

2,4,6-Trichloro-1,3,5-triazine (TCT) mediated one-pot sequential functionalisation of glycosides for the generation of orthogonally protected monosaccharide building blocks

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General information: ^1H and ^{13}C NMR spectra were recorded on 200, 400 and 500 MHz spectrometers with TMS as the internal standard. Chemical shifts are expressed in parts per million (δ ppm). Silica gel coated aluminium plates were used for TLC. The products were purified by column chromatography on silica gel (60-120/100-200 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. Elemental analyses were performed on Elementar. Reagents used were mostly purchased from Sigma Aldrich.

General procedure for 4,6-*O*-arylidene: To a mixture (suspension) of unprotected saccharide (1 mmol) and arylidene dimethyl acetal (1.2 mmol) in CH_3CN (5 mL) was added TCT (0.3 mmol). The reaction mixture was subjected to sonication at 60 $^\circ\text{C}$ for 10 minutes under a nitrogen atmosphere. The completion of the reaction was monitored through TLC. The solvent was evaporated and the residue was purified by flash chromatography to give the corresponding 4,6-*O*-arylidene product.

General procedure for one-pot 4,6-*O*-arylidene/acetylation reaction:

To a mixture (suspension) of unprotected saccharide (1 mmol) and arylidene dimethyl acetal (1.2 mmol) in CH_3CN (5 mL) was added TCT (0.3 mmol). The reaction mixture was subjected to sonication at 60 $^\circ\text{C}$ for 10 minutes under a nitrogen atmosphere. Acetic anhydride (3 mmol) was then added and the obtained solution was stirred for a further 8 hours at 90 $^\circ\text{C}$ under sonication. Acetonitrile was evaporate and DCM (30 mL) was added. The reaction mixture was filtered and the filtrate was concentrated to yield the crude product. The crude product was purified by column chromatography to give the corresponding protected monosaccharides.

General procedure for one-pot 4,6-*O*-arylidene/acetylation/reductive ring opening reaction:

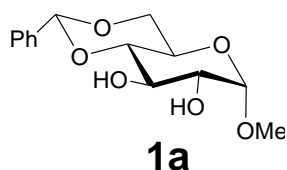
To a mixture (suspension) of unprotected saccharide (1 mmol) and arylidene dimethyl acetal (1.2 mmol) in CH_3CN (5 mL) was added TCT (0.3 mmol). The reaction mixture was subjected to sonication at 60 $^\circ\text{C}$ for 10 minutes under a nitrogen atmosphere. Acetic anhydride (3 mmol) and additional 0.2 mmol of TCT was then added and the obtained solution was stirred for a further 8 hours at 90 $^\circ\text{C}$ under sonication to get completely acetylated product followed by the addition of 8 equiv. of NaCNBH_3 and additional 6 mmol of TCT. The reaction mixture was allowed to stirred at 90 $^\circ\text{C}$ for further 6h. The completion of the reaction was monitored through TLC. The reaction mixture was passed through short celite pad and washed with 20 mL of DCM. The filtrate was evaporated to yield the crude

product which was subjected to column chromatography to yield the corresponding orthogonally protected monosaccharides.

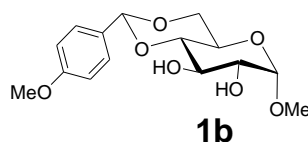
Procedure for large scale benzylidene protection:

To a mixture (suspension) of unprotected saccharide (20 grams) and arylidene dimethyl acetal (1.2 mol) in CH₃CN (50 mL) was added TCT (10 mol%). The reaction mixture was subjected to sonication at 60 °C for 0.5 h under a nitrogen atmosphere. The completion of the reaction was monitored through TLC. The solvent was evaporated and the residue was purified by flash chromatography to give the corresponding 4,6-*O*-arylidene product.

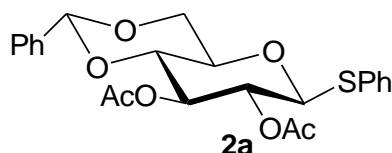
Spectral Analysis:



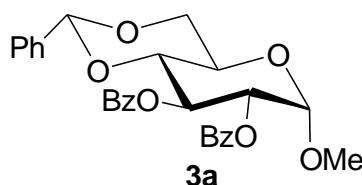
Methyl 4,6-*O*-benzylidene- α -D-glucopyranoside 1a. Prepared by general procedure **1** using methyl- α -D-glucopyranoside **1** (194 mg, 1mmol) to give the corresponding product **1a** in >99% yield. IR (CHCl₃) ν 3368, 2940, 1452, 1372, 1074, 1040, 999, 748, 696 cm⁻¹. ¹H NMR (200MHz, MeOD), δ , 7.40-7.33 (m, 5H, Ar), 5.37 (s, 1H, PhCH), 4.65 (d, J = 3.3 Hz, 1H, H-1), 3.83-3.70 (m, 1H), 3.67-3.50 (m, 4H), 3.66-3.65 (m, 1H), 3.40 (bs, 3H, -OMe). ¹³C NMR (50MHz, MeOD), δ , 137.0, 129.2, 128.2 x 2, 126.3 x 2, 101.8, 99.8, 80.9, 72.7, 71.4, 68.8, 62.3, 55.4. ESI MS (m/z): 305 [M+Na]. Anal. Cal.for C₁₄H₁₈O₆: C, 59.57, H, 6.43; Found: C, 59.50, H, 6.52.



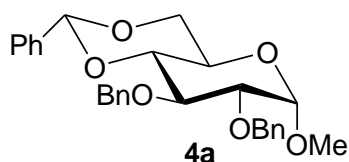
Methyl 4,6-*O*-*p*-methoxybenzylidene- α -D-glucopyranoside 1b. Prepared by general procedure **1** using methyl- α -D-glucopyranoside **1** (194 mg, 1 mmol) to give the corresponding product **1b** in >99% yield. IR (CHCl₃) ν 3362, 2491, 1370, 1043, 997 cm⁻¹; ¹H NMR (200MHz, MeOD), δ , 7.89 (d, J = 8.5 Hz, 1H, Ar), 7.35 (d, J = 8.5 Hz, 1H, Ar), 7.10 (d, J = 8.5 Hz, 1H, Ar), 6.92 (d, J = 8.5 Hz, 1H, Ar), 5.31 (s, PhCH), 4.68 (d, J = 3.4 Hz, 1H, H-1), 3.89-3.71 (m, 3H), 3.67-3.49 (m, 2H), 3.40 (bs, 3H, -OMe), 3.36-3.32 (m, 1H). ¹³C NMR (50MHz, MeOD), δ , 160.2, 129.6, 127.6 x 2, 113.7 x 2, 101.9, 99.8, 81.0, 72.7, 68.9, 62.4, 55.5, 55.3. ESI MS (m/z): 335 [M+Na]. Anal. Cal.for C₁₅H₂₀O₇: C, 57.69, H, 6.45; Found: C, 57.77, H, 6.53.



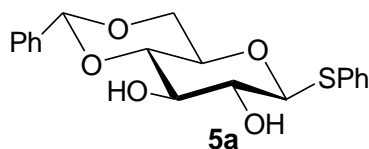
Prepared by general procedure **1** using thiophenyl- β -D-glucopyranoside **2** (356 mg, 1 mmol) to give the corresponding product **2a** in 99% yield. The spectroscopic data was found in agreement with the reported one.^{S1}



Prepared by general procedure **1** using methyl- α -D-glucopyranoside **3** (374 mg, 1 mmol) to give the corresponding product **3a** in 93% yield. IR (CHCl₃) ν 3066, 2934, 2863, 1728, 1602, 1584, 1482, 1416, 1451, 1377, 1276, 1096, 996, 751, 710 cm⁻¹; ¹H NMR (200 MHz, CDCl₃), δ , 8.01-7.92 (m, 5H, Ar), 7.51-7.29 (m, 10H, Ar), 6.06 (t, J = 9.7 Hz, 1H), 5.57 (s, 1H, PhCH), 5.28 (d, J = 3.3 Hz, 1H, H-1), 5.21-5.17 (m, 2H), 4.39 (dd, J = 4.4, 10.0 Hz, 1H), 4.12-3.60 (m, 2H), 3.43 (bs, 3H, -OMe). ¹³C NMR (50MHz, MeOD), δ , 166.6, 165.5, 136.9, 133.6, 133.3, 129.9, 129.8 x 2, 129.7, 129.6 x 2, 129.0 x 2, 128.4 x 2, 128.2 x 2, 128.1 x 2, 126.1, 101.6, 97.8, 79.4, 72.5, 69.5, 68.9, 62.5, 55.6. ESI MS (m/z): 335 [M+Na]. Anal. Cal. for C₂₈H₂₆O₈: C, 68.56, H, 5.34; Found: C, 68.59, H, 5.39.

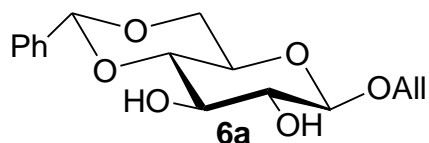


Prepared by general procedure **1** using methyl- α -D-glucopyranoside **4** (402 mg, 1 mmol) to give the corresponding product **4a** in 98% yield. The spectroscopic data was found in agreement with the reported one.^{S3}

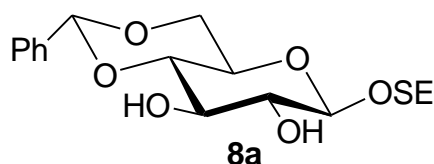


Prepared by general procedure **1** using thiophenyl- β -D-glucopyranoside **5** (272 mg, 1 mmol) to give the corresponding product **5a** in 95% yield. IR (CHCl₃) ν 3381, 2920, 1583, 1451, 1370, 1106, 1069, 985, 743, 697 cm⁻¹; ¹H NMR (200MHz, MeOD), δ , 7.57-7.30 (m, 5H, Ar), 5.56 (s, 1H, PhCH), 4.73 (d, J = 10 Hz, 1H, H-1), 4.26 (dd, J = 4.0, 10.0 Hz, 1H), 3.74-3.62

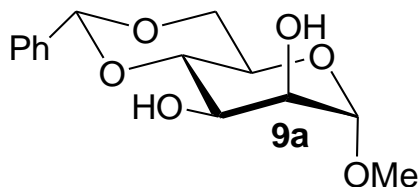
(m, 2H), 3.49-3.43 (m, 2H), 3.34-3.33 (m, 1H). ^{13}C NMR (50MHz, MeOD), δ , 136.8, 133.0 x 2, 131.2, 129.3, 129.1 x 2, 128.4, 128.3 x 2, 126.2 x 2, 101.9, 88.5, 80.5, 74.5, 72.5, 70.5, 68.5. ESI MS (m/z): 383 [M+Na]. Anal. Cal. for $\text{C}_{19}\text{H}_{20}\text{O}_5\text{S}$: C, 63.32, H, 5.59; Found: C, 63.39, H, 5.67.



Prepared by general procedure **1** using allyl- β -D-glucopyranoside **6** (220 mg, 1 mmol) to give the corresponding product **6a** in 99% yield. IR (CHCl_3) ν 3509, 2925, 2864, 1606, 1452, 1085, 928, 771, 748 cm^{-1} ; ^1H NMR (400MHz, MeOD), δ , 7.52-7.50 (m, 2H, Ar), 7.40-7.38 (m, 2H, Ar), 5.96-5.94 (m, 1H), 5.55 (bs, 1H), 5.38 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.34 (dd, $J = 1.2, 17.2$ Hz, 1H), 4.48 (d, $J = 7.6$ Hz, 1H), 4.40-4.37 (m, 2H), 4.18 (dd, $J = 6.0, 12.4$ Hz, 1H), 3.86-3.60 (m, 3H). ^{13}C NMR (50MHz, MeOD), δ , 136.9, 133.4, 129.3, 128.3 x 2, 126.2 x 2, 118.3, 102.1, 101.9, 80.5, 79.5, 74.5, 73.1, 70.6, 68.6, 66.3, 50.7. ESI MS (m/z): 331 [M+Na]. Anal. Cal. for $\text{C}_{16}\text{H}_{20}\text{O}_6$: C, 62.33, H, 6.54; Found: C, 62.39, H, 6.60.

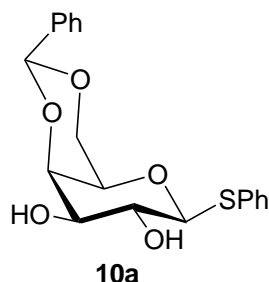


Prepared by general procedure **1** using silylethanol- β -D-glucopyranoside **8** (280 mg, 1 mmol) to give the corresponding product **8a** in 95% yield. ^1H NMR (200MHz, MeOD), δ , 7.46-7.36 (m, 5H, Ar), 5.55 (s, 1H, PhCH), 4.39 (d, $J = 7.6$ Hz, 1H, H-1), 4.24-4.21 (m, 1H), 3.94-3.90 (m, 2H), 3.79-3.60 (m, 4H), 3.45-3.42 (m, 2H), 0.99-0.97 (m, 2H), 0.03, 0.01, 0.001 (s, 3 x -Si(CH₃)₃). ESI MS (m/z): 274 [M+Na]. Anal. Cal. for $\text{C}_{13}\text{H}_{15}\text{O}_5$: C, 62.14, H, 6.02; Found: C, 62.19, H, 6.09.

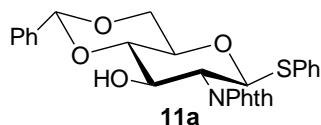


Prepared by general procedure **1** using methyl- α -D-mannopyranoside **9** (194 mg, 1 mmol) to give the corresponding product **9a** in 98% yield. IR (CHCl_3) ν 3400, 3060, 2869, 1583, 1480, 1439, 1402, 1362, 1099, 1069, 1026, 997, 817, 735, 696 cm^{-1} ; ^1H NMR (200MHz, MeOD), δ , 7.50-7.32 (m, 5H, Ar), 5.59 (s, 1H, PhCH), 4.66 (bs, 1H, H-1), 4.23 (dd, $J = 4.0, 10.0$ Hz, 1H), 3.89-3.74 (m, 5H), 3.38 (bs, 3H, -OMe). ^{13}C NMR (50MHz, MeOD), δ , 137.8,

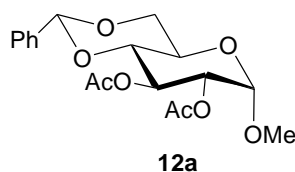
128.7, 127.9 x 2, 126.2 x 2, 101.9, 101.1, 78.4, 70.7, 67.9, 67.5, 63.6, 54.2. ESI MS (m/z): 305 [M+Na]. Anal. Cal. for C₁₄H₁₈O₆: C, 59.57, H, 6.43; Found: C, 59.54, H, 6.55.



Prepared by general procedure **1** using thiophenyl-β-D-galactopyranoside **10** (272 mg, 1 mmol) to give the corresponding product **10a** in 96% yield. IR (CHCl₃) ν 3368, 2872, 1583, 1480, 1362, 1069, 734, 695 cm⁻¹; ¹H NMR (200MHz, MeOD), δ, 7.65-7.26 (m, 10H, Ar), 5.58 (s, 1H, PhCH), 4.60 (d, *J* = 9.3 Hz, 1H, H-1), 4.18 (dd, *J* = 1.2, 6.9 Hz, 1H), 3.73-3.56 (m, 4H), 3.32-3.29 (m, 1H). ¹³C NMR (50MHz, MeOD), δ, 138.5, 133.8, 130.4 x 2, 128.6, 128.5 x 2, 127.7 x 2, 126.4, 126.2 x 2, 105.8, 88.0, 75.9, 73.0, 69.0, 68.5, 67.8. ESI MS (m/z): 383 [M+Na]. Anal. Cal. for C₁₉H₂₀O₅S: C, 63.32, H, 5.59; Found: C, 63.37, H, 5.70.

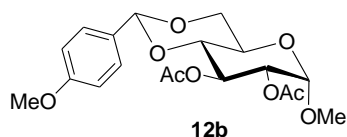


Prepared by general procedure **1** using 2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside **11** (401 mg, 1 mmol) to give the corresponding product **11a** in 70% yield. The spectroscopic data was found in agreement with the reported one.^{S1}

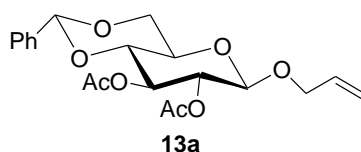


Prepared by general procedure **2** using methyl-α-D-glucopyranoside **1** (194 mg, 1 mmol) to give the corresponding product **12a** in 95% yield. IR (CHCl₃) ν 2933, 1753, 1451, 1372, 1241, 1224, 1033, 974, 891cm⁻¹; ¹H NMR (CDCl₃, 200MHz), δ, 7.46-7.34 (m, 5H, Ar), 5.51 (bs, 1H), 5.59 (t, *J* = 9.2 Hz, 1H), 4.95 (d, *J* = 3.0 Hz, 1H), 4.90 (bd, *J* = 3.0Hz, 1H), 4.32 (dd, *J* = 4.4, 9.8 Hz, 1H), 4.00-3.60 (m, 3H), 4.42 (bs, 3H, -OMe), 2.10 (s, 3H, -OAc), 2.06 (s, 3H, -OAc). ¹³C NMR (50MHz, MeOD), δ, 166.6, 165.6, 136.9, 129.6, 129.0, 128.4, 128.2, 126.1,

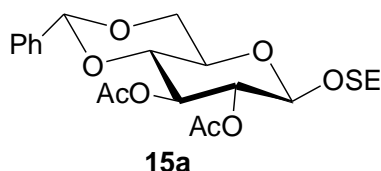
101.6, 97.8, 79.4, 72.5, 69.5, 68.9, 62.5, 55.7, 23.7, 22.9. ESI MS (m/z): 389 [M+Na]. Anal. Cal. for C₁₈H₂₂O₈: C, 59.01, H, 6.05; Found: C, 59.09, H, 6.10.



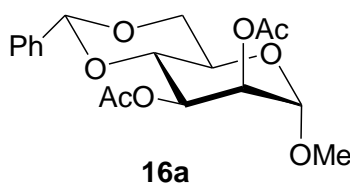
Prepared by general procedure **2** using methyl- α -D-mannopyranoside **9** (194 mg, 1 mmol) to give the corresponding product **16b** in 80% yield. IR (CHCl₃) ν 2937, 1751, 1615, 1589, 1432, 1371, 1056, 1034, 990, 831 cm⁻¹; ¹H NMR (200 MHz, CDCl₃), δ , 7.39 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 5.62 (t, J = 9.4 Hz, 1H), 5.74 (s, 1H), 4.93–4.87 (m, 2H), 4.30 (dd, J = 4.3, 10.0 Hz, 1H), 3.91 (dd, J = 4.3, 10.0 Hz, 1H), 3.80 (bs, 3H, -OMe, Ar), 3.70 (bs, 3H, -OMe), 2.10 (bs, 3H, -OAc), 2.05 (s, 3H, -OAc), ¹³C NMR (CDCl₃, 50 MHz), δ , 170.4, 169.7, 160.1, 129.5, 127.5 x 4, 113.6, 101.5, 97.6, 79.2, 71.6, 69.0, 68.8, 62.4, 55.3, 55.2, 20.8, 20.7. ESI MS (m/z): 419 [M+Na]. Anal. Cal. for C₁₉H₂₄O₉: C, 57.57, H, 6.10; Found: C, 57.50, H, 6.18.



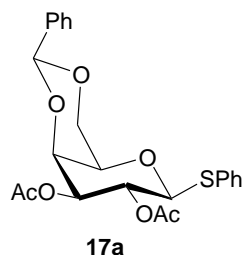
Prepared by general procedure **2** using allyl- α -D-glucopyranoside **6** (220 mg, 1 mmol) to give the corresponding product **13a** in 95% yield. IR (CHCl₃) ν 2924, 1749, 1458, 1374, 1238, 1222, 1090, 1060, 992, 762, 695 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz), δ , 7.44–7.41 (m, 2H, Ar), 7.35–7.34 (m, 3H, Ar), 5.97–5.95 (m, 1H), 5.50 (bs, 1H), 5.34–5.29 (m, 2H), 5.03 (dd, J = 8, 11.8 Hz, 1H), 4.64 (d, J = 8.0 Hz, 1H), 4.38–4.31 (m, 2H), 4.11 (dd, J = 6.0, 13.2 Hz, 1H), 3.80 (t, J = 10.4 Hz, 1H), 3.70 (t, J = 9.6 Hz, 1H), 3.54–3.48 (m, 1H), 2.06 (bs, 3H, -OAc), 2.04 (bs, 3H, -OAc). ¹³C NMR (50 MHz, MeOD), δ , 170.1, 169.5, 136.8, 133.3, 129.1, 128.2 x 2, 126.1 x 2, 117.6, 101.5, 100.3, 78.3, 71.8, 70.2, 68.6, 66.3, 20.7, 20.6. ESI MS (m/z): 415 [M+Na]. Anal. Cal. for C₂₀H₂₄O₈: C, 61.22, H, 6.16; Found: C, 61.29, H, 6.10



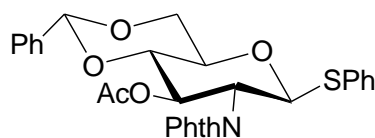
Prepared by general procedure **2** using silylethanol- β -D-glucopyranoside **8** (280 mg, 1 mmol) to give the corresponding product **15a** in 95% yield. ^1H NMR (200 MHz, CDCl_3), δ , 7.47-7.33 (m, 5H, Ar), 5.50 (bs, 1H, PhCH), 5.36-5.27 (m, 2H), 4.99 (t, $J = 8.0$ Hz, 1H), 4.61 (d, $J = 8.0$ Hz, 1H), 4.39 (dd, $J = 4.8, 10.4$ Hz, 1H), 4.04-3.99 (m, 2H), 3.86-3.56 (m, 2H), 2.05, 2.04 (s, 6H, 2 x $-\text{OAc}$), 1.03-0.91 (m, 2H), 0.07, 0.02, 0.01 (s, 9H, $-\text{Si}(\text{CH}_3)_3$). ESI MS (m/z): 358 $[\text{M}+\text{Na}]$. Anal. Cal. for $\text{C}_{17}\text{H}_{19}\text{O}_7$: C, 60.89, H, 5.71; Found: C, 60.80, H, 5.79.



Prepared by general procedure **2** using methyl- α -D-mannopyranoside **9** (194 mg, 1 mmol) to give the corresponding product **16a** in 95% yield. IR (CHCl_3) ν 1750, 1456, 1370, 1242, 1220, 1030, 894, 759 cm^{-1} ; ^1H NMR (200MHz, CDCl_3), δ , 7.47-7.26 (m, 5H, Ar), 5.58 (bs, 1H), 5.43-5.34 (m, 2H), 4.67 (d, $J = 3.3$ Hz, 1H), 4.31 (dd, $J = 2.7, 8.6$ Hz, 1H), 4.05-3.81 (m, 3H), 3.41 (bs, 3H, $-\text{OMe}$), 2.17 (s, 3H, $-\text{OAc}$), 2.02 (s, 3H, $-\text{OAc}$). ^{13}C NMR (CDCl_3 , 50MHz), δ , 169.9, 169.8, 137.2, 129.6, 128.4 x 2, 126.9 x 2, 101.9, 98.3, 75.7, 70.1, 68.7, 68.3, 63.8, 55.1, 20.8, 20.7. ESI MS (m/z): 389 $[\text{M}+\text{Na}]$. Anal. Cal. for $\text{C}_{18}\text{H}_{22}\text{O}_8$: C, 59.01, H, 6.05; Found: C, 59.09, H, 6.11.

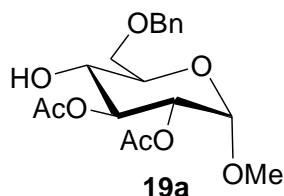


Prepared by general procedure **2** using thio- β -D-galactopyranoside **10** (272 mg, 1 mmol) to give the corresponding product **17a** in 95% yield. The spectroscopic data was found in agreement with the reported one.^{S1}



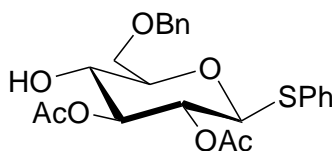
18a

Prepared by general procedure **2** using 2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside **11** (401 mg, 1 mmol) to give the corresponding product **18a** in 95% yield. The spectroscopic data was found in agreement with the reported one.^{S1}



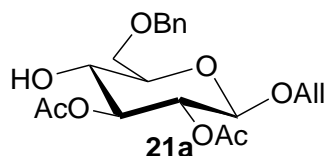
19a

Prepared by general procedure **3** using methyl- α -D-glucopyranoside **1** (194 mg, 1 mmol) to give the corresponding product **19a** in 95% yield. The spectroscopic data was found in agreement with the reported one.^{S2} IR (CHCl₃) ν 3462, 2922, 1747, 1496, 1453, 1371, 1241, 1053 cm⁻¹; ¹H NMR (400MHz, CDCl₃), δ , 7.37-7.29 (m, 5H, -Ar), 5.30 (t, J = 10.0 Hz, 1H), 4.91 (d, J = 3.6 Hz, 1H), 4.87 (dd, J = 3.6, 10.4 Hz, 1H), 4.61 (dd, J = 12.0, 20.4 Hz, 2H), 3.82-3.72 (m, 4H), 3.39 (bs, 3H, -OMe), 2.09 (s, 3H, -OAc), 2.07 (s, 3H, -OAc). ¹³C NMR (CDCl₃, 50MHz), δ , 171.0, 170.3, 137.9, 128.4, 127.9, 127.8, 127.7, 127.6, 97.0, 73.7, 70.7, 70.3, 70.7, 69.4, 53.9. ESI MS (m/z): 381 [M+Na]. Anal. Cal. for C₁₈H₂₄O₈: C, 58.69, H, 6.57; Found: C, 58.61, H, 6.70.

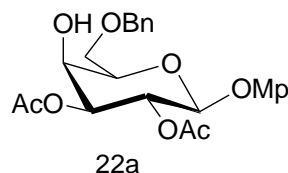


20a

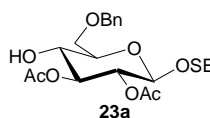
Prepared by general procedure **3** using thio- β -D-glucopyranoside **5** (272 mg, 1 mmol) to give the corresponding product **20a** in 85% yield. The spectroscopic data was found in agreement with the reported one.^{S1}



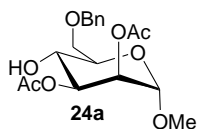
Prepared by general procedure **3** using allyl- β -D-glucopyranoside **6** (220 mg, 1 mmol) to give the corresponding product **21a** in 85% yield. IR (CHCl₃) ν 3467, 2925, 2858, 1751, 1496, 1454, 1367, 1242, 1221, 1055 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ , 7.34-7.30 (m, 5H, Ar), 5.94-5.75 (m, 1H), 5.30-5.10 (m, 2H), 5.00-4.85 (m, 2H), 4.68-4.50 (m, 3H), 4.37-4.29 (m, 1H), 4.09 (dd, J = 6.0, 13.0 Hz, 1H), 3.80-3.72 (m, 3H), 3.55 (dd, J = 4.6, 9.4 Hz, 1H), ¹³C NMR (CDCl₃, 50MHz), δ , 171.6, 170.3, 137.7, 133.5, 128.4 x 2, 127.7 x 2, 117.3, 99.5, 94.8, 75.6, 74.2, 73.1, 71.4, 70.7, 69.8, 68.3, 20.9, 20.7. ESI MS (m/z): 417 [M+Na]. Anal. Cal. for C₂₀H₂₆O₈: C, 60.90, H, 6.64; Found: C, 60.98, H, 6.69.



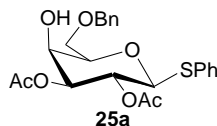
Prepared by general procedure **3** using *p*-methoxybenzyl- β -D-glucopyranoside **7** (286 mg, 1 mmol) to give the corresponding product **22a** in 87% yield. The spectroscopic data was found in agreement with the reported one.^{S2}



Prepared by general procedure **3** using silylethanol- β -D-glucopyranoside **8** (280 mg, 1 mmol) to give the corresponding product **23a** in 95% yield. IR (CHCl₃) ν 3461, 3952, 1753, 4996, 1419, 1365, 1247, 1222, 1055, 859, 838 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ , 7.33-7.27 (m, 5H, Ar), 5.03 (t, J = 9.2 Hz, 1H), 4.88 (dd, J = 8.0, 9.6 Hz, 1H), 4.59 (d, J = 6.4 Hz, 2H), 4.48 (d, J = 7.6 Hz, 1H), 3.96 (ddd, J = 5.6, 10.0, 15.6 Hz, 1H), 3.78 (d, J = 4.8 Hz, 2H), 3.73 (d, J = 9.6 Hz, 1H), 3.57-3.56 (m, 2H), 2.05 (s, 3H, -OAc), 2.02 (s, 3H, -OAc), 0.96-0.88 (m, 2H), -0.00 (bs, 9H, -Si(CH₃)₃). ¹³C NMR (CDCl₃); δ , 172.7, 171.0, 139.0, 129.0, 129.8, 129.3, 129.2, 129.1, 101.5, 77.2, 75.1, 75.0, 72.9, 72.0, 71.4, 68.1, 22.2, 22.1, 19.3, -0.0. ESI MS (m/z): 477 [M+Na]. Anal. Cal. for C₂₂H₃₄O₈Si: C, 58.13, H, 7.54; Found: C, 58.19, H, 7.59.



Prepared by general procedure **3** using methyl- α -D-mannopyranoside **9** (194 mg, 1 mmol) to give the corresponding product **24a** in 98% yield. IR (CHCl₃) ν 3467, 2917, 1749, 1496, 1453, 1370, 1245, 1225, 1054, 1080 cm⁻¹; ¹H NMR (200MHz, CDCl₃), δ , 7.27-7.21 (m, 5H, Ar), 5.14-5.09 (m, 2H), 4.61-4.60 (m, 2H), 4.52 (dd, J = 11.4 Hz, 1H), 4.12-4.00 (m, 1H), 3.82-3.76 (m, 2H), 3.33 (s, 3H, -OMe), 2.02 (s, 3H, -OAc), 2.01 (s, 3H, -OAc). ¹³C NMR (50 MHz, CDCl₃), δ 171.5, 170.9, 138.5, 128.5, 128.4, 127.8, 127.7, 127.6, 99.4, 80.3, 75.1, 74.9, 74.8, 72.0, 69.0, 53.4, 20.2, 20.1. ESI MS (m/z): 391 [M+Na]. Anal. Cal. for C₁₈H₂₄O₈: C, 58.69, H, 6.57; Found: C, 58.72, H, 6.50

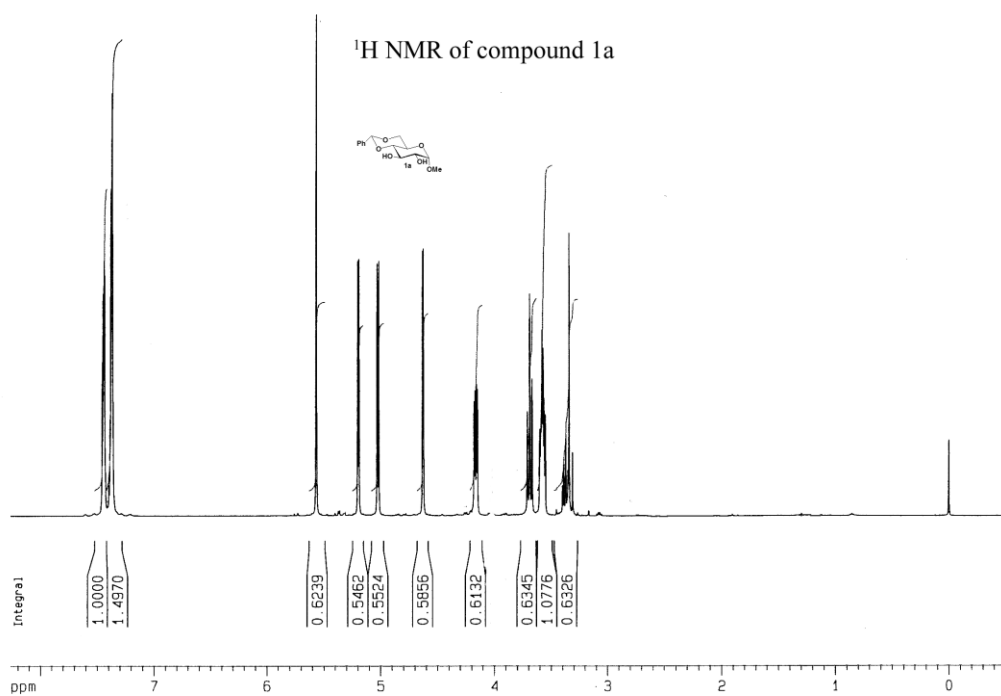


Prepared by general procedure **3** using thio- β -D-galactopyranoside **10** (272 mg, 1 mmol) to give the corresponding product **25a** in 96% yield. The spectroscopic data was found in agreement with the reported one.^{S1}

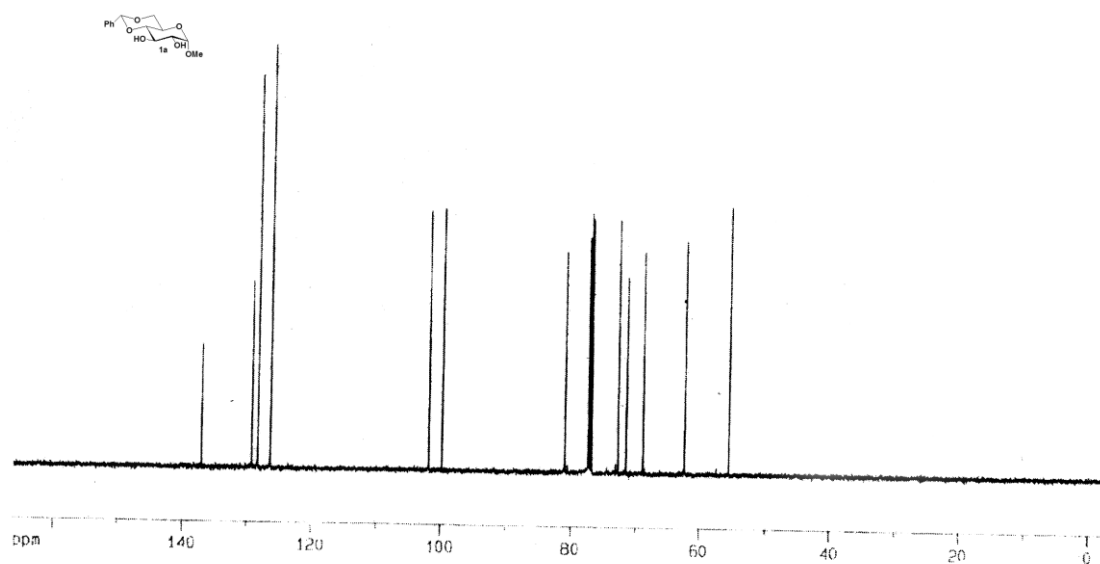
References:

1. A-T, Tran, R. A. Jones, J. Pastor, J. Boisson, N. Smith, M. C. Galan, *Adv. Synt. Catal.*, 2011, **353**, 2593-2598.
2. R. Panchadhayee, A. K. Misra, *Synlett*, 2010, **8**, 1193-1196.
3. K. V. Rao, P. R. Patil, S. Atmakuri, K. P. R. Kartha. *Carbohydr. Res.* 2010, **45**, 2709-2713.

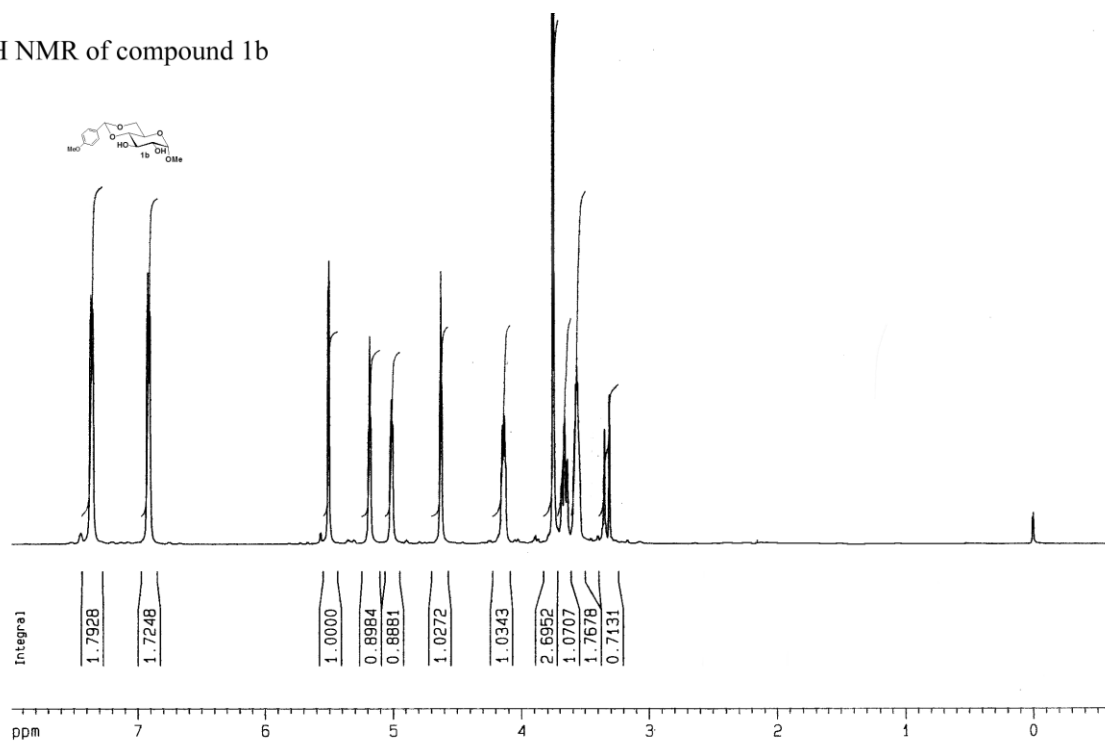
Copies of ^1H NMR and ^{13}C NMR of the representative compounds.



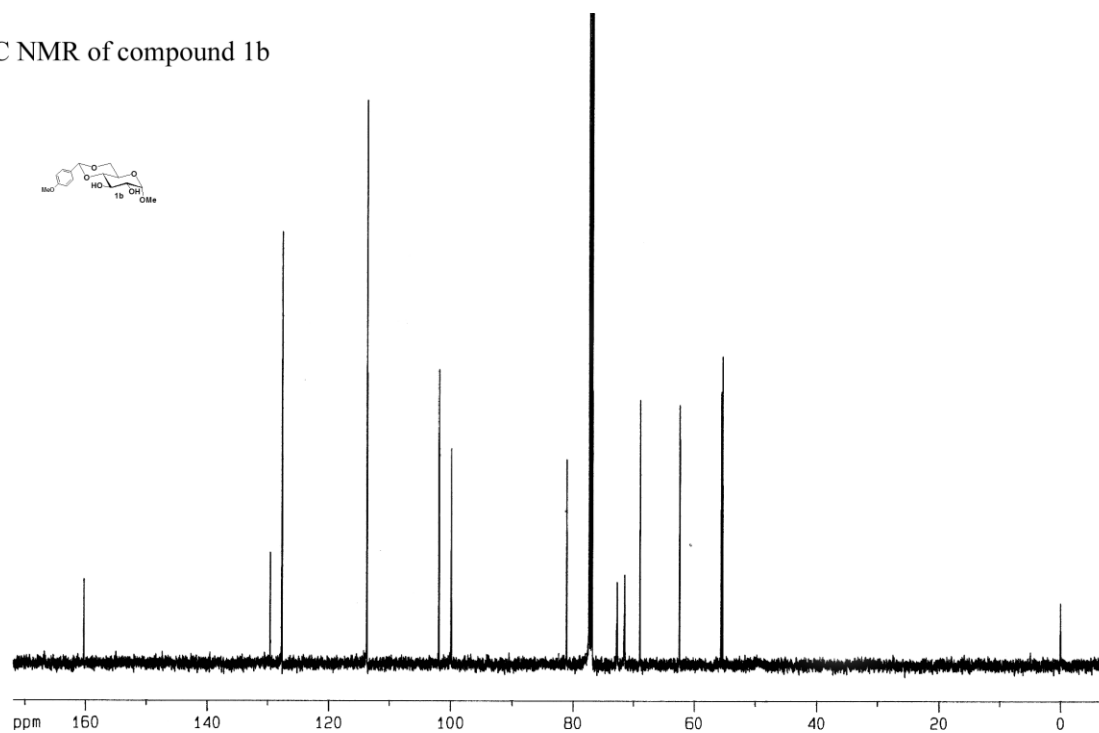
^{13}C NMR of compound 1a

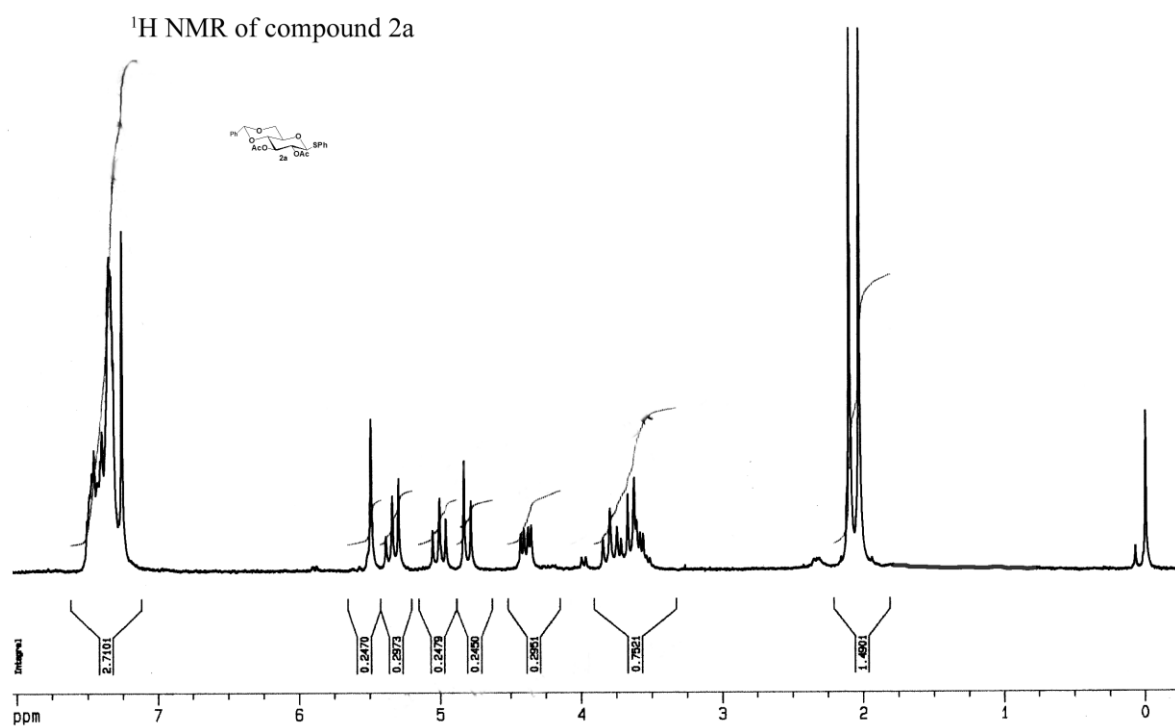


¹H NMR of compound 1b

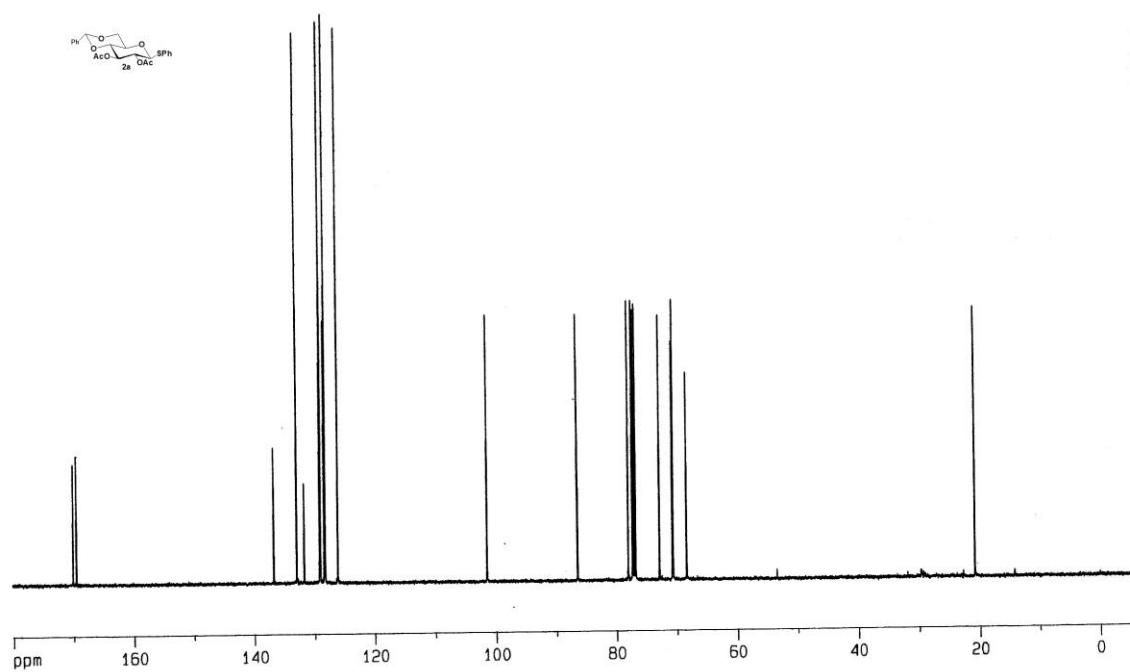


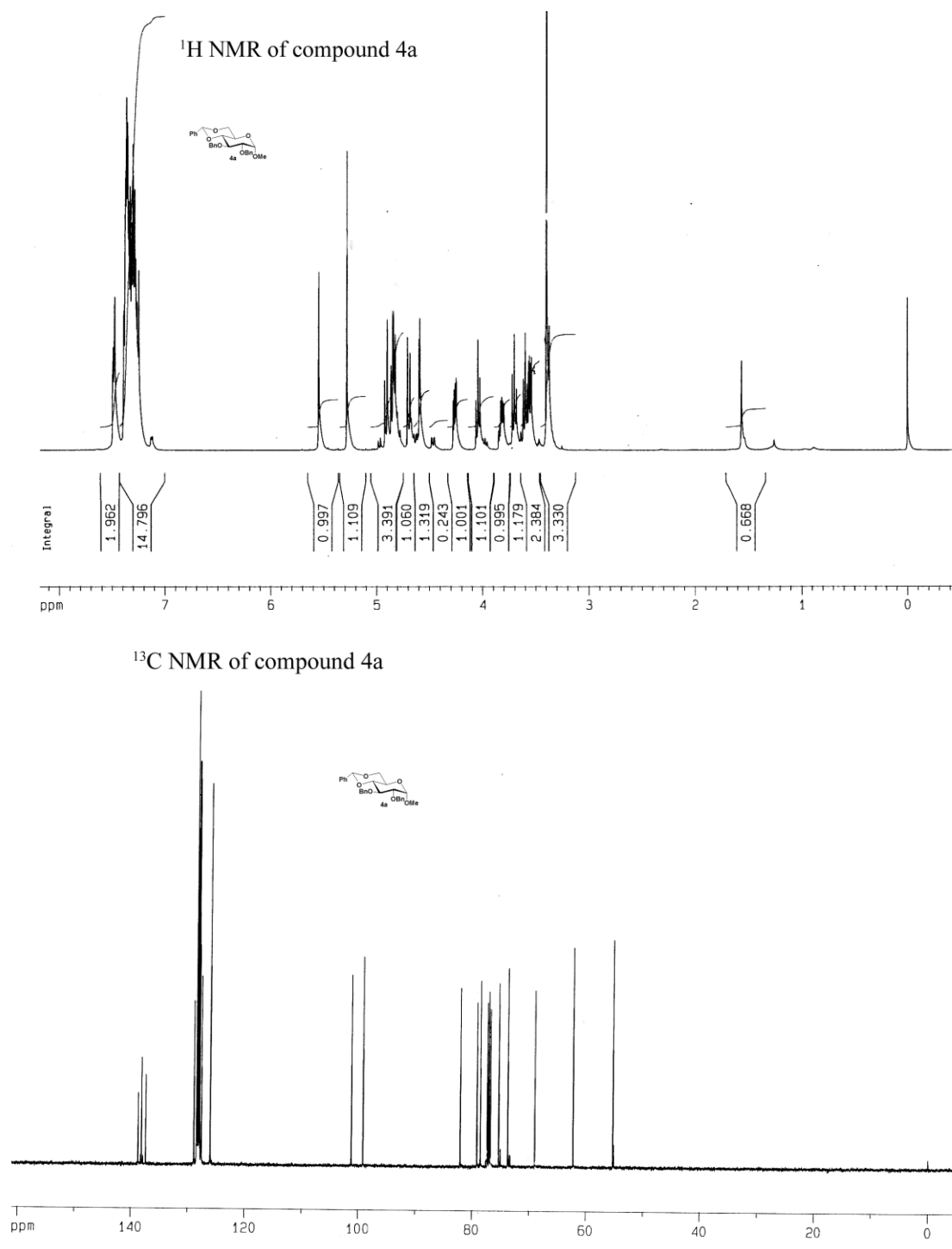
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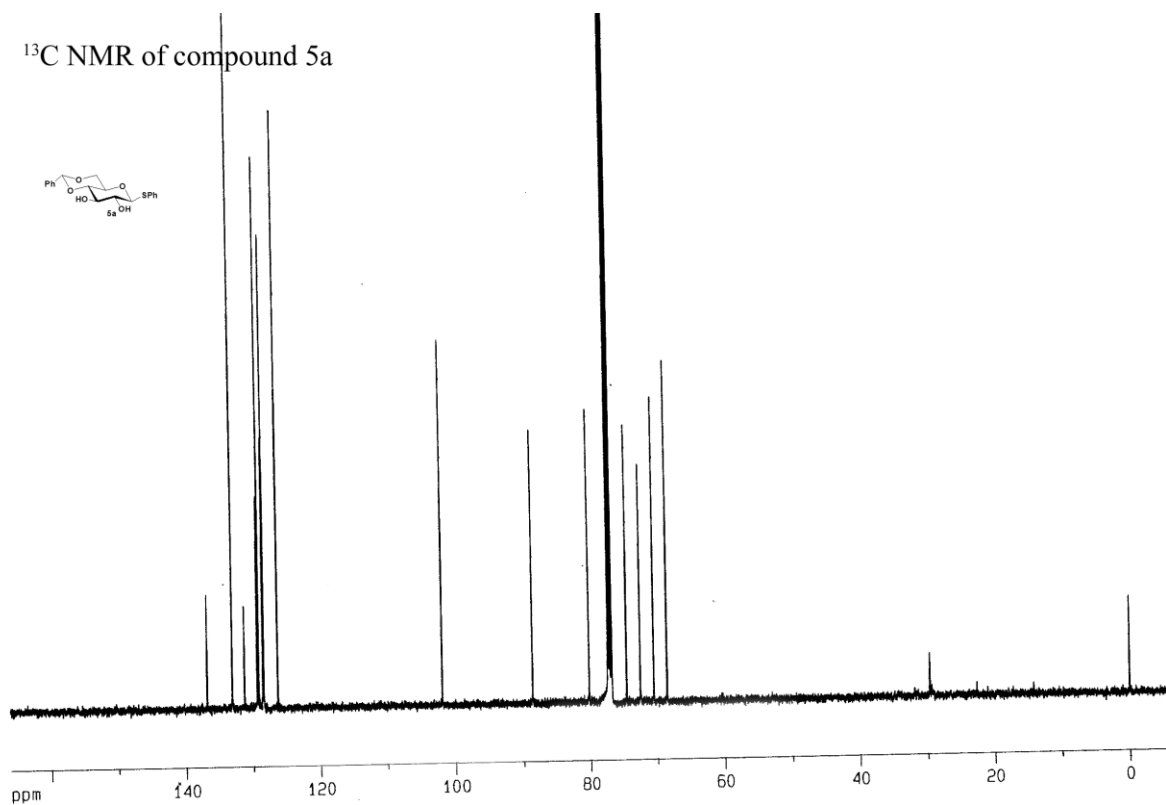
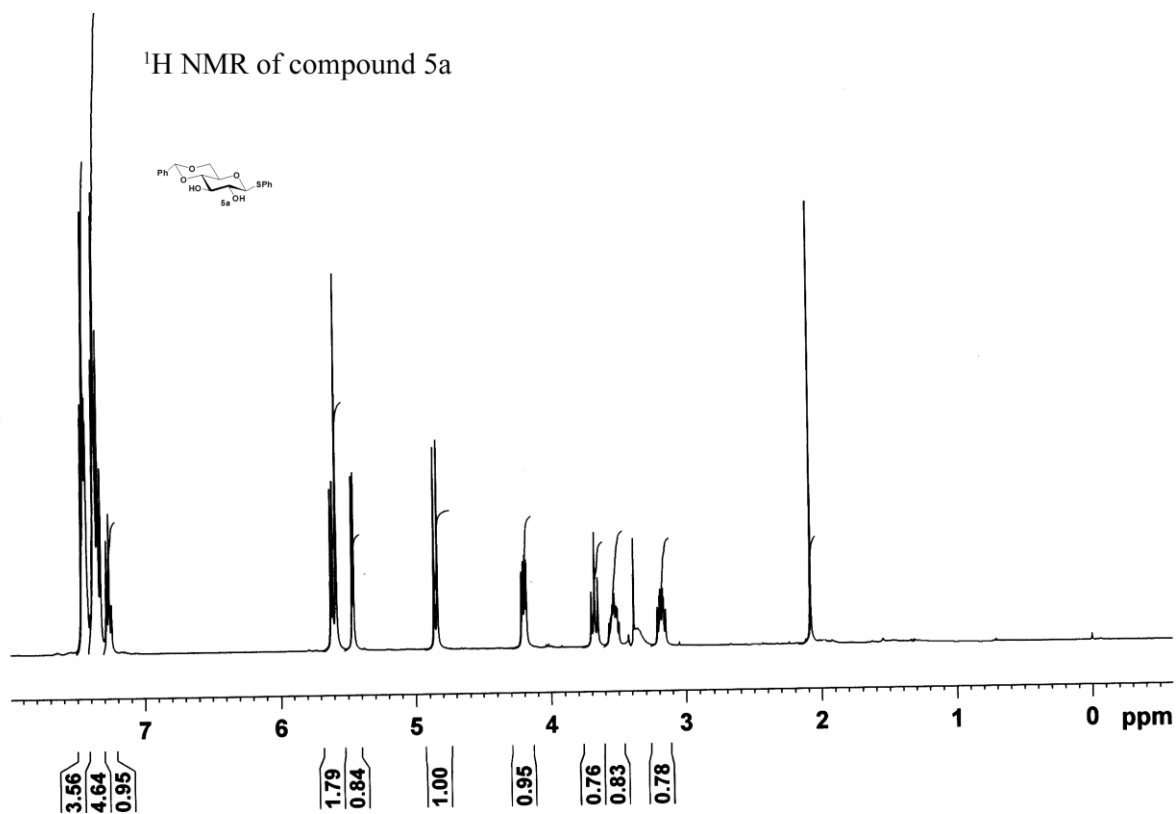




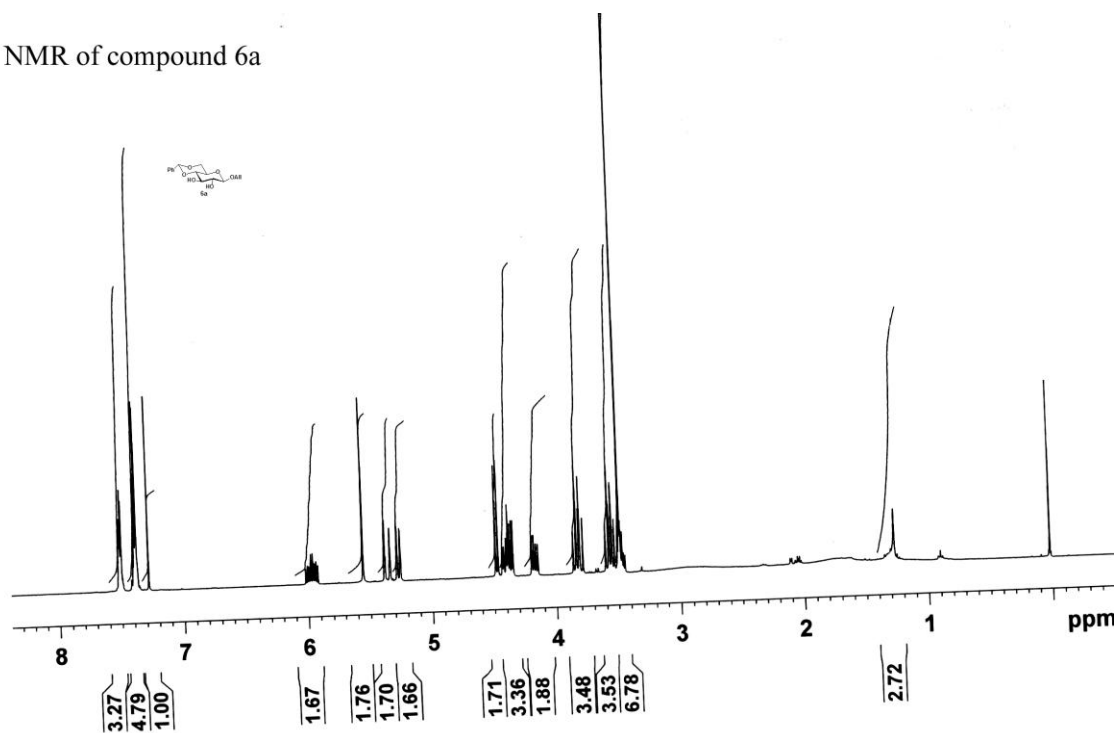
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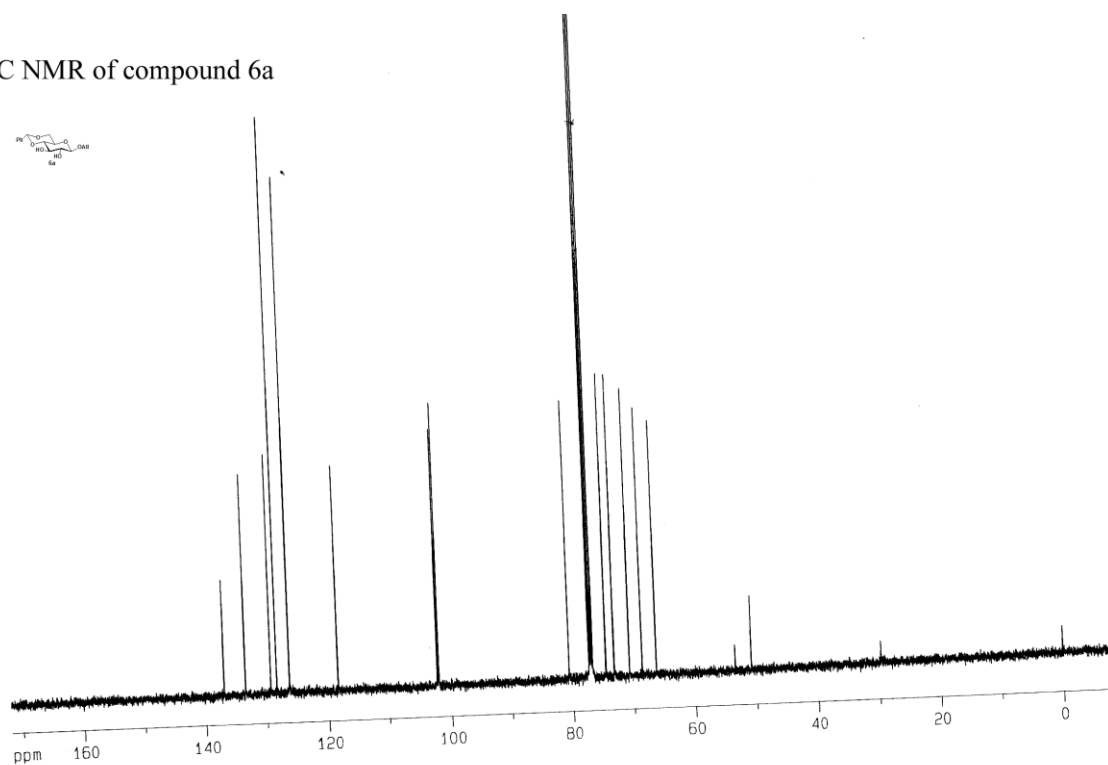




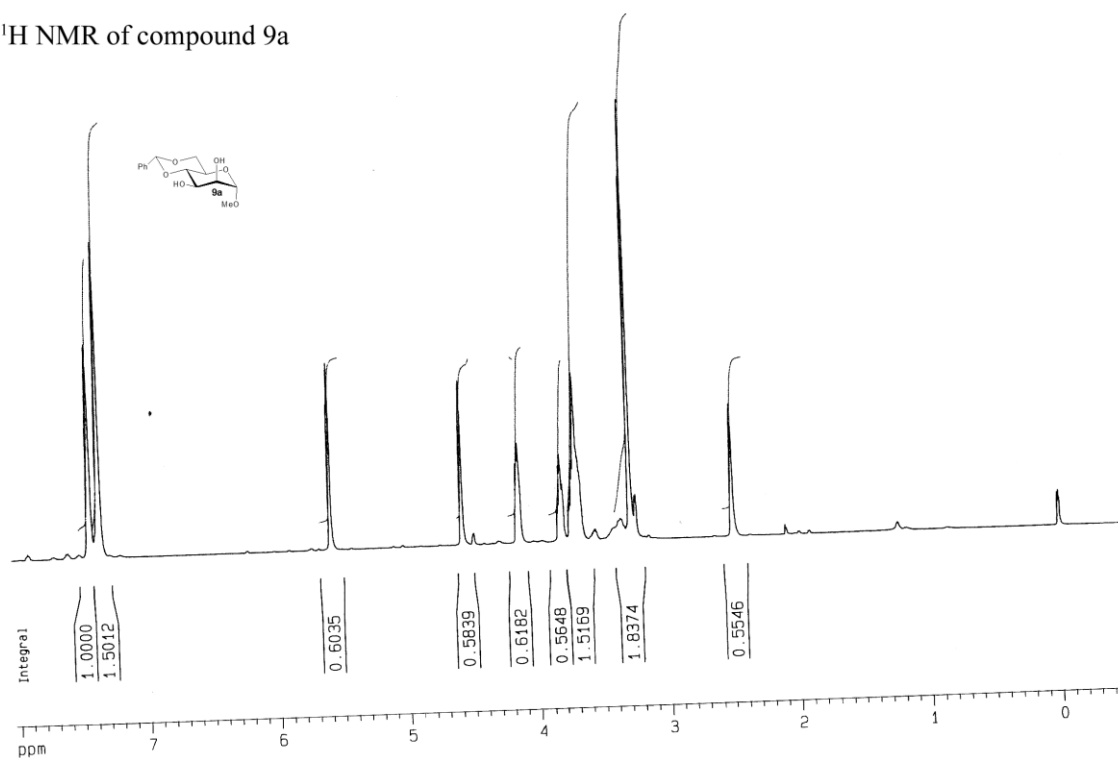
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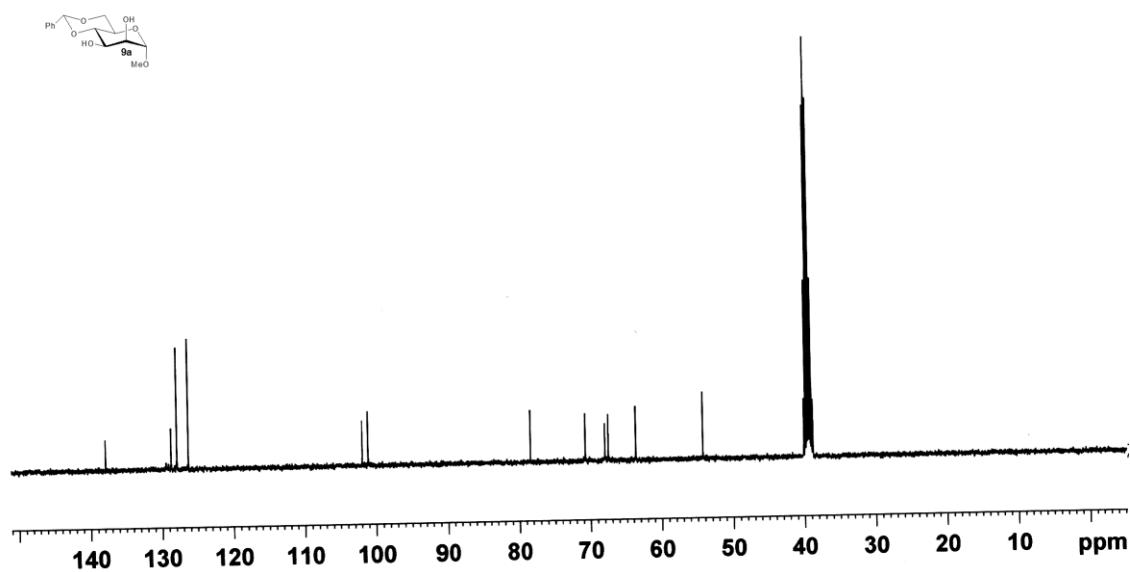
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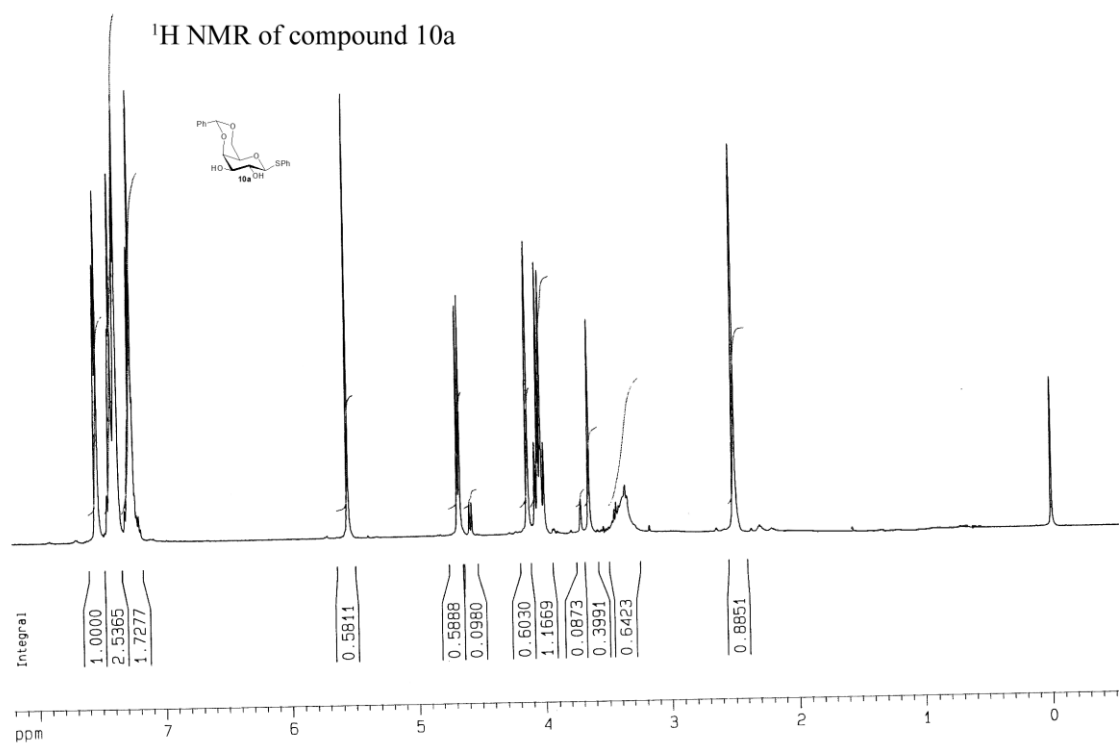


^1H NMR of compound 9a

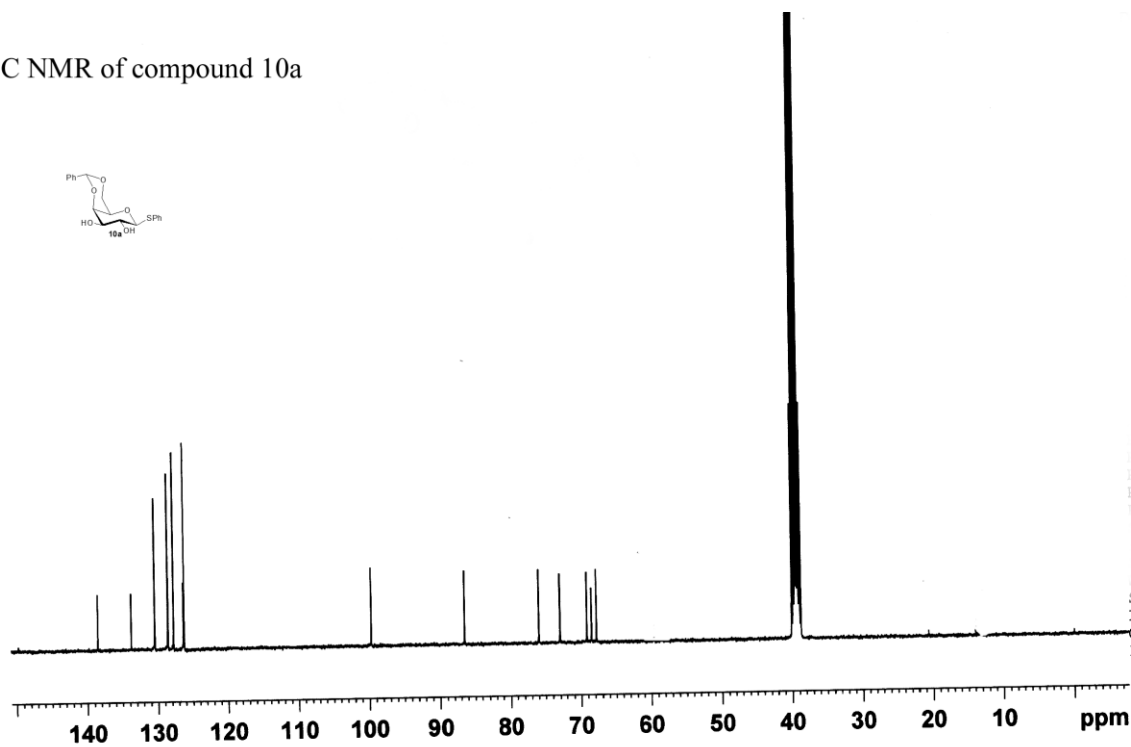


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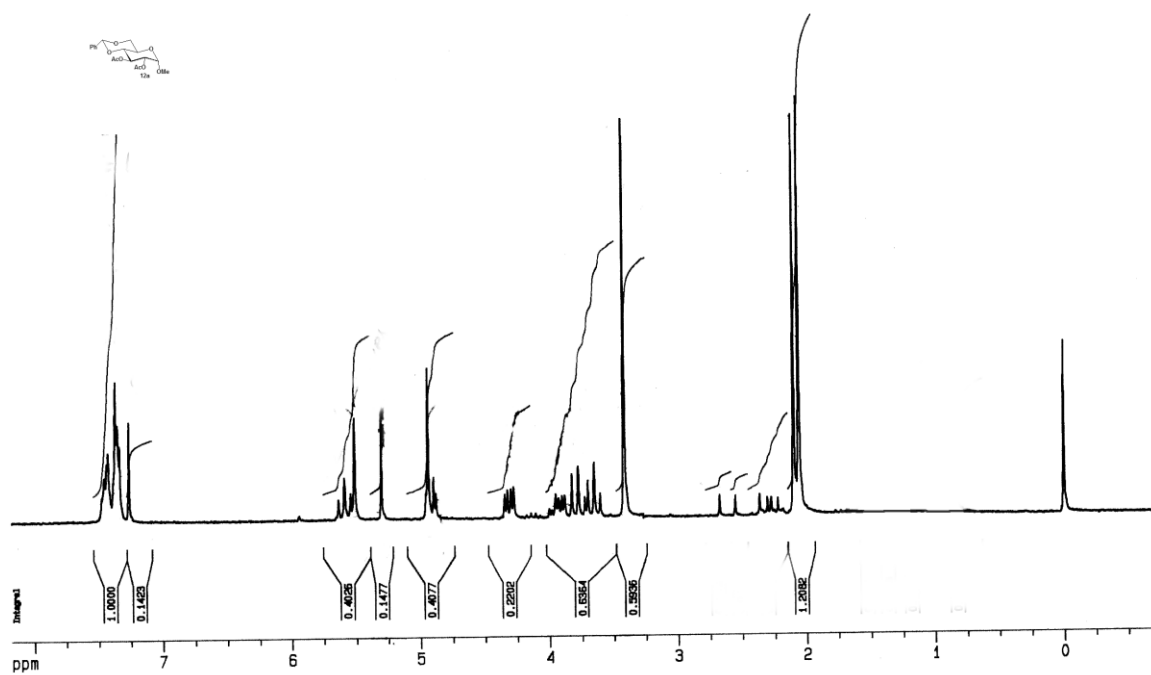




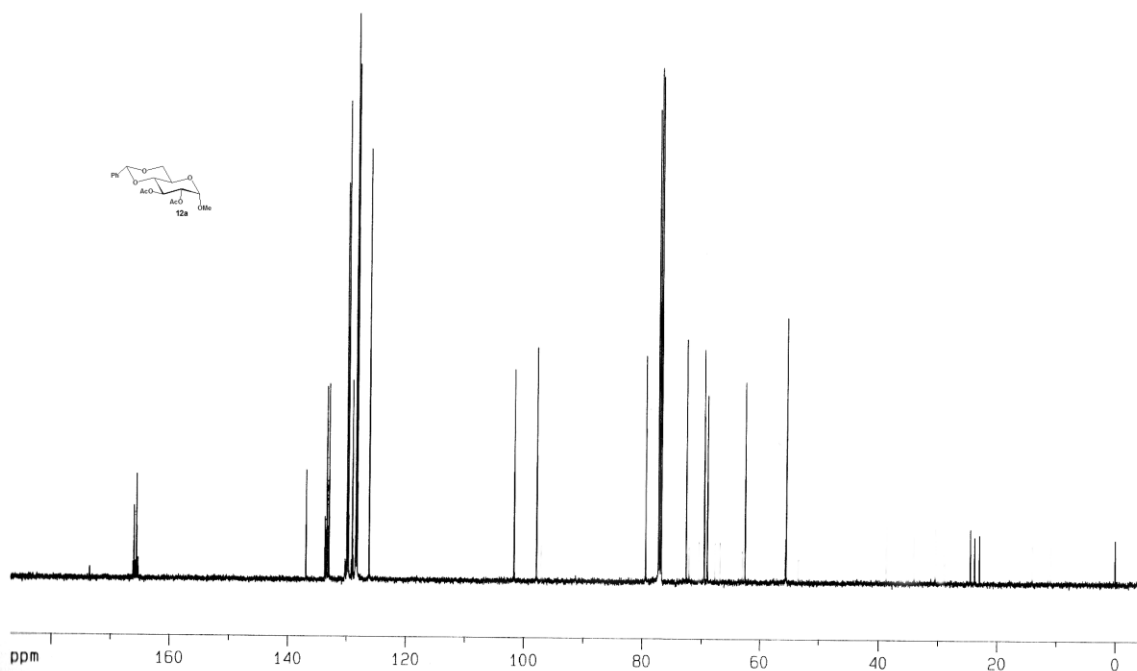
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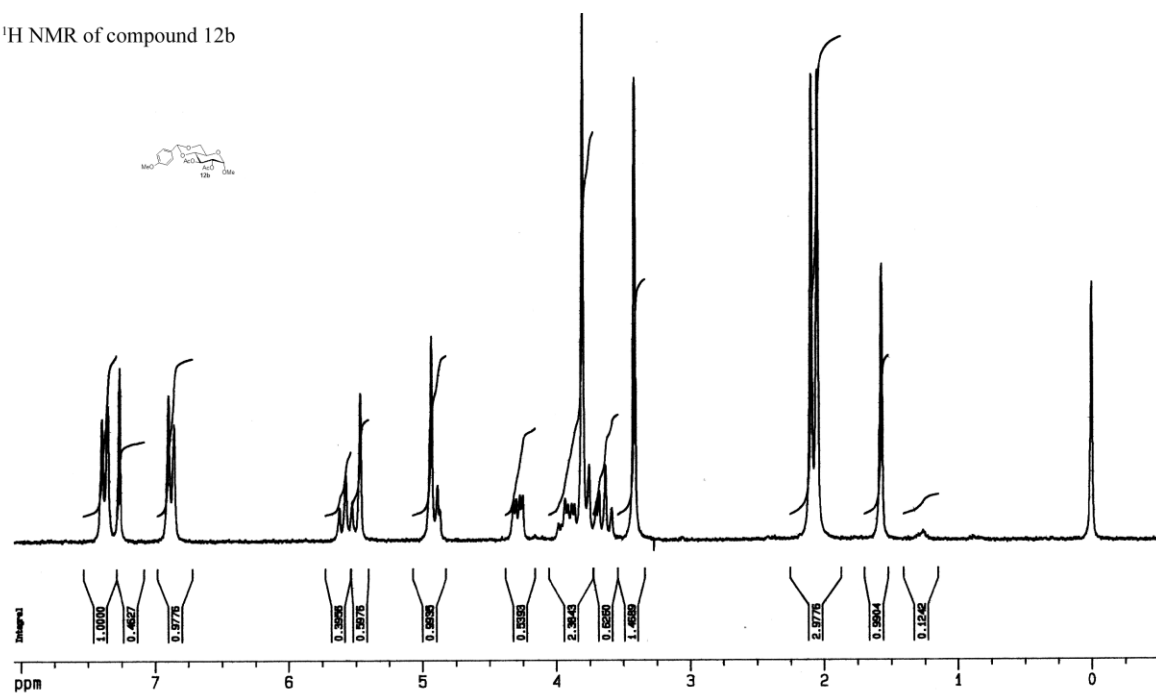
^1H NMR of compound 12a



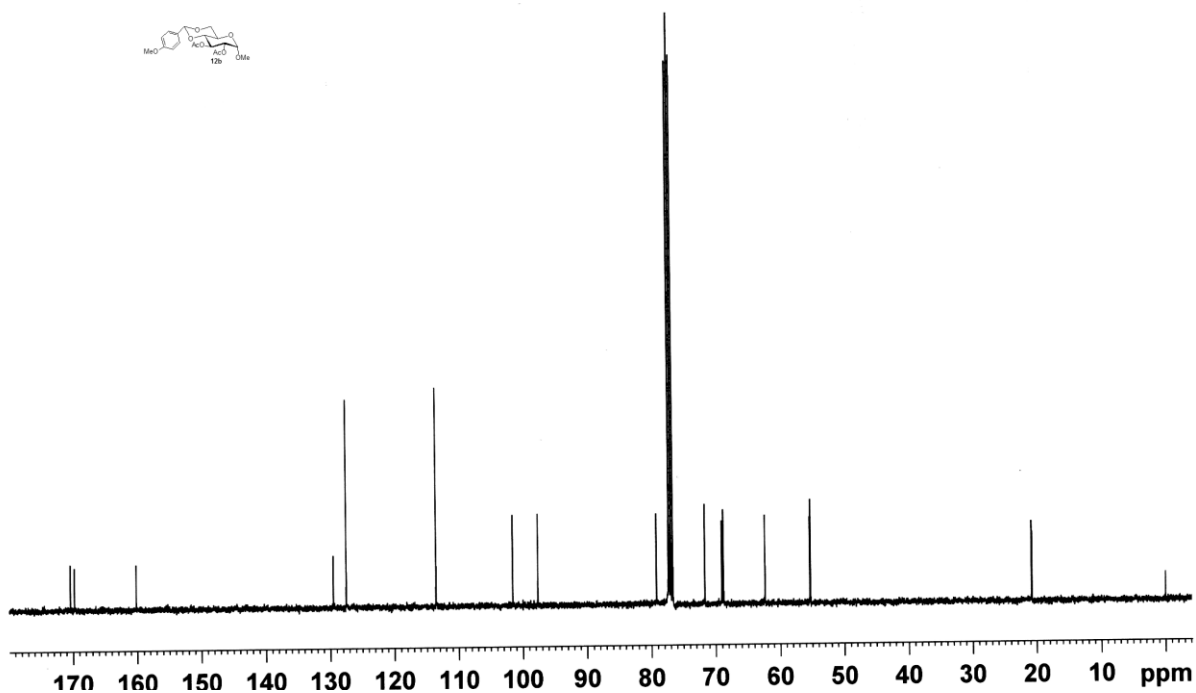
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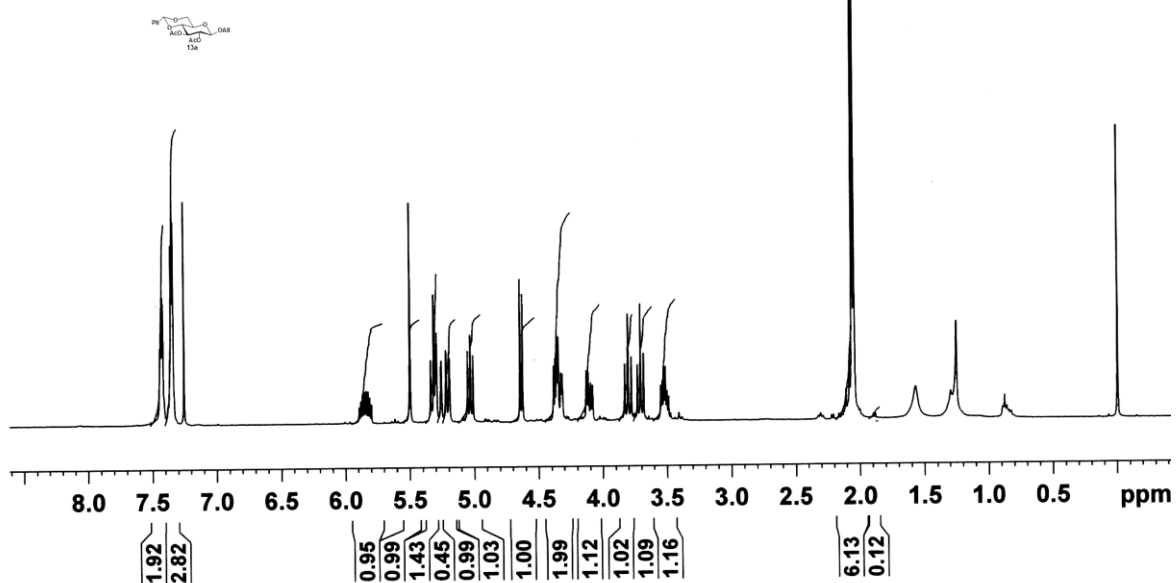
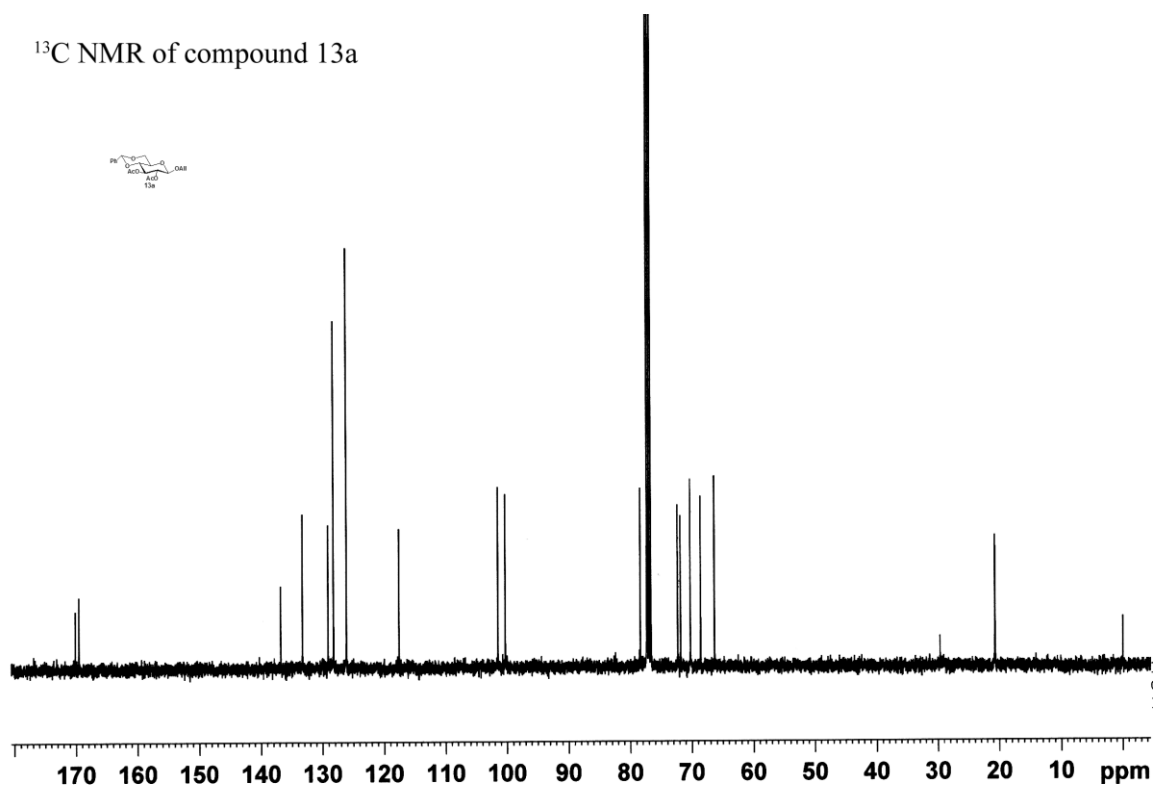


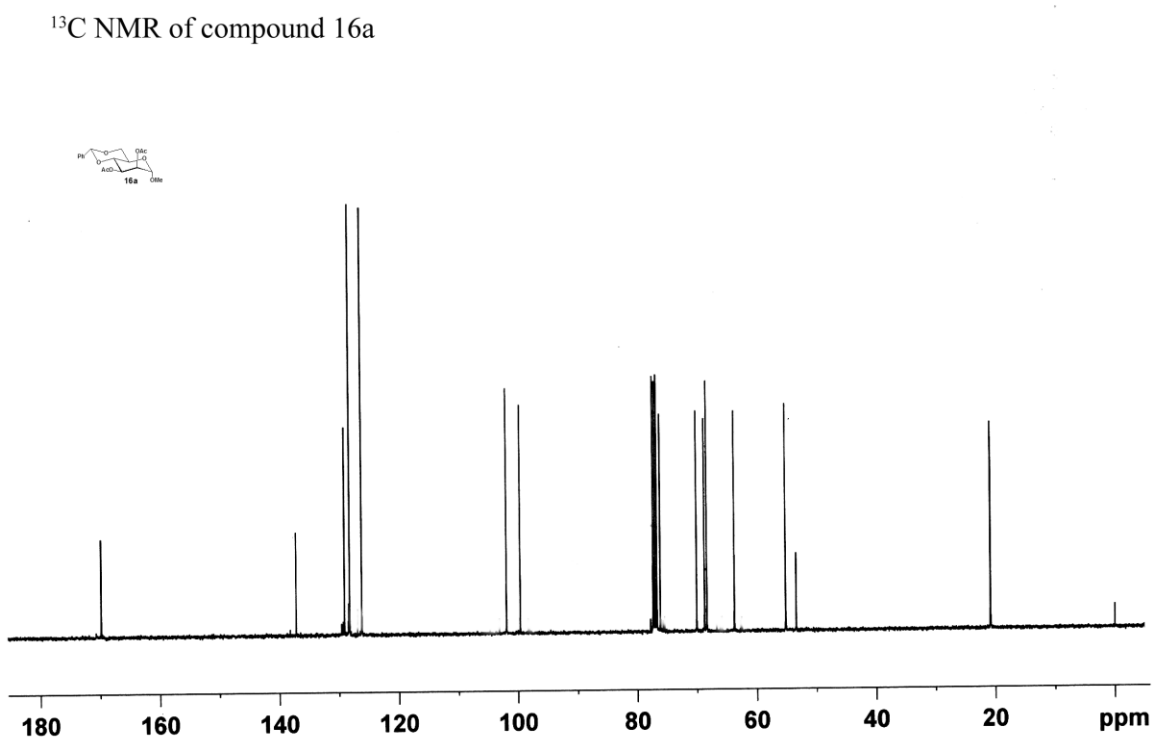
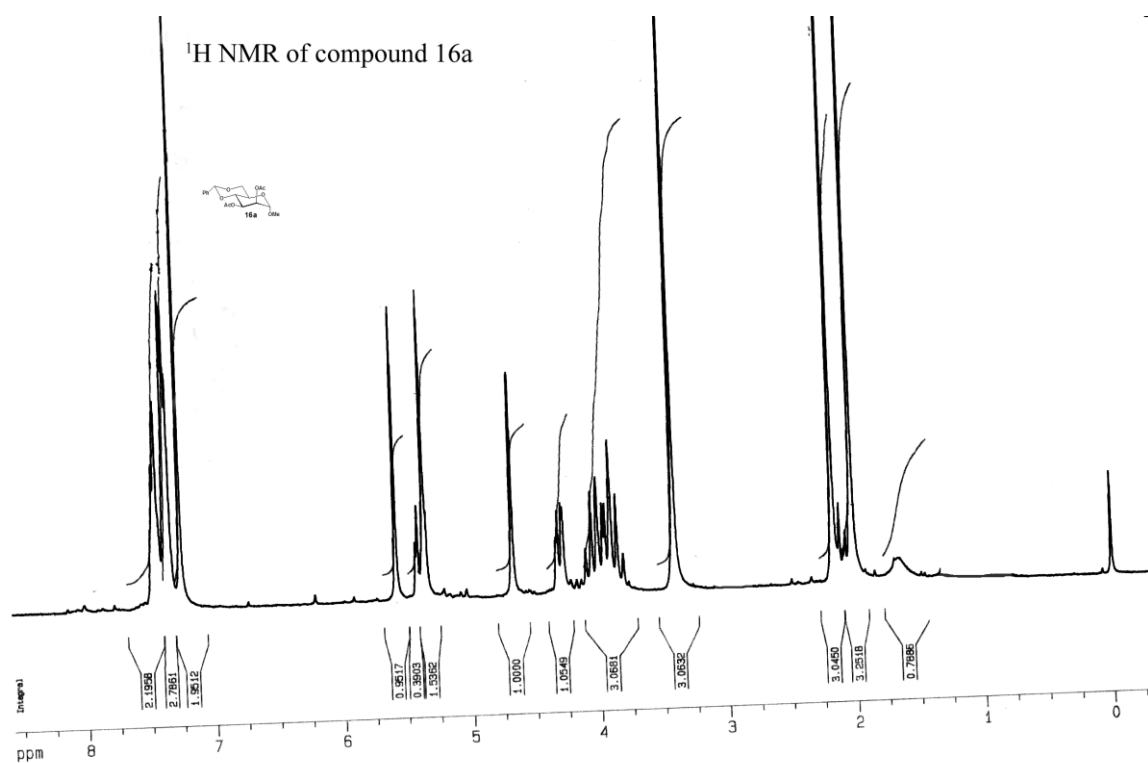
^1H NMR of compound 12b

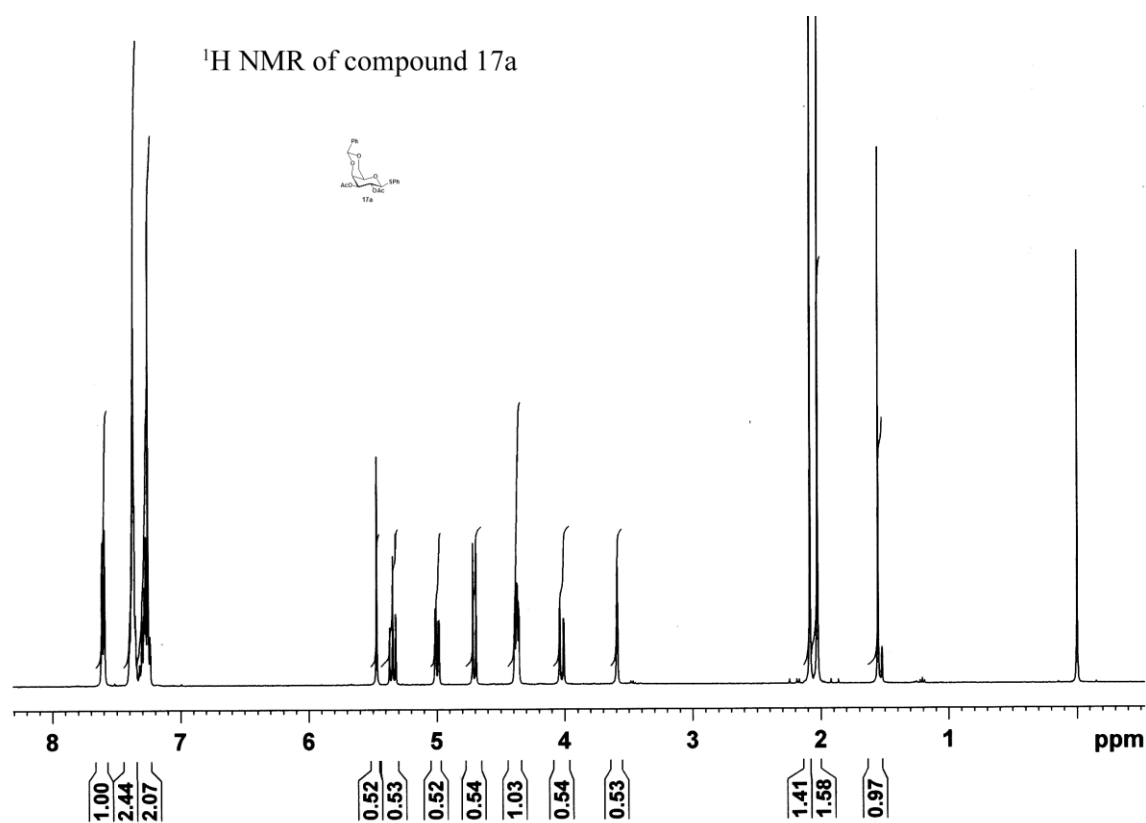


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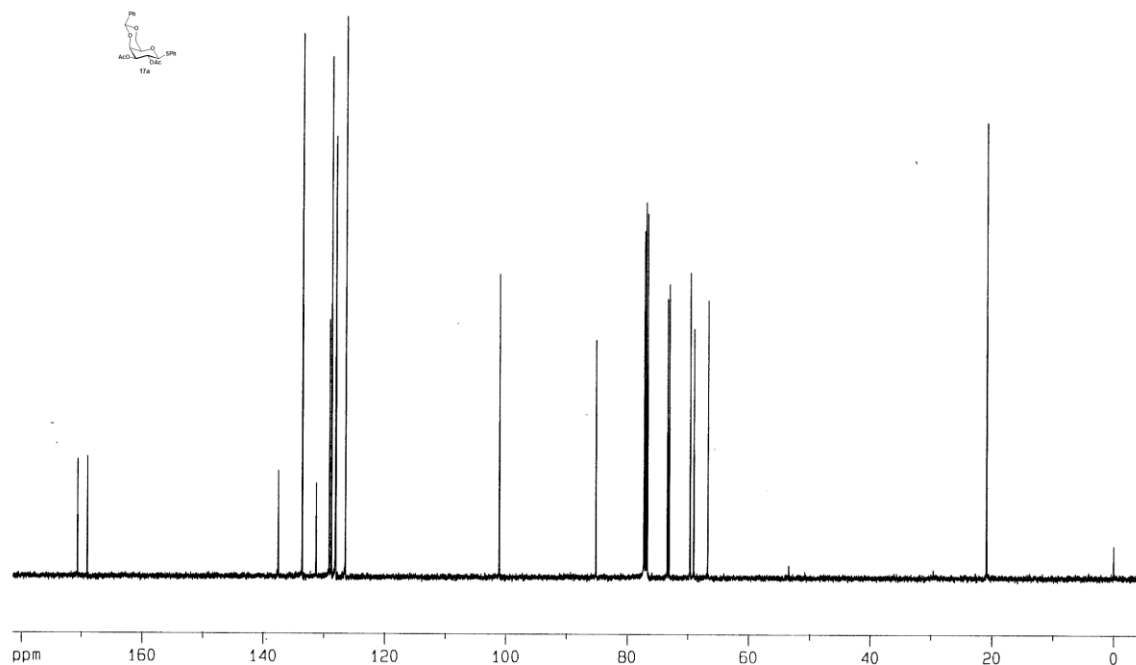


¹H NMR of compound 13a¹³C NMR of compound 13a

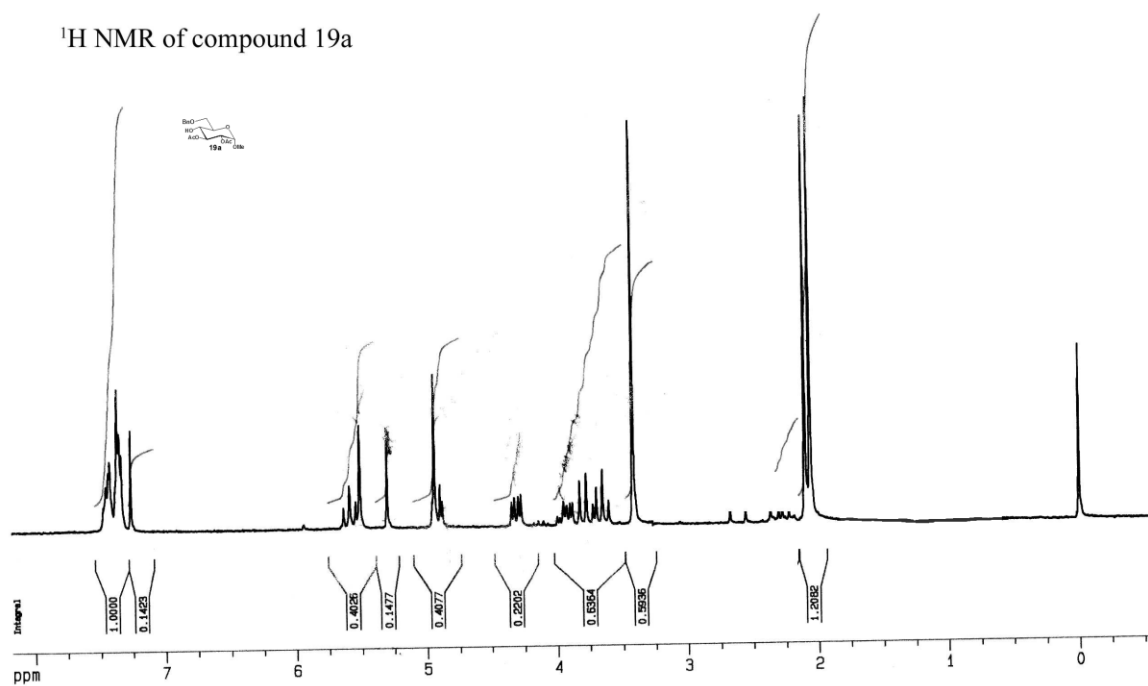




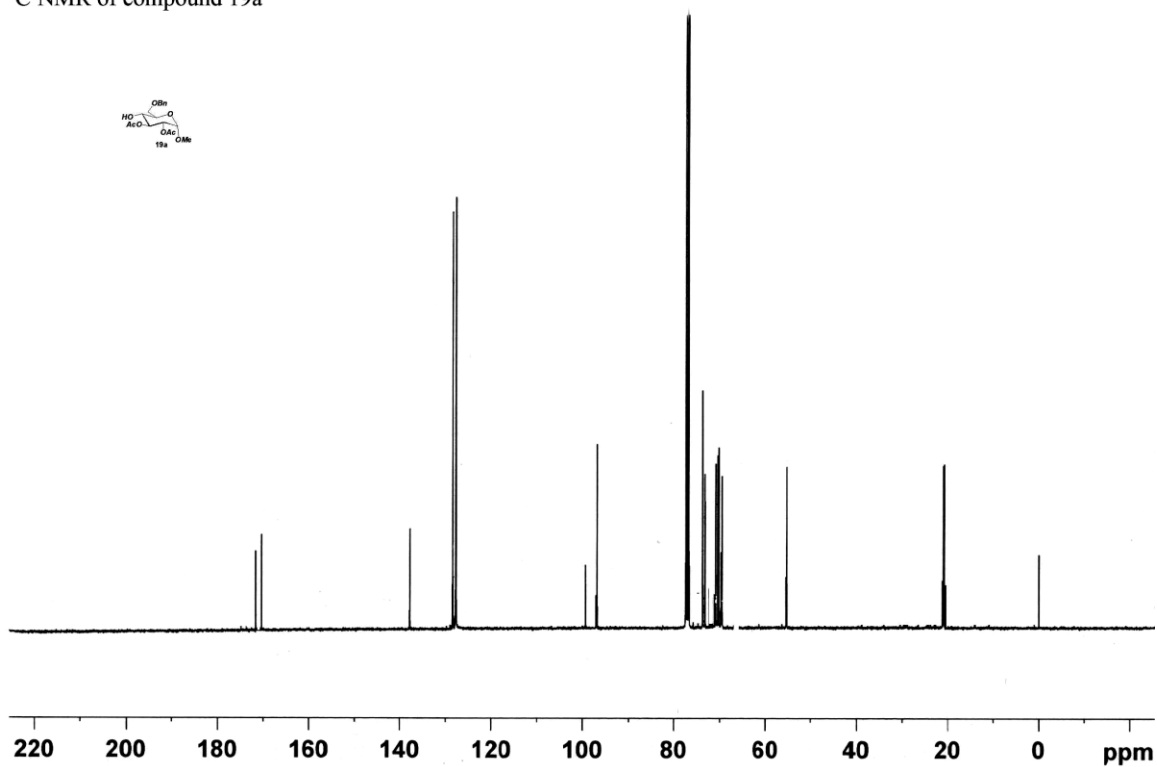
¹³C NMR of compound 17a

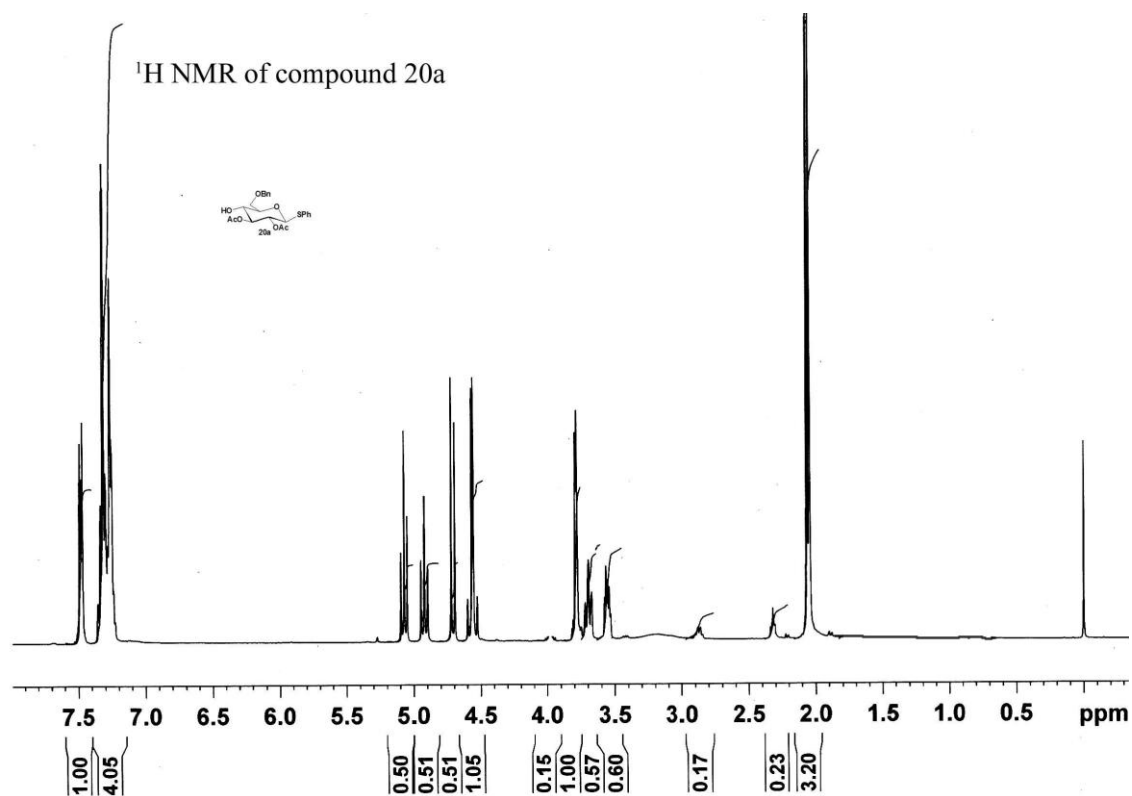


^1H NMR of compound 19a

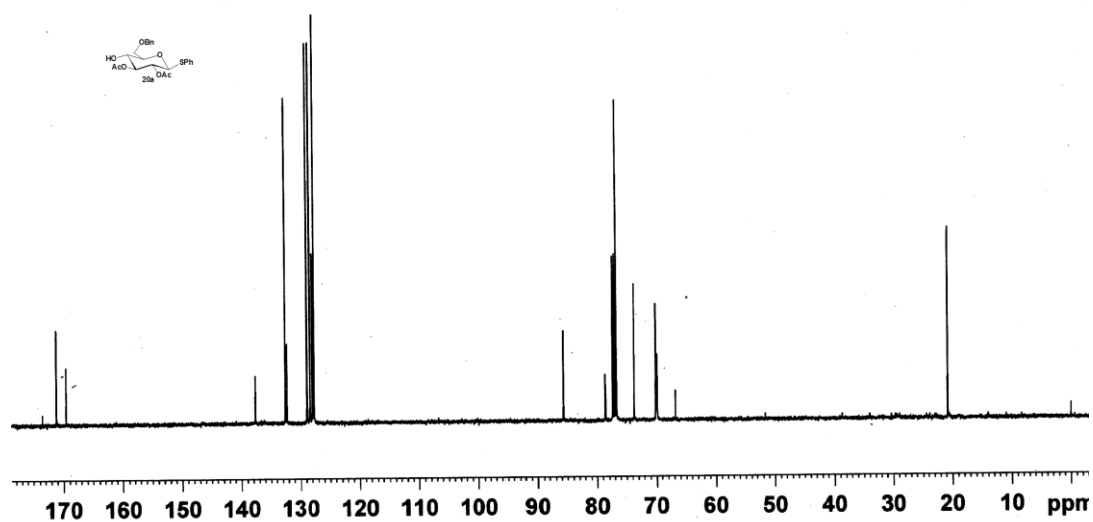


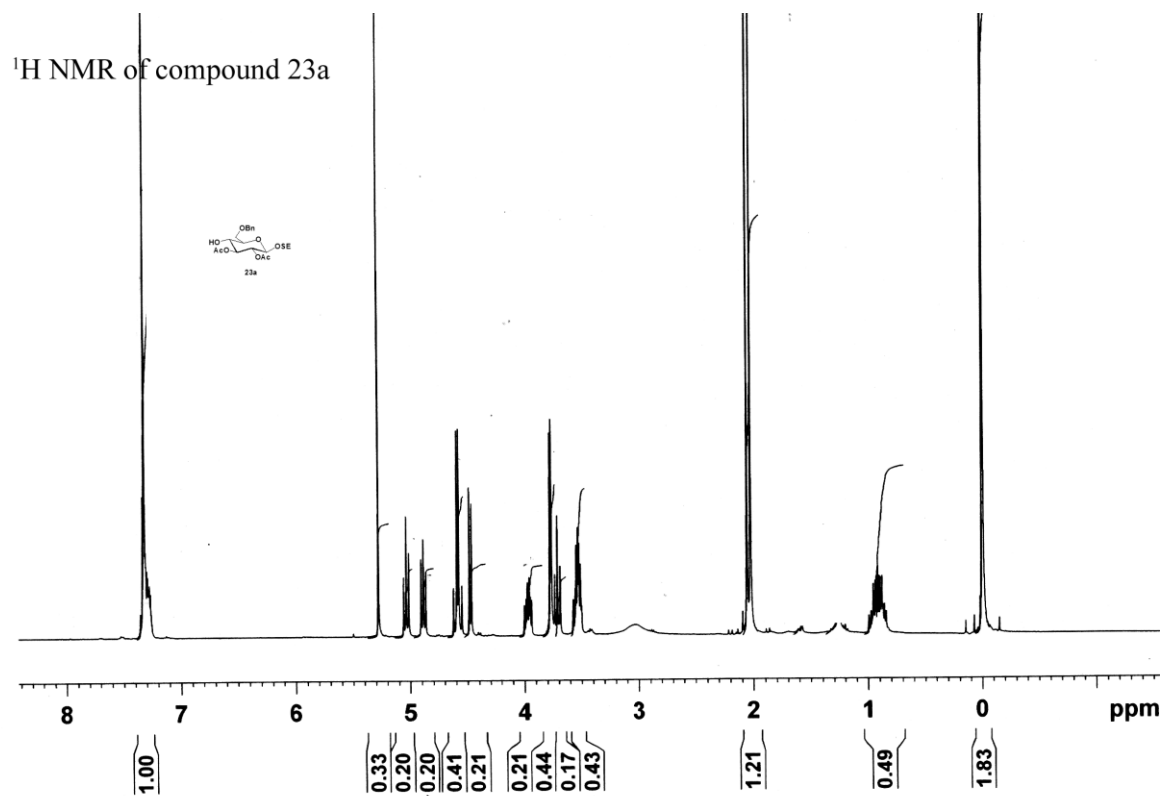
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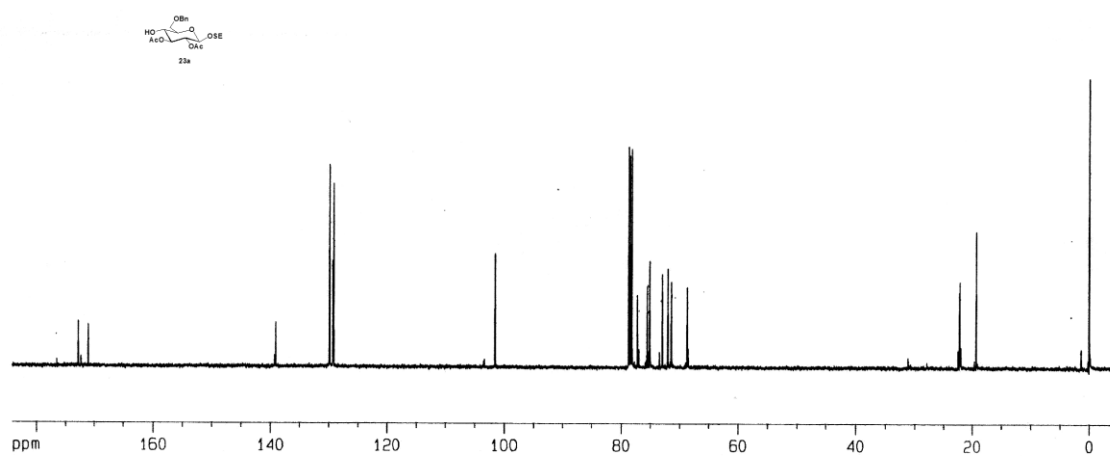


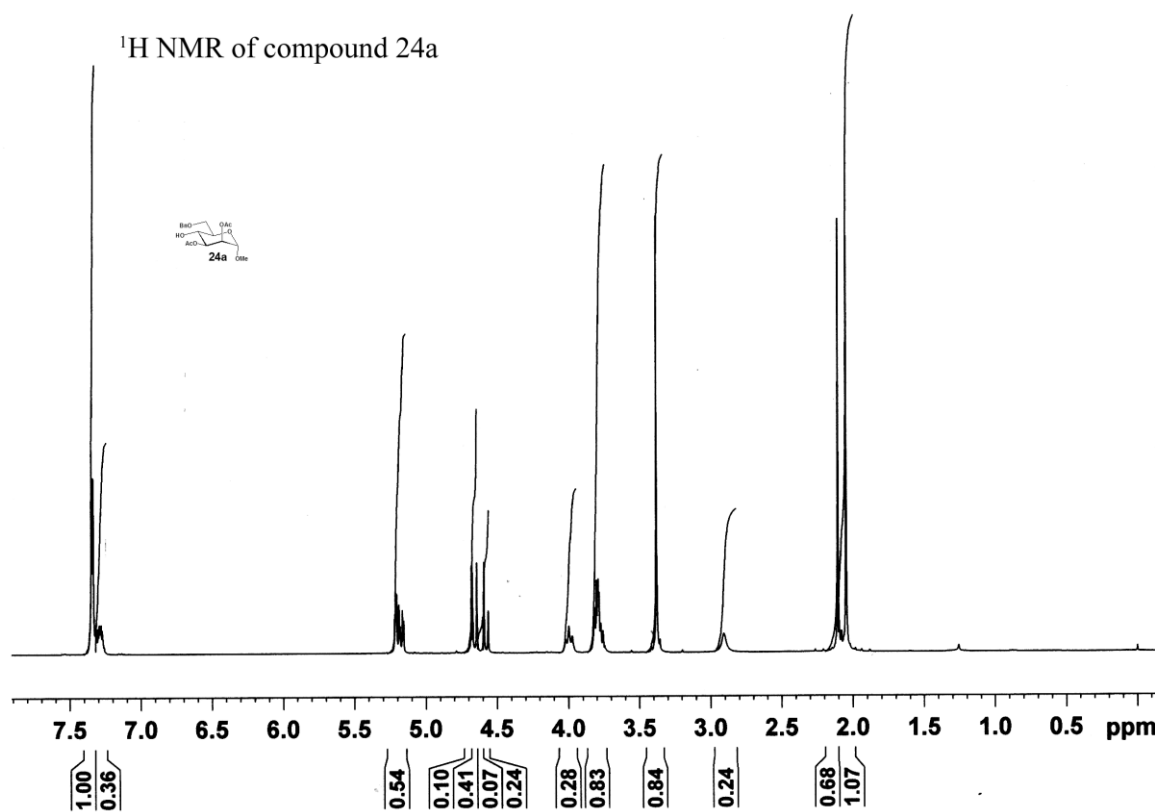
¹³C NMR of compound 20a





¹³C NMR of compound 23a





¹³C NMR of compound 24a

