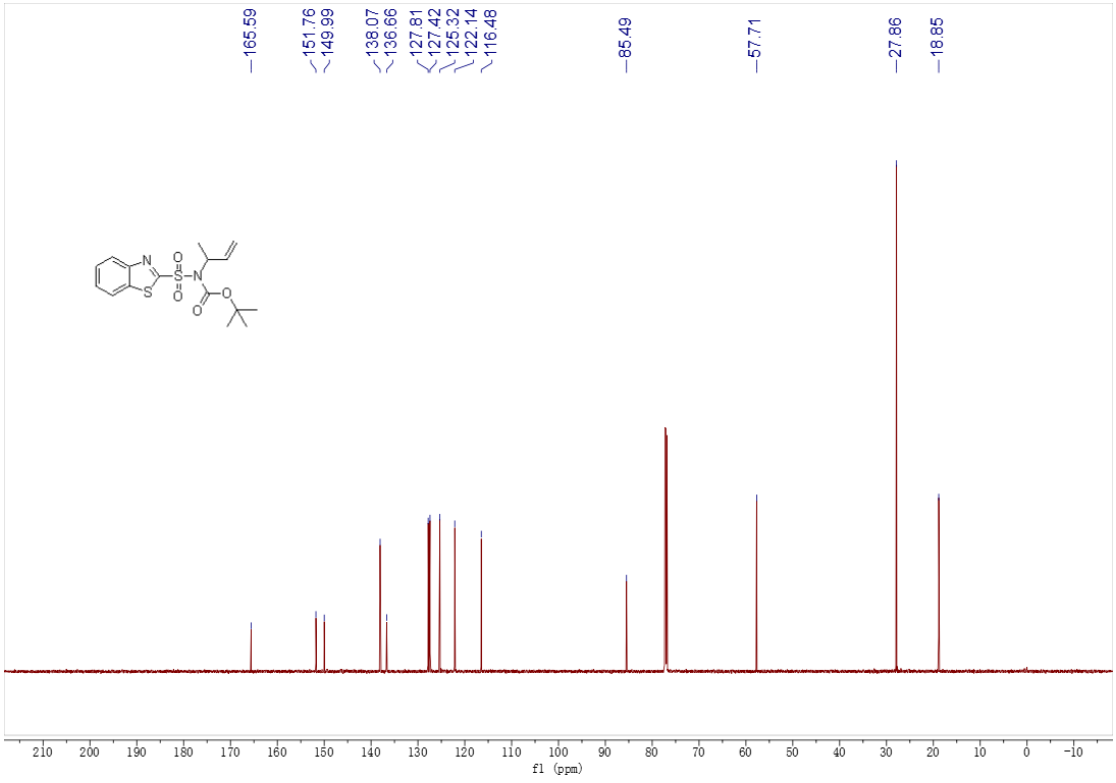
(S)-*N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(but-3-en-2-yl)acetamide (1v)



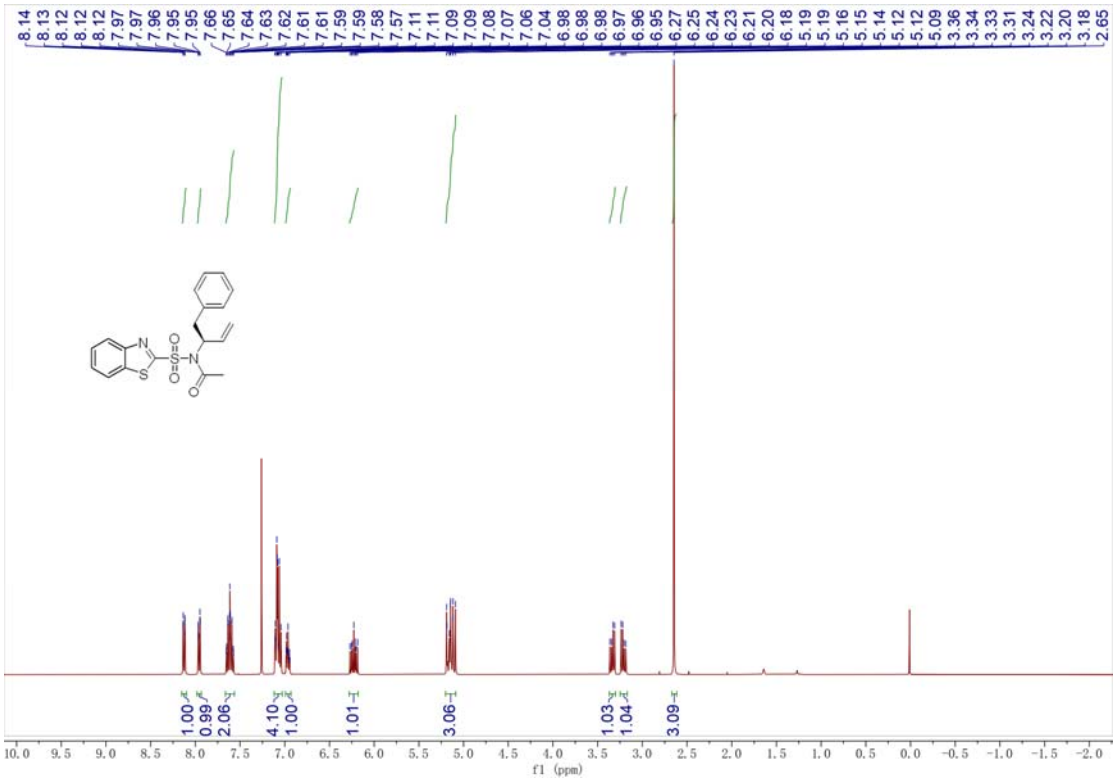


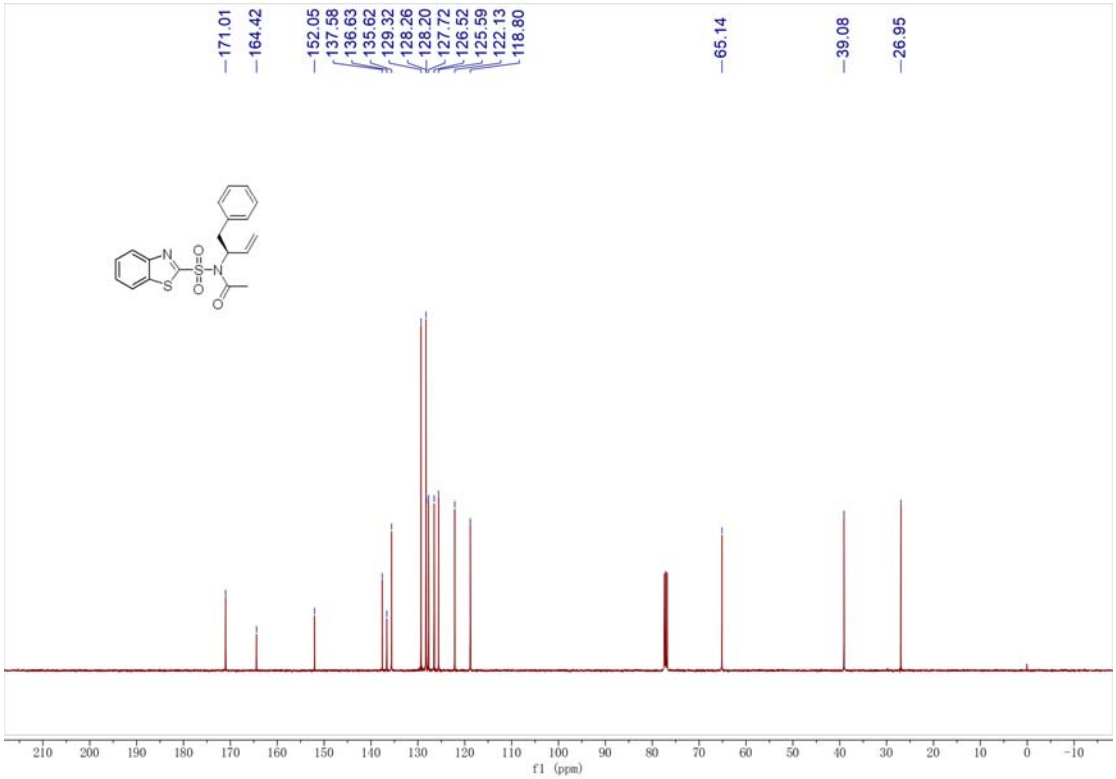
Tert-butyl (benzo[d]thiazol-2-ylsulfonyl)(but-3-en-2-yl)carbamate (1v')



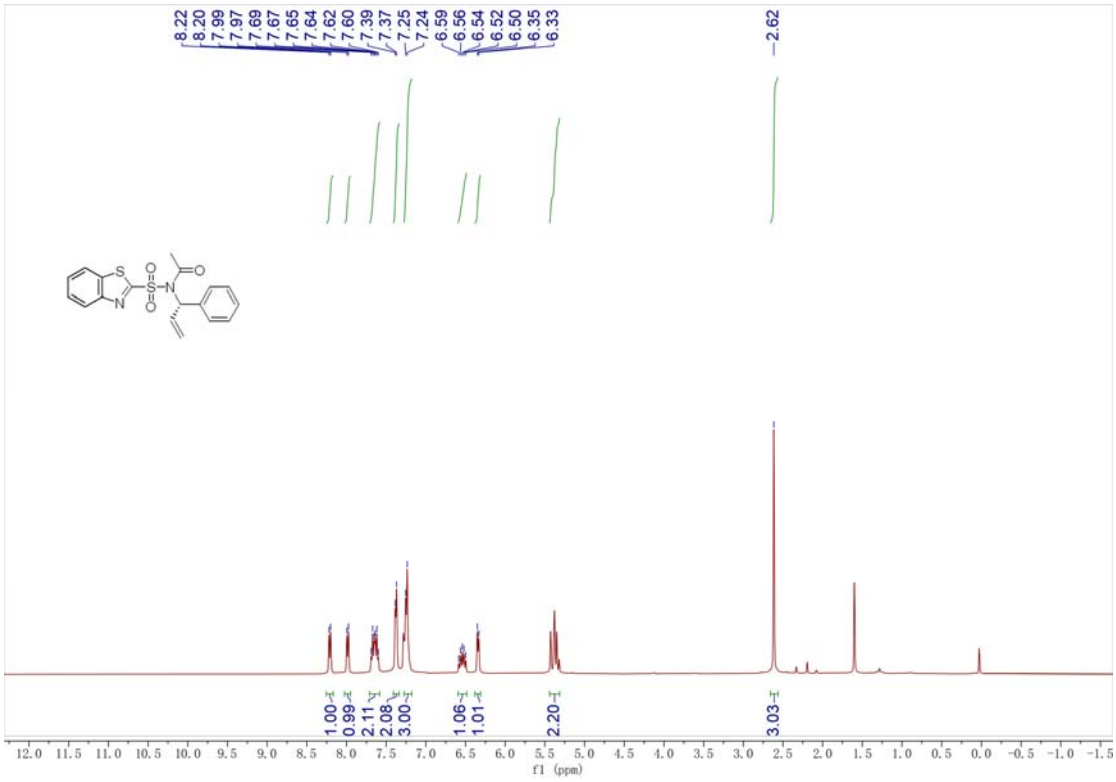


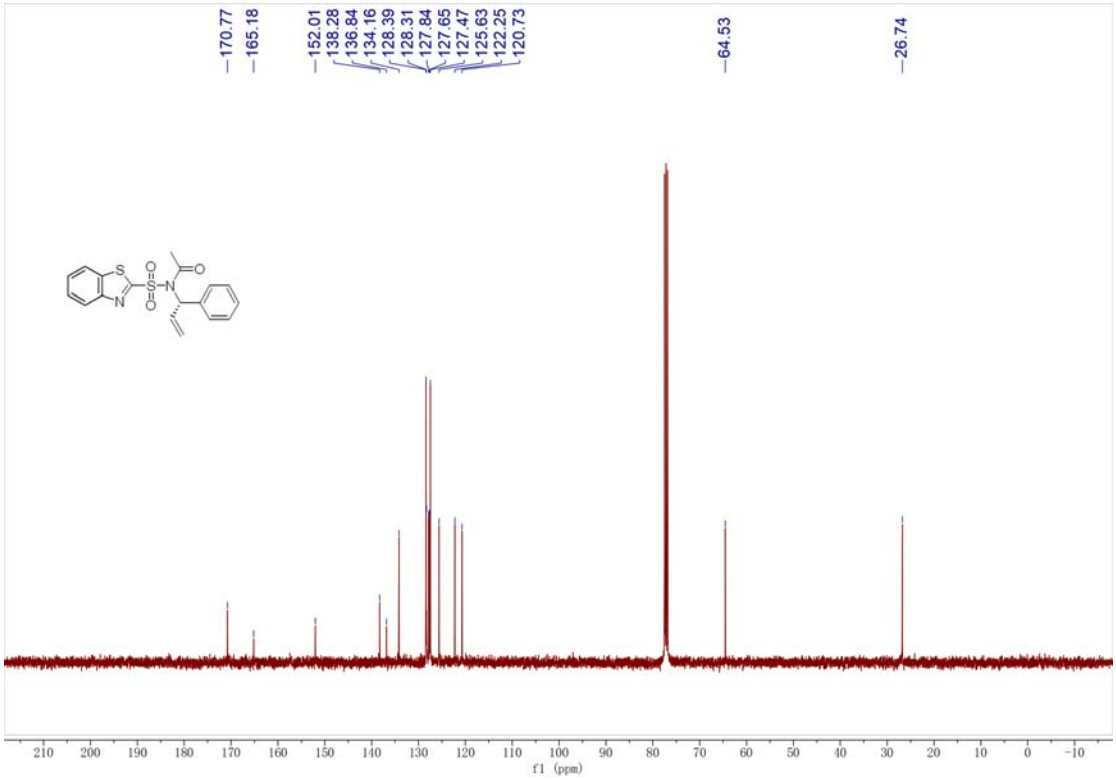
(S)-*N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(1-phenylbut-3-en-2-yl)acetamide (1w)



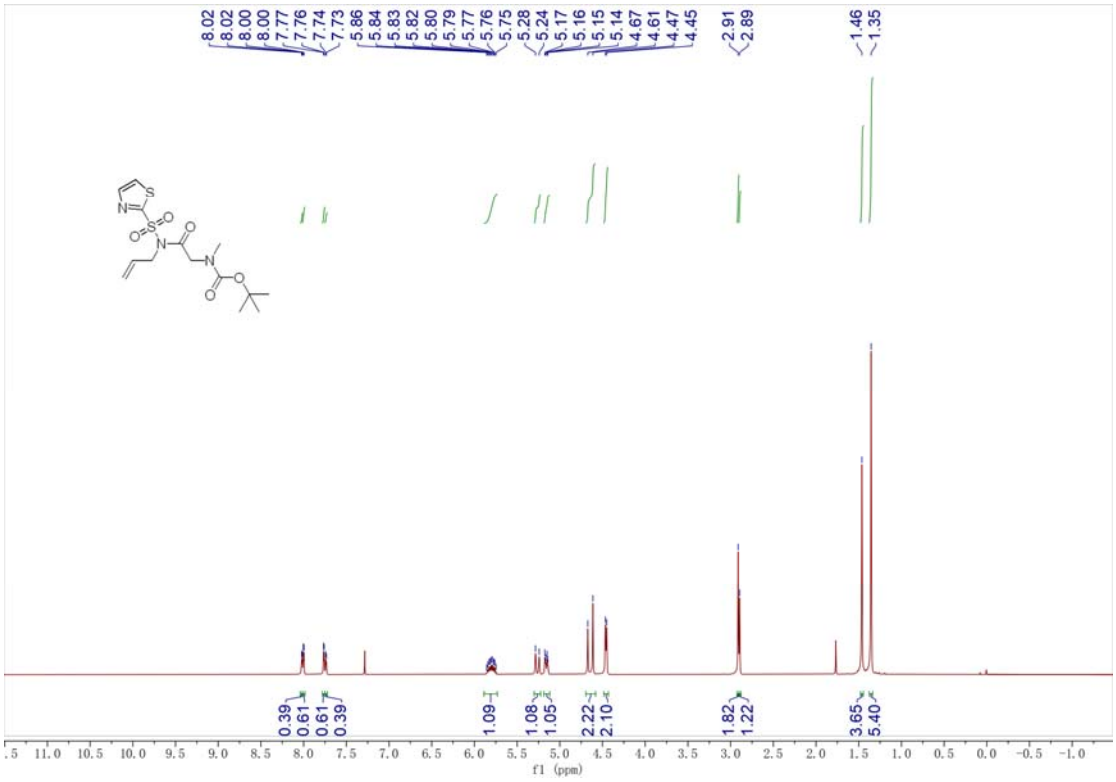


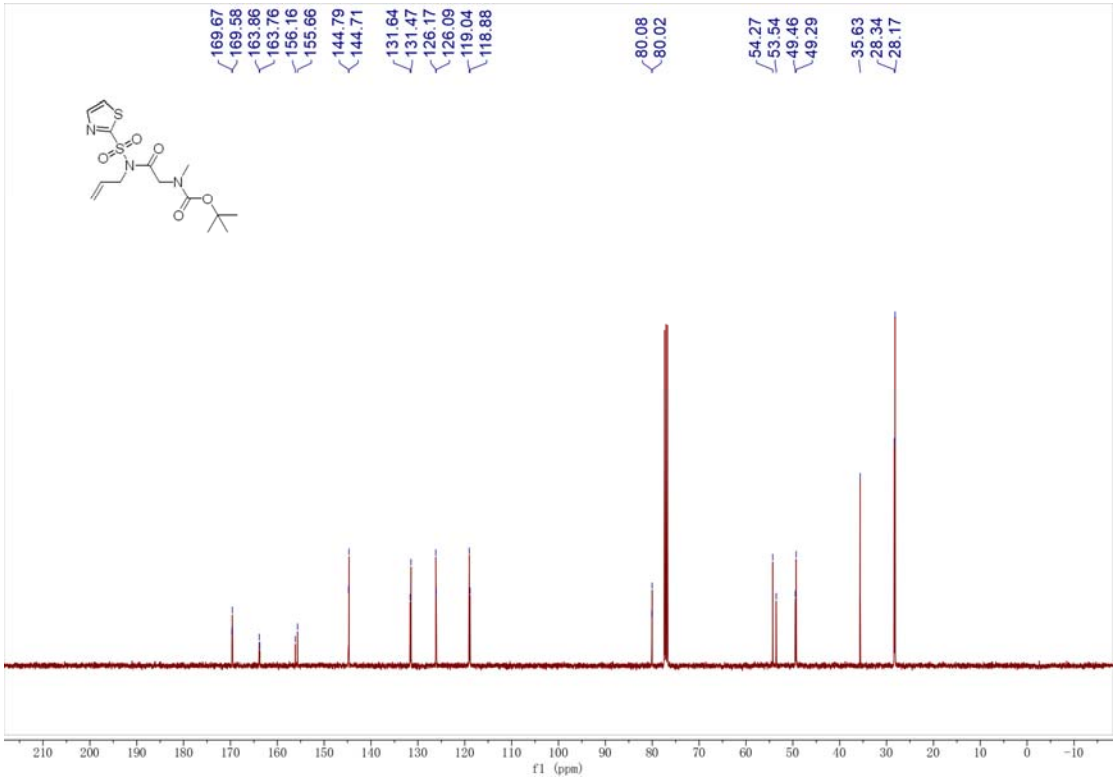
(S)-*N*-(benzo[d]thiazol-2-ylsulfonyl)-*N*-(1-phenylallyl)acetamide (1x)



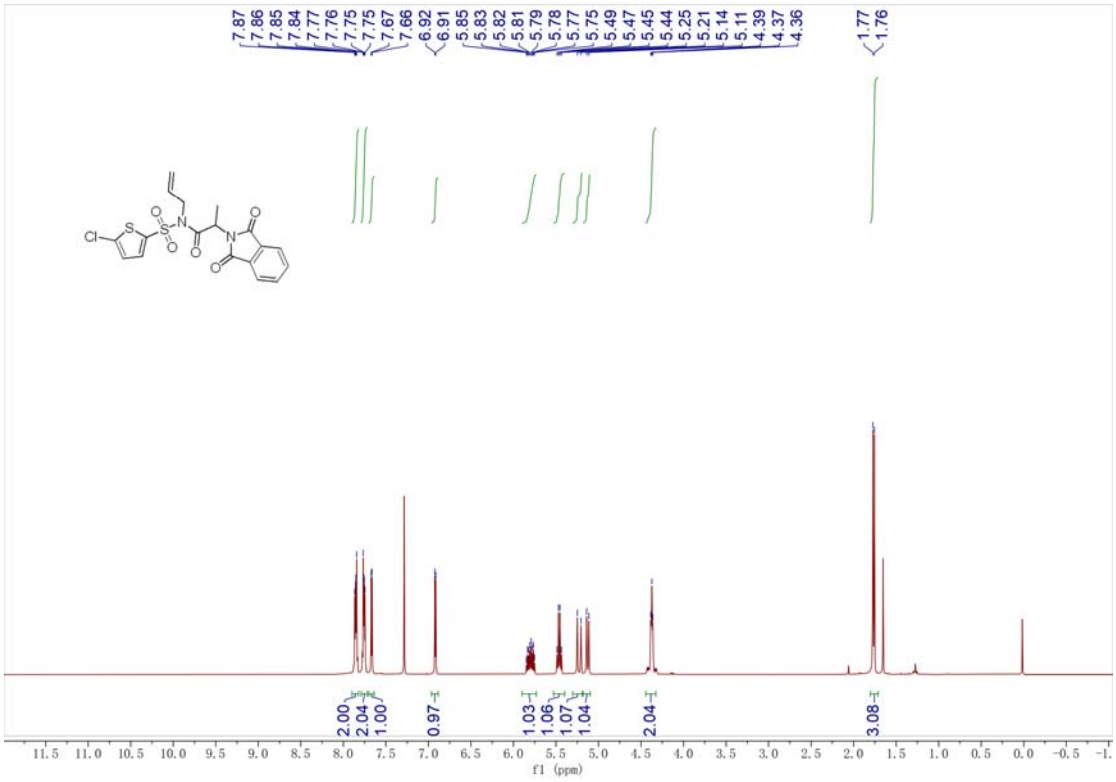


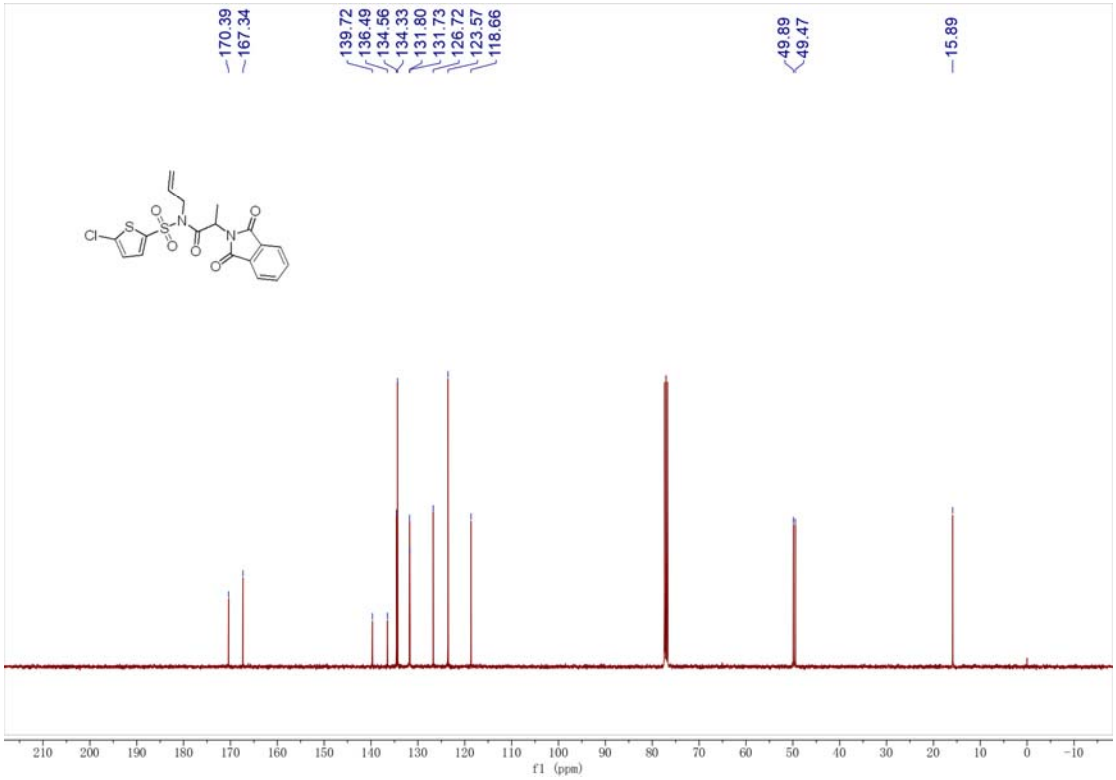
tert-butyl (2-(*N*-allylthiazole-2-sulfonamido)-2-oxoethyl)(methyl)carbamate (1y)



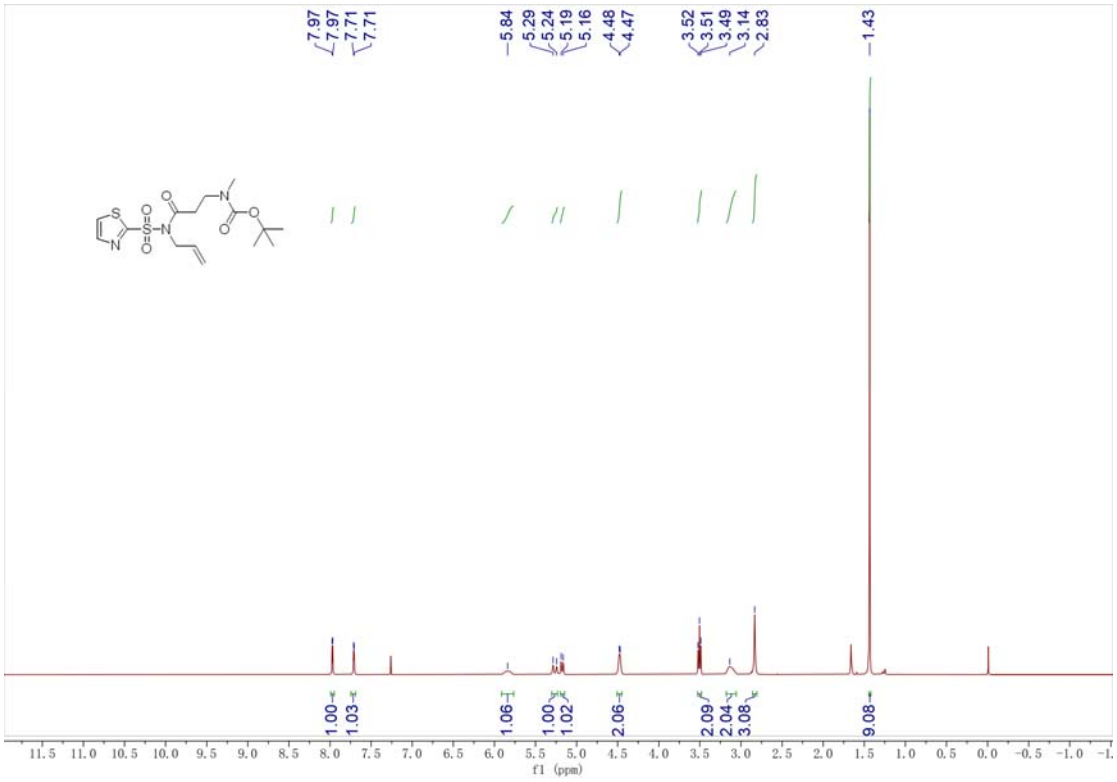


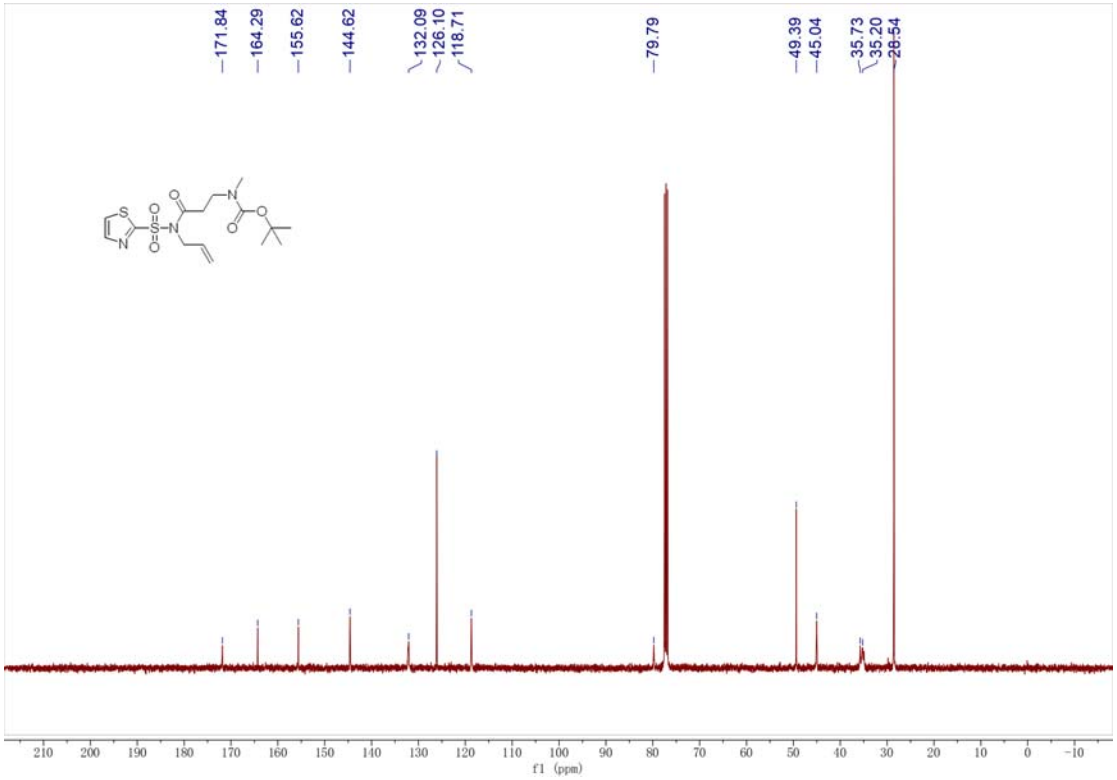
***N*-allyl-*N*-((5-chlorothiophen-2-yl)sulfonyl)-2-(1,3-dioxoisoindolin-2-yl)propenamide (1z)**



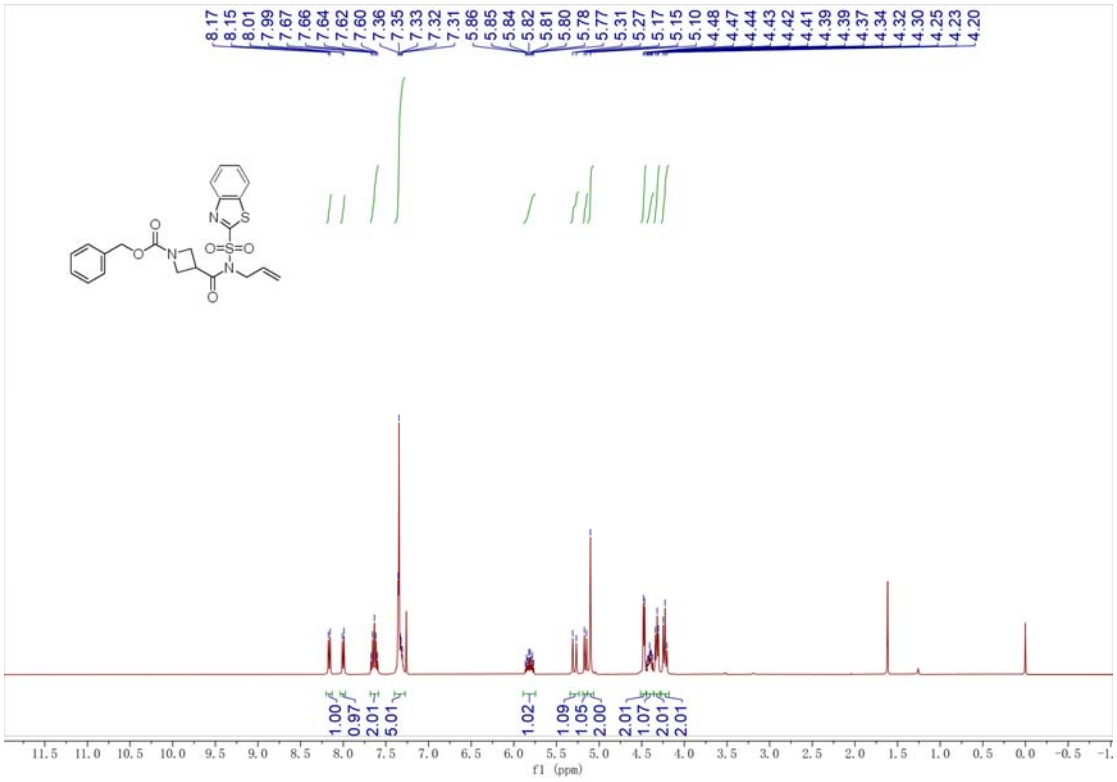


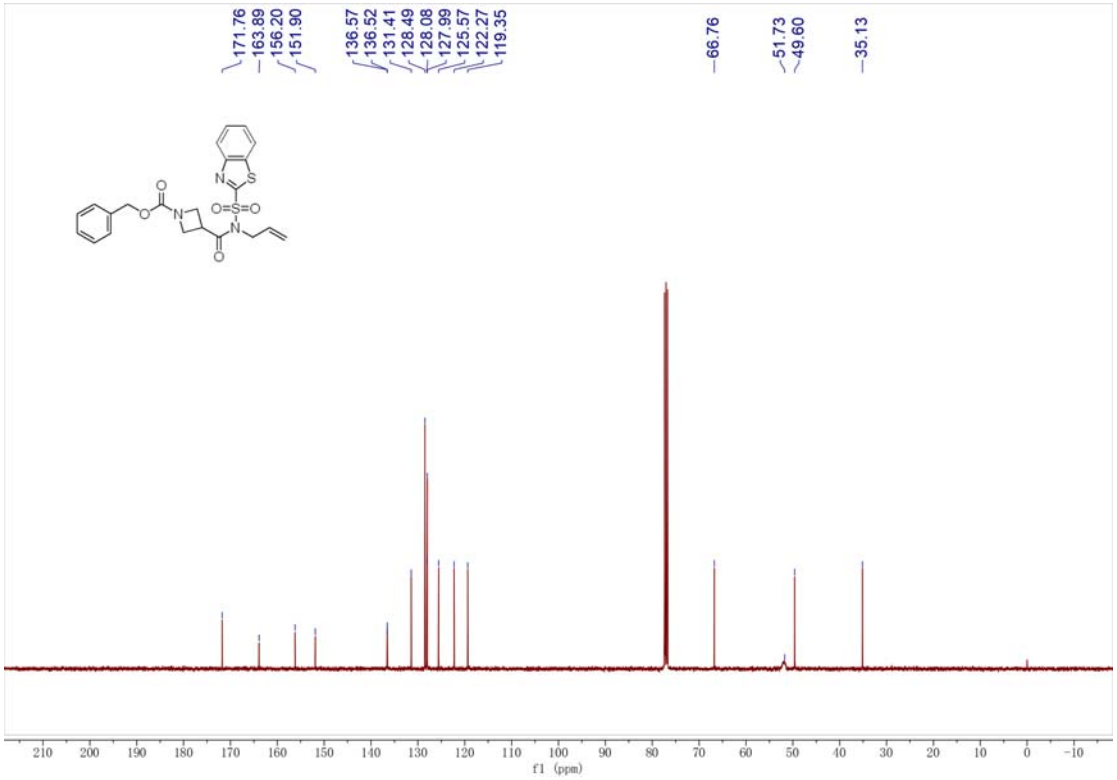
tert-butyl (3-(*N*-allylthiazole-2-sulfonamido)-3-oxopropyl)(methyl)carbamate (1z1)



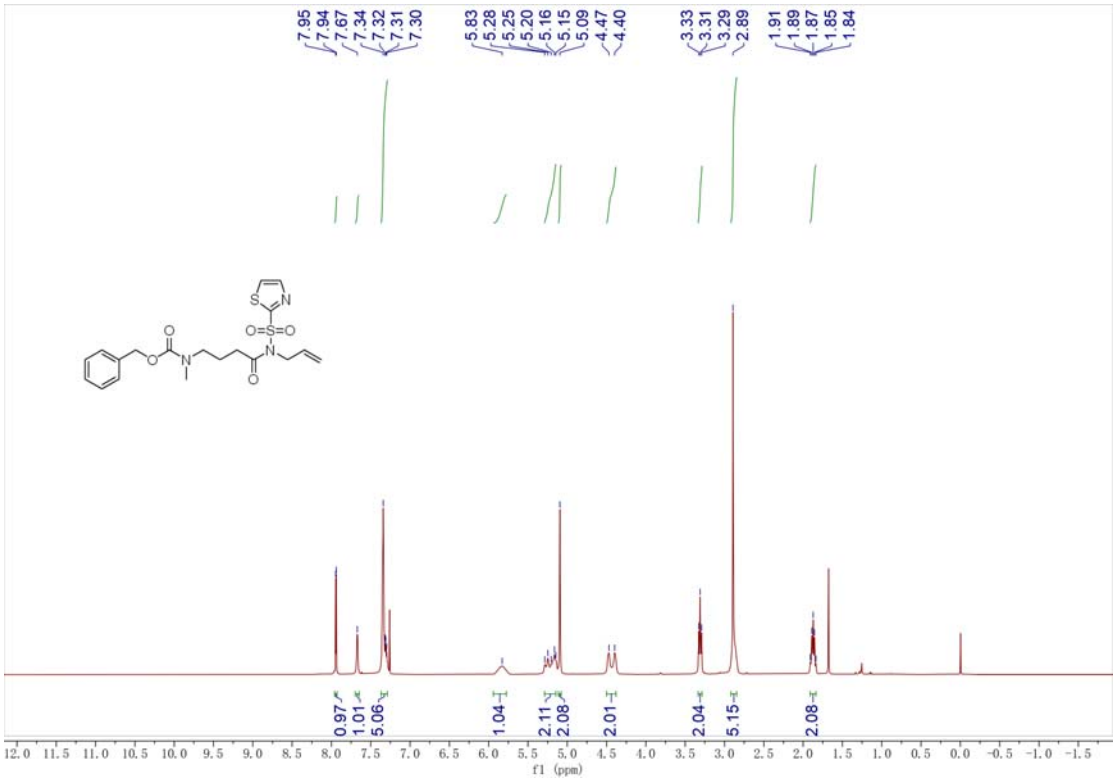


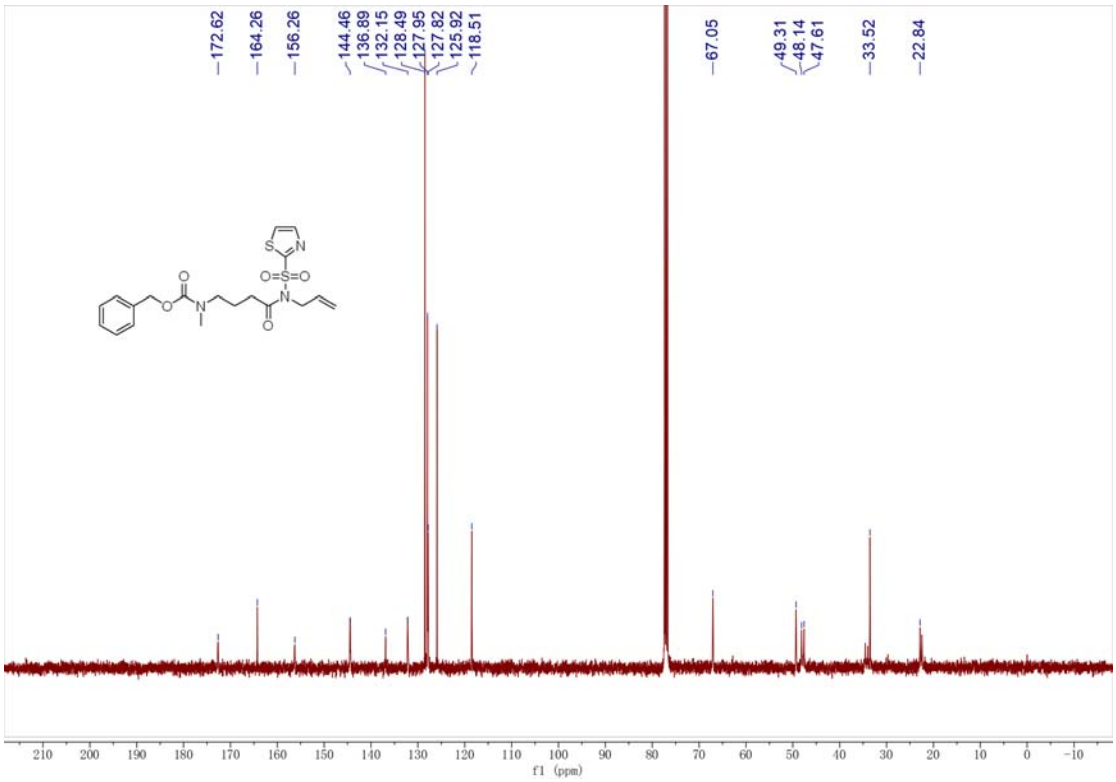
benzyl 3-(allyl(benzo[d]thiazol-2-ylsulfonyl)carbamoyl)azetidine-1-carboxylate (1z2)



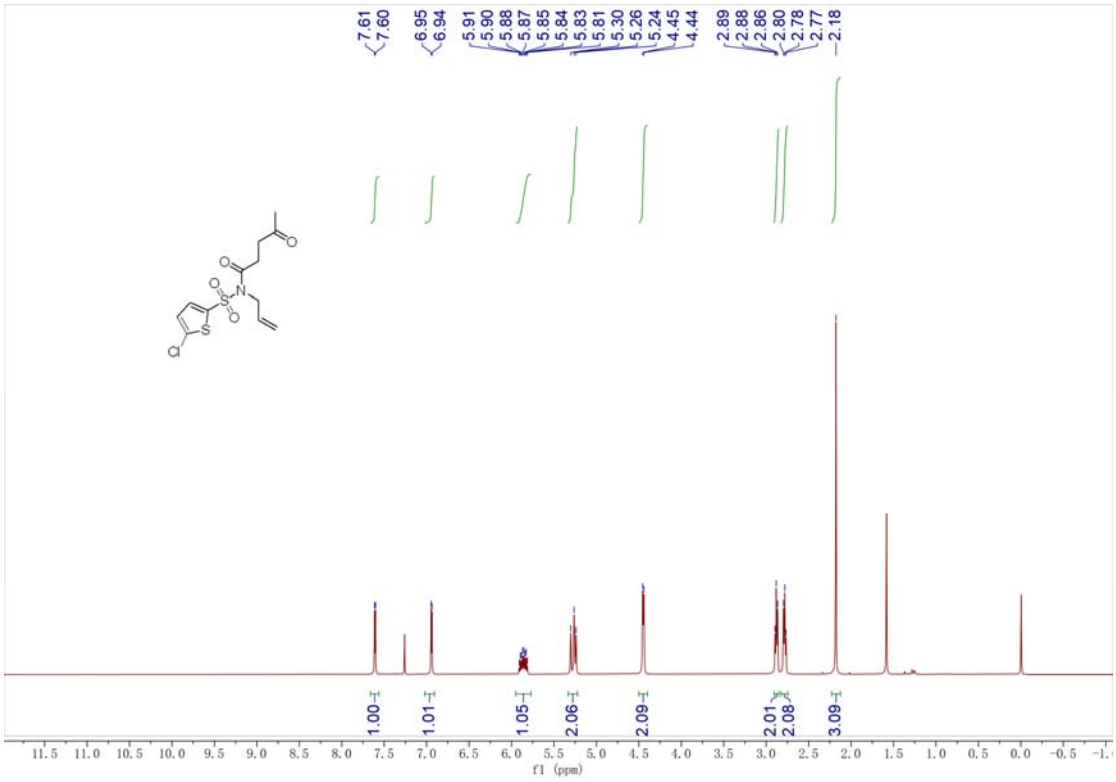


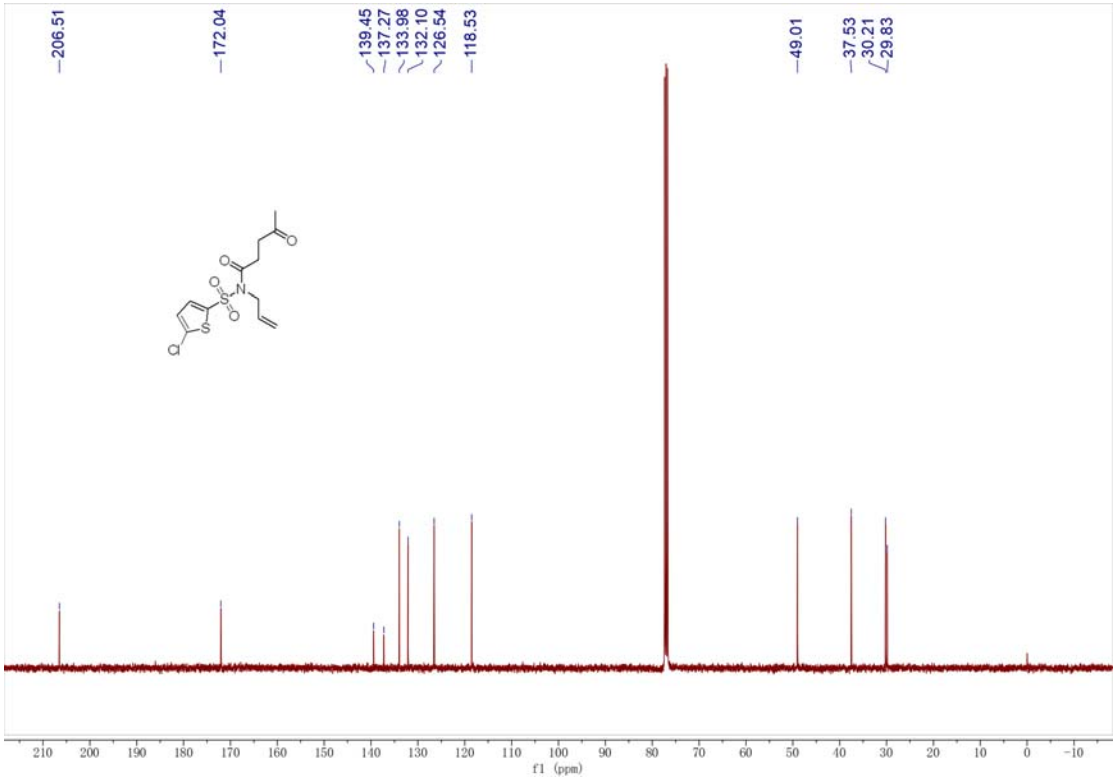
benzyl (4-(*N*-allylthiazole-2-sulfonamido)-4-oxobutyl)(methyl)carbamate (1z3)



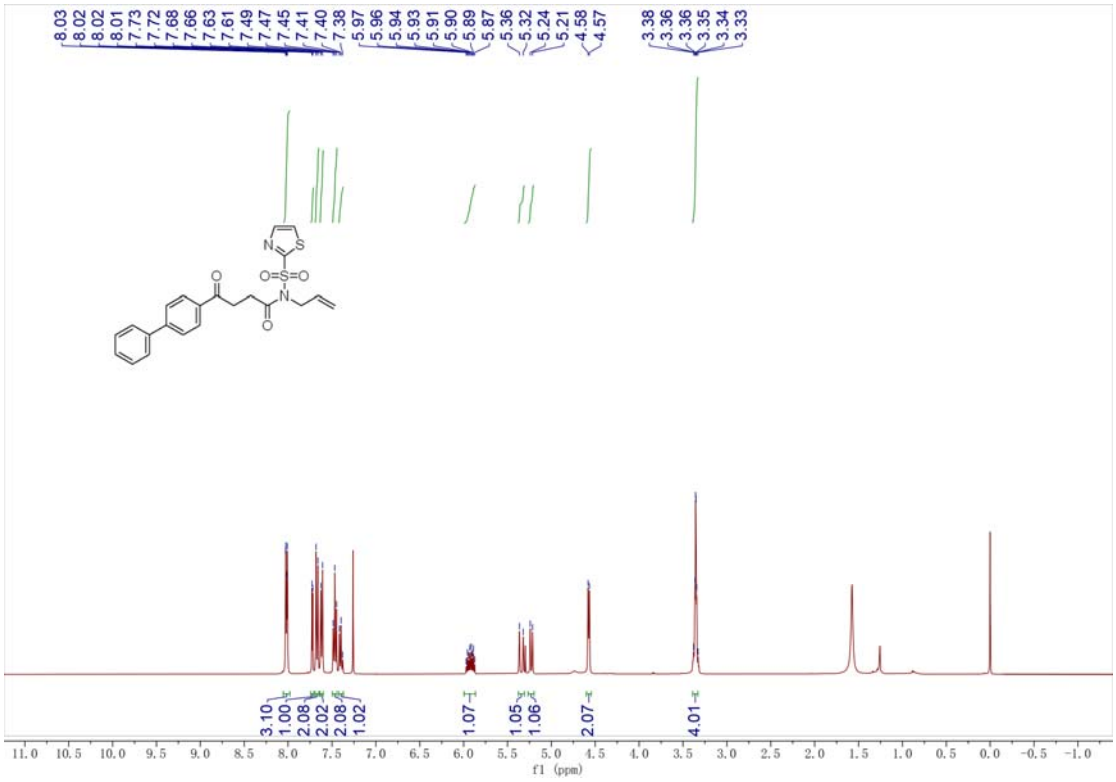


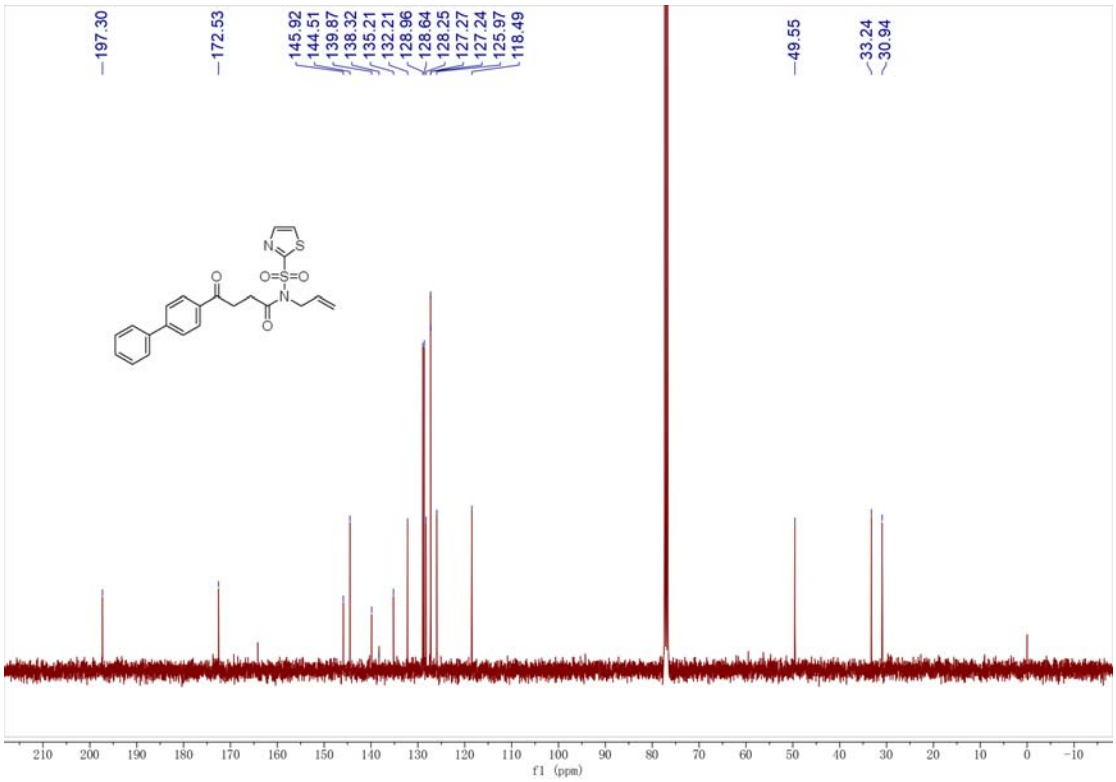
***N*-allyl-*N*-((5-chlorothiophen-2-yl)sulfonyl)-4-oxopentanamide (1z4)**



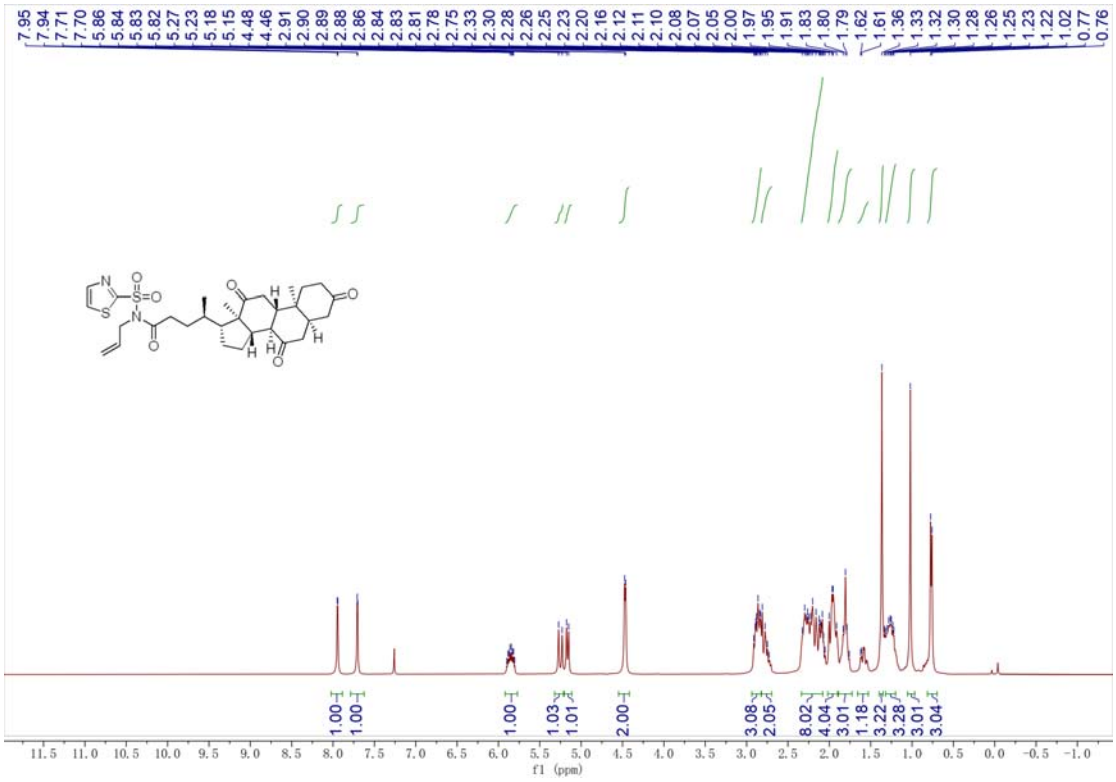


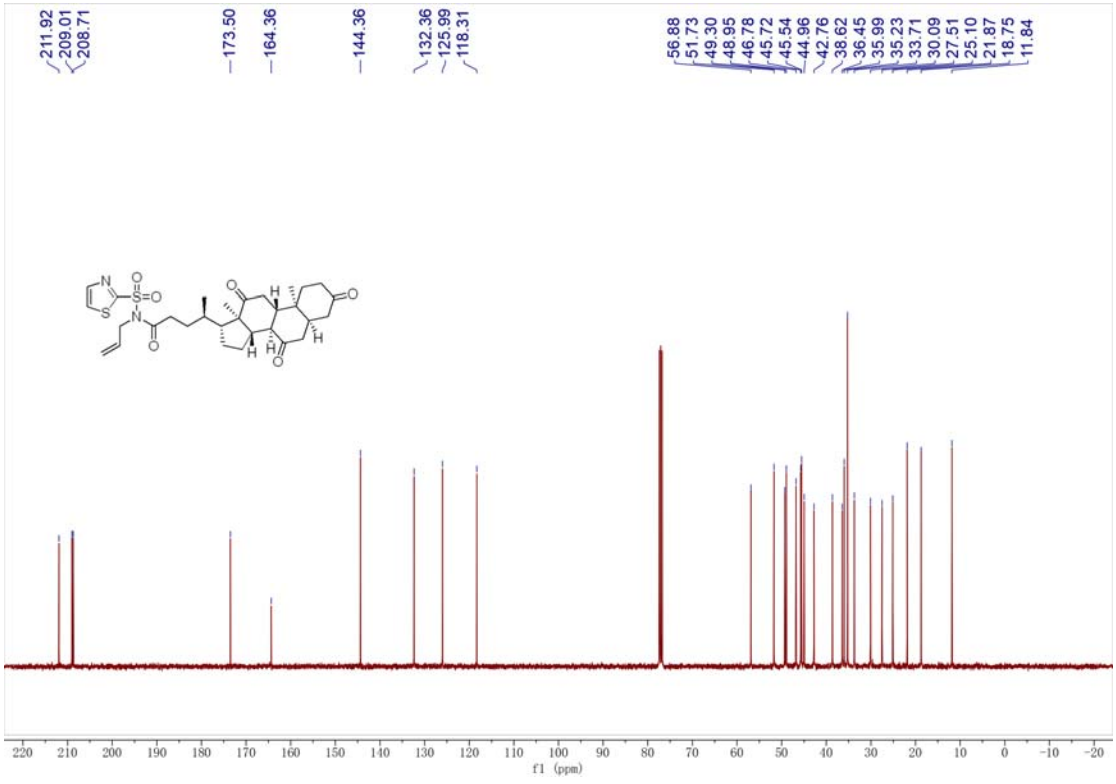
***N*-allyl-*N*-((5-chlorothiophen-2-yl)sulfonyl)-4-oxopentanamide (1z5)**



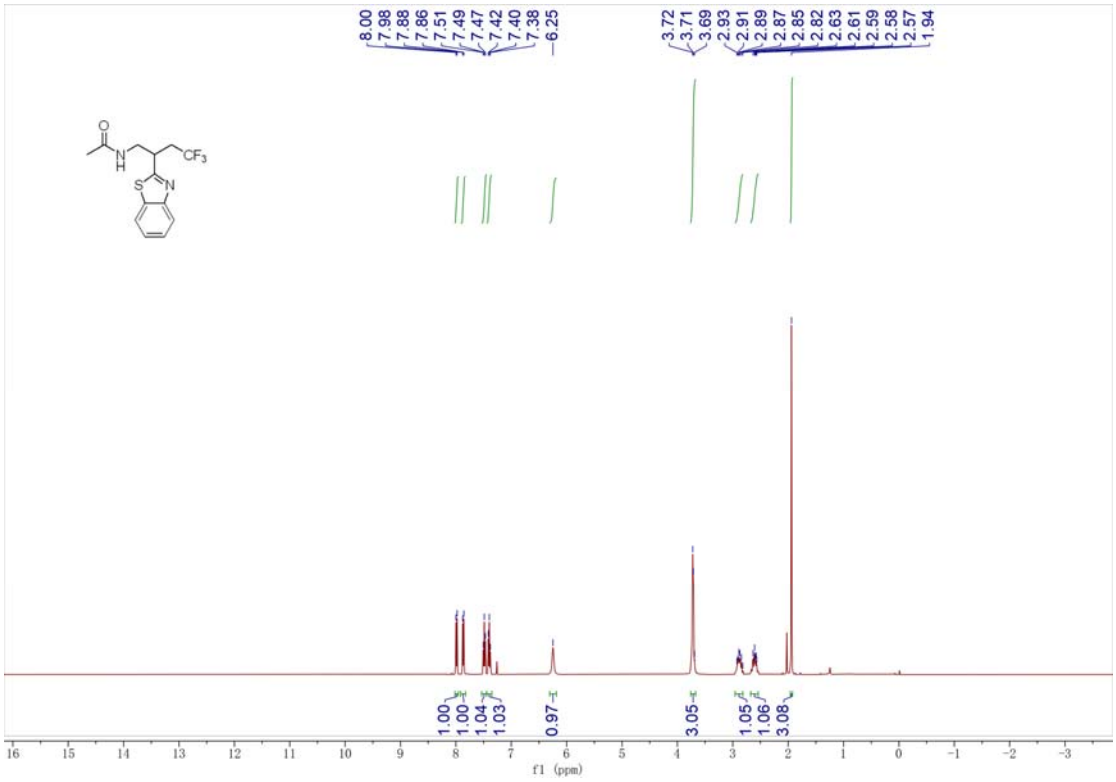


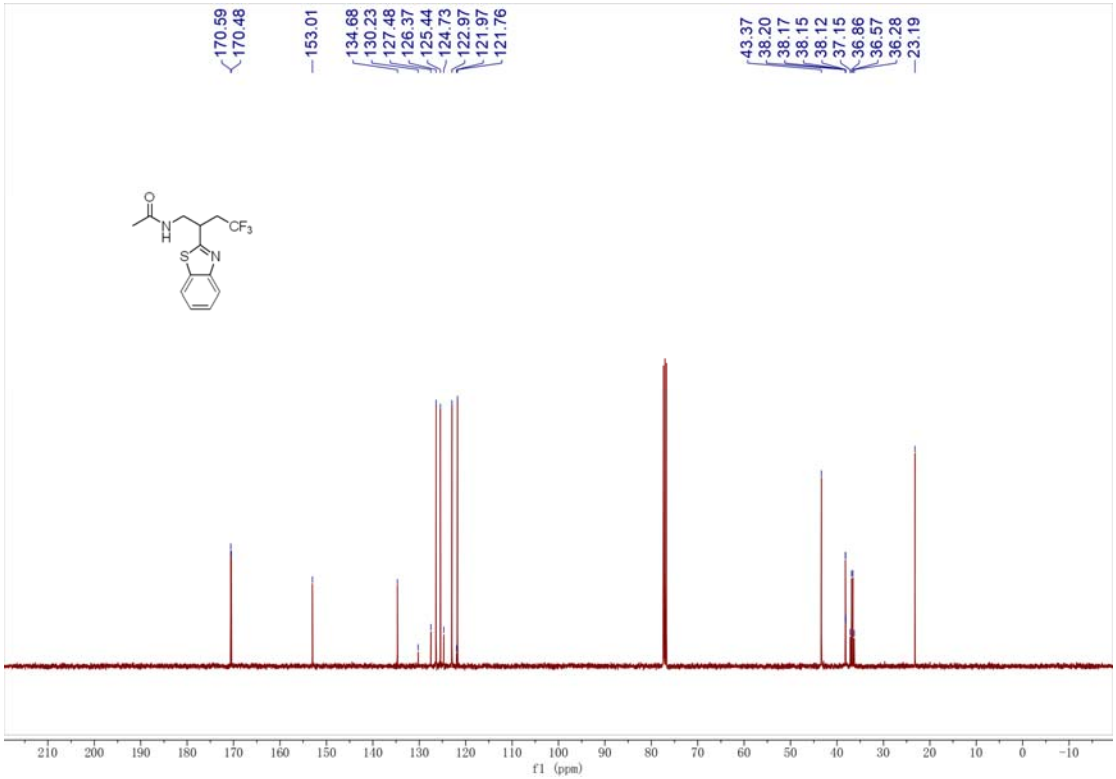
(R)-*N*-allyl-4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)-*N*-(thiazol-2-ylsulfonyl)pentanamide (1z6)

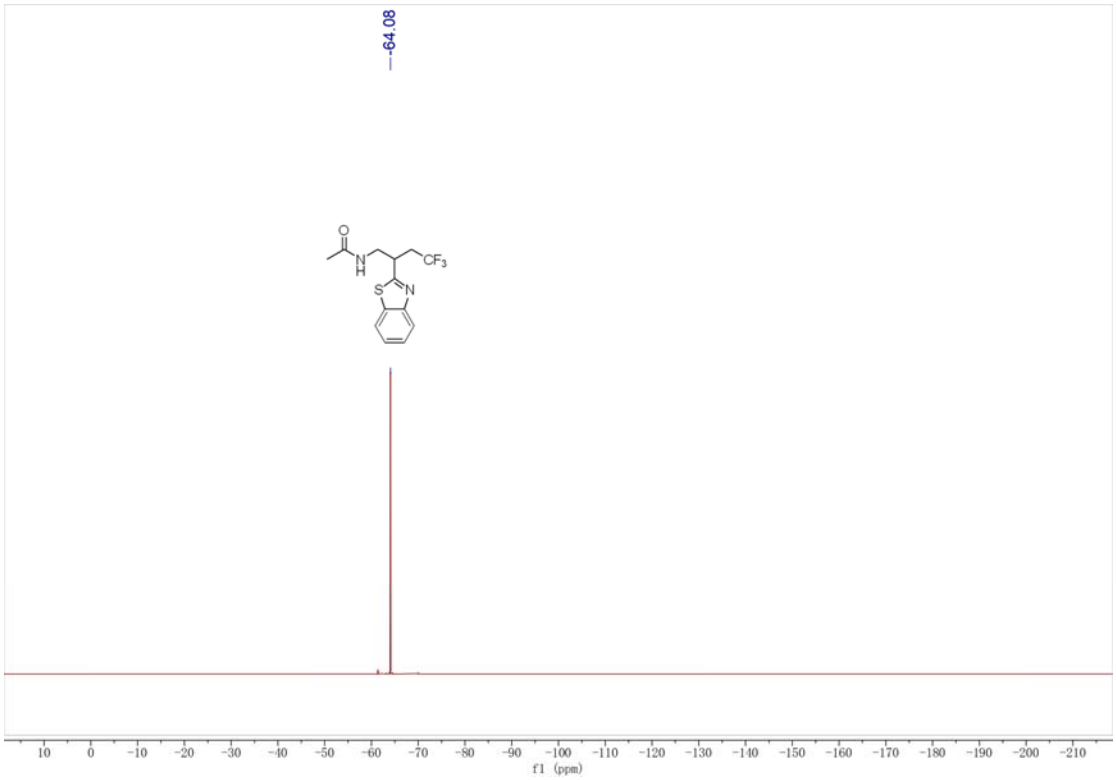




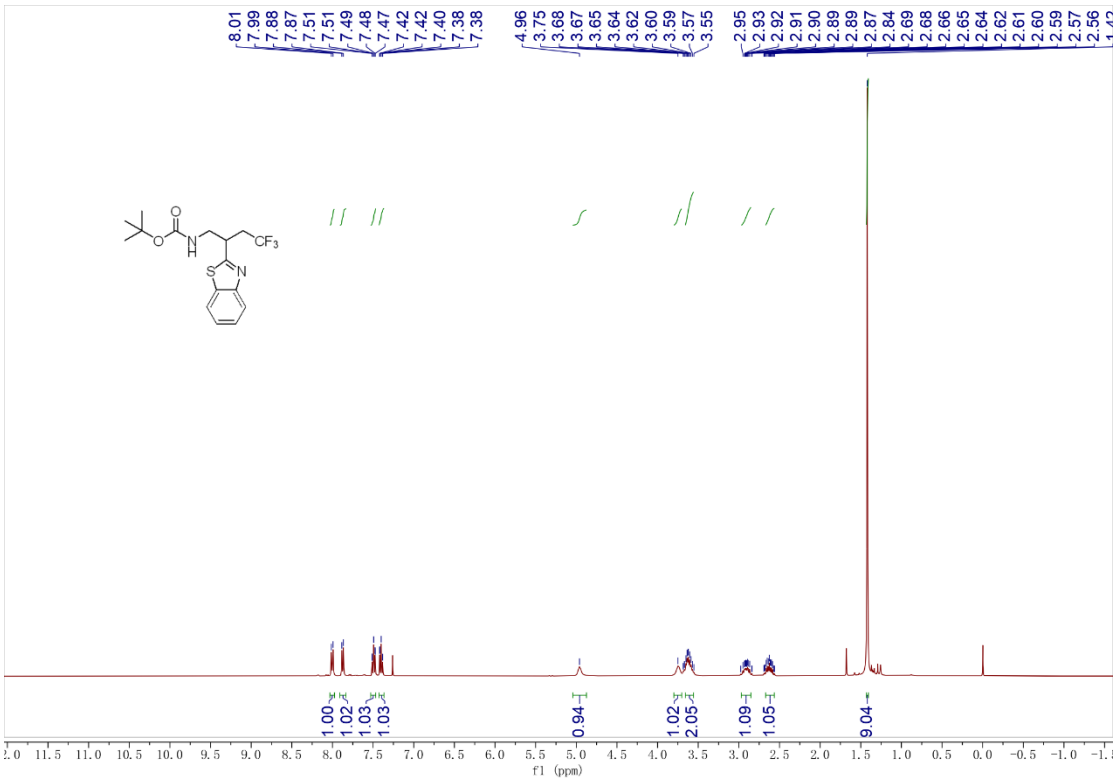
***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)acetamide (3a)**

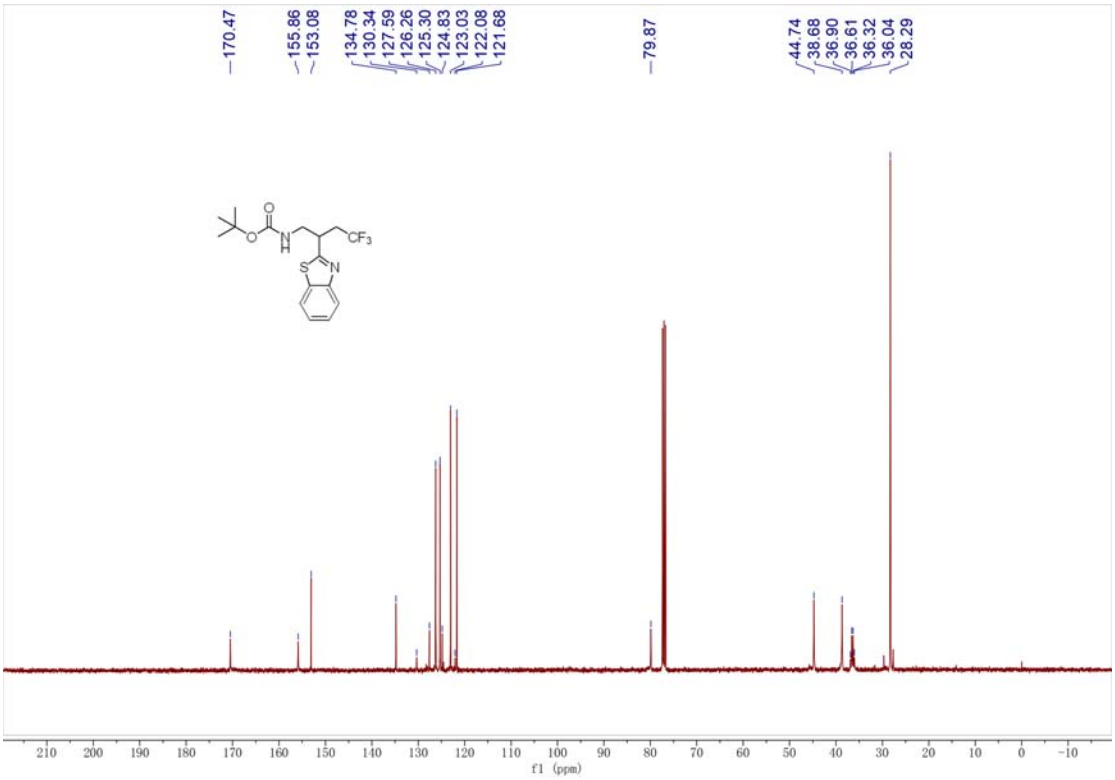


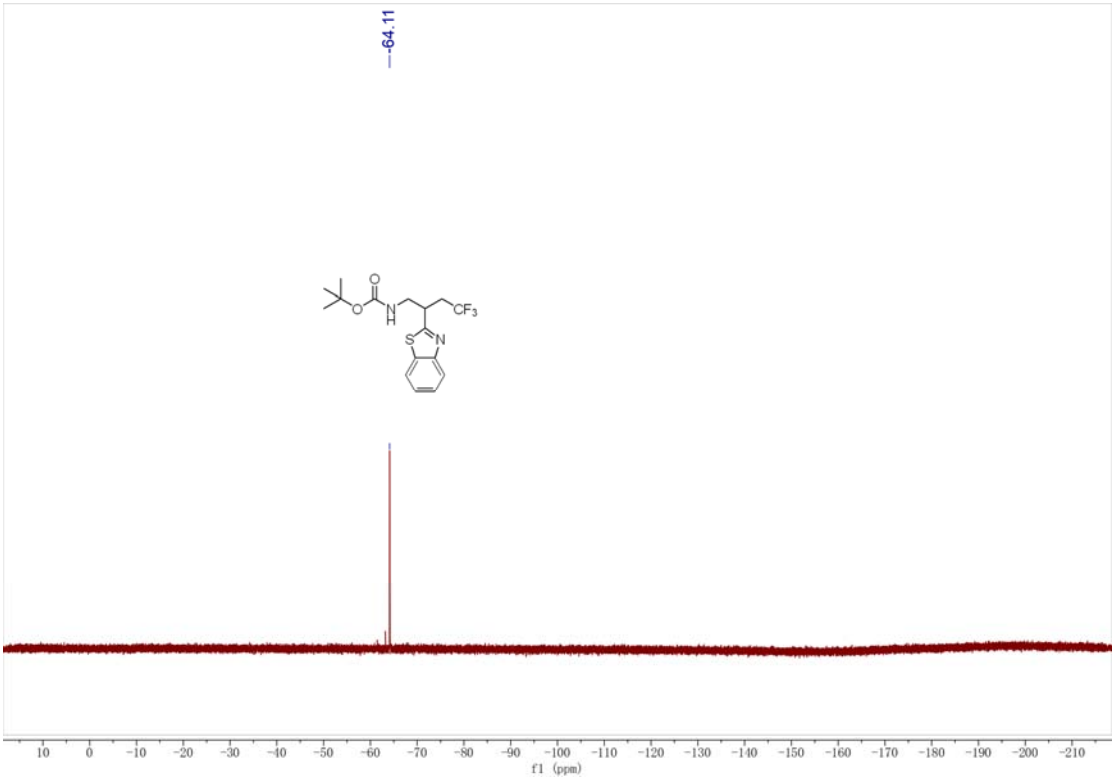




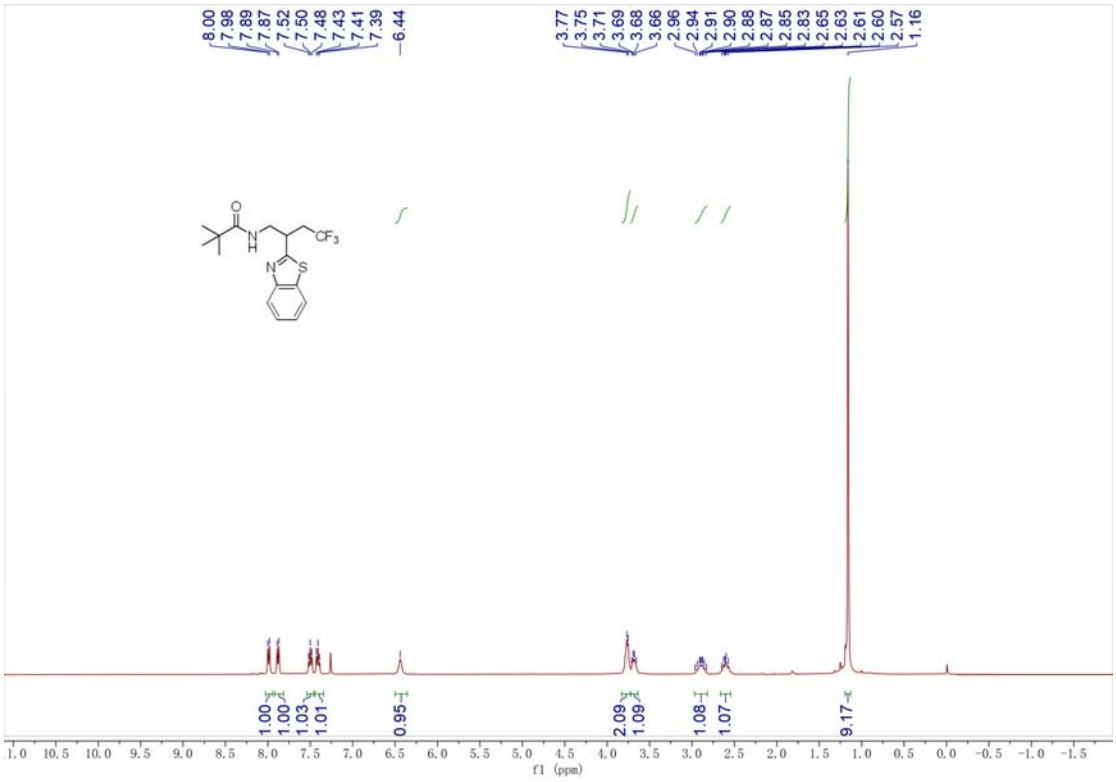
tert-butyl (2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)carbamate (3b)

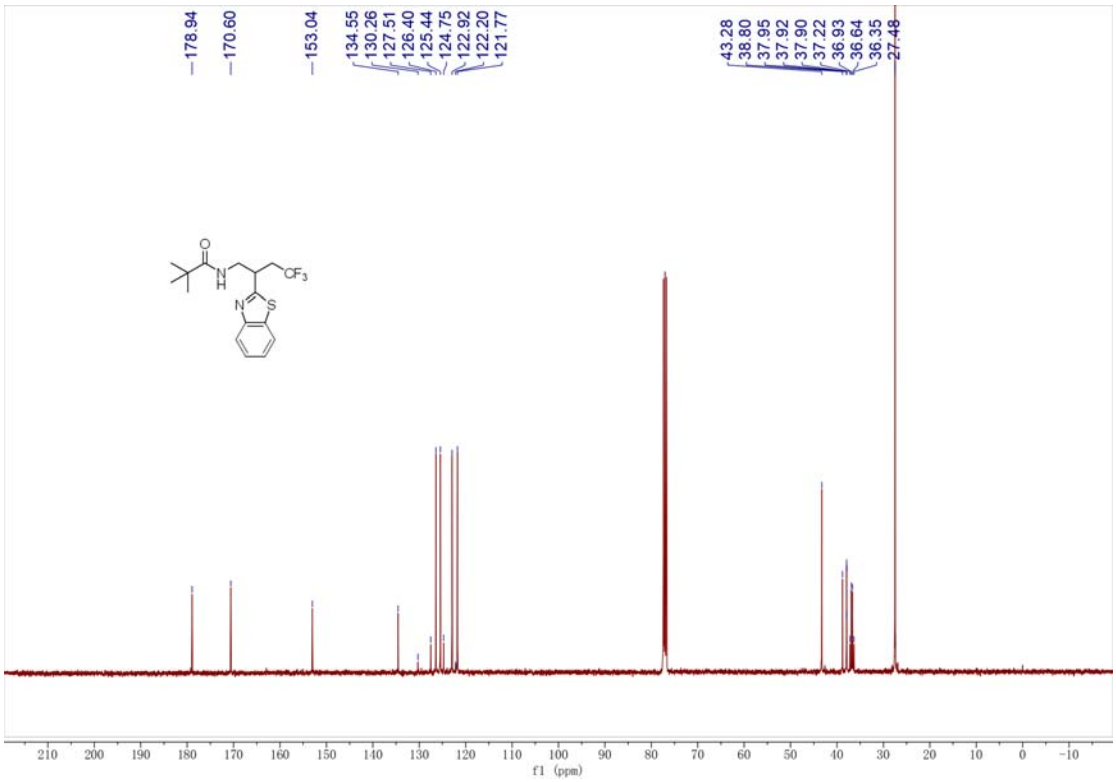


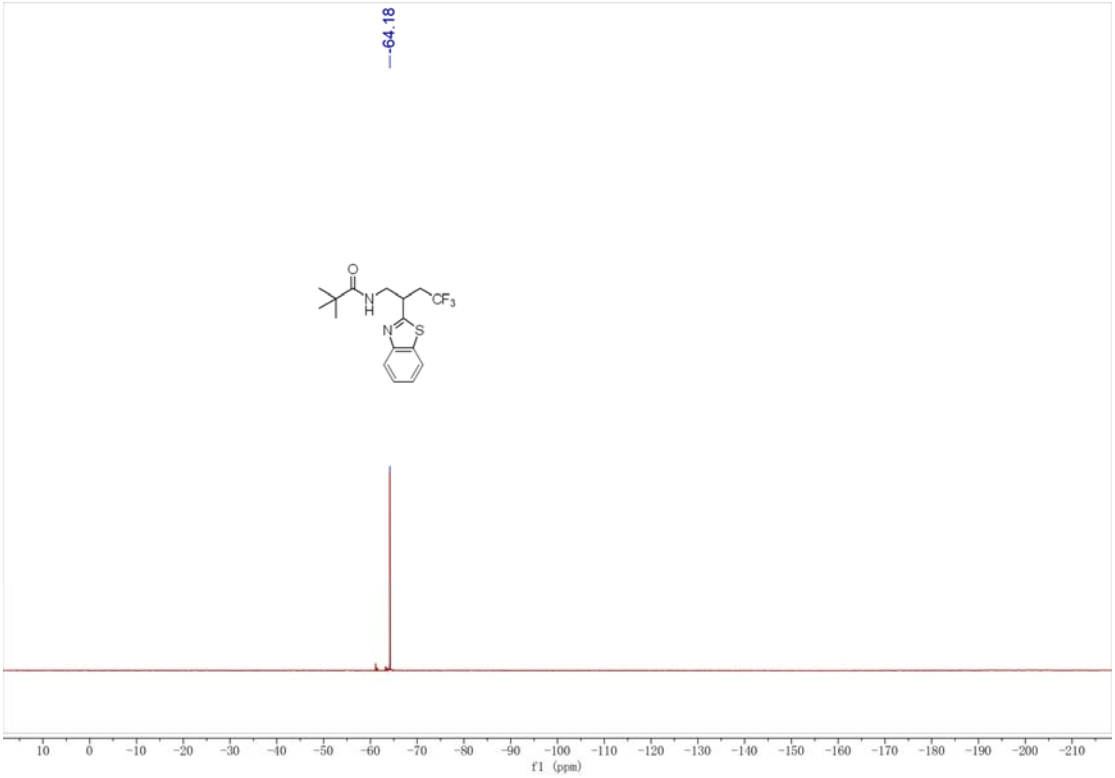

170.47
155.86
153.08
134.78
130.34
127.59
126.26
125.30
124.83
123.03
122.08
121.68
79.87
44.74
38.68
36.90
36.61
36.32
36.04
28.29
CF3
S
N
O
H
f1 (ppm)


-64.11
CF3
S
N
O
H
f1 (ppm)

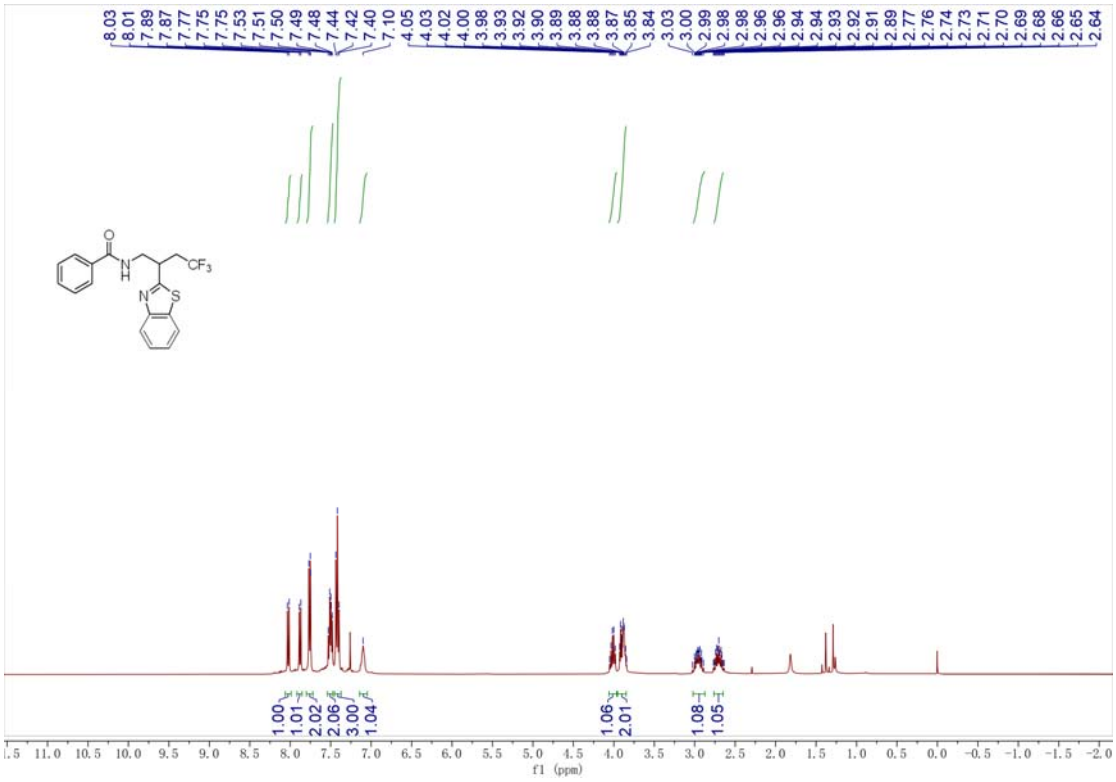
***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)pivalamide (3c)**

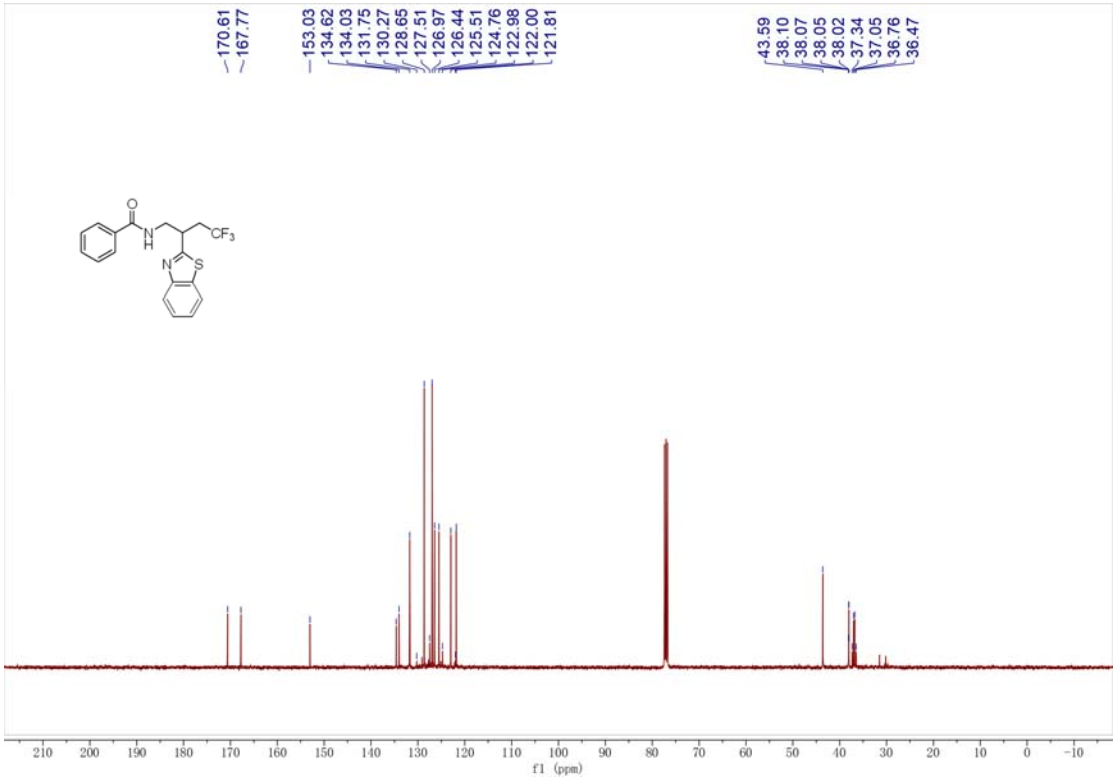


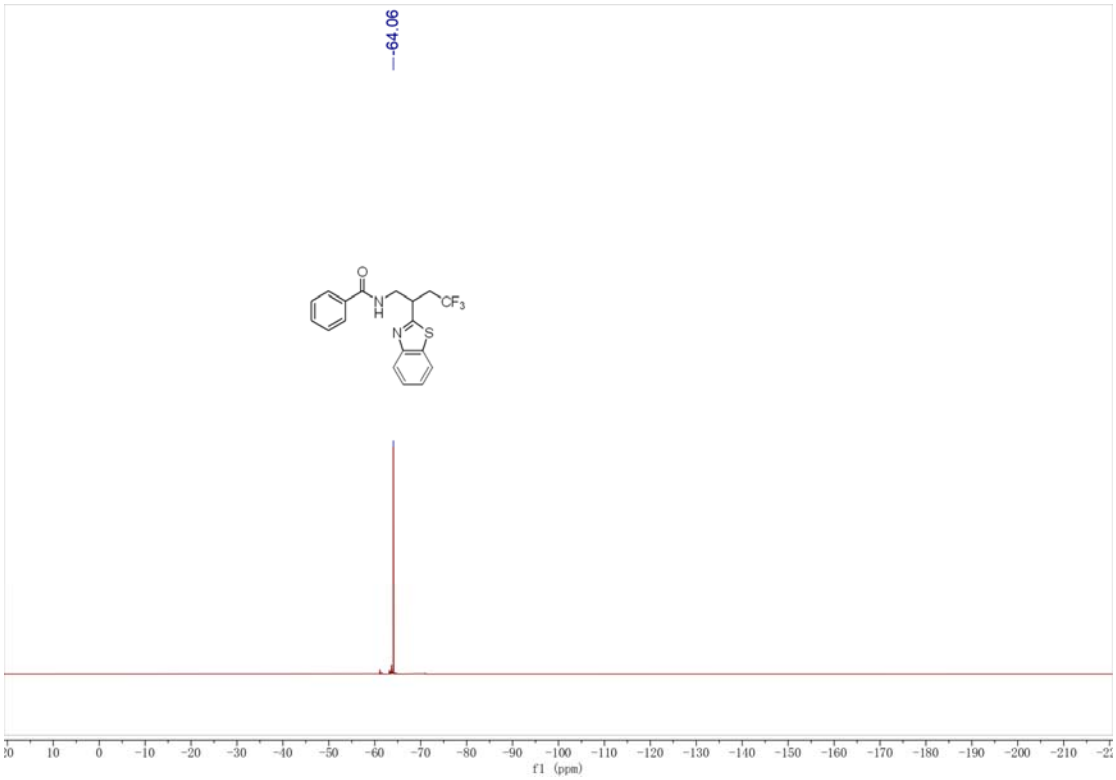



-64.18
O
N
H
CF3
N
S
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

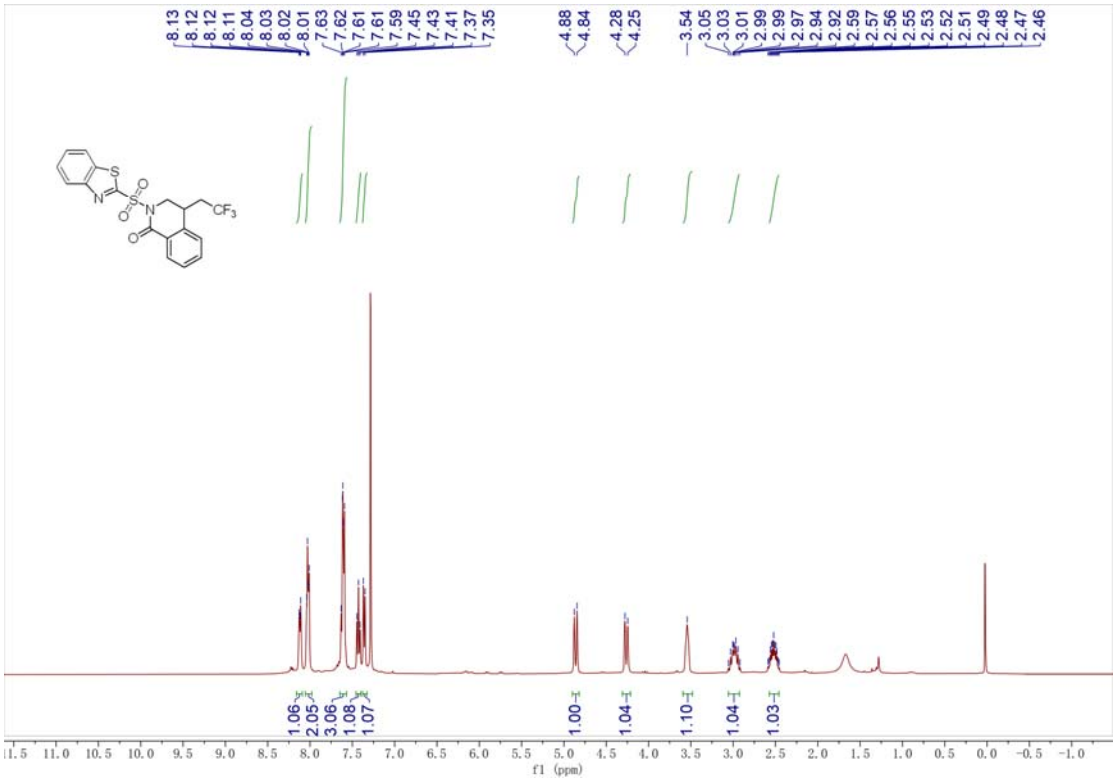
***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)benzamide (3d)**

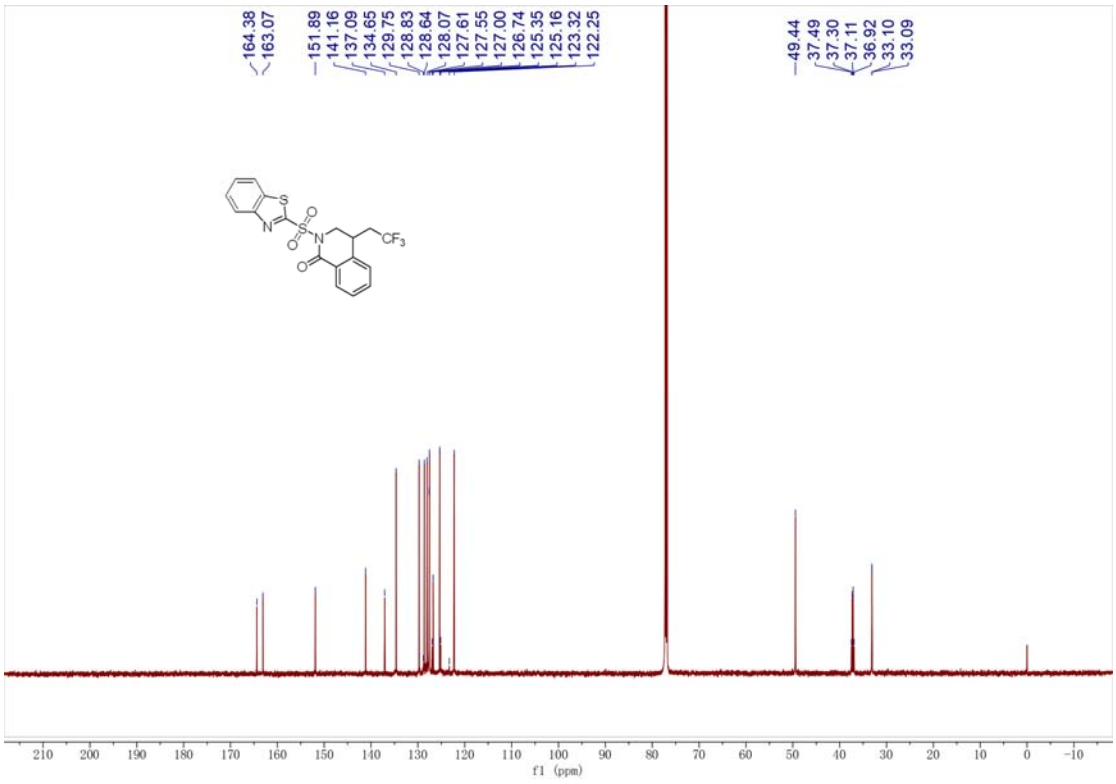


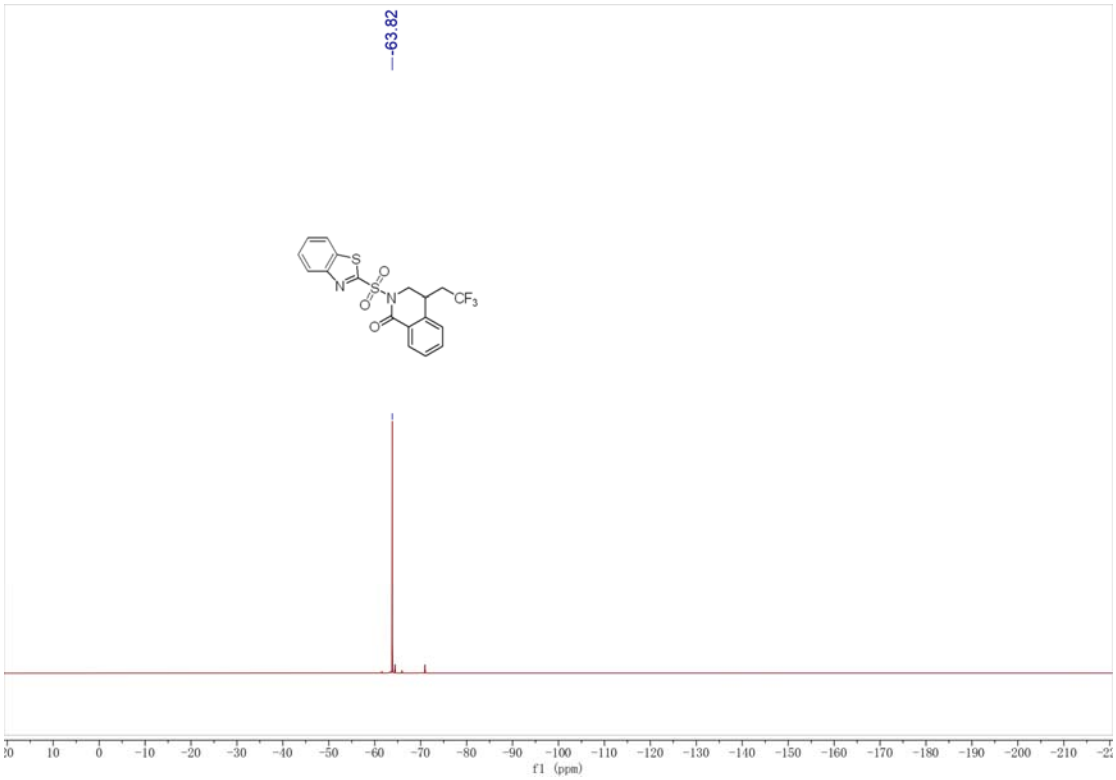



-64.06
O
N
H
CF3
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

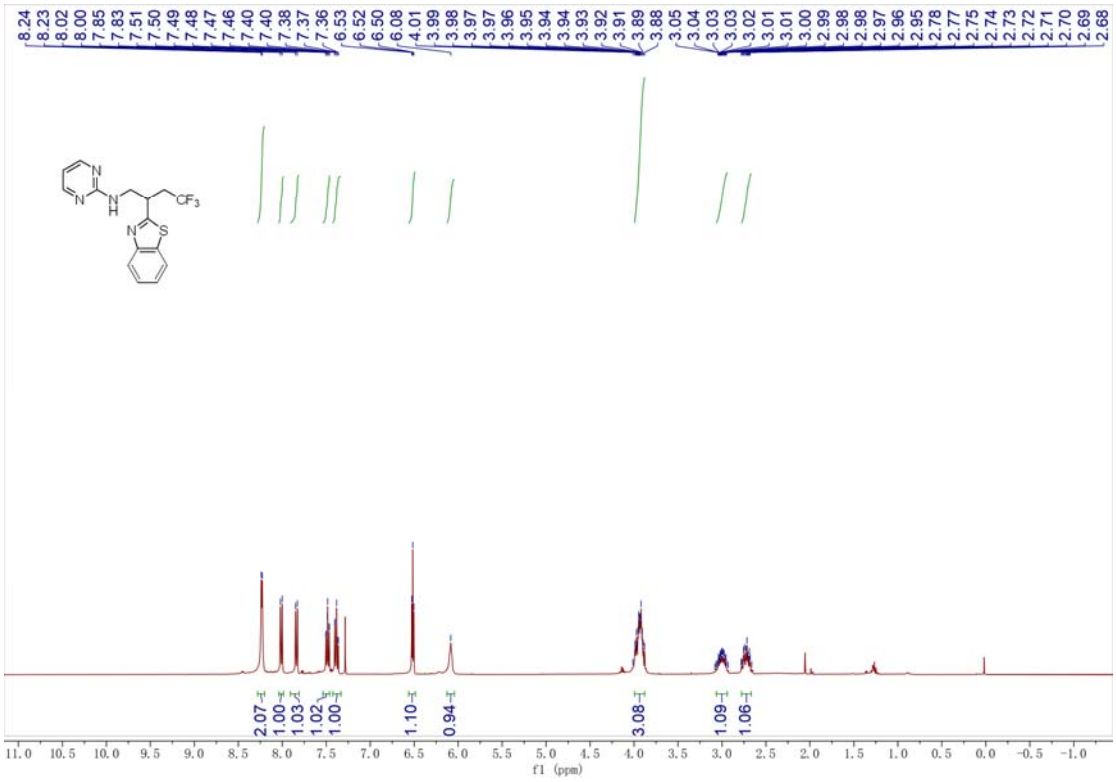
2-(benzo[d]thiazol-2-ylsulfonyl)-4-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinolin-1(2H)-one（3d'）

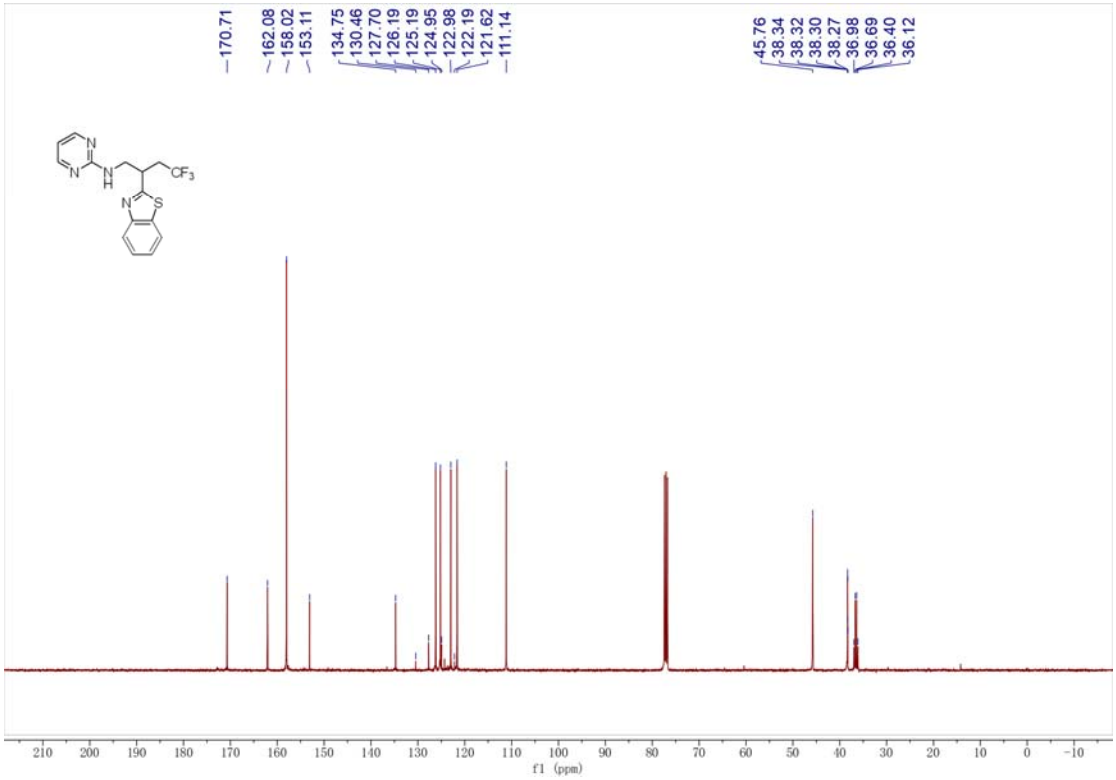


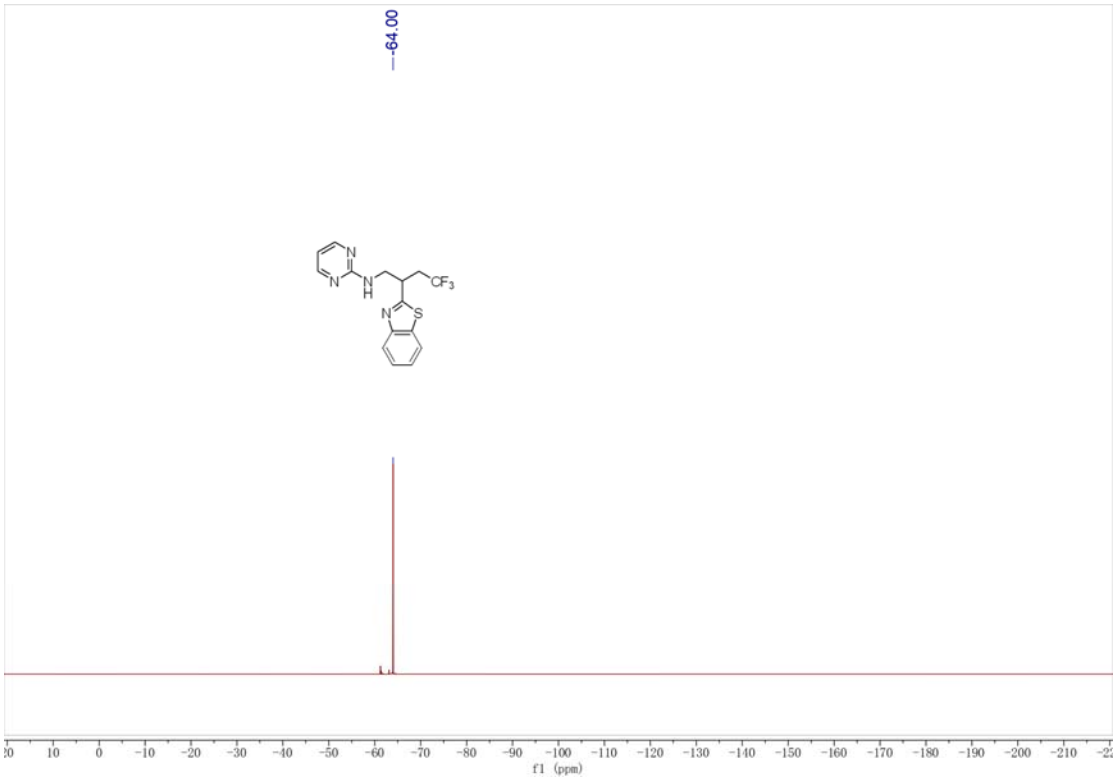



-63.82
S
N
O
O
S
N
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

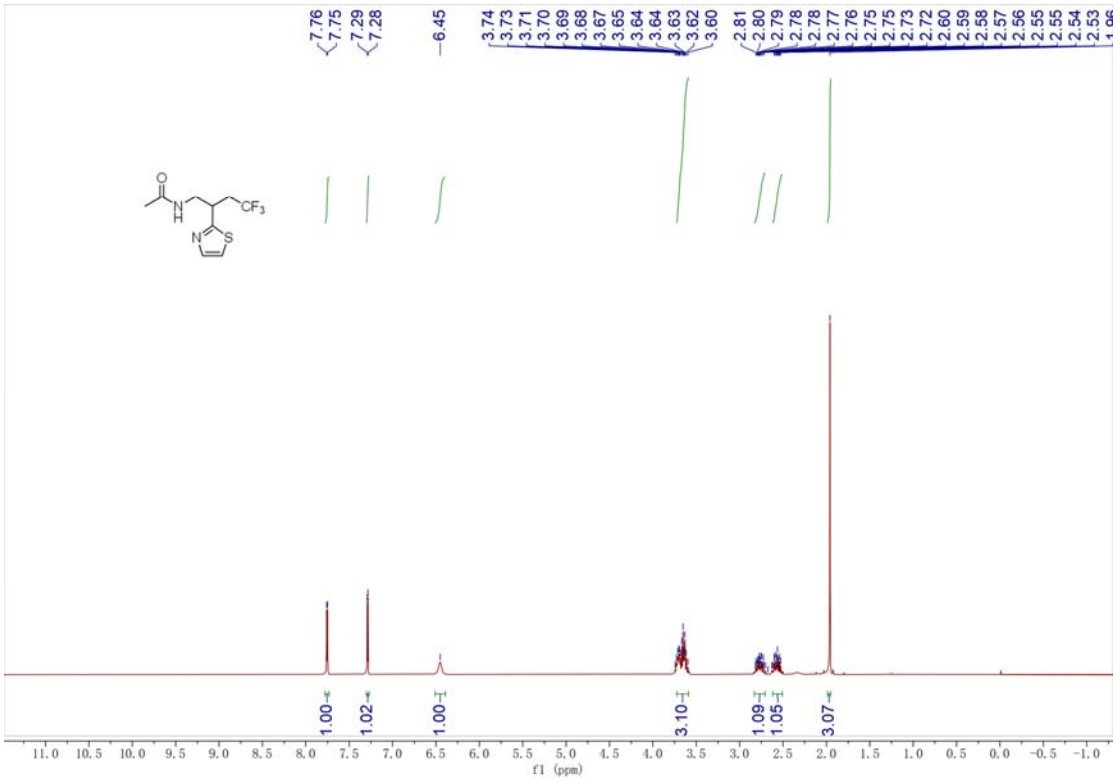
***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-*trifluorobutyl*)pyrimidin-2-amine (3e)**

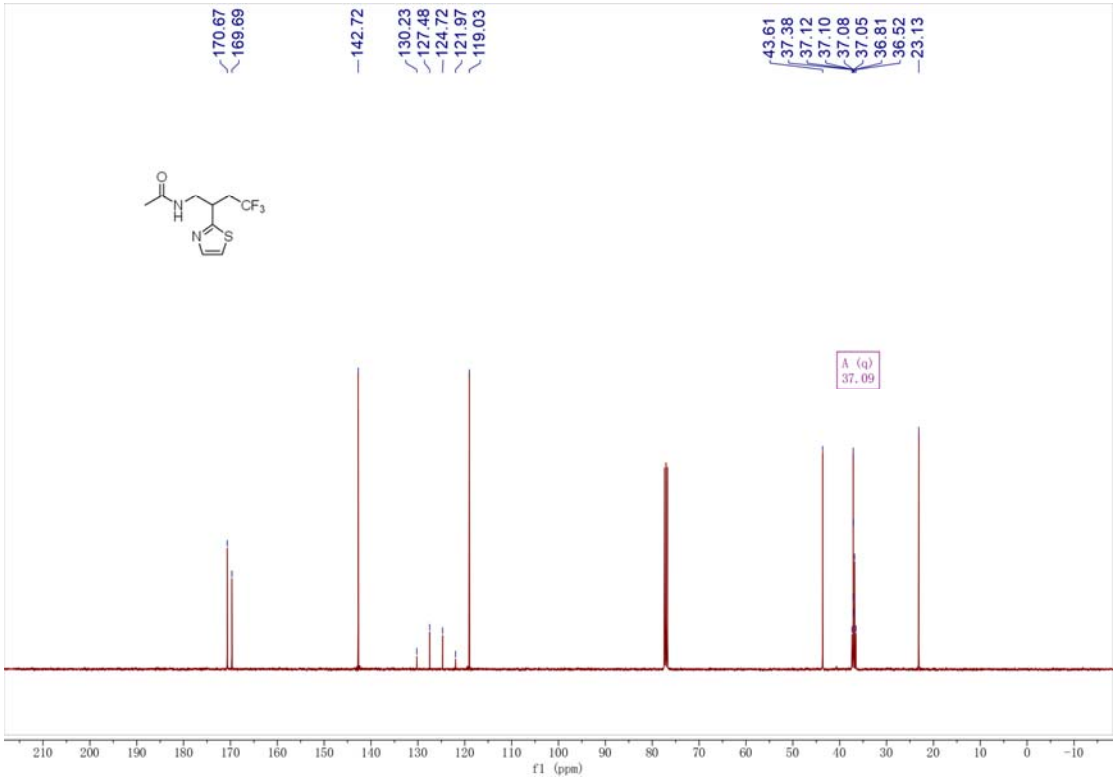


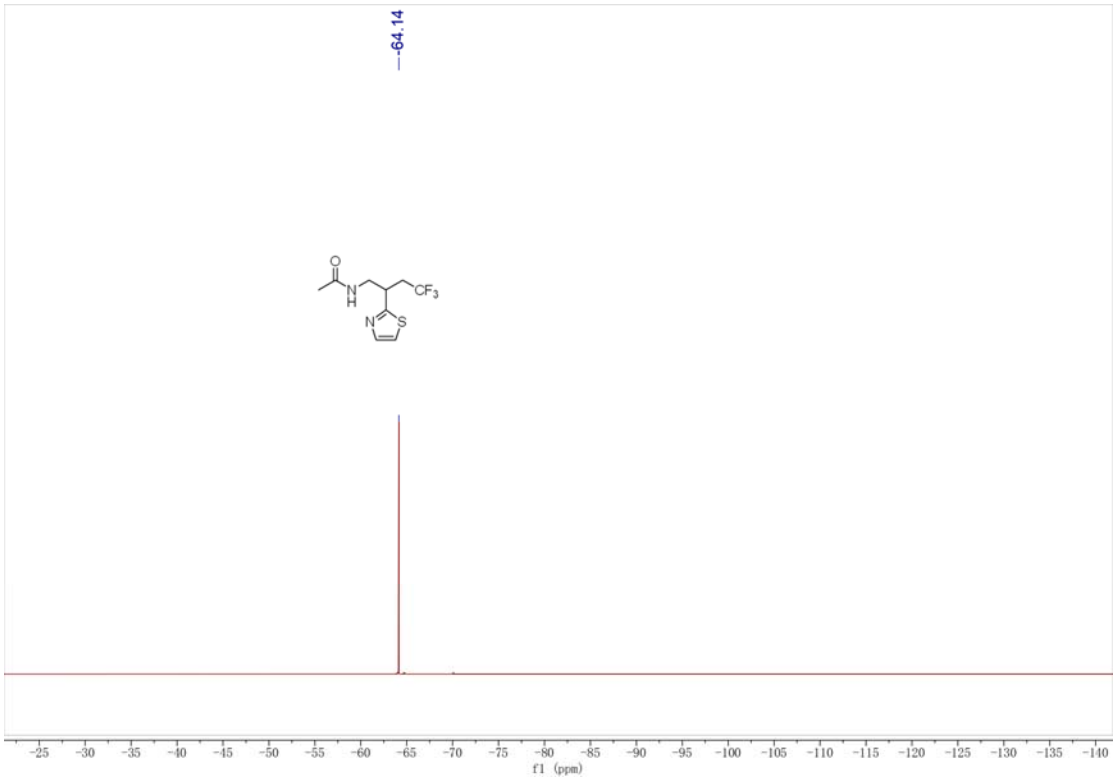



-64.00
N
N
H
N
S
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

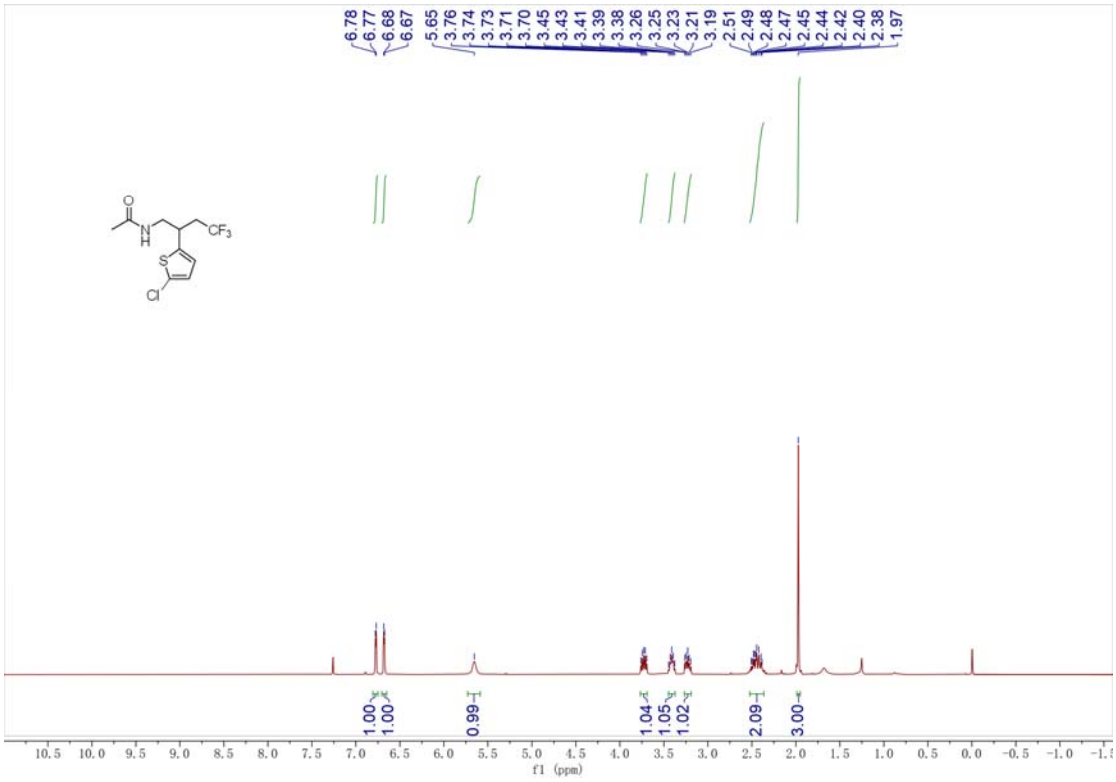
***N*-(4,4,4-trifluoro-2-(thiazol-2-yl)butyl)acetamide (3f)**

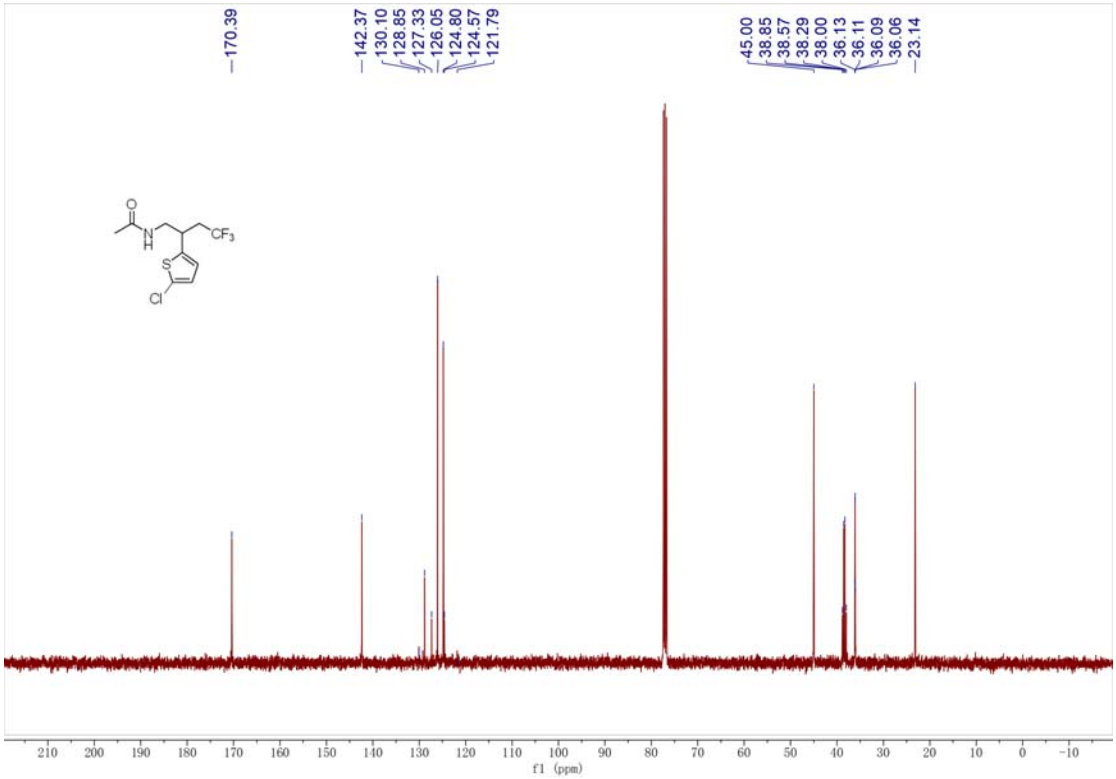


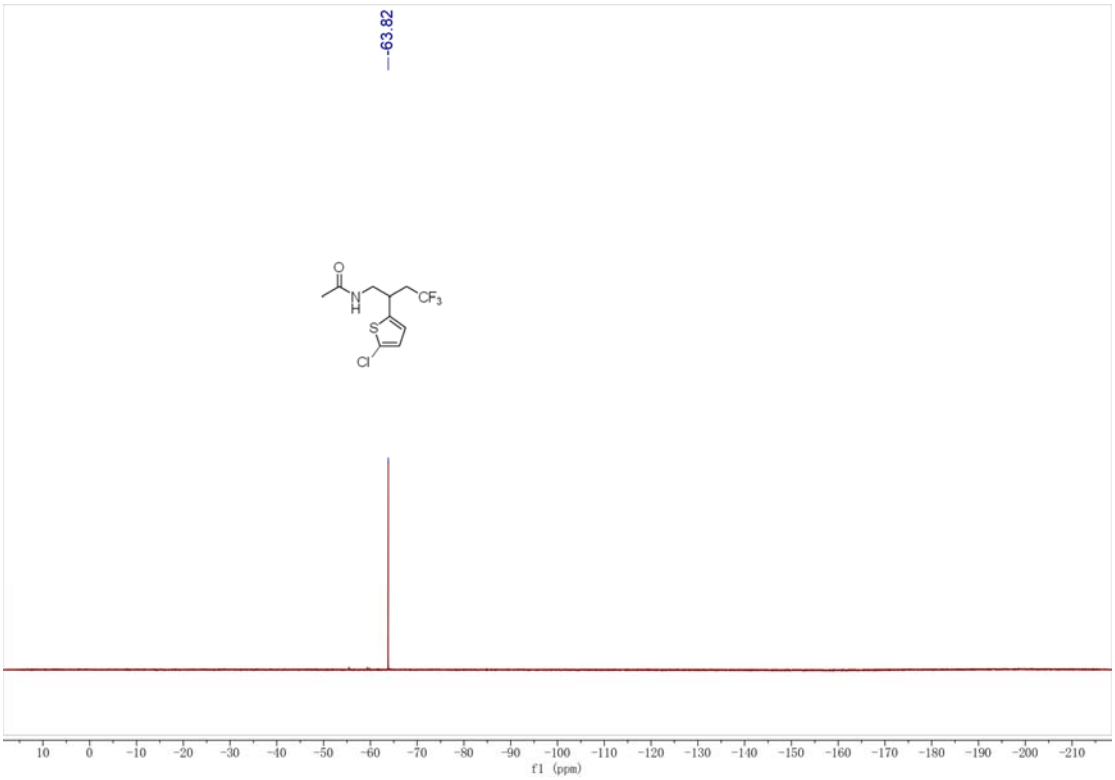



-64.14
O
N
H
CF3
N
S
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)

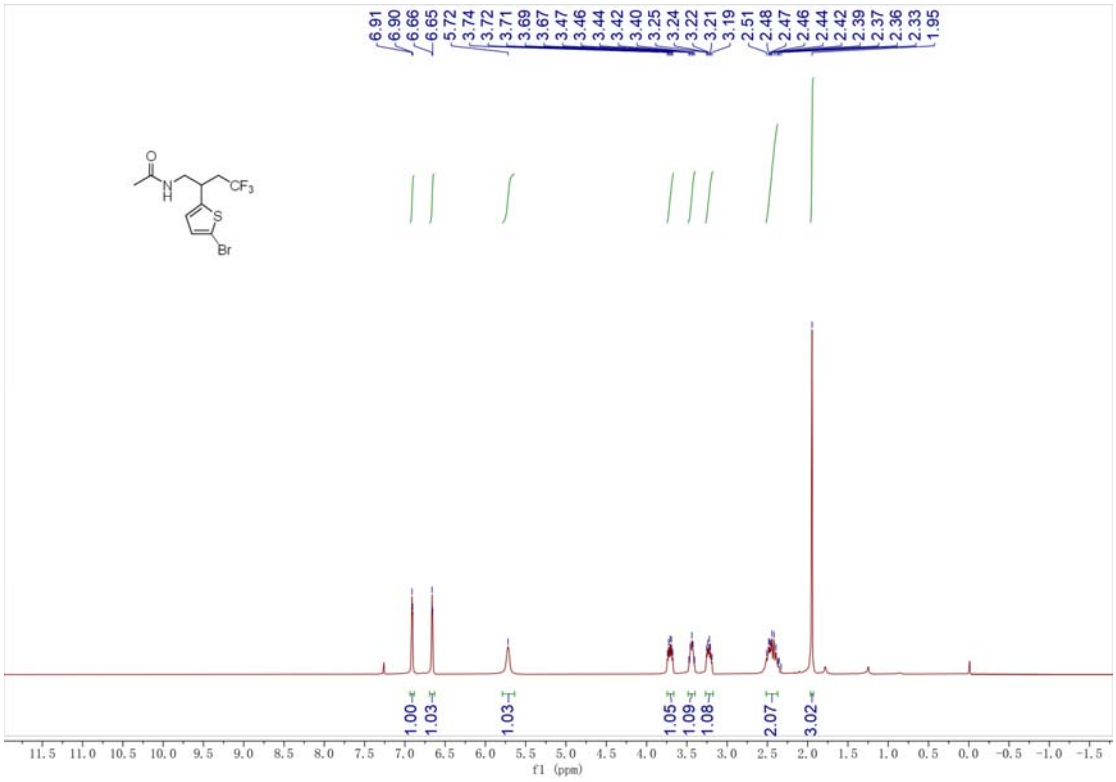
***N*-(2-(5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)acetamide (3g)**

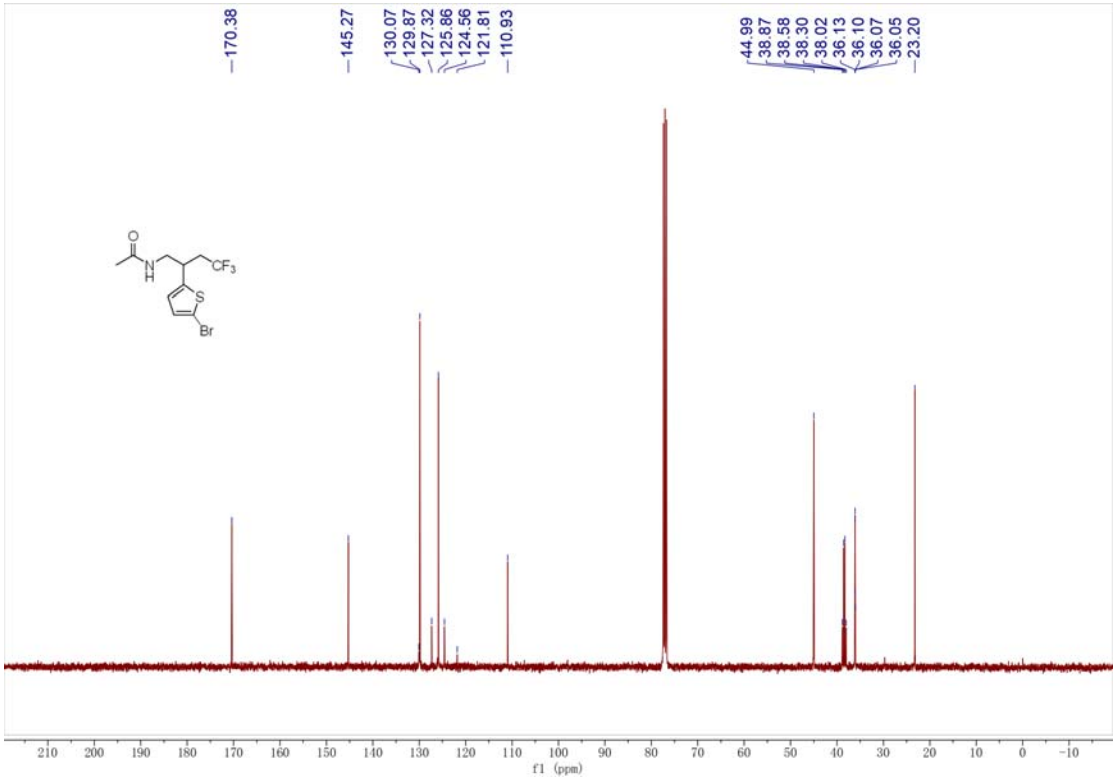


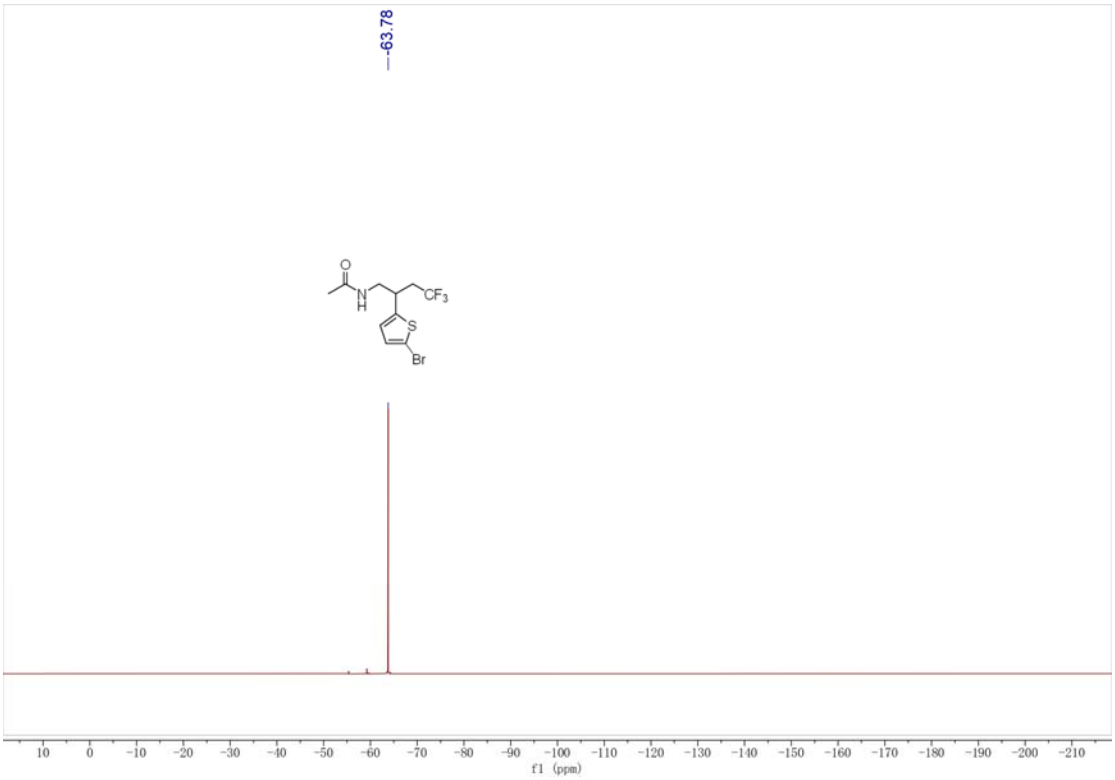



-63.82
O
N
H
CF3
S
Cl
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

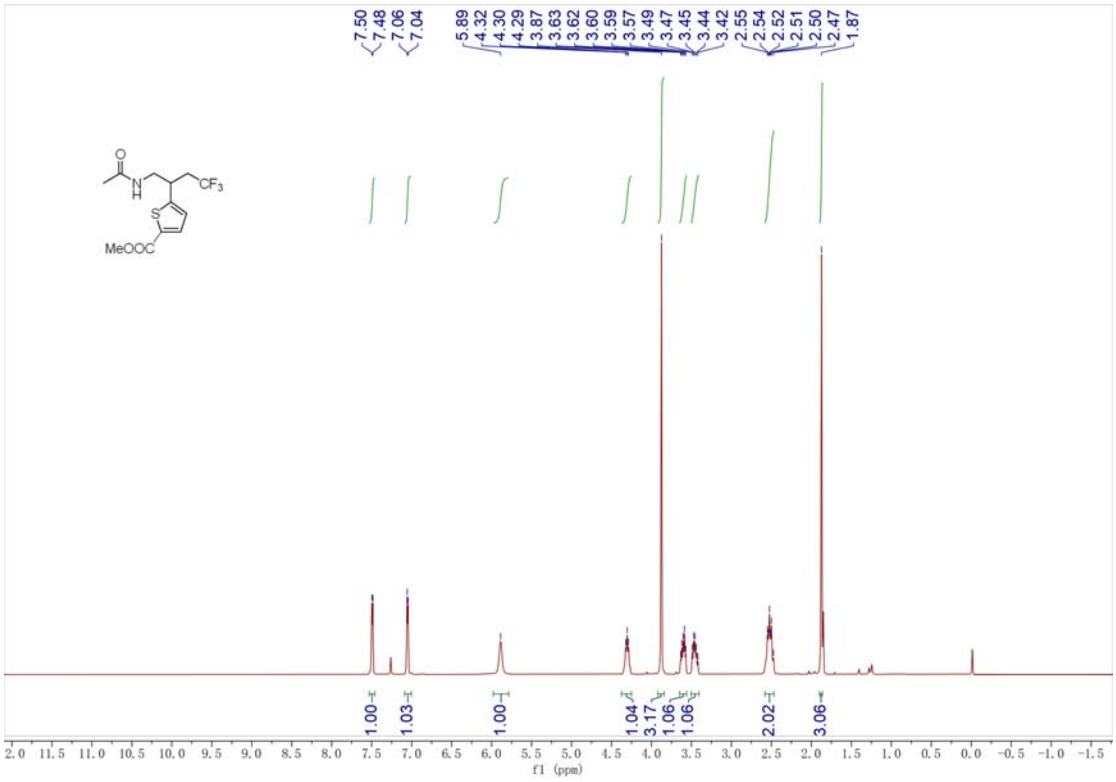
***N*-(2-(5-bromothiophen-2-yl)-4,4,4-trifluorobutyl)acetamide (3h)**

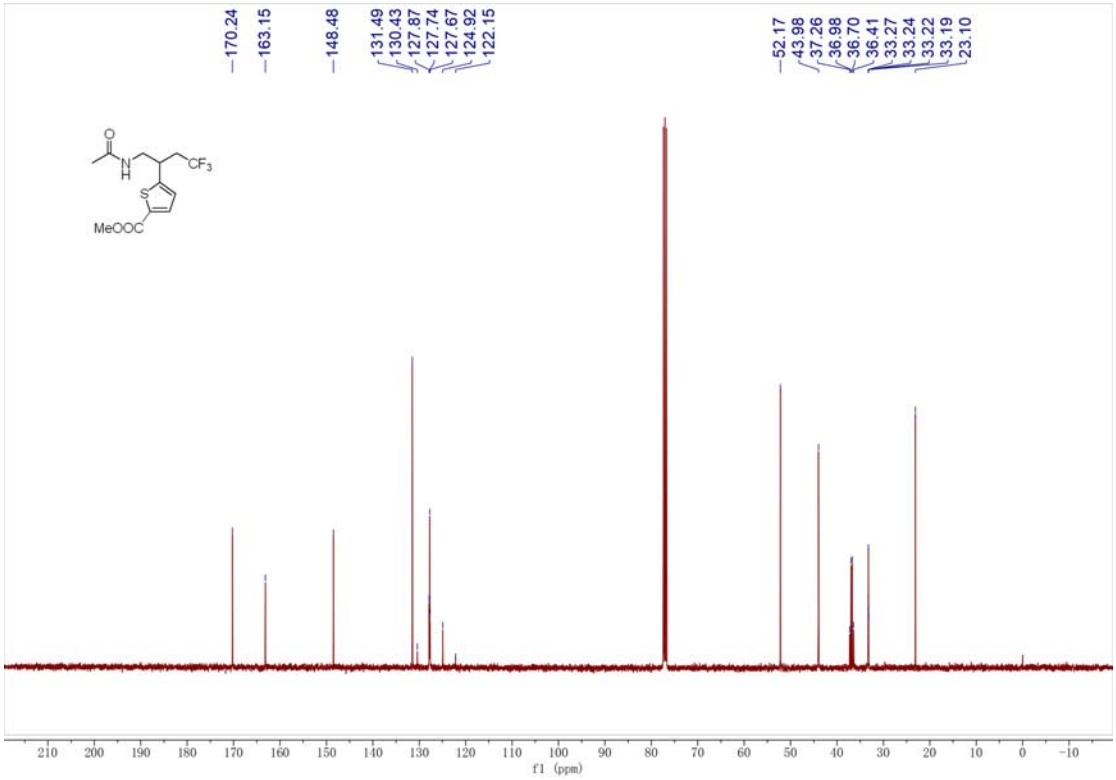


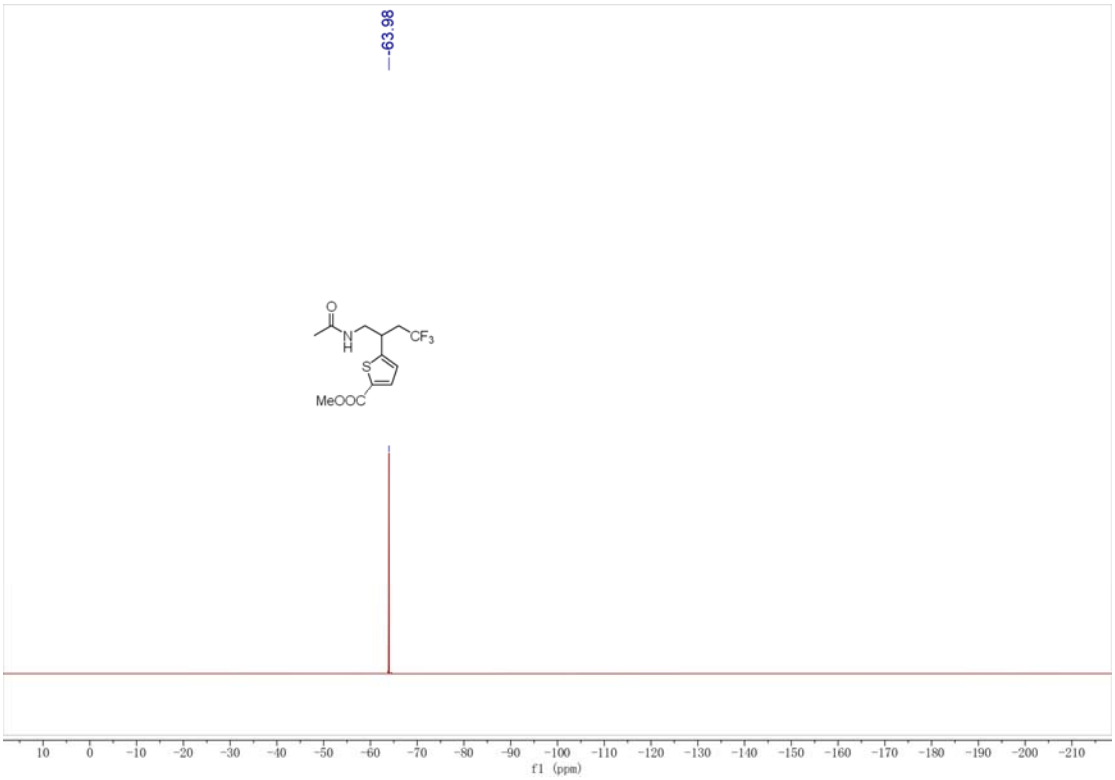



-63.78
O
N
H
CF3
S
Br
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

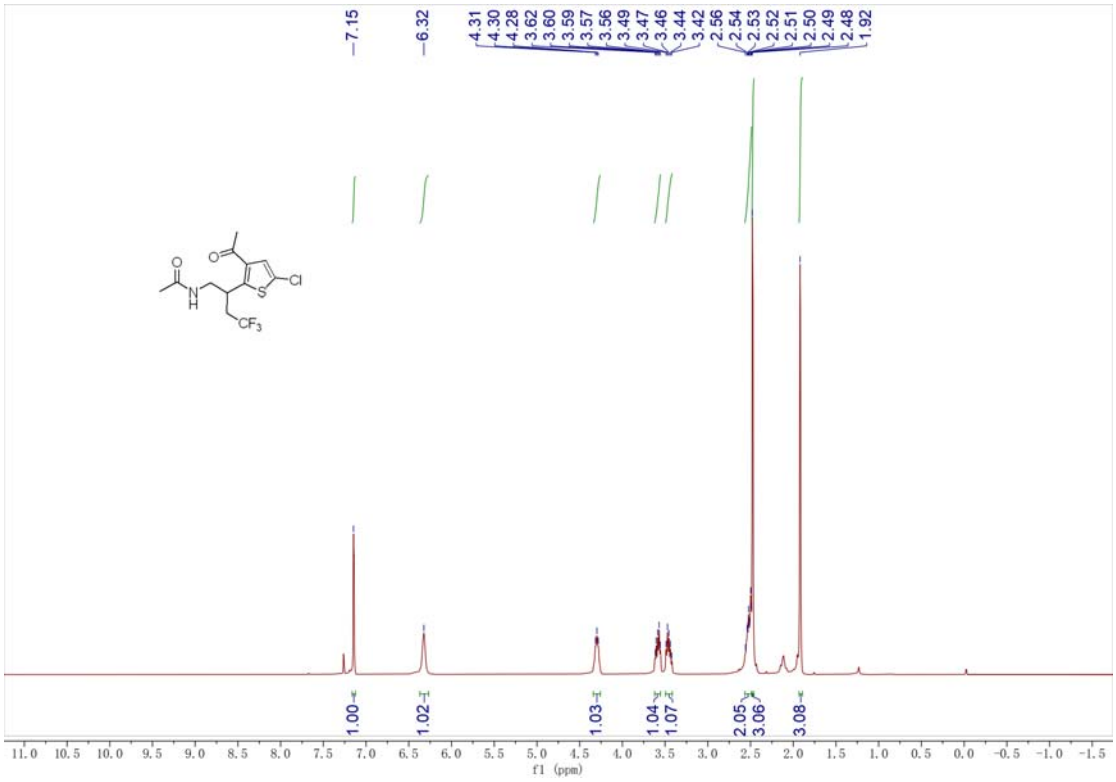
methyl 5-(1-acetamido-4,4,4-trifluorobutan-2-yl)thiophene-2-carboxylate (3i)

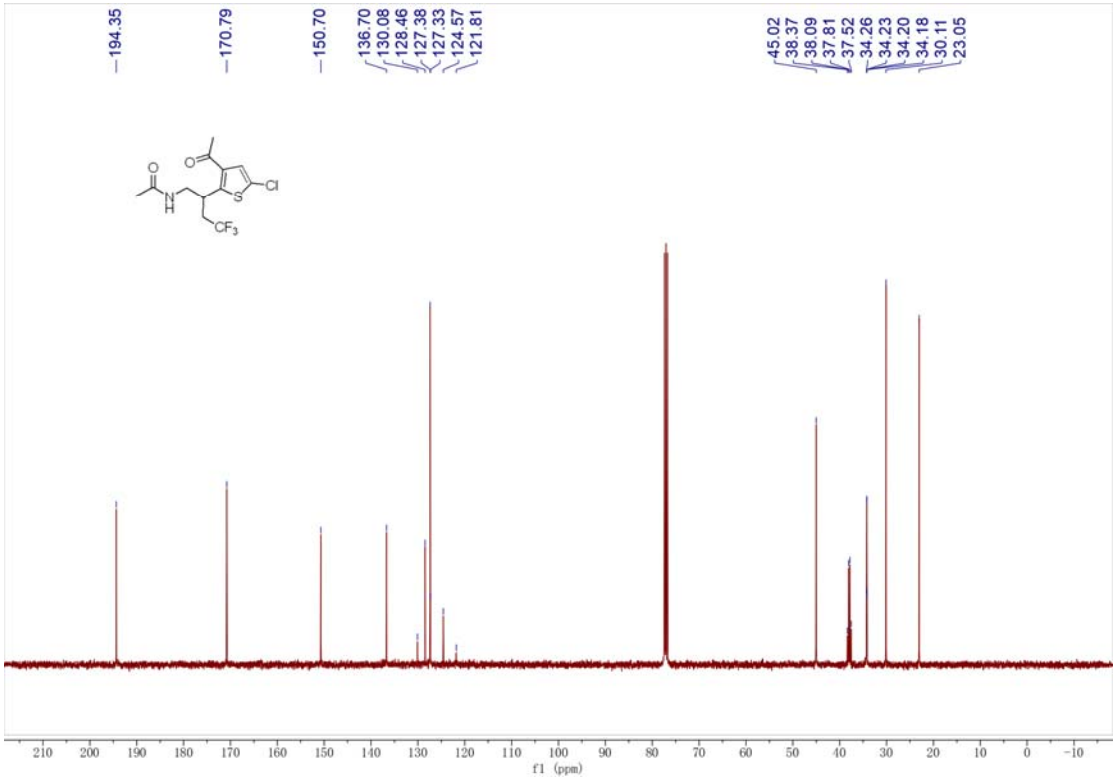


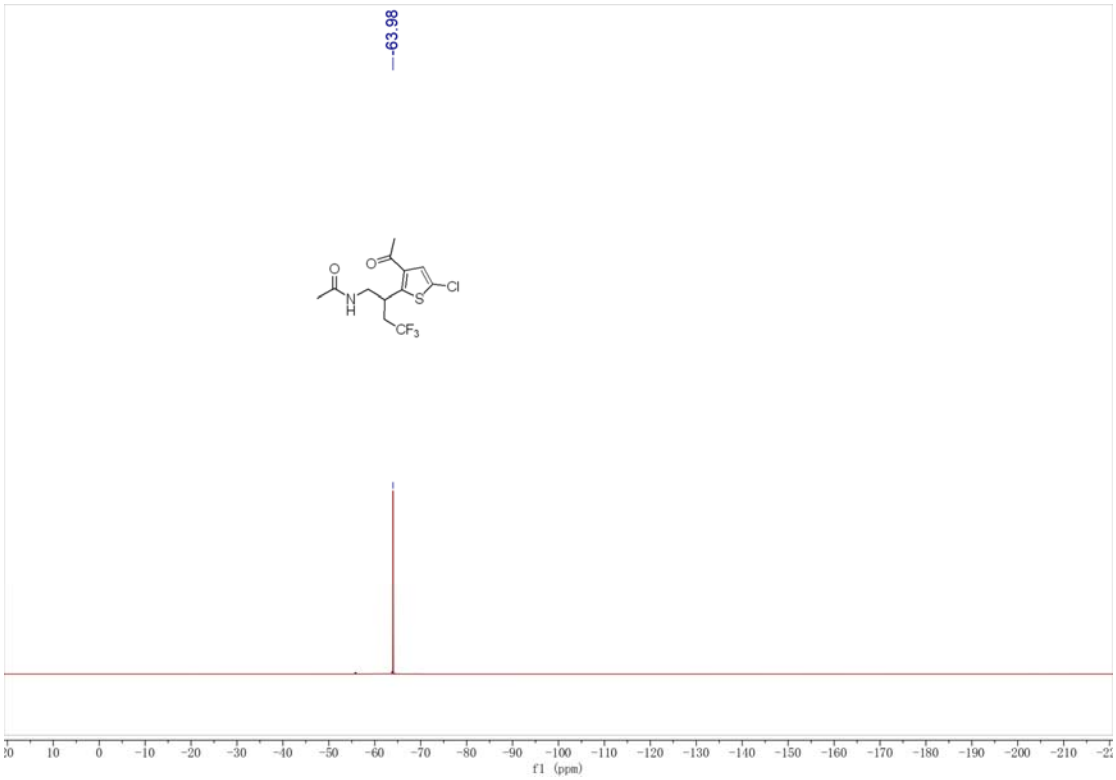



-63.98
O
N
H
CF3
S
MeOOC
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

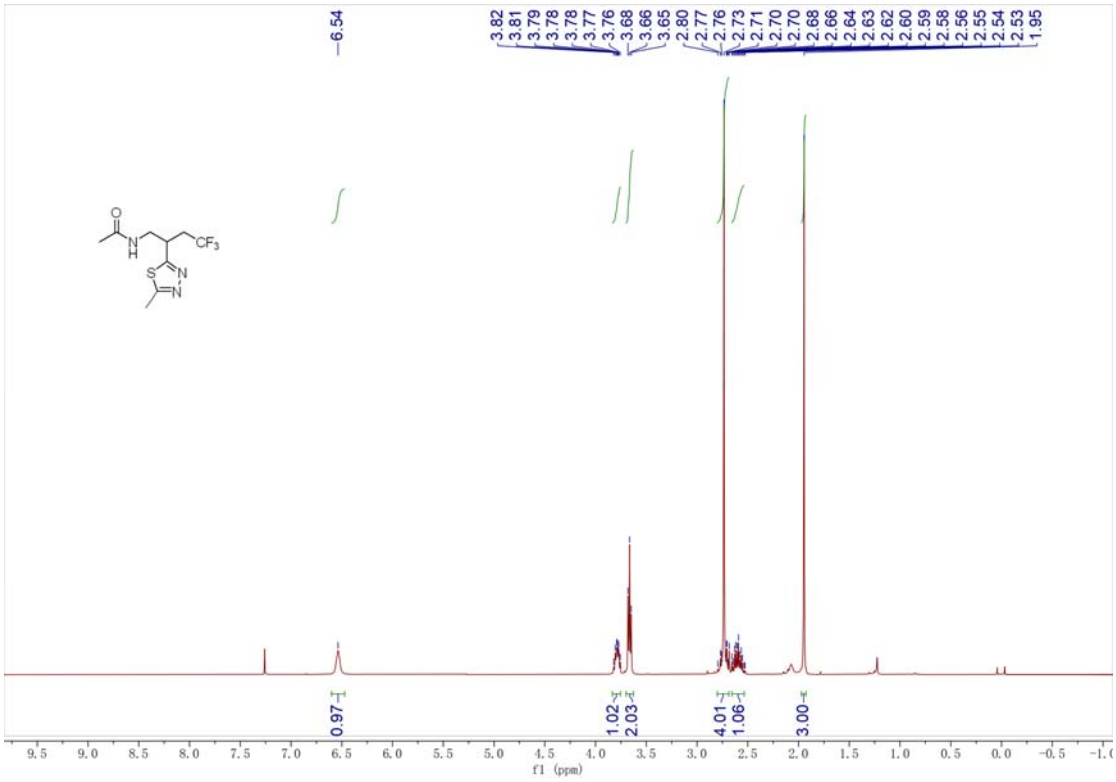
***N*-(2-(3-acetyl-5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)acetamide (3j)**

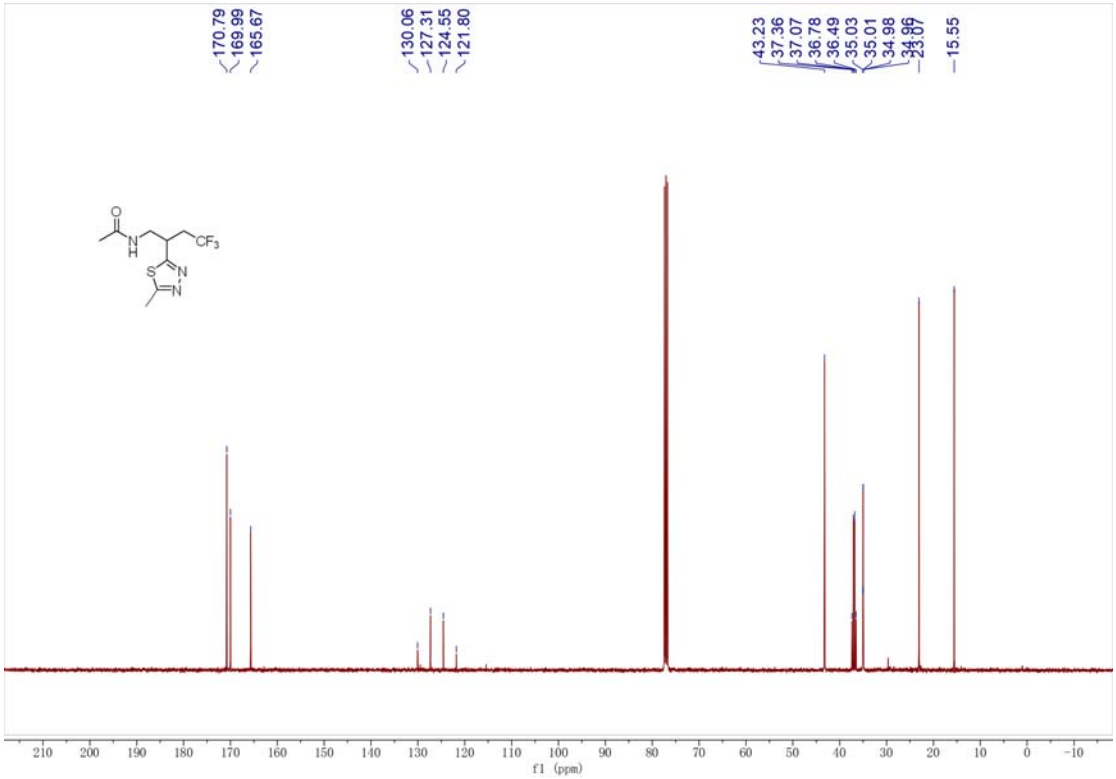


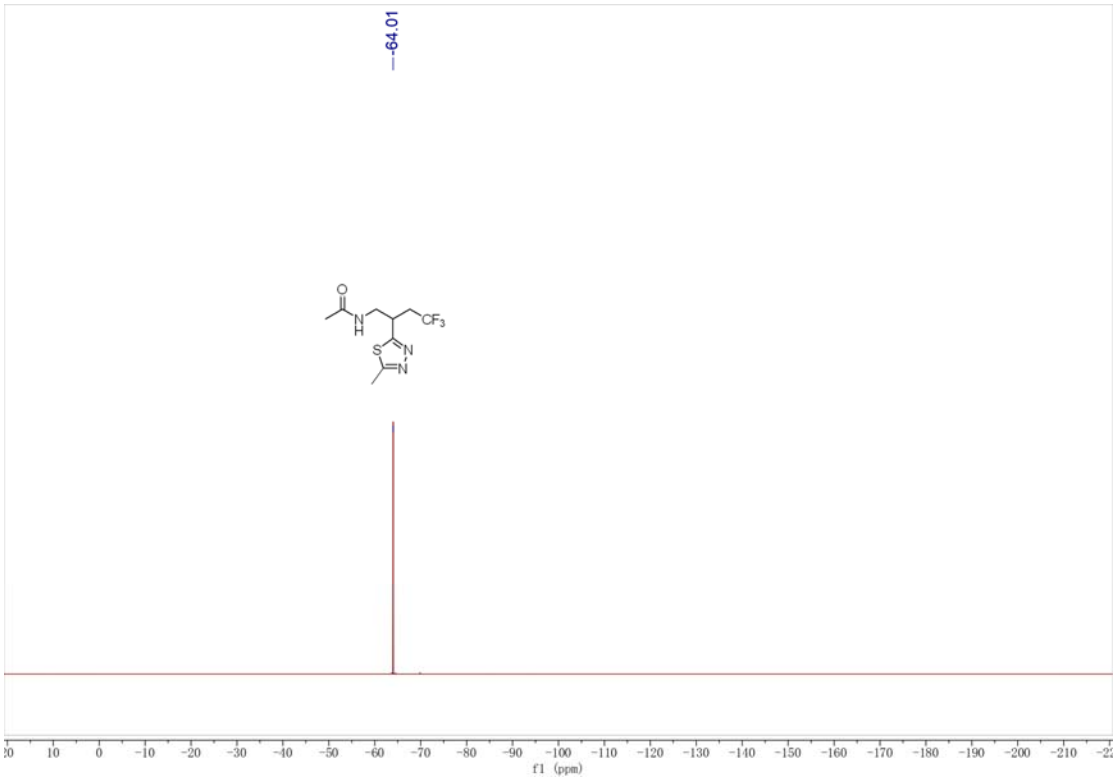



-63.98
O
O
N
H
S
Cl
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

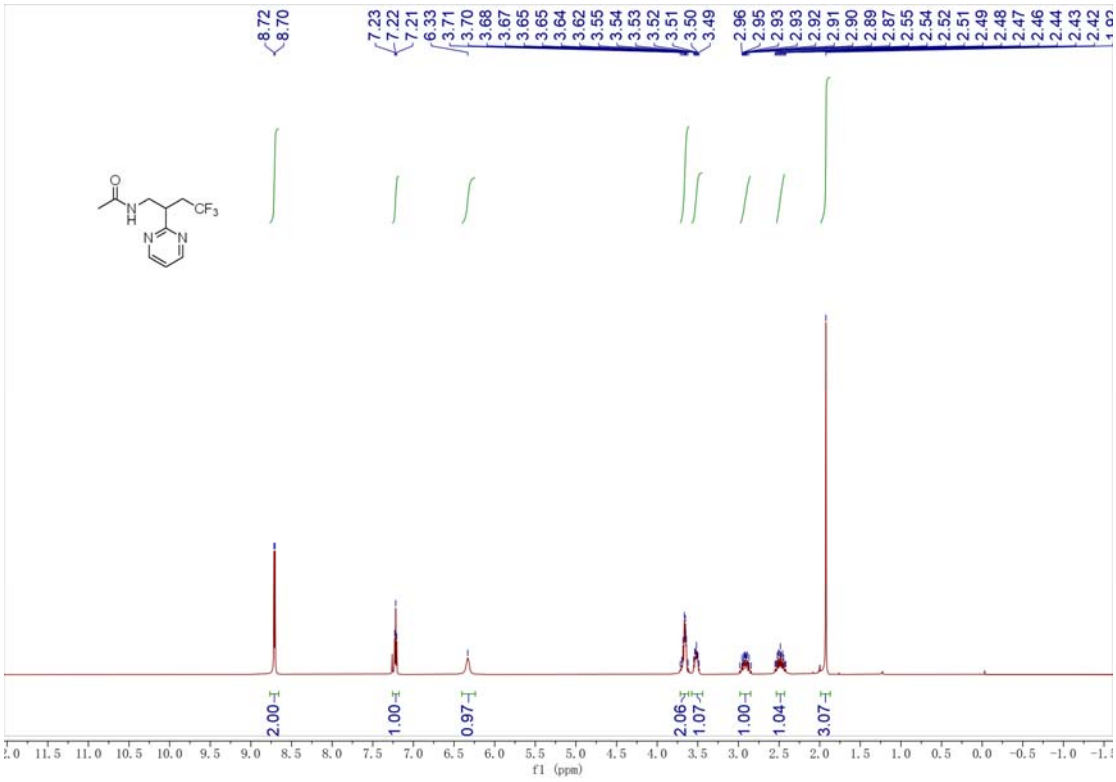
***N*-(4,4,4-trifluoro-2-(5-methyl-1,3,4-thiadiazol-2-yl)butyl)acetamide (3k)**

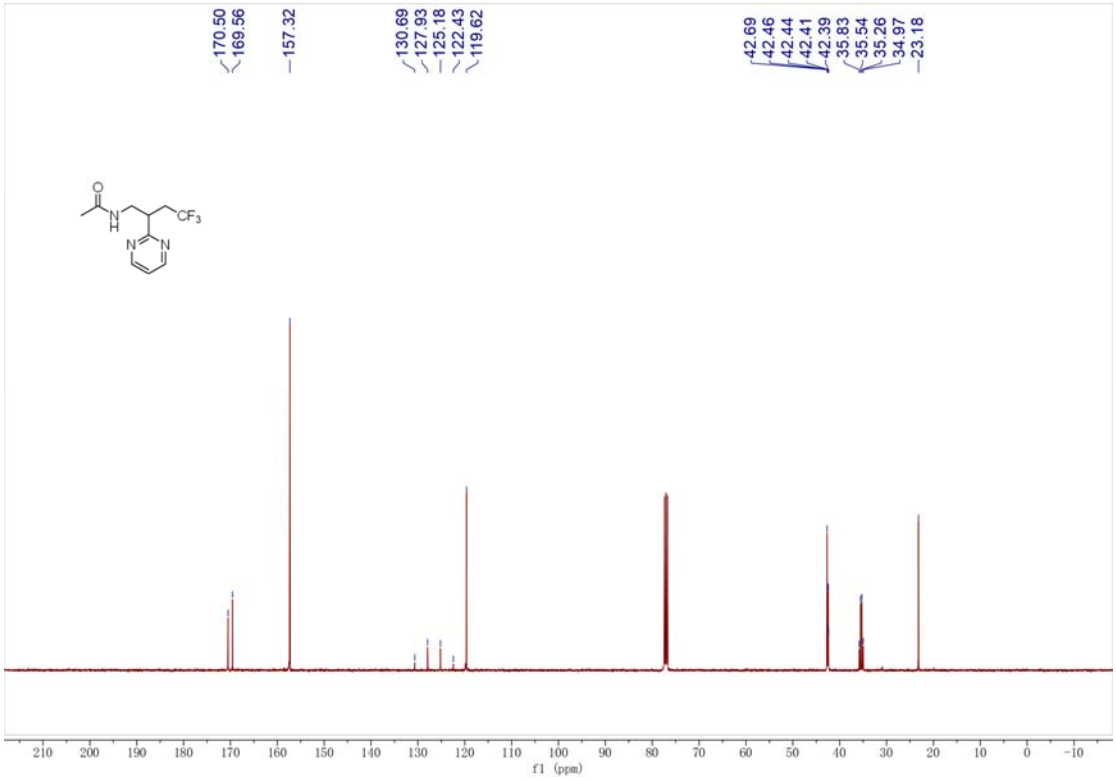


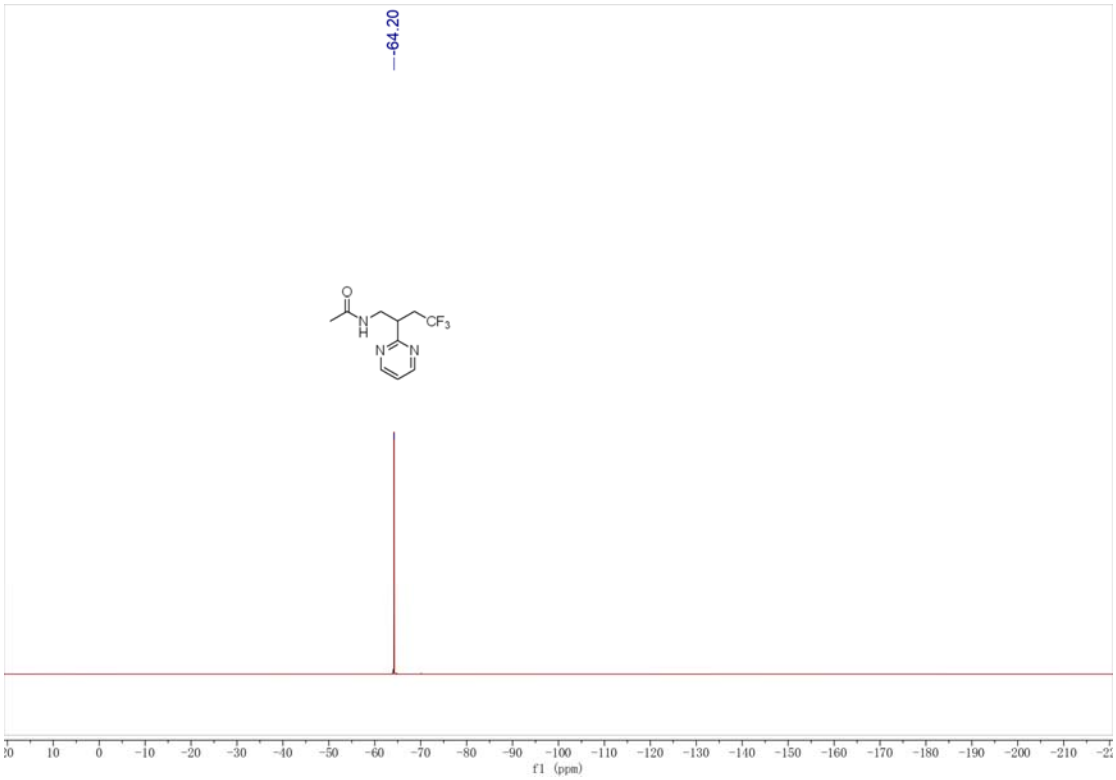



-64.01
O
N
H
CF3
S
N
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

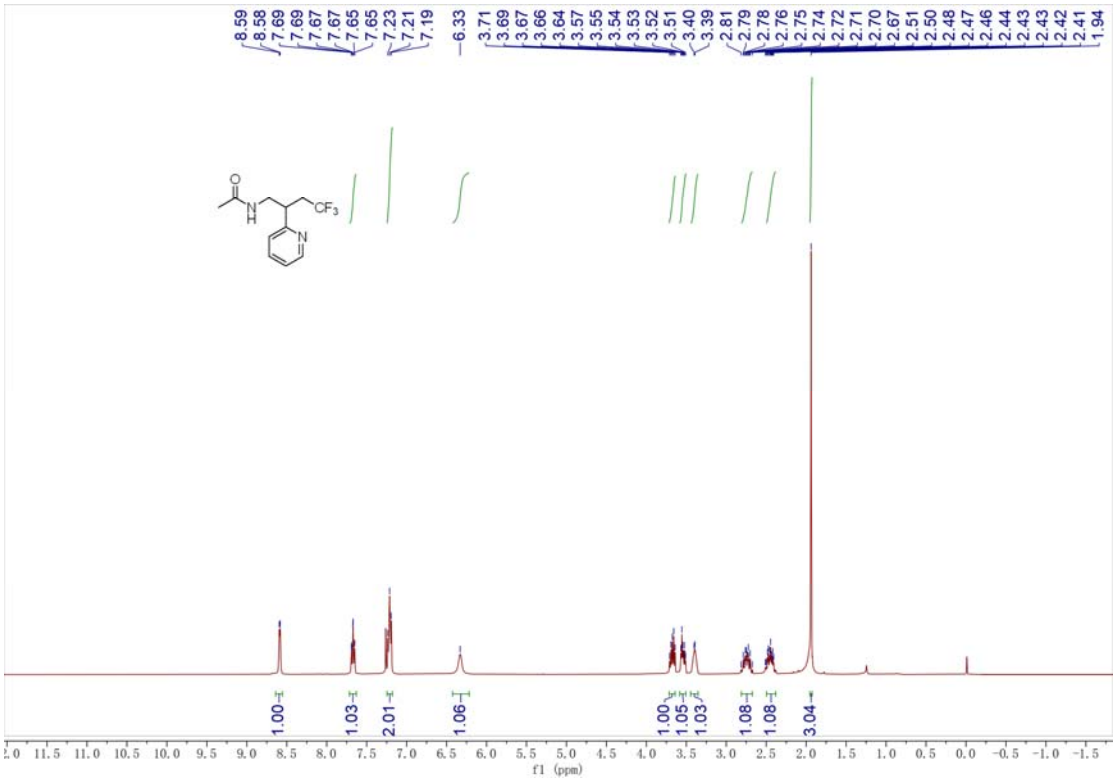
***N*-(4,4,4-trifluoro-2-(pyrimidin-2-yl)butyl)acetamide (3l)**

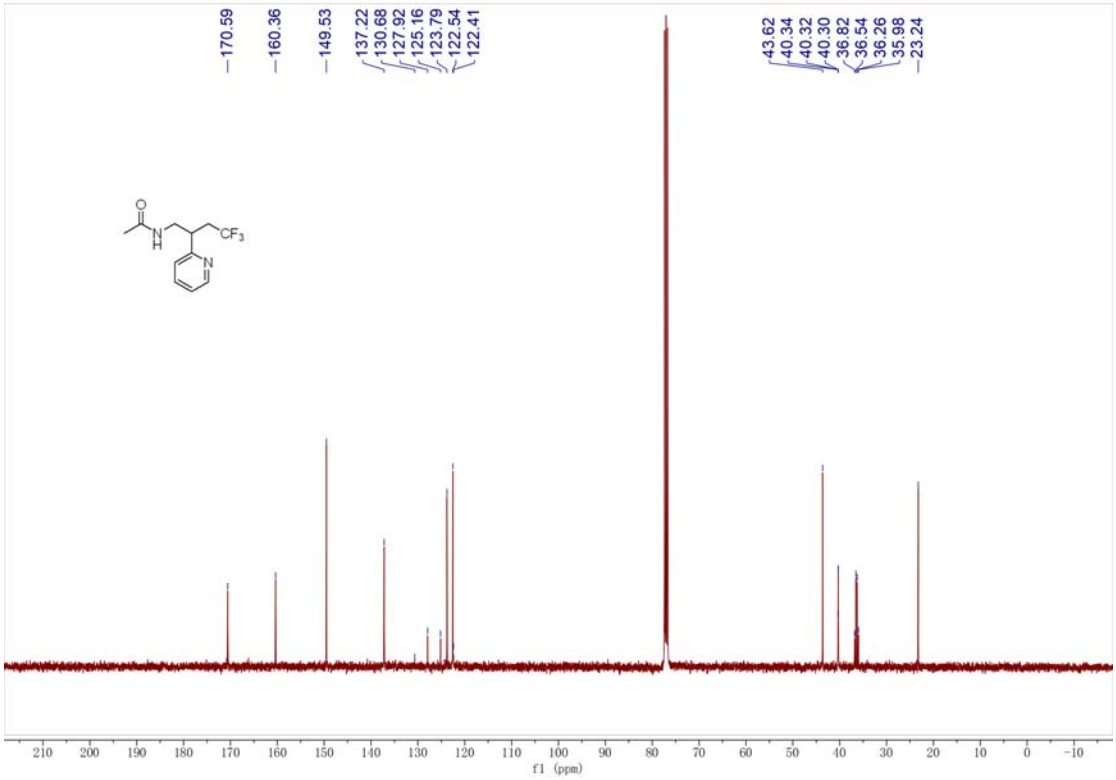


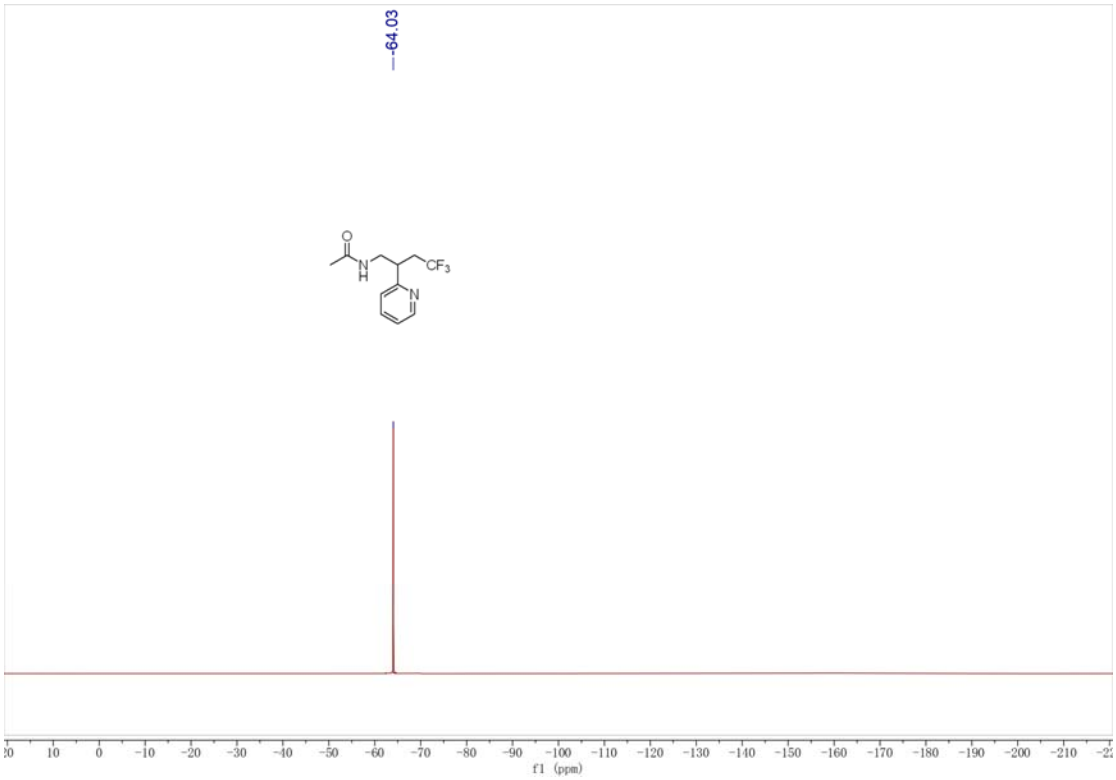



-64.20
O
N
H
CF3
N
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

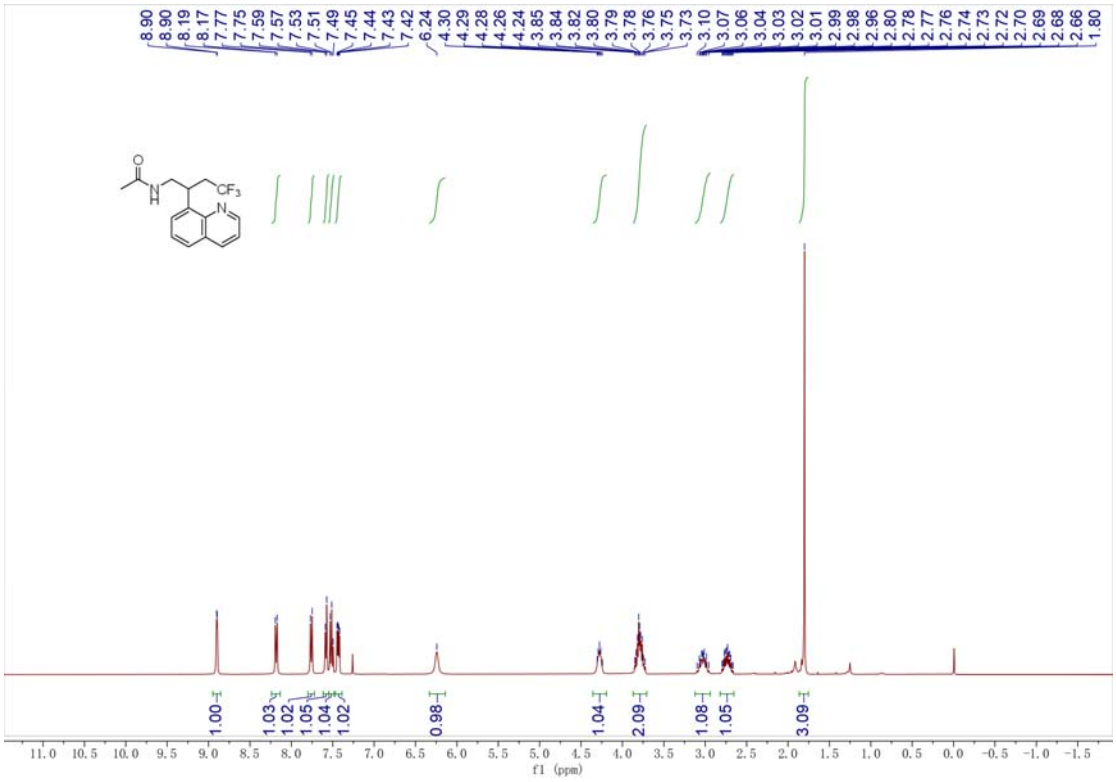
***N*-(4,4,4-trifluoro-2-(pyridin-2-yl)butyl)acetamide (3m)**

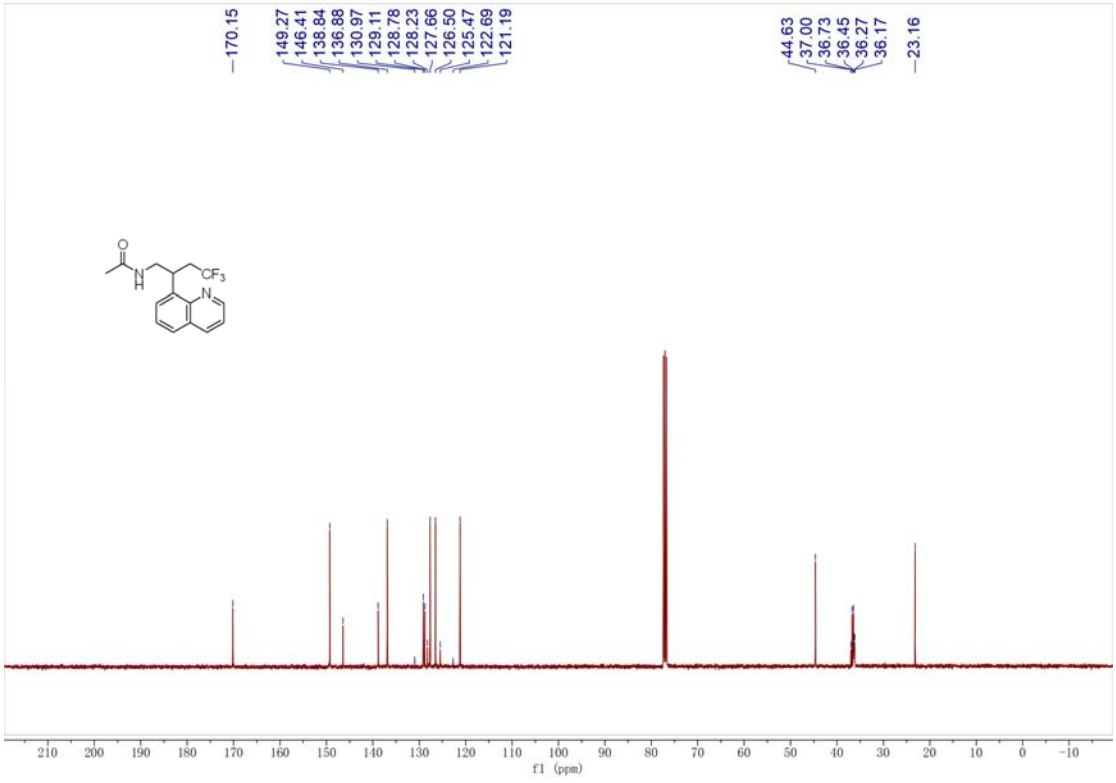


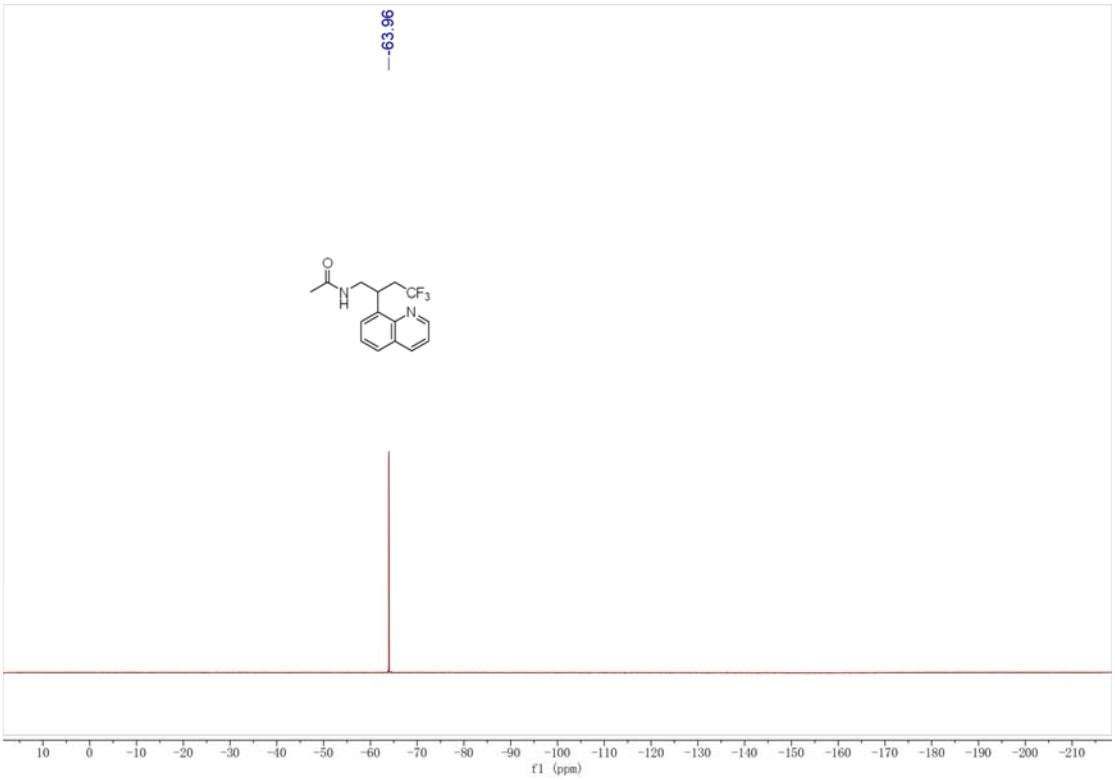



-64.03
O
N
H
CF3
N
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

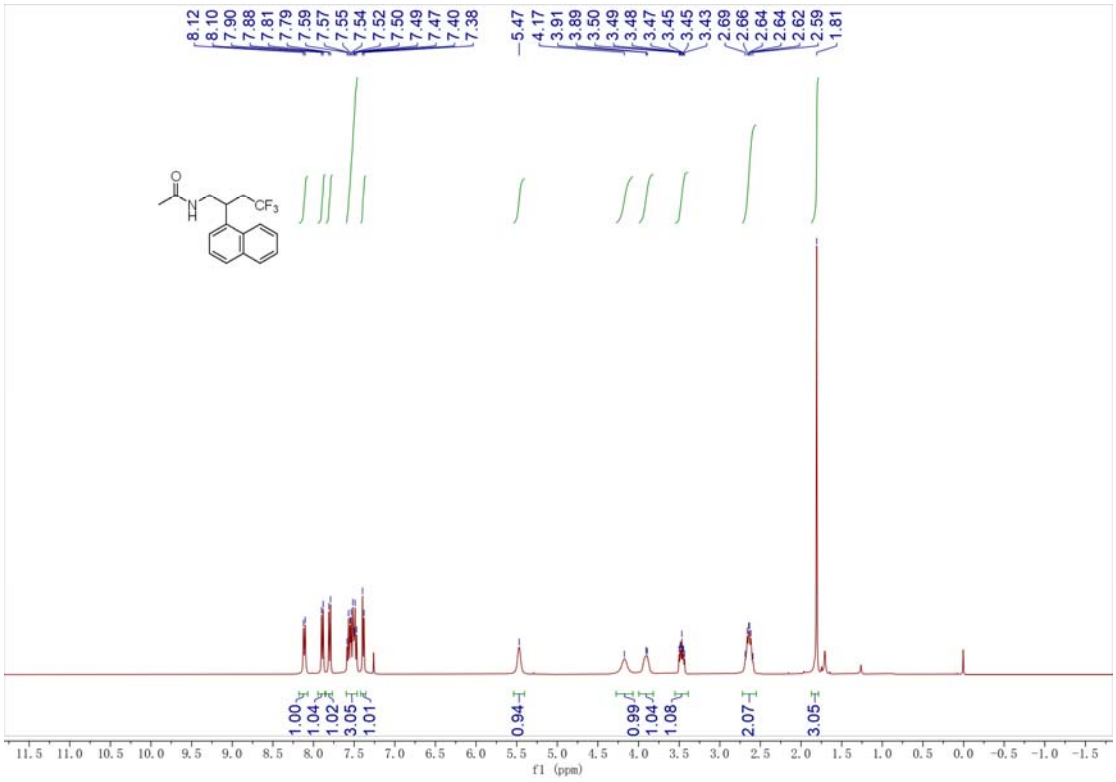
***N*-(4,4,4-trifluoro-2-(quinolin-8-yl)butyl)acetamide (3n)**

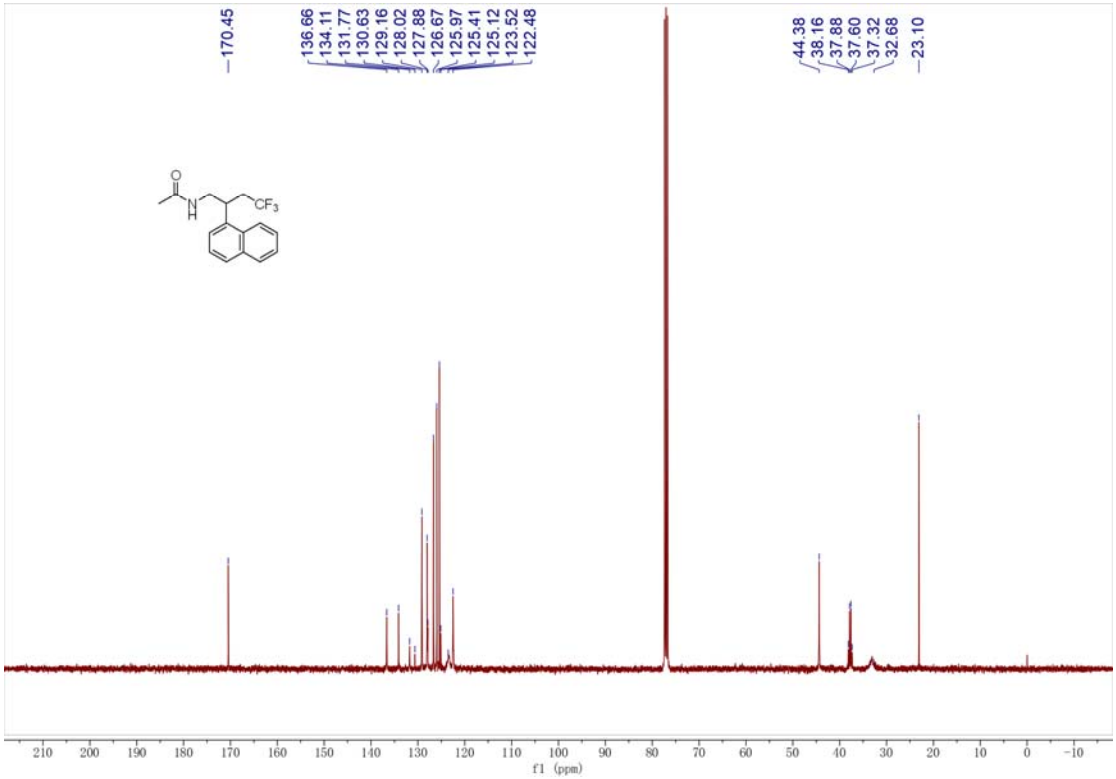


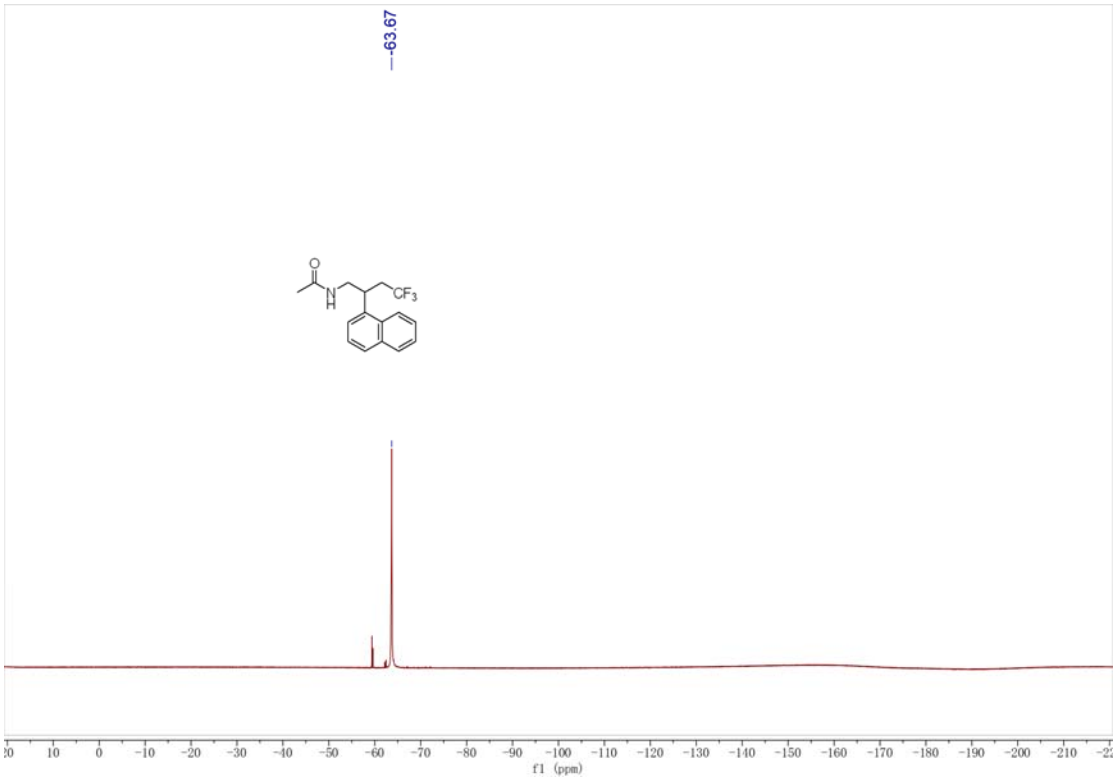



-63.96
O
N
H
CF3
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

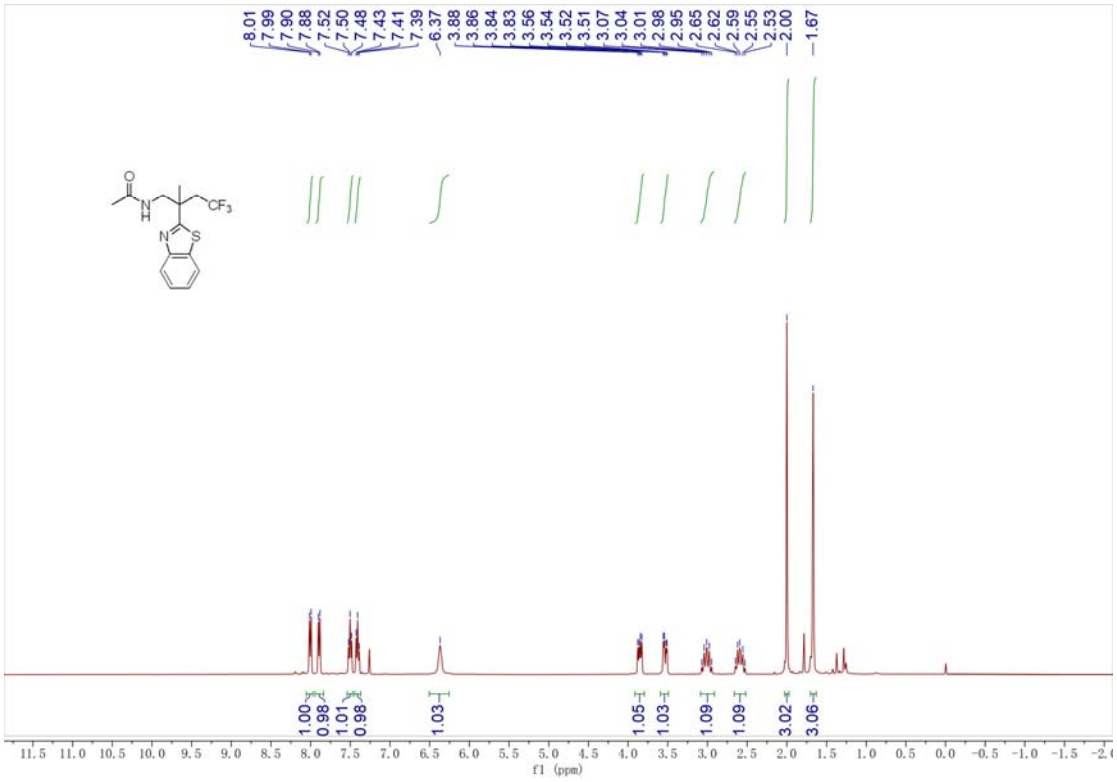
***N*-(4,4,4-trifluoro-2-(naphthalen-1-yl)butyl)acetamide (3o)**

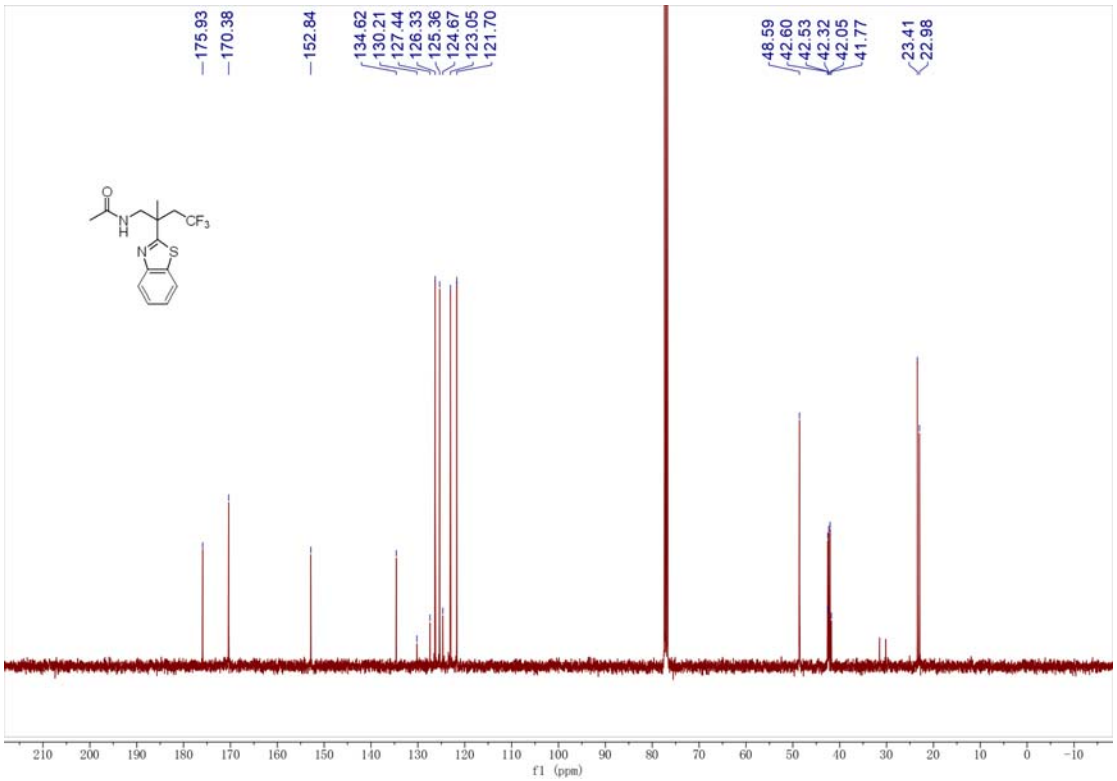


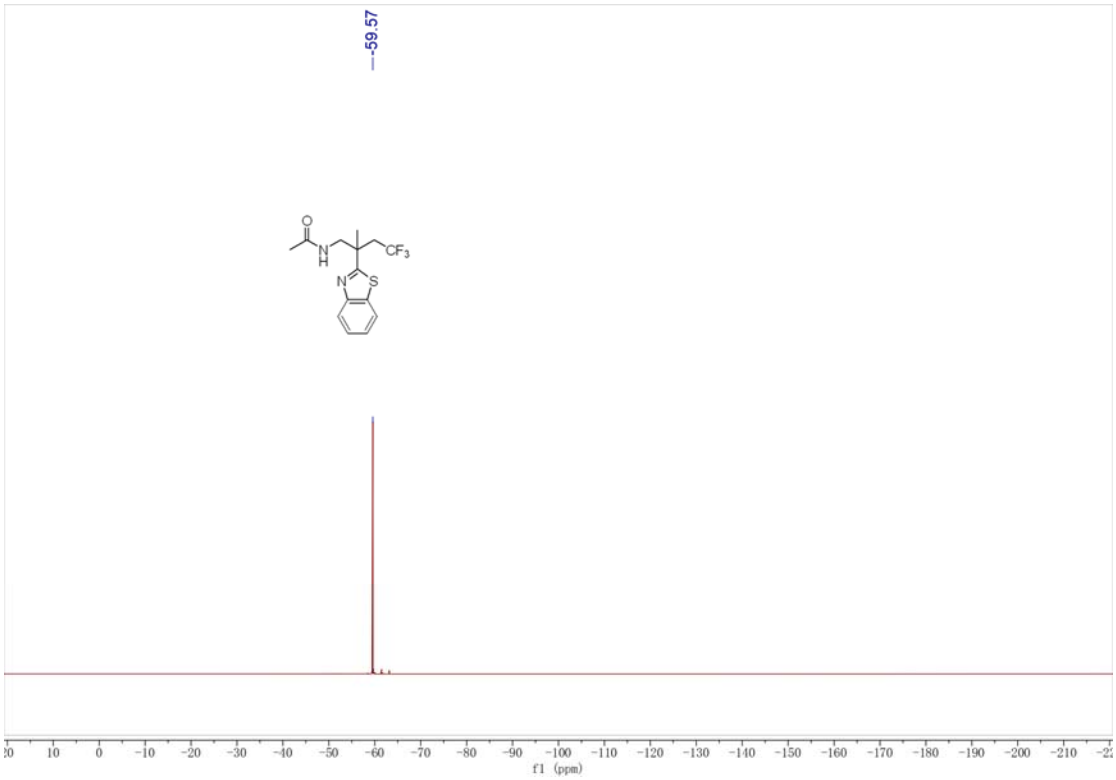



-63.67
O
N
H
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

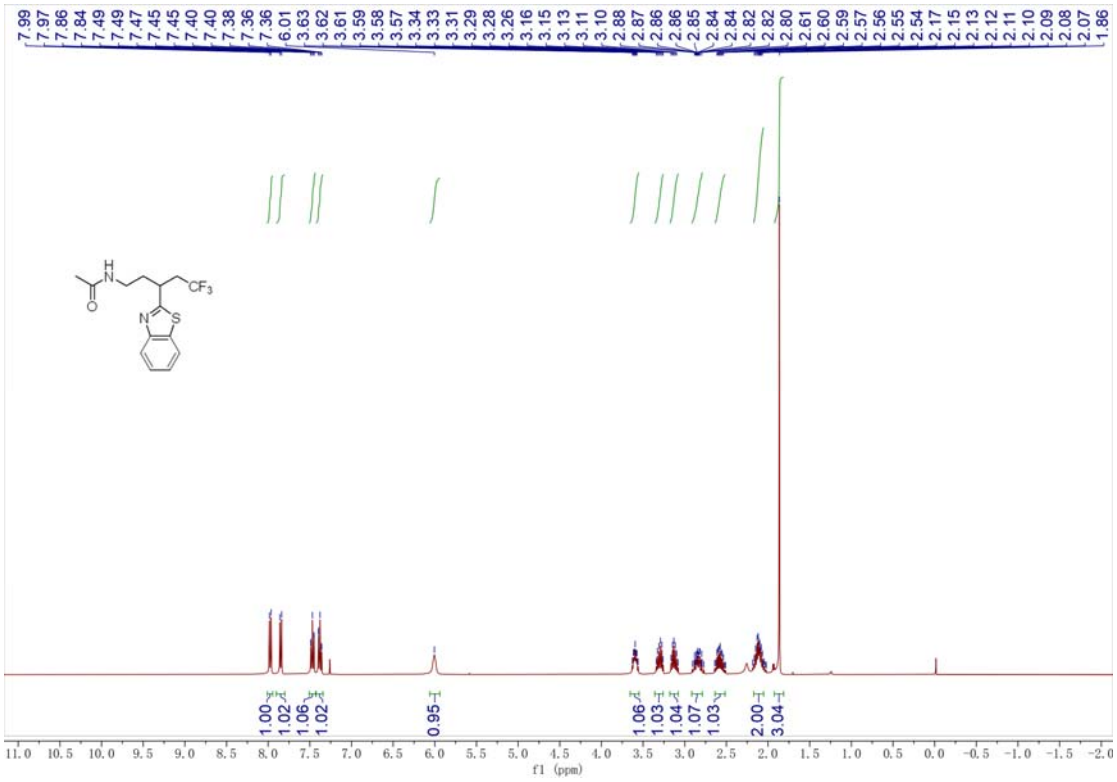
***N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluoro-2-methylbutyl)acetamide (3p)**

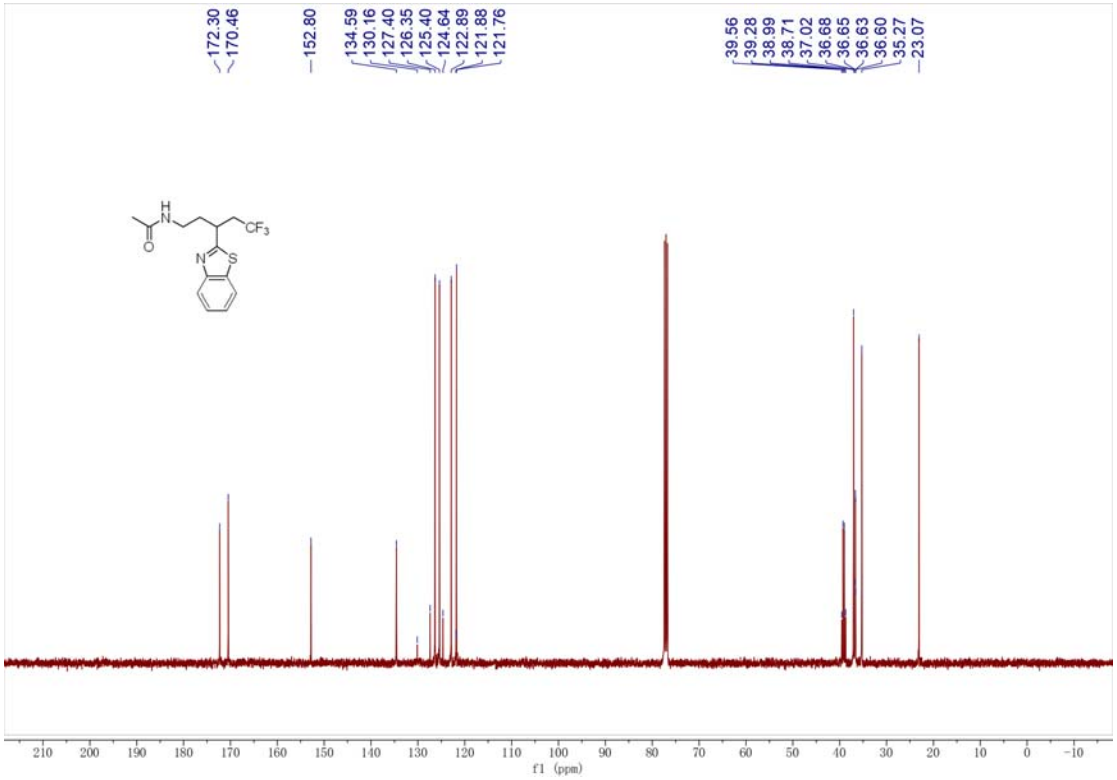


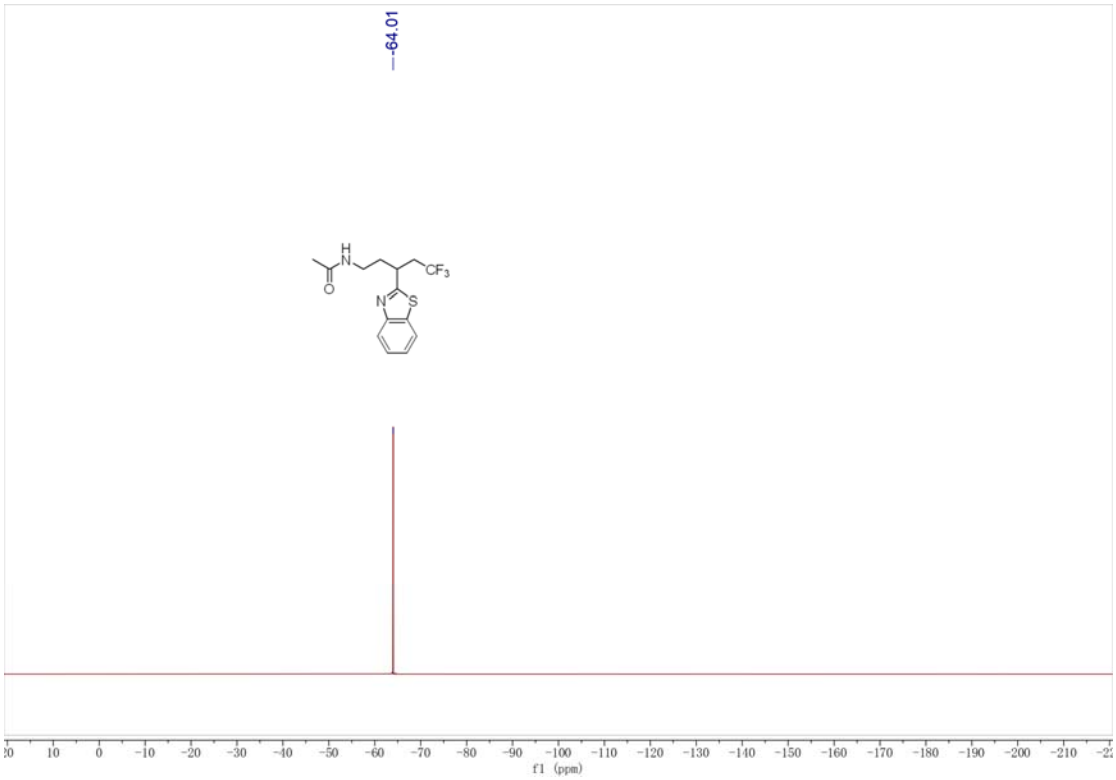



-59.57
O
N
H
CF3
N
S
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

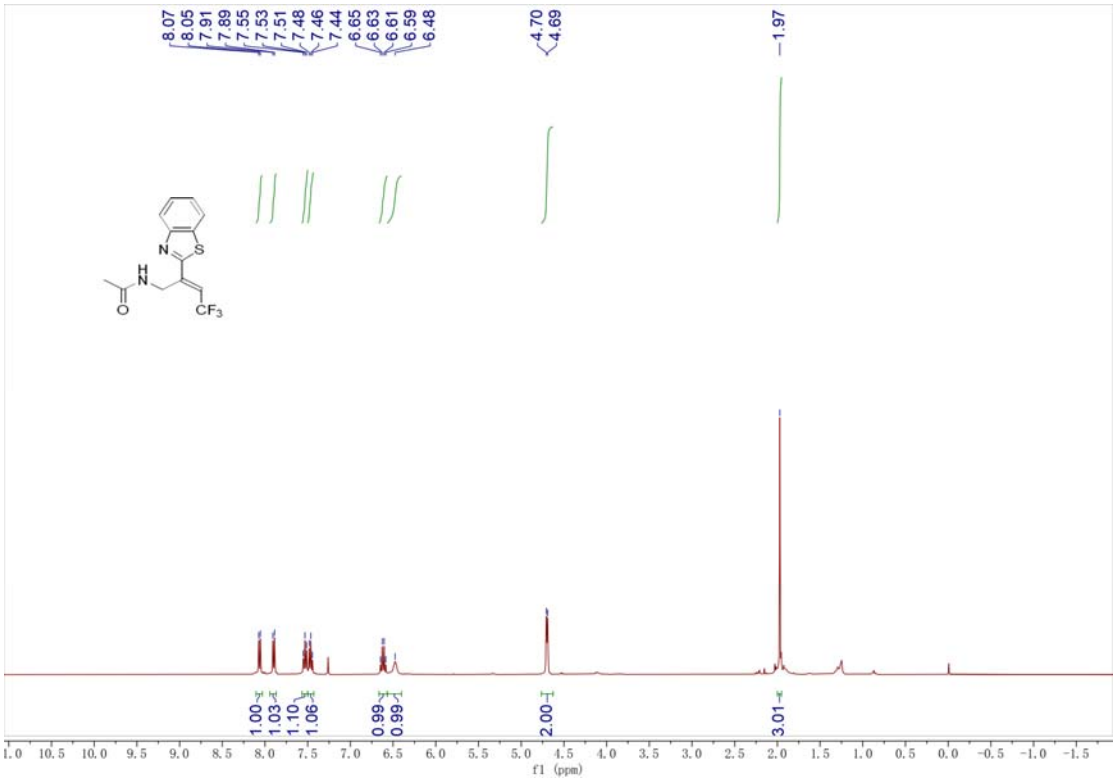
***N*-(3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentyl)acetamide (3q)**

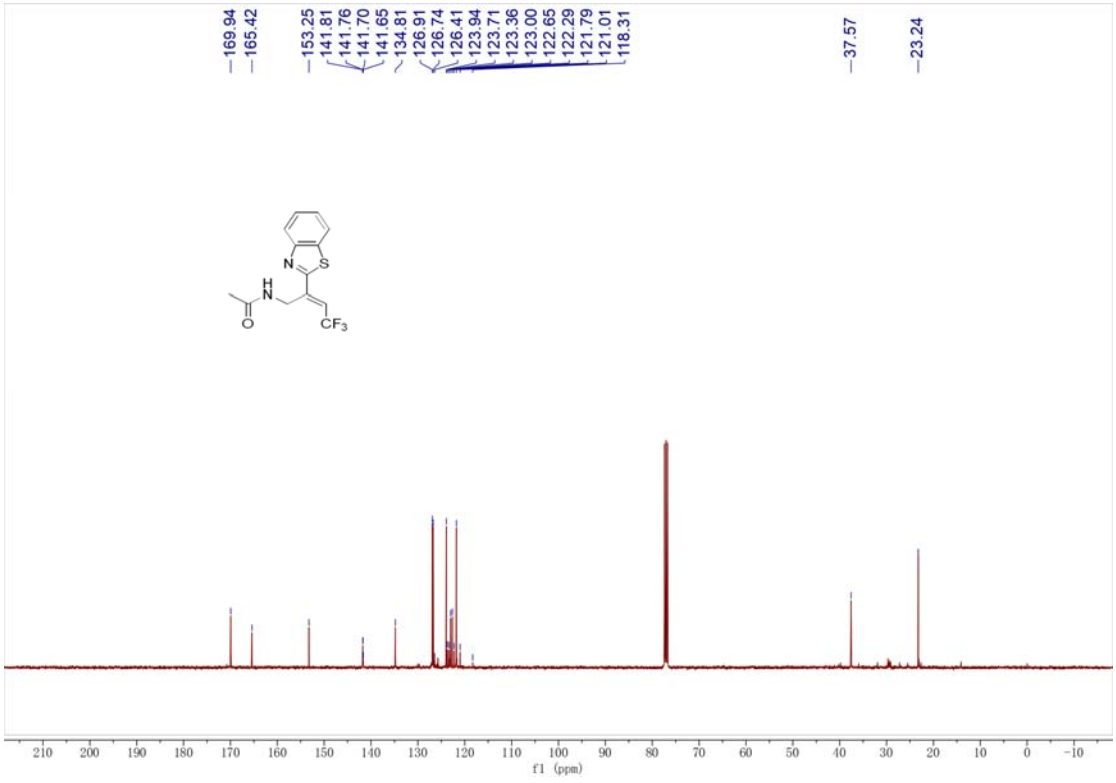


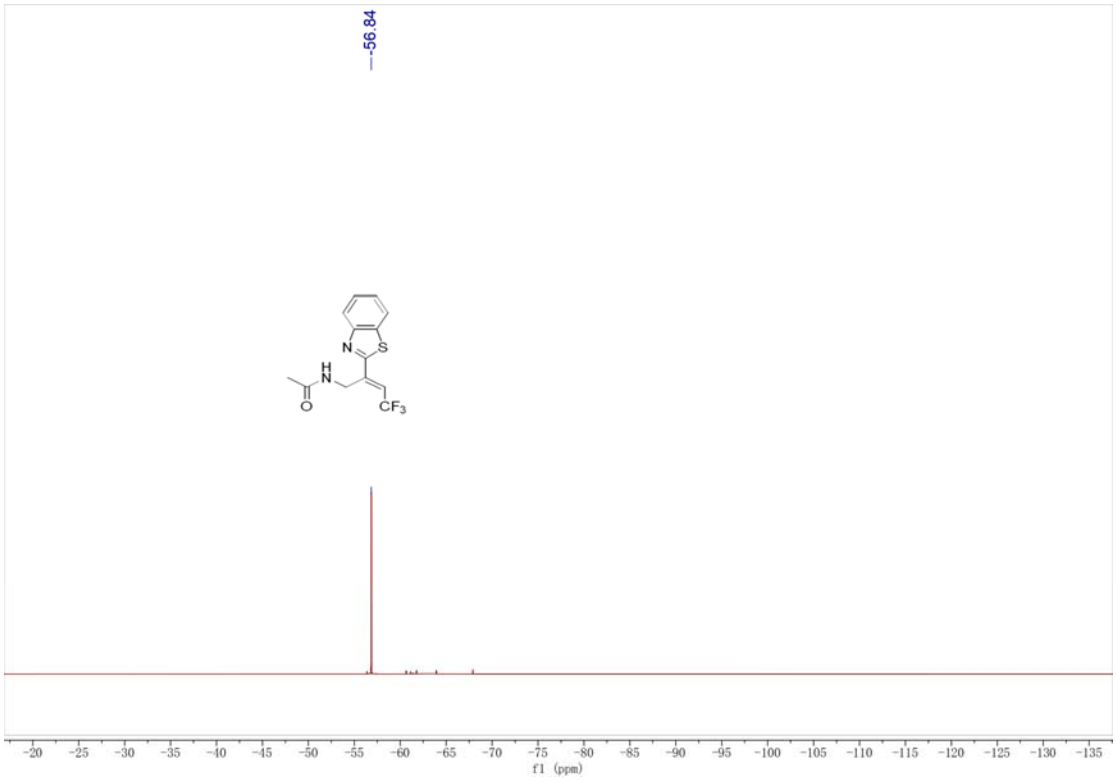



-64.01
H
N
O
CF3
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

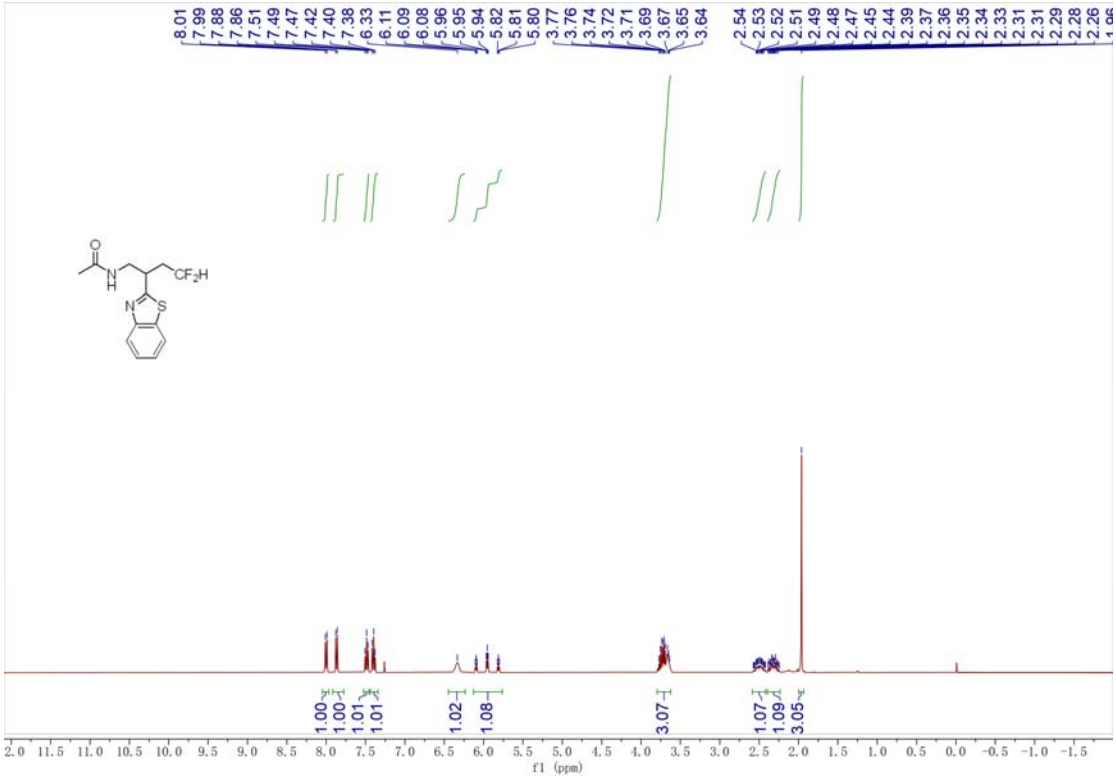
(E)-*N*-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobut-2-en-1-yl)acetamide (3r)

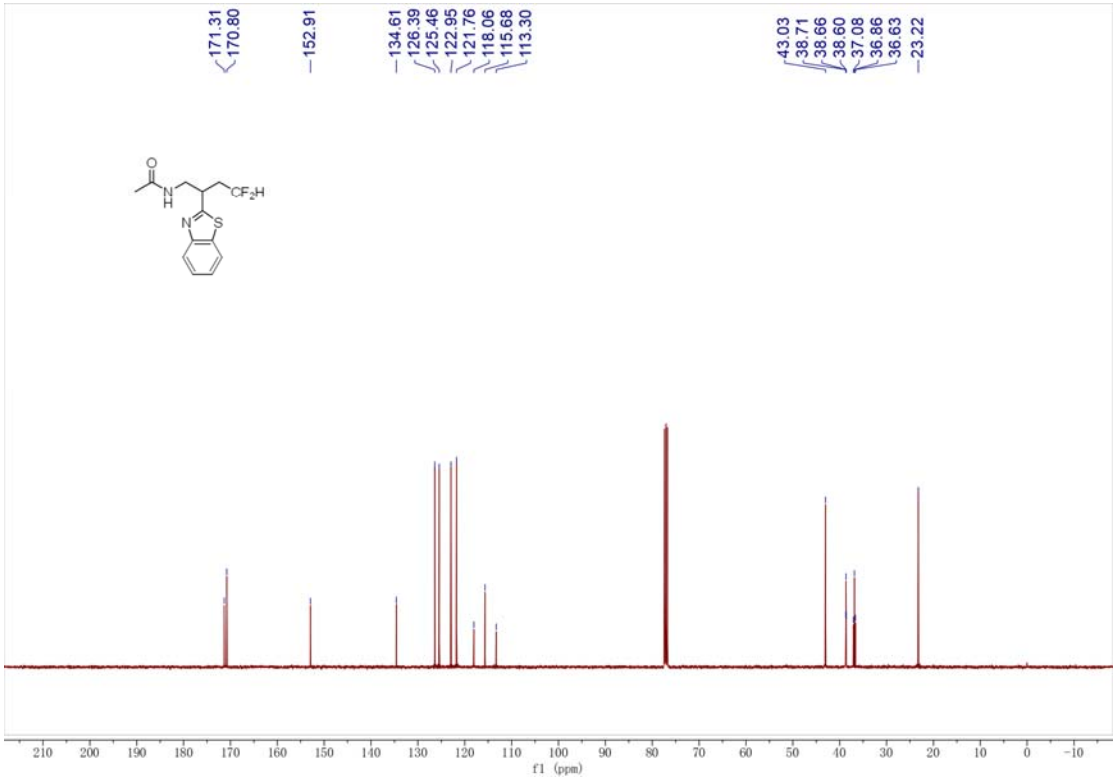


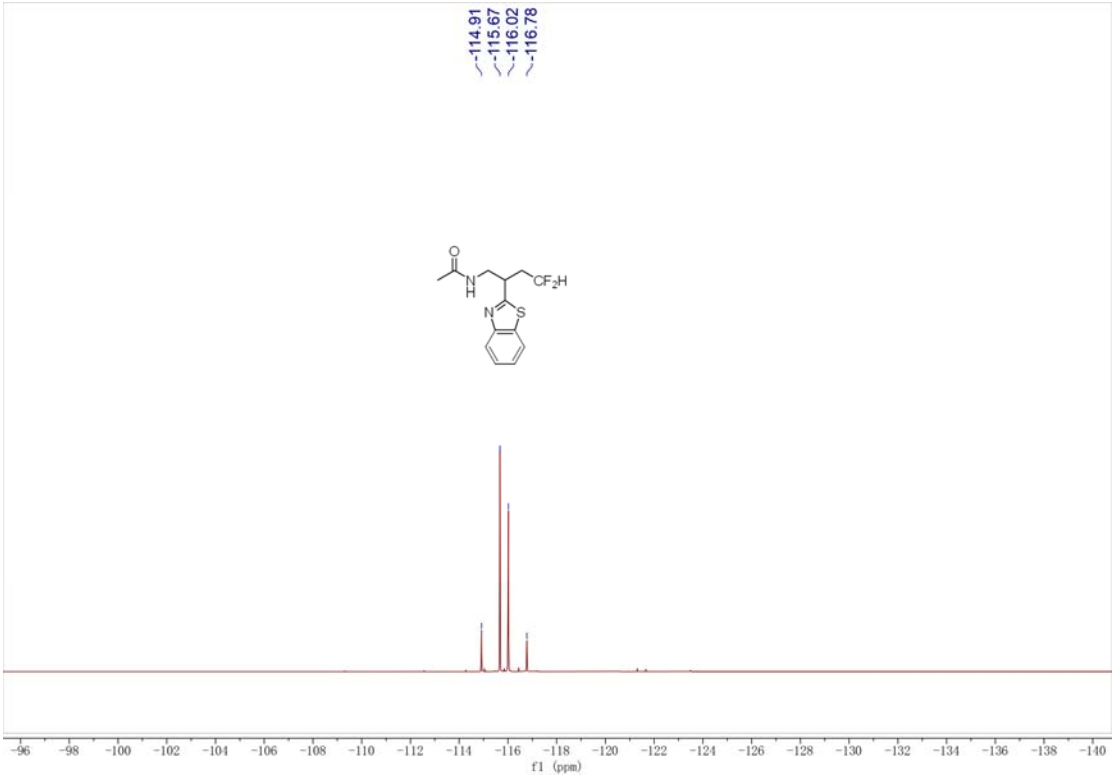



-56.84
N
S
HN
O
CF3
-20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)

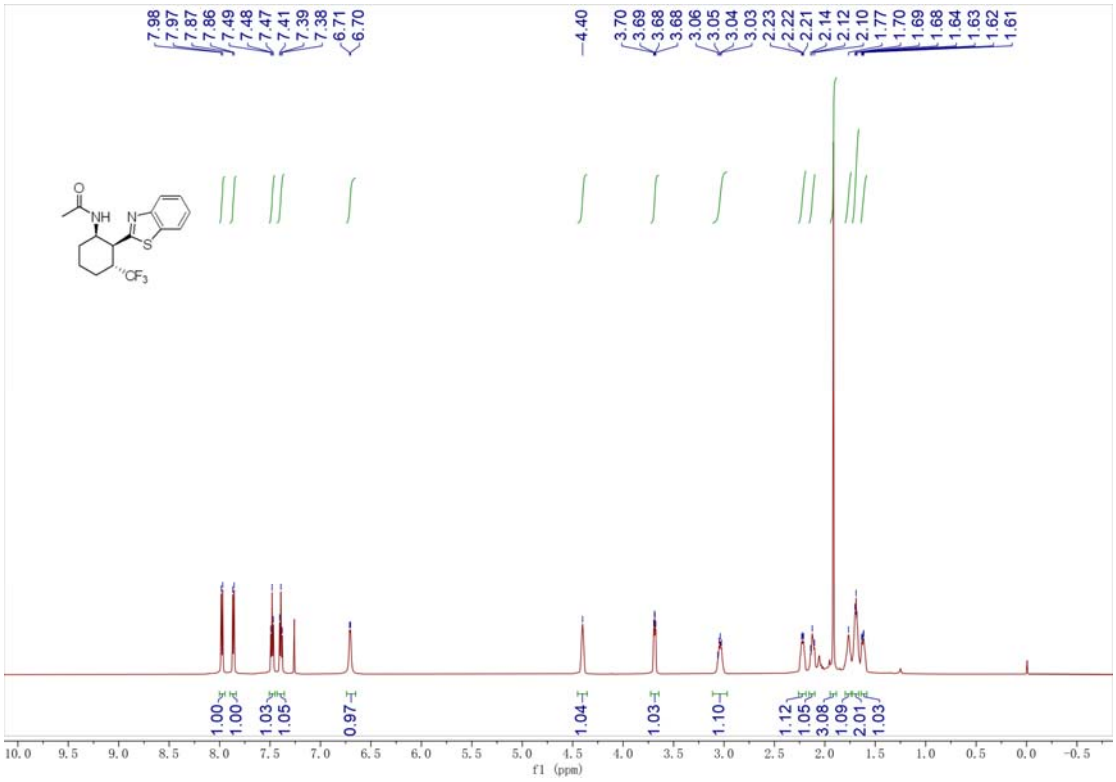
***N*-(2-(benzo[d]thiazol-2-yl)-4,4-difluorobutyl)acetamide (3s)**

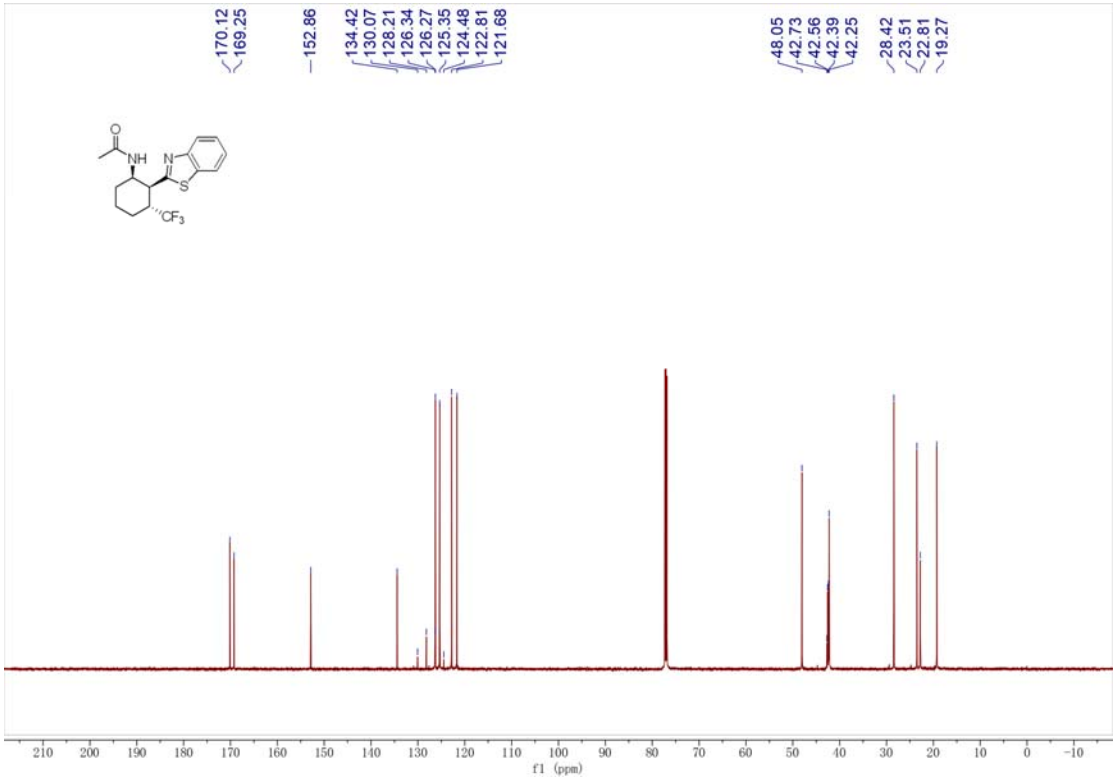


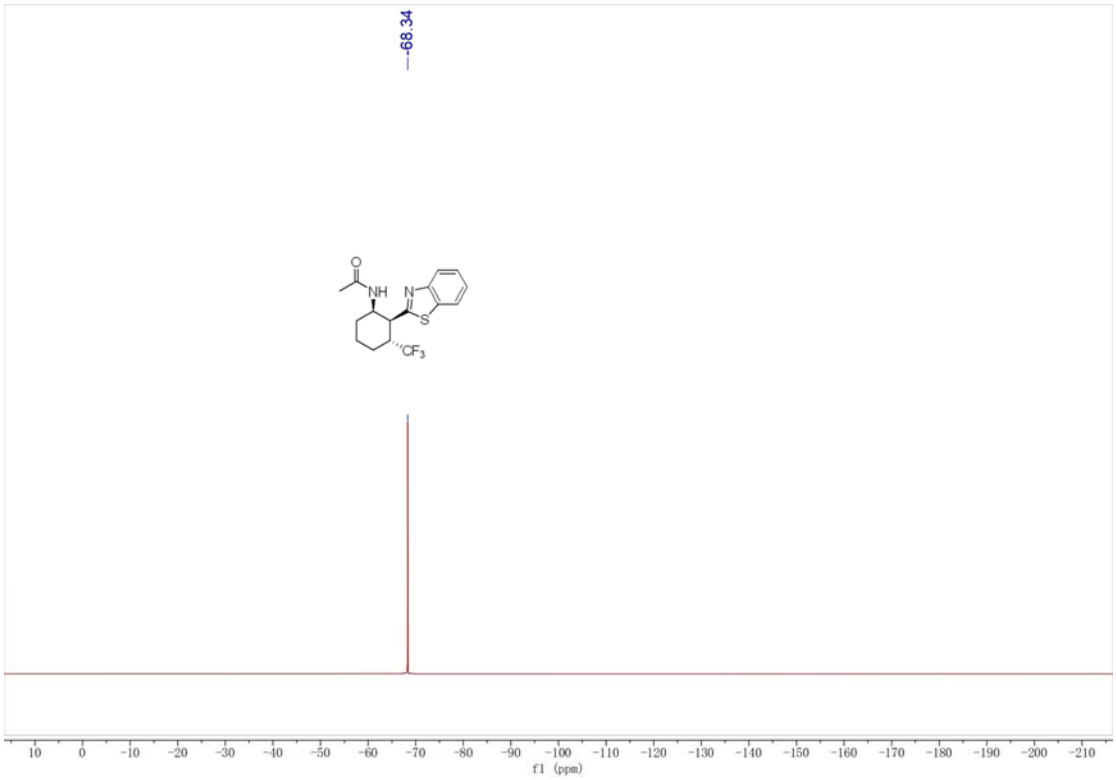


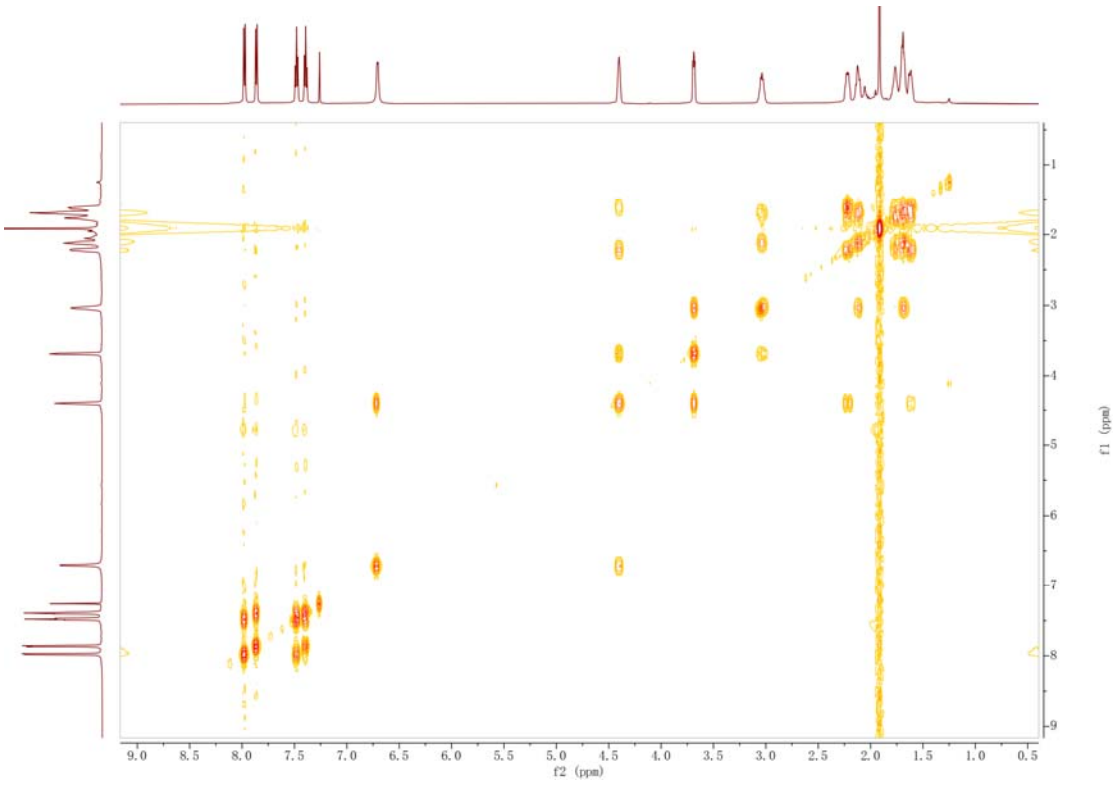

-114.91
-115.67
-116.02
-116.78
O
N
H
CF2H
N
S
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
-136
-138
-140
f1 (ppm)

***N*-((1R,2S,3R)-2-(benzo[d]thiazol-2-yl)-3-(trifluoromethyl)cyclohexyl)acetamide (3u):**

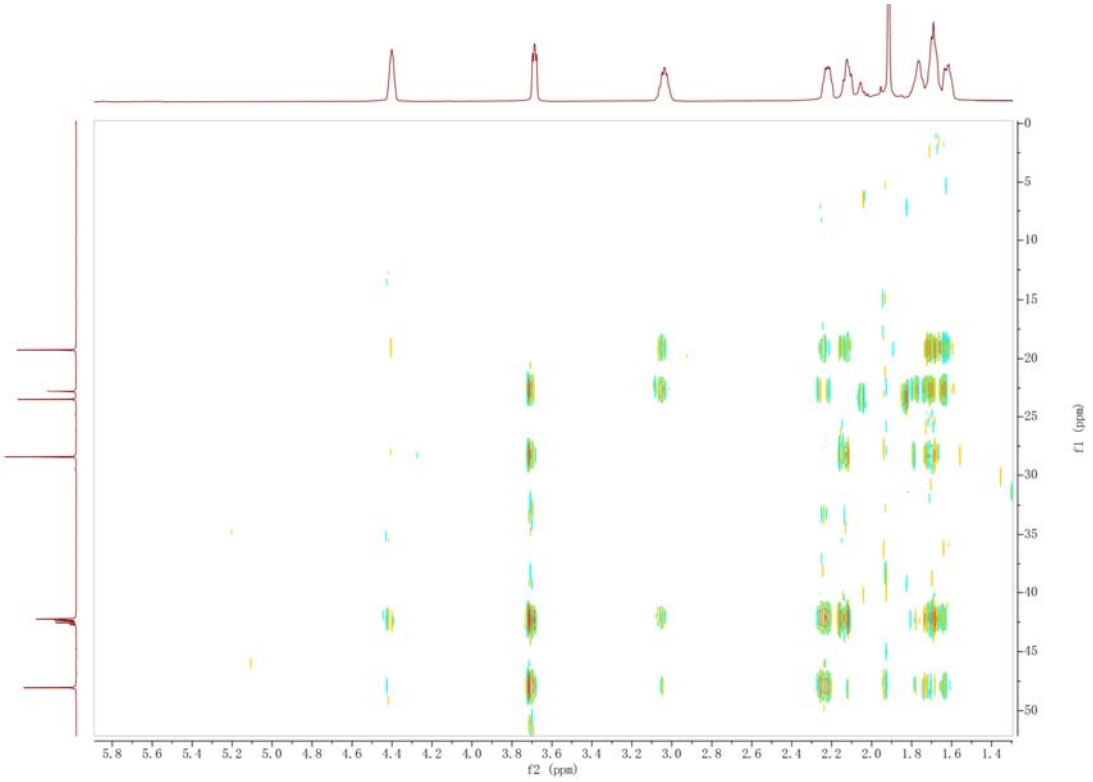




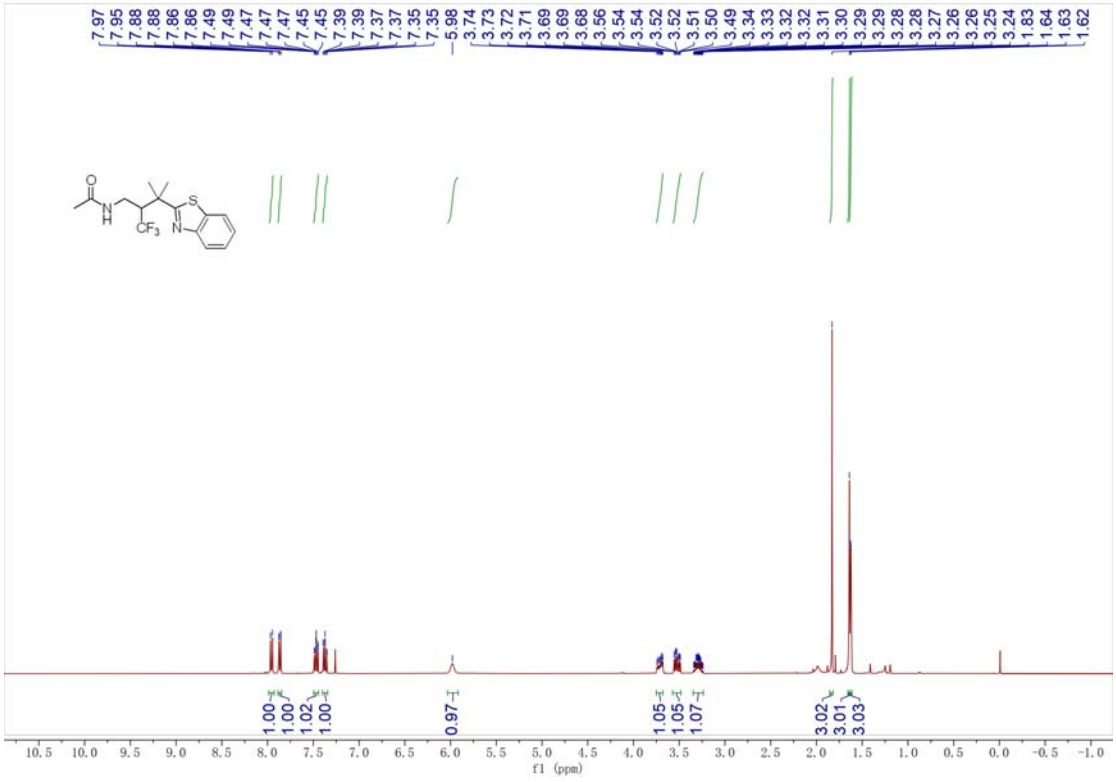

-68.34
NH
N
S
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

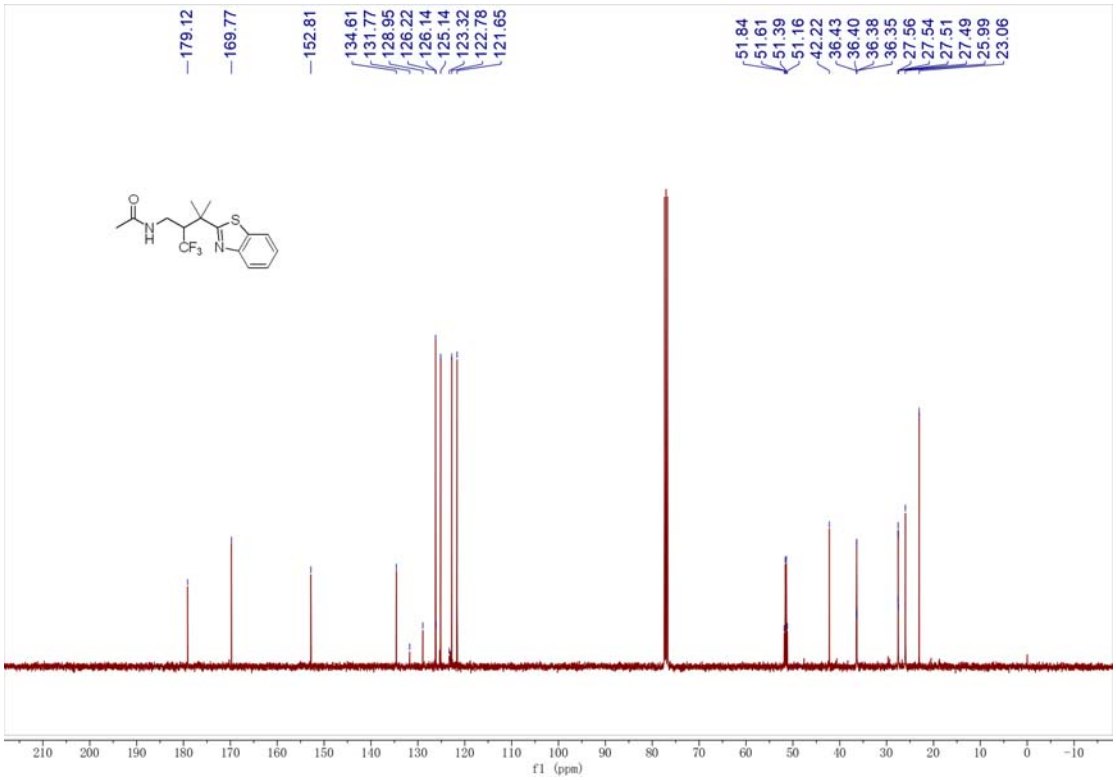

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)
f1 (ppm)

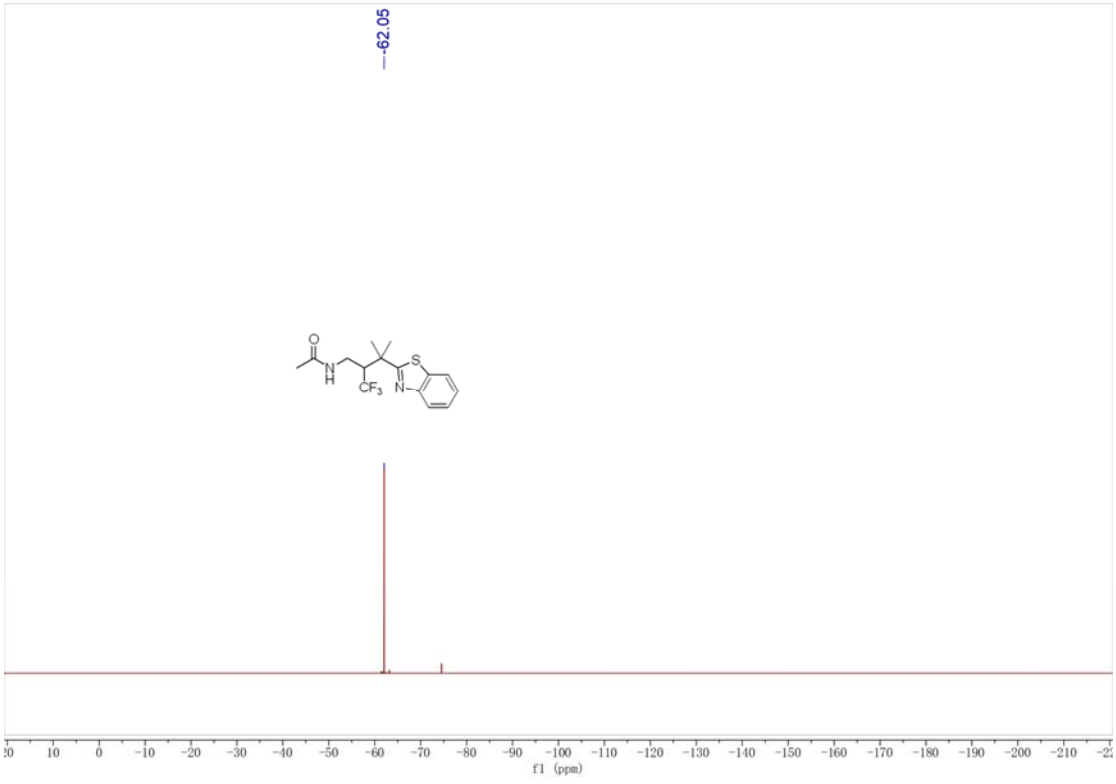
HMBC



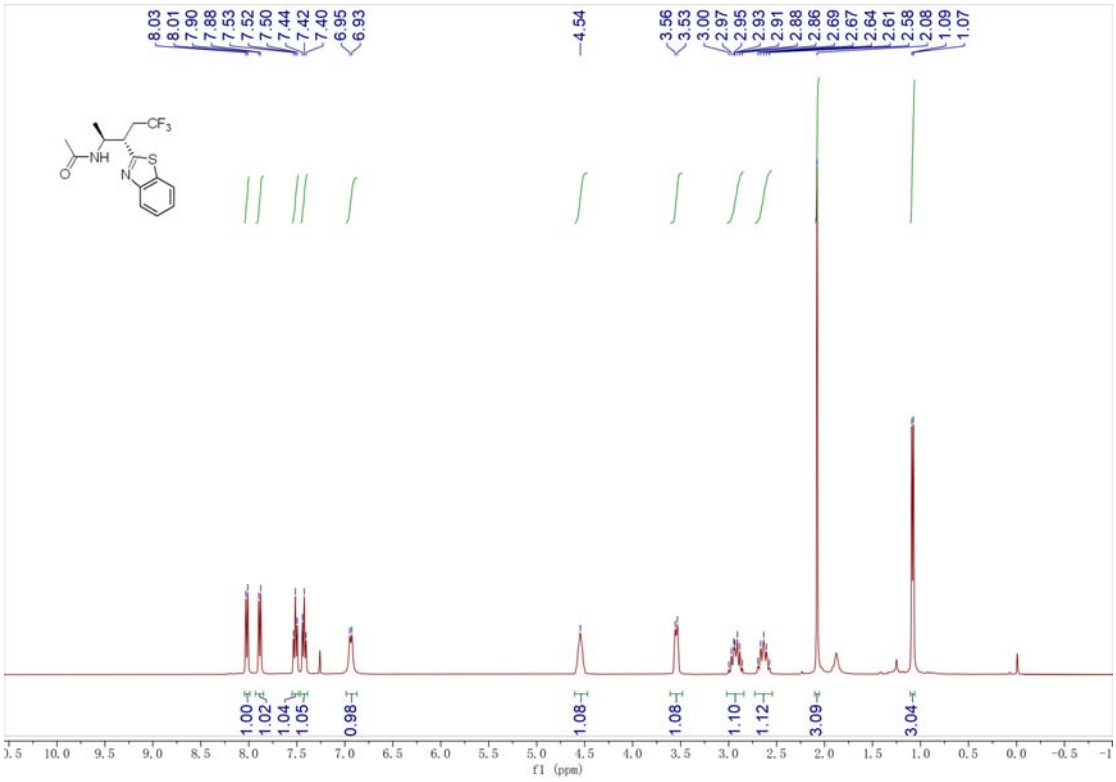
***N*-(3-(benzo[d]thiazol-2-yl)-3-methyl-2-(trifluoromethyl)butyl)acetamide (3t)**

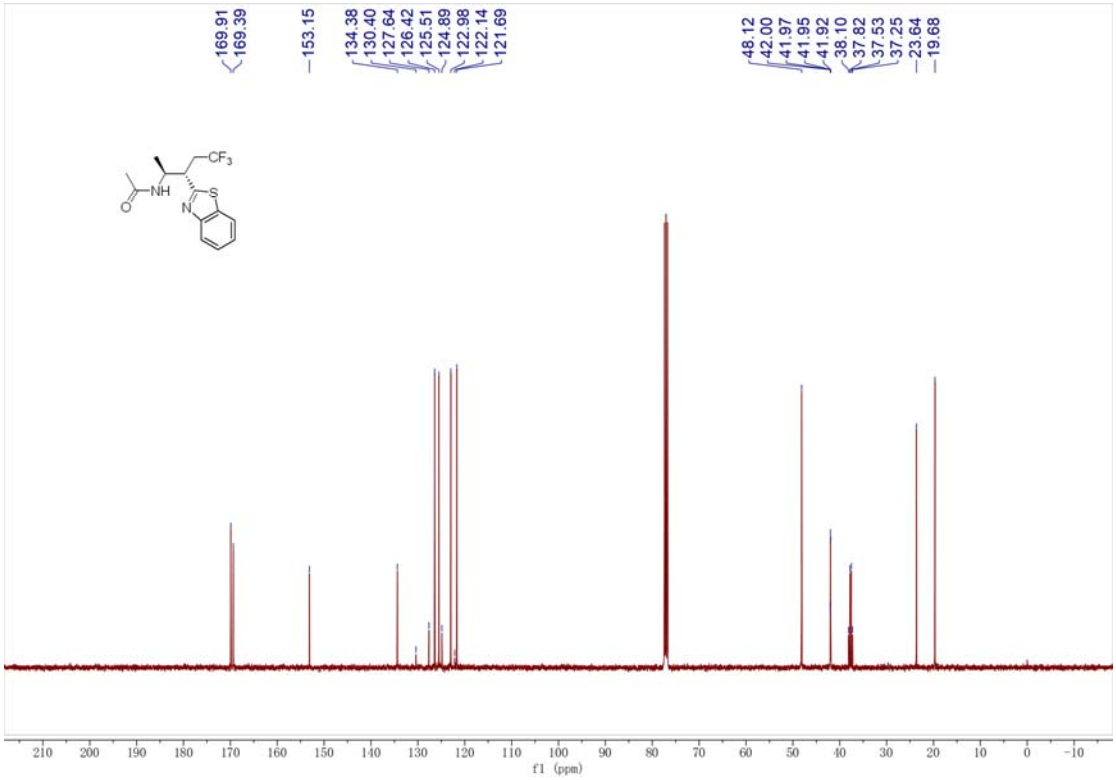


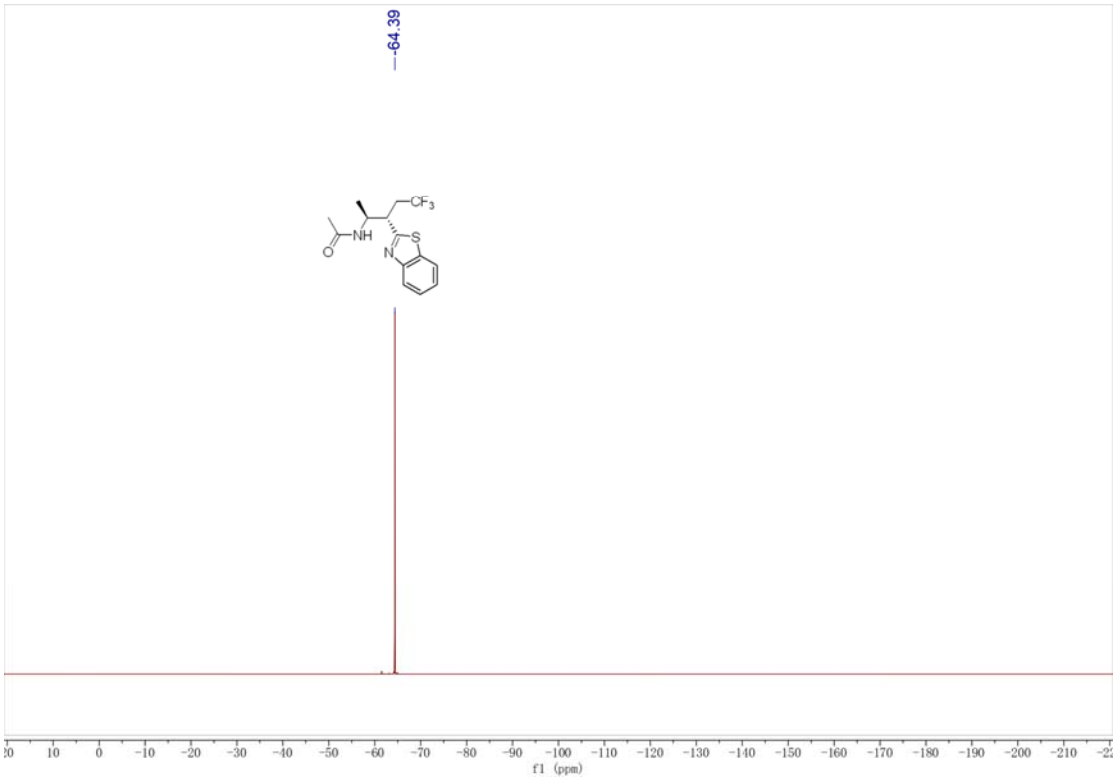

179.12
169.77
152.81
134.61
131.77
128.95
126.22
126.14
125.14
123.32
122.78
121.65
51.84
51.61
51.39
51.16
42.22
36.43
36.40
36.38
36.35
27.56
27.54
27.51
27.49
25.99
23.06
f1 (ppm)


-62.05
f1 (ppm)

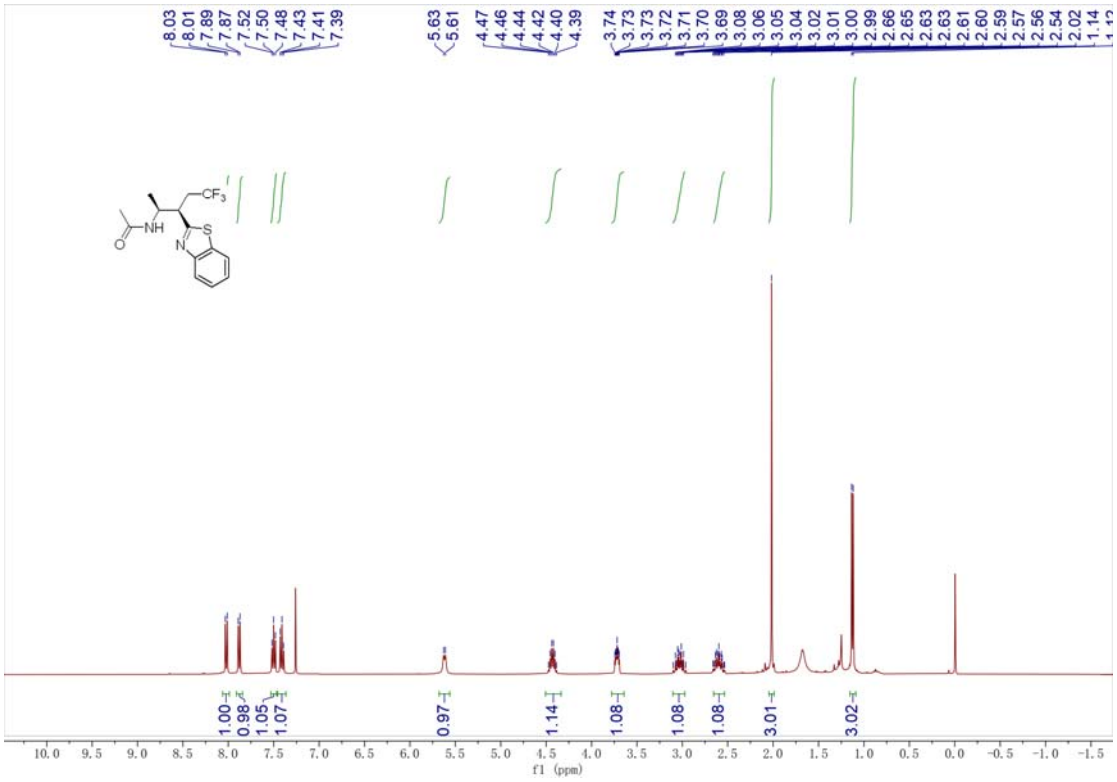
***N*-((2S,3S)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentan-2-yl)acetamide (3v)**

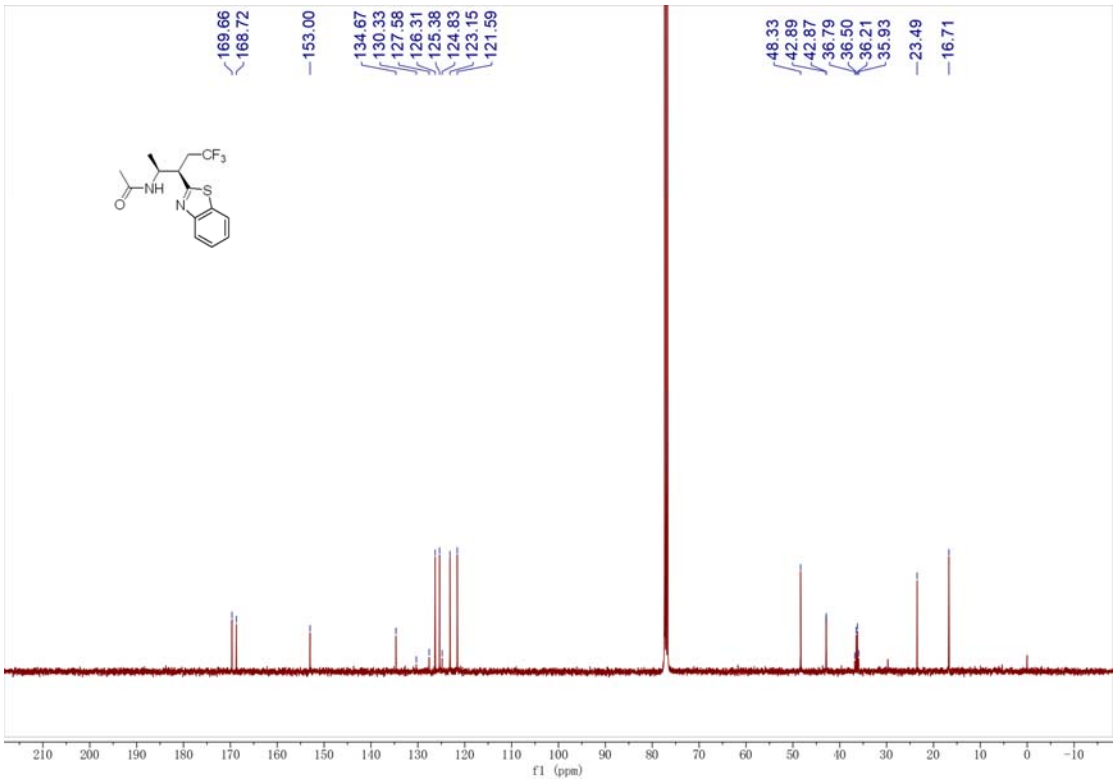


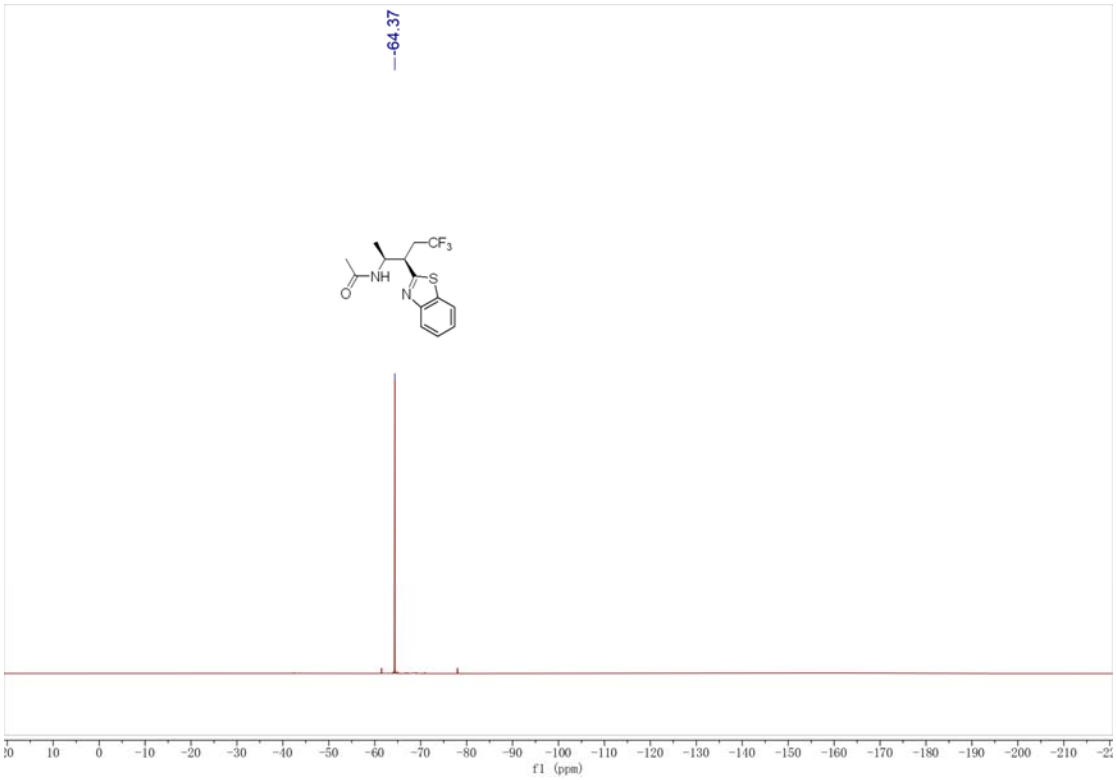



-64.39
CF3
NH
O
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

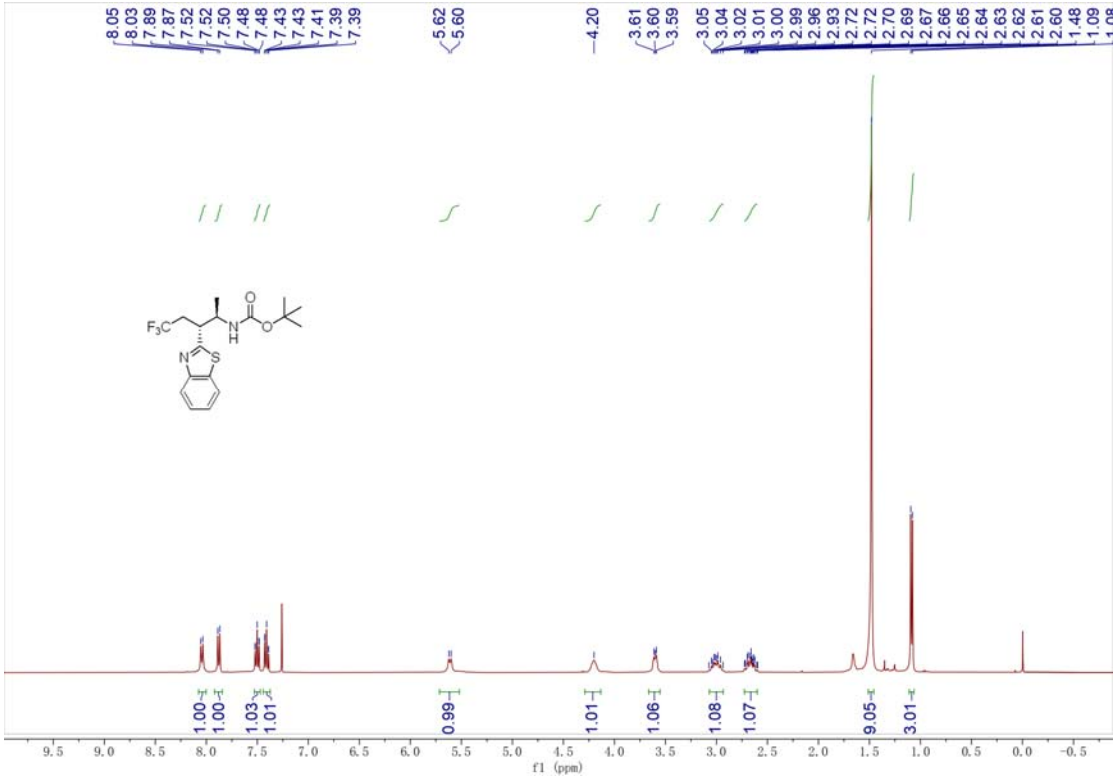
***N*-((2S,3R)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentan-2-yl)acetamide (3v2)**

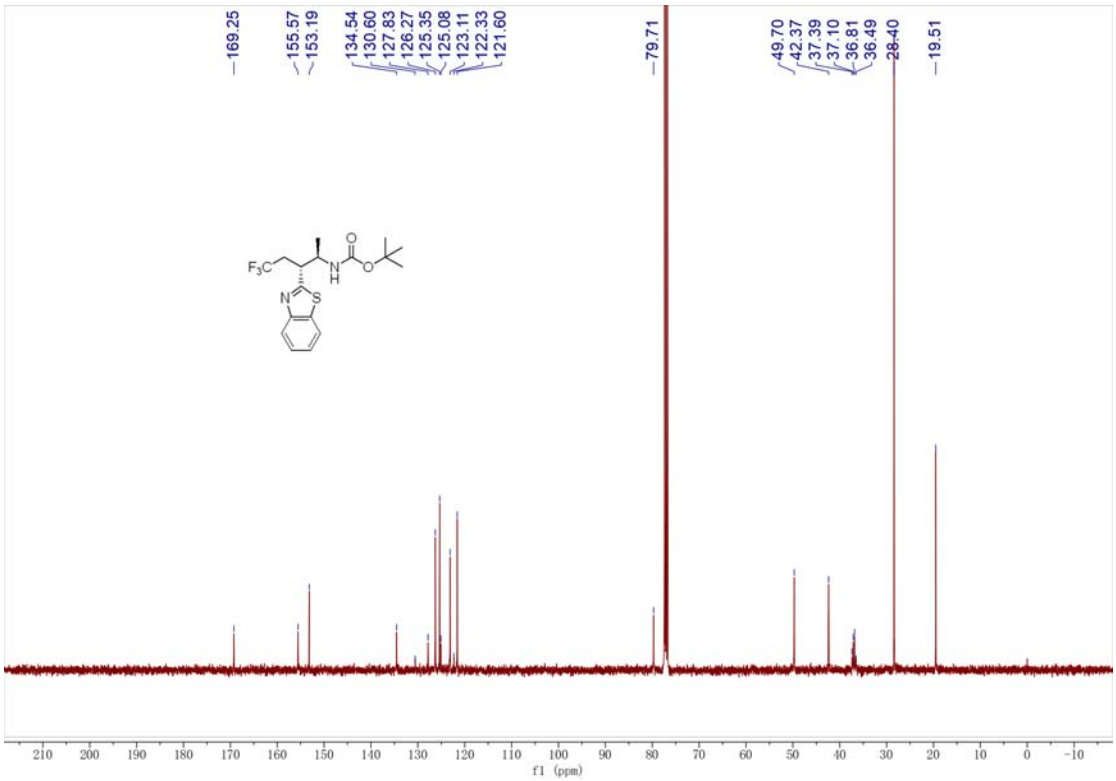


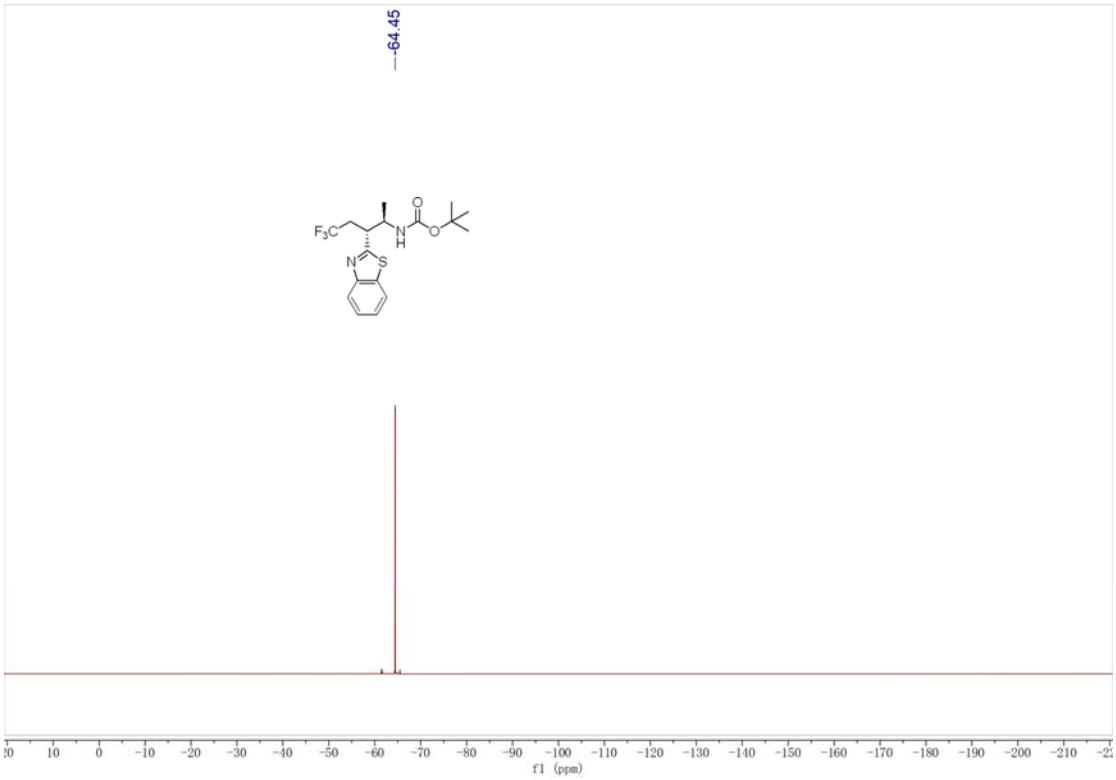



-64.37
CF3
NH
O
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

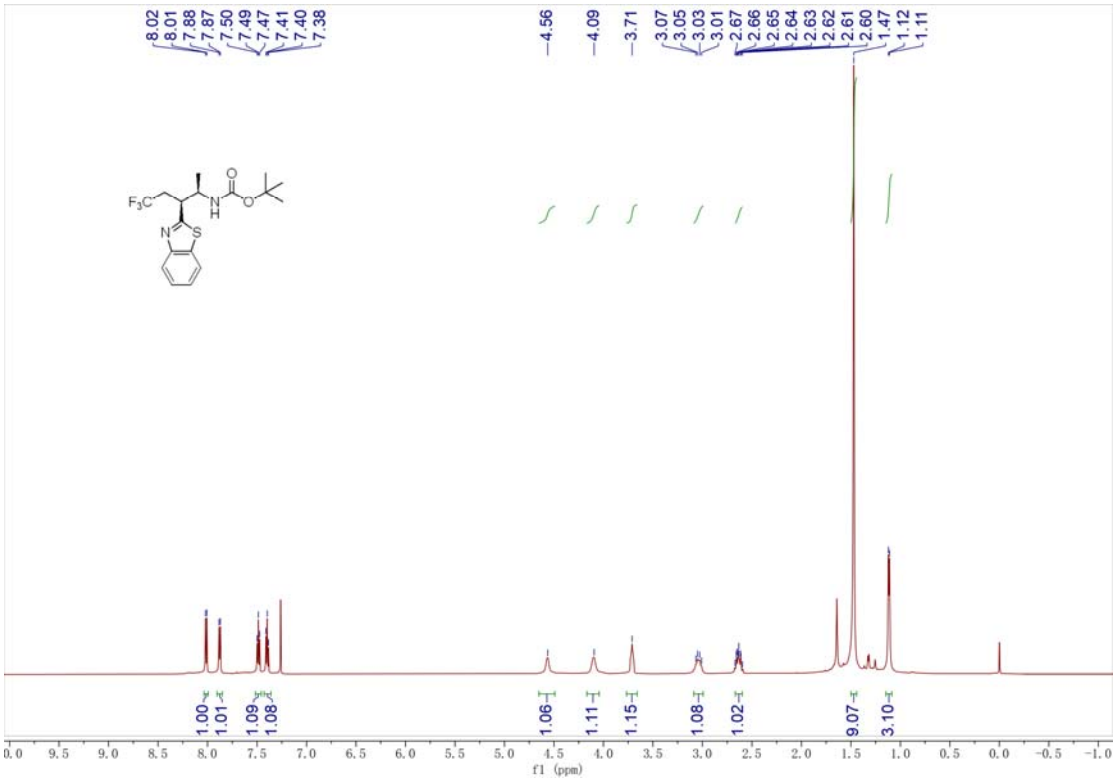
Tert-butyl ((2R,3R)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentan-2-yl)carbamate (3v')

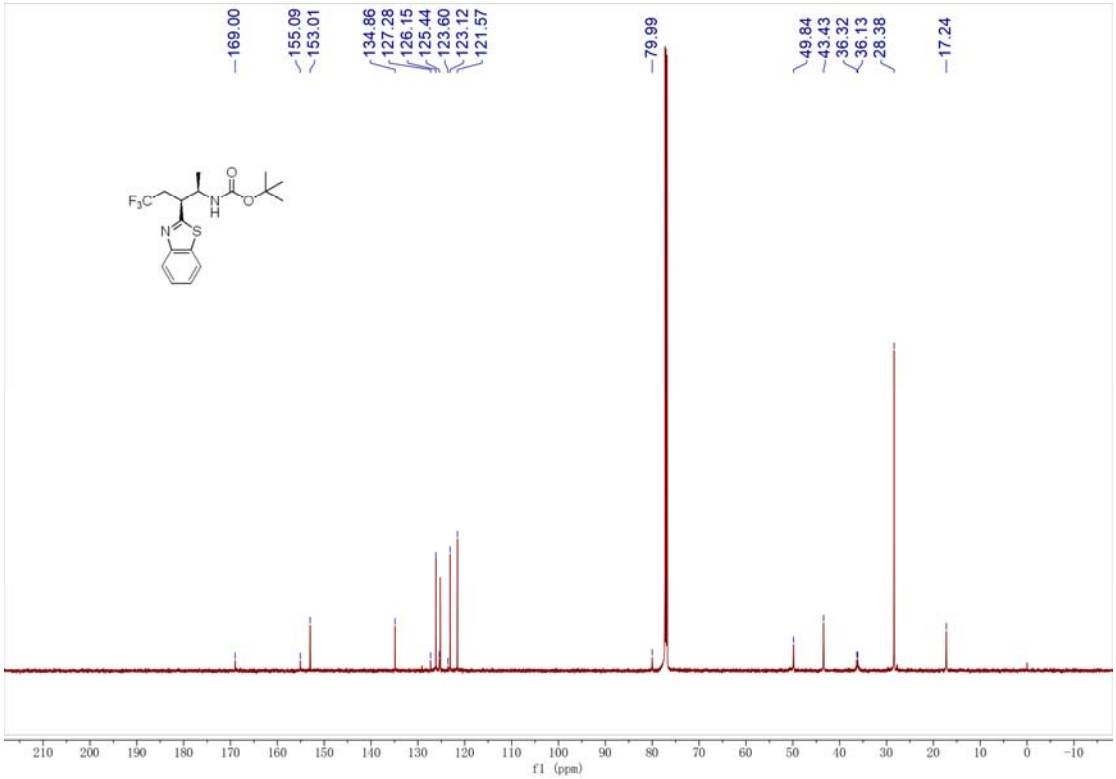


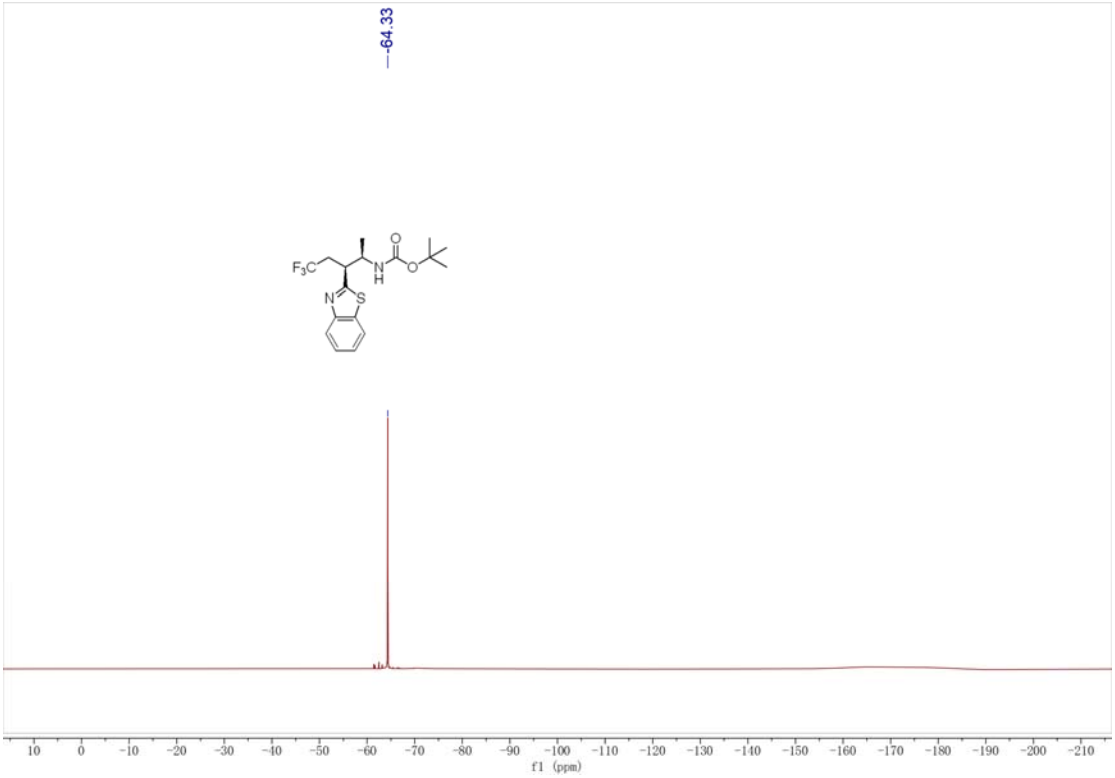



-64.45
F3C
N
H
O
O
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

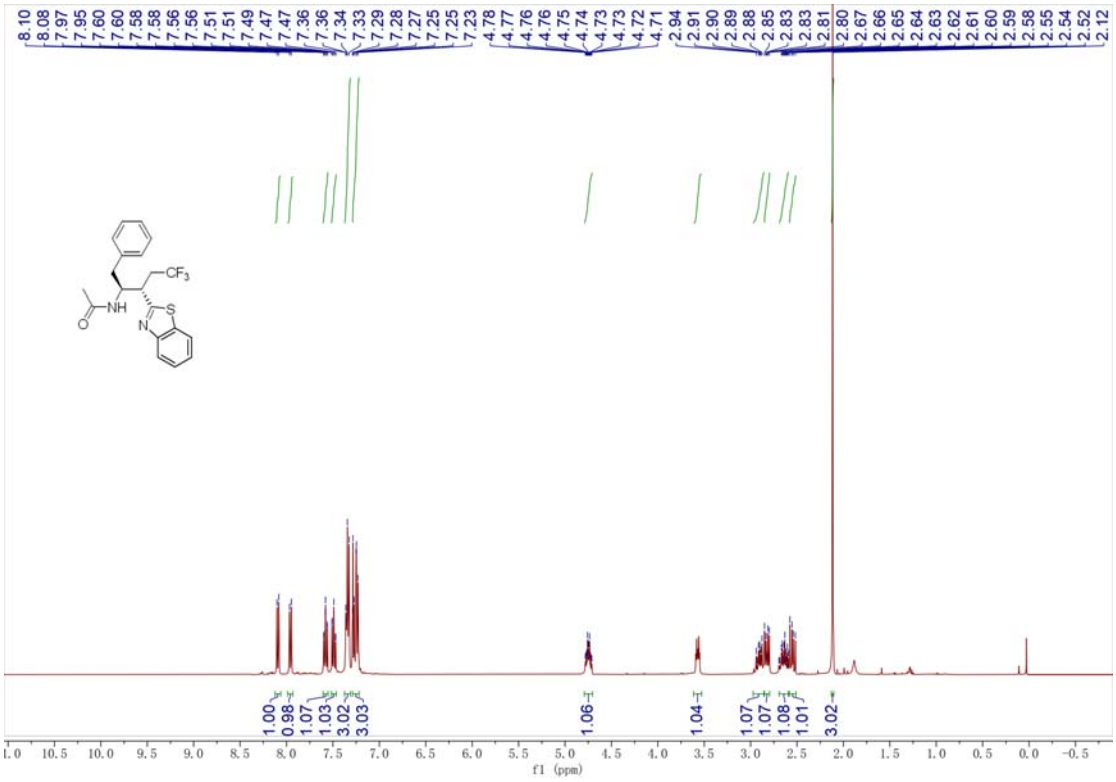
tert-butyl ((2R,3S)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoropentan-2-yl)carbamate (3v'2)

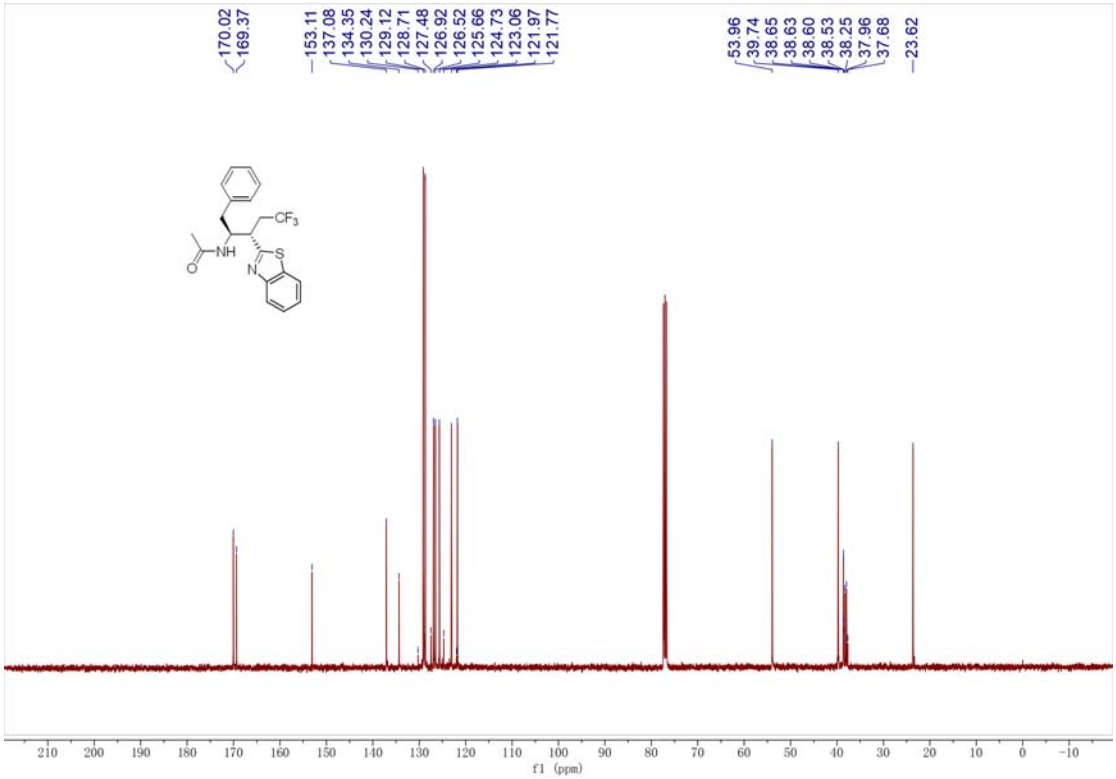


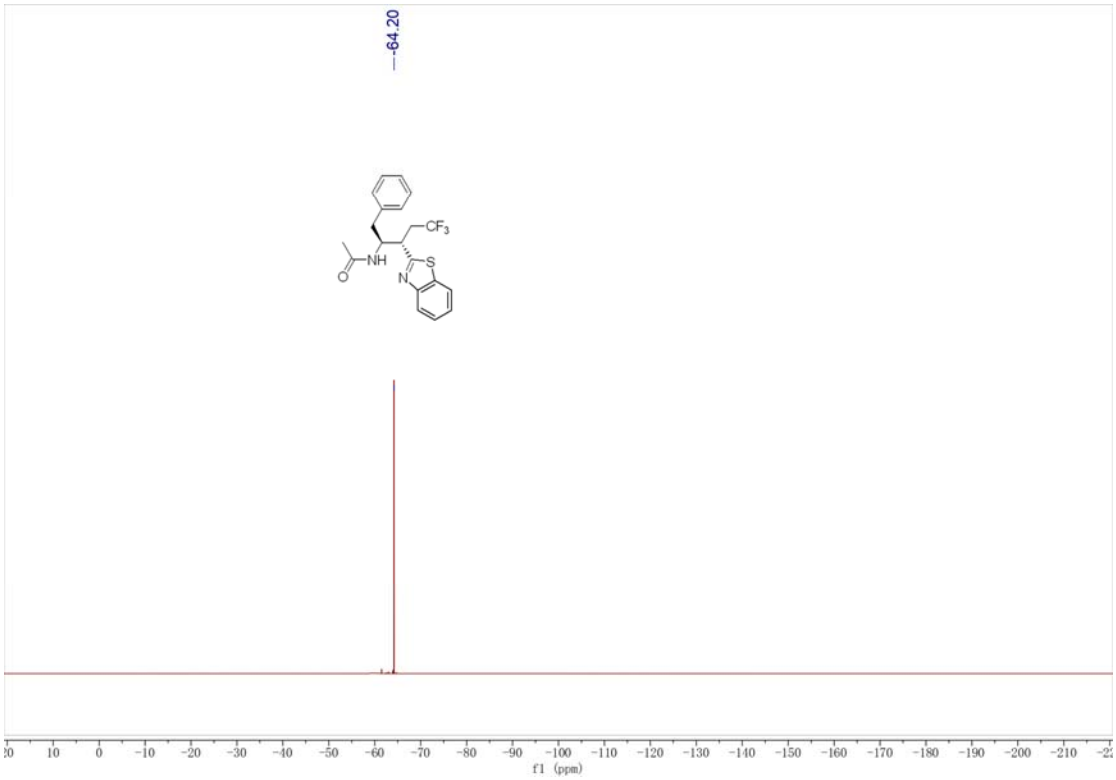



-64.33
F3C
N
H
O
O
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

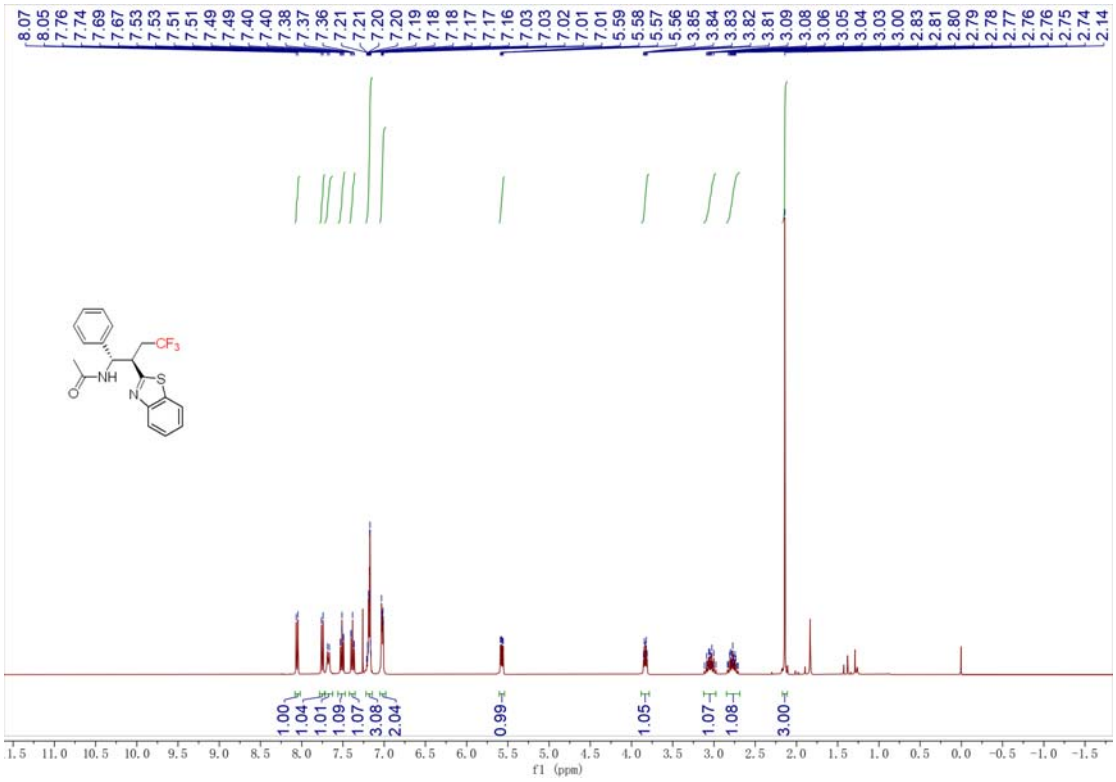
***N*-((2S,3S)-3-(benzo[d]thiazol-2-yl)-5,5,5-trifluoro-1-phenylpentan-2-yl)acetamide (3w)**

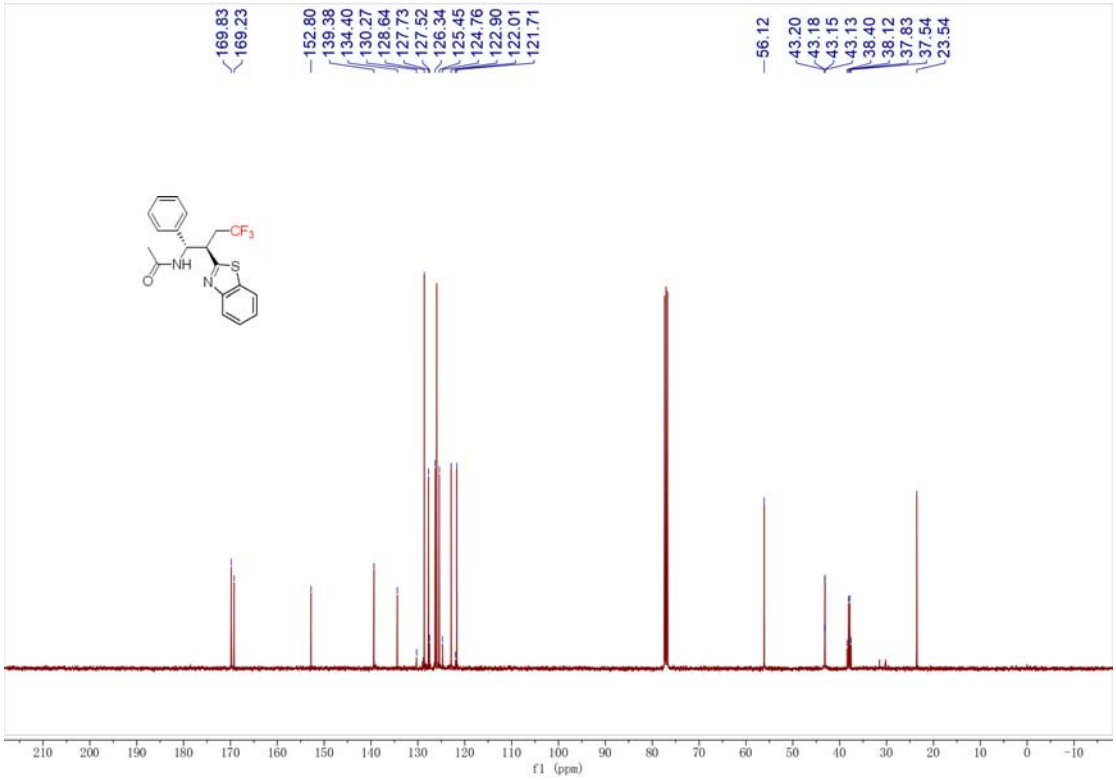


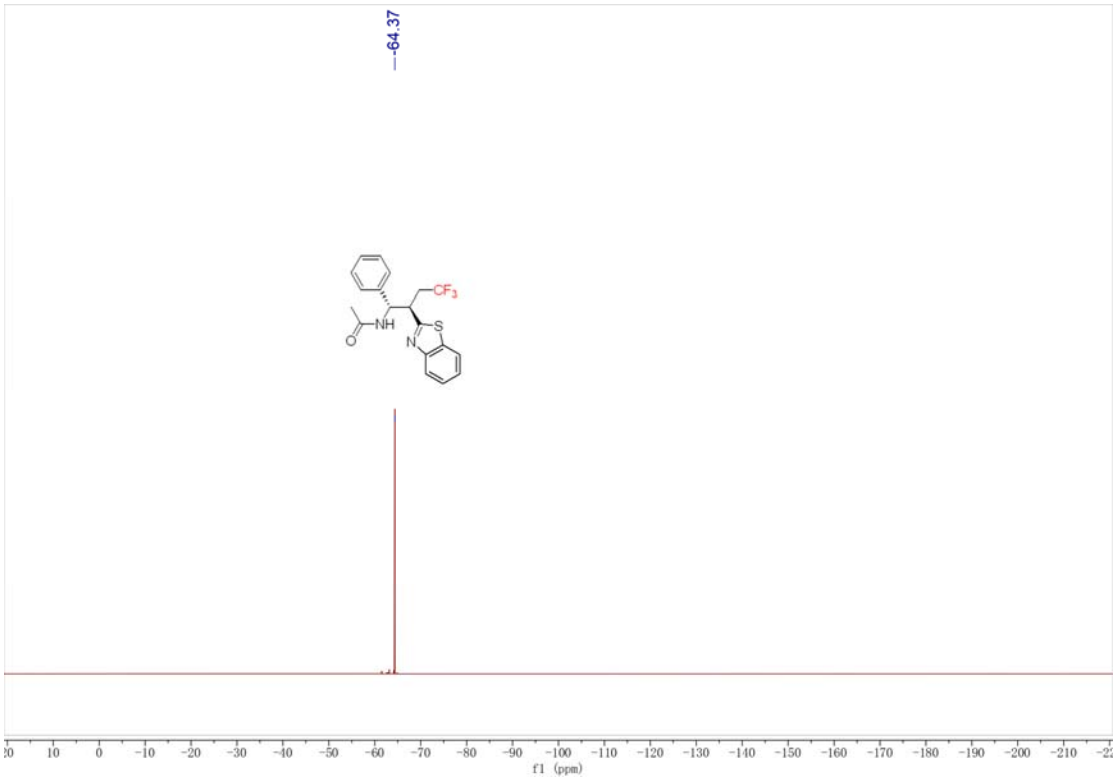



-64.20
CF3
NH
O
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

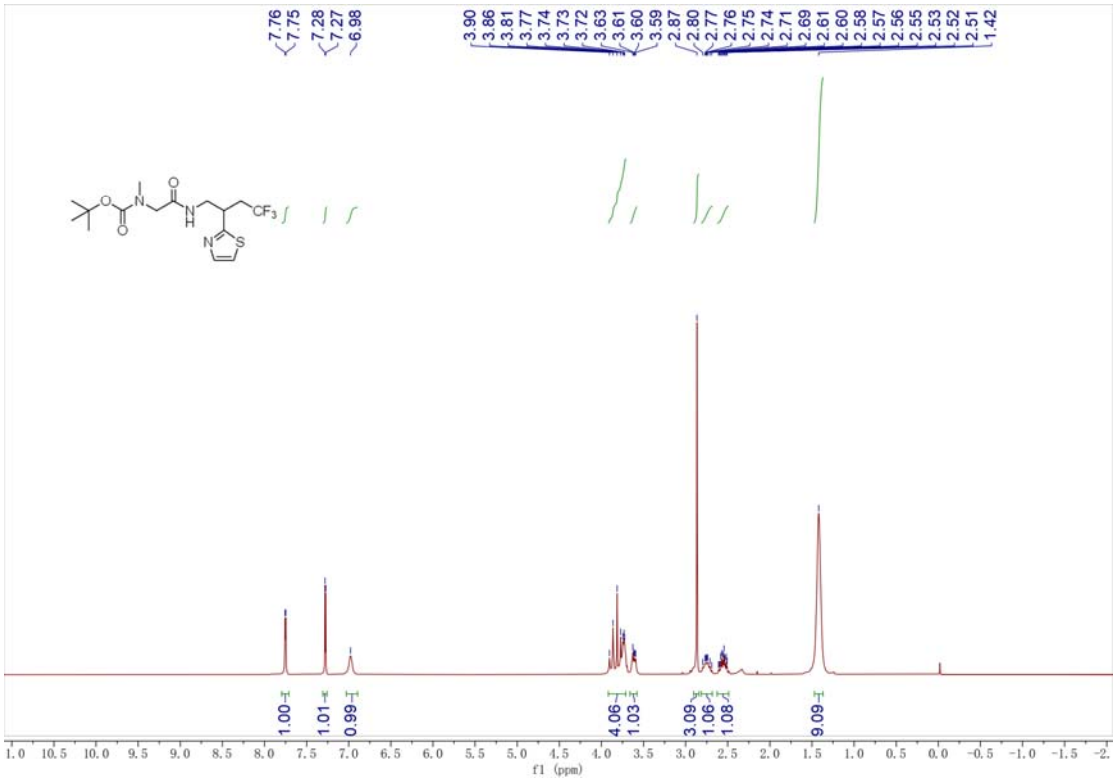
***N*-((1S,2R)-2-(benzo[d]thiazol-2-yl)-4,4,4-trifluoro-1-phenylbutyl)acetamide (3x)**

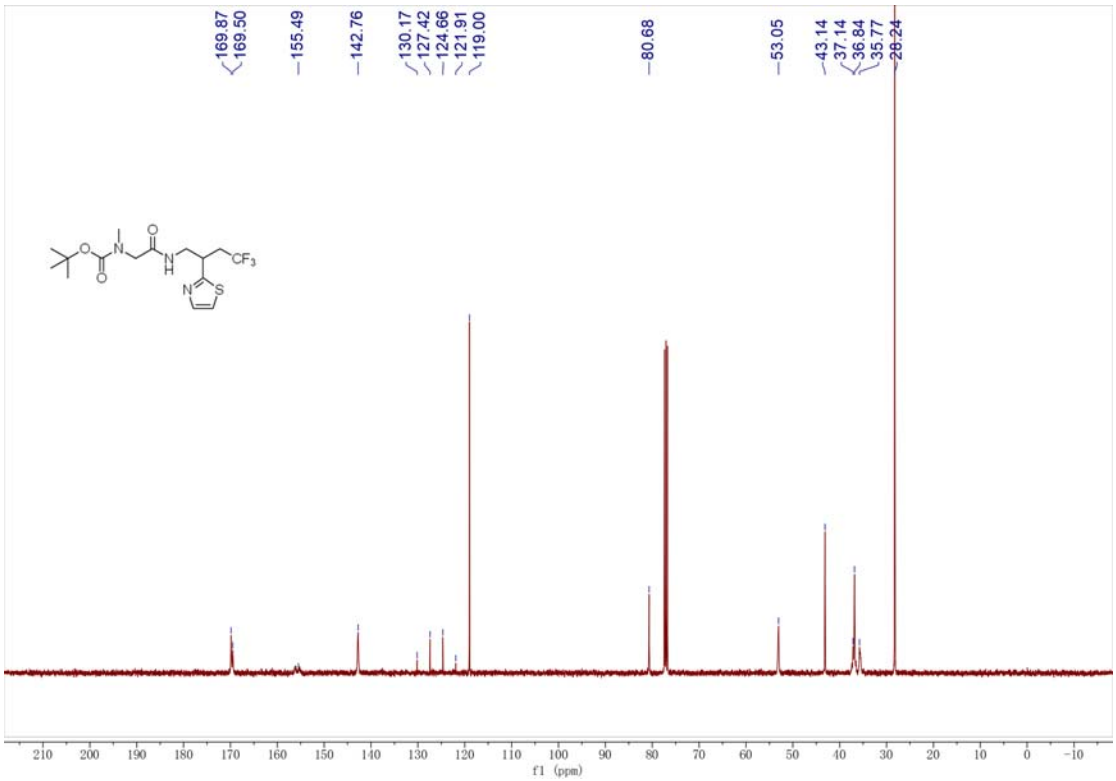


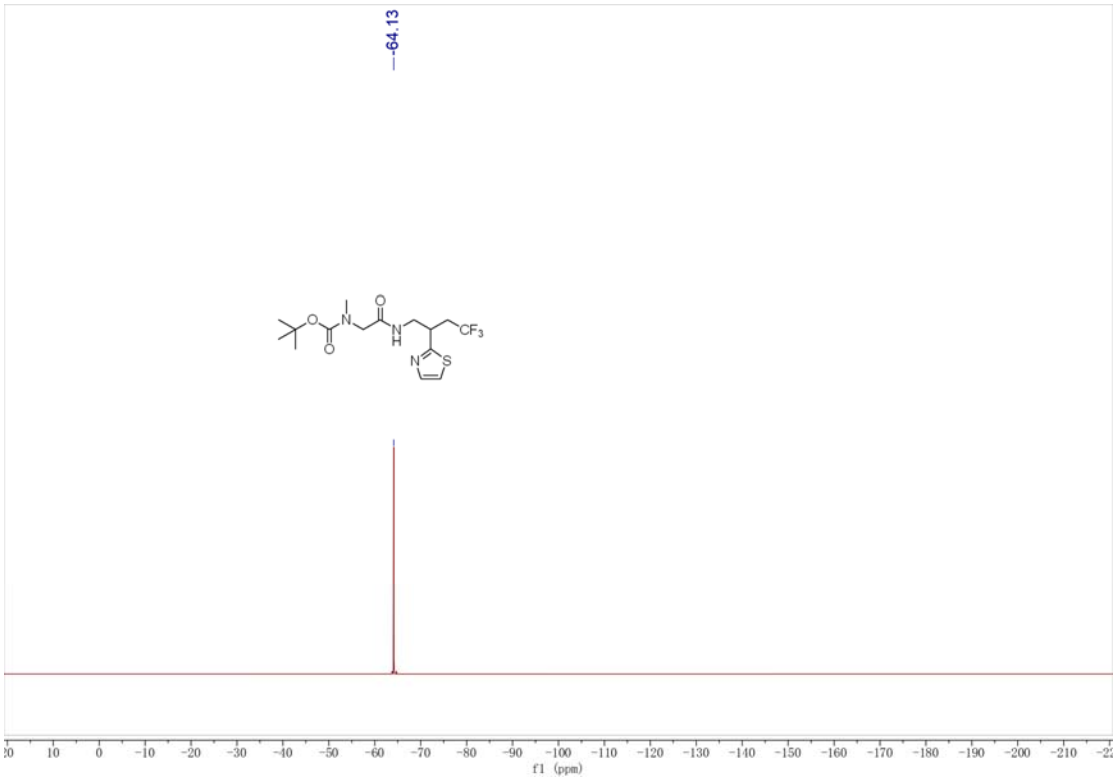



-64.37
CF3
NH
O
S
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

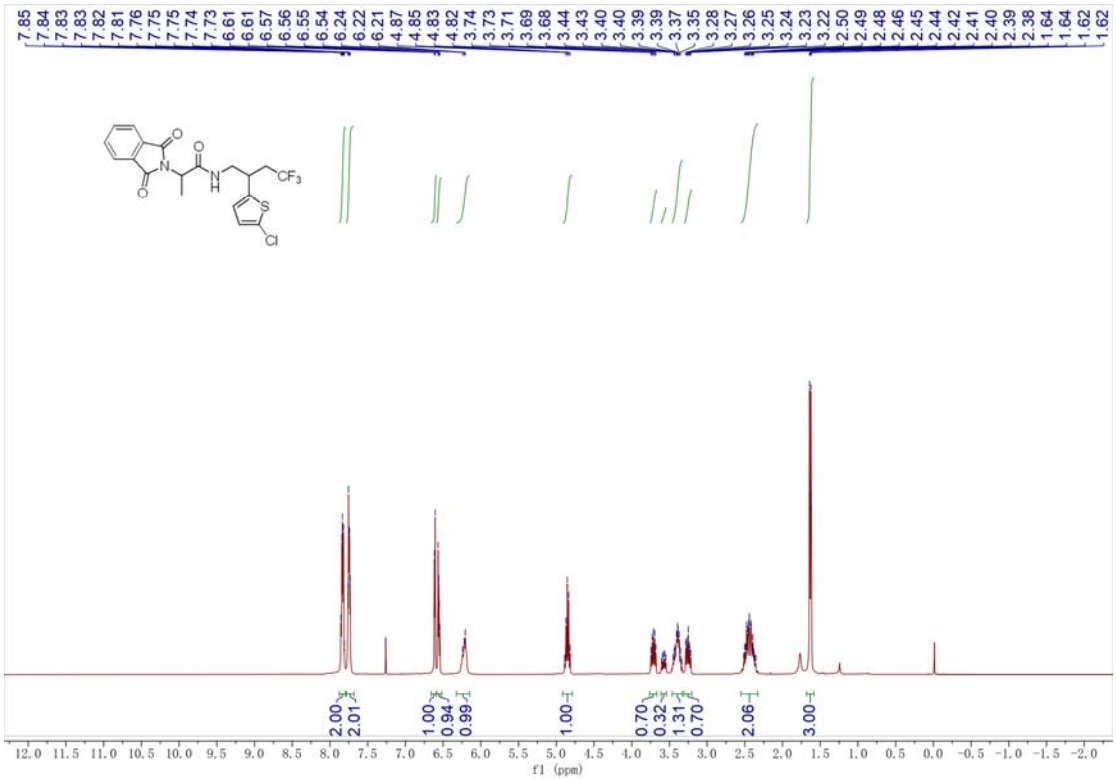
tert-butyl methyl(2-oxo-2-((4,4,4-trifluoro-2-(thiazol-2-yl)butyl)amino)ethyl)carbamate (3y)

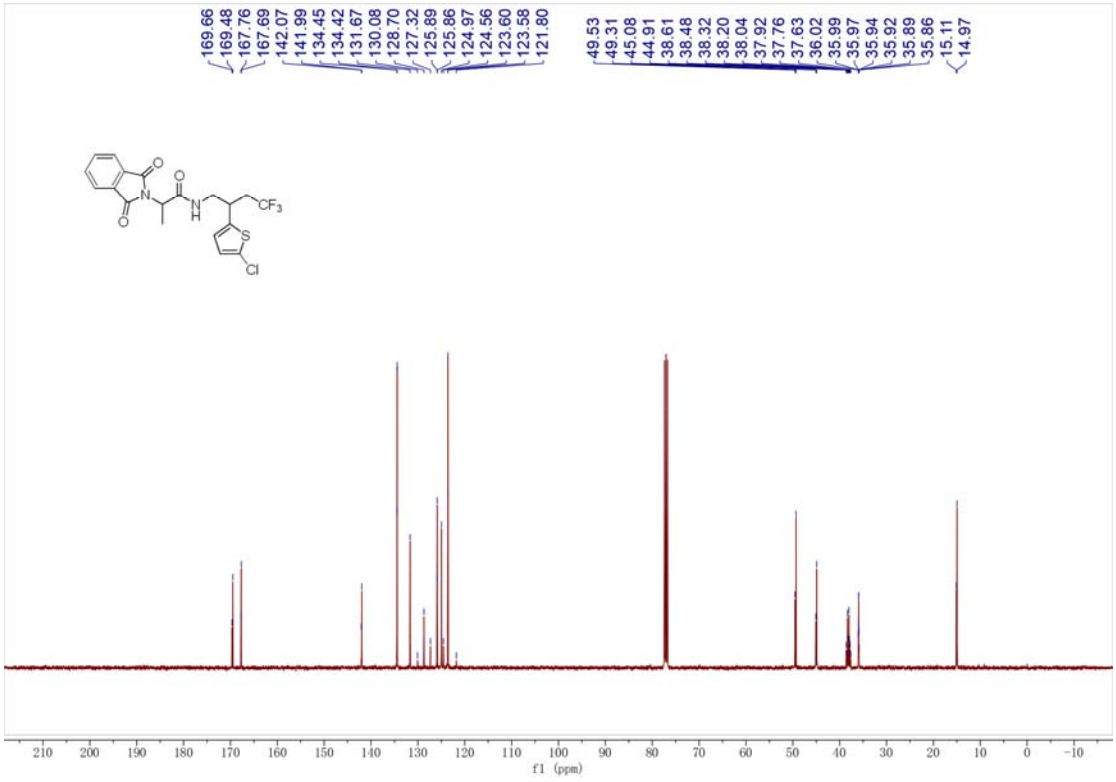


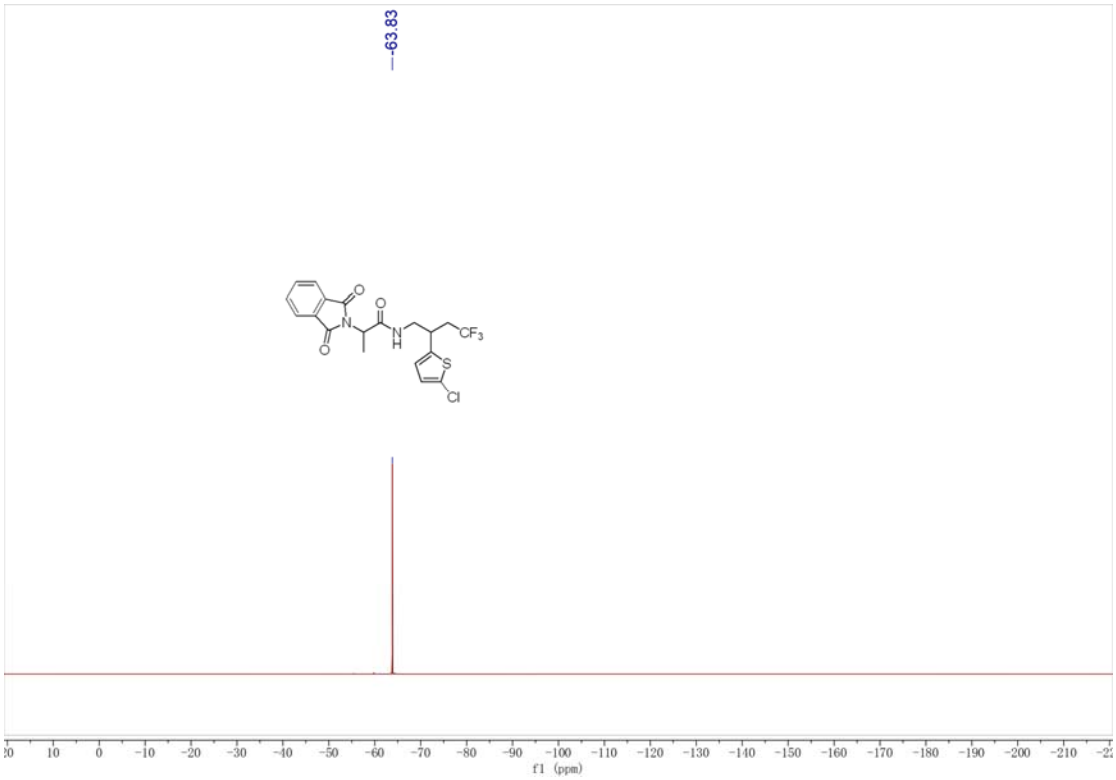



-64.13
CF3
N
S
f1 (ppm)

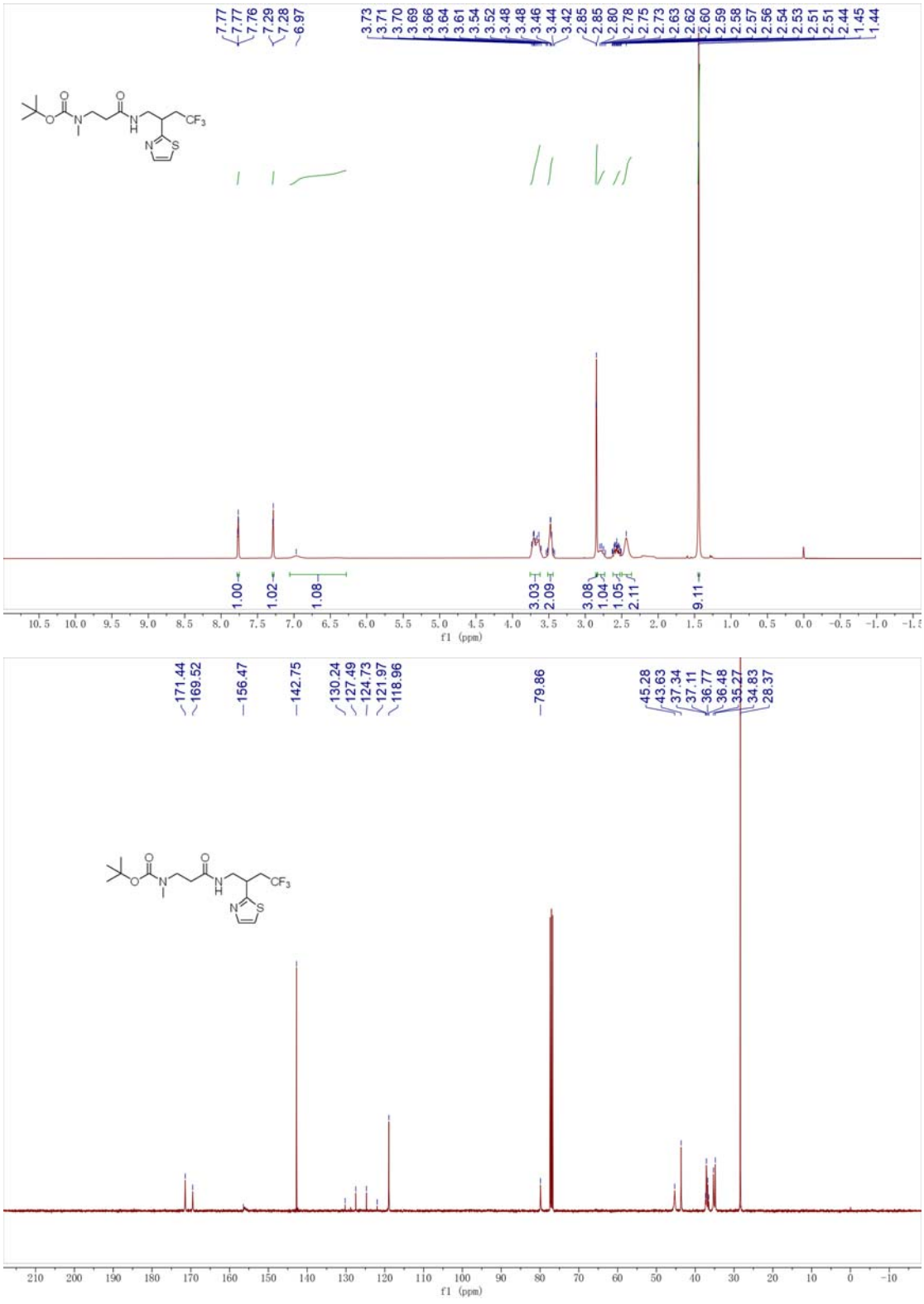
***N*-(2-(5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)-2-(1,3-dioxoisoindolin-2-yl)propenamide (3z)**

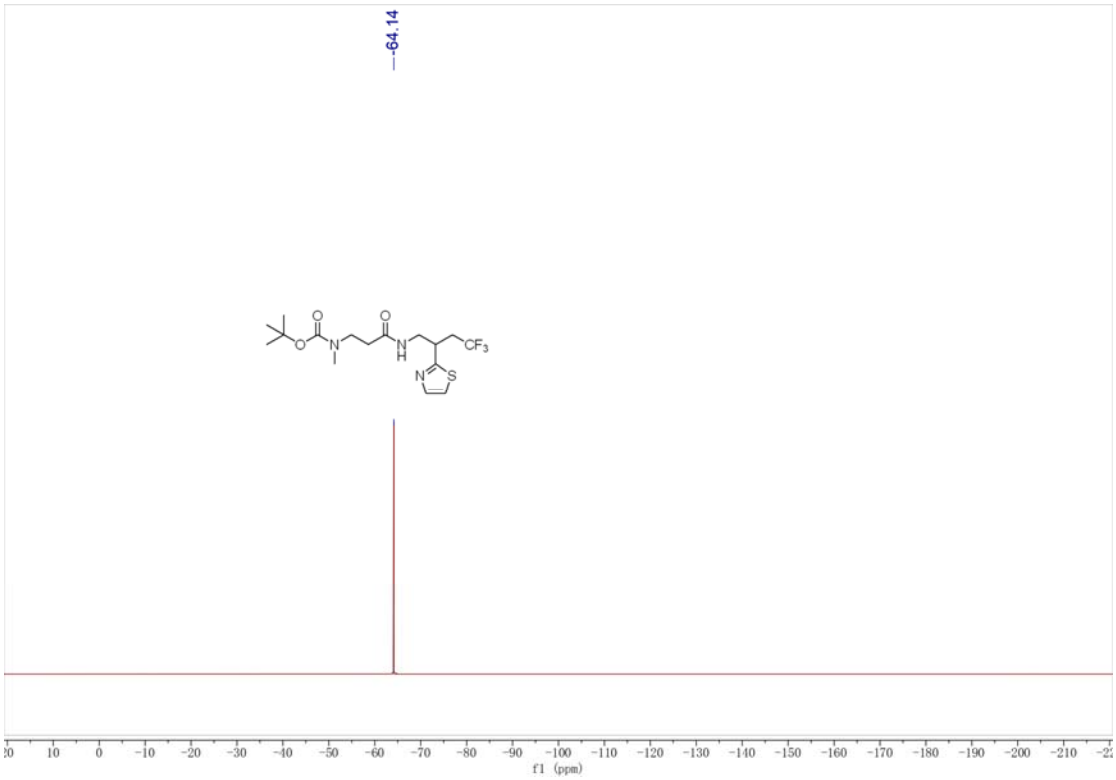




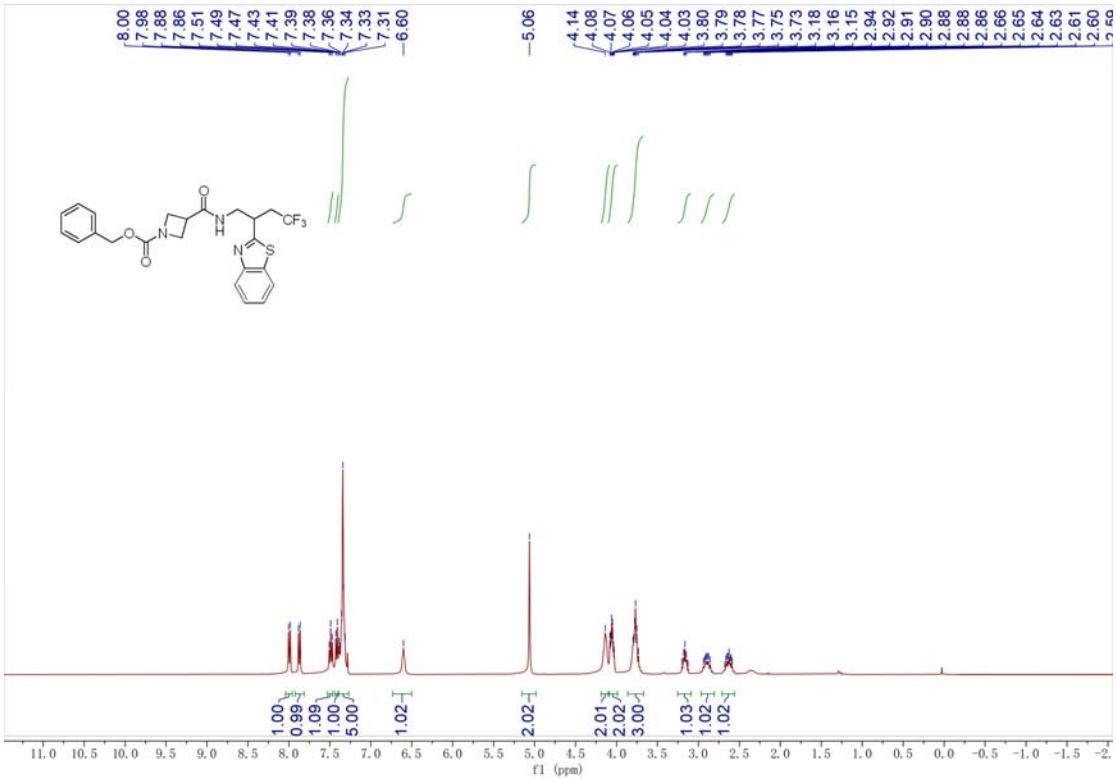

-63.83
O
O
N
O
NH
CF3
S
Cl
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

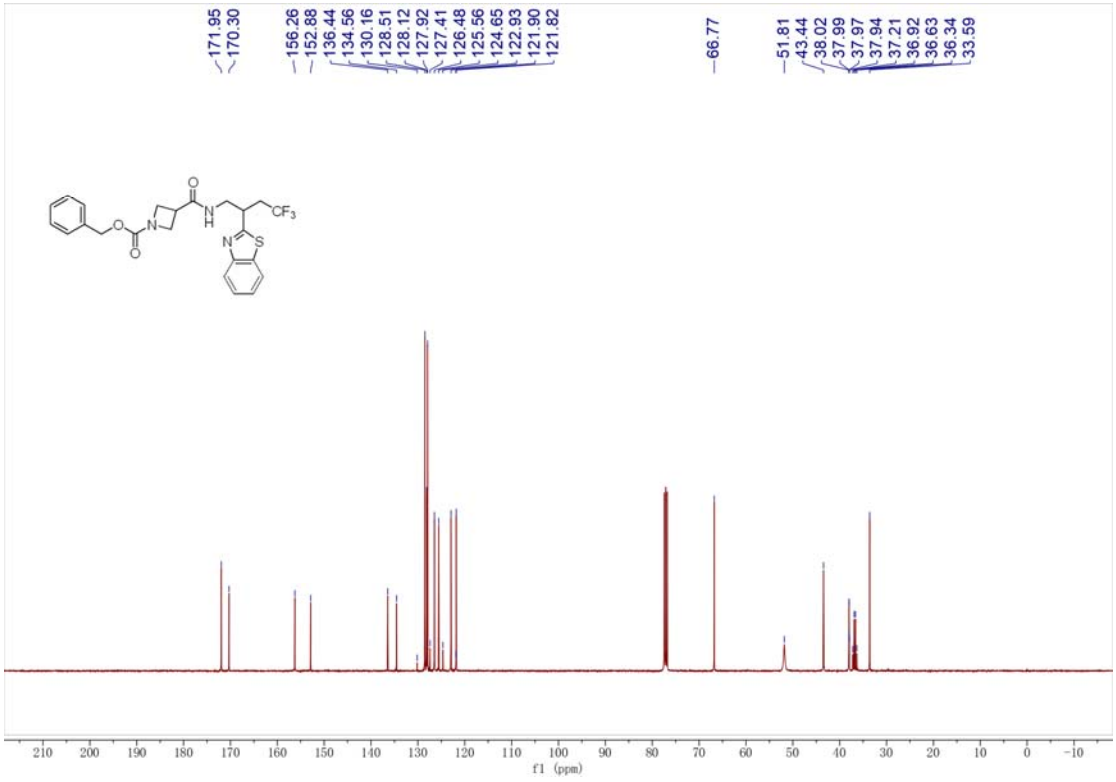
tert-butyl methyl(3-oxo-3-((4,4,4-trifluoro-2-(thiazol-2-yl)butyl)amino)propyl)carbamate (3z1)

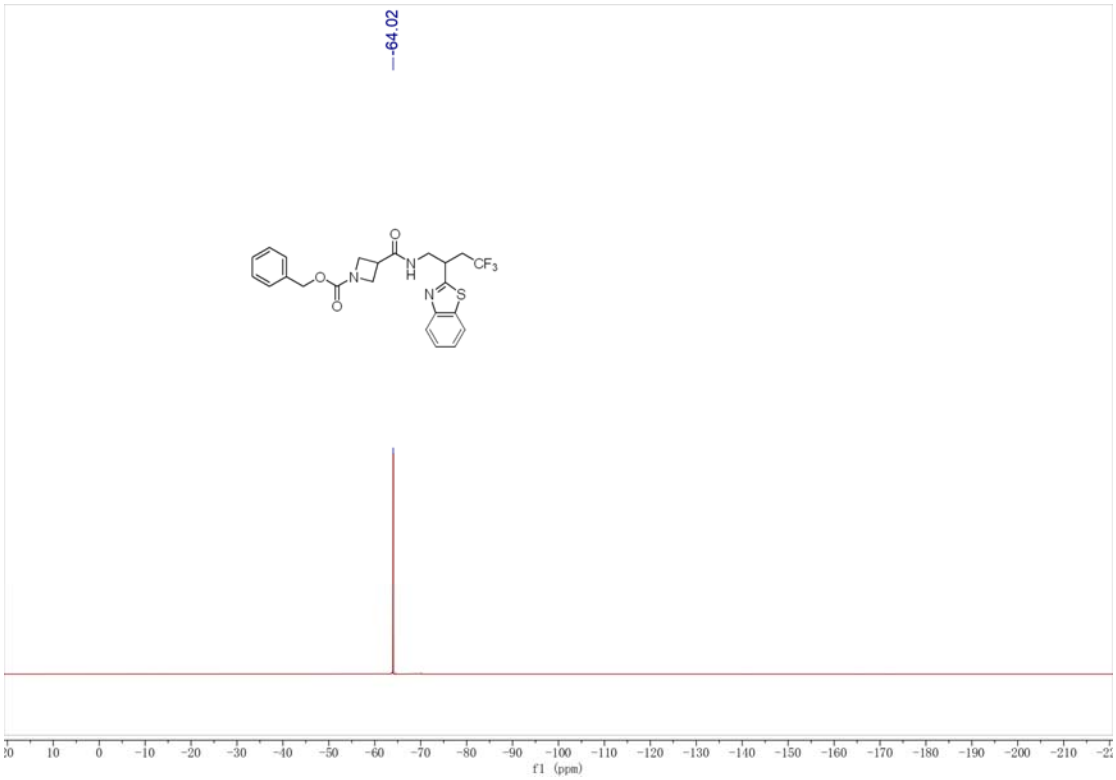



-64.14
O
O
N
H
CF3
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

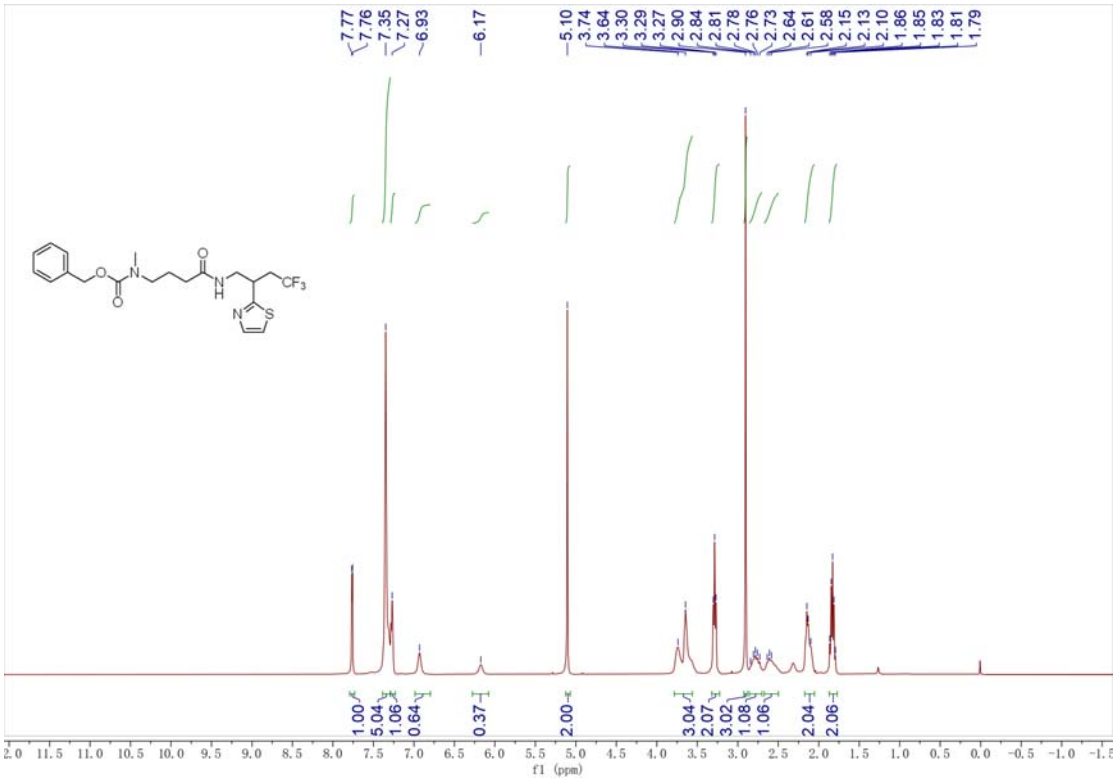
benzyl 3-((2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)carbamoyl)azetidine-1-carboxylate (3z2)

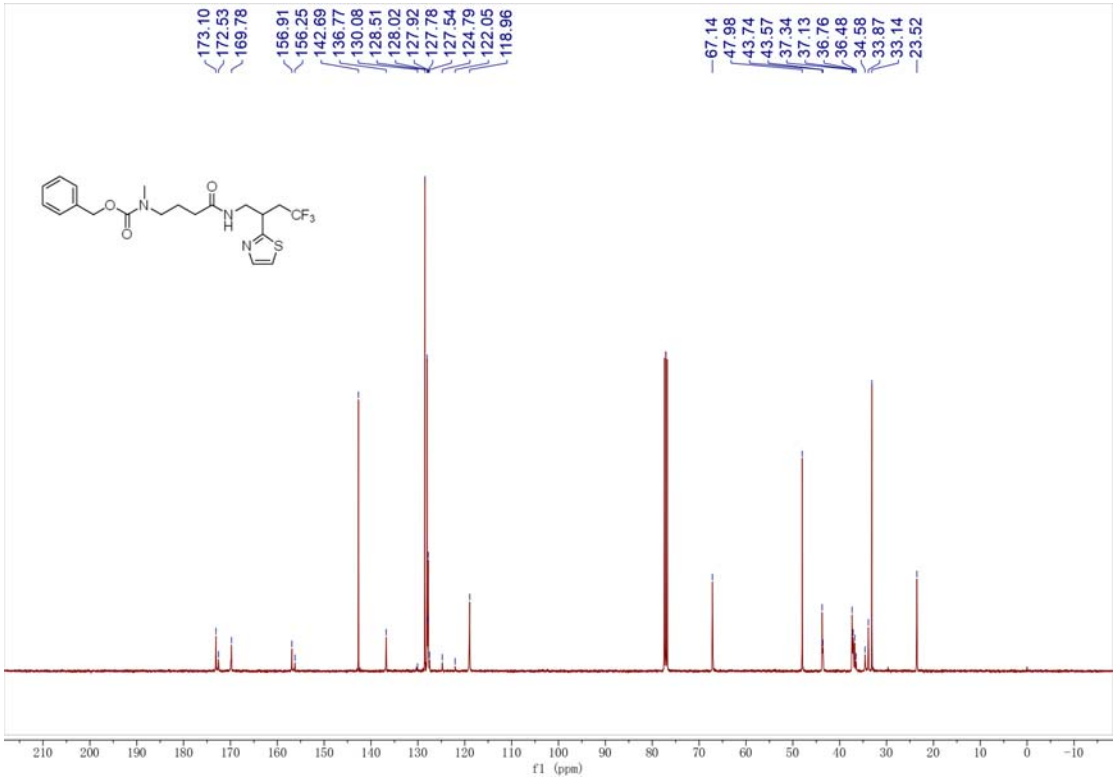


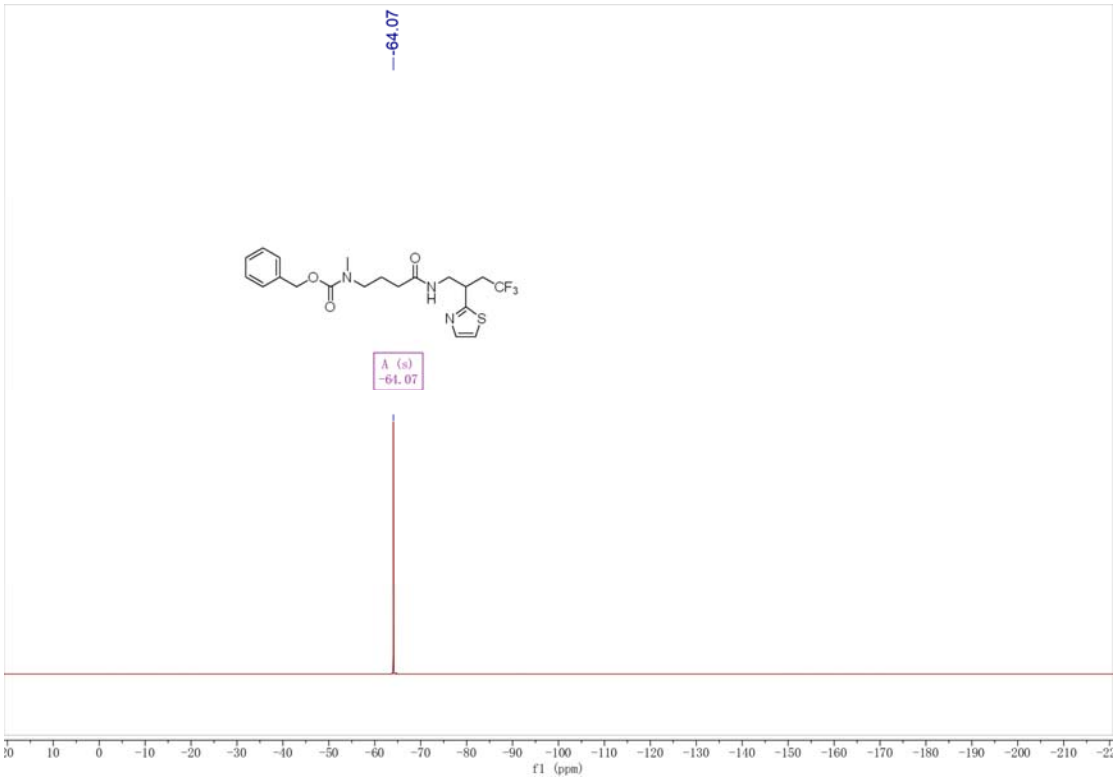



-64.02
O
N
H
CF3
N
S
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

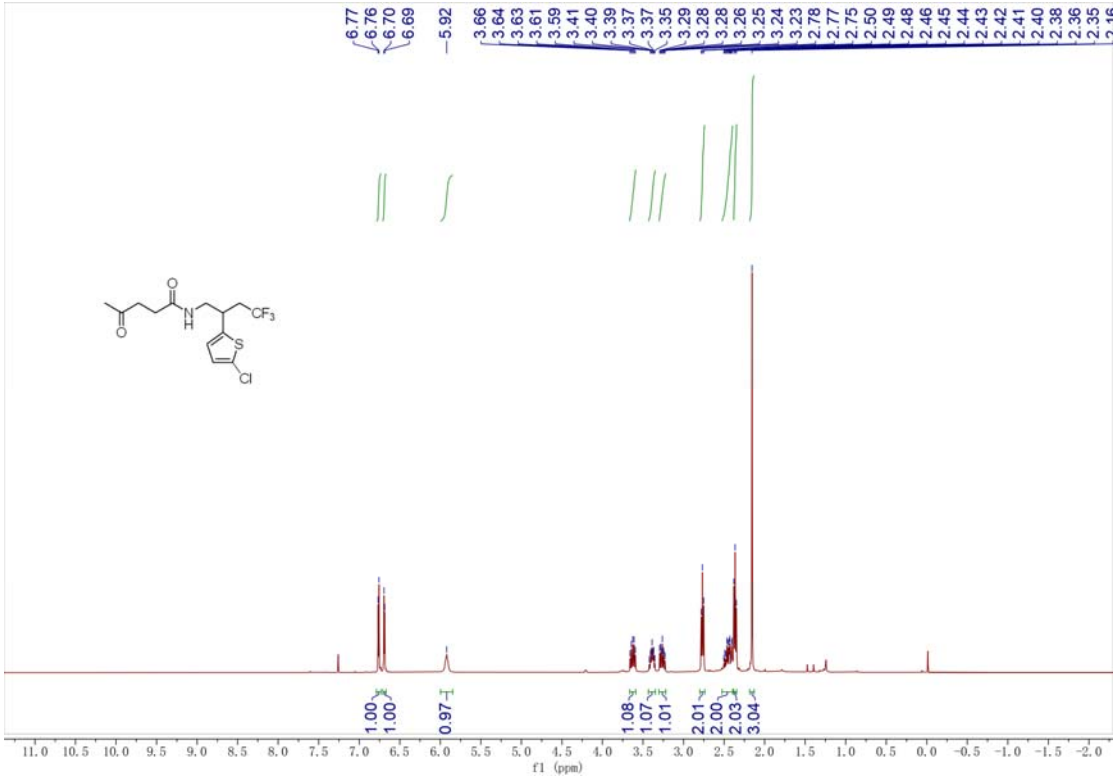
benzyl methyl(4-oxo-4-((4,4,4-trifluoro-2-(thiazol-2-yl)butyl)amino)butyl)carbamate (3z3)

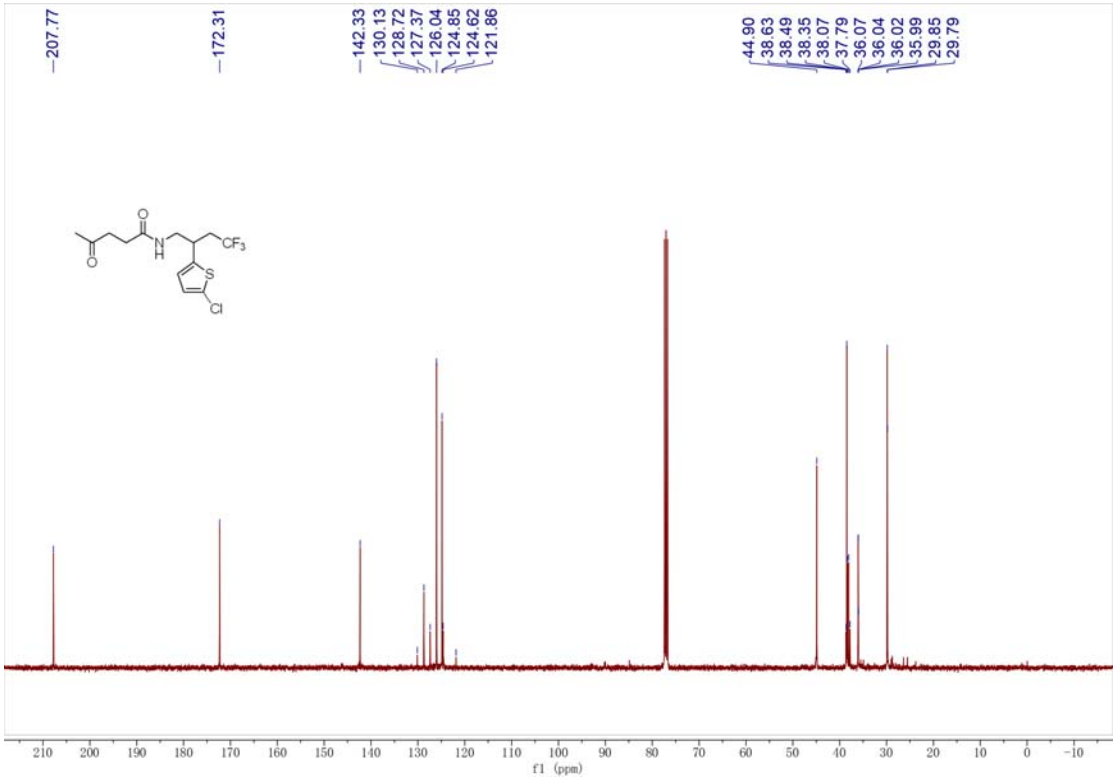


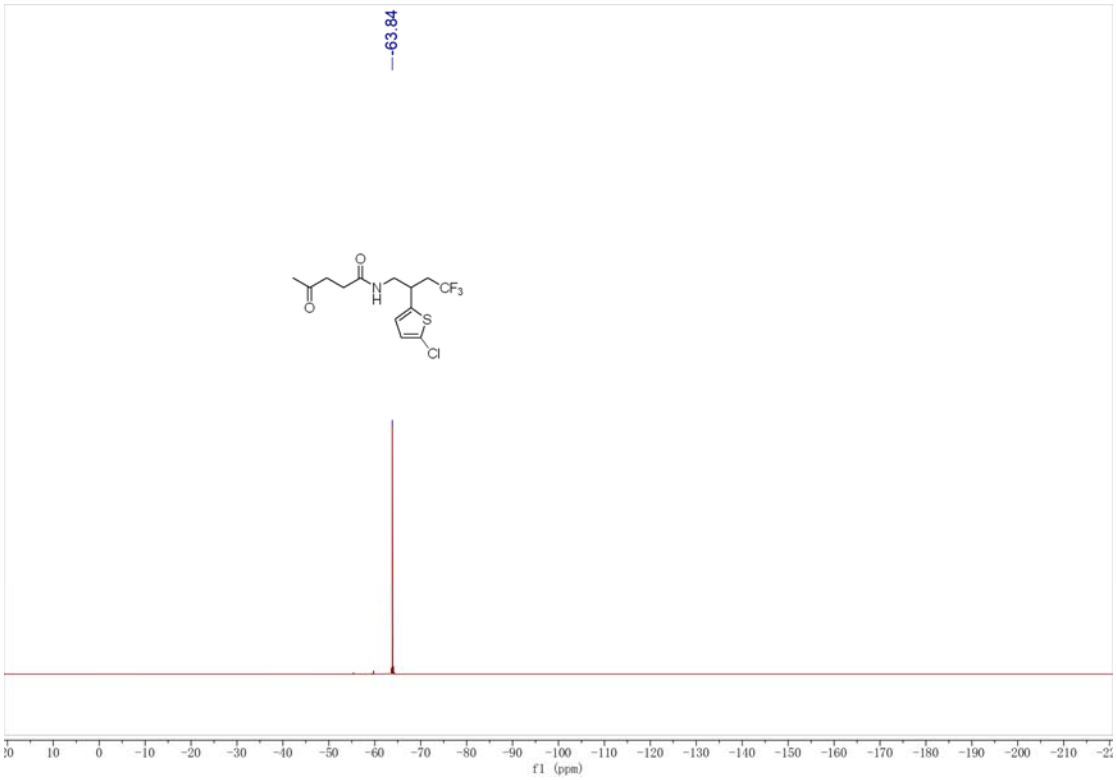



-64.07
A (s)
-64.07
f1 (ppm)

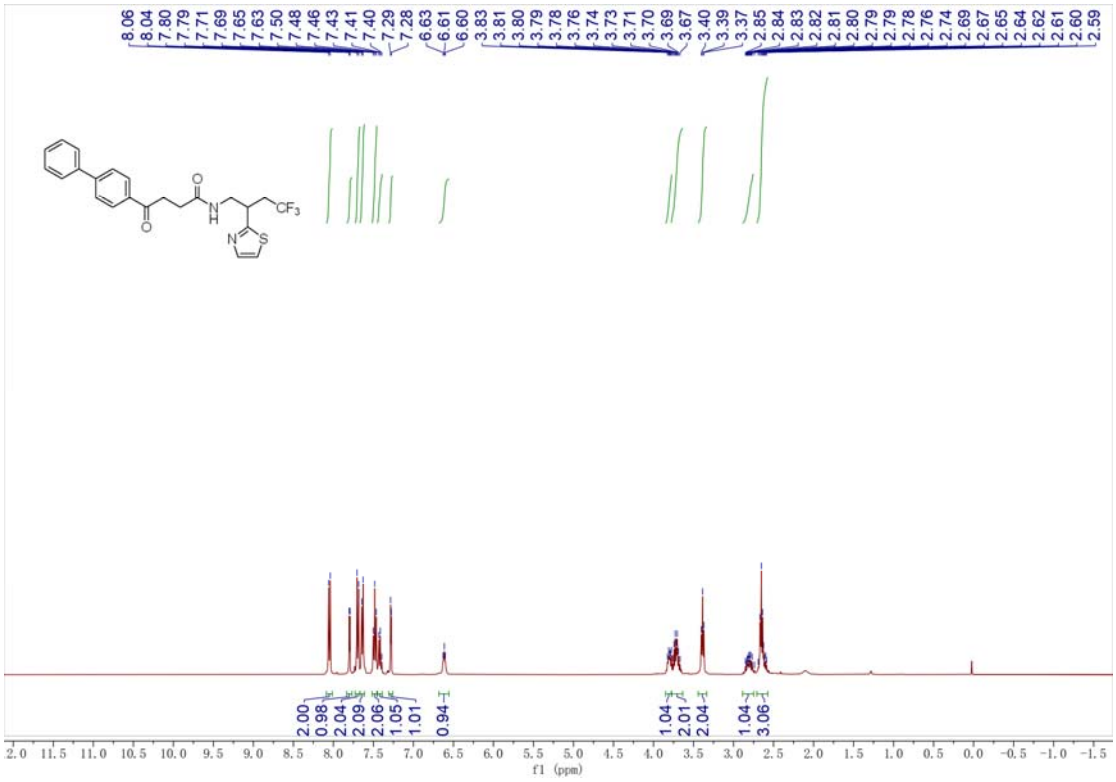
***N*-(2-(5-chlorothiophen-2-yl)-4,4,4-trifluorobutyl)-4-oxopentanamide (3z4)**

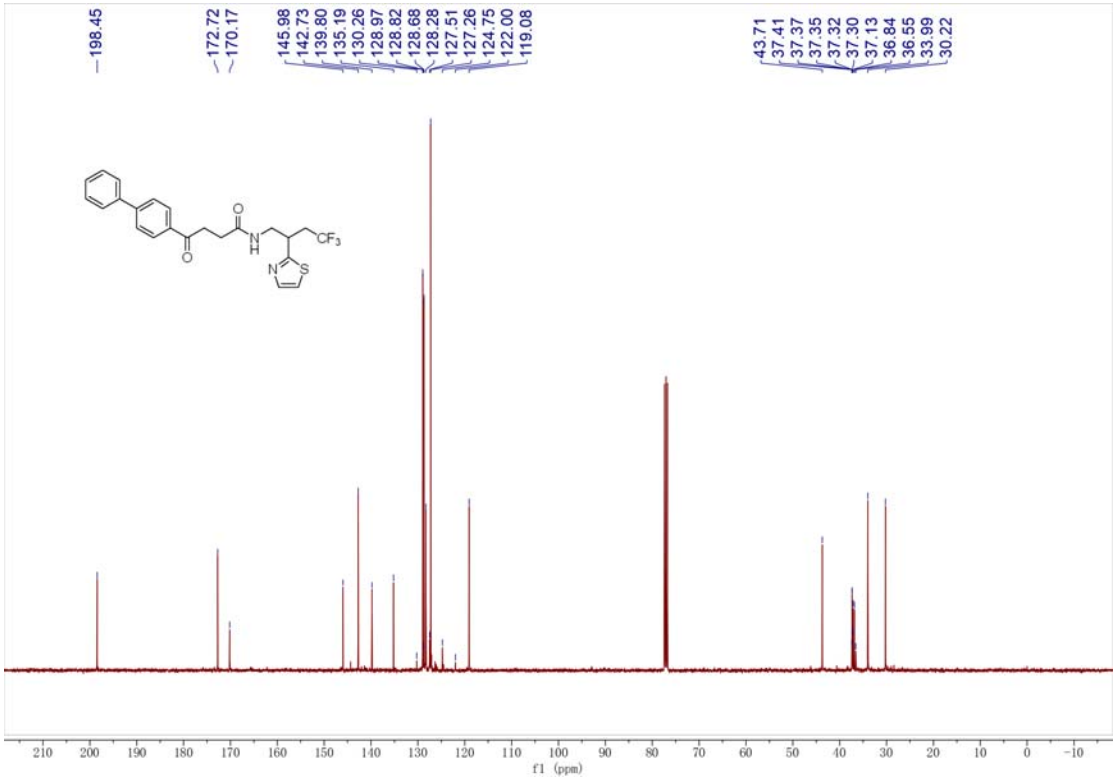


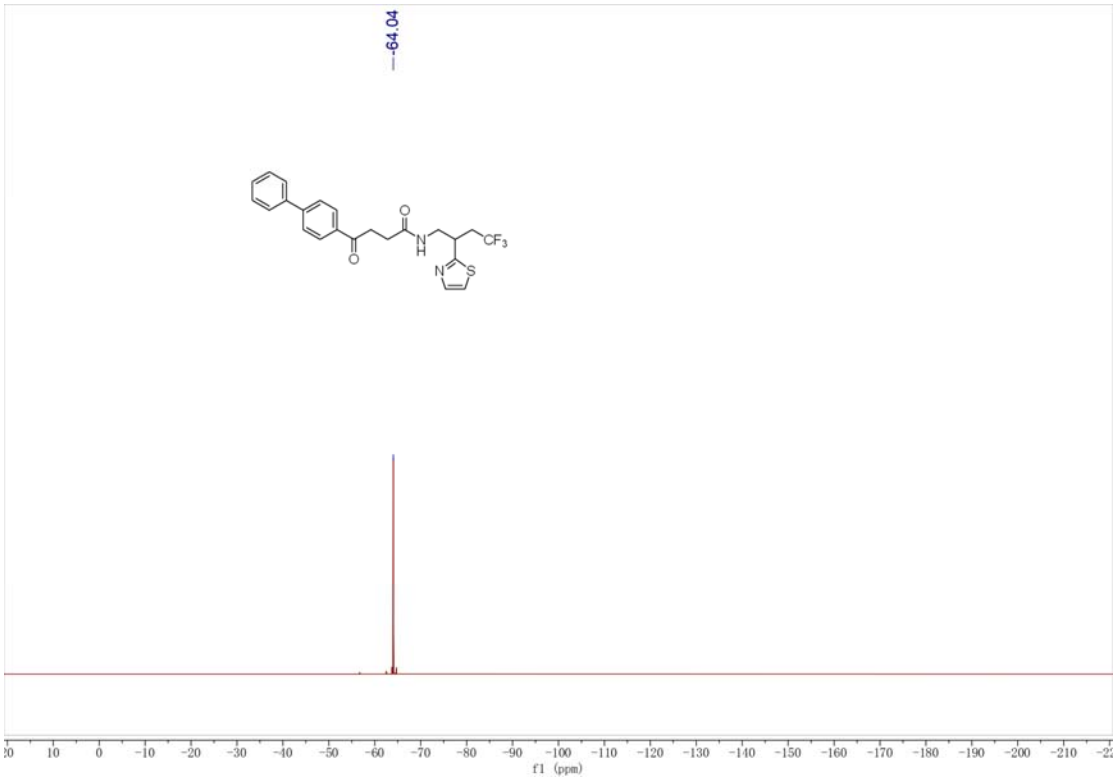



-63.84
O
O
N
H
CF3
S
Cl
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

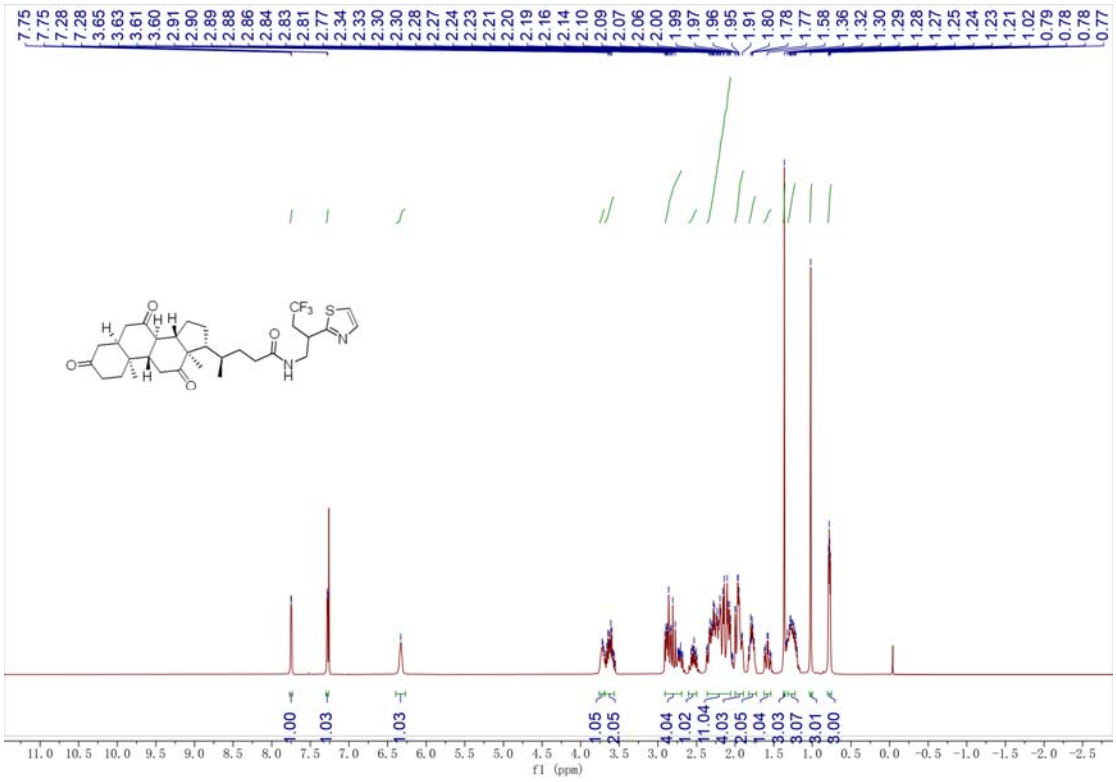
4-([1,1'-biphenyl]-4-yl)-4-oxo-*N*-(4,4,4-trifluoro-2-(thiazol-2-yl)butyl)butanamide (3z5)

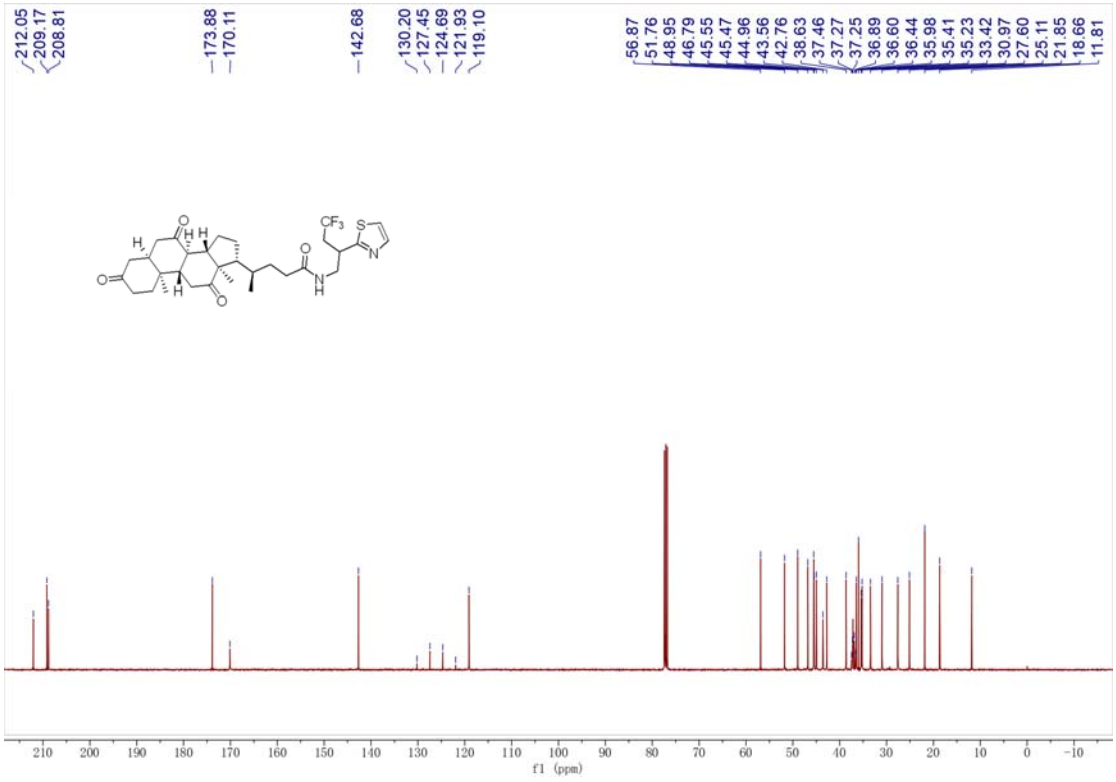


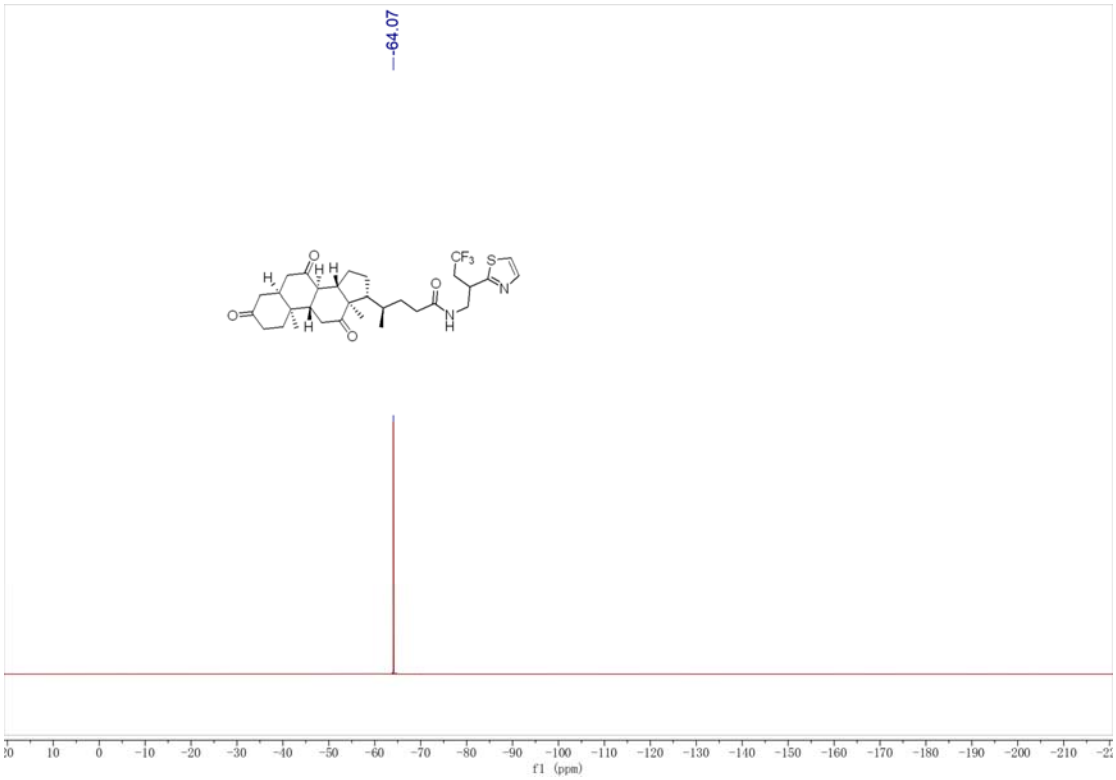



-64.04
O
O
N
H
CF3
N
S
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

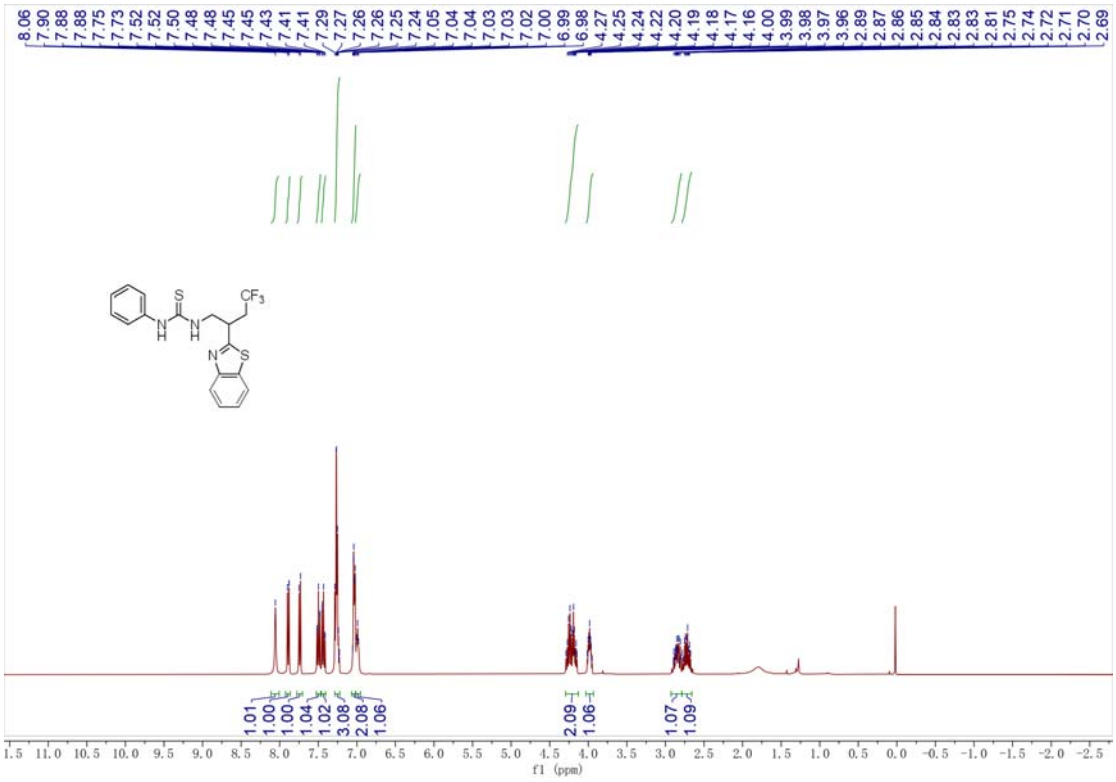
(4R)-4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)-N-(4,4,4-trifluoro-2-(thiazol-2-yl)butyl)pentanamide (3z6)

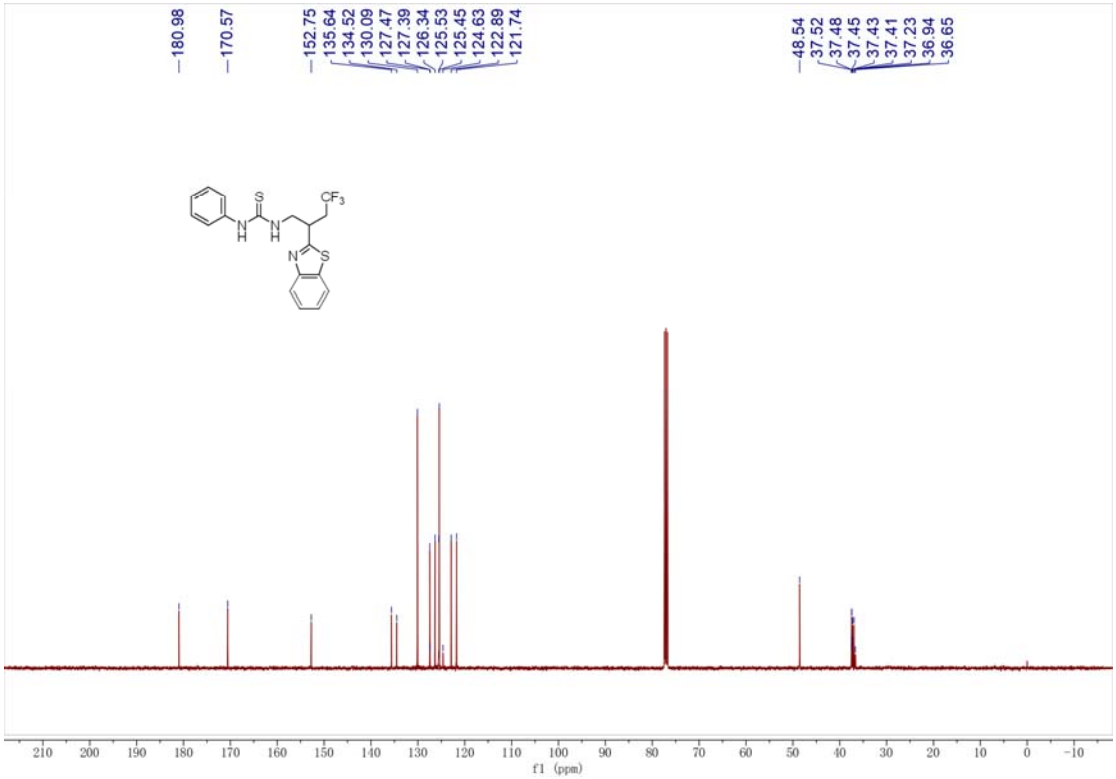


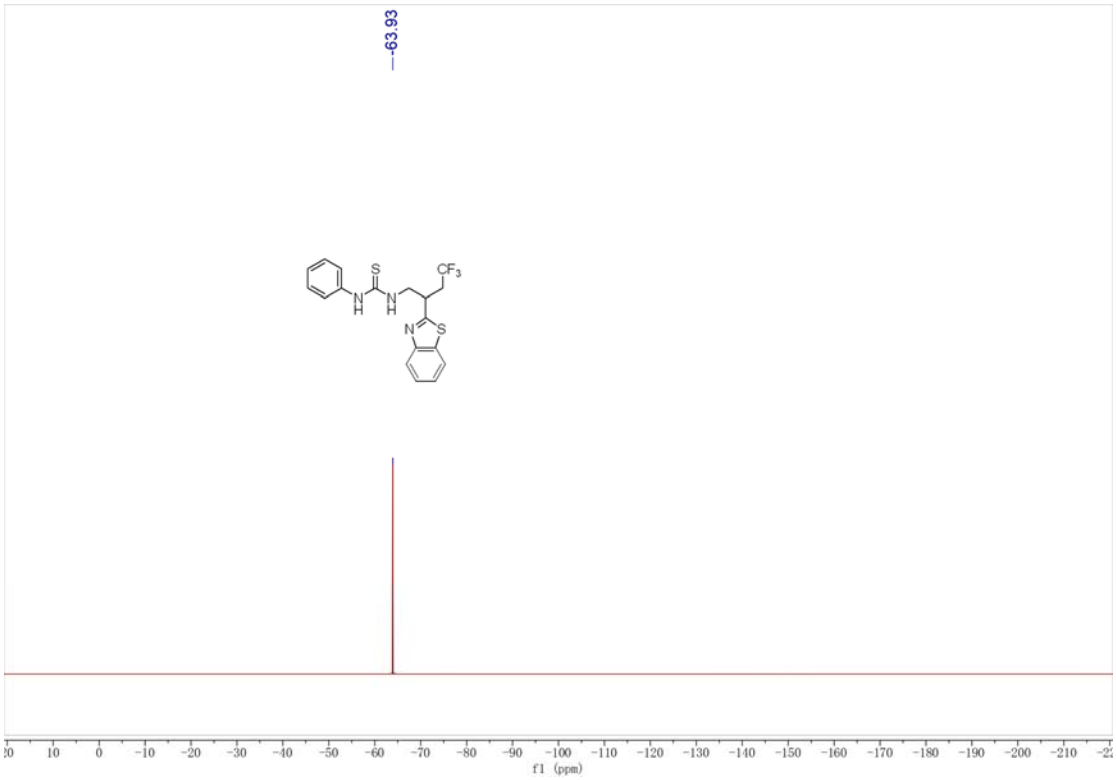



-64.07
CF3
S
N
O
H
H
H
O
O
N
H
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

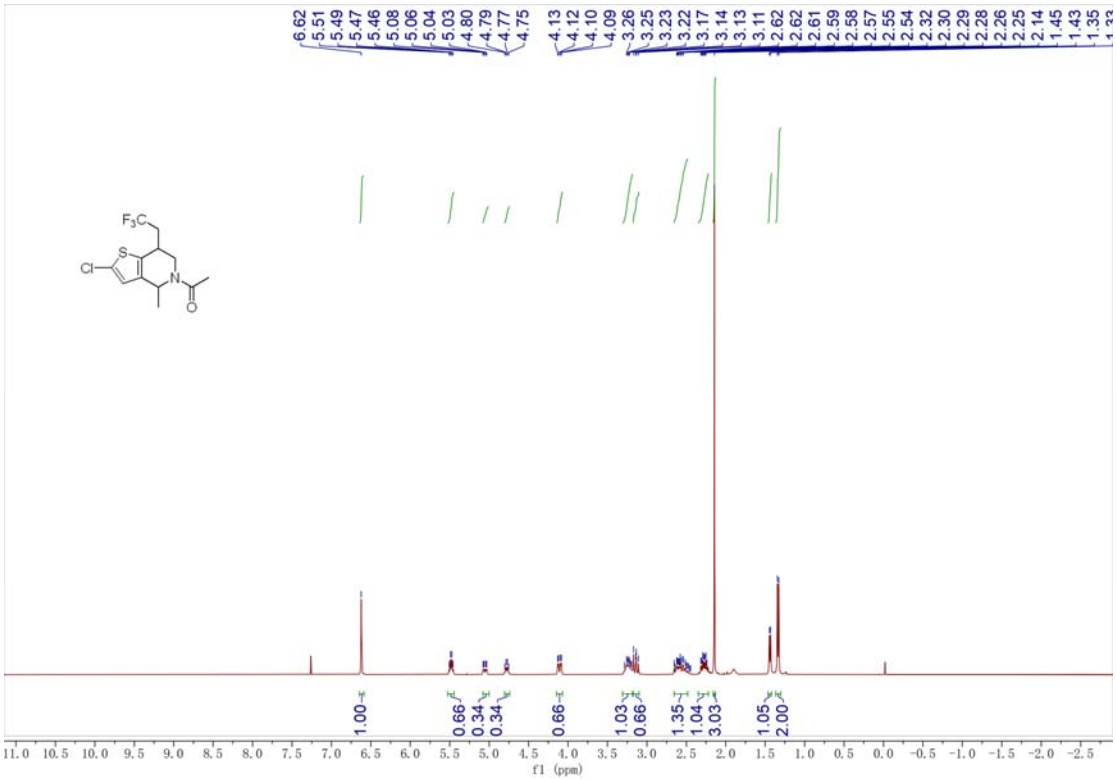
1-(2-(benzo[d]thiazol-2-yl)-4,4,4-trifluorobutyl)-3-phenylthiourea (4)

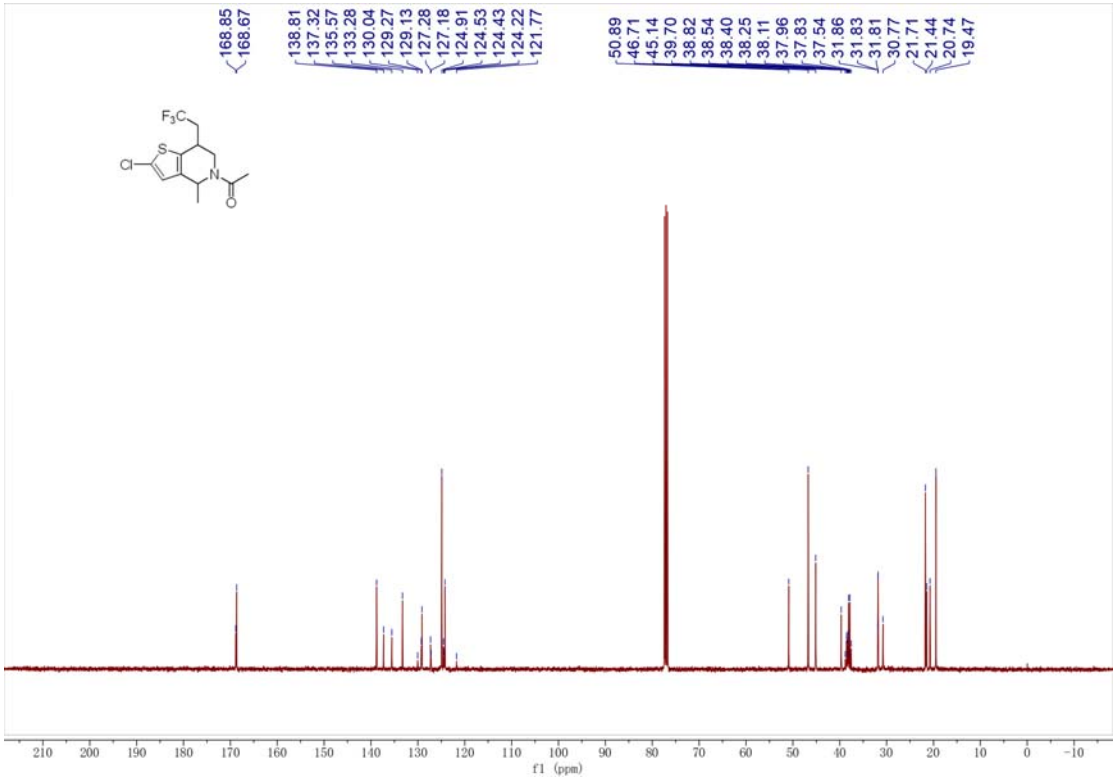


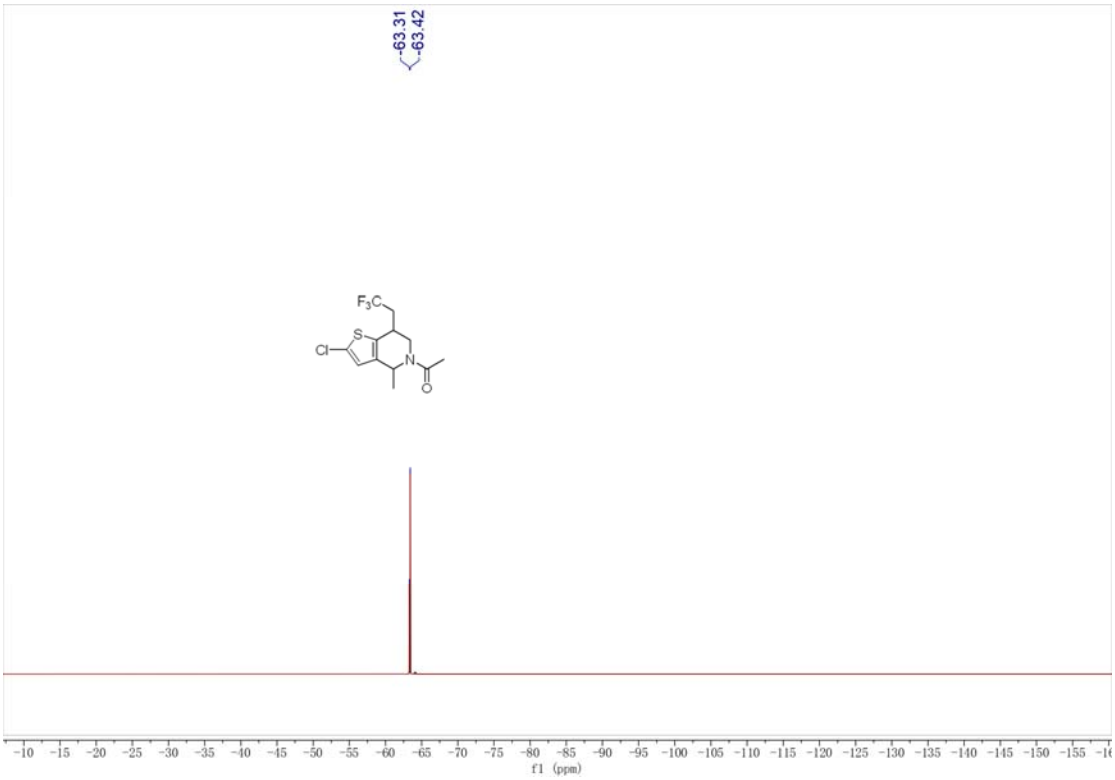



-63.93
CF3
S
N
H
N
H
N
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1-(2-chloro-4-methyl-7-(2,2,2-trifluoroethyl)-6,7-dihydrothieno[3,2-c]pyridin-5(4H)-yl)ethan-1-one (5)






-63.31
-63.42
F3C
S
Cl
N
O
−10 −15 −20 −25 −30 −35 −40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155
f1 (ppm)

9. Reference

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