Electronic Supplementary Material (ESI) for ChemComm.

Peroxodisulfate Assisted Synthesis of 2-Thiocyanato Glycals and their Transformation to C-2-Thio Acrylo/Aryl Nitrile Substituted Glycals

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1. General Consideration:

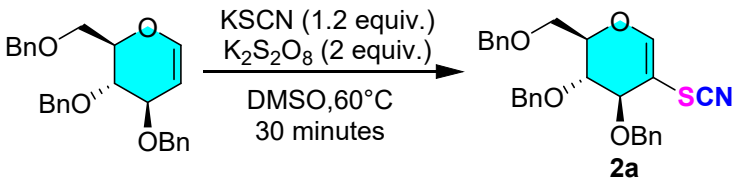
^{1}H and ^{13}C NMR spectra were recorded using 400 MHz and 101 MHz spectrometers with TMS as internal standards. Chemical shifts are expressed in parts per million (δ ppm). Silica gel-coated aluminium plates were used for TLC.The products were purified by column chromatography on silica gel (60- 120 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. The Exact masses of all products were derived by using HRMS having QTOF analyzer. Reagents used were mostly purchased from Sigma Aldrich, TCI and Avra.

2.0 Optimization studies for compound 3a

Entry	Pd-Source (10 mol%)	Ligand (20 mol%)	Base (2.0 equiv.)	Solvent	Temp (°C)	Yield (%)
1	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMF	80 °C	13
2	$Pd(OAc)_2$	PPh_3	K_2CO_3	Toluene	110 °C	27
3	$Pd(OAc)_2$	PPh_3	K_2CO_3	ACN	70 °C	37
4	$Pd(OAc)_2$	PPh_3	Et_3N	ACN	70 °C	23
5	$Pd(OAc)_2$	Xantphos	K_2CO_3	ACN	70 °C	65
6	$Pd(dba)_2$	Xantphos	K_2CO_3	ACN	70 °C	33
7	$Pd(dba)_2$	Xantphos	K_2CO_3	Toluene	110 °C	19
8	$Pd(PPh_3)_4$		K_2CO_3	Toluene	110 °C	31
9	$Pd(PPh_3)_4$		K_2CO_3	ACN	70 °C	42

2.1 General procedures

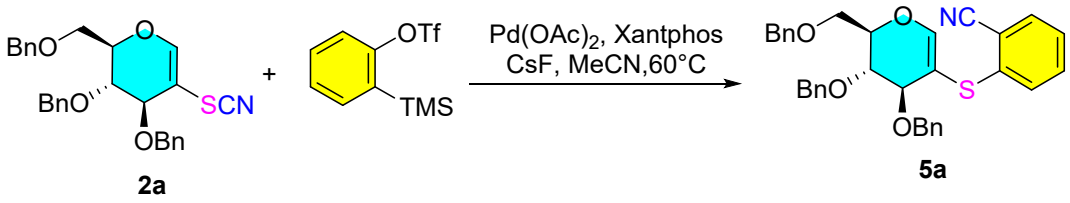
2.1.1 General experimental procedure for the synthesis of 2-thiocyanato glycals:



2a

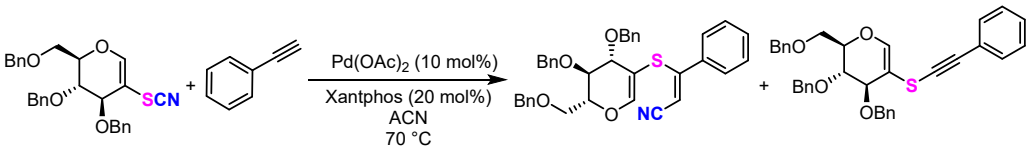
By taking Tri-O-benzyl-D-glucal as an example. An oven dried round bottom flask equipped with a magnetic stir bar was charged with Tri-O-benzyl-D-glucal (1 equiv.) and dissolved in DMSO. To this stirred solution was added KSCN (1.2 equiv.) and $K_2S_2O_8$ (2 equiv.) and stirred at 60°C for 30 minutes. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was treated with water and then extracted with ethyl acetate (3 × 20 mL), the organic phase was dried over sodium sulfate and evaporated under reduced pressure to get the crude product which was purified by filtration thru a short-pad of silica gel column (hexane:ethyl acetate;95:5) to afford 2a.

2.1.2 General experimental procedure for the synthesis of 2-thioarylnitrile glycals:



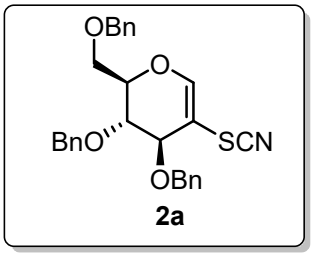
By taking **5a** as an example.To solid $Pd(OAc)_2$ (2.2 mg, 10 µmol, 10 mol%), Xantphos (11.6 mg, 0.20 µmol, 20 mol%) and CsF (50 mg, 331 µmol, 3.30 eq.) was added acetonitrile (4 mL) and prestirred for 2-3 min. Afterwards the corresponding glycal thiocyanate (100 µmol, 1.00 eq.) was added and the reaction was stirred for additional 2 min. Subsequently, the corresponding aryne precursor (140 µmol, 1.40 eq.) was added and the reaction was heated to 60 °C and stirred for 1 hour in sealed tube. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel.

2.1.3 General experimental procedure for the synthesis of 2-thioacrylonitrile glycals:



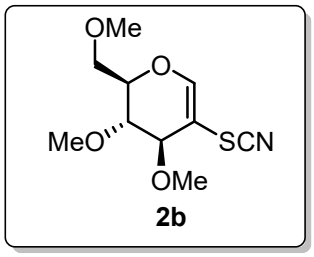
By taking **3a** as an example.Glycal thiocyanate was dissolved in CAN, to this was added phenyl acetylene,solid $Pd(OAc)_2$ (2.2 mg, 10 µmol, 10 mol%), Xantphos (11.6 mg, 0.20 µmol, 20 mol%) and stirred for 2-3 hours at 70 °C in sealed tube. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel.

3. Characterization of the products:



Prepared by general procedure **2.1.1** using Tri-O-benzyl-D-glucal (50 mg, 0.12 mmol), KSCN (50 mg, 1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 95:5) to afford **2a** as yellow oil in 73 % yield, 41.45 mg.

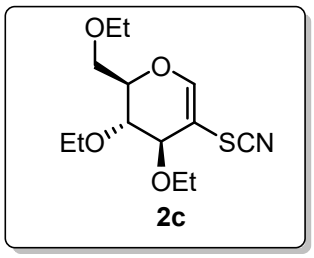
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 11H), 7.21 – 7.16 (m, 4H), 6.90 (s, 1H), 4.66 (d, J = 11.3 Hz, 1H), 4.60 – 4.54 (m, 2H), 4.51 (d, J = 7.6 Hz, 1H), 4.41 (s, 2H), 4.36 – 4.30 (m, 1H), 4.03 (d, J = 3.6 Hz, 1H), 3.89 – 3.85 (m, 1H), 3.71 – 3.66 (m, 1H), 3.61 – 3.57 (m, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.6, 137.6(C_q),137.3(C_q),137.3(C_q), 128.6, 128.6, 128.55, 128.48, 128.2, 128.1, 128.0, 127.9, 127.8, 111.8(C_q), 97.4 (C_q), 77.2, 75.0, 73.5 (CH_2), 73.3, 72.9 (CH_2), 67.4 (CH_2). **HRMS** (ESI), m/z calcd. for $C_{28}H_{31}N_2O_4S$ $[M+NH_4]^+$ 491.1996, found 491.2005.



2b

Prepared by general procedure **2.1.1** using Tri-*O*-methyl-D-glucal (50 mg, 0.26 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 92:8) to afford 2b as yellow oil in 61 % yield, 38.87 mg.

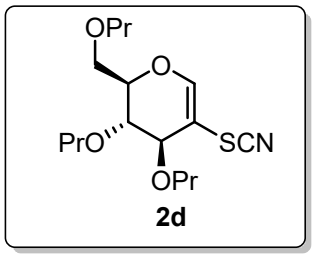
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 4.30 (tdt, *J* = 5.9, 3.8, 1.0 Hz, 1H), 4.12 (dd, *J* = 7.2, 0.9 Hz, 1H), 3.85 (dq, *J* = 4.5, 1.0 Hz, 1H), 3.67 – 3.63 (m, 1H), 3.62 (s, 3H), 3.60 – 3.57 (m, 1H), 3.53 (s, 3H), 3.40 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.2, 111.7(C_q), 97.6 (C_q), 77.3, 76.9, 75.2, 69.7 (CH_2), 59.2, 58.9, 58.7. **HRMS** (ESI), m/z calcd. for $C_{10}H_{19}N_2O_4S$ $[M+NH_4]^+$ 263.1034, found 263.1066.



2c

Prepared by general procedure 2.1.1 using Tri-*O*-ethyl-D-glucal (50 mg, 0.22 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 93:7) to afford 2c as yellow oil in 76 % yield, 48.00 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 4.19 – 4.13 (m, 1H), 3.86 (d, *J* = 4.3 Hz, 1H), 3.75 (tdd, *J* = 11.1, 5.7, 2.6 Hz, 2H), 3.69 – 3.64 (m, 2H), 3.59 (ddd, *J* = 10.8, 6.8, 2.8 Hz, 3H), 3.50 – 3.41 (m, 2H), 1.22 (td, *J* = 7.0, 0.6 Hz, 3H), 1.16 (dd, *J* = 6.8, 0.6 Hz, 3H), 1.13 (dd, *J* = 6.9, 0.6 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.2, 111.8(C_q), 97.8(C_q), 77.7, 76.4, 74.3, 67.8 (CH_2), 67.3 (CH_2), 66.9 (CH_2), 66.8 (CH_2), 15.5 (CH_3), 15.4 (CH_3), 15.1 (CH_3). **HRMS** (ESI), m/z calcd. for $C_{13}H_{25}N_2O_4S$ $[M+NH_4]^+$ 305.1509, found 305.1529.

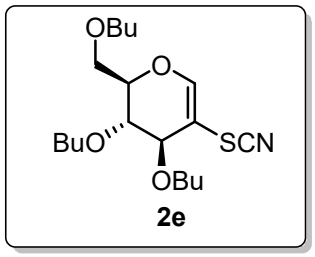


2d

Prepared by general procedure **2.1.1** using Tri-*O*-propyl-D-glucal (50 mg, 0.18 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 94:6) to afford 2d as yellow oil in 79 % yield, 46.80 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 4.18 (dd, *J* = 9.8, 5.8 Hz, 1H), 3.85 (d, *J* = 4.7 Hz, 1H), 3.65 (dd, *J* = 6.3, 1.7 Hz, 2H), 3.64 – 3.60 (m, 2H), 3.59 – 3.54 (m, 2H), 3.52 – 3.47 (m, 1H), 3.38 – 3.32 (m, 2H), 1.62 (dd, *J* = 14.1, 7.1 Hz, 2H), 1.55 (d, *J* = 7.0 Hz, 2H), 1.52 (d, *J* = 7.0 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.88 – 0.86 (m, 3H), 0.86 – 0.83 (m, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.3, 111.9 (C_q), 97.9 (C_q),77.7, 76.3, 74.3, 73.5 (CH_2), 73.3 (CH_2), 73.1 (CH_2), 68.1, 23.3 (CH_2), 23.2 (CH_2), 22.8 (CH_2), 10.6 (CH_3), 10.6 (CH_3), 10.5(CH_3). **HRMS** (ESI), m/z calcd. for $C_{16}H_{31}N_2O_4S$ $[M+NH_4]^+$ 347.2009, found 347.2005.

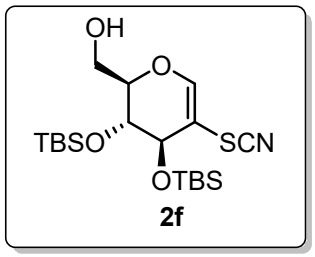
Prepared by general procedure **2.1.1** using Tri-*O*-propyl-D-glucal (50 mg, 0.16 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30



2e

minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 95:5) to afford 2e as yellow oil in 81 % yield, 48.10 mg.

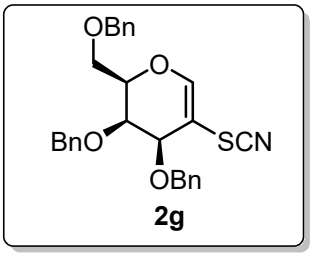
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 4.16 (dd, *J* = 9.7, 5.7 Hz, 1H), 3.83 (d, *J* = 4.8 Hz, 1H), 3.69 (dd, *J* = 6.8, 1.9 Hz, 1H), 3.65 (dd, *J* = 9.9, 3.9 Hz, 2H), 3.62 – 3.58 (m, 2H), 3.56 (d, *J* = 3.8 Hz, 1H), 3.52 (dd, *J* = 6.6, 2.5 Hz, 1H), 3.41 – 3.35 (m, 2H), 1.60 – 1.54 (m, 2H), 1.50 (dd, *J* = 6.1, 2.3 Hz, 2H), 1.47 (s, 1H), 1.37 (dd, *J* = 11.7, 4.2 Hz, 2H), 1.33 (d, *J* = 2.6 Hz, 1H), 1.31 (d, *J* = 2.0 Hz, 1H), 1.29 (s, 1H), 1.27 (d, *J* = 1.8 Hz, 1H), 1.26 (s, 1H), 1.22 – 1.17 (m, 1H), 0.88 (t, *J* = 4.7 Hz, 3H), 0.87 – 0.85 (m, 3H), 0.85 – 0.82 (m, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.3, 111.9 (C_q), 97.9 (C_q), 77.7, 76.3, 74.4, 71.7 (CH_2), 71.4 (CH_2), 71.3 (CH_2), 68.1 (CH_2), 32.2 (CH_2), 32.1 (CH_2), 31.7 (CH_2), 19.3 (CH_2), 13.9 (CH_3), 13.9 (CH_3), 13.9 (CH_3). **HRMS** (ESI), m/z calcd. for $C_{19}H_{37}N_2O_4S$ $[M+NH_4]^+$ 389.2477, found 389.2475.



2f

Prepared by general procedure **2.1.1** using Tri-O-tertbutyldimethylsilyl-D-glucal (50 mg, 0.10 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 98:2) to afford 2f as yellow oil in 66 % yield, 28.46 mg.

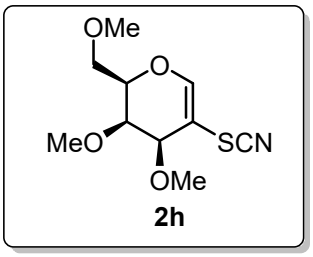
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 4.13 (s, 1H), 4.01 (dt, *J* = 7.1, 5.9 Hz, 1H), 3.90 – 3.83 (m, 2H), 3.61 (d, *J* = 12.3 Hz, 1H), 0.81 (d, *J* = 2.4 Hz, 9H), 0.77 (d, *J* = 2.4 Hz, 9H), 0.16 (d, *J* = 2.4 Hz, 3H), 0.10 (d, *J* = 2.4 Hz, 3H), 0.02 (d, *J* = 2.4 Hz, 3H), -0.00 (d, *J* = 2.4 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.5, 111.5 (C_q), 96.9 (C_q), 80.0, 70.9, 68.7, 61.4 (CH_2), 25.7 (CH_3), 25.5 (CH_3), 18.0 (CH_3), 17.9 (CH_3), -4.6 (CH_3), -4.6 (CH_3), -4.7 (CH_3), -4.8 (CH_3). HRMS (ESI), m/z calcd. for $C_{19}H_{41}N_2O_4SSi_2$ $[M+NH_4]^+$ 449.2329, found 449.2325.



2g

Prepared by general procedure **2.1.1** using Tri-*O*-benzyl-D-galactal (50 mg, 0.12 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 95:5) to afford 2g as yellow oil in 71 % yield, 40.31 mg.

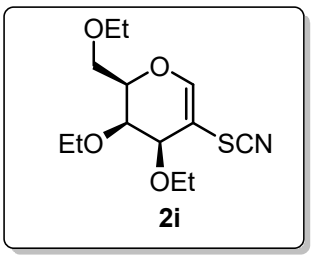
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 4H), 7.22 – 7.13 (m, 11H), 6.74 (s, 1H), 4.69 (d, *J* = 5.0 Hz, 2H), 4.49 (s, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.8 Hz, 1H), 4.29 (d, *J* = 11.8 Hz, 1H), 4.19 (s, 1H), 4.13 (d, *J* = 3.8 Hz, 1H), 3.90 (dd, *J* = 3.6, 2.9 Hz, 1H), 3.63 (dd, *J* = 10.4, 7.3 Hz, 1H), 3.57 (dd, *J* = 10.6, 5.0 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.1, 137.6 (C_q), 137.6 (C_q), 137.5 (C_q), 128.5, 128.5, 128.5, 128.1, 128.0, 127.9, 127.9, 112.0 (C_q), 98.2 (C_q), 74.1 (CH_2), 73.7 (CH_2), 73.5 (CH_2), 72.9, 67.5. HRMS (ESI), m/z calcd. for $C_{28}H_{31}N_2O_4S$ $[M+NH_4]^+$ 491.2006, found 491.2005.



2h

Prepared by general procedure **2.1.1** using Tri-*O*-methyl-D-galactal (50 mg, 0.26 mmol), KSCN (1.2 equiv.) and K2S2O8 (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 92:8) to afford 2h as yellow oil in 69 % yield, 43.97 mg.

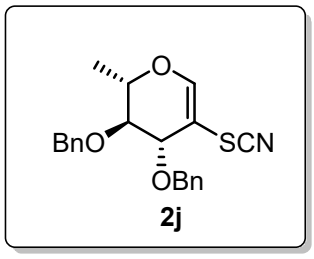
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 1H), 4.29 – 4.23 (m, 1H), 3.98 (dt, *J* = 3.8, 1.1 Hz, 1H), 3.81 – 3.77 (m, 1H), 3.65 – 3.58 (m, 3H), 3.58 (s, 3H), 3.52 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 152.6, 111.8 (C_q), 98.2 (C_q),76.6, 74.7, 73.7, 69.7 (CH_2), 60.2 (CH_3), 59.9 (CH_3), 59.3 (CH_3). HRMS (ESI), m/z calcd. for $C_{10}H_{19}N_2O_4S$ $[M+NH_4]^+$ 463.1034, found 263.1066.



2i

Prepared by general procedure **2.1.1** using Tri-*O*-ethyl-D-galactal (50 mg, 0.22 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 93:7) to afford **2i** as yellow oil in 83 % yield, 52.43 mg.

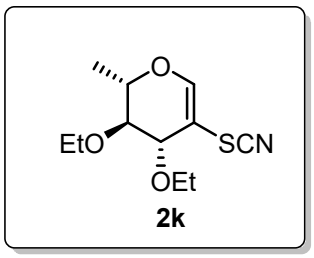
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 1H), 4.21 (t, *J* = 4.7 Hz, 1H), 4.03 (d, *J* = 3.7 Hz, 1H), 3.84 (t, *J* = 3.2 Hz, 1H), 3.79 (dd, *J* = 6.4, 2.9 Hz, 1H), 3.75 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.72 – 3.66 (m, 1H), 3.64 (d, *J* = 2.5 Hz, 1H), 3.63 (d, *J* = 0.7 Hz, 1H), 3.58 – 3.53 (m, 1H), 3.50 (dd, *J* = 7.2, 2.2 Hz, 1H), 3.46 (d, *J* = 7.3 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H), 1.19 – 1.17 (m, 3H), 1.14 (t, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 152.5, 112.0 (C_q), 98.6 (C_q), 73.3, 67.9 (CH_2), 67.8 (CH_2), 67.7 (CH_2), 66.9 (CH_2), 15.5(CH_3), 15.4 (CH_3), 15.1(CH_3). HRMS (ESI), m/z calcd. for $C_{13}H_{25}N_2O_4S$ $[M+NH_4]^+$ 305.1509, found 305.1535.



2j

Prepared by general procedure **2.1.1** using Di-*O*-benzyl-L-rhamnal (50 mg, 0.16 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 93:7) to afford **2j** as yellow oil in 67 % yield, 39.35 mg.

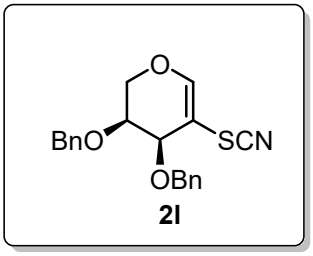
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 6.5, 1.0 Hz, 4H), 7.27 – 7.20 (m, 6H), 6.87 (s, 1H), 4.74 (d, *J* = 11.3 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 4.60 (t, *J* = 6.0 Hz, 1H), 4.54 – 4.48 (m, 1H), 4.29 – 4.20 (m, 1H), 4.05 (d, *J* = 4.4 Hz, 1H), 3.53 (dd, *J* = 5.5, 4.5 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.7, 137.5 (C_q), 137.3 (C_q), 128.63, 128.56, 128.2, 128.1, 127.9, 112.0 (C_q), 97.3 (C_q), 77.7, 75.6, 74.8, 73.7 (CH_2), 73.2 (CH_2), 16.4 (CH_3). HRMS (ESI), m/z calcd. for $C_{21}H_{25}N_2O_3S$ $[M+NH_4]^+$ 385.1566, found 385.1586.



2k

Prepared by general procedure **2.1.1** using Di-*O*-benzyl-L-rhamnal (50 mg, 0.27 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 93:7) to afford 2k as yellow oil in 85 % yield, 55.78 mg.

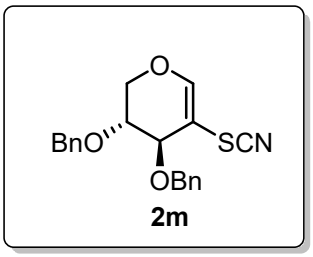
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 1H), 4.11 – 4.07 (m, 1H), 3.86 (d, J = 5.3 Hz, 1H), 3.83 – 3.78 (m, 1H), 3.76 (dd, J = 7.1, 2.0 Hz, 1H), 3.74 – 3.69 (m, 1H), 3.64 – 3.59 (m, 1H), 3.31 (dd, J = 7.1, 5.4 Hz, 1H), 1.31 (d, J = 6.7 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.0 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.4, 112.1 (C_q), 98.0 (C_q), 79.3, 76.9, 75.3, 67.6 (CH_2), 67.4 (CH_2), 16.6 (CH_3), 15.6 (CH_3), 15.5 (CH_3). HRMS (ESI), m/z calcd. for $C_{11}H_{21}N_2O_3S$ $[M+NH_4]^+$ 261.1274, found 261.1278.



2l

Prepared by general procedure **2.1.1** using 3,4-Di-*O*-benzyl-L-arabinal (50 mg, 0.17 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 96:4) to afford **2l** as yellow oil in 68 % yield, 40.81 mg.

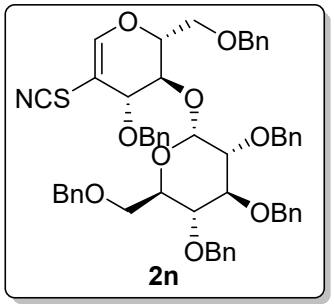
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.38 – 7.33 (m, 8H), 6.90 (s, 1H), 4.95 (d, J = 11.2 Hz, 1H), 4.80 (d, J = 11.2 Hz, 1H), 4.70 – 4.65 (m, 2H), 4.27 – 4.24 (m, 1H), 4.06 (dd, J = 5.1, 3.9 Hz, 2H), 3.90 – 3.82 (m, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 154.66, 137.83 (C_q), 137.36 (C_q), 128.69, 128.58, 128.50, 128.40, 128.22, 128.04, 127.71, 127.65, 127.01, 111.87 (C_q), 97.03 (C_q), 74.66 (CH_2), 74.09, 72.09 (CH_2), 71.91, 63.41 (CH_2). HRMS (ESI), m/z calcd. for $C_{20}H_{23}N_2O_3S$ $[M+NH_4]^+$ 371.1509, found 371.1529.



2m

Prepared by general procedure **2.1.1** using 3,4-Di-*O*-benzyl-D-xylal (50 mg, 0.17 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 96:4) to afford **2m** as yellow oil in 77 % yield, 46.21 mg.

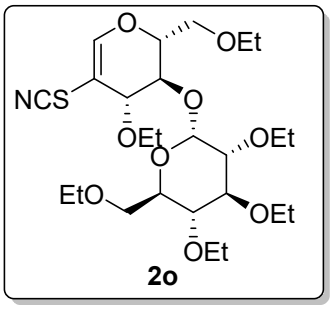
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 7H), 7.22 – 7.18 (m, 3H), 6.95 (s, 1H), 4.54 (d, J = 6.9 Hz, 2H), 4.44 (s, 2H), 4.13 (dt, J = 12.0, 2.1 Hz, 1H), 3.86 – 3.82 (m, 2H), 3.61 (dd, J = 4.0, 2.4 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 155.4, 137.4 (C_q), 137.2 (C_q), 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 128.0, 127.6, 127.0, 112.0 (C_q), 96.6 (C_q), 72.6 (CH_2), 72.4, 71.8, 71.4 (CH_2), 64.4 (CH_2). HRMS (ESI), m/z calcd. for $C_{20}H_{23}N_2O_3S$ $[M+NH_4]^+$ 371.1509, found 371.1535.



2n

Prepared by general procedure **2.1.1** using benzyl protected maltal (50 mg, 0.059 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 90:10) to afford 2n as yellow oil in 84 % yield, 44.87 mg.

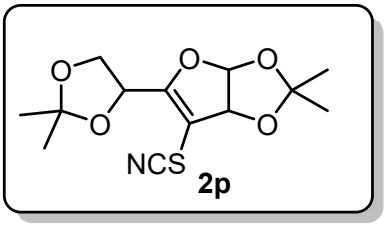
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 9H), 7.22 – 7.21 (m, 7H), 7.19 (d, *J* = 3.1 Hz, 7H), 7.14 (d, *J* = 2.0 Hz, 2H), 6.88 (s, 1H), 4.85 (d, *J* = 11.6 Hz, 1H), 4.68 (t, *J* = 8.3 Hz, 2H), 4.62 (t, *J* = 4.5 Hz, 5H), 4.56 – 4.49 (m, 2H), 4.33 (t, *J* = 3.8 Hz, 3H), 4.28 (d, *J* = 9.5 Hz, 2H), 4.16 (t, *J* = 3.4 Hz, 1H), 4.14 – 4.11 (m, 1H), 3.78 (d, *J* = 2.9 Hz, 1H), 3.72 – 3.67 (m, 2H), 3.51 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.41 (dd, *J* = 5.5, 3.3 Hz, 2H), 3.39 – 3.35 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.42, 138.55 (C_q), 138.49 (C_q), 138.41 (C_q), 137.77 (C_q), 137.74 (C_q), 137.68 (C_q), 128.60, 128.53, 128.48, 128.41, 128.38, 128.34, 128.28, 128.18, 128.03, 127.94, 127.90, 127.84, 127.75, 127.73, 127.65, 127.62, 127.52, 127.03, 111.98 (C_q), 103.20, 97.35 (C_q), 82.07, 79.19, 76.65, 75.38(CH_2), 74.75, 74.70 (CH_2), 73.67, 73.61 (CH_2), 73.49, 73.31 (CH_2), 73.09 (CH_2), 72.91 (CH_2), 72.85, 68.79 (CH_2), 67.05 (CH_2). HRMS (ESI), m/z calcd. for $C_{55}H_{59}N_2O_9S$ $[M+NH_4]^+$ 923.3941, found 923.3947.



2o

Prepared by general procedure **2.1.1** using ethyl protected maltal (50 mg, 0.10 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 70:30) to afford 2o as yellow oil in 83 % yield, 44.26 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 4.41 (s, 1H), 4.29 (d, *J* = 7.7 Hz, 1H), 4.06 (d, *J* = 3.0 Hz, 1H), 3.96 (s, 1H), 3.88 – 3.81 (m, 1H), 3.74 – 3.64 (m, 4H), 3.63 – 3.54 (m, 6H), 3.53 – 3.47 (m, 4H), 3.46 – 3.41 (m, 3H), 3.34 – 3.26 (m, 1H), 3.11 (dd, *J* = 9.7, 3.0 Hz, 1H), 1.20 – 1.17 (m, 6H), 1.15 (dd, *J* = 4.0, 2.9 Hz, 6H), 1.12 – 1.11 (m, 3H), 1.08 (td, *J* = 7.0, 1.1 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 152.9, 111.8 (C_q), 103.3, 97.1 (C_q), 82.2, 78.7, 76.5, 74.9, 74.2, 73.6, 73.0, 68.8 (CH_2), 68.7 (CH_2), 68.5 (CH_2), 67.5 (CH_2), 66.9 (CH_2), 66.8 (CH_2), 66.5 (CH_2), 66.1 (CH_2),15.7 (CH_3), 15.6 (CH_3), 15.6 (CH_3), 15.3 (CH_3), 15.2 (CH_3), 15.1 (CH_3). HRMS (ESI), m/z calcd. for $C_{25}H_{47}N_2O_9S$ $[M+NH_4]^+$ 551.3007, found 551.3002.

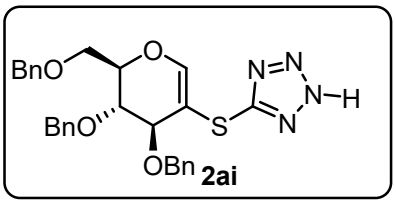


2p

Prepared by general procedure **2.1.1** using diacetonide-3,4-endofuranose (50 mg, 0.21 mmol), KSCN (1.2 equiv.) and $K_2S_2O_8$ (2.0 equiv.). The reaction mixture was stirred at 70 °C for 30 minutes. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine,

dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 80:20) to afford 2p as yellow oil in 70 % yield, 43.96 mg.

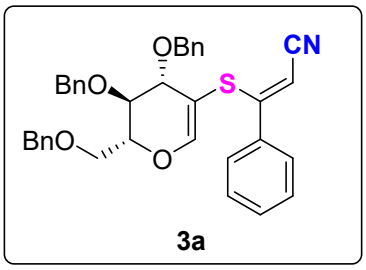
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (d, *J* = 5.3 Hz, 1H), 5.32 (d, *J* = 5.3 Hz, 1H), 4.98 (t, 1H), 4.20 (dd, *J* = 8.7, 6.9 Hz, 1H), 4.07 (dd, *J* = 8.7, 5.7 Hz, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 164.2 (C_q), 114.3 (C_q), 111.5 (C_q), 106.1, 94.9 (C_q), 84.6, 77.2, 69.3, 66.5 (CH_2), 27.8(CH_3), 25.7 (CH_3), 25.4 (CH_3). HRMS (ESI), m/z calcd. for $C_{13}H_{21}N_2O_5S$ $[M+NH_4]^+$ 317.1175, found 317.1172.



2ai

Prepared by the reaction of 2a (50 mg, 0.105 mmol) with NaN_3 (3 equiv.) and $ZnCl_2$ (1.5 equiv.) using iso-propanol as solvent at 50 °C for 30 minutes. The reaction mixture was filtered, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 80:20) to get 2ai as white powder in 90 % yield, 49.1mg.

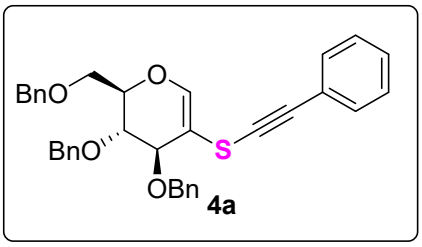
^{1}H NMR (400 MHz, CDCl3) δ 7.31 – 7.19 (m, 14H), 7.05 (d, J = 1.8 Hz, 1H), 7.02 (s, 1H), 4.59 (q, J = 11.6 Hz, 2H), 4.53 – 4.46 (m, 3H), 4.44 (d, 2H), 4.05 – 4.00 (m, 2H), 3.68 (dd, J = 10.5, 6.5 Hz, 1H), 3.60 (dd, J = 10.4, 5.3 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 171.3(C_q), 156.1, 137.3 (C_q), 136.5 (C_q), 136.1 (C_q), 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.8, 97.4 (C_q), 75.9, 75.8, 73.5 (CH_2), 73.1 (CH_2), 72.6 (CH_2), 72.1, 67.4(CH_2). HRMS (ESI), m/z calcd. for $C_{28}H_{29}N_4O_4S$ $[M+H]^+$ 517.1910, found 517.1908.



3a

Prepared by general procedure **2.1.3** using 2a (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) in ACN. The reaction mixture was stirred at 70 °C for 3 hours. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 98:2) to afford 3a as yellow oil in 65 % yield, 21.984 mg.

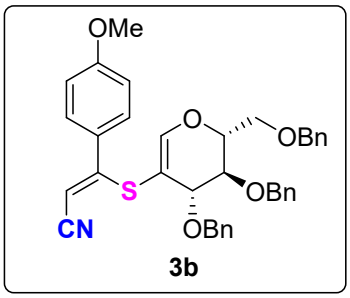
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 12H), 7.28 – 7.20 (m, 4H), 7.15 (td, J = 7.9, 1.9 Hz, 4H), 6.83 (s, 1H), 5.34 (d, J = 1.4 Hz, 1H), 4.62 – 4.48 (m, 2H), 4.47 (d, J = 11.8 Hz, 1H), 4.43 – 4.34 (m, 2H), 4.32 (d, J = 11.9 Hz, 1H), 4.20 (q, J = 5.2 Hz, 1H), 3.77 (d, J = 3.9 Hz, 1H), 3.71 (t, J = 4.7 Hz, 1H), 3.36 (d, J = 5.2 Hz, 2H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 163.8 (C_q), 153.4, 137.8 (C_q), 137.7 (C_q), 137.5 (C_q), 136.6 (C_q), 130.1,128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 127.99, 127.97, 127.8, 127.76, 127.7, 127.67, 116.6 (C_q), 102.6 (C_q), 94.9, 76.5, 75.7, 73.3 (CH_2), 73.1, 72.7 (CH_2), 72.5 (CH_2), 67.4 (CH_2). HRMS (ESI), m/z calcd. for $C_{36}H_{33}NO_4NaS$ $[M+Na]^+$ 598.2029, found 598.2028.



4a

Prepared by general procedure 2.1.3 as a side product, using 2a (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) in ACN. The reaction mixture was stirred at 70 °C for 3 hours. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 99:1) to afford 3a as yellow oil in 10 % yield, 4.604 mg.

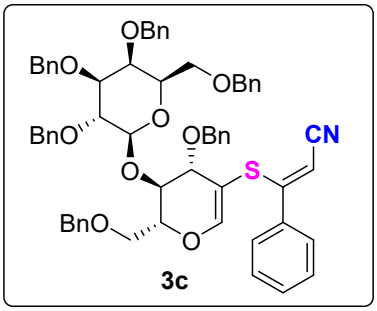
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 3H), 7.32 (dd, *J* = 5.1, 3.3 Hz, 5H), 7.30 – 7.28 (m, 4H), 7.27 (d, *J* = 2.2 Hz, 5H), 7.26 – 7.24 (m, 3H), 6.91 (s, 1H), 4.85 (d, *J* = 11.3 Hz, 1H), 4.73 – 4.64 (m, 2H), 4.60 – 4.55 (m, 1H), 4.52 (d, *J* = 1.2 Hz, 2H), 4.36 (tdd, *J* = 5.6, 4.1, 1.3 Hz, 1H), 4.28 (d, *J* = 4.3 Hz, 1H), 3.97 (ddd, *J* = 9.8, 5.7, 3.8 Hz, 1H), 3.82 – 3.75 (m, 1H), 3.70 (dd, *J* = 10.7, 4.1 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 148.7, 138.0 (C_q), 137.8 (C_q), 137.6 (C_q), 131.6 (C_q), 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.87, 127.8, 127.7, 123.2, 104.0 (C_q), 92.4 (C_q), 78.8, 76.9, 74.0, 73.9, 73.4 (CH_2), 73.2 (CH_2), 72.8 (CH_2), 67.9 (CH_2). HRMS (ESI), m/z calcd. for $C_{35}H_{32}O_4NaS$ $[M+Na]^+$ 571.1915, found 571.1919.



3b

Prepared by general procedure 2.1.3 using 2a (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) in ACN. The reaction mixture was stirred at 70 °C for 3 hours. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 97:3) to afford 3b as yellow oil in 63 % yield, 32.02 mg.

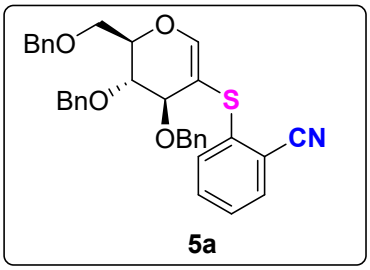
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (q, *J* = 2.2 Hz, 3H), 7.23 (dd, *J* = 3.6, 2.0 Hz, 4H), 7.21 (d, *J* = 2.1 Hz, 3H), 7.20 – 7.13 (m, 4H), 7.07 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.07 – 7.00 (m, 2H), 6.77 (s, 1H), 6.71 (s, 1H), 6.68 (s, 1H), 5.21 (s, 1H), 4.48 (d, *J* = 5.0 Hz, 2H), 4.36 (d, *J* = 8.3 Hz, 1H), 4.32 (d, *J* = 3.3 Hz, 1H), 4.25 (d, *J* = 9.9 Hz, 1H), 4.17 (qd, *J* = 5.1, 1.3 Hz, 1H), 3.76 (d, *J* = 6.0 Hz, 1H), 3.70 (d, *J* = 3.9 Hz, 1H), 3.64 (s, 3H), 3.32 (d, *J* = 5.2 Hz, 2H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 162.8 (Cq), 161.3 (Cq), 153.0, 137.8 (Cq), 137.7 (Cq), 137.5 (Cq), 130.1, 128.9 (Cq), 128.5, 128.5, 128.4, 128.4, 128.35, 128.3, 128.0, 127.9, 127.8, 127.76, 127.7, 127.7, 117.1 (Cq), 113.8, 103.1 (Cq), 93.7, 76.5, 75.4, 73.4, 73.3, 73.2 (CH_2), 72.7, 72.66 (CH_2), 72.4 (CH_2), 67.4 (CH_2), 55.3 (CH_3). HRMS (ESI), m/z calcd. for $C_{37}H_{35}NO_5S$ $[M+Na]^+$ 628.2134, found 628.2136.



3c

Prepared by general procedure 2.1.3 using 2a (30 mg, 0.033 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) in ACN. The reaction mixture was stirred at 70 °C for 3 hours. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 94:6) to afford 3c as yellow oil in 60 % yield, 19.98 mg.

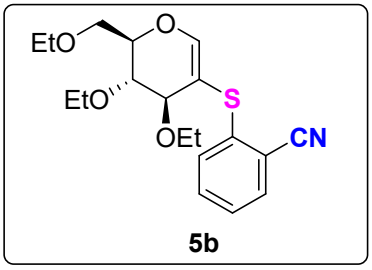
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 6H), 7.30 – 7.20 (m, 22H), 7.21 – 7.09 (m, 6H), 7.10 – 7.01 (m, 2H), 6.71 (s, 1H), 6.19 (s, 1H), 5.30 (s, 1H), 4.86 (d, *J* = 11.5 Hz, 2H), 4.82 – 4.72 (m, 2H), 4.71 – 4.54 (m, 3H), 4.52 – 4.36 (m, 3H), 4.32 – 4.19 (m, 3H), 4.02 – 3.89 (m, 3H), 3.88 – 3.78 (m, 3H), 3.65 (dd, *J* = 3.3, 1.5 Hz, 1H), 3.54 (m, *J* = 10.9, 4.5, 3.3 Hz, 1H), 3.23 (m, *J* = 10.9, 4.4, 3.2 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 163.5 (Cq), 153.0, 138.7 (Cq), 138.6 (Cq), 138.5 (Cq), 138.0 (Cq), 137.9 (Cq), 137.7 (Cq), 136.7 (Cq), 129.9, 128.8, 128.5, 128.4, 128.4, 128.4, 128.38, 128.36, 128.34, 128.32, 128.3, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.56,116.7 (Cq), 103.5, 102.5 (Cq), 96.2, 81.9, 79.1, 76.0, 75.2 (CH_2), 75.0, 74.9 (CH_2), 73.8, 73.6 (CH_2), 73.4, 73.2 (CH_2), 73.1 (CH_2), 72.8, 72.3 (CH_2), 68.8 (CH_2), 66.9 (CH_2). HRMS (ESI), m/z calcd. for $C_{63}H_{65}N_2O_9S$ $[M+NH_4]^+$ 1025.4411, found 1025.4415.



5a

Prepared by general procedure **2.1.2** using 2a (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) and CsF (3.30 eq.) in ACN. The reaction mixture was stirred at 40 °C for 1 hour. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 94:6) to afford 3a as yellow oil in 90 % yield, 41.52 mg.

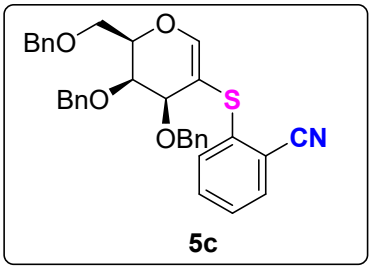
^{1}H NMR (400 MHz, $CDCl_3$) ***δ*** 7.42 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.20 (m, 9H), 7.18 – 7.11 (m, 6H), 7.05 – 7.00 (m, 2H), 6.89 (s, 1H), 4.49 (d, *J* = 0.9 Hz, 2H), 4.48 (d, *J* = 5.1 Hz, 1H), 4.46 (d, *J* = 5.6 Hz, 2H), 4.43 (d, *J* = 12.7 Hz, 2H), 3.87 (t, *J* = 3.9 Hz, 1H), 3.82 (dd, *J* = 3.5, 1.2 Hz, 1H), 3.77 (dd, *J* = 10.6, 6.7 Hz, 1H), 3.64 (dd, *J* = 10.6, 4.5 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** ***δ*** 154.1, 143.7 (C_q), 137.8 (C_q), 137.6 (C_q), 137.5 (C_q), 133.4, 132.7, 128.6, 128.5, 128.1, 127.9, 127.86, 127.8, 126.9, 125.3, 117.0 (C_q), 110.3 (C_q), 101.3 (C_q), 76.5, 74.0, 73.5 (CH_2), 73.3, 72.8 (CH_2), 72.4 (CH_2), 67.9 (CH_2). HRMS (ESI), m/z calcd. for $C_{34}H_{35}N_2O_4S$ $[M+NH_4]^+$ 567.2323, found 567.2318.



5b

Prepared by general procedure **2.1.2** using 2c (50 mg, 0.139 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) and CsF (3.30 eq.) in ACN. The reaction mixture was stirred at 40 °C for 1 hour. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 92:8) to afford 3b as yellow oil in 81 % yield, 40.88 mg.

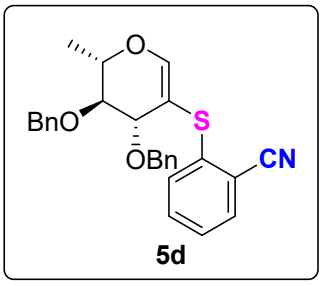
^{1}H NMR (400 MHz, $CDCl_3$) ***δ*** 7.53 – 7.43 (m, 2H), 7.37 (td, J = 7.8, 1.5 Hz, 2H), 7.11 (td, J = 7.6, 1.3 Hz, 1H), 6.86 (s, 1H), 4.30 (ddt, J = 7.6, 5.9, 2.9 Hz, 1H), 3.73 – 3.66 (m, 3H), 3.64 – 3.59 (m, 3H), 3.53 (dd, J = 7.0, 1.4 Hz, 2H), 3.49 (dd, J = 7.1, 1.4 Hz, 2H), 1.18 (t, 3H), 1.14 (t, J = 2.1 Hz, 3H), 0.98 (t, J = 7.1, 1.4 Hz, 1H)..51 – 7.44 (m, 2H), 7.40 – 7.35 (m, 1H), 7.11 (td, *J* = 7.6, 1.3 Hz, 1H), 6.86 (s, 1H), 3.68 (d, *J* = 1.4 Hz, 2H), 3.61 (d, *J* = 1.3 Hz, 2H), 3.60 (d, *J* = 1.2 Hz, 1H), 3.53 (dd, *J* = 7.0, 1.4 Hz, 2H), 3.49 (dd, *J* = 7.1, 1.4 Hz, 2H), 1.18 (t, 3H), 1.14 (t, *J* = 2.1 Hz, 3H), 0.98 (t, *J* = 7.1, 1.4 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** ***δ*** 153.8, 144.0(C_q), 133.3, 132.5, 127.2, 125.2, 116.9 (C_q), 110.3 (C_q), 102.0 (C_q), 75.6, 74.3, 68.4 (CH_2), 66.9 (CH_2), 66.5 (CH_2), 66.4 (CH_2), 15.6 (CH_3), 15.4 (CH_3), 15.1 (CH_3). HRMS (ESI), m/z calcd. for $C_{19}H_{25}NO_4NaS$ $[M+Na]^+$ 386.1380, found 386.1402.



5c

Prepared by general procedure **2.1.2** using 2g (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) and CsF (3.30 eq.) in ACN. The reaction mixture was stirred at 40 °C for 1 hour. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 94:6) to afford 3c as yellow oil in 85 % yield, 39.21 mg.

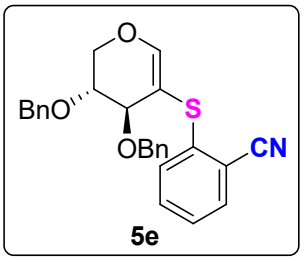
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.0 Hz, 1H), 7.40 (dd, J = 7.5, 1.7 Hz, 1H), 7.28 – 7.23 (m, 9H), 7.20 – 7.17 (m, 3H), 7.14 – 7.11 (m, 3H), 7.05 (dd, J = 7.8, 1.8 Hz, 1H), 6.97 – 6.92 (m, 2H), 6.79 (s, 1H), 4.75 (d, J = 11.4 Hz, 1H), 4.58 (s, 2H), 4.52 (d, J = 11.4 Hz, 1H), 4.45 (d, J = 14.9 Hz, 2H), 4.33 – 4.28 (m, 1H), 4.18 (d, J = 3.5 Hz, 1H), 4.00 (dd, J = 3.7, 2.3 Hz, 1H), 3.75 (dd, J = 10.1, 6.9 Hz, 1H), 3.69 (dd, J = 10.1, 5.6 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.9,144.9 (C_q),137.9 (C_q), 137.8 (C_q), 137.6 (C_q), 132.8, 132.3, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.6, 127.5, 127.4, 124.9, 117.1(C_q),109.46 (C_q), 102.3 (C_q), 77.3,75.2,74.0 (CH_2),73.6 (CH_2), 73.6 (CH_2), 68.0 (CH_2). HRMS (ESI), m/z calcd. for $C_{34}H_{35}N_2O_4S$ $[M+NH_4]^+$ 567.2313, found 567.2318.



5d

Prepared by general procedure **2.1.2** using 2j (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) and CsF (3.30 eq.) in ACN. The reaction mixture was stirred at 40 °C for 1 hour. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 94:6) to afford 3d as yellow oil in 75 % yield, 27.25 mg.

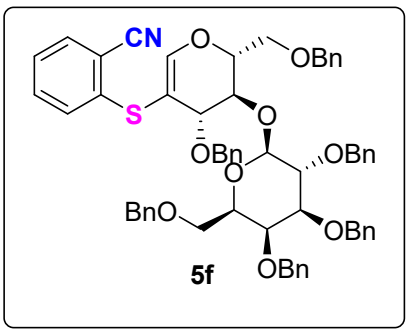
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 7.8 Hz, 3H), 7.24 – 7.16 (m, 5H), 7.15 (m, 2H), 7.10 – 7.01 (m, 2H), 6.88 (s, 1H), 4.56 (dd, J = 11.7, 3.3 Hz, 2H), 4.52 (s, 1H), 4.50 (s, 1H), 4.41 – 4.33 (m, 1H), 3.90 (d, J = 3.8 Hz, 1H), 3.59 (t, J = 4.3 Hz, 1H), 1.38 (d, J = 6.8 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 154.2, 144.0 (C_q), 137.8 (C_q), 137.6 (C_q), 133.4, 132.5, 128.5, 128.3, 128.0, 127.8, 127.7, 127.7, 126.9, 125.1, 116.9 (C_q), 110.3 (C_q), 101.2 (C_q), 75.0, 74.0, 73.0, 72.6, 16.6 (CH_3). HRMS (ESI), m/z calcd. for $C_{27}H_{29}N_2O_3S$ $[M+NH_4]^+$ 461.1884, found 461.1899.



5e

Prepared by general procedure **2.1.2** using 2l (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) and CsF (3.30 eq.) in ACN. The reaction mixture was stirred at 40 °C for 1 hour. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 94:6) to afford 3e as yellow oil in 77 % yield, 37.33 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (ddd, J = 13.5, 7.7, 1.5 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.23 (td, J = 5.6, 2.4 Hz, 3H), 7.19 – 7.12 (m, 4H), 7.06 (ddd, J = 15.1, 7.7, 1.5 Hz, 2H), 6.99 (s, 1H), 4.55 – 4.49 (m, 3H), 4.47 (d, J = 8.2 Hz, 1H), 4.28 (dt, J = 12.0, 2.1 Hz, 1H), 4.02 (d, J = 11.9 Hz, 1H), 3.68 (d, J = 1.9 Hz, 2H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 156.0, 144.1 (C_q), 137.6 (C_q), 137.5 (C_q), 133.4, 132.7, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 127.97, 127.9, 127.89, 127.8, 127.6, 126.7, 125.1, 117.0 (C_q), 110.0 (C_q), 100.6 (C_q), 72.2, 72.1 (CH_2), 71.5, 71.1 (CH_2), 63.7 (CH_2). HRMS (ESI), m/z calcd. for $C_{26}H_{27}N_2O_3S$ $[M+NH_4]^+$ 447.1728, found 447.1742.

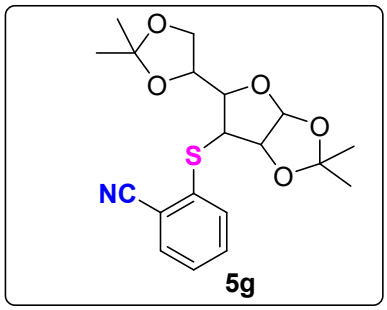


5f

Prepared by general procedure **2.1.2** using 2n (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) and CsF (3.30 eq.) in ACN. The reaction mixture was stirred at 40 °C for 1 hour. After cooling to room temperature, the reaction mixture was filtered

through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 96:4) to afford 3f as yellow oil in 86 % yield, 37.13 mg

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.29 (td, *J* = 4.0, 3.2, 1.8 Hz, 4H), 7.22 (dddd, *J* = 16.0, 8.9, 5.1, 3.3 Hz, 20H), 7.14 – 7.09 (m, 5H), 7.07 – 7.00 (m, 3H), 6.93 (s, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 1H), 4.75 – 4.64 (m, 3H), 4.56 (ddt, *J* = 7.3, 4.9, 2.0 Hz, 1H), 4.46 (d, *J* = 2.4 Hz, 1H), 4.45 – 4.42 (m, 2H), 4.40 (dd, *J* = 8.2, 5.9 Hz, 2H), 4.26 – 4.17 (m, 2H), 4.09 (t, *J* = 2.4 Hz, 1H), 3.98 (t, *J* = 2.3 Hz, 1H), 3.80 (d, *J* = 3.0 Hz, 1H), 3.74 (ddd, *J* = 14.6, 10.1, 7.7 Hz, 2H), 3.57 (dd, *J* = 10.5, 5.1 Hz, 1H), 3.46 – 3.37 (m, 2H), 3.30 (dd, *J* = 9.0, 7.0 Hz, 1H), 3.16 (dd, *J* = 9.0, 5.8 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 153.4, 143.4 (C_q), 138.6 (C_q), 138.4 (C_q), 138.3 (C_q), 138.0 (C_q), 137.8 (C_q), 137.6 (C_q), 133.2, 133.1, 128.5, 128.47, 128.4, 128.4, 128.4, 128.3, 128.2, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 127.0, 124.8, 117.1 (C_q), 109.4 (C_q), 104.1, 100.8 (C_q), 81.9, 79.1, 76.5, 75.4 (CH_2), 75.1 (CH_2), 74.0, 73.6 (CH_2), 73.4, 73.3 (CH_2), 73.1 (CH_2), 72.9, 72.4 (CH_2), 68.5 (CH_2), 67.7 (CH_2). HRMS (ESI), m/z calcd. for $C_{61}H_{59}NNaO_9S$ $[M+Na]^+$ 1004.3008, found 1004.3009.

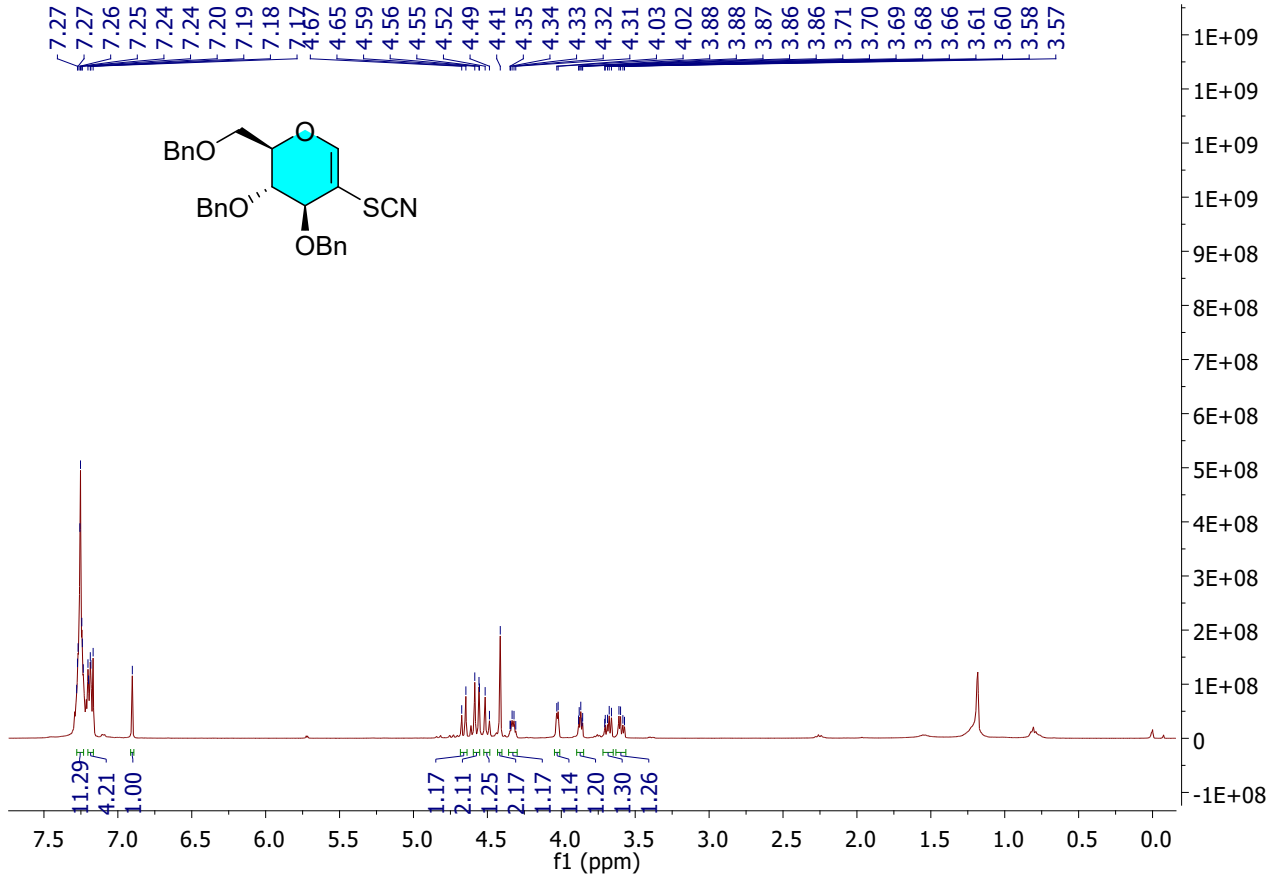


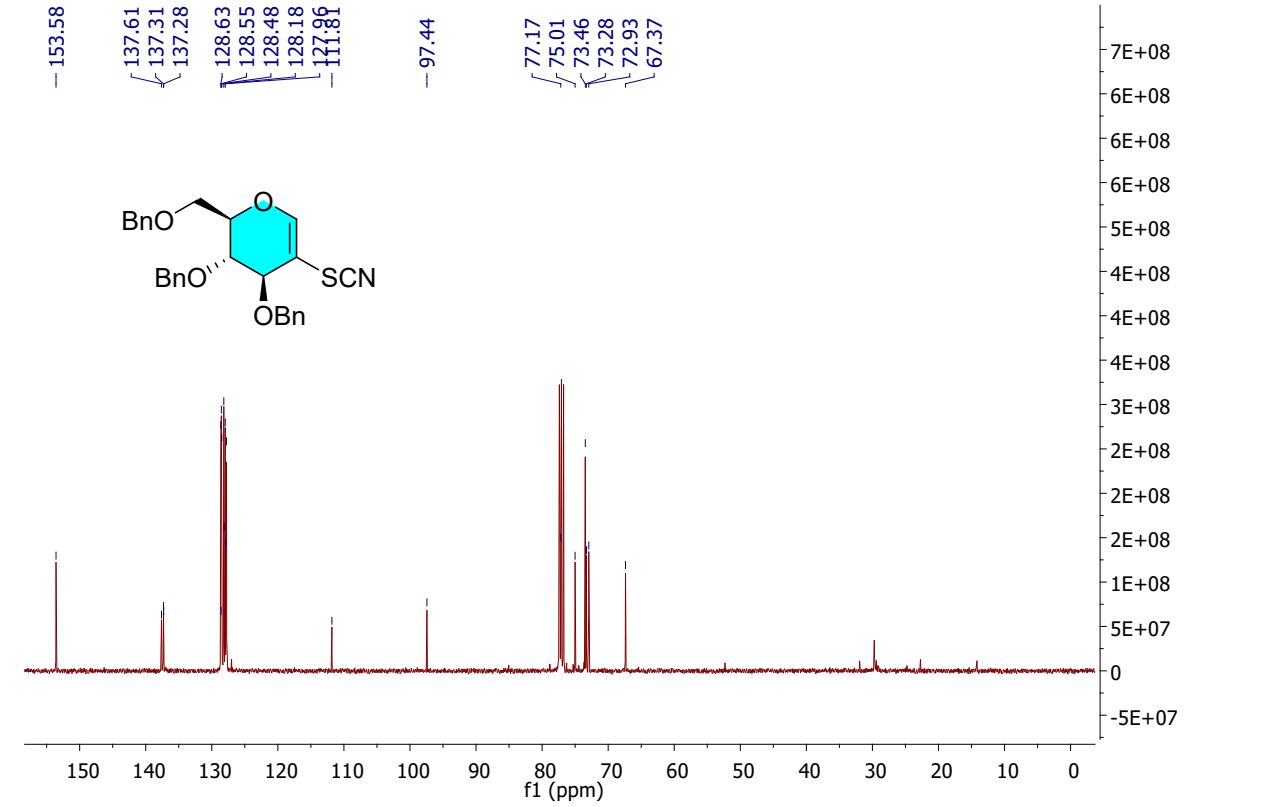
5g

Prepared by general procedure **2.1.2** using 2p (50 mg, 0.084 mmol), Pd $(OAc)_2$ (10 mol%), Xantphos (20 mol%) and CsF (3.30 eq.) in ACN. The reaction mixture was stirred at 40 °C for 1 hour. After cooling to room temperature, the reaction mixture was filtered through celite, solvent removed in vacuo and the crude product was purified by column chromatography on silica gel. (Hexane: EtOAc; 94:6) to afford 3g as yellow oil in 89 % yield, 44.40 mg.

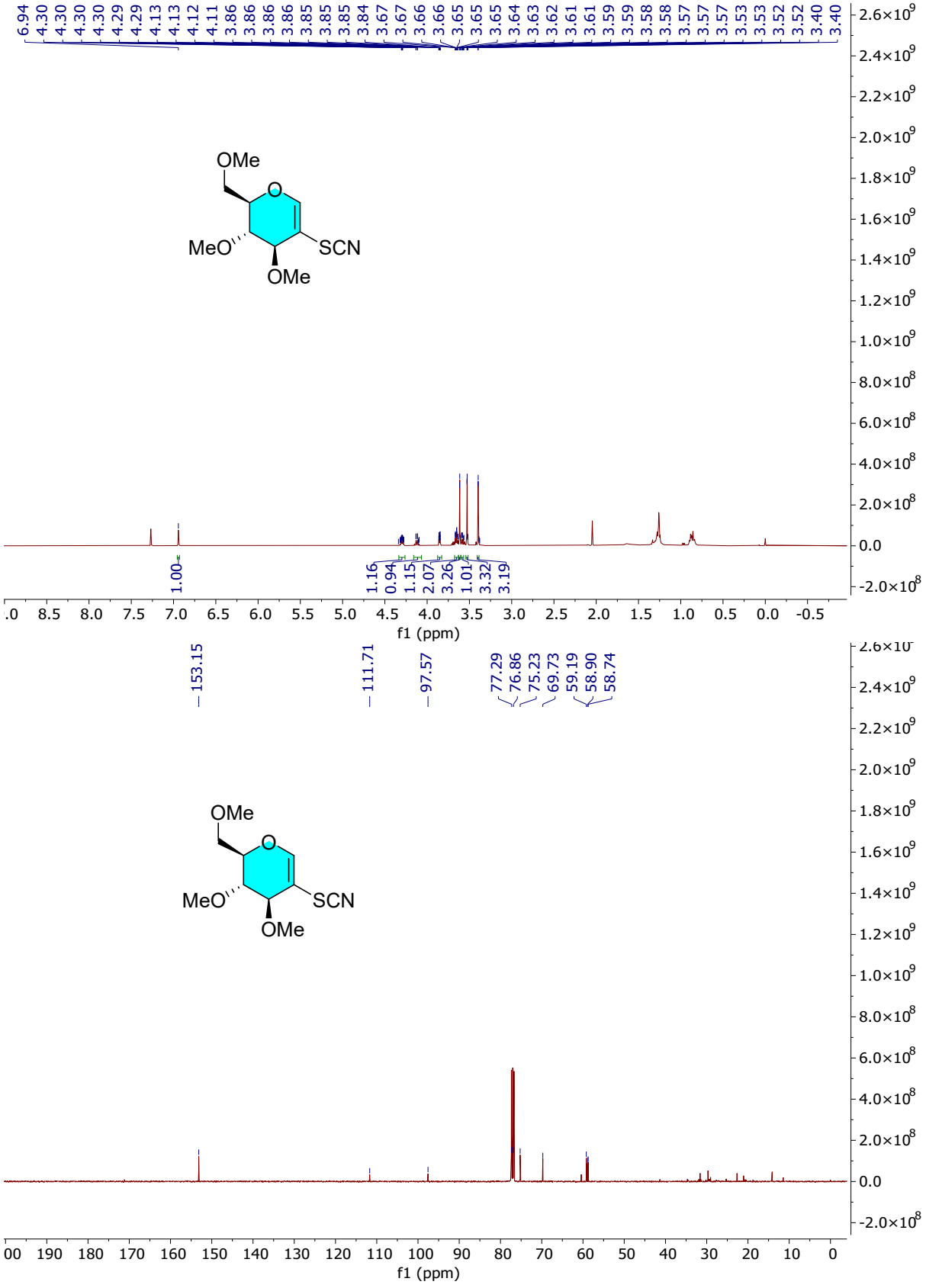
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.24 (ddd, *J* = 7.6, 6.4, 2.3 Hz, 1H), 6.10 (d, *J* = 5.3 Hz, 1H), 5.13 (dd, *J* = 6.8, 5.6 Hz, 1H), 4.98 (d, *J* = 5.3 Hz, 1H), 4.10 (dd, *J* = 8.6, 6.8 Hz, 1H), 4.03 (dd, *J* = 8.6, 5.6 Hz, 1H), 1.42 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 163.7 (C_q), 139.4 (C_q), 134.1, 133.6, 133.1, 132.8, 130.6, 127.1, 113.7 (C_q), 110.9 (C_q), 105.9, 103.5 (C_q), 84.1, 69.1, 66.6, 27.9 (CH_3), 27.8 (CH_3), 25.9 (CH_3), 25.6 (CH_3). HRMS (ESI), m/z calcd. for $C_{19}H_{21}NNaO_5S$ $[M+Na]^+$ 398.1038, found 398.0977.

^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2a** in $CDCl_3$

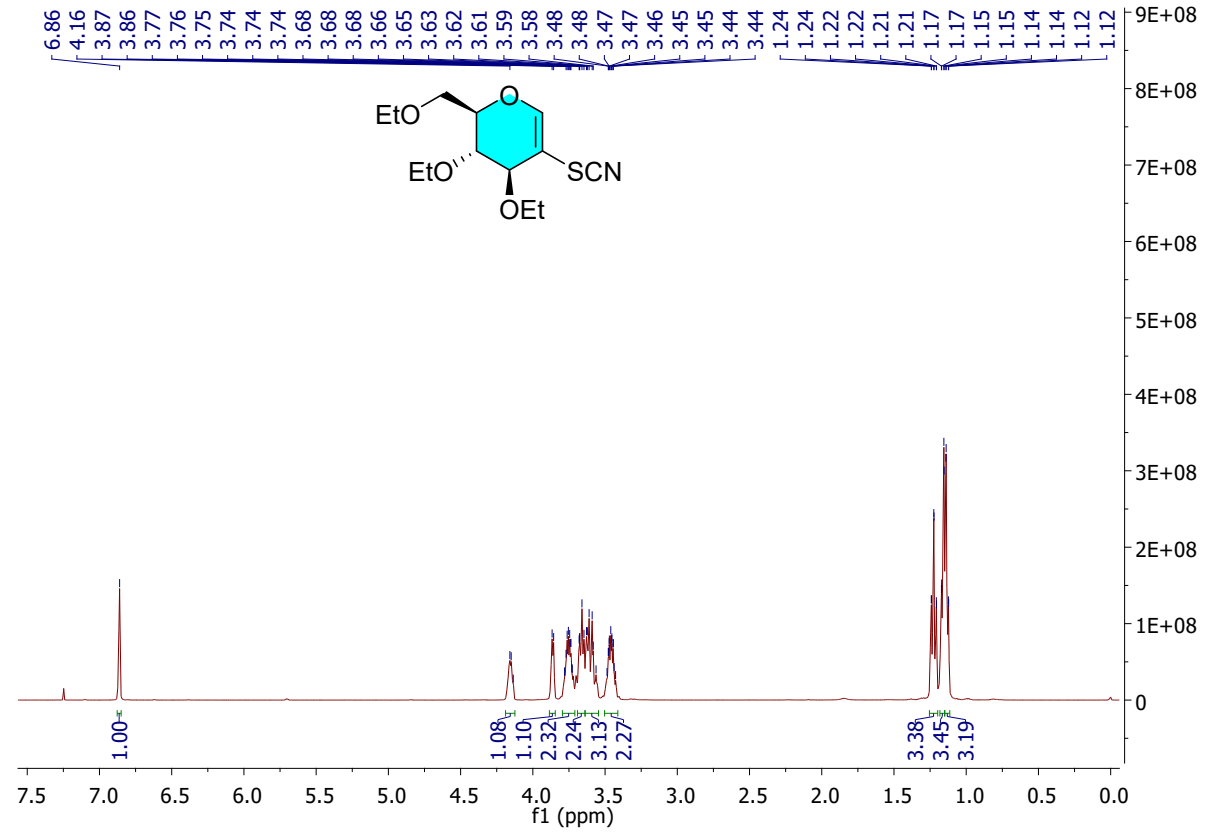


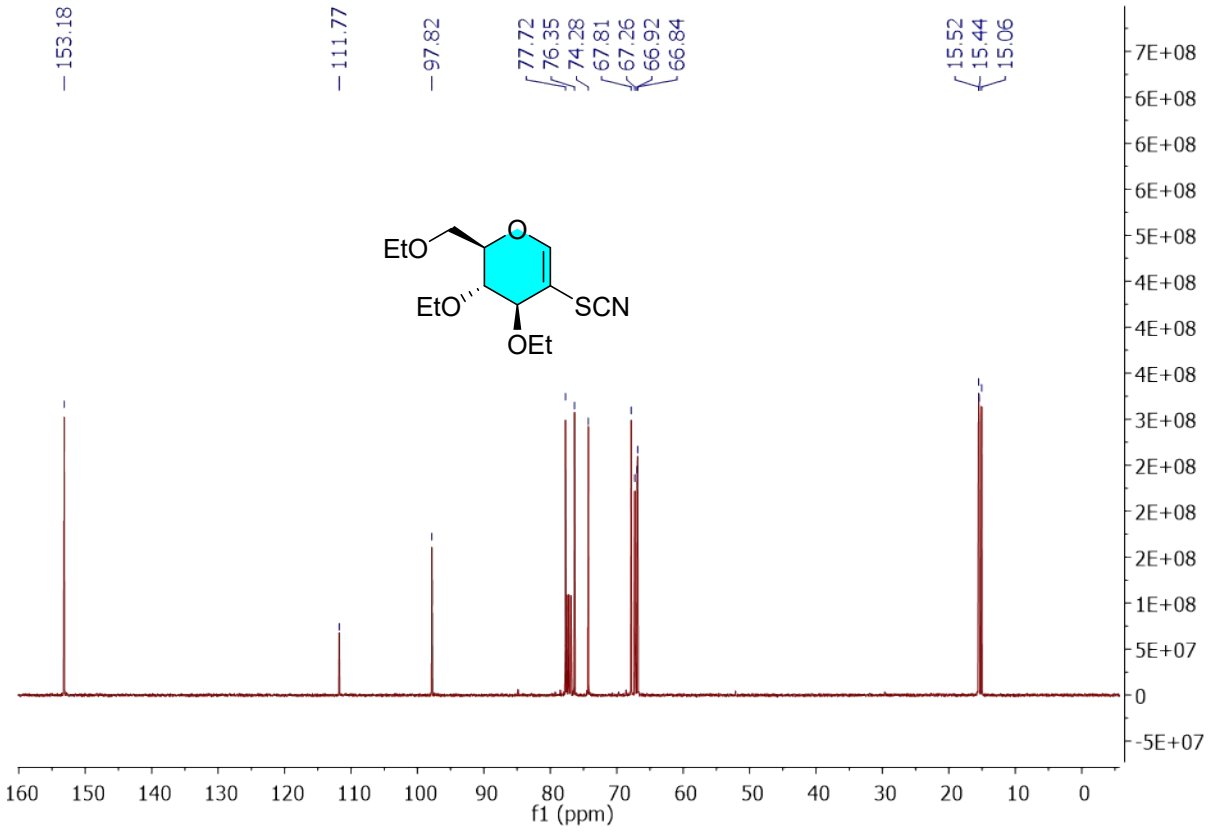


^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2b** in $CDCl_3$

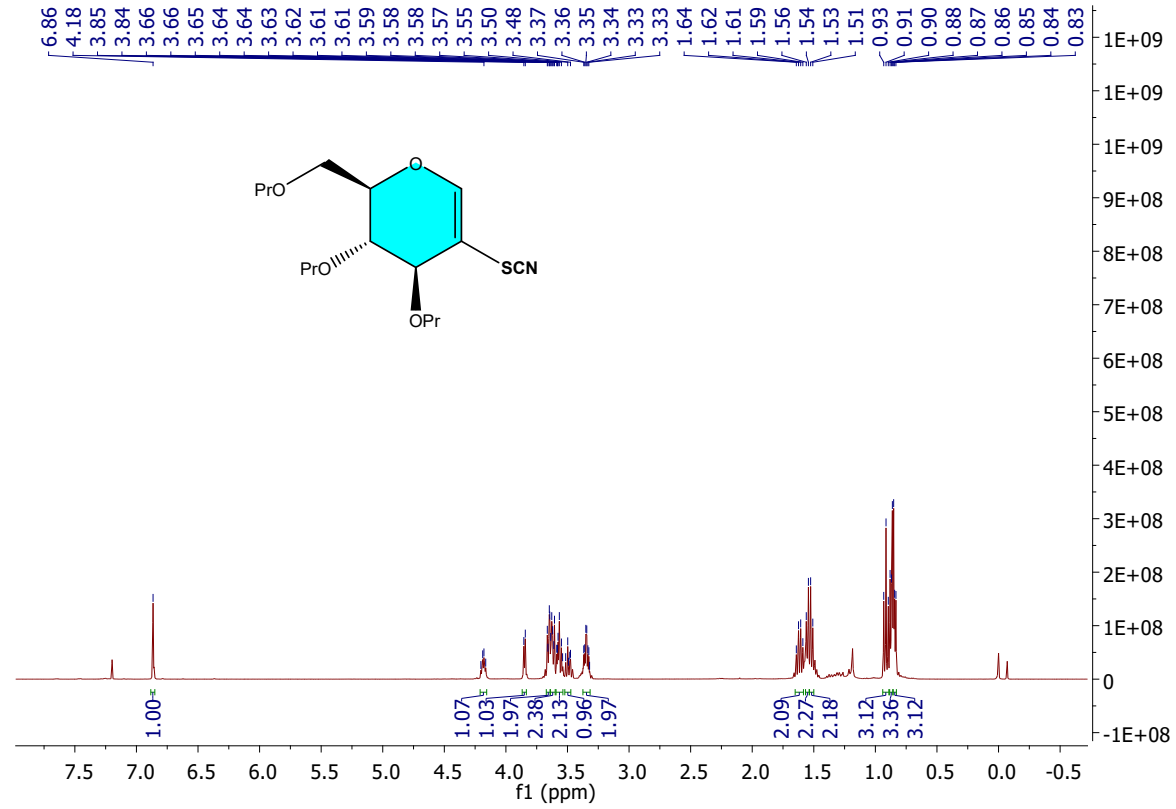


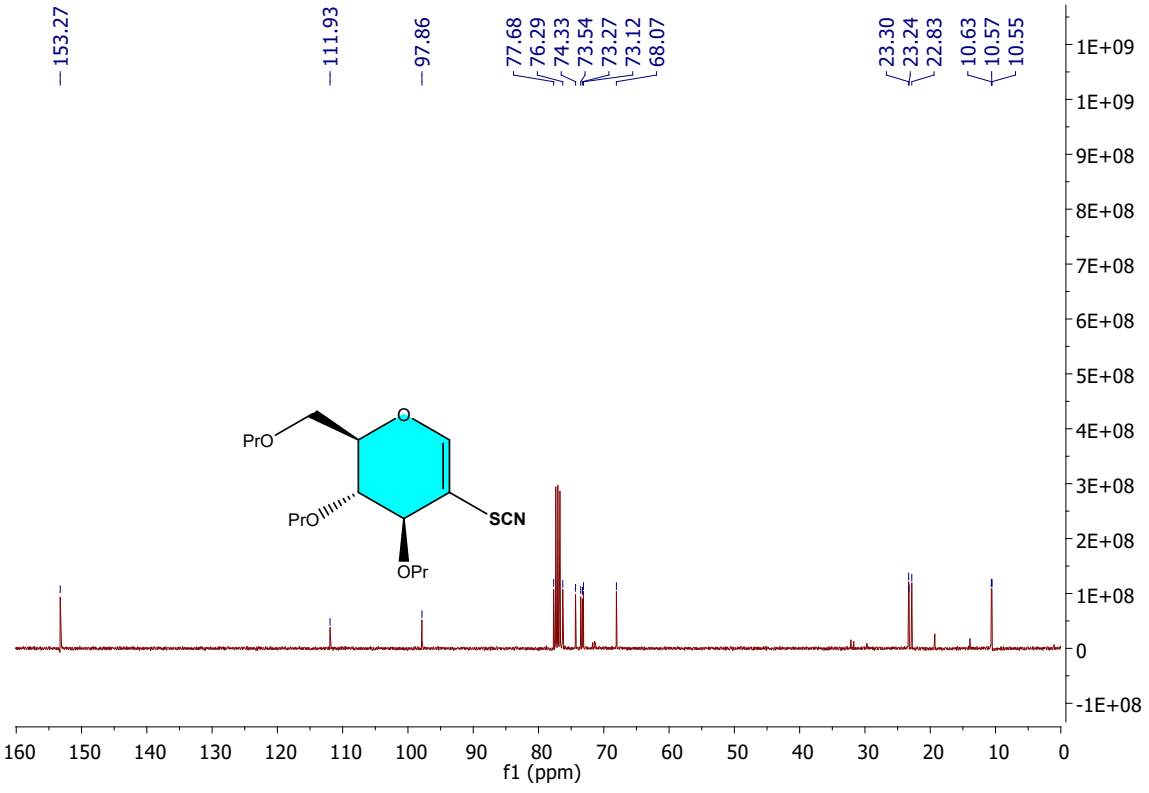
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2c** in $CDCl_3$



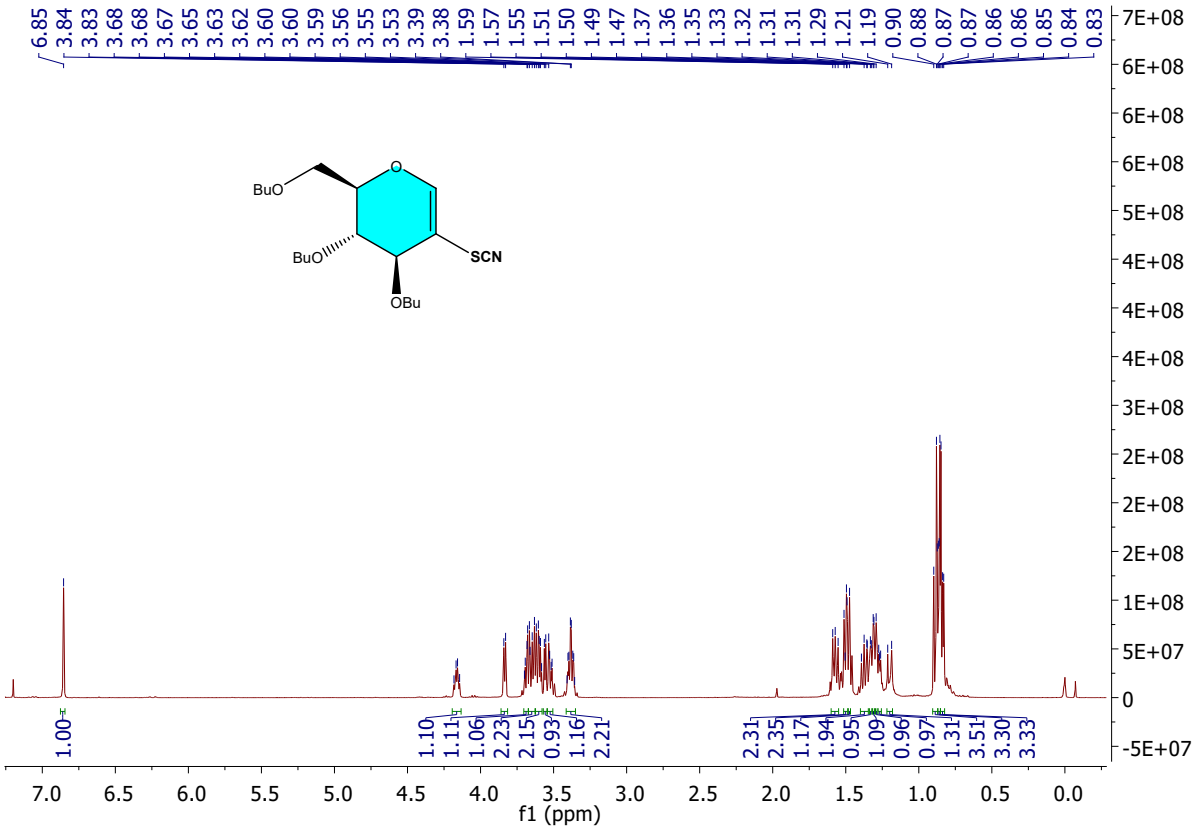


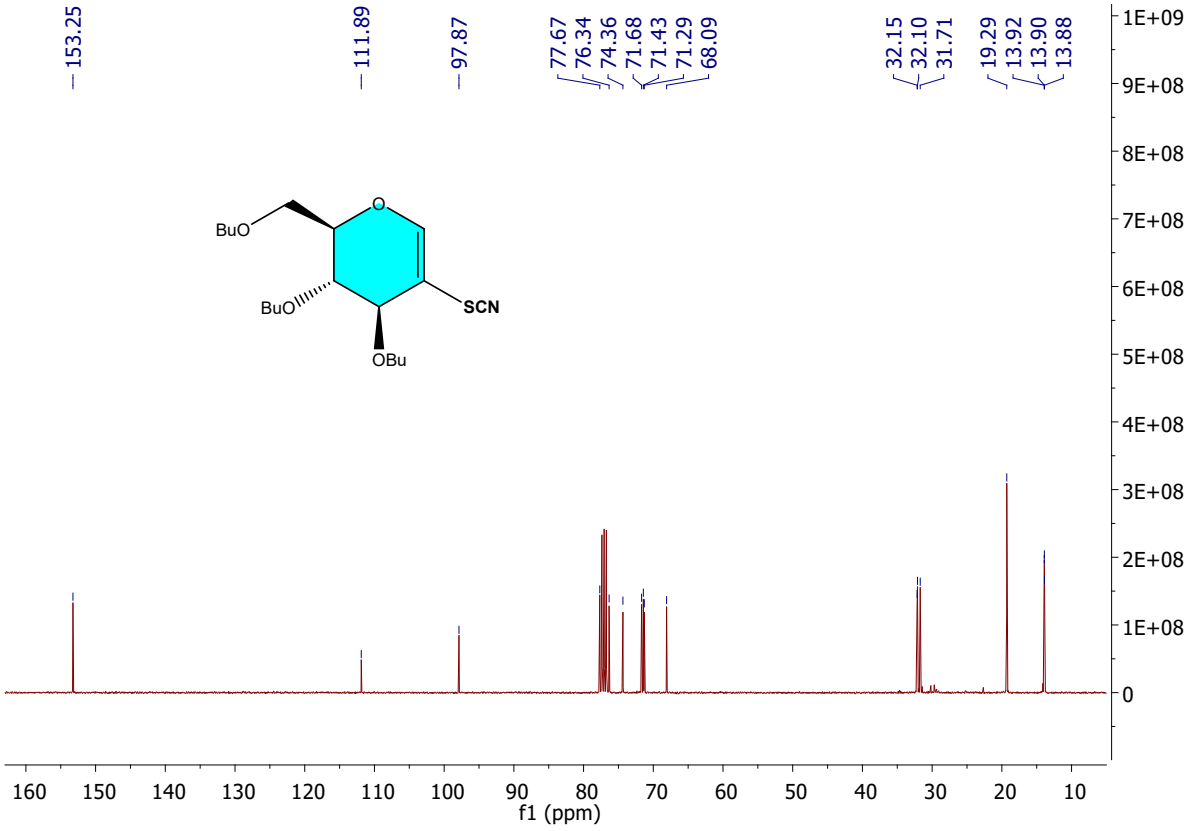
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2d** in $CDCl_3$



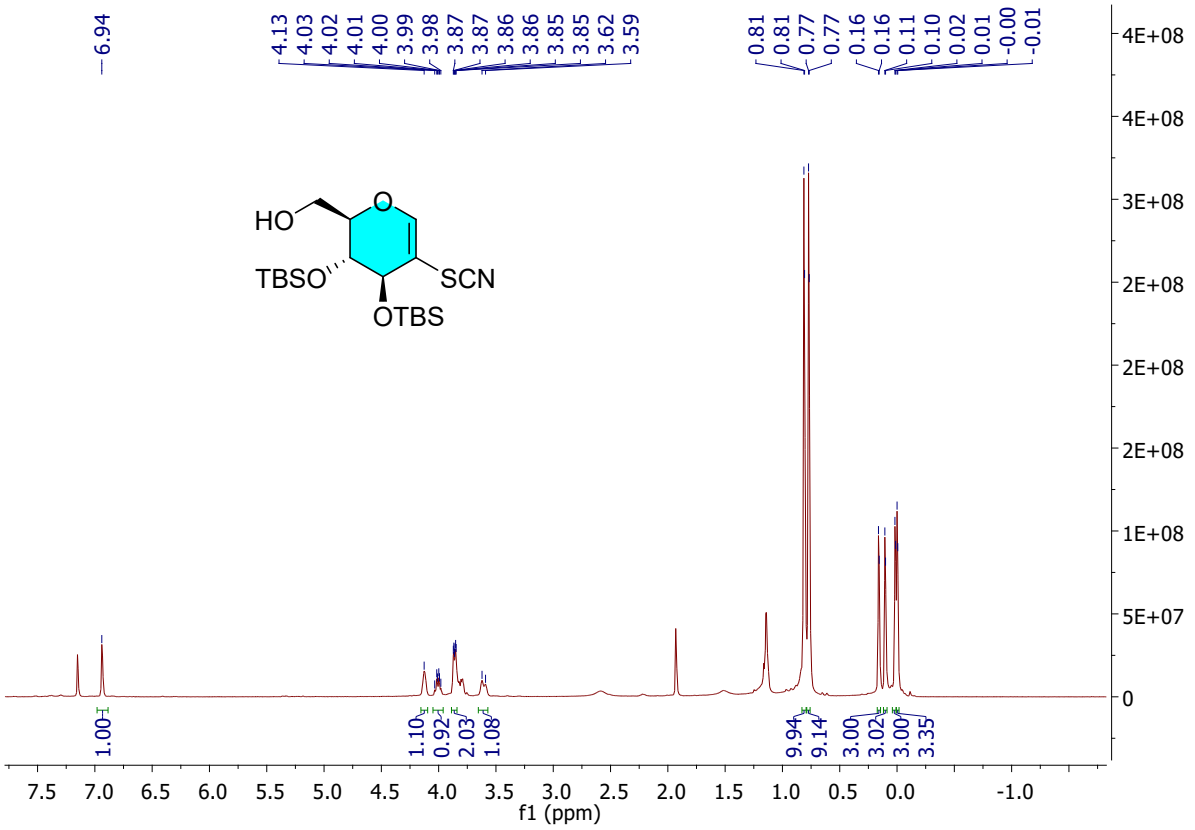


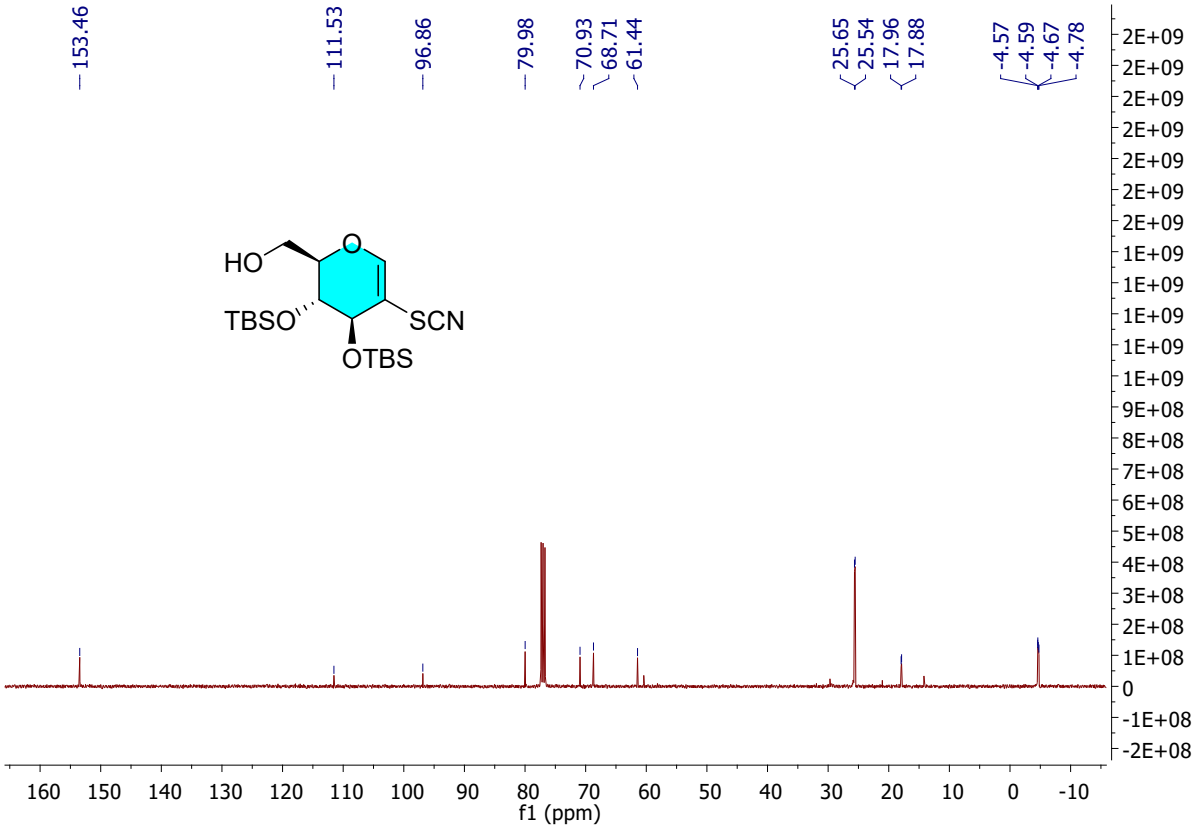
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2e** in $CDCl_3$



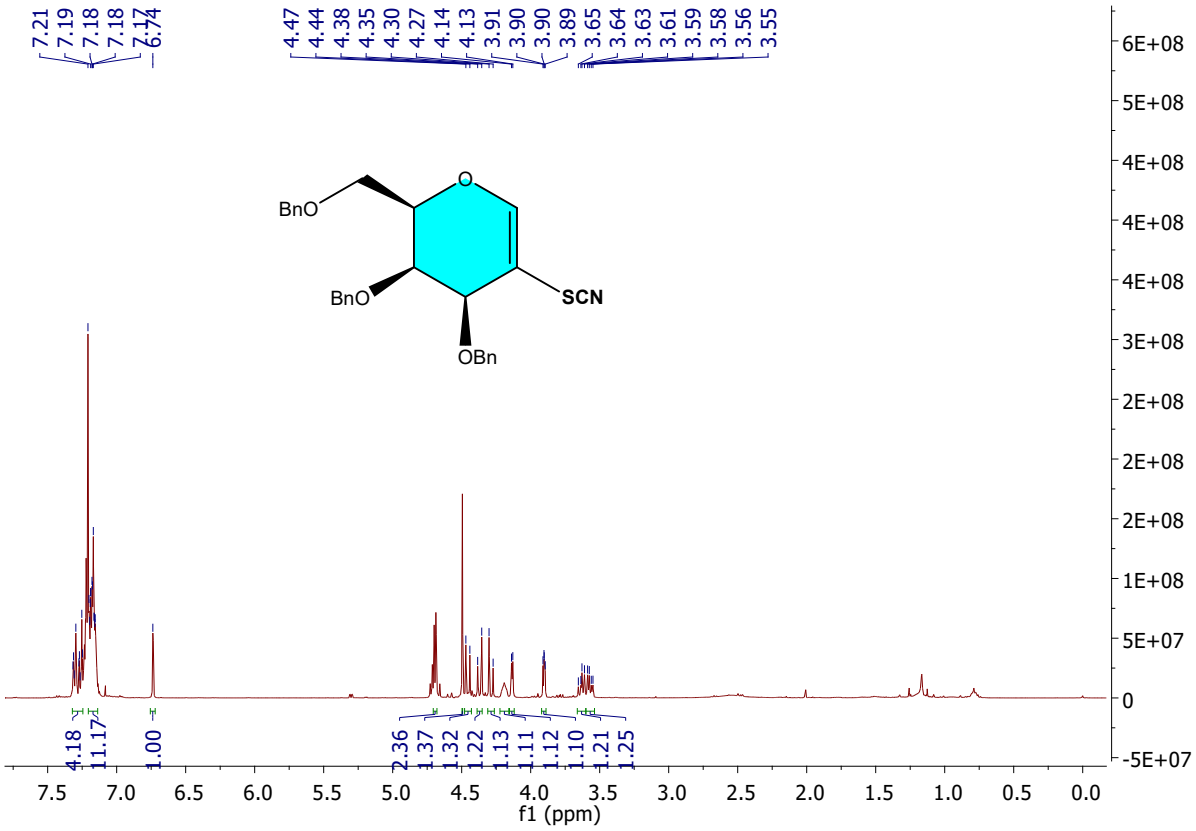


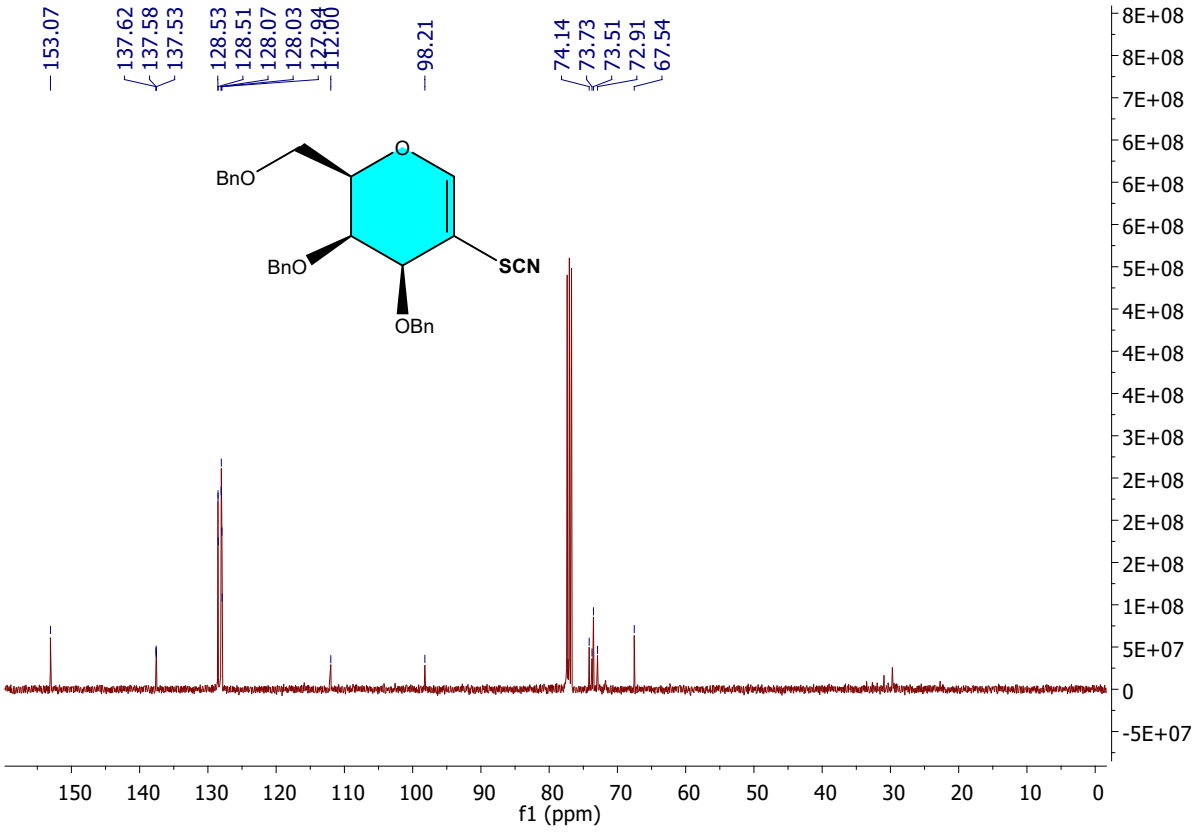
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2f** in $CDCl_3$



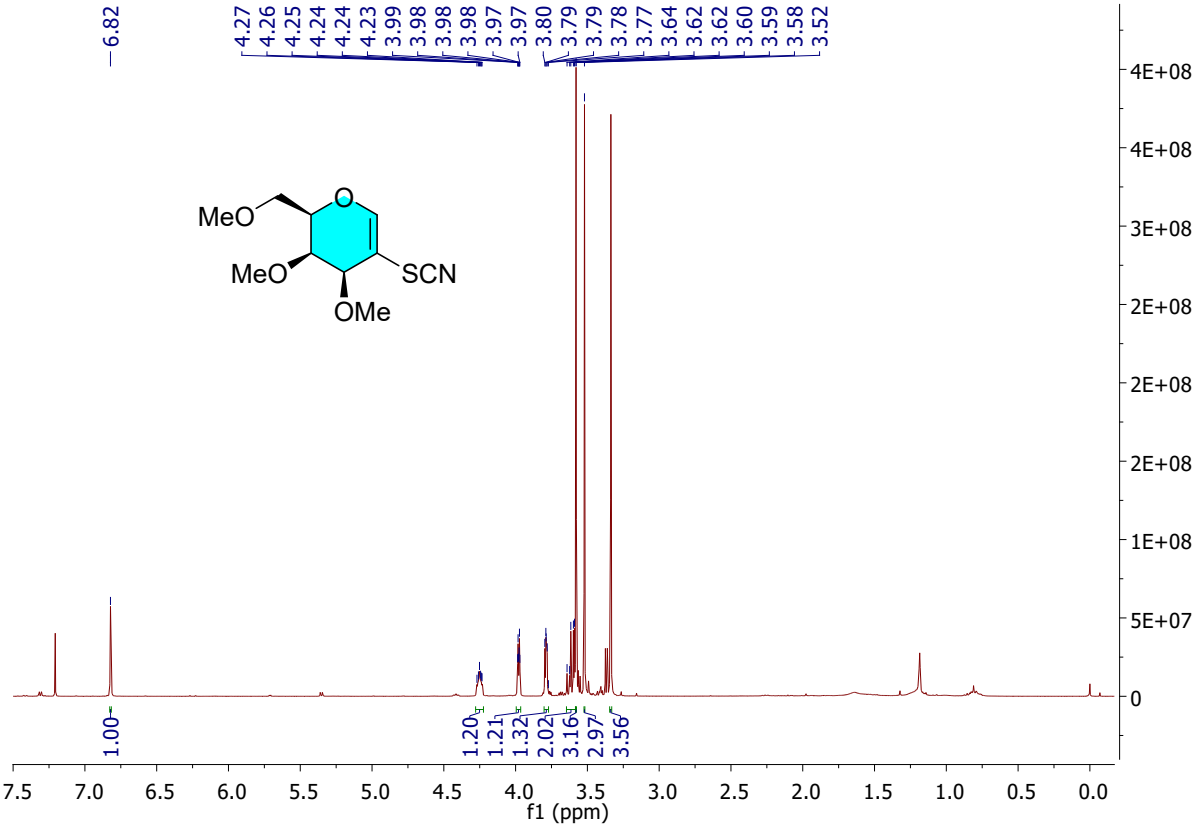


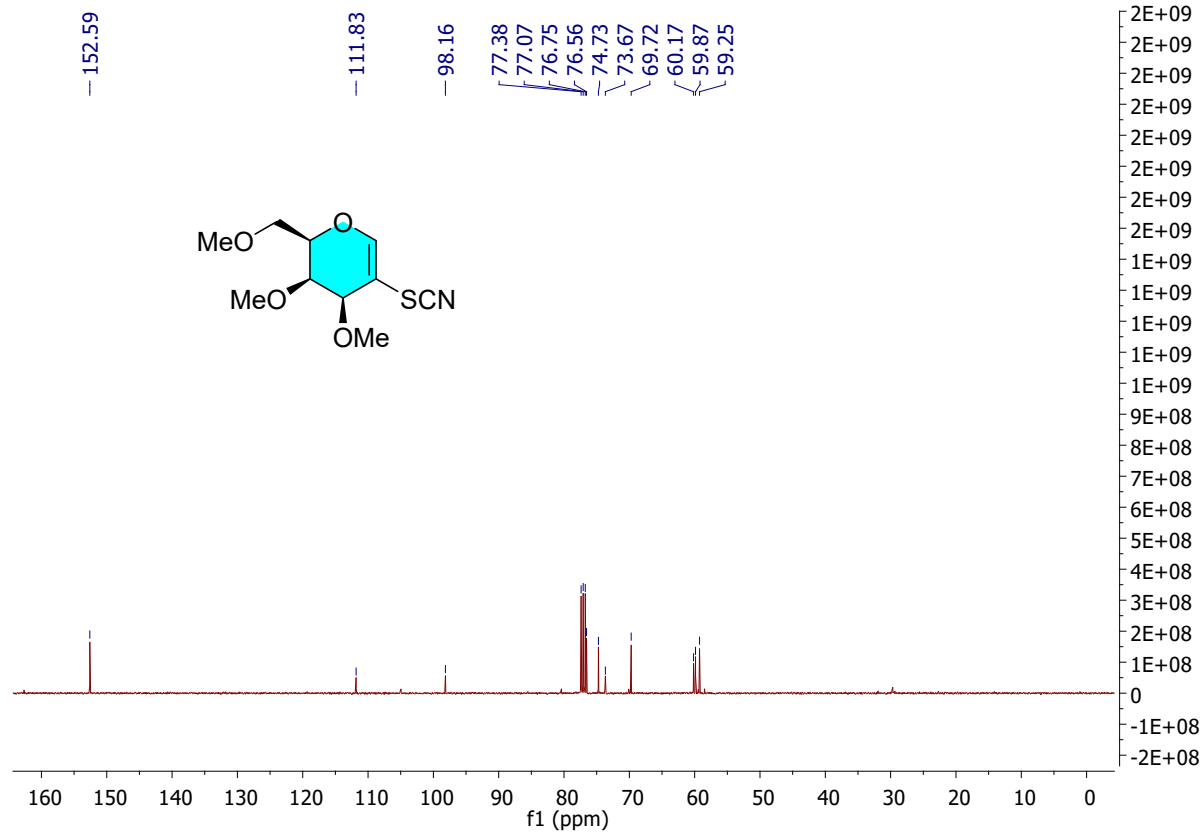
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2g** in $CDCl_3$



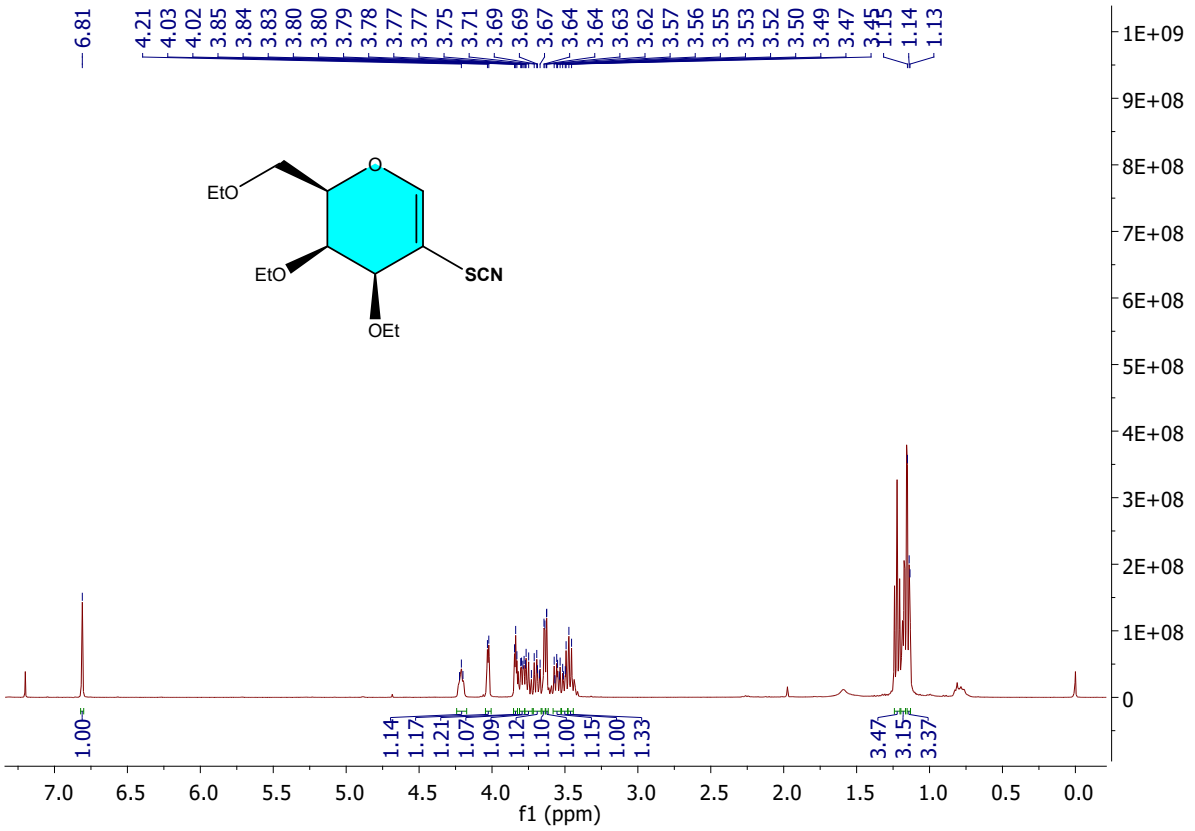


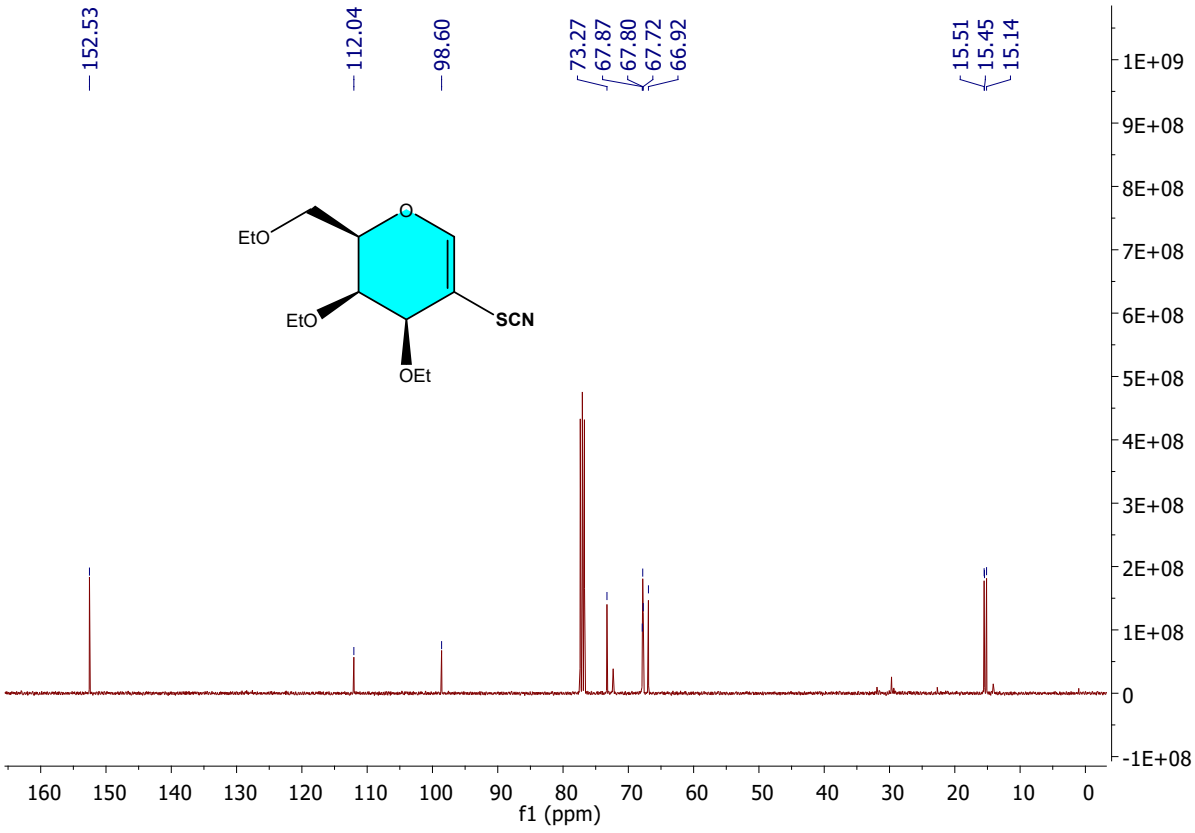
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2h** in $CDCl_3$



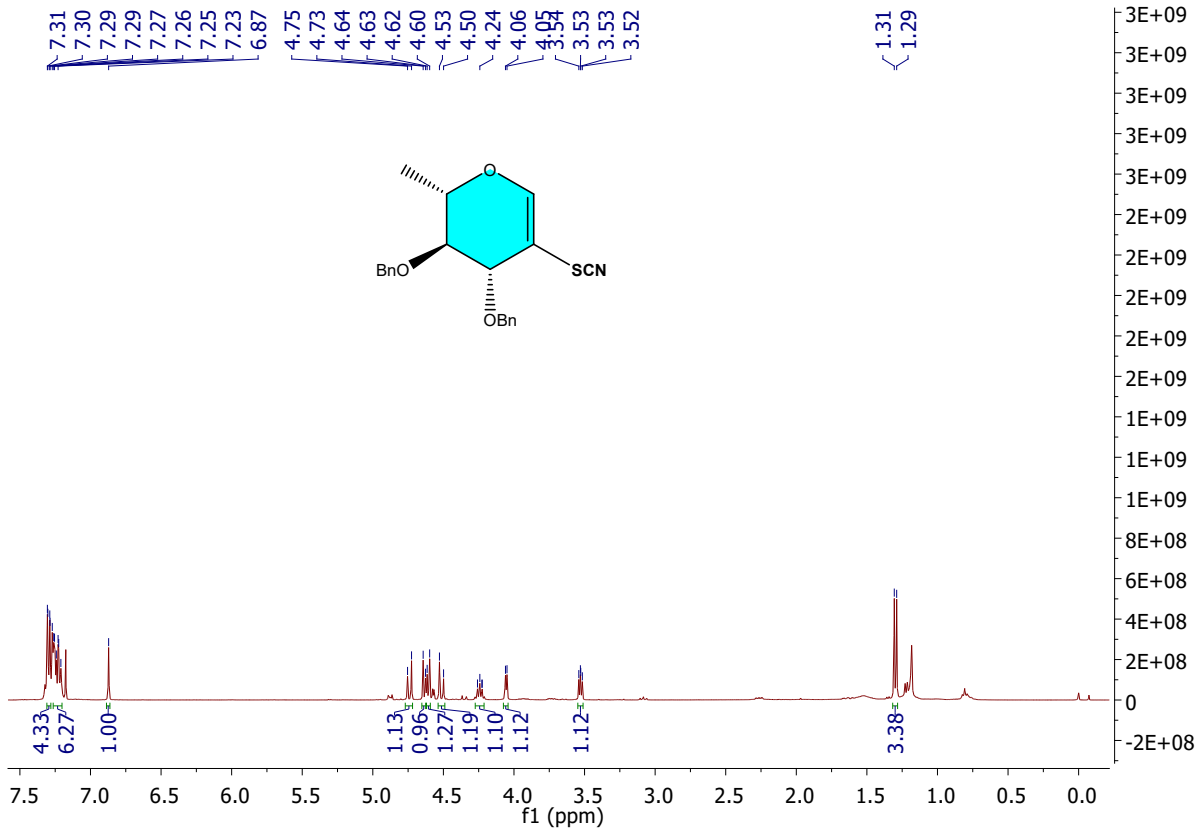


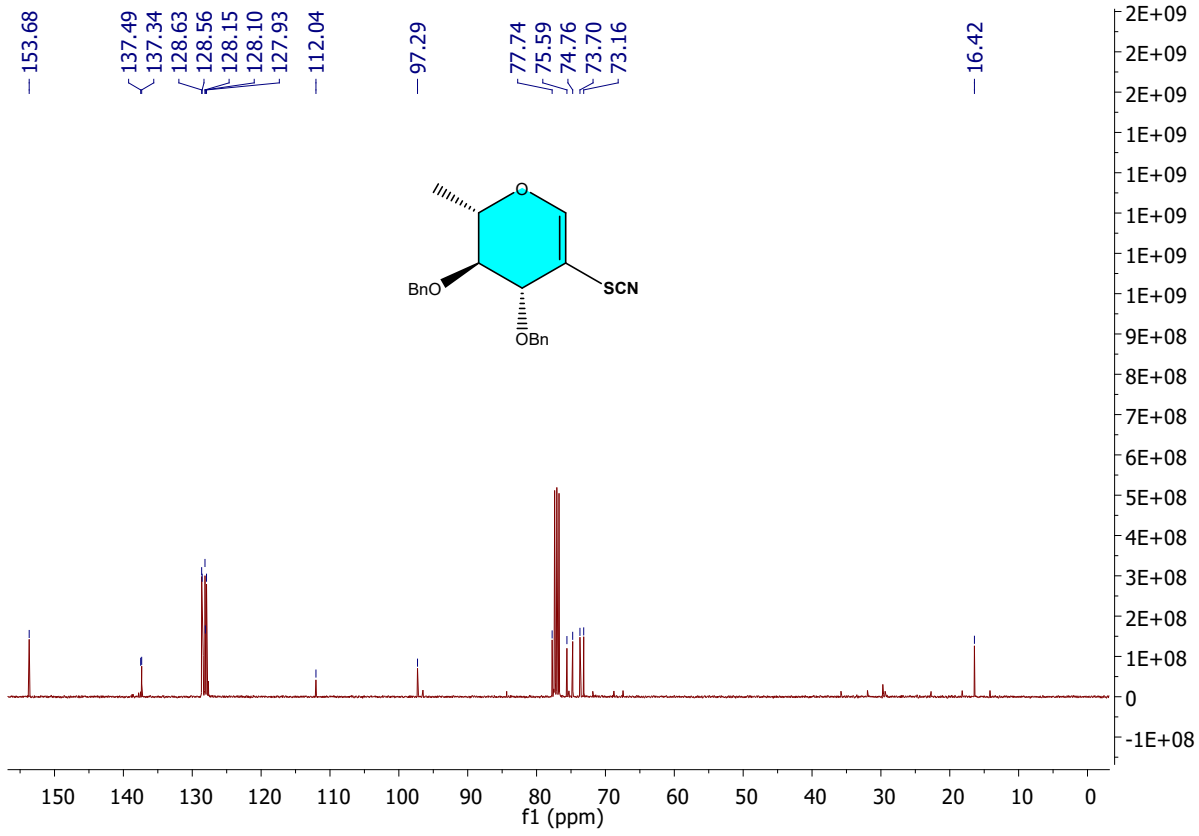
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2i** in $CDCl_3$



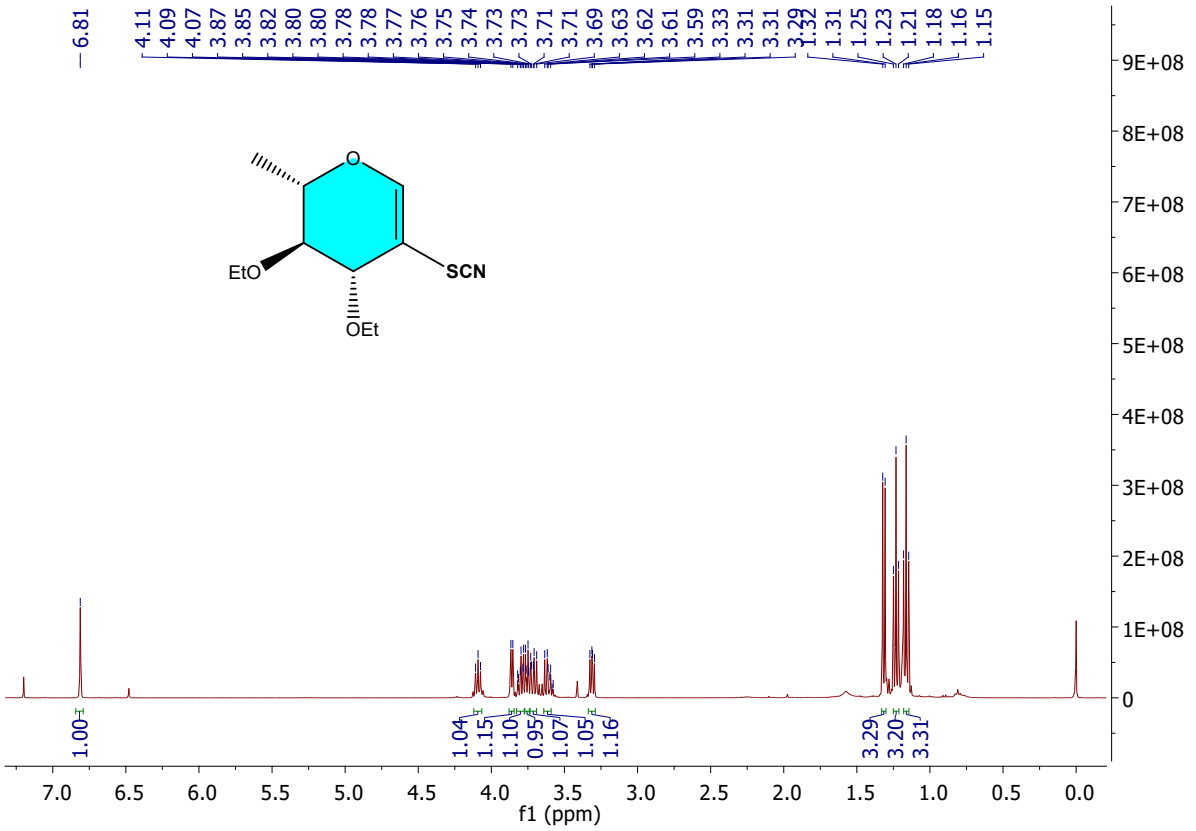


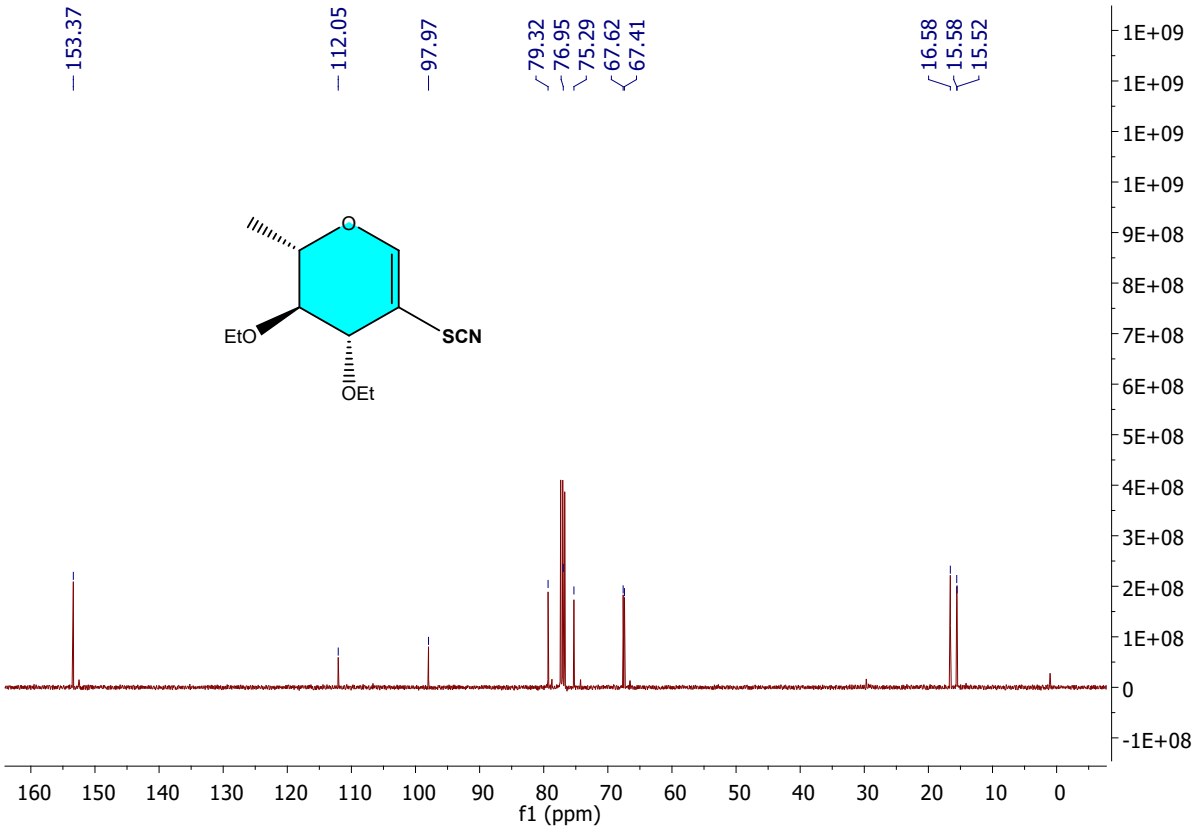
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2j** in $CDCl_3$



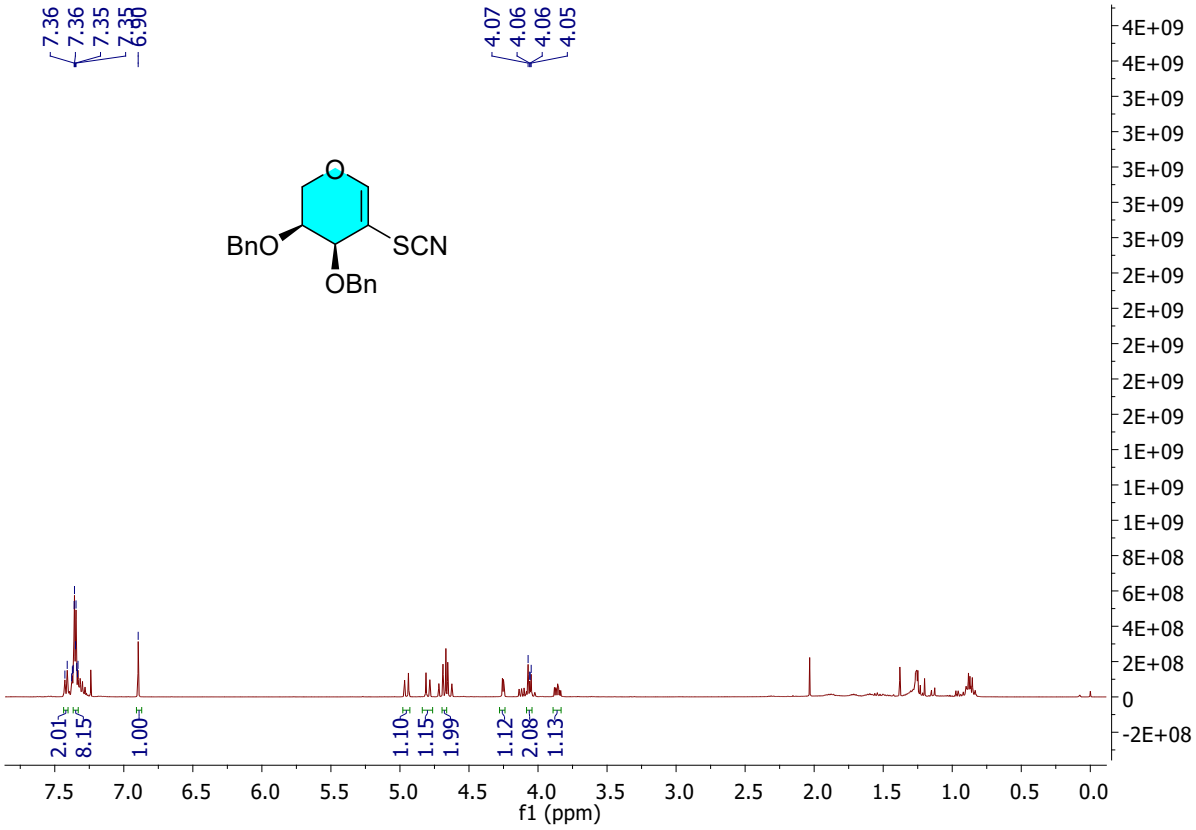


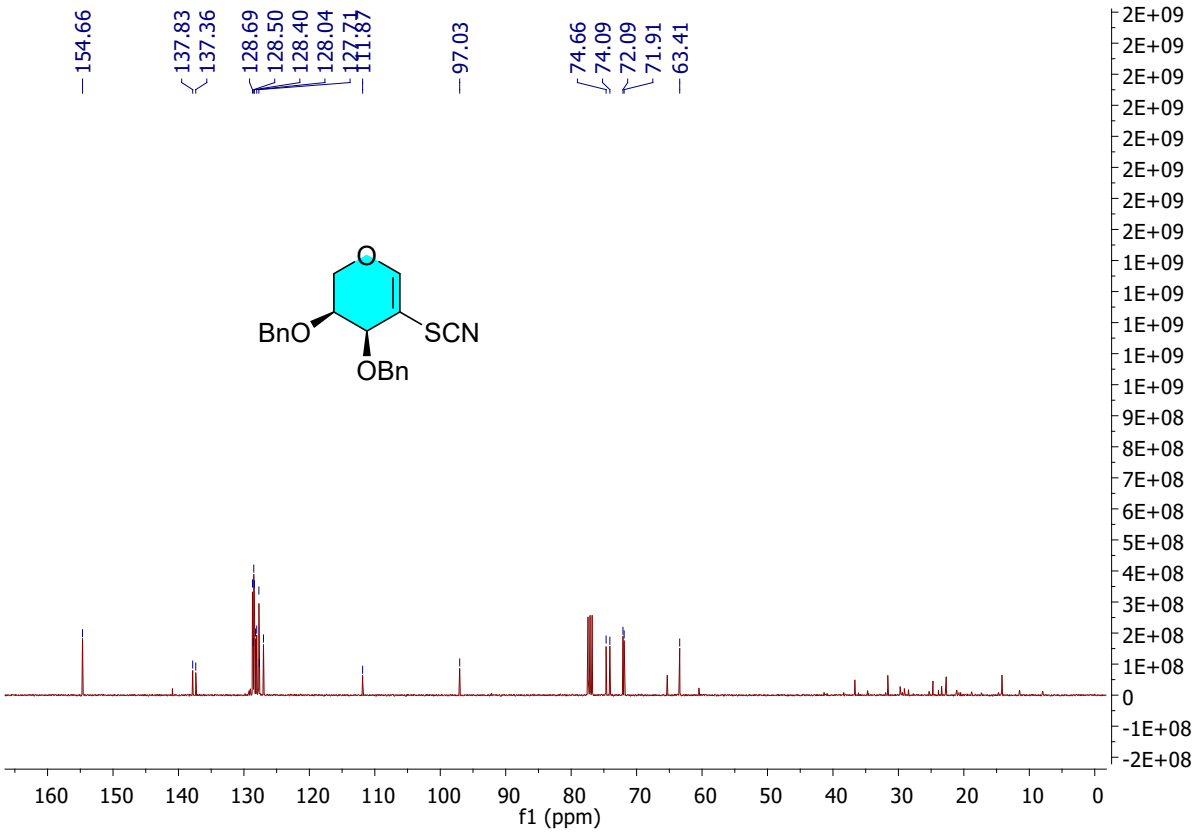
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2k** in $CDCl_3$



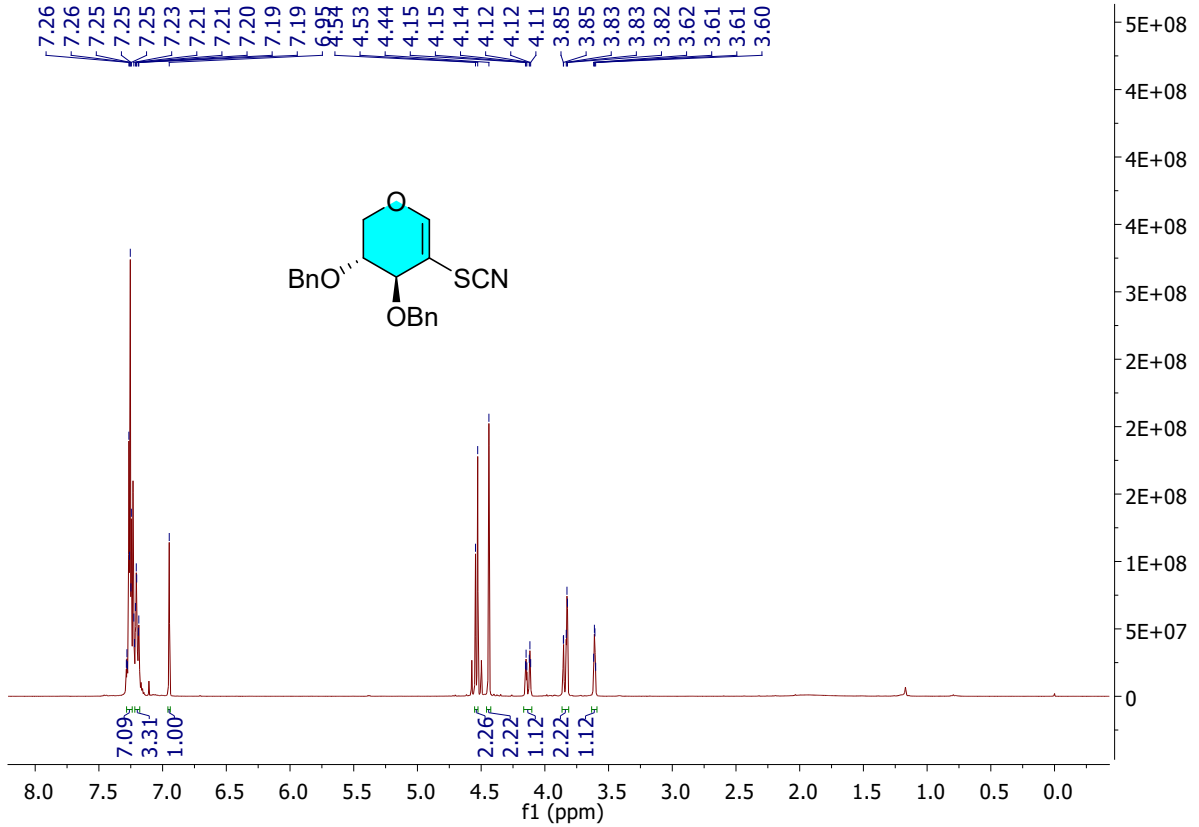


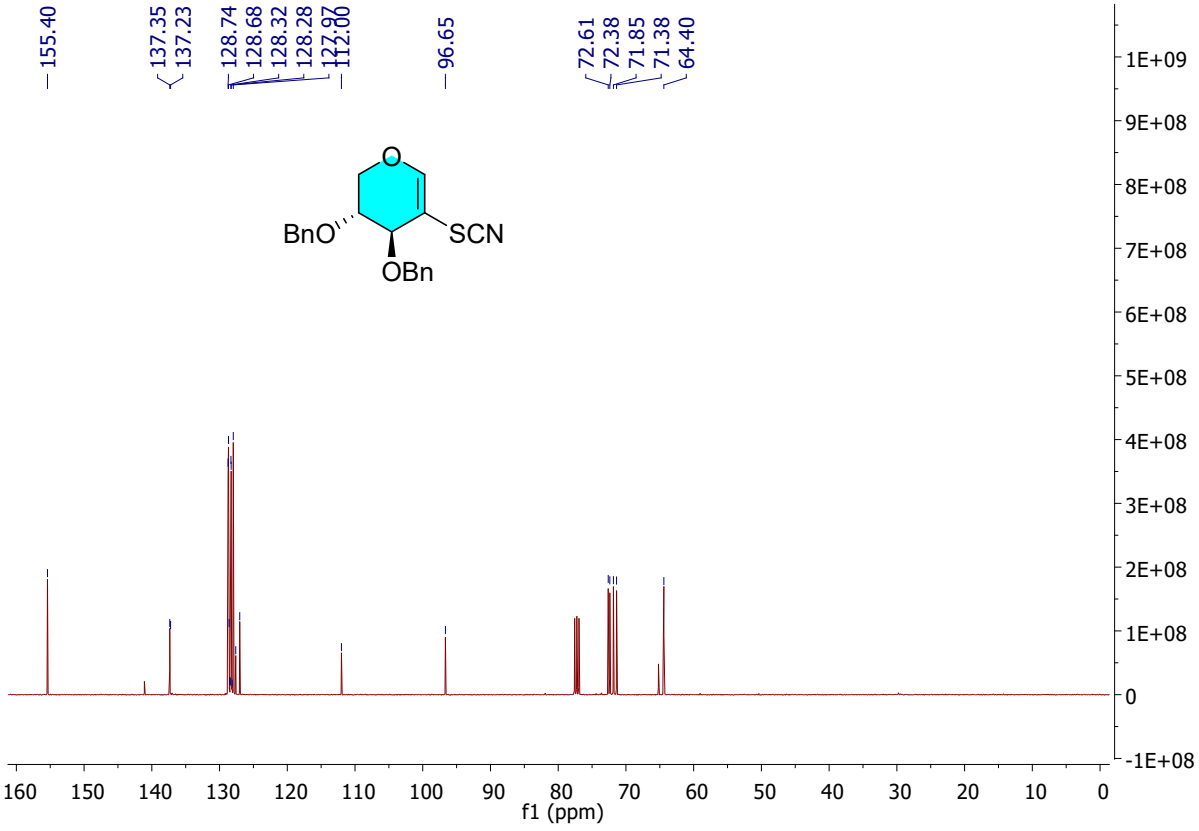
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2l** in $CDCl_3$



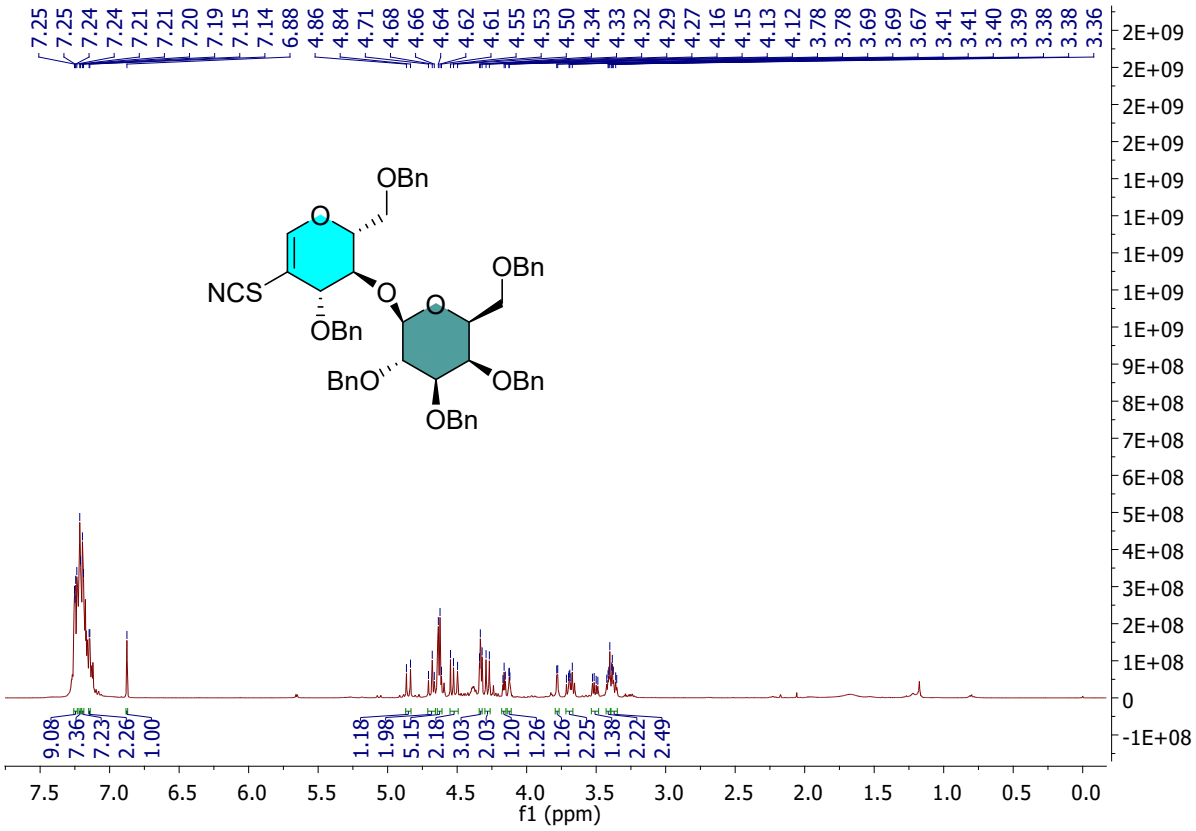


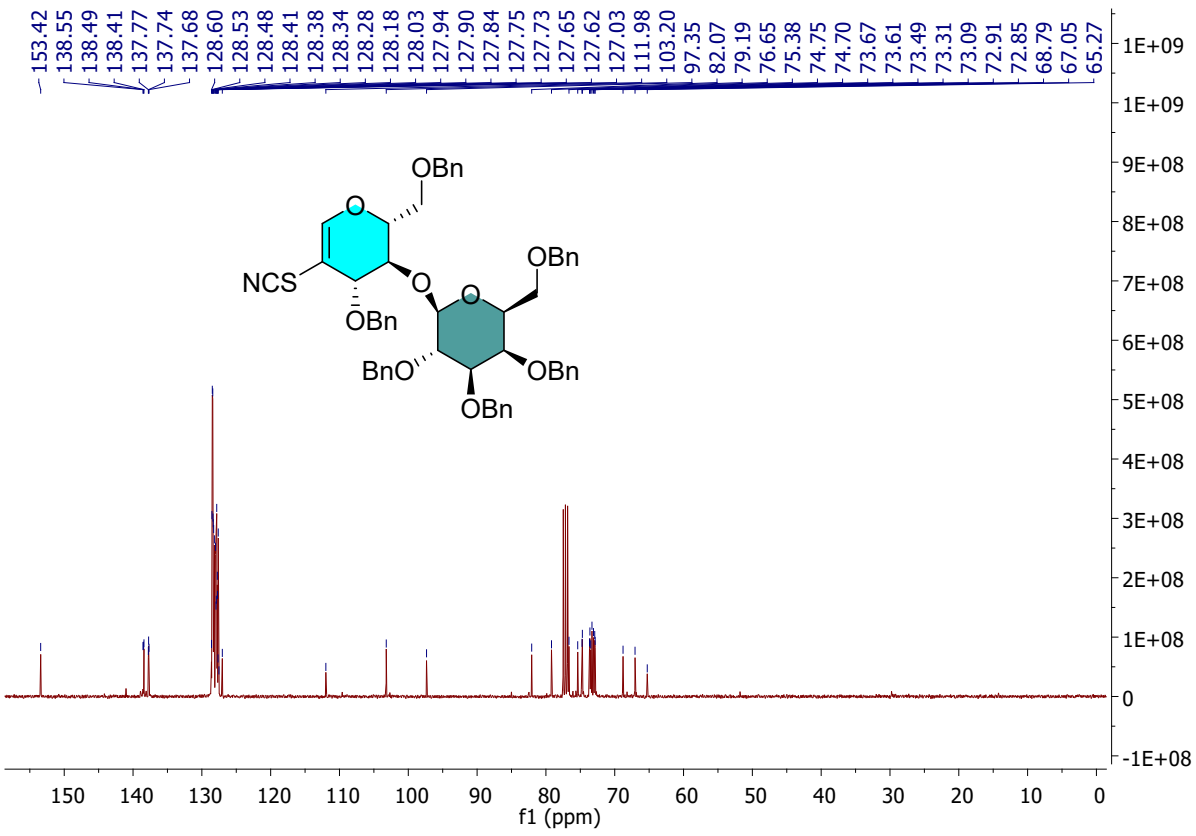
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2m** in $CDCl_3$



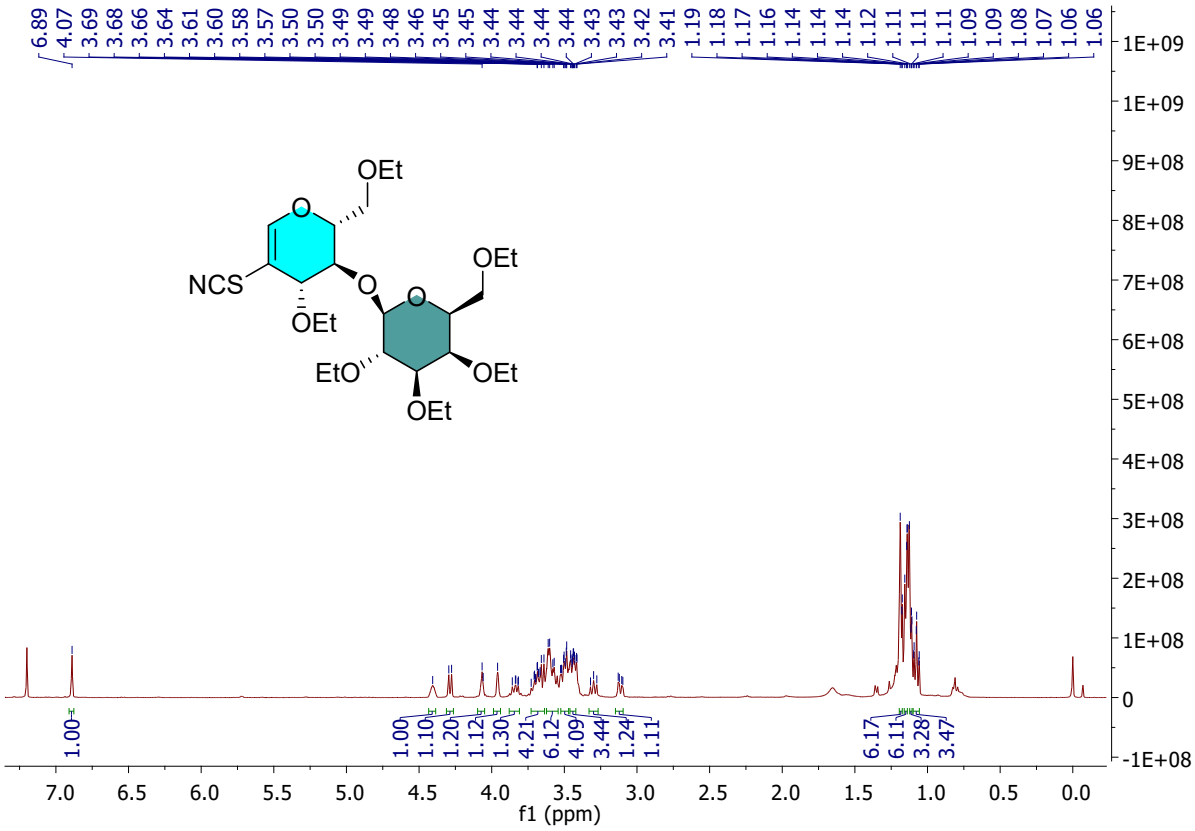


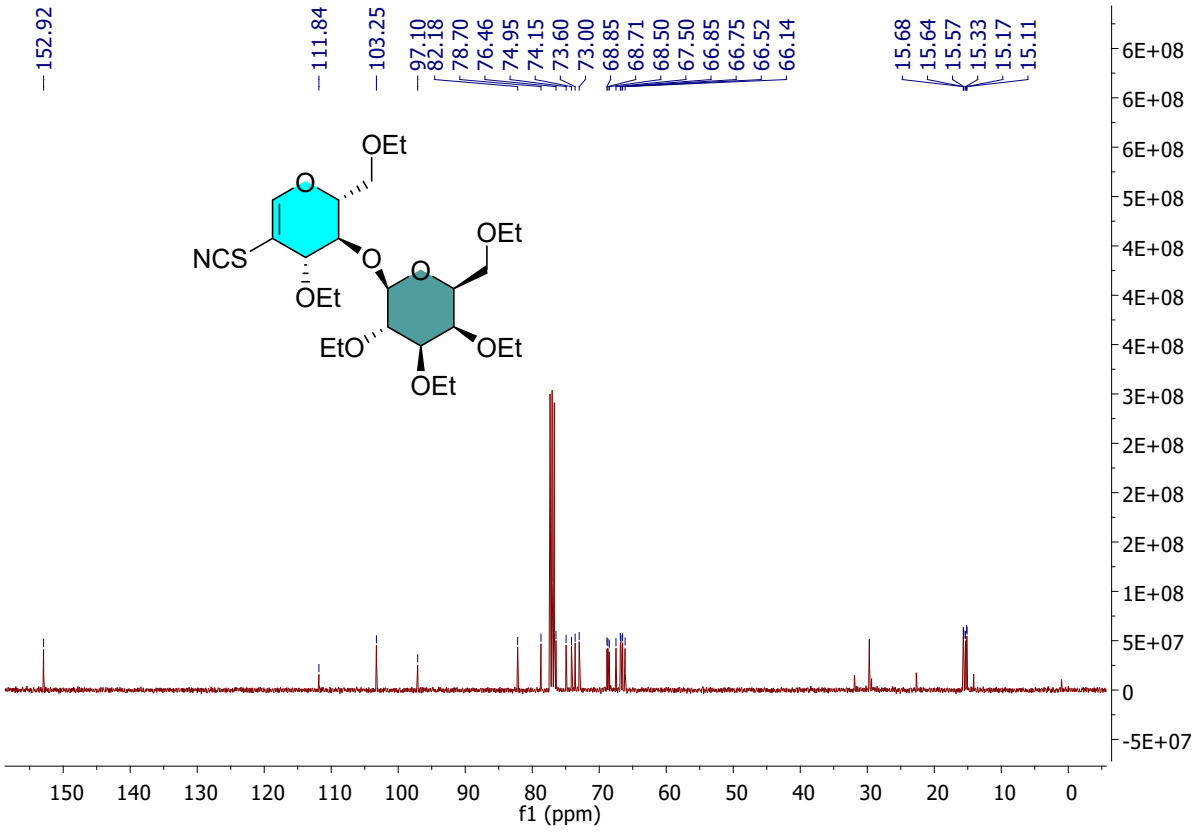
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2n** in $CDCl_3$



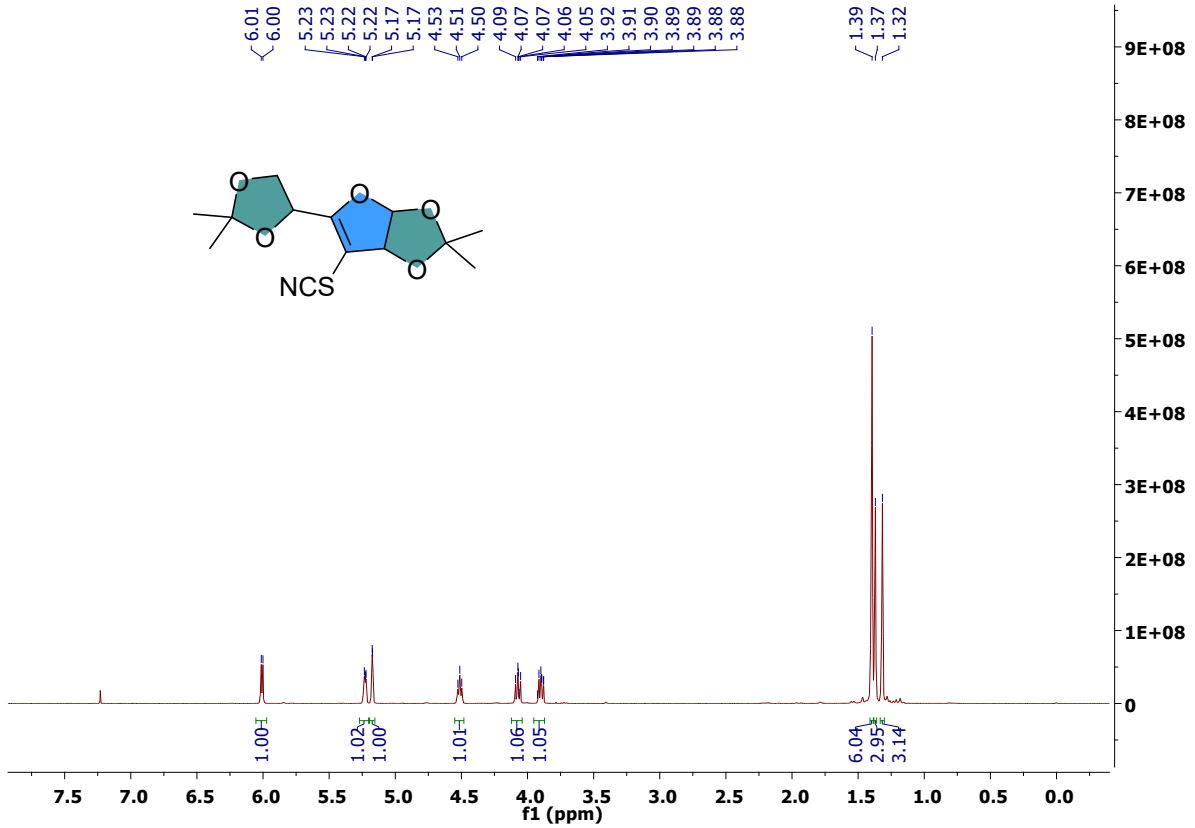


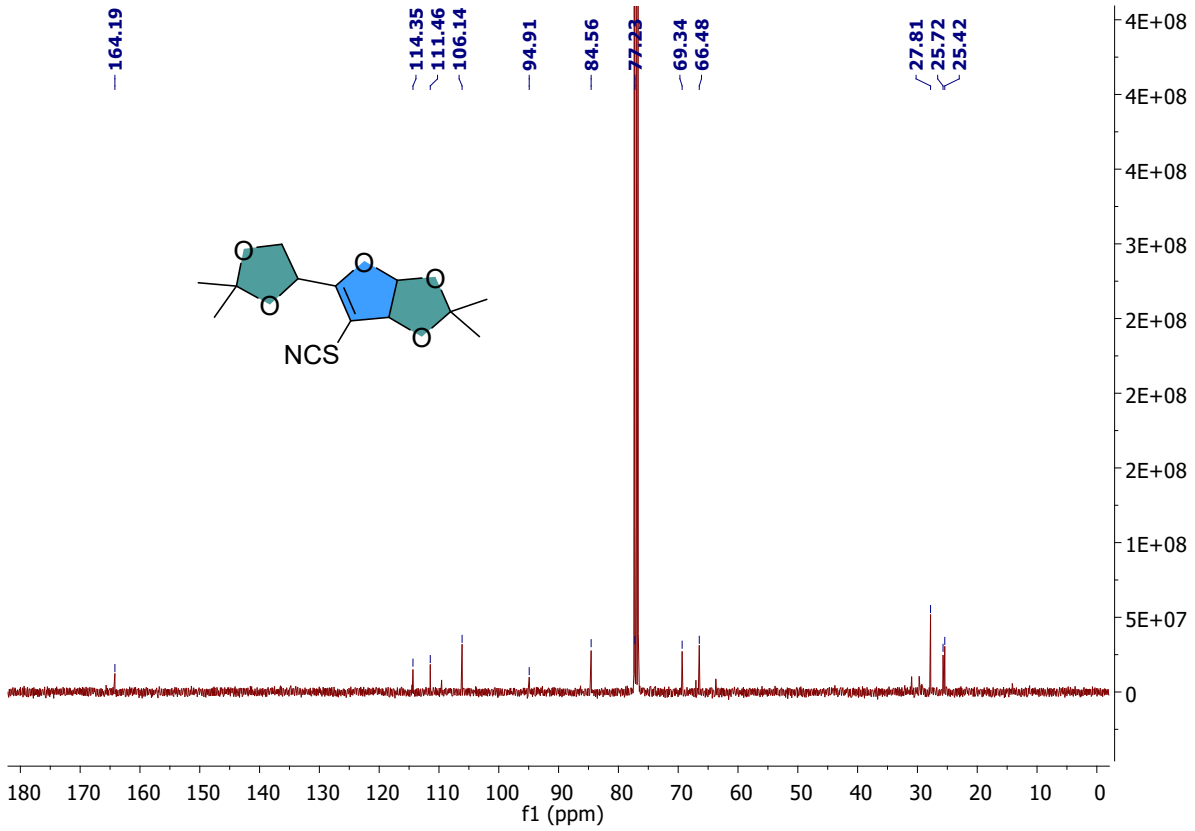
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2o** in $CDCl_3$



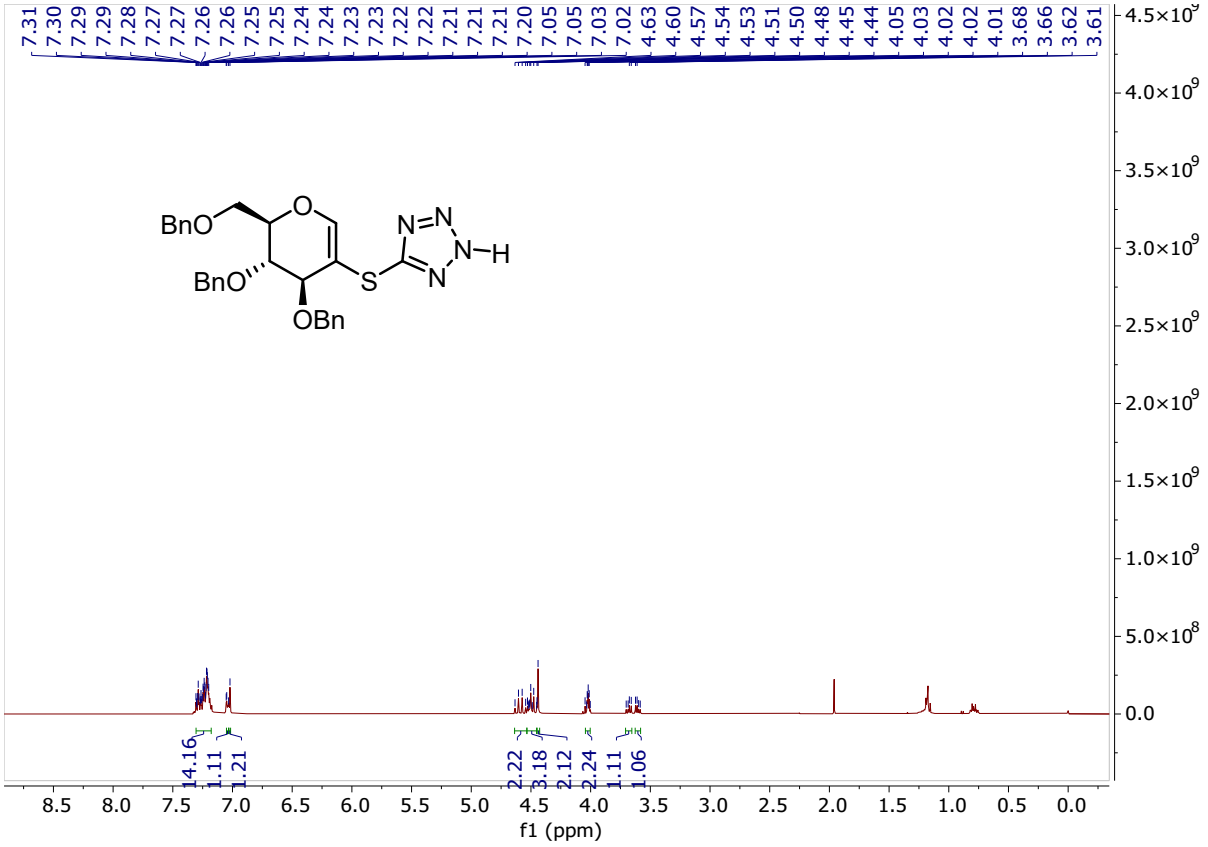


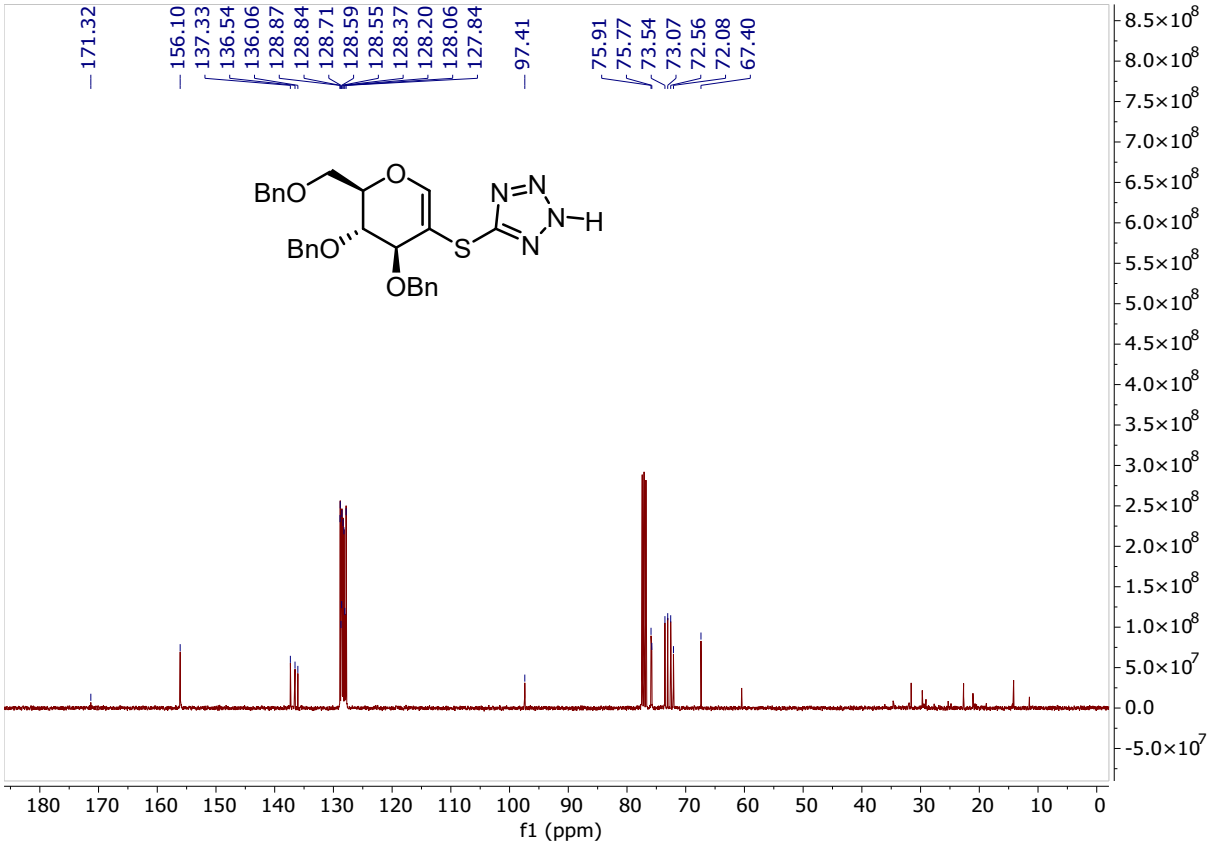
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2p** in $CDCl_3$



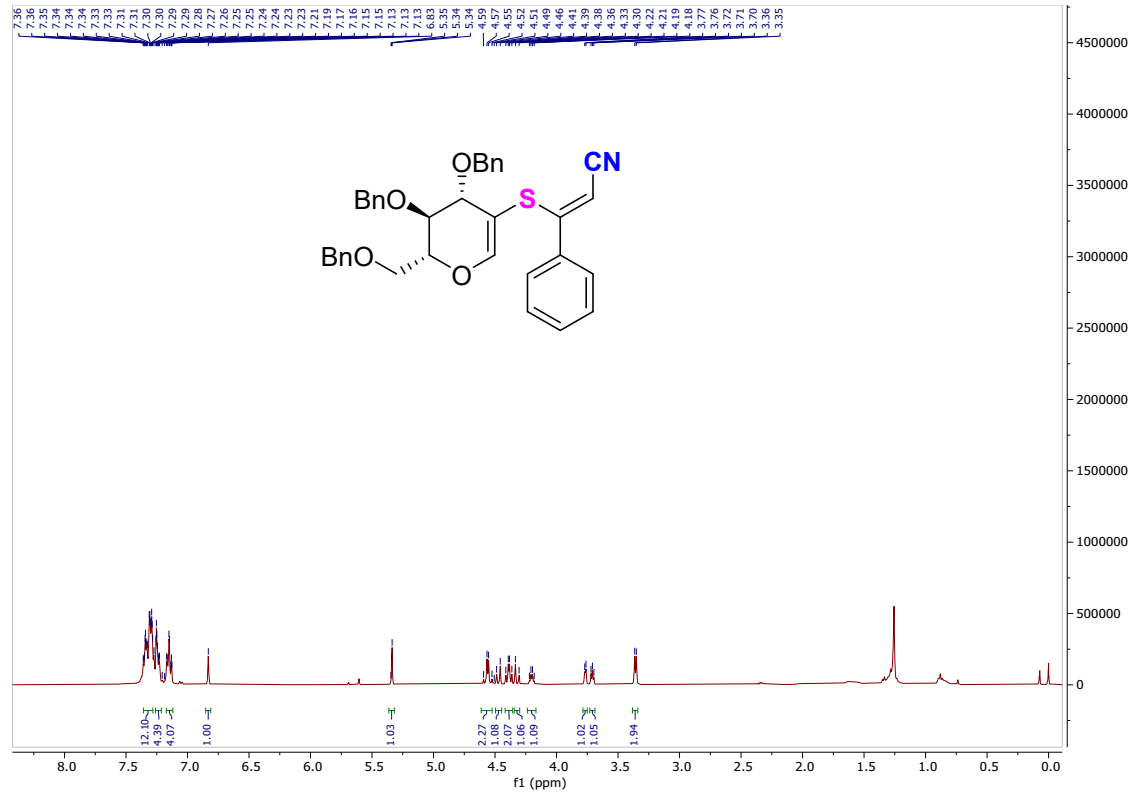


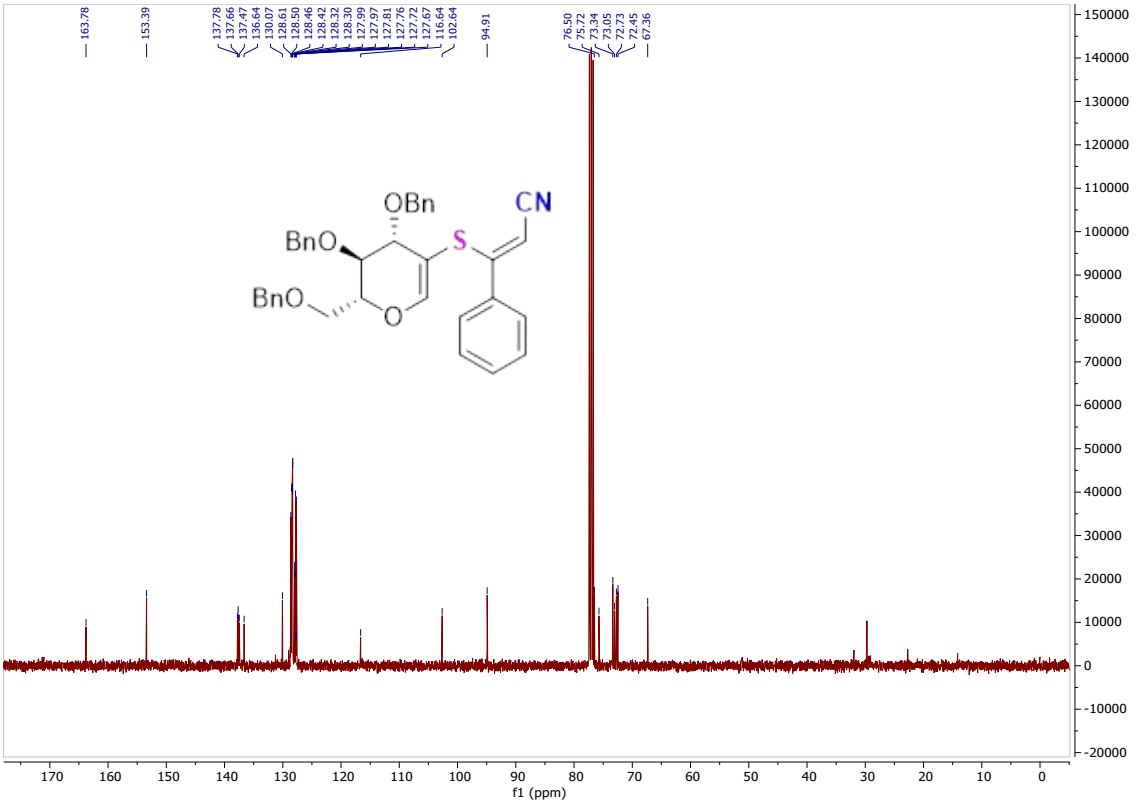
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **2ai** in $CDCl_3$



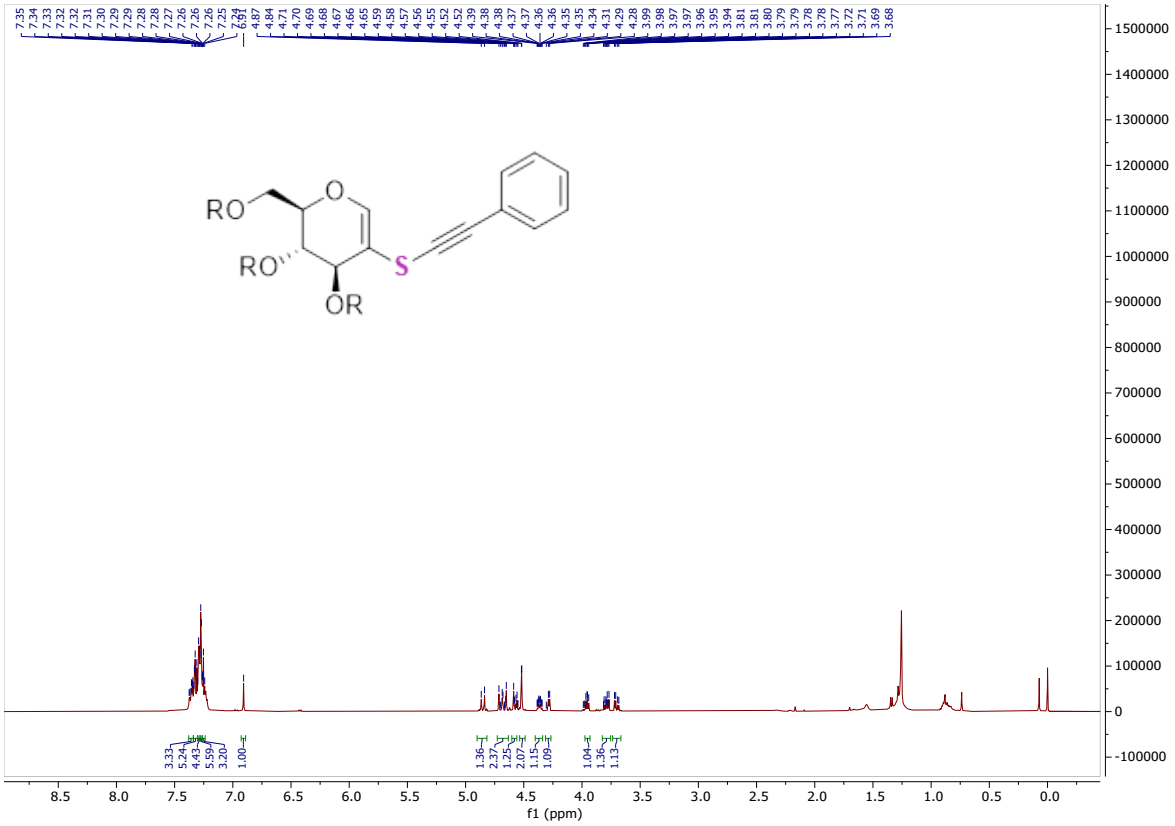


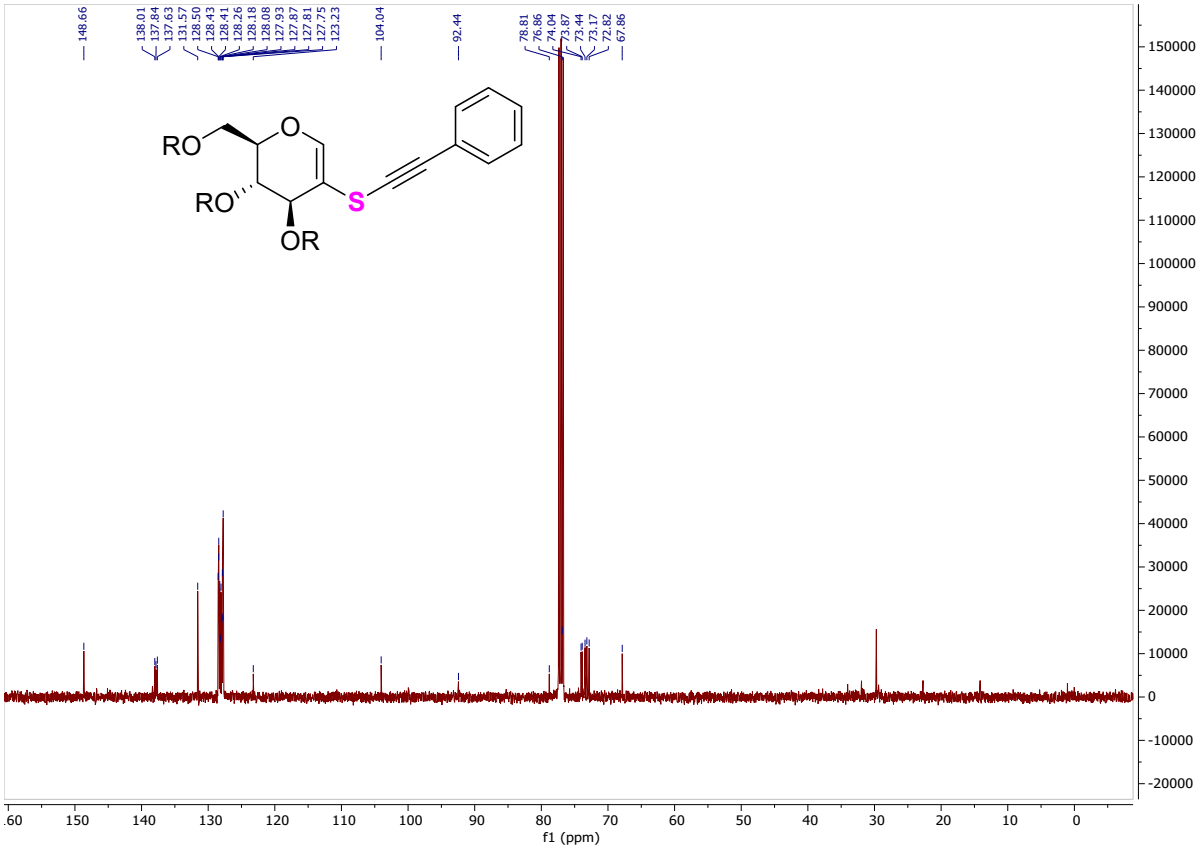
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **3a** in $CDCl_3$



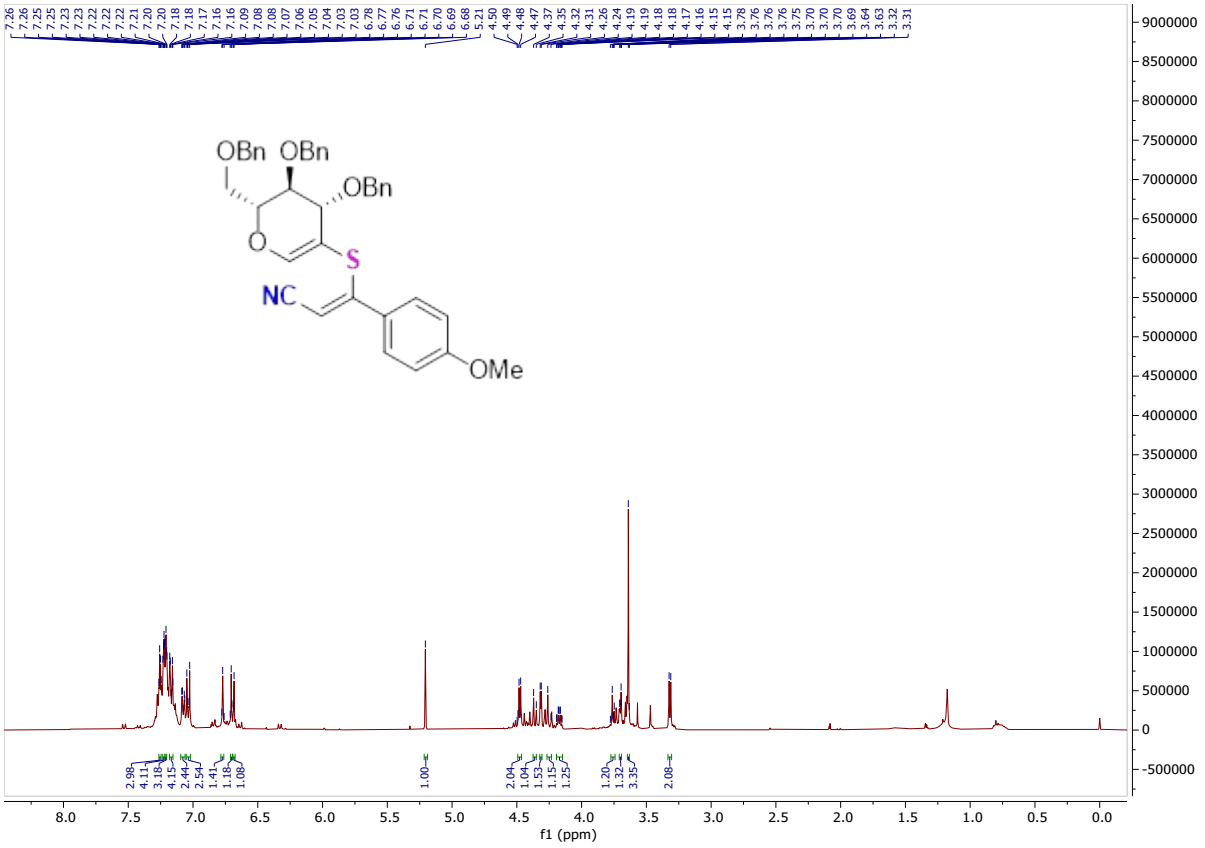


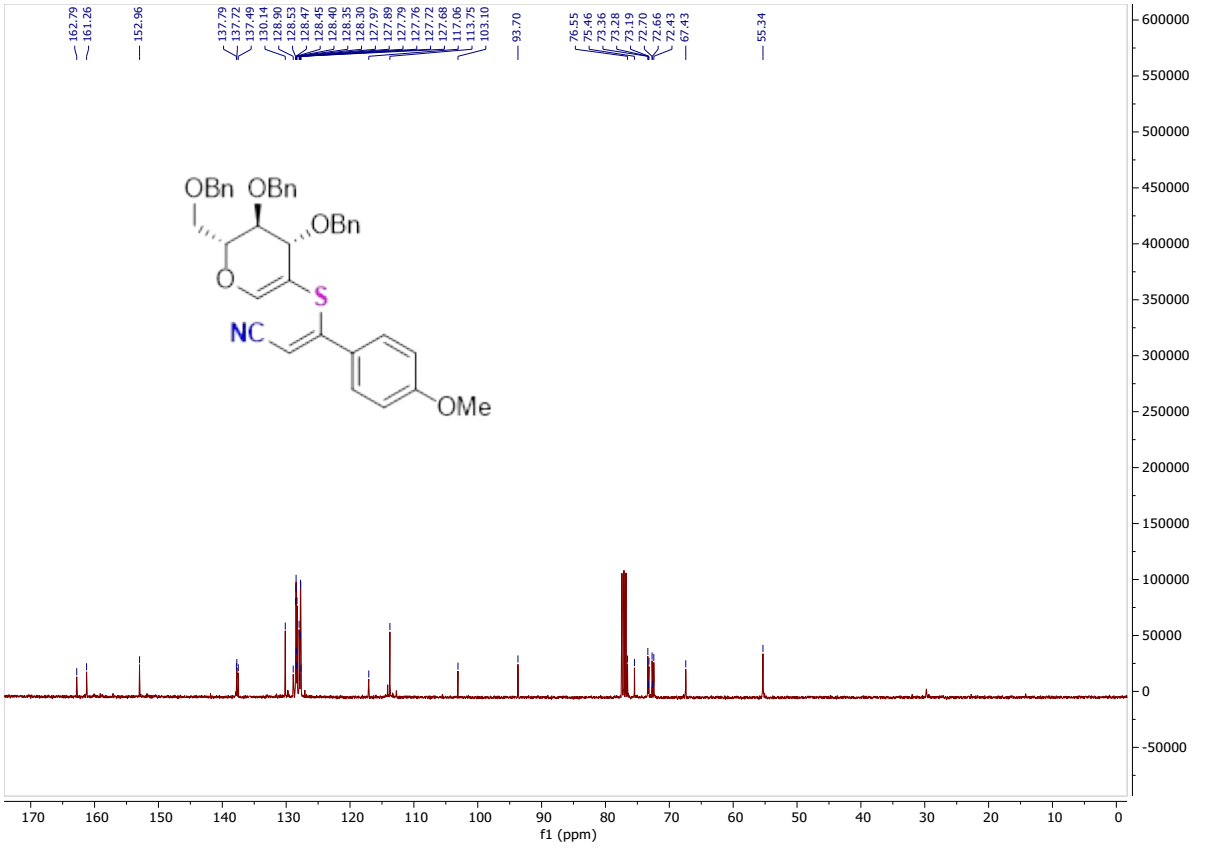
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **4a** in $CDCl_3$



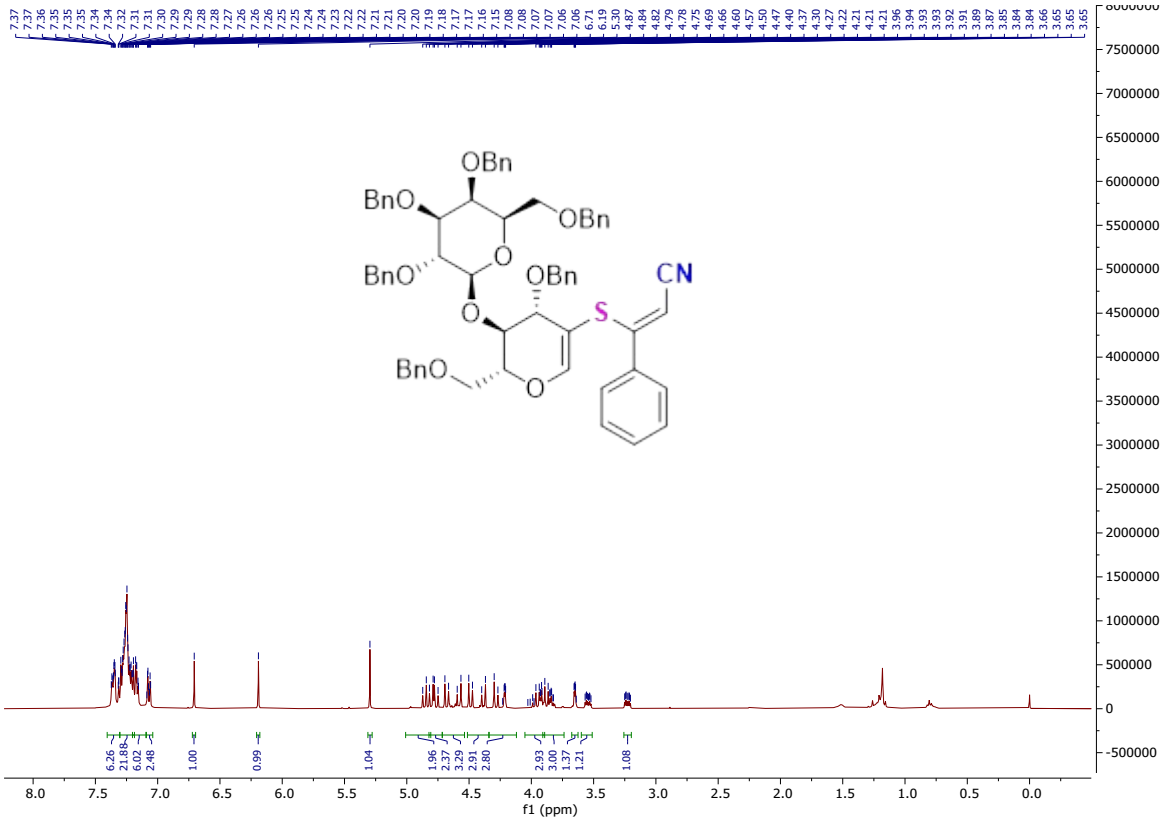


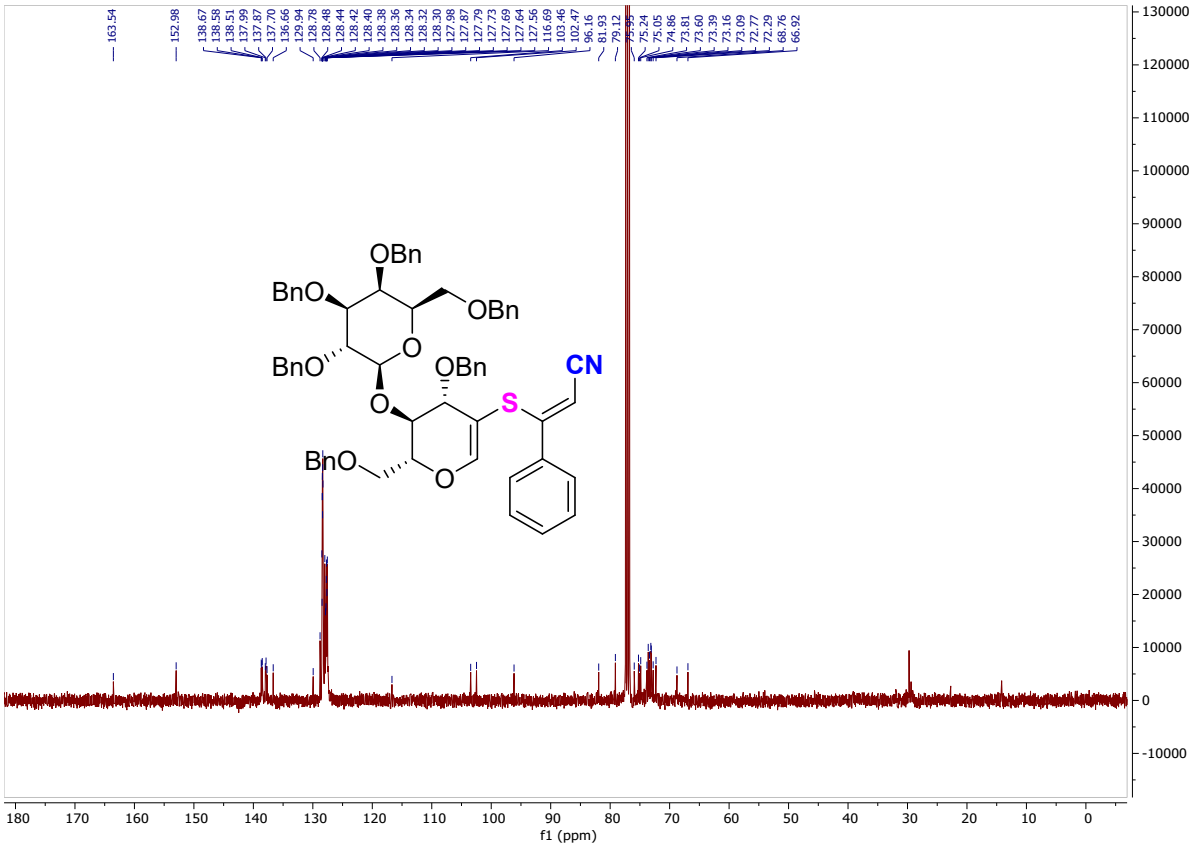
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **3b** in $CDCl_3$



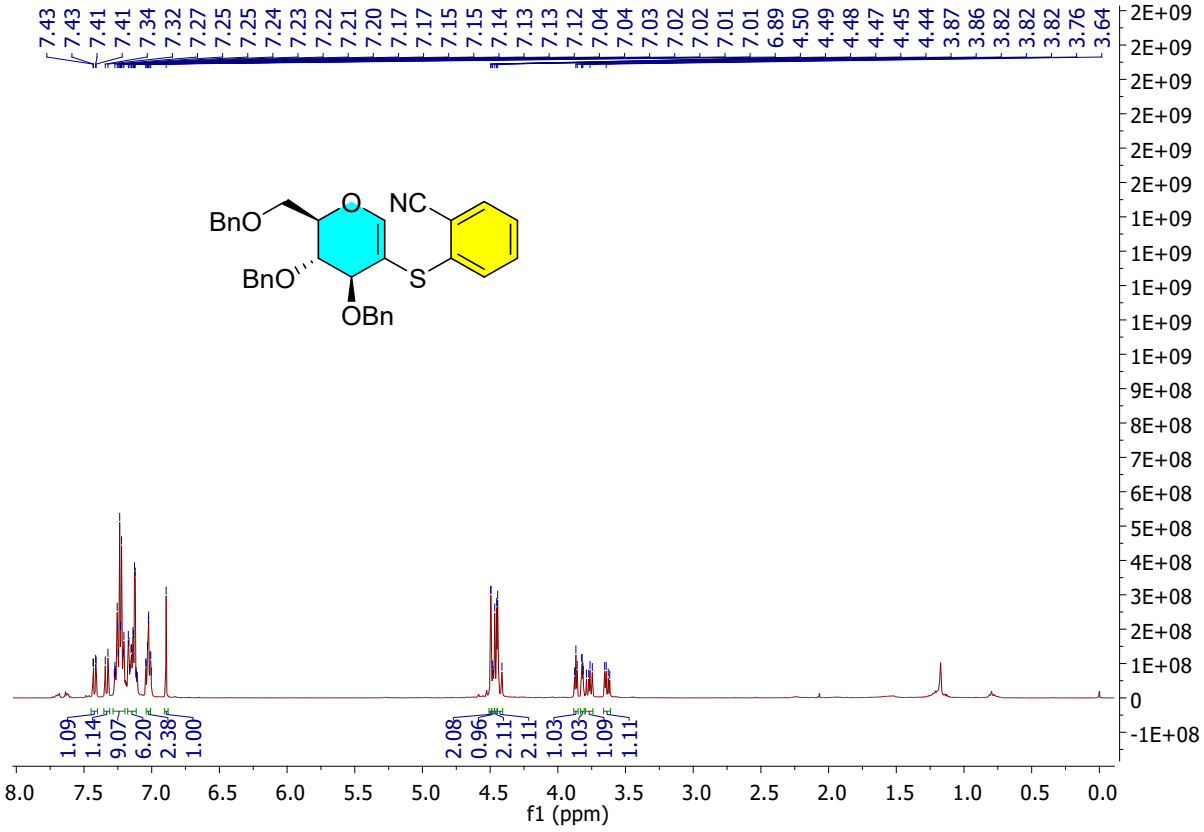


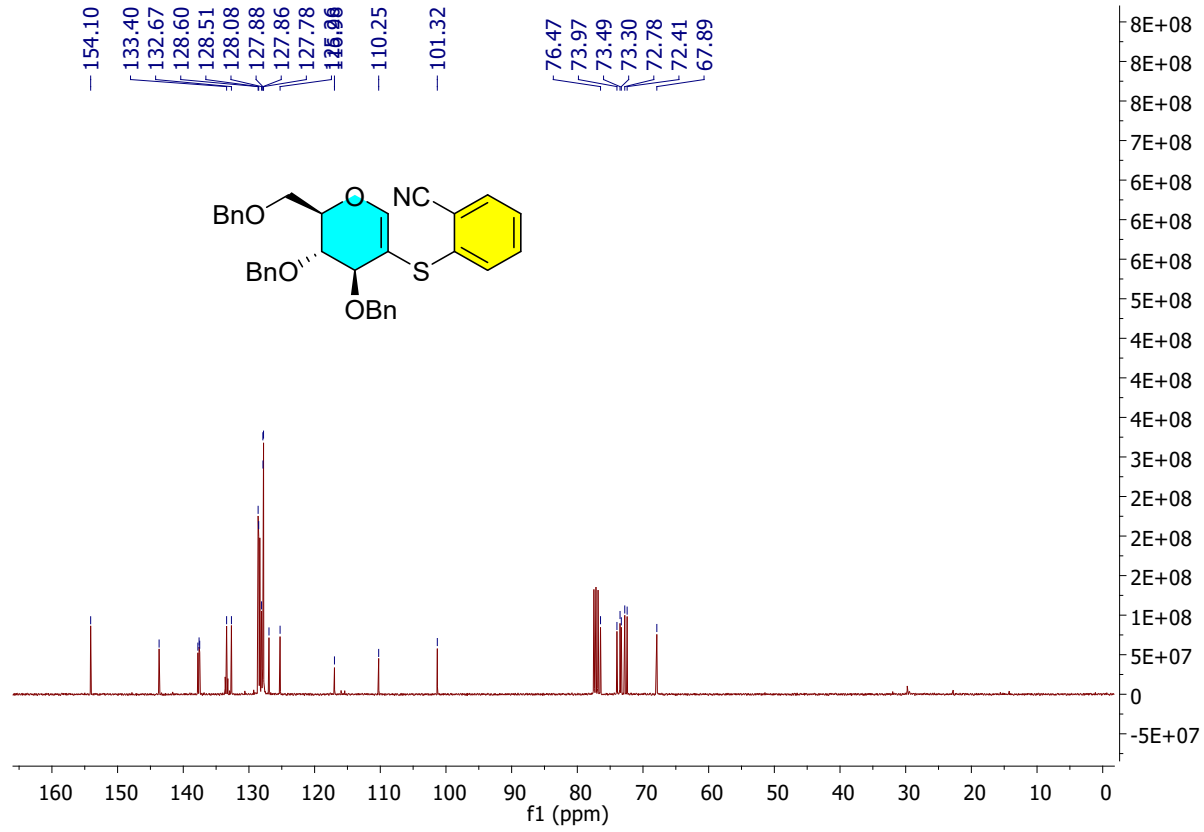
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **3c** in $CDCl_3$



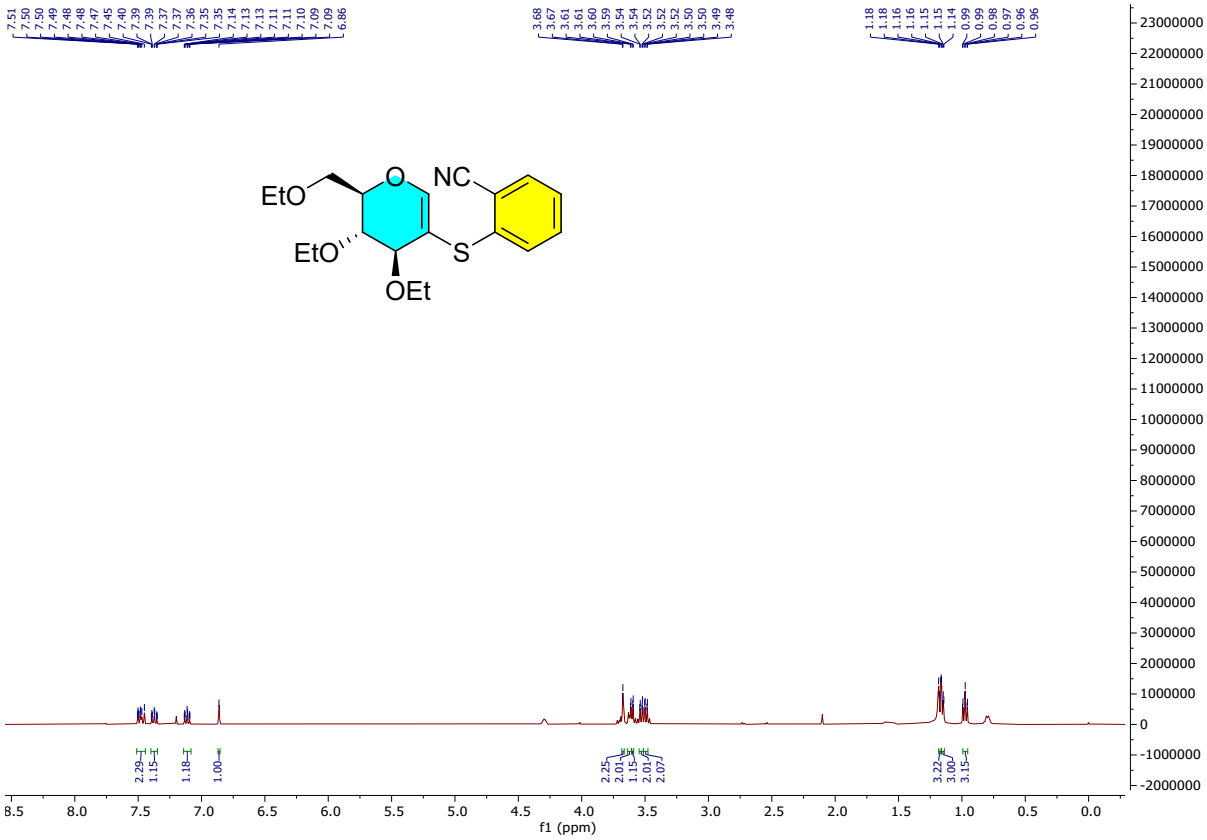


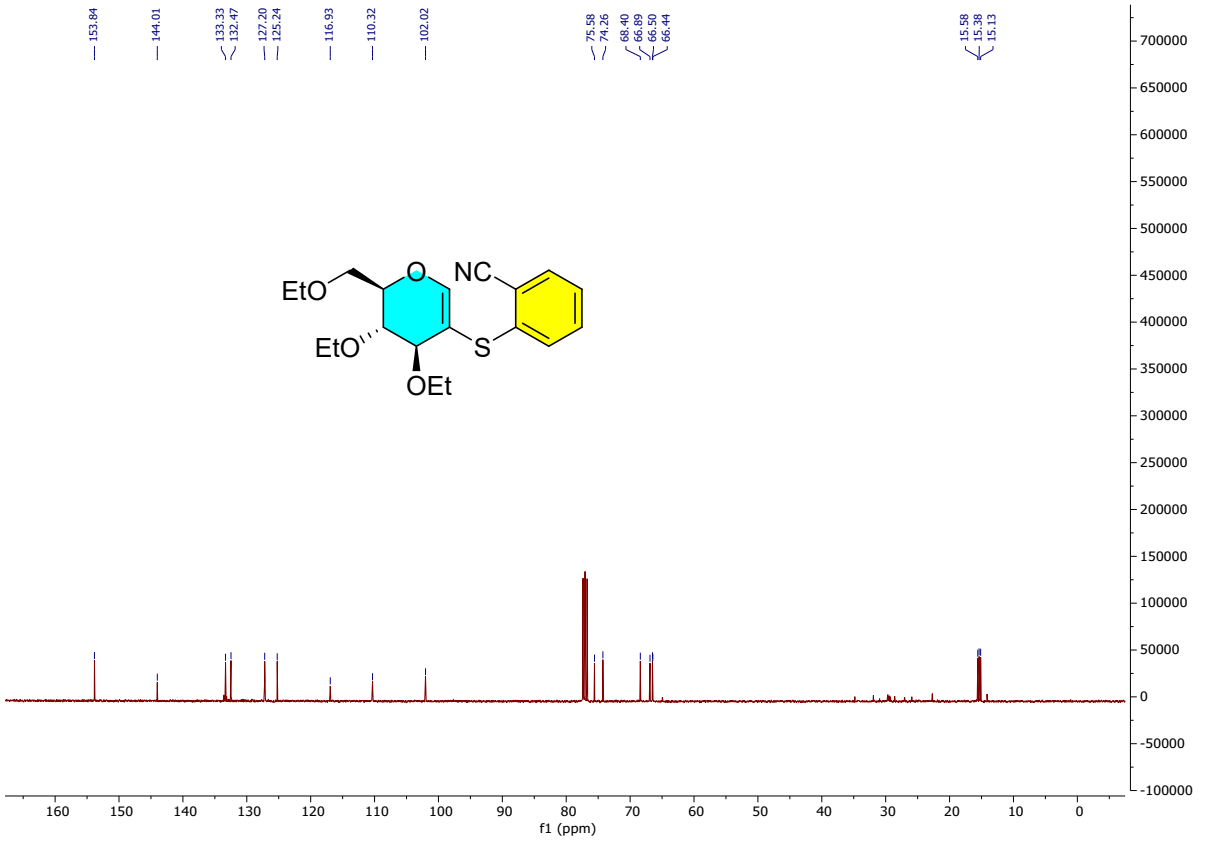
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **5a** in $CDCl_3$



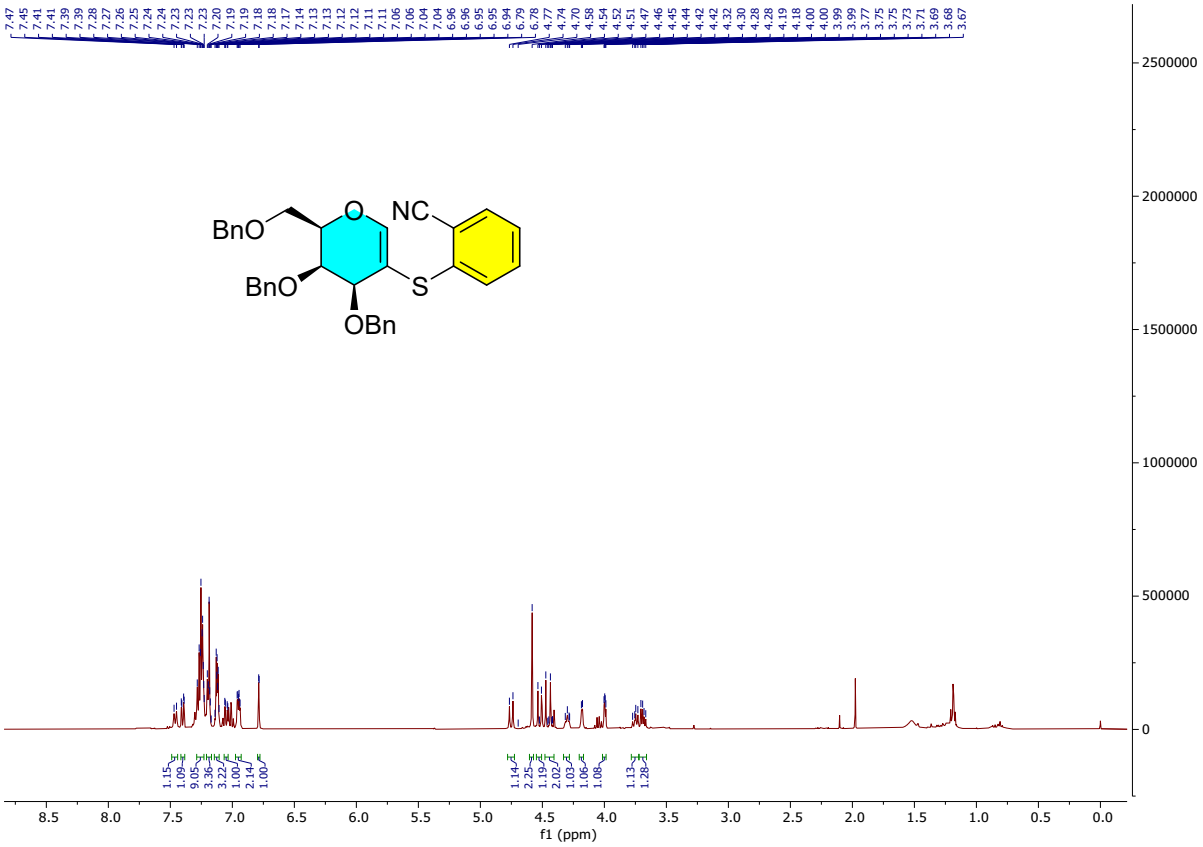


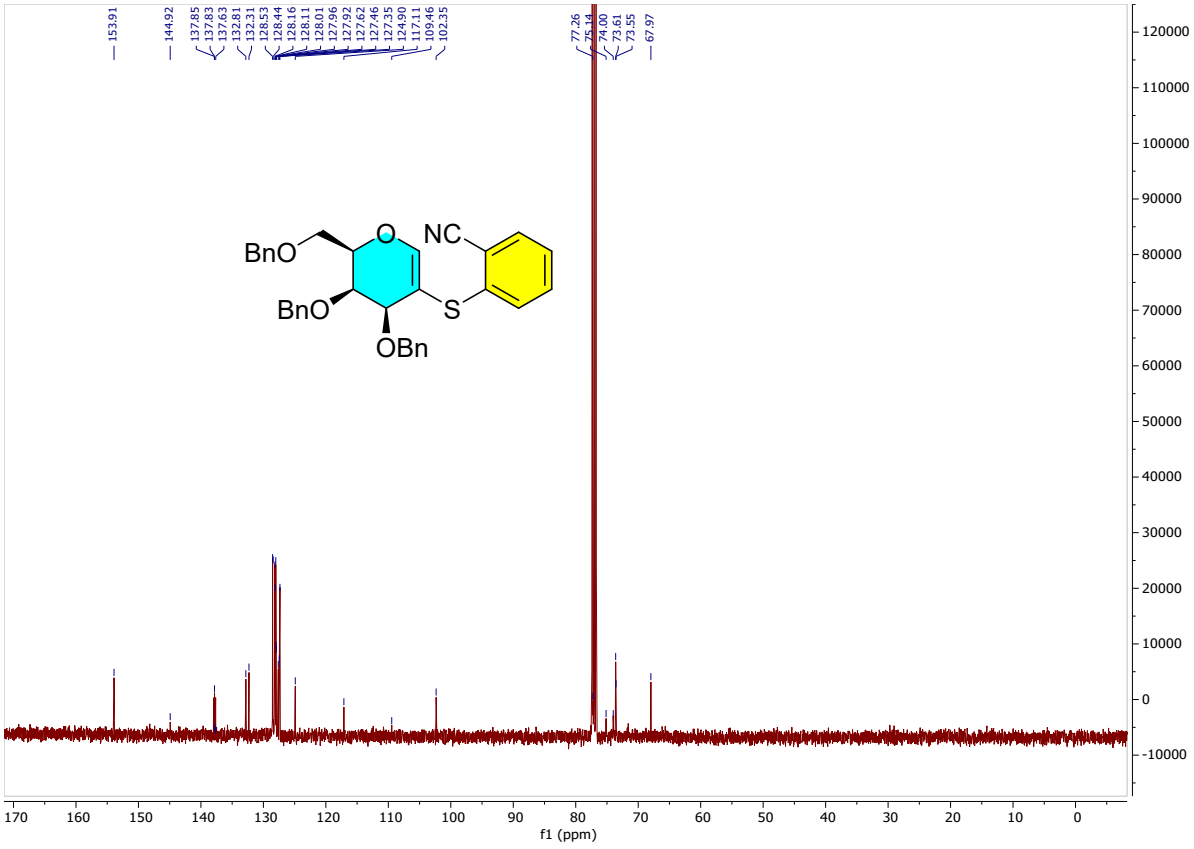
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **5b** in $CDCl_3$



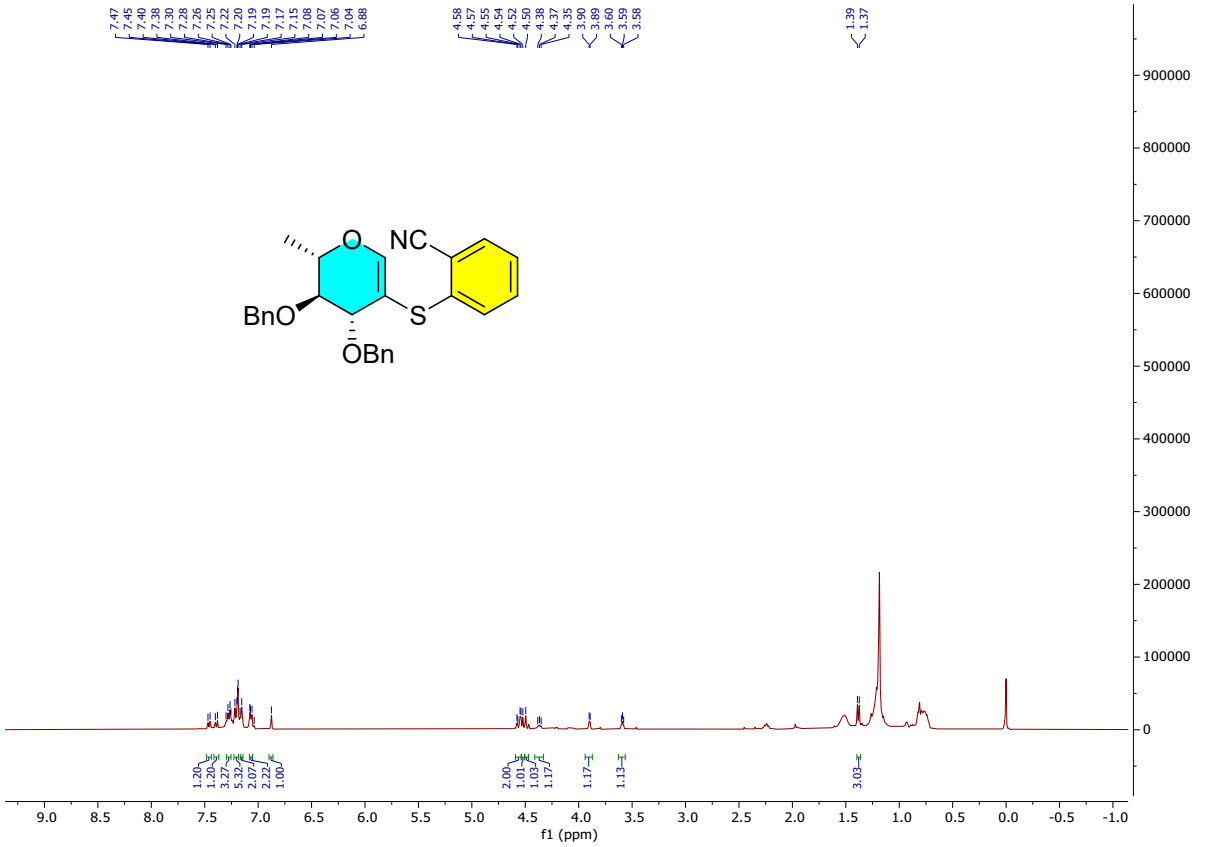


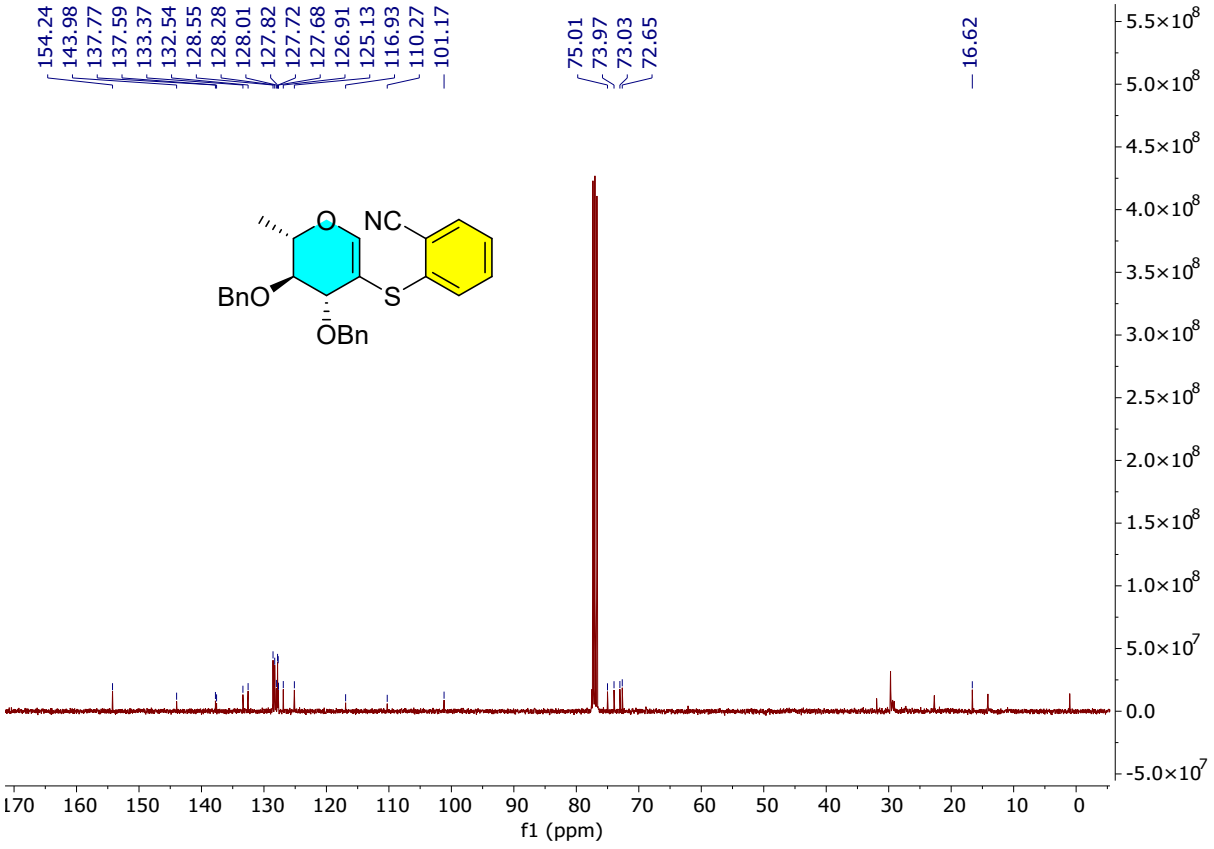
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **5c** in $CDCl_3$



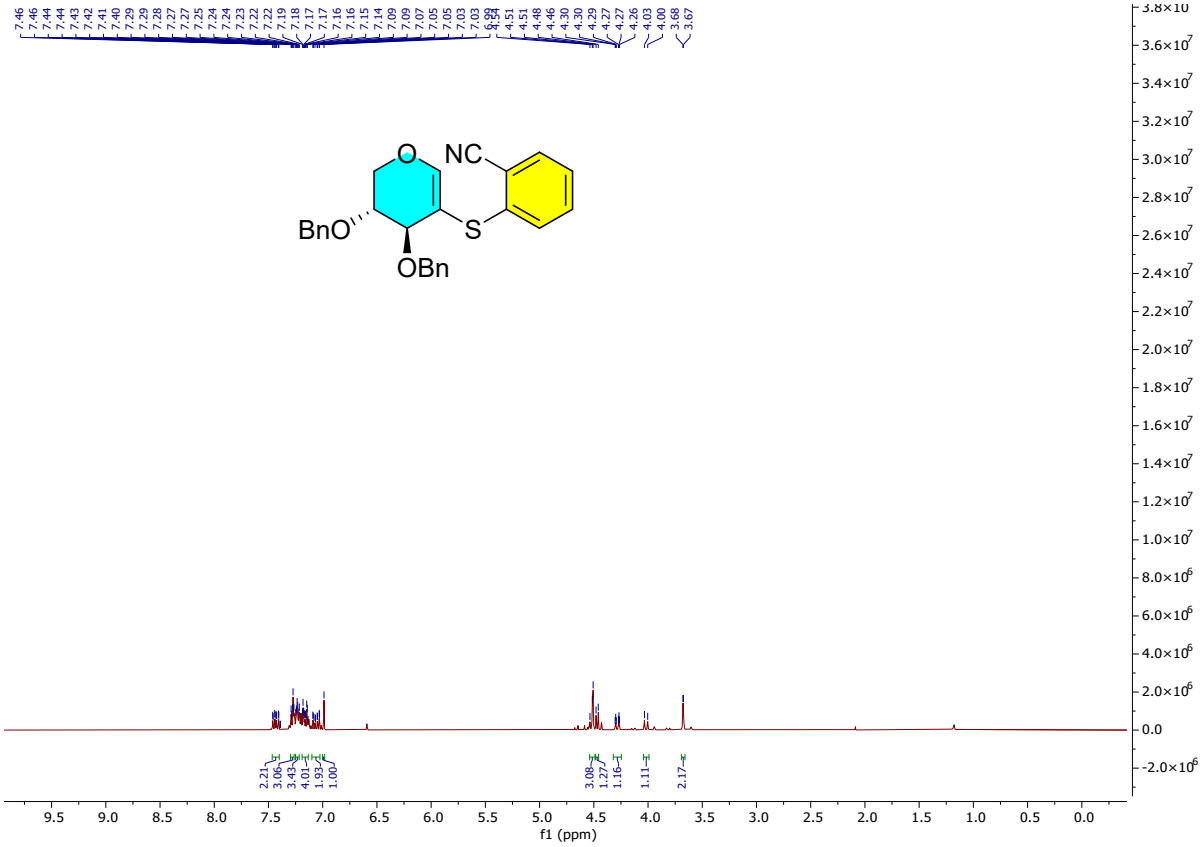


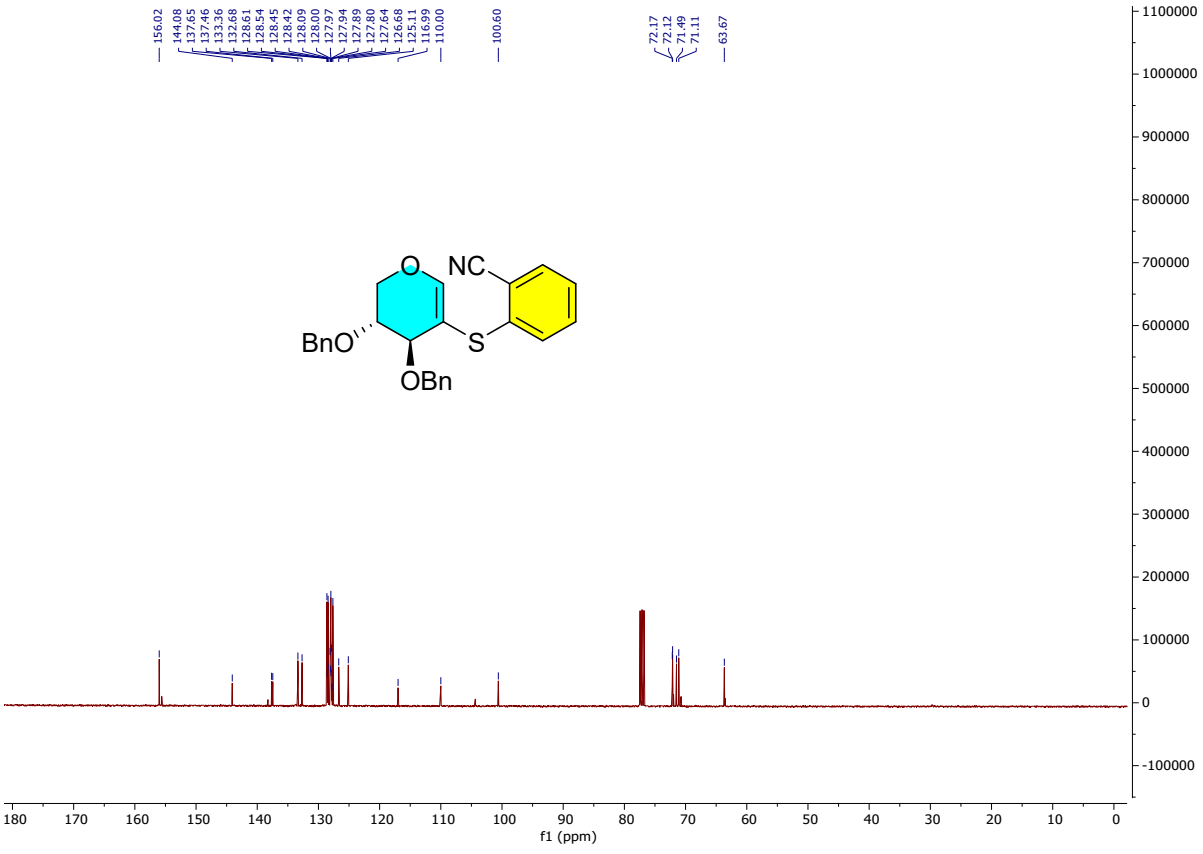
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **5d** in $CDCl_3$



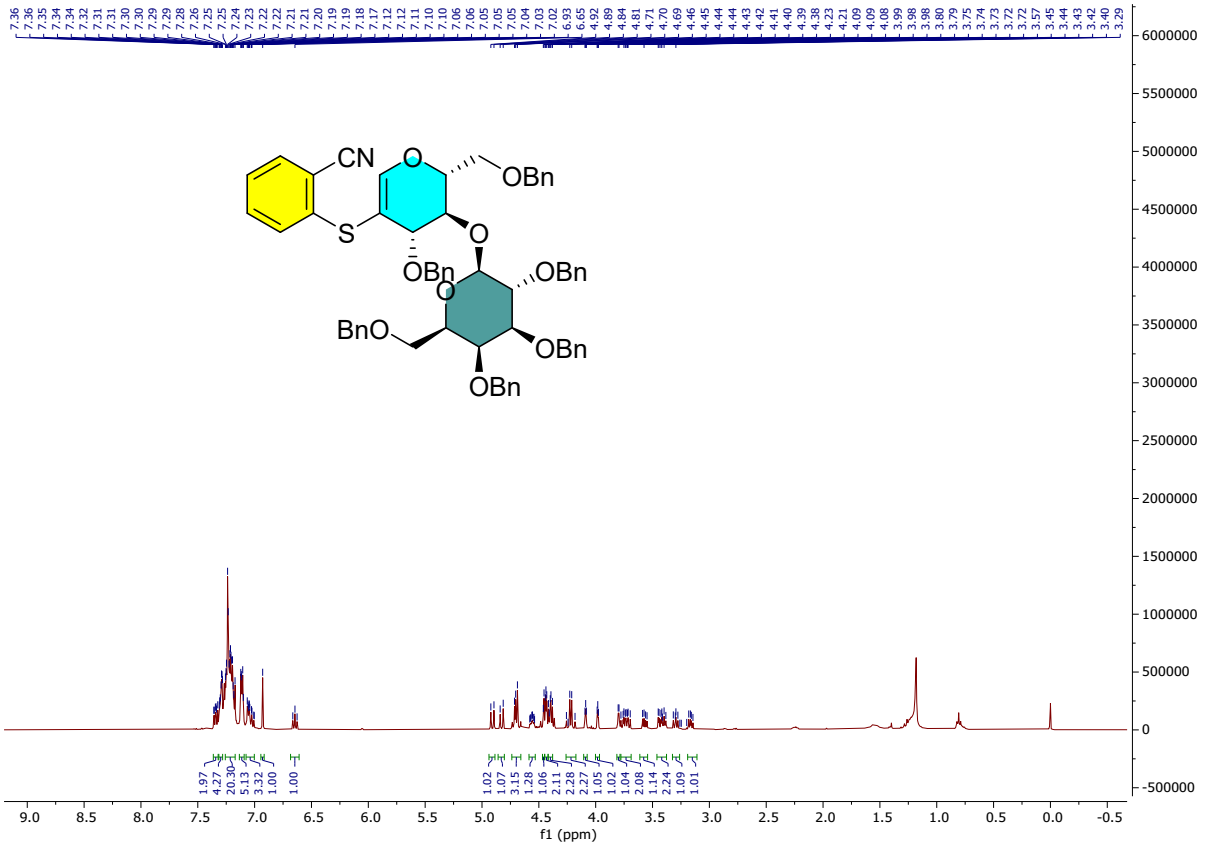


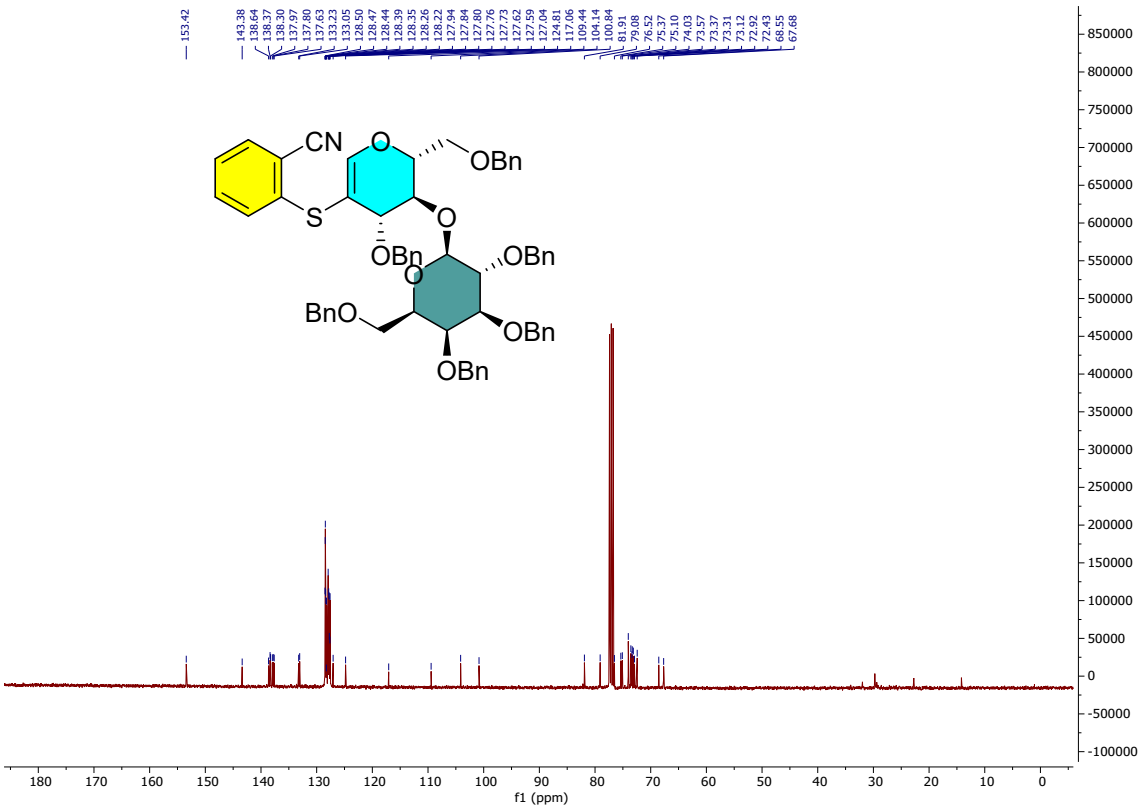
^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **5e** in $CDCl_3$





^{1}H NMR (400 MHz) & ^{13}C NMR {^{1}H} (101 MHz) of **5f** in $CDCl_3$





^{1}H NMR (400 MHz) & ^{13}C NMR $\{^{1}H\}$ (101 MHz) of **5g** in $CDCl_3$