Electronic Supplementary Information

Catalyst-free regioselective acetylation of primary hydroxy groups in partially protected and unprotected thioglycosides with acetic acid

Polina I. Abronina,*[a] Nelly N. Malysheva,[a] Alexander I. Zinin,[a] Natalya G. Kolotyrkina,[a] Elena V. Stepanova[a,b] and Leonid O. Kononov*[a]

[a] N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, Leninsky prosp., 47, Moscow 119991, Russian Federation.

[b] Research School of Chemistry and Applied Biomedical Sciences, Tomsk Polytechnic University, Lenin avenue 30, Tomsk 634050, Russian Federation.

e-mail: *polina-abronina@yandex.ru, leonid.kononov@gmail.com*

Contents

Copies of NMR spectra

General methods

All reactions sensitive to air and/or moisture were carried out under argon atmosphere. The reactions were performed with the use of commercial reagents (Aldrich, Fluka, Acros Organics) Anhydrous solvents were purified and dried (where appropriate) according to standard procedures. Column chromatography was performed on silica gel 60 (40–63 μm, Merck). Thin-layer chromatography was carried out on plates with silica gel 60 on aluminum foil (Merck). Spots of compounds were visualized under UV light and by heating the plates (at *ca.* 150 °C) after immersion in a 1:10 (v/v) mixture of 85% aq H_3PO_4 and 95% EtOH. ^{1}H and ^{13}C NMR spectra were recorded for solutions in Me_2CO-d_6, $CDCl_3$, or CD_3OD on a Bruker AM-300 instrument (300.13 and 75.48 MHz for ^{1}H and ^{13}C, respectively), a Bruker DRX-400 instrument (400.16 and 100.63 MHz for ^{1}H and ^{13}C, respectively) or on a Bruker AVANCE 600 spectrometer (600.13 and 150.90 MHz for ^{1}H and ^{13}C, respectively). The ^{1}H NMR chemical shifts are referred to the residual signal of $CHCl_3$ (δ_H 7.27), CHD_2OD (δ_H 3.31), or CHD_2COCD_3 (δ_H 2.05), the ^{13}C NMR shifts – to the central line of $CDCl_3$ signal (δ_C 77.00), CD_3OD signal (δ_C 49.00) or $(CD_3)_2CO$ signal (δ_C 29.84). Assignments of the signals in the NMR spectra were performed using 2D-spectroscopy (COSY, HSQC, HMBC) and DEPT-135 experiments. High resolution mass spectra (electrospray ionization, HRESIMS) were recorded in positive mode on a Bruker micrOTOF II mass spectrometer for 2×10^{-5} M solutions in MeCN or MeOH. Optical rotations were measured using a JASCO P-2000 automatic digital polarimeter (Japan).

General procedure for deprotection of benzylidene acetals 2, 3, 11, 15 and acetylation of alcohols 4, 16, 17

To thioglycosides **2**, **3**, **4**, **11**, **15-17** (0.1–0.5 mmol) 60–100% (v/v) AcOH was added and the reaction mixture (c = 10–100 mmol/L) was stirred at T °C according to methods ***A***–***C*** (Table 1). Then the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with satd aq $NaHCO_3$ (50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL) and the combined organic extracts were filtered through a cotton wool plug, concentrated, and dried *in vacuo*. The products were purified by silica gel column chromatography in gradient of EtOAc in light petroleum (1→20%) for isolating of silyl (TBDPS or TIPS)-containing thioglycosides **4**–**10** and in gradient of EtOAc in light petroleum (5→60%) for isolating of benzyl-containing thioglycosides **16**–**19**. The yields of purified products are shown in Figs. 1–3 (see also Tables 1S-4S in ESI).

Ethyl 4,6-*O*-benzylidene-1-thio-α-D-galactopyranoside (**1**)

To a suspension of ethyl 1-thio-α-D-galactopyranoside [1] (3.92 mmol, 880 mg) in dry MeCN (10 ml), $PhCH(OMe)_2$ (5.88 mmol, 0.86 ml) and CSA (0.58 mmol, 135 mg) were added. The reaction mixture was stirred at 20 °C for 3 h, then neutralized with Et_3N (0.1 mL) and concentrated under reduced pressure. The crystalline residue was thoroughly washed with light petroleum, then with EtOAc, and dried to give alcohol **1** (857 mg, 70%). The organic extract was washed with satd aq $NaHCO_3$, dried and concentrated under reduced pressure to give an additional portion of **1** (280 mg, 23%). Total yield of **1** 1.137 g (93%). R_f = 0.47 (PhMe–Me_2CO, 2:1); $[\alpha]_D^{21}$ +191.5 (c 2.1 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{31}H_{38}O_5SSi+Na^+$: 573.2101 $[M+Na]^+$; found: 573.2096; ^{1}H NMR (300 MHz, MeOD): δ = 1.30 (t, J = 7.4 Hz, 3H, C<u>H</u>$_3$CH$_2$S), 2.58 (dq, J = 7.5 Hz, J = 12.9 Hz, 1H, CH$_3$C<u>H</u>$_2$S), 2.64 (dq, J = 7.5 Hz, J = 12.9 Hz, 1H, CH$_3$C<u>H</u>$_2$S), 3.77 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,2}$ = 10.2 Hz, 1H, H-3), 4.07–4.10 (m, 1H, H-5), 4.08–4.14 (m, 1H, H-6a), 4.14–4.20 (m, 1H, H-6b), 4.20 (dd, $J_{2,1}$ = 5.4 Hz, $J_{2,3}$ = 10.2 Hz, 1H, H-2), 4.26 (dd, $J_{4,5}$ = 1.2 Hz, $J_{4,3}$ = 3.6 Hz, 1H, H-4), 5.48 (d, $J_{1,2}$ = 5.4 Hz, 1H, H-1), 5.61 (s, 1H, PhC<u>H</u>), 7.27–7.42 (m, 3H, Ph (H-3, H-4, H-5)), 7.47–7.59 (m, 2H, Ph (H-2, H-6)); ^{13}C NMR (75 MHz, MeOD): δ = 15.3 (<u>C</u>H$_3$CH$_2$S), 25.2 (CH$_3$<u>C</u>H$_2$S), 64.7 (C-5), 69.5 (C-2), 70.4 (C-6), 71.0 (C-3), 77.9 (C-4), 87.8 (C-1), 102.3 (Ph<u>C</u>H), 127.5 (Ph (C-2, C-6)), 129.0 (Ph (C-3, C-5)), 129.9 (Ph (C-4)), 139.7 (Ph (C-1)).

Ethyl 4,6-*O*-benzylidene-2,3-bis-*O*-triisopropylsilyl-1-thio-α-D-galactopyranoside (2)

To a solution of ethyl 4,6-*O*-benzylidene-1-thio-α-D-galactopyranoside (**1**) (0.10 g, 0.32 mmol) in 2,4,6-collidine (2.0 mL), *i*-Pr_3SiOTf (0.26 mL, 0.96 mmol) was added. The reaction mixture was stirred at 80 °C for 12 h and then diluted with CH_2Cl_2 (50 mL), washed with H_2O (50 mL), 1 M aq $KHSO_4$ (50 mL), H_2O (50 mL) and satd aq $NaHCO_3$ (50 mL). Each aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic extracts were filtered through a cotton wool plug, concentrated under reduced pressure and purified by silica gel column chromatography (1→4% EtOAc in light petroleum) to give benzylidene derivative **2** (190 mg, 95%). R_f = 0.65 (light petroleum– EtOAc, 8:2). $[\alpha]_D^{21}$ +143.6 (c 1.8 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{33}H_{60}O_5SSi_2+Na^+$: 647.3592 $[M+Na]^+$; found: 647.3588; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.09–1.18 (m, 42H, 2 × $((CH_3)_2CH)_3Si$), 1.29 (t, *J* = 7.4 Hz, 3H, $C\underline{H}_3CH_2S$), 2.52 (dq, *J* = 7.4 Hz, *J* = 12.9 Hz, 1H, $CH_3C\underline{H}_2S$), 2.58 (dq, *J* = 7.4 Hz, *J* = 12.9 Hz, 1H, $CH_3C\underline{H}_2S$), 4.07 (ddd~q, $J_{app.}$ = 1.5 Hz, 1H, H-5), 4.10 (dd, $J_{6a,5}$ = 1.8 Hz, $J_{6a,6b}$ = 12.4 Hz, 1H, H-6a), 4.18 (dd, $J_{4,5}$ = 1.3 Hz, $J_{4,3}$ = 3.3 Hz, 1H, H-4), 4.22 (dd, $J_{6b,5}$ = 1.6 Hz, $J_{6b,6a}$ = 12.4 Hz, 2H, H-6b), 4.23 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,2}$ = 9.6 Hz, 1H, H-3), 4.65 (dd, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 9.6 Hz, 1H, H-2), 5.49 (d, $J_{1,2}$ = 5.0 Hz, 1H, H-1), 5.54 (s, 1H, PhC$\underline{H}$), 7.29–7.41 (m, 3H, Ph), 7.49–7.60 (m, 2H, Ph (H-2, H-6)); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 13.2, 13.4 ($((CH_3)_2\underline{C}H)_3Si$), 14.7 ($\underline{C}H_3CH_2S$), 18.0, 18.2 ($((\underline{C}H_3)_2CH)_3Si$), 18.3 (2 × $((\underline{C}H_3)_2CH)_3Si$), 23.8 ($CH_3\underline{C}H_2S$), 63.3 (C-5), 69.5 (C-6), 69.9 (C-2), 71.7 (C-3), 77.7 (C-4), 87.0 (C-1), 100.4 (Ph$\underline{C}$H), 126.0 (Ph (C-2, C-6)), 127.9 (Ph (C-3, C-5)), 128.5 (Ph (C-4)), 138.2 (Ph (C-1)).

Ethyl 4,6-*O*-benzylidene-2,3-bis-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-galactopyranoside (3)

To a solution of ethyl 4,6-*O*-benzylidene-1-thio-α-D-galactopyranoside **1** (0.838 g, 2.68 mmol) in dry DMF (5 mL), TBDPS-Cl (0.57 mL, 2.19 mmol) and imidazole (0.912 g, 13.4 mmol) were added. Then the reaction mixture was stirred at 20 °C for 3.5 h. Then an additional portion of TBDPS-Cl (0.1 mL, 0.38 mmol) was added and the reaction mixture was stirred at 20 °C for 18 h. The reaction mixture was quenched with satd aq NH_4Cl (100 mL) and diluted with *t*-BuOMe (100 mL). The organic layer was separated and the aqueous phase was extracted with *t*-BuOMe (4 × 10 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL), dried and concentrated. After silica gel column chromatography (2→12% EtOAc in light petroleum), a mixture of monosilyl ethers was obtained (1.28 g, 90% based on TBDPS-Cl).

To the solution of the obtained mixture (1.25 g, 2.27 mmol) in THF (12 mL), NaH (65% dispersion in mineral oil, 326 mg, 8.83 mmol) was added at 0 °C (bath temperature). After 20 min, TBDPS-Cl (1.18 mL, 4.54 mmol) was added. The reaction mixture was stirred at 20 °C for 24 h, cooled (ice–water), quenched with MeOH (0.5 mL) and concentrated under reduced pressure. The residue was diluted with *t*-BuOMe, washed twice with H_2O, concentrated and dried in *vacuo*. After purification by silica gel column chromatography (2→9% EtOAc in light petroleum), silyl ether **3** was obtained (1.62 g, 90% based on monosilylated intermediates). R_f = 0.35 (light petroleum–EtOAc 10:1); $[\alpha]_D^{25}$ +115.0 (c 2.0 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{47}H_{56}O_5SSi_2+Na^+$: 811.3279 $[M+Na]^+$; found: 811.3264; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 3H, $C\underline{H}_3CH_2S$), 1.14 (s, 9H, $(CH_3)_3CSi$)[1], 1.20 (s, 9H, $(CH_3)_3CSi$), 1.97–2.15 (m, 2H, $CH_3C\underline{H}_2S$), 3.11 (d, $J_{4,3}$ = 3.6 Hz, 1H, H-4), 3.49 (dd, $J_{6a,5}$ = 1.8 Hz, $J_{6a,6b}$ = 12.4 Hz, 1H, H-6a), 3.59 (m~s, 1H, H-5), 3.85 (dd, $J_{6b,5}$ = 1.5 Hz, $J_{6b,6a}$ = 12.4 Hz, 1H, H-6b), 4.44 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,2}$ = 9.6 Hz, 1H, H-3), 4.59 (d, $J_{1,2}$ = 5.2 Hz, 1H, H-1), 4.79 (s, 1H, PhC$\underline{H}$), 4.92 (dd, $J_{2,1}$ = 5.2 Hz, $J_{2,3}$ = 9.6 Hz, 1H, H-2), 7.27–7.52 (m, 17H, Ph), 7.82–7.86 (m, 2H, PhSi (H-2, H-6)), 7.88–7.92 (m, 2H, PhSi (H-2, H-6)), 7.93–7.97 (m, 2H, PhSi (H-2, H-6)), 7.97–8.01 (m, 2H, PhSi (H-2, H-6)); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.5 ($\underline{C}H_3CH_2S$), 19.1, 19.3 ($(CH_3)_3\underline{C}Si$), 24.0 ($CH_3\underline{C}H_2S$), 27.1, 27.4 (($\underline{C}H_3)_3CSi$), 62.6 (C-5), 69.2 (C-6), 70.4 (C-2), 72.5 (C-3), 75.2 (C-4), 86.3 (C-1), 99.9 (Ph$\underline{C}$H), 126.0 ($\underline{Ph}$CH (C-2, C-6)), 127.5, 127.6, 127.7, 127.8, 127.9, 128.5, 129.5, 129.7, 129.9 (Ph), 132.9, 134.8, 135.4 (PhSi (C-1)), 135.9, 136.1, 136.36, 136.44 (PhSi (C-2, C-6)), 138.0 ($\underline{Ph}$CH (C-1)).

Ethyl 2,3-bis-*O*-triisopropylsilyl-1-thio-α-D-galactopyranoside (4)

R_f = 0.32 (light petroleum–EtOAc 8:2); $[\alpha]_D^{21}$ +125.9 (c 1.2 in $CHCl_3$); HRMS (ESI): m/z calcd for $C_{26}H_{56}O_5SSi_2+Na^+$: 539.3279 $[M+Na]^+$; found: 539.3274; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02–1.22 (m, 42H, 2 × $((CH_3)_2CH)_3Si$), 1.28 (t, *J* = 7.4 Hz, 3H, $C\underline{H}_3CH_2S$), 2.42 (br.s, 1H, HO-6), 2.50 (dq, *J* = 7.4 Hz, *J* = 12.7 Hz, 1H, $CH_3C\underline{H}_2S$), 2.56 (dq, *J* = 7.4 Hz, *J* = 12.7 Hz, 1H, $CH_3C\underline{H}_2S$), 2.71 (br.s, 1H, HO-4), 3.82 (dd, $J_{6a,5}$ = 4.0 Hz, $J_{6a,6b}$ = 11.7 Hz, 1H, H-6a), 3.97 (dd, $J_{4,5}$ = 1.9 Hz, $J_{4,3}$ = 3.4 Hz, 1H, H-4), 3.98 (dd, $J_{6b,5}$ = 5.8 Hz, $J_{6b,6a}$ = 11.7

[1] The ^{13}C nuclei of the three CH groups in a triisopropylsilyloxy group next to a chiral center are chemically equivalent and appear as one peak, while those of the two CH_3 groups of each isopropyl moiety are diastereotopic and generally have close but distinct chemical shifts (two signals per one *O*-TIPS group). Such behavior is consistent over a large number of *O*-TIPS derivatives of sugars that we have dealt with.

Hz, 1H, H-6b), 4.13 (dd, $J_{3,4}$ = 3.4 Hz, $J_{3,2}$ = 9.3 Hz, 1H, H-3), 4.27 (ddd~t, J = 5.1 Hz, 1H, H-5), 4.38 (dd, $J_{2,1}$ = 5.1 Hz, $J_{2,3}$ = 9.3 Hz, 1H, H-2), 5.42 (d, $J_{1,2}$ = 5.1 Hz, 1H, H-1); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 13.3 (((CH$_3$)$_2$<u>C</u>H)$_3$Si), 14.6 (<u>C</u>H$_3$CH$_2$S), 18.20 (((<u>C</u>H$_3$)$_2$CH)$_3$Si), 18.23 (2 × ((<u>C</u>H$_3$)$_2$CH)$_3$Si), 18.30 (((<u>C</u>H$_3$)$_2$CH)$_3$Si), 23.4 (CH$_3$<u>C</u>H$_2$S), 63.2 (C-6), 69.5 (C-5), 70.4 (C-2), 72.2 (C-4), 72.7 (C-3), 85.9 (C-1).

Ethyl 6-*O*-acetyl-2,3-bis-*O*-triisopropylsilyl-1-thio-α-D-galactopyranoside (5)

R_f = 0.56 (light petroleum–EtOAc 8:2); $[\alpha]_D^{21}$ +136.3 (c 1.5 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{28}H_{58}O_6SSi_2$+Na^+: 601.3385 $[M+Na]^+$; found: 601.3376; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.02–1.25 (m, 42H, 2 × ((CH$_3$)$_2$CH)$_3$Si), 1.29 (t, J = 7.4 Hz, 3H, C<u>H</u>$_3$CH$_2$S), 2.07 (s, 3H, CH$_3$CO), 2.46–2.54 (m, 2H, CH$_3$C<u>H</u>$_{2a}$S, HO-4), 2.57 (dq, J = 7.4 Hz, J = 12.8 Hz, 1H, CH$_3$C<u>H</u>$_{2b}$S), 3.88–3.91 (m, 1H, H-4), 4.12 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,2}$ = 9.2 Hz, 1H, H-3), 4.31 (dd, $J_{6a,5}$ = 8.0 Hz, $J_{6a,6b}$ = 11.5 Hz, 1H, H-6a), 4.37 (dd, $J_{2,1}$ = 5.1 Hz, $J_{2,3}$ = 9.2 Hz, 1H, H-2), 4.39 (dd, $J_{6b,5}$ = 4.0 Hz, $J_{6b,6a}$ = 11.5 Hz, 1H, H-6b), 4.40–4.44 (m, 1H, H-5), 5.39 (d, $J_{1,2}$ = 5.1 Hz, 1H, H-1); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 13.2, 13.3 (((CH$_3$)$_2$<u>C</u>H)$_3$Si), 14.7 (<u>C</u>H$_3$CH$_2$S), 18.18, 18.22, 18.23, 18.29 (((<u>C</u>H$_3$)$_2$CH)$_3$Si), 20.8 (<u>C</u>H$_3$CO), 23.5 (CH$_3$<u>C</u>H$_2$S), 63.7 (C-6), 68.2 (C-5), 70.5 (C-2), 70.7 (C-4), 72.8 (C-3), 85.8 (C-1), 170.7 (CO).

Ethyl 6-*O*-acetyl-2-*O*-triisopropylsilyl-1-thio-α-D-galactopyranoside (6)

R_f = 0.09 (light petroleum–EtOAc 8:2); $[\alpha]_D^{23}$ +156.0 (*c* 1.32 in $CHCl_3$); HRMS (ESI): m/z calcd for $C_{19}H_{38}O_6SSi$ +Na^+: 445.2051 $[M+Na]^+$; found: 445.2043; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01–1.19 (m, 21H, ((CH$_3$)$_2$CH)$_3$Si), 1.29 (t, J = 7.4 Hz, 3H, C<u>H</u>$_3$CH$_2$S), 2.08 (s, 3H, CH$_3$CO), 2.44 (br.d, J = 3.7 Hz, 1H, HO-3), 2.43–2.66 (m, 2H, CH$_3$C<u>H</u>$_2$S), 2.56 (br.s, 1H, HO-4), 3.80 (m~dt, J = 2.8 Hz, J = 10.3 Hz, 1H, H-3), 4.01 (d, $J_{4,3}$ = 3.5 Hz, 1H, H-4), 4.21–4.47 (m, 4H, H-6a, H-2, H-6b, H-5), 5.41 (d, $J_{1,2}$ = 5.4 Hz, 1H, H-1); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.5 (((CH$_3$)$_2$<u>C</u>H)$_3$Si), 14.7 (<u>C</u>H$_3$CH$_2$S), 17.97, 18.02 (((<u>C</u>H$_3$)$_2$CH)$_3$Si), 20.8 (<u>C</u>H$_3$CO), 23.5 (CH$_3$<u>C</u>H$_2$S), 63.4 (C-6), 68.0 (C-5), 69.1 (C-4), 70.3 (C-2), 71.5 (C-3), 85.4 (C-1), 170.8 (CO).

Ethyl 4-*O*-acetyl-2,3-bis-*O*-triisopropylsilyl-1-thio-α-D-galactopyranoside (7)

R_f = 0.38 (light petroleum–EtOAc 8:2); $[\alpha]_D^{23}$ +131.0 (c 0.79 in $CHCl_3$); HRMS (ESI): m/z calcd for $C_{28}H_{58}O_6SSi_2$+Na^+: 601.3385 $[M+Na]^+$; found: 601.3381; ^{1}H NMR (300

MHz, $CDCl_3$): δ = 1.00–1.19 (m, 42H, 2 × $((CH_3)_2CH)_3Si$), 1.28 (t, *J* = 7.4 Hz, 3H, $C\underline{H}_3CH_2S$), 2.15 (s, 3H, CH_3CO), 2.40–2.64 (m, 2H, $CH_3C\underline{H}_2S$), 2.70 (br.s, 1H, HO-6), 3.44 (dd, $J_{6a,5}$ = 8.0 Hz, $J_{6a,6b}$ = 11.5 Hz, 1H, H-6a), 3.52–3.68 (br.m, 1H, H-6b), 4.27 (dd, $J_{3,4}$ = 3.0 Hz, $J_{3,2}$ = 9.4 Hz, 1H, H-3), 4.32–4.40 (m, 1H, H-5), 4.47 (dd, $J_{2,1}$ = 4.9 Hz, $J_{2,3}$ = 9.4 Hz, 1H, H-2), 5.22 (dd, $J_{4,5}$ = 1.2 Hz, $J_{4,3}$ = 3.0 Hz, 1H, H-4), 5.37 (d, $J_{1,2}$ = 4.9 Hz, 1H, H-1); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.25, 13.27 ($((CH_3)_2\underline{C}H)_3Si$), 14.7 ($\underline{C}H_3CH_2S$), 18.17 ($((\underline{C}H_3)_2CH)_3Si$), 18.26 (3 × $((\underline{C}H_3)_2CH)_3Si$), 20.9 ($\underline{C}H_3CO$), 23.7 ($CH_3\underline{C}H_2S$), 60.4 (C-6), 69.8 (C-5), 70.8, 70.9 (C-2, C-3), 73.1 (C-4), 86.1 (C-1), 172.4 (CO).

Ethyl 2,3-bis-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-galactopyranoside (8)

R_f = 0.19 (light petroleum–EtOAc 8:2); $[\alpha]_D^{23}$ +117.3 (c 1.4 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{40}H_{52}O_5SSi_2+Na^+$: 723.2966 $[M+Na]^+$; found: 723.2974; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 3H, $C\underline{H}_3CH_2S$), 1.20 (s, 9H, $(CH_3)_3CSi$), 1.21 (s, 9H, $(CH_3)_3CSi$), 1.93 (br.s, *J* = 6.3 Hz, 1H, HO-6), 2.01 (dq, *J* = 7.4 Hz, *J* = 12.6 Hz, 1H, $CH_3C\underline{H}_2S$), 2.10 (dq, *J* = 7.4 Hz, *J* = 12.6 Hz, 1H, $CH_3C\underline{H}_2S$), 2.35 (br.s, 1H, HO-4), 2.94 (dd, $J_{4,5}$ = 1.4 Hz, $J_{4,3}$ = 3.2 Hz, 1H, H-4), 3.34 (br.d, $J_{app.}$ = 11.1 Hz, 1H, H-6a), 3.52 (dd, $J_{6b,5}$ = 5.8 Hz, $J_{6b,6a}$ = 11.9 Hz, 1H, H-6b), 3.77 (ddd, $J_{5,4}$ = 1.4 Hz, $J_{5,6a}$ = 4.1 Hz, $J_{5,6b}$ = 5.8 Hz, 1H, H-5), 4.36 (dd, $J_{3,4}$ = 3.2 Hz, $J_{3,2}$ = 9.5 Hz, 1H, H-3), 4.44 (d, $J_{1,2}$ = 5.2 Hz, 1H, H-1), 4.71 (dd, $J_{2,1}$ = 5.2 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H-2), 7.33–7.54 (m, 12H, 4 × PhSi (H-3, H-4, H-5)), 7.77–7.84 (m, 2H, PhSi (H-2, H-6)), 7.84–7.99 (m, 6H, 3 × PhSi (H-2, H-6)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 ($\underline{C}H_3CH_2S$), 19.16, 19.25 ($(CH_3)_3\underline{C}Si$), 23.7 ($CH_3\underline{C}H_2S$), 27.3, 27.5 ($(\underline{C}H_3)_3CSi$), 63.0 (C-6), 69.1 (C-5), 70.6, 70.7 (C-2, C-4), 73.8 (C-3), 85.6 (C-1), 127.6, 127.7, 127.9, 128.2 (PhSi (C-3, C-5)), 129.7, 130.0, 130.1, 130.4 (PhSi (C-4)), 132.1, 133.0, 134.6, 134.7 (PhSi (C-1)), 135.5, 136.0, 136.1, 136.3 (PhSi (C-2, C-6)).

Ethyl 6-*O*-acetyl-2,3-bis-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-galactopyranoside (9)

R_f = 0.42 (light petroleum–EtOAc 8:2); $[\alpha]_D^{22}$ +120.5 (*c* 1.6 in $CHCl_3$); HRMS (ESI): m/z calcd for $C_{42}H_{54}O_6SSi_2+Na^+$: 765.3072 $[M+Na]^+$; found: 765.3083; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.4 Hz, 3H, $C\underline{H}_3CH_2S$), 1.197 (s, 9H, $(CH_3)_3CSi$), 1.203 (s, 9H, $(CH_3)_3CSi$), 1.86 (s, 3H, CH_3CO), 2.06 (q, *J* = 7.4 Hz, 2H, $CH_3C\underline{H}_2S$), 2.17 (br.d, *J* = 1.4 Hz, 1H, HO-4), 2.91 (br.s, 1H, H-4), 3.78–3.99 (m, 3H, H-6a, H-6b, H-5), 4.36 (dd, $J_{3,4}$ = 3.2 Hz, $J_{3,2}$ = 9.5 Hz, 1H, H-3), 4.40 (d, $J_{1,2}$ = 5.3 Hz, 1H, H-1), 4.71 (dd, $J_{2,1}$ = 5.3 Hz, $J_{2,3}$ = 9.5 Hz,

1H, H-2), 7.32–7.55 (m, 12H, 4 × PhSi (H-3, H-4, H-5)), 7.78–7.85 (m, 2H, PhSi (H-2, H-6)), 7.85–7.98 (m, 6H, 3 × PhSi (H-2, H-6)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6 ($\underline{C}H_3CH_2S$), 19.16, 19.24 (($CH_3)_3\underline{C}Si$), 20.7 ($\underline{C}H_3CO$), 23.8 ($CH_3\underline{C}H_2S$), 27.3, 27.5 (($\underline{C}H_3)_3CSi$), 62.9 (C-6), 67.3 (C-5), 68.8 (C-4), 70.7 (C-2), 73.8 (C-3), 85.7 (C-1), 127.6, 127.7, 127.9, 128.2 (PhSi (C-3, C-5)), 129.7, 129.9, 130.1, 130.3 (PhSi (C-4)), 132.1, 132.9, 134.6, 134.8 (PhSi (C-1)), 135.5, 136.0, 136.1, 136.3 (PhSi (C-2, C-6)), 170.3 (CO).

Ethyl 4-*O*-acetyl-2,3-bis-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-galactopyranoside (**10**)

R_f = 0.28 (light petroleum–EtOAc 8:2); $[\alpha]_D^{23}$ +110.5 (c 1.6 in $CHCl_3$); HRMS (ESI): m/z calcd for $C_{42}H_{54}O_6SSi_2+K^+$: 781.2811 $[M+K]^+$; found: 781.2835; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.4 Hz, 4H, $C\underline{H}_3CH_2S$), 1.18 (s, 9H, $(CH_3)_3CSi$), 1.19 (s, 9H, $(CH_3)_3CSi$), 2.06 (s, 3H, CH_3CO), 1.98–2.17 (m, 2H, $CH_3C\underline{H}_2S$), 2.33 (br.s, 1H, HO-6), 2.87–3.04 (br.m, 1H, H-6a), 3.06–3.24 (br.m, 1H, H-6b), 3.82 (ddd~dd, *J* = 6.0 Hz, *J* = 8.4 Hz, 1H, H-5), 4.22 (br.s, 1H, H-4), 4.37 (d, $J_{1,2}$ = 5.0 Hz, 1H, H-1), 4.45 (dd, $J_{3,4}$ = 2.9 Hz, $J_{3,2}$ = 9.8 Hz, 1H, H-3), 4.76 (dd, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 9.8 Hz, 1H, H-2), 7.33–7.53 (m, 12H, 4 × PhSi (H-3, H-4, H-5)), 7.67–7.74 (m, 2H, PhSi (H-2, H-6)), 7.83–7.95 (m, 4H, 2 × PhSi (H-2, H-6)), 7.95–8.04 (m, 2H, PhSi (H-2, H-6)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 ($\underline{C}H_3CH_2S$), 19.1, 19.2 (($CH_3)_3\underline{C}Si$), 20.8 ($\underline{C}H_3CO$), 23.9 ($CH_3\underline{C}H_2S$), 27.2, 27.4 (($\underline{C}H_3)_3CSi$), 59.8 (C-6), 69.0 (C-5), 71.0 (C-2), 71.7 (C-3), 72.1 (C-4), 86.0 (C-1), 127.6, 127.7, 127.8, 128.0 (PhSi (C-3, C-5)), 129.7, 129.9, 130.1, 130.2 (PhSi (C-4)), 132.8, 132.9, 134.0, 134.6 (PhSi (C-1)), 135.9, 136.0, 136.27, 136.33 (PhSi (C-2, C-6)), 171.9 (CO).

Ethyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-thio-β-D-galactopyranoside (13)

R_f = 0.33 (light petroleum–EtOAc 1:1); $[\alpha]_D^{23}$ +7.9 (*c* 1.1 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{24}H_{30}O_6S+Na^+$: 469.1655 $[M+Na]^+$; found: 469.1651; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.4 Hz, 3H, $C\underline{H}_3CH_2S$), 2.20 (s, 3H, CH_3CO), 2.41 (br.s, 1H, HO-6), 2.75 (dq, *J* = 7.3 Hz, *J* = 12.5 Hz, 1H, $CH_3C\underline{H}_2S$), 2.80 (dq, *J* = 7.5 Hz, *J* = 12.7 Hz, 1H, $CH_3C\underline{H}_2S$), 3.50 (dd, $J_{6a,5}$ = 6.4 Hz, $J_{6a,6b}$ = 11.1 Hz, 1H, H-6a), 3.62 (td, $J_{5,4}$ = 0.9 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 6.4 Hz, 1H, H-5), 3.64–3.70 (m, 2H, H-3, H-2), 3.72 (dd, $J_{6b,5}$ = 6.4 Hz, $J_{6b,6a}$ = 11.1 Hz, 1H, H-6b), 4.47–4.53 (m, 1H, H-1), 4.58 (d, *J* = 11.4 Hz, 1H, $PhC\underline{H}_2$), 4.71 (d, *J* = 11.4 Hz, 1H, $PhC\underline{H}_2$), 4.79 (d, *J* = 10.1 Hz, 1H, $PhC\underline{H}_2$), 4.86 (d, *J* = 10.1 Hz, 1H, $PhC\underline{H}_2$), 5.47 (dd~d, *J* = 2.2 Hz, 1H, H-4), 7.28–7.44 (m, 10H, 2 × Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 ($\underline{C}H_3CH_2S$), 20.9

(CH_3CO), 25.1 (CH_3CH_2S), 60.9 (C-6), 67.4 (C-4), 71.9, 75.9 (PhCH_2), 77.1 (C-5), 78.0, 80.7 (C-2, C-3), 85.6 (C-1), 127.80, 127.88, 127.92, 128.28, 128.31, 128.45 (Ph), 137.5, 138.1 (Ph (C-1)), 171.8 (CO).

Ethyl 6-*O*-acetyl-2,3-di-*O*-benzyl-1-thio-β-D-galactopyranoside (14)

R_f = 0.52 (light petroleum–EtOAc 1:1); $[\alpha]_D^{22}$ +2.0 (*c* 2.6 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{24}H_{30}O_6S$ +Na^+: 469.1655 $[M+Na]^+$; found: 469.1649; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.4 Hz, 3H, CH_3CH_2S), 2.08 (s, 3H, CH_3CO), 2.48 (br.s, 1H, HO-4), 2.65–2.88 (m, 2H, CH_3CH_2S), 3.56 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,2}$ = 9.0 Hz, 1H, H-3), 3.59–3.65 (m, 1H, H-5), 3.67 (dd, $J_{2,3}$ = 9.0 Hz, $J_{2,1}$ = 9.6 Hz, 1H, H-2), 3.99 (dd~d, *J* = 2.7 Hz, 1H, H-4), 4.27–4.38 (m, 2H, H-6a, H-6b), 4.43 (d, $J_{1,2}$ = 9.6 Hz, 1H, H-1), 4.73 (s, 2H, 3-*O*-PhCH_2), 4.77 (d, *J* = 10.4 Hz, 1H, 2-*O*-PhCH_2), 4.89 (d, *J* = 10.4 Hz, 1H, 2-*O*-PhCH_2), 7.20–7.50 (m, 10H, 2 × Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 (CH_3CH_2S), 20.8 (CH_3CO), 24.9 (CH_3CH_2S), 63.3 (C-6), 66.7 (C-4), 72.3 (3-*O*-PhCH_2), 75.5 (C-5), 75.8 (2-*O*-PhCH_2), 77.7 (C-2), 82.1 (C-3), 85.1 (C-1), 127.80, 127.83, 128.0, 128.30, 128.32, 128.5 (Ph), 137.6 (3-*O*-PhCH_2 (C-1)), 138.0 (2-*O*-PhCH_2 (C-1)), 170.8 (CO).

Phenyl 6-*O*-acetyl-2,3-di-*O*-benzyl-1-thio-β-D-glucopyranoside (17) [2]

^{1}H NMR spectrum was identical to that described [2].

R_f = 0.70 (light petroleum–EtOAc 4:6); HRMS (ESI): m/z calcd for $C_{28}H_{30}O_6S$+Na^+: 517.1655 $[M+Na]^+$; found: 517.1653.

Phenyl 4-*O*-acetyl-2,3-di-*O*-benzyl-1-thio-β-D-glucopyranoside (18)

R_f = 0.50 (light petroleum–EtOAc 4:6); $[\alpha]_D^{22}$ −20.5 (*c* 1.2 in $CHCl_3$); HRMS (ESI): m/z calcd for $C_{28}H_{30}O_6S$+Na^+: 517.1655 $[M+Na]^+$; found: 517.1657; ^{1}H NMR (300 MHz, Me_2CO-d_6): δ = 1.99 (s, 3H, CH_3CO), 3.49 (dd, $J_{2,3}$ = 8.7 Hz, $J_{2,1}$ = 9.8 Hz, 1H, H-2), 3.51–3.68 (m, 3H, H-6a, H-6b, H-5), 3.83 (dd, $J_{3,2}$ = 8.7 Hz, $J_{3,4}$ = 9.4 Hz, 1H, H-3), 4.70 (d, *J* = 11.4 Hz, 1H, 3-*O*-PhCH_{2a}), 4.76 (d, *J* = 10.6 Hz, 1H, 2-*O*-PhCH_{2a}), 4.82 (d, *J* = 11.4 Hz, 1H, 3-*O*-PhCH_{2b}), 4.87 (d, $J_{1,2}$ = 9.8 Hz, 2H, H-1), 4.88 (d, *J* = 10.6 Hz, 2H, 2-*O*-PhCH_{2b}), 4.94 (dd~t, $J_{app.}$ = 9.5 Hz, 1H, H-4), 7.19–7.48 (m, 13H, Ph), 7.52–7.66 (m, 2H, PhS (H-2, H-6)); ^{13}C NMR (75 MHz, Me_2CO-d_6): δ = 21.0 (CH_3CO), 62.2 (C-6), 71.4 (C-4), 75.7, 75.8 (PhCH_2), 79.7 (C-5),

81.7 (C-2), 84.8 (C-3), 87.7 (C-1), 128.0, 128.3, 128.4, 128.5, 128.9, 129.0, 129.1, 129.8 (Ph), 131.9 (PhS (C-2, C-6)), 135.3 (PhS (C-1)), 139.4, 139.7 (PhCH$_2$ (C-1)), 170.4 (CO).

General procedure for acetylation of thioglycoside 20

To thioglycoside **20** (150 mg, 0.55 mmol) 60–100% (v/v) AcOH (27.5 mL) was added and the reaction mixture (c = 20 mmol/L) was stirred at T °C according to methods ***C***–***I*** (Table 1). Then the reaction mixture was concentrated under reduced pressure and dried *in vacuo*. The products were purified by silica gel column chromatography in gradient of EtOAc in light petroleum (5→60%) to afford acetylated products **21**–**28**. The yields of purified products are shown in Figs. 4, 5 (see also Table 5S in ESI).

Phenyl 6-*O*-acetyl-1-thio-β-D-glucopyranoside (21)

R_f = 0.30 (light petroleum–EtOAc 1:9); $[\alpha]_D^{23}$ −61.7 (c 2.0 in $CHCl_3$); HRMS (ESI): m/z calcd for $C_{14}H_{18}O_6S+Na^+$: 337.0716 $[M+Na]^+$; found: 337.0715; ^{1}H NMR (300 MHz, MeOD): δ = 2.04 (s, 3H, CH_3CO), 3.22 (dd, $J_{2,3}$ = 8.5 Hz, $J_{2,1}$ = 9.7 Hz, 1H, H-2), 3.24–3.33 (m, 1H, H-4), 3.40 (dd~t, $J_{app.}$ = 8.8 Hz, 1H, H-3), 3.50 (ddd, $J_{5,6b}$ = 2.2 Hz, $J_{5,6a}$ = 6.6 Hz, $J_{5,4}$ = 9.8 Hz, 1H, H-5), 4.19 (dd, $J_{6a,5}$ = 6.6 Hz, $J_{6a,6b}$ = 11.9 Hz, 1H, H-6a), 4.40 (dd, $J_{6b,5}$ = 2.2 Hz, $J_{6b,6a}$ = 11.9 Hz, 1H, H-6b), 4.59 (d, $J_{1,2}$ = 9.7 Hz, 1H, H-1), 7.19–7.38 (m, 3H, PhS (H-3, H-4, H-5)), 7.45–7.61 (m, 2H, PhS (H-2, H-6)); ^{13}C NMR (75 MHz, MeOD): δ = 20.8 ($\underline{C}H_3CO$), 64.9 (C-6), 71.4 (C-4), 73.7 (C-2), 79.0 (C-5), 79.4 (C-3), 89.0 (C-1), 128.5 (PhS (C-4)), 129.8 (PhS (C-3, C-5)), 133.0 (PhS (C-2, C-6)), 134.8 (PhS (C-1)), 172.7 (CO).

Phenyl 3,6-di-*O*-acetyl-1-thio-β-D-glucopyranoside (22)

R_f = 0.70 (light petroleum–EtOAc 1:9); $[\alpha]_D^{23}$ −46.9 (c 1.0 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{16}H_{20}O_7S+Na^+$: 379.0822 $[M+Na]^+$; found: 379.0815; ^{1}H NMR (300 MHz, MeOD): δ = 2.05 (s, 3H, CH_3CO), 2.10 (s, 3H, CH_3CO), 3.27–3.36 (m, 1H, H-2), 3.41 (dd~t, $J_{app.}$ = 9.6 Hz, 1H, H-4), 3.59 (ddd, $J_{5,6b}$ = 2.2 Hz, $J_{5,6a}$ = 6.2 Hz, $J_{5,4}$ = 10.0 Hz, 1H, H-5), 4.21 (dd, $J_{6a,5}$ = 6.2 Hz, $J_{6a,6b}$ = 11.9 Hz, 1H, H-6a), 4.40 (dd, J = 2.2 Hz, J = 11.9 Hz, 1H, H-6b), 4.66 (d, J = 9.8 Hz, 1H, H-1), 4.96 (t, J = 9.2 Hz, 1H, H-3), 7.24–7.39 (m, 3H, PhS (H-3, H-4, H-5)), 7.50–7.61 (m, 2H, PhS (H-2, H-6)); ^{13}C NMR (75 MHz, MeOD): δ = 20.8 ($\underline{C}H_3CO$), 21.1 ($\underline{C}H_3CO$), 64.6 (C-6), 69.8 (C-4), 71.9 (C-2), 78.9 (C-5), 80.2 (C-3), 88.7 (C-1), 128.8 (PhS (C-4)), 129.9 (PhS (C-3, C-5)), 133.5 (PhS (C-2, C-6)), 134.2 (PhS (C-1)), 172.60, 172.65 (CO).

Phenyl 4,6-di-*O*-acetyl-1-thio-β-D-glucopyranoside (23)

R_f = 0.50 (light petroleum–EtOAc 1:9); $[\alpha]_D^{22}$ −28.7 (c 1.36 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{16}H_{20}O_7S+Na^+$: 379.0822 $[M+Na]^+$; found: 379.0813; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.09 (s, 3H, CH_3CO), 2.12 (s, 3H, CH_3CO), 2.68–3.02 (br.m, 2H, 2 × HO), 3.41 (dd, $J_{2,3}$ = 8.8 Hz, $J_{2,1}$ = 9.7 Hz, 1H, H-2), 3.67 (ddd, $J_{5,6a}$ = 2.8 Hz, $J_{5,6b}$ = 5.1 Hz, $J_{5,4}$ = 10.0 Hz, 1H, H-5), 3.69 (dd, $J_{3,2}$ = 8.8 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H-3), 4.18 (dd, $J_{6a,5}$ = 2.8 Hz, $J_{6a,6b}$ = 12.2 Hz, 1H, H-6a), 4.24 (dd, $J_{6b,5}$ = 5.1 Hz, $J_{6b,6a}$ = 12.2 Hz, 1H, H-6b), 4.53 (d, $J_{1,2}$ = 9.7 Hz, 1H, H-1), 4.87 (dd~t, $J_{app.}$ = 9.7 Hz, 1H, H-4), 7.28–7.40 (m, 3H, PhS (H-3, H-4, H-5)), 7.51–7.62 (m, 2H, PhS (H-2, H-6)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 20.9 ($\underline{C}H_3CO$), 62.5 (C-6), 70.2 (C-4), 72.3 (C-2), 75.8 (C-5), 76.1 (C-3), 87.6 (C-1), 128.4 (PhS (C-4)), 129.0 (PhS (C-3, C-5)), 131.2 (PhS (C-1)), 133.1 (PhS (C-2, C-6)), 170.6, 170.7 (CO).

Phenyl 3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (24)

R_f = 0.80 (light petroleum–EtOAc 1:9); $[\alpha]_D^{22}$ −20.5 (c 1.97 in $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{18}H_{22}O_8S+Na^+$: 421.0928 $[M+Na]^+$; found: 421.0929; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 3H, 4-*O*-CH_3CO), 2.07 (s, 3H, CH_3CO), 2.09 (s, 3H, CH_3CO), 2.56 (br.s, 1H, HO-2), 3.51 (ddd~td, $J_{2,HO}$ = 1.7 Hz, $J_{app.}$ = 9.6 Hz, 1H, H-2), 3.73 (ddd, $J_{5,6a}$ = 2.7 Hz, $J_{5,6b}$ = 4.9 Hz, $J_{5,4}$ = 10.0 Hz, 1H, H-5), 4.18 (dd, $J_{6a,5}$ = 2.7 Hz, $J_{6a,6b}$ = 12.3 Hz, 1H, H-6a), 4.24 (dd, $J_{6b,5}$ = 4.9 Hz, $J_{6b,6a}$ = 12.3 Hz, 1H, H-6b), 4.57 (d, $J_{1,2}$ = 9.8 Hz, 1H, H-1), 4.98 (dd~t, $J_{app.}$ = 9.7 Hz, 1H, H-4), 5.13 (dd~t, $J_{app.}$ = 9.3 Hz, 1H, H-3), 7.29–7.41 (m, 3H, PhS (H-3, H-4, H-5)), 7.52–7.62 (m, 2H, PhS (H-2, H-6)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6 (4-*O*-$\underline{C}H_3CO$), 20.7, 20.8 (3-*O*-$\underline{C}H_3CO$, 6-*O*-$\underline{C}H_3CO$), 62.2 (C-6), 68.1 (C-4), 70.3 (C-2), 75.8 (C-3), 75.9 (C-5), 88.0 (C-1), 128.7 (PhS (C-4)), 129.1 (PhS (C-3, C-5)), 130.6 (PhS (C-1)), 133.5 (PhS (C-2, C-6)), 169.6 (4-*O*-$CH_3\underline{C}O$), 170.6, 170.7 (3-*O*-$CH_3\underline{C}O$, 6-*O*-$CH_3\underline{C}O$).

Table 1S The yields (%) of products **4**–**7** obtained from compounds **2**, **4** under acetylation conditions according to method ***B***. See also Fig. 1.

Entry	Method	c, mmol/L	Substrate	**4** (%)	**5** (%)	**6** (%)	**7** (%)
1	***B***	48	**2**	19	22	7	3
2	***B***	48	**4**	22	32	9	6

Table 2S The yields (%) of products **3**, **8**–**10** obtained from compound **3** under acetylation conditions according to method ***B***. See also Fig. 1.

Entry	Method	c, mmol/L	Substrate	**3** (%)	**8** (%)	**9** (%)	**10** (%)
1	***B***	10	**3**	0	34	31	5
2	***B***	48	**3**	0	39	35	0
3	***B***	100	**3**	2	45	36	4

Table 3S The yields (%) of products **11**–**14** obtained from compound **11** under acetylation conditions according to method ***B***. See also Fig. 2.

Entry	Method	c, mmol/L	Substrate	**11** (%)	**12** (%)	**13** (%)	**14** (%)
1	***B***	58	**11**	5	36	11	41
2	***B***	68	**11**	0	30	8	43

Table 4S The yields (%) of products **16**–**19** obtained from compounds **15**–**17** under acetylation conditions according to methods ***A***–***C***. See also Fig. 3.

Entry	Method	c, mmol/L	Substrate	**16** (%)	**17** (%)	**18** (%)	**19** (%)
1	***A***	20	**15**	54	27	1	0
2	***B***	20	**15**	43	45	6	0
3	***A***	20	**16**	51	28	2	0
4	***B***	20	**16**	43	30	8	0
5	***C***	20	**16**	35	42	4	3
6	***B***	20	**17**	24	53	4	0

Table 5S The yields (%) of compounds **20**–**28** after acetylation of compound **20** according to methods ***C***–***I***. Concentration of **20** c = 20 mmol/L. See also Figs. 4 and 5.

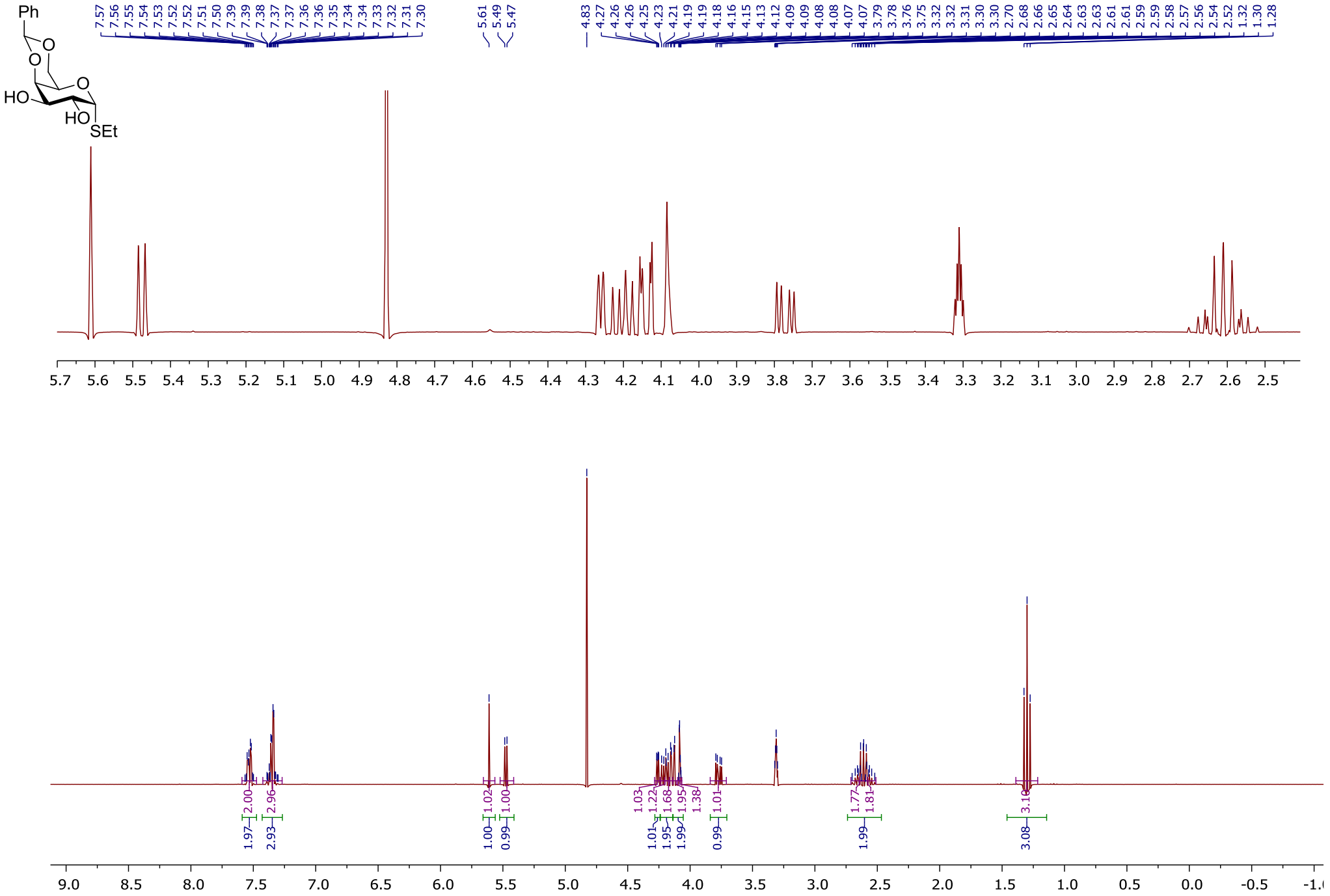
	Method						
Cmpd	***C***	***D***	***E***	***F***	***G***	***H***	***I***
20	34	5	0	20	35	50	19
21	47	34	0	49	36	33	42
22	5	0	0	7	5	2	7
23	0	0	0	0	5	0	3
24	0	0	0	2	0	0	0
25	0	0	17	0	0	0	0
26	5	5	14	8	8	7	10
27	5	21	40	8	0	2	5
28	0	10	29	0	0	0	2

References

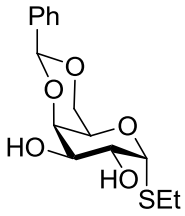
1. L. Käsbeck and H. Kessler, *Liebigs Ann./Recl.*, 1997, 169–173.

2. M. M. Mukherjee, N. Basu, S. Nandi, and R. Ghosh, *Carbohydr. Res.*, 2019, **476**, 36–43.

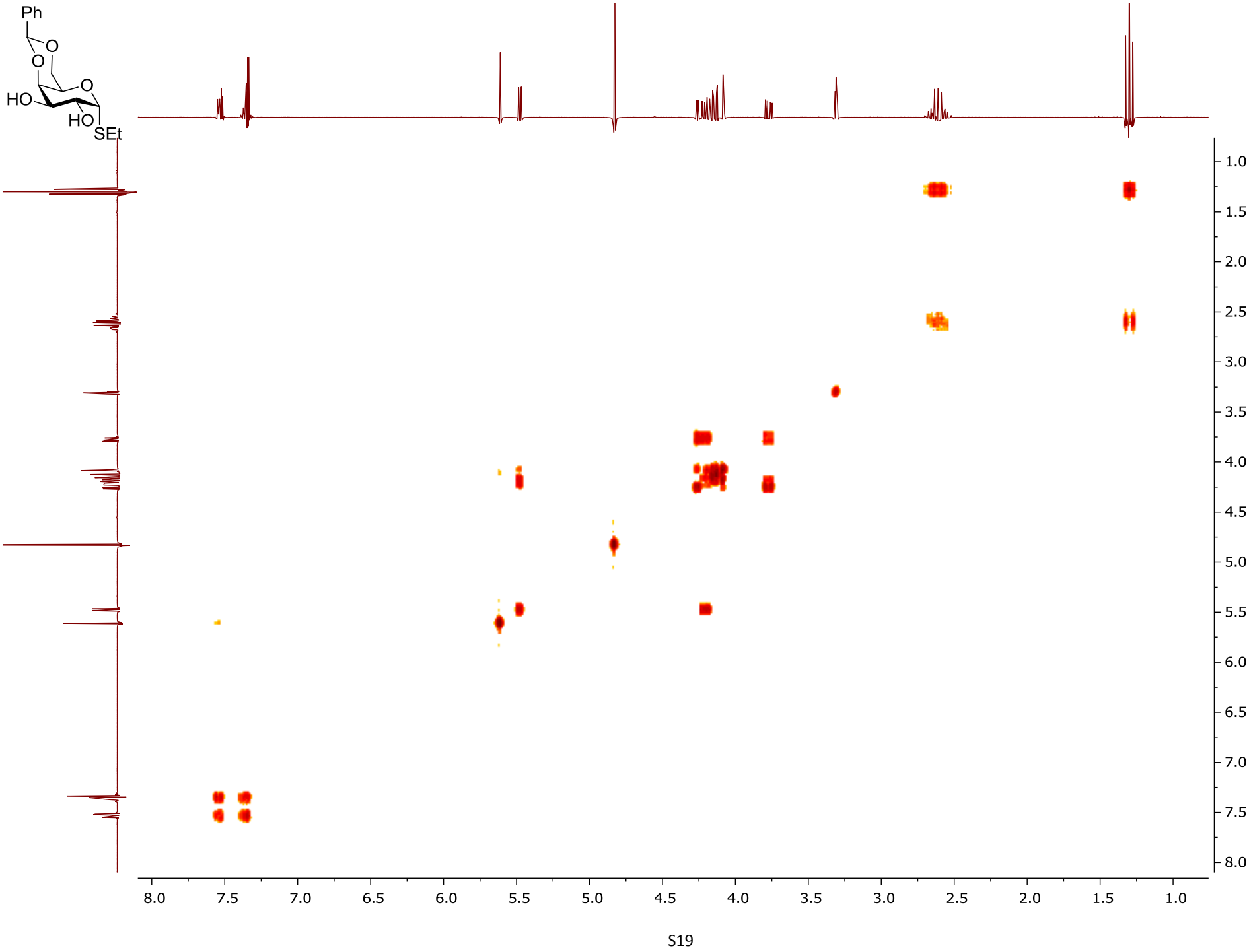
^{1}H NMR (300 MHz) spectrum of compound 1 in CD_3OD



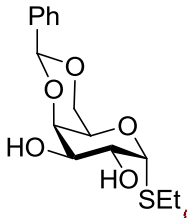
^{13}C NMR (75 MHz) spectrum of compound 1 in CD_3OD

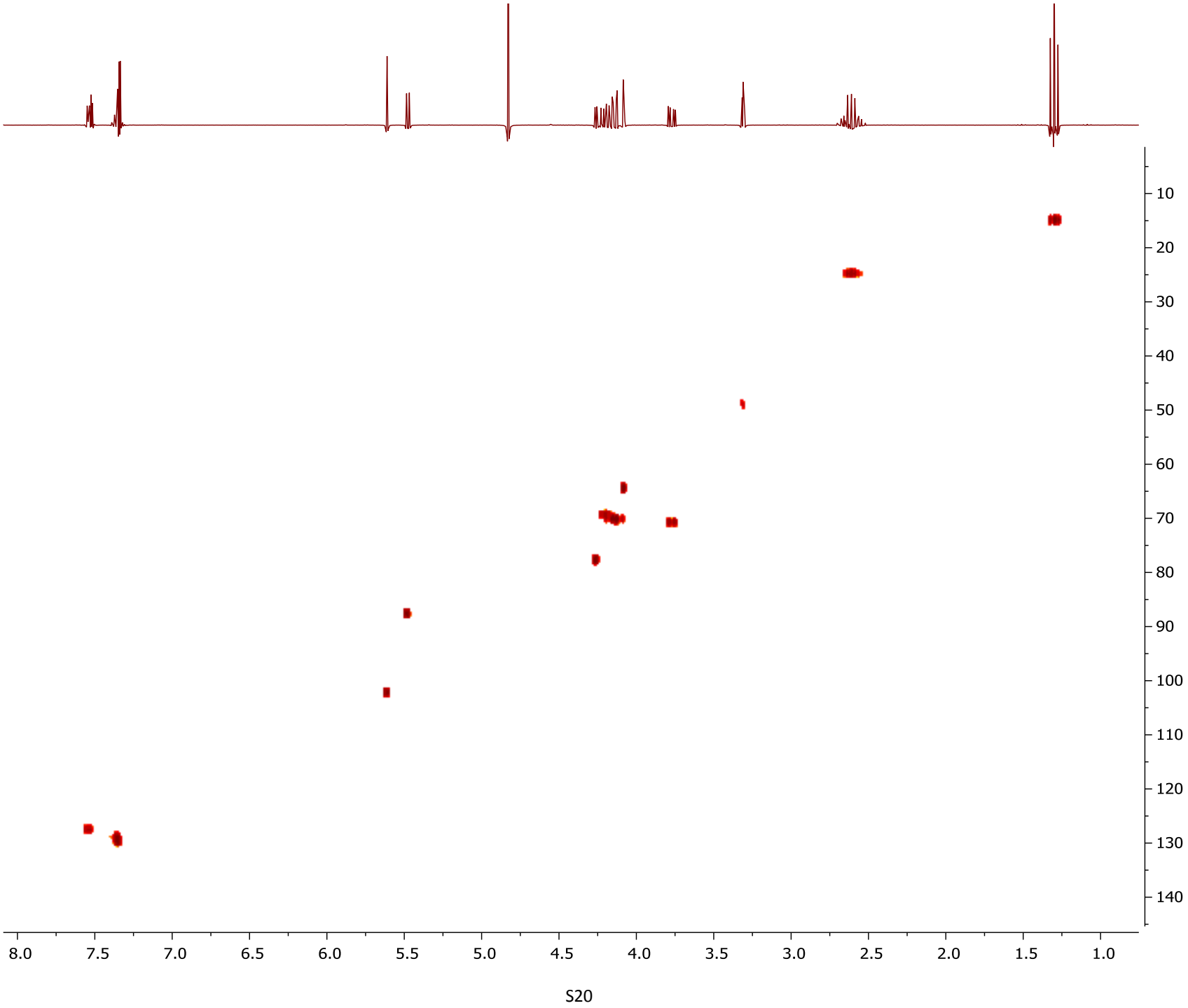


COSY spectrum of compound 1 in CD_3OD (300 MHz)

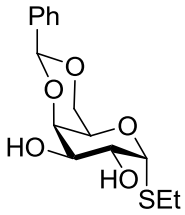


HSQC spectrum of compound 1 in CD_3OD (300 MHz)

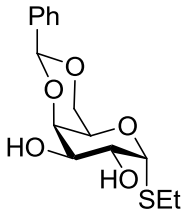




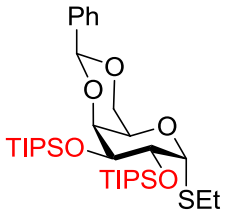
HMBC spectrum of compound 1 in CD_3OD (300 MHz)



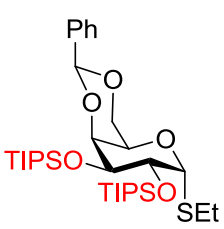
DEPT spectrum of compound 1 in CD_3OD (75 MHz)



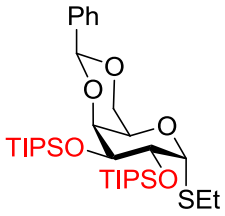
^{1}H NMR (600 MHz) spectrum of compound 2 in $CDCl_3$

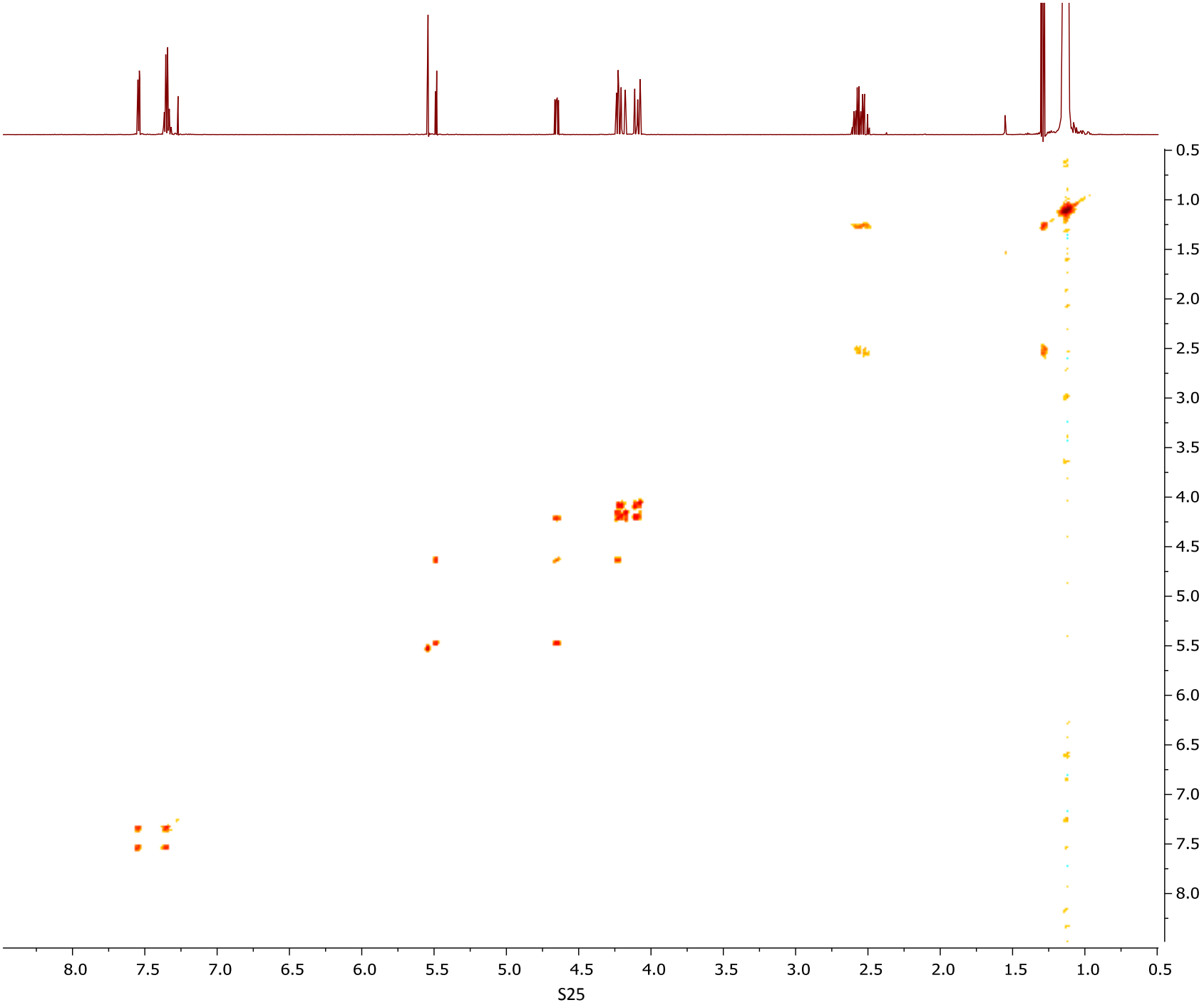


^{13}C NMR (151 MHz) spectrum of compound 2 in $CDCl_3$

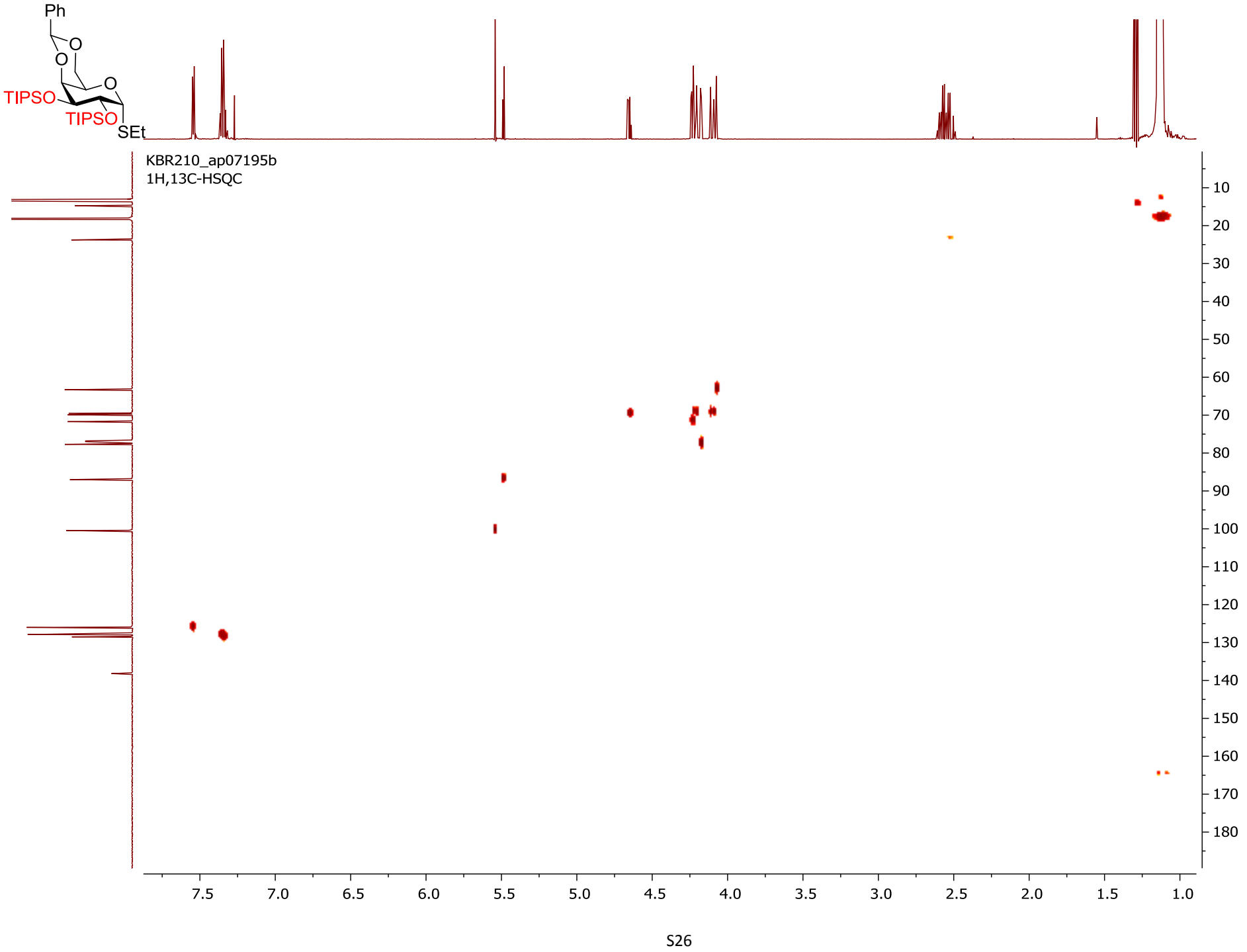


COSY spectrum of compound 2 in $CDCl_3$ (600 MHz)

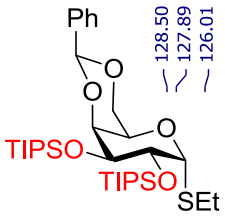




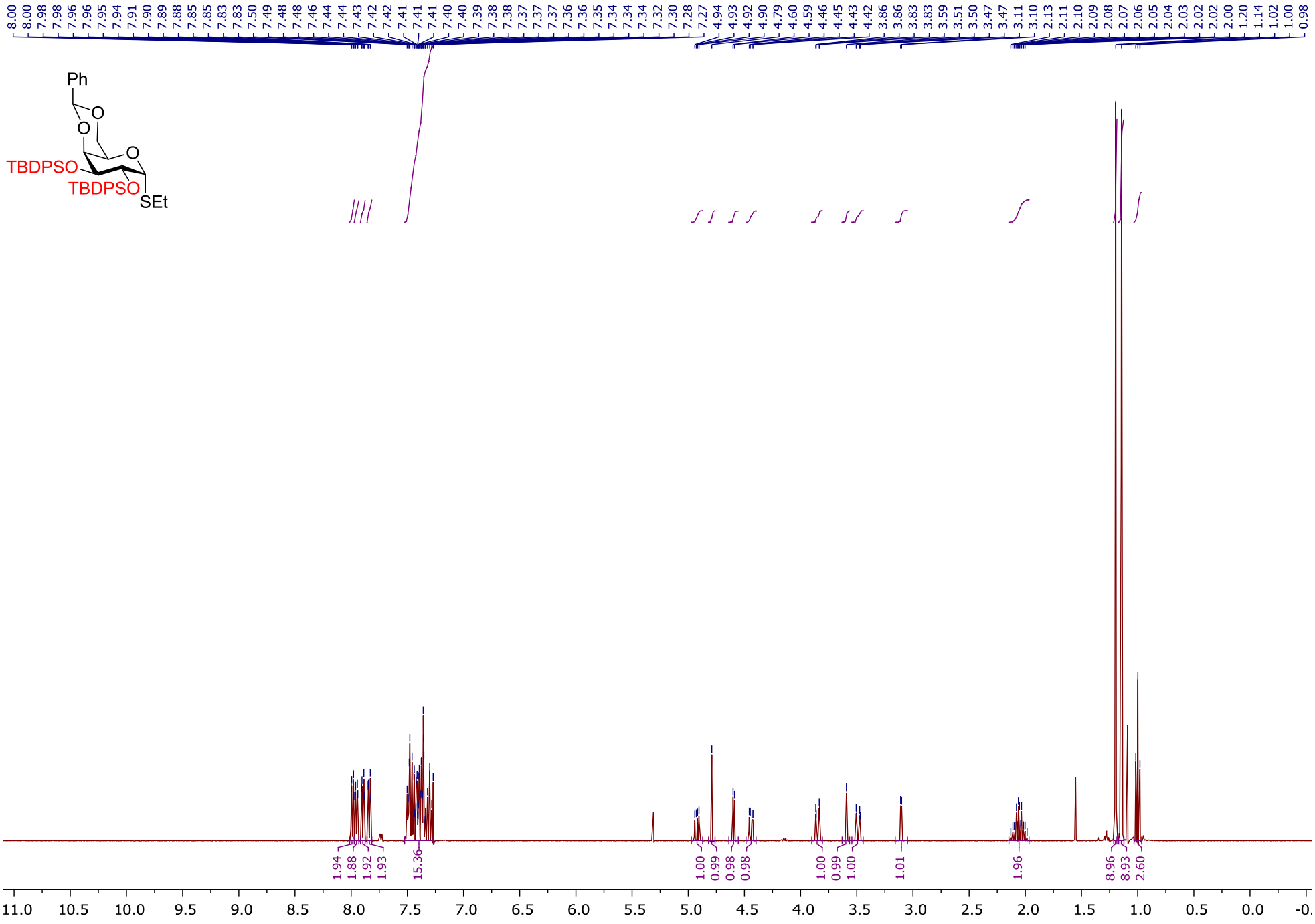
HSQC spectrum of compound 2 in $CDCl_3$ (600 MHz)



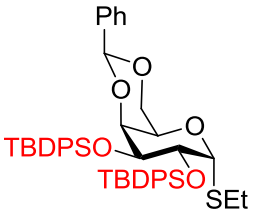
DEPT spectrum of compound 2 in $CDCl_3$ (151 MHz)



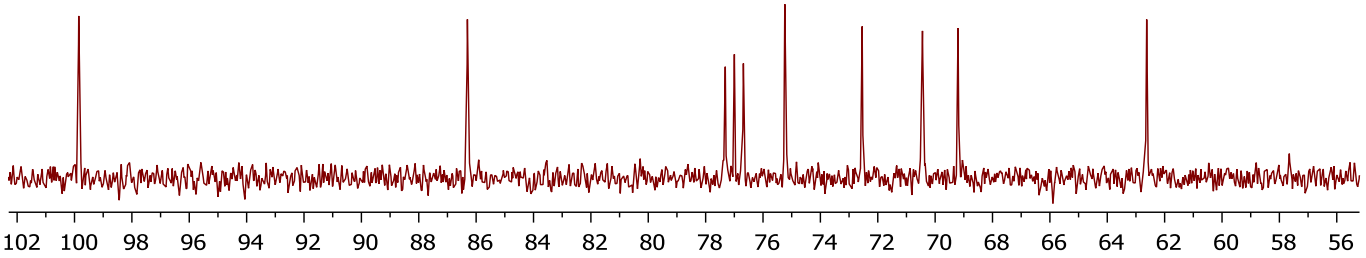
^{1}H NMR (400 MHz) spectrum of compound 3 in $CDCl_3$

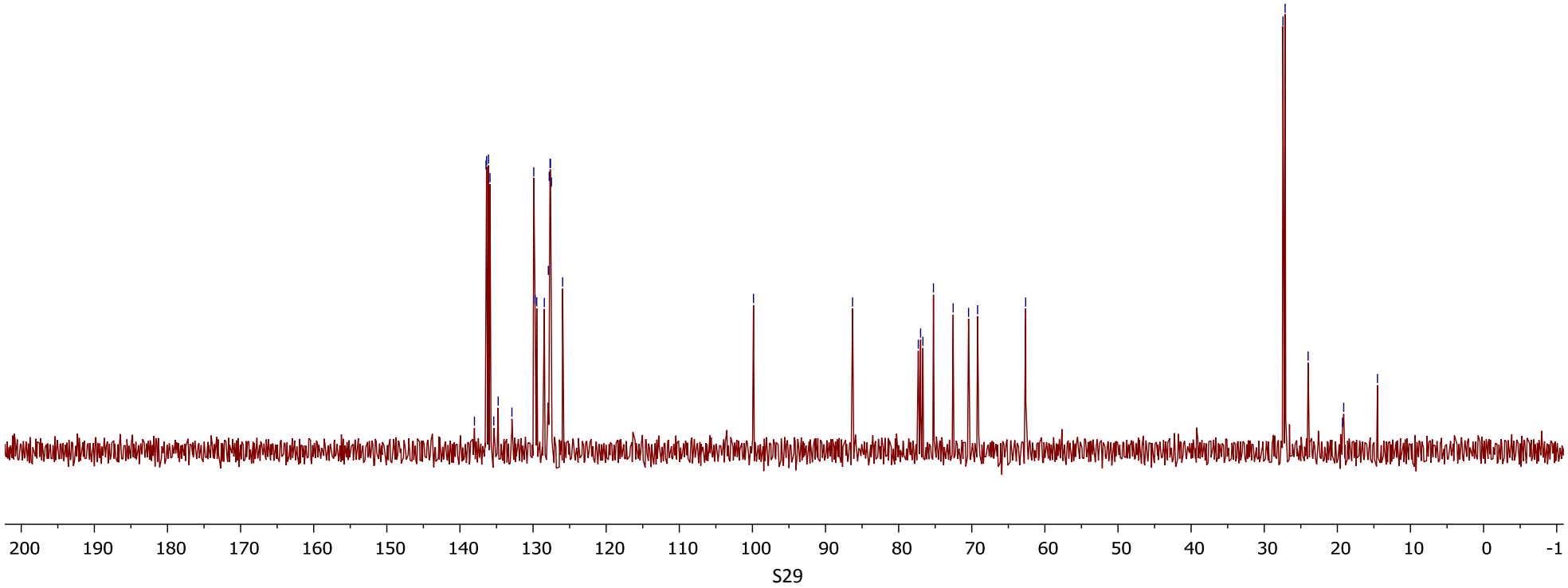


^{13}C NMR (101 MHz) spectrum of compound 3 in $CDCl_3$

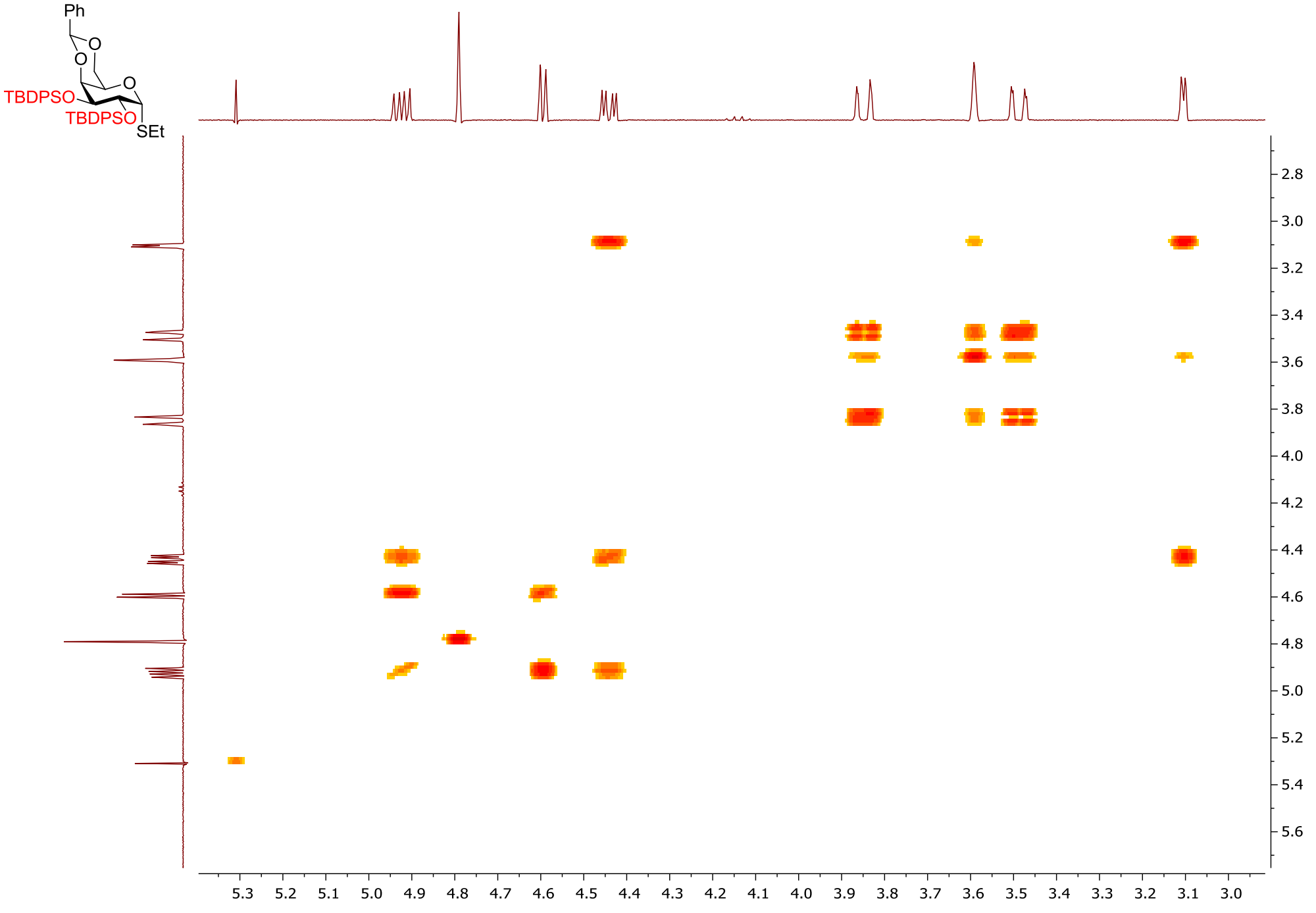


138.02
136.44
136.36
136.10
135.89
135.37
134.77
132.89
129.91
129.73
129.49
128.46
127.91
127.79
127.68
127.62
127.48
125.96
99.85
86.30
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
75.24
72.54
70.44
69.20
62.63
27.44
27.14
24.00
19.30
19.13
14.52

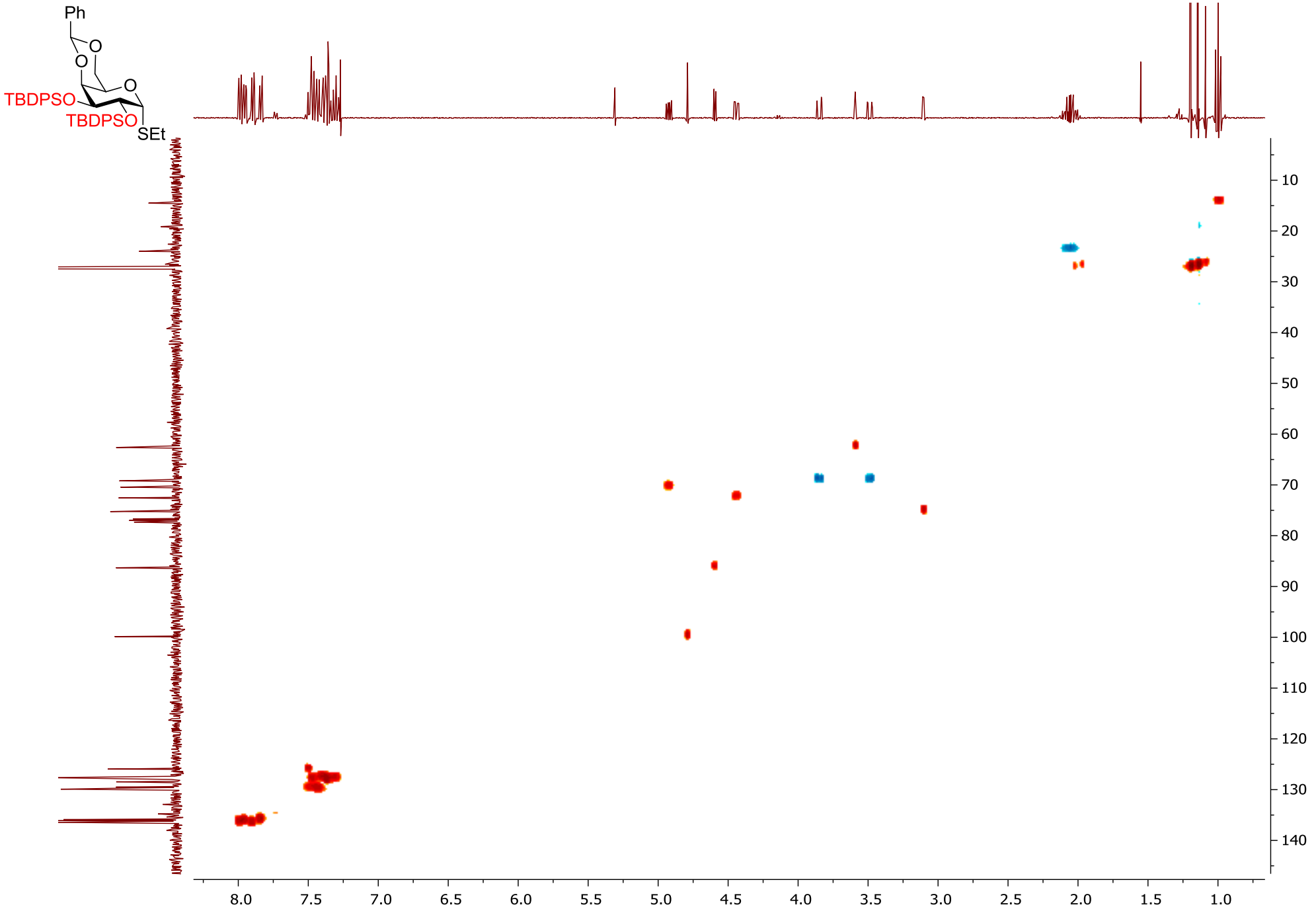




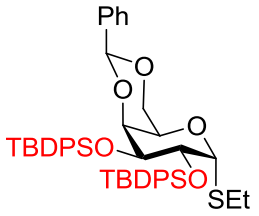
COSY spectrum of compound 3 in $CDCl_3$ (400 MHz)

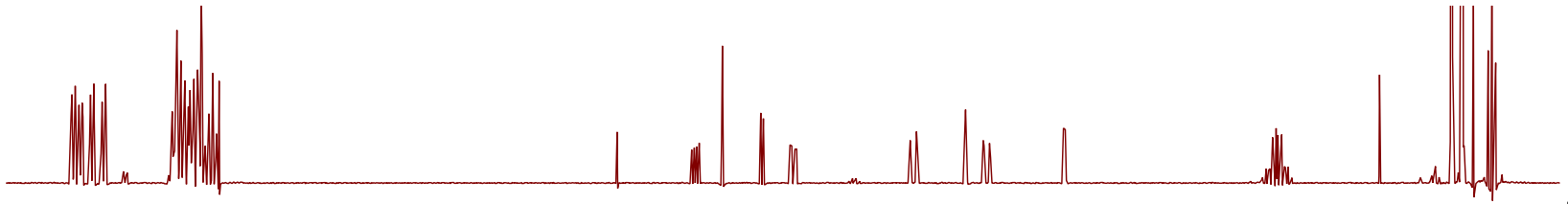


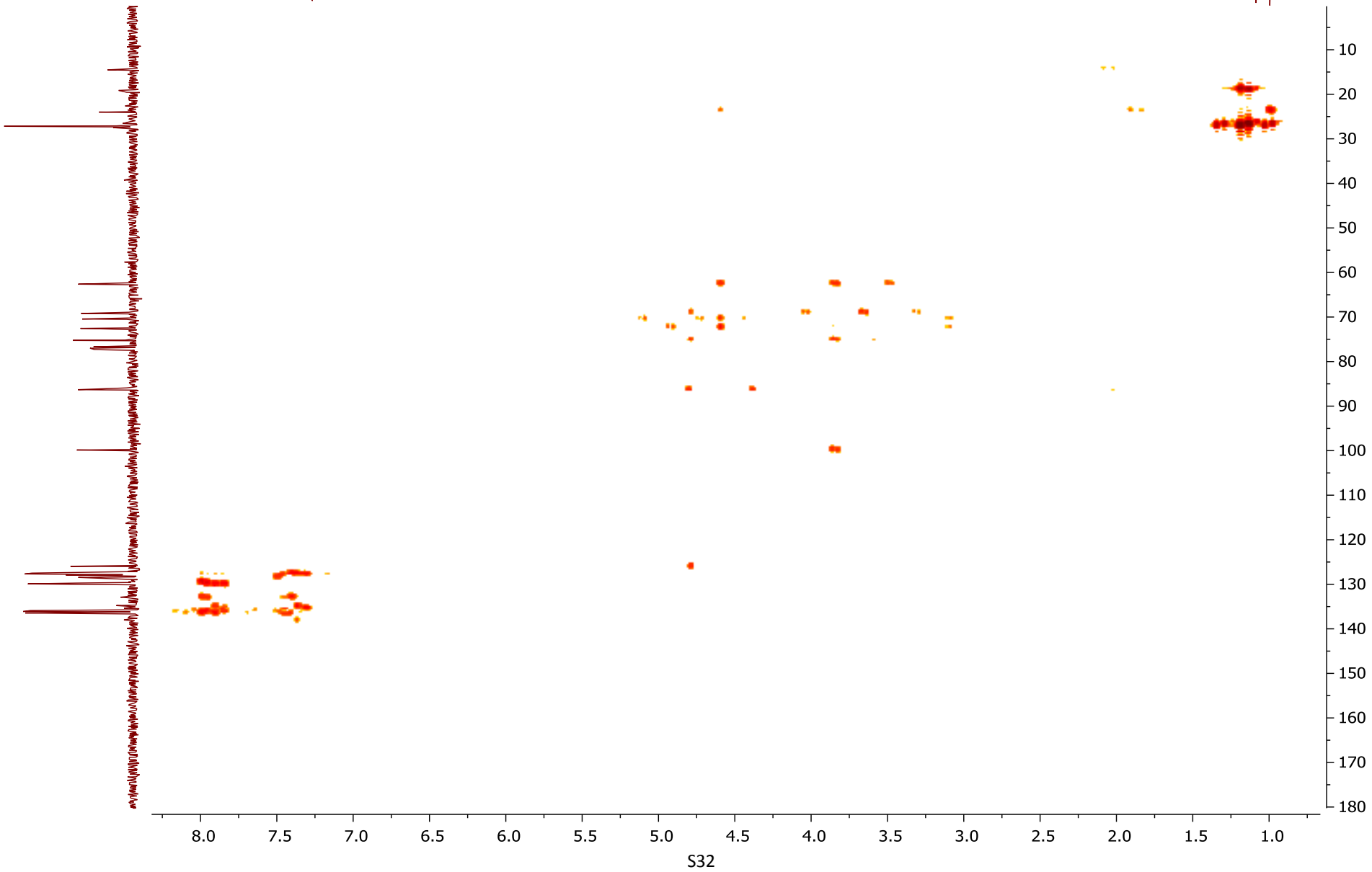
HSQC spectrum of compound 3 in $CDCl_3$ (400 MHz)



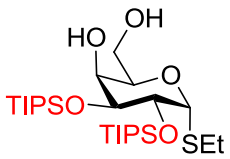
HMBC spectrum of compound 3 in $CDCl_3$ (400 MHz)



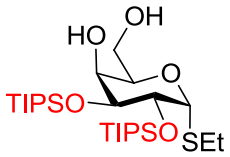




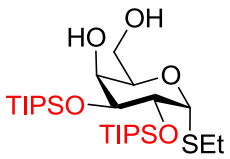
^{1}H NMR (300 MHz) spectrum of compound 4 in $CDCl_3$



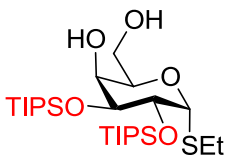
^{13}C NMR (75 MHz) spectrum of compound 4 in $CDCl_3$



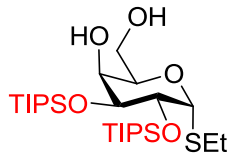
COSY spectrum of compound 4 in $CDCl_3$ (300 MHz)

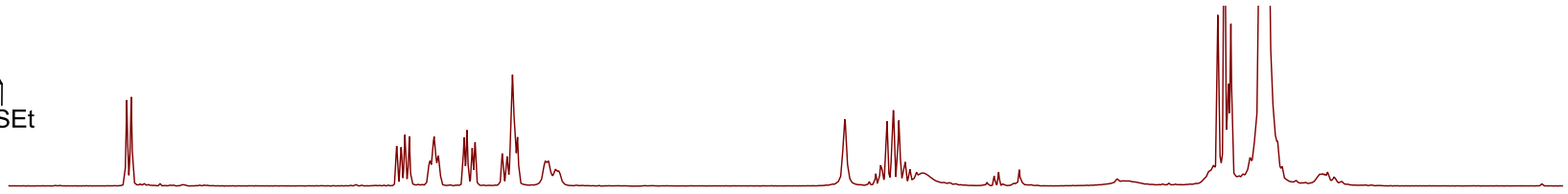


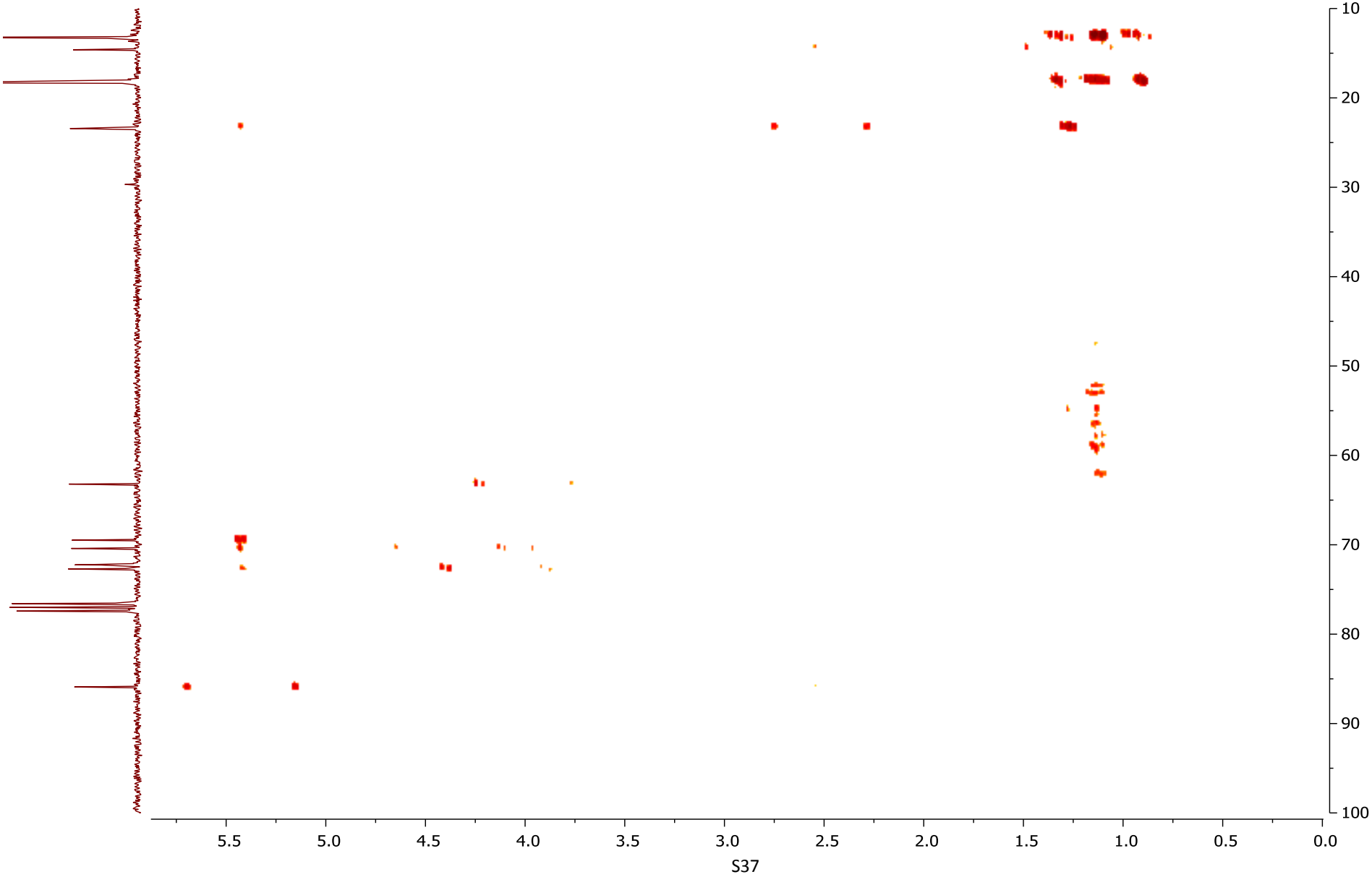
HSQC spectrum of compound 4 in $CDCl_3$ (300 MHz)



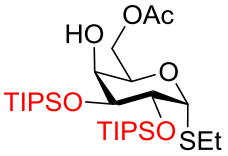
HMBC spectrum of compound 4 in $CDCl_3$ (300 MHz)



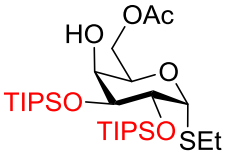




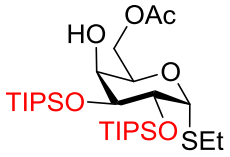
^{1}H NMR (300 MHz) spectrum of compound 5 in $CDCl_3$



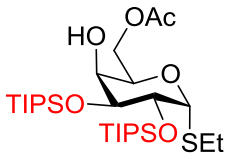
^{13}C NMR (151 MHz) spectrum of compound 5 in $CDCl_3$



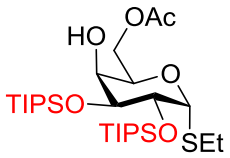
COSY spectrum of compound 5 in $CDCl_3$ (600 MHz)



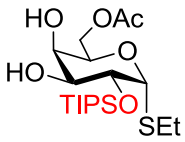
HSQC spectrum of compound 5 in $CDCl_3$ (600 MHz)



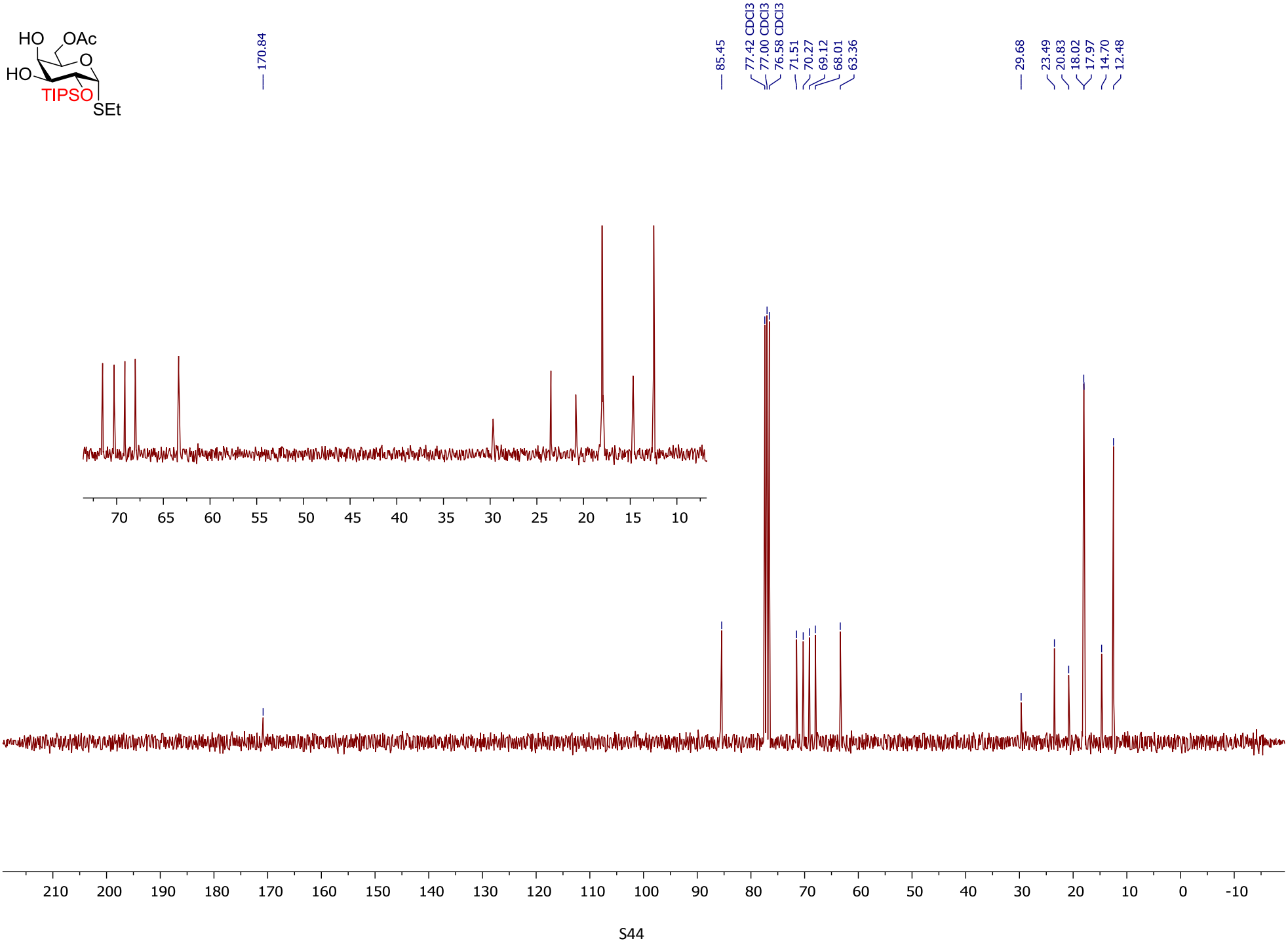
DEPT spectrum of compound 5 in $CDCl_3$ (151 MHz)



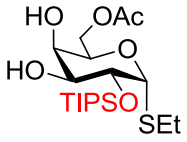
^{1}H NMR (300 MHz) spectrum of compound 6 in $CDCl_3$



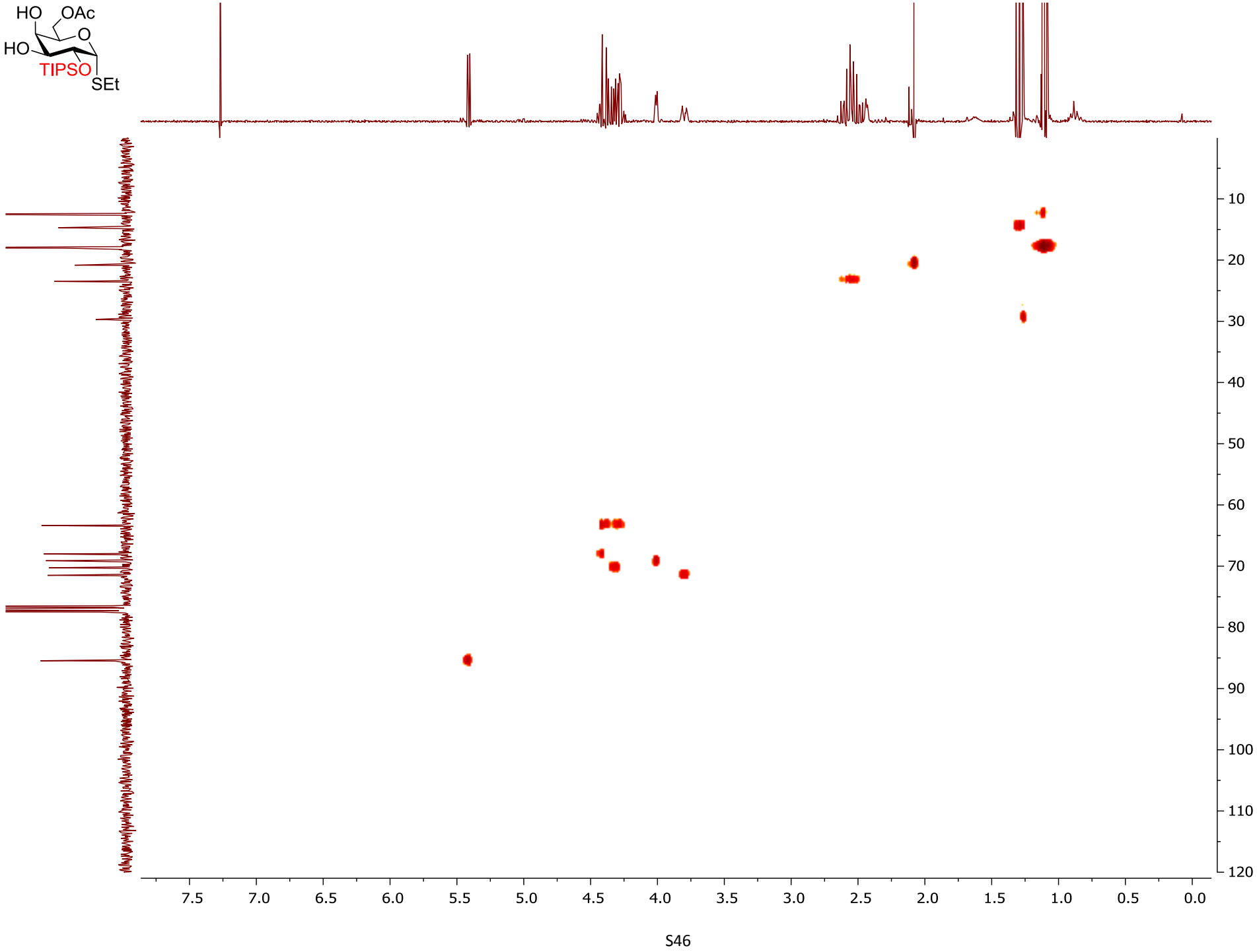
^{13}C NMR (75 MHz) spectrum of compound 6 in $CDCl_3$



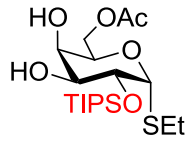
COSY spectrum of compound 6 in $CDCl_3$ (300 MHz)



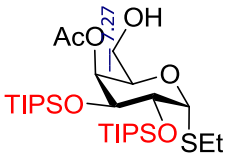
HSQC spectrum of compound 6 in $CDCl_3$ (300 MHz)



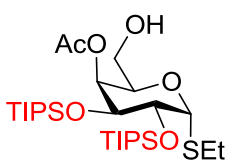
DEPT spectrum of compound 6 in $CDCl_3$ (75 MHz)



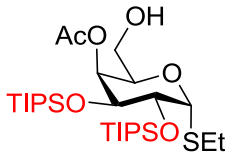
^{1}H NMR (300 MHz) spectrum of compound 7 in $CDCl_3$

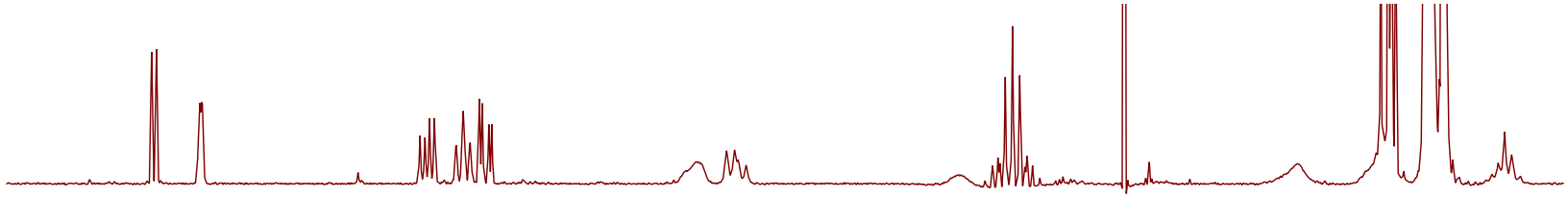


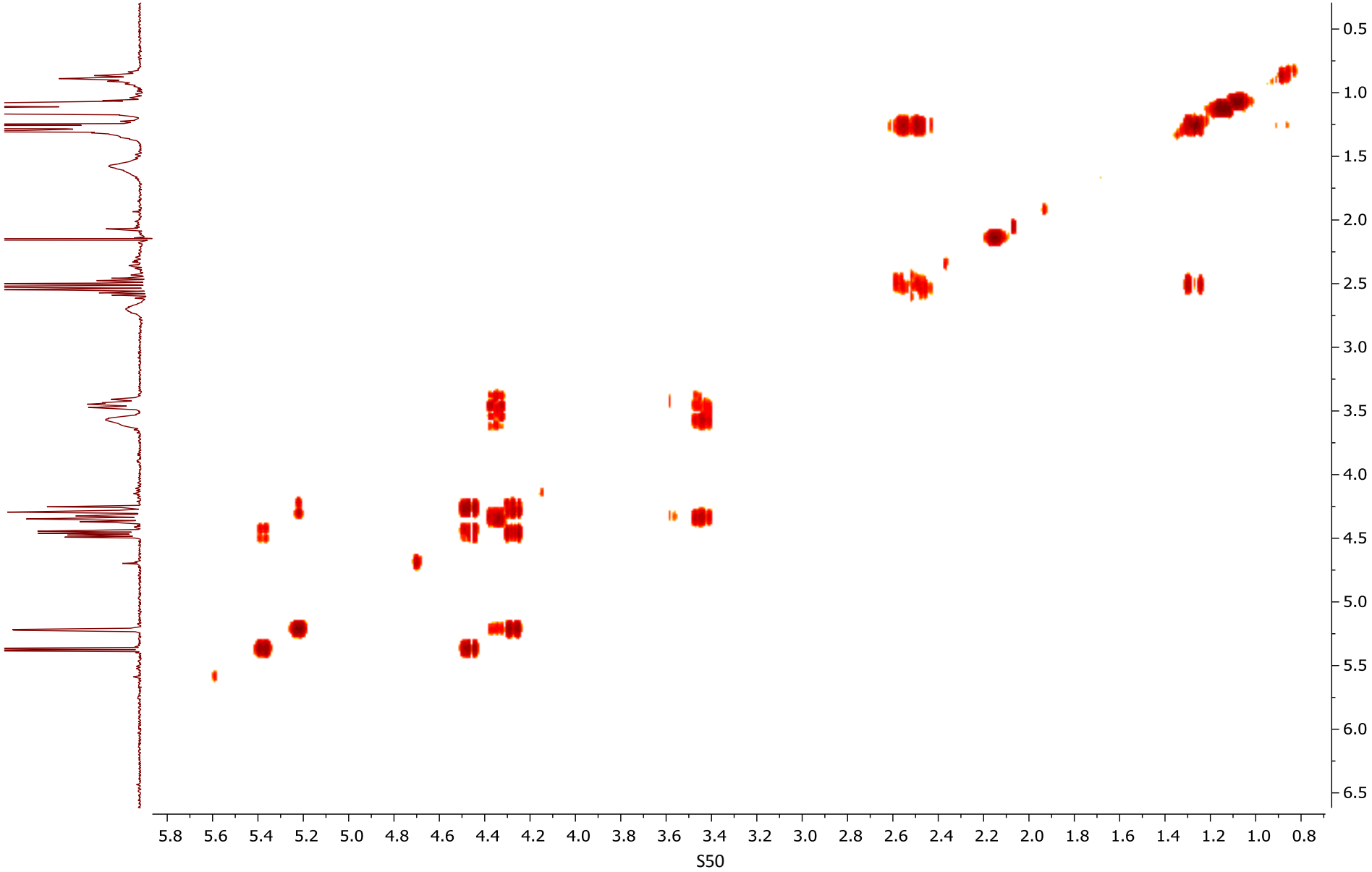
^{13}C NMR (75 MHz) spectrum of compound 7 in $CDCl_3$



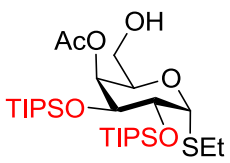
COSY spectrum of compound 7 in $CDCl_3$ (300 MHz)

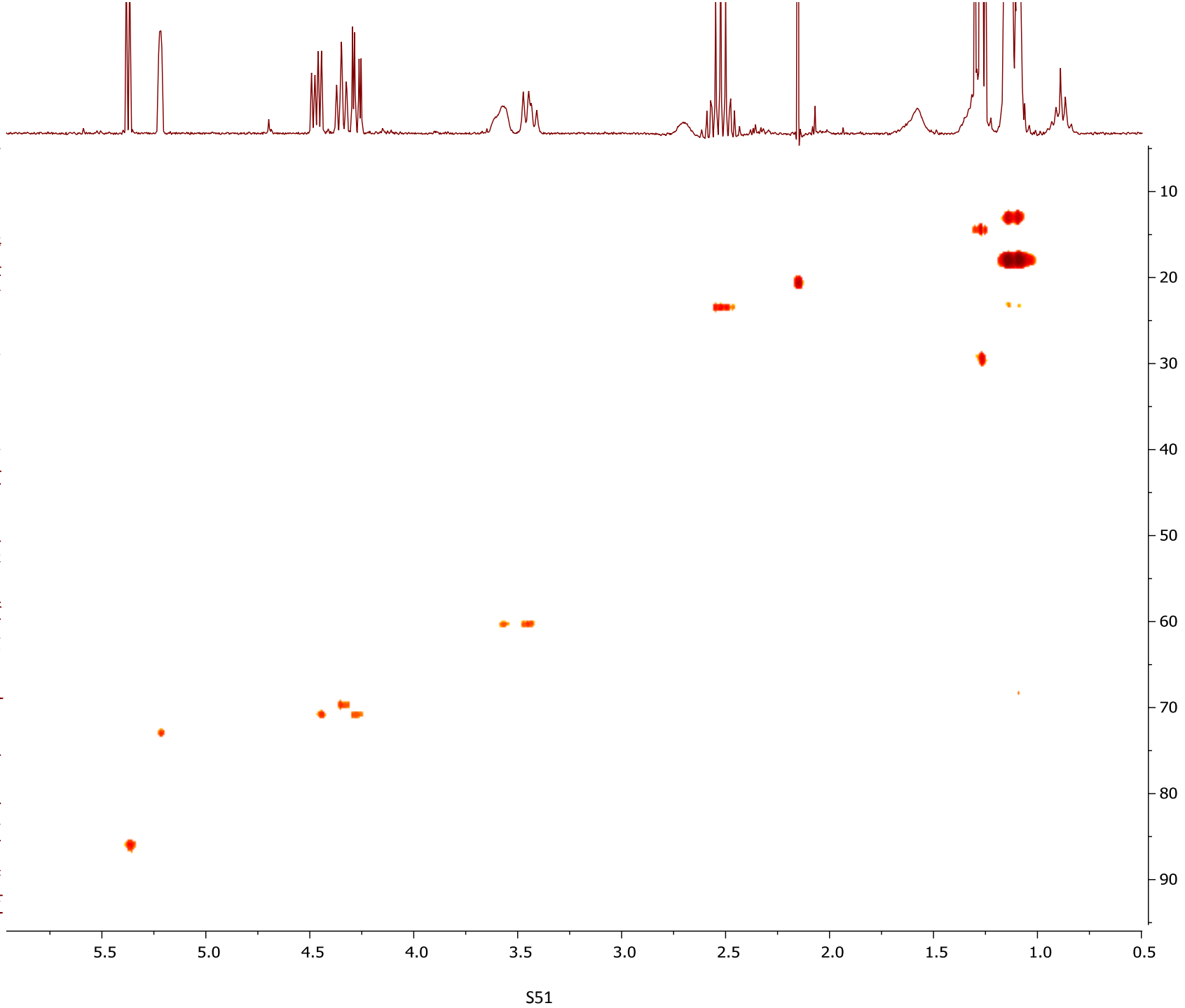




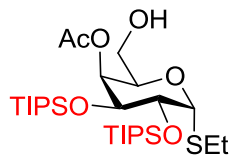


HSQC spectrum of compound 7 in $CDCl_3$ (300 MHz)

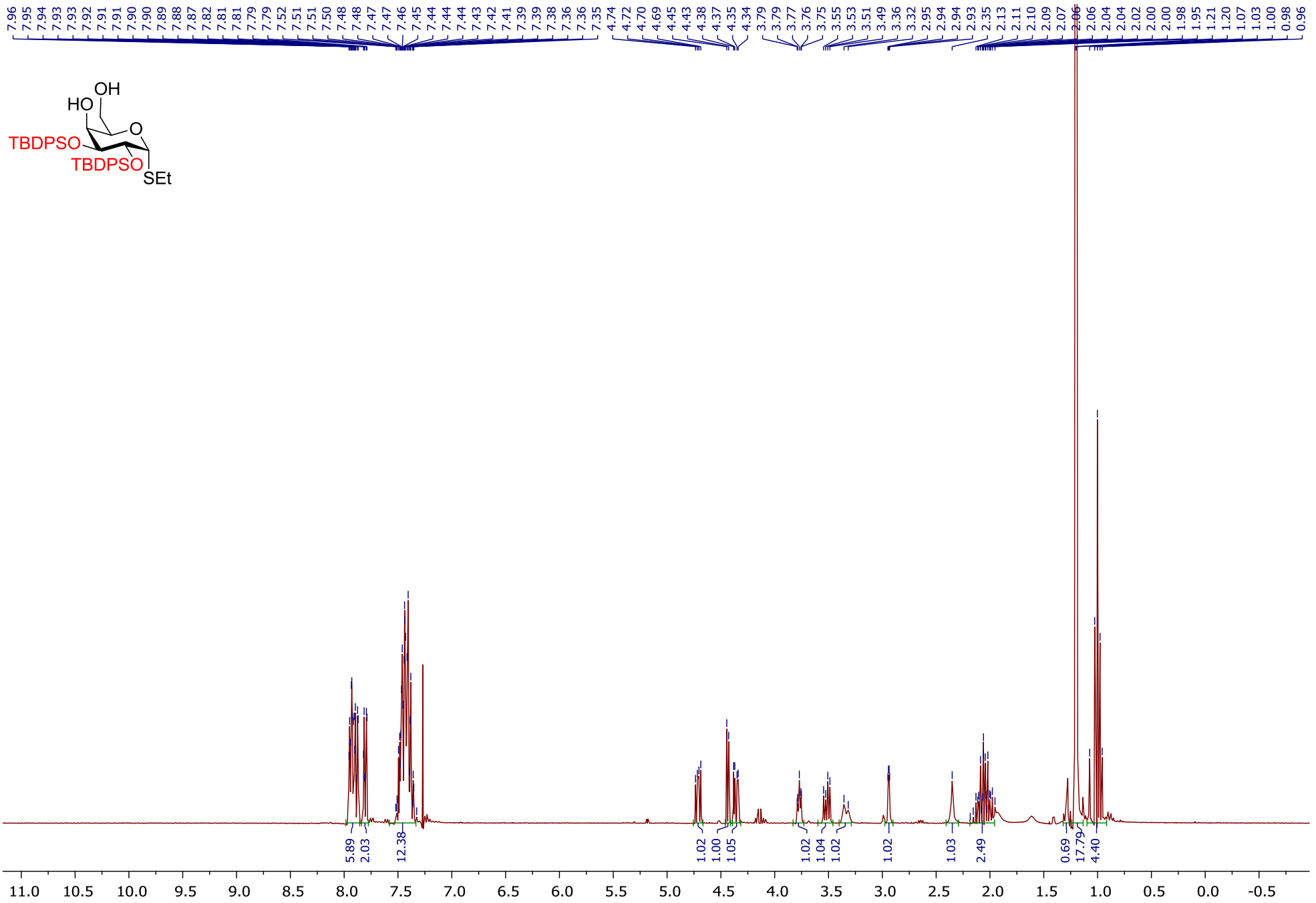




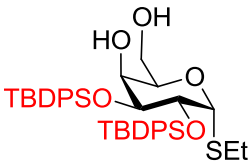
HMBC spectrum of compound 7 in $CDCl_3$ (300 MHz)

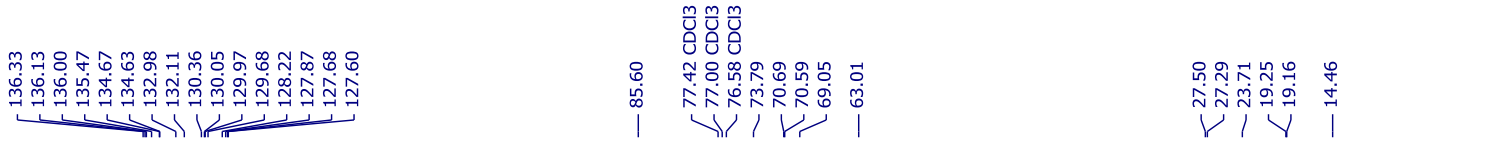


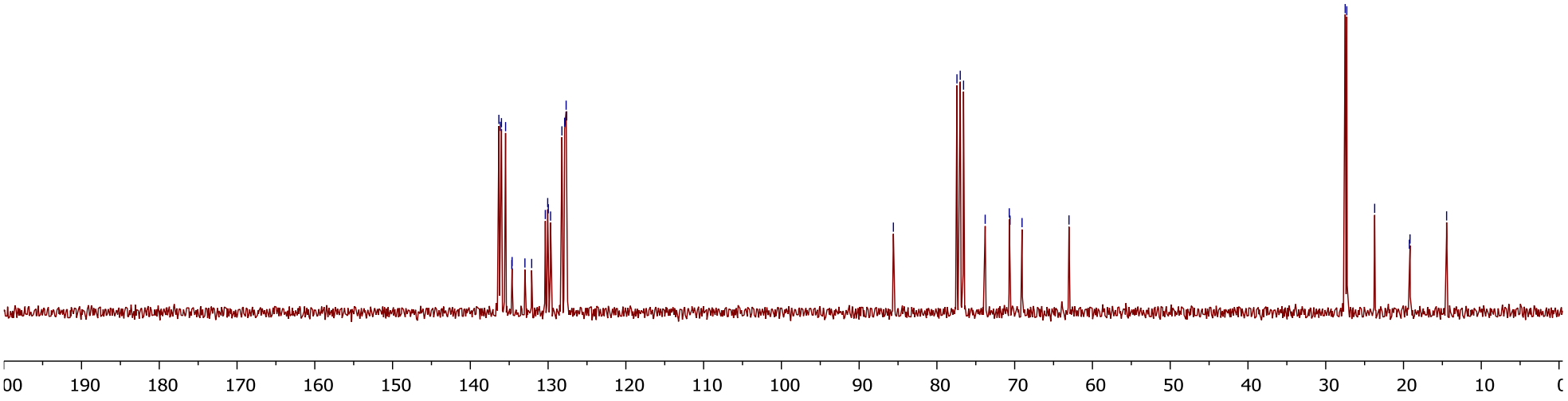
^{1}H NMR (300 MHz) spectrum of compound 8 in $CDCl_3$



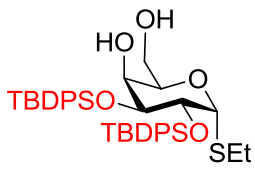
^{13}C NMR (151 MHz) spectrum of compound 8 in $CDCl_3$

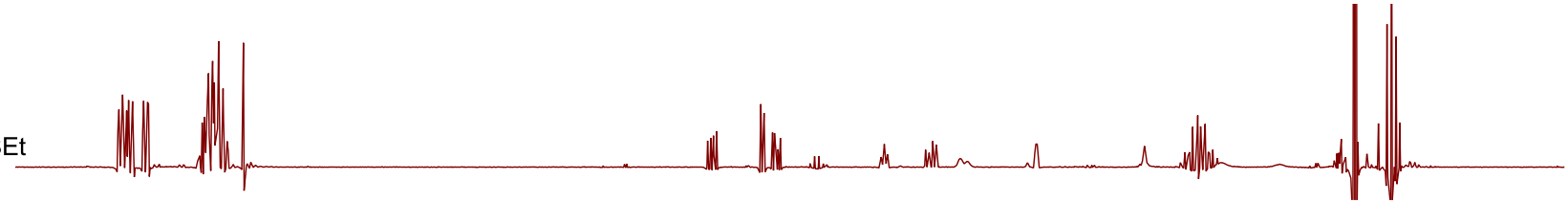


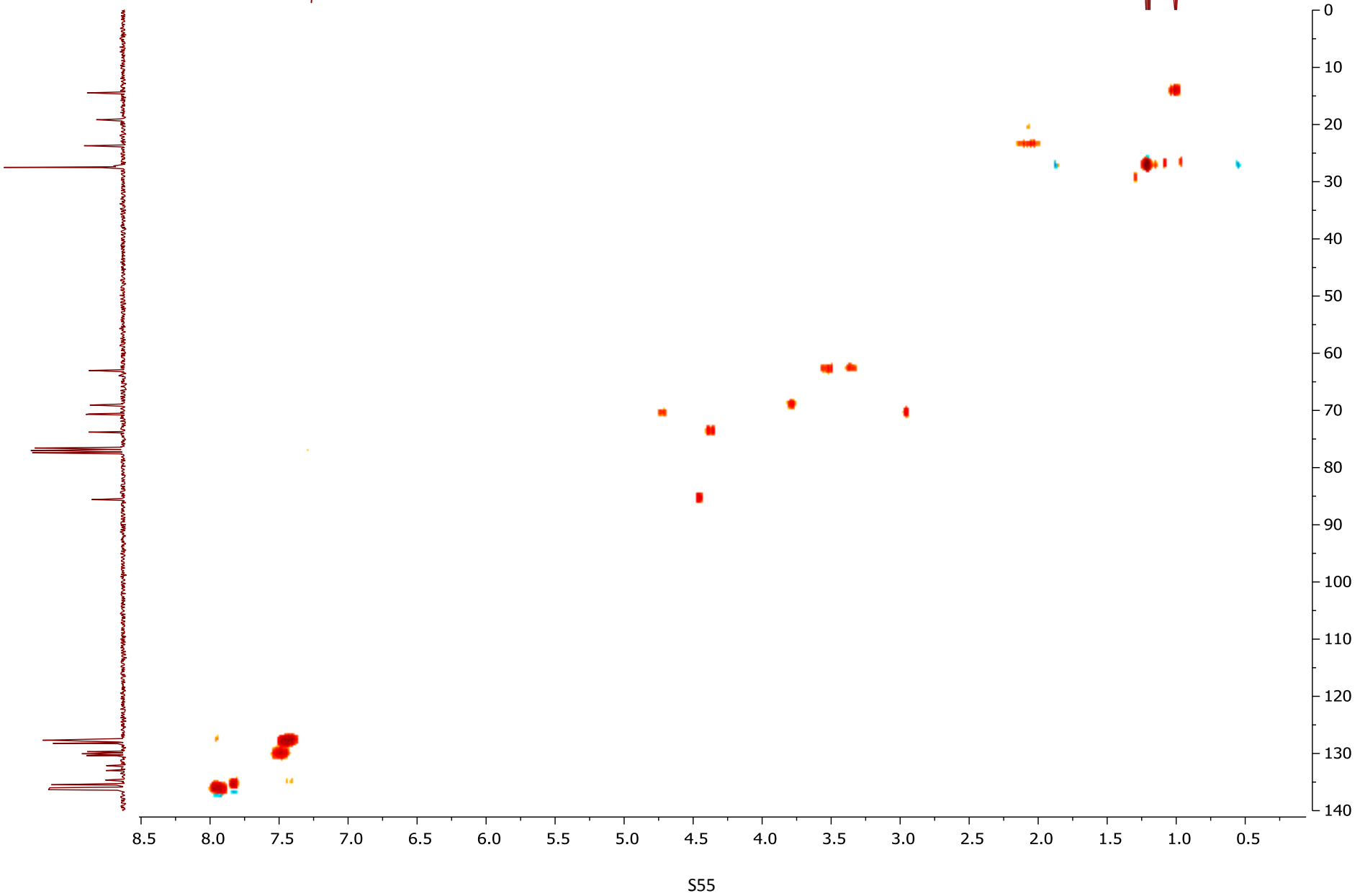




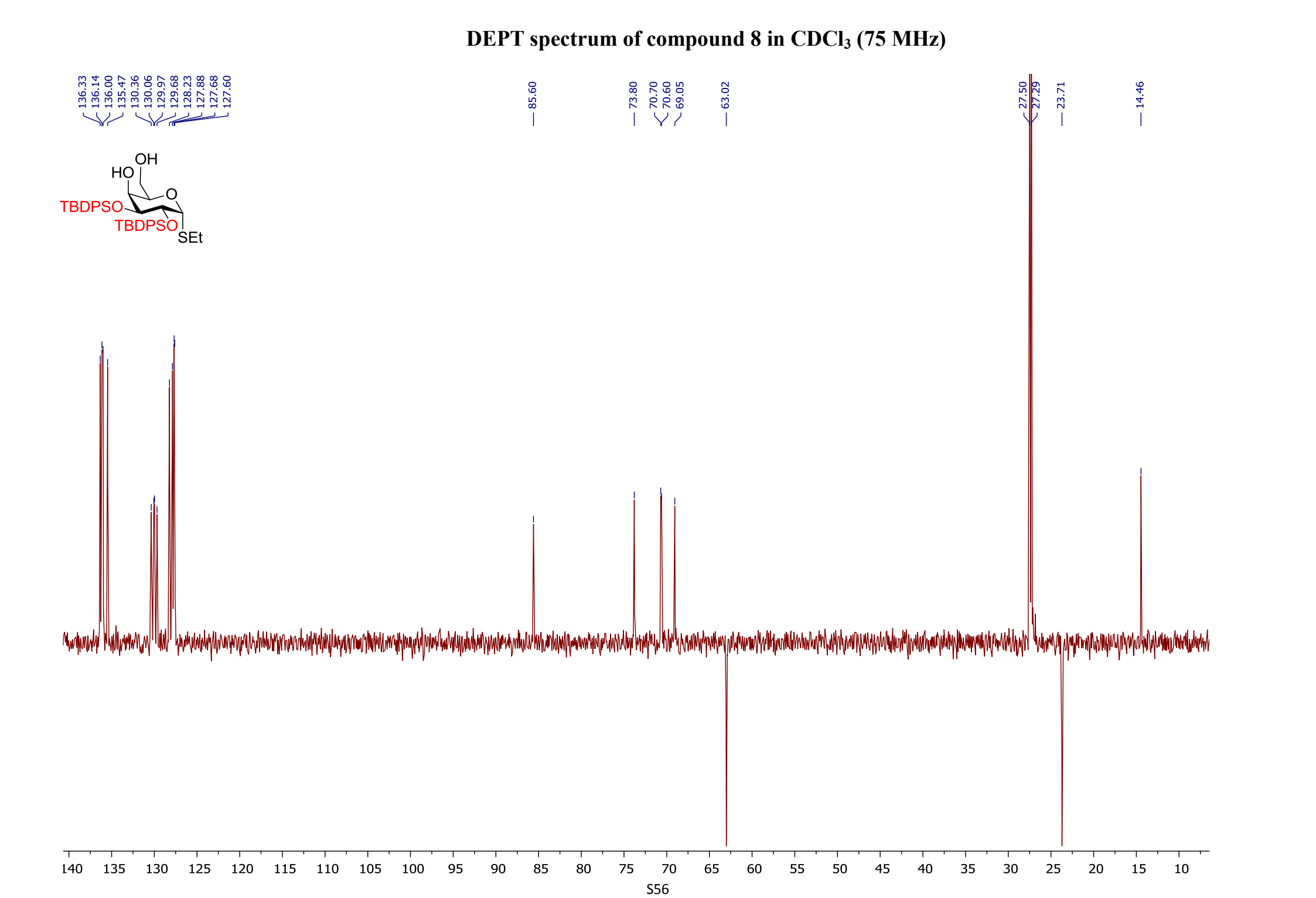
HSQC spectrum of compound 8 in $CDCl_3$ (600 MHz)



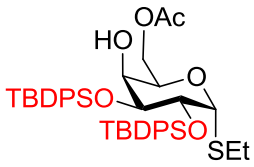




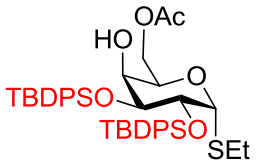
DEPT spectrum of compound 8 in $CDCl_3$ (75 MHz)



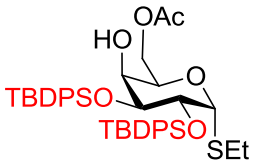
^{1}H NMR (300 MHz) spectrum of compound 9 in $CDCl_3$

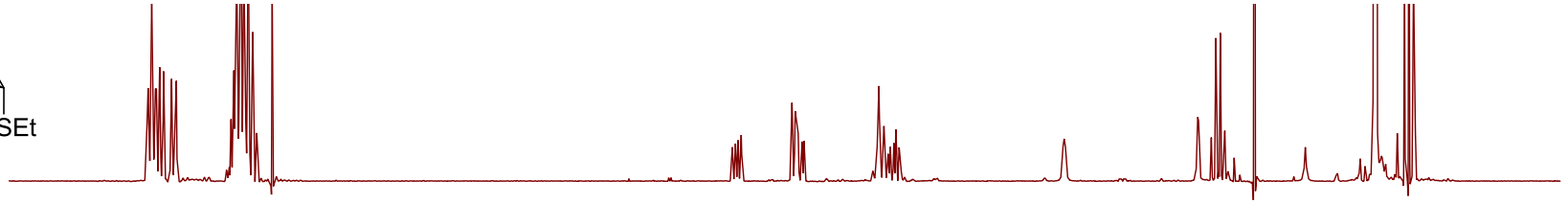


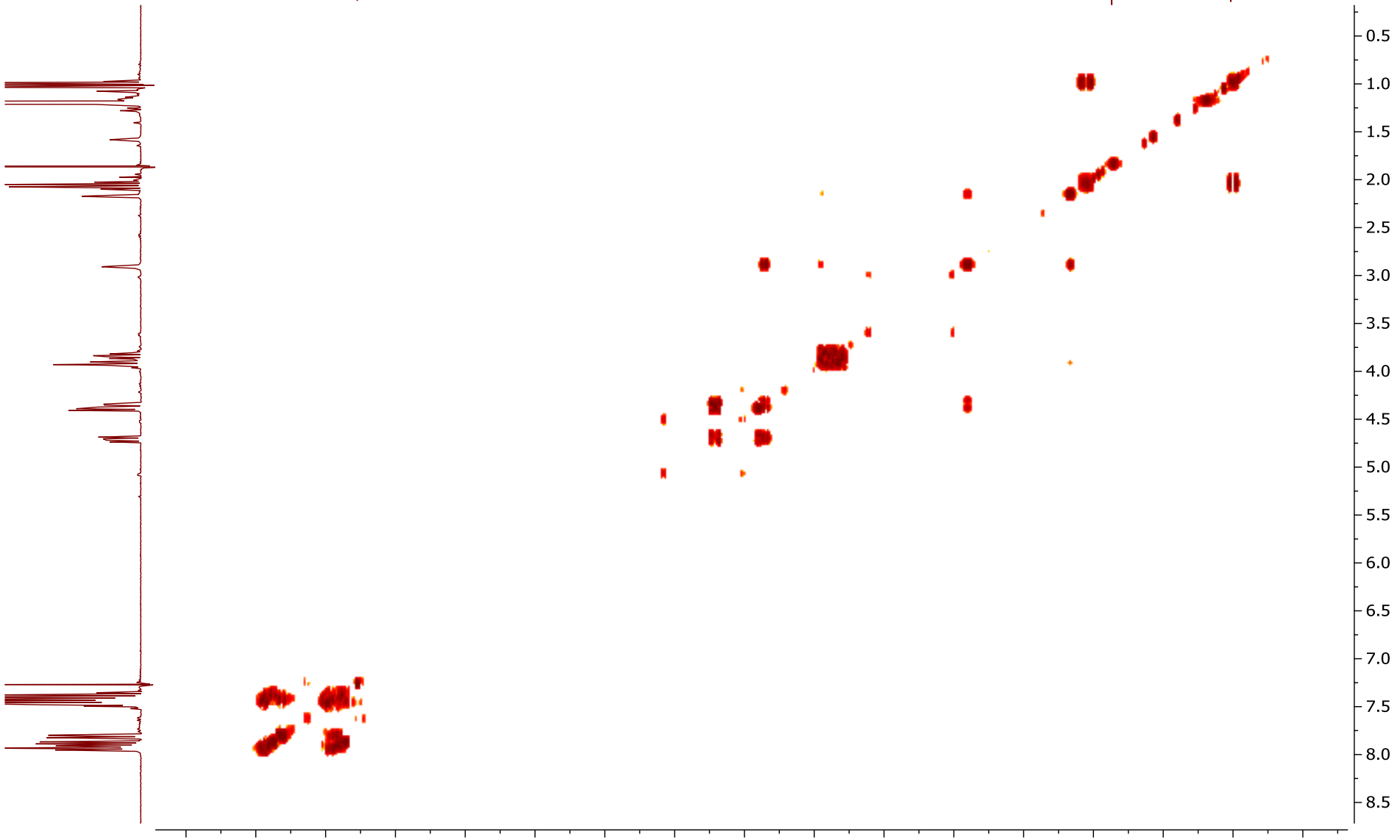
^{13}C NMR (75 MHz) spectrum of compound 9 in $CDCl_3$



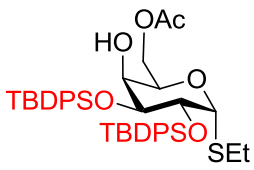
COSY spectrum of compound 9 in $CDCl_3$ (300 MHz)



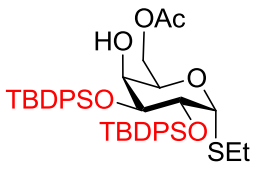




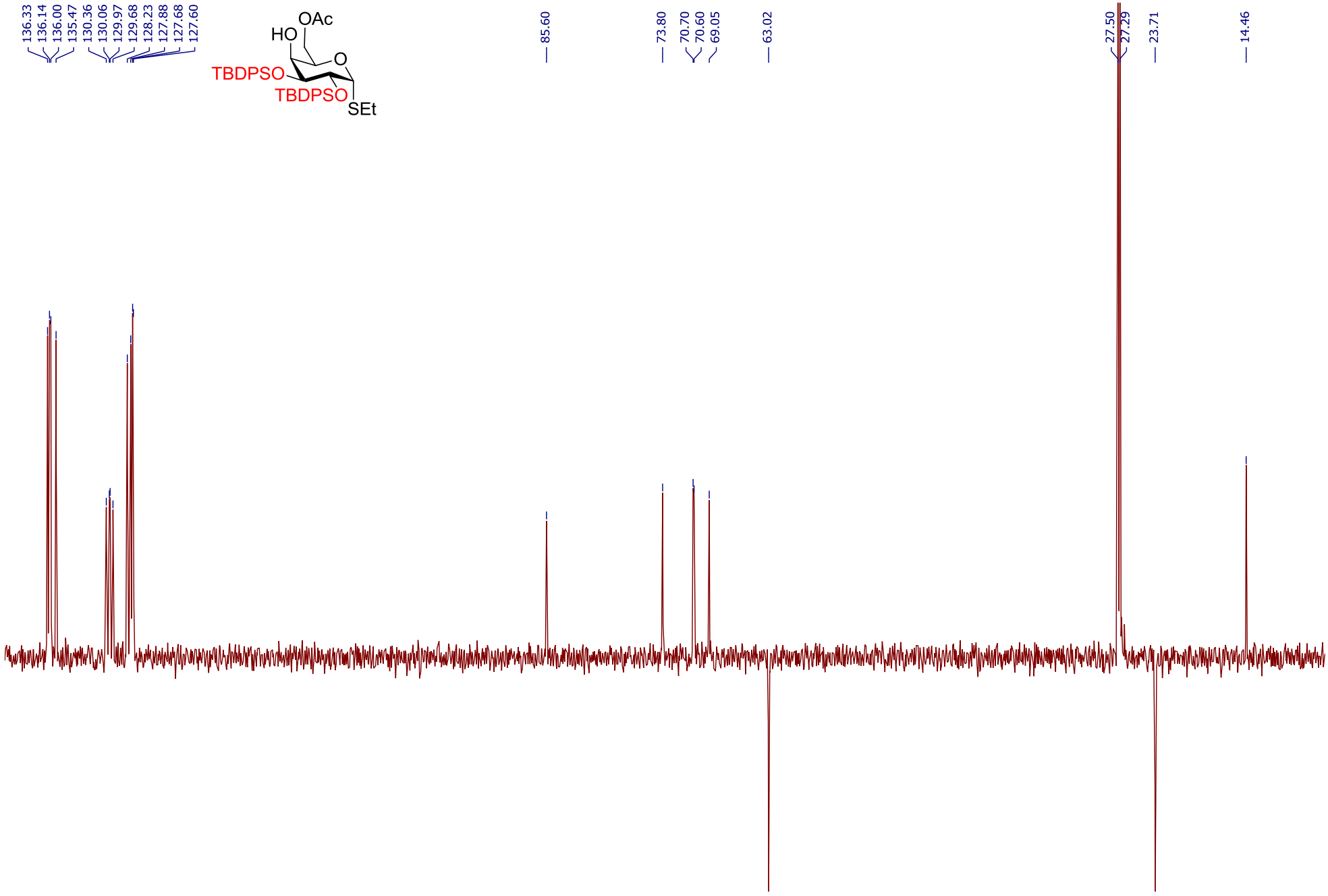
HSQC spectrum of compound 9 in $CDCl_3$ (300 MHz)



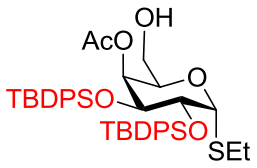
HMBC spectrum of compound 9 in $CDCl_3$ (300 MHz)



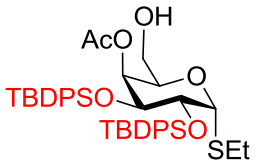
DEPT spectrum of compound 9 in $CDCl_3$ (75 MHz)



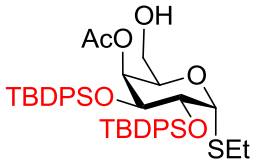
^{1}H NMR (300 MHz) spectrum of compound 10 in $CDCl_3$

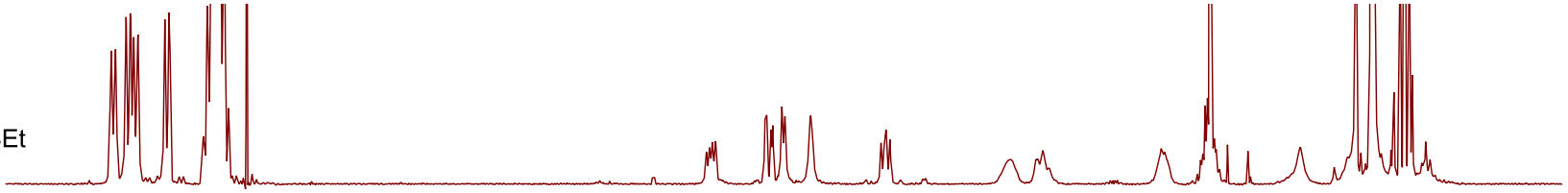


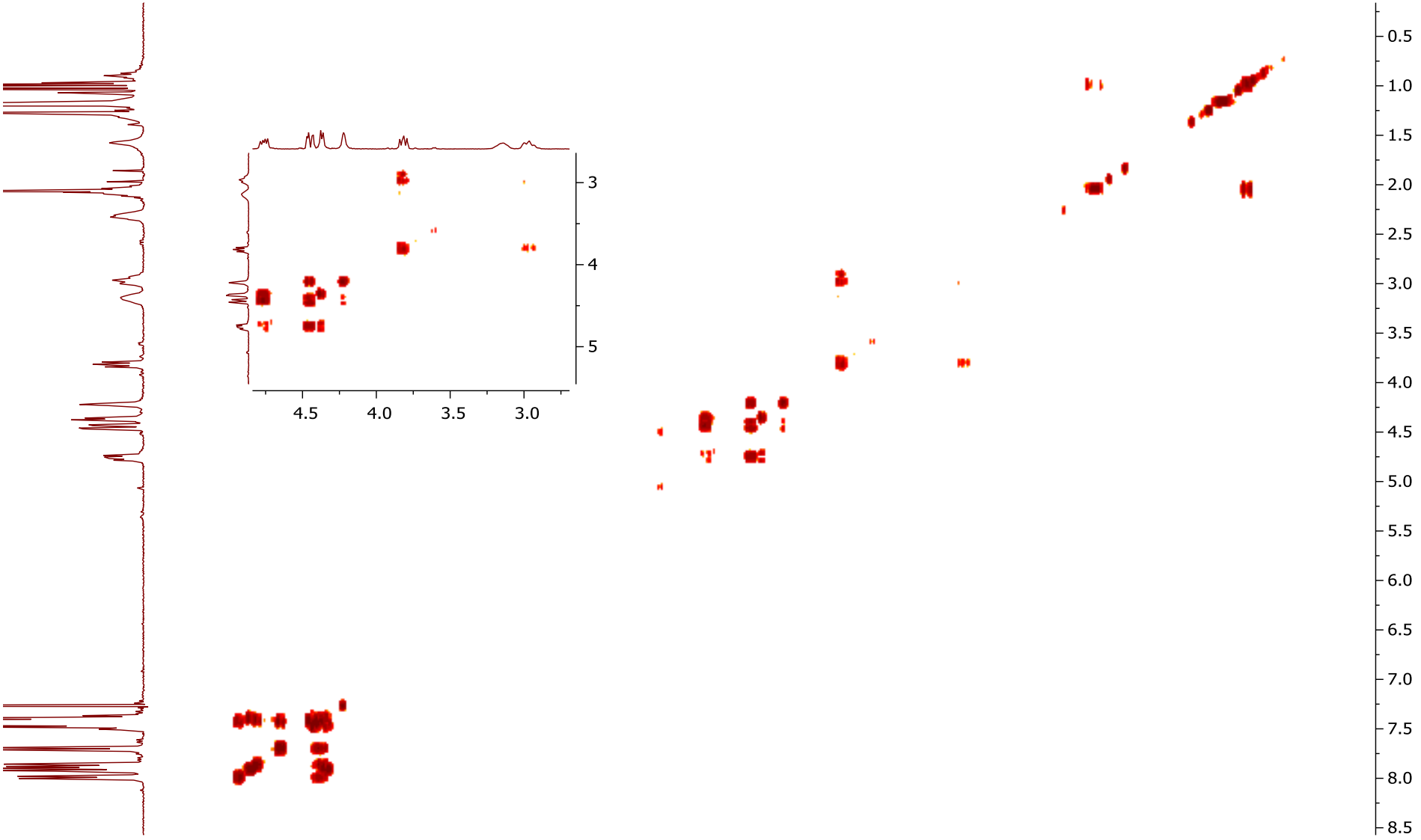
^{13}C NMR (75 MHz) spectrum of compound 10 in $CDCl_3$



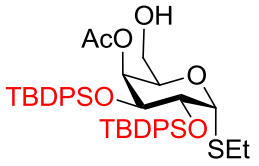
COSY spectrum of compound 10 in $CDCl_3$ (300 MHz)

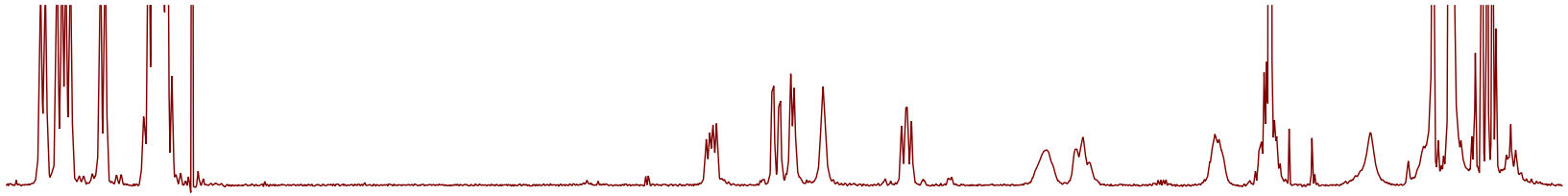


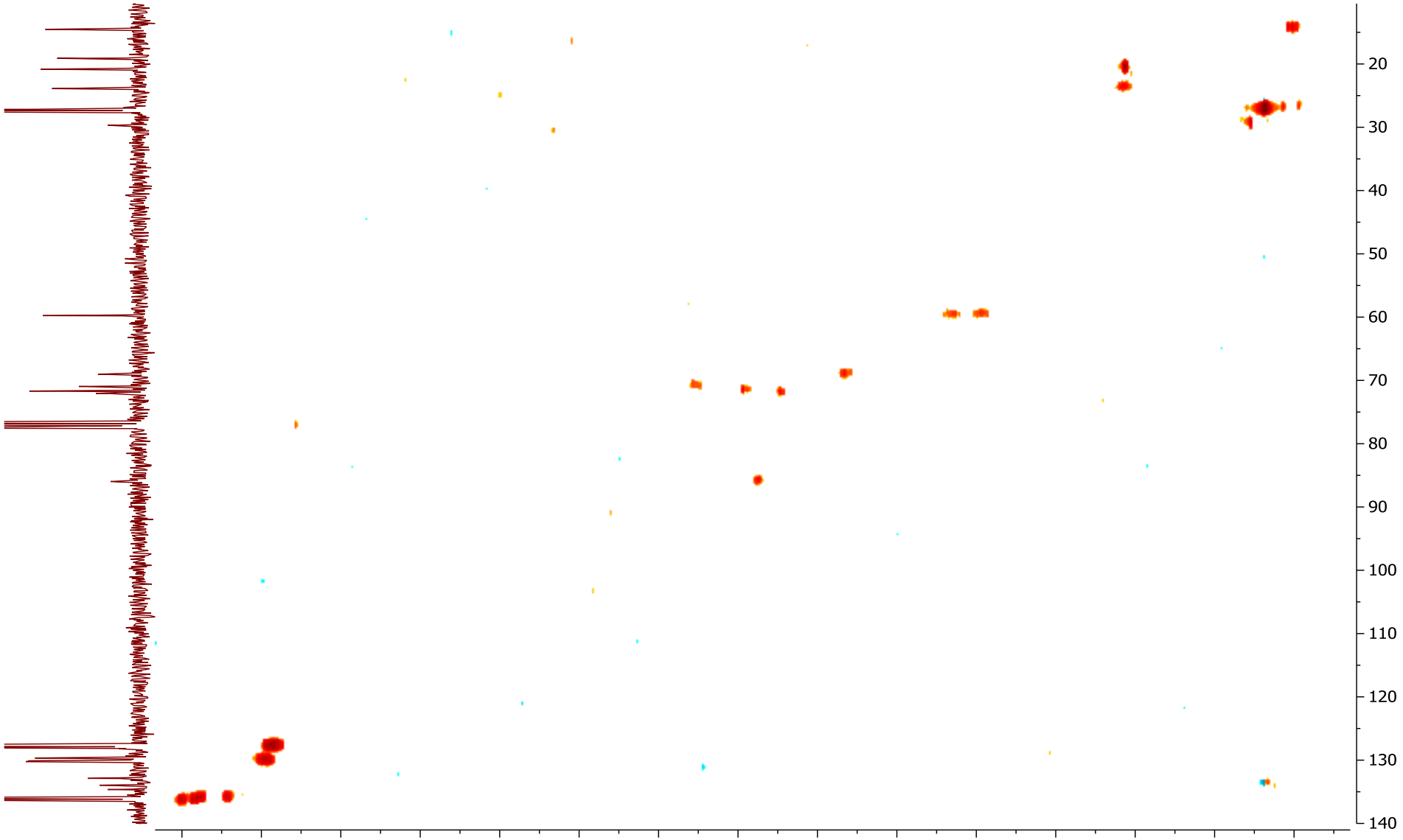




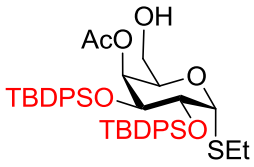
HSQC spectrum of compound 10 in $CDCl_3$ (300 MHz)



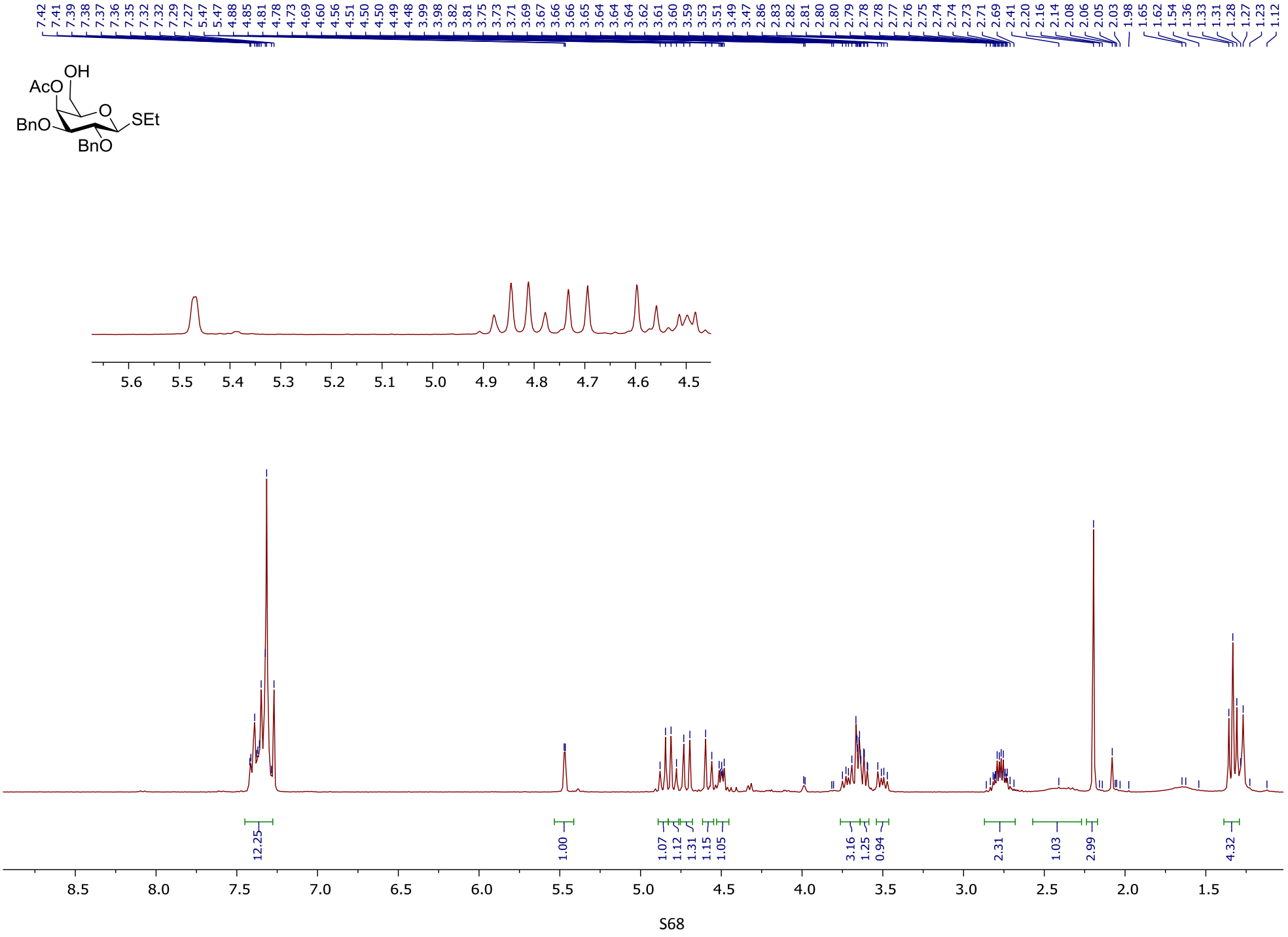




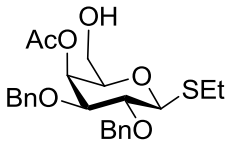
HMBC spectrum of compound 10 in $CDCl_3$ (300 MHz)



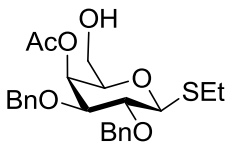
^{1}H NMR (300 MHz) spectrum of compound 13 in $CDCl_3$



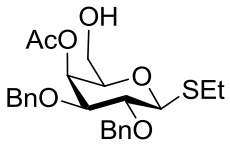
^{13}C NMR (75 MHz) spectrum of compound 13 in $CDCl_3$



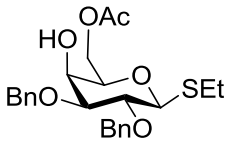
COSY spectrum of compound 13 in $CDCl_3$ (300 MHz)



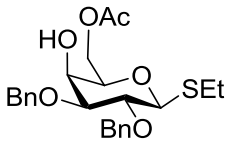
HSQC spectrum of compound 13 in $CDCl_3$ (300 MHz)



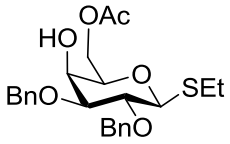
^{1}H NMR (300 MHz) spectrum of compound 14 in $CDCl_3$



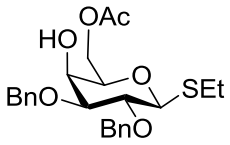
^{13}C NMR (75 MHz) spectrum of compound 14 in $CDCl_3$

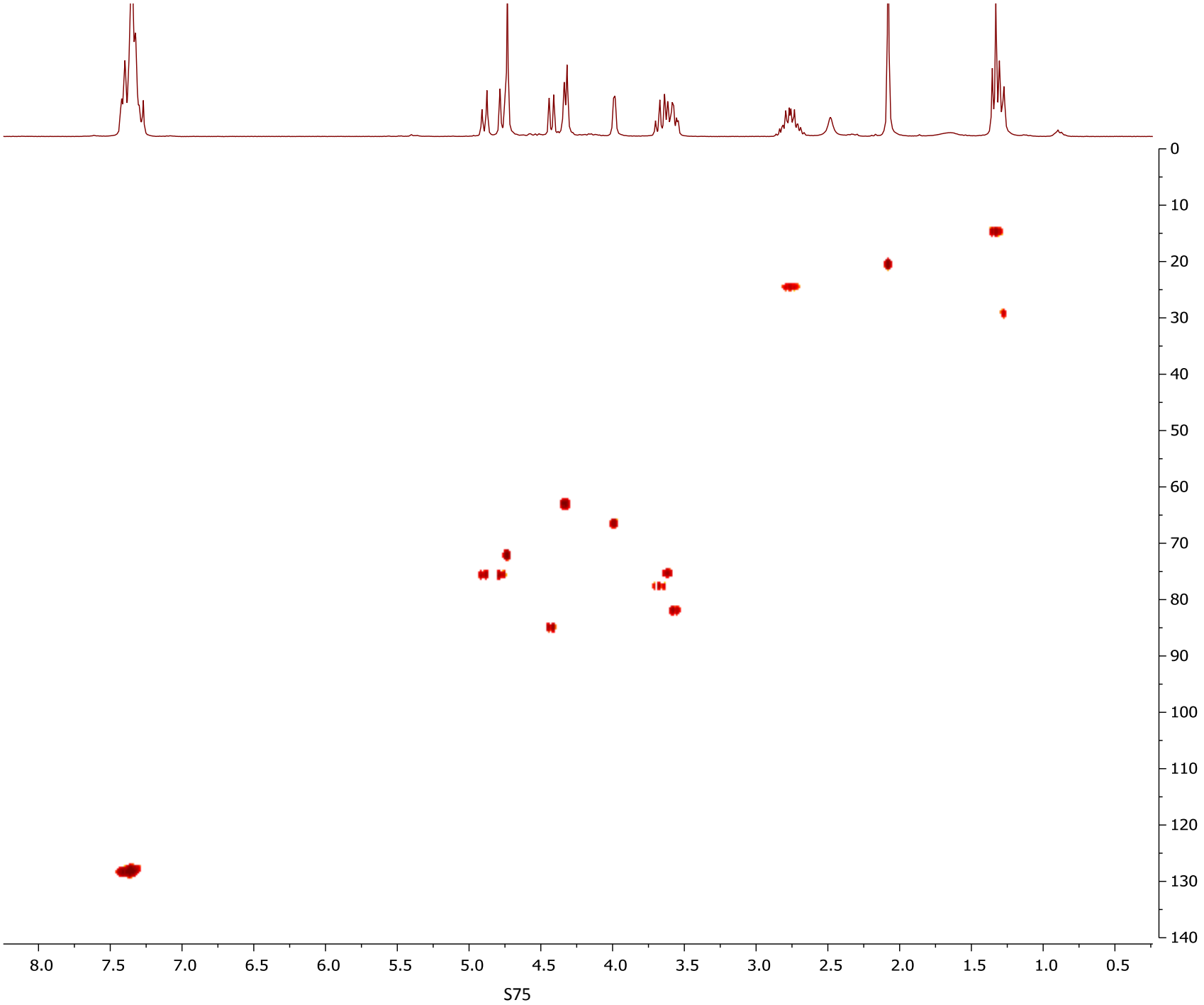


COSY spectrum of compound 14 in $CDCl_3$ (300 MHz)

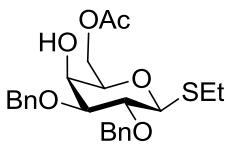


HSQC spectrum of compound 14 in $CDCl_3$ (300 MHz)

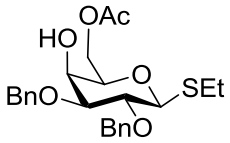


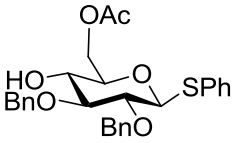


HMBC spectrum of compound 14 in $CDCl_3$ (300 MHz)

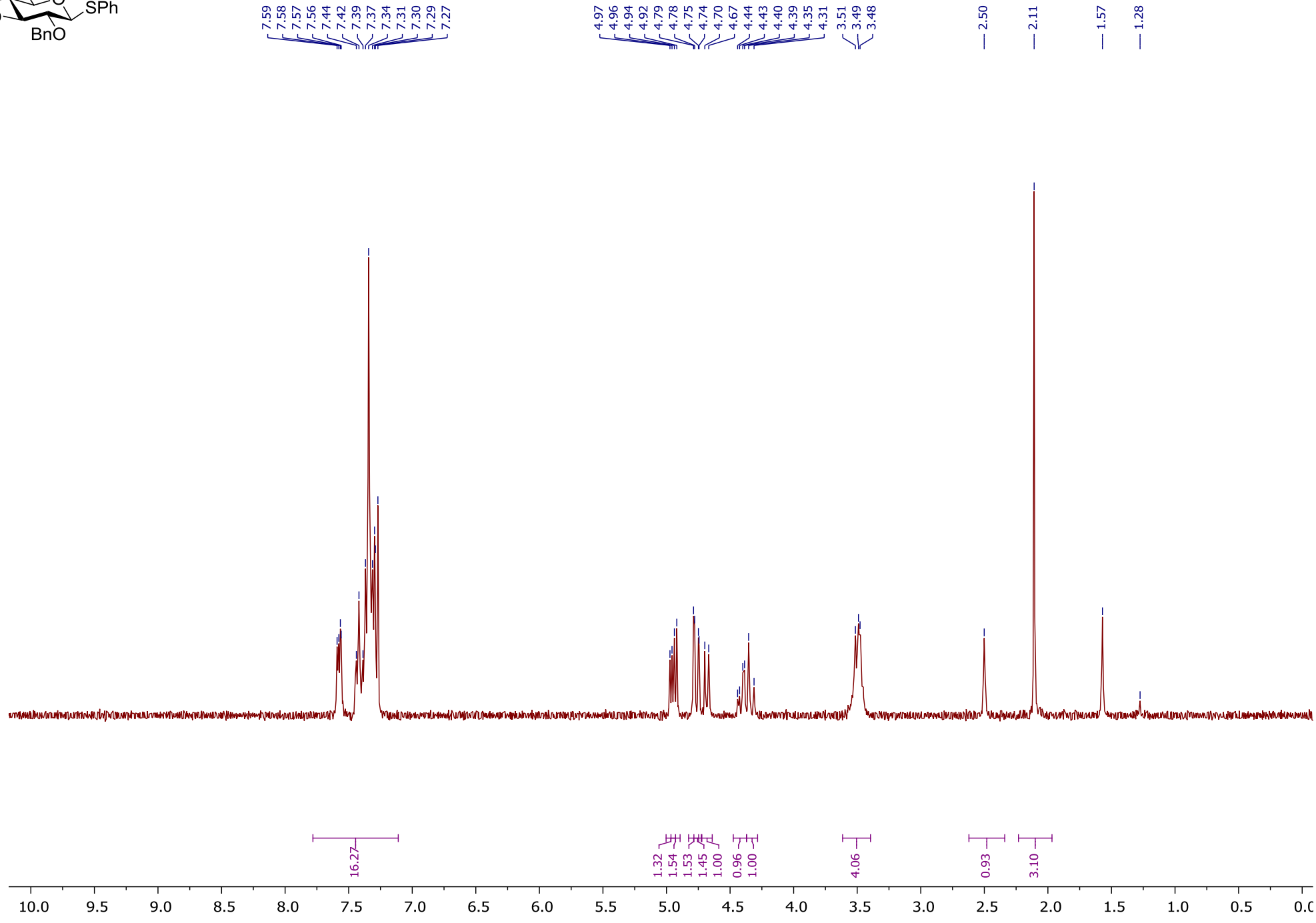


DEPT spectrum of compound 14 in $CDCl_3$ (75 MHz)

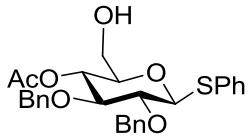




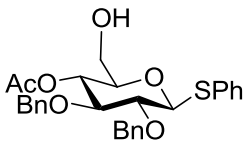
^{1}H NMR (300 MHz) spectrum of compound 17 in $CDCl_3$ (300 MHz)



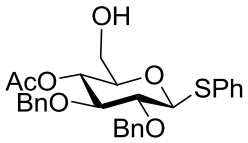
^{1}H NMR (300 MHz) spectrum of compound 18 in Me_2CO-d_6



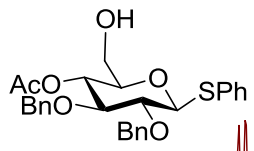
^{13}C NMR (75 MHz) spectrum of compound 18 in Me_2CO-d_6



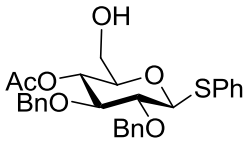
COSY spectrum of compound 18 in Me_2CO-d_6 (300 MHz)



HSQC spectrum of compound 18 in Me_2CO-d_6 (300 MHz)



DEPT spectrum of compound 18 in Me_2CO-d_6 (75 MHz)

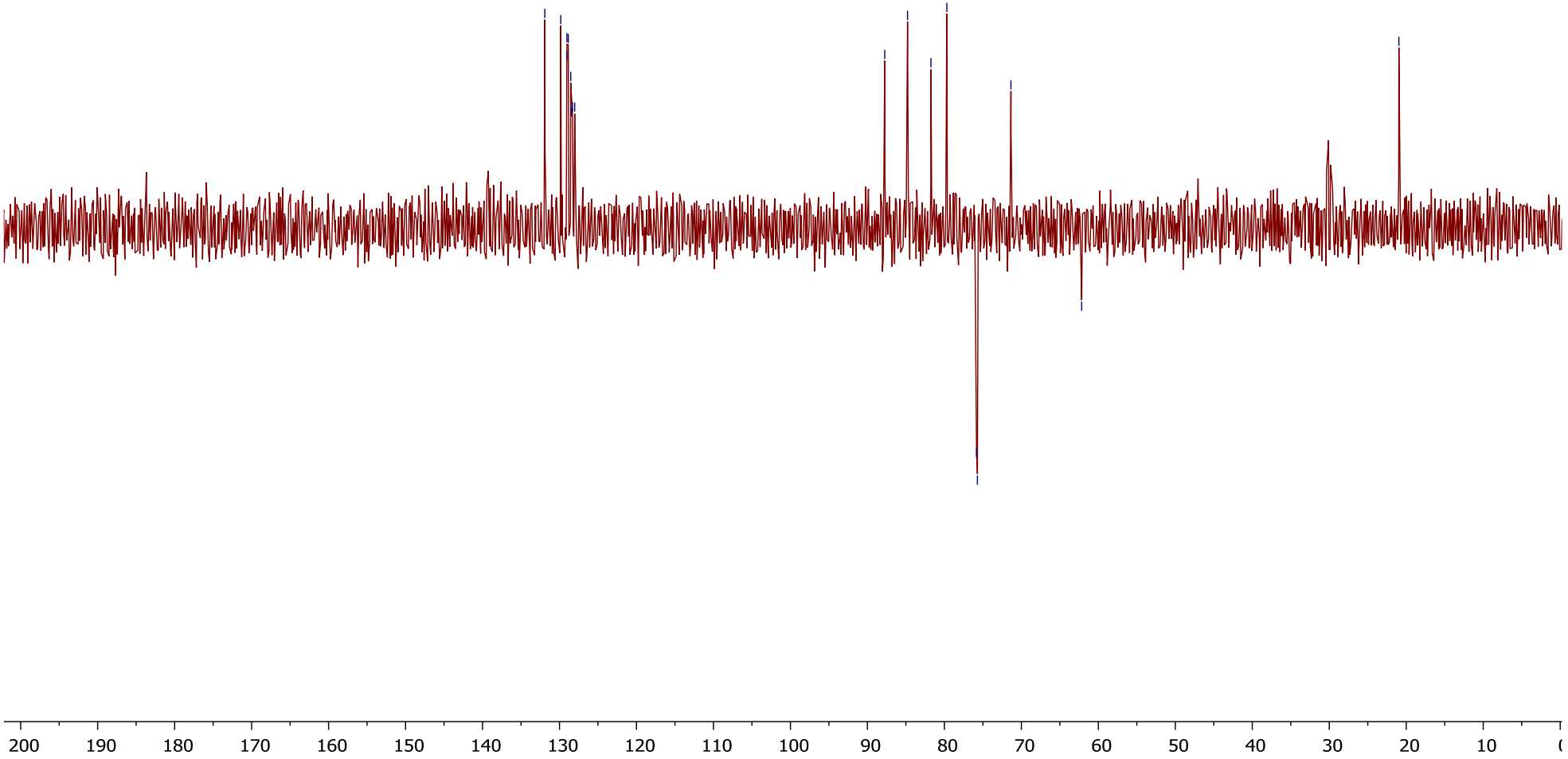


131.91
129.84
129.07
129.04
128.86
128.54
128.43
128.32
128.02

87.75
84.79
81.74
79.68
75.83
75.71
71.35

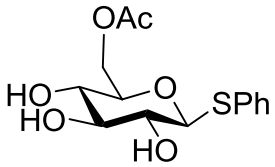
62.16

20.95

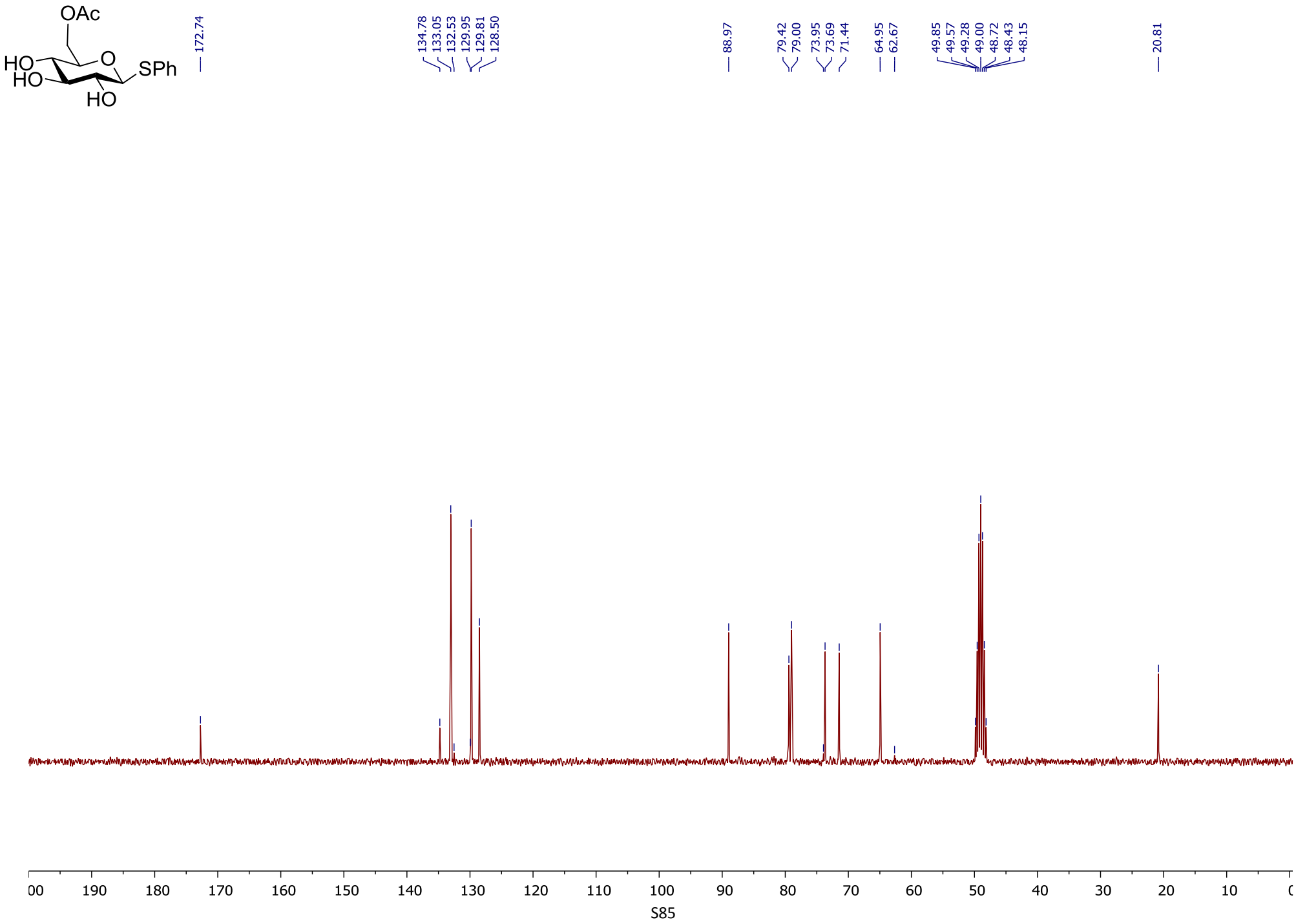


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

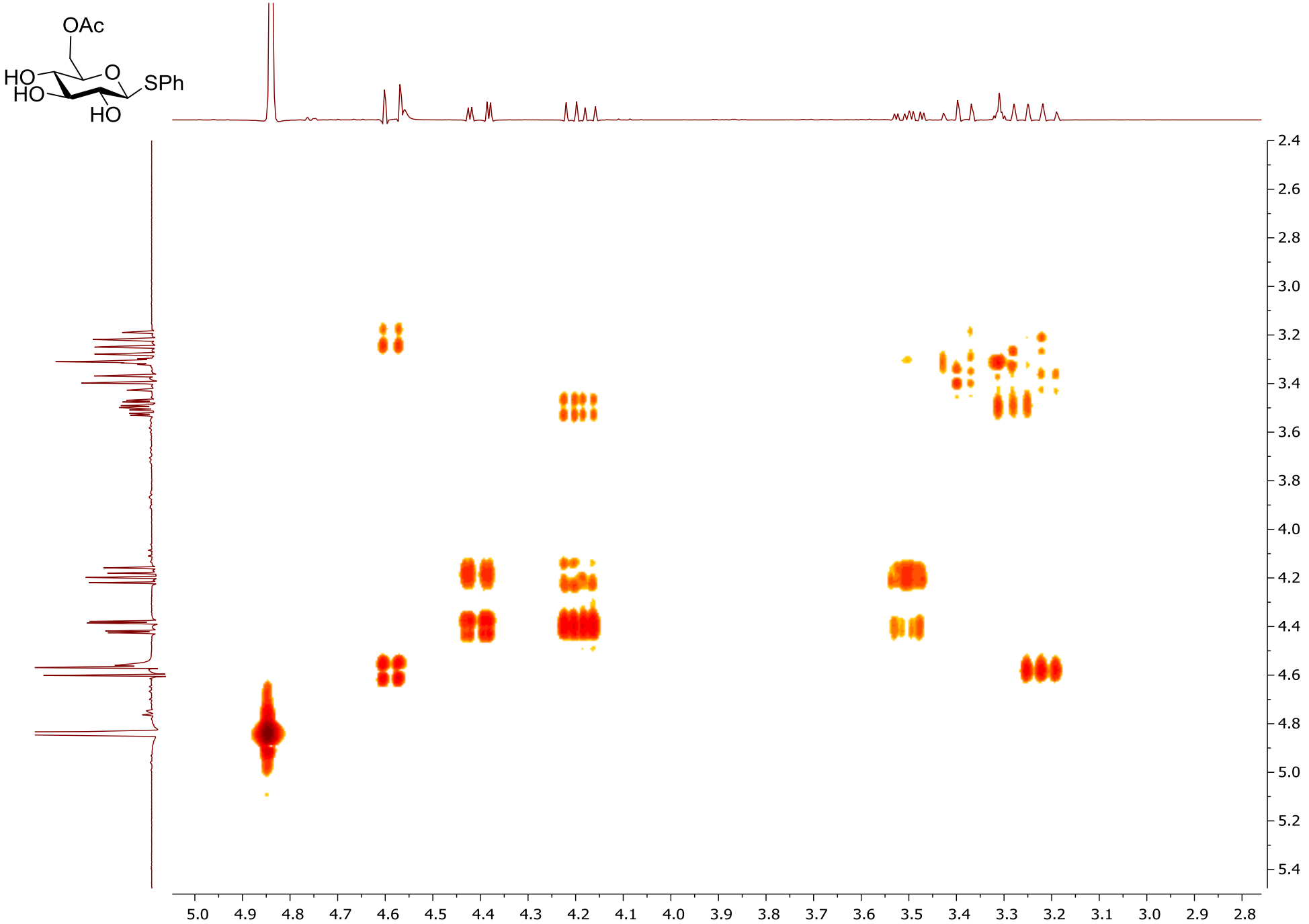
^{1}H NMR (300 MHz) spectrum of compound 21 in CD_3OD



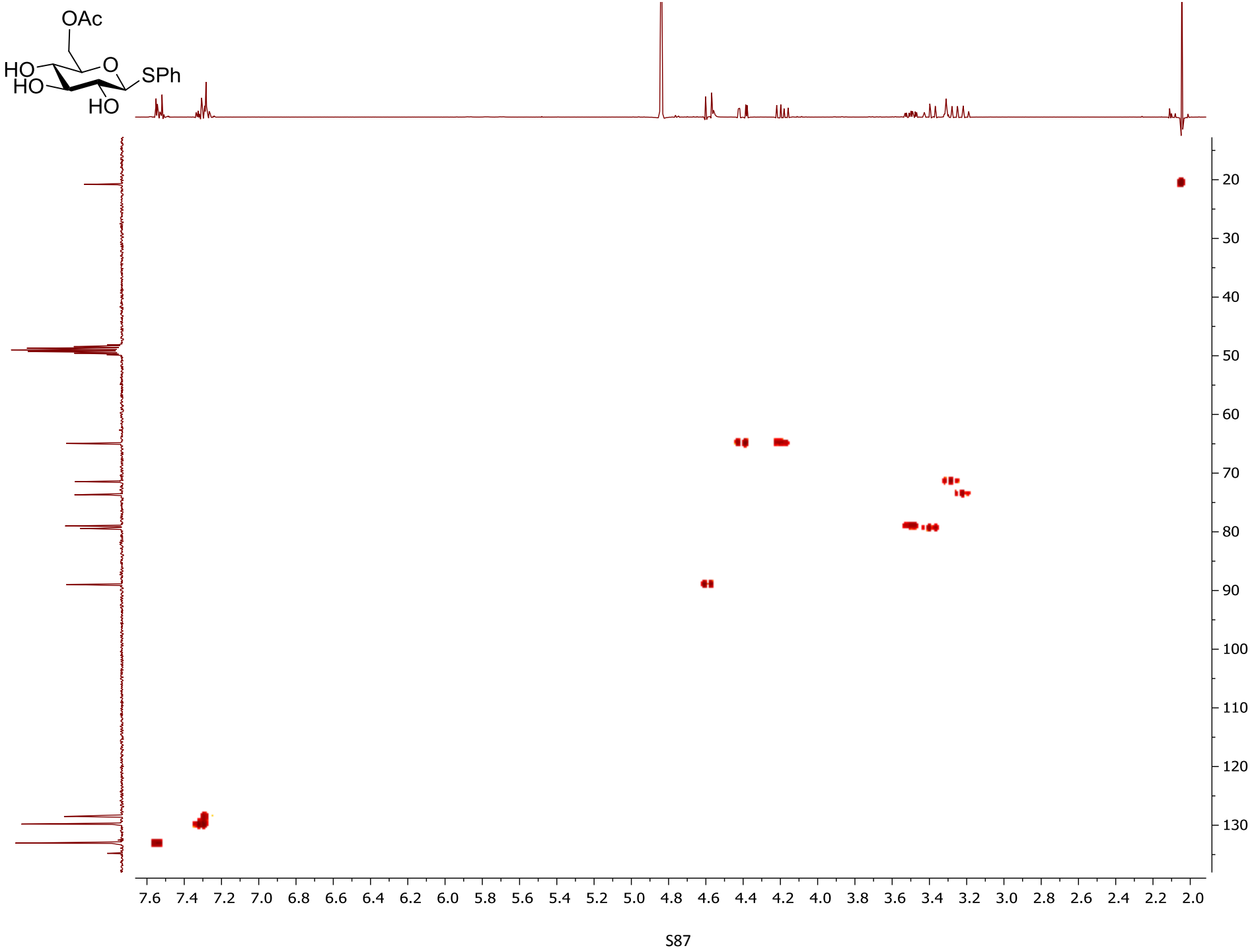
^{13}C NMR (75 MHz) spectrum of compound 21 in CD_3OD



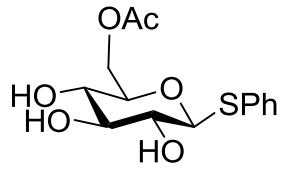
COSY spectrum of compound 21 in CD_3OD (300 MHz)



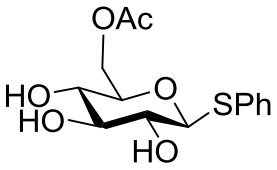
HSQC spectrum of compound 21 in CD_3OD (300 MHz)



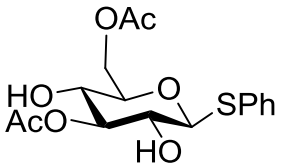
HMBC spectrum of compound 21 in CD_3OD (300 MHz)

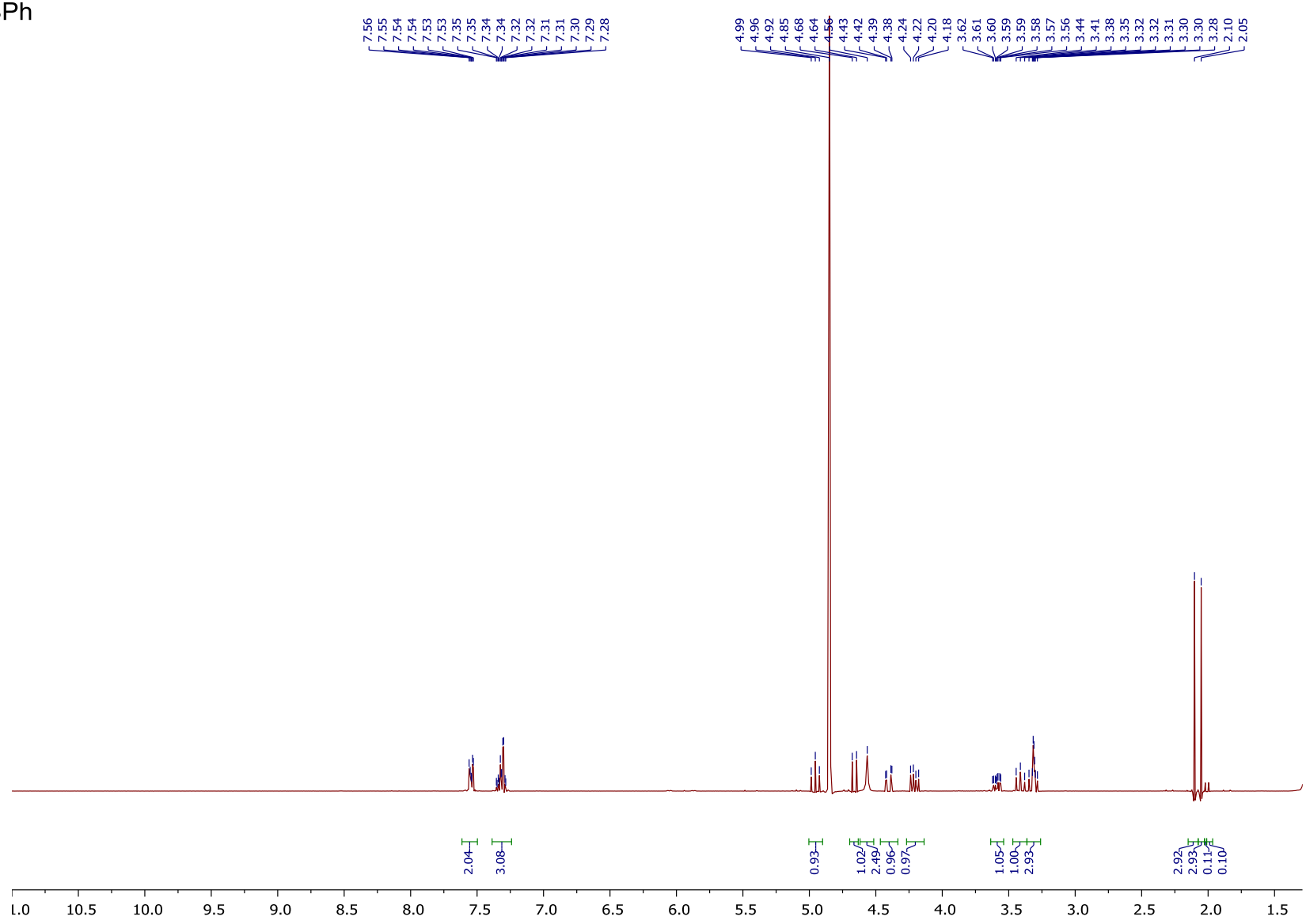


DEPT spectrum of compound 21 in CD_3OD (75 MHz)

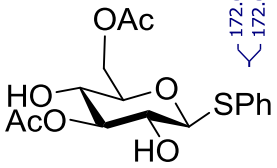


^{1}H NMR (300 MHz) spectrum of compound 22 in CD_3OD

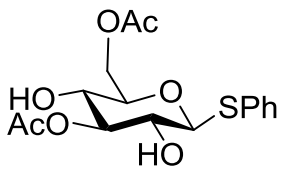




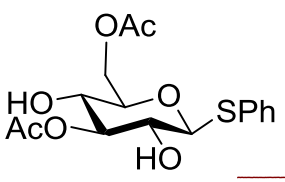
^{13}C NMR (75 MHz) spectrum of compound 22 in CD_3OD



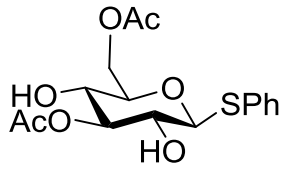
COSY spectrum of compound 22 in CD_3OD (300 MHz)



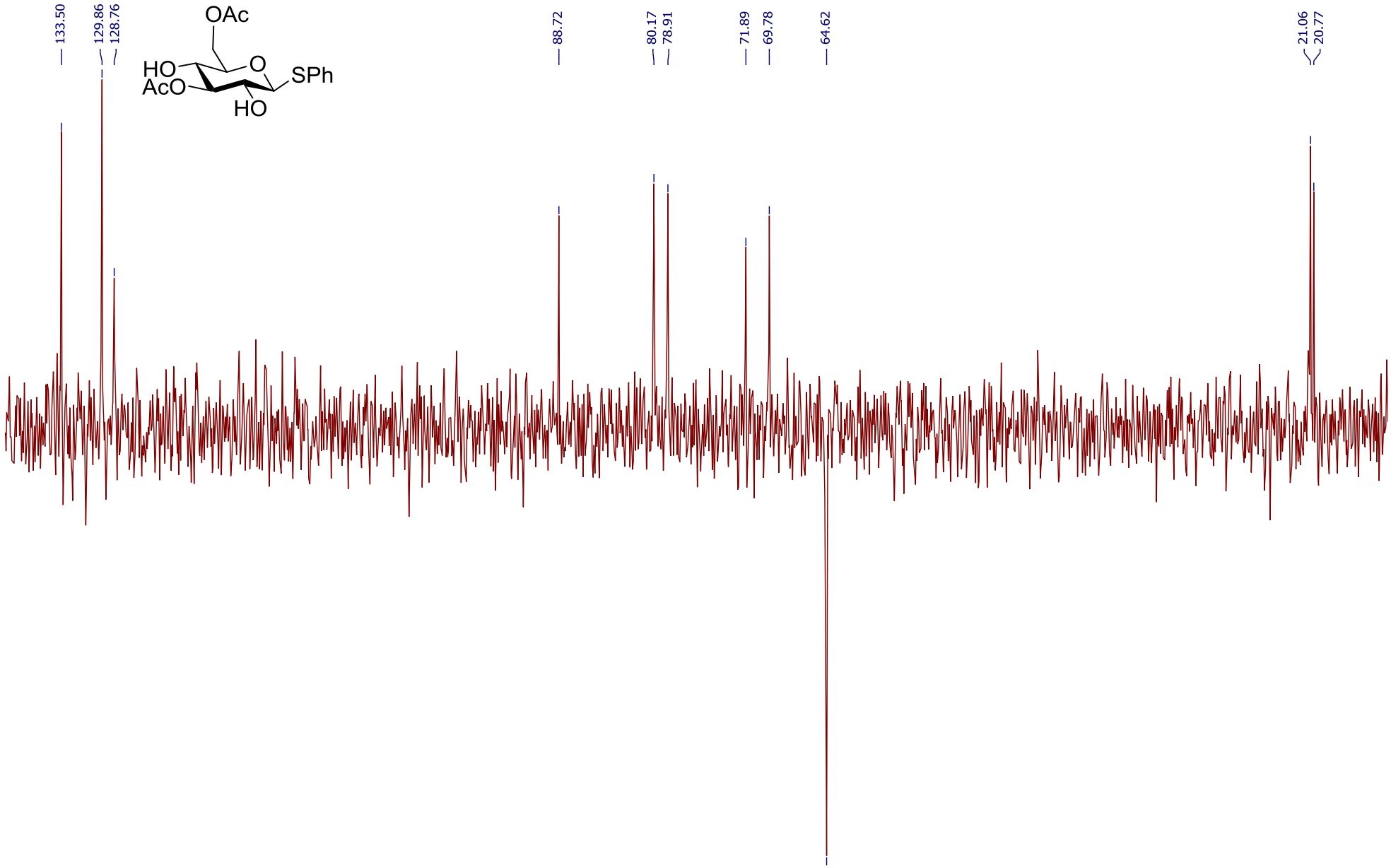
HSQC spectrum of compound 22 in CD_3OD (300 MHz)



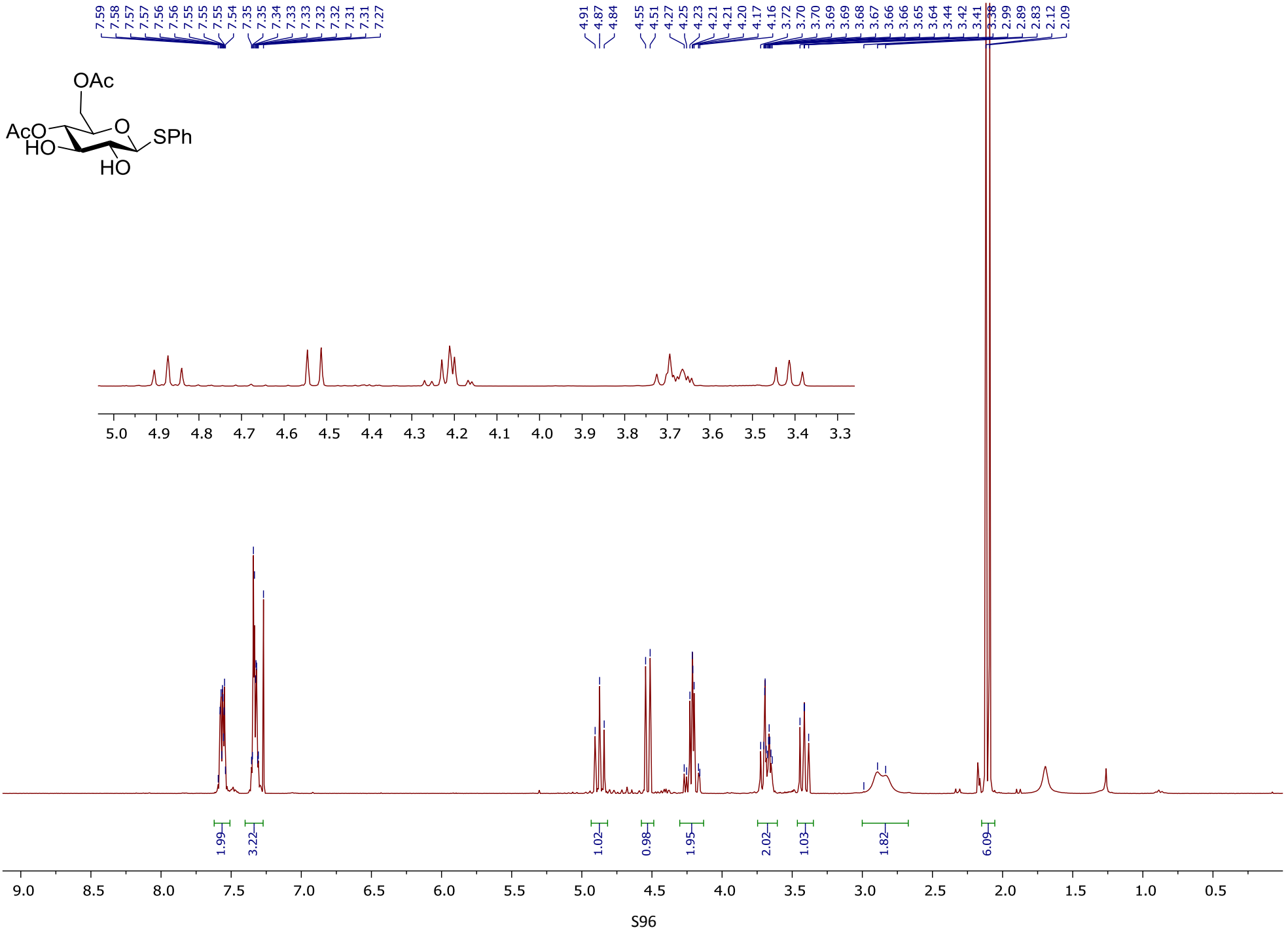
HMBC spectrum of compound 22 in CD_3OD (300 MHz)



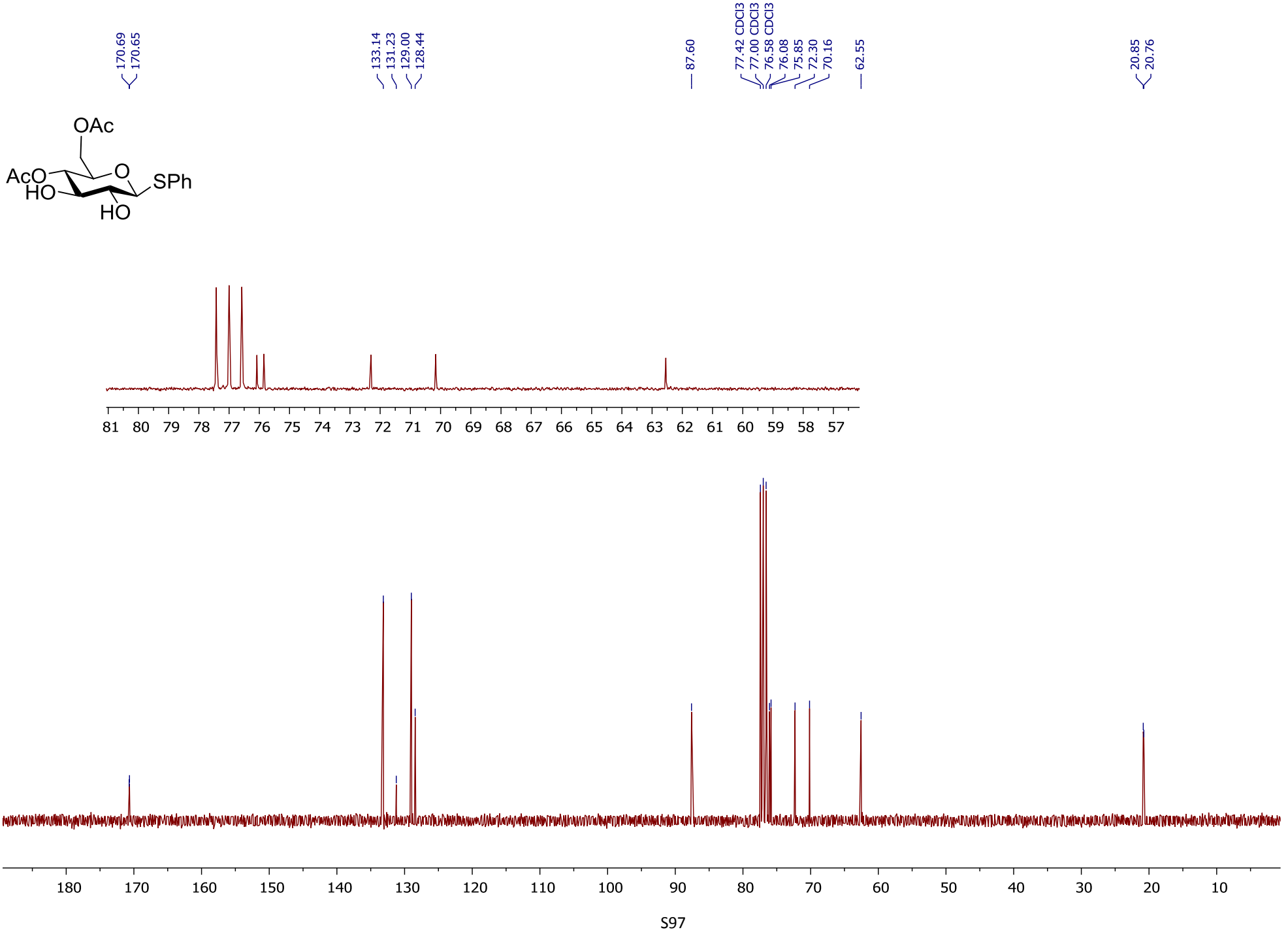
DEPT spectrum of compound 22 in CD_3OD (75 MHz)



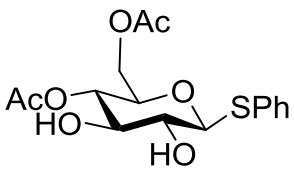
^{1}H NMR (300 MHz) spectrum of compound 23 in $CDCl_3$



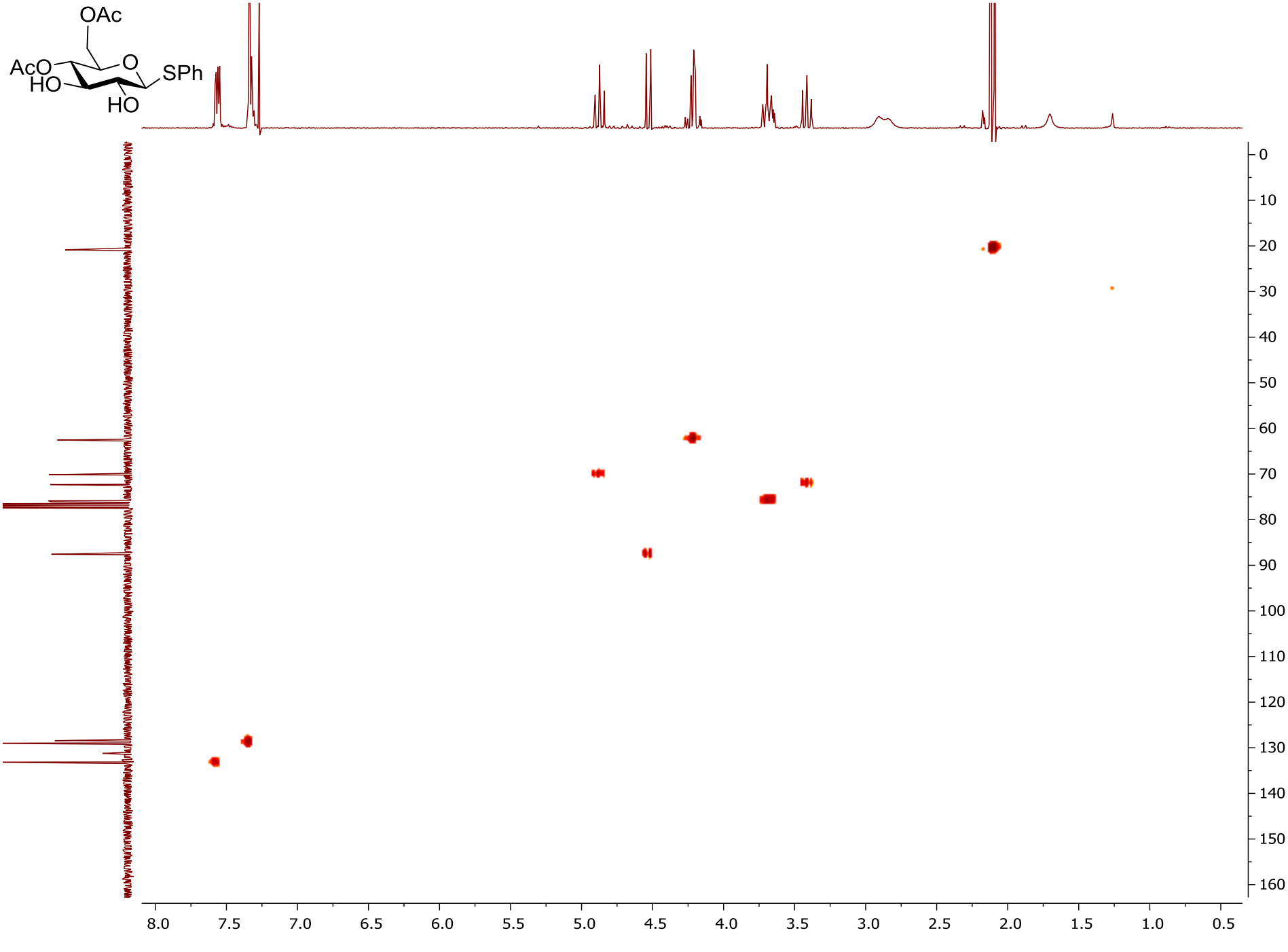
^{13}C NMR (75 MHz) spectrum of compound 23 in $CDCl_3$



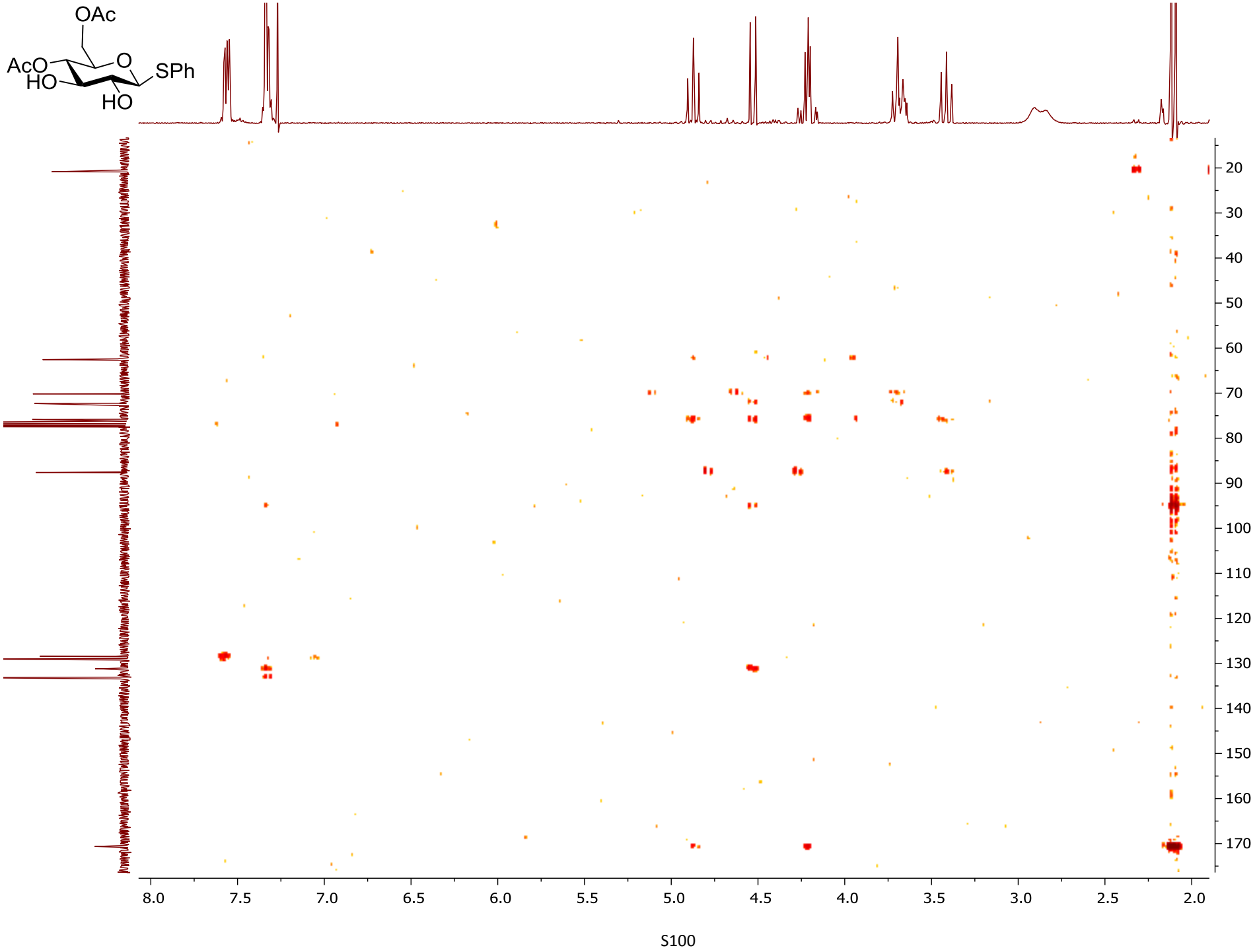
COSY spectrum of compound 23 in $CDCl_3$ (300 MHz)



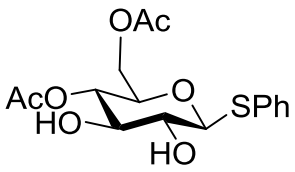
HSQC spectrum of compound 23 in $CDCl_3$ (300 MHz)



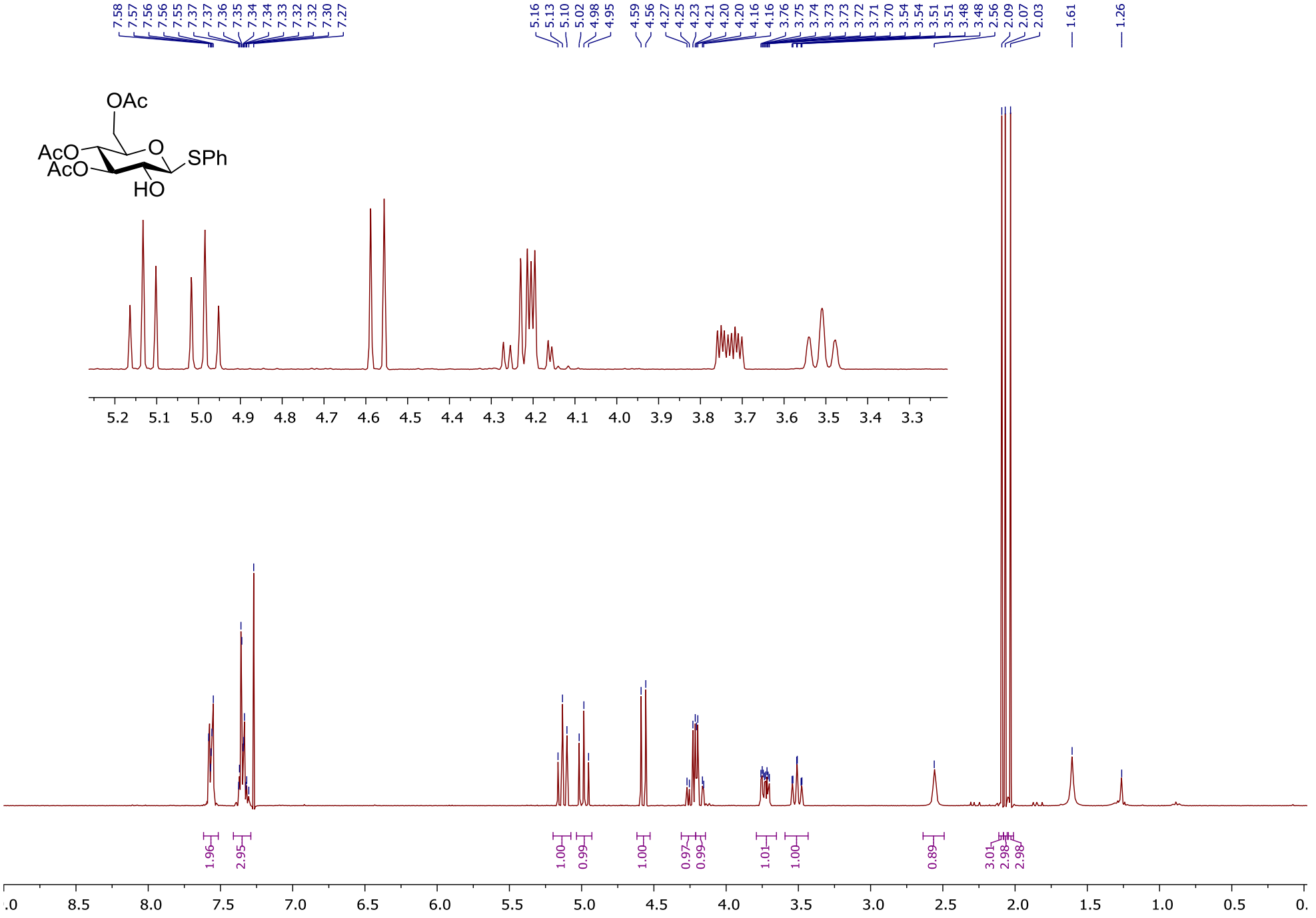
HMBC spectrum of compound 23 in $CDCl_3$ (300 MHz)

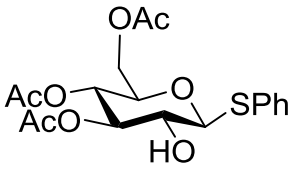


DEPT spectrum of compound 23 in $CDCl_3$ (75 MHz)

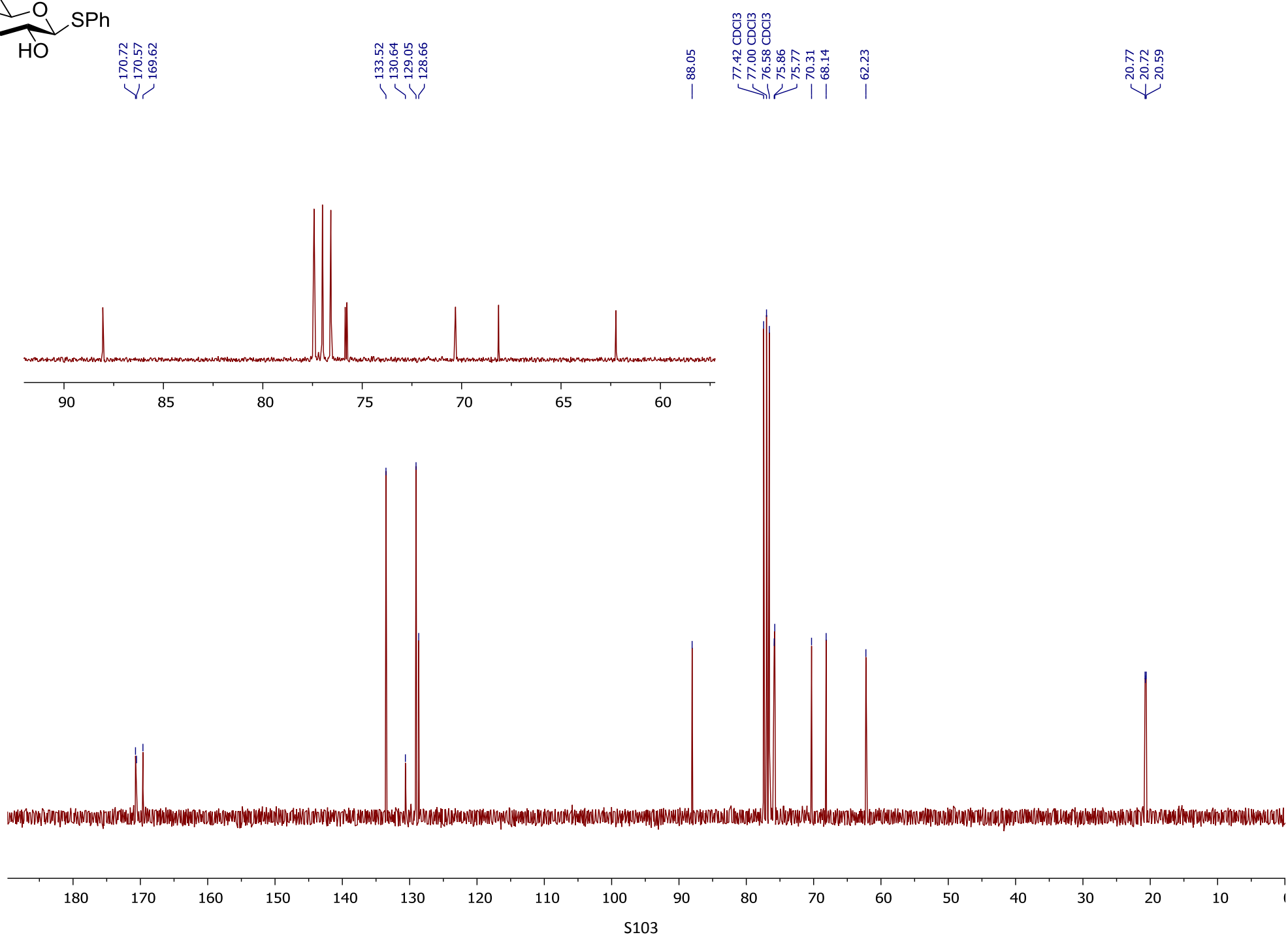


^{1}H NMR (300 MHz) spectrum of compound 24 in $CDCl_3$

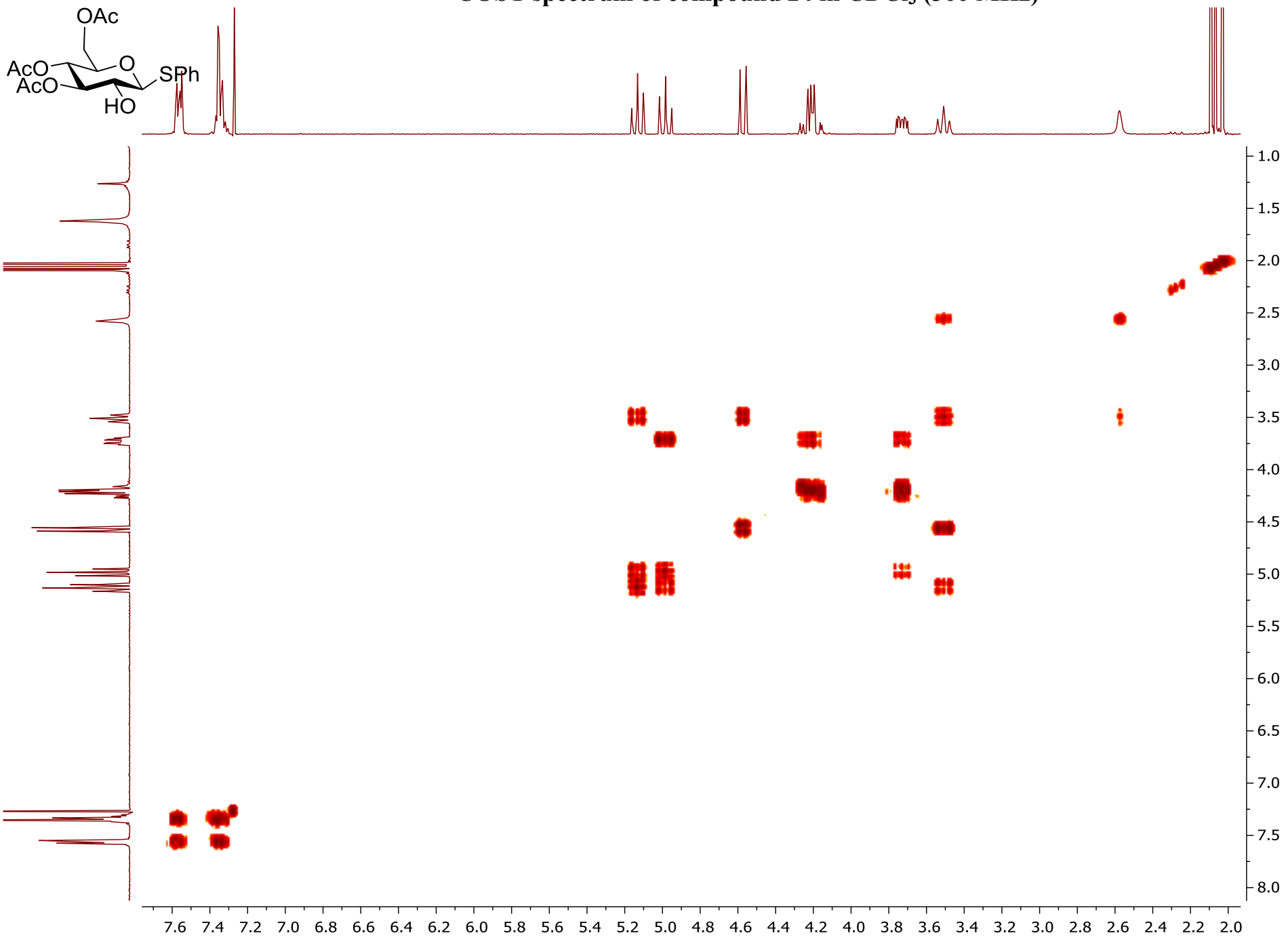




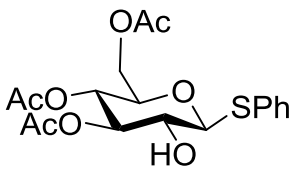
^{13}C NMR (75 MHz) spectrum of compound 24 in $CDCl_3$



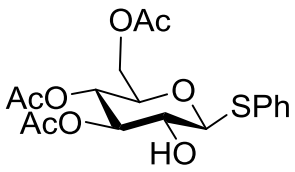
COSY spectrum of compound 24 in $CDCl_3$ (300 MHz)

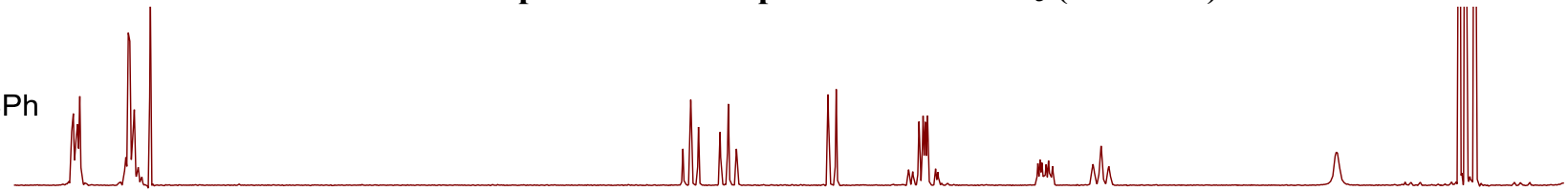


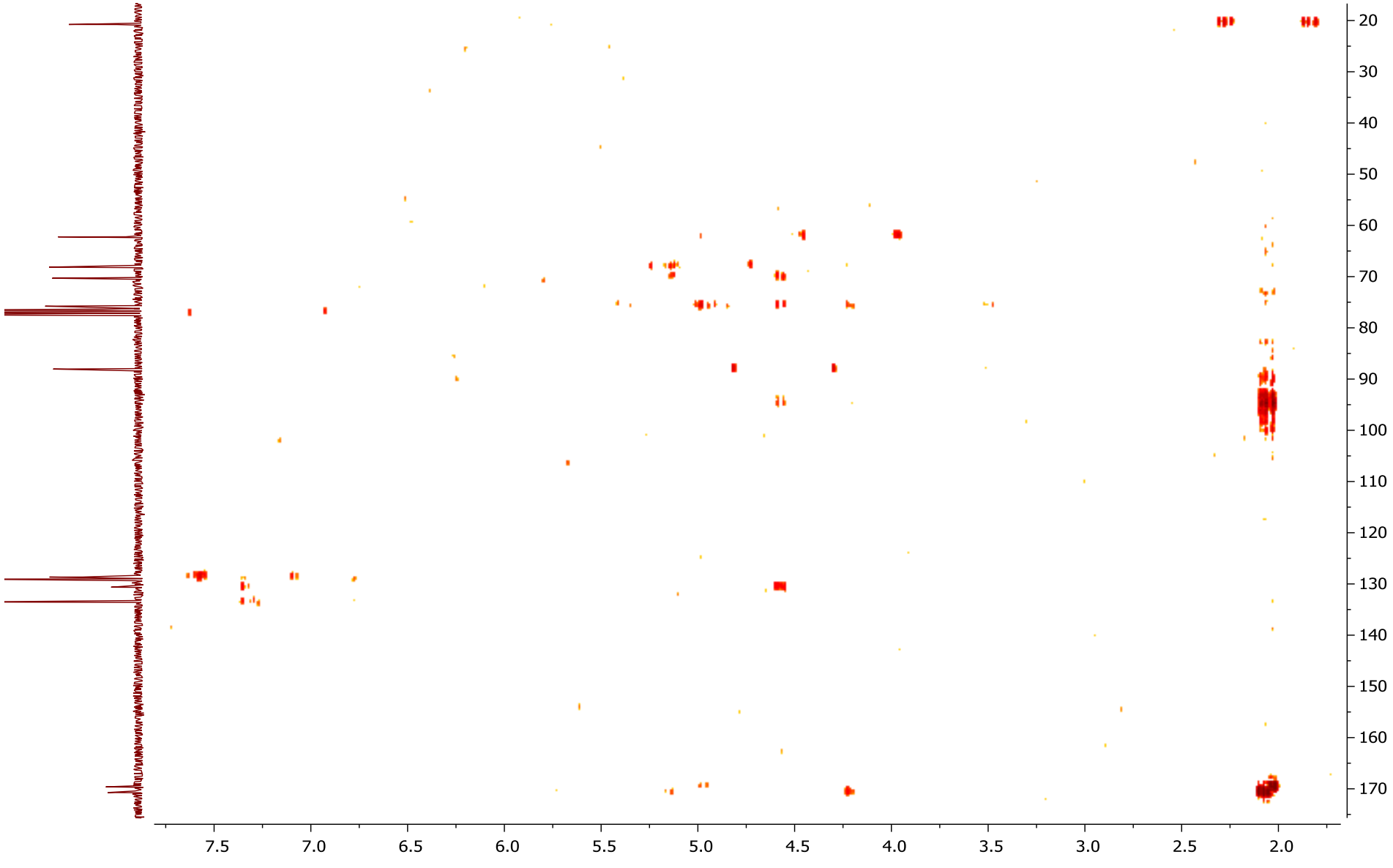
HSQC spectrum of compound 24 in $CDCl_3$ (300 MHz)



HMBC spectrum of compound 24 in $CDCl_3$ (300 MHz)







DEPT spectrum of compound 24 in $CDCl_3$ (75 MHz)