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Supporting Information
for
Regioselective Ring Opening of N-H-Aziridines with *S*-nucleophiles in Liquid SO_2

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1. General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a *Bruker Avance* 300 MHz in $CDCl_3$, $DMSO_{d6}$, D_2O, or $MeOD_{d4}$. Chemical shifts (δ) values are reported in ppm. The residual solvent peaks are used as the internal reference ($CDCl_3$ 7.26 ppm, $DMSO_{d6}$ 2.50 ppm, D_2O 4.79 ppm, $MeOD_{d4}$ 3.78 ppm for ^{1}H-NMR, $CDCl_3$ 77.0 ppm, $DMSO_{d6}$ 39.52 ppm $MeOD_{d4}$ 49.15 ppm for ^{13}C-NMR). Coupling constants *J* are reported in Hz and coupling patterns are described as br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. IR spectra were recorded as thin films on KBr plates or in KBr with *FT-IR Perkin Elmer Spectrum BX*. Wave numbers are given in reciprocal centimeters (cm^{-1}). HRMS spectra were performed using *Agilent 1290 Infinity series* UHPLC chromatographic system connected with *Agilent 6230 TOF LC/MS* mass-selective detector (ESI+). All solvents were dried and distilled prior to use. Other chemicals were used as received without further purification. Column chromatography was performed on silica gel (60 Å, 40-63 µm, ROCC). All reactions were followed by TLC on *E. Merck Kieselgel 60 F_{254}*, and the UV-active products were visualized by UV detection (λ = 254 nm). Optical rotation was measured at 25 °C on a *Anton Paar MCP 500* polarimeter (1 dm cell) using a sodium lamp as the light source (589 nm).

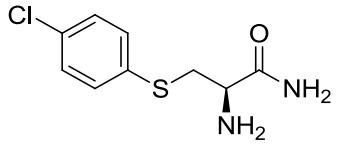
2. General Procedures

General procedure 1 for aziridine ring opening at 20 – 60 °C: *(S)*-Aziridine-2-carboxamide **1** (0.05 g, 0.58 mmol, 1 equiv.) and 4-chlorobenzenethiol **2a** (0.17 g, 1.16 mmol, 2 equiv.), were placed into a stainless steel vessel. Three vacuum/nitrogen cycles were accomplished via Schlenk line. Sulfur dioxide (25 ± 2 g) was transferred into the vessel at – 78 °C. Reaction was carried out under pressure (p = 4 bar) at 25 °C for 16 h. Then the SO_2-collecting vessel was cooled to – 78 °C, connected to reaction vessel and the excess of SO_2 was transferred. Residue was purified by column chromatography (4 % DCM/EtOH) to obtain to obtain (*R*)-2-amino-3-((4-chlorophenyl)thio)propanamide **3a** (130 mg, 97%) as an amorphous powder.

General procedure 2 for aziridine ring opening at -10 °C: (*S*)-aziridine-2-carboxamide **1** (0.05 g, 0.58 mmol, 1 equiv.) and glucose-derived thiol **2g** (0.23 g, 0.64 mmol, 1.1 equiv.), were placed into a two-neck round bottom flask equipped with dry ice condenser under inert atmosphere. Sulfur dioxide (35 ± 5 mL) was condensed into the flask at – 78 °C. The resulting reaction mixture was allowed to warm up to the boiling point of SO_2 (- 10 °C) and the reaction was performed in liquid SO_2 under reflux (-10 °C) for 5 h. Once the ring opening was complete (^{1}H-NMR control), the flask was connected to SO_2-collecting vessel and the excess of SO_2 was transferred at -78 °C. The solid was residue purified by column chromatography (DCM/EtOH 29:1 → 4:1) to obtain 258 mg (98%) of **3g** as a colorless oil.

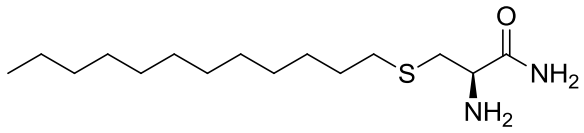
3. Analytical Data

(*R*)-2-Amino-3-((4-chlorophenyl)thio)propanamide 3a



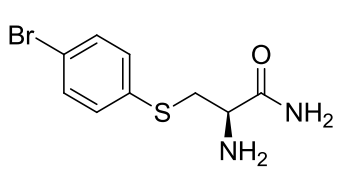
According to general procedure **1**: compound **3a** was prepared from (*S*)-aziridine-2-carboxamide **1** (0.05 g, 0.58 mmol, 1 equiv.), 4-chlorothiophenol **2a** (0.17 g, 1.16 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 16 h, purified by column chromatography (4 % DCM/EtOH) to obtain 130 mg (97%) of (*R*)-2-amino-3-((4-chlorophenyl)thio)propanamide **3a** as an amorphous powder. $[\alpha]_D^{25}$= - 53.5 (*c*=1, $CHCl_3$). IR (KBr): 3380, 3330, 3075, 3185, 1655, 1635, 1575, 1540, 1505, 1495, 1475, 1425, 1390, 1095, 1010, 815, 810, 730, 705, 675. ^{1}H-NMR ($DMSO_{d6}$, 300 MHz): δ = 7.41 (br.s, 1H, CONH), 7.40 – 7.31 (m, 4H, H-C(Ar)), 7.10 (br.s, 1H, CONH), 3.33 – 3.19 (m, 2H, Ha-C(3), H-C(2)), 2.98 (dd, 1H, ^2J = 12.4 Hz, ^3J = 7.0 Hz, Hb-C(3)), 1.99 (br.s, 1H, H_2N-C(2)). ^{13}C-NMR ($DMSO_{d6}$, 75.5 MHz): δ = 175.1, 135.6, 130.1, 129.7, 128.8, 54.0, 38.4. HRMS: calculated [$C_9H_{11}ClN_2OS + H^+$] 231.0354; found 231.0355.

(*R*)-2-amino-3-(dodecylthio)propanamide 3b



According to general procedure **1**: compound **3b** was prepared from (*S*)-aziridine-2-carboxamide **1** (0. 05 g, 0.58 mmol, 1 equiv.), dodecane-1-thiol **2b** (280 µL, 1.16 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 14 h, purified by column chromatography (4 % DCM/EtOH) to obtain 147 mg (87%) of (*R*)-2-amino-3-(dodecylthio)propanamide **3b** as an amorphous powder. $[\alpha]_D^{25}$= - 51.5 (*c*=1, $CHCl_3$). IR (KBr): 3370, 3320, 3185, 2955, 2920, 2870, 2850, 1635, 1470, 1315, 1090, 720. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.26 (br.s, 1H, CONH), 5.65 (br.s, 1H, CONH), 3.49 (dd, ^3J = 9.0, 3.8 Hz, 1H, H-C(2)), 3.05 (dd, ^2J = 13.8 Hz, ^3J = 3.8 Hz, 1H, Ha-C(3)), 2.67 (dd, ^2J = 13.8 Hz, ^3J = 9.1 Hz, 1H, Hb-C(3)), 2.52 (t, ^3J = 7.4 Hz, 2H, $\underline{CH_2}$-S), 1.77 (br.s, 2H, H_2N-C(2)), 1.64 – 1.51 (m, 2H, CH_2), 1.43 – 1.14 (m, 18H, $9CH_2$), 0.87 (t, ^3J = 6.6 Hz, 3H, CH_3). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 176.5, 54.0, 37.6, 32.1, 31.9, 29.6, 29.6 (3C), 29.5, 29.3, 29.2, 28.8, 22.7, 14.1. HRMS: calculated [$C_{15}H_{32}N_2OS + H^+$] 289.23032; found 289.2310.

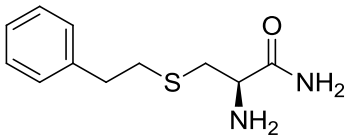
(*R*)-2-Amino-3-((4-bromophenyl)thio)propanamide 3c



According to general procedure **1**: compound **3c** was prepared from (*S*)-aziridine-2-carboxamide **1** (0.05 g, 0.58 mmol, 1 equiv.), 4-bromobenzenethiol **2c** (0.22 g, 1.16 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 14 h, purified by column chromatography (4 % DCM/EtOH) to obtain 136 mg (85%) of (*R*)-2-amino-3-((4-bromophenyl)thio)propanamide **3c** as an amorphous powder. $[\alpha]_D^{25}$= - 41.2 (*c*=1, $CHCl_3$). IR (KBr): 3370, 3325, 3175, 3075, 3005, 1655, 1635, 1585, 1470, 1425, 1335,1090, 1005, 810, 805, 725, 690. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.42 (d, ^3J = 8.5 Hz, 2H, H-C(Ar)), 7.26 (d, ^3J = 8.5 Hz, 2H, H-C(Ar)), 7.21(br.s, 1H, CONH), 5.59 (br.s, 1H,

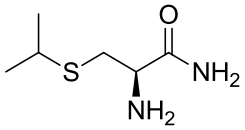
CONH), 3.57 (dd, 1H, ^{2}J = 13.7 Hz, ^{3}J = 3.2 Hz, Ha-C(3)), 3.45 (dd, ^{3}J = 9.4, 3.2 Hz, 1H, H-C(2)), 2.91 (dd, ^{2}J = 13.7 Hz, ^{3}J = 9.5 Hz, 1H, Hb-C(3)), 1.70 (br.s, 2H, H_2N-C(2)). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 175.8, 133.7, 132.2, 131.4, 120.7, 53.7, 39.4. HRMS: calculated [$C_9H_{11}BrN_2OS + H^+$] 274.9843; found 274.9869.

(*R*)-2-amino-3-(phenethylthio)propanamide 3d



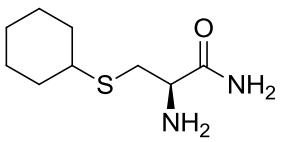
According to general procedure **1**: compound **3d** was prepared from (*S*)-aziridine-2-carboxamide **1** (0. 05 g, 0.58 mmol, 1 equiv.), 2-phenylethanethiol **2d** (160 µL, 1.16 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 13 h, purified by column chromatography (4 % DCM/EtOH) to obtain 130 mg (71%) of (*R*)-2-amino-3-(phenethylthio)propanamide **3d** as an amorphous powder. $[\alpha]_D^{25}$= - 39.5 (*c*=1, $CHCl_3$). IR (KBr): 3370, 3195, 3065, 3030, 2910, 1635, 1495, 1445, 1425, 1335, 1245, 1095, 1080, 850, 815, 805, 720, 700. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.84 – 7.10 (m, 6H, H-C(Ar), CONH), 5.65 (br.s, 1H, CONH), 3.46 (dd, ^{3}J = 8.6, 3.9 Hz, 1H, H-C(2)), 3.03 (dd, ^{2}J = 13.6 Hz, ^{3}J = 3.9 Hz, 1H, Ha-C(3)), 2.96 – 2.58 (m, 5H, Hb-C(3), $2CH_2$), 1.80 (br.s, 2H, H_2N-C(2)). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 176.4, 140.1, 128.5, 128.5, 126.4, 53.9, 37.5, 36.1, 33.5. HRMS: calculated [$C_{11}H_{16}N_2OS + H^+$] 225.1051; found 225.1068.

(*R*)-2-amino-3-(isopropylthio)propanamide 3e



According to general procedure **1**: compound **3e** was prepared from (*S*)-aziridine-2-carboxamide **1** (0.05 g, 0.58 mmol, 1 equiv.), propane-2-thiol **2e** (110 µL, 1.16 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 15 h, purified by column chromatography (4 % DCM/EtOH) to obtain 92 mg (93%) of (*R*)-2-amino-3-(isopropylthio)propanamide **3e** as an amorphous powder. $[\alpha]_D^{25}$= 4.8 (*c*=1, H_2O). IR (KBr): 3400, 3275, 3225, 3170, 2975, 1675, 1610, 1595, 1505, 1475, 1460, 1315, 1120, 620. ^{1}H-NMR (D_2O, 300 MHz) δ = 4.20 (dd, ^{3}J = 7.0, 5.6 Hz, 1H, H-C(2)), 3.22 – 2.94 (m, 3H, H_2C(3), $(CH_3)_2$-CH-S), 1.25 (d, ^{3}J = 6.6 Hz, 6H, $(CH_3)_2$-CHS). ^{13}C-NMR (D_2O, 75.5 MHz) δ = 170.7, 52.2, 35.2, 30.4, 22.2. HRMS: calculated [$C_6H_{14}N_2OS + H^+$] 163.0895; found 163.0902.

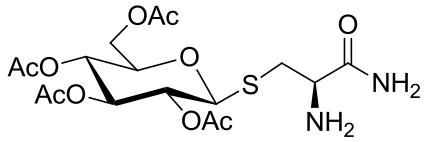
(*R*)-2-amino-3-(cyclohexylthio)propanamide 3f



According to general procedure **1**: compound **3f** was prepared from (*S*)-aziridine-2-carboxamide **1** (0.05 g, 0.58 mmol, 1 equiv.), cyclohexanethiol **2f** (142 µL, 1.16 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 17 h, purified by column chromatography (4 % DCM/EtOH) to obtain 72 mg (78%) of (*R*)-2-amino-3-(cyclohexylthio)propanamide **3f** as an amorphous powder. $[\alpha]_D^{25}$= 10.2 (*c*=1, H_2O). IR (KBr): 3400, 3275, 3220, 3160, 2975, 2930, 2855, 1670, 1610, 1590, 1465, 1450, 1355, 1315, 1115, 1040, 620. ^{1}H-NMR (D_2O, 300 MHz) δ = 4.23 – 4.12 (m, 1H, H-C(2)),

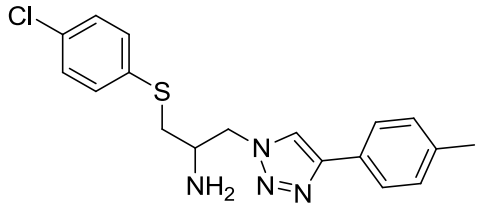
3.19 – 2.98 (m, 2H, $H_2C(3)$), 2.87 – 2.72 (m, 1H, H-C(Cy)), 2.04 – 1.85 (m, 2H, H-C(Cy)), 1.80 – 1.64 (m, 2H, H-C(Cy)), 1.61 – 1.50 (m, 1H, H-C(Cy)), 1.42 – 1.12 (m, 5H, H-C(Cy)). ^{13}C-NMR (D_2O, 75.5 MHz) δ = 170.9, 52.3, 43.5, 32.9, 32.8, 29.9, 25.4, 25.3, 25.1. HRMS: calculated [$C_9H_{18}N_2OS + H^+$] 203.1208; found 203.1212.

Amino acid – carbohydrate conjugate 3g



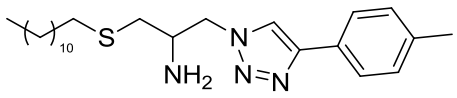
According to general procedure **2**: compound **3g** was prepared from (*S*)-aziridine-2-carboxamide **1** (0.05 g, 0.58 mmol, 1 equiv.), thiocarbohydrate **2g** (0.23 g, 0.64 mmol, 1.1 equiv.), SO_2 (35 ± 5 mL) at -10 °C in 5 h, purified by column chromatography (DCM/EtOH 29:1 → 4:1) to obtain 258 mg (98%) of **3g** as a colorless oil. IR (KBr): 3445, 3355, 3200, 3060, 2950, 2885, 1745, 1695, 1675, 1600, 1435, 1385, 1370, 1335, 1275, 1230, 1095, 1040, 980, 915, 735, 605. ^{1}H-NMR ($DMSO_{d6}$, 300 MHz): 7.32 (br.s, 1H, CONH), 7.08 (br.s, 1H, CONH), 5.26 (dd, 1H, ^3J = 9.4, 9.2 Hz, H-C(3Carb.)), 5.00 – 4.80 (m, 3H, H-C(1,2,4Carb.)), 4.13 (dd, 1H, ^2J = 13.0 Hz, ^3J = 6.2 Hz, Ha-C(6Carb.)), 4.08 – 3.93 (m, 2H, Hb-C(6Carb.), H-C(5Carb.)), 3.35 – 3.19 (m, 1H, H-C(2)), 2.94 (dd, 1H, ^2J = 13.2 Hz, ^3J = 4.5 Hz, Ha-C(3)), 2.64 (dd, 1H, ^2J = 13.2 Hz, ^3J = 7.9 Hz, Hb-C(3)), 2.02, 2.01, 1.98, 1.95 (4s, 12H, 4OAc). ^{13}C-NMR ($DMSO_{d6}$, 75.5 MHz): δ 175.1, 169.9, 169.4, 169.1, 169.0, 82.0, 74.3, 72.9, 69.5, 68.0, 61.8, 54.6, 35.4, 20.4, 20.3, 20.2, 20.1. HRMS: calculated [$C_{17}H_{26}N_2O_{10}S + H^+$] 451.1381; found 451.1382.

1-((4-Chlorophenyl)thio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8a



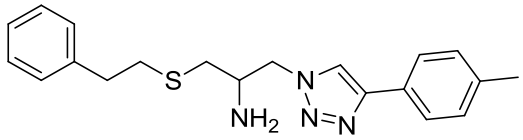
According to general procedure **1**: compound **8a** was prepared from 1-(aziridin-2-ylmethyl)-4-(p-tolyl)-1H-1,2,3-triazole **5** (0.07 g, 0.35 mmol, 1 equiv.), 4-chlorothiophenol **2a** (0.10 g, 0.70 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 14 h, purified by column chromatography (3 % DCM/MeOH) to obtain 78 mg (62%) of **8a** as an amorphous powder. IR (KBr): 3340, 3330, 3255, 3165, 3110, 2920, 2905, 2860, 1615, 1500, 1475, 1455, 1390, 1220, 1110, 1095, 1055, 1010, 810, 730, 660, 610. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.74 (s, 1H, H-C(triaz.)), 7.69 (d, 2H, ^3J = 8.0 Hz, H-C(Ar)), 7.29 (d, 2H, ^3J = 8.6 Hz, H-C(Ar)), 7.25 – 7.17 (m, 4H, H-C(Ar)), 4.51 (dd, ^2J = 13.7 Hz, ^3J = 4.6 Hz, 1H, Ha-C(3)), 4.35 (dd, ^2J = 13.7 Hz, ^3J = 6.8 Hz, 1H, Hb-C(3)), 3.51 – 3.34 (m, 1H, H-C(2)), 3.04 (dd, ^2J = 13.7 Hz, ^3J = 5.3 Hz, 1H, Ha-C(1)), 2.84 (dd, ^2J = 13.6 Hz, ^3J = 7.4 Hz, 1H, Hb-C(1)), 2.37 (s, 3H, Me-C(Ar)), 1.71 (s, 2H, -NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 147.8, 138.1, 133.4, 133.0, 131.5, 129.5, 129.4, 127.5, 125.6, 120.4, 55.3, 50.7, 39.7, 21.3. HRMS: calculated [$C_{18}H_{19}ClN_4S + H^+$] 359.1087; found 359.1102.

1-(Dodecylthio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8b



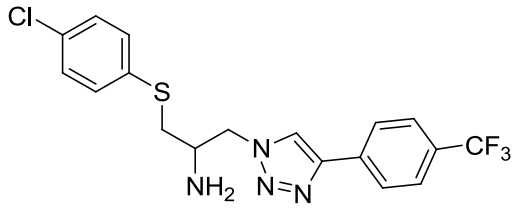
According to general procedure **1**: compound **8b** was prepared from 1-(aziridin-2-ylmethyl)-4-(p-tolyl)-1H-1,2,3-triazole **5** (0.07 g, 0.35 mmol, 1 equiv.), dodecane-1-thiol **2b** (170 µL, 0.70 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 14 h, purified by column chromatography (3 % DCM/MeOH) to obtain 86 mg (57%) of **8b** as an amorphous powder. IR (KBr): 3380, 3315, 3135, 3025, 2955, 2920, 2875, 2850, 1600, 1500, 1470, 1455, 1380, 1225, 1190, 1075, 980, 815, 720, 665, 605. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.84 (s, 1H, H-C(triaz.)), 7.71 (d, ^{3}J = 8.1 Hz, 2H, H-C(Ar)), 7.22 (d, ^{3}J = 7.9 Hz, 2H, H-C(Ar)), 4.51 (dd, ^{2}J = 13.7 Hz, ^{3}J = 4.4 Hz, 1H, Ha-C(3)), 4.31 (dd, ^{2}J = 13.7 Hz, ^{3}J = 7.3 Hz, 1H, Hb-C(3)), 3.50 – 3.38 (m, 1H, H-C(2)), 2.65 (dd, ^{2}J = 13.4 Hz, ^{3}J = 5.3 Hz, Ha-C(1)), 2.58 – 2.42 (m, 3H, Hb-C(1), CH_2-S), 2.37 (s, 3H, Me-C(Ar)), 1.69 – 1.47 (m, 4H, CH_2, -NH_2), 1.42 – 1.15 (m, 18H, 9CH_2), 0.87 (t, ^{3}J = 6.6 Hz, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 147.7, 138.0, 129.5, 127.6, 125.5, 120.4, 55.6, 50.9, 37.4, 32.7, 31.8, 29.6 (3C), 29.5 (2C), 29.3, 29.1, 28.8, 22.6, 21.2, 14.0. HRMS: calculated [$C_{24}H_{40}N_4S$ + H^+] 417.3041; found 417.3051.

1-(Phenethylthio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8c



According to general procedure **1**: compound **8c** was prepared from 1-(aziridin-2-ylmethyl)-4-(p-tolyl)-1H-1,2,3-triazole **5** (0.07 g, 0.34 mmol, 1 equiv.), 2-phenylethanethiol **2d** (90 µL, 0.70 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 14 h, purified by column chromatography (3 % DCM/MeOH) to obtain 59 mg (50%) of **8c** as an amorphous powder. IR (KBr): 3380, 3315, 3140, 3065, 3025, 2950, 2920, 2855, 1603, 1545, 1495, 1455, 1355, 1225, 1185, 1075, 1055, 810, 740, 695, 610. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.80 (s, 1H, H-C(triaz.)), 7.71 (d, ^{3}J = 8.0 Hz, 2H, H-C(Ar)), 7.33 - 7.27 (m, 2H, H-C(Ar)), 7.26 – 7.14 (m, 5H, H-C(Ar)), 4.47 (dd, ^{2}J = 13.7 Hz, ^{3}J = 4.5 Hz, 1H, Ha-C(3)), 4.29 (dd, ^{2}J = 13.7 Hz, ^{3}J = 7.2 Hz, 1H, Hb- C(3)), 3.47 – 3.35 (m, 1H, H-C(2)), 2.93 – 2.76 (m, 4H, Ph-($\underline{CH_2}$)$_2$-S), 2.64 (dd, ^{2}J = 13.4 Hz, ^{3}J = 5.3 Hz, 1H, Ha-C(1)), 2.47 (dd, ^{2}J = 13.4 Hz, ^{3}J = 7.5 Hz, 1H, Ha-C(1)), 2.37 (s, 3H, Me-C(Ar)), 1.53 (s, 2H, -NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 147.7, 140.0, 138.0, 129.5, 128.5 (2C), 127.6, 126.5, 125.6, 120.4, 55.5, 50.9, 37.6, 36.2, 34.2, 21.3. HRMS: calculated [$C_{20}H_{14}N_4S$ + H^+] 353.1789; found 353.1806.

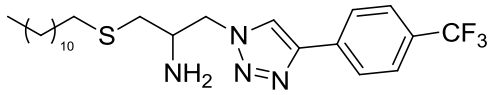
1-((4-Chlorophenyl)thio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9a



According to general procedure **1**: compound **9a** was prepared from 1-(aziridin-2-ylmethyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole **6** (0.07 g, 0.26 mmol, 1 equiv.), 4-

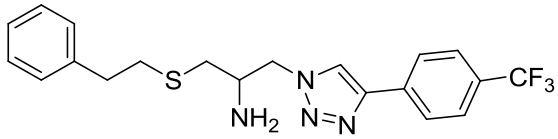
chlorothiophenol **2a** (0.07 g, 0.52 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 16 h, purified by column chromatography (3 % DCM/MeOH) to obtain 94 mg (88%) of **9a** as an amorphous powder. IR (KBr): 3340, 3330, 3260, 3130, 2905, 2855, 1620, 1475, 1330, 1220, 1170, 1130, 1110, 1100, 1080, 1065, 845, 815, 805, 600. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.93 (d, ^3J = 8.0 Hz, 2H, H-C(Ar)), 7.88 (s, 1H, H-C(triaz.)), 7.68 (d, ^3J = 8.2 Hz, 2H, H-C(Ar)), 7.34 – 7.27 (m, 4H, H-C(Ar)), 4.56 (dd, ^2J = 13.7 Hz, ^3J = 4.4 Hz, 1H, Ha-C(3)), 4.39 (dd, ^2J = 13.7 Hz, ^3J = 6.9 Hz, 1H, Hb- C(3)), 3.51 – 3.40 (m, 1H, H-C(2)), 3.07 (dd, ^2J = 13.7 Hz, ^3J = 5.4 Hz, 1H, Ha-C(1)), 2.86 (dd, ^2J = 13.7 Hz, ^3J = 7.4 Hz, 1H, Hb-C(1)), 1.59 (s, 2H, -NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 146.3, 133.8, 133.3, 133.1, 131.6, 130.0 (q, $^2J_{C\text{-}F}$ = 32 Hz), 129.4, 125.8 (q, $^3J_{C\text{-}F}$ = 4 Hz), 125.8, 124.4 (q, $^1J_{C\text{-}F}$ = 271 Hz), 121.6, 55.3, 50.7, 39.8. HRMS: calculated [$C_{18}H_{16}ClF_3N_4S$ + H^+] 413.0804; found 413.0814.

1-(Dodecylthio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9b



According to general procedure 1: compound **9b** was prepared from 1-(aziridin-2-ylmethyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole **6** (0.05 g, 0.19 mmol, 1 equiv.), dodecane-1-thiol **2b** (89 µL, 0.37 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 14 h, purified by column chromatography (3 % DCM/MeOH) to obtain 83 mg (95%) of **9b** as an amorphous powder. IR (KBr): 3385, 3315, 3135, 3115, 2965, 2920, 2850, 1620, 1470, 1335, 1230, 1190, 1170, 1125, 1065, 845, 825, 720, 695, 600. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.99 (s, 1H, H-C(triaz.)), 7.95 (d, ^3J = 8.2 Hz, 2H, H-C(Ar)), 7.67 (d, ^3J = 8.2 Hz, 2H, H-C(Ar)), 4.56 (dd, ^2J = 13.7 Hz, ^3J = 4.2 Hz, 1H, Ha-C(3)), 4.34 (dd, ^2J = 13.7 Hz, ^3J = 7.3 Hz, 1H, Hb-C(3)), 3.53 – 3.40 (m, 1H, H-C(2)), 2.67 (dd, ^2J = 13.4 Hz, ^3J = 5.4 Hz, 1H, Ha-C(1)), 2.58 – 2.44 (m, 3H, Hb-C(1), $\underline{CH_2}$-S), 1.66 – 1.49 (m, 4H, CH_2, -NH_2), 1.44 – 1.14 (m, 18H, 9CH_2), 0.87 (t, ^3J = 6.6 Hz, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 146.2, 134.0, 130.0 (q, $^2J_{C\text{-}F}$ = 32 Hz), 125.8 (q, $^3J_{C\text{-}F}$ = 4 Hz), 125.8, 124.5(q, $^1J_{C\text{-}F}$ = 272 Hz), 121.6, 55.7, 50.9, 37.5, 32.7, 31.9, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 28.8, 22.6, 14.1. HRMS: calculated [$C_{24}H_{37}F_3N_4S$ + H^+] 471.2759; found 471.2780.

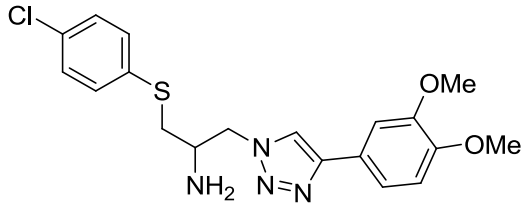
1-(Phenethylthio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9c



According to general procedure **1**: compound **9c** was prepared from 1-(aziridin-2-ylmethyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole **6** (0.04 g, 0.16 mmol, 1 equiv.), 2-phenylethanethiol **2d** (42 µL, 0.31 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 13 h, purified by column chromatography (3 % DCM/MeOH) to obtain 56 mg (90%) of **9c** as an amorphous powder. IR (KBr): 3375, 3345, 3295, 3140, 2940, 2910, 2850, 1620, 1605, 1585, 1565, 1500, 1455, 1415, 1335, 1155, 1115, 1075, 1065, 1050, 855, 820, 770, 735, 700, 660, 600. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.95 (s, 1H, H-C(triaz.)), 7.94 (d, ^3J = 8.0 Hz, 2H, H-C(Ar)), 7.68 (d,

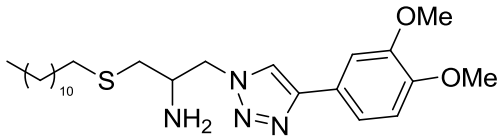
^3J = 8.2 Hz, 2H, H-C(Ar)), 7.34 – 7.21 (m, 5H, H-C(Ar)), 4.52 (dd, ^2J = 13.7 Hz, ^3J = 4.3 Hz, 1H, Ha-C(3)), 4.32 (dd, ^2J = 13.7 Hz, ^3J = 7.2 Hz, 1H, Hb-C(3)), 3.50 – 3.35 (m, 1H, H-C(2)), 2.95 – 2.76 (m, 4H, Ph-($\underline{CH_2}$)$_2$-S), 2.65 (dd, ^2J = 13.4 Hz, ^3J = 5.4 Hz, 1H, Ha-C(1)), 2.48 (dd, ^2J = 13.4 Hz, ^3J = 7.4 Hz, 1H, Hb-C(1)), 1.65 (s, 2H, -NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 146.2, 140.0, 133.9, 130.0 (q, $^2J_{C\text{-}F}$ = 33 Hz), 128.5 (2C), 126.5, 125.8 (q, $^3J_{C\text{-}F}$ = 4 Hz), 125.8, 124.3 (q, $^1J_{C\text{-}F}$ = 271 Hz), 121.6, 55.6, 50.9, 37.6, 36.2, 34.2. HRMS: calculated [$C_{20}H_{21}F_3N_4S + H^+$] 407.1507; found 407.1526.

1-((4-Chlorophenyl)thio)-3-(4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 10a



According to general procedure **1**: compound **10a** was prepared from 1-(aziridin-2-ylmethyl)-4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazole **7** (0.05 g, 0.21 mmol, 1 equiv.), 4-chlorothiophenol **2a** (0.06 g, 0.42 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 14 h, purified by column chromatography (3 % DCM/MeOH) to obtain 73 mg (86%) of **10a** as an amorphous powder. IR (KBr): 3370, 3305, 3125, 3095, 3005, 2960, 2935, 2840, 1610, 1585, 1560, 1510, 1475, 1455, 1440, 1370, 1255, 1230, 1170, 1140, 1095, 1025, 1010, 810, 765, 630, 620. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.72 (s, 1H, H-C(triaz.)), 7.43 (d, ^4J = 1.4 Hz, 1H, H-C(Ar)), 7.31 – 7.19 (m, 4H, H-C(Ar)), 6.88 (d, ^3J = 8.4 Hz, 2H, H-C(Ar)), 4.50 (dd, ^2J = 13.7 Hz, ^3J = 4.3 Hz, 1H, Ha-C(3)), 4.36 (dd, ^2J = 13.8 Hz, ^3J = 6.7 Hz, 1H, Hb-C(3)), 3.93, 3.89 (2s, 6H, 2OMe), 3.51 – 3.34 (m, 1H, H-C(2)), 3.03 (dd, ^2J = 13.7 Hz, ^3J = 5.4 Hz, 1H, Ha-C(1)), 2.86 (dd, ^2J = 13.7 Hz, ^3J = 7.3 Hz, 1H, Hb-C(1)), 2.22 (s, 2H, -NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 149.3, 149.1, 147.6, 133.3, 132.9, 131.4, 129.3, 123.2, 120.2, 118.1, 111.3, 108.8, 55.9, 55.9, 54.8, 50.7, 39.2. HRMS: calculated [$C_{19}H_{21}ClN_4O_2S + H^+$] 405.1142; found 405.1153.

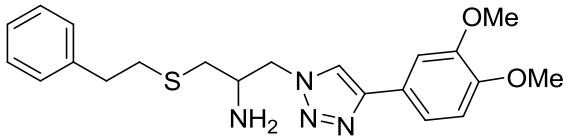
1-(4-(3,4-Dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)-3-(dodecylthio)propan-2-amine 10b



According to general procedure 1: compound **10b** was prepared from 1-(aziridin-2-ylmethyl)-4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazole **7** (0.05 g, 0.20 mmol, 1 equiv.), dodecane-1-thiol **2b** (96 µL, 0.40 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 16 h, purified by column chromatography (3 % DCM/MeOH) to obtain 71 mg (77%) of **10b** as an amorphous powder. IR (KBr): 3360, 3295, 3125, 3105, 2955, 2920, 2850, 1610, 1590, 1515, 1470, 1445, 1370, 1265, 1235, 1170, 1145, 1025, 860, 815, 765, 720, 620. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.82 (s, 1H, H-C(triaz.)), 7.49 (d, ^4J = 1.8 Hz, 1H, H-C(Ar)), 7.29 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz, 1H, H-C(Ar)), 6.91 (d, ^3J = 8.3 Hz, 1H, H-C(Ar)), 4.53 (dd, ^2J = 13.7 Hz, ^3J = 4.3 Hz, 1H, Ha-C(3)), 4.33 (dd, ^2J = 13.7 Hz, ^3J = 7.3 Hz, 1H, Hb-C(3)), 3.97, 3.92 (2s, 6H, 2OMe), 3.53 – 3.40 (m, 1H, H-C(2)), 2.67 (dd, ^2J = 13.4 Hz, ^3J = 5.3 Hz, 1H, Ha-C(1)), 2.54 (t, ^3J = 7.3 Hz, 2H, $\underline{CH_2}$-S), 2.50 (dd, ^2J = 13.4 Hz, ^3J = 7.6 Hz, 1H, Hb-C(1)), 1.65 – 1.50 (m, 4H, CH_2, -NH_2), 1.44 – 1.16 (m, 18H,

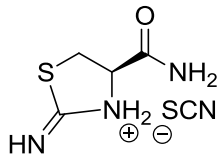
9CH_2), 0.88 (t, ^3J = 6.6 Hz, 3H, Me).^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 149.3, 149.1, 147.6, 123.5, 120.1, 118.1, 111.3, 108.9, 56.0, 55.9, 55.7, 50.9, 37.5, 32.8, 31.9, 29.7, 29.6 (3C), 29.50, 29.3, 29.2, 28.8, 22.7, 14.1. HRMS: calculated [$C_{25}H_{42}N_4O_2S$ + H^+] 463.3096; found 463.3114.

1-(4-(3,4-Dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)-3-(phenethylthio) propan- 2-amine 10c



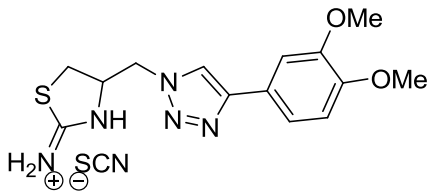
According to general procedure **1**: compound **10c** was prepared from 1-(aziridin-2-ylmethyl)-4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazole **7** (0.05 g, 0.21 mmol, 1 equiv.), 2-phenylethanethiol **2d** (57 µL, 0.42 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 25 °C in 14 h, purified by column chromatography (3 % DCM/MeOH) to obtain 75 mg (90%) of **10c** as an amorphous powder. IR (KBr): 3365, 3305, 3130, 3025, 2935, 2835, 1595, 1505, 1465, 1455, 1365, 1255, 1235, 1140, 1025, 865, 805, 765, 700, 630. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.78 (s, 1H, H-C(triaz.)), 7.48 (d, ^4J = 1.8 Hz, 1H, H-C(Ar)), 7.32 – 7.14 (m, 6H, H-C(Ar)), 6.90 (d, ^3J = 8.3 Hz, 1H, H-C(Ar)), 4.47 (dd, ^2J = 13.7 Hz, ^3J = 4.5 Hz, 1H, Ha-C(3)), 4.29 (dd, ^2J = 13.7 Hz, ^3J = 7.2 Hz, 1H, Hb-C(3)), 3.95, 3.90 (2s, 6H, 2OMe), 3.49 – 3.34 (m, 1H, H-C(2)), 2.94 – 2.75 (m, 4H, Ph-($\underline{CH_2}$)$_2$-S), 2.65 (dd, ^2J = 13.4 Hz, ^3J = 5.3 Hz, 1H, Ha-C(1)), 2.48 (dd, ^2J = 13.4 Hz, ^3J = 7.5 Hz, 1H, Hb-C(1)), 1.67 (s, 2H, -NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 149.3, 149.1, 147.5, 140.0, 128.5 (2C), 126.4, 123.4, 120.1, 118.1, 111.3, 108.9, 55.9, 55.9, 55.5, 50.9, 37.5, 36.2, 34.1. HRMS: calculated [$C_{21}H_{26}N_4O_2S$ + H^+] 399.1844; found 399.1858.

(*R*)-4-carbamoyl-2-iminothiazolidin-3-ium rhodanide 11



According to general procedure **1**: compound **11** was prepared from (*S*)-aziridine-2-carboxamide **1** (0.05 g, 0.58 mmol, 1 equiv.), KSCN (0.11 g, 1.16 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 60 °C in 18 h, purified by column chromatography (10 % DCM/EtOH) to obtain 74 mg (62%) of (*R*)-4-carbamoyl-2-iminothiazolidin-3-ium rhodanide **11** as an amorphous powder. Single crystals of **11** were obtained by crystallization of EtOH. $[\alpha]_D^{25}$= - 61.6 (*c*=1, H_2O). IR (KBr): 3450, 3245, 2980, 2785, 2085, 2075, 1680, 1660, 1585, 1430, 1405, 1305, 1260, 665. ^{1}H-NMR (D_2O, 300 MHz) δ = 4.95 (dd, ^3J = 9.0, 4.7 Hz, 1H, H-C(4)), 3.99 (dd, ^2J = 11.7 Hz, ^3J = 9.0 Hz, 1H, Ha-C(5)), 3.69 (dd, ^2J = 11.7 Hz, ^3J = 4.7 Hz, 1H, Hb-C(5)).^{13}C-NMR (D_2O, 75.5 MHz) δ = 175.2, 172.0, 133.5, 66.0, 35.6. HRMS: calculated [$C_4H_7N_3OS$ + H^+] 146,0378; found 146,0383.

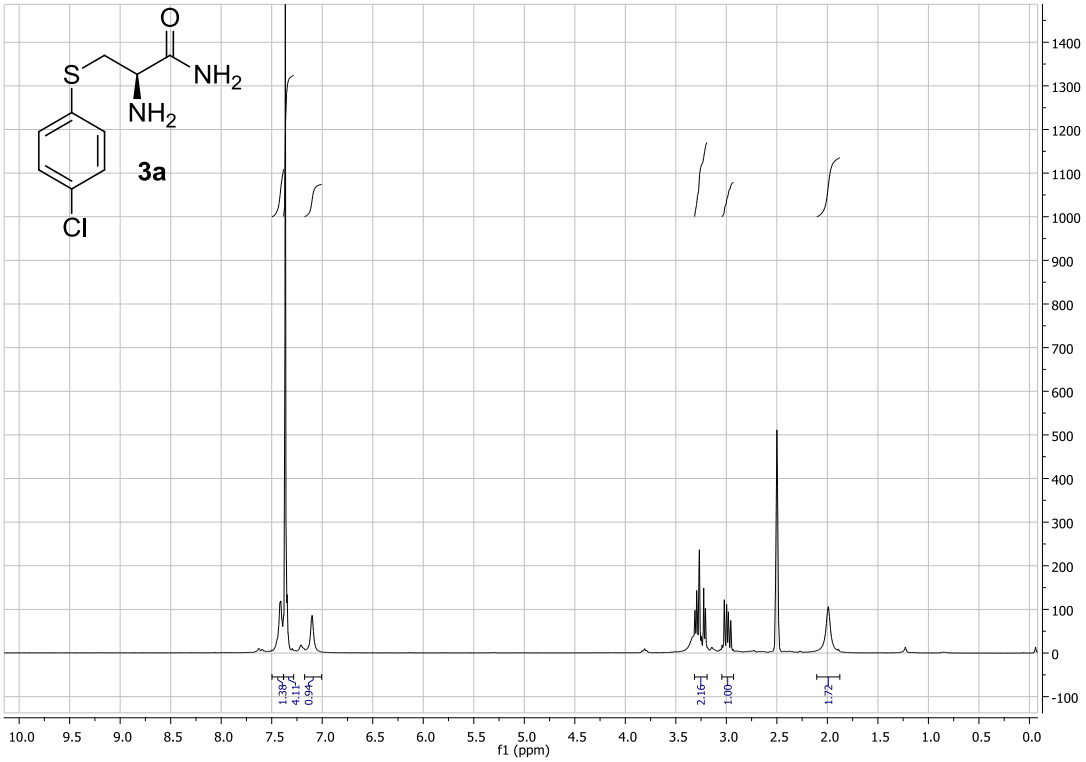
4-((4-(3,4-Dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)methyl)thiazolidin-2-iminium rhodanide 12



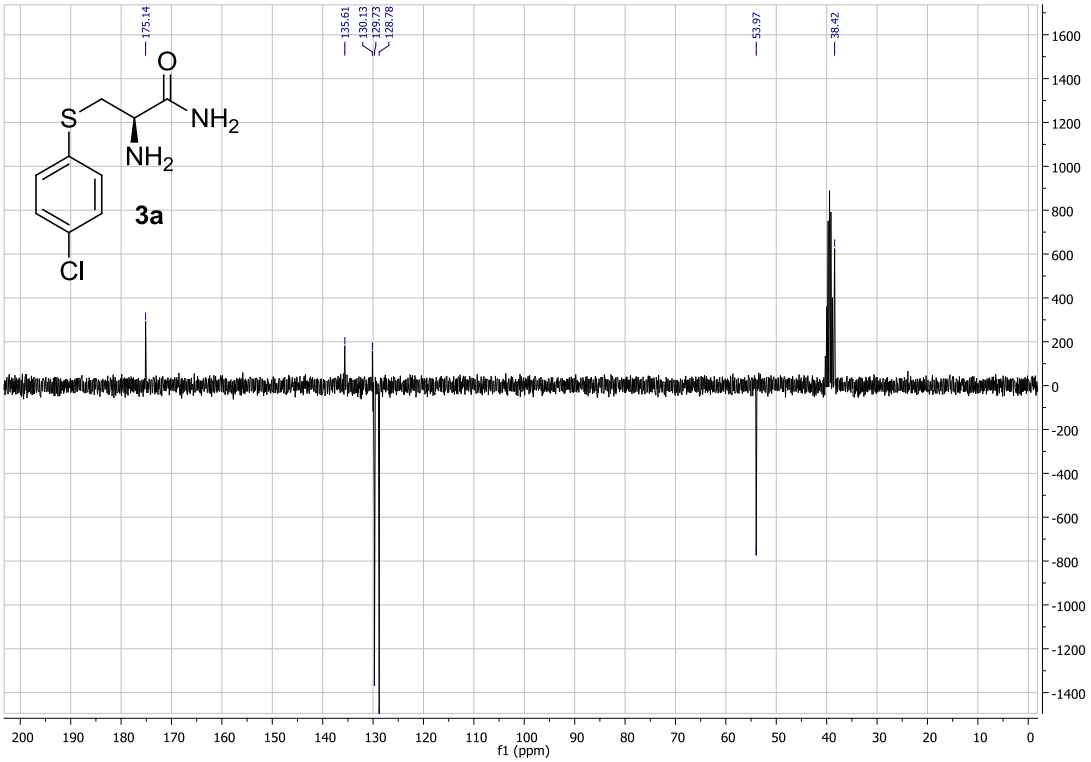
According to general procedure 1: compound **12** was prepared from 1-(aziridin-2-ylmethyl)-4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazole **7** (0.04 g, 0.17 mmol, 1 equiv.), KSCN (0.03 g, 0.35 mmol, 2 equiv.), SO_2 (25 ± 2 g) at 60 °C in 13 h, purified by column chromatography (3 % DCM/MeOH) to obtain 62 mg (95%) of **12** as an amorphous powder. IR (KBr): 3315, 3135, 3000, 2960, 2835, 2055, 1655, 1645, 1505, 1460, 1440, 1255, 1235, 1165, 1140, 1025, 865, 805, 765, 730, 630. ^{1}H-NMR (MeOD$_{d4}$, 300 MHz) δ = 8.31 (s, 1H, H-C(triaz.)), 7.42 (d, ^{4}J = 1.7 Hz, 1H, H-C(Ar)), 7.36 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.8 Hz, 1H, H-C(Ar)), 7.00 (d, ^{3}J = 8.3 Hz, 1H, H-C(Ar)), 4.86 – 4.75 (m, 1H, H-C(4)), 4.72 – 4.61 (m, 2H, H_2C(4')) 3.88, 3.85 (2s, 6H, 2OMe), 3.74 (dd, ^{2}J = 11.6 Hz, ^{3}J = 8.1 Hz, 1H, Ha-C(5)), 3.47 (dd, ^{2}J = 11.6 Hz, ^{3}J = 4.3 Hz, 1H, Hb-C(5)). ^{13}C-NMR (MeOD$_{d4}$, 75 MHz) δ = 172.2, 150.8, 150.8, 149.0, 133.8, 124.5, 122.8, 119.6, 113.3, 110.6, 65.6, 56.6, 56.5, 53.6, 35.6. HRMS: calculated [$C_{14}H_{17}N_5O_2S + H^+$] 320.1171; found 320.1183.

4. ^{1}H and ^{13}C NMR Spectra

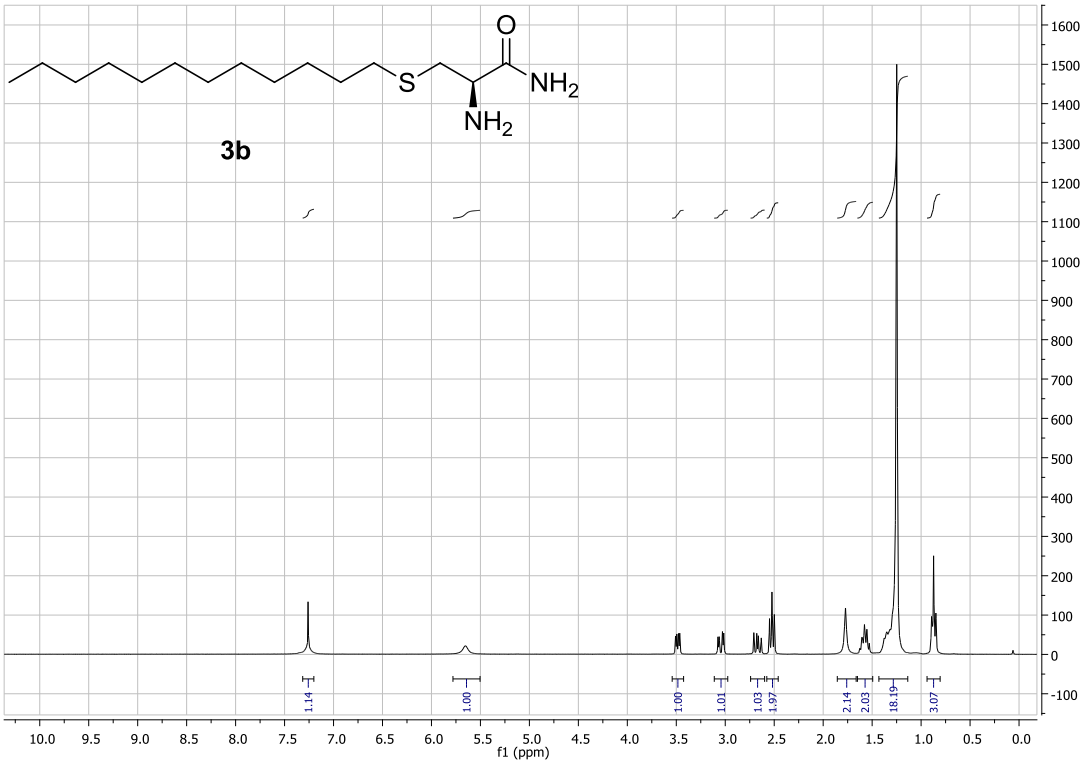
^{1}H-NMR (DMSO$_{d6}$, 300 MHz) spectrum of (*R*)-2-amino-3-((4-chlorophenyl) thio)propanamide 3a:



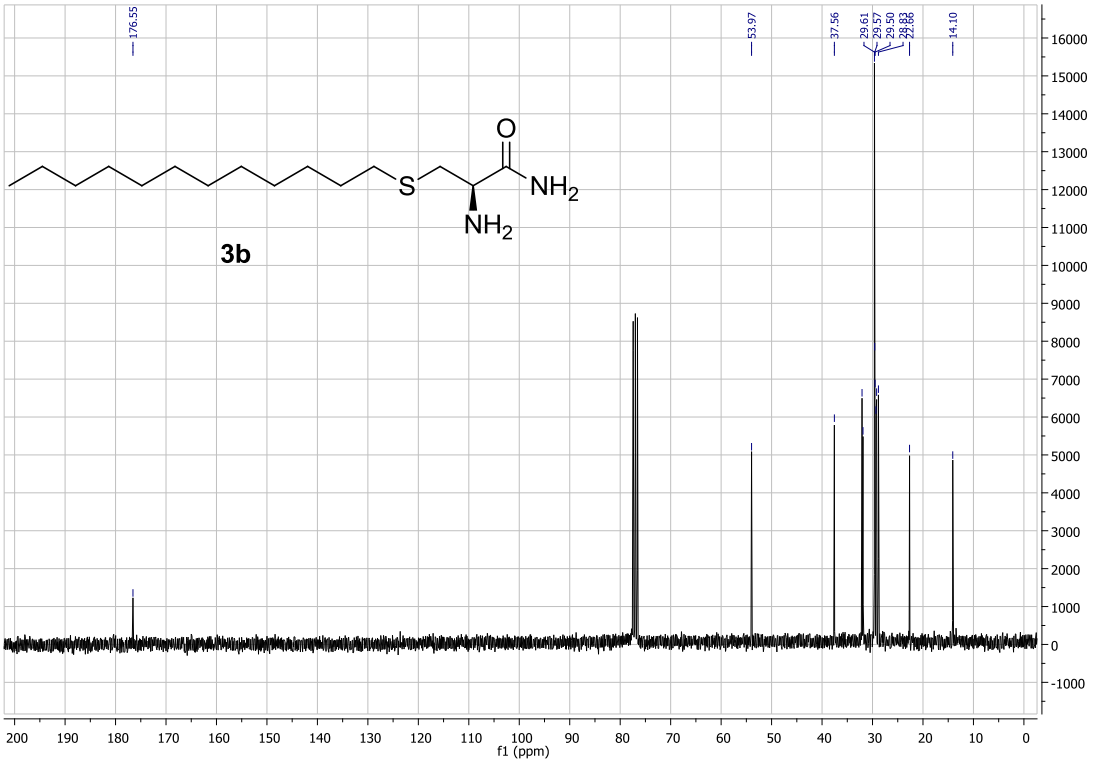
^{13}C-NMR (DMSO$_{d6}$, 75.5 MHz) spectrum of (*R*)-2-amino-3-((4-chlorophenyl) thio)propanamide 3a:



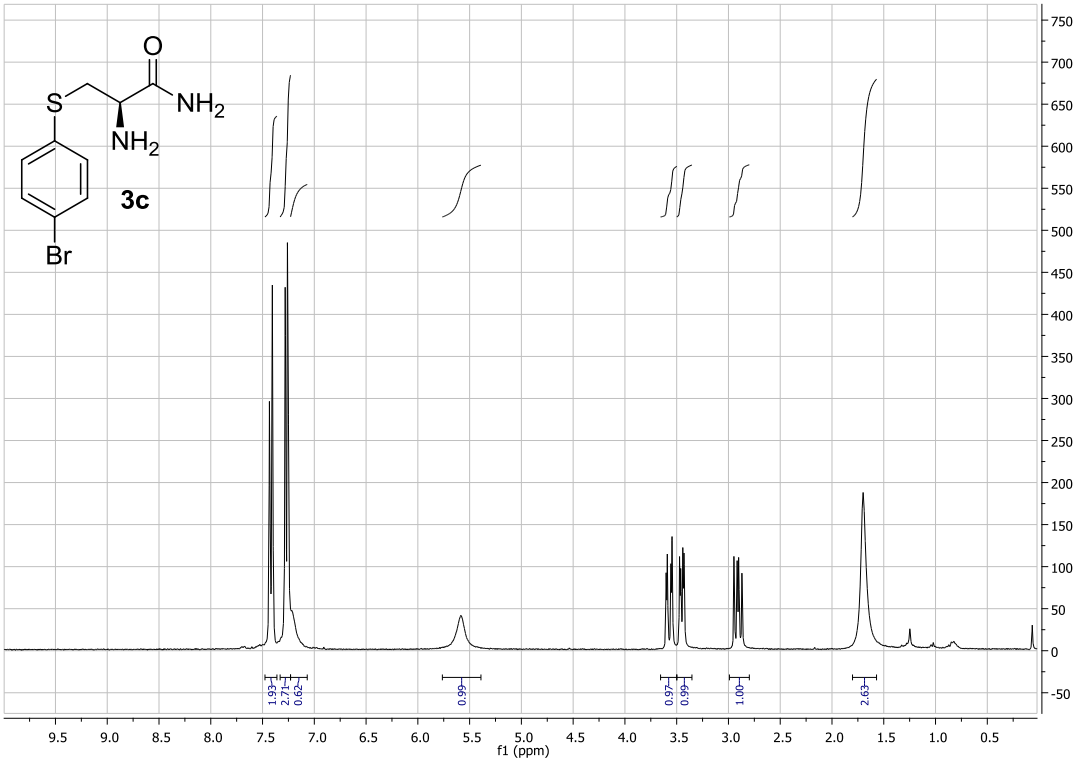
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of (*R*)-2-amino-3-(dodecylthio)propanamide 3b:



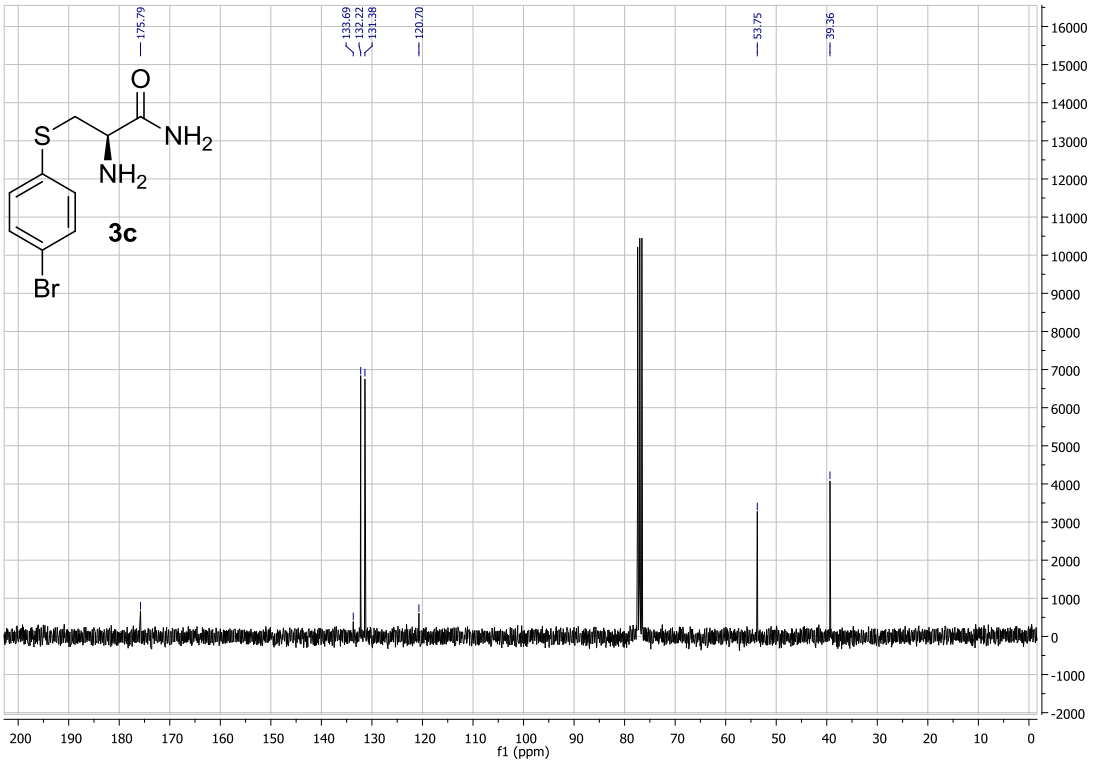
^{13}C-NMR ($CDCl_3$, 75.5 MHz) spectrum of (*R*)-2-amino-3-(dodecylthio)propanamide 3b:



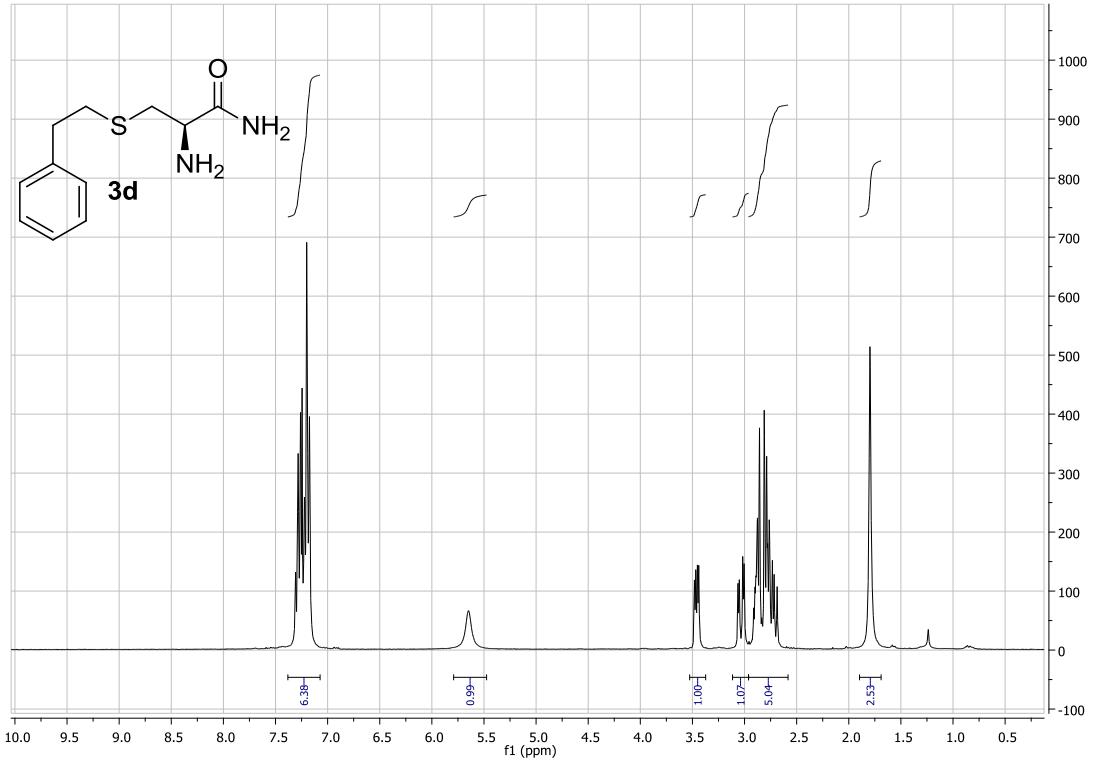
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of (*R*)-2-amino-3-((4-bromophenyl) thio)propanamide 3c:



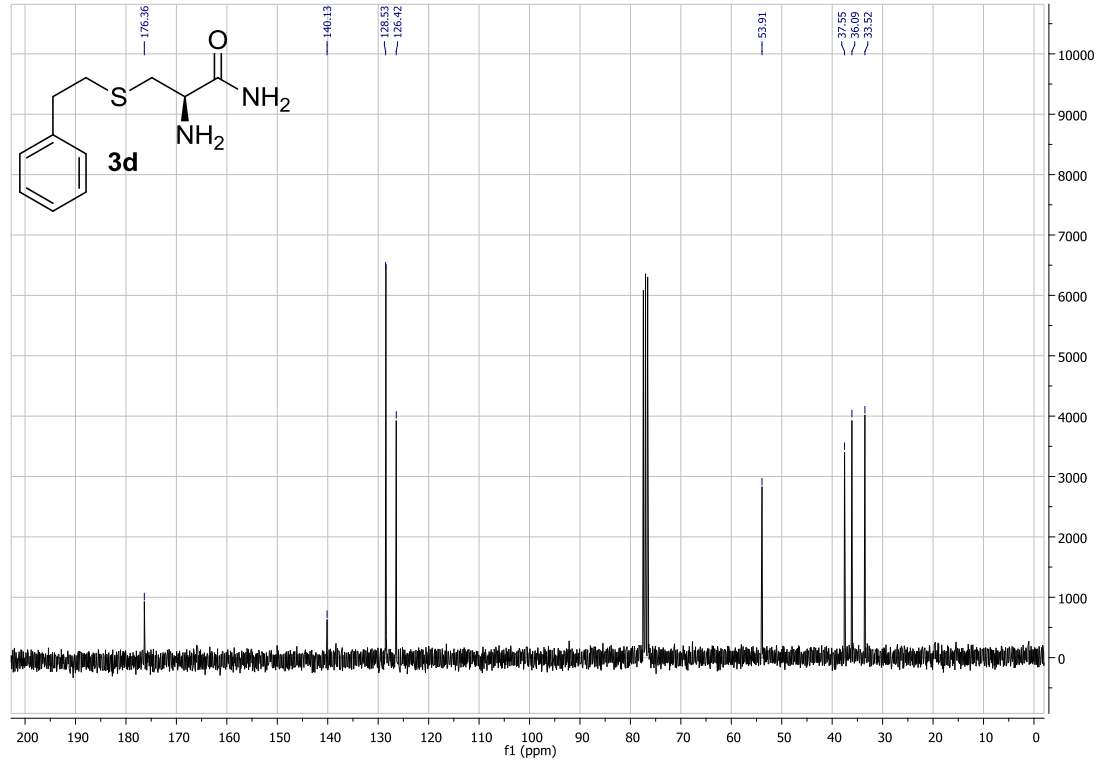
^{13}C-NMR ($CDCl_3$, 75.5 MHz) spectrum of (*R*)-2-amino-3-((4-bromophenyl) thio)propanamide 3c:



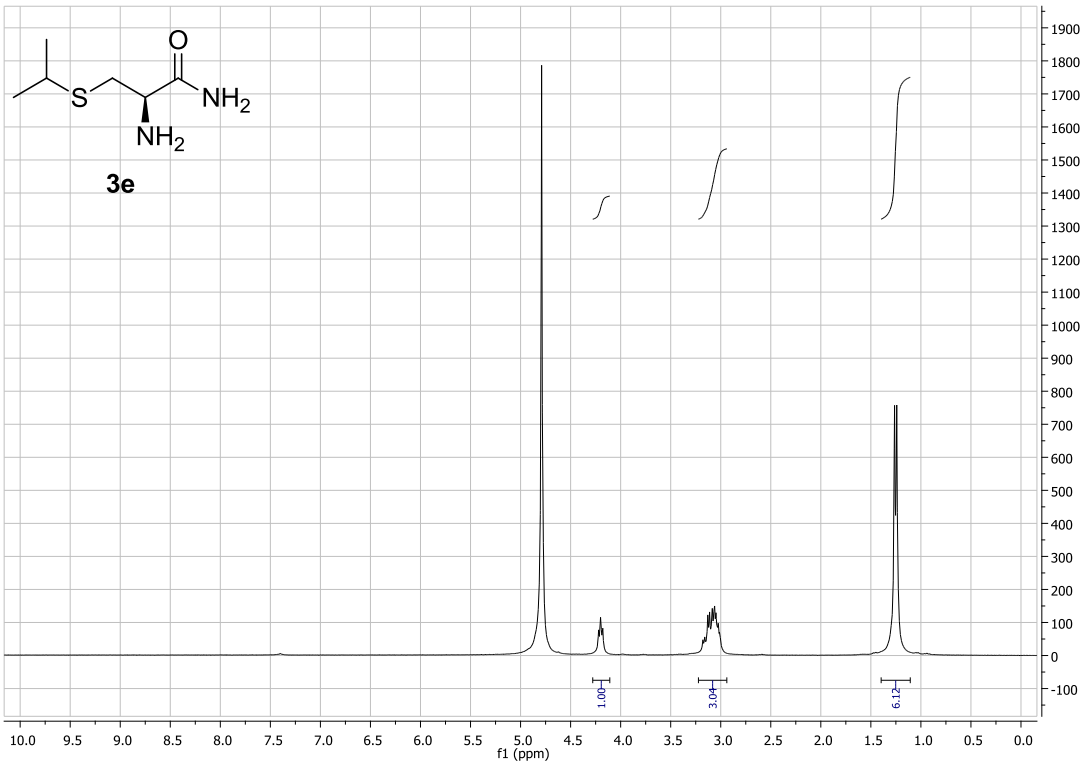
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of (*R*)-2-amino-3-(phenethylthio)propanamide 3d:



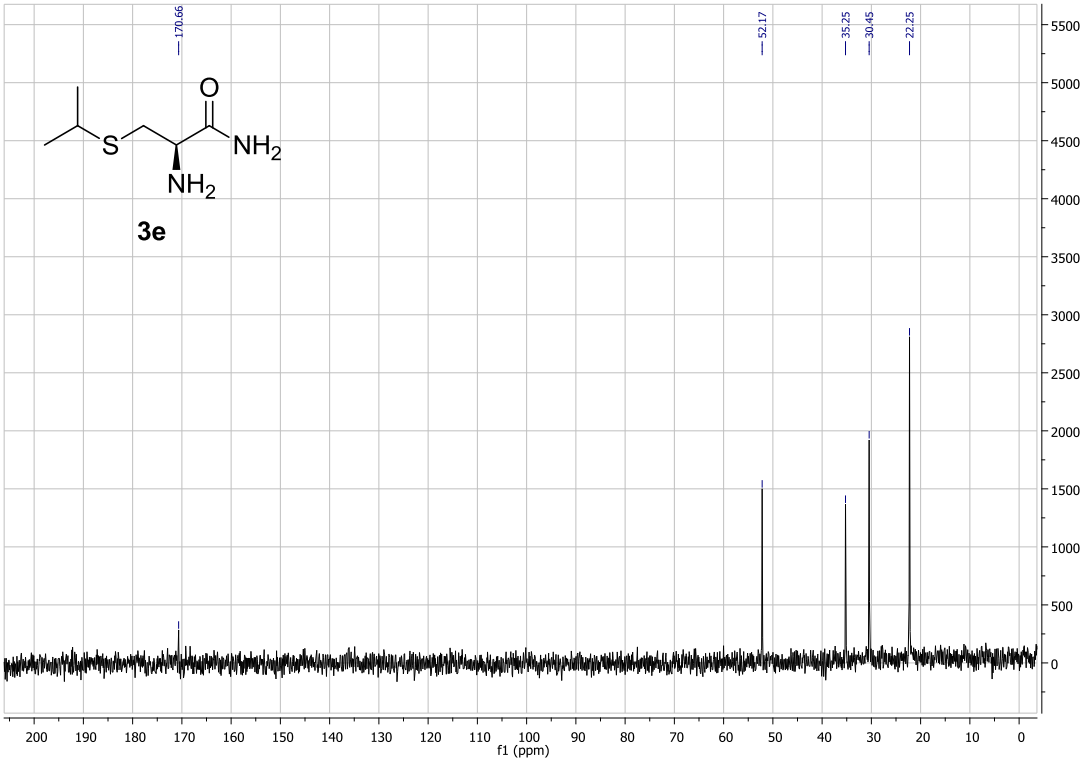
^{13}C-NMR ($CDCl_3$, 75.5 MHz) spectrum of (*R*)-2-amino-3-(phenethylthio)propanamide 3d:



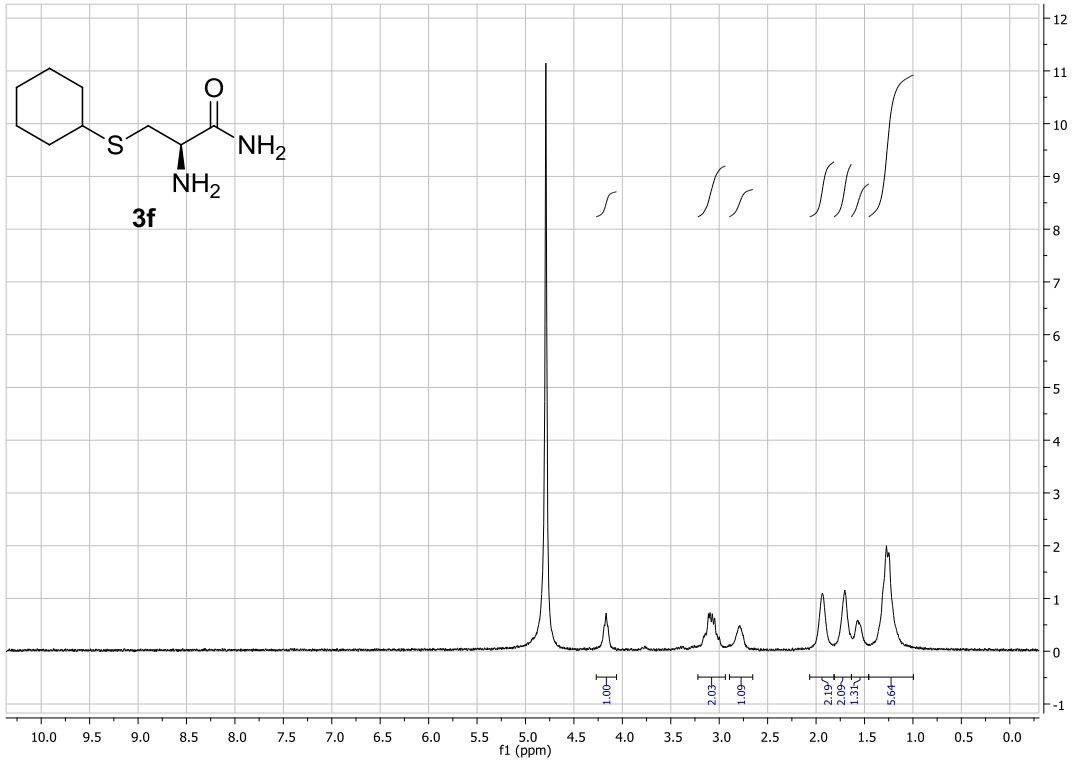
^{1}H-NMR (D_2O, 300 MHz) spectrum of (*R*)-2-amino-3-(isopropylthio)propanamide 3e:



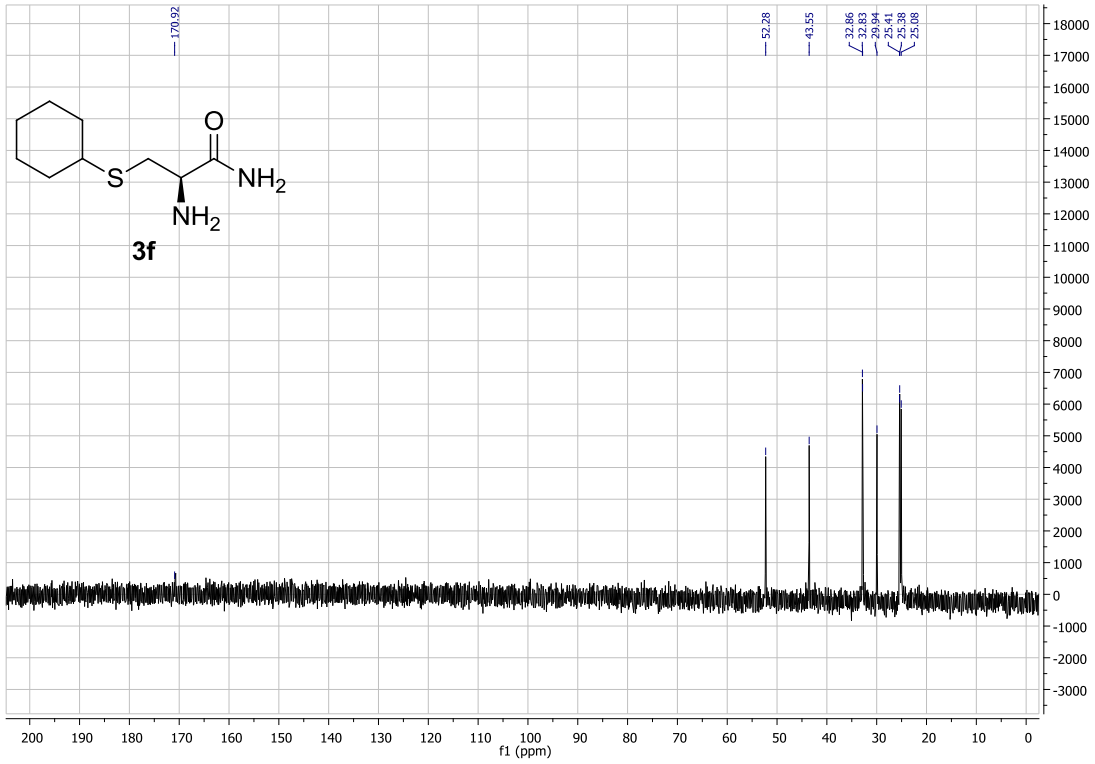
^{13}C-NMR (D_2O, 75.5 MHz) spectrum of (*R*)-2-amino-3-(isopropylthio)propanamide 3e:



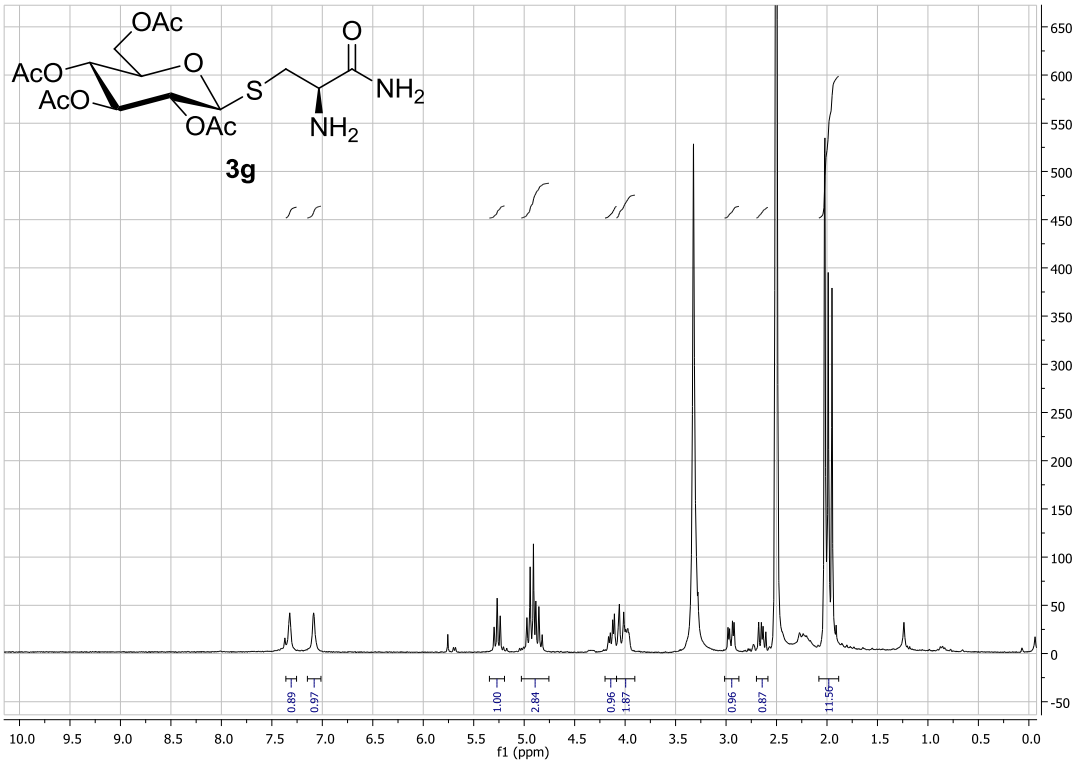
^{1}H-NMR (D_2O, 300 MHz) spectrum of (*R*)-2-amino-3-(cyclohexylthio)propanamide 3f:



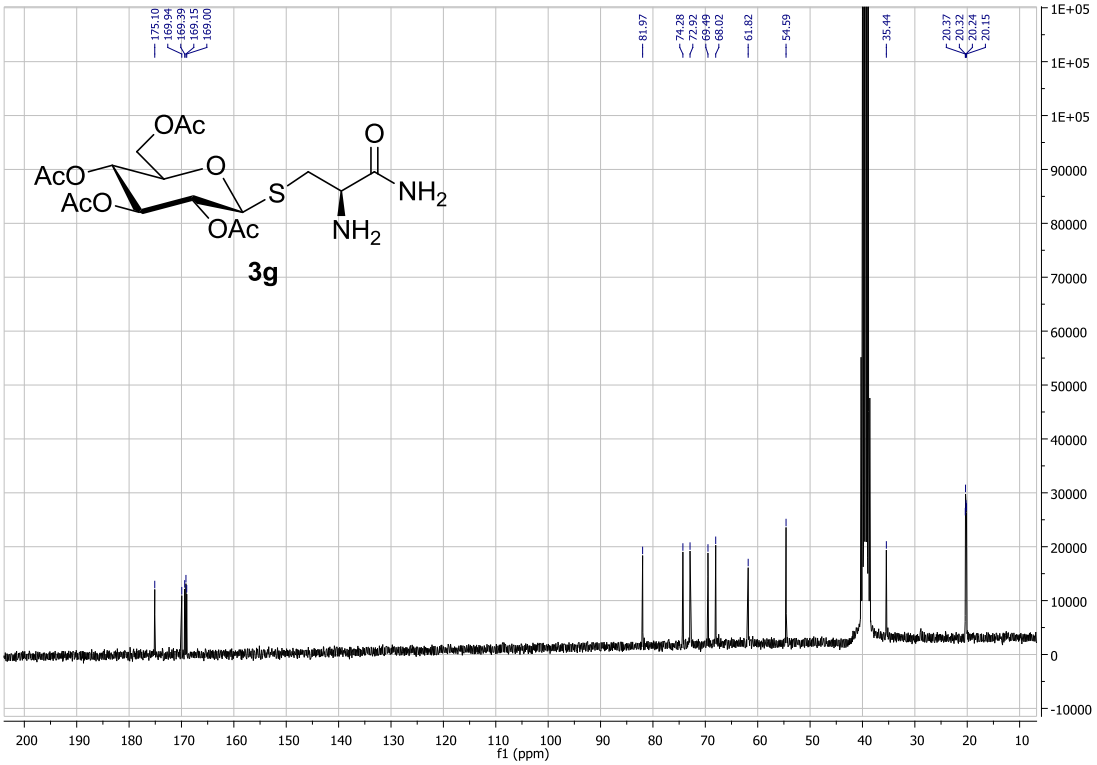
^{13}C-NMR (D_2O, 75.5 MHz) spectrum of (*R*)-2-amino-3-(cyclohexylthio)propanamide 3f:



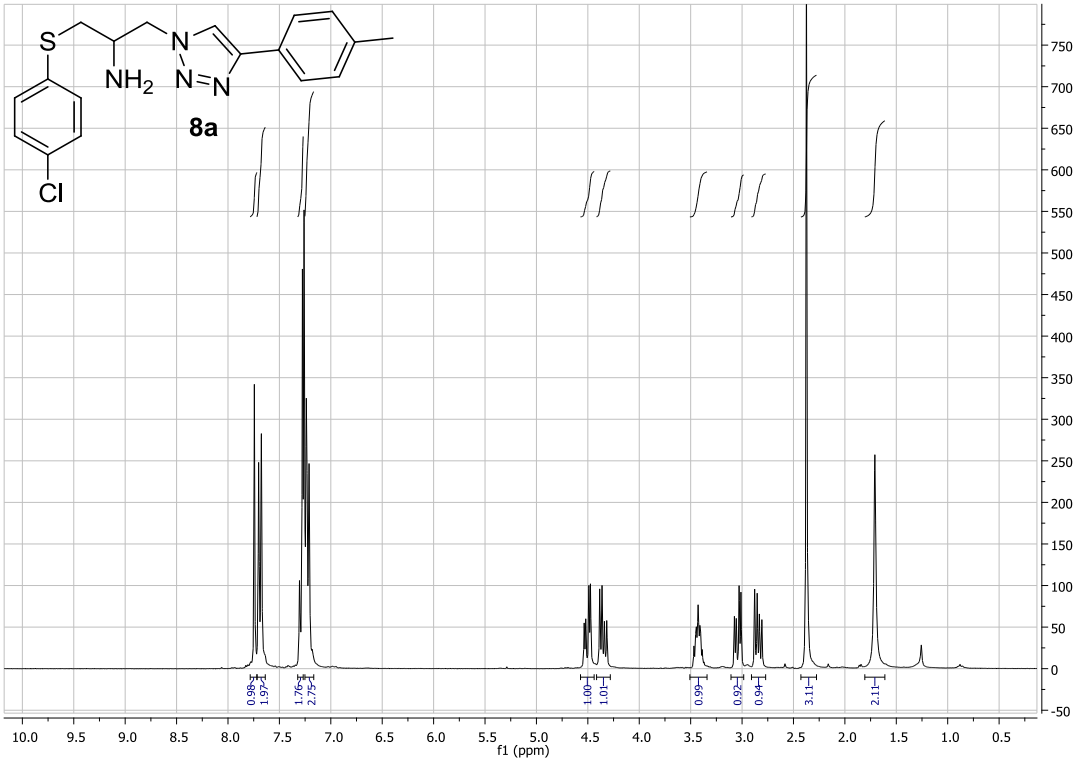
^{1}H-NMR (DMSO$_{d6}$, 300 MHz) spectrum of amino – acid carbohydrate conjugate 3g:



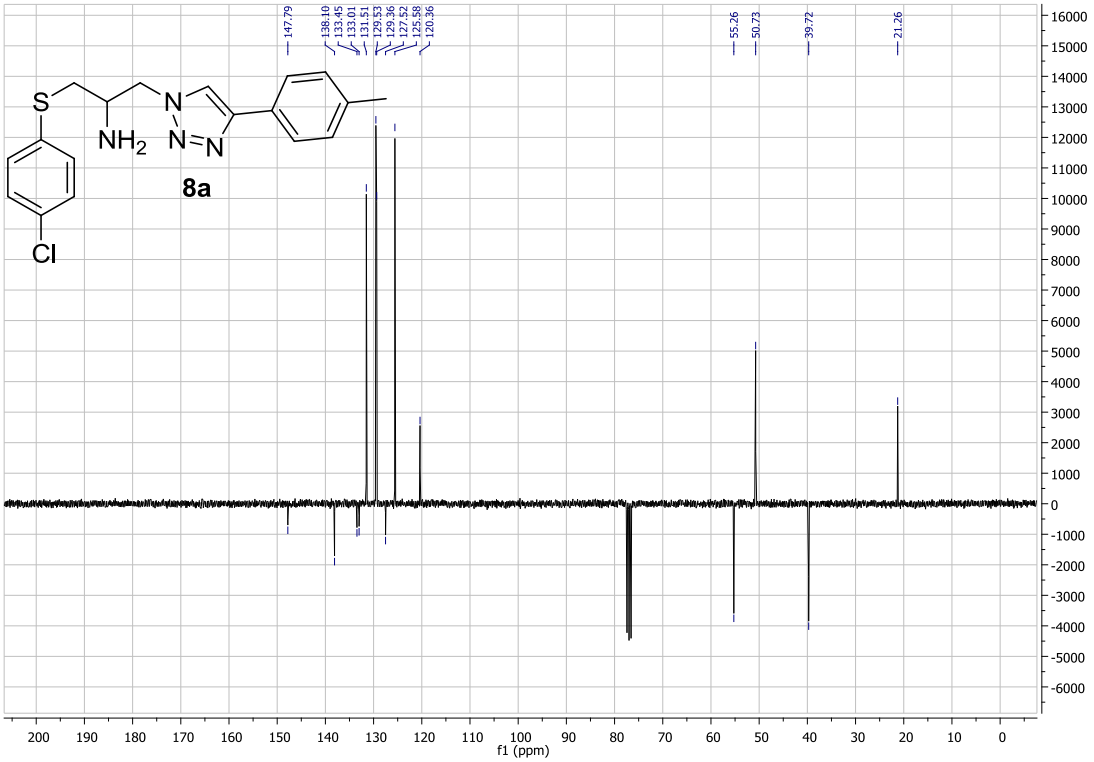
^{13}C-NMR (DMSO$_{d6}$, 75.5 MHz) spectrum of amino – acid carbohydrate conjugate 3g:



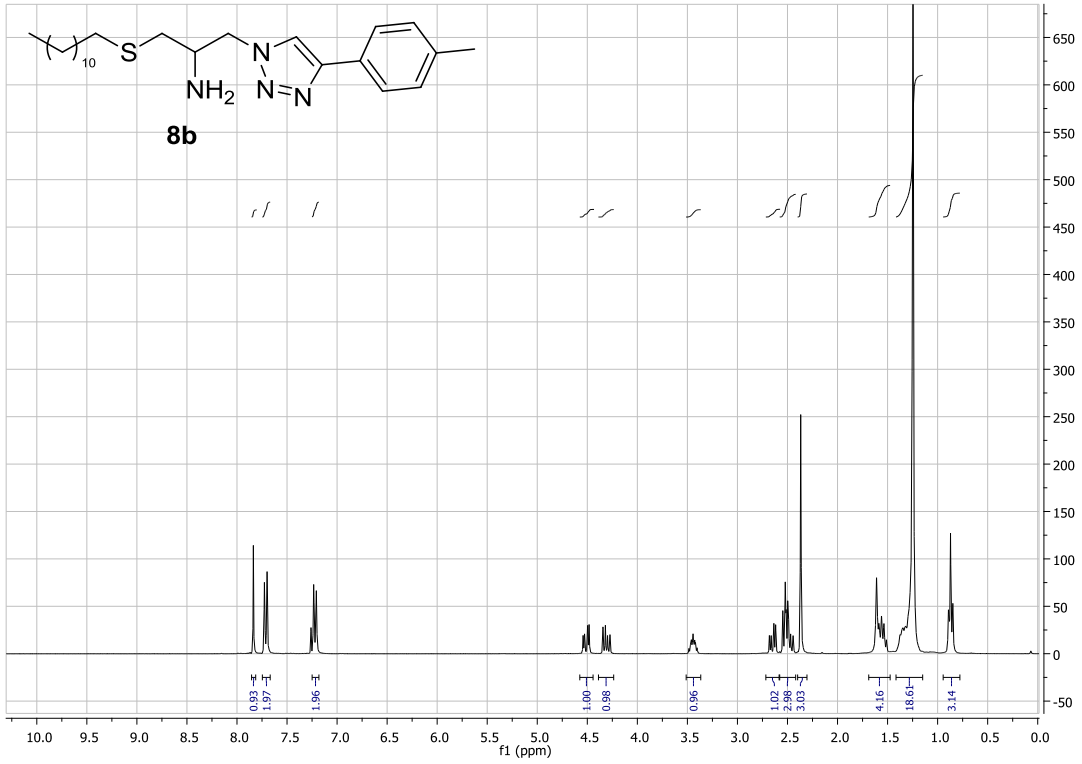
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-((4-chlorophenyl)thio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8a:



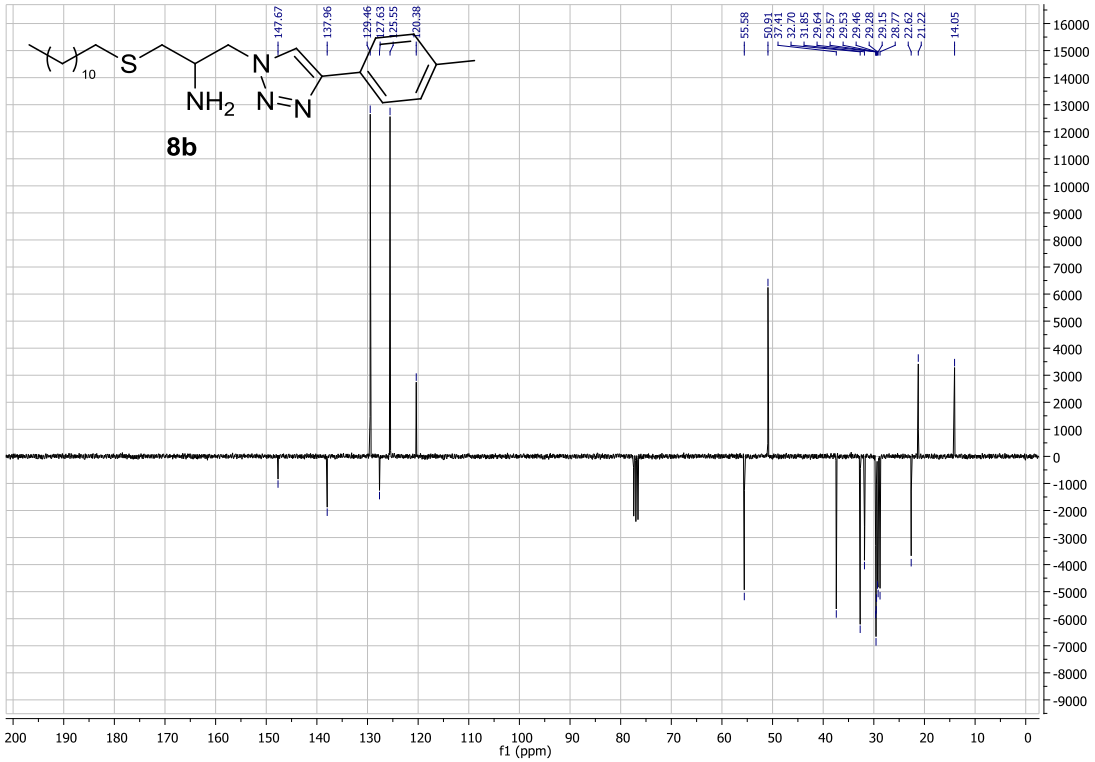
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-((4-chlorophenyl)thio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8a:



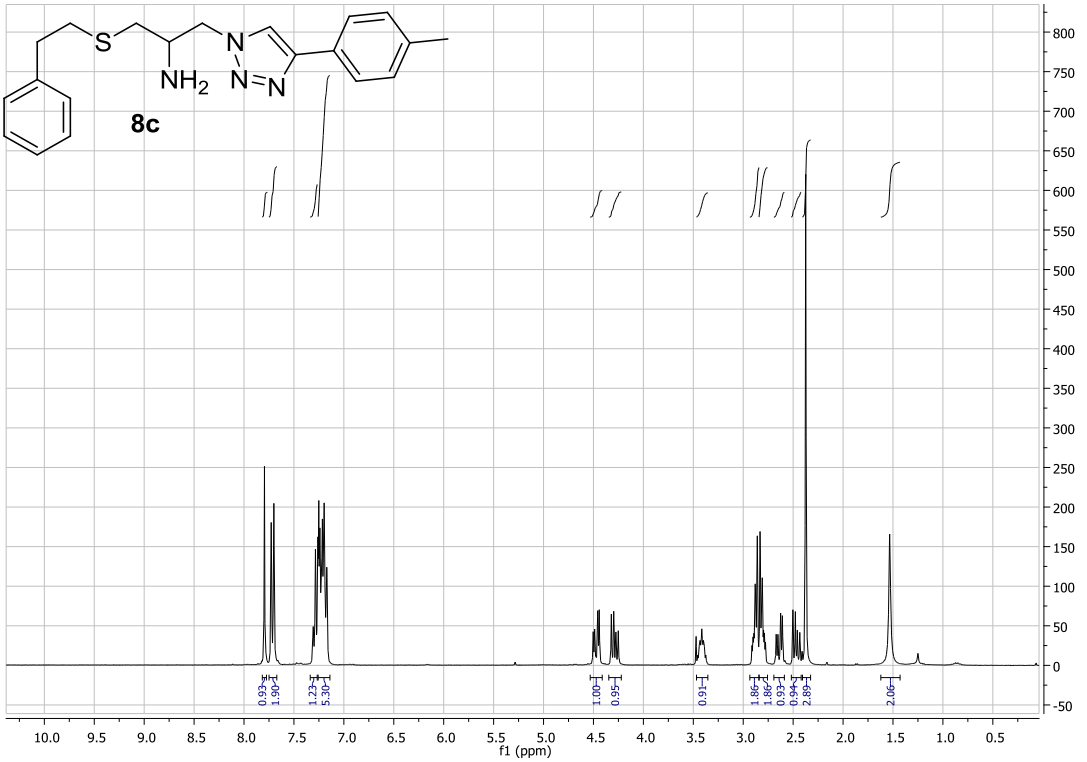
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-(dodecylthio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8b:



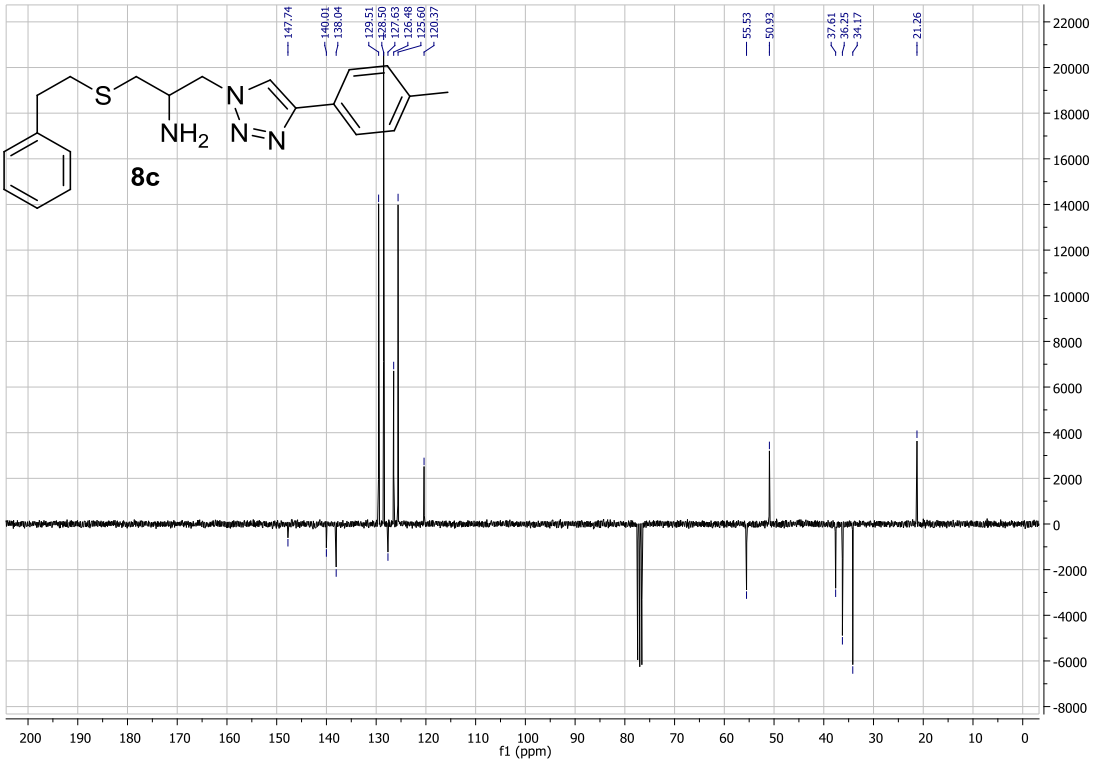
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-(dodecylthio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8b:



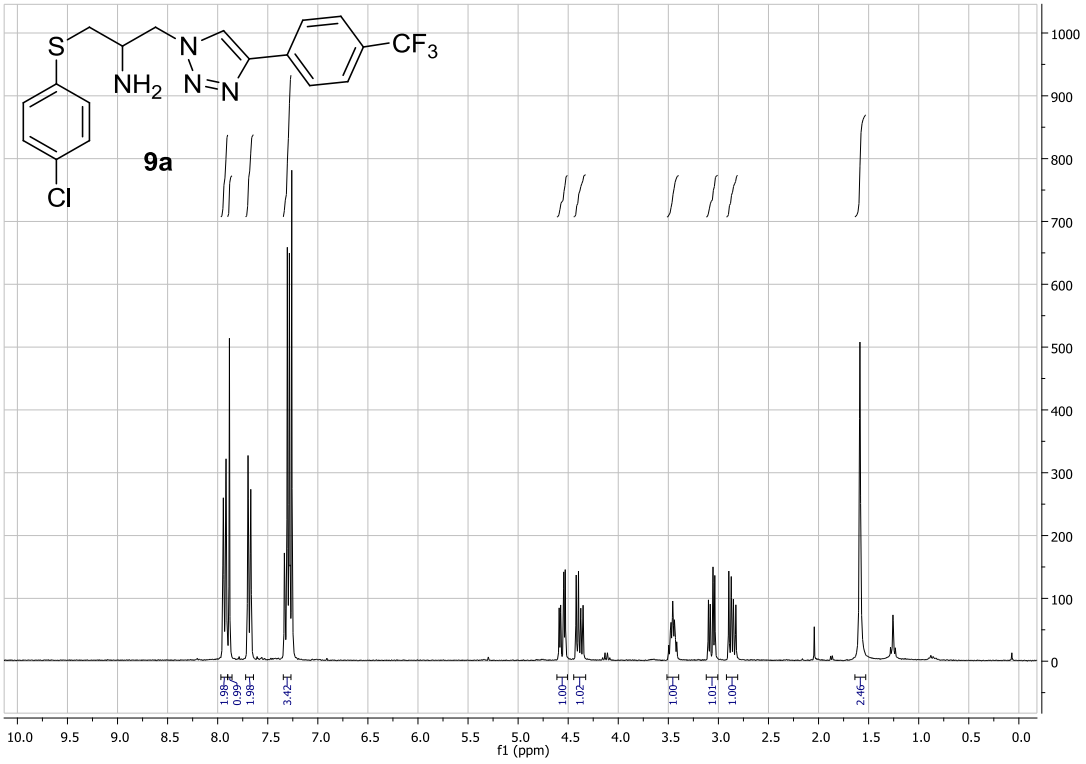
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-(phenethylthio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8c:



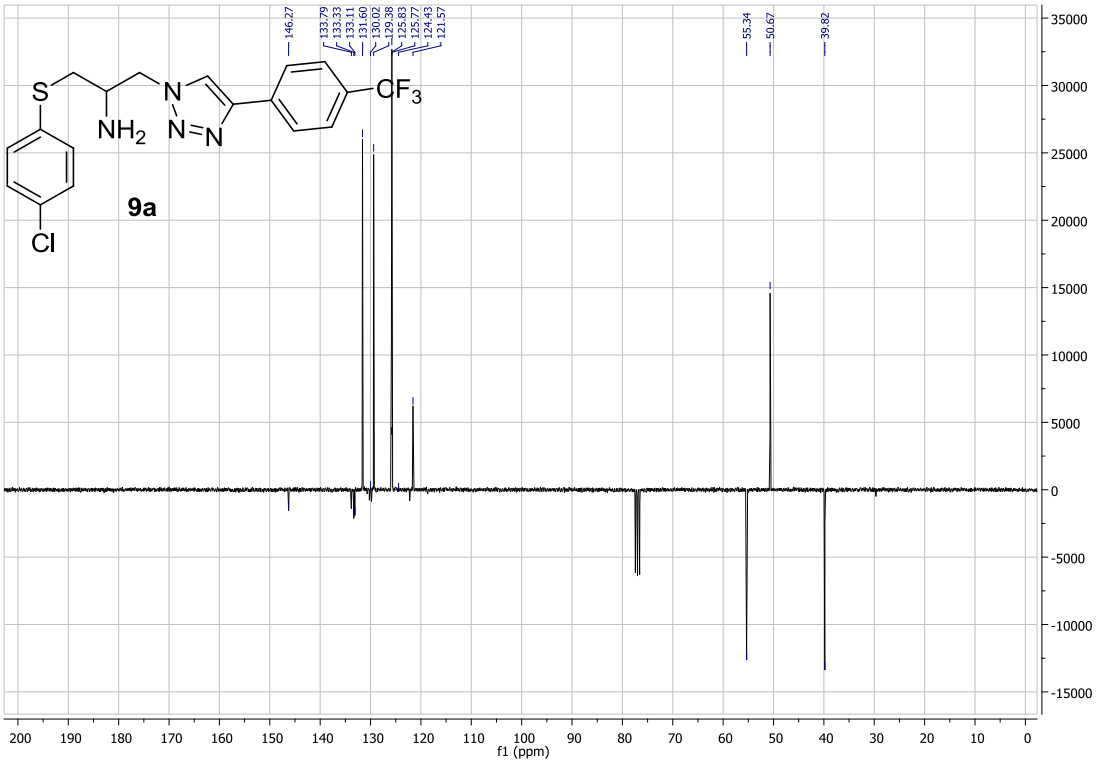
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-(phenethylthio)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 8c:



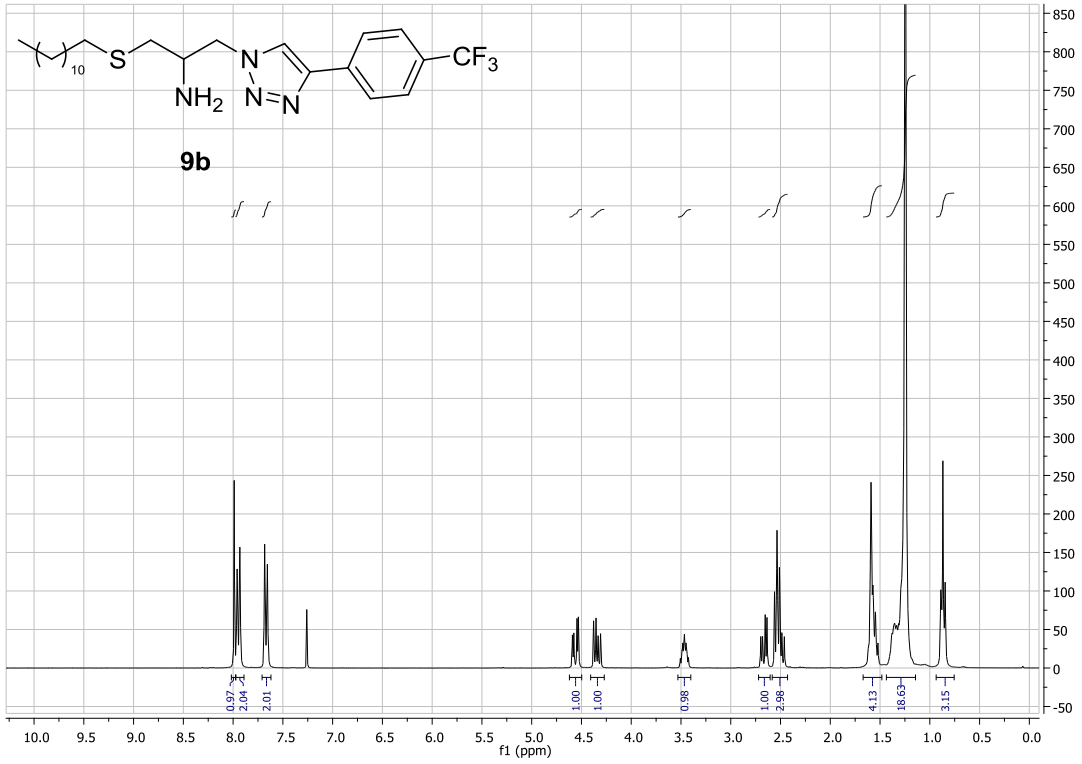
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-((4-chlorophenyl)thio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9a:



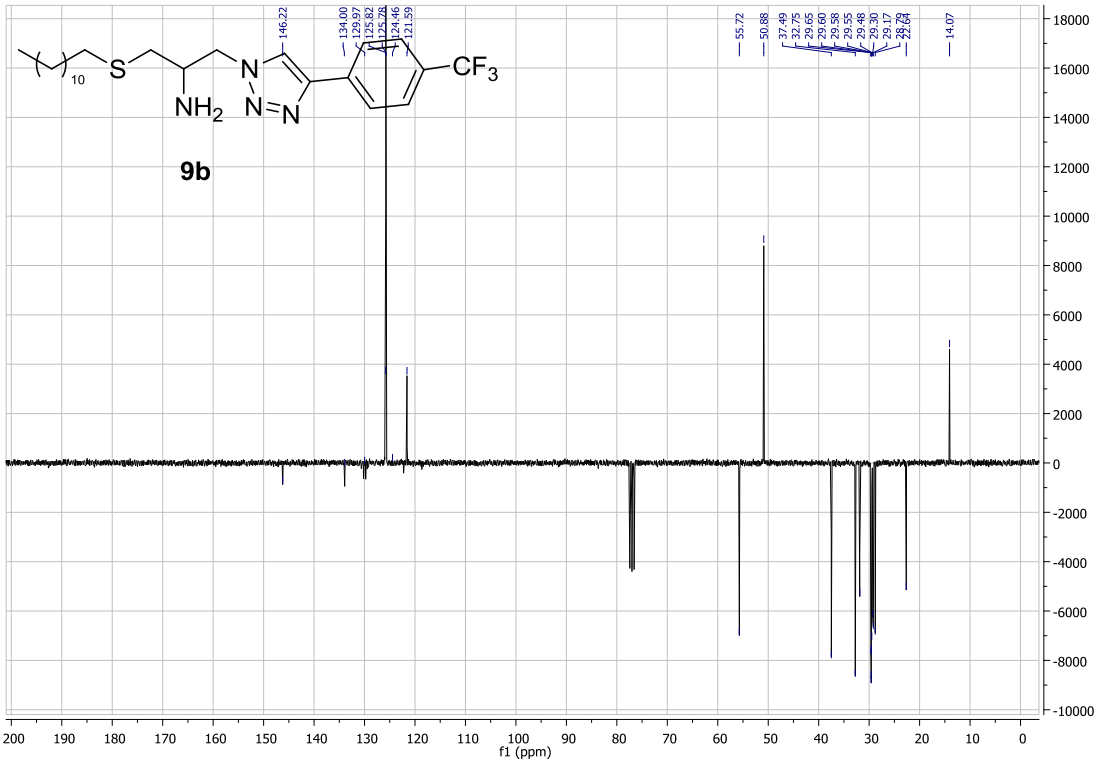
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-((4-chlorophenyl)thio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9a:



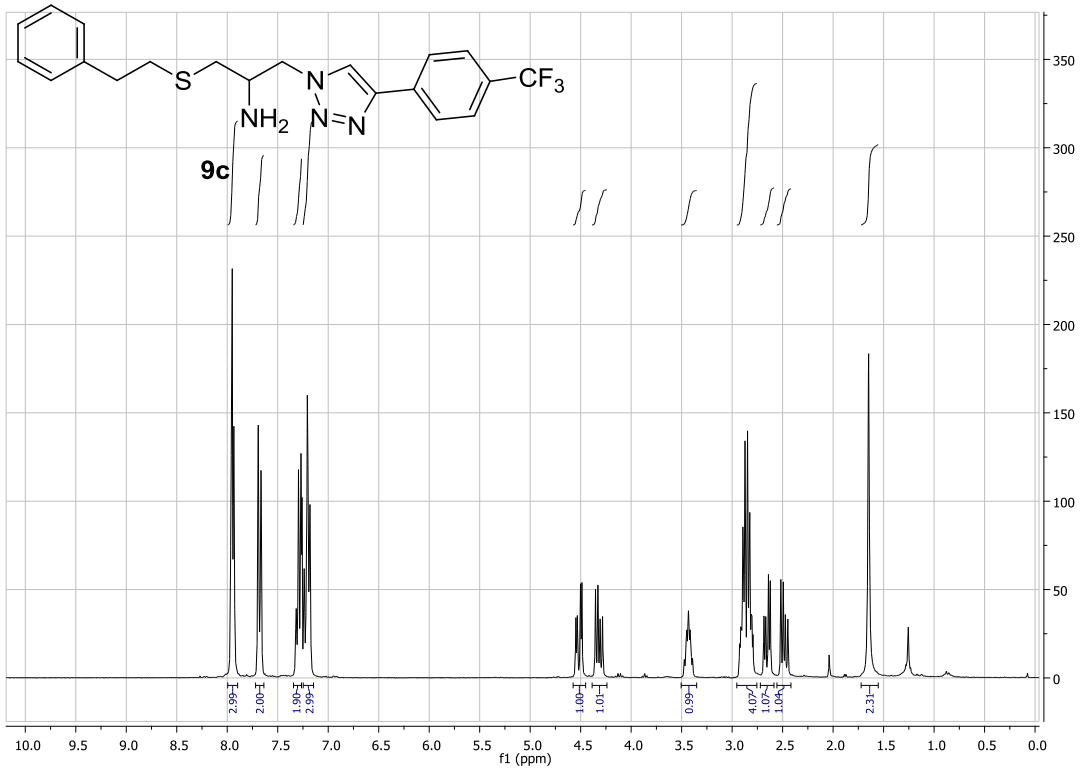
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-(dodecylthio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9b:



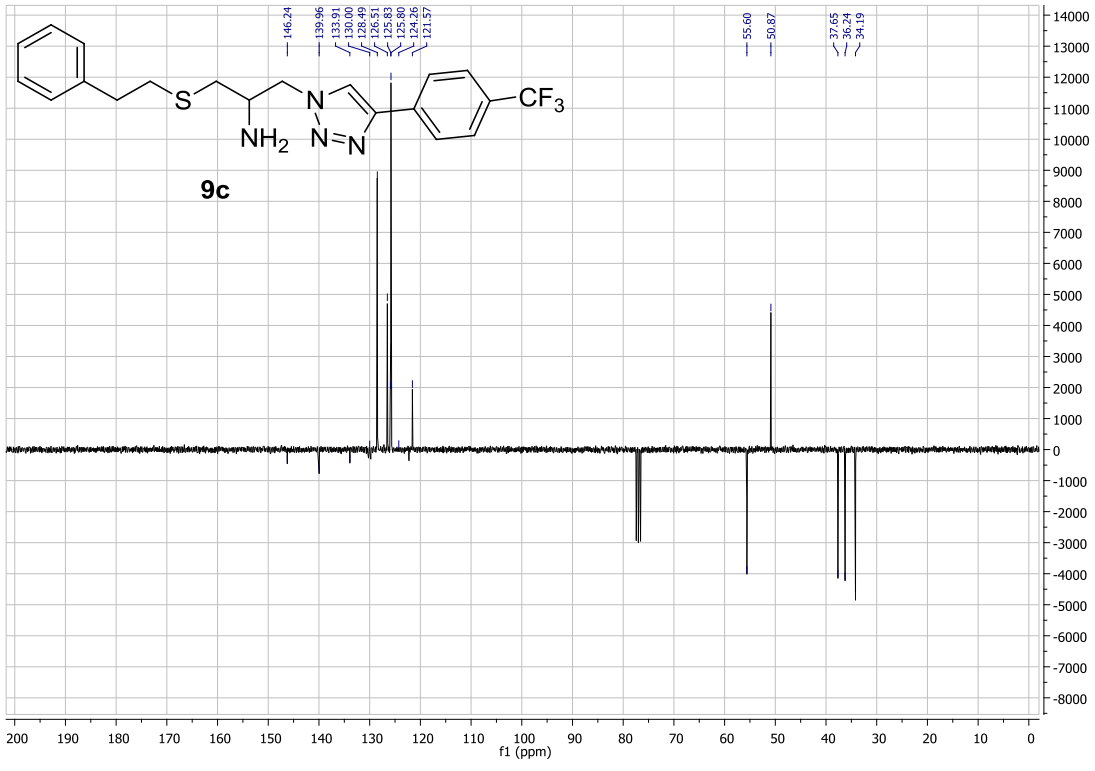
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-(dodecylthio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9b:



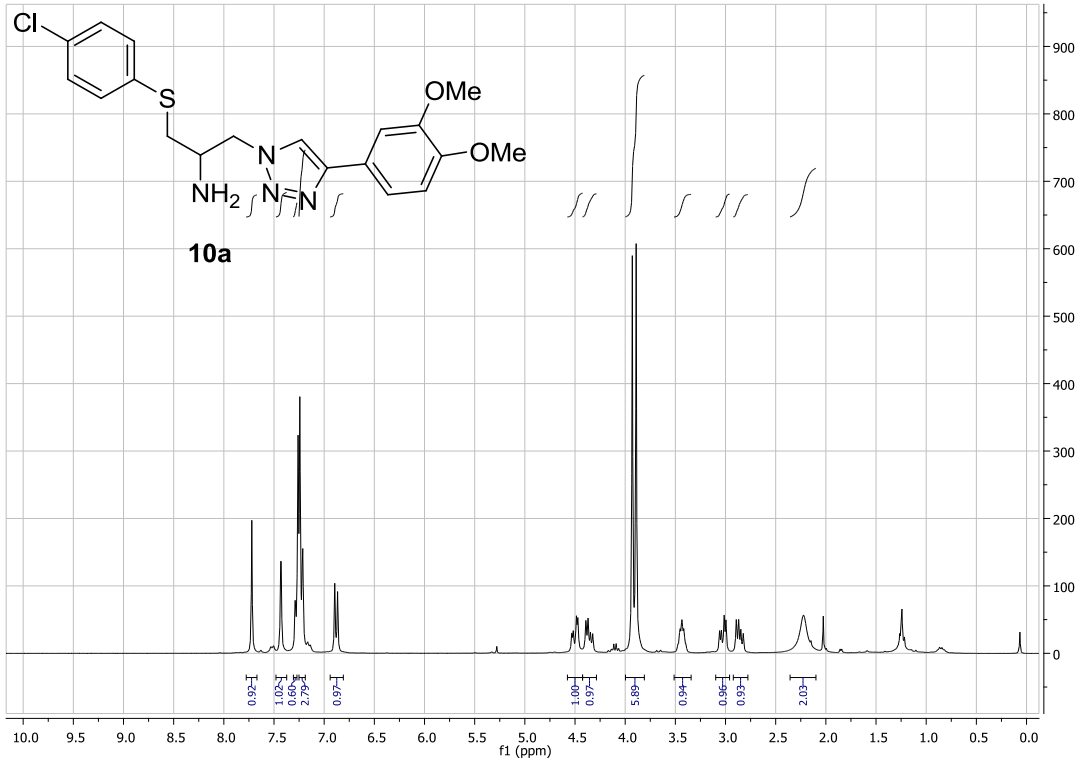
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-(phenethylthio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9c:



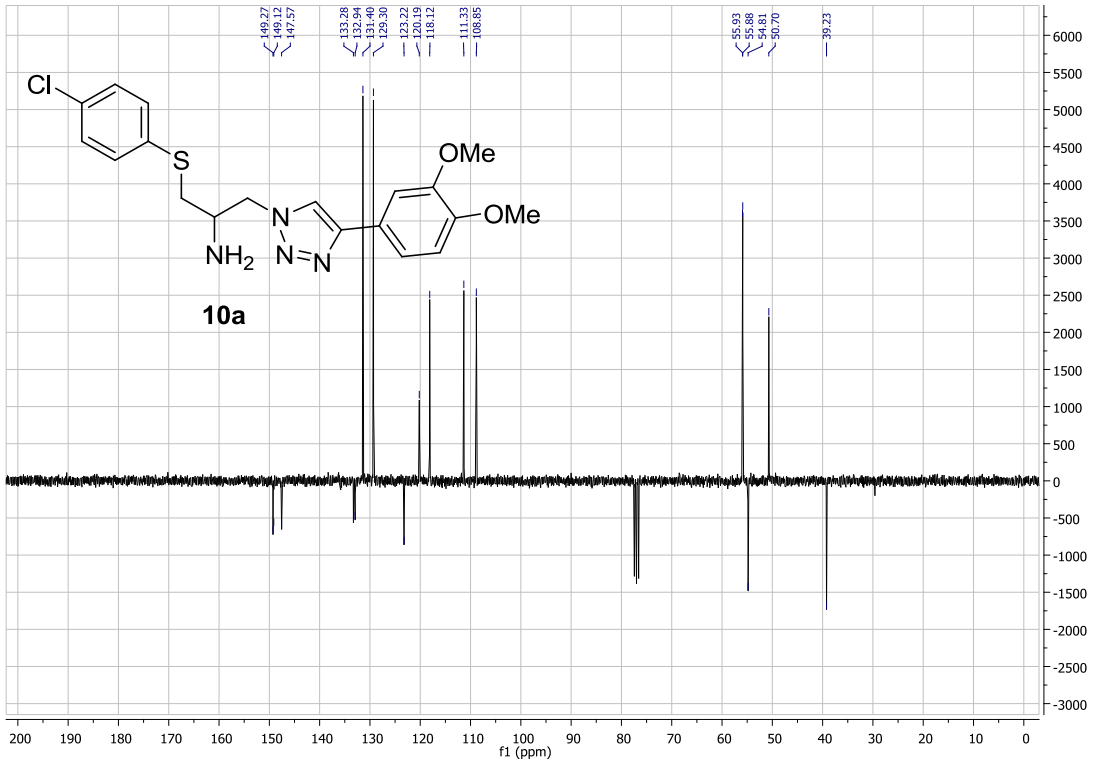
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-(phenethylthio)-3-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 9c:



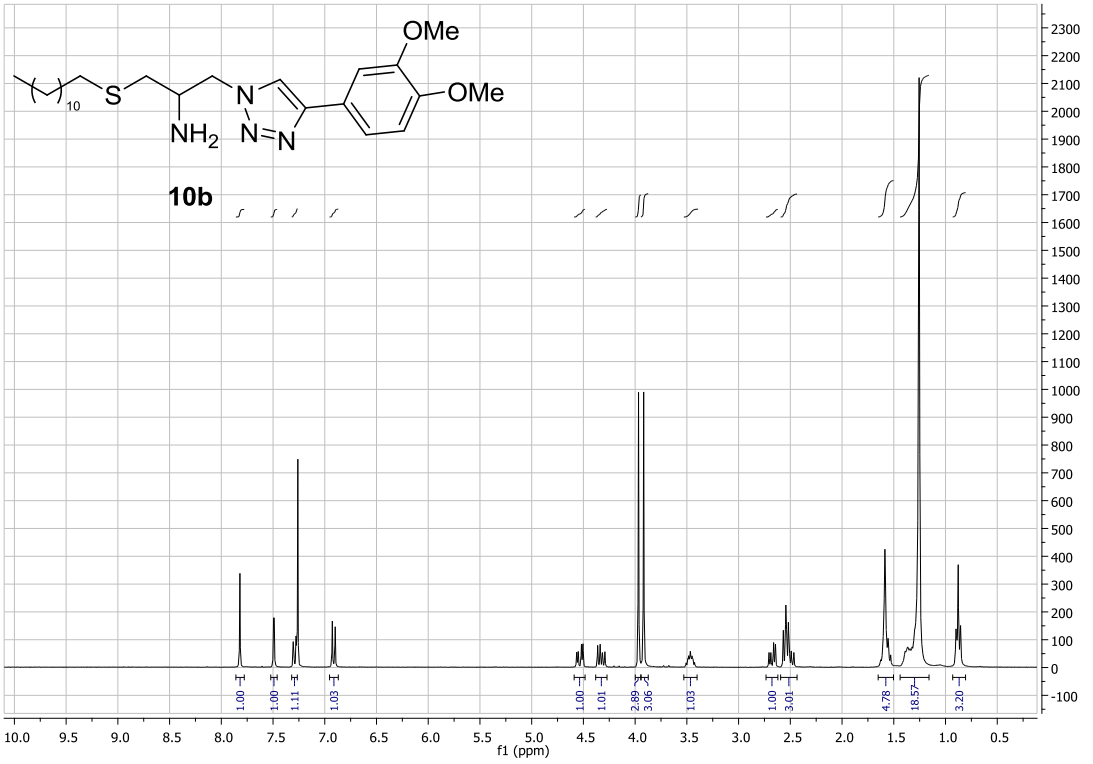
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-((4-chlorophenyl)thio)-3-(4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 10a:



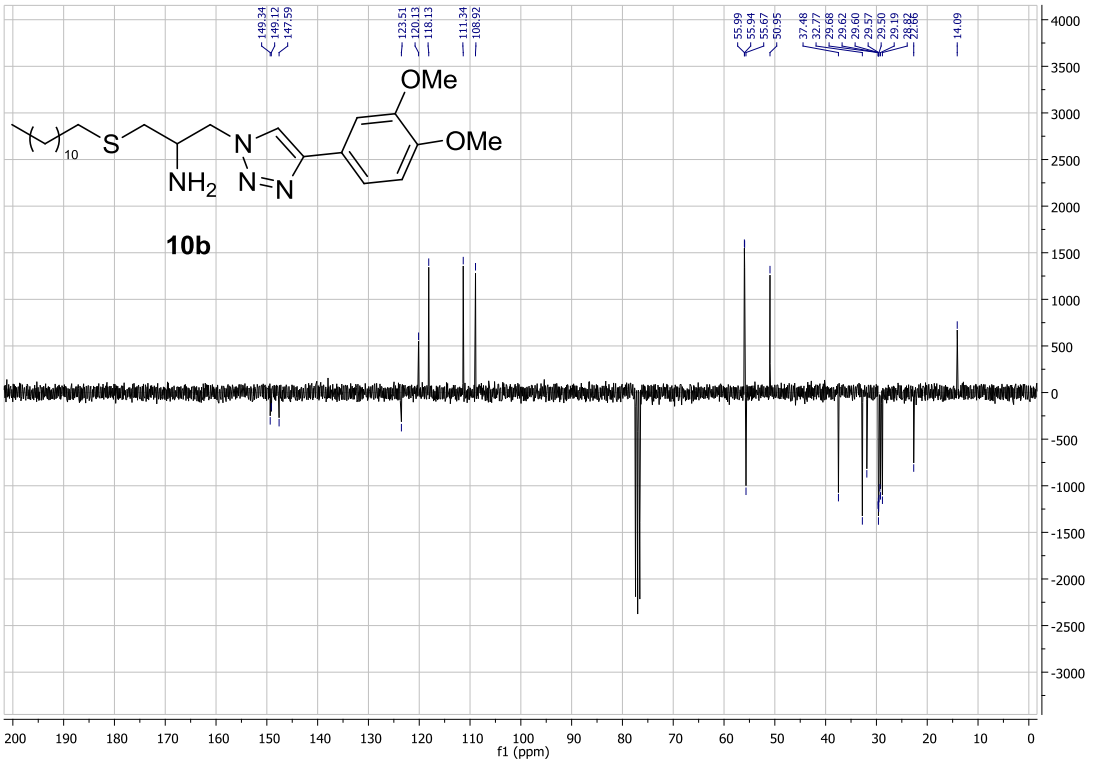
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-((4-chlorophenyl)thio)-3-(4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)propan-2-amine 10a:



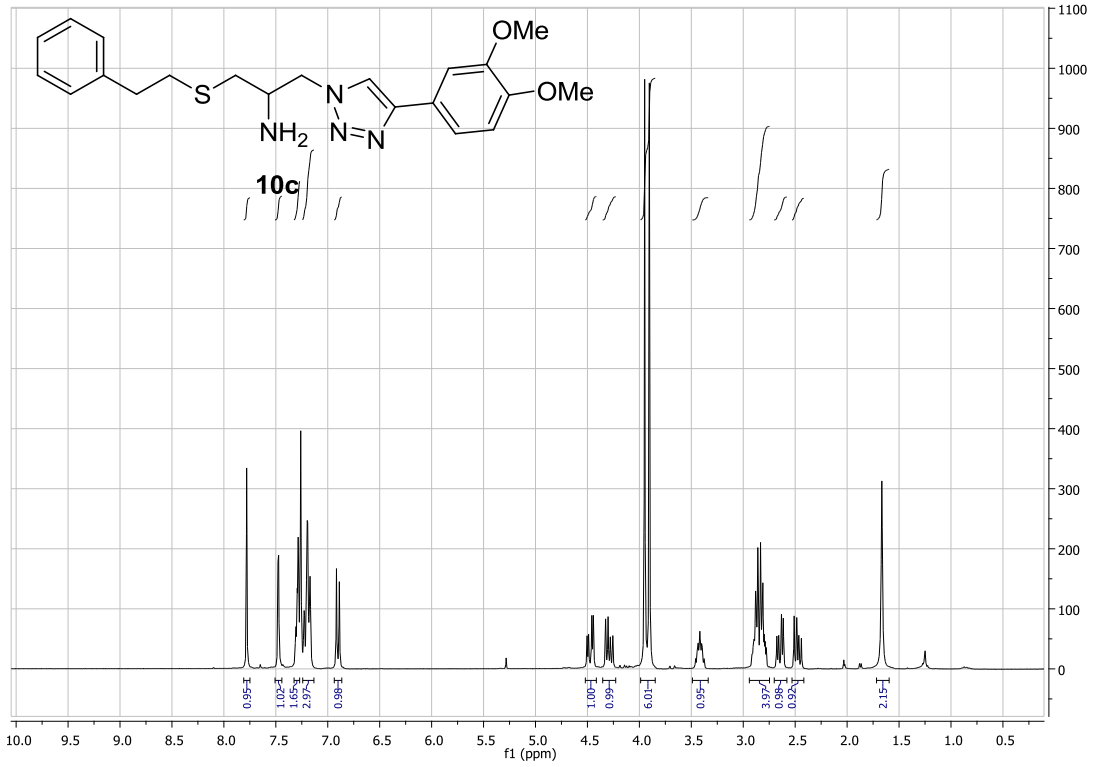
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-(4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)-3-(dodecylthio)propan-2-amine 10b:



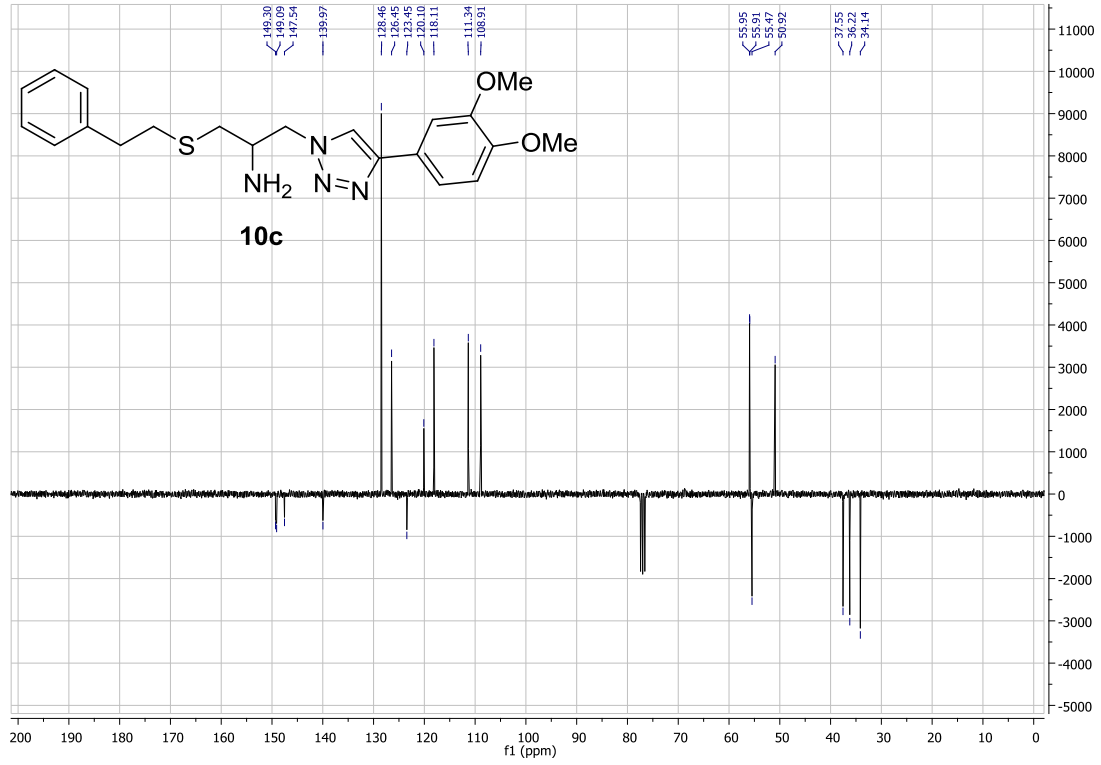
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-(4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)-3-(dodecylthio)propan-2-amine 10b:



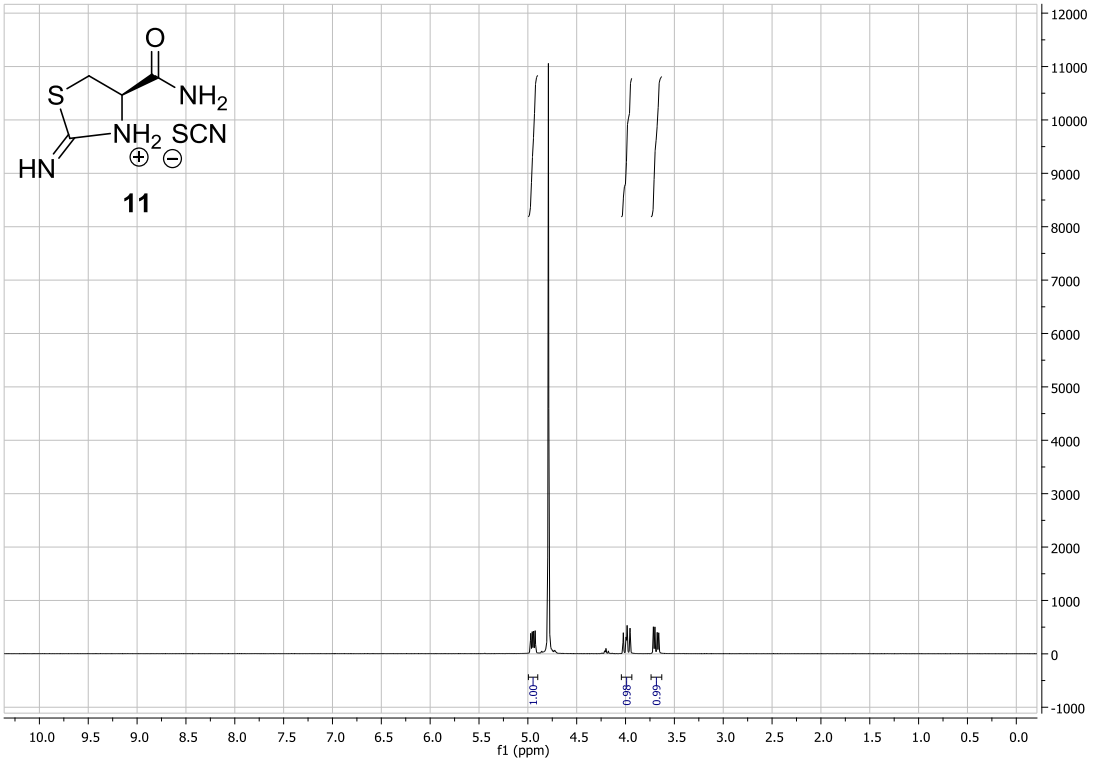
^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of 1-(4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)-3-(phenethylthio) propan- 2-amine 10c:



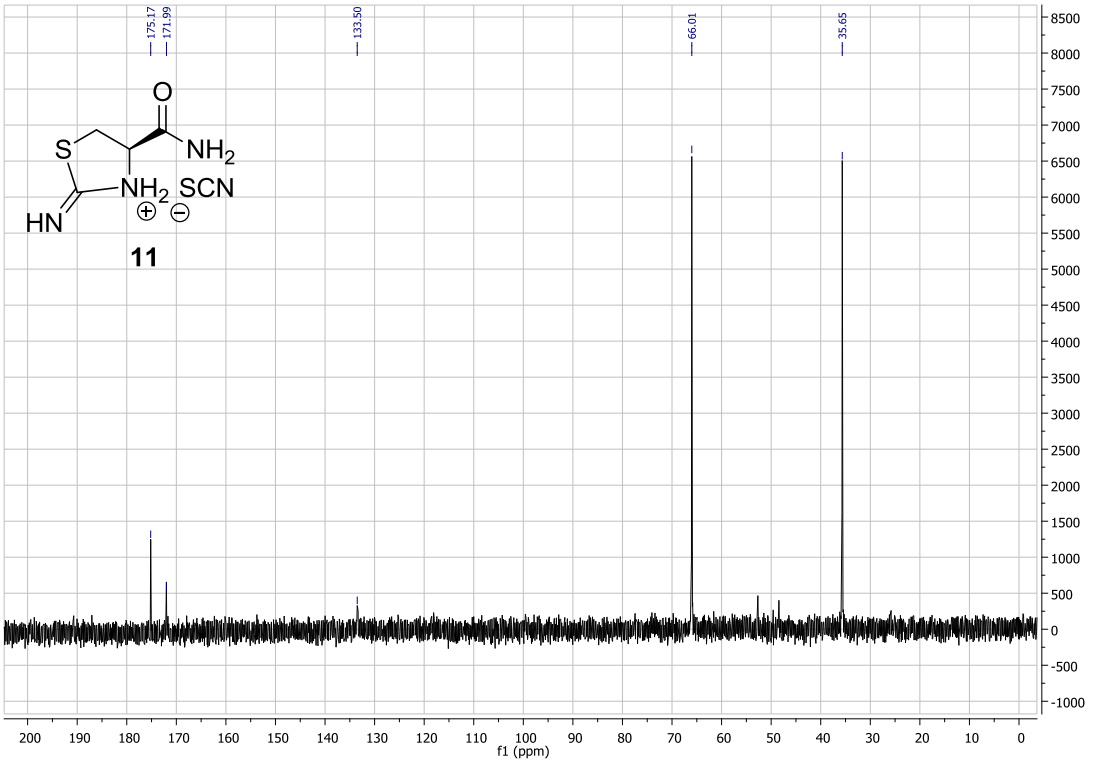
^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of 1-(4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)-3-(phenethylthio) propan- 2-amine 10c:



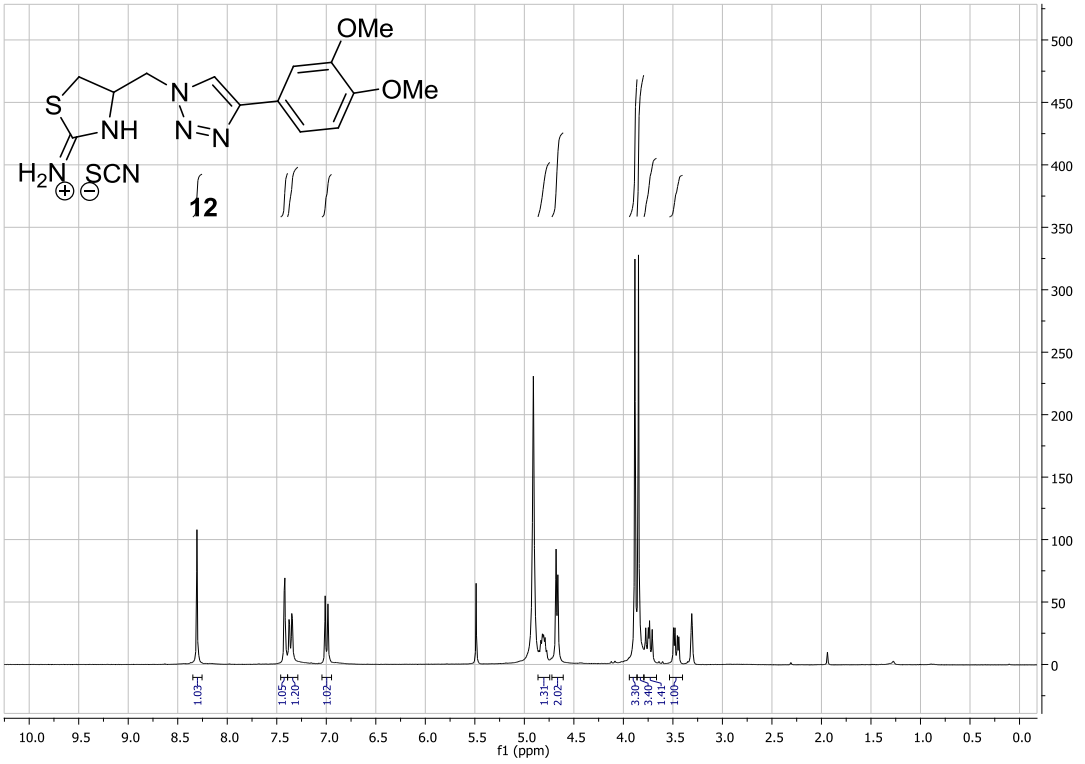
^{1}H-NMR (D_2O, 300 MHz) spectrum of (*R*)-4-carbamoyl-2-iminothiazolidin-3-ium rhodanide 11:



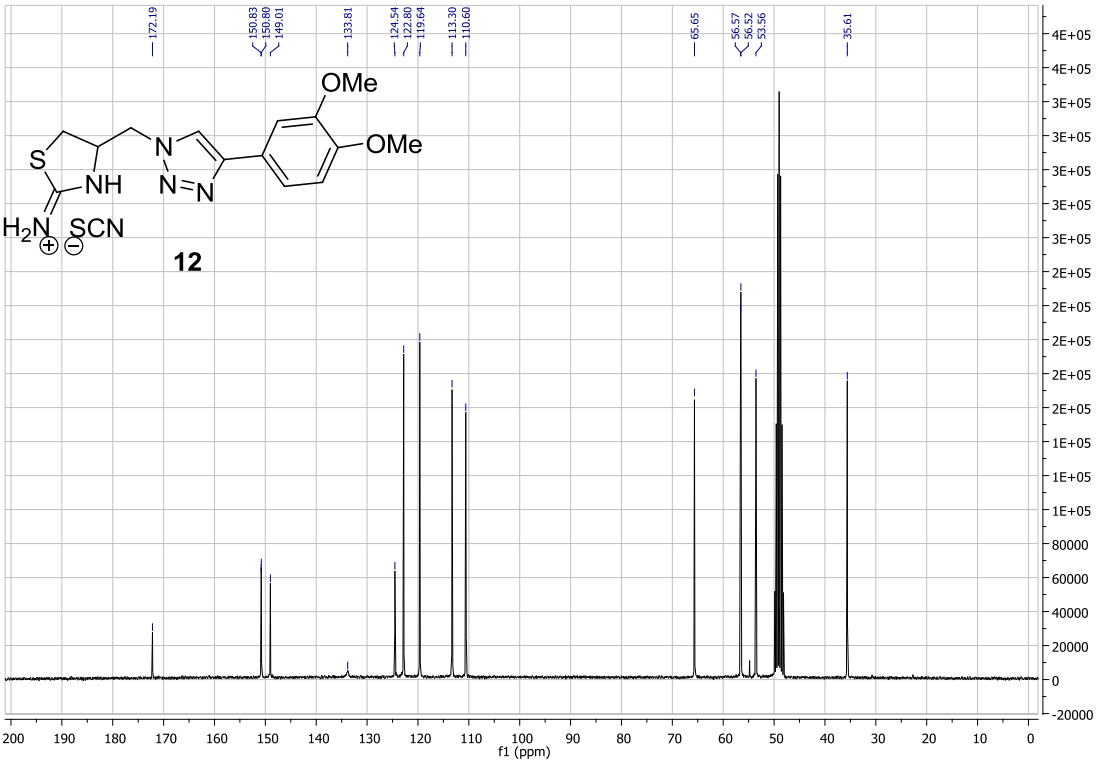
^{13}C-NMR (D_2O, 75.5 MHz) spectrum of (*R*)-4-carbamoyl-2-iminothiazolidin-3-ium rhodanide 11:



^{1}H-NMR (MeOD$_{d4}$, 300 MHz) spectrum of 4-((4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)methyl)thiazolidin-2-iminium rhodanide 12:



^{13}C-NMR (MeOD$_{d4}$, 75.5 MHz) spectrum of 4-((4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-1-yl)methyl)thiazolidin-2-iminium rhodanide 12:

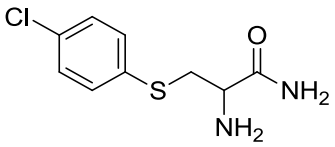


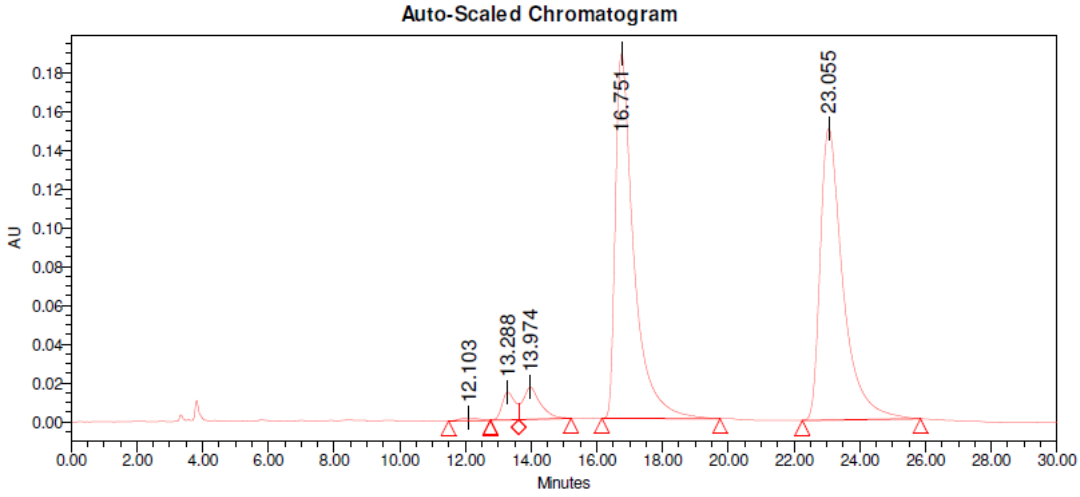
5. HPLC Chromatograms

HPLC analysis for the estimation of enantiomeric purity was performed with Chiralpak IC column (0.46 × 25 cm); isocratic regime: 4% isopropanol in hexanes (prepared by parallel pumping of 80% hexanes and 20% of an eluent containing 20% isopropanol in hexanes); flow rate 1.0 ml/min; sample: 1 mg/ml in 20 % isopropanol in hexanes (for **3a** and **3b**), 1 mg/ml in 40 % isopropanol in hexanes (for **3c** and **3d**), injection volume 10 µL, detector wavelength 210 nm.

General procedure for derivatization of amine with Cbz- group: (*R*)-**3e** (5 mg, 0.031 mmol, 1 equiv.) was dissolved in solution of 0.5 mL H_2O and 0.5 mL THF, reaction mixture was cooled to 0 °C and K_2CO_3 (5 mg, 0.034 mmol, 1.1 equiv.) was added. Solution of Cbz-O-Suc (9 mg, 0.037 mmol, 1.2 equiv.) in 0.5 mL THF was added dropwise and the mixture allowed to warm to rt and stirred for 20 h. The resulting reaction mixture was filtrated through silica gel and the filtrate was subsequently analyzed by HPLC (same conditions as above).

5.1. HPLC Traces for racemic **3a**

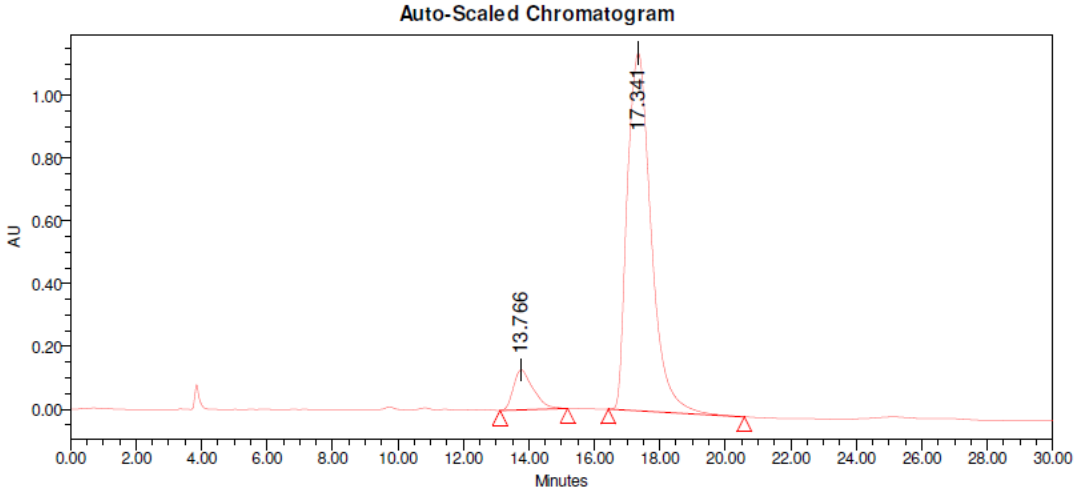




Peak Results

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
1	11.483	12.750	12.103	1410	53568	0.34
2	12.767	13.617	13.288	14401	386907	2.48
3	13.617	15.217	13.974	16646	614147	3.93
4	16.150	19.750	16.751	188106	7334952	46.93
5	22.250	25.850	23.055	150489	7240984	46.33

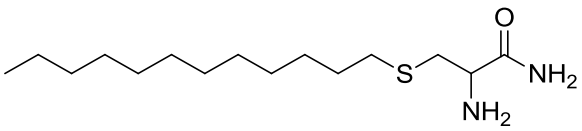
5.2.HPLC Traces for enantioenriched (*R*)-3a

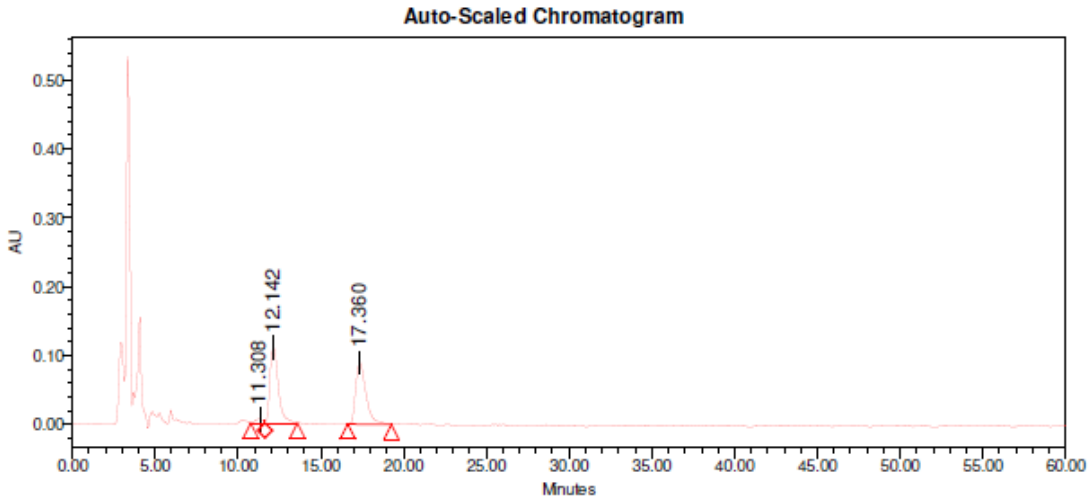


Peak Results

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
1	13.117	15.183	13.766	127703	5307764	8.43
2	16.433	20.583	17.341	1139456	57627813	91.57

5.3.HPLC Traces for racemic **3b**

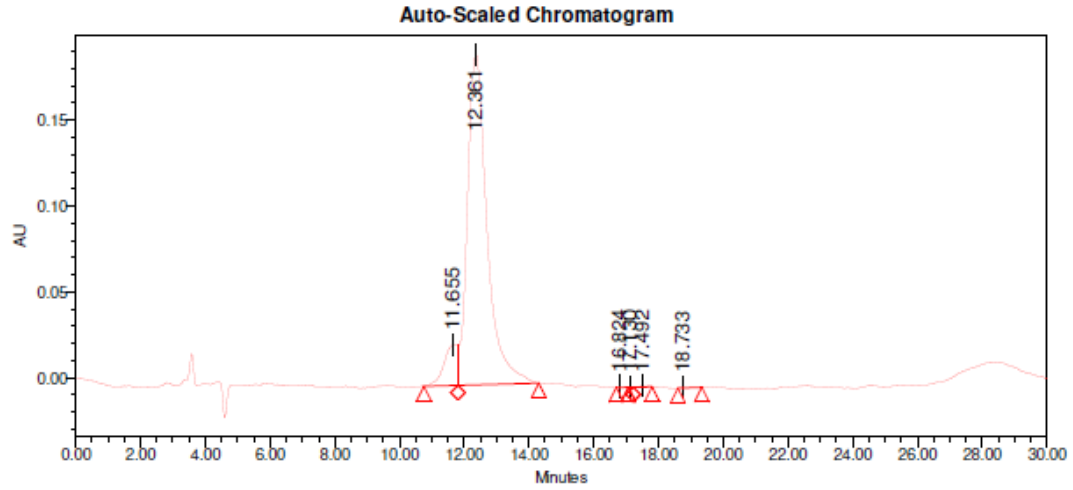




Peak Results

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
1	10.767	11.633	11.308	5480	179749	2.28
2	11.633	13.583	12.142	110059	3833073	48.68
3	16.633	19.267	17.360	88702	3861393	49.04

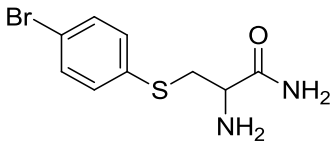
5.4. HPLC Traces for enantioenriched (*R*)-**3b**

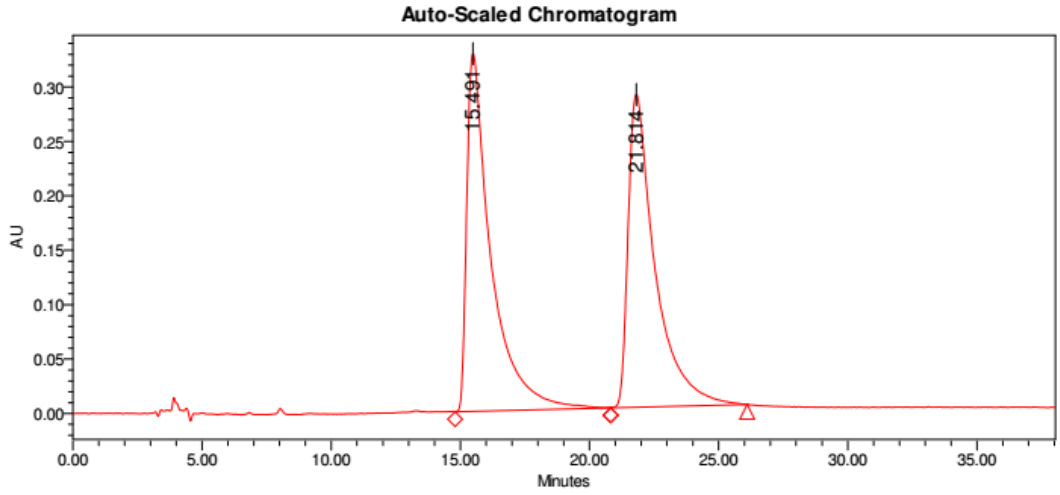


Peak Results

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
1	10.750	11.800	11.655	23780	671699	7.64
2	11.800	14.300	12.361	192583	8088524	92.00
3	16.700	17.067	16.824	562	7591	0.09
4	17.067	17.217	17.130	259	1260	0.01
5	17.217	17.800	17.492	733	12957	0.15

5.5.HPLC Traces for racemic **3c**

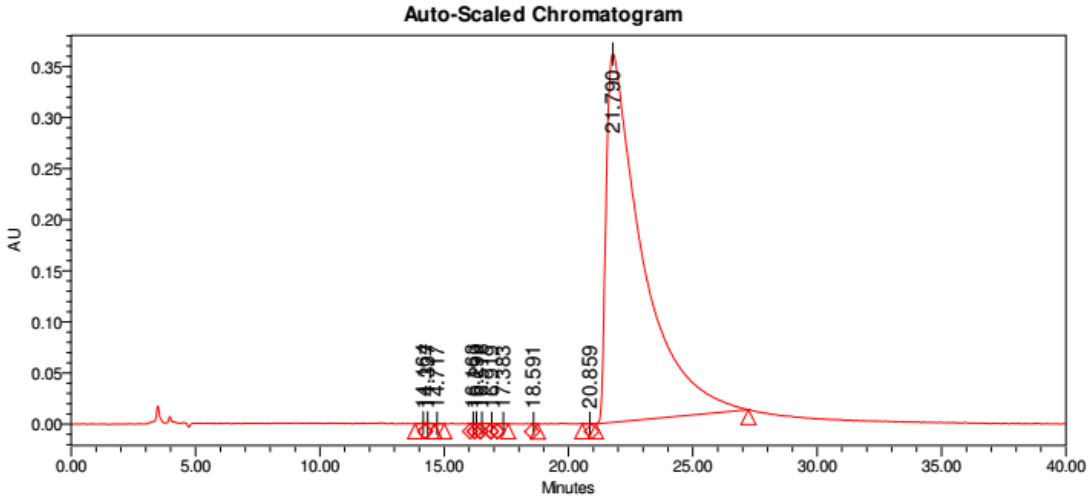




Peak Results

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
1	14.800	20.817	15.491	328607	21375465	50.69
2	20.817	26.100	21.814	287434	20790828	49.31

5.6.HPLC Traces for enantioenriched (*R*)-**3c**

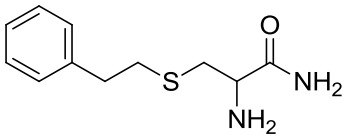


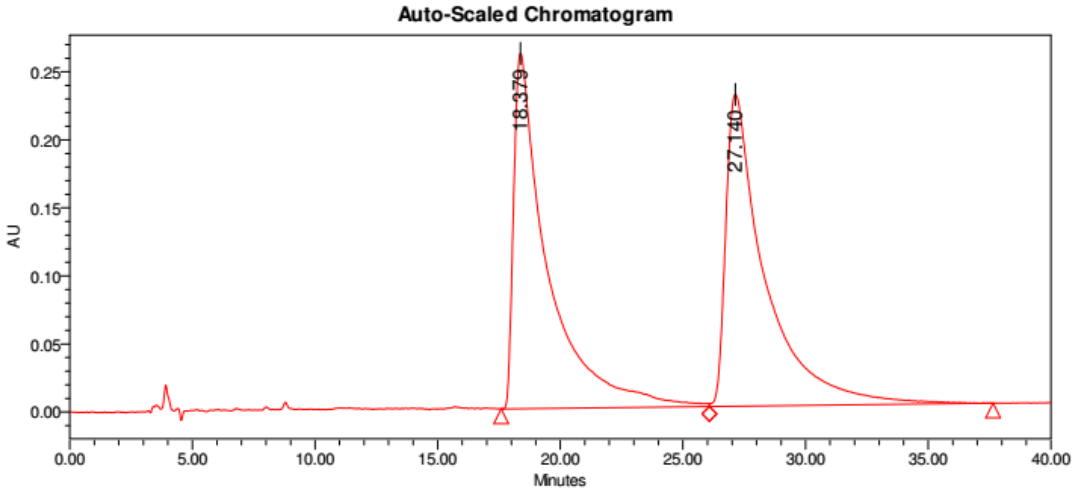
Peak Results

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
1	13.833	14.233	14.164	882	13163	0.04
2	14.233	14.600	14.337	960	13353	0.04
3	14.600	15.000	14.717	445	6447	0.02
4	16.033	16.233	16.163	897	8751	0.02
5	16.233	16.450	16.299	996	11011	0.03

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
6	16.450	16.867	16.516	902	16323	0.04
7	16.867	17.133	16.919	486	5466	0.02
8	17.133	17.567	17.383	429	7147	0.02
9	18.533	18.767	18.591	472	5003	0.01
10	20.550	20.933	20.859	495	6085	0.02
11	21.100	27.233	21.790	360317	36249999	99.74

5.7.HPLC Traces for racemic **3d**

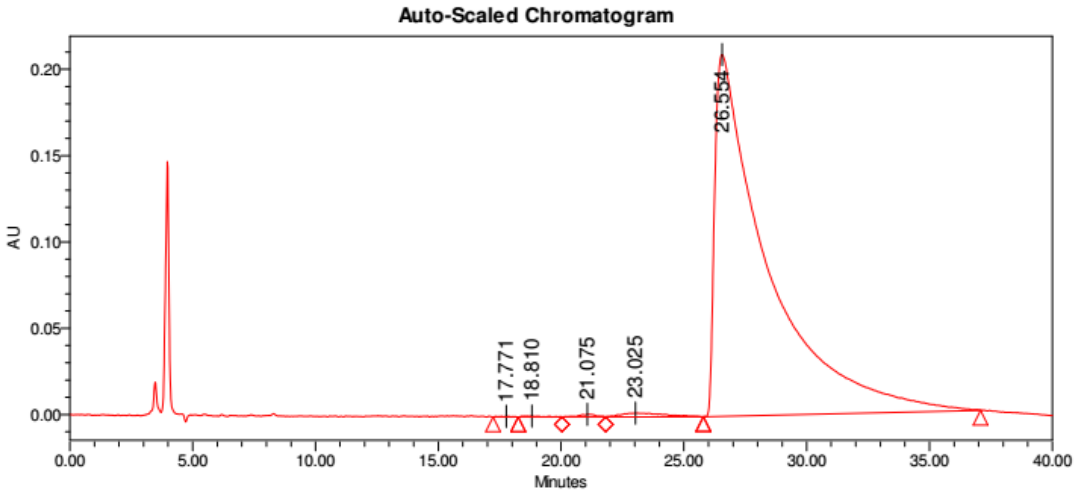




Peak Results

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
1	17.583	26.083	18.379	261151	25132045	49.49
2	26.083	37.650	27.140	229110	25652626	50.51

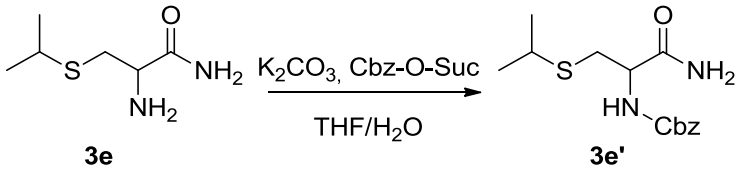
5.8.HPLC Traces for enantioenriched (*R*)-3d



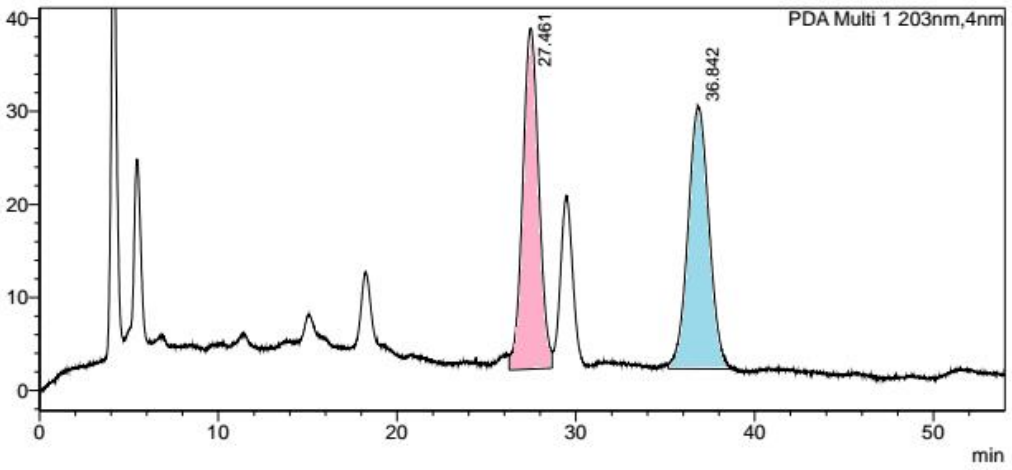
Peak Results

	Start Time (min)	End Time (min)	RT	Height	Area	% Area
1	17.233	18.250	17.771	450	16510	0.05
2	18.250	20.033	18.810	672	39045	0.12
3	20.033	21.817	21.075	1605	79349	0.25
4	21.817	25.783	23.025	2287	284871	0.90
5	25.800	37.083	26.554	209683	31095768	98.67

5.9.HPLC Traces for freshly derivatized racemic **3e**



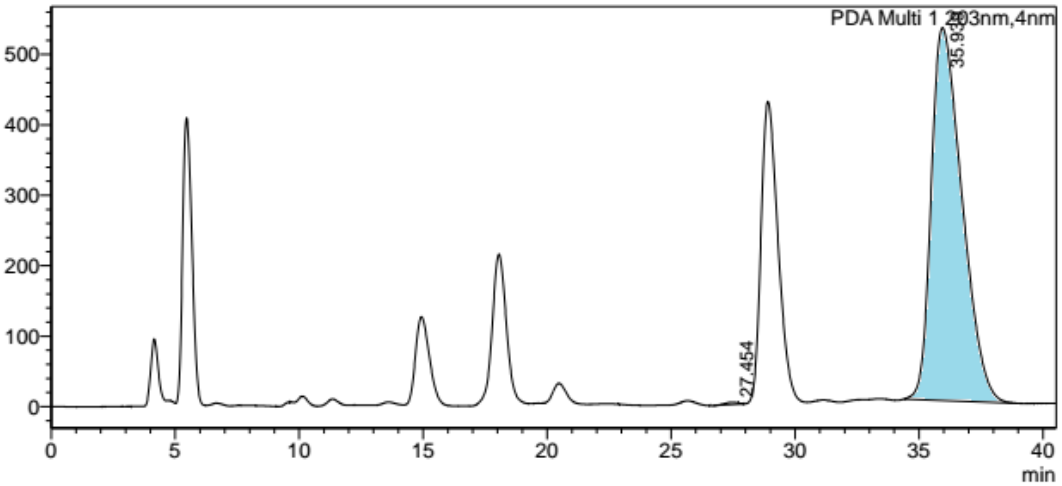
3e **3e'**



PDA Ch1 203nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark
1	27.461	2295509	36622	49.901		V
2	36.842	2304592	28146	50.099		V
Total		4600100	64768			

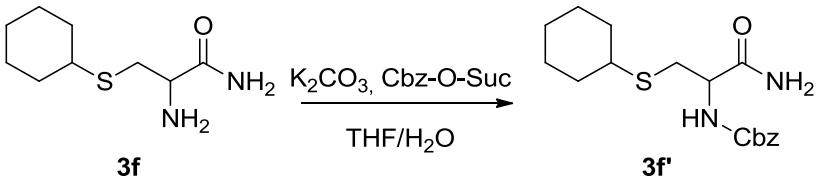
6.0. HPLC Traces for freshly derivatized enantioenriched (*R*)-**3e**



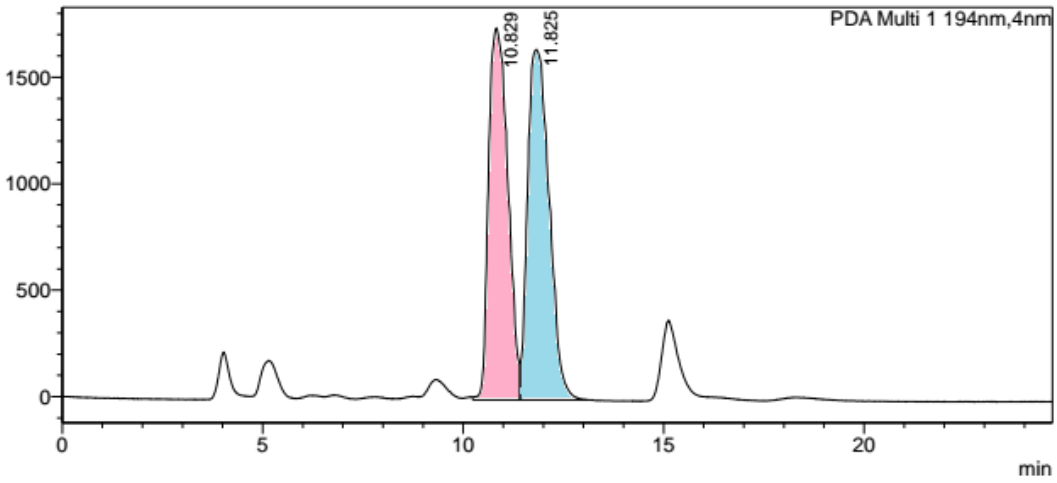
PDA Ch1 203nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark
1	27.454	110340	2959	0.241		
2	35.939	45682671	529334	99.759		
Total		45793011	532294			

6.1. HPLC Traces for freshly derivatized racemic **3f**



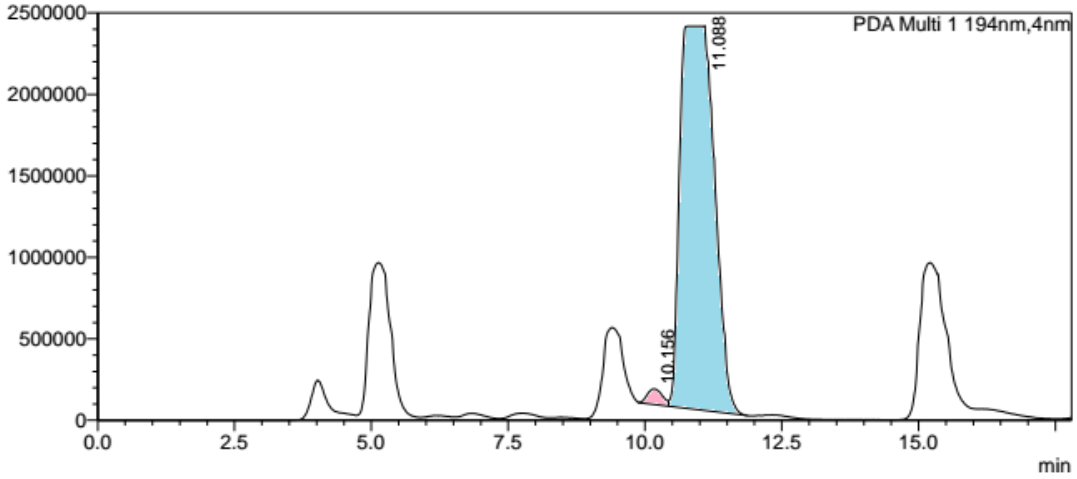
3f **3f'**



PDA Ch1 194nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.829	58249397	1745017	48.659
2	11.825	61458950	1644556	51.341
Total		119708347	3389573	

6.2. HPLC Traces for freshly derivatized enantioenriched (*R*)-**3f**



PDA Ch1 194nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.156	1844479	94956	1.779
2	11.088	101841909	2359295	98.221
Total		103686389	2454251	