Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Orthogonal cleavage of 2-naphthylmethyl group in the presence of p-methoxy phenyl-protected anomeric position and its use in carbohydrate synthesis

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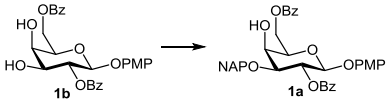
General methods for chemical synthesis of oligosaccharides

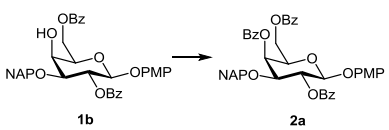
All chemicals were of reagent grade, and were used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on Silica Gel 60 F_{254} (Sigma Aldrich); after examination under UV light, compounds were visualized by heating with 10% (v/v) ethanolic H_2SO_4. In the work up procedures, organic solutions were washed with the amounts of the indicated aqueous solutions, then dried with anhydrous Na_2SO_4, and concentrated under reduced pressure at 30-50ºC on a water bath. Column chromatography was performed on pre-packed silica cartridges RediSep (Teledyne-Isco, 0.040–0.063 nm) or Biotage SNAP Ultra (0.050 nm irregular silica). Unless otherwise specified, a gradient 0 $\rightarrow$ 100% of the elution mixture was applied in a CombiflashR$_f$ (Teledyne-Isco) or Isolera (Biotage) instrument. Solvent mixtures less polar than those used for TLC were used at the onset of separation. ^{1}H NMR spectra were measured at 400 MHz and 298 K with a Bruker Avance^{III} spectrometer; δ_H values were reported in ppm, relative to the internal standard Me_4Si (δ_H = 0.00, $CDCl_3$) or the water signal (δ_H = 4.79 ppm, D_2O). ^{13}C NMR spectra were measured at 100 MHz and 298 K with a Bruker Avance^{III} spectrometer; δ_C values are reported in ppm relative to the signal of $CDCl_3$ (δ_C = 77.0, $CDCl_3$). NMR signals were assigned by homonuclear and heteronuclear 2-dimensional correlation spectroscopy. When reporting assignments of NMR signals, sugar residues in oligosaccharides are indicated with capital letters, uncertain attributions are denoted "/". Nuclei associated with the linker are denoted with a prime. Exact masses were measured by electron spray ionization cut-off spectroscopy, using a Q-Tof *micro*Macromass (Waters) instrument. Optical rotation was measured with a P-2000 Jasco polarimeter at 25°C.



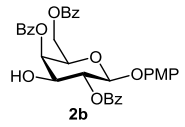
4-Methoxyphenyl 2,6-di-O-benzoyl-3-O-naphtylmethyl-β-D-galactopyranoside 1a: Compound **1b**[1] (2.57 g, 5.2 mmol) and Bu_2SnO (1.55 g, 6.2 mmol) were refluxed in toluene (50 ml) for 2 h using a Dean Stark apparatus. Then temperature was lowered to 50 °C, NAPBr (1.3 g, 6.2 mmol) and TBAI (2.3 g, 6.2 mmol) were added, and stirring was continued for 12 h. Chromatography (cyclohexane-EtOAc) provided 3.03 g of product **1** (92%).

^{1}H NMR ($CDCl_3$): δ 8.07–6.61 (m, 22H, H-Ar), 5.75 (t, *J* = 8.8 Hz, 1H, H-2), 4.89 (d, *J* = 7.3 Hz, H-1), 4.89, 4.72 (2 d, *J* = 12.2 Hz, 1H, C*H*$_2$NAP), 4.77–4.65 (m, 2H, H-6), 4.24 (d, *J* = 2.3 Hz, 1H, H-4), 3.98–3.95 (m, 1H, H-5), 3.79 (dd, 1H, H-3), 3.66 (s, 3H, OCH_3).

^{13}C NMR ($CDCl_3$): δ 166.3, 165.4 (2 CO), 155.4–113.4 (C-Ar), 100.8 (C-1), 78.0 (C-3), 72.7 (C-5), 71.7 (*C*H$_2$NAP), 70.9 (C-2) 66.1 (C-4), 63.6 (C-6), 55.5 (OCH_3). HR ESI MS $C_{38}H_{34}O_9$: $[M+Na]^+$ calc 657.2101; found 657.2116.

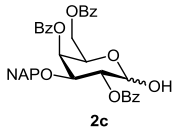


4-Methoxyphenyl 2,4,6-tri-O-benzoyl-3-O-naphtylmethyl-β-D-galactopyranoside 2a: Compound **1b** (500 mg, 0.79 mmol) was dissolved in 4:1 CH_2Cl_2-Pyridine (10 ml), and BzCl (0.5 ml, 4 mmol) was added at 0°C. After stirring overnight, allowing reaching room temperature, the mixture was concentrated and the residue was purified on silica gel to afford product **2a** in theoretically quantitative yield. $[\alpha]_D^{25}$ = +79.4˚ (c 0.40, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 8.10–6.56 (m, 19H, H-Ar), 5.73 (d, *J* = 3.2 Hz, 1H, H-4), 5.55 (t, *J* = 8.7 Hz, 1H, H-2), 5.08 (d, *J* = 8.0 Hz, H-1), 4.53–4.46 (m, 2H, H-6), 4.22–4.18 (m, 1H, H-5), 4.16 (dd, 1H, H-3), 3.64 (s, 3H, OCH_3).
^{13}C NMR ($CDCl_3$): δ 166.8, 166.2, 166.0 (3 CO), 155.6–112.3 (C-Ar), 100.7 (C-1), 73.8 (C-2), 71.8 (C-3,5), 70.3 (C-4), 62.4 (C-6), 55.5 (OCH_3). HR ESI MS $C_{45}H_{38}O_{10}$: $[M+Na]^+$ calc 761.2363; found 761.2346.



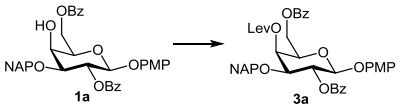
2b

4-Methoxyphenyl 2,4,6-tri-O-benzoyl- β-D-galactopyranoside 2b: Yield 78%. $[\alpha]_D^{25}$ = +17.3˚ (c 0.40, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.10–6.58 (m, 19H, H-Ar), 5.73 (d, *J* = 3.1 Hz, 1H, H-4), 5.55 (t, *J* = 8.6 Hz, 1H, H-2), 5.07 (d, *J* = 7.9 Hz, H-1), 4.53–4.44 (m, 2H, H-6), 4.22–4.18 (m, 1H, H-5), 4.16 (dd, 1H, H-3), 3.64 (s, 3H, OCH_3).
^{13}C NMR ($CDCl_3$): δ 166.8, 166.2, 166.0 (3 x CO), 155.6–112.3 (C-Ar), 100.7 (C-1), 73.3 (C-2), 71.8, 70.8 (C-3,4), 70.3 (C-5), 62.6 (C-6), 55.6 (OCH_3). HR ESI MS $C_{34}H_{30}O_{10}$: $[M+H]^+$ calc 599.1997; found 599.1995.

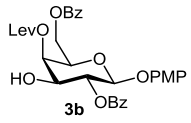


2c

2,4,6-Tri-O-benzoyl-3-O-naphtylmethyl-α,β-D-galactopyranoside 2c: Yield 68%.^{1}H NMR ($CDCl_3$): δ 8.18–7.40 (m, H-Ar), 5.81 (d, *J* = 2.7 Hz, H-4$^{\alpha}$), 5.81 (d, *J* = 2.8 Hz, H-4$^{\beta}$), 5.75 (d, *J* = 3.5 Hz, H-1$^{\alpha}$), 5.43 (dd, *J* = 9.0 Hz, H-2$^{\alpha}$), 5.31 (dd, *J* = 7.9, 9.9 Hz, H-2$^{\beta}$), 4.94 (d, H-1$^{\beta}$), 4.73–4.38 (m, H-5$^{\alpha}$,3$^{\alpha}$,6b$^{\alpha}$,6$^{\beta}$), 4.26–4.20 (m, H-3$^{\beta}$,5$^{\beta}$). ^{13}C NMR ($CDCl_3$): δ 166.8, 166.5, 166.2 (3 x CO), 133.7–128.3 (C-Ar), 96.0 (C-1$^{\beta}$), 91.1 (C-1$^{\alpha}$), 75.5 (C-2$^{\beta}$), 72.2 (C-2$^{\alpha}$), 71.7 (C-4$^{\alpha}$), 71.6 (C-4$^{\beta}$), 70.7 (C-5$^{\alpha}$), 67.1 (C-3$^{\alpha}$), 68.0 (C-3$^{\beta}$), 66.0 (C-5$^{\beta}$), 62.7 (C-6$^{\alpha}$), 62.6 (C-6$^{\beta}$). HR ESI MS $C_{38}H_{32}O_9$: $[M+H]^+$ calc 632.2046; found 632.2035.



4-Methoxyphenyl 2,6-di-O-benzoyl-4-O-levulinoyl-3-O-naphtylmethyl-β-D-galactopyranoside 3a: Compound **1a** (500 mg, 0.79 mmol) was dissolved in CH_2Cl_2 (10 ml), to which levulinic acid (140 mg, 1.2 mmol), DCC (247 mg, 1.2 mmol) and DMAP (146 mg, 1.2 mmol) were added. After stirring overnight the mixture was concentrated and the residue was purified on silica gel to afford 512 mg of product **3a** (89%), as a white solid (m.p 119–121°C from ethyl acetate). $[\alpha]_D^{25}$ = +48.7˚ (c 0.43, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 8.08–6.59 (m, 22H, H-Ar), 5.73 (d, *J* = 2.3 Hz, 1H, H-4), 5.68 (t, *J* = 9.0 Hz, 1H, H-2), 4.91 (d, *J* = 7.8 Hz, H-1), 4.82, 4.58 (2 d, *J* = 12.3 Hz, 1H, C*H*$_2$NAP), 4.57–4.50 (m, 2H, H-6), 4.11–4.08 (m, 1H, H-5), 3.79 (dd, 1H, H-3), 3.67 (s, 3H, OCH_3), 2.93–2.78 (m, 4H, CH_2CH_2), 2.19 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$): δ 206.3, 172.3, 166.1, 165.2 (4 CO), 155.5–114.3 (C-Ar), 101.0 (C-1), 75.9 (C-3), 71.4 (C-5), 71.2 (*C*H_2Nap), 70.8 (C-2), 66.1 (C-4), 62.3 (C-6), 55.5 (OCH_3), 38.1, 29.71 (2 CH_2^{Lev}), 28.2 (CH_3). HR ESI MS $C_{43}H_{40}O_{11}$: $[M+H]^+$ calc 733.2649; found 733.2646.

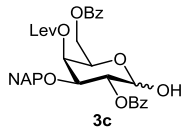


3b

2,6-Di-O-benzoyl-4-O-levulinoyl-β-D-galactopyranoside 3b: Yield 76%. $[\alpha]_D^{25}$ = +25.1˚ (c 0.23, $CHCl_3$).

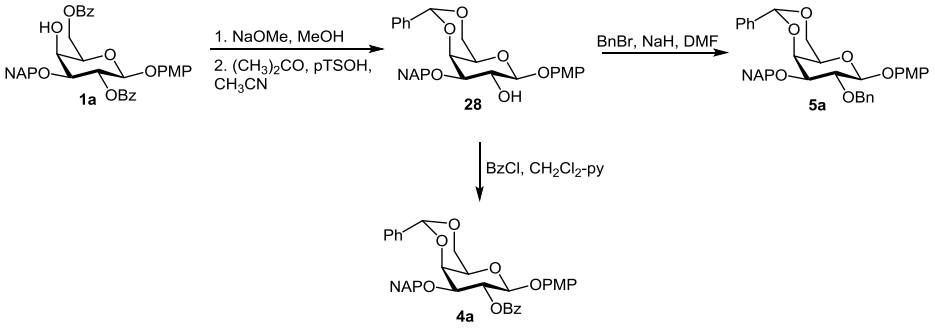
^{1}H NMR ($CDCl_3$): δ 8.03–6.58 (m, 14H, H-Ar), 5.54 (d, *J* = 2.9 Hz, 1H, H-4), 5.45 (t, *J* = 8.8 Hz, 1H, H-2), 5.00 (d, *J* = 7.6 Hz, H-1), 4.54–4.40 (m, 2H, H-6), 4.14–4.11 (m, 1H, H-5), 4.04 (dd, 1H, H-3), 3.66 (s, 3H, OCH_3), 2.86–2.72 (m, 4H, CH_2CH_2), 2.19 (s, 3H, CH_3).

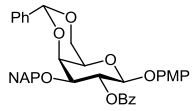
^{13}C NMR ($CDCl_3$): δ 208.0, 172.4, 166.5, 166.1 (4 CO), 155.6–114.3 (C-Ar), 100.8 (C-1), 73.0 (C-3), 71.5 (C-4,5), 70.1 (C-2), 62.4 (C-6), 55.5 (OCH_3), 38.4, 29.71 (2 CH_2), 28.2 (CH_3). HR ESI MS $C_{32}H_{31}O_{11}$: $[M+H]^+$ calc 592.1945; found 592.1955.



3c

2,6-Di-O-benzoyl-4-O-levulinoyl-3-O-naphtylmethyl-α,β-D-galactopyranoside 3c: Yield 61%, α/β anomers in ~3:2 ratio. ^{1}H NMR ($CDCl_3$): δ 8.07–7.27 (m, H-Ar), 5.81 (d, *J* = 2.1 Hz, H-4$^\alpha$), 5.78 (d, *J* = 2.3 Hz, H-4$^\beta$), 5.61 (d, *J* = 2.6 Hz, H-1$^\alpha$), 5.38 (dd, *J* = 10.2 Hz, H-2$^\alpha$), 5.35 (t, *J* = 8.7 Hz, H-2$^\beta$), 4.82 (t, *J* = 11 Hz, H-6a$^\alpha$), 4.70 (d, H-1$^\beta$), 4.71–4.33 (m, H-5$^\alpha$,5$^\beta$,6b$^\alpha$,6$^\beta$), 4.22 (dd, H-3$^\alpha$), 4.05 (dd, H-3$^\beta$), 3.77 (br. s, OH), 2.85–2.68 (m, CH_2CH_2), 2.10, 2.04 (2x s, 2 x CH_3). HR ESI MS $C_{36}H_{34}O_{10}$: $[M+H]^+$ calc 627.2230; found 627.2245.



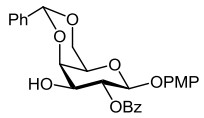


4a

4-Methoxyphenyl 2-O-benzoyl-4,6-O-benzylidene-3-O-naphtylmethyl-β-D-galactopyranoside 4a: Compound **28** was prepared from **1a** (730 mg, 1 mmol) by deacylation with NaOMe in MeOH (5 ml) at pH 12 for 48 h. The reaction crude was neutralized with Dowex H^+, then filtered and concentrated.

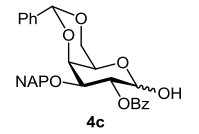
The material was dissolved in CH_3CN (5 ml) and benzylidene dimethyl acetal (1 ml) was added in the presence of catalytic p-TsOH (100 mg). After stirring for 6 h, the reaction was quenched by addition of TEA, concentrated and rapidly purified on silica gel (cyclohexane-EtOAc). Fractions containing sugar were concentrated and dissolved in DMF (5 ml) and 60% NaH in mineral oil (2 equiv) followed by BnBr (0.5 ml) was added at 0°C under nitrogen. After stirring overnight at r.t., the mixture was partitioned with water, and combined organic layers were concentrated. Purification on silica gel of the residue gave 450 mg of product (73%), as a white solid (m.p. 139–140°C from cyclohexane-EtOAc). $[\alpha]_D^{25}$ = +3.7˚ (c 0.15, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 8.00–6.70 (m, 22H, H-Ar), 5.90 (dd, *J* = 8.0, 9.9 Hz, 1H, H-2), 5.56 (s, 1H, C*H*Ph), 4.99 (d, 1H, H-1), 4.88, 4.79 (2 d, *J* = 12.0 Hz, 2H, CH_2NAP), 4.92, 4.11 (2 d, *J* = 12.1 Hz, 2H, H-6), 4.32 (d, *J* = 2.5 Hz, 1H, H-4), 3.84 (dd, 1H, H-3), 3.71 (s, 3H, OCH_3), 3.49 (br. s 1H, H-5). HR ESI MS $C_{38}H_{34}O_8$: $[M+H]^+$ calc 619.2332; found 619.2334.



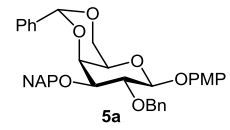
4b

4-Methoxyphenyl 2-O-benzoyl-4,6-O-benzylidene-D-galactopyranoside 4b: Yield 82%. $[\alpha]_D^{25}$ = -2.2˚ (c 0.15, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 8.13–6.80 (m, 14H, H-Ar), 5.65 (s, 1H, C*H*Ph), 5.45 (dd, *J* = 8.0, 9.2 Hz, 1H, H-2), 5.18 (d, 1H, H-1), 4.47–4.44 (m, 1H, H-6a), 4.21 (d, *J* = 3.5 Hz, 1H, H-4), 4.15 (t, *J* = 10.0 Hz, 1H, H-6b), 3.98 (dd, 1H, H-3), 3.77 (s, 3H, OCH_3), 3.71–3.68 (br. s 1H, H-5).
^{13}C NMR ($CDCl_3$): δ 166.1 (CO), 133.6–114.6 (C-Ar), 102.1 (Ph*C*H), 100.2 (C-1), 80.7 (C-3), 74.8 (C-4), 72.7 (C-2), 68.6 (C-6), 66.42 (C-5), 55.6 (OCH_3). HR ESI MS $C_{27}H_{26}O_8$: $[M+H]^+$ calc 501.1525; found 501.1531.



4c

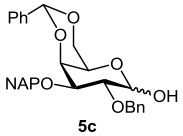
2-O-Benzoyl-4,6-O-benzylidene-3-O-naphtylmethyl-β-D-galactopyranoside 4c: Yield 45%, α/β anomers in ~3:2 ratio. ^{1}H NMR ($CDCl_3$): δ 8.06–6.89 (m, H-Ar), 5.69 (d, *J* = 3.6 Hz, H-1$^{\alpha}$), 5.61 (dd, *J* = 10.2 Hz, H-2$^{\alpha}$), 5.54 (d, *J* = 8.0 Hz, H-1$^{\beta}$), 5.52 (s, C*H*Ph), 4.89–4.81 (m, C*H*Ph, H-2$^{\beta}$,6$_a^{\alpha/\beta}$), 4.324.22 (m, H-3$^{\beta}$,5$^{\beta}$,6$^{\alpha/\beta}$), 4.16–4.09 (m, H-6$_b^{\alpha/\beta}$), 4.40 (t, *J* = 9.0 Hz, H-3$^{\alpha}$), 3.91 (d, *J* = 2.3 Hz, H-4$^{\alpha}$), 3.88–3.85 (m, H-5$^{\alpha}$), 3.92 (dd, *J* = 2.3, 9.9 Hz, H-3$^{\alpha}$), 3.48 (d, *J* = 2.3 Hz, H-4$^{\beta}$).
^{13}C NMR ($CDCl_3$): δ 167.1, 166.0, 137.7–125.2 (C-Ar), 101.2 (C*H*Ph, C-1$^{\beta}$), 92.6 (C*H*Ph), 97.8 (C-1$^{\beta}$), 91.3 (C-1$^{\alpha}$), 74.2, 73.5, 73.1, 71.8, 70.8, 69.4, 62.5, 60.4. HR ESI MS $C_{31}H_{28}O_7$: $[M+H]^+$ calc 513.1913; found 513.1925.



5a

4-Methoxyphenyl 2-O-benzyl-4,6-O-benzylidene-3-O-naphtylmethyl-β-D-galactopyranoside 5a: This compound was prepared from **1a** (730 mg, 1 mmol) by deacylation with NaOMe in MeOH (5 ml) at pH 12 for 48 h**.** The reaction crude was neutralized with Dowex H^+, then filtered and concentrated. The residue was dissolved in DMF (5 ml) and 60% NaH in mineral oil (2 equiv) and BnBr (0.5 ml) was added under nitrogen. After stirring overnight the mixture was partitioned with water, and combined organic layers were concentrated. Purification on silica gel of the residue gave 510 mg of product (84%).). $[\alpha]_D^{25}$ = -0.3˚ (c 2.1, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.90–6.86 (m, 22H, H-Ar), 5.55 (s, 1H, C*H*Ph), 5.10, 4.91 (2 d, *J* = 10.9 Hz, 2H, C*H*$_2$Ar), 5.11, 4.97 (2 d, *J* = 12.0 Hz, 2H, C*H*$_2$Ar), 4.92 (d, *J* = 7.6 Hz H-1), 4.32, 4.01 (2 d, *J* = 12.1 Hz, 2H, H-6), 4.22–4.18 (m, 2H, H-2,5), 3.80 (s, 3H, OCH_3), 3.72 (dd, *J* = 3.2 Hz, 1H, H-3), 3.33 (s, 1H, H-4).
^{13}C NMR ($CDCl_3$): δ 155.5–114.1 (C-Ar), 103.2 (*C*HPh), 100.2 (C-1), 79.2 (C-3), 78.2 (C-5), 75.5 (*C*H$_2$Ar), 73.8 (C-4), 72.1 (C-2), 69.1 (C-6), 55.6 (OCH_3). HR ESI MS $C_{38}H_{36}O_7$: $[M+Na]^+$ calc 627.2359; found 627.2363.

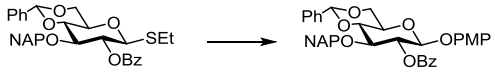
4-Methoxyphenyl 2-O-benzyl-4,6-O-benzylidene-D-galactopyranoside: The product of NAP removal from **5a** was identical to the compound described in literature.[2]



5c

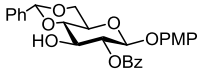
2-O-Benzyl-4,6-O-benzylidene-3-O-naphtylmethyl-β-D-galactopyranoside 5c: Yield 68%, α/β anomers in ~3:2 ratio. ^{1}H NMR ($CDCl_3$): δ 7.93–7.33 (m, H-Ar), 5.52 (s, C*H*Ph$^{\beta}$) 5.51 (s, C*H*Ph$^{\alpha}$), 5.41 (d, *J* = 3.5 Hz, H-1$^{\alpha}$), 5.09–4.75 (m, C*H*$_2$Ar), 4.72 (d, *J* = 7.5 Hz, H-1$^{\beta}$), 4.25 (br. s, H-4$^{\alpha}$), 4.25–4.22 (m, H-6$_a^{\alpha}$), 4.18–4.15 (m, H-6$_a^{\beta}$), 4.14–4.00 (m, H-2$^{\alpha}$,3$^{\alpha}$,5$^{\beta}$,6$_b^{\alpha/\beta}$), 3.87 (br. s, H-5$^{\alpha}$), 3.84 (dd, J = 7.0, 9.3 Hz, H-2$^{\beta}$), 3.67 (dd, J = 2.3, 9.7 Hz, H-3$^{\beta}$), 3.40 (d, *J* = 2.3 Hz, H-4$^{\beta}$).

^{13}C NMR ($CDCl_3$): δ 129.9–125.2 (C-Ar), 101.3 (C*H*Ph$^{\beta}$), 101.1 (C*H*Ph$^{\alpha}$), 97.5 (C-1β), 92.5 (C-1$^{\alpha}$), 79.2, 77.2, 75.8, 75.3, 73.9, 72.1, 69.5, 66.8, 62.8. HR ESI MS $C_{31}H_{30}NO_6$: $[M+Na]^+$ calc 521.1940; found 521.1955.



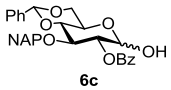
29 **6a**

4-Methoxyphenyl 2-O-Benzoyl-4,6-O-benzylidene-3-O-naphtylmethyl-β-D-glucopyranoside 6a: Compound **29**[3] (800 mg, 1.4 mmol) was reacted with p-methoxy phenol (620 mg, 5 mmol), NIS (450 mg, 2.5 mmol) and TfOH (28 ul, 0. 32 mmol) and CH_2Cl_2 (5 ml) at -10°C to room temperature, under nitrogen. After stirring overnight the mixture was quenched with TEA, and filtered. The filtrate was concentrated and purified on silica gel (cyclohexane-EtOAc) to give 514 mg of product **6a** (74%), as a white solid (m.p. 133–135°C from EtOAc). $[\alpha]_D^{25}$ = +7.5˚ (c 0.17, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.89–5.39 (m, 22H, H-Ar), 5.62 (s, 1H, C*H*Ph), 5.53 (t, J = 7.2 Hz, 1H, H-2), 5.00 (d, *J* = 8.0 Hz H-1), 4.97, 4.86 (2 d, J = 11.6 Hz, 2H, C*H*$_2$NAP), 4.37 (dd, *J* = 4.5, 9.5 Hz, 1H, H-6$_a$), 3.97–3.96 (m, 2H, H-3,4), 3.86 (t, J = 9.5 Hz, 1H, H-6$_b$), 3.67 (s, 3H, OCH_3), 3.57–3.51 (m, 1H, H-5).
^{13}C NMR ($CDCl_3$): δ 165.1 (CO), 155.6–114.5 (C-Ar), 101.4 (*C*HPh,C-1), 81.5 (C-4), 77.6 (C-3), 74.05 (C*H*$_2$NAP), 73.3 (C-2), 68.7 (C-6), 66.4 (C-5), 55.6 (OCH_3). HR ESI MS $C_{31}H_{29}O_6$: $[M+H]^+$ calc 513.1878; found 520.1913.



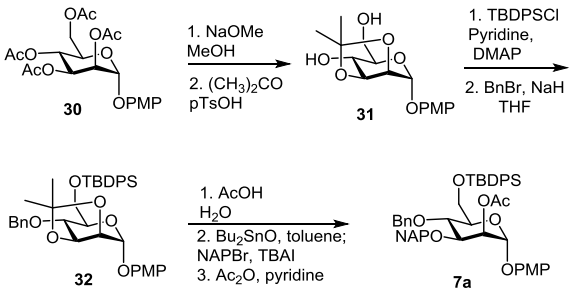
6b

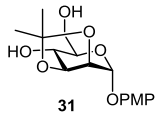
4-Methoxyphenyl 2-O-Benzoyl-4,6-O-benzylidene-β-D-glucopyranoside 6b: Yield 82%. $[\alpha]_D^{25}$ = +18.7˚ (c 0.41, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.57–6.07 (m, 14H, H-Ar), 5.55 (s, 1H, C*H*Ph), 5.36 (t, *J* = 7.6 Hz, 1H, H-2), 5.08 (d, *J* = 7.5 Hz H-1), 4.38 (dd, *J* = 4.6, 9.5 Hz, 1H, H-6$_a$), 4.07 (t, *J* = 8.0 Hz, 1H, H-3), 3.83 (t, J = 9.5 Hz, 1H, H-6$_b$), 3.73 (t, *J* = 9.1 Hz, 1H, H-4), 3.69 (s, 3H, OCH_3), 3.61–3.55 (m, 1H, H-5).
^{13}C NMR ($CDCl_3$): δ 151.3 (CO), 133.7–114.5 (C-Ar), 102.0 (*C*HPh), 101.2 (C-1), 80.7 (C-4), 74.8 (C-2), 72.5 (C-3), 68.6 (C-6), 66.4 (C-5), 55.6 (OCH_3). HR ESI MS $C_{27}H_{26}O_8$: $[M+H]^+$ calc 479.1712; found 479.1706.



6c

2-O-Benzoyl-4,6-O-benzylidene-3-O-naphtylmethyl-α,β-D-glucopyranoside 6c: Yield 78%, α/β anomers in ~2:1 ratio.^{1}H NMR ($CDCl_3$): δ 8.14–7.35 (m, H-Ar), 5.70 (s, C*H*Ph$^{\beta}$), 5.60 (d, *J* = 3.9 Hz, H-1$^{\alpha}$), 5.34 (s, C*H*Ph$^{\alpha}$), 5.13 (dd, J = 8.5 Hz, H-2$^{\alpha}$), 5.09–4.83 (m, C*H*$_2$Ar, H-2$^{\beta}$), 4.70 (d, *J* = 7.5 Hz, H-1$^{\beta}$), 4.17 (t, *J* = 11.0 Hz, H-6$_b^{\beta}$), 4.06–3.51 (m, H-3$^{\alpha/\beta}$,4$^{\alpha/\beta}$,6$_b$), 3.30–3.20 (m, 5$^{\alpha/\beta}$). HR ESI MS $C_{31}H_{28}O_7$: $[M+H]^+$ calc 535.1733; found 535.1716.

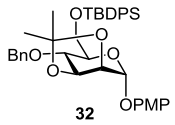




4-Methoxyphenyl 2,3-O-isopropylidene-α-D-mannopyranoside 31: Mannoside **30** (2 g, 4.1 mmol) was deacetylated with NaOMe in 20 of MeOH at pH strongly basic. After neutralization with Dowex H^+, the mixture was filtered. The filtrate was concentrated and re-dissolved in 20 ml of 1:1 acetone:dimethyl acetone, containing catalytic p-TsOH (200 mg, 0.4 mmol) and stirred for 1 h at r.t. Then water was added (50 ml) and the mixture was stirred for 2 h until the faster moving spot (cyclohexane–EtOAc 1:1) disappeared. The mixture was concentrated and chromatographed (cyclohexane-EtOAc) to give 0.88 g of product **30** (67%). $[\alpha]_D^{25}$ = +74.9° (c 0.97, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.67–6.78 (m, 27H, H-Ar), 5.62 (s, 1H, H-1), 4.31 (d, *J* = 5.0 Hz, 1H, H-2), 4.26 (t, *J* = 5.0 Hz, 1H, H-3), 3.80–3.69 (m, 7H, H-4,5,6,OCH_3), 3.53 (br. s, 1H, OH-2), 2.65 (br. s, 1H, OH-3), 1.67, 1.48 (2 s, 3H each, 2 x C*H*$_3$).

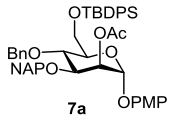
^{13}C NMR ($CDCl_3$): δ 170.1 (CO), 155.1–114.7 (C-Ar), 109.8 (*C*(OCH_3)$_2$), 96.5 (C-1), 78.5 (C-3), 75.6 (C-2), 70.2 (C-4,5), 69.2 (C-6), 55.7 (OCH_3), 27.0, 26.2 (2 x *C*H_3). HR ESI MS $C_{16}H_{22}O_7$: $[M+H]^+$ calc 327.1416; found 327.1444.



4-Methoxyphenyl 4-O-benzyl-2,3-O-isopropylidene-6-O-tertbutyldiphenylsilyl-α-D-mannopyranoside 32: Diol **31** (500 mg, 1.5 mmol) was dissolved in pyridine (5 ml) and treated with TBDPSCl (600 µl, 2.3 mmol) in the presence of DMAP (40 µg, 0.2 mmol) at r.t. After stirring for 6 h (TLC, 4:1 cyclohexane-EtOAc) the reaction was complete. The reaction crude was concentrated and purified on silica gel (cyclohexane-EtOAc) to give the 6-TBDPS mannoside, which was dissolved in dry THF (5 ml) and treated with NaH in mineral oil (150 mg, 4.5 mmol) for 15 min at °C. The BnBr (0.53 ml, 4.5 mmol) was added and stirring was continued overnight at r.t. After TLC (9:1 cyclohexane-EtOAc) showed complete reaction, the mixture was diluted with CH_2Cl_2 and partitioned with water. Combined organic layers were concentrated and chromatographed on silica gel (cyclohexane-EtOAc) to yield compound **32** (780 mg, 78% over two steps). $[\alpha]_D^{25}$ = +24.3° (c 1.6, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.77–6.79 (m, 19H, H-Ar), 5.73 (s, 1H, H-1), 4.99, 4.70 (2 d, J = 11.3 Hz, 2H, C*H*$_2$Ph), 4.55 (t, *J* = 6.5 Hz, 1H, H-4), 4.42 (d, *J* = 5.3 Hz, 1H, H-2), 3.99–3.96 (m, 1H, H-6_a), 3.92–3.82 (m, 3H, H-3,5,6_b), 3.77 (br. s, 3H, OCH_3), 1.66, 1.49 (2 s, 3H each, 2 x C*H*$_3$).

^{13}C NMR ($CDCl_3$): δ 155.0–114.6 (C-Ar), 109.6 (*C*(OCH_3)$_2$), 96.3 (C-1), 78.9 (C-4), 75.9 (C-2), 75.4 C-3), 73.2 (*C*H_2Ph), 72.2 (C-5), 62.9 (C-6), 55.8 (OCH_3), 28.0 (*C*H_3), 26.6 (tBuSi), 26.2 (*C*H_3). HR ESI MS $C_{39}H_{46}O_7Si$: $[M+Na]^+$ calc 677.2911; found 677.2864.



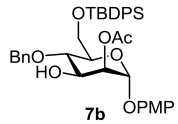
7a

4-Methoxyphenyl 2-O-acetyl-4-O-benzyl-3-O-napthylmethyl-6-O-tertbutyldiphenylsilyl-α-D-mannopyranoside 7a: Compound **32** (1.95 g, 3 mmol) was stirred overnight in 15 ml of 9:1 AcOH-H_2O at 50°C**.** The reaction crude was concentrated and purified on silica gel to give 550 mg of the diol which was used for the following step.

The material (1.55 g, 3 mmol) and Bu_2SnO (830 mg, 3.3 mmol) were suspended in toluene (30 ml) and refluxed for 2 h at the Dean Stark apparatus. The temperature was lowered to 50°C, then NAPBr (680 mg, 3.3 mmol) and TBAI (1.2 g, 3.3 mmol) were added. After stirring overnight, TLC (4:1 cyclohexane-EtOAc) showed complete reaction. The mixture was concentrated and re-dissolved in 1:1 Ac_2O-pyridine (10 ml). After 6 h, TLC (9:1 cyclohexane-EtOAc) showed formation of a faster moving spot. The reagents were evaporated and the residue was purified on silica gel to yield the product **7a** (1.55 g, 65% over three steps). $[\alpha]_D^{25}$ = +2.8˚ (c 1.74, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.67–6.78 (m, 27H, H-Ar), 5.66 (br. s, 1H, H-2), 5.50 (s, 1H, H-1), 5.06, 4.76 (2 d, *J* = 10.9 Hz, 2H, C*H*$_2$Ar), 5.00, 4.85 (2 d, *J* = 11.3 Hz, 2H, C*H*$_2$Ar), 4.33 (dd, *J* = 2.9, 9.6 Hz, H-3), 4.22 (t, *J* = 9.6 Hz, 1H, H-4), 4.22 (dd, *J* = 3.4, 10.6 Hz, H-6a), 3.93–3.88 (m, 2H, H-5,6b), 3.79 (m, 3H, OCH_3), 2.19 (s, 3H, C*H*$_3$CO), 1.15 (s, 9H, tBuSi).

^{13}C NMR ($CDCl_3$): δ 170.1 (CO), 155.5–114.7 (C-Ar), 96.9 (C-1), 78.1 (C-3), 75.5 (CH_2Ar), 74.1 (C-4), 73.1 (C-5), 75.3 (CH_2Ar), 70.9 (C-2), 70.0 (C-6), 55.7 (OCH_3), 26.8 (tBuSi), 21.2 (*C*H_3CO). HR ESI MS $C_{49}H_{52}O_8Si$: $[M+Na]^+$ calc 819.3329; found 819.3347.

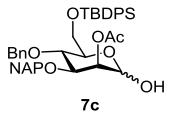


7b

4-Methoxyphenyl 2-O-acetyl-4-O-benzyl-6-O-tertbutyldiphenylsilyl-α-D-mannopyranoside 7b: Yield 88%. $[\alpha]_D^{25}$ = +36.1˚ (c 0.52, $CHCl_3$).

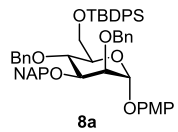
^{1}H NMR ($CDCl_3$): δ 7.67–6.78 (m, 19H, H-Ar), 5.53 (br. s, 1H, H-2), 5.39 (s, 1H, H-1), 4.99, 4.84 (2 d, *J* = 11.3 Hz, 2H, C*H*$_2$Ph), 4.44 (dd, *J* = 2.9, 9.6 Hz, H-3), 4.14 (t, *J* = 9.6 Hz, 1H, H-4), 4.09 (dd, *J* = 3.4, 10.6 Hz, H-6a), 3.96 (d, *J* = 10.8 Hz, H-6b), 3.87–3.85 (m, 1H, H-5), 3.80 (m, 3H, OCH_3), 2.26 (s, *3*H, C*H*$_3$CO), 1.19 (s, 9H, tBuSi).

^{13}C NMR ($CDCl_3$): δ 170.9 (CO), 155.3–114.0 (C-Ar), 97.4 (C-1), 75.4 (C-4), 75.2 (CH_2Ar), 73.0 (C-2), 73.8 (C-5), 70.1 (C-3), 62.7 (C-6), 55.7 (OCH_3), 26.9 (tBuSi), 21.3 (*C*H_3CO). HR ESI MS $C_{38}H_{44}O_8Si$: $[M+Na]^+$ calc 679.2703; found 679.2787.



7c

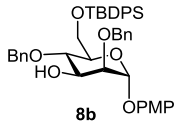
2-O-Acetyl-4-O-benzyl-3-O-napthylmethyl-6-O-tertbutyldiphenylsilyl-α,β-D-mannopyranoside 7c: Yield, 58%. Yield 77%, 3:1 α/β mixture. ^{1}H NMR ($CDCl_3$): δ 8.30–7.05 (m, 23H, H-Ar), 5.42 (dd, *J* = 1.3, 2.3 Hz, H-2$^{\beta}$), 5.31 (br. s, H-2$^{\alpha}$), 5.28 (d, H-1$^{\beta}$), 5.19 (d, J = 2.5 Hz, H-1$^{\alpha}$), 4.89–4.603 (m, C*H*$_2$Ar), 4.27 (dd, H-3$^{\alpha}$), 4.16 (dd, H-3$^{\beta}$), 4.09–3.87 (m, H-4$^{\alpha/\beta}$,5$^{\alpha/\beta}$,6$^{\alpha/\beta}$), 2.20, 2.18 (2 x s, 2 x C*H*$_3$CO), 1.27 (s, tBuSi). HR ESI MS $C_{42}H_{46}O_7Si$: $[M+Na]^+$ calc 713.2911; found 713.2918.



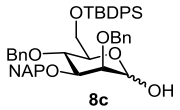
8a

4-Methoxyphenyl 2,4-di-O-benzyl-3-O-napthylmethyl-6-O-tertbutyldiphenylsilyl-α-D-mannopyranoside 8a: This compound was prepared from compound **32** (1.95 g, 3 mmol) as described for 20, except that after 3-ONAP introduction the material was dissolved in 10 ml of dry THF and treated with NaH in mineral oil (300 mg, 9 mmol) at °C, followed by BnBr (1 ml, 9 mmol) at 0°C. The mixture was stirred overnight at r.t., when TLC (9:1 cyclohexane-EtOAc) showed complete reaction. The mixture was diluted with CH_2Cl_2 and partitioned

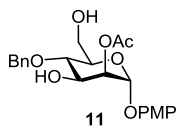
with water. Combined organic layers were concentrated and chromatographed on silica gel (cyclohexane-EtOAc) to give compound **8a** (1.8 g, 72% over two steps). $[\alpha]_D^{25}$ = +81.5˚ (c 0.80, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.64–6.78 (m, 32H, H-Ar), 5.51 (s, 1H, H-1), 5.01–4.72 (m, 6H, 3 x CH_2Ar), 4.25 (br. s, 1H, H-2), 4.41–4.34 (m, 2H, H-2,4), 4.19–4.12 (m, 2H, H-3,6a), 4.01–3.95 (m, 2H, H-5,6b), 3.84 (s, 3H, OCH_3), 1.21 (s, 9H, tBuSi).
^{13}C NMR ($CDCl_3$): δ 155.3–114.6 (C-Ar), 97.2 (C-1), 80.2 (C-4), 75.5, 75.4, 74.8 (3 x CH_2Ar), 73.7 (C-2), 73.0 (C-5), 72.6 (C-3), 63.2 (C-6), 55.7 (OCH_3), 26.9 (tBuSi). HR ESI MS $C_{57}H_{56}O_7Si$: $[M+Na]^+$ calc 844.3795; found 844.3793.



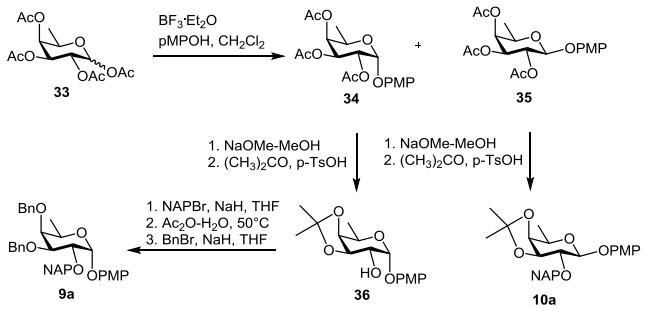
4-Methoxyphenyl 2,4-di-O-benzyl-6-O-tertbutyldiphenylsilyl-α-D-mannopyranoside 8b: Yield 81%. $[\alpha]_D^{25}$ = +21.2˚ (c 0.43, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.75–6.78 (m, 24H, H-Ar), 5.52 (s, 1H, H-1), 4.99, 4.67 (2 d, J = 11.0 Hz, 2H, CH_2Ph), 4.83, 4.71 (2 d, J = 11.3 Hz, 2H, CH_2Ph), 4.24–4.22 (m, 1H, H-3), 3.99–3.87 (m, 4H, H-2,4,6), 3.79–3.77 (m, 1H, H-5), 3.77 (s, 3H, OCH_3), 1.09 (s, 9H, tBuSi).
^{13}C NMR ($CDCl_3$): δ 158.8–114.3 (C-Ar), 95.9 (C-1), 78.6 (C-4), 76.3 (C-2), 75.0, 73.1 (2 x CH_2Ar), 72.6 (C-5), 71.7 (C-3), 62.9 (C-6), 55.7 (OCH_3), 26.8 (tBuSi). HR ESI MS $C_{43}H_{48}O_7Si$: $[M+Na]^+$ calc 727.3067; found 727.3091.



2,4-Di-O-benzyl-3-O-napthylmethyl-6-O-tertbutyldiphenylsilyl-α,β-D-mannopyranoside 8c: Yield 77%, almost exclusively α-anomer. ^{1}H NMR ($CDCl_3$): δ 7.55–7.16 (m, 28H, H-Ar), 5.47 (s, 1H, H-1), 5.02–4.63 (m, 6H, 3 x CH_2Ph), 4.21 (t, *J* = 7.6 Hz, 1H, H-4), 4.13 (dd, *J* = 3.5, 8 Hz, 1H, H-3), 4.00–3.95 (m, 2H, H-2,6), 3.88–3.85 (m, 1H, H-5), 1.28 (s, 9H, tBuSi).
^{13}C NMR ($CDCl_3$): δ 168.4 (CO), 138.1–122.7 (C-Ar), 99.9 (C-1), 80.4 (C-3), 75.3 (CH_2Ar), 75.1 (C-4), 74.4, 74.1 (2 x CH_2Ar), 73.2 (C-2), 72.7 (C-5), 62.9 (C-6), 26.7 (tBuSi). HR ESI MS $C_{47}H_{50}O_6Si$: $[M+Na]^+$ calc 761.3274; found 761.3261.



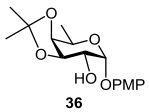
4-Methoxyphenyl 4-O-benzyl-α-D-mannopyranoside 11: Compound **7a** (1 g, 1.25 mmol) was first desilylated by treatment with 1 M TBAF (300 ul) in 10 ml of THF. After fast purification on a silica gel pad eluting with CH_2Cl_2, the material was concentrated and then treated with DDQ according to the general procedure for NAP removal. Chromatography on silica gel (cyclohexane-EtOAc) gave compound **11** (370 mg, 71% over two steps).). $[\alpha]_D^{25}$ = +15.1˚ (c 0.21, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.67–6.78 (m, 9H, H-Ar), 5.43 (s, 1H, H-1), 5.32 (br. s, 1H, H-2), 4.92, 4.88 (2 d, J = 10.8 Hz, 2H, CH_2Ph), 4.38 (dd, *J* = 3.0, 7.6 Hz, H-3), 4.32–4.27 (m, 1H, H-5), 3.87–3.84 (m, 3H, H-4,6), 3.78 (s, 3H, OCH_3), 2.20 (s, 3H, CH_3CO).
^{13}C NMR ($CDCl_3$): δ 170.8 (CO), 155.2–114.6 (C-Ar), 96.7 (C-1), 72.4 (C-4, CH_2Ar), 72.2 (C-2), 70.1 (C-3,5), 70.1 (C-3), 61.7 (C-6), 55.4 (OCH_3), 21.1 (CH_3CO). HR ESI MS $C_{22}H_{26}O_8$: $[M+Na]^+$ calc 441.1525; found 441.1533.



2,3,4,6-tetra-O-acetyl-α-D-fucopyranoside 34 and 2,3,4,6-tetra-O-acetyl-β-D-fucopyranoside 35: To a solution of D-fucose peracetate **33** (2 g, 6 mmol) and p-methoxyphenol (2,2 g, 18 mmol) in CH_2Cl_2 (30 ml) containing preactived 4 Å MS, $BF_3{\cdot}Et_2O$ (3.7 ml, 30 mmol) was added and the mixture was stirred for 2 h at r.t., at which time TLC (3:2 cyclohexane-EtOAc) showed disappearance of the starting material. After stirring, TLC (3:2 toluene-EtOAc) showed that the reaction was complete. The reaction was quenched with TEA, the crude mixture was concentrated and purified on silica gel to give the α- product **34** (1.25 g, 52%) and the β- product **35** (1.1 g, 45%). The β-anomer **35** was identical to the compound described in literature;[4] α-anomer **34**, $[\alpha]_D^{25}$ = +113.0˚ (c 3.50, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 6.92–6.72 (m, 4H, H-Ar), 5.52 (d, *J* = 4.5 Hz H-1, 1H), 5.66 (dd, J = 3.1, 10.9 Hz, 1H, H-3), 5.27 (d, 1H, H-4), 5.15 (dd, 1H, H-2), 4.07 (t, J = 8.0 Hz, 1H, H-3), 4.23–4.19 (m, 1H, H-5), 3.66 (s, 3H, OCH_3), 2.08, 1.98, 1.92 (3 x s, 3H each, 3 x C*H*$_3$CO), 1.03 (d, *J* = 6.7 Hz, 3H, H-6).

^{13}C NMR ($CDCl_3$): δ 170.6, 710.4 170.1 (CO), 155.7–114.3 (C-Ar), 95.7 (C-1), 71.0 (C-4), 67.9 (C-2,3), 65.2 (C-5), 55.6 (OCH_3), 20.7, 20.6, 20.5 (C-5), 15.8 (C-6). HR ESI MS $C_{19}H_{24}O_9$: $[M+Na]^+$ calc 419.1318; found 419.1328.

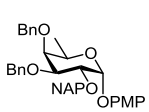


36

4-Methoxyphenyl 2,3-O-isopropylidene-α-D-fucopyranoside 36: α-Fucoside **34** (1 g, 2.5 mmol) was deacetyled by treatment with NaOMe in 10 ml of MeOH at pH strongly basic. After neutralization with Dowex H^+, the resin was filtered off. The filtrate was concentrated and re-dissolved in acetone dimethyl acetal (30 ml) containing p-TsOH (100 mg) as catalyst. After stirring overnight at r.t., the mixture was neutralized with TEA, concentrated and purified on silica gel (cyclohexane-EtOAc) to afford **36** (660 mg, 85%). $[\alpha]_D^{25}$ = +17.2˚ (c 0.41, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 6.98–6.77 (m, 4H, H-Ar), 5.32 (d, *J* = 3.6 Hz H-1, 1H), 5.30 (t, J = 5.6 Hz, 1H, H-3), 4.24–4.19 (m, 1H, H-5), 4.06 (d, J = 6.0 Hz, 1H, H-4), 3.87–3.82 (m, 1H, H-2), 3.71 (s, 3H, OCH_3), 1.48, 1.32 (2 x s, 3H each, 2 x CH_3), 1.25 (d, *J* = 6.7 Hz, 3H, H-6).

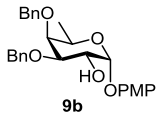
^{13}C NMR ($CDCl_3$): δ 155.5–114.5 (C-Ar), 109.3 (*C*$(CH_3)_2$), 97.5 (C-1), 76.2 (C-3), 74.6 (C-4), 69.6 (C-2), 64.5 (C-5), 55.6 (OCH_3), 27.9, 26.0 (2 x CH_3), 16.2 (C-6). HR ESI MS $C_{16}H_{22}O_6$: $[M+Na]^+$ calc 333.1314; found 333.1318.



9a

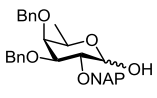
4-Methoxyphenyl 3,4-di-O-benzyl-2-O-naphtylmethyl-α-D-fucopyranoside 9a: To a solution of compound **36** (600 mg, 1 mmol) in THF (5 ml), 60% NaH in mineral oil (117 mg, 3 mmol) was added at 0°C under nitrogen. After 15 min, NAPBr (660 mg, 3 mmol) was added and the mixture was stirred overnight at r.t. After washing with water, combined organic layers were concentrated and purified on silica gel (cyclohexane-EtOAc). Fractions containing the product were concentrated and dissolved in 10 ml of 9:1 AcOH-H_2O and kept at 50°C

overnight, and then it was concentrated. The mixture was washed with ad $NaHCO_3$, and organic layers were combined and concentrated. The residue was dissolved in THF (10 ml) and treated with 60% NaH in mineral oil (235 mg, 6 mmol) and BnBr (0.71 ml, 6 mmol). After stirring overnight, the mixture was concentrated and purified on silica gel (cyclohexane-EtOAc) to afford **9a** (407 mg, 69% over three steps), as a white solid (m.p. 133–135°C from EtOAc). $[\alpha]_D^{25}$ = +7.5˚ (c 0.17, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.77–6.77 (m, 22H, H-Ar), 5.43 (d, *J* = 3.6 Hz H-1,1H), 5.06–4.69 (m, 6H, 3 x C*H*$_2$Ar), 4.27 (dd, *J* = 9.8 Hz, 1H, H-5), 4.32 (dd, *J* = 2.6 Hz, H-3), 4.10–4.06 (m, 1H, H-5), 3.80 (s, 3H, OCH_3), 3.77 (d, 1H, H-4), 1.13 (d, *J* = 6.3 Hz, 3H, H-6).
^{13}C NMR ($CDCl_3$): δ 155.5–114.5 (C-Ar), 97.3 (C-1), 79.3 (C-3), 77.7 (C-4), 76.6 (C-3), 75.2 (*C*H_2Ar), 73.4 (2 x *C*H_2Ar), 67.1 (C-5), 55.6 (OCH_3), 16.6 (C-6). HR ESI MS $C_{38}H_{38}O_6$: $[M+K]^+$ calc 629.2195; found 629.2305.



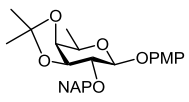
9b

4-Methoxyphenyl 3,4-di-O-benzyl-α-D-fucopyranoside 9b: Yield 94%.). $[\alpha]_D^{25}$ = +38.7˚ (c 0.42, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.40–6.37 (m, 14H, H-Ar), 5.41 (d, *J* = 3.8 Hz H-1,1H), 4.92, 4.61 (2 d, J = 12.0 Hz, 2H, C*H*$_2$Ph), 4.74 (s, 2 H, C*H*$_2$Ph), 4.28–4.22 (m, 1H, H-2), 4.00–3.94 (m, 1H, H-5), 3.83 (dd, *J* = 2.3, 9.9 Hz, H-3), 3.70–3.68 (m, 4H, H-4,OCH_3), 3.77 (d, 1H, H-4), 1.10 (d, *J* = 6.7 Hz, 3H, H-6b).
^{13}C NMR ($CDCl_3$): δ 155.5–114.6 (C-Ar), 98.7 (C-1), 79.9 (C-5), 76.7 (C-4), 74.9 (*C*H_2Ar), 72.6 (*C*H_2Ar), 68.7 (C-2), 67.5 (C-3), 55.6 (OCH_3), 16.7 (C-6). HR ESI MS $C_{27}H_{30}O_6$: $[M+Na]^+$ calc 473.1940; found 473.1917.



9c

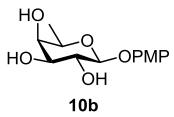
3,4-Di-O-benzyl-2-O-naphtylmethyl-α,β-D-fucopyranoside 9c: ^{1}H NMR ($CDCl_3$) showed α/β anomers in ratio 2:3. δ 7.79–6.58 (m, H-Ar), 5.27 (d, *J* = 3.7 Hz, H-1$^{\alpha}$), 5.00–4.61 (m, 6 x C*H*$_2$Ph, incl. d, 4.61, J = 8.0 Hz, H-1$^{\beta}$), 4.11–4.04 (m, H-2$^{\alpha}$,3$^{\beta}$), 4.00–3.94 (m, 1H, H-5$^{\alpha}$), 3.92 (dd, *J* = 2.3, 9.9 Hz, H-3$^{\alpha}$), 3.80 (dd, *J* = 7.0, 8.9 Hz, H-2$^{\beta}$), 3.62 (d, 1H, H-4$^{\alpha}$), 3.51–3.42 (m, H-4$^{\beta}$,5$^{\beta}$), 1.19 (d, *J* = 6.6 Hz, H-6$^{\beta}$), 1.11 (d, *J* = 6.6 Hz, H-6$^{\alpha}$).
^{13}C NMR ($CDCl_3$): δ 133.0–116.1 (C-Ar), 97.8 (C-1$^{\beta}$), 91.8 (C-1$^{\alpha}$), 82.5, 80.7, 77.4, 76.5, 75.1, 74.9, 74.8, 73.5, 73.1, 70.8, 66.8, 16.9 (C-6$^{\beta}$), 16.8 (C-6$^{\alpha}$). HR ESI MS $C_{31}H_{32}O_5$: $[M+H]^+$ calc 485.2328; found 485.2358.



10a

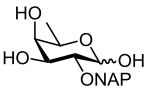
4-Methoxyphenyl 3,4-O-isopropylidene-2-O-naphtylmethyl-β-D-fucopyranoside 10a: Compound **35** (1 g, 2.5 mmol) was first deacetyled by treatment with NaOMe in 10 ml of MeOH at pH strongly basic. After neutralization with Dowex H^+, the resin was filtered off. The filtrate was concentrated and re-dissolved in acetone dimethyl acetal (30 ml) containing p-TsOH (100 mg) as catalyst. After stirring overnight at r.t., the mixture was quenched with TEA and concentrated. The residue was dissolved in THF (10 ml) and treated with 60% NaH in mineral oil (195 mg, 5 mmol) at 0°C under nitrogen. After 15 min, NAPBr (1.1 g, 5 mmol) and stirred overnight at r.t. After TLC (4:1 cyclohexane-EtOAc) showed complete reaction, the mixture was concentrated and chromatography of the residue on silica gel (cyclohexane-EtOAc) gave compound **10a** (630 mg, 81%). $[\alpha]_D^{25}$ = +76.0˚ (c 0.70, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.81–6.79 (m, 12H, H-Ar), 5.04, 5.12 (2 d, *J* = 12.0 Hz, 2H, C*H*$_2$NAP), 4.76 (d, *J* = 8.1 Hz, 1H, H-1), 4.12 (t, *J* = 6.2 Hz, 1H, H-3), 3.98 (d, J = 1.0, 5.0 Hz, 1H, H-4), 3.90–3.83 (m, 1H, H-5), 3.73 (s, 3H, OCH_3), 3.64 (t, *J* = 7.0 Hz, 1H, H-2), 1.37 (d, *J* = 6.4 Hz, 3H, H-6), 1.32, 1.31 (2 x s, 3H each, 2 x C*H*$_3$).

^{13}C NMR ($CDCl_3$): δ 152.3–115.5 (C-Ar), 102.1 (C-1), 79.3 (C-3), 71.2 (C-2), 76.3 (C-4), 73.7 (CH_2Ar), 68.9 (C-5), 55.6 (OCH_3), 27.8, 26.4 (2 x CH_3), 16.7 (C-6). HR ESI MS $C_{27}H_{30}O_6$: $[M+H]^+$ calc 468.2351; found 468.2386.



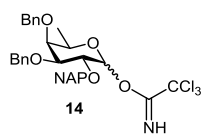
10b

4-Methoxyphenyl β-D-fucopyranoside 10b: Yield 45%.[4] ^{1}H NMR ($CDCl_3$): δ 7.03–6.71 (m, 4H, H-Ar), 4.72 (d, *J* = 8.0 Hz, 1H, H-1), 3.84 (t, *J* = 8.2 Hz, 1H, H-2), 3.80–3.68 (m, 6H, H-3,4,5, incl. 3.77 s, OCH_3), 1.39 (d, *J* = 6.3 Hz, 3H, H-6). ^{13}C NMR ($CDCl_3$): δ 118.2–114.5 (C-Ar), 102.1 (C-1), 77.2 (C-3), 73.7 (C-2), 71.2 (C-4), 70.8 (C-5), 55.6 (OCH_3), 16.3 (C-6). HR ESI MS $C_{13}H_{18}O_6$: $[M+H]^+$ calc 293.1003; found 293.1001.



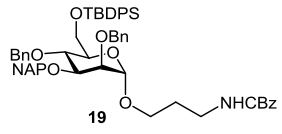
10c

2-O-Naphtylmethyl α,β-D-fucopyranoside 10c: Yield 41%, α/β anomers in 2:1 ratio. ^{1}H NMR ($CDCl_3$): δ 7.78–7.10 (m, H-Ar), 5.25 (d, *J* = 2.5 Hz, 1H, H-1_α), 4.88–4.71 (m, CH_2NAP), 4.66 (d, *J* = 7.5 Hz, 1H, H-1_β), 4.17–4.05 (m, H-$5_{\alpha,\beta}$), 3.96 (dd, J = 7.7 Hz, 1H, H-2_α), 3.75 (d, J = 3.2 Hz, 1H, H-$4_{\alpha,\beta}$), 3.70–3.63 (m, H-3_α,4_β), 3.59–3.58 (m, H-3_β), 3.41 (t, J =8.5 Hz, H-2_β), 1.28 (d, *J* = 6.0 Hz, H-6_β), 1.21 (d, *J* = 6.3 Hz, H-6_α). HR ESI MS $C_{17}H_{20}O_5$: $[M+Na]^+$ calc 327.1188; found 327.1208.



14

3,4-Di-O-benzyl-α,β-D-fucopyranosyl trichloroacetimidate 14: The 1-OH fucoside **9c** (110 mg, 0.22 mmol) was dissolved in 5 ml of CH_2Cl_2, and CCl_3CN (0.1 ml, 1.1 mmol) followed by DBU (7 µl, 0.044 mmol) was added. The reaction was complete in 30 min (7:3 cyclohexane-EtOAc). The mixture was concentrated and purified on silica gel to give 85 mg of product **34** (62%) as α/β anomers in 3:2 ratio. ^{1}H NMR ($CDCl_3$): δ 8.45 (NH), 7.76–6.51 (m, 14H, H-Ar), 6.51 (d, *J* = 2.3 Hz, H-1α), 5.35 (d, *J* = 10.0 Hz, H-1β), 4.79–4.61 (m, 6 x CH_2Ph), 4.35 (dd, *J* = 3.3, 10.5 Hz, H-3β), 4.27 (dd, *J* = 8.0, 9.9 Hz, H-2β), 4.11–4.04 (m, H-2α,5β), 4.06–4.03 (m, 1H, H-5α), 4.00 (dd, *J* = 2.3, 9.3 Hz, H-3α), 3.80 (dd, *J* = 7.0, 8.9 Hz, H-2β), 3.79–3.55 (m, H-4 α,4β,5β), 1.15 (d, *J* = 6.6 Hz, H-6β), 1.11 (d, *J* = 6.6 Hz, H-6α). ^{13}C NMR ($CDCl_3$): δ 161.5 (CNH), 138.5–126.4 (C-Ar), 102.0 (C-1β), 95.4 (C-1α), 82.9, 82.1, 81.9, 78.2, 77.4, 76.5, 74.9, 74.8, 73.2, 72.9, 70.4, 69.6, 68.4, 16.7 (C-6β), 14.9 (C-6α). HR ESI MS $C_{31}H_{32}O_5$: $[M+H]^+$ calc 650.1244; found 650.1248.



19

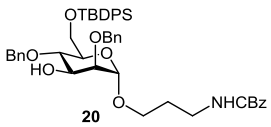
3-(Benzyloxycarbonyl)aminopropyl 2,4-di-O-benzyl-3-O-naphtylmethyl-6-O-tertbutyldiphenylsilyl-α-D-mannopyranoside 19: Compound **8c** (500 mg, 0.65 mmol) was dissolved in 20 ml of CH_2Cl_2 and Cl_3CCN (0.35 ml, 3.25 mmol) followed by DBU (30 µl, 0.2 mmol) was added. After stirring for 3 h the mixture was concentrated and purified on silica gel (cyclohexane-EtOAc with 0.1% TEA) to give the trichloroacetimidate **18** (344 mg, 67%). ^{1}H NMR ($CDCl_3$): δ 8.70 (s 1H, NH), 7.88–7.18 (m, 28H, H-Ar), 6.63 (d, *J* = 3.5 Hz, H-1), 5.04–4.66 (m, 3 x CH_2Ph), 4.21 (t, J = 8.5 Hz, 1H, H-4), 4.18–4.09 (m, 4H, H-3,5,6), 3.98 (br. s, 1H, H-2).

To a solution of donor **18** (400 mg, 0.5 mmol) and 3-(benzyloxycarbonylamino)-1-propanol (151 mg, 0.72 mmol) in CH_2Cl_2 (5 ml) containing preactivated 4 Å MS, NIS (162 mg, 0.72 mmol) followed by TfOH (13 µl, 0.14 mmol) was added at -20°C. The mixture was stirred for 30 min, when TLC (7:3 cyclohexane-EtOAc) showed complete reaction. The mixture was neutralized with TEA, filtered and

concentrated. Purification of the residue on silica gel (cyclohexane-EtOAc) gave the product **19** (340 mg, 73%). $[\alpha]_D^{25}$ = +4.1˚ (c 0.55, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.89–7.21 (m, 33H, H-Ar), 5.15, 5.08 (2 d, J = 11.7 Hz, 2H, CH_2^{Cbz}), 4.99–4.62 (m, 7H, 3 x C*H*$_2$Ph, incl., s, 4.82, H-1), 4.11 (t, J = 8.8 Hz, 1H, H-4), 4.03–3.96 (m, 3H, H-5,6), 3.83 (br. s, 1H, H-2), 3.82–3.77 (m, 1H, H-1'a), 3.71 (dd, J = 3.2, 9.1 Hz, 1H, H-3), 3.47–3.42 (s, 1H, H-1'b), 3.31–3.22 (m, 2H, H-3'), 1.88–1.75 (m, 2H, H-2'), 1.10 (s, 9H, tBuSi).

^{13}C NMR ($CDCl_3$): δ 156.3 (CONH), 138.2–125.5 (C-Ar), 97.8 (C-1), 80.3 (C-2), 75.5, 75.1, 74.7 (CH_2Ar), 73.8 (C-3), 72.8 (C-5), 72.4 (C-5), 66.6 (*C*H_2^{Cbz}), 65.4 (C-6), 63.3 (C-1'), 38.9 (C-3'), 29.4 (C-2'), 26.7 (tBuSi). HR ESI MS $C_{58}H_{63}NO_8Si$: $[M+Na]^+$ calc 952.4221; found 952.4234.



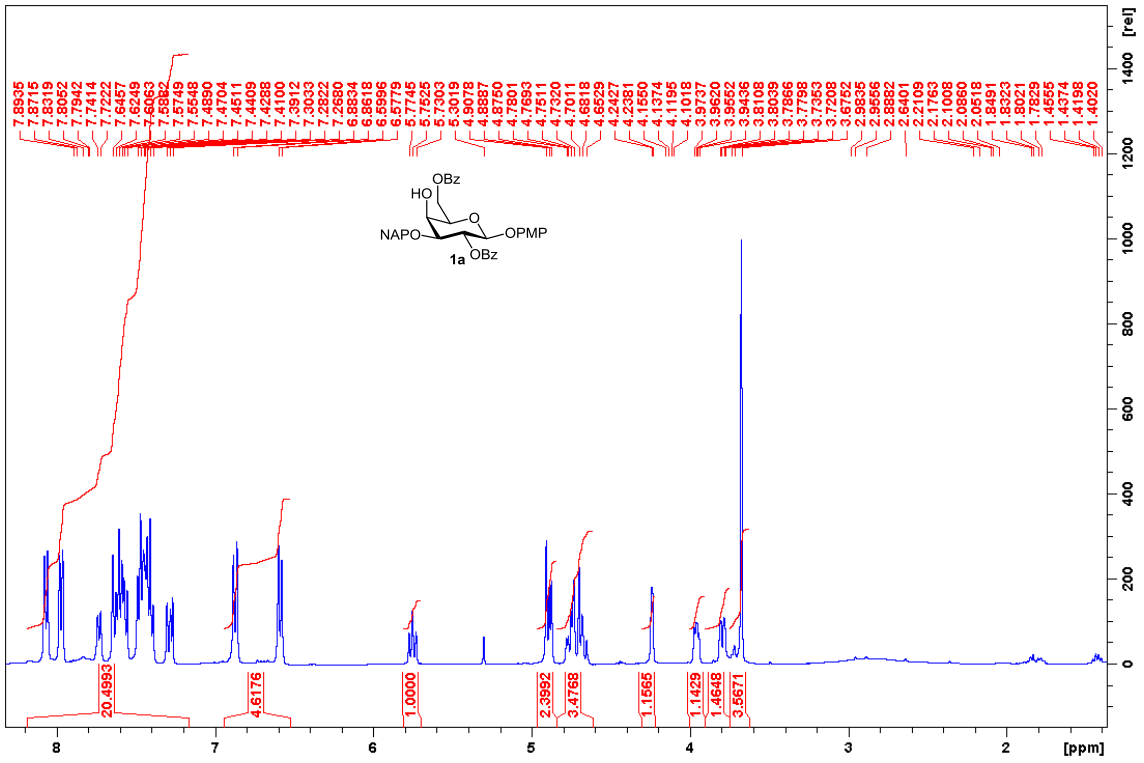
20

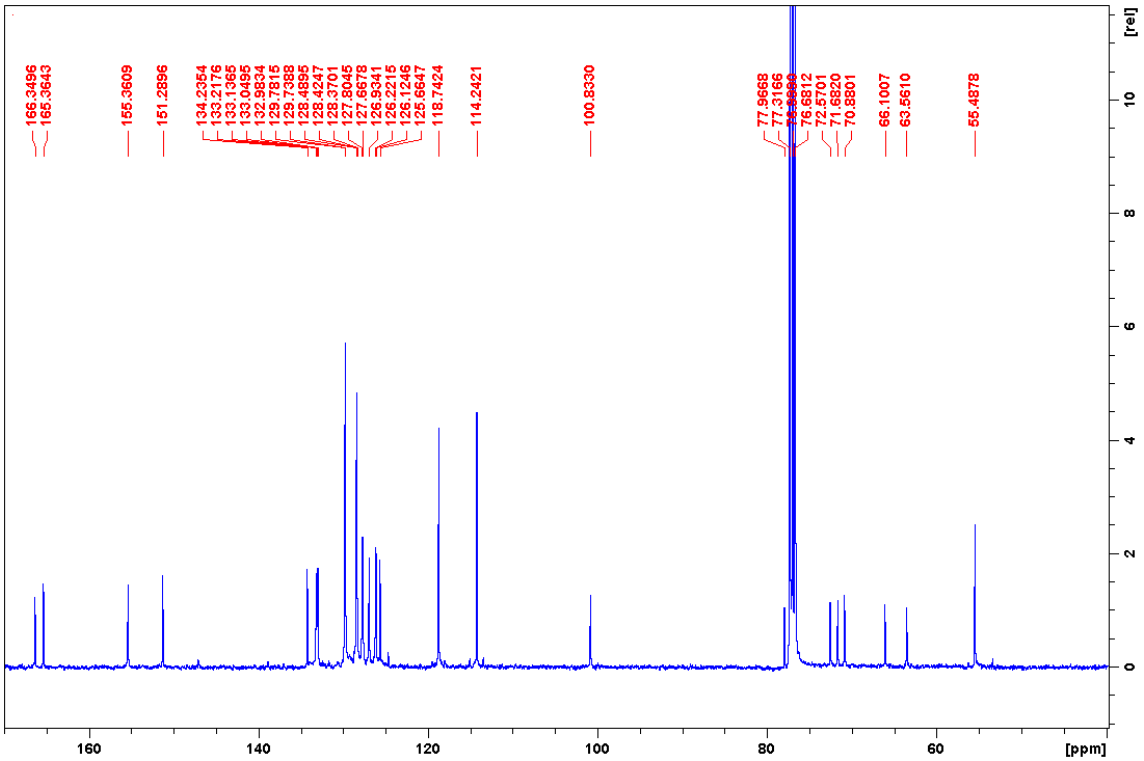
3-(Benzyloxycarbonyl)aminopropyl 2,4-di-O-benzyl-6-O-tertbutyldiphenylsilyl-α-D-mannopyranoside 20: The general procedure for NAP removal was followed, yield 78%.). $[\alpha]_D^{25}$ = +9.6˚ (c 0.78, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.82–7.30 (m, 24H, H-Ar), 5.31 (br. s, 2H, CH_2^{Cbz}), 4.96, 4.64 (2 d, J = 11.9 Hz, 2H, C*H*$_2$Ph), 4.95 (s, 1H, H-1), 4.82, 4.70 (2 d, J = 11.0 Hz, 2H, C*H*$_2$Ph), 4.07–3.97 (m, 3H, H-1'a,3,6a), 3.87–3.79 (m, 3H, H-4,5,6b), 3.68 (d, J = 7.8 Hz, 1H, H-2), 3.48–3.45 (s, 1H, H-1'b), 3.35–3.27 (m, 2H, H-3'), 1.87–1.77 (m, 2H, H-2'), 1.13 (s, 9H, tBuSi).

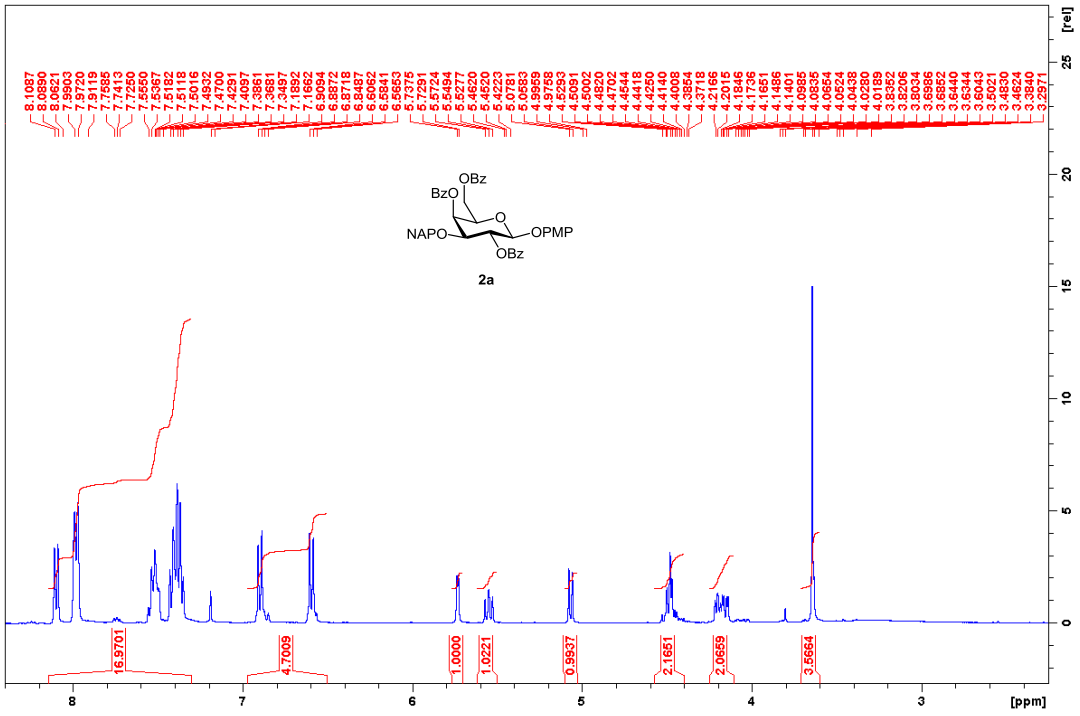
^{13}C NMR ($CDCl_3$): δ 156.3 (CONH), 138.6–127.5 (C-Ar), 96.9 (C-1), 78.8 (C-2), 76.4 (C-4), 74.8, 72.5 (CH_2Ar), 72.3 (C-3), 71.7 (C-5), 63.5 (*C*H_2^{Cbz}), 61.5 (C-6), 63.2 (C-1'), 38.6 (C-3'), 29.2 (C-2'), 27.4 (tBuSi). HR ESI MS $C_{47}H_{53}NO_7Si$: $[M+Na]^+$ calc 794.3489; found 794.3492.

Compound 1a





Compound 2a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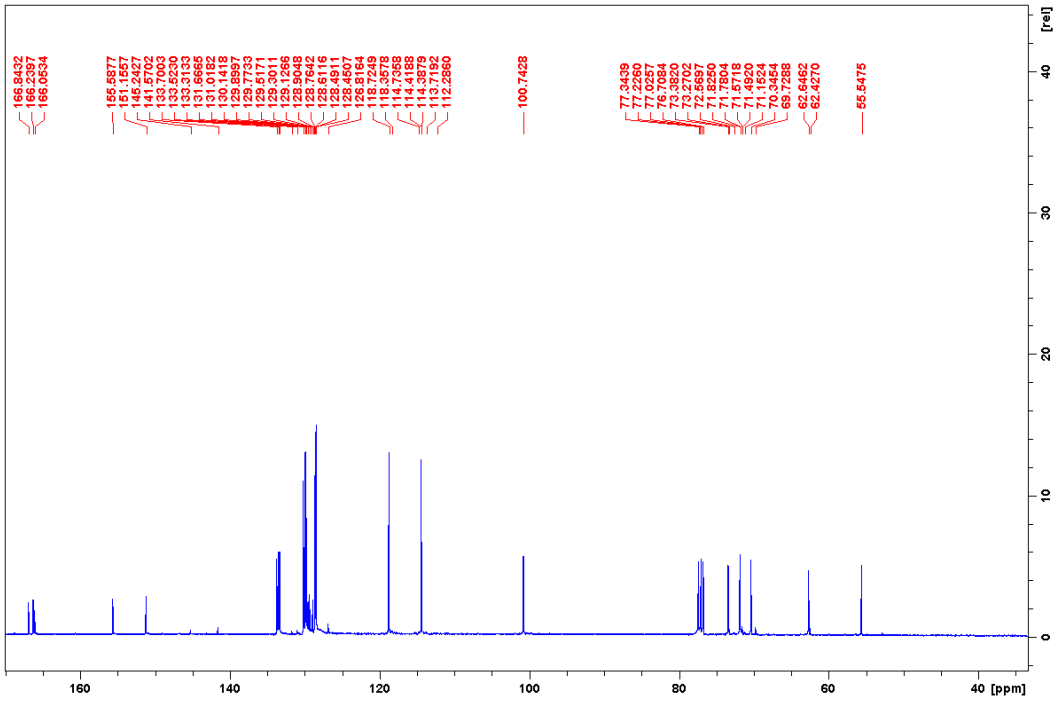
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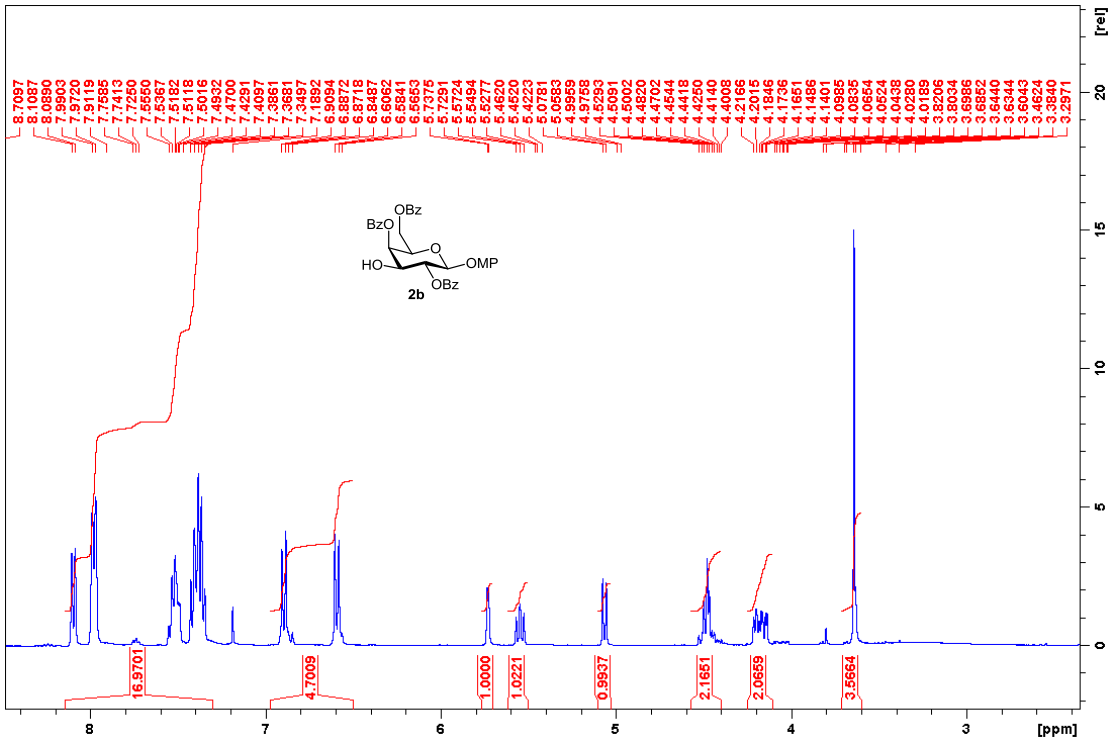
Compound 2b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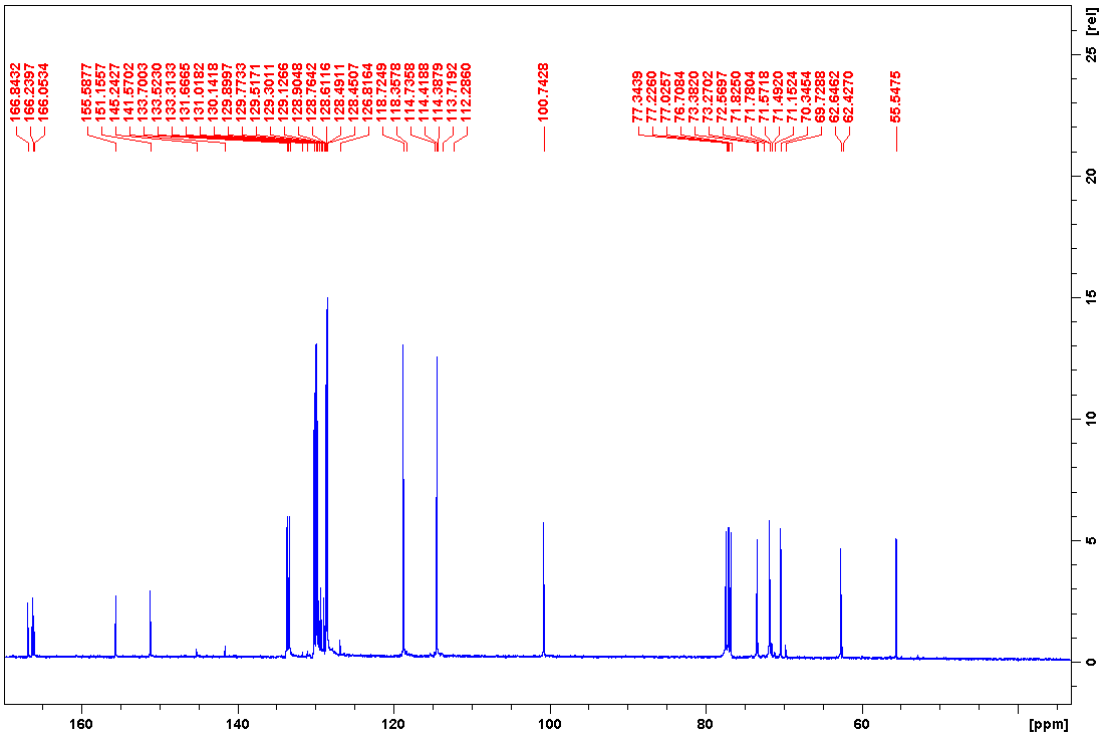
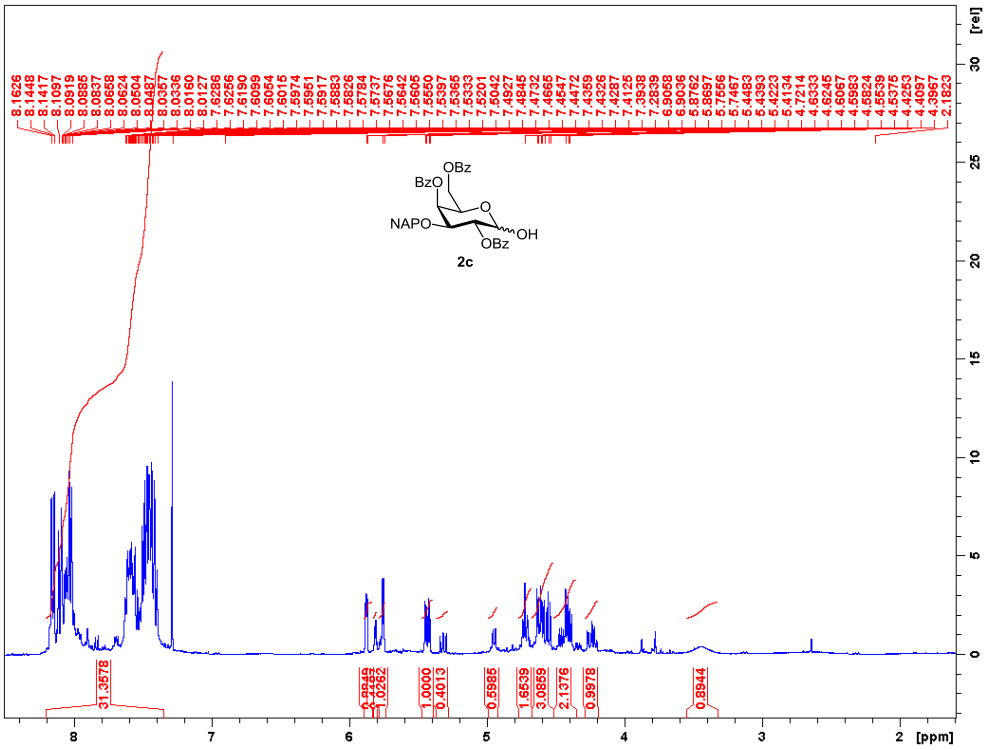
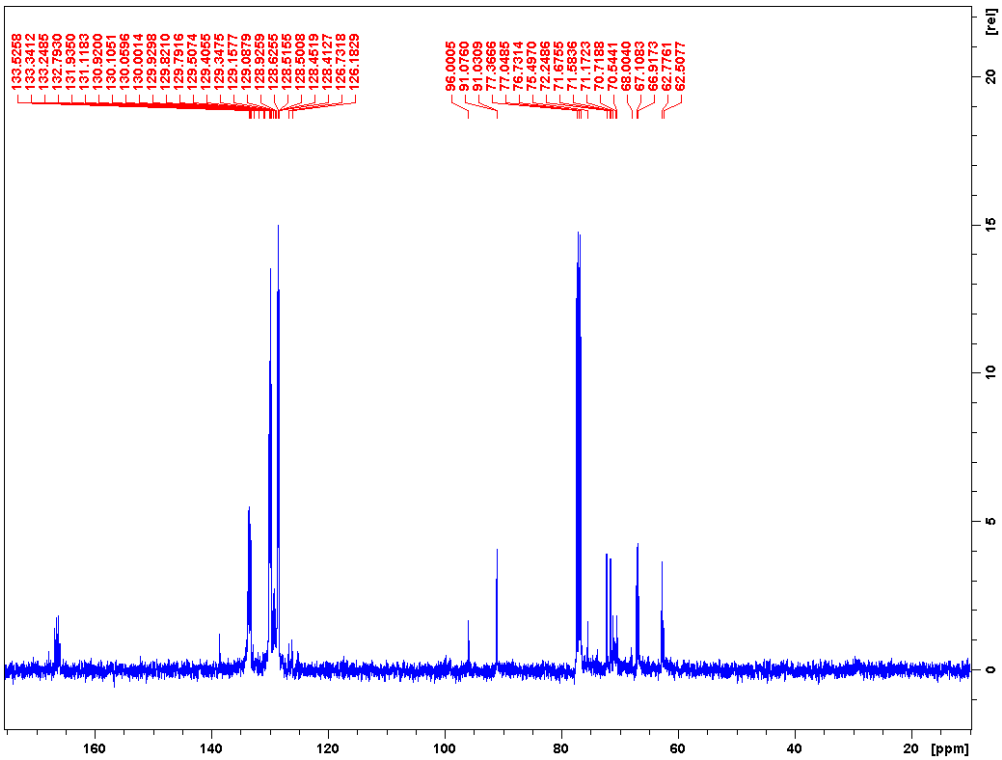
8.0890
7.9903
7.9720
7.9119
7.7585
7.7413
7.7250
7.5550
7.5367
7.5182
7.5118
7.5016
7.4832
7.4700
7.4291
7.4097
7.3861
7.3681
7.3497
7.1892
6.9094
6.8872
6.8718
6.8487
6.6062
6.5841
6.5655
6.5455
5.7291
5.5724
5.5494
5.5277
5.4620
5.4520
5.4223
5.0781
5.0583
4.9959
4.9758
4.5293
4.5091
4.5002
4.4820
4.4702
4.4544
4.4418
4.4250
4.4140
4.4008
4.2166
4.2015
4.1846
4.1736
4.1651
4.1486
4.1401
4.0985
4.0835
4.0654
4.0524
4.0438
4.0280
4.0189
3.8206
3.8034
3.6986
3.6852
3.6440
3.6344
3.6043
3.4624
3.3840
3.2971
OBz
BzO
O
HO
OMP
OBz
2b
16.9701
4.7009
1.0000
1.0221
0.9937
2.1651
2.0659
3.5664
[rel]
[ppm]

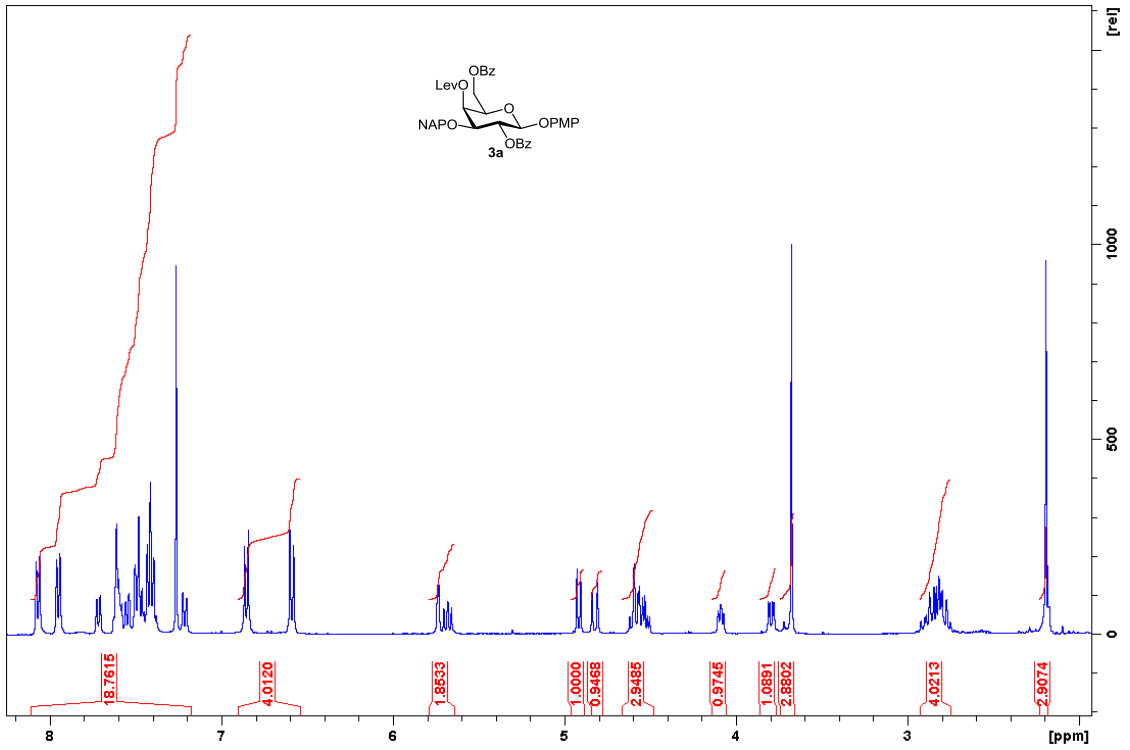

166.8432
166.2397
166.0534
155.5877
151.1557
145.2427
141.5702
133.7003
133.5230
133.3133
131.6665
131.0182
130.1418
129.8997
129.7733
129.5171
129.3011
129.1266
128.9048
128.7642
128.6116
128.4911
128.4601
128.4164
118.7248
118.3578
114.7588
114.4188
114.3979
113.7192
112.2860
100.7428
77.3439
77.2260
77.0257
76.7084
73.3820
73.2702
72.5697
71.8250
71.7804
71.5718
71.4920
71.1524
70.3454
69.7288
62.6462
62.4270
55.5475
[rel]
[ppm]

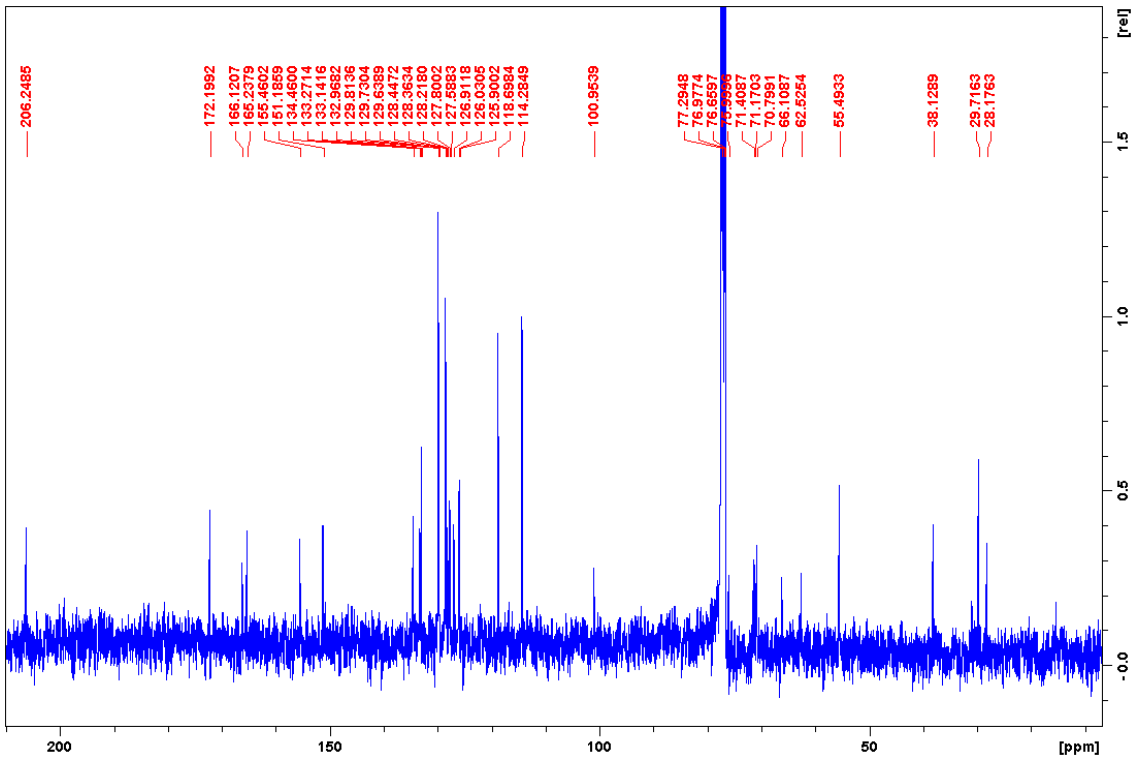
Compound 2c



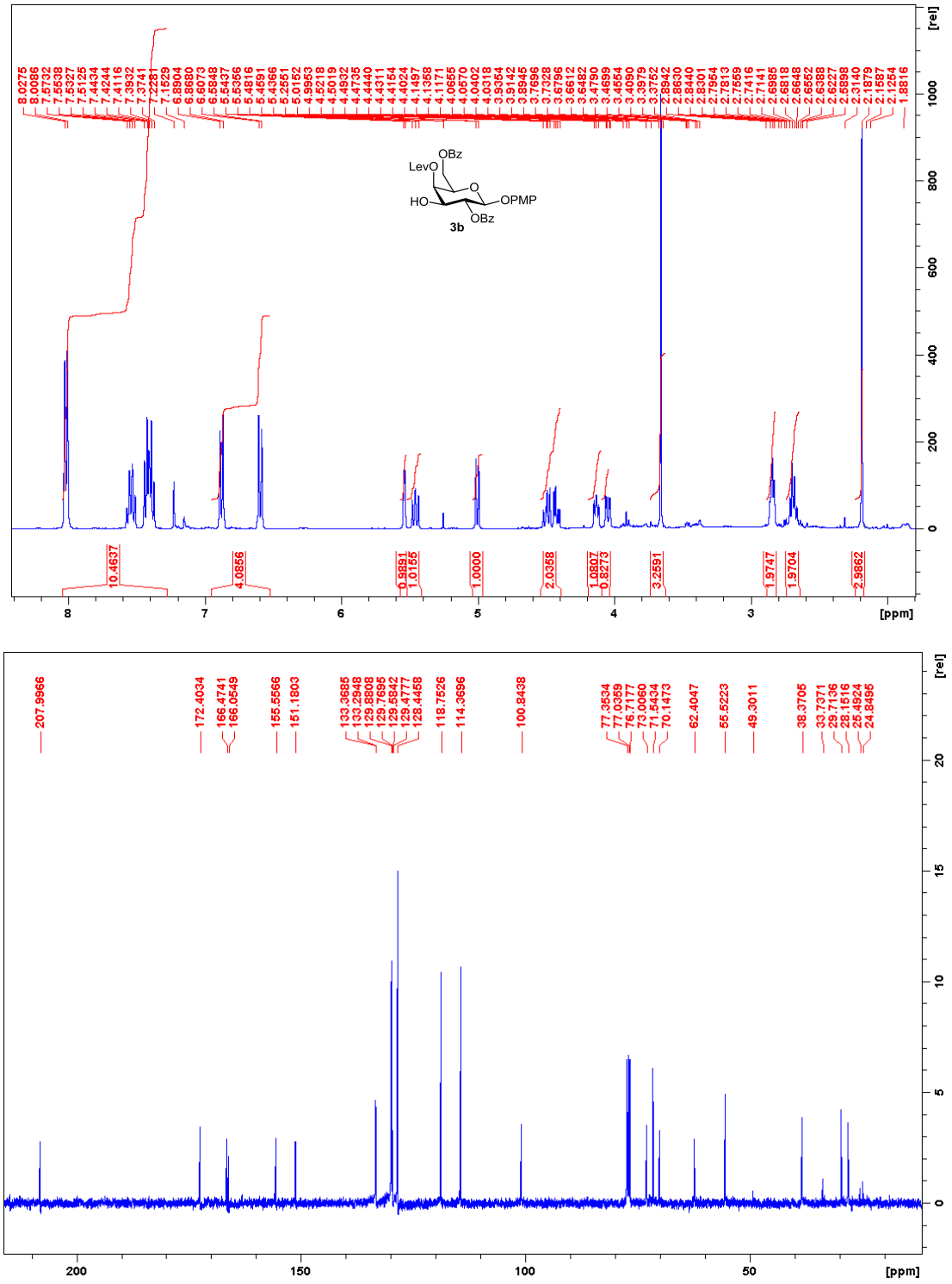


Compound 3a

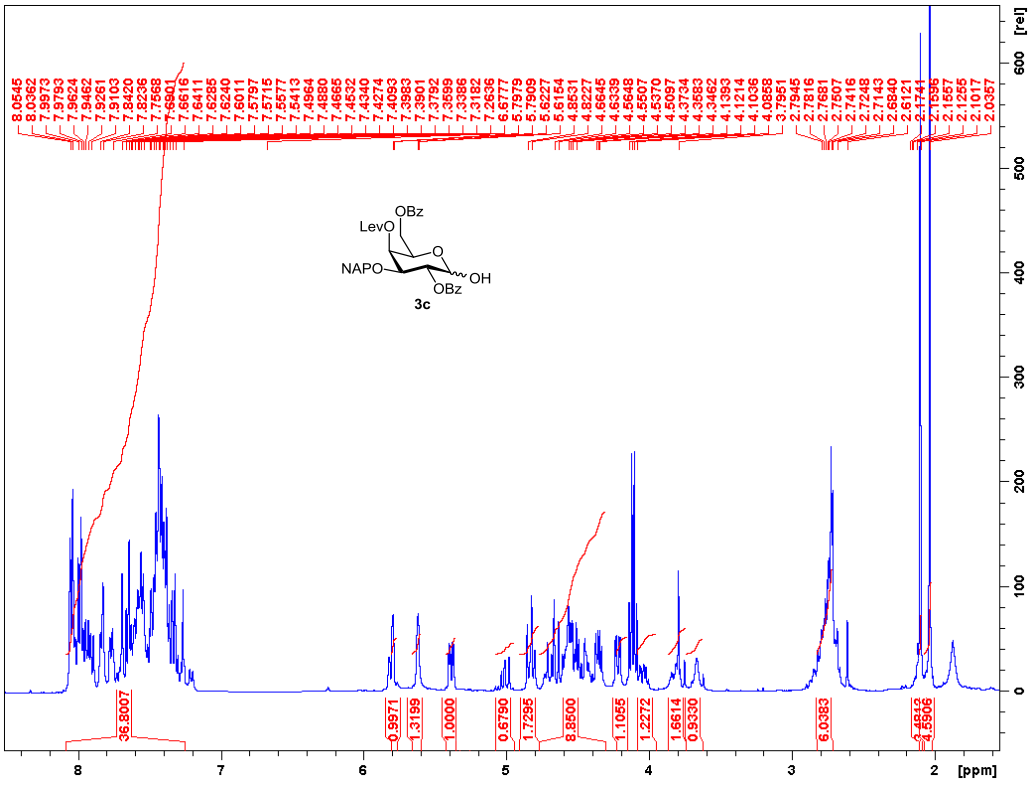

OBz
LevO
O
NAPO
OPMP
OBz
3a
[rel]
1000
500
0
18.7615
4.0120
1.8533
1.0000
0.9468
2.9485
0.9745
1.0891
2.8802
4.0213
2.9074
8
7
6
5
4
3
[ppm]


206.2485
172.1992
166.1207
165.2379
155.4602
151.1859
134.4800
133.2714
133.1416
132.9682
129.8136
129.7304
129.6389
128.4472
128.3634
128.2180
127.8002
127.5883
126.9118
126.0305
125.9002
118.6984
114.2849
100.9539
77.2948
76.9774
76.6597
71.4087
71.1703
70.7991
66.1087
62.5254
55.4933
38.1289
29.7163
28.1763
[rel]
1.5
1.0
0.5
-0.0
200
150
100
50
[ppm]

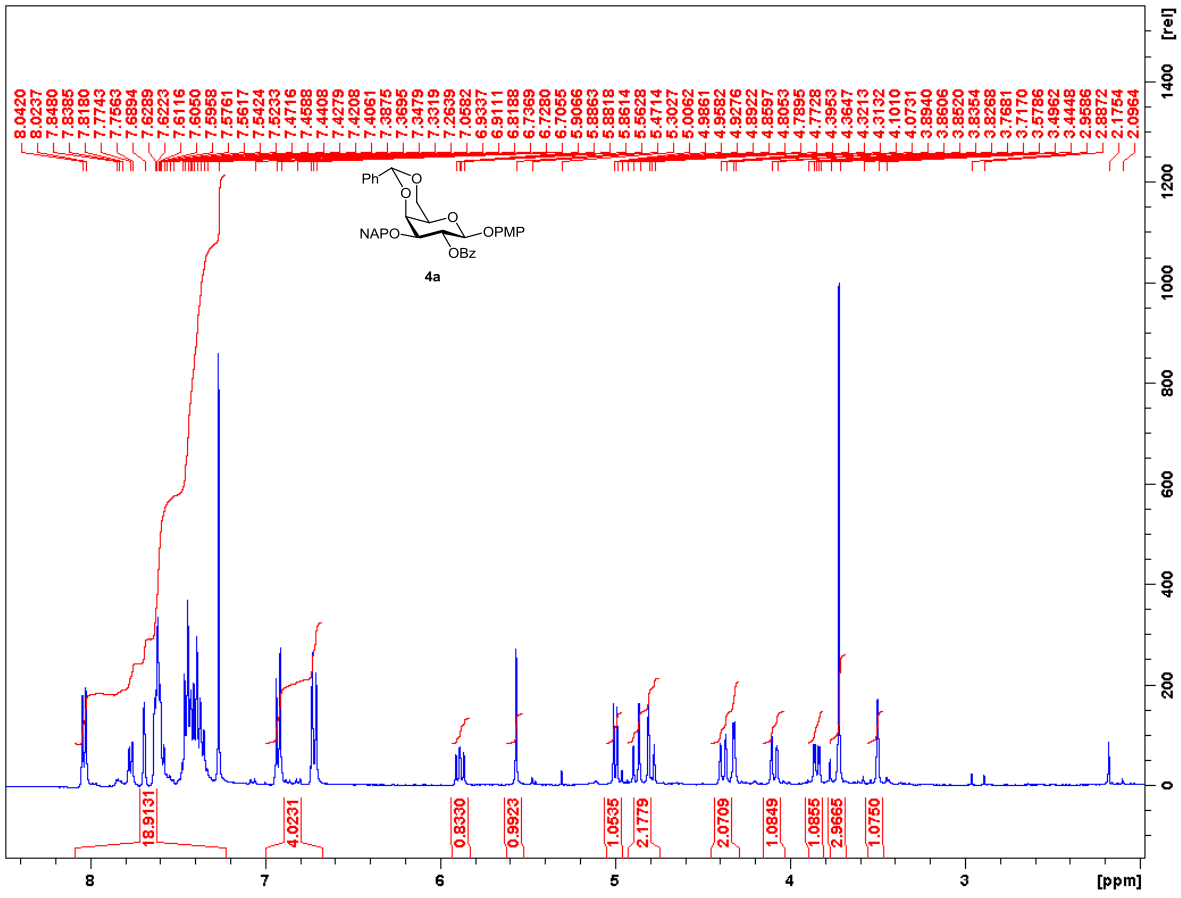
Compound 3b



Compound 3c



Compound 4a


8.0420
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7.8480
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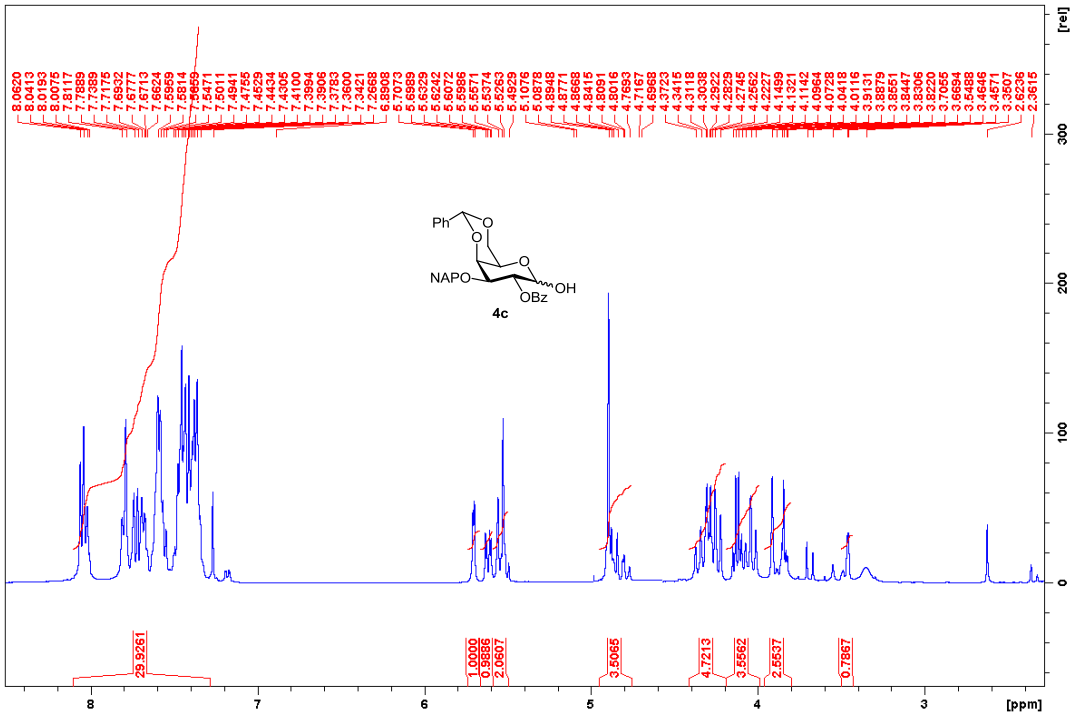
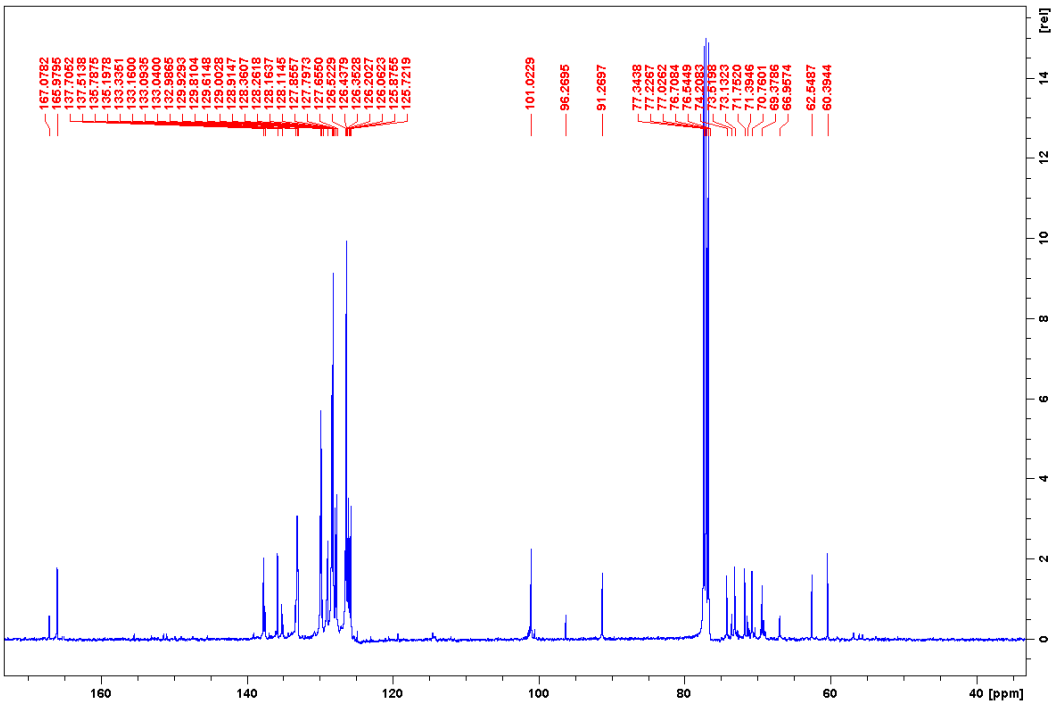
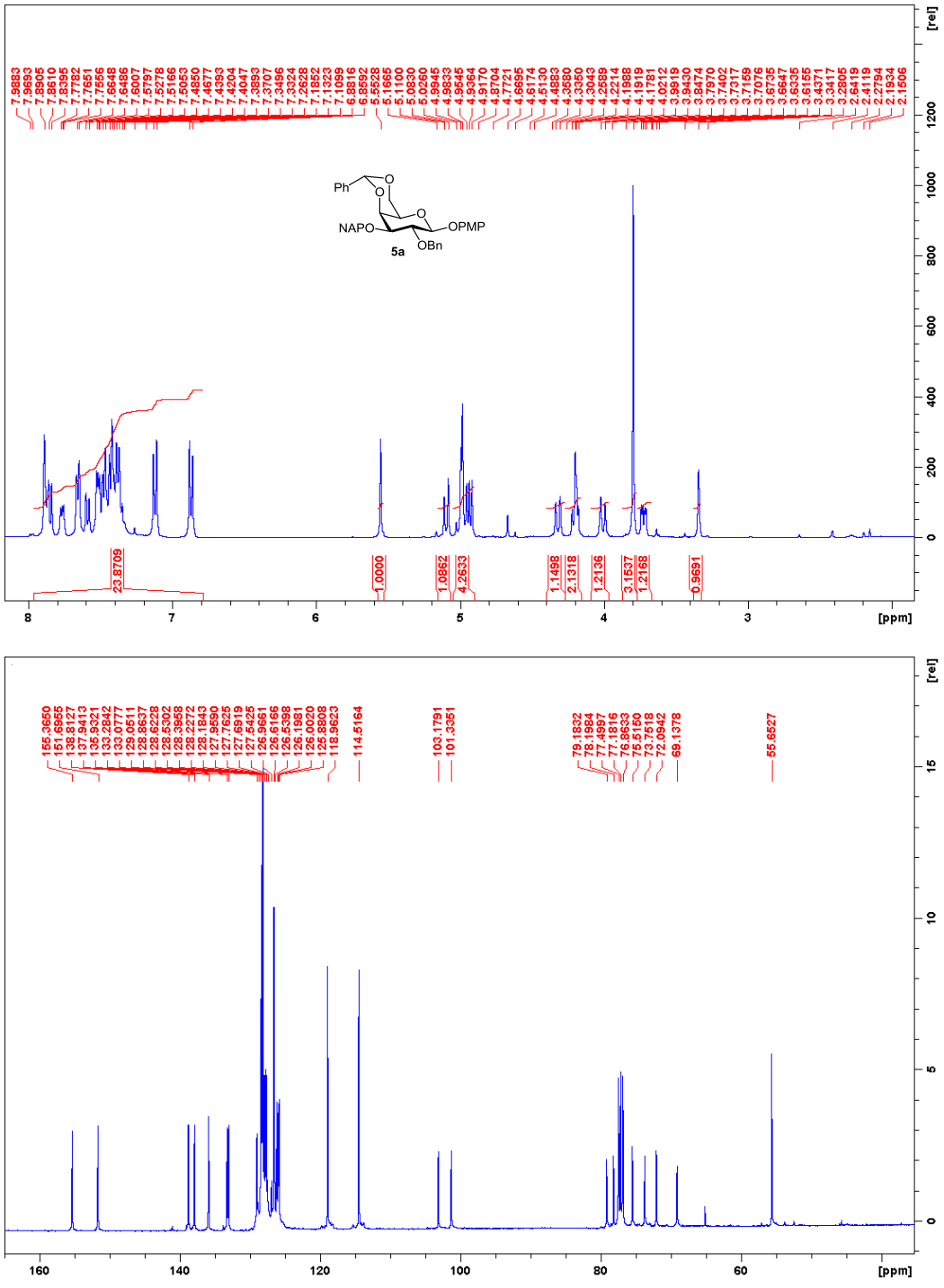
7.8180
7.7743
7.7563
7.6894
7.6289
7.6223
7.6116
7.6050
7.5958
7.5761
7.5617
7.5424
7.5233
7.4716
7.4588
7.4408
7.4279
7.4208
7.4061
7.3875
7.3695
7.3479
7.3319
7.2639
7.0582
6.9337
6.9111
6.8188
6.7369
6.7280
6.7055
5.9066
5.8863
5.8818
5.8614
5.5628
5.4714
5.3027
5.0062
4.9861
4.9582
4.9276
4.8922
4.8597
4.8053
4.7895
4.7728
4.3953
4.3647
4.3213
4.3132
4.1010
4.0731
3.8940
3.8606
3.8520
3.8354
3.8268
3.7681
3.7170
3.5786
3.4962
3.4448
2.9586
2.8872
2.1754
2.0964
Ph
O
O
O
NAPO
OPMP
OBz
4a
[rel]
1400
1200
1000
800
600
400
200
0
18.9131
4.0231
0.8330
0.9923
1.0535
2.1779
2.0709
1.0849
1.0855
2.9665
1.0750
8
7
6
5
4
3
[ppm]

Compound 4c





Compound 5a


Ph
O
O
O
NAPO
OPMP
OBn
5a
[rel]
[ppm]
23.8709
1.0000
1.0862
4.2633
1.1498
2.1318
1.2136
3.1537
1.2168
0.9691
155.3650
151.6955
138.8127
137.9413
135.5321
133.2842
133.0777
129.0611
128.8537
128.6328
128.5302
128.3958
128.1843
128.2272
127.9590
127.7625
127.6919
127.5425
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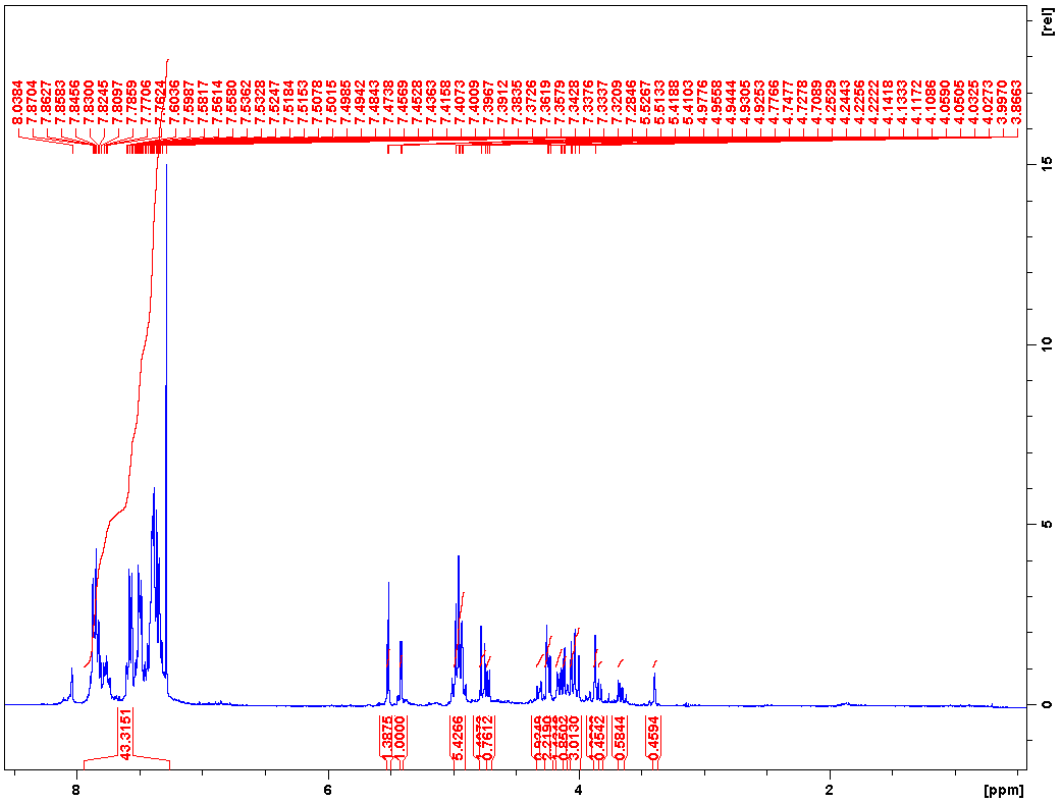
126.6166
126.5398
126.1981
126.0020
125.8808
118.9623
114.5164
103.1791
101.3351
79.1832
78.1984
77.4997
77.1816
76.8633
75.5150
73.7618
72.0942
69.1378
55.6527

Compound 5c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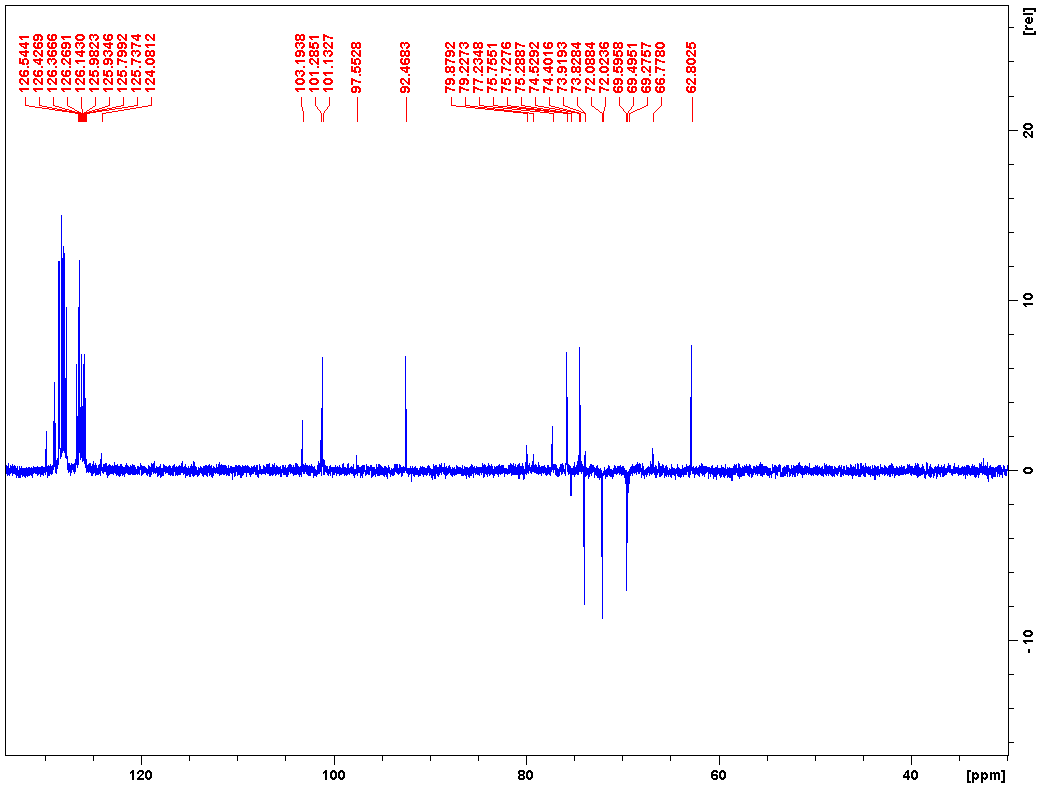
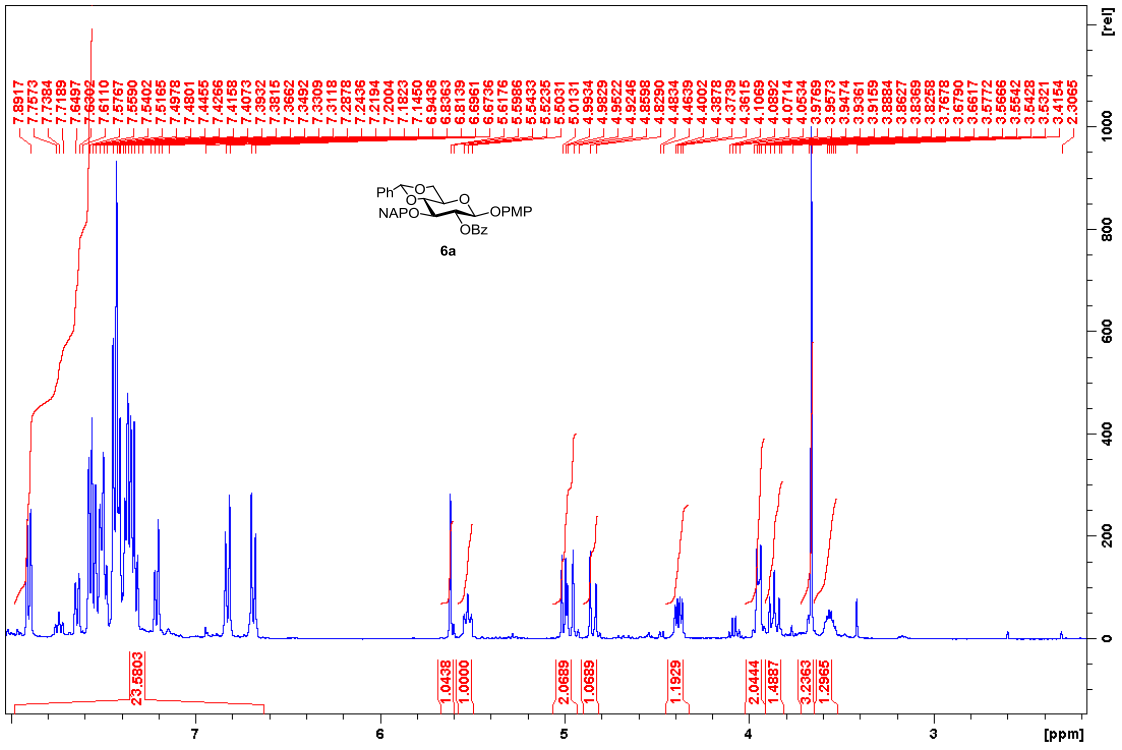
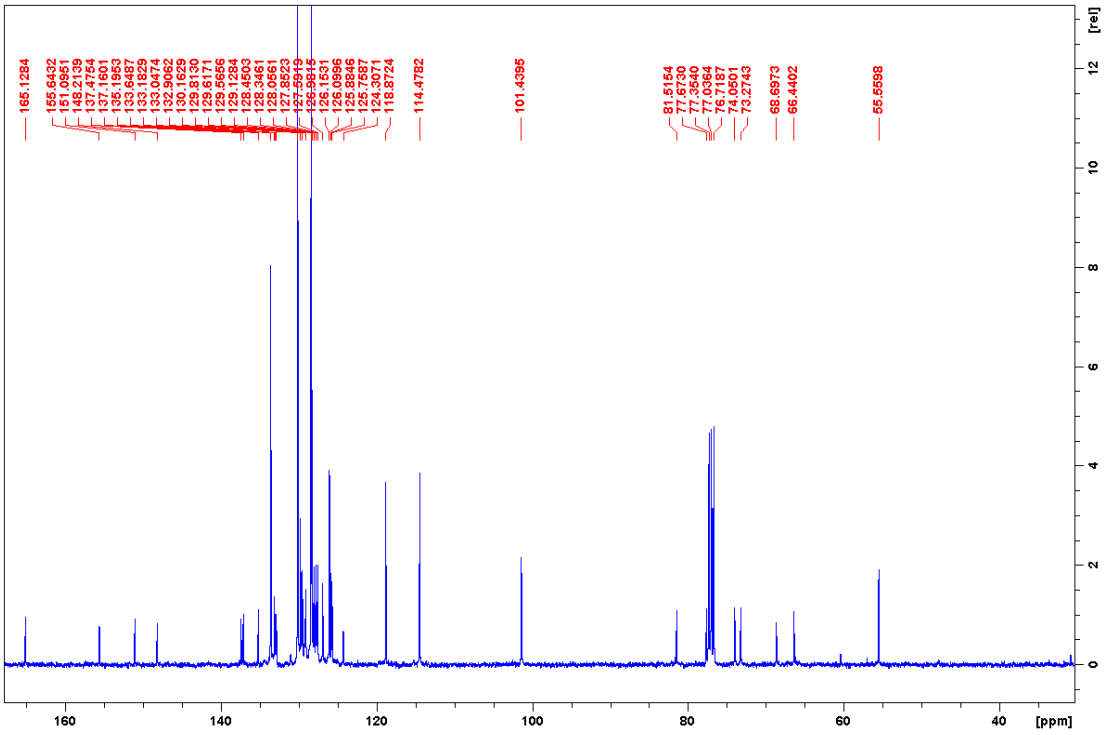
7.8627
7.8583
7.8456
7.8300
7.8245
7.8097
7.7859
7.7706
7.7624
7.6036
7.5987
7.5817
7.5614
7.5580
7.5362
7.5328
7.5247
7.5184
7.5153
7.5078
7.5015
7.4985
7.4942
7.4843
7.4738
7.4669
7.4528
7.4363
7.4158
7.4073
7.4009
7.3967
7.3912
7.3835
7.3726
7.3619
7.3579
7.3428
7.3376
7.3337
7.3209
7.2846
5.5267
5.5133
5.4188
5.4103
4.9776
4.9558
4.9444
4.9305
4.9253
4.7766
4.7477
4.7278
4.7089
4.2529
4.2443
4.2256
4.2222
4.1418
4.1333
4.1172
4.1086
4.0590
4.0506
4.0325
4.0273
3.9970
3.8663
43.3151
1.3875
1.0000
5.4266
0.7612
0.5844
0.4594
[rel]
[ppm]

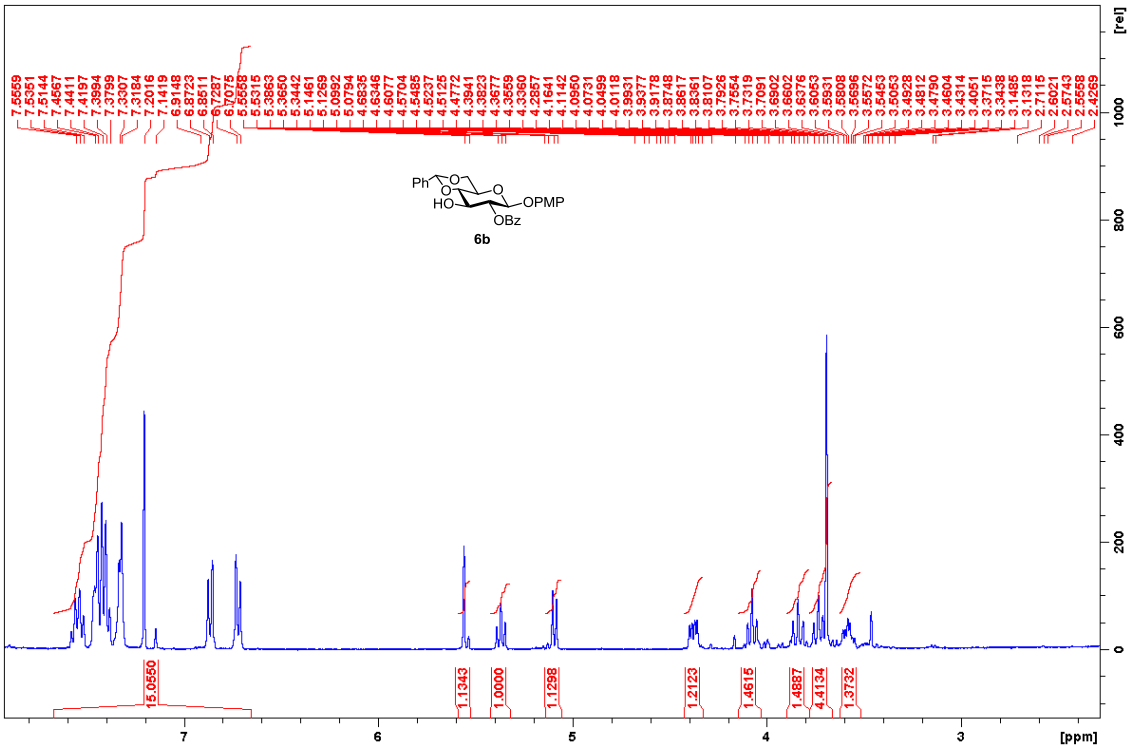

126.5441
126.4269
126.3666
126.2691
126.1430
125.9823
125.9346
125.7992
125.7374
124.0812
103.1938
101.2851
101.1327
97.5528
92.4683
79.8792
79.2273
77.2348
75.7651
75.7216
75.2887
74.5292
74.4016
73.9193
73.8234
72.0884
72.0236
69.5958
69.4951
69.2757
66.7780
62.8025
[rel]
[ppm]

Compound 6a





Compound 6b


6b
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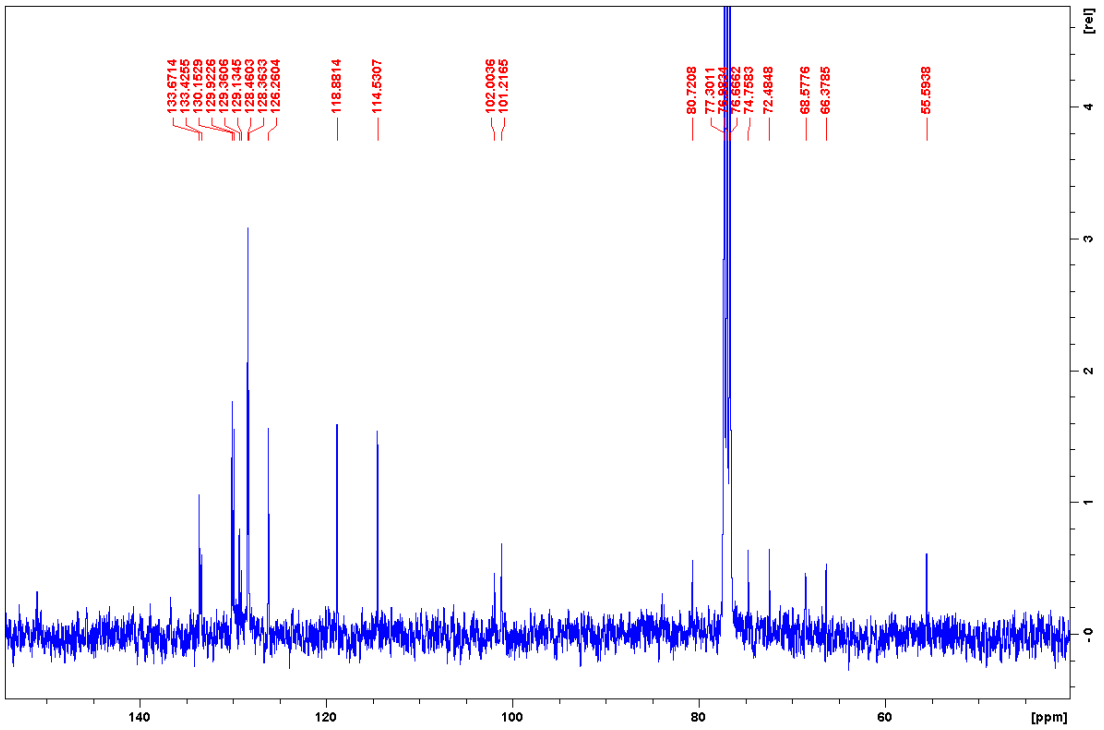
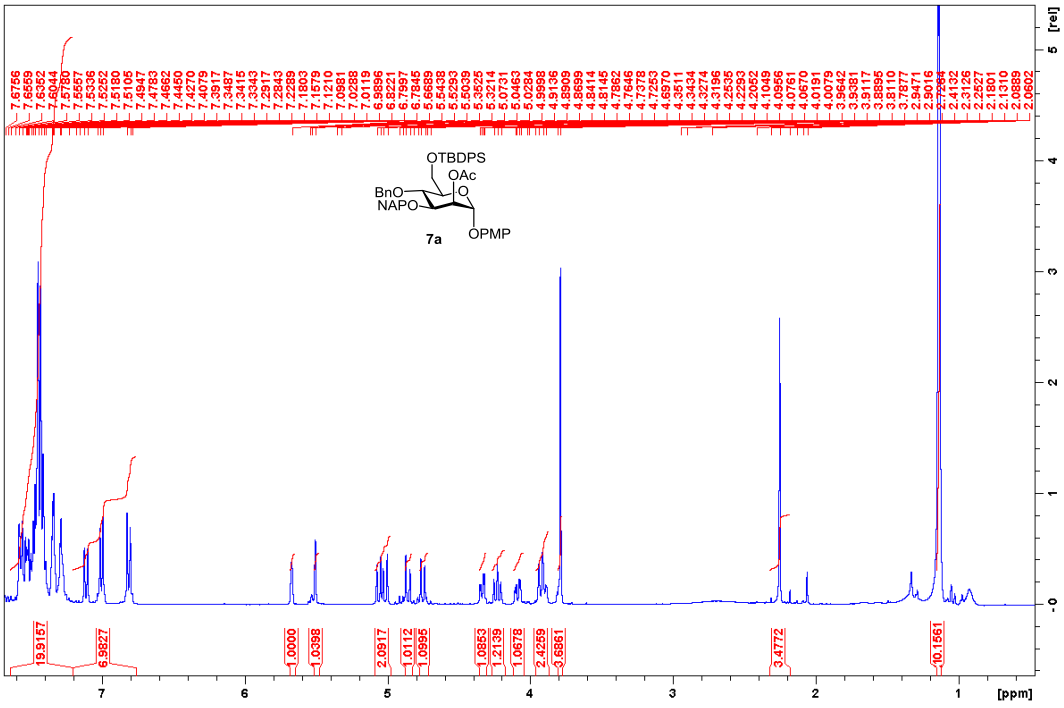
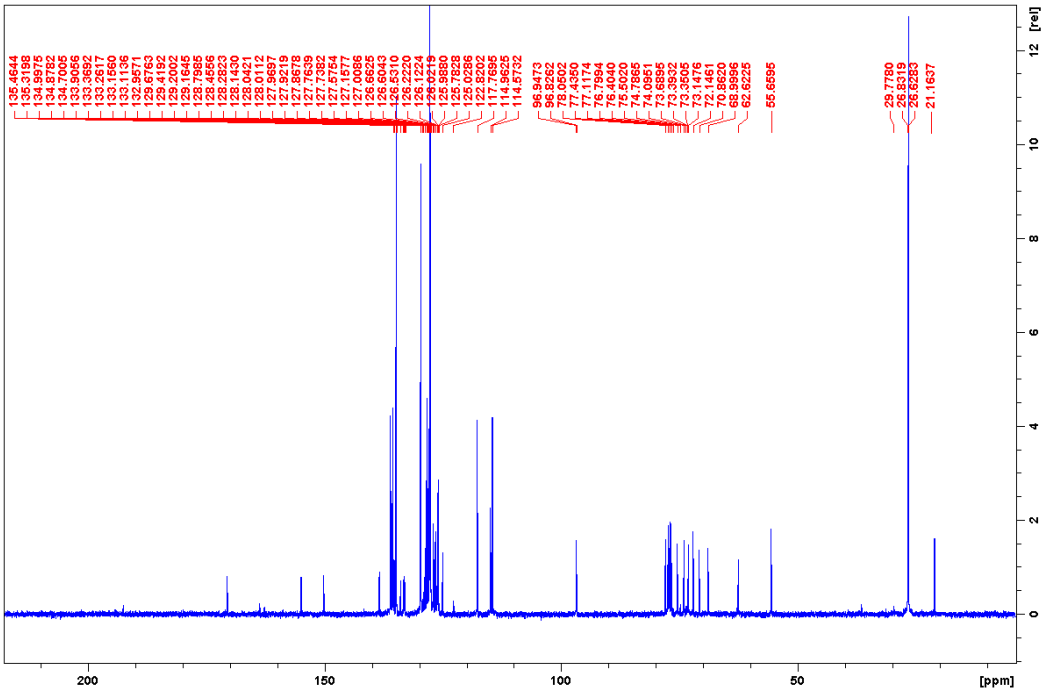
1.0000
1.1298
1.2123
1.4615
1.4887
4.4134
1.3732
[ppm]
[rel]

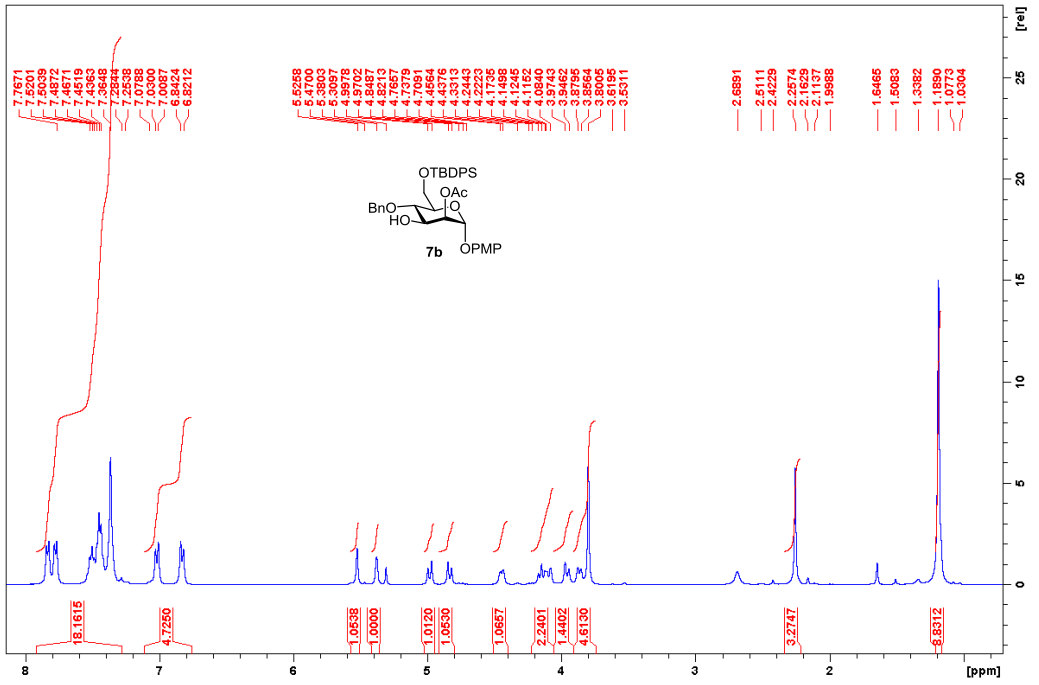

133.6714
130.4255
130.4529
129.9226
129.3606
129.1345
128.4603
128.3633
126.2604
118.8814
114.5307
102.0036
101.2165
80.7208
77.3011
76.9824
76.6662
74.7583
72.4848
68.5776
66.3785
55.5938
[ppm]
[rel]

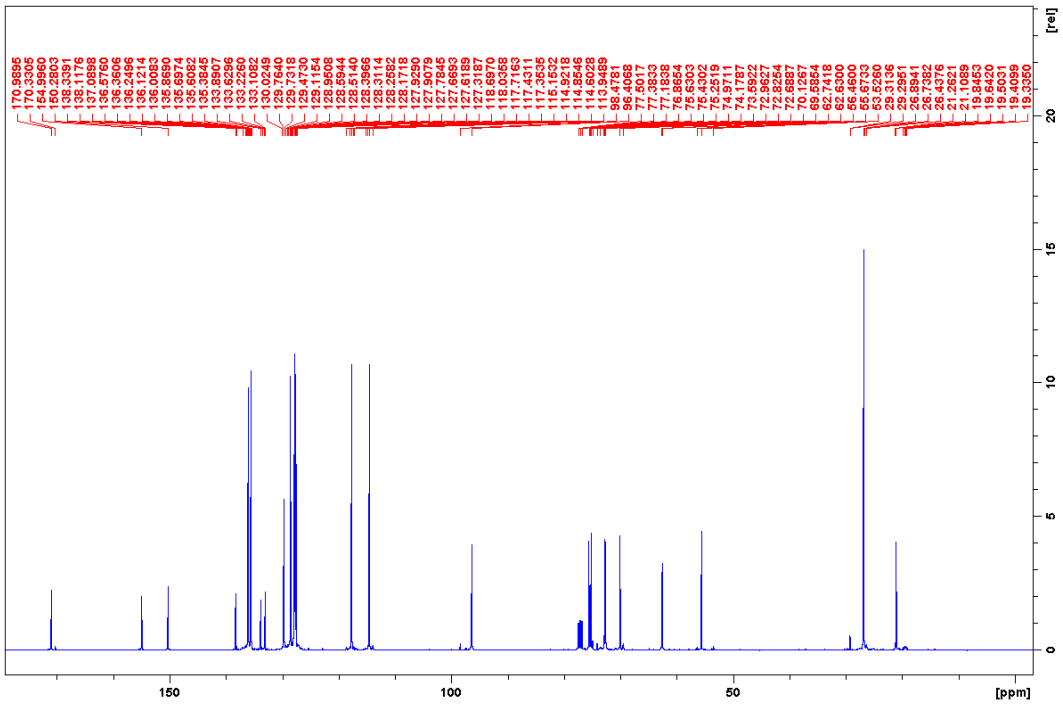
Compound 7a



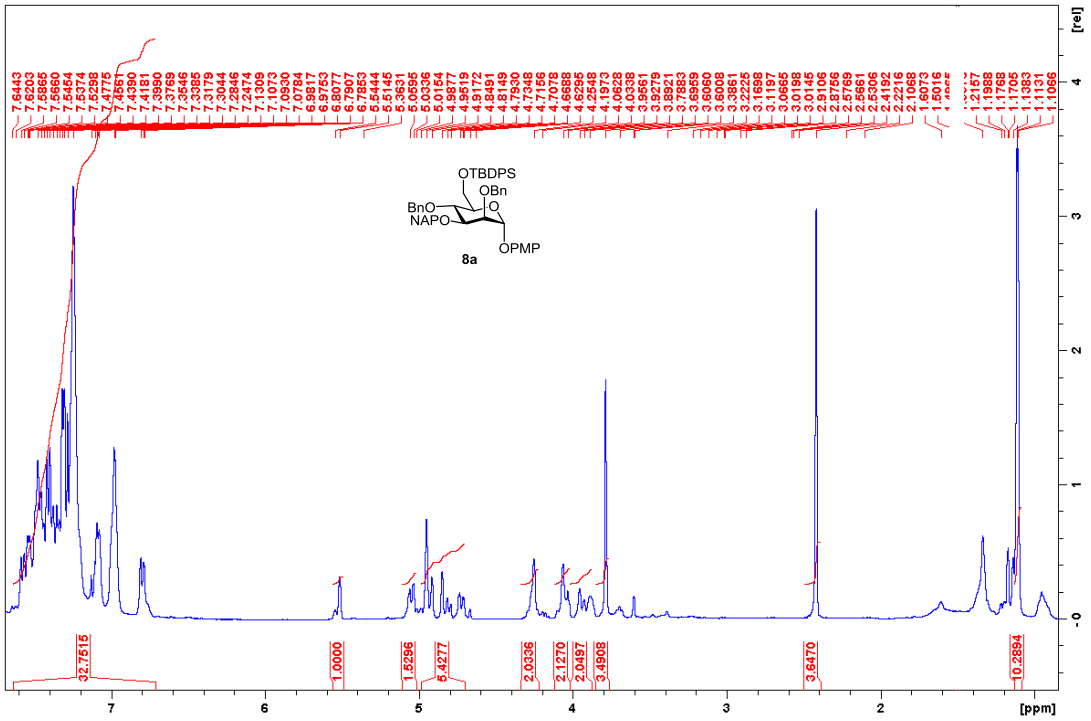


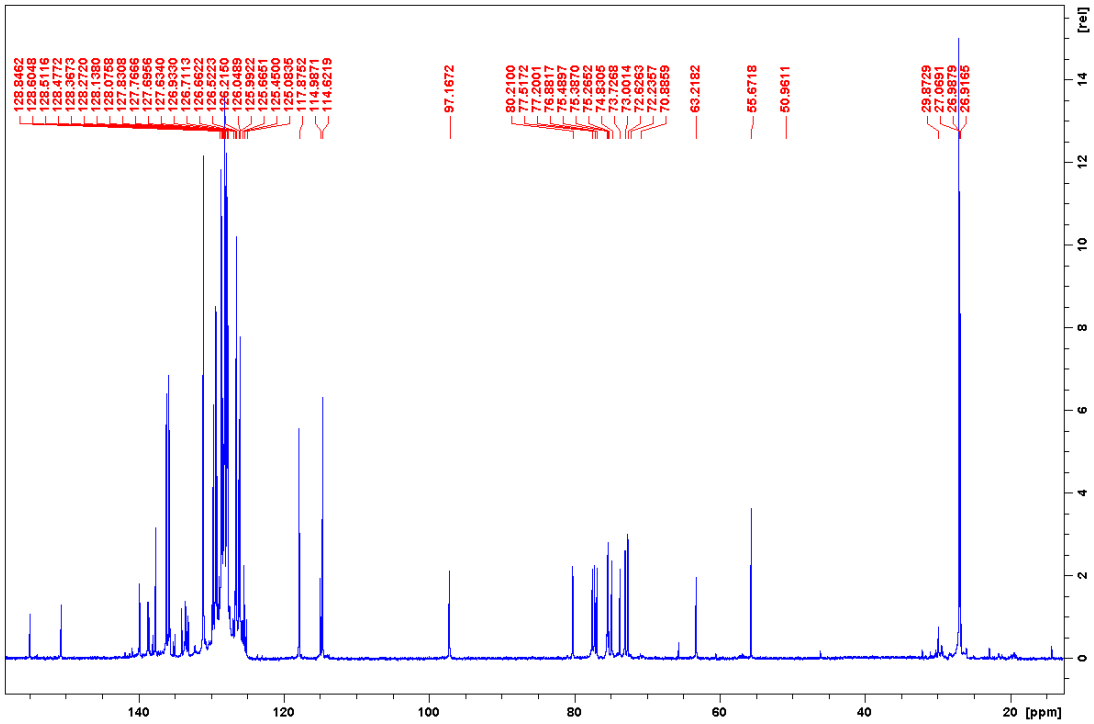
Compound 7b



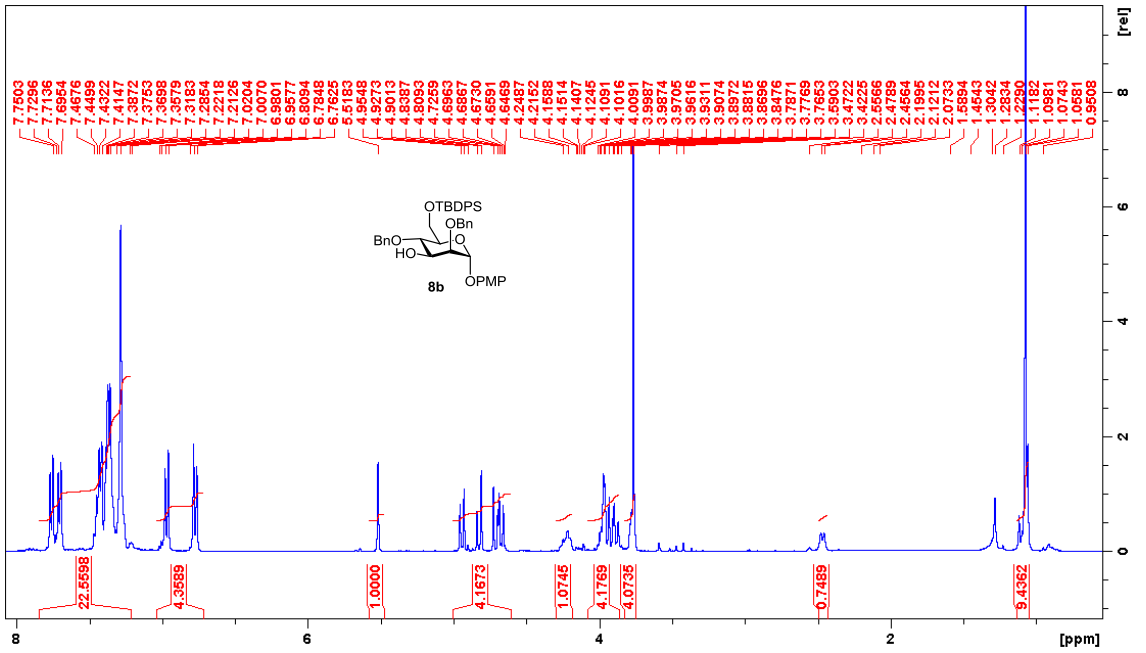


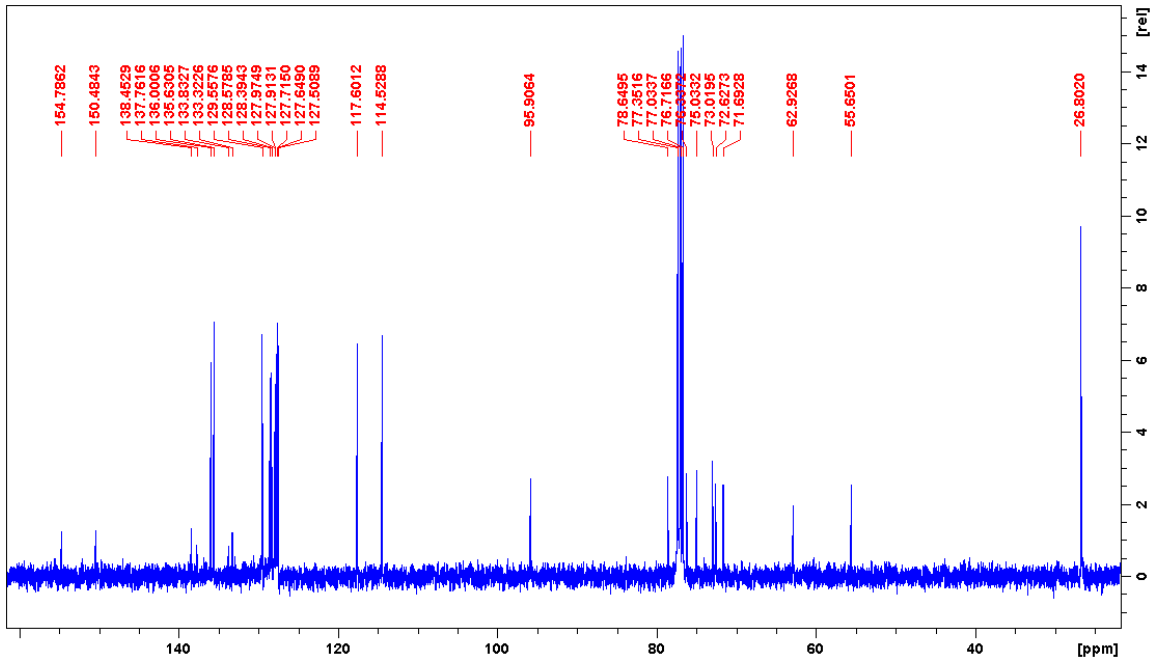
Compound 8a



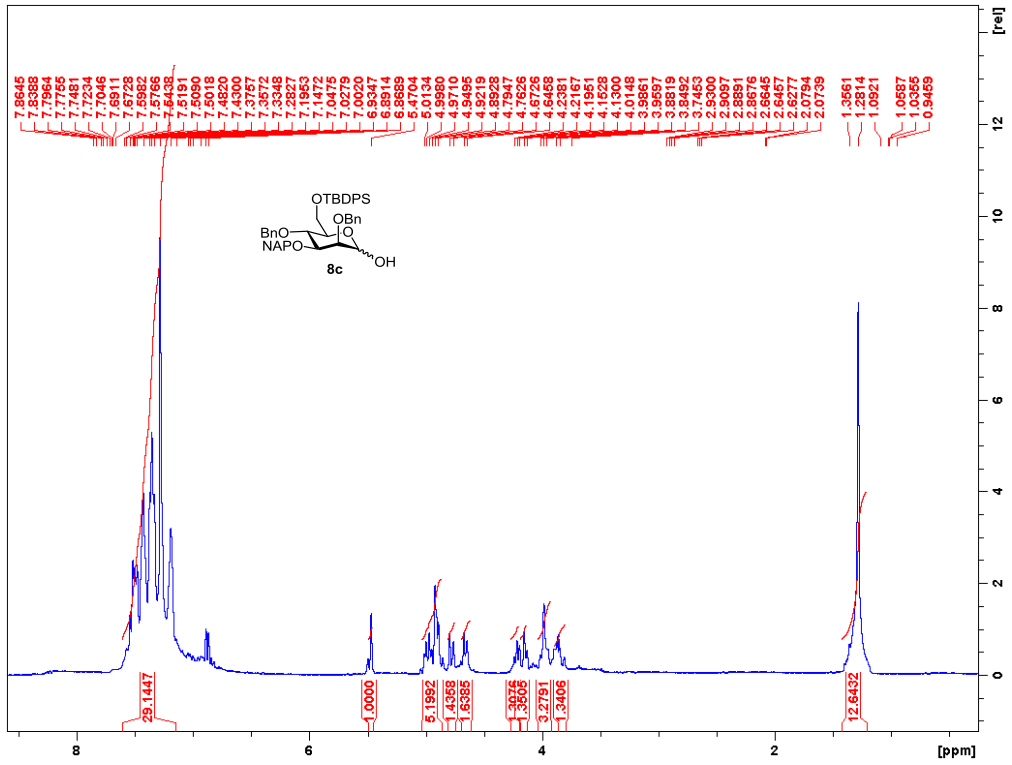


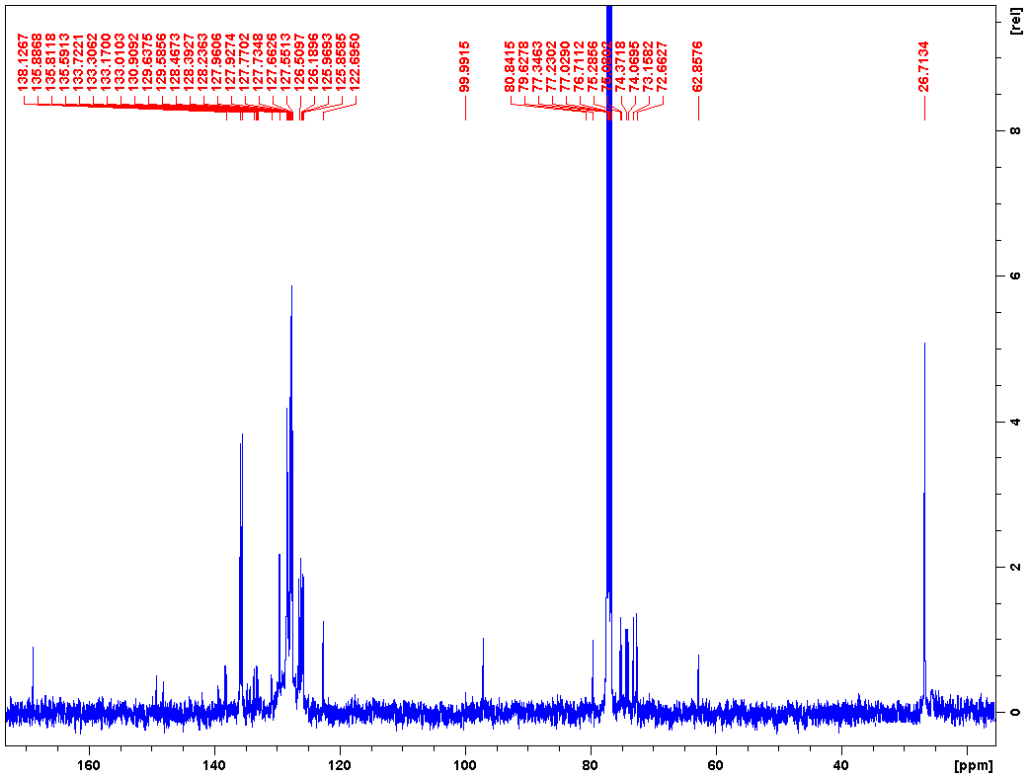
Compound 8b



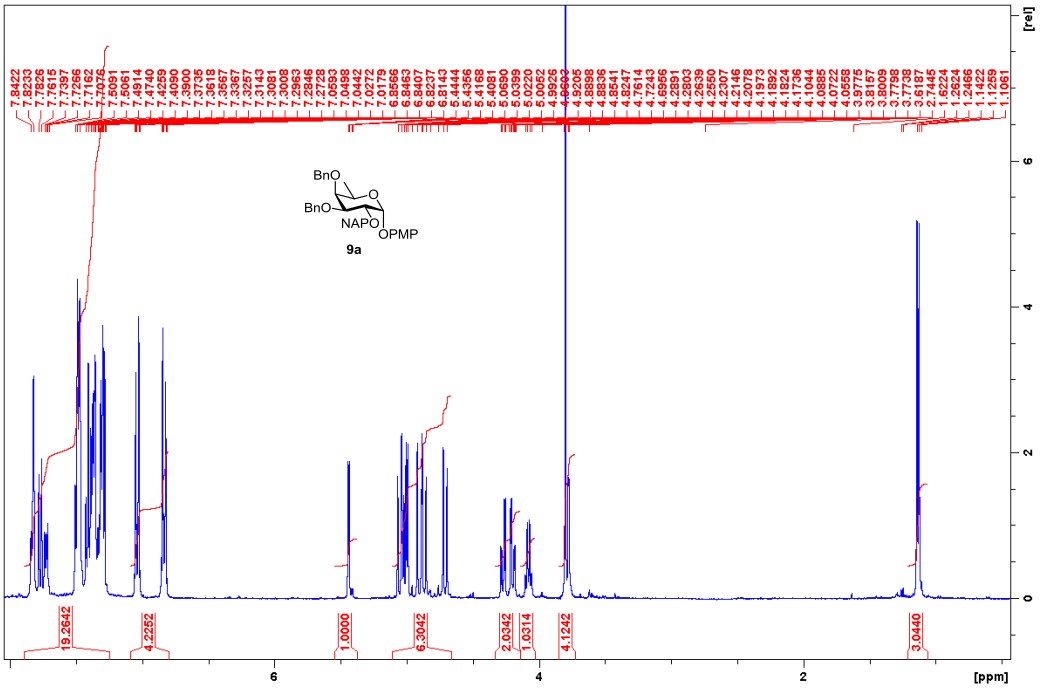


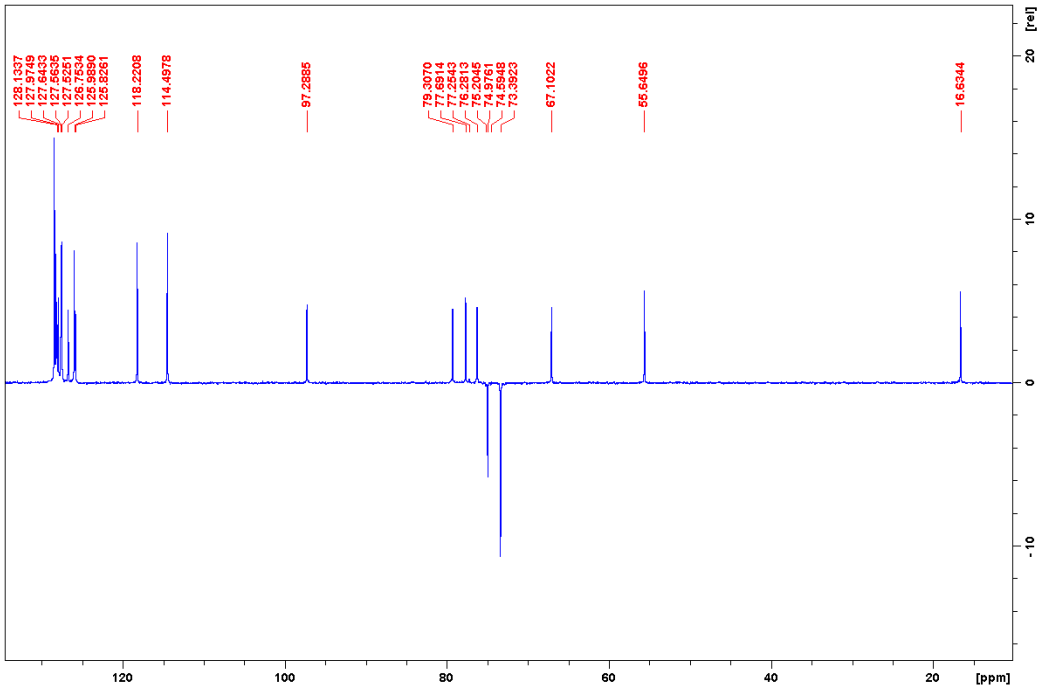
Compound 8c



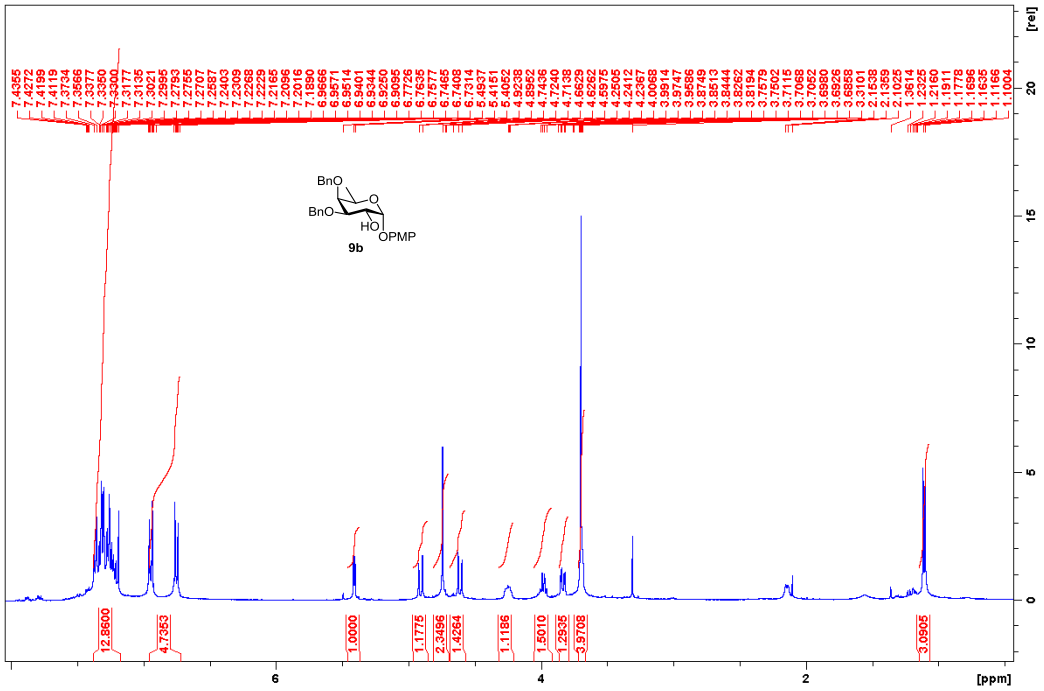


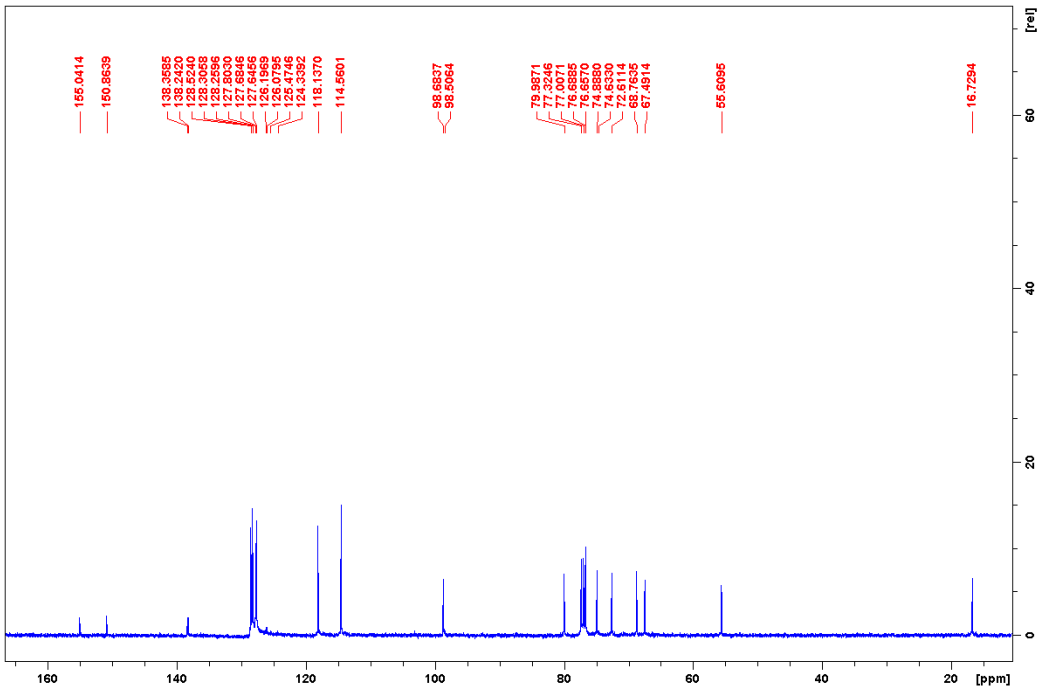
Compound 9a



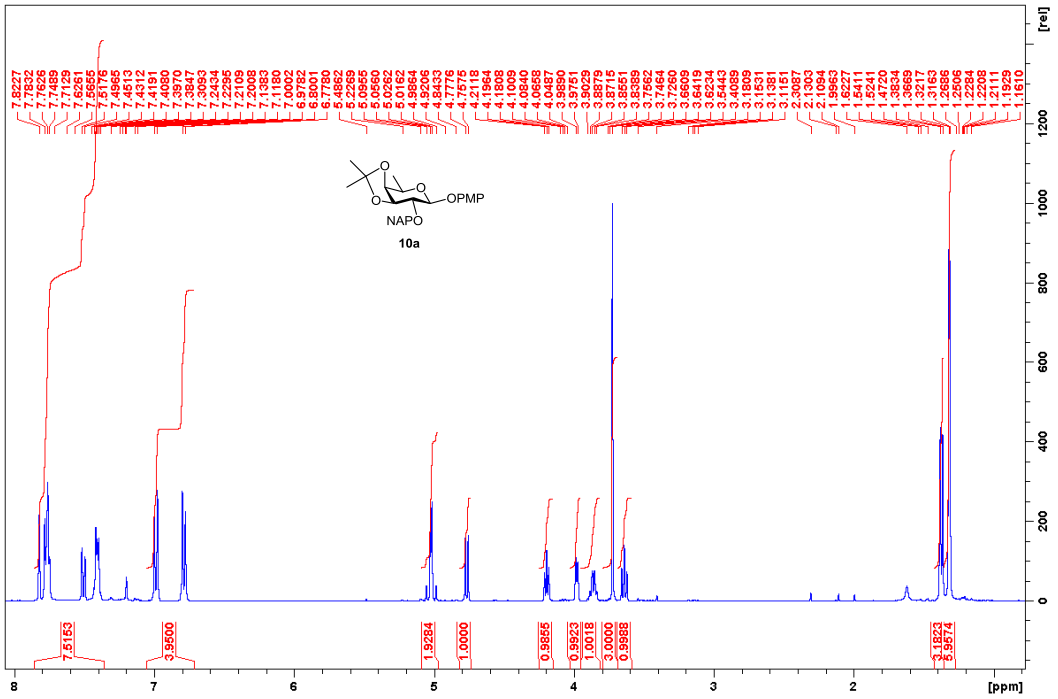


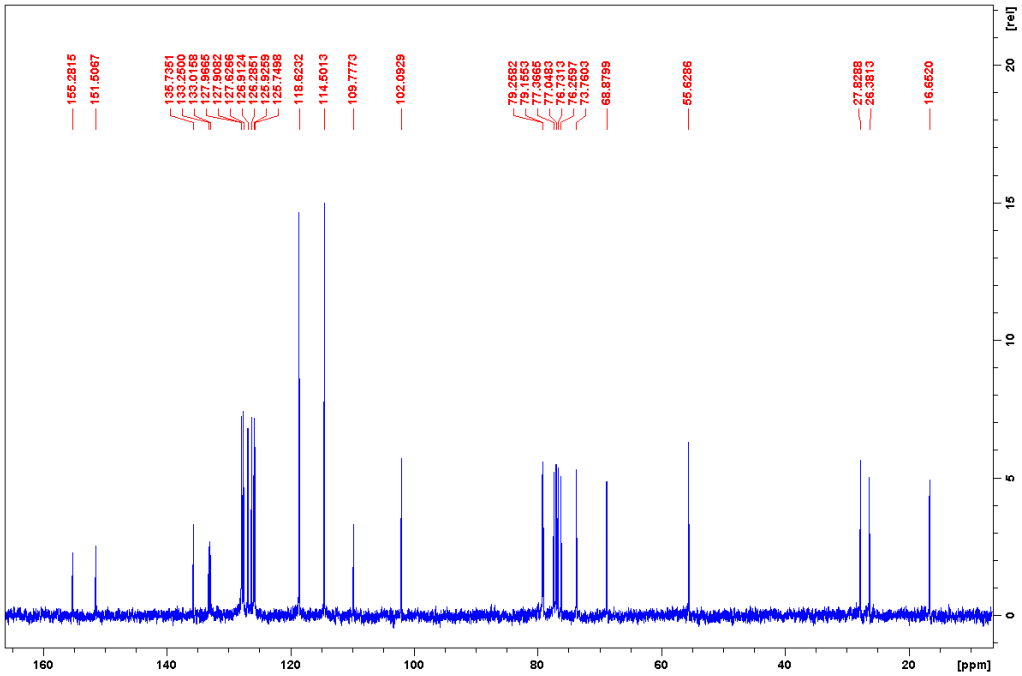
Compound 9b



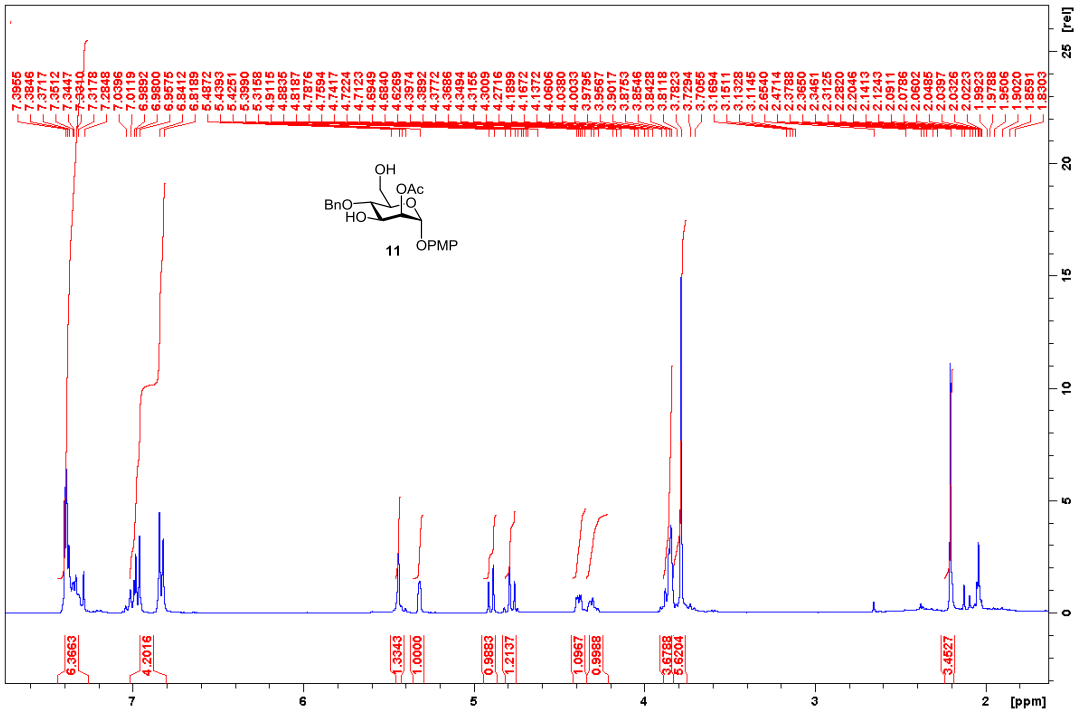


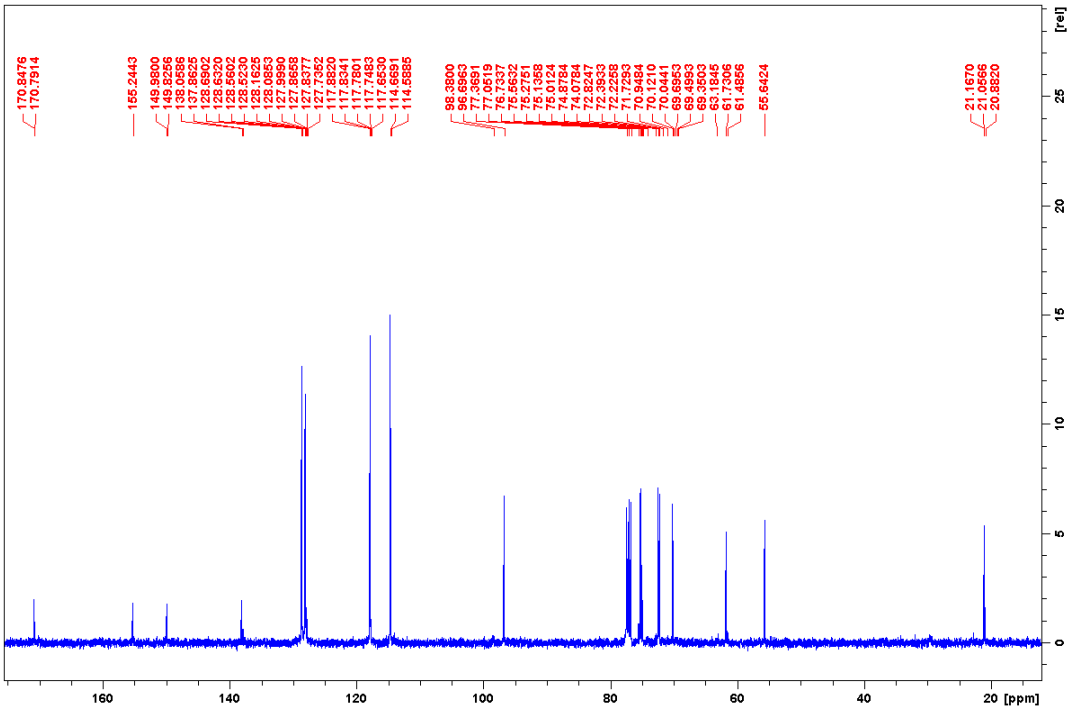
Compound 10a



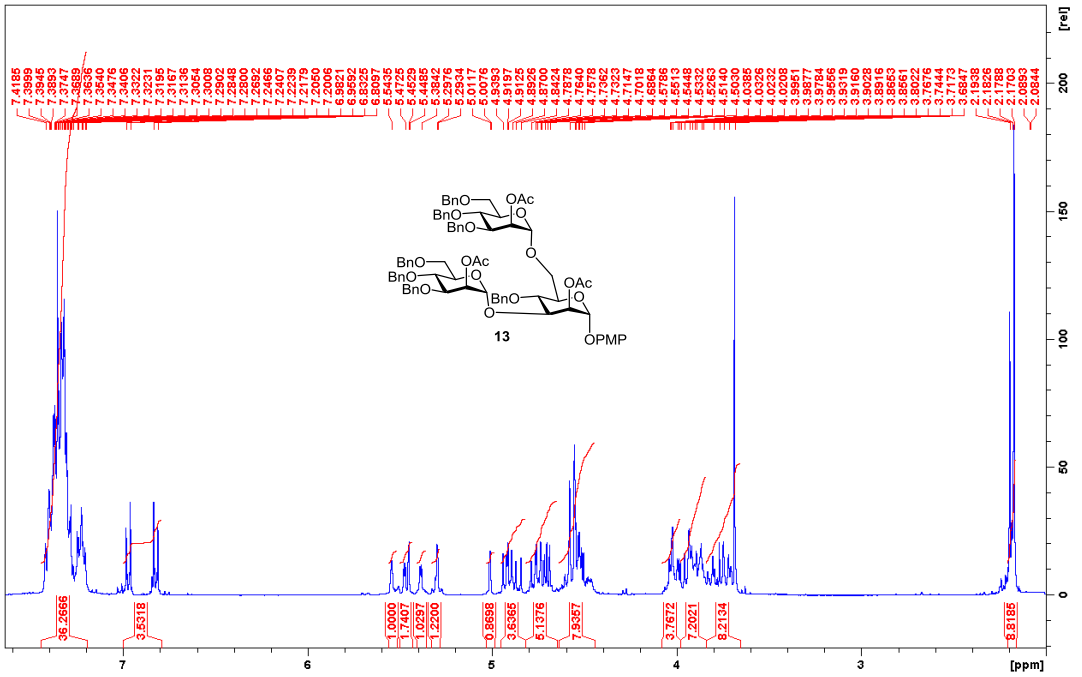


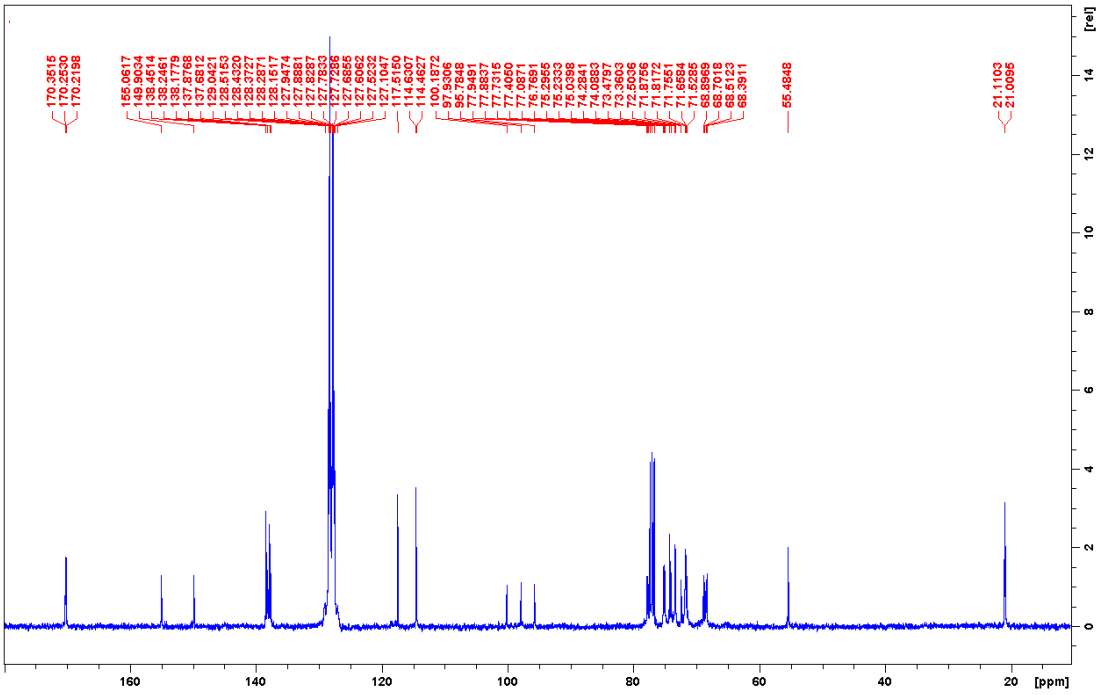
Compound 11



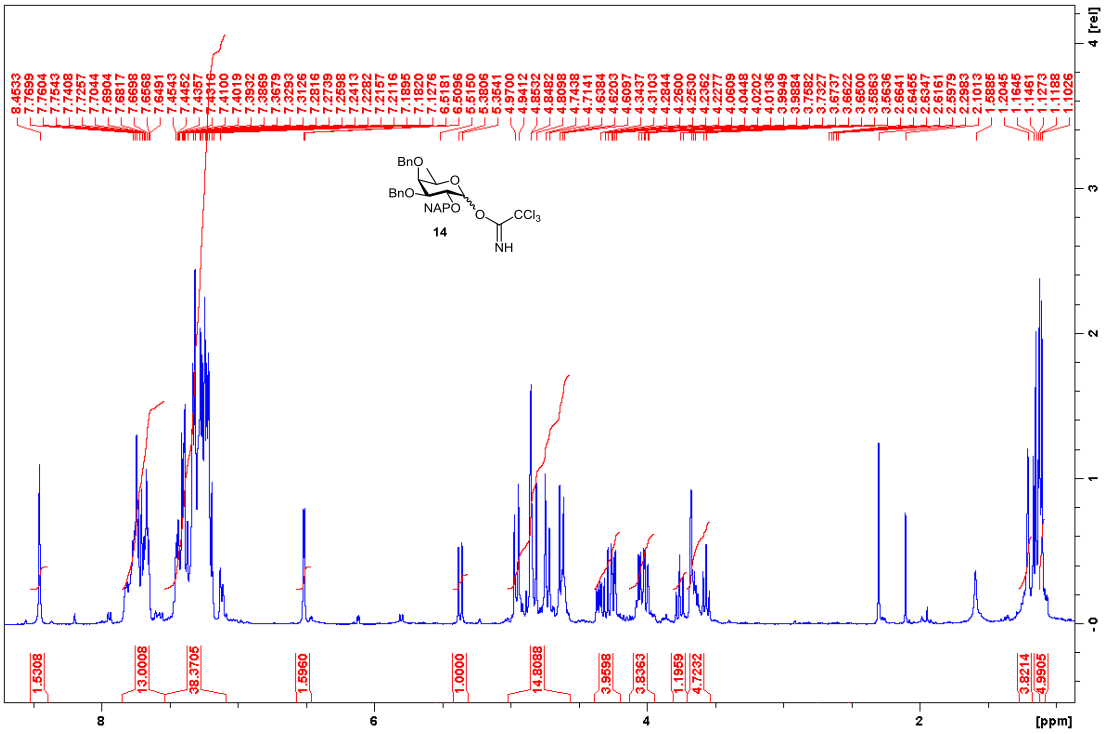


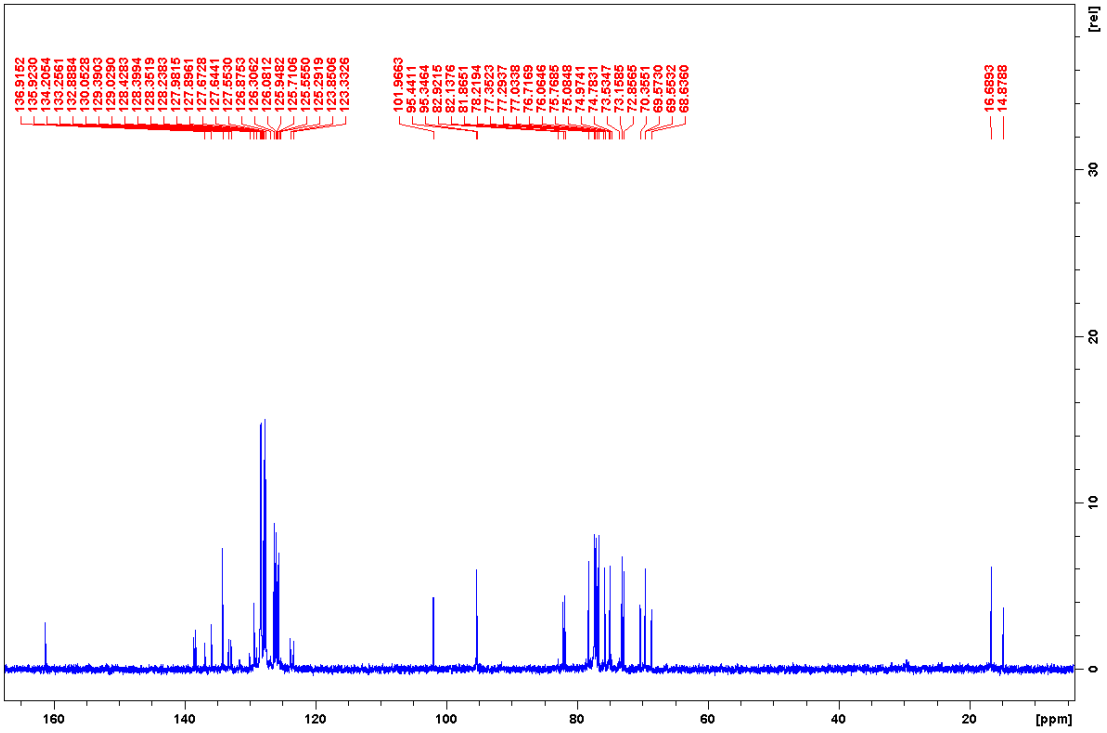
Compound 13



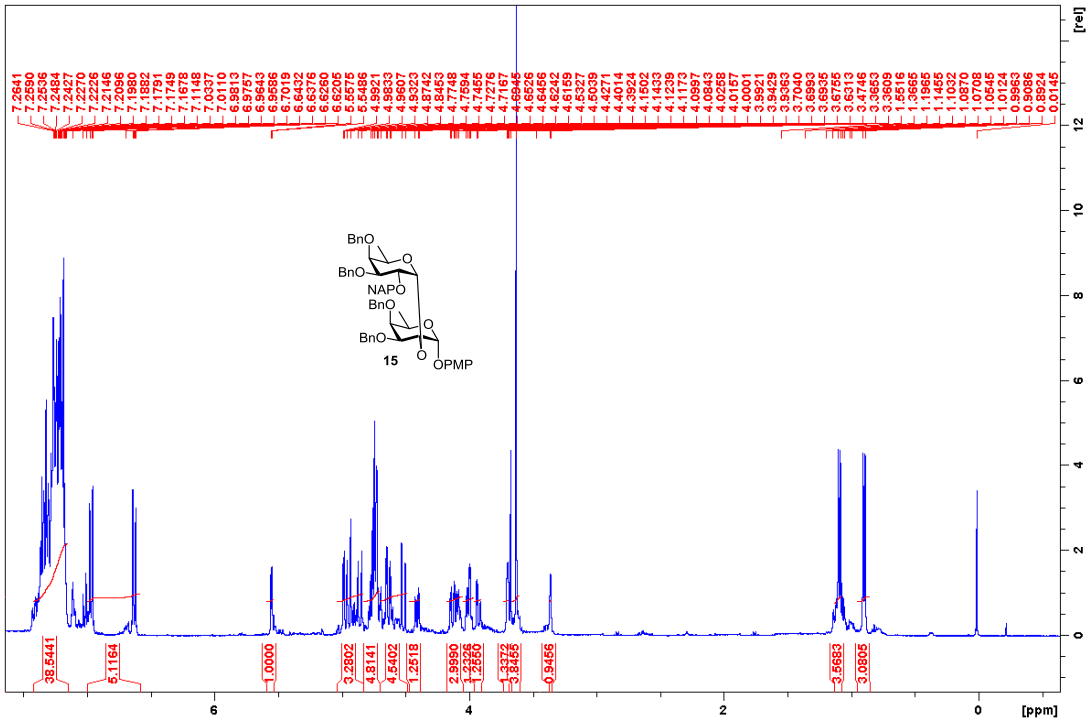


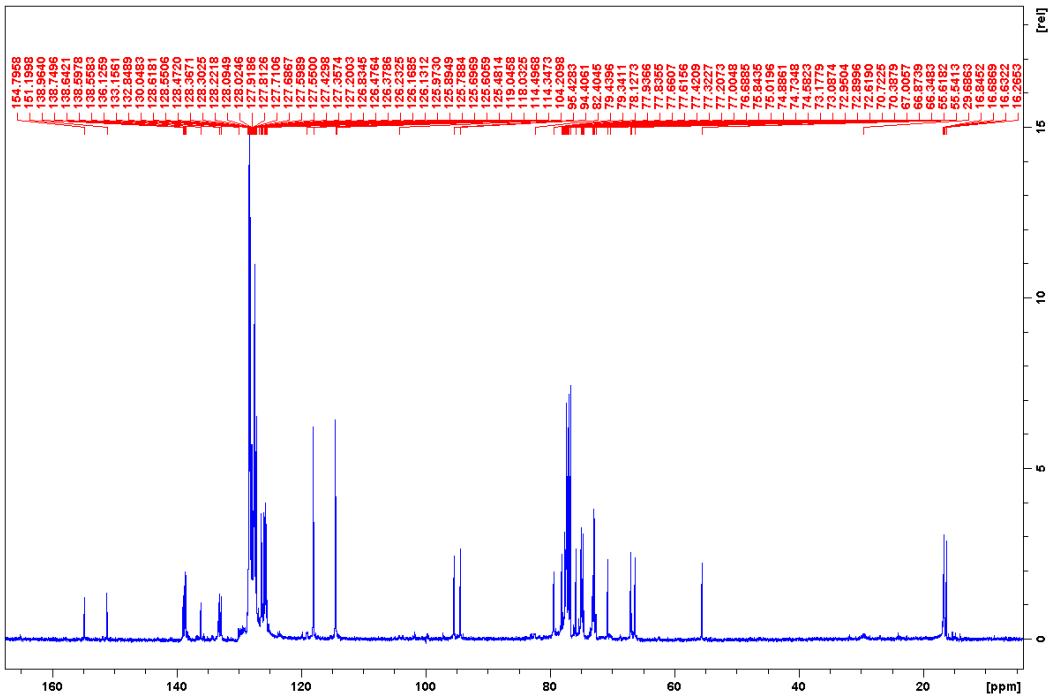
Compound 14



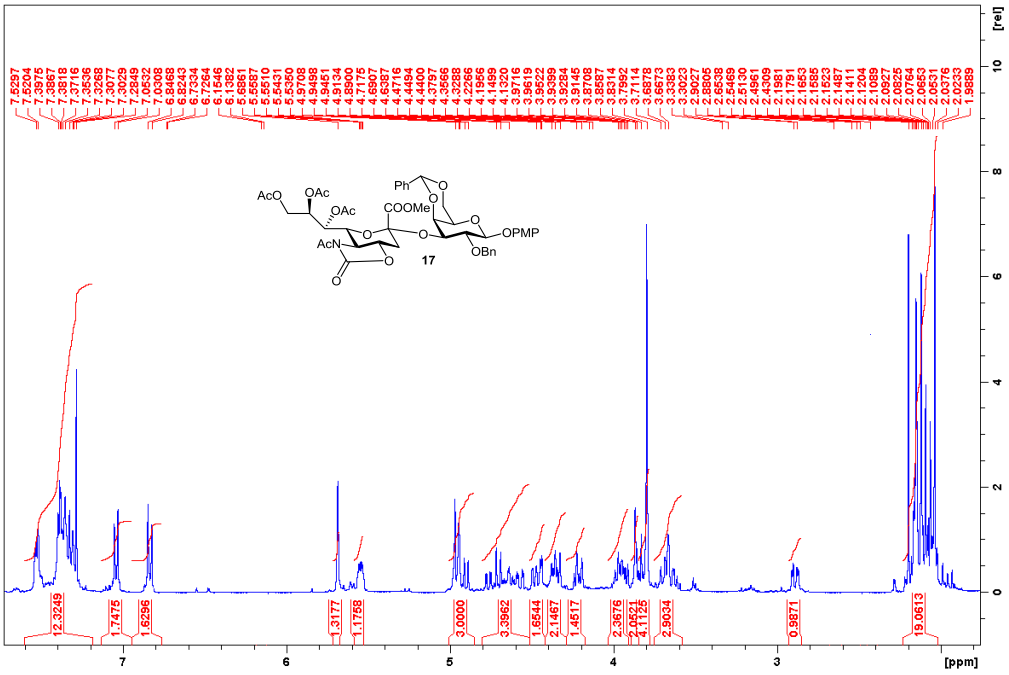


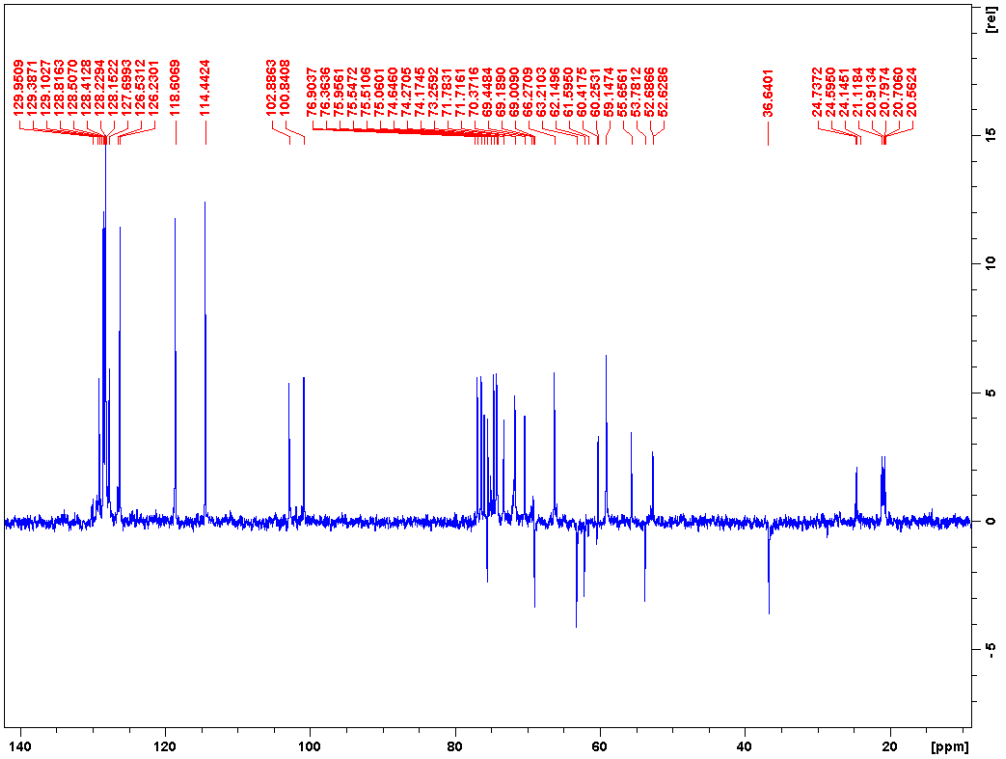
Compound 15



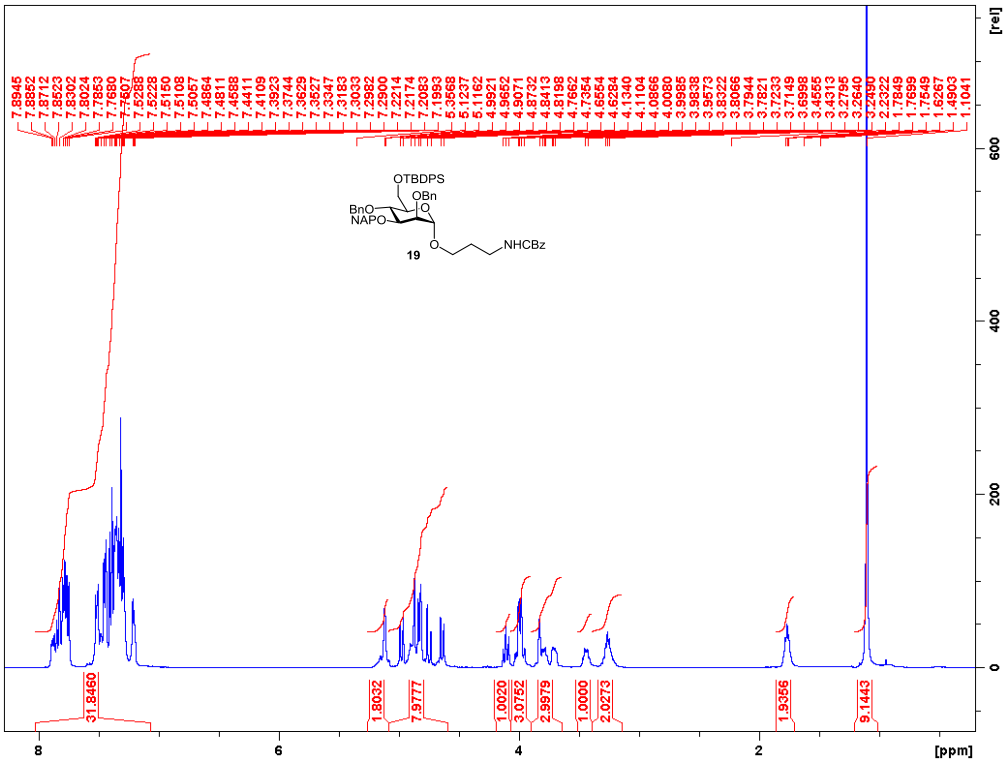


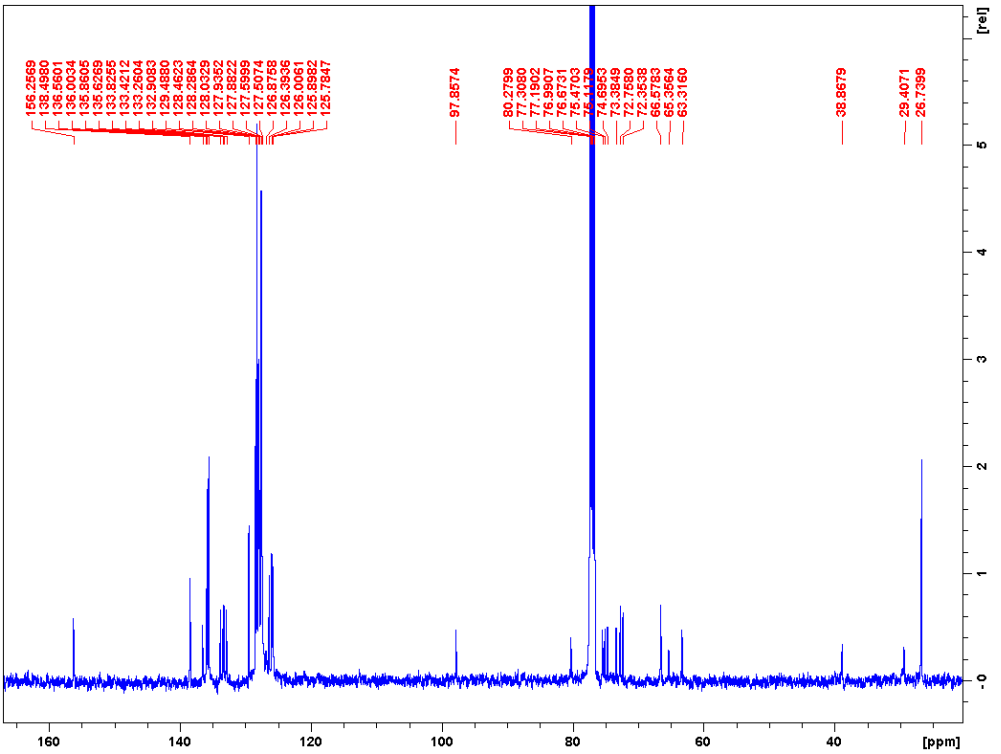
Compound 17





Compound 19





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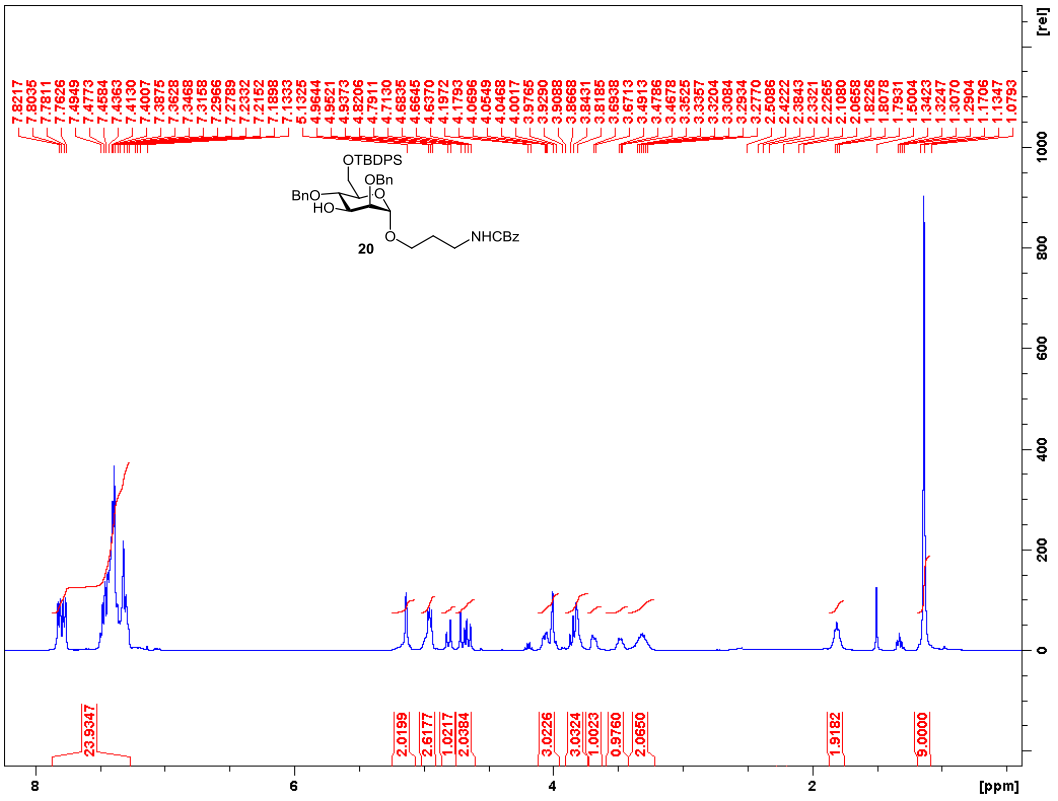

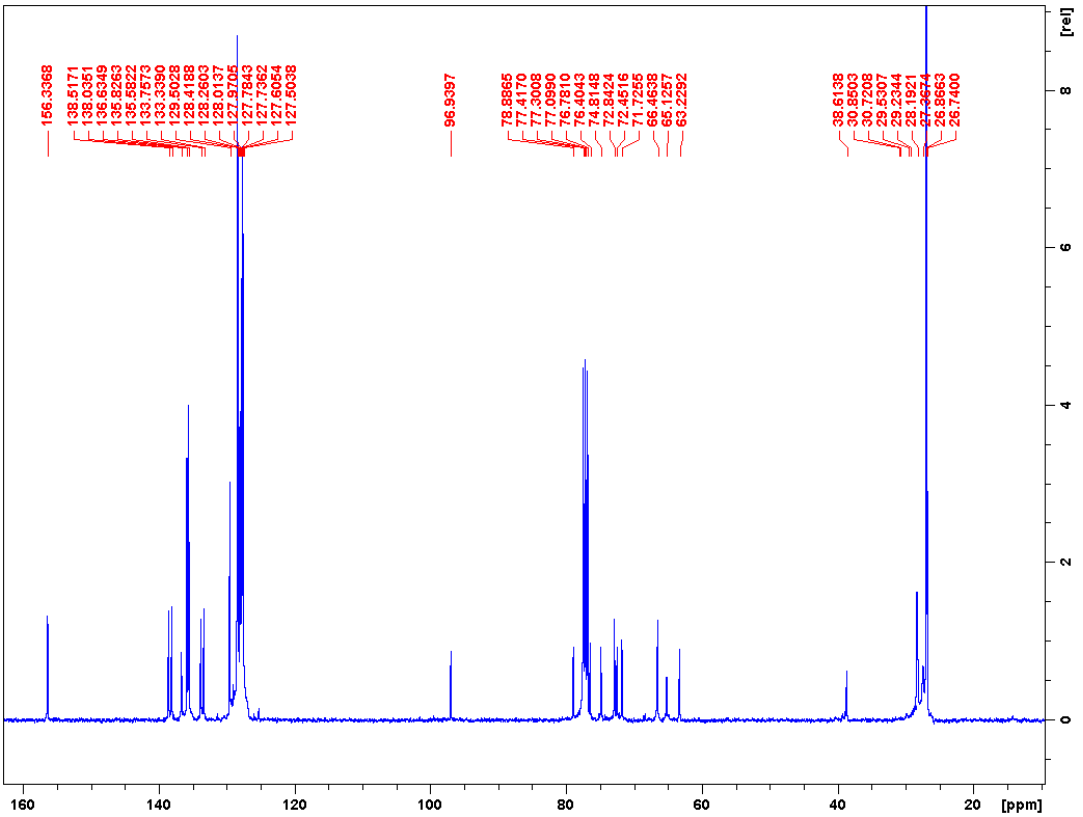

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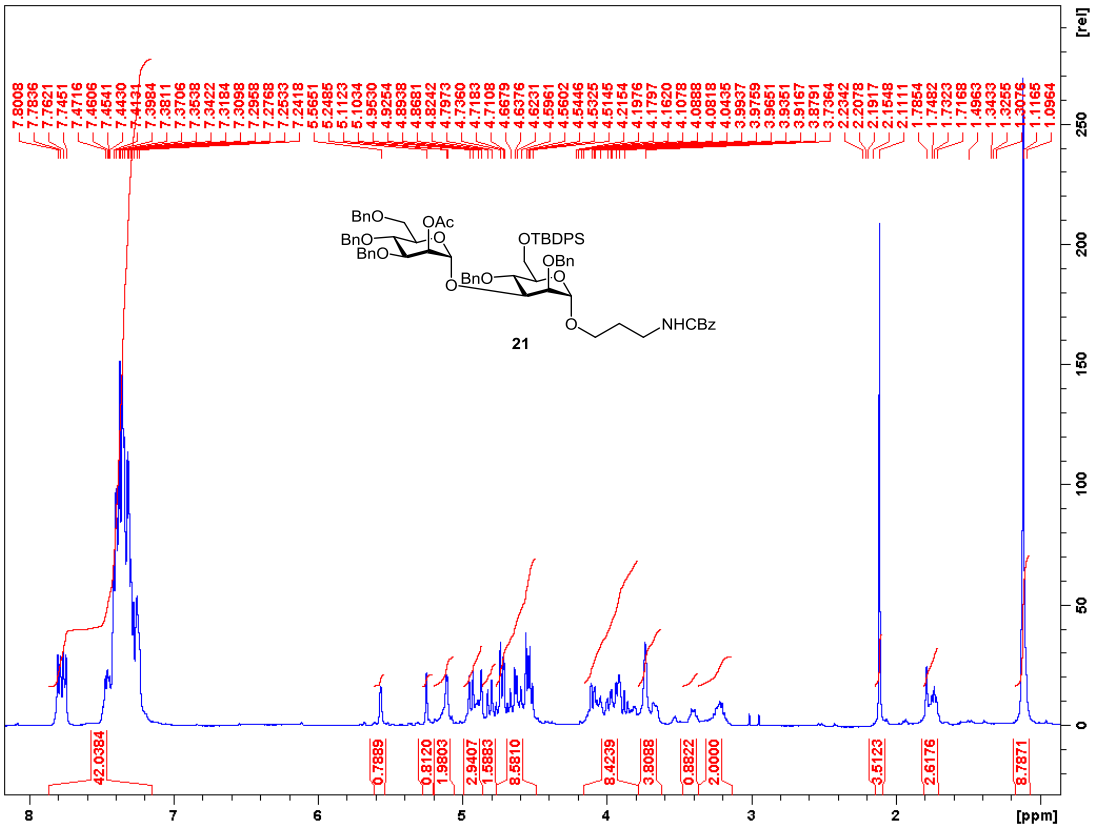
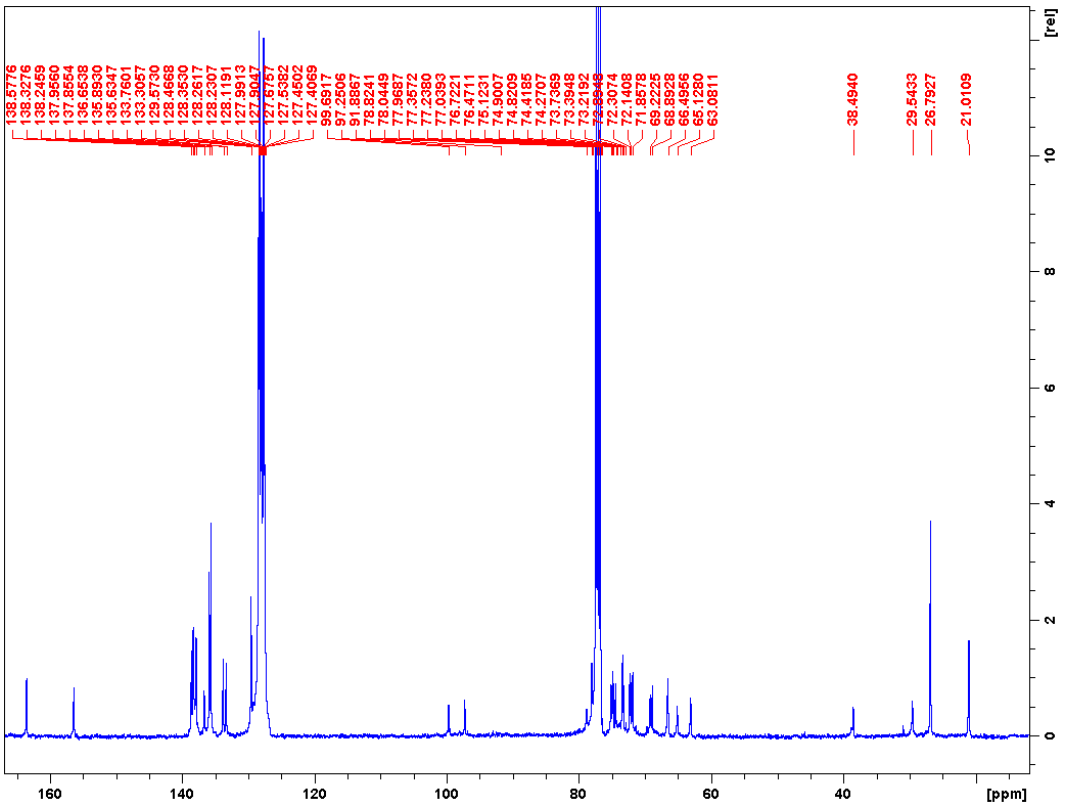
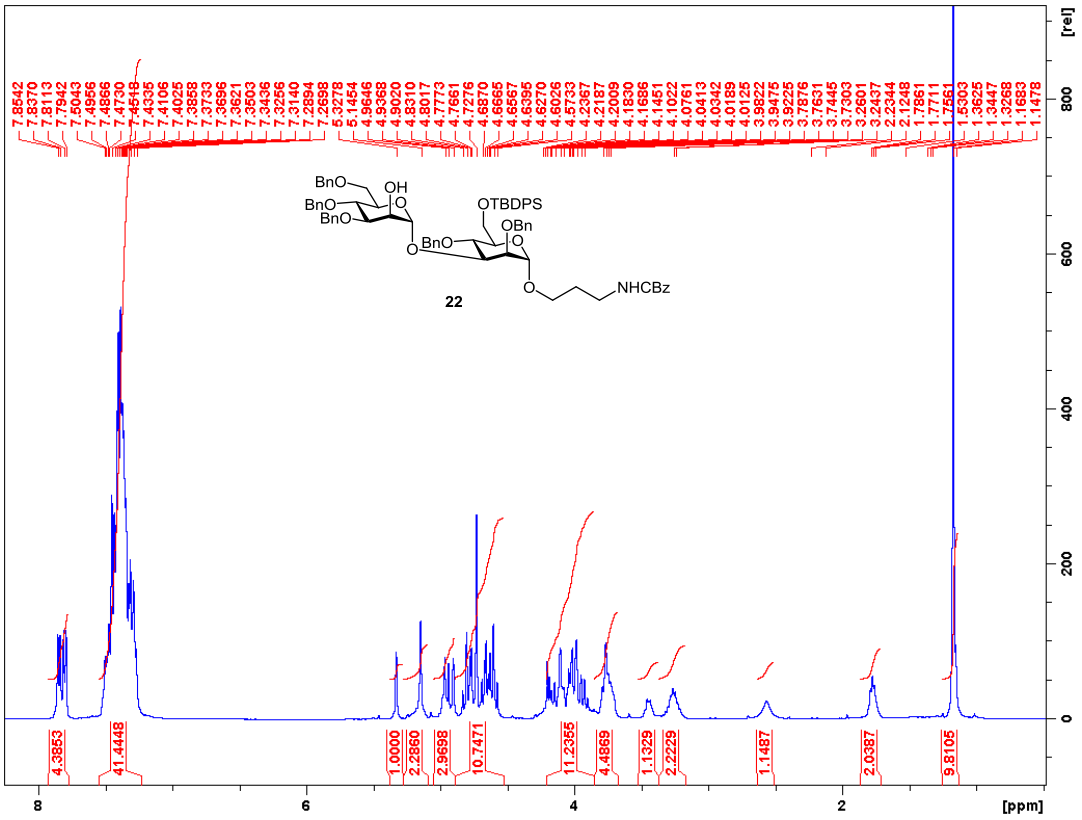
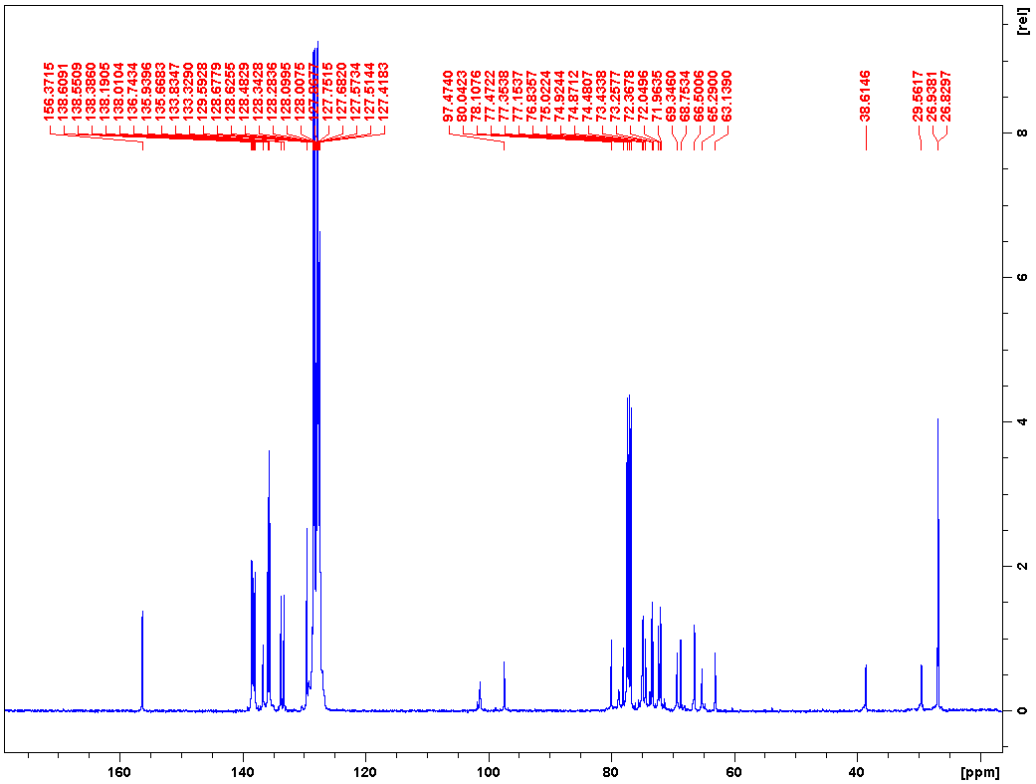




Compound 22





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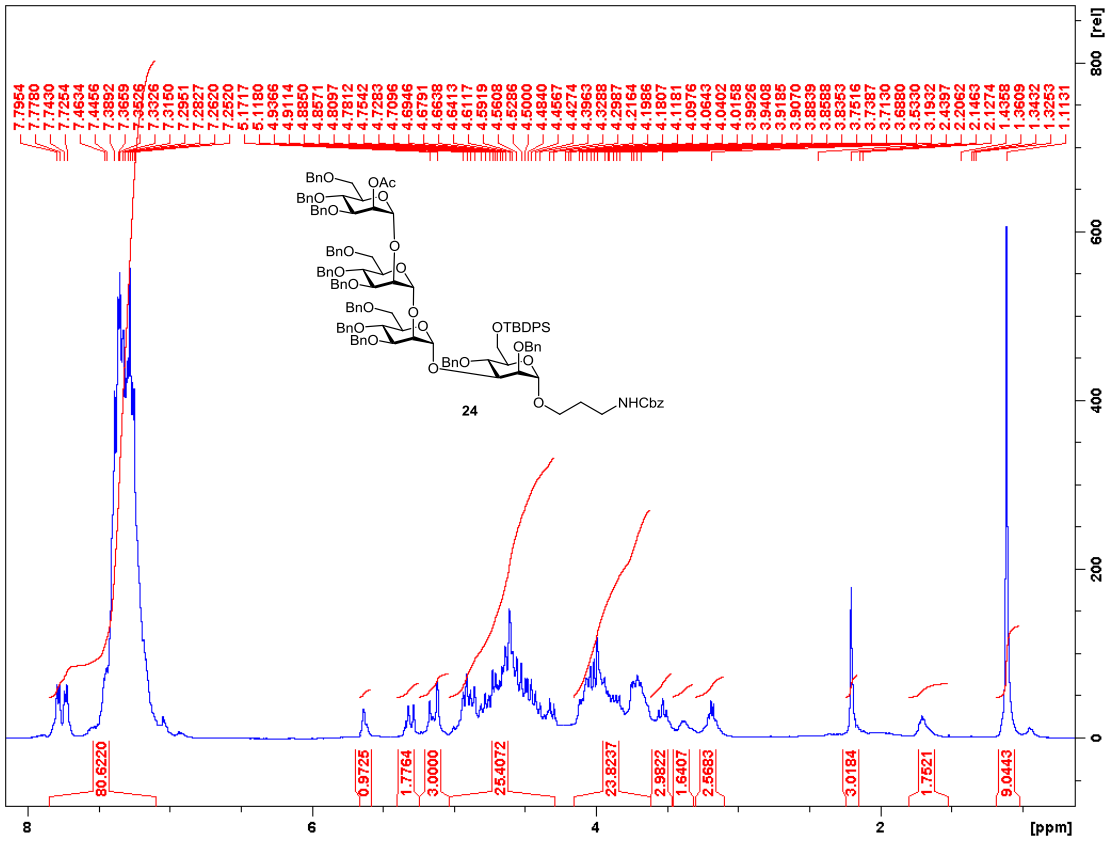
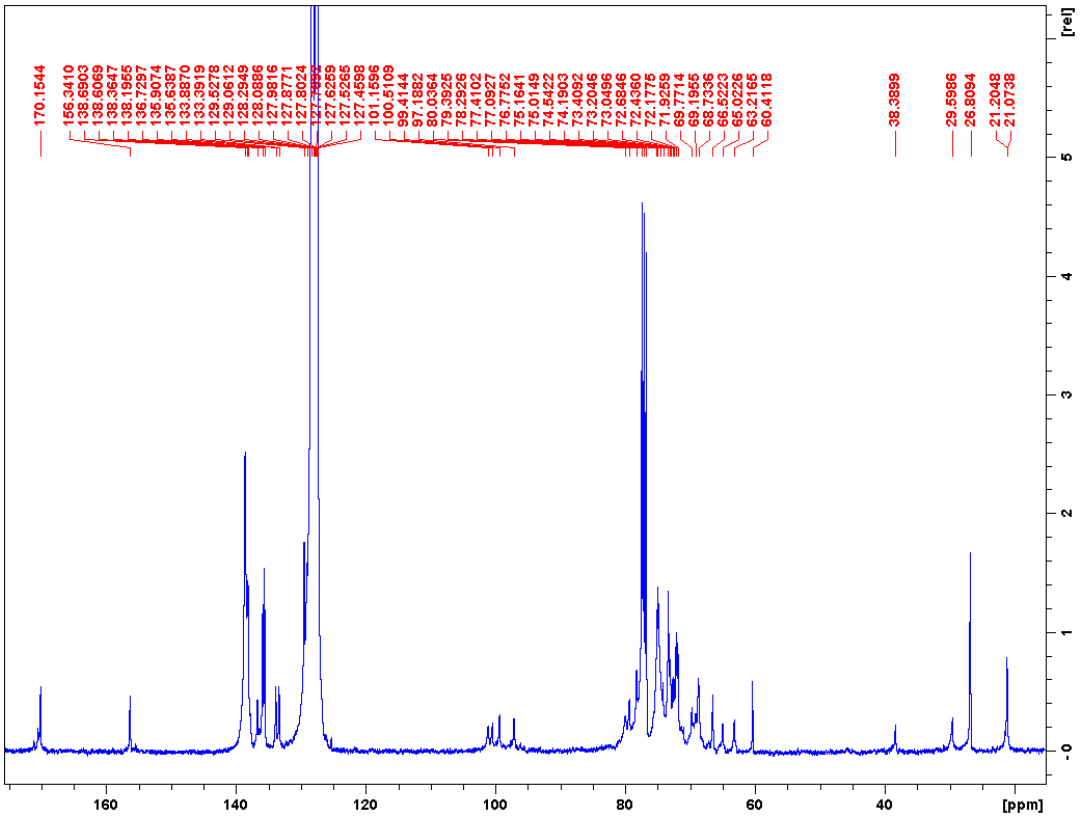
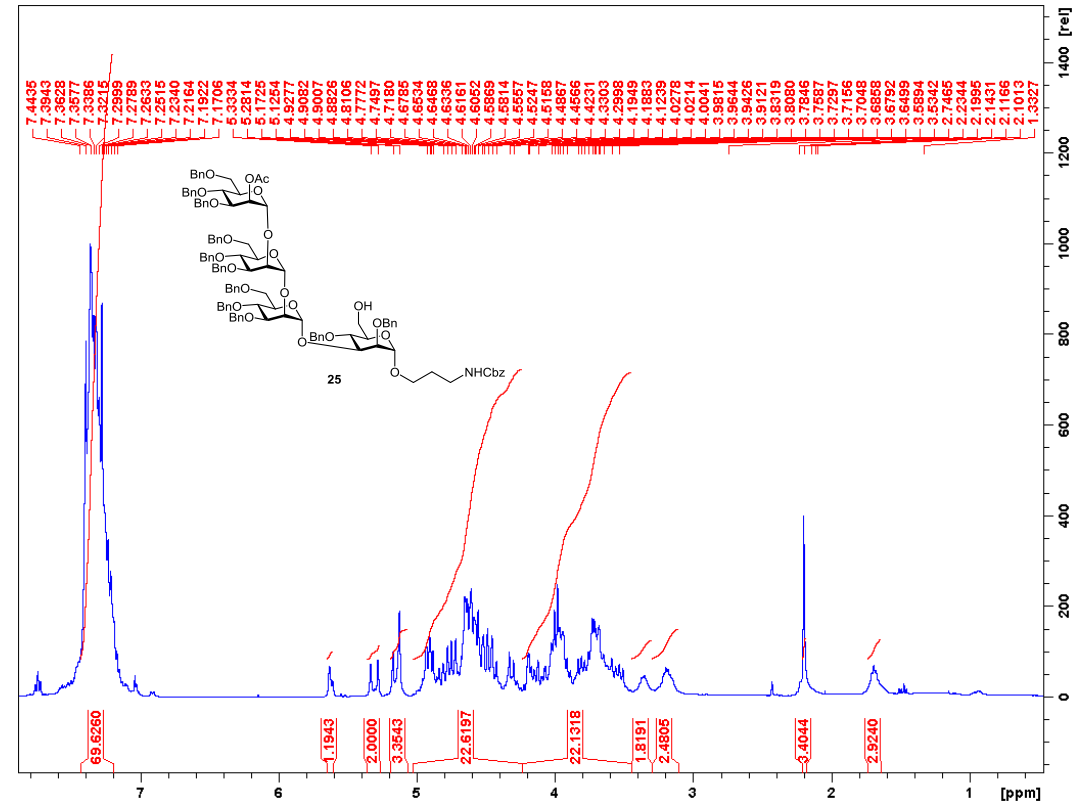
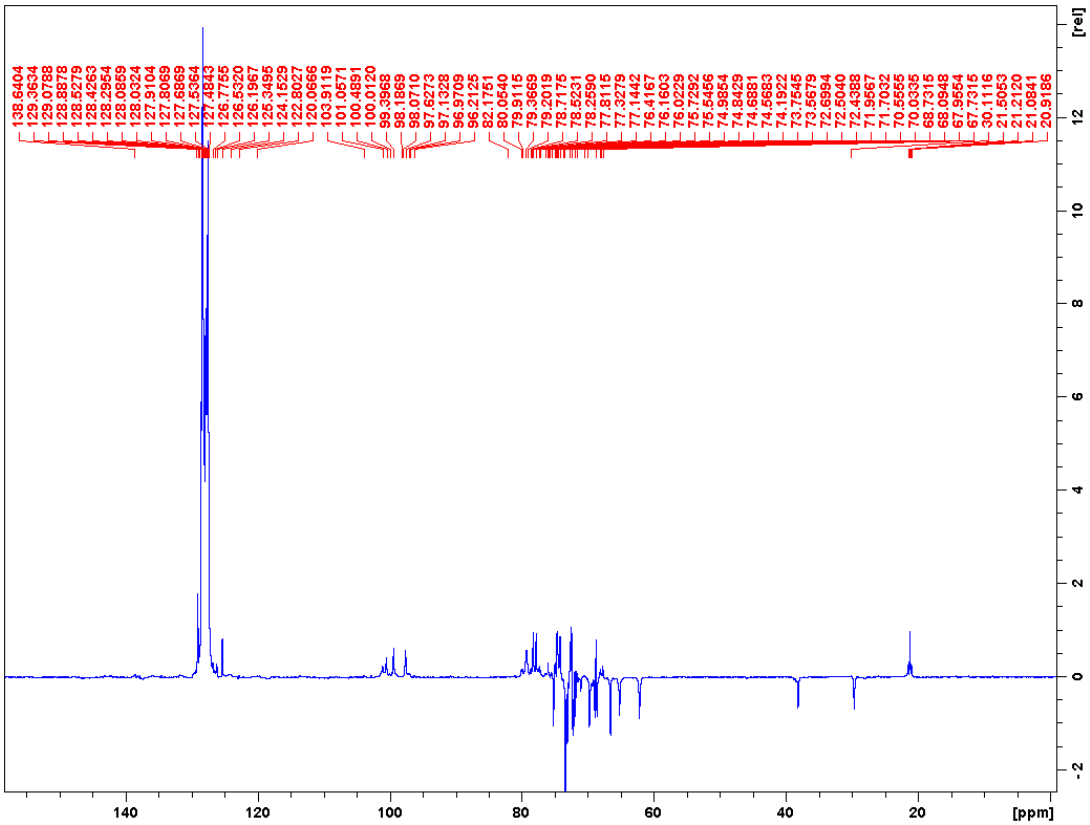


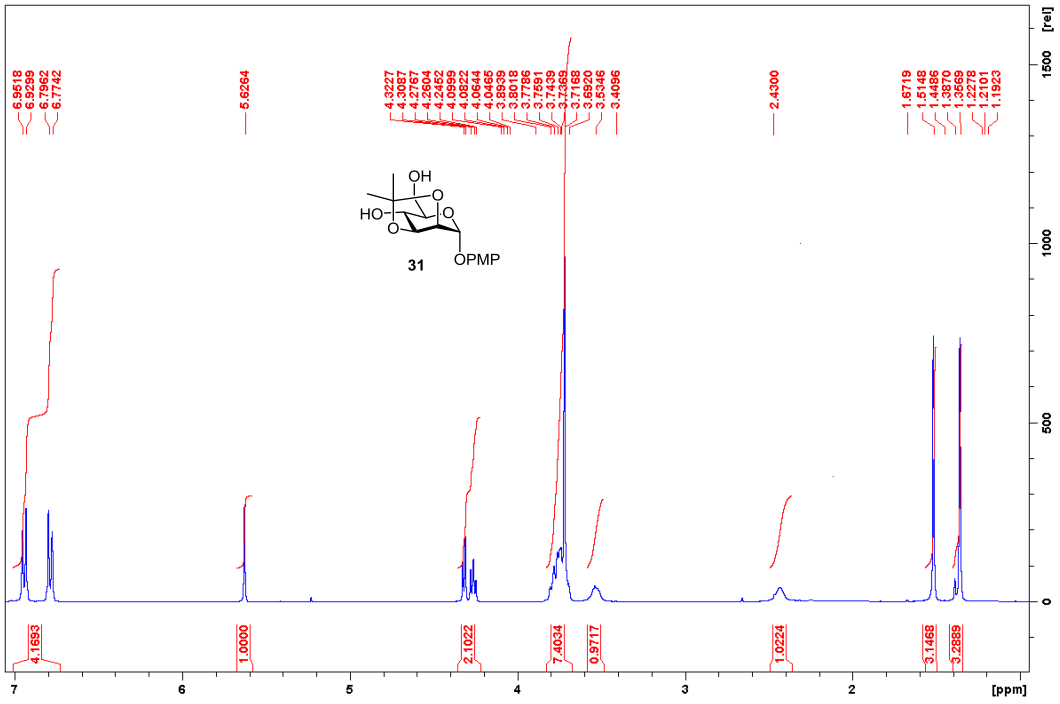


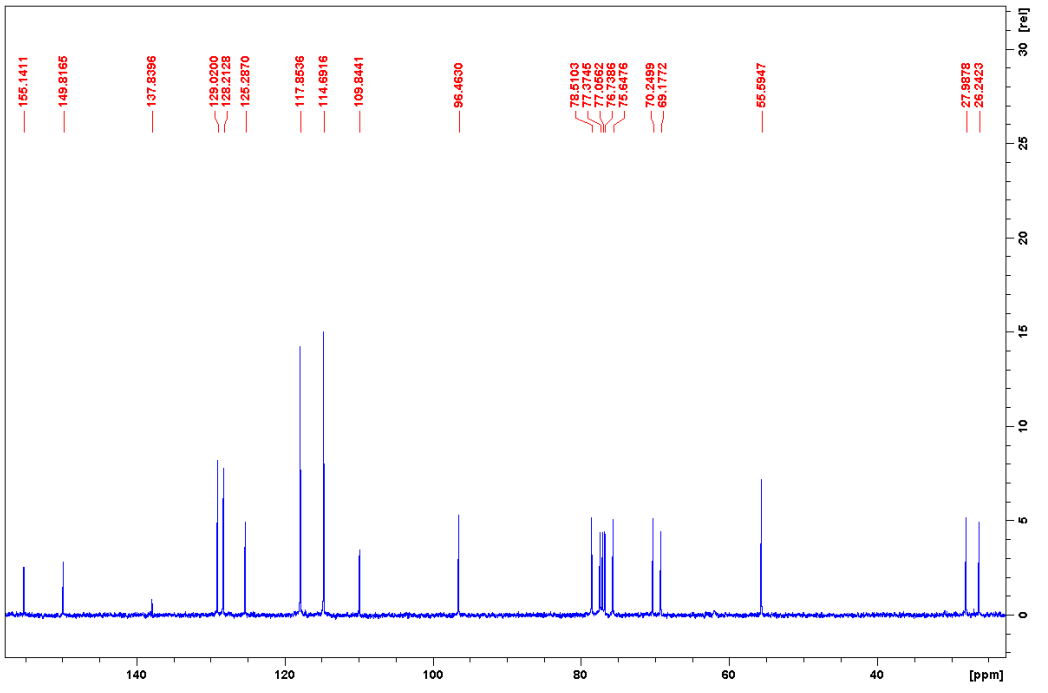
Compound 25


25
69.6260
1.1943
2.0000
3.3543
22.6197
22.1318
1.8191
2.4805
3.4044
2.9240
[ppm]
[rel]


[ppm]
[rel]

Compound 31


6.9618
6.9299
6.7962
6.7742
5.6264
4.3227
4.3067
4.2757
4.2604
4.2452
4.0999
4.0822
4.0644
4.0486
3.8939
3.8018
3.7786
3.7591
3.7439
3.7369
3.7168
3.6920
3.5346
3.4096
2.4300
1.6719
1.5148
1.4486
1.3870
1.3569
1.2278
1.2101
1.1923
OH
HO
O
O
O
OPMP
31
4.1693
1.0000
2.1022
7.4034
0.9717
1.0224
3.1468
3.2889
[rel]
[ppm]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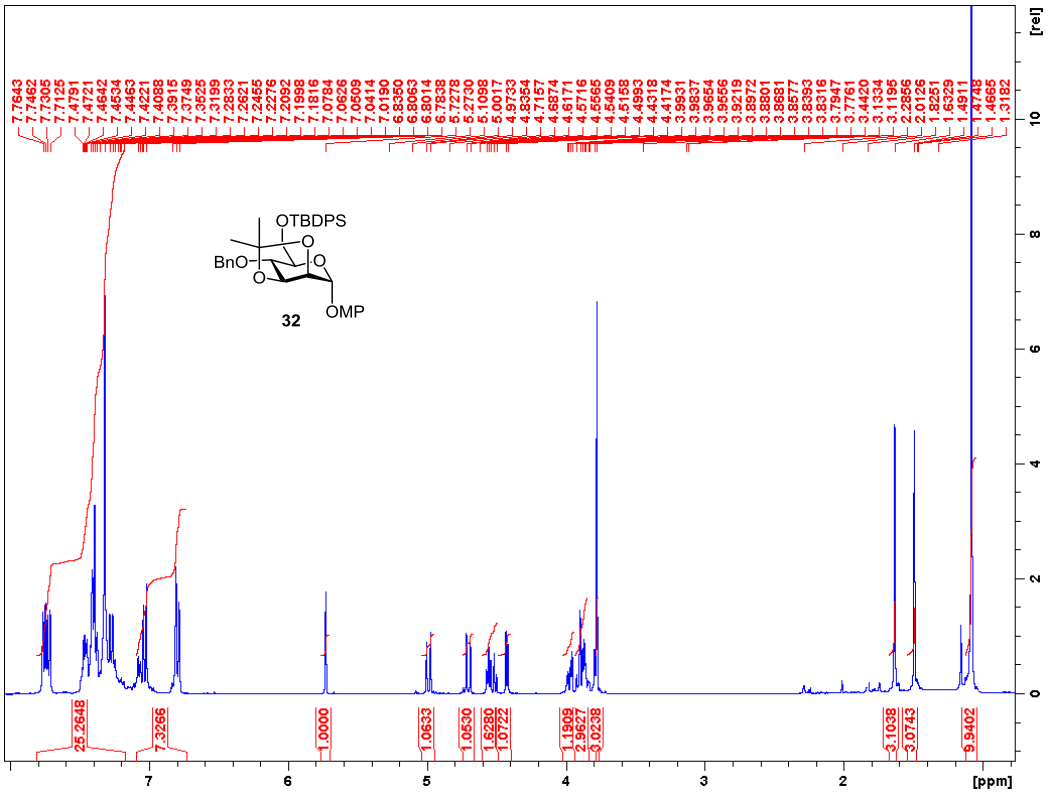
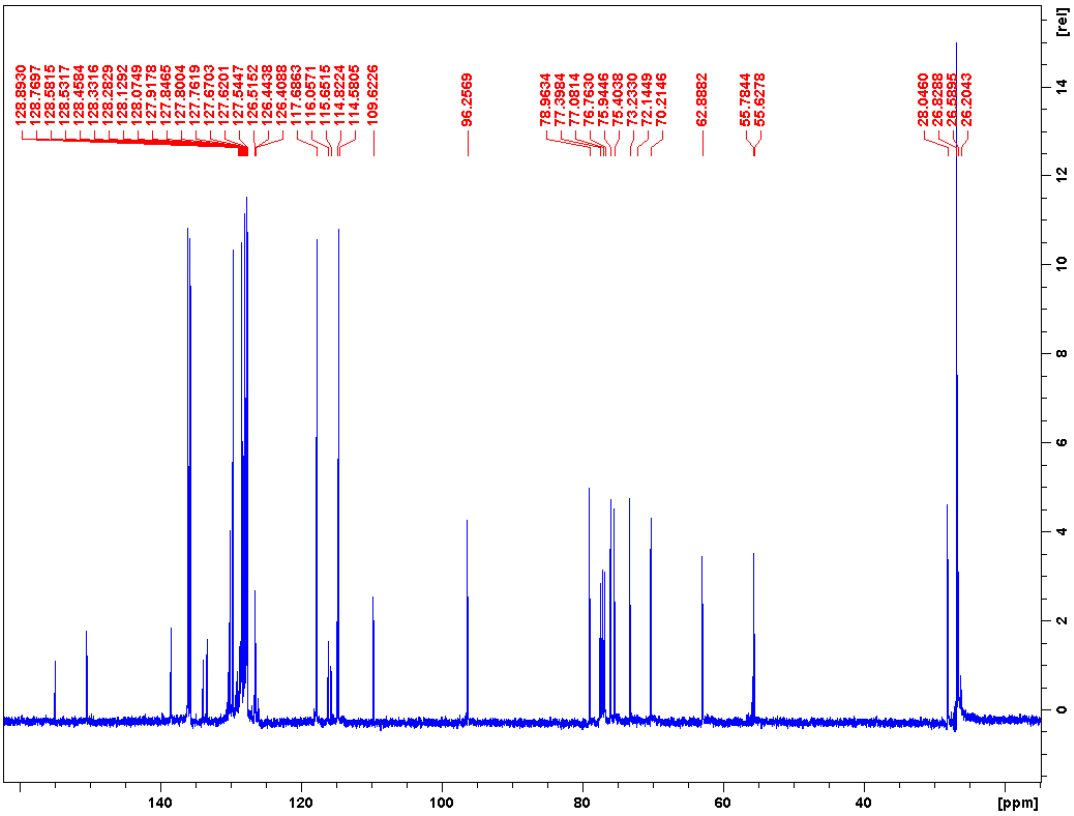
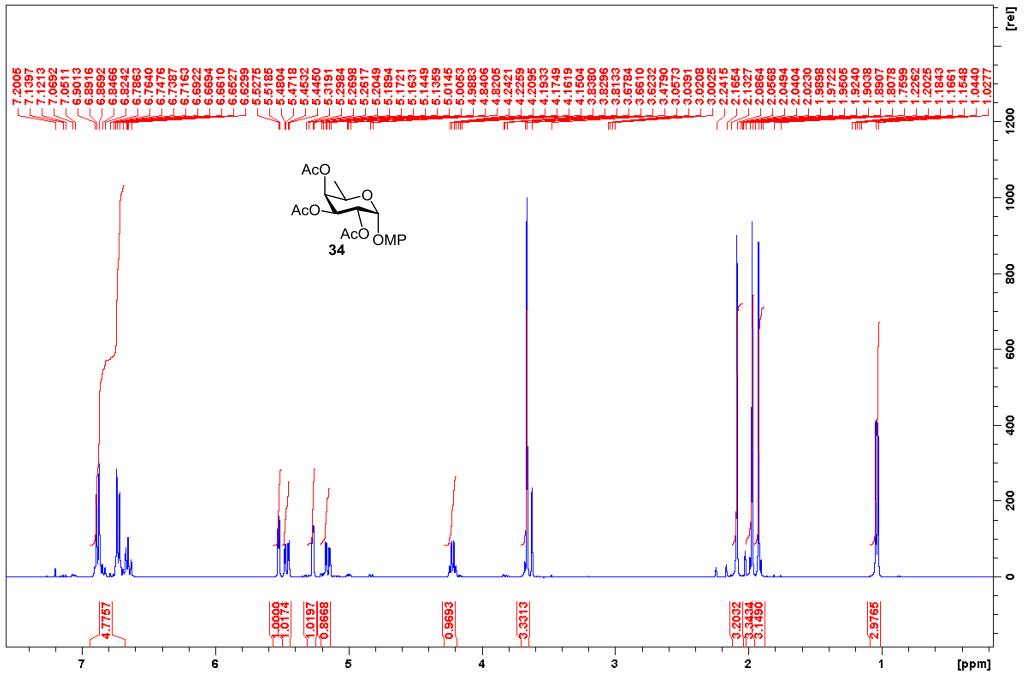
149.8165
137.8396
129.0200
128.2128
125.2870
117.8536
114.6916
109.8441
96.4630
78.5103
77.3745
77.0582
76.7386
75.6476
70.2499
69.1772
55.5947
27.9878
26.2423
[rel]
[ppm]

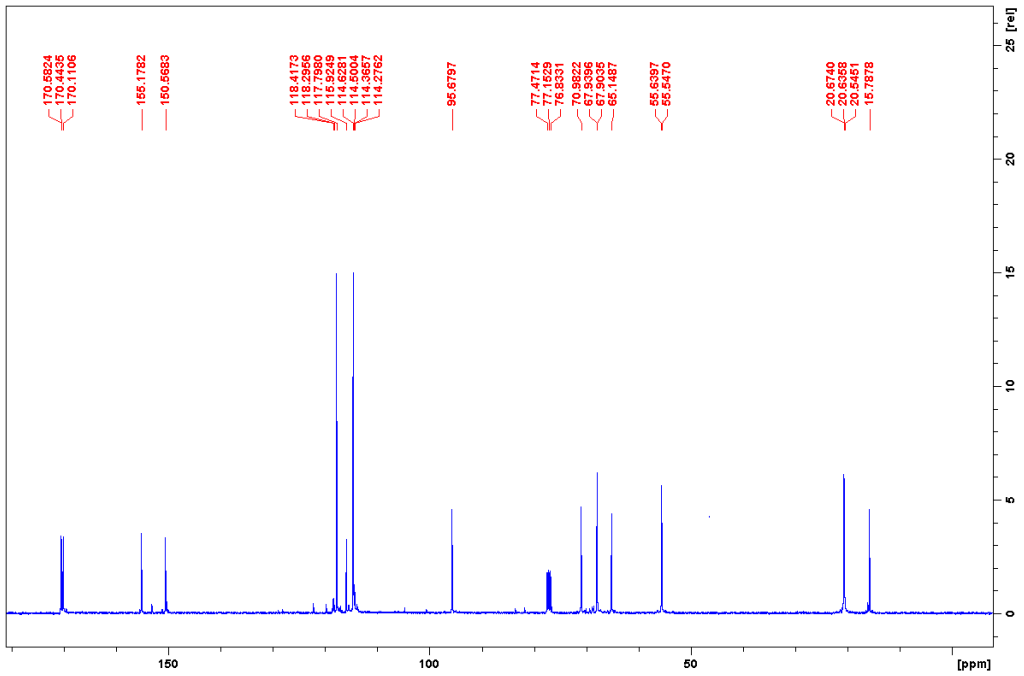
Compound 32



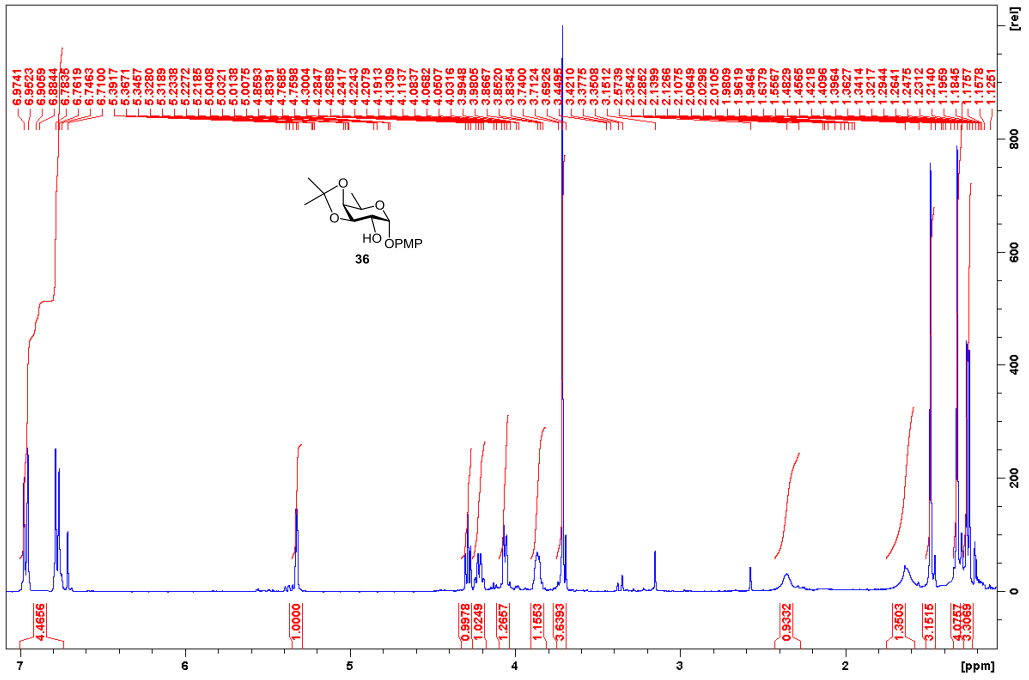


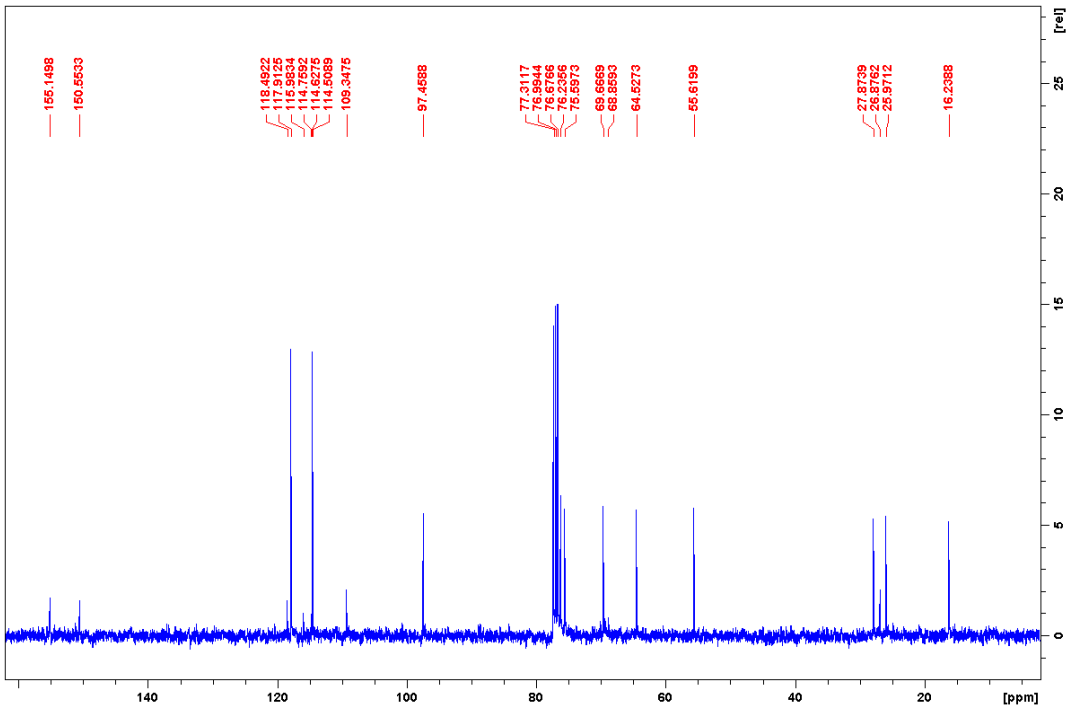
Compound 34





Compound 36


HO
OPMP
36
[rel]
[ppm]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117.9125
115.9834
114.7592
114.6275
114.5089
109.3475
97.4588
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76.9944
76.6766
76.2356
75.5973
69.6669
68.8593
64.5273
55.6199
27.8739
26.8762
25.9712
16.2388
[rel]
[ppm]

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