## Supporting Information

# Preparation and X-ray analysis of 2,3-dichlorophenylglucosinolate

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**Table contents**



| Compound Number | Page | $^{1}$H NMR Spectrum | $^{13}$C NMR Spectrum | ORTEP Plot |
|---|---|---|---|---|
| **2** | S5 | √ | √ | |
| **3** | S6 | √ | √ | |
| **8** | S7 | √ | √ | |
| **9** | S8 | √ | √ | |
| **10** | S9 | √ | √ | |
| **11** | S10 | √ | √ | |
| **9** | S11 | | | √ |
| **11** | S12 | | | √ |

# 1. Synthesis

## 1.1. General Procedures

Melting points (mp) were recorded on a hot stage apparatus and are uncorrected. Optical rotations were measured at the stated temperatures in the stated solvent on a polarimeter at the sodium d-line (589 nm); $[\alpha]_D$ values are given in $10^{-1}$ degcm$^2$g$^{-1}$. Infrared spectra ($\nu_{max}$) were recorded on a FT-IR spectrometer. Samples were analyzed as KBr drift (for solids) or as thin films on NaCl plates (for liquids/oils). Unless otherwise specified, proton ($^1$H) and carbon ($^{13}$C) NMR spectra were recorded on a 300 MHz spectrometer operating at 300 MHz for proton and 75 MHz for carbon nuclei. Chemical shifts were recorded as $\delta$ values in parts per million (ppm). Spectra were acquired in deuterated chloroform ($CDCl_3$) at 300 K unless otherwise stated. For $^1$H NMR spectra recorded in $CDCl_3$, the peak due to residual $CHCl_3$ ($\delta_H$ 7.24) was used as the internal reference, while the central peak ($\delta_C$ 77.0) of the $CDCl_3$ triplet was used as the reference for proton-decoupled $^{13}$C NMR spectra. Low-resolution mass spectra were measured on a mass spectrometer at 300 ˚C and scan rate of 5500 *m/z*/second using either water/methanol/acetic acid in a ratio of 0/99/1 or 50/50/1 as a mobile phase. Accurate mass measurement was by mass spectrometry with a heated electrospray ionisation (HESI) source. The mass spectrometer was operated with full scan (50-1000 amu) in positive or negative FT mode (at a resolution of 100,000). The analyte was dissolved in water/methanol/acetic acid in a ratio of 0/99/1 or 50/50/1 and infused via syringe pump at a rate of 5 μl/min. The heated capillary was maintained at 320 °C with a source heater temperature of 350 °C and the sheath, auxiliary and sweep gases were at 40, 15 and 8 units respectively. Source voltage was set to 4.2 kV. Solvents were dried over standard drying agents and freshly distilled before use. Ethyl acetate and hexane used for chromatography were distilled prior to use. All solvents were purified by distillation. Reactions were monitored by TLC on silica gel 60 $F_{254}$ plates with detection by UV fluorescence or charring with a basic potassium permanganate stain. Flash column chromatography was performed on silica gel 60 particle size 0.040-0.063 μm (230–400 mesh).

## 1.2. 2,3-Dichlorobenzaldehyde oxime 2.

Hydroxylamine hydrochloride (2.50 g, 36 mmol) was added to a solution of the aldehyde **1** (5.25 g, 30 mmol) in MeOH (60 mL) followed by pyridine (3.0 mL, 30 mmol). The reaction

was stirred at rt for 2.5 h. After the MeOH was removed *in vacuo*, the residue was suspended in DCM (120 mL) and washed with 1 M HCl solution (3 × 30 mL), $H_2O$ (3 × 30 mL) and brine solution. The organic phase was dried ($Na_2SO_4$) and then concentrated at reduced pressure. The compound **2** was obtained by re-crystallization with hexane/EtOAc as white crystals (5.64 g, 99%). $R_f$ 0.61 in hexane/ethyl acetate (7:3), mp 121-122 ˚C. $\delta_H$ (300 MHz, $CDCl_3$, 300 K) 8.57 (s, 1H, CH=N), 8.13 (s, 1H, OH), 7.73 (dd, $J_{4,5}$ 8.1, 1H, H4), 7.49 (dd, $J_{5,6}$ 7.8, 1H, H6), 7.20 (dd, $J_{5,6}$ 7.8, $J_{4,5}$8.1, 1H, H5). $\delta_C$ (75 MHz, $CDCl_3$, 300 K) 147.2 (C=N), 133.4 (C-3), 131.8 (C-2), 131.5 (C-4), 131.2 (C-1), 127.1 (C-6), 125.0 (C-5). HRMS (ESI) *m/z* for $C_7H_5Cl_2NO$ $[M+H]^+$, calcd 189.9821, found 189.9813.

### 1.3. 2,3-Dichlorobenzohydroxymoyl chloride 3

One-fifth of *N*-chlorosuccinimide (4.46 g, 33.4 mmol) (CAUTION: induction period) was added initially to a solution of the oxime 2 (5.90 g, 31.4 mmol) in DMF (60 ml). The reaction was cooled and stirred in an ice bath (for about 30 minutes) for the reaction happened (as indicated by a slight temperature rise). The reaction temperature was kept under 35 ˚C, while the addition of the NCS was repeated until all the rest of NCS was added. The reaction mixture was allowed to reach rt over 4 h. After that, the reaction mixture was poured into ice-water and extracted with $Et_2O$ (3 × 20 ml). The organic layers were washed with water, dried over $MgSO_4$ and concentrated under reduced pressure. The pure hydroxymoyl chloride **3** obtained by chromatograph eluting with 80% hexane/EtOAc as white crystals (6.04 g, 87%). $R_f$ 0.63 in hexane/ethyl acetate (2:3), mp 112-113 ˚C. $\nu_{max}$ (NaCl)/$cm^{-1}$ 3392 (OH), 1629 (C=N), 1462, 1409, 1242. $\delta_H$ (300 MHz, $CDCl_3$, 300 K) 8.76 (s, 1H, OH), 7.55 (d, *J* 8.1, 1H, H4), 7.36 (d, *J* 7.8, 1H, H6), 7.27 (dd, $J_{4,5}$ 8.1, $J_{5,6}$ 7.8, 1H, H5). $\delta_C$ (75 MHz, $CDCl_3$, 300 K) 136.4 (C=N), 134.2 (C-3), 133.8 (C-2), 131.7 (C-4), 131.6 (C-1), 128.8 (C-6), 127.1 (C-5). HRMS (ESI) *m/z* for $C_7H_5Cl_3NO$ $[M+H]^+$, calcd 223.9431, found 223.9421.

### 1.4.2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl thiol 8

To a solution of D-glucose **4** (3.00 g, 16.6 mmol) in dry pyridine (33 mL) at 0 ˚C under a nitrogen atmosphere was slowly added acetic anhydride (31.5 mL, 333 mmol). The reaction mixture was stirred at 0 ˚C for 1 h before a catalytic amount of DMAP (200 mg, 1.67 mmol) was added. As the reaction mixture was allowed to reach rt, it becomes slightly exothermic.

After 6 h, the clear yellow mixture was slowly poured into rapidly stirred ice-water (125 mL), giving a sticky solid. After EtOAc extraction (3 × 45 mL), evaporation of the solvent and co-evaporations with dry toluene (3 × 20 mL), peracetylated glucose was obtained as a yellow solid (5.84 g, 90%). A solution of pentaacetyl-D-glucopyranose **5** (2.00 g, 5.1 mmol) in DCM (20 mL) was stirred in an ice bath while HBr/HOAc (6 mL, 45 wt%) was added drop-wise. After an hour, the solution was washed with ice-water and cold saturated $NaHCO_3$ solution, dried over $MgSO_4$ and concentrated to leave the glucosyl bromide **6** as a pale yellow oil (1.83 g). The oil was dissolved in dry acetone (20 mL), and the solution was added to freshly activated 4Å molecular sieves (2 g) and thiourea (500 mg, 6.6 mmol). The mixture was maintained at reflux temperature (60 ˚C) under a nitrogen atmosphere for 2.5 h, cooled and filtered through Celite. Solvent removal and trituration of the syrupy residue with hexane (3 × 20 mL) gave the isothiouronium bromide 7 as a colorless amorphous power. The crude product was dissolved in DCM (20 mL), a solution of $Na_2S_2O_5$ (2.00 g) in water (20 mL) was added, and the mixture was maintained at reflux under a nitrogen atmosphere for an hour. After cooling, the organic layer was separated and washed with water, saturated NaCl solution, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to give a residue. Pure **8** was obtained by flash column chromatography on silica gel eluting with 0-3% MeOH/DCM as a solid (1.60 g, 86%). $R_f$ 0.3 in 50% hexane/EtOAc, mp 114–115 ˚C (Lit. 113–114 ˚C)(Fujihira *et al.*, 2003). $[\alpha]_D^{20}$ +10.5 (*c* 1.0, $CHCl_3$) (Lit. +11)(Fujihira *et al.*, 2003). $\delta_H$ (300 MHz, $CDCl_3$, 300 K) 5.02–5.18 (m, 2H, H3 and H4), 4.93 (dd, $J_{1,2}$ 9.6, $J_{2,3}$ 9.3, 1H, H2), 4.51 (dd,$J_{1,2}$ 9.6, $J_{1,SH}$ 9.9, 1H, H1), 4.23 (dd, $J_{5,6b}$ 4.8, $J_{6a,6b}$ 12.3, 1H, H6b), 4.11 (dd, $J_{5,6a}$ 2.4, $J_{6a,6b}$ 12.3, 1H, H6b), 3.66–3.17 (m, 1H, H5), 2.29 (d, $J_{1,SH}$ 9.9, 1H, SH), 1.96–2.08 (4 × br s, 12H, $CH_3COO$). $\delta_C$ (75 MHz, $CDCl_3$, 300 K) 170.2, 169.7, 169.2, 168.9 (4 × $CH_3COO$), 87.3 (C-1), 75.9 (C-3), 73.2 (C-2, C-3), 67.7 (C-4), 61.6 (C-6), 20.6, 20.3(2), 20.2 (4 × $CH_3COO$). HRMS (ESI) *m/z* for $C_{14}H_{19}O_9S$ $[M-H]^-$, calcd 363.0755, found 363.0746.

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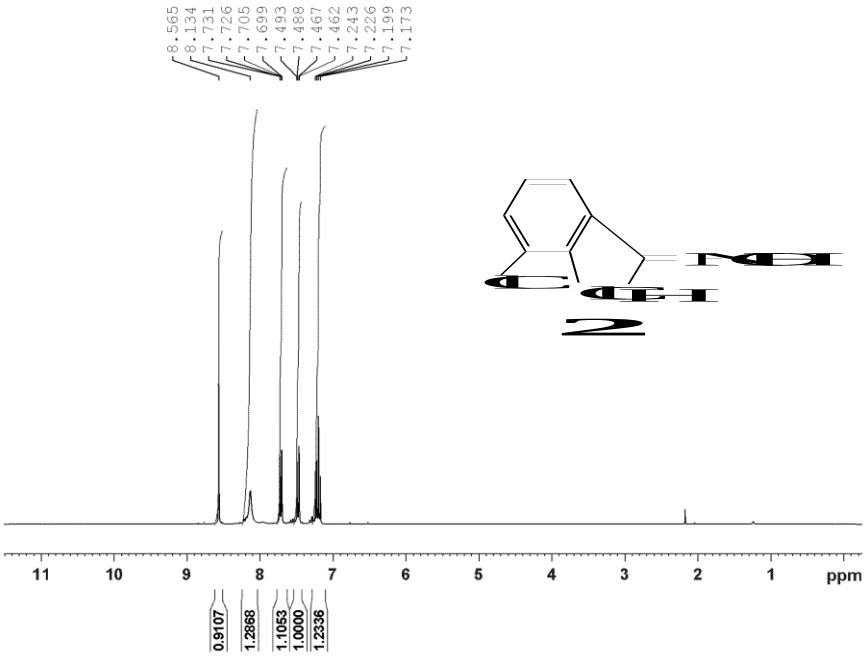





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TD0                     1

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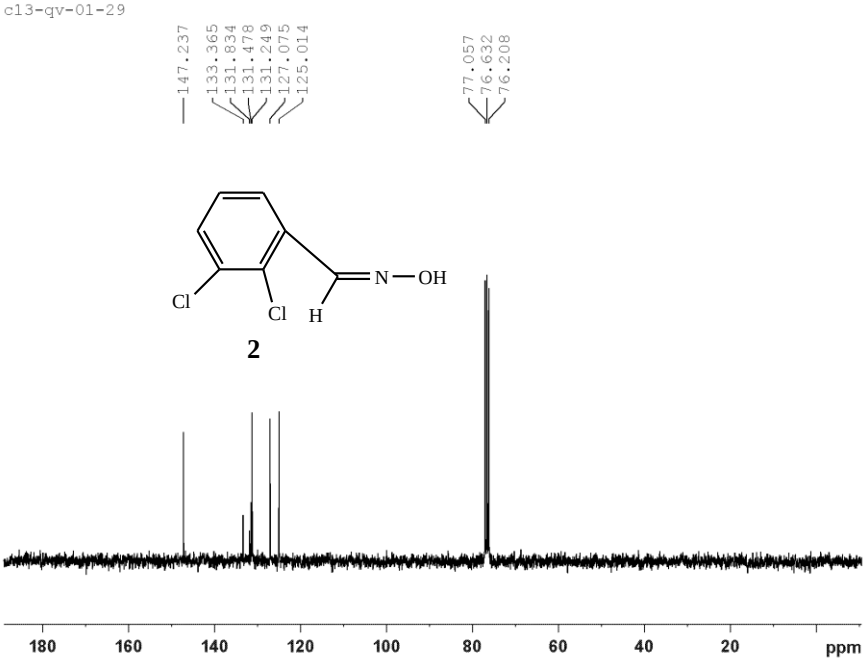


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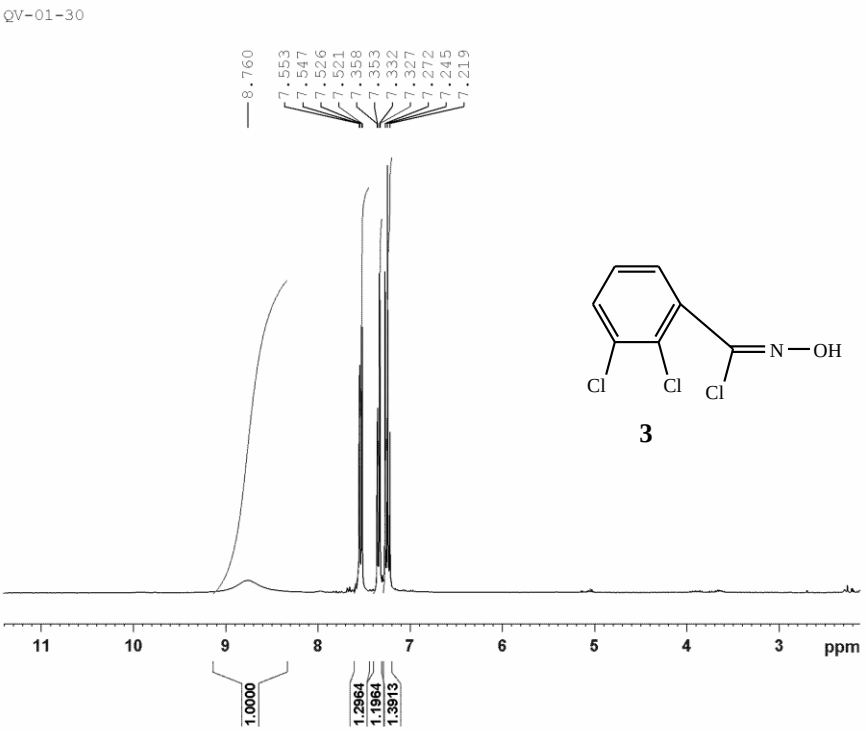


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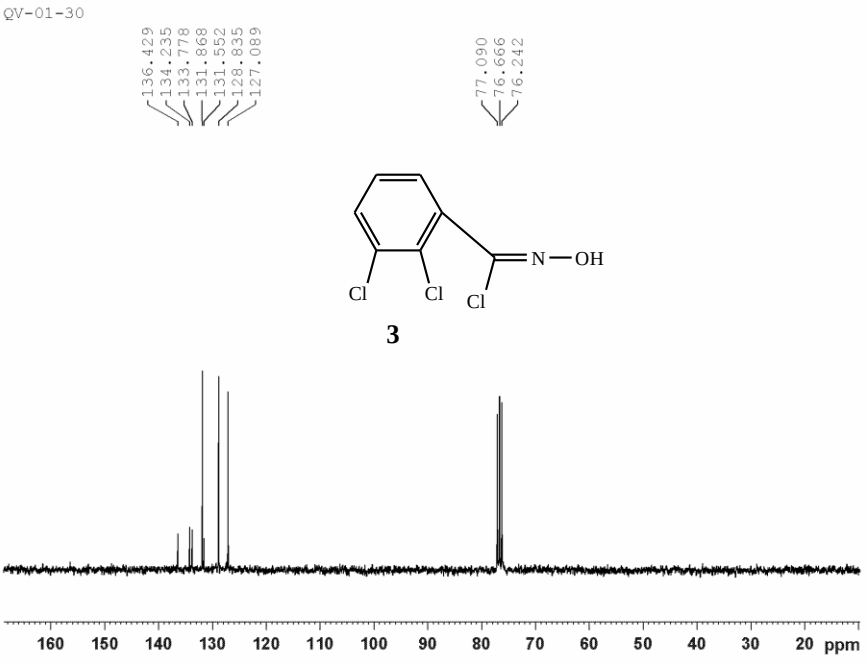


**3**

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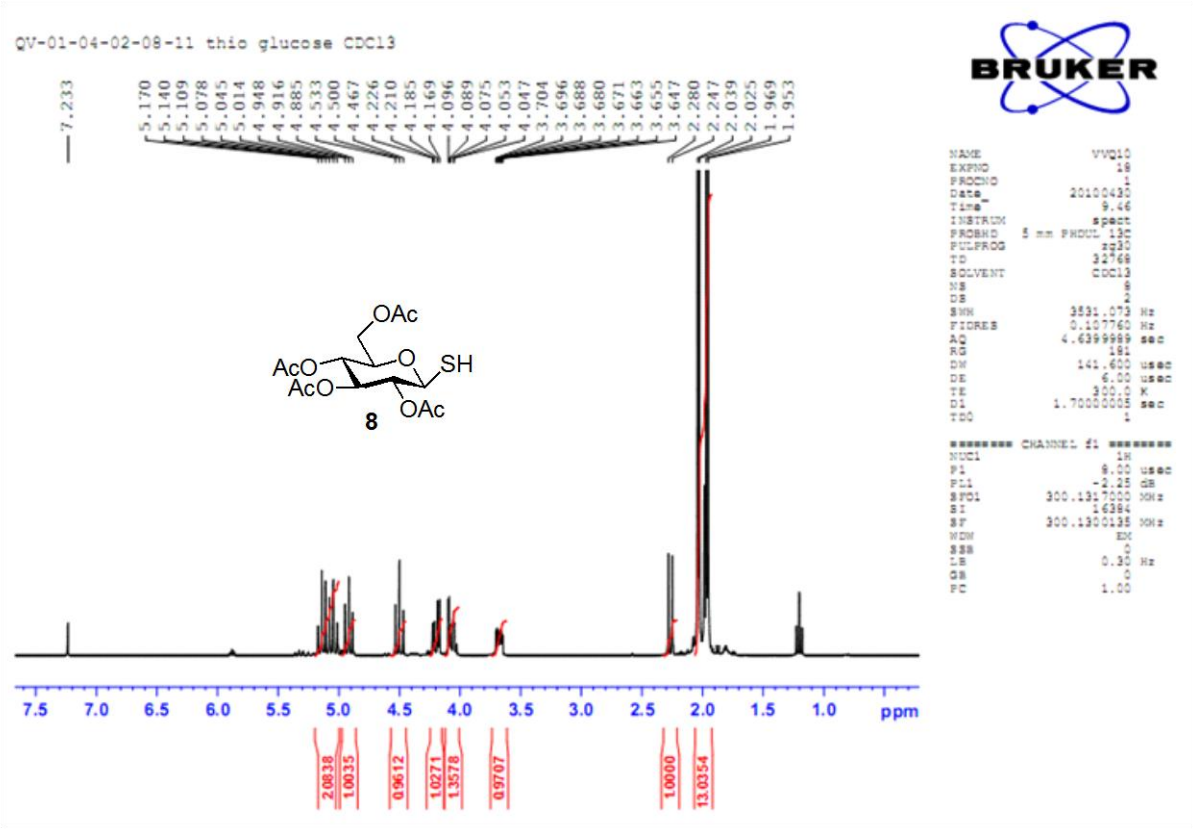
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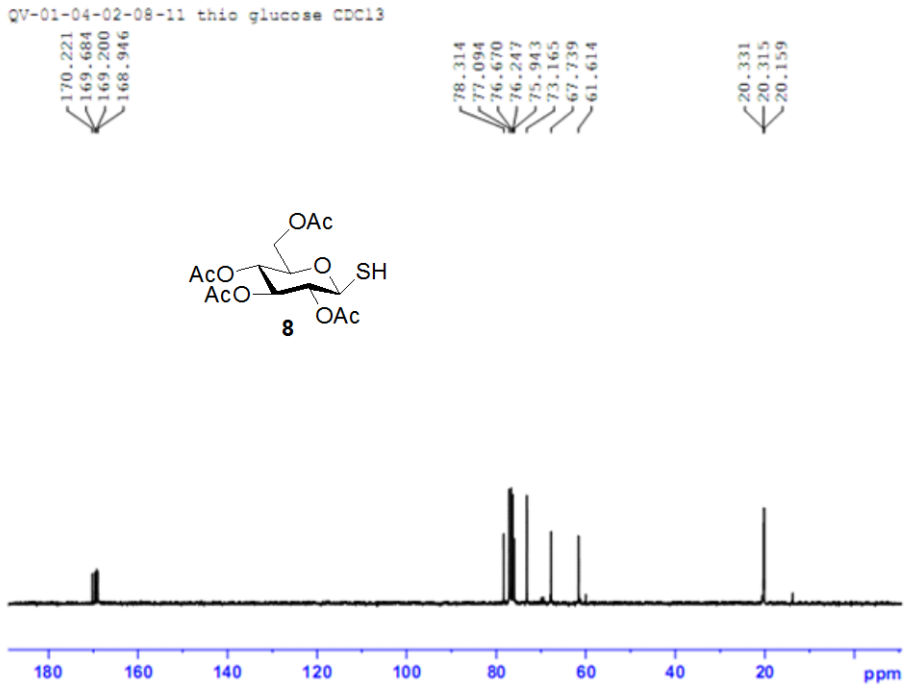
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ppm


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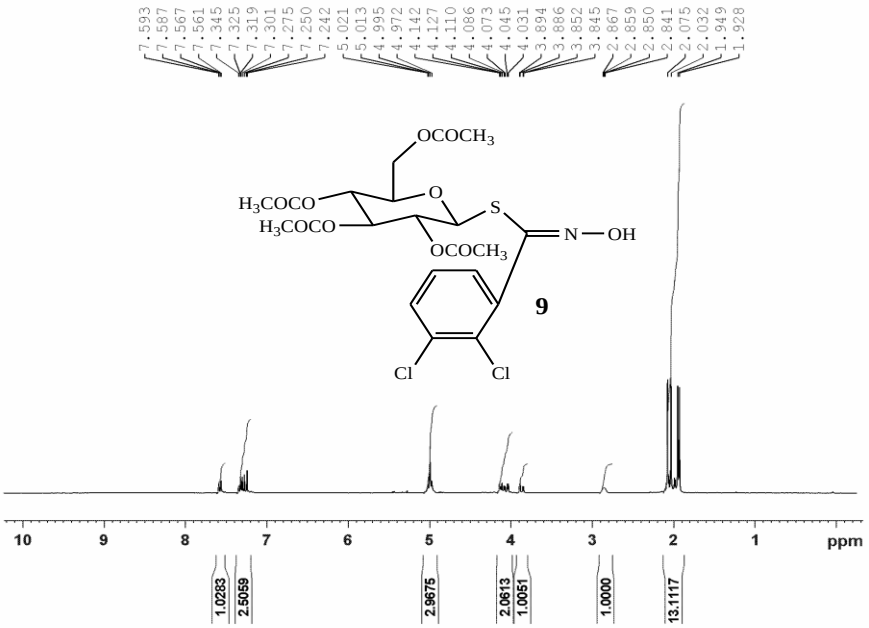


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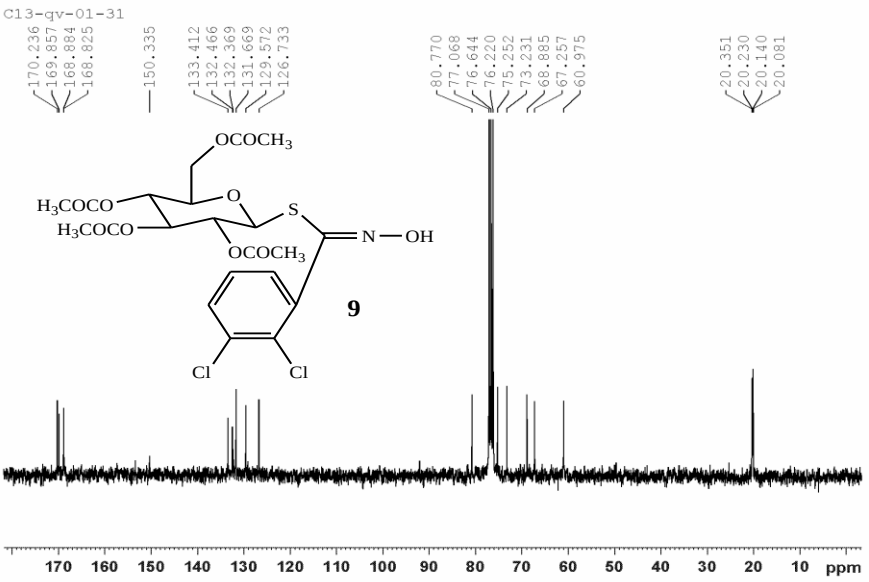


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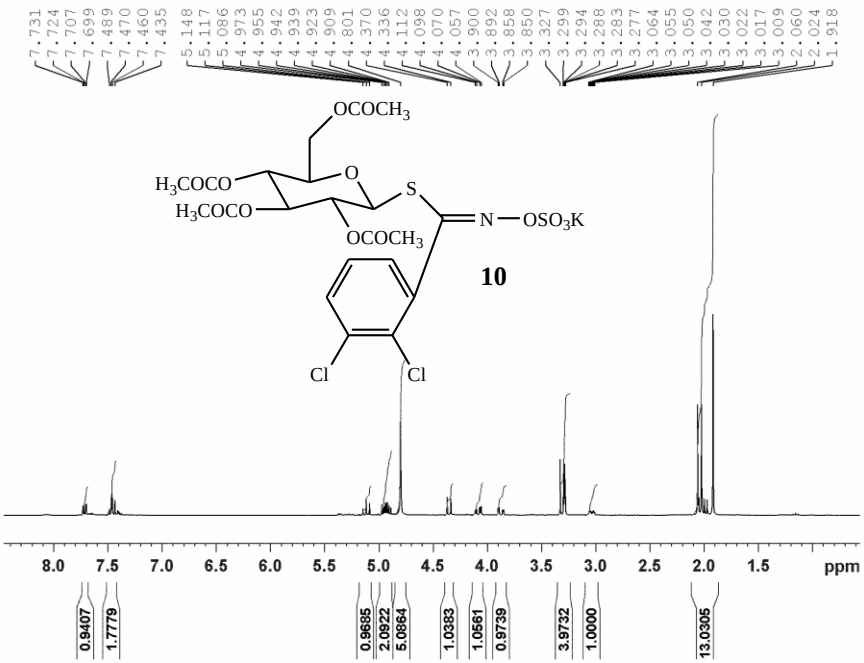


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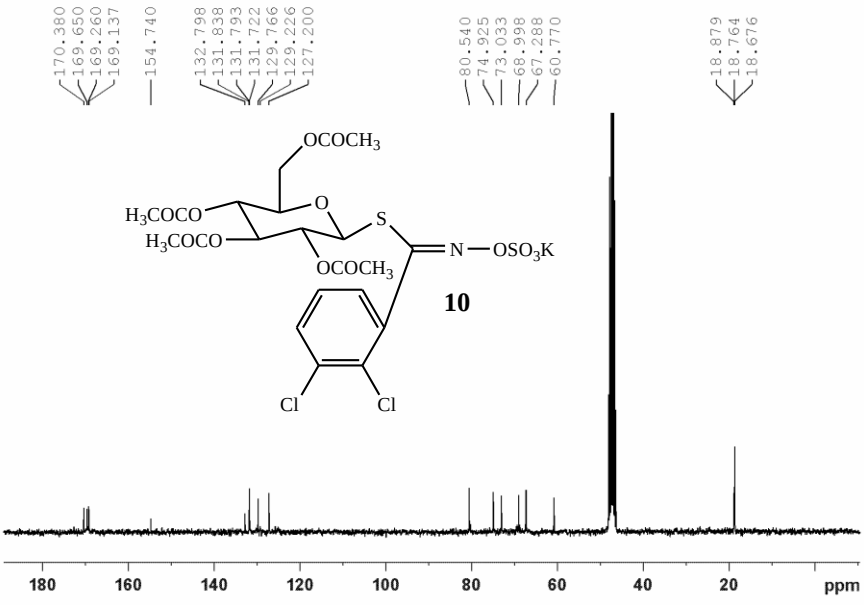


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TE                300.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

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P1                  3.00 usec
PL1                -1.00 dB
SFO1         75.4745111 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2              77.00 usec
PL2                -1.00 dB
PL12               17.00 dB
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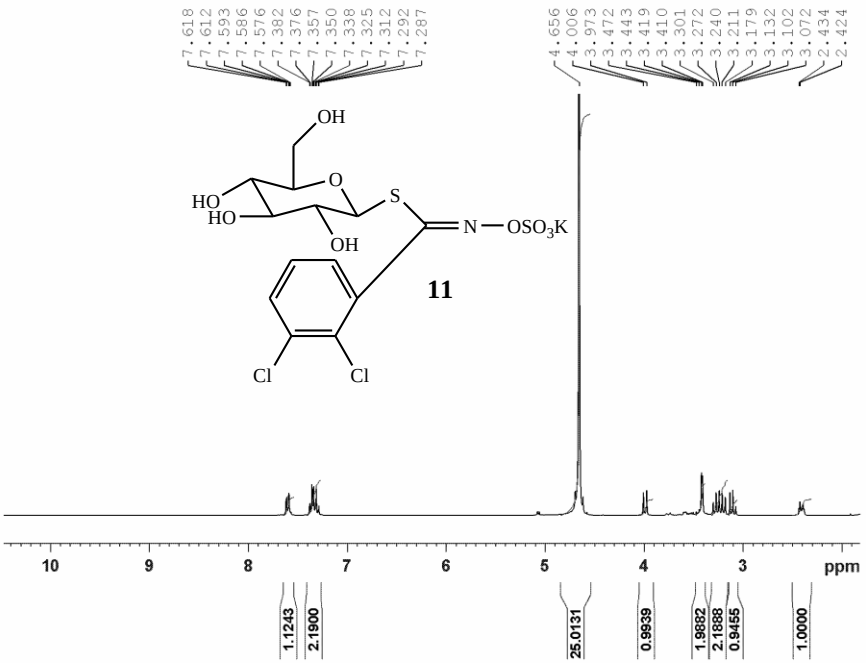
```

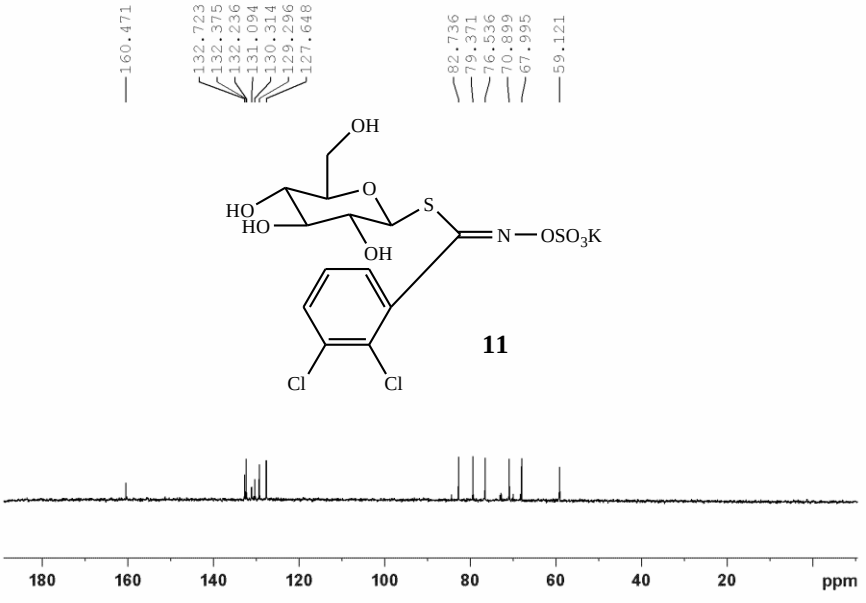
H1-QV-01-33-01




```
NAME                VVQ10
EXPNO                 201
PROCNO                  1
Date_            20100926
Time_                11.22
INSTRUM              spect
PROBHD   5 mm PHDUL 13C
PULPROG               zg30
TD                   32768
SOLVENT                D2O
NS                       8
DS                       2
SWH              3531.073 Hz
FIDRES           0.107760 Hz
AQ               4.6399989 sec
RG                   322.5
DW                141.600 usec
DE                  6.00 usec
TE                 294.6 K
D1              1.70000005 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -2.25 dB
SFO1         300.1317000 MHz
SI                   16384
SF           300.1300110 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

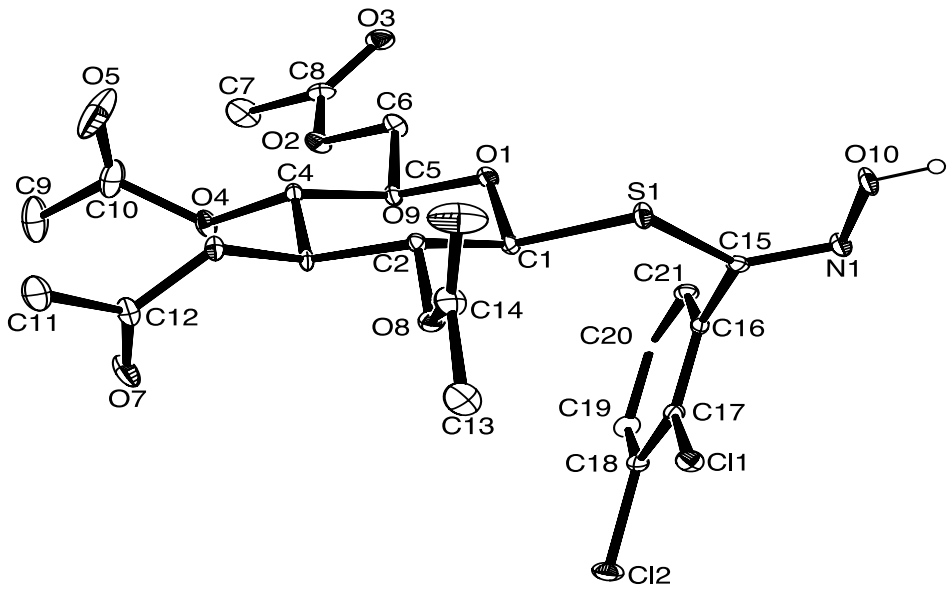
C13-QV-01-33



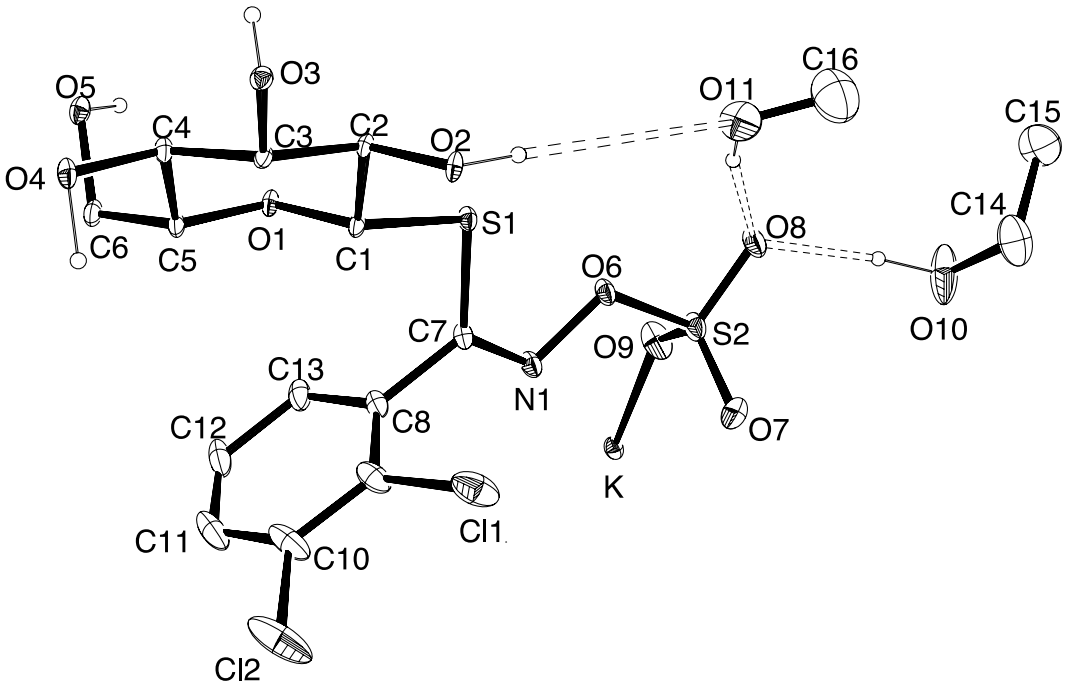

```
NAME                VVQ10
EXPNO                 203
PROCNO                  1
Date_            20100926
Time_                16.39
INSTRUM              spect
PROBHD   5 mm PHDUL 13C
PULPROG             zgpg
TD                   32768
SOLVENT                D2O
NS                    6000
DS                       2
SWH             15060.241 Hz
FIDRES           0.459602 Hz
AQ               1.0879476 sec
RG                14596.5
DW                 33.200 usec
DE                  6.00 usec
TE                 296.2 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   3.00 usec
PL1                 -1.00 dB
SFO1         75.4745111 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2               77.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
PL13                17.00 dB
SFO2         300.1317000 MHz
SI                   16384
SF           75.4677770 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.40
```




ORTEP plot of Compound **9.**




ORTEP plot of compound **11**.