Supporting Information for

A Direct and Efficient Preparation of 1-Phenyltetrazol-5-yl Sulfides from Alcohols

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1. General Experimental

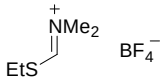
All reactions were carried out under argon with dry solvents. Dry toluene, dichloromethane and diethyl ether were obtained by passage through activated alumina columns under nitrogen. All other chemicals were used as obtained from commercial sources.

Flash column chromatography was carried out on silica gel (Kieselgel 600) or weakly acidic alumina (50-200 μm). "Petrol" refers to the fraction of petroleum ether that boils in the range 40–60 ˚C.

IR spectra were recorded of neat solids or liquids or of solvent casts, using a PerkinElmer Spectrum 100 instrument fitted with an ATR accessory. ^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AVANCE DRX600 spectrometer. Mass spectra were recorded by Dr Lisa Harris of the Christopher Ingold Laboratories on a VG70-SE instrument or a Thermo MAT 900 instrument. Melting points were measured on a Reichert-Jung THERMOVAR instrument or an Electrothermal 9100 apparatus and are uncorrected.

2. Experimental Procedures

2.1 *N*-(Ethylsulfanylmethylene)-*N*,*N*-dimethylammonium tetrafluoroborate (6)

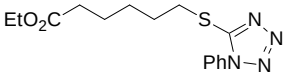


To a solution of triethyloxonium tetrafluoroborate (5.57 g, 29.3 mmol) in CH_2Cl_2 (50 mL) was added *N*,*N*-dimethylthioformamide **5** (2.3 mL, 26.7 mmol) and the solution stirred at room temperature for 18 h. The mixture was concentrated *in vacuo* to approximately half of its original volume and then added dropwise to stirred Et_2O (100 mL); the solution was then placed in a refrigerator for 2 h. The resulting precipitate was collected by filtration under argon, washed with cold Et_2O (2 × 25 mL) and dried *in vacuo* for 10 min to give salt **6** (5.26 g, 96%) as a white crystalline solid which was stored at –25 ºC under argon; m.pt. 20-21 ºC; ν_{max}/cm^{-1} (solid) 3076, 1650, 1634, 1463; δ_H ($CDCl_3$, 600 MHz) 1.51 (3H, t, *J* 7.5 Hz, $CH_2C\underline{H}_3$), 3.40 (3H, s, $NC\underline{H}_3CH_3$), 3.41 (2H, q, *J* 7.5 Hz, $C\underline{H}_2$), 3.73 (3H, s, $NCH_3C\underline{H}_3$), 9.57 (1H, s, C<u>H</u>); δ_C ($CDCl_3$, 150 MHz) 15.6 ($CH_2\underline{C}H_3$), 30.1 ($\underline{C}H_2$), 42.4 and 49.4 ($N(\underline{C}H_3)_2$), 183.1 (<u>C</u>H); *m*/*z* (CI) 118 ($[EtSCH{=}NMe_2]^+$, 100%), 90 (48); HRMS found 118.0686, $C_5H_{12}NS$ ($[EtSCH{=}NMe_2]^+$) requires 118.0691.

2.2 General procedure for preparation of 1-phenyl-1(*H*)-tetrazol-5-yl sulfides.

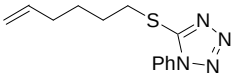
To a solution of alcohol **2** in toluene (0.4-0.5 M) were added salt **6** (1.5 equiv.), imidazole (1.0 to 5.0 equiv) and 1-phenyl-1(*H*)-tetrazole-5-thiol **7** (1.2 to 2.0 equiv.), and the mixture heated to 90 °C. Upon completion of the reaction (monitored by TLC or ^{1}H NMR analysis), the solvent was removed *in vacuo*. Purification by flash chromatography afforded pure sulfide **8**.

2.2.1 Ethyl 6-(1-phenyl-1(*H*)-tetrazol-5-ylsulfanyl)hexanoate (8a)



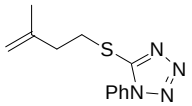
Purification by flash chromatography (Al_2O_3, petrol/EtOAc 19:1→9:1) gave sulfide **8a** as a yellow oil in 76% yield; ν_{max}/cm^{-1} ($CHCl_3$ cast) 2980, 2937, 2865, 1729, 1597, 1500; δ_H ($CDCl_3$, 600 MHz) 1.24 (3H, t, *J* 7.3 Hz, $C\underline{H}_3$), 1.48 (2H, app. quin, *J* 7.5 Hz, $C\underline{H}_2CH_2CH_2S$), 1.67 (2H, app. quin, *J* 7.5 Hz, $C\underline{H}_2CH_2C{=}O$), 1.85 (2H, app. quin, *J* 7.5 Hz, $C\underline{H}_2CH_2S$), 2.30 (2H, t, *J* 7.5 Hz, $C\underline{H}_2C{=}O$), 3.39 (2H, t, *J* 7.4 Hz, $C\underline{H}_2S$), 4.11 (2H, q, *J* 7.3 Hz, $C\underline{H}_2CH_3$), 7.51-7.59 (5H, m, aromatic C<u>H</u>); δ_C ($CDCl_3$, 150 MHz) 14.4 ($\underline{C}H_3$), 24.4 ($\underline{C}H_2CH_2C{=}O$), 28.2 ($\underline{C}H_2CH_2CH_2S$), 28.9 ($\underline{C}H_2CH_2S$), 33.2 ($\underline{C}H_2S$), 34.2 ($\underline{C}H_2C{=}O$), 60.4 ($\underline{C}H_2CH_3$), 124.0, 129.9 and 130.2 (aromatic <u>C</u>H), 133.8 (aromatic <u>C</u>), 154.5 (N<u>C</u>S), 173.6 (<u>C</u>=O); *m*/*z* (CI) 321 (MH^+, 100%), 275 (MH^+–EtOH, 41), 119 (55); HRMS found 321.1379, $C_{15}H_{21}N_4O_2S$ (MH^+) requires 321.1385.

2.2.2 5-(Hex-5-enylsulfanyl)-1-phenyl-1(*H*)-tetrazole (8b)[1]



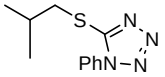
Purification by flash chromatography (Al_2O_3, petrol→petrol/EtOAc 19:1) gave sulfide **8b** as a colorless oil in 70% yield; ν_{max}/cm^{-1} (CH_2Cl_2 cast) 3071, 2927, 2856, 2640, 1597, 1499; δ_H ($CDCl_3$, 600 MHz) 1.54 (2H, app. quin, *J* 7.4 Hz, C$\underline{H}_2$CH$_2$CH=CH$_2$), 1.83 (2H, app. quin, *J* 7.4 Hz, C$\underline{H}_2$CH$_2$S), 2.08 (2H, q, *J* 7.0 Hz, C$\underline{H}_2$CH=CH$_2$), 3.39 (2H, t, *J* 7.4 Hz, C$\underline{H}_2$S), 4.95 (1H, d, *J* 10.0 Hz) and 5.00 (1H, d, *J* 17.1 Hz, C$\underline{H}_2$=CH), 5.77 (1H, ddt, *J* 17.1, 10.0, 7.0 Hz, CH$_2$=C$\underline{H}$), 7.50-7.59 (5H, m, aromatic C$\underline{H}$); δ_C ($CDCl_3$, 150 MHz) 27.9 (C$\underline{H}_2$CH$_2$CH=CH$_2$), 28.6 (C$\underline{H}_2$CH$_2$S), 33.2 (C$\underline{H}_2$S), 33.3 (C$\underline{H}_2$CH=CH$_2$), 115.2 (C$\underline{H}_2$=CH), 123.9, 130.0 and 130.2 (aromatic C$\underline{H}$), 133.8 (aromatic C$\underline{C}$), 138.1 (CH$_2$=C$\underline{H}$), 154.6 (N$\underline{C}$S); *m*/*z* (CI) 261 (MH^+, 100%), 207 (28); HRMS found 261.1165, $C_{13}H_{17}N_4S$ (MH^+) requires 261.1174.

2.2.3 5-(3-Methylbut-3-enylsulfanyl)-1-phenyl-1(*H*)-tetrazole (8c)[2]



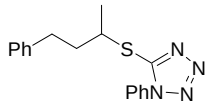
Purification by flash chromatography (SiO_2, petrol→petrol/EtOAc 24:1) gave sulfide **8c** as a pale yellow oil in 67% yield; ν_{max}/cm^{-1} ($CDCl_3$ cast) 3078, 2970, 2937, 1649, 1597, 1499; δ_H ($CDCl_3$, 600 MHz) 1.77 (3H, s, C$\underline{H}_3$), 2.53 (2H, t, *J* 7.5 Hz, C$\underline{H}_2$CH$_2$S), 3.53 (2H, t, *J* 7.3 Hz, C$\underline{H}_2$S), 4.77 (1H, s) and 4.83 (1H, s, C$\underline{H}_2$=C), 7.51-7.59 (5H, m, aromatic C$\underline{H}$); δ_C ($CDCl_3$, 150 MHz) 22.2 (C$\underline{H}_3$), 31.5 (C$\underline{H}_2$CH$_2$S), 37.0 (C$\underline{H}_2$S), 112.6 (C$\underline{H}_2$=C), 124.0, 129.9 and 130.2 (aromatic C$\underline{H}$), 133.8 (aromatic C$\underline{C}$), 142.6 (CH$_2$=C$\underline{C}$), 154.5 (S$\underline{C}$N); *m*/*z* (EI) 246 (M^+, 40%), 159 (45), 135 (32), 85 (100); HRMS found 246.0935, $C_{12}H_{14}N_4S$ (M^+) requires 246.0939.

2.2.4 5-(2-Methylpropylsulfanyl)-1-phenyl-1(*H*)-tetrazole (8d)[3]



Purification by flash chromatography (SiO_2, petrol→petrol/Et_2O 19:1) gave sulfide **8d** as a colorless oil in 75% yield; ν_{max}/cm^{-1} (film) 2960, 2929, 2871, 1597, 1499; δ_H ($CDCl_3$, 600 MHz) 1.05 (6H, d, *J* 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 2.10 (1H, nonet, *J* 6.8 Hz, C$\underline{H}$(CH$_3$)$_2$), 3.31 (2H, d, *J* 6.8 Hz, C$\underline{H}_2$), 7.52-7.60 (5H, m, aromatic C$\underline{H}$); δ_C ($CDCl_3$, 150 MHz) 21.8 (CH(C$\underline{H}_3$)$_2$), 28.4 (C$\underline{H}$(CH$_3$)$_2$), 41.9 (C$\underline{H}_2$), 124.0, 129.9 and 130.2 (aromatic C$\underline{H}$), 133.9 (aromatic C$\underline{C}$), 154.8 (S$\underline{C}$N); *m*/*z* (CI) 235 (MH^+, 100%); HRMS found 235.1022, $C_{11}H_{15}N_4S$ (MH^+) requires 235.1017.

2.2.5 1-Phenyl-5-(4-phenylbutan-2-ylsulfanyl)-1(*H*)-tetrazole (8e)



Purification by flash chromatography (SiO_2, petrol→petrol/EtOAc 24:1) gave sulfide **8e** as a colorless oil in 83% yield; ν_{max}/cm^{-1} ($CDCl_3$ cast) 3063, 3027, 2926, 2859, 1597, 1499, 1455, 1387; δ_H ($CDCl_3$, 600 MHz) 1.56 (3H, d, *J* 6.8 Hz, C$\underline{H}_3$), 2.02 (1H, ddt, *J* 13.7, 9.5, 6.8 Hz) and 2.14 (1H, ddt, *J* 13.7, 9.5, 6.8 Hz, C$\underline{H}_2$CHS), 2.72-2.83 (2H, m, PhC$\underline{H}_2$), 4.07 (1H, sext., *J* 6.8 Hz, C$\underline{H}$S), 7.15-7.21 (3H, m), 7.25-7.30 (2H, m) and 7.51-7.60 (5H, m, aromatic C$\underline{H}$); δ_C ($CDCl_3$, 150 MHz) 21.6 (C$\underline{H}_3$), 33.3 (PhC$\underline{H}_2$), 38.3 (C$\underline{H}_2$CHS), 44.5 (C$\underline{H}$S), 124.2, 126.3, 128.5, 128.6, 129.9 and 130.2 (aromatic C$\underline{H}$), 133.8 and 141.0 (aromatic C$\underline{C}$), 154.0 (S$\underline{C}$N); *m*/*z* (CI) 311 (MH^+, 100%), 119 (58); HRMS found 311.1327, $C_{17}H_{19}N_4S$ (MH^+) requires 311.1330.

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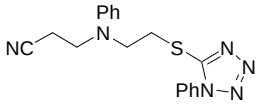
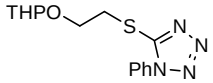
[1] A. K. Ghosh and B. Zajc, *J. Org. Chem.* 2009, **74**, 8531.
[2] S. Hosokawa, K. Yokota, K. Imamura, Y. Suzuki, M. Kawarasaki and K. Tatsuta, *Tetrahedron Lett.* 2006, **47**, 5415.
[3] C. M. DiBlasi, D. E. Macks and D. S.Tan, *Org. Lett.* 2005, **7**, 1777.

2.2.6 3-{Phenyl[2-(1-phenyl-1(*H*)-tetrazol-5-ylsulfanyl)ethyl]amino}propanenitrile (8f)



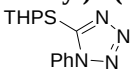
Purification by flash chromatography (SiO_2, petrol/EtOAc 17:3→4:1) gave sulfide **8f** as a viscous colorless oil in 88% yield; ν_{max}/cm^{-1} (neat) 3063, 2932, 2248, 1693, 1597, 1499; δ_H ($CDCl_3$, 600 MHz) 2.65 (2H, t, *J* 6.8 Hz, C$\underline{H}_2$CN), 3.53 (2H, t, *J* 7.2 Hz, C$\underline{H}_2$S), 3.77 (2H, t, *J* 6.8 Hz, C$\underline{H}_2$CH$_2$CN), 3.89 (2H, t, *J* 7.2 Hz, C$\underline{H}_2$CH$_2$S), 6.80-6.84 (3H, m), 7.27-7.32 (2H, m) and 7.53-7.60 (5H, m, aromatic C$\underline{H}$); δ_C ($CDCl_3$, 150 MHz) 16.3 (C$\underline{H}_2$CN), 30.1 (C$\underline{H}_2$S), 47.6 (C$\underline{H}_2$CH$_2$CN), 50.9 (C$\underline{H}_2$CH$_2$S), 113.2 (aromatic C$\underline{H}$), 118.4 (C$\underline{N}$), 118.7, 123.9, 130.0, 130.0 and 130.4 (aromatic C$\underline{H}$), 133.6 (aromatic C$\underline{N}_{tetrazole}$), 145.7 (aromatic C$\underline{N}_{amine}$), 154.0 (SC$\underline{N}$); *m*/*z* ($ES^+$) 373 ($MNa^+$, 100%); HRMS found 373.1211, $C_{18}H_{18}N_6NaS$ (MNa^+) requires 373.1211.

2.2.7 1-Phenyl-5-[2-(tetrahydro-2(*H*)-pyran-2-yloxy)ethylsulfanyl]-1(*H*)-tetrazole (8g)



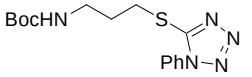
Purification by flash chromatography (Al_2O_3, petrol/EtOAc 9:1→4:1) gave sulfide **8g** as a colorless oil in 80% yield; ν_{max}/cm^{-1} ($CDCl_3$ cast) 2942, 2871, 1597, 1499; δ_H ($CDCl_3$, 600 MHz) 1.45-1.60 (4H, m, OCH$_2$C$\underline{H}$HC$\underline{H}$HC$\underline{H}_2$), 1.68 (1H, m, OCH$_2$CH$\underline{H}$CH$_2$), 1.77 (1H, m, OCH$_2$CH$_2$CH$\underline{H}$), 3.49 (1H, m, OC$\underline{H}$HCH$_2$CH$_2$), 3.61 (1H, dt, *J* 13.6, 5.9 Hz) and 3.66 (1H, dt, *J* 13.6, 5.9 Hz, C$\underline{H}_2$S), 3.80-3.85 (2H, m, OCH$\underline{H}$CH$_2$CH$_2$ and OC$\underline{H}$HCH$_2$S), 4.08 (1H, dt, *J* 10.7, 5.9 Hz, OCH$\underline{H}$CH$_2$S), 4.63 (1H, dd, *J* 4.1, 2.9 Hz, OC$\underline{H}$O), 7.51-7.59 (5H, m, aromatic C$\underline{H}$); δ_C ($CDCl_3$, 150 MHz) δ 19.5 (OCH$_2$CH$_2$C$\underline{H}_2$), 25.4 (CH$\underline{C}$H$_2$), 30.5 (OCH$_2$C$\underline{H}_2$CH$_2$), 33.6 (C$\underline{H}_2$S), 62.5 (OC$\underline{H}_2$CH$_2$CH$_2$), 65.6 (OC$\underline{H}_2$CH$_2$S), 99.1 (O$\underline{C}$HO), 124.0, 129.9 and 130.3 (aromatic C$\underline{H}$), 133.8 (aromatic C$\underline{C}$), 154.4 (S$\underline{C}$N); *m*/*z* (ES^+) 329 (MNa^+, 80%), 301 (31), 223 (100); HRMS found 329.1052, $C_{14}H_{18}N_4O_2NaS$ (MNa^+) requires 329.1048.

2.2.8 1-Phenyl-5-(tetrahydro-2(*H*)-pyran-2-ylsulfanyl)-1(*H*)-tetrazole (9)



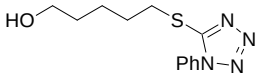
Obtained in the reaction of **2f** in the presence of 1 equiv. imidazole. Purification by flash chromatography (Al_2O_3, petrol→petrol/EtOAc 19:1) gave sulfide **9** as a white solid in 39% yield; m.pt. 69-71 ºC; ν_{max}/cm^{-1} (solid) 2966, 2941, 2851, 1595, 1498; δ_H ($CDCl_3$, 600 MHz) 1.68 (1H, m, OCH$_2$C$\underline{H}$H), 1.73-1.83 (2H, m, OCH$_2$CH$\underline{H}$C$\underline{H}$H), 2.04 (1H, m, SCHC$\underline{H}$H), 2.11-2.20 (1H, m, OCH$_2$CH$_2$CH$\underline{H}$), 2.36 (1H, dddd, *J* 13.1 11.8, 10.1, 4.2 Hz, SCHCH$\underline{H}$), 3.80 (1H, td, *J* 11.5, 2.7 Hz) and 4.16 (1H, m, OC$\underline{H}_2$), 5.98 (1H, dd, *J* 10.1, 2.8 Hz, OC$\underline{H}$S), 7.48-7.57 (3H, m) and 7.90-7.93 (2H, m, aromatic C$\underline{H}$); δ_C ($CDCl_3$, 150 MHz) 22.3 (OCH$_2$CH$_2$C$\underline{H}_2$), 24.8 (OCH$_2$C$\underline{H}_2$), 29.1 (SCH$\underline{C}$H$_2$), 68.5 (OC$\underline{H}_2$), 83.5 (O$\underline{C}$HS), 124.2, 129.4 and 129.8 (aromatic C$\underline{H}$), 134.6 (aromatic C$\underline{C}$), 163.7 (S$\underline{C}$N); *m*/*z* (CI) 263 (MH^+, 100%), 179 (100), 85 (23); HRMS found 263.0958, $C_{12}H_{15}ON_4S$ (MH^+) requires 263.0967.

2.2.9 *tert*-Butyl 3-(1-phenyl-1(*H*)-tetrazol-5-ylsulfanyl)propylcarbamate (8h)



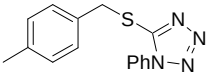
Purification by flash chromatography (Al_2O_3, petrol/EtOAc 9:1→17:3) gave sulfide **8h** as a cloudy yellow oil; ν_{max}/cm^{-1} ($CDCl_3$ cast) 3342 br, 2978, 2929, 1696, 1597, 1500; δ_H ($CDCl_3$, 600 MHz) 1.43 (9H, s, C(C$\underline{H}_3$)$_3$), 2.00-2.07 (2H, m, C$\underline{H}_2$CH$_2$N), 3.22-3.30 (2H, m, C$\underline{H}_2$N), 3.43 (2H, td, *J* 6.9, 2.0 Hz, C$\underline{H}_2$S), 4.81-5.00 (1H, br s, N$\underline{H}$), 7.51-7.60 (5H, m, aromatic C$\underline{H}$); δ_C ($CDCl_3$, 150 MHz) 28.5 (C($\underline{C}$H$_3$)$_3$), 29.8 (C$\underline{H}_2$CH$_2$N), 30.6 (C$\underline{H}_2$S), 38.9 (C$\underline{H}_2$N), 79.5 (C($\underline{C}$H$_3$)$_3$), 124.0, 129.9 and 130.3 (aromatic C$\underline{H}$), 133.7 (aromatic C$\underline{C}$), 154.5 (S$\underline{C}$N), 156.2 (C$\underline{C}$=O); *m*/*z* (EI) 335 (M^+, 8%), 279 (100); HRMS found 335.1420, $C_{15}H_{21}N_5O_2S$ (M^+) requires 335.1416.

2.2.10 5-(1-Phenyl-1(*H*)-tetrazol-5-ylsulfanyl)pentan-1-ol (8i)



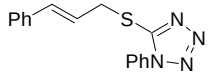
Purification by flash chromatography (SiO_2, petrol/EtOAc 7:3→1:1) gave sulfide **8i** as a colorless oil; ν_{max}/cm^{-1} ($CDCl_3$ cast) 3414 br, 2941, 2865, 1597, 1500; δ_H ($CDCl_3$, 600 MHz) 1.54 (2H, m, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.62 (2H, m, C<u>H</u>$_2$CH$_2$O), 1.88 (2H, quin., *J* 7.3 Hz, C<u>H</u>$_2$CH$_2$S), 3.40 (2H, t, *J* 7.3 Hz, C<u>H</u>$_2$S), 3.66 (2H, t, *J* 6.3 Hz, C<u>H</u>$_2$O), 7.51-7.60 (5H, m, aromatic C<u>H</u>); δ_C ($CDCl_3$, 150 MHz) 25.0 (<u>C</u>H$_2$CH$_2$CH$_2$O), 29.0 (<u>C</u>H$_2$CH$_2$S), 32.1 (<u>C</u>H$_2$CH$_2$O), 33.3 (<u>C</u>H$_2$S), 62.7 (<u>C</u>H$_2$O), 124.0, 129.9 and 130.0 (aromatic <u>C</u>H), 133.8 (aromatic <u>C</u>), 154.5 (S<u>C</u>N); *m*/*z* (CI) 265 (MH^+, 100%); HRMS found 265.1114, $C_{12}H_{17}ON_4S$ (MH^+) requires 265.1123.

2.2.11 5-[(4-Methylphenyl)methylsulfanyl]-1-phenyl-1(*H*)-1,2,3,4-tetrazole (8j)[4]



Purification by flash chromatography (SiO_2, petrol→petrol/EtOAc 19:1) gave sulfide **8j** as a thick pale yellow oil; ν_{max}/cm^{-1} ($CDCl_3$ cast) 3043, 2922, 1597, 1515, 1499; δ_H ($CDCl_3$, 600 MHz) 2.33 (3H, s, C<u>H</u>$_3$), 4.60 (2H, s, C<u>H</u>$_2$), 7.13 (2H, d, *J* 7.9 Hz, CH$_3$CC<u>H</u>), 7.31 (2H, d, *J* 7.9 Hz, SCH$_2$CC<u>H</u>), 7.50-7.54 (5H, m, aromatic C<u>H</u>); δ_C ($CDCl_3$, 150 MHz) 21.3 (<u>C</u>H$_3$), 37.6 (<u>C</u>H$_2$), 123.9, 129.3, 129.6, 129.9 and 130.2 (aromatic <u>C</u>H), 132.2 (SCH$_2$<u>C</u>), 133.7 (N<u>C</u>CH), 138.2 (CH$_3$<u>C</u>), 154.1 (S<u>C</u>N); *m*/*z* (EI) 282 (M^+, 30%), 221 (22), 137 (21), 118 (19), 105 (100); HRMS found 282.0927, $C_{15}H_{14}N_4S$ (M^+) requires 282.0934.

2.2.12 (*E*)-5-(3-Phenylprop-2-enylsulfanyl)-1-phenyl-1(*H*)-tetrazole (8k)[5]



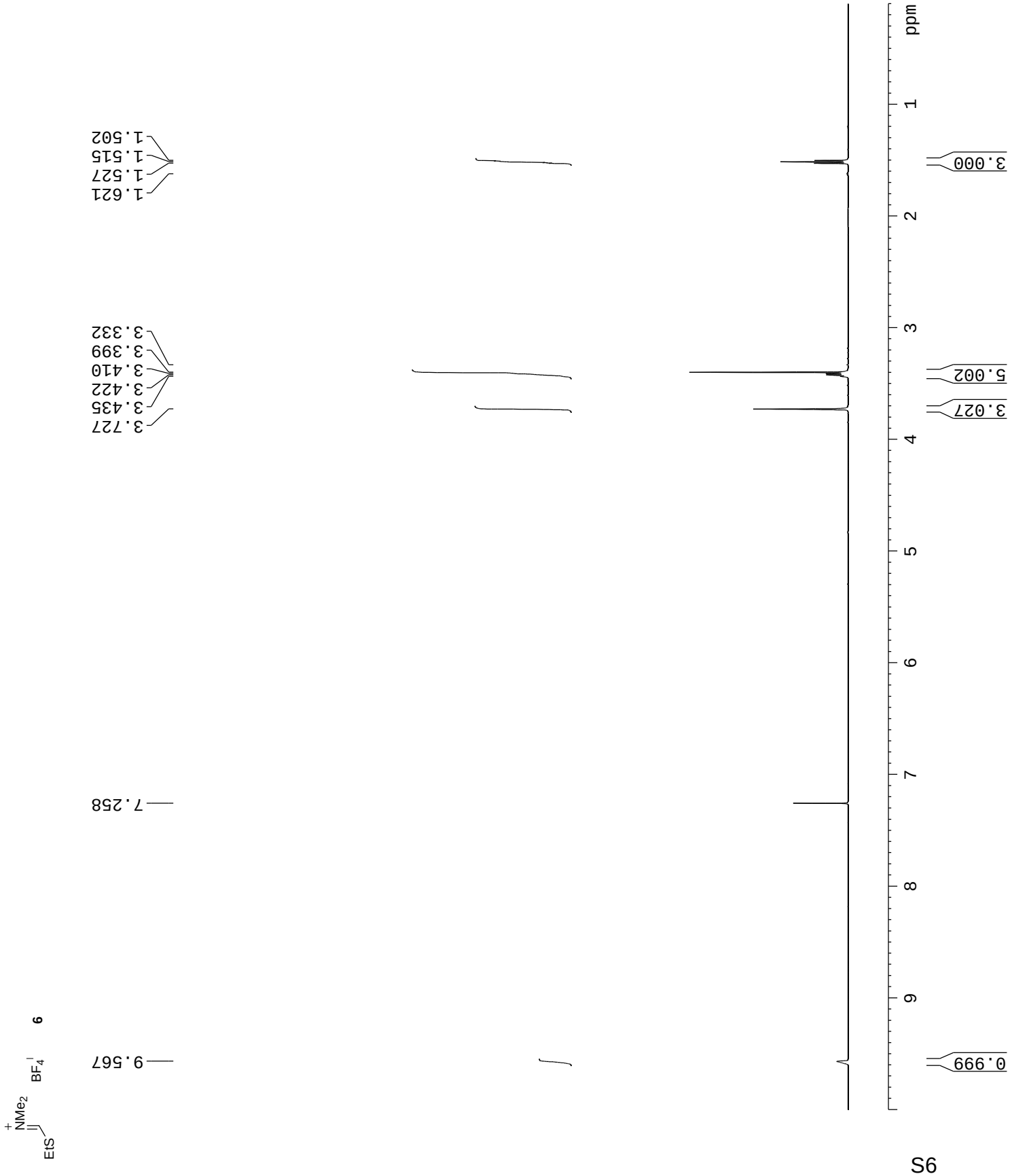
Purification by flash chromatography (SiO_2, petrol→petrol/EtOAc 19:1) gave sulfide **8k** as a thick pale yellow oil; ν_{max}/cm^{-1} ($CDCl_3$ cast) 3060, 3027, 1597, 1499; δ_H ($CDCl_3$, 600 MHz) 4.21 (2H, dd, *J* 7.5, 1.1 Hz, SC<u>H</u>$_2$), 6.36 (1H, dt, *J* 15.7, 7.5 Hz, SCH$_2$C<u>H</u>), 6.71 (1H, d, *J* 15.7 Hz, PhC<u>H</u>), 7.24 (1H, m), 7.28-7.32 (2H, m), 7.34-7.37 (2H, m) and 7.51-7.60 (5H, m, aromatic C<u>H</u>); δ_C ($CDCl_3$, 150 MHz) 36.0 (S<u>C</u>H$_2$), 122.5 (SCH$_2$<u>C</u>H), 124.0, 126.7, 128.3, 128.8, 129.9 and 130.3 (aromatic <u>C</u>H), 133.7 (N<u>C</u>CH), 135.3 (Ph<u>C</u>H), 136.1 (<u>C</u>CH=CH), 153.9 (S<u>C</u>N); *m*/*z* (EI) 294 (M^+, 17%), 266 (16), 265 (16), 233 (15), 147 (17), 118 (22), 117 (100); HRMS found 294.0925, $C_{16}H_{14}N_4S$ (M^+) requires 294.0934.

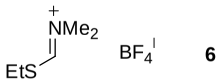
[4] K. Waisser, J. Adamec, J. Kuneš and J. Kaustová, *Chem. Pap.* 2004, **58**, 214.

[5] (a) K. Takeda, K. Tsuboyama, K. Torii, M. Murata and H. Ogura, *Tetrahedron Lett.* 1988, **29**, 4105; (b) K. Tsuboyama, K. Takeda, K. Torii and H. Ogura, *Chem. Pharm. Bull.* 1990, **38**, 2357.

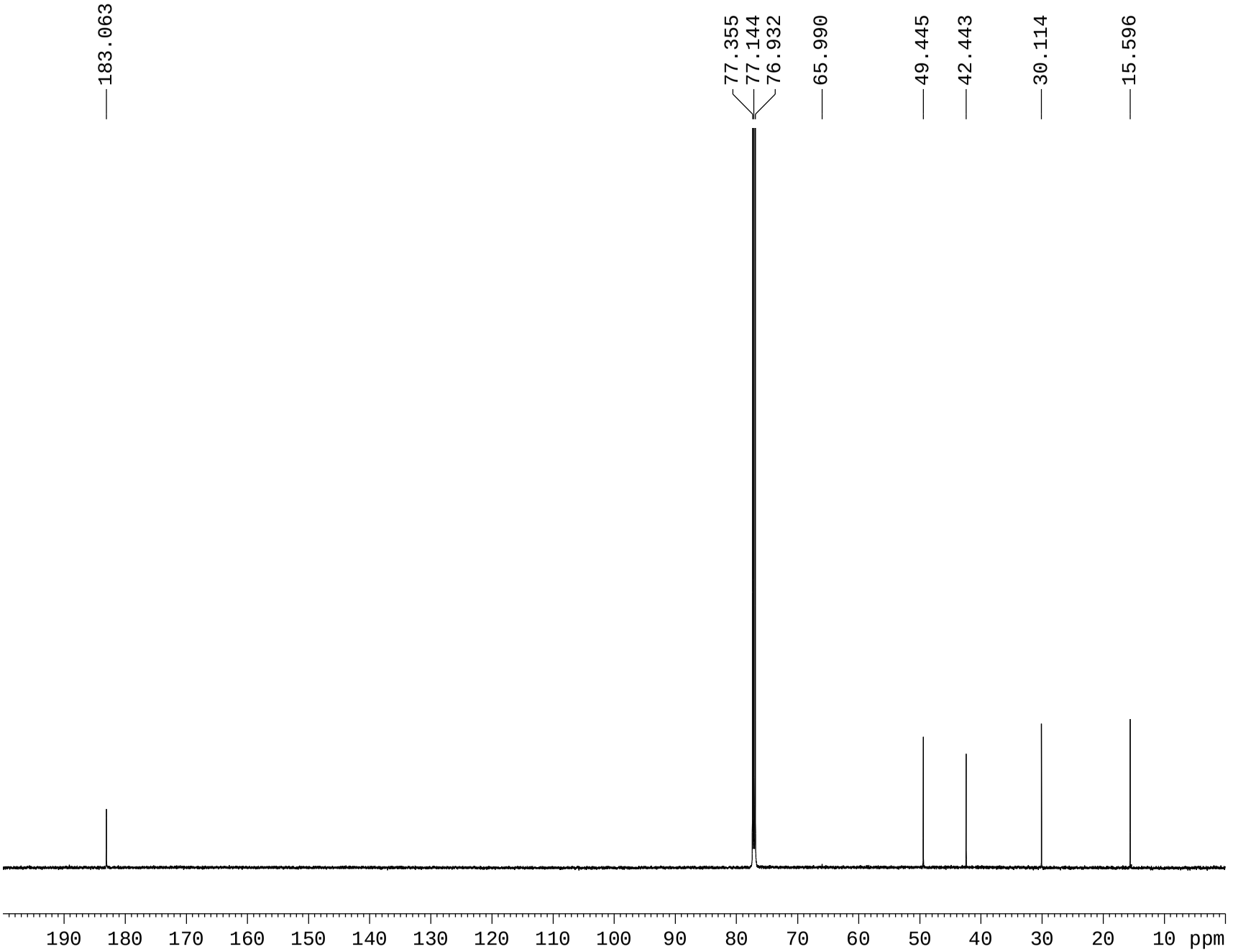
3. NMR Spectra

3.1 *N*-(Ethylsulfanylmethylene)-*N*,*N*-dimethylammonium tetrafluoroborate

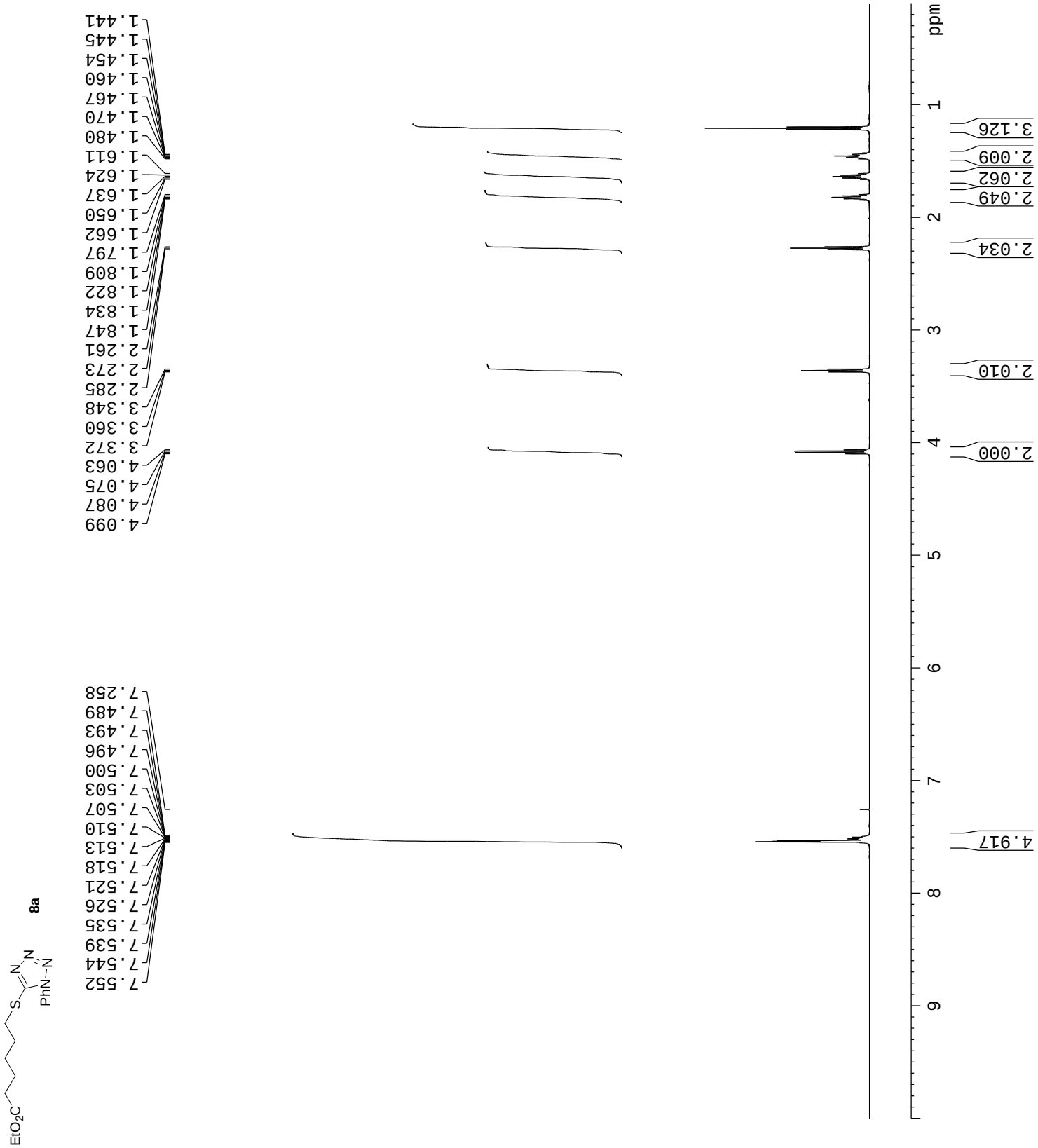


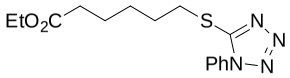

NMe2
EtS
BF4

6


183.063
77.355
77.144
76.932
65.990
49.445
42.443
30.114
15.596
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

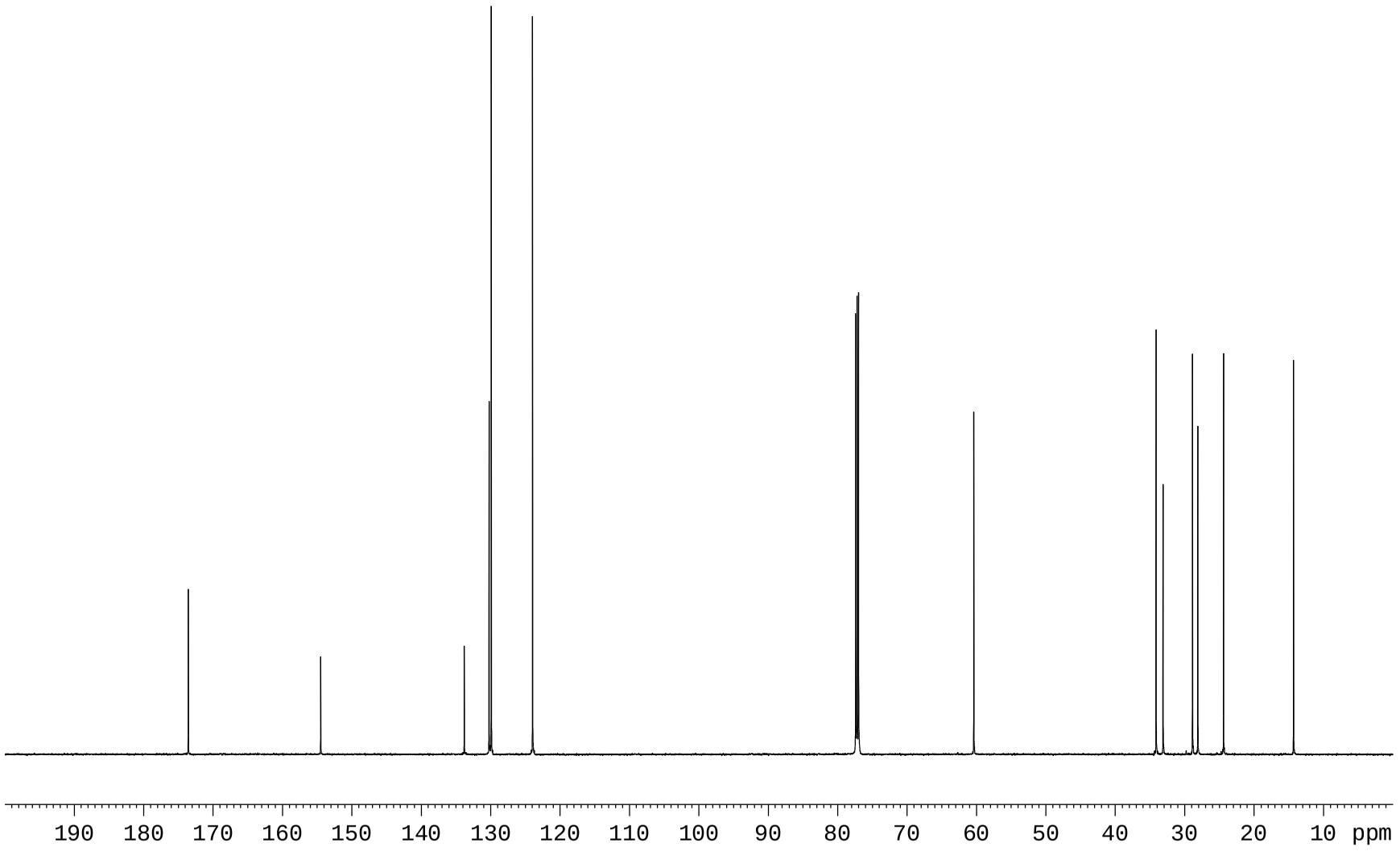
3.2 Ethyl 6-(1-phenyl-1(*H*)-tetrazol-5-ylsulfanyl)hexanoate (8a)



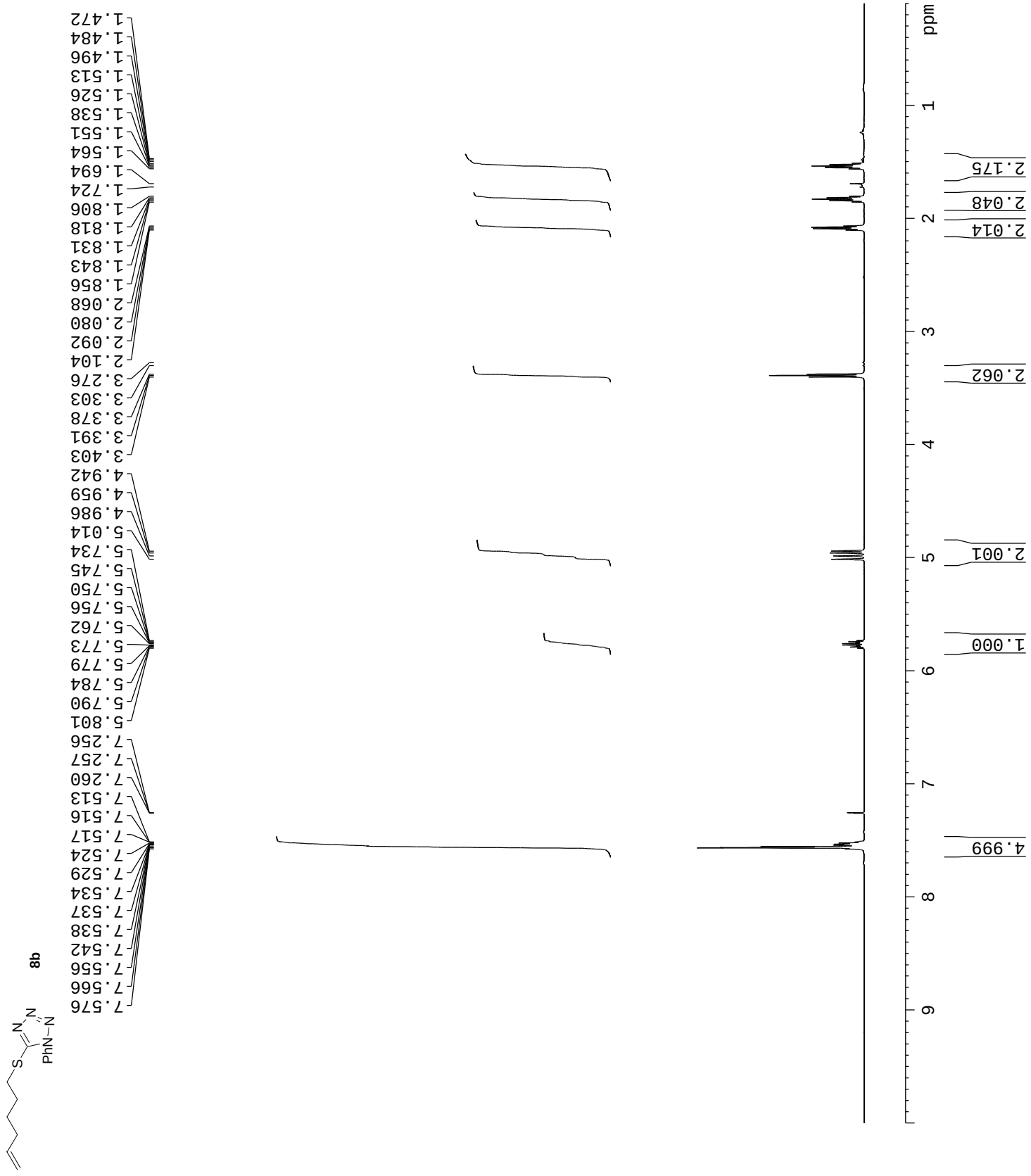


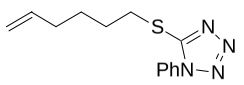
8a

173.533
154.464
133.970
133.763
133.534
130.211
130.093
129.971
129.890
129.692
124.122
123.925
123.713
123.685
77.426
77.214
77.002
62.686
60.396
34.350
34.233
34.123
33.921
33.129
29.785
28.880
28.779
28.220
28.131
24.760
24.520
24.417
24.293
14.457



3.3 5-(Hex-5-enylsulfanyl)-1-phenyl-1(*H*)-tetrazole (8b)





8b

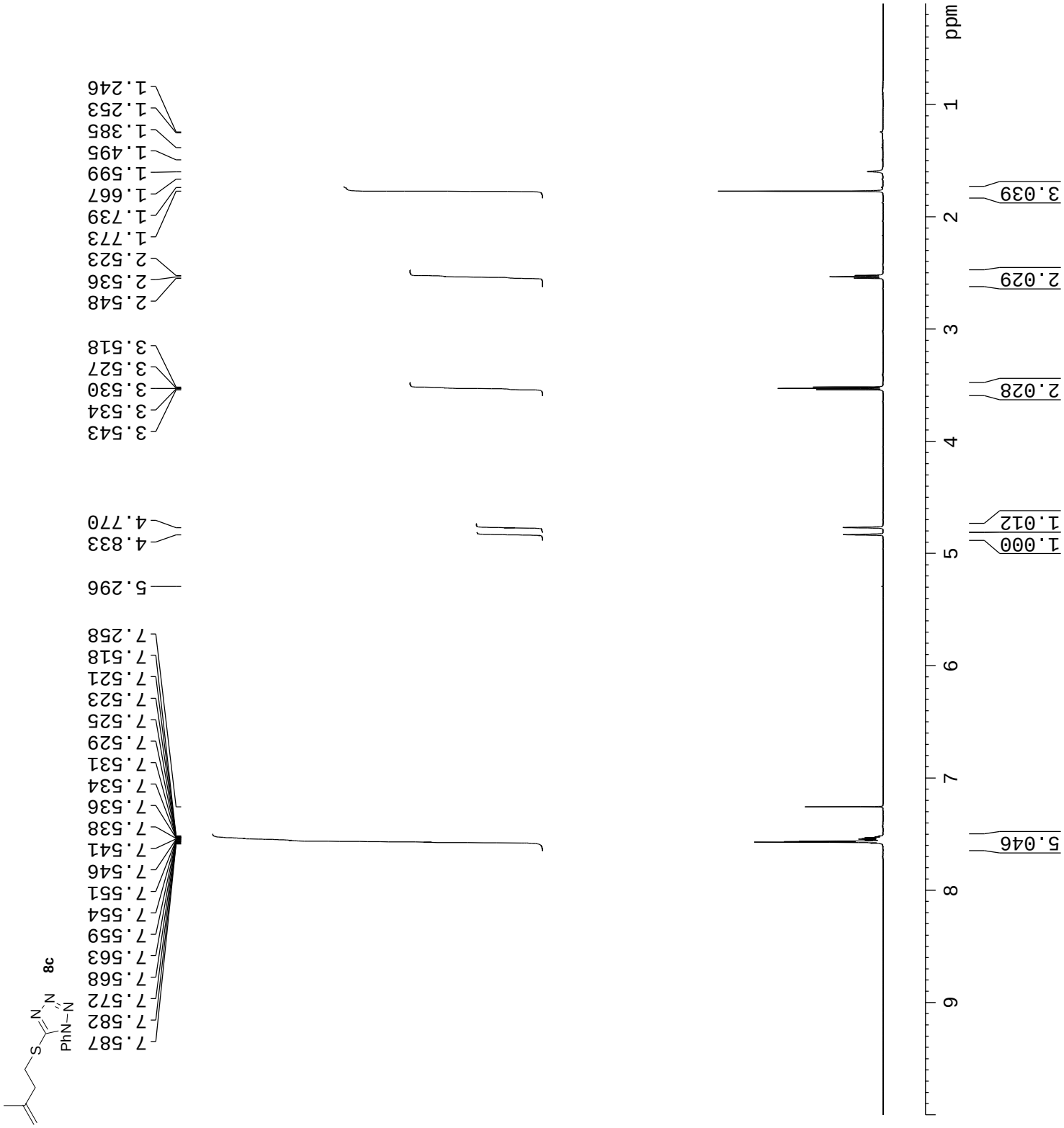
154.555
138.130
133.806
130.211
130.094
129.978
129.897
129.699
124.144
124.113
123.947
123.735
123.707
115.393
115.191

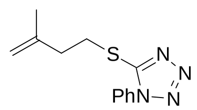
77.385
77.173
76.961

39.462
36.377
33.263
33.197
32.568
29.814
29.143
28.618
28.516
27.889
26.146
24.293
21.530
15.001
14.691
14.260

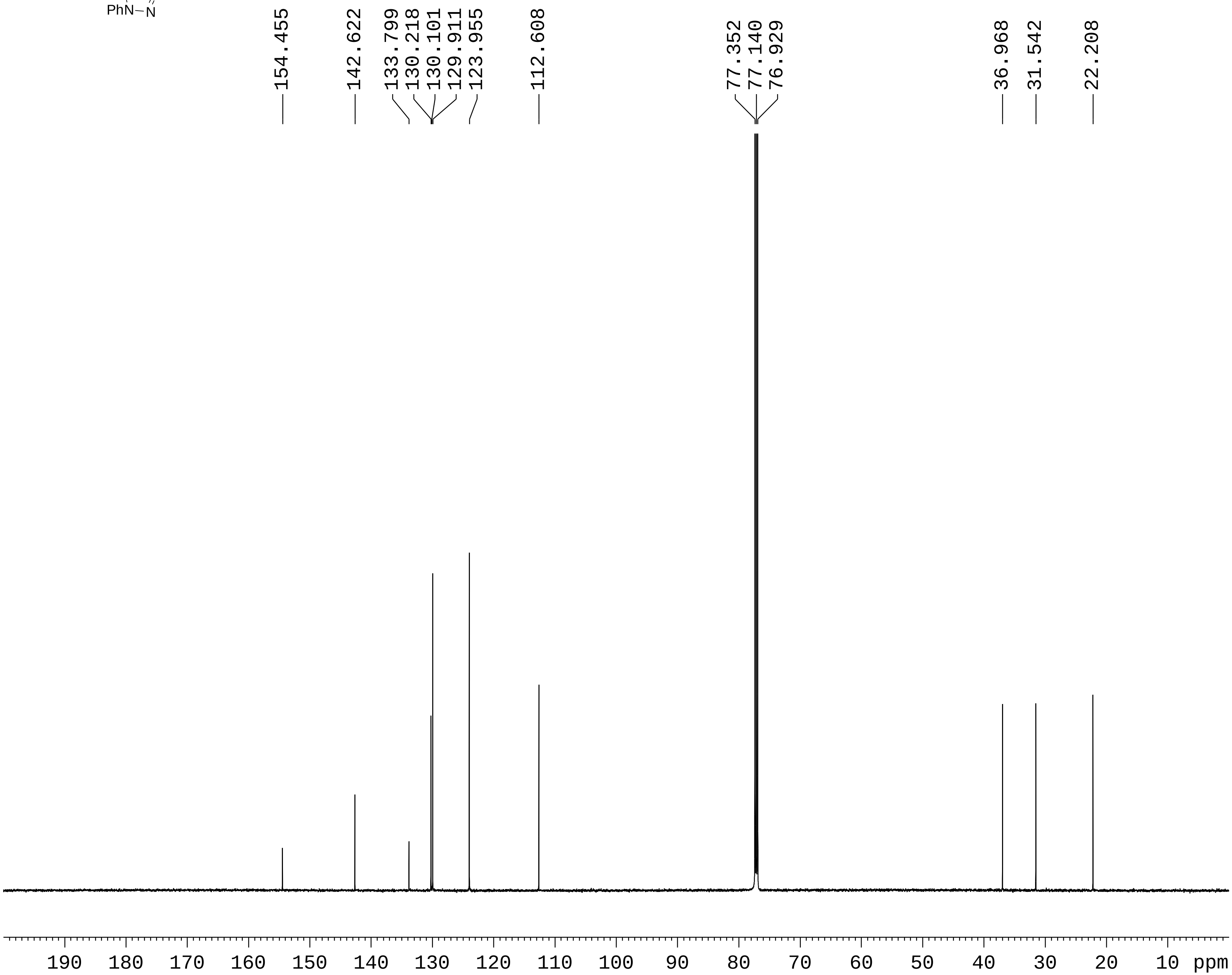
200 180 160 140 120 100 80 60 40 20 0 ppm

3.4 5-(3-Methylbut-3-enylsulfanyl)-1-phenyl-1(*H*)-tetrazole (8c)

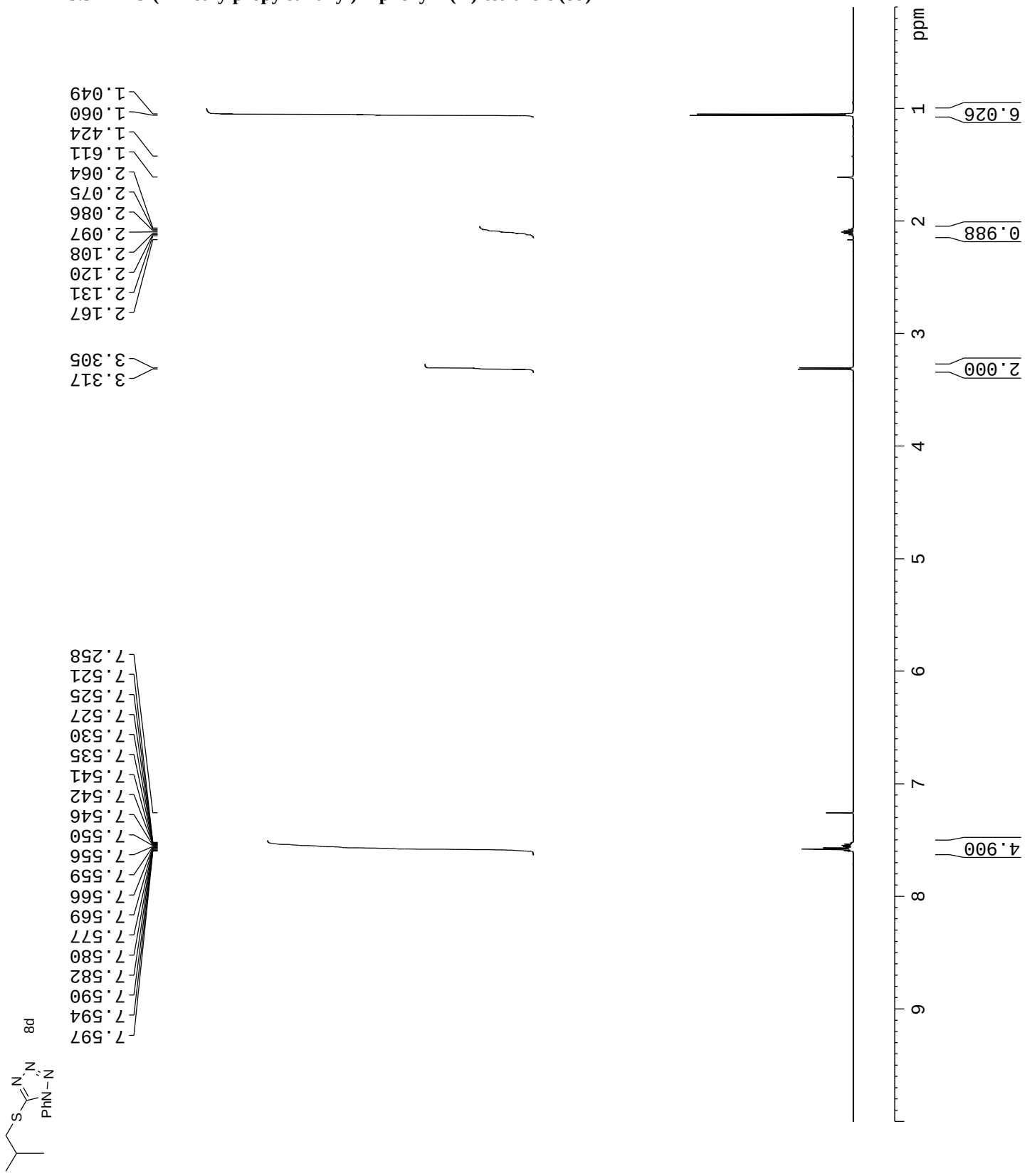


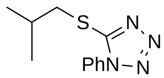

S
N
N
N
PhN

8c

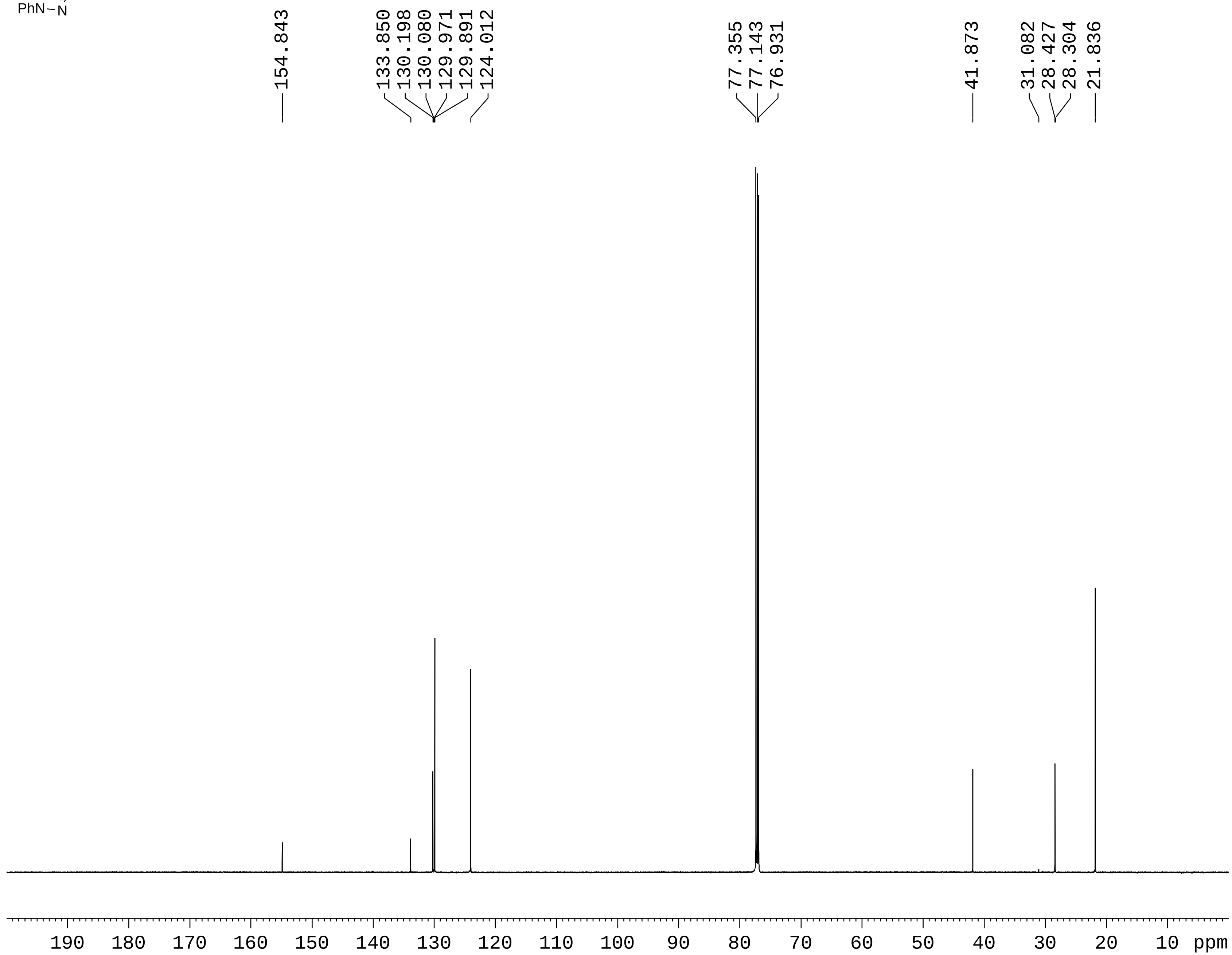

154.455
142.622
133.799
130.218
130.101
129.911
123.955
112.608
77.352
77.140
76.929
36.968
31.542
22.208
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3.5 5-(2-Methylpropylsulfanyl)-1-phenyl-1(*H*)-tetrazole (8d)



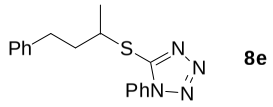


8d



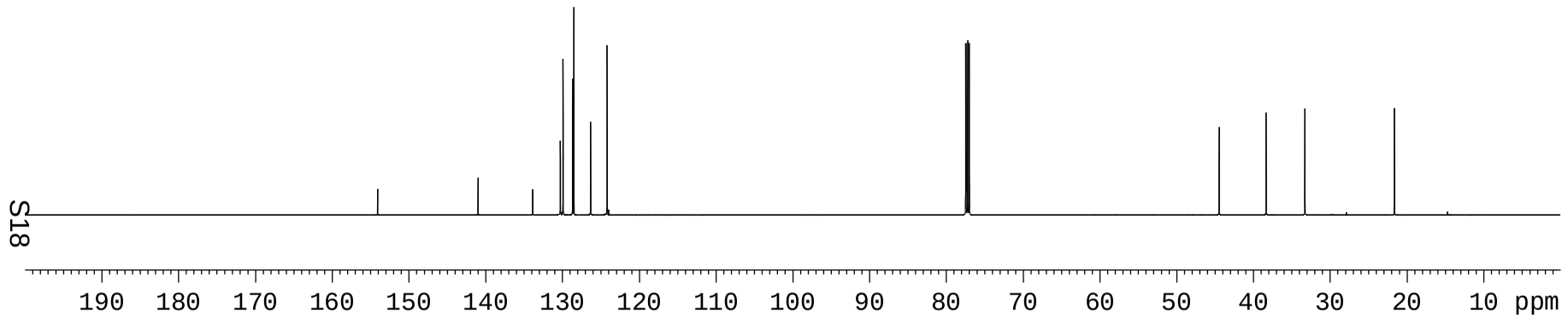
154.843
133.850
130.198
130.080
129.971
129.891
124.012
77.355
77.143
76.931
41.873
31.082
28.427
28.304
21.836
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3.6 1-Phenyl-5-(4-phenylbutan-2-ylsulfanyl)-1(*H*)-tetrazole (8e)

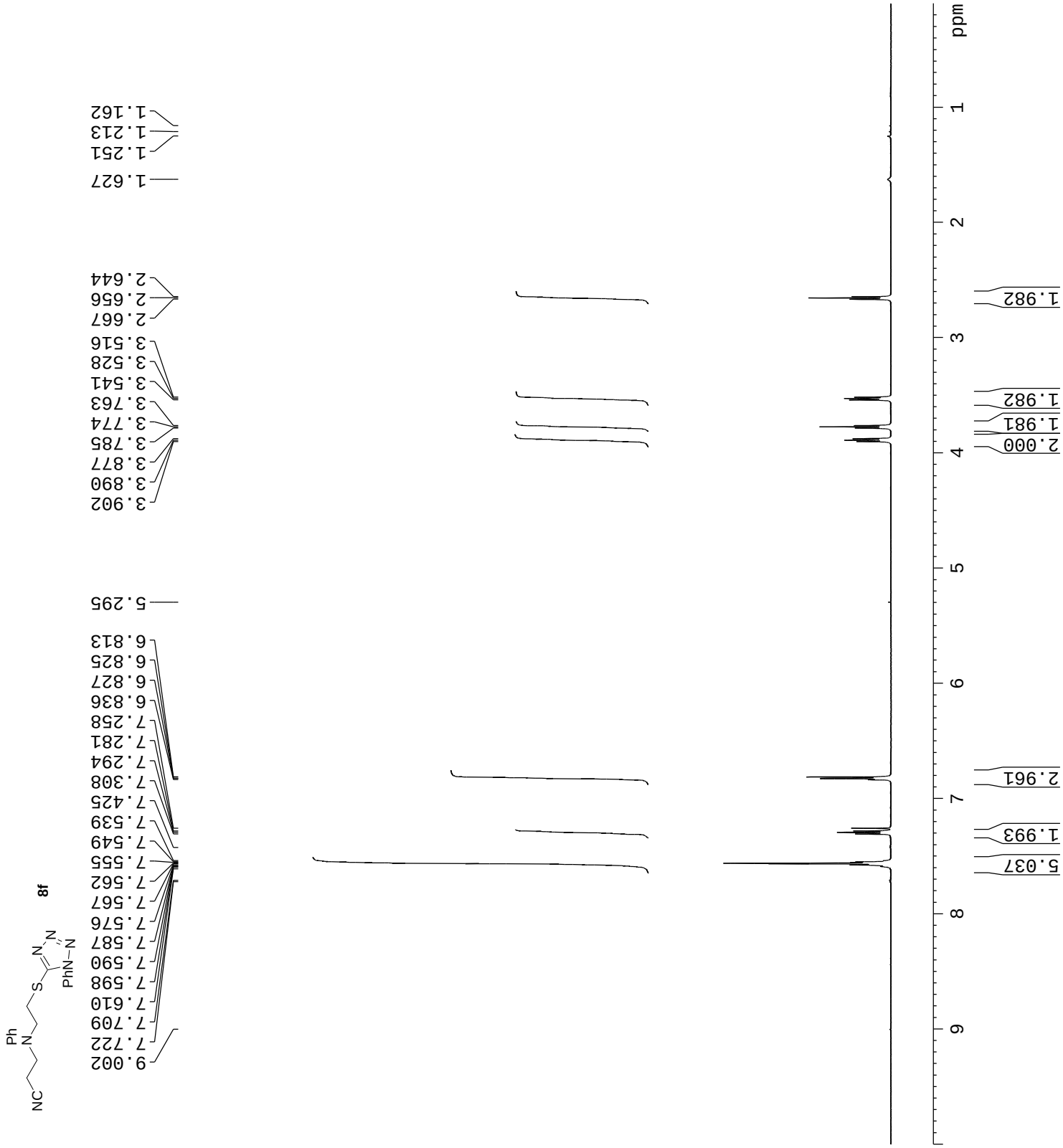


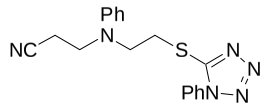
8e

154.425
154.022
141.141
140.969
140.763
133.847
130.668
130.253
130.124
130.058
129.970
129.910
129.881
129.680
129.386
128.826
128.646
128.558
128.519
128.468
128.262
126.441
126.288
126.072
124.588
124.355
124.320
124.158
123.961
123.918
77.424
77.212
77.001
60.534
44.579
44.464
44.345
38.442
38.339
38.218
37.418
33.292
33.169
33.139
29.836
27.866
22.835
21.733
21.625
14.719
14.347



3.7 3-{Phenyl[2-(1-phenyl-1(*H*)-tetrazol-5-ylsulfanyl)ethyl]amino}propanenitrile (8f)



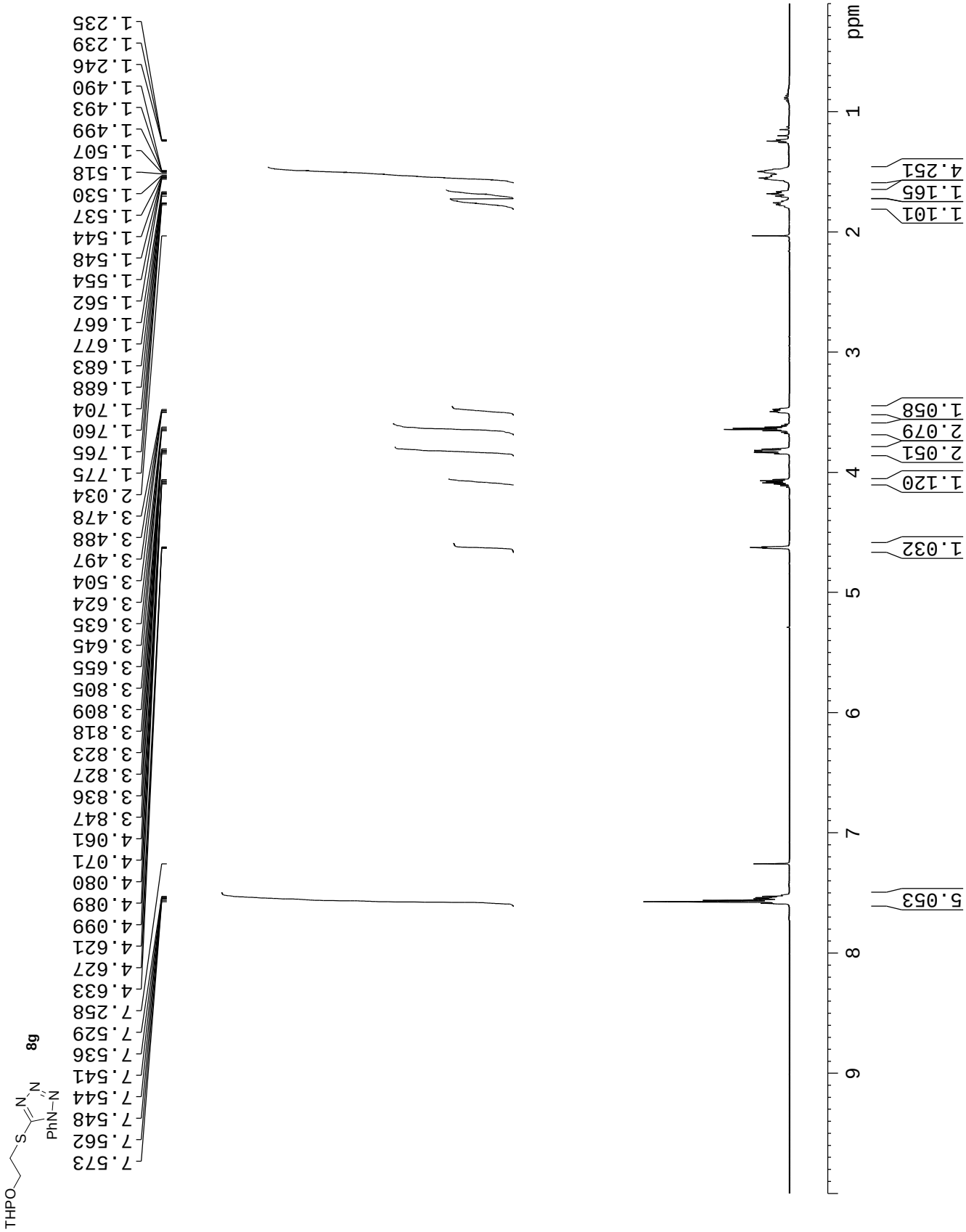


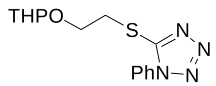
8f

153.968
145.723
133.602
130.422
130.355
130.014
129.992
123.920
123.711
121.358
118.665
118.372
113.187
77.386
77.174
76.962
50.896
47.634
30.136
16.323

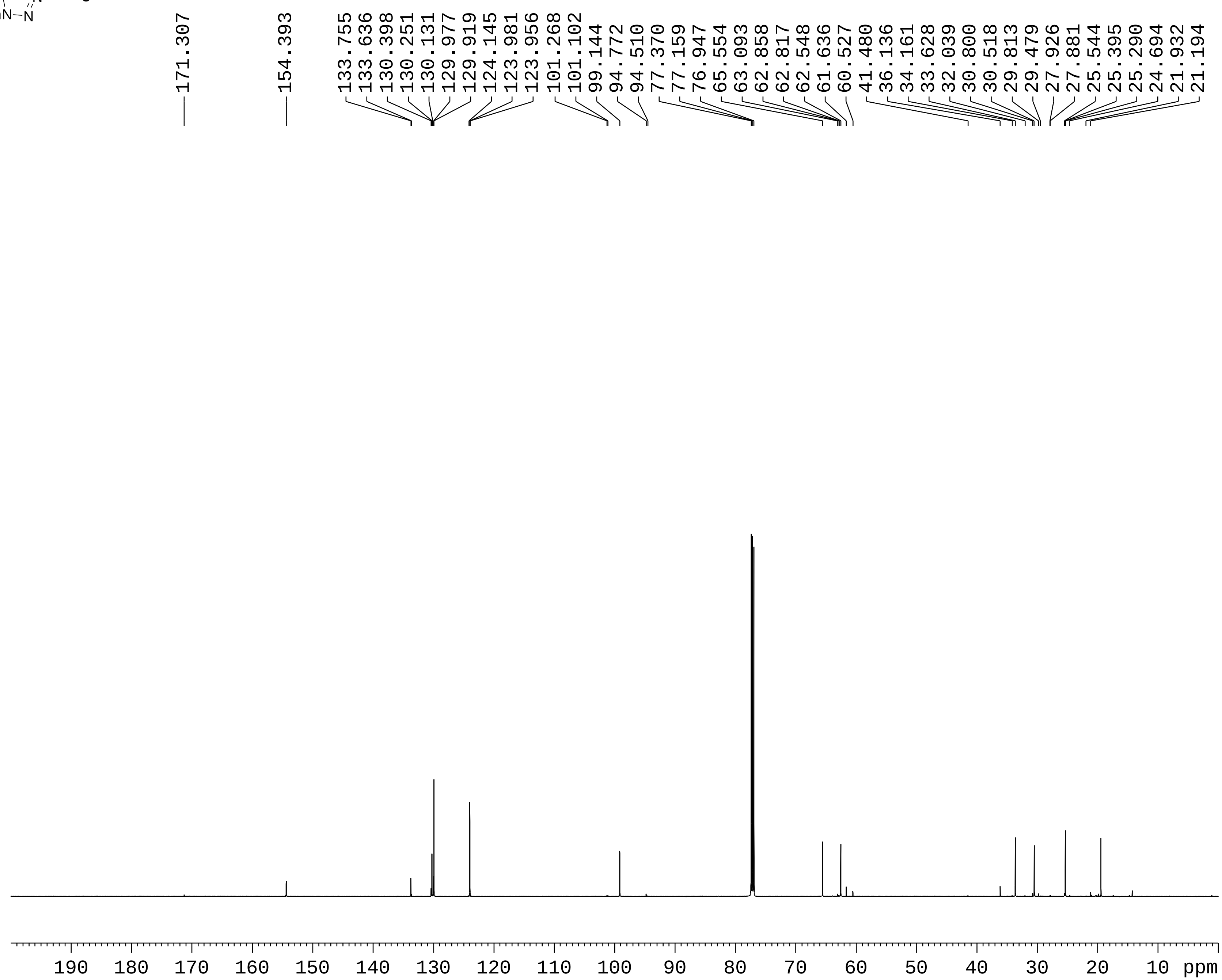
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3.8 1-Phenyl-5-[2-(tetrahydro-2(*H*)-pyran-2-yloxy)ethylsulfanyl]-1(*H*)-tetrazole (8g)

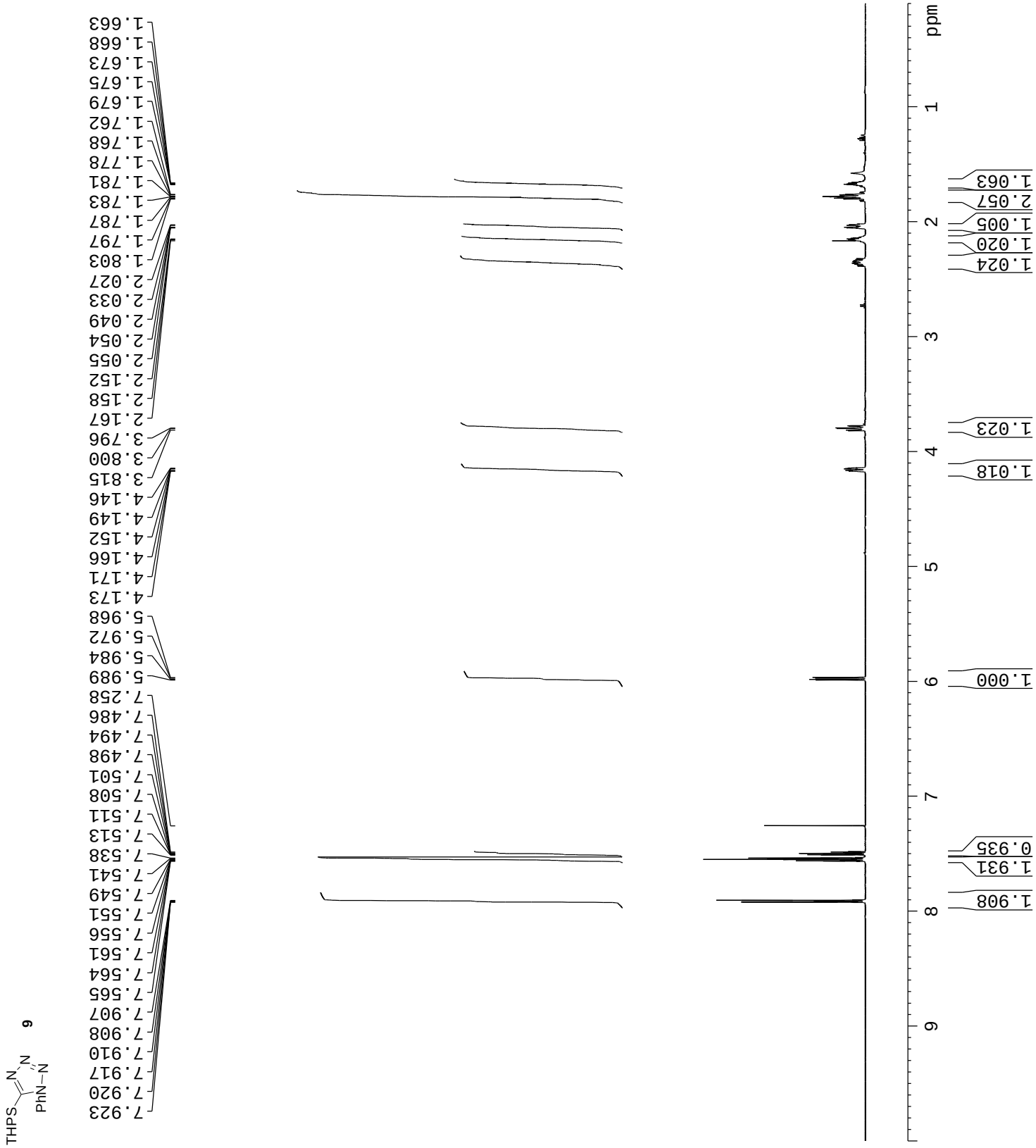


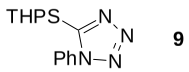


8g

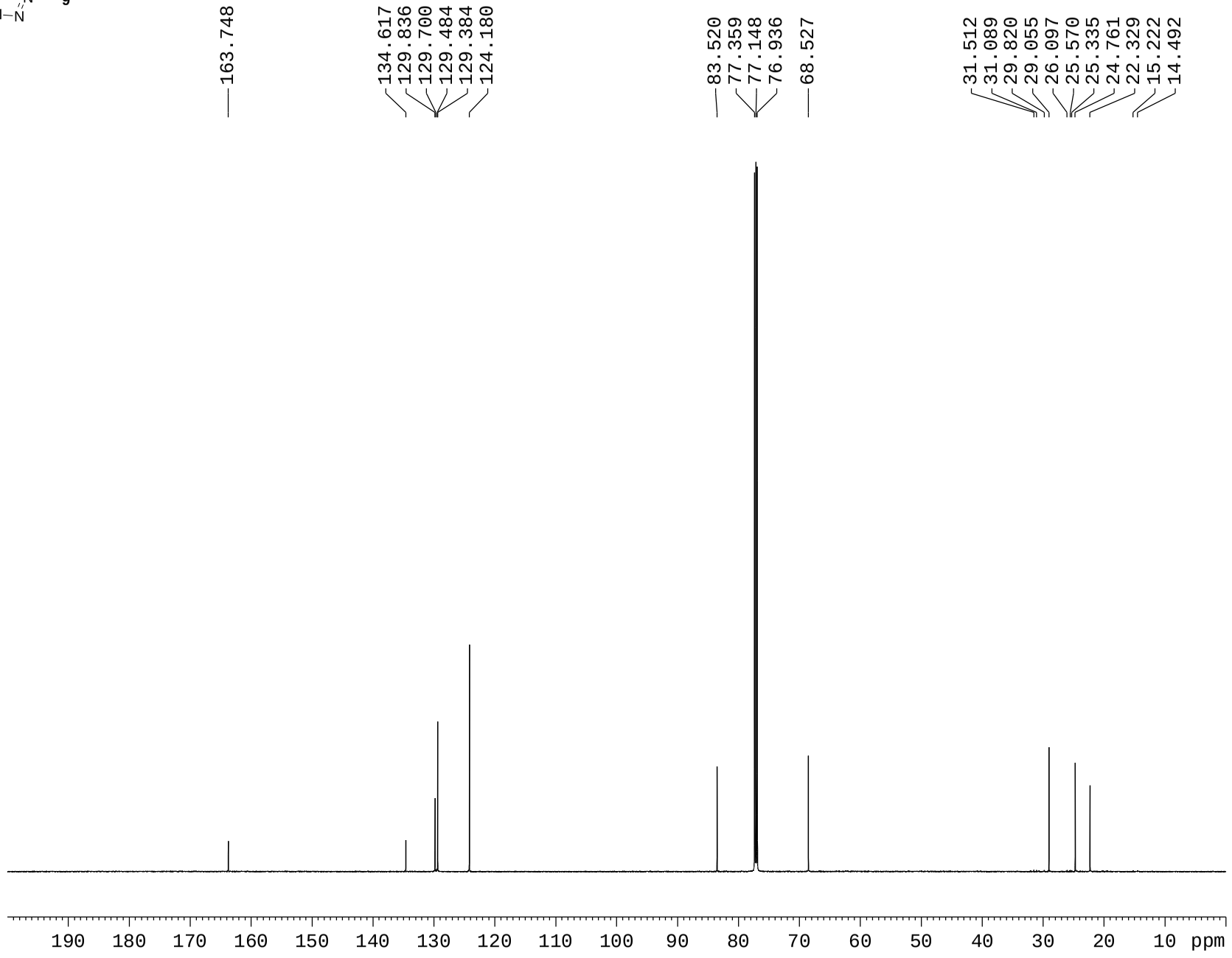

171.307
154.393
133.755
133.636
130.398
130.251
130.131
129.977
129.919
124.145
123.981
123.956
101.268
101.102
99.144
94.772
94.510
77.370
77.159
76.947
65.554
63.093
62.858
62.817
62.548
61.636
60.527
41.480
36.136
34.161
33.628
32.039
30.800
30.518
29.813
29.479
27.926
27.881
25.544
25.395
25.290
24.694
21.932
21.194
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3.9 1-Phenyl-5-(tetrahydro-2(*H*)-pyran-2-ylsulfanyl)-1(*H*)-tetrazole (9)

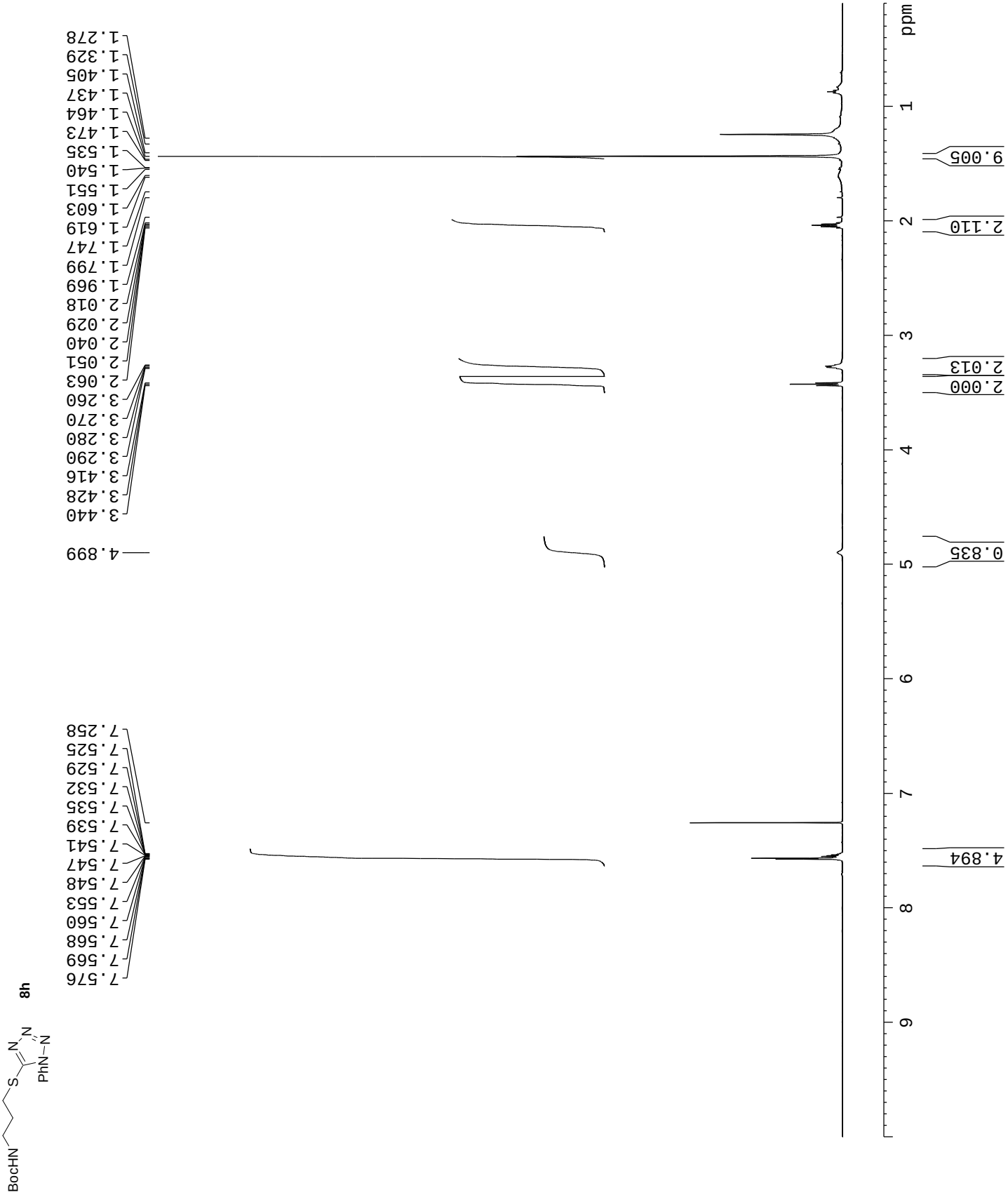


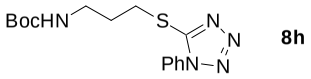

THPS
N
N
PhN
N

9


163.748
134.617
129.836
129.700
129.484
129.384
124.180
83.520
77.359
77.148
76.936
68.527
31.512
31.089
29.820
29.055
26.097
25.570
25.335
24.761
22.329
15.222
14.492
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3.10 *tert*-Butyl 3-(1-phenyl-1(*H*)-tetrazol-5-ylsulfanyl)propylcarbamate (8h)



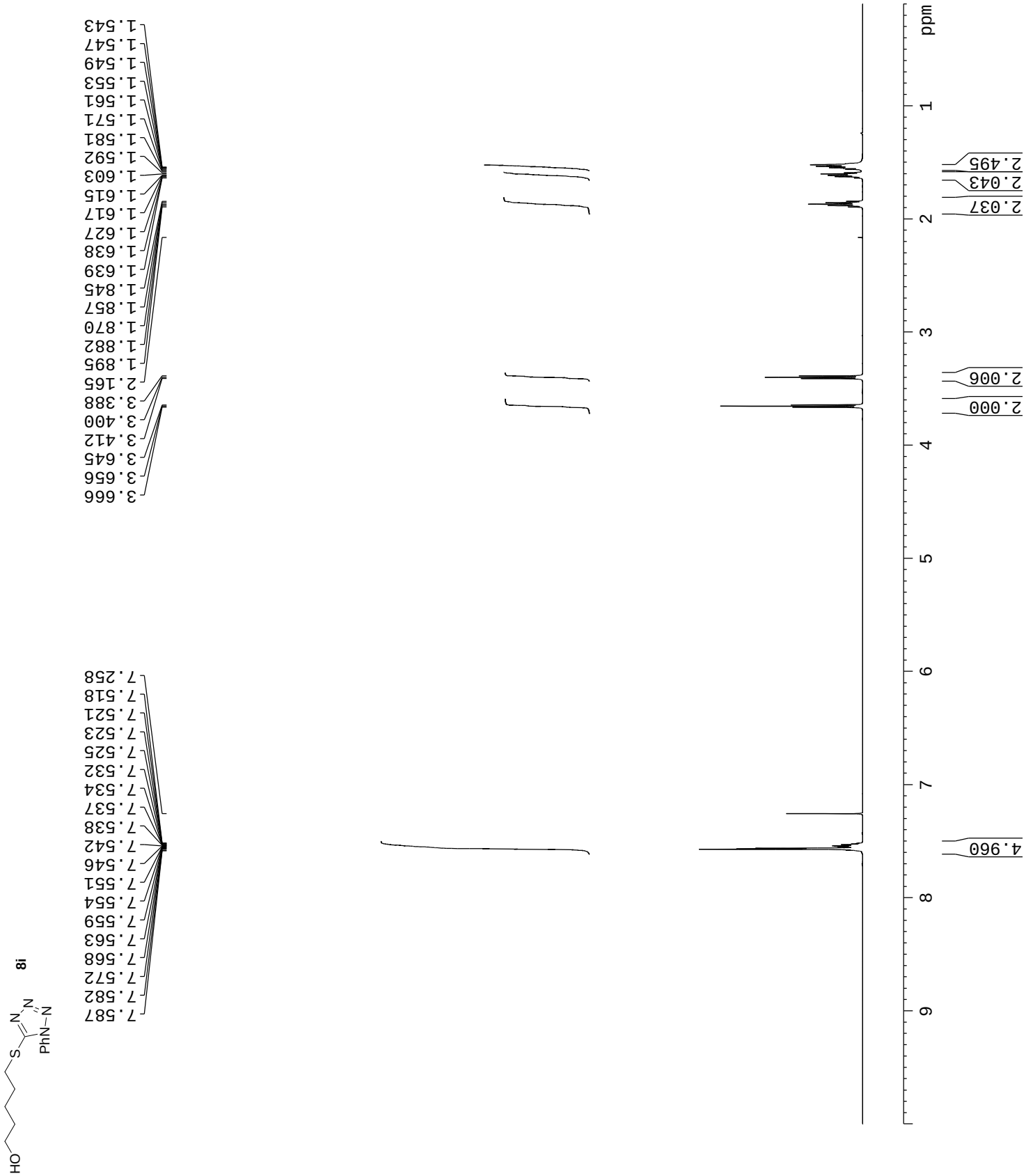


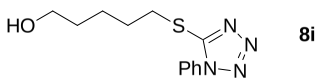
8h

156.188
154.564
133.703
130.298
129.943
123.959
79.561
77.341
77.130
76.918
38.929
32.050
30.619
30.279
29.982
29.827
28.511

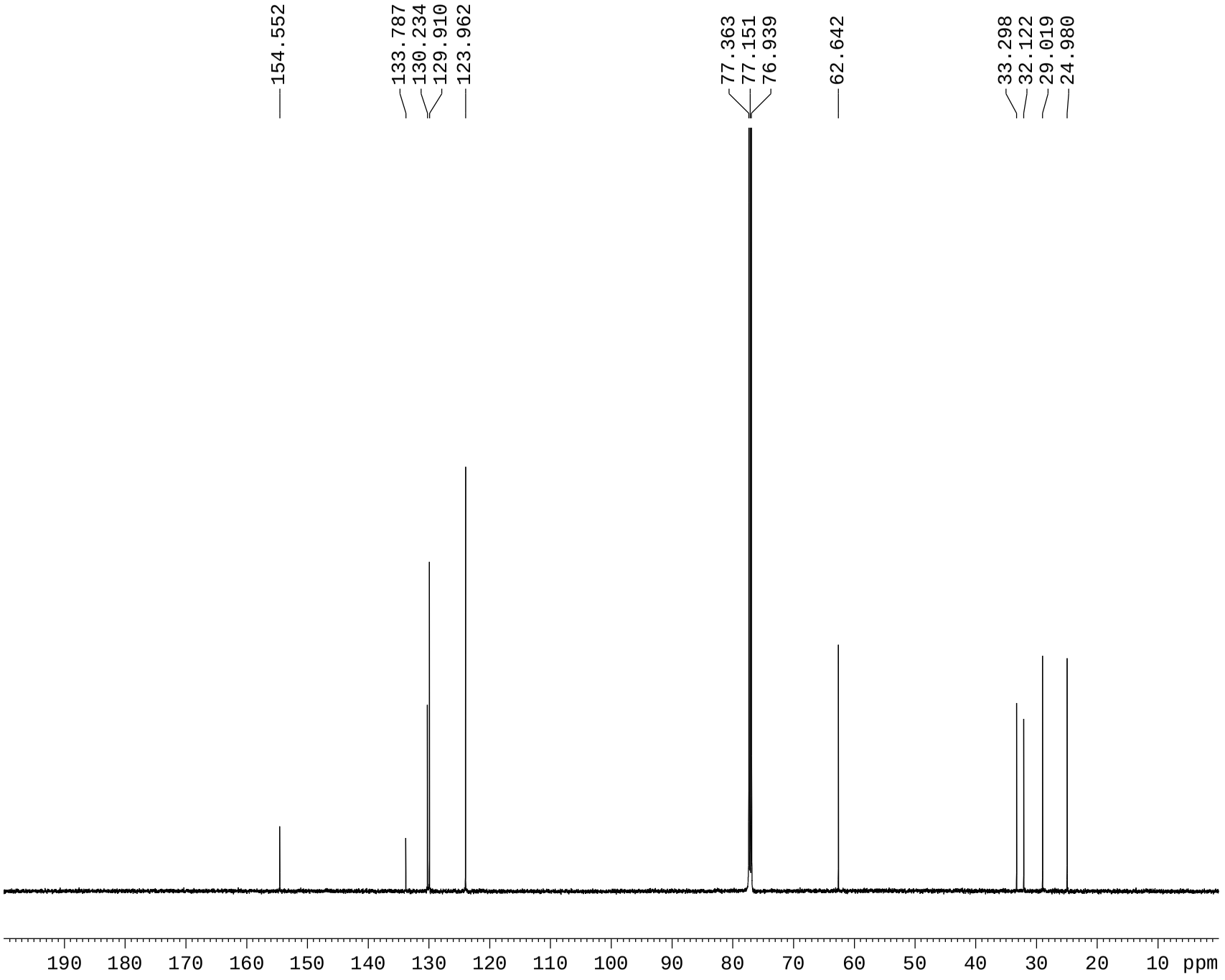
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3.11 5-(1-Phenyl-1(*H*)-tetrazol-5-ylsulfanyl)pentan-1-ol (8i)

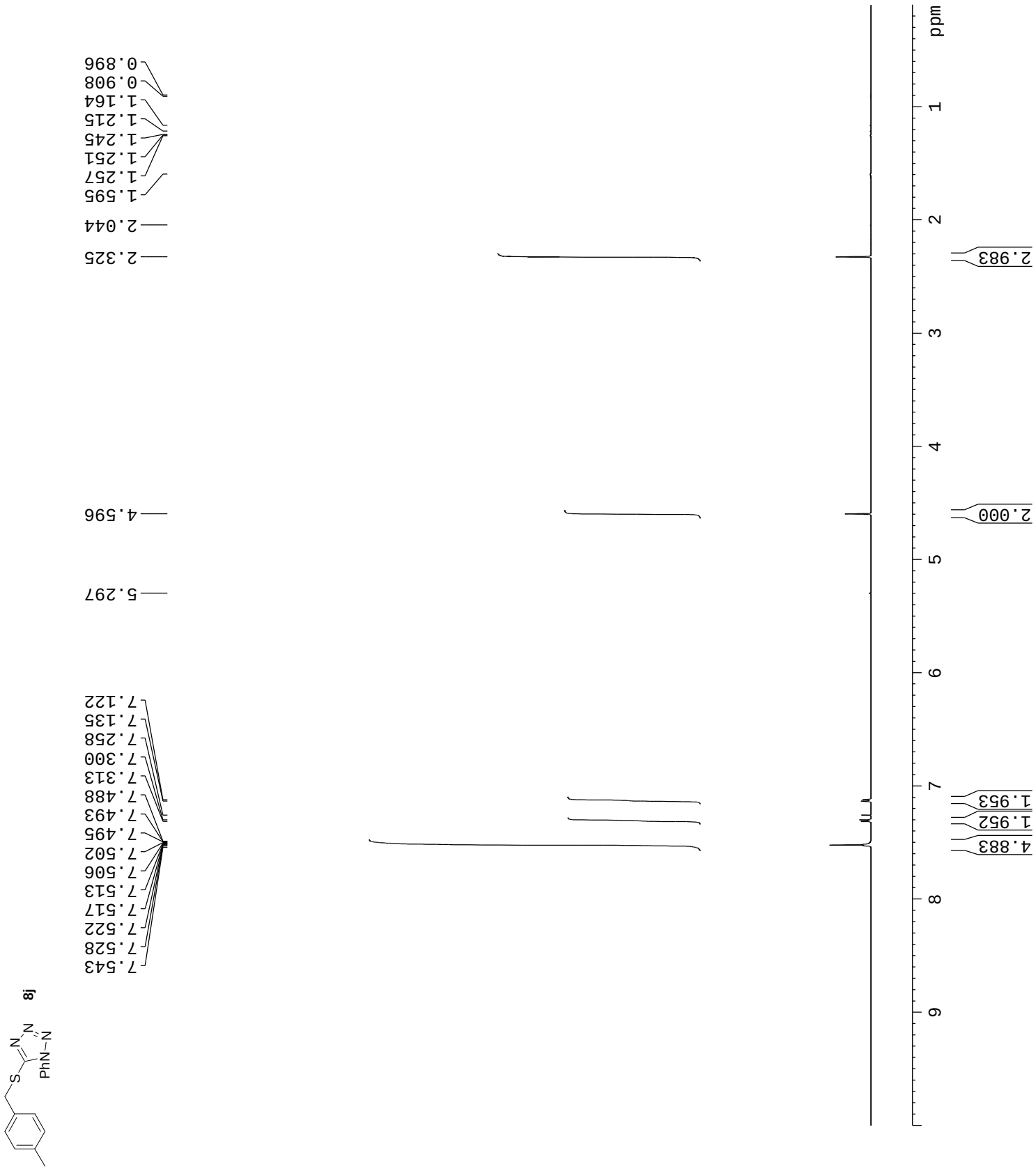


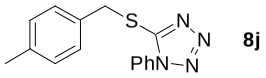

HO
S
N
N
PhN
N

8i

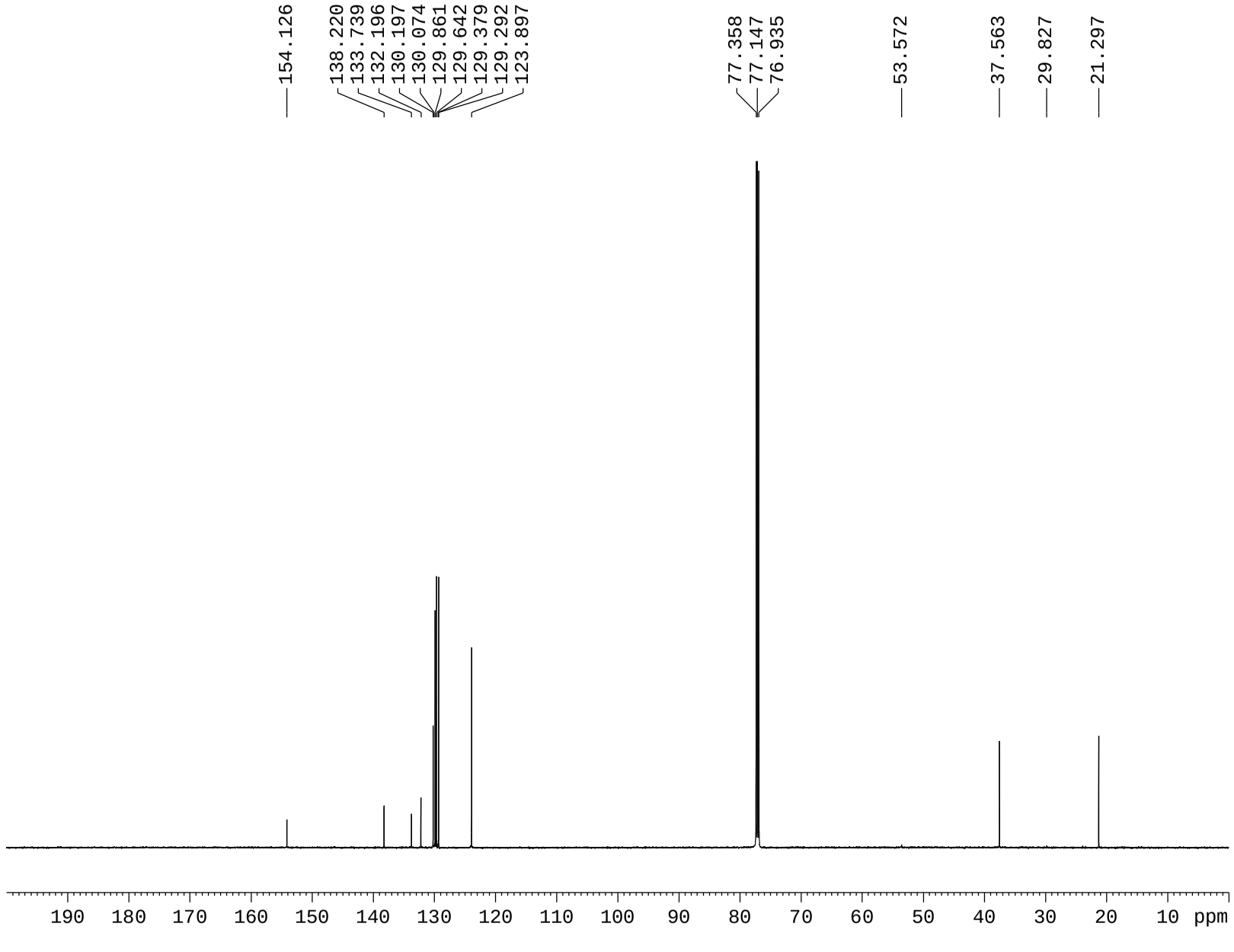

154.552
133.787
130.234
129.910
123.962
77.363
77.151
76.939
62.642
33.298
32.122
29.019
24.980
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3.12 5-[(4-Methylphenyl)methylsulfanyl]-1-phenyl-1(*H*)-1,2,3,4-tetrazole (8j)

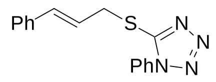



S
N
N
PhN
N

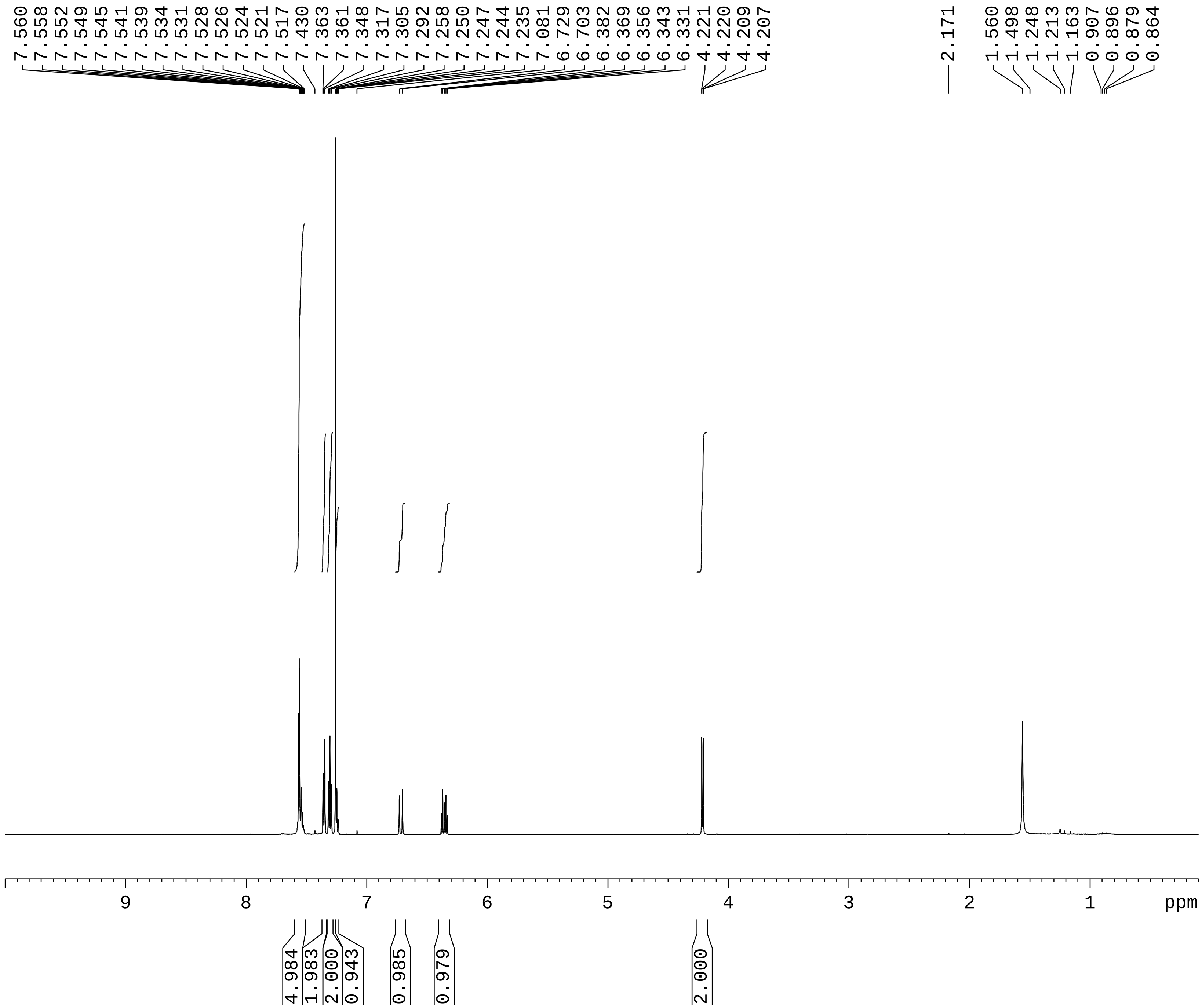
8j

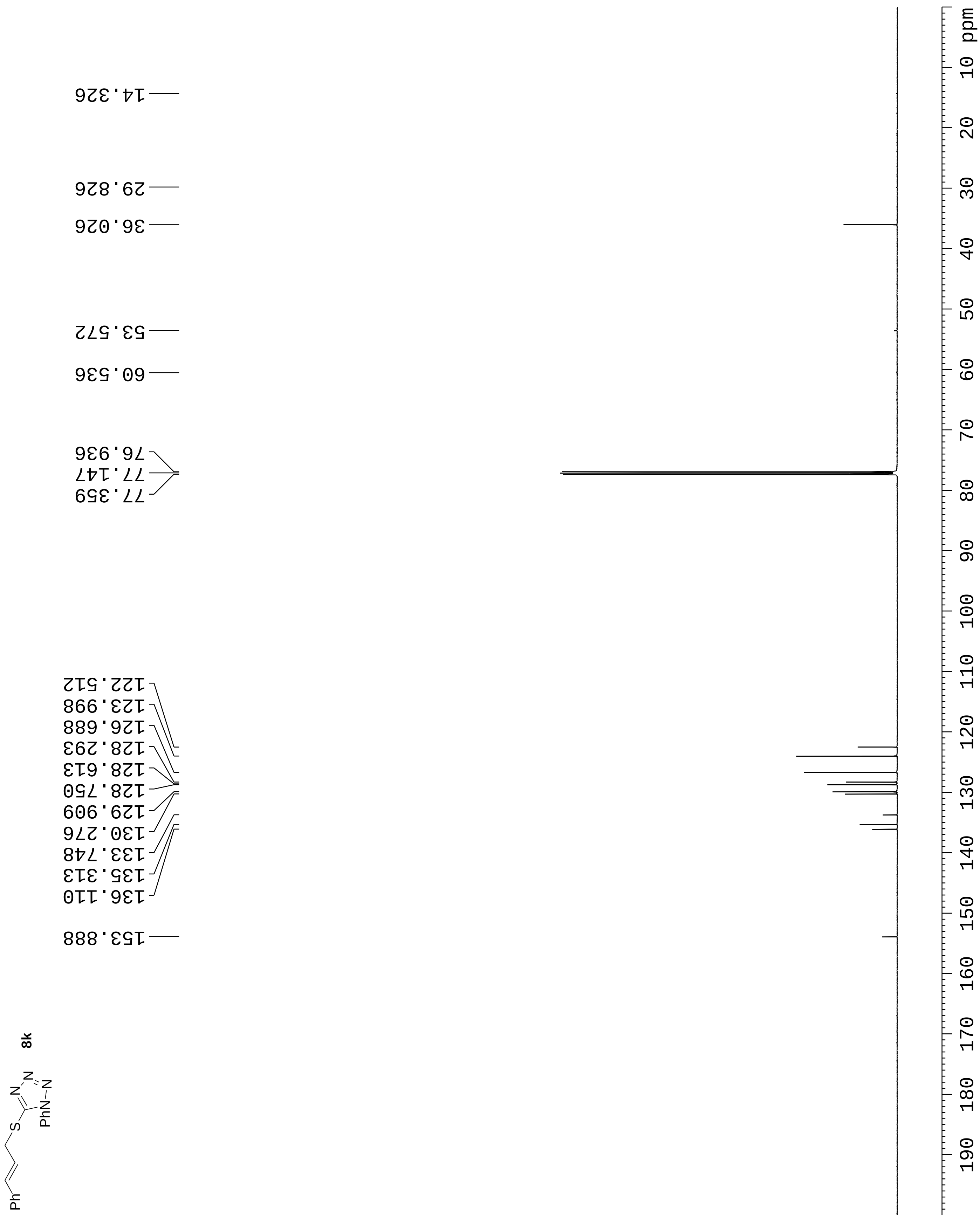

154.126
138.220
133.739
132.196
130.197
130.074
129.861
129.642
129.379
129.292
123.897
77.358
77.147
76.935
53.572
37.563
29.827
21.297
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3.13 (*E*)-5-(3-Phenylprop-2-enylsulfanyl)-1-phenyl-1(*H*)-tetrazole (8k)


Ph
S
N
N
PhN−N

8k


7.560 7.558 7.552 7.549 7.545 7.541 7.539 7.534 7.531 7.528 7.526 7.524 7.521 7.517 7.430 7.363 7.361 7.348 7.317 7.305 7.292 7.258 7.250 7.247 7.244 7.235 7.081 6.729 6.703 6.382 6.369 6.356 6.343 6.331 4.221 4.220 4.209 4.207
2.171
1.560 1.498 1.248 1.213 1.163 0.907 0.896 0.879 0.864
9 8 7 6 5 4 3 2 1 ppm
4.984 1.983 2.000 0.943 0.985 0.979 2.000


8k
Ph
S
N
N
N
PhN
14.326
29.826
36.026
53.572
60.536
76.936
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77.359
122.512
123.998
126.688
128.293
128.613
128.750
129.909
130.276
133.748
135.313
136.110
153.888
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
ppm