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Investigation into the Role of the Hydrogen Bonding Network in Cyclodextrin-based Self-assembling Mesophases

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General Methods

Analytical TLC was performed on Silica Gel 60-F_{254} (Merck, Darmstadt) with detection by quenching of fluorescence and/or by charring with 5% sulfuric acid in water or with a ceric ammonium molybdate dip. All commercial reagents were used as supplied unless otherwise stated. Column chromatography was performed on Silica Gel 60 (Silicycle, Ontario). Organic solutions from extractions were concentrated under vacuum at < 40 °C (bath). ^{1}H NMR spectra were recorded at 400 MHz on Bruker spectrometers. The first order proton chemical shifts δ_H and δ_C are reported in δ (ppm) and referenced to either residual $CHCl_3$ (δ_H 7.24, δ_C 77.0, $CDCl_3$), residual CD_2HOD (δ_H 3.30, δ_C 49.5, CD_3OD), residual CD_3SOCD_2H (δ_H 2.50, δ_C 39.51, CD_3SOCD_3) or residual C_5D_4HN (δ_H 7.22, δ_C 123.87, C_5D_5N). ^{1}H and ^{13}C NMR spectra were assigned with the assistance of GCOSY, GHSQC spectra. Matrix-assisted laser desorption / ionization and time-of-flight mass spectra (MALDI-TOF MS) were recorded on a Bruker Daltonics AUTOFLEX III spectrometer using DHP as a matrix. High resolution ESI-QTOF mass spectra were recorded on an Agilent 6520 Accurate Mass Quadrupole Time-of-Flight LC/MS spectrometer. Polarized optical microscopy was performed on OLYMPUS BX-41 equipped with a Linkam hot stage. Thermal analyses were performed using TA-Q200 differential scanning calorimetry instrument with a heating and cooling rate of 5 °C. All data were obtained by the analytical services of the Department of Chemistry, University of Calgary.

Per-6-*O*-acetyl-2,3-di-*O*-benzyl-β-cyclodextrin (10)

Perbenzylated compound **9** (600 mg, 0.198 mmol) in acetic anhydride (10 mL) was cooled to -40 °C. TMSOTf (0.25 mL, 1.39 mmol) in anhydrous dichloromethane (0.5 mL) was added dropwise into the reaction mixture. After stirring at -40 °C for 1.5 hrs, the reaction was quenched by the addition of saturated $NaHCO_3$ (15 mL) at 0 °C. The reaction mixture was then diluted with water (15 mL) and extracted with EtOAc (25 mL); the organic solution was washed with saturated $NaHCO_3$ (25 mL), H_2O (25 mL), saturated brine (25 mL), dried over anhydrous Na_2SO_4 and evaporated under reduce pressure. The pure product **10** was obtained as a white solid (424 mg, 80.5% yield) by column chromatography on silica gel using 50% hexane - EtOAc as eluent. R_f 0.4 (EtOAc : hexane, 60 : 40). $[\alpha]_D$ +33.5 (*c* 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.10 (m, 70H, 14 × Ph), 5.02 (d, J = 11.0 Hz, 7H, 7 ×

Ha_Bn), 4.96 (d, *J* = 3.4 Hz, 7H, 7 × H-1), 4.75 (d, *J* = 11.0 Hz, 7H, 7 × Hb_Bn), 4.58 (d, *J* = 12.5 Hz, 7H, 7 × Ha_Bn), 4.48-4.34 (m, 21H, 7 × Hb_Bn + 7 × H-6a + 7 × H-6b), 4.11 – 4.05 (m, 7H, 7 × H-5), 4.01 (d, *J* = 8.6, 8.9 Hz, 7H, 7 × H-3), 3.70 (dd, *J* = 8.6, 9.2 Hz, 7H, 7 × H-4), 3.48 (dd, *J* = 9.4, 3.5 Hz, 7H, 7 × H-2), 2.05 (s, 21H, 7 × Ac). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.45 (CO), 139.06, 138.30, 128.24, 128.07, 127.94, 127.65, 127.16, 127.09 (Ar), 98.99 (C-1), 80.44 (C-3), 79.79 (C-4), 78.68 (C-2), 75.36 (*C*H_2Ph), 73.07 (*C*H_2Ph), 69.92 (C-5), 63.48 (C-6), 20.82 (Ac). *m/z* (HRMS ESI-TOF) calcd for $[C_{154}H_{168}O_{42} + Na]^+$ 2712.0902, found 2712.0849.

Per-2,3-di-*O*-benzyl-β-cyclodextrin (11)

The per-6-*O*-acetylated compound **10** (300 mg, 0.11 mmol) was dissolved in MeOH (2 mL) and anhydrous THF (0.5 mL); a solution of NaOMe in MeOH (0.1 M, 1 mL) was added. After stirring overnight, the reaction mixture was neutralized with Amberlite IR-120 (H^+) resin. After stirring for 30 minutes, the solution was filtered off and evaporated under reduced pressure to give the desired compound **11** as a white solid (0.270 g, 100% yield). R_f 0.5 (CH_2Cl_2 : MeOH, 95 : 5). $[\alpha]_D$ +18.2 (*c* 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD) δ 7.22 – 7.05 (m, 70H, 14 × Ph), 5.26 (d, *J* = 3.4 Hz, 7H, 7 × H-1), 4.94 (d, *J* = 11.2 Hz, 7H, 7 × Ha_Bn), 4.64 (d, *J* = 11.2 Hz, 7H, 7 × Hb_Bn), 4.56 (d, *J* = 12.0 Hz, 7H, 7 × Ha_Bn), 4.50 (d, *J* = 12.0 Hz, 7H, 7 × Hb_Bn), 4.05 – 3.81 (m, 35H, 7 × H-3 + 7 × H-4 + 7 × H-5 + 7 × H-6a + 7 × H-6b), 3.49 (dd, *J* = 3.4, 9.3 Hz, 7H, 7 × H-2). ^{13}C NMR (100 MHz, CD_3OD) δ 139.01, 138.33, 127.86, 127.72, 127.69, 127.23, 127.20, 126.77 (Ar), 97.84 (C-1), 80.54 (C-3), 78.89 (C-2), 78.00 (C-4), 74.98 (*C*H_2Ph), 72.70 (C-5), 72.55 (*C*H_2Ph), 60.98 (C-6). *m/z* (HRMS ESI-TOF) calcd for $[C_{140}H_{154}O_{35} + Na]^+$ 2418.0163, found 2418.0121.

Per-2,3-di-*O*-benzyl-6-*O*-methanesulfonyl-β-cyclodextrin (12)

A solution of compound **11** (200 mg, 0.084 mmol) in anhydrous dichloromethane (2 mL) and pyridine (0.5 mL) was cooled to 0 °C using an ice-bath, and methanesulfonyl chloride (0.06 mL, 0.7 mmol) was added dropwise. The ice-bath was removed and the reaction was left stirring overnight at room temperature. The reaction was quenched with a sat. solution of $NaHCO_3$, diluted with water (20 mL), and extracted with EtOAc (50 mL). The organic layer was washed with $NaHCO_3$ (30 mL), H_2O (30 mL) and sat. brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified

by column chromatography on silica gel using a mixture of 50% EtOAc - hexane as the eluent to afford the pure compound **12** as a white solid (220 mg, 90% yield). R_f 0.5 (EtOAc : hexane, 80 : 20). $[\alpha]_D$ +45.2 (*c* 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 70H, 14 × Ph), 5.08 (d, *J* = 3.5 Hz, 7H, 7 × H-1), 5.00 (d, *J* = 11.0 Hz, 7H, 7 × Ha_Bn), 4.75 (d, *J* = 11.0 Hz, 7H, 7 × Hb_Bn), 4.64 – 4.58 (m, 14H, 7 × H-6a + 7 × H-6b), 4.57 (d, *J* = 12.3 Hz, 7H, 7 × Ha_Bn), 4.45 (d, *J* = 12.3 Hz, 7H, 7 × Hb_Bn), 4.10 – 4.05 (m, 7H, 7 × H-5), 3.99 (dd, *J* = 8.8 Hz, 7H, 7 × H-3), 3.77 (dd, *J* = 8.3, 9.6 Hz, 7H, 7 × H-4), 3.49 (dd, *J* = 9.4, 3.6 Hz, 7H, 7 × H-2), 3.05 (s, 21H, 7 × C*H*$_3$SO$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.80, 137.89, 128.32, 128.12, 127.92, 127.80, 127.21, 115.11 (Ar), 98.66 (C-1), 80.15 (C-3), 78.75 (C-4), 78.33 (C-2), 75.43 (*C*H$_2$Ph), 73.09, (*C*H$_2$Ph), 69.83 (C-5), 69.51 (C-6), 37.10 (C*H*$_3$SO$_2$). *m/z* (HRMS ESI-TOF) calcd for $[C_{147}H_{168}O_{49}S_7 + Na]^+$ 2963.8591, found 2963.8600.

Per-2,3-di-*O*-benzyl-6-deoxy-6-octadecylthio-β-cyclodextrin (3)

A solution of compound **12** (100 mg, 0.034 mmol) and 1- octadecanethiol (200 mg, 0.713 mmol) in anhydrous THF (5 mL) was purged with argon; then a solution of KOBu-*t* (53 mg, 0.476 mmol,) in anhydrous THF (2 mL) was added. After stirring at 70 °C for 3 days, the reaction mixture was concentrated under reduced pressure. MeOH (30 mL) was added, and the mixture was refluxed, after cooling to room temperature, the liquid (containing excess amount of 1-octadecanethiol) was decanted. The residue was purified by column chromatography on silica gel using a mixture of 5% EtOAc - hexane as the eluent to afford the desired compound **3** (111 mg, 76% yield). R_f 0.36 (EtOAc : hexane, 5 : 95). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.06 (m, 70H, 14 × Ph), 5.18 (br s, 7H, 7 × H-1), 5.03 (d, *J* = 10.5 Hz, 7H, 7 × Ha_Bn), 4.73 (d, *J* = 11.0 Hz, 7H, 7 × Hb_Bn), 4.54 (d, *J* = 12.5 Hz, 7H, 7 × Ha_Bn), 4.47 (d, *J* = 12.4 Hz, 7H, 7 × Hb_Bn), 4.17 – 4.07 (m, 7H, 7 × H-5), 3.99 (dd, *J* = 8.8, 8.8 Hz, 7H, 7 × H-3), 3.89 (dd, *J* = 8.5, 8.5 Hz, 7H, 7 × H-4), 3.46 (dd, *J* = 9.4, 3.4 Hz, 7H, 7 × H-2), 3.18 – 3.04 (m, 14H, 7 × H-6a + 7 × H-6b), 2.56 (t, *J* = 7.4 Hz, 14H, 7 × SC*H*$_2$-), 1.45 – 1.15 (m, 224H, alkyl), 0.90 (t, *J* = 6.8 Hz, 21H, 7 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.25, 138.33, 128.16, 127.96, 127.79, 127.41, 127.25, 126.91 (Ar), 98.27 (C-1), 80.58 (C-4), 80.54 (C-3), 78.94 (C-2), 72.73 (× 2, *C*H$_2$Ph), 71.70 (C-5), 34.57 (C-6), 33.86 (S*C*H$_2$-), 31.95, 30.14, 29.92, 29.87, 29.84, 29.81, 29.77, 29.70, 29.39, 29.28, 22.70 (CH_2), 14.12 (CH_3). Anal. calcd for $C_{266}H_{406}O_{28}S_7$: C, 74.74; H, 9.58; found: C, 74.62; H,

9.73.

Per-6-*O*-methanesulfonyl-2,3-di-*O*-methyl-β-cyclodextrin (14)

Compound **13**[15] (20 mg, 0.015 mmol) was reacted with MsCl (0.20 mL) in anhydrous CH_2Cl_2 (1 mL) and pyridine (0.20 mL, 2.3 mmol) in a similar manner as **12**. The obtained crude product was purified by column chromatography on silica gel using a gradient of 1 → 10% MeOH - dichloromethane as the eluent to afford the heptamesylate **14** as a white solid (23 mg, 82% yield). R_f 0.48 (CH_2Cl_2 : MeOH, 95 : 5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (d, J = 3.6 Hz, 7H, 7 × H-1), 4.60 (dd, J = 1.9, 11.4 Hz, 7H, 7 × H-6a), 4.55 (dd, J = 11.4, 3.6 Hz, 7H, 7 × H-6b), 3.96 (m, 7H, 7 × H-5), 3.70 – 3.45 (m, 56H, 7 × H-3 + 7 × H-4 + 14 × OCH_3), 3.19 (dd, J = 9.5, 3.6 Hz, 7H, 7 × H-2), 3.10 (s, 21H, 7 × CH_3SO_2-). ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.80 (C-1), 81.64 (C-3), 81.45 (C-2), 79.73 (C-4), 69.54 (C-5), 69.38 (C-6), 61.52 (OCH_3), 58.87 (OCH_3), 37.12 (CH_3SO_2).

Per-2,3-di-*O*-methyl-6-deoxy-6-octadecylthio-β-cyclodextrin (4)

The per-6-*O*-mesylate **14** (23 mg, 0.012 mmol) was reacted with 1-octadecanethiol (73.3 mg, 0.26 mmol) and KOBu-*t* (26 mg, 0.23 mmol) in anhydrous DMF (3 mL) under argon in a similar manner as **3**. After stirring overnight at 70 °C, the crude mixture was purified by column chromatography on silica gel using 1% methanol - dichloromethane as the eluent to afford compound **4** as a white solid (17.8 mg, 45% yield). R_f 0.53 (CH_2Cl_2 : MeOH, 95 : 5). $[\alpha]_D$ +7.6 (*c* 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (d, J = 3.5 Hz, 7H, 7 × H-1), 3.98 – 3.91 (m, 7H, 7 × H-5), 3.68 – 6.63 (m, 28H, 7 × H-4 + 7 × OCH_3), 3.54 (s, 21H, 7 × OCH_3), 3.48 (dd, J = 9.4, 9.4 Hz, 7H, 7 × H-3), 3.18 (dd, J = 3.5, 9.8 Hz, 7H, 7 × H-2), 3.10 (dd, J = 5.4, 14.2 Hz, 7H, 7 × H-6a), 3.01 (dd, J = 2.6, 14.2 Hz, 7H, 7 × H-6b), 2.59 (t, J = 7.3, 14H, 7 × SCH_2-), 1.62 – 1.54 (m, 14H, 7 × SCH_2CH_2-), 1.42 – 1.34 (m, 14H, 7 × $SCH_2CH_2CH_2$-), 1.30 – 1.10 (m, 196H, alkyl), 0.90 (t, J = 6.8 Hz, 21H, 7 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.44 (C-1), 82.28 (C-4), 82.01 (C-2), 81.85 (C-3), 71.44 (C-5), 61.49 (OCH_3), 58.62 (OCH_3), 34.19 (C-6), 33.75 (SCH_2-), 31.93, 30.09, 29.85, 29.82, 29.80, 29.78, 29.76, 29.74, 29.68, 29.59, 29.37, 29.21, 22.68, 14.09 (CH_3). *m/z* (HRMS MALDI-TOF) calcd for $[C_{182}H_{350}O_{28}S_7 + Na]^+$ 3231.3901, found 3231.3979.

Per-2-*O*-methyl-3,6-di-*O*-*tert*-butyldimethylsilyl–β-cyclodextrin (16)

To a solution of compound **15** (2.60 g, 0.95 mmol) in anhydrous THF (60 mL), was added

NaH (60% in mineral oil, 0.87 g, 23.8 mmol) in portions. After stirring for 1.5 hrs at room temperature, methyl iodide (1.5 mL, 23.8 mmol) was added drop wise, and the reaction was left stirring for 3 days. MeOH (20 mL) was added to quench the reaction. The reaction mixture was concentrated and redissolved in EtOAc (150 mL); the organic solution was washed with water (2 × 75 mL), saturated brine (2 × 75 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using 0.5% EtOAc - hexane as the eluent to provide compound **16** as a white powder (1.81 g, 67.2% yield). R_f 0.84 (EtOAc : hexane, 5 : 95). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.29 (d, J = 3.4 Hz, 7H, 7 × H-1), 4.22 (dd, J = <2.0, 11.5 Hz, 7H, 7 × H-6a), 4.14 (dd, J = 8.0, 6.2 Hz, 7H, 7 × H-3), 3.87 – 3.76 (m, 14H, 7 × H-4 + 7 × H-5), 3.71 (dd, J = 11.3, 1.7 Hz, 7 × H, 7 × H-6b), 3.36 (s, 21H, 7 × OCH_3), 3.05 (dd, J = 8.1, 3.6 Hz, 7H, 7 × H-2), 0.90 (s, 63H, 7 × *t*-butyl), 0.90 (s, 63H, 7 × *t*-butyl), 0.12 (s, 21H, 7 × $SiCH_3$), 0.10 (s, 21H, 7 × $SiCH_3$), 0.04 (s, 42H, 14 × $SiCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 96.17 (C-1), 81.15 (C-2), 78.04 (C-4), 73.09 (C-3), 72.14 (C-5), 62.84 (C-6), 57.26 (OCH_3), 26.29 ($C(CH_3)_3$), 25.99 ($C(CH_3)_3$), 18.37 ($C(CH_3)_3$), 18.28 ($C(CH_3)_3$), -3.75 ($SiCH_3$), -3.83 ($SiCH_3$), -4.76 ($SiCH_3$), -5.08 ($SiCH_3$). *m/z* (MALDI-TOF) calcd for $[C_{133}H_{280}O_{35}Si_{14} + Na]^+$ 2855.7, found: 2855.5.

Per-2-*O*-methyl–β-cyclodextrin (17)

Compound **16** (0.100 g, 0.035 mmol) was dissolved in THF (1 mL) and DMF (1 mL), and tetra-*n*-butylammonium fluoride (0.10 mL, 1.0 M solution in THF) was added to the reaction mixture and left at room temperature overnight. The solvent was removed under reduced pressure. The residue was dissolved in MeOH (10 mL) and stirred with Dowex MR-3 for 1 h. The solvent was removed under reduced pressure and the product was purified by column chromatography on silica gel using 20% MeOH - CH_2Cl_2 as eluent. Compound **17** was obtained as a white powder (0.410 g, 86.6% yield). R_f 0.1 (CH_2Cl_2 : MeOH, 8 : 2). ^{1}H NMR (CD_3OD, 400 MHz) δ 5.09 (d, J = 3.6 Hz, 7H, 7 × H-1), 3.94 (t, J = 9.3, 9.3 Hz, 7H, 7 × H-3), 3.88 – 3.80 (m, 14H, 7 × H-6a + 7 × H-6b), 3.72 – 3.68 (m, 7H, 7 × H-5), 3.50 (dd, J = 9.3, 9.3 Hz, 7H, 7 × H-4), 3.37 (s, 21H, 7 × OCH_3), 3.30 (dd, J = 9.8, 3.6 Hz, 7H, 7 × H-2). ^{13}C NMR (CD_3OD, 100 MHz): δ 100.53 (C-1), 82.56 (C-4), 82.23 (C-2), 73.05 (C-3), 71.78 (C-5), 60.41 (C-6), 59.20 (OCH_3). *m/z* (MS MALDI-TOF) calcd for $[C_{49}H_{84}O_{35} + Na]^+$ 1255.4, found: 1255.5.

Per-6-deoxy-6-iodo-2-*O*-methyl–β-cyclodextrin (18)

Triphenylphosphine (0.33 g, 1.26 mmol) and iodine (0.32 g, 1.25 mmol) were dissolved in DMF (2 mL) and stirred at room temperature for 0.5 h. Compound **17** (0.100 g, 0.075 mmol) was added to the mixture and the reaction was left stirring at 80 °C overnight. Saturated $NaHCO_3$ (3 mL) was added drop wise to the reaction mixture until a red solid was formed. The red tar was isolated by decanting which was dissolved in MeOH (20 mL); solid KOBu-*t* (~0.50 g) was added until the pH 10, and a white precipitate was formed. The precipitate was isolated by filtration which was purified by column chromatography on silica gel using 1% MeOH-CH_2Cl_2 to afford the heptaiodide **18** as a white powder (0.061 g, 40.3 % yield). R_f 0.6 (MeOH : CH_2Cl_2, 5 : 95). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.07 – 5.03 (m, 14H, 7 × H-1 + 7 × OH), 3.95 (dd, J = 9.2, 9.2 Hz, 7H, 7 × H-3), 3.68 – 3.65 (m, 28H, 7 × H-6a, 7 × OCH_3), 3.59 – 3.51 (m, 7H, 7 × H-5), 3.50 (dd, J = 9.2, 4.8 Hz, 7H, 7 × H-6b), 3.30 (dd, J = 9.7, 3.6 Hz, 7H, 7 × H-2), 3.24 (dd, J = 8.9, 8.9 Hz, 7H, 7 × H-4). ^{13}C NMR (CD_3OD, 100 MHz) δ 101.04 (C-1), 87.62 (C-4), 81.77 (C-2), 72.55 (C-3), 70.40 (C-5), 60.57 (OCH_3), 7.58 (C-6).

Per-6-deoxy-2-*O*-methyl-6-octadecylthio–β-cyclodextrin (5)

A solution of compound **18** (0.178 g, 0.090 mmol) in a mixture of THF (3 mL) and CH_2Cl_2 (1 mL) was added to a solution of KOBu-*t* (0.140 g, 1.25 mmol) and thiooctadecane (0.357 g, 1.25 mmol) in THF (3 mL) under argon; and the reaction mixture was heated at 65 °C for 21 hrs. After removing the solvents under reduced pressure, the residue was dissolved in CH_2Cl_2 (20 mL); the organic solution was washed with water (1 × 30 mL) and dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by column chromatography on silica gel using 1% MeOH - CH_2Cl_2 as eluent to afford compound **5** as a white solid (0.175 g, 64.4% yield). R_f 0.45 (MeOH : CH_2Cl_2, 5 : 95). $[\alpha]_D$ +58.6 (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.02 (d, J = 3.4 Hz, 7H, 7 × H-1), 3.92 (dd, J = 9.3, 9.3 Hz, 7H, 7 × H-3), 3.89 – 3.82 (m, 7H, 7 × H-5), 3.66 (s, 21H, 7 × OCH_3), 3.50 (dd, J = 9.1, 9.1 Hz, 7H, 7 × H-4), 3.27 (dd, J = 9.7, 3.5 Hz, 7H, 7 × H-2), 3.04 – 2.88 (m, 14H, 7 × H-6a + 7 × H-6b), 2.60 (t, J = 7.4, 14H, 7 × S-CH_2), 1.63-1.51 (m, 14H, 7 × S-CH_2CH_2), 1.43-1.33 (m, 14H, 7 × S-CH_2CH_2CH_2), 1.35 – 1.20 (m, 196H, alkyl), 0.89 (t, J = 6.7 Hz, 21H, 7 × CH_3). ^{13}C NMR (CD_3OD, 100 MHz) δ 100.91 (C-1), 85.80 (C-4), 82.12 (C-2), 72.98 (C-3), 70.96 (C-5), 60.35 (OCH_3), 33.79 (C-6), 33.71 (S-*C*H_2), 31.94, 29.93, 29.82, 29.76, 29.69, 29.49, 29.38, 29.10, 22.69, 14.11. *m/z* (HRMS MALDI-TOF) calcd for

$[C_{1175}H_{336}O_{28}S_7 + Na]^+$ 3133.2805, found: 3133.2754.

Per-2-*O*-ethyl-6-*O*-*tert*-butyldimethylsilyl–β-cyclodextrin (20)

To a solution of **19** (2.00 g, 1.04 mmol) in anhydrous THF (15 mL), was added NaH (60% in mineral oil, 0.433 g, 10.8 mmol) in portions at 0 °C. After 20 mins, ethyl iodide (0.987 mL, 14.56 mmol) was added, and the reaction mixture was stirred at room temperature overnight. More ethyl iodide (0.500 mL, 7.38 mmol) was added, and the reaction was continued. After 48 hrs, MeOH was added to quench the reaction until no bubbles formed. The mixture was dilutred with EtOAc (75 mL), and washed with H_2O (1 × 40 mL) and saturated brine (1 × 40 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude mixture was purified by column chromatography on silica gel using EtOAc – hexane (10 : 90) as eluent to afford pure **20** as a white solid (0.593 g, 30% yield). R_f 0.40 (EtOAc : toluene, 30 : 70). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (s, 7H, 7 × OH-3), 4.90 (d, J = 3.5 Hz, 7H, 7 × H-1), 4.04 (dq, J = 9.2, 7.1 Hz, 7H, 7 × OC*Ha*HbCH$_3$), 3.93 (m, 14H, 7 × H-3 + 7 × H-6a), 3.70 (dq, J = 9.3, 7.1 Hz , 7H, 7 × OCHa*Hb*CH$_3$), 3.65 (dd, , J = ~1, 11 Hz, 7 × H-6b), 3.56 (m, 7H, 7 × H-5), 3.48 (dd, J = 9.2, 9.2 Hz, 7 × H-4), 3.24 (dd, J = 9.6, 3.5 Hz, 7H, 7 × H-2), 1.24 (t, J = 7.0 Hz, 21H, 7 × OCHaHbC*H*$_3$), 0.87 (s, 63H, 7 × SiBu-*t*), 0.04 (s, 21H, 7 × SiMe), 0.03 (s, 21H, 7 × SiMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.21 (C-1), 82.16 (C-4), 80.49 (C-2), 73.26 (C-3), 71.61 (C-5), 67.97 (O*C*HaHb), 61.68 (C-6), 25.86 (SiBu-*t*), 18.23 (SiBu-*t*), 15.32 (OCHaHb*C*H$_3$), -5.09 (SiMe), -5.24 (SiMe).

Per-2-*O*-allyl-6-*O*-*tert*-butyldimethylsilyl–β-cyclodextrin (21)

To a solution of **19** (2.00 g, 1.04 mmol) in anhydrous DMF (10 mL), was added NaH (60% in mineral oil, 0.31 g, 8.0 mmol) in portions at 0 °C, and the reaction was allowed to warm to room temperature. After 2 hrs, the reaction mixture was cooled to 0 °C again and allyl bromide (0.63 mL, 7.3 mmol) was added dropwise. The reaction was allowed to warm to room temperature and left overnight. The mixture was diluted with CH_2Cl_2 (40 mL) and the organic solution was washed with H_2O (1 × 60 mL) and saturated brine (1 × 60 mL) and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the crude mixture was purified by column chromatography on silica gel using acetone – hexane (5 : 95) as eluent to afford pure **21** as a white solid (0.89 g, 39% yield). R_f 0.23 (EtOAc : hexane, 20 : 80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (dddd, J = 17.1, 10.3, 6.8, 5.4 Hz, 7H, 7 × CH_2C*H*=CH_2), 5.36– 5.28 (m, 7H, 7 × CH_2CH=C*Ha*Hb), 5.25–5.20 (m, 7H, 7 ×

CH_2CH=CHa*Hb*), 4.92 (d, *J* = 3.5 Hz, 7H, 7 × H-1), 4.90 (s, 7H, 7 × OH), 4.54– 4.46 (m, 7H, 7 × $CH_aH_bCH=CH_2$), 4.258 – 4.22 (m, 7H, 7 × $CH_aH_bCH=CH_2$), 3.98 (dd, *J* = 9.0, 9.0 Hz, 7H, 7 × H-3), 3.94 (dd, *J* = 11.1, 2.7 Hz, 7H, 7 × H-6a), 3.71 – 3.65 (m, 7H, 7 × H-6b), 3.58 (m, 7H, 7 × H-5), 3.53 (dd, *J* = 9.6, 9.6 Hz, 7H, 7 × H-4), 3.33 (dd, *J* = 9.6, 3.5 Hz, 7H, 7 × H-2), 0.90 (s, 63H, 7 × Si $C(CH_3)_3$), 0.06 (s, 21H, 7 × SiMe), 0.05 (s, 21H, 7 × SiMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.42 ($CH_2CH=CH_2$), 118.17 ($CH_2CH=CH_2$), 101.19 (C-1), 82.14 (C-4), 79.56 (C-2), 73.27 (C-3), 73.23 ($CH_2CH=CH_2$), 71.68 (C-5), 25.90 ($SiC(CH_3)_3$), 18.24($SiC(CH_3)_3$), (-5.06 (SiMe), -5.21 (SiMe).

Per-2-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-β-cyclodextrin (22)

To a solution of **19** (2.00 g, 1.04 mmol) in anhydrous DMF (10 mL), was added NaH (60% in mineral oil, 0.31 g, 8.0 mmol) in small portions at 0 °C, and the reaction was allowed to warm to room temperature. After 2 hrs, the reaction mixture was cooled to 0 °C again and benzyl bromide (0.86 mL, 7.3 mmol) was added dropwise. The mixture was warmed up to room temperature and left stirring overnight. CH_2Cl_2 (40 mL) was added and the organic solution was washed with H_2O (1 × 60 mL), saturated brine (1 × 60 mL) and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the crude mixture was further purified by column chromatography on silica gel using acetone – hexane (5 : 95) as eluent to obtain pure compound **22**[15] as a white solid (0.87 g, 32% yield). R_f 0.42 (EtOAc : hexane, 20 : 80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (d, *J* = 11.7 Hz, 7H, 7 × Ha_Bn), 4.94 (s, 7H, 7 × OH), 4.80 (d, *J* = 3.6 Hz, 7H, 7 × H-1), 4.75 (d, *J* = 11.8, 7H, 7 × Hb_Bn), 4.04 (dd, *J* = 9.3, 9.3 Hz, 7H, 7 × H-3), 3.89 (dd, *J* = 11.3, 2.9 Hz, 7H, 7 × H-6a), 3.64 (dd, *J* = 1.3, 11.3 Hz, 7H, 7 × H-6b), 3.58 (m, 7H, 7 × H-5), 3.47 (dd, *J* = 9.2, 9.2 Hz, 7H, 7 × H-4), 3.36 (dd, *J* = 9.6, 3.6 Hz, 7H, 7 × H-2), 0.88 – 0.85 (m, 63H, 7 × $SiC(CH_3)_3$), 0.01 (s, 21H, 7 × SiMe), -0.00 (s, 21H, 7 × SiMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.80, 128.71, 128.34, 127.86 (Ar), 101.26 (C-1), 82.13 (C-4), 79.10 (C-2), 73.98 (CH_2Ph), 73.61 (C-3), 71.70 (C-5), 61.76 (C-6), 25.92 ($SiC(CH_3)_3$),18.27($SiC(CH_3)_3$), -5.10 (SiMe), -5.23 (SiMe).

Per-6-bromo-6-deoxy–2-*O*-ethyl-β-cyclodextrin (23)

Triphenylphosphine (103 mg, 0.39 mmol) was dissolved in anhydrous CH_2Cl_2 (3 mL) under argon. Bromine (20 μL, 0.39 mmol) was added dropwise at 0 °C to produce a slight reddish solution. A few crystals of triphenylphosphine were added until the solution became

colourless. A white precipitate formed and the ice bath was removed. A solution of compound **20** (60 mg, 0.028 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added dropwise, and the reaction was left stirring overnight at room temperature. EtOAc (20 mL) was added and the organic solution was washed with saturated $NaHCO_3$ (10 mL), saturated brine (10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel using 20% EtOAc – toluene as eluent to afford **23** which is contaminated with triphenylphosphine oxide. Pure **23** was obtained by stirring the mixture in ethanol (28 mg, 56% yield). R_f 0.30 (EtOAc : toluene, 50 : 50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 7H, 7 × OH)), 4.99 (d, J = 3.4 Hz, 7H, 7 × H-1), 4.06 (dq, J = 7.1, 9.3 Hz, 7H, 7 × OC*Ha*Hb), 3.93 (dd, J = 9.1, 9.1 Hz, 7H, 7 × H-3), 3.89 – 3.80 (m, 14H, 7 × H-5 + 7 × H-6a), 3.77 – 3.66 (m, 14H, 7 × OCHa*Hb* + 7 × H-6b), 3.39 (dd, J = 9.6, 3.5 Hz, 7H, 7 × H-2), 3.33 (dd, J = 9.0, 9.0 Hz, 7H, 7 × H-4), 1.23 (t, J = 7.0 Hz, 21H, 7 × OCHaHbCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.80 (C-1), 86.08 (C-4), 79.84 (C-2), 72.84 (C-3), 70.54 (C-5), 68.53 (OCHaHb), 33.29 (C-6), 15.23 (CH_3).

Per-2-*O*-allyl-6-bromo-6-deoxy–β-cyclodextrin (24)

Triphenylphosphine (41 mg, 0.16 mmol) was dissolved in anhydrous CH_2Cl_2 (0.5 mL) under argon. Bromine (8 μL, 0.16 mmol) was added dropwise at 0 °C to produce a slight reddish solution. PPh_3 was added until the solution became colourless again. A white precipitate formed and the ice bath was removed. A solution of compound **21** (50 mg, 0.02 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added dropwise, and the reaction was left stirring overnight at room temperature. EtOAc (20 mL) was added and the organic solution was washed with saturated $NaHCO_3$ (20 mL), H_2O (1 × 60 mL), saturated brine (1 × 60 mL) and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the residue was suspended in EtOH (5 mL) by sonication; the precipitate was collected by filtration to afford compound **24**[15] as a white solid (19 mg, 46% yield). R_f 0.25 (acetone : hexane, 70 : 30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (dddd, J = 17.1, 10.3, 6.8, 5.4 Hz, 7H, 7 × CH_2C*H*=CH_2), 5.38 – 5.23 (m, 14H, 7 × CH_2CH=C*Ha*Hb), 5.00 (d, J = 3.6 Hz, 7H, 7 × H-1), 4.97 (s, 7H, 7 × OH), 4.55– 4.47 (m, 7H, 7 × C*H*aHbCH=CH_2), 4.30– 4.22 (m, 7H, 7 × CHa*H*bCH=CH_2), 3.98 (dd, J = 9.1, 9.1 Hz, 7H, 7 × H-3), 3.91 – 3.81 (m, 14H, 7 × H-5 + 7 × H-6a), 3.72 (dd, J = 11.5, 6.1 Hz, 7H, 7 × H-6b), 3.48 (dd, J = 9.7, 3.6 Hz, 7H, 7 × H-2), 3.35 (dd, J = 9.1, 9.1 Hz, 7H, 7 × H-4). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.81 (CH_2*C*H=CH_2), 119.07 (CH_2CH=*C*H_2),

101.79 (C-1), 86.06 (C-4), 78.74 (C-2), 73.62 (*C*H_2CH=CH_2), 72.89 (C-3), 70.58 (C-5), 33.18 (C-6).

Per-2-*O*-benzyl-6-bromo-6-deoxy–β-cyclodextrin (25)

Method 1: Compound **22** (100 mg, 0.04 mmol) was reacted with triphenylphosphine (72 mg, 0.27 mmol) and bromine (15 μL, 0.27 mmol) in a similar fashion as above to afford pure **25** (28 mg, 33% yield).

Method 2: Compound **22** (250 mg, 0.097 mmol) was reacted with triphenylphosphine (358 mg, 1.36 mmol) and bromine (70 μL, 1.36 mmol) in a similar fashion as above. After stirring at room temperature for 6 hrs, the desired compound **25** (202 mg, 94% yield) was isolated by column chromatography using 8→10% EtOAc – toluene as an eluent. R_f 0.9 (EtOAc : hexane, 50 : 50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 35H, 7 × Ph), 5.04 (s, 7H, 7 × OH), 5.01 (d, J = 11.7 Hz, 7H, 7 × Ha_Bn), 4.81 (d, J = 3.7 Hz, 7H, 7 × H-1), 4.77 (d, J = 11.7 Hz, 7H, 7 × Hb_Bn), 4.03 (dd, J = 9.2, 9.2 Hz, 7H, 7 × H-3), 3.83 (ddd, J = 9.6, 5.8, 1.4 Hz, 7H, 7 × H-5), 3.78 (dd, J = 2.0, 11.4 Hz, 7H, 7 × H-6a), 3.63 (dd, J = 6.1, 11.4 Hz, 7H, 7 × H-6b), 3.48 (dd, J = 9.6, 3.6 Hz, 7H, 7 × H-2), 3.28 (dd, J = 9.1, 9.1 Hz, 7H, 7 × H-4). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.10, 129.02, 128.55, 128.34 (Ar), 101.83 (C-1), 85.98 (C-4), 78.06 (C-2), 74.34 (*C*H_2Ph), 73.19 (C-3), 70.58 (C-5), 33.06 (C-6).

Per-6-deoxy-2-*O*-ethyl-6-octadecylthio–β-cyclodextrin (6)

Compound **23** (50 mg, 28 μmol) was dissolved in a mixture of anhydrous DMF (1.5 mL) and THF (1 mL) under argon; 1-octadecanethiol (113 mg, 0.40 mmol) and Cs_2CO_3 (125 mg, 0.40 mmol) were added and the reaction was heated to 60 °C for 2 days. Then the temperature was raised to 80 °C for 1 hr. The reaction mixture was diluted with EtOAc (20 mL) and washed with H_2O (1 × 40 mL), saturated brine (2 × 40 mL) and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the crude mixture was purified by column chromatography on silica gel using EtOAc – toluene (15 : 85) as eluent to afford pure compound **6** as a white solid (58 mg, 64% yield). R_f 0.24 (EtOAc : Toluene, 20 : 80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (s, 7H, 7 × OH-3), 4.97 (d, J = 3.5 Hz, 7H, 7 × H-1), 4.06 (dq, J = 7.1, 9.3 Hz, 7H, 7 × OC*Ha*HbCH_3), 3.97 – 3.80 (m, 14H, 7 × H-3 + 7 × H-5), 3.72 (dq, J = 7.1, 9.3 Hz, 7 × OCHa*Hb*CH_3), 3.47 (dd, J = 9.2, 9.2 Hz, 7H, 7 × H-4), 3.35 (dd, J = 9.6, 3.4 Hz, 7H, 7 × H-2), 3.00 (dd, J = 2.2, 13.8 Hz, 7 × H-6a), 2.93 (dd, J = 5.3, 13.8 Hz, 7

× H-6b), 2.60 (t, *J* = 7.4 Hz, 14H, S-C*H*$_2$), 1.63-1.53 (m, 14H, 7 × S-CH$_2$C*H*$_2$), 1.47 – 1.16 (m, 231H, 7 × S-CH$_2$CH$_2$(C*H*$_2$)$_{15}$ + 7 × OCHaHbC*H*$_3$), 0.89 (t, *J* = 6.7 Hz, 21H, 7 × CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 101.56 (C-1), 85.83 (C-4), 80.24 (C-2), 73.09 (C-3), 70.81 (C-5), 68.25 (OCHaHb), 33.86 (C-6), 33.66 (S-CH$_2$), 31.92, 29.91, 29.81, 29.80, 29.78, 29.75, 29.67, 29.48, 29.37, 29.09, 22.67, 15.26 (OCHaHb*C*H$_3$), 14.09 (CH$_3$). *m/z* (HRMS MALDI-TOF) calcd for [C$_{182}$H$_{350}$O$_{28}$S$_7$ + Na]$^+$ 3231.3906, found: 3231.4020.

Per-2-*O*-allyl-6-deoxy-6-octadecylthio–β-cyclodextrin (7)

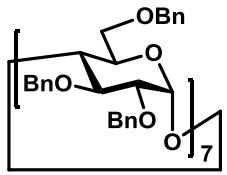
To a solution of compound **24** (50 mg, 0.03 mmol) and 1-octadecanethiol (130 mg, 0.45 mmol) in a mixture of DMF (1 mL) and THF (0.5 mL) under argon, was added a solution of KOBu-*t* (42 mg, 0.38 mmol) in DMF (1 mL) at room temperature, and the solution was left stirring at 70 °C overnight. The reaction mixture was diluted with EtOAc (20 mL) and washed with H$_2$O (1 × 40 mL), saturated brine (2 × 40 mL) and dried over anhydrous Na$_2$SO$_4$. After concentration under reduced pressure, the crude mixture was purified by column chromatography on silica gel using acetone – hexane (1 : 99) as eluent to afford pure compound **7** as a white solid (35 mg, 39% yield). R_f 0.33 (acetone : hexane, 10 : 90). [α]$_D$ +55.9 (*c* 1.0, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.96 (dddd, *J* = 17.2, 10.3, 6.9, 5.4 Hz, 7H, 7 × CH$_2$C*H*=CH$_2$), 5.36–5.30 (m, 7H, 7 ×CH$_2$CH=C*H*aHb), 5.26–5.20 (m, 7H, 7 ×CH$_2$CH=CHa*H*b), 4.97 (s, 7H, 7 × OH), 4.96 (d, *J* = 3.9 Hz, 7H, 7 × H-1), 4.50 (dd, *J* = 12.5, 5.4 Hz, 7H, 7 × C*H*aHbCH=CH$_2$), 4.26 (dd, *J* = 12.5, 6.9 Hz, 7H, 7 × CHa*H*bCH=CH$_2$), 3.94 (dd, *J* = 9.2, 9.2 Hz, 7H, 7 × H-3), 3.88 (ddd , *J* = 9.4, 5.2, 3.3 Hz, 7H, 7 × H-5), 3.48 (dd, *J* = 9.1, 9.1 Hz, 7H, 7 × H-4), 3.42 (dd, *J* = 9.6, 3.6 Hz, 7H, 7 × H-2), 3.01 (dd, *J* = 13.7, 2.6 Hz, 7H, 7 × H-6a), 2.94 (dd, *J* = 13.9, 5.5 Hz, 7H, 7 × H-6b), 2.61 (t, *J* = 7.4 Hz, 14H, 7 × SC*H*$_2$-), 1.64–1.54 (m, 14H, 7 × SCH$_2$C*H*$_2$-), 1.43 – 1.33 (m, 14H, 7 × SCH$_2$CH$_2$C*H*$_2$-), 1.32 – 1.24 (m, 196H, alkyl), 0.90 (t, *J* = 6.9 Hz, 21H, 7 × CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.16 (CH$_2$*C*H=CH$_2$), 118.53 (CH$_2$CH=*C*H$_2$), 101.54 (C-1), 85.84 (C-4), 79.22 (C-2), 73.38 (*C*H$_2$CH=CH$_2$), 73.12 (C-3), 70.85 (C-5), 33.71 (C-6), 31.93 (-S*C*H$_2$-), 29.94, 29.82, 29.77, 29.68, 29.50, 29.37, 29.10, 22.68, 14.09. *m/z* (HRMS MALDI-TOF) calcd for [C$_{189}$H$_{350}$O$_{28}$S$_7$ + Na]$^+$ 3315.3901, found 3315.3901.

Per-2-*O*-benzyl-6-deoxy-6-octadecylthio–β-cyclodextrin (8)

Compound **25** (100 mg, 45 μmol) was reacted with 1-octadecanethiol (185.6 mg, 0.63 mmol)

and Cs_2CO_3 (207 mg, 0.63 mmol) in a mixture of anhydrous DMF (1.5 mL) and THF (1.0 mL) a similar fashion as **23**. The desired compound **8** was obtained as a white solid by column chromatography on silica gel using EtOAc – toluene (4 : 96) as eluent (133 mg, 80% yield). R_f 0.36 (EtOAc : hexane, 10 : 90). $[\alpha]_D$ +38.5 (*c* 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 35H, 7 × Ph), 5.04 (s, 7H, 7 × OH), 4.99 (d, *J* = 11.7 Hz, 7H, 7 × Ha_Bn), 4.81 (d, *J* = 3.7 Hz, 7H, 7 × H-1), 4.77 (d, *J* = 11.8 Hz, 7H, 7 × Hb_Bn), 4.00 (dd, *J* = 9.3, 9.3 Hz, 7H, 7 × H-3), 3.85 (ddd, 2.7, 5.6, 9.3 Hz, 7H, 7 × H-5), 3.44 (dd, *J* = 9.6, 3.5 Hz, 7H, 7 × H-2), 3.39 (dd, *J* = 9.1, 9.1 Hz, 7H, 7 × H-4), 2.96 (dd, *J* = 2.4, 13.6 Hz, 7H, 7 × H-6a), 2.86 (dd, *J* = 5.8, 13.7 Hz, 7H, 7 × H-6b), 2.54 (t, *J* = 7.4, 14H, 7 × -SC*H*$_2$-), 1.55–1.48 (m, 14H, 7 × -SCH_2CH_2-), 1.35 – 1.22 (m, 210H, alkyl), 0.89 (t, *J* = 6.6 Hz, 21H, 7 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.48, 128.90, 128.40, 128.05 (Ar), 101.60 (C-1), 85.86 (C-4), 78.58 (C-2), 74.07 (*C*H_2Ph), 73.45 (C-3), 70.80 (C-5), 33.85 (C-6), 33.64 (-S*C*H_2-), 31.93, 29.91, 29.81, 29.79, 29.75, 29.69, 29.48, 29.37, 29.08, 22.68, 14.09. *m/z* (HRMS MALDI-TOF) calcd for $[C_{217}H_{364}O_{28}S_7 + Na]^+$ 3665.4996, found 3665.4954.

^{1}H NMR in $CDCl_3$ (400 MHz)



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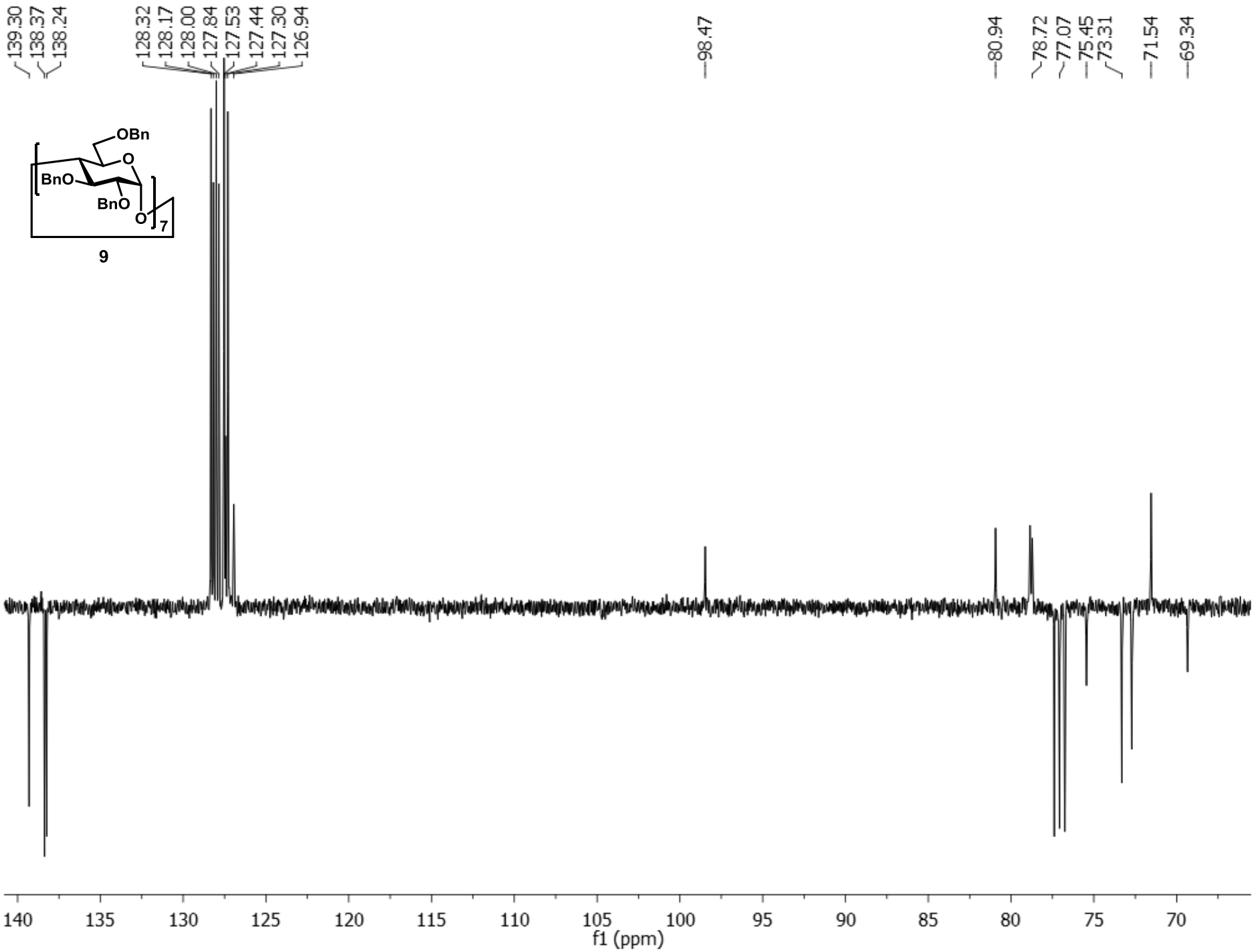
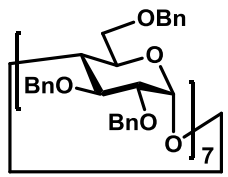
^{13}C APT NMR in $CDCl_3$ (100 MHz)



^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



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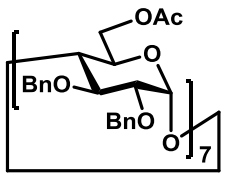
^{1}H NMR in $CDCl_3$ (400 MHz)



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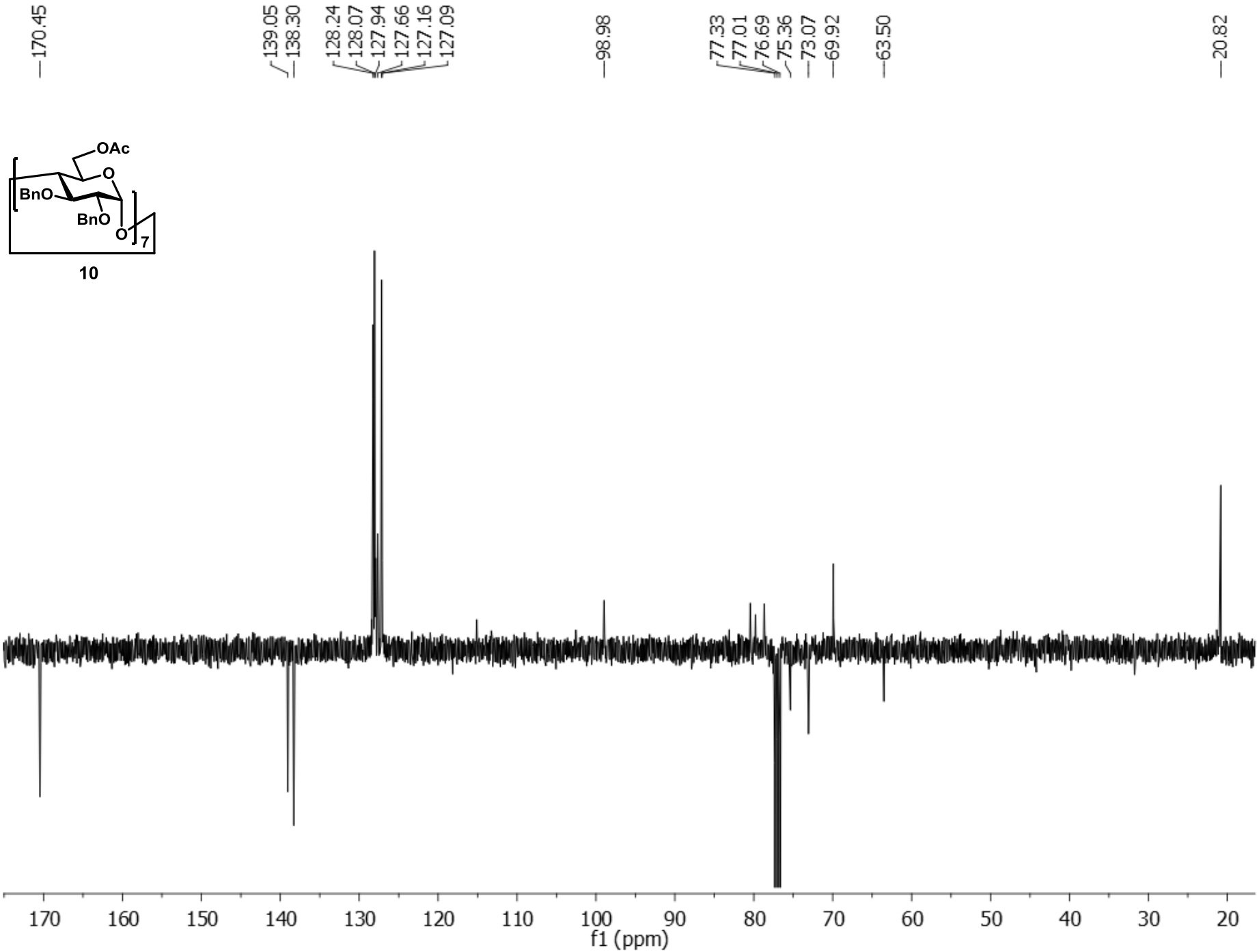
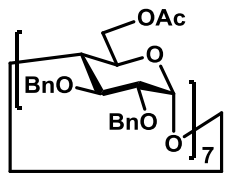


^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



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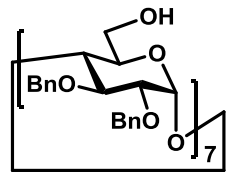
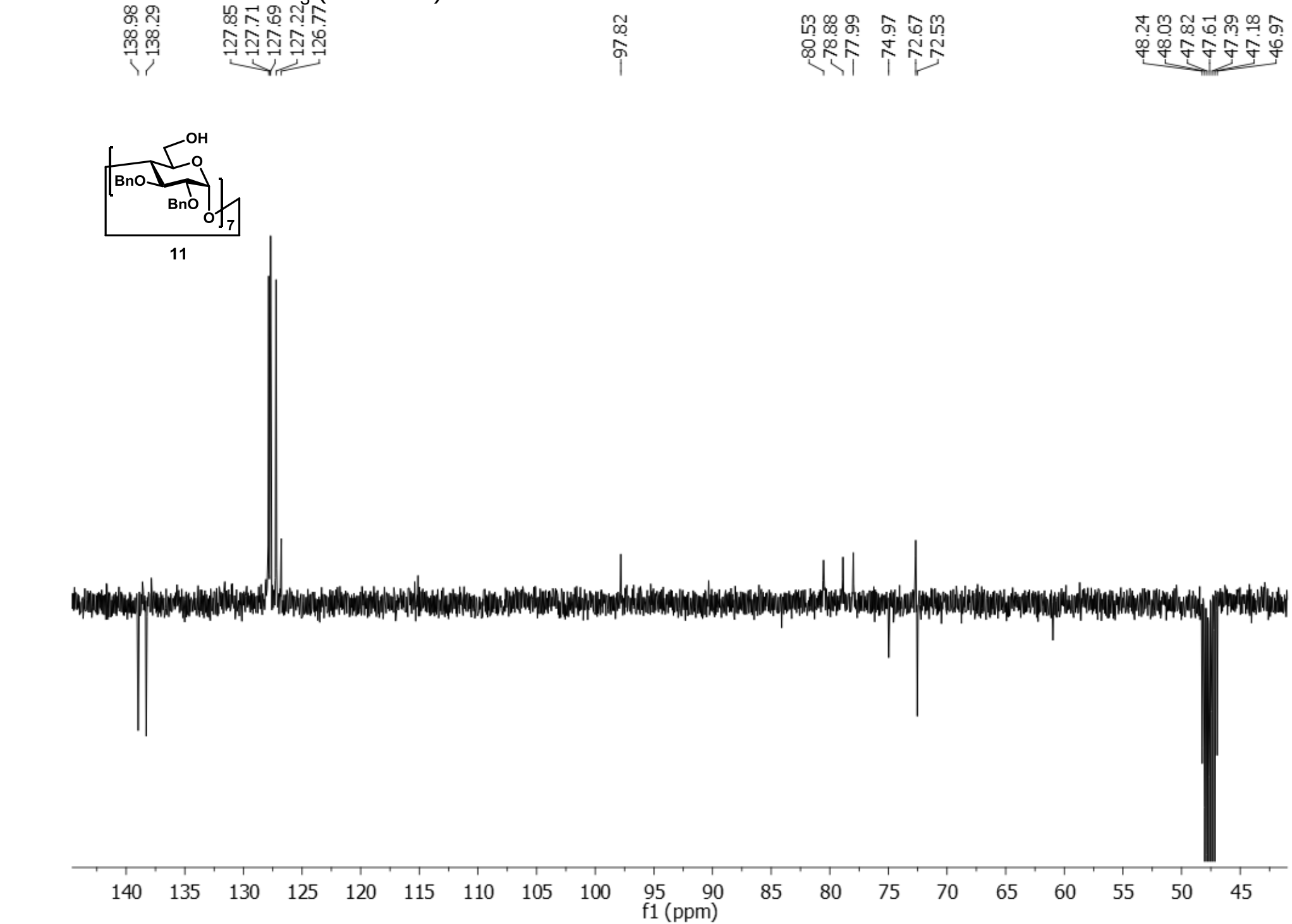
^{1}H NMR in $CDCl_3$ (400 MHz)

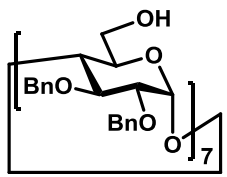


11

^{13}C APT NMR in $CDCl_3$ (100 MHz)

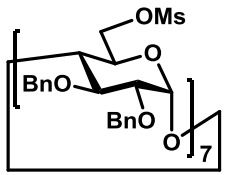


^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



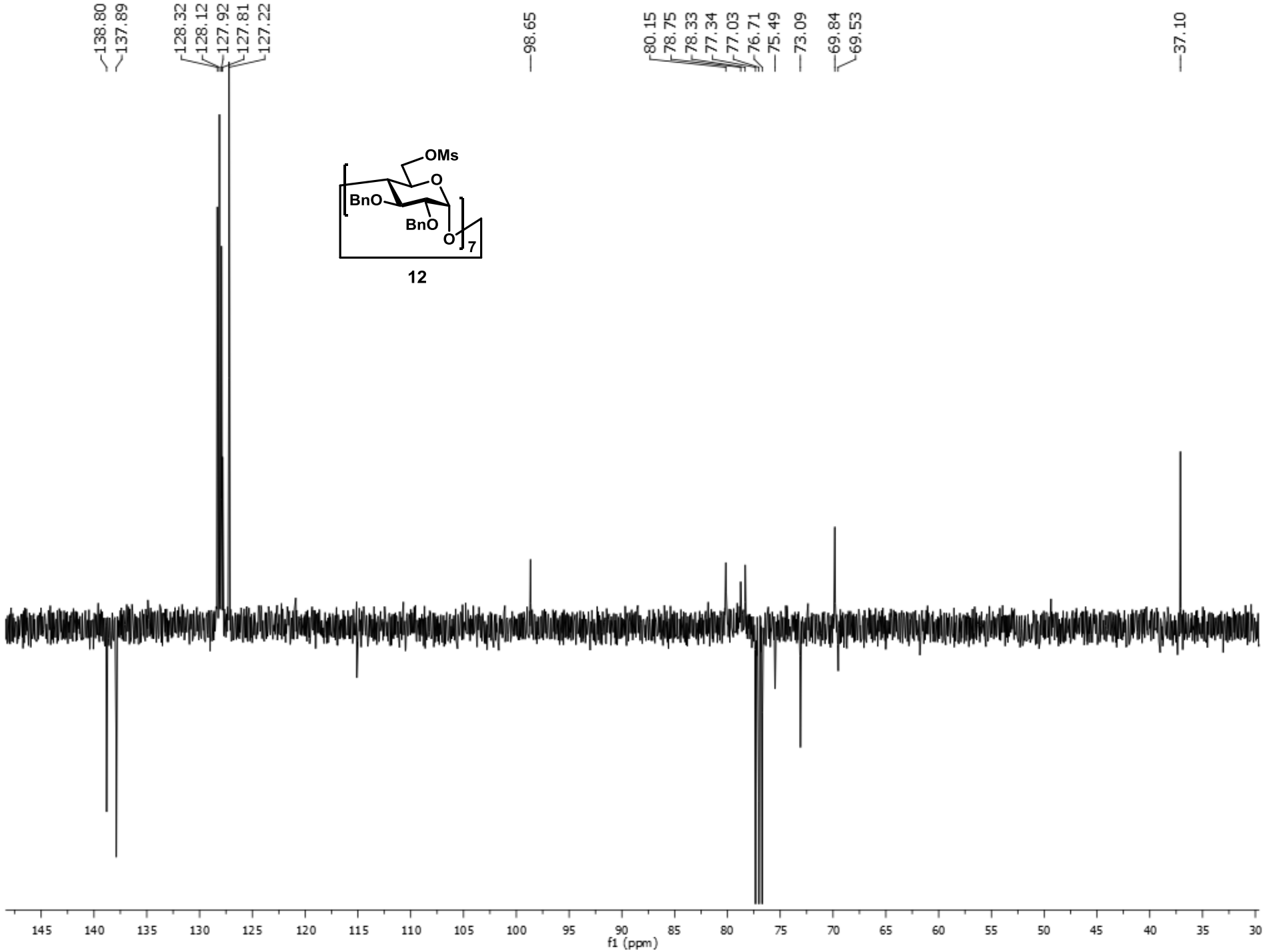
11

^{1}H NMR in $CDCl_3$ (400 MHz)

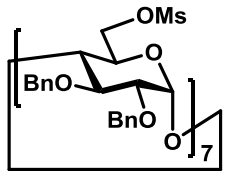


12

^{13}C APT NMR in $CDCl_3$ (100 MHz)



^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



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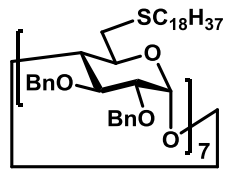
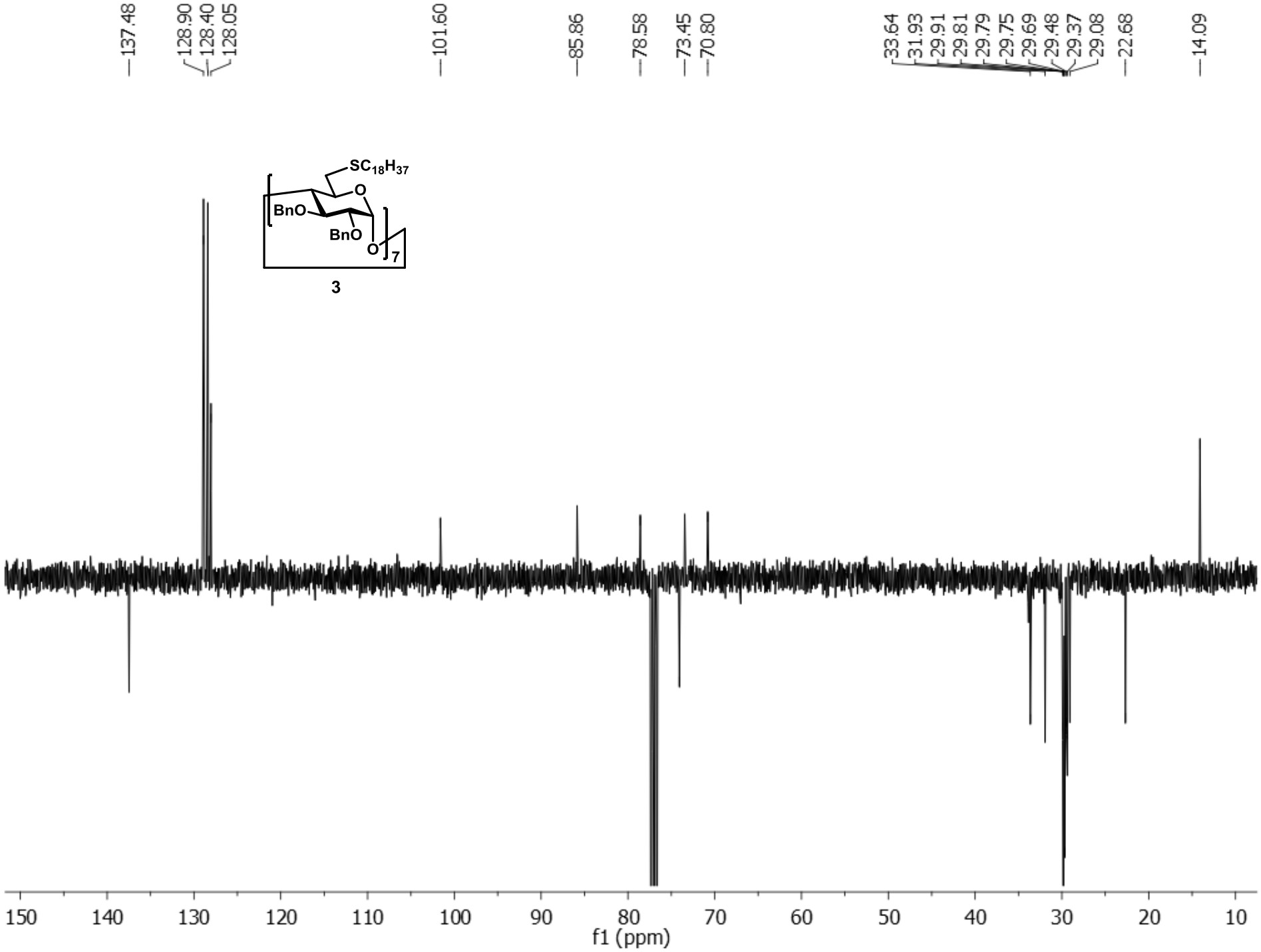
^{1}H NMR in $CDCl_3$ (400 MHz)

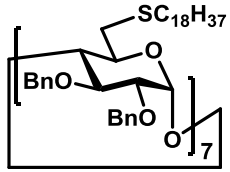


3

^{13}C APT NMR in $CDCl_3$ (100 MHz)



^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



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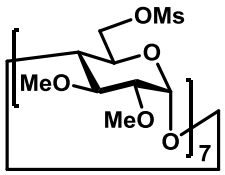
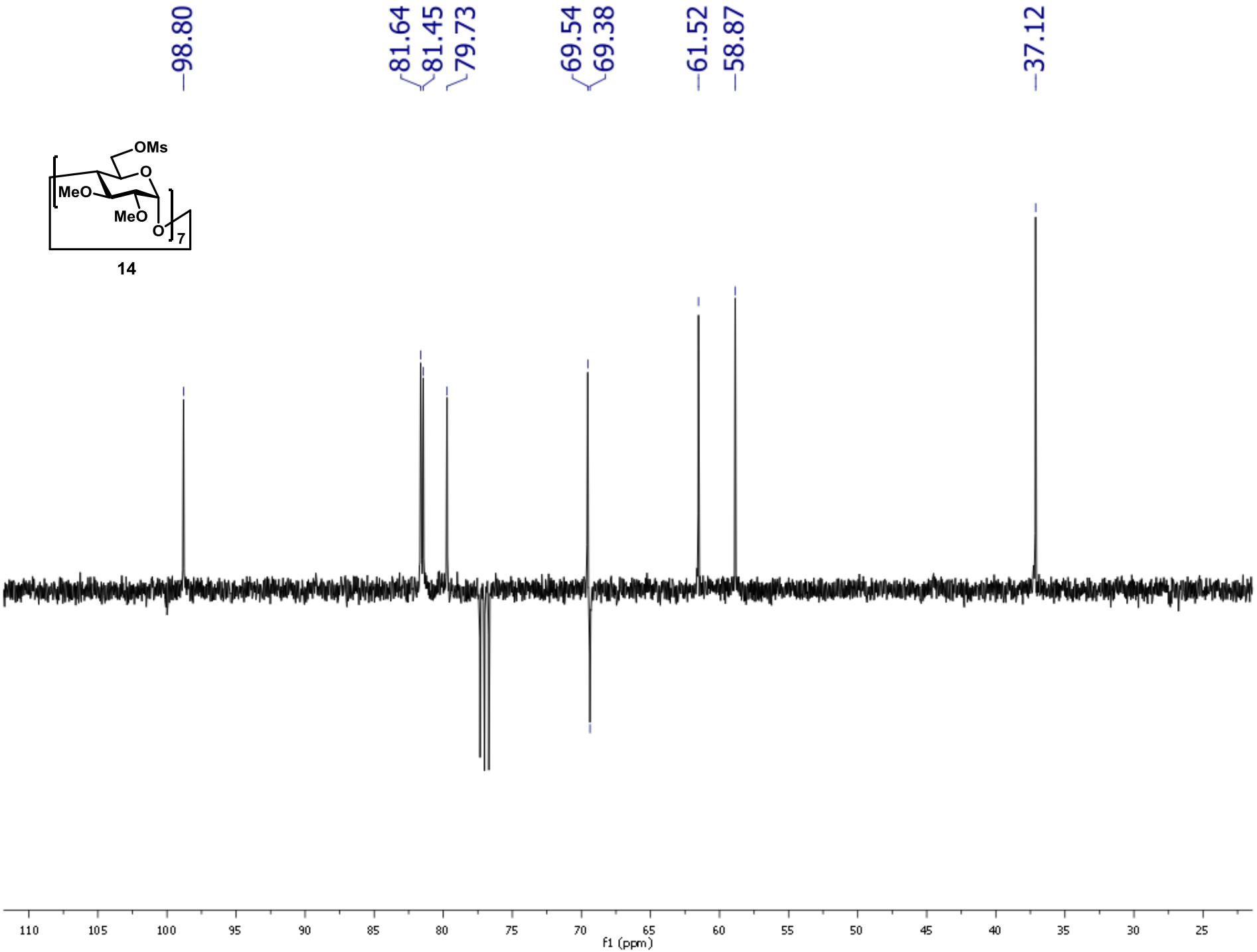
^{1}H NMR in $CDCl_3$ (400 MHz)

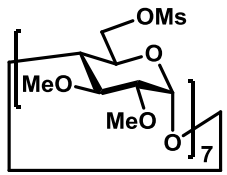


14

^{13}C APT NMR in $CDCl_3$ (100 MHz)

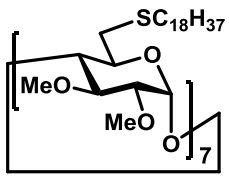


^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



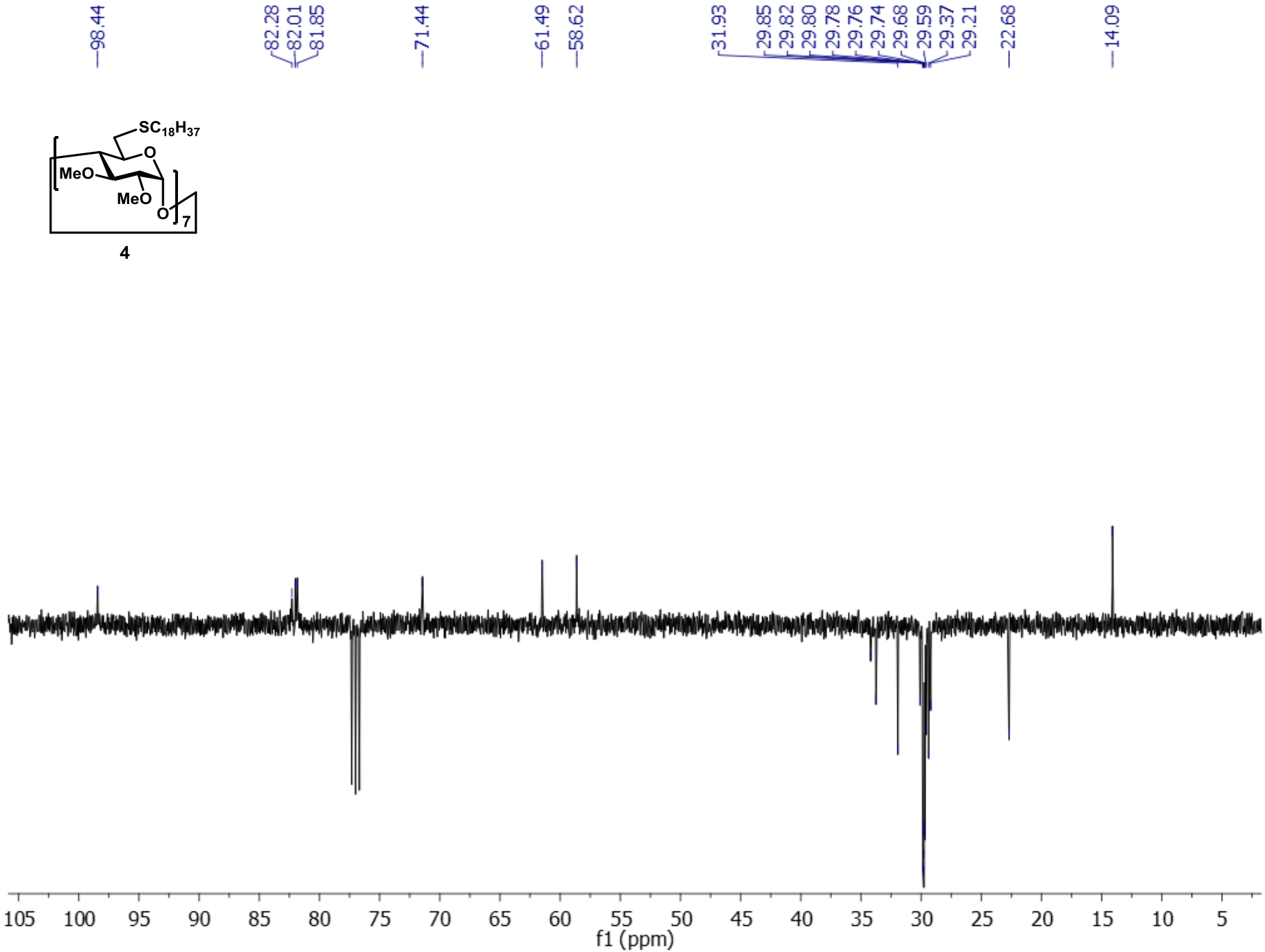
14

^{1}H NMR in $CDCl_3$ (400 MHz)



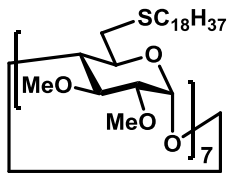
4

^{13}C APT NMR in $CDCl_3$ (100 MHz)



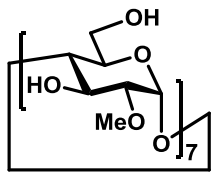
4

^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



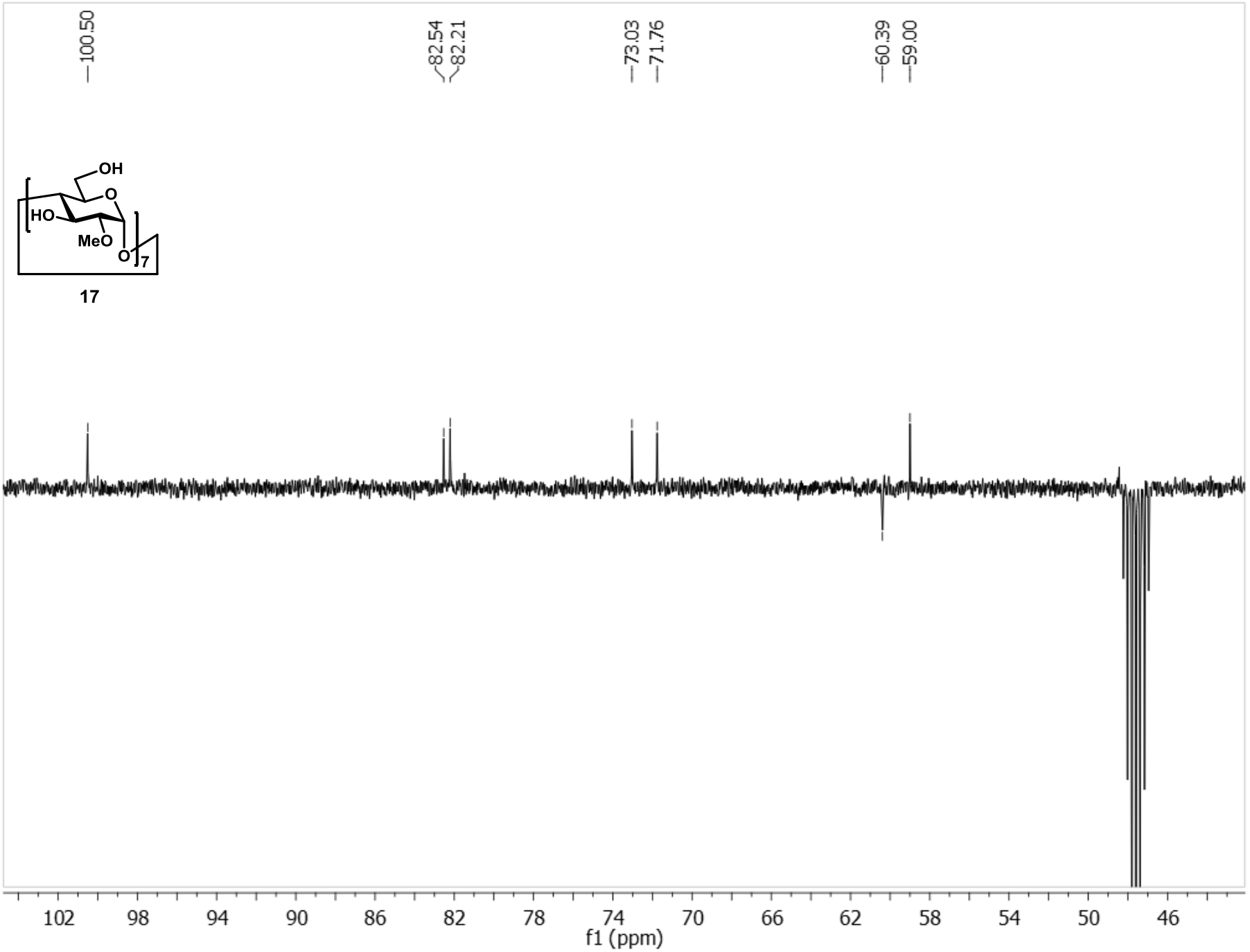
4

^{1}H NMR in $CDCl_3$ (400 MHz)

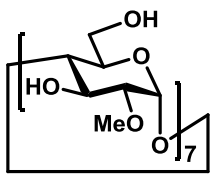


17

^{13}C APT NMR in $CDCl_3$ (100 MHz)

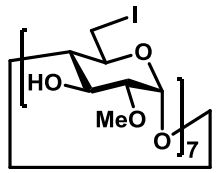


^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



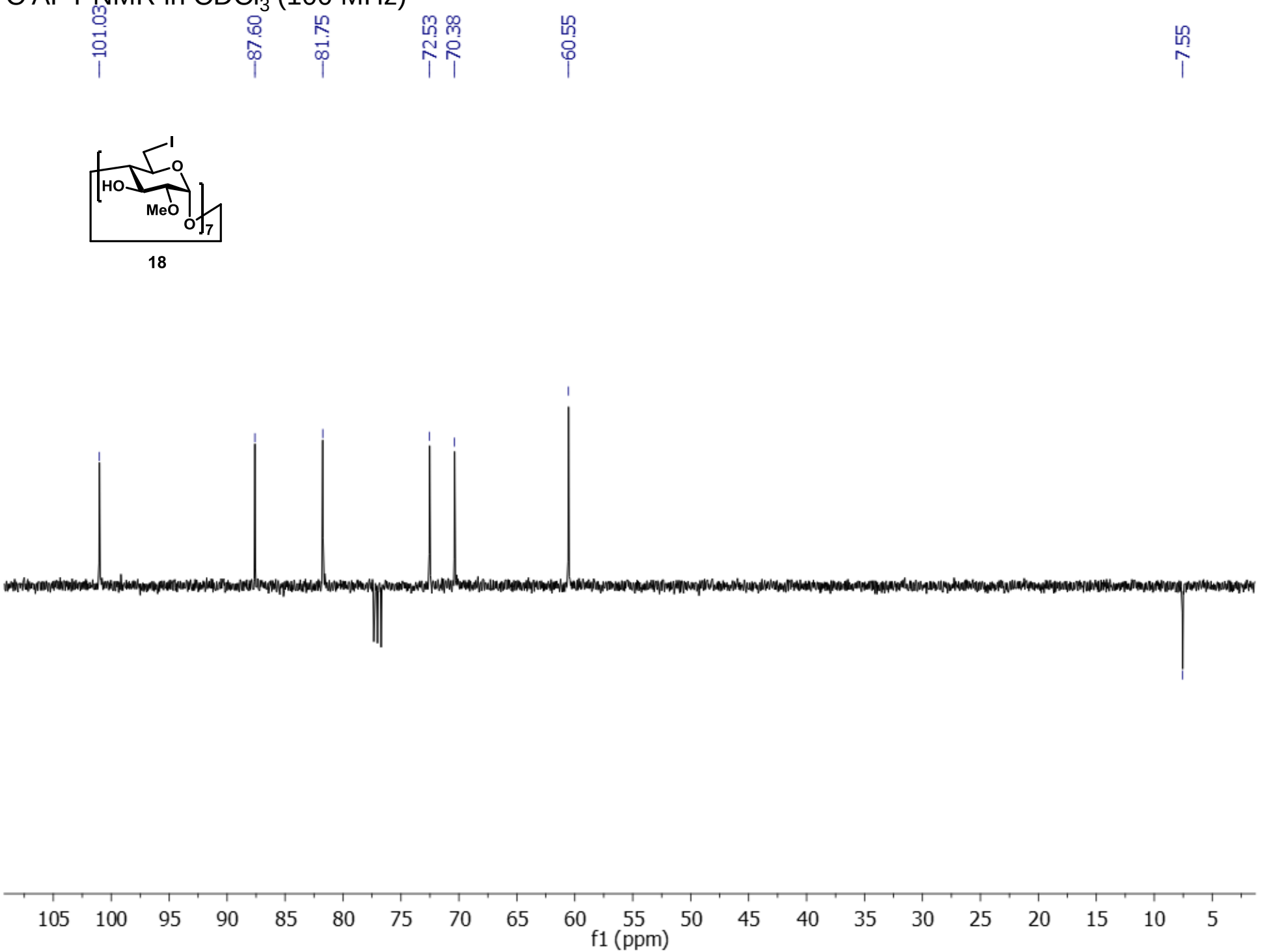
17

^{1}H NMR in $CDCl_3$ (400 MHz)



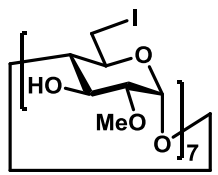
18

^{13}C APT NMR in $CDCl_3$ (100 MHz)



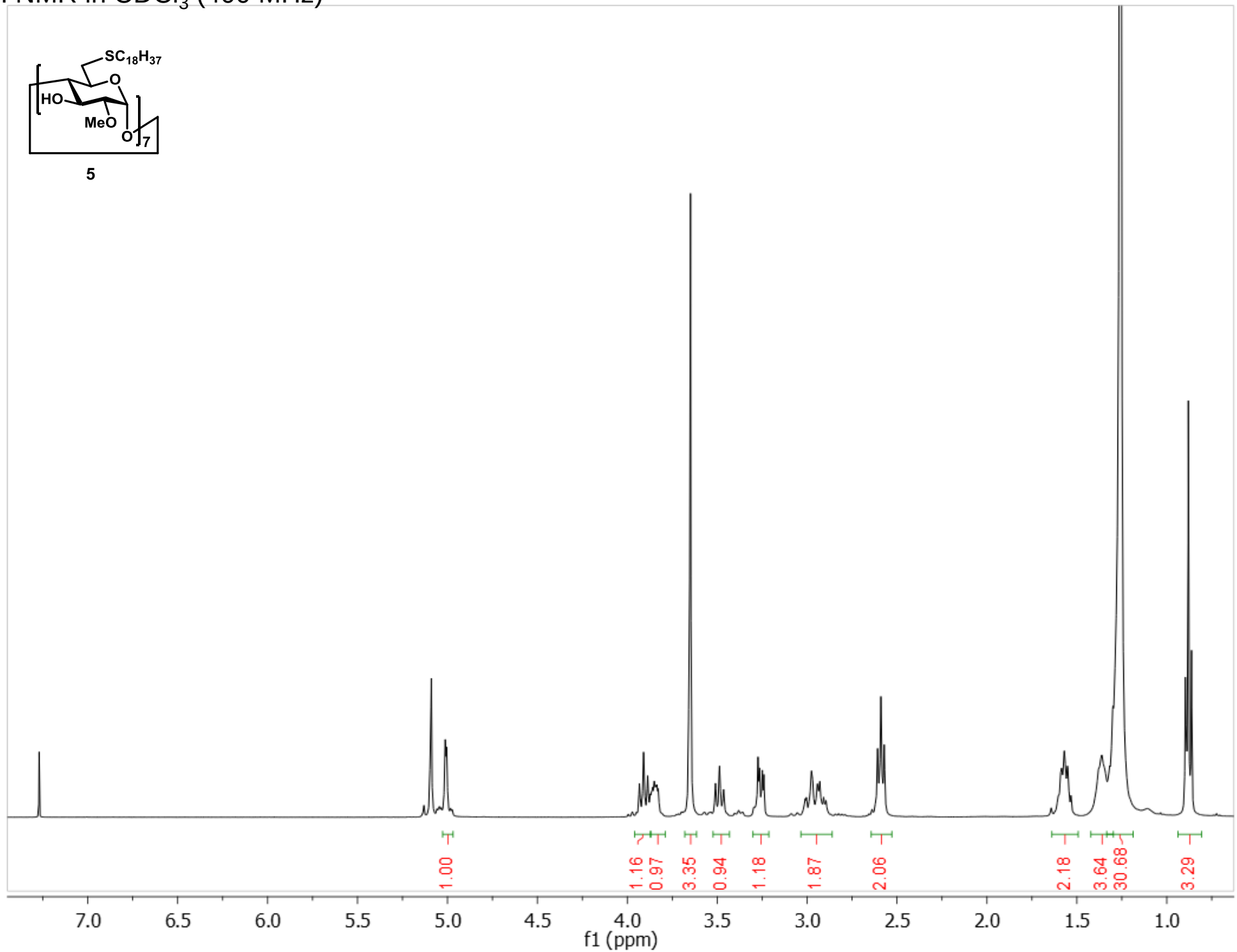
18

^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)

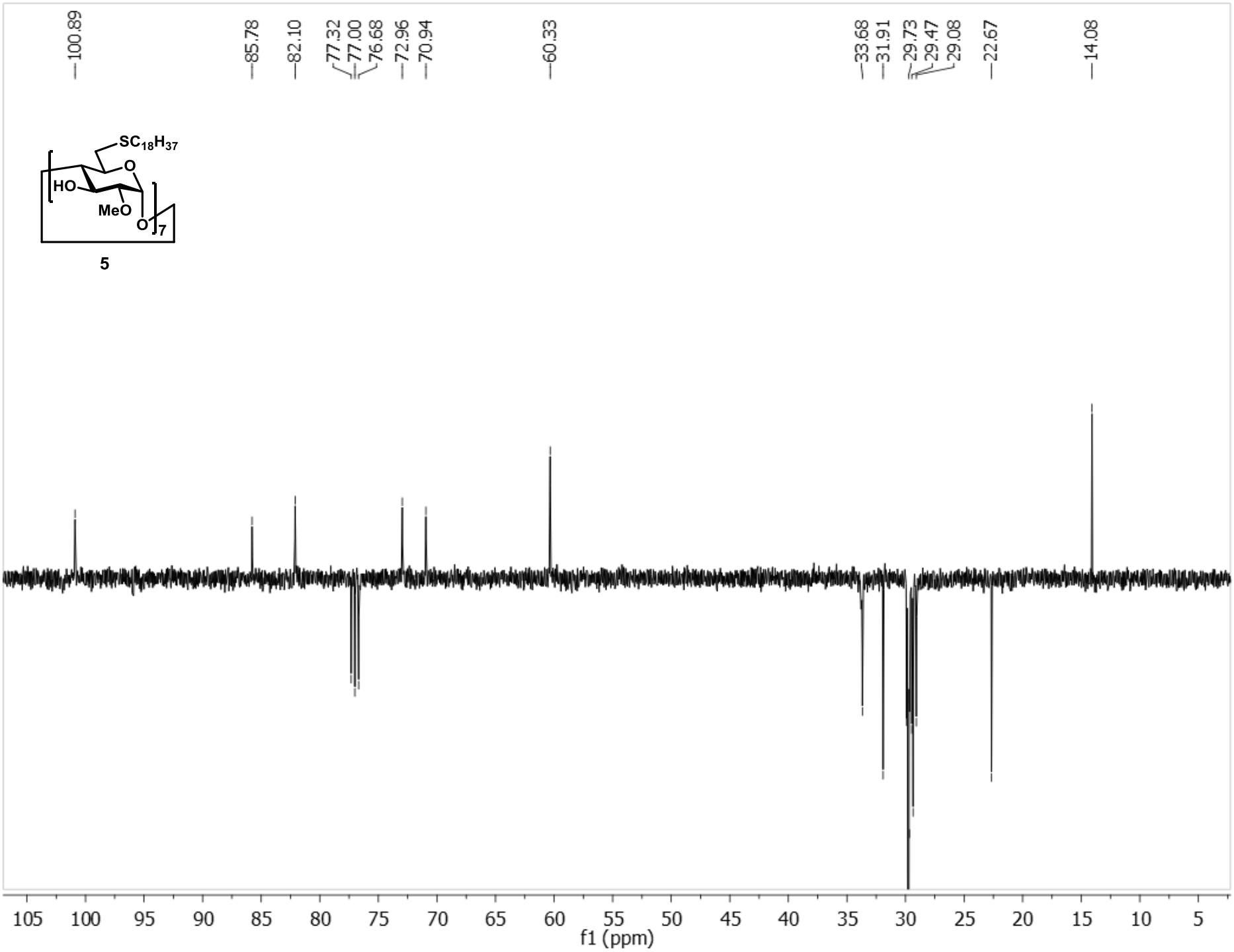


18

^{1}H NMR in $CDCl_3$ (400 MHz)

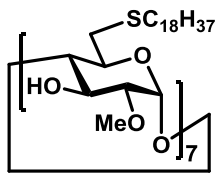


^{13}C APT NMR in $CDCl_3$ (100 MHz)



5

^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



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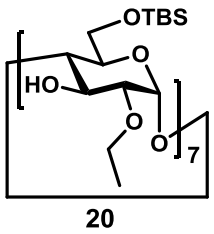
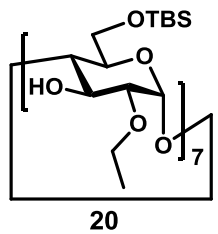
^{1}H NMR in $CDCl_3$ (400 MHz)



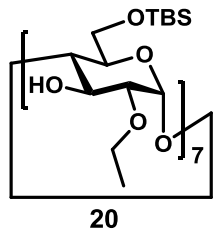
20

^{13}C NMR in $CDCl_3$ (100 MHz)



20

^{1}H-^{1}H gCOSY NMR in $CDCl_3$ (400 MHz)



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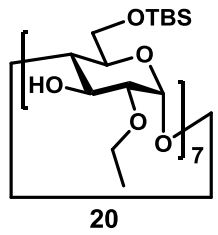
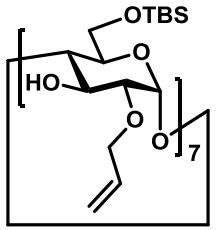
^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



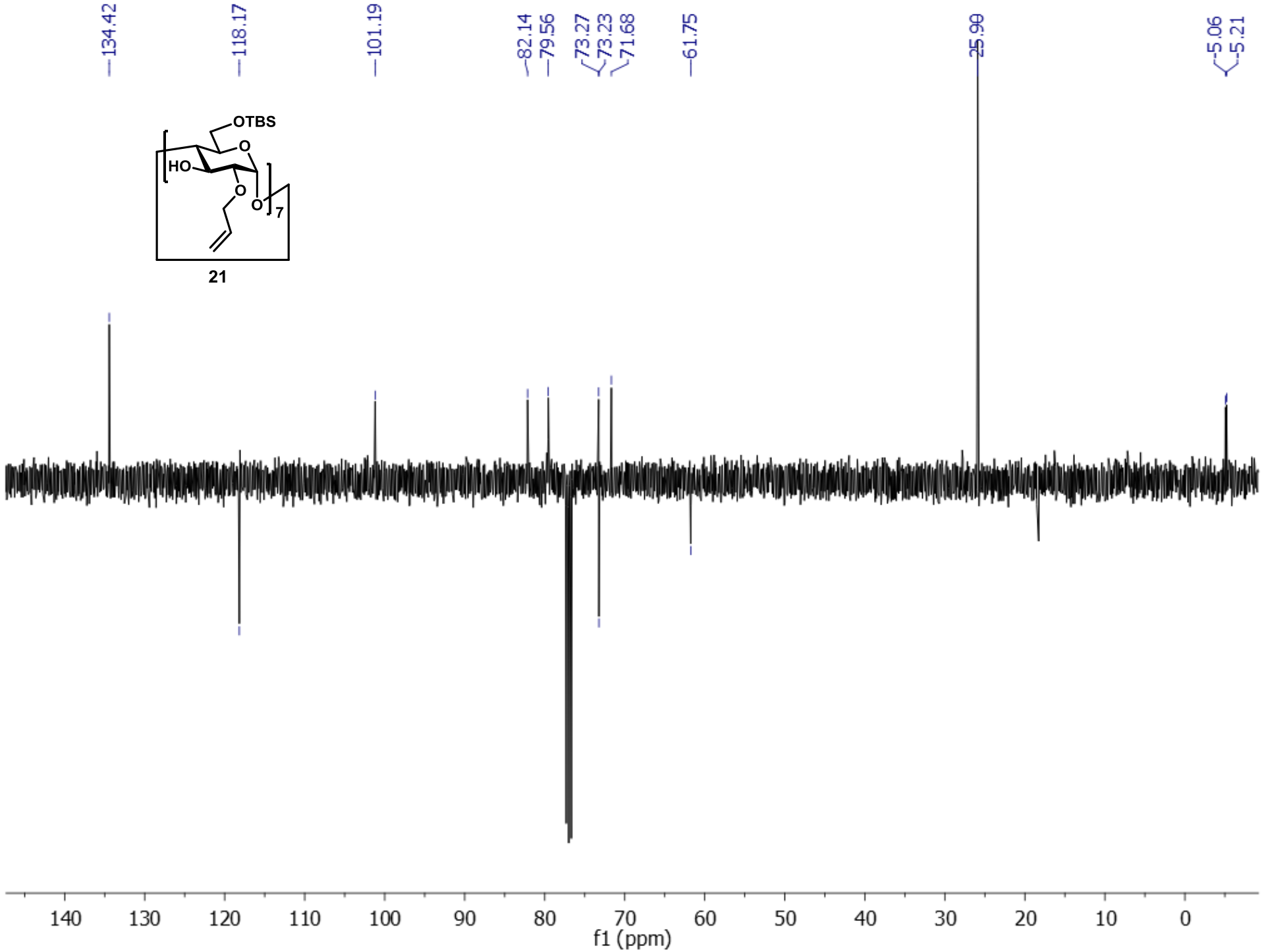
20

^{1}H NMR in $CDCl_3$ (400 MHz)

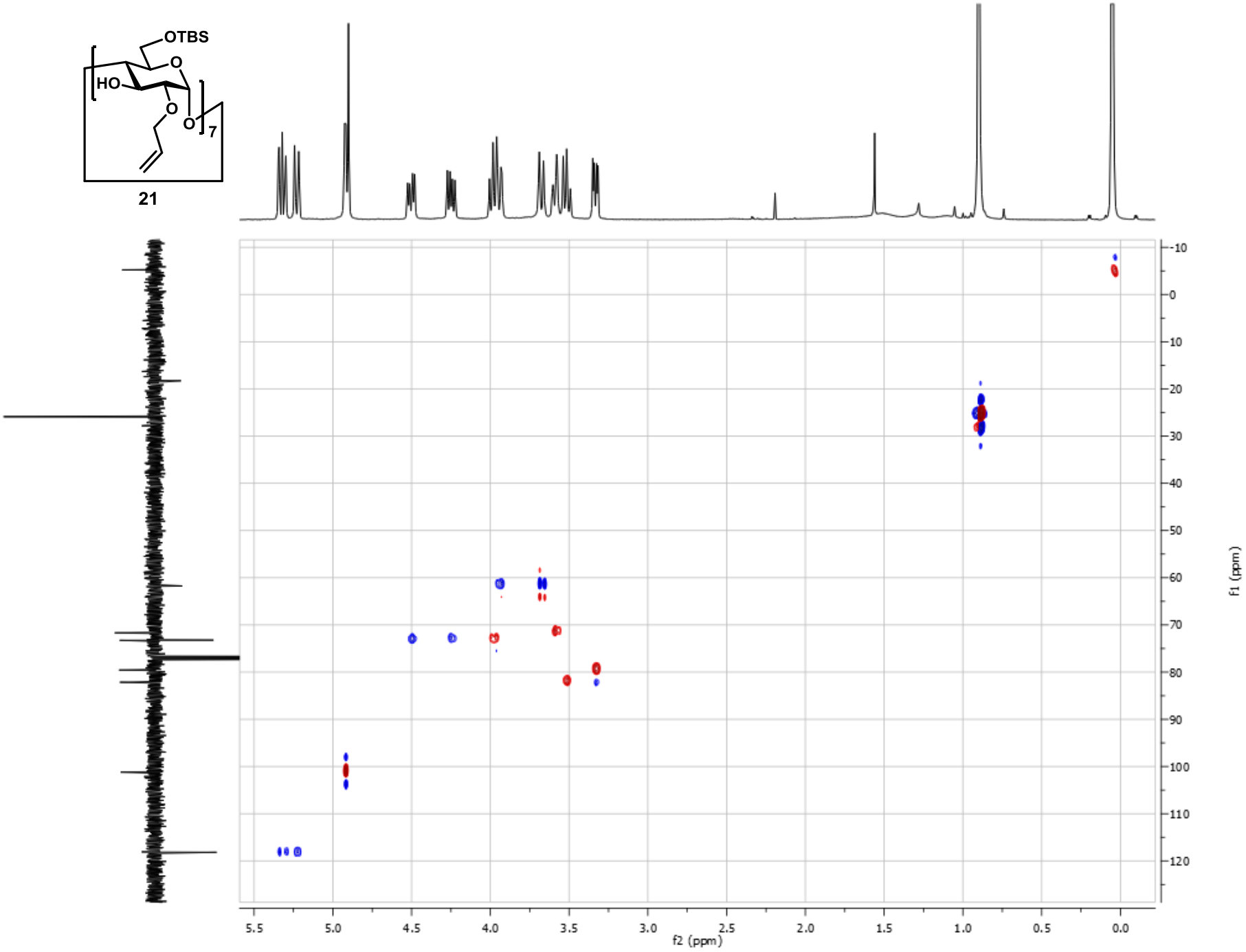


21

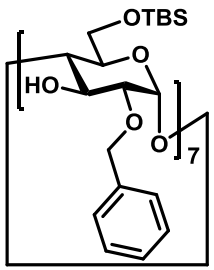
^{13}C APT NMR in $CDCl_3$ (100 MHz)



^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)

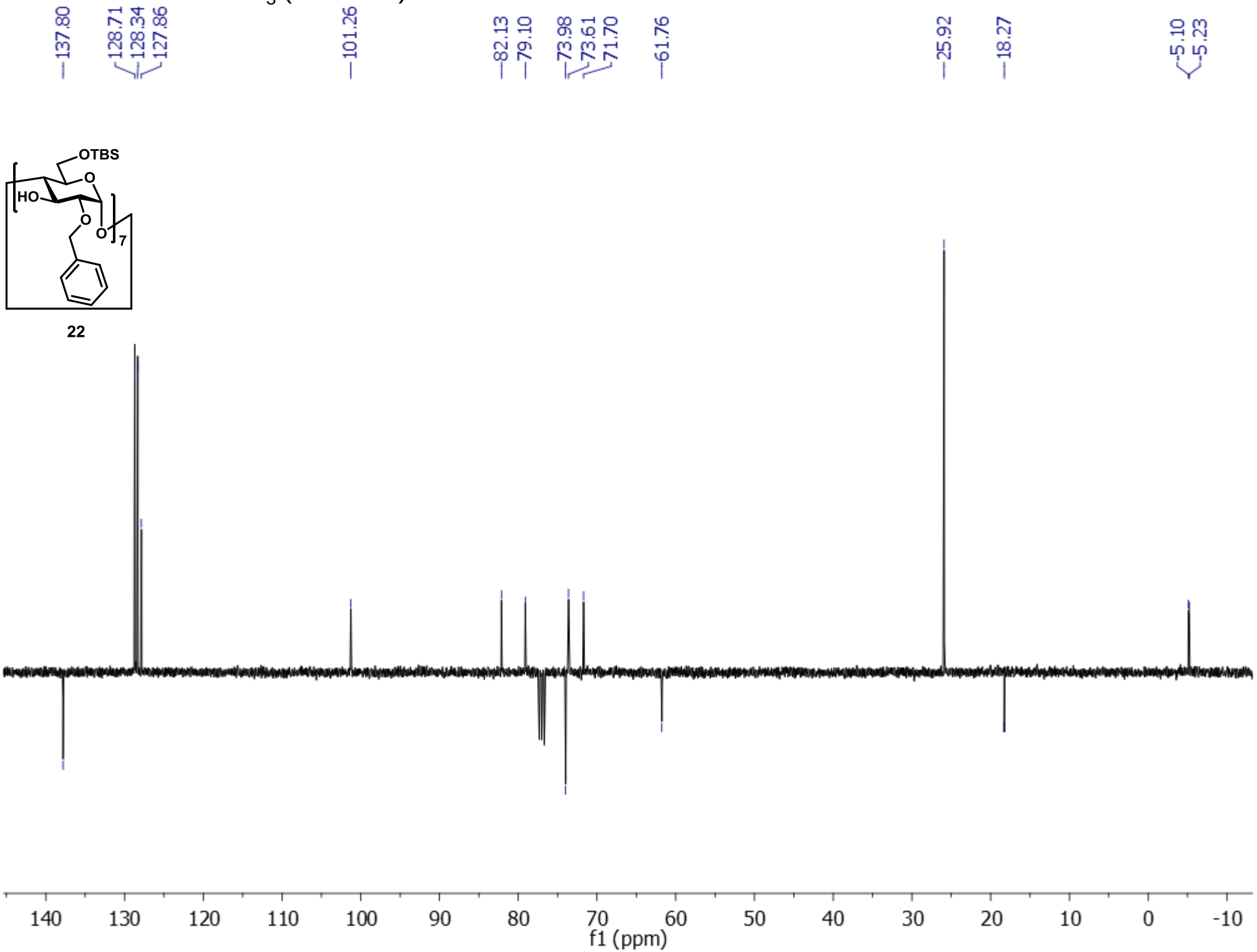


^{1}H NMR in $CDCl_3$ (400 MHz)



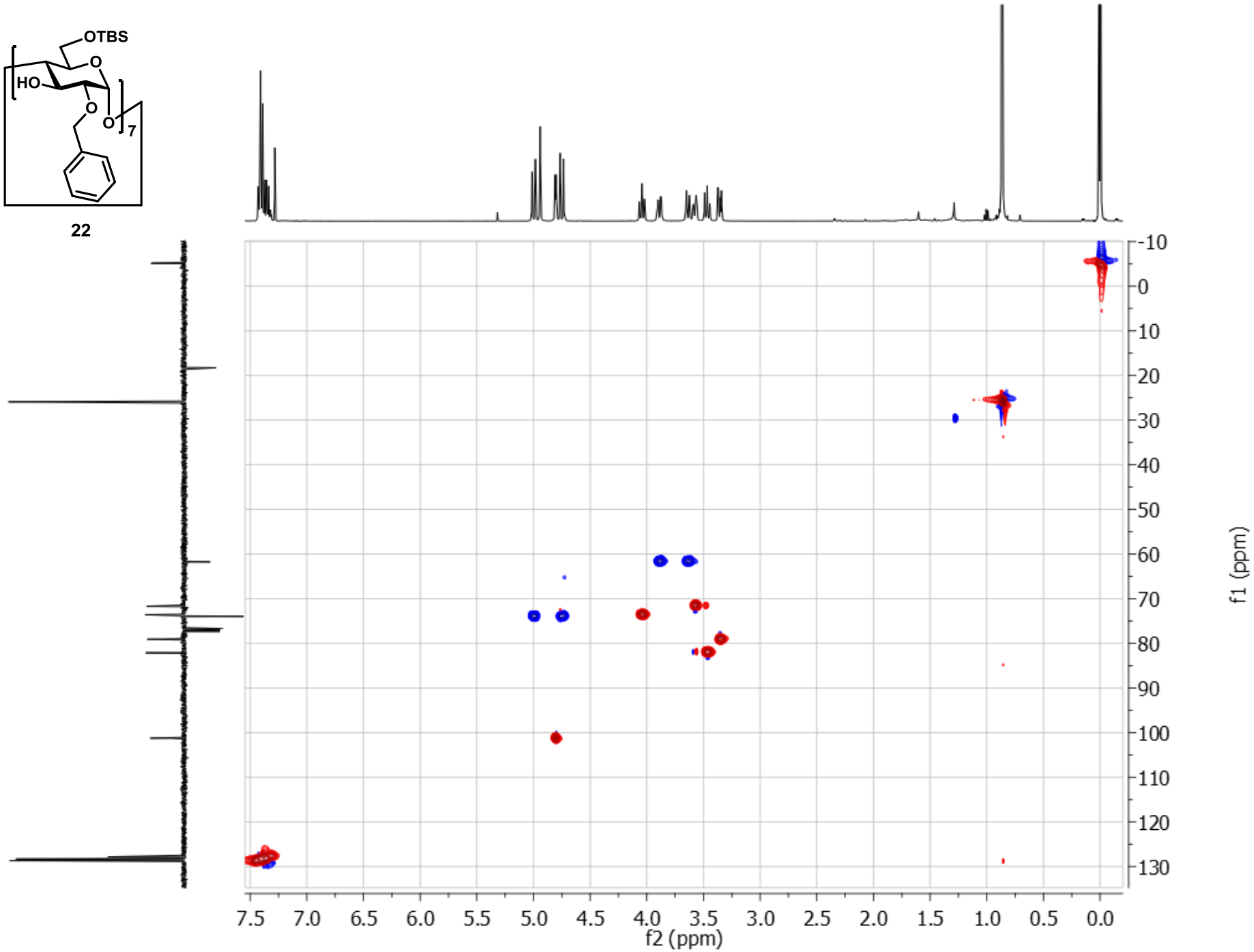
22

^{13}C APT NMR in $CDCl_3$ (100 MHz)

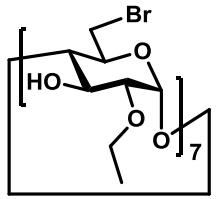


22

^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



^{1}H NMR in $CDCl_3$ (400 MHz)



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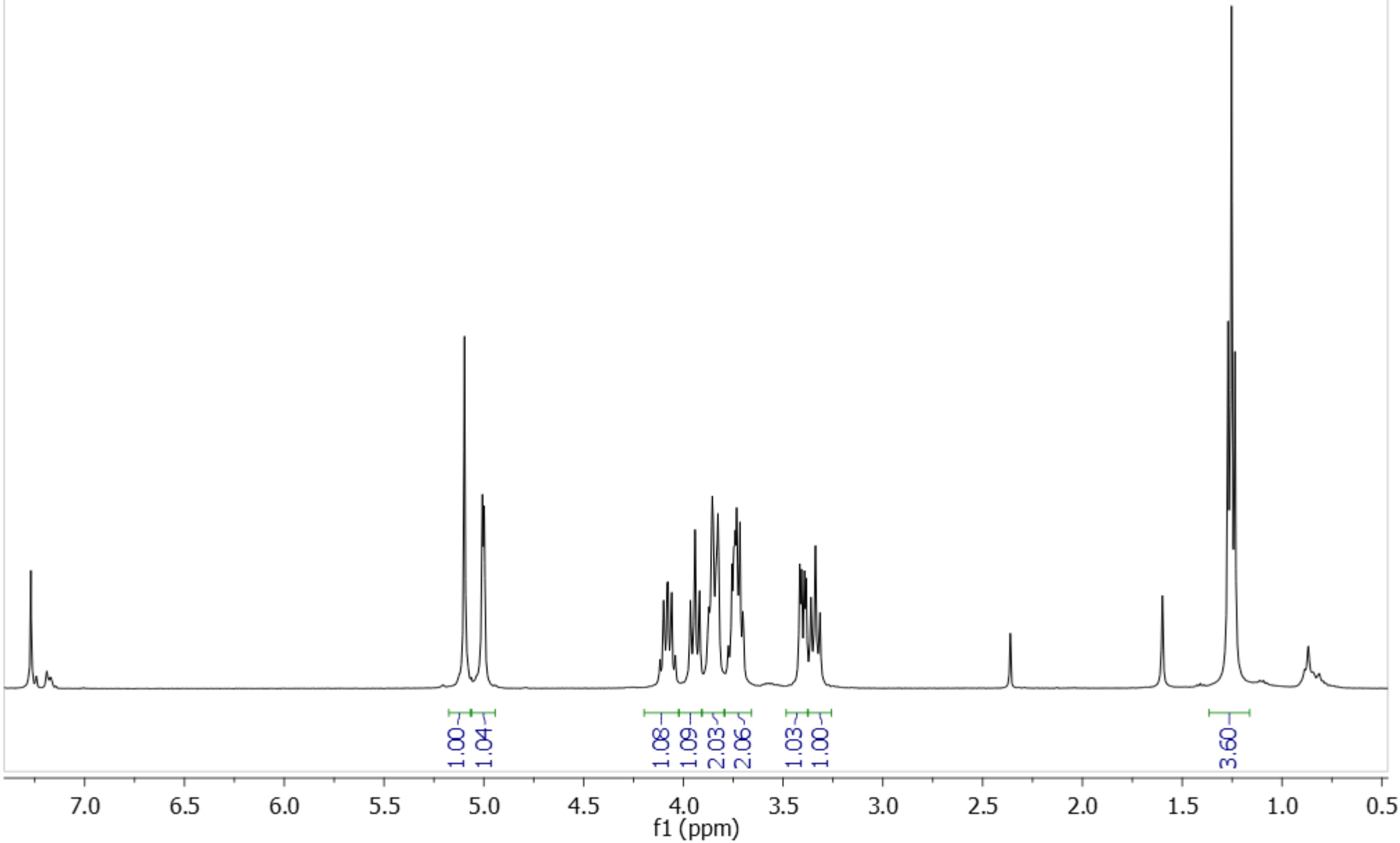
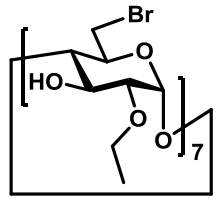
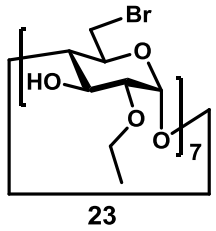


^{13}C APT NMR in $CDCl_3$ (100 MHz)



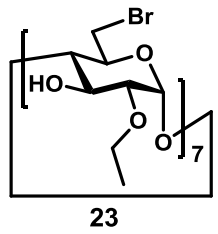
23

^{1}H-^{1}H gCOSY NMR in $CDCl_3$ (400 MHz)



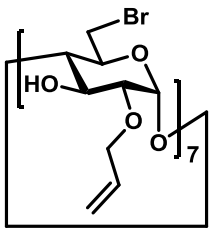
23

^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



23

^{1}H NMR in $CDCl_3$ (400 MHz)



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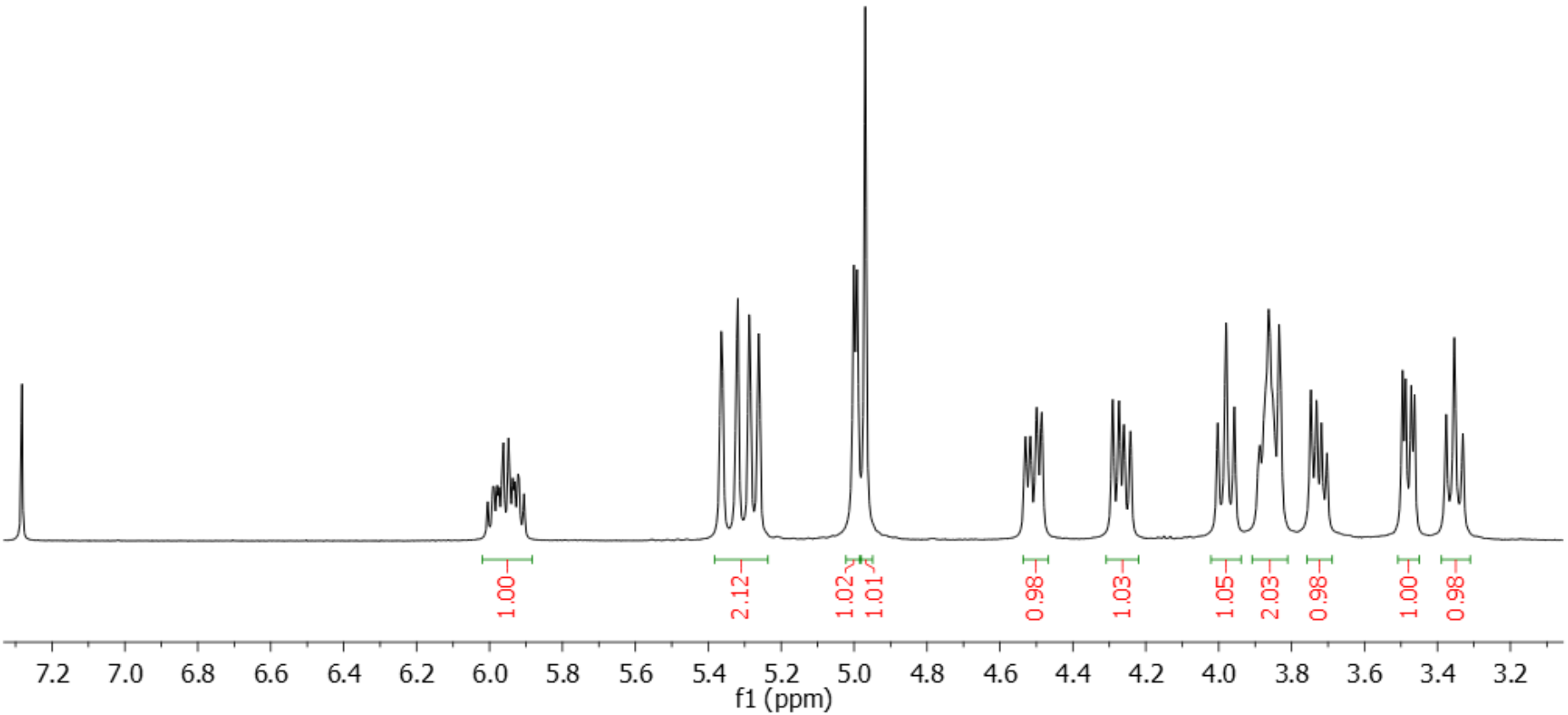
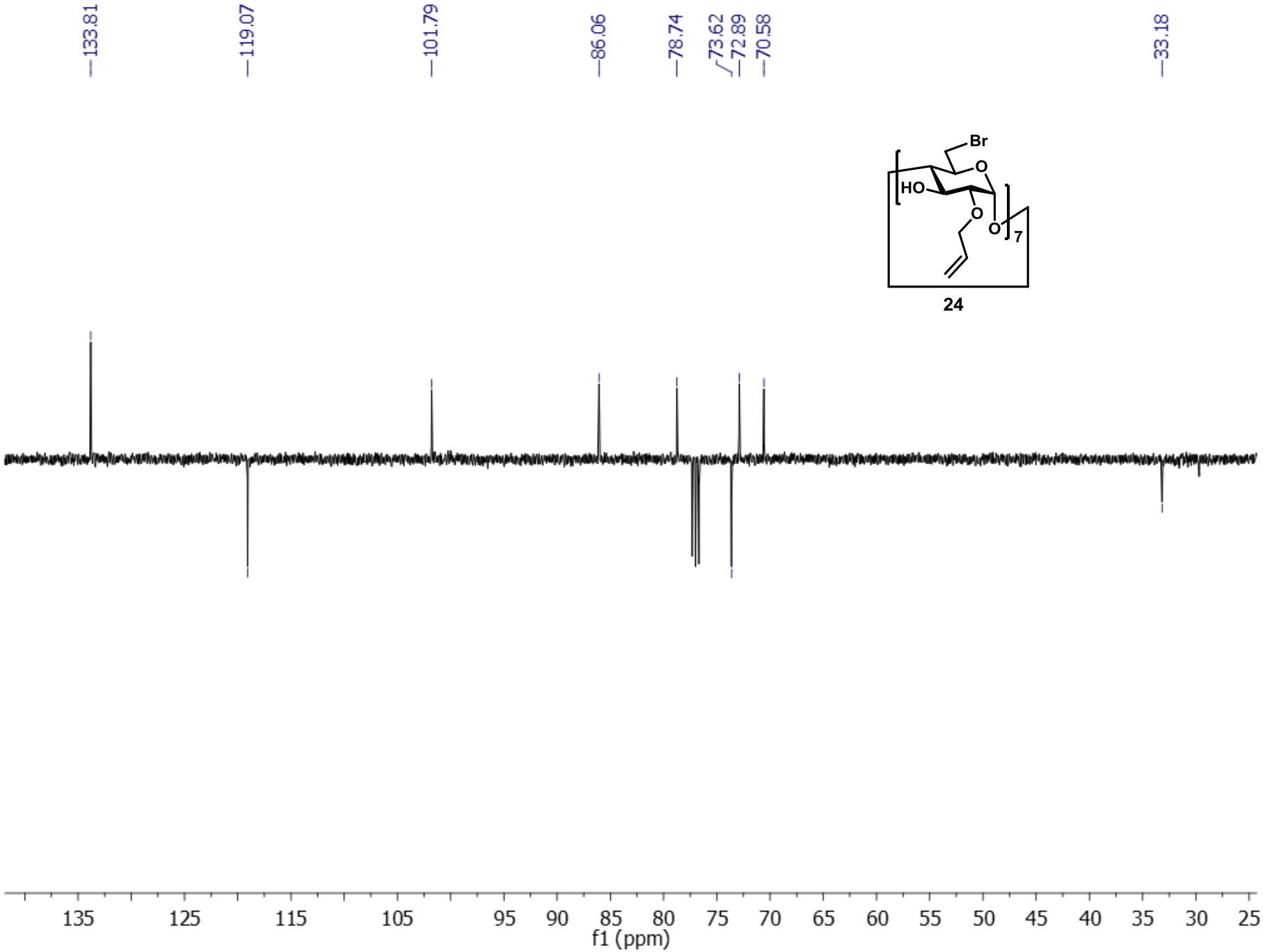
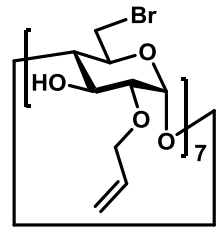


^{13}C APT NMR in $CDCl_3$ (100 MHz)



^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



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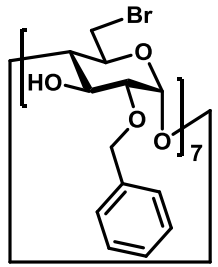
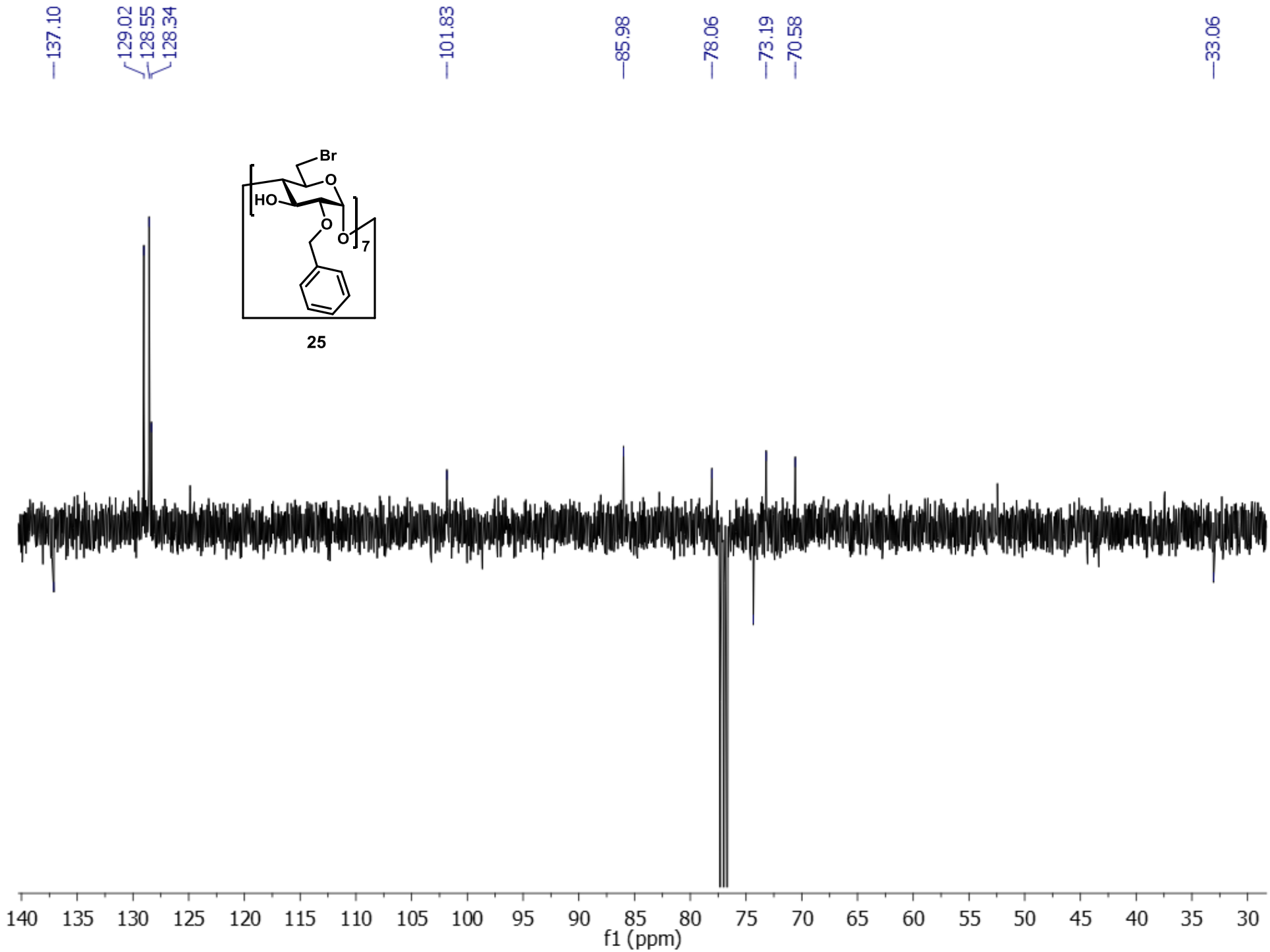
^{1}H NMR in $CDCl_3$ (400 MHz)

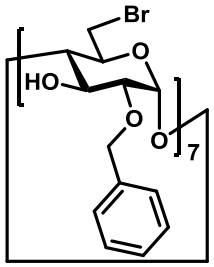


25

^{13}C APT NMR in $CDCl_3$ (100 MHz)



^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



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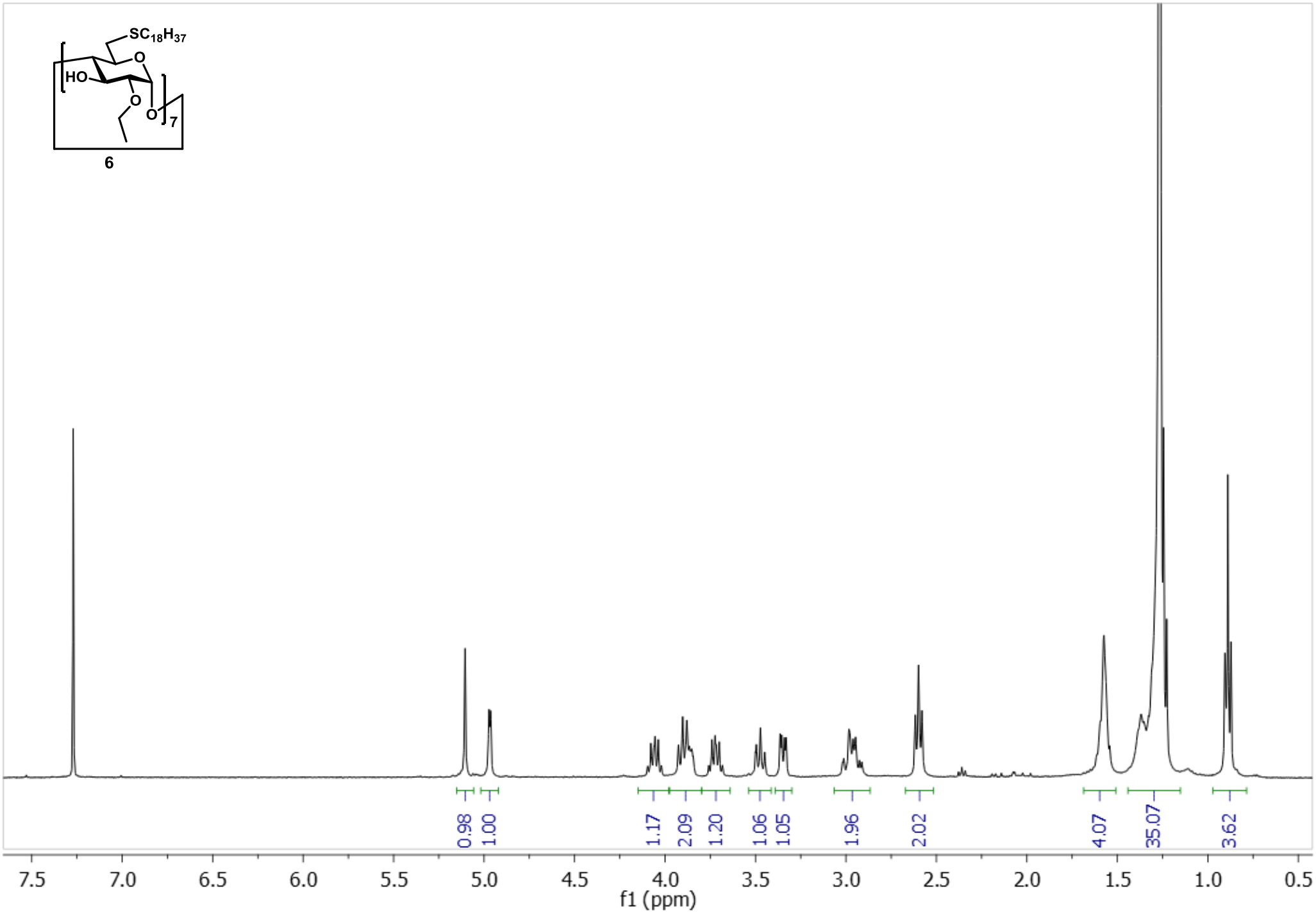
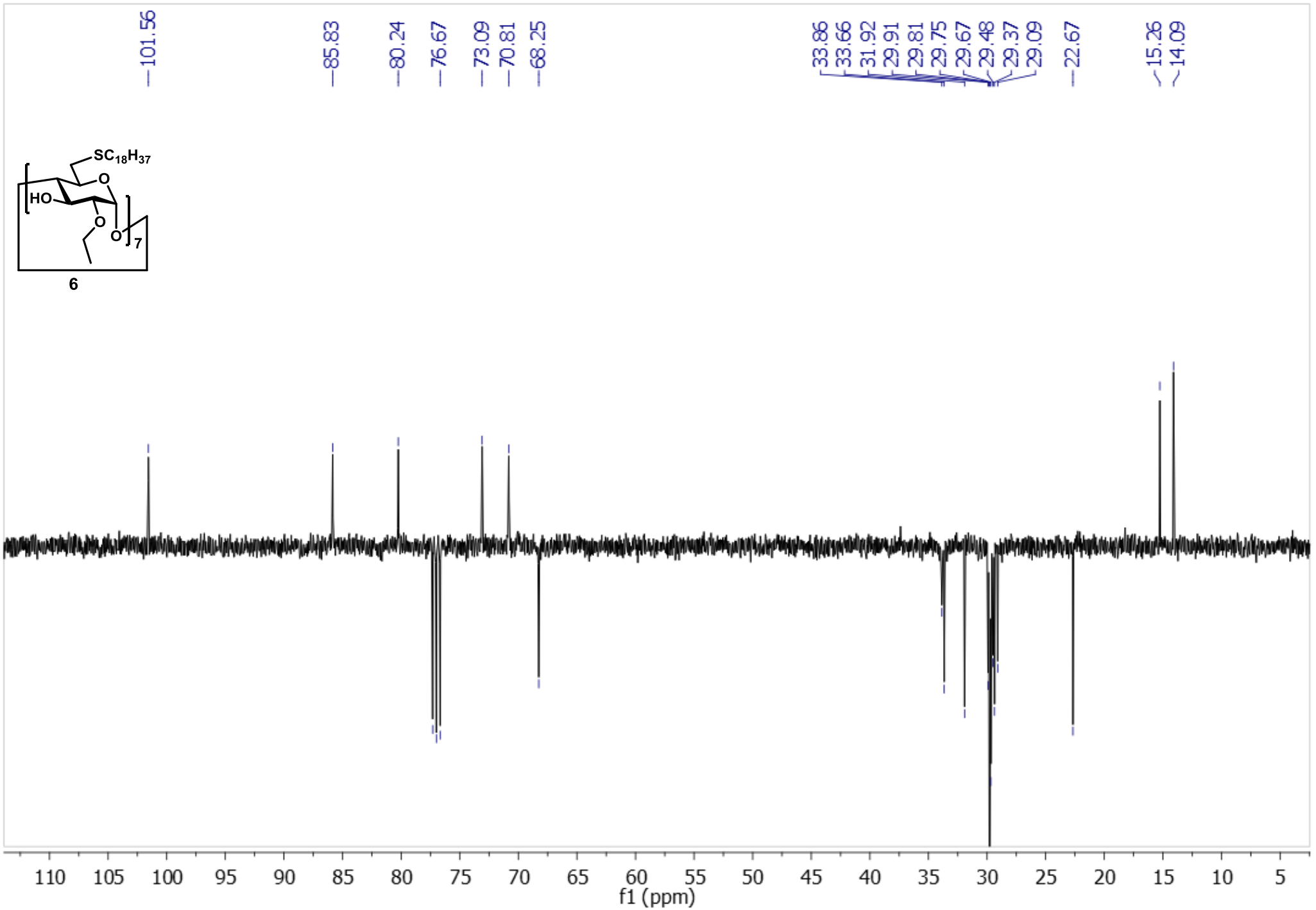
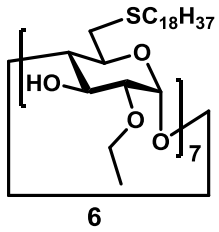
^{1}H NMR in $CDCl_3$ (400 MHz)



^{13}C APT NMR in $CDCl_3$ (100 MHz)

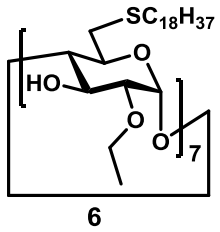


^{1}H-^{1}H gCOSY NMR in $CDCl_3$ (400 MHz)



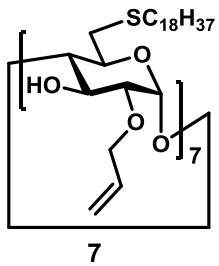
6

^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)



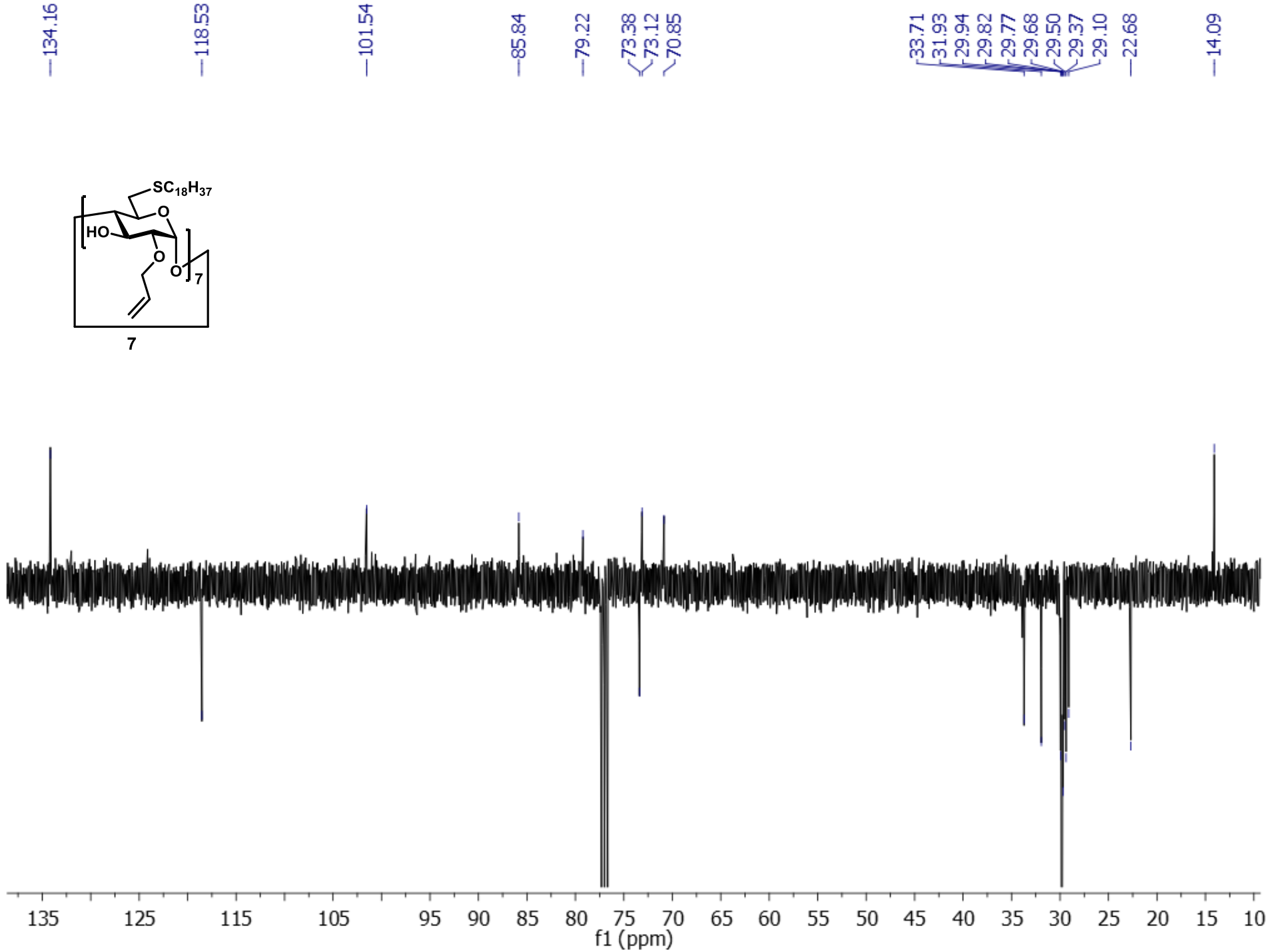
6

^{1}H NMR in $CDCl_3$ (400 MHz)

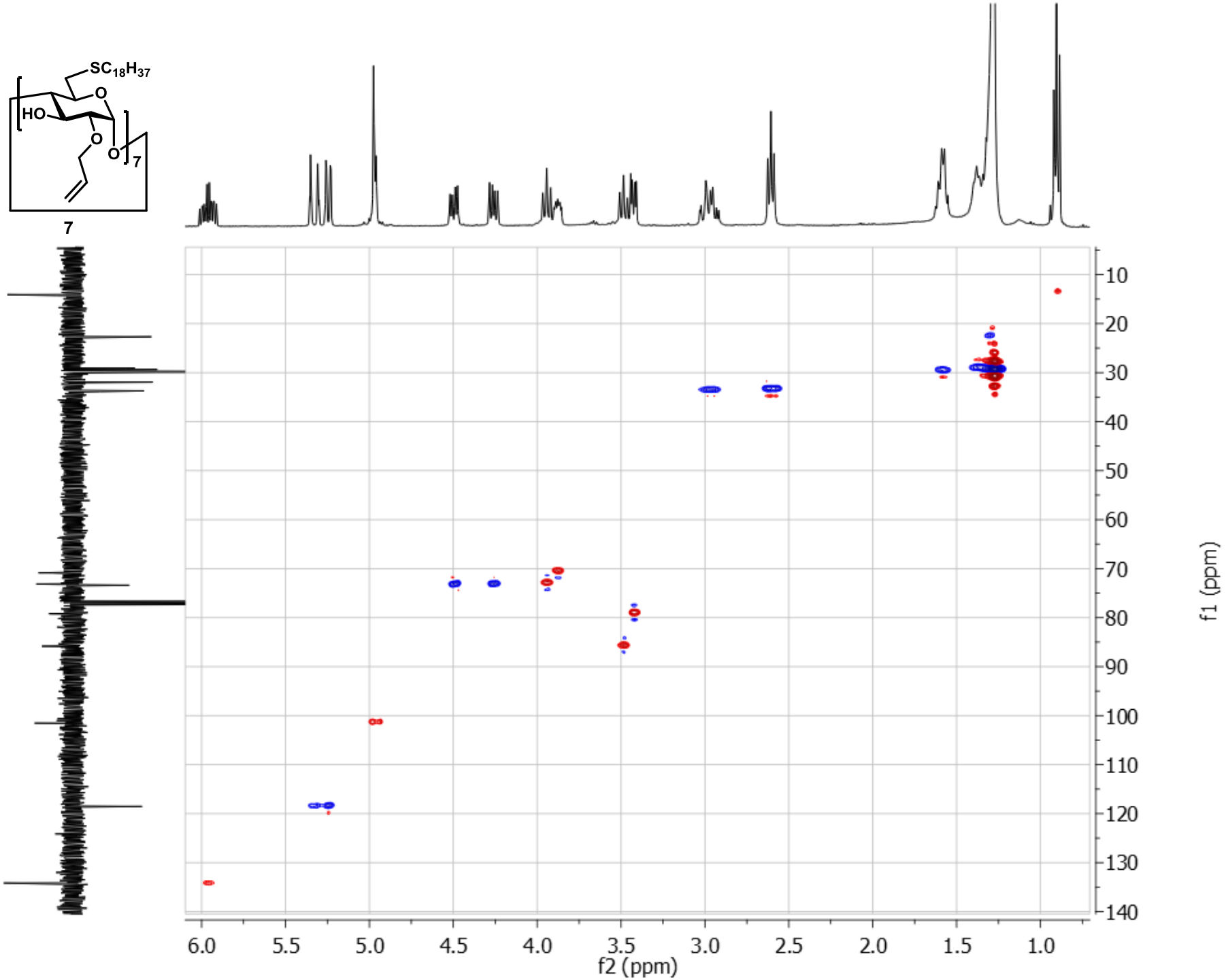


7

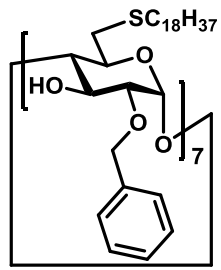
^{13}C APT NMR in $CDCl_3$ (100 MHz)



^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)

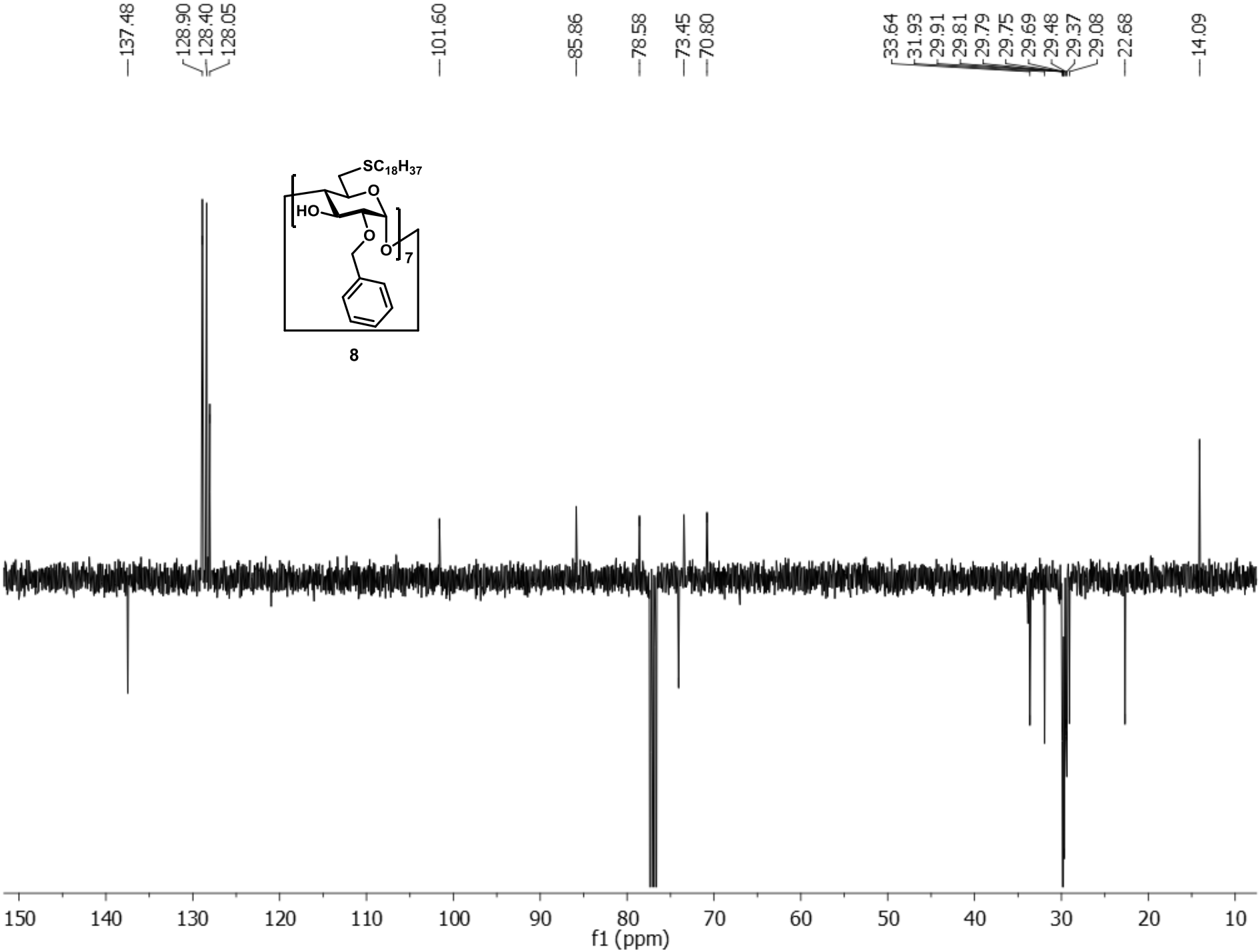


^{1}H NMR in $CDCl_3$ (400 MHz)

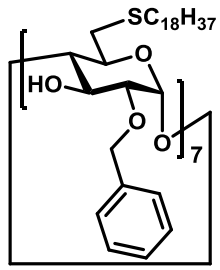


8

^{13}C APT NMR in $CDCl_3$ (100 MHz)



^{1}H-^{13}C gHSQC NMR in $CDCl_3$ (400 MHz)

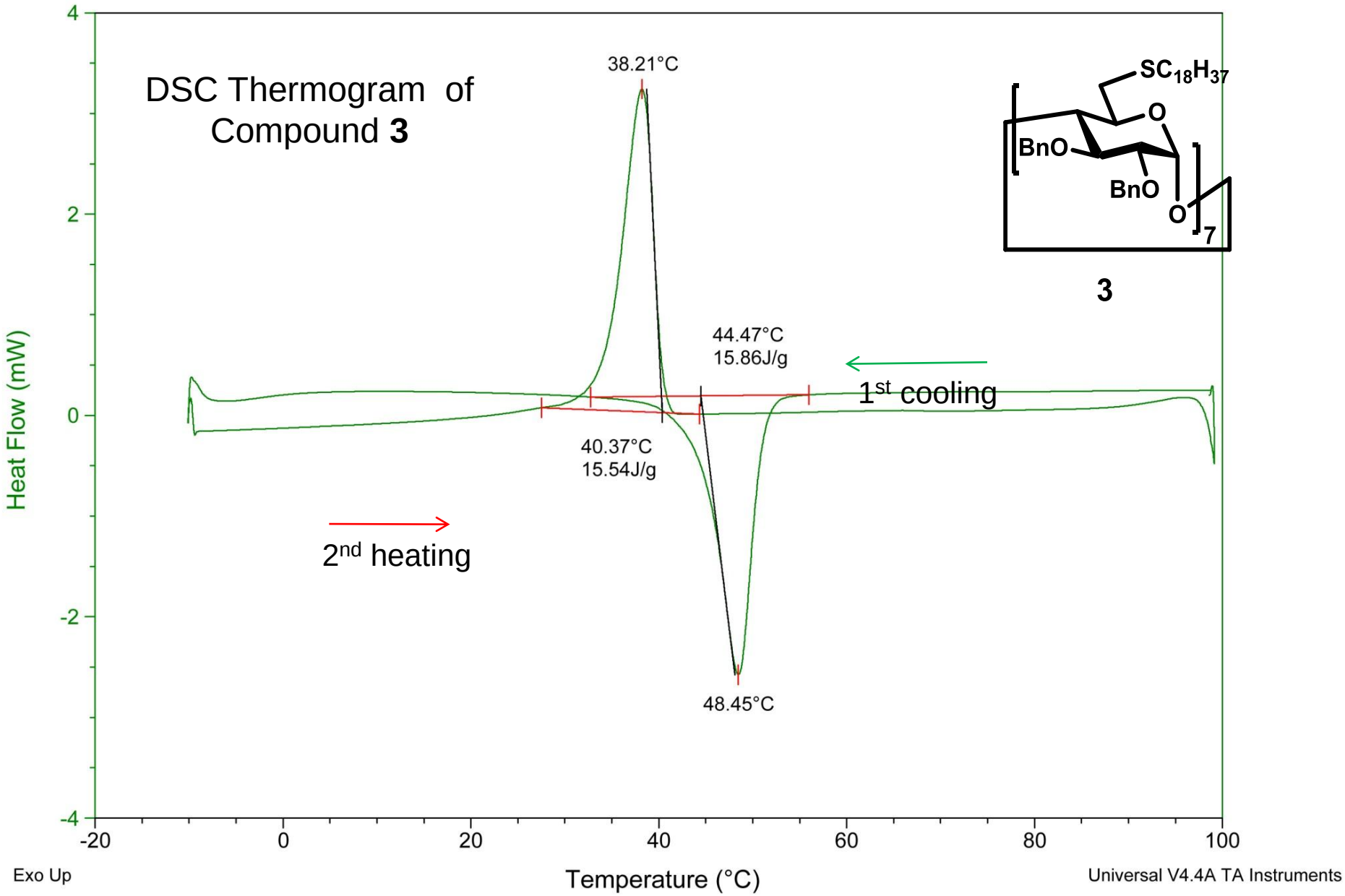


8

Sample: SWC18DiBn
Size: 5.0000 mg at 25.00°C
Method: Cyclic Robin1

DSC

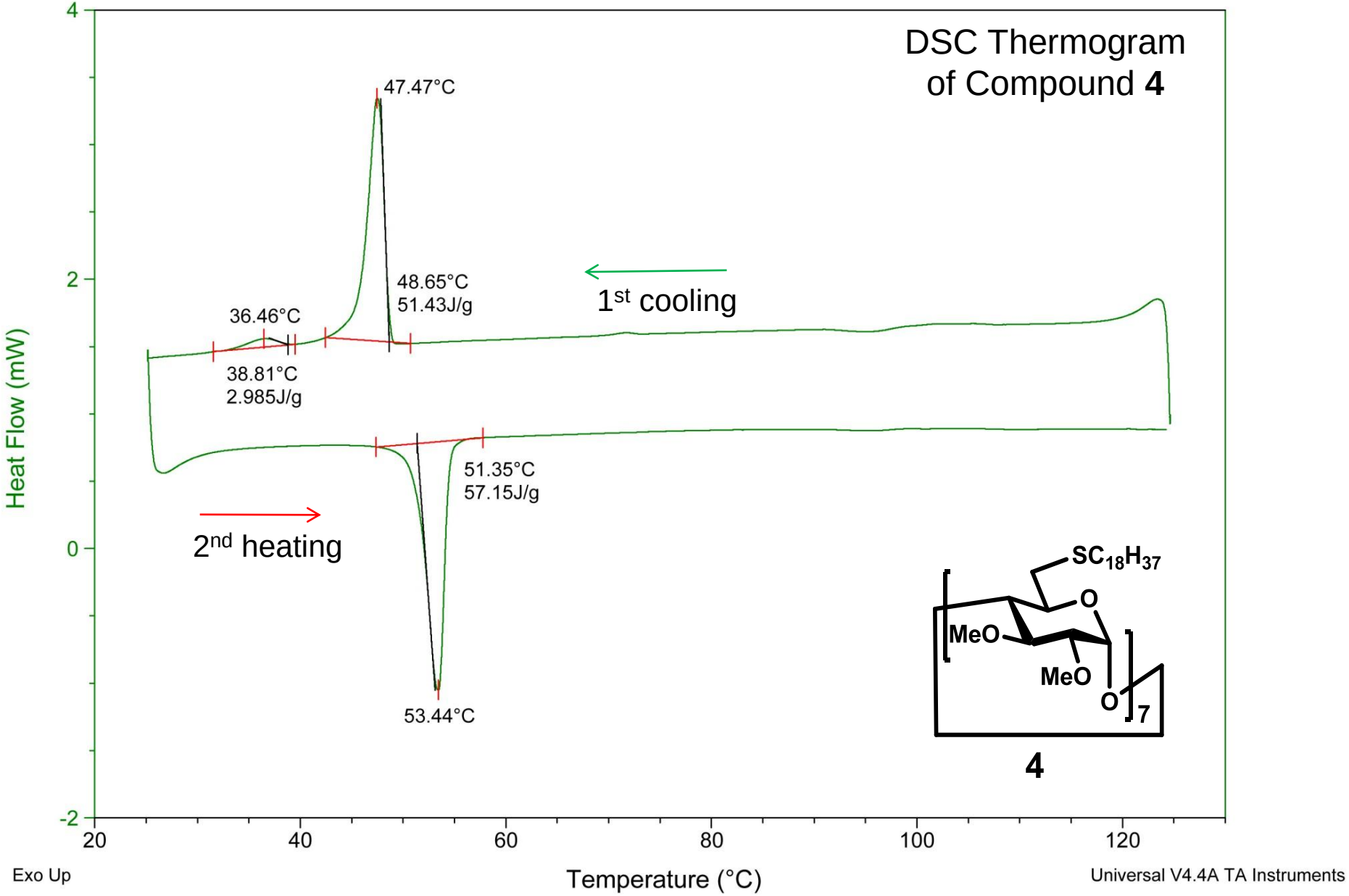
File: C:\TA\Data\DSC\CCL\SandraW\SWC18DiBn.00
Operator: SW
Run Date: 31-Oct-2011 13:41
Instrument: DSC Q200 V23.12 Build 103



Sample: Sandra_diMeS18
Size: 2.1000 mg at 25.00°C
Method: Heat/Cool/Heat

DSC

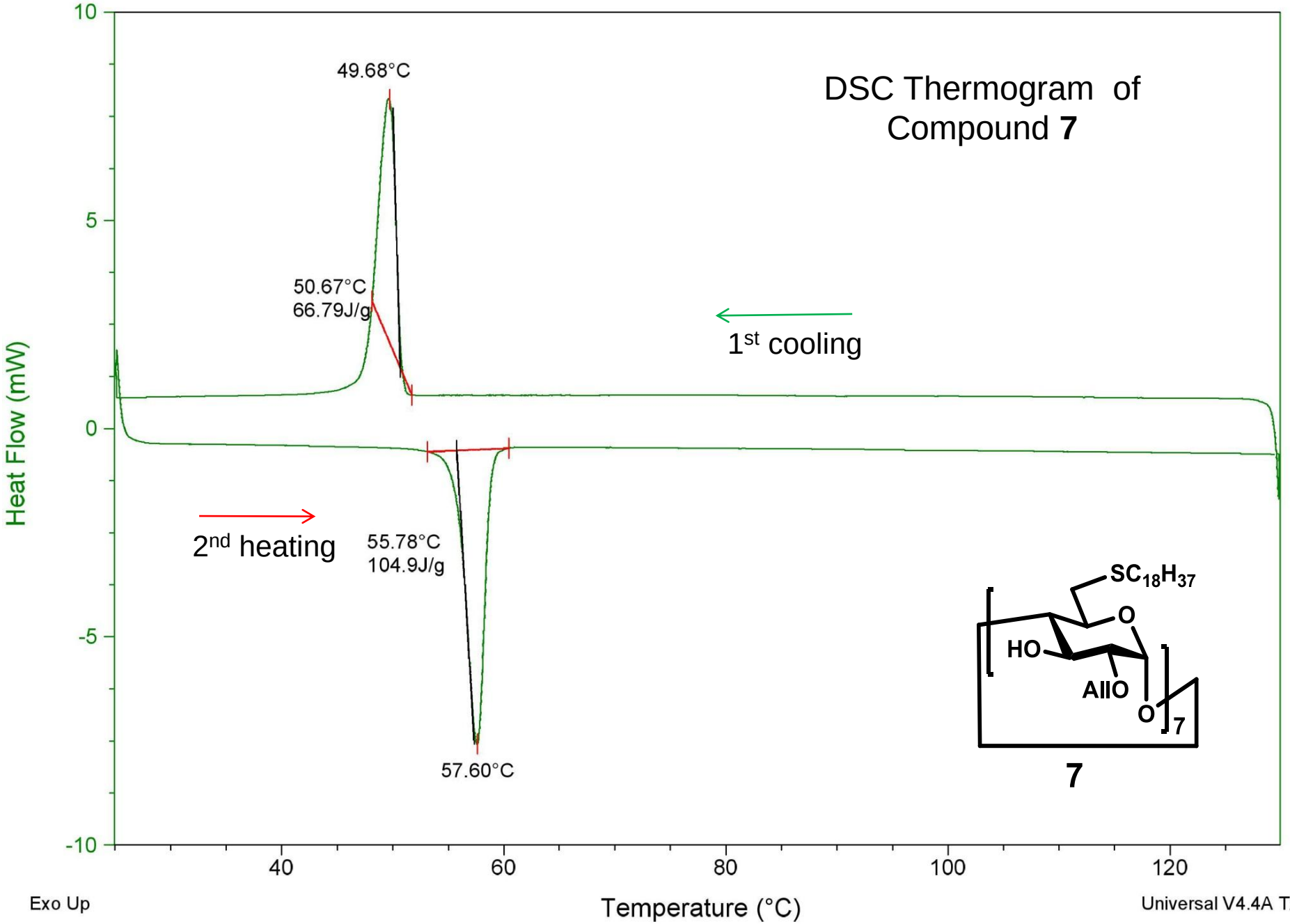
File: C:...\DSC\CCL\SandraW\Sandra_diMeS18.002
Operator: CCL
Run Date: 18-Feb-2014 10:29
Instrument: DSC Q200 V24.8 Build 120



Sample: 130417PZ5041-DSC
Size: 4.0000 mg at 25.00°C
Method: Heat/Cool/Heat
Comment: allyl

DSC

File: C:...\CCL\SandraW\130417PZ5041-DSC.001
Operator: Ping
Run Date: 17-Apr-2013 12:09
Instrument: DSC Q200 V23.12 Build 103

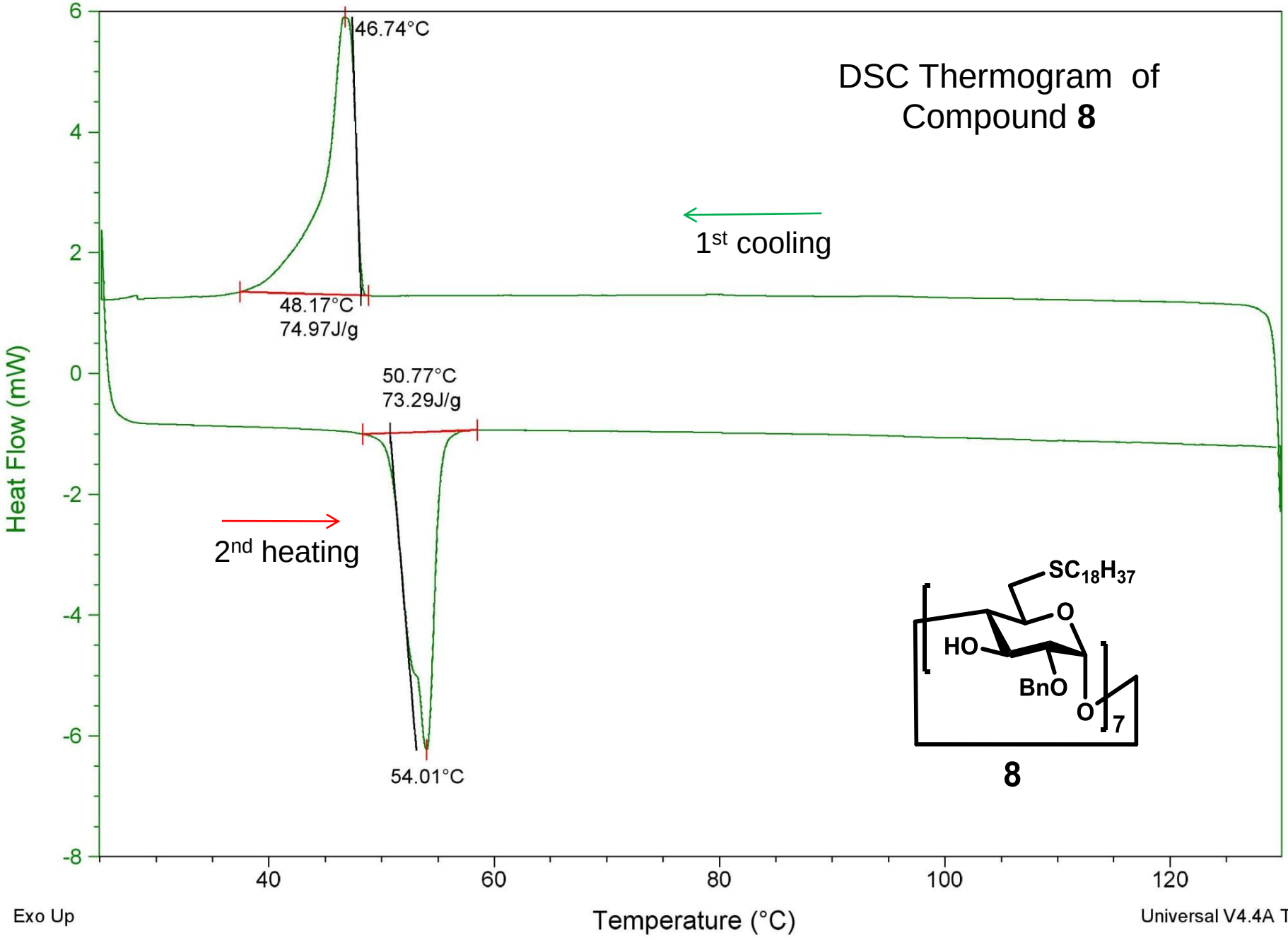


7

Sample: 130417PZ5044-DSC
Size: 6.0000 mg at 25.00°C
Method: Heat/Cool/Heat
Comment: Bn

DSC

File: C:...\CCL\SandraW\130417PZ5044-DSC.001
Operator: Ping
Run Date: 17-Apr-2013 15:06
Instrument: DSC Q200 V23.12 Build 103

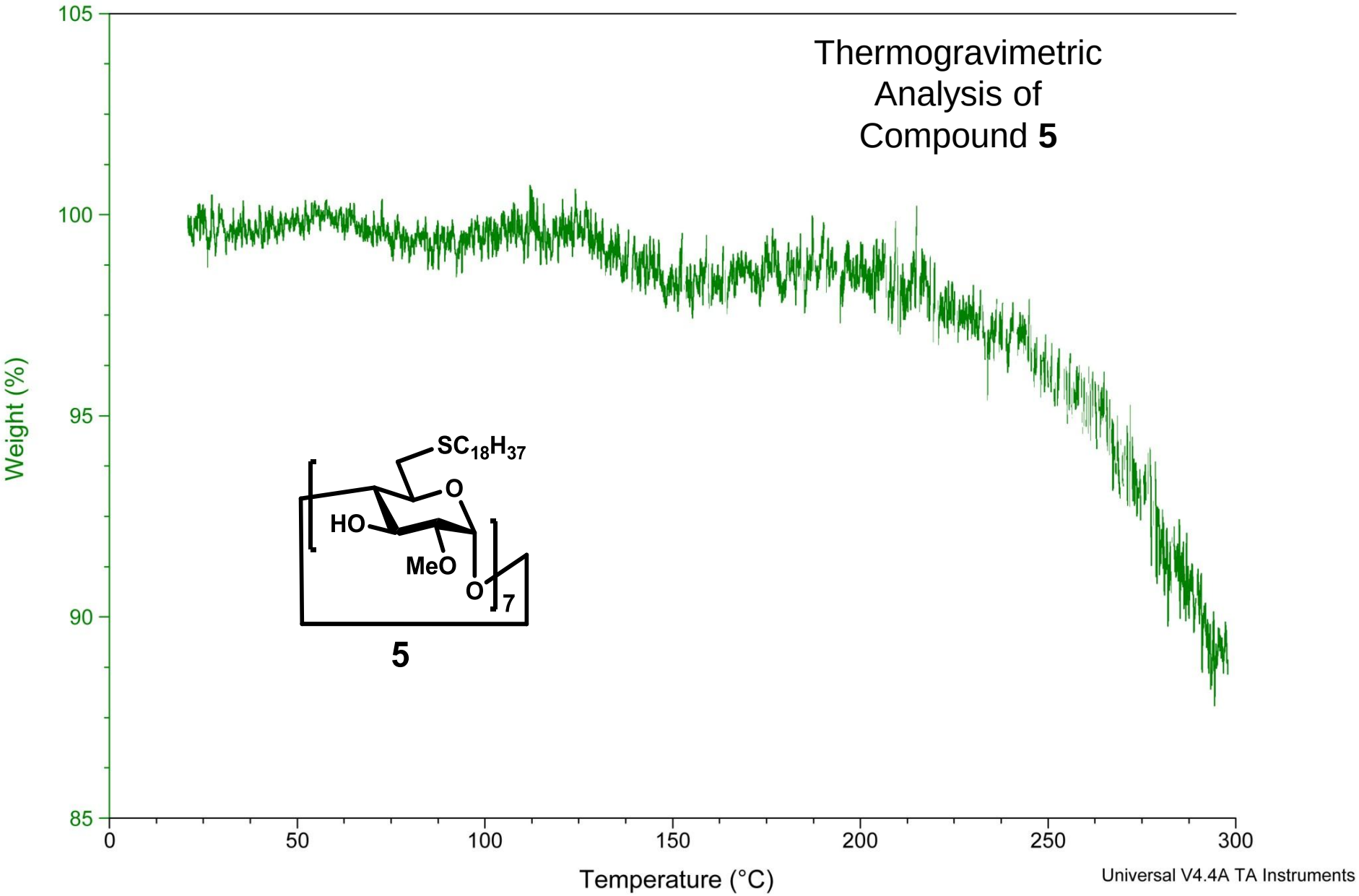


8

Sample: SWIII.3
Size: 4.1090 mg
Method: Ramp

TGA

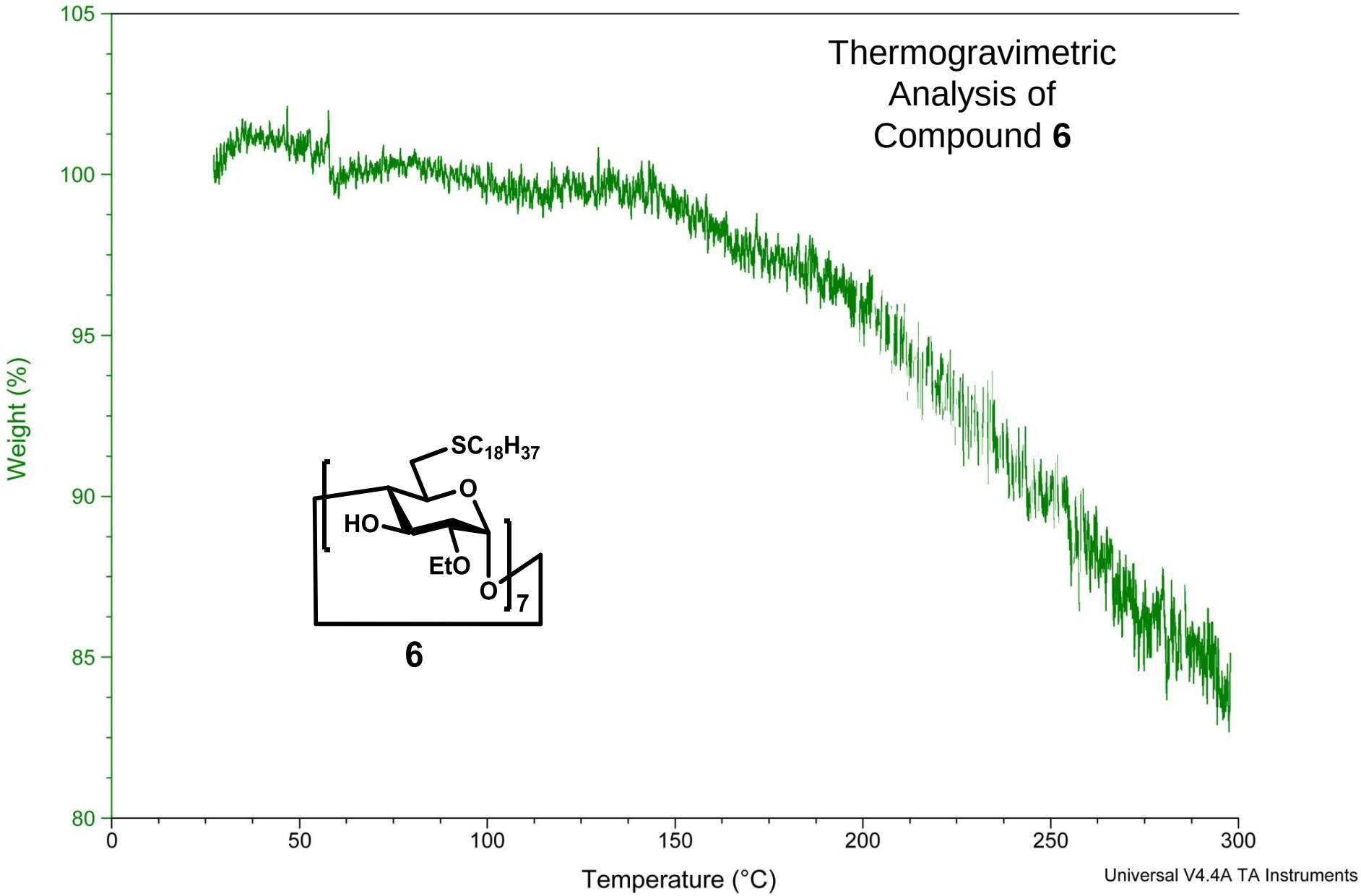
File: \\...\Data\TGA\CC-Group\Sandra\SWIII.300
Operator: MS
Run Date: 14-Feb-2014 13:43
Instrument: TGA Q50 V20.7 Build 32



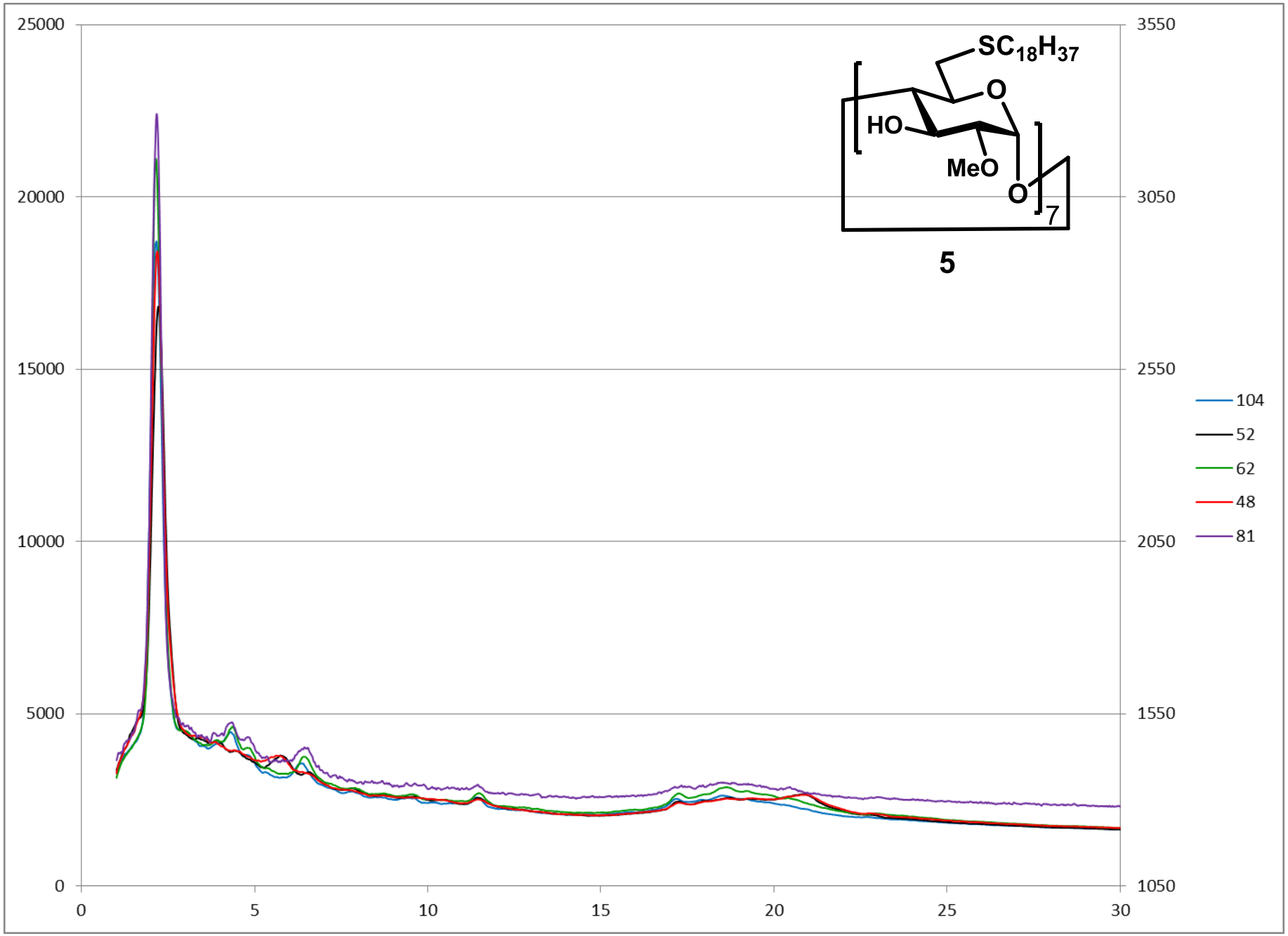
Sample: Matt6
Size: 3.9200 mg
Method: Ramp

TGA

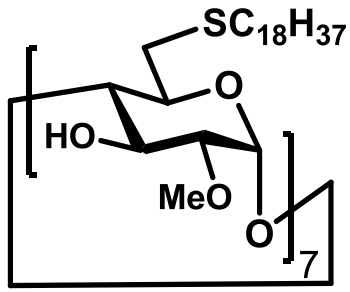
File: C:\TA\Data\TGA\CC-Group\Sandra\Matt6.001
Operator: MS
Run Date: 14-Feb-2014 16:53
Instrument: TGA Q50 V20.7 Build 32



Variable Temperature XRD Plots. Recorded at 104, 81, 62, 52, 48°C



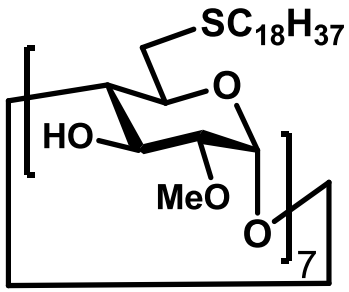
Variable Temperature Results



5

Temp (°C)	d-spacing (Å)	Intensity(%)	Miller index (*hkl*)	Phase
105	40.7	100	(001)	Smectic
	20.5	7.4	(002)	(a = 40.7Å)
	13.9	4.9	(003)	
	9.3	0.6	(???)	
	7.7	1.1	(???)	
	5.2	0.7	(???)	
	4.8	2.4	*alkyl halo*	
52	39.9	100	(???)	???
	26.3	1.3	(???)	
	22.8	1.2	(???)	
	15.4	3.9	(???)	
	7.7	1.6	(???)	
	4.7	1	(???)	
	4.2	4.4	*alkyl halo*	

Variable Temperature Results



5

Temp (°C)	d-spacing (Å)	Intensity(%)	Miller index (*hkl*)	Phase
81	40.7	100	(001)	Smectic
	20.4	3.9	(002)	(a = 40.7Å)
	13.7	3.4	(003)	
	7.7	1.1	(???)	
	5.2	0.7	(???)	
	4.8	2.4	*alkyl halo*	
48	40.3	100	(???)	???
	15.4	2.1	(???)	
	7.7	1.2	(???)	
	4.2	3.9	*alkyl halo*	