Supporting Information

Pre-treatment of Lignocellulosic Feedstocks Using Biorenewable Alcohols: Towards Complete Biomass Valorisation

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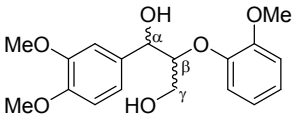
General Information

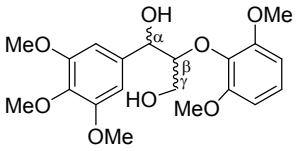
Commercially available compounds were purchased and used as received unless otherwise stated. ^{1}H and ^{13}C spectra were obtained with a Bruker Avance II 400 MHz, Bruker Avance 500 MHz or a Bruker Avance III 500 MHz spectrometer with the solvent peak used as the internal standard. Multiplicities are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet and the J couplings are reported in Hz. NMR spectra were processed using TopSpin 3.1 (PC version) or MestReNova. Column chromatography was performed using Merck Geduran® Si 60 silica gel. Thin layer chromatography was performed on pre-coated glass plates (Silica Gel 60A, Fluorochem) and visualised under UV light (254 nm) or by staining with KMnO4. IR spectra were obtained on a Shimadzu IRAffinity-1 FourierTransform IR spectrophotometer as thin films. Analysis was carried out using Shimadzu IRsolution v1.50 and only characteristic peaks are reported. Melting points were recorded on an Electrothermal 9100 melting point apparatus. Mass spectrometry data were acquired through the University of St Andrews School of Chemistry mass spectrometry service or through the EPSRC national mass spectrometry service centre (Swansea, UK).

Figure S1 Photos showing the consistency of the pulps obtained after high alcohol pretreatments (0.2 M HCl, 6 hours).

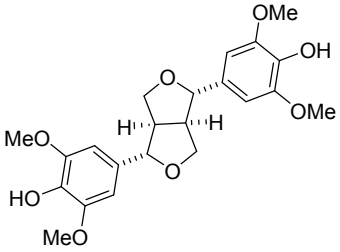
Models Compound Synthesis



S1



S2

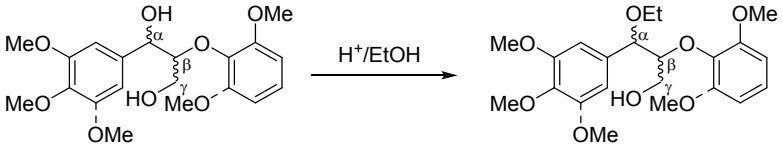


S3

Model compounds **S1-3** were synthesised according to previous reports.[1, 2]

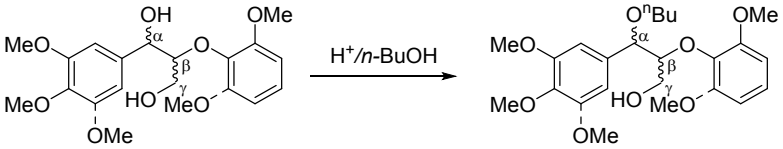
General Procedures

General Procedure A: Ethanol substitution of β-O-4 model compound



To a solution of β-O-4 model compound (1 eq.) in ethanol was added concentrated hydrochloric acid. The reaction mixture was then heated to reflux for 16 h. The mixture was then quenched by addition of $NaHCO_3$ and extracted with EtOAc (x 3). The combined organic layers were then washed with brine and dried $MgSO_4$, then concentrated by rotary evaporation. Quantities of reagents, reactants and solvents are specified below for each reaction.

General Procedure B: Butanol substitution of β-O-4 model compound

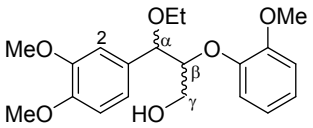


To a solution of β-O-4 model compound (1 eq.) in *n*-butanol was added concentrated hydrochloric acid. The reaction mixture was then heated to reflux for 5 h. The mixture was then quenched by addition of $NaHCO_3$ and extracted with EtOAc (x 3). The combined organic layers were then washed

with brine and dried $MgSO_4$, then concentrated by rotary evaporation. Quantities of reagents, reactants and solvents will be specified for each reaction.

Organosolv Models

3-(3,4-Dimethoxyphenyl)-3-ethoxy-2-(2-methoxyphenoxy)propan-1-ol (S4)

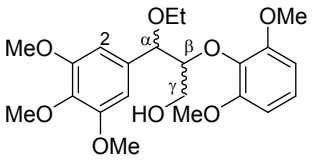


S4 was prepared from β-O-4 model compound **S1** (0.25 g, 0.74 mmol, 1 eq.) and hydrochloric acid (12 M, 0.15 mL) in ethanol (5 mL) using general procedure **A**. Purification was achieved by column chromatography (10-30% EtOAc/petroleum ether), followed by washing with 50 wt% sodium bisulfite solution. Compound **S4** was obtained as a pale yellow oil (0.21 g, 0.58 mmol, 78%, *major:minor = 2.07:1*). **^{1}H NMR** (400 MHz, Acetone) δ 7.02 (dt, *J* = 11.5, 8.4 Hz, 1H, 6), 6.80 – 6.62 (m, 6H, 6 x Ar-H), 4.77 (dd, *J* = 22.4, 6.1 Hz, 1H, Hα), 4.20 – 4.11 (m, 1H, Hβ), 3.85 (s, 3H, OCH_3), 3.84 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.75 – 3.71 (m, 1H, Hγ), 3.59 – 3.50 (m, 1H, Hγ), 3.45 – 3.31 (m, 2H, OCH_2), 1.19 (t, *J* = 7.0 Hz, 3H, $CH_2C\underline{H}_3$), 1.13 – 1.08 (m, 3H, $CH_2C\underline{H}_3$).

^{1}H NMR (400 MHz, CDCl3) δ 7.29 (dd, J = 7.8, 1.7 Hz, 1H, *minor*), 7.02 (ddd, J = 7.7, 7.7, 1.6 Hz, 1H, *minor*), 6.99 – 6.88 (m, 3H *major*, 4H *minor*), 6.87 – 6.81 (m, 2H, *major*, 1H, *minor*), 6.75 (ddd, J = 7.8, 7.8, 1.6 Hz, 1H, *major*), 6.50 (dd, J = 7.8, 1.6 Hz, 1H, *major*), 4.53 (d, J = 7.5 Hz, 1H, *major*), 4.50 (d, J = 7.3 Hz, 1H, *minor*), 4.18 (ddd, J = 6.9, 6.9, 3.5 Hz, 1H, *minor*), 4.07 (ddd, J = 7.8, 4.2, 4.2 Hz, 1H, *major*), 3.97 – 3.80 (m, 11H, *major*, 9H, *minor*), 3.57 – 3.20 (m, 2H, *major*, 4H, *minor*), 3.28 – 3.20 (m, 1H, *major*, 1H, *minor*, -O*H*), 1.21 (t, 3H, *major*), 1.19 (t, 3H, *minor*).

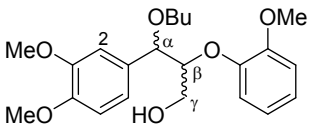
Analytical data are in accordance with those previously reported.[3]

2-(2,6-Dimethoxyphenoxy)-3-ethoxy-3-(3,4,5-trimethoxyphenyl)propan-1-ol (S5)



S5 was prepared from β-O-4 model compound **S2** (0.26 g, 0.66 mmol, 1eq.) and hydrochloric acid (12 M, 0.15 mL) in ethanol (5 mL) using general procedure A. Purification was achieved by column chromatography (10-30% EtOAc/petroleum ether), followed by washing with 50 wt% sodium bisulfite solution. Compound **S2** was obtained as a pale yellow oil (0.10 g, 0.24 mmol, 36%, major:minor = *1.7:1*). **HRMS** (ESI) calculated for $C_{22}H_{30}O_8Na$ $[M + Na]^+$ 445.1833; found 445.1824. **^{1}H NMR** (500 MHz, Acetone) δ 7.03 (t, J = 8.2 Hz, 3H, *minor*), 7.00 (t, *J* = 8.4 Hz, 1H, *major*), 6.80 – 6.68 (m, 4H, *major,* 4H, *minor*), 4.80 (d, *J* = 5.8 Hz, 1H, *minor*), 4.74 (d, *J* = 6.4 Hz, 1H, *major*), 4.18 (m, 1H, *minor*), 4.13 (m, 1H, *major*), 3.90 - 3.69 (m, 16H, *major*, 15H, *minor*), 3.59 - 3.29 (m, 3H, *major,* 3H, *minor*), 3.23 (dd, J = 11.9, 5.8 Hz, 1H, *minor*), 1.19 (t, *J* = 7.0 Hz, 3H, *major*), 1.10 (t, *J* = 7.0 Hz, 3H, *minor*). **^{13}C NMR** (126 MHz, Acetone) δ 153.50, 153.14, 137.58, 137.50, 137.29, 136.05, 135.89, 135.02, 123.67, 123.45, 105.66, 104.83, 104.64, 86.31, 85.71, 81.72, 80.62, 64.43, 61.38, 59.67, 59.54, 55.55, 55.47, 54.09, 14.84. **IR** (thin film) 3508, 2937, 1591, 1492, 1477, 1456, 1419, 1325, 1294, 1253, 1228, 1103.

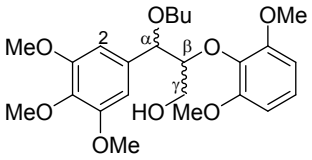
3-Butoxy-3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propan-1-ol (S6)



S6 was prepared from β-O-4 model compound **S1** (0.26 g, 0.78 mmol, 1 eq.) and hydrochloric acid (12 M, 0.15 mL) in *n*-butanol (5 mL) using general procedure B. Purification was achieved by column chromatography (10-30% EtOAc/petroleum ether), followed by washing with 50 wt% sodium bisulfite solution. Compound **S1** was obtained as a pale yellow oil (0.14 g, 0.36 mmol, 46%, *major:minor =*

1:1.1). **HRMS** (ESI) calculated for $C_{22}H_{30}O_6Na$ $[M + Na]^+$ 413.1935; found 413.1921. **^{1}H NMR** (500 MHz, Acetone) δ 7.17 (dd, *J* = 7.9, 1.5 Hz, 1H, *minor*), 7.11 – 7.05 (m, 1H, *major*, 1H, *minor*), 7.02 – 6.76 (m, 6H, *major*, 5H, *minor*), 4.55 (ap. d, *J* = 6.2 Hz, 1H, *major*, 1H, *minor*), 4.37 – 4.27 (m, 1H, *major*, 1H, *minor*), 3.89 – 3.71 (m, 11H, *major*, 9H, *minor*), 3.69 – 3.53 (m, 1H, *minor*), 3.48 – 3.39 (m, 1H, *minor*), 3.39 – 3.35 (m, 2H, *major*, 2H, *minor*), 1.60 – 1.48 (m, 2H, *major*, 2H, *minor*), 1.46 – 1.33 (m, 2H, *major*, 2H. *minor*), 0.90 (t, *J* = 7.0 Hz, 3H, *major/minor*), 0.87 (t, *J* = 7.0 Hz, 3H, *major/minor*). **^{13}C NMR** (126 MHz, Acetone) δ 150.92, 149.04, 148.30, 131.69, 122.14, 120.91, 120.36, 119.87, 118.26, 112.62, 111.33, 111.10, 85.61, 84.71, 81.50, 80.74, 68.51, 61.30, 60.84, 55.10, 31.87, 19.19, 13.28. **IR** (thin film) 3508, 2931, 1591, 1498, 1456, 1251, 1220, 1091, 1024.

3-Butoxy-2-(2,6-dimethoxyphenoxy)-3-(3,4,5-trimethoxyphenyl)propan-1-ol (S7)

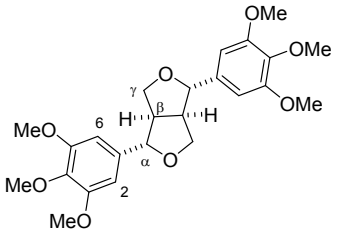


S7 was prepared from β-O-4 model compound **S2** (0.25 g, 0.63 mmol, 1 eq.) and hydrochloric acid (12 M, 0.15 mL) in *n*-butanol (5 mL) using general procedure B. Purification was achieved by column chromatography (10-30% EtOAc/petroleum ether), followed by washing with 50 wt% sodium bisulfite solution. Compound **S7** was obtained as a pale yellow oil (0.18 g, 0.39 mmol, 62%, *major:minor = 1.94:1*). **HRMS** (ESI) calculated for $C_{24}H_{34}O_8Na$ $[M + Na]^+$ 473.2146; found 473.2138; **^{1}H NMR** (500 MHz, Acetone) δ 7.03 (t, J = 7.7 Hz, 1H, *minor*), 7.00 (t, J = 7.7 Hz, 1H, *major*), 6.80 (s, 2H, *minor*), 6.73 (s, 2H, *major*), 6.72 (d, *J* = 8.2 Hz, 2H, *minor*), 6.67 (d, J = 8.4 Hz, 2H, *major*), 4.80 (d, J = 5.7 Hz, 1H, *minor*), 4.72 (d, J = 6.4 Hz, 1H, *major*), 4.18 (td, *J* = 5.8, 3.2 Hz, 1H, *minor*), 4.13 (ddd, J = 6.6, 4.0, 2.8 Hz, 1H, *major*), 3.91 – 3.76 (m, 13H, *major*, 12H, *minor*), 3.74 (s, 3H, *minor*), 3.73 (s, 3H, *major*), 3.55 – 3.50 (m, 1H, *major*, 1H, *minor*), 3.49 – 3.36 (m, 2H, *major*, 2H, *minor*), 3.23 (dd, J = 11.5, 6.0 Hz, 1H, *minor*), 1.67 – 1.26 (m,

4H, *major*, 4H, *minor*), 0.92 (t, J = 7.4 Hz, 3H, *major*), 0.88 (t, J = 7.3 Hz, 3H, *minor*). **^{13}C NMR** (126 MHz, Acetone) δ 153.51, 153.12, 137.49, 135.86, 134.98, 123.67, 105.67, 104.85, 86.31, 85.75, 81.74, 80.74, 68.75, 61.36, 59.67, 55.46, 31.90, 19.23, 13.32. **IR** (thin film) 3510, 2933, 1591, 1477, 1325, 1294, 1253, 1226, 1105, 1029.

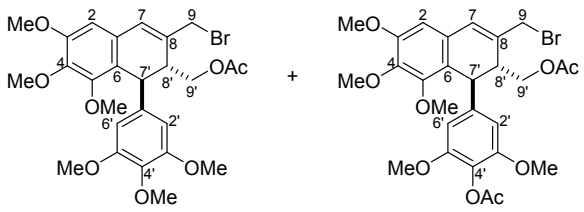
AcBr/AcOH Model Reactions for Assignment of Whole Cell Wall NMR spectra

Syringaresinol dimethyl ether (S8)



To a solution of syringaresinol **S3** (500 mg, 1.19 mmol) in acetone (10 mL) was added Cs_2CO_3 (1.23 g, 3.78 mmol, 2.00 eq.) followed by methyl iodide (1.76 mL, 28.3 mmol, 15.0 eq.). The mixture was then heated at reflux for 16 hours and then allowed to cool to room temperature before being filtered through a plug of Celite and concentrated *in vacuo* to give the product syringaresinol dimethyl ether (**S8**) as a white solid (531 mg, 100%). Crystallisation from EtOH gave colourless needles (451 mg). **M.p.** 110-111 °C (lit.[4] 119-120 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.57 (s, 4H, 2 x H2, 2 x H6), 4.75 (d, *J* = 4.0 Hz, 2H, 2 x Hα), 4.36 – 4.25 (m, 2H, 2 x Hγ), 3.94 (dd, *J* = 9.3, 3.3 Hz, 2H, 2 x Hγ), 3.88 (s, 12H, 4 x OMe), 3.84 (s, 6H, s, 2 x OMe), 3.15 – 3.04 (m, 2H, 2 x Hβ). Analytical data are in accordance with those previously reported.[4]

***rel.* ((1S,2R)-3-(Bromomethyl)-6,7,8-trimethoxy-1-(3,4,5-trimethoxyphenyl)-1,2-dihydronaphthalen-2-yl)methyl acetate (S9) and *rel.* ((1S,2R)-1-(4-acetoxy-3,5-dimethoxyphenyl)-3-(bromomethyl)-6,7,8-trimethoxy-1,2-dihydronaphthalen-2-yl)methyl acetate (S10)**



S9 **S10**

To a solution of acetyl bromide in acetic acid (1:3, 4 mL) was added syringaresinol dimethyl ether (**S8**) (98 mg, 0.22 mmol, 1.0 eq.) and the mixture was stirred at 50 °C for 1 hour. The mixture was

then concentrated *in vacuo* and purified by column chromatography (10-20% EtOAc/petroleum ether) to give, in order of elution, **S9** (26 mg, 21%), a mixture of **S9** and **S10** (46 mg), and **S10** (26 mg, 20%) as colourless oils.

S9: **HRMS** (ESI) calculated for $C_{26}H_{31}O_8Br^{79}Na$ $[M + Na]^+$ 573.1095; found 573.1087. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 6.80 (s, 1H, H7), 6.78 (s, 1H, H2), 6.41 (s, 2H, H2'/6'), 4.46 (d, *J* = 1.1 Hz, 1H, H7'), 4.33 (dd, *J* = 10.1, 1.0 Hz, 1H, H9), 4.29 (d, *J* = 10.1 Hz, 1H, H9), 4.18 (dd, *J* = 10.8, 5.4 Hz, 1H, H9'), 3.93 – 3.88 (m, 1H, H9'), 3.86 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.70 (s, 6H, 2xOMe), 3.64 (s, 3H, OMe), 3.62 (s, 3H, OMe), 3.00 (ddd, *J* = 8.5, 5.4, 1.3 Hz, 1H, H8'), 2.01 (s, 3H, OAc). **^{13}C NMR** (126 MHz, Acetone) δ 170.9 ($CH_3\underline{C}OOR$), 153.9 (C5'/3'), 152.7, 143.8 (C4), 140.3 (C1'), 138.0 (C4'), 134.1 (C8), 129.9 (C7), 129.1 (C1 or C6), 121.9 (C1 or C6), 107.9 (C2), 106.3 (C6'/2'), 65.4 (9'), 61.0 (OMe), 60.8 (OMe), 60.5 (OMe), 56.3 (2xOMe), 44.0 (C8'), 40.1 (C7'), 38.1 (C9), 20.7 (OAc). **IR** (thin film) 2938, 1737, 1587, 1489, 1454, 1406, 1344, 1220, 1200, 1120, 1095, 1028, 995.

S10: **HRMS** (ESI) calculated for $C_{27}H_{31}O_9Br^{79}Na$ $[M + Na]^+$ 601.1044; found 601.1033. **^{1}H NMR** (500 MHz, Acetone-d_6) δ 6.83 – 6.80 (m, 1H, H7), 6.78 (s, 1H, H2), 6.48 (s, 2H, H2'/6'), 4.53 – 4.47 (m, 1H, H7'), 4.37 – 4.27 (m, 2H, H9), 4.20 (dd, *J* = 10.9, 5.3 Hz, 1H, H9'), 3.92 (dd, *J* = 10.9, 8.4 Hz, 1H, H9'), 3.86 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.68 (s, 6H, 2xOMe), 3.64 (s, 3H, OMe), 3.03 (ddd, *J* = 8.4, 5.4, 1.3 Hz, 1H, H8'), 2.16 (s, 3H, ArOAc), 2.00 (s, 3H, OAc). **^{13}C NMR** (126 MHz, Acetone) δ 170.9 ($CH_3\underline{C}OOR$), 168.5 ($CH_3\underline{C}OOAr$), 153.8 (Q), 152.7 (C3'/C5'), 143.8 (C4), 143.1 (C1'), 134.1 (C8), 130.0 (C7), 129.0 (C1 or C6), 128.3 (C4'), 121.6 (C1 or C6), 108.0 (C2), 105.4 (C2'/6'), 65.3 (C9'), 61.0 (OMe), 60.9 (OMe), 56.3 (2xOMe), 43.8 (C8'), 40.3 (C7'), 37.9 (C9), 20.7 ($\underline{C}H_3OOR$), 20.3 ($\underline{C}H_3OOAr$). **IR** (thin film) 2939, 1765, 1738, 1598, 1456, 1408, 1346, 1219, 1197, 1122, 1097, 1030.

The molecular ion observed for these compounds $[M + Na]^+$ on MS analysis was found to be quite weak. This was assigned to the reactivity under the ionisation conditions of the allyl bromide substituent. Indeed, when the mass spectral analysis was performed in methanol the mass of the major observed compound was consistent with substitution of the bromide with methanol (For **S9** observed m/z $[M(OMe) + Na]^+$ 525.2079; theorectical m/z 525.2095. For **S10** observed m/z $[M(OMe) + Na]^+$ 553.2028; theorectical m/z 553.2044.

The stereochemistry of **S9** and **S10** was tentatively assigned based on the small coupling constant observed between H7' and H8'. This indicated that the *anti* geometry is likely based on the predicted dihedral angles of the *anti* and *syn* isomers (Figure S3).

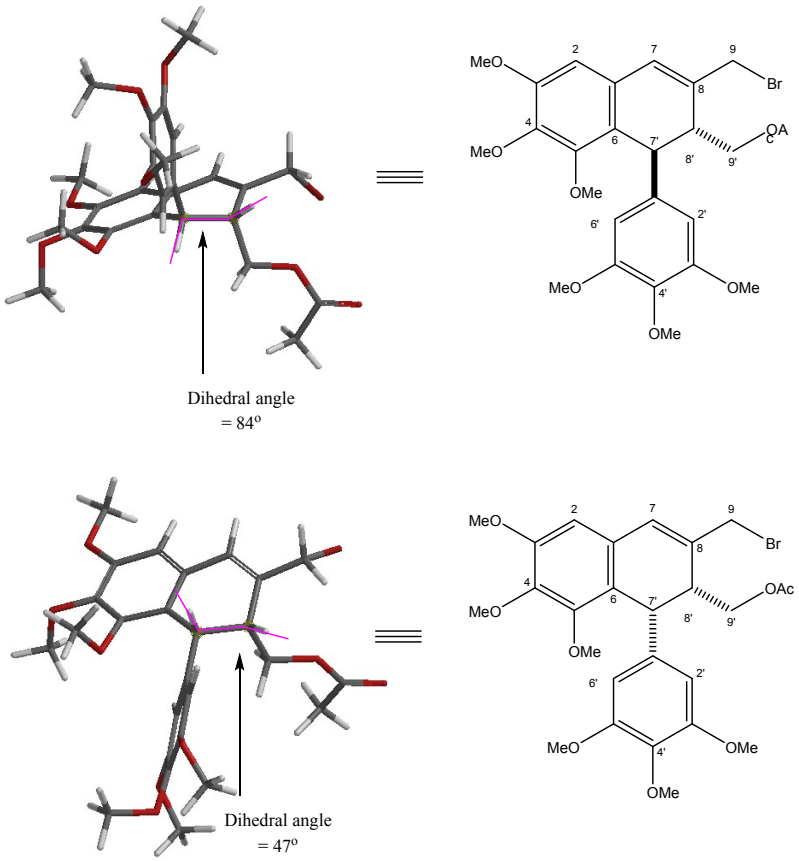
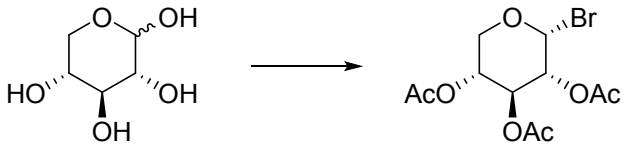


Figure S2 Showing the *anti* and *syn* isomers of **S9** optimised using the RM1 semi-empirical method as implemented in Spartan'14 (Wavefunction).

General Procedure C

To a stirred solution/suspension of model substrate (50-100 mg) in AcOH (75 mL/g) was added AcBr (25 mL/g) and the mixture stirred at 50 ˚C for 3 hours. The mixture was then concentrated *in vacuo* and used for 2D HSQC NMR analysis without further purification. Model substrates used: D-xylose, D-glucose, cellulose filter paper (Fisherbrand, qualitative), cellobiose, S-G-β-O-4[1] and S-G- β-O-4 / β-β[2] model polymers.

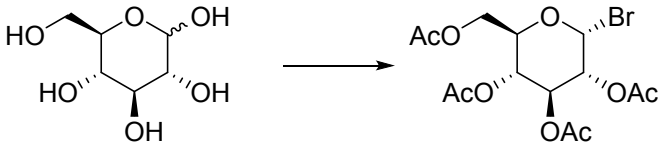
D-Xylose gave α-bromotriacetylxylose (2,3,4-tri-O-acetyl- a-D-xylopyranosyl bromide) as the major product as identified by ^{1}H NMR.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.54 (d, *J* = 4.0 Hz, 1H), 5.52 (t, *J* = 9.7 Hz, 1H), 5.00 (dq, *J* = 8.9, 5.8 Hz, 1H), 4.74 (dd, *J* = 10.0, 3.9 Hz, 1H), 4.01 (dd, *J* = 11.4, 5.9 Hz, 1H), 3.84 (t, *J* = 11.1 Hz, 1H), 2.09 – 2.03 (m, 9H). Analytical data are consistent with those previously reported.[5]

^{1}H NMR (400 MHz, Acetone-d_6) δ 6.75 (d, *J* = 3.8 Hz, 1H), 5.54 (t, *J* = 9.8 Hz, 1H), 5.13 (ddd, *J* = 10.9, 9.6, 6.0 Hz, 1H), 4.93 (dd, *J* = 10.0, 3.9 Hz, 1H), 4.13 (dd, *J* = 11.5, 5.9 Hz, 1H), 3.84 (ddd, *J* = 11.5, 10.9, 0.8 Hz, 1H), 2.08 – 2.02 (m, 9H).

D-Glucose gave α-bromotetraacetylglucose as the major product as identified by ^{1}H NMR.



^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.62 (d, *J* = 4.0 Hz, 1H), 5.56 (t, *J* = 9.8 Hz, 1H), 5.17 (t, *J* = 9.8 Hz, 1H), 4.84 (dd, *J* = 9.8, 4.0 Hz, 1H), 4.41 – 4.23 (m, 2H), 4.19 – 4.06 (m, 1H), 2.16 – 1.99 (m, 12H). Analytical data are consistent with those previously reported.[6]

^{1}H NMR (400 MHz, Acetone) δ 6.78 (d, *J* = 3.9 Hz, 1H), 5.55 (t, *J* = 10.0 Hz, 1H), 5.24 (t, *J* = 10.0 Hz, 1H), 4.96 (dd, *J* = 10.0, 3.9 Hz, 1H), 4.40 – 4.26 (m, 2H), 4.22 – 4.13 (m, 1H), 2.12 – 1.96 (m, 12H).

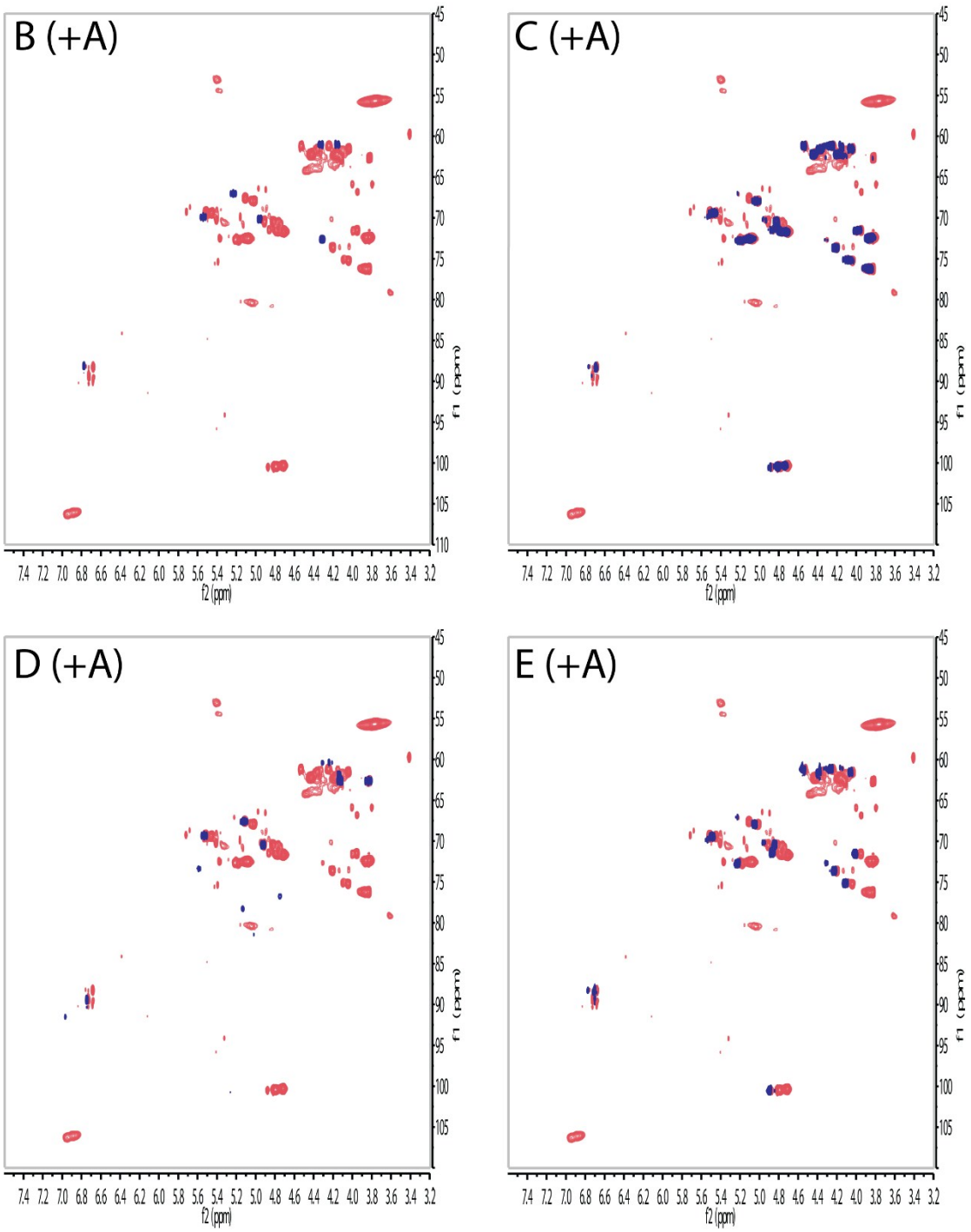


Figure S3 Comparison of the ^{1}H-^{13}C HSQC NMR spectra (d_6-acetone) obtained from: A) beech wood after AcBr/AcOH treatment (red) with the crude reaction mixtures obtained from B) D-glucose, C) filter paper, D) D-xylose and E) cellobiose (blue) after the same treatment.

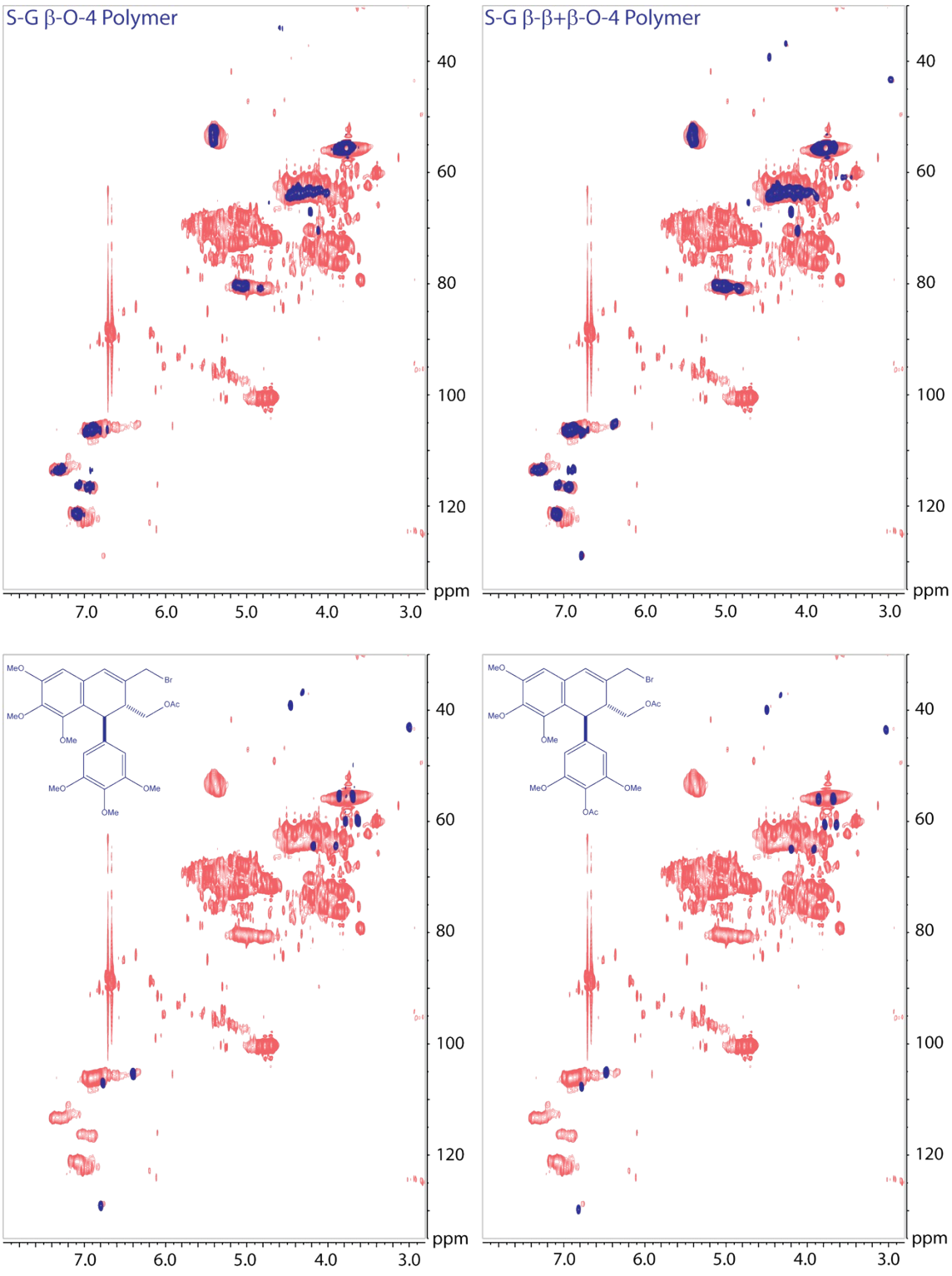
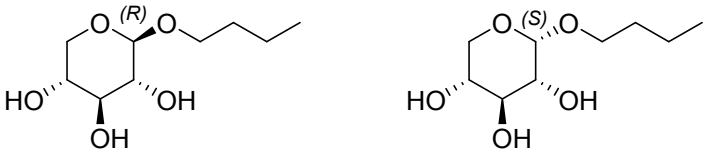


Figure S4 A comparison of a selected region of the ^{1}H-^{13}C HSQC NMR spectrum of beech cell walls (red) overlaid with that of S-G β-O-4 polymer, S-G β-β/β-O-4 polymer and syringaresinol dimethyl ether (blue) following AcBr/AcOH treatment.

Preparation of butyl D-xylose and butyl D-mannose

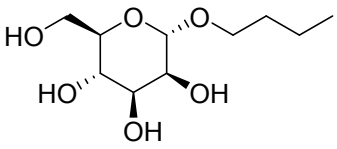
Butyl D-Xylose ((2R/S,3R,4S,5R)-2-butoxytetrahydro-2H-pyran-3,4,5-triol)



D-Xylose (100 mg) was heated at reflux in 95% *n*-BuOH/5% H_2O containing 0.2 M HCl (10 mL) for 6 hours. The reaction mixture was then concentrated *in vacuo* to give the product (mixture of anomers *ca.* 2:1) as a viscous very pale yellow oil which was characterised without further purification.

^{13}C NMR (101 MHz, D_2O) δ 102.9, 98.2, 75.8, 73.2, 73.0, 71.3, 70.4, 69.4, 69.2, 68.1, 65.1, 61.0, 30.9, 30.8, 18.8, 18.5, 13.2, 13.1. Analytical data are consistent with those previously reported.[7]

Butyl α-D-Mannose ((2S,3S,4S,5S,6R)-2-butoxy-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol)



D-Mannose (100 mg) was heated at reflux in 95% *n*-BuOH/5% H_2O containing 0.2 M HCl (10 mL) for 6 hours. The reaction mixture was then concentrated *in vacuo* to give the product as a viscous colourless oil which was characterised without further purification. The crude mixture appeared to contain essentially exclusively the α isomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (s, 1H), 4.07 – 3.71 (m, 5H), 3.65 (dt, *J* = 11.5, 6.9 Hz, 1H), 3.53 (s, 1H), 3.41 (q, *J* = 7.3 Hz, 1H), 1.56 (pt, *J* = 6.9, 3.7 Hz, 2H), 1.38 (dtd, *J* = 15.3, 7.0, 5.1 Hz, 2H), 0.94 (dt, *J* = 11.9, 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 100.2, 72.4, 71.7, 71.1, 67.6, 66.3, 61.1, 31.6, 19.4, 14.0. Analytical data are consistent with those previously reported.[8]

^{1}H NMR (400 MHz, D_2O) δ 4.71 (s, 1H), 3.82 – 3.71 (m, 2H), 3.67 – 3.56 (m, 3H), 3.56 – 3.45 (m, 2H), 3.40 (dt, *J* = 9.9, 6.0 Hz, 1H), 1.57 – 1.36 (m, 2H), 1.33 – 1.16 (m, 2H), 0.78 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, D_2O) δ 99.6, 72.6, 70.6, 70.1, 67.5, 66.7, 60.9, 30.6, 18.8, 13.1.

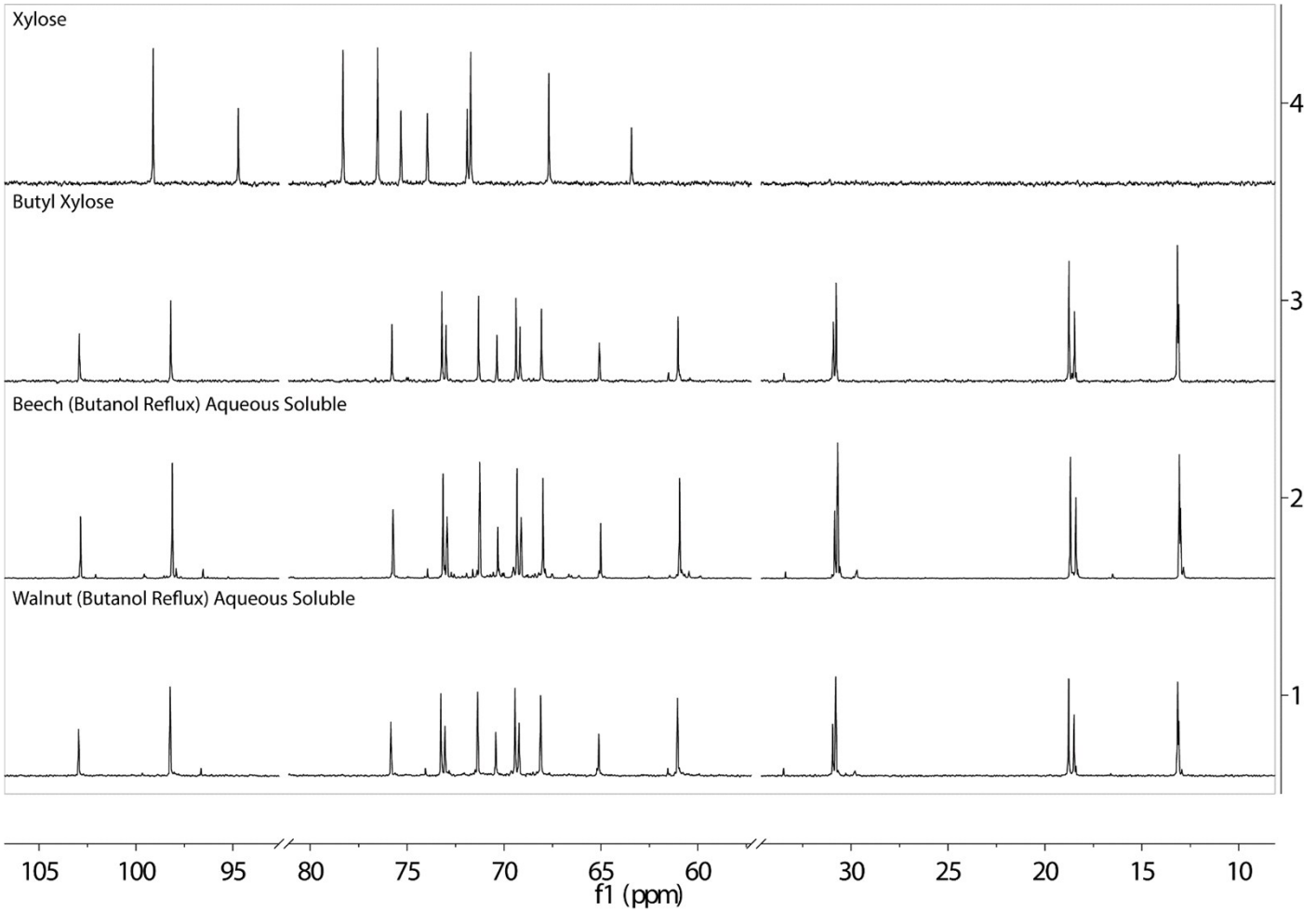


Figure S5 Comparison of ^{13}C NMR spectra (D_2O) obtained from the aqueous soluble fraction from butanol pretreatment of walnut shell and beech sawdust with D-xylose and the prepared sample of butyl xylose (mixture of anomers).

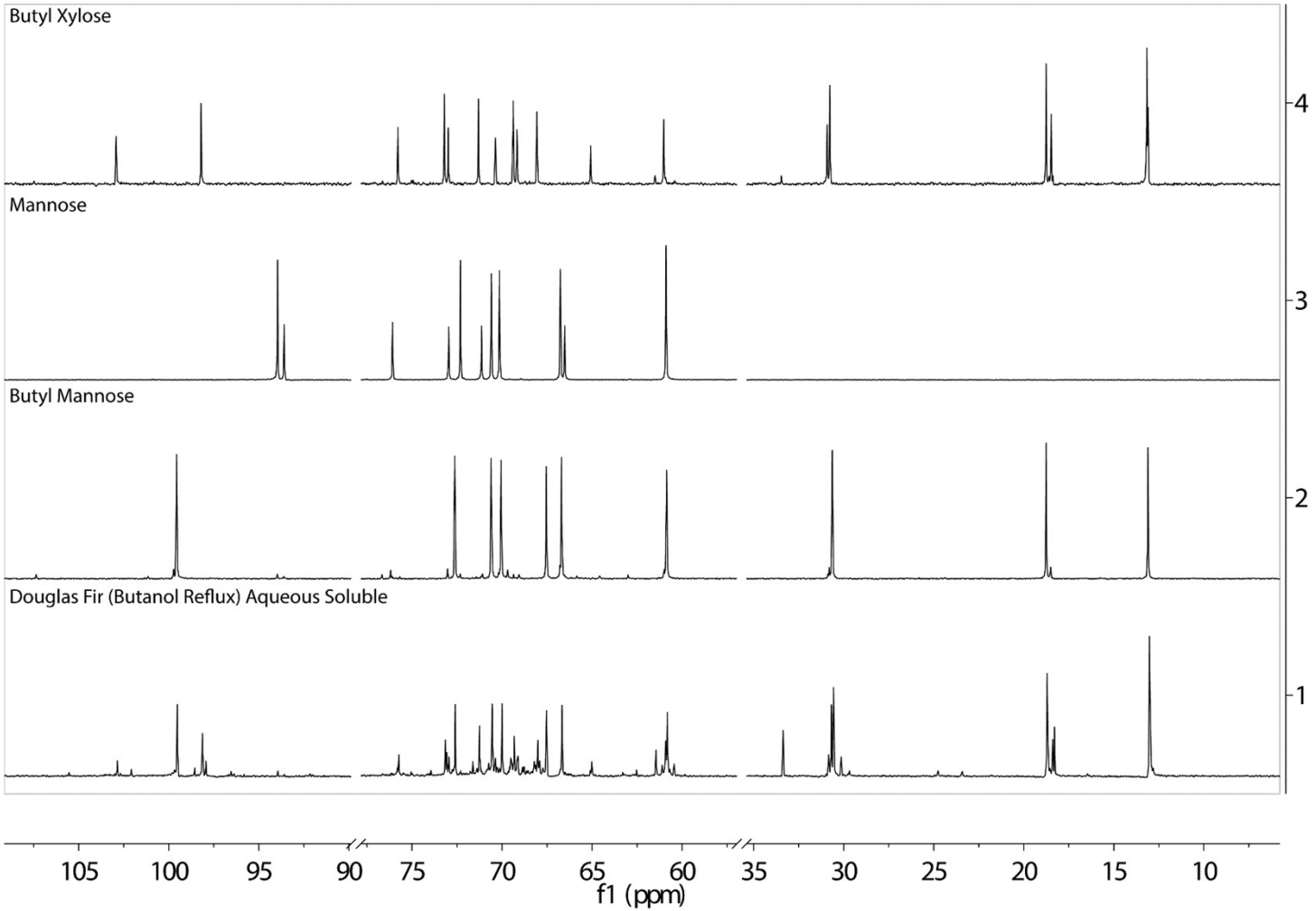


Figure S6 Comparison of ^{13}C NMR spectra (D_2O) obtained from the aqueous soluble fraction from butanol pretreatment of Douglas fir with the prepared sample of butyl xylose (mixture of anomers), commercially available D-mannose and the prepared sample of butyl α-D-mannose.

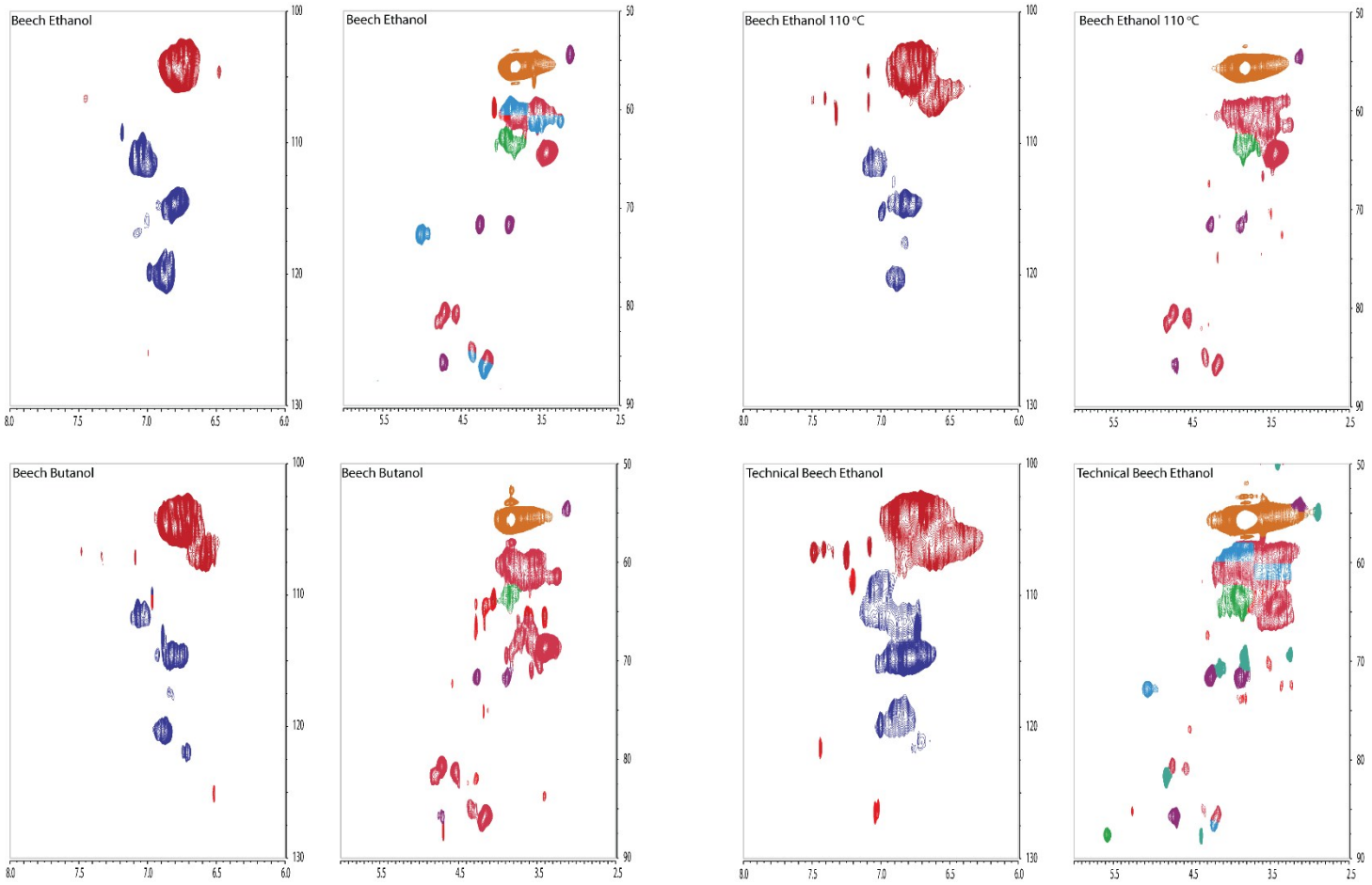


Figure S7 ^{1}H-^{13}C HSQC NMR spectra (d_6-acetone) of beech organosolv lignins. For each lignin both the aromatic and linkage regions are shown. For a detailed analysis of the spectra see Table 2, entries 1-4 in the main manuscript. For colour coding please see Figure 5 in the main manuscript.

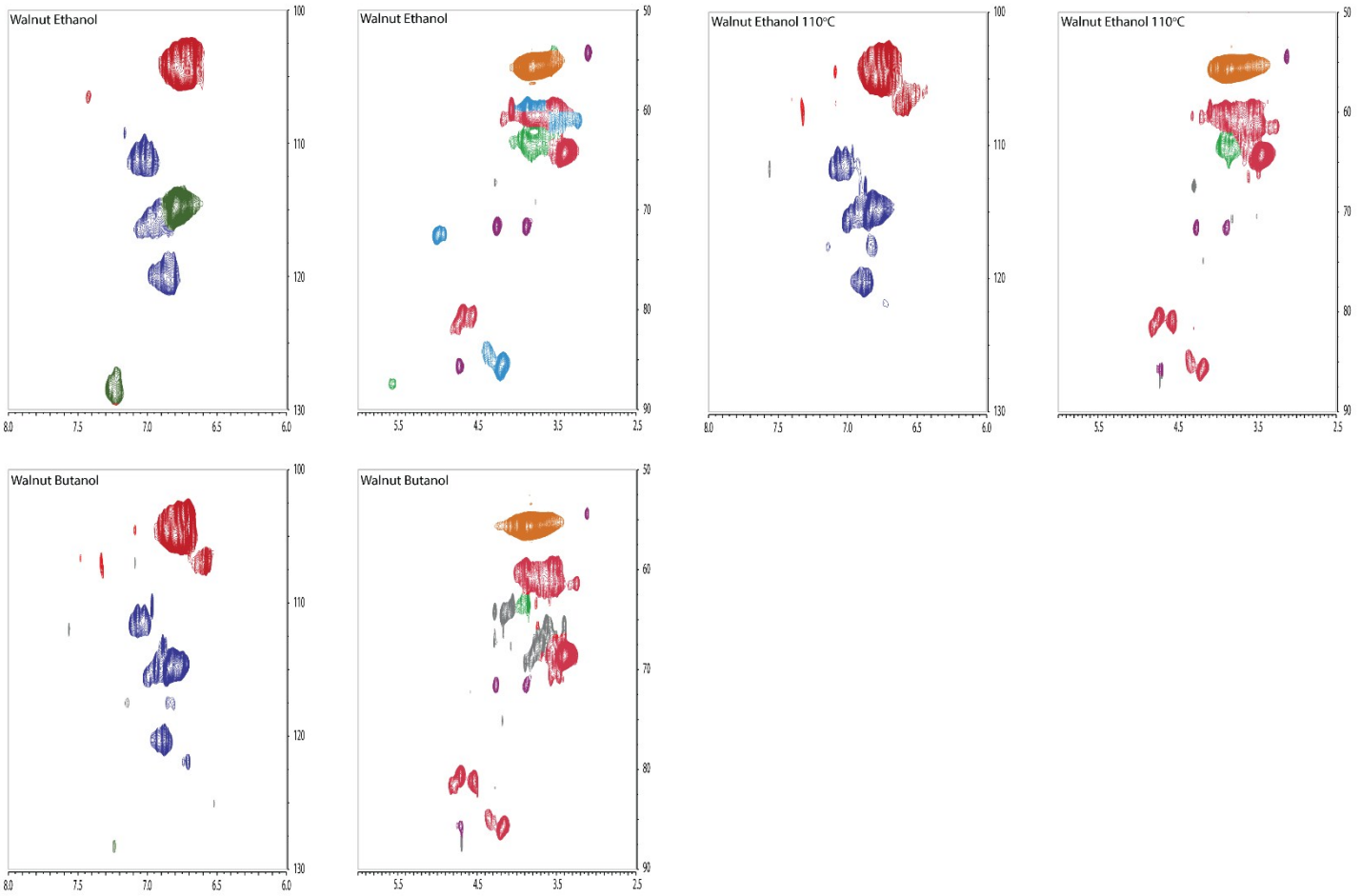


Figure S8 ^{1}H-^{13}C HSQC NMR spectra (d_6-acetone) of walnut shell organosolv lignins. See Table 2 and Figure 5 for additional analysis and a colour coding key. The green coloured aromatic cross-peaks correspond to H units.

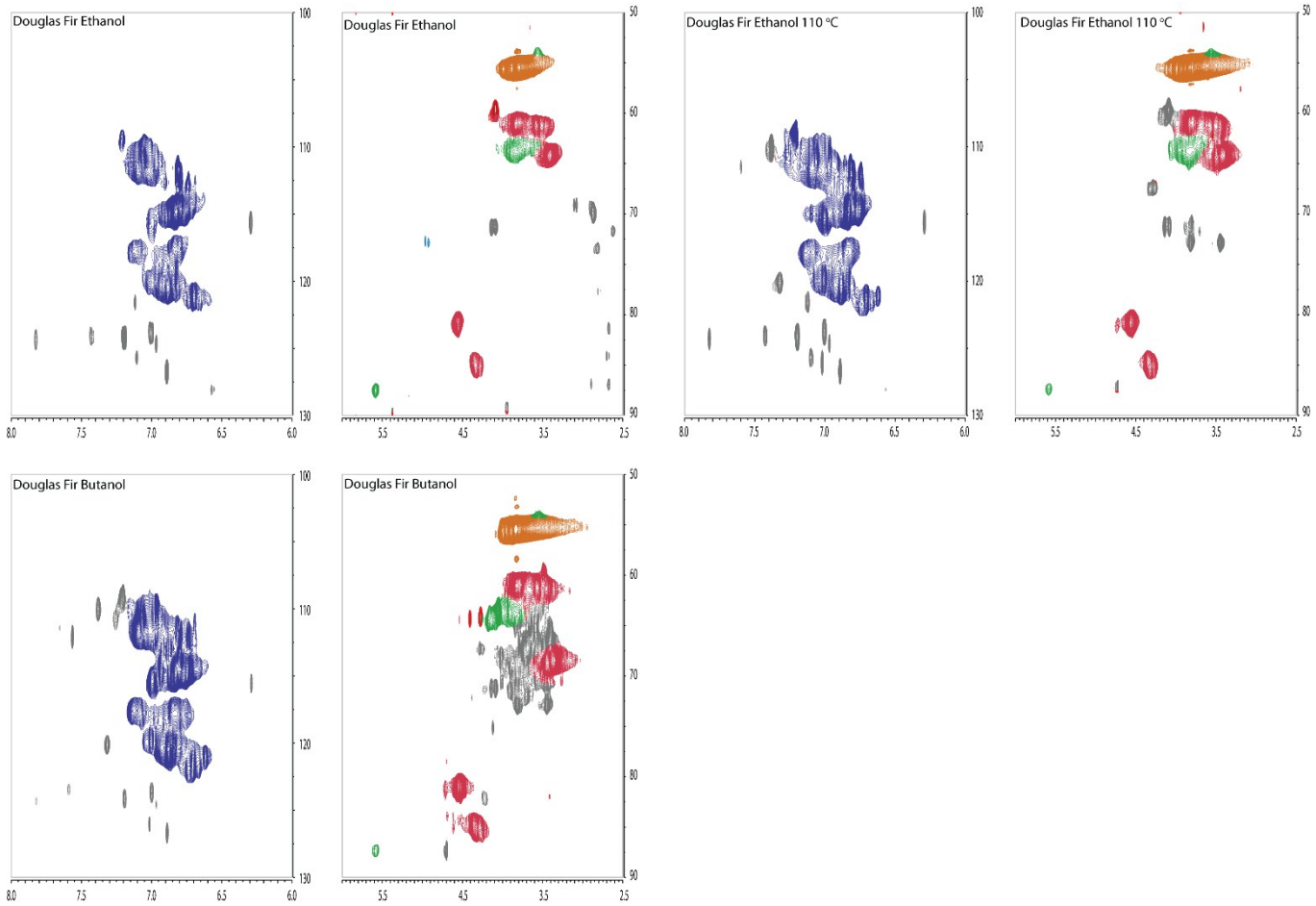


Figure S9 ^{1}H-^{13}C HSQC NMR spectra (d_6-acetone) of douglas fir organosolv lignins. Please see Table 2 and Figure 5 in the main manuscript for additional details.

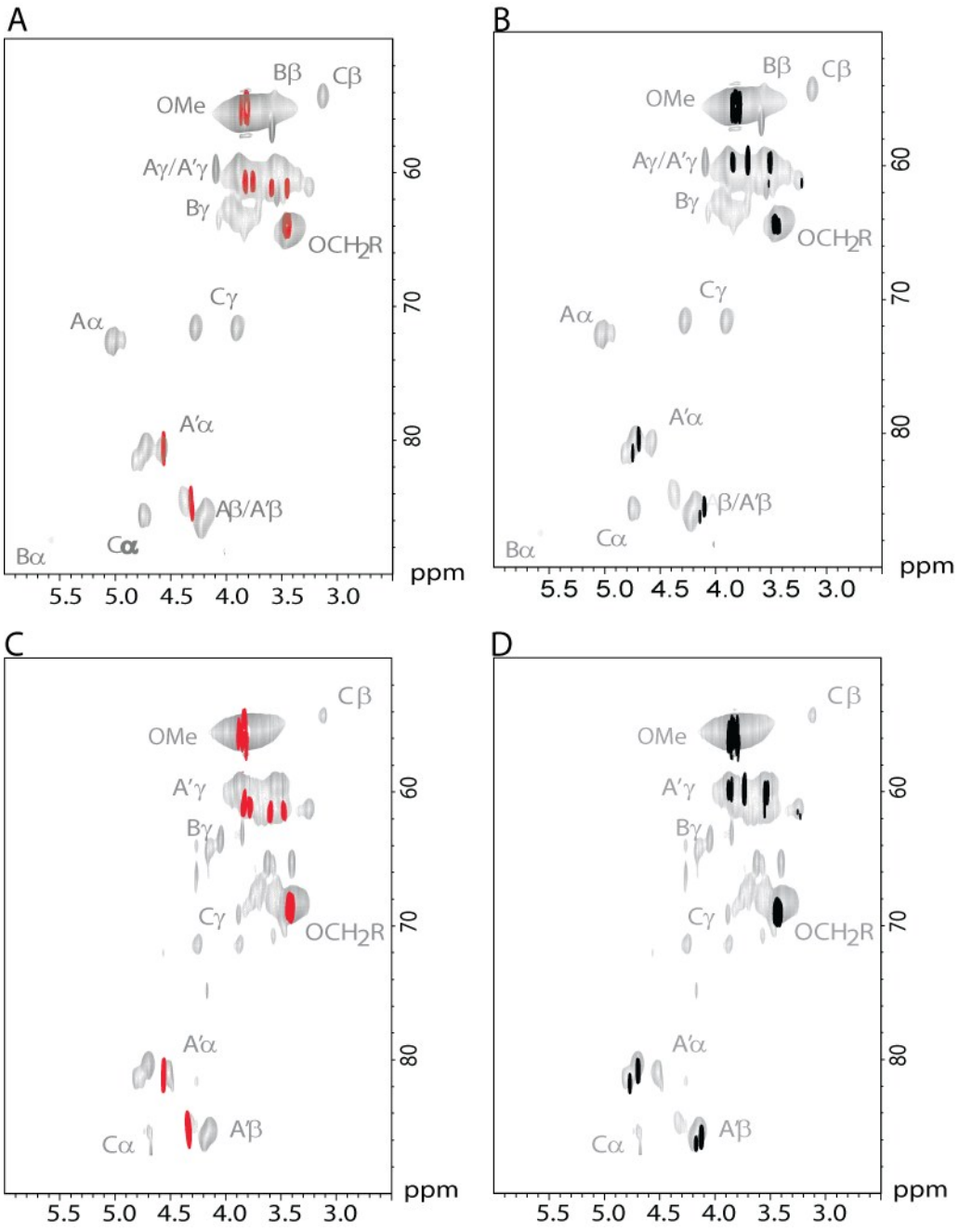


Figure S10 Comparison of the ^{1}H-^{13}C HSQC NMR spectra of models: A) S4 (red – GG-OEt) and B) S6 (black – SS-OEt) with a walnut ethanol lignin (grey) and C) S5 (red – GG-O^{n}Bu) and D) S7 (black - SS-O^{n}Bu) with a walnut butanol lignin (grey) in d_6-acetone showing the characteristic peaks in the oxygenated aliphatic region indicting α-etherification of β-O-4 units. See above in ESI for the synthesis of these model compounds.

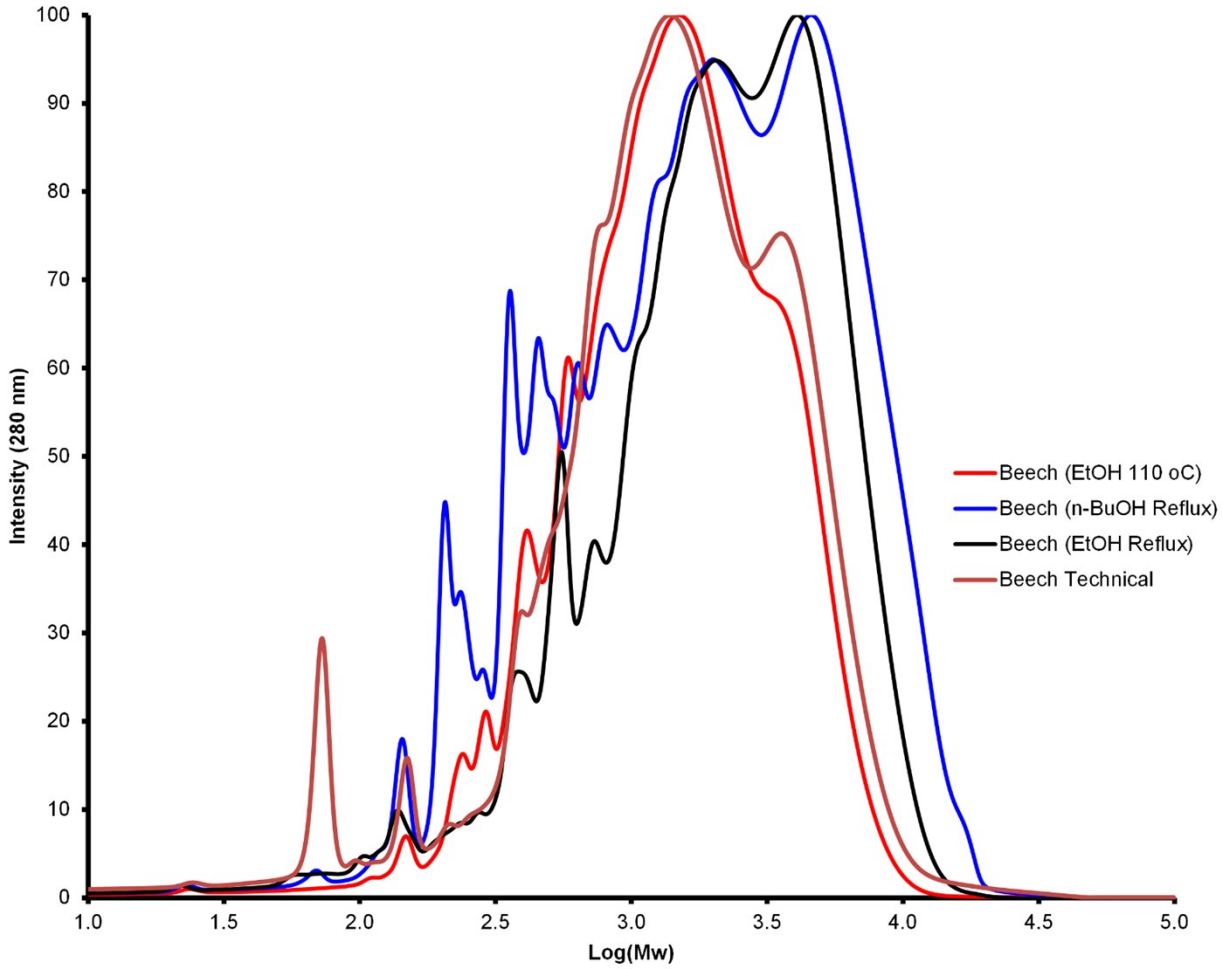


Figure S11 GPC analysis of beech organosolv lignins.

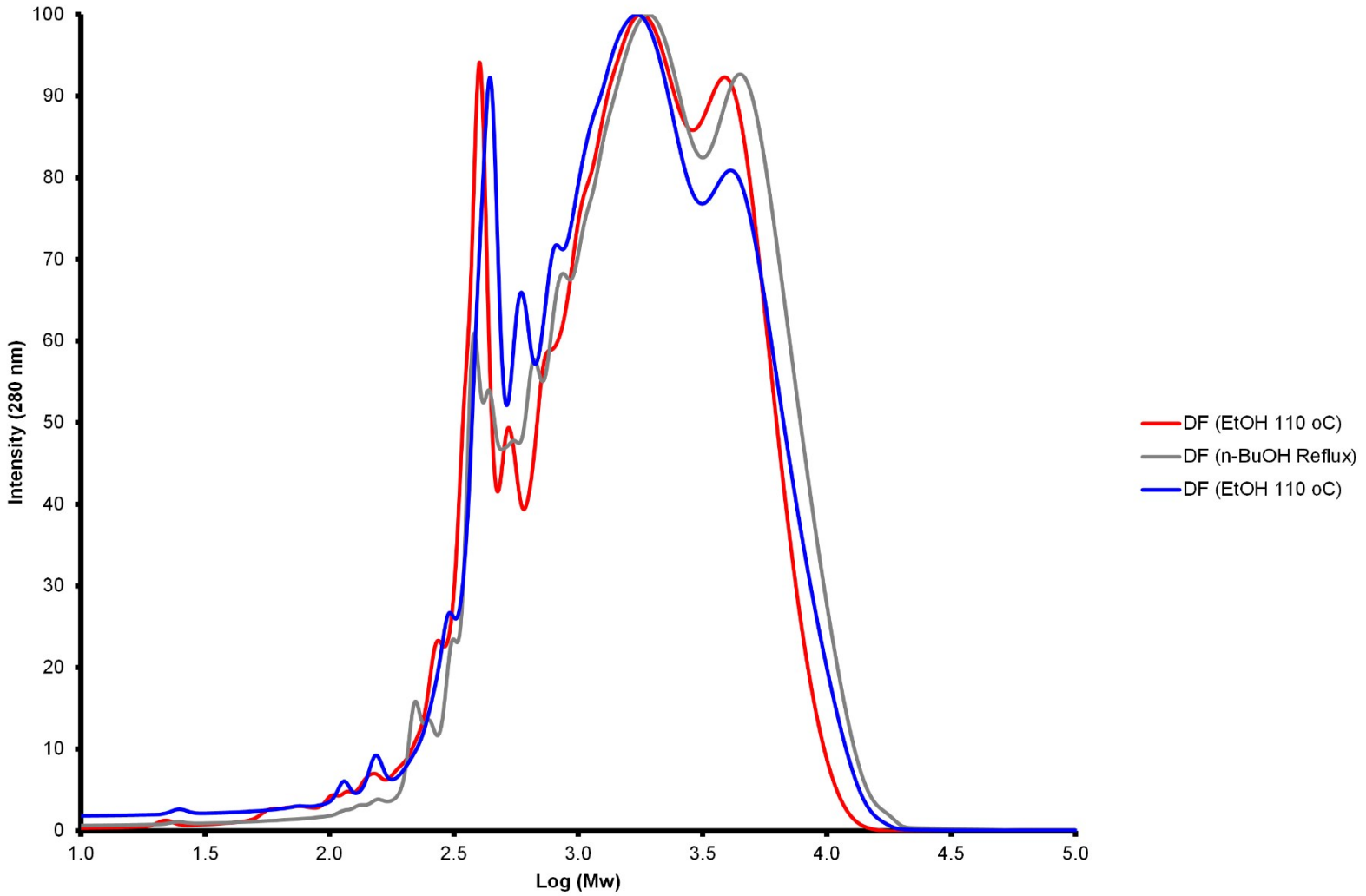


Figure S12 GPC analysis of Douglas fir organosolv lignins.

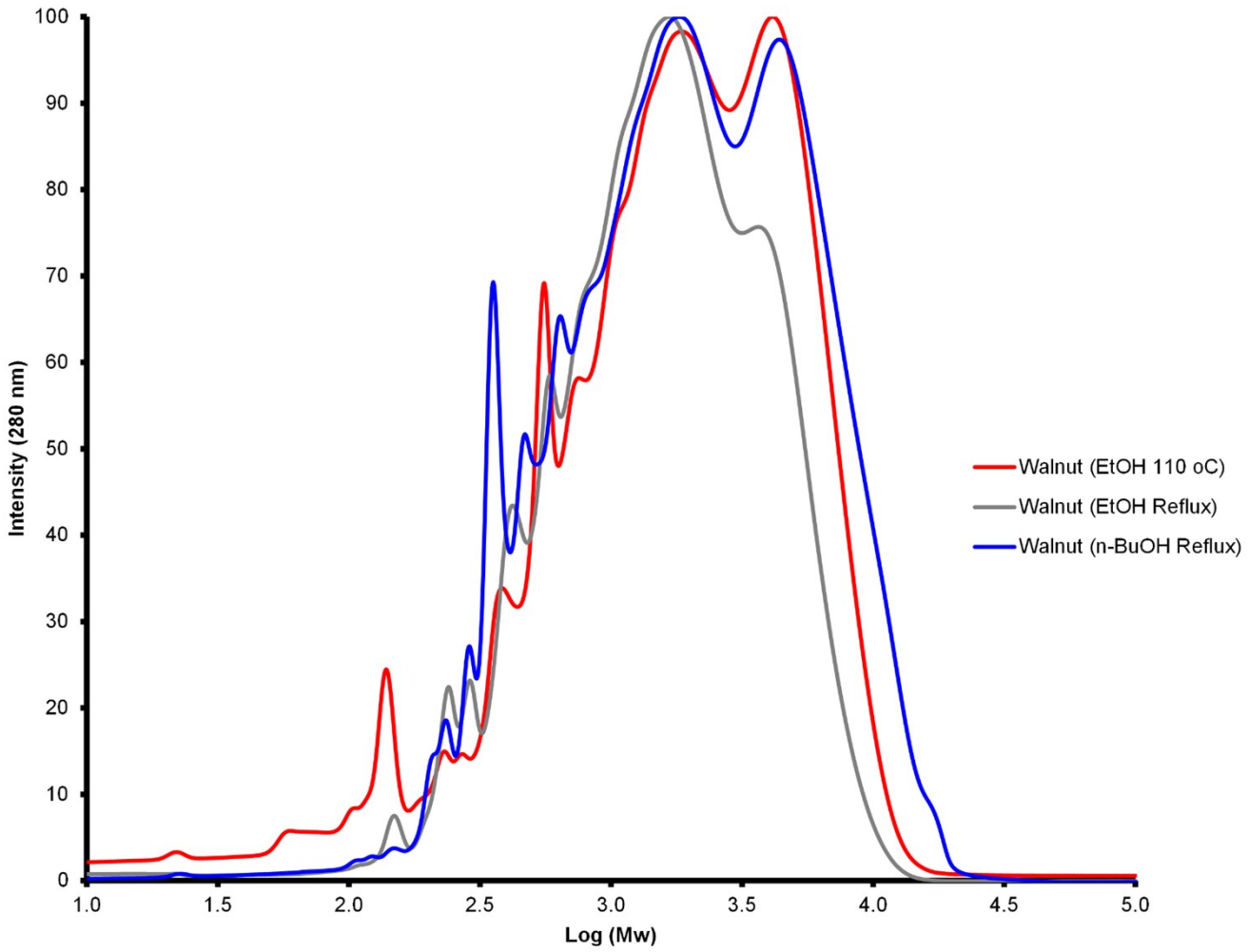


Figure S13 GPC analysis of walnut shell organosolv lignins.

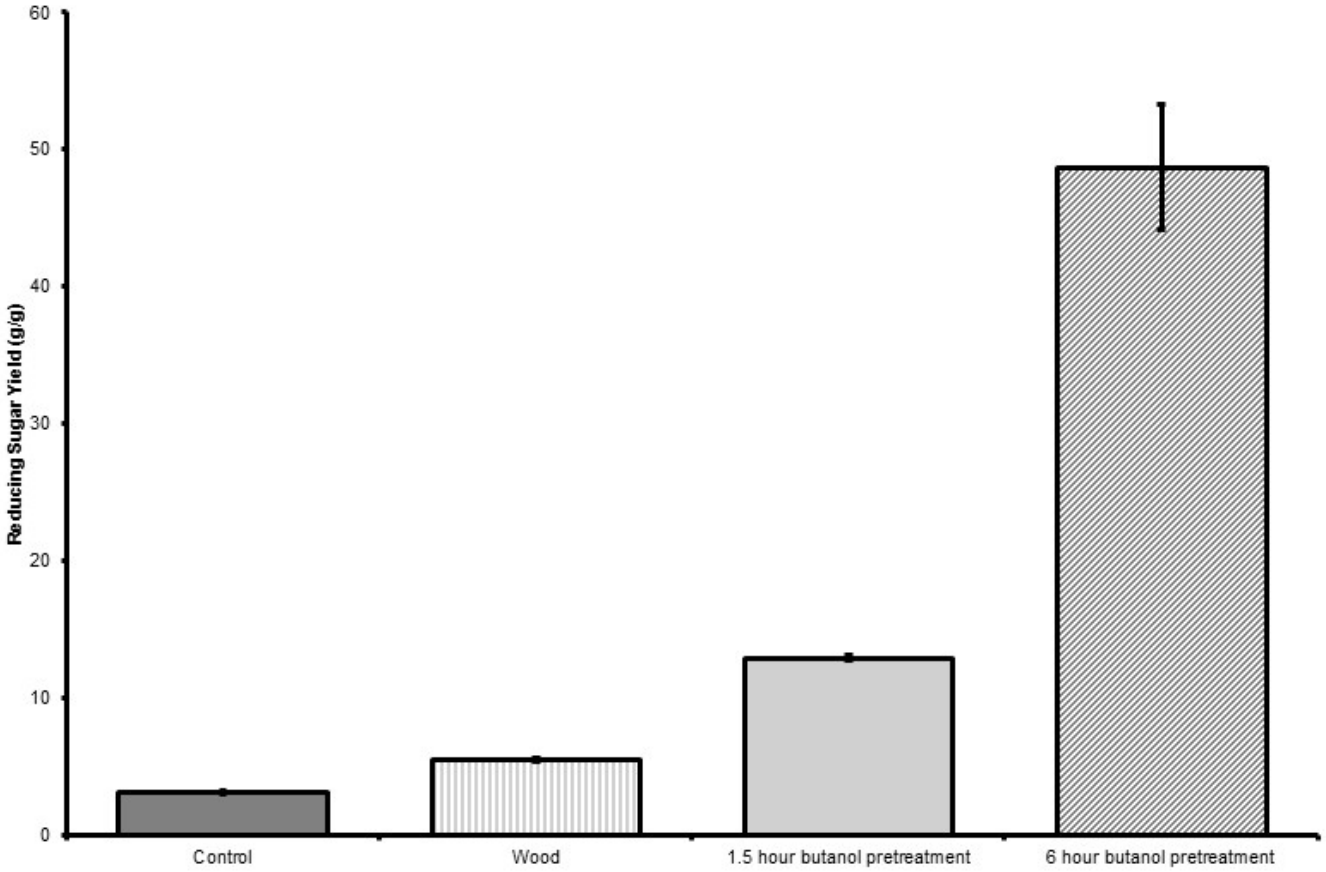
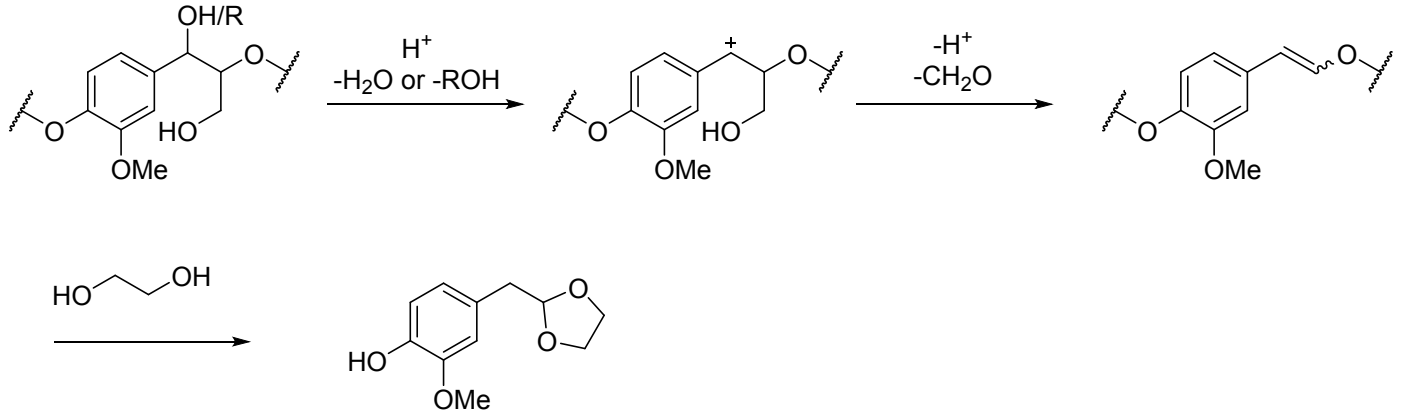


Figure S14 Preliminary enzymatic hydrolysis experiments with beech wood. Conditions: pH 5.5 acetate buffer, 5 wt% loading, 22 FPU/g CTec 2, 50 ^{o}C, 24 hrs. Control = no wood/pulp

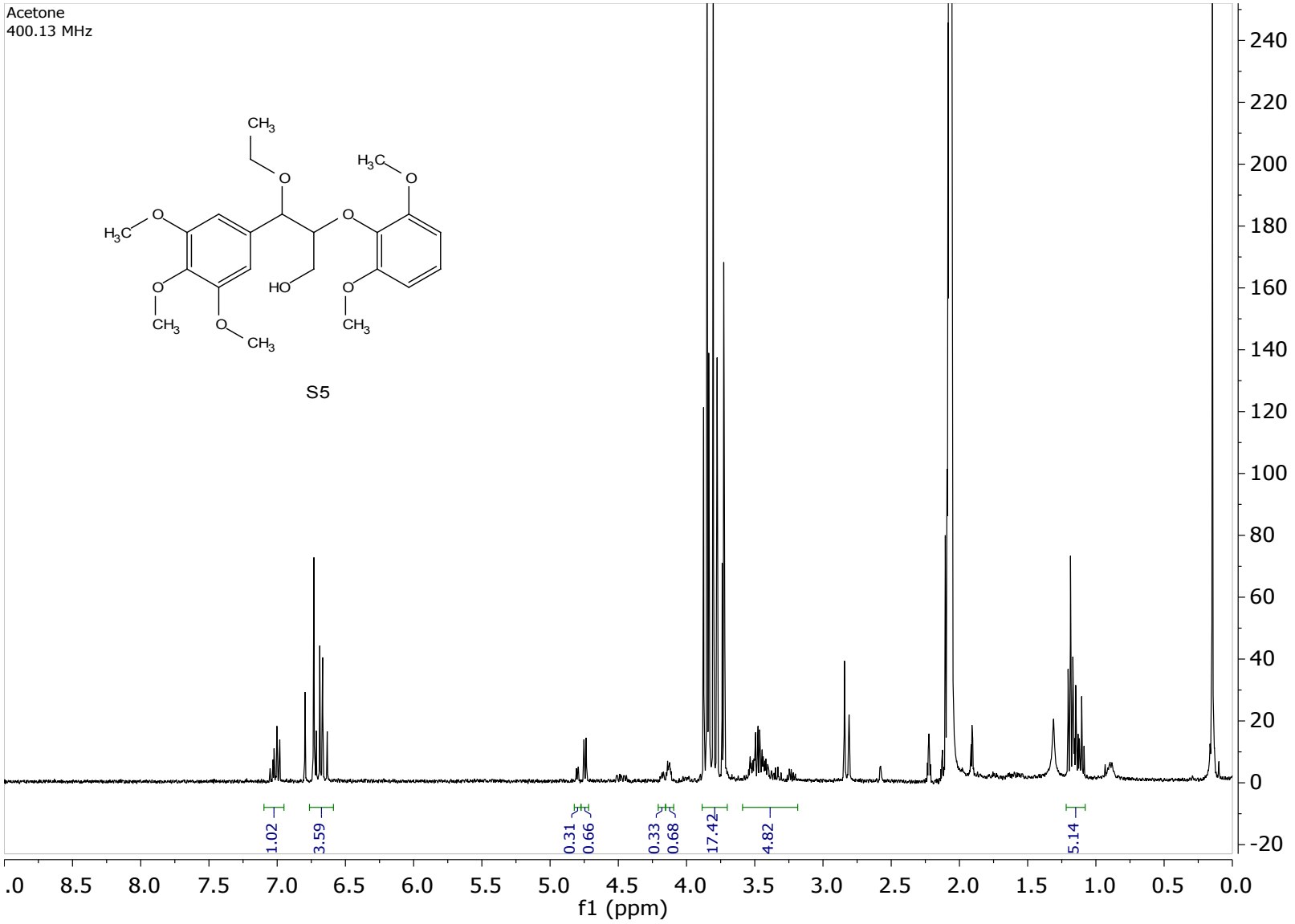
Table S1 GC quantification of acetal monomers from lignin depolymerisation reactions

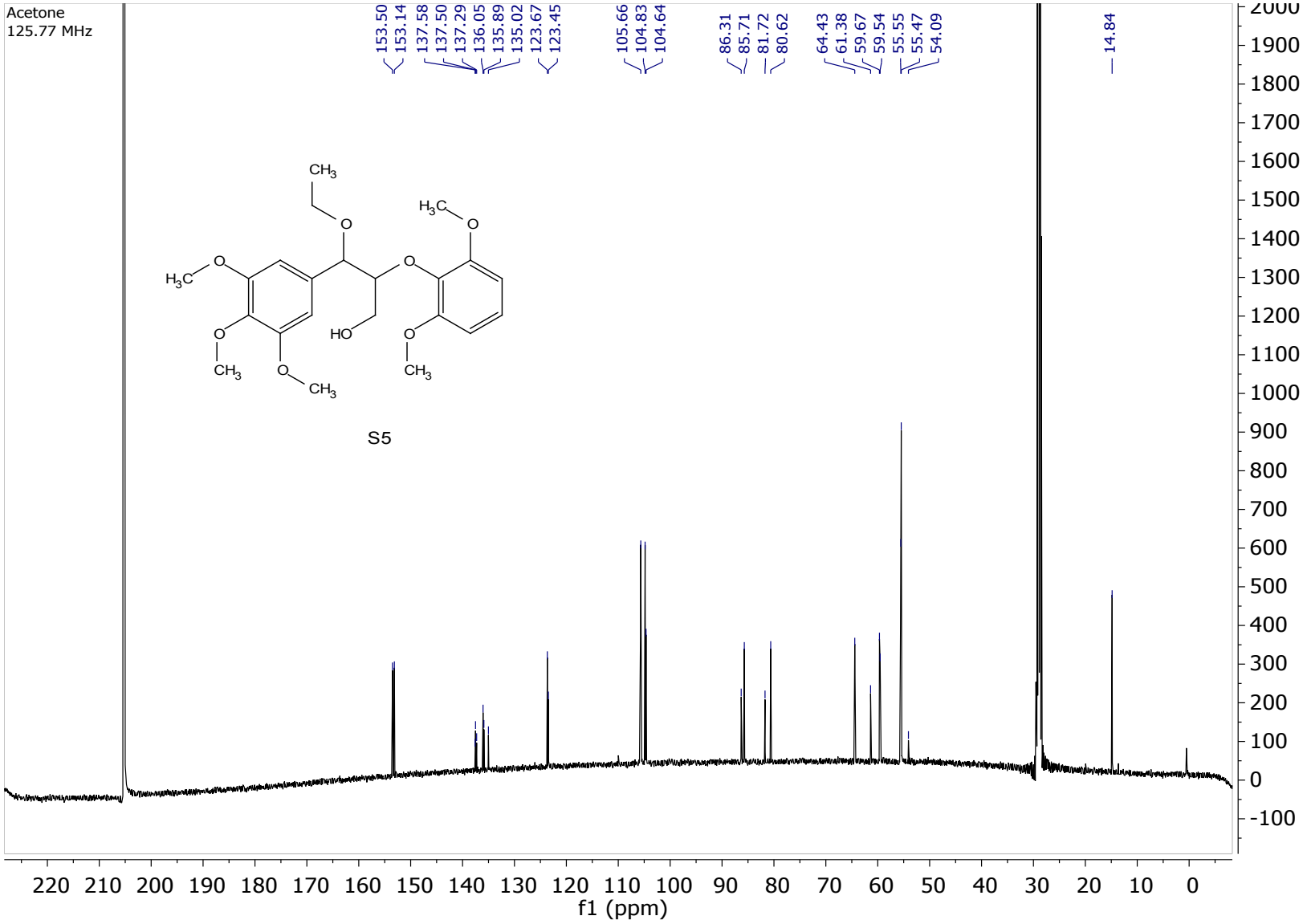
Entry	Lignin	Cat.	**P1** Wt%	**P2** Wt%	**P3** Wt%	Tot. **P1**-**3** (Wt%) +/- (Stdev)	H : G : S (rel%)
1a	Subicat	$Bi(OTf)_3$	0.0	0.6	0.9	1.5	0 : 39 : 61
1b	Subicat	$Bi(OTf)_3$	0.0	1.2	1.7	2.8	0 : 41 : 59
1av	Subicat	$Bi(OTf)_3$	0.0	0.9	1.3	2.1 (+/- 1.0)	0 : 40 : 60
2a	Walnut EtOH	$Bi(OTf)_3$	2.3	8.5	6.9	17.8	13 : 48 : 39
2b	Walnut EtOH	$Bi(OTf)_3$	2.3	8.8	7.4	18.5	13 : 47 : 40
2av	Walnut EtOH	$Bi(OTf)_3$	2.3	8.7	7.9	18.1 (+/- 0.5)	13 : 48 : 39
3a	Beech EtOH	$Bi(OTf)_3$	0.0	8.3	10.4	18.8	0 : 44 : 56
3b	Beech EtOH	$Bi(OTf)_3$	0.0	6.9	8.4	15.3	0 : 45 : 55
3av	Beech EtOH	$Bi(OTf)_3$	0.0	7.6	9.4	17.0 (+/- 2.5)	0 : 45 : 55
4a	Douglas Fir EtOH	$Bi(OTf)_3$	0.3	12.2	0.0	12.5	2 : 98 : 0
4b	Douglas Fir EtOH	$Bi(OTf)_3$	0.2	9.8	0.0	10.0	2 : 98 : 0
4av	Douglas Fir EtOH	$Bi(OTf)_3$	0.3	11.0	0.0	11.3 (+/- 1.8)	2 : 98 : 0
5a	Walnut Butanol	$Bi(OTf)_3$	0.4	3.9	5.5	9.8	4 : 39 : 57
5b	Walnut Butanol	$Bi(OTf)_3$	0.4	4.0	5.8	10.2	4 : 39 : 57
5av	Walnut Butanol	$Bi(OTf)_3$	0.4	4.0	5.7	10.0 (+/- 0.3)	4 : 39 : 57
6a	Beech Butanol	$Bi(OTf)_3$	0.0	3.1	6.7	9.7	0 : 32 : 68
6b	Beech Butanol	$Bi(OTf)_3$	0.0	3.1	6.8	9.9	0 : 31 :69
6av	Beech Butanol	$Bi(OTf)_3$	0.0	3.1	6.7	9.8 (+/- 0.2)	0 : 32 : 68
7a	Douglas Fir Butanol	$Bi(OTf)_3$	0.1	8.6	0.0	8.8	1 : 99 : 0
7b	Douglas Fir Butanol	$Bi(OTf)_3$	0.1	7.9	0.0	8.0	1 : 99 : 0
7av	Douglas Fir Butanol	$Bi(OTf)_3$	0.1	8.2	0.0	8.4 (+/- 0.5)	1 : 99 : 0
8a	Walnut Butanol	MsOH	0.5	4.3	4.5	9.2	5 : 46 : 49
8b	Walnut Butanol	MsOH	0.3	3.4	3.6	7.3	5 : 46 : 49
8av	Walnut Butanol	MsOH	0.4	3.8	4.0	8.2 (+/- 1.4)	5 : 46 : 49
9a	Walnut Butanol	TsOH	0.4	3.6	3.9	7.8	4 : 46 : 50
9b	Walnut Butanol	TsOH	0.3	3.2	3.4	6.9	5 : 46 : 49
9av	Walnut Butanol	TsOH	0.4	3.4	3.6	7.4 (+/- 0.7)	4 : 46 : 50
10a	Walnut Butanol	$Bi(OTf)_3$	0.3	2.6	3.6	6.2	4 : 40 : 56
10b	Walnut Butanol	$Bi(OTf)_3$	0.3	2.3	3.0	5.3	5 : 41 : 54
10av	Walnut Butanol	$Bi(OTf)_3$	0.3	2.4	3.3	6.0 (+/- 0.7)	5 : 40 : 55



Scheme 1 Acid catalysed depolymerisation and in-situ acetal formation for the production of aromatic monomers from lignin.

NMR Spectra of Model Compounds


Acetone
400.13 MHz
S5
1.02
3.59
0.31
0.66
0.33
0.68
17.42
4.82
5.14
f1 (ppm)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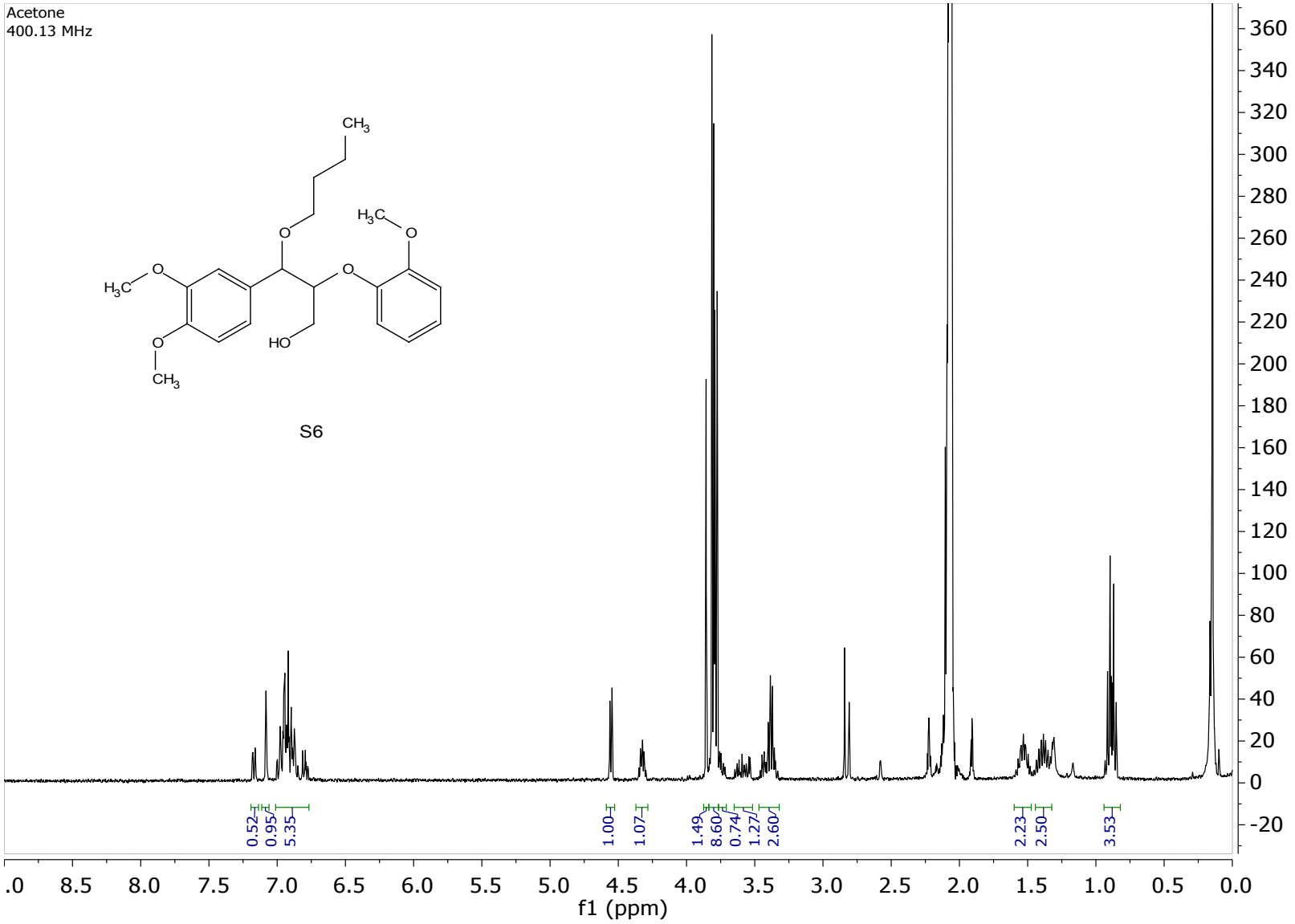
153.50
153.14
137.58
137.50
137.29
136.05
135.89
135.02
123.67
123.45
105.66
104.83
104.64
86.31
85.71
81.72
80.62
64.43
61.38
59.67
59.54
55.55
55.47
54.09
14.84
S5
f1 (ppm)


Acetone
400.13 MHz
S6
0.52
0.95
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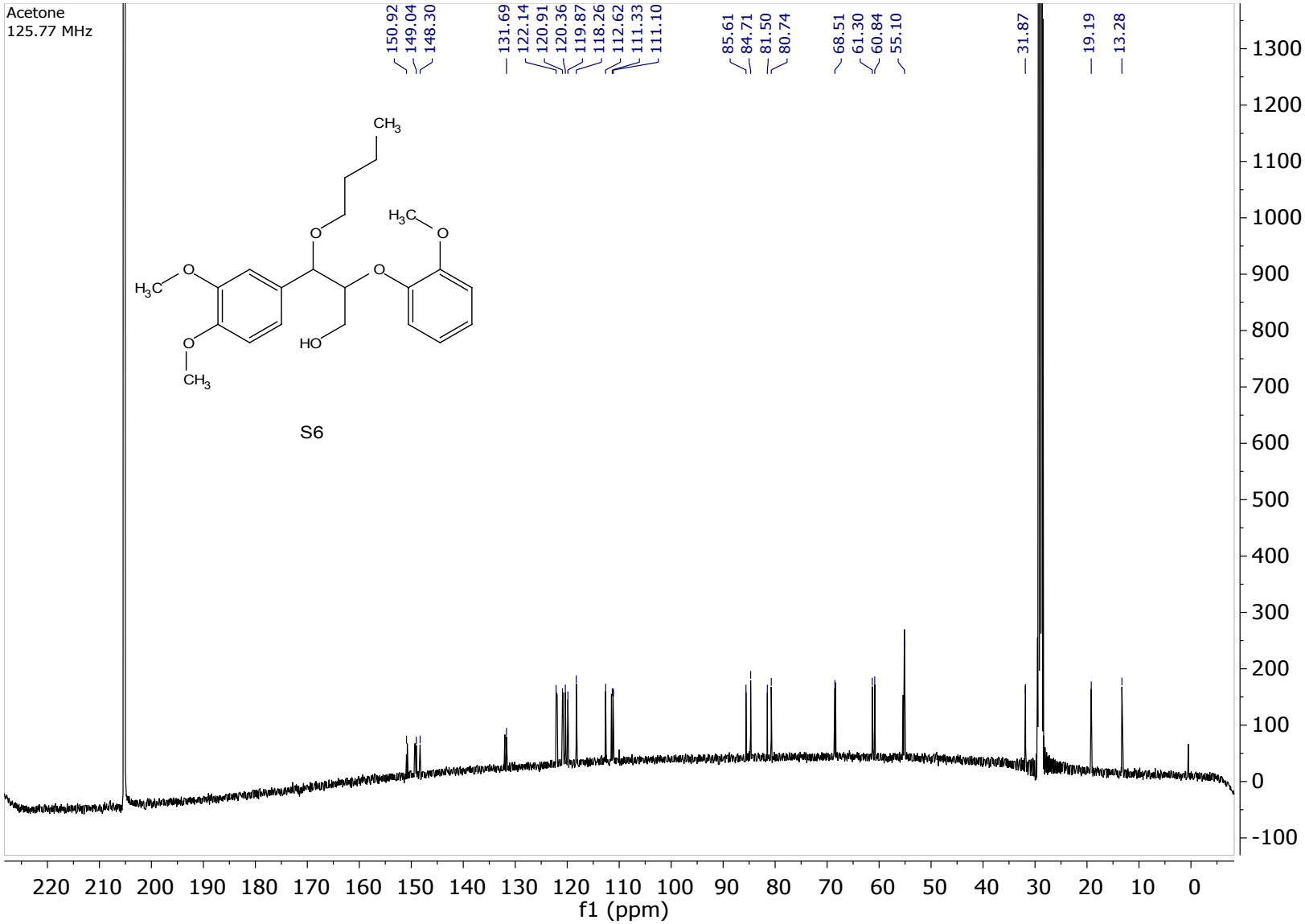
1.00
1.07
1.49
8.60
0.74
1.27
2.60
2.23
2.50
3.53
f1 (ppm)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149.04
148.30
131.69
122.14
120.91
120.36
119.87
118.26
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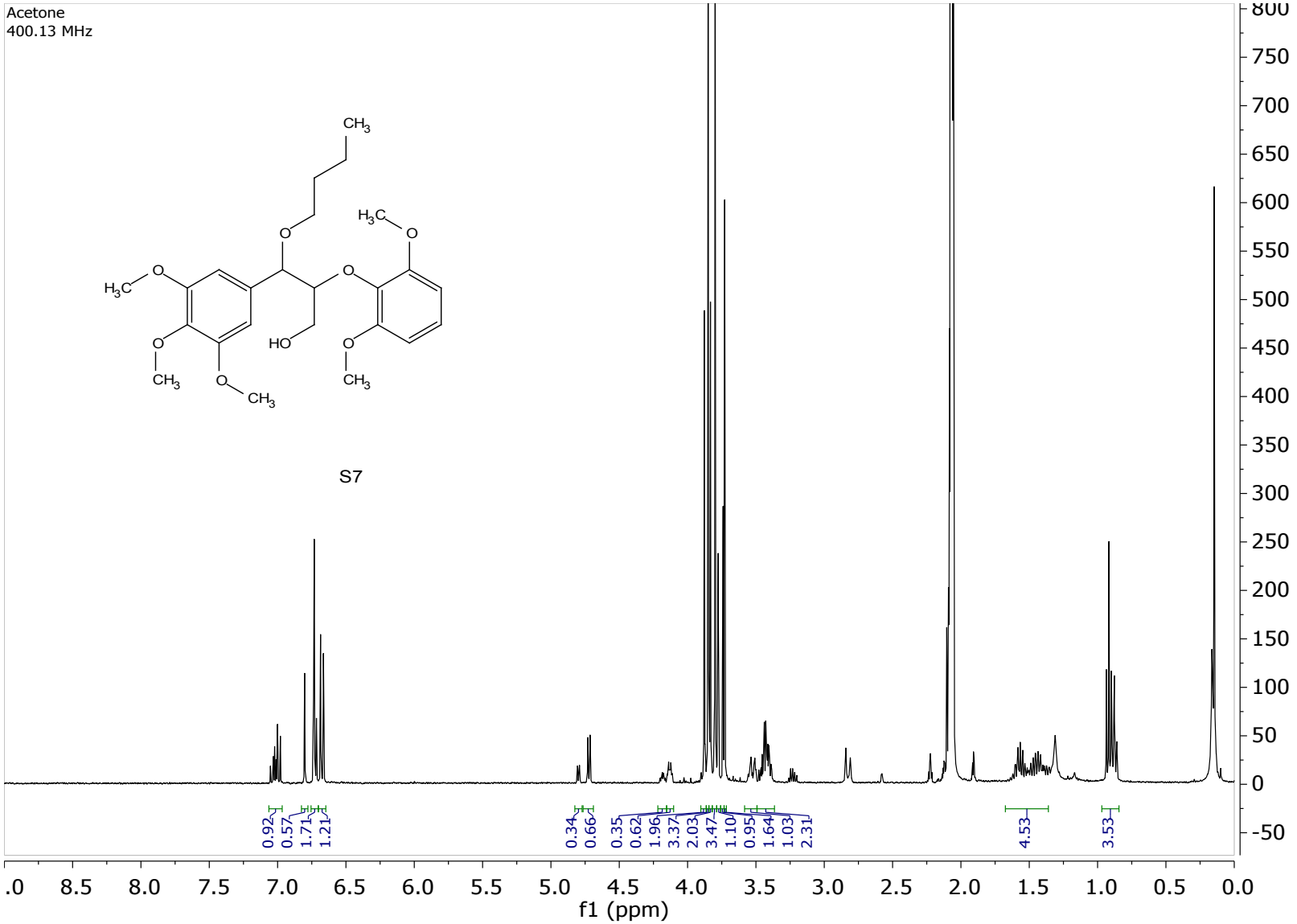
111.33
111.10
85.61
84.71
81.50
80.74
68.51
61.30
60.84
55.10
31.87
19.19
13.28
CH3
H3C
O
O
O
O
O
H3C
HO
CH3
S6
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Acetone
400.13 MHz
S7
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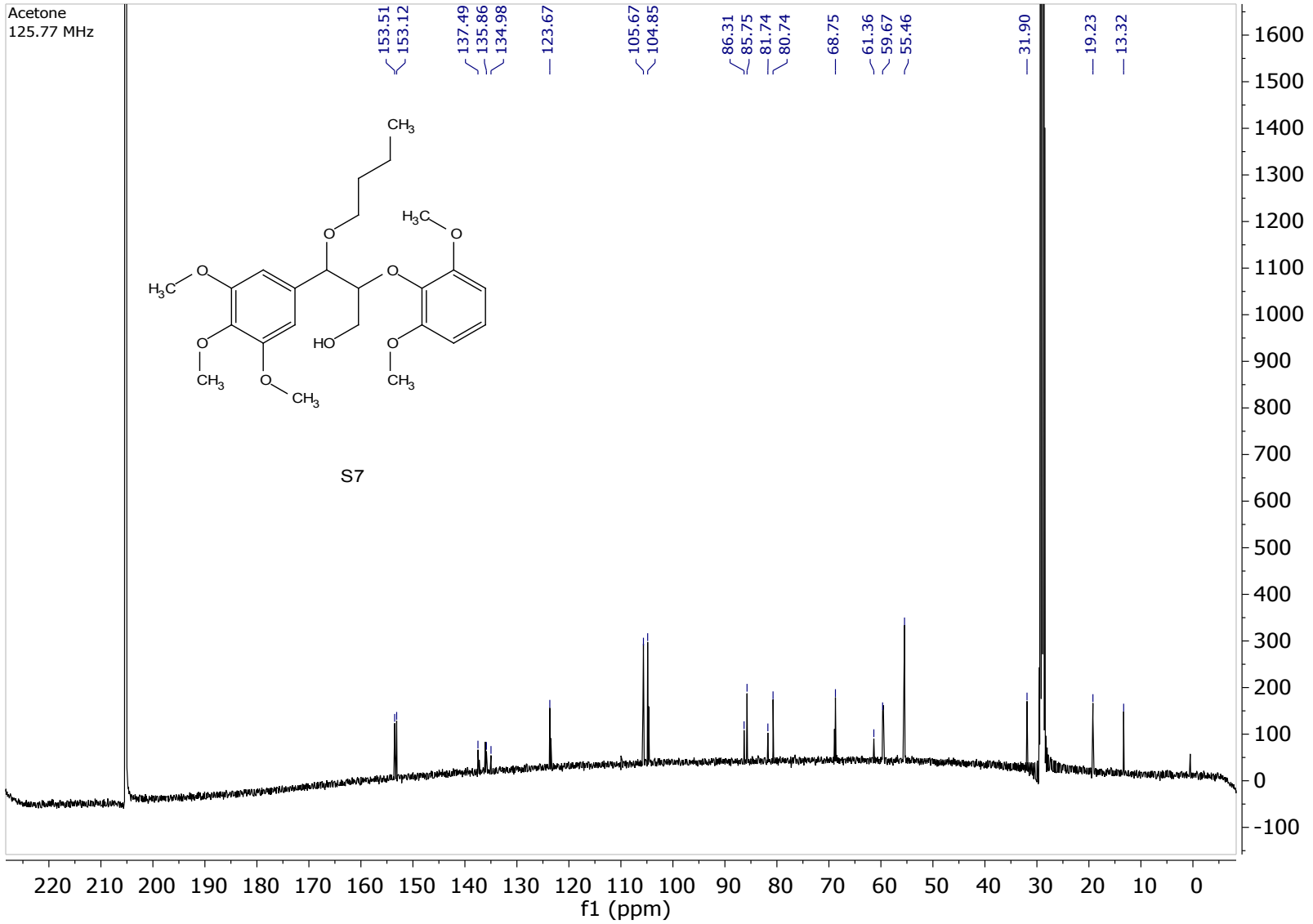
0.57
1.71
1.21
0.34
0.66
0.35
0.62
1.96
3.37
2.03
3.47
1.10
0.95
1.64
1.03
2.31
4.53
3.53
f1 (ppm)


Acetone
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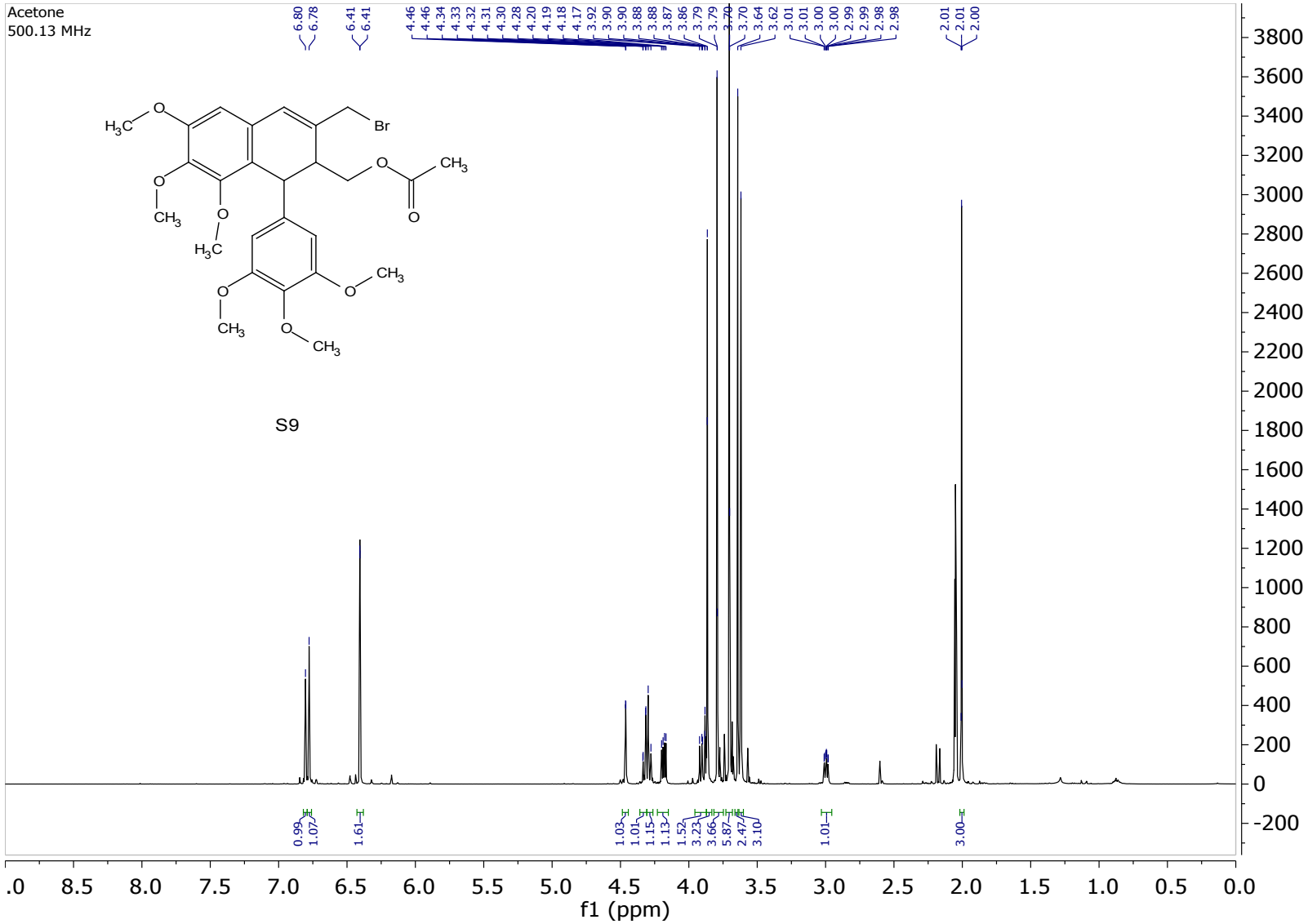
137.49
135.86
134.98
123.67
105.67
104.85
86.31
85.75
81.74
80.74
68.75
61.36
59.67
55.46
31.90
19.23
13.32
CH3
H3C
O
HO
f1 (ppm)

S7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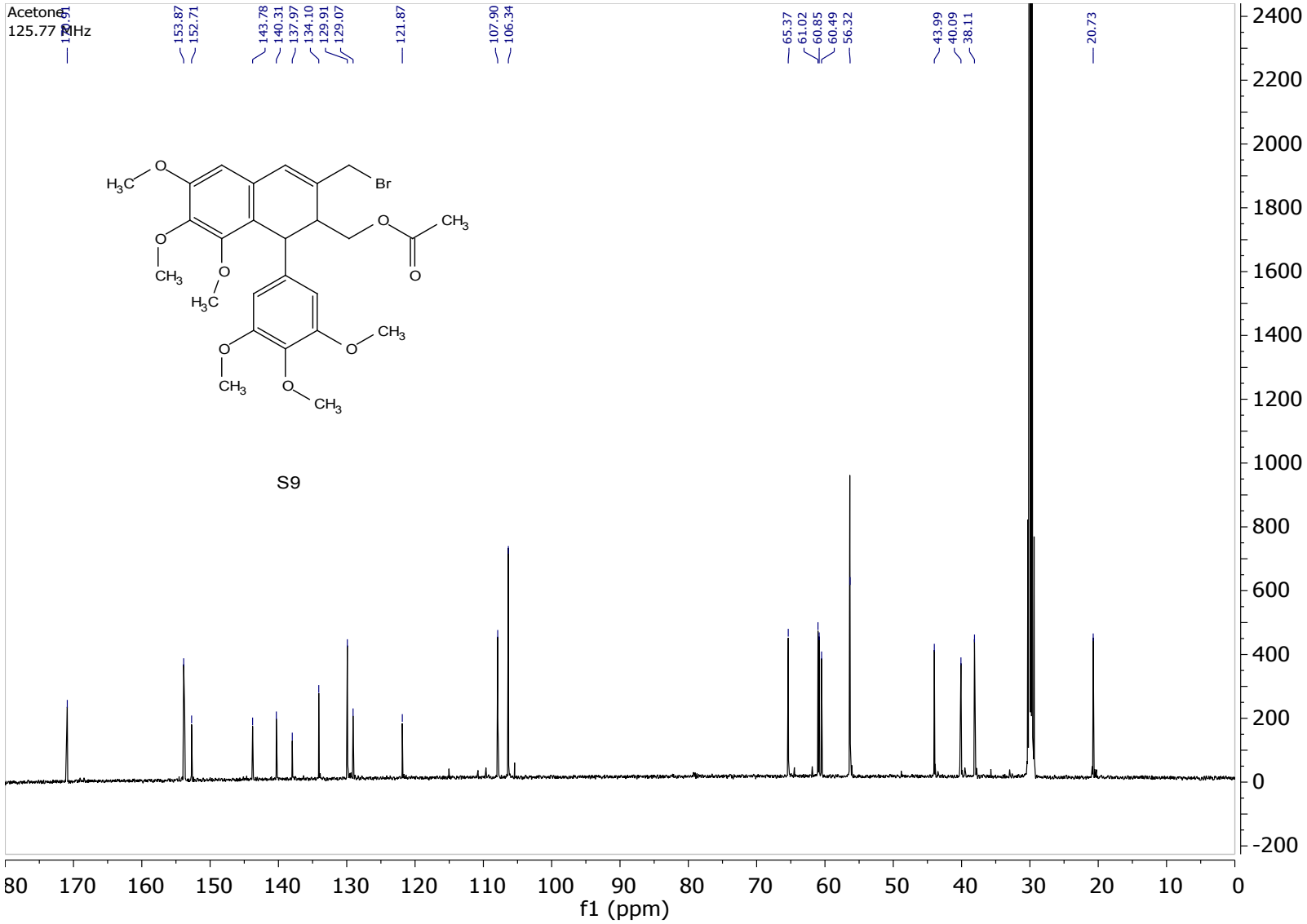
6.41
6.41
4.46
4.46
4.34
4.33
4.32
4.31
4.30
4.28
4.20
4.19
4.18
4.17
3.92
3.90
3.90
3.88
3.88
3.87
3.86
3.79
3.79
3.70
3.70
3.64
3.62
3.01
3.01
3.00
3.00
2.99
2.99
2.98
2.98
2.01
2.01
2.00
Br
S9
0.99
1.07
1.61
1.03
1.01
1.15
1.13
1.52
3.23
3.66
5.87
2.47
3.10
1.01
3.00
f1 (ppm)


Acetone
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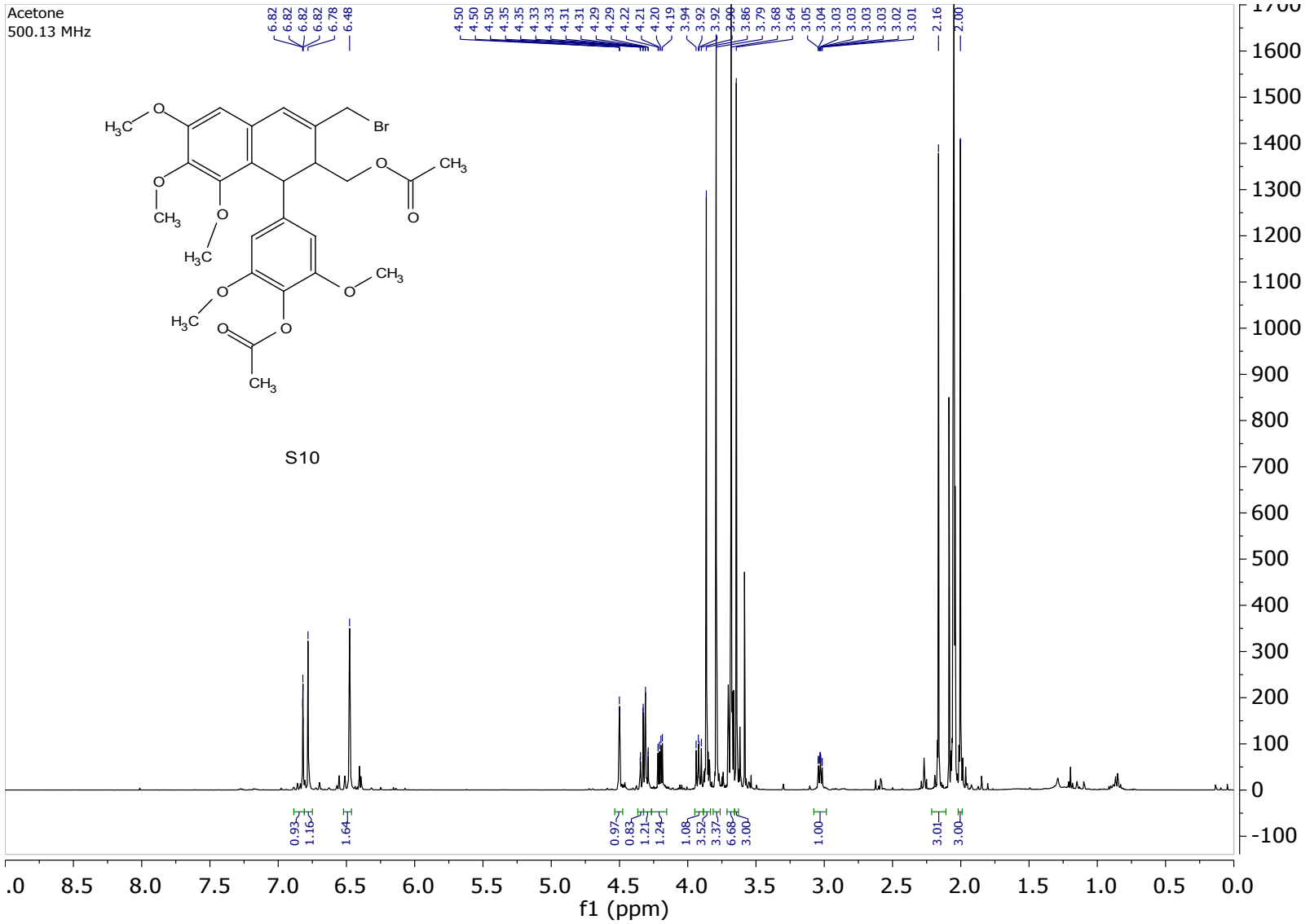
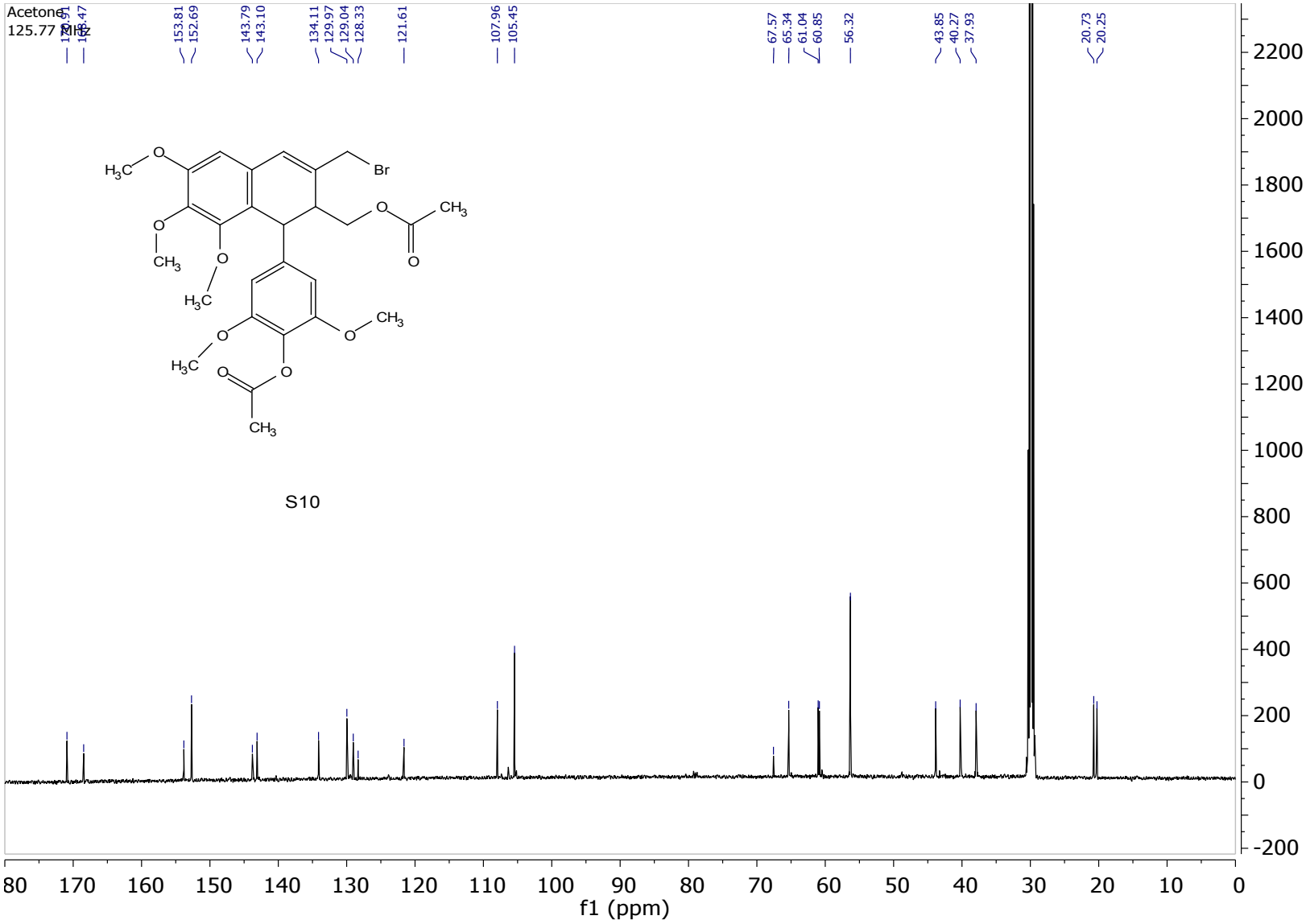
152.71
143.78
140.31
137.97
134.10
129.91
129.07
121.87
107.90
106.34
65.37
61.02
60.85
60.49
56.32
43.99
40.09
38.11
20.73
Br
S9
f1 (ppm)


Acetone
500.13 MHz
S10
f1 (ppm)


Acetone
125.77 MHz
170.91
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153.81
152.69
143.79
143.10
134.11
129.97
129.04
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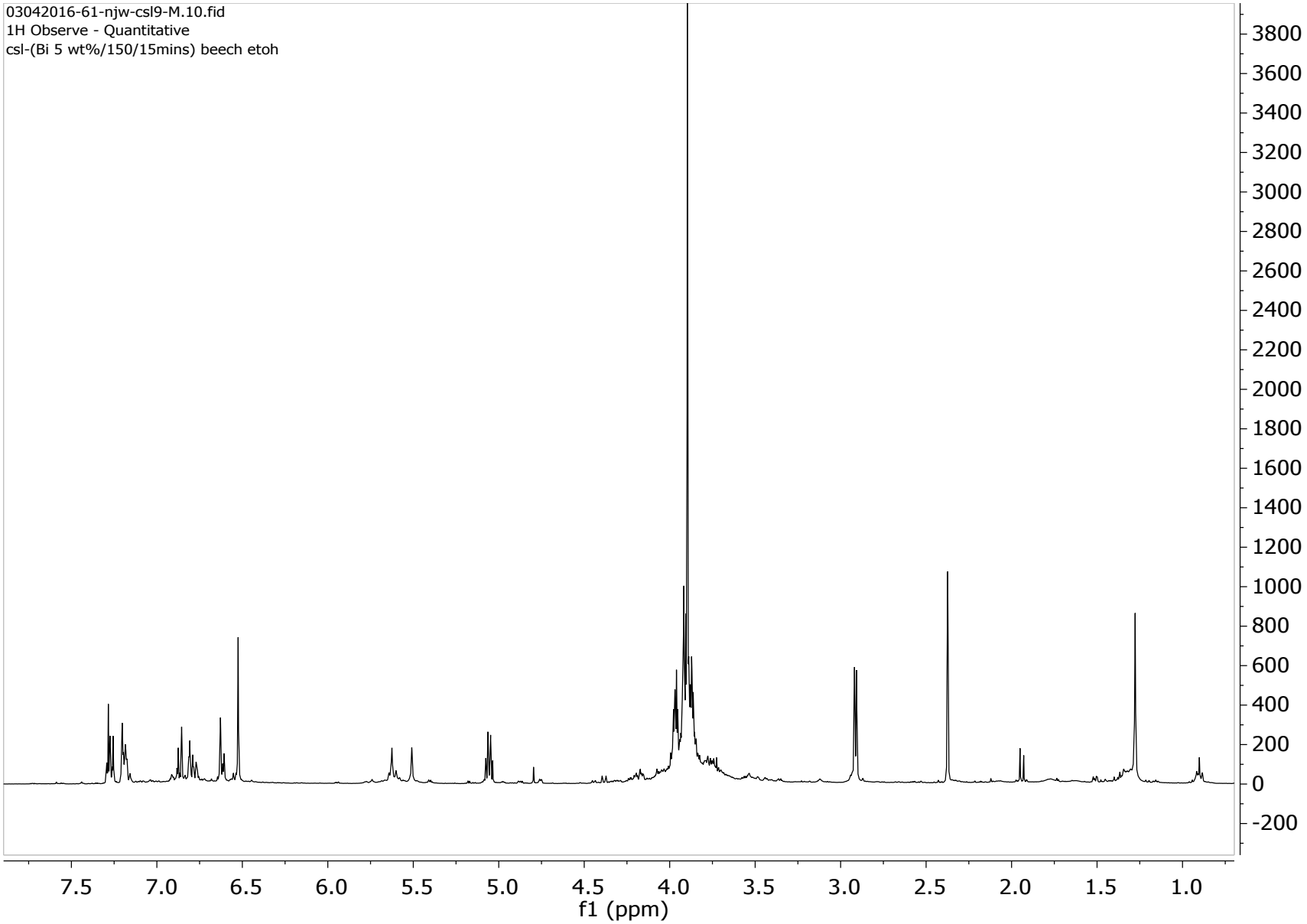
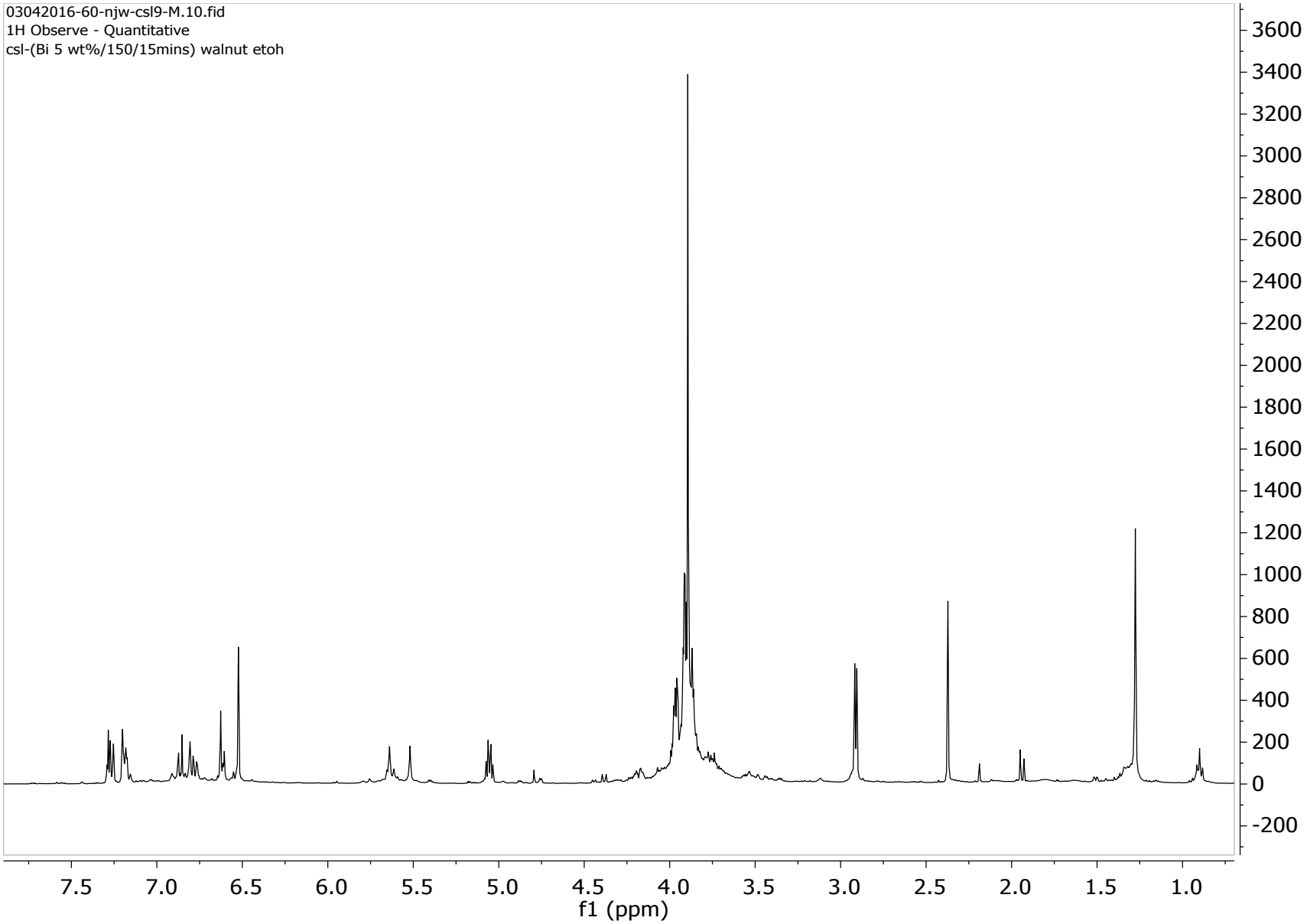
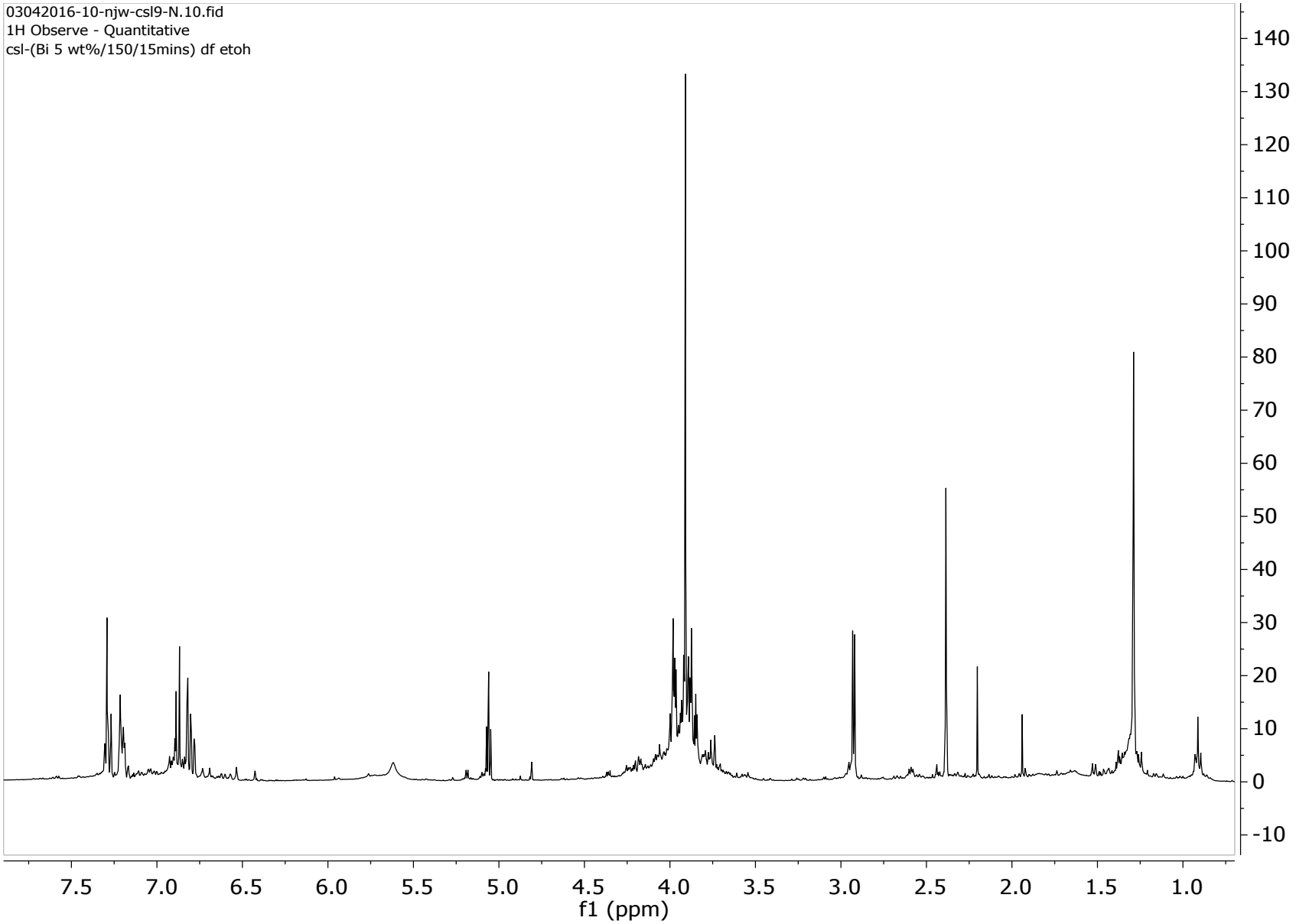
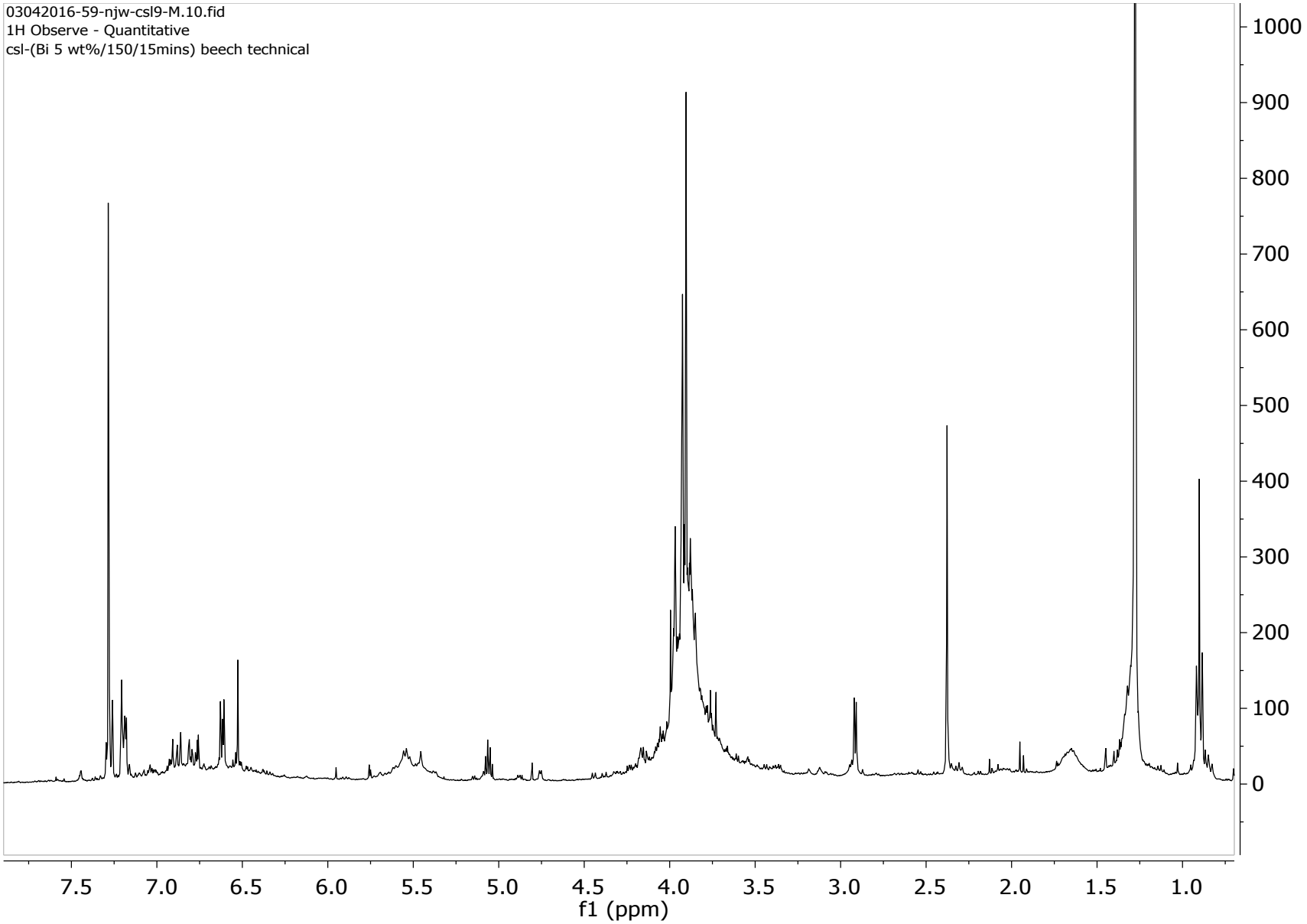
121.61
107.96
105.45
67.57
65.34
61.04
60.85
56.32
43.85
40.27
37.93
20.73
20.25
Br
S10
f1 (ppm)

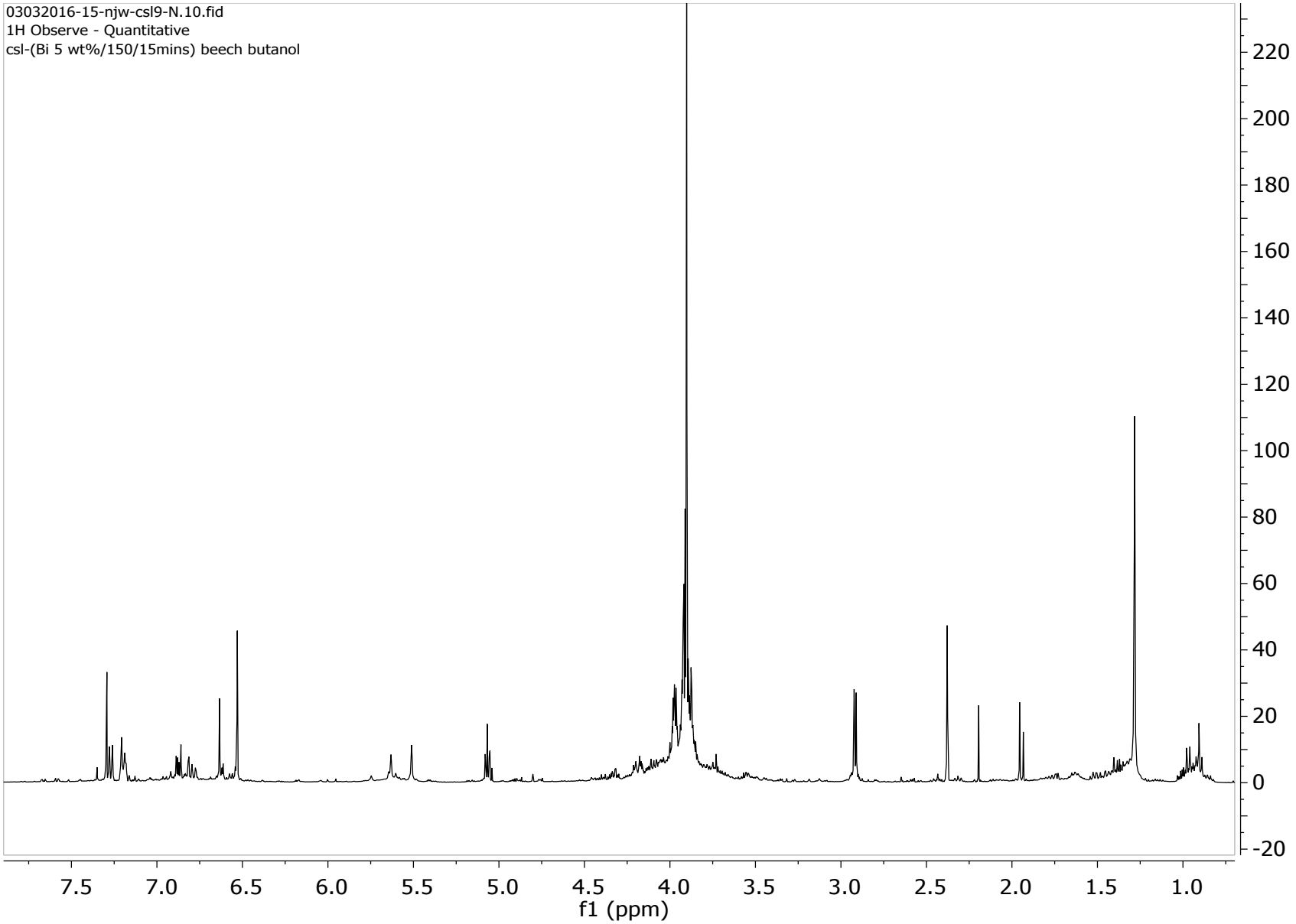
Lignin Depolymerisation NMR's

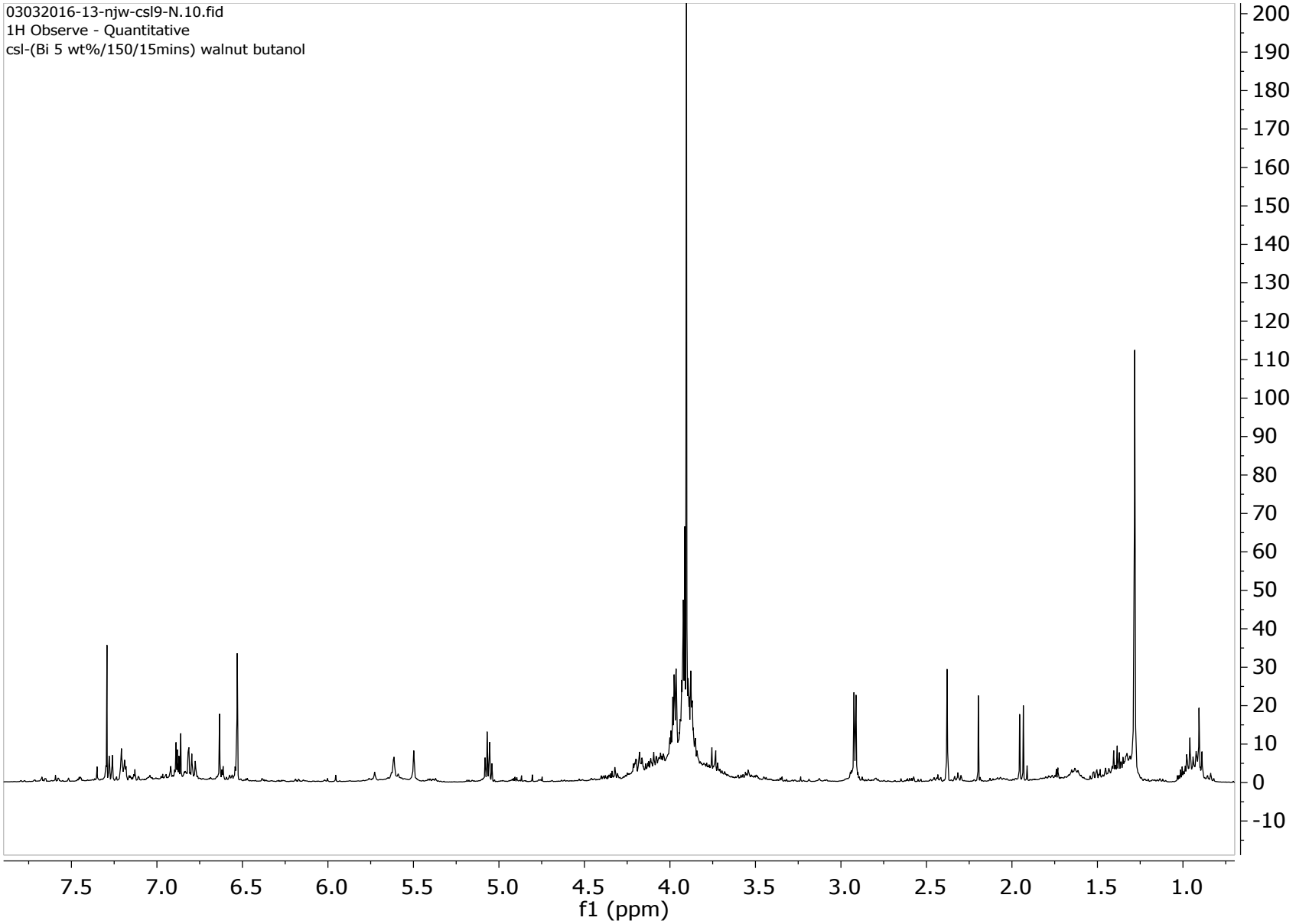

03042016-61-njw-csl9-M.10.fid
1H Observe - Quantitative
csl-(Bi 5 wt%/150/15mins) beech etoh
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

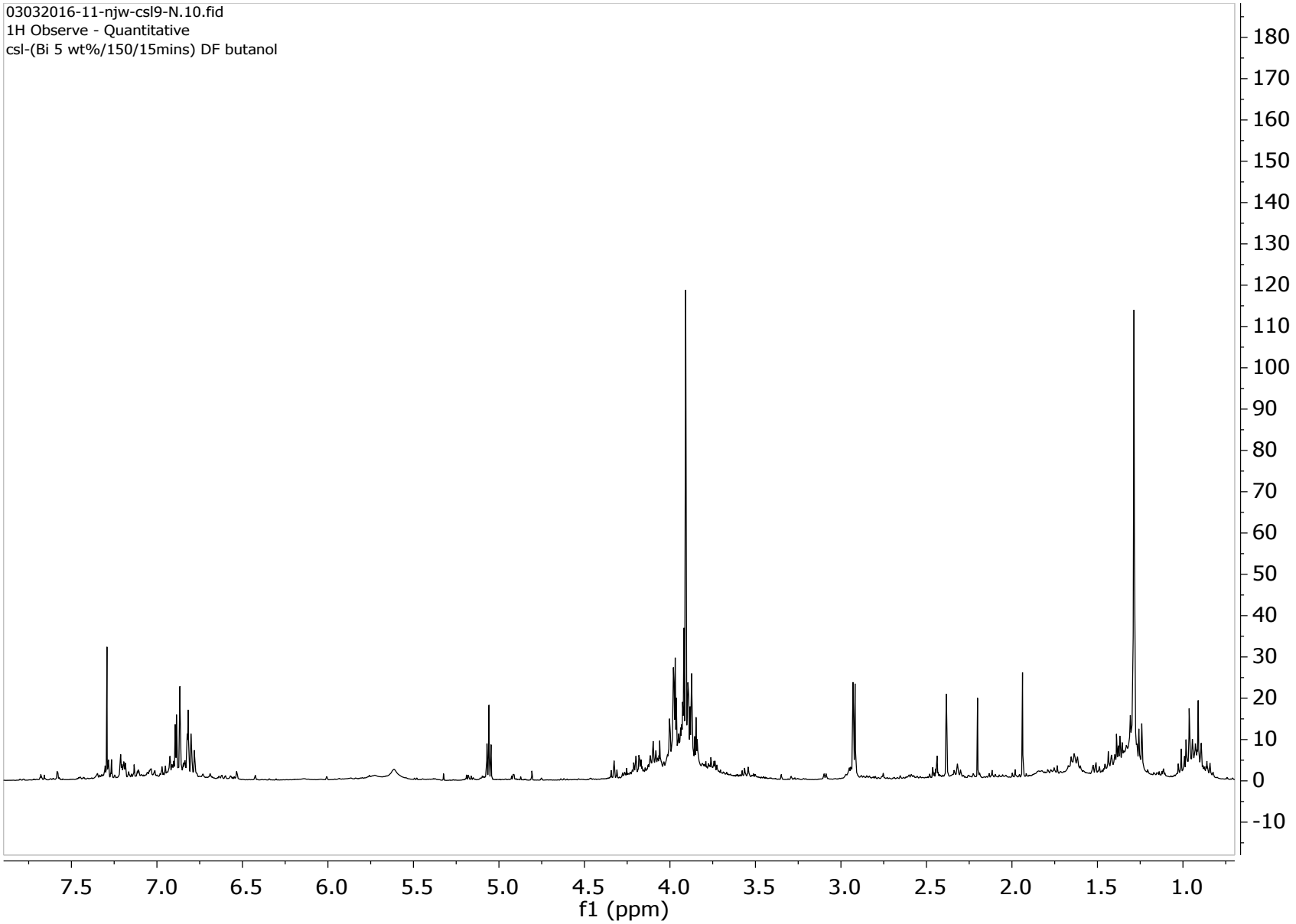

03042016-60-njw-csl9-M.10.fid
1H Observe - Quantitative
csl-(Bi 5 wt%/150/15mins) walnut etoh
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

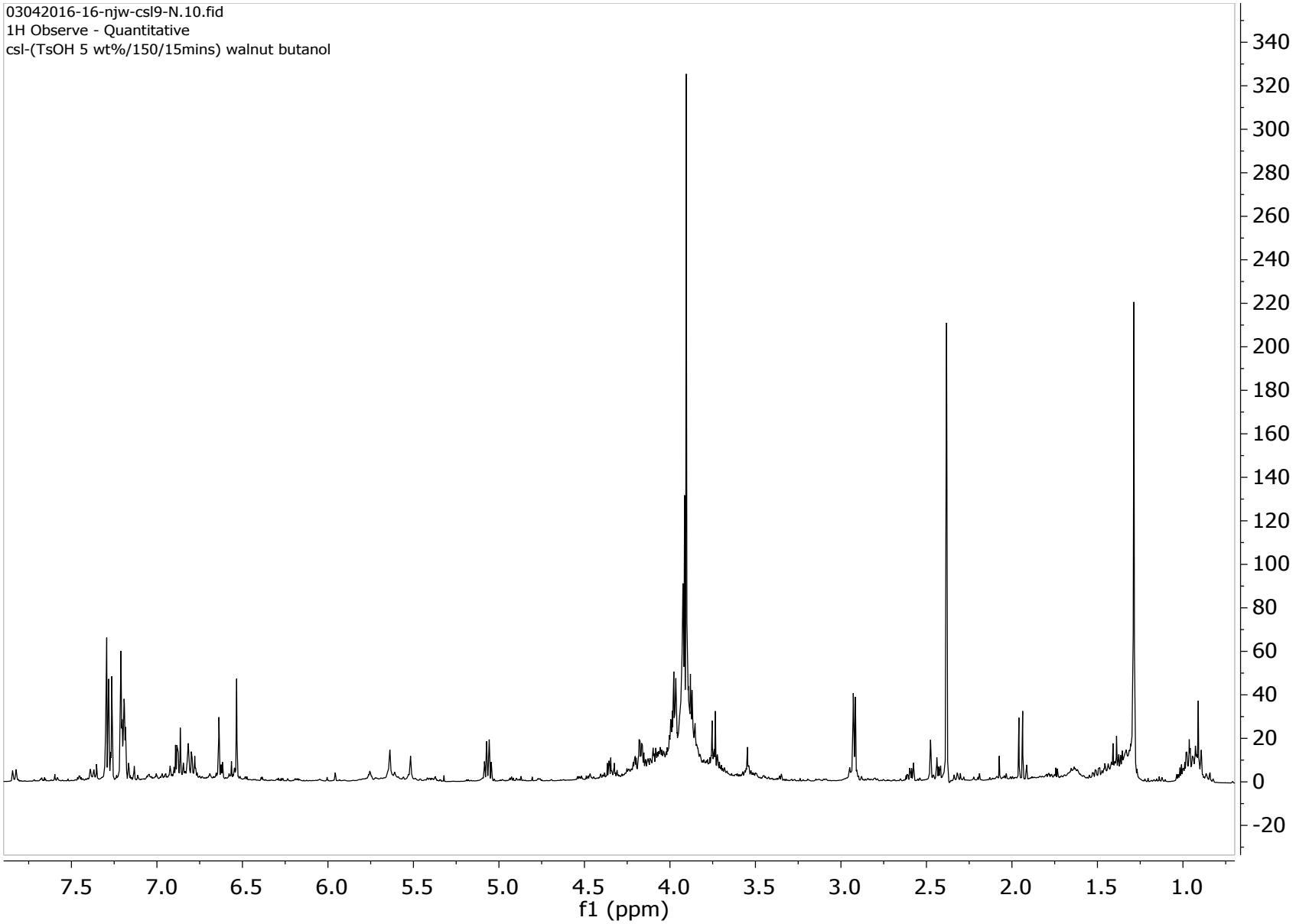

03042016-10-njw-csl9-N.10.fid
1H Observe - Quantitative
csl-(Bi 5 wt%/150/15mins) df etoh
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

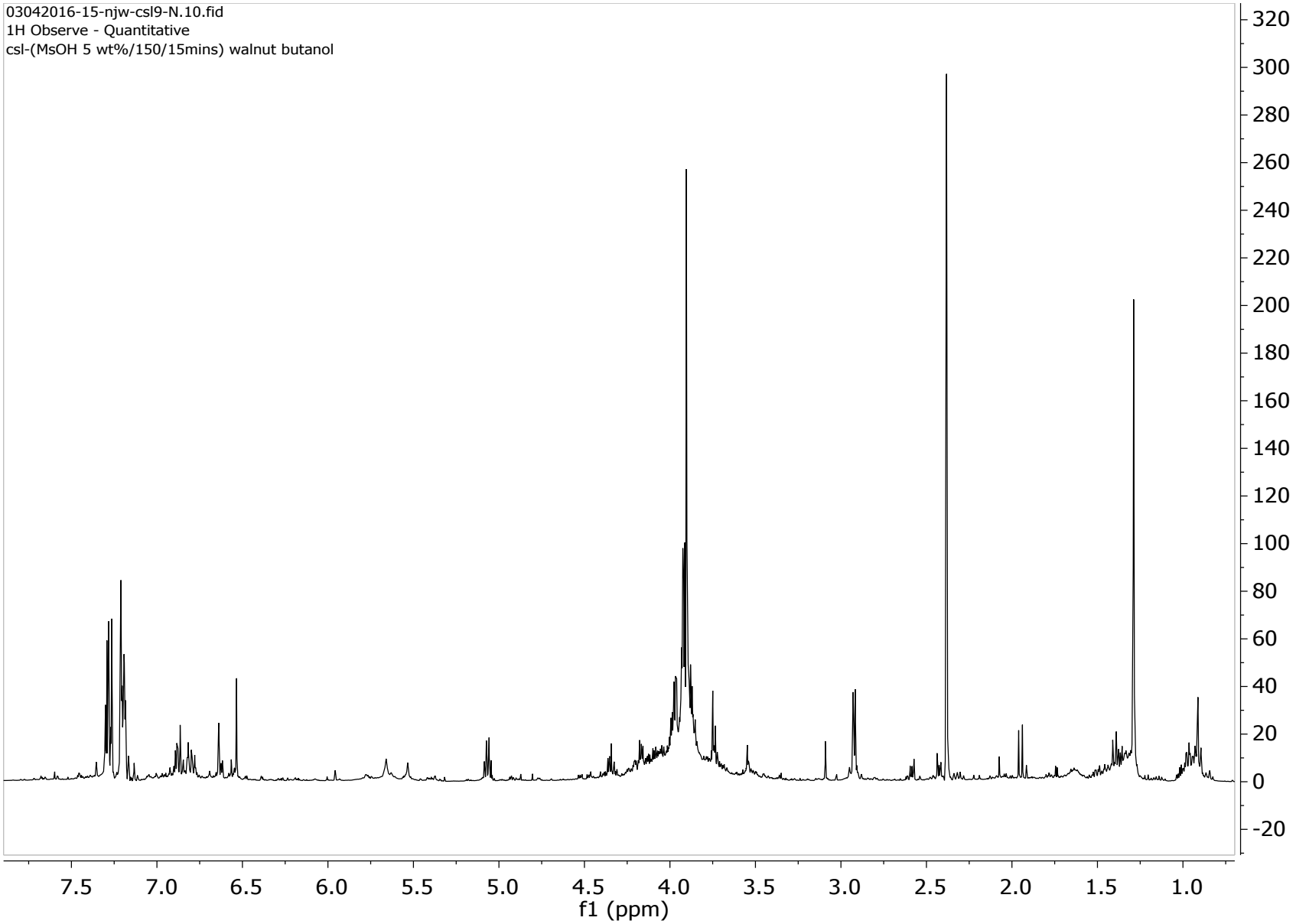

03042016-59-njw-csl9-M.10.fid
1H Observe - Quantitative
csl-(Bi 5 wt%/150/15mins) beech technical
1000
900
800
700
600
500
400
300
200
100
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


03032016-15-njw-csl9-N.10.fid
1H Observe - Quantitative
csl-(Bi 5 wt%/150/15mins) beech butanol
220
200
180
160
140
120
100
80
60
40
20
0
-20
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
f1 (ppm)

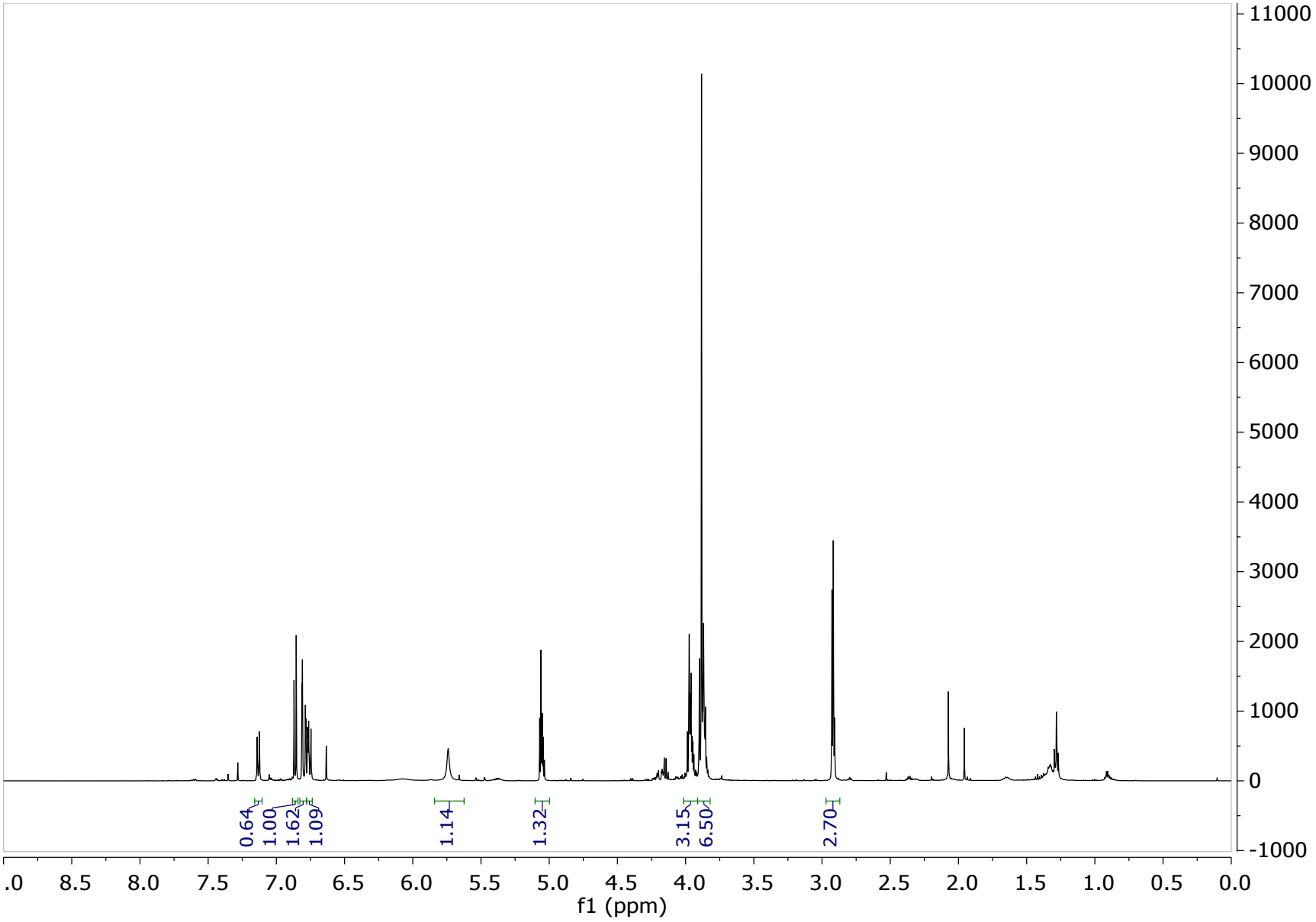

03032016-13-njw-csl9-N.10.fid
1H Observe - Quantitative
csl-(Bi 5 wt%/150/15mins) walnut butanol
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

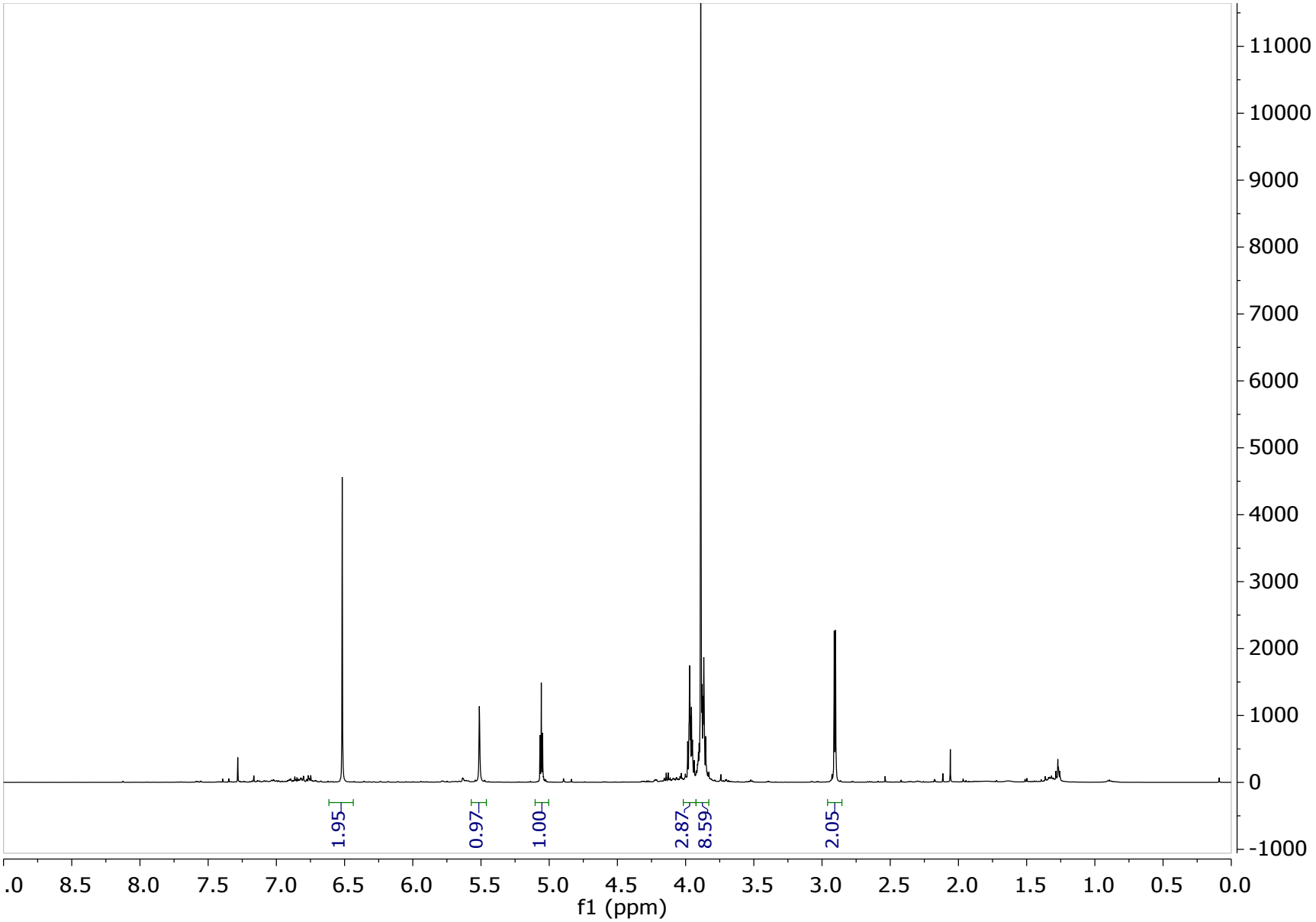

03032016-11-njw-csl9-N.10.fid
1H Observe - Quantitative
csl-(Bi 5 wt%/150/15mins) DF butanol
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


03042016-16-njw-csl9-N.10.fid
1H Observe - Quantitative
csl-(TsOH 5 wt%/150/15mins) walnut butanol
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
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
f1 (ppm)


03042016-15-njw-csl9-N.10.fid
1H Observe - Quantitative
csl-(MsOH 5 wt%/150/15mins) walnut butanol
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
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
f1 (ppm)

NMRs of Isolated Acetals


11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0.64
1.00
1.62
1.09
1.14
1.32
3.15
6.50
2.70
.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
f1 (ppm)


11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.95
0.97
1.00
2.87
8.59
2.05
.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
f1 (ppm)

References

S1. C. S. Lancefield, O. S. Ojo, F. Tran and N. J. Westwood, *Angewandte Chemie International Edition*, 2015, **54**, 258-262.

S2. C. S. Lancefield and N. J. Westwood, *Green Chem.*, 2015, **17**, 4980-4990.

S3. J. D. Nguyen, B. S. Matsuura and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2013, **136**, 1218-1221.

S4. N. Mori, H. Watanabe and T. Kitahara, *Synthesis*, 2006, **2006**, 400-404.

S5. J. Camponovo, C. Hadad, J. Ruiz, E. Cloutet, S. Gatard, J. Muzart, S. Bouquillon and D. Astruc, *The Journal of Organic Chemistry*, 2009, **74**, 5071-5074.

S6. S. Pearson, W. Scarano and M. H. Stenzel, *Chem. Commun. (Cambridge, U. K.)*, 2012, **48**, 4695-4697.

S7. F. Bouxin, S. Marinkovic, J. L. Bras and B. Estrine, *Carbohydr. Res.*, 2010, **345**, 2469-2473.

S8. M. Meldal, M. K. Christensen and K. Bock, *Carbohydr. Res.*, 1992, **235**, 115-127.