Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Chemical synthesis of uridine 5'-diphospho 2,3-diacetamido-2,3-dideoxy-D-glucuronic acid (UDP-Glc-2,3-diNAcA), a key intermediate in cell surface O antigen polysaccharide biosynthesis in the human respiratory pathogens *Bordetella pertussis* and *Pseudomonas aeruginosa*

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Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (5). *N*-Acetyl-α-D-glucosamine (**3**) (20.0 g, 90.4 mmol) was suspended in benzyl alcohol (140 mL) and the suspension was warmed to 95°C under stirring. A saturated solution of anhydrous HCl in benzyl alcohol (10 mL) was added. The suspended material dissolved and turned dark over 20 min. The solution was filtered through sintered glass into vigorously stirring diethyl ether (500 mL). The precipitated solid was removed by filtration, washed thoroughly with diethyl ether, air dried to give crude benzyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**4**)[1] (26.7 g) that was used without further purification. Fused zinc chloride (27.0 g) dried in an oven was added to a stirred mixture of the benzyl glycoside (**4**) in freshly distilled benzaldehyde (80 mL) and stirring was continued overnight at room temperature. The homogenous reaction mixture was then dispersed between ice – water and light petroleum. The solid that formed was filtered off, washed repeatedly with hexane and air dried. Recrystallisation gave **5** (32.2 g, 89 % over 2 steps) as elongated prisms. R_f = 0.10 (hexane / ethyl acetate 1:2); mp 263-265°C (1,4-dioxane / propan-2-ol) (lit.,[2] mp 263-264°C); $[\alpha]^{23}_D$ +118 (*c* 1.0, pyridine) (lit.,[2] $[\alpha]^{26}_D$ +120); δ_H (400 MHz; DMSO-d_6; referenced to solvent residual peak at 2.54 ppm) 8.07 (d, 1H, $^3J_{2,NH}$ = 7.6 Hz, NH), 7.49-7.34 (m, 10H, aromatic), 5.66 (s, 1H, C*H*Ph), 5.26 (d, 1H, $^3J_{3,OH}$ = 4.8 Hz, 3-OH), 4.83 (bs, 1H, H1), 4.74 (d, 1H, $^2J_{a,b}$ = 12.4 Hz, CH_aH$_b$Ph), 4.53 (d, 1H, $^2J_{a,b}$ = 12.4 Hz, CH$_a$$H_b$Ph), 4.22-4.17 (m, 1H, H6$_a$), 3.91-3.86 (m, 1H, H2), 3.79-3.75 (m, 3H, H3, H5, H6$_b$), 3.60-3.55 (m, 1H, H4), 1.89 (s, 3H, CH_3CONH); δ_C (100 MHz; DMSO-d_6, referenced to solvent peak at 40.45 ppm) 170.5 (s, 1C, CH$_3$*C*ONH), 138.7 (s, 2C, aromatic), 129.9, 129.2, 129.0, 128.6, 128.5, 127.4 (d, 10C, aromatic), 101.8 (d, 1C, *C*HPh), 97.9 (d, 1C, C1), 83.1 (d, 1C, C4), 69.5 (t, 1C, *C*H$_2$Ph), 69.0 (t, 1C, C6), 68.2 (d, 1C, C3), 63.8 (d, 1C, C5), 55.1 (d, 1C, C2), 23.5 (q, 1C, *C*H$_3$CONH); m/z (ESI$^+$) 422 ([M+Na]$^+$, 100%), 400 ([M+H]$^+$, 14.8%), 292 (14.8%), 126 (13.5%); m/z (ESI$^-$) 398 ([M-H]$^-$, 12.2%), 121 (100); HR-MS calcd for $C_{22}H_{26}NO_6$ [M+H]$^+$ 400.1755, found 400.1756. NMR spectra

(^{1}H in $CDCl_3$ and ^{13}C in DMSO-d_6) were in good agreement with literature[3] data. Assignment of the spectra differs from Kohlbau *et al*.[1] The situation was clarified with the aid of HSQC data.

Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside (7). To a stirred solution of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**5**) (12.6 g, 32.0 mmol) in pyridine (79 mL), was added methanesulfonyl chloride (6.3 mL, 82.0 mmol) under cooling to 0°C. The mixture was stored at 0°C for 16 h and poured into ice and water. The crystalline product was collected by filtration and washed with diethyl ether (20 mL). The crystals were dissolved in dichloromethane, aqueous layer was separated. The organic layer was dried over Na_2SO_4 and evaporated to give crude benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-methanesulfonyl-α-D-glucopyranoside (**6**) (14.8 g) that was used without further purification. The crude methanesulfonate **6** was dissolved in ethylene glycol monomethyl ether (methyl cellosolve) (176.0 mL) and water (9.3 mL), and sodium acetate (14.8 g, 180 mmol) was added. The solution was refluxed for 48 h. After cooling, the mixture was poured into water and the precipitated product was collected by filtration. The solid was dissolved in dichloromethane and the aqueous layer was separated. The organic layer was dried over $MgSO_4$ and evaporated. The solid was crystallised to give **7** (11.24 g, 89 % over 2 steps) as colourless needles. R_f = 0.20 (hexane / ethyl acetate 1:1); mp 204-206°C (MeOH) (lit.,[4] mp 203-206°C); $[\alpha]^{23}_D$ +116.8 (*c* 1.0, DMSO) (lit.,[4] $[\alpha]^{20}_D$ +118.5); δ_H (400 MHz; DMSO-d_6; referenced to solvent residual peak at 2.54 ppm) 7.91 (d, 1H, $^3J_{2,NH}$ = 8.8 Hz, NH), 7.51-7.33 (m, 10H, aromatic), 5.69 (s, 1H, C*H*Ph), 5.20 (bs, 1H, 3-OH), 4.76 (d, 1H, $^3J_{1,2}$ = 4.4 Hz, H1), 4.72 (d, 1H, $^2J_{a,b}$ = 12.8 Hz, CH_aH$_b$Ph), 4.53 (d, 1H, $^2J_{a,b}$ = 12.8 Hz, CH$_a$$H_b$Ph), 4.22-4.07 (m, 3H, H6$_a$, H5, H2), 4.02-3.96 (m, 1H, H3), 3.75-3.70 (m, 2H, H6$_b$, H4), 1.94 (s, 3H, CH_3CONH); δ_C (100 MHz; DMSO-d_6; referenced to solvent peak at 40.45 ppm) 170.1 (s, 1C, CH$_3$*C*ONH), 139.0 (s, 1C, aromatic), 138.8 (s, 1C, aromatic), 129.8, 129.1, 128.9,

128.7, 128.4, 127.4 (d, 10C, aromatic), 101.6 (d, 1C, *C*HPh), 97.4 (d, 1C, C1), 79.2 (d, 1C, C4), 69.9 (t, 1C, *C*H_2Ph), 69.3 (t, 1C, C6), 67.5 (d, 1C, C3), 58.3 (d, 1C, C5), 50.7 (d, 1C, C2), 23.4 (q, 1C, *C*H_3CONH); m/z (ESI^+) 422 ($[M+Na]^+$, 100%), 400 ($[M+H]^+$, 2.7), 292 (10.8), 149 (18.9); m/z (ESI^-) 398 ($[M-H]^-$, 100%), 147 (21.6); HR-MS calcd for $C_{22}H_{26}NO_6$ $[M+H]^+$ 400.1755, found 400.1759. The ^{1}H NMR spectrum (in $CDCl_3$) published by Jordaan *et al.*[5] is incomplete and assigned differently. The situation was clarified with the aid of HSQC data.

Benzyl 2-acetamido-3-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranoside (9). To a solution of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside (**7**) (10.0 g, 25.1 mmol) in pyridine (83.2 mL) was added methanesulfonyl chloride (6.6 mL, 85.5 mmol) with cooling to 0°C. The mixture was stored at 0°C overnight and then poured into ice and water. The mixture was extracted with chloroform (3 x 100 mL). The combined organic extracts were washed with 1 M H_2SO_4 (50 mL), dilute aqueous $NaHCO_3$ (50 mL), water (50 mL) and dried over $MgSO_4$. Evaporation gave crude benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-methanesulfonyl-α-D-allopyranoside (**8**) (11.2 g) that was used without further purification. The crude methanesulfonate (**8**) was dissolved in DMF (150 mL) and sodium azide (14.6 g, 224.0 mmol) and tetrabutylammonium hydrogen sulfate (TBAHS) (8.0 g, 23.5 mmol) were added.[6] The mixture was heated to 100°C for 20 h under vigorous stirring. The mixture was allowed to cool down and poured into water and ice (500 mL). The resulting solid was collected by filtration on sintered glass, washed with water (50 mL) and air dried. The solid was dissolved in chloroform and the solvent was evaporated under reduced pressure. The resulting solid was crystallised twice to give pure **9** (8.7 g, 82 % over 2 steps). R_f = 0.70 (hexane / ethyl acetate 1:2); ν_{max}(film)/cm^{-1} 2120 (azido group); mp 245.0-245.5°C (EtOH) (lit.,[4] mp 244-245°C); $[\alpha]^{23}_D$ +97.5 (*c* 1.0, DMSO) (lit.,[4] $[\alpha]^{20}_D$ +97.0); δ_H (400 MHz; $CDCl_3$; TMS) 7.50-7.26 (m, 10H, aromatic), 5.69 (d, 1H, $^3J_{2,NH}$

= 10.0 Hz, NH), 5.61 (s, 1H, C*H*Ph), 4.87 (d, 1H, $^{3}J_{1,2}$ = 3.6 Hz, H1), 4.74 (d, 1H, $^{2}J_{a,b}$ = 11.6 Hz, CH_aH$_b$Ph), 4.49 (d, 1H, $^{2}J_{a,b}$ = 11.6 Hz, CH$_a$$H_b$Ph), 4.30-4.24 (m, 2H, H6$_a$, H2), 3.95-3.90 (m, 1H, H3), 3.84-3.75 (m, 2H, H6$_b$, H5), 3.66 (t, $^{3}J_{3,4}$ = $^{3}J_{4,5}$ = 9.6 Hz, H4), 1.99 (s, 3H, CH_3CONH); δ_C (100 MHz; $CDCl_3$; TMS) 168.9 (s, 1C, CH$_3$*C*ONH), 135.7 (s, 1C, aromatic), 135.5 (s, 1C, aromatic), 128.1, 127.7, 127.5, 127.3, 127.2, 124.9 (d, 10C, aromatic), 100.4 (d, 1C, *C*HPh), 96.0 (d, 1C, C1), 79.5 (d, 1C, C4), 69.2 (t, 1C, *C*H$_2$Ph), 67.8 (t, 1C, C6), 62.3 (d, 1C, C3), 60.1 (d, 1C, C5), 50.4 (d, 1C, C2), 22.3 (q, 1C, *C*H$_3$CONH); m/z (ESI$^+$) 447 ([M+Na]$^+$, 29.7%), 425 ([M+H]$^+$, 13.5), 91 (100); m/z (ESI$^-$) 423 ([M-H]$^-$, 71.6%), 136 (100); HR-MS calcd for $C_{22}H_{24}N_4O_5Na$ [M+Na]$^+$ 447.1639, found 447.1642.

Benzyl 2,3-diacetamido-2,3-dideoxy-α-D-glucopyranoside (11). A solution of benzyl 2-acetamido-3-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranoside (**9**) (3.53 g, 8.3 mmol) in acetic acid 80% (176.0 mL) was heated to 90°C for 45 min. The solution was evaporated under reduced pressure and the remaining acetic acid was removed by co-evaporation with water to give crude benzyl 2-acetamido-3-azido-2,3-dideoxy-α-D-glucopyranoside (**10**) (2.78 g) that was used without further purification. The crude azide **10** was dissolved in MeOH (246 mL) and palladium, 10% on carbon (700 mg) was added. The mixture was hydrogenated for 1.5 h at 1 atm. The catalyst was removed by filtration through 2 filter papers and washed with MeOH, acetic anhydride (2.5 mL, 26.0 mmol) was added to the filtrate and the solution was evaporated under reduced pressure. The residue was re-crystallised to give pure **11** (2.46 g, 84 % over 2 steps). R_f = 0.54 (dichloromethane / methanol 5:1); mp 265.0-267.0°C (EtOH) (lit.,[4] mp 267-268°C); $[\alpha]^{23}_D$ +145.3 (*c* 1.0, DMSO) (lit.,[4] $[\alpha]^{20}_D$ +146.5); δ_H (400 MHz; DMSO-d_6; referenced to solvent residual peak at 2.54 ppm) 7.78 (d, 1H, $^{3}J_{3,NH}$ = 8.8 Hz, 3-NH), 7.54 (d, 1H, $^{3}J_{2,NH}$ = 8.8 Hz, 2-NH), 7.47-7.33 (m, 5H, aromatic), 5.04 (d, 1H, $^{3}J_{4,OH}$ = 14.8 Hz, 4-OH), 4.75-4.73 (m, 2H, H1,

C*H*$_a$H$_b$Ph), 4.65 (bt, 1H, $^3J_{6,OH}$ = 6.0 Hz, 6-OH), 4.49 (d, 1H, $^2J_{a,b}$ = 12.4 Hz, CH$_a$*H*$_b$Ph), 4.08-4.00 (m, 1H, H3), 3.87-3.82 (m, 1H, H2), 3.71-3.67 (m, 1H, H6$_a$), 3.60-3.52 (m, 2H, H5, H6$_b$), 3.36-3.29 (m, 1H, H4), 1.79 (s, 6H, 2 x C*H*$_3$CONH); δ_C (100 MHz; DMSO-d_6; referenced to solvent peak at 40.45 ppm) 171.3, 170.6 (s, 2C, 2 x CH$_3$*C*ONH), 138.8 (s, 1C, aromatic), 129.2, 128.8, 128.5 (d, 5C, aromatic), 96.4 (d, 1C, C1), 74.6 (d, 1C, C5), 69.2 (d, 1C, C4), 68.8 (t, 1C, *C*H$_2$Ph), 61.6 (t, 1C, C6), 53.2 (d, 1C, C2), 52.4 (d, 1C, C3), 23.9, 23.5 (q, 2C, 2 x *C*H$_3$CONH); m/z (ESI$^+$) 375 ([M+Na]$^+$, 100%), 353 ([M+H]$^+$, 12.2), 245 (20.3), 138 (62.2); m/z (ESI$^-$) 351 ([M-H]$^-$, 100%), 243 (82.4), 153 (91.9); HR-MS calcd for $C_{17}H_{25}N_2O_6$ [M+H]$^+$ 353.1707, found 353.1708.

2,3-Diacetamido-2,3-dideoxy-α,β-D-glucose (12). A solution of benzyl 2,3-diacetamido-2,3-dideoxy-α-D-glucopyranoside (**11**) (2.30 g, 6.5 mmol) in MeOH (50 mL) was hydrogenated with $Pd(OH)_2$ (20 wt. % Pd on carbon; 230 mg). After 24 h TLC showed incomplete conversion. The mixture was filtered and a new batch of the catalyst (230 mg) was added. After a further 24 h the conversion was complete (by TLC). The catalyst was removed by filtration through 2 filter papers and washed with MeOH. The filtrate was evaporated under reduced pressure and the residue was recrystallised by dissolving it in minimum EtOH and by adding a few drops of diethyl ether to induce turbidity. The crystallisation gave pure **12** (1.58 g, 92 %) as a 3.3:1 α / β equilibrium (by ^{13}C NMR). R_f = 0.15 (dichloromethane / methanol 5:1); mp 250.0-252.0°C (EtOH / Et_2O) (lit.,[4] mp 250-251°C); $[\alpha]^{23}_D$ -21.0 to -41.0 (*c* 1.0, DMSO) (lit.,[4] $[\alpha]^{20}_D$ -21.0 to –41.0); δ_H (400 MHz; D_2O, referenced to the methyl resonance of internal acetone at 2.22 ppm) 5.18 (d, $^3J_{1,2}$ = 2.4 Hz, H1$_\alpha$), 4.82 (d, H1$_\beta$ overlapping with HDO signal), 4.14 (t, $^3J_{3,4}$ = $^3J_{2,3}$ = 10.4 Hz, H3$_\alpha$), 3.98-3.89 (m, H2$_\alpha$, H5$_\alpha$, H3$_\beta$, H6$_\beta$), 3.86-3.76 (m, H6$_{\alpha,\beta}$), 3.74-3.63 (m, H2$_\beta$), 3.56-3.51 (m, H4 $_{\alpha,\beta}$, H5$_\beta$), 1.99, 1.98 (s, 2 x C*H*$_3$CONH); δ_C (100 MHz; D_2O; referenced to the methyl resonance of internal acetone at 30.89 ppm) 175.5, 174.9 (s, 2C, 2 x CH$_3$*C*ONH α anomer), δ 175.3, 175.0 (s, 2C, 2 x

CH_3CONH β anomer), 95.7 (d, 1C, $C1_\beta$), 91.0 (d, 1C, $C1_\alpha$), 77.8 (d, 1C, $C5_\beta$), 72.4 (d, 1C, $C5_\alpha$), 68.4 (d, 1C, $C4_\alpha$), 68.3 (d, 1C, $C4_\beta$), 61.4 (d, 1C, $C6_\beta$), 61.2 (t, 1C, $C6_\alpha$), 56.1 (d, 1C, $C3_\beta$), 55.7 (d, 1C, $C2_\beta$), 53.0 (d, 1C, $C2_\alpha$), 52.6 (d, 1C, $C3_\alpha$), 22.7, 22.4 (q, 4C, 4 x CH_3CONH); m/z (ESI^+) 285 ($[M+Na]^+$, 100%), 138 (25.7); m/z (ESI^-) 261 ($[M-H]^-$, 21.6%), 202 (13.5), 142 (100); HR-MS calcd for $C_{10}H_{18}N_2O_6Na$ $[M+H]^+$ 285.1057, found 285.1060. NMR spectra (^1H and ^{13}C in benzene-d_6 / DMSO-d_6 4:1[7] and ^1H and ^{13}C NMR in D_2O[8]) were in good agreement with literature data.

Table 1 ^{1}H NMR data for a series of UDP sugar nucleotides

UDP-α-D-sugar	H-5	H-6	H-1'	H-2'	H-3'	H-4'	H-5'a	H-5'b	H-1''	H-2''	H-3''	H-4''	H-5''	H-6''a	H-6''b	Acetyl
GlcNAc [9,a]	5.97 d $J_{5,6}$ 8.13	7.96 d	5.99 d $J_{1',2'}$ 4.46	~4.37	~4.37	~4.29 m	4.19 ddd $J_{5'a,P}$ 5.6 $J_{4,5'a}$ 3.1 $J_{5'a,5'b}$ 11.8	4.25 ddd $J_{5'b,P}$ 4.5 $J_{4,5'b}$ 2.6	5.52 dd $J_{1'',2''}$ 3.2 $J_{1'',P}$ 7.2	3.99 dt $J_{2'',3''}$ 10.3 $J_{2'',P}$ 3.0	3.81 dd $J_{3'',4''}$ 9.3	3.50 dd $J_{4'',5''}$ 10.1	3.93 ddd $J_{5'',6''a}$ 4.9 $J_{5'',6''b}$ 2.3	3.80 dd $J_{6''a,6''b}$ 12.5	3.87 dd	2.00 s
GlcNAc3N [9,10,a]	5.97 d $J_{5,6}$ 8.13	7.96 d	5.99 d $J_{1',2'}$ 4.36	~4.37	~4.37	~4.30 m	4.20 ddd $J_{5'a,P}$ 5.7 $J_{4,5'a}$ 3.2 $J_{5'a,5'b}$ 11.8	4.26 ddd $J_{5'b,P}$ 4.5 $J_{4,5'b}$ 2.6	5.54 dd $J_{1'',2''}$ 3.3 $J_{1'',P}$ 6.9	~4.21 dt[b] $J_{2'',3''}$ 9.8	3.39 m	3.67 m $J_{4'',5''}$ 10.0	3.97 ddd $J_{5'',6''a}$ 4.2 $J_{5'',6''b}$ 2.2	3.82 dd $J_{6''a,6''b}$ 12.6	3.88 dd	2.01 s
GlcNAcA [11,c]	5.96 d $J_{5,6}$ 8.2	7.95 d $J_{5,6}$ 8.2	5.98 d $J_{1',2'}$ 4.4	4.38-4.34 m	4.38-4.34 m	4.29-4.27 m	4.24-4.20 m	4.18-4.13 m	5.52 dd $J_{1'',2''}$ 3.2 $J_{1'',P\beta}$ 7.6	4.02 dt $J_{2'',3''}$ 10.6 $J_{1'',2''}$ 3.2 $J_{2'',P\beta}$ 3.0	3.81 dd $J_{3'',4''}$ 9.4 $J_{2'',3''}$ 10.6	3.58 dd $J_{3'',4''}$ 9.4 $J_{4'',5''}$ 10.5	4.16 d $J_{4'',5''}$ 10.5	-	-	2.03 s
Glc-2,3-diNAc [d]	5.94 d $J_{5,6}$ 8.2	7.93 d $J_{5,6}$ 8.2	6.00 d $J_{1',2'}$ 4.0	4.38-4.34 m	4.38-4.34 m	4.29-4.27 m	4.25-4.23 m	4.22-4.19 m	5.53 dd $J_{1'',2''}$ 3.2 $J_{1'',P\beta}$ 7.2	4.08 dt $J_{2'',3''}$ 11.2 $J_{1'',2''}$ 3.2 $J_{2'',P\beta}$ 2.8	4.12 dd $J_{3'',4''}$ 9.6 $J_{2'',3''}$ 11.2	3.62 dd $J_{3'',4''}$ 9.6 $J_{4'',5''}$ 10.0	3.98 ddd $J_{4'',5''}$ 10.0 $J_{5'',6''a}$ 4.0 $J_{5'',6''b}$ 2.4	3.81 dd $J_{6''a,6''b}$ 12.6 $J_{5'',6''a}$ 4.0	3.87 dd $J_{6''a,6''b}$ 12.6 $J_{5'',6''b}$ 2.4	2.04 s 2.09 s
Glc-2,3-diNAcA [12,e]	5.91 d $J_{5,6}$ 8.0	7.85 d $J_{5,6}$ 8.0	6.01 d $J_{1',2'}$ 4.4	4.37-4.33 m	4.37-4.33 m	4.28-4.20 m	4.19-4.16 m	4.28-4.20 m	5.56 dd $J_{1'',2''}$ 2.4 $J_{1'',P\beta}$ 7.2	4.16-4.12 m	4.19-4.16 m	3.65 dd $J_{3'',4''}$ 9.6 $J_{4'',5''}$ 9.6	4.28-4.20 m			2.03 s 2.09 s

[a] 600 MHz, D_2O, relative to internal 2,2-dimethylsilapentane-5-sulfonic acid, pD 7.8, 25°C, disodium salt. [b] Overlaps ribose H-5'a, coupling constant estimated from the resolved H-3'' signal. [c] 400 MHz, D_2O, relative to methyl resonance of internal acetone at δ_H 2.22 ppm, 25°C, triammonium salt. [d] 400 MHz, D_2O, referenced to the methyl resonance of internal acetone at 2.22 ppm, 25°C, diammonium salt. [e] 400 MHz, D_2O, referenced to the methyl resonance of internal acetone at 2.22 ppm, 25°C, triammonium salt.

Table 2 ^{13}C NMR data for a series of UDP sugar nucleotides

UDP-α-D-sugar	C-2	C-4	C-5	C-6	C-1'	C-2'	C-3'	C-4'	C-5'	C-1''	C-2''	C-3''	C-4''	C-5''	C-6''	Acetyl
GlcNAc [9,a]	154.5 s	168.9 s	105.2 d	144.2 d	91.0 d	76.3 d	72.0 d	85.8 dd $J_{C4',P}$ 9.08	67.5 dt $J_{C5',P}$ 5.88	97.0 dd $J_{C1'',P}$ 6.41	56.2 dd $J_{C2'',P}$ 8.54	73.5 d	72.2 d	75.5 d	62.9 t	24.6 q 177.3 s
GlcNAc3N [9,10,a, b]	~154.4	~168.9	~105.2	~144.2	~91.0	~76.3	~72.2	~85.7	~67.7	~96.4	~54.0	~56.4	~69.8	~75.4	~62.8	24.5 177.3
GlcNAcA [11,c]	152.5 s	167.0 s	103.3 d	142.3 d	89.0 d	74.4 d	70.3 d	83.9 dd $J_{C4',P\alpha}$ 9.2	65.7 td $J_{C5',P\alpha}$ 5.6	94.9 dd $J_{C1'',P\beta}$ 6.1	54.1 dd $J_{C2'',P\beta}$ 8.3	71.3 d	72.8 d	73.8 d	177.0 s	22.7 q 175.5 s
Glc-2,3-diNAc [d]	153.4 s	168.1 s	103.3 d	142.1 d	89.1 d	74.4 d	70.3 d	83.8 dd $J_{C4',P\alpha}$ 9.9	65.7 dt $J_{C5',P\alpha}$ 5.3	94.6 dd $J_{C1'',P\beta}$ 6.0	52.6 dd $J_{C2'',P\beta}$ 9.2	53.1 d	67.9 d	73.8 d	60.9 t	22.7 q 22.5 q 175.4 s 175.1 s
Glc-2,3-diNAcA [12,e]	156.2 s[f]	167.0 s[f]	103.5 d	141.6 d	89.1 d	74.3 d	70.3 d	83.5 dd $J_{C4',P\alpha}$ 9.3	65.8 dt $J_{C5',P\alpha}$ 5.5	94.3 dd $J_{C1'',P\beta}$ 5.6	52.3 dd $J_{C2'',P\beta}$ 8.8	52.6 d	70.6 d	74.0 d	176.7 s	22.7 q 22.5 q 175.5 s 175.1 s

[a] 150 MHz, D_2O, relative to internal 2,2-dimethylsilapentane-5-sulfonic acid, pD 7.8, 25°C, disodium salt. [b] Shift data estimated from heteronuclear multi-quantum correlation two-dimensional map at coarse digitisation. [c] 100 MHz, D_2O, relative to methyl resonance of internal acetone at δ_C 30.89 ppm, 25°C, triammonium salt. [d] 100 MHz, D_2O, referenced to the methyl resonance of internal acetone at 30.89 ppm, 25°C, diammonium salt. [e] 100 MHz, D_2O, referenced to the methyl resonance of internal acetone at 30.89 ppm, 25°C, triammonium salt. [f] C-2 or C-4 carbonyle was observed in equilibrium with its enol form at 159.8 ppm at basic pD.

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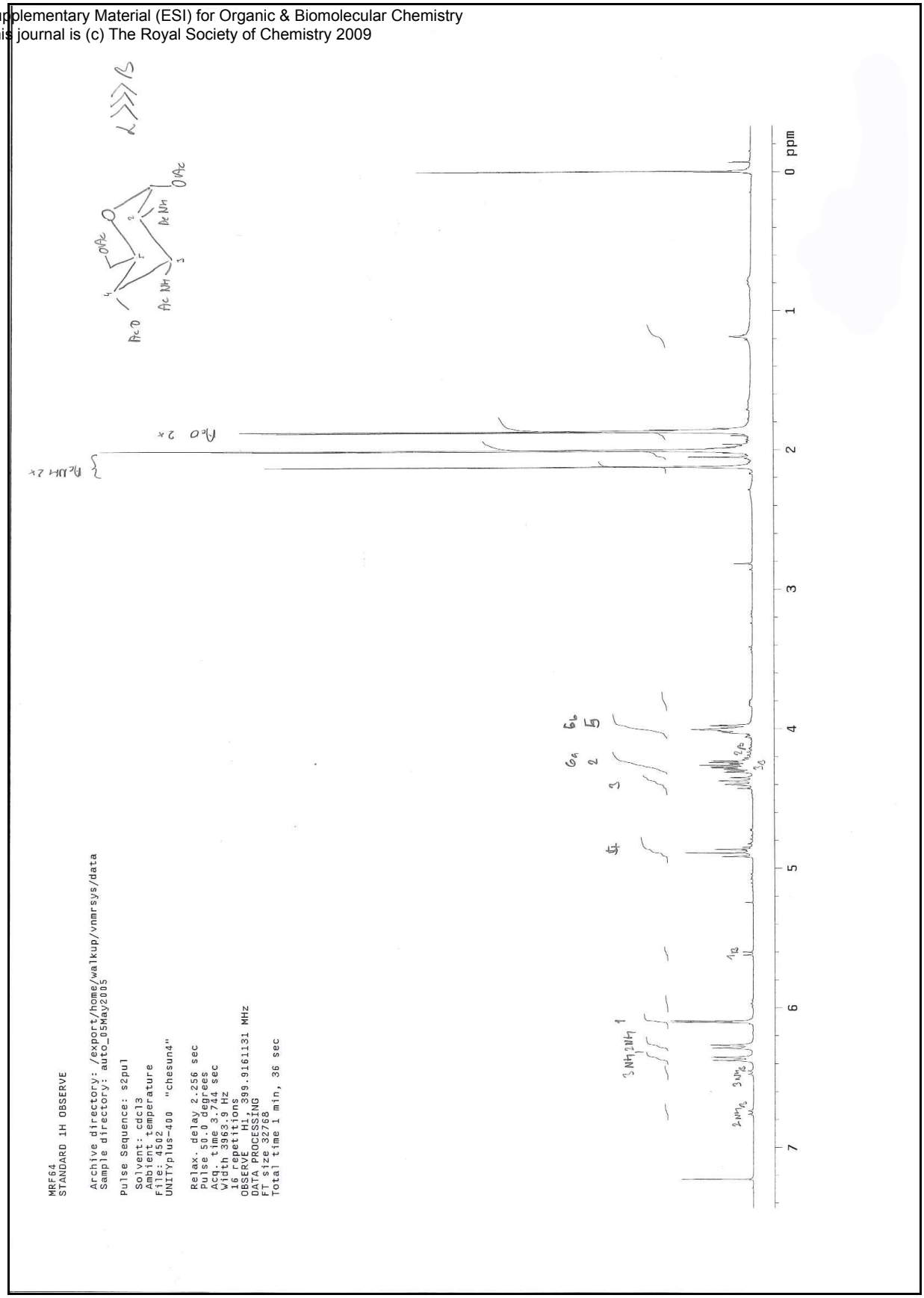
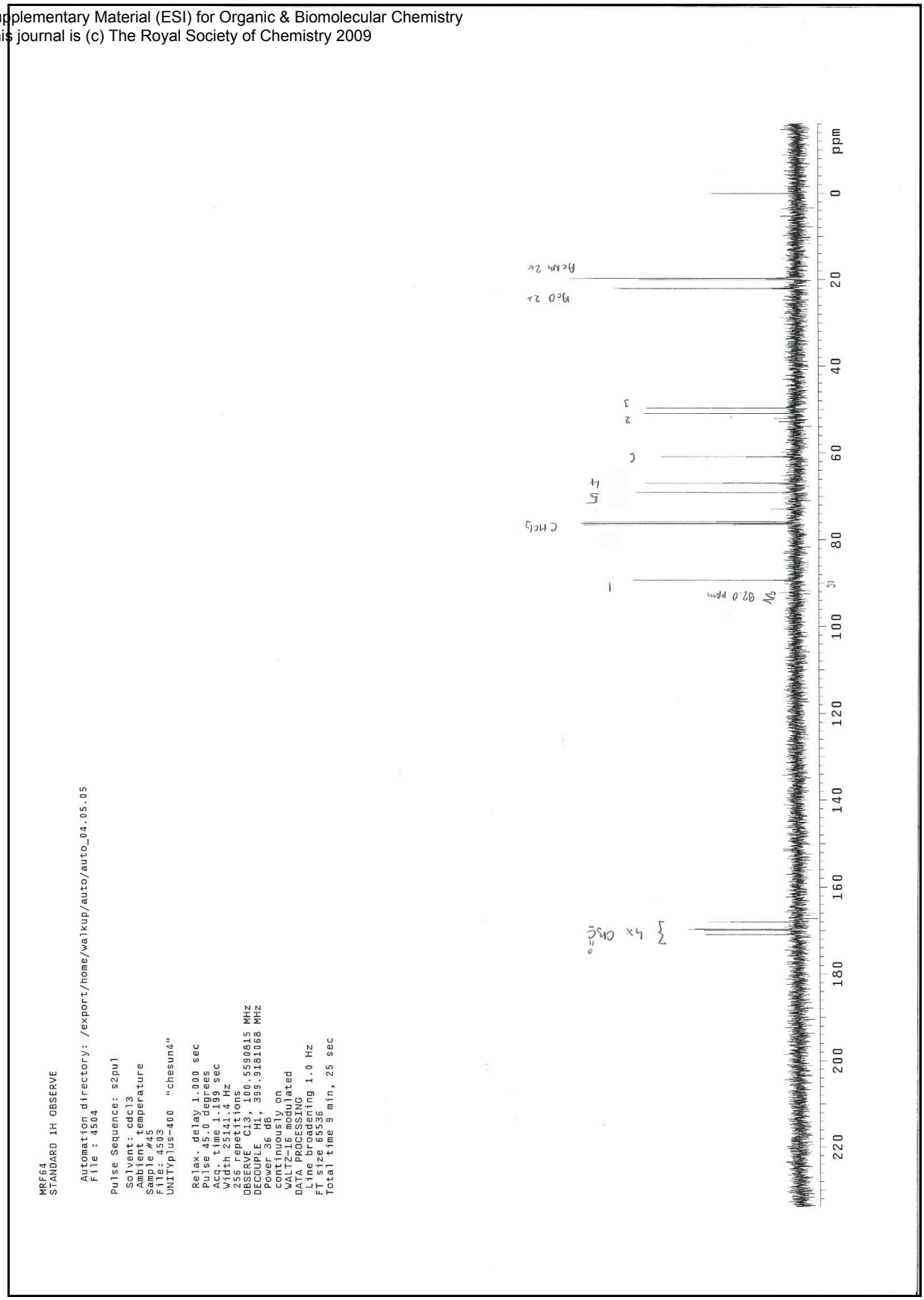
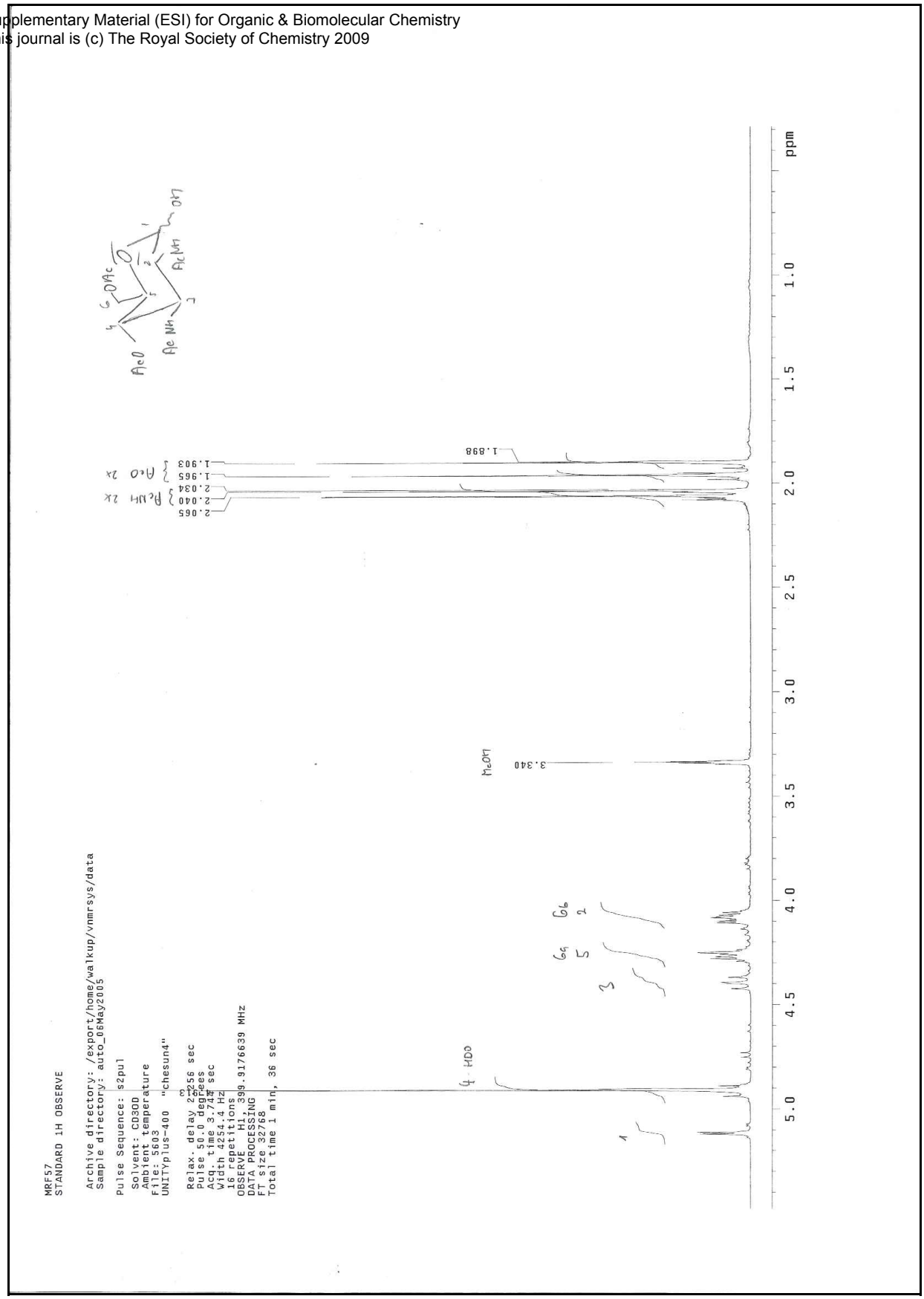
^{1}H NMR Spectrum of Compound **13**



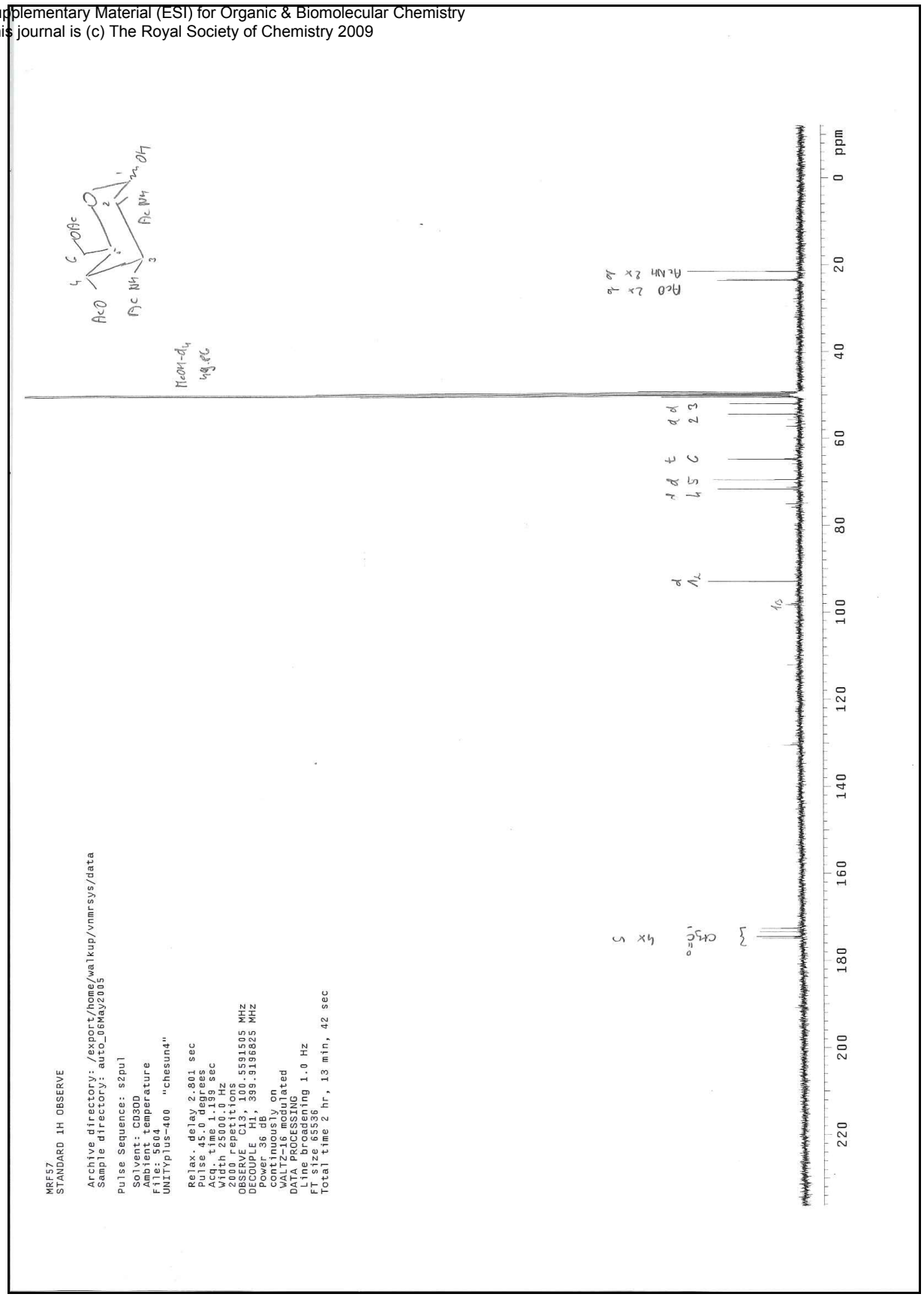
^{13}C NMR Spectrum of Compound **13**



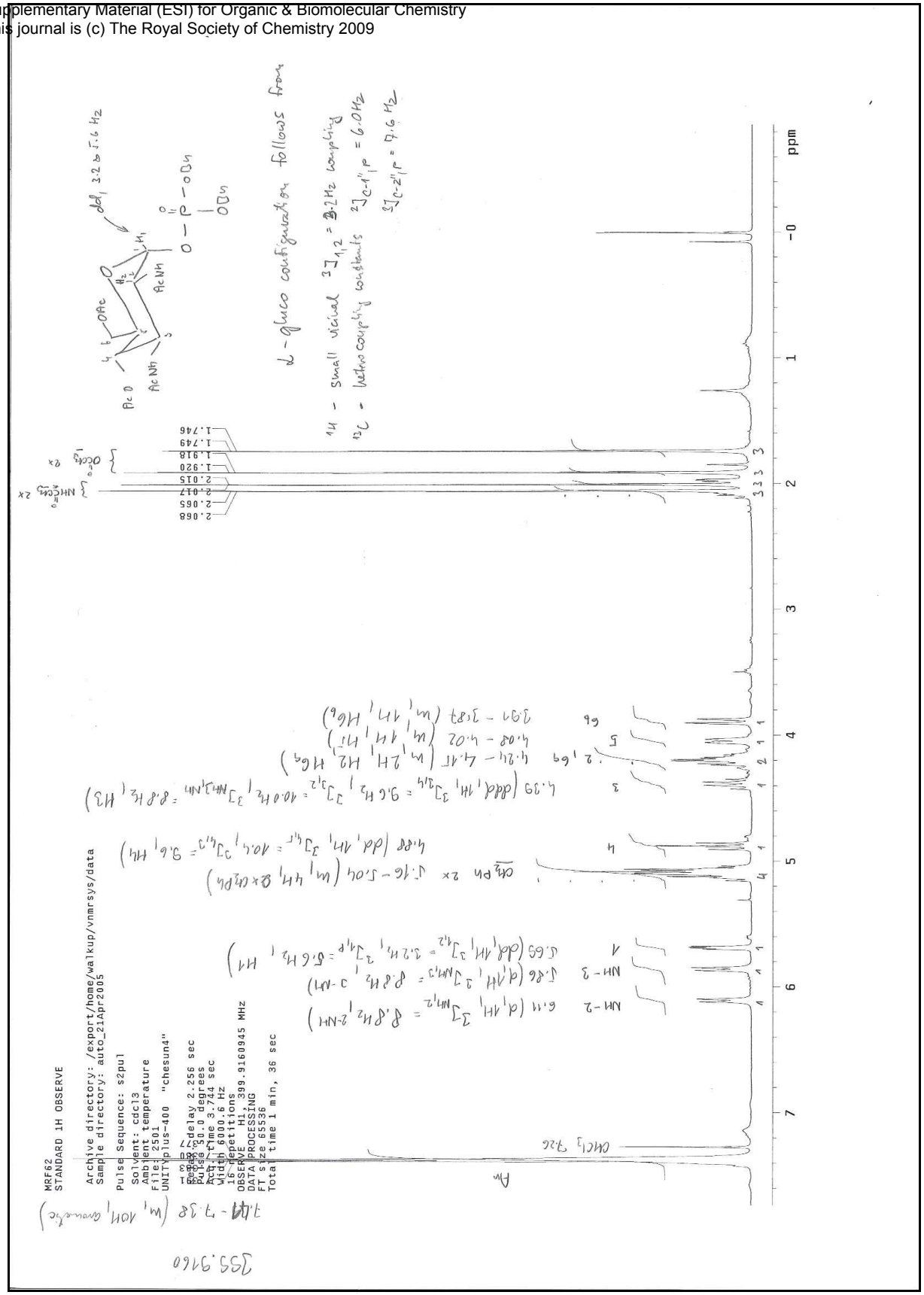
^{1}H NMR Spectrum of Compound **14**



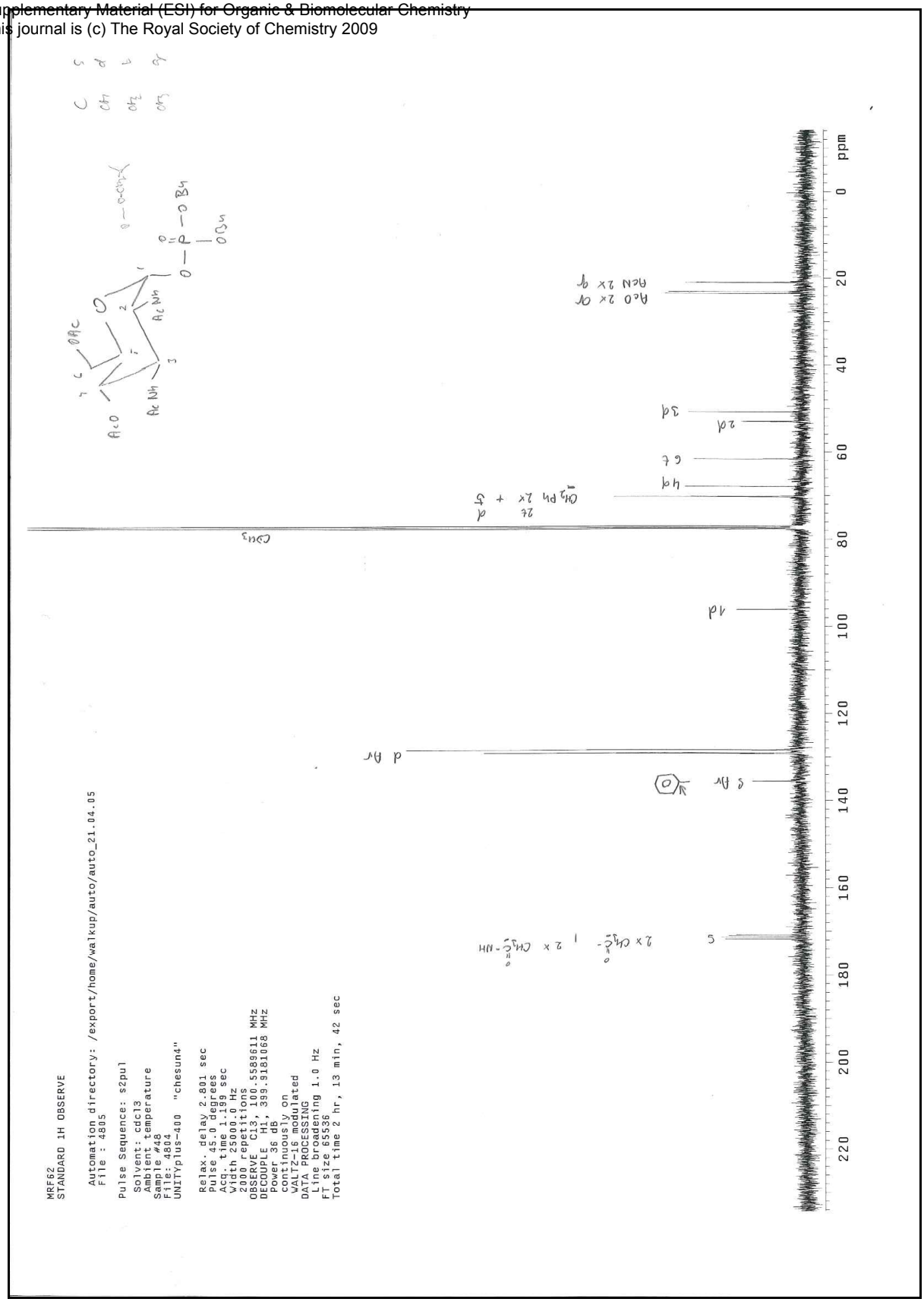
^{13}C NMR Spectrum of Compound **14**



^{1}H NMR Spectrum of Compound **15**



^{13}C NMR Spectrum of Compound **15**



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