Synthesis of Structurally-Defined Polymeric Glycosylated Phosphoprenols as Potential Lipopolysaccharide Biosynthetic Probes

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Supporting Information

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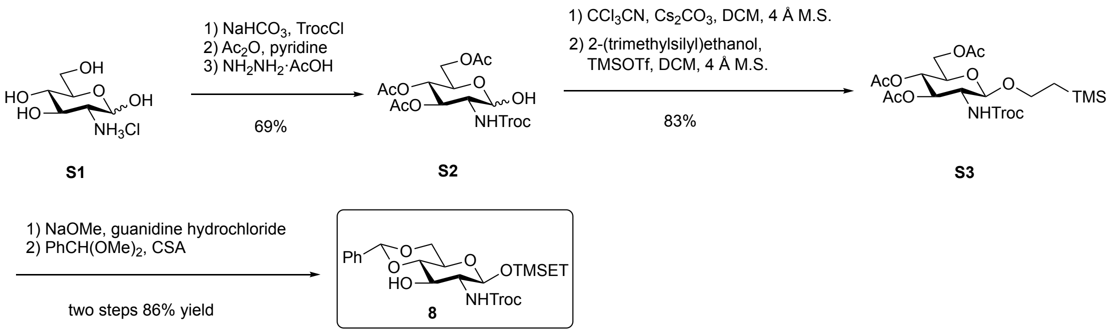
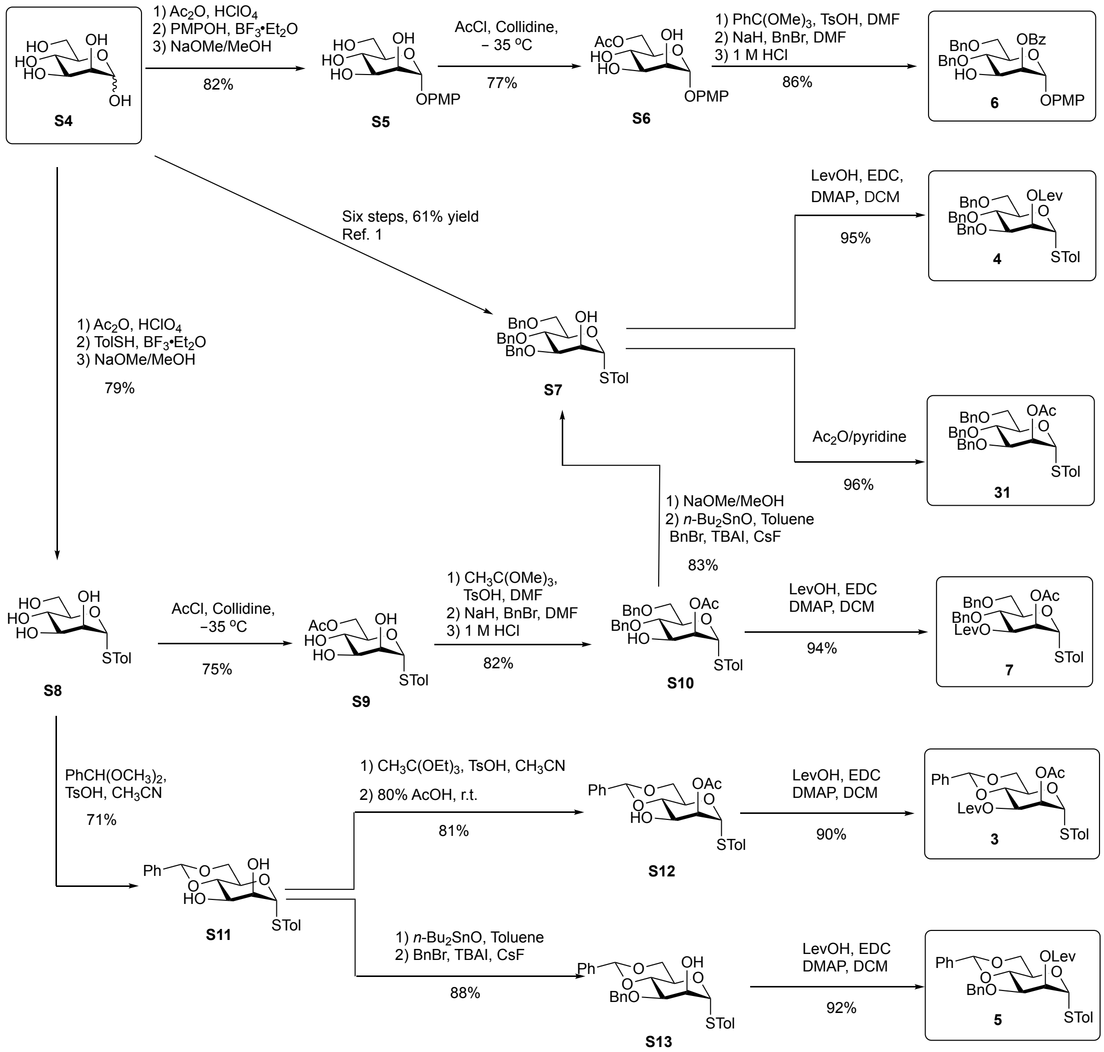


Scheme S1: Synthesis of glucosamine-based building block **8**.



Scheme S2: Synthesis of mannose-based building blocks **3–7** and **31**.

Figure S1. Overlaid partial ^{1}H NMR spectra of **1** (top) and **2** (bottom) from 3.5–5.6 ppm.

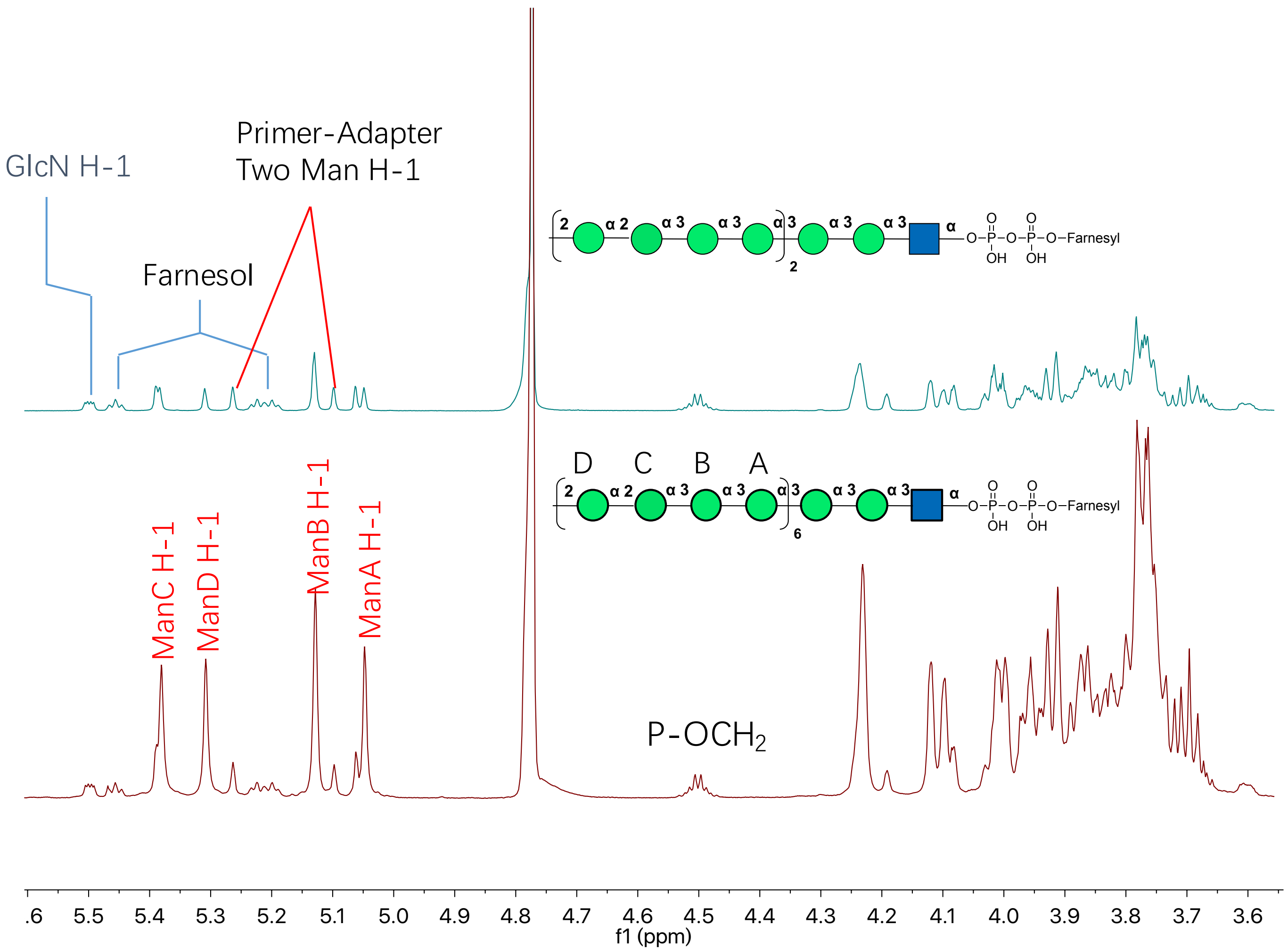
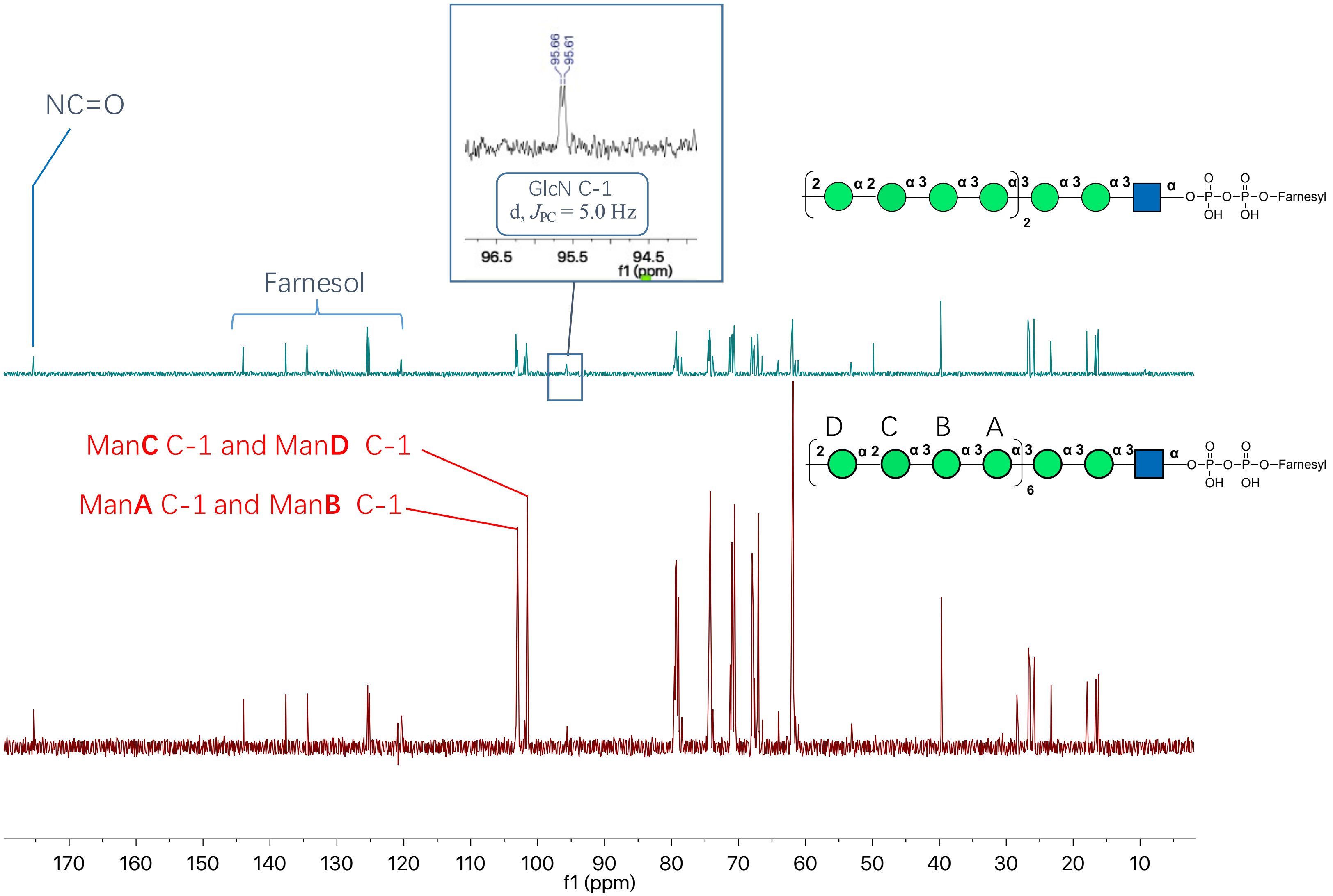


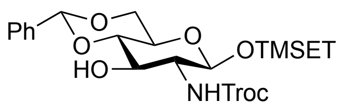
Figure S2. Overlaid ^{13}C NMR spectra of **1** (top) and **2** (bottom).



4.5 Experimental section

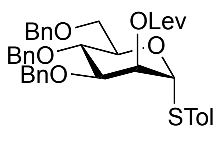
General Methods: Reactions were carried out in oven-dried glassware. All reagents used were purchased from commercial sources and were used without further purification unless noted. Solvents used in reactions were purified by successive passage through columns of alumina and copper under nitrogen. Unless stated otherwise, all reactions were carried out at r.t. under a positive pressure of argon and were monitored by TLC on silica gel 60 F_{254} (0.25 mm, E. Merck). Spots were detected under UV light or by charring with a solution of ammonium molybdate (12 g), ceric ammonium nitrate (0.42 g) and concentrated sulfuric acid (15 mL) in H_2O (235 mL). Unless otherwise indicated, all column chromatography was performed on silica gel 60 (40–60 μM). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured at 22 ± 2 °C at the sodium D line (589 nm) and are in units of deg·mL(dm·g)$^{-1}$. ^{1}H NMR spectra were recorded at 500 or 700 MHz, and chemical shifts are referenced to either TMS (0.0 ppm, $CDCl_3$) or HOD (4.78 ppm, D_2O and CD_3OD). ^{13}C NMR spectra were recorded at 150 or 175 MHz, and ^{13}C chemical shifts were referenced to internal $CDCl_3$ (77.23 ppm, $CDCl_3$), external dioxane (67.40 ppm, D_2O) or CD_3OD (48.9 ppm, CD_3OD). The stereochemistry of the newly formed glycosidic linkages was confirmed by measuring $^1J_{C\text{-}1,\ H\text{-}1}$ values via an ^{1}H-coupled HSQC experiment. In the processing of reaction mixtures, solutions of organic solvents were washed with equal amounts of aqueous solutions. Organic solutions were concentrated under vacuum at < 40˚C (bath). Electrospray mass spectra (time-of-light analyzer) were recorded on samples suspended in mixtures of THF with CH_3OH and added NaCl. MALDI mass spectrum was obtained in the linear positive mode of ionization on a MALDI TOF/TOF mass spectrometer using sinaoinic acid as the matrix.

General procedure A. Removal of PMP protecting group and formation of an trichloroacetimidate donors: CAN (5 equiv.) was added to a solution of compound **32**, **10**, **50** or **52** (1 equiv.) in 1:3:6 H_2O–CH_2Cl_2–CH_3CN (10 mL–300 mL, depending upon the amount of substrate) at 0 °C. The mixture was slowly warmed and vigorously stirred for 2 h at r.t.. The solution was then diluted with EtOAc and the organic layer was washed with H_2O, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography to afford the corresponding hemiacteal. Then, to a solution of the hemiacetal in dry CH_2Cl_2 (10 mL–200 mL) was added CCl_3CN (25 equiv.) and DBU (0.2 equiv.) at 0 °C and the mixture was stirred at r.t. for 1 h. The solution was then concentrated and the resulting residue was subjected to chromatography to afford the trichloroacetimidate intermediate for glycosylation reactions.

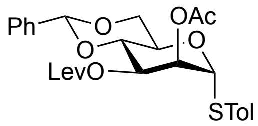


2-(Trimethylsilyl)ethyl 4,6-*O*-Benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (8): To a solution of guanidine chloride (0.4 g, 62.8 mmol) in CH_3OH (40 mL) was added 1 M of $NaOCH_3$ (2 mL). Then, this mixture was added to a solution of **S3**[1] (6 g, 10.4 mmol) in CH_3OH (90 mL). The reaction mixture was stirred at r.t. for 20 min and then neutralized with Amberlite IR120 H^+ ion-exchange resin and concentrated to dryness. The resulting residue, benzaldehyde dimethyl acetal (1.89 g, 12.4 mmol) and CSA (0.58 g, 2.5 mmol) were dissolved in anhydrous CH_3CN

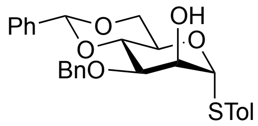
(40 mL) and the mixture was stirred at r.t. for 4 h. After the addition of Et_3N, the mixture was diluted with EtOAc, washed with a satd aq solution of $NaHCO_3$, brine, dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by chromatography (gradient 17→25% EtOAc in hexane) to afford **8** (4.85 g, 86% yield) as a white solid. R_f 0.53 (3:2 hexane–EtOAc); $[\alpha]_D$ = −30.5 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.49–7.47 (m, 2 H, ArH), 7.38–7.35 (m, 3 H, ArH), 5.54 (s, 1 H, PhC*H*(O)$_2$), 5.25 (br, 1 H, N*H*), 4.75 (d, 1 H, *J* = 12.0 Hz, C*H*$_2$CCl$_3$), 4.70 (d, 1 H, *J* = 8.0 Hz, H-1), 4.70 (d, 1 H, *J* = 12.0 Hz, C*H*$_2$CCl$_3$), 4.35 (dd, 1 H, *J* = 10.5, 5.0 Hz, H-6), 4.17 (br, 1 H, H-3), 3.96 (ddd, 1 H, *J* = 10.8, 9.7 5.5 Hz, TMSCH$_2$C*H*$_2$O), 3.78 (app t, 1 H, *J* = 10.5 Hz, H-6), 3.57 (ddd, 1 H, *J* = 11.0, 9.7 6.0 Hz, TMSCH$_2$C*H*$_2$O), 3.54 (app t, 1 H, *J* = 9.0 Hz, H-4), 3.49–3.45 (m, 1 H, H-5), 3.35–3.17 (m, 1 H, H-2), 3.04 (br, 1 H, OH), 0.97 (ddd, 1 H, *J* = 13.8, 11.2, 6.0 Hz, TMSC*H*$_2$CH$_2$O), 0.92 (ddd, 1 H, *J* = 13.8, 10.8, 5.5 Hz, TMSC*H*$_2$CH$_2$O), 0.01 (s, 9 H, (C*H*$_3$)$_3$Si); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.5 (NHC=O), 137.0 (Ar), 129.3 (Ar), 128.3 (Ar), 126.3 (Ar), 101.9 (Ph*C*H(O)$_2$), 100.3 (C-1), 81.5 (C-4), 74.6 (*C*H$_2$CCl$_3$), 70.7 (C-3), 68.7 (C-6), 67.8 (TMSCH$_2$*C*H$_2$O), 66.0 (C-5), 59.1 (C-2), 18.2 (TMS*C*H$_2$CH$_2$O), −1.4 (*C*H$_3$)$_3$Si); HRMS (ESI) calcd for (M+NH$_4$) $C_{21}H_{34}Cl_3N_2O_7Si$: 559.1195. Found: 559.1183.



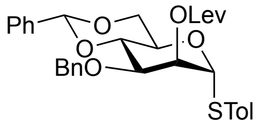
***p*-Tolyl 3,4,6-tri-*O*-Benzyl-2-*O*-levulinyl-1-thio-α-D-mannopyranoside (4):** To a solution of **S7**[2] (200 mg, 0.36 mmol) in CH_2Cl_2 (15 mL) was added levulinic acid (83 mg, 0.72 mmol), EDC (137 mg, 0.72 mmol) and DMAP (4.4 mg, 0.036 mmol). The mixture was stirred at r.t. overnight and then water was added and the mixture was extracted with CH_2Cl_2. The organic phase was washed with a satd aq solution of $NaHCO_3$, brine, dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified by chromatography (gradient 16→20% EtOAc in hexane) to afford **4** (222 mg, 95% yield) as a colorless oil. R_f 0.38 (2:1 hexane–EtOAc); $[\alpha]_D$ = +71.0 (*c* 0.3, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 7.35–7.26 (m, 15 H, ArH), 7.20–7.19 (m, 2 H, ArH), 7.05–7.04 (m, 2 H, ArH), 5.58 (dd, 1 H, *J* = 3.0, 1.5 Hz, H-2), 5.43 (d, 1 H, *J* = 1.5 Hz, H-1), 4.87 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.70 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.63 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.54 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.53 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.46 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.33 (ddd, 1 H, *J* = 9.0, 5.0, 1.5 Hz, H-5), 3.93 (dd, 1 H, *J* = 9.0, 3.0 Hz, H-3), 3.90 (app t, 1 H, *J* = 9.0 Hz, H-4), 3.83 (dd, 1 H, *J* = 11.0, 5.0 Hz, H-6), 3.73 (dd, 1 H, *J* = 11.0, 2.0 Hz, H-6), 2.71–2.66 (m, 4 H, $CH_3C{=}OCH_2$, $OC{=}OCH_2CH_2$), 2.30 (s, 3 H, CH_3PhS), 2.11 (s, 3 H, $CH_3C{=}OCH_2$); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 206.2 ($CH_3C{=}OCH_2$), 171.9 ($OC{=}OCH_2CH_2$), 138.3 (Ar), 138.2 (Ar), 137.9 (Ar), 137.7 (Ar), 132.4 (Ar), 129.8 (Ar), 129.7 (Ar), 128.4 (Ar), 128.33 (Ar), 128.28 (Ar), 128.16 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.67 (Ar), 127.54 (Ar), 86.4 (C-1), 78.4 (C-3), 75.2 (Ph*C*H$_2$), 74.5 (C-4), 73.3 (Ph*C*H$_2$), 72.4 (C-5), 71.7 (Ph*C*H$_2$), 70.4 (C-2), 68.9 (C-6), 37.9 ($CH_3C{=}OCH_2$), 29.8 ($CH_3C{=}OCH_2$), 28.1 ($CH_3C{=}OCH_2CH_2$), 21.1 (CH_3); HRMS (ESI) calcd for (M+Na) $C_{39}H_{42}NaO_7S$: 677.2543. Found: 677.2554.



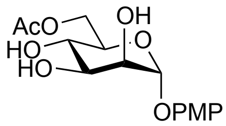
***p*-Tolyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-levulinyl-1-thio-α-D-mannopyranoside (3):** To a solution of **S12**[3] (240 mg, 0.58 mmol) in CH_2Cl_2 (250 mL) was added levulinic acid (133 mg, 1.15 mmol), EDC (219 mg, 1.15 mmol) and DMAP (7.3 mg, 0.06 mmol). The mixture was stirred at r.t. overnight and then water was added and the mixture was extracted with EtOAc. The organic phase was washed with a satd aq solution of $NaHCO_3$, brine, dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified by chromatography (gradient 20→25% EtOAc in hexane) to afford **3** (266 mg, 90% yield) as a colorless oil. R_f 0.31 (3:2 hexane–EtOAc); $[\alpha]_D$ = +145.0 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.48–7.47 (m, 2 H, ArH), 7.38–7.35 (m, 5 H, ArH), 7.13–7.11 (m, 2 H, ArH), 5.59 (s, 1H, PhC*H*(O)$_2$), 5.58 (d, 1 H, *J* = 3.5 Hz, H-2), 5.38 (dd, 1 H, *J* = 10.0, 3.5 Hz, H-3), 5.35 (s, 1 H, H-1), 4.46 (app td, 1 H, *J* = 10.0, 5.0 Hz, H-5), 4.24 (dd, 1 H, *J* = 10.0, 5.0 Hz, H-6), 4.12 (app t, 1 H, *J* = 10.0 Hz, H-4), 3.85 (dd, 1 H, *J* = 11.0, 1.5 Hz, H-6), 2.74–2.71 (app t, 2 H, *J* = 6.5 Hz, CH_3C=OCH_2), 2.60 (dt, 1 H, *J* = 17.0, 6.5 Hz, OC=OCH_2CH$_2$), 2.52 (dt, 1 H, *J* = 17.0, 6.5 Hz, OC=OCH_2CH$_2$), 2.32 (s, 3 H, CH_3PhS), 2.15 (s, 3 H, CH_3C=OCH$_2$), 2.14 (s, 3 H, OC=OCH_3); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 206.1 (CH$_3$*C*=OCH$_2$), 171.7 (O*C*=OCH$_2$CH$_2$), 169.8 (O*C*=OCH$_3$), 138.4 (Ar), 137.0 (Ar), 132.8 (Ar), 129.9 (Ar), 129.1 (Ar), 129.0 (Ar), 128.3 (Ar), 126.2 (Ar), 101.9 (Ph*C*H(O)$_2$), 87.1 (C-1), 76.2 (C-4), 71.4 (C-2), 68.9 (C-3), 68.4 (C-6), 65.1 (C-5), 37.9 (CH$_3$C=O*C*H$_2$), 29.8 (*C*H$_3$C=OCH$_2$), 27.9 (CH$_3$C=OCH$_2$*C*H$_2$), 21.1 (CH$_3$), 20.8 (OC=O*C*H$_3$); HRMS (ESI) calcd for (M+Na) $C_{27}H_{30}NaO_8S$: 537.1554. Found: 537.1552.



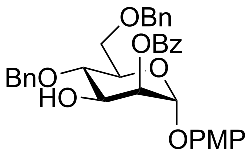
***p*-Tolyl 3-*O*-Benzyl-4,6-di-*O*-benzylidene-1-thio-α-D-mannopyranoside (S13):** Compound **S11**[4] (5.0 g, 13.3 mmol) was suspended in toluene (120 mL) treated with *n*-Bu_2SnO (4.0 g, 1.6 mmol) and heated at reflux for 6 h with a Dean–Stark trap. The reaction mixture was cooled to r.t. and then BnBr (3.18 g, 18.6 mmol), cesium fluoride (2.2 g, 14.6 mmol) and TBAI (5.38 g, 14.6 mmol) were added. The resulting mixture was stirred at 110 °C for 2 h. After cooling to r.t., the mixture was diluted with EtOAc, washed with brine, dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified by chromatography (gradient 16→25% EtOAc in hexane) to afford **S13** (5.21 g, 85% yield) as a white foam; R_f 0.50 (2:1 hexane–EtOAc); $[\alpha]_D$ = +230.5 (*c* 0.6, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 7.51–7.50 (m, 2 H, ArH), 7.39–7.31 (m, 10 H, ArH), 7.12–7.11 (m, 2 H, ArH), 5.61 (s, 1 H, PhC*H*$(O)_2$), 5.51 (d, 1 H, *J* = 1.0 Hz, H-1), 4.89 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.74 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.42 (app td, 1 H, *J* = 10.0, 5.0 Hz, H-5), 4.27 (app dt, 1 H, *J* = 3.5, 1.4 Hz, H-2), 4.20 (dd, 1 H, *J* = 10.3, 5.0 Hz, H-6), 4.16 (app t, 1 H, *J* = 10.5 Hz, H-4), 3.96 (dd, 1 H, *J* = 9.5, 3.5 Hz, H-3), 3.84 (app t, 1 H, *J* = 10.3 Hz, H-6), 2.81 (d, 1 H, *J* = 1.4 Hz, OH), 2.33 (s, 3 H, CH_3PhS); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.1 (Ar), 137.8 (Ar), 137.5 (Ar), 132.5 (Ar), 130.0 (Ar), 129.4 (Ar), 129.0 (Ar), 128.6 (Ar), 128.3 (Ar), 128.1 (Ar), 127.9 (Ar), 126.1 (Ar), 101.6 (PhCH$(O)_2$), 88.2 (C-1), 79.1 (C-4), 75.7 (C-3), 73.2 (Ph*C*H_2), 71.4 (C-2), 68.6 (C-6), 64.5 (C-5), 21.1 (CH_3); HRMS (ESI) calcd for (M+Na) $C_{27}H_{28}NaO_5S$: 487.1550. Found: 487.1560.



***p*-Tolyl 3-*O*-Benzyl-4,6-di-*O*-benzylidene-2-*O*-levulinyl-1-thio-α-D-mannopyrano side (5):** To a solution of **S13** (1.2 g, 2.37 mmol) in CH_2Cl_2 (100 mL) was added levulinic acid (0.55 g, 4.74 mmol), EDC (0.91 g, 4.74 mmol) and DMAP (30 mg, 0.24 mmol). The mixture was stirred at r.t. overnight and then water was added and the mixture was extracted with EtOAc. The organic phase was washed with a satd aq solution of $NaHCO_3$, brine, dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified by chromatography (gradient 16→25% EtOAc in hexane) to afford **5** (1.24 g, 92% yield) as a white foam. R_f 0.16 (3:1 hexane−EtOAc); $[\alpha]_D$ = +91.0 (*c* 0.4, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 7.52−7.51 (m, 2 H, ArH), 7.39−7.26 (m, 10 H, ArH), 7.12−7.11 (m, 2 H, ArH), 5.63 (s, 1 H, PhC*H*(O)$_2$), 5.59 (dd, 1 H, *J* = 3.3, 1.2 Hz, H-2), 5.38 (d, 1 H, *J* = 1.0 Hz, H-1), 4.70 (d, 1 H, *J* = 12.5 Hz, PhC*H*$_2$), 4.67 (d, 1 H, *J* = 12.5 Hz, PhC*H*$_2$), 4.36 (app td, 1 H, *J* = 10.0, 5.0 Hz, H-5), 4.22 (dd, 1 H, *J* = 10.3, 5.0 Hz, H-6), 4.09 (app t, 1 H, *J* = 9.5 Hz, H-4), 4.00 (dd, 1 H, *J* = 9.5, 3.5 Hz, H-3), 3.84 (app t, 1 H, *J* = 10.3 Hz, H-6), 2.79−2.65 (m, 4 H, 2 x CH_2), 2.32 (s, 3 H, CH_3PhS), 2.16 (s, 3 H, CH_3C=O); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.1 (CH_3*C*=OCH_2), 171.9 (O*C*=OCH_2), 138.4 (Ar), 137.8 (Ar), 137.4 (Ar), 132.7 (Ar), 130.0 (Ar), 129.1 (Ar), 129.0 (Ar), 128.4 (Ar), 128.2 (Ar), 127.8 (Ar), 127.7 (Ar), 126.1 (Ar), 101.6 (PhCH(O)$_2$), 87.3 (C-1), 78.6 (C-4), 74.0 (C-3), 72.3 (Ph*C*H$_2$), 71.5 (C-2), 68.5 (C-6), 65.0 (C-5), 38.0 (CH_3C=O*C*H$_2$), 29.8 (*C*H$_3$C=OCH_2), 28.0 (CH_3C=OCH_2*C*H$_2$), 21.1 (CH_3); HRMS (ESI) calcd for (M+Na) $C_{32}H_{34}NaO_7S$: 585.1920. Found: 585.1917.

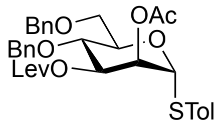


***p*-Methoxyphenyl 6-*O*-Acetyl-α-D-mannopyranoside (S6):** *p*-Methoxyphenyl α-D-mannopyranoside **S5**[5] (4.2 g, 14.7 mmol) was dissolved in sym-collidine (100 mL) and the solution was cooled to −35 °C. Acetyl chloride (2.3 g, 29.4 mmol) was then added dropwise over 30 min under vigorous stirring. After 2 h, CH_3OH (5 mL) was added, and the reaction was warmed to r.t. The crude mixture was concentrated and purified by chromatography (gradient 10→33% acetone in CH_2Cl_2) to afford **S6** (3.7 g, 77% yield) as a white solid. R_f 0.14 (1:3 hexane−EtOAc); $[\alpha]_D$ = +63.9 (*c* 0.9, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 6.96−6.95 (m, 2 H, ArH), 6.78−6.76 (m, 2 H, ArH), 5.43 (s, 1 H, H-1), 4.46 (dd, 1 H, *J* = 12.1, 5.5 Hz, H-6), 4.22 (dd, 1 H, *J* = 12.1, 2.0 Hz, H-6), 4.16 (dd, 1 H, *J* = 3.4, 1.5 Hz, H-2), 4.04 (dd, 1 H, *J* = 9.4, 3.4 Hz, H-3), 3.86 (ddd, 1 H, *J* = 9.8, 5.5, 2.0 Hz, H-5), 3.74 (app t, 1 H, *J* = 9.8 Hz, H-4), 3.73 (s, 3 H, OCH_3), 2.01 (s, 3 H, OC=OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 172.2 (C=O), 155.1 (Ar), 150.0 (Ar), 117.8 (Ar), 114.6 (Ar), 98.8 (C-1), 71.4 (C-3), 71.0 (C-5), 70.5 (C-2), 67.6 (C-4), 63.5 (C-6), 55.6 (CH_3O), 20.9 (OC=OCH_3); HRMS (ESI) calcd for (M+Na) $C_{15}H_{20}NaO_8$: 351.1050. Found: 351.1045.

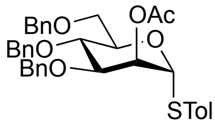


***p*-Methoxyphenyl 2-*O*-Benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (6):** *p*-Toluenesulfonic acid monohydrate (95 mg, 0.5 mmol) was added to a solution of **S6** (0.73 g, 2.22 mmol) and trimethylorthobenzoate (3 mL) in DMF (0.7 mL) under N_2. After 1 h additional

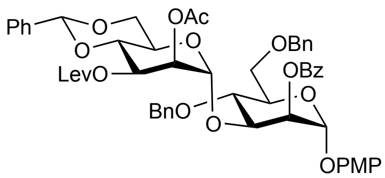
DMF (4.2 mL) was added and the suspension was cooled to 0 °C. NaH (60% in mineral oil, 528 mg, 13.2 mmol) was added and the mixture was stirred at 0 °C for 15 min. Then, benzyl bromide (1.14 g, 6.66 mmol) was added dropwise. After a further 1 h, ice water was added to the solution and the mixture was warmed to r.t. The organic phase was extracted with CH_2Cl_2. The organic extract was stirred vigorously in the presence of 1 M HCl for 1 h. At this time the mixture was diluted with CH_2Cl_2 and washed with a satd aq solution of $NaHCO_3$, brine, dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by chromatography (gradient 14→25% EtOAc in hexane) to afford **6** (1.09 g, 86% yield) as a colorless oil; R_f 0.56 (3:2 hexane–EtOAc); $[\alpha]_D$ = +36.8 (*c* 1.9, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.05–8.03 (m, 2 H, ArH), 7.58–7.55 (m, 1 H, ArH), 7.40–7.26 (m, 12 H, ArH), 7.00–6.99 (m, 2 H, ArH), 6.80–6.78 (m, 2 H, ArH), 5.57 (d, 1 H, *J* = 1.9 Hz, H-1), 5.52 (dd, 1 H, *J* = 3.4, 1.9 Hz, H-2), 4.81 (d, 1 H, *J* = 11.1 Hz, PhC*H*₂), 4.71 (d, 1 H, *J* = 11.8 Hz, PhC*H*₂), 4.66 (d, 1 H, *J* = 11.1 Hz, PhC*H*₂), 4.50 (d, 1 H, *J* = 11.8 Hz, PhC*H*₂), 4.45 (ddd, 1 H, *J* = 9.6, 5.2, 3.4 Hz, H-3), 4.10 (app t, 1 H, *J* = 9.6 Hz, H-4), 3.98 (ddd, 1 H, *J* = 9.6, 3.7, 1.8 Hz, H-5), 3.90 (dd, 1 H, *J* = 11.0, 3.7 Hz, H-6), 3.75 (dd, 1 H, *J* = 11.0, 1.8 Hz, H-6), 3.74 (s, 3 H, OCH_3), 2.14 (d, 1 H, *J* = 5.2 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1 (C=O), 155.1 (Ar), 150.0 (Ar), 138.3 (Ar), 138.1 (Ar), 133.3 (Ar), 129.9 (Ar), 129.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 127.9 (Ar), 127.6 (Ar), 127.5 (Ar), 117.8 (Ar), 114.6 (Ar), 96.6 (C-1), 75.6 (C-4), 74.9 (Ph*C*H₂), 73.4 (Ph*C*H₂), 72.6 (C-2), 71.9 (C-5), 70.4 (C-3), 68.8 (C-6), 55.6 (CH_3O); ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^1J_{C\text{-}1,H\text{-}1}$ = 174.6 Hz (C-1, H-1); HRMS (ESI) calcd for (M+Na) $C_{34}H_{34}NaO_8$: 593.2146. Found: 593.2154.



***p*-Tolyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-1-thio-α-D-mannopyranoside (7):** To a solution of **S10**[6] (10.62 g, 21 mmol) in CH_2Cl_2 (250 mL) was added levulinic acid (4.85 g, 42 mmol), EDC (8.0 g, 42 mmol) and DMAP (256 mg, 2.1 mmol). The mixture was stirred at r.t. overnight and then water was added and the mixture was extracted with EtOAc. The organic phase was washed with a satd aq solution of $NaHCO_3$, brine, dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified by chromatography (gradient 20→28% EtOAc in hexane) to afford **7** (12.1 g, 94% yield) as a colorless oil. R_f 0.35 (3:2 hexane–EtOAc); $[\alpha]_D$ = +97.9 (*c* 0.8, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 7.40–7.23 (m, 12 H, ArH), 7.09–7.08 (m, 2 H, ArH), 5.51 (dd, 1 H, *J* = 3.5, 1.5 Hz, H-2), 5.45 (d, 1 H, *J* = 1.5 Hz, H-1), 5.34 (dd, 1 H, *J* = 10.0, 3.5 Hz, H-3), 4.72 (d, 1 H, *J* = 11.0 Hz, $PhCH_2$), 4.71 (d, 1 H, *J* = 12.0 Hz, $PhCH_2$), 4.56 (d, 1 H, *J* = 11.0 Hz, $PhCH_2$), 4.50 (d, 1 H, *J* = 12.0 Hz, $PhCH_2$), 4.42 (ddd, 1 H, *J* = 11.0, 10.0, 1.5 Hz, H-5), 4.07 (app t, 1 H, *J* = 10.0 Hz, H-4), 3.89 (dd, 1 H, *J* = 11.0, 4.5 Hz, H-6), 3.73 (dd, 1 H, *J* = 11.0, 1.5 Hz, H-6), 2.81–2.67 (m, 2 H, $CH_3C{=}OCH_2$), 2.58–2.47 (m, 2 H, $OC{=}OCH_2CH_2$), 2.33 (s, 3 H, CH_3PhS), 2.20 (s, 3 H, $CH_3C{=}OCH_2$), 2.16 (s, 3 H, $OC{=}OCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2 ($CH_3C{=}OCH_2$), 171.8 ($OC{=}OCH_2CH_2$), 170.0 ($OC{=}OCH_3$), 138.1 (Ar), 138.0 (Ar), 137.9 (Ar), 132.4 (Ar), 129.8 (Ar), 129.6 (Ar), 128.4 (Ar), 128.3 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 86.2 (C-1), 74.9 ($PhCH_2$), 73.5 ($PhCH_2$), 73.3 (C-4), 72.6 (C-3), 72.4 (C-5), 71.5 (C-2), 68.7 (C-6), 37.9 ($CH_3C{=}OCH_2$), 29.8 ($CH_3C{=}OCH_2$), 27.9 ($CH_3C{=}OCH_2CH_2$), 21.1 (CH_3), 21.0 ($OC{=}OCH_3$); HRMS (ESI) calcd for (M+Na) $C_{34}H_{38}NaO_8S$: 629.2180. Found: 629.2179.

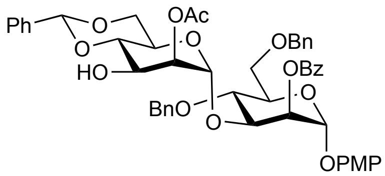


***p*-Tolyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (31):** Compound **S7**[2] (200 mg, 0.36 mmol) was dissolved in 3:2 pyridine−Ac_2O (5 mL) and the mixture was stirred at r.t. for 2 h. Then, the solution was concentrated, dissolved in CH_2Cl_2 (100 mL) followed by washing with 1M of HCl, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography (gradient 16→20% EtOAc in hexane) to afford **31** (222 mg, 96% yield) as a white solid; R_f 0.62 (2:1 hexane−EtOAc); $[\alpha]_D$ = +91.1 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.35−7.26 (m, 15 H, ArH), 7.20−7.18 (m, 2 H, ArH), 7.05−7.04 (m, 2 H, ArH), 5.59 (app t, 1 H, *J* = 2.0, H-2), 5.45 (d, 1 H, *J* = 2.0 Hz, H-1), 4.88 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.71 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.65 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.56 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.51 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.46 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.34−4.32 (m, 1 H, H-5), 3.95−3.93 (m, 2 H, H-3, H-4), 3.84 (dd, 1 H, *J* = 11.0, 4.5 Hz, H-6), 3.72 (dd, 1 H, *J* = 11.0, 1.5 Hz, H-6), 2.29 (s, 3 H, CH_3PhS), 2.13 (OC=OC*H*$_3$); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 170.4 (O*C*=OCH$_3$), 138.3 (Ar), 138.2 (Ar), 137.9 (Ar), 137.6 (Ar), 132.3 (Ar), 129.9 (Ar), 129.8 (Ar), 128.4 (Ar), 128.33 (Ar), 128.26 (Ar), 128.17 (Ar), 127.9 (Ar), 127.73 (Ar), 127.66 (Ar), 127.52 (Ar), 86.5 (C-1), 78.5 (C-3), 75.2 (Ph*C*H$_2$), 74.6 (C-4), 73.3 (Ph*C*H$_2$), 72.4 (C-5), 71.9 (Ph*C*H$_2$), 70.3 (C-2), 68.9 (C-6), 21.1 (OC=O*C*H$_3$); HRMS (ESI) calcd for (M+Na) $C_{36}H_{38}NaO_6S$: 621.2281. Found: 621.2283.



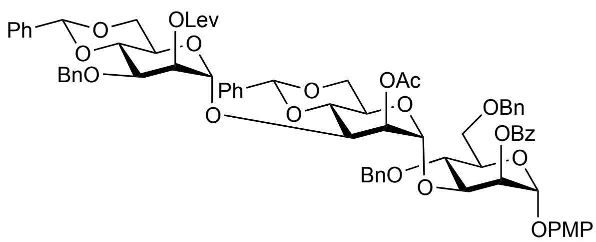
***p*-Methoxyphenyl 2-*O*-Acetyl-4,6-di-*O*-benzylidene-3-*O*-levulinyl-α-D-manno pyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (11):** A mixture of donor **3** (160 mg, 0.31 mmol), acceptor **6** (161 mg, 0.28 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (20 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (94 mg, 0.42 mmol) and AgOTf (22 mg, 0.08 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h. Et_3N (0.1 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→33% EtOAc in hexane) to afford **11** (176 mg, 65% yield) as a white foam; R_f 0.24 (3:2 hexane–EtOAc); $[\alpha]_D$ = +31.6 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.12–8.11 (m, 2 H, ArH), 7.60–7.58 (m, 1 H, ArH), 7.42–7.26 (m, 15 H, ArH), 7.18–7.17 (m, 2 H, ArH), 7.00–6.99 (m, 2 H, ArH), 6.79–6.78 (m, 2 H, ArH), 5.61 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.59 (d, 1 H, *J* = 2.0 Hz, H-1), 5.48 (dd, 1 H, *J* = 3.5, 1.5 Hz, H-2′), 5.43 (s, 1 H, PhC*H*(O)$_2$), 5.31 (dd, 1 H, *J* = 10.0, 3.0 Hz, H-3′), 5.15 (d, 1 H, *J* = 1.5 Hz, H-1′), 4.92 (d, 1 H, *J* = 10.5 Hz, PhC*H*$_2$), 4.68 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.64 (d, 1 H, *J* = 10.5 Hz, PhC*H*$_2$), 4.48 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.47 (dd, 1 H, *J* = 9.5, 3.0 Hz, H-3), 4.29 (app t, 1 H, *J* = 9.5 Hz, H-4), 4.16 (dd, 1 H, *J* = 10.0, 5.0 Hz, H-6′), 4.00–3.97 (m, 2 H, H-5, H-4′), 3.93 (td, 2 H, *J* = 10.0, 5.0 Hz, H-5′), 3.89 (dd, 1 H, *J* = 11.0, 3.5 Hz, H-6), 3.75 (s, 3 H, OCH_3), 3.73–3.70 (m, 2 H, H-6, H-6′), 2.65 (t, 2 H, *J* = 7.0 Hz, CH_3C=OC*H*$_2$), 2.54 (dt, 1 H, *J* = 17.0, 7.0 Hz, OC=OC*H*$_2$CH$_2$), 2.46 (dt, 1 H, *J* = 17.0, 7.0 Hz, OC=OC*H*$_2$CH$_2$), 2.13 (s, 3 H, C*H*$_3$C=OCH$_2$), 2.09 (s, 3 H, OC=OC*H*$_3$); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 206.1

(CH_3C=OCH_2), 171.7 (O*C*=OCH_2), 169.7, (O*C*=OCH_3), 166.1 (PhC=O), 155.1 (Ar), 149.9 (Ar), 138.2 (Ar), 137.8 (Ar), 137.1 (Ar), 133.4 (Ar), 130.0 (Ar), 129.4 (Ar), 129.0 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 126.4 (Ar), 117.7 (Ar), 114.6 (Ar), 101.9 (Ph*C*H$(O)_2$), 100.8 (C-1′), 96.1 (C-1), 79.7 (C-3), 75.7 (PhCH_2), 75.6 (C-4′), 73.9 (C-4), 73.4 (PhCH_2), 72.1 (C-2), 72.0 (C-5), 69.9 (C-2′), 68.8 (C-3′), 68.7 (C-6), 68.5 (C-6′), 64.9 (C-5′), 55.6 (CH_3O), 37.8 (CH_3C=OCH_2), 29.7 (CH_3C=OCH_2), 27.9 (CH_3C=OCH_2CH_2), 20.7 (OC=OCH_3); HRMS (ESI) calcd for (M+NH_4) $C_{54}H_{60}NO_{16}$: 978.3907. Found: 978.3919.

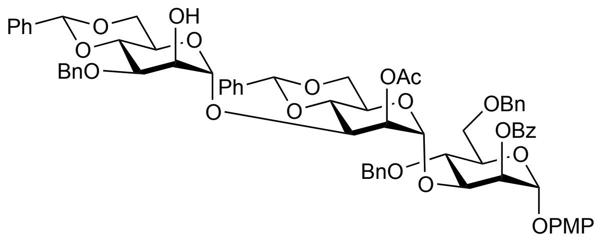


***p*-Methoxyphenyl 2-*O*-Acetyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)- 2-*O*-benzoyl-4,6-di-*O*- benzyl-α-D-mannopyranoside (13):** A solution of **11** (190 mg, 0.2 mmol) and hydrazine acetate (37 mg, 0.4 mmol) in 9:1 CH_2Cl_2−CH_3OH (30 mL) was stirred at r.t. for 3 h. Then, the solution was concentrated and the resulting residue was purified by chromatography (gradient 20→33% EtOAc in hexane) to afford **13** (156 mg, 93% yield) as a white foam; R_f 0.30 (3:2 hexane−EtOAc); $[\alpha]_D$ = +45.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.11−8.10 (m, 2 H, ArH), 7.62−7.60 (m, 1 H, ArH), 7.43−7.24 (m, 17 H, ArH), 7.01−7.00 (m, 2 H, ArH), 6.80−6.79 (m, 2 H, ArH), 6.00−5.59 (m, 2 H, H-2, H-1), 5.48 (s, 1 H, PhC*H*$(O)_2$), 5.28 (dd, 1 H, *J* = 3.5, 1.5 Hz, H″-2), 5.20 (s, 1 H, H-1′), 4.83 (d, 1 H, *J* = 10.5 Hz, PhCH_2), 4.70 (d, 1 H, *J* = 11.5 Hz, PhCH_2), 4.62 (d, 1 H, *J* = 10.5 Hz, PhCH_2), 4.49 (d, 1 H, *J* = 11.5 Hz, PhCH_2), 4.48 (dd, 1 H, *J* = 9.0, 3.0 Hz, H-3), 4.29 (app t, 1 H, *J* = 9.5 Hz, H-

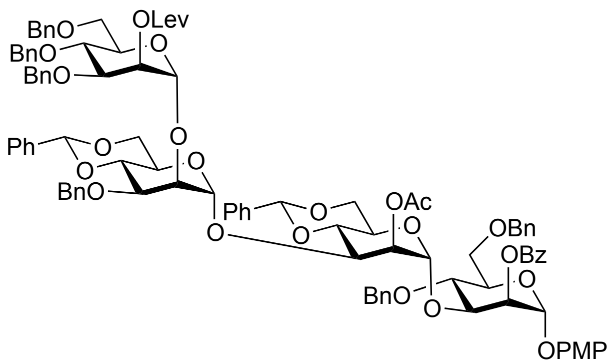
4), 4.21 (dd, 1 H, *J* = 10.0, 4.0 Hz, H-6′), 4.11–4.09 (m, 1 H, H-3′), 4.00–3.98 (m, 1 H, H-5), 3.88 (dd, 1 H, *J* = 10.5, 3.5 Hz, H-6), 3.86–3.81 (m, 2 H, H-5′, H-4′), 3.75 (s, 3 H, OCH_3), 3.73–3.70 (m, 2 H, H-6′, H-6), 2.15 (d, 1 H, *J* = 4.0 Hz, OH), 2.13 (s, 3 H, $OC{=}OCH_3$); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 170.2, ($OC{=}OCH_3$), 165.9 (PhC=O), 155.1 (Ar), 149.9 (Ar), 138.2 (Ar), 137.8 (Ar), 137.1 (Ar), 133.4 (Ar), 129.9 (Ar), 129.5 (Ar), 129.2 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3 (Ar), 128.17 (Ar), 128.14 (Ar), 127.9 (Ar), 127.6 (Ar), 126.4 (Ar), 117.8 (Ar), 114.6 (Ar), 102.2 ($PhCH(O)_2$), 100.6 (C-1′), 96.2 (C-1), 78.6 (C-4′), 78.2 (C-3), 75.4 ($PhCH_2$), 74.3 (C-4), 73.4 ($PhCH_2$), 72.1 (C-2, C-5), 71.9 (C-2′), 68.6 (C-6), 68.4 (C-6′), 67.2 (C-3′), 64.2 (C-5′), 55.6 (CH_3O), 20.9 ($OC{=}OCH_3$); HRMS (ESI) calcd for (M+Na) $C_{49}H_{50}NaO_{14}$: 885.3093. Found: 885.3092.



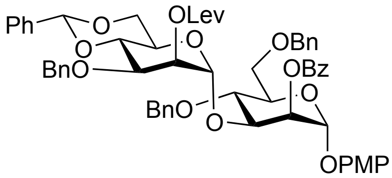
***p*-Methoxyphenyl 3-*O*-Benzyl-4,6-di-*O*-benzylidene-2-*O*-levulinyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (14):** A mixture of donor **5** (118 mg, 0.21 mmol), acceptor **13** (140 mg, 0.16 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (15 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (61 mg, 0.27 mmol) and AgOTf (16 mg, 0.06 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (0.2 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→25% EtOAc in hexane) to afford **14** (141 mg, 67% yield) as a white foam; R_f 0.33 (3:2 hexane–EtOAc); $[\alpha]_D$ = +14.5 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.09–8.08 (m, 2 H, ArH), 7.59–7.57 (m, 1 H, ArH), 7.46–7.22 (m, 27 H, ArH), 7.00–6.99 (m, 2 H, ArH), 6.80–6.78 (m, 2 H, ArH), 5.60 (app t, 1 H, *J* = 2.0 Hz, H-2), 5.56 (d, 1 H, *J* = 2.0 Hz, H-1), 5.52 (s, 1 H, PhC*H*(O)$_2$), 5.51 (s, 1 H, PhC*H*(O)$_2$), 5.39 (dd, 1 H, *J* = 3.0, 1.5 Hz, H‴-2), 5.32 (dd, 1 H, *J* = 3.0, 1.0 Hz, H-2′), 5.20 (s, 1 H, H-1′), 5.07 (s, 1 H, H-1″), 4.82 (d, 1 H, *J* = 10.5 Hz, PhC*H*$_2$), 4.70 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.64–4.58 (m, 3 H, PhC*H*$_2$), 4.51 (dd, 1 H, *J* = 9.0, 3.0 Hz, H-3), 4.48 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.29 (app t, 1 H, *J* = 9.5 Hz, H-4), 4.22–4.19 (m, 2 H, H-3′, H-6′), 3.99–3.97 (m, 2 H, H-5, H-4′), 3.93–3.83 (m, 4 H), 3.80–3.70 (m, 4 H), 3.75 (s, 3 H, OCH_3), 3.58–3.55 (m, 1 H), 2.64–2.56 (m, 4 H, CH_3C=OC*H*$_2$, OC=OC*H*$_2$CH$_2$), 2.11 (s, 3 H, C*H*$_3$C=OCH$_2$), 2.00 (s, 3 H, OC=OC*H*$_3$); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 206.1 (CH_3*C*=OCH$_2$), 171.6 (O*C*=OCH$_2$), 170.2, (O*C*=OCH$_3$), 165.8 (PhC=O), 155.2 (Ar), 149.9 (Ar), 138.2 (Ar), 138.1 (Ar), 137.6 (Ar), 137.2 (Ar), 133.4 (Ar), 129.9 (Ar), 129.5 (Ar), 128.8 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 128.05 (Ar), 127.97 (Ar), 127.89 (Ar), 127.6 (Ar), 127.56 (Ar), 127.54 (Ar), 127.49 (Ar), 126.20 (Ar), 126.16 (Ar), 117.8 (Ar), 114.6 (Ar), 101.5 (Ph*C*H(O)$_2$), 101.3 (Ph*C*H(O)$_2$), 100.3 (C-1″), 99.5 (C-1′), 96.3 (C-1), 78.5, 78.4, 77.4 (C-3), 75.4 (Ph*C*H$_2$), 74.4 (C-4), 73.5 (Ph*C*H$_2$), 73.3, 72.1 (C-5), 71.96 (Ph*C*H$_2$), 71.9 (C-2), 71.6 (C-2′), 71.3 (C-3′), 69.6 (C-2″), 68.6, 68.5, 68.4, 64.5, 64.3, 55.6 (CH_3O), 38.0 (CH_3C=O*C*H$_2$), 29.7 (*C*H$_3$C=OCH$_2$), 28.0 (CH_3C=OCH$_2$*C*H$_2$), 20.7 (OC=O*C*H$_3$); HRMS (ESI) calcd for (M+NH$_4$) $C_{74}H_{80}NO_{21}$: 1318.5217. Found: 1318.5246.



***p*-Methoxyphenyl 3-*O*-Benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)- 2-*O*-acetyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*- benzyl-α-D-mannopyranoside (15):** A solution of **14** (110 mg, 0.08 mmol) and hydrazine acetate (23 mg, 0.25 mmol) in 9:1 CH_2Cl_2–CH_3OH (30 mL) was stirred at r.t. for 3 h. Then, the solution was concentrated and the resulting residue was subjected to chromatography (gradient 20→33% EtOAc in hexane) to afford **15** (101 mg, 99% yield) as a white foam; R_f 0.44 (3:2 hexane–EtOAc); $[\alpha]_D$ = +34.7 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.10–8.09 (m, 2 H, ArH), 7.59–7.57 (m, 1 H, ArH), 7.45–7.25 (m, 27 H, ArH), 7.01–6.99 (m, 2 H, ArH), 6.80–6.78 (m, 2 H, ArH), 5.61 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.57 (d, 1 H, *J* = 2.0 Hz, H-1), 5.51 (s, 1 H, PhC*H*(O)$_2$), 5.49 (s, 1 H, PhC*H*(O)$_2$), 5.35 (dd, 1 H, *J* = 3.5, 1.5 Hz, H-2′), 5.20 (d, 1 H, *J* = 1.5 Hz, H-1′), 5.10 (s, 1 H, H-1″), 4.86 (d, 1 H, *J* = 10.5 Hz, PhC*H*$_2$), 4.80 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.70 (d, 1 H, *J* = 11.5 Hz, PhC*H*$_2$), 4.65 (d, 1 H, *J* = 11.5 Hz, PhC*H*$_2$), 4.61 (d, 1 H, *J* = 10.5 Hz, PhC*H*$_2$), 4.51 (dd, 1 H, *J* = 9.0, 3.0 Hz, H-3), 4.49 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.29 (app t, 1 H, *J* = 9.5 Hz, H-4), 4.22–4.19 (m, 2 H, H-3′, H-6′), 4.01–3.86 (m, 7 H), 3.79–3.70 (m, 4 H), 3.75 (s, 3 H, OCH_3), 3.58 (app t, 1 H, *J* = 10.5 Hz), 2.49 (d, 1 H, *J* = 1.0 Hz, OH), 2.07 (s, 3 H, OC=OC*H*$_3$); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 169.6 (O*C*=OCH$_3$), 165.8 (PhC=O), 155.2 (Ar), 149.9 (Ar), 138.2 (Ar), 138.1 (Ar), 137.6 (Ar), 137.5 (Ar), 137.3 (Ar), 133.4 (Ar), 129.9 (Ar), 129.5 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.40 (Ar), 128.38 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.61 (Ar), 127.57 (Ar), 126.17 (Ar), 126.15 (Ar), 117.8 (Ar), 114.6 (Ar), 101.6 (Ph*C*H(O)$_2$), 101.5 (Ph*C*H(O)$_2$), 101.4 (C-1″), 100.3 (C-1′), 96.3 (C-1), 78.8, 78.2, 77.8 (C-3), 75.4 (Ph*C*H$_2$), 75.1, 74.3 (C-4), 73.5 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.3, 72.1, 71.94, 71.88, 69.9, 68.62, 68.60, 68.5, 64.6, 63.9, 55.6 (CH_3O), 20.8 (OC=O*C*H$_3$); HRMS (ESI) calcd for (M+Na) $C_{69}H_{70}NaO_{19}$: 1225.4404. Found: 1225.4413.

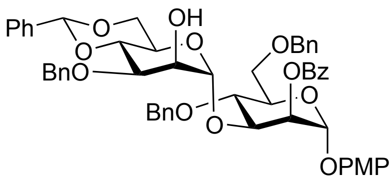


***p*-Methoxyphenyl 3,4,6-tri-*O*-Benzyl-2-*O*-levulinyl-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (16):** A mixture of donor **4** (38 mg, 0.058 mmol), acceptor **15** (54 mg, 0.045 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (5 mL) and stirred at r.t. for 10 min. The solution was then cooled to −5 °C, and then NIS (18 mg, 0.08 mmol) and AgOTf (5.8 mg, 0.022 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (0.2 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→25% EtOAc in hexane) to afford **16** (48 mg, 63% yield) as a white foam; R_f 0.41 (3:2 hexane−EtOAc); $[\alpha]_D$ = +20.8 (*c* 0.2, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.11−8.09 (m, 2 H, ArH), 7.58−7.55 (m, 1 H, ArH), 7.48−7.11 (m, 42 H, ArH), 7.02−7.00 (m, 2 H, ArH), 6.81–6.79 (m, 2 H, ArH), 5.61 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.57 (d, 1 H, *J* = 2.0 Hz), 5.54 (s, 1 H), 5.51 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.40 (s, 1 H), 5.34 (dd, 1 H, *J* = 3.5, 1.5 Hz), 5.20 (d, 1 H, *J* = 1.5 Hz), 5.11 (d, 1 H, *J* = 1.5 Hz), 5.08 (d, 1 H, *J* = 1.5 Hz), 4.87–4.80 (m, 3 H), 4.73–4.70 (m, 2 H), 4.63 (d, 1 H, *J* = 11.5 Hz), 4.60 (d, 1 H, *J* = 12.5 Hz, $PhCH_2$), 4.54–4.50 (m, 2 H), 4.43 (d, 1 H, *J* = 11.5 Hz), 4.41 (d, 1 H, *J* = 10.5 Hz), 4.30 (app t, 1 H, *J* = 9.5 Hz), 4.24–4.17 (m, 3 H), 4.01–3.86 (m, 7 H), 3.79–3.70 (m, 4 H), 4.02–3.85 (m, 8 H), 3.81 (dd, 1 H, *J* = 10.5, 3.5 Hz), 3.76 (s, 3 H), 3.75–3.68 (m, 4 H), 3.56–3.51 (m, 2 H), 3.25 (dd, 1 H, *J* = 11.0, 3.0 Hz), 3.03 (dd, 1 H, *J* = 11.0, 1.5 Hz), 2.67–2.61 (m, 4 H), 2.08 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2, 171.6, 169.5, 165.8, 155.2, 149.9, 138.6, 138.5, 138.2, 138.1, 137.7, 137.6, 137.3, 133.4, 130.0, 129.4, 128.9, 128.8, 128.6, 128.46, 128.37, 128.29, 128.25, 128.13, 128.11, 128.07, 127.9, 127.7, 127.6, 127.56, 127.48, 127.41, 127.3, 126.24, 126.15, 117.8, 114.6, 101.7, 101.5, 100.6, 100.3, 99.4, 96.4, 79.1, 78.5, 77.8, 77.2, 75.6, 75.5, 75.3, 75.2, 74.5, 73.9, 73.5, 73.2, 73.0, 72.2, 72.0, 71.9, 71.65, 71.64, 70.6, 68.63, 68.59, 68.52, 68.45, 68.0, 64.6, 64.5, 55.6, 30.0, 29.7, 28.2, 20.7; HRMS (ESI) calcd for ($M+NH_4$) $C_{101}H_{108}NO_{26}$:1750.7154. Found: 1750.7189.

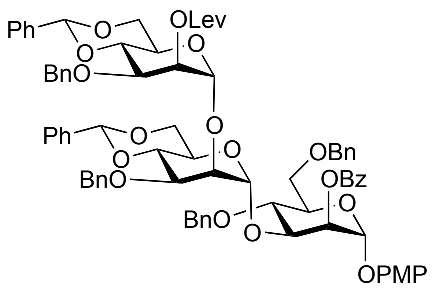


***p*-Methoxyphenyl 3-*O*-Benzyl-4,6-di-*O*-benzylidene-2-*O*-levulinyl-α-D-manno-pyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (17):** A mixture of donor **5** (6.40 g, 11.4 mmol), acceptor **6** (5.0 g, 8.77 mmol) and powdered 4Å molecular sieves was suspended in anhydrous CH_2Cl_2 (480 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (3.52 g, 15.8 mmol) and AgOTf (673 mg, 2.63 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (2.0 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→25% EtOAc in hexane) to afford **17** (6.4 g, 72% yield) as a white foam; R_f 0.26 (2:1 hexane–EtOAc); $[\alpha]_D$ = +31.7 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.06–8.05 (m, 2 H, ArH), 7.58–7.56 (m, 1 H, ArH), 7.38–7.15 (m, 22 H, ArH), 7.00–6.99 (m, 2 H, ArH), 6.79–6.78 (m, 2 H, ArH), 5.58 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.56 (d, 1 H, *J* = 2.0 Hz, H-1), 5.50 (s, 1 H, PhC*H*(O)$_2$), 5.38 (dd, 1 H, *J* = 3.5, 1.5 Hz, H-2′), 5.18 (d, 1 H, *J* = 1.5 Hz, H-1′), 4.74 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.60 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.52 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.50–4.45 (m, 4 H, PhC*H*$_2$, H-3), 4.22 (app t, 1 H, *J* = 10.0 Hz, H-4′), 4.16 (dd, 1 H, *J* = 10.5, 4.5 Hz, H-6′), 3.98–3.96 (m, 1 H, H-5′), 3.96 (app t, 1 H, *J* = 9.5 Hz, H-4), 3.88–3.84 (m, 3 H, H-3′, H-5, H-6), 3.74 (s, 3 H, OCH_3), 3.71 (app t, 1 H, *J* = 10.5 Hz, H-6′), 3.66 (dd, 1 H, *J* = 11.0, 1.6 Hz, H-6), 2.74–2.60 (m, 4 H, CH_3C=OC*H*$_2$, CH_3C=OCH_2C*H*$_2$), 2.14 (s, 3 H, C*H*$_3$C=OCH_2,); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 206.1 (CH_3*C*=OCH_2), 171.7 (O*C*=OCH_2), 165.8 (PhC=O), 155.1 (Ar), 149.9 (Ar), 138.3 (Ar), 137.9 (Ar), 137.8 (Ar), 137.5 (Ar), 133.3 (Ar), 129.9 (Ar), 129.6 (Ar), 128.8 (Ar), 128.5

(Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 126.3 (Ar), 117.8 (Ar), 114.6 (Ar), 101.6 (Ph*C*H(O)$_2$), 100.6 (C-1′), 96.2 (C-1), 78.2 (C-4), 78.0 (C-3), 75.4 (Ph*C*H$_2$), 74.4 (C-4′), 73.6 (C-3′), 73.4 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 72.0 (C-5), 71.9 (C-2), 70.2 (C-2′), 68.6 (C-6), 68.5 (C-6′), 64.7 (C-5′), 55.6 (CH$_3$O), 38.0 (CH$_3$C=O*C*H$_2$), 29.8 (*C*H$_3$C=OCH$_2$), 28.0 (CH$_3$C=OCH$_2$*C*H$_2$); ^{1}H-coupled HSQC (700 MHz, CDCl$_3$) $^1J_{\text{C-1, H-1}}$ = 171.5 Hz (C-1, H-1), $^1J_{\text{C-1′, H-1′}}$ = 171.5 Hz (C-1′, H-1′); HRMS (ESI) calcd for (M+NH$_4$) $C_{59}H_{64}NO_{15}$: 1026.4270. Found: 1026.4257.

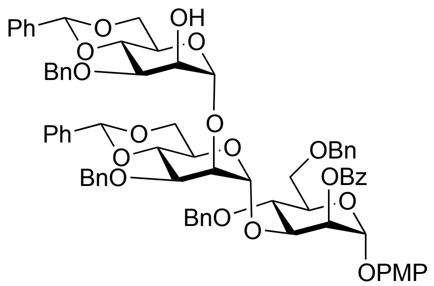


***p*-Methoxyphenyl 3-*O*-Benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)- 2-*O*-benzoyl-4,6-di-*O*- benzyl-α-D-mannopyranoside (18):** A solution of **17** (6.40 g, 6.35 mmol) and hydrazine acetate (1.05 g, 11.4 mmol) in 9:1 CH$_2$Cl$_2$–CH$_3$OH (300 mL) was stirred at r.t. for 3 h. Then, the solution was concentrated and the resulting residue was subjected to chromatography (gradient 16→25% EtOAc in hexane) to afford **18** (5.6 g, 92% yield) as a white foam; R_f 0.28 (2:1 hexane–EtOAc); $[\alpha]_D$ = +40.1 (*c* 0.3, CH$_2$Cl$_2$); ^{1}H NMR (700 MHz, CDCl$_3$, δ_H) 8.10–8.09 (m, 2 H, ArH), 7.59–7.57 (m, 1 H, ArH), 7.41–7.20 (m, 22 H, ArH), 7.02–7.00 (m, 2 H, ArH), 6.80–6.79 (m, 2 H, ArH), 5.61 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.57 (d, 1 H, *J* = 2.0 Hz, H-1), 5.49 (s, 1 H, PhC*H*(O)$_2$), 5.24 (d, 1 H, *J* = 1.0 Hz, H-1′), 4.74 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.71 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.68 (d, 1 H, *J* = 10.5 Hz, PhC*H*$_2$), 4.57 (d, 1 H, *J* = 10.5 Hz, PhC*H*$_2$), 4.53 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.48 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.47 (dd, 1 H, *J* = 9.5, 3.0 Hz, H-3), 4.24 (app t, 1 H, *J* = 10.0 Hz, H-4′), 4.19 (dd, 1 H, J = 10.0, 4.5 Hz, H-6′), 4.03 (app t, 1 H, J = 9.5 Hz, H-4), 3.99 (ddd, J = 10.0, 3.0, 1.5 Hz, H-5), 3.95 (dd, J = 3.0, 1.5 Hz, H-2′), 3.87 (dd, 1 H, J = 11.0, 3.0 Hz, H-6), 3.84 (td, 1 H, J = 10.0, 4.5 Hz, H-5′), 3.78 (dd, 1 H, J = 9.5, 3.0 Hz, H-3′), 3.75 (s, 3 H, OCH_3), 3.73 (app t, 1 H, J = 10.0 Hz, H-6′), 3.72 (dd, 1 H, J = 11.0, 1.5 Hz, H-6), 2.54 (s, 1 H, OH); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.8 (PhC=O), 155.2 (Ar), 150.0 (Ar), 138.3 (Ar), 138.0 (Ar), 137.9 (Ar), 137.7 (Ar), 133.3 (Ar), 129.9 (Ar), 129.8 (Ar), 128.8 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 126.3 (Ar), 117.9 (Ar), 114.6 (Ar), 102.3 (C-1′), 101.6 (Ph*C*H(O)$_2$), 96.4 (C-1), 78.6 (C-4′), 78.1 (C-3), 75.5 (C-3′), 75.4 (Ph*C*H$_2$), 74.5 (C-4), 73.5 (Ph*C*H$_2$), 73.1 (Ph*C*H$_2$), 72.2 (C-2), 72.1 (C-5), 70.4 (C-2′), 68.8 (C-6), 68.7 (C-6′), 64.2 (C-5′), 55.6 (CH_3O); HRMS (ESI) calcd for (M+NH_4) $C_{54}H_{58}NO_{13}$: 928.3903. Found: 928.3899.

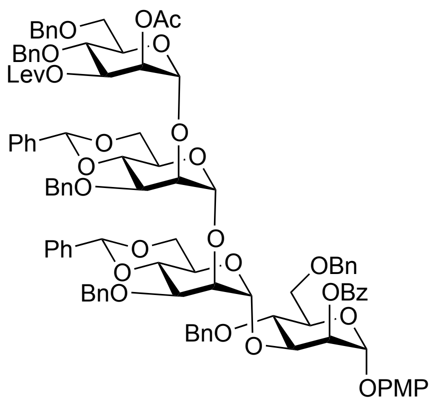


***p*-Methoxyphenyl 3-*O*-Benzyl-4,6-di-*O*-benzylidene-2-*O*-levulinyl-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (19):** A mixture of donor **5** (4.70 g, 8.35 mmol), acceptor **18** (5.24 g, 5.76 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (480 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (2.58 g, 11.52 mmol) and AgOTf (442 mg, 1.73 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (2.0 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→25% EtOAc in hexane) to afford **19** (5.82 g, 73% yield) as a white foam; R_f 0.27 (2:1 hexane–EtOAc); $[\alpha]_D$ = +5.9 (*c* 1.1, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 8.10−8.09 (m, 2 H, ArH), 7.61−7.58 (m, 1 H, ArH), 7.51−7.50 (m, 1 H, ArH), 7.42−7.20 (m, 31 H, ArH), 7.03−7.02 (m, 2 H, ArH), 6.79−6.78 (m, 2 H, ArH), 5.60 (s, 1 H, PhC*H*$(O)_2$), 5.59−5.57 (m, 2 H, H-1, H-2), 5.56 (dd, 1 H, *J* = 3.5, 1.5 Hz, H-2″), 5.48 (s, 1 H, PhC*H*$(O)_2$), 5.11 (d, 1 H, *J* = 1.5 Hz, H-1′), 4.98 (d, 1 H, *J* = 1.5 Hz, H-1″), 4.72–4.66 (m, 4 H, 4 X PhCH_2), 4.62 (d, 1 H, *J* = 11.5 Hz, PhCH_2), 4.51 (d, 1 H, *J* = 11.5 Hz, PhCH_2), 4.45 (d, 1 H, *J* = 11.5 Hz, PhCH_2), 4.43 (d, 1 H, *J* = 11.5 Hz, PhCH_2), 4.40 (dd, 1 H, *J* = 9.5, 2.5 Hz, H-3), 4.19 (app t, 1 H, *J* = 10.0 Hz, H-4), 4.14 (dd, 1 H, *J* = 10.0, 4.5 Hz, H-6′), 4.07 (dd, 1 H, *J* = 10.0, 5.0 Hz, H-6″), 4.03 (dd, 1 H, *J* = 10.0, 3.0 Hz, H-3″), 4.00 (app t, 1 H, *J* = 10.0 Hz, H-4″), 3.98 (ddd, 1 H, *J* = 10.0, 3.5, 1.5 Hz, H-5), 3.94 (app t, 1 H, *J* = 9.5 Hz, H-4′), 3.89 (td, 1 H, *J* = 10.0, 5.0 Hz, H-5″), 3.86 (dd, 1 H, *J* = 3.0, 1.5 Hz, H-2′), 3.83 (dd, 1 H, *J* = 11.0, 3.5 Hz, H-6), 3.81 (dd, 1 H, *J* = 10.0, 3.0 Hz, H-3′), 3.77–3.74 (m, 1 H, H-5′), 3.75 (s, 3 H, OCH_3), 3.72–3.65 (m, 3 H, H-6, H-6′, H-6′), 2.79–2.63 (m, 4 H, $CH_3C{=}OCH_2$, $CH_3C{=}OCH_2CH_2$), 2.16 (s, 3 H, $CH_3C{=}OCH_2$,); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.1 ($CH_3C{=}OCH_2$), 171.6 ($OC{=}OCH_2$), 165.8 (PhC=O), 155.1 (Ar), 149.9 (Ar), 138.4 (Ar), 138.3 (Ar), 138.1 (Ar), 137.9 (Ar), 137.7 (Ar), 137.4 (Ar), 133.3 (Ar), 129.9 (Ar), 129.7 (Ar), 128.9 (Ar), 128.8 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.28 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.76 (Ar), 127.7 (Ar), 127.6 (Ar), 127.56 (Ar), 127.54 (Ar), 127.52 (Ar), 126.4 (Ar), 126.1 (Ar), 117.8 (Ar), 114.6 (Ar), 102.3 (C-1′), 101.6 (Ph*C*H$(O)_2$), 101.5 (Ph*C*H$(O)_2$), 100.7

(C-1″), 96.2 (C-1), 79.2 (C-3), 78.7 (C-4′), 78.5 (C-4″), 77.2 (C-2′), 75.4 (PhCH$_2$), 75.2 (C-3′), 74.2 (C-4), 73.7 (C-3″), 73.4 (PhCH$_2$), 73.2 (PhCH$_2$), 72.3 (PhCH$_2$), 72.2 (C-2), 72.1 (C-5), 69.7 (C-2″), 68.7 (C-6), 68.5 (C-6′, C-6″), 64.9 (C-5′), 64.5 (C-5″), 55.6 (CH_3O), 38.1 ($CH_3C{=}OCH_2$), 29.8 ($CH_3C{=}OCH_2$), 28.1 ($CH_3C{=}OCH_2CH_2$); ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^1J_{C\text{-}1,\,H\text{-}1}$ = 174.8 Hz (C-1, H-1), $^1J_{C\text{-}1',\,H\text{-}1'}$ = 170.2 Hz (C-1′, H-1′), $^1J_{C\text{-}1'',\,H\text{-}1''}$ = 171.9 Hz (C-1″, H-1″); HRMS (ESI) calcd for (M+NH_4) $C_{79}H_{84}NO_{20}$: 1366.5581. Found: 1366.5570.

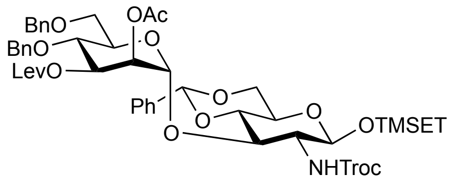


***p*-Methoxyphenyl 3-*O*-Benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-di-*O*- benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopy- ranoside (20):** A solution of **19** (5.53 g, 4.10 mmol) and hydrazine acetate (676 mg, 7.34 mmol) in 9:1 CH_2Cl_2–CH_3OH (300 mL) was stirred at r.t. for 3 h. Then, the solution was concentrated and the resulting residue was subjected to chromatography (gradient 16→25% EtOAc in hexane) to afford **20** (4.9 g, 97% yield) as a white foam; R_f 0.33 (2:1 hexane–EtOAc); $[\alpha]_D$ = +30.7 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.10–8.09 (m, 2 H, ArH), 7.61–7.59 (m, 1 H, ArH), 7.51–7.49 (m, 2 H, ArH), 7.42–7.16 (m, 30 H, ArH), 7.04–7.03 (m, 2 H, ArH), 6.80–6.78 (m, 2 H, ArH), 5.60 (s, 1 H, PhCH(O)$_2$), 5.59–5.58 (m, 2 H, H-1, H-2), 5.47 (s, 1 H, PhCH(O)$_2$), 5.14 (d, 1 H, J = 1.5 Hz, H-1′), 5.12 (d, 1 H, J = 1.0 Hz, H-1″), 4.89 (d, 1 H, J = 11.7 Hz, PhCH_2), 4.74 (d, 1 H, J = 11.7 Hz, PhCH_2), 4.69 (d, 1 H, *J* = 12.2 Hz, PhC*H*$_2$), 4.68 (d, 1 H, *J* = 11.6 Hz, PhC*H*$_2$), 4.63 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.51 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.46 (d, 1 H, *J* = 12.2 Hz, PhC*H*$_2$), 4.46 (d, 1 H, *J* = 11.6 Hz, PhC*H*$_2$), 4.41 (dd, 1 H, *J* = 9.5, 2.5 Hz, H-3), 4.22–4.21 (m, 1 H, H-2″), 4.20 (app t, 1 H, *J* = 10.0 Hz, H-4), 4.15 (dd, 1 H, *J* = 10.0, 4.5 Hz, H-6′), 4.11 (app t, 1 H, *J* = 9.5 Hz, H-4″), 4.07 (dd, 1 H, *J* = 10.5, 5.0 Hz, H-6″), 3.98 (ddd, 1 H, *J* = 10.0, 3.5, 1.5 Hz, H-5), 3.97 (dd, 1 H, *J* = 9.5, 3.5 Hz, H-3″), 3.94–3.93 (m, 1 H, H-2′), 3.94 (app t, 1 H, *J* = 9.5 Hz, H-4′), 3.89 (td, 1 H, *J* = 10.0, 5.0 Hz, H-5″), 3.84 (dd, 1 H, *J* = 11.0, 3.5 Hz, H-6), 3.82 (dd, 1 H, *J* = 10.0, 3.0 Hz, H-3′), 3.76 (td, 1 H, *J* = 10.0, 5.0 Hz, H-5′), 3.75 (s, 3 H, OCH_3), 3.74–3.67 (m, 3 H, H-6, H-6′, H-6′), 2.58 (d, 1 H, *J* = 1.3 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.9 (PhC=O), 155.2 (Ar), 149.9 (Ar), 138.3 (Ar), 138.2 (Ar), 138.1 (Ar), 137.9 (Ar), 137.7 (Ar), 137.5 (Ar), 133.3 (Ar), 129.9 (Ar), 129.7 (Ar), 128.9 (Ar), 128.8 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.95 (Ar), 127.92 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 126.4 (Ar), 126.1 (Ar), 117.8 (Ar), 114.6 (Ar), 102.6 (C-1′), 102.1 (C-1″), 101.6 (Ph*C*H(O)$_2$), 101.5 (Ph*C*H(O)$_2$), 96.2 (C-1), 79.3 (C-3), 78.9 (C-4″), 78.7 (C-4′), 77.2 (C-2′), 75.5 (Ph*C*H$_2$), 75.4 (C-3′, C-3″), 74.2 (C-4), 73.4 (Ph*C*H$_2$), 73.3 (Ph*C*H$_2$), 73.2 (Ph*C*H$_2$), 72.3 (C-2), 72.1 (C-5), 69.9 (C-2″), 68.7, 68.6, 68.5 (C-6, C-6′, C-6″), 64.9 (C-5′), 64.0 (C-5″), 55.6 (CH_3O); HRMS (ESI) calcd for (M+Na) $C_{74}H_{74}NaO_{18}$: 1273.4767. Found: 1273.4772.



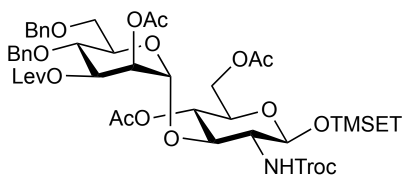
***p*-Methoxyphenyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D-mannopyrano- syl-(1→2)-3-*O*-benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-manno-pyranoside (21):** A mixture of acceptor **20** (4.60 g, 3.72 mmol), donor **7** (2.92 g, 4.83 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (400 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (1.58 g, 7.07 mmol) and AgOTf (285 mg, 1.11 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (2.0 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→33% EtOAc in hexane) to afford **21** (5.53 g, 86% yield) as a white solid; R_f 0.14 (2:1 hexane–EtOAc); $[\alpha]_D$ = +27.6 (*c* 1.2, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 8.08–8.06 (m, 2 H, ArH), 7.59–7.57 (m, 1 H, ArH), 7.50–7.49 (m, 2 H, ArH), 7.39–7.09 (m, 40 H, ArH), 7.06–7.01 (m, 3 H, ArH), 6.79–6.77 (m, 2 H, ArH), 5.65 (s, 1 H, PhC*H*(O)$_2$), 5.57–5.55 (m, 2 H, H-1, H-2), 5.45–5.44 (m, 2 H, H′′′′-2, PhC*H*(O)$_2$), 5.40 (dd, 1 H, *J* = 10.0, 3.5 Hz, H′′′′-3), 5.17 (d, 1 H, *J* = 1.5 Hz, H-1′′′), 5.12 (d, 1 H, *J* = 1.5 Hz, H-1′′), 5.10 (d, 1 H, *J* = 1.5 Hz, H-1′), 4.89 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.66 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.63 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.61 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.57 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.55 (d, 1 H, *J* = 12.0

Hz, PhCH_2), 4.54 (d, 1 H, J = 12.5 Hz, PhCH_2), 4.46–4.39 (m, 5 H, PhCH_2, H-3), 4.22 (d, 1 H, J = 12.0 Hz, PhCH_2), 4.19 (dd, 1 H, J = 1.5 Hz, H-2″), 4.16 (app t, 1 H, J = 9.5 Hz, H-4), 4.13 (dd, 1 H, J = 10.0, 4.5 Hz, H-6′), 3.99 (dd, 1 H, J = 10.5, 5.0 Hz, H-6″), 4.00–3.95 (m, 4 H), 3.93 (dd, 1 H, J = 3.0, 1.5 Hz, H-2′), 3.88 (app t, 1 H, J = 9.5 Hz, H-4′), 3.83–3.76 (m, 4 H), 3.74 (s, 3 H, OCH_3), 3.74–3.70 (m, 2 H), 3.67 (dd, 1 H, J = 11.0, 2.0 Hz), 3.65 (app t, 1 H, J = 10.0 Hz), 3.55 (dd, 1 H, J = 11.0, 3.0 Hz), 3.39 (dd, 1 H, J = 11.0, 2.0 Hz), 2.78 (dt, 1 H, J = 18.0, 7.5 Hz, $CH_3C{=}OCH_2$), 2.65 (dt, 1 H, J = 18.0, 6.5 Hz, $CH_3C{=}OCH_2$), 2.53 (dt, 1 H, J = 17.0, 7.0 Hz, $OC{=}OCH_2CH_2$), 2.44 (dt, 1 H, J = 17.0, 6.5 Hz, $OC{=}OCH_2CH_2$), 2.16 (s, 3 H, $CH_3C{=}OCH_2$), 2.07 (s, 3 H, $OC{=}OCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.3 ($CH_3C{=}OCH_2$), 171.8 ($OC{=}OCH_2$), 169.8 ($CH_3C{=}O$),165.8 (PhC=O), 155.1 (Ar), 149.9 (Ar), 138.6 (Ar), 138.4 (Ar), 138.3 (Ar), 138.1 (Ar), 138.0 (Ar), 137.8 (Ar), 137.7 (Ar), 137.6 (Ar), 133.3 (Ar), 129.9 (Ar), 129.7 (Ar), 128.8 (Ar), 128.6 (Ar), 128.5 (Ar), 128.33 (Ar), 128.32 (Ar), 128.28 (Ar), 128.22 (Ar), 128.1 (Ar), 128.0 (Ar), 127.99 (Ar), 127.92 (Ar), 127.89 (Ar), 127.87 (Ar), 127.7 (Ar), 127.69 (Ar), 127.63 (Ar), 127.5 (Ar), 127.4 (Ar), 127.3 (Ar), 126.4 (Ar), 126.1 (Ar), 117.8 (Ar), 114.6 (Ar), 102.5 (C-1′), 101.6 (C-1″), 101.5 ($PhCH(O)_2$), 101.3 ($PhCH(O)_2$), 99.4 (C-1‴), 96.2 (C-1), 79.2 (C-3), 78.8, 77.2, 76.5, 75.8, 75.5, 75.4 ($PhCH_2$), 75.3, 74.9 ($PhCH_2$), 74.1, 73.5 ($PhCH_2$), 73.4 ($PhCH_2$), 73.3 ($PhCH_2$), 72.9 ($PhCH_2$), 72.8, 72.3, 72.0, 71.8, 69.7, 68.7, 68.5, 68.4, 68.1, 64.9, 64.8, 55.6 (CH_3O), 37.9 ($CH_3C{=}OCH_2$), 29.8 ($CH_3C{=}OCH_2$), 28.0 ($CH_3C{=}OCH_2CH_2$), 20.9 ($OC{=}OCH_3$); ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^1J_{C\text{-}1,\,H\text{-}1}$ = 175.4 Hz (C-1, H-1), $^1J_{C\text{-}1',\,H\text{-}1'}$ = 170.1 Hz (C-1′, H-1′), $^1J_{C\text{-}1'',\,H\text{-}1''}$ = 173.1 Hz (C-1″, H-1″), $^1J_{C\text{-}1''',\,H\text{-}1'''}$ = 173.3 Hz (C-1‴, H-1‴); HRMS (ESI) calcd for (M+Na) $C_{101}H_{104}NaO_{26}$: 1755.6708. Found: 1755.6690.

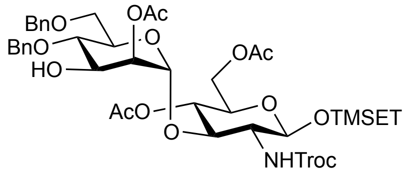


2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D-manno- pyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino) -β-D-glucopyranoside (22): A mixture of thioglycoside **7** (2 g, 3.68 mmol), acceptor **8** (2.45 g, 4.05 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (70 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (1.21 g, 5.43 mmol and AgOTf (282 mg, 1.1 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (1.0 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 25→33% EtOAc in hexane) to afford **22** (3.21 g, 85% yield) as a white solid; R_f 0.72 (1:1 hexane–EtOAc); $[\alpha]_D$ = +1.5 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.39–7.26 (m, 13 H, ArH), 7.20–7.19 (m, 2 H, ArH), 5.55 (d, 1 H, *J* = 8.8 Hz, N*H*), 5.52 (s, 1 H, PhC*H*(O)$_2$), 5.37 (app t, 1 H, *J* = 2.1, H-2′), 5.24 (dd, 1 H, *J* = 10.3, 2.1 Hz, H-3′), 5.22 (s, 1 H, H-1′), 4.65 (d, 1 H, *J* = 11.5 Hz, PhC*H*$_2$), 4.64 (d, 1 H, *J* = 11.2 Hz, PhC*H*$_2$), 4.64 (d, 1 H, *J* = 12.0 Hz, C*H*$_2$CCl$_3$), 4.50 (d, 1 H, *J* = 12.0 Hz, C*H*$_2$CCl$_3$), 4.50 (d, 1 H, *J* = 11.5 Hz, PhC*H*$_2$), 4.47 (d, 1 H, *J* = 11.2 Hz, PhC*H*$_2$), 4.34–4.32 (m, 2 H, H-1, H-6), 4.09 (app t, 1 H, *J* = 10.0 Hz, H-3), 4.06–4.04 (m, 1 H, H-5′), 3.88–3.84 (m, 1 H, TMSCH$_2$C*H*$_2$O), 3.79 (app t, 1 H, *J* = 9.0 Hz, H-4′), 3.76 (app t, 1 H, *J* = 10.0 Hz, H-6), 3.71–3.63 (m, 2 H, H-6′), 3.67 (app t, 1 H, *J* = 10.0 Hz, H-4), 3.44–3.40 (m, 2 H, H-2, TMSCH$_2$C*H*$_2$O), 3.35 (app td, 1 H, *J* = 10.0, 5.0 Hz, H-5), 2.71 (dt, 1 H, *J* = 18.3, 7.0 Hz, CH$_3$C=OC*H*$_2$), 2.64 (dt, 1 H, *J* = 18.3, 6.5 Hz, CH$_3$C=OC*H*$_2$), 2.48 (dt, 1

H, J = 17.2, 7.0 Hz, OC=OCH_2CH$_2$), 2.43 (dt, 1 H, J = 17.2, 6.5 Hz, OC=OCH_2CH$_2$), 2.14 (s, 3 H, CH_3C=OCH$_2$), 2.04 (s, 3 H, OC=OCH_3), 0.90–0.86 (m, 2 H, TMSCH_2CH$_2$O), 0.00 (s, 9 H, (CH_3)$_3$Si); ^{13}C NMR (175 MHz, CDCl$_3$, δ_C) 206.2 (CH$_3$$C$=OCH$_2$), 171.6 (O$C$=OCH$_2CH_2$), 169.6 (O$C$=OCH$_3$), 153.9 (NHC=O), 138.0 (Ar), 137.8 (Ar), 137.0 (Ar), 133.8 (Ar), 130.0 (Ar), 128.8 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 125.9 (Ar), 101.2 (C-1), 100.9 (PhCH(O)$_2$), 98.3 (C-1′), 81.9 (C-4), 74.6 (PhCH$_2$), 74.5 (C-3), 74.4 (CH$_2$CCl$_3$), 73.7 (PhCH$_2$), 73.3 (C-4′), 72.1 (C-3′), 71.3 (C-5′), 69.8 (C-2′), 69.1 (C-6′), 68.6 (C-6), 67.7 (TMSCH$_2$$CH_2$O), 65.8 (C-5), 56.8 (C-2), 37.8 (CH$_3$C=OCH$_2$), 29.8 (CH$_3$C=OCH$_2$), 27.9 (CH$_3$C=OCH$_2$$CH_2$), 20.7 (OC=O$CH_3$), 18.1 (TMS$CH_2CH_2$O), −1.4 ($CH_3$)$_3$Si); HRMS (ESI) calcd for (M+NH$_4$) $C_{48}H_{64}Cl_3N_2O_{15}Si$: 1041.3136. Found: 1041.3120.

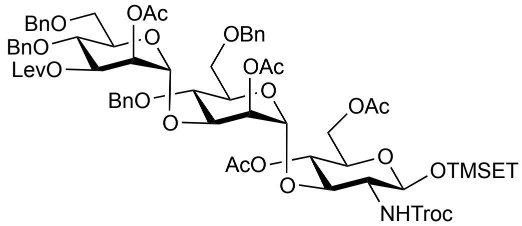


2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D- mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl- amino)-β-D-glucopyranoside (23): Disaccharide **22** (3.15 g, 3.08 mmol) was dissolved in 4:1 AcOH–H$_2$O (50 mL) and the solution was heated at 60 °C for 6 h. After cooling to r.t., the solvent was evaporated, the residue was dissolved with EtOAc, washed with a satd aq solution of NaHCO$_3$, brine, dried over Na$_2$SO$_4$, filtered and concentrated. Then, the residue was dissolved in 2:3 Ac$_2$O–pyridine (25 mL) and stirred at r.t. for 2 h. The solvent was evaporated under high vacuum and the residue was diluted with CH$_2$Cl$_2$, washed with 1M HCl, a satd aq solution of NaHCO$_3$, brine, dried over Na$_2$SO$_4$, filtered and concentrated. The resulting residue was purified by chromatography (gradient 33→50% EtOAc in hexane) to afford **23** (2.95 g, 94% yield) as a white foam; R_f 0.26 (1:1 hexane–EtOAc); $[\alpha]_D$ = +19.2 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.39–7.25 (m, 8 H, ArH), 7.17–7.16 (m, 2 H, ArH), 5.90 (d, 1 H, *J* = 6.9 Hz, N*H*), 5.23 (dd, 1 H, *J* = 8.5, 3.0 Hz, H-3′), 5.04 (app t, 1 H, *J* = 9.5 Hz, H-4), 5.01 (app t, 1 H, *J* = 3.0 Hz, H-2′), 4.90 (s, 1 H, H-1′), 4.70 (d, 1 H, *J* = 11.8 Hz, CH_2CCl_3), 4.64 (d, 1 H, *J* = 11.2 Hz, $PhCH_2$), 4.60 (d, 1 H, *J* = 11.8 Hz, $PhCH_2$), 4.59 (d, 1 H, *J* = 8.5 Hz, H-1), 4.51 (d, 1 H, *J* = 11.8 Hz, $PhCH_2$), 4.46 (d, 1 H, *J* = 11.8 Hz, CH_2CCl_3), 4.44 (d, 1 H, *J* = 11.2 Hz, $PhCH_2$), 4.19 (dd, 1 H, *J* = 12.2, 5.0 Hz, H-6), 4.15 (app t, 1 H, *J* = 9.5 Hz, H-3), 4.05 (dd, 1 H, *J* = 12.2, 2.5 Hz, H-6), 4.02–4.00 (m, 1 H, H-5′), 3.86 (app td, 1 H, *J* = 10.0, 6.2 Hz, $TMSCH_2CH_2O$), 3.78 (app t, 1 H, *J* = 8.5 Hz, H-4′), 3.66–3.59 (m, 2 H, H-6′), 3.55–3.52 (m, 1 H, H-5), 3.44 (app td, 1 H, *J* = 10.0, 6.2 Hz, $TMSCH_2CH_2O$), 3.22–3.21 (m, 1 H, H-2), 2.68 (t, 2 H, *J* = 6.8 Hz, $CH_3C{=}OCH_2$), 2.45 (t, 2 H, *J* = 6.8 Hz, $CH_3C{=}OCH_2$), 2.13 (s, 3 H, $CH_3C{=}OCH_2$), 2.09 (s, 3 H, $OC{=}OCH_3$), 2.07 (s, 3 H, $OC{=}OCH_3$), 2.05 (s, 3 H, $OC{=}OCH_3$), 0.90–0.83 (m, 2 H, $TMSCH_2CH_2O$), −0.03 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.1 ($CH_3C{=}OCH_2$), 171.4 ($OC{=}OCH_2CH_2$), 170.8 ($OC{=}OCH_3$), 169.9 ($OC{=}OCH_3$), 169.5 ($OC{=}OCH_3$), 154.1 (NHC=O), 137.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 99.7 (C-1), 98.8 (C-1′), 78.0 (C-3), 74.4 (CH_2CCl_3), 74.3 ($PhCH_2$), 73.7 ($PhCH_2$), 73.5 (C-4′), 71.5 (C-3′, C-5′, C-5), 70.7 (C-4), 70.5 (C-2′), 69.1 (C-6′), 67.5 ($TMSCH_2CH_2O$), 62.3 (C-6), 57.6 (C-2), 37.9 ($CH_3C{=}OCH_2$), 29.8 ($CH_3C{=}OCH_2$), 27.9 ($CH_3C{=}OCH_2CH_2$), 20.9 ($OC{=}OCH_3$), 20.8 ($OC{=}OCH_3$), 20.7 ($OC{=}OCH_3$), 18.1 ($TMSCH_2CH_2O$), −1.4 ($(CH_3)_3Si$); HRMS (ESI) calcd for (M+NH_4) $C_{45}H_{64}Cl_3N_2O_{17}Si$: 1037.3034. Found: 1037.3014.

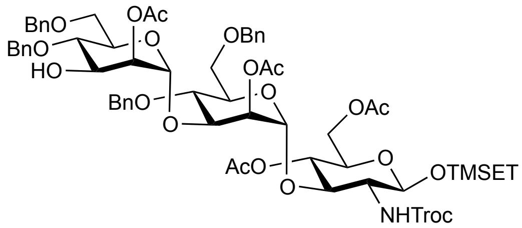


2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)- 4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (24): A solution of **23** (2.86 g, 2.8 mmol) and hydrazine acetate (515 mg, 5.6 mmol) in 9:1 CH_2Cl_2–CH_3OH (100 mL) was stirred at r.t. for 3 h. Then, the solution was concentrated and the resulting residue was subjected to chromatography (gradient 33→50% EtOAc in hexane) to afford **24** (2.52 g, 98% yield) as a white foam; R_f 0.30 (1:1 hexane–EtOAc); $[\alpha]_D$ = +10.3 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.37–7.26 (m, 8 H, ArH), 7.22–7.21 (m, 2 H, ArH), 5.94 (d, 1 H, *J* = 7.3 Hz, N*H*), 5.02 (dd, 1 H, *J* = 9.9, 9.2 Hz, H-4), 4.92 (s, 1 H, H-1′), 4.86 (dd, 1 H, *J* = 3.5, 1.8 Hz, H-2′), 4.74 (d, 1 H, *J* = 10.8 Hz, PhC*H*$_2$), 4.68 (d, 1 H, *J* = 11.8 Hz, C*H*$_2$CCl$_3$), 4.62 (d, 1 H, *J* = 11.4 Hz, PhC*H*$_2$), 4.58–4.51 (m, 4 H, H-1, C*H*$_2$CCl$_3$, PhC*H*$_2$), 4.21 (dd, 1 H, *J* = 12.3, 5.0 Hz, H-6), 4.12–4.09 (m, 1 H, H-3), 4.06 (dd, 1 H, *J* = 12.3, 2.6 Hz, H-6), 4.03 (dd, 1 H, *J* = 8.8, 3.5 Hz, H-3′), 3.96–3.94 (m, 1 H, H-5′), 3.87 (td, 1 H, *J* = 10.0, 6.5 Hz, TMSCH$_2$C*H*$_2$O), 3.72 (dd, 1 H, *J* = 10.2, 1.7 Hz, H-6′), 3.66–3.64 (m, 1 H, H-4′, H-6′), 3.55–3.54 (m, 1 H, H-5), 3.48–3.44 (m 1 H, TMSCH$_2$C*H*$_2$O), 3.26–3.23 (m, 1 H, H-2), 2.11 (s, 3 H, OC=OC*H*$_3$), 2.10 (s, 3 H, OC=OC*H*$_3$), 2.05 (s, 3 H, OC=OC*H*$_3$), 0.90–0.86 (m, 2 H, TMSC*H*$_2$CH$_2$O), −0.01 (s, 9 H, (C*H*$_3$)$_3$Si); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.8 (O*C*=OCH$_3$), 170.4 (O*C*=OCH$_3$), 169.9 (O*C*=OCH$_3$), 154.1 (NHC=O), 138.0 (Ar), 137.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 99.8 (C-1), 98.9 (C-1′), 78.5 (C-3), 76.0 (C-4′), 74.9 (Ph*C*H$_2$), 74.4 (*C*H$_2$CCl$_3$), 73.6 (Ph*C*H$_2$), 72.9 (C-2′), 71.6 (C-5′), 71.5 (C-5), 70.8 (C-4), 70.0(C-3′), 69.2 (C-6′), 67.5 (TMSCH$_2$*C*H$_2$O), 62.3 (C-6), 57.6 (C-2),

21.0 (OC=OCH_3), 20.9 (OC=OCH_3), 20.8 (OC=OCH_3), 18.1 (TMSCH_2CH_2O), −1.4 ($(CH_3)_3Si$); HRMS (ESI) calcd for ($M+NH_4$) $C_{40}H_{58}Cl_3N_2O_{15}Si$: 939.2667. Found: 939.2649.

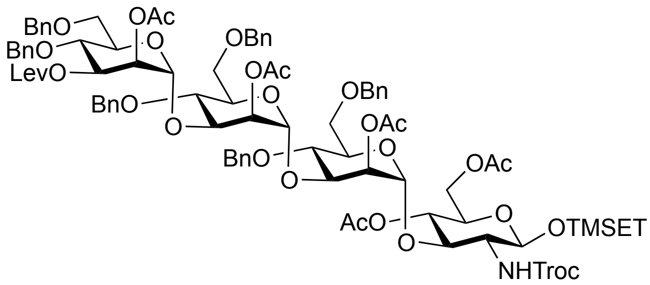


2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D- mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (25): A mixture of thioglycoside **7** (1.44 g, 2.38 mmol), acceptor **24** (2.0 g, 2.12 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (50 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (0.73 g, 3.25 mmol and AgOTf (166 mg, 0.65 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (1.0 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 25→40% EtOAc in hexane) to afford **25** (2.75 g, 91% yield) as a white foam; R_f 0.46 (1:1 hexane–EtOAc); $[\alpha]_D$ = +33.4 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.37–7.22 (m, 14 H, ArH), 7.18–7.16 (m, 6 H, ArH), 5.94 (d, 1 H, *J* = 7.5 Hz, N*H*), 5.30 (dd, 1 H, *J* = 3.3, 1.9 Hz, H-2″), 5.26 (dd, 1 H, *J* = 9.6, 3.2 Hz, H-3″), 5.06 (d, 1 H, *J* = 1.7 Hz, H-1″), 5.00 (dd, 1 H, *J* = 9.9, 9.2 Hz, H-4′), 4.91 (dd, 1 H, *J* = 3.0, 1.8 Hz, H-2′), 4.89 (s, 1 H, H-1′), 4.76 (d, 1 H, *J* = 11.9 Hz, PhCH_2), 4.75 (d, 1 H, *J* = 10.0 Hz, PhCH_2), 4.68 (d, 1 H, *J* = 11.8 Hz, C$H_2$$CCl_3$), 4.61 (d, 1 H, *J* = 11.3 Hz, PhCH_2), 4.60–4.49 (m, 5 H, H-1, C$H_2$$CCl_3$, PhC$H_2$), 4.47 (d, 1 H, *J* = 12.4 Hz, PhCH_2), 4.43 (d, 1 H, *J* = 10.0 Hz, PhCH_2), 4.21 (dd, 1 H, *J* = 12.5, 5.5 Hz, H-6), 4.12–4.09 (m, 1 H, H-3), 4.06 (dd, 1 H, J = 6.3, 3.3 Hz, H-3′), 4.05–4.03 (m, 2 H, H-6, H-4″), 3.94–3.92 (m, 1 H, H-5′), 3.88 (td, 1 H, J = 10.0, 6.0 Hz, TMSCH$_2$C*H*$_2$O), 3.82 (dd, 1 H, J = 11.0, 2.5 Hz, H-6″), 3.76 (app t, 1 H, J = 10.0 Hz, H-4′), 3.72 (app dt, 1 H, J = 9.7, 2.0 Hz, H-5″), 3.68 (dd, 1 H, J = 11.0, 1.8 Hz, H-6″), 3.66 (dd, 1 H, J = 10.0, 1.5 Hz, H-6′), 3.61–3.59 (m, 1 H, H-6′), 3.55–3.54 (m, 1 H, H-5), 3.48–3.44 (m 1 H, TMSCH$_2$C*H*$_2$O), 3.22–3.19 (m, 1 H, H-2), 2.69 (dt, 1 H, J = 18.4, 7.0 Hz, CH$_3$C=OC*H*$_2$), 2.61 (dt, 1 H, J = 18.4, 6.5 Hz, CH$_3$C=OC*H*$_2$), 2.46 (dt, 1 H, J = 17.3, 7.0 Hz, OC=OC*H*$_2$CH$_2$), 2.41 (dt, 1 H, J = 17.3, 6.5 Hz, OC=OC*H*$_2$CH$_2$), 2.13 (s, 3 H, C*H*$_3$C=OCH$_2$), 2.08 (s, 6 H, 2 x OC=OC*H*$_3$), 2.06 (s, 3 H, OC=OC*H*$_3$), 2.05 (s, 3 H, OC=OC*H*$_3$), 0.90–0.86 (m, 2 H, TMSC*H*$_2$CH$_2$O), −0.01 (s, 9 H, (C*H*$_3$)$_3$Si); ^{13}C NMR (125 MHz, CDCl$_3$, δ_C) 206.1 (CH$_3$*C*=OCH$_2$), 171.8 (O*C*=OCH$_2$CH$_2$), 170.7 (O*C*=OCH$_3$), 170.4 (O*C*=OCH$_3$), 169.9 (O*C*=OCH$_3$), 169.6 (O*C*=OCH$_3$), 154.1 (NHC=O), 138.4 (Ar), 138.3 (Ar), 137.7 (Ar), 128.4 (Ar), 128.3 (Ar), 128.28 (Ar), 128.25 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 99.7 (C-1), 99.6 (C-1″), 98.7 (C-1′), 78.6 (C-3), 77.3(C-3′), 75.2 (Ph*C*H$_2$), 74.6 (C-4′), 74.5 (Ph*C*H$_2$), 74.4 (*C*H$_2$CCl$_3$), 73.6 (Ph*C*H$_2$), 72.5 (C-4″, C-5″), 72.2 (C-2′), 72.0 (C-3″), 71.9 (C-5′), 71.5 (C-5), 70.6 (C-4), 69.9 (C-2″), 68.9 (C-6′), 68.1 (C-6″), 67.6 (TMSCH$_2$*C*H$_2$O), 62.4 (C-6), 57.6 (C-2), 37.8 (CH$_3$C=O*C*H$_2$), 29.8 (*C*H$_3$C=OCH$_2$), 27.9 (CH$_3$C=OCH$_2$*C*H$_2$), 21.3 (OC=O*C*H$_3$), 20.9 (OC=O*C*H$_3$), 20.8 (OC=O*C*H$_3$), 18.1 (TMS*C*H$_2$CH$_2$O), −1.4 (*C*H$_3$)$_3$Si); ^{1}H-coupled HSQC (700 MHz, CDCl$_3$) $^1J_{\text{C-1, H-1}}$ = 165.3 Hz (C-1, H-1), $^1J_{\text{C-1′, H-1′}}$ = 174.8 Hz (C-1′, H-1′), $^1J_{\text{C-1″, H-1″}}$ = 174.9 Hz (C-1″, H-1″); HRMS (ESI) calcd for (M+NH$_4$) $C_{67}H_{88}Cl_3N_2O_{23}Si$: 1421.4607. Found: 1421.4579.



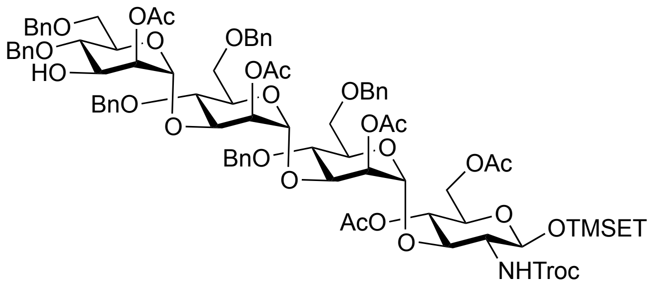
2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)- 2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (26): A solution of **25** (2.73 g, 1.9 mmol) and hydrazine acetate (320 mg, 3.5 mmol) in 9:1 CH_2Cl_2–CH_3OH (100 mL) was stirred at r.t. for 3 h. Then, the solution was concentrated and the resulting residue was subjected to chromatography (gradient 33→50% EtOAc in hexane) to afford **26** (2.35 g, 93% yield) as a white foam; R_f 0.53 (1:1 hexane–EtOAc); $[\alpha]_D$ = +33.2 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.38–7.25 (m, 16 H, ArH), 7.21–7.17 (m, 4 H, ArH), 5.88 (d, 1 H, *J* = 6.7 Hz, N*H*), 5.15 (dd, 1 H, *J* = 3.0, 1.5 Hz, H-2″), 5.10 (s, 1 H, H-1″), 5.00 (app t, 1 H, *J* = 9.5 Hz, H-4′), 4.88 (s, 1 H, H-1′), 4.88 (s, 1 H, H-2′), 4.77 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.73 (d, 1 H, *J* = 11.2 Hz, PhCH_2), 4.68 (d, 1 H, *J* = 11.2 Hz, C$H_2$$CCl_3$), 4.65 (d, 1 H, *J* = 11.3 Hz, PhCH_2), 4.61–4.48 (m, 5 H, H-1, C$H_2$$CCl_3$, PhC$H_2$), 4.45 (d, 1 H, *J* = 12.3 Hz, PhCH_2), 4.43 (d, 1 H, *J* = 10.8 Hz, PhCH_2), 4.21 (dd, 1 H, *J* = 12.1, 5.0 Hz, H-6), 4.14–4.01 (m, 1 H, H-3), 4.07 (dd, 1 H, *J* = 7.0, 2.7 Hz, H-3′), 4.05 (dd, 1 H, *J* = 12.1, 2.3 Hz, H-6), 3.98 (dd, 1 H, *J* = 9.5, 3.3 Hz, H-3″), 3.93–3.90 (m, 1 H, H-5′), 3.90–3.87 (m, 1 H, TMSCH_2CH_2O), 3.86 (app t, 1 H, *J* = 9.5 Hz, H-4″), 3.82 (dd, 1 H, *J* = 11.3, 3.0 Hz, H-6″), 3.79 (app t, 1 H, *J* = 9.0 Hz, H-4′), 3.71 (dd, 1 H, *J* = 11.3, 1.5 Hz, H-6″), 3.63–3.57 (m, 3 H, H-5″, H-6′), 3.55–3.53 (m, 1 H, H-5), 3.48–3.44 (m 1 H, TMSCH_2CH_2O), 3.22–3.19 (m, 1 H, H-2), 2.08 (s, 3 H, OC=OCH_3), 2.07 (s, 3 H, OC=OCH_3), 2.06 (s, 3 H, OC=OCH_3), 2.05 (s, 3 H, OC=OCH_3), 0.90–0.86 (m, 2

H, TMSCH_2CH$_2$O), −0.02 (s, 9 H, (CH_3)$_3$Si); ^{13}C NMR (125 MHz, CDCl$_3$, δ_C) 170.8 (O*C*=OCH$_3$), 170.6 (O*C*=OCH$_3$), 170.1 (O*C*=OCH$_3$), 169.6 (O*C*=OCH$_3$), 154.1 (NHC=O), 138.3 (Ar), 137.8 (Ar), 137.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.02 (Ar), 127.99 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 99.7 (C-1), 99.5 (C-1″), 98.8 (C-1′), 78.6 (C-3), 76.5(C-3′), 75.3 (C-4″), 75.1 (Ph*C*H$_2$), 74.8 (C-4′), 74.6 (Ph*C*H$_2$), 74.4 (*C*H$_2$CCl$_3$), 73.7 (Ph*C*H$_2$), 73.6 (Ph*C*H$_2$), 72.3 (C-2′), 72.2 (C-2″), 72.0 (C-5″, C-5′), 71.5 (C-5), 70.7 (C-4), 70.1 (C-1″), 68.9 (C-6′), 68.2 (C-6″), 67.6 (TMSCH$_2$*C*H$_2$O), 62.4 (C-6), 57.6 (C-2), 21.02 (OC=O*C*H$_3$), 20.99 (OC=O*C*H$_3$), 20.84 (OC=O*C*H$_3$), 20.82 (OC=O*C*H$_3$), 18.1 (TMS*C*H$_2$CH$_2$O), −1.4 (*C*H$_3$)$_3$Si); HRMS (ESI) calcd for (M+NH$_4$) $C_{62}H_{82}Cl_3N_2O_{21}Si$: 1323.4239. Found: 1323.4213.

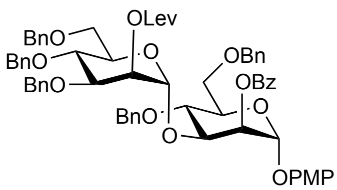


2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D- mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*- acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2- trichloroeth-oxycarbonylamino)-β-D-glucopyranoside (27): A mixture of thioglycoside **7** (1.25 g, 2.06 mmol), acceptor **26** (2.43 g, 1.87 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (50 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (0.63 g, 2.81 mmol and AgOTf (143 mg, 0.56 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (0.5 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 25→40% EtOAc in hexane) to afford **27** (2.75 g, 83% yield) as a white solid; R_f 0.42 (1:1 hexane−EtOAc); $[\alpha]_D$ = +36.3 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.37–7.30 (m, 8 H), 7.28–7.18 (m, 18 H), 7.16–7.12 (m, 4 H), 5.85 (d, 1 H, *J* = 7.1 Hz), 5.30 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.28–5.27 (m, 1 H), 5.26 (dd, 1 H, *J* = 9.5, 3.0 Hz), 5.10 (s, 1 H), 5.08 (d, 1 H, *J* = 1.5 Hz), 4.99 (app t, 1 H, *J* = 9.5 Hz), 4.90 (s, 1 H), 4.87 (app t, 1 H, *J* = 2.5 Hz), 4.78 (d, 1 H, *J* = 10.5 Hz), 4.73 (d, 1 H, *J* = 12.1 Hz), 4.71 (d, 1 H, *J* = 10.9 Hz), 4.65 (d, 1 H, *J* = 11.5 Hz), 4.62–4.54 (m, 3 H), 4.53–4.43 (m, 5 H), 4.34 (d, 1 H, *J* = 10.5 Hz), 4.21–4.16 (m, 2 H), 4.13–4.02 (m, 5 H), 3.97 (app t, 1 H, *J* = 10.0 Hz), 3.90–3.85 (m, 2 H), 3.81–3.73 (m, 3 H), 3.65 (dd, 1 H, *J* = 11.0, 2.0 Hz), 3.63 (dd, 1 H, *J* = 11.0, 2.5 Hz), 3.59–3.52 (m, 4 H), 3.47–3.43 (m, 1 H), 3.40 (dd, 1 H, *J* = 11.0, 1.5 Hz), 3.19–3.16 (m, 1 H), 2.68 (dt, 1

H, J = 18.5, 7.0 Hz), 2.61 (dt, 1 H, J = 18.5, 6.5 Hz), 2.46 (dt, 1 H, J = 17.5, 7.0 Hz), 2.41 (dt, 1 H, J = 17.5, 6.5 Hz), 2.12 (s, 3 H), 2.11 (s, 3 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 2.01 (s, 3 H), 0.90–0.86 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2, 171.8, 170.8, 170.4, 170.3, 169.8, 169.6, 154.0, 138.3, 138.2, 138.1, 138.0, 137.8, 137.6, 128.5, 128.4, 128.3, 128.27, 128.25, 128.22, 127.9, 127.86, 127.83, 127.64, 127.60, 127.5, 100.0, 99.7, 98.6, 95.6, 78.6, 77.6, 75.3, 75.1, 74.5, 74.4, 74.3, 74.2, 73.6, 73.5, 73.3, 72.6, 72.5, 72.4, 72.1, 72.0, 71.8, 71.5, 70.7, 70.0, 68.9, 68.1, 68.0, 67.5, 62.4, 60.4, 57.6, 37.9, 29.8, 27.9, 21.1, 21.0, 20.84, 20.82, 18.1, −1.4; ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^1J_{C\text{-}1,\,H\text{-}1}$ = 173.6, 170.8, 170.8, 161.0 Hz; HRMS (ESI) calcd for (M+NH_4) $C_{89}H_{112}Cl_3N_2O_{29}Si$: 1805.6180. Found: 1805.6149.

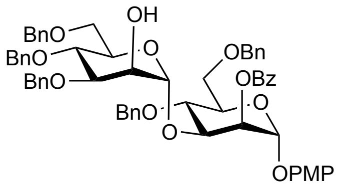


2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)- 2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-β-D-glucopyranoside (28): A solution of **27** (2.70 g, 1.5 mmol) and hydrazine acetate (250 mg, 2.7 mmol) in 9:1 CH_2Cl_2–CH_3OH (100 mL) was stirred at r.t. for 3 h. Then, the solution was concentrated and the resulting residue was subjected to chromatography (gradient 33→40% EtOAc in hexane) to afford **28** (2.39 g, 94% yield) as a white solid; R_f 0.53 (1:1 hexane–EtOAc); $[\alpha]_D$ = +38.6 (c 0.5, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.36–7.19 (m, 24 H), 7.18–7.15 (m, 6 H), 5.85 (d, 1 H, J = 6.7 Hz), 5.23 (dd, 1 H, J = 3.0, 2.0 Hz), 5.14 (dd, 1 H, J = 3.3, 1.7 Hz), 5.10 (d, 1 H, J = 1.5 Hz), 5.09 (d, 1 H, J = 1.5 Hz), 4.99 (app t, 1 H, J = 9.5 Hz), 4.90 (s, 1 H), 4.89 (app t, 1 H, J = 2.5 Hz), 4.79 (d, 1 H, J = 10.0 Hz), 4.72 (d, 1 H, J = 11.7 Hz), 4.69 (d, 1 H, J = 10.9 Hz), 4.65 (d, 1 H, J = 11.9 Hz), 4.62–4.54 (m, 3 H), 4.51–4.43 (m, 6 H), 4.34 (d, 1 H, J = 10.5 Hz), 4.21–4.16 (m, 2 H), 4.13–3.98 (m, 6 H), 3.90–3.85 (m, 2 H), 3.81–3.74 (m, 3 H), 3.69 (app dt, 1 H, J = 9.5, 2.0 Hz), 3.65 (dd, 1 H, J = 11.0, 2.0 Hz), 3.62 (dd, 1 H, J = 11.0, 3.0 Hz), 3.59–3.52 (m, 4 H), 3.47–3.43 (m, 1 H), 3.40 (dd, 1 H, J = 11.0, 1.5 Hz), 3.19–3.16 (m, 1 H), 2.08 (s, 6 H), 2.07 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 0.90–0.86 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.8, 170.4, 170.3, 170.1, 169.6, 154.0, 138.4, 138.3, 138.1, 138.0, 137.8, 137.6, 128.6, 128.5, 128.4, 128.3, 128.28, 128.27, 128.0, 127.96, 127.94, 127.86, 127.84, 127.81, 127.6, 127.5, 99.9, 99.7, 99.6, 98.6, 78.5, 77.8, 77.1, 75.3, 75.2, 75.0, 74.5, 74.4, 74.3, 73.5, 73.4, 72.6, 72.5, 72.3, 71.9, 71.8, 71.5, 70.7, 70.0, 68.9, 68.3, 68.1, 67.5, 62.4, 57.6, 21.1, 21.0, 20.9, 20.84, 20.82, 18.1, −1.4; ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^{1}J_{C\text{-}1,\,H\text{-}1}$ = 176.8, 172.3, 172.3, 162.2 Hz HRMS (ESI) calcd for (M+NH_4) $C_{84}H_{106}Cl_3N_2O_{27}Si$: 1707.5812. Found: 1707.5801.

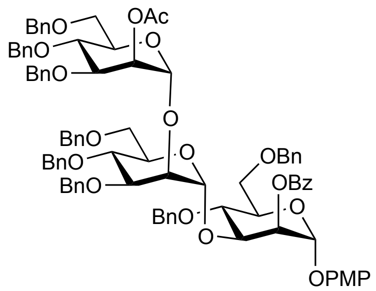


***p*-Methoxyphenyl 3,4,6-tri-*O*-Benzyl-2-*O*-levulinyl-α-D-mannopyranosyl-(1→3)- 2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (29):** A mixture of acceptor **6** (1.08 g, 1.90 mmol), donor **4** (1.37 g, 2.09 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (100 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (702 mg, 3.13 mmol) and AgOTf (146 mg, 0.57 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h before Et_3N (1.0 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→33% EtOAc in hexane) to afford **29** (1.96 g, 94% yield) as a white foam; R_f 0.24 (2:1 hexane–EtOAc); $[\alpha]_D$ = +32.9 (*c* 1.2, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 8.03–8.02 (m, 2 H, ArH), 7.56–7.54 (m, 1 H, ArH), 7.36–7.16 (m, 25 H, ArH), 7.07–7.05 (m, 2 H, ArH), 6.97–6.96 (m, 2 H, ArH), 6.77–6.76 (m, 2 H, ArH), 5.59 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.57 (d, 1 H, *J* = 2.0 Hz, H-1), 5.36 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2′), 5.23 (d, 1 H, *J* = 2.0 Hz, H-1′), 4.77 (d, 1 H, *J* = 10.5 Hz, PhC*H*$_2$), 4.75 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.67 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.65 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.54 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.52 (dd, 1 H, *J* = 9.5, 3.0 Hz, H-3), 4.47 (d, 1 H, *J* = 11.5 Hz, PhC*H*$_2$), 4.45 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.43 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.42 (d, 1 H, *J* = 12.0 Hz, PhC*H*$_2$), 4.32 (d, 1 H, *J* = 11.0 Hz, PhC*H*$_2$), 4.22 (app t, 1 H, *J* = 9.5 Hz, H-4), 3.96 (ddd, 1 H, *J* = 10.0, 3.0, 1.5 Hz, H-5), 3.88 (app t, 1 H, *J* = 9.5 Hz, H-4′), 3.86–3.83 (m, 3 H, H-3′, H-5′, H-6), 3.74 (s, 3 H, OCH_3), 3.68 (dd, 1 H, *J* = 11.0, 2.0 Hz, H-6), 3.63 (dd, 1 H, *J* = 11.0, 3.0 Hz, H-6′), 3.59 (dd, 1 H, *J* = 11.0, 1.5 Hz, H-6′), 2.65–2.61 (m, 4 H, $CH_3C{=}OC$*H*$_2$, $CH_3C{=}OCH_2C$*H*$_2$), 2.08 (s, 3 H, C*H*$_3$C=OCH$_2$,); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 206.1 (CH$_3$*C*=OCH$_2$), 171.8 (O*C*=OCH$_2$), 165.7 (PhC=O), 155.1 (Ar), 149.9 (Ar), 138.6 (Ar), 138.3 (Ar), 138.2 (Ar), 137.9 (Ar), 137.8 (Ar), 133.3 (Ar), 129.9 (Ar), 129.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.22 (Ar), 128.20 (Ar), 128.1 (Ar), 127.92 (Ar), 127.90 (Ar), 127.8 (Ar), 127.7 (Ar), 127.55 (Ar), 127.53 (Ar), 127.52 (Ar), 127.4 (Ar), 127.3 (Ar), 117.8 (Ar), 114.6 (Ar), 99.7 (C-1′), 96.2 (C-1), 77.7 (C-3′), 77.0 (C-3), 75.3 (Ph*C*H$_2$), 74.54 (C-4), 74.53 (Ph*C*H$_2$), 73.9 (C-4′), 73.4 (Ph*C*H$_2$), 72.3 (C-5′), 72.1 (C-5), 72.0 (C-2), 71.7 (Ph*C*H$_2$), 69.2 (C-2′), 68.7

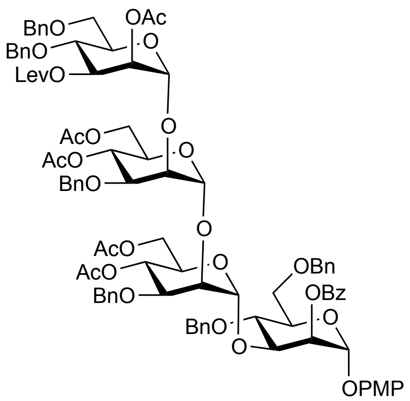
(C-6), 68.4 (C-6′), 55.6 (CH_3O), 38.0 ($CH_3C{=}OCH_2$), 29.7 ($CH_3C{=}OCH_2$), 28.2 ($CH_3C{=}OCH_2CH_2$); ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^1J_{C\text{-}1,\,H\text{-}1}$ = 174.5 Hz (C-1, H-1), $^1J_{C\text{-}1',\,H\text{-}1'}$ = 174.5 Hz (C-1′, H-1′); HRMS (ESI) calcd for (M+Na) $C_{66}H_{68}NaO_{15}$: 1123.4450. Found: 1123.4434.



***p*-Methoxyphenyl 3,4,6-tri-*O*-Benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl- 4,6-di-*O*-benzyl-α-D-mannopyranoside (30):** A solution of **29** (1.88 g, 1.71 mmol) and hydrazine acetate (282 mg, 3.07 mmol) in 9:1 CH_2Cl_2–CH_3OH (100 mL) was stirred at r.t. for 2 h. Then, the solution was concentrated and the resulting residue was subjected to chromatography (gradient 33→40% EtOAc in hexane) to afford **30** (1.60 g, 93% yield) as a white foam; R_f 0.24 (2:1 hexane–EtOAc); $[\alpha]_D$ = +53.1 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.06–8.04 (m, 2 H, ArH), 7.57–7.55 (m, 1 H, ArH), 7.38–7.19 (m, 25 H, ArH), 7.09–7.07 (m, 2 H, ArH), 6.98–6.97 (m, 2 H, ArH), 6.78–6.77 (m, 2 H, ArH), 5.61 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.57 (d, 1 H, *J* = 2.0 Hz, H-1), 5.27 (d, 1 H, *J* = 2.0 Hz, H-1′), 4.72 (d, 1 H, *J* = 11.0 Hz, $PhCH_2$), 4.70–4.68 (m, 2 H, $PhCH_2$), 4.65 (d, 1 H, *J* = 12.0 Hz, $PhCH_2$), 4.55 (d, 1 H, *J* = 11.0 Hz, $PhCH_2$), 4.53 (d, 1 H, *J* = 11.5 Hz, $PhCH_2$), 4.51 (dd, 1 H, *J* = 9.5, 3.0 Hz, H-3), 4.48–4.43 (m, 4 H, $PhCH_2$), 4.21 (app t, 1 H, *J* = 9.5 Hz, H-4), 3.98 (ddd, 1 H, *J* = 10.0, 3.0, 1.5 Hz, H-5), 3.90–3.84 (m, 4 H, H-2′, H-5′, H-6, H-4′), 3.74 (s, 3 H, OCH_3), 3.72 (dd, 1 H, *J* = 9.0, 3.0 Hz, H-3′), 3.69 (dd, 1 H, *J* = 11.0, 2.0 Hz, H-6), 3.63–3.60 (m, 2 H, H-6′), 3.59 (dd, 1 H, *J* = 11.0, 1.5 Hz, H-6′), 2.35 (d, 1 H, *J* = 3.0 Hz, OH); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 165.7 (PhC=O), 155.1 (Ar), 150.0 (Ar), 138.5 (Ar), 138.3 (Ar), 138.2 (Ar), 137.93 (Ar), 137.91 (Ar), 133.2 (Ar), 129.9 (Ar), 129.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 127.86 (Ar), 127.84 (Ar), 127.82 (Ar), 127.80 (Ar), 127.77 (Ar), 127.57 (Ar), 127.55 (Ar), 127.53 (Ar), 127.4 (Ar), 127.3 (Ar), 117.8 (Ar), 114.6 (Ar), 101.6 (C-1′), 96.3 (C-1), 79.7 (C-3′), 77.4 (C-3), 75.2 (Ph*C*H$_2$), 74.6 (C-4), 74.5 (Ph*C*H$_2$), 73.9 (C-4′), 73.4 (Ph*C*H$_2$), 72.3 (C-2), 72.15 (Ph*C*H$_2$), 72.11 (C-5), 71.9 (C-5′), 69.0 (C-2′), 68.7 (C-6), 68.4 (C-6′), 55.6 (CH$_3$O); HRMS (ESI) calcd for (M+Na) $C_{61}H_{62}NaO_{13}$: 1025.4083. Found: 1025.4066.

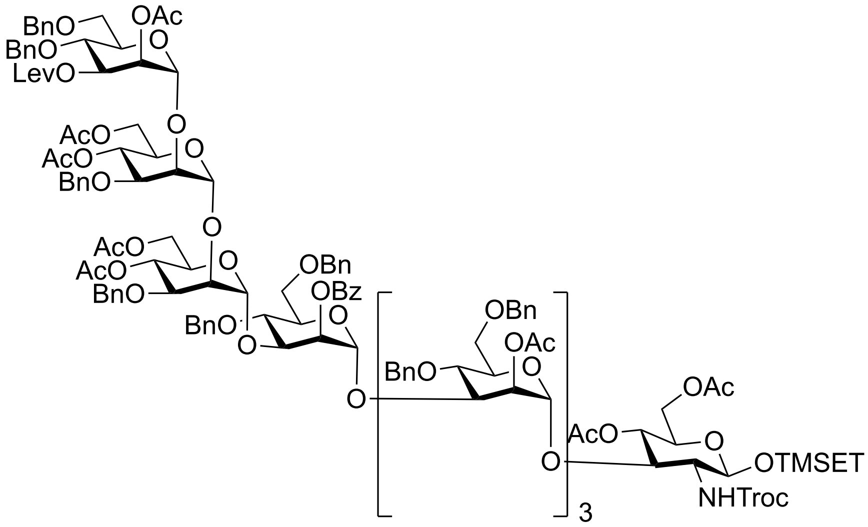


***p*-Methoxyphenyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)- 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (32):** A mixture of acceptor **30** (1.57 g, 1.56 mmol), donor **31** (1.08 g, 1.80 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (100 mL) and stirred at r.t. for 10 min. The solution was then cooled to −15 °C, and then NIS (602 mg, 2.69 mmol) and AgOTf (119 mg, 0.49 mmol) were added. The solution was slowly warmed to 0 °C and stirred for 1 h. Et_3N (1.0 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→25% EtOAc in hexane) to afford **32** (2.0 g, 86% yield) as a white foam; R_f 0.44 (2:1 hexane−EtOAc); $[\alpha]_D$ = +37.6 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.06−8.04 (m, 2 H, ArH), 7.57–7.55 (m, 1 H, ArH), 7.38–7.06 (m, 42 H, ArH), 6.95–6.94 (m, 2 H, ArH), 6.75–6.74 (m, 2 H, ArH), 5.62 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.57 (d, 1 H, *J* = 2.0 Hz, H-1), 5.48 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2″), 5.31 (d, 1 H, *J* = 1.5 Hz, H-1′), 5.02 (d, 1 H, *J* = 1.5 Hz, H-1″), 4.79 (d, 1 H, *J* = 11.0 Hz, PhC*H*2), 4.75 (d, 1 H, *J* = 11.0 Hz, PhC*H*2), 4.74 (d, 1 H, *J* = 11.0 Hz, PhC*H*2), 4.66 (d, 1 H, *J* = 12.0 Hz, PhC*H*2), 4.62 (d, 1 H, *J* = 12.0 Hz, PhC*H*2), 4.58 (d, 1 H, *J* = 12.5 Hz, PhC*H*2), 4.57 (d, 1 H, *J* = 11.5 Hz, PhC*H*2), 4.52–4.49 (m, 3 H, PhC*H*2), 4.48 (dd, 1 H, *J* = 9.5, 3.0 Hz, H-3), 4.42–4.39 (m, 4 H, PhC*H*2), 4.36 (d, 1 H, *J* = 12.0 Hz, PhC*H*2), 4.28 (d, 1 H, *J* = 11.0 Hz, PhC*H*2), 4.17 (app t, 1 H, *J* = 9.5 Hz, H-4), 3.95–3.90 (m, 5 H, H-2′, H-4′, H-5, H-3″, H-5″), 3.85 (app t, 1 H, *J* = 9.5 Hz, H-4″), 3.81–3.77 (m, 3 H, H-6, H-3′, H-5′), 3.74 (s, 3 H, OCH_3), 3.67–3.63 (m, 2 H, H-6, H-6″), 3.57 (dd, 1 H, *J* = 11.0, 3.5 Hz, H-6′), 3.54 (dd, 1 H, *J* = 11.0, 1.5 Hz, H-6′), 3.69 (dd, 1 H, *J* = 10.5, 1.0 Hz, H-6″), 2.10 (s, 3 H, OC=OC*H*3); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 170.1 (O*C*=OCH3), 165.7 (PhC=O), 155.1 (Ar), 150.0 (Ar), 138.7 (Ar), 138.6 (Ar), 138.5 (Ar), 138.3 (Ar), 138.28 (Ar), 138.26 (Ar), 138.19 (Ar), 138.0 (Ar), 133.2 (Ar), 129.9 (Ar), 129.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.17 (Ar), 128.12 (Ar), 128.11 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.56 (Ar), 127.54 (Ar), 127.48 (Ar), 127.46 (Ar), 127.44 (Ar), 127.39 (Ar), 127.37 (Ar), 127.26 (Ar), 127.21 (Ar), 117.9 (Ar), 114.5 (Ar), 101.0 (C-1′), 99.4 (C-1″), 96.3 (C-1), 79.1 (C-3′), 78.4 (C-3), 78.2 (C-3′), 75.3, 75.1 (Ph*C*H2), 74.9 (Ph*C*H2), 74.4 (Ph*C*H2), 74.3 (C-4), 74.1 (C-4″), 73.34 (Ph*C*H2), 73.3 (Ph*C*H2), 73.2 (Ph*C*H2), 72.8, 72.2, 72.1 (Ph*C*H2), 72.0, 71.97, 71.9 (Ph*C*H2), 68.8, 68.7, 68.6 68.5, 55.6 (CH_3O), 21.1 (OC=O*C*H3); ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^1J_{C\text{-}1, H\text{-}1}$ = 176.2 Hz (C-1, H-1), $^1J_{C\text{-}1', H\text{-}1'}$ = 170.5 Hz (C-1′, H-1′), $^1J_{C\text{-}1'', H\text{-}1''}$ = 171.9 Hz (C-1″, H-1″); HRMS (ESI) calcd for (M+Na) $C_{90}H_{92}NaO_{19}$: 1499.6125. Found: 1499.6120.

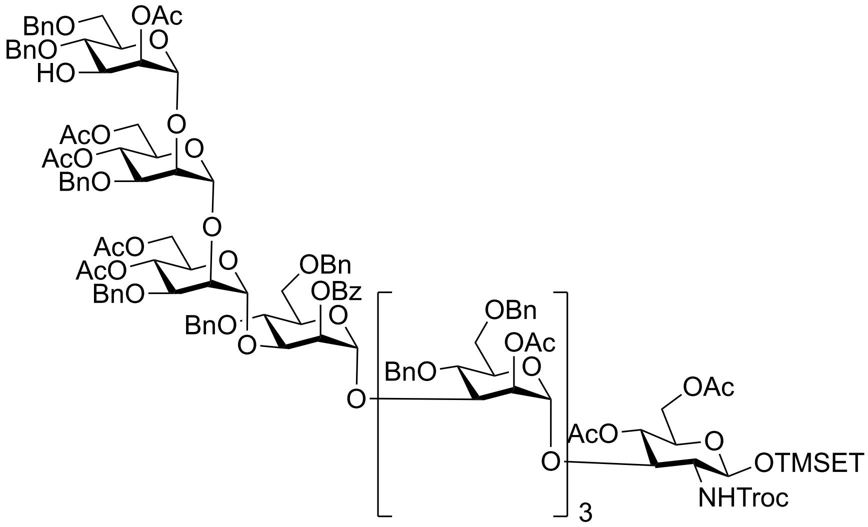


***p*-Methoxyphenyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D- mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D- mannopyranoside (10):** Tetrasaccharide **21** (1.40 g 0.81 mmol) was dissolved in a 1% solution of I_2 in CH_3OH (w/v, 120 mL) and the solution was heated at reflux for 6 h. The solution was cooled, a few crystals of $Na_2S_2O_3$ were added, and the suspension was stirred until the dark red solution went colorless. Then, the mixture was filtered and water was added. The mixture was extracted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated to dryness. The resulting residue was dissolved in 5:4 pyridine–Ac_2O (90 mL) and the mixture was stirred at r.t. for 2 h. Then, the solution was concentrated to dryness and the residue was dissolved in a 2% solution of HCl in acetone (30 mL). After 0.5 h, CH_2Cl_2 (150 mL) was added and the mixture was washed with 1M of HCl, a satd aq solution of $NaHCO_3$, brine, dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by chromatography (gradient 33→66% EtOAc in hexane) to afford **10** (1.22 g, 88% yield) as a white solid. R_f 0.18 (1:1 hexane–EtOAc); $[\alpha]_D$ = +50.0 (*c* 0.2, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 8.08–8.07 (m, 2 H, ArH), 7.62–7.60 (m, 1 H, ArH), 7.43–7.41 (m, 2 H, ArH), 7.36–7.01 (m, 30 H, ArH), 6.98–6.96 (m, 3 H, ArH), 6.79–6.77 (m, 2 H, ArH), 5.57 (d, 1 H, *J* = 2.0 Hz, H-1), 5.54 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.39 (dd, 1 H, *J* = 9.5, 3.5 Hz, H-3‴), 5.31 (dd, 1 H, *J* = 3.5, 2.0 Hz, H-2‴), 5.30 (s, 1 H, H-1′), 5.25 (app t, 1 H, *J* = 10.0 Hz, H-4″), 5.16 (app t, 1 H, *J* = 10.0 Hz, H-4′), 4.94 (d, 1 H, *J* = 2.0 Hz, H-1″), 4.88 (d, 1 H, *J* = 1.5 Hz, H-1‴), 4.67 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.62–4.52 (m, 5 H, PhCH_2), 4.46–4.44 (m, 2 H, PhCH_2), 4.42 (dd, 1 H, *J* = 9.5, 3.0 Hz, H-3), 4.36 (d, 1 H, *J* = 11.0 Hz, PhCH_2), 4.28–4.23 (m, 3 H, PhCH_2), 4.16 (app t, 1 H, *J* = 9.5 Hz, H-4), 4.08 (dd, 1 H, *J* = 12.0, 2.5 Hz), 4.04 (dd, 1 H, *J* = 12.0, 6.0 Hz), 4.02 (app t, 1 H, *J* = 2.5 Hz, H-2″), 3.96–3.79 (m, 9 H), 3.74 (s, 3 H, OCH_3), 3.69 (app t, 1 H, *J* = 2.0 Hz), 3.66–3.64 (m, 2 H), 3.57 (dd, 1 H, *J* = 10.5, 3.5 Hz), 3.42 (dd, 1 H, *J* = 11.0, 1.5 Hz), 2.77 (dt, 1 H, *J* = 18.0, 7.0 Hz, $CH_3C{=}OCH_2$), 2.63 (dt, 1 H, *J* = 18.0, 6.5 Hz, $CH_3C{=}OCH_2$), 2.52 (dt, 1 H, *J* = 17.0, 7.0 Hz, $OC{=}OCH_2CH_2$), 2.42 (dt, 1 H, *J* = 17.0, 6.5 Hz, $OC{=}OCH_2CH_2$), 2.14 (s, 3 H, $CH_3C{=}OCH_2$), 2.07 (s, 3 H, $OC{=}OCH_3$), 2.01 (s, 3 H, $OC{=}OCH_3$), 1.98 (s, 3 H, $OC{=}OCH_3$), 1.94 (s, 3 H, $OC{=}OCH_3$), 1.90 (s, 3 H, $OC{=}OCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.4 ($CH_3C{=}OCH_2$), 171.2 ($OC{=}OCH_2$), 170.8 ($CH_3C{=}O$), 170.7 ($CH_3C{=}O$), 169.7 ($CH_3C{=}O$), 169.6 ($CH_3C{=}O$), 169.3 ($CH_3C{=}O$), 165.6 (PhC=O), 155.3 (Ar), 149.7 (Ar), 138.3 (Ar), 138.1 (Ar), 138.0 (Ar), 137.8 (Ar), 137.7 (Ar), 137.5 (Ar), 133.5 (Ar), 129.8 (Ar), 129.6 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.32 (Ar), 128.31 (Ar), 128.25 (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.77 (Ar), 127.73 (Ar), 127.68 (Ar), 127.64 (Ar), 127.57 (Ar), 127.54 (Ar), 127.51 (Ar), 125.49 (Ar), 117.7 (Ar), 114.6 (Ar), 100.9 (C-1′，C-1″), 98.6 (C-1‴), 96.4 (C-1), 77.4 (C-3), 76.9, 75.7, 75.3 (PhCH_2), 74.7 (PhCH_2), 74.5, 73.5, 73.40 (PhCH_2), 73.39 (PhCH_2), 72.9, 72.3, 72.2 (PhCH_2), 72.1, 71.9 (PhCH_2), 71.8, 71.7, 69.9, 69.75, 69.74, 68.6, 68.5, 67.4, 67.3, 62.8， 62.6, 55.6 (CH_3O), 37.9 ($CH_3C{=}OCH_2$), 29.8

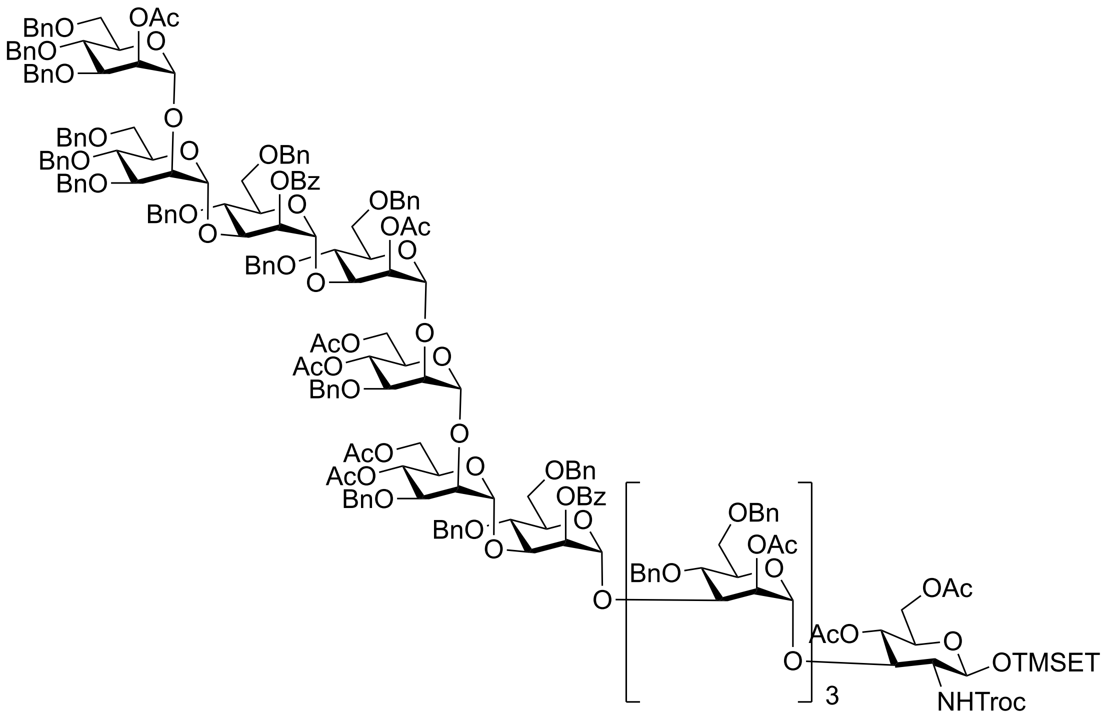
(CH_3C=OCH_2), 27.9 (CH_3C=OCH_2CH_2), 20.9 (OC=OCH_3), 20.8 (OC=OCH_3), 20.79 (OC=OCH_3), 20.7 (OC=OCH_3), 20.6 (OC=OCH_3); ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^1J_{C-1, H-1}$ = 173.3 Hz (C-1, H-1), $^1J_{C-1', H-1'}$ = 174.4 Hz (C-1′, H-1′), $^1J_{C-1'', H-1''}$ = 172.8 Hz (C-1″, H-1″), $^1J_{C-1''', H-1'''}$ = 175.0 Hz (C-1‴, H-1‴); HRMS (ESI) calcd for ($M+NH_4$) $C_{95}H_{108}NO_{30}$: 1742.6951. Found: 1742.6827.



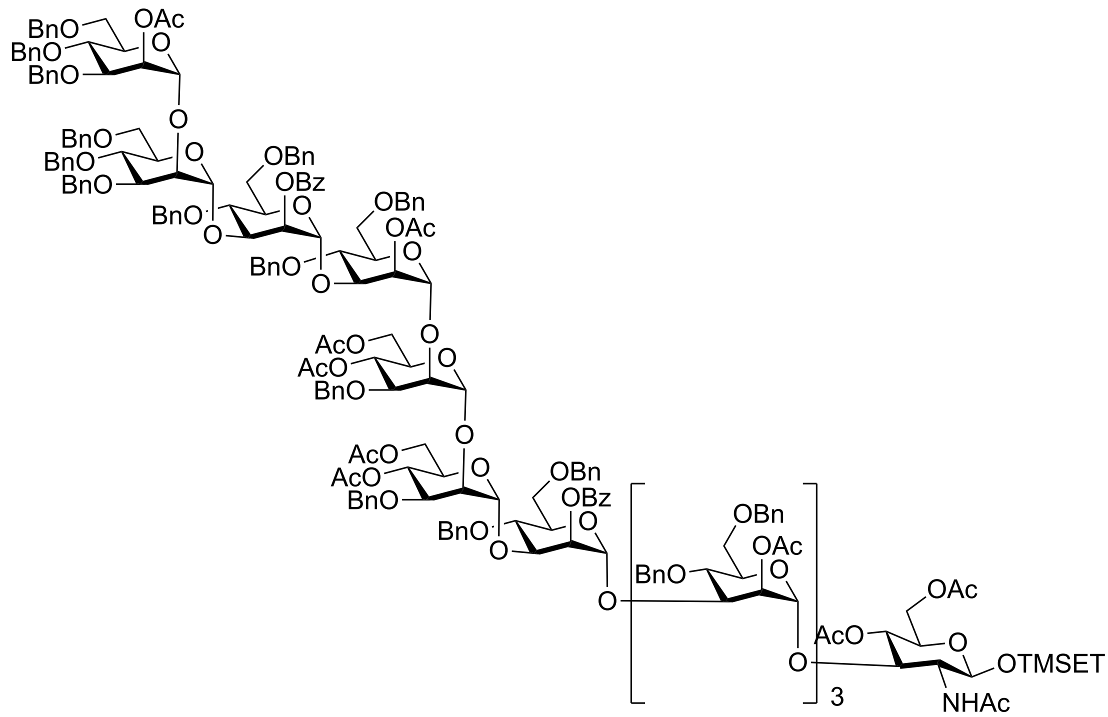
2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D- mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*- acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-β-D-glucopyranoside (38): Trichloroacetimidate **36** (780 mg) was prepared from tetrasaccharide **10** (1.19 g) in 65% yield following general procedure A described above. A mixture of tetrasaccharide acceptor **28** (532 mg, 0.31 mmol), trichloroacetimidate donor **36** (460 mg, 0.29 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (100 mL) and stirred at r.t. for 10 min. The solution was then cooled to 0 °C, and then TBSOTf (20 μL) was added. The solution was stirred for 1 h before Et_3N (0.2 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 30→60% EtOAc in hexane) to afford **38** (750 mg, 86%) yield as a white solid; R_f 0.09 (1:1 hexane–EtOAc); $[\alpha]_D$ = +27.9 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.99–7.98 (m, 2 H), 7.58–7.56 (m, 1 H), 7.37–7.06 (m, 60 H), 6.99–6.97 (m, 2 H), 5.84 (d, 1 H, *J* = 6.5 Hz), 5.47 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.37 (dd, 1 H, *J* = 9.5, 3.5 Hz), 5.30 (dd, 1 H, *J* = 3.5, 2.0 Hz), 5.28 (dd, 1 H, *J* = 3.0, 1.5 Hz), 5.26−5.21 (m, 3 H), 5.18−5.15 (m, 2 H), 5.12 (d, 1 H, *J* = 1.5 Hz), 5.09 (s, 1 H), 4.98 (dd, 1 H, *J* = 10.0, 9.0 Hz), 4.91 (d, 1 H, *J* = 1.5 Hz), 4.89 (s, 1 H), 4.86 (d, 1 H, *J* = 1.5 Hz), 4.84 (app t, 1 H, *J* = 2.5 Hz), 4.80 (d, 1 H, *J* = 10.5 Hz), 4.74 (d, 1 H, *J* = 10.5 Hz), 4.71 (d, 1 H, *J* = 10.5 Hz), 4.70 (d, 1 H, *J* = 12.0 Hz), 4.65−4.48 (m, 9 H), 4.44−4.42 (m, 5 H), 4.38−4.32 (m, 4 H), 4.25−4.06 (m, 11 H), 4.04−3.96 (m, 5 H), 3.92−3.72 (m, 14 H), 3.64−3.51 (m, 11 H), 3.46−3.34 (m, 4 H), 3.18−3.15 (m, 1 H), 2.77 (dt, 1 H, *J* = 18.5, 7.0 Hz), 2.63 (dt, 1 H, *J* = 18.5, 6.5 Hz), 2.51 (dt, 1 H, *J* = 17.0, 7.0 Hz), 2.41 (dt, 1 H, *J* = 17.0, 6.5 Hz), 2.14 (s, 3 H), 2.05−2.04 (m, 18 H), 1.93 (s, 3 H), 1.91 (s, 3 H), 1.89 (s, 3 H), 1.88 (s, 3 H), 0.89−0.82 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 206.5, 171.3, 171.0, 170.8, 170.6, 170.3, 170.2, 170.0, 169.7, 169.6, 169.5, 169.3, 165.2, 154.0, 138.4, 138.3, 138.0, 137.9, 137.87, 137.84, 137.77, 137.73, 137.6, 137.5, 133.4, 129.8, 129.7, 128.5, 128.4, 128.3, 128.29, 128.28, 128.27, 128.24, 128.2, 128.1, 128.0, 127.9, 127.86, 127.84, 127.80, 127.78, 127.72, 127.70, 127.65, 127.62, 127.58, 127.54, 127.48, 127.47, 127.43, 127.37, 100.7, 99.8, 99.6, 98.7, 98.5, 78.2, 77.2, 76.7, 75.9, 75.8, 75.3, 75.1, 74.9, 74.7, 74.3, 74.1, 74.0, 73.5, 73.46, 73.39, 73.37, 73.33, 73.2, 72.9, 72.5, 72.4, 72.3, 72.2, 72.0, 71.9, 71.8, 71.76, 71.4, 70.7, 69.8, 69.6, 68.9, 68.4, 68.3, 68.0, 67.5, 67.2, 67.1, 62.5, 62.4, 62.3, 57.6, 37.9, 29.8, 27.9, 21.1, 21.0, 20.97, 20.92, 20.80, 20.78, 20.75, 20.67, 20.61, 18.0, −1.4; ^{1}H-coupled HSQC (700 MHz, $CDCl_3$) $^{1}J_{C\text{-}1,H\text{-}1}$ = 175.0, 175.0, 174.3, 174.3, 174.3, 173.6, 172.2, 161.7 Hz; HRMS (ESI) calcd for $(M+3Na)^{+3}$ $C_{172}H_{198}Cl_3NNa_3O_{55}Si$: 1119.7080. Found: 1119.7119.



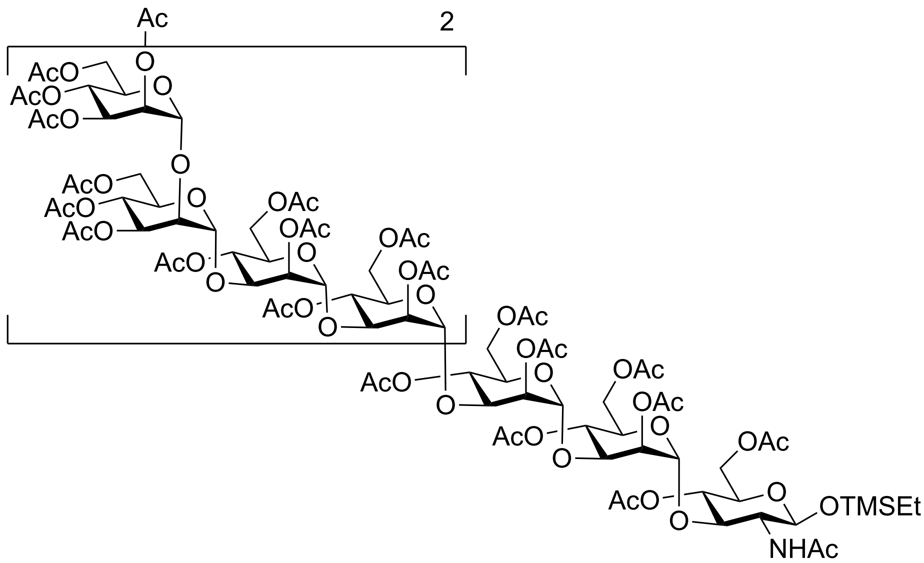
2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)- 4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (40): A solution of **38** (0.95 g, 0.29 mmol) and hydrazine acetate (53 mg, 0.58 mmol) in 9:1 CH_2Cl_2–CH_3OH (50 mL) was stirred at r.t. for 1 h. Then, the solution was concentrated at 40 °C for 0.5 h to achieve complete deproection of the levulinyl group. The resulting residue was subjected to chromatography (gradient 16→33% EtOAc in hexane) to afford **40** (0.86 g, 94% yield) as a white solid; R_f 0.13 (1:1 hexane–EtOAc); $[\alpha]_D$ = +29.0 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.00–7.99 (m, 2 H), 7.59–7.56 (m, 1 H), 7.37–7.07 (m, 60 H), 7.02–7.00 (m, 2 H), 5.83 (d, 1 H, *J* = 7.0 Hz), 5.47 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.28 (dd, 1 H, *J* = 3.0, 1.5 Hz), 5.25 (d, 1 H, *J* = 1.5 Hz), 5.22 (app t, 1 H, *J* = 2.0 Hz), 5.19–5.16 (m, 4 H), 5.11 (d, 1 H, *J* = 1.5 Hz), 5.08 (s, 1 H), 5.01 (d, 1 H, *J* = 1.5 Hz), 4.98 (app t, 1 H, *J* = 9.5 Hz), 4.88 (s, 1 H), 4.84 (app t, 1 H, *J* = 2.5 Hz), 4.79 (d, 1 H, *J* = 10.5 Hz), 4.78–4.70 (m, 5 H), 4.64 (d, 1 H, *J* = 11.5 Hz), 4.59–4.42 (m, 13 H), 4.37 (d, 1 H, *J* = 10.5 Hz), 4.34 (d, 1 H, *J* = 11.0 Hz), 4.33 (d, 1 H, *J* = 10.5 Hz), 4.28 (d, 1 H, *J* = 12.0 Hz), 4.23–4.06 (m, 11 H), 4.04–3.94 (m, 5 H), 3.91–3.81 (m, 9 H), 3.76–3.71 (m, 5 H), 3.65–3.34 (m, 15 H), 3.18–3.14 (m, 1 H), 2.08 (s, 3 H), 2.05–2.03 (m, 15 H), 1.92 (s, 3 H), 1.91 (s, 3 H), 1.89 (s, 3 H), 1.84 (s, 3 H), 0.88–0.84 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 170.8, 170.6, 170.5, 170.3, 170.2, 170.0, 169.6, 169.5, 165.2, 154.0, 138.4, 138.3, 138.28, 138.1, 137.9, 137.83, 137.78, 137.75, 137.6, 137.5, 133.4, 129.8, 129.7, 128.5, 128.47, 128.41, 128.38, 128.32, 128.29, 128.27, 128.20, 128.1, 128.0, 127.93, 127.91, 127.80, 127.78, 127.74, 127.72, 127.69, 127.62, 127.57, 127.50, 127.49, 127.43, 127.35, 100.8, 100.7, 99.8, 99.6, 99.2, 98.5, 78.2, 75.8, 75.5, 75.4, 75.3, 75.1, 75.04, 74.99, 74.94, 74.4, 74.3, 74.1, 74.0, 73.5, 73.4, 73.33, 73.28, 73.24, 72.5, 72.4, 72.26, 72.25, 72.18, 72.0, 71.9, 71.8, 71.6, 71.4, 70.7, 70.6, 69.6, 69.4, 68.8, 68.3, 68.0, 67.5, 67.2, 67.1, 62.5, 62.3, 57.6, 21.1, 21.0, 20.92, 20.82, 20.79, 20.78, 20.76, 20.65, 20.61, 18.0, −1.4; HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{167}H_{200}Cl_3N_3O_{53}Si$: 1614.0935. Found: 1614.0952.



2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)- 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (41): 742 mg of trichloroacetimidate donor **33** (742 mg) was formed from trisaccharide **32** (1.1 g) in 65% yield following general procedure A described above. Then, a mixture of acceptor **40** (650 mg, 0.20 mmol), trichloroacetimidate donor **33** (370 mg, 0.24 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (30 mL) and stirred at r.t. for 10 min. The solution was then cooled to 0 °C, and then TBSOTf (20 μL) was added. The solution was stirred for 1 h at r.t. before Et_3N (0.2 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 25→50% EtOAc in hexane) to afford **41** (800 mg, 86% yield) as a white solid; R_f 0.53 (1:1 hexane–EtOAc); $[\alpha]_D$ = +16.3 (*c* 0.4, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 8.00–7.97 (m, 4 H), 7.58–7.56 (m, 1 H), 7.53–7.51 (m, 1 H), 7.36–6.98 (m, 104 H), 5.83 (d, 1 H, J = 6.5 Hz), 5.57 (s, 1 H), 5.47 (s, 1 H), 5.46 (s, 1 H), 5.30 (s, 1 H), 5.27 (s, 1 H), 5.25 (s, 1 H), 5.22–5.14 (m, 6 H), 5.11 (s, 1 H), 5.08 (s, 1 H), 5.02 (s, 1 H), 4.99–4.96 (m, 2 H), 4.89 (s, 1 H), 4.84–4.79 (m, 4 H), 4.76–4.64 (m, 8 H), 4.58–4.41 (m, 18 H), 4.38–4.32 (m, 7 H), 4.26–3.95 (m, 22 H), 3.93–3.69 (m, 24 H), 3.64–3.32 (m, 19 H), 3.18–3.14 (m, 1 H), 2.07 (s, 3 H), 2.06–2.04 (m, 12 H), 2.02 (s, 3 H), 2.00 (s, 3 H), 1.91 (s, 3 H), 1.89 (s, 3 H), 1.82 (s, 3 H), 1.77 (s, 3 H), 0.88–0.84 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 170.8, 170.7, 170.5, 170.3, 170.2, 170.03, 169.98, 169.90, 169.6, 169.5, 169.0, 165.4, 165.2, 154.0, 139.1, 138.8, 138.7, 138.6, 138.5, 138.4, 138.32, 138.30, 138.29, 138.1, 138.07, 137.97, 137.94, 137.85, 137.81, 137.78, 137.6, 137.5, 133.4, 133.0, 129.9, 129.8, 129.7, 128.6, 128.5, 128.42, 128.38, 128.36, 128.32, 128.27, 128.23, 128.19, 128.14, 128.12, 128.10, 128.0, 127.90, 127.88, 127.81, 127.77, 127.75, 127.71, 127.69, 127.66, 127.63, 127.59, 127.55, 127.50, 127.47, 127.40, 127.38, 127.35, 127.31, 127.18, 127.12, 101.1, 100.8, 99.8, 99.6, 99.4, 99.1, 99.0, 98.5, 79.3, 78.3, 78.2, 77.7, 76.5, 75.7, 75.5, 75.4, 75.3, 75.1, 75.0, 74.9, 74.87, 74.7, 74.6, 74.3, 74.2, 74.18, 74.14, 74.0, 73.9, 73.5, 73.4, 73.32, 73.29, 73.23, 73.18, 73.09, 72.7, 72.6, 72.48, 72.46, 72.43, 72.3, 72.19, 72.13, 72.0, 71.95, 71.89, 71.83, 71.7, 71.4, 70.7, 69.6, 69.5, 68.63, 68.58, 68.33, 68.27, 68.20, 68.0, 67.4, 67.23, 67.18, 62.6, 62.5, 62.3, 57.6, 21.1, 21.05, 21.04, 21.0, 20.9, 20.78, 20.76, 20.70, 20.6, 20.5, 18.0, −1.4; HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{250}H_{284}Cl_3N_3O_{70}Si$: 2290.3790. Found: 2290.3814.

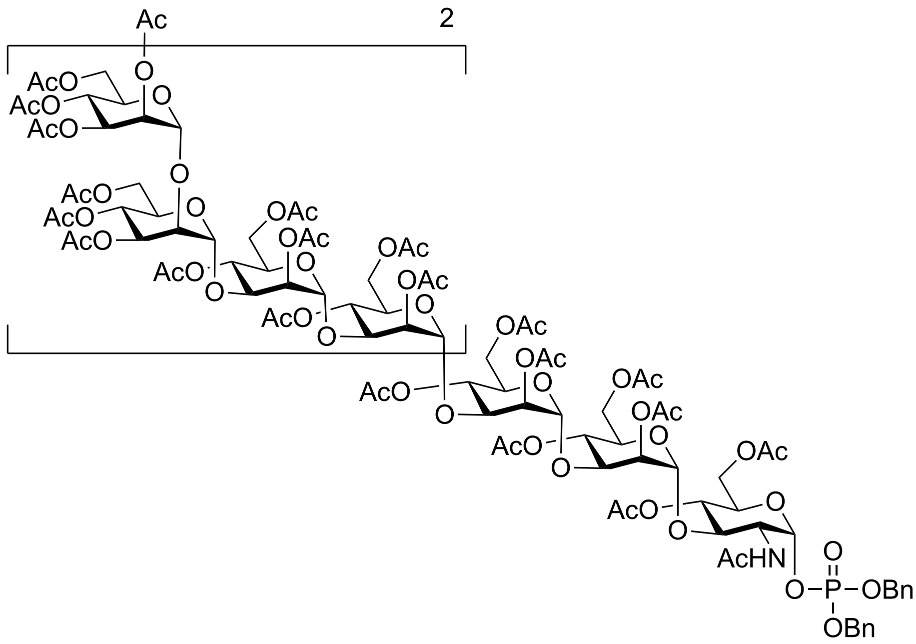


2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)- 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (42): To a solution of substrate **41** (800 mg, 0.18 mmol) in 3:1 THF–AcOH (84 mL) was added freshly activated zinc dust (2 g). After stirring for 3 h at r.t., the mixture was filtered and the filtrate was concentrated. The resulting residue was dissolved in 3:2 pyridine–Ac_2O (25 mL) and the mixture was stirred at r.t. for 2 h. Then, the solution was concentrated, dissolved in CH_2Cl_2 (100 mL) followed by washing with 1M HCl, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography (gradient 40→66% EtOAc in hexane) to afford **42** (698 mg, 90% yield) as a white solid; R_f 0.19 (1:1 hexane–EtOAc); $[\alpha]_D$ = +9.8 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.00–7.98 (m, 4 H), 7.59–7.57 (m, 1 H), 7.54–7.52 (m, 1 H), 7.37–6.99 (m, 104 H), 6.49 (d, 1 H, *J* = 7.0 Hz), 5.58 (s, 1 H), 5.48 (app t, 1 H *J* = 2.0 Hz), 5.46 (app t, 1 H *J* = 2.0 Hz), 5.31 (d, 1 H *J* = 1.5 Hz), 5.28 (dd, 1 H *J* = 2.5, 1.5 Hz), 5.25 (d, 1 H *J* = 1.5 Hz), 5.23–5.16 (m, 6 H), 5.12 (s, 1 H), 5.10 (s, 1 H), 5.07 (d, 1 H *J* = 8.0 Hz), 5.03 (d, 1 H *J* = 1.5 Hz), 4.98 (s, 1 H), 4.90 (dd, 1 H *J* = 10.0, 9,0 Hz), 4.85–4.81 (m, 4 H), 4.77–4.67 (m, 8 H), 4.59–4.30 (m, 24 H), 4.27–4.12 (m, 14 H), 4.09–4.01 (m, 5 H), 3.98–3.70 (m, 25 H), 3.65–3.34 (m, 20 H), 2.96–2.93 (m, 1 H), 2.07 (s, 3 H), 2.06–2.04 (m, 12 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.92 (s, 3 H), 1.89 (s, 3 H), 1.83 (s, 3 H), 1.79 (s, 3 H), 1.77 (s, 3 H), 0.96–0.82 (m, 2 H), −0.01 (s, 9 H); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 171.4, 170.83, 170.81, 170.5, 170.22, 170.20, 170.04, 169.97, 169.91, 169.6, 169.5, 169.0, 165.4, 165.2, 154.0, 139.1, 138.8, 138.7, 138.6, 138.5, 138.4, 138.33, 138.30, 138.10, 138.08, 138.00, 137.98, 137.88, 137.82, 137.78, 137.6, 137.5, 137.2, 133.4, 133.0, 129.9, 129.8, 129.7, 128.6, 128.56, 128.53, 128.51, 128.43, 128.39, 128.37, 128.33, 128.31, 128.28, 128.24, 128.20, 128.16, 128.14, 128.12, 128.10, 128.04, 128.00, 127.97, 127.89, 127.83, 127.77, 127.74, 127.71, 127.67, 127.64, 127.61, 127.56, 127.55, 127.51, 127.48, 127.44, 127.43, 127.41, 127.39, 127.35, 127.34, 127.32, 127.19, 127.14, 101.2, 100.8, 99.8, 99.6, 99.5, 99.4, 99.1, 99.0, 98.7, 80.3, 79.3, 78.3, 78.0, 77.7, 77.6, 77.3, 76.5, 75.7, 75.5, 75.49, 75.33, 75.27, 75.16, 75.04, 74.94, 74.89, 74.85, 74.7, 74.6, 74.3, 74.2, 74.19, 74.16, 74.07, 73.97, 73.6, 73.5, 73.32, 73.31, 73.24, 73.19, 73.09, 72.7, 72.6, 72.47, 72.44, 72.3, 72.19, 72.14, 71.99, 71.97, 71.89, 71.85, 71.7, 71.2, 70.3, 69.6, 69.5, 69.4, 68.4, 68.35, 68.28, 68.21, 68.12, 68.06, 67.28, 67.25, 67.19, 62.6, 62.51, 62.49, 58.7, 23.4, 21.1, 21.06, 21.05, 21.0, 20.9, 20.79, 20.75, 20.71, 20.6, 20.5, 18.0, −1.4; HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{249}H_{285}N_3O_{69}Si$: 2224.4321. Found: 2224.4363.

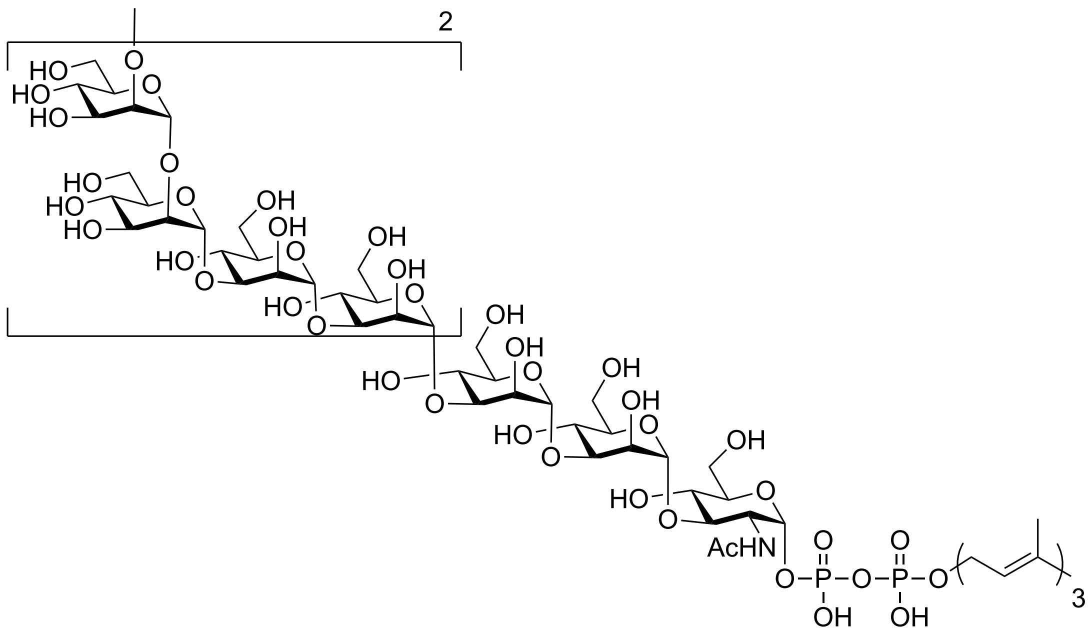


2-(Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-Acetyl-α-D-mannopyranosyl-(1→2)- 3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl- (1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-manno- pyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (43): Compound **42** (120 mg, 27.1 μmol) was dissolved in CH_3OH (10 mL), treated with $NaOCH_3$ (0.5 M solution in CH_3OH, 124 μL) and stirred at r.t. for 5 h. Water (0.10 mL) and then Amberlite IR120 H^+ ion-exchange resin was added. The mixture was then filtered and concentrated to provide crude half-deprotected compound. Next, ammonia was condensed at −78 °C into 50 mL round-bottom flask equipped with a Dewar condenser and a magnetic stir bar (total volume 15 mL). Freshly cut sodium metal (60 mg) was added and the mixture was stirred at −78 °C for 10 min. A solution of crude half-deprotected compound in THF (0.50 mL) was introduced via syringe and the mixture was stirred at −78 °C for 1 h before CH_3OH (2 mL) was added. The colorless solution was warmed to r.t. and then concentrated. The residue was dissolved in water (4 mL) and neutralized with Amberlite IR120 H^+ ion-exchange resin, filtered and concentrated to afford crude fully deprotected compound. This compound was then suspended in 3:2 pyridine−Ac_2O (25 mL) and the mixture was stirred at r.t. for 1 day. Then, the solution was concentrated, dissolved in CH_2Cl_2 (100 mL) followed by washing with 1M of HCl, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography (gradient 66→95% EtOAc in hexane) to afford **43** (59 mg, 65% yield) as a white solid; R_f 0.57 (EtOAc); $[\alpha]_D$ = +14.8 (*c* 0.3, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 6.25 (d, 1 H, *J* = 7.0 Hz), 5.58 (s, 1 H), 5.36 (dd, 1 H *J* = 10.0, 3.0 Hz), 5.32 (app t, 1 H *J* = 10.0 Hz), 5.30–5.16 (m, 12 H), 5.12–5.09 (m, 2 H), 5.06–4.94 (m, 9 H), 4.91–4.89 (m, 5 H), 4.84 (d, 1 H *J* = 1.5 Hz), 4.82 (s, 1 H), 4.50 (app t, 1 H *J* = 9.5 Hz), 4.26–4.19 (m, 9 H), 4.17–3.85 (m, 29 H), 3.84–3.77 (m, 5 H), 3.64 (ddd, 1 H, *J* = 10.0, 5.0, 2.5 Hz), 3.54 (td, 1 H, *J* = 10.0, 6.5 Hz), 3.09–3.05 (m, 1 H), 2.15–2.07 (m, 69 H), 2.05–2.02 (m, 15 H), 2.00–1.97 (m, 18 H), 0.96–0.84 (m, 2 H), −0.01 (s, 9 H); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 171.1, 170.8, 170.69, 170.66, 170.63, 170.59, 170.56, 170.41, 170.38, 170.32,

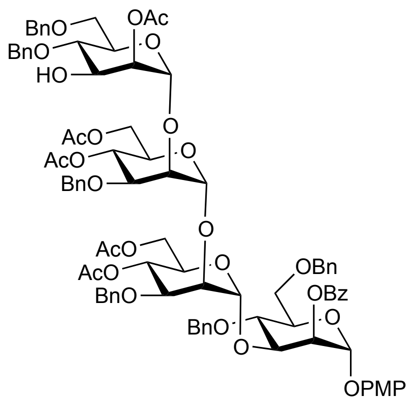
170.22, 170.18, 170.16, 170.0, 169.85, 169.82, 169.79, 169.71, 169.67, 169.50, 169.45, 169.37, 169.35, 169.2, 99.9, 99.8, 99.49, 99.44, 99.40, 99.34, 99.25, 99.1, 98.8, 98.6, 80.6, 77.6, 77.4, 75.6, 75.4, 75.1, 75.0, 74.0, 73.7, 71.25, 71.23, 71.16, 71.13, 70.9, 70.7, 70.4, 69.9, 69.7, 69.63, 69.61, 69.56, 69.52, 69.48, 68.9, 68.6, 68.3, 67.31, 67.29, 67.23, 66.9, 66.73, 66.68, 66.1, 65.9, 65.3, 63.7, 62.4, 62.3, 62.23, 62.18, 61.96, 61.94, 61.8, 61.7, 61.6, 61.5, 58.3, 45.8, 23.6, 20.93, 20.90, 20.83, 20.81, 20.76, 20.73, 20.71, 20.68, 20.65, 20.64, 20.62, 20.58, 20.56, 20.53, 17.9, −1.4; HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{139}H_{201}N_3O_{89}Si$: 1682.0526. Found: 1682.0530.



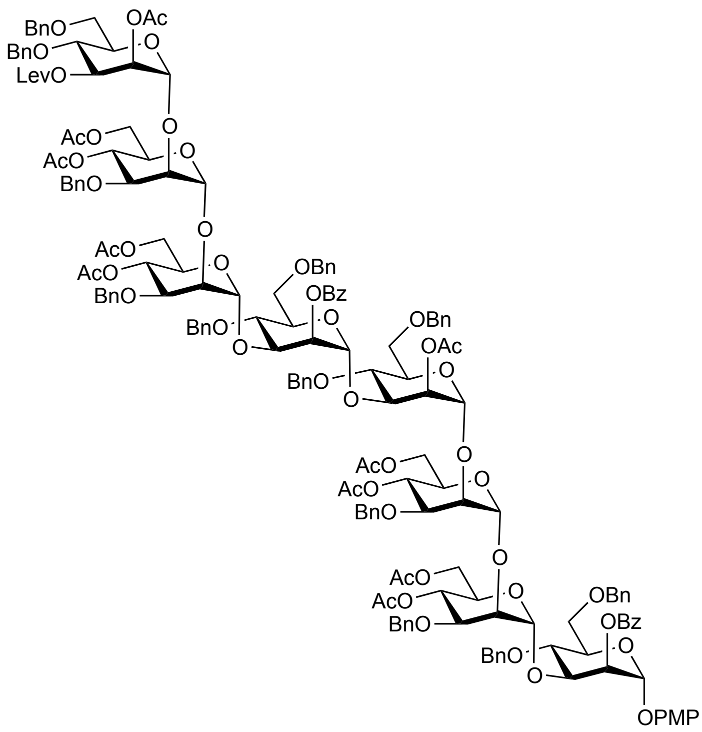
2,3,4,6-tetra-*O*-Acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-α-D-glucopyranosyl dibenzyl phosphate (45): To a solution of **43** (58 mg, 17.4 μmol) in dry CH_2Cl_2 (3 mL) was added TFA (1 mL) dropwise at 0 °C. After stirring for 3 h at r.t., the solution was concentrated, dissolved in CH_2Cl_2 (20 mL), washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography to afford hemiacital (47 mg, 83% yield) as a white solid. Then, hemiacital (47 mg, 14.4 μmol) was dissolved in dry CH_2Cl_2 (5 mL) before tetraazole (20.2 mg, 288 μmol) was added and the reaction mixture was cooled to 0 °C. After 10 min, dibenzyl *N*,*N*-diisopropylphosphoramidite (50 mg, 144 μmol) was added dropwise and the mixture was stirred at r.t. for 4 h. The mixture was cooled to −78 °C and *m*-CPBA (37 mg, 216 μmol) was added in one portion. The reaction mixture was warmed to r.t. and after stirring at r.t. for 2 h, CH_2Cl_2 was added. The mixture was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography (gradient 50→95% EtOAc in hexane) to afford phosphate **45** (38 mg, 75% yield) as a white solid; R_f 0.19 (1:10 hexane−EtOAc); $[\alpha]_D$ = +21.1 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 7.36−7.30 (m, 10 H), 5.85 (d, 1 H, *J* = 9.5 Hz), 5.58 (dd, 1 H, *J* = 6.0, 3.0 Hz), 5.36 (dd, 1 H *J* = 10.0, 3.0 Hz), 5.31 (app t, 1 H *J* = 10.0 Hz), 5.29−5.25 (m, 4 H), 5.22−5.15 (m, 8 H), 5.11−4.88 (m, 20 H), 4.86 (dd, 1 H, *J* = 3.0, 2.0 Hz), 4.83 (d, 1 H *J* = 2.0 Hz), 4.33−4.18 (m, 8 H), 4.16−3.92 (m, 25 H), 3.89−3.72 (m, 10 H), 3.12−3.09 (m, 1 H), 2.14−2.12 (m, 24 H), 2.10−2.02 (m, 60 H), 1.99−1.97 (m, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.9, 170.75, 170.69, 170.66, 170.59, 170.54, 170.45, 170.41, 170.36, 170.27, 170.25, 170.22, 170.21, 170.14, 170.07, 170.03, 169.88, 169.86, 169.83, 169.73, 169.71, 169.53, 169.48, 169.42, 169.40, 169.3, 135.3, 135.2 (d, J_{PC} = 6.4 Hz), 135.1(d, J_{PC} = 6.4 Hz), 129.1, 128.8, 128.24, 128.20, 99.9, 99.8, 99.6, 99.5, 99.3, 99.2, 99.1, 98.4, 96.7 (d, $J_{PC\text{-}1}$ = 6.5 Hz), 77.7, 77.5, 76.5, 75.6, 75.5, 75.1, 75.0, 74.7, 74.0, 71.3, 71.0, 70.9, 70.13, 70.10, 70.09, 70.06, 69.85, 69.80, 69.72, 69.68, 69.62, 69.58, 68.7, 68.3, 67.4, 67.4, 67.0, 66.9, 66.7, 66.1, 66.0, 65.4, 62.7, 62.5, 62.4, 62.3, 62.0, 61.9, 61.8, 61.7, 61.6, 61.2, 60.4, 51.8 (d, $J_{PC\text{-}2}$ = 7.3 Hz), 22.9, 21.1, 20.96, 20.92, 20.87, 20.83, 20.79, 20.71, 20.69, 20.62, 20.59; ^{31}P NMR (200 MHz, $CDCl_3$, δ_C) 2.4; HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{148}H_{202}N_3O_{92}P$: 1762.0473. Found: 1762.0501.



α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl- (1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl- (1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl- (1→3)-α-D-mannopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranosyl farnesyl diphosphate diammonium salt (1): To a solution of **45** (38 mg, 0.011 mmol) in THF (5 mL) was added palladium on charcoal (10%, 30 mg). The mixture was subjected to a hydrogen atmosphere for 4 h before being filtered through Celite and concentrated. The residue **46** was used in the next step without further purification. To a solution of the crude phosphate **46** in dry CH_2Cl_2 (3 mL) was added 1,1'-carbonyldiimidazole (26 mg, 0.16 mmol). After stirring at r.t. for 2 h, a solution of 5% (v/v) anhydrous CH_3OH in CH_2Cl_2 (0.16 mL) was added to quench unreacted 1,1'-carbonyldiimidazole and the mixture stirred for 30 min. The solvent was concentrated and the residue was dissolved in DMF (0.6 mL). Farnesyl phosphate **47** (53 mg, 0.16 mmol) was added and the reaction mixture stirred at r.t. for 7 days. The solvent was removed in vacuo and the residue was purified by Sephadex LH-20 (1:1 CH_3OH–CH_2Cl_2) to afford **48** as a crude product. To a solution of crude phosphate **48** in CH_3OH (5 mL) was added freshly prepared $NaOCH_3$ (1M solution in CH_3OH, 0.5 mL). The reaction mixture was stirred at r.t. for 3 h, and then the $NaOCH_3$ was quenched by addition of Amberlite IR120 (NH_4^+ form). The mixture was filtered, concentrated in vacuo and the residue purified by C_{18} chromatography (gradient 0→50% CH_3OH in H_2O) to afford **1** (13 mg, 56% yield) as a white solid. R_f 0.36 (2:3 H_2O–CH_3OH); $[\alpha]_D$ = +100.4 (*c* 0.1, CH_2Cl_2); ^1H NMR (700 MHz, D_2O, δ_H) 5.50 (dd, 1 H, *J* = 7.0, 3.0 Hz), 5.46 (app t, 1 H *J* = 7.5 Hz), 5.39 (s, 1 H), 5.38 (s, 1 H), 5.31 (s, 1 H), 5.26 (s, 1 H), 5.23–5.19 (m, 2 H), 5.13–5.10 (m, 4 H), 5.06 (s, 1 H), 5.05 (s, 1 H), 4.53–4.47 (m, 2 H), 4.25–4.19 (m, 6 H), 4.12–4.08 (m, 5 H), 4.03–3.66 (m, 53 H), 3.61–3.59 (m, 1 H), 3.22–3.18 (m, 1 H), 2.19–2.10 (m, 6 H), 2.08 (s, 3 H), 2.04 (t, 1 H *J* = 7.5 Hz), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.64 (s, 6 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 175.3, 144.0, 137.7, 134.5, 125.4, 125.2, 120.4 (d, J_{PC} = 8.0 Hz)， 103.25, 103.23, 103.18, 103.07, 103.05, 101.9, 101.68, 101.64, 101.61, 95.6 (d, J_{PC} = 6.3 Hz)， 79.6, 79.5, 79.4, 79.3, 79.24, 79.20, 79.0, 78.5, 74.5, 74.4, 74.35, 74.30, 74.28, 74.24, 74.20, 73.9, 71.30, 71.28, 71.06, 70.99, 70.94, 70.68, 70.65, 70.57, 68.0, 67.8, 67.7, 67.17, 67.13, 67.10, 66.5, 64.0 (d, J_{PC} = 5.3 Hz), 62.1, 62.0, 61.94, 61.90, 61.5, 61.1, 53.2 (d, J_{PC} = 8.3 Hz), 39.7, 26.7, 26.5, 25.8, 23.3, 18.0, 16.6, 16.3; ^{31}P NMR (200 MHz, D_2O, δ_C) −10.6, −13.3; HRMS (ESI) calcd for $(M{-}2H)^{-2}$ $C_{83}H_{141}NO_{62}P_2$: 1101.8620. Found: 1101.8628.



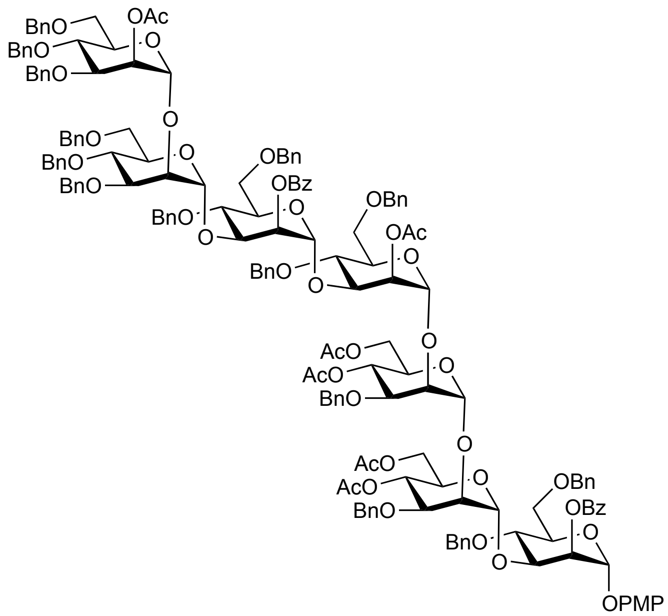
***p*-Methoxyphenyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6- di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (49):** A solution of **10** (1.04 g, 0.60 mmol) and hydrazine acetate (100 mg, 1.08 mmol) in 9:1 CH_2Cl_2–CH_3OH (150 mL) was stirred at r.t. for 2 h. Then, the solution was concentrated and the resulting residue was subjected to chromatography (gradient 33→50% EtOAc in hexane) to afford **49** (0.91 g, 93% yield) as a white solid; R_f 0.18 (1:1 hexane–EtOAc); $[\alpha]_D$ = +50.0 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.10–8.09 (m, 2 H, ArH), 7.64–7.61 (m, 1 H, ArH), 7.44–7.42 (m, 2 H, ArH), 7.39–7.06 (m, 30 H, ArH), 6.99–6.97 (m, 3 H, ArH), 6.80–6.78 (m, 2 H, ArH), 5.58 (d, 1 H, *J* = 2.0 Hz, H-1), 5.56 (dd, 1 H, *J* = 3.0, 2.0 Hz, H-2), 5.30 (d, 1 H, *J* = 1.5 Hz, H-1′), 5.22–5.18 (m, 3 H, H-2‴, H-4′, H-4″), 5.06 (d, 1 H, *J* = 2.0 Hz, H-1″), 4.81 (d, 1 H, *J* = 1.5 Hz, H-1‴), 4.78 (d, 1 H, *J* = 11.5 Hz, PhC*H*2), 4.68 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.60 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.56 (d, 1 H, *J* = 11.0 Hz, PhCH_2), 4.54 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.49–4.43 (m, 5 H, PhCH_2, H-3), 4.33 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.27 (d, 1 H, *J* = 11.5 Hz, PhCH_2), 4.25 (d, 1 H, *J* = 12.0 Hz, PhCH_2), 4.21 (app dt, 1 H, *J* = 9.0, 4.0 Hz, H-3‴), 4.17 (app t, 1 H, *J* = 9.5 Hz, H-4), 4.09 (dd, 1 H, *J* = 12.0, 2.5 Hz), 4.06 (dd, 1 H, *J* = 12.0, 5.6 Hz), 3.99 (ddd, 1 H, *J* = 10.0, 5.5, 2.5 Hz), 3.96–3.94 (m, 2 H), 3.91–3.80 (m, 6 H), 3.75 (s, 3 H, OCH_3), 3.74–3.70 (m, 2 H), 3.68–3.65 (m, 2 H), 3.59 (dd, 1 H, *J* = 11.0, 4.0 Hz), 3.45 (dd, 1 H, *J* = 10.5, 1.5 Hz), 2.11 (d, *J* = 4.0 Hz, OH), 2.10 (s, 3 H, $OC{=}OCH_3$), 2.02 (s, 3 H, $OC{=}OCH_3$), 1.96 (s, 3 H, $OC{=}OCH_3$), 1.95 (s, 3 H, $OC{=}OCH_3$), 1.90 (s, 3 H, $OC{=}OCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.8 ($OC{=}OCH_3$), 170.7 ($OC{=}OCH_3$), 170.6 ($OC{=}OCH_3$), 169.7 ($OC{=}OCH_3$), 169.6 ($OC{=}OCH_3$), 165.6 (PhC=O), 155.3 (Ar), 149.7 (Ar), 138.4 (Ar), 138.3 (Ar), 138.1 (Ar), 137.8 (Ar), 137.5 (Ar), 133.5 (Ar), 129.9 (Ar), 129.7 (Ar), 128.6 (Ar), 128.52 (Ar), 128.51 (Ar), 128.37 (Ar), 128.35 (Ar), 128.33 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.75 (Ar), 127.72 (Ar), 127.64 (Ar), 127.62 (Ar), 127.53 (Ar), 127.51 (Ar), 117.8 (Ar), 114.7 (Ar), 101.0 (C-1″), 100.9 (C-1′), 99.2 (C-1‴), 96.4 (C-1), 77.4 (C-3), 75.8, 75.6, 75.5, 75.4 ($PhCH_2$), 75.3, 75.0 ($PhCH_2$), 74.6 (C-4), 73.5 ($PhCH_2$), 73.4 ($PhCH_2$), 72.5, 72.3, 72.28 ($PhCH_2$), 72.2, 72.0 ($PhCH_2$), 71.6, 70.6, 69.8, 69.7, 68.9, 68.4, 67.5, 67.2, 55.6 (CH_3O), 21.9 ($OC{=}OCH_3$), 20.9 ($OC{=}OCH_3$), 20.8 ($OC{=}OCH_3$), 20.71 ($OC{=}OCH_3$), 20.70 ($OC{=}OCH_3$); HRMS (ESI) calcd for $(M+NH_4)^+$ $C_{90}H_{102}NO_{28}$: 1644.6583. Found: 1644.6555.



***p*-Methoxyphenyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D- mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (50):** A mixture of tetrasaccharide acceptor **49** (2.30 g, 1.42 mmol), trichloroacetimidate donor **36** (2.73 g, 1.57 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (100 mL) and stirred at r.t. for 10 min. The solution was then cooled to 0 °C and then TBSOTf (50 μL) was added. The solution was stirred for 2 h before Et_3N (0.5 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 33→66% EtOAc in hexane) to afford **50** (4.05 g, 88%) yield as a white solid; R_f 0.42 (2:3 hexane–EtOAc); $[\alpha]_D$ = +30.4 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.08–8.06

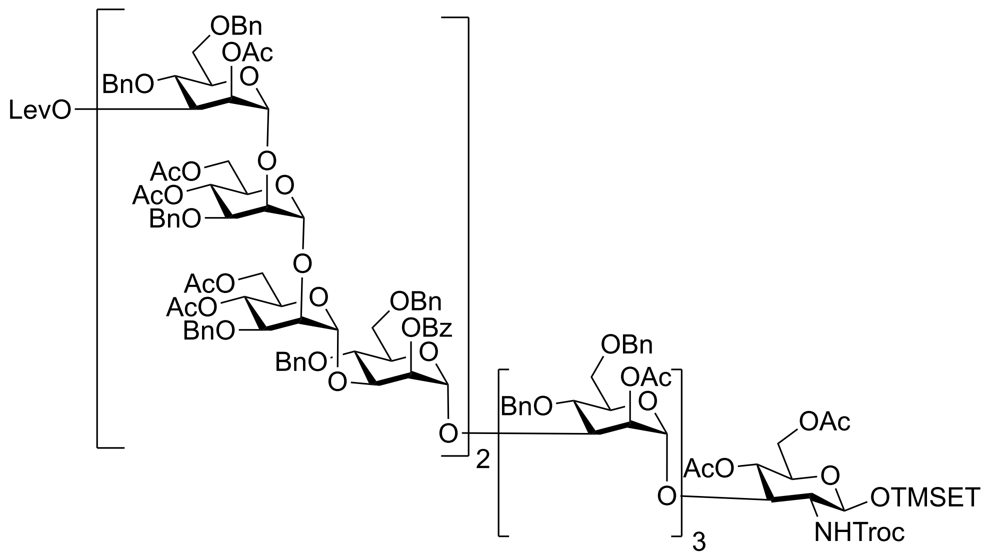
(m, 2 H), 8.01−7.99 (m, 2 H), 7.62−7.59 (m, 1 H), 7.58−7.55 (m, 1 H), 7.42−6.99 (m, 66 H), 6.78−6.76 (m, 2 H), 5.56 (d, 1 H, *J* = 2.0 Hz), 5.54 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.50 (app t, 1 H, *J* = 2.0 Hz), 5.37 (dd, 1 H, *J* = 9.5, 3.5 Hz), 5.31 (d, 1 H, *J* = 1.5 Hz), 5.30 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.29 (s, 1 H), 5.25 (app t, 1 H, *J* = 10.0 Hz), 5.22 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.20−5.15 (m, 4 H), 5.00 (d, 1 H, *J* = 2.0 Hz), 4.92 (d, 1 H, *J* = 2.0 Hz), 4.85 (d, 1 H, *J* = 2.0 Hz), 4.79 (d, 1 H, *J* = 2.0 Hz), 4.76 (d, 1 H, *J* = 12.0 Hz), 4.75 (d, 1 H, *J* = 10.5 Hz), 4.67 (d, 1 H, *J* = 12.0 Hz),4.60−4.37 (m, 17 H), 4.30−4.20 (m, 6 H), 4.18−4.13 (m, 4 H), 4.08−4.01 (m, 3 H), 3.96−3.78 (m, 21 H), 3.72−3.70 (m, 1 H), 3.65−3.60 (m, 4 H), 4.57−4.53 (m, 2 H), 3.40 (dd, 1 H, *J* = 11.0, 1.5 Hz), 3.35 (d, 1 H, *J* = 11.0 Hz), 2.76 (dt, 1 H, *J* = 18.5, 7.5 Hz), 2.62 (dt, 1 H, *J* = 18.5, 6.5 Hz), 2.50 (dt, 1 H, *J* = 17.0, 7.0 Hz), 2.41 (dt, 1 H, *J* = 17.0, 6.5 Hz), 2.13 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.00 (s, 3 H), 1.94 (s, 3 H), 1.92 (s, 3 H), 1.91 (s, 3 H), 1.89 (s, 3 H), 1.88 (s, 3 H), 1.87 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.5, 171.3, 171.1, 170.8, 170.7, 170.6, 169.8, 169.69, 169.68, 169.6, 169.3, 169.2, 165.6, 165.4, 155.3, 149.7, 139.1, 138.3, 138.1, 138.02, 138.00, 137.94, 137.8, 137.6, 137.5, 133.6, 133.3, 129.9, 129.8, 129.7, 128.7, 128.55, 128.50, 128.46, 128.39, 128.36, 128.34, 128.28, 128.25, 128.1, 128.0, 127.88, 127.87, 127.85, 127.76, 127.73, 127.62, 127.59, 127.53, 127.3, 117.8, 114.7, 101.01, 100.97, 100.87, 100.7, 99.3, 99.2, 98.8, 96.4, 77.5, 77.2, 76.6, 76.1, 75.93, 75.88, 75.76, 75.48, 75.44, 75.39, 74.97, 74.94, 74.8, 74.6, 74.5, 73.7, 73.47, 73.44, 73.41, 73.37, 72.94, 72.88, 72.4, 72.30, 72.27, 72.23, 72.19, 72.02, 71.96, 71.93, 71.91, 71.83, 71.79, 69.9, 69.8, 69.71, 69.69, 69.62, 68.5, 68.4, 68.3, 67.5, 67.3, 62.91, 62.88, 62.55, 62.44, 55.6, 37.9, 29.9, 28.0, 21.09, 21.08, 21.0, 20.9, 20.82, 20.81, 20.76, 20.72, 20.69, 20.63; ^{1}H-coupled HSQC (700

MHz, $CDCl_3$) $^{1}J_{C\text{-}1,H\text{-}1}$ = 176.0, 176.0, 175.6, 175.6, 175.5, 173.3, 173.2, 173.1 Hz HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{178}H_{202}N_2O_{56}$: 1631.6505. Found: 1631.6521.

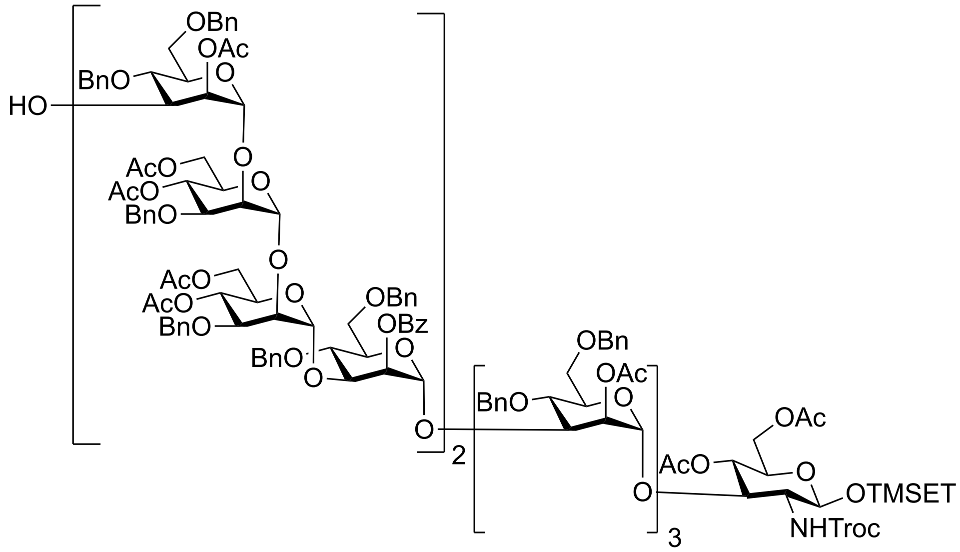


***p*-Methoxyphenyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)- 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (52):** A mixture of tetrasaccharide acceptor **49** (941 mg, 0.56 mmol), trisaccharide trichloroacetimidate **33** (1070 mg, 0.70 mmol) and powdered 4Å molecular sieves was suspended in anhydrous CH_2Cl_2 (100 mL) and stirred at r.t. for 10 min. The solution was then cooled to 0 °C and then TBSOTf (40 µL) was added. The solution was stirred for 2 h at r.t. before Et_3N (0.2 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 16→33% EtOAc in hexane) to afford **52** (1.48 g, 87% yield) as a white solid; R_f 0.67 (1:1 hexane–EtOAc); $[\alpha]_D$ = +22.8 (*c* 0.2, CH_2Cl_2); ^{1}H NMR

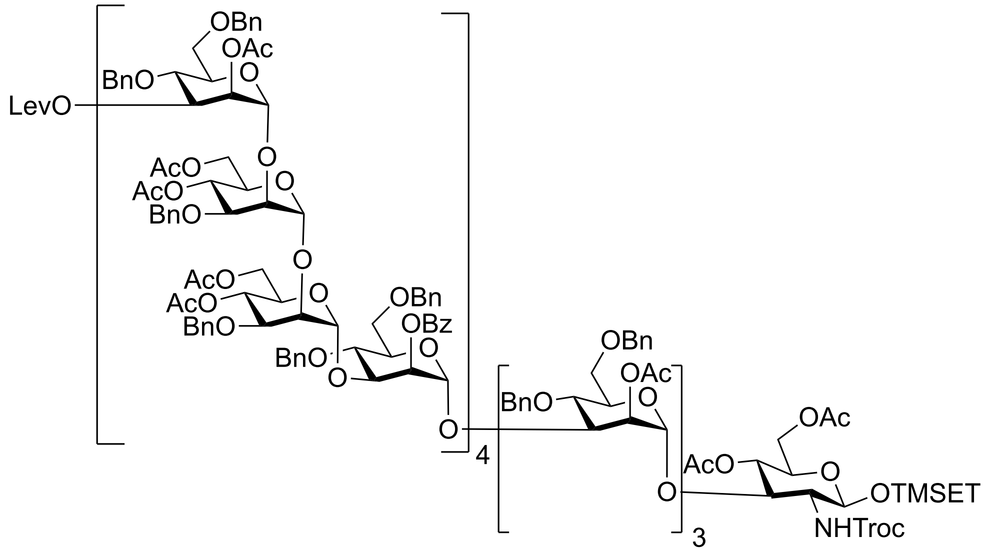
(700 MHz, $CDCl_3$, δ_H) 8.08–8.06 (m, 2 H), 7.99–7.98 (m, 2 H), 7.62–7.60 (m, 1 H), 7.54–7.52 (m, 1 H), 7.43–7.40 (m, 2 H), 7.36–7.25 (m, 72 H), 6.99–6.96 (m, 2 H), 6.78–6.77 (m, 2 H), 5.58 (app t, 1 H, J = 2.0 Hz), 5.56 (d, 1 H, J = 2.0 Hz), 5.54 (dd, 1 H, J = 3.0, 2.0 Hz), 5.48 (dd, 1 H, J = 3.0, 2.0 Hz), 5.31 (d, 1 H, J = 1.5 Hz), 5.29 (s, 1 H), 5.24 (dd, 1 H, J = 3.0, 2.0 Hz), 5.20–5.15 (m, 3 H), 5.03 (d, 1 H, J = 1.5 Hz), 5.00 (d, 1 H, J = 2.0 Hz), 4.85–4.84 (m, 2 H), 4.75 (d, 1 H, J = 11.0 Hz), 4.73–4.66 (m, 4 H), 4.59–4.53 (m, 5 H), 5.00–4.40 (m, 8 H), 4.38–4.32 (m, 4 H), 4.30–4.18 (m, 9 H), 4.15 (app t, 1 H, J = 9.5 Hz), 4.07 (dd, 1 H, J = 12.5, 2.5 Hz), 4.04 (dd, 1 H, J = 12.5, 5.0 Hz), 3.96–3.78 (m, 17 H), 3.75–3.70 (m, 4 H), 3.74 (s, 3 H), 3.65–3.63 (m, 2 H), 3.59 (dd, 1 H, J = 11.0, 3.5 Hz), 3.53–3.49 (m, 2 H), 3.41–3.34 (m, 3 H), 2.07 (s, 3 H), 2.02 (s, 3 H), 2.01 (s, 3 H), 1.91 (s, 3 H), 1.89 (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$, δ_C) 170.8, 170.7, 170.0, 169.9, 169.6, 169.1, 165.6, 165.4, 155.2, 149.7, 139.1, 138.8, 138.7, 138.6, 138.5, 138.32, 138.29, 138.11, 138.07, 137.9, 137.8, 137.4, 133.5, 133.0, 129.9, 129.8, 129.6, 128.62, 128.59, 128.46, 128.44, 128.39, 128.33, 128.29, 128.25, 128.23, 128.20, 128.19, 128.15, 128.14, 128.13, 128.11, 128.0, 127.9, 127.8, 127.70, 127.66, 127.59, 127.57, 127.51, 127.47, 127.44, 127.41, 127.38, 127.33, 127.31, 127.18, 127.14, 127.13, 117.7, 114.7, 101.2, 100.98, 100.94, 99.4, 99.1, 98.9, 96.4, 79.2, 78.3, 77.7, 77.3, 77.2, 76.5, 75.6, 75.55, 75.4, 75.2, 74.94, 74.88, 74.80, 74.6, 74.5, 74.24, 74.18, 73.9, 73.4, 73.3 73.24, 73.19, 73.09, 72.8, 72.6, 72.4, 72.27, 72.19, 72.16, 72.12, 72.0, 71.9, 71.86, 71.83, 69.72, 69.67, 68.7, 68.6, 68.3, 68.2, 67.4, 67.3, 62.84, 62.80, 60.4, 55.6, 21.13, 21.06, 20.80, 20.75, 20.65, 20.57; ^1H-coupled HSQC (700 MHz, $CDCl_3$) $^1J_{C\text{-}1,\ H\text{-}1}$ = 176.4, 175.7, 175.7, 175.0, 175.0, 174.3, 172.9 Hz; HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{173}H_{190}N_2O_{45}$: 1507.6315. Found: 1507.6323.



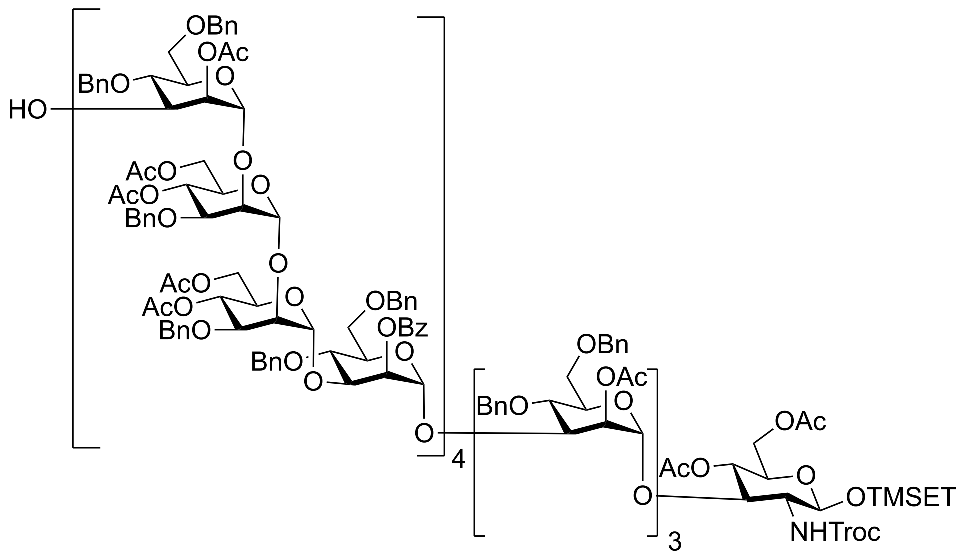
2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D- mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6- di-*O*-ace-tyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-ace-tyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (54): The formation of octasaccharide trichloroacetimidate **51** (2.5 g) was achieved from octasaccharide **50** (4.0 g) in 63% yield following general procedure A described above. A mixture of adaptor **28** (460 mg, 0.50 mmol), octasaccharide trichloroacetimidate **51** (740 mg, 0.23 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (40 mL) and stirred at r.t. for 10 min. The solution was then cooled to 0 °C and then TBSOTf (20 μL) was added. The solution was stirred at r.t. for 2 h before Et_3N (0.5 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 50→60% EtOAc in hexane) to afford **54** (950 mg, 86%) yield as a white solid; R_f 0.48 (2:3 hexane−EtOAc); $[\alpha]_D$ = +15.1 (*c* 0.7, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.01−7.99 (m, 4 H), 7.58−7.55 (m, 2 H), 7.38−6.99 (m, 94 H), 5.83 (d, 1 H, *J* = 6.5 Hz), 5.49 (s, 1 H), 5.46 (s, 1 H), 5.37 (dd, 1 H, *J* = 9.5, 3.5 Hz), 5.31−5.15 (m, 13 H), 5.11 (s, 1 H), 5.08 (s, 1 H), 4.99−4.97 (m, 2 H), 4.93 (s, 1 H), 4.88 (s, 1 H), 4.85−4.70 (m, 9 H), 4.65−4.32 (m, 25 H), 4.27−3.70 (m, 50 H), 3.64−3.52 (m, 14 H), 3.46−3.34 (m, 5 H), 3.18−3.15 (m, 1 H), 2.76 (dt, 1 H, *J* = 18.0, 7.0 Hz), 2.63 (dt, 1 H, *J* = 18.0, 6.5 Hz), 2.50 (dt, 1 H, *J* = 17.0, 7.0 Hz), 2.41 (dt, 1 H, *J* = 17.0, 6.5 Hz), 2.14 (s, 3 H), 2.06–2.04 (m, 18 H), 2.02 (s, 3 H), 1.94 (s, 3 H), 1.92 (s, 3 H), 1.91 (s, 3 H), 1.90 (s, 3 H), 1.89 (s, 3 H), 1.88 (s, 3 H), 1.83 (s, 3 H), 1.77 (s, 3 H), 0.88–0.79 (m, 2 H), –0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.5, 171.3, 171.1, 170.8, 170.77, 170.5, 170.3, 170.2, 170.0, 169.8, 169.66, 169.61, 169.57, 169.3, 169.1, 165.4, 165.2, 154.0, 139.1, 138.5, 138.3, 138.15, 138.14, 137.98, 137.96, 137.93, 137.89, 137.8, 137.63, 137.61, 133.4, 133.3, 129.9, 129.83, 129.79, 129.7, 128.53, 128.47, 128.43, 128.38, 128.32, 128.30, 128.26, 128.22, 128.14, 127.93, 127.89, 127.85, 127.82, 127.73, 127.69, 127.62, 127.59, 127.57, 127.52, 127.45, 127.38, 127.3, 100.84, 100.79, 100.64, 99.9, 99.7, 99.3, 99.2, 98.8, 98.5, 95.5, 78.2, 76.5, 76.1, 75.9, 75.83, 75.79, 75.6, 75.48, 75.43, 75.3, 75.1, 74.92, 74.88, 74.75, 74.45, 74.39, 74.2, 74.1, 73.6, 73.54, 73.51, 73.42, 73.37, 73.33, 73.29, 72.92, 72.85, 72.51, 72.47, 72.38, 72.32, 72.26, 72.17, 72.04, 72.02, 71.93, 71.88, 71.81, 71.78, 71.75, 71.5, 70.7, 69.9, 69.7, 69.65, 69.60, 69.5, 68.5, 68.4, 68.3, 68.1, 67.5, 67.2, 62.7, 62.5, 62.41, 62.38, 57.6, 37.9, 29.9, 28.0, 21.08, 21.06, 21.04, 20.97, 20.95, 20.83, 20.81, 20.79, 20.76, 20.73, 20.67, 20.66, 20.59, 18.1, −1.4; HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{255}H_{296}Cl_3N_3O_{81}Si$: 2414.3980. Found: 2414.3971.



2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)- 4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (55): A solution of **54** (0.9 g, 0.19 mmol) and hydrazine acetate (86 mg, 0.93 mmol) in 9:1 CH_2Cl_2–CH_3OH (30 mL) was stirred at r.t. for 1 h. Then, the solution was concentrated at 40 °C for 0.5 h to achieve complete deproection of the levulinyl group. The resulting residue was subjected to chromatography (gradient 50→60% EtOAc in hexane) to afford **55** (0.77 g, 87% yield) as a white solid; R_f 0.47 (2:3 hexane–EtOAc); $[\alpha]_D$ = +20.0 (*c* 0.5, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 8.02–7.98 (m, 4 H), 7.59–7.57 (m, 2 H), 7.38–6.99 (m, 94 H), 5.83 (d, 1 H, *J* = 7.0 Hz), 5.50 (s, 1 H), 5.46 (dd, 1 H, *J* = 3.0, 2.0 Hz), 5.31 (d, 1 H, *J* = 1.5 Hz), 5.28 (dd, 1 H, *J* = 3.0, 1.5 Hz), 5.25 (d, 1 H, *J* = 1.5 Hz), 5.22–5.15 (m, 9 H), 5.11 (s, 1 H), 5.09 (s, 1 H), 4.99–4.97 (m, 2 H), 4.89 (s, 1 H), 4.88 (s, 1 H), 4.84 (dd, 1 H, *J* = 3.0, 2.0 Hz), 4.80–4.70 (m, 8 H), 4.65–4.12 (m, 20 H), 4.39–4.32 (m, 4 H), 4.28–3.70 (m, 51 H), 3.67–3.51 (m, 14 H), 3.46–3.34 (m, 4 H), 3.18–3.15 (m, 1 H), 2.09 (s, 3 H), 2.06–2.04 (m, 15 H), 2.02 (s, 3 H), 1.93 (s, 3 H), 1.92 (s, 3 H), 1.905 (s, 3 H), 1.902 (s, 3 H), 1.899 (s, 3 H), 1.85 (s, 3 H), 1.83 (s, 3 H), 1.77 (s, 3 H), 0.88–0.79 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.9, 170.80, 170.77, 170.6, 170.5, 170.26, 170.20, 170.0, 169.7, 169.62, 169.57, 169.50, 169.1, 165.4, 165.3, 154.0, 139.1, 138.5, 138.4, 138.3, 138.2, 137.98, 137.95, 137.89, 137.85, 137.79, 137.78, 137.6, 133.4, 133.3, 129.9, 129.83, 129.79, 129.7, 128.53, 128.49, 128.46, 128.44, 128.38, 128.31, 128.29, 128.23, 128.14, 127.98, 127.95, 127.93, 127.87, 127.80, 127.78, 127.73, 127.69, 127.62, 127.58, 127.56, 127.52, 127.4, 127.3, 127.2, 100.8, 100.7, 99.9, 99.7, 99.3, 99.28, 99.21, 98.5, 78.2, 77.2, 76.0, 75.8, 75.7, 75.6, 75.5, 75.4, 75.3, 75.1, 74.95, 74.88, 74.5, 74.4, 74.2, 74.1, 73.53, 73.51, 73.37, 73.33, 73.28, 72.83, 72.51, 72.46, 72.36, 72.32, 72.27, 72.24, 72.03, 71.93, 71.90, 71.77, 71.74, 71.6, 71.5, 70.7, 70.6, 69.59, 69.52, 69.49, 68.8, 68.3, 68.1, 67.5, 67.3, 67.2, 62.7, 62.5, 62.4, 57.6, 21.08, 21.05, 20.97, 20.85, 20.83, 20.81, 20.76, 20.71, 20.67, 20.65, 20.59, 18.1, −1.4; HRMS (ESI) calcd for $(M+2(NH_4))^{+2}$ $C_{250}H_{290}Cl_3N_3O_{79}Si$: 2365.3796. Found: 2365.3757.



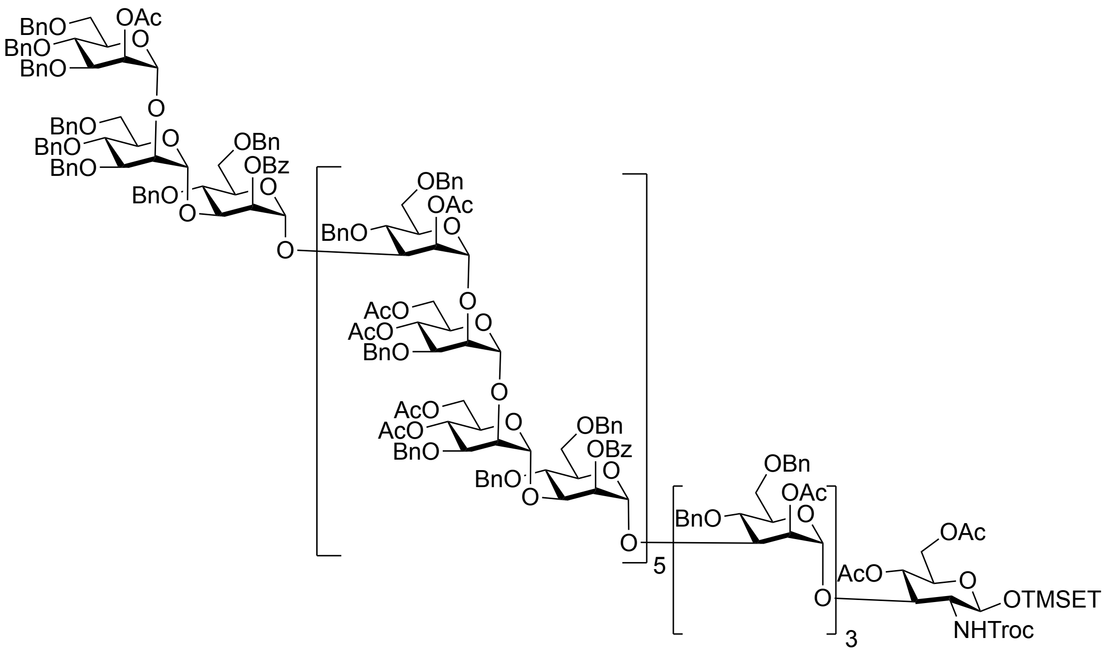
2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-3-*O*-levulinyl-α-D- mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6- di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-ace-tyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D- mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*- benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D- mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D- mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D- mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (56): A mixture of acceptor **55** (800 mg, 0.17 mmol), octasaccharide trichloroacetimidate **51** (772 mg, 0.24 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (40 mL) and stirred at r.t. for 10 min. The solution was then cooled to 0 °C and then TBSOTf (20 μL) was added. The solution was stirred at r.t. overnight before Et_3N (0.5 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 50→66% EtOAc in hexane) to afford **56** (944 mg, 71% yield) as a white solid; R_f 0.25 (2:3 hexane–EtOAc); $[\alpha]_D$ = +18.0 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.01–7.99 (m, 8 H), 7.58–7.56 (m, 4 H), 7.39–6.97 (m, 158 H), 5.83 (d, 1 H, *J* = 7.0 Hz), 5.50–5.47 (m, 4 H), 5.38 (dd, 1 H, *J* = 9.5, 3.5 Hz), 5.31–5.15 (m, 21 H), 5.11 (s, 1 H), 5.09 (s, 1 H), 5.00–4.97 (m, 4 H), 4.94 (s, 1 H), 4.89 (s, 1 H), 4.86–4.70 (m, 14 H), 4.65–4.32 (m, 39 H), 4.26–4.01 (m, 34 H), 3.99–3.71 (m, 56 H), 3.66–3.51 (m, 20 H), 3.46–3.34 (m, 6 H), 3.18–3.15 (m, 1 H), 2.77 (dt, 1 H, *J* = 18.0, 7.0 Hz), 2.63 (dt, 1 H, *J* = 18.0, 6.5 Hz), 2.51 (dt, 1 H, *J* = 17.0, 7.0 Hz), 2.42 (dt, 1 H, *J* = 17.0, 6.5 Hz), 2.14 (s, 3 H), 2.07–2.03 (m, 24 H), 1.94–1.92 (m, 15 H), 1.90–1.89 (m, 15 H), 1.849 (s, 3 H), 1.846 (s, 3 H), 1.835 (s, 3 H), 1.78 (s, 9 H), 0.88–0.79 (m, 2 H), –0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.5, 171.2, 171.1, 170.9, 170.80, 170.77, 170.55, 170.53, 170.26, 170.21, 170.0, 169.76, 169.72, 169.66, 169.59, 169.3, 169.1, 165.3, 165.2, 154.0, 139.14, 139.10, 138.5, 138.3, 138.16, 138.14, 138.07, 138.01, 137.99, 137.95, 137.89, 137.89, 137.81, 137.65, 137.61, 133.4, 133.3, 129.9, 129.8, 129.7, 128.53, 128.44, 128.38, 128.34, 128.31, 128.26, 128.24, 128.22, 128.14, 127.94, 127.87, 127.85, 127.83, 127.80, 127.79, 127.76, 127.74, 127.73, 127.67, 127.61, 127.59, 127.56, 127.4, 100.8, 100.6, 99.9, 99.7, 99.3, 99.2, 98.8, 98.6, 78.2, 77.9, 77.2, 76.6, 76.1, 75.96, 75.84, 75.68, 75.61, 75.51, 75.40, 75.31, 75.07, 75.01, 74.88, 74.75, 74.48, 74.39, 74.2, 74.1, 73.61, 73.54, 73.51, 73.42, 73.38, 73.33, 73.29, 72.92, 72.84, 72.51, 72.47, 72.36, 72.27, 72.22, 72.18, 72.03, 71.93, 71.88, 71.81, 71.78, 71.74, 71.5, 69.9, 69.70, 69.65, 69.60, 69.52, 68.5, 68.4, 68.3, 68.0, 67.5, 67.3, 67.2, 62.7, 62.56, 62.53, 62.41, 62.37, 57.6, 37.9, 29.8, 27.9, 21.08, 21.07, 21.04, 20.97, 20.95, 20.84, 20.81, 20.79, 20.76, 20.73, 20.67, 20.61, 20.59, 18.1, −1.4; HRMS (ESI) calcd for $(M+3(NH_4))^{+3}$ $C_{421}H_{480}Cl_3N_4O_{133}Si$: 2617.3251. Found: 2617.3245.



2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)- 4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbo-nylamino)-β-D-glucopyranoside (57): A solution of **56** (0.94 g, 0.12 mmol) and hydrazine acetate (222 mg, 2.4 mmol) in 9:1

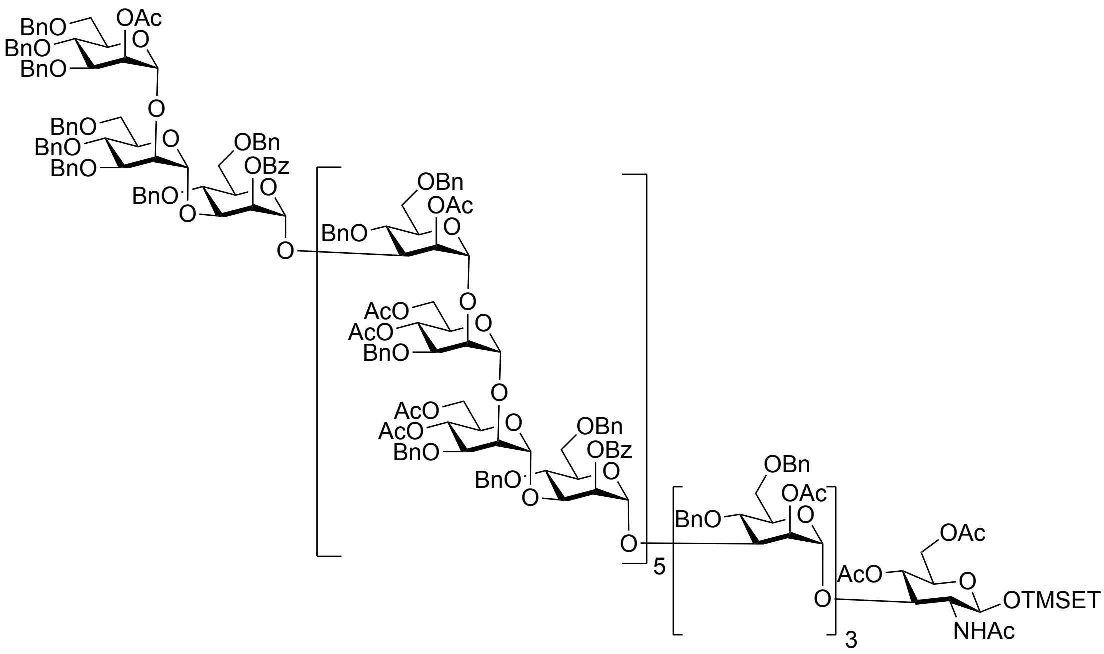
CH_2Cl_2–CH_3OH (40 mL) was stirred at r.t. for 1 h. Then, the solution was concentrated at 40 °C for 1.5 h to achieve complete deproection of the levulinyl group. The resulting residue was subjected to chromatography (gradient 50→66% EtOAc in hexane) to afford **57** (806 mg, 87% yield) as a white solid; R_f 0.30 (2:3 hexane–EtOAc); $[\alpha]_D$ = +13.0 (*c* 0.2, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 8.03–7.99 (m, 8 H), 7.59–7.56 (m, 4 H), 7.39–6.97 (m, 158 H), 5.83 (d, 1 H, *J* = 6.0 Hz), 5.51–5.47 (m, 4 H), 5.32–5.27 (m, 4 H), 5.25 (s, 1 H), 5.22–5.15 (m, 16 H), 5.11 (s, 1 H), 5.09 (s, 1 H), 5.04 (d, 1 H, *J* = 1.5 Hz), 5.00–4.97 (m, 3 H), 4.89 (s, 1 H), 4.85 (app t, 1 H, *J* = 2.0 Hz), 4.86–4.70 (m, 14 H), 4.65–4.32 (m, 39 H), 4.26–4.01 (m, 34 H), 3.99–3.71 (m, 57 H), 3.66–3.51 (m, 20 H), 3.46–3.34 (m, 6 H), 3.18–3.15 (m, 1 H), 2.09 (s, 3 H), 2.06–2.03 (m, 24 H), 1.94–1.92 (m, 12 H), 1.91–1.89 (m, 15 H), 1.855 (s, 3 H), 1.852 (s, 3 H), 1.845 (s, 3 H), 1.835 (s, 3 H), 1.78–1.77 (m, 9 H), 0.88–0.79 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.94, 170.90, 170.80, 170.77, 170.62, 170.53, 170.26, 170.21, 170.0, 169.73, 169.64, 169.52, 169.1, 165.3, 165.2, 154.0, 139.14, 139.13, 139.10, 138.5, 138.4, 138.3, 138.16, 138.01, 137.99, 137.97, 137.95, 137.89, 137.86, 137.81, 137.78, 137.61, 133.4, 133.3, 129.9, 129.8, 129.7, 128.53, 128.49, 128.45, 128.37, 128.31, 128.24, 128.22, 128.14, 127.99, 127.96, 127.94, 127.87, 127.80, 127.79, 127.76, 127.73, 127.70, 127.67, 127.63, 127.61, 127.58, 127.56, 127.4, 127.3, 100.77, 100.74, 100.66, 99.9, 99.7, 99.3, 99.2, 98.5, 78.2, 77.2, 76.0, 75.96, 75.84, 75.69, 75.63, 75.51, 75.40, 75.31, 75.07, 75.01, 74.96, 74.89, 74.55, 74.50, 74.39, 74.35, 74.2, 74.1, 73.54, 73.51, 73.38, 73.37, 73.33, 73.29, 72.84, 72.51, 72.47, 72.36, 72.26, 72.22, 72.03, 71.93, 71.90, 71.78, 71.74, 71.63, 71.48, 70.7, 70.6, 69.65, 69.59, 69.52, 68.8, 68.5, 68.3, 68.0, 67.5, 67.3, 67.27, 67.20, 62.7, 62.56, 62.53, 62.37, 57.6, 21.09, 21.04, 20.97, 20.87, 20.84, 20.81, 20.77, 20.71, 20.68, 20.61, 20.59, 18.1, −1.4;

MALDI-TOF calcd for $(M+Na)^+$ $C_{416}H_{462}Cl_3NNaO_{131}Si$: 7722.8. Found: 7722.5.



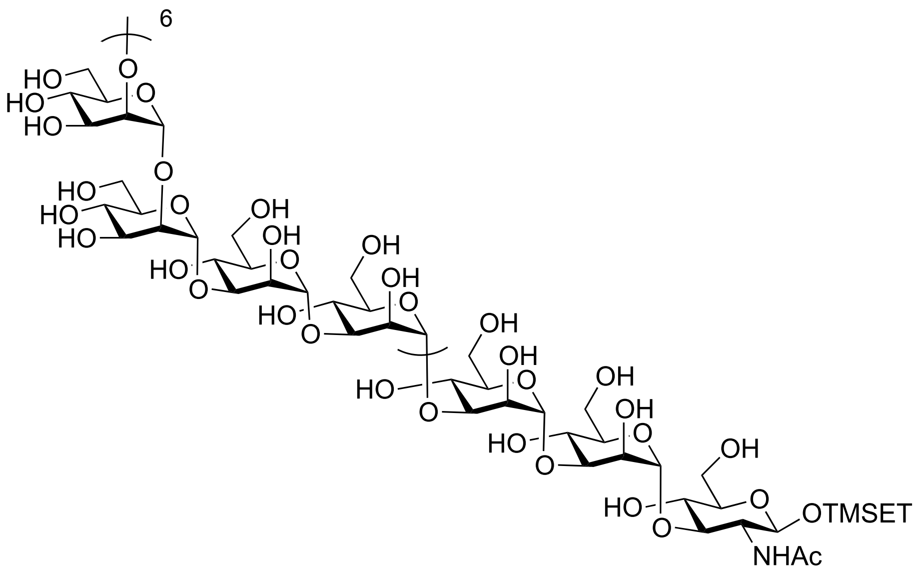
2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl- (1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-

mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (58): Trichloroacetimidate **53** (0.94 g) was synthesized from heptasaccharide **52** (1.49 g) in 63% yield. following general procedure A described above. A mixture of acceptor **57** (963 mg, 0.125 mmol), heptasaccharide trichloroacetimidate **53** (530 mg, 0.175 mmol) and powdered 4 Å molecular sieves was suspended in anhydrous CH_2Cl_2 (80 mL) and stirred at r.t. for 10 min. The solution was then cooled to 0 °C and then TBSOTf (50 μL) was added. The solution was stirred at r.t. overnight before Et_3N (1.0 mL) was added and the mixture was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (gradient 50→63% EtOAc in hexane) to afford **58** (963 mg, 73%) yield as a white solid; R_f 0.53 (2:3 hexane–EtOAc); $[\alpha]_D$ = +6.1 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (700 MHz, $CDCl_3$, δ_H) 8.01–7.98 (m, 12 H), 7.58–7.52 (m, 6 H), 7.39–6.98 (m, 232 H), 5.83 (d, 1 H, *J* = 6.0 Hz), 5.58 (s, 1 H), 5.50–5.47 (m, 6 H), 5.31–5.28 (m, 6 H), 5.25 (s, 1 H), 5.23–5.16 (m, 21 H), 5.11 (s, 1 H), 5.09 (s, 1 H), 5.03 (d, 1 H, *J* = 1.5 Hz), 5.00–4.97 (m, 5 H), 4.89 (s, 1 H), 4.85–4.64 (m, 24 H), 4.59–4.33 (m, 54 H), 4.27–4.13 (m, 37 H), 4.12–4.00 (m, 8 H), 3.98–3.71 (m, 79 H), 3.66–3.50 (m, 25 H), 3.47–3.34 (m, 9 H), 3.18–3.15 (m, 1 H), 2.07 (s, 3 H), 2.06–2.04 (m, 24 H), 2.03 (s, 3 H), 2.01 (s, 3 H), 1.93–1.92 (m, 15 H), 1.90–1.89 (m, 15 H), 1.85–1.84 (m, 15 H), 1.78–1.77 (m, 15 H), 0.88–0.79 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.99, 170.94, 170.81, 170.78, 170.53, 170.26, 170.21, 170.07, 170.00, 169.93, 169.7, 169.6, 169.1, 169.0, 165.4, 165.3, 165.2, 154.0, 139.16, 139.13, 139.10, 138.8, 137.72, 138.68, 138.53, 138.49, 138.37, 138.34, 138.33, 138.16, 138.11, 138.08, 138.01, 137.99, 137.95, 137.89, 137.86, 137.81, 137.78, 137.61, 133.4, 133.3, 133.2, 129.9, 129.8, 129.7, 128.6, 128.53, 128.44, 128.41, 128.38, 128.34, 128.30, 128.26, 128.24, 128.22, 128.18, 128.14, 128.06, 127.94, 127.85, 127.80, 127.76, 127.73, 127.67, 127.63, 127.61, 127.56, 127.54, 127.51, 127.46, 127.44, 127.41, 127.38, 127.36, 127.25, 127.21, 127.15, 101.2, 100.78, 100.65, 99.9, 99.7, 99.6, 99.4, 99.27, 99.17, 99.09, 98.5, 79.2, 78.4, 78.2, 77.2, 76.9, 76.4, 75.96, 75.84, 75.64, 75.51, 75.39, 75.31, 75.07, 75.00, 74.89, 74.79, 74.65, 74.50, 74.39, 74.30, 74.2, 74.1, 74.0, 73.54, 73.52, 73.38, 73.33, 73.29, 73.22, 73.13, 72.84, 72.63, 72.51, 72.47, 72.36, 72.27, 72.22, 72.15, 72.03, 71.93, 71.90, 71.78, 71.74, 71.48, 70.7, 69.65, 69.58, 69.52, 68.65, 68.62, 68.49, 68.39, 68.25, 68.14, 68.06, 67.5, 67.3, 67.2, 62.7, 62.53, 62.37, 57.6, 21.18, 21.11, 21.09, 21.04, 20.97, 20.87, 20.84, 20.81, 20.77, 20.68, 20.61, 18.1, −1.4; MALDI-TOF calcd for $(M+Na)^+$ $C_{582}H_{636}Cl_3NNaO_{174}Si$: 10578. Found: 10578.



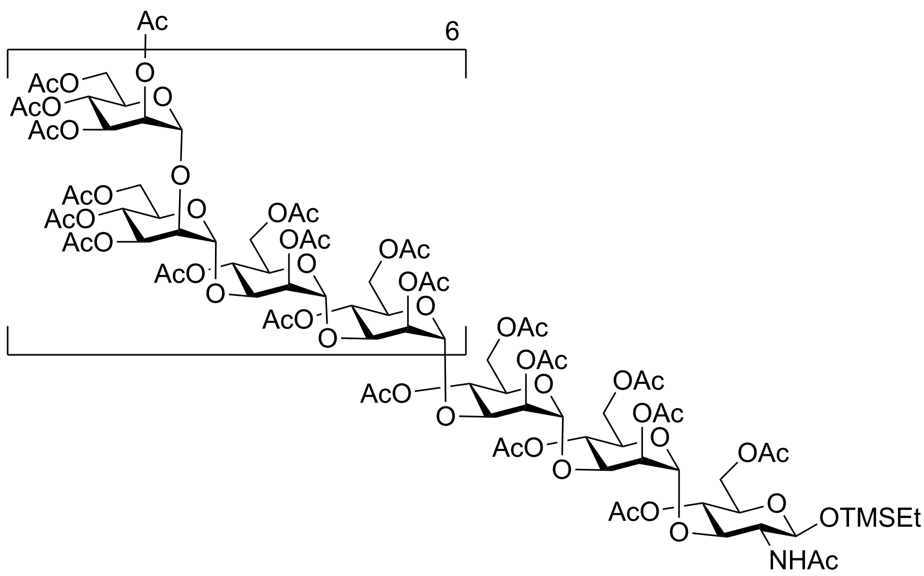
2-(Trimethylsilyl)ethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl- (1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benz-oyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-

mannopyranosyl-(1→2)-4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (59): To a solution of substrate **58** (940 mg, 0.09 mmol) in 3:1 THF–AcOH (40 mL) was added freshly activated zinc dust (2 g). After stirring for 3 h at r.t., the mixture was filtered and the filtrate was concentrated. The resulting residue was dissolved in 3:2 pyridine–Ac_2O (25 mL) and the mixture was stirred at r.t. for 2 h. Then, the solution was concentrated, dissolved in CH_2Cl_2 (100 mL) followed by washing with 1M HCl, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography (gradient 50→60% EtOAc in hexane) to afford **59** (742 mg, 80% yield) as a white solid; R_f 0.17 (2:3 hexane–EtOAc); $[\alpha]_D$ = +6.4 (*c* 0.3, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 8.01–7.98 (m, 12 H), 7.58–7.51 (m, 6 H), 7.39–6.98 (m, 232 H), 6.48 (d, 1 H, *J* = 7.0 Hz), 5.57 (s, 1 H), 5.50–5.47 (m, 6 H), 5.30–5.28 (m, 6 H), 5.25 (s, 1 H), 5.22–5.15 (m, 21 H), 5.11 (s, 1 H), 5.09 (s, 1 H), 5.06 (d, 1 H, *J* = 8.5 Hz), 5.02 (d, 1 H, *J* = 1.5 Hz), 4.99–4.98 (m, 5 H), 4.93 (dd, 1 H, *J* = 10.0, 9.0 Hz), 4.84–4.67 (m, 23 H), 4.58–4.30 (m, 53 H), 4.27–4.12 (m, 38 H), 4.09–4.00 (m, 6 H), 3.98–3.70 (m, 78 H), 3.66–3.48 (m, 26 H), 3.45–3.34 (m, 9 H), 2.95–2.92 (m, 1 H), 2.07 (s, 3 H), 2.05–2.03 (m, 24 H), 2.02 (s, 3 H), 2.01 (s, 3 H), 1.93–1.92 (m, 15 H), 1.90–1.89 (m, 15 H), 1.84–1.83 (m, 15 H), 1.78–1.77 (m, 18 H), 0.94–0.80 (m, 2 H), –0.02 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 171.4, 170.99, 170.94, 170.83, 170.80, 170.53, 170.24, 170.21, 170.07, 169.98, 169.93, 169.7, 169.6, 169.1, 169.0, 165.4, 165.3, 165.2, 139.16, 139.13, 139.10, 138.8, 137.72, 138.68, 138.53, 138.48, 138.37, 138.34, 138.32, 138.16, 138.11, 138.08, 138.01, 137.99, 137.95, 137.90, 137.86, 137.81, 137.78, 137.61, 137.5, 137.2, 133.4, 133.3, 133.1, 129.9, 129.8, 129.7, 128.62, 128.59, 128.53, 128.44, 128.38, 128.34, 128.30, 128.26, 128.23, 128.21, 128.18, 128.14, 128.11, 128.06, 128.02, 129.99, 127.85, 127.80, 127.76, 127.73, 127.70, 127.63, 127.61, 127.56, 127.54, 127.51, 127.46, 127.44, 127.41, 127.38, 127.36, 127.25, 127.21, 127.15, 101.2, 100.77, 100.64, 99.8, 99.66, 99.58, 99.42, 99.28, 99.18, 99.08, 98.8, 80.4, 79.2, 78.4, 78.1, 77.7, 77.6, 77.2, 76.9, 76.4, 75.96, 75.84, 75.64, 75.53, 75.39, 75.30, 75.07, 75.00, 74.89, 74.79, 74.65, 74.50, 74.39, 74.30, 74.2, 74.1, 74.0, 73.63, 73.53, 73.38, 73.35, 73.33, 73.28, 73.22, 73.13, 72.83, 72.64, 72.51, 72.47, 72.36, 72.27, 72.22, 72.15, 72.03, 71.93, 71.88, 71.78, 71.74, 71.2, 70.4, 69.65, 69.62, 69.52, 68.65, 68.50, 68.39, 68.25, 68.17, 68.09, 67.3, 67.2, 62.7, 62.53, 57.8, 23.4, 21.18, 21.10, 21.09, 21.04, 20.97, 20.87, 20.84, 20.78, 20.76, 20.67, 20.61, 20.59, 18.0, −1.4; MALDI-TOF calcd for $(M+Na)^+$ $C_{581}H_{637}NNaO_{173}Si$: 10446. Found: 10446.



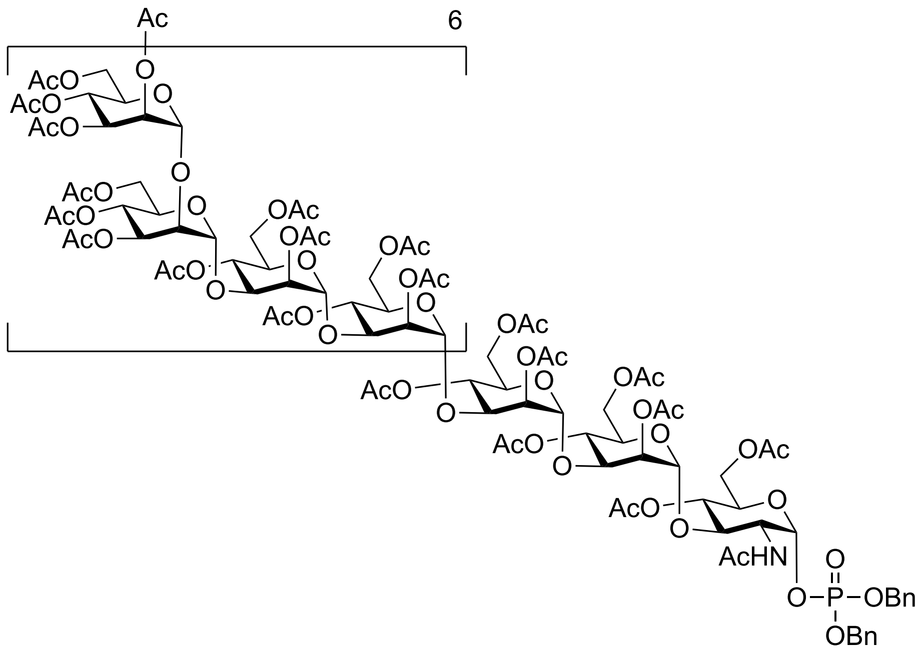
2-(Trimethylsilyl)ethyl α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3) -α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopy-ranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranos-yl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (S14): Ammonia was condensed at −78 °C into 50 mL round bottom flask equipped with a Dewar condenser and a magnetic stir bar (total volume 14 mL). Freshly cut sodium metal (70 mg) was added and the mixture was stirred at −78 °C for 5 min. A solution of compound **59** (25 mg, 2.4 μmol) in THF (0.40 mL) was introduced via syringe and the mixture was stirred at −80 °C for 1.5 h before CH_3OH (2 mL) was added. The colorless solution was warmed to r.t. and then concentrated. The residue was dissolved in water

(4 mL) and the solution was neutralized with Amberlite IR120 H^+ ion-exchange resin, filtered, concentrated. The residue purified by C_{18} chromatography (gradient 0→30% CH_3OH in H_2O) to afford **S14** (6.6 mg, 61% yield) as a white solid. $[\alpha]_D$ = +88.8 (*c* 0.2, H_2O); ^1H NMR (700 MHz, D_2O, δ_H) 5.39–5.38 (m, 6 H), 5.31–5.28 (m, 6 H), 5.15–5.13 (m, 7 H), 5.09 (s, 1 H), 5.06–5.05 (m, 6 H), 4.58 (d, 1 H, *J* = 8.5 Hz), 4.23–4.18 (m, 13 H), 4.12–4.05 (m, 13 H), 4.03–3.99 (m, 13 H), 3.97–3.64 (m, 119 H), 3.63–3.58 (m, 3 H), 2.95–2.92 (m, 1 H), 2.04 (s, 3 H), 1.02–0.86 (m, 2 H), 0.02 (s, 9 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 174.9, 103.25, 103.22, 103.17, 103.07, 101.71, 101.68, 101.63, 101.1, 80.7, 79.6, 79.5, 79.39, 79.36, 79.31, 79.2, 76.6, 74.50, 74.44, 74.37, 74.29, 74.26, 74.21, 71.8, 71.3, 71.05, 71.01, 70.96, 70.91, 70.64, 70.57, 69.3, 68.0, 67.9, 67.8, 67.14, 67.10, 66.5, 62.07, 61.99, 61.96, 61.91, 61.62, 61.54, 55.1, 23.5, 18.1, −1.4; MALDI-TOF calcd for $(M+Na)^+$ $C_{169}H_{287}NNaO_{136}Si$: 4557.6. Found: 4558.0.



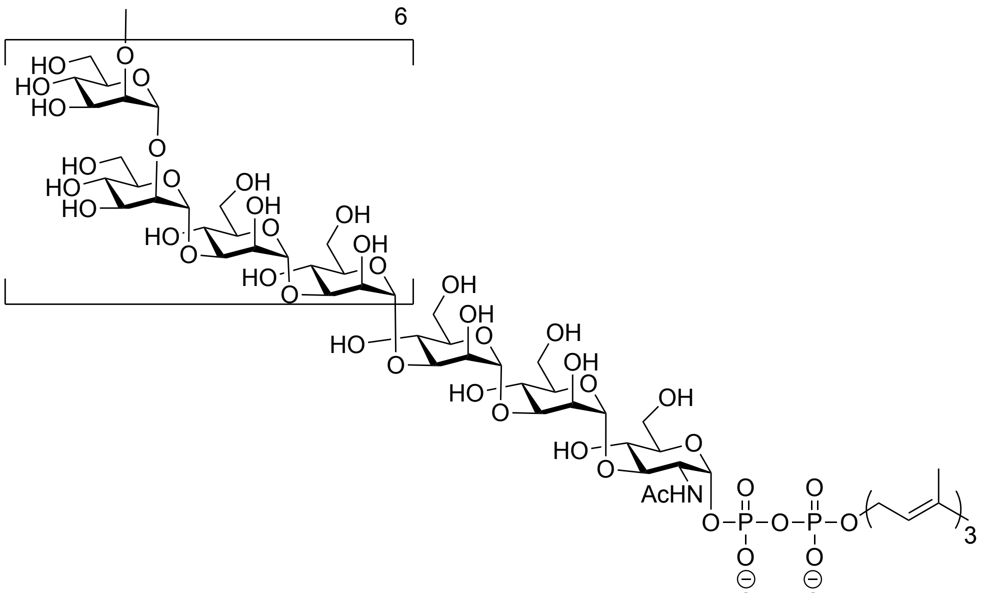
2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6- tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl- (1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-manno- pyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-manno-pyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-

deoxy-β-D-glucopyranoside (60): Compound **S14** (64 mg, 14.1 µmol) was suspended in 3:2 pyridine–Ac_2O (5 mL) and the mixture was stirred at 45 °C overnight. Then, the solution was concentrated, dissolved in CH_2Cl_2 (100 mL) followed by washing with 1M HCl, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography (gradient 60→75% acetone in hexane) to afford **60** (86 mg, 77% yield) as a white solid; R_f 0.24 (4:7 hexane-acetone); $[\alpha]_D$ = +18.9 (*c* 0.3, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 6.25 (d, 1 H, *J* = 7.0 Hz), 5.37 (dd, 1 H, *J* = 10.0, 3.5 Hz), 5.34–5.17 (m, 32 H), 5.31–5.28 (m, 6 H), 5.14–5.10 (m, 6 H), 5.06–4.90 (m, 31 H), 4.84 (s, 1 H), 4.83 (s, 1 H), 4.50 (app t, 1 H, *J* = 9.0 Hz), 4.27–4.21 (m, 17 H), 4.16–3.89 (m, 79 H), 3.85–3.78 (m, 9 H), 3.72 (s, 2 H), 3.66–3.64 (m, 1 H), 3.54 (td, 1 H, *J* = 10.0, 6.5 Hz), 3.09–3.05 (m, 1 H), 2.16–2.12 (m, 69 H), 2.11–2.08 (m, 87 H), 2.05–2.03 (m, 39 H), 2.00–1.98 (m, 51 H), 0.97–0.83 (m, 2 H), 0.00 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 171.1, 170.9, 170.72, 170.68, 170.61, 170.59, 170.44, 170.40, 170.36, 170.26, 170.21, 170.19, 170.07, 169.85, 169.82, 169.71, 169.69, 169.52, 169.47, 169.43, 169.41, 169.39, 169.37, 169.28, 99.95, 99.83, 99.59, 99.54, 99.50, 99.42, 99.30, 99.15, 98.8, 98.6, 80.7, 77.7, 77.5, 77.2, 77.1, 75.6, 75.4, 75.2, 75.1, 74.3, 74.0, 73.7, 71.3, 71.2, 70.94, 70.89, 70.79, 70.5, 70.0, 69.8, 69.63, 69.58, 69.51, 69.0, 68.7, 68.4, 67.38, 67.31, 67.22, 67.0, 66.8, 66.7, 66.1, 66.0, 65.4, 63.8, 62.5, 62.37, 62.28, 62.23, 62.0, 61.87, 61.80, 61.76, 61.71, 61.6, 58.4, 23.7, 20.98, 20.95, 20.88, 20.86, 20.82, 20.79, 20.76, 20.72, 20.68, 20.62, 20.59, 20.56, 18.0, −1.4; MALDI-TOF calcd for $(M+Na)^+$ $C_{331}H_{449}NNaO_{217}Si$: 7960.4. Found: 7960.6.



2,3,4,6-tetra-*O*-Acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-α-D-

mannopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-α-D-glucopyranosyl dibenzyl phosphate (62): To a solution of **60** (81 mg, 10.2 μmol) in dry CH_2Cl_2 (3 mL) was added TFA (1 mL) dropwise at 0 °C. After stirring for 3 h at r.t., the solution was concentrated, dissolved in CH_2Cl_2 (20 mL), washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered and concentrated. The residue was purified by chromatography (gradient 60→95% acetone in hexane) to afford hemiacital (62 mg, 78% yield) as a white solid. The hemiacital (62 mg, 7.9 μmol) was dissolved in dry CH_2Cl_2 (5 mL), tetraazole (28 mg, 395 μmol) was added and the reaction mixture was cooled to 0 °C. After 10 min, dibenzyl *N*,*N*-diisopropylphosphoramidite (82 mg, 237 μmol) was added dropwise and the mixture was stirred at r.t. for 4 h. The mixture was cooled to −78 °C and *m*-CPBA (61 mg, 355 μmol) was added in one portion and then the solition was warmed to r.t. After stirring at r.t. for 2 h, CH_2Cl_2 was added and the mixture was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by Sephadex LH-20 (1:1CH_3OH–CH_2Cl_2) to afford phosphate **62** (82 mg, 92% yield) as a white solid; R_f 0.12 (4:7 hexane–acetone); $[\alpha]_D$ = +17.3 (*c* 0.2, CH_2Cl_2); ^1H NMR (700 MHz, $CDCl_3$, δ_H) 7.37−7.31 (m, 10 H), 5.86 (d, 1 H, *J* = 9.5 Hz), 5.60 (dd, 1 H, *J* = 6.0, 3.0 Hz), 5.37 (dd, 1 H, *J* = 10.0, 3.0 Hz), 5.34 (app t, 1 H, *J* = 10.0 Hz), 5.30−5.25 (m, 13 H), 5.23−5.19 (m, 13 H), 5.18−5.09 (m, 10 H), 5.08−5.01 (m, 9 H), 5.00−4.97 (m, 14 H), 4.91−4.87 (m, 9 H), 4.84 (d, 1 H, *J* = 1.5 Hz), 4.34−4.19 (m, 16 H), 4.17−4.11 (m, 23 H), 4.08−3.93 (m, 46 H), 3.90−3.73 (m, 22 H), 2.17−2.13 (m, 51 H), 2.12−2.06 (m, 99 H), 2.05−2.03 (m, 42 H), 2.00−1.98 (m, 54 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.9, 170.75, 170.68, 170.59, 170.54, 170.44, 170.40, 170.37, 170.26, 170.21, 170.14, 170.07, 170.02, 169.86, 169.82, 169.72, 169.70, 169.52, 169.47, 169.43, 169.41, 169.40, 169.39, 169.28, 135.2 (d, J_{PC} = 6.1 Hz), 135.1(d, J_{PC} = 6.1 Hz), 129.8, 129.10, 129.08, 128.85, 128.24, 128.20, 99.95, 99.83, 99.59, 99.56, 99.50, 99.30, 99.18, 99.10, 98.4, 96.7 (d, J_{PC-1} = 6.4 Hz), 77.7, 77.5, 77.2, 77.1, 76.5, 75.6, 75.4, 75.1, 75.0, 74.7, 74.3, 74.0, 71.3, 70.94, 70.89, 70.77, 70.13, 70.10, 70.04, 69.86, 69.80, 69.67, 69.63, 69.58, 69.49, 68.7, 68.4, 67.37, 67.31, 67.22, 67.02, 66.96, 66.7, 66.1, 66.0, 65.4, 62.7, 62.5, 62.37, 62.28, 62.03, 61.88, 61.81, 61.75, 61.71, 61.6, 61.2, 51.8 (d, J_{PC-2} = 7.3 Hz), 22.9, 20.95, 20.91, 20.86, 20.82, 20.79, 20.72, 20.68, 20.66, 20.62, 20.59, 20.56; ^{31}P NMR (160 MHz, $CDCl_3$, δ_C) –2.4; MALDI-TOF calcd for $(M+Na)^+$ $C_{340}H_{450}NNaO_{220}P$: 8125.0. Found: 8124.8.



α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl- (1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-

α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranosyl farnesyl diphosphate diammonium salt (2): To a solution of **62** (20 mg, 2.5 μmol) in THF (5 mL) was added palladium on charcoal (10%, 10 mg) and the solution was subjected to hydrogen atmosphere for 4 h. The mixture was filtered through Celite and the filtrate was concentrated. The residue **63** was used in the next step without further purification. To a solution of the crude phosphate **63** in dry CH_2Cl_2 (3 mL) was added 1,1'-carbonyldiimidazole (16 mg, 0.1 mmol). After stirring at r.t. for 2 h, a solution of 5% (v/v) solution of anhydrous CH_3OH in CH_2Cl_2 (0.10 mL) was added to quench the unreacted 1,1'-carbonyldiimidazole and the mixture was stirred for 30 min. The solvent was concentrated and the residue dissolved in DMF-d_7 (0.6 mL). Farnesyl phosphate **47** (41 mg, 0.125 mmol) was added and the reaction mixture stirred at r.t. for 7 days. ^{31}P NMR spectroscopy showed that at this point all of the activated intermediate was consumed. The solvent was removed in vacuo and the residue purified by Sephadex LH-20 (1:1 CH_3OH-CH_2Cl_2) to afford farnesyl-linked compound as a crude product. To a solution of crude farnesyl-linked compound in CH_3OH–CH_2Cl_2 (5 mL, 4:1) was added freshly prepared $NaOCH_3$ (1M solution in CH_3OH, 1.0 mL). The reaction mixture was stirred at r.t. for 6 h, and the $NaOCH_3$ was quenched by addition of Amberlite IR120 (NH_4^+ form). The mixture was filtered, concentrated in vacuo and the residue purified by C_{18} chromatography (gradient 0→15% CH_3OH in H_2O) to afford **2** (6.5 mg, 55%

yield) as a white solid. $[\alpha]_D$ = +40.6 (*c* 0.1, CH_2Cl_2); ^1H NMR (700 MHz, D_2O, δ_H) 5.50 (dd, 1 H, *J* = 7.0, 3.0 Hz), 5.46 (app t, 1 H *J* = 8.0 Hz), 5.39−5.38 (m, 6 H), 5.31 (s, 5 H), 5.26 (s, 1 H), 5.23−5.19 (m, 2 H), 5.13 (s, 7 H), 5.10 (s, 1 H), 5.06 (s, 1 H), 5.05 (s, 5 H), 4.53−4.47 (m, 2 H), 4.22−4.19 (m, 14 H), 4.12−4.08 (m, 13 H), 4.03−3.73 (m, 126 H), 3.72−3.66 (m, 13 H), 3.61−3.59 (m, 1 H), 2.19−2.10 (m, 6 H), 2.08 (s, 3 H), 2.04 (t, 1 H *J* = 7.5 Hz), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.64 (s, 6 H); ^{13}C NMR (125 MHz, D_2O, δ_C) 175.3, 144.0, 137.7, 134.5, 125.4, 125.2, 120.4 (d, J_{PC} = 8.5 Hz)， 103.25, 103.23, 103.18, 103.06, 101.98, 101.68, 101.63, 95.6 (d, J_{PC} = 6.5 Hz)， 79.6, 79.5, 79.35, 79.30, 79.25, 79.22, 79.0, 78.5, 74.5, 74.4, 74.35, 74.30, 74.28, 74.24, 74.25, 74.20, 73.9, 71.30, 71.04, 71.00, 70.95, 70.63, 70.57, 68.0, 67.8, 67.7, 67.14, 67.10, 66.5, 64.0 (d, J_{PC} = 5.8 Hz), 62.06, 61.95, 61.90, 61.5, 61.1, 53.2 (d, J_{PC} = 7.5 Hz), 39.7, 26.7, 26.5, 25.8, 23.3, 18.0, 16.6, 16.2; ^{31}P NMR (200 MHz, D_2O, δ_C) −10.6 (d, J_{PP} = 20.0 Hz), −13.3 (d, J_{PP} = 20.0 Hz); HRMS (ESI) calcd for $(M-3H)^{-3}$ $C_{179}H_{298}NO_{142}P_2$: 1598.5201. Found: 1598.5180.

References:

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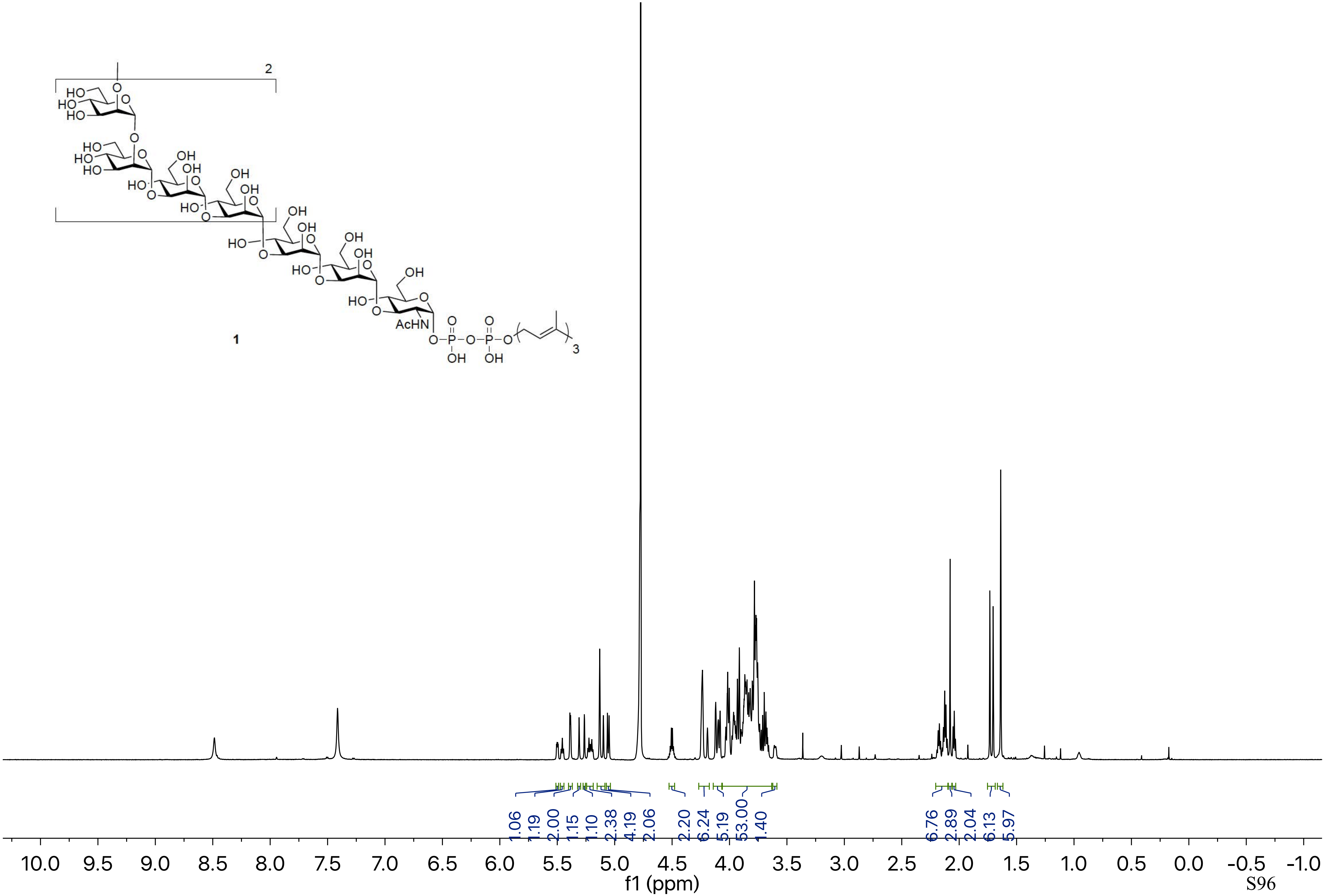
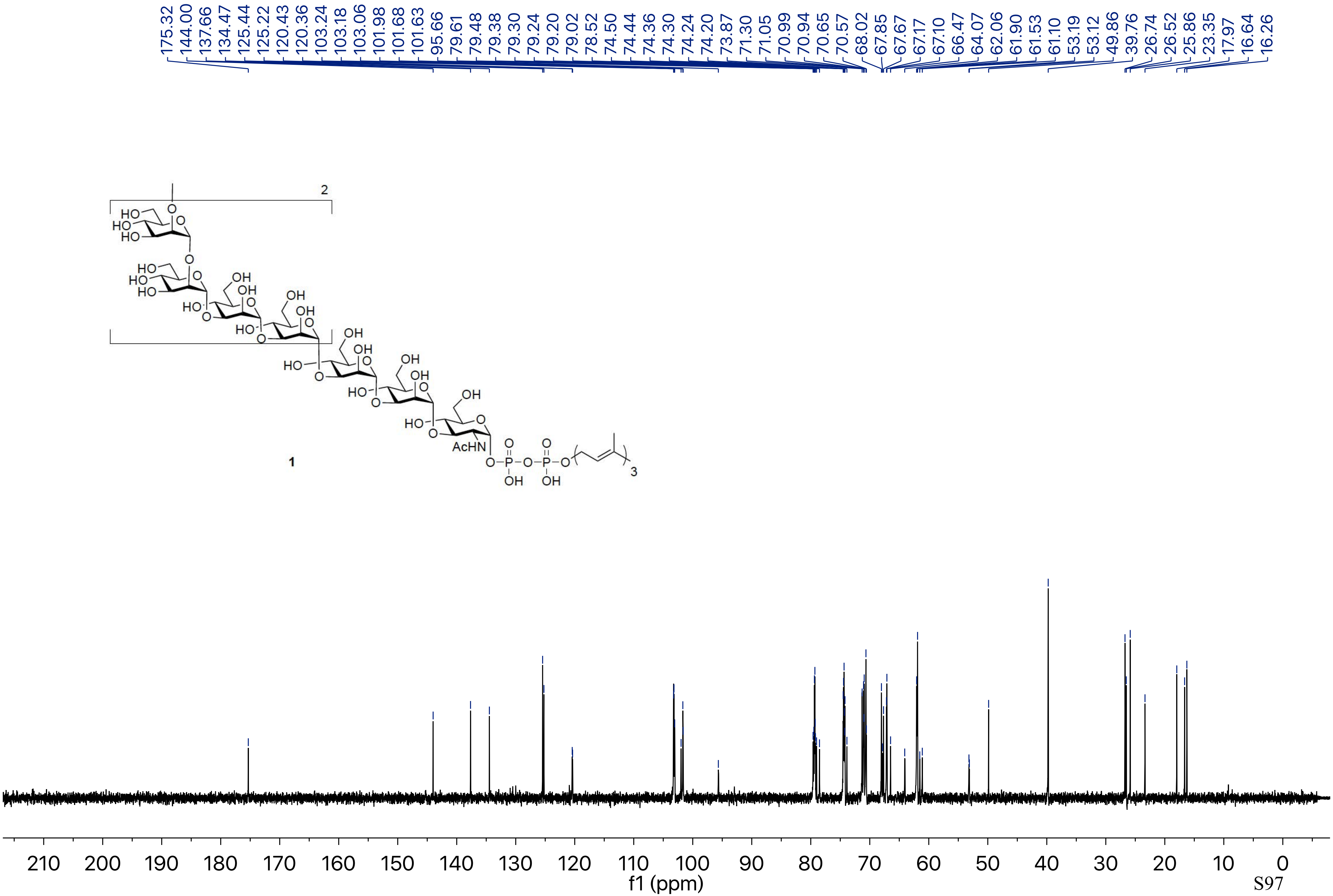
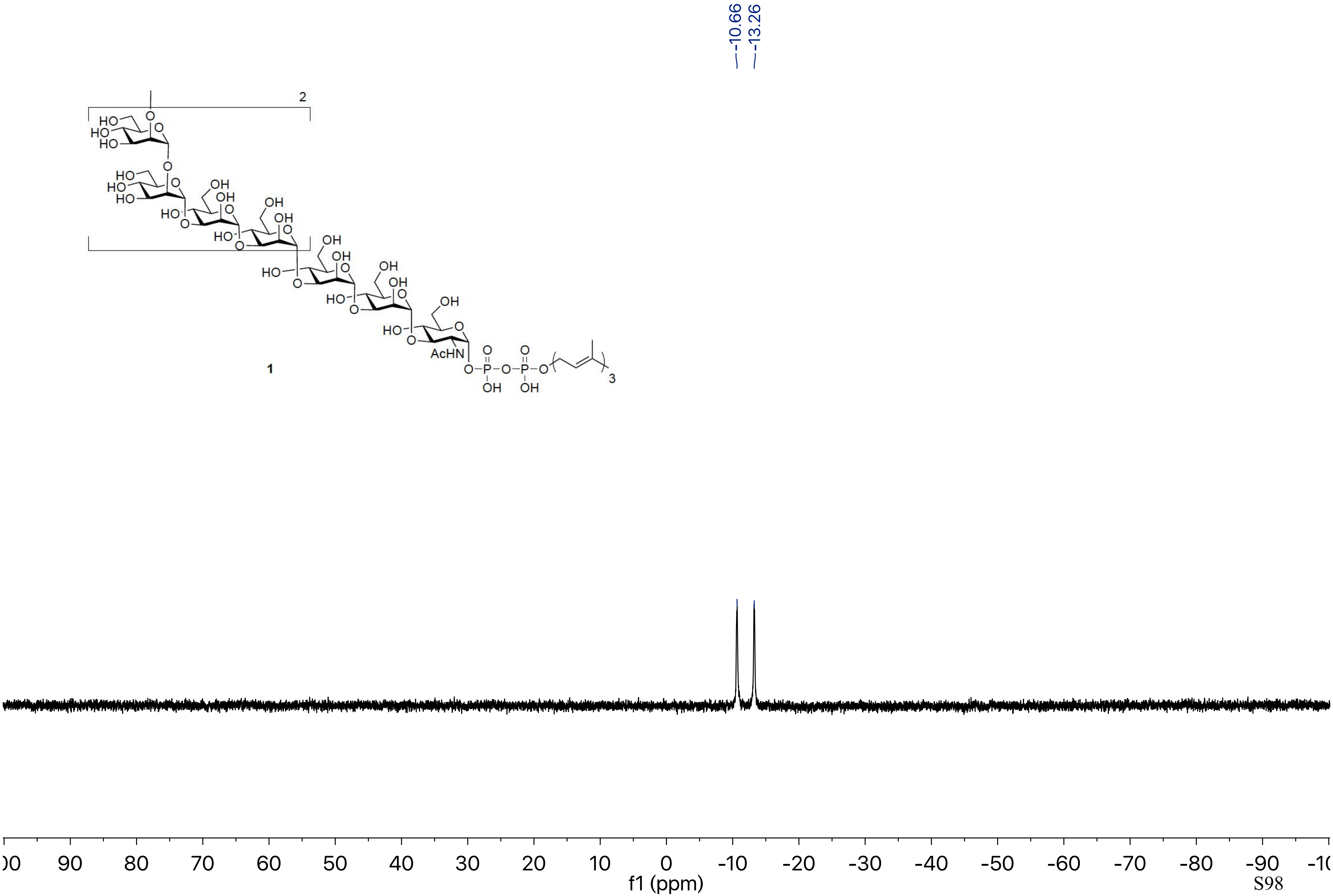
2015.09.25.v7_WL-6-020-prod_loc48_17.29_H1_1D — Lei, WL-6-020-prod — 699.764 MHz H1 PRESAT in d2o (ref. to external acetone @ 2.225 pp

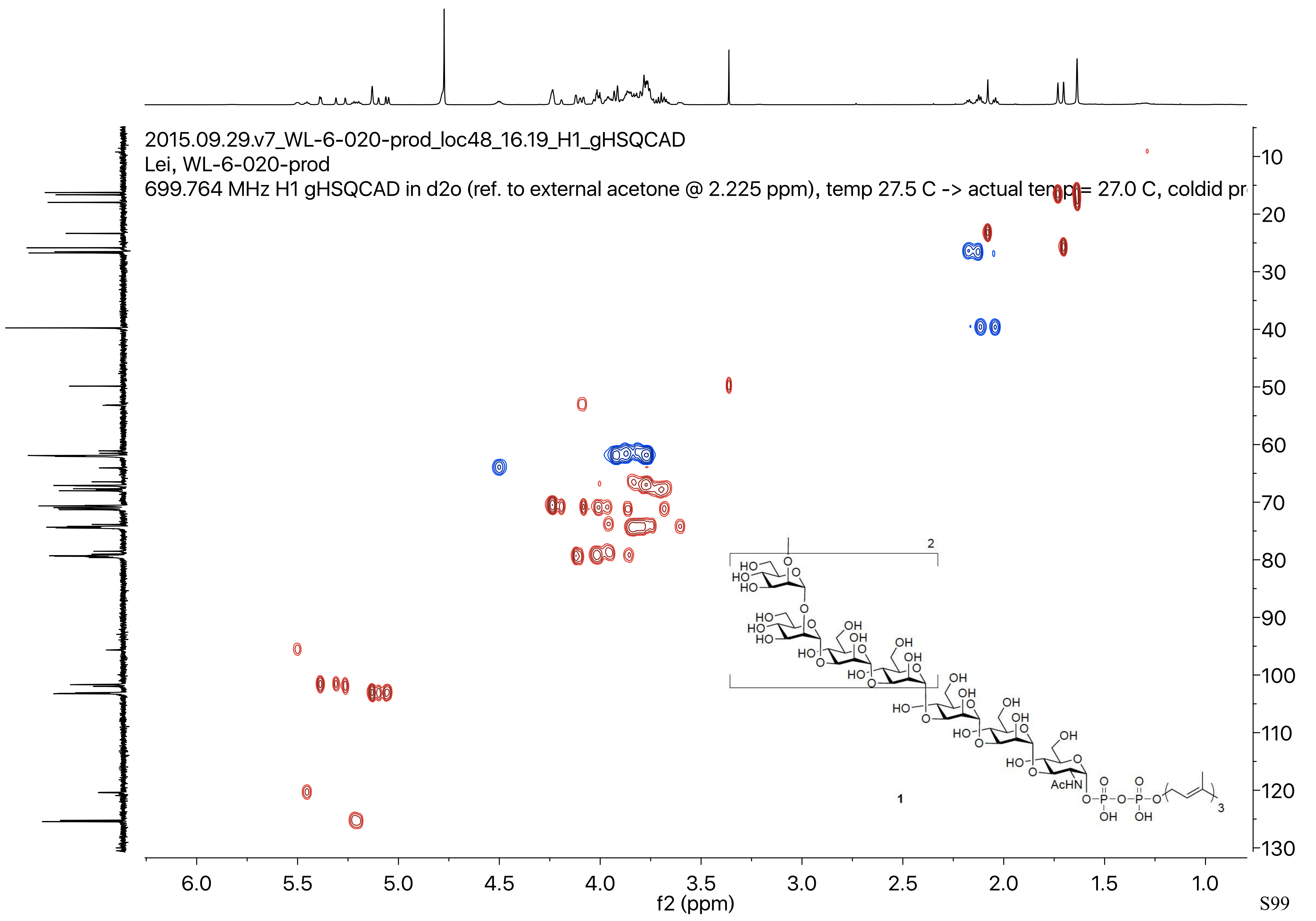


2015.09.29.u5_WL-6-020-prod_loc12_20.04_C13_1D — Lei, WL-6-020-prod — 125.691 MHz C13[H1] 1D in d2o (ref. to external acetone @ 31.07 p



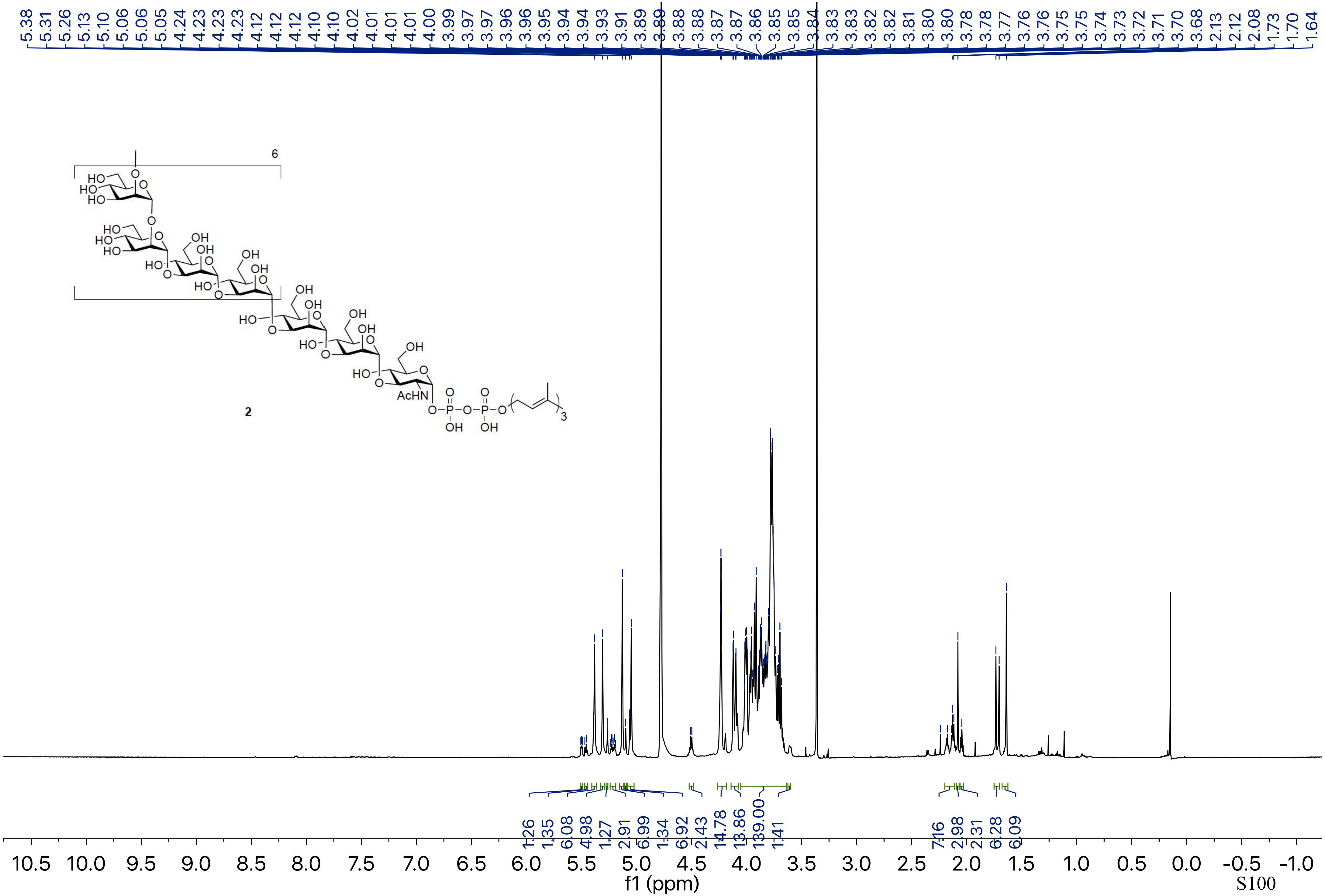
2015.10.08.i5_WL-6-020-prod_P31_1D — WL-6-020-prod — 201.641 MHz P31[H1] 1D in d2o, temp 26.4 C -> actual temp = 27.0 C, autoxdb prob



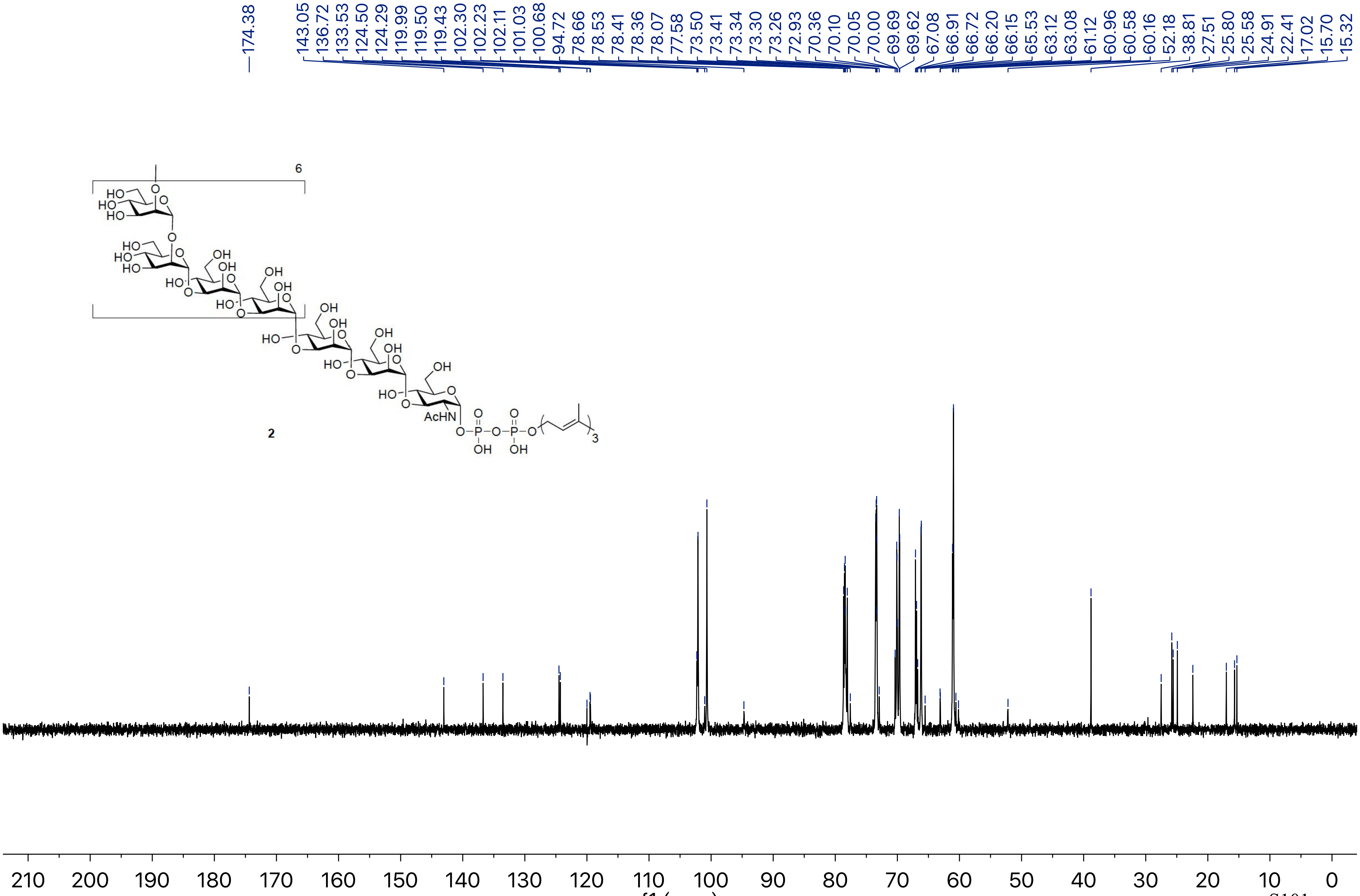


2015.09.29.v7_WL-6-020-prod_loc48_16.19_H1_gHSQCAD
Lei, WL-6-020-prod
699.764 MHz H1 gHSQCAD in d2o (ref. to external acetone @ 2.225 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid pr
f1 (ppm)
f2 (ppm)
2
1

2016.06.27.v7_WL-6-053-final-prod_loc43_15.53_H1_1D — Lei, WL-6-053-final-prod — 699.764 MHz H1 PRESAT in d2o (ref. to external acetone



2016.06.29.u5_WL-6-053-final-prod_C13_1D — Lei, WL-6-053-final-prod — 125.691 MHz C13[H1] 1D in d2o (ref. to external acetone @ 31.07 ppm



2

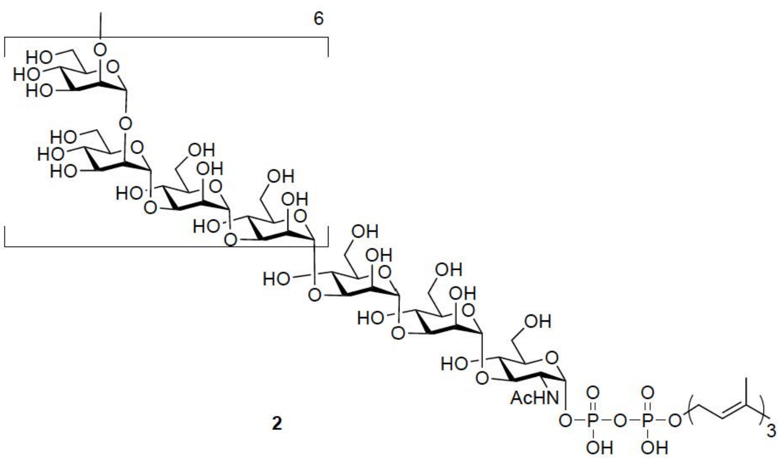
Department of Chemistry, University of Alberta

Agilent Technologies

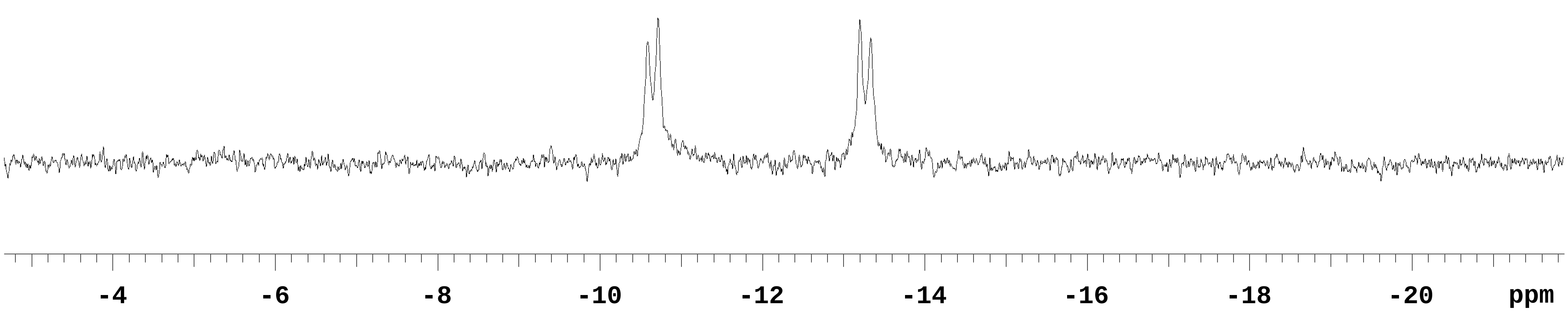
Recorded on: mr400, Jun 12 2016	Sweep Width(Hz): 32051.3	Acquisiton Time(s): 1	Relaxation Delay(s): 0.1
Pulse Sequence: s2pul	Digital Res.(Hz/pt): 0.49	Hz per mm(Hz/mm): 12.96	Completed Scans 46128

WL-6-053-prod

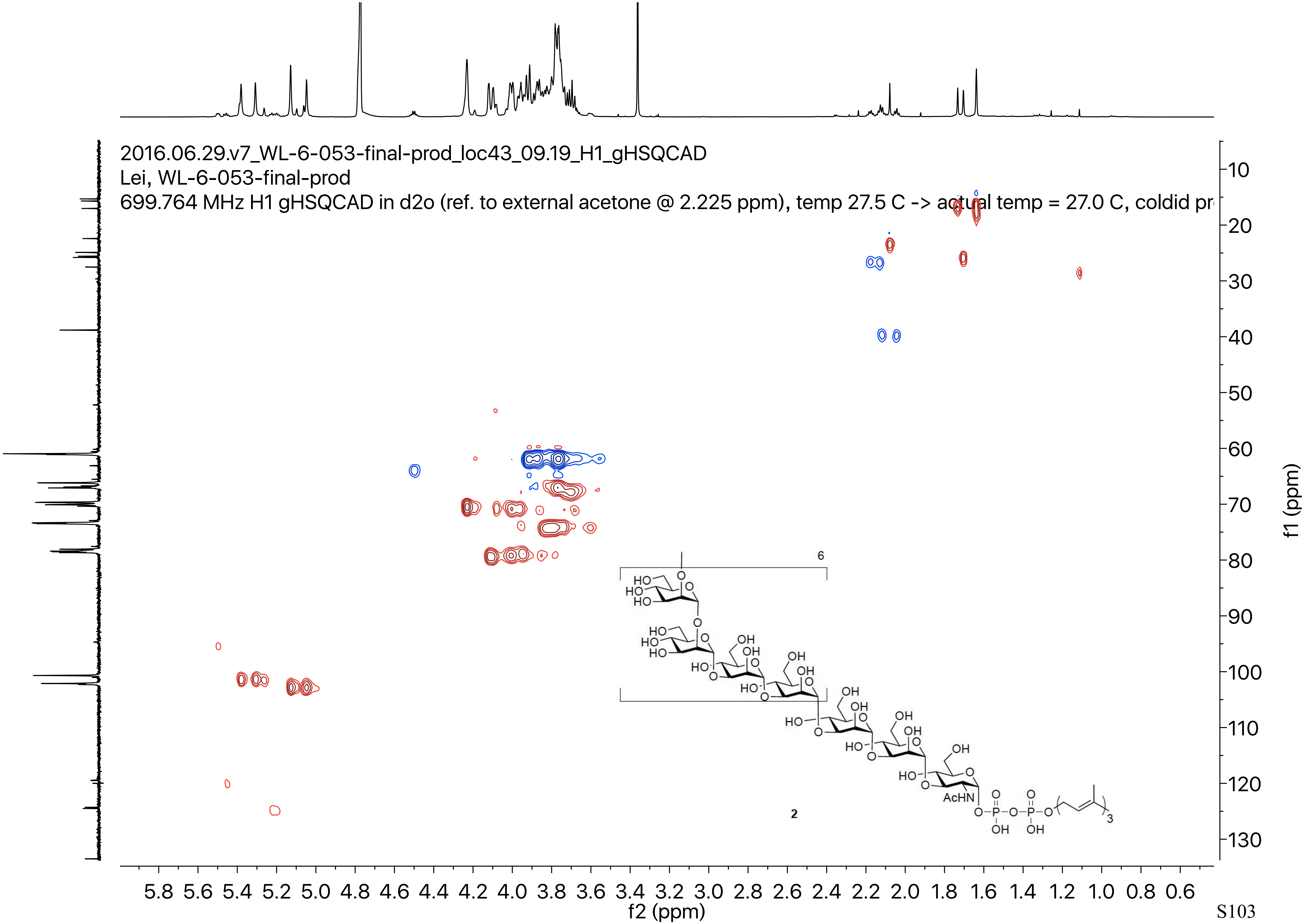
161.914 MHz P31[H1] 1D in d2o, temp 25.9 C -> actual temp = 27.0 C, onenmr probe



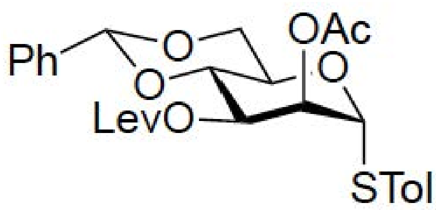
2



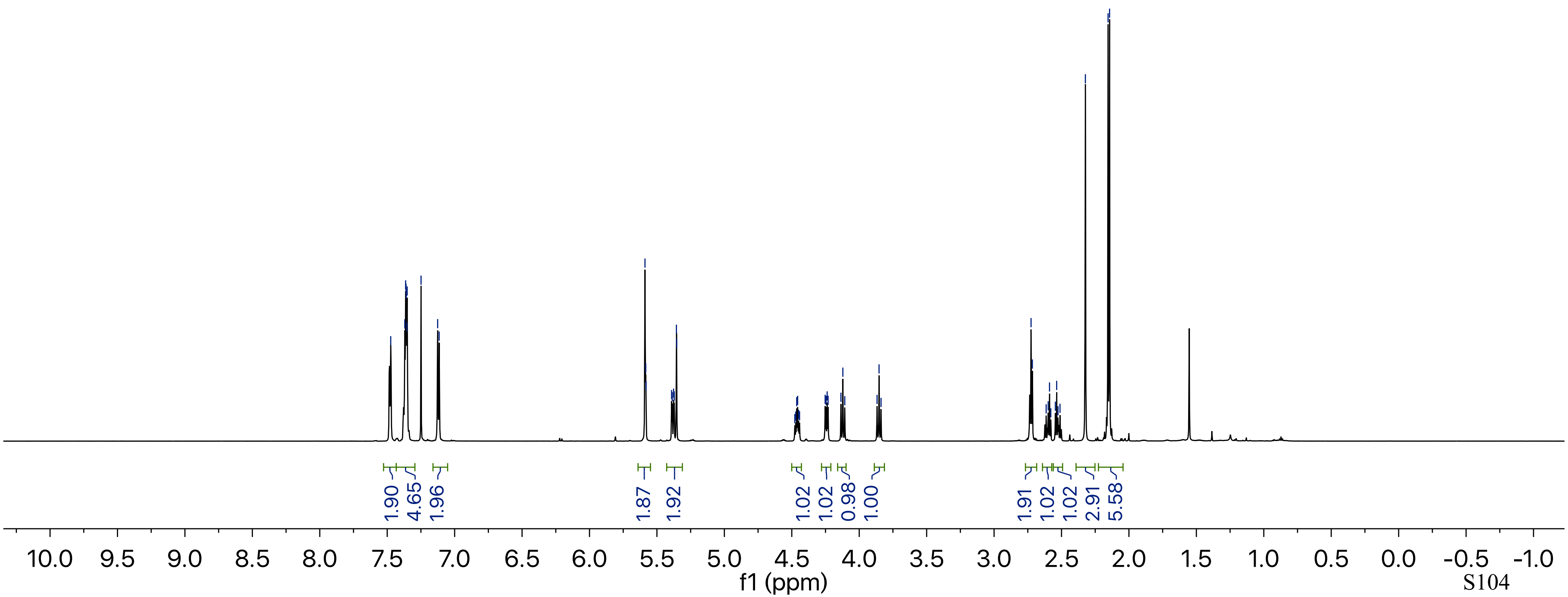
File: /mnt/d600/home9/tllnmr/nmrdata/lei_wang/2016.06.12.mr4_WL-6-053-prod_P31_1D

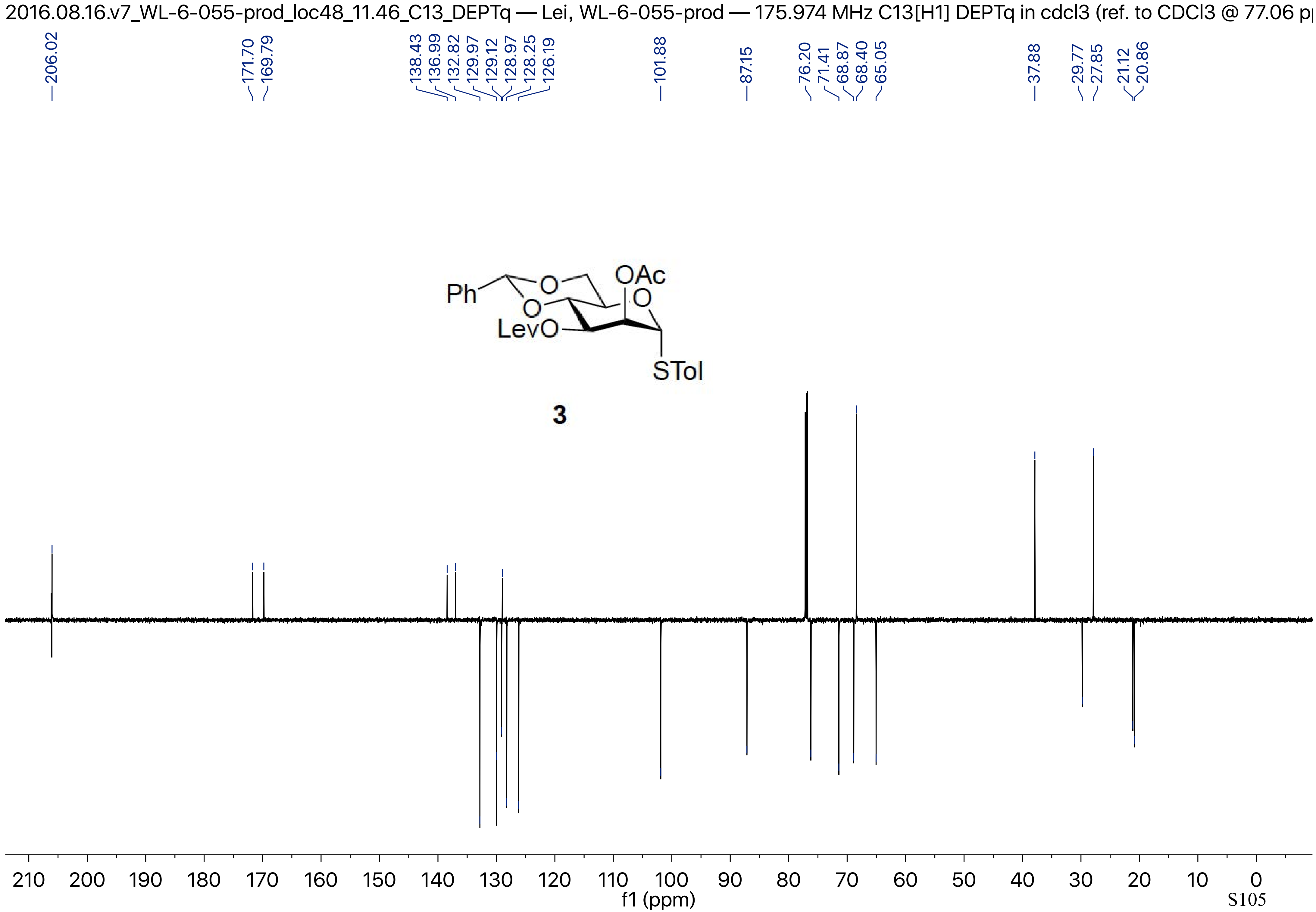

2016.06.29.v7_WL-6-053-final-prod_loc43_09.19_H1_gHSQCAD
Lei, WL-6-053-final-prod
699.764 MHz H1 gHSQCAD in d2o (ref. to external acetone @ 2.225 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid pr
f1 (ppm)
f2 (ppm)
6
AcHN
2

2016.08.16.v7_WL-6-055-prod_loc48_11.44_H1_1D — Lei, WL-6-055-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp

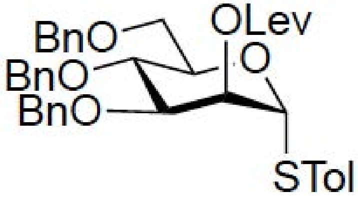


3

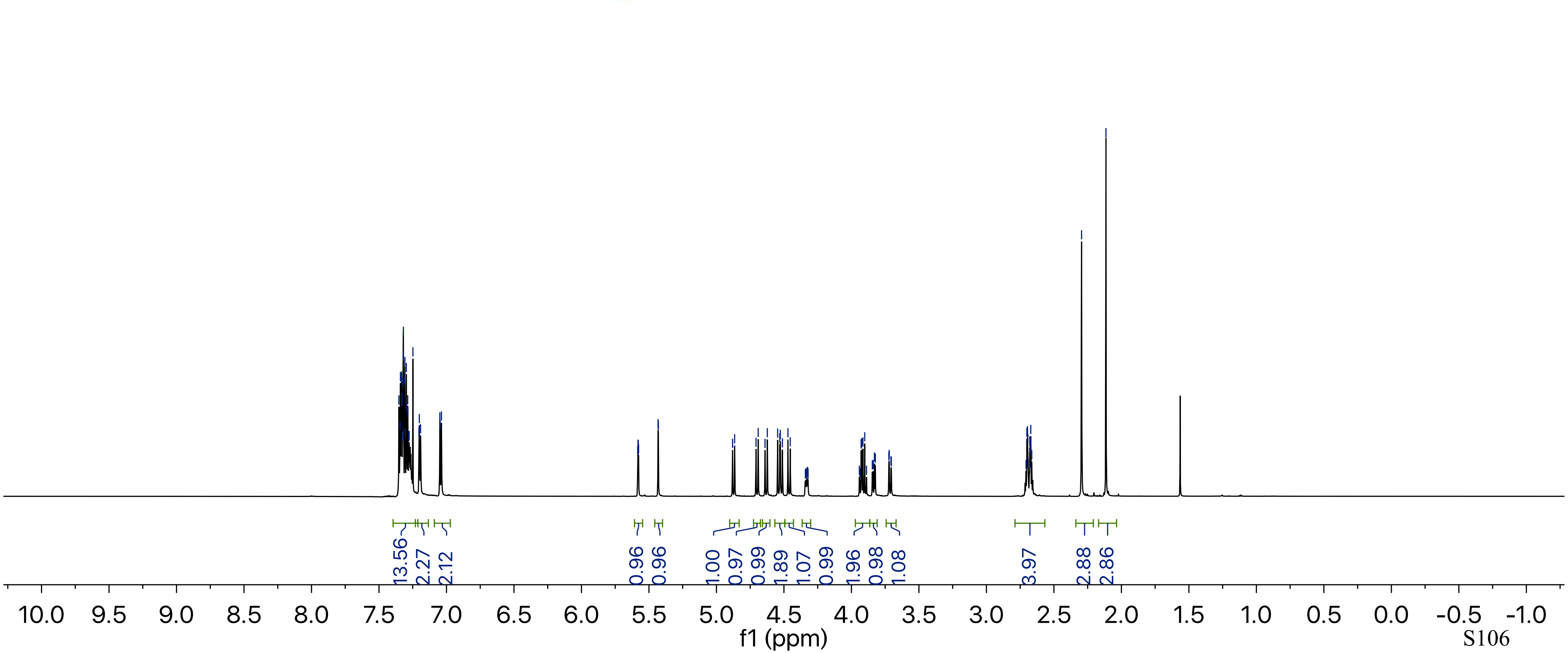



2016.08.16.v7_WL-6-055-prod_loc48_11.46_C13_DEPTq — Lei, WL-6-055-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p
206.02
171.70
169.79
138.43
136.99
132.82
129.97
129.12
128.97
128.25
126.19
101.88
87.15
76.20
71.41
68.87
68.40
65.05
37.88
29.77
27.85
21.12
20.86
Ph
O
O
OAc
O
LevO
STol
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

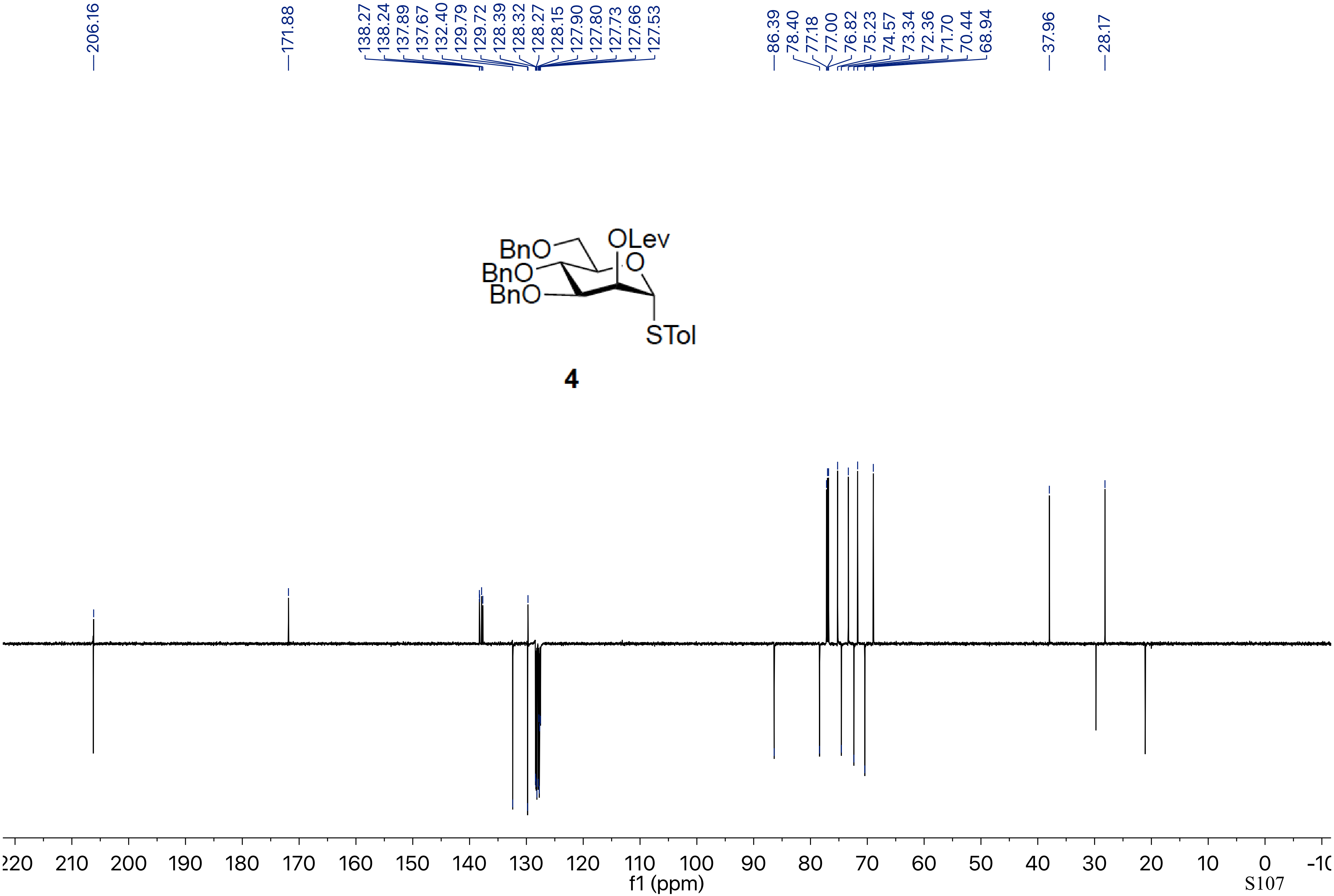
2016.08.18.v7_WL-6-058-prod_loc48_10.35_H1_1D — Lei, WL-6-058-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



4

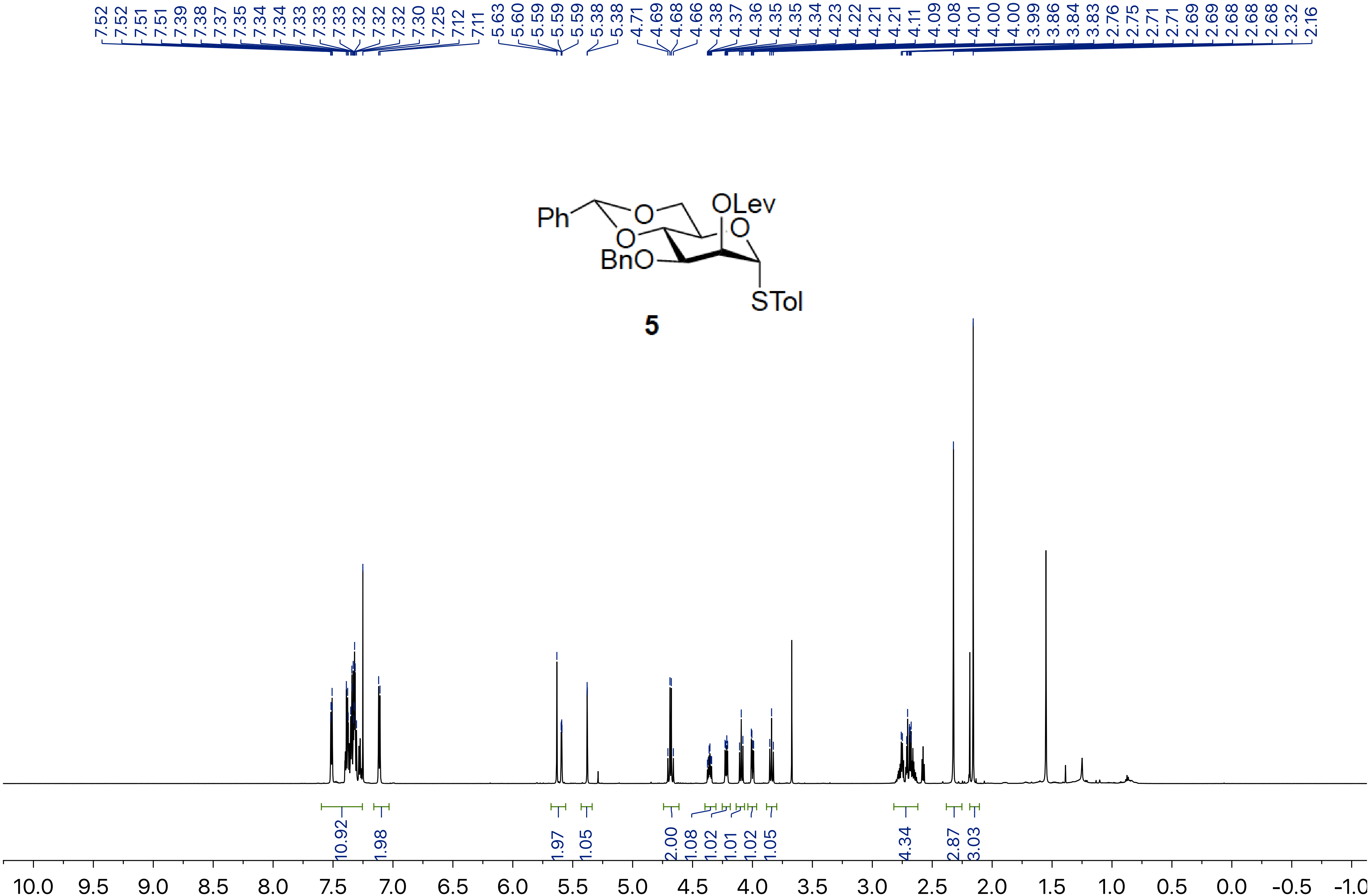


2016.08.18.v7_WL-6-058-prod_loc48_10.37_C13_DEPTq — Lei, WL-6-058-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



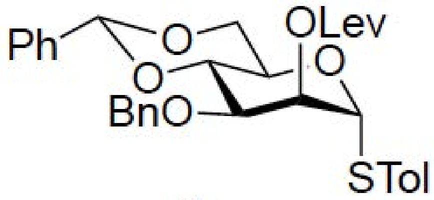
4

2016.07.8.v7_WL-5-075-prod_loc46_14.12_H1_1D — Lei, WL-5-075-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2

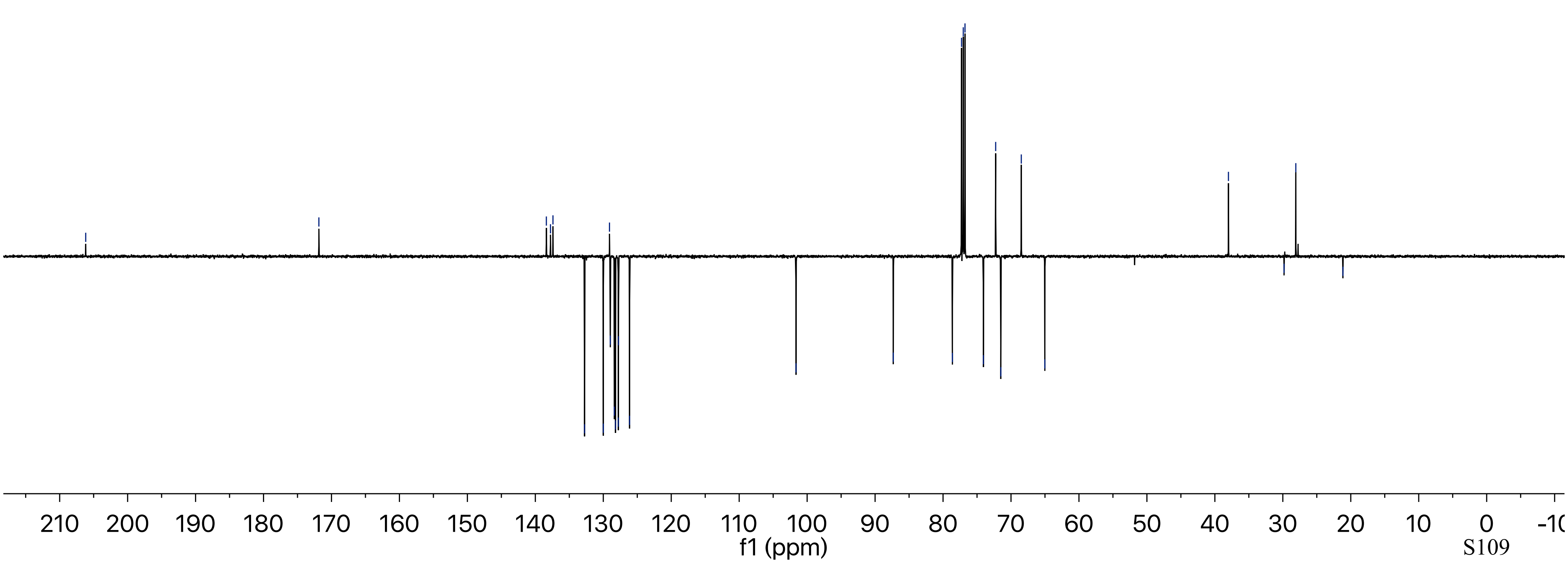


f1 (ppm)

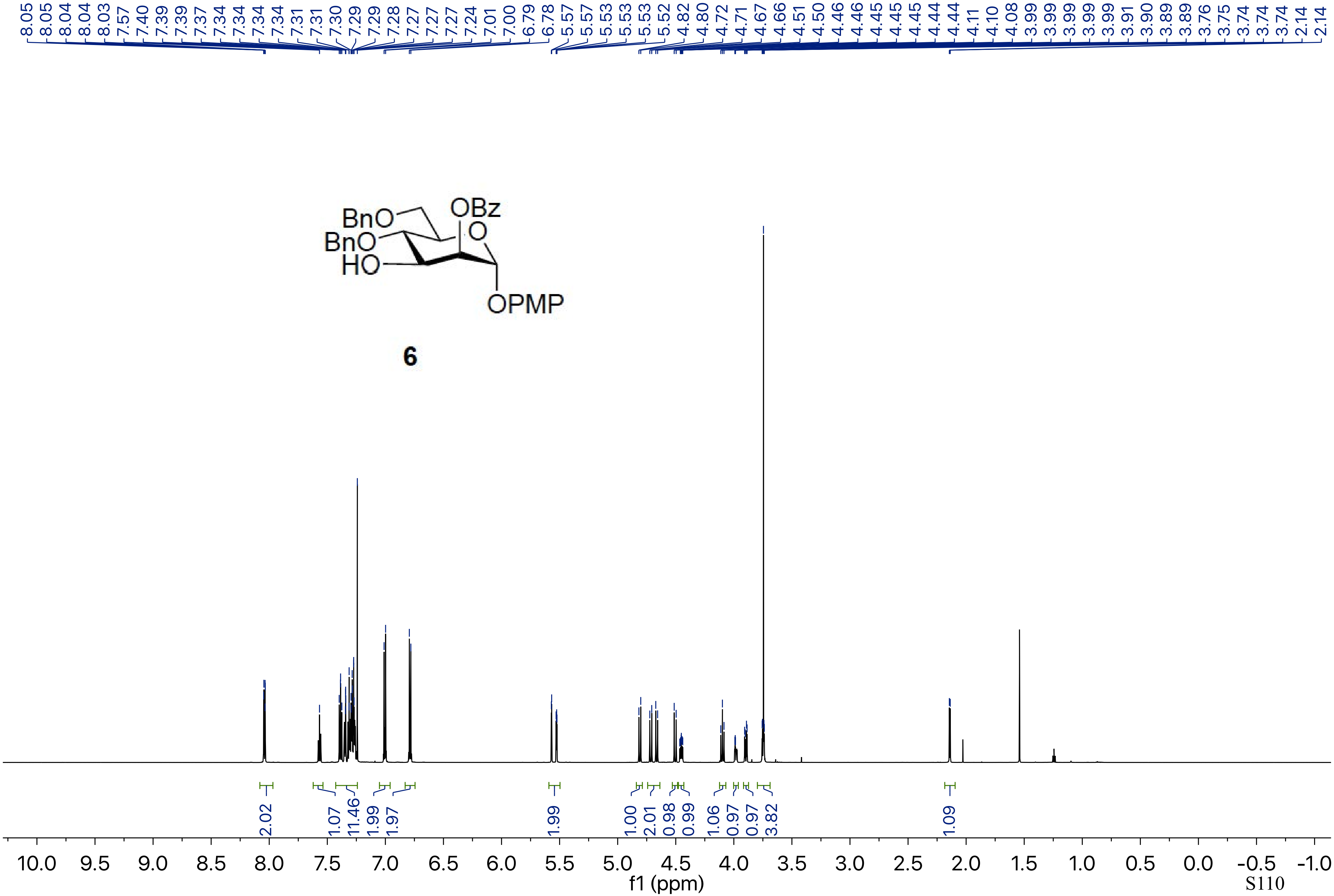
2016.07.08.u5_WL-5-075-prod_loc10_15.58_C13_DEPTq — Lei, WL-5-075-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



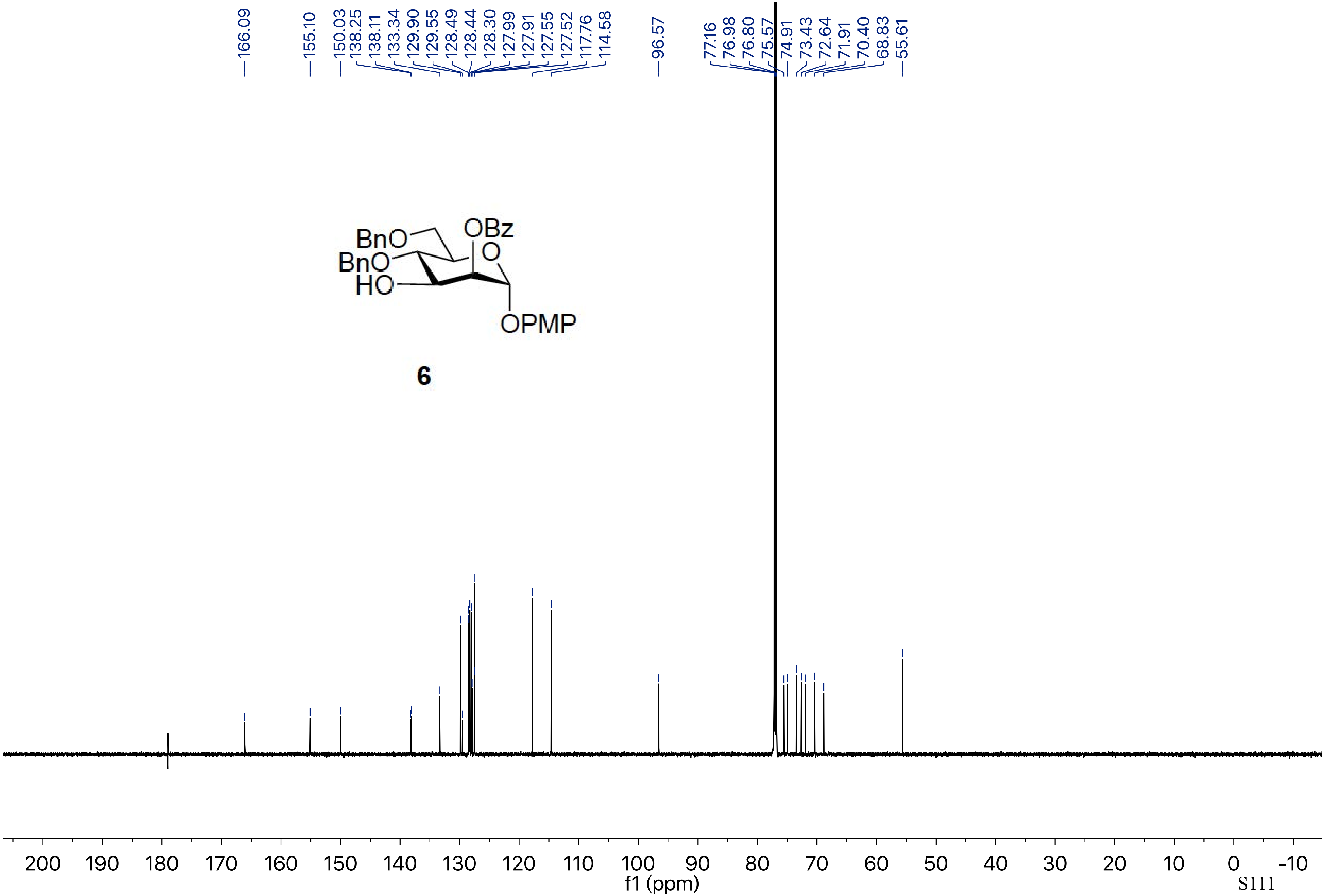
5



2015.03.11.v7_WL-5-028-prod_loc12_20.03_H1_1D — Lei, WL-5-028-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp

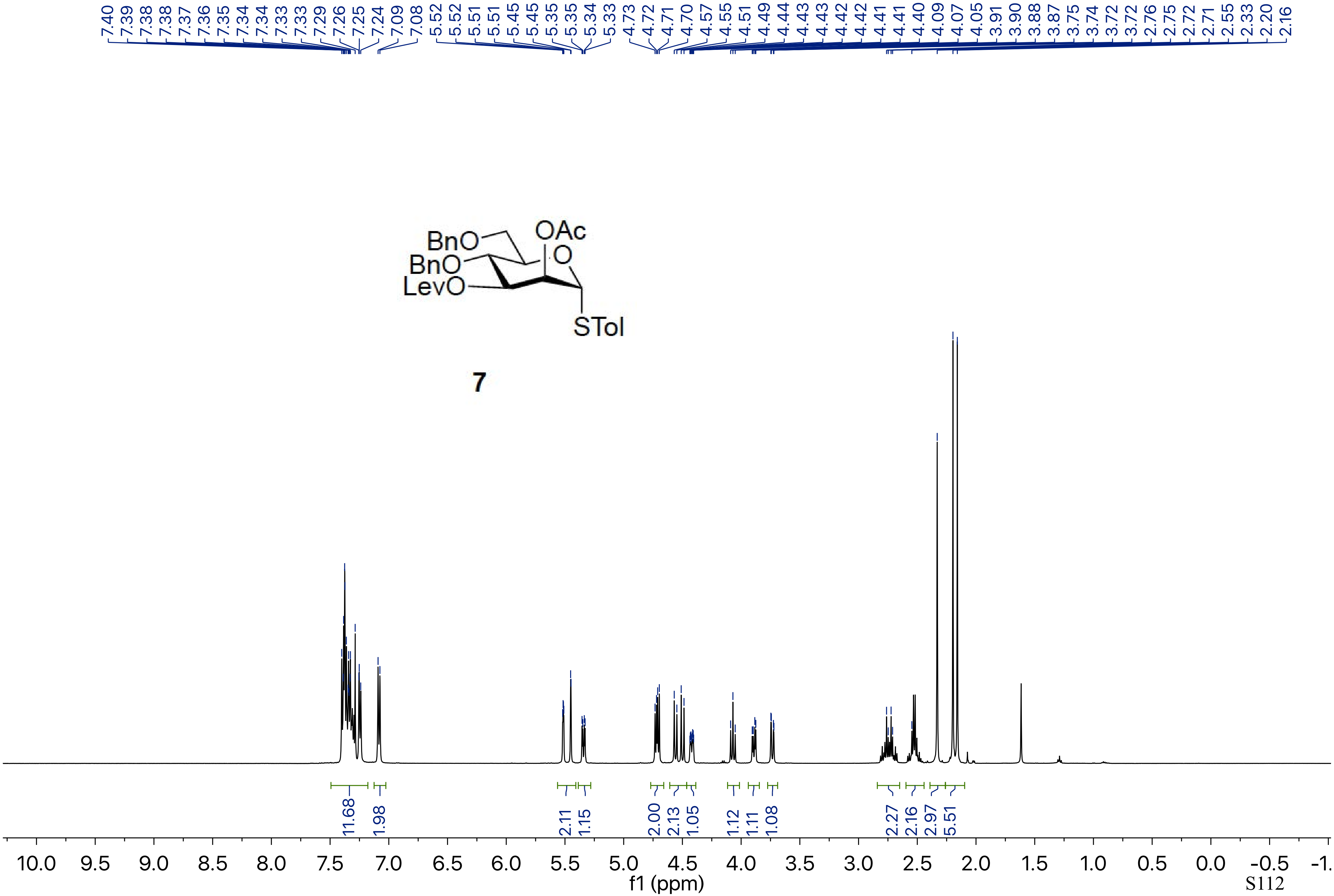


2015.03.11.v7_WL-5-028-prod_loc12_20.04_C13_1D — Lei, WL-5-028-prod — 175.976 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), tem

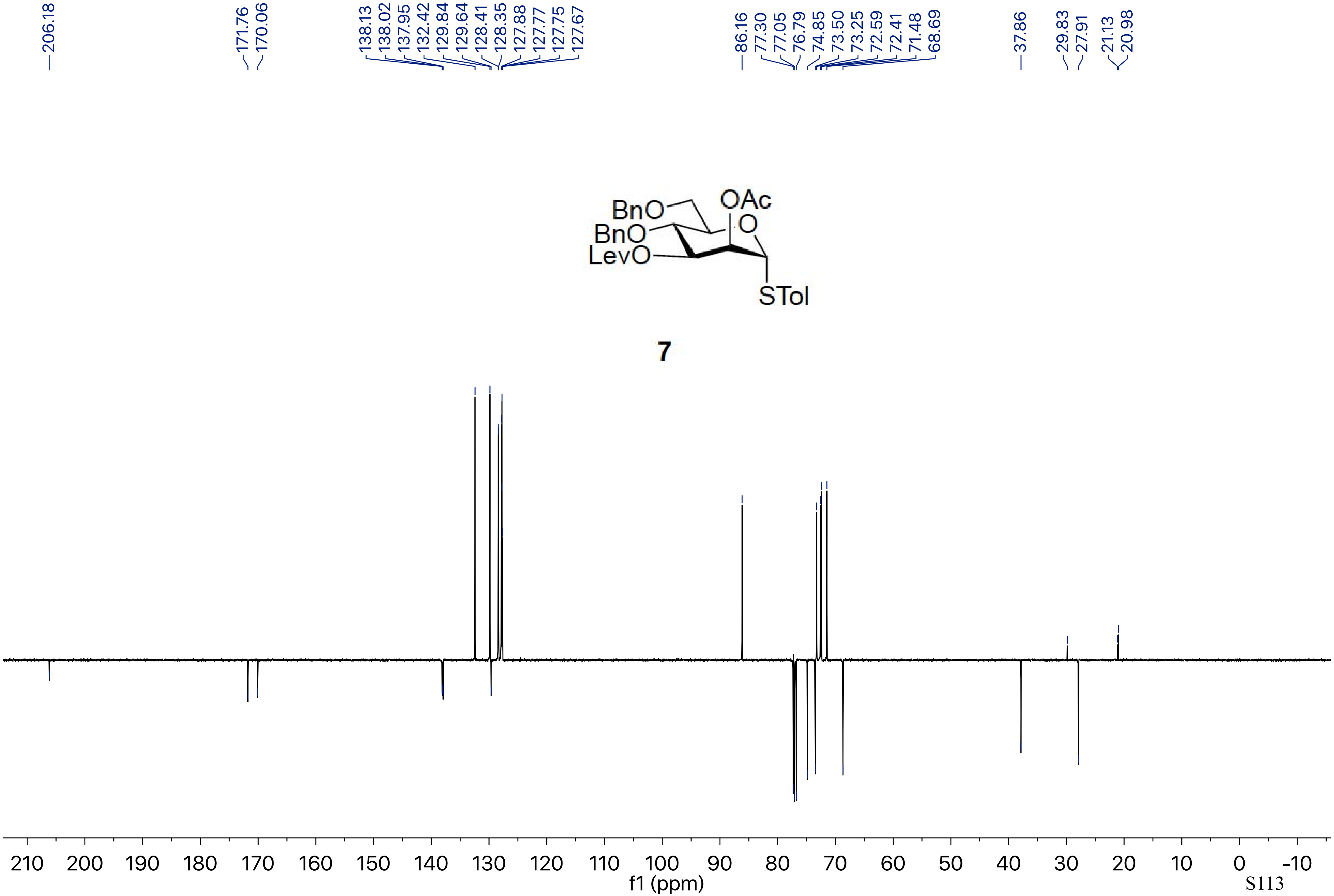


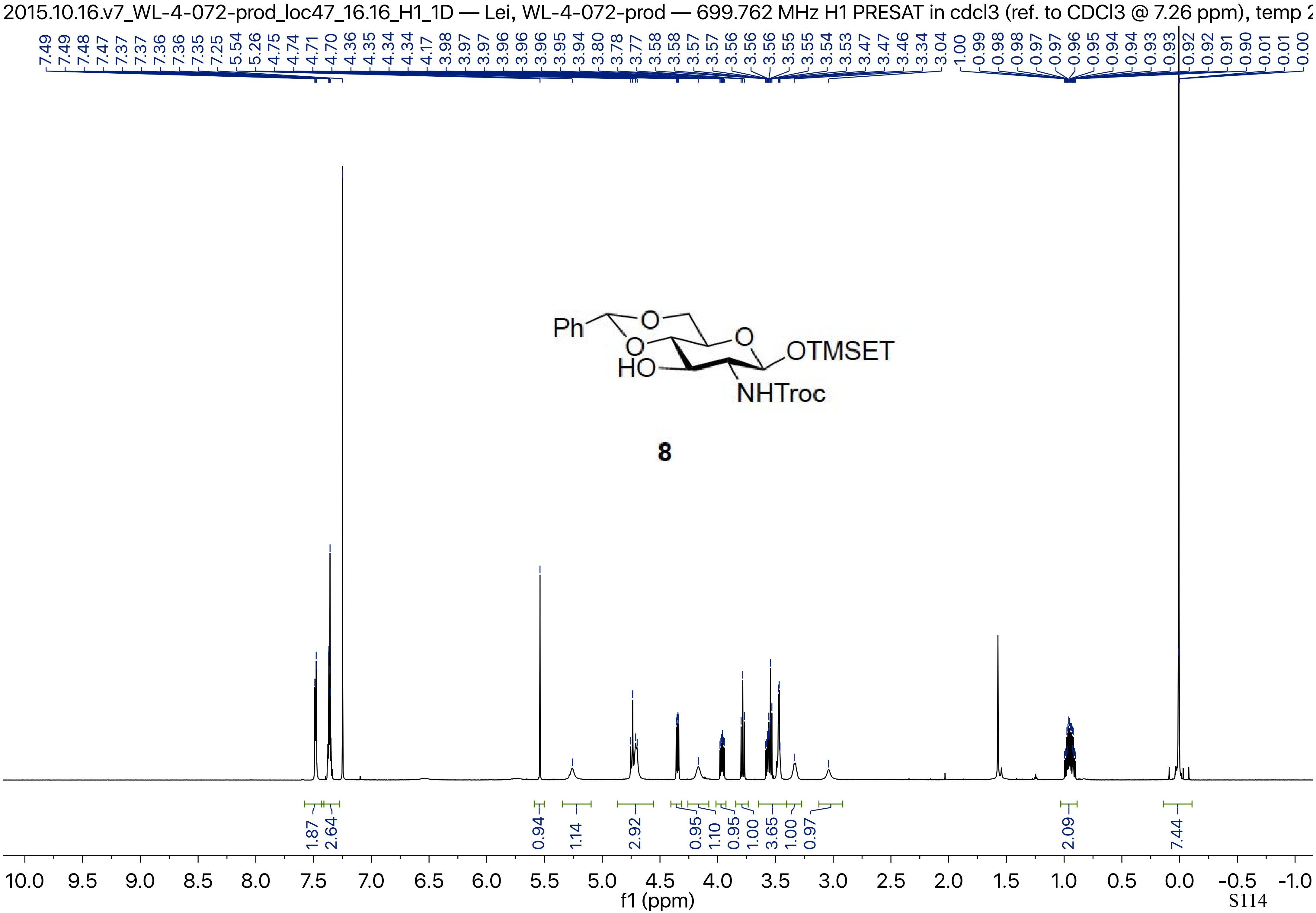
6

2015.05.15.u5_WL-5-061-PROD_loc11_16.50_H1_1D — Lei, WL-5-061-PROD — 499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), ten

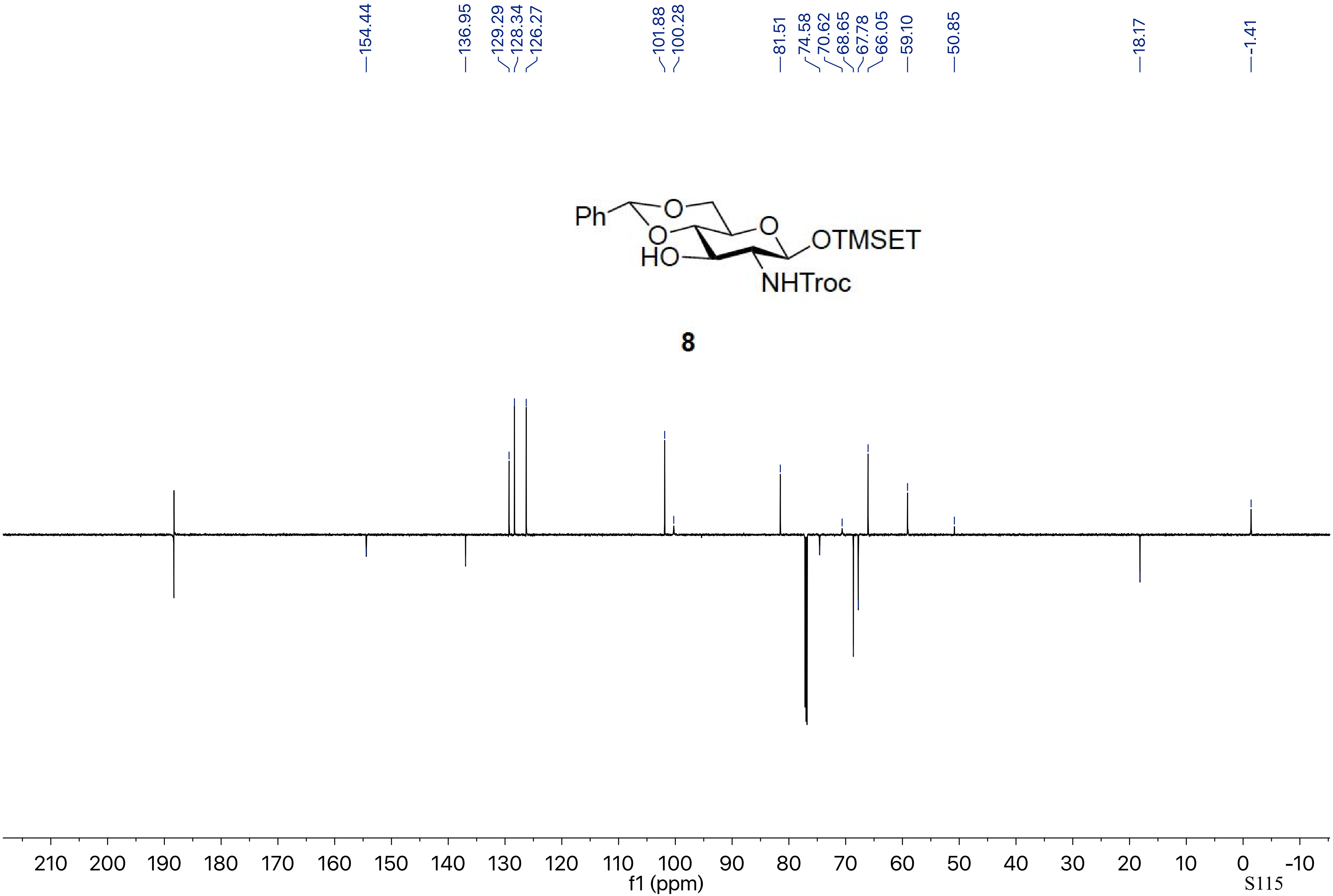


2015.05.15.u5_WL-5-061-PROD_loc11_16.52_C13_DEPTq — Lei, WL-5-061-PROD — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06

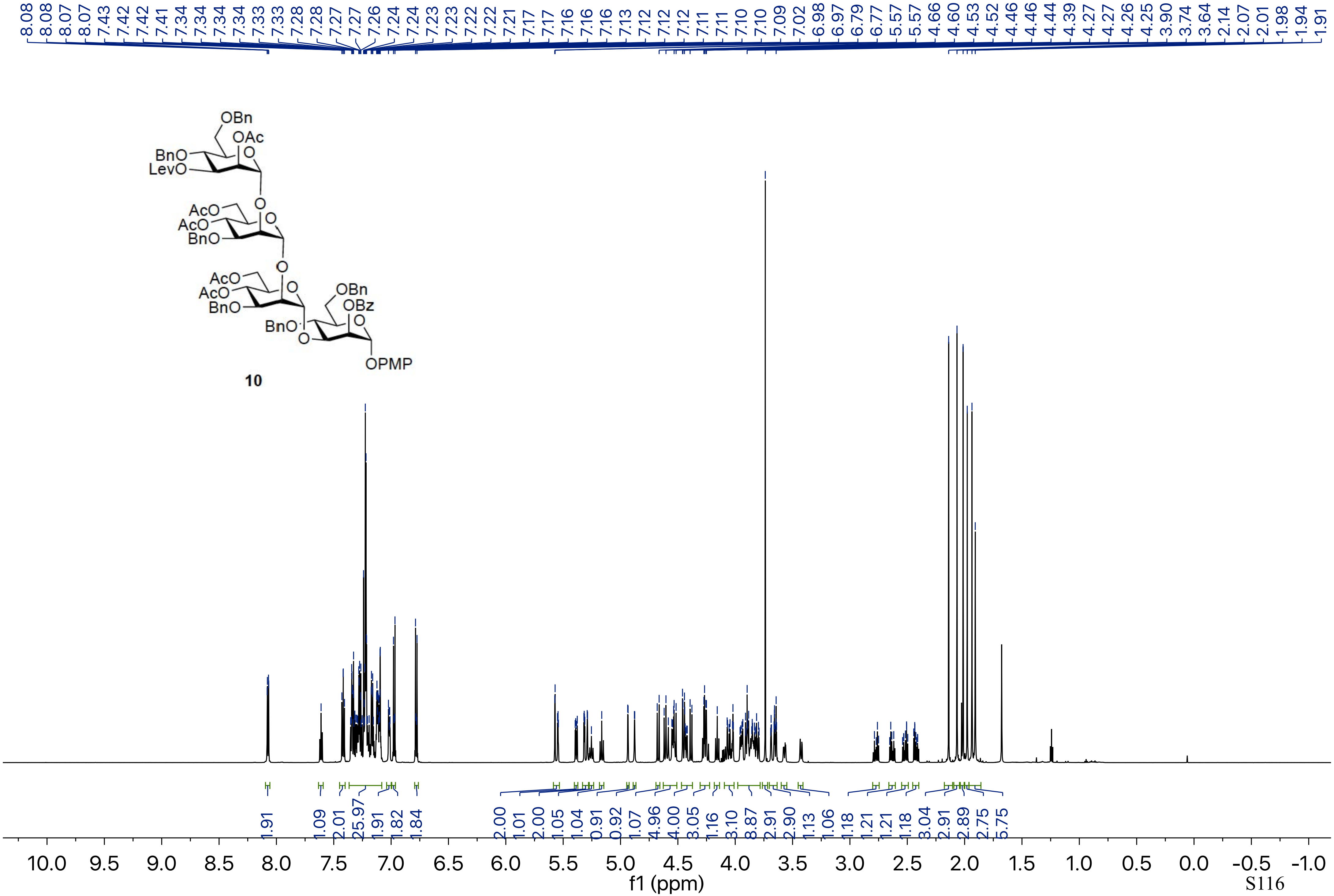



2015.10.16.v7_WL-4-072-prod_loc47_16.16_H1_1D — Lei, WL-4-072-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2
7.49 7.49 7.48 7.47 7.37 7.37 7.36 7.36 7.35 7.25 5.54 5.26 4.75 4.74 4.71 4.70 4.36 4.35 4.34 4.34 4.17 3.98 3.97 3.97 3.96 3.96 3.96 3.95 3.94 3.80 3.78 3.77 3.58 3.58 3.57 3.57 3.56 3.56 3.56 3.55 3.55 3.54 3.53 3.47 3.47 3.46 3.34 3.04 1.00 0.99 0.98 0.98 0.97 0.97 0.96 0.95 0.94 0.94 0.93 0.93 0.92 0.92 0.91 0.90 0.01 0.01 0.00
Ph
O
O
O
HO
OTMSET
NHTroc
8
1.87 2.64 0.94 1.14 2.92 0.95 1.10 0.95 1.00 3.65 1.00 0.97 2.09 7.44
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

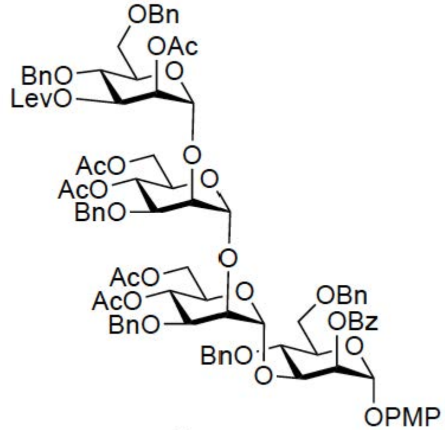
2015.10.16.v7_WL-4-072-prod_loc47_22.50_C13_DEPTq — Lei, WL-4-072-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp



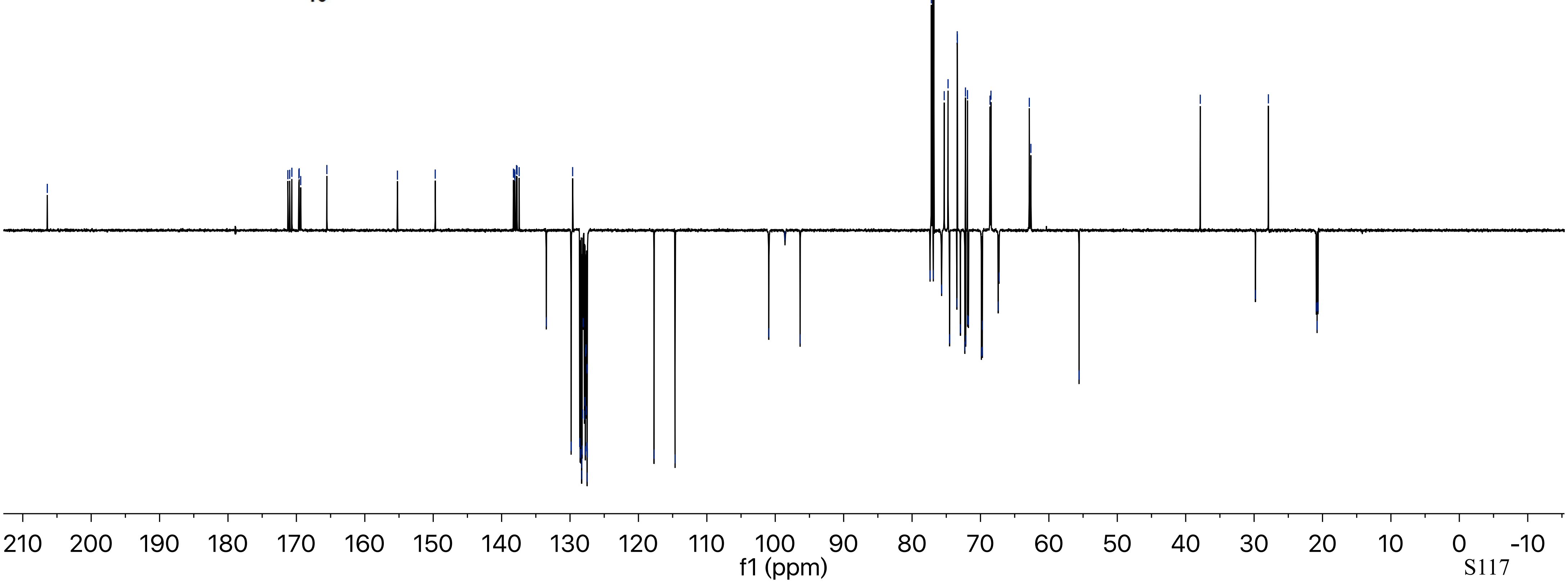
2015.06.25.v7_WL-5-063-prod_loc3_00.15_H1_1D — Lei, WL-5-063-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp :



2015.06.25.v7_WL-5-063-prod_loc3_00.17_C13_DEPTq — Lei, WL-5-063-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp



10

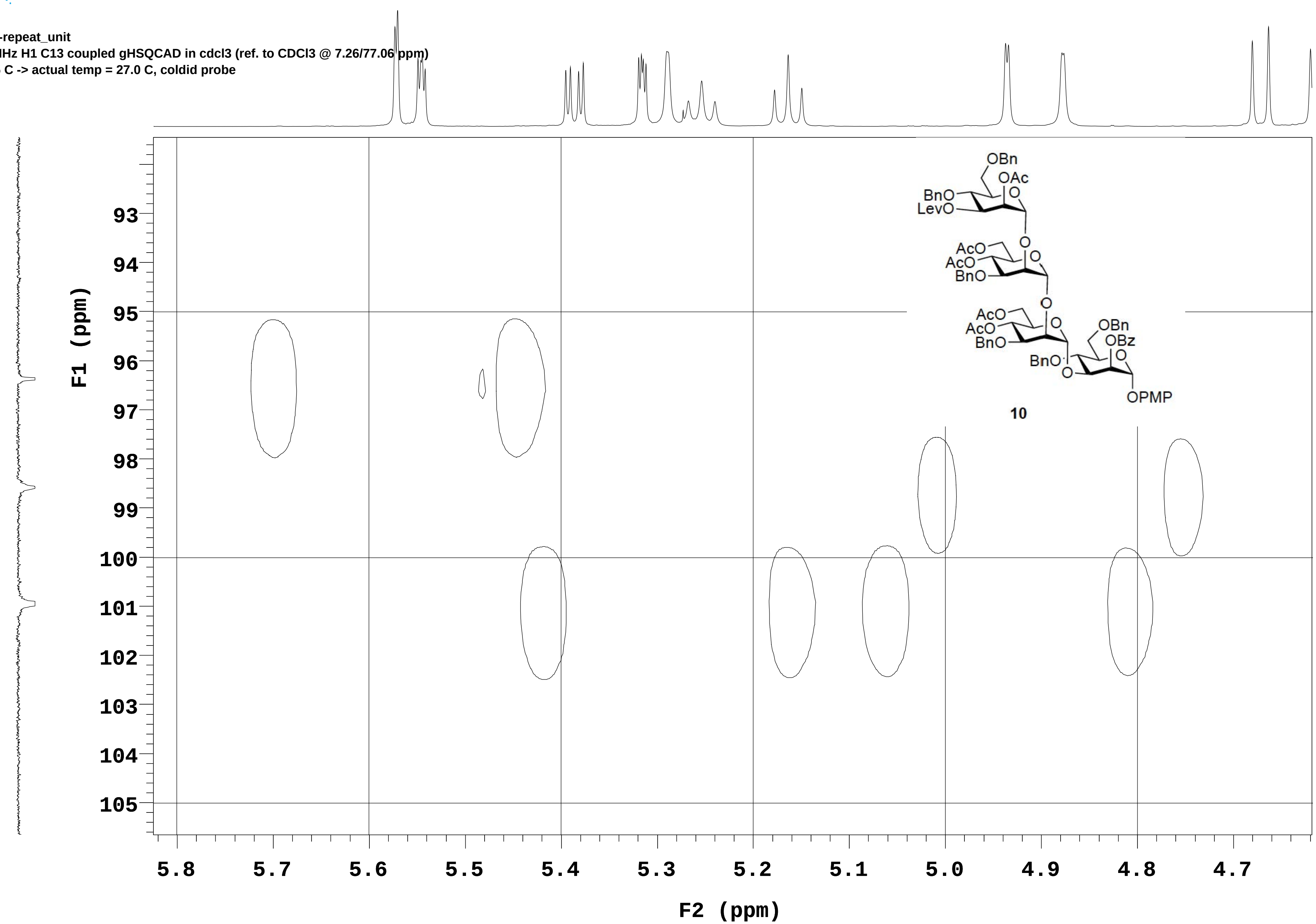


Department of Chemistry, University of Alberta

Agilent Technologies

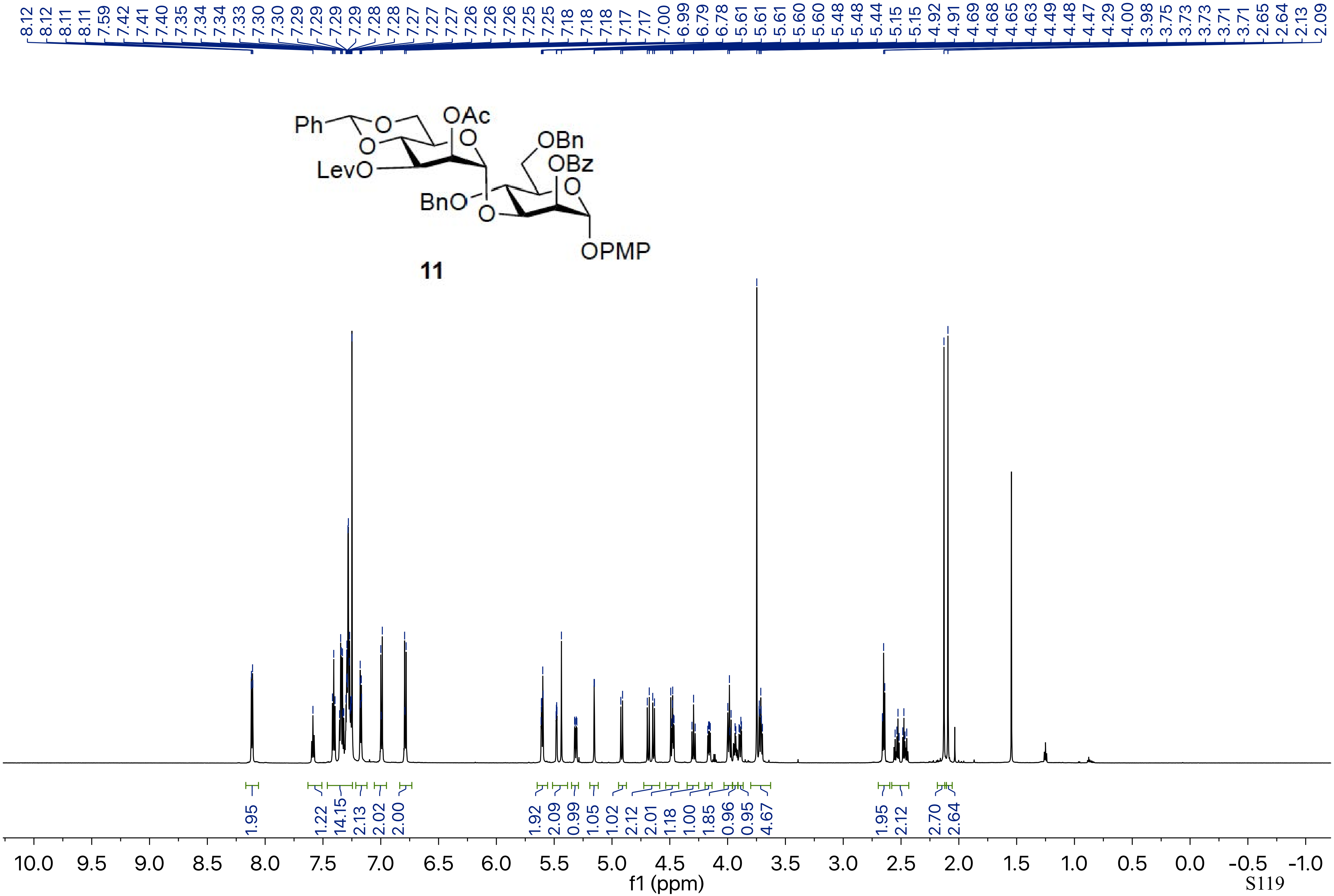
Recorded on: v700, Jan 16 2017
Pulse Sequence: gHSQCAD
Sweep Width F2|F1(Hz): 8389.26 | 38722.17
Digital Res. F2|F1(Hz/pt): 2.05 | 75.63
Acquisiton Time(s): 0.1
Hz per mm F2|F1(Hz/mm): 3.60 | 17.26
Relaxation Delay(s): 1.89999
No. of Scans|Increments 2 | 128

Lei, WL-5-repeat_unit
699.762 MHz H1 C13 coupled gHSQCAD in cdcl3 (ref. to CDCl3 @ 7.26/77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe

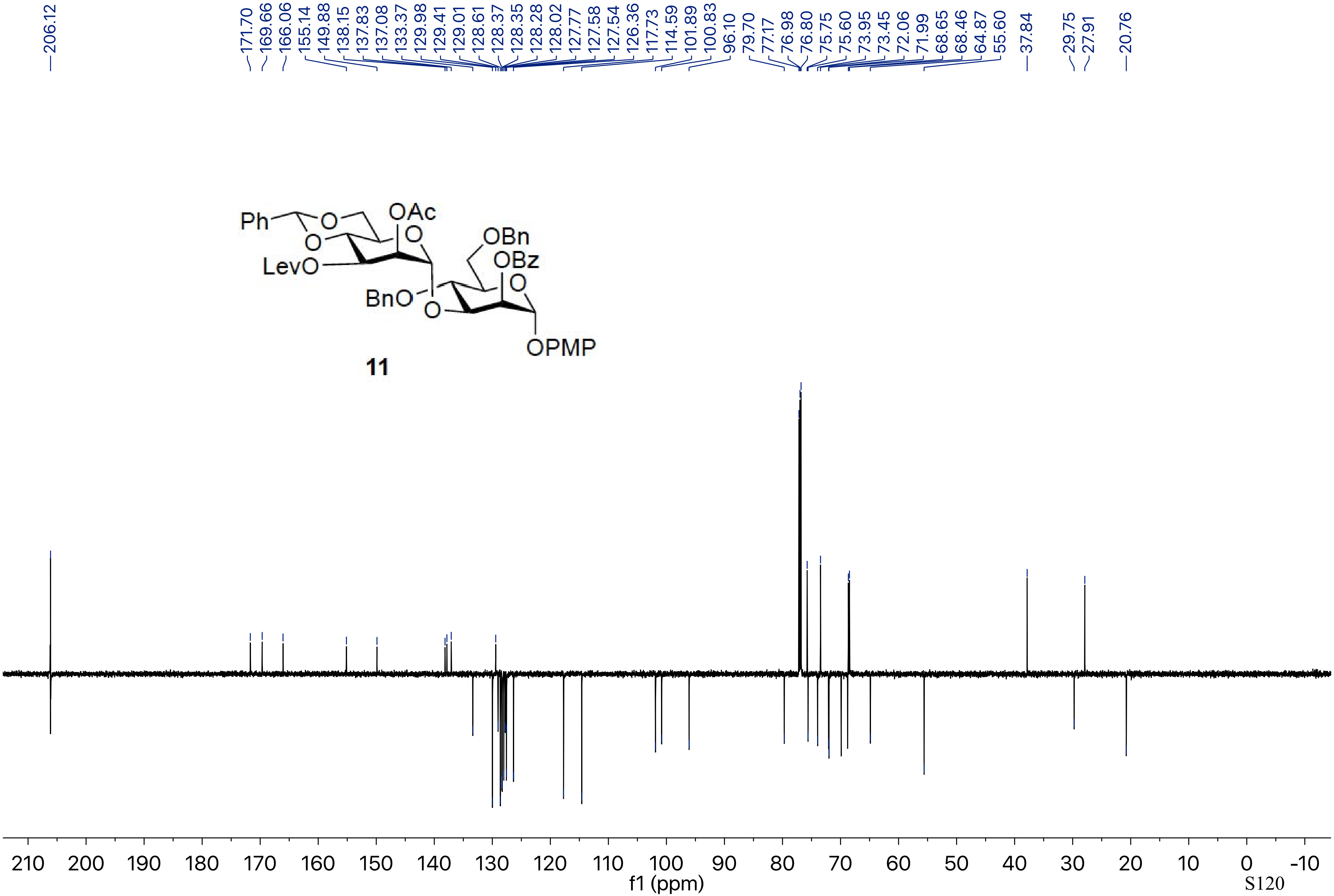


File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Lei/2017.01/2017.01.16.v7_WL-5-repeat_unit_loc48_09.36_coupled_H1_gHSQCAD

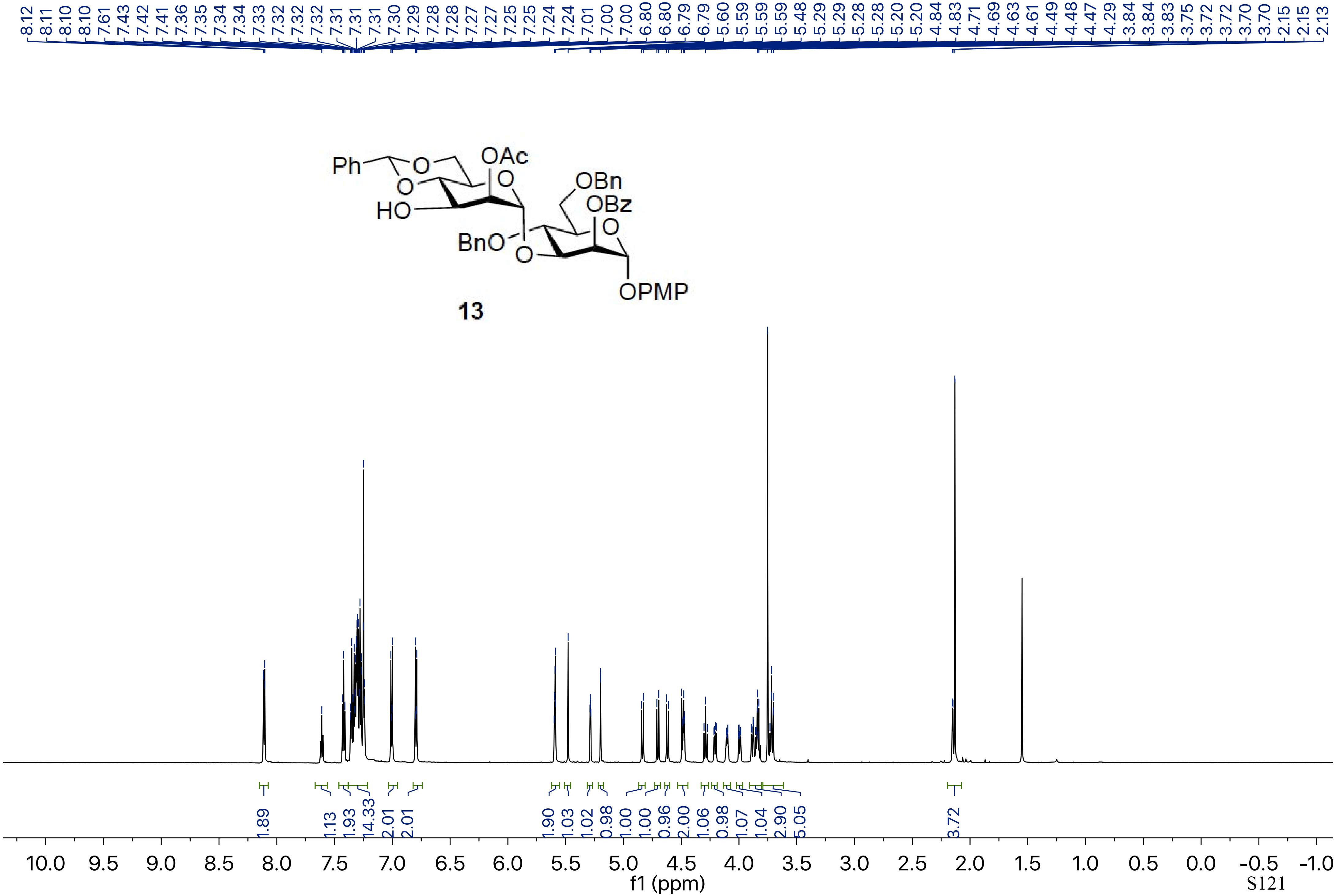
2016.08.16.v7_WL-6-057-prod_loc48_17.42_H1_1D — Lei, WL-6-057-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



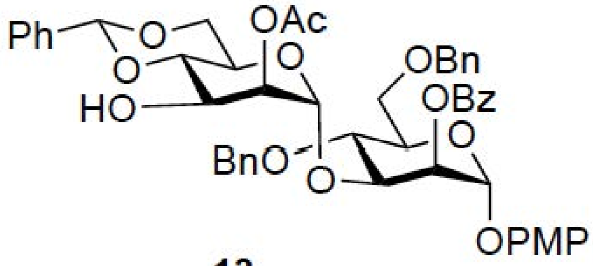
2016.08.16.v7_WL-6-057-prod_loc48_17.44_C13_DEPTq — Lei, WL-6-057-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



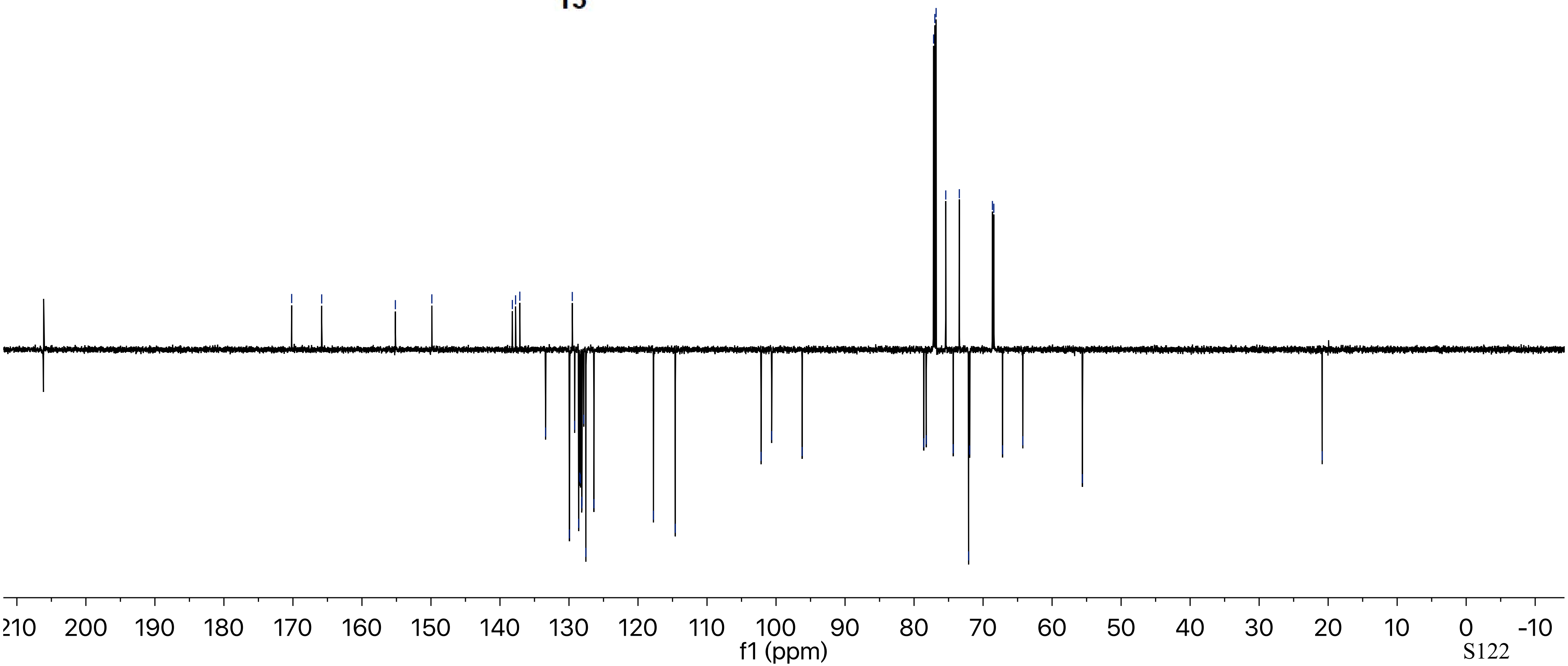
2016.08.17.v7_WL-6-060-prod_loc48_12.30_H1_1D — Lei, WL-6-060-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



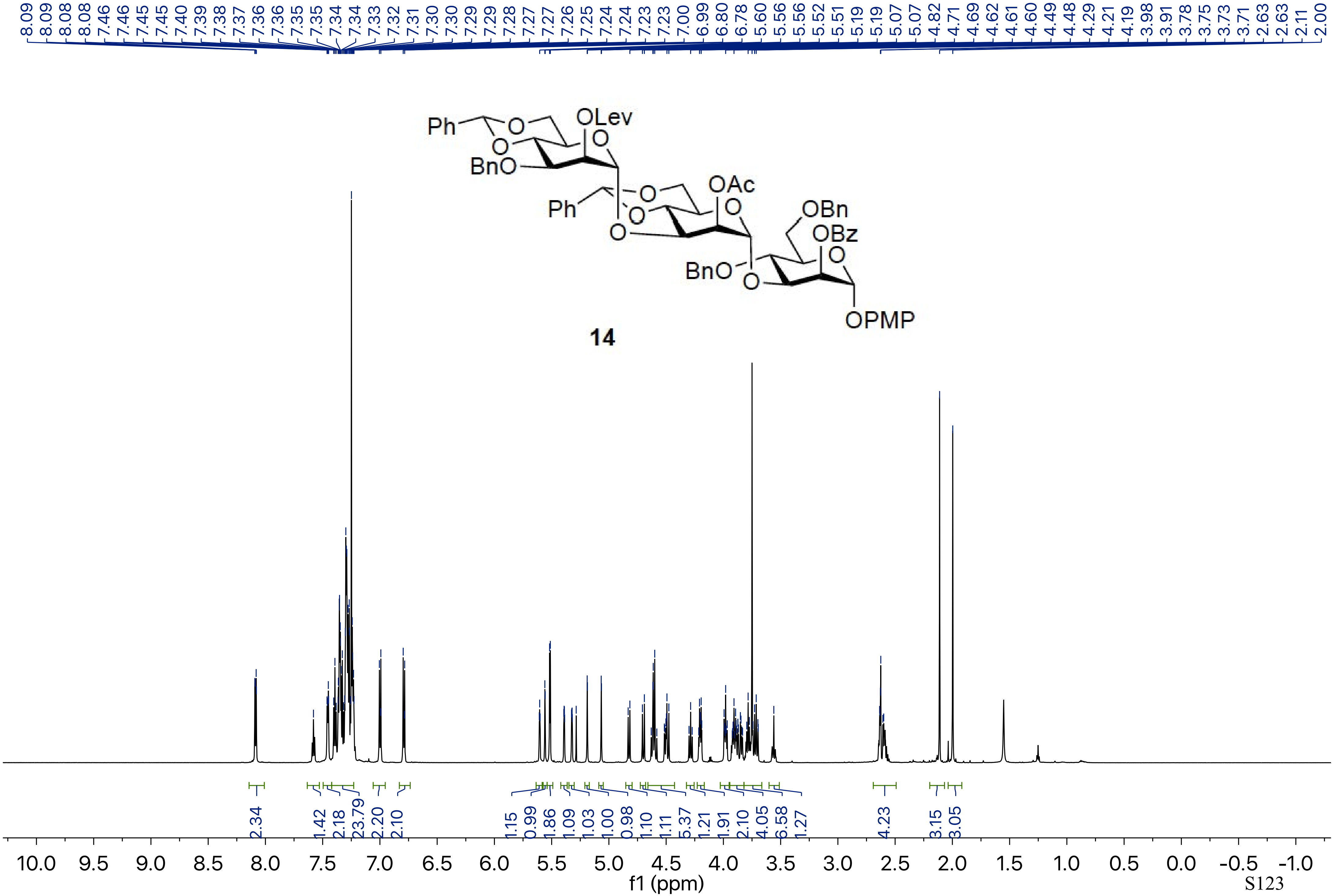
2016.08.17.v7_WL-6-060-prod_loc48_12.32_C13_DEPTq — Lei, WL-6-060-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



13

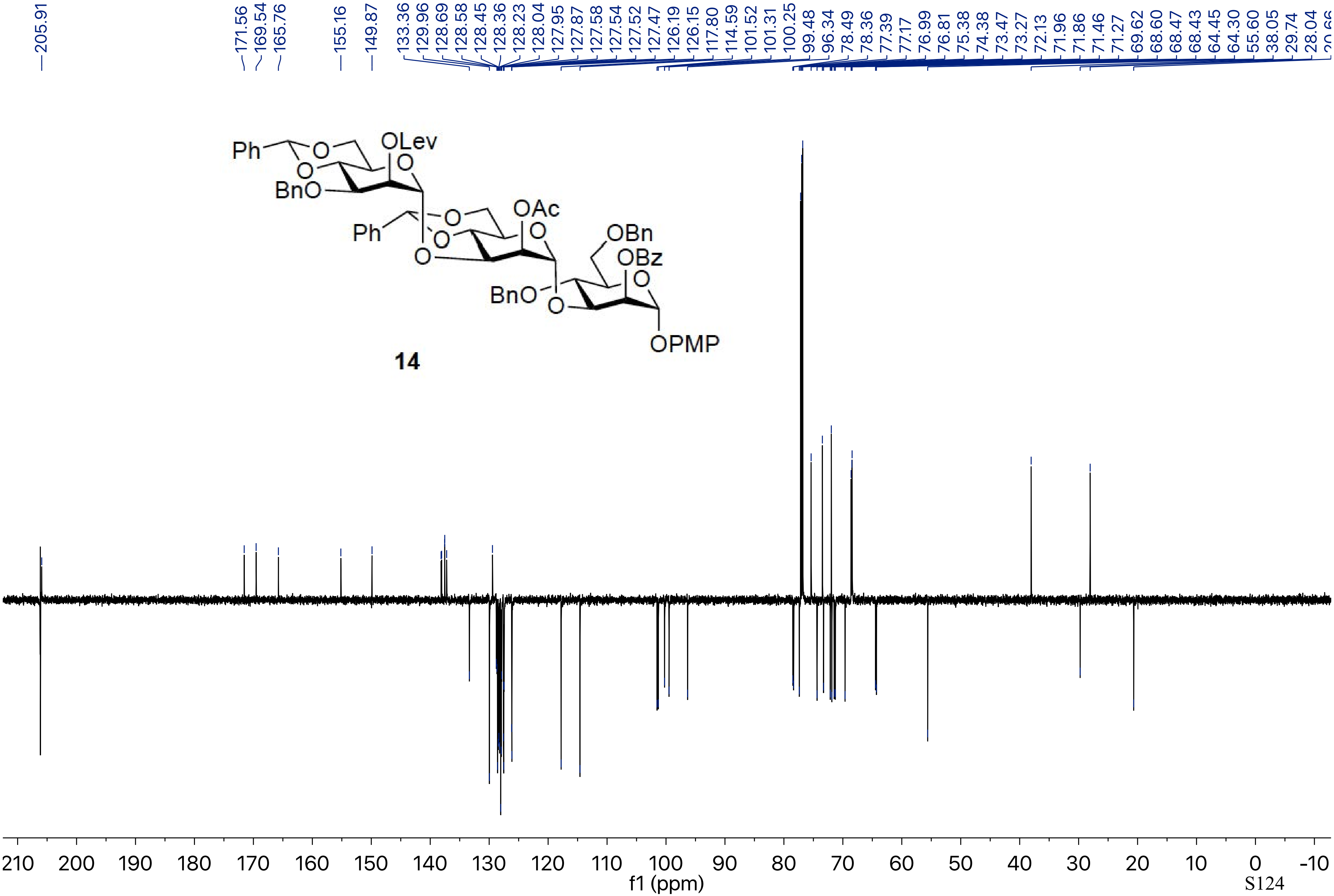


2016.08.17.v7_WL-6-061-prod_loc47_16.56_H1_1D — Lei, WL-6-061-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp

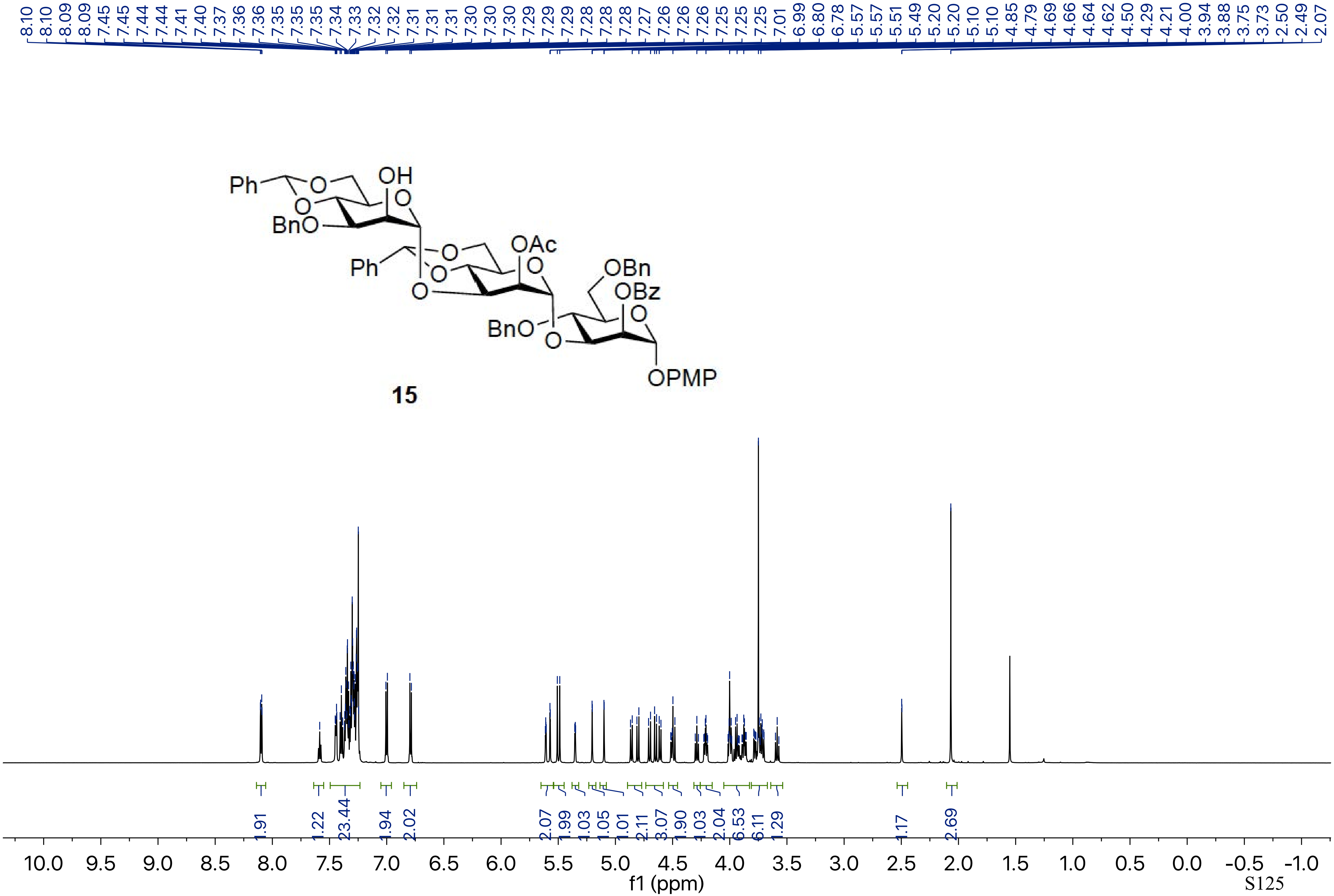


14

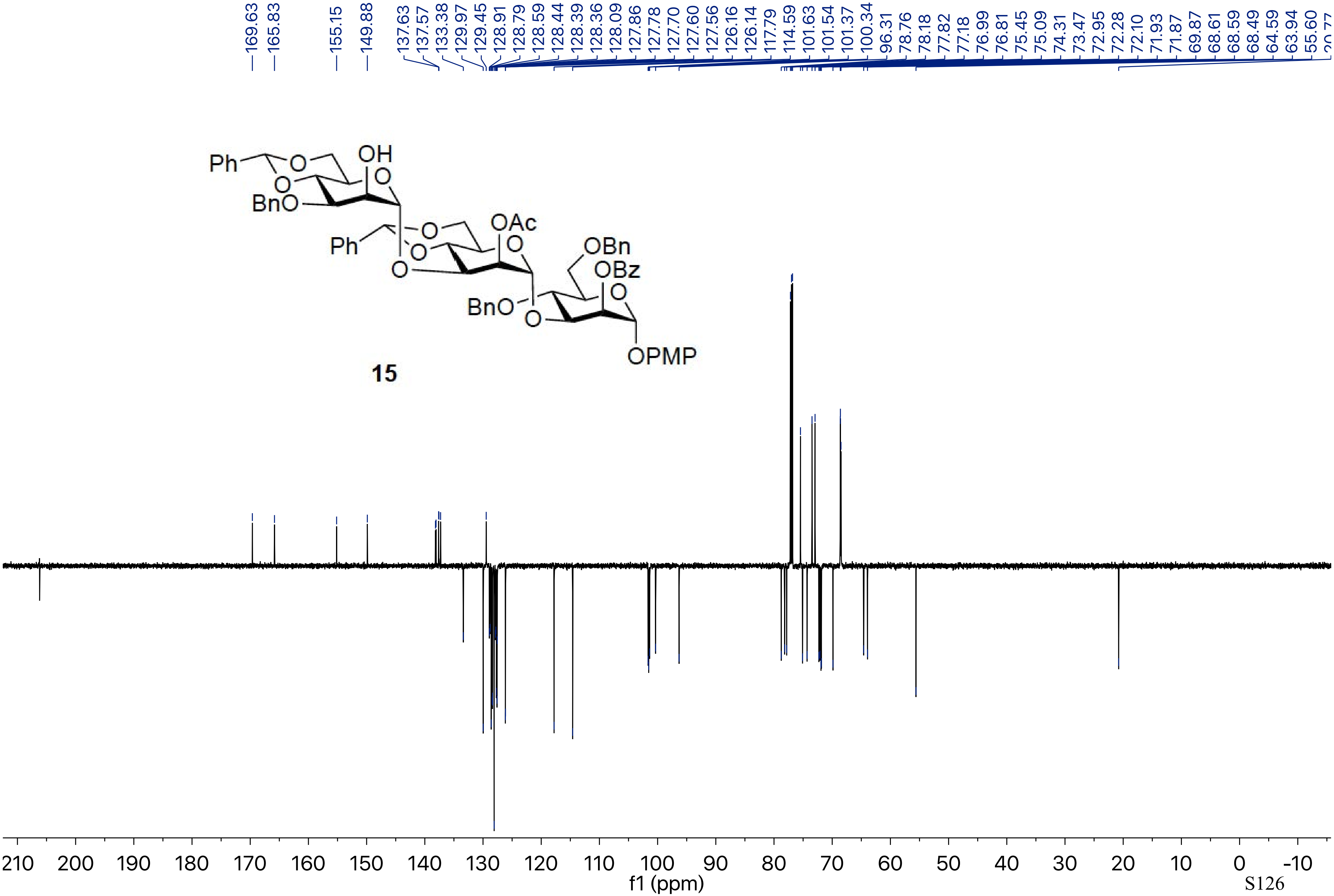
2016.08.17.v7_WL-6-061-prod_loc47_16.58_C13_DEPTq — Lei, WL-6-061-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp



2016.08.18.v7_WL-6-062-prod_loc47_13.57_H1_1D — Lei, WL-6-062-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp

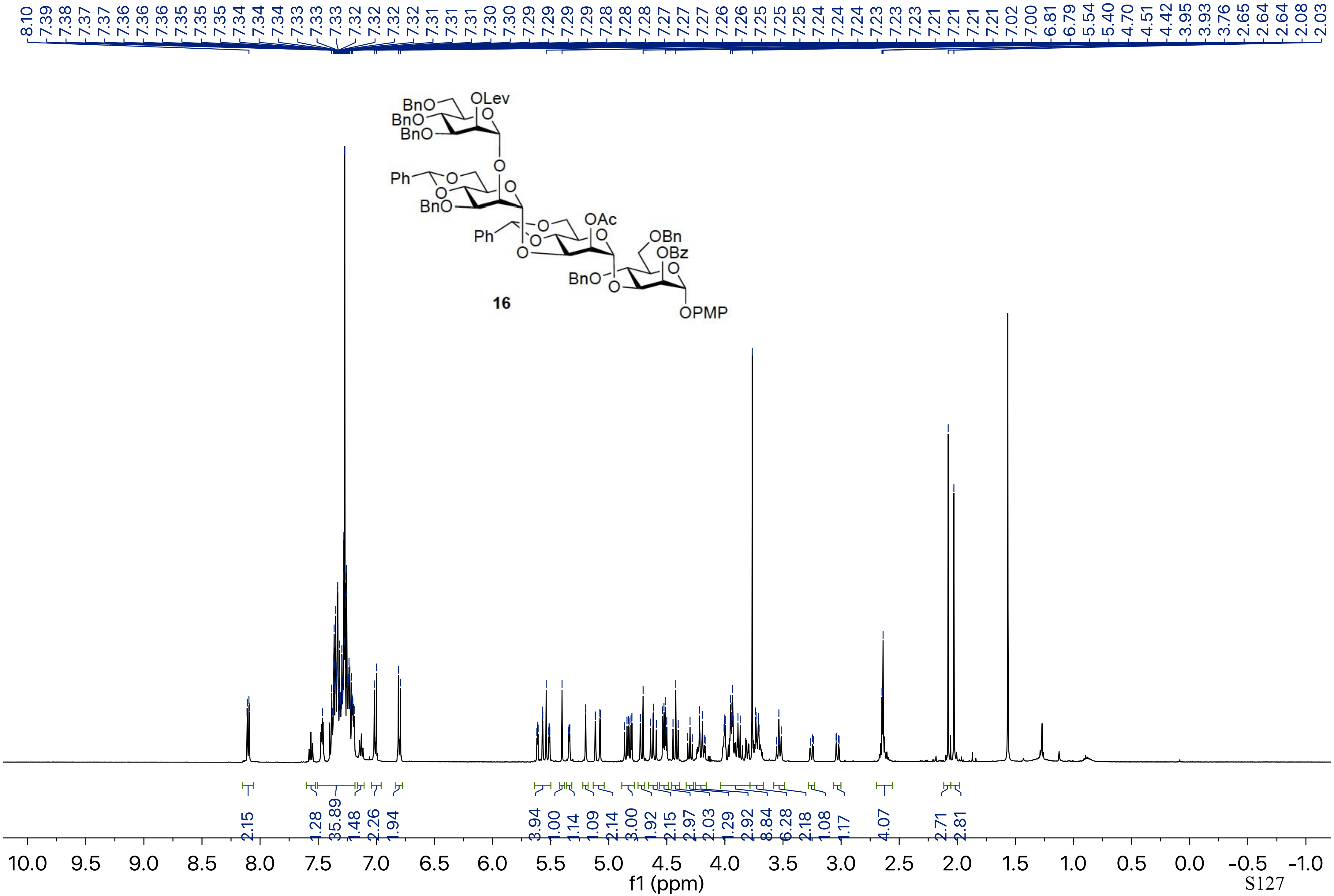


2016.08.18.v7_WL-6-062-prod_loc47_13.58_C13_DEPTq — Lei, WL-6-062-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p

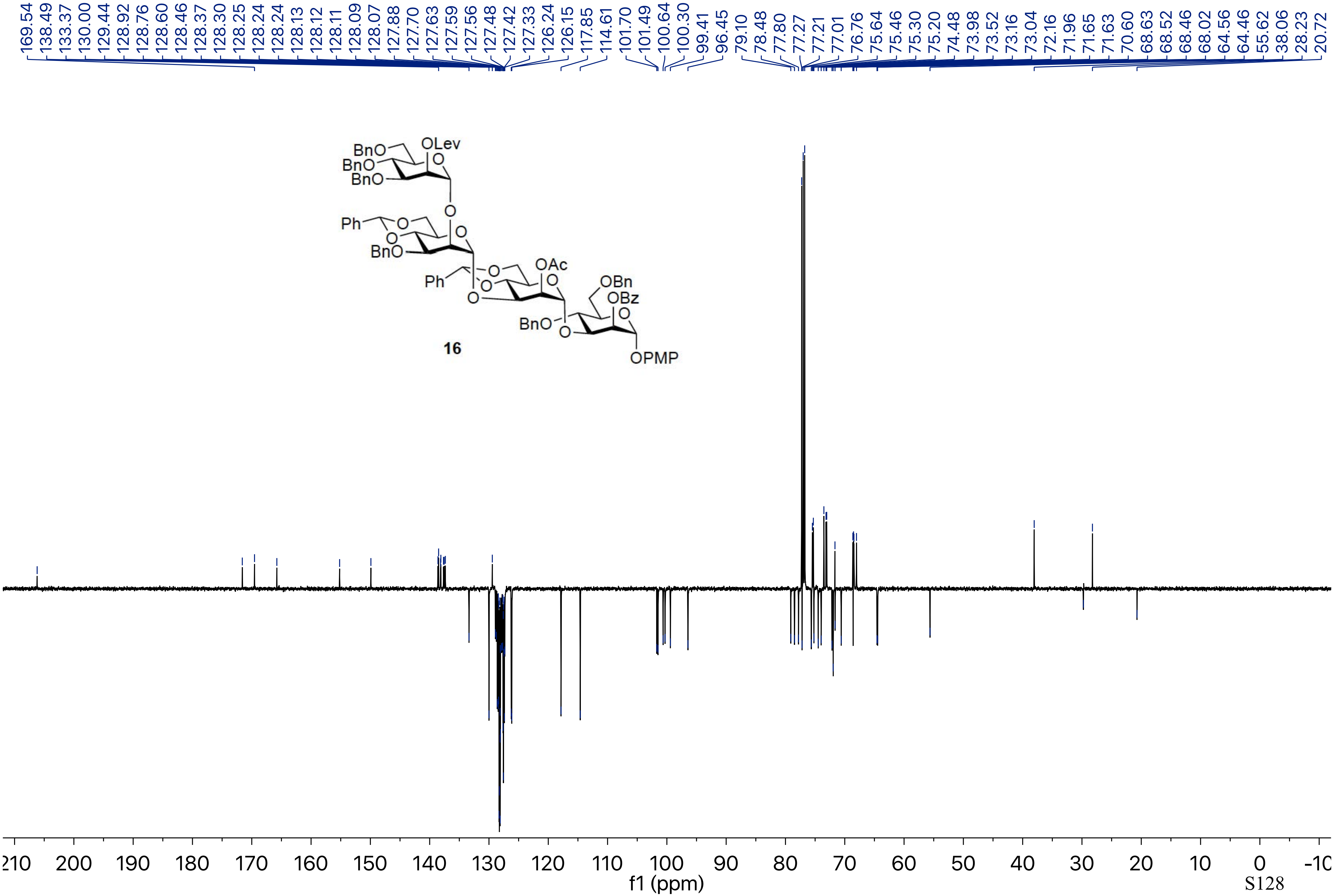


15

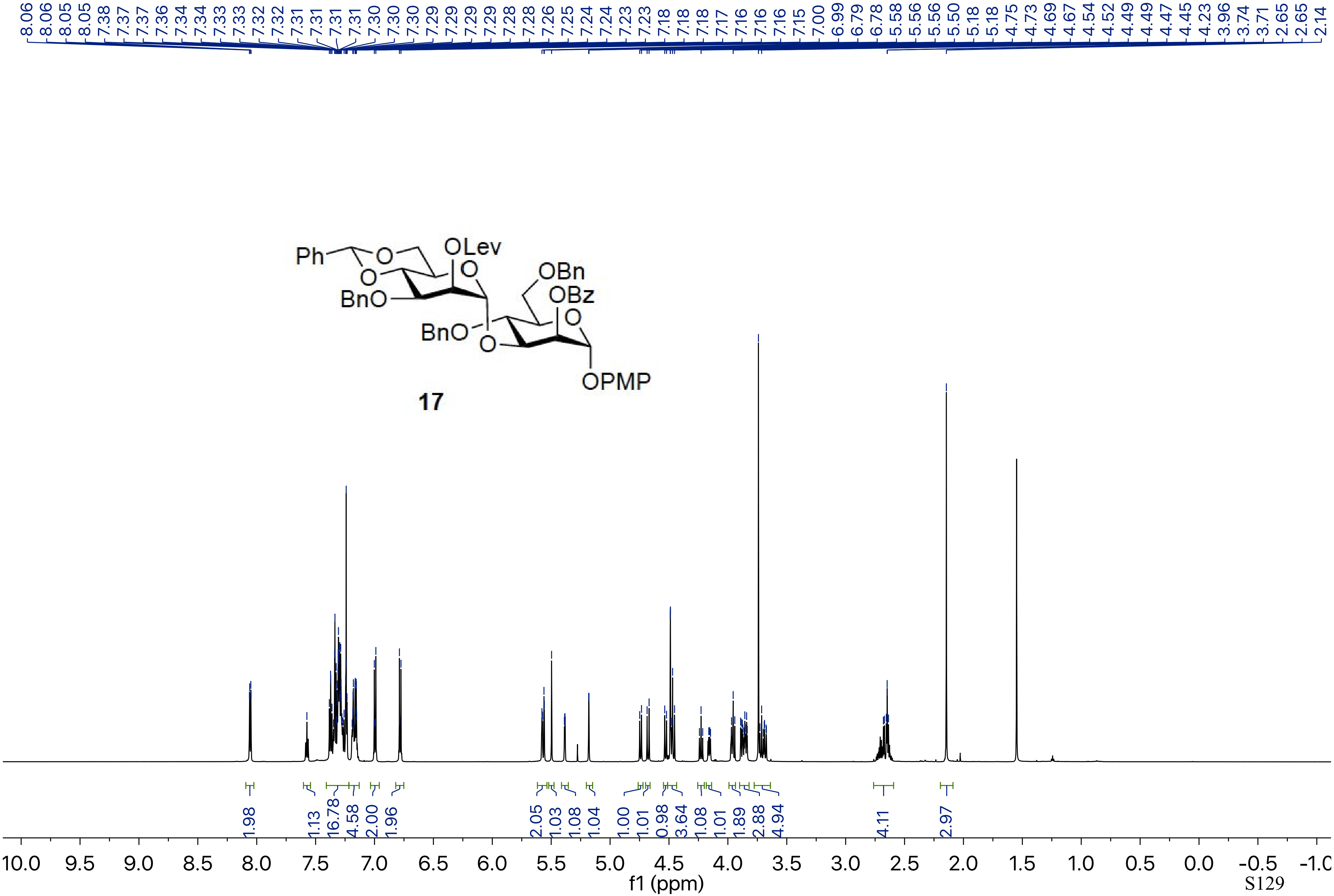
2016.08.19.u5_WL-6-063-prod_loc3_23.55_H1_1D — Lei, WL-6-063-prod — 499.797 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



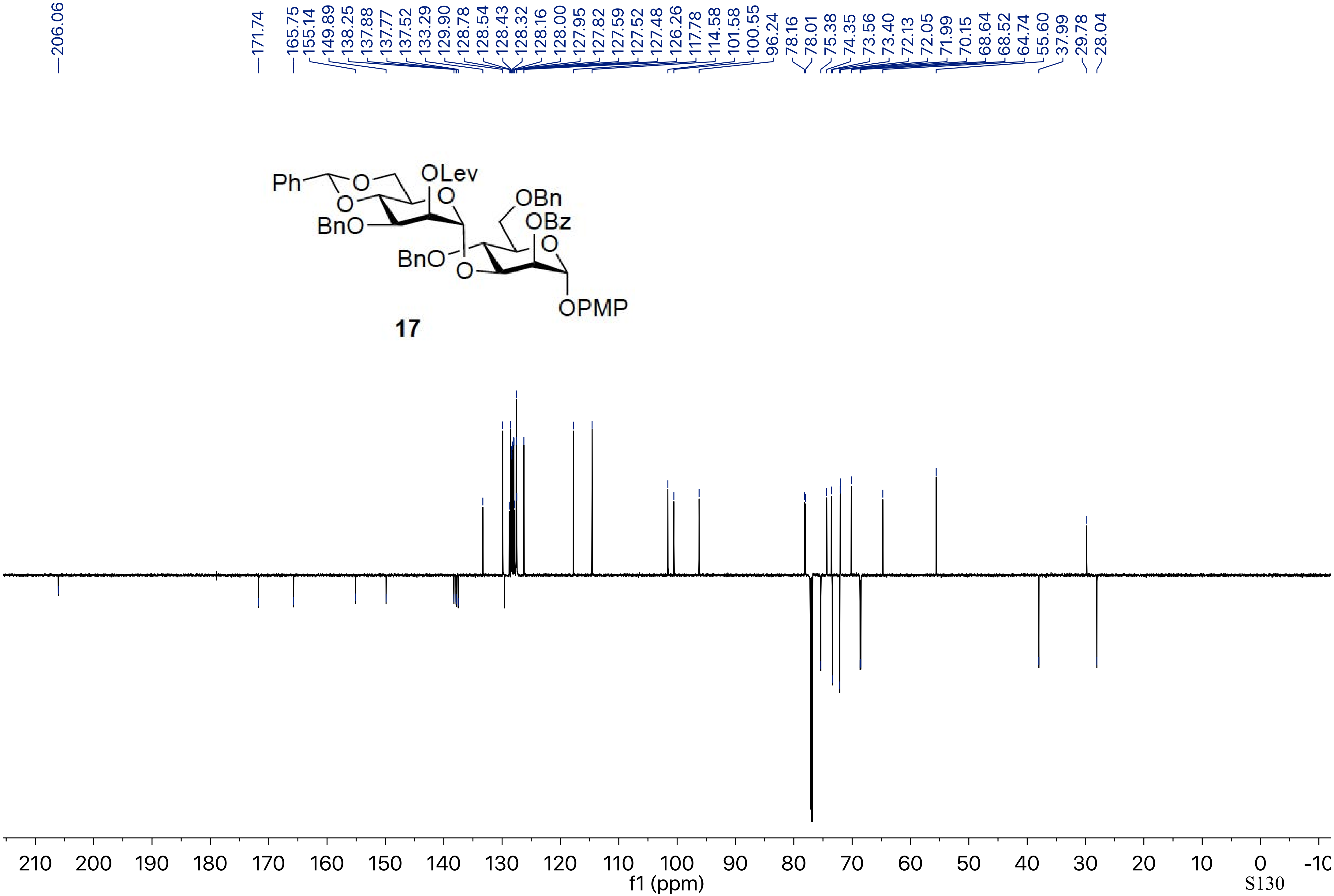
2016.08.20.u5_WL-6-063-prod_loc3_00.04_C13_DEPTq — Lei, WL-6-063-prod — 125.688 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p

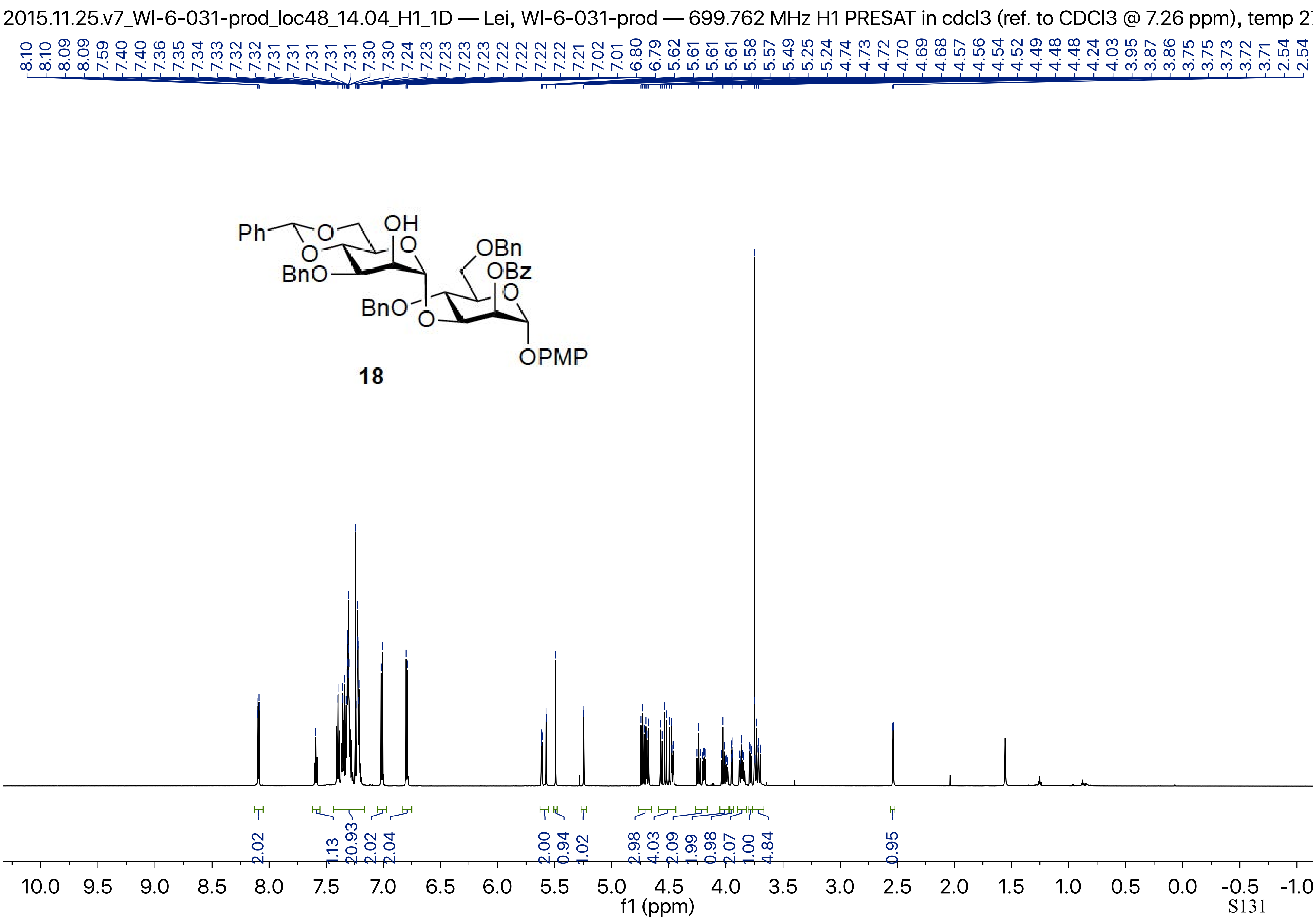


2015.06.5.v7_WL-5-080-prod_loc27_17.22_H1_1D — Lei, WL-5-080-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2

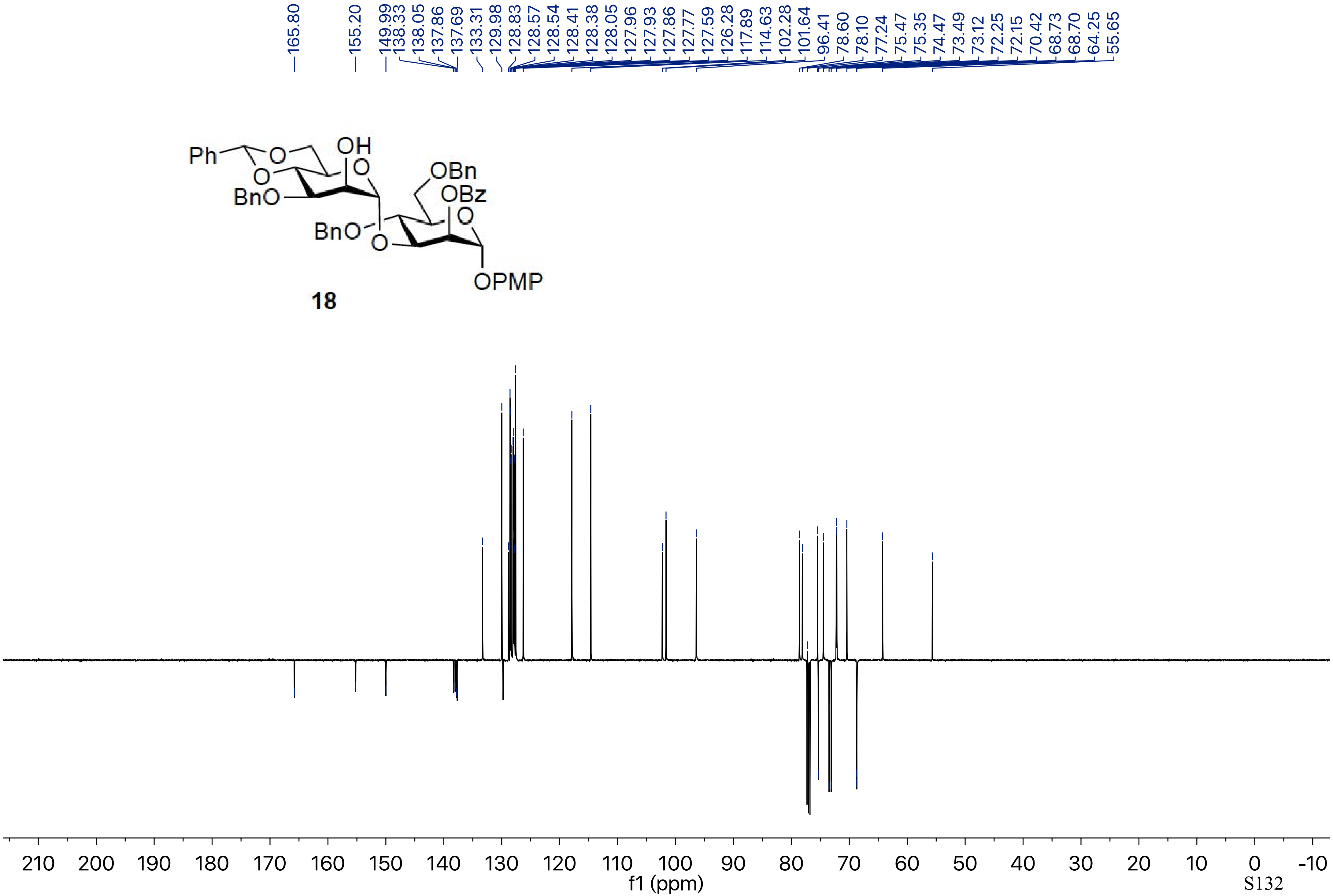


2015.06.5.v7_WL-5-080-prod_loc27_22.57_C13_DEPTq — Lei, WL-5-080-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp

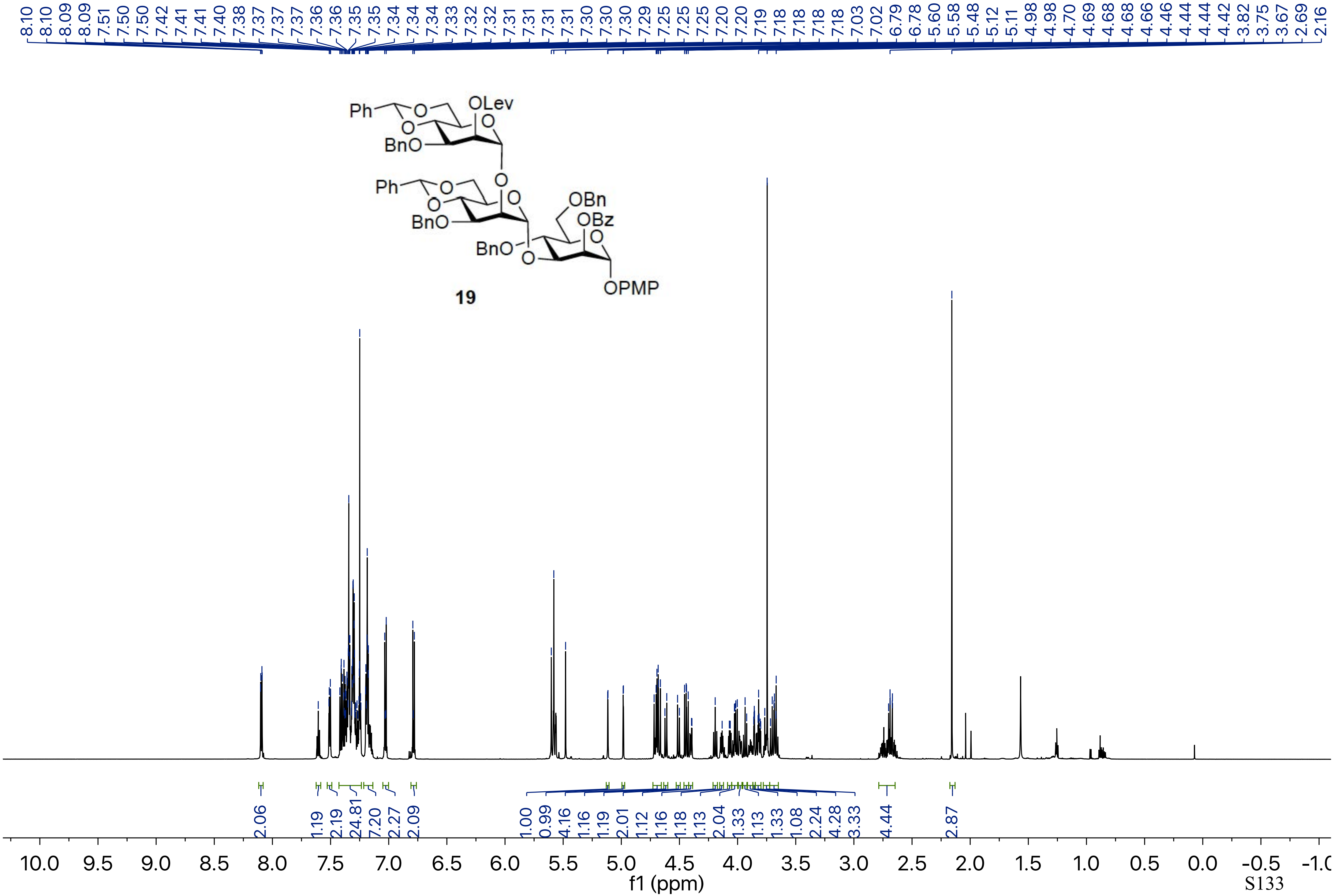



2015.11.25.v7_WI-6-031-prod_loc48_14.04_H1_1D — Lei, WI-6-031-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2
8.10 8.10 8.09 8.09 7.59 7.40 7.40 7.36 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.31 7.31 7.31 7.30 7.30 7.24 7.23 7.23 7.23 7.23 7.22 7.22 7.22 7.22 7.22 7.21 7.02 7.01 6.80 6.79 5.62 5.61 5.61 5.61 5.58 5.57 5.49 5.25 5.24 4.74 4.73 4.72 4.70 4.69 4.68 4.57 4.56 4.54 4.52 4.49 4.48 4.48 4.24 4.03 3.95 3.87 3.86 3.75 3.75 3.73 3.72 3.71 2.54 2.54
Ph
O
OH
BnO
OBn
OBz
BnO
OPMP
18
2.02 1.13 20.93 2.02 2.04 2.00 0.94 1.02 2.98 4.03 2.09 1.99 0.98 2.07 1.00 4.84 0.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

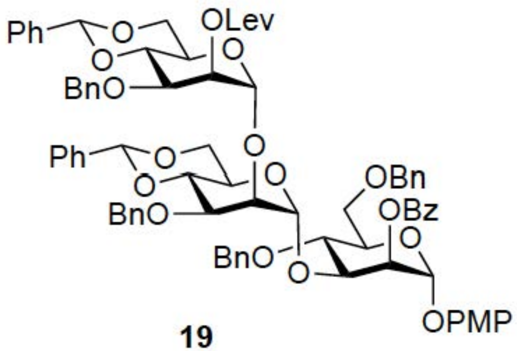
2015.11.25.u5_WL-6-031-prod_loc12_14.37_C13_DEPTq — Lei, WL-6-031-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp



2015.11.26.v7_WL-6-032-prod_loc48_15.51_H1_1D — Lei, WL-6-032-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



2015.11.27.u5_WL-6-032-prod_loc12_10.05_C13_DEPTq — Lei, WL-6-032-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp



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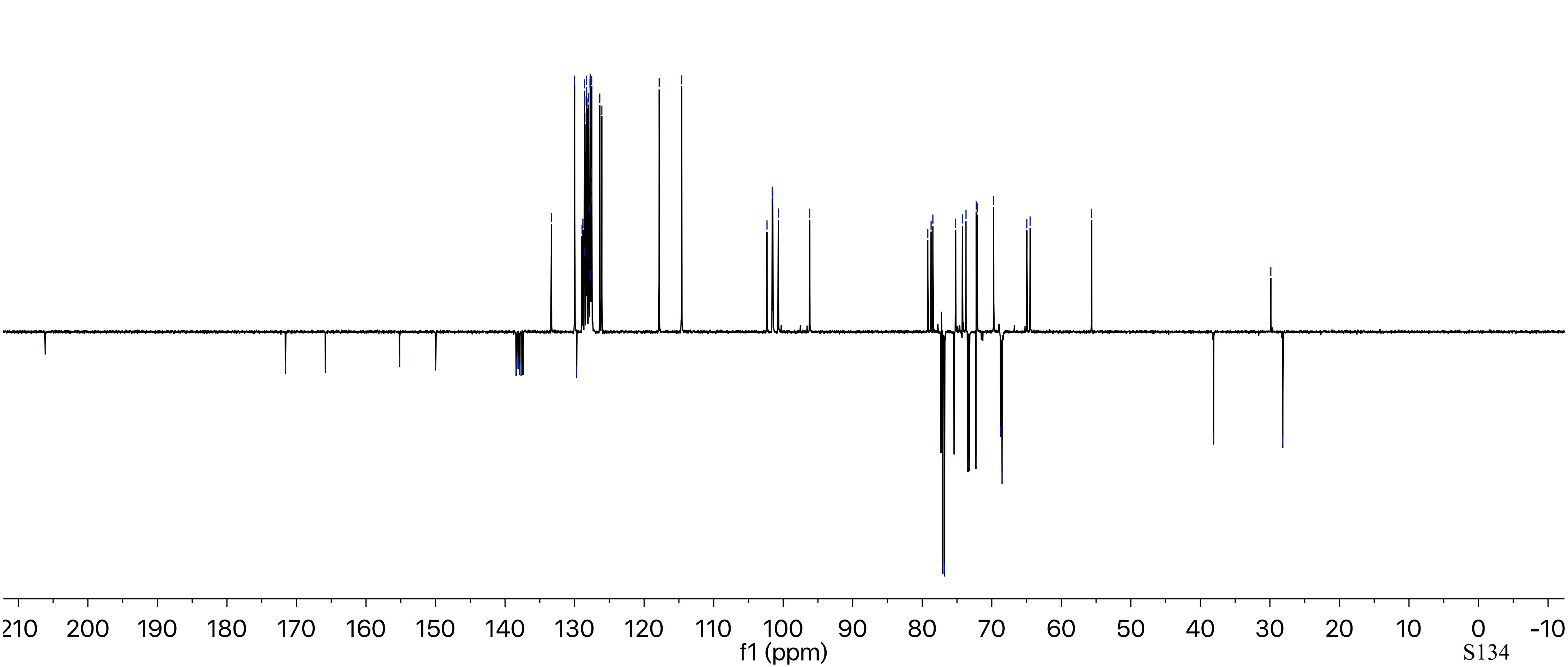
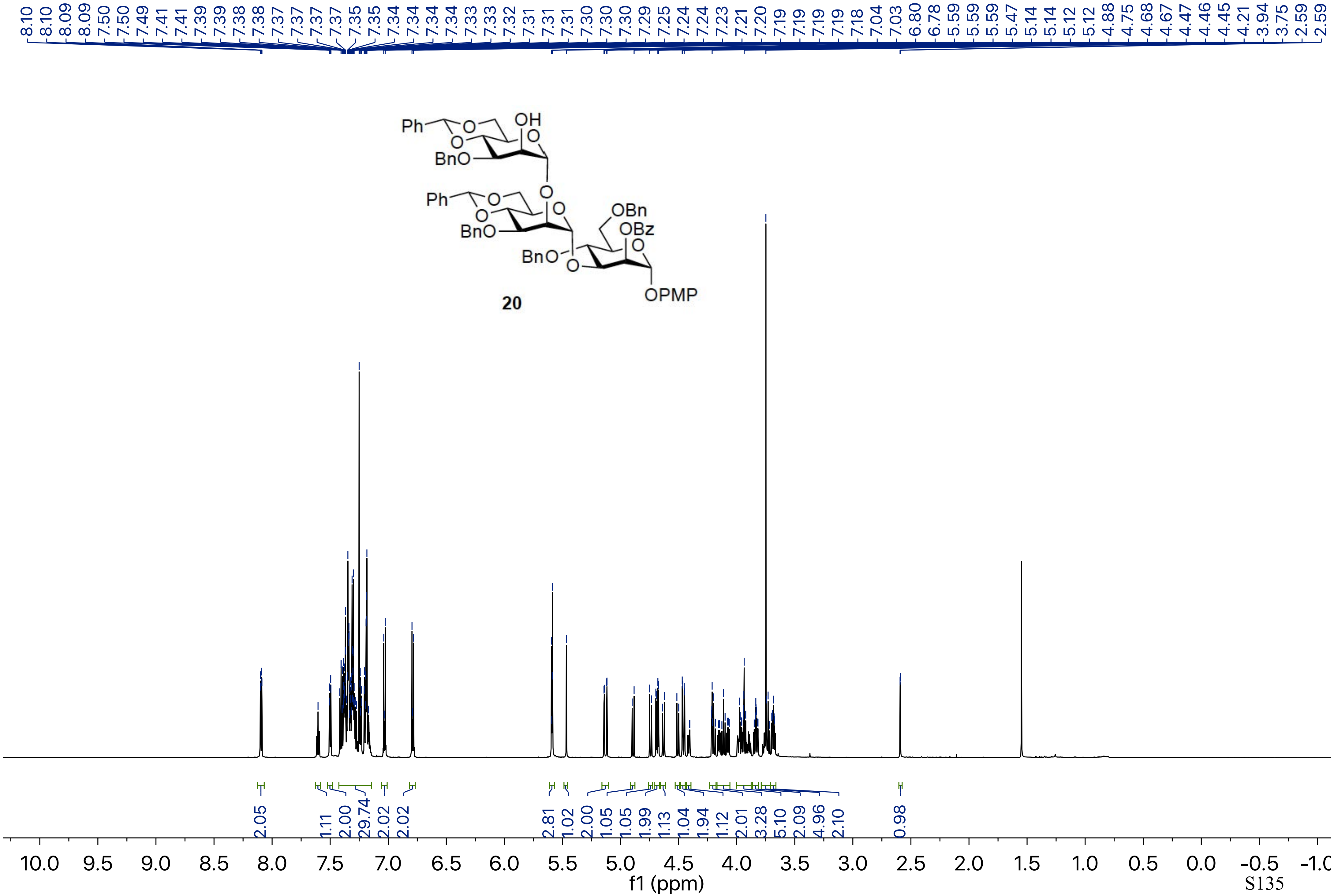
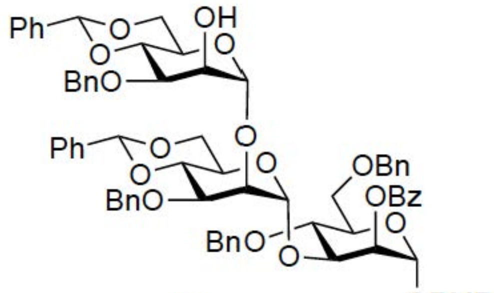


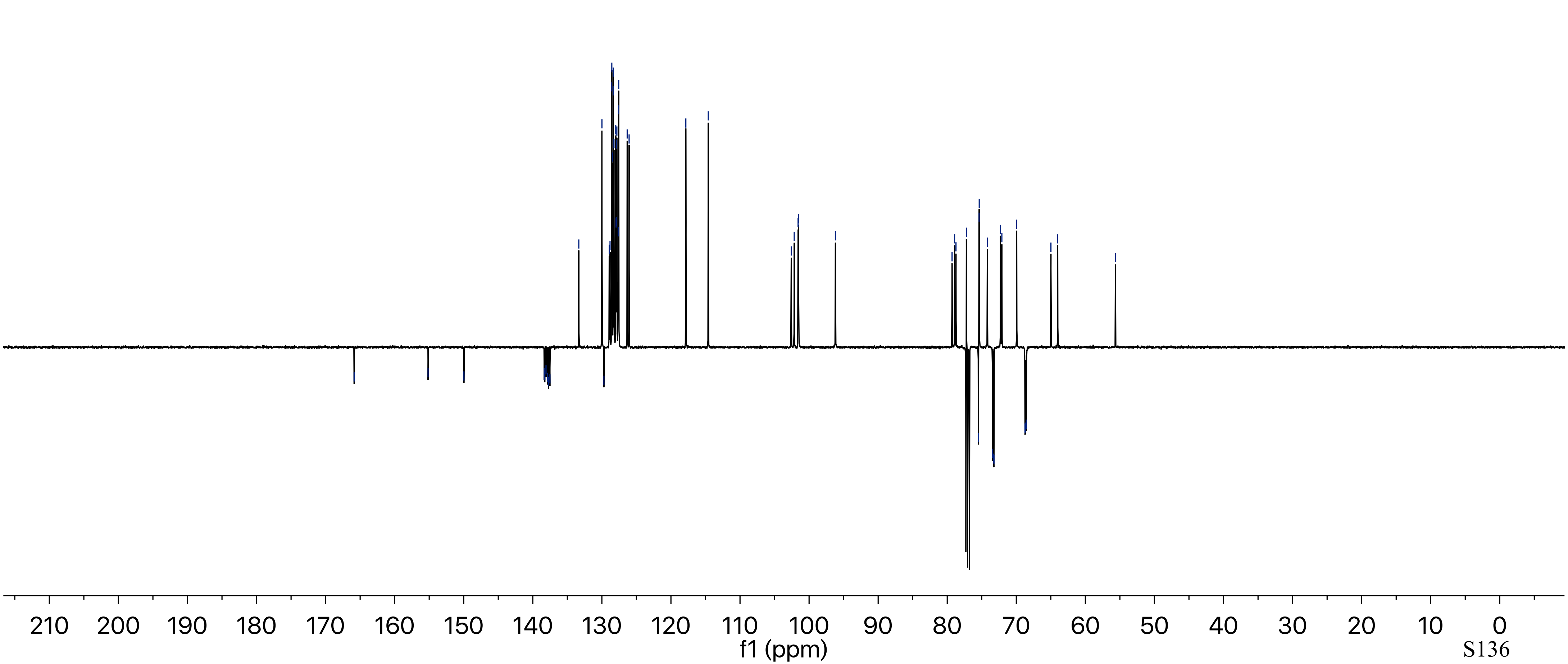
2015.12.2.v7_WL-6-033-prod_loc48_09.20_H1_1D — Lei, WL-6-033-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



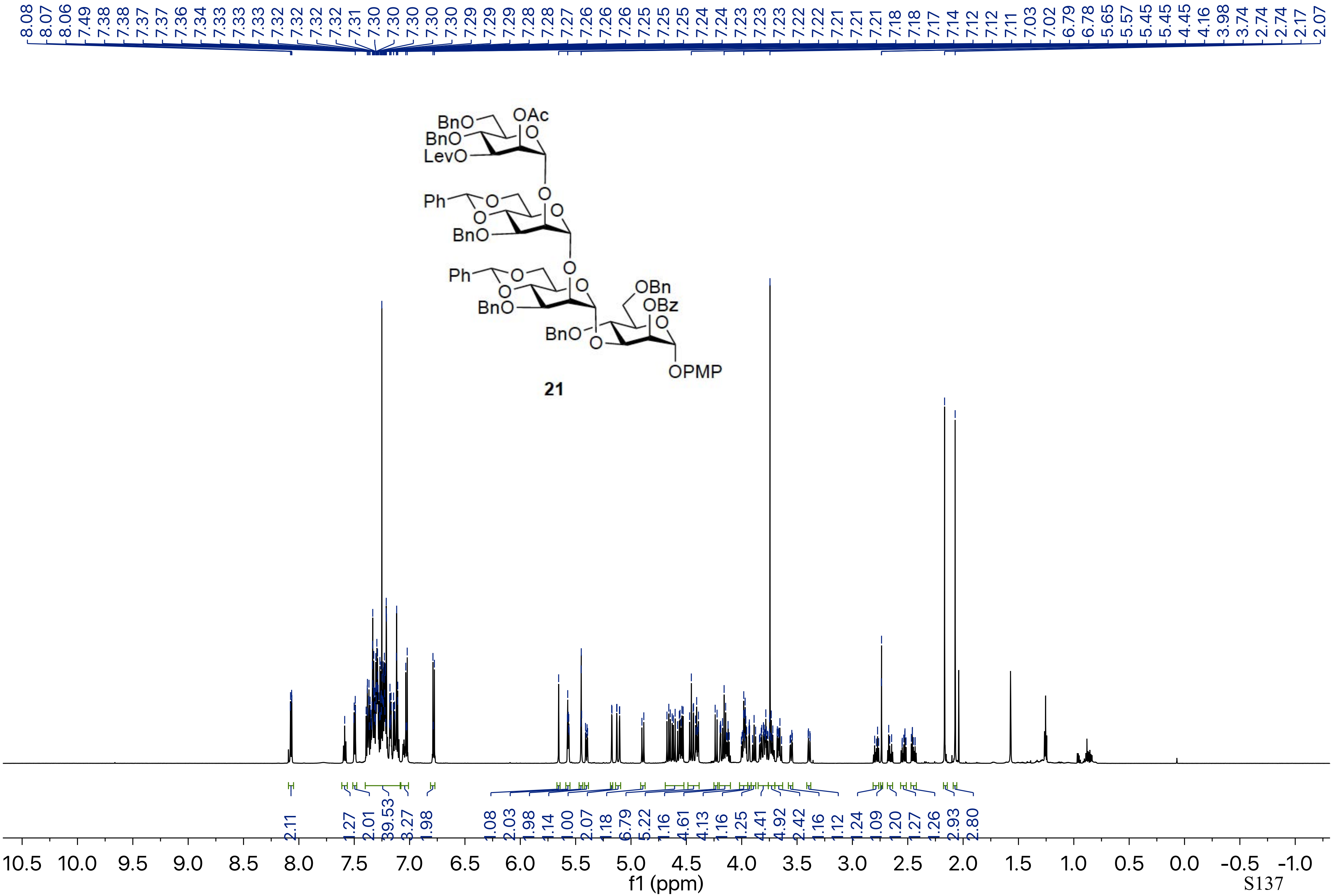
2015.12.03.u5_WL-6-033-prod_loc10_12.31_C13_DEPTq — Lei, WL-6-033-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



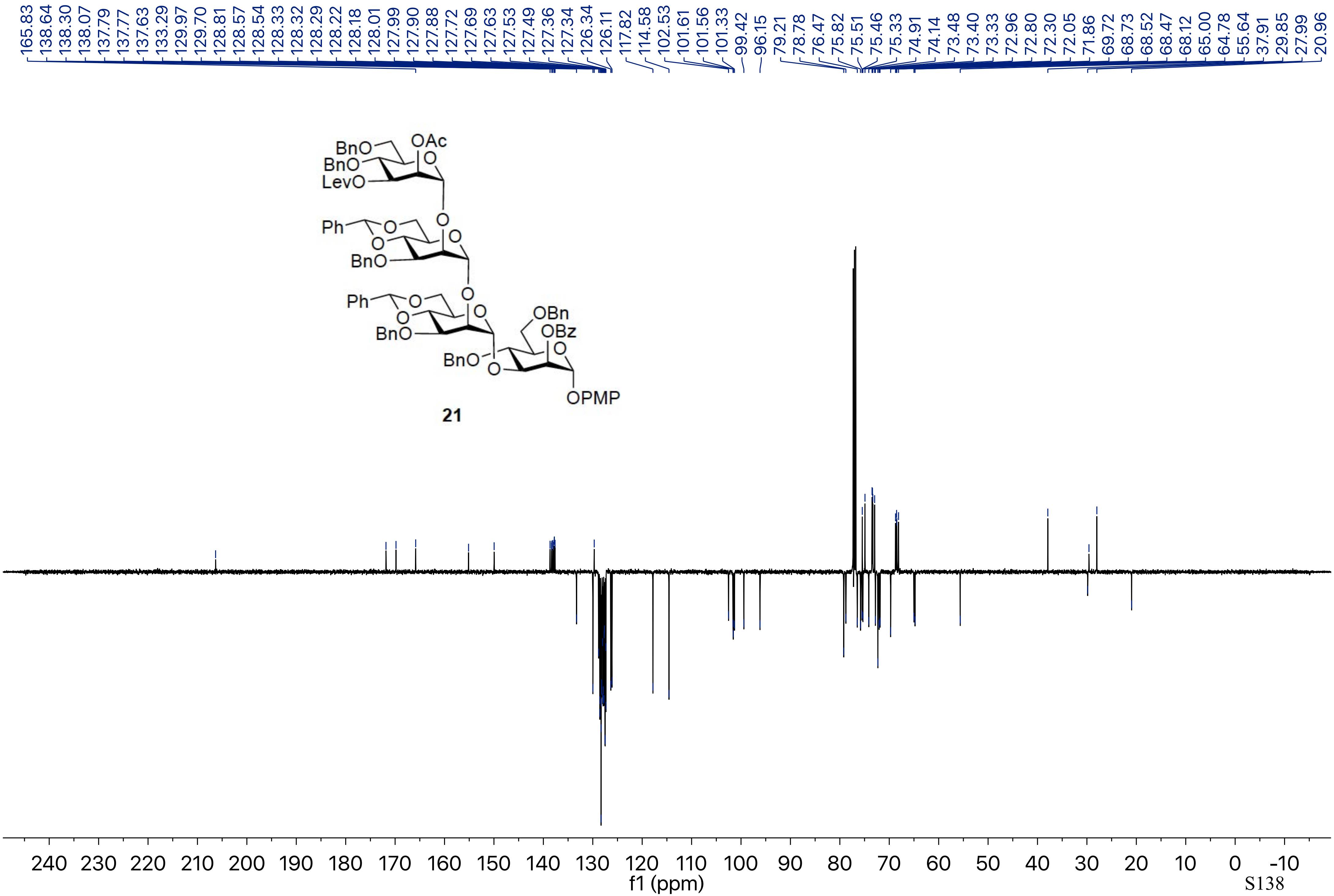
20

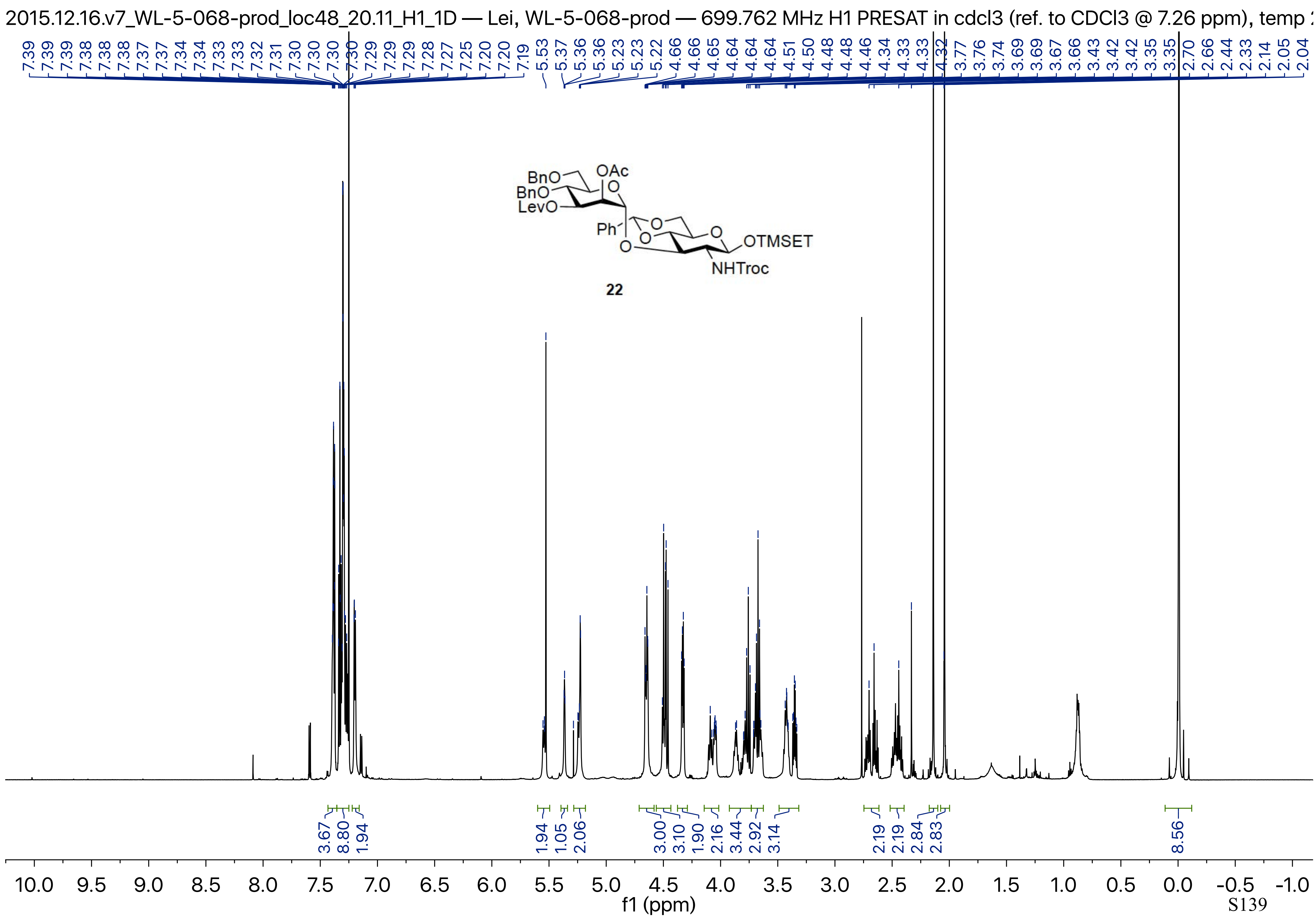


2015.12.2.v7_WL-6-034-prod_loc47_19.10_H1_1D — Lei, WL-6-034-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2

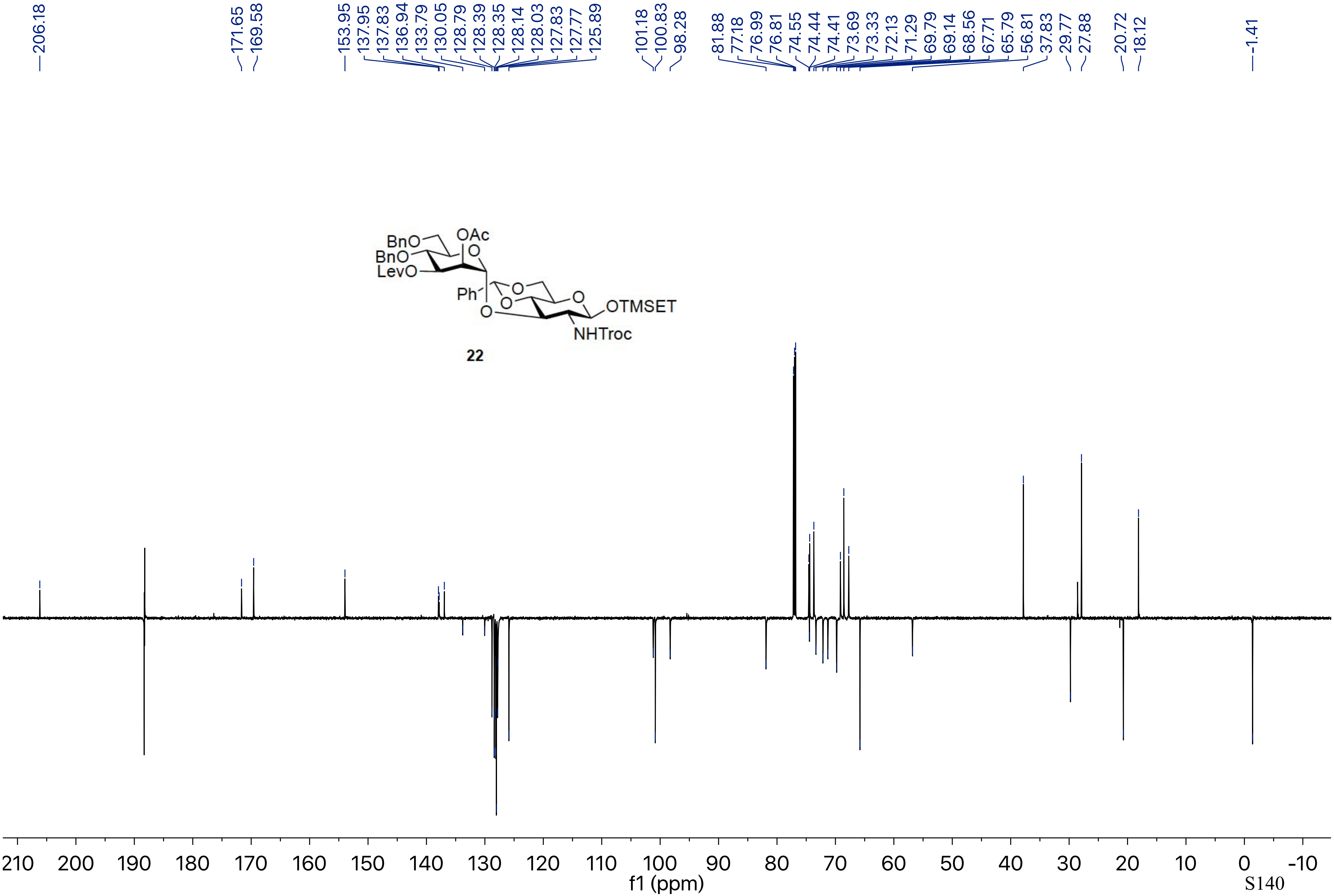


2015.12.03.u5_WL-6-034-prod_loc10_17.26_C13_DEPTq — Lei, WL-6-034-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p

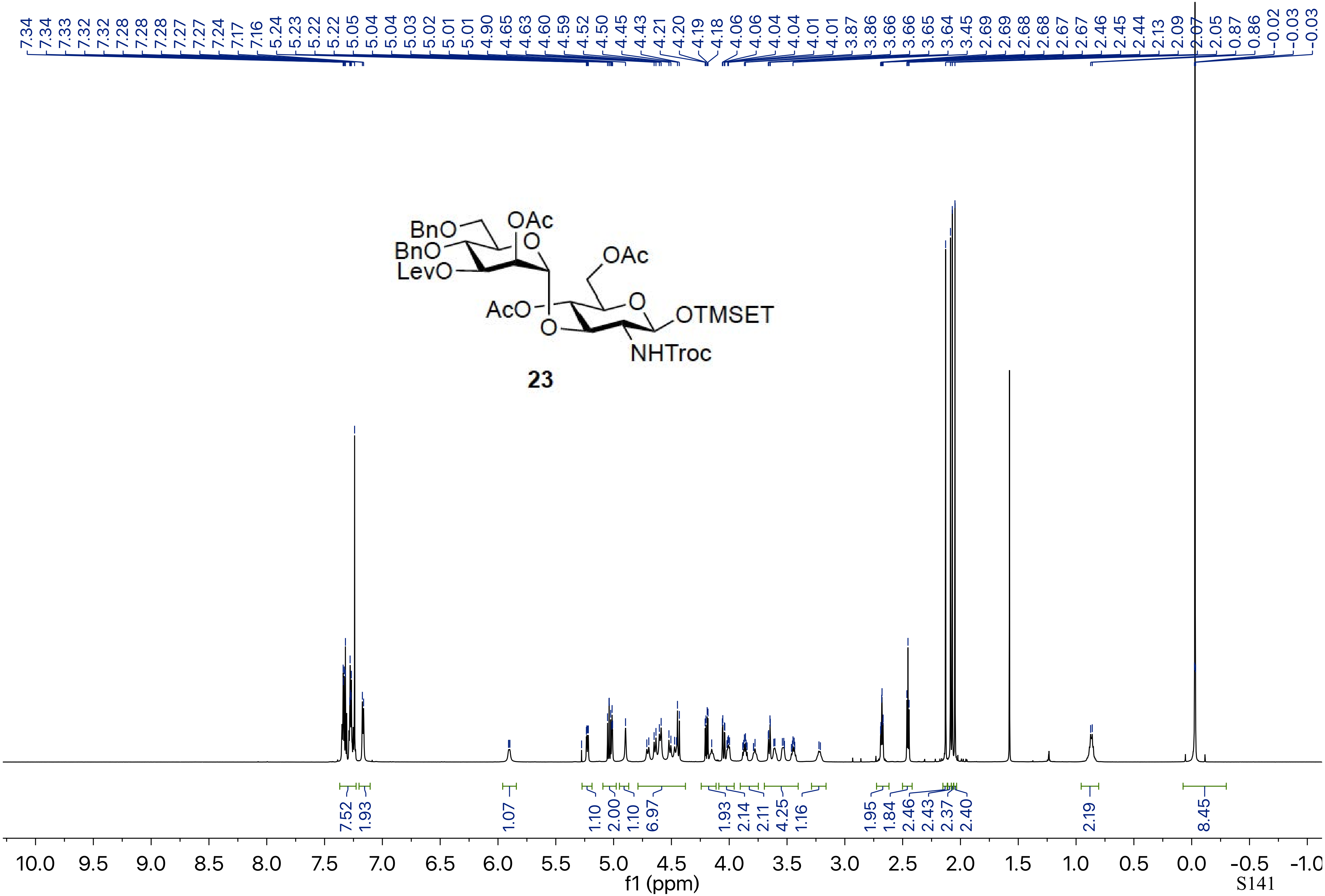


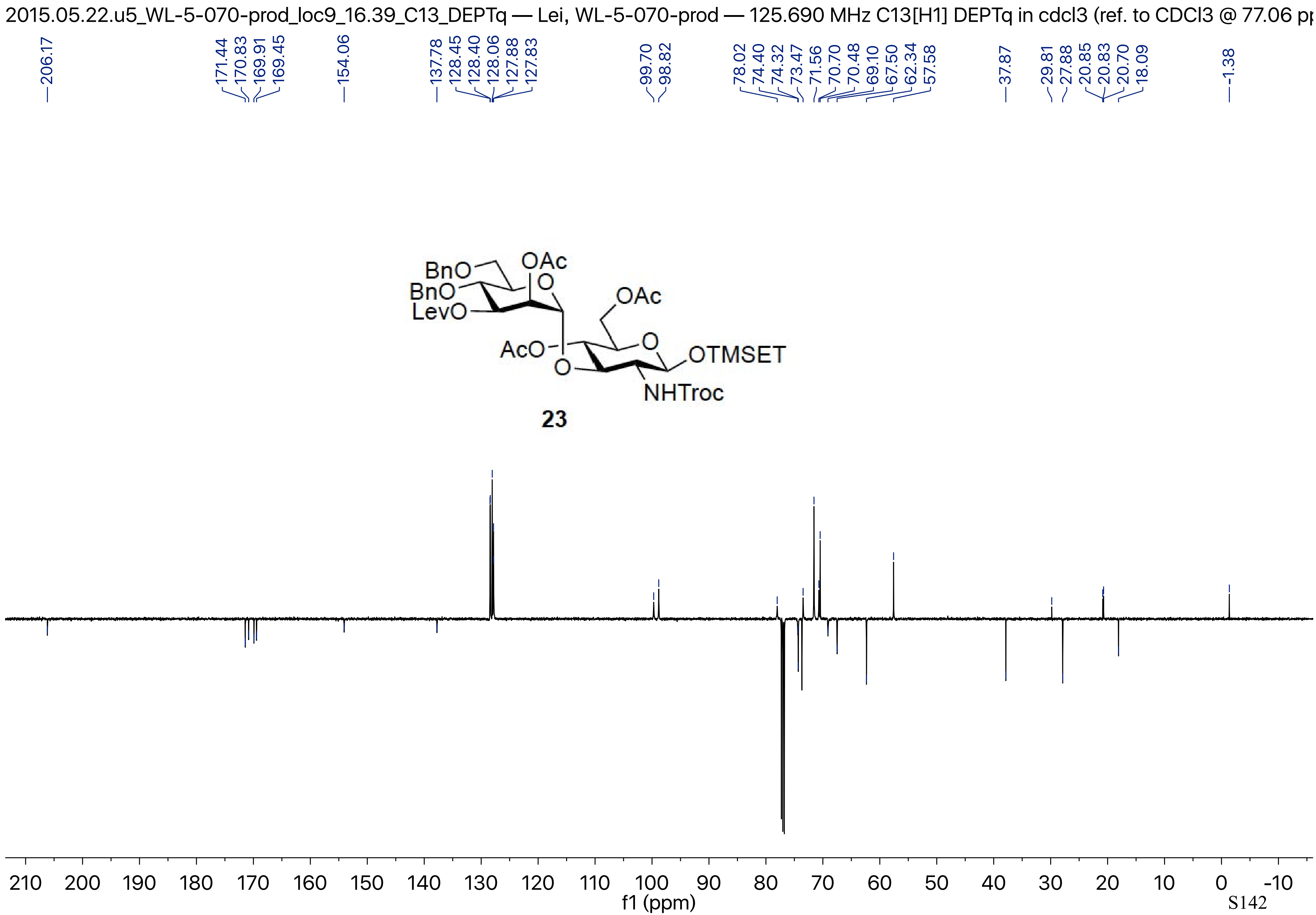

2015.12.16.v7_WL-5-068-prod_loc48_20.11_H1_1D — Lei, WL-5-068-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp
7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.34 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.27 7.25 7.20 7.20 7.19 5.53 5.37 5.36 5.36 5.23 5.23 5.22 4.66 4.66 4.65 4.64 4.64 4.64 4.51 4.50 4.48 4.48 4.46 4.34 4.33 4.33 4.32 3.77 3.76 3.74 3.69 3.69 3.67 3.66 3.43 3.42 3.35 3.35 2.70 2.66 2.44 2.33 2.14 2.05 2.04
BnO
BnO
LevO
OAc
O
Ph
O
O
O
O
OTMSET
NHTroc
22
3.67 8.80 1.94 1.94 1.05 2.06 3.00 3.10 1.90 2.16 3.44 2.92 3.14 2.19 2.19 2.84 2.83 8.56
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

2015.12.16.v7_WL-5-068-prod_loc48_20.17_C13_DEPTq — Lei, WL-5-068-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp

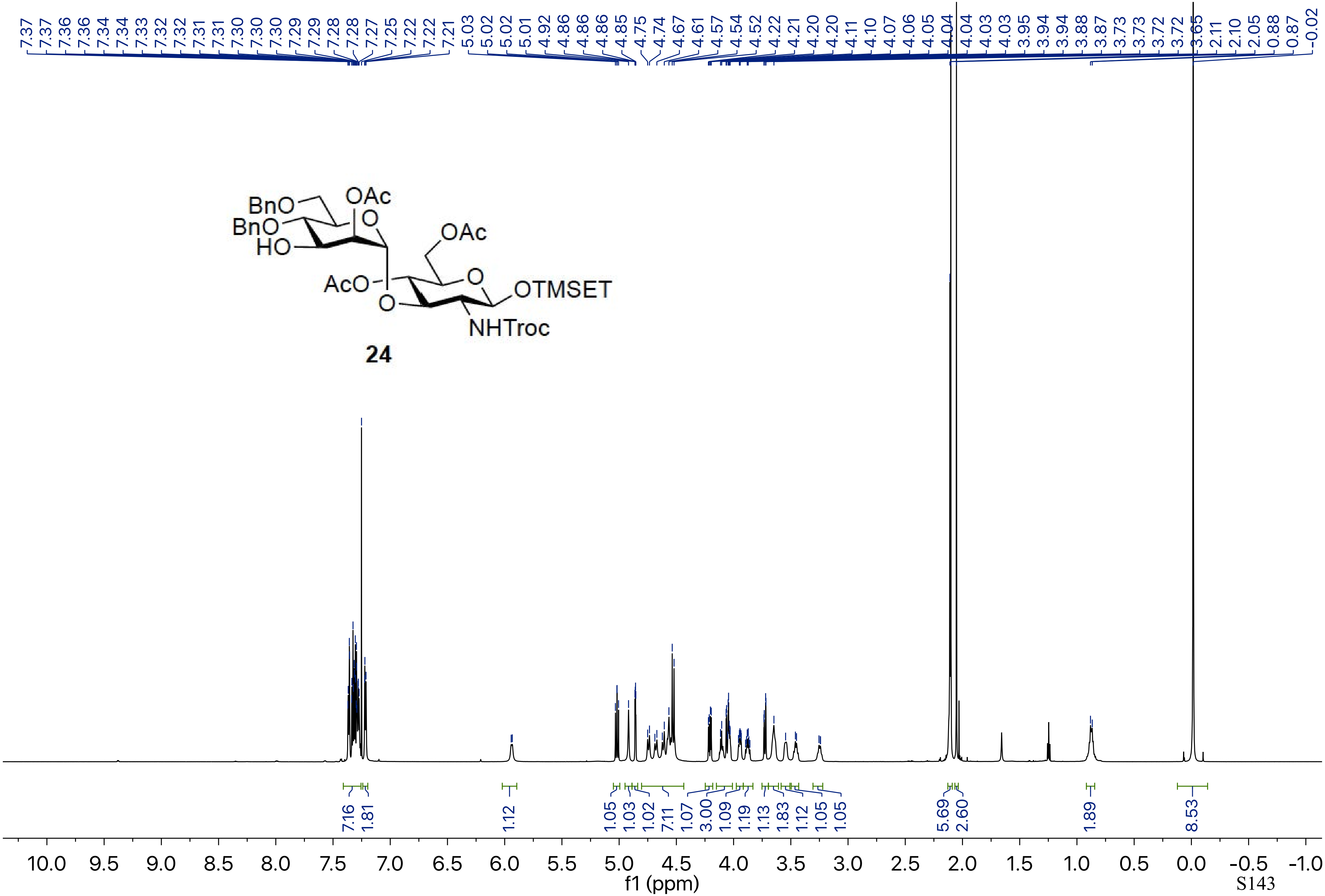


2015.05.25.v7_WL-5-070-prod_loc8_16.17_H1_1D — Lei, WL-5-070-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2




2015.05.22.u5_WL-5-070-prod_loc9_16.39_C13_DEPTq — Lei, WL-5-070-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp
206.17
171.44
170.83
169.91
169.45
154.06
137.78
128.45
128.40
128.06
127.88
127.83
99.70
98.82
78.02
74.40
74.32
73.47
71.56
70.70
70.48
69.10
67.50
62.34
57.58
37.87
29.81
27.88
20.85
20.83
20.70
18.09
-1.38
BnO
BnO
LevO
OAc
O
OAc
AcO
O
O
OTMSET
NHTroc
23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2015.12.23.v7_WL-5-072-prod_loc48_12.02_H1_1D — Lei, WL-5-072-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



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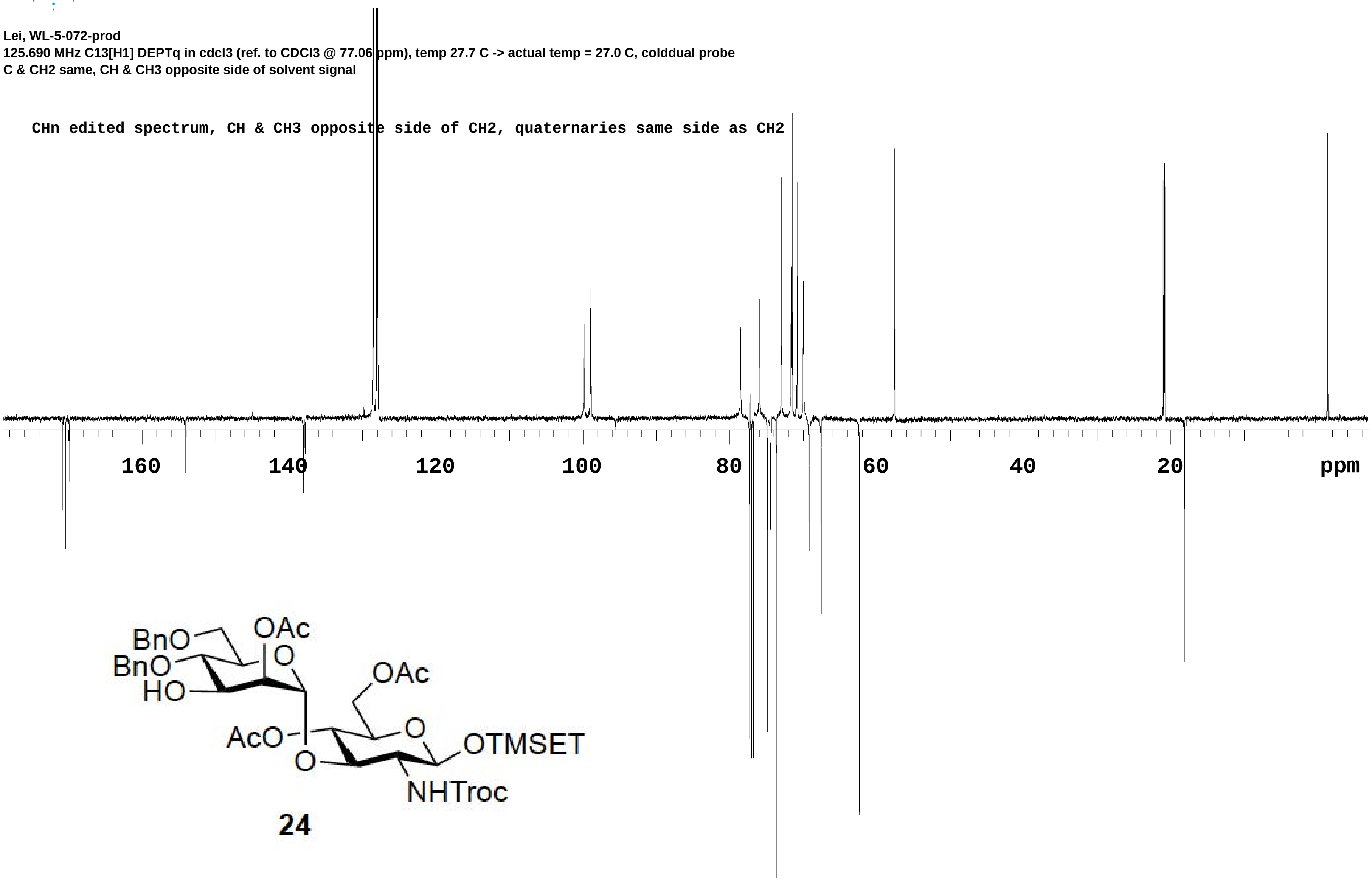
Recorded on: **u500, Dec 23 2015**	Sweep Width(Hz): **33783.8**	Acquisiton Time(s): **1**	Relaxation Delay(s): **1**
Pulse Sequence: **DEPT_chempack**	Digital Res.(Hz/pt): **0.26**	Hz per mm(Hz/mm): **97.28**	Completed Scans **556**

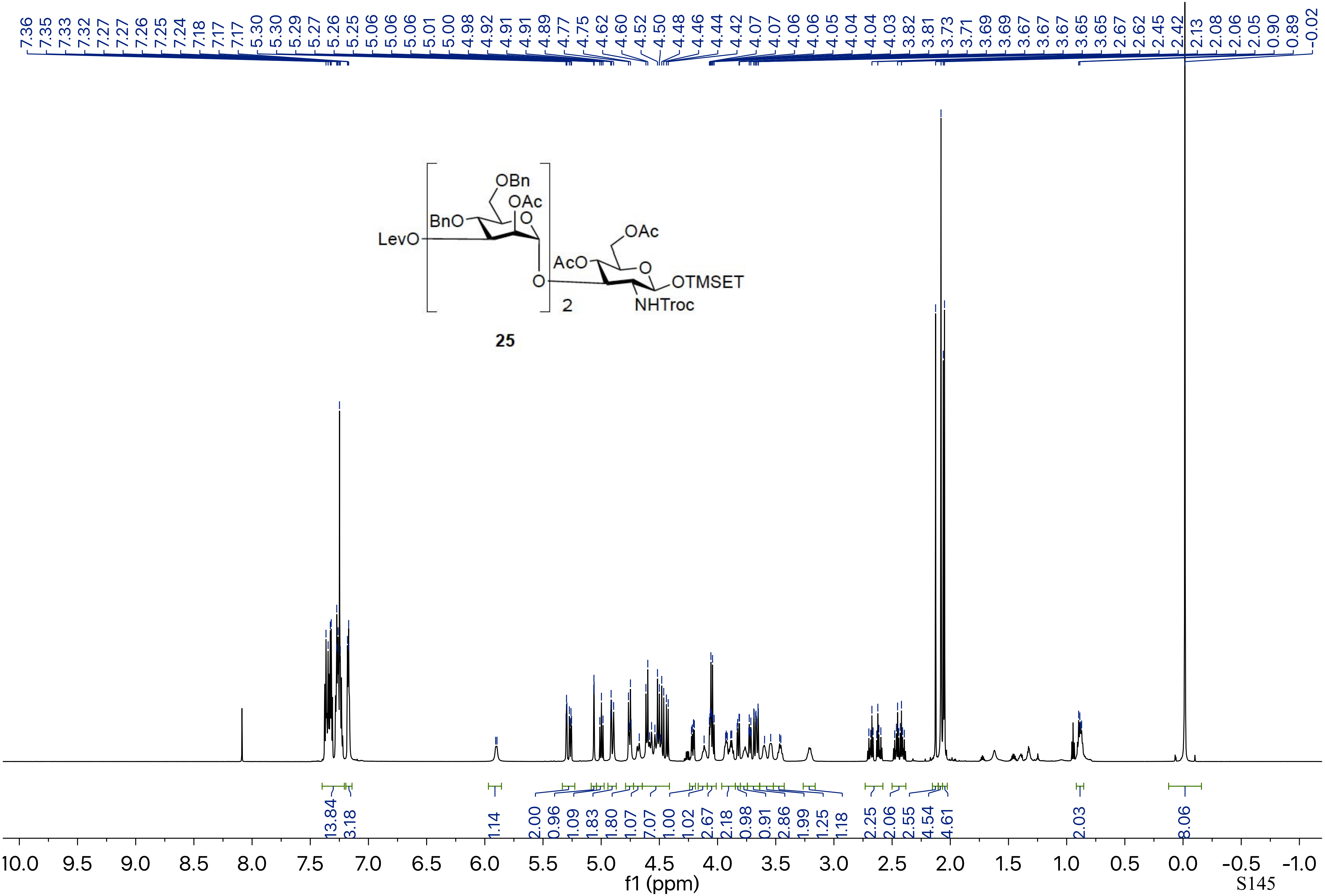
Lei, WL-5-072-prod
125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal



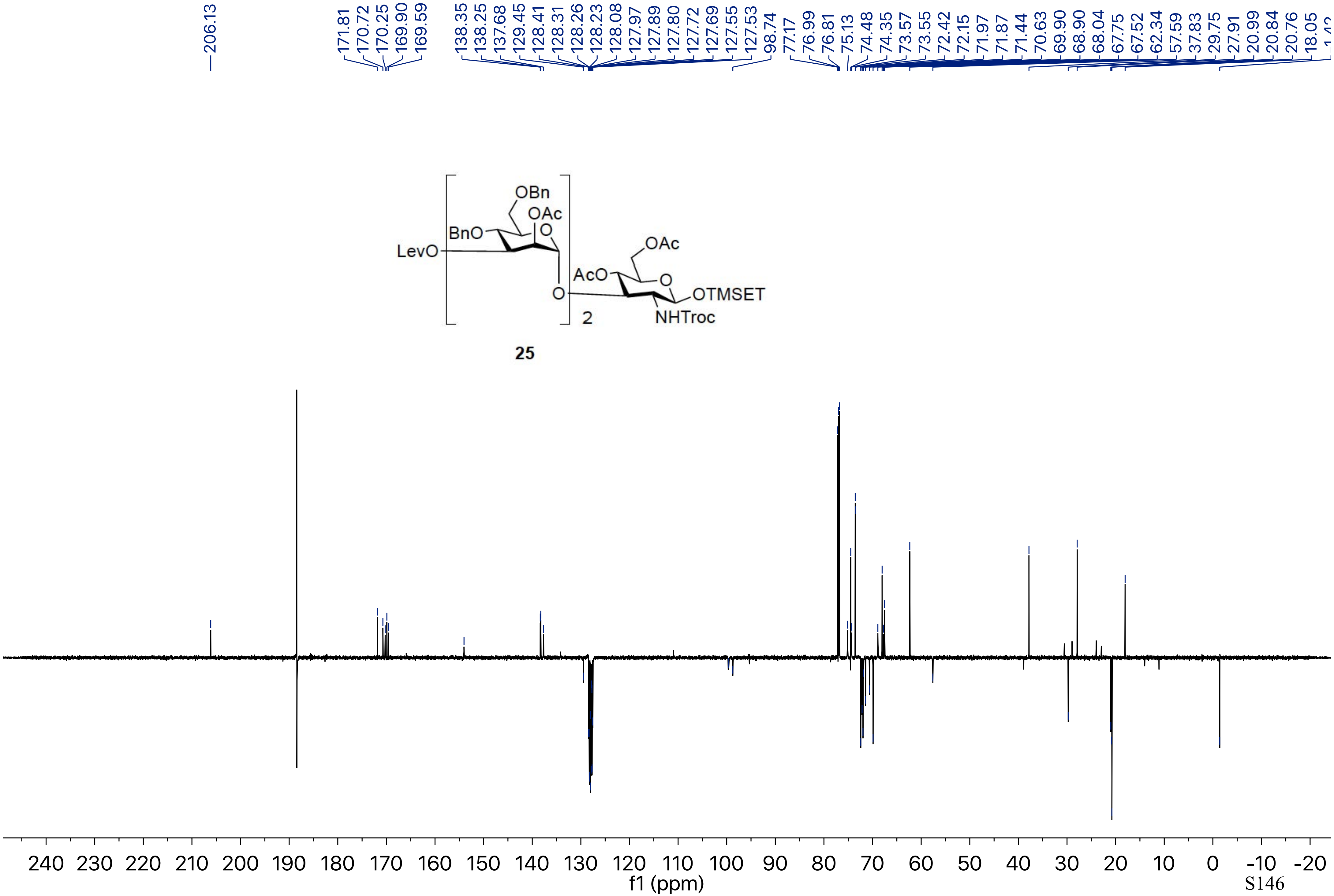
24

File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Lei/2015.12/2015.12.23.u5_WL-5-072-prod_loc5_14.44_C13_DEPTq

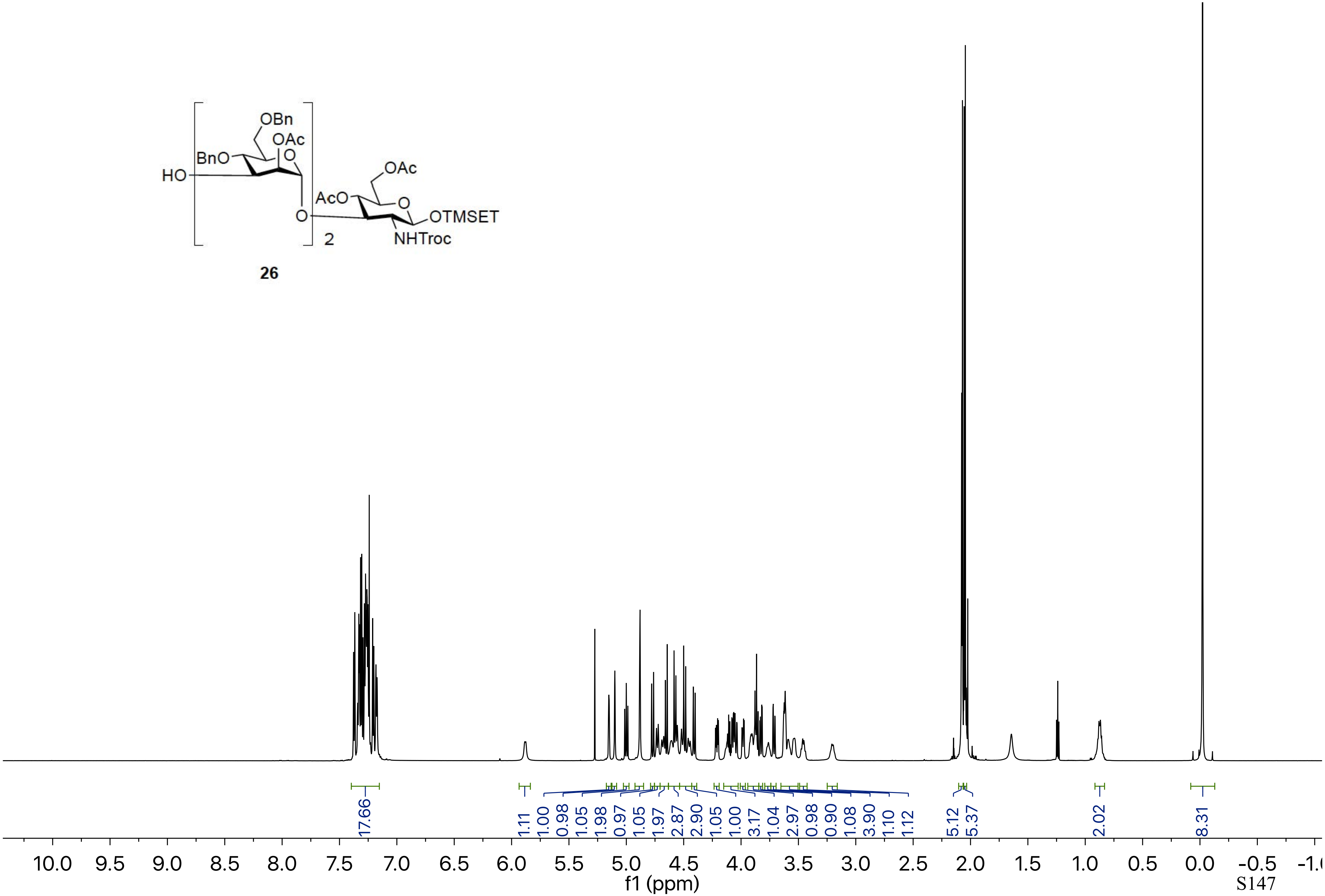
2016.01.4.v7_WL-5-073-prod_loc48_16.03_H1_1D — Lei, WL-5-073-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



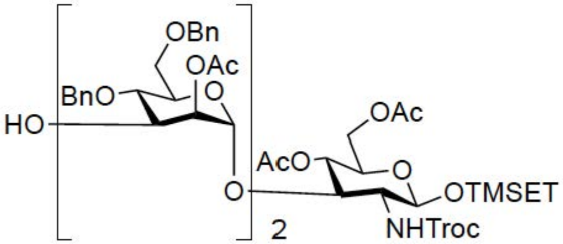
2016.01.4.v7_WL-5-073-prod_loc48_16.05_C13_DEPTq — Lei, WL-5-073-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp



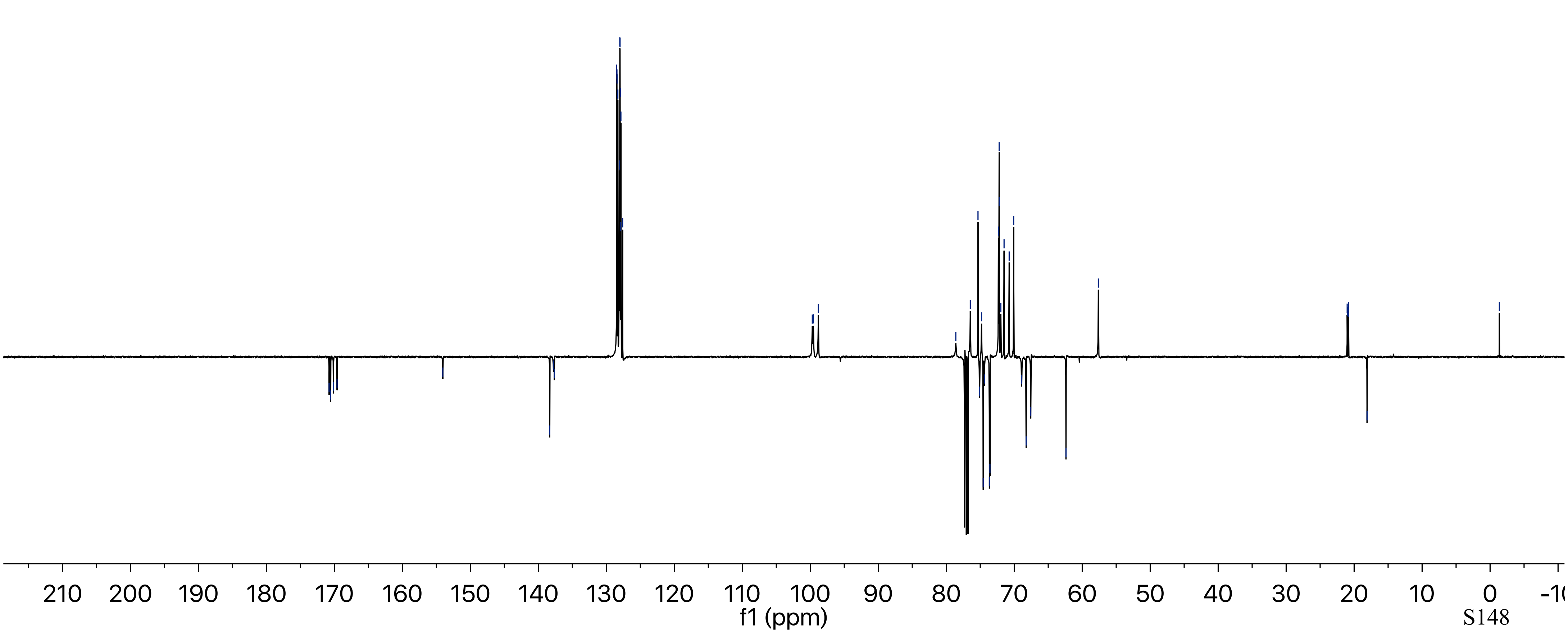
2015.05.28.v7_WL-5-074-prod_loc5_14.33_H1_1D — Lei, WL-5-074-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



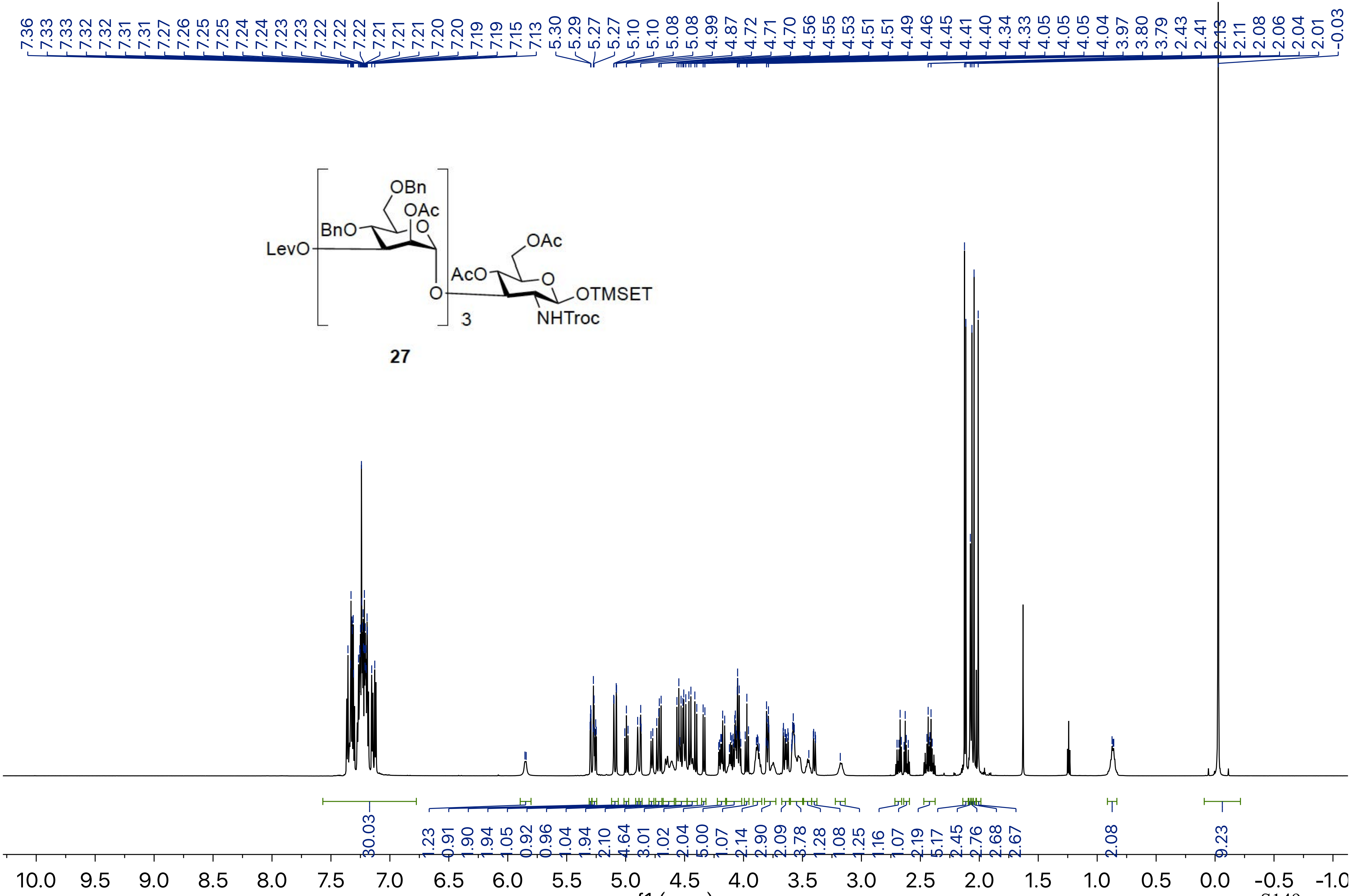
2015.05.28.u5_WL-5-074-prod_loc11_21.51_C13_DEPTq — Lei, WL-5-074-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp

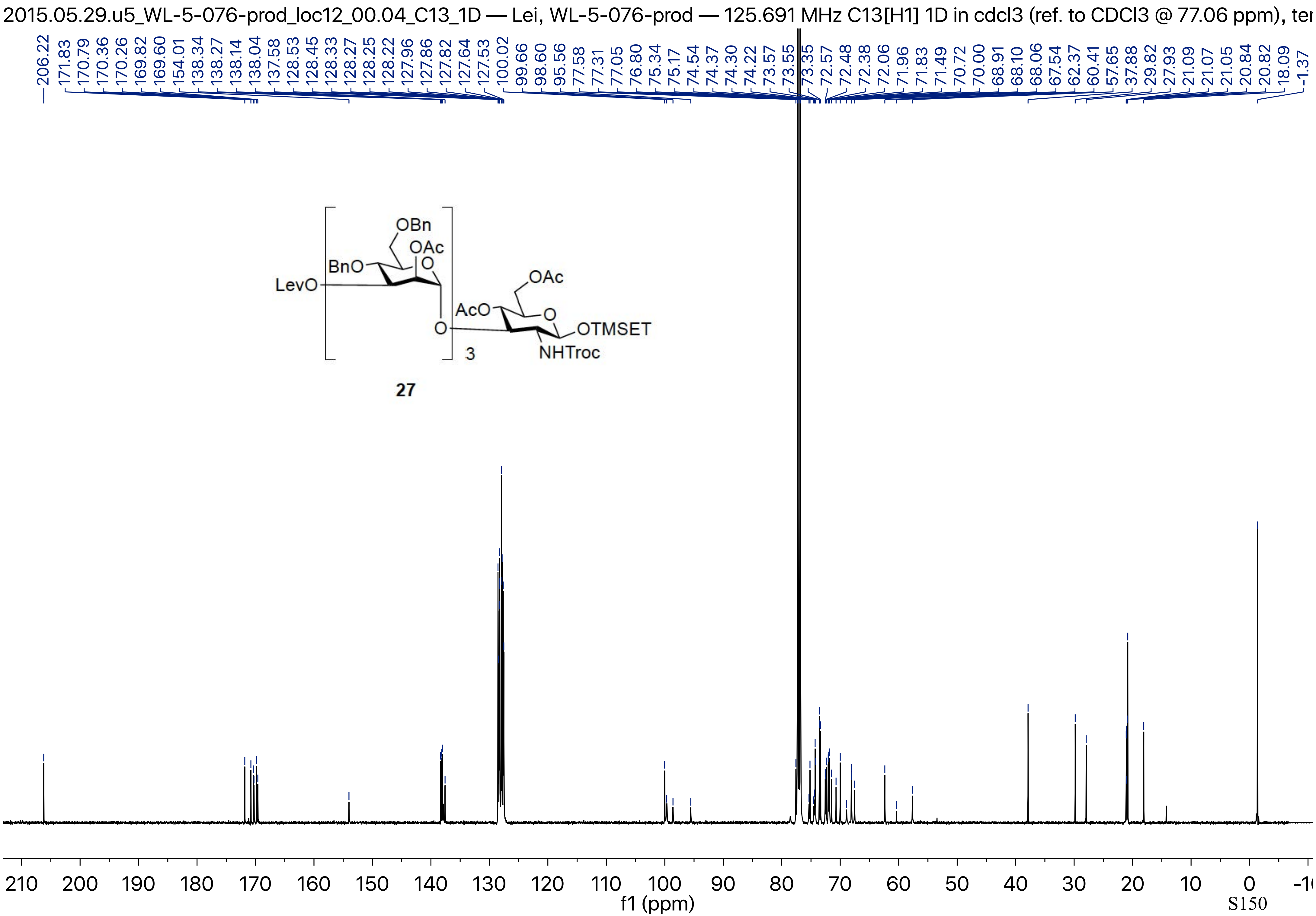


26



2015.05.28.v7_WL-5-076-prod_loc6_14.40_H1_1D — Lei, WL-5-076-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2




2015.05.29.u5_WL-5-076-prod_loc12_00.04_C13_1D — Lei, WL-5-076-prod — 125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), ter
206.22
171.83
170.79
170.36
170.26
169.82
169.60
154.01
138.34
138.27
138.14
138.04
137.58
128.53
128.45
128.33
128.27
128.25
128.22
127.96
127.86
127.82
127.64
127.53
100.02
99.66
98.60
95.56
77.58
77.31
77.05
76.80
75.34
75.17
74.54
74.37
74.30
74.22
73.57
73.55
73.35
72.57
72.48
72.38
72.06
71.96
71.83
71.49
70.72
70.00
68.91
68.10
68.06
67.54
62.37
60.41
57.65
37.88
29.82
27.93
21.09
21.07
21.05
20.84
20.82
18.09
-1.37
OBn
OAc
BnO
O
LevO
OAc
AcO
O
O
OTMSET
3
NHTroc
27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

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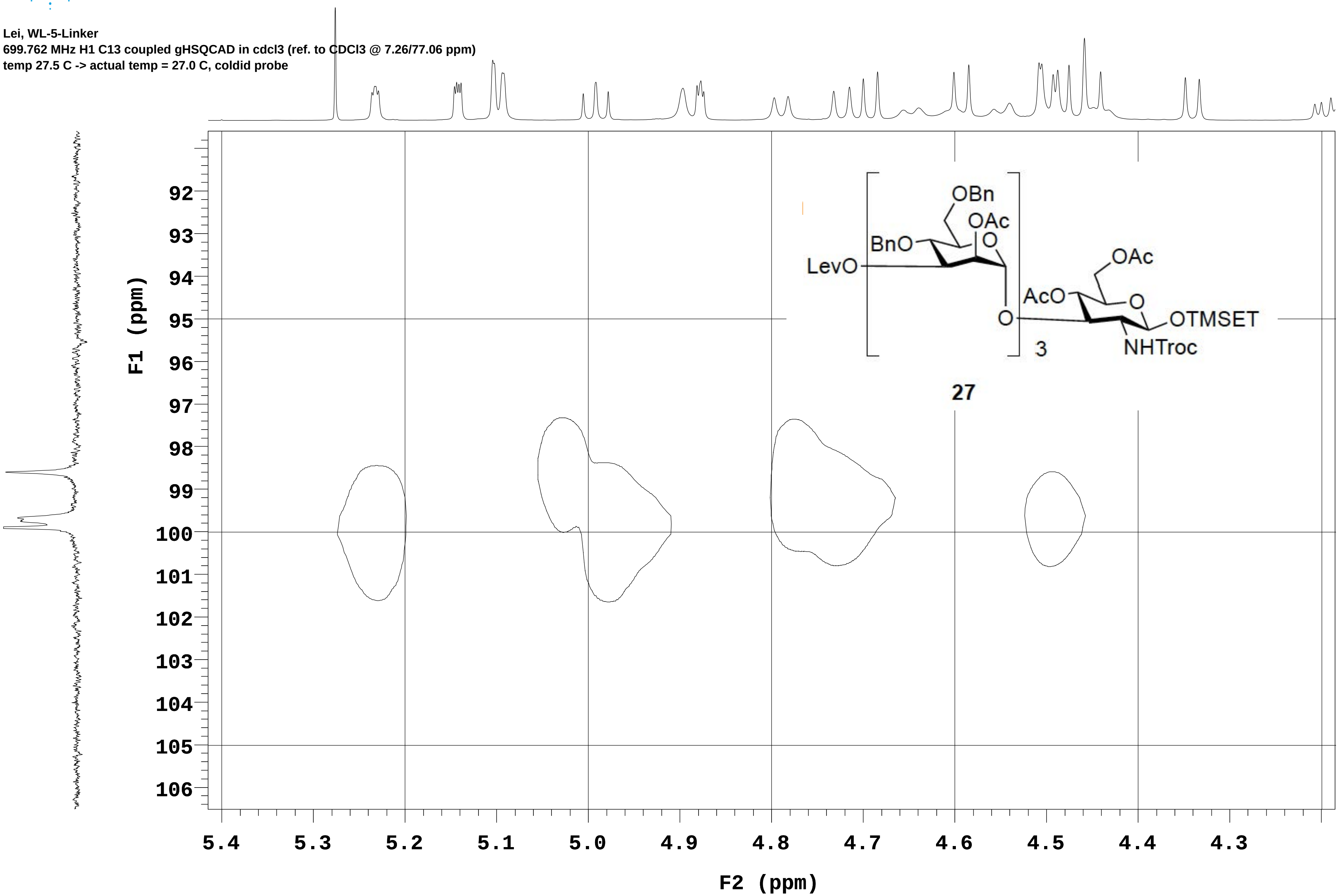
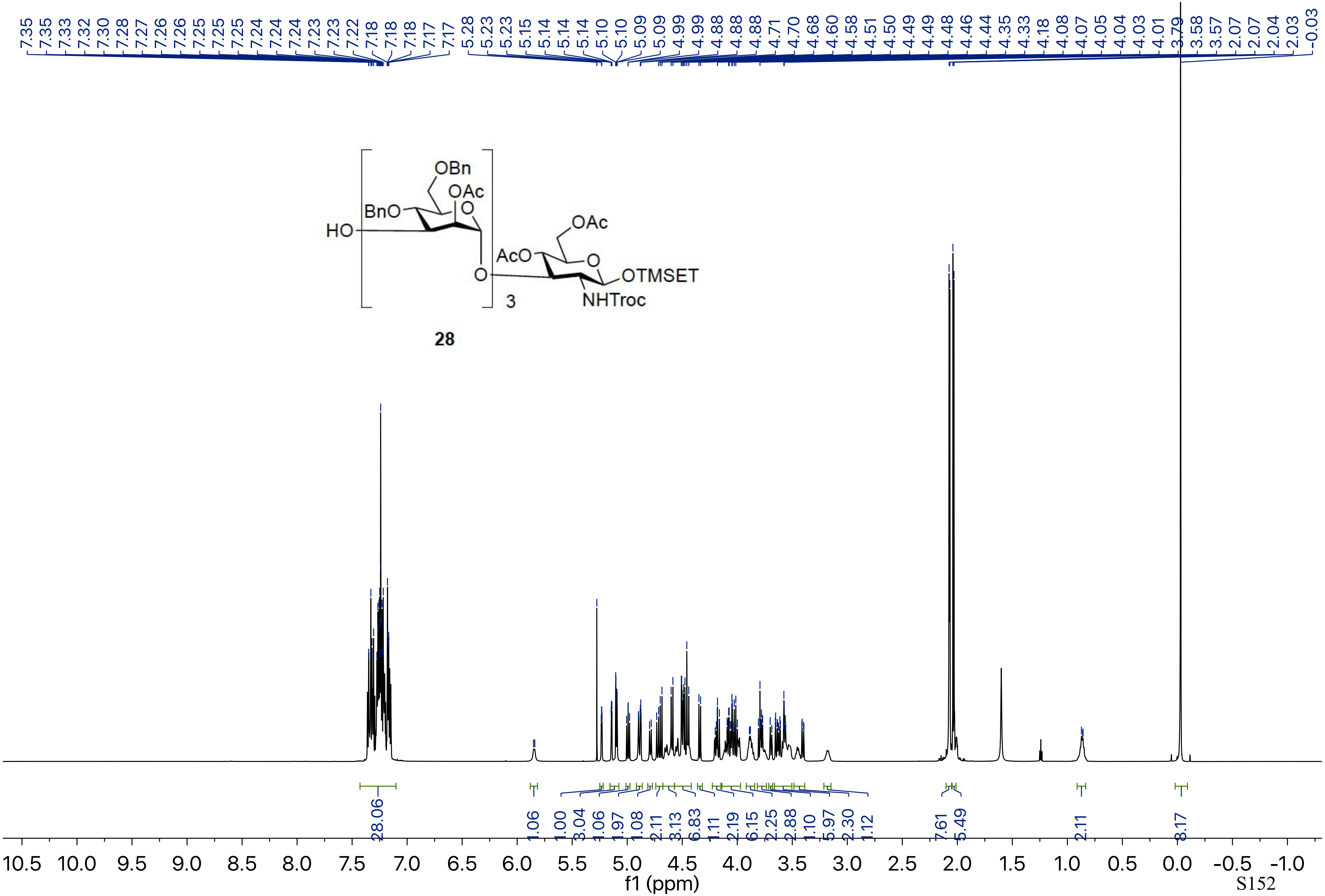
Recorded on:	v700, Jan 16 2017	Sweep Width F2|F1(Hz):	8389.26 | 38722.17	Acquisiton Time(s):	0.1	Relaxation Delay(s):	1.89999
Pulse Sequence:	gHSQCAD	Digital Res. F2|F1(Hz/pt):	2.05 | 75.63	Hz per mm F2|F1(Hz/mm):	3.67 | 19.35	No. of Scans|Increments	2 | 128

Lei, WL-5-Linker
699.762 MHz H1 C13 coupled gHSQCAD in cdcl3 (ref. to CDCl3 @ 7.26/77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe

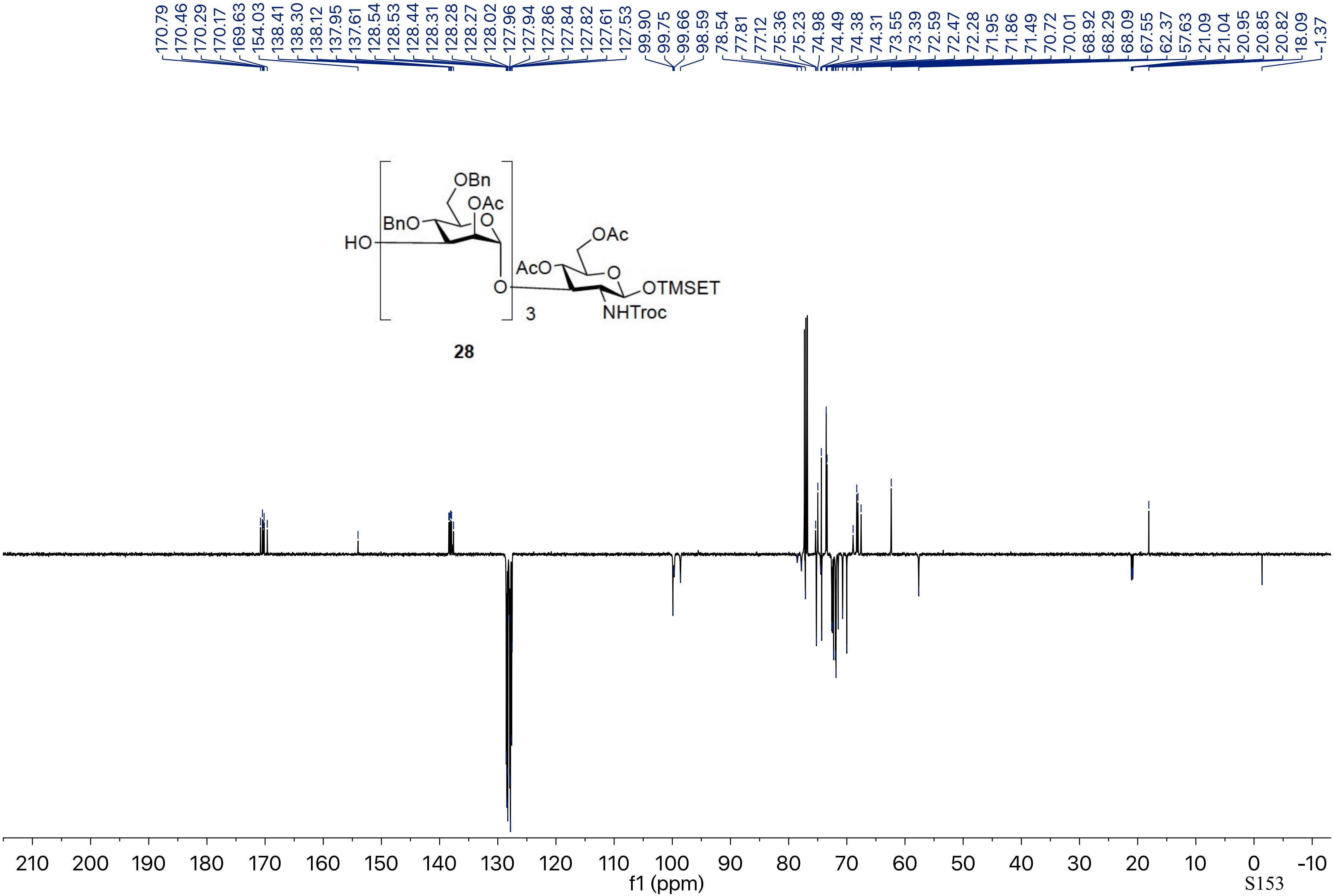


File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Lei/2017.01/2017.01.16.v7_WL-5-Linker_loc47_09.15_coupled_H1_gHSQCAD

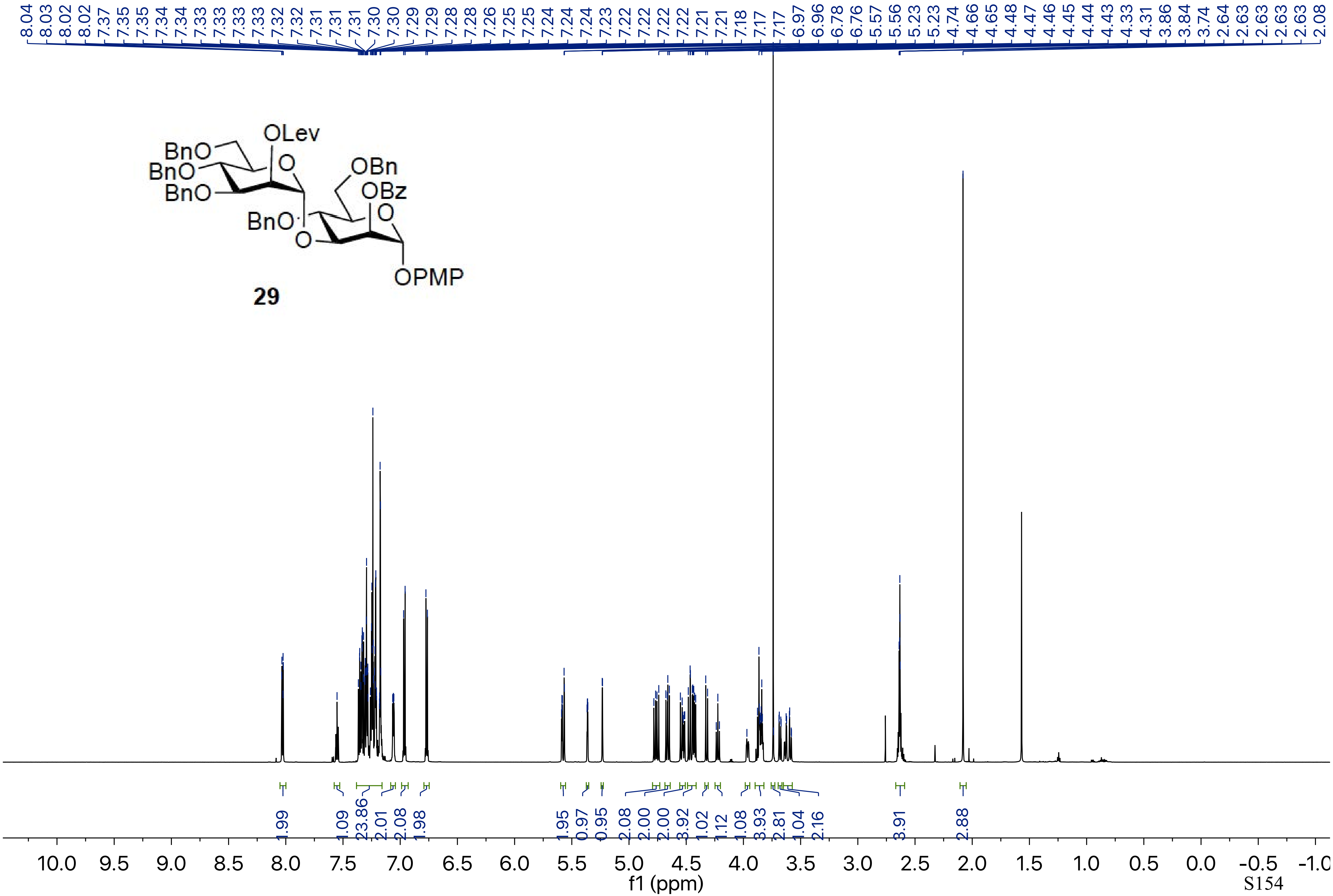
2015.06.4.v7_WL-5-077-prod_loc26_11.04_H1_1D — Lei, WL-5-077-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



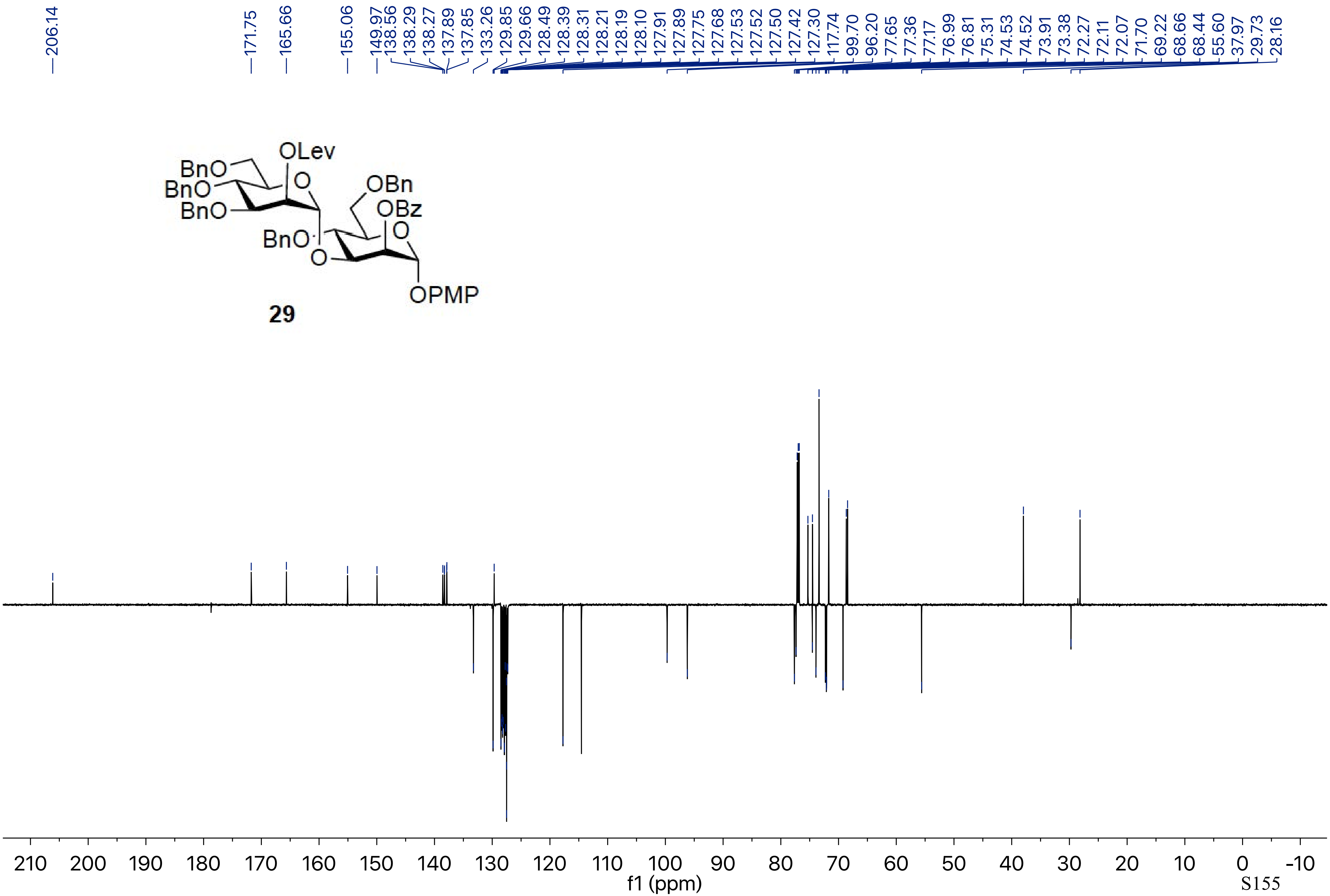
2015.06.04.u5_WL-5-077-prod_loc4_11.17_C13_DEPTq — Lei, WL-5-077-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppm



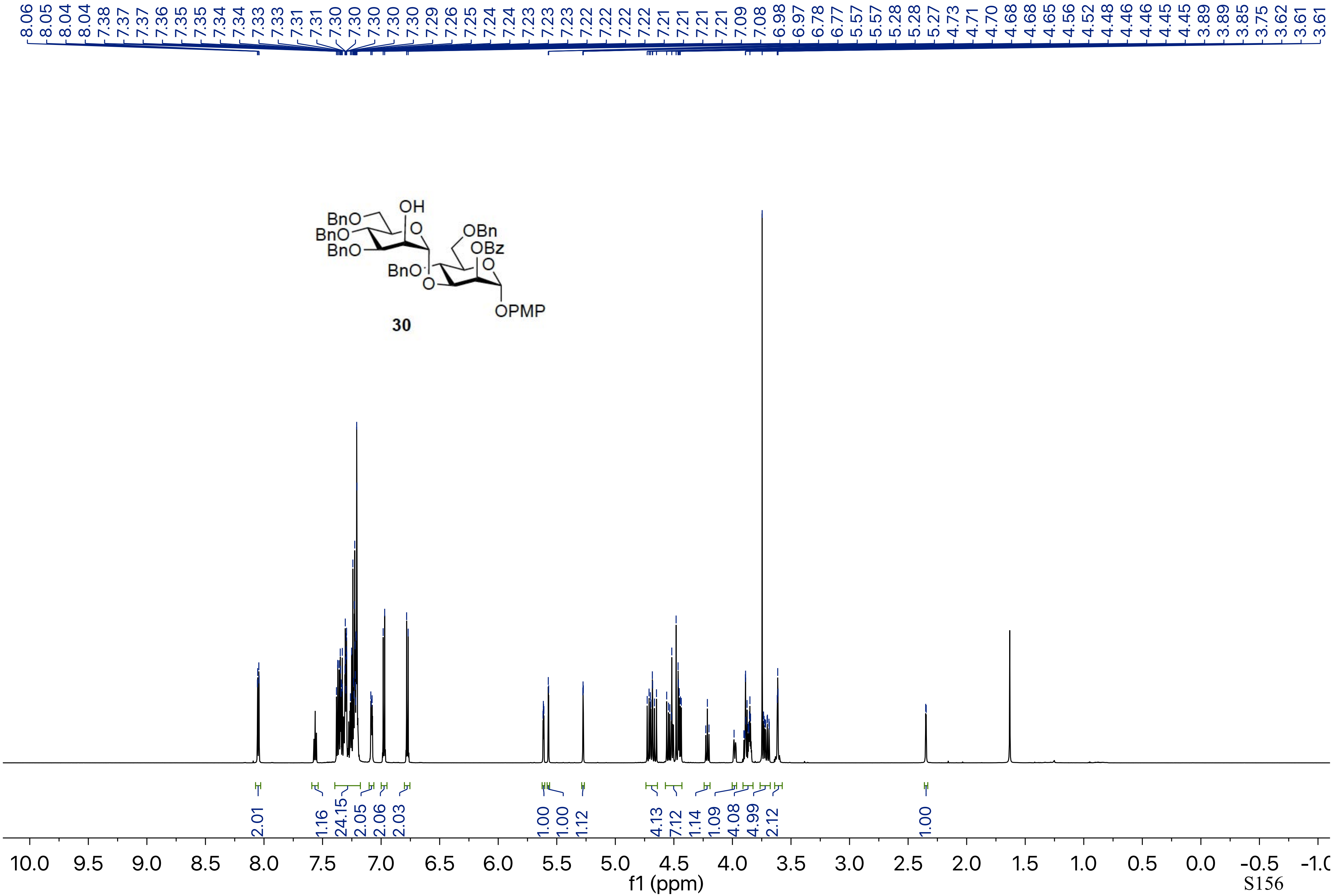
2015.07.8.v7_WL-5-090-prod_loc4_19.27_H1_1D — Lei, WL-5-090-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27



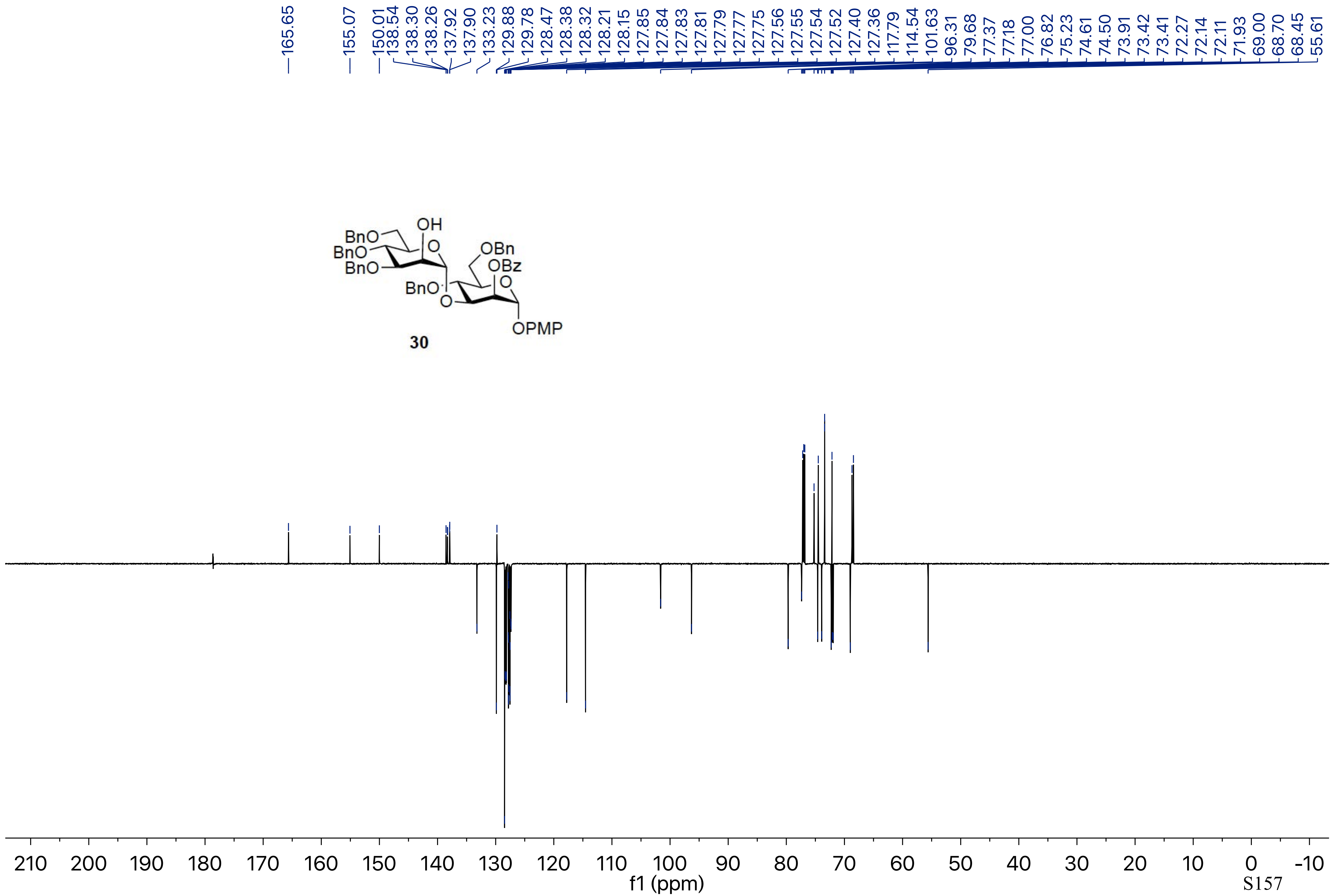
2015.07.8.v7_WL-5-090-prod_loc4_23.35_C13_DEPTq — Lei, WL-5-090-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppr



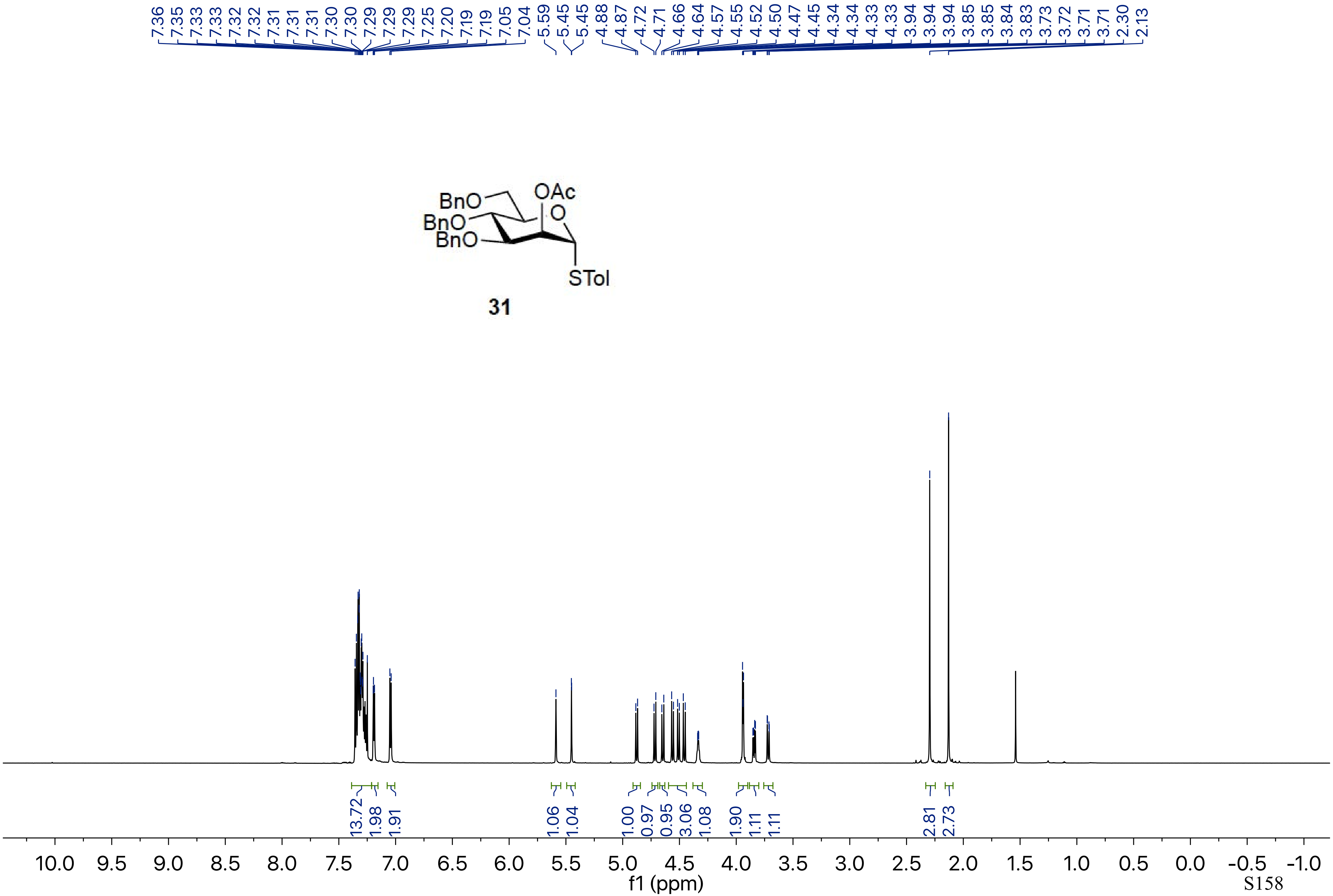
2015.07.12.v7_WL-5-091-prod_loc6_22.18_H1_1D — Lei, WL-5-091-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27



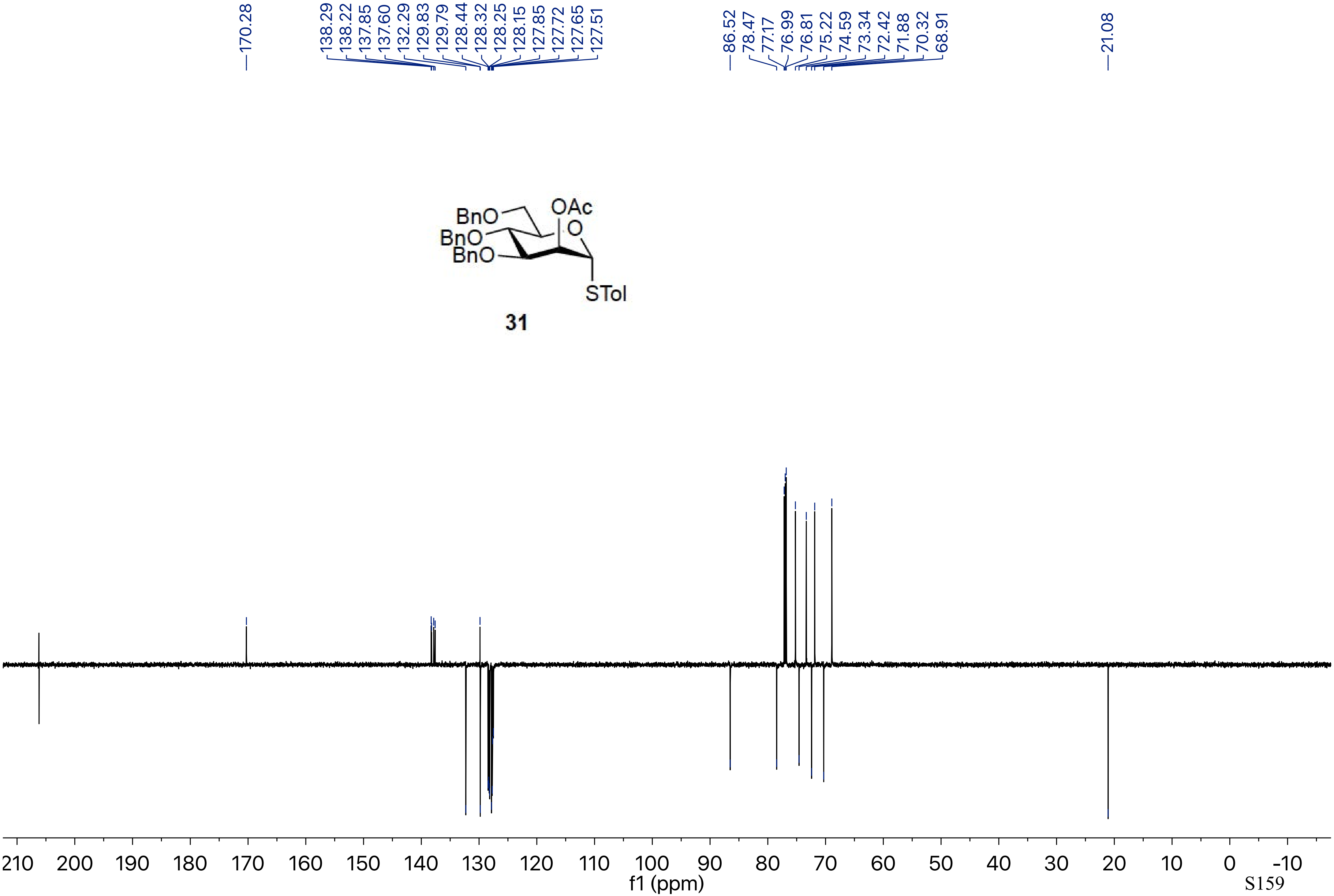
2015.07.12.v7_WL-5-091-prod_loc6_22.20_C13_DEPTq — Lei, WL-5-091-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppr



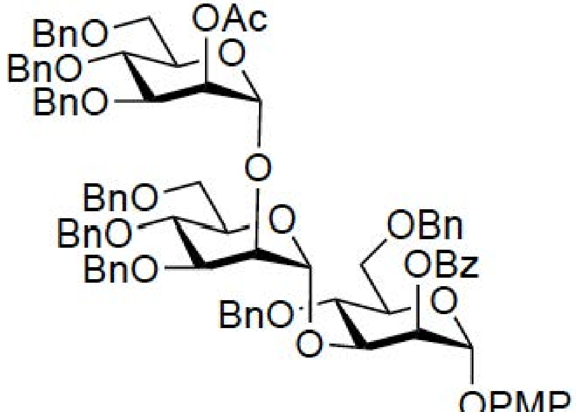
2016.08.22.v7_WL-6-059-prod_loc43_10.47_H1_1D — Lei, WL-6-059-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



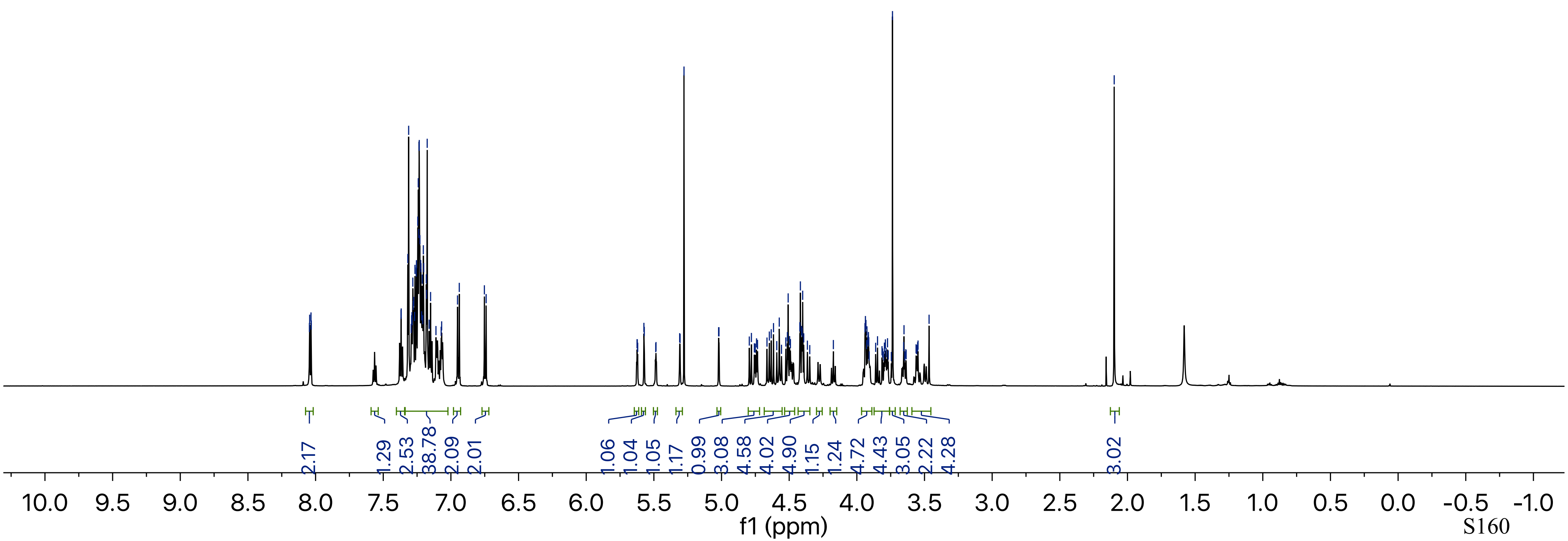
2016.08.22.v7_WL-6-059-prod_loc43_10.48_C13_DEPTq — Lei, WL-6-059-prod — 175.974 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



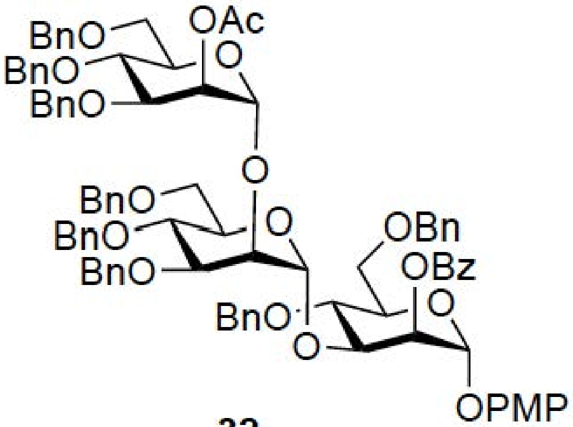
2015.07.13.v7_WL-5-092-prod_loc7_01.29_H1_1D — Lei, WL-5-092-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



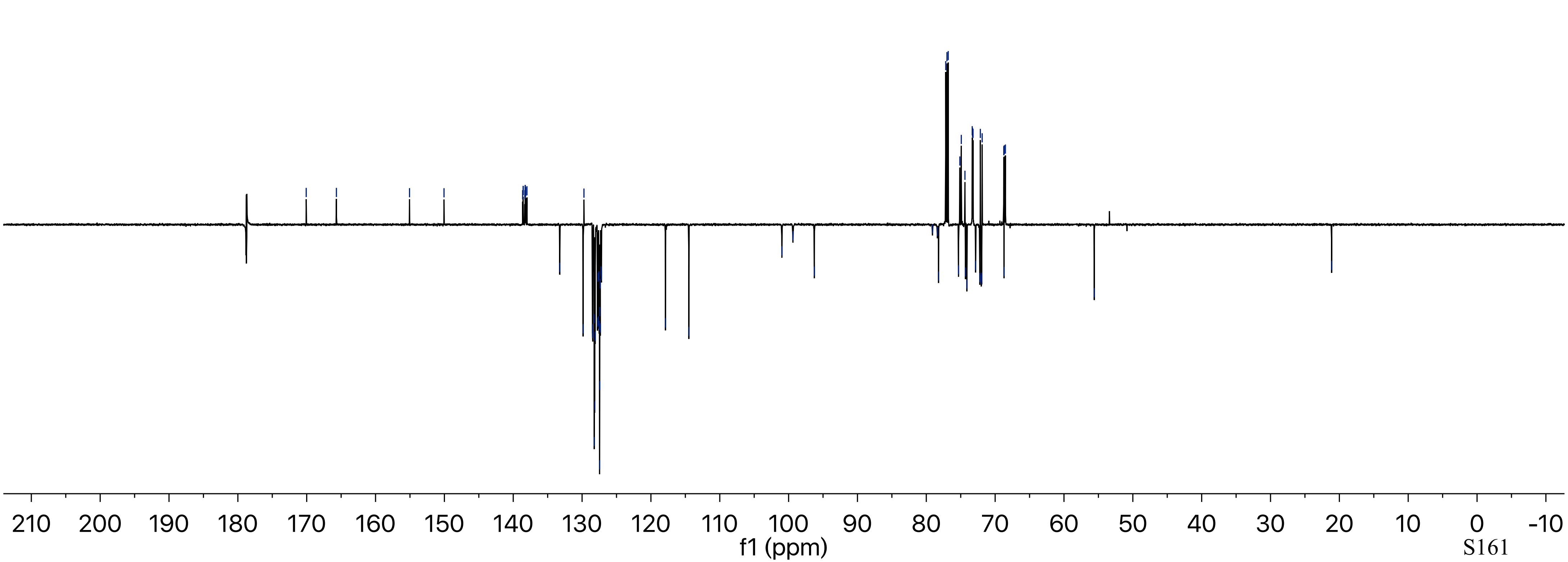
32



2015.07.13.v7_WL-5-092-prod_loc7_01.31_C13_DEPTq — Lei, WL-5-092-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppm



32



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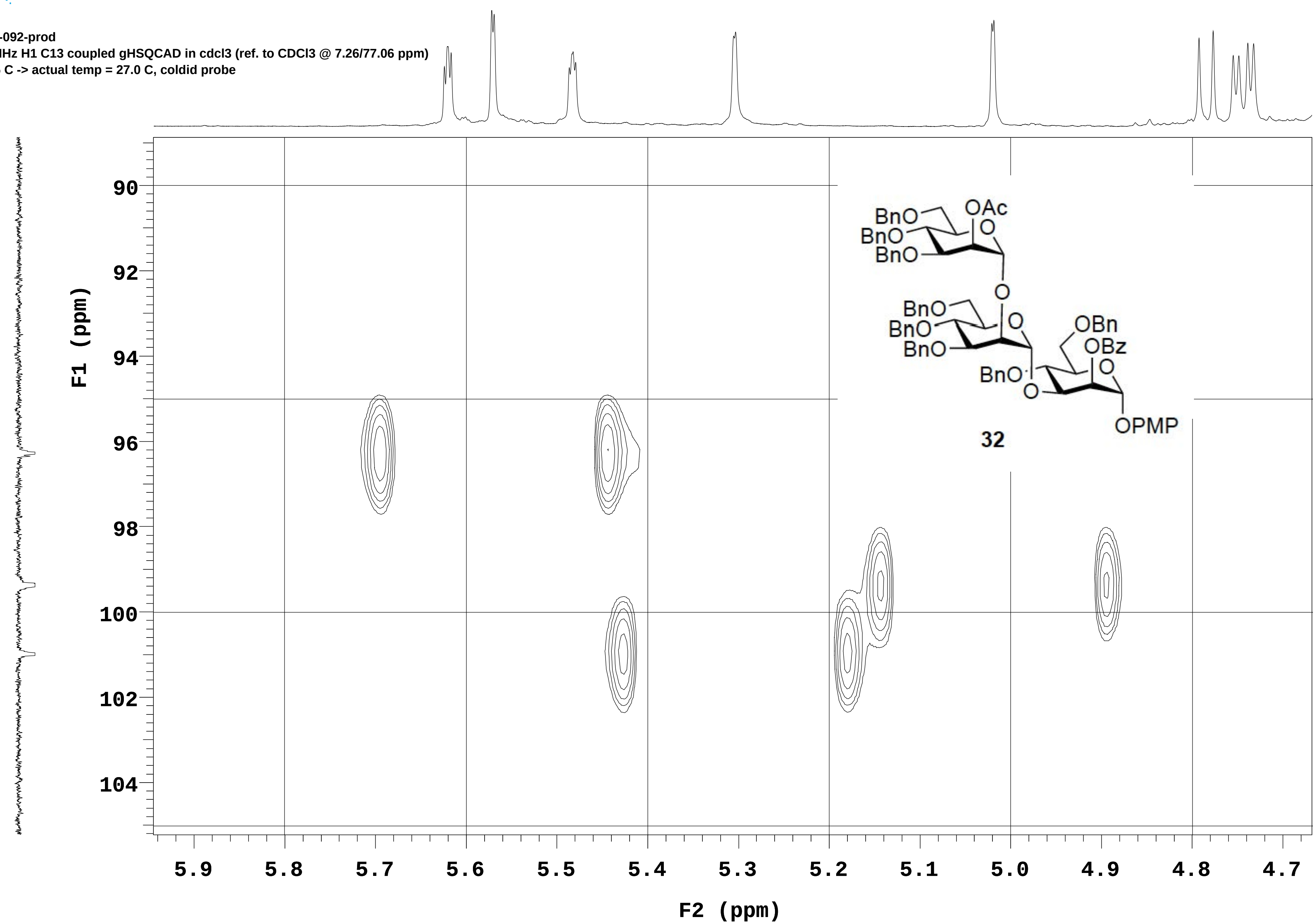
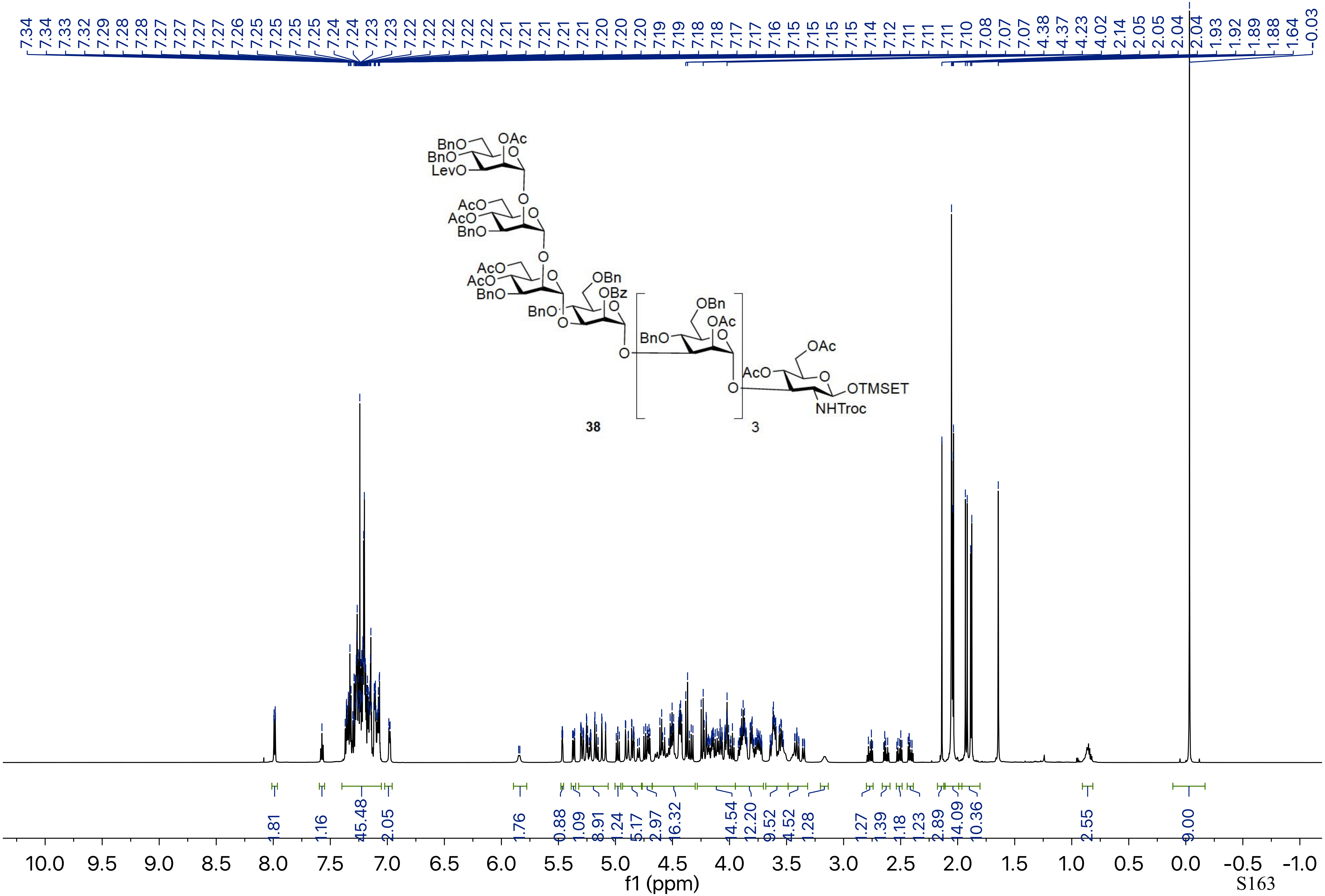
Recorded on: v700, Feb 21 2017 | Sweep Width F2|F1(Hz): 8389.26 | 38722.17 | Acquisiton Time(s): 0.1 | Relaxation Delay(s): 1.89999
Pulse Sequence: gHSQCAD | Digital Res. F2|F1(Hz/pt): 2.05 | 75.63 | Hz per mm F2|F1(Hz/mm): 3.81 | 19.88 | No. of Scans|Increments 4 | 128

Lei, WL-5-092-prod
699.762 MHz H1 C13 coupled gHSQCAD in cdcl3 (ref. to CDCl3 @ 7.26/77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Lei/2017.02/2017.02.21.v7_WL-5-092-prod_loc42_23.20_coupled_H1_gHSQCAD

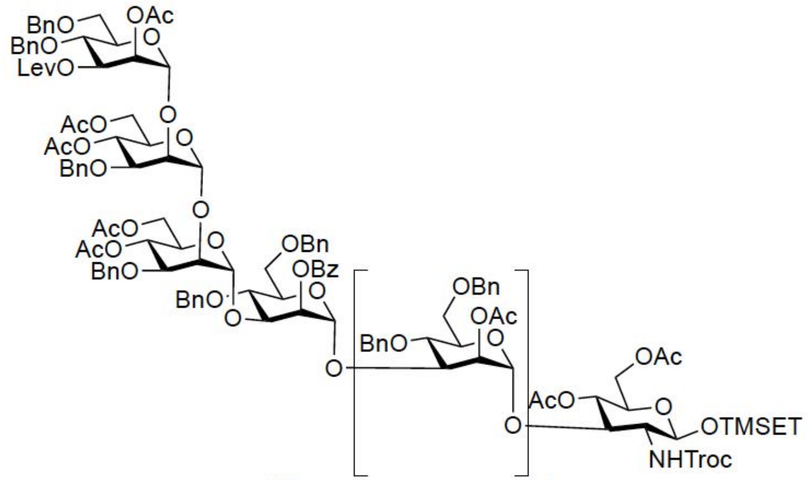
2015.07.19.v7_WL-5-098-prod_loc48_18.48_H1_1D — Lei, WL-5-098-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



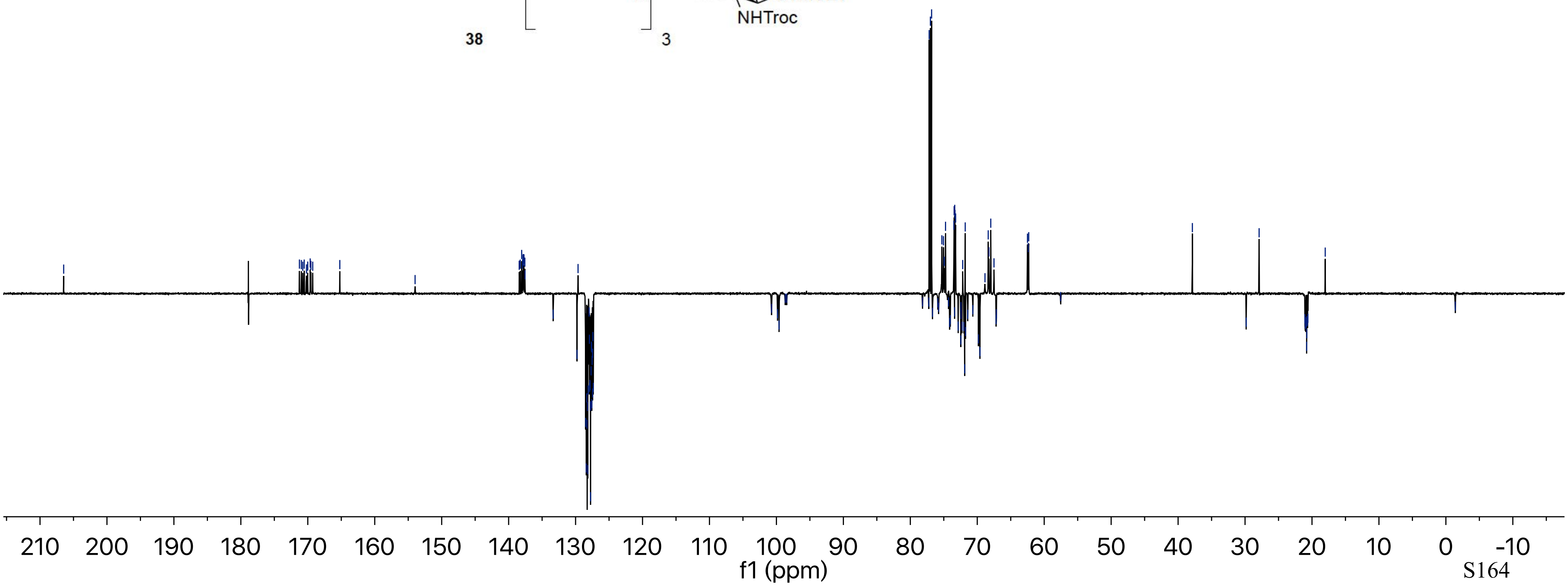
38

2015.07.19.v7_WL-5-098-prod_loc48_23.18_C13_DEPTq — Lei, WL-5-098-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p

138.05 129.79 128.50 128.41 128.31 128.28 128.27 128.22 128.19 128.12 127.93 127.91 127.85 127.83 127.79 127.77 127.71 127.69 127.63 127.60 127.57 127.53 127.47 127.45 127.42 127.35 99.61 77.18 77.00 76.82 75.29 75.05 74.74 74.13 74.03 73.49 73.45 73.37 73.33 73.23 72.85 72.46 72.28 72.00 71.88 71.80 71.76 69.83 69.60 68.36 68.26 67.98 67.19 62.50 62.38 62.31 37.87 29.83 27.90 21.01 20.96 20.91 20.80 20.79 20.78 20.75 20.67 18.02



38



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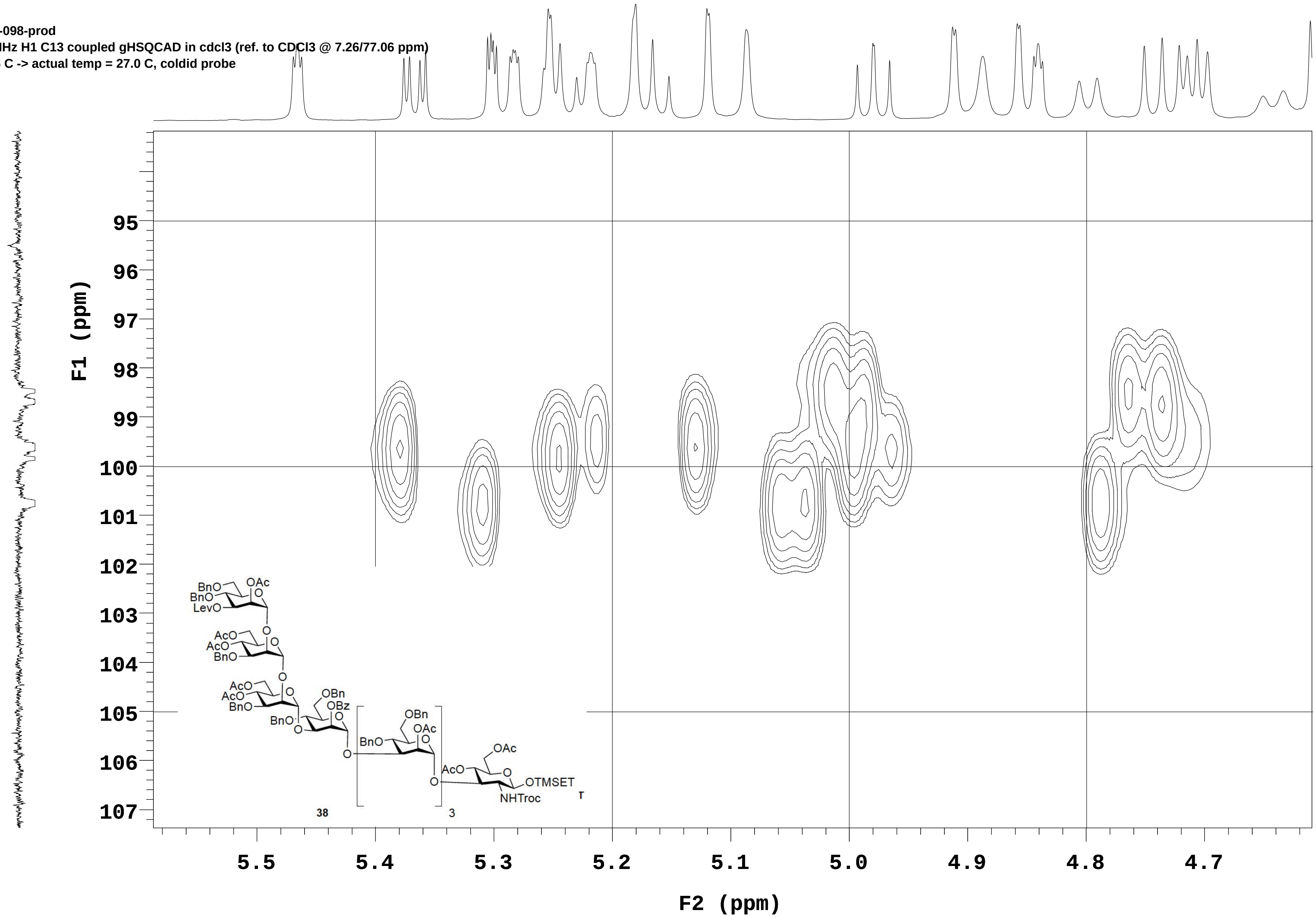
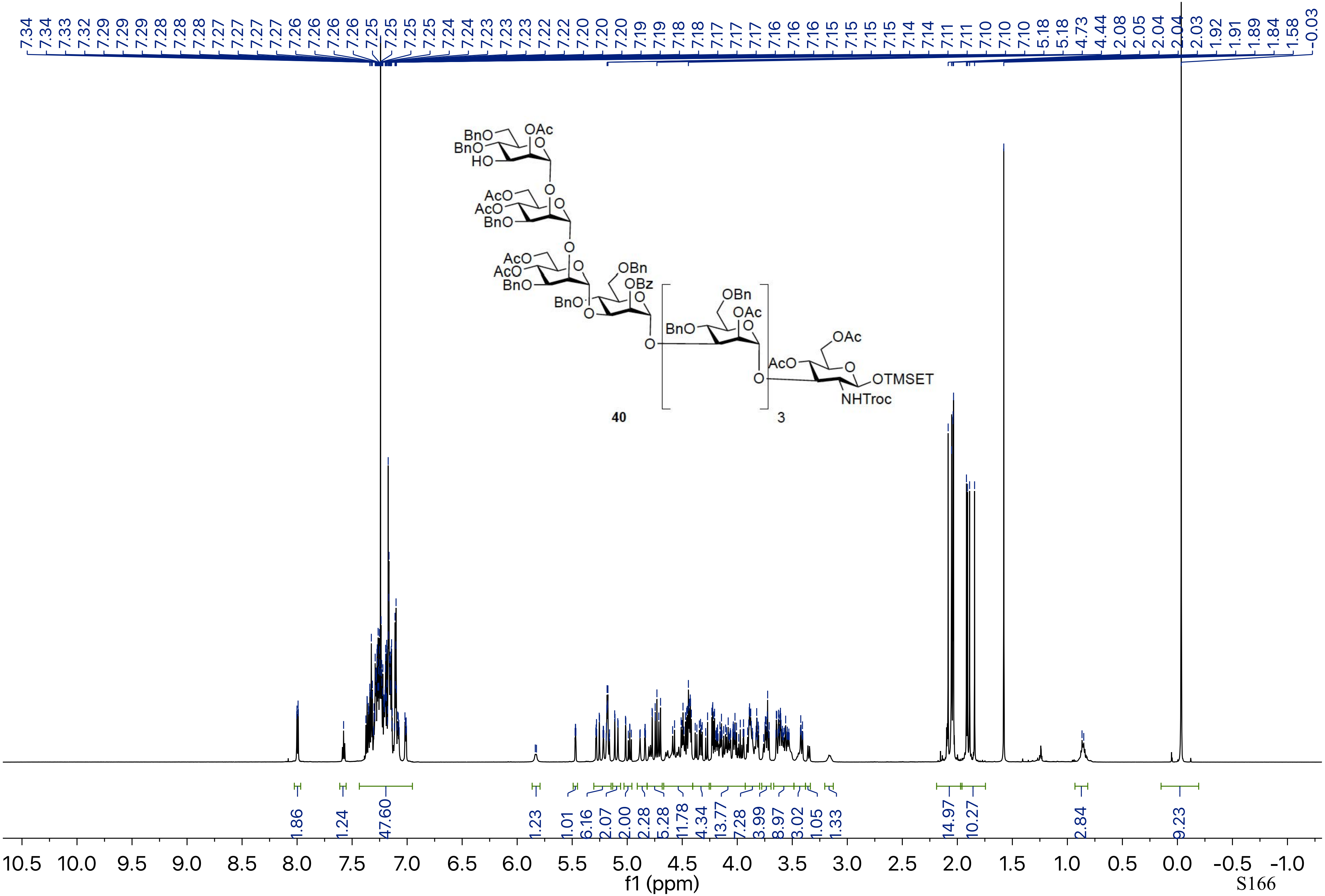
Recorded on: **v700, Feb 22 2017** | Sweep Width F2|F1(Hz): **8389.26 | 38722.17** | Acquisiton Time(s): **0.1** | Relaxation Delay(s): **1.89999**
Pulse Sequence: **gHSQCAD** | Digital Res. F2|F1(Hz/pt): **2.05 | 75.63** | Hz per mm F2|F1(Hz/mm): **2.91 | 17.26** | No. of Scans|Increments **8 | 128**

Lei, WL-5-098-prod
699.762 MHz H1 C13 coupled gHSQCAD in cdcl3 (ref. to CDCl3 @ 7.26/77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe

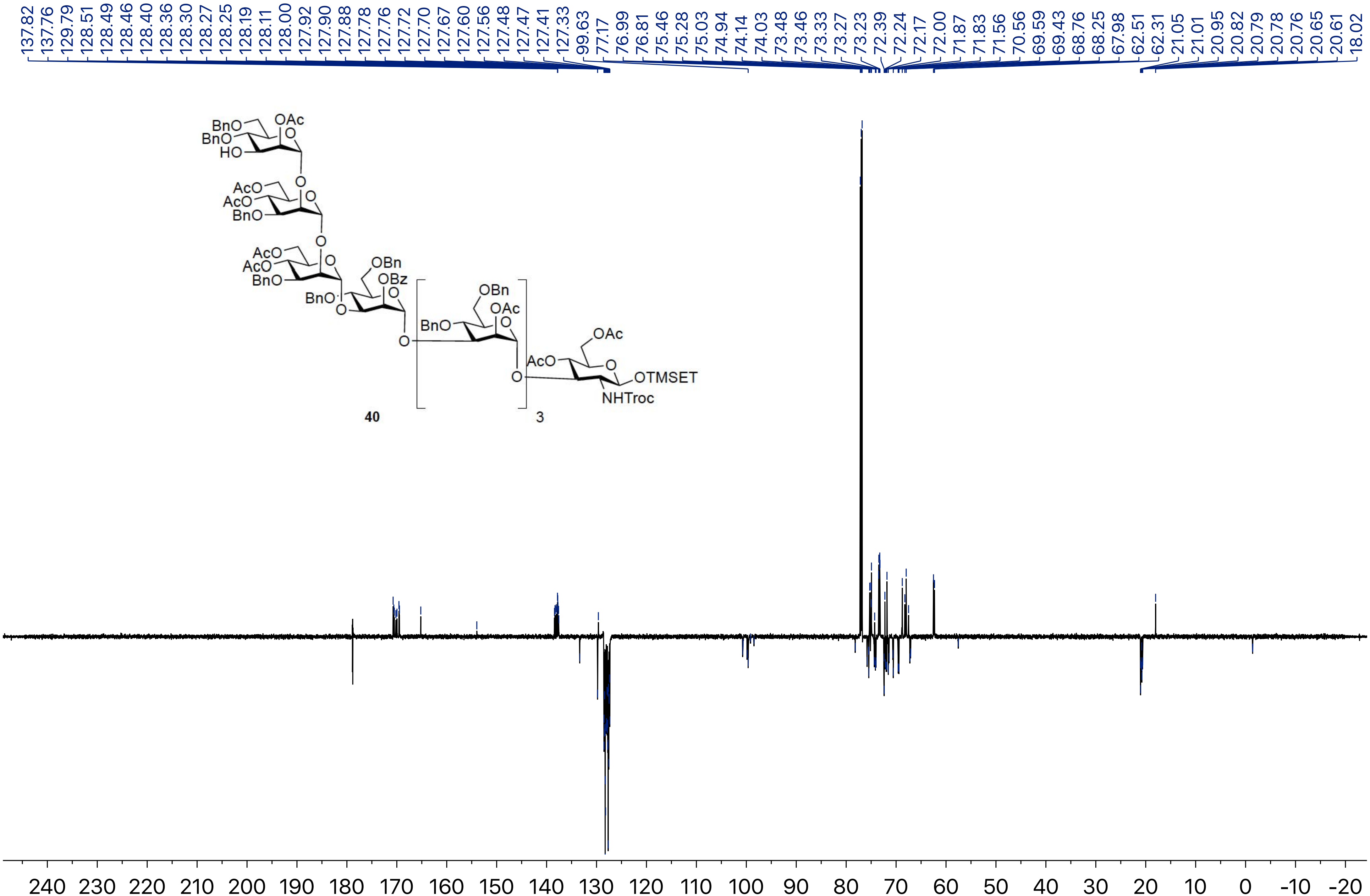


File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Lei/2017.02/2017.02.22.v7_WL-5-098-prod_loc44_01.13_coupled_H1_gHSQCAD

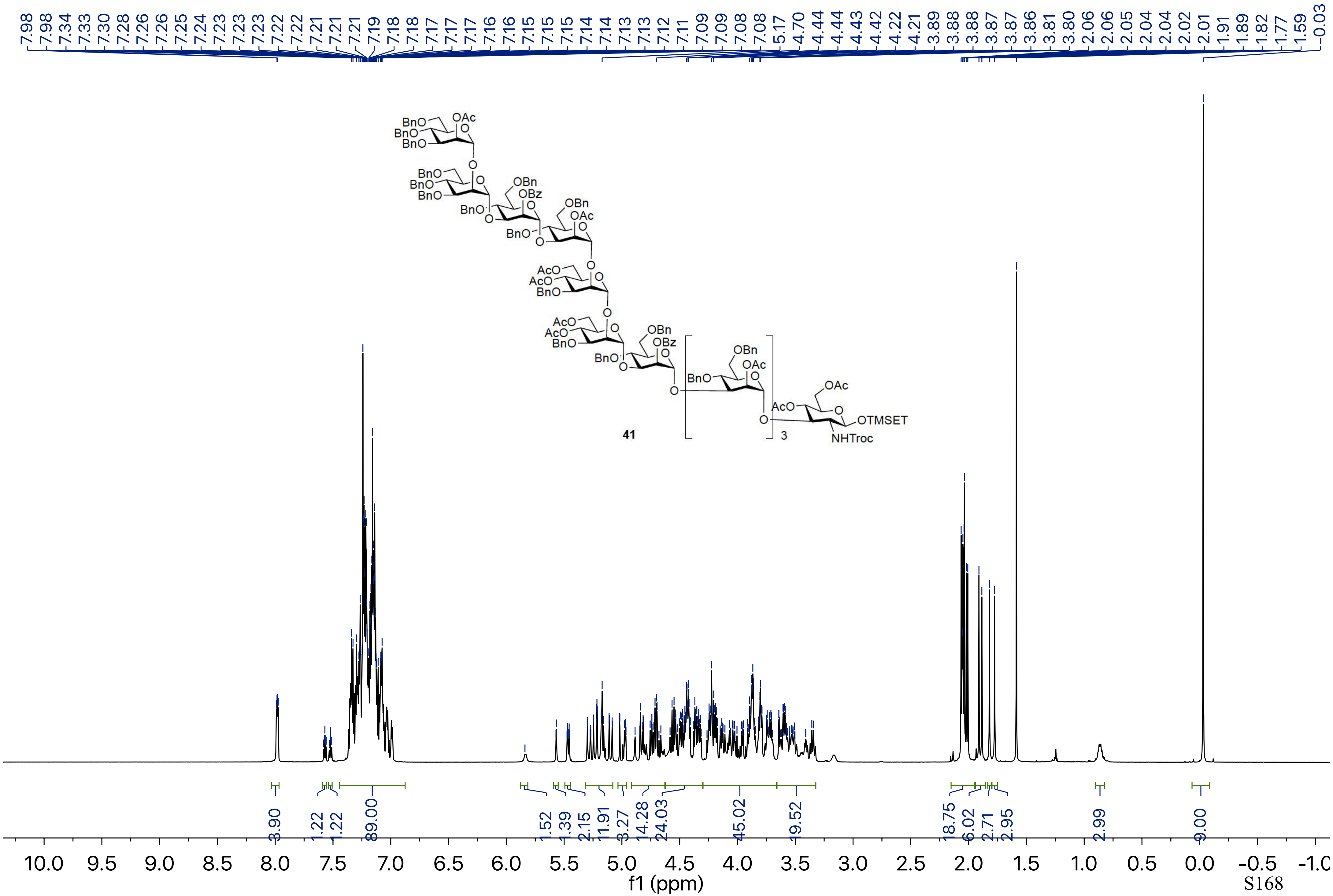
2015.07.19.v7_WL-5-094-prod_loc47_18.42_H1_1D — Lei, WL-5-094-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



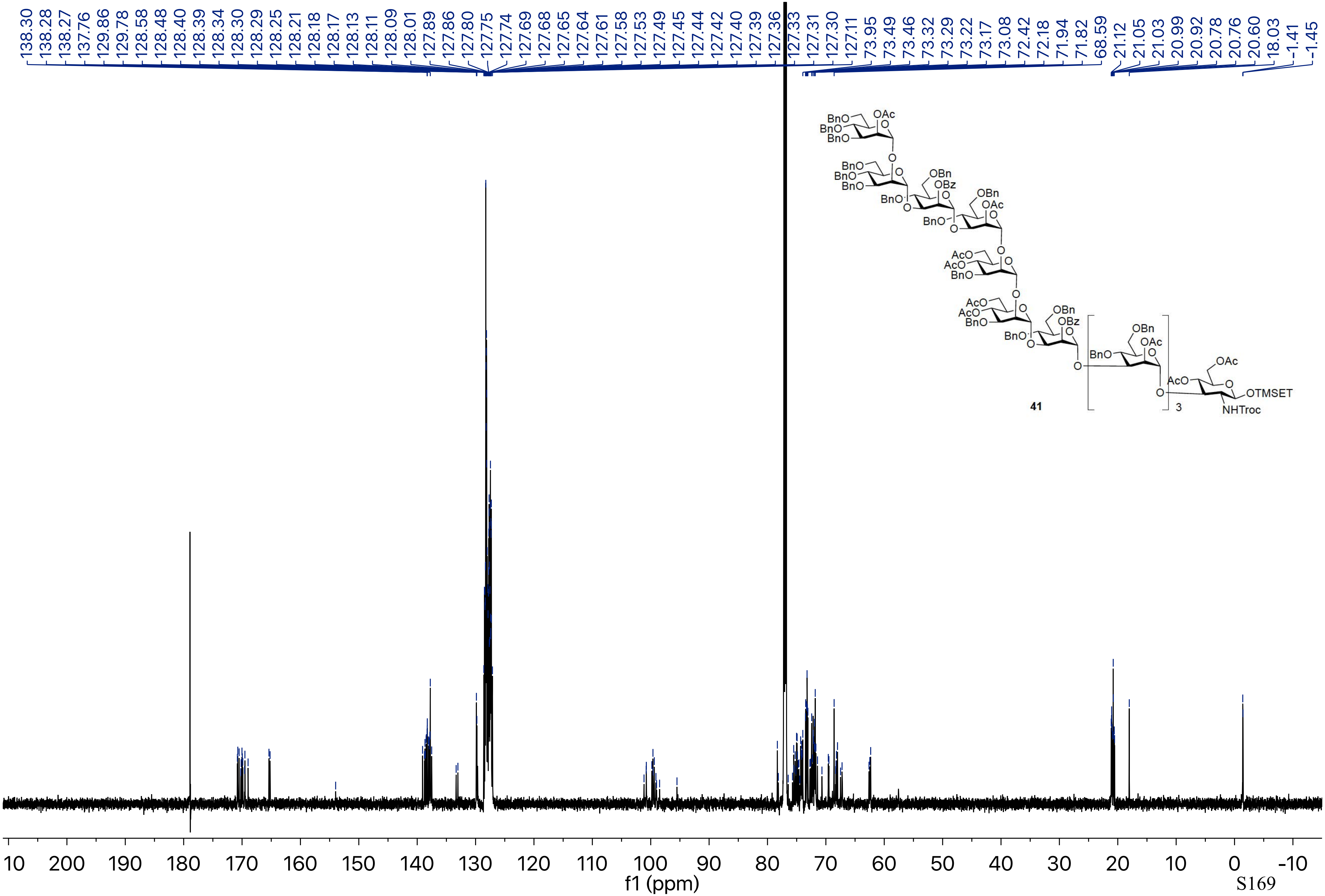
2015.07.19.v7_WL-5-094-prod_loc47_20.02_C13_DEPTq — Lei, WL-5-094-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



2015.07.14.v7_WL-5-096-prod_loc15_17.54_H1_1D — Lei, WL-5-096-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp :



2015.07.14.v7_WL-5-096-prod_loc15_20.16_C13_1D — Lei, WL-5-096-prod — 175.976 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), tem



Department of Chemistry, University of Alberta

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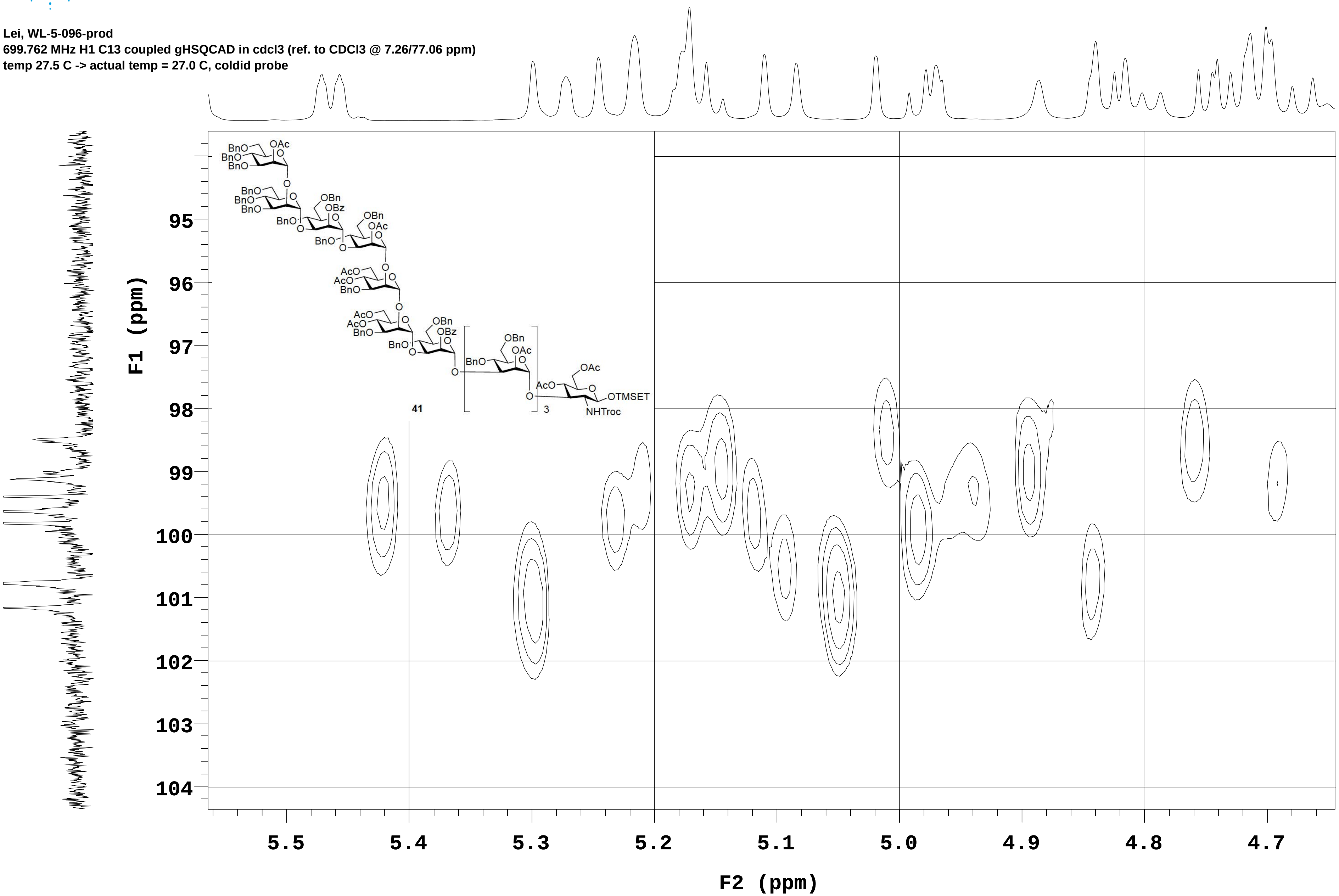
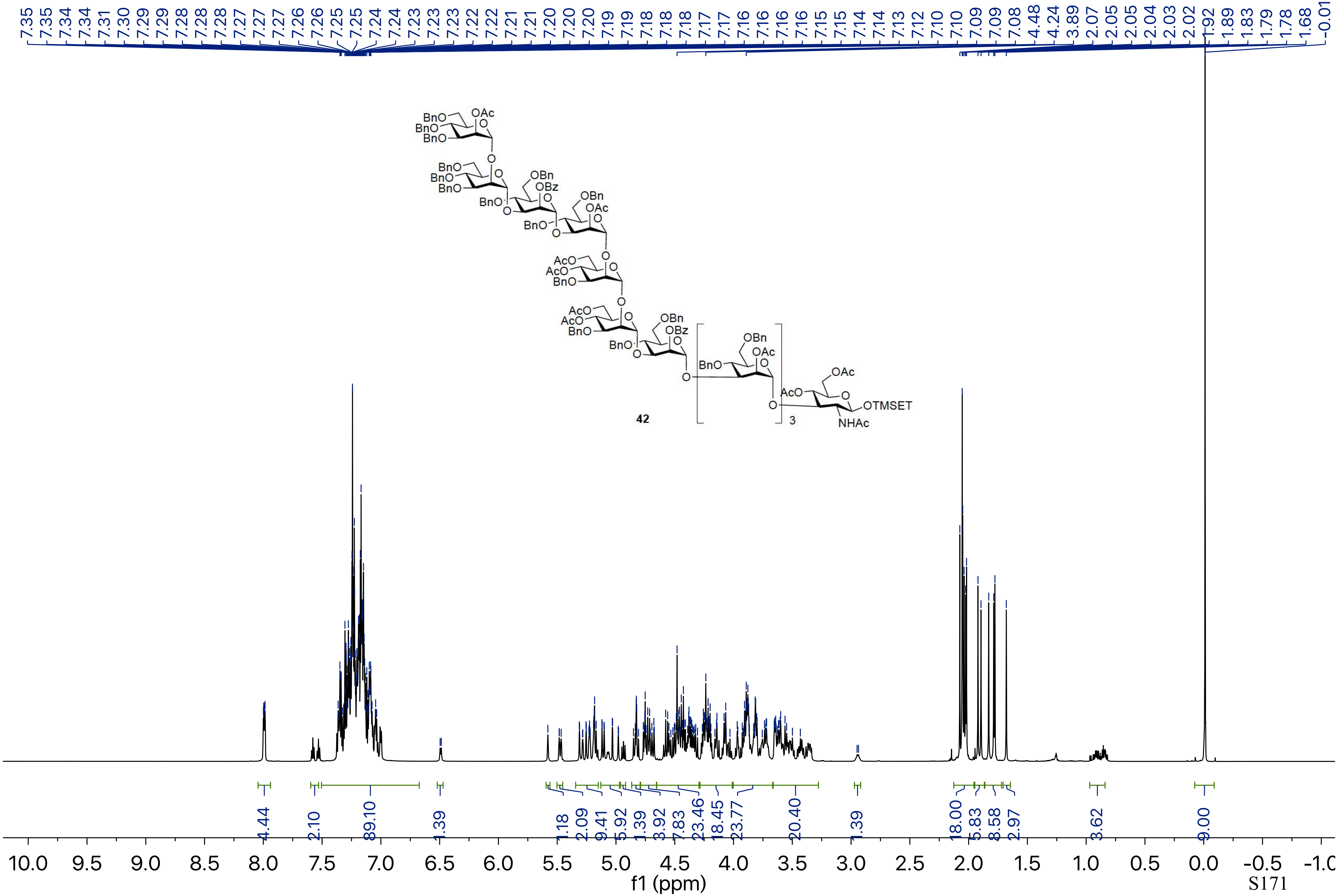
Recorded on:	v700, Feb 21 2017	Sweep Width F2|F1(Hz):	8389.26 | 38722.17	Acquisiton Time(s):	0.1	Relaxation Delay(s):	1.89999
Pulse Sequence:	gHSQCAD	Digital Res. F2|F1(Hz/pt):	2.05 | 75.63	Hz per mm F2|F1(Hz/mm):	2.74 | 13.08	No. of Scans|Increments	8 | 128

Lei, WL-5-096-prod
699.762 MHz H1 C13 coupled gHSQCAD in cdcl3 (ref. to CDCl3 @ 7.26/77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe

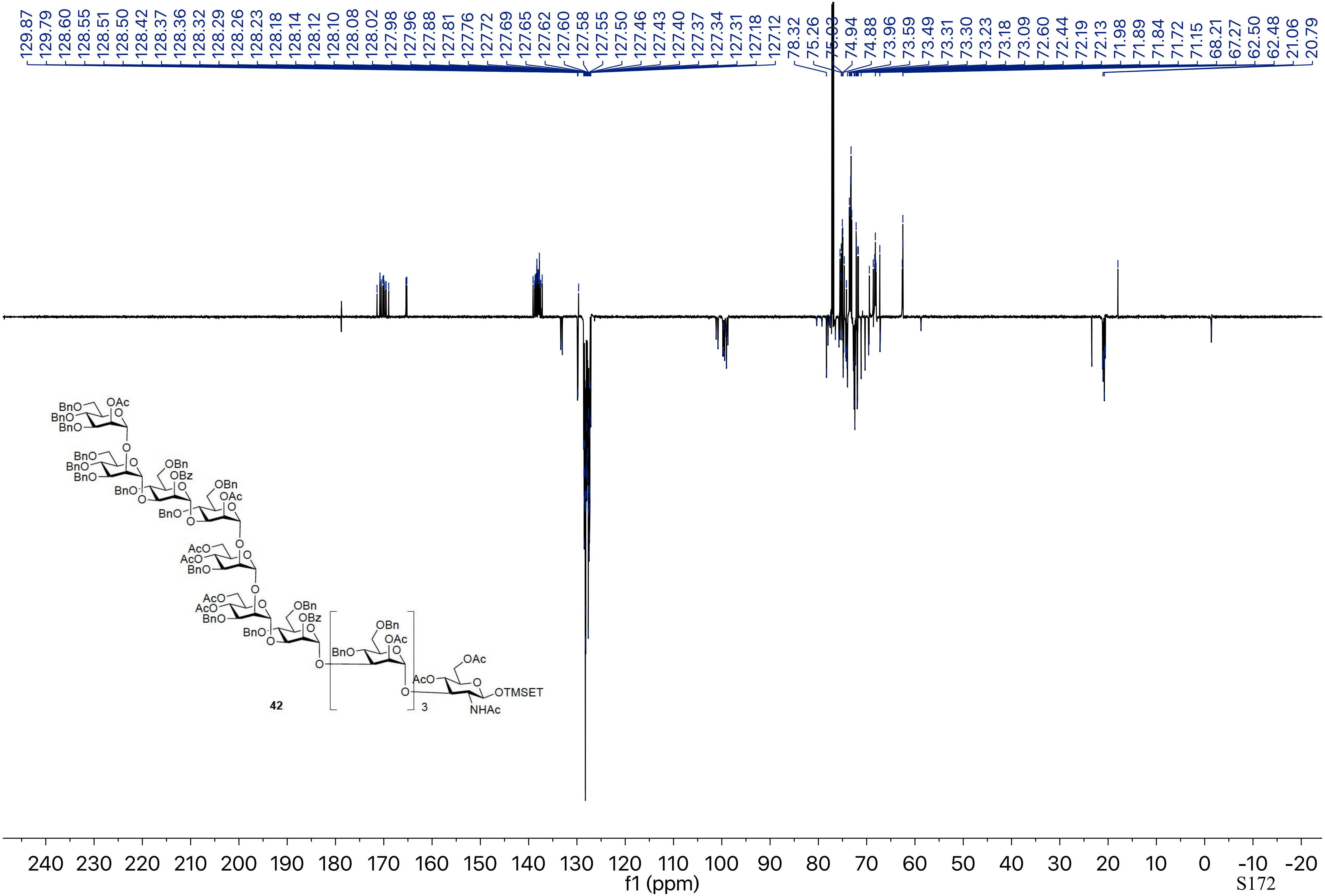


File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Lei/2017.02/2017.02.21.v7_WL-5-096-prod_loc43_23.59_coupled_H1_gHSQCAD

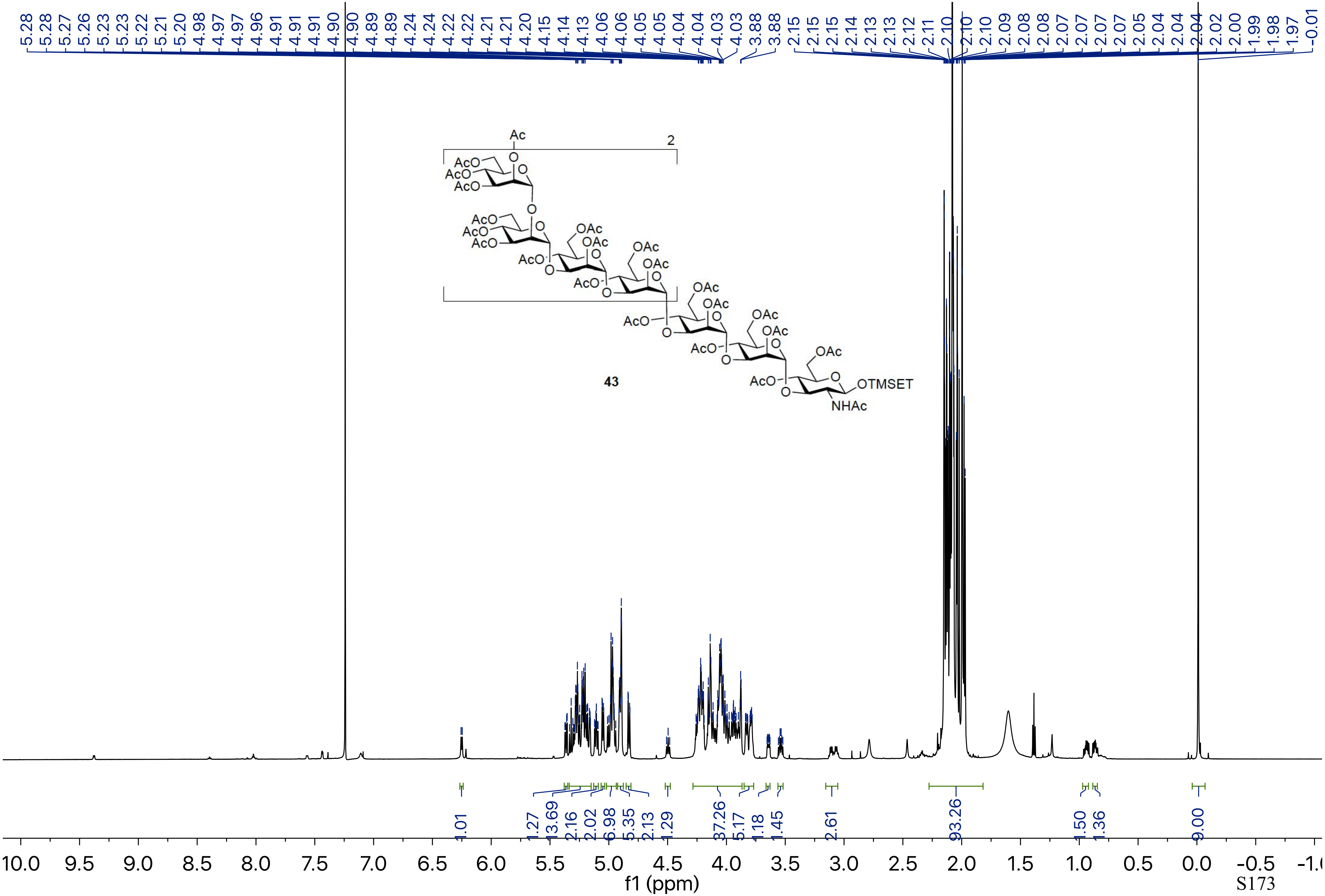
2015.07.15.v7_WL-5-097-prod_loc48_22.16_H1_1D — Lei, WL-5-097-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



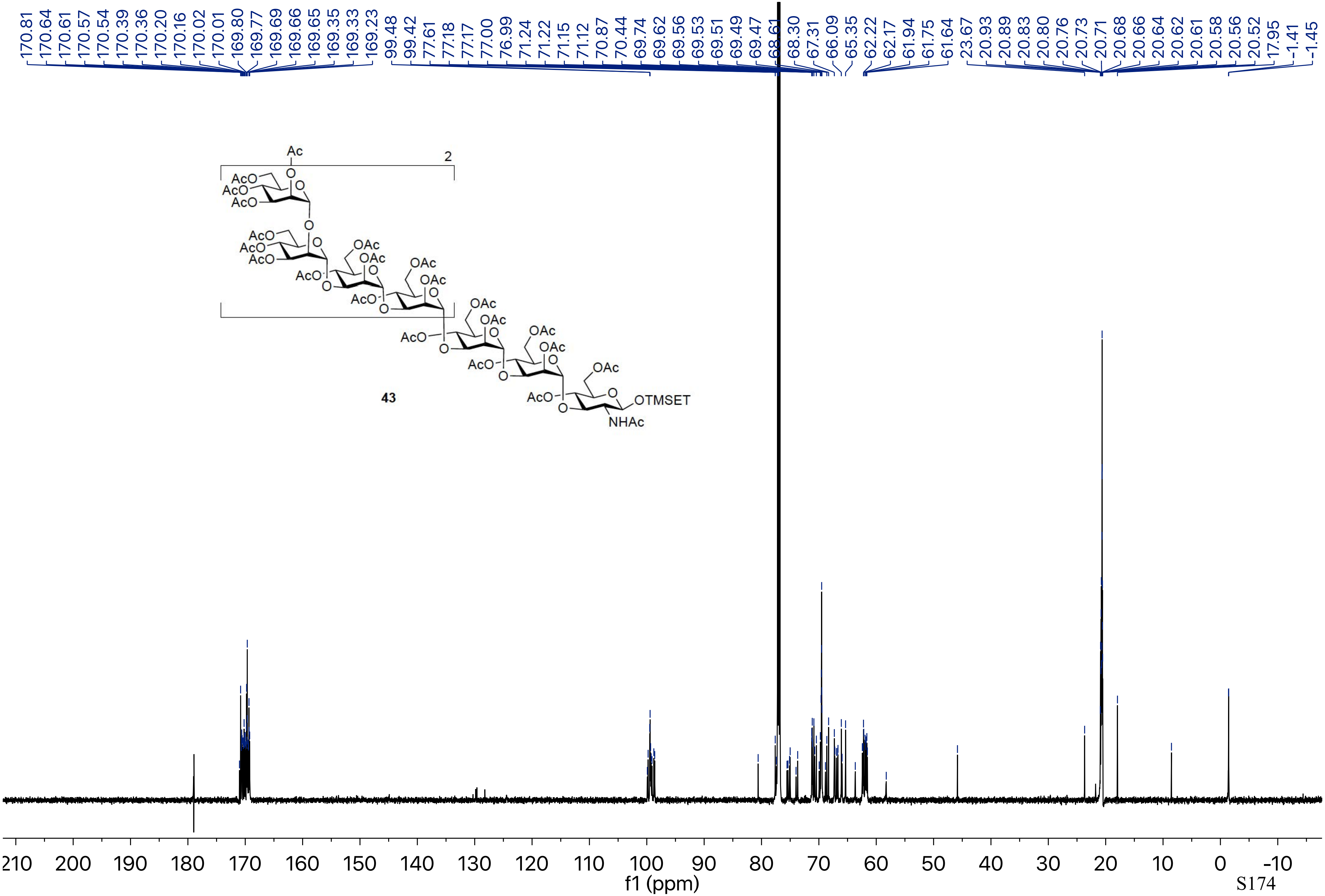
2015.07.15.v7_WL-5-097-prod_loc48_22.23_C13_DEPTq — Lei, WL-5-097-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p

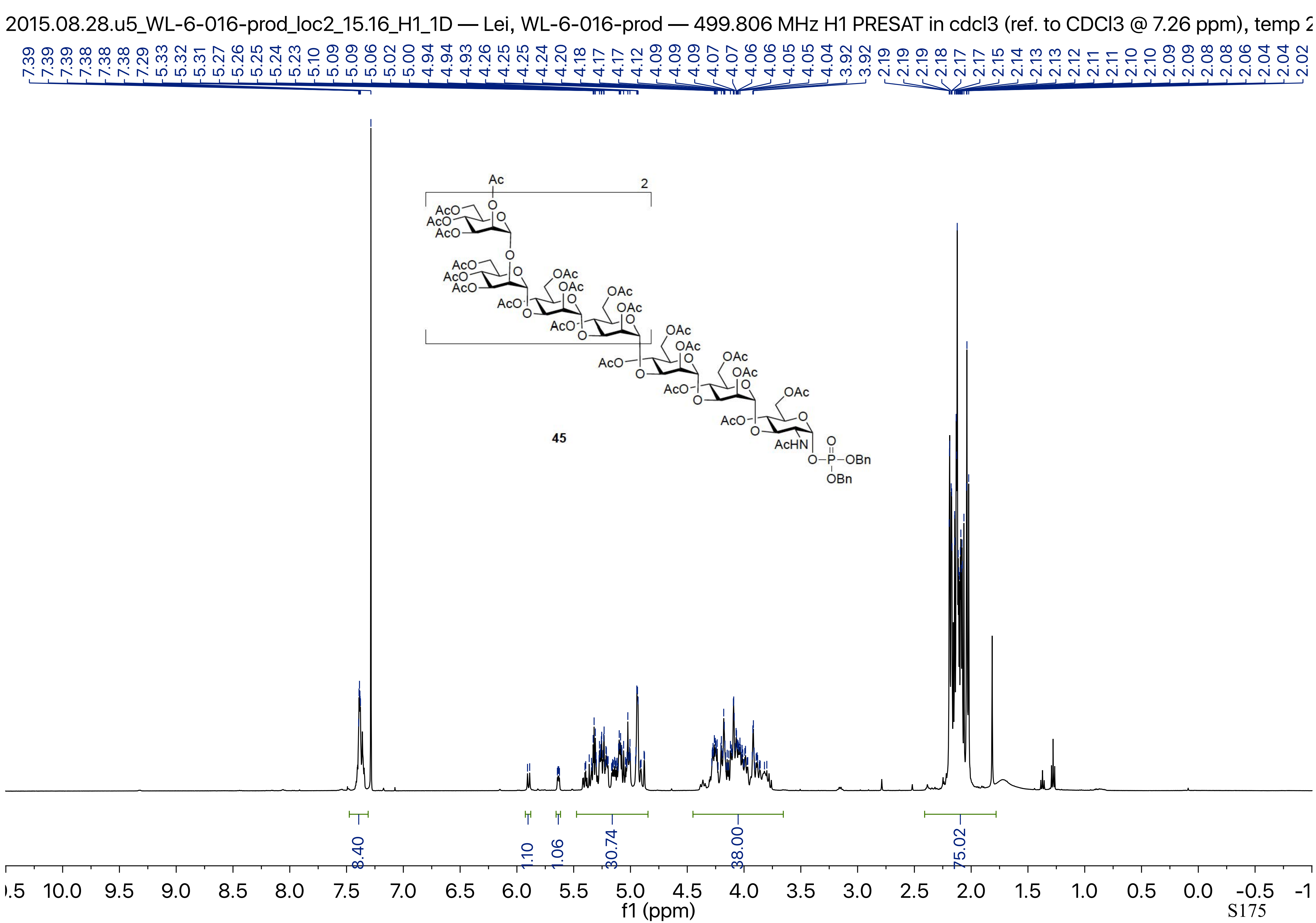


2015.08.25.v7_WL-6-007-prod_loc48_10.03_H1_1D — Lei, WL-6-007-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



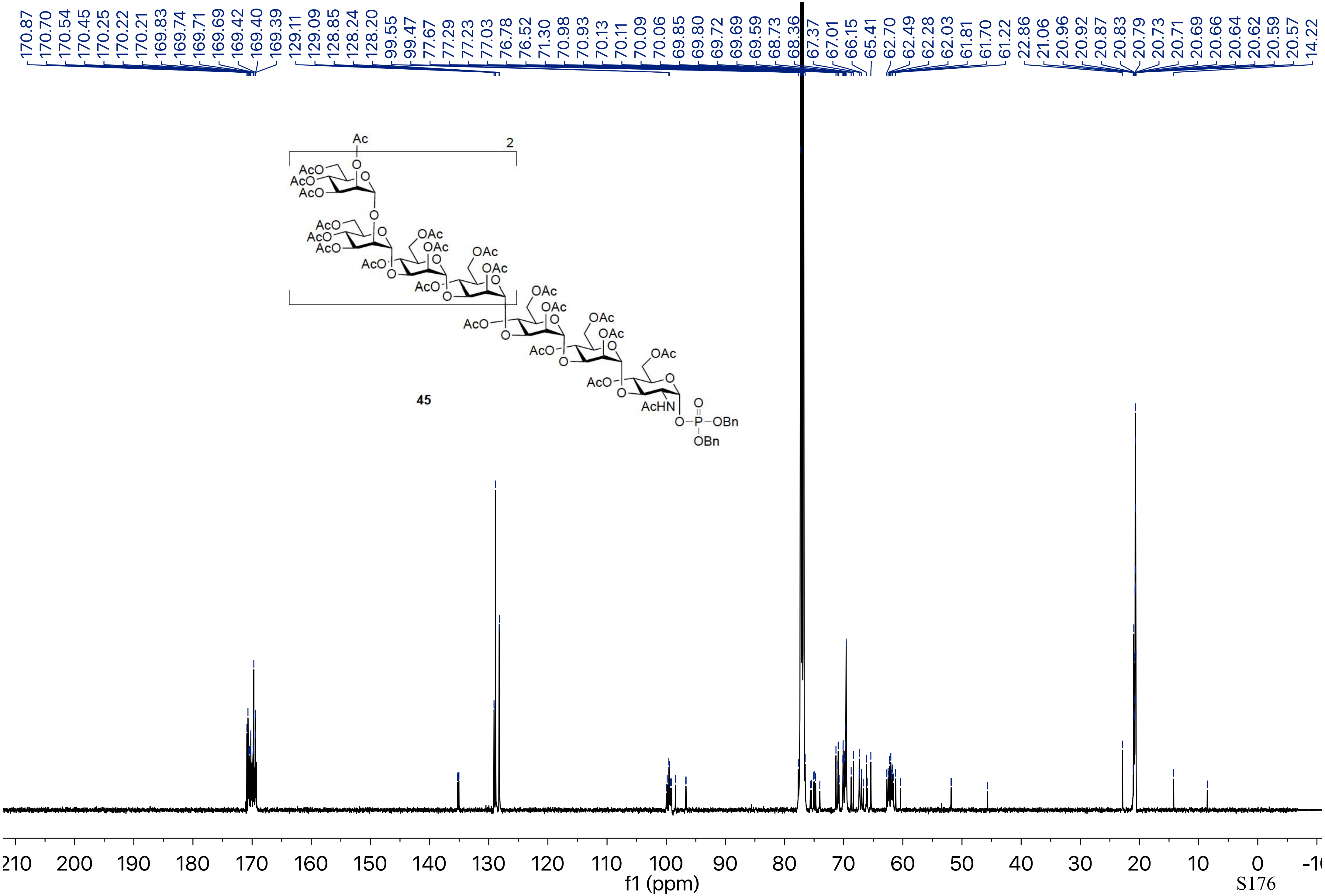
2015.08.24.v7_WL-6-007-prod_loc48_20.19_C13_1D — Lei, WL-6-007-prod — 175.976 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), ter



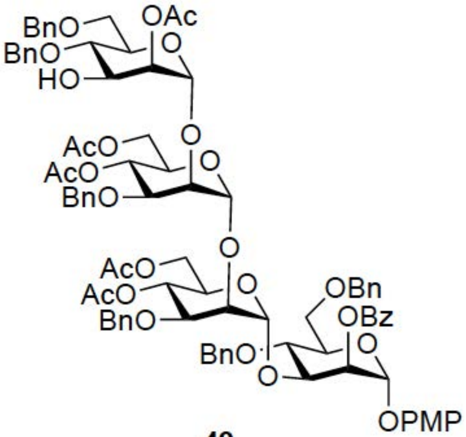


2015.08.28.u5_WL-6-016-prod_loc2_15.16_H1_1D — Lei, WL-6-016-prod — 499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2
7.39 7.39 7.39 7.38 7.38 7.38 7.29 5.33 5.32 5.31 5.27 5.26 5.25 5.24 5.23 5.10 5.09 5.09 5.06 5.02 5.00 4.94 4.94 4.93 4.26 4.25 4.25 4.24 4.20 4.18 4.17 4.17 4.12 4.09 4.09 4.09 4.07 4.07 4.06 4.06 4.05 4.05 4.04 3.92 3.92 2.19 2.19 2.19 2.18 2.17 2.17 2.15 2.14 2.13 2.13 2.12 2.11 2.11 2.10 2.10 2.09 2.09 2.08 2.08 2.06 2.04 2.04 2.02
Ac
2
AcO
AcO
AcO
O
O
OAc
AcO
AcHN
O-P-OBn
OBn
45
8.40
1.10
1.06
30.74
38.00
75.02
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

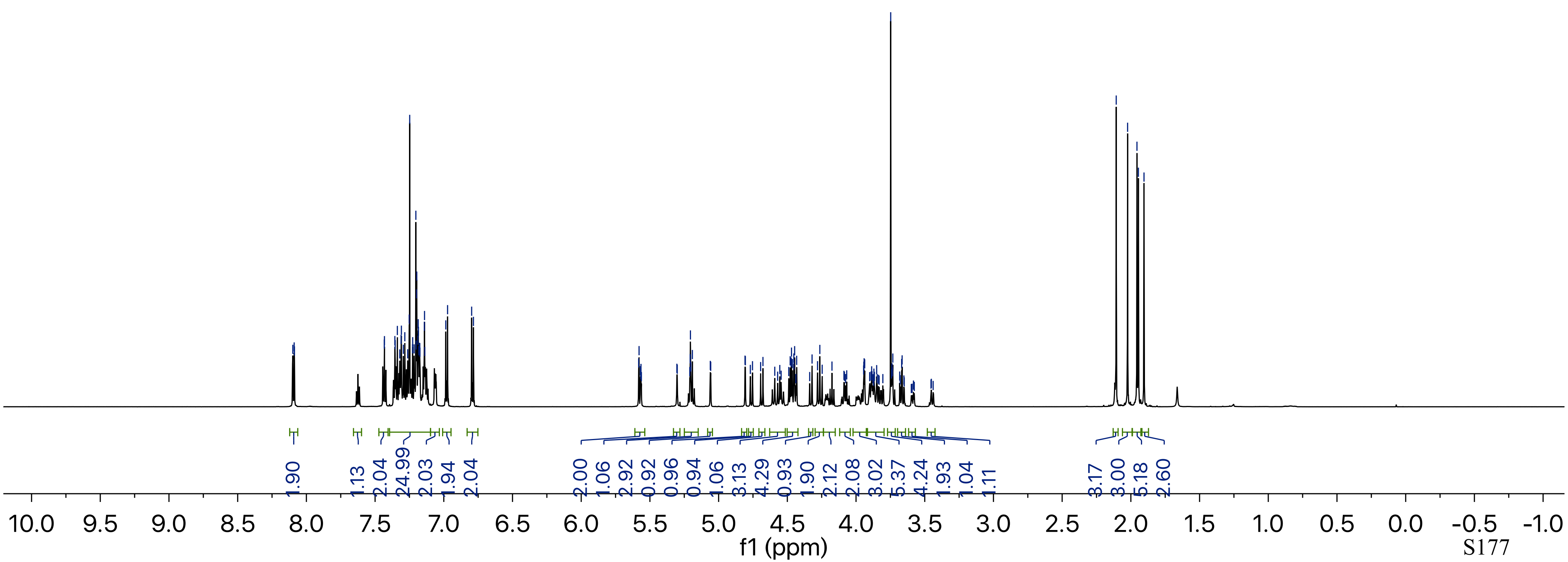
2015.08.28.u5_WL-6-016-prod_loc2_20.02_C13_1D — Lei, WL-6-016-prod — 125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), tem



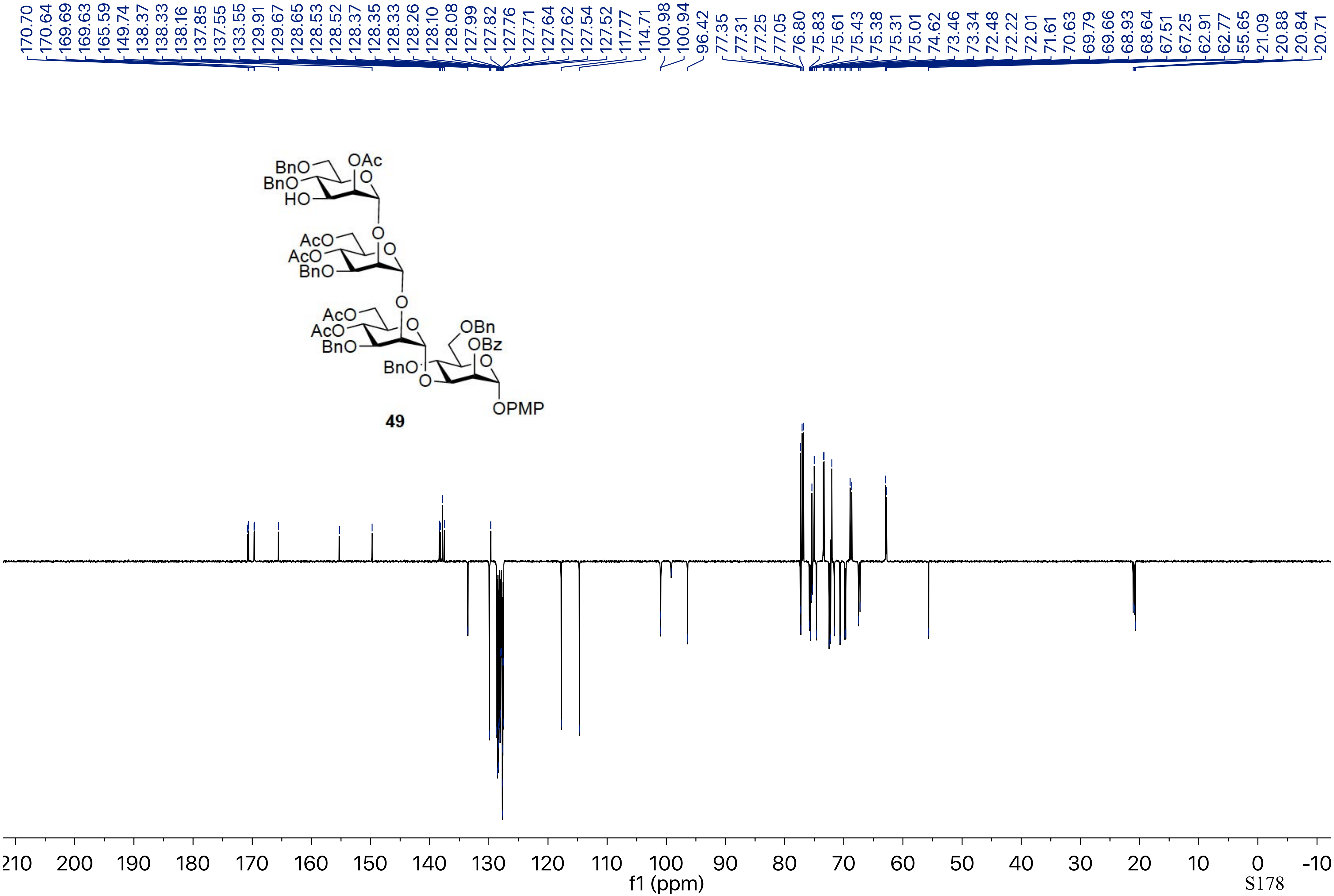
2015.12.10.v7_WL-5-065-prod_loc48_17.18_H1_1D — Lei, WL-5-065-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



49

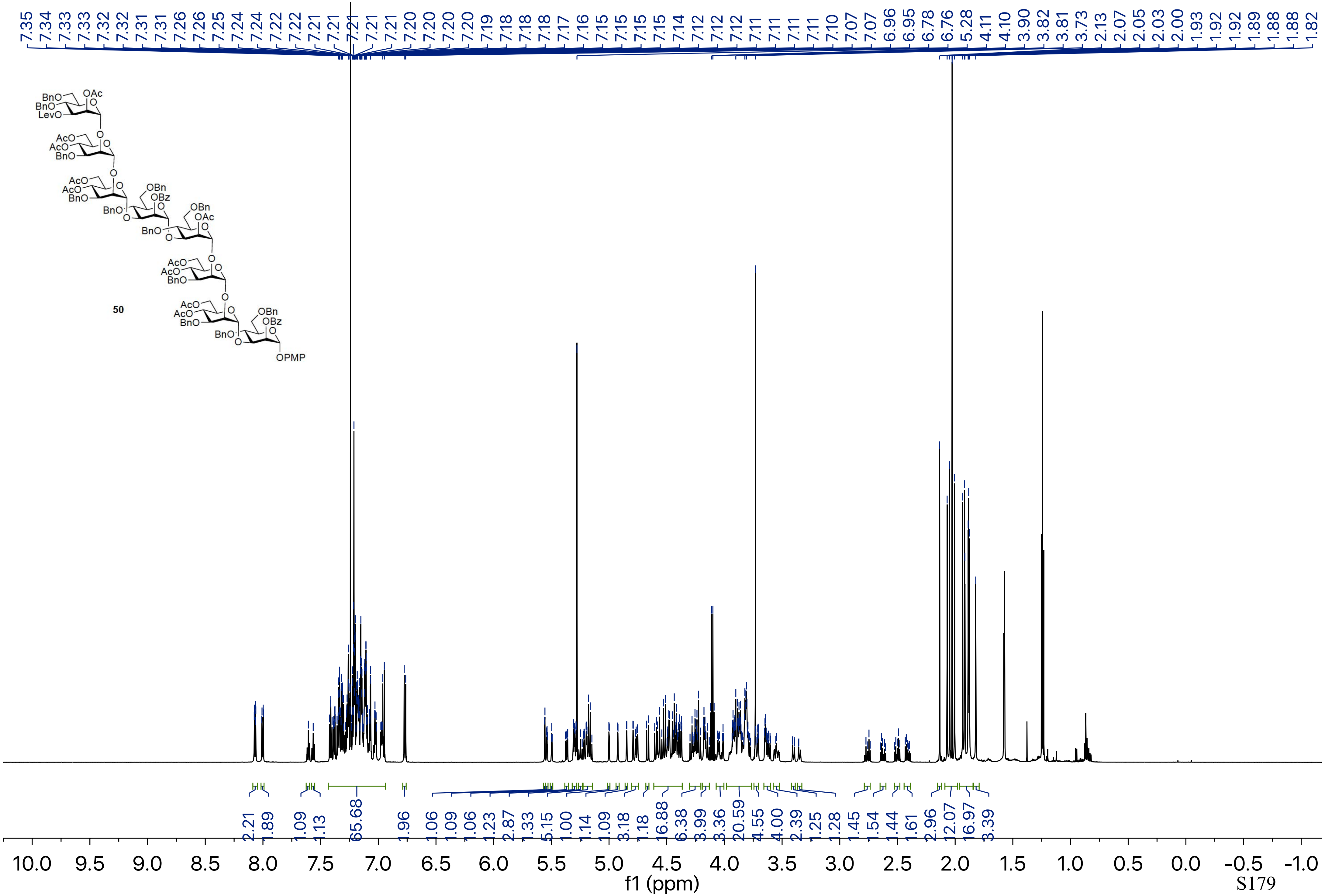


2015.12.10.u5_WL-5-065-prod_loc12_17.29_C13_DEPTq — Lei, WL-5-065-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp

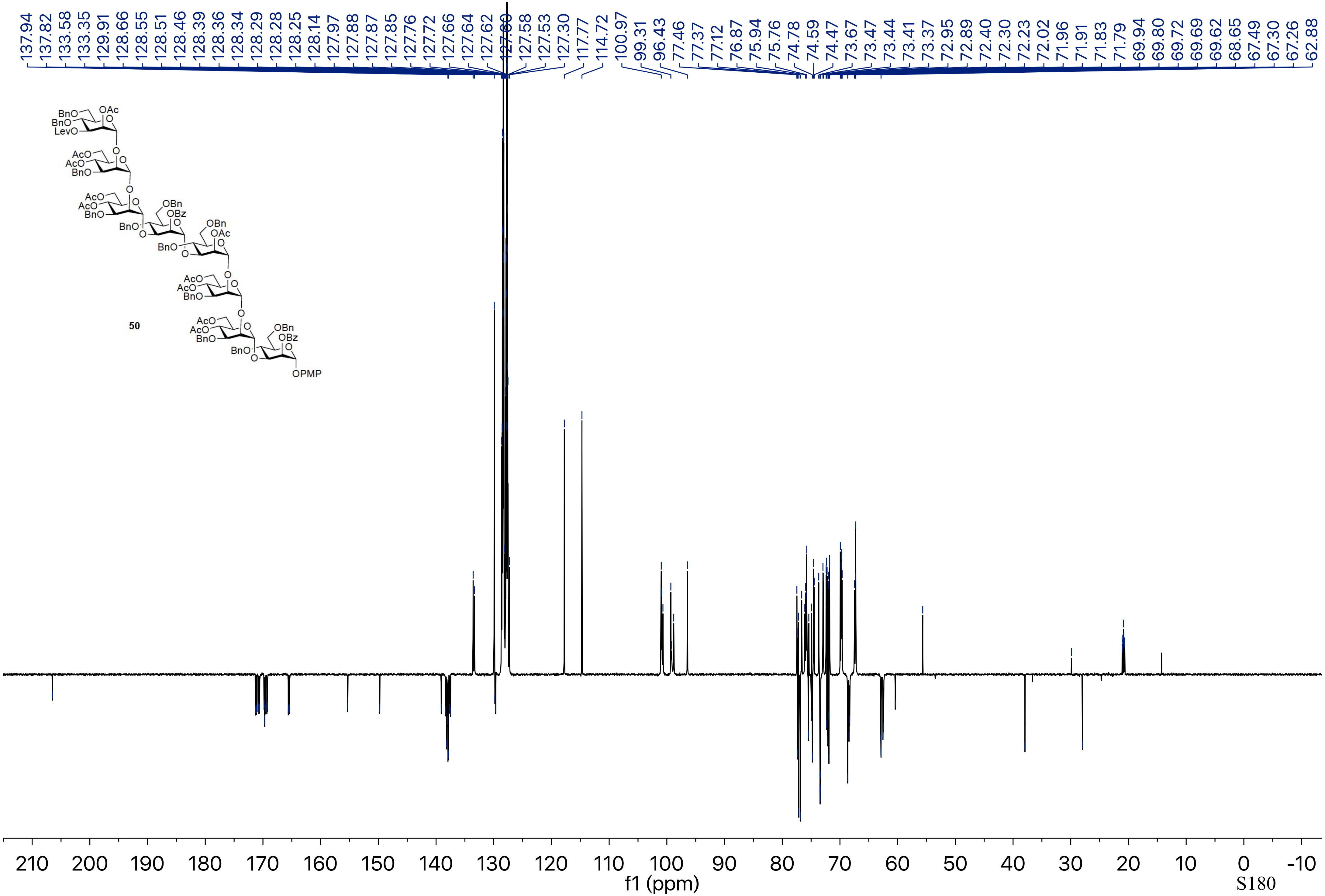


49

2015.05.15.v7_WL-5-067-prod1_loc26_16.27_H1_1D — Lei, WL-5-067-prod1 — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), tem



2015.05.15.u5_WL-5-067-prod1_loc8_14.44_C13_DEPTq — Lei, WL-5-067-prod1 — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06

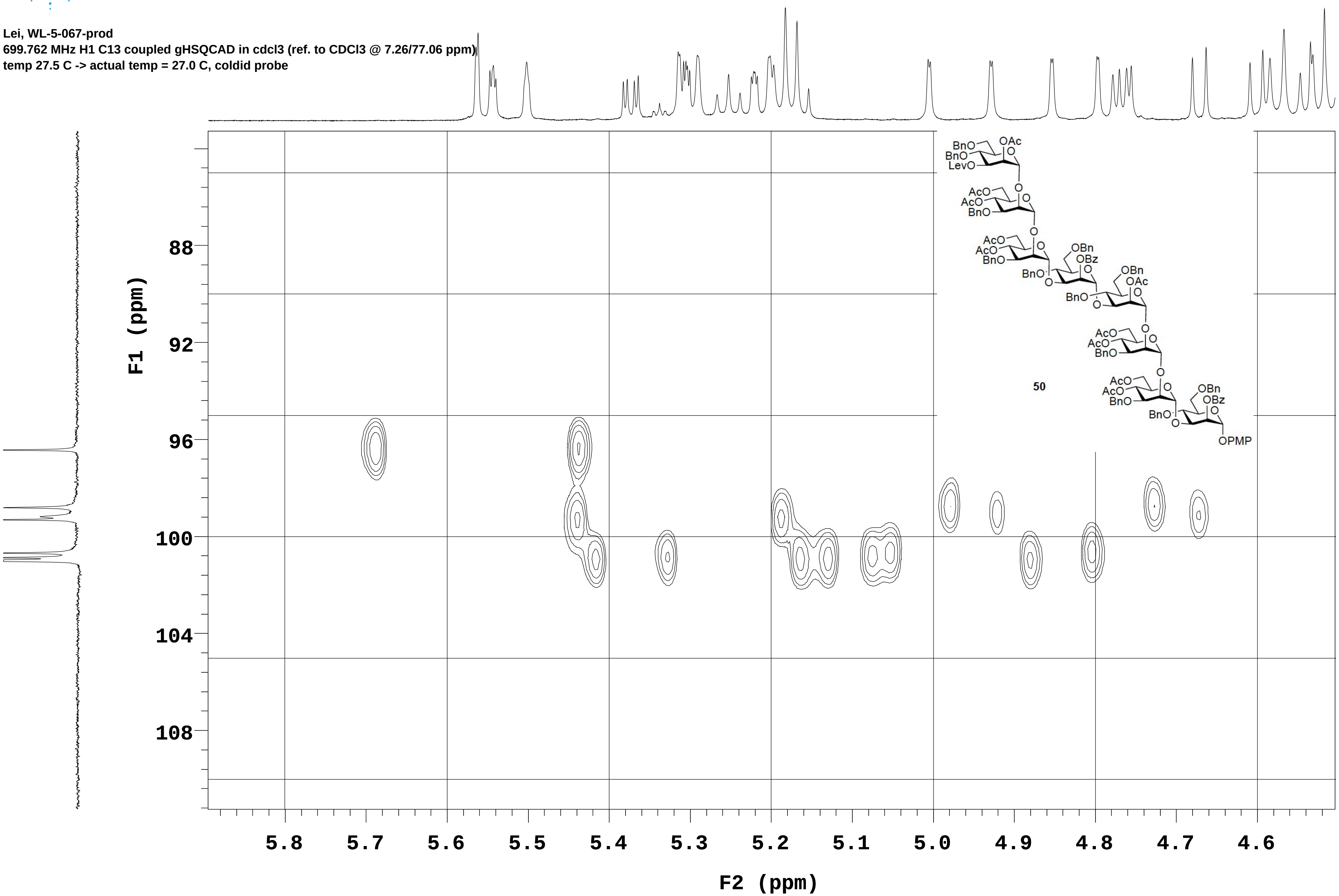


Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on: v700, Jan 16 2017
Pulse Sequence: gHSQCAD
Sweep Width F2|F1(Hz): 8389.26 | 38722.17
Digital Res. F2|F1(Hz/pt): 2.05 | 75.63
Acquisiton Time(s): 0.1
Hz per mm F2|F1(Hz/mm): 4.15 | 34.00
Relaxation Delay(s): 1.89999
No. of Scans|Increments 4 | 128

Lei, WL-5-067-prod
699.762 MHz H1 C13 coupled gHSQCAD in cdcl3 (ref. to CDCl3 @ 7.26/77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



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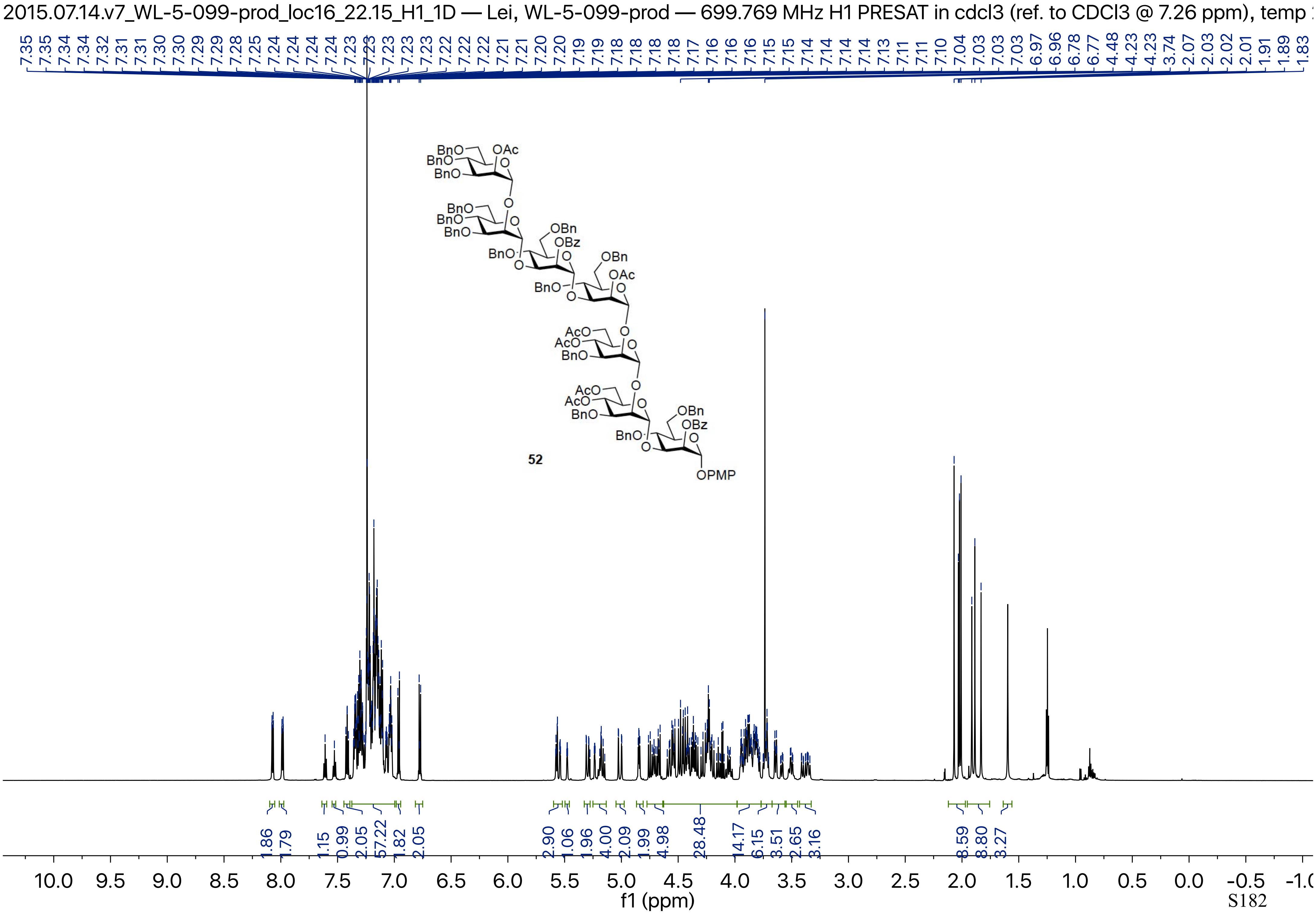
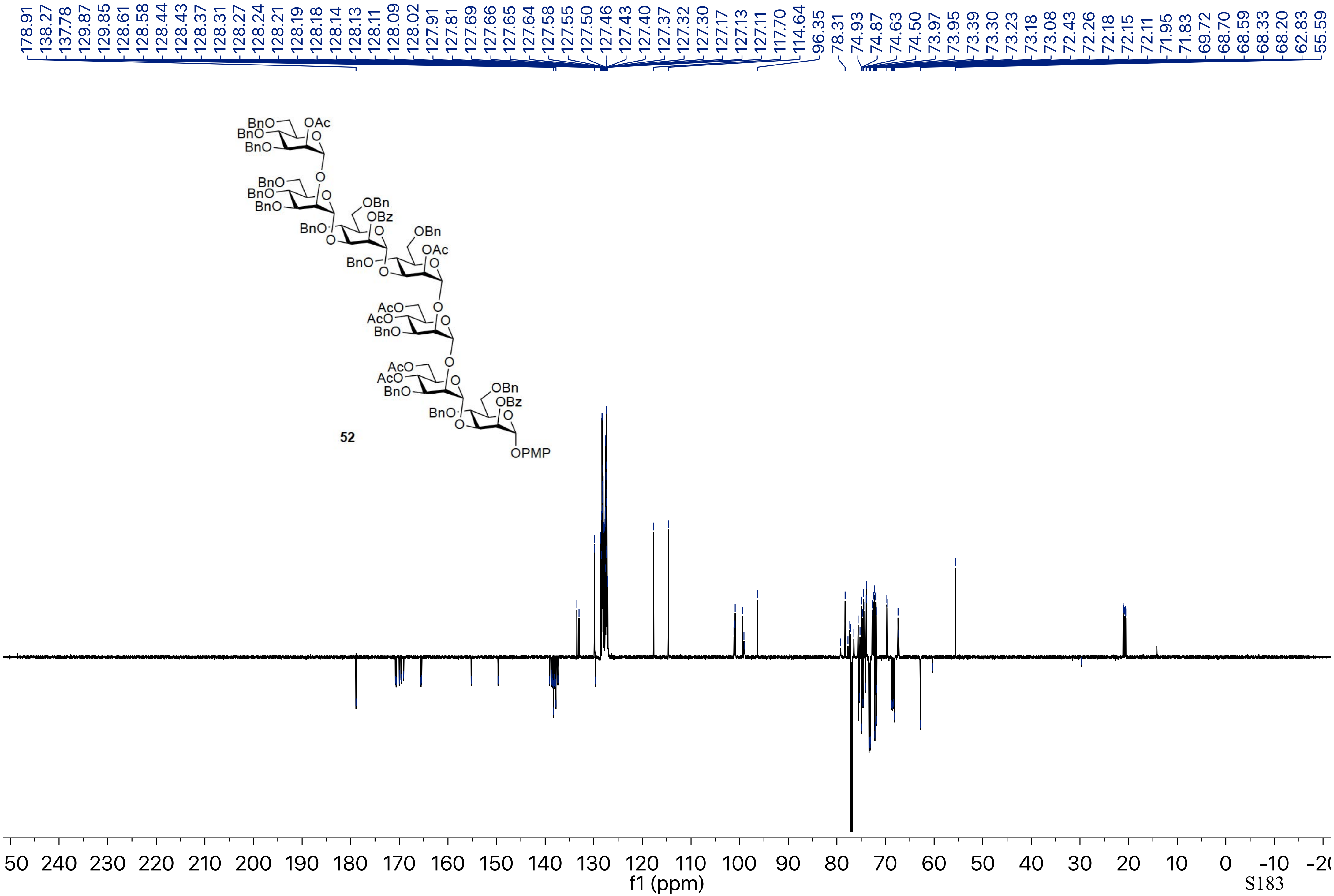
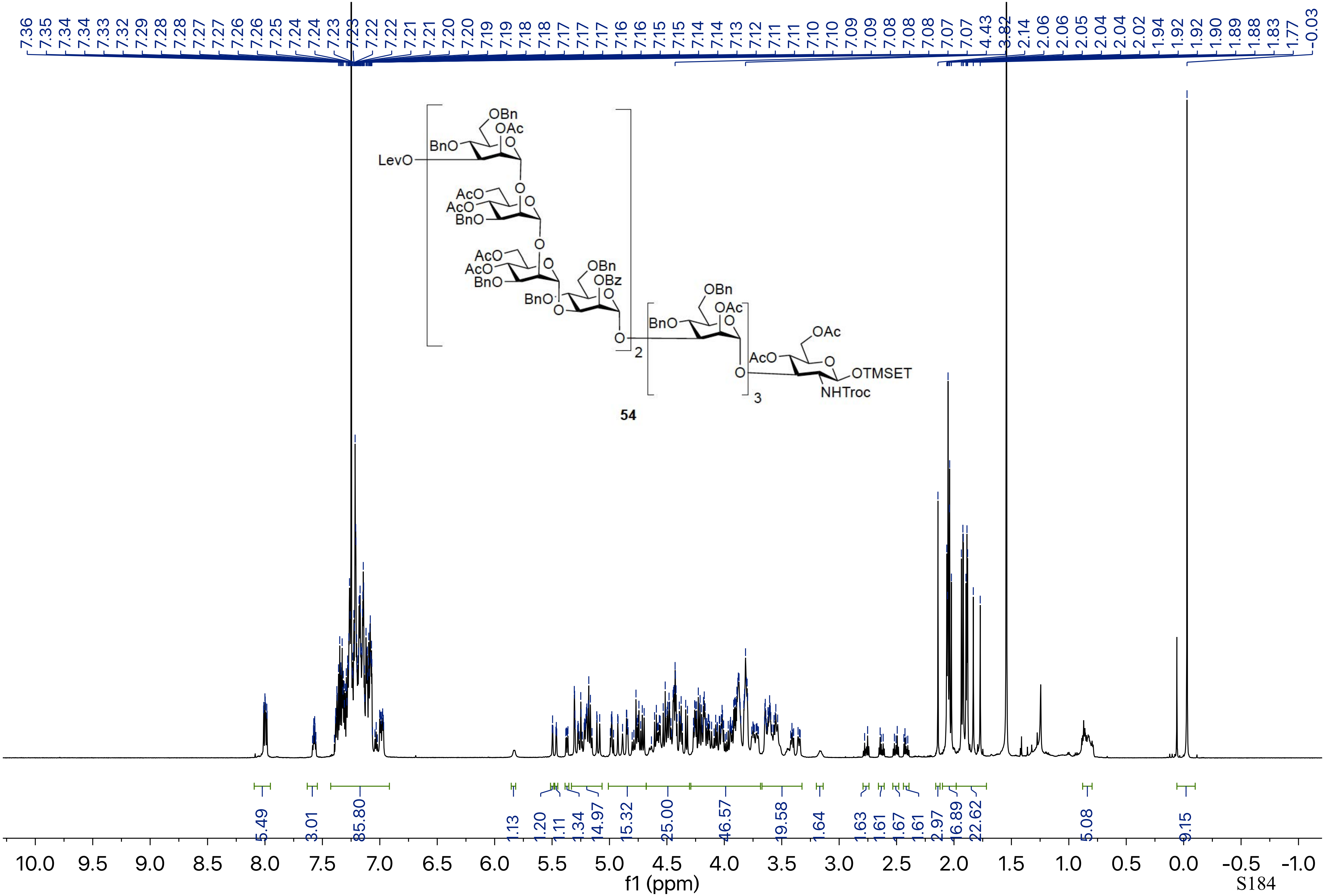
File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Lei/2017.01/2017.01.16.v7_WL-5-067-prod_loc42_12.53_coupled_H1_gHSQCAD


2015.07.14.v7_WL-5-099-prod_loc16_22.15_H1_1D — Lei, WL-5-099-prod — 699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp
7.35 7.35 7.34 7.34 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.25 7.24 7.24 7.24 7.24 7.23 7.23 7.23 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.18 7.18 7.17 7.16 7.16 7.16 7.15 7.15 7.14 7.14 7.14 7.14 7.13 7.11 7.11 7.10 7.04 7.03 7.03 7.03 6.97 6.96 6.78 6.77 4.48 4.23 4.23 3.74 2.07 2.03 2.02 2.01 1.91 1.89 1.83
BnO
BnO
BnO
OAc
O
O
BnO
BnO
BnO
O
OBn
OBz
BnO
O
O
OBn
OAc
BnO
O
O
O
AcO
AcO
BnO
O
O
AcO
AcO
BnO
O
OBn
OBz
BnO
O
O
OPMP
52
1.86 1.79 1.15 0.99 2.05 57.22 1.82 2.05 2.90 1.06 1.96 4.00 2.09 1.99 4.98 28.48 14.17 6.15 3.51 2.65 3.16 8.59 8.80 3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

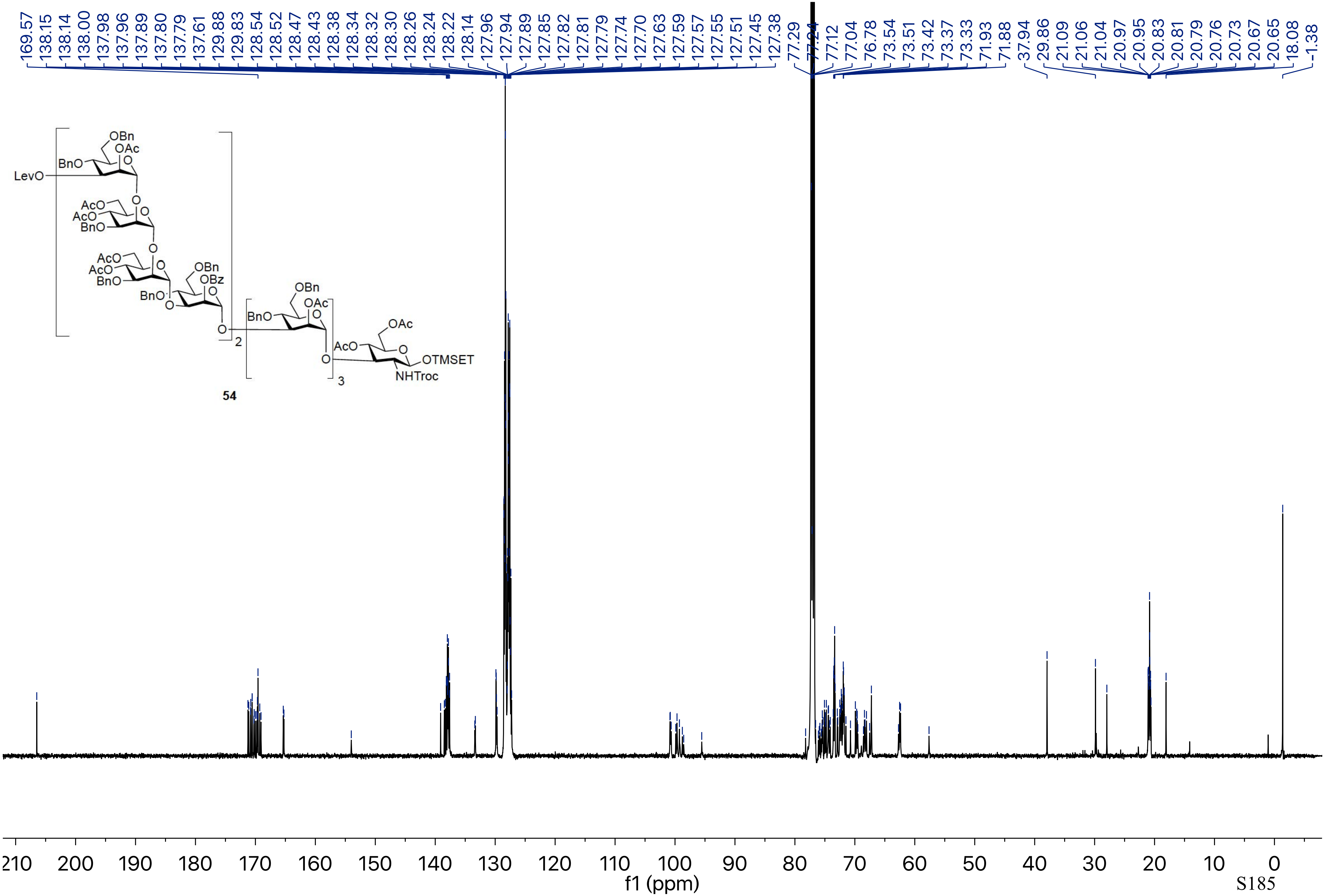
2015.07.14.v7_WL-5-099-prod_loc16_22.22_C13_DEPTq — Lei, WL-5-099-prod — 175.976 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



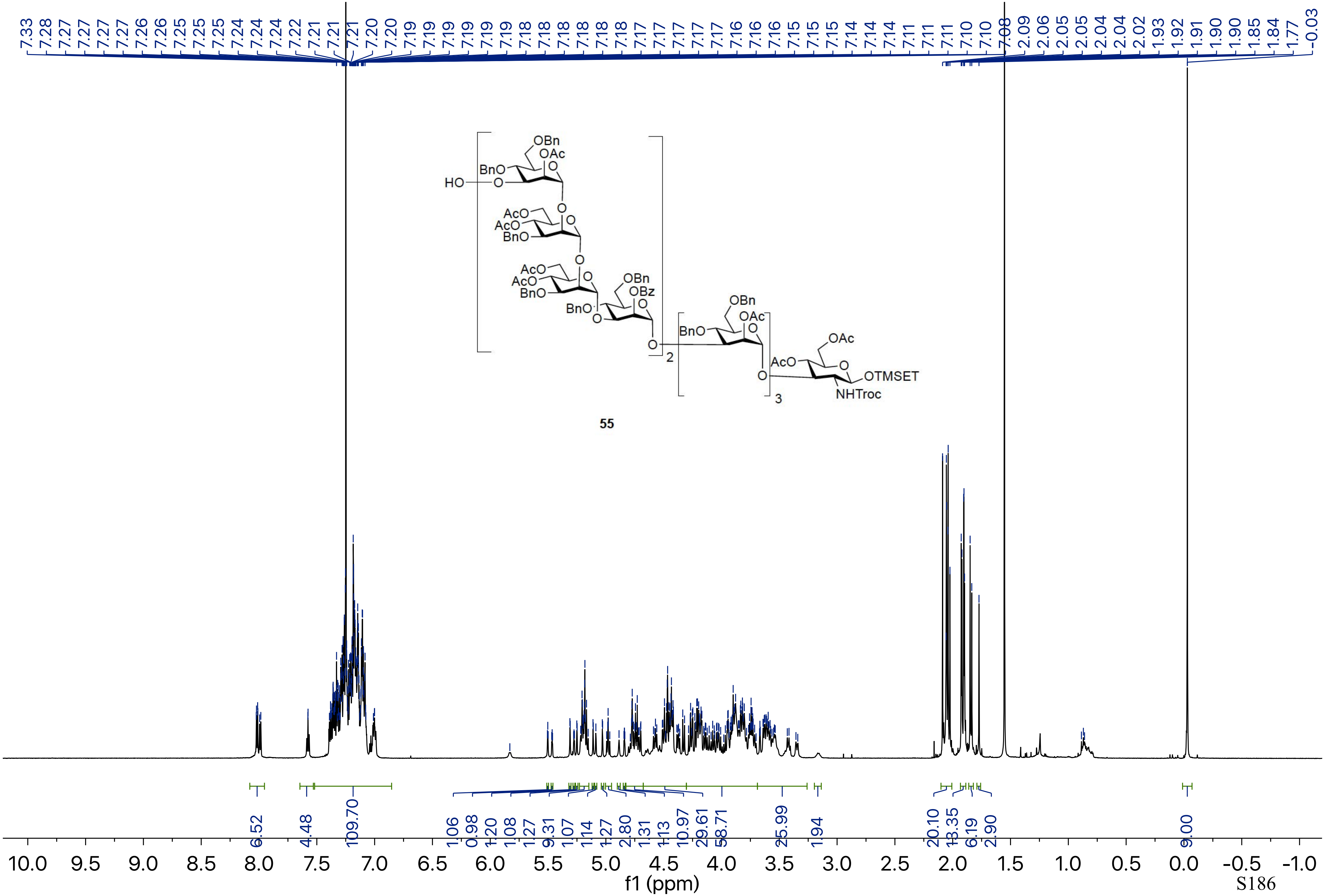
2015.10.26.v7_WL-6-026-prod_loc46_10.54_H1_1D — Lei, WL-6-026-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



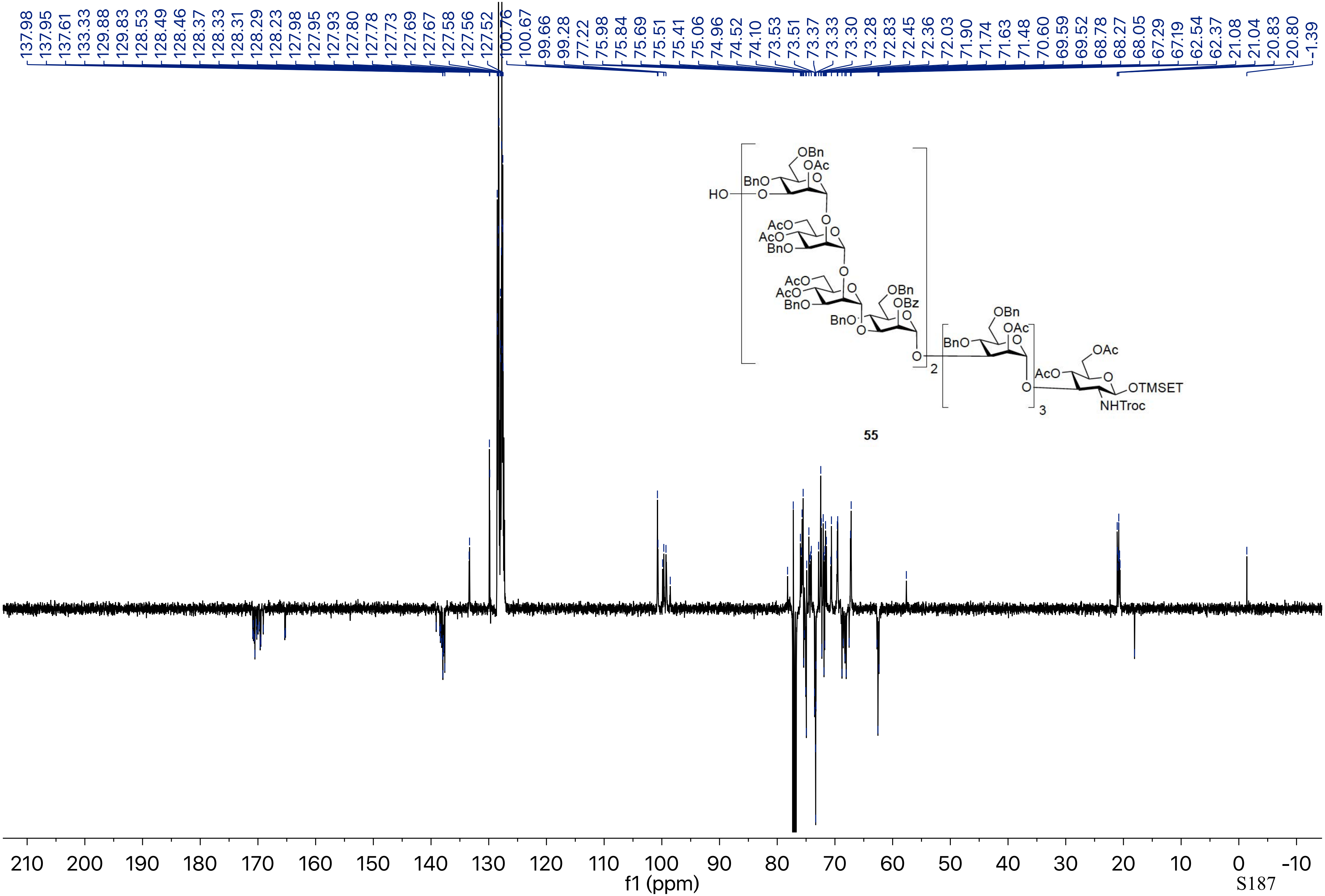
2015.10.28.u5_WL-6-026-prod_loc12_03.27_C13_1D — Lei, WL-6-026-prod — 125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), ten



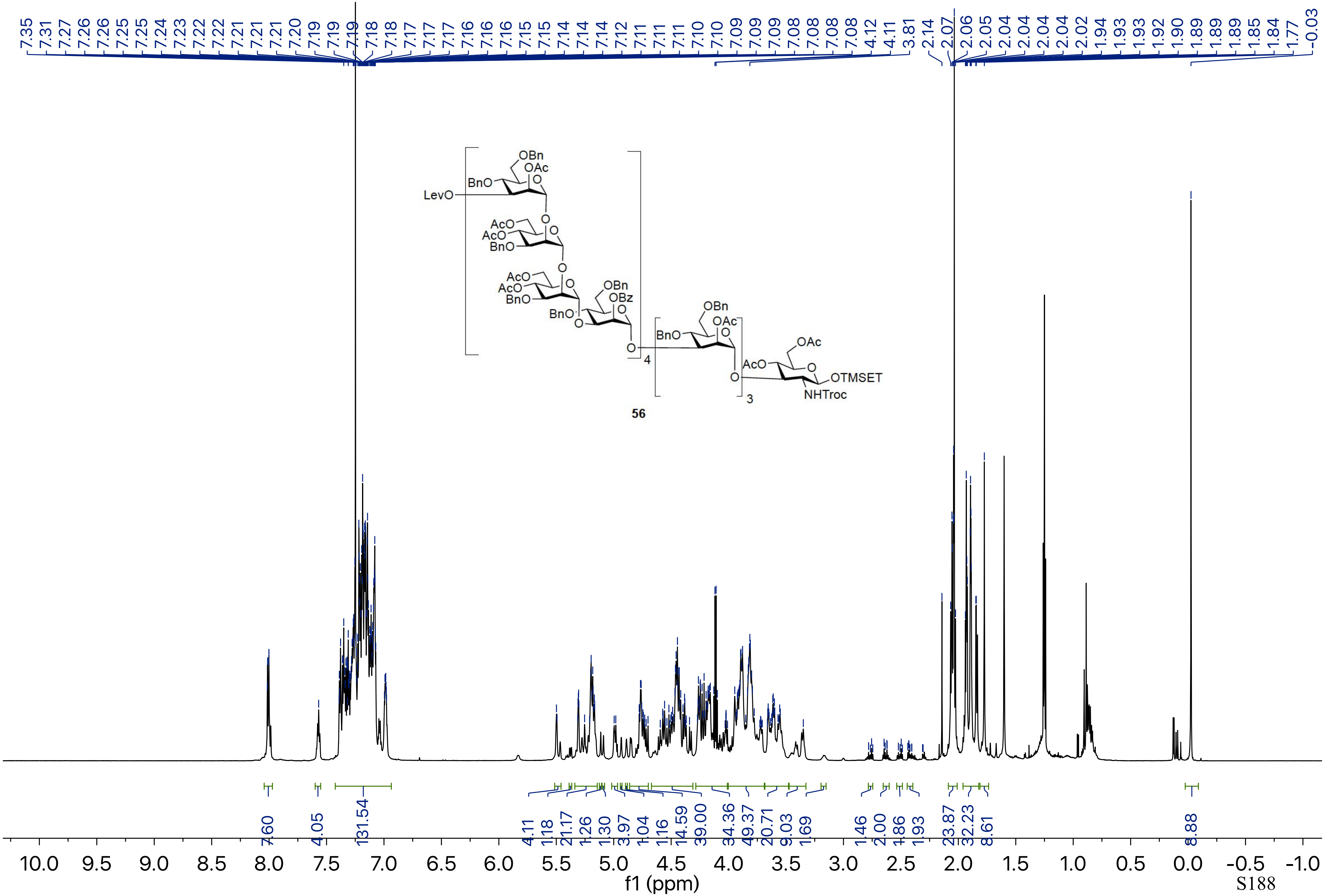
2016.04.26.v7_WL-6-027-prod_loc48_08.49_H1_1D — Lei, WL-6-027-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp

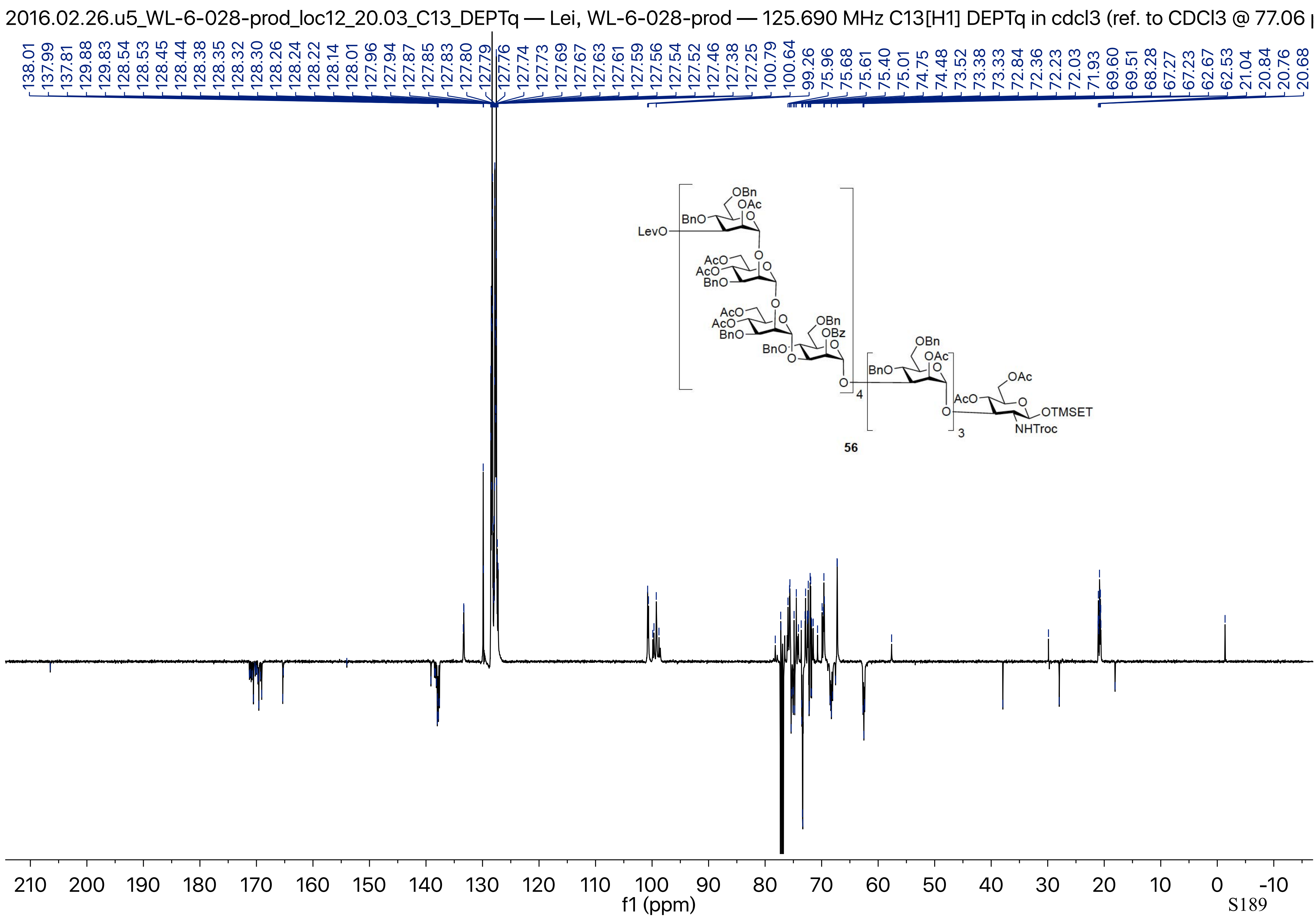


2016.04.25.u5_WL-6-027-prod_loc9_22.12_C13_DEPTq — Lei, WL-6-027-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp

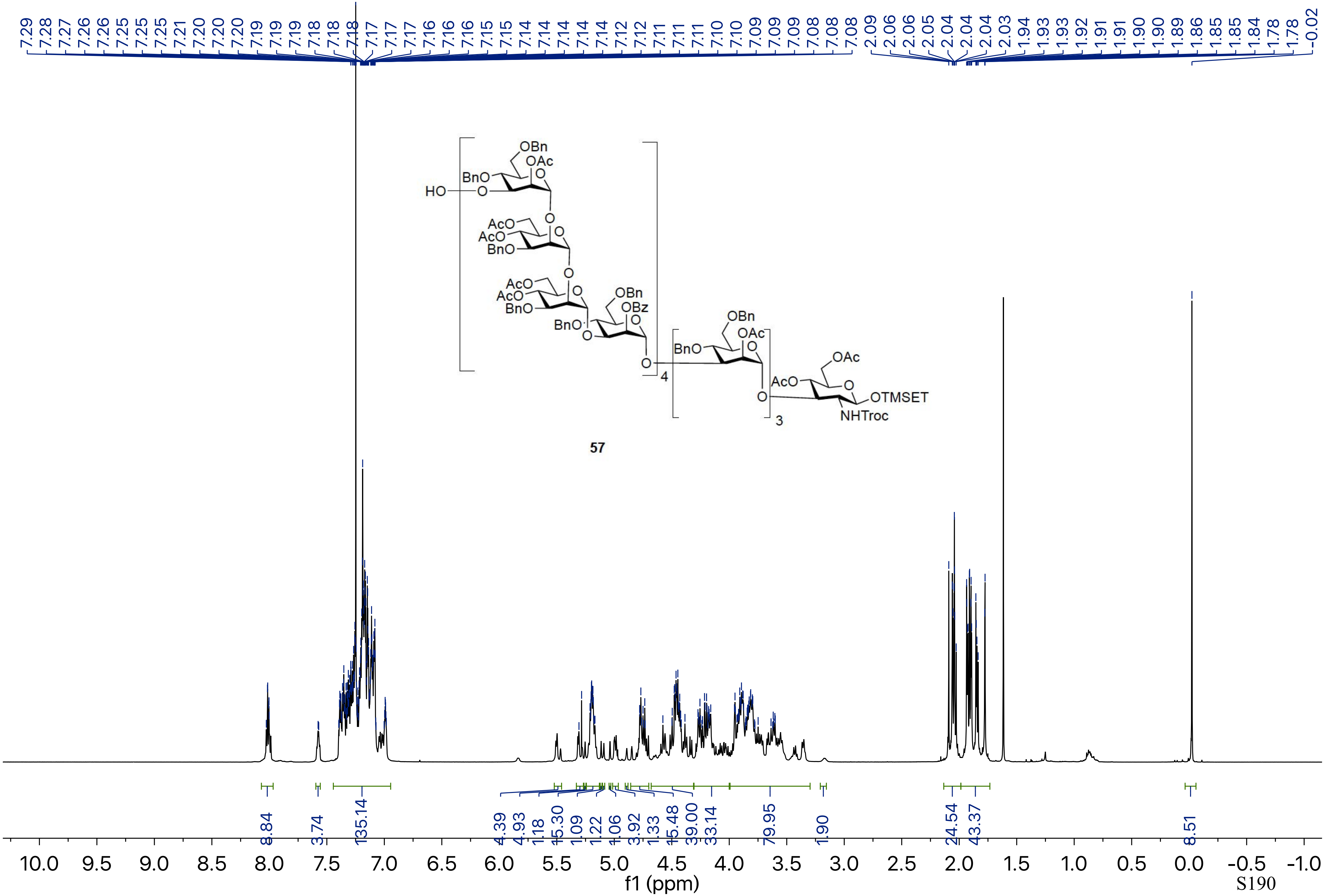


2016.02.25.v7_WL-6-028-run4_loc48_11.31_H1_1D — Lei, WL-6-028-run4 — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp

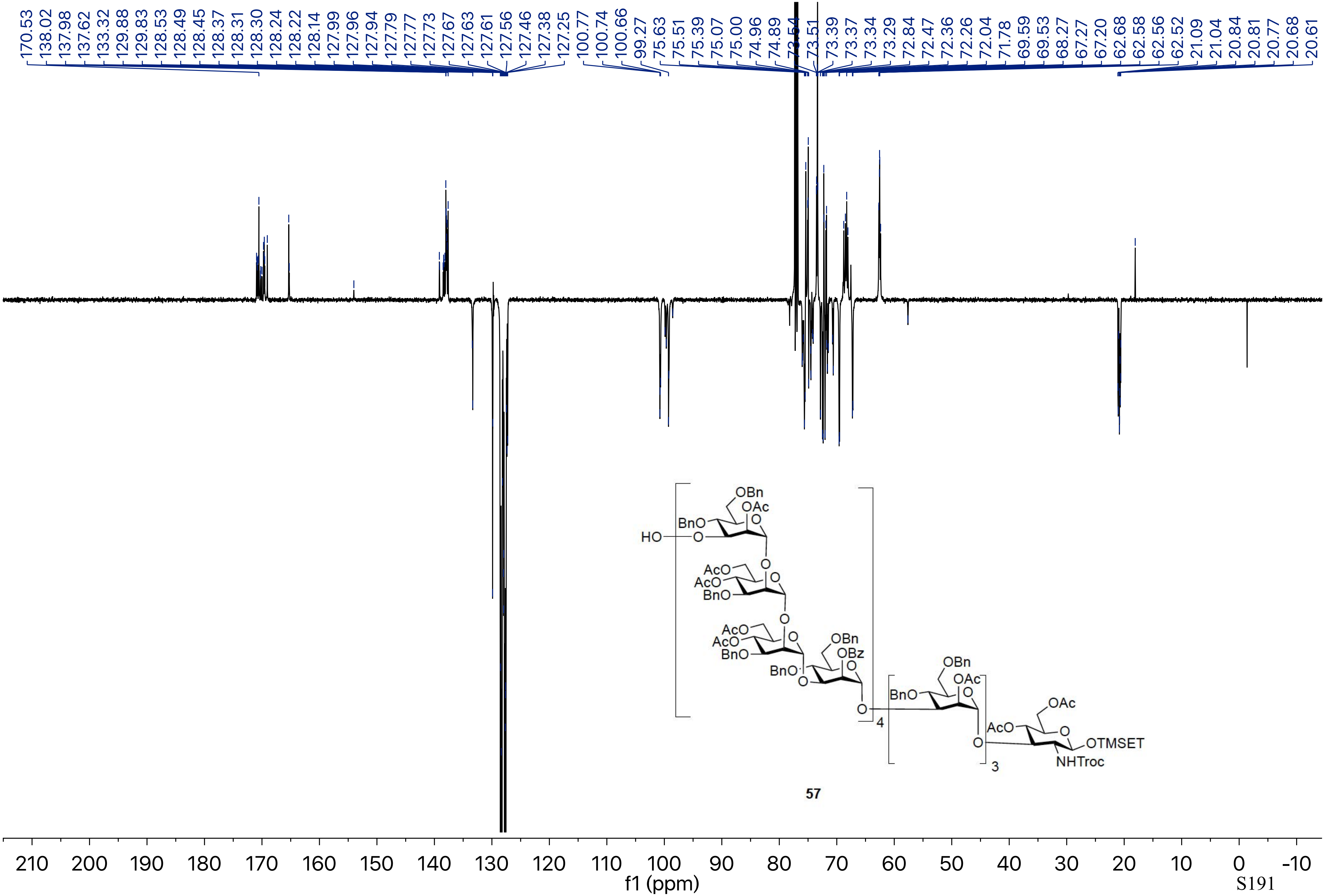



2016.02.26.u5_WL-6-028-prod_loc12_20.03_C13_DEPTq — Lei, WL-6-028-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06
138.01 137.99 137.81 129.88 129.83 128.54 128.53 128.45 128.44 128.38 128.35 128.32 128.30 128.26 128.24 128.22 128.14 128.01 127.96 127.94 127.87 127.85 127.83 127.80 127.79 127.76 127.74 127.73 127.69 127.67 127.63 127.61 127.59 127.56 127.54 127.52 127.46 127.38 127.25 100.79 100.64 99.26 75.96 75.68 75.61 75.40 75.01 74.75 74.48 73.52 73.38 73.33 72.84 72.36 72.23 72.03 71.93 69.60 69.51 68.28 67.27 67.23 62.67 62.53 21.04 20.84 20.76 20.68
LevO
BnO
OBn
OAc
AcO
AcO
BnO
BnO
OBz
4
3
OTMSET
NHTroc
56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2016.03.8.v7_WL-6-043-prod_loc48_16.13_H1_1D — Lei, WL-6-043-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



2016.03.08.u5_WL-6-043-prod_loc8_20.03_C13_DEPTq — Lei, WL-6-043-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



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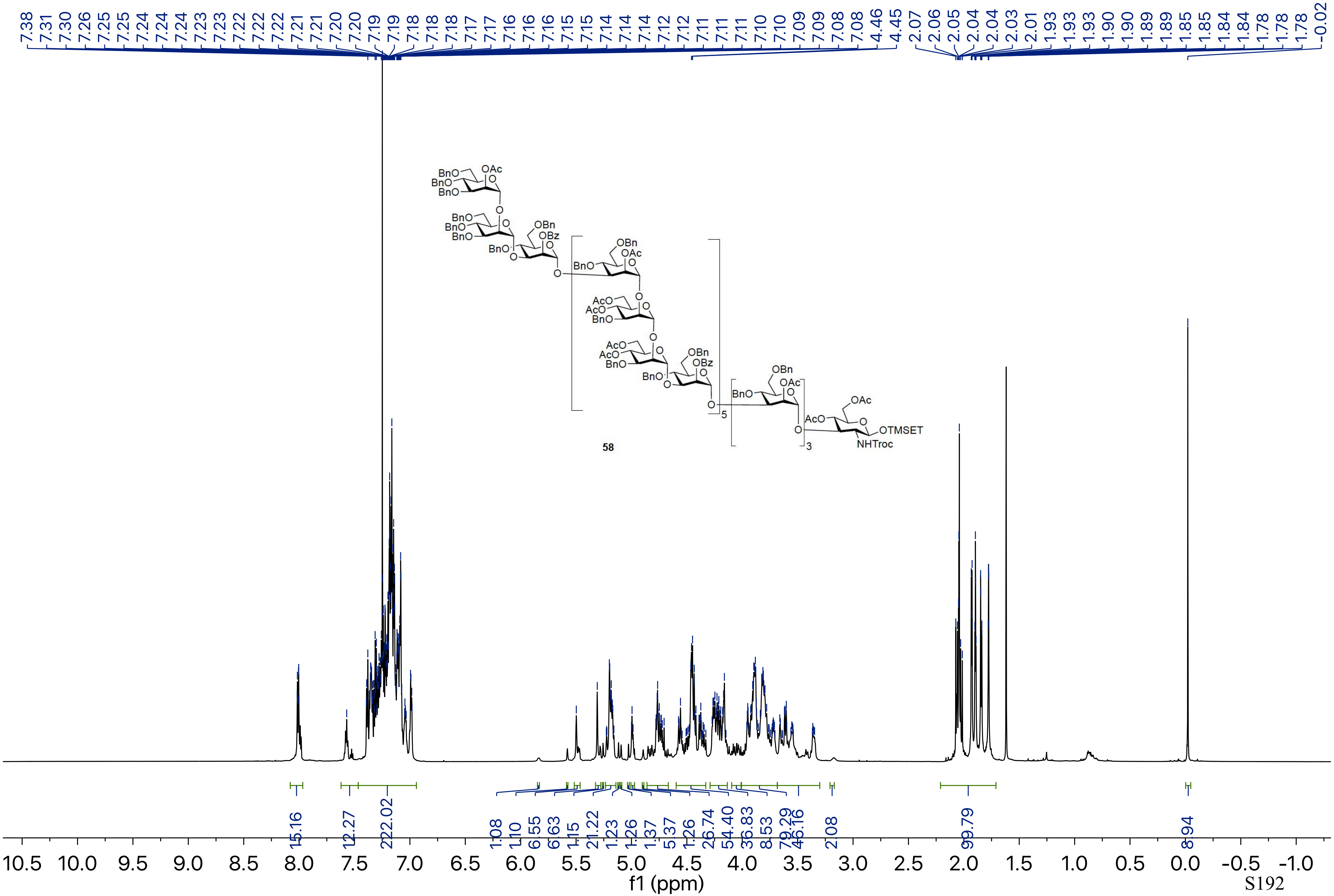
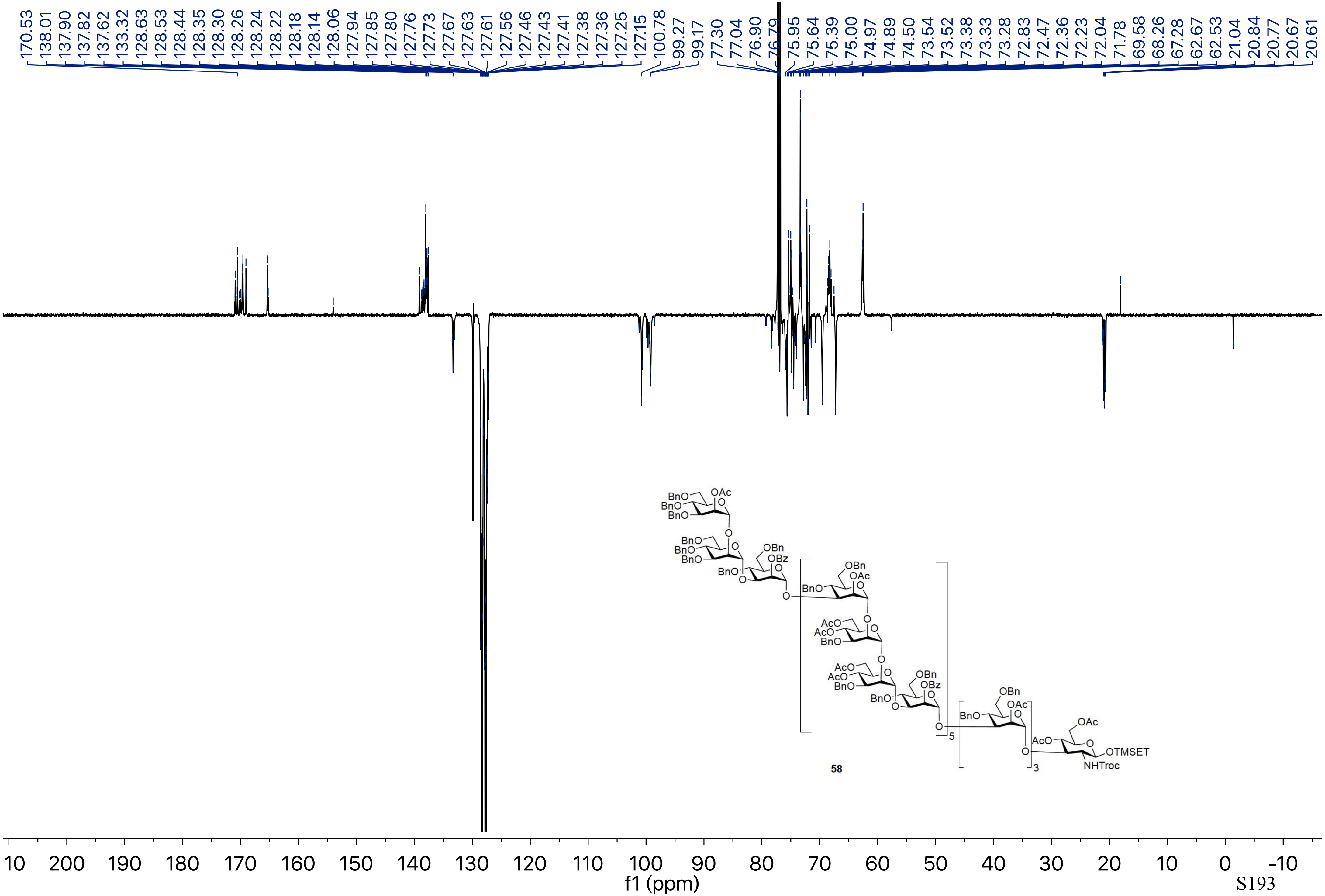
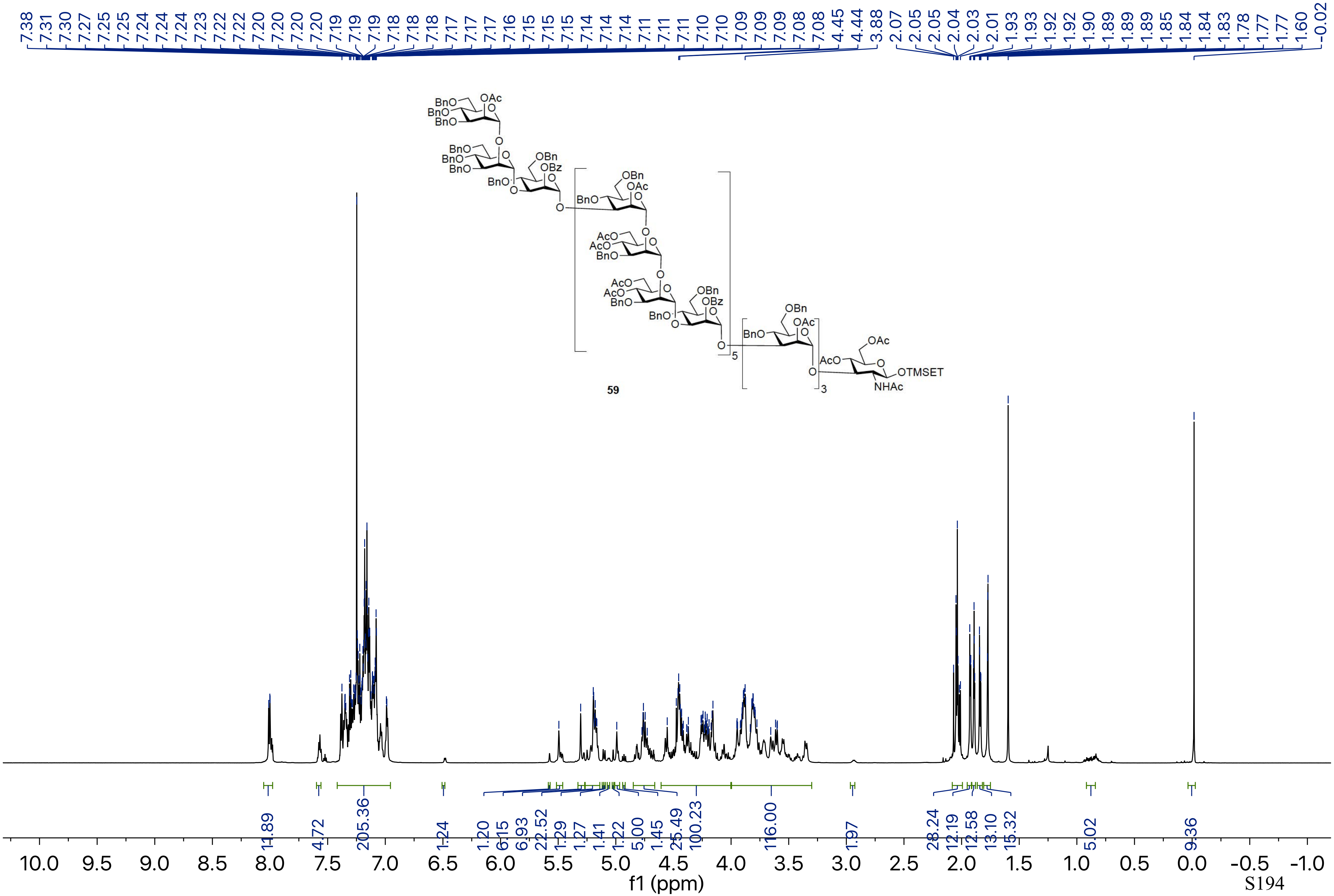
2016.04.27.v7_WL-6-045-prod_loc85_18.11_H1_1D — Lei, WL-6-045-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



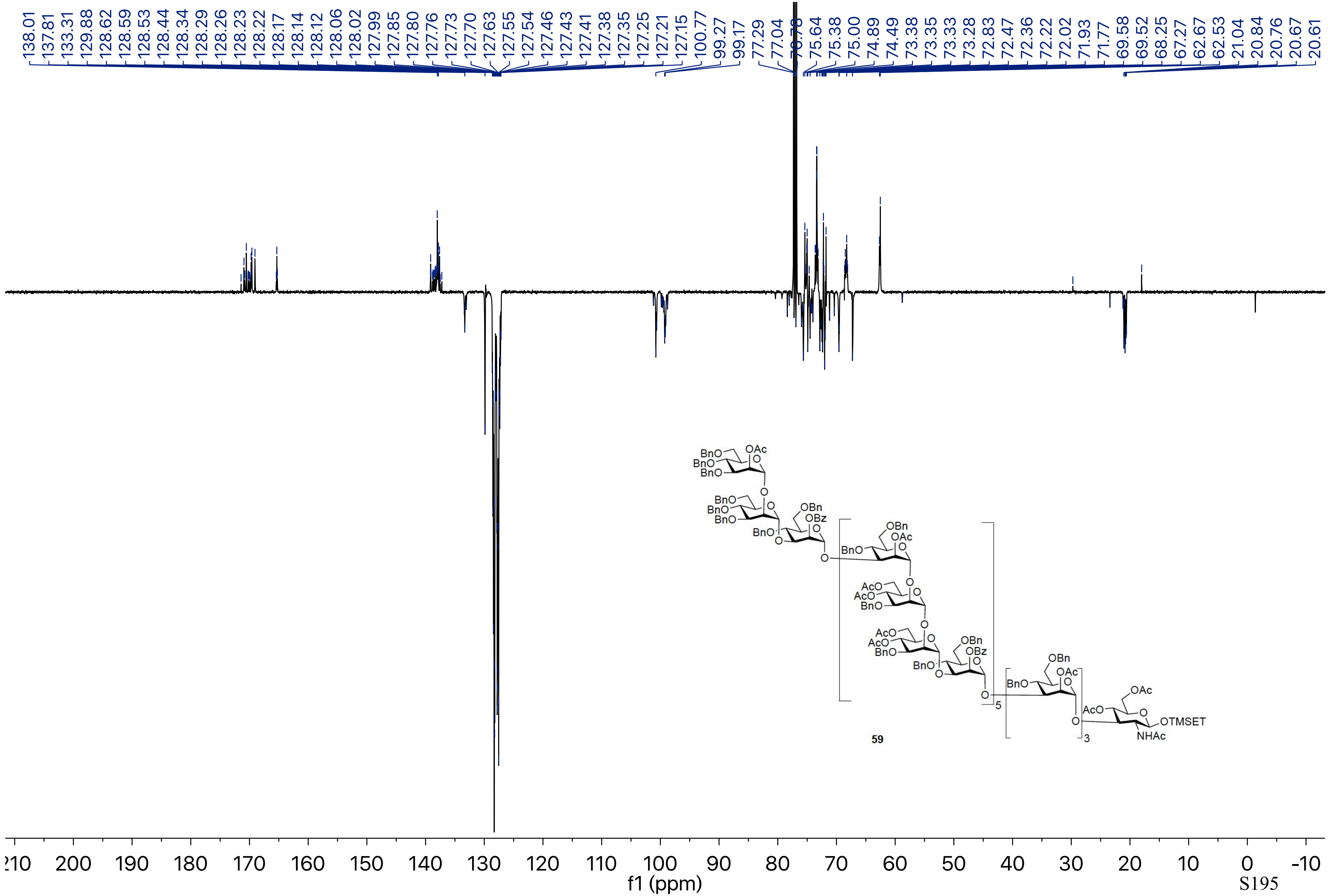
2016.04.27.u5_WL-6-045-prod_loc11_20.03_C13_DEPTq — Lei, WL-6-045-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p

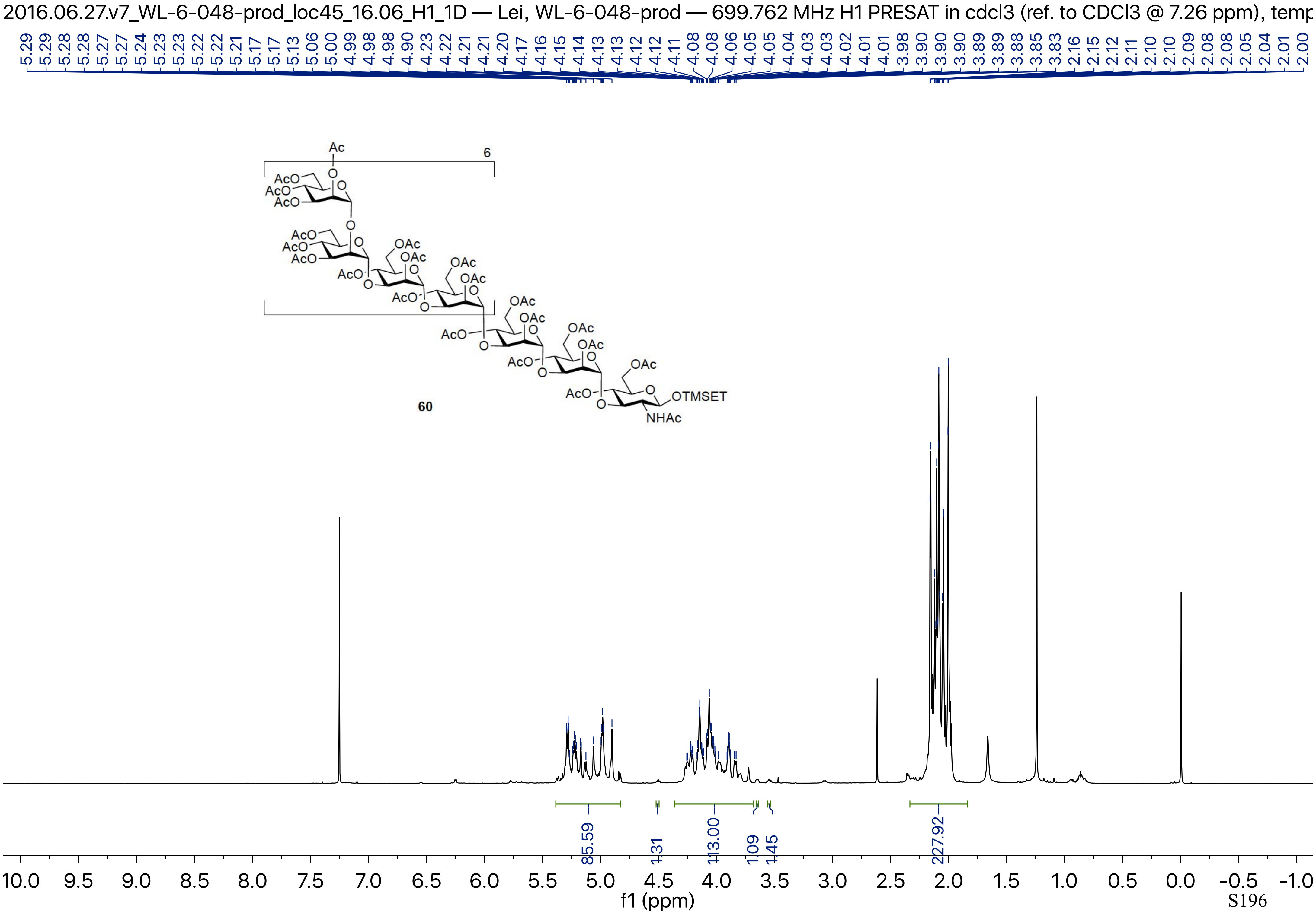


2016.05.2.v7_WL-6-046-prod_loc48_15.23_H1_1D — Lei, WL-6-046-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp

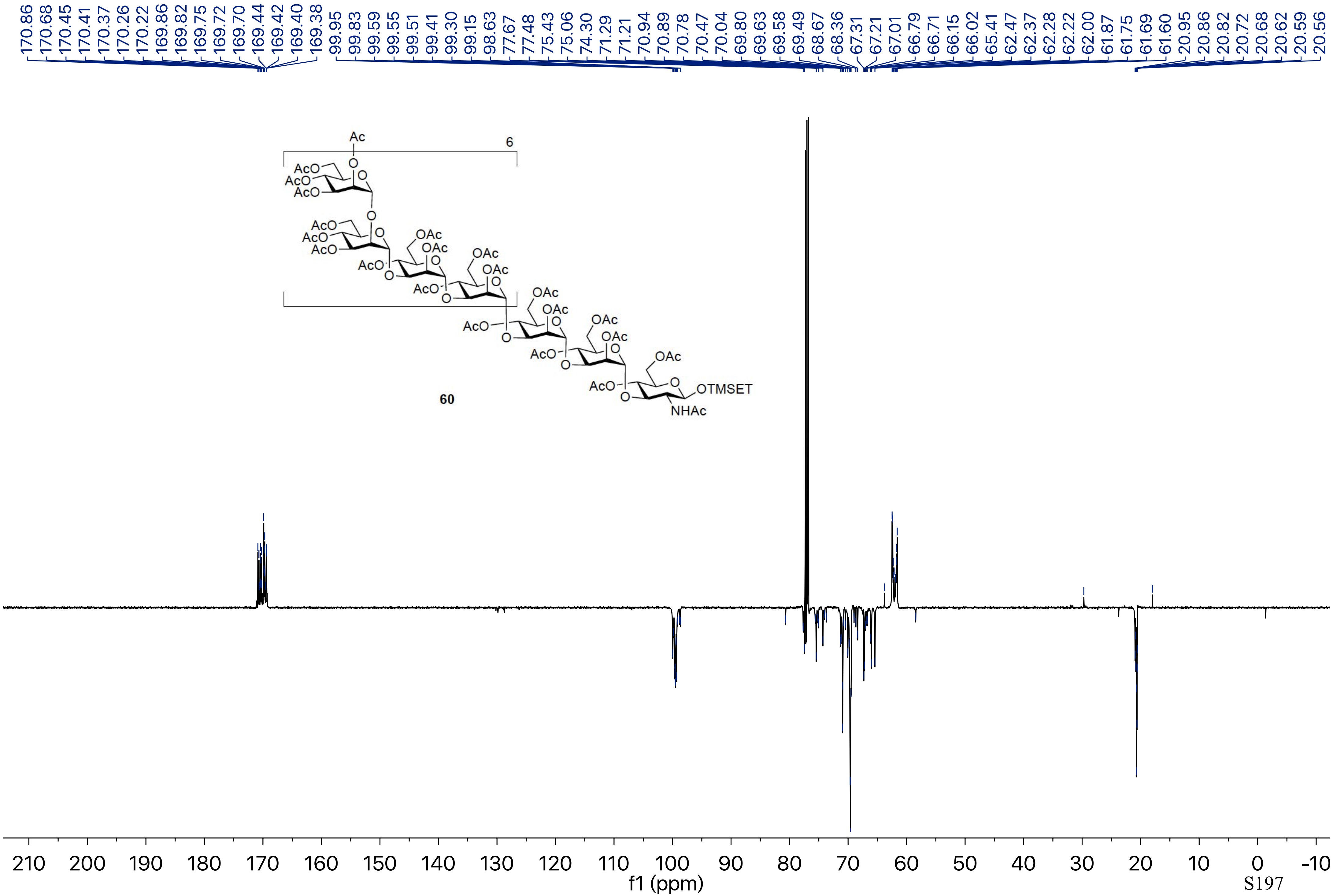


2016.05.02.u5_WL-6-046-prod_loc8_20.03_C13_DEPTq — Lei, WL-6-046-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p

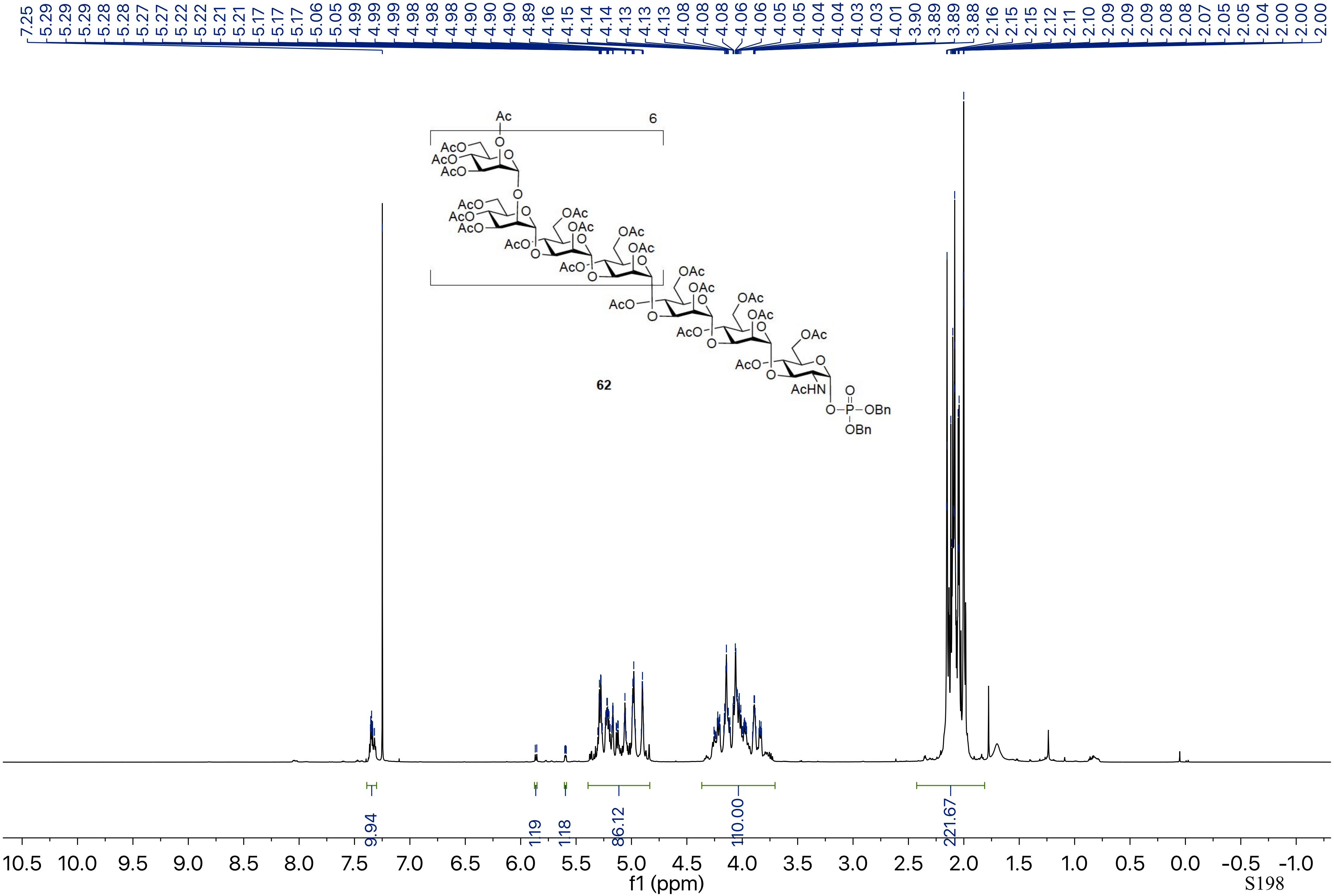



2016.06.27.v7_WL-6-048-prod_loc45_16.06_H1_1D — Lei, WL-6-048-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp
5.29 5.29 5.28 5.28 5.27 5.27 5.24 5.23 5.23 5.22 5.22 5.21 5.17 5.17 5.13 5.06 5.00 4.99 4.98 4.98 4.90 4.23 4.22 4.21 4.21 4.20 4.17 4.16 4.15 4.14 4.13 4.13 4.12 4.12 4.11 4.08 4.08 4.06 4.05 4.05 4.04 4.03 4.03 4.02 4.01 4.01 3.98 3.90 3.90 3.90 3.89 3.89 3.88 3.85 3.83 2.16 2.15 2.12 2.11 2.10 2.10 2.09 2.08 2.08 2.05 2.04 2.01 2.00
Ac
6
AcO
OAc
O
OTMSET
NHAc
60
85.59
1.31
113.00
1.09
1.45
227.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

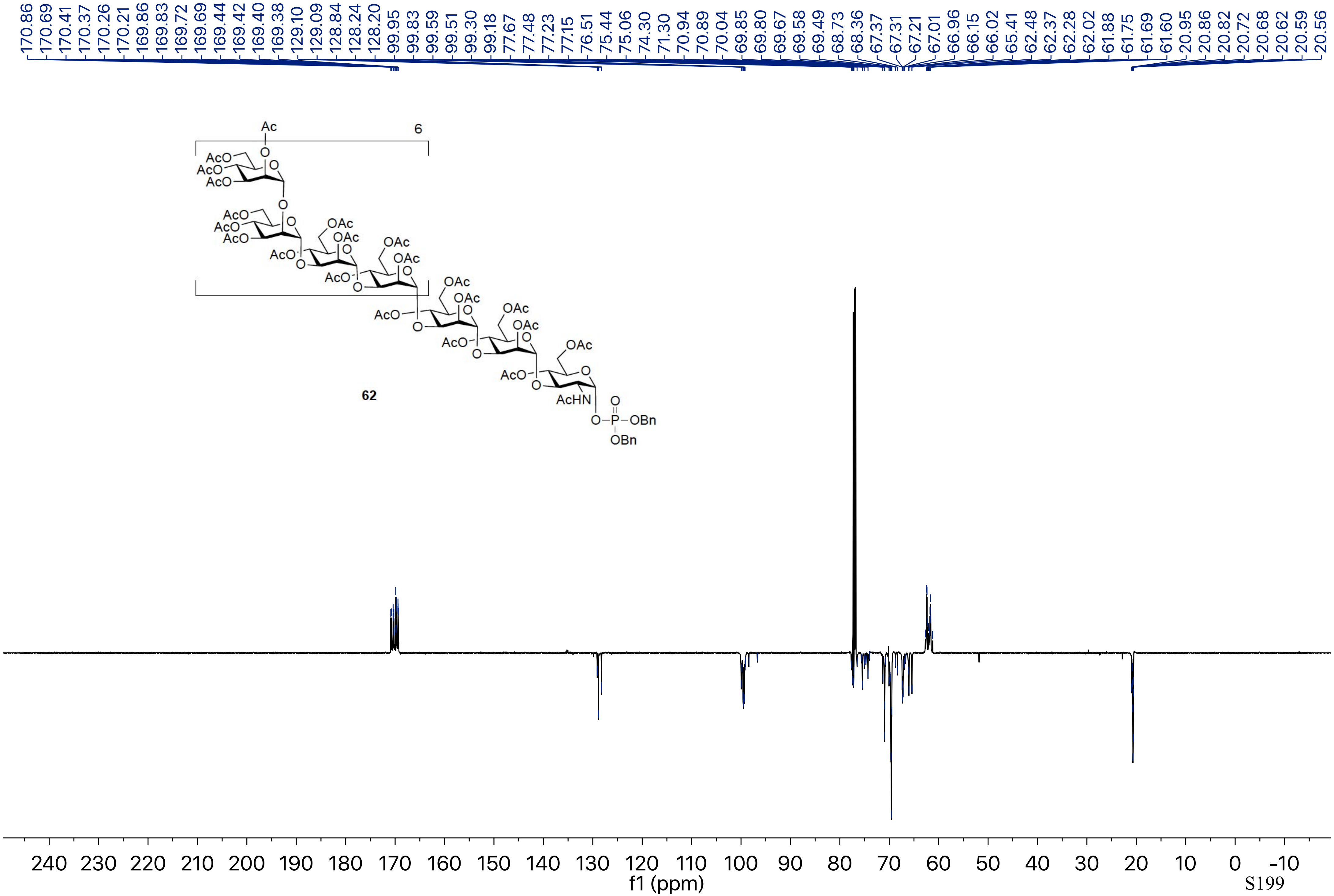
2016.05.28.u5_WL-6-048-prod_loc12_20.02_C13_DEPTq — Lei, WL-6-048-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06



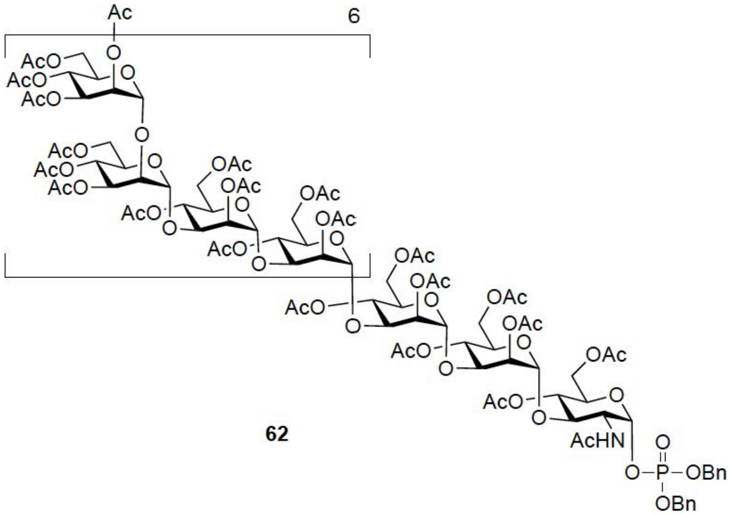
2016.05.30.v7_WL-6-050-prod_loc45_10.12_H1_1D — Lei, WL-6-050-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp



2016.05.29.u5_WL-6-050-prod_loc10_21.10_C13_DEPTq — Lei, WL-6-050-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 p



2016.05.31.mr4_WL-6-050-prod_P31_1D — WL-6-050-prod — 161.913 MHz P31[H1] 1D in cdcl3, temp 25.9 C -> actual temp = 27.0 C, onenmr pı



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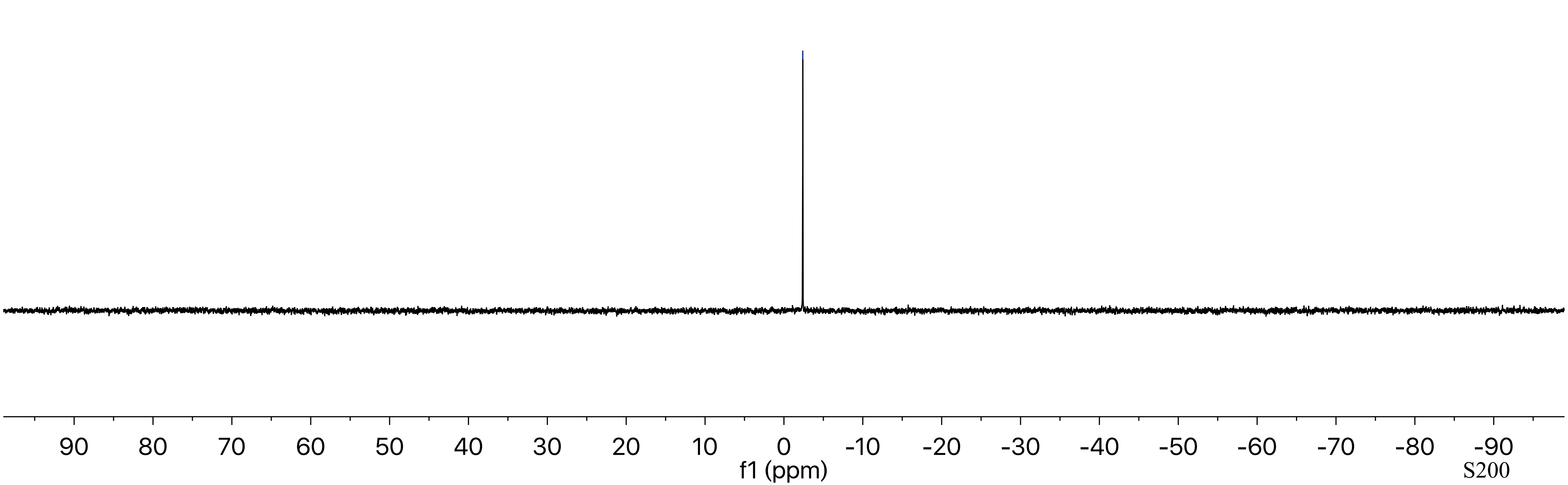
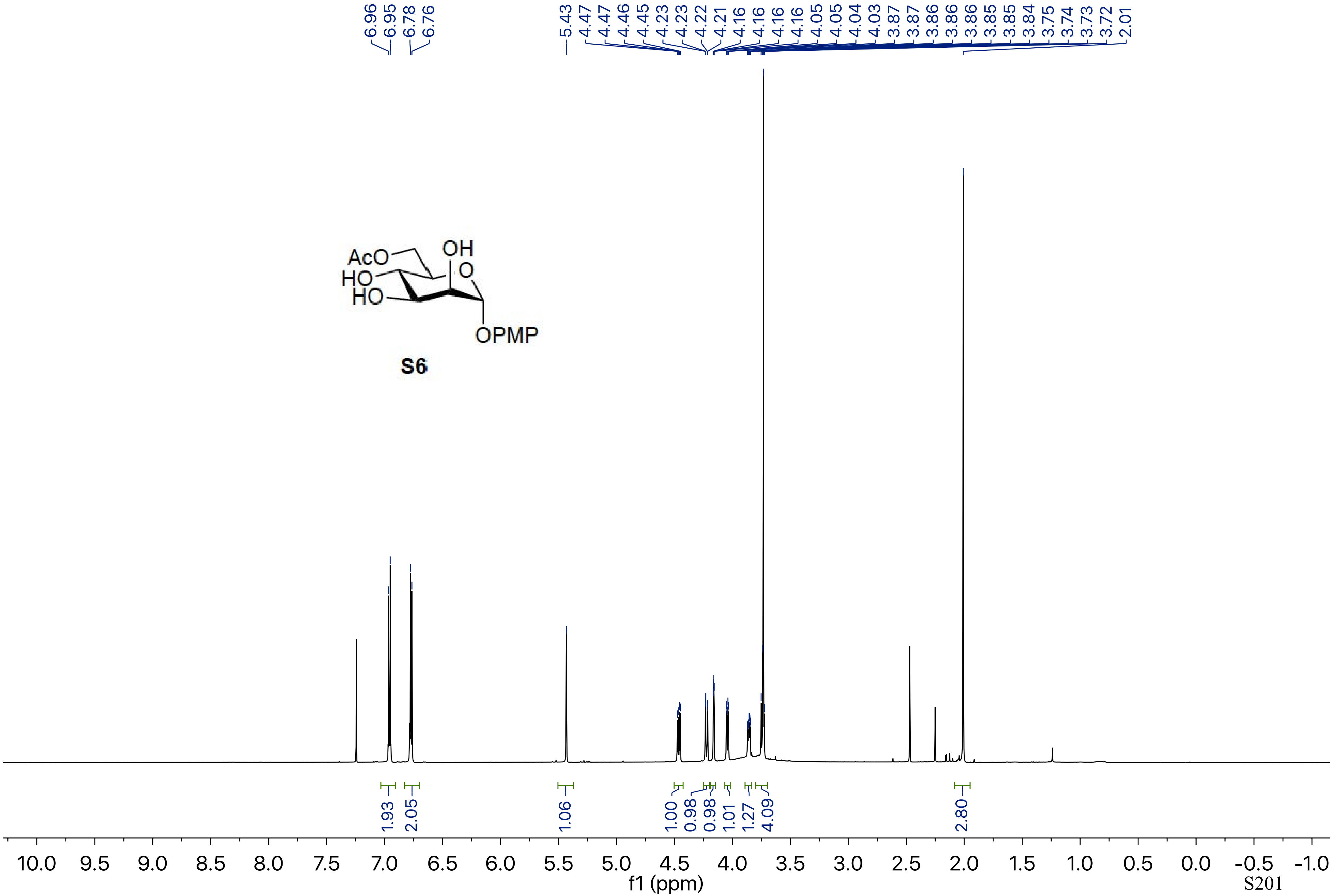
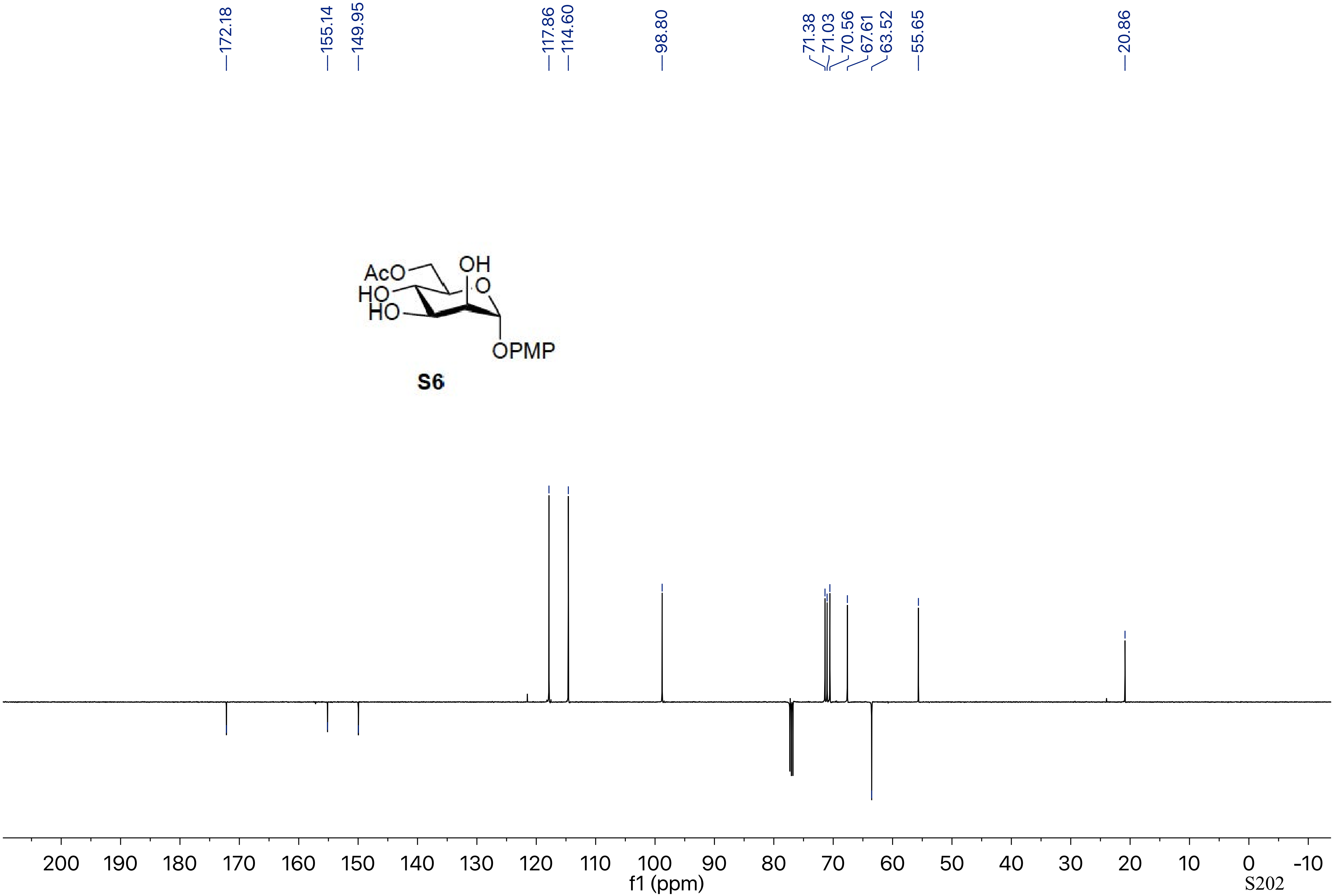


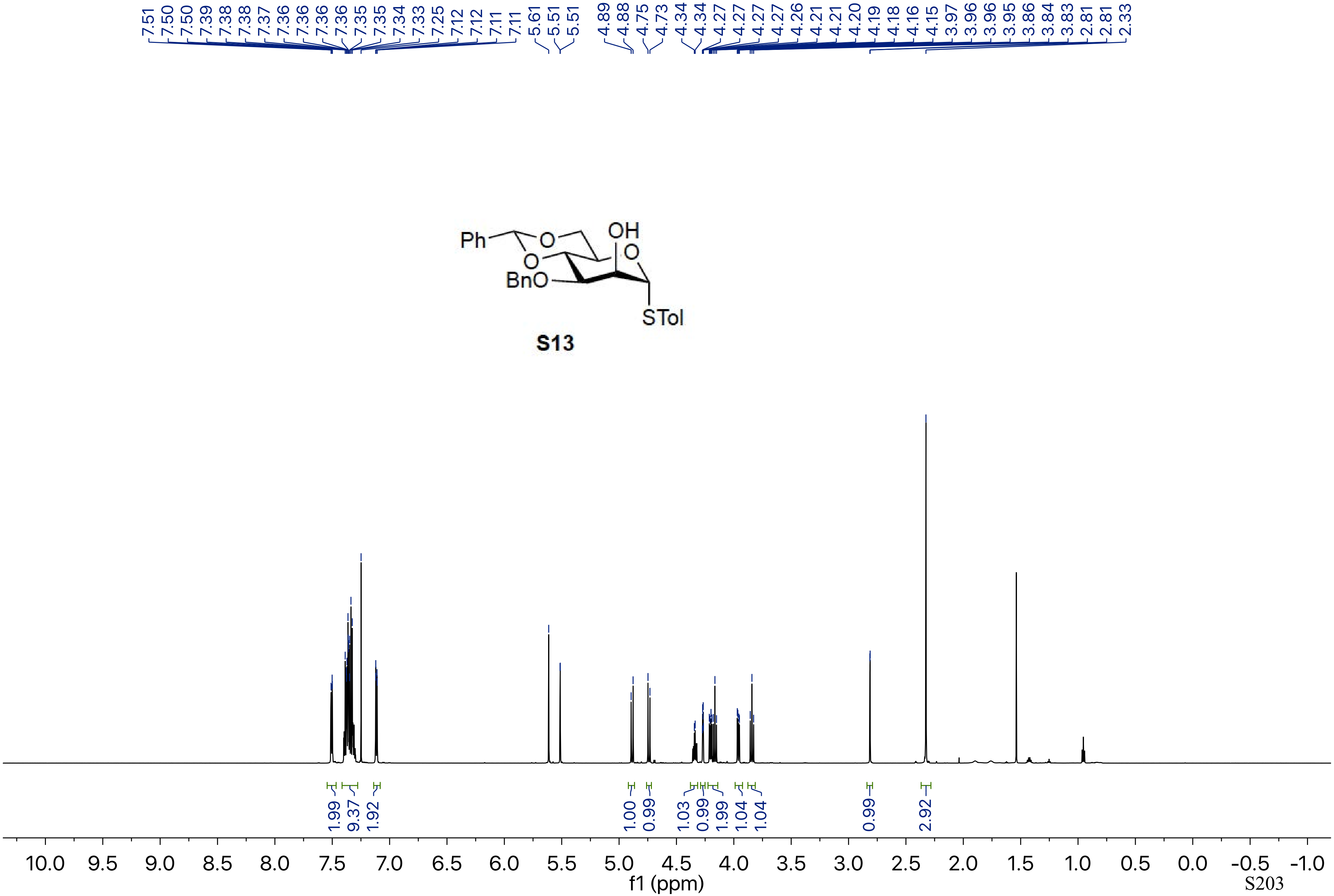
2015.11.16.v7_WL-5-027-prod_loc47_10.05_H1_1D — Lei, WL-5-027-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



2015.11.16.u5_WL-5-027-prod_loc12_14.02_C13_DEPTq — Lei, WL-5-027-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 pp



2015.11.19.v7_WL-5-071-prod_loc47_15.29_H1_1D — Lei, WL-5-071-prod — 699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 2



2015.11.19.u5_WL-5-071-prod_loc12_17.38_C13_DEPTq — Lei, WL-5-071-prod — 125.690 MHz C13[H1] DEPTq in cdcl3 (ref. to CDCl3 @ 77.06 ppr