Supplementary Material

Mechanistic Investigation of β-galactosidase-activated MR Contrast Agents

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Part 1. Experimental details and characterization of S-diastereomers and racemic mixtures.

S-(-)-2-bromopropan-1-ol (7b). The same procedure was used as described for **7a** beginning with 3.0 mL (5.09 g, 0.033 mol) of S-(-)-2-bromopropionic acid. Yield: 72% ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (d, 3H, C*H*$_3$CHBrCH$_2$OH, J = 8), 2.14-2.24 (s, 1H, CH$_3$CHBrCH$_2$O*H*), 3.60-3.82 (m, 2H, CH$_3$C*H*BrC*H*$_2$OH), 4.20-4.36 (m, 1H, CH$_3$CHBrC*H*$_2$OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 53.74, 68.90.

2-bromopropan-1-ol (7c). The same procedure was used as described for **7a** beginning with 10.0 ml (16.96 g, 0.111 mol) of 2-bromopropionic acid. Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52-1.62 (d, 3H, C*H*$_3$CHBrCH$_2$OH, J = 8), 3.1 (s, 1H, CH$_3$CHBrCH$_2$O*H*), 3.54-3.70 (m, 2H, CH$_3$C*H*BrC*H*$_2$OH), 4.02-4.15 (m, 1H, CH$_3$CHBrC*H*$_2$OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.23, 52.73, 67.42.

S-(-)-2-bromopropan-1-β-D-galactose tetraacetate (8b). The S-diastereomer was synthesized by the same procedure described for **8a** beginning with 0.2820 g (0.0020 mol) **7b** in a 74.4% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66-1.67 (d, 3H, methyl, J = 6.5), 1.99-2.16 (m, 12H, OAc), 3.65-3.69 (m, 2H, CH$_3$CHBrC*H*$_2$O-sugar), 3.90-3.93 (m, 1H, CH$_3$C*H*BrCH$_2$O-sugar), 4.00-4.03 (m, 2H, H-6), 4.11-4.20 (m, 1H, H-4), 4.53-4.55 (m, 1H, H-5), 5.02-5.05 (m, 1H, H-3), 5.22-5.26 (m, 2H, H-2), 5.40-5.40 (m, 1H, H-1). ^{13}C NMR (125 MHz) δ 20.87, 20.95, 21.14, 22.69, 46.15, 61.44, 67.14, 68.80, 70.91, 70.97, 75.14, 101.91, 170.28, 170.36, 170.54. ESI-MS *m/z* = 492.8 (M + Na$^+$).

2-bromopropan-1-β-D-galactose tetraacetate (8c). The racemic mixture of **8** was synthesized by the same procedure as for **8a** beginning with 6.46 g (0.046 mol) **7c** in a yield of 70%. ^{1}H NMR (400 MHz) δ 1.62-1.76 (d, 3H, methyl, J = 6.5), 1.88-2.18 (m, 12H, OAc), 3.60-3.68 (m, 2H, CH$_3$CHBrC*H*$_2$O-sugar), 3.86-3.92 (m, 1H, CH$_3$C*H*BrCH$_2$O-sugar), 4.16-4.22 (m, 3H, H-5 and H-6), 4.52-4.58 (m, 1H, H-4), 5.0-5.18 (m, 1H, H-2), 5.20-5.28 (m, 1H, H-3), 5.39 (m, 1H, H-1). ^{13}C NMR (100 MHz) δ 20.49, 20.57, 20.78, 20.94, 22.19, 22.37, 45.95, 46.34, 60.27, 61.19, 66.96, 68.53, 68.60, 70.67, 74.84, 75.07, 101.31, 101.60, 169.36, 169.99, 170.14, 170.26. ESI-MS *m/z* = 492.8 (M+Na$^+$).

S-(-)-(2-(1,4,7,10-tetraazacyclododecyl)propan)-1-β-D-galactose tetraacetate (9b). Synthesized **9b** according to the procedure for **9a** beginning with 1.8441 g (0.00393 mol) of **8a**. ^{1}H NMR (400 MHz, CD_3CN) δ 0.78-0.84 (d, 3H, methyl, J = 6.0), 1.85-2.22 (m, 12H, OAc), 2.74-3.35(br, 16H, cyclen), 3.92-4.08 (m, 2H, methylene on linker), 4.16-4.2

(m, 1H, methine on linker), 4.38-4.42 (m, 3H, H-5 and H-6), 4.72 (m, d, 1H, H-4), 4.98-5.08 (m, 1H, H-2), 5.10-5.18 (m, 1H, H-3), 5.40 (m 1H, H-1). ^{13}C NMR (125 MHz, CD_3CN) δ 7.92, 20.15, 20.30, 20.37, 20.40, 53.41, 61.52, 67.47, 68.76, 70.56, 72.04, 73.49. 104.5, 170.02, 170.75, 170.79, 171.28. ESI-MS *m/z* = 561.3 ($M + H^+$).

(2-(1,4,7,10-tetraazacyclododecyl)propan)-1-β-D-galactose tetraacetate (9c): Compound **9c** was synthesized using the procedure described for **9a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82-0.98 (d, 3H, methyl, J = 6.0), 1.95-2.18(m, 12H, OAc), 2.8-3.42 (br, 16H, cyclen), 3.80-4.1 (m, 3H, methylene and methine on linker), 4.18-4.22 (m, 2H, H-6), 4.48 (d, 1H, H-4), 4.96-4.98 (m, 1H, H-5), 5.0-5.06 (m, 1H, H-3), 5.40 (m, 2H, H-2 and H-1). ^{13}C NMR (125 MHz, CD_3CN) δ 7.85, 8.20, 20.09, 20.21, 20.34, 53.11, 53.43, 61.29, 61.52, 67.47, 67.66, 68.77, 69.09, 70.31, 70.56, 70.89, 71.55, 72.07, 101.5, 104.5, 170.02, 170.26, 170.55, 171.27, 171.49. ESI-MS *m/z* = 561.2 ($M + H^+$).

(S)-(-)-(2-(4,7,10-trismethylcarboxymethyl-(1,4,7,10-tetraazacyclododecyl))propan)-1-β-D-galactose tetraacetate (10b). The S-diastereomer **10b**, was synthesized according to the procedure for **10a** beginning with 1.1828 g of **9b**. The yield was calculated over last two reactions beginning with **8a**: 25%. ^{1}H NMR (500 MHz, CD_3CN) δ 1.3 (d, 3H, methyl, J = 6), 1.98-2.2 (m, 12H, OAc), 2.3-3.6 (m, 16H, cyclen), 3.8-3.98 (m, 9H, $-OCH_3$), 4.0-4.15 (m, 5H, methylene and methine on linker and H-6), 4.55-4.80 (br, 3H, H-5, H-4, and H-3), 5.1 (s, 1H, H-2), 5.4 (s, 1H, H-1). ^{13}C NMR (CD_3CN, 125 MHz) δ 20.72, 20.76, 20.90, 54.40, 60.33, 67.32, 68.72, 70.25, 71.43, 71.54, 101.24, 169.46, 169.93, 170.75, 171.48. ESI-MS: *m/z* = 777.6 ($M + H^+$), 799.5 ($M + Na^+$).

(2-(4,7,10-trismethylcarboxymethyl-(1,4,7,10-tetraazacyclododecyl))propan)-1-β-D-galactose tetraacetate (10c). The racemic mixture was synthesized according to procedure described for **10a** beginning with 1.0148 g of **9c**. Yield was calculated over the last two reactions beginning with **8c**: 37%. ^{1}H NMR (500 MHz, CD_3CN) δ 1.2-1.3 (d, 3H, methyl, J = 6.0), 1.9-2.2 (m, 12H, OAc), 2.4-3.6 (br, 16H, cyclen), 3.65-3.8 (m, 9H, $-OCH_3$), 3.9-4.2 (br, methylene and methine on linker and H-6), 4.6 (m, 1H, H-4), 4.7 (m, 1H, H-5), 5.0-5.2 (m, 1H, H-3), 5.4 (m, 1H, H-2), 5.5 (s, 1H, H-1). ^{13}C NMR (125 MHz, CD_3CN) δ 20.05, 20.10, 20.20, 20.35, 20.38, 51.17, 51.41, 51.46, 52.18, 52.28, 52.38, 52.52, 55.12, 55.57, 55.67, 61.49, 61.55, 67.55, 67.62, 68.95, 69.06, 69.14, 70.68, 70.80, 70.96, 71.13, 100.48, 101.24, 170.05, 170.48, 171.30, 171.51, 171.57, 174.33, 174.76, 175.15. ESI-MS: *m/z* = 777.2 ($M + H^+$), 799.2 ($M + Na^+$).

Kinetic resolution of S-(-)-propylene oxide (11b). Propylene oxide was kinetically resolved as described above beginning with 5 mL (4.15 g, 0.071 mol) of propylene oxide and 0.008 eq. of (S,S)-(+)-N,N'-bis (3,5-di-tertbutylsalicylidene)-1,2-cyclohexane diaminocobalt(II). (S)-propylene oxide was obtained after distillation in 23% yield (vapor temperature = 33 ^{o}C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26-1.34 (d, 3H, methyl, J = 5), 2.42-2.46 (m, 1H, methylene), 2.74-2.78 (m, 1H, methylene), 2.96-3.00 (m, 1H, methine). ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.12, 48.16, 48.39.

S-(-)-1-bromopropan-2-ol (12b). The S-diastereomer was synthesized using the procedure described for **12a** beginning with 8 mL (6.63 g, 0.11 mol) of **11b**. Yield: 57%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28-1.36 (d, 3H, methyl, J = 6.0), 1.88 (br, 1H, -O*H*), 3.34-3.40 (m, 1H, methylene), 3.48-3.04 (m, 1H, methylene), 3.96-4.02 (m, 1H, methine). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.22, 41.50, 68.11.

1-bromopropan-2-ol (12c). The racemic mixture of **12** was synthesized according to the procedure described for **12a** beginning with 10 mL (8.29 g, 0.14 mol) of **11c**. Yield: 76%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25-1.32 (d, 3H, methyl, J = 6.0), 1.85 (br, 1H, -O*H*), 3.32-3.38 (m, 1H, methylene), 3.45-3.51 (m, 1H, methylene), 3.94-4.02 (m, 1H, methine). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.23, 41.51, 68.11.

S-(-)-1-bromopropan-2-β-D-galactose tetraacetate (13b). The S-diastereomer was synthesized using the procedure described for **13a** beginning with 4.3867 g (0.0315 mol) of **12b** and 10.1832 g (0.026 mol) of β-D-galactosepentaacetate. Single crystals of compound **13b** were obtained from a solution of ether/pet. ether, methanol, and ethyl acetate. Yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30-1.38 (d, 3H, methyl, J = 6.5), 1.98-2.40 (m, 12H, OAc), 3.28-3.36 (m, 2H, -CH_2Br), 3.86-3.98 (m, 2H, methine on linker and H-5), 4.05-4.20 (m, 2H, H-6), 4.55-4.64 (m, 1H, H-4), 4.96-5.02 (m, 1H, H-3), 5.18-5.24 (m, 1H, H-2), 5.38 (m, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.85, 20.94, 21.01, 21.28, 36.23, 61.18, 67.13, 68.86, 70.79, 70.98, 76.98, 101.67, 168.57, 176.13, 170.27, 170.37. ESI-MS: *m/z* = 493.0 ($M + Na^+$), 509.2 ($M + K^+$).

1-bromo-propan-2-β-D-galactose tetraacetate (13c). The racemic mixture was synthesized using the procedure described for **13a** beginning with 5.2619 g (0.038 mol) of **12c** and 12.2332 g (0.031 mol) of β-D-galactosepentaacetate. Yield: 45%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33-1.38 (d, 3H, methyl, J = 6.5), 1.92-2.20 (m, 12H, OAc), 3.32-3.40 (m, 1H, -CH_2Br), 3.42-3.48 (m, 1H, -CH_2Br), 3.88-3.98 (m, 2H, methine on linker and H-5), 4.12-4.20 (m, 2H, H-6), 4.50-4.58 (m, 1H, H-4), 4.98-5.10 (m, 1H, H-3), 5.28-5.40 (m, 2H, H-1 and H-2). ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.92, 20.55, 20.89, 20.92, 20.98, 36.18, 36.52, 61.54, 62.09, 62.14, 66.77, 67.17, 67.66, 67.71, 68.22, 68.30, 68.39, 68.47, 70.87, 71.03, 75.00, 75.37, 95.25, 96.70, 170.46, 170.67, 170.69, 170.88. ESI-MS: *m/z* = 493.1 ($M + Na^+$), 509.1 ($M + K^+$).

S-(-)-1-(1,4,7,10-tetraazacyclododecyl)propan-2-β-D-galactose tetraacetate (14b). The S-diastereomer was synthesized using the method described for **14a** beginning with 3.1863 g (0.0068 mol) of **13b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08-1.18 (d, 3H, methyl, J = 6.5), 1.95-2.28 (m, 12H, OAc), 2.70 (s, 2H, methylene on linker), 2.90-3.50 (br, 16H, cyclen), 3.90-4.02 (m, 1H, methine on linker), 4.16-4.24 (m, 1H, H-5), 4.25-4.36 (m, 2H, H-6), 4.62-4.68 (m, 1H, H-4), 4.90-4.98 (m, 1H, H-3), 5.02-5.12 (m, 1H, H-2), 5.42 (m, 1H, H-1). ESI-MS: *m/z* = 561.2 ($M + H^+$).

1-(1,4,7,10-tetraazacyclododecyl)propan-2-β-D-galactose tetraacetate (14c). The racemic mixture was synthesized according to the method described for **14a** beginning with 3.5534 g (0.0076 mol) of **13c.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08-1.16 (d, 3H, methyl, J = 6.5), 1.95-2.30 (m, 12H, OAc), 2.70 (s, 2H, methylene on linker), 2.92-3.52 (br, 16H, cyclen), 3.90-4.02 (m, 1H, methine on linker), 4.18-4.28 (m, 1H, H-5), 4.25-

4.36 (m, 2H, H-6), 4.62-4.68 (m, 1H, H-4), 4.90-4.98 (m, 1H, H-3), 5.02-5.12 (m, 1H, H-2), 5.42 (m, 1H, H-1). ESI-MS: *m/z* = 561.2 ($M + H^+$).

S-(-)-1-(4,7,10-trismethylcarboxymethyl-(1,4,7,10-tetraazacyclododecyl))propan-2-β-D-galactose tetraacetate (15b). The S-diastereomer was synthesized using the procedure described for **15a** beginning with 1.6147 g (0.0029 mol) of **14b**. The yield over last two reactions starting from **13b**: 39%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18-1.19 (d, 3H, methyl, J = 6.5), 1.89-2.09 (m, 12H, acetates), 2.73-3.42 (m, 16H, cyclen), 3.64-3.74 (m, 9H, -OCH_3), 3.90-4.15 (br, methylene and methine on linker and H-6), 4.55-4.62 (m, 1H, H-4), 4.91-5.00 (m, 2H, H-3 and H-5), 5.07-5.15 (m, 1H, H-2), 5.32 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.39, 20.74, 20.89, 21.41, 48.31, 50.69, 51.96, 52.09, 52.89, 52.96, 55.69, 55.99, 55.87, 61.56, 67.26, 67.38, 69.31, 69.42, 70.87, 70.94, 71.41, 73.25, 95.01, 100.98, 169.66, 169.96, 170.08, 170.17, 170.42, 170.62, 171.40, 171.82, 174. 20. ESI-MS: *m/z* = 777.2 ($M + H^+$), 799.3 ($M + Na^+$).

1-(4,7,10-trismethylcarboxymethyl-(1,4,7,10-tetraazacyclododecyl))propan-2-β-D-galactose tetraacetate (15c). The racemic mixture was synthesized using the method described for **15a** beginning with 1.6173 g (0.0029 mol) of **14c**. Yield over last two reactions starting with **13c**: 51%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17-1.18 (d, 3H, methyl, J = 6.5), 1.89-2.09 (m, 12H, acetates), 2.65-3.60 (m, 16H, cyclen), 3.64-3.75 (m, 9H, -OCH_3), 3.92-3.98 (br, methylene and methine on linker and H-6), 4.99-5.36 (m, 4H, H-3, H-5, H-2, H-1). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.93, 48.24, 50.99, 52.13, 52.73, 52.98, 55.87, 56.16, 61.59, 66.86, 67.51, 67.94, 70.63, 94.51, 95.01, 170.39, 170.54, 170.72, 171.24, 171.41, 171.59, 174.27, 174.92. ESI-MS: *m/z* = 777.2 ($M + H^+$), 799.3 ($M + Na^+$).

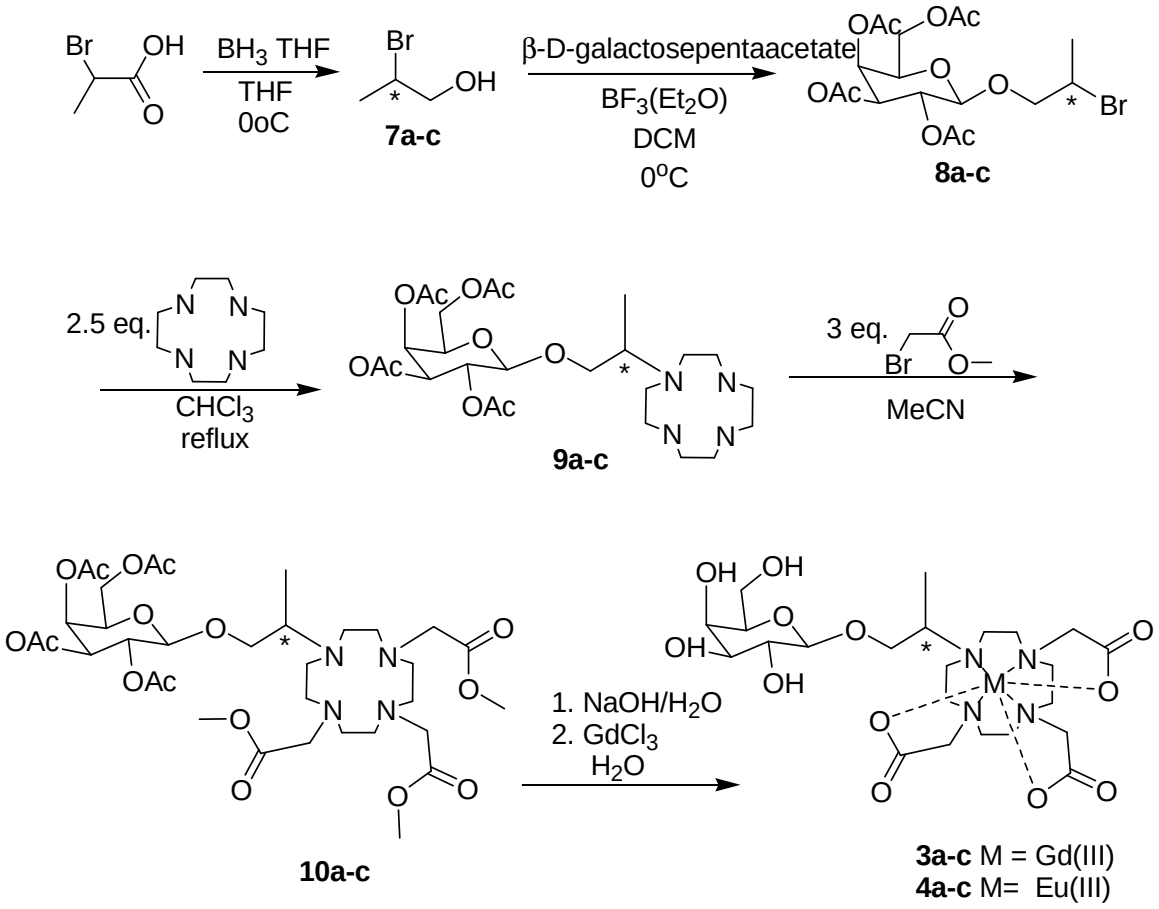


Figure S1. Synthetic Scheme for preparationof α-series.

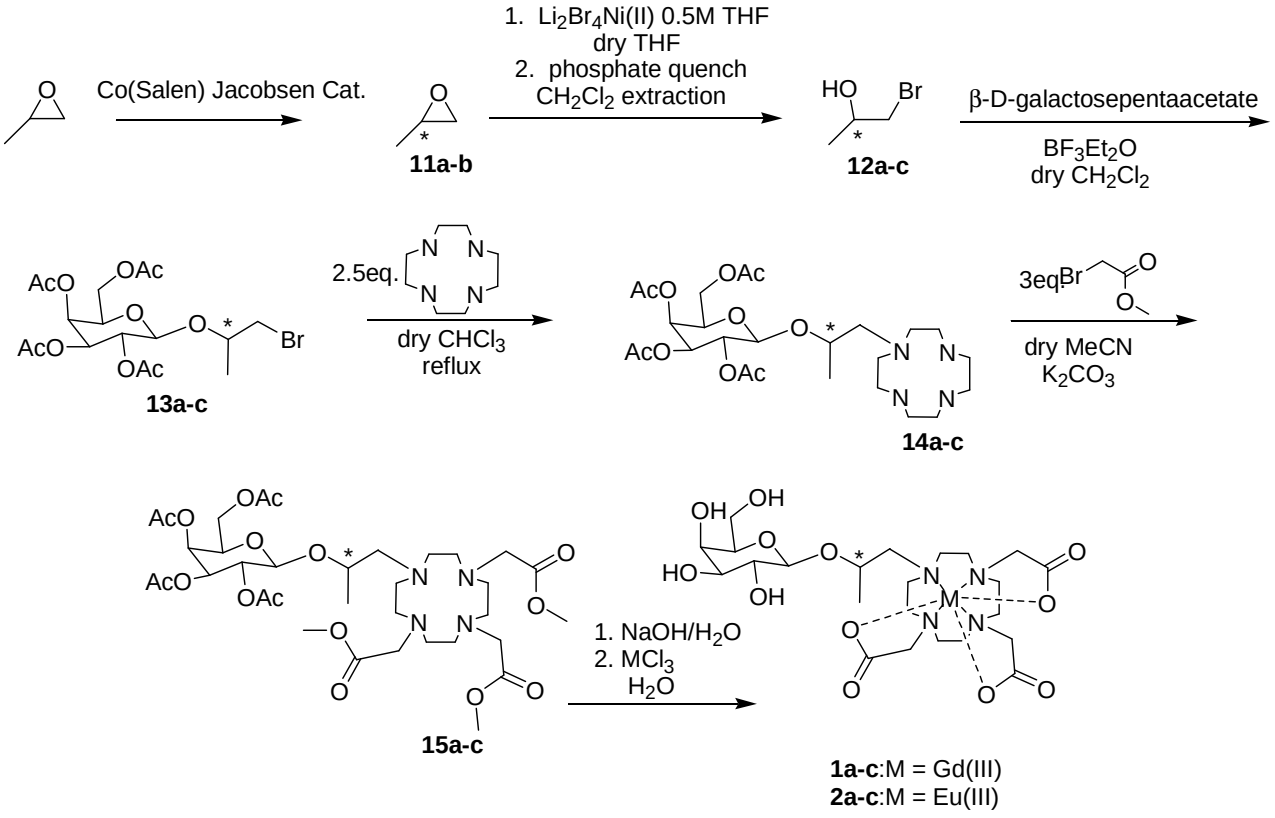


Figure S2. Synthetic Scheme for the preparation of the β-series.

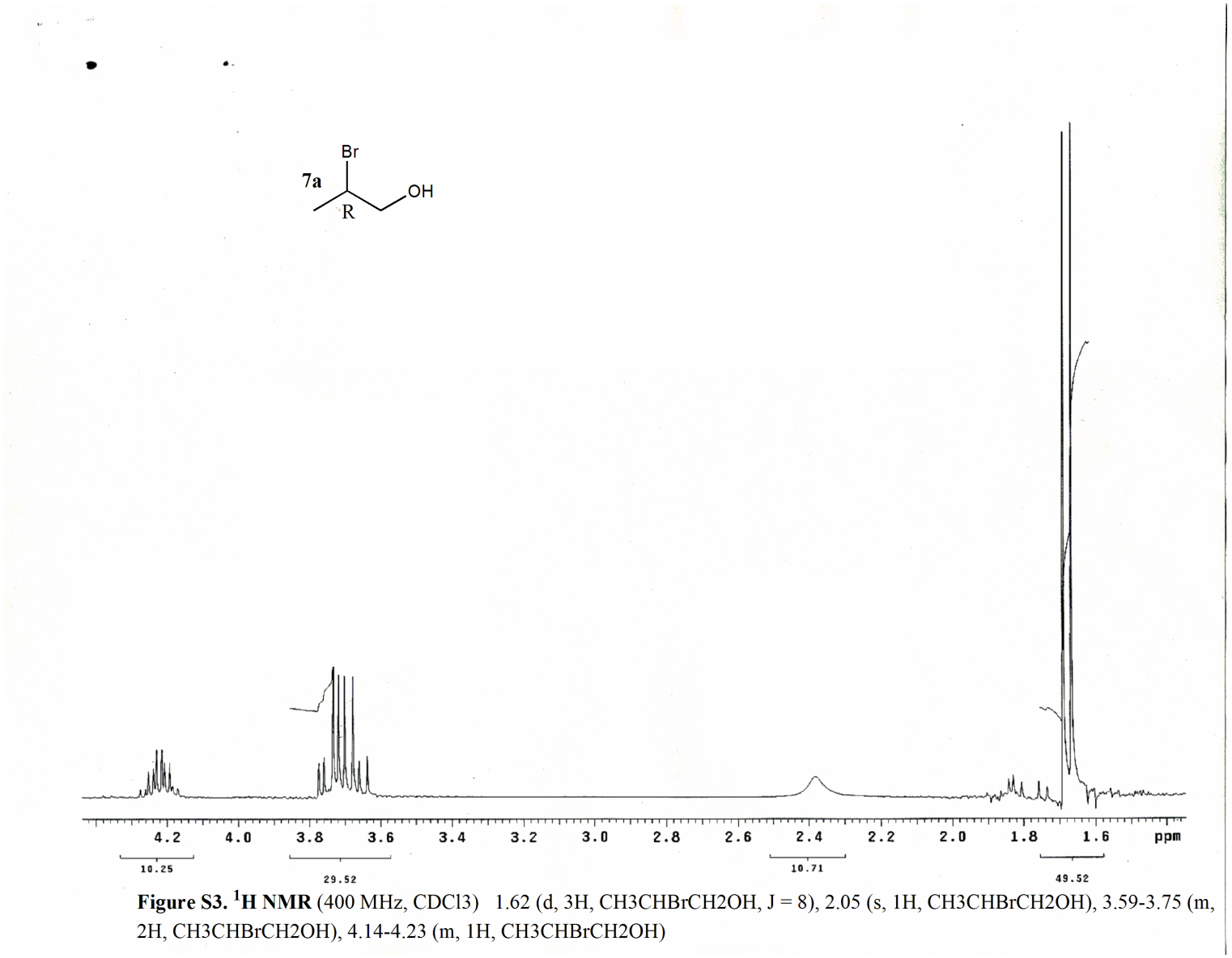


Figure S3. ^{1}H NMR (400 MHz, CDCl3) 1.62 (d, 3H, CH3CHBrCH2OH, J = 8), 2.05 (s, 1H, CH3CHBrCH2OH), 3.59-3.75 (m, 2H, CH3CHBrCH2OH), 4.14-4.23 (m, 1H, CH3CHBrCH2OH)

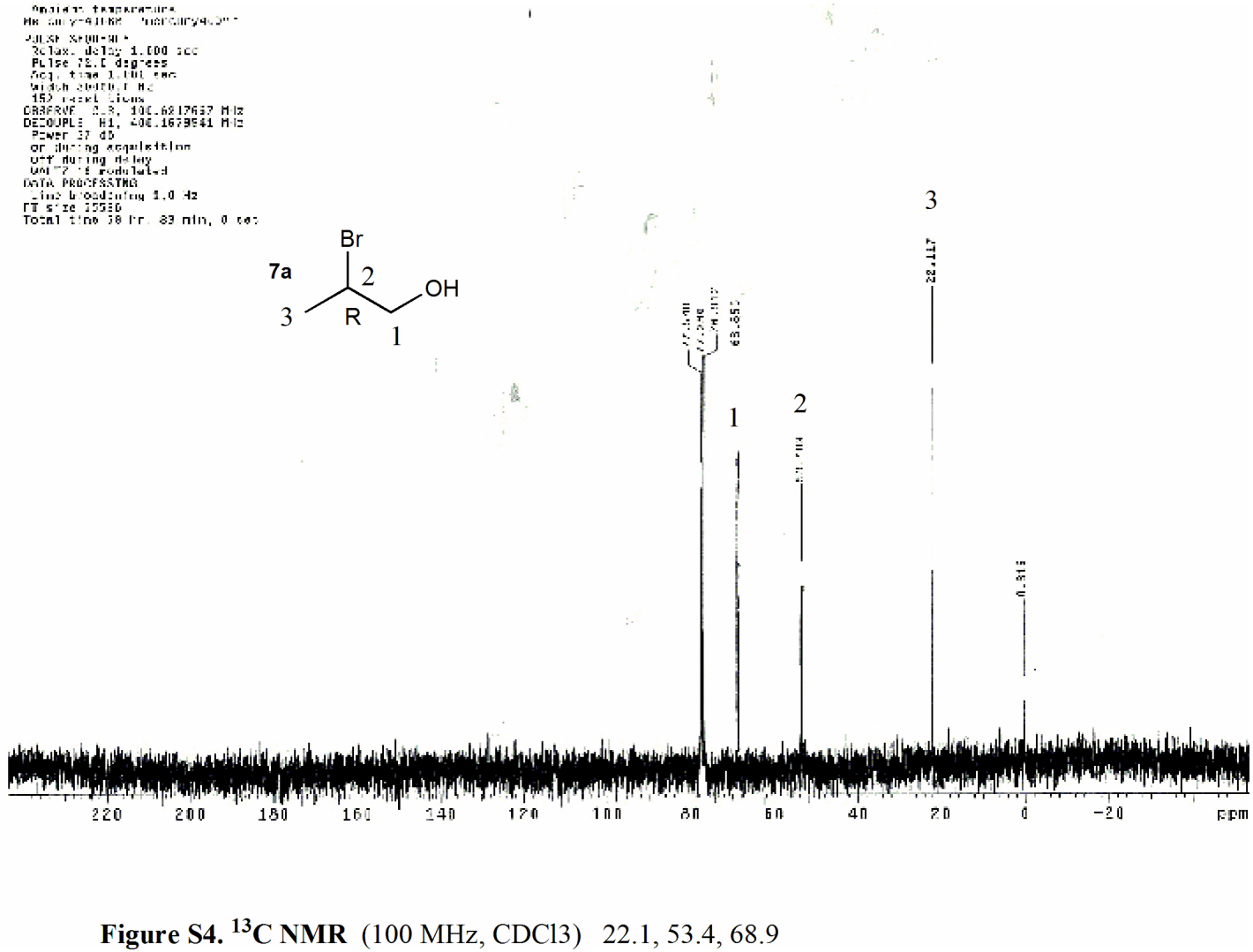


Figure S4. ^{13}**C NMR** (100 MHz, CDCl3) 22.1, 53.4, 68.9

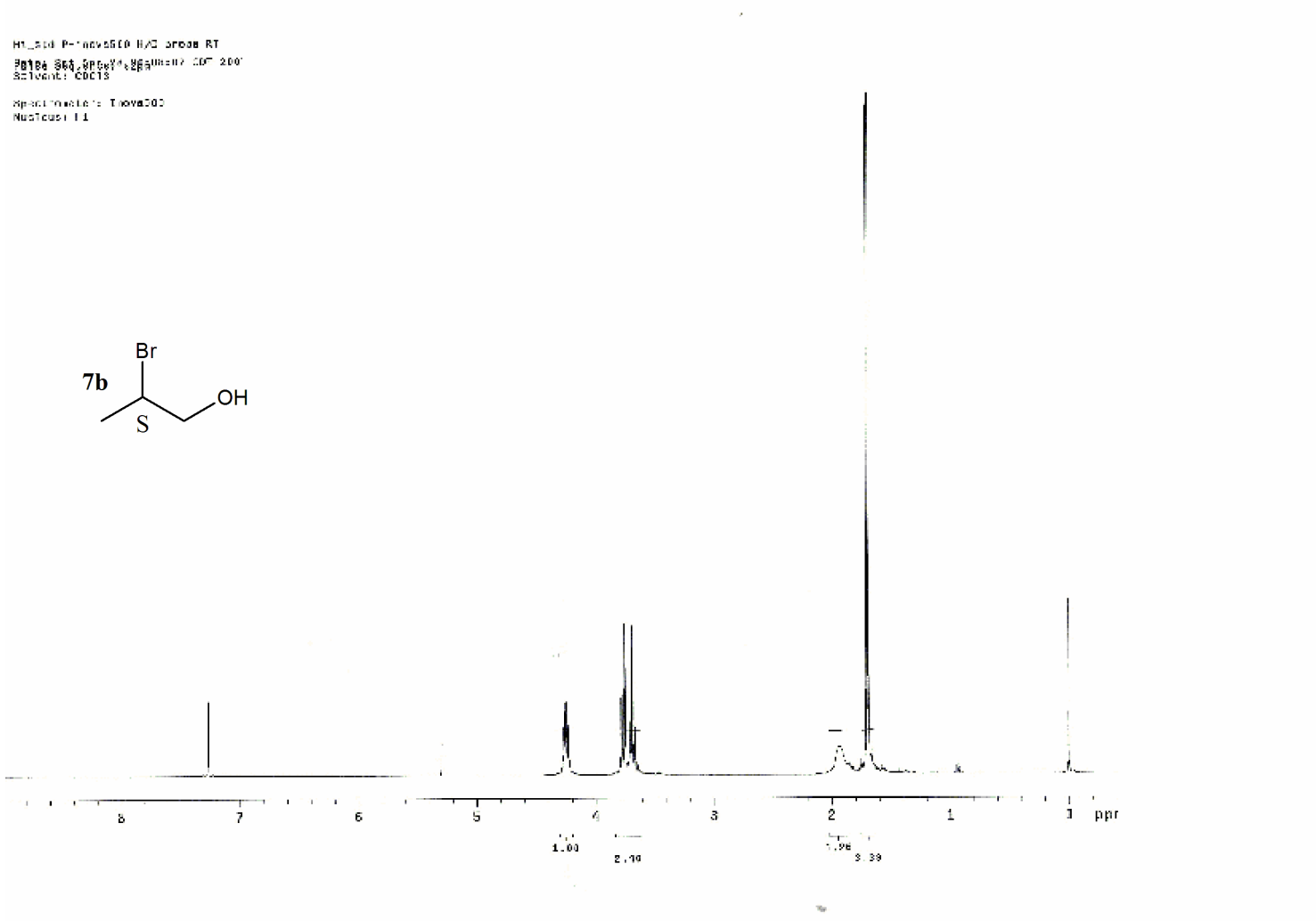


Figure S5. **^{1}H NMR** (400 MHz, CDCl3) 1.62 (d, 3H, CH3CHBrCH2OH, J = 8), 2.14-2.24 (s, 1H, CH3CHBrCH2OH), 3.60-3.82 (m, 2H, CH3CHBrCH2OH), 4.20-4.36 (m, 1H, CH3CHBrCH2OH)

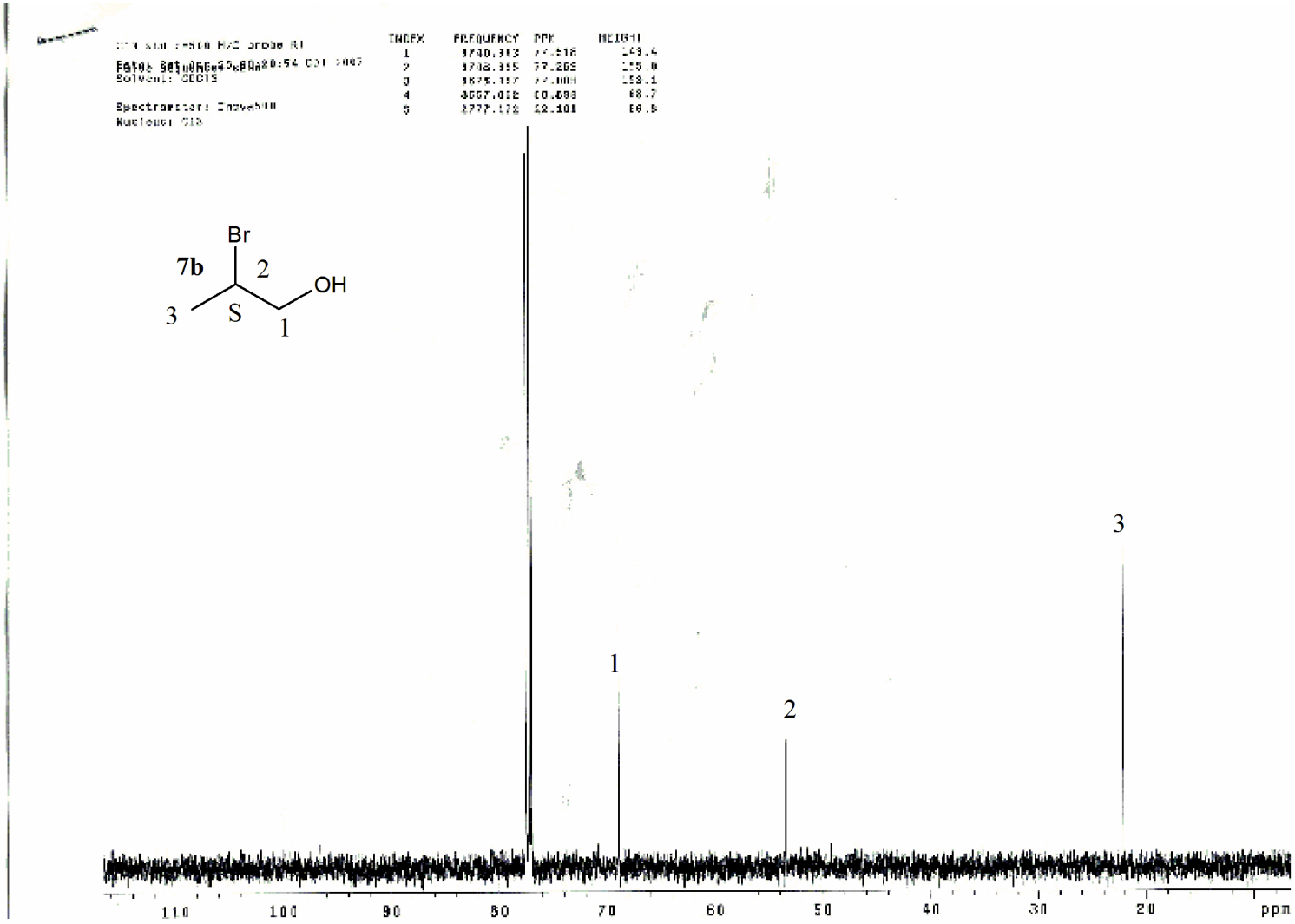


Figure S6. **^{1}C NMR** (100 MHz, CDCl3) 22.1, 53.74, 68.90

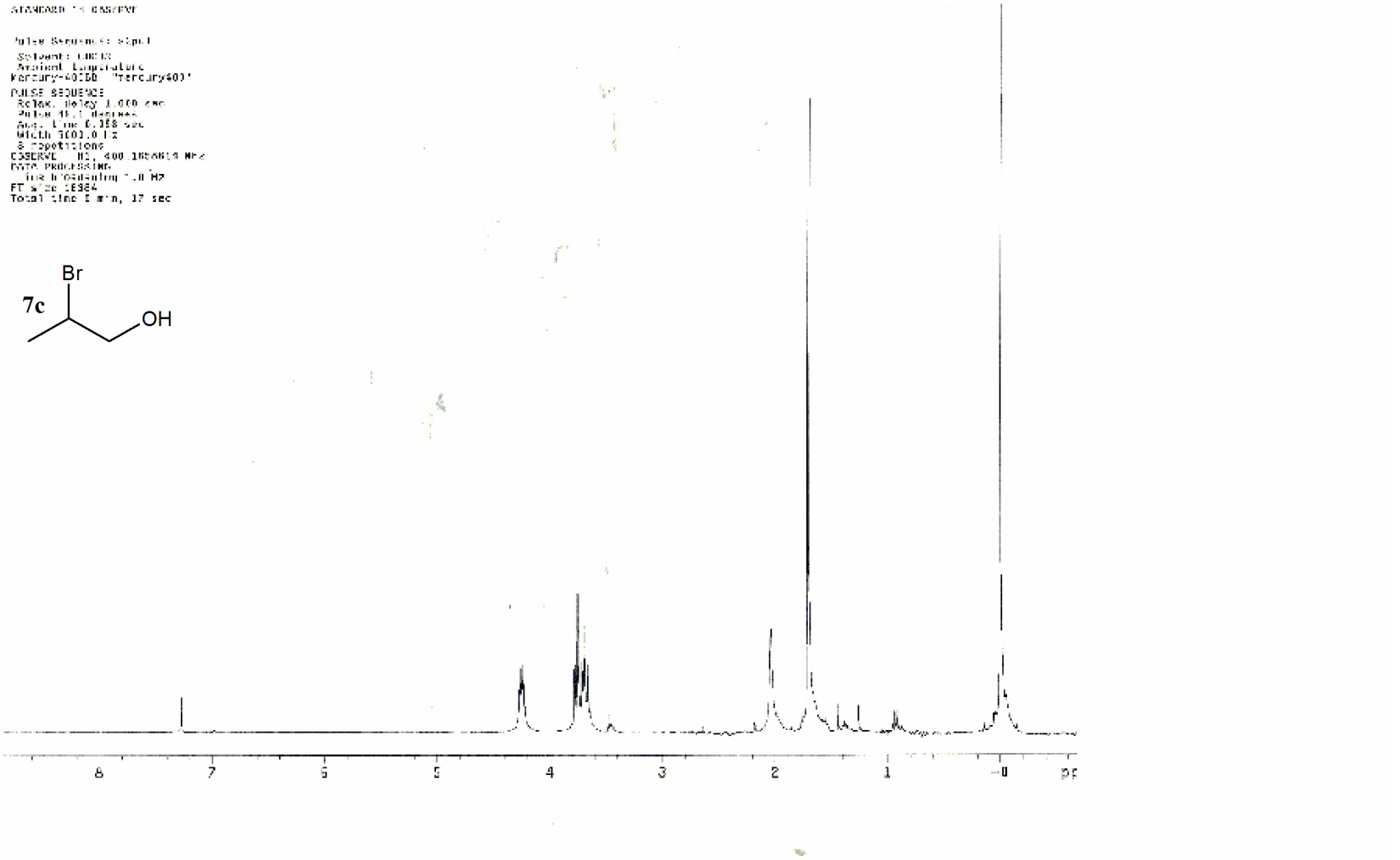


Figure S7. **^{1}H NMR** (400 MHz, CDCl3) 1.52-1.62 (d, 3H, CH3CHBrCH2OH, J = 8), 3.1 (s, 1H, CH3CHBrCH2OH), 3.54-3.70 (m, 2H, CH3CHBrCH2OH), 4.02-4.15 (m, 1H, CH3CHBrCH2OH)

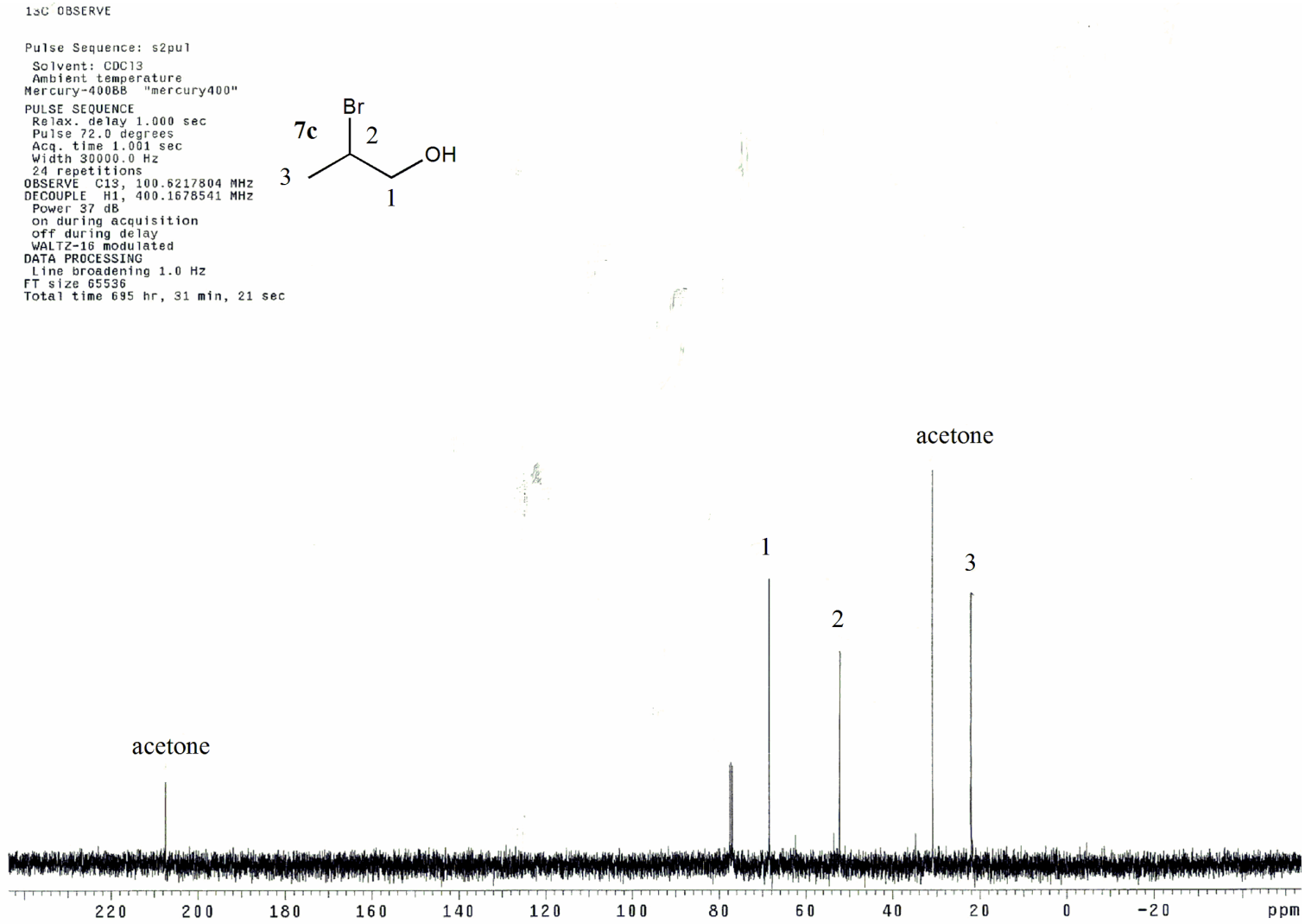


Figure S8. **^{13}C NMR** (100 MHz, CDCl3) 21.23, 52.73, 67.42

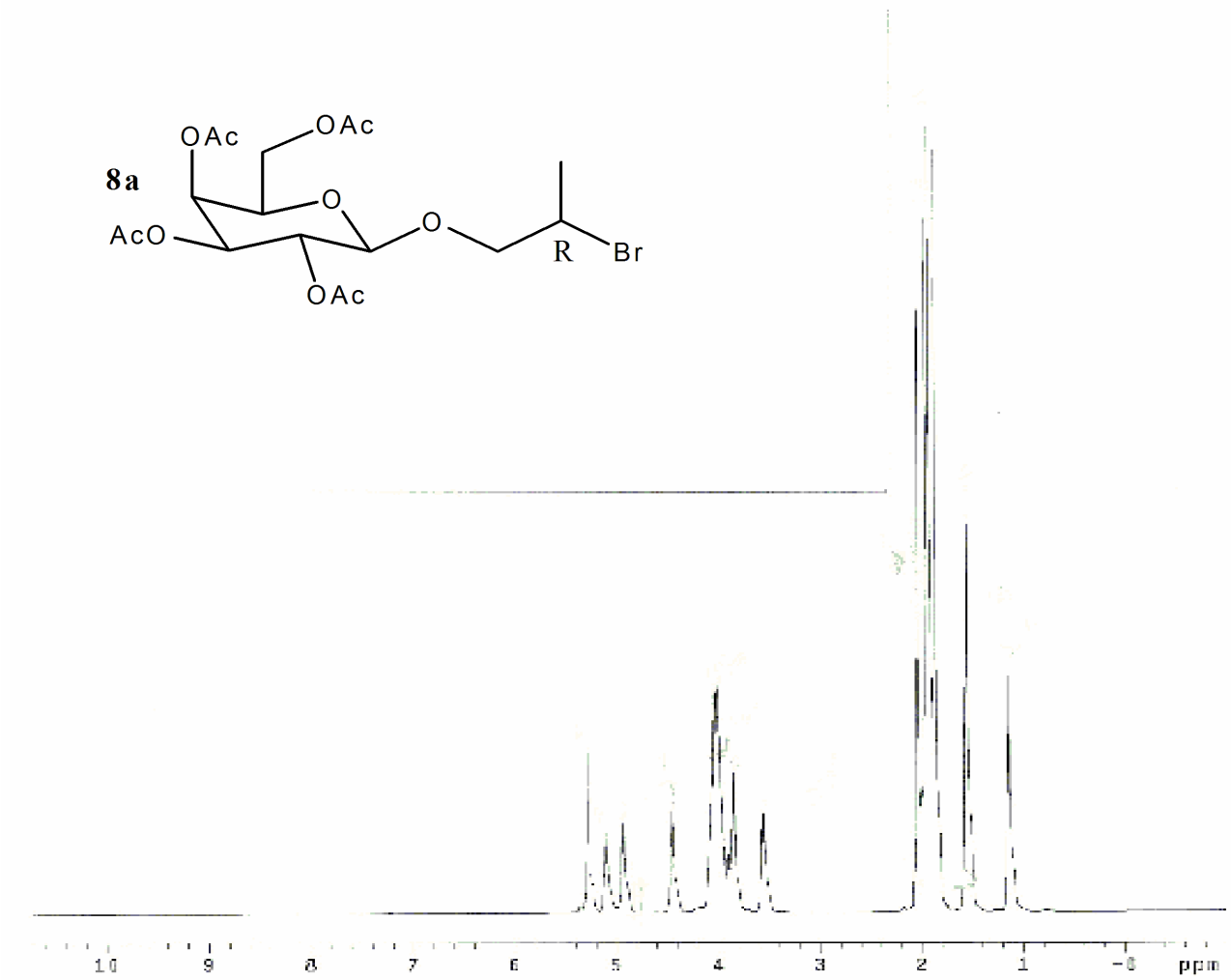


Figure S9. **^{1}H NMR** (500 MHz, CDCl3) 1.51 (d, 3H, methyl, J = 6.5), 1.80-2.05 (m, 12H, OAc), 3.54-3.59 (m, 2H, CH3CHBrCH2O-sugar), 3.84-3.91 (m, 1H, CH3CHBrCH2O-sugar), 3.97-4.11 (m, 3H, H-5 and H-6) 4.45-4.49 (m, 1H, H-4), 4.93-4.95 (m, 1H, H-2), 5.09-5.13 (m, 1H, H-3), 5.23-5.29 (m, 1H, sugar anomeric H)

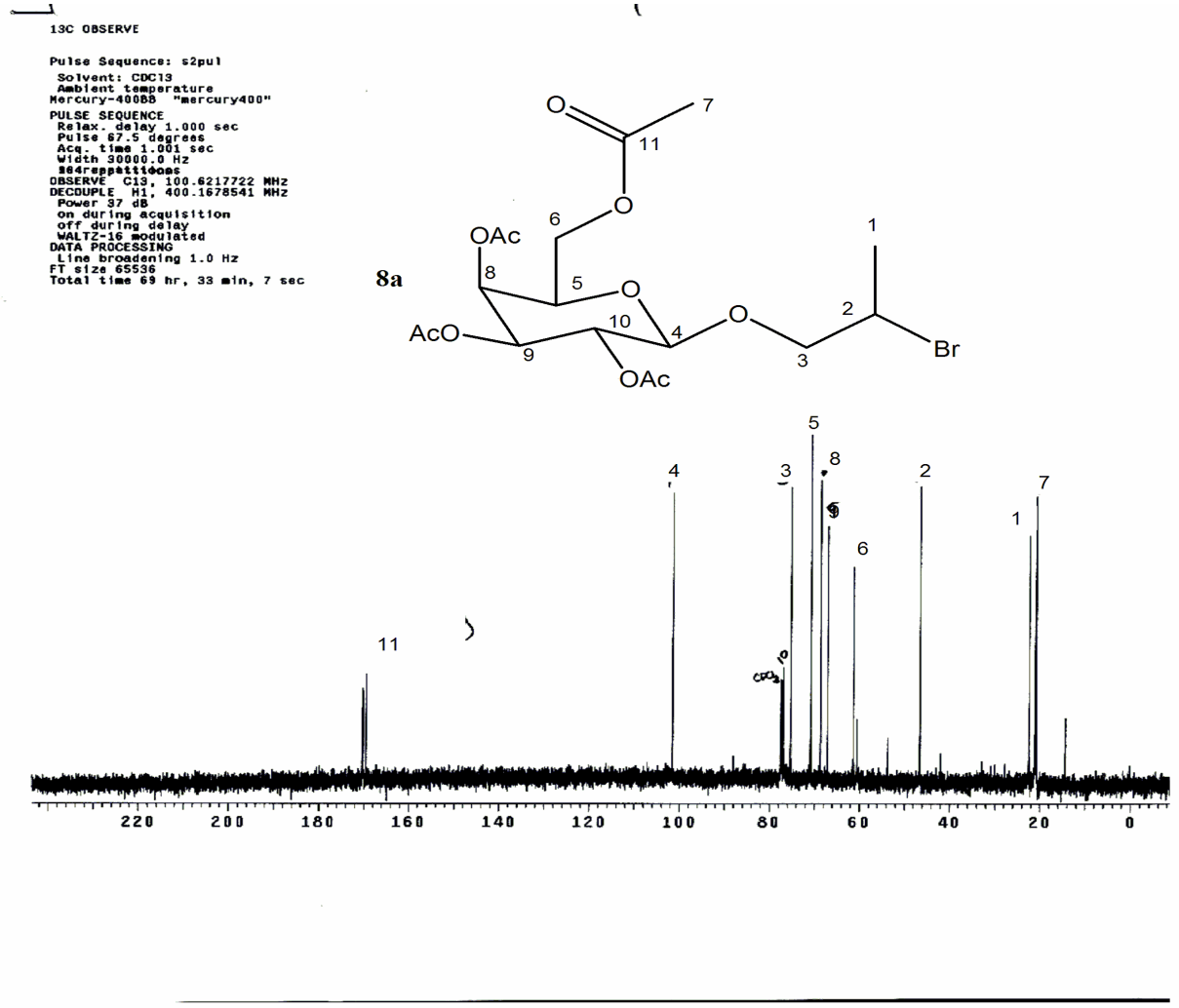


Figure S10. ^{13}**C NMR** (100 MHz, CDCl3) 20.80, 20.88, 21.08, 22.45, 46.58, 61.41, 67.11, 68.70, 70.12, 70.68, 70.91, 75.08, 101.48, 170.21, 170.30

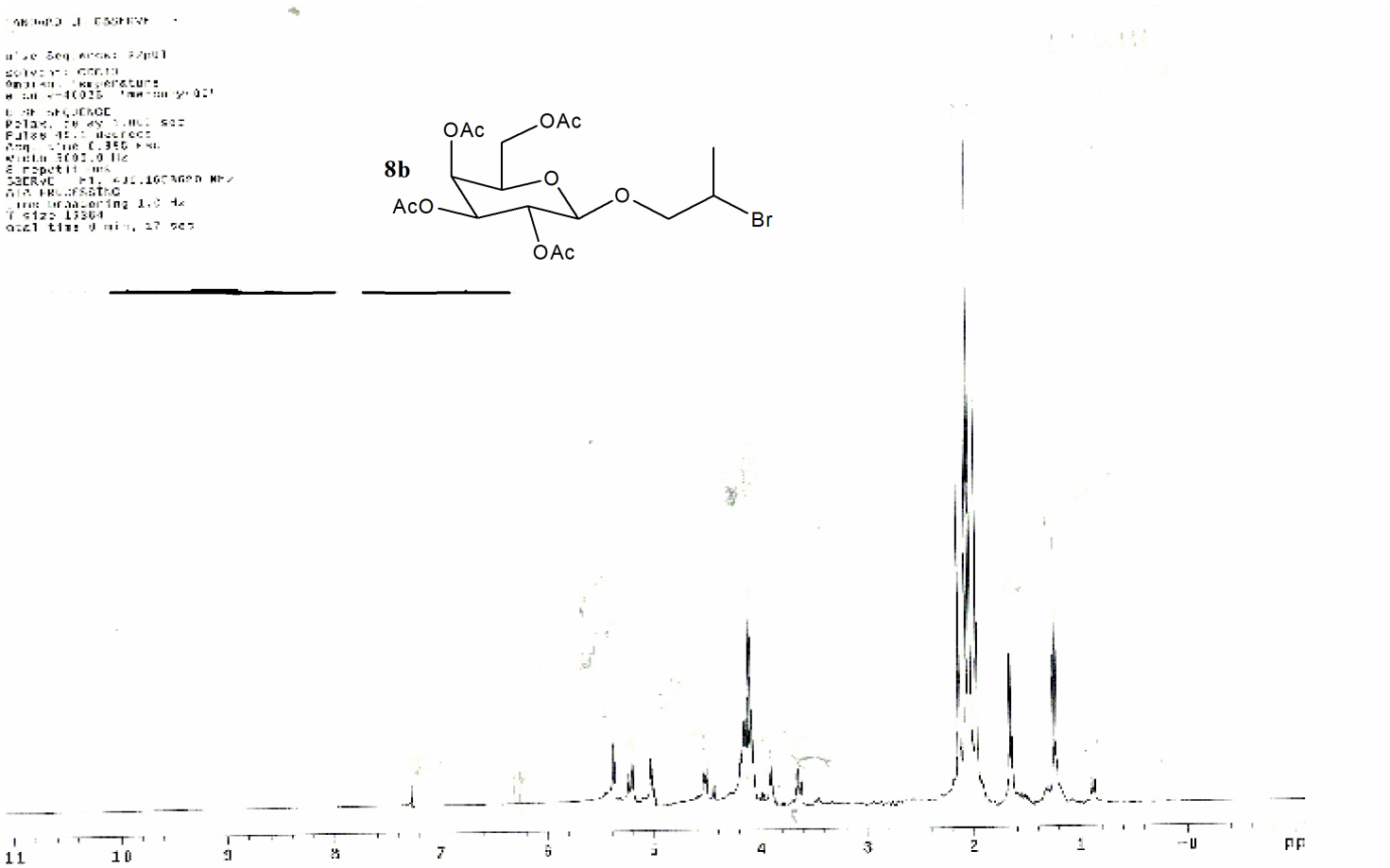


Figure S11. **^{1}H NMR** (500 MHz, CDCl3) 1.66-1.67 (d, 3H, methyl, J = 6.5), 1.99-2.16 (m, 12H, OAc), 3.65-3.69 (m, 2H, CH3CHBrCH2O-sugar), 3.90-3.93 (m, 1H, CH3CHBrCH2O-sugar), 4.00-4.03 (m, 2H, H-6), 4.11-4.20 (m, 1H, H-4), 4.53-4.55 (m, 1H, H-5), 5.02-5.05 (m, 1H, H-3), 5.22-5.26 (m, 2H, H-2), 5.40-5.40 (m, 1H, H-1)

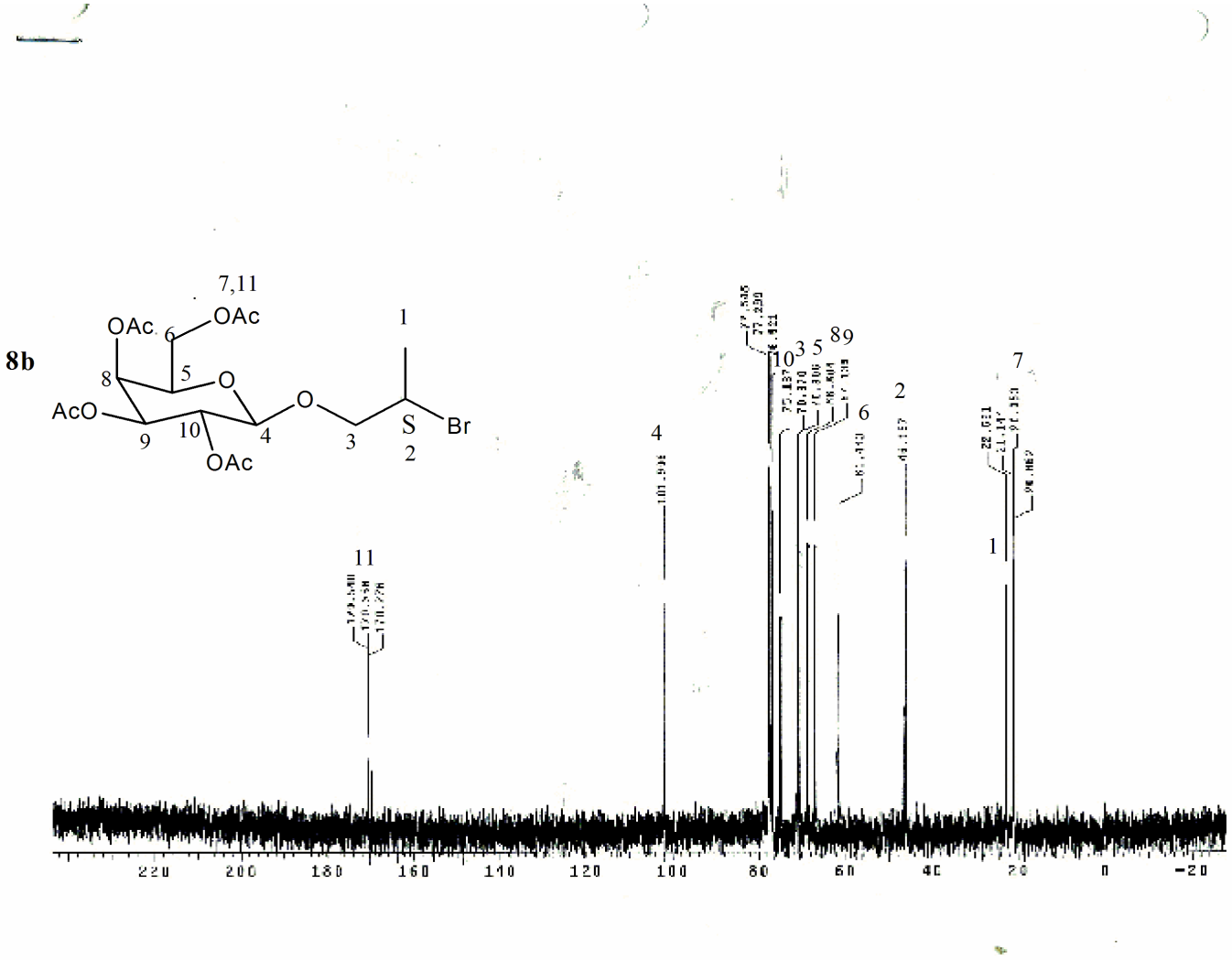


Figure S12. ^{13}**C NMR** (125 MHz) 20.87, 20.95, 21.14, 22.69, 46.15, 61.44, 67.14, 68.80, 70.91, 70.97, 75.14, 101.91, 170.28, 170.36, 170.54

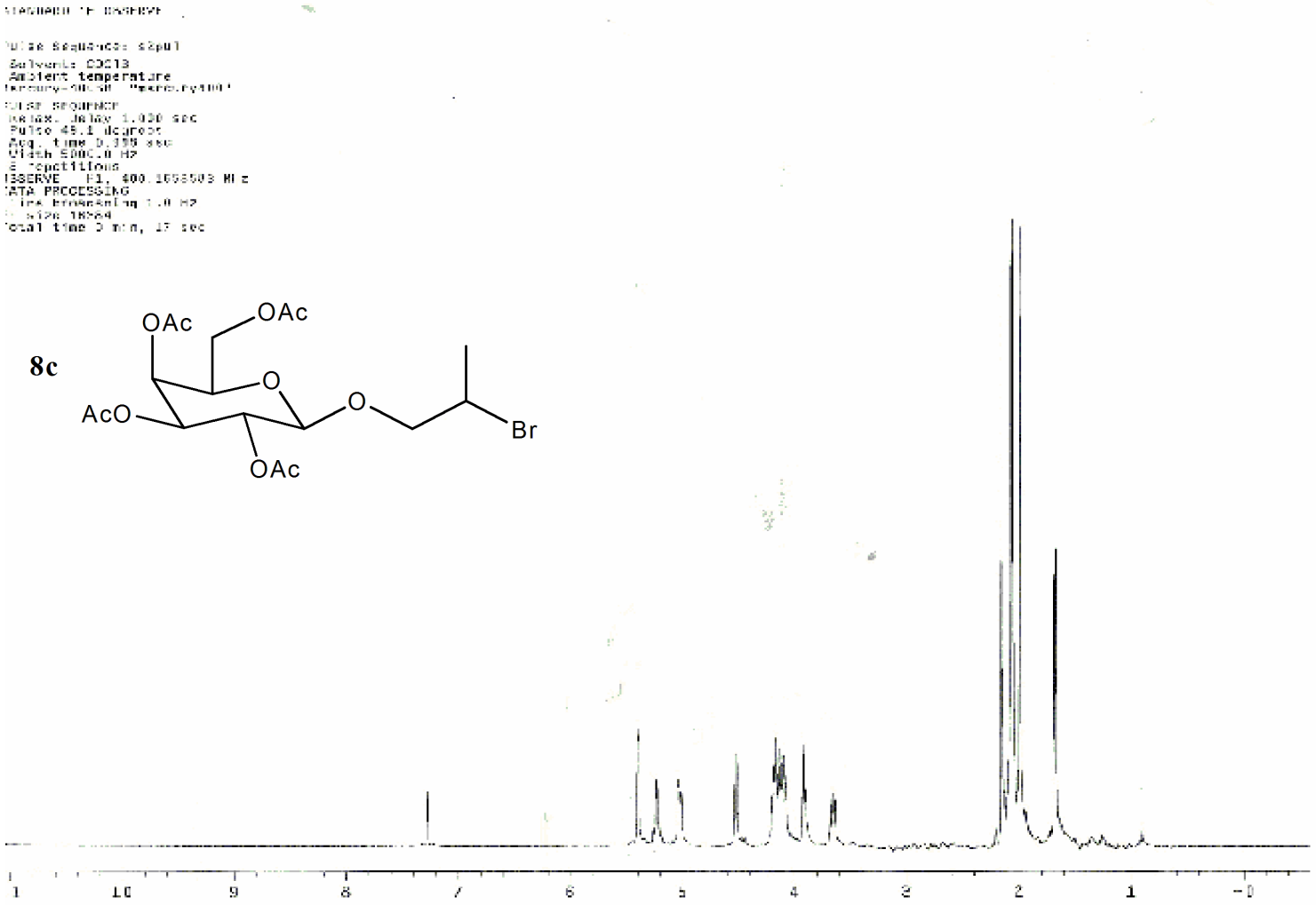


Figure S13. **^{1}H NMR** (400 MHz) 1.62-1.76 (d, 3H, methyl, J = 6.5), 1.88-2.18 (m, 12H, OAc), 3.60-3.68 (m, 2H, CH3CHBrCH2O-sugar), 3.86-3.92 (m, 1H, CH3CHBrCH2O-sugar), 4.16-4.22 (m, 3H, H-5 and H-6), 4.52-4.58 (m, 1H, H-4), 5.0-5.18 (m, 1H, H-2), 5.20-5.28 (m, 1H, H-3), 5.39 (m, 1H, H-1)

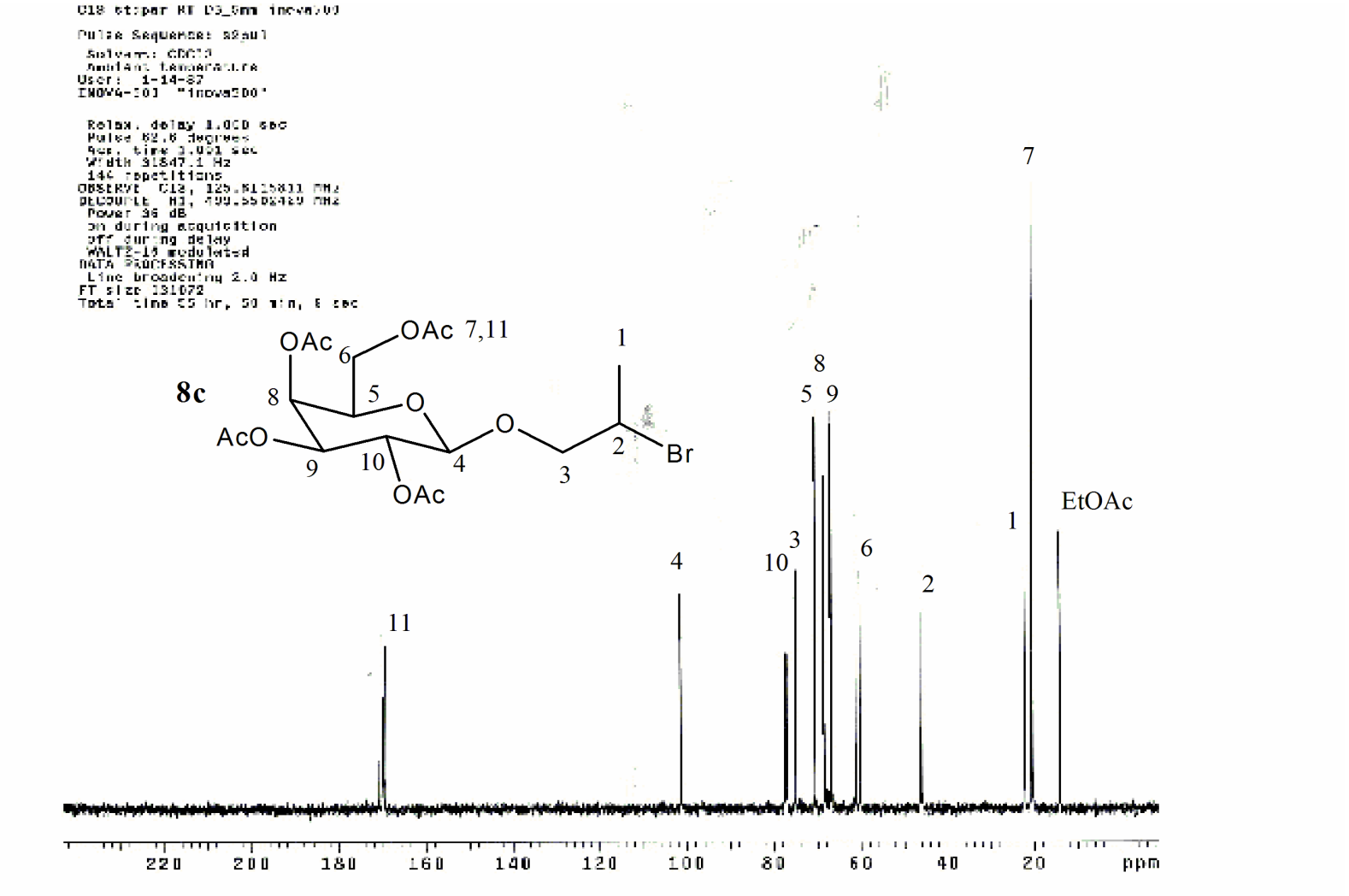


Figure S14. (100 MHz) 20.49, 20.57, 20.78, 20.94, 22.19, 22.37, 46.34, 60.27, 61.19, 66.96, 68.53, 68.60, 70.67, 74.84, 75.07, 101.31, 101.60, 169.36, 169.99, 170.14, 170.26

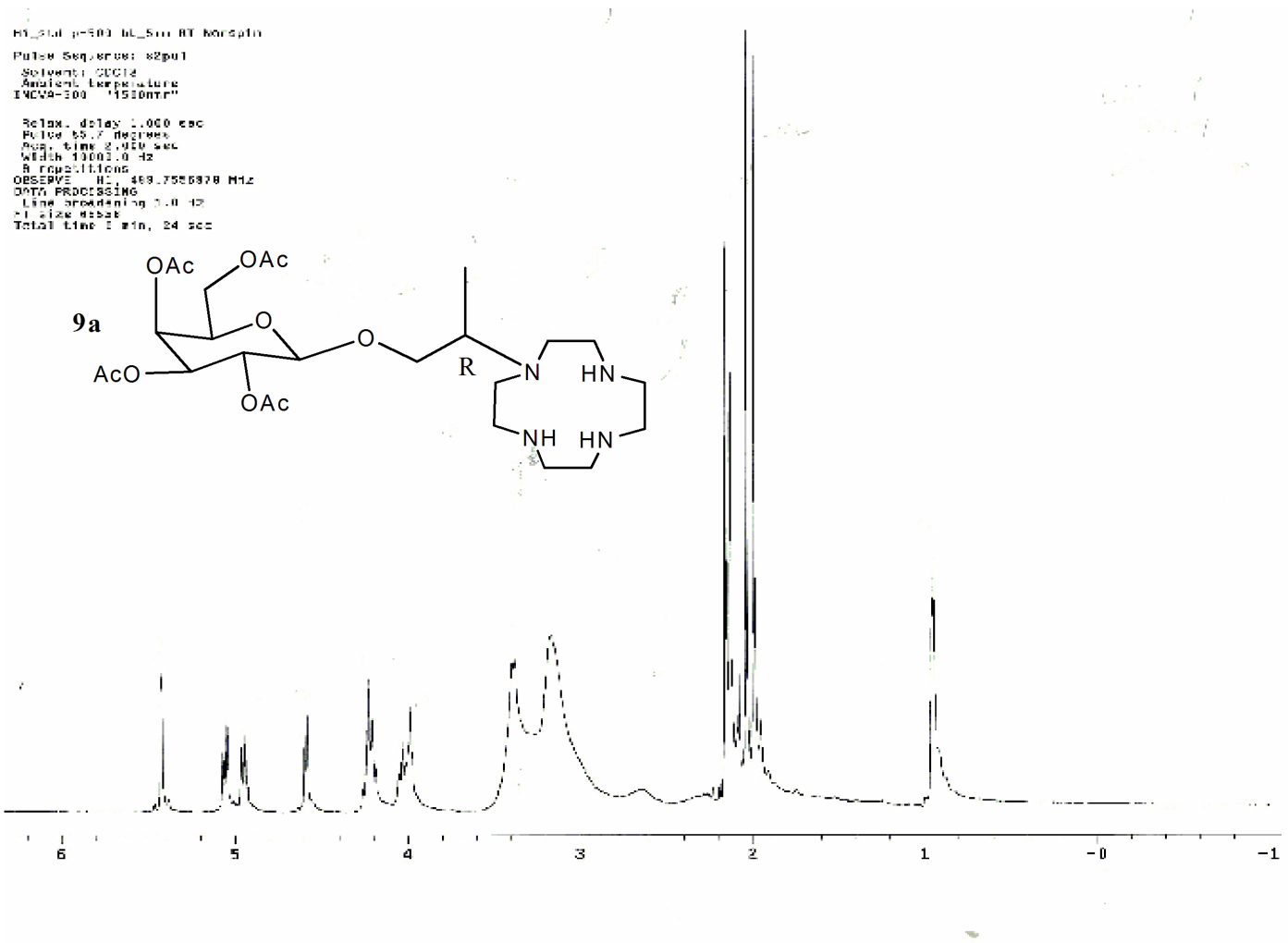


Figure S15. **^{1}H NMR** (500 MHz, CDCl3) 0.82-0.98 (d, 3H, methyl, J = 6.0), 1.85-2.18 (m, 12H, sugar acetate CH3), 3.0-3.5 (br, 16H, cyclen), 3.95-4.04 (m, 3H, methylene and methine on linker), 4.18-4.28 (m, 3H, H-6 and H-5), 4.50 (d, 1H H-4), 4.92-4.99 (m, 1H, H-2), 5.02-5.15 (m, 1H, H-3), 5.42 (m, 1H, H-1)

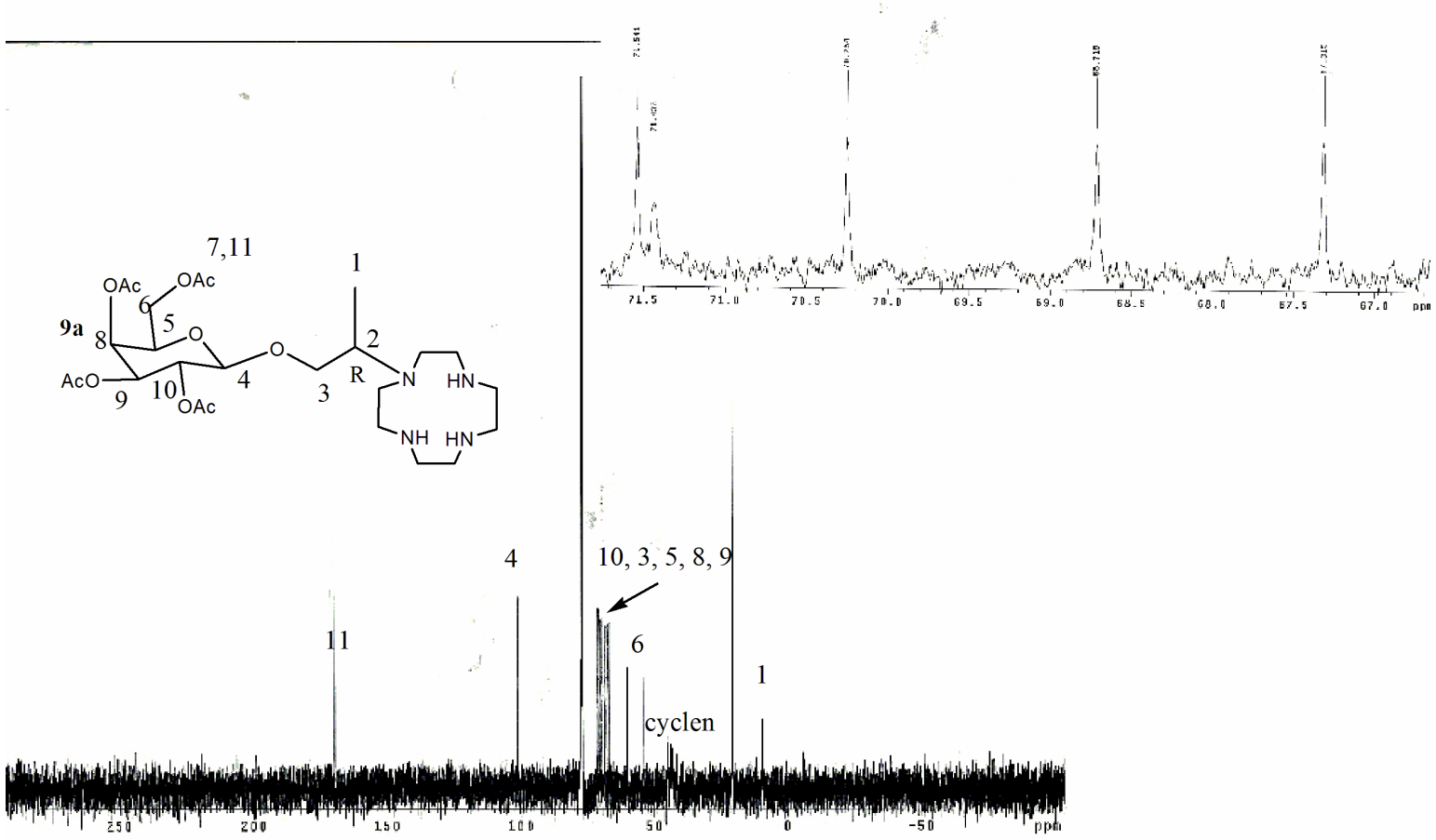


Figure S16. (125 MHz, CDCl3) 9.54, 20.72, 20.76, 20.90, 54.40, 60.33, 67.32, 68.72, 70.25, 71.43, 71.54, 110.2, 169.46, 169.93, 170.75, 171.48. Enlargement of peaks found between 76-71.6 ppm. Only one peak is seen for each of the sugar carbons.

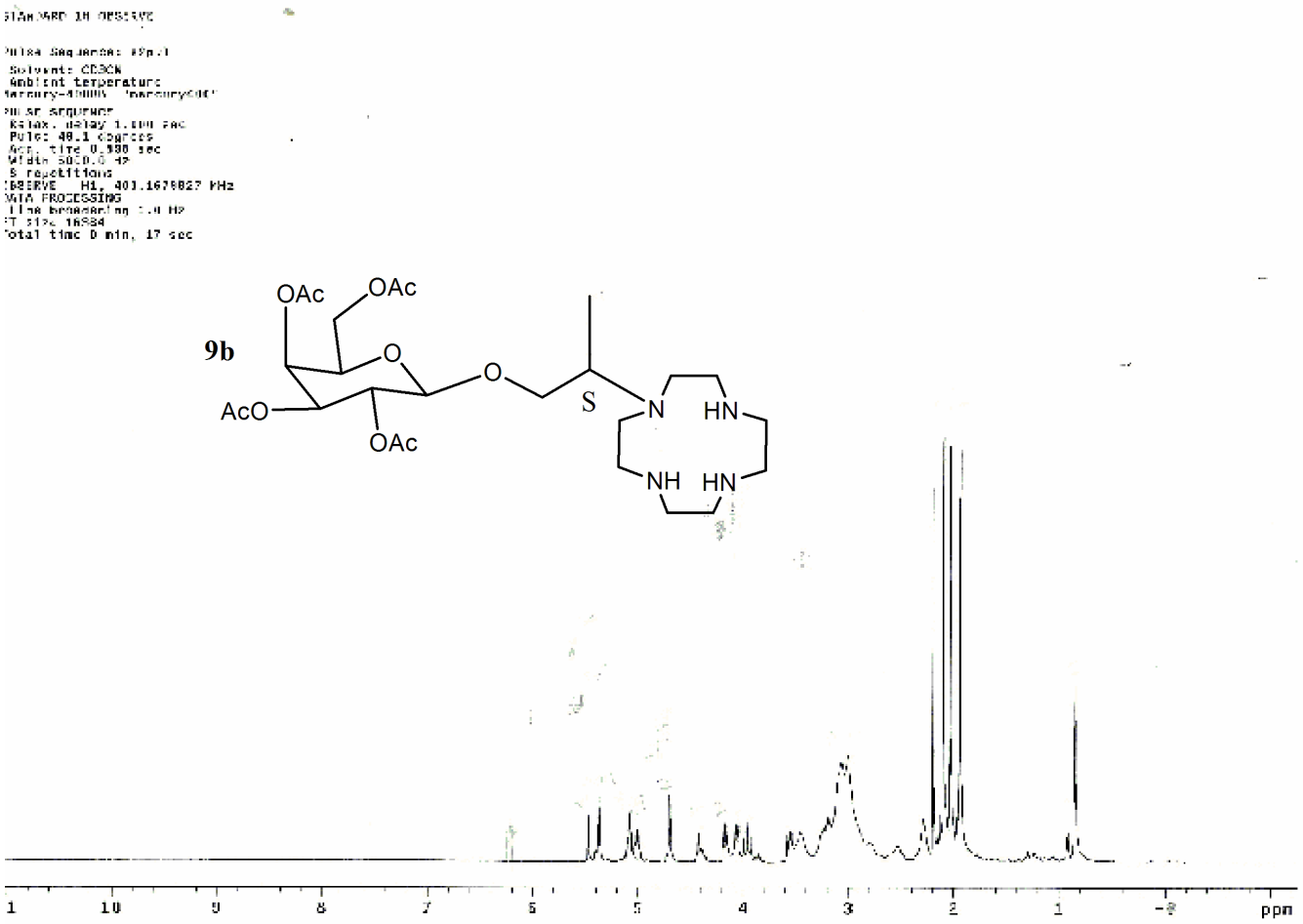


Figure S17. **^{1}H NMR** (400 MHz, CD3CN) 0.78-0.84 (d, 3H, methyl, J = 6.0), 1.85-2.22 (m, 12H, OAc), 2.74-3.35(br, 16H, cyclen), 3.92-4.08 (m, 2H, methylene on linker), 4.16-4.2 (m, 1H, methine on linker), 4.38-4.42 (m, 3H, H-5 and H-6), 4.72 (m, d, 1H, H-4), 4.98-5.08 (m, 1H, H-2), 5.10-5.18 (m, 1H, H-3), 5.40 (m 1H, H-1)

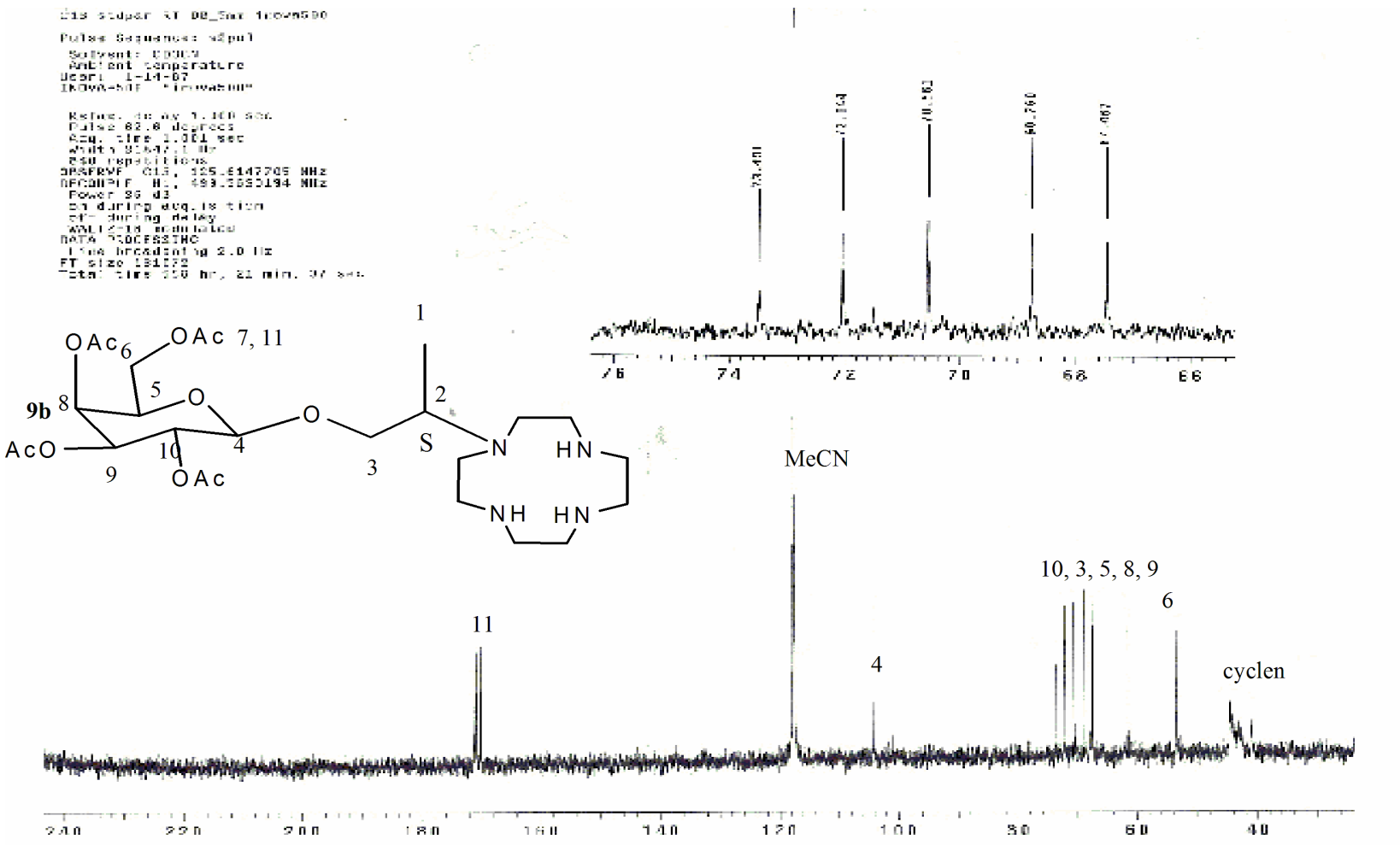


Figure S18. ^{13}**C NMR** (125 MHz, CD3CN) 7.92, 20.15, 20.30, 20.37, 20.40, 53.41, 61.52, 67.47, 68.76, 70.56, 72.04, 73.49. 104.5, 170.02, 170.75, 170.79, 171.28. Enlargement of peaks between 66 ppm and 76 ppm. Only one peak is seen for each of the sugar carbons.

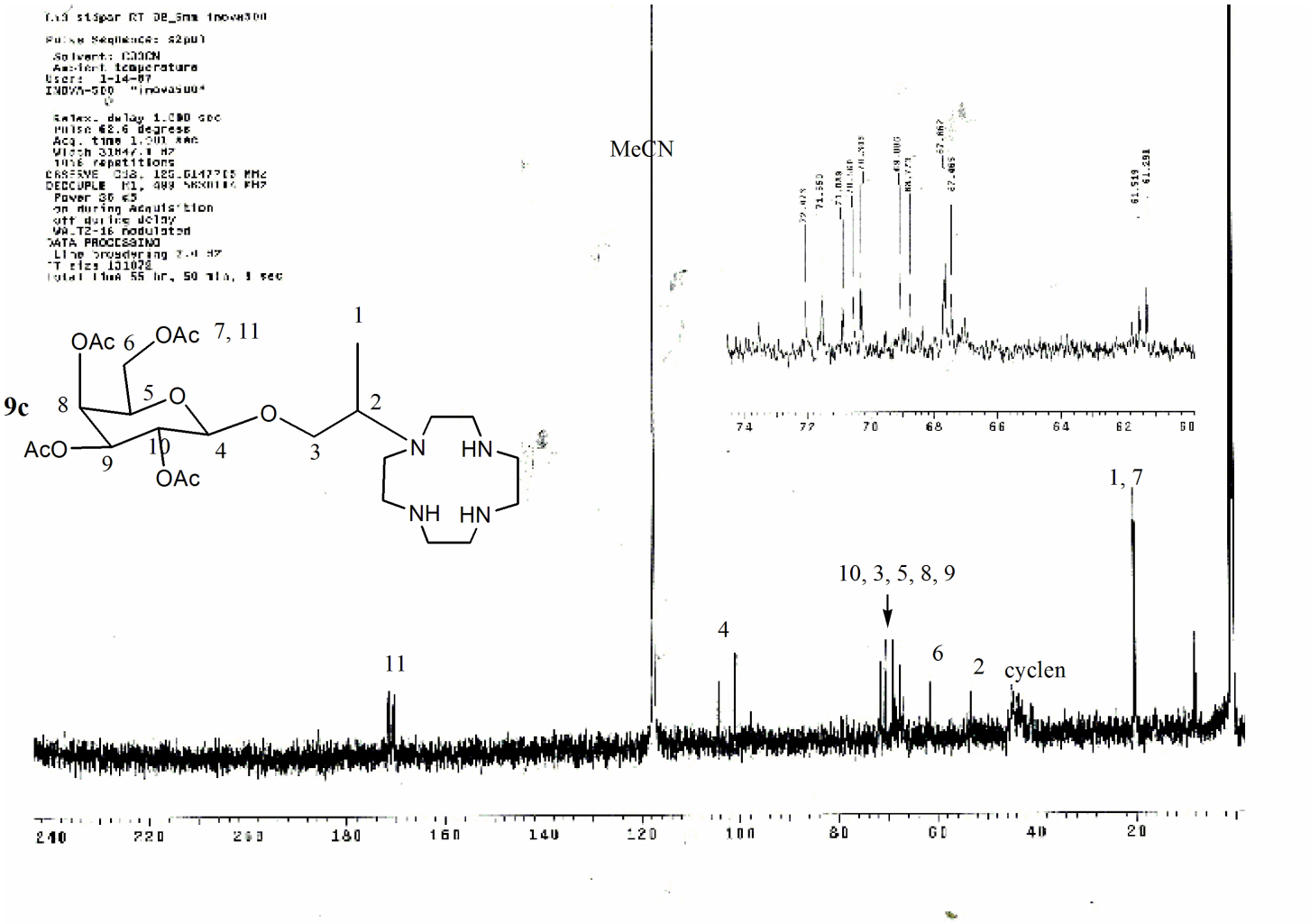
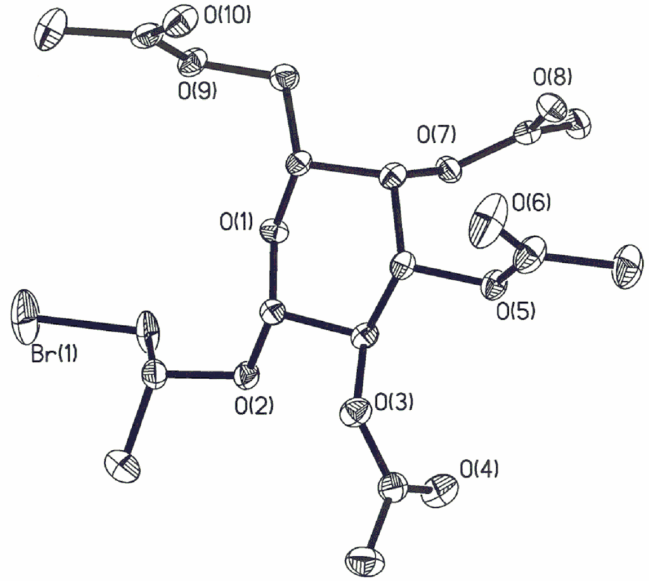
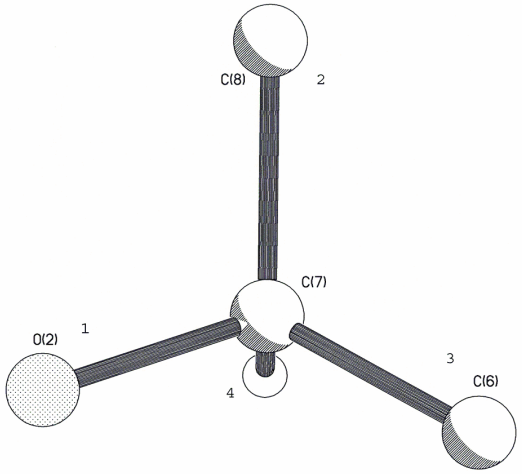


Figure S19. **^{13}C NMR** (125 MHz, CD3CN) 7.85, 8.20, 20.09, 20.21, 20.34, 53.11, 53.43, 61.29, 61.52, 67.47, 67.66, 68.77, 69.09, 70.31, 70.56, 70.89, 71.55, 72.07, 101.5, 104.5, 170.02, 170.26, 170.55, 171.27, 171.49. Enlargement of peaks found between 60-74 ppm. Two peaks are seen for each of the sugar carbons.

X-ray Crystal Structure: *R*-Bromo-Galactose Pentaacetate



Chirality: Clockwise (*R*)



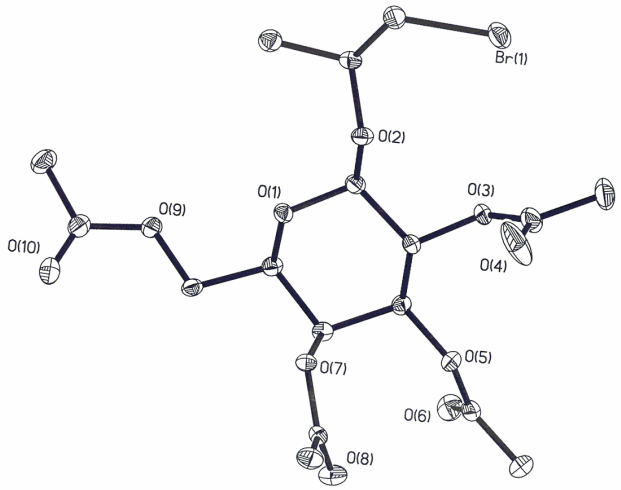
Monoclinic
$P2_1$

a = 9.6159(8)
b = 10.7202(9)
c = 10.6943(8)

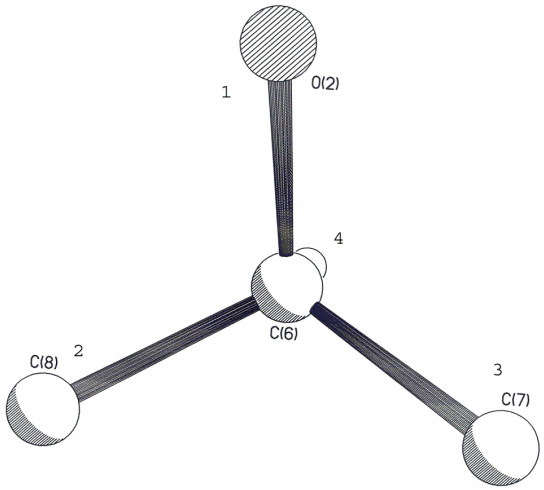
$\alpha = \gamma = 90°$ $\beta = 103.868(1)°$

Figure S22. Crystal structure of R-(+)-1-bromopropan-2- -D-galactose tetraacetate (13a). CIF file is attached as supplementary material.

X-ray Crystal Structure: *S*-Bromo-Galactose Pentaacetate



Chirality: CounterClockwise (*S*)



Orthorhombic
$P2_12_12_1$

$\alpha = \beta = \gamma = 90°$

a = 8.9183(7)
b = 10.5142(8)
c = 22.198(2)

Figure S23. Crystal structure of structure S-(-)-1-bromopropan-2- -D-galactose tetraacetate (13b). CIF file attached as supplementary material.

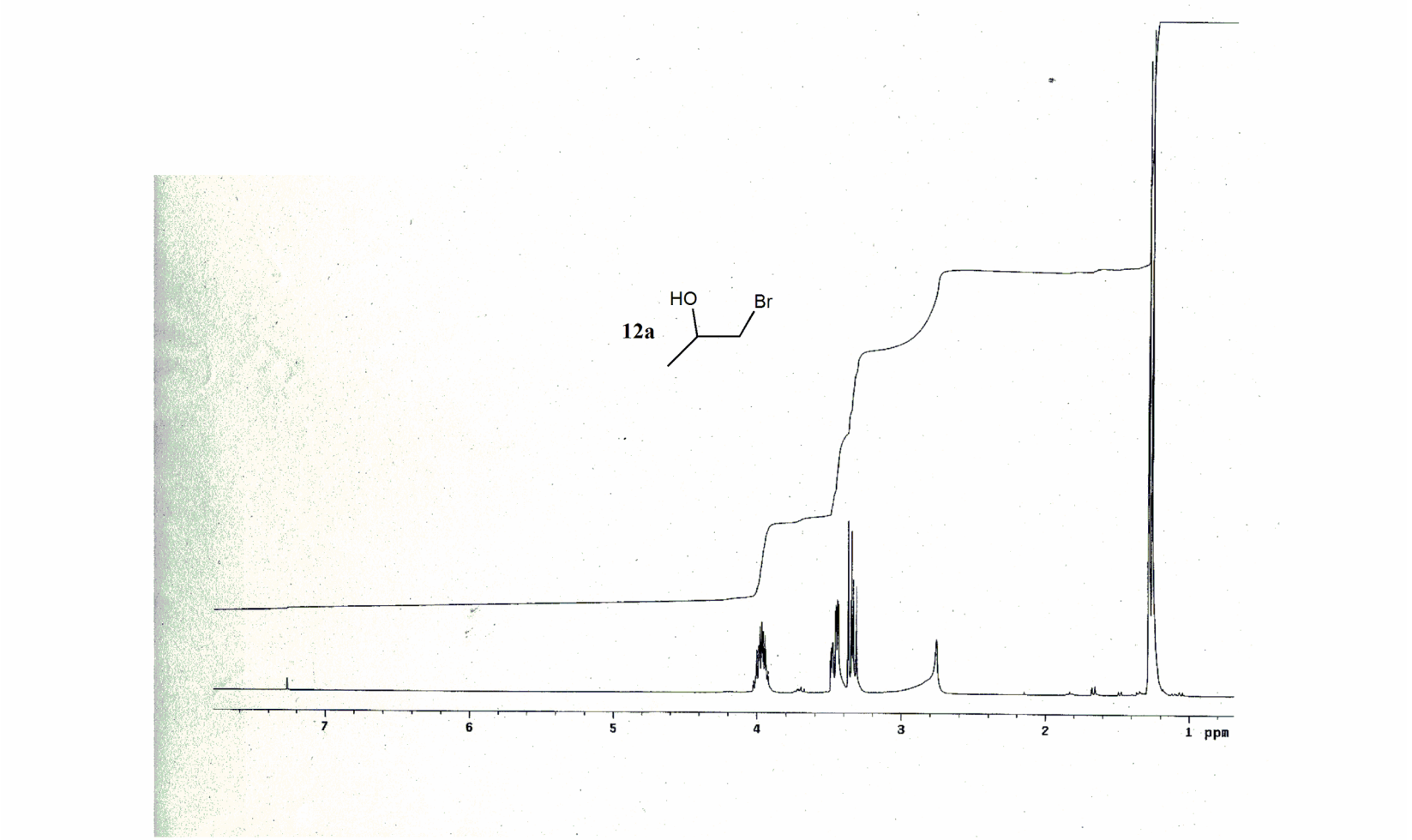


Figure S24. **^{1}H NMR** 1H NMR (500 MHz, CDCl3) 1.25-1.32 (d, 3H, methyl, J = 6.0), 1.85 (br, 1H, -OH), 3.32-3.38 (m, 1H, methylene), 3.45-3.51 (m, 1H, methylene), 3.94-4.02 (m, 1H, methine)

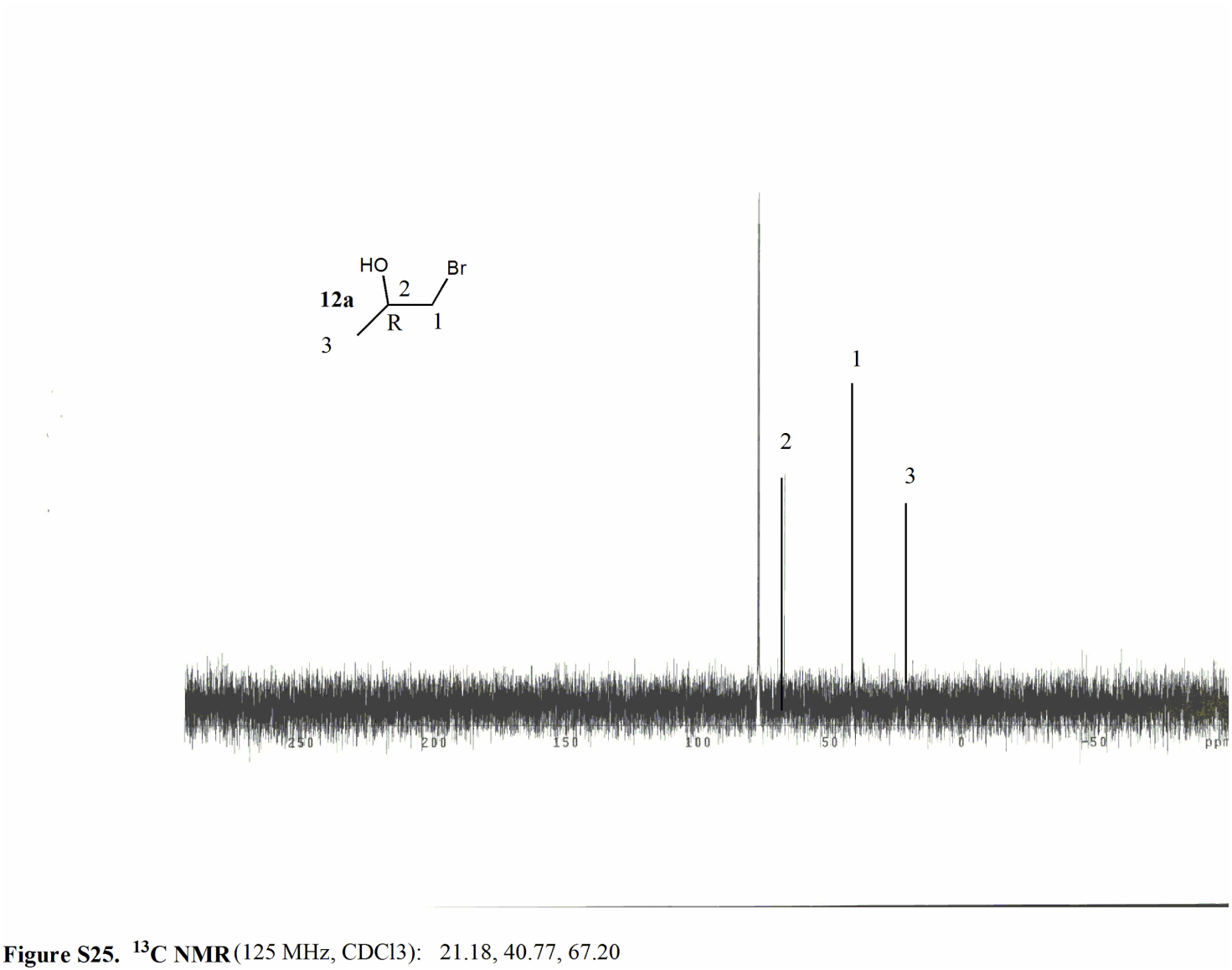


Figure S25. **^{13}C NMR** (125 MHz, CDCl3): 21.18, 40.77, 67.20

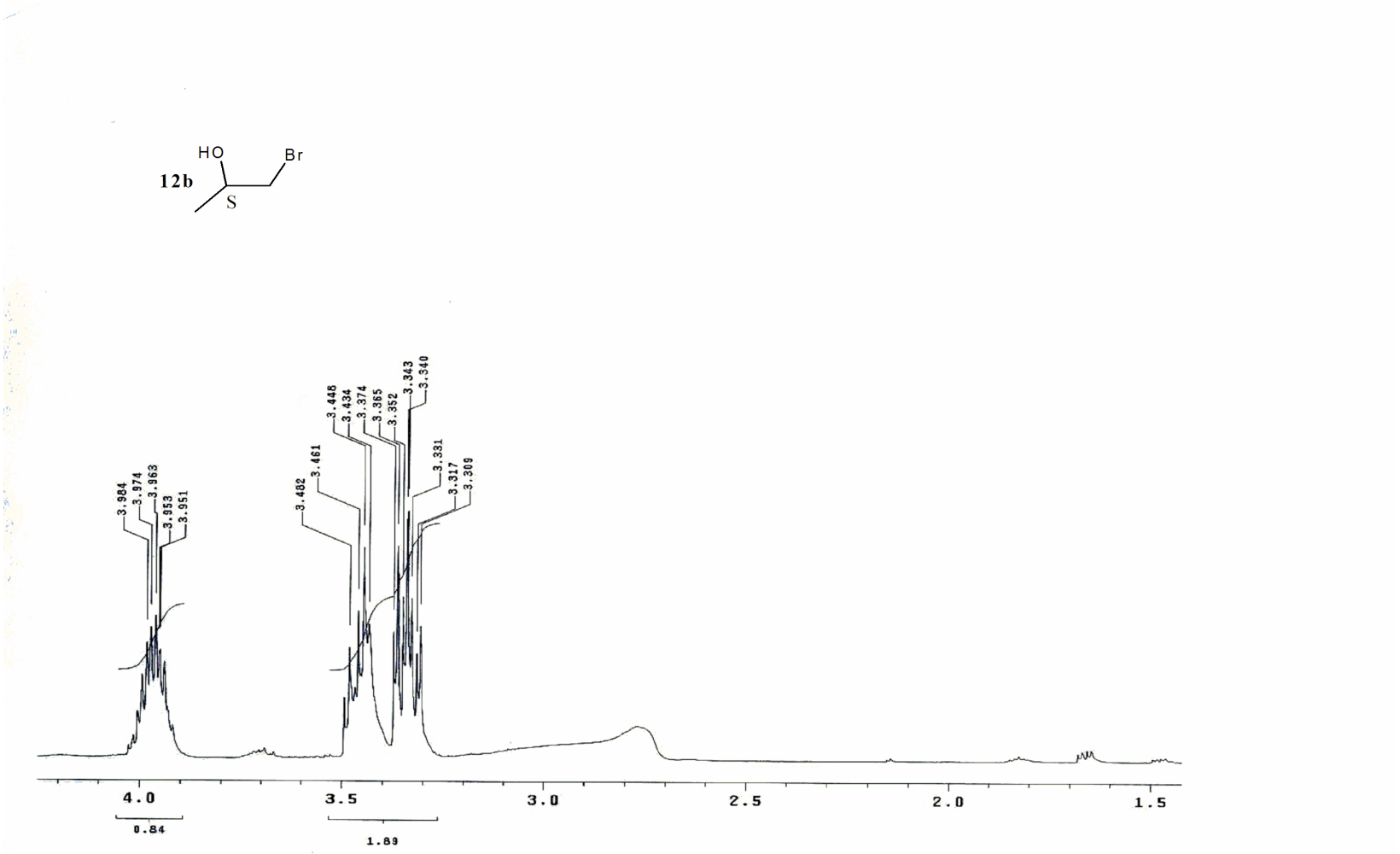


Figure S26. **^{1}H NMR** (500 MHz, CDCl3) 1.28-1.36 (d, 3H, methyl, J = 6.0), 1.88 (br, 1H, -OH), 3.34-3.40 (m, 1H, methylene), 3.48-3.04 (m, 1H, methylene), 3.96-4.02 (m, 1H, methine)

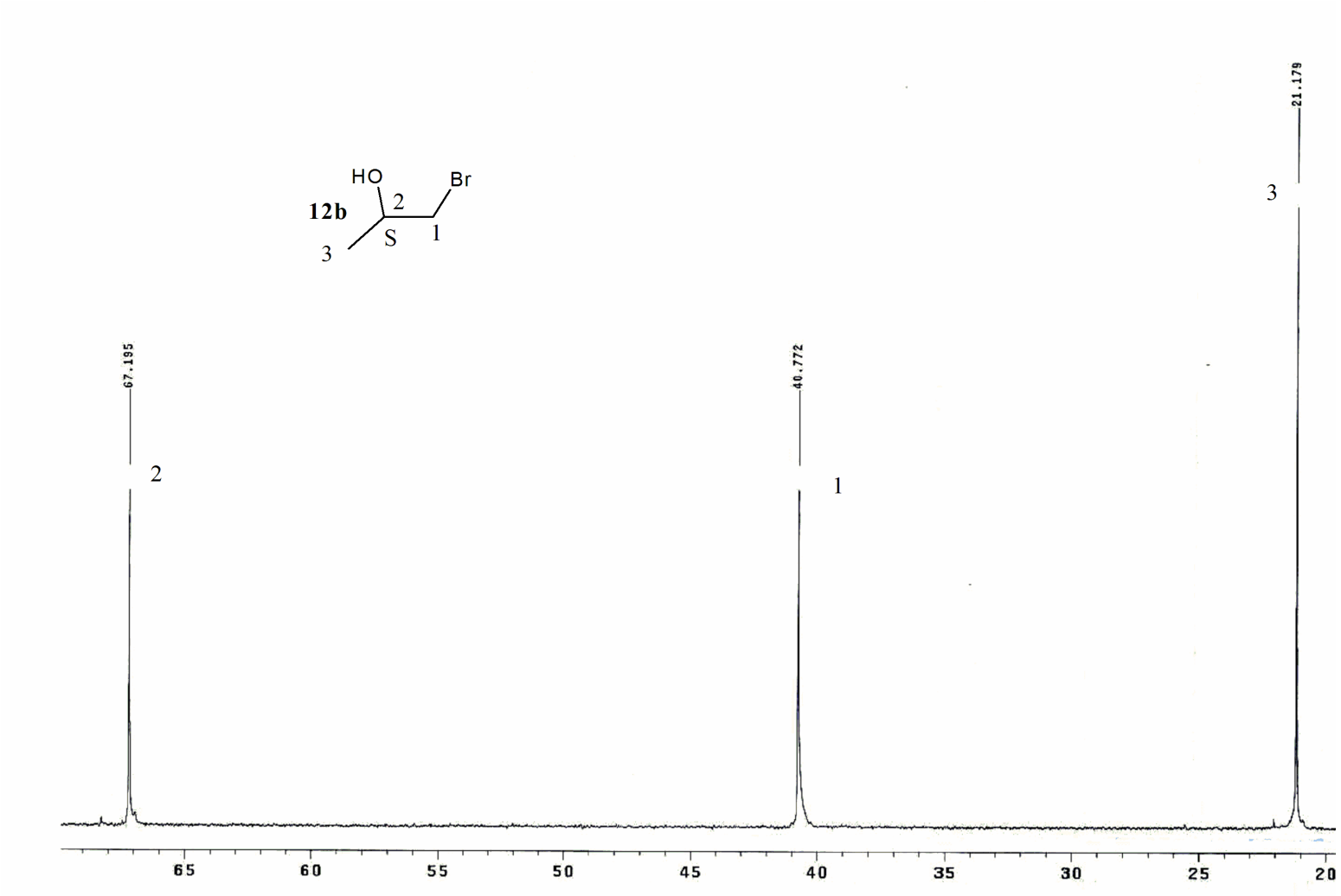


Figure S27. ^{13}**C NMR.** (125 MHz, CDCl3) 21.22, 41.50, 68.11

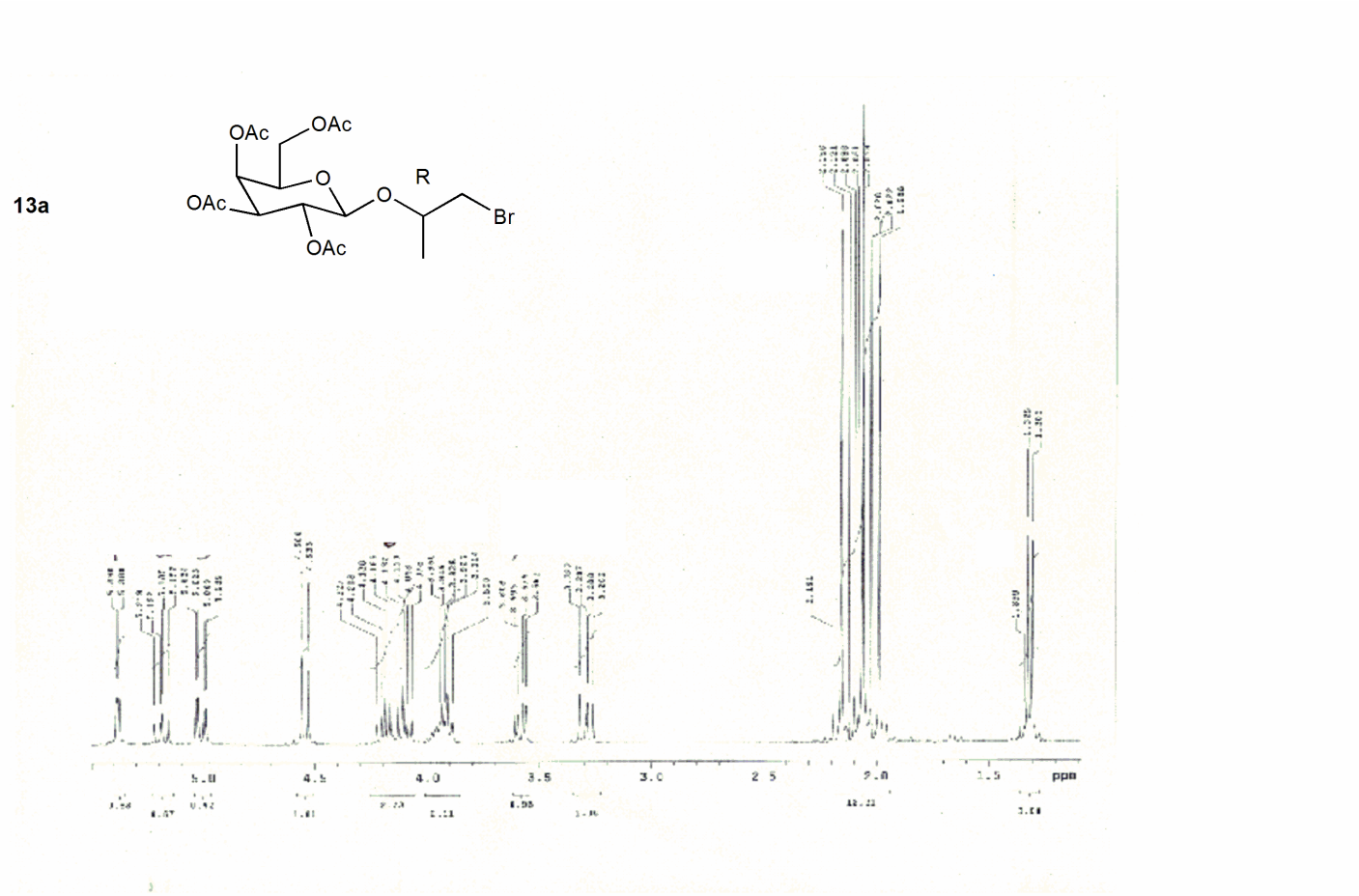


Figure S28. **^{1}H NMR** (500 MHz, CDCl3) 1.26-1.32 (d, 3H, methyl, J = 6.5), 1.85-2.32 (m, 12H, OAc), 3.24-3.32 (m, 1H, -CH2Br), 3.50-3.12 (m, 1H, -CH2Br), 3.89-4.02 (m, 2H, methine on linker, H-5), 4.05-4.22 (m, 2H, H-6), 4.52-4.64 (m, 1H, H-4), 4.98-5.08 (m, 1H, H-3), 5.24-5.34 (m, 1H, H-2), 5.40 (m, 1H, H-1)

13a

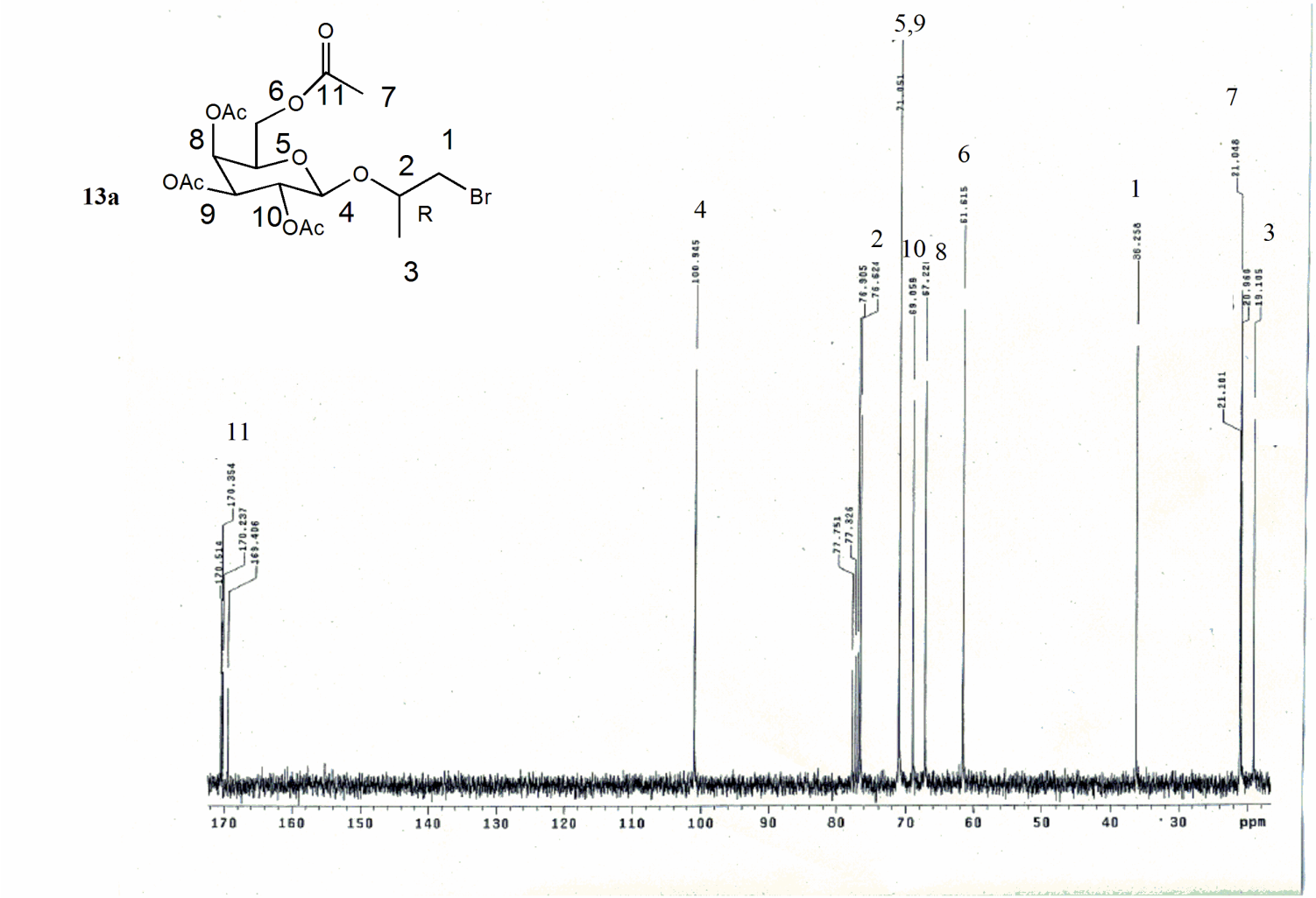


Figure S29. (125 MHz, CDCl3) 19.11, 20.96, 21.05, 21.10, 36.25, 61.62, 67.23, 69.06, 71.05, 76.62, 76.91, 100.95, 169.41, 170.24, 170.35, 170.52

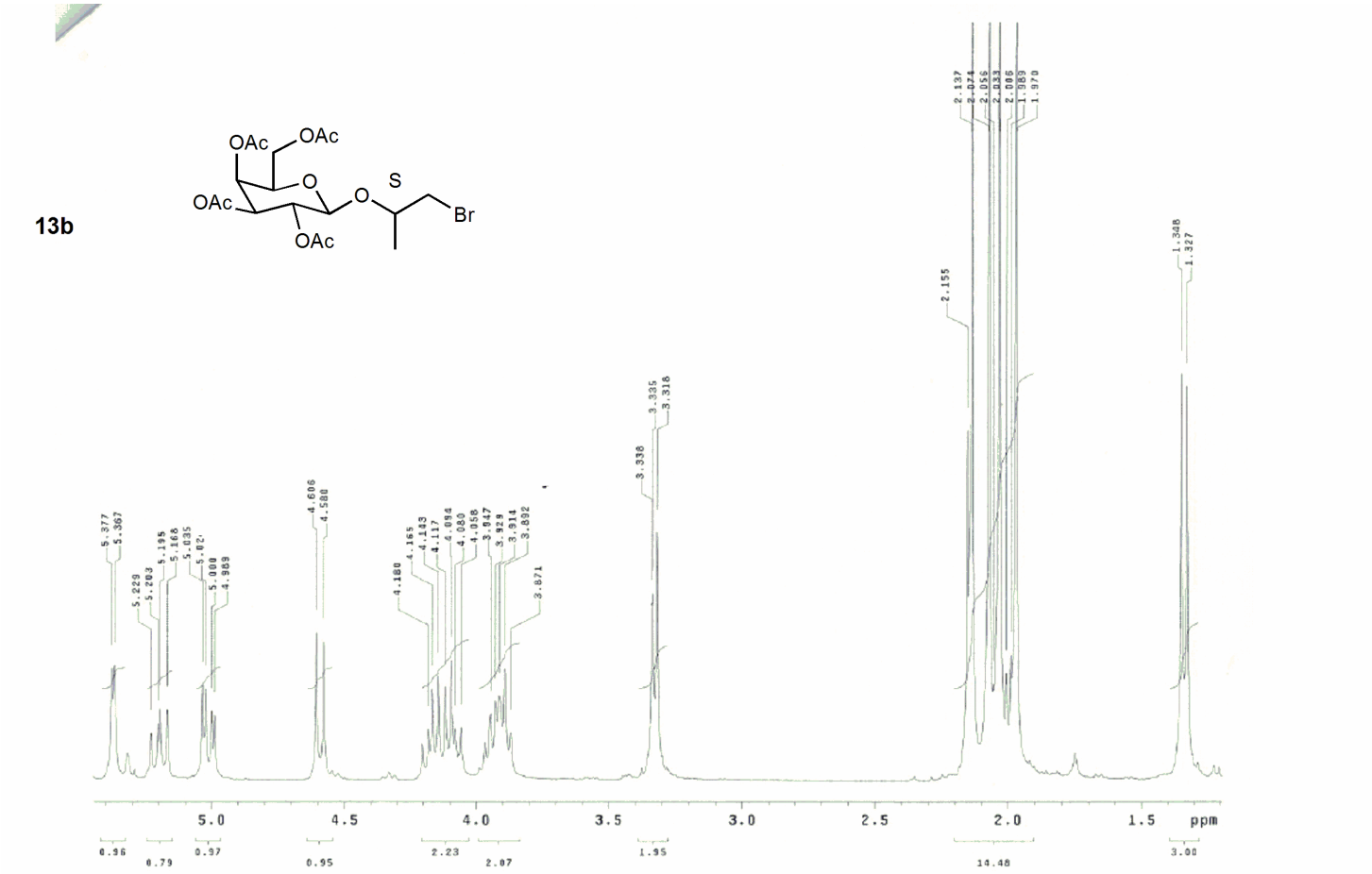


Figure S30. **^{1}H NMR** (500 MHz, CDCl3) 1.30-1.38 (d, 3H, methyl, J = 6.5), 1.98-2.40 (m, 12H, OAc), 3.28-3.36 (m, 2H, -CH2Br), 3.86-3.98 (m, 2H, methine on linker and H-5), 4.05-4.20 (m, 2H, H-6), 4.55-4.64 (m, 1H, H-4), 4.96-5.02 (m, 1H, H-3), 5.18-5.24 (m, 1H, H-2), 5.38 (m, 1H, H-1)

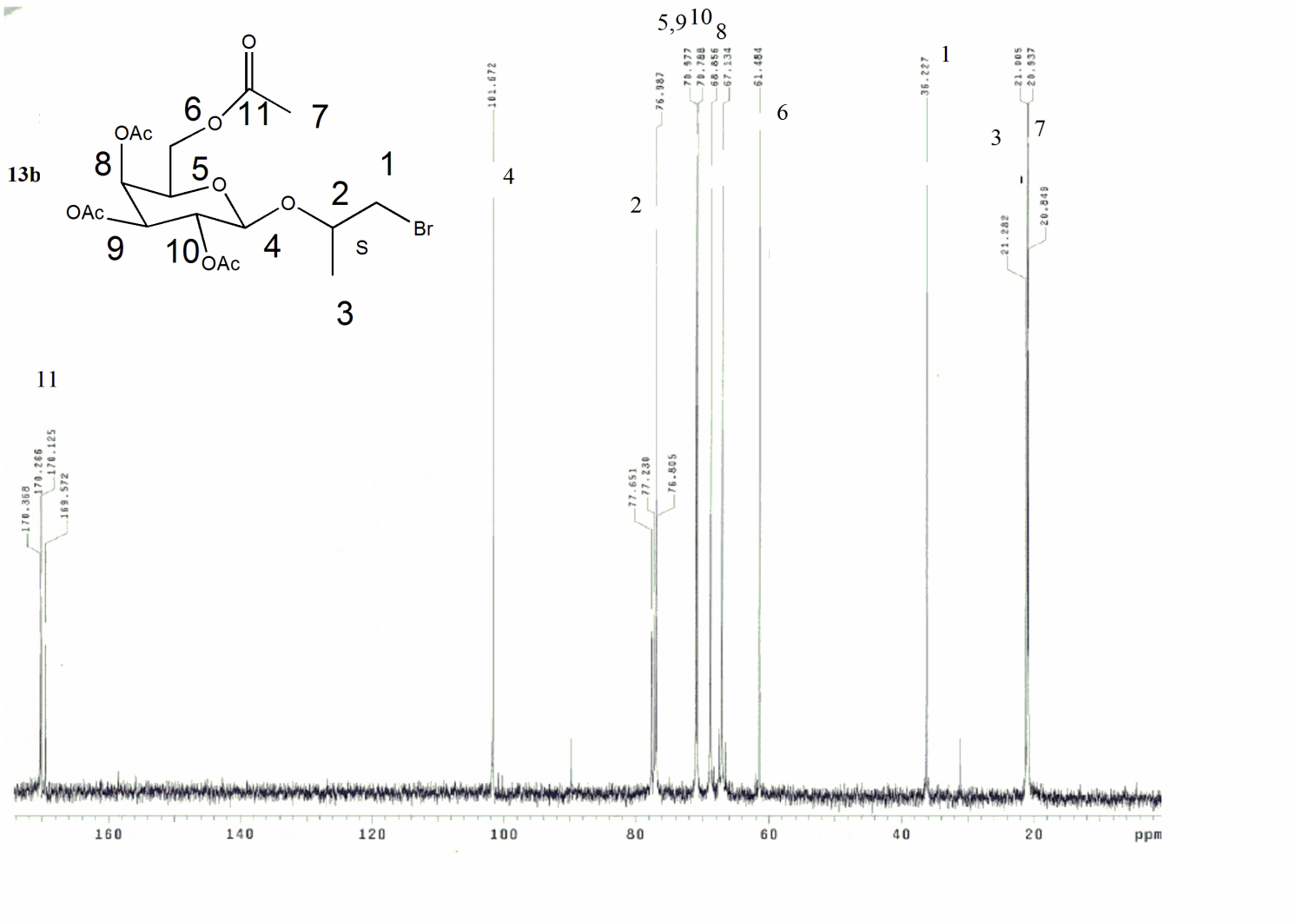


Figure S31. (125 MHz, CDCl3) 20.85, 20.94, 21.01, 21.28, 36.23, 61.18, 67.13, 68.86, 70.79, 70.98, 76.98, 101.67, 168.57, 176.13, 170.27, 170.37

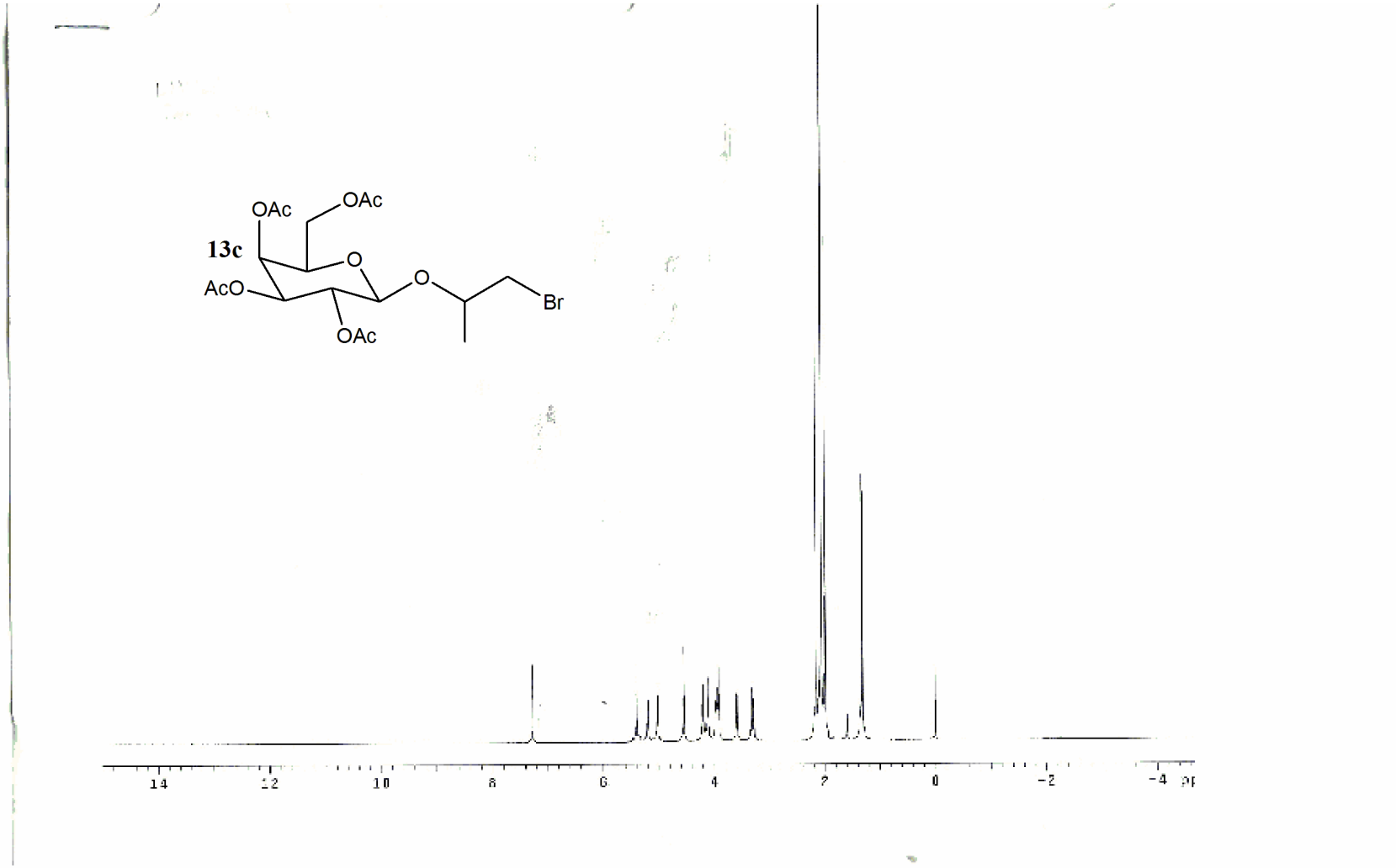


Figure S32. **^{1}H NMR.** (500 MHz, CDCl3) 1.33-1.38 (d, 3H, methyl, J = 6.5), 1.92-2.20 (m, 12H, OAc), 3.32-3.40 (m, 1H, -CH2Br), 3.42-3.48 (m, 1H, -CH2Br), 3.88-3.98 (m, 2H, methine on linker and H-5), 4.12-4.20 (m, 2H, H-6), 4.50-4.58 (m, 1H, H-4), 4.98-5.10 (m, 1H, H-3), 5.28-5.40 (m, 2H, H-1 and H-2).

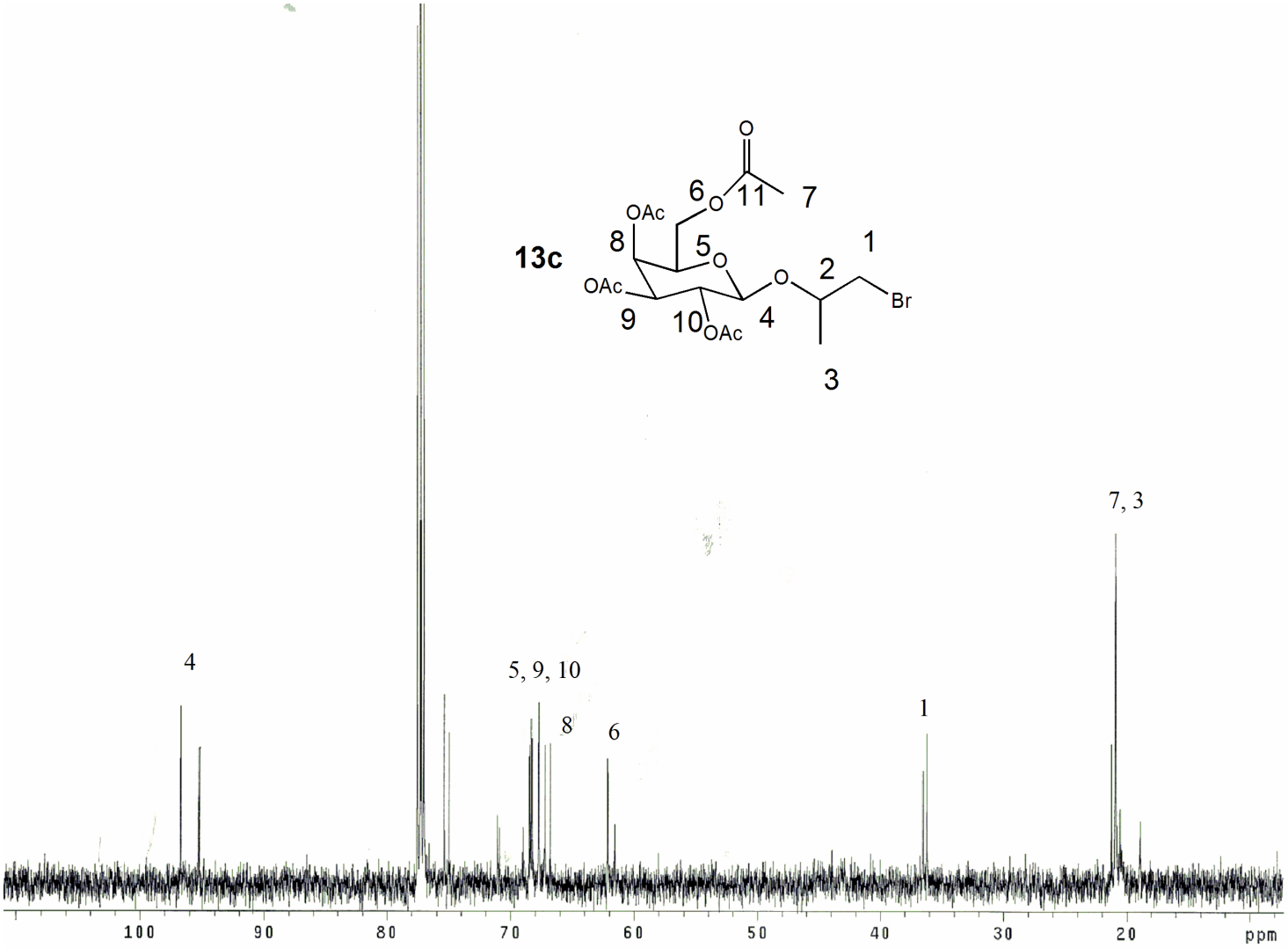


Figure S33. ^{13}**C NMR** (125 MHz, CDCl3) 18.92, 20.55, 20.89, 20.92, 20.98, 36.18, 36.52, 61.54, 62.09, 62.14, 66.77, 67.17, 67.66, 67.71, 68.22, 68.30, 68.39, 68.47, 70.87, 71.03, 75.00, 75.37, 95.25, 96.70, 170.46, 170.67, 170.69, 170.88