Supporting Information

Multifunctional Biomass Based Chemicals: H_2S Scavenging

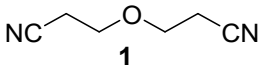
SI.1 General synthetic methods

The chemicals were directly applied to the reactions without further purifications prior to use. Dry solvent were collected from an Innovative Technology PS-MD-05 solvent drying system. All air and water sensitive reactions were carried out in an inert atmosphere of nitrogen. The plates used for thin layer chromatography (TLC) were Silica gel (60F) coated on aluminum sheets. The TLC plates were analyzed first with UV-light then stained in a 10 % solution of H_2SO_4 in ethanol. The concentration of the samples was performed under reduced pressure at 40 °C. Sodium hydride was added as a 60 % dispersion in mineral oil. Purifications by flash column chromatography were carried out by using silica gel (40-63 μm).

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 500 MHz Ultra Shield Plus spectrograph equipped with a cryoprobe. ^{1}H-NMR were recorded at 500 MHz and ^{13}C-NMR at 126 MHz. The spectra were referenced to the chemical shifts of the deuterated solvents ($CDCl_3$: ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm), (D_2O: ^{1}H: 4.790 ppm). High-resolution mass spectrometry (HRMS) was performed on a Bruker SolariX XR7T ESI/MALDI-FT-ICR-MS instrument using matrix-assisted laser desorption ionization (MALDI) with dithranol as the matrix.

SI.2 Chemical synthesis

2-Cyanoethyl ether (1)[1]



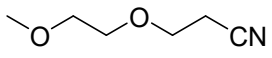
1

Acrylonitrile (5.00 g, 94.2 mmol) was dissolved in H_2O (4 mL), 40% NaOH (1 mL) was added to the solution. The reaction was carried out while stirring at rt. After 3 hours the pH of the reacting mixture was lowered to 7 by adding aq. HCl (1 M). The reaction mixture was then extracted with $CHCl_3$ and the combined organic phases were washed twice with aq. $NaHCO_3$ (sat.) and once with brine. Then the organic phase was dried over $MgSO_4$ and concentrated in vacuo to give the product **1** (0.70 g, 5.67 mmol, 12%) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (t, *J* = 6.2 Hz, 4H, O-CH_2), 2.60 (t, *J* = 6.2 Hz, 4H, CH_2-CN) ppm.

HRMS (ESP+): Calculated for $C_6H_8ON_2Na^+$ 147.05288 *m/z* found 147.05299 *m/z.*

3-(2-methoxyethoxy)propanenitrile (2)[2]



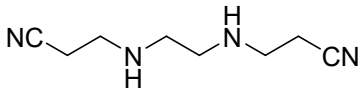
2

Acrylonitrile was added to a mixture of 2-methoxyethanol (2.00 g, 26.3 mmol) and aq. NaOH (2 M, 1 mL). The temperature of the reaction was maintained at 25 °C and stirred for 18 hour, whereupon the pH of the reaction was lowered to 7 by adding aq. HCl (1 M). The reaction mixture was then extracted with CH_2Cl_2 and organic phase was separated, washed once with aq. NaOH (1 M) and once with brine. The organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo to give the product **2** (1.3 g, 10.1 mmol, 38%) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (t, *J* = 6.3, 0.9 Hz, 2H, O-CH_2), 3.57 – 3.53 (t, *J* = 4.07 Hz, 2H O-CH_2), 3.46 (t, *J* = 5.3 Hz, 2H, O-CH_2), 3.29 (s, 3H, CH_3-O), 2.54 (d, *J* = 6.9, Hz, 2H CH_2-CN) ppm.

HRMS (ESP+): Calculated for $C_6H_{11}O_2N_1H^+$ 130.08625 *m/z* found 130.08710 *m/z.*

N,N'-bis-(2-cyanoethyl)ethylenediamine (3)[3]



3

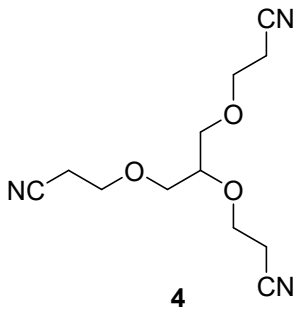
Ethylenediamine (5.00 g, 83.19 mmol) was dissolved in H_2O and N_2 was bubbled through the solution before acrylonitrile (9.71 g, 183.03 mmol) was added over 10 minutes while stirring at room temperature. After 2 hours the reaction was evaporated to give product **3** (13.01 g, 78.27 mmol, 94%) in the form of a light yellow oil.

R_f (EtOAc) = 0.33

^{1}H NMR (500 MHz, D_2O) δ 2.93 (t, *J* = 6.7 Hz, 4H, O-CH_2), 2.76 (s, 4H, O-CH_2), 2.69 (t, *J* = 7.1 Hz, 4H, CH_2-CN) ppm.

HRMS (MALDI+): Calculated for $C_8H_{14}N_4H^+$ 167.12912 *m/z* found 167.12965 *m/z.*

1,2,3-Tri(2-cyanoethoxy)propane (4)[4]



4

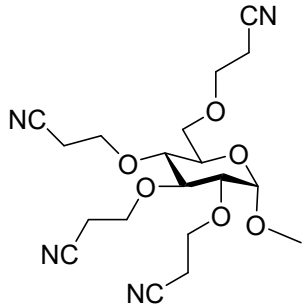
NaOH (0.04 g, 0.94 mmol) was added to aq. glycerol 87% (1.00 g, 9.45 mmol) and heated to 65 °C while stirring until the until all NaOH had dissolved. The reaction mixture was then cooled to room temperature and acrylonitrile (1.75 g, 33.06 mmol) was slowly added to the reaction over five minutes. The reaction was stirred for 22 hours whereupon the pH of the reaction was lowered to 7 by adding aq. HCl (1 M). The reaction mixture was extracted with CH_2Cl_2 and the organic phase was washed twice with H_2O and once with brine, dried over $MgSO_4$, filtered and concentrated. The product was purified using flash column chromatography, (SiO2, 7/3 to 8/2 EtOAc/heptane) to give **4** (1.51 g, 6.01 mmol, 64%) as a clear syrup.

$\mathbf{R_f}$ (5% methanol in CH_2Cl_2) = 0.58

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (t, *J* = 6.2 Hz, 2H, O-CH_2), 3.66 (m, 5H, O-CH_2, and O-CH), 3.59 (dd, *J* = 10.3, 4.1 Hz, 2H, O-CH_2), 3.54 (dd, *J* = 10.3, 5.9 Hz, 2H, O-CH_2), 2.57 (td, *J* = 6.1, 1.1 Hz, 6H, CH_2-CN) ppm.

HRMS (MALDI+): Calculated for $C_{12}H_{17}O_3N_3Na^+$ 274.11621 *m/z* found 274.11596 *m/z.*

Methyl 2,3,4,6-tetra-*O*-(2-cyanoethyl)-α-D-glucopyranoside (5)



5

Methyl-*a*-$_D$-glucopyranoside (5.00 g, 25.75 mmol) was dissolved in aq. Na_2CO_3 (0.2 M) (13 mL). Acrylonitrile (10.93 g, 206 mmol) was added to the reaction mixture, which was then stirred at 80 °C. After 5 hours the heating was removed and the reaction mixture was cooled to rt. and the pH of the reaction lowered to 7 by adding aq. HCl (1 M). The reaction mixture was then extracted with CH_2Cl_2 and the organic phase was washed twice with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated in vacuo and purified with flash column chromatography, (SiO2, 8/2 to 9/1 EtOAc/heptane) to give **5** (3.09 g, 7.60 mmol, 30%) as a clear syrup.

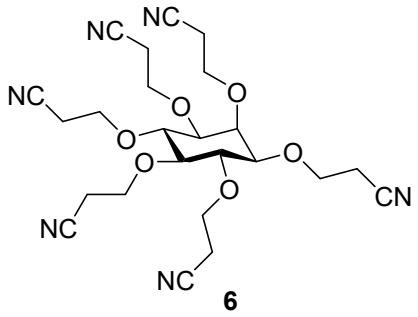
R_f (5% methanol in CH_2Cl_2) = 0.61

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (d, *J* = 3.5 Hz, 1H, H-1), 4.18 – 4.07 (m, 2H, H-6), 3.97 – 3.86 (m, 3H, H-5, O-CH_2), 3.86 – 3.77 (m, 2H, O-CH_2), 3.74 (ddd, *J* = 9.5, 7.9, 5.0 Hz, 2H, O-CH_2), 3.69 – 3.62 (m, 3H, H-4 O-CH_2), 3.49 (t, *J* = 9.5 Hz, 1H, H-3), 3.41 (s, 3H, H-2, CH_3), 2.70 – 2.57 (m, 8H, CH_2-CN) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 118.8 (CN), 118.7 (CN), 118.1 (CN), 117.8 (CN), 97.3 (C-1), 81.0 (C-2), 77.0 (C-3), 69.9 (C-4), 69.2 (O-CH_2), 67.8 (C-5), 67.7 (C-6), 66.2 (O-CH_2,O-CH_2), 65.8 (O-CH_2), 55.5 (CH_3), 19.5 (C-CN), 19.5 (C-CN), 19.3 (C-CN), 19.0 (C-CN) ppm.

HRMS (MALDI+): Calculated for $C_{19}H_{26}O_6N_4Na^+$ 429.17445 *m/z* found 429.17518 *m/z.*

1,2,3,4,5,6-Hexa-*O*-(2-cyanoethyl)-*meso*-D-*myo*-inositol (6)



6

Myo-inositol (3.00 g, 16.65 mmol) was suspended in acrylonitrile (8.84 g, 166.52 mmol) to which NaOH (0.133 g, 3.33 mmol) was added along with H_2O (2 mL). The reaction mixture was stirred at room temperature for 4 hours whereupon the pH of the reaction was lowered to 7 by adding aq. HCl (1 M). The reaction mixture was then extracted with CH_2Cl_2 and the organic phase was washed twice with brine, dried over $MgSO_4$ and concentrated in vacuo. The product was purified with flash column chromatography, (SiO2, 9/1 to 10/0 EtOAc/heptane) to give **6** (1.97 g, 3.95 mmol, 24%) as a white solid.

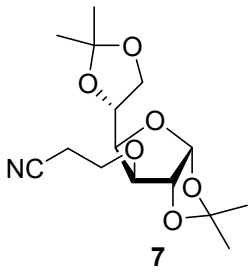
R_f (5% methanol in CH_2Cl_2) = 0.68

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.05 – 4.00 (m, 9H, O-CH_2 and H-2), 3.93 (ddd, *J* = 9.1, 6.2, 4.6 Hz, 2H, O-CH_2), 3.83 (ddd, *J* = 9.1, 7.9, 4.2 Hz, 2H, O-CH_2), 3.67 (t, *J* = 9.6 Hz, 2H, H-4 and H-6), 3.20 (dd, *J* = 9.8, 2.4 Hz, 2H, H-1 and H-3), 3.12 (t, *J* = 9.4 Hz, 1H, H-5), 2.72 (dd, *J* = 7.9, 4.6 Hz, 2H, CH_2-CN), 2.67 – 2.61 (m, 10H, CH_2-CN) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 118.9 (CN), 118.8 (CN), 118.4 (CN), 118.3 (CN), 82.5 (H-5), 80.8 (H-1 and H-3), 80.6 (H-4 and H-6), 76.4 (H-2), 68.4 (O-CH_2), 68.2 (O-CH_2), 68.1 (O-CH_2), 66.2 (O-CH_2), 19.8 (CH_2-CN), 19.5 (CH_2-CN) (d, *J* = 6.2 Hz) ppm.

HRMS (MALDI+): Calculated for $C_{15}H_{26}O_6N_6Na^+$ 521.21190 *m/z* found 521.21254 *m/z.*

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-cyanoethyl)-α-D-glucofuranose (7)



7

1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3.07 g, 11.79 mmol) was suspended in acrylonitrile (3.76 g, 70.77 mmol) to which NaOH (0.05 g, 1.18 mmol) was added along with H_2O (2 mL). The reaction mixture was stirred at rt. for 16 hours, whereupon the pH of the reaction lowered to 7 by adding aq. HCl (1 M). The reaction mixture was extracted with EtOAc and the organic phase was washed two times with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The product was purified with flash column chromatography, (SiO2, 4/6 to 5/5 EtOAc/heptane) to give **7** (2.57 g, 8.20 mmol, 70%) as a clear syrup.

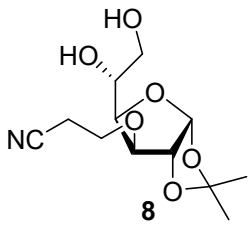
R_f (2/1 EtOAc/Heptane) = 0.50

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (d, *J* = 3.6 Hz, 1H, H-1,), 4.55 (d, *J* = 3.7 Hz, 1H, H-2), 4.28 (ddd, *J* = 8.5, 6.2, 5.2 Hz, 1H, H-5), 4.11 (dd, *J* = 8.7, 6.2 Hz, 1H, H-6), 4.06 (dd, *J* = 8.4, 3.0 Hz, 1H, H-4), 3.98 (dd, *J* = 8.7, 5.2 Hz, 1H, H-6), 3.92 (d, *J* = 3.0 Hz, 1H, H-3), 3.83 (td, *J* = 6.1, 2.6 Hz, 2H, O-CH_2), 2.61 (td, *J* = 6.3, 3.6 Hz, 2H, CH_2-CN), 1.49 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.31 (s, 3H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 117.6 (CN), 112.2 (O-C-O), 109.4 (O-C-O), 105.4 (C-1), 82.9 (C-2 or C-3), 82.9 (C-2 or C-3), 81.3 (C-4), 72.3 (C-5), 67.6 (C-6), 65.6 (O-CH_2), 27.0 (CH_3), 26.9 (CH_3), 26.3 (CH_3), 25.4 (CH_3), 19.1 (CH_2-CN) ppm.

HRMS (MALDI+): Calculated for $C_{15}H_{23}O_6N_1Na^+$ 336.14176 *m/z* found 362.14182 *m/z.*

1,2-*O*-Isopropylidene-3-*O*-(2-cyanoethyl)-α-D-glucofuranose (8)



8

7 (0.43 g, 1.38 mmol) was dissolved in a solution of 70 wt. % acetic acid and 30 wt. % H_2O (8 mL). The reacting mixture was stirred for 2 hours at rt. where after it was heated to 60 °C. After 1 hour the heating was removed and the reaction mixture was cooled to room temperature. The reacting mixture was quenched by neutralizing it by adding $NaHCO_3$. The crude mixture was extracted with EtOAc (3 times 5 mL) and the combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. The product was purified with flash column chromatography, (SiO2, 5% MeOH in DMC) to give **8** (0.16 g, 0.59 mmol, 43%) as a clear syrup.

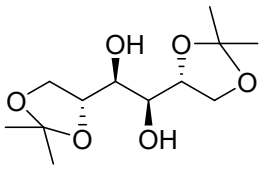
R_f (5 % methanol in CH_2Cl_2) =0.26

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.91 (d, *J* = 3.8 Hz, 1H, H-1), 4.57 (d, *J* = 3.8 Hz, 1H, H-2), 4.13 (dd, *J* = 8.7, 3.1 Hz, 1H, H-3), 4.02 (dd, *J* = 6.8, 3.2 Hz, 2H, H-4, H-5), 3.89 (ddd, *J* = 15.0, 10.5, 7.2 Hz, 2H, H-6, O-CH), 3.82 – 3.67 (m, 2H, H-6, O-CH), 2.65 (t, *J* = 6.0 Hz, 2H, CH_2-CN), 1.49 (s, 3H, CH_3), 1.31 (s, 3H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 118.2 (CN), 112.1 (O-C-O), 105.2 (C-1), 83.3 (C-4), 82.0 (C-2), 79.8 (C-3), 68.7 (C-5), 65.2 (CH_2-O), 64.5 (C-6), 26.8 (CH_3), 26.3 (CH_3), 19.3 (C-CN) ppm.

HRMS (MALDI+): Calculated for $C_{12}H_{19}O_6N_1Na^+$ 296.11046 *m/z* found 296.11038 *m/z*.

1,2:5,6-Di-*O*-isopropylidene-D-mannitol (9)[5]



9

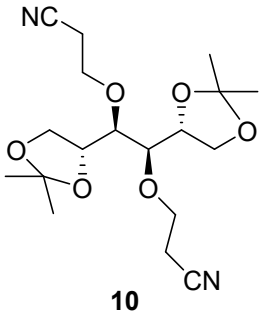
D-Mannitol (4.07 g, 22.34 mmol) was dissolved in DMF (15 mL) to which 2,2-dimethoxypropane (5.12 g, 48.15 mmol) and *p*-toluenesulfonic acid monohydrate (0.425 g, 2.23 mmol) were added. The reaction mixture was stirred at room temperature for 15 hours after which the reaction was quenched with aq. $NaHCO_3$ (4 mL) whereupon the reaction was diluted with water. The reaction mixture was extracted five times with EtOAc (10 mL) and the combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. The product was purified with flash column chromatography, (SiO2, 5/5 to 7/3 EtOAc/heptane) to give **9** (2.36 g, 9.00 mmol, 40%) as a white solid.

$\mathbf{R_f}$ (2/1 EtOAc/heptane) = 0.49

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (q, *J* = 6.3 Hz, 2H, CH), 4.12 (ddt, *J* = 7.8, 5.6, 2.4 Hz, 2H, CH_2), 4.01 – 3.93 (m, 2H, CH_2), 3.75 (td, *J* = 6.9, 2.0 Hz, 2H, CH), 2.52 (dd, *J* = 6.8, 2.6 Hz, 2H, -OH), 1.42 (d, *J* = 2.6 Hz, 6H, CH_3), 1.36 (d, *J* = 2.8 Hz, 6H, CH_3) ppm.

HRMS (ESP+): Calculated for $C_{12}H_{22}O_6Na^+$ 285.13086 *m/z* found 285.13248 *m/z.*

1,2:5,6-Di-*O*-isopropylidene-3,4-di-*O*-(2-cyanoethyl)-D-mannitol (10)



10

9 (1.50 g, 5.72 mmol) was suspended in acrylonitrile (1.52 g, 28.59 mmol) to which NaOH (0.023 g, 0.57 mmol) was added along with H_2O (0.8 mL). The reaction mixture was stirred at room temperature for 21 hours whereupon the pH of the reaction was lowered to 7 by adding aq. HCl (1 M). The reaction mixture was extracted with EtOAc and the organic phase was washed twice with

brine, dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified with flash column chromatography, (SiO2, 6/4 to 10/0 EtOAc/heptan) to give **10** (1.56 g, 4.23 mmol, 74 %) as a clear syrup.

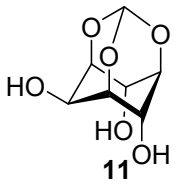
R_f (7/3 EtOAc/Heptane) = 0.56

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.23 (qd, *J* = 6.2, 1.6 Hz, 2H, CH), 4.14 (dd, *J* = 8.2, 6.3 Hz, 2H,), 3.95 (d, 6.1 Hz, 2H, CH_2), 3.94 – 3.86 (m, 4H, O-CH_2), 3.62 (dt, *J* = 5.2, 1.6 Hz, 2H, CH), 2.60 (tt, *J* = 6.5, 2.3 Hz, 4H, CH_2-CN), 1.41 (d, *J* = 1.4 Hz, 6H, CH_3), 1.35 (d, *J* = 1.4 Hz, 6H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 117.9 (CN), 109.1 (C), 81.0 (CH), 75.2 (CH), 67.4 (O-CH_2), 66.5 (CH_2), 26.8 (CH_3), 25.1 (CH_3), 19.4 (CH_2-CN) ppm.

HRMS (ESP+): Calculated for $C_{18}H_{28}O_6N_2Na^+$ 391.18396 *m/z* found 391.18351 *m/z.*

***Meso*-D-*myo*-inositol-1,3,5-*O*-orthoformate (11)**[6]



11

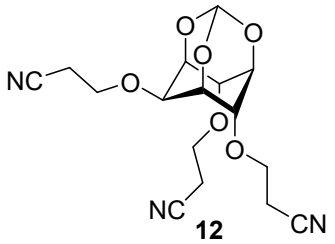
Myo-inositol (3.01 g, 16.71 mmol) was dissolved in DMF (20 mL), to which triethyl orthoformate (3.70 g, 24.98 mmol) and *p*-toluenesulfonic acid monohydrate (0.32 g, 1.67 mmol) were added. The reaction mixture was heated to 110 °C and stirred for 5 hours. The reaction was quenched with trimethylamine (2 mL), concentrated and the resulting syrup was crystallized from hot methanol to yield **11** (1.67 g, 8.78 mmol, 53%) as a white solid.

R_f (5% methanol in CH_2Cl_2) = 0.3

^{1}H NMR (500 MHz, D_2O) δ 5.49 (s, 1H, CHO_3), 4.48 (t, *J* = 3.7 Hz, 2H, H-4 and H-6), 4.23 (dq, *J* = 3.8, 2.0 Hz, 1H, H-5), 4.18 – 4.15 (m, 1H, H-2), 4.14 – 4.11 (m, 2H, H-1 and H-3) ppm.

HRMS (MALDI+): Calculated for $C_7H_{10}O_6H^+$ 191.05501 *m/z* found 191.05556 *m/z.*

2,4,6-Tri-*O*-(2-cyanoethyl)-*meso*-D-*myo*-inositol-1,3,5-*O*-orthoformate (12)



12

11 (2.02 g, 10.6 mmol) was suspended in acrylonitrile (3.35 g, 63.1 mmol) to which NaOH (0.050 g, 1.3 mmol) was added along with H_2O (1 mL). The reaction mixture was stirred at room temperature. After 5 hours more acrylonitrile (1.24 g, 23.4 mmol) was added to the reaction. After 21 hours the pH of the reaction was lowered to 7 by adding aq. HCl (1 M) and the reaction mixture was extracted with CH_2Cl_2. The organic phase was washed twice with H_2O and once with brine. The organic phase was then dried over $MgSO_4$ and concentrated in vacuo. The product was purified using flash column chromatography, (SiO2, 7/3 to 8/2 EtOAc/heptane) to give **12** (2.54 g, 7.27 mmol, 68%) as a white solid.

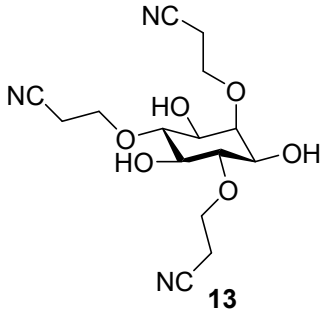
R_f (5% methanol in CH_2Cl_2) = 0.47

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 (s, 1H, CHO_3), 4.49 (dt, *J* = 3.5, 1.7 Hz, 1H, H-5), 4.39 (dt, *J* = 4.4, 1.7 Hz, 2H, H-1 and H-3), 4.33 – 4.30 (m, 2H, H-4 and H-6), 3.99 (d, *J* = 1.6 Hz, 1H, H-2), 3.93 (t, *J* = 6.3 Hz, 2H, O-CH_2), 3.87 (ddd, *J* = 8.8, 6.8, 5.3 Hz, 2H, O-CH_2), 3.75 (ddd, *J* = 8.8, 6.1, 5.2 Hz, 2H, O-CH_2), 2.73 (t, *J* = 6.3 Hz, 2H, CH_2-CN), 2.69 (ddd, *J* = 6.1, 5.2, 2.0 Hz, 4H, CH_2-CN) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 118.1 (CN), 102.7 (HCO_3), 74.1 (C-4, C-6), 69.5 (C-1, C-3), 68.5 (C-2), 67.21 (C-5), 64.3 (O-CH_2), 19.0 (CH_2-CN) ppm.

HRMS (MALDI+): Calculated for $C_{16}H_{19}O_6N_3Na^+$ 372.11661 *m/z* found 372.11661 *m/z*.

2,4,6-Tri-*O*-(2-cyanoethyl)-*meso*-D-*myo*-inositol (13)



13

12 (5.70 g, 16.32 mmol) was dissolved in THF (50 mL) and MeOH (25 mL) whereupon acid resin (Amberlite IR120 hydrogen form) was added. The reaction mixture was stirred at 45 °C for 50 hours. The reaction was cooled to rt. and the acid resin was removed by filtration. The reaction mixture was concentrated in vacuo and purified with flash column chromatography, (SiO2, 1/9 MeOH/CH_2Cl_2) to give **13** (3.64 g, 10.73 mmol, 66%) as a white solid.

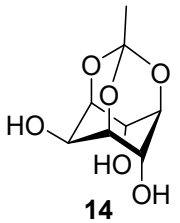
R_f (5% methanol in CH_2Cl_2) = 0.19

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.09 – 4.02 (m, 6H, O-CH_2), 3.90 (t, *J* = 2.7 Hz, 1H, H-2), 3.55 (dd, *J* = 8.7, 2.6 Hz, 2H, H-1, H-3), 3.53 – 3.45 (m, 3H,H-4, H-5, H-6), 2.67 (m, 6H, CH_2-CN).

^{13}C NMR (126 MHz, $CDCl_3$) δ 118.9 (CN), 82.9 (C-1, C-3), 80.9 (C-2), 74.6 (C-5), 72.1 (C-4, C-6), 67.6 (O-CH_2), 19.7 (CH_2-CN).

HRMS (MALDI+): Calculated for $C_{15}H_{21}O_6N_3Na^+$ 362.13226 *m/z* found 362.13219 *m/z.*

***Meso*-D-*myo*-inositol-1,3,5-*O*-orthoacetate (14)**[7]



14

Myo-inositol (2.01 g, 11.16 mmol) was dissolved in DMF (15 mL), to which trimethyl orthoacetate (2.01g, 16.74 mmol) and *p*-toluenesulfonic acid monohydrate (0.192 g, 1.12 mmol) were added. The reaction mixture was heated to 110 °C for 5 hours whereupon the reaction was quenched with

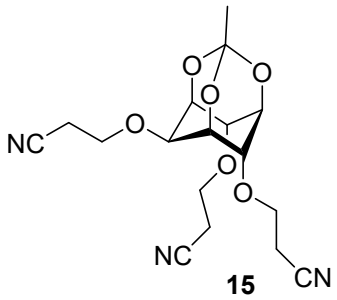
trimethylamine (1 mL) and then the reaction mixture was concentrated in vacuo followed by purification by flash column chromatography, (SiO2, EtOAc) to give **14** (1.62 g, 7.93 mmol, 71%) as white crystals

R_f (5% methanol in CH_2Cl_2) = 0.44

^{1}H NMR (500 MHz, D_2O) δ 4.43 (t, *J* = 3.7 Hz, 2H, H-4, H-6), 4.18 – 4.09 (m, 4H, H-1, H-2, H-3, H-5), 1.35 (s, Hz, 3H, CH_3) ppm.

HRMS (MALDI+): Calculated for $C_{12}H_{19}O_6N_1Na^+$ 296.11046 *m/z* found 296.11038 *m/z.*

2,4,6-Tri-*O*-(2-cyanoethyl)-*meso*-D-*myo*-inositol-1,3,5-orthoacetate (15)



15

14 (1.40 g, 6.86 mmol) was suspended in acrylonitrile (2.18 g, 41.14 mmol) to which NaOH (0.027 g, 0.69 mmol) was added along with H_2O (1.4 mL). The reaction mixture was stirred at room temperature and after 16 hours the pH of the reaction lowered to 7 by adding aq. HCl (1 M) and the reaction mixture was extracted with CH_2Cl_2. The organic phase was washed twice with H_2O and once with brine, dried over $MgSO_4$ and concentrated in vacuo. The product was purified with flash column chromatography, (SiO2, 7/3 to 8/2 EtOAc/heptane) to give **15** (1.37 g, 3.77 mmol, 55%) as a white solid.

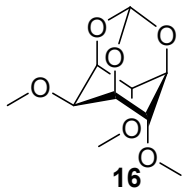
R_f (8/2 EtOAc/Heptane) = 0.43

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.40 (m, 1H, H-5), 4.37 (m, 2H, H-1, H-3), 4.26 (t, *J* = 3.8 Hz, 2H, H-4, H-6), 3.92 – 3.89 (m, 3H, H-2, O-CH_2), 3.85 – 3.82 (m, 2H, O-CH_2), 3.73 (m, 2H, O-CH_2), 2.71 (t, *J* = 6.3 Hz, 2H, CH_2-CN), 2.68 – 2.65 (m, 4H, CH_2-CN), 1.45 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 118.07 (CN), 117.88 (CN), 109.22 (CO_3), 74.62 (H-4, H-6), 70.62 (H-1, H-3), 67.97 (H-2), 67.74 (H-5), 64.58 (O-CH_2), 24.30 (CH_3), 19.39 (CH_2-CN), 19.37 (CH_2-CN).

HRMS (MALDI+): Calculated for $C_{17}H_{21}O_6N_3Na^+$ 386.13226 *m/z* found 386.13265 *m/z*

2,4,6-Tri-*O*-methyl-*meso*-D-*myo*-inositol-1,3,5-*O*-orthoformate (16)[8]



16

11 (0.202 g, 1.06 mmol) was dissolved in DMF (2 mL) and the solution was cooled to 0 °C, where NaH (0.170 g, 4.25 mmol) was added. The reaction mixture was then stirred for 30 minutes at 0 °C whereupon MeI (0.754 g, 5.31 mmol) was added over 10 minutes at 0 °C. The cooling was removed and the reaction mixture was stirred at rt. overnight. The reaction was quenched by adding MeOH and then extracted with EtOAc (10 mL). The organic phase was separated and washed 3 times with water and 1 time with brine, dried over $MgSO_4$, filtered and evaporated to dryness. The product was purified by flash column chromatography, (SiO2, 4/6 EtOAc/heptane) to give **16** (0.12 g, 0.5 mmol, 47%) as a white solid.

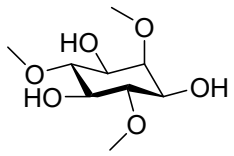
$\mathbf{R_f}$ (3/7 EtOAc/Heptane) = 0.12

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (s, 1H, CH), 4.47 (td, *J* = 3.4, 1.7 Hz, 1H, H-5), 4.39 (dt, *J* = 3.4, 1.7 Hz, 2H, H-1, H-3), 4.16 (t, *J* = 3.7 Hz, 2H, H-4, H-6), 3.63 (q, *J* = 1.7 Hz, 1H, H-2), 3.53 (s, 3H, CH_3), 3.46 (s, 6H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 103.3 (HCO_3), 76.1 (C-4, C-6), 69.3 (C-5, C-1, H-3), 67.6 (C-2), 58.0 (CH_3), 57.0 (CH_3) ppm.

HRMS (MALDI+): Calculated for $C_{10}H_{16}O_6H^+$ 233.10196 *m/z* found 233.10197 *m/z.*

2,4,6-Tri-*O*-methyl-*meso*-D-Inositol (17)



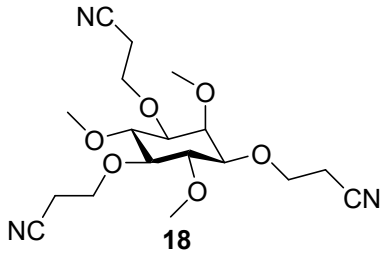
17

16 (1.00 g, 4.31 mmol) was dissolved in THF (10 mL) and MeOH (5 mL). To the solution was then added acidic resin (Amberlite IR120 hydrogen form) and it was stirred at 45 °C for 18 hours. The reaction was cooled to rt. and the acid resin removed by filtration. The reaction mixture was concentrated to give **17** (0.931 g, 4.19 mmol, quantitative yield) as a white solid.

R_f (5% methanol in CH_2Cl_2) = 0.51

^{1}H NMR (500 MHz, D_2O) δ 3.66 (t, *J* = 3.0 Hz, 1H, H-2), 3.57 (d, *J* = 3.1 Hz, 1H, H-1 or H-3), 3.56 (s, 4H, CH_3, H-1 or H-3), 3.54 (s, 6H, CH_3), 3.31 (dq, *J* = 23.4, 9.4 Hz, 3H, H-4, H-6, H-5) ppm.

1,3,5-Tri-*O*-(2-cyanoethyl)-2,4,6-tri-*O*-methyl-*meso*-D-*myo*-inositol (18)



18

17 (3.72 g, 16.7 mmol) was suspended in acrylonitrile (7.99 g, 151 mmol) to which NaOH (0.067 g, 1.67 mmol) was added along with H_2O (2 mL). The reaction mixture was stirred at room temperature and after 20 hours the pH of the reaction mixture was lowered to 7 by adding aq. HCl (1 M). The reaction mixture was then extracted with CH_2Cl_2 and the organic phase was washed twice with H_2O and once with brine, then dried over $MgSO_4$ and concentrated in vacuo. The product was purified using flash column chromatography, (SiO2, 9/1 to 10/0 EtOAc/heptane) to give **18** (1.79 g, 4.69 mmol, 28%) as a white solid.

R_f (5% methanol in CH_2Cl_2) = 0.71

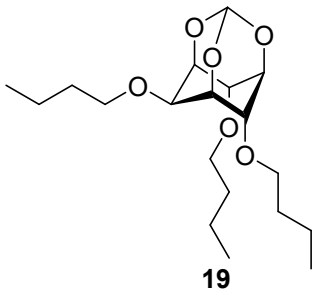
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (t, *J* = 6.1 Hz, 2H, O-CH_2), 3.86 – 3.76 (m, 4H, O-CH_2), 3.74 (t, *J* = 2.5 Hz, 1H, H-2), δ 3.58 (s, 3H, O-CH_3), 3.57 (s, 6H, O-CH_3), 3.42 (t, *J* = 9.5 Hz, 2H, H-4, H-6),

3.07 (dd, J = 9.8, 2.5 Hz, 2H, H-1, H-3), 2.94 (t, J = 9.2 Hz, 1H, H-5), 2.66 – 2.55 (m, 6H, CH_2-CN) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 118.2 (CN), 117.9 (CN), 84.0 (C-5), 82.2 (C-4, C-6), 81.5 (C-1, C-3), 77.7 (C-2), 67.7 (O-CH_2), 66.1 (O-CH_2), 61.5 (O-CH_3), 19.4 (CH_2-CN) ppm.

HRMS (MALDI+): Calculated for $C_{18}H_{27}O_6N_3Na^+$ 404.17921 *m/z* found 404.17791 *m/z.*

2,4,6-Tri-*O*-butyl-*meso*-D-*myo*-inositol-1,3,5-orthoacetate (19)



19

11 (2.01 g, 10.6 mmol) was dissolved in DMF (10 mL) and the solution was cooled to 0 ℃ where NaH (1.69 g, 42.28 mmol) was added. The reaction mixture was the stirred for 30 minutes at 0 ℃ whereupon 1-bromobutane (11.59 g, 84.56 mmol) was added over 10 minutes at 0 ℃. The cooling was removed and the reaction mixture was stirred at room temperature overnight. The reaction was stopped by adding MeOH and then diluted by EtOAc (50 mL). The organic phase was washed 3 times with water, 1 time with brine and then dried over Na_2SO_4, filtered and evaporated to dryness. The product was purified using flash column chromatography, (SiO2, 1/9 EtOAc/heptane) to give **19** (1.53 g, 4.27 mmol, 40%) in the form of clear oil.

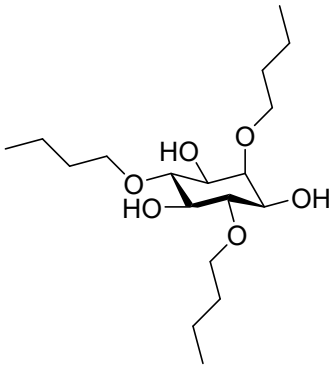
R_f (1/9 EtOAc/Heptane) = 0.45

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (d, J = 1.4 Hz, 1H, CH), 4.39 (dt, J = 3.5, 1.7 Hz, 1H, H-5), 4.27 (dt, J = 3.5, 1.7 Hz, 2H, H-1, H-3), 4.18 (t, J = 3.7 Hz, 2H, H-4, H-6), 3.74 (t, J = 1.6 Hz, 1H, H-2), 3.59 (t, J = 6.7 Hz, 2H, CH_2-O), 3.56 – 3.53 (m, 2H, CH_2-O), 3.47 (dt, J = 9.1, 6.6 Hz, 2H, CH_2-O), 1.67 – 1.61 (m, 2H, -CH_2-), 1.56 – 1.48 (m, 4H, -CH_2-), 1.43 – 1.31 (m, 6H, -CH_2-), 0.91 (dt, J = 9.7, 7.4 Hz, 9H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 103.3 (CH), 74.6 (C-4, C-6), 70.6 (C-1, C-3), 69.5 (CH_2-O), 69.4 (CH_2-O), 68.4 (C-6), 68.1 (C-2), 32.0 (-CH_2-), 32.0 (-CH_2-), 19.3 (-CH_2-), 19.3 (-CH_2-), 14.0 (CH_3), 13.9 (CH_3) ppm.

HRMS (MALDI+): Calculated for $C_{19}H_{34}O_6H^+$ 359.24281 *m/z* found 359.24273 *m/z*.

2,4,6-Tri-*O*-butyl-*meso*-D-*myo*-inositol (20)



20

19 (0.24 g, 0.67 mmol) was dissolved in THF (6 mL) and MeOH (3 mL). To the solution was added *p*-toluenesulfonic acid monohydrate (0.15 g, 0.77 mmol). Then the reaction was stirred at 45 °C for 16 hours, followed by cooling to room temperature. The concentrated residue was purified by flash column chromatography, (SiO2, 5 % MeOH in CH_2Cl_2) to give **20** (0.17 g, 0.53 mmol, 80 %) in the form of clear syrup.

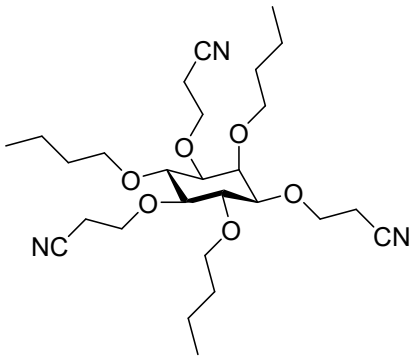
R_f (5 % methanol in CH_2Cl_2) = 0.47

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (qd, *J* = 6.6, 5.8, 2.8 Hz, 7H, CH_2-O, H-2), 3.44 (m, 2H, H-1, H-3), 3.39 – 3.32 (m, 2H, H-4, H-6), 2.42 (d, *J* = 5.8 Hz, 1H, H-5), 1.63 – 1.52 (m, 6H, -CH_2-), 1.37 (ttd, *J* = 9.5, 7.4, 5.3 Hz, 6H, -CH_2-), 0.92 (td, *J* = 7.4, 4.7 Hz, 9H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 82.1 (C-1, C-3), 79.6 (C-5), 74.7 (C-4, C-6), 73.6 (CH_2-O), 72.9 (CH_2-O), 72.6 (C-2), 32.5 (-CH_2-), 19.3 (-CH_2-), 14.0 (CH_3) ppm.

HRMS (MALDI+): Calculated for $C_{18}H_{36}O_6H^+$ 371.24041 *m/z* found 371.24032 *m/z*.

1,3,5-Tri-*O*-(2-cyanoethyl)-2,4,6-tri-*O*-butyl-*meso*-D-*myo*-Inositol (21)



21

20 (0.18 g, 0.50 mmol) was suspended in acrylonitrile (0.19 g, 3.52 mmol) and KOH (0.014 g, 0.25 mmol) was added. The reaction mixture was stirred at 80 °C for three hour after which the reaction mixture was cooled to room temperature and diluted with CH_2Cl_2. The reaction mixture was washed 3 times with water and 1 time with brine. The organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified using flash column chromatography, (SiO2, 6/4 to 7/3 EtOAc/heptane) to give **21** (0.092 g, 0.18 mmol, 36%) in the form of clear oil.

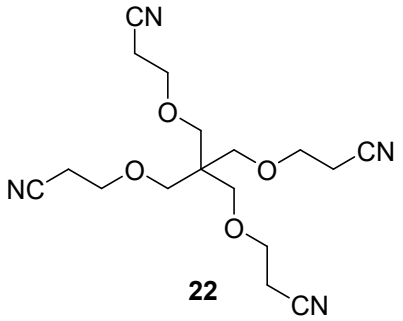
R_f (2/1 EtOAc/Heptane) = 0.41

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95 (t, *J* = 6.4 Hz, 2H, CH_2-O), 3.87 – 3.82 (m, 3H, CH_2-O, H-2), 3.81 – 3.77 (m, 2H, CH_2-O), 3.77 – 3.68 (m, 2H, CH_2-O), 3.56 (t, *J* = 9.5 Hz, 2H, H-4, H-6), 3.05 (dd, *J* = 9.8, 2.4 Hz, 2H, H-1, H-3), 2.98 (t, *J* = 9.3 Hz, 1H, H-5), 2.65 – 2.53 (m, 6H, CH_2-CN), 1.59 – 1.50 (m, 6H, -CH_2-), 1.37 (ddt, *J* = 15.0, 11.1, 7.4 Hz, 6H, -CH_2-), 0.92 (t, *J* = 7.4 Hz, 9H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 118.0 (CN), 117.8 (CN), 84.1 (C-5), 81.7 (C-1, C-3), 80.6 (C-4, C-6), 76.1 (C-2), 73.6 (CH_2-O), 73.3 (CH_2-O), 67.8 (CH_2-O), 65.9 (CH_2-O), 32.7 (-CH_2-), 32.3 (-CH_2-), 19.4 (CH_2-CN), 19.3 (CH_2-CN), 19.2 (-CH_2-), 19.2 (-CH_2-), 14.0 (CH_3), 13.9 (CH_3) ppm.

HRMS (MALDI+): Calculated for $C_{27}H_{45}O_6N_3H^+$ 530.32006 *m/z* found 530.31959 *m/z.*

Tetrakis-[(2-cyanoethoxy)methyl]methane (22)[9]



22

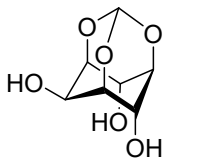
Pentaerythritol (0.50 g, 3.67 mmol) was suspended in acrylonitrile (1.56 g, 29.38 mmol) and aq. Na_2CO_3 (0.05 M) (3 mL) was added. The reaction was stirred at 80°C and after 14 hours the heating was removed and the reaction mixture cooled to room temperature whereupon the pH of the reaction was lowered to 7 by adding aq. HCl (1M). The reaction mixture was then extracted with CH_2Cl_2 and the combined organic phases were washed twice with H_2O and once with brine. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The product was purified using flash column chromatography, (SiO2, 8/2 to 9/1 EtOAc/heptane) to give **22** (0.36 g, 1.04 mmol, 28%) as a clear oil.

R_f (5 % methanol in CH_2Cl_2) = 0.68

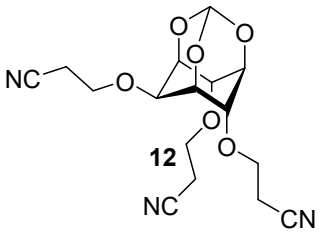
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.64 (t, *J* = 6.0 Hz, 8H, O-CH_2), 3.50 (s, 8H, O-CH_2), 2.59 (t, *J* = 6.0 Hz, 8H, CH_2-CN) ppm.

HRMS (MALDI+): Calculated for $C_{17}H_{24}O_4N_4H^+$ 349.18703 *m/z* found 349.18722 *m/z.*

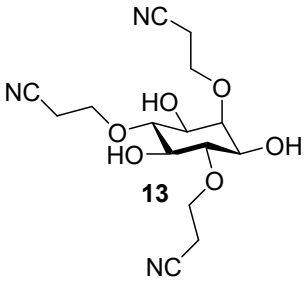
SI.3 Molecules List



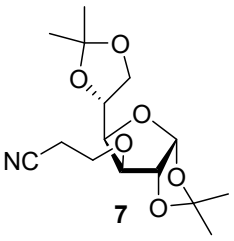
11



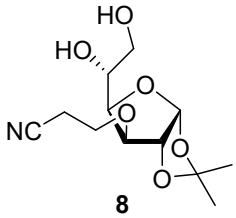
12



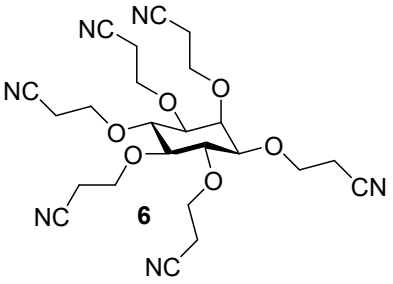
13



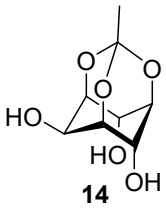
7



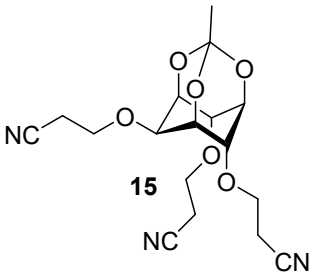
8



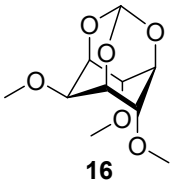
6



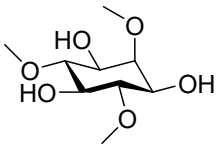
14



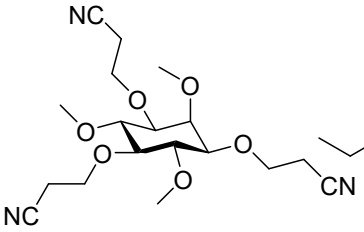
15



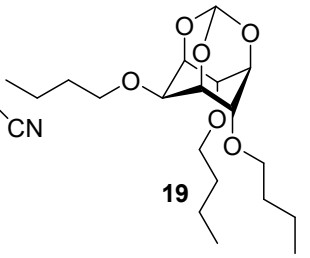
16



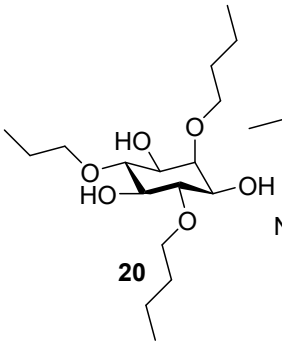
17



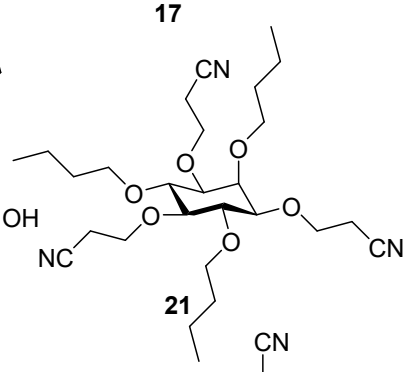
18



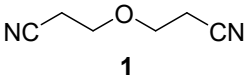
19



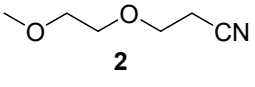
20



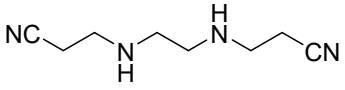
21



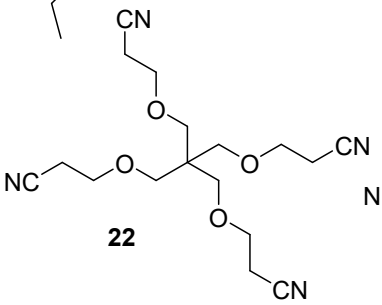
1



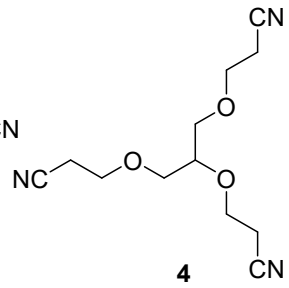
2



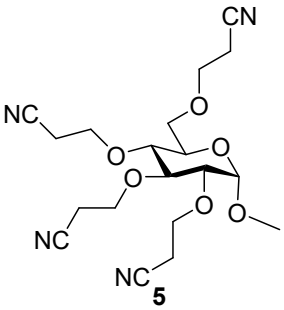
3



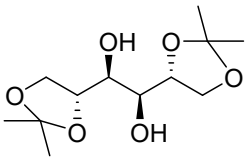
22



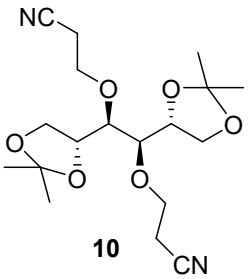
4



5



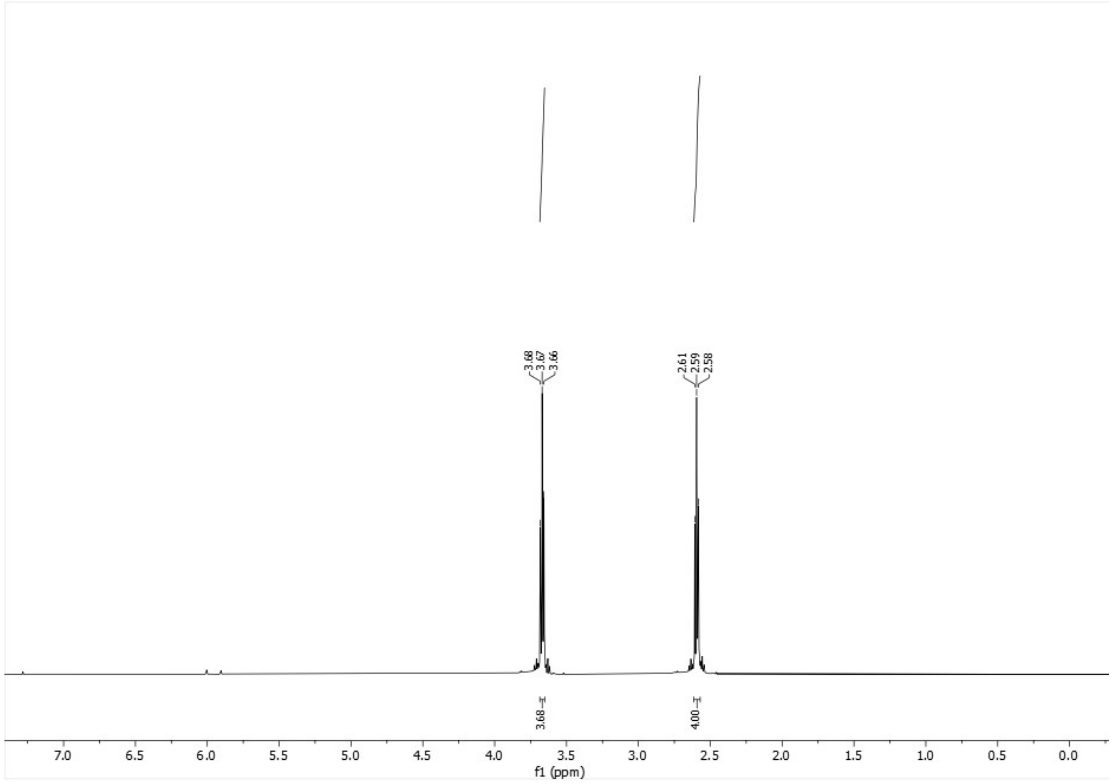
9

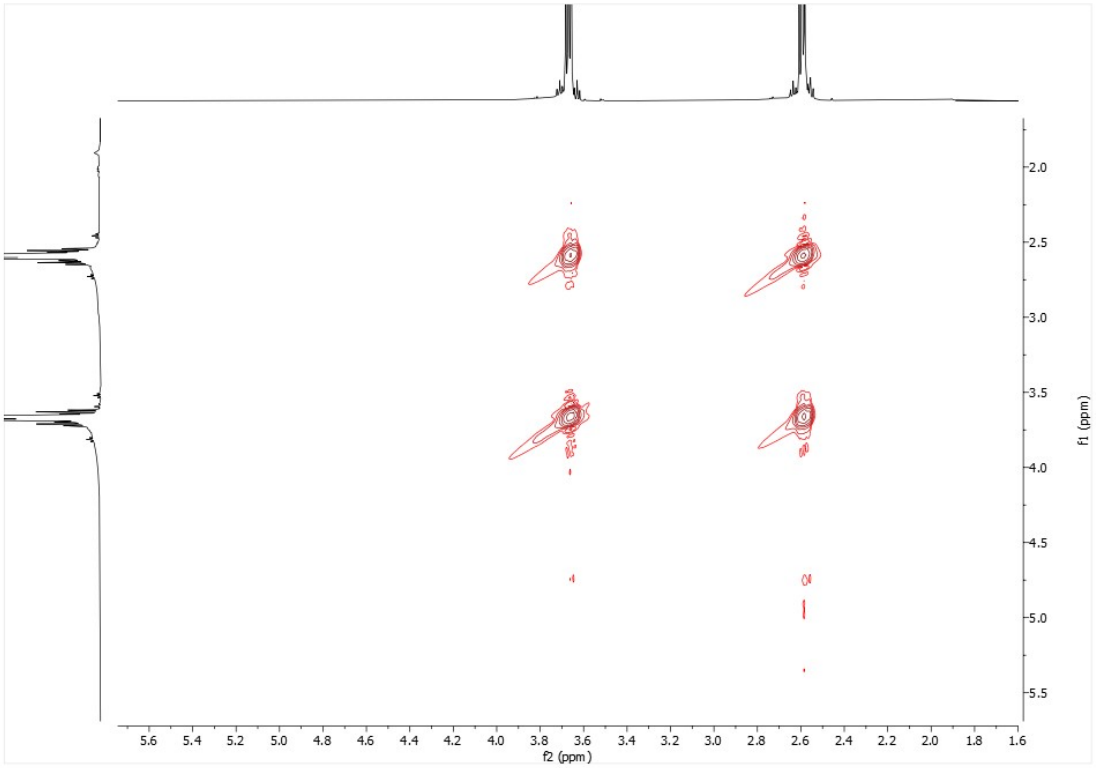


10

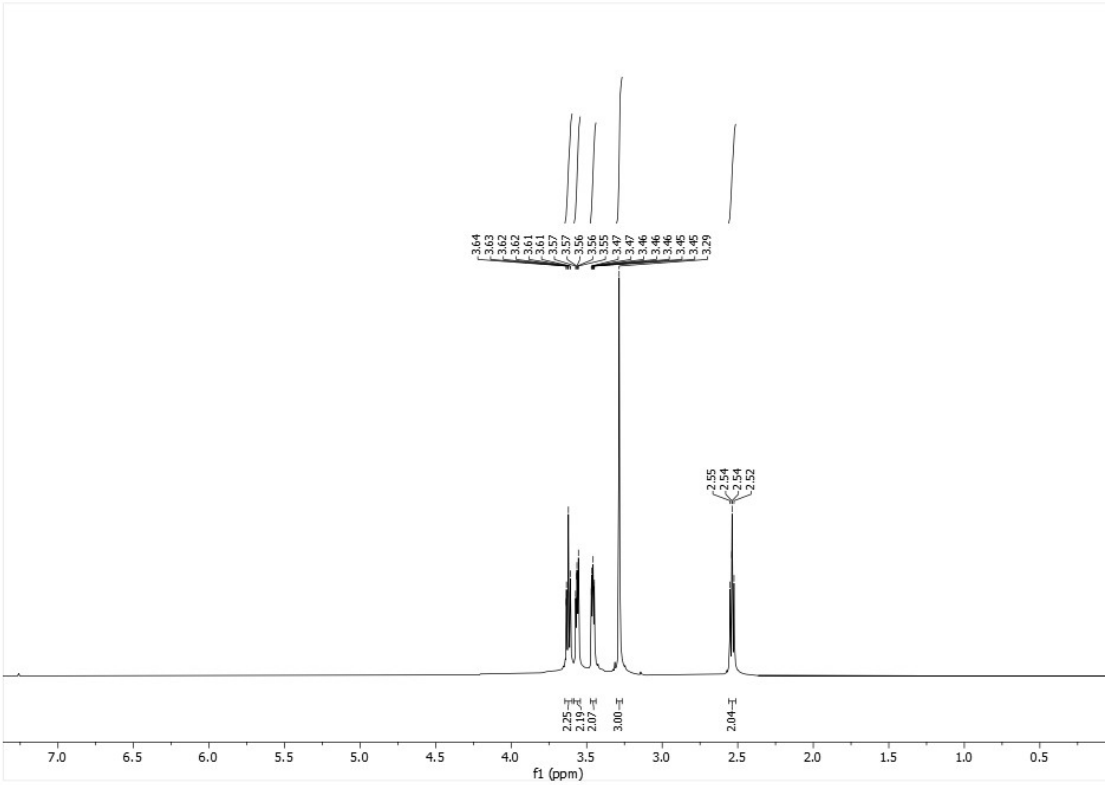
SI.4 NMR data

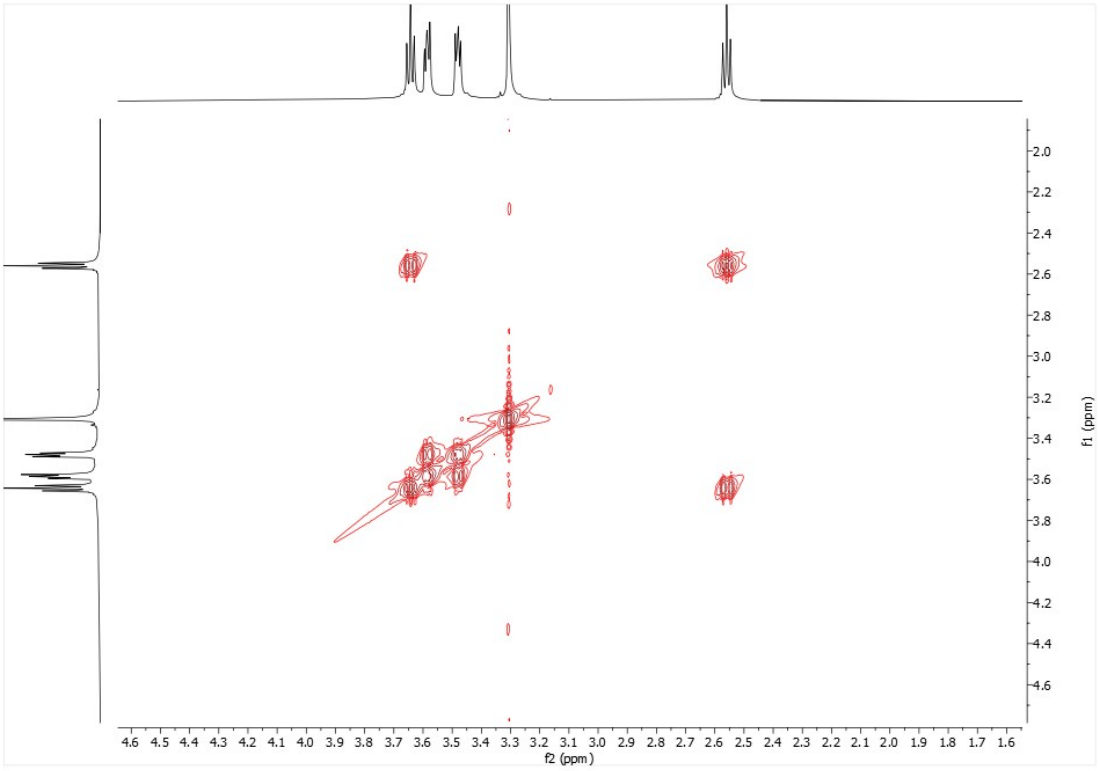
2-Cyanoethyl ether (1)



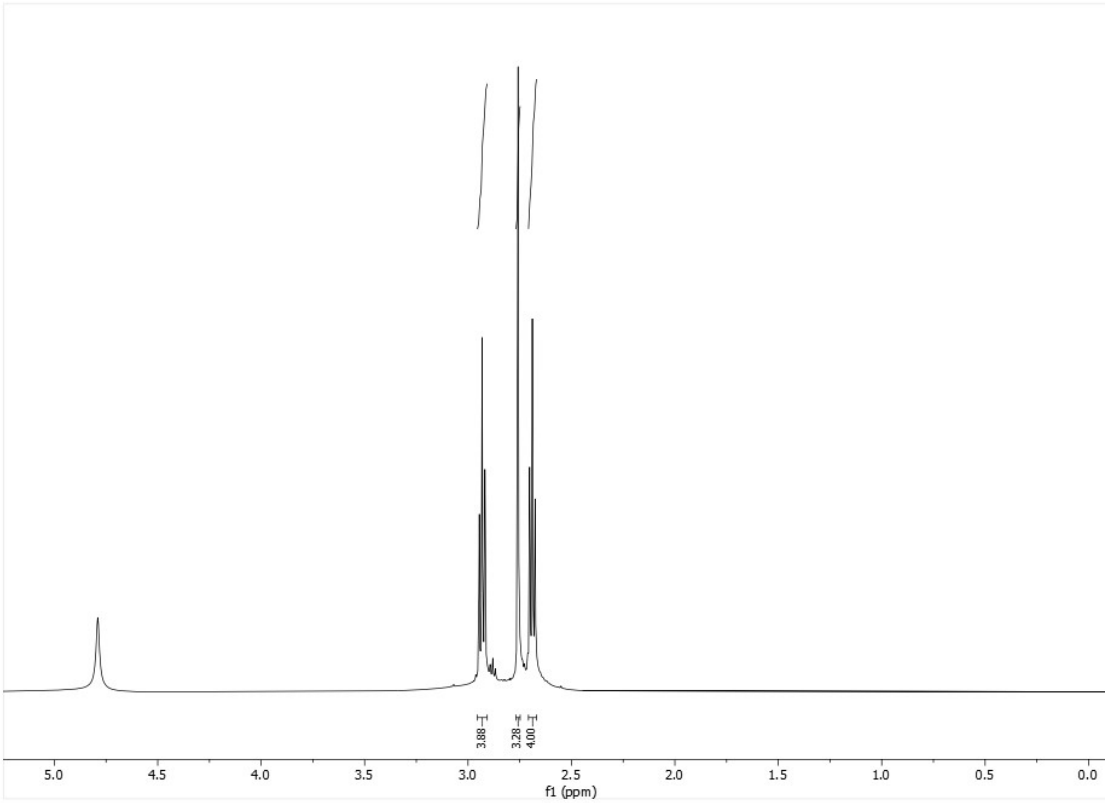


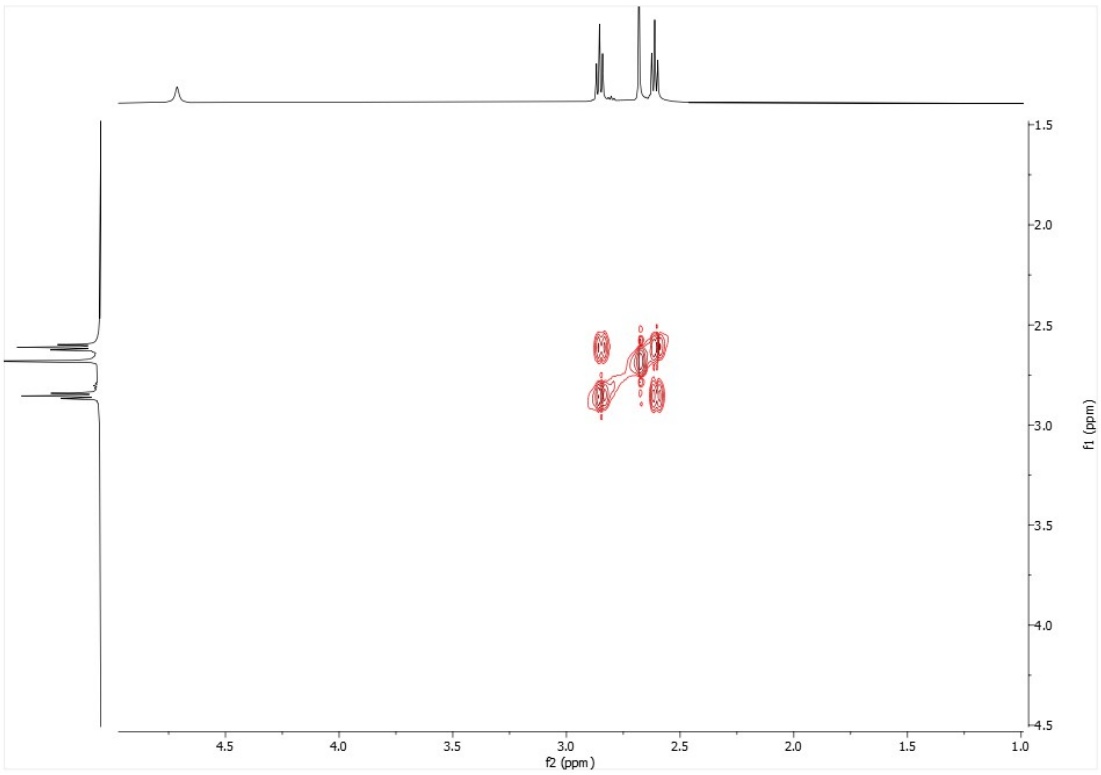
3-(2-methoxyethoxy)propanenitrile (2)



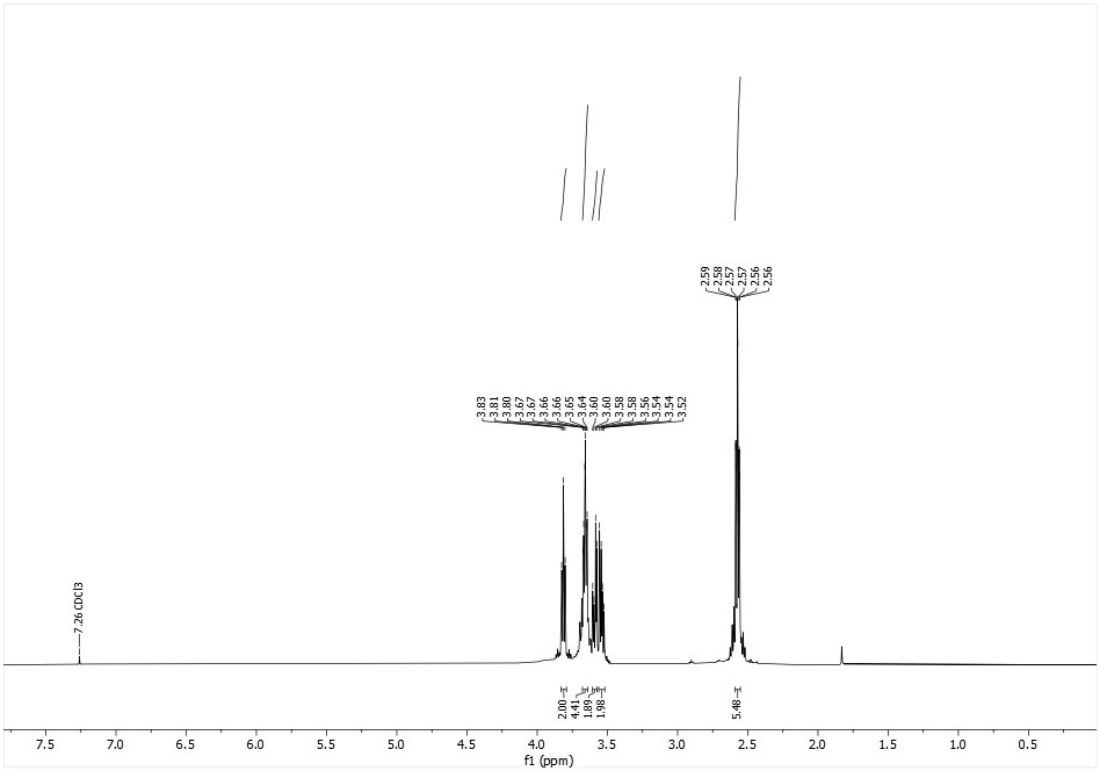


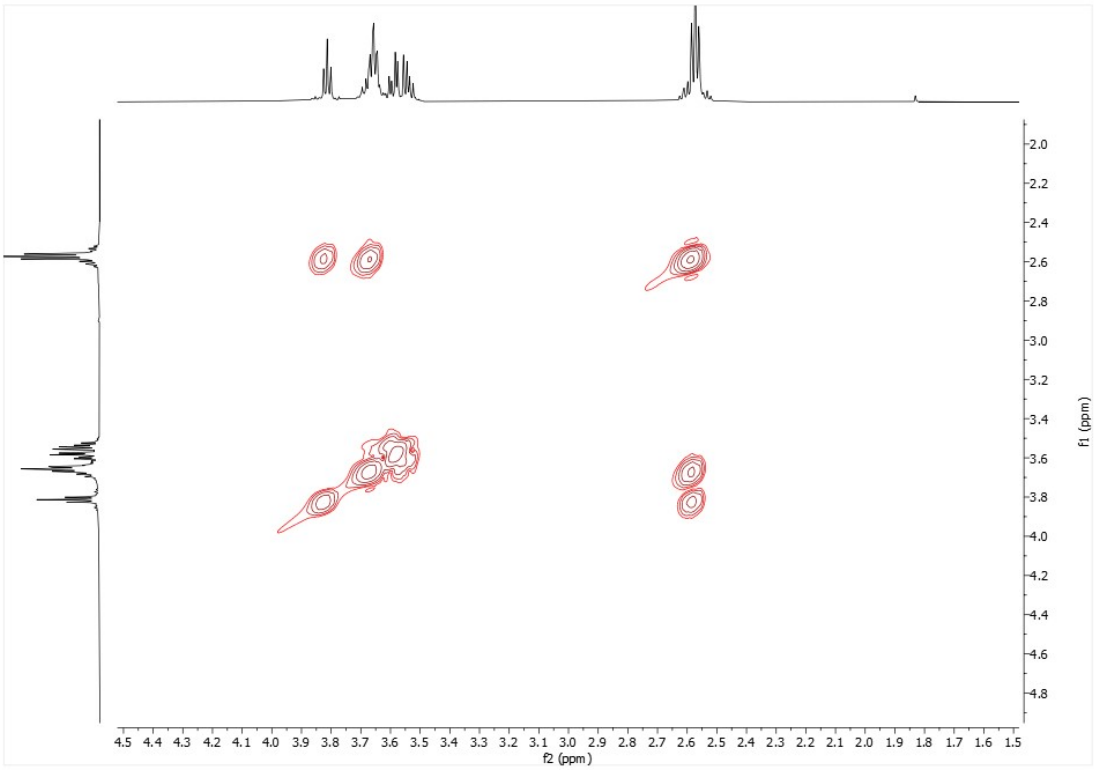
N,N'-bis-(2-cyanoethyl)ethylenediamine (3)



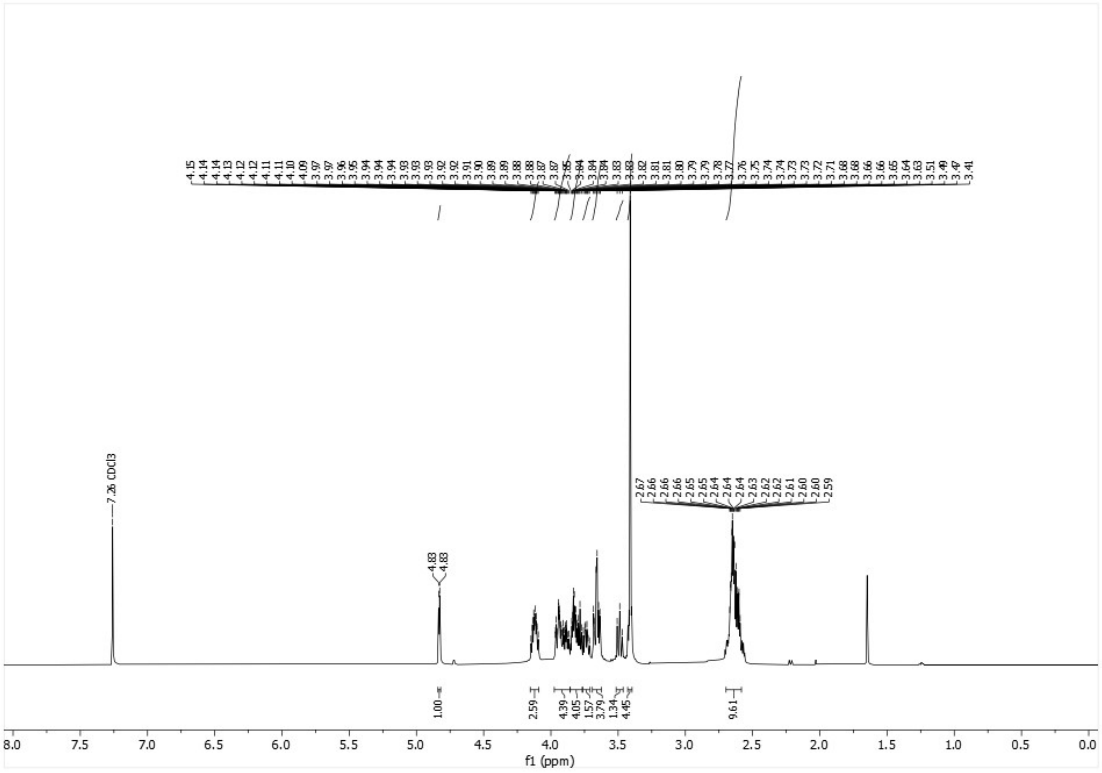


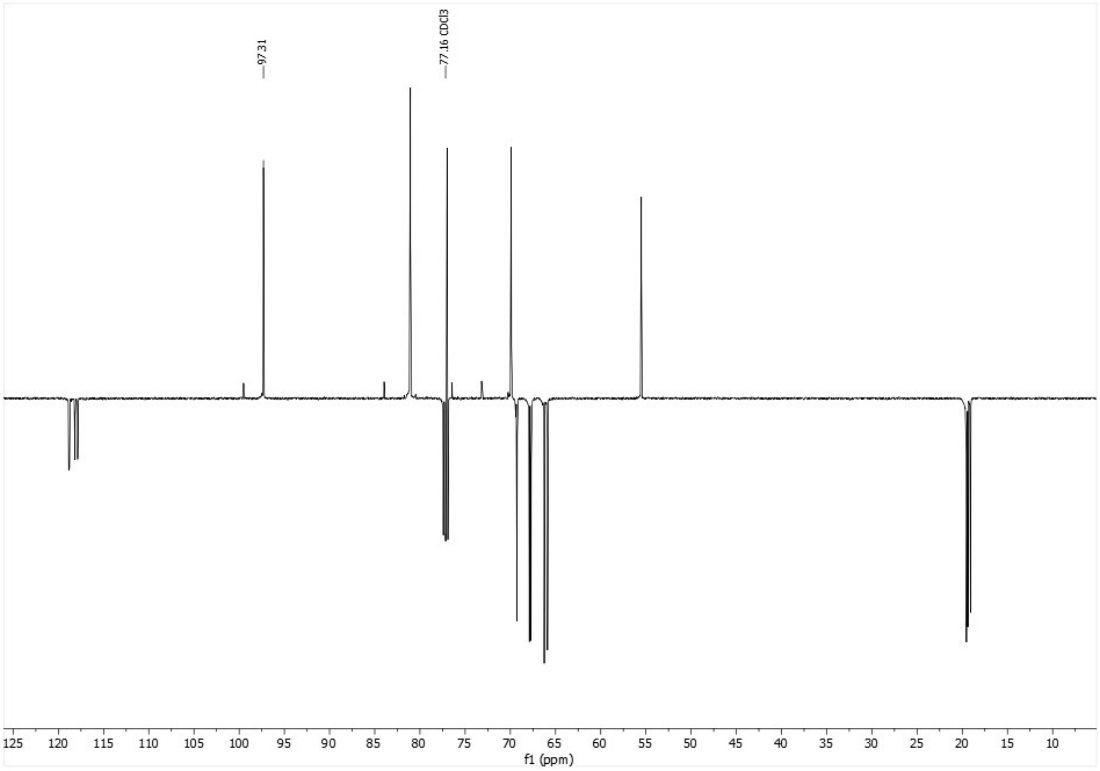
1,2,3-Tri(cyanoethoxy)propane (4)

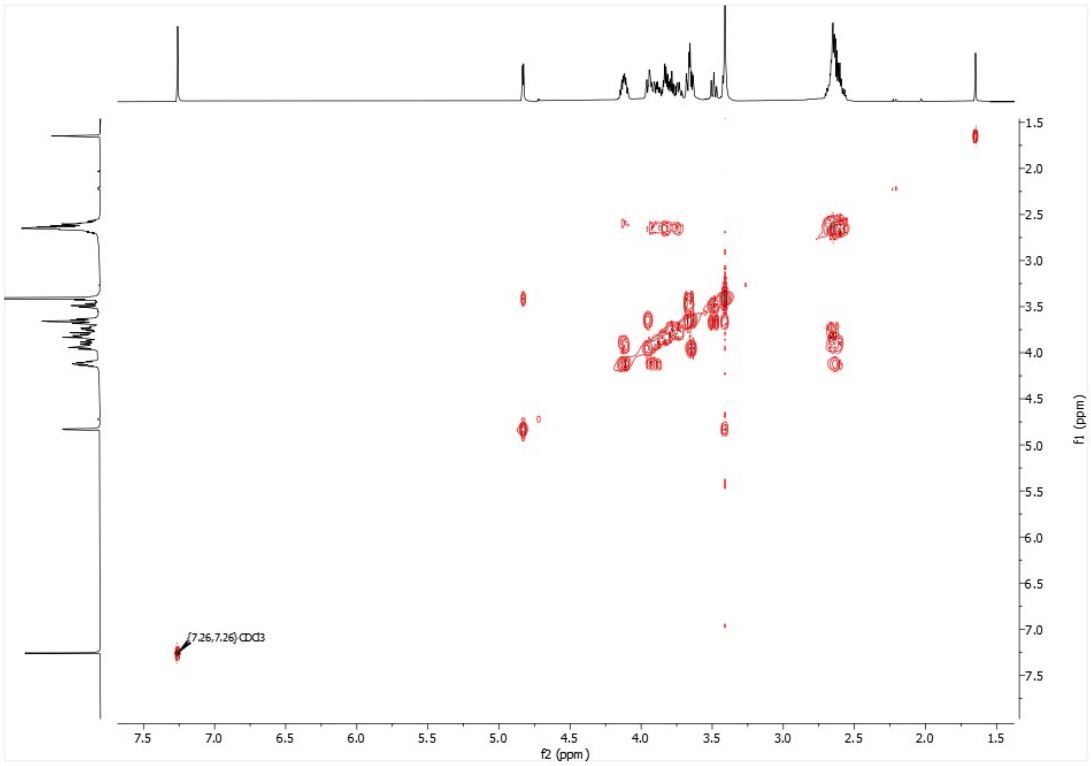


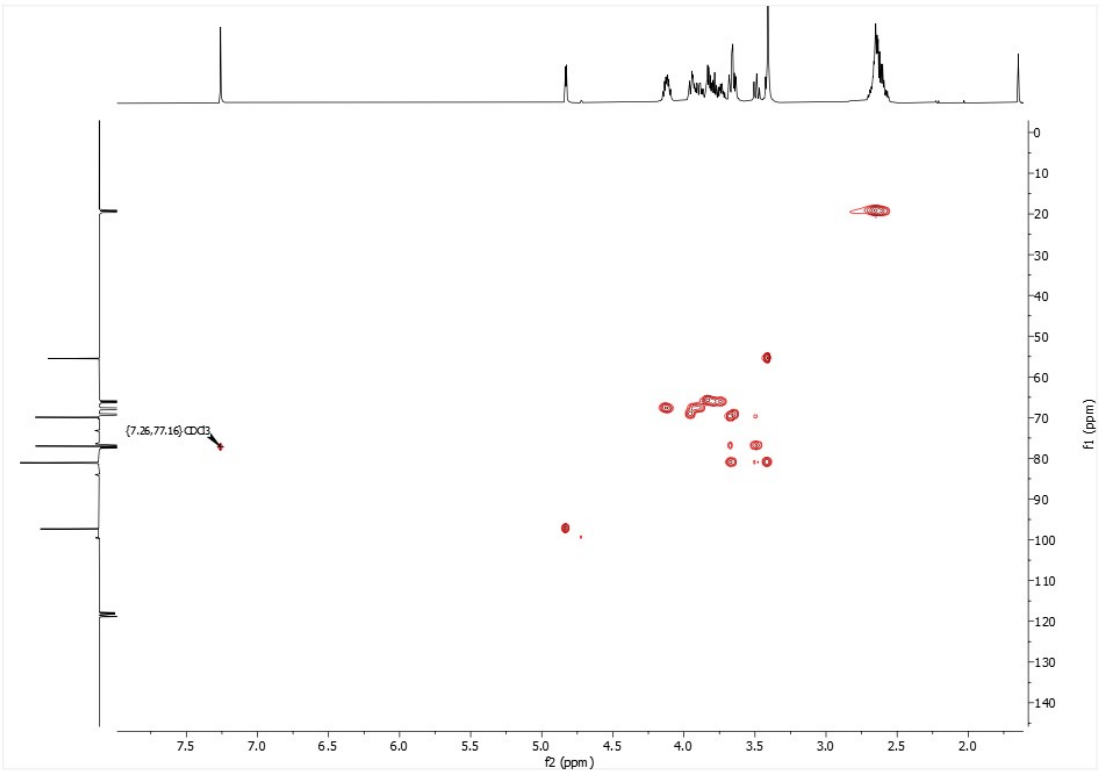


Methyl 2,3,4,6-tetra-*O*-(2-cyanoethyl)-α-D-glucopyranoside (5)

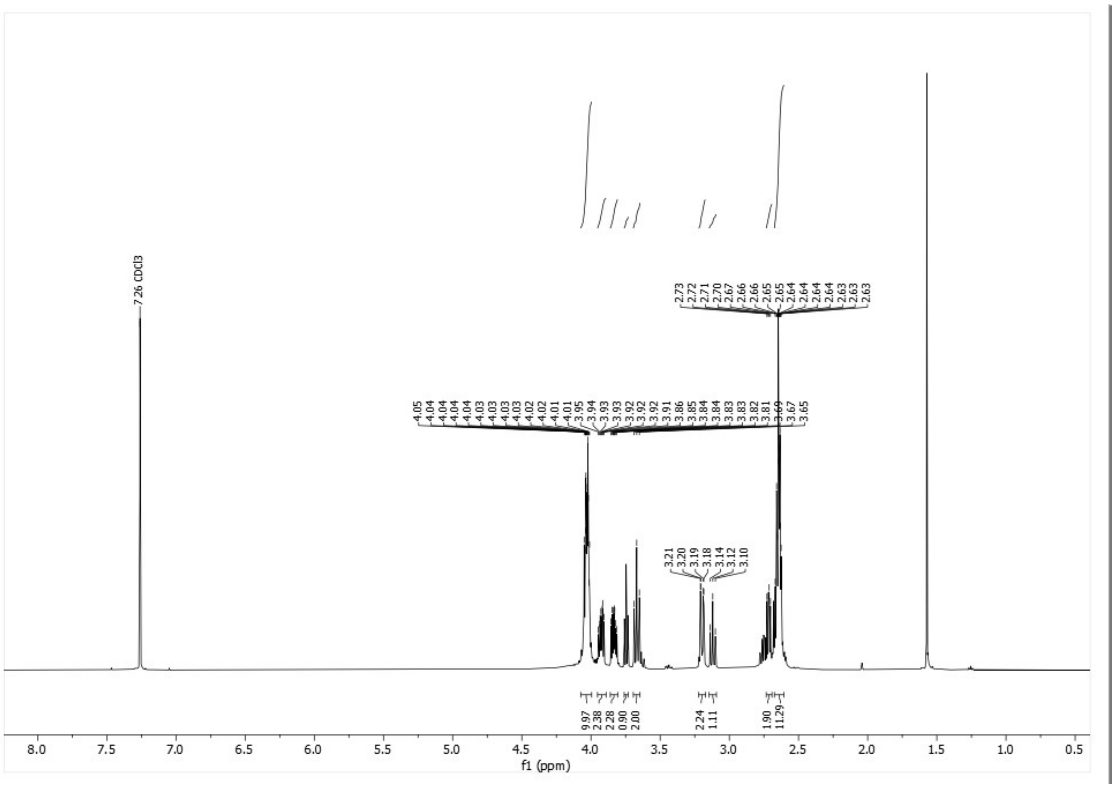


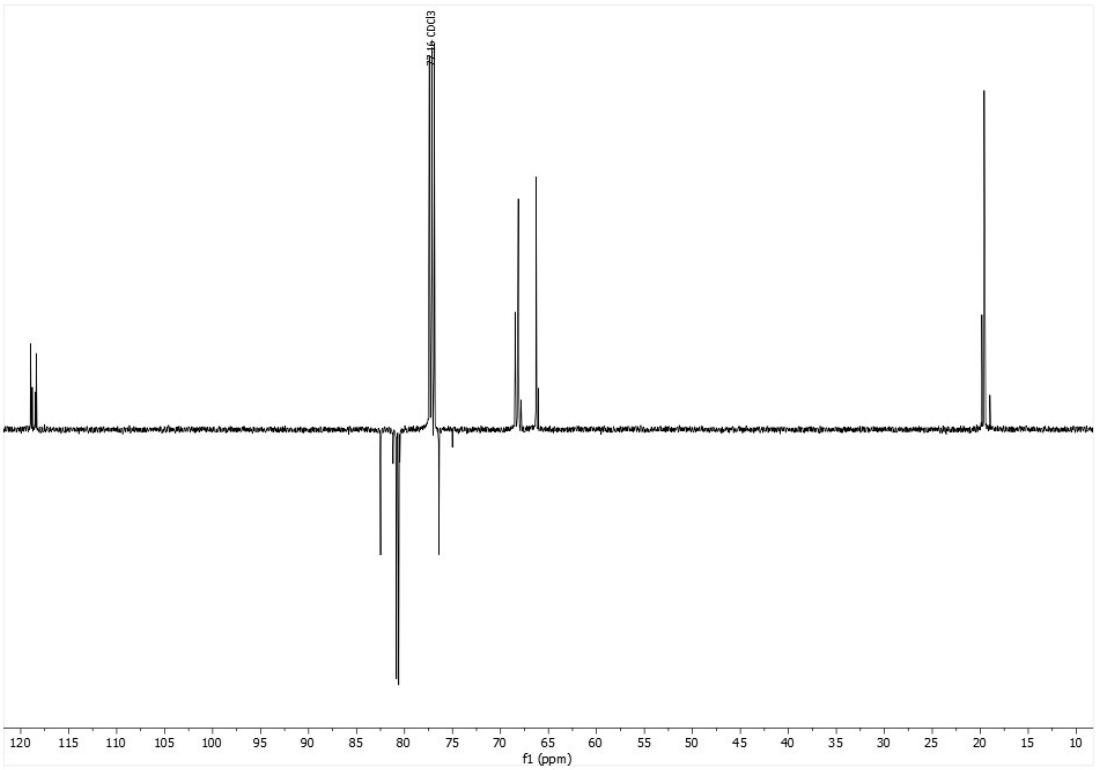


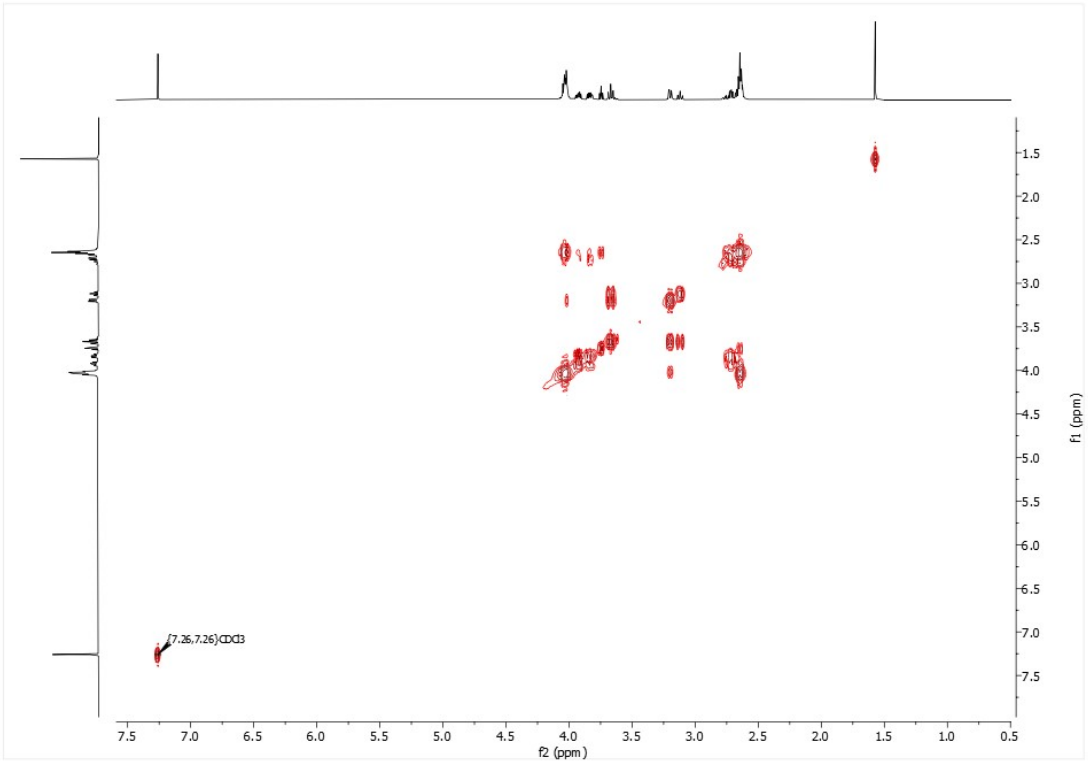

(7.26,7.26) CDCl3
f2 (ppm)
f1 (ppm)

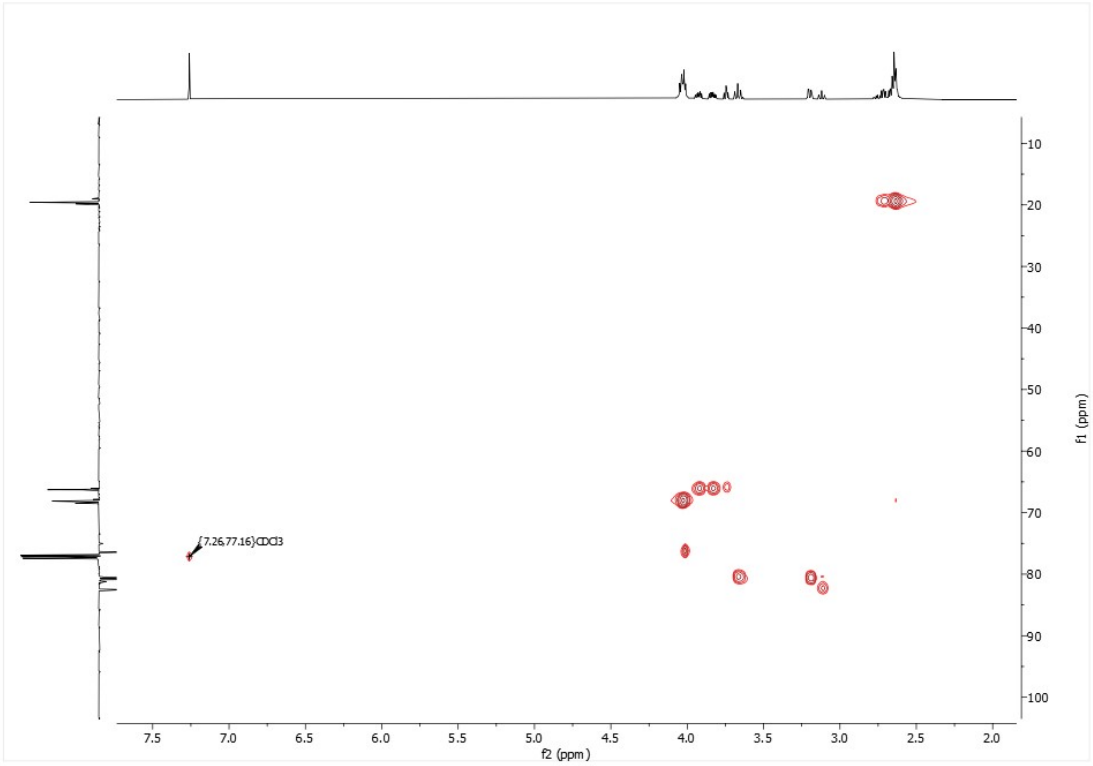

(7.26,77.16) CDCl3
f2 (ppm)
f1 (ppm)

1,2,3,4,5,6-Hexa-*O*-(2-cyanoethyl)-*meso*-D-*myo*-inositol (6)

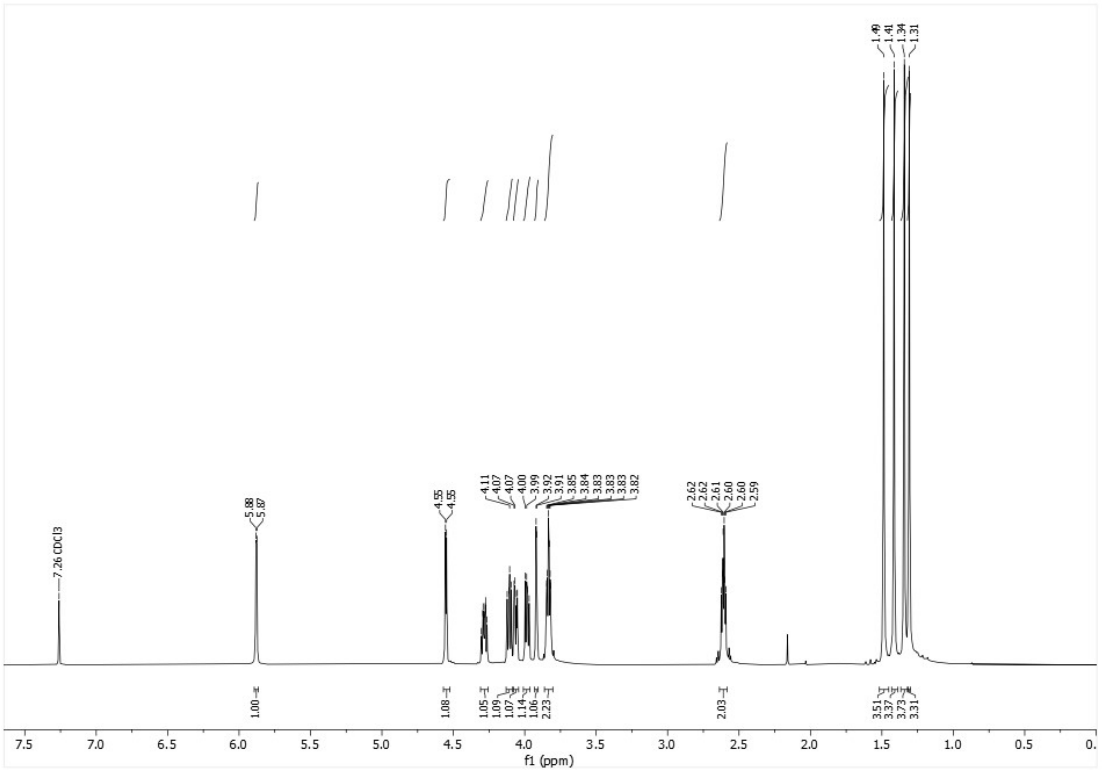


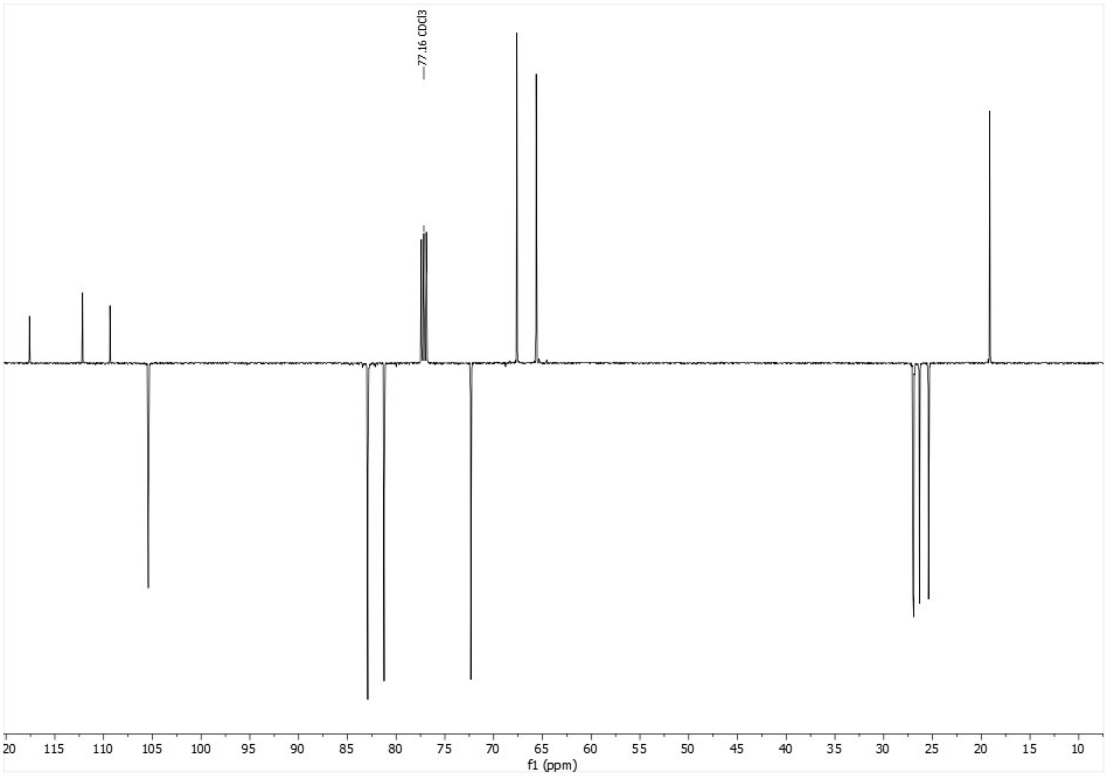


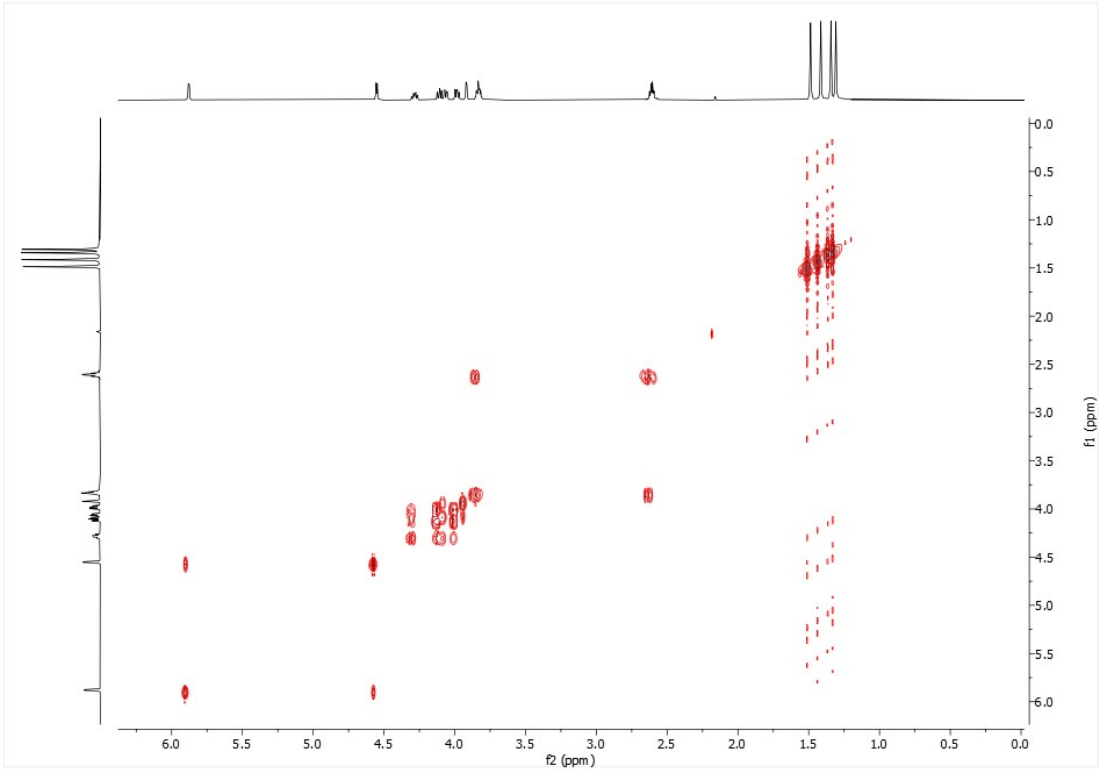

{7.26,7.26}CDCl3
f2 (ppm)
f1 (ppm)

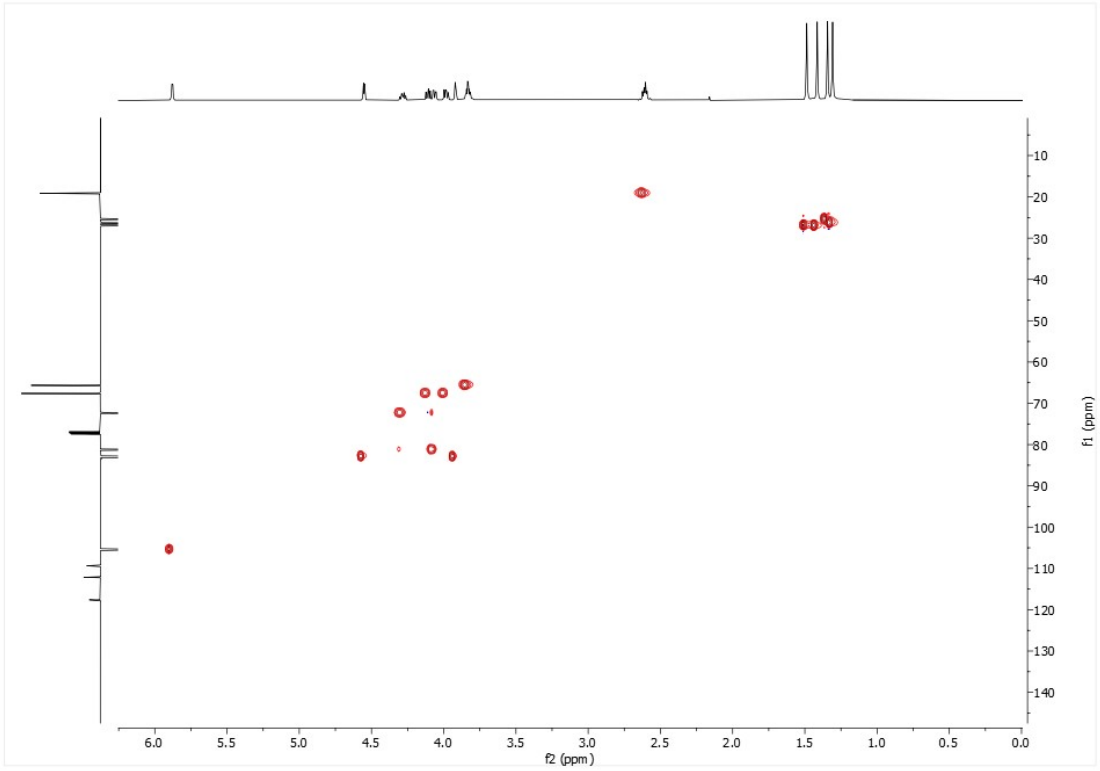

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-cyanoethyl)-α-D-glucofuranose (7)

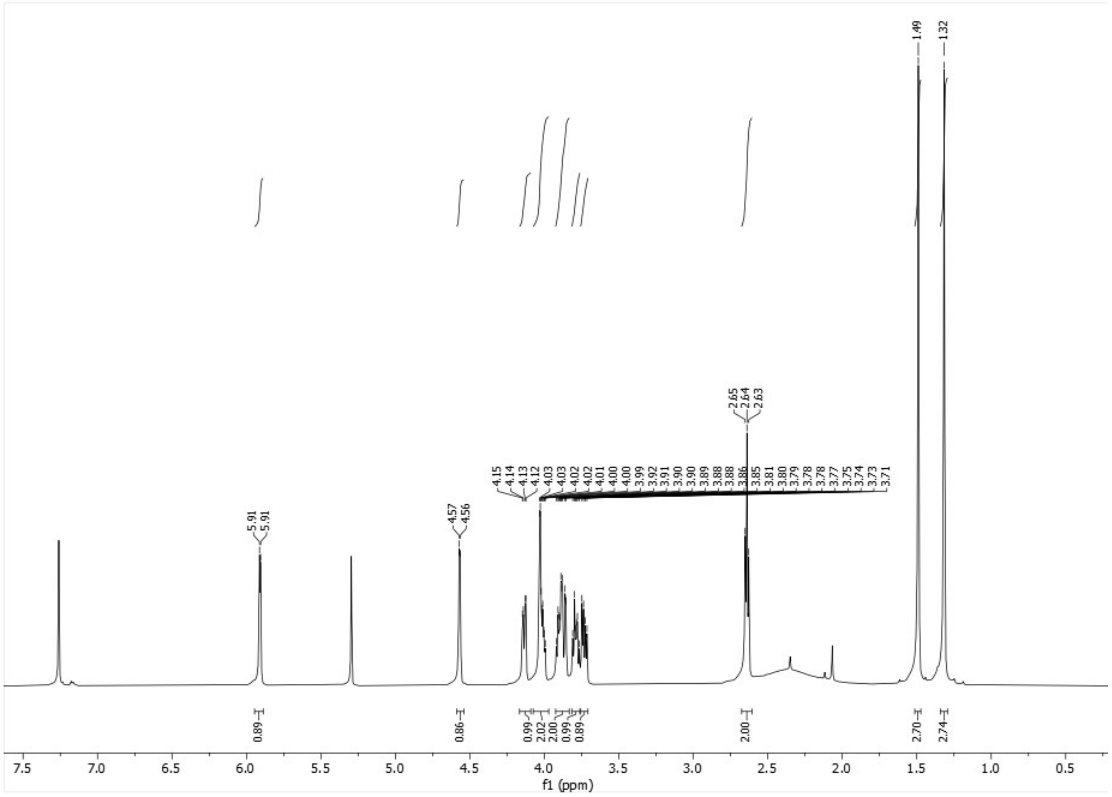


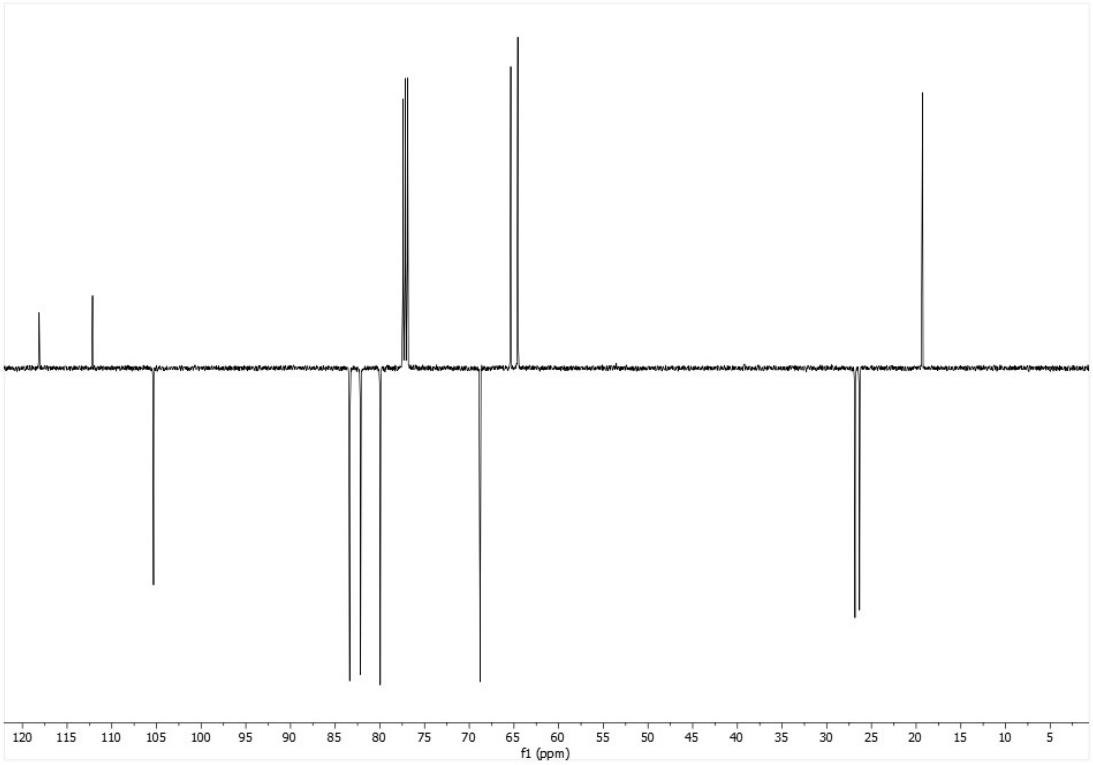


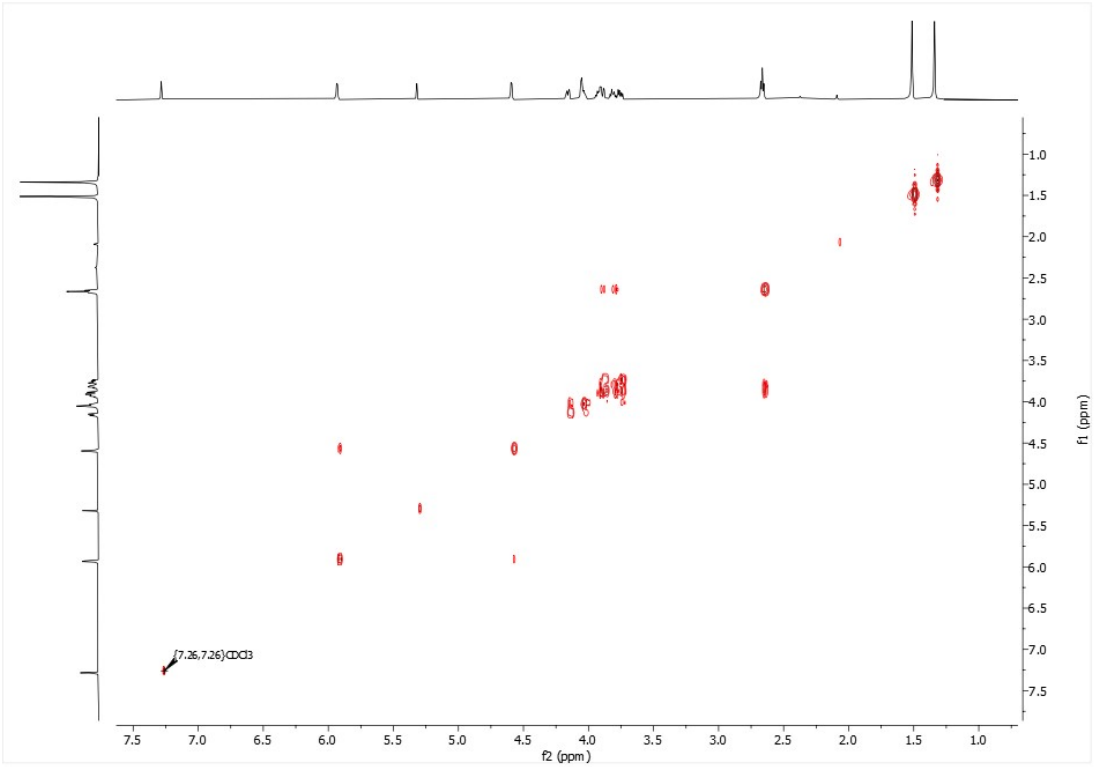

f2 (ppm)
f1 (ppm)

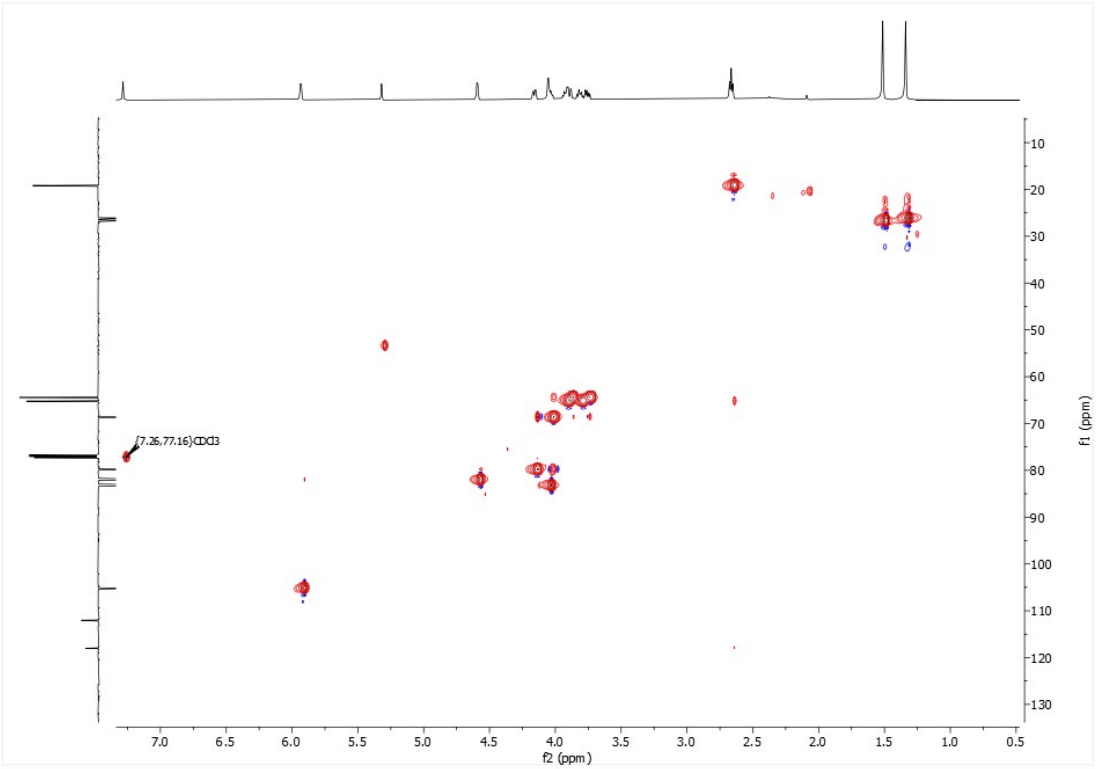

f2 (ppm)
f1 (ppm)

1,2-*O*-Isopropylidene-3-*O*-(2-cyanoethyl)-α-D-glucofuranose (8)

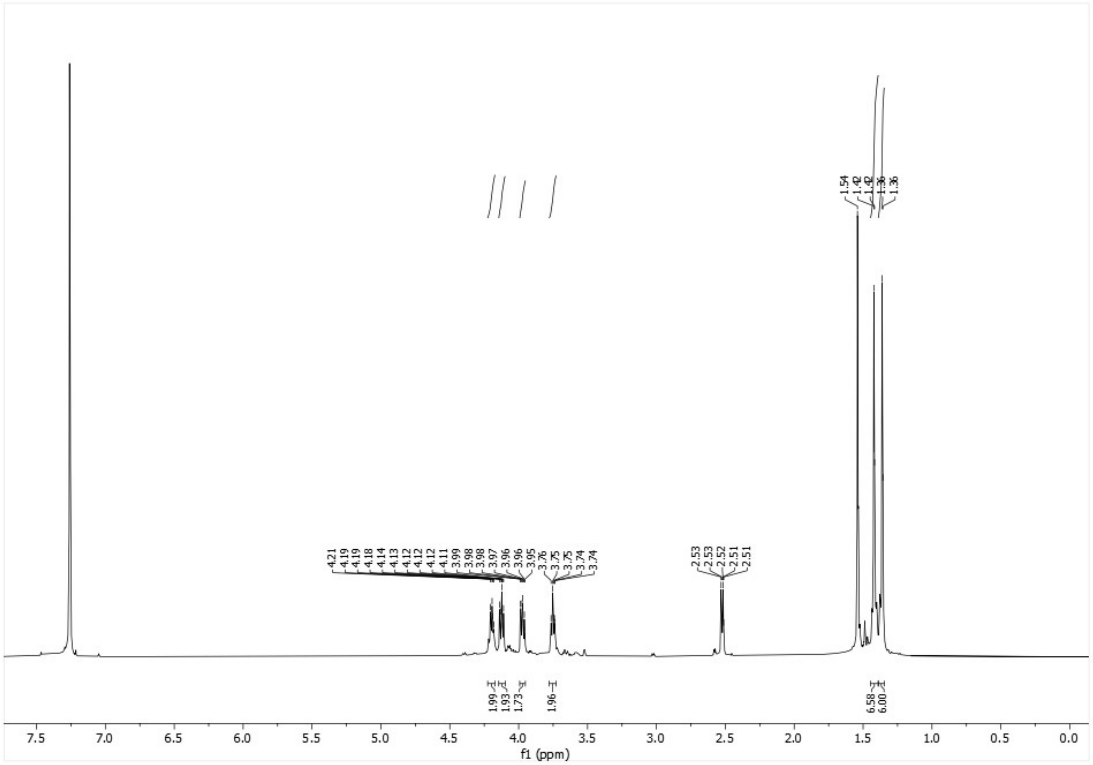


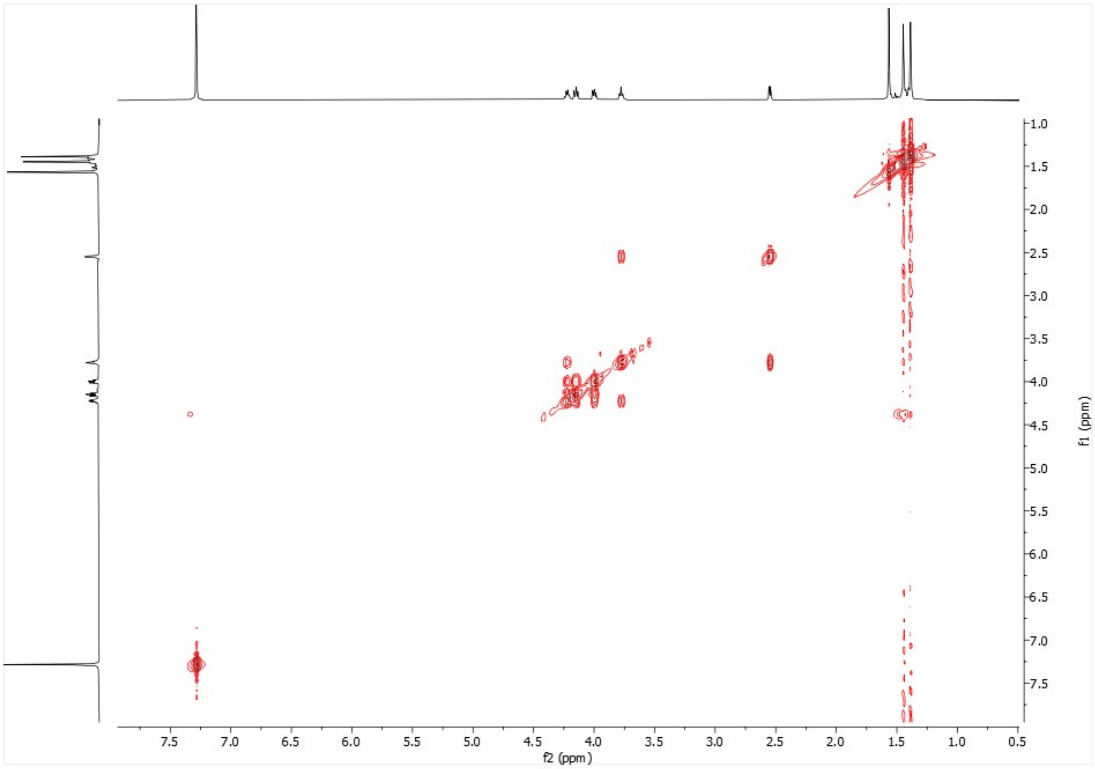



(7.26,7.26)CDCl3
f2 (ppm)
f1 (ppm)

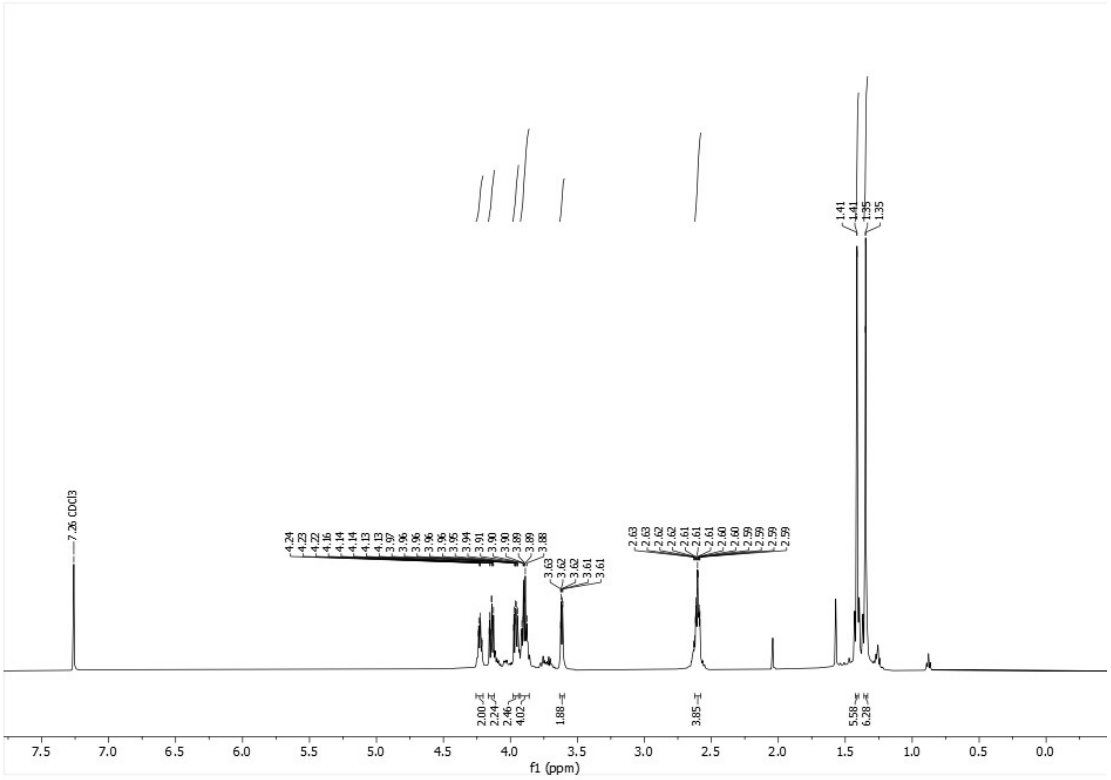

(7.26,77.16)CDCl3
f2 (ppm)
f1 (ppm)

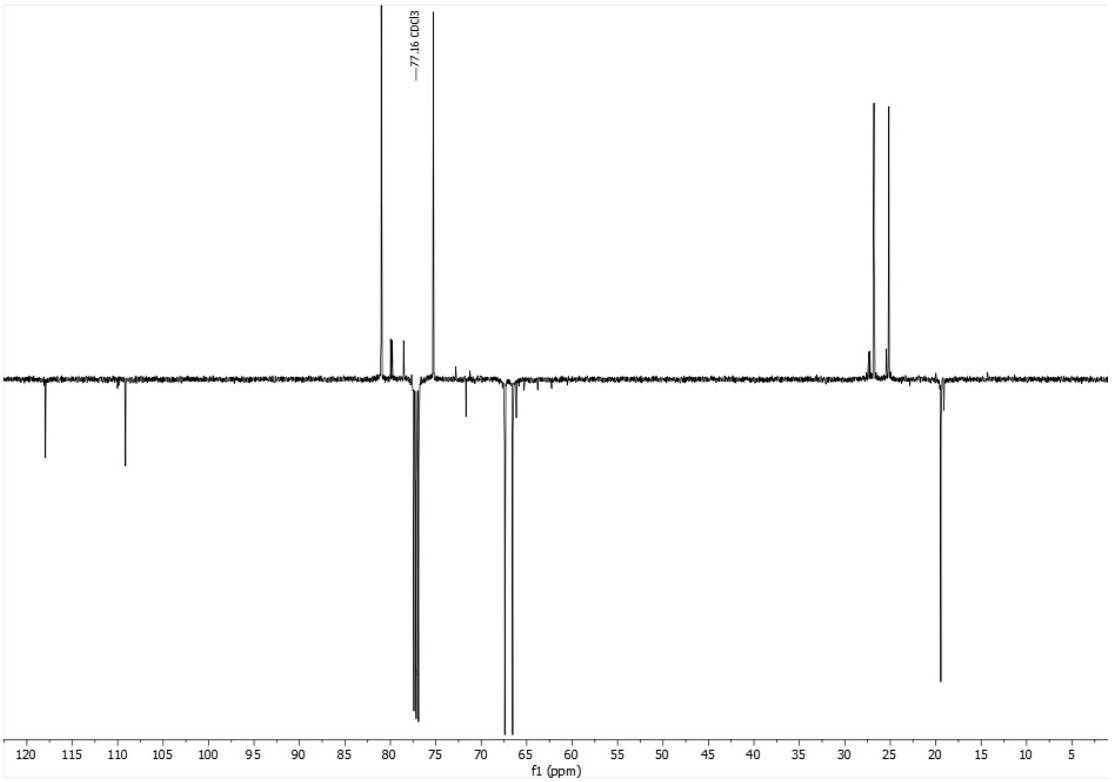
1,2:5,6-Di-*O*-isopropylidene-D-mannitol (9)

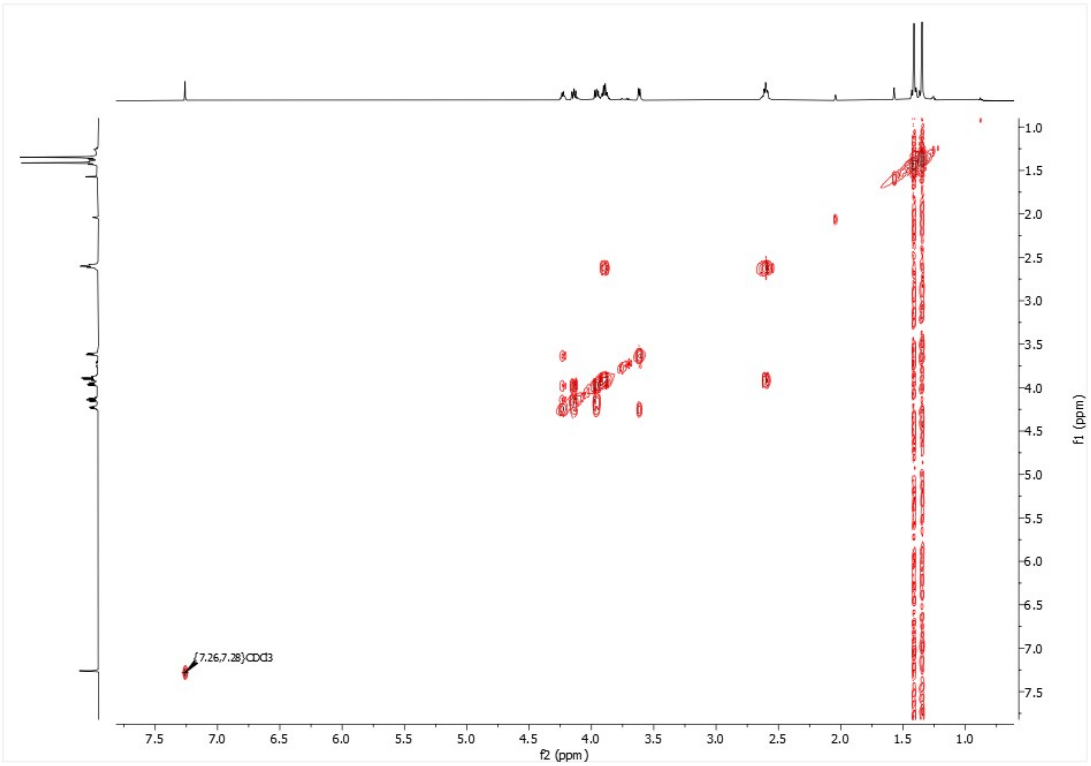


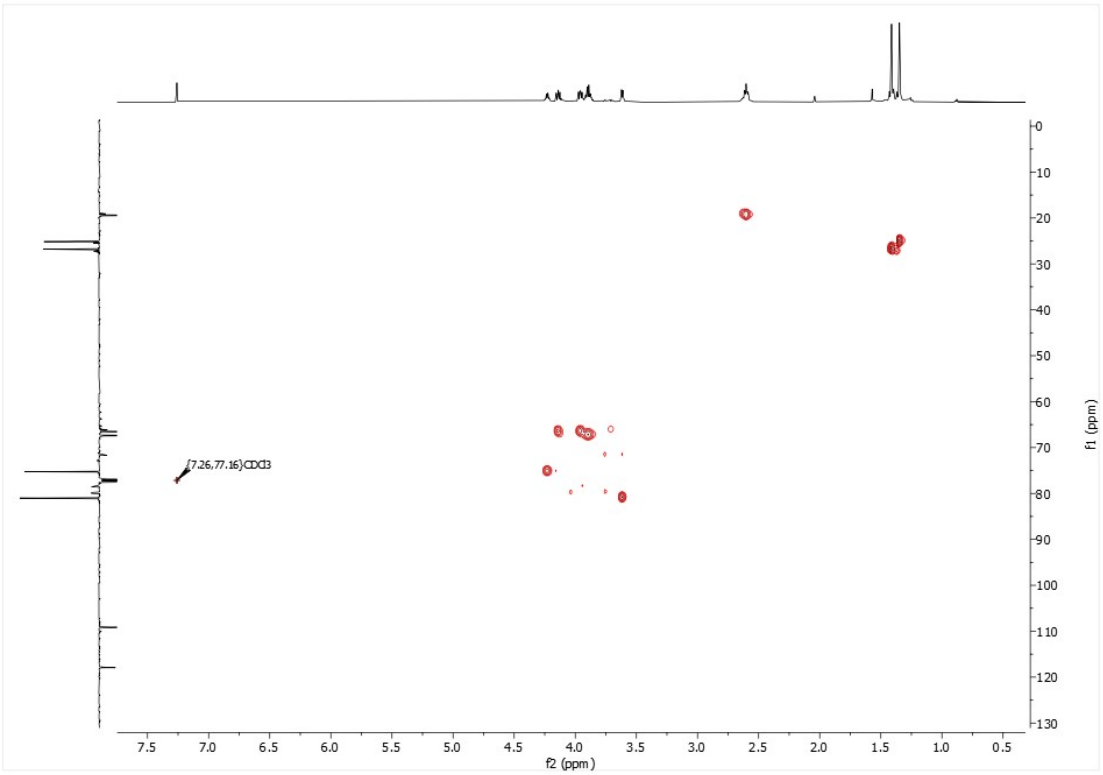


1,2:5,6-Di-*O*-isopropylidene-3,4-di-*O*-(2-cyanoethyl)-D-mannitol (10)

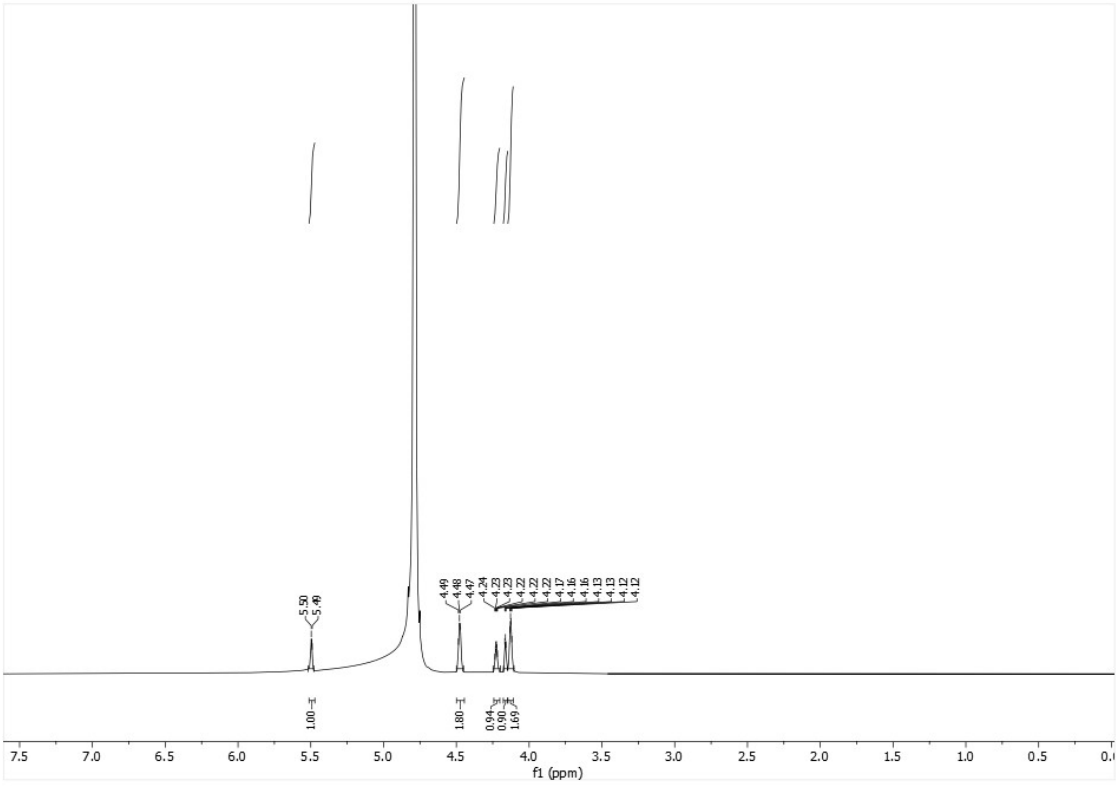


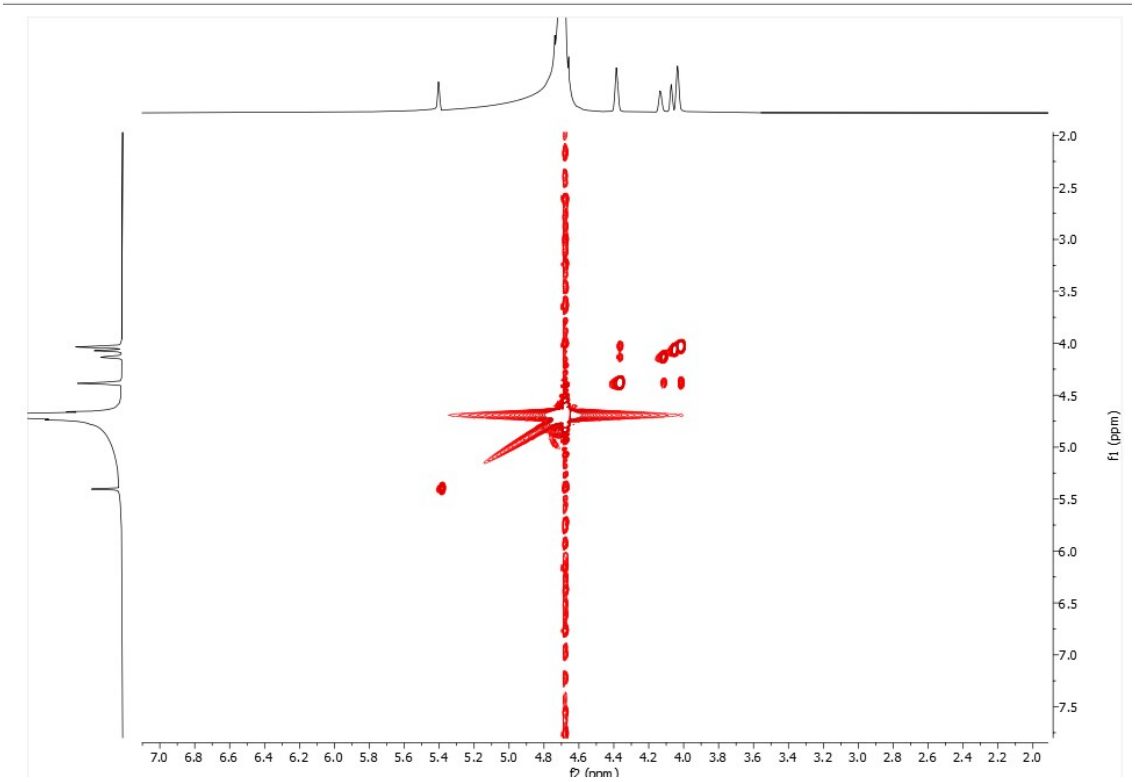



{7.26,7.28}CDCl3
f2 (ppm)
f1 (ppm)

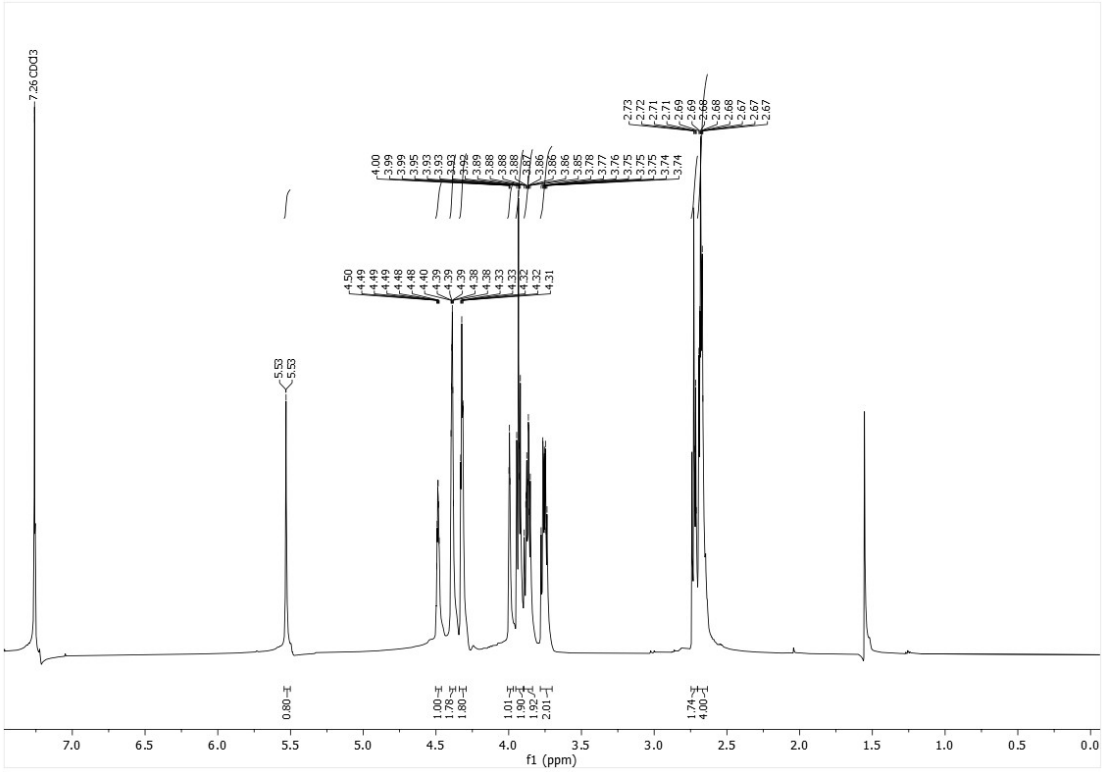

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

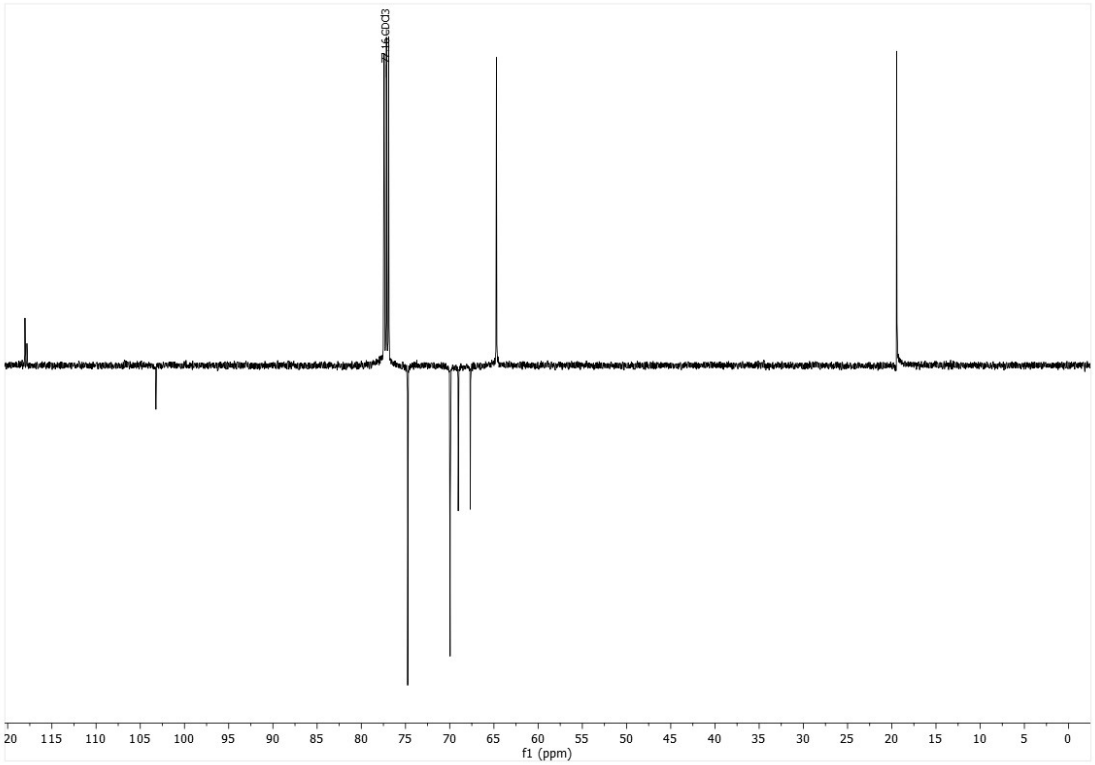
***Meso*-D-*myo*-inositol-1,3,5-*O*-orthoformate (11)**

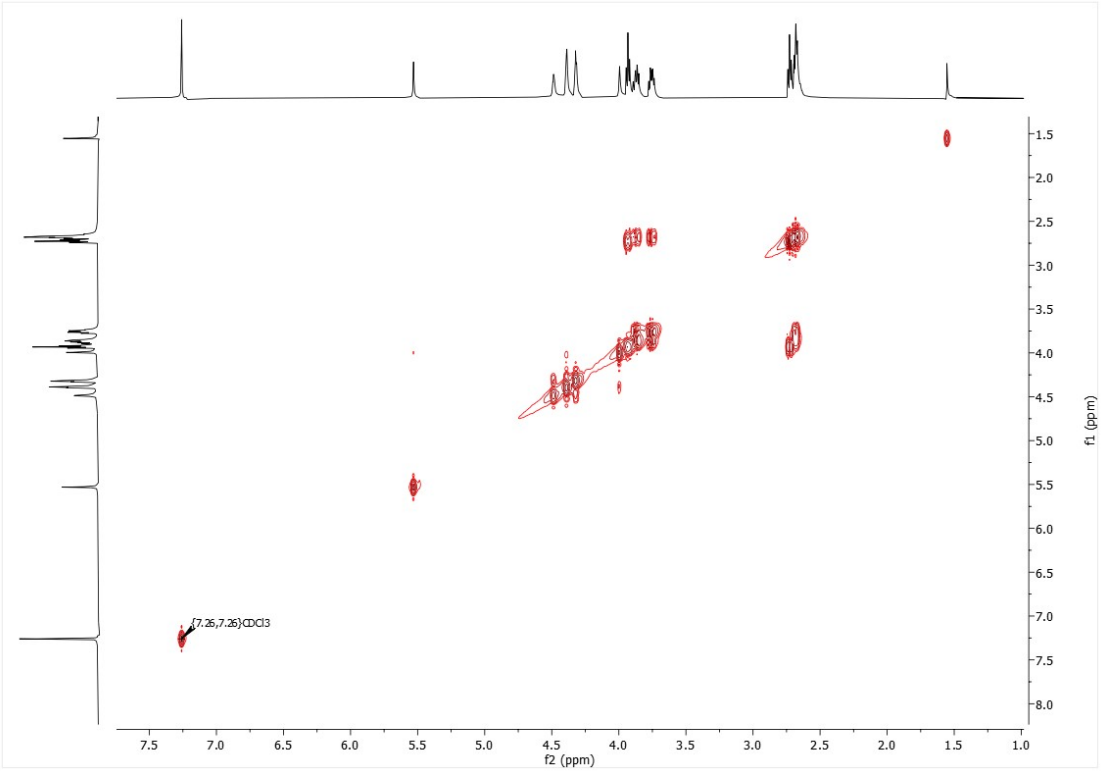


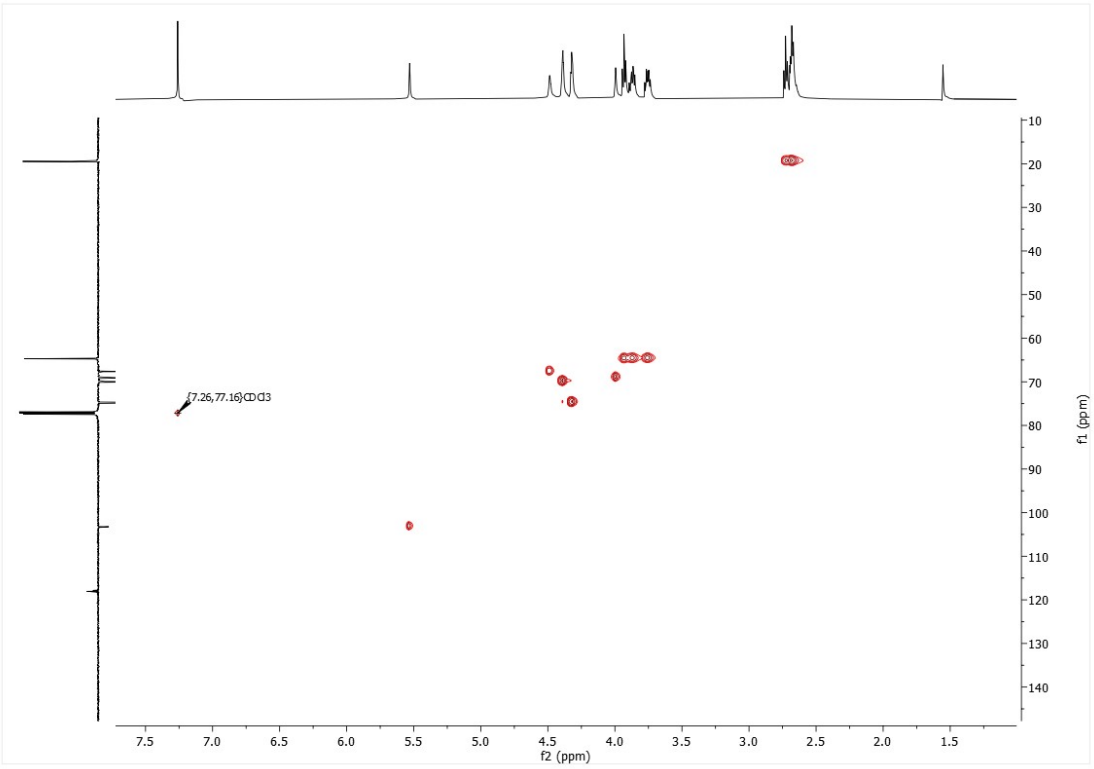


2,4,6-Tri-*O*-(2-cyanoethyl)-*meso*-D-*myo*-inositol-1,3,5-*O*-orthoformate (12)

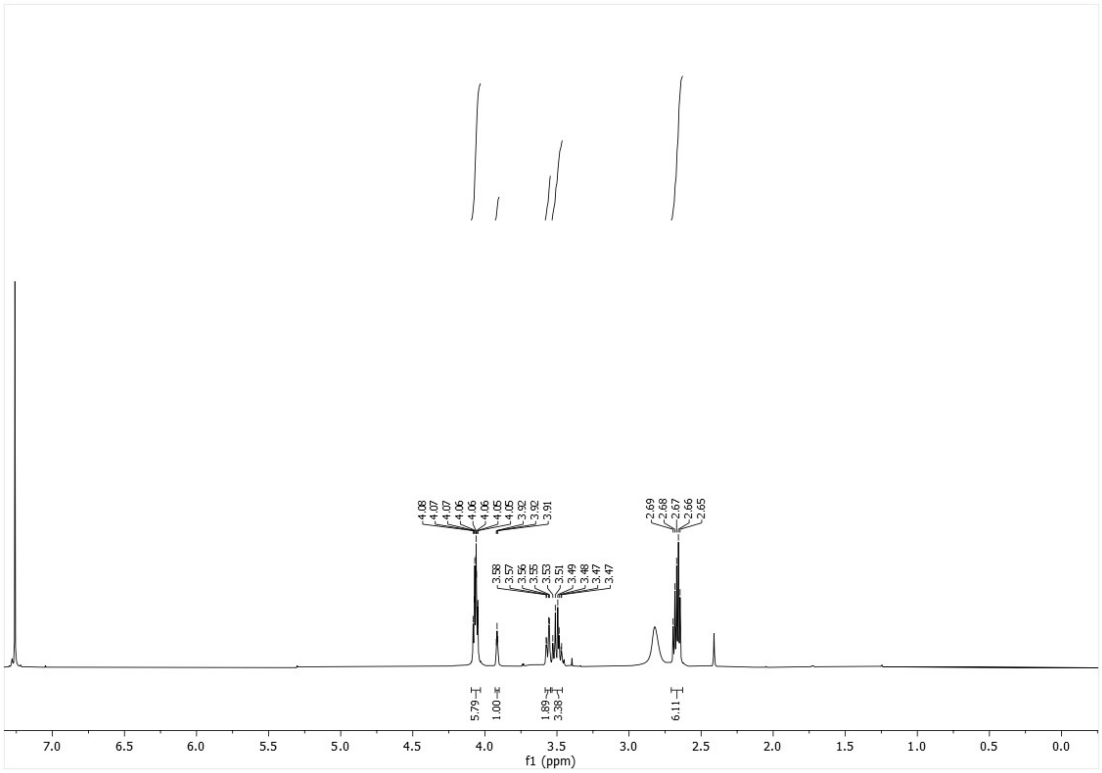


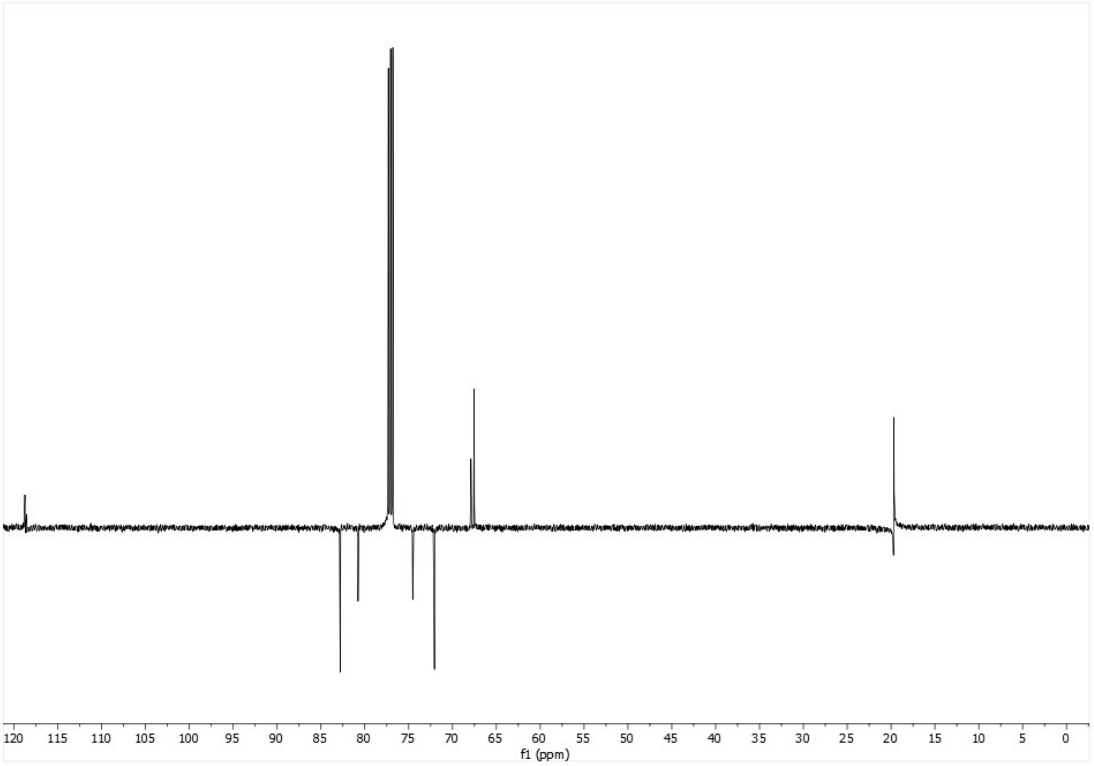


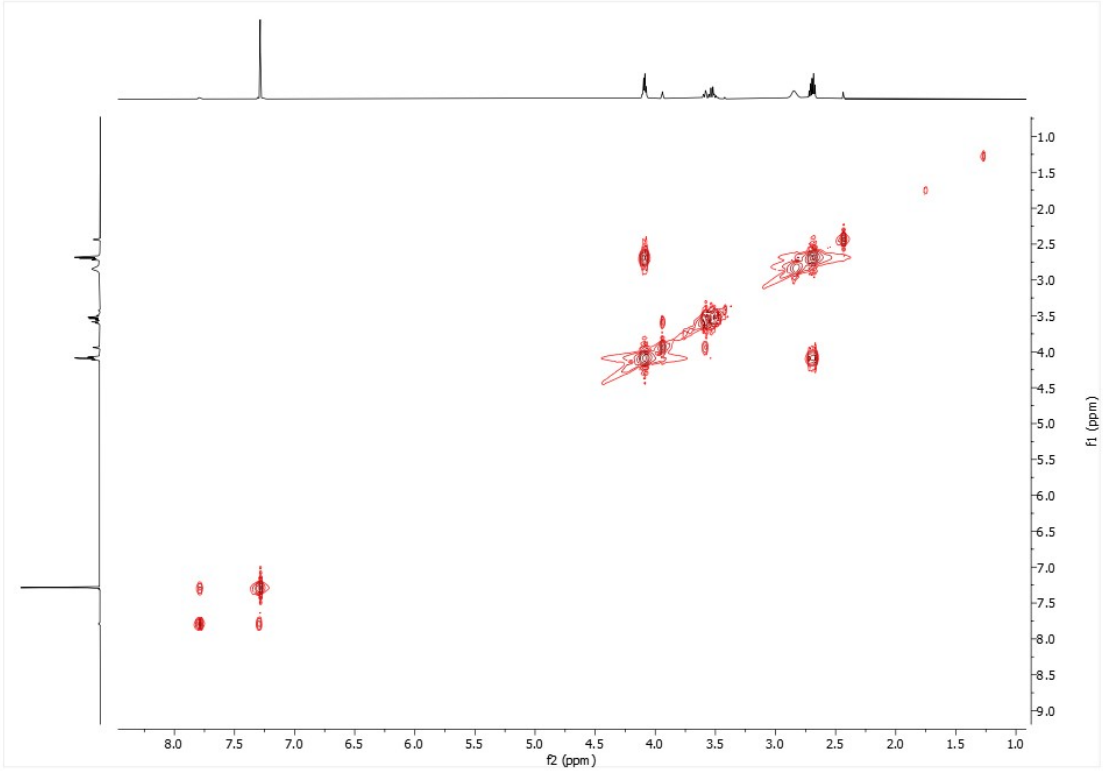

{7.26,7.26}CDCl3
f2 (ppm)
f1 (ppm)

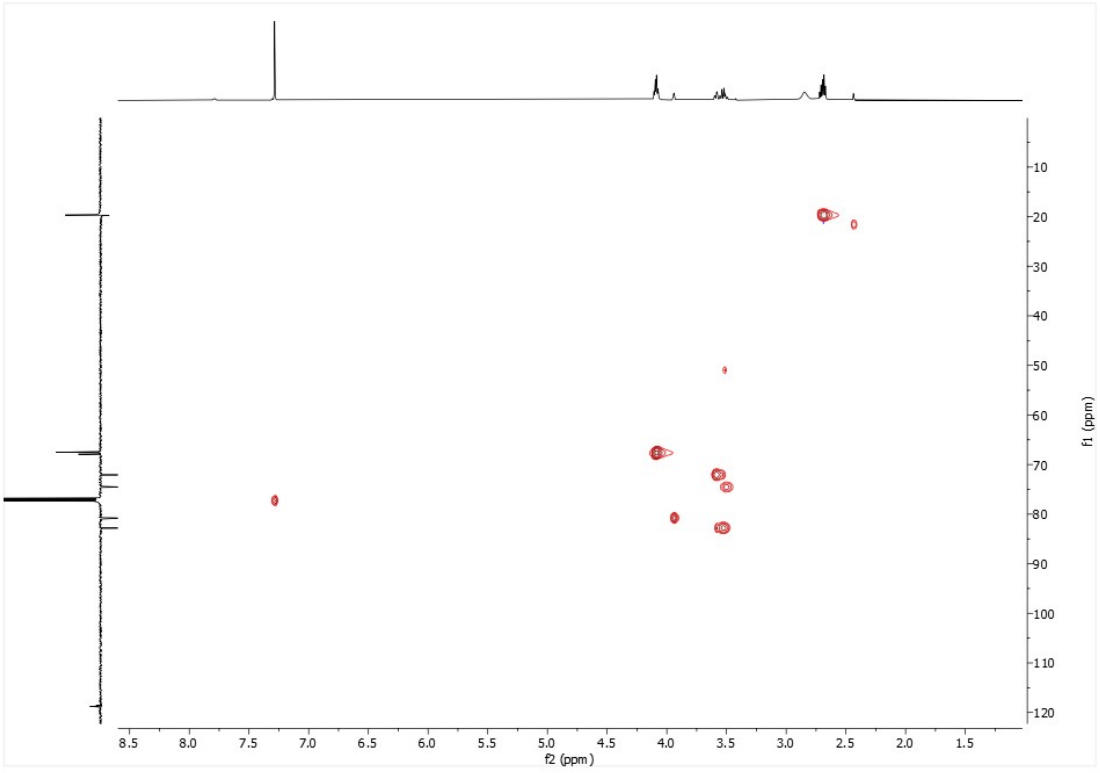

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

2,4,6-Tri-*O*-(2-cyanoethyl)-*meso*-D-*myo*-inositol (13)

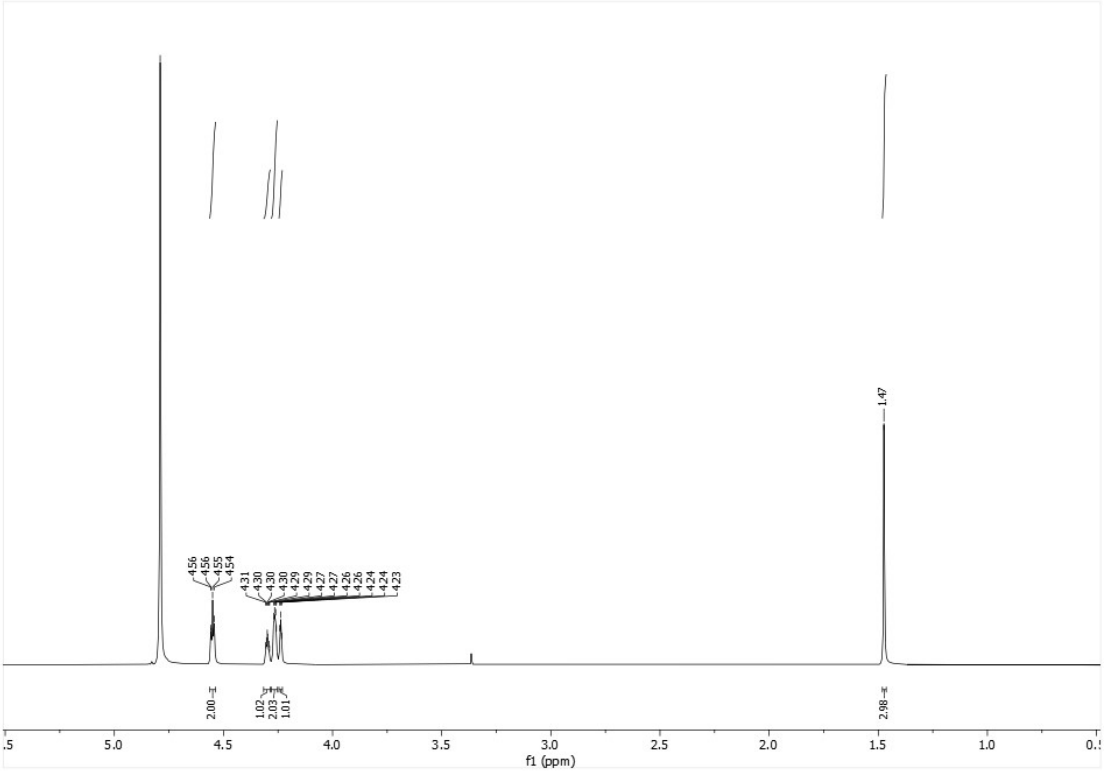


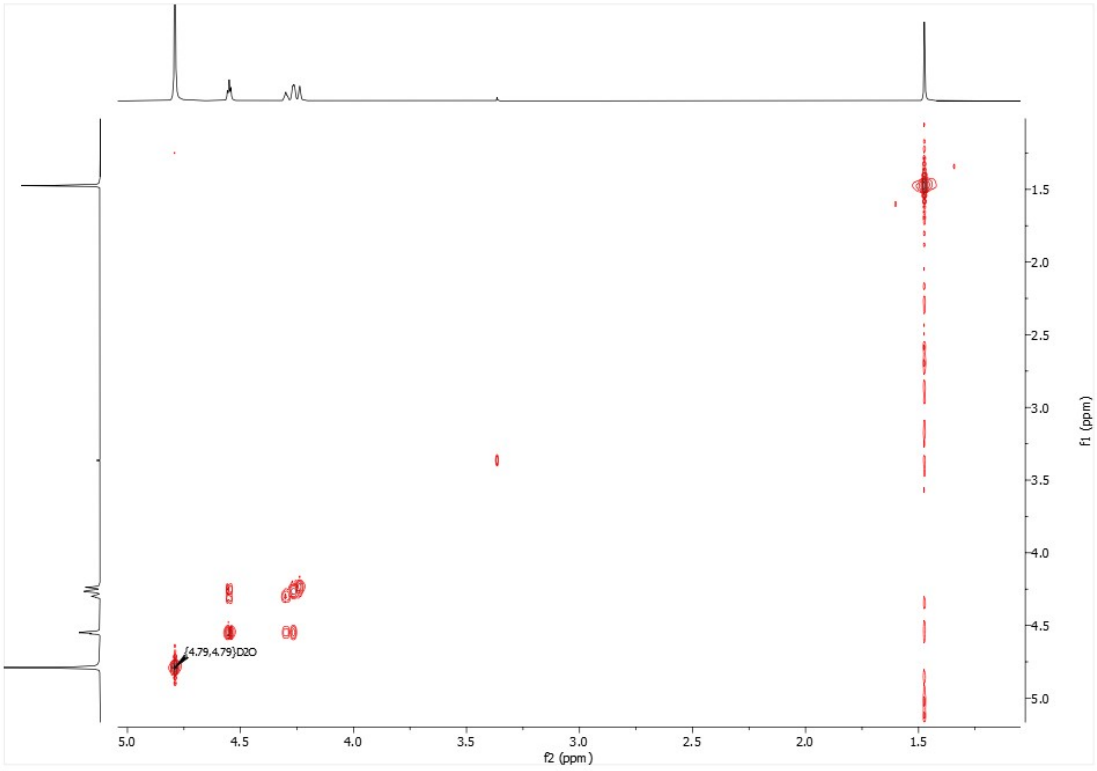



f2 (ppm)
f1 (ppm)

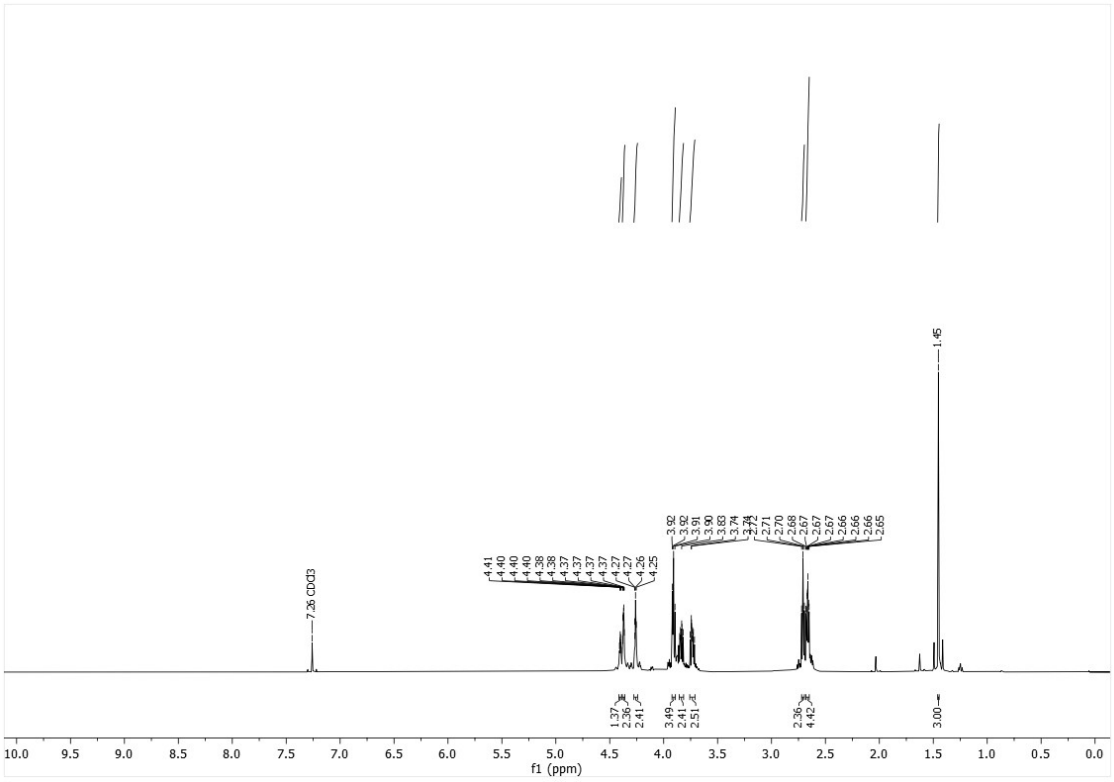

f2 (ppm)
f1 (ppm)

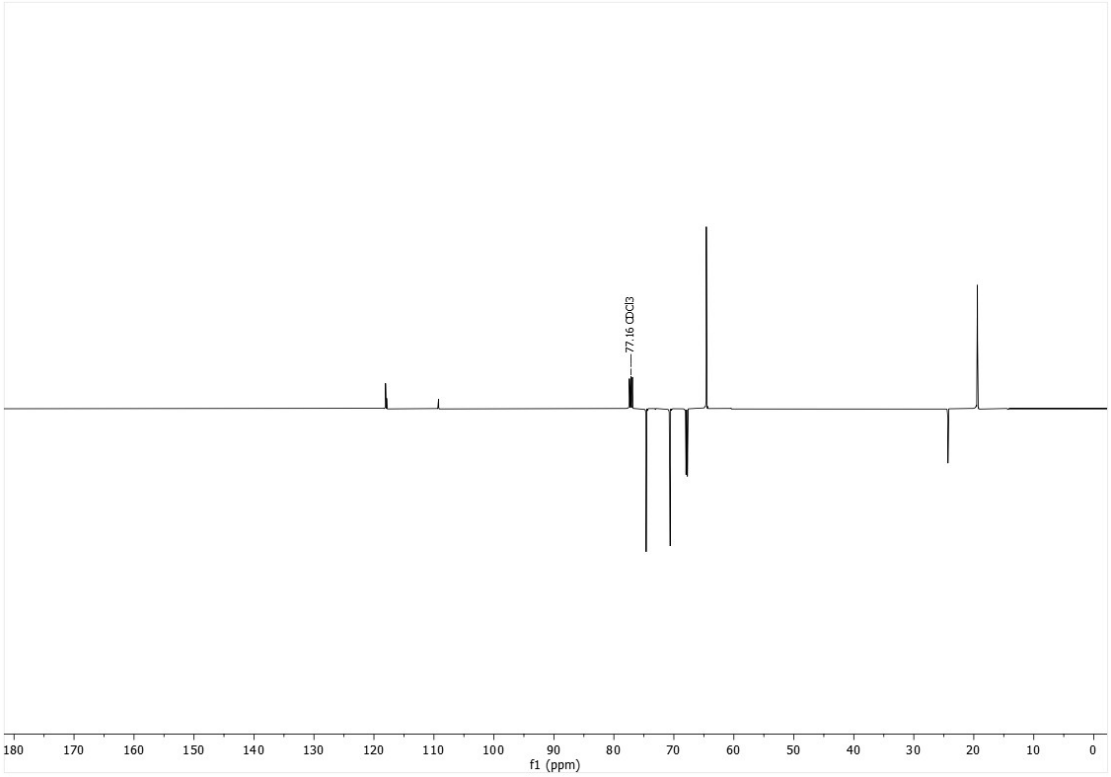
***Meso*-D-*myo*-inositol-1,3,5-*O*-orthoacetate (14)**

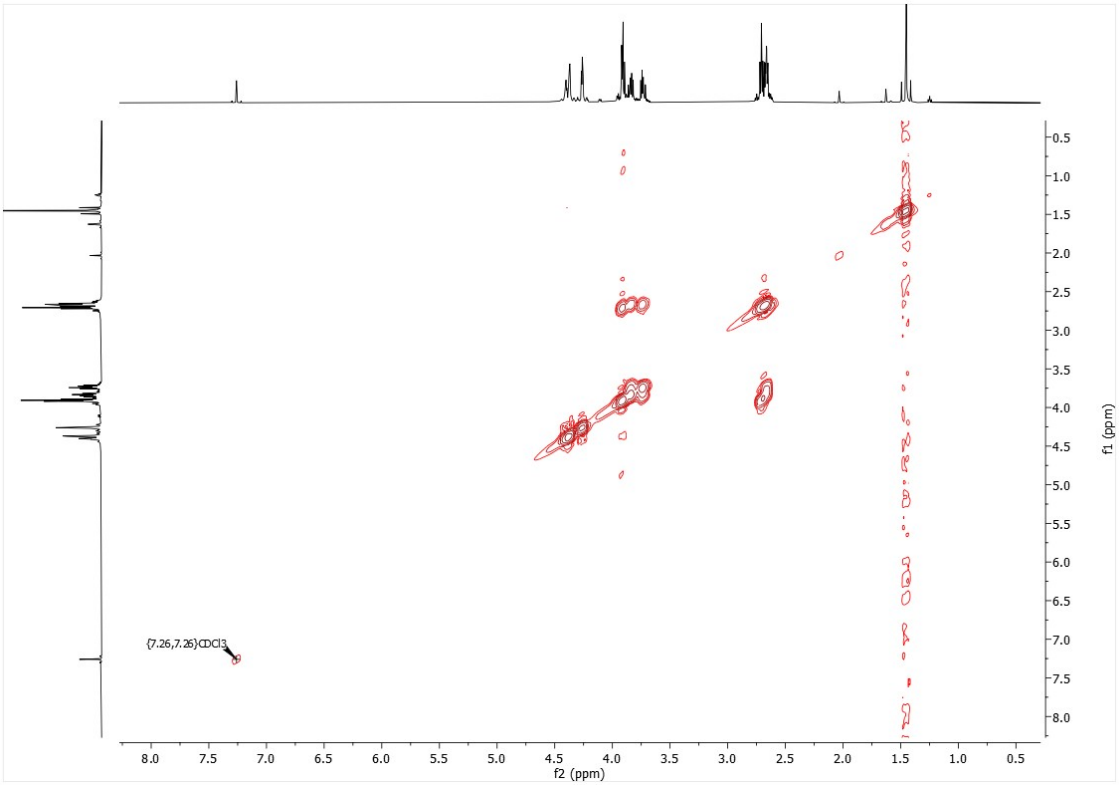


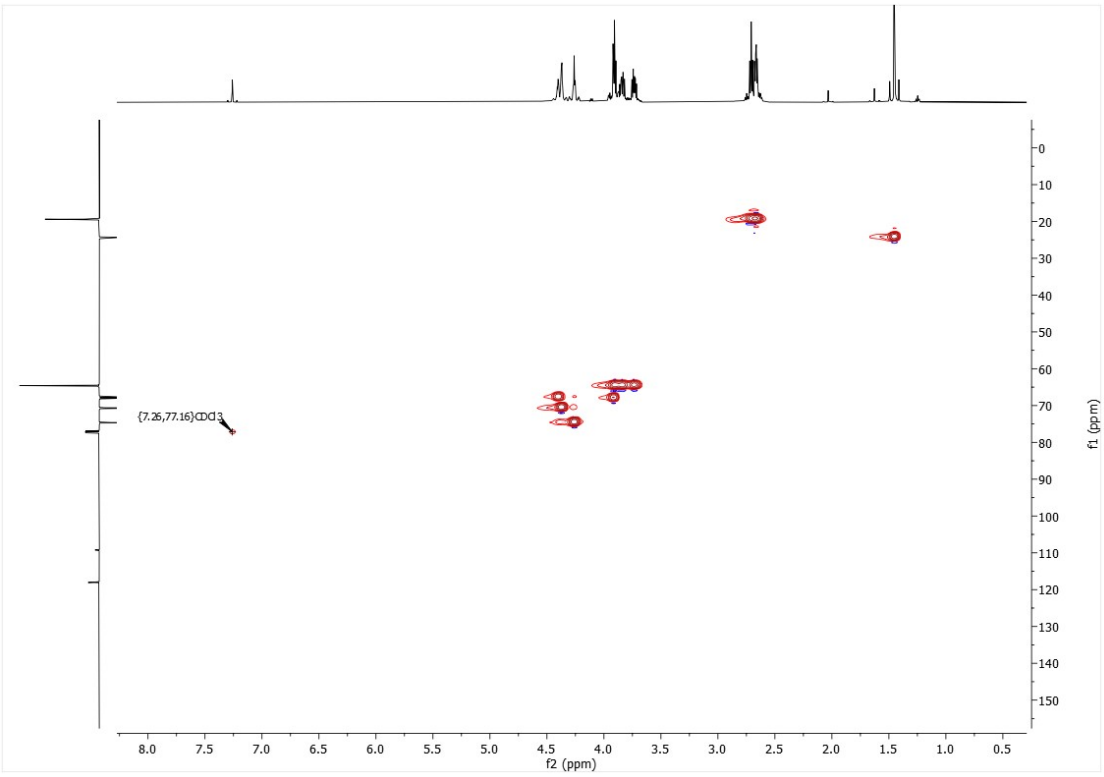


2,4,6-Tri-*O*-(2-cyanoethyl)-*meso*-D-*myo*-inositol-1,3,5-orthoacetate (15)

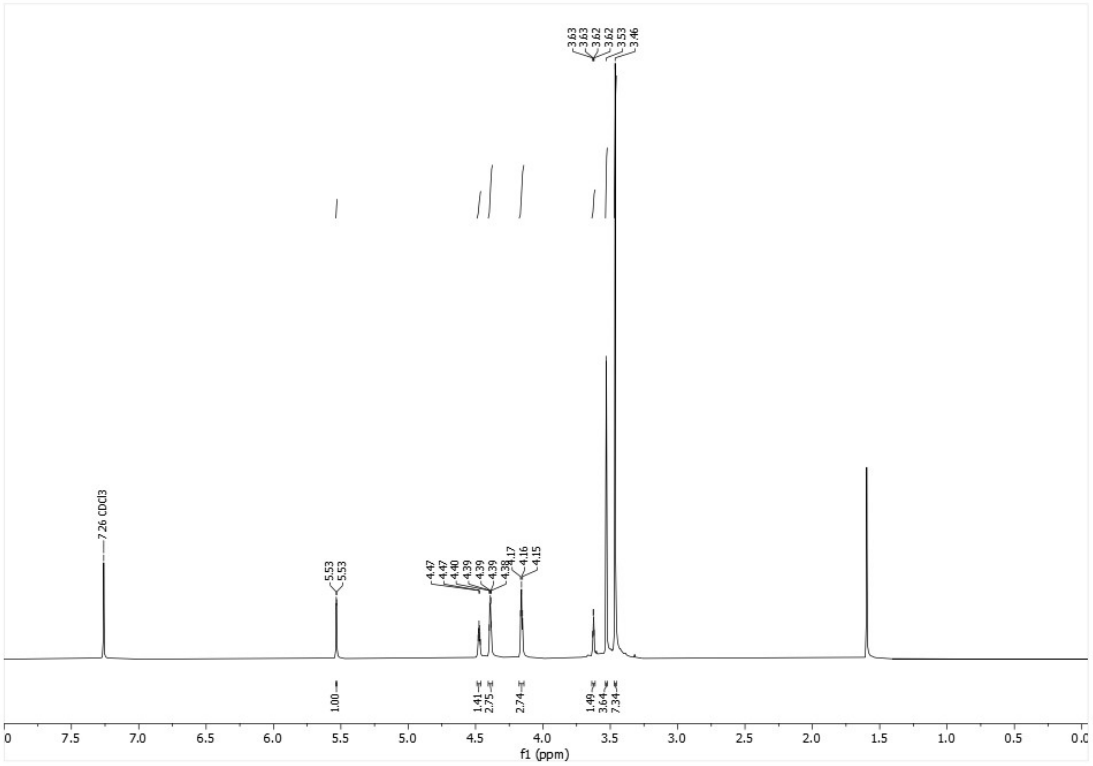


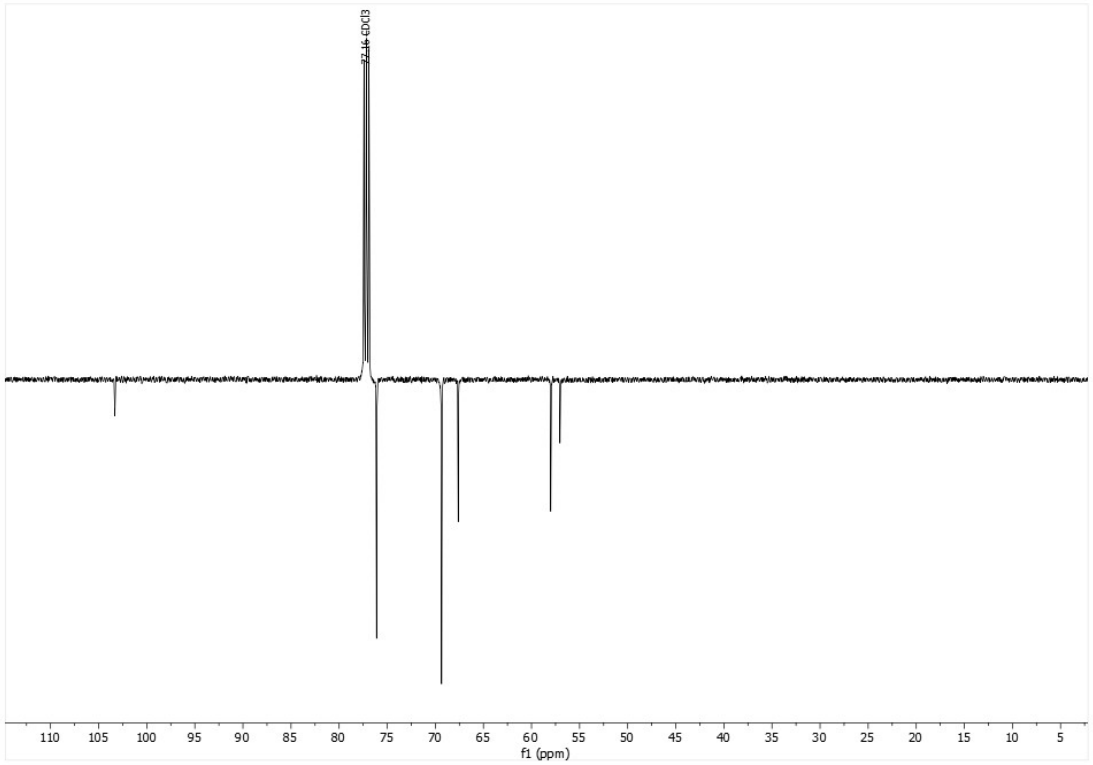


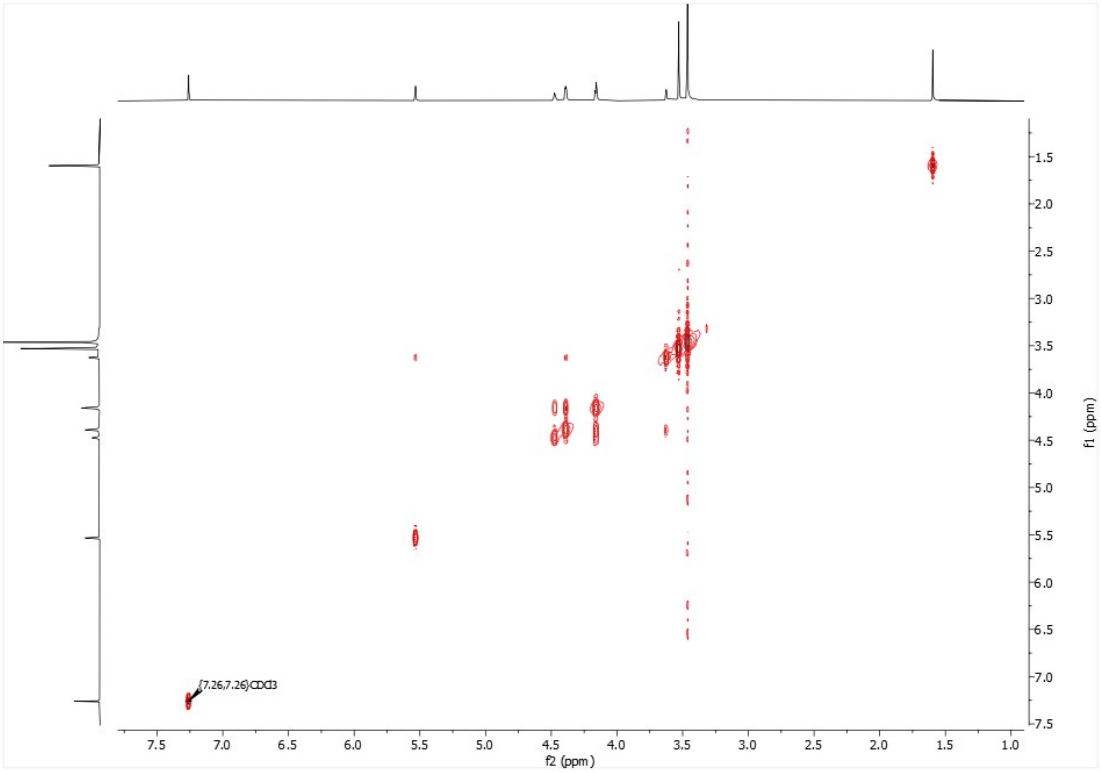

{7.26,7.26}CDCl3
f2 (ppm)
f1 (ppm)

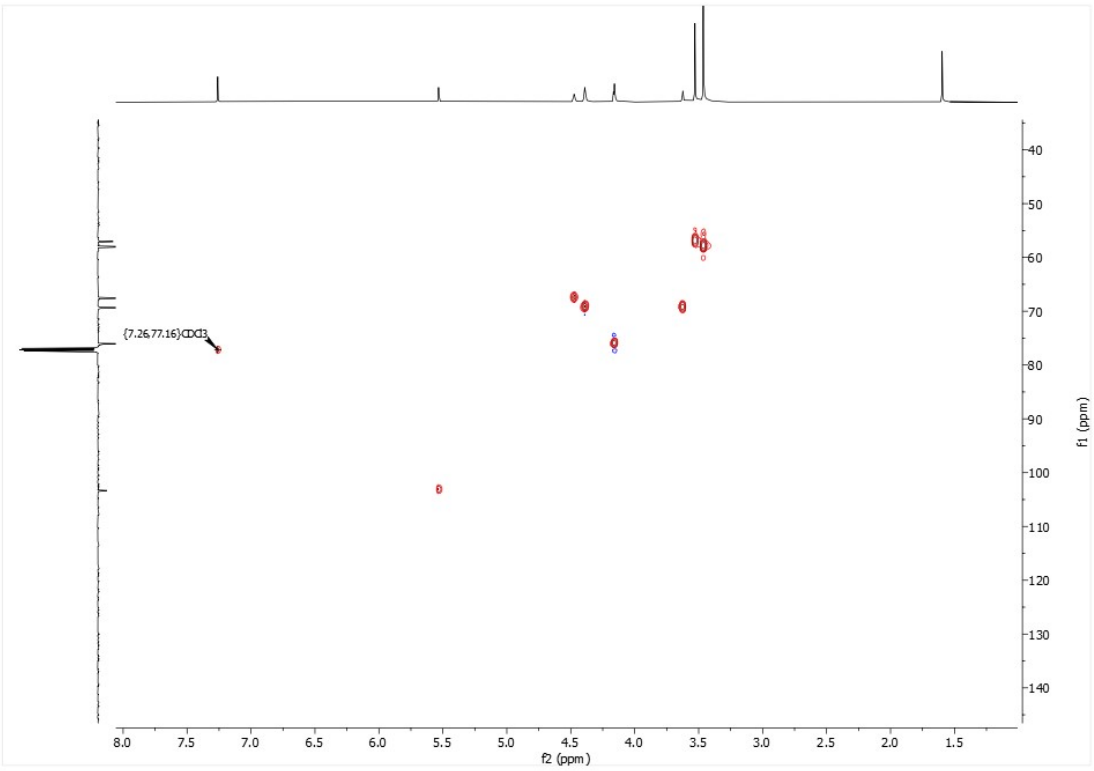

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

2,4,6-Tri-*O*-methyl-*meso*-D-*myo*-inositol-1,3,5-*O*-orthoformate (16)

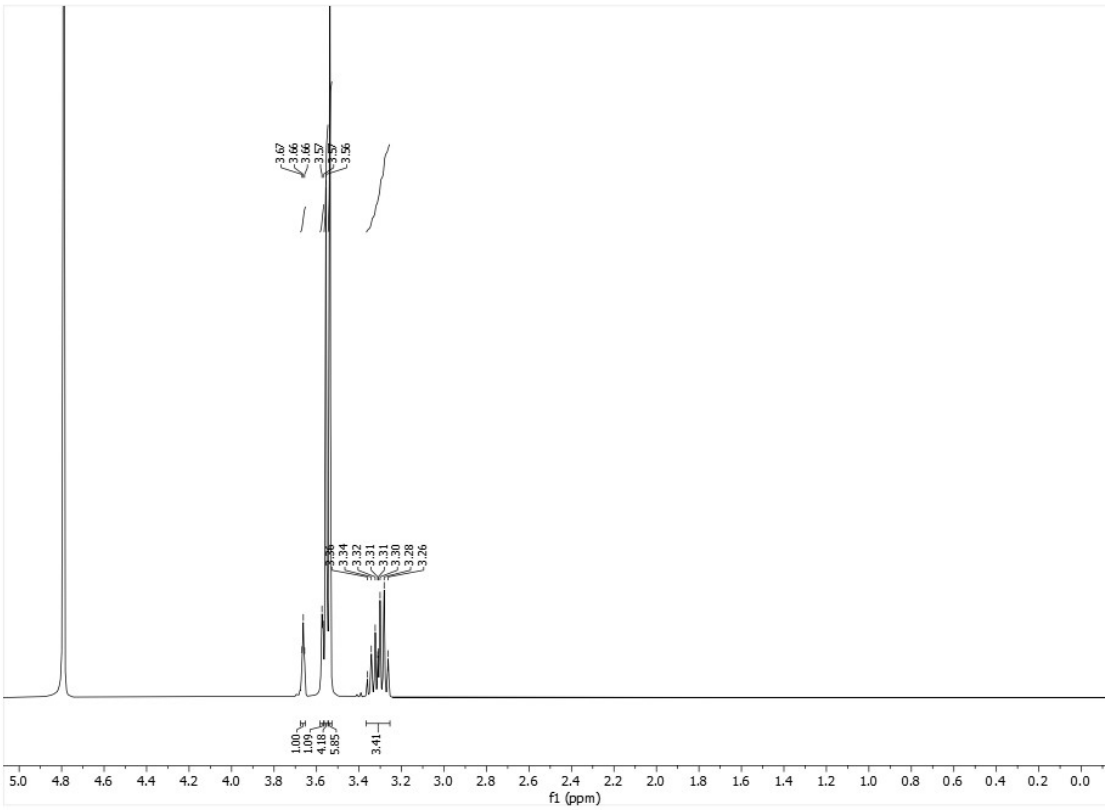


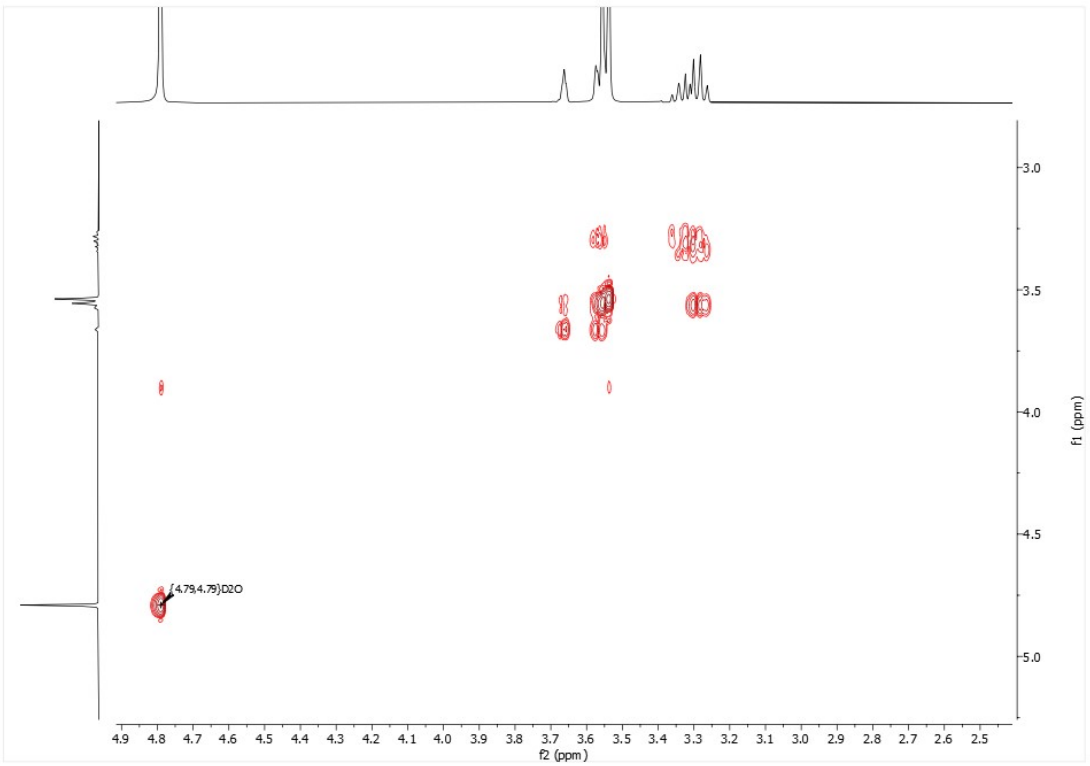



{7.26,7.26}CDCl3
f2 (ppm)
f1 (ppm)

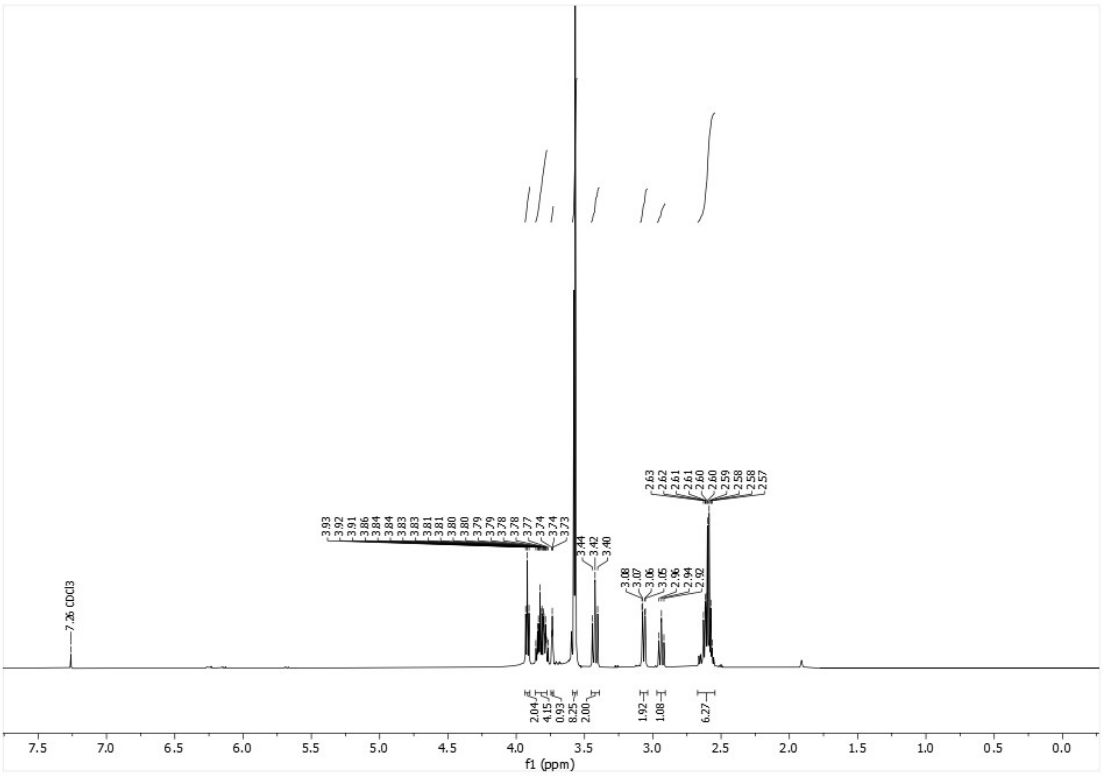

{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)

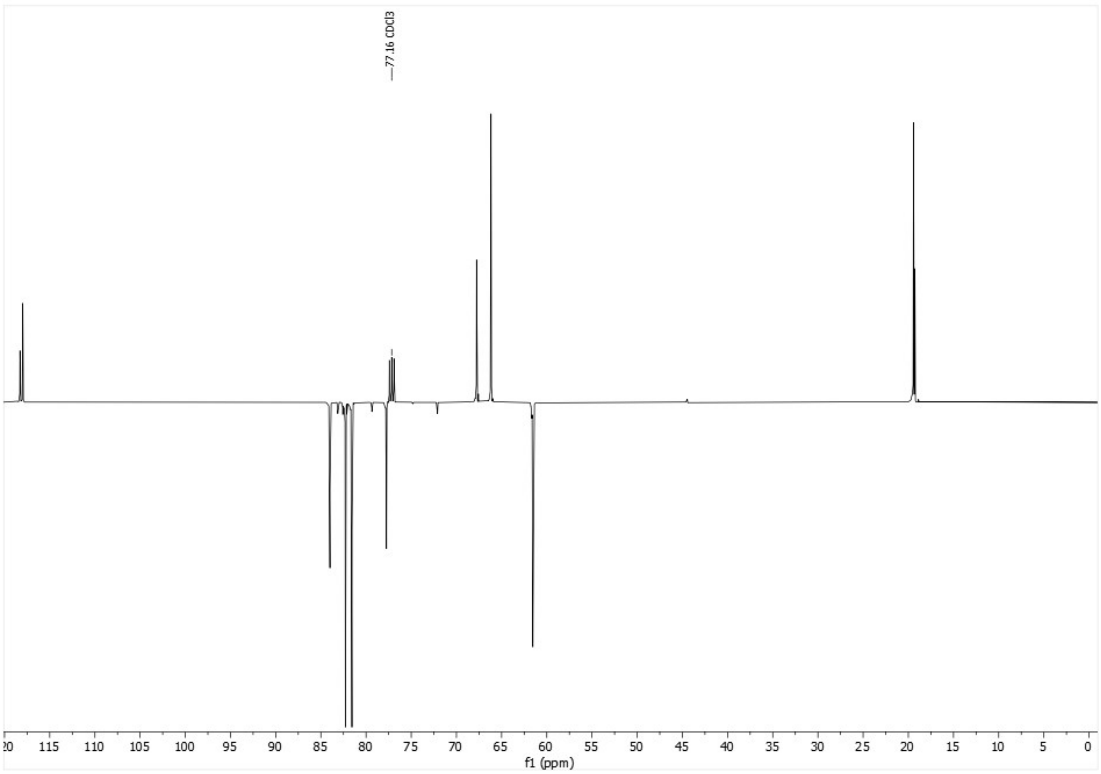
2,4,6-Tri-*O*-methyl-*meso*-D-Inositol (17)

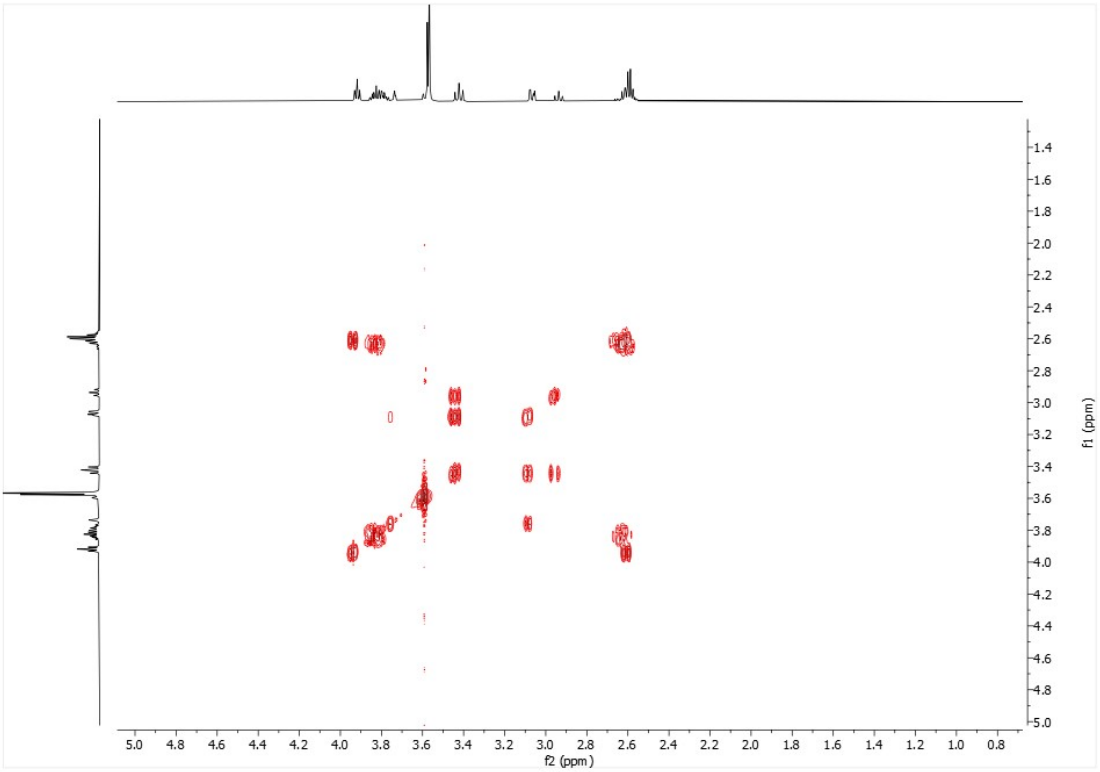


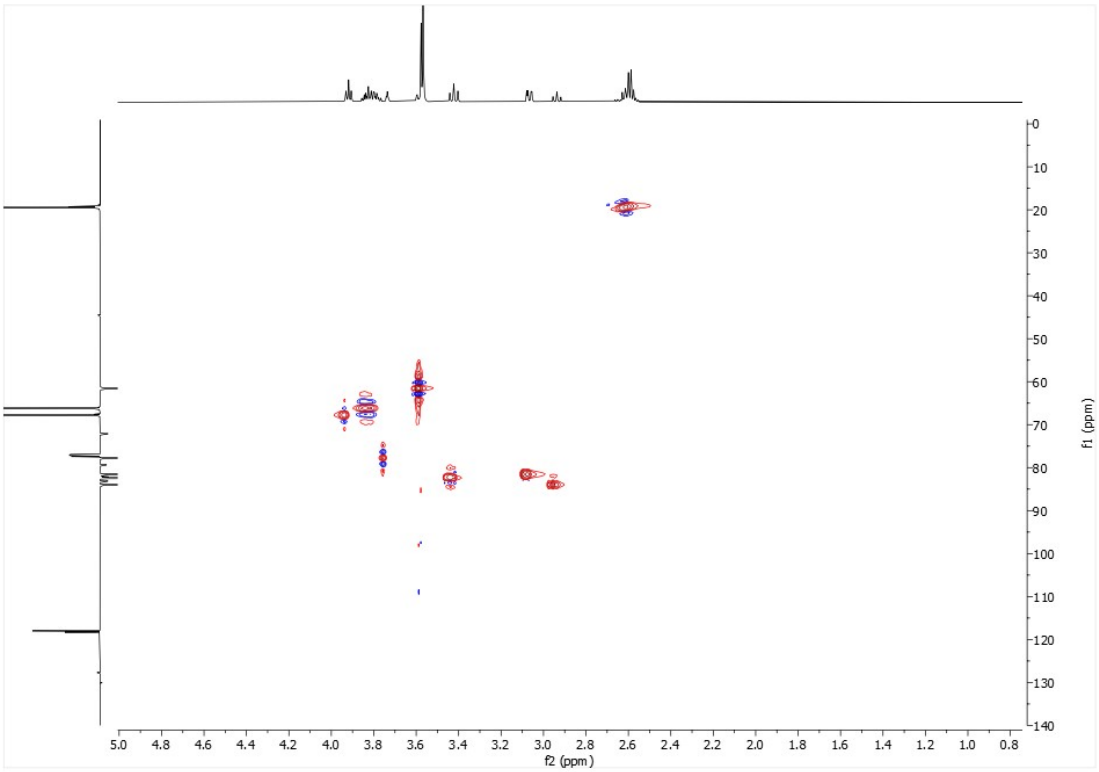


1,3,5-Tri-*O*-(2-cyanoethyl)-2,4,6-tri-*O*-methyl-*meso*-D-*myo*-inositol (18)

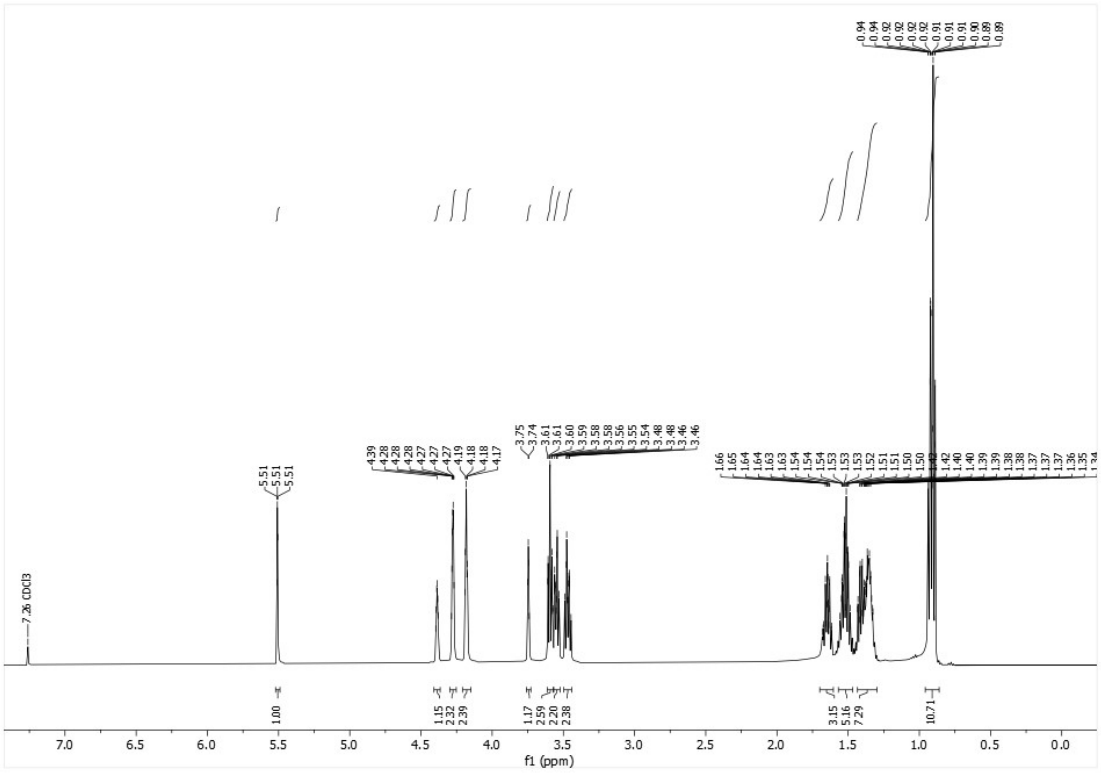


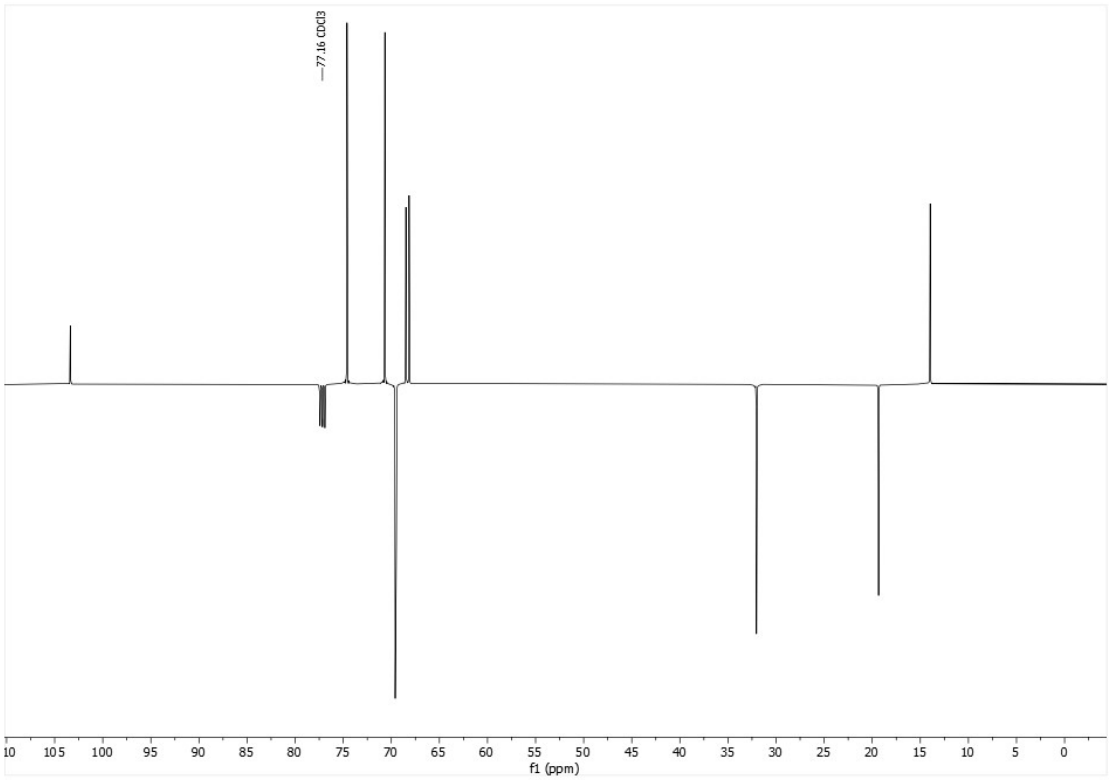


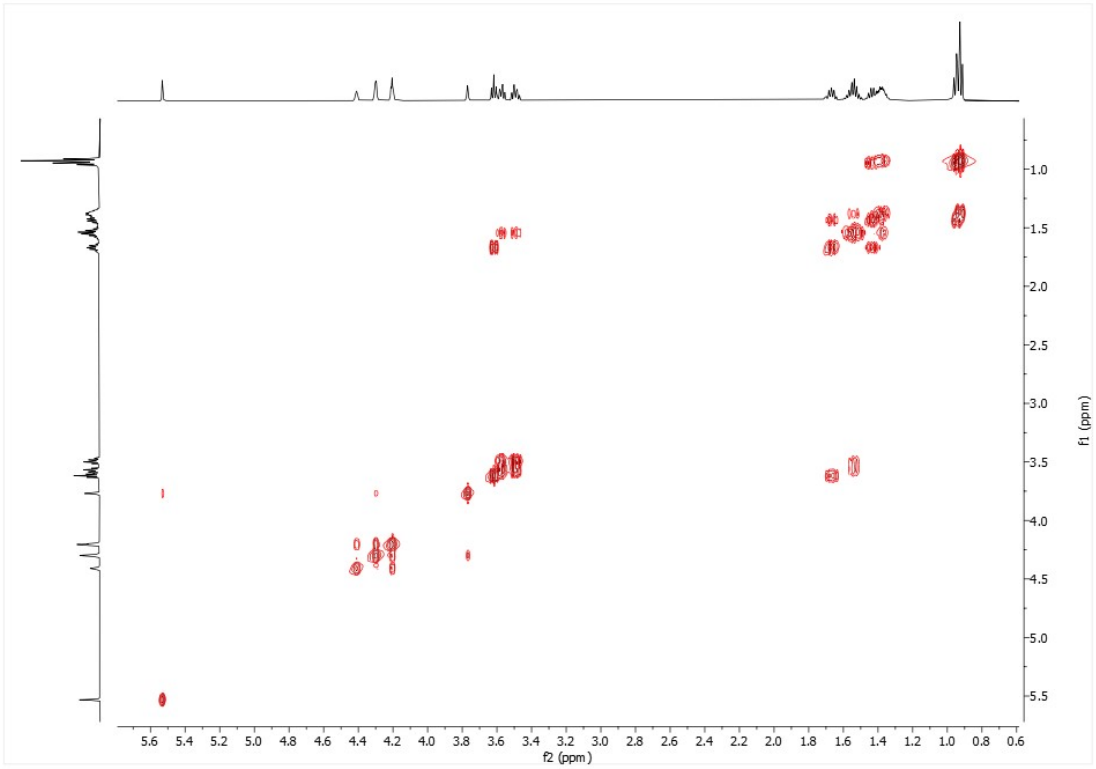

f2 (ppm)
f1 (ppm)

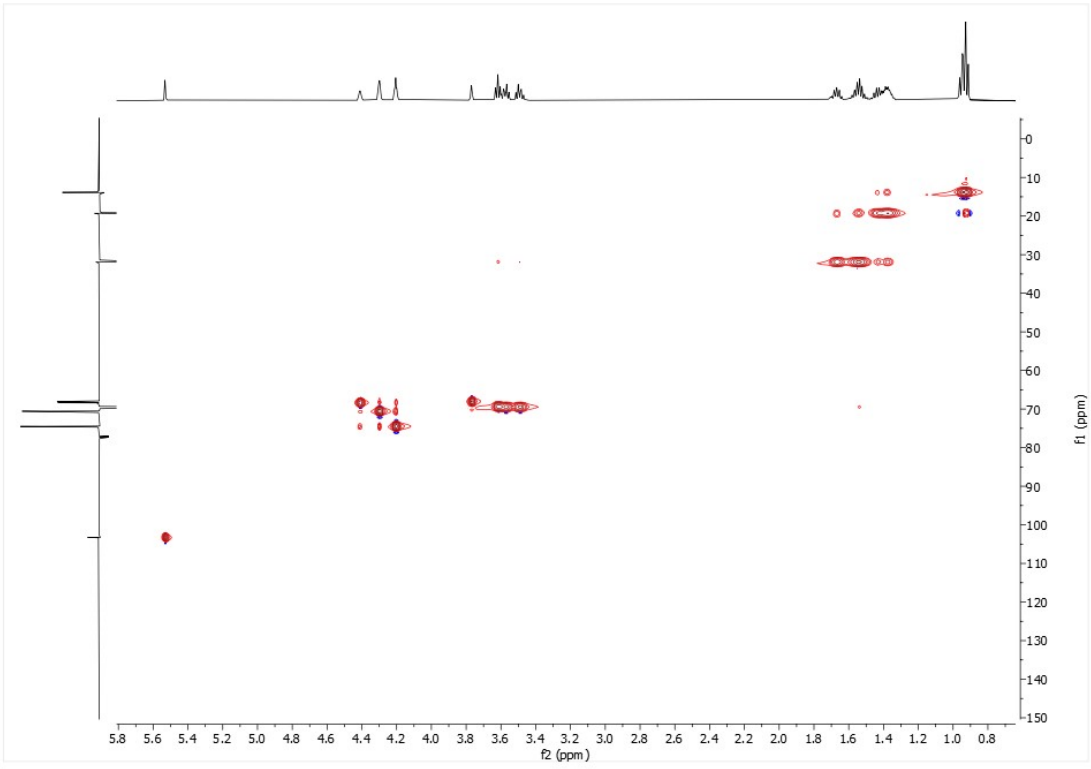

f2 (ppm)
f1 (ppm)

2,4,6-Tri-*O*-butyl-*meso*-D-*myo*-inositol-1,3,5-orthoacetate (19)

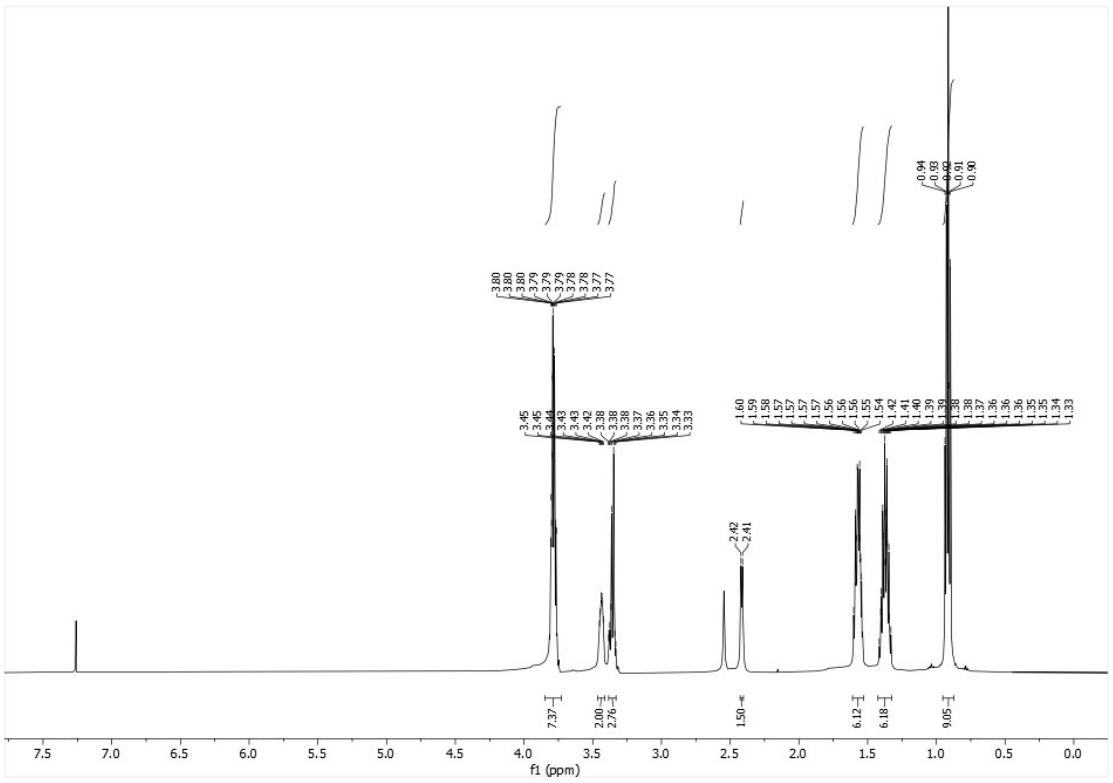


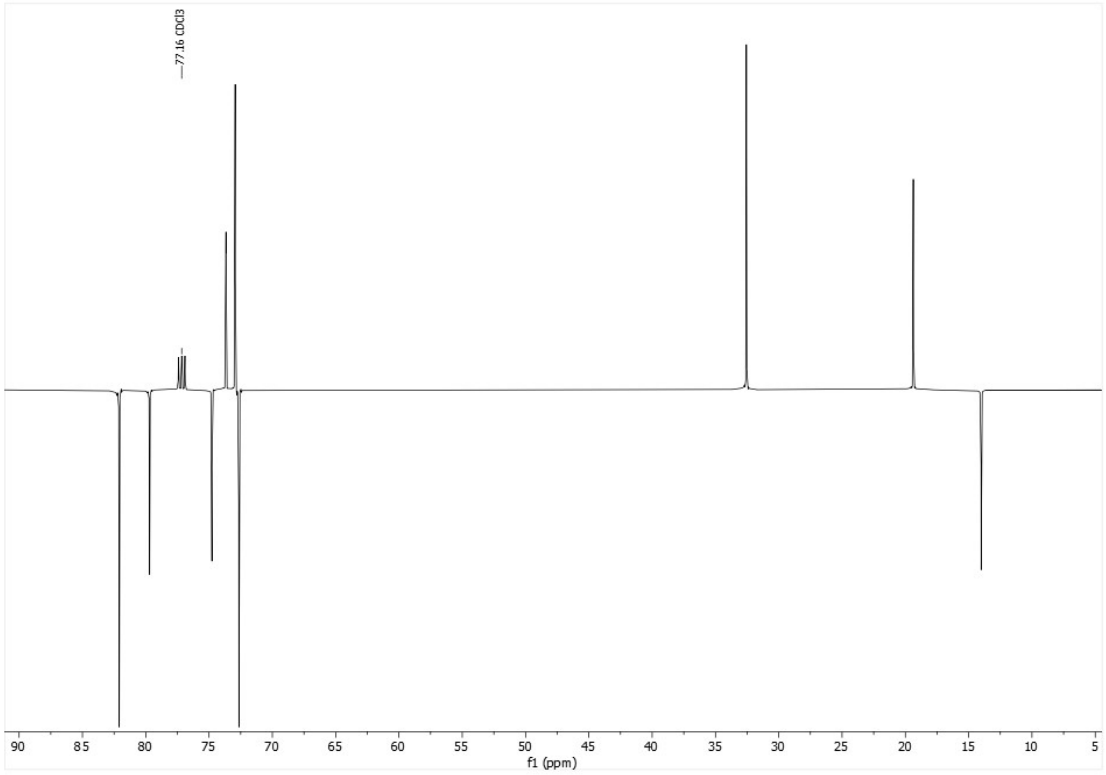


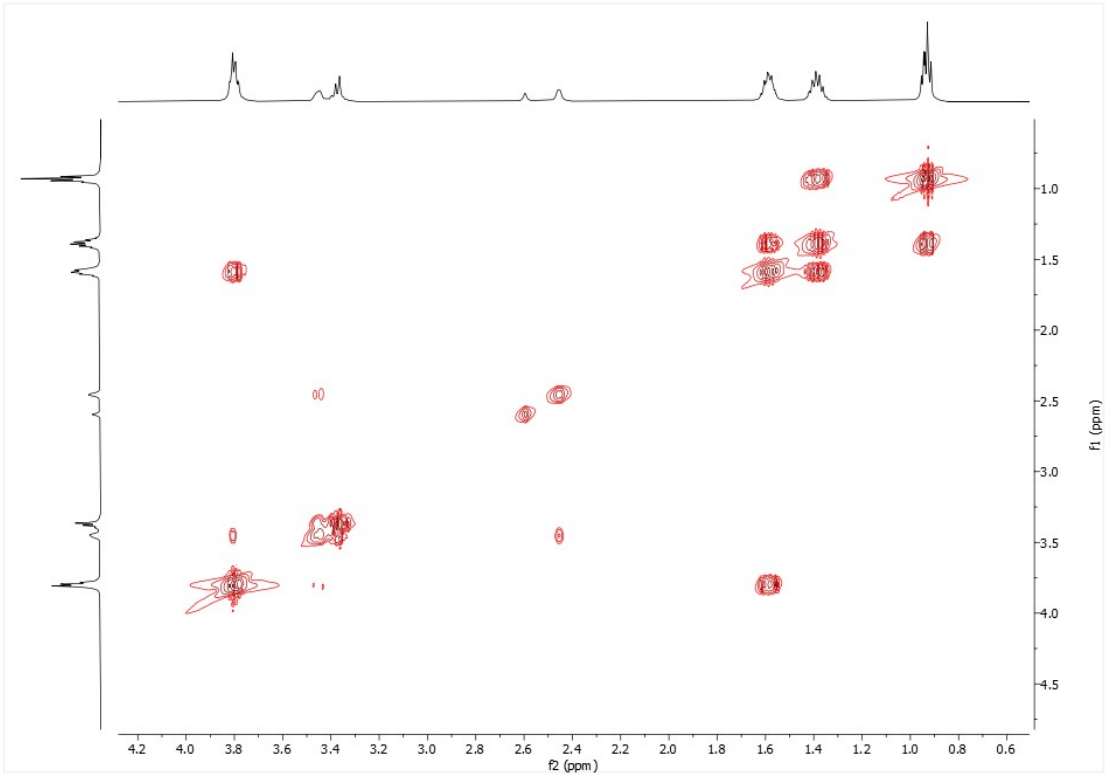

f2 (ppm)
f1 (ppm)

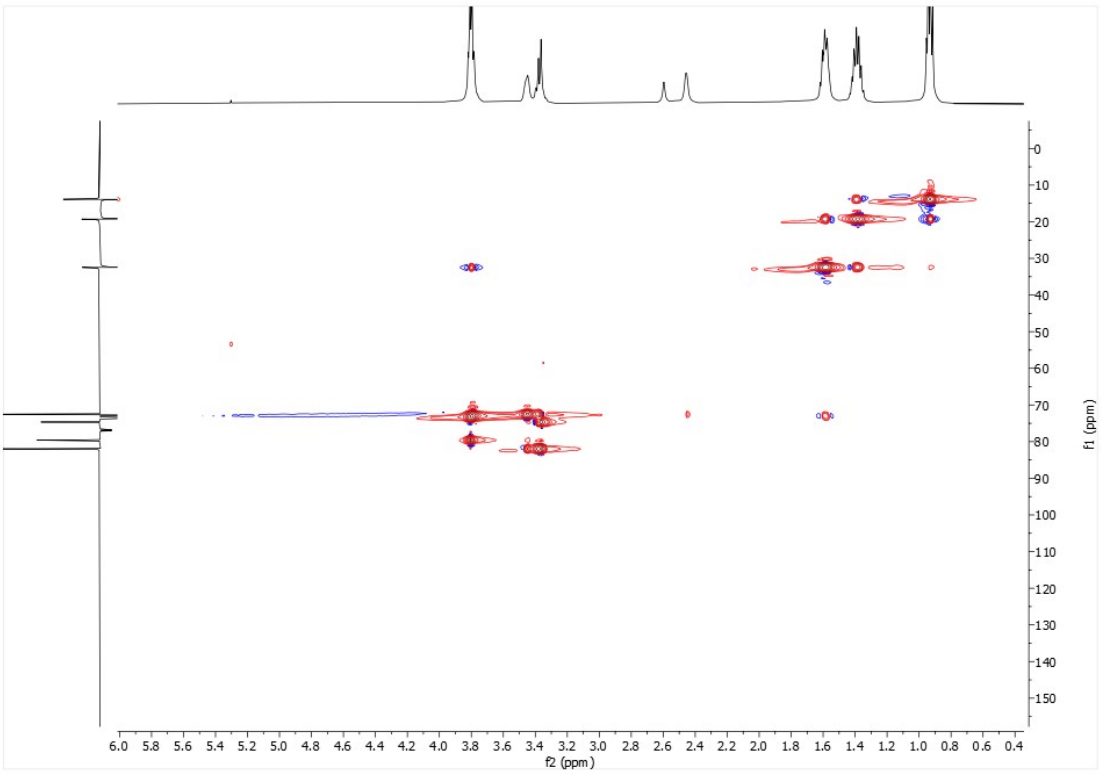

f2 (ppm)
f1 (ppm)

2,4,6-Tri-*O*-butyl-*meso*-D-*myo*-inositol (20)

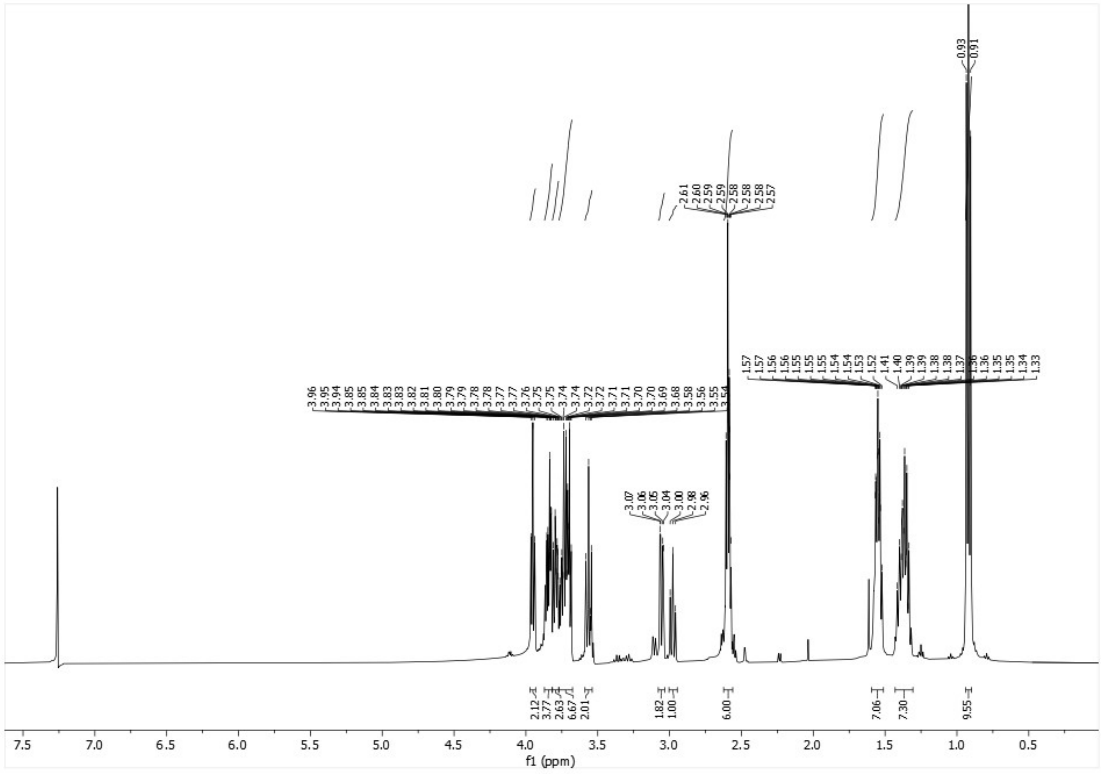


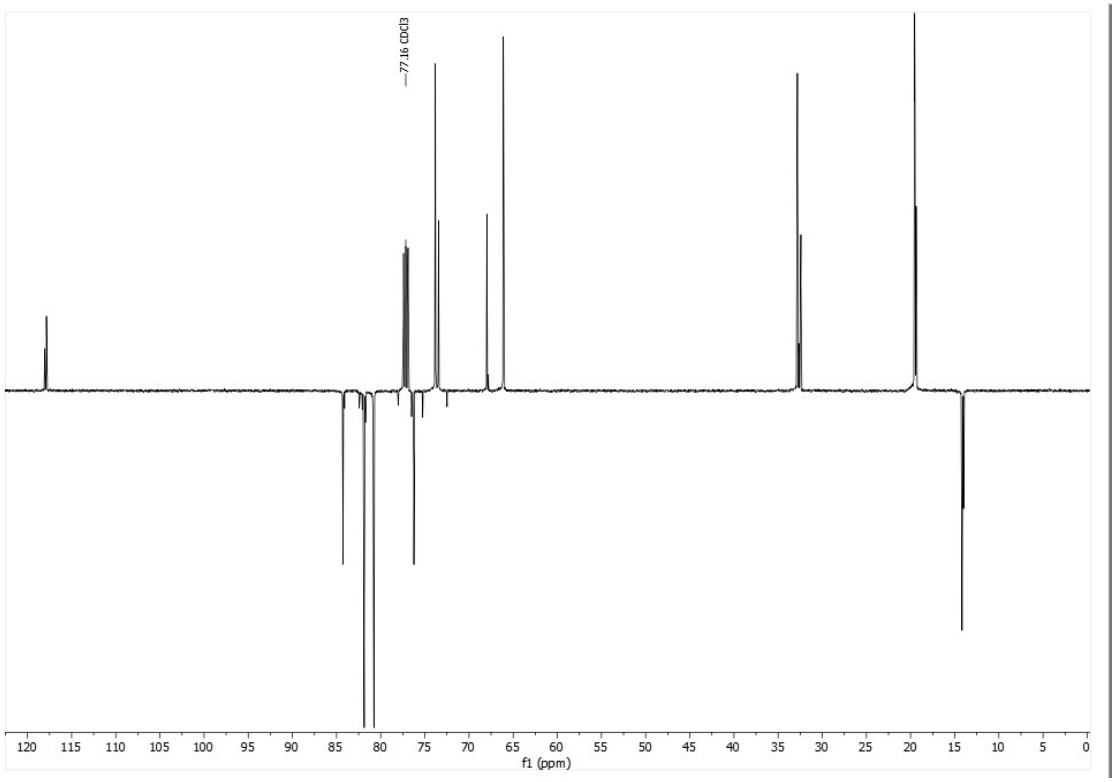


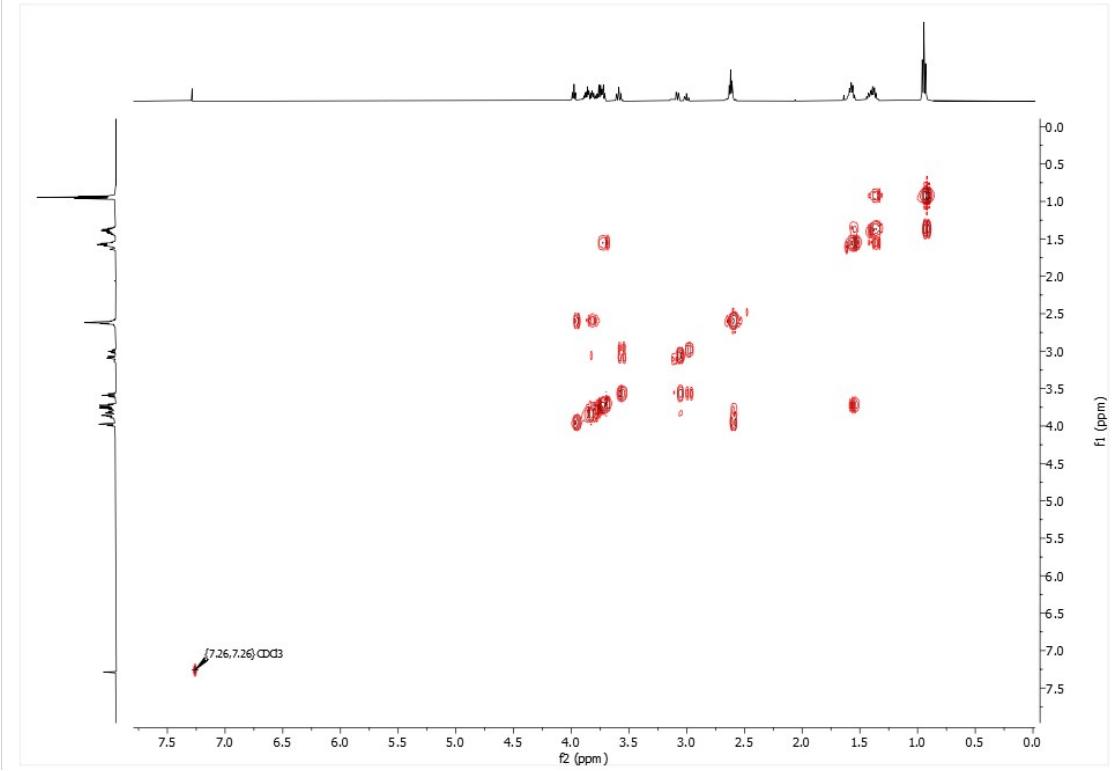

f1 (ppm)
f2 (ppm)

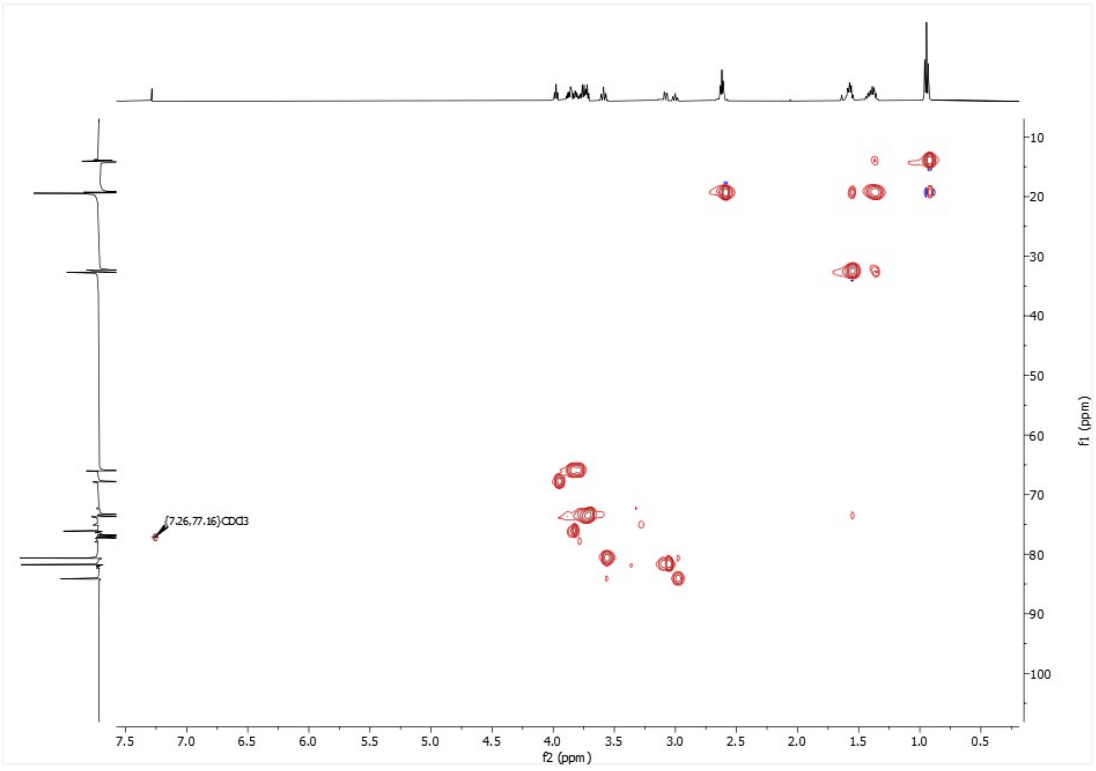

f1 (ppm)
f2 (ppm)

1,3,5-Tri-*O*-(2-cyanoethyl)-2,4,6-tri-*O*-butyl-*meso*-D-*myo*-Inositol (21)

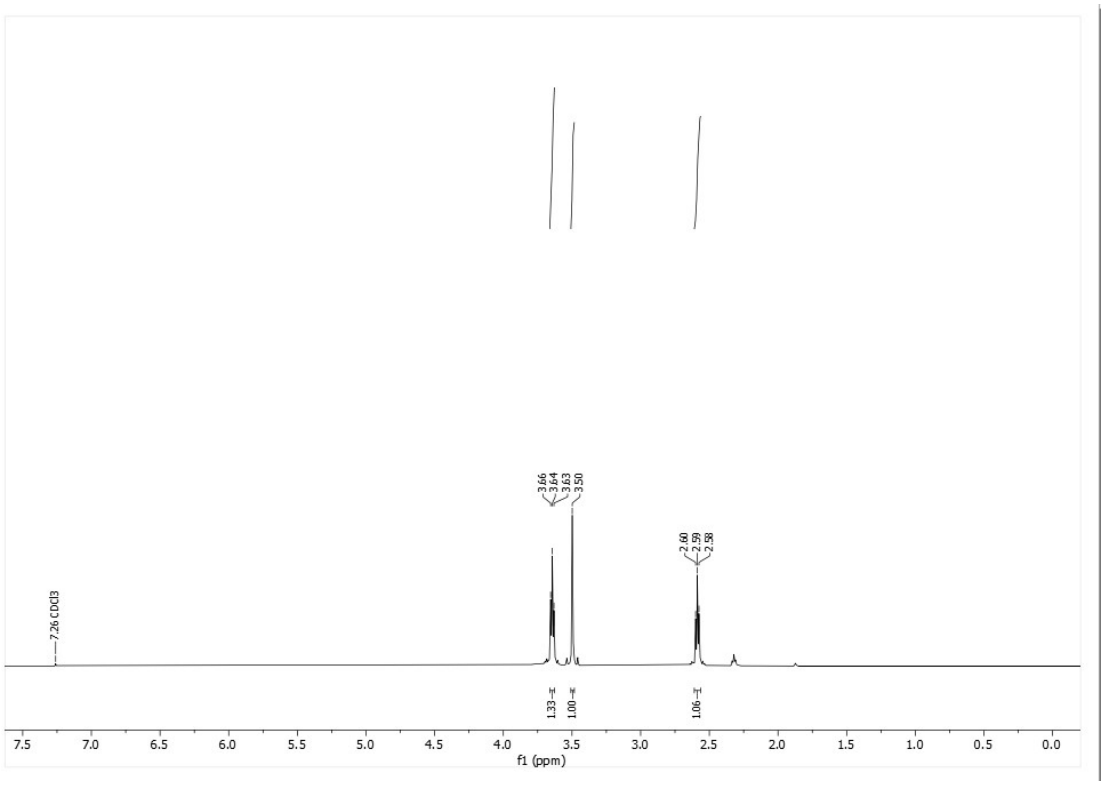


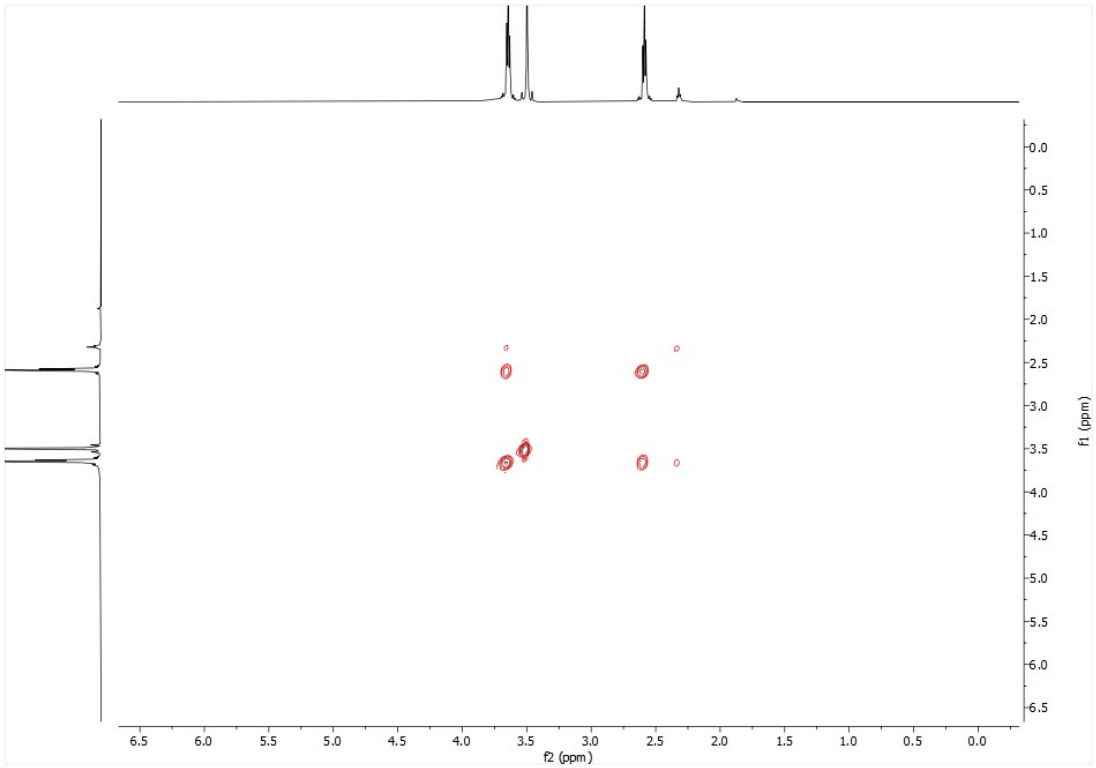



f1 (ppm)
f2 (ppm)
{7.26,7.26}-CDCl3


f1 (ppm)
f2 (ppm)
{7.26,77.16}-CDCl3

Tetrakis-[(2-cyanoethoxy)methyl]methane (22)





SI.5 H_2S scavenging reactions in basic aqueous phase: Methodology

The scavenging reactions with the chemicals synthesized in this work, as well as with MEA-triazine for benchmarking purpose, were monitored in basic aqueous solutions. Under these conditions, the prevailing form of H_2S is bisulfide (HS^-). All reactions were homogeneous, with no signs of de-mixing or precipitation being observed.

Bisulfide solutions were prepared using disodium sulfide about trihydrate ($Na_2S \cdot \sim 3H_2O$; CAS 27610-45-3) from VWR Chemical (product ID 83756.230). The degree of hydration of the salt was determined via Karl Fisher titration. The mass fraction of water in the salt was found to be 0.391 ± 0.002 (five repetitions). Phenylacetic acid (PAA; CAS 103-82-2, purity > 99 wt%) from Sigma-Aldrich (product ID P16621-100G) was used as internal standard (IS) for Raman Spectroscopy.

The scavenging reactions were carried out by loading 20 mL of an aqueous solution of bisulfide and IS, with pH adjusted to 10 ± 0.2, into a 45 mL glass vial (batch reactor). The content of the reactor is kept stirred, and it is brought to and kept at 75 °C. Subsequently, 10 mL of an aqueous solutions of the biomass-based scavenger synthesized in this work, also with pH adjusted to 10 ± 0.2, is injected into the bisulfide solution. The pH of the two solutions to be mixed is referred to as initial pH in the following. The concentrations of the two solutions are fixed in such a way to have 100 mM of bisulfide, 100 mM of scavenger, and 200 mM of IS immediately after the injection (reaction time t = 0). A schematic and a photo of the experimental setup, together with additional details on the experimental methodology, can be found elsewhere (Romero *et al*., Temperature- and pH-dependent kinetics of the aqueous phase hydrogen sulfide scavenging reaction with MEA-triazine, Industrial and Engineering Chemistry Research 62 (2023) 8269-8280). In this work, the reaction monitoring time was 1 hour in most of the experiments (longer in a few experiments) and the spectra acquisition was every 30 seconds in most of the experiments, while being every 20 seconds in a few experiments.

Additional scavenging reaction monitoring experiments were conducted at 25 °C and 50 °C and initial pH 10, and at 60 °C and initial pH 8 for 2,4,6-Tri-*O*-(2-cyanoethyl)-meso-D-myo-inositol-1,3,5-*O*-orthoformate **12** only. Also, some additional Raman monitoring experiments were performed to check the stability of the compounds in the absence of bisulfide (control experiments).

SI.6 H_2S scavenging reactions in basic aqueous phase: Results

Scavenging reactions at 75 °C and initial pH 10.

Figure SI.6.1 shows the trends of the concentration of HS^- over time with different biomass-based scavengers.

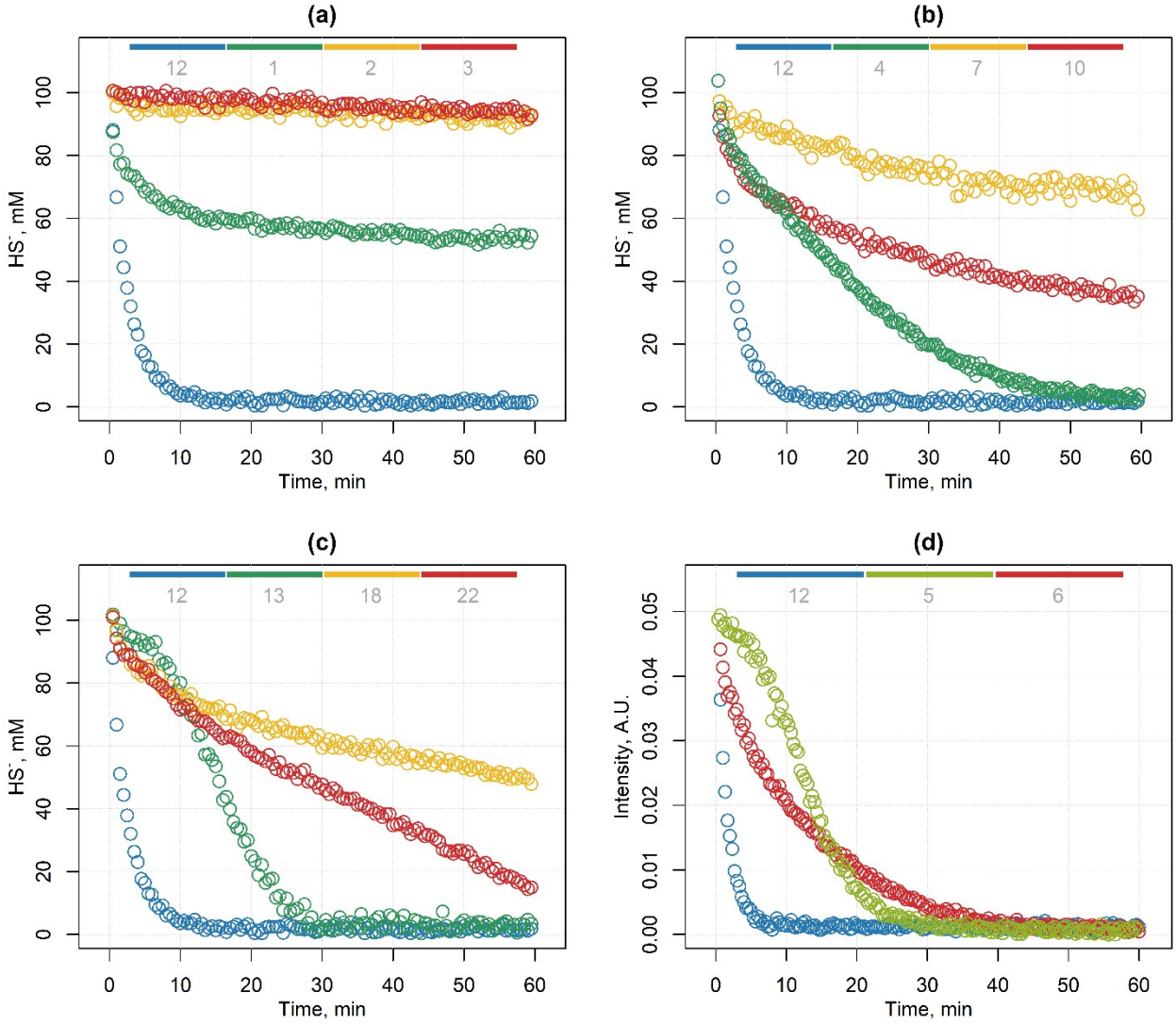


Fig. SI.6.1 Trend of the concentration of HS^- in the scavenging reactions for different biomass-based scavengers. Figures a, b and c report concentration of HS^- in mM, and figure d reports Raman intensity of HS^- peak.

In all runs, 2,4,6-Tri-*O*-(2-cyanoethyl)-meso-D-myo-inositol-1,3,5-*O*-orthoformate, identified as the biomass-based scavenger **12**, lead to a total depletion of HS^- in the shortest time compared to the other scavengers.

Scavenging reactions with 12 at different temperatures

Figure SI.6.2 shows the trend of the concentration of bisulfide when using 2,4,6-Tri-*O*-(2-cyanoethyl)-meso-D-myo-inositol-1,3,5-*O*-orthoformate as scavenger at different temperatures. The initial pH was 10 in all runs. As can be seen, the reaction rate is strongly dependent on temperature. Complete depletion of bisulfide is observed also at 50 °C, even though in approximately 100 min instead of approximately 15 min at 75 °C. At 25 °C complete depletion of bisulfide was not reached within 3 hours, even though the concentration of bisulfide was still decreasing.

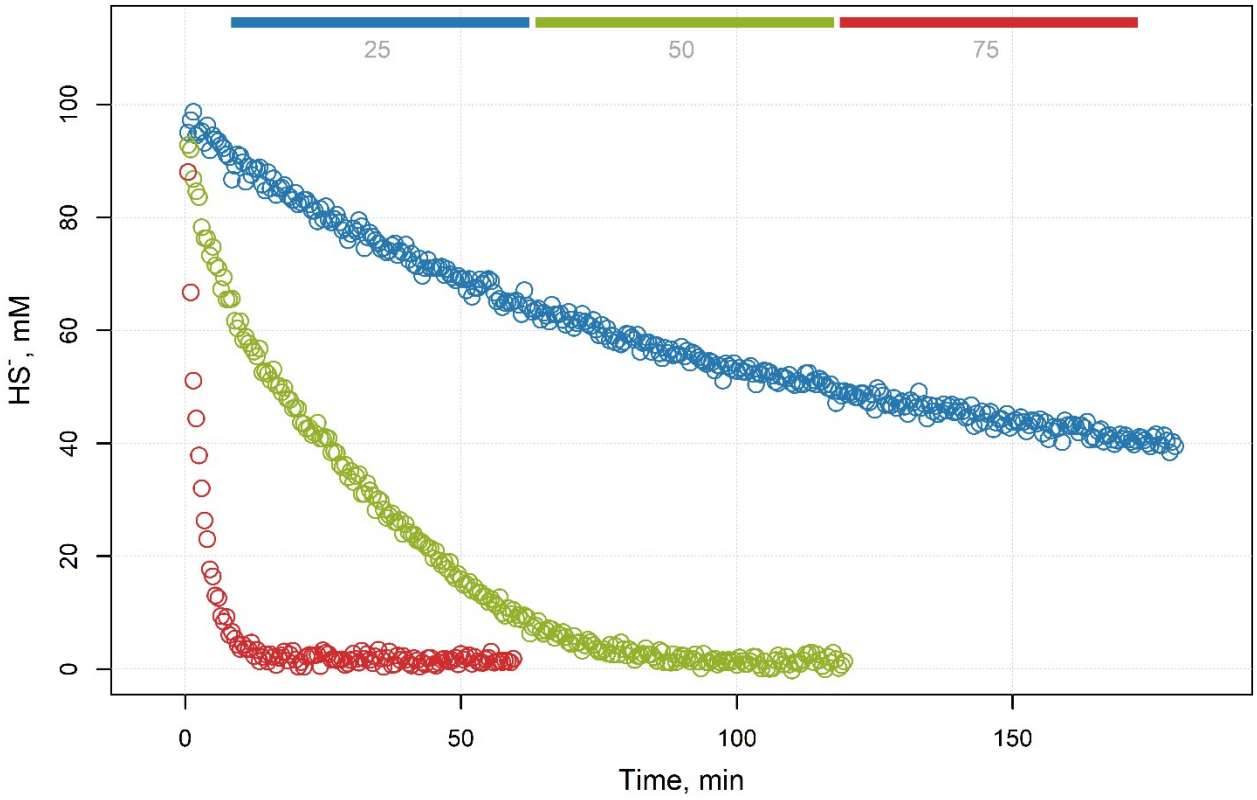
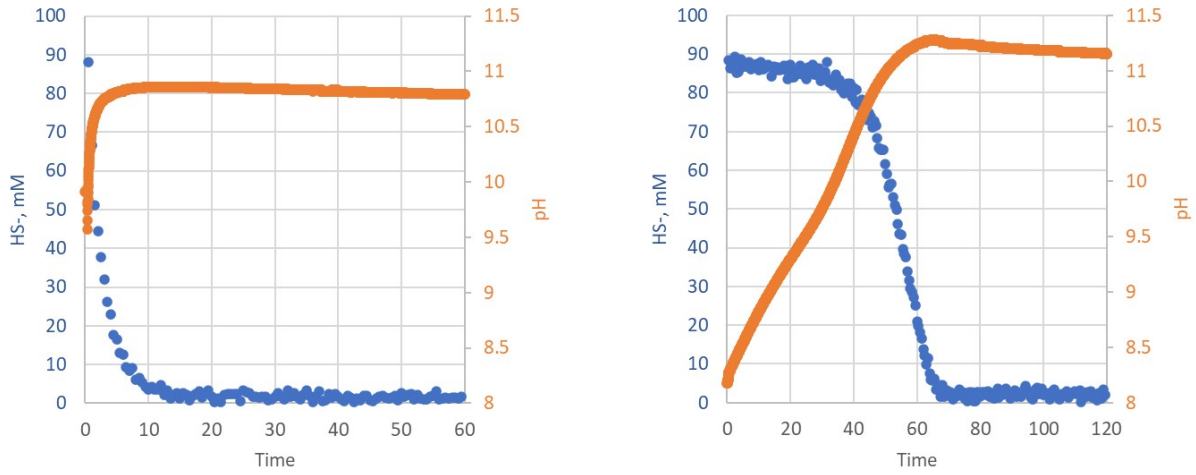


Fig. SI.6.2 Concentration of bisulfide as a function of time for the scavenging reactions carried out with the biomass-based scavenger **12** at different temperatures 25, 50 and 75 °C.

Scavenging reactions with 12 at initial pH 8

Figure SI.6.3 shows the scavenging reaction using 2,4,6-Tri-*O*-(2-cyanoethyl)-meso-D-myo-inositol-1,3,5-*O*-orthoformate at 60 °C and initial pH 8. As can be seen, the reaction at initial pH 8 is much slower than the case with the same chemical at initial pH 10. In approximately 40 min, the concentration of bisulfide is reduced to approximately 80 mM only, while the reduction was to 0 mM or below 30 mM at 75 °C and 50 °C, respectively, for the same scavenger at initial pH 10. It is also noted that the pH increases during the reaction, with values above 10 reached in approximately 30-40

min. When the pH reaches values between 10.5 – 11.0, the scavenging reaction becomes much faster, and complete depletion is ultimately achieved at a final pH of approximately 11.

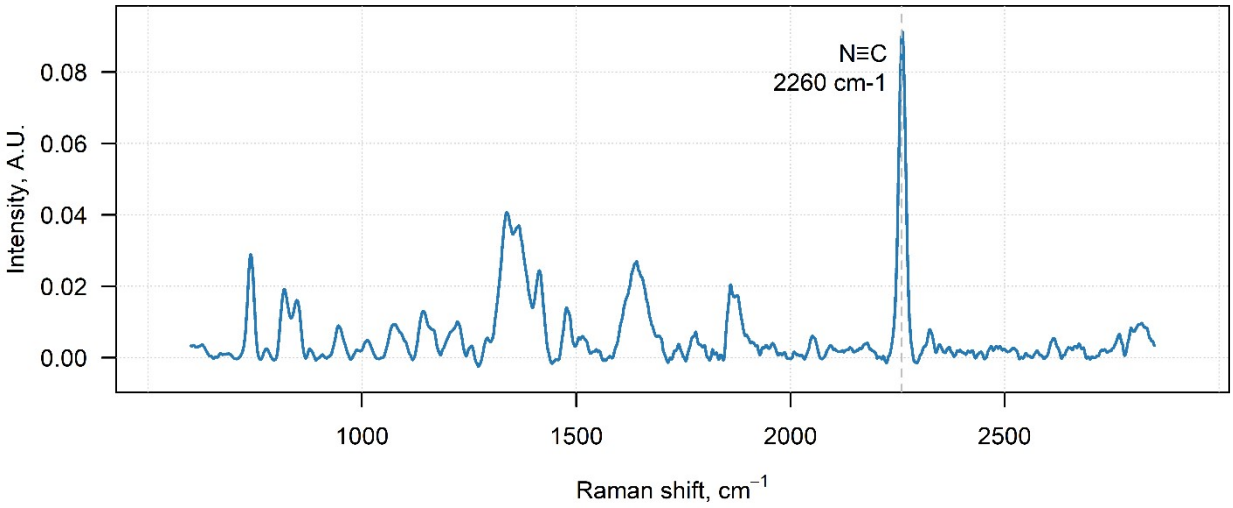


Scavenger 12 – at 75 °C – initial pH 10 **Scavenger 12 – at 60 °C – initial pH 8**

Fig. SI.6.3 Concentration of bisulfide and pH as a function of time for the scavenging reaction with the biomass-based scavenger **12** at 60 ºC and initial pH 8

Monitoring of Raman peaks during reactions with 12

Figure SI.6.4 shows the Raman spectrum of the biomass-based scavenger **12**. The peak corresponding to the nitrile bond (2260 cm^{-1}) is indicated. In addition, figures SI.6.5 and SI.6.6 shows the trends of key region of the Raman spectra as monitored during the scavenging reaction for experiments with initial pH 10 and 75 °C and initial pH 8 and 60 °C, respectively.



+

Fig. SI.6.4 Raman spectrum of the biomass-based scavenger **12** in aqueous solution at pH 10.6. Acquisition conditions: 3 acc x 5 sec.

As can be seen, the dissolution of the scavenger at pH 10 is associated to the onset of a new peak at 2235 cm^{-1}, which is not present in the pure scavenger. The nitrile bond can present a distinct vibration mode around 2200 to 2260 cm^{-1}.[10] The previously mentioned peak at 2235 cm^{-1} is associated to the nitrile bond and is subsequently consumed during the reaction, while the peak of bisulfide (peak at 2574 cm^{-1}) reduces. A peak at 1607 cm^{-1}, possibly associated with carbon-carbon double bonds[10] presented a similar trend, meaning its intensity also decreases over the reaction. The characteristic peak for bisulfide (2574 cm^{-1}) was totally depleted in the first stages of the reaction. The expected peak for thioamide (713 cm^{-1})[11] did not appear during the reaction; however, a peak, possibly associated with sulfur-carbon single bond (657 cm^{-1})[10,11], was observed. The peak of phenylacetic acid (PAA, IS) was stable during the experimental execution.

These observations suggest that the reaction, instead of occurring via direct formation of a thioamide from the scavenger, occurs in the presence of a nitrile bond and a carbon-carbon double bond.

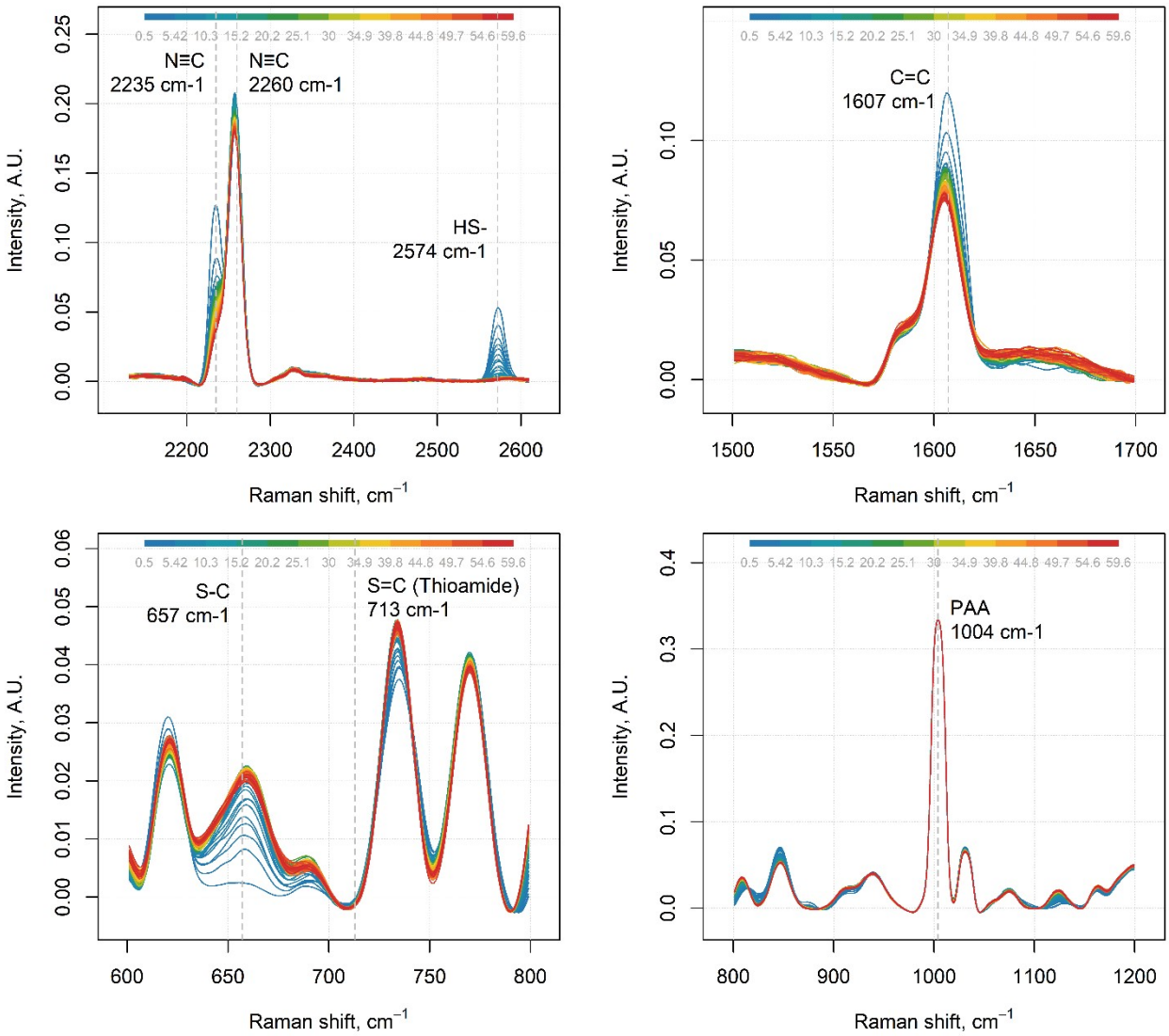


Fig. SI.6.5 Raman spectra during scavenging reaction using biomass-based scavenger **12** at initial pH 10 and 75 °C.

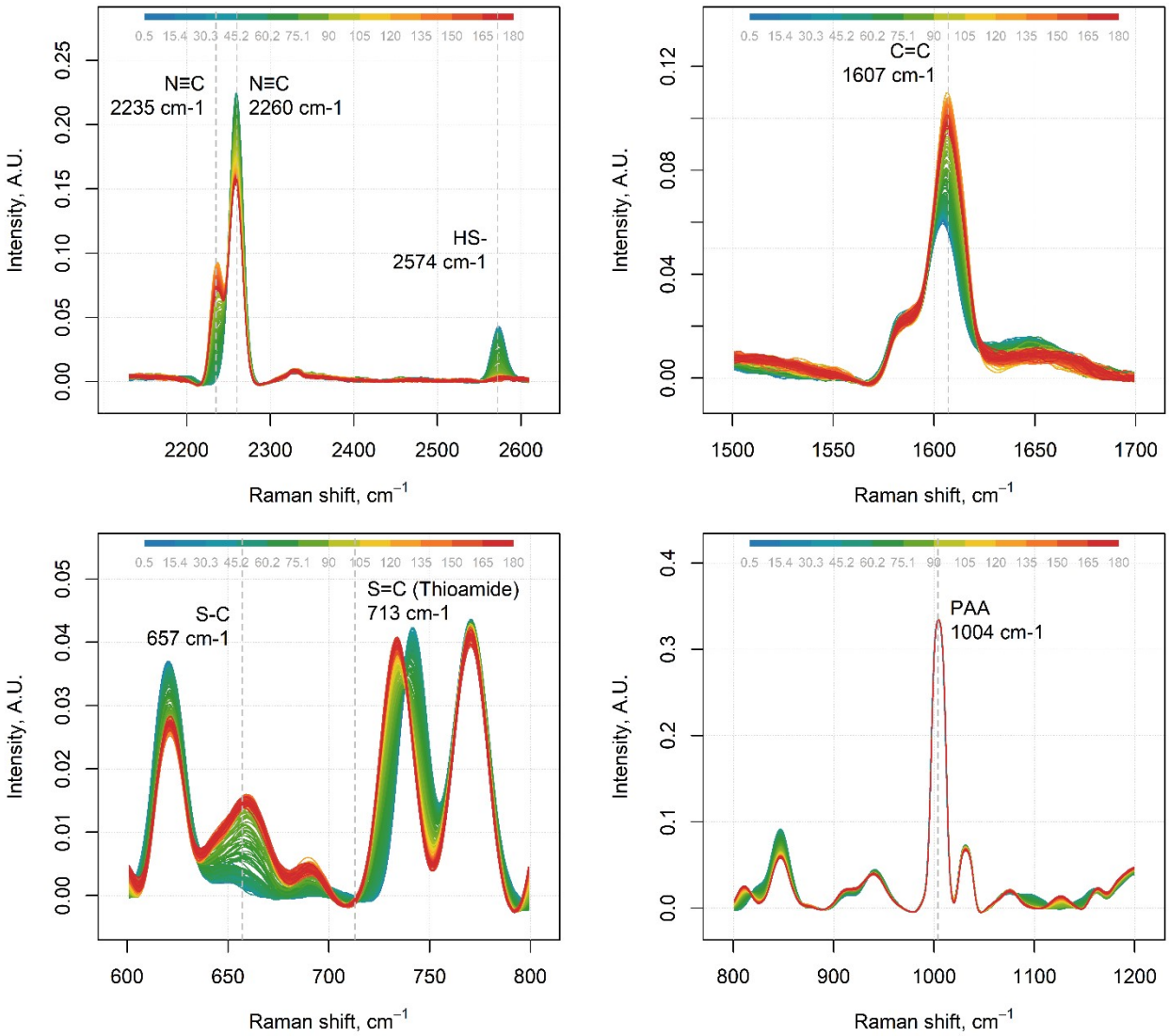


Fig. SI.6.6 Raman spectra during scavenging reaction using biomass-based scavenger **12** at initial pH 8 and 60 °C.

Stability of biomass-based scavenger 12 at different pH values

In order to elucidate if the scavenger **12** can undergo chemical reactions due to pH changes, control experiments were carried out in the absence of bisulfide. The biomass-based scavenger **12** was monitored at different pH levels to check its stability over time. Three initial pH levels were considered, with values of 9, 10 and 11. The solutions were monitored for 1 hour for each pH level. Figure SI.6.7 shows the trend over time, where the color bar varies from blue (0 minutes) to red (60 minutes).

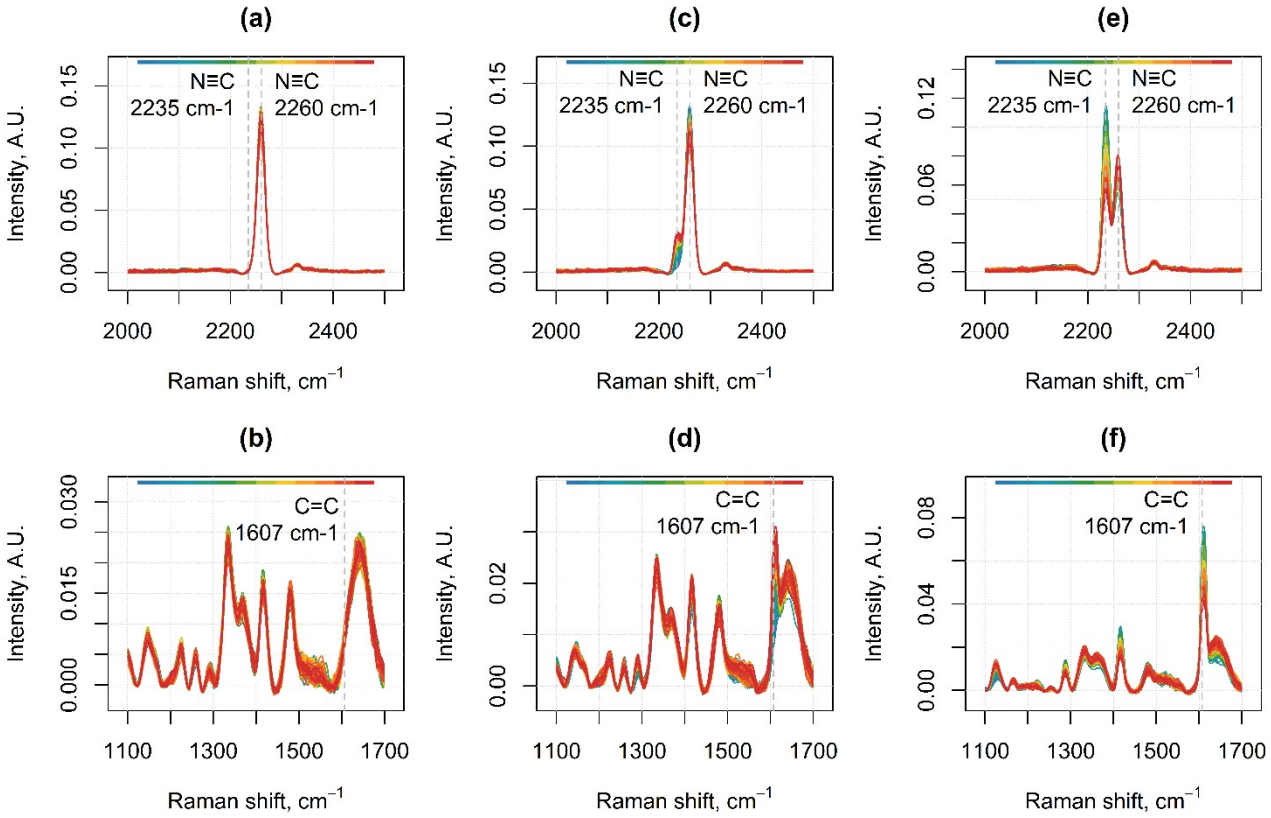


Fig. SI.6.7 Control experiments in the absence of bisulfide ran at 60 °C. Raman spectra over time at different initial pH values for the biomass-based scavenger 12. Initial pH values around 9 (a, b), 10 (c, d) and 11 (e, f).

As can be seen at pH 9 the Raman spectrum is stable. However, at pH 10 and 11 the Raman spectra show the onset of new peaks appearing at 2235 cm^{-1} and 1607 cm^{-1}. The characteristic peak at 2235 cm^{-1} corresponds to the nitrile bond located in an acrylonitrile molecule. This is in agreement with the literature which reports different Raman shifts of the nitrile bond depending on the perturbation generated by the surrounding group.[12] In addition, the peak observed at 1607 cm^{-1} is related to the appearance of carbon-carbon double bond,[10] also part of the acrylonitrile molecule. Fig. SI.6.9 shows the Raman spectra of acrylonitrile.

Figure SI.6.8 shows the pH monitored during the stability analyses performed using scavenger **12**.

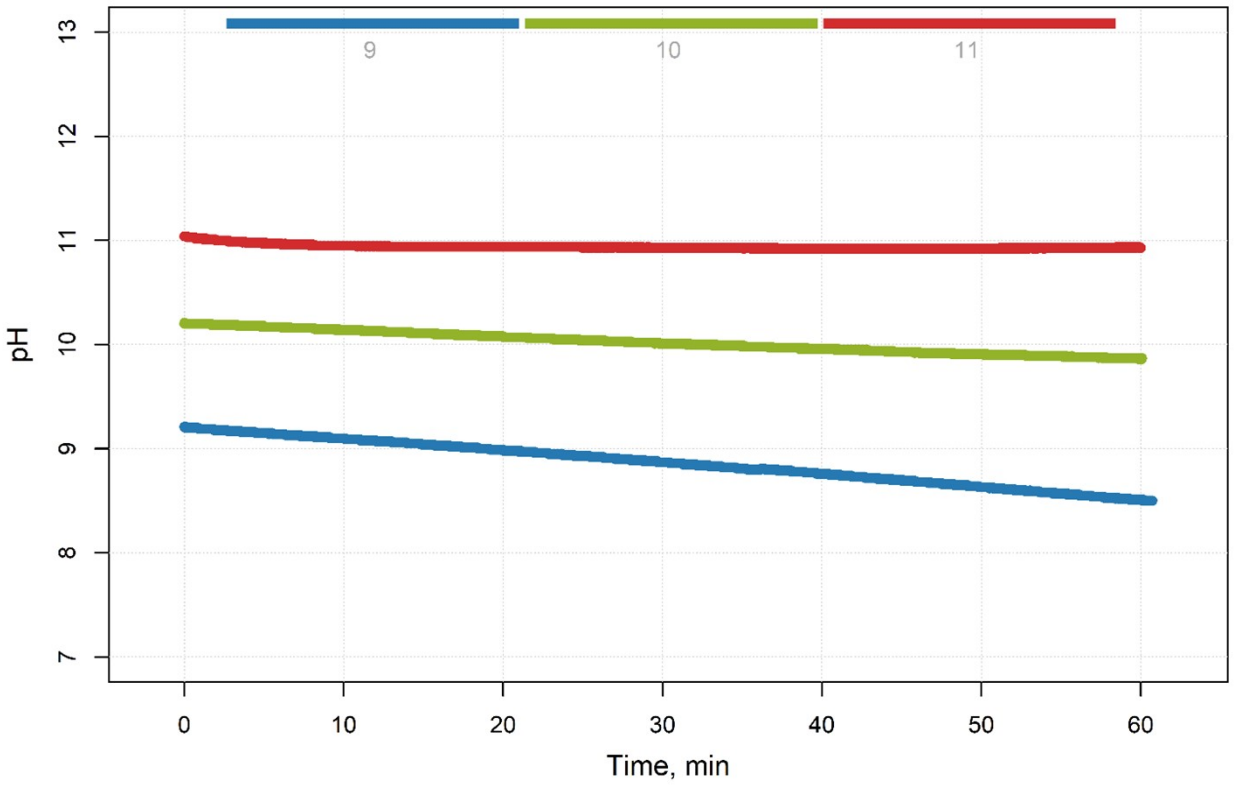


Fig. SI.6.8 Control experiments in the absence of bisulfide ran at 60 °C. pH over time.

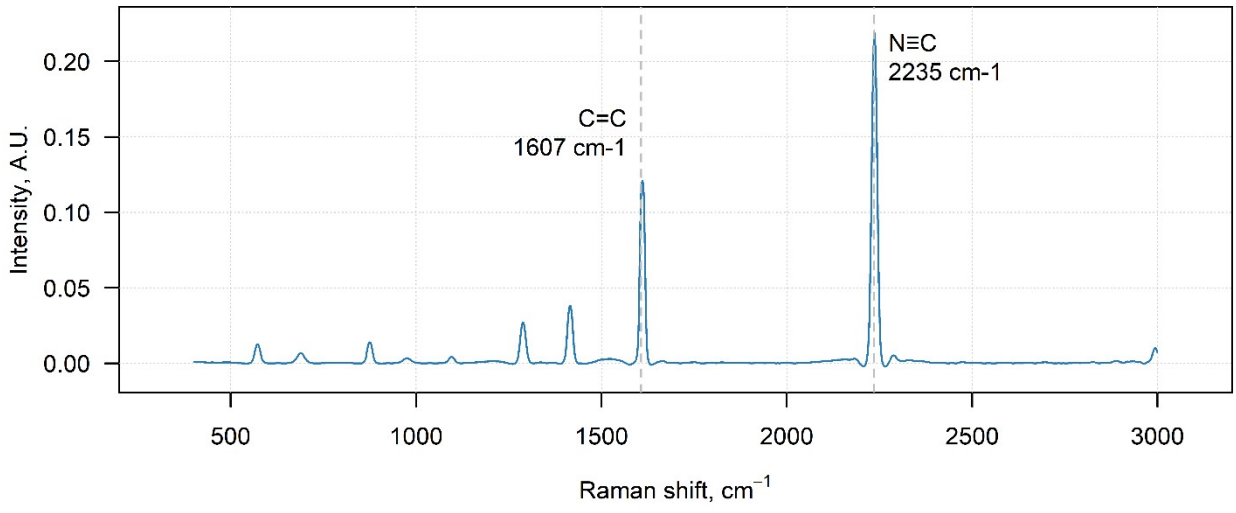


Fig. SI.6.9 Raman spectra of pure acrylonitrile. Acquisition conditions: 3 acc x 5 sec.

It was therefore hypothesized that the biomass-based scavenger **12** decomposes into acrylonitrile at high pH (approx. above 10). The hypothesis was proved by NMR (see Figure SI.6.10). When the pH

is increased from 7 to 10 in a solution of **12** in D_2O at rt. signals that match acrylonitrile can be observed. The broad signals in the blue spectrum is due to lack of solubility of **12** in D_2O at rt.

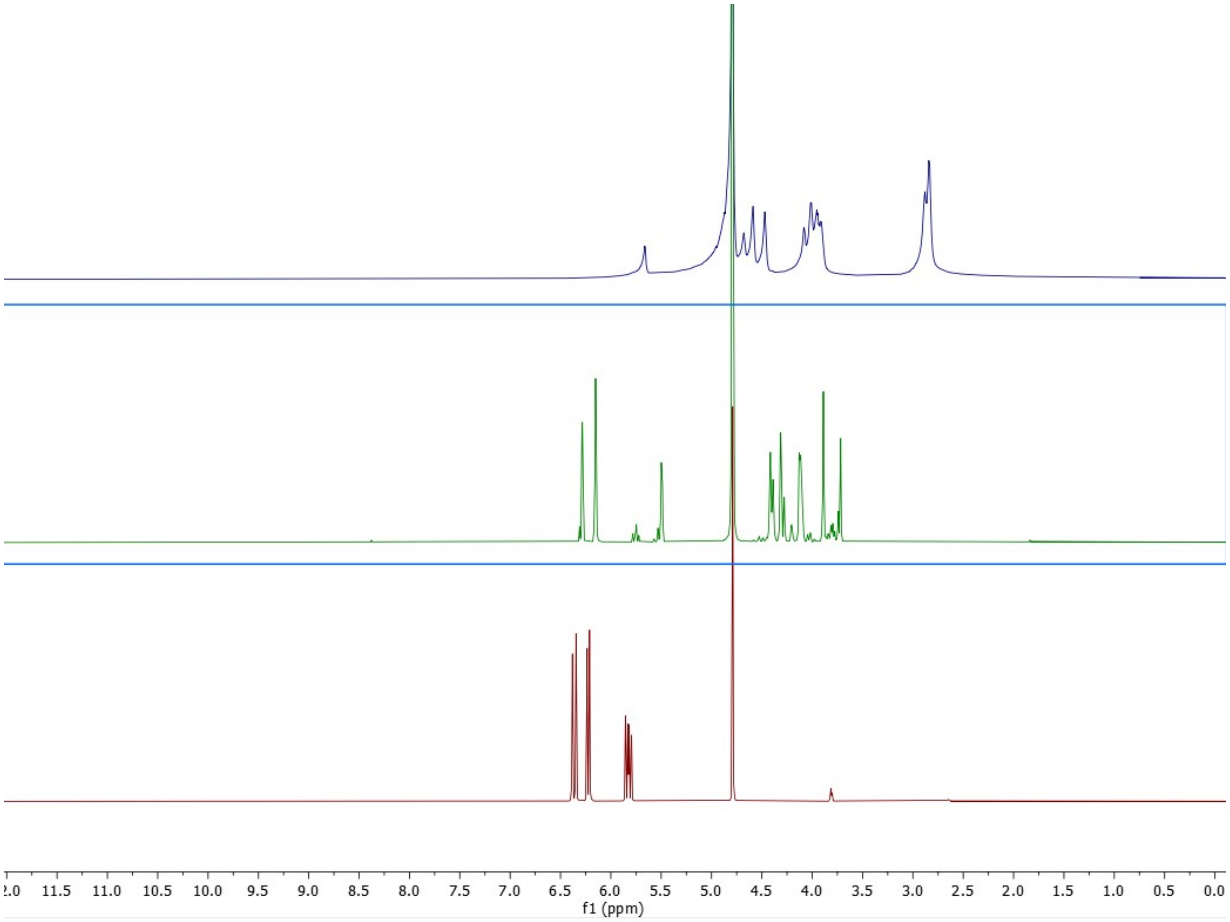


Fig. SI.6.10 ^{1}H-NMR of **12** in D_2O at pH 7 (Blue spectra), **12** in D_2O at pH 10 (Green spectra) and acrylonitrile at pH 10 (Red spectra).

Possible reaction pathway

It was therefore hypothesized that the biomass-based scavenger **12** acts as bisulfide scavenger via an acrylonitrile release mechanism, according to the mechanism below:

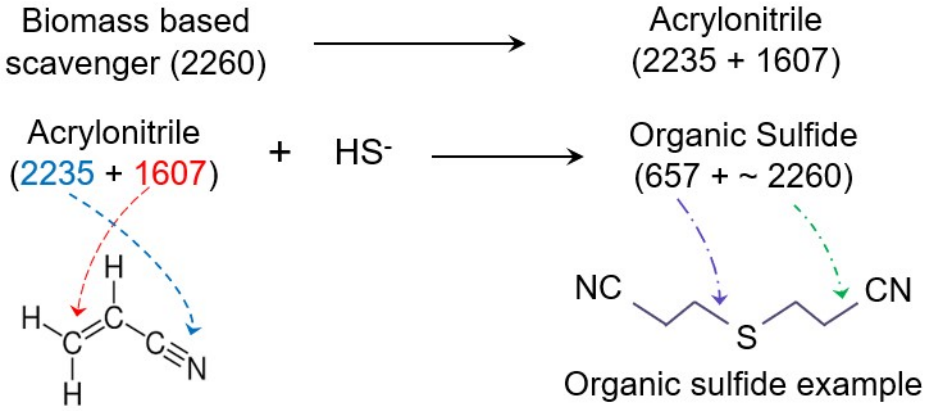


Fig. SI.6.11 Possible reactions mechanism for biomass-based scavengers via acrylonitrile release mechanism. Raman shifts in cm^{-1} for characteristics bonds shown inside parentheses**.**

The biomass-based scavenger **12** presents a characteristic Raman peak at 2260 cm^{-1}, corresponding to the nitrile group present in the molecule. At pH values higher than 10, scavenger **12** decomposes into acrylonitrile, which presents two characteristic Raman peaks at 2235 cm^{-1} and 1607 cm^{-1}. The former corresponds to the nitrile group in acrylonitrile, which has shifted from 2260 to 2235 cm^{-1} due to the perturbance produced by the carbon-carbon double bond (1607 cm^{-1}) present in the acrylonitrile molecule. The acrylonitrile molecule reacts with bisulfide forming an organic sulfide compound with two characteristic Raman peaks: 2260 cm^{-1} (nitrile bond) and 657 cm^{-1} (carbon-sulfur single bond).

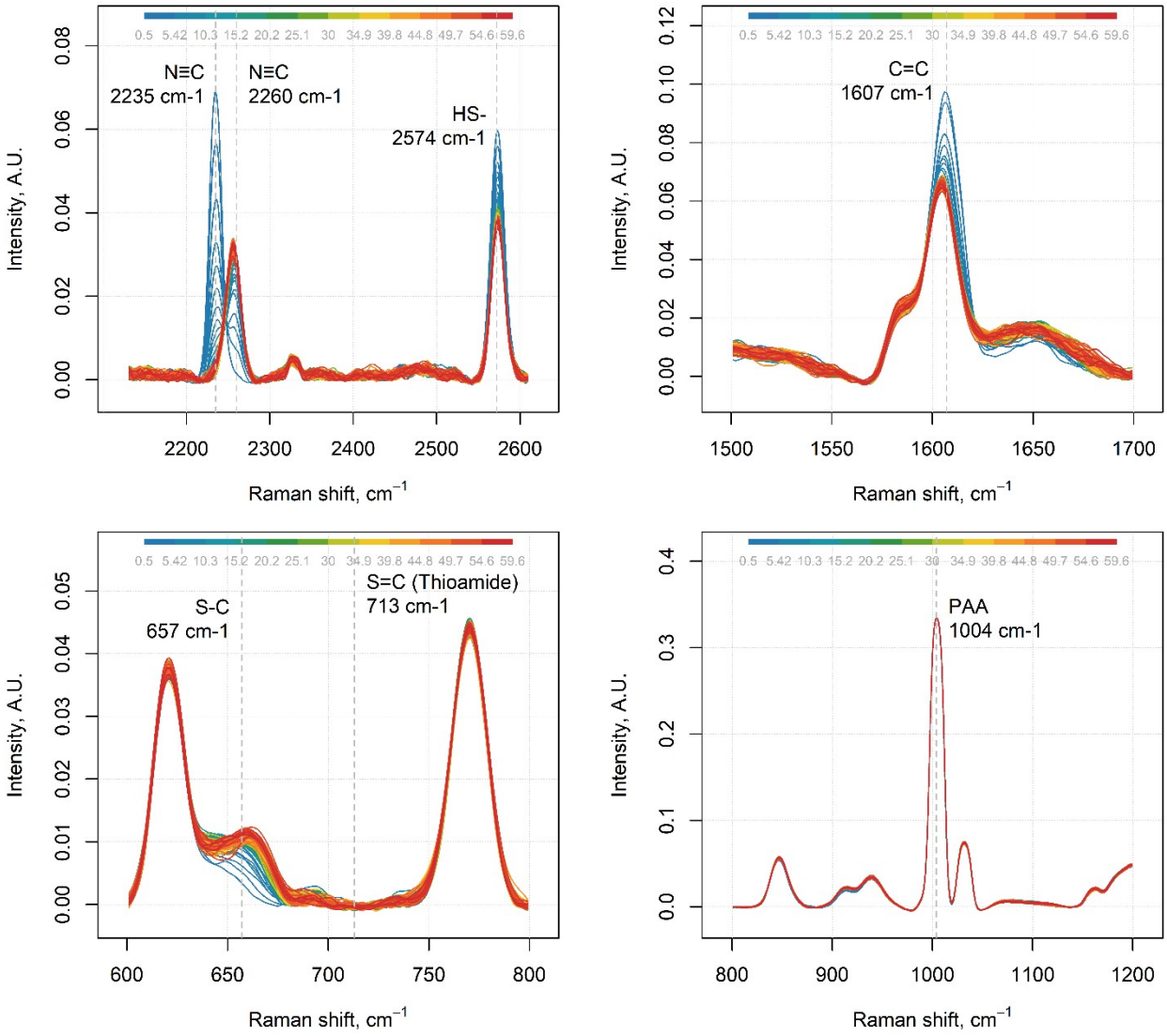


Fig. SI.6.12 Raman spectra during scavenging reaction using acrylonitrile at initial pH 10 and 60 °C.

As can be seen, the peak at 2235 cm^{-1}, previously associated to the nitrile bond, is totally consumed during the reaction, while the peak of bisulfide (peak at 2574 cm^{-1}) reduces. A peak at 1607 cm^{-1}, previously associated to carbon-carbon double bonds, is also consumed during the reaction. In addition, the peak at 2260 cm^{-1}, also associated to a nitrile bond, appears during the reaction confirming the formation of a different compound containing the nitrile group. The characteristic peak for bisulfide (2574 cm^{-1}) was not totally depleted, probably due to the volatilization of acrylonitrile during the experiment. The expected peak for thioamide (713 cm^{-1}) did not appear during the reaction; however, the peak possibly associated with sulfur-carbon single bond (657 cm^{-1}), was observed. The peak of phenylacetic acid (PAA, IS) was stable during the experimental execution.

These observations suggest that the reaction, instead of occurring via direct formation of a thioamide from the scavenger, occurs in the presence of a nitrile bond and a carbon-carbon double bond.

SI.7 stability test

To check how stable the 2-cyanoethyl groups are at neutral pH, a simple NMR experiment was performed. Compound **13** was dissolved in D_2O at pH 7. A ^{1}H-NMR spectrum was taken every 7 days of **13**. Figure SI.7.1 shows the ^{1}H-NMR spectrums of **13** at rt. pH 7. No changes in the ^{1}H-NMR spectrum of **13** could be observed, over 21 days at room temperature and a pH of 7. This indicates that the 2-cyanoethyl groups are stable in water at neutral pH.

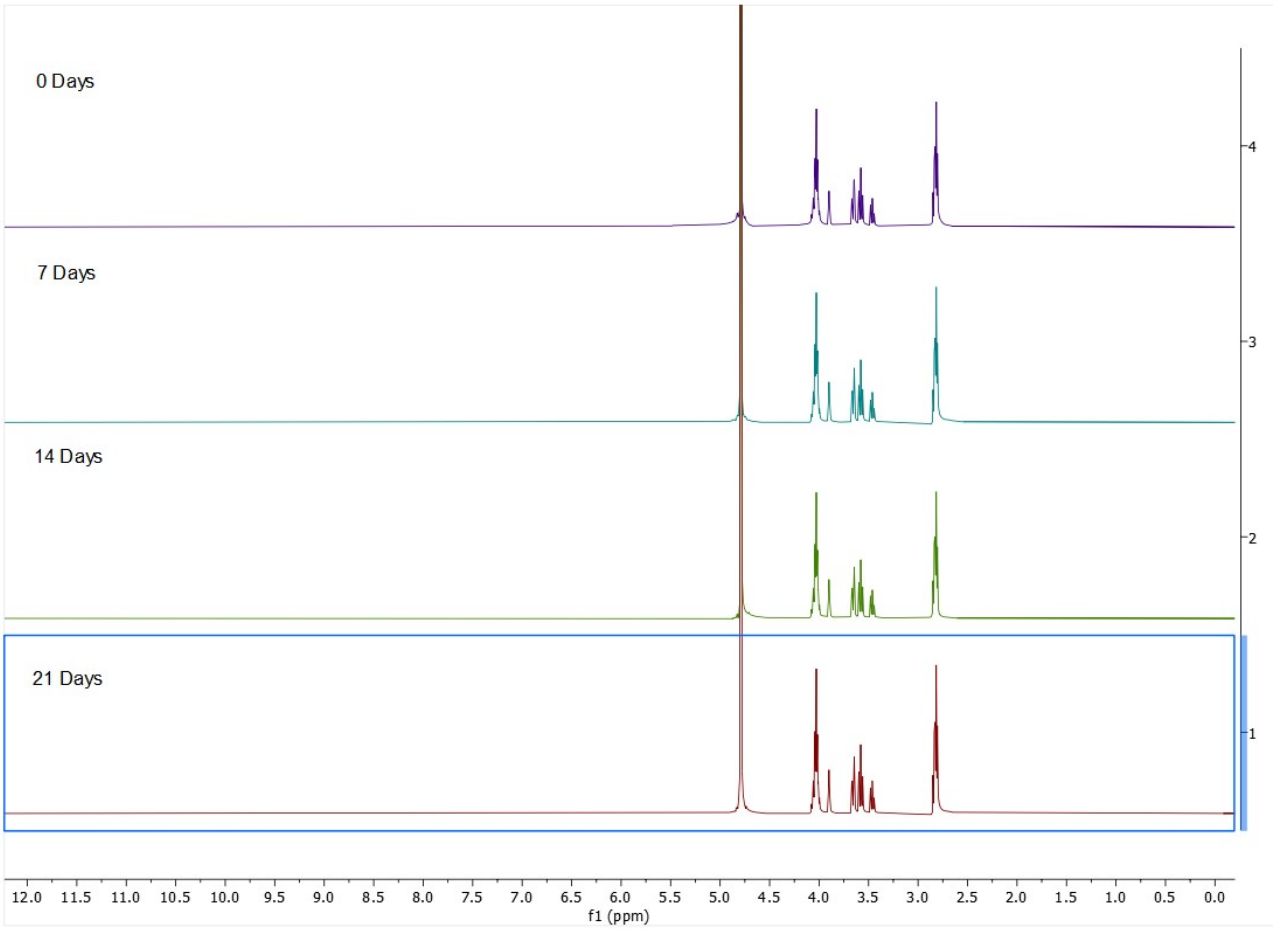


Fig. SI.7.1 ^{1}H-NMR (500 MHz, D_2O) spectrums of compound **13** in D_2O over 21 days, rt. pH 7.

SI.8 Environmental impact assessment materials and method

Ecotoxicity of multifunctional biomass based H_2S scavengers towards regulatory relevant organisms

Inhibition of luminescence was quantified with Microtox test kits (ABOATOX, Finland) using ISO standard 11348-3 with modifications (ISO, 2007).[15] Freeze-dried bacteria, *Aliivibrio fishecri* (formerly *Vibrio fishceri*) were reconstituted in 12 mL saltwater solution (2 wt%) and acclimated for 20 min before the start of the experiment. Five test concentrations were prepared by weighed off the respective H_2S scavengers (**4**, **12** and **13**) yielding twice the final concentration e.g. 12.5, 25, 50, 100 and 200 mg/L. Background luminescence of the 2% saltwater solution was corrected for by measuring 200 µL of the solution in 2 mL glass vials (Thermo Fisher Scientific™). Initial bacterial luminescence was measured by pipetting 100 µL of bacteria suspension into 2 mL glass vials (Thermo Fisher Scientific™) and immediately measuring the luminescence using a luminometer (Luminoskan TL Plus, Thermo Labsystems) denoting the luminescence at time 0 followed by immediate dilution with the test solutions yielding an exposure concentration of 6.25, 12.5, 25, 50 and 100 mg/L. The experiment was carried out in duplicates for each tested concentration and a set of unexposed controls. Luminescence were denoted after 15 and 30 min of exposure. The test were considered valid if the parallel determination of the controls did not deviate more than 3% and the reference compound 3,5-dichlorophenol caused between 20% and 80% decrease in luminescence after 30 min of exposure. A correction factor (f_{kt}) was calculated for controls according to ISO 11348-3 to determine the water-dependent decrease in luminescence (equation 1). The were considered valid if the correction factor was between 0.6 and 1.8 (ISO, 2007).

$$f_{kt} = \frac{I_{kt}}{I_0} \qquad (1)$$

Where f_{kt} is the correction factor at time t (15 or 30 min), I_{kt} is the luminescence at time t (15 or 30 min) and I_0 is the luminescence at time 0. The relative decrease in luminescence for each sample was calculated according to Equation 2.

$$Rel_t = 1 - \frac{I_{kt}}{f_{kt} \cdot I_0} \qquad (2)$$

Where Rel_t is the relative decrease in luminescence at time t (15 or 30 min), I_{kt} is the luminescence at time t (15 or 30 min) and I_0 is the luminescence at time 0.

Growth inhibition tests with marine and freshwater algae for 72 h were conducted according to ISO 10253 and OECD 201 respectively (ISO, 2016,[16] OECD, 2011[17]). Mono cultures of algae was obtained from Norwegian Institute for Water Research, Oslo, Norway (NIVA). Cultures were grown continuously in respective media in 20 mL glass vials fitted with a perforated screw cap to allow for

CO_2 diffusion from the atmosphere. The vials were placed on an orbital shaker (300 rpm) (IKA® Schütler MTS 4) with continuous illumination from below by fluorescent tubes (30 W/33; Philips Amsterdam, The Netherlands) with an intensity of 100±20 µmol m^{-2} s^{-1} measured by LI-189 Quantum/Radiometer/Photometer (LI-COR, Nebraska, USA) at a temperature of 20±2 °C. Test concentrations were prepared in the range 6.25 – 100 mg/L with a factor of two between concentrations. Solutions were inoculated with an initial cell density of $2*10^4$ cells/mL of exponentially growing algal culture. In practice, 250 µL of an exponentially growing algal culture of approximately $2 \cdot 10^6$ cells/mL was added to 25 mL of each exposure concentration and 4 mL was transferred to 20 mL scintillation vials (n = 3, n = 6 for the control group), and placed on an orbital shaker (IKA® Schüttler MTS 4) mounted with a rack and continuously illuminated from below with fluorescent tubes (30 W/33; Philips, Amsterdam, The Netherlands) with an intensity of 90 ± 8 µmol m^{-2} s^{-1} measured by LI-189 Quantum/Radiometer/Photometer (LI-COR, Nebraska, USA). The validity criteria stated in ISO 10253 and OECD 201 were met for all tests, i.e., control growth rate of minimum 0.9 day^{-1} and a maximum change in pH of 1 unit during the 72 hours of incubation. Samples of 0.4 mL were taken at times 0 and 72 h and extracted with 1.6 mL acetone. The algal growth rates were calculated based on the *in vitro* fluorescence of algal pigments as a surrogate for biomass as described by Mayer et al. (1997).[13] The fluorescence was 430 nm and 670 nm for excitation and emission wavelengths. Background fluorescence was corrected by measuring a blank sample containing medium and acetone. For the marine algae the supernatant of each sample was gently transferred to a new vial before fluorescence measurement to avoid interference with precipitates. The algal growth rates were calculated assuming exponential growth following Equation 3.

$$\mu = \frac{\ln N_n - \ln N_0}{t_d} \qquad (3)$$

Where µ is the growth rate (d^{-1}), N_0 is the initial biomass, N_n is the final biomass and t_d is the length of the test period (d). Additionally, the inhibition is calculated as the growth rate of the control related to the growth in each individual exposure following Equation 4.

$$I_i = \left(1 - \frac{\mu_i}{\mu_c}\right) * 100 \qquad (4)$$

Where I_i is the percentage inhibition of growth for concentration i, and μ_i is the mean growth rate for concentration I and μ_c is the mean growth for the control.

Acute toxicity tests with crustaceans were conducted according to the OECD TG 202 Daphnia sp. Acute Immobilisation Test test protocol (OECD, 2004). The crustacean tests were carried out in 100 mL glass beakers in four replicates of 25 mL each, with approximately five organisms in each beaker. Nominal concentrations ranging from 6.25 – 100 mg/L were used with a factor of two between each concentration. pH and dissolved oxygen concentrations were measured initially and at the end of the test and were within the acceptable limits (OECD, 2004). The test was incubated in the dark at 20°C for 48 h. Organisms were considered immobile after gentle prodding or stirring of the beakers. Immobility were assessed after 24 h and 48 h. The percent of immobile organisms was calculated based on number of immobile organisms compared to the total number of exposed organisms.

For each ecotoxicological test the respective inhibition of luminescence, growth rate and immobility were plotted using the statistical software R loaded with the drc-package to fit concentration-response curves, EC-values and their corresponding 95 % confidence intervals using a log-normal function (Ritz and Streibig, 2005).[14]

Biodegradation of multifunctional biomass based H_2S scavengers

Biodegradation test was conducted following OECD 301F (Manometric respirometry test) with few modifications. One day prior to the start of the experiment activated sludge was collected from Mølleåværket waste water treatment plant (Lundtofte, Denmark) in 1 L blue cap bottles. The sludge was filtered through a 500 um sieve and aerated until use. For TSS determination 20 mL MilliQ water was filtered through microfiber filters and dried at 104 °C for 12 hours. After being dried, 5 mL sludge was filtered and final TSS content was determined and the required volume to reach a TSS content in the range of 20-30 mg/L was calculated. The theoretical oxygen (ThOD) demand was calculated from the chemical structure of the proposed H_2S scavengers and was added to reach a final ThOD of approximately 80 mg ThOD/L in a final volume of 365 mL. Controls included inoculum blanks, positive control (NaAC) and abiotic control (H_2S scavengers, without inoculum). Each bottle included a magnetic rod and were equipped with a rubber sleeve containing a NaOH pellet covering the top of the bottle without being submerged in the aqueous phase. The bottles were then attached with a manometric device (OxiTop®-IDS, WTW, Fagerberg, Denmark), closed tightly and incubated on a magnetic stirrer for 28 days (time resolution, 360 measuring points). Quality criteria for the test include the oxygen uptake o fthe inoculum blank to be in the range of 20-30 mg O_2/L and not exceed 60 mg O_2/L and the pH should be in the range of 6-8.5 at the end of the test. The percent of biodegradation was calculated according to equation 5:

$$\%\ degradation = \frac{BOD}{ThOD} * 100 \qquad (5)$$

Where BOD is the biological oxygen demand (mg O_2/mg test substance) and ThOD is the theoretical oxygen demand (mg O_2/mg test substance).

SI.9 References

1 T. R. Krishna and N. Jayaraman, *J. Org. Chem.*, 2003, **68**, 9694–9704.

2 H. Surya Prakash Rao, M. Babu and A. Desai, *RSC Adv.*, 2014, **4**, 11064–11072.

3 B. Majumdar, S. Mandani, T. Bhattacharya, D. Sarma and T. K. Sarma, *J. Org. Chem.*, 2017, **82**, 2097–2106.

4 F. Nadeau, M. Sindt and N. Oget, *New J. Chem.*, 2015, **39**, 9155–9161.

5 M. Kadirvel, W. T. Stimpson, S. Moumene-Afifi, B. Arsic, N. Glynn, N. Halliday, P. Williams, P. Gilbert, A. J. McBain, S. Freeman and J. M. Gardiner, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 2625–2628.

6 F. Song, J. Zhang, Y. Zhao, W. Chen, L. Li and Z. Xi, *Org. Biomol. Chem.*, 2012, **10**, 3642–3654.

7 K. M. Sureshan, S. Devaraj and M. S. Shashidhar, *Tetrahedron*, 2009, **65**, 2703–2710.

8 L. A. Paquette and J. Tae, *J. Am. Chem. Soc.*, 2001, **123**, 4974–4984.

9 K. W. Felling, C. R. Youngstrom and R. J. Lagow, *J. Fluor. Chem.*, 2004, **125**, 749–754.

10 G. Socrates, *Infrared and Raman Characteristic Group Frequencies, Tables and Charts*, John Wiley & Sons, LTD.; West Sussex, 2001.

11 D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press; San Diego, California, 1991.

12 E. R. E. Mojica, N. Abbas, L. O. Wyan, J. Vedad and R. Z. B. Desamero, in *ACS Symposium Series*, American Chemical Society, 2018, vol. 1305, pp. 181–197.

13 P. Mayer, R. Cuhel and N. Nyholm, *Water Res.*, 1997, **31**, 2525–2531.

14 C. Ritz and J. C. Streibig, *J. Stat. Softw.*, 2005, **12**, 1–22.

15 International Organization for Standardization, ISO 11348-3:2007 Water quality - Determination of inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test) - Part 3: Method using freeze-dried bacteria, (2007). https://www.iso.org/standard/40518.html

16 International Organization for Standardization, ISO 10253:2016 Water quality - Marine algal growth inhibition test with Skeletoma sp. and Phaeodacttylum tricornutum, (2016). https://www.iso.org/standard/66657.html

17 OECD, 2011. Test No. 201: Freshwater Alga and Cyanobacteria, Growth Inhibition Test. https://doi.org/10.1787/9789264069923-en