**Supporting Information of the Manuscript: "Highly Diastereoselective Oxidation of 2-amino-2-deoxy-1-thio-β-D-Glucopyranosides: Synthesis of Imino Sulfinylglycosides"**

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- X-Ray data of compound **15*S*$_S$**
- Copies of $^1$H (500 MHZ) and the $^{13}$C NMR (125 MHz) spectra of compounds:
  - **3** ($^1$H and the $^{13}$C NMR).
  - **8** ($^1$H NMR)
  - **9*R/S*** ($^1$H and the $^{13}$C NMR)
  - **13** ($^1$H NMR)
  - **14*R/S*** ($^1$H NMR)
  - **17*S*$_S$** ($^1$H NMR)
  - **9*S*$_S$** ($^1$H and the $^{13}$C NMR)
  - **14*S*$_S$** ($^1$H and the $^{13}$C NMR)
  - **22** ($^1$H NMR)
  - **24** ($^1$H NMR)

**Crystal data for 15*S*$_S$**: $C_{22}H_{21}Cl_4NO_{10}S$, 0.59($H_2O$), $M_r$ = 643.79, colourless needle (0.68 × 0.11 × 0.09 mm) from hexanes /ethyl acetate, monoclinic, space group *P21* (no. 4), a = 6.169(10) Å, b = 11.94(2) Å, c = 19.10(3) Å, $\beta$ = 93.59(4)°, $V$ = 1404(4) Å$^3$, $Z$ = 2, $D_x$ = 1.523 Mg/m$^3$, $\lambda$(Mo Kα) = 0.71073 Å, $\mu$ = 0.552 mm$^{-1}$, $T$ = 100(2) K.

X-ray diffraction data were collected on a Bruker SMART diffractometer equipped with a APEX CCD detector, graphite monochromated Mo Kα radiation, and a Kryoflex low-temperature device.[1] Four sets of frames covering a hemisphere of the reciprocal space were recorded (606, 435, 230 y 100 frames to φ = 0º, 90º, 180º and 0º respectively, ω-scans, Δω = 0.3°, time per frame 10 s). Data reduction up to $\theta$ = 30° by program SAINT, corrections for absorption with program SADABS, 6248 reflections measured, 3286 independent, $R_{int}$ = 0.038.[1] Structure solution with direct methods and program SHELXS97, structure refinement on $F^2$ using program SHELXL97.[2]

The asymmetric unit of the structure is formed by one molecule of **15*S*$_S$** and one structural water molecule with an occupancy factor refined to 0.58. This water molecule appears to be hydrogen bonded to the carbonyl oxygen ($O_9$) of the tetrachlorophtalimide moiety [displaying $H_{11Aw}\cdots O_9$ and $O_{11w}\cdots O_9$ distances of 2.03(3) Å and 3.00(10) Å, respectively, and an $O_{11w}$-$H_{11Aw}\cdots O_9$ angle of 176(13)º ] and on to the carbonyl oxygen ($O_{7A}$) of an acetate moiety of a second symmetrical **15*S*$_S$** disordered in two positions. The occupancy factors for this disordered moiety $O_{7A}$ was refined to 0.58, displaying $H_{11Bw}\cdots O_{7A}$ and $O_{11w}\cdots O_{7A}$ distances of 2.25(13) Å and 2.99(2) Å, respectively, and an $O_{11w}$-$H_{11Bw}\cdots O_{7A}$ angle of 131(13)º.

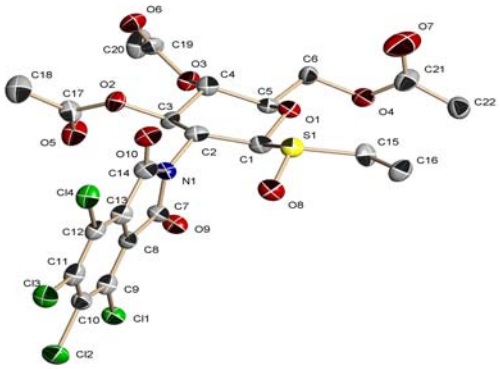
All non-hydrogen atoms were refined with anisotropic displacement parameters. The $O_{11w}$-bound hydrogen atoms $H_{11Aw}$ and $H_{11Bw}$ of the water molecule, located on a difference Fourier map, were refined with isotropic displacement parameters and geometric restraints (DFIX commands). All the others hydrogen atoms were included from calculated positions and refined riding on the atoms which they are bonded with isotropic thermal parameter. Final refinement with 3286 data, 3 restraints, and 385 parameters gave $R1$ = 0.0600, $wR2$ = 0.0983 (all data), and $R1$ = 0.0490, $wR2$ = 0.0949 [$I > 2\sigma(I)$], (S = 1.007). The highest residual peak, 0.960 Å$^{-3}$, and deepest hole, -0.245 Å$^{-3}$, were located close to the heavier atoms S1 and Cl3 and have no chemical sense.

The absolute structure was determined by examination of the Flack parameter x = -0.11(9). The results of configurational analysis by X-ray crystallographic

examination of **15*S*$_S$** showed that this molecule possesses the S-configuration at sulfur as shown in the ORTEP representation in Figure 1**.**


1. Bruker, Programs SMART, version 5.054; SAINT, version 6.2.9; SADABS version 2.03; XPREP, version 5.1; SHELXTL, version 5.1. / Bruker AXS Inc., Madison, WI, USA, 2001.
2. G.M. Sheldrick, Programs SHELXS97 (crystal structure solution) and SHELXL97 (crystal structure refinement), University of Göttingen, Germany, 1997.


**Figure 1**[a]




[a]ORTEP drawing of $S_S$of sulfoxide **15***S*$_s$

**Table 1**. Crystal data and structure refinement for **15*S*$_S$**.

| | | |
|---|---|---|
| Empirical formula | C22 H22.17 Cl4 N O10.59 S | |
| Formula weight | 643.79 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21 | |
| Unit cell dimensions | a = 6.169(10) Å | α= 90°. |
| | b = 11.94(2) Å | β= 93.59(4)°. |
| | c = 19.10(3) Å | γ = 90°. |
| Volume | 1404(4) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.523 Mg/m$^3$ | |
| Absorption coefficient | 0.552 mm$^{-1}$ | |
| F(000) | 660 | |
| Crystal size | 0.68 x 0.11 x 0.09 mm$^3$ | |
| Theta range for data collection | 2.01 to 23.23°. | |
| Index ranges | -6<=h<=6, -12<=k<=13, -21<=l<=19 | |
| Reflections collected | 6248 | |
| Independent reflections | 3286 [R(int) = 0.0383] | |
| Completeness to theta = 23.23° | 99.4 % | |
| Max. and min. transmission | 0.9541 and 0.7053 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3286 / 3 / 385 | |
| Goodness-of-fit on F$^2$ | 1.007 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0490, wR2 = 0.0949 | |
| R indices (all data) | R1 = 0.0600, wR2 = 0.0983 | |
| Absolute structure parameter | -0.11(9) | |
| Largest diff. peak and hole | 0.960 and -0.245 e.Å$^{-3}$ | |

**Table 2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **15*S*$_S$**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 5892(2) | 5750(1) | 1974(1) | 25(1) |
| Cl(2) | 2658(3) | 6933(1) | 859(1) | 35(1) |
| Cl(3) | -1490(3) | 5668(2) | 237(1) | 33(1) |
| Cl(4) | -2566(2) | 3248(1) | 788(1) | 29(1) |
| S(1) | 4630(3) | 44(1) | 1542(1) | 22(1) |
| O(1) | 6171(6) | -362(3) | 2845(2) | 19(1) |
| O(2) | 1903(6) | 1734(3) | 3769(2) | 23(1) |
| O(3) | 5747(6) | 671(4) | 4627(2) | 23(1) |
| O(4) | 9956(7) | -1293(4) | 3510(2) | 25(1) |
| O(5) | 3391(7) | 3075(4) | 4492(2) | 37(1) |
| O(6) | 2493(8) | 218(4) | 5048(2) | 38(1) |
| O(7A) | 8750(50) | -3085(18) | 3307(13) | 69(7) |
| O(11) | 10195(15) | 4559(8) | 3087(5) | 42(4) |
| O(7B) | 8300(60) | -2750(20) | 3095(13) | 34(6) |
| O(8) | 4423(7) | 1051(3) | 1083(2) | 29(1) |
| O(9) | 6121(6) | 3298(4) | 2642(2) | 24(1) |
| O(10) | -218(7) | 1575(4) | 1838(2) | 26(1) |
| N(1) | 3020(7) | 2232(4) | 2369(2) | 18(1) |
| C(1) | 5523(10) | 586(5) | 2435(3) | 21(1) |
| C(2) | 3599(10) | 1190(5) | 2740(3) | 18(1) |
| C(3) | 4001(9) | 1434(6) | 3539(3) | 20(2) |
| C(4) | 4947(10) | 384(5) | 3918(3) | 20(2) |
| C(5) | 6935(9) | -14(6) | 3539(3) | 18(1) |
| C(6) | 8081(10) | -1003(6) | 3893(3) | 28(2) |
| C(7) | 4344(9) | 3187(5) | 2328(3) | 18(1) |
| C(8) | 3107(9) | 3968(5) | 1831(3) | 16(1) |
| C(9) | 3587(9) | 5067(6) | 1627(3) | 21(2) |
| C(10) | 2137(10) | 5583(6) | 1141(3) | 23(2) |
| C(11) | 239(10) | 5035(6) | 861(3) | 24(2) |
| C(12) | -249(10) | 3934(5) | 1087(3) | 20(2) |
| C(13) | 1221(9) | 3437(5) | 1578(3) | 18(1) |
| C(14) | 1162(10) | 2307(6) | 1904(3) | 23(2) |
| C(15) | 7104(10) | -689(6) | 1362(3) | 26(2) |

| | | | | |
|---|---|---|---|---|
| C(16) | 7083(11) | -989(6) | 585(3) | 33(2) |
| C(17) | 1817(11) | 2587(5) | 4241(3) | 23(2) |
| C(18) | -521(10) | 2793(6) | 4403(4) | 41(2) |
| C(19) | 4363(11) | 526(6) | 5154(3) | 29(2) |
| C(20) | 5467(11) | 803(7) | 5855(3) | 42(2) |
| C(21) | 9969(12) | -2262(6) | 3166(3) | 33(2) |
| C(22) | 11893(11) | -2399(6) | 2740(3) | 34(2) |

**Table 3**. Bond lengths [Å] and angles [°] for **15*S*$_S$**.

| | | | |
|---|---|---|---|
| Cl(1)-C(9) | 1.735(6) | C(6)-H(6A) | 0.9416 |
| Cl(2)-C(10) | 1.736(7) | C(6)-H(6B) | 0.9416 |
| Cl(3)-C(11) | 1.724(6) | C(7)-C(8) | 1.503(8) |
| Cl(4)-C(12) | 1.715(7) | C(8)-C(13) | 1.385(8) |
| S(1)-O(8) | 1.488(4) | C(8)-C(9) | 1.405(9) |
| S(1)-C(15) | 1.811(7) | C(9)-C(10) | 1.393(8) |
| S(1)-C(1) | 1.876(6) | C(10)-C(11) | 1.416(9) |
| O(1)-C(1) | 1.419(7) | C(11)-C(12) | 1.422(9) |
| O(1)-C(5) | 1.441(6) | C(12)-C(13) | 1.395(8) |
| O(2)-C(17) | 1.364(7) | C(13)-C(14) | 1.487(9) |
| O(2)-C(3) | 1.438(7) | C(15)-C(16) | 1.526(8) |
| O(3)-C(19) | 1.372(7) | C(15)-H(15A) | 0.9342 |
| O(3)-C(4) | 1.454(7) | C(15)-H(15B) | 0.9342 |
| O(4)-C(21) | 1.331(8) | C(16)-H(16A) | 0.9676 |
| O(4)-C(6) | 1.449(7) | C(16)-H(16B) | 0.9676 |
| O(5)-C(17) | 1.205(7) | C(16)-H(16C) | 0.9676 |
| O(6)-C(19) | 1.216(8) | C(17)-C(18) | 1.514(9) |
| O(7A)-C(21) | 1.28(3) | C(18)-H(18A) | 0.9471 |
| O(11)-H(11A) | 0.98(2) | C(18)-H(18B) | 0.9471 |
| O(11)-H(11B) | 0.98(2) | C(18)-H(18C) | 0.9471 |
| O(7B)-C(21) | 1.19(3) | C(19)-C(20) | 1.500(9) |
| O(9)-C(7) | 1.224(7) | C(20)-H(20A) | 0.8641 |
| O(10)-C(14) | 1.221(7) | C(20)-H(20B) | 0.8641 |
| N(1)-C(7) | 1.408(8) | C(20)-H(20C) | 0.8641 |
| N(1)-C(14) | 1.408(7) | C(21)-C(22) | 1.489(9) |
| N(1)-C(2) | 1.465(7) | C(22)-H(22A) | 0.9051 |
| C(1)-C(2) | 1.534(8) | C(22)-H(22B) | 0.9051 |
| C(1)-H(1) | 0.9488 | C(22)-H(22C) | 0.9051 |
| C(2)-C(3) | 1.557(8) | | |
| C(2)-H(2) | 0.9735 | O(8)-S(1)-C(15) | 108.7(3) |
| C(3)-C(4) | 1.543(9) | O(8)-S(1)-C(1) | 105.5(3) |
| C(3)-H(3) | 0.9841 | C(15)-S(1)-C(1) | 97.8(3) |
| C(4)-C(5) | 1.537(8) | C(1)-O(1)-C(5) | 110.0(4) |
| C(4)-H(4) | 1.0931 | C(17)-O(2)-C(3) | 117.4(5) |
| C(5)-C(6) | 1.514(8) | C(19)-O(3)-C(4) | 117.6(5) |
| C(5)-H(5) | 0.9979 | C(21)-O(4)-C(6) | 119.1(5) |

| | | | |
|---|---|---|---|
| H(11A)-O(11)-H(11B) | 110(10) | C(5)-C(6)-H(6B) | 109.9 |
| C(7)-N(1)-C(14) | 111.4(5) | H(6A)-C(6)-H(6B) | 108.3 |
| C(7)-N(1)-C(2) | 126.2(5) | O(9)-C(7)-N(1) | 124.4(6) |
| C(14)-N(1)-C(2) | 121.6(5) | O(9)-C(7)-C(8) | 130.2(6) |
| O(1)-C(1)-C(2) | 111.3(5) | N(1)-C(7)-C(8) | 105.3(5) |
| O(1)-C(1)-S(1) | 106.5(4) | C(13)-C(8)-C(9) | 121.2(5) |
| C(2)-C(1)-S(1) | 108.5(4) | C(13)-C(8)-C(7) | 108.6(5) |
| O(1)-C(1)-H(1) | 110.2 | C(9)-C(8)-C(7) | 130.2(5) |
| C(2)-C(1)-H(1) | 110.2 | C(10)-C(9)-C(8) | 117.4(6) |
| S(1)-C(1)-H(1) | 110.2 | C(10)-C(9)-Cl(1) | 121.6(5) |
| N(1)-C(2)-C(1) | 112.7(5) | C(8)-C(9)-Cl(1) | 121.0(5) |
| N(1)-C(2)-C(3) | 109.5(5) | C(9)-C(10)-C(11) | 122.0(6) |
| C(1)-C(2)-C(3) | 112.3(5) | C(9)-C(10)-Cl(2) | 119.6(5) |
| N(1)-C(2)-H(2) | 107.3 | C(11)-C(10)-Cl(2) | 118.5(5) |
| C(1)-C(2)-H(2) | 107.3 | C(10)-C(11)-C(12) | 119.9(6) |
| C(3)-C(2)-H(2) | 107.3 | C(10)-C(11)-Cl(3) | 121.3(5) |
| O(2)-C(3)-C(4) | 112.3(5) | C(12)-C(11)-Cl(3) | 118.8(5) |
| O(2)-C(3)-C(2) | 104.7(5) | C(13)-C(12)-C(11) | 117.2(6) |
| C(4)-C(3)-C(2) | 109.9(5) | C(13)-C(12)-Cl(4) | 120.9(5) |
| O(2)-C(3)-H(3) | 109.9 | C(11)-C(12)-Cl(4) | 121.9(5) |
| C(4)-C(3)-H(3) | 109.9 | C(8)-C(13)-C(12) | 122.4(6) |
| C(2)-C(3)-H(3) | 109.9 | C(8)-C(13)-C(14) | 108.1(5) |
| O(3)-C(4)-C(5) | 106.1(5) | C(12)-C(13)-C(14) | 129.4(6) |
| O(3)-C(4)-C(3) | 110.0(5) | O(10)-C(14)-N(1) | 123.6(6) |
| C(5)-C(4)-C(3) | 108.6(4) | O(10)-C(14)-C(13) | 129.9(6) |
| O(3)-C(4)-H(4) | 110.7 | N(1)-C(14)-C(13) | 106.4(5) |
| C(5)-C(4)-H(4) | 110.7 | C(16)-C(15)-S(1) | 110.0(4) |
| C(3)-C(4)-H(4) | 110.7 | C(16)-C(15)-H(15A) | 109.7 |
| O(1)-C(5)-C(6) | 107.6(5) | S(1)-C(15)-H(15A) | 109.7 |
| O(1)-C(5)-C(4) | 107.3(5) | C(16)-C(15)-H(15B) | 109.7 |
| C(6)-C(5)-C(4) | 113.3(5) | S(1)-C(15)-H(15B) | 109.7 |
| O(1)-C(5)-H(5) | 109.5 | H(15A)-C(15)-H(15B) | 108.2 |
| C(6)-C(5)-H(5) | 109.5 | C(15)-C(16)-H(16A) | 109.5 |
| C(4)-C(5)-H(5) | 109.5 | C(15)-C(16)-H(16B) | 109.5 |
| O(4)-C(6)-C(5) | 109.0(5) | H(16A)-C(16)-H(16B) | 109.5 |
| O(4)-C(6)-H(6A) | 109.9 | C(15)-C(16)-H(16C) | 109.5 |
| C(5)-C(6)-H(6A) | 109.9 | H(16A)-C(16)-H(16C) | 109.5 |
| O(4)-C(6)-H(6B) | 109.9 | H(16B)-C(16)-H(16C) | 109.5 |

| | |
|---|---|
| O(5)-C(17)-O(2) | 124.1(6) |
| O(5)-C(17)-C(18) | 126.5(5) |
| O(2)-C(17)-C(18) | 109.4(5) |
| C(17)-C(18)-H(18A) | 109.5 |
| C(17)-C(18)-H(18B) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |
| C(17)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |
| O(6)-C(19)-O(3) | 122.9(6) |
| O(6)-C(19)-C(20) | 126.1(6) |
| O(3)-C(19)-C(20) | 111.0(6) |
| C(19)-C(20)-H(20A) | 109.5 |
| C(19)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 |
| C(19)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |
| O(7B)-C(21)-O(7A) | 28.9(15) |
| O(7B)-C(21)-O(4) | 117.1(16) |
| O(7A)-C(21)-O(4) | 122.9(13) |
| O(7B)-C(21)-C(22) | 126.8(16) |
| O(7A)-C(21)-C(22) | 122.0(13) |
| O(4)-C(21)-C(22) | 113.3(6) |
| C(21)-C(22)-H(22A) | 109.5 |
| C(21)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| C(21)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

**Table 4**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **15*S*$_S$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Cl(1) | 22(1) | 21(1) | 32(1) | 1(1) | 4(1) | -2(1) |
| Cl(2) | 41(1) | 26(1) | 37(1) | 9(1) | 7(1) | 4(1) |
| Cl(3) | 34(1) | 41(1) | 22(1) | 6(1) | -1(1) | 12(1) |
| Cl(4) | 19(1) | 42(1) | 26(1) | -8(1) | -4(1) | 3(1) |
| S(1) | 25(1) | 25(1) | 17(1) | -3(1) | 1(1) | 2(1) |
| O(1) | 23(2) | 17(2) | 19(2) | 1(2) | 2(2) | 1(2) |
| O(2) | 18(2) | 26(3) | 25(2) | -6(2) | 8(2) | -3(2) |
| O(3) | 26(2) | 27(3) | 16(2) | -3(2) | 7(2) | -3(2) |
| O(4) | 21(2) | 21(3) | 34(2) | 0(2) | 8(2) | 1(2) |
| O(5) | 22(3) | 42(3) | 47(3) | -21(3) | 6(2) | -2(3) |
| O(6) | 38(3) | 44(3) | 34(3) | 3(2) | 18(2) | -2(3) |
| O(7A) | 78(15) | 20(11) | 115(19) | -6(9) | 53(14) | -13(9) |
| O(11) | 40(6) | 39(7) | 48(6) | -16(5) | 8(4) | -14(5) |
| O(7B) | 49(13) | 21(15) | 33(9) | 0(8) | 26(8) | -17(11) |
| O(8) | 39(3) | 22(3) | 24(2) | 4(2) | 1(2) | 1(2) |
| O(9) | 21(2) | 20(3) | 29(2) | -1(2) | -4(2) | -2(2) |
| O(10) | 19(2) | 25(3) | 33(2) | -1(2) | 5(2) | -6(2) |
| N(1) | 17(3) | 17(3) | 19(3) | -2(2) | 2(2) | -5(2) |
| C(1) | 18(3) | 20(4) | 24(3) | -3(3) | 3(3) | -10(3) |
| C(2) | 16(3) | 15(4) | 23(3) | 1(3) | 3(3) | 1(3) |
| C(3) | 9(3) | 24(4) | 27(3) | -1(3) | 4(3) | -3(3) |
| C(4) | 20(4) | 21(4) | 21(3) | 2(3) | 2(3) | -4(3) |
| C(5) | 17(3) | 18(3) | 19(3) | -2(3) | 1(3) | -4(3) |
| C(6) | 30(4) | 33(4) | 23(3) | 2(3) | 13(3) | 5(3) |
| C(7) | 23(3) | 17(4) | 15(3) | -6(3) | 3(3) | -2(3) |
| C(8) | 9(3) | 22(4) | 16(3) | -4(3) | 5(2) | 0(3) |
| C(9) | 15(3) | 35(4) | 12(3) | -8(3) | 3(3) | 2(3) |
| C(10) | 23(3) | 25(4) | 22(3) | -2(3) | 17(3) | 2(3) |
| C(11) | 27(4) | 34(4) | 12(3) | -7(3) | 9(3) | 13(3) |
| C(12) | 17(3) | 24(4) | 19(3) | -7(3) | 10(3) | 3(3) |
| C(13) | 14(3) | 21(4) | 18(3) | 0(3) | 4(3) | 4(3) |
| C(14) | 18(4) | 30(4) | 22(3) | -1(3) | 6(3) | -4(3) |
| C(15) | 29(4) | 24(4) | 25(3) | -7(3) | 2(3) | 1(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(16) | 31(4) | 43(5) | 24(4) | 1(3) | 10(3) | 1(4) |
| C(17) | 27(4) | 15(4) | 28(3) | -8(3) | 4(3) | 6(3) |
| C(18) | 23(4) | 40(5) | 59(5) | -23(4) | -1(4) | -1(4) |
| C(19) | 36(5) | 30(4) | 24(4) | 3(3) | 19(3) | 10(4) |
| C(20) | 49(5) | 54(5) | 25(4) | 1(4) | 11(3) | 16(5) |
| C(21) | 33(5) | 27(5) | 39(4) | -6(4) | 7(3) | -10(4) |
| C(22) | 27(4) | 35(5) | 39(4) | -14(4) | 8(3) | 2(3) |

**Table 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **15*S*$_S$**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(11A) | 8840(140) | 4160(120) | 2970(80) | 110(60) |
| H(11B) | 10100(300) | 5320(60) | 2890(80) | 120(80) |
| H(1) | 6710(80) | 1090(30) | 2405(3) | 25 |
| H(2) | 2350(80) | 690(30) | 2684(4) | 22 |
| H(3) | 5010(70) | 2070(40) | 3611(5) | 24 |
| H(4) | 3730(70) | -280(40) | 3925(3) | 25 |
| H(5) | 7980(60) | 620(40) | 3505(3) | 22 |
| H(6A) | 8520(20) | -819(9) | 4360(20) | 34 |
| H(6B) | 7130(40) | -1620(30) | 3900(3) | 34 |
| H(15A) | 8300(50) | -235(19) | 1484(6) | 31 |
| H(15B) | 7223(12) | -1340(30) | 1632(12) | 31 |
| H(16A) | 5920(60) | -1520(30) | 471(7) | 49 |
| H(16B) | 8460(50) | -1320(30) | 486(6) | 49 |
| H(16C) | 6850(60) | -320(20) | 306(10) | 49 |
| H(18A) | -950(30) | 2250(30) | 4730(20) | 61 |
| H(18B) | -1420(40) | 2730(40) | 3985(16) | 61 |
| H(18C) | -654(18) | 3520(30) | 4590(20) | 61 |
| H(20A) | 4500(40) | 900(40) | 6159(15) | 63 |
| H(20B) | 6210(70) | 1410(30) | 5822(7) | 63 |
| H(20C) | 6330(70) | 260(30) | 5988(14) | 63 |
| H(22A) | 12100(40) | -3140(30) | 2653(18) | 50 |
| H(22B) | 13080(50) | -2120(30) | 2980(13) | 50 |
| H(22C) | 11670(30) | -2030(30) | 2330(18) | 50 |

**Table 6**. Torsion angles [°] for **15*S*$_S$**.

| | |
|---|---|
| O(1)-C(1)-C(2)-C(3) | 50.3(7) |
| C(1)-C(2)-C(3)-C(4) | -45.3(7) |
| C(2)-C(3)-C(4)-C(5) | 52.4(6) |
| C(3)-C(4)-C(5)-O(1) | -64.8(6) |
| C(4)-C(5)-O(1)-C(2) | 39.3(5) |
| C(5)-O(1)-C(2)-C(3) | -11.8(5) |

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **15*S*$_S$** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(11)-H(11B)...O(7B)#1 | 0.98(2) | 2.60(11) | 3.41(3) | 141(13) |
| O(11)-H(11B)...O(7A)#1 | 0.98(2) | 2.25(13) | 2.99(2) | 131(13) |
| O(11)-H(11A)...O(9) | 0.98(2) | 2.03(3) | 3.006(10) | 175(14) |

Symmetry transformations used to generate equivalent atoms:

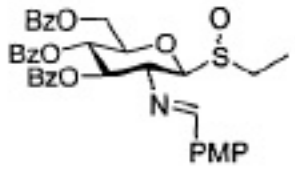
#1 x,y+1,z

Integral
1.7586
2.8488
1.9190
0.9736
0.9095
2.0728
1.0174
2.8990
3.0355
3.0419
ppm
AcO
AcO
TCPN
3
OAc
O
S
Ph

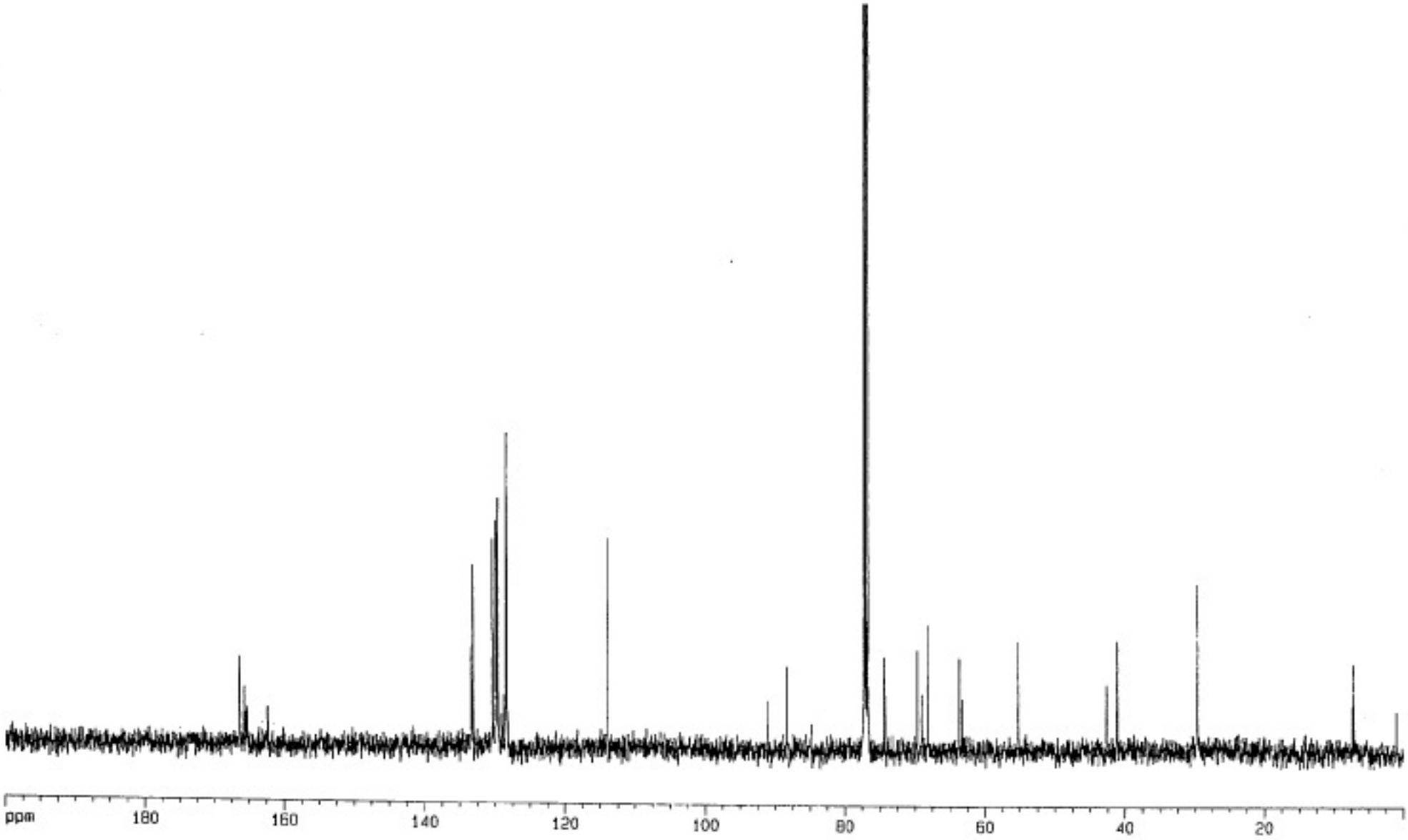
ppm
200
180
160
140
120
100
80
60
40
20
ppm
170.561
170.535
169.361
163.253
162.159
140.823
140.602
133.287
130.511
129.011
128.584
AcO
AcO
TCPN
3
OAc
O
S
Ph
77.326
77.071
75.817
75.022
71.674
68.429
62.132
54.407
20.752
20.590
20.459

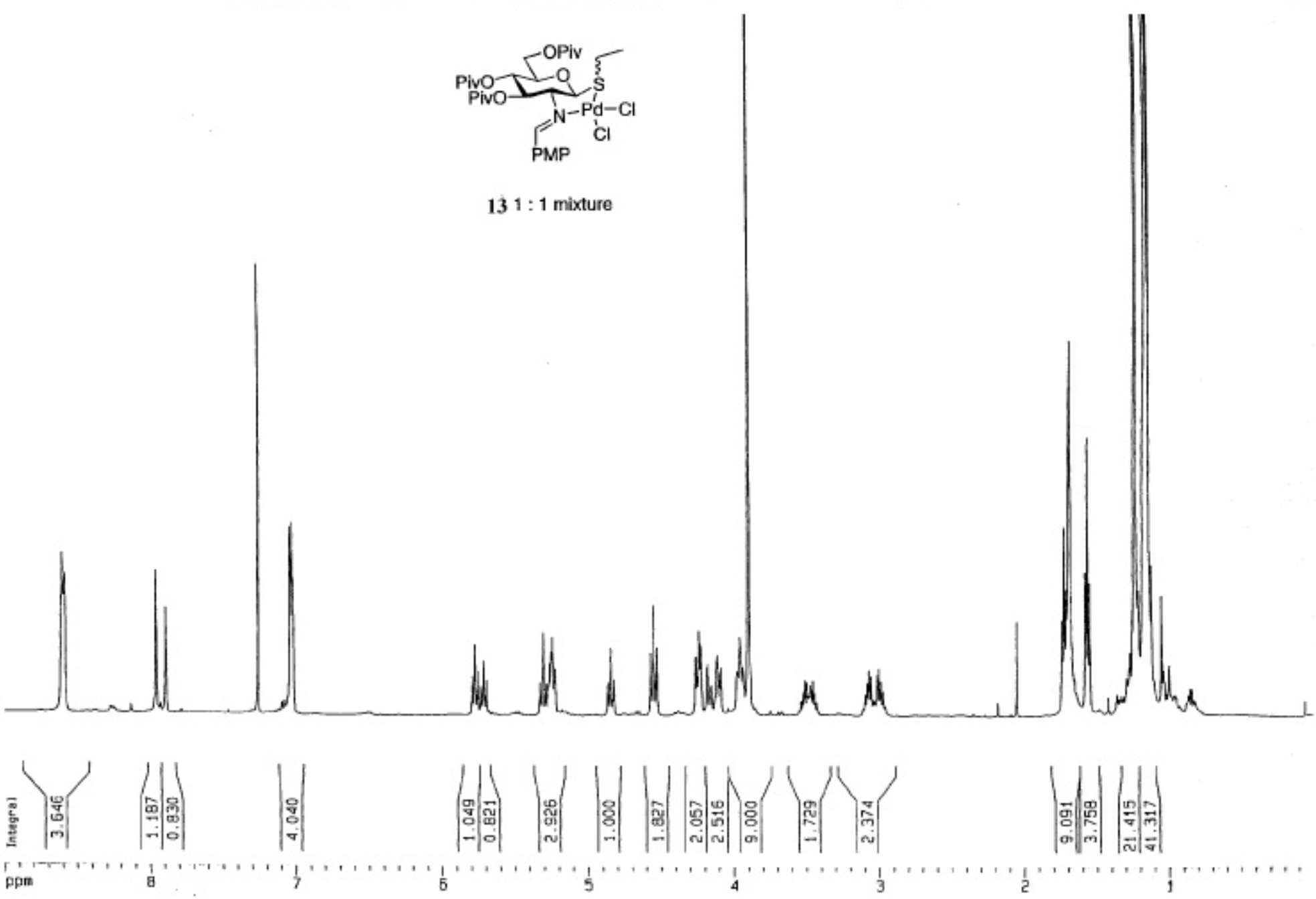
**8** 65 : 35 mixture

Integral
1.042
0.642
3.198
3.240
2.978
20.089
3.258
1.000
0.585
1.631
0.589
1.719
2.948
3.781
5.134
1.130
2.434
0.914
17.505
3.485
ppm
BzO
BzO
BzO
O
O
S
N
PMP
9 ($R_S$ : $S_S$; 65: 35)




**9** ($R_S$ : $S_S$; 65: 35)






**13** 1 : 1 mixture

ppm
Integral
1.106
0.924
3.682
3.659
1.000
0.785
1.946
0.092
0.785
2.367
0.945
2.139
4.200
6.092
1.242
1.904
0.878
1.119
29.518
19.967
18.595
PivO
PivO
PivO
O
O
S
N
PMP
14
($R_S$ : $S_S$; 55: 45)


PivO
PivO
PivO
O
O
S
TCPN

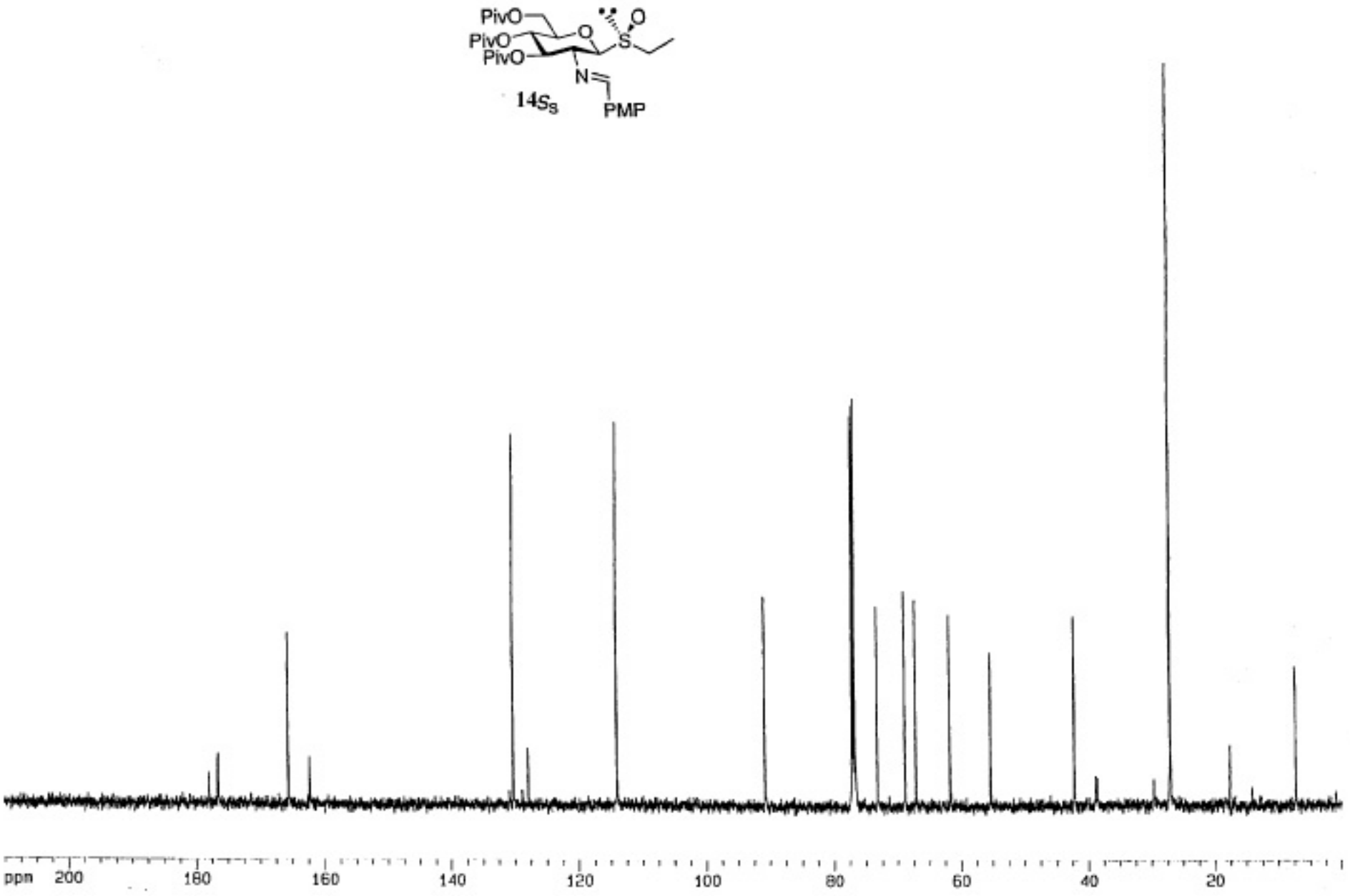
**17** $S_S$


Integral
1.089
1.113
1.187
1.029
1.249
1.269
1.243
1.203
1.209
3.496
10.008
10.300
10.242
ppm
7
6
5
4
3
2
1

Integral
1.0316
1.8012
1.8765
1.8537
6.9972
4.2580
2.0193
1.0000
1.0085
1.0400
1.0588
1.0792
2.1621
0.6838
1.1060
1.0633
1.2851
4.6664
ppm
BzO
BzO
BzO
O
N
PMP
S
O
9 Ss

ppm
200
180
160
140
120
100
80
60
40
20
BzO
BzO
BzO
O
S
N
PMP
9 Ss

Integral
1.035
1.881
1.810
0.969
0.915
1.000
0.159
1.187
2.161
3.077
0.995
1.040
12.673
8.823
8.557
ppm
PivO
PivO
PivO
O
N
PMP
S
O
14 Ss


PivO
PivO
PivO
O
S
O
N
PMP
14Ss
ppm
200
180
160
140
120
100
80
60
40
20

Integral
1.000
0.484
2.375
2.130
12.129
13.288
6.603
7.454
0.808
0.764
6.837
6.723
1.349
5.928
1.964
0.438
17.390
8.627
4.466
20.218
29.460
24.616
ppm
AcO
AcO
AcO
O
NTCP
S
O
22

Integral
41.664
3.809
2.907
0.598
1.229
3.350
0.971
1.000
0.554
2.318
4.135
5.028
0.822
4.030
0.701
11.365
16.106
13.720
AcO
AcO
AcO
O
NPht
O
S
24