Supporting information

Coupling of anhydro-aldose tosylhydrazones with hydroxy compounds and carboxylic acids: A new route for the synthesis of *C*-β-D-glycopyranosylmethyl ethers and esters

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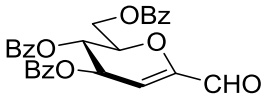
Experimental

General methods

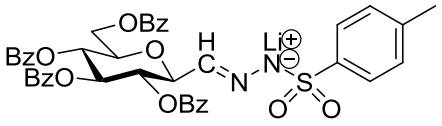
Optical rotations were determined with a Perkin–Elmer 241 polarimeter at room temperature. NMR spectra were recorded with Bruker 360 (360/90 MHz for $^{1}H/^{13}C$) or Bruker 400 (400/100 MHz for $^{1}H/^{13}C$) spectrometers. Chemical shifts are referenced to TMS as the internal reference (^{1}H), or to the residual solvent signals (^{13}C). The assignments of the ^{1}H and ^{13}C NMR signals of compounds **3**, **6**, **7**, **9** were performed by their COSY (**3**, **6c**, **7a**, **7c-g**, **7k**, **7m-p**, **9a-b**, **9d**), HSQC (**3**, **6c**, **7a**, **7c-d**, **7f**, **7k**, **7m-p**, **9b-d**) and HMBC (**3**, **6c**, **7f**, **7k**, **7n-p**, **9d**) spectra. Microanalyses were performed on an Elementar Vario Micro Cube instrument. Mass spectra were recorded with a Thermo LTQ XL or Bruker micrOTOF-Q mass spectrometers operated in a full scan positive ion ESI mode or positive ion APCI mode. TLC was performed on DCAlurolle Kieselgel 60 F254 (Merck). TLC plates were visualized under UV light, and by gentle heating. For column chromatography Kieselgel 60 (Merck, particle size (0.063–0.200 mm) was applied. 1,4-Dioxane and THF was distilled from sodium benzophenone ketyl and stored over sodium wires.



2,6-Anhydro-4,5,7-tri-*O*-benzoyl-3-deoxy-D-*arabino*-hept-2-enose (*C*-(3,4,6-tri-*O*-benzoyl-2-deoxy-D-*arabino*-hex-1-enopyranosyl)formaldehyde) (3)

Isolated from a mixture obtained in transformation of 1 in the presence of K_2CO_3.$[\alpha]_D$ +29 (c 0.65 in $CHCl_3$); Rf: 0.39 (1:2 EtOAc–hexane). ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 9.33 (1H, s, H-1, CHO), 8.20–7.90 (6H, m, aromatics), 7.67–7.28 (9H, m, aromatics), 6.13 (1H, d, $J_{3,4}$ 3.6 Hz, H-3), 5.96–5.85 (2H, m, H-4, H-5), 4.89 (1H, ddd, $J_{5,6}$ 10.6, $J_{6,7a}$ 5.9, $J_{6,7b}$ 4.4 Hz,

H-6), 4.77 (1H, dd, $J_{6a,6b}$ 12.2 Hz, H-7_a), 4.70 (1H, dd, H-7_b). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 185.8 (C-1, CHO), 166.2, 165.6, 165.0 (3×CO), 151.9 (C-2), 134.0–128.0 (aromatics), 113.8 (C-3), 74.9 (C-6), 67.3 (C-4, C-5), 61.6 (C-7). MS (ESI, m/z): 509.50 $[M+Na]^+$, $C_{28}H_{22}O_8$ (486.13). Found: C, 69.21; H, 4.54; O, 26.35. Calc. for $C_{28}H_{22}O_8$: C, 69.13; H, 4.56; O, 26.31.



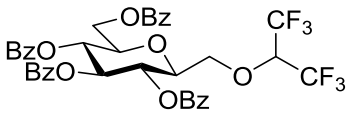
2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptose tosylhydrazon lithium salt (5)

1.00 g (1.29 mmol) 2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptose tosylhydrazone was dissolved in dry THF (8mL) and cooled to -78 °C under N_2 atmosphere. Then 1.6 M solution of *n*-BuLi in hexane (1.2 equiv., 0,965 mL) was added, and the mixture was stirred at -78 °C. After 10 minutes hexane (10 mL) was added and the precipitate was filtered off to yield 0.96 g (96%) of **5** as a yellow amorphous product. $[\alpha]_D$ +9.5 (c 0.78 in DMSO). ^{1}H NMR (400 MHz, DMSO-*d*6) δ (ppm) 8.10–7.04 (22H, m, aromatics), 6.83 (1H, d, $J_{1,2}$ 7.2 Hz, H-1), 6.77–6.62 (2H, d, aromatics), 5.95, 5.57, 5.45 (3H, 3×pseudo t, J = 9.5, 9.8 Hz, H-3, H-4, H-5), 4.56–4.37 (4H, m, H-2, H-6, H-7_a, H-7_b), 2.14 (s, 3H, CH_3). ^{13}C NMR (90 MHz, DMSO-*d*6) δ (ppm) 165.4, 165.3, 164.8, 164.7 (4×CO), 156.7 (C-1), 137.9–123.6 (aromatics), 78.4, 74.5, 74.0, 71.0, 69.6 (C-2, C-3, C-4, C-5, C-6), 63.1 (C-7), 20.8 (CH_3). MS (ESI, m/z): 782.70 $[M^-+Li^++H]^+$, $C_{42}H_{35}N_2O_{11}SLi$ (782.21). Found: C, 64.49; H, 4.50; Li, 0.90; N, 3.56; O, 22.45; S, 4.12. Calc. for $C_{42}H_{35}N_2O_{11}SLi$: C, 64.45; H, 4.51; Li, 0.89; N, 3.58; O, 22.48; S, 4.10.

General procedure I for the synthesis of 2,6-anhydro-1-*O*-aryl-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptitols (aryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl ethers) (6)

A phenol (20 or 33 equiv., 2.57 or 4.25 mmol) and LiO*t*Bu (1.2 or 1.5 equiv., 0.15 or 0.19 mmol) was added to dry 1,4-dioxane (2 mL) in a sealed tube. The suspension was stirred and heated to 110 °C. Then a solution of **6** *C*-(β-D-glucopyranosyl)anhydro-aldose tosylhydrazone (**1**, 0.10 g, 0.13 mmol) in dry 1,4-dioxane (2 mL) was added. When the reaction was complete (TLC, eluent: 1:2 EtOAc–hexane), the mixture was cooled and the insoluble material was filtered off. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (eluent: 1:6 or 1:8 acetone–hexane) to give 2,6-anhydro-1-*O*-aryl-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptitols (aryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl ethers).

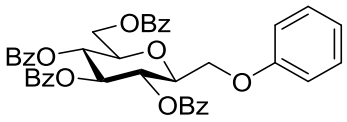
Characterization of the glycosylmethyl ethers



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(1,1,1,3,3,3-hexafluoropropan-2-yl)-D-*glycero*-D-*gulo*-heptitol (1,1,1,3,3,3-hexafluoropropan-2-yl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl ether) (6a)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), 1,1,1,3,3,3-hexafluoro-2-propanol (20 equiv., 0,27 mL, 0.43 g, 2.57 mmol) and LiO*t*Bu (1.2 equiv., 0.01 g, 0.12 mmol) according to General procedure I. Purified by column chromatography (1:8 acetone–hexane) to yield 35 mg (35%) of **6a** as a white amorphous product. $[\alpha]_D$ 37 (c 0.65 in $CHCl_3$); Rf: 0.59 (1:2 ereEtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15–7.74 (8H, m, aromatics),

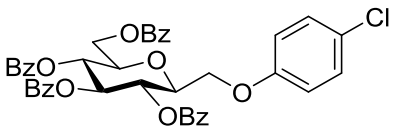
7.63–7.15 (12H, m, aromatics), 5.93 (1H, pseudo t, $J_{4,5}$ 9.6 Hz, H-4), 5.66 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.44 (1H, pseudo t, $J_{3,4}$ 9.8 Hz, H-3), 4.73 (1H, dd, $J_{7a,7b}$ 12.4 Hz, H-7_a), 4.55 (1H, hept, J 5.9 Hz, CH), 4.41 (1H, dd, H-7_b), 4.15 (1H, ddd, $J_{6,7a}$ 2.6, $J_{6,7b}$ 5.0 Hz, H-6), 4.09 (1H, ddd, $J_{1a,2}$ 3.1, $J_{1b,2}$ 6.6, $J_{2,3}$ 9.9 Hz, H-2), 4.07 (1H, dd, $J_{1a,1b}$ 12.6 Hz, H-1_a), 3.97 (1H, dd, H-1_b). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.4, 166.0, 165.4, 165.3 (4×CO), 144.3–126.6 (aromatics), 123.1–117.4 (2×CF_3), 79.0 (C-2), 76.6 (C-6), 76.7–75.7 (CH), 74.2 (C-4), 72.4 (C-1), 69.3 (C-3), 69.1 (C-5), 62.8 (C-7). MS (ESI, m/z): 783.33 $[M+Na]^+$, $C_{38}H_{30}F_6O_{10}$ (760.17). Found: C, 60.10; H, 4.00; F, 14.92; O, 21.00. Calc. for $C_{38}H_{30}F_6O_{10}$: C, 60.00; H, 3.98; F, 14.99; O, 21.03.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-phenyl-D-*glycero*-D-*gulo*-heptitol (phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl ether) (6b)

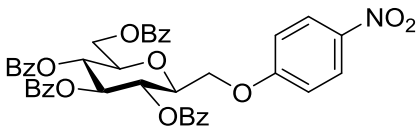
From tosylhydrazone **1** (0.10 g, 0.13 mmol), phenol (33 equiv., 0.40 g, 4.25 mmol) and Li*O*t*B*u (1.5 equiv., 0.02 g, 0.15 mmol) according to General procedure I. Purified by column chromatography (1:6 acetone–hexane) to yield 22 mg (25%) of **6b** as a white amorphous product. $[\alpha]_D$ +18 (c 0.29 in $CHCl_3$); Rf: 0.39 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21–7.76 (8H, m, aromatics), 7.67–7.14 (14H, m, aromatics), 6.96–6.88 (1H, m, aromatic), 6.85–6.77 (2H, m, aromatics), 5.97 (1H, pseudo t, $J_{4,5}$ 9.6 Hz, H-4), 5.71 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.67 (1H, pseudo t, $J_{3,4}$ 9.5 Hz, H-3), 4.64 (1H, dd, $J_{6,7a}$ 3.1, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.49 (1H, dd, $J_{6,7b}$ 5.7 Hz, H-7_b), 4.24–4.16 (4H, m, H-1_a, H-1_b, H-2, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.3, 166.1, 165.5, 165.4 (4×CO), 134.5–114.1 (aromatics), 77.3 (C-2), 76.3 (C-6), 74.5 (C-4), 70.1 (C-3), 69.8 (C-5), 67.6 (C-1), 63.4 (C-7).

MS (ESI, m/z): 709.50 $[M+Na]^+$, $C_{41}H_{34}O_{10}$ (686.21). Found: C, 71.52; H, 4.96; O, 23.36. Calc. for $C_{41}H_{34}O_{10}$: C, 71.71; H, 4.99; O, 23.30.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(4-chlorophenyl)-D-*glycero*-D-gulo-heptitol (4-chlorophenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl ether) (6d)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), 4-chlorophenol (20 equiv., 0.33 g, 2.57 mmol) and Li*O*t*B*u (1.2 equiv., 0.01 g, 0.12 mmol) according to General procedure I. Purified by column chromatography (1:6 acetone–hexane) to yield 27 mg (30%) of **6d** as a white amorphous product. $[\alpha]_D$ +7.9 (c 0.38 in $CHCl_3$); Rf: 0.39 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.17–7.70 (8H, m, aromatics), 7.67–6.99 (14H, m, aromatics), 6.83–6.67 (2H, m, aromatics), 5.97 (1H, pseudo t, $J_{4,5}$ 9.6 Hz, H-4), 5.70 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.67 (1H, pseudo t, $J_{3,4}$ 9.4 Hz, H-3), 4.64 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.49 (1H, dd, H-7_b), 4.22 (1H, ddd, $J_{6,7a}$ 3.0, $J_{6,7b}$ 5.2 Hz, H-6), 4.21 (1H, ddd, $J_{1a,2}$ 3.3, $J_{1b,2}$ 5.5, $J_{2,3}$ 9.7 Hz, H-2), 4.16 (2H, m, H-1_a, H-1_b). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.3, 166.1, 165.5, 165.4 (4×CO), 158.1–115.7 (aromatics), 77.2 (C-2), 76.4 (C-6), 74.4 (C-4), 70.1 (C-3), 69.8 (C-5), 68.0 (C-1), 63.4 (C-7). MS (ESI, m/z): 721.17 $[M+H]^+$, $C_{41}H_{33}ClO_{10}$ (720.18). Found: C, 68.34; H, 4.63; Cl, 4.91; O, 22.16. Calc. for $C_{41}H_{33}ClO_{10}$: C, 68.29; H, 4.61; Cl, 4.92; O, 22.19.



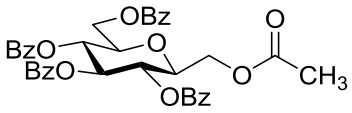
2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(4-nitrophenyl)-D-*glycero*-D-*gulo*-heptitol (4-nitrophenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl ether) (6e)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), 4-nitrophenol (20 equiv., 0.36 g, 2.57 mmol) and LiO*t*Bu (1.2 equiv., 0.01 g, 0.12 mmol) according to General procedure I. Purified by column chromatography (1:6 acetone–hexane) to yield 32 mg (34%) of **6e** as a white amorphous product. $[\alpha]_D$ -10 (c 0.31 in $CHCl_3$); Rf: 0.26 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23–7.77 (10H, m, aromatics), 7.66–7.19 (12H, m, aromatics), 6.93–6.81 (2H, m, aromatics), 5.99 (1H, pseudo t, $J_{4,5}$ 9.6 Hz, H-4), 5.71 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.68 (1H, pseudo t, $J_{3,4}$ 9.4 Hz, H-3), 4.65 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.49 (1H, dd, H-7_b), 4.30 (1H, dd, $J_{1a,1b}$ 12.3 Hz, H-1_a), 4.27 (1H, dd, H-1_b), 4.22 (1H, ddd, $J_{6,7a}$ 2.9, $J_{6,7b}$ 5.3 Hz, H-6), 4.21 (1H, ddd, $J_{1a,2}$ 2.7, $J_{1b,2}$ 5.2, $J_{2,3}$ 9.8 Hz, H-2). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 166.3, 166.1, 165.6, 165.4 (4×CO), 163.6–114.1 (aromatics), 77.0 (C-2), 76.5 (C-6), 74.3 (C-4), 70.0 (C-3), 69.6 (C-5), 68.0 (C-1), 63.2 (C-7). MS (ESI, m/z): 731.83 $[M+H]^+$, $C_{41}H_{34}NO_{12}$ (731.20). Found: C, 67.22; H, 4.58; N, 1.90; O, 26.21. Calc. for $C_{41}H_{34}NO_{12}$: C, 67.30; H, 4.55; N, 1.91; O, 26.24.

General procedure II for the synthesis of 2,6-anhydro-1,3,4,5,7-penta-*O*-acyl-heptitols (2,3,4,6-tetra-*O*-acyl-β-D-glycopyranosylmethyl esters) (7, 9)

A carboxylic acid (3-40 equiv., 0.39-5.15 mmol) and K_3PO_4 (3-25 equiv., 0.39-3.22 mmol) was added to dry 1,4-dioxane (2 mL). The suspension was stirred and heated to reflux, and then a solution of a tosylhydrazone (0.10 g, **1** (0.13 mmol), or **8** (0.19 mmol) in dry 1,4-dioxane (2 mL) was added dropwise. When the reaction was complete (TLC, eluent: 1:2 EtOAc–hexane for **7**; 1:1 EtOAc–hexane for **9**), the mixture was cooled and the insoluble material filtered off. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (eluent: 1:3 or 1:4 EtOAc–hexane or 1:3, 1:5 or 1:6 acetone–hexane for **7**; 1:2 EtOAc–hexane for **9**) to give the title compounds.

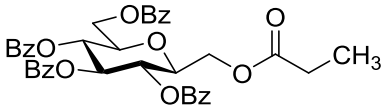
Characterization of the glycosylmethyl esters



1-*O*-Acetyl-2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl acetate) (7a)

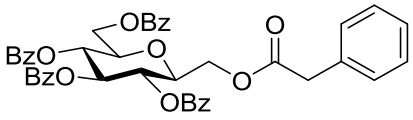
From tosylhydrazone **1** (0.10 g, 0.13 mmol), acetic acid (20 equiv., 0.15 mL, 0.15 g, 2.57 mmol) and K_3PO_4 (10 equiv., 0.27 g, 1.28 mmol) according to General procedure II. Purified by column chromatography (1:4 EtOAc–hexane) to yield 26 mg (31%) of **7a** as a white amorphous product. $[\alpha]_D$ +25 (c 0.63 in $CHCl_3$); Rf: 0.26 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13–7.69 (8H, m, aromatics), 7.62–7.21 (12H, m, aromatics), 5.93 (1H, pseudo t, $J_{4,5}$ 9.5 Hz, H-4), 5.68 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.61 (1H, pseudo t, $J_{3,4}$ 9.5 Hz, H-3), 4.63 (1H, dd, $J_{7a,7b}$ 12.1 Hz, H-7_a), 4.48 (1H, dd, H-7_b), 4.31 (1H, dd, $J_{1a,1b}$ 12.4 Hz, H-1_a), 4.27 (1H, dd, H-1_b), 4.16 (1H, ddd, $J_{6,7a}$ 3.1, $J_{6,7b}$ 5.7 Hz, H-6), 4.05 (1H, ddd, $J_{1a,2}$

3.1, $J_{1b,2}$ 5.0, $J_{2,3}$ 9.8 Hz, H-2), 2.00 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 166.3, 166.0, 165.4 (5×CO), 134.0–125.2 (aromatics), 76.4 (C-2), 76.3 (C-6), 74.4 (C-4), 69.7 (C-5), 69.5 (C-3), 63.4 (C-7), 62.9 (C-1), 20.8 (CH_3). MS (ESI, m/z): 653.75 $[M+H]^+$, $C_{37}H_{32}O_{11}$ (652.19). Found: C, 68.11; H, 4.99; O, 26.88. Calc. for $C_{37}H_{32}O_{11}$: C, 68.09; H, 4.94; O, 26.97.



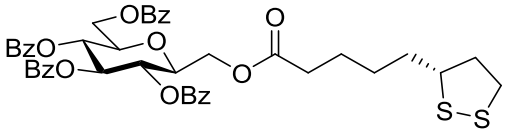
2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-propanoyl-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl propanoate) (7b)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), propanoic acid (20 equiv., 0.19 mL, 0.19 g, 2.57 mmol) and K_3PO_4 (10 equiv., 0.27 g, 1.28 mmol) according to General procedure II. Purified by column chromatography (1:4 EtOAc–hexane) to yield 42 mg (49%) of **7b** as a white amorphous product. $[\alpha]_D$ +20 (c 0.64 in $CHCl_3$); Rf: 0.29 (1:2 EtOAc–hexane). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08–7.75 (8H, m, aromatics), 7.64–7.18 (12H, m, aromatics), 5.92 (1H, pseudo t, $J_{4,5}$ 9.8 Hz, H-4), 5.67 (1H, pseudo t, $J_{5,6}$ 8.9 Hz, H-5), 5.61 (1H, pseudo t, $J_{3,4}$ 9.4 Hz, H-3), 4.62 (1H, dd, $J_{7a,7b}$ 12.1 Hz, H-7_a), 4.47 (1H, dd, H-7_b), 4.31 (1H, dd, $J_{1a,1b}$ 12.4 Hz, H-1_a), 4.28 (1H, dd, H-1_b), 4.15 (1H, ddd, $J_{6,7a}$ 2.7, $J_{6,7b}$ 5.0 Hz, H-6), 4.05 (1H, ddd, $J_{1a,2}$ 4.0, $J_{1b,2}$ 8.1, $J_{2,3}$ 9.8 Hz, H-2), 2.31 (1H, dd, $J_{CH2a,CH2b}$ 3.3, 7.6 Hz, CH_{2a}), 2.27 (1H, dd, CH_{2b}), 1.08 (3H, t, *J* 7.6 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.2, 166.3, 166.1, 165.4 (5×CO), 133.9–127.8 (aromatics), 76.4 (C-2, C-6), 74.4 (C-4), 69.8 (C-5), 69.5 (C-3), 63.4 (C-7), 62.7 (C-1), 27.4 (CH_2), 9.1 (CH_3). MS (ESI, m/z): 667.42 $[M+H]^+$, $C_{38}H_{34}O_{11}$ (666.21). Found: C, 68.52; H, 5.10; O, 26.42. Calc. for $C_{38}H_{34}O_{11}$: C, 68.46; H, 5.14; O, 26.40.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(2-phenylacetyl)-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 2-phenylacetate) (7c)

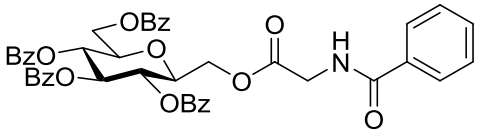
From tosylhydrazone **1** (0.10 g, 0.13 mmol), 2-phenylacetic acid (20 equiv., 0.35 g, 2.57 mmol) and K_3PO_4 (10 equiv., 0.27 g, 1.28 mmol) according to General procedure II. Purified by column chromatography (1:4 EtOAc–hexane) to yield 54 mg (58%) of **7c** as a pale orange amorphous product. $[\alpha]_D$ +15 (c 0.43 in $CHCl_3$); Rf: 0.29 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08–7.77 (8H, m, aromatics), 7.60–7.19 (17H, m, aromatics), 5.90 (1H, pseudo t, $J_{4,5}$ 9.6 Hz, H-4), 5.63 (1H, pseudo t, $J_{5,6}$ 9.9 Hz, H-5), 5.57 (1H, pseudo t, $J_{3,4}$ 9.6 Hz, H-3), 4.59 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.45 (1H, dd, H-7_b), 4.34 (1H, dd, $J_{1a,1b}$ 12.3 Hz, H-1_a), 4.29 (1H, dd, H-1_b), 4.12 (1H, ddd, $J_{6,7a}$ 3.1, $J_{6,7b}$ 5.3 Hz, H-6), 4.02 (1H, ddd, $J_{1a,2}$ 3.0, $J_{1b,2}$ 5.1, $J_{2,3}$ 10.0 Hz, H-2), 3.58 (2H, s, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.3, 166.3, 166.0, 165.4 (5×CO), 133.9–125.2 (aromatics), 76.3 (C-2, C-6), 74.4 (C-4), 69.8 (C-5), 69.5 (C-3), 63.5 (C-7), 63.1 (C-1), 41.0 (CH_2). MS (ESI, m/z): 729.83 $[M+H]^+$, $C_{43}H_{36}O_{11}$ (728.23). Found: C, 70.78; H, 4.02; O, 24.21. Calc. for $C_{43}H_{36}O_{11}$: C, 70.87; H, 4.98; O, 24.15.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-lipoyl-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl lipoate) (7d)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), α-lipoic acid (5 equiv., 0.13 g, 0.64 mmol) and K_3PO_4 (5 equiv., 0.14 g, 0.64 mmol) according to General procedure II. Purified by column chromatography (1:6 acetone–hexane) to yield 40 mg (39%) of **7d** as a pale yellow product.

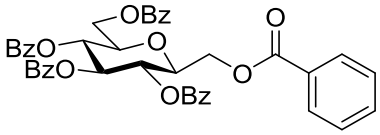
$[\alpha]_D$ +9 (c 0.83 in $CHCl_3$); Rf: 0.26 (1:2 EtOAc–hexane). ^1H NMR (360 MHz, $CDCl_3$) δ (ppm) 8.18–7.67 (8H, m, aromatics), 7.63–6.98 (12H, m, aromatics), 5.92 (1H, pseudo t, $J_{4,5}$ 9.5 Hz, H-4), 5.67 (1H, pseudo t, $J_{5,6}$ 9.9 Hz, H-5), 5.60 (1H, pseudo t, $J_{3,4}$ 9.5 Hz, H-3), 4.62 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.48 (1H, dd, H-7_b), 4.29 (2H, dd, $J_{1a,1b}$ 12.0 Hz, H-1_a, H-1_b), 4.16 (1H, ddd, $J_{6,7a}$ 2.8, $J_{6,7b}$ 5.2 Hz, H-6), 4.05 (1H, ddd, $J_{1a,2}$ 3.9, $J_{1b,2}$ 6.1, $J_{2,3}$ 9.9 Hz, H-2), 3.61–3.45 (1H, m, CH), 3.23–3.00 (2H, m, CH_2), 2.53–2.13 (3H, m, CH_2, CH_{2a}), 2.00–1.79 (1H, m, CH_{2b}), 1.78–1.18 (6H, m, 3×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.1, 166.2, 166.0, 165.3 (5×CO), 134.1–126.1 (aromatics), 76.3 (C-2, C-6), 74.4 (C-4), 69.8 (C-5), 69.5 (C-3), 63.4 (C-7), 62.7 (C-1), 56.4 (CH), 40.3, 38.6, 34.7, 33.8, 28.8, 24.5 (6×CH_2). MS (ESI, m/z): 816.67 $[M+H_2O]^+$, $C_{43}H_{42}O_{11}S_2$ (798.22). Found: C, 64.62; H, 5.32; O, 22.05; S, 7.99. Calc. for $C_{43}H_{42}O_{11}S_2$: C, 64.65; H, 5.30; O, 22.03; S, 8.03.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(*N*-benzoylglycyl)-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl *N*-benzoylglycinate) (7e)

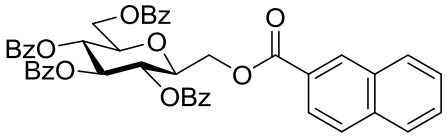
From tosylhydrazone **1** (0.10 g, 0.13 mmol), *N*-benzoylglycine (hippuric acid, 5 equiv., 0.12 g, 0.64 mmol) and K_3PO_4 (5 equiv., 0.14 g, 0.64 mmol) according to General procedure II. Purified by column chromatography (1:3 EtOAc–hexane) to yield 28 mg (28%) of **7e** as a white amorphous product. $[\alpha]_D$ +9 (c 0.75 in $CHCl_3$); Rf: 0.35 (1:1 EtOAc–hexane). ^1H NMR (360 MHz, $CDCl_3$) δ (ppm) 8.24–7.71 (10H, m, aromatics), 7.66–7.12 (15H, m, aromatics), 6.69 (1H, dd, $J_{NH,CH2a}$ 4.5, $J_{NH,CH2b}$ 4.7 Hz, NH), 5.94 (1H, pseudo t, $J_{4,5}$ 9.6 Hz, H-4), 5.66 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.60 (1H, pseudo t, $J_{3,4}$ 9.6 Hz, H-3), 4.63 (1H, dd, $J_{7a,7b}$ 12.3 Hz, H-7_a), 4.47 (1H, dd, H-7_b), 4.42 (1H, dd, $J_{1a,1b}$ 12.1 Hz, H-1_a), 4.40 (1H, dd, H-1_b), 4.25 (2H, dd, $J_{CH2a,CH2b}$ 5.0 Hz, CH_{2a}, CH_{2b}), 4.15 (1H, ddd, $J_{6,7a}$ 3.1, $J_{6,7b}$ 5.2 Hz, H-6), 4.08 (1H,

ddd, $J_{1a,2}$ 3.6, $J_{1b,2}$ 6.8, $J_{2,3}$ 9.9 Hz, H-2). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 169.8, 166.3, 166.0, 165.6, 165.3 (6×CO), 134.1–126.9 (aromatics), 76.5 (C-2), 76.2 (C-6), 74.3 (C-4), 69.8 (C-5), 69.5 (C-3), 63.7 (C-7), 63.3 (C-1), 41.9 (CH_2). MS (ESI, m/z): 772.50 $[M+H]^+$, $C_{44}H_{37}NO_{12}$ (771.23). Found: C, 68.53; H, 4.82; N, 1.79; O, 24.95. Calc. for $C_{44}H_{37}NO_{12}$: C, 68.48; H, 4.83; N, 1.81; O, 24.88.



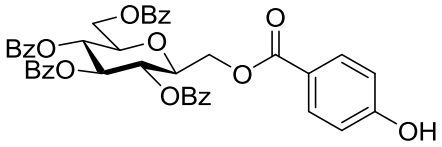
2,6-Anhydro-1,3,4,5,7-penta-*O*-benzoyl-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl benzoate) (7f)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), benzoic acid (40 equiv., 0.63 g, 5.15 mmol) and K_3PO_4 (20 equiv., 0.55 g, 2.57 mmol) according to General procedure II. Purified by column chromatography (1:4 EtOAc–hexane) to yield 20 mg (22%) of **7f** as a white amorphous product. $[\alpha]_D$ +1 (c 0.55 in $CHCl_3$); Rf: 0.29 (1:2 EtOAc–hexane). ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 8.08–7.78 (10H, m, aromatics), 7.56–7.20 (15H, m, aromatics), 5.96 (1H, pseudo t, $J_{4,5}$ 9.6 Hz, H-4), 5.68 (2H, pseudo t, $J_{2,3}$ 9.5, $J_{3,4}$ 9.6, $J_{5,6}$ 9.5 Hz, H-3, H-5), 4.63 (2H, dd, $J_{1a,1b}$ 12.2, $J_{7a,7b}$ 12.2 Hz, H-1_a, H-7_a), 4.47 (2H, dd, H-1_b, H-7_b), 4.19 (2H, ddd, $J_{1a,2}$ 3.0, $J_{1b,2}$ 5.4, $J_{6,7a}$ 3.0, $J_{6,7b}$ 5.4 Hz, H-2, H-6). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 166.3, 166.1, 165.4 (5×CO), 134.0–128.2 (aromatics), 76.5 (C-2, C-6), 74.4 (C-4), 69.8 (C-3, C-5), 63.5 (C-1, C-7). MS (ESI, m/z): 715.67 $[M+H]^+$, $C_{42}H_{34}O_{11}$ (714.21). Found: C, 70.48; H, 4.84; O, 24.56. Calc. for $C_{42}H_{34}O_{11}$: C, 70.58; H, 4.80; O, 24.62.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(2-naphthoyl)-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 2-naphthoate) (7g)

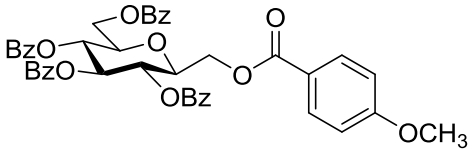
From tosylhydrazone **1** (0.10 g, 0.13 mmol), 2-naphthoic acid (20 equiv., 0.44 g, 2.57 mmol) and K_3PO_4 (10 equiv., 0.27 g, 1.28 mmol) according to General procedure II. Purified by column chromatography (1:4 EtOAc–hexane) to yield 36 mg (37%) of **7g** as a pale brown amorphous product. $[\alpha]_D$ –5 (c 0.91 in $CHCl_3$); Rf: 0.26 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.18–7.72 (10H, m, aromatics), 7.70–7.18 (17H, m, aromatics), 5.98 (1H, pseudo t, $J_{4,5}$ 9.7 Hz, H-4), 5.72 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.71 (1H, pseudo t, $J_{3,4}$ 9.8 Hz, H-3), 4.69 (1H, dd, $J_{7a,7b}$ 12.3 Hz, H-7_a), 4.65 (1H, dd, $J_{1a,1b}$ 12.4 Hz, H-1_a), 4.56 (1H, dd, H-7_b), 4.49 (1H, dd, H-1_b), 4.25 (1H, ddd, $J_{6,7a}$ 3.2, $J_{6,7b}$ 5.6 Hz, H-6), 4.21 (1H, ddd, $J_{1a,2}$ 3.0, $J_{1b,2}$ 5.6, $J_{2,3}$ 9.7 Hz, H-2). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 166.4, 166.3, 166.1, 165.4 (5×CO), 136.4–124.9 (aromatics), 76.5 (C-2, C-6), 74.5 (C-4), 70.0 (C-3), 69.8 (C-5), 63.7 (C-7), 63.5 (C-1). MS (ESI, m/z): 787.75 $[M+Na]^+$, $C_{46}H_{36}O_{11}$ (764.23). Found: C, 72.18; H, 4.76; O, 23.06. Calc. for $C_{46}H_{36}O_{11}$: C, 72.24; H, 4.74; O, 23.01.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(4-hydroxybenzoyl)-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 4-hydroxybenzoate) (7h)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), 4-hydroxybenzoic acid (20 equiv., 0.36 g, 2.57 mmol) and K_3PO_4 (20 equiv., 0.55 g, 2.57 mmol) according to General procedure II. Purified by column chromatography (1:5 acetone–hexane) to yield 40 mg (43%) of **7h** as a pale brown

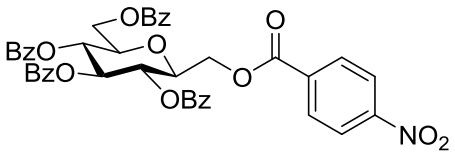
amorphous product. $[\alpha]_D$ –3 (c 1.06 in $CHCl_3$); Rf: 0.44 (1:1 EtOAc–hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 8.18–7.66 (10H, m, aromatics), 7.65–7.15 (12H, m, aromatics), 6.79–6.70 (2H, m, aromatics), 5.95 (1H, pseudo t, $J_{4,5}$ 9.9 Hz, H-4), 5.69 (1H, pseudo t, $J_{5,6}$ 9.7 Hz, H-5), 5.69 (1H, pseudo t, $J_{3,4}$ 9.9 Hz, H-3), 4.63 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.60 (1H, dd, $J_{1a,1b}$ 12.1 Hz, H-1_a), 4.47 (1H, 1H, H-7_b), 4.44 (1H, dd, H-1_b), 4.19 (1H, ddd, $J_{6,7a}$ 2.7, $J_{6,7b}$ 5.4 Hz, H-6), 4.18 (1H, ddd, $J_{1a,2}$ 2.5, $J_{1b,2}$ 5.4, $J_{2,3}$ 9.9 Hz, H-2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.1, 166.0, 165.4 (5×CO), 160.3–115.0 (aromatics), 76.5 (C-2), 76.4 (C-6), 74.5 (C-4), 69.8 (C-3, C-5), 63.5 (C-7), 63.1 (C-1). MS (ESI, m/z): 731.17 $[M+H]^+$, $C_{42}H_{34}O_{12}$ (730.21). Found: C, 69.10; H, 4.66; O, 26.30. Calc. for $C_{42}H_{34}O_{12}$: C, 69.04; H, 4.69; O, 26.27.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(4-methoxybenzoyl)-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 4-methoxybenzoate) (7i)

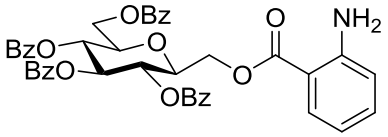
From tosylhydrazone **1** (0.10 g, 0.13 mmol) and 4-methoxybenzoic acid (20 equiv., 0.39 g, 2.57 mmol) and K_3PO_4 (25 equiv., 0.68 g, 3.22 mmol) according to General procedure II. Purified by column chromatography (1:5 acetone–hexane) to yield 28 mg (29%) of **7i** as a white amorphous product. $[\alpha]_D$ –3 (c 0.68 in $CHCl_3$); Rf: 0.24 (1:2 EtOAc–hexane). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20–7.65 (10H, m, aromatics), 7.61–7.15 (12H, m, aromatics), 6.85–6.76 (2H, m, aromatics), 5.95 (1H, pseudo t, $J_{3,4}$ 9.7, $J_{4,5}$ 9.7 Hz, H-4), 5.68 (2H, pseudo t, H-3, H-5), 4.63 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.60 (1H, dd, $J_{1a,1b}$ 12.1 Hz, H-1_a), 4.47 (1H, dd, H-7_b), 4.43 (1H, dd, H-1_b), 4.19 (1H, ddd, $J_{5,6}$ 9.7, $J_{6,7a}$ 3.1, $J_{6,7b}$ 5.5 Hz, H-6), 4.18 (1H, ddd, $J_{1a,2}$ 3.0, $J_{1b,2}$ 5.5, $J_{2,3}$ 9.7 Hz, H-2), 3.84 (3H, s, CH_3). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 166.3, 166.1, 166.0, 165.4 (5×CO), 164.0–113.5 (aromatics), 76.5 (C-2), 76.4 (C-6),

74.5 (C-4), 69.8 (C-3, C-5), 63.5 (C-7), 63.2 (C-1), 55.6 (CH_3). MS (ESI, m/z): 767.50 $[M+Na]^+$, $C_{43}H_{36}O_{12}$ (744.22). Found: C, 69.42; H, 4.86; O, 25.80. Calc. for $C_{43}H_{36}O_{12}$: C, 69.35; H, 4.87; O, 25.78.



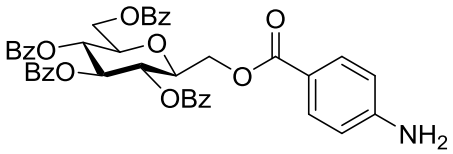
2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-*O*-(4-nitrobenzoyl)-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 4- nitrobenzoate) (7j)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), 4-nitrobenzoic acid (20 equiv., 0.43 g, 2.57 mmol) and K_3PO_4 (25 equiv., 0.68 g, 3.22 mmol) according to General procedure II. Purified by column chromatography (1:5 acetone–hexane) to yield 50 mg (51%) of **7j** as a yellow amorphous product. $[\alpha]_D$ +2 (c 1.25 in $CHCl_3$); Rf: 0.27 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.37–8.07 (4H, m, aromatics), 8.04–7.70 (8H, m, aromatics), 7.66–7.07 (12H, m, aromatics), 5.98 (1H, pseudo t, $J_{4,5}$ 9.8 Hz, H-4), 5.71 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.69 (1H, pseudo t, $J_{3,4}$ 9.8 Hz, H-3), 4.66 (2H, dd, H-1_a, H-7_a), 4.52 (1H, dd, $J_{1a,1b}$ 12.2 Hz, H-7_b), 4.44 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-1_b), 4.22 (1H, ddd, $J_{6,7a}$ 3.0, $J_{6,7b}$ 5.4 Hz, H-6), 4.19 (1H, ddd, $J_{1a,2}$ 3.1, $J_{1b,2}$ 5.5, $J_{2,3}$ 9.6 Hz, H-2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.1, 166.0, 165.4, 164.3 (5×CO), 150.7–123.1 (aromatics), 76.5 (C-2), 76.0 (C-6), 74.2 (C-4), 69.6 (C-3, C-5), 63.9 (C-7), 63.2 (C-1). MS (APCI, m/z): 759.83 $[M+H]^+$, $C_{42}H_{33}NO_{13}$ (759.20). Found: C, 66.36; H, 4.36; N, 1.83; O, 27.35. Calc. for $C_{42}H_{33}NO_{13}$: C, 66.40; H, 4.38; N, 1.84; O, 27.38.



1-*O*-(2-Aminobenzoyl)-2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 2-aminobenzoate) (7k)

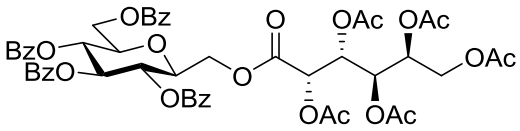
From tosylhydrazone **1** (0.10 g, 0.13 mmol), 2-aminobenzoic acid (20 equiv., 0.35 g, 2.57 mmol) and K_3PO_4 (15 equiv., 0.41 g, 1.93 mmol) according to General procedure II. Purified by column chromatography (1:5 acetone–hexane) to yield 48 mg (51%) of **7k** as an orange amorphous product. $[\alpha]_D$ +2 (c 1.10 in $CHCl_3$); Rf: 0.27 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07–7.67 (9H, m, aromatics), 7.63–7.09 (13H, m, aromatics), 6.63–6.55 (1H, m, aromatic), 6.55–6.46 (1H, m, aromatic), 5.96 (1H, pseudo t, $J_{4,5}$ 9.9 Hz, H-4), 5.69 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.67 (2H, br s, NH_2), 5.66 (1H, pseudo t, $J_{3,4}$ 9.8 Hz, H-3), 4.63 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.59 (1H, dd, $J_{1a,1b}$ 12.1 Hz, H-1_a), 4.46 (1H, dd, H-7_b), 4.43 (1H, dd, H-1_b), 4.19 (1H, ddd, $J_{6,7a}$ 2.8, $J_{6,7b}$ 5.4 Hz, H-6), 4.18 (1H, ddd, $J_{1a,2}$ 2.9, $J_{1b,2}$ 5.7, $J_{2,3}$ 9.8 Hz, H-2). ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.6, 166.3, 166.1, 165.4 (5×CO), 151.0–116.0 (aromatics), 76.6 (C-2), 76.4 (C-6), 74.5 (C-4), 69.9 (C-3), 69.8 (C-5), 63.4 (C-7), 62.8 (C-1). MS (ESI, m/z): 752.42 $[M+Na]^+$, $C_{42}H_{35}NO_{11}$ (729.22). Found: C, 69.01; H, 4.85; N, 1.93; O, 24.18. Calc. for $C_{42}H_{35}NO_{11}$: C, 69.13; H, 4.83; N, 1.92; O, 24.12.



1-*O*-(4-Aminobenzoyl)-2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 4-aminobenzoate) (7l)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), 2-aminobenzoic acid (3 equiv., 0.05 g, 0.39 mmol) and K_3PO_4 (8 equiv., 0.22 g, 1.03 mmol) according to General procedure II. Purified

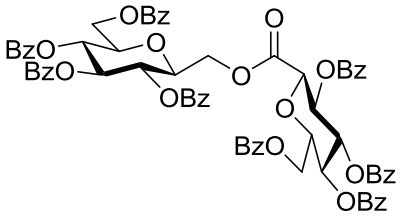
by column chromatography (1:4 EtOAc–hexane) to yield 34 mg (36%) of **7l** as a yellow amorphous product. $[\alpha]_D$ -5 (c 0.38 in $CHCl_3$); Rf: 0.36 (1:1 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10–7.68 (10H, m, aromatics), 7.62–7.11 (12H, m, aromatics), 6.57–6.48 (2H, m, aromatics), 5.95 (1H, pseudo t, $J_{4,5}$ 9.5 Hz, H-4), 5.68 (1H, pseudo t, $J_{5,6}$ 10.0 Hz, H-5), 5.67 (1H, pseudo t, $J_{2,3}$ 10.0, $J_{3,4}$ 9.5 Hz, H-3), 4.62 (1H, dd, $J_{6,7a}$ 2.7, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.59 (1H, dd, $J_{1a,1b}$ 12.2, $J_{1a,2}$ 2.7, Hz, H-1_a), 4.47 (1H, dd, $J_{6,7b}$ 5.5 Hz, H-7_b), 4.40 (1H, dd, $J_{1b,2}$ 5.5, H-1_b), 4.25 (2H, br s, NH_2), 4.19 (2H, ddd, H-2, H-6). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.3, 166.1, 165.4 (5×CO), 151.7–113.1 (aromatics), 76.6 (C-2), 76.4 (C-6), 74.5 (C-4), 69.8 (C-3, C-5), 63.5 (C-7), 63.0 (C-1). MS (ESI, m/z): 752.42 $[M+Na]^+$, $C_{42}H_{35}NO_{11}$ (729.22). Found: C, 69.10; H, 4.81; N, 1.92; O, 24.11. Calc. for $C_{42}H_{35}NO_{11}$: C, 69.13; H, 4.83; N, 1.92; O, 24.12.



2,6-Anhydro-1-*O*-(2,3,4,5,6-penta-*O*-acetyl-D-galactonoyl)-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptitol (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 2,3,4,5,6-penta-*O*-acetyl-D-galactonate) (7m)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), 2,3,4,5,6-penta-*O*-acetyl-D-galactonic acid (5 equiv., 0.26 g, 0.64 mmol) and K_3PO_4 (5 equiv., 0.14 g, 0.64 mmol) according to General procedure II. Purified by column chromatography (1:3 EtOAc–hexane) to yield 62 mg (48%) of **7m** as a white amorphous product. $[\alpha]_D$ +13 (c 1.06 in $CHCl_3$); Rf: 0.24 (1:1 EtOAc–hexane). ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 8.15–7.75 (8H, m, aromatics), 7.60–7.19 (12H, m, aromatics), 5.90 (1H, pseudo t, $J_{4,5}$ 9.8 Hz, H-4), 5.70 (1H, pseudo t, $J_{5,6}$ 10.1 Hz, H-5), 5.56 (1H, dd, $J_{3',4'}$ 9.9 Hz, H-3'), 5.54 (1H, pseudo t, $J_{3,4}$ 9.5 Hz, H-3), 5.44 (1H, dd, $J_{4',5'}$ 1.8 Hz, H-4'), 5.33 (1H, ddd, $J_{5',6a'}$ 5.3, $J_{5',6b'}$ 7.1 Hz, H-5'), 5.16 (1H, d, $J_{2',3'}$ 1.6 Hz, H-2'), 4.62

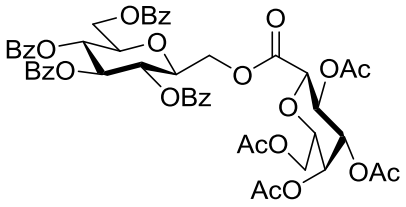
(1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_a), 4.48 (1H, dd, H-7_b), 4.43 (1H, dd, $J_{1a,1b}$ 12.1 Hz, H-1_a), 4.27 (1H, dd, $J_{6a',6b'}$ 11.6 Hz, H-6_a'), 4.22 (1H, dd, H-1_b), 4.15 (1H, ddd, $J_{6,7a}$ 3.2, $J_{6,7b}$ 4.7 Hz, H-6), 4.07 (1H, ddd, $J_{1a,2}$ 2.2, $J_{1b,2}$ 5.5, $J_{2,3}$ 9.6 Hz, H-2), 3.91 (1H, dd, H-6_b'), 2.18, 2.10, 2.08, 2.04, 1.96 (15H, 5s, 5×CH_3). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 170.5, 170.2, 169.6, 169.3, 167.0, 166.3, 166.0, 165.4 (9×CO), 133.9–127.9 (aromatics), 100.1 (C-1'), 76.3 (C-6), 76.2 (C-2), 74.5 (C-4), 69.7 (C-5), 69.4, 69.3 (C-2', C-3), 68.0 (C-3'), 67.8 (C-4'), 67.7 (C-5'), 64.5 (C-1), 63.5 (C-7), 62.1 (C-6'), 20.9, 20.8, 20.7, 20.5 (5×CH_3). MS (ESI, m/z): 1016.42 $[M+H_2O]^+$, $C_{51}H_{20}O_{21}$ (998.28). Found: C, 61.41; H, 5.10; O, 33.58. Calc. for $C_{51}H_{20}O_{21}$: C, 61.32; H, 5.05; O, 33.63.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-deoxy-D-*glycero*-D-*gulo*-heptitol-1-yl 2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonate (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formate) (7n)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formic acid (5 equiv., 0.40 g, 0.64 mmol) and K_3PO_4 (4 equiv., 0.11 g, 0.51 mmol) according to General procedure II. Purified by column chromatography (1:4 EtOAc–hexane) to yield 94 mg (60%) of **7n** as a white amorphous product. $[\alpha]_D$ –1 (c 0.08 in $CHCl_3$); Rf: 0.49 (1:1 EtOAc–hexane). ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 8.16–7.71 (16H, m, aromatics), 7.65–7.14 (24H, m, aromatics), 5.85 (1H, pseudo t, $J_{3',4'}$ 9.6 Hz, H-3'), 5.78 (1H, pseudo t, $J_{4,5}$ 9.6 Hz, H-4), 5.68 (1H, pseudo t, $J_{4',5'}$ 9.5 Hz, H-4'), 5.66 (1H, pseudo t, $J_{2',3'}$ 9.3 Hz, H-2'), 5.59 (1H, pseudo t, $J_{5,6}$ 9.3 Hz, H-5), 5.44 (1H, pseudo t, $J_{3,4}$ 9.6 Hz, H-3), 4.59 (1H, dd, $J_{6a',6b'}$ 12.3 Hz, H-6_a'), 4.47 (1H, dd, H-6_b'), 4.45 (1H, dd, H-1_a), 4.40 (1H, dd, H-7_a),

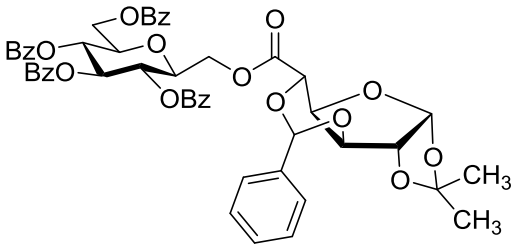
4.32 (1H, dd, $J_{7a,7b}$ 12.2 Hz, H-7_b), 4.19 (1H, dd, $J_{1a,1b}$ 12.1 Hz, H-1_b), 4.14 (1H, d, $J_{1',2'}$ 9.8 Hz, H-1'), 4.00 (1H, ddd, $J_{5',6a'}$ 3.0, $J_{5',6b'}$ 5.1 Hz, H-5'), 3.96 (1H, ddd, $J_{6,7a}$ 3.4, $J_{6,7b}$ 5.1 Hz, H-6), 3.85 (1H, ddd, $J_{1a,2}$ 3.0, $J_{1b,2}$ 6.8, $J_{2,3}$ 9.8 Hz, H-2). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 166.5, 166.3, 166.2, 166.0, 165.9, 165.4, 165.3, 165.2 (9×CO), 134.0–126.4 (aromatics), 76.7 (C-1'), 76.5 (C-5'), 76.2 (C-2, C-6), 74.2 (C-4), 73.8 (C-3'), 70.2 (C-2'), 70.0 (C-3), 69.7 (C-5), 69.4 (C-4'), 64.9 (C-1), 63.3 (C-6', C-7). MS (ESI, m/z): 1217.58 $[M+H]^+$, $C_{70}H_{56}O_{20}$ (1216.31). Found: C, 69.18; H, 4.55; O, 26.37. Calc. for $C_{70}H_{56}O_{20}$: C, 69.07; H, 4.64; O, 26.29.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-deoxy-D-*glycero*-D-*gulo*-heptitol-1-yl 2,6-anhydro-3,4,5,7-tetra-*O*-acetyl-D-*glycero*-L-*manno*-heptonate (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)formate) (7o)

From tosylhydrazone **1** (0.10 g, 0.13 mmol), *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)formic acid (5 equiv., 0.24 g, 0.64 mmol) and K_3PO_4 (3 equiv., 0.08 g, 0.39 mmol) according to General procedure II. Purified by column chromatography (1:3 acetone–hexane) to yield 72 mg (58%) of **7o** as a white amorphous product. $[\alpha]_D$ +11 (c 0.55 in $CHCl_3$); Rf: 0.31 (1:1 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14–7.71 (8H, m, aromatics), 7.64–7.13 (12H, m, aromatics), 5.93 (1H, pseudo t, $J_{4,5}$ 9.7 Hz, H-4), 5.70 (1H, pseudo t, $J_{5,6}$ 9.9 Hz, H-5), 5.50 (1H, pseudo t, $J_{3,4}$ 9.5 Hz, H-3), 5.42 (1H, dd, $J_{4',5'}$ 0.8 Hz, H-4'), 5.38 (1H, pseudo t, $J_{2',3'}$ 10.2 Hz, H-2'), 5.03 (1H, dd, $J_{3',4'}$ 3.4 Hz, H-3'), 4.63 (1H, dd, $J_{7a,7b}$ 12.3 Hz, H-7_a), 4.49 (1H, dd, H-7_b), 4.49 (1H, dd, H-1_a), 4.19 (1H, dd, $J_{1a,1b}$ 12.2 Hz, H-1_b), 4.17 (1H, ddd, $J_{6,7a}$ 3.0, $J_{6,7b}$ 5.0 Hz, H-6), 4.14 (1H, dd, $J_{6a',6b'}$ 11.5 Hz, H-6_a'), 4.10 (1H,

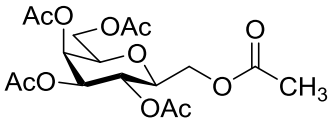
dd, H-6_b'), 4.07 (1H, ddd, $J_{1a,2}$ 2.5, $J_{1b,2}$ 7.1, $J_{2,3}$ 9.7 Hz, H-2), 3.89 (1H, dd, $J_{1',2'}$ 12.3 Hz, H-1'), 3.84 (1H, ddd, $J_{5',6a'}$ 6.5, $J_{5',6b'}$ 6.6 Hz, H-5'), 2.13, 2.04, 2.03, 2.00 (12H, 4s, 4×CH_3). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 170.4, 170.1, 169.7, 166.7, 166.2, 166.0, 165.4, 165.3 (9×CO), 134.0–127.8 (aromatics), 76.6 (C-1'), 76.3 (C-2, C-5), 74.6 (C-5'), 74.3 (C-4), 71.6 (C-3'), 69.7 (C-3, C-5), 67.1 (C-4'), 66.5 (C-2'), 64.5 (C-1), 63.3 (C-7). 61.5 (C-6'), 20.7 (4×CH_3). MS (ESI, m/z): 991.58 $[M+Na]^+$, $C_{50}H_{48}O_{20}$ (968.27). Found: C, 61.90; H, 4.98; O, 32.98. Calc. for $C_{50}H_{48}O_{20}$: C, 61.98; H, 4.99; O, 33.02.



2,6-Anhydro-3,4,5,7-tetra-*O*-benzoyl-1-deoxy-D-*glycero*-D-*gulo*-heptitol-1-yl 1,2-*O*-isopropylidene-3,5-*O*-benzylidene-α-D-glucofuranuronate (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylmethyl 1,2-*O*-isopropylidene-3,5-*O*-benzylidene-α-D-glucofuranuronate) (7p)

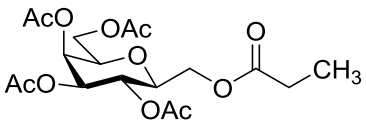
From tosylhydrazone **1** (0.10 g, 0.13 mmol), *C*-(1,2-*O*-isopropylidene-3,4-*O*-benzylidene-α-D-glucofuranosyl)uronic acid (5 equiv., 0.21 g, 0.64 mmol) and K_3PO_4 (5 equiv., 0.14 g, 0.64 mmol) according to General procedure II. Purified by column chromatography (1:3 acetone–hexane) to yield 78 mg (66%) of **7p** as a white amorphous product. $[\alpha]_D$ +11 (c 0.53 in $CHCl_3$); Rf: 0.26 (1:2 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14–7.66 (8H, m, aromatics), 7.62–7.16 (17H, m, aromatics), 6.09 (1H, d, $J_{1',2'}$ 3.7 Hz, H-1'), 6.02 (1H, s, CH), 5.95 (1H, pseudo t, $J_{4,5}$ 9.7 Hz, H-4), 5.64 (1H, pseudo t, $J_{5,6}$ 9.8 Hz, H-5), 5.57 (1H, pseudo t, $J_{3,4}$ 9.7 Hz, H-3), 5.00 (1H, s, H-5'), 4.67 (1H, d, H-2'), 4.58 (1H, s, H-3'), 4.57 (1H, dd, H-7_a), 4.55 (1H, s, H-4'), 4.49 (1H, dd, $J_{1a,1b}$ 12.4 Hz, H-1_a), 4.45 (1H, dd, $J_{7a,7b}$ 11.8

Hz, H-7_b), 4.42 (1H, dd, 1H, H-1_b), 4.14 (1H, ddd, $J_{6,7a}$ 3.1, $J_{6,7b}$ 5.0 Hz, H-6), 4.18 (1H, ddd, $J_{1a,2}$ 2.5, $J_{1b,2}$ 4.5, $J_{2,3}$ 10.0 Hz, H-2), 1.58, 1.36 (6H, 2s, 2×CH_3). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 169.1, 166.2, 166.0, 165.4, 165.2 (5×CO), 137.8–125.7 (aromatics), 112.4 (quat. C, isopropylidene), 105.3 (C-1'), 96.2 (CH, benzylidene), 84.0 (C-2'), 77.9 (C-3'), 76.5 (C-6), 76.1 (C-2), 74.2 (C-4), 74.0 (C-5'), 72.6 (C-4'), 69.7 (C-5), 69.3 (C-3), 63.4 (C-7), 63.3 (C-1), 26.9, 26.4 (2×CH_3). MS (ESI, m/z): 937.58 $[M+Na]^+$, $C_{51}H_{46}O_{16}$ (914.28). Found: C, 66.89; H, 5.08; O, 27.94. Calc. for $C_{51}H_{46}O_{16}$: C, 66.95; H, 5.07; O, 27.98.



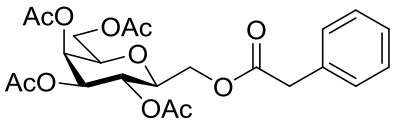
1,3,4,5,7-Penta-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptitol (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosylmethyl acetate) (9a)

From tosylhydrazone **8** (0.10 g, 0.19 mmol), acetic acid (20 equiv., 0.22 mL, 3.78 mmol) and K_3PO_4 (10 equiv., 0.40 g, 1.89 mmol) according to General procedure II. Purified by column chromatography (1:2 EtOAc–hexane) to yield 39 mg (51%) of **9a** as a white amorphous product. $[\alpha]_D$ +8 (c 0.48 in $CHCl_3$); Rf: 0.24 (1:1 EtOAc–hexane). ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 5.44 (1H, dd, $J_{5,6}$ 0.8 Hz, H-5), 5.25 (1H, pseudo t, $J_{3,4}$ 10.1 Hz, H-3), 5.06 (1H, dd, $J_{4,5}$ 3.4 Hz, H-4), 4.26 (1H, dd, $J_{1a,1b}$ 12.3 Hz, H-1_a), 4.15 (1H, dd, $J_{7a,7b}$ 11.4 Hz, H-7_a), 4.13 (1H, dd, H-1_b), 4.10 (1H, dd, H-7_b), 3.91 (1H, ddd, $J_{6,7a}$ 6.6, $J_{6,7b}$ 6.6 Hz, H-6), 3.67 (1H, ddd, $J_{1a,2}$ 2.4, $J_{1b,2}$ 5.6, $J_{2,3}$ 9.9 Hz, H-2), 2.17, 2.10, 2.05, 1.99 (15H, 4s, 5×CH_3). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 170.8, 170.5, 170.3, 169.7 (5×CO), 76.5 (C-2), 74.4 (C-6), 72.1 (C-4), 67.6 (C-5), 66.1 (C-3), 62.8 (C-1), 61.6 (C-7), 20.9, 20.8, 20.7 (5×CH_3). MS (ESI, m/z): 427.50 $[M+Na]^+$, $C_{17}H_{24}O_{11}$ (404.13). Found: C, 50.42; H, 5.97; O, 43.56. Calc. for $C_{17}H_{24}O_{11}$: C, 50.50; H, 5.98; O, 43.52.



3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-1-*O*-propanoyl-D-*glycero*-L-*manno*-heptitol (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosylmethyl propanoate) (9b)

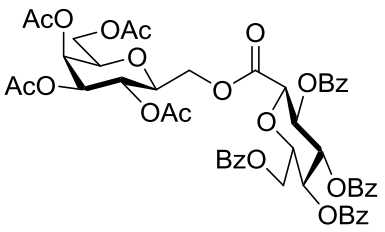
From tosylhydrazone **8** (0.10 g, 0.19 mmol), propanoic acid (5 equiv., 0.07 mL, 0.95 mmol) and K_3PO_4 (4 equiv., 0.16 g, 0.76 mmol) according to General procedure II. Purified by column chromatography (1:2 EtOAc–hexane) to yield 27 mg (30%) of **9b** as a white amorphous product. $[\alpha]_D$ +7 (c 0.72 in $CHCl_3$); Rf: 0.27 (1:1 EtOAc–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.43 (1H, dd, $J_{5,6}$ 0.7 Hz, H-5), 5.26 (1H, pseudo t, $J_{3,4}$ 10.1 Hz, H-3), 5.05 (1H, dd, $J_{4,5}$ 3.4 Hz, H-4), 4.25 (1H, dd, $J_{1a,1b}$ 12.3 Hz, H-1_a), 4.16 (1H, dd, H-1_b), 4.11 (1H, dd, $J_{7a,7b}$ 11.4 Hz, H-7_a), 4.10 (1H, dd, H-7_b), 3.91 (1H, ddd, $J_{6,7a}$ 6.6, $J_{6,7b}$ 6.6 Hz, H-6), 3.67 (1H, ddd, $J_{1a,2}$ 2.4, $J_{1b,2}$ 5.4, $J_{2,3}$ 9.8 Hz, H-2), 2.47–2.31 (2H, m, CH_2), 2.16, 2.05, 1.99 (12, 4s, 4×CH_3), 1.16 (3H, t, J 7.6 Hz, CH_3). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 174.1, 170.5, 170.3, 170.2, 169.7 (5×CO), 76.6 (C-2), 74.5 (C-6), 72.2 (C-4), 67.7 (C-5), 66.2 (C-3), 62.6 (C-1), 61.7 (C-7), 27.6 (CH_2), 20.8, 20.7 (4×CH_3), 9.1 (CH_3). MS (ESI, m/z): 419.00 $[M+H]^+$, $C_{18}H_{26}O_{11}$ (418.15). Found: C, 51.61; H, 6.29; O, 42.01. Calc. for $C_{18}H_{26}O_{11}$: C, 51.67; H, 6.26; O, 42.06.



3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-1-*O*-(2-phenylacetyl)-D-*glycero*-L-*manno*-heptitol (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosylmethyl 2-phenylacetate) (9c)

From tosylhydrazone **8** (0.10 g, 0.19 mmol), 2-phenylacetic acid (2 equiv., 0.05 g, 0.38 mmol) and K_3PO_4 (2 equiv., 0.08 g, 0.38 mmol) according to General procedure II. Purified by column chromatography (1:2 EtOAc–hexane) to yield 22 mg (25%) of **9c** as a white

amorphous product. $[\alpha]_D$ +3 (c 0.18 in $CHCl_3$); Rf: 0.30 (1:1 EtOAc–hexane). ^1H NMR (360 MHz, $CDCl_3$) δ (ppm) 7.38–7.20 (5H, m, aromatics), 5.43 (1H, dd, $J_{5,6}$ 0.8 Hz, H-5), 5.25 (1H, pseudo t, $J_{3,4}$ 10.1 Hz, H-3), 5.05 (1H, dd, $J_{4,5}$ 3.4 Hz, H-4), 4.25 (1H, dd, $J_{1a,1b}$ 12.3 Hz, H-1_a), 4.19 (1H, dd, H-1_b), 4.13 (1H, dd, $J_{7a,7b}$ 11.3 Hz, H-7_a), 4.09 (1H, dd, H-7_b), 3.89 (1H, ddd, $J_{6,7a}$ 6.6, $J_{6,7b}$ 6.6 Hz, H-6), 3.68 (2H, s, CH_2), 3.66 (1H, ddd, $J_{1a,2}$ 2.5, $J_{1b,2}$ 5.7, $J_{2,3}$ 10.0 Hz, H-2), 2.16, 2.05, 2.03, 1.99 (12H, 4s, 4×CH_3). ^{13}C NMR (90 MHz, $CDCl_3$) δ 171.4, 170.5, 170.3, 169.8 (5×CO), 134.1–126.9 (aromatics) 76.6 (C-2), 74.5 (C-6), 72.2 (C-4), 67.7 (C-5), 66.3 (C-3), 63.3 (C-1), 61.6 (C-7), 41.2 (CH_2), 20.8, 20.7 (4×CH_3). MS (ESI, m/z): 481.33 $[M+H]^+$, $C_{23}H_{28}O_{11}$ (480.16). Found: C, 57.56; H, 5.88; O, 36.68. Calc. for $C_{23}H_{28}O_{11}$: C, 57.50; H, 5.87; O, 36.63.

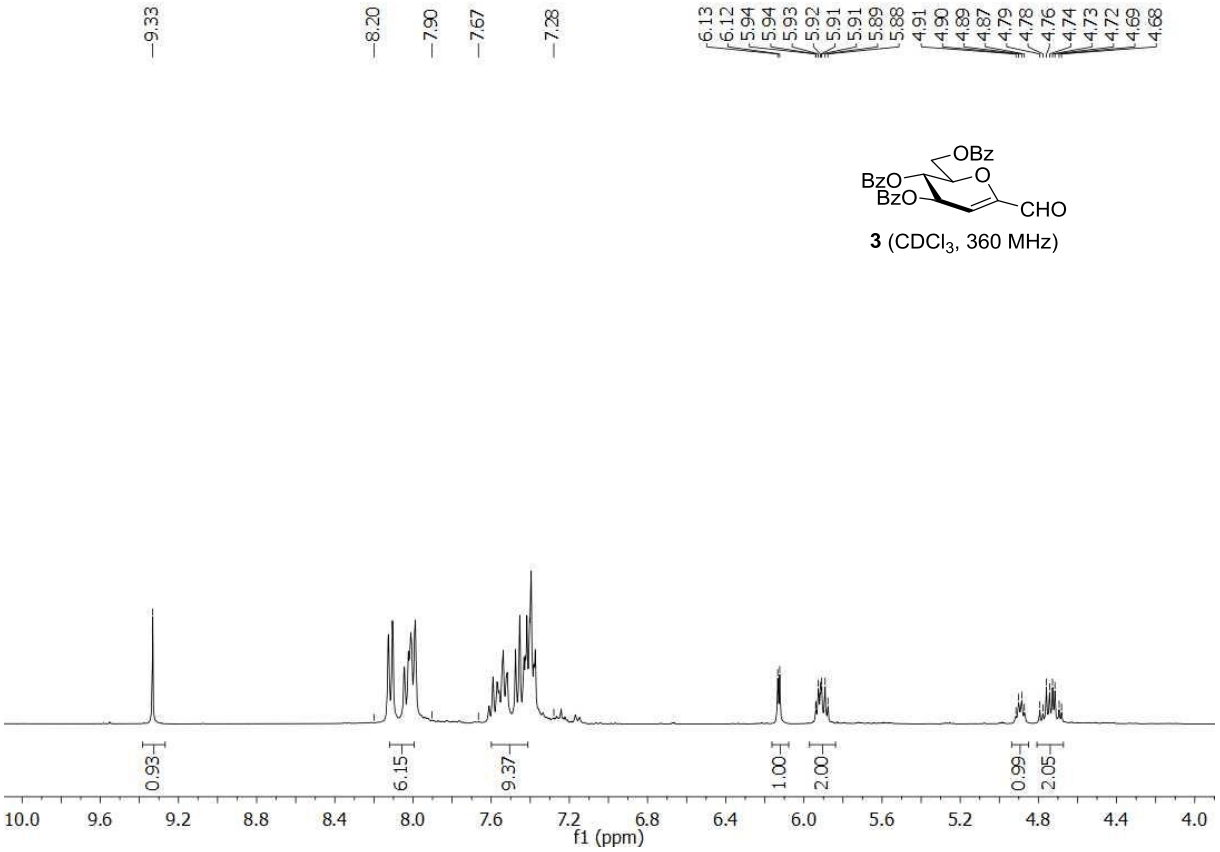


3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-1-deoxy-D-*glycero*-L-*manno*-heptitol-1-yl 2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonate (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosylmethyl *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formate) (9d)

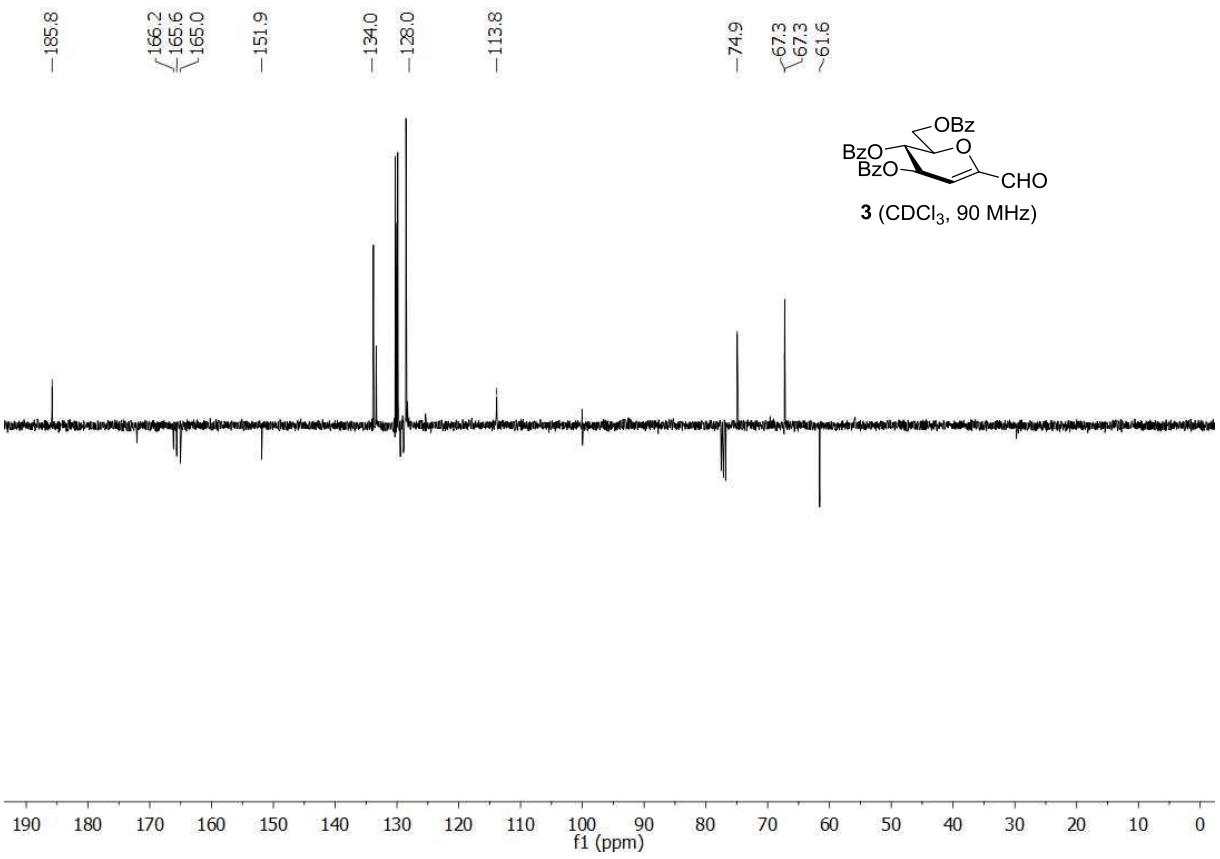
From tosylhydrazone **8** (0.10 g, 0.19 mmol), *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formic acid (5 equiv., 0.59 g, 0.95 mmol) and K_3PO_4 (3 equiv., 0.12 g, 0.57 mmol) according to General procedure II. Purified by column chromatography (1:2 EtOAc–hexane) to yield 138 mg (75%) of **9d** as a white amorphous product. $[\alpha]_D$ –12 (c 0.83 in $CHCl_3$); Rf: 0.21 (1:1 EtOAc–hexane). ^1H NMR (360 MHz, $CDCl_3$) δ (ppm) 8.16–7.76 (8H, m, aromatics), 7.64–7.19 (12H, m, aromatics), 5.97 (1H, pseudo t, $J_{3',4'}$ 9.8 Hz, H-3'), 5.74 (1H, pseudo t, $J_{4',5'}$ 9.6 Hz, H-4'), 5.71 (1H, pseudo t, $J_{2',3'}$ 9.5 Hz, H-2'), 5.38 (1H, dd, $J_{5,6}$ 0.7 Hz, H-5), 5.08 (1H, pseudo t, $J_{3,4}$ 10.0 Hz, H-3), 4.95 (1H, dd, $J_{4,5}$ 3.4 Hz, H-4), 4.66 (1H,

dd, $J_{6a',6b'}$ 12.3 Hz, H-6_a'), 4.54 (1H, dd, H-6_b'), 4.41 (1H, d, $J_{1',2'}$ 9.8 Hz, H-1'), 4.31 (1H, dd, $J_{1a,2}$ 12.1 Hz, H-1_a), 4.21 (1H, ddd, $J_{5',6a'}$ 3.2, $J_{5',6b'}$ 5.0 Hz, H-5'), 4.08 (1H, dd, H-1_b), 4.00 (1H, dd, $J_{7a,7b}$ 11.2 Hz, H-7_a), 3.92 (1H, dd, H-7_b), 3.78 (1H, ddd, $J_{6,7a}$ 6.1, $J_{6,7b}$ 7.4 Hz, H-6), 3.60 (1H, ddd, $J_{1a,2}$ 2.3, $J_{1b,2}$ 7.4, $J_{2,3}$ 9.7 Hz, H-2), 2.12, 2.02, 1.97, 1.96 (12H, 4s, 4×CH_3). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 170.3, 170.1, 169.8, 166.6, 166.2, 165.9, 165.2 (9×CO), 133.8–127.9 (aromatics), 77.0 (C-1'), 76.5 (C-5'), 76.3 (C-2), 74.0 (C-6), 73.7 (C-3'), 71.9 (C-4), 70.4 (C-2'), 69.3 (C-4'), 67.4 (C-5), 66.4 (C-3), 64.9 (C-1), 63.3 (C-6'), 61.1 (C-7), 20.7, 20.6 (5×CH_3). MS (ESI, m/z): 969.00 $[M+H]^+$, $C_{50}H_{48}O_{20}$ (968.27). Found: C, 61.92; H, 5.02; O, 33.06. Calc. for $C_{50}H_{48}O_{20}$: C, 61.98; H, 4.99; O, 33.02.

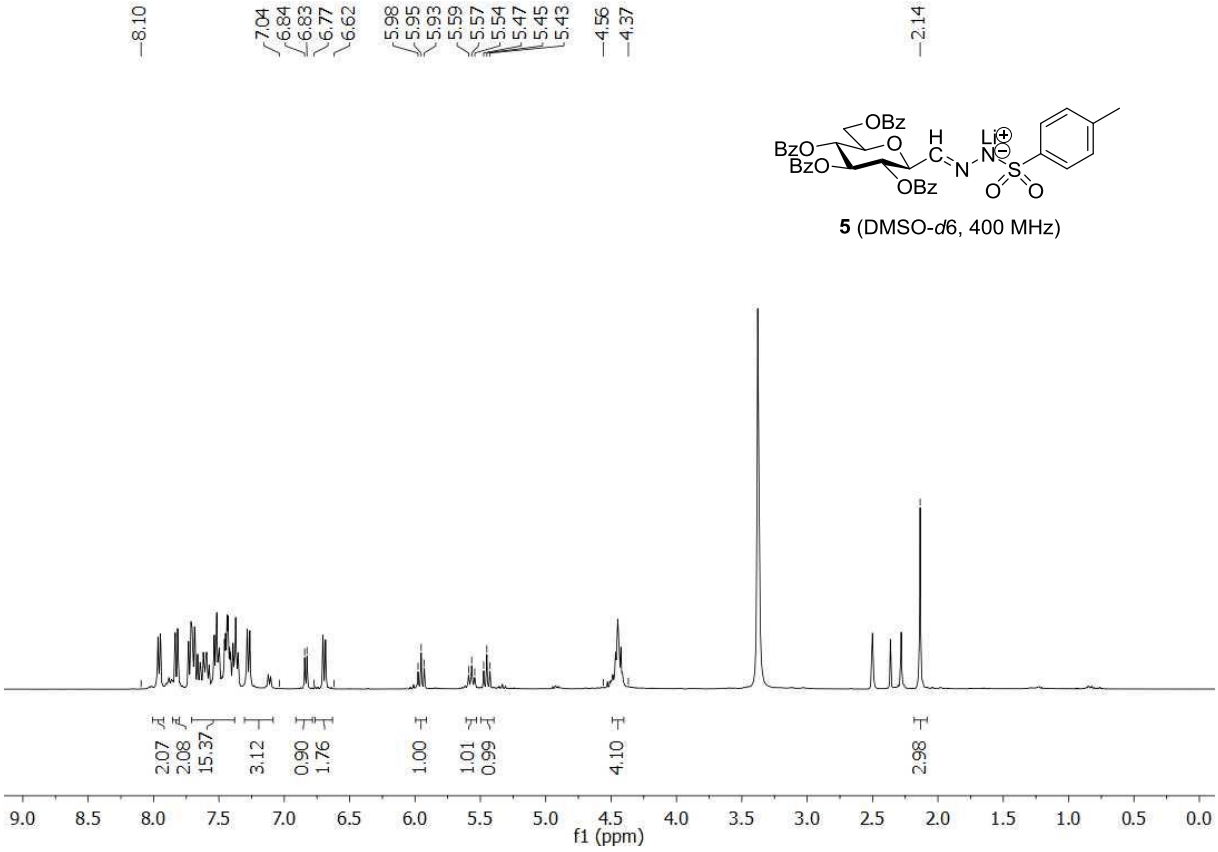
Copies of the NMR spectra



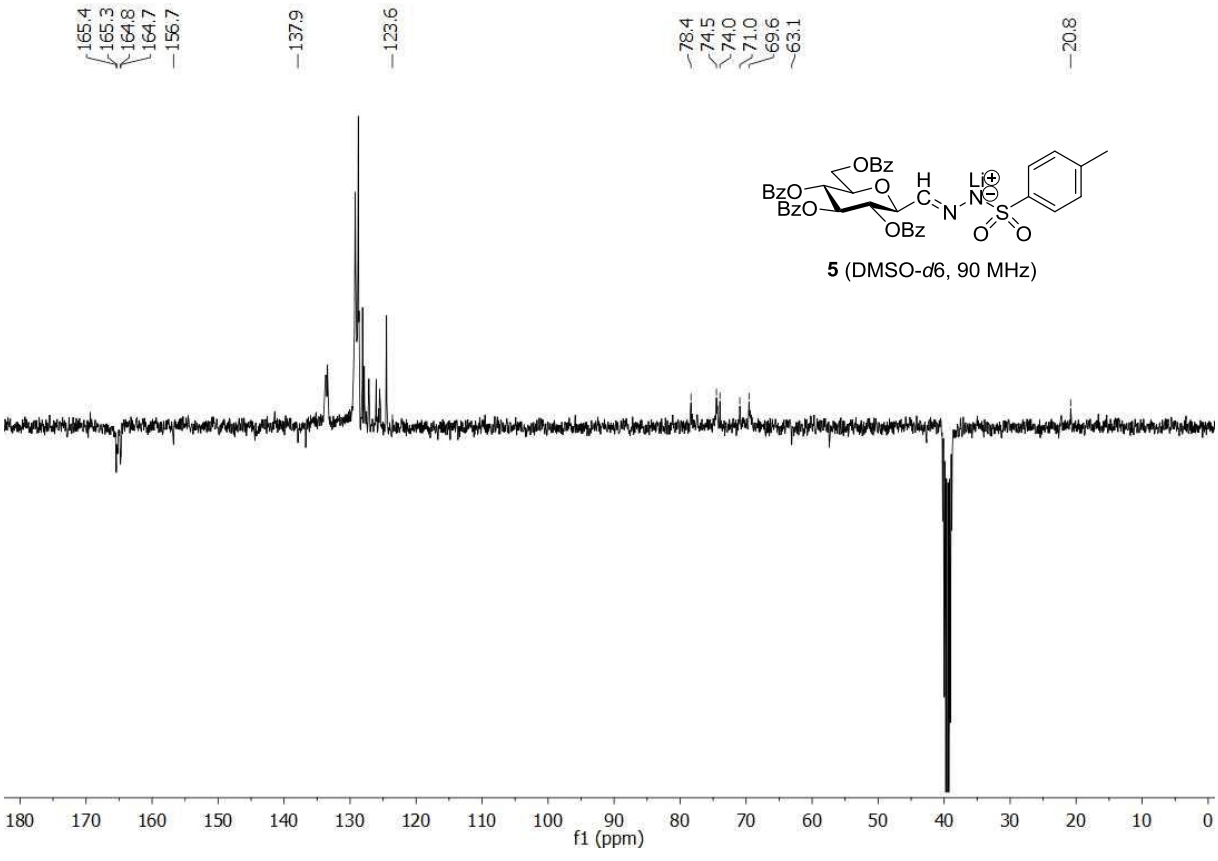
3 ($CDCl_3$, 360 MHz)



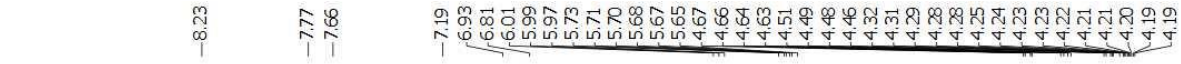
3 ($CDCl_3$, 90 MHz)

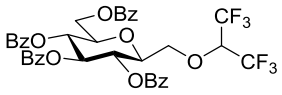


5 (DMSO-*d*6, 400 MHz)

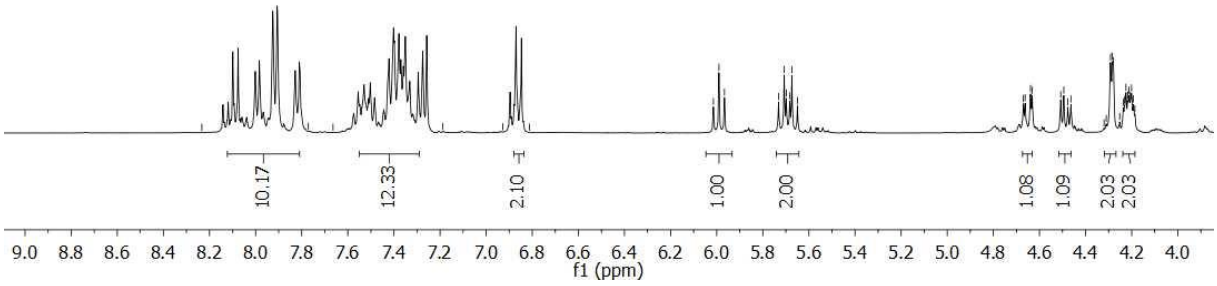


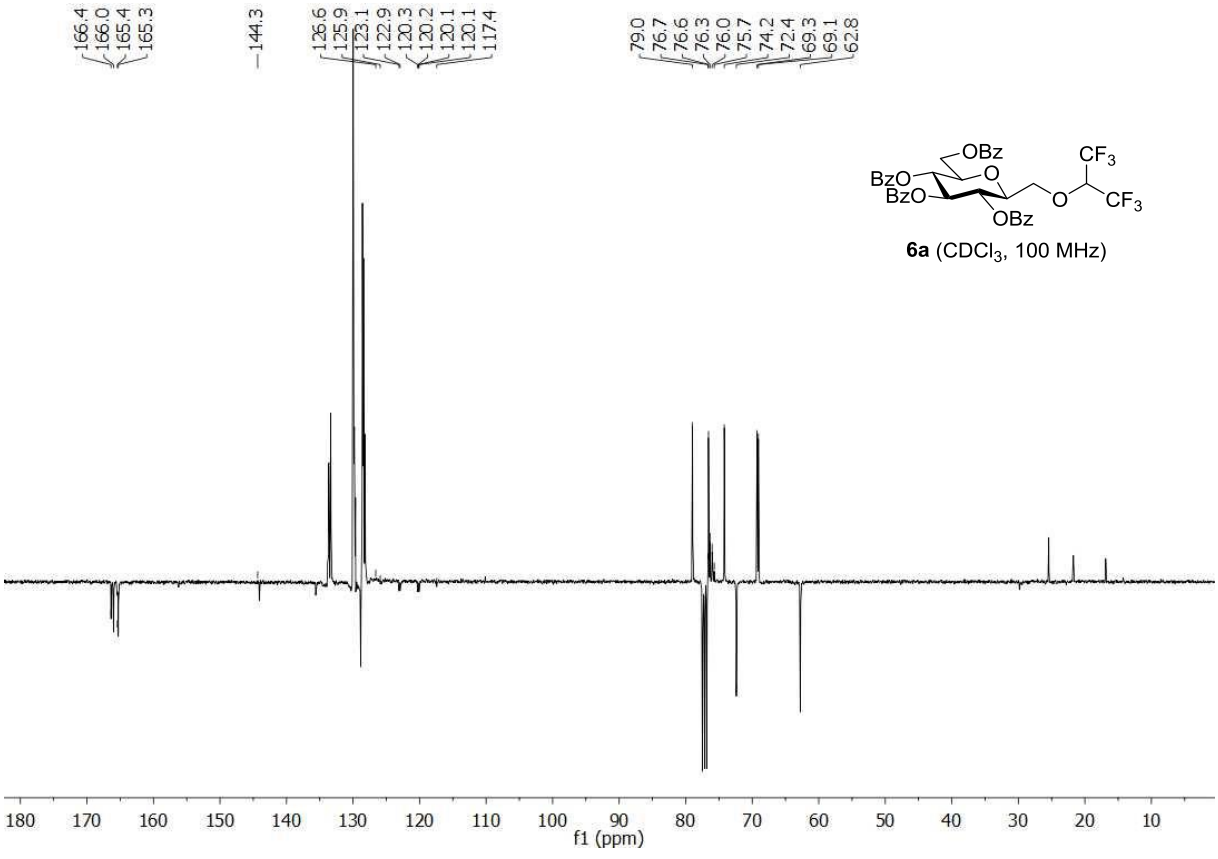
5 (DMSO-*d*6, 90 MHz)



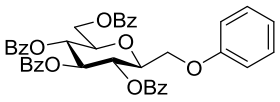


6a ($CDCl_3$, 400 MHz)

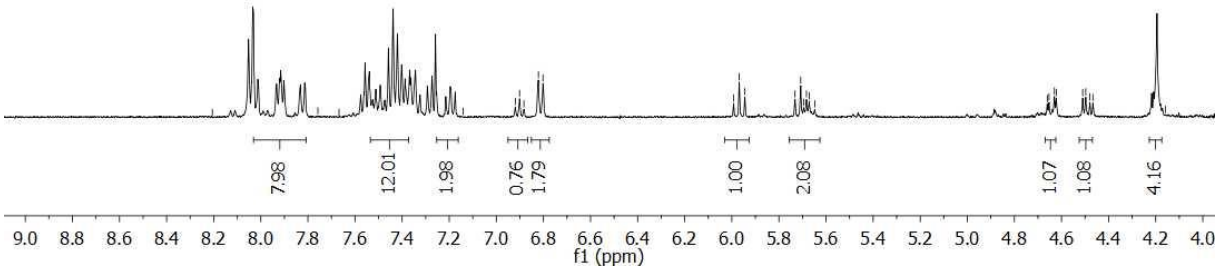


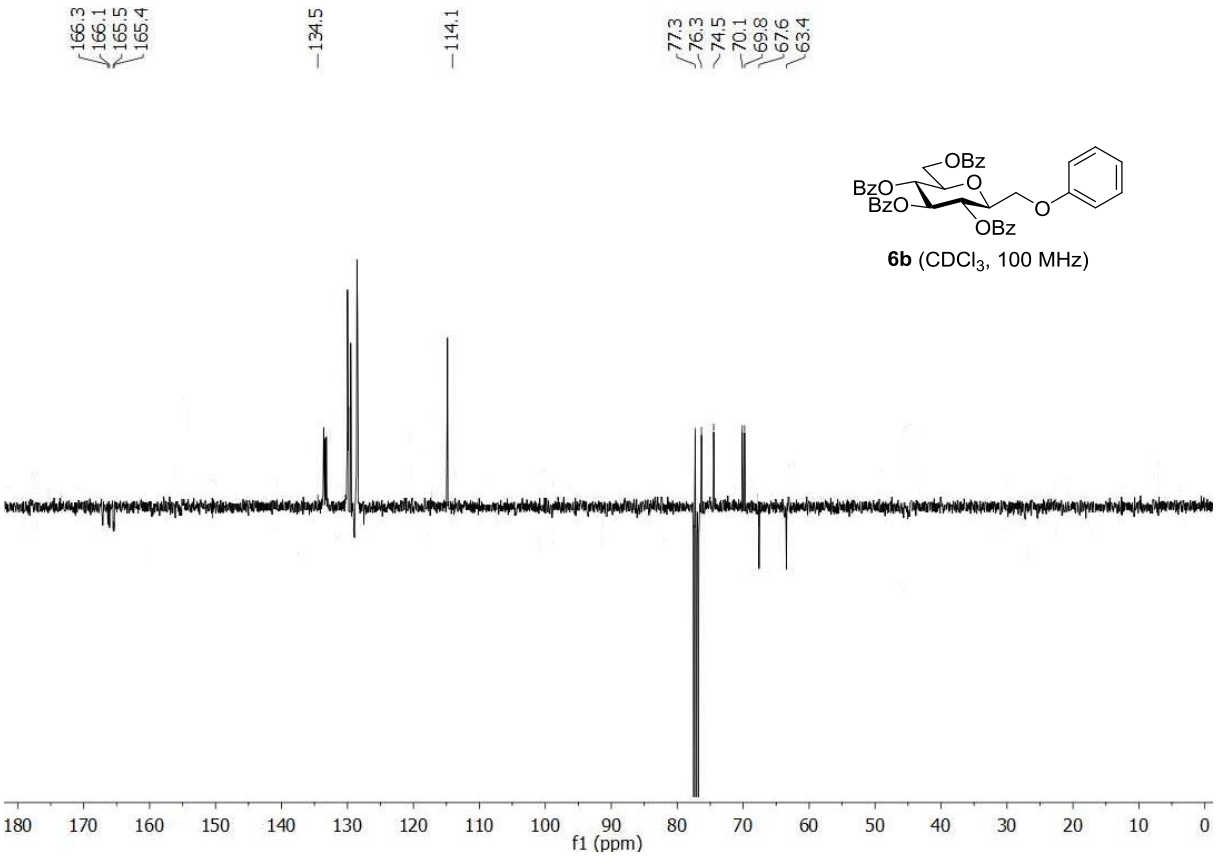


6a ($CDCl_3$, 100 MHz)

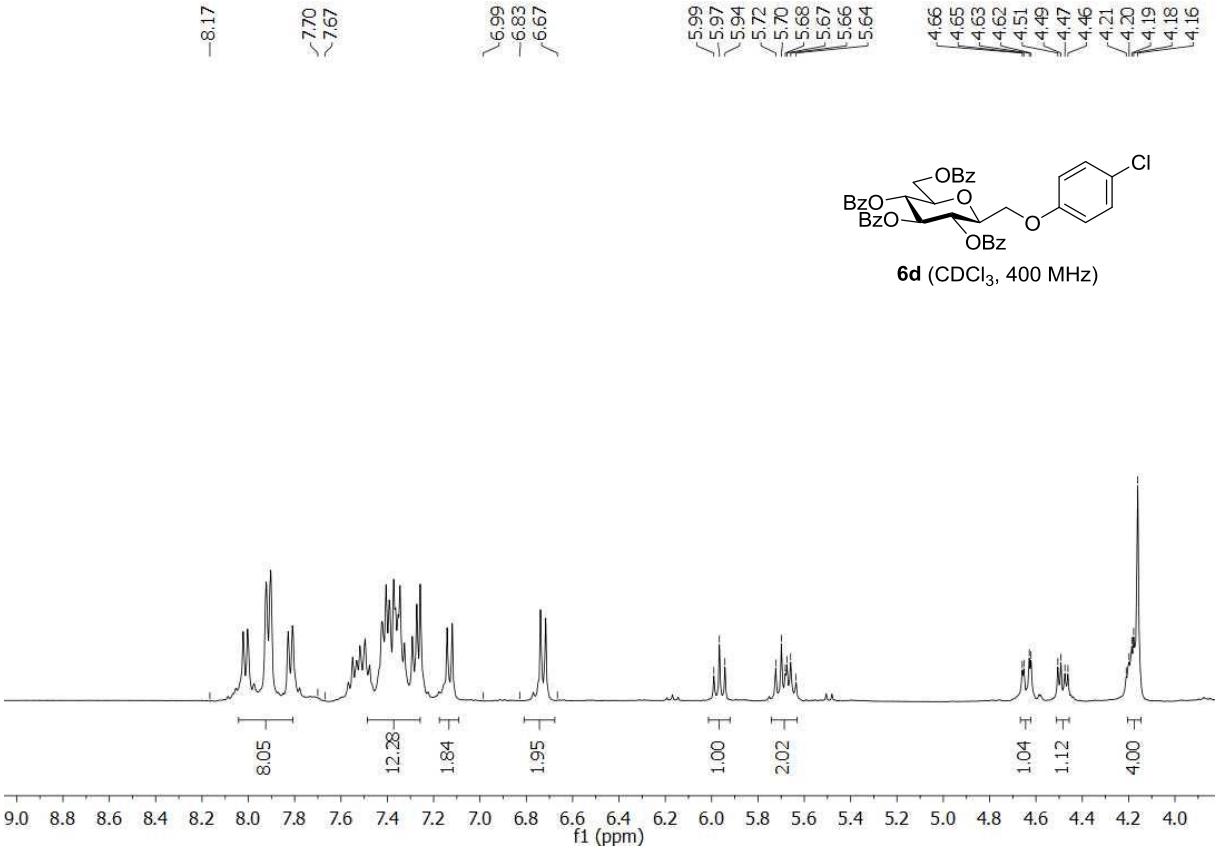


6b ($CDCl_3$, 400 MHz)

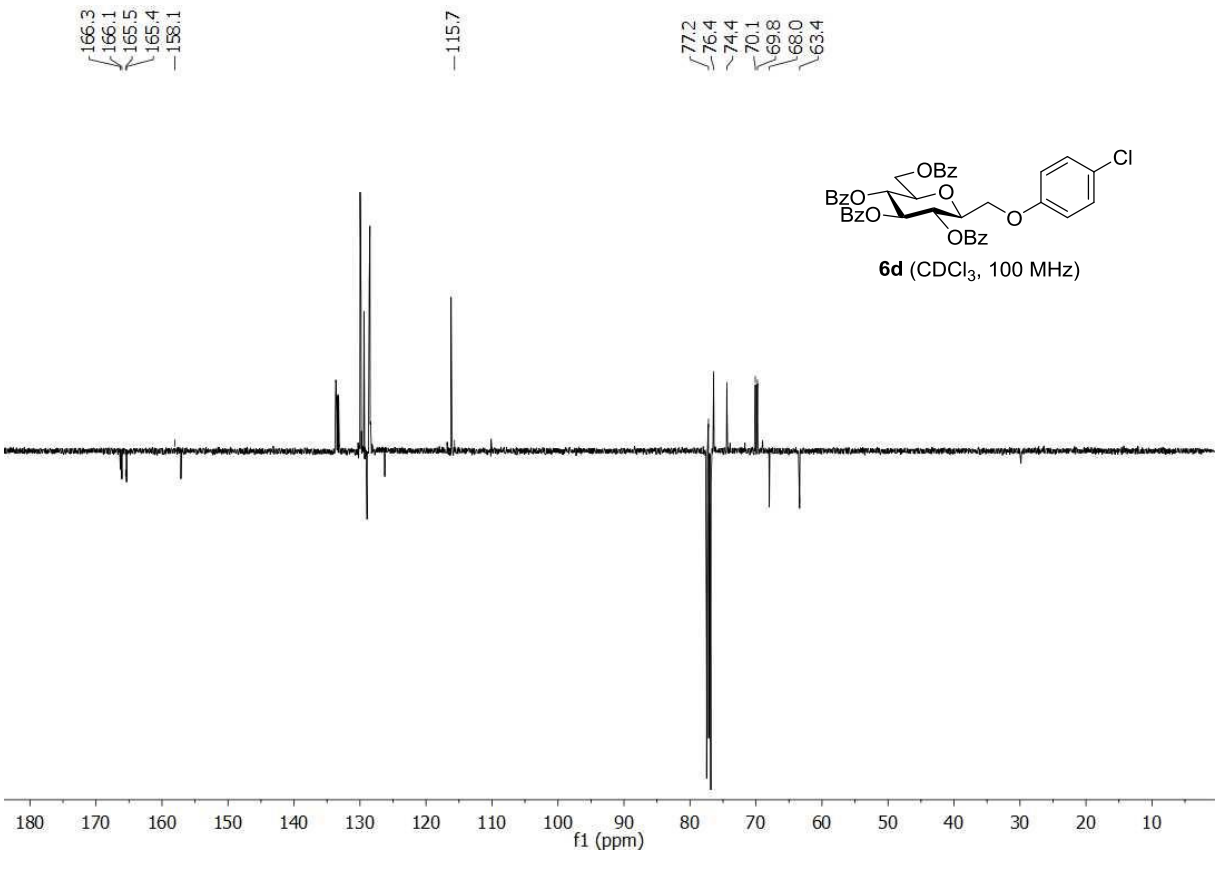




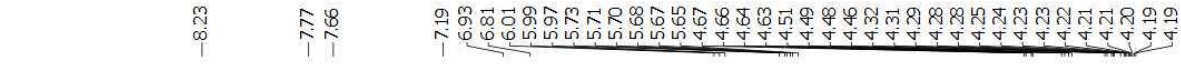
6b ($CDCl_3$, 100 MHz)

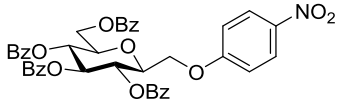


6d ($CDCl_3$, 400 MHz)

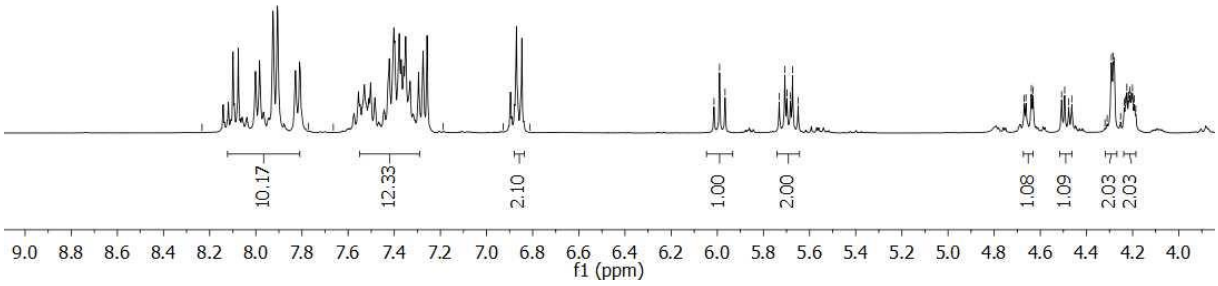


6d ($CDCl_3$, 100 MHz)

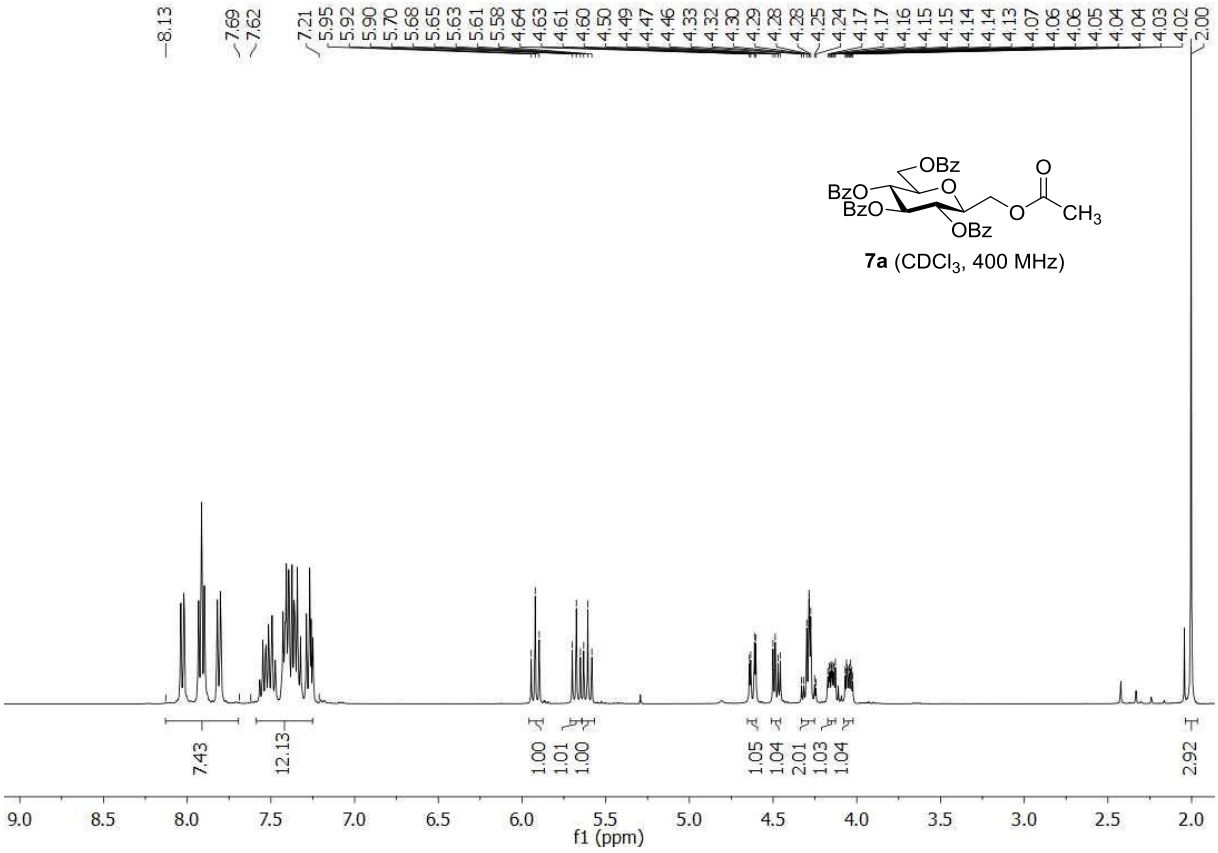




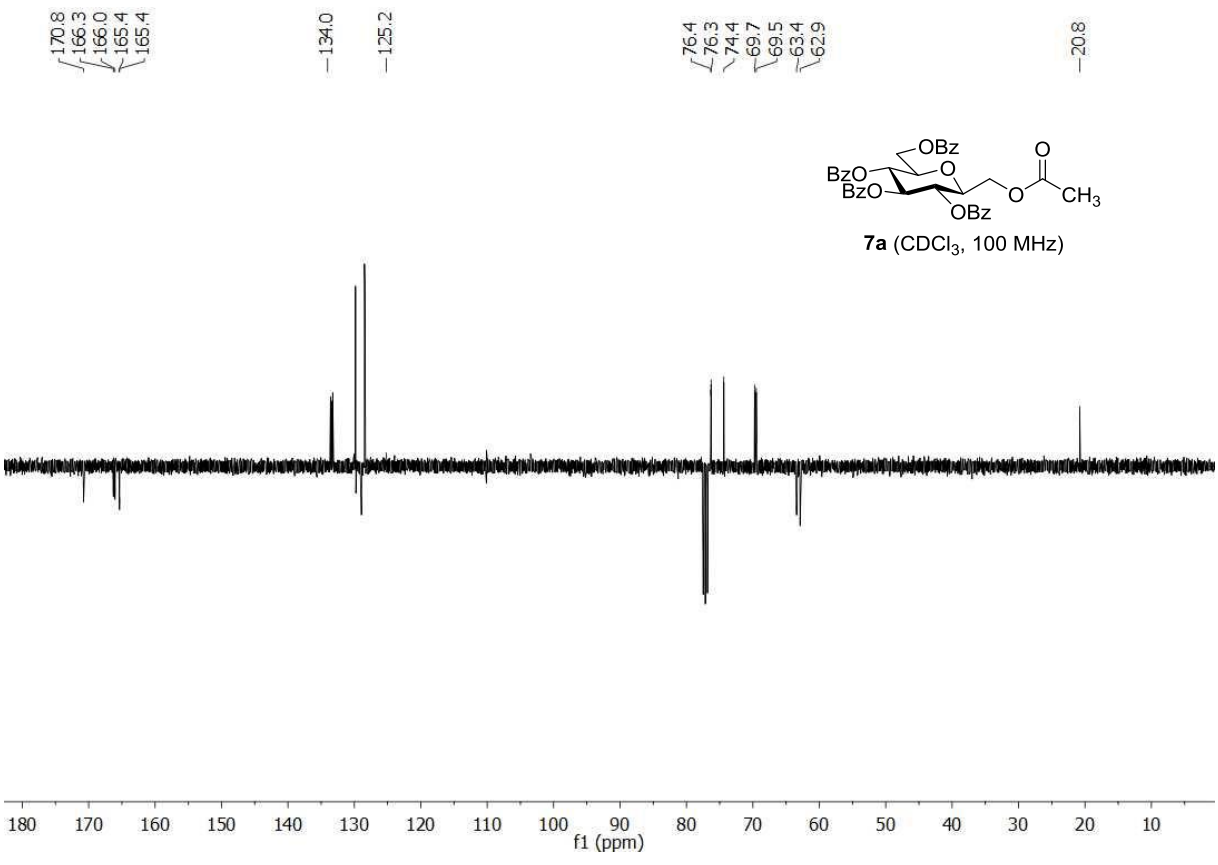
6e ($CDCl_3$, 400 MHz)



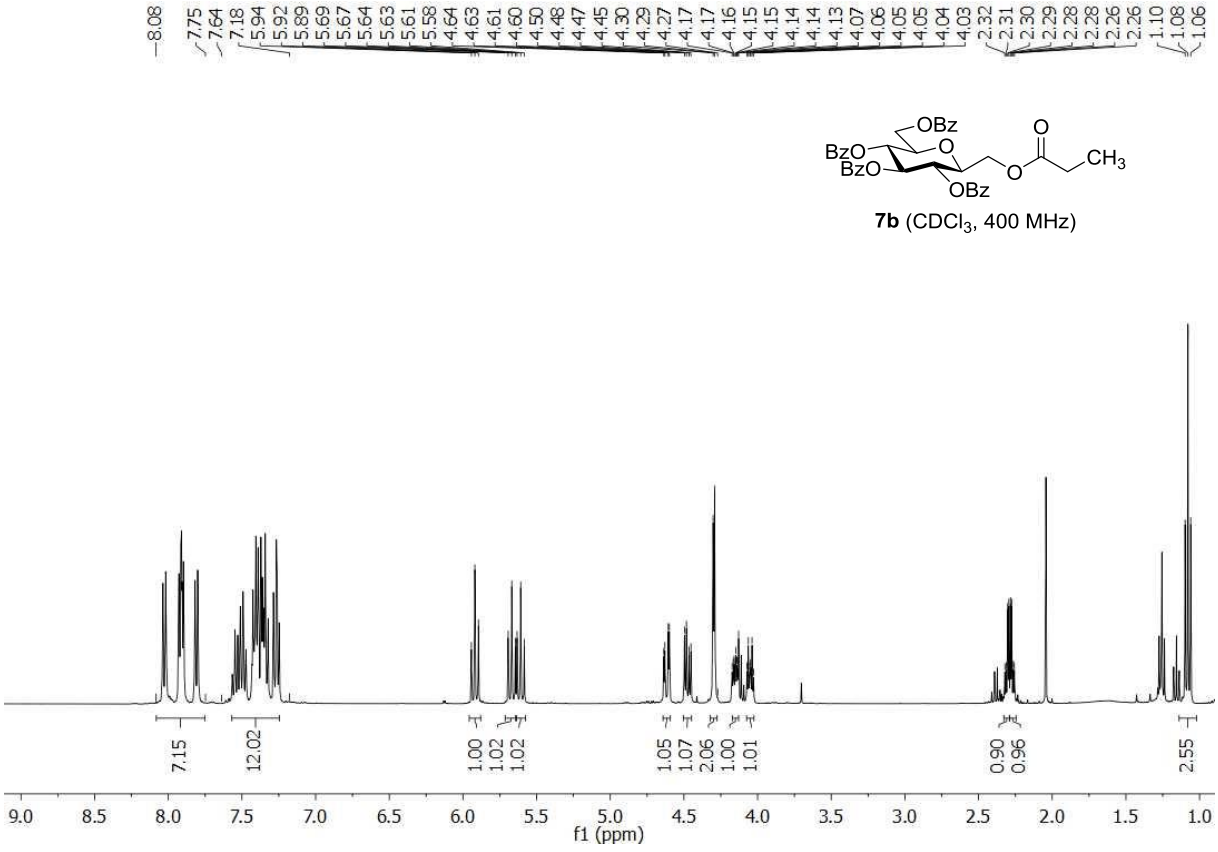
6e ($CDCl_3$, 90 MHz)



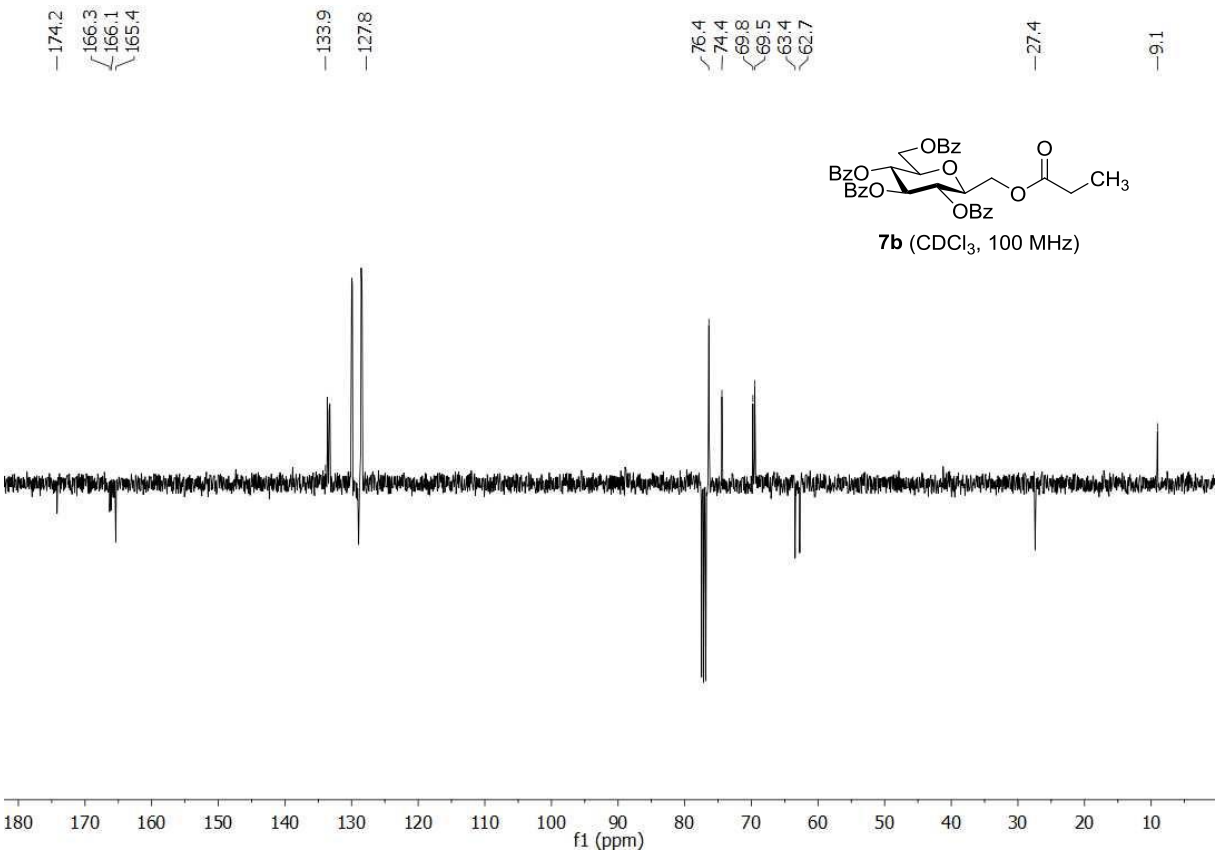
7a ($CDCl_3$, 400 MHz)



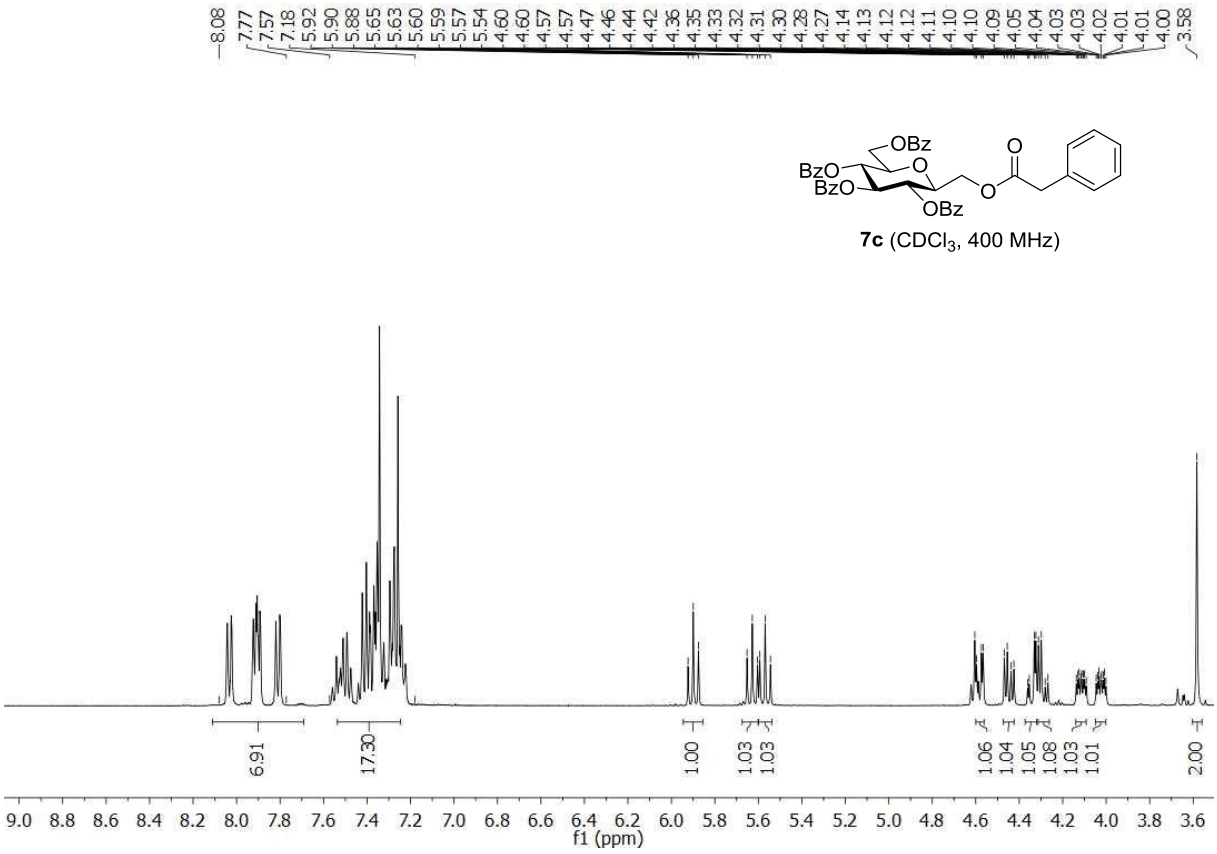
7a ($CDCl_3$, 100 MHz)



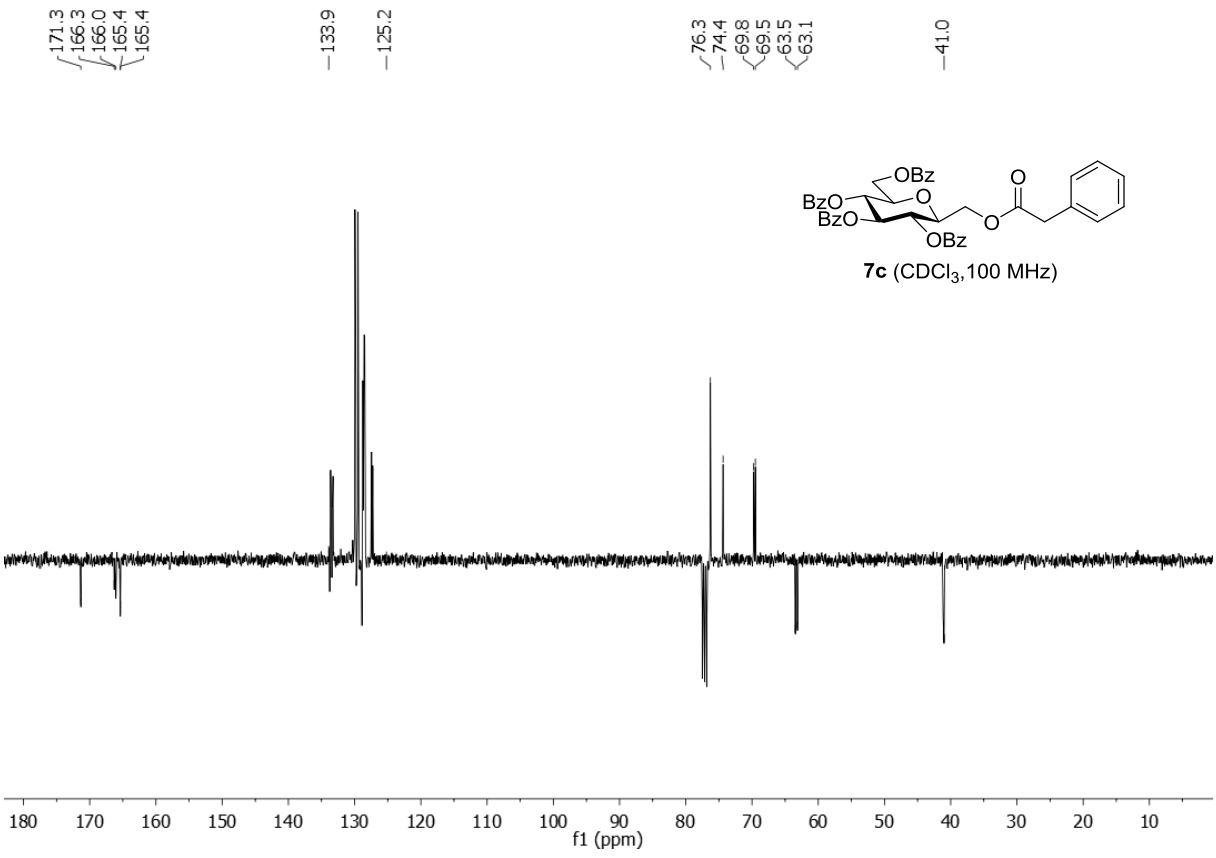
7b ($CDCl_3$, 400 MHz)



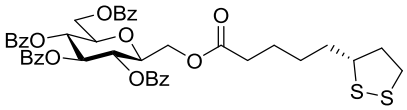
7b ($CDCl_3$, 100 MHz)



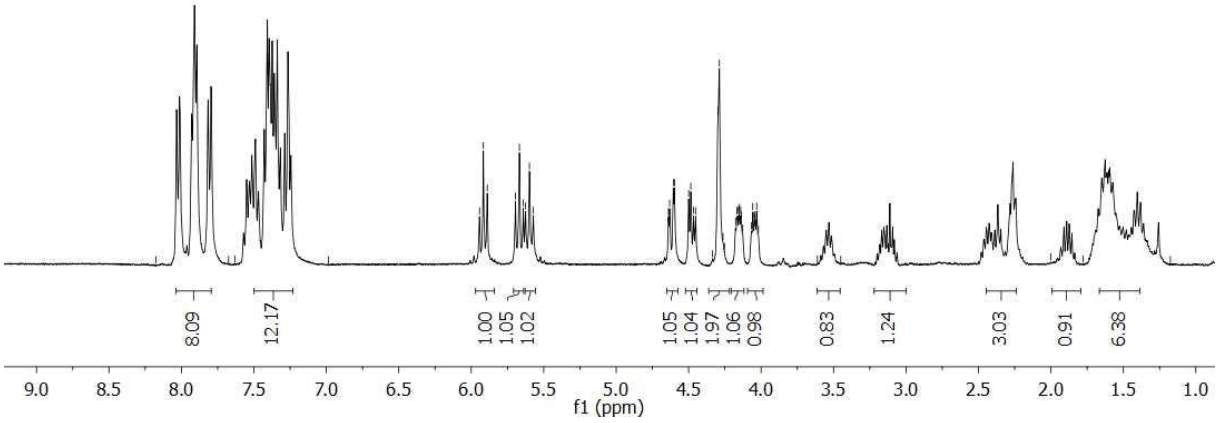
7c ($CDCl_3$, 400 MHz)

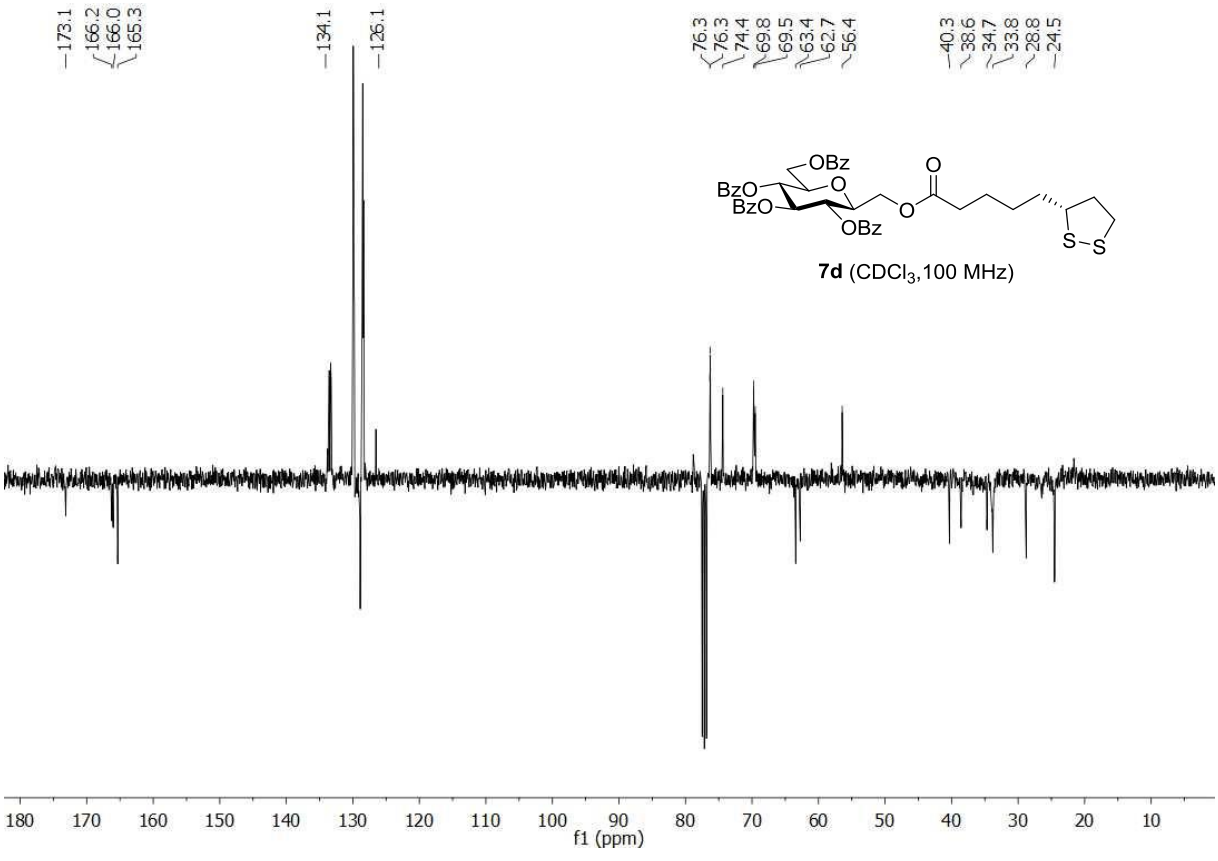


7c ($CDCl_3$,100 MHz)

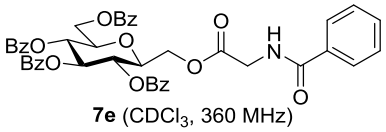


7d ($CDCl_3$,360 MHz)

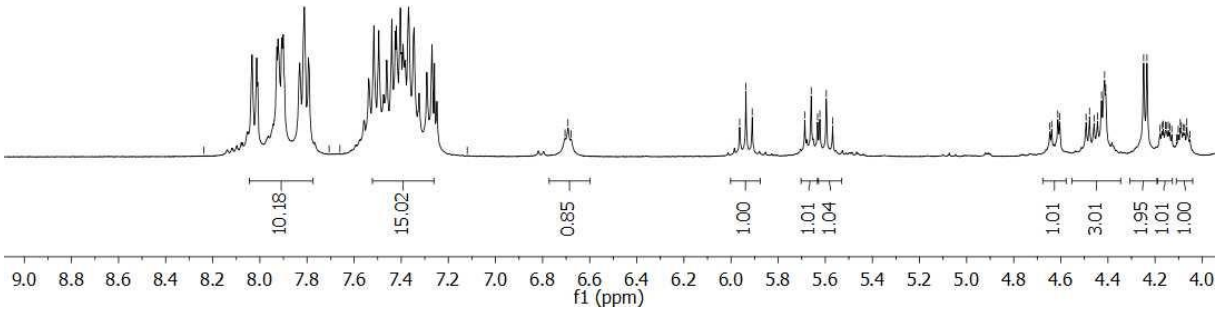


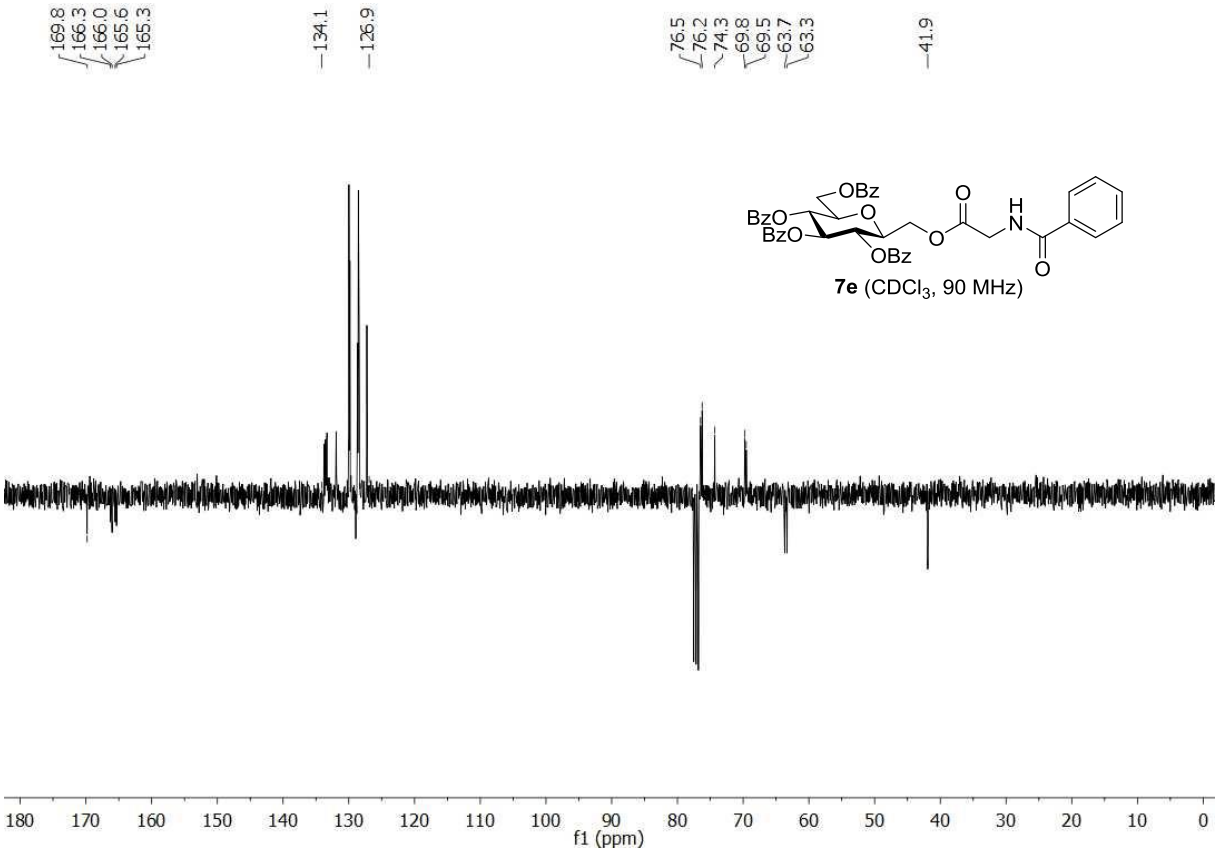


7d ($CDCl_3$,100 MHz)

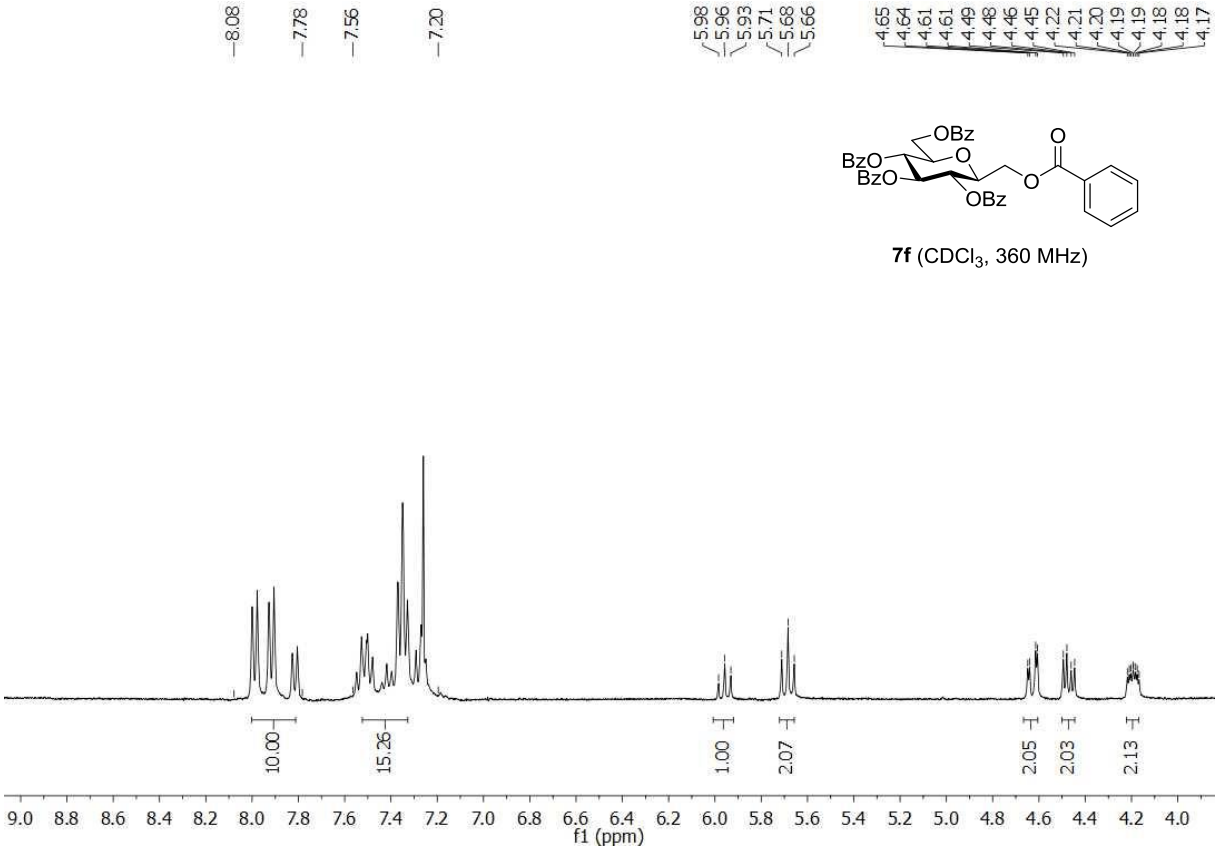


7e ($CDCl_3$, 360 MHz)

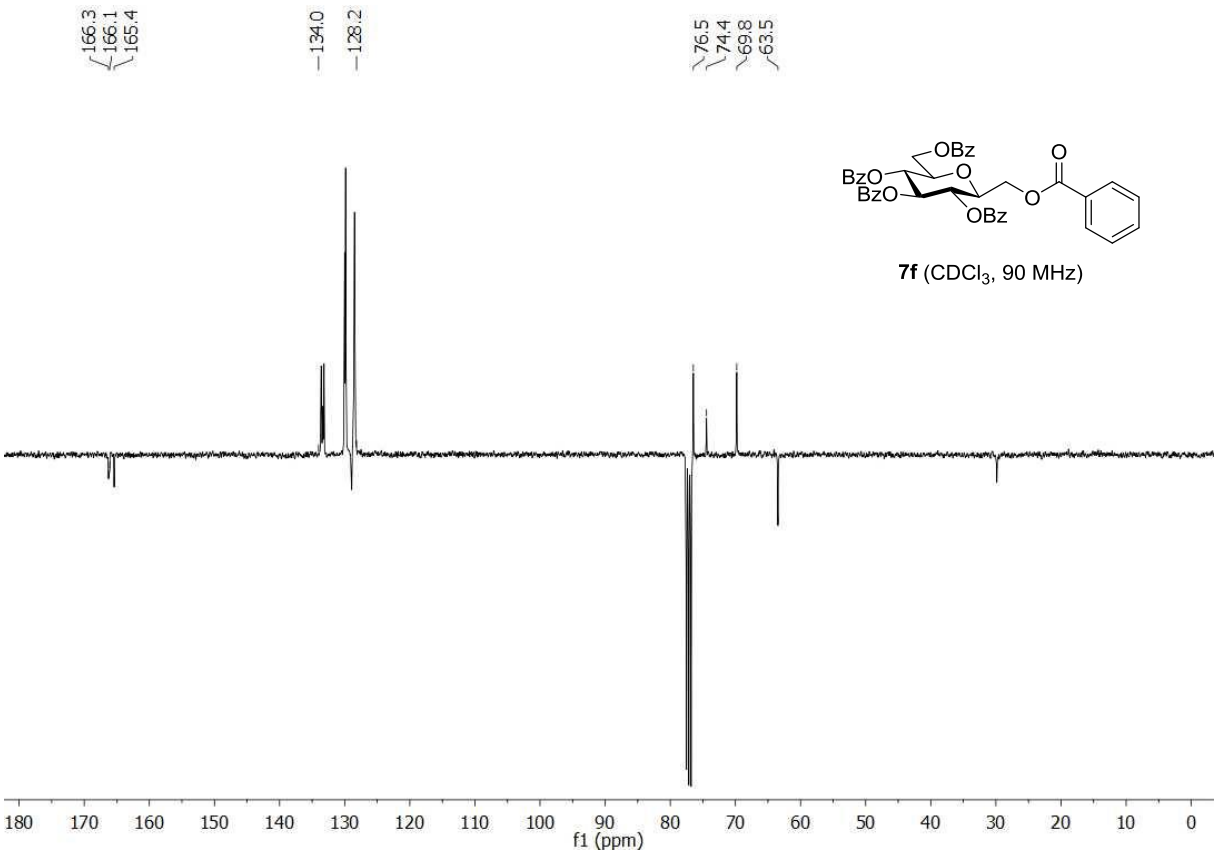




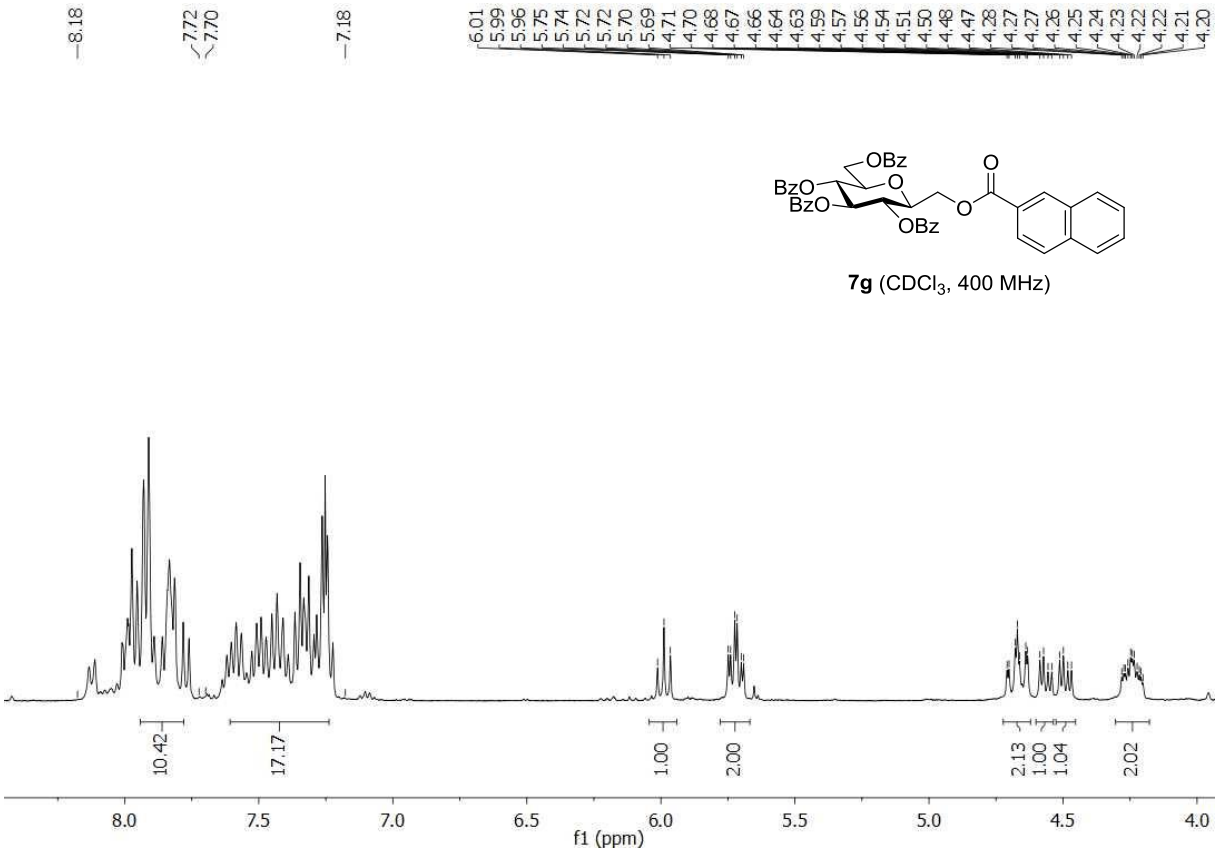
7e ($CDCl_3$, 90 MHz)



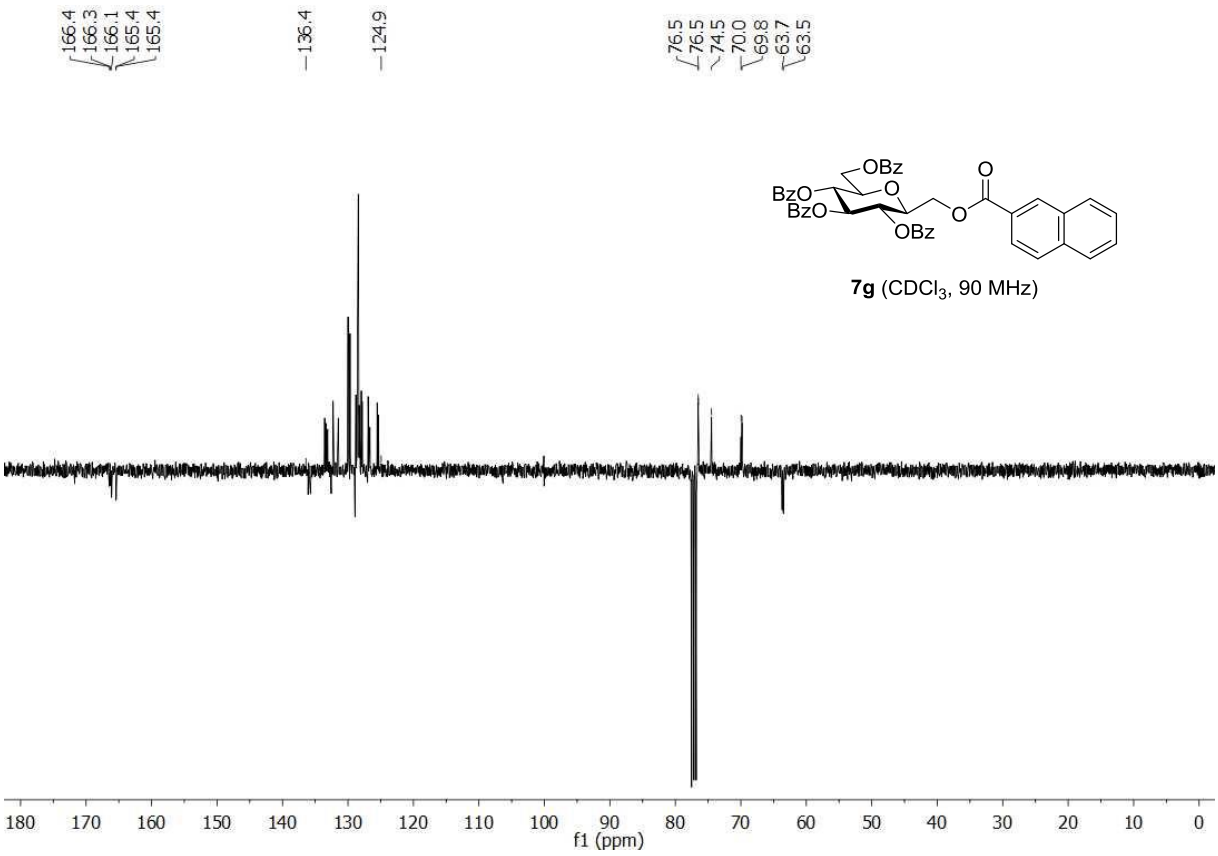
7f ($CDCl_3$, 360 MHz)



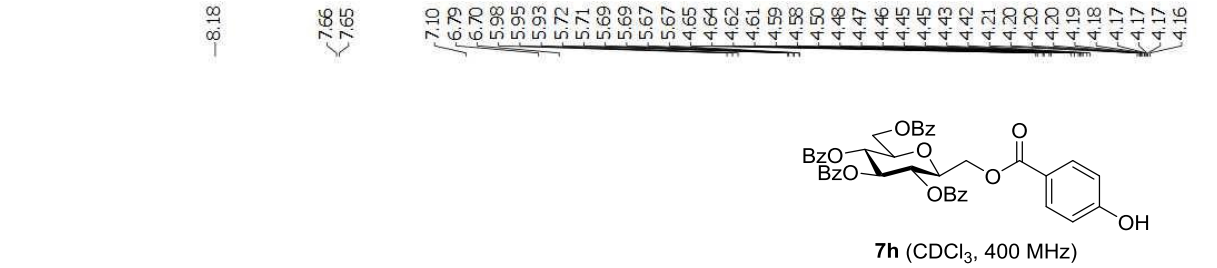
7f ($CDCl_3$, 90 MHz)



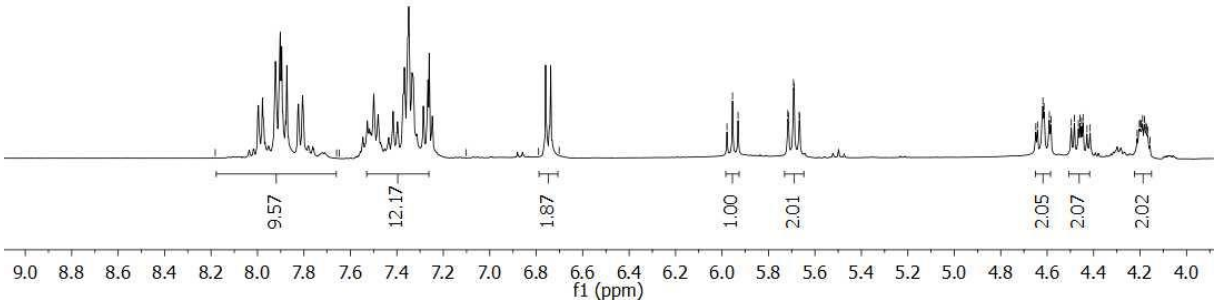
7g ($CDCl_3$, 400 MHz)

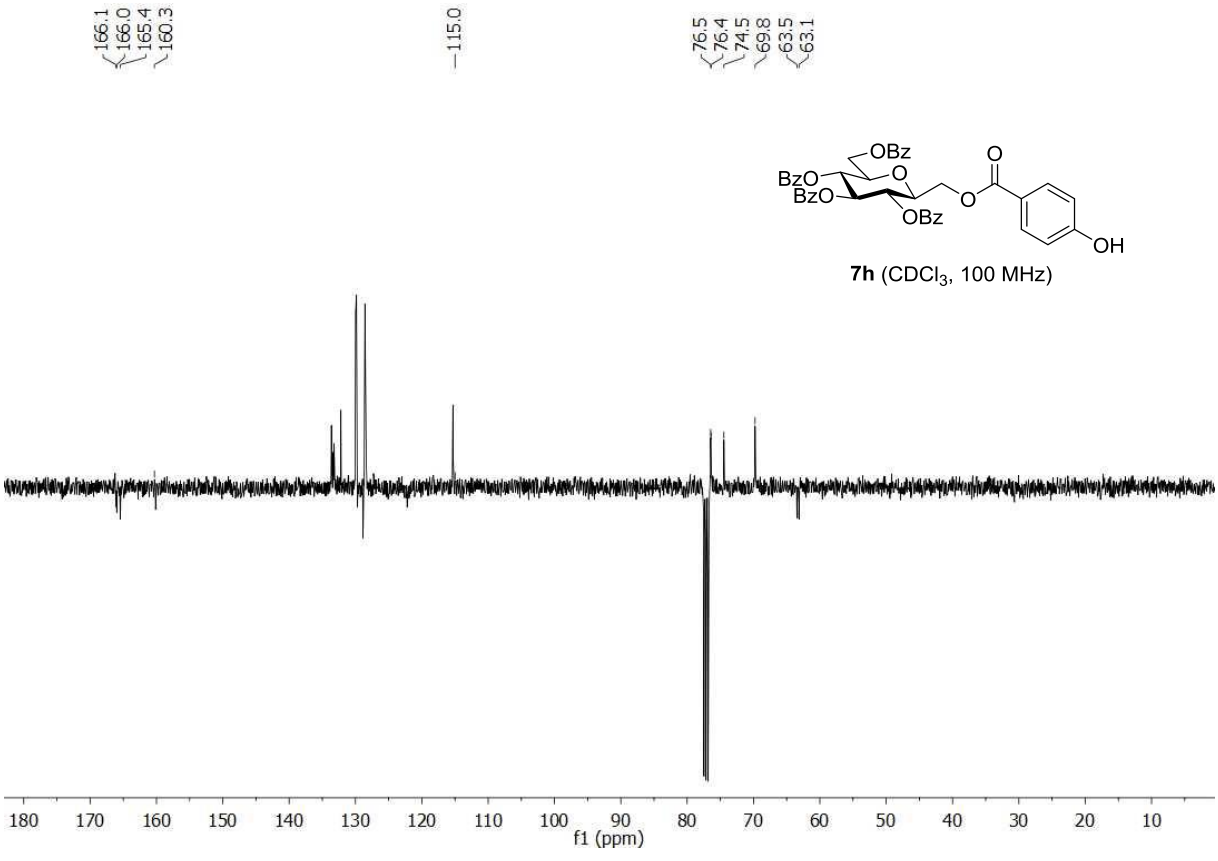


7g ($CDCl_3$, 90 MHz)

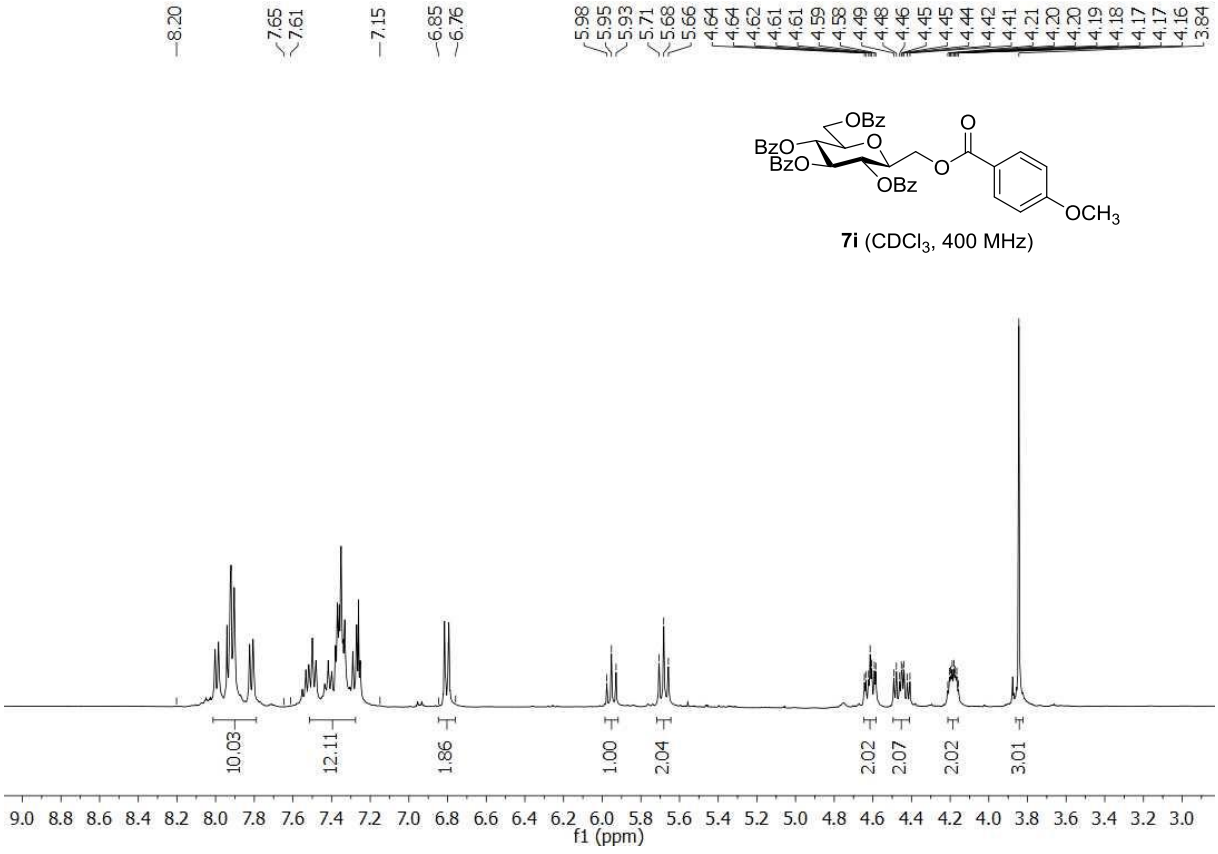


7h ($CDCl_3$, 400 MHz)

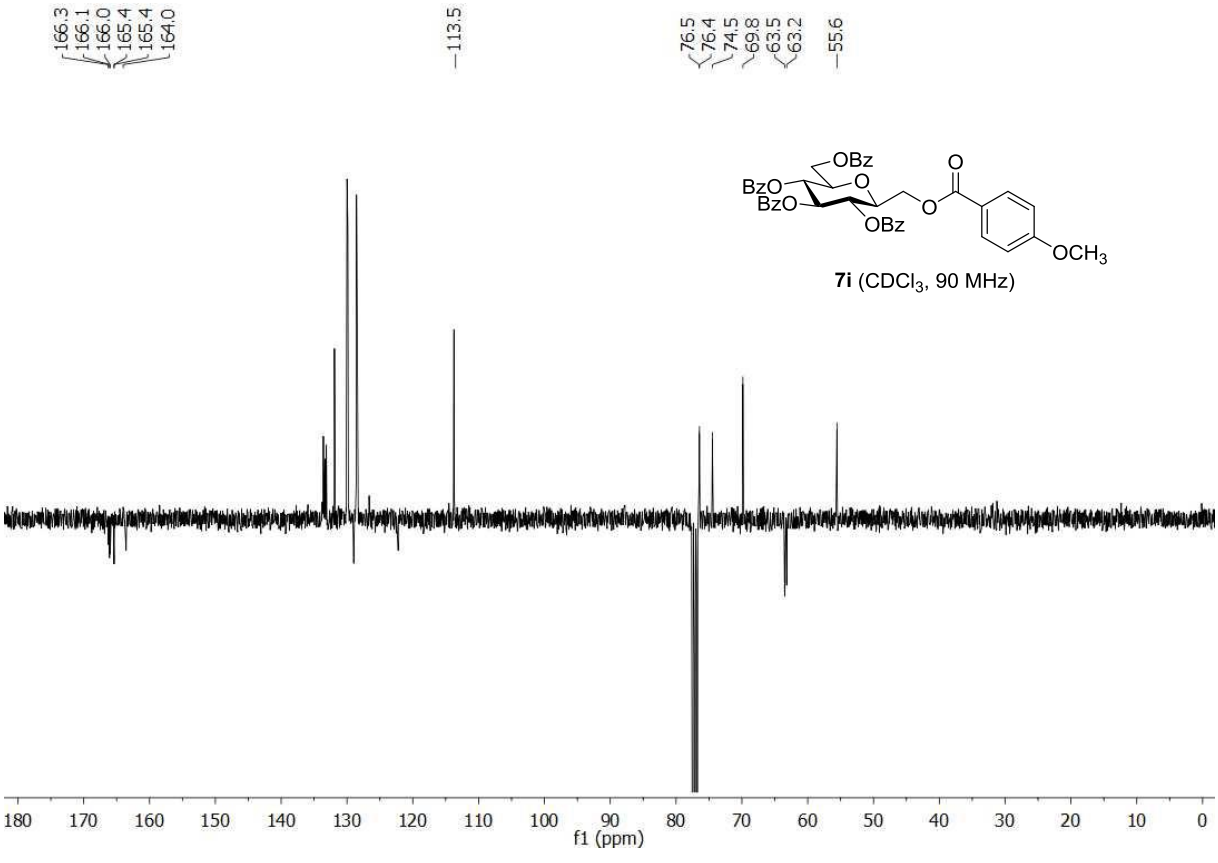




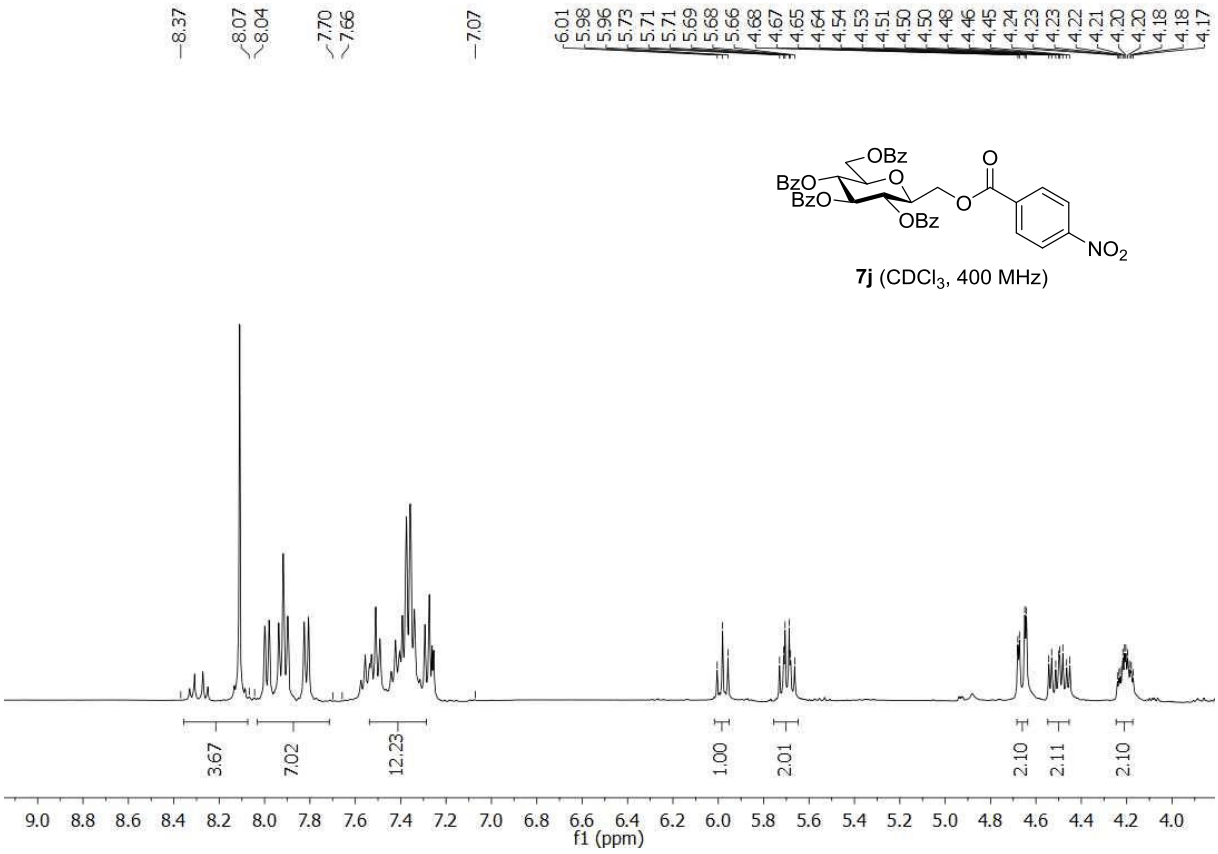
7h ($CDCl_3$, 100 MHz)



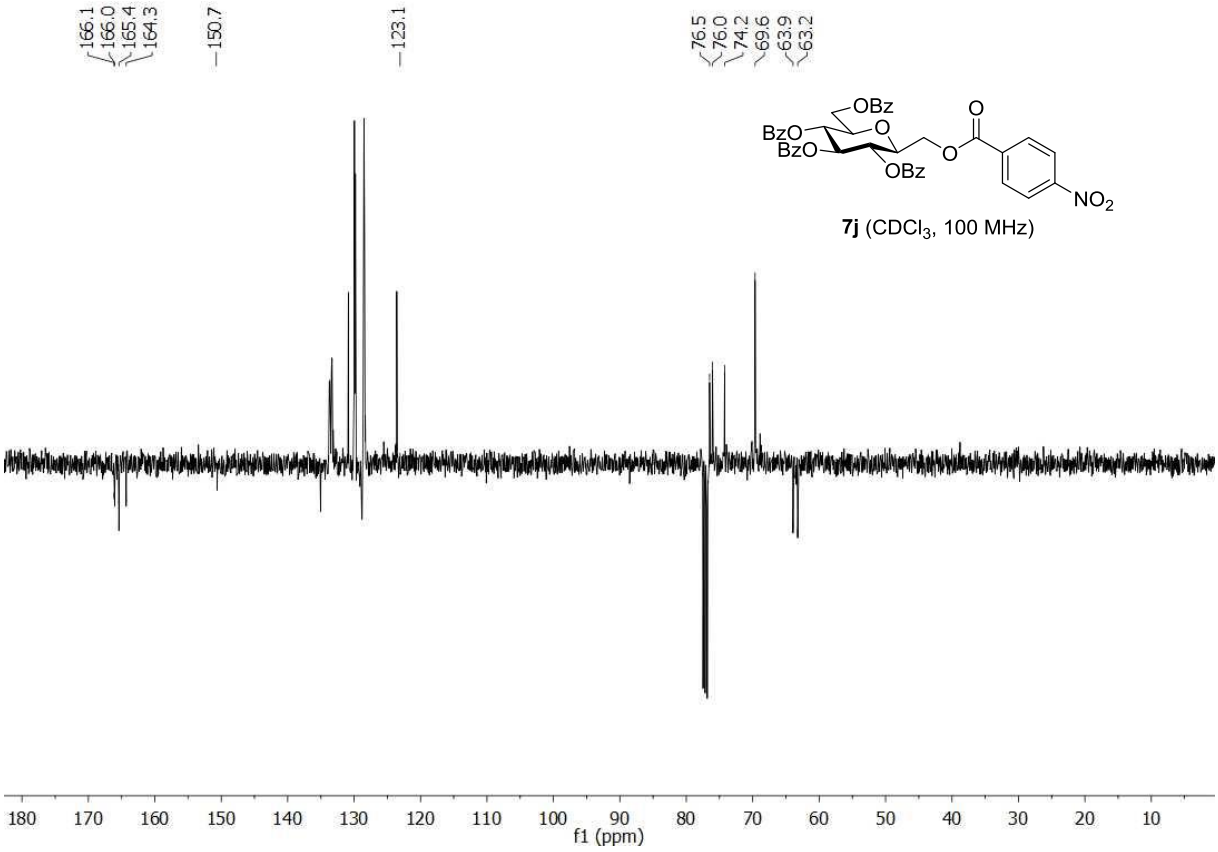
7i ($CDCl_3$, 400 MHz)



7i ($CDCl_3$, 90 MHz)

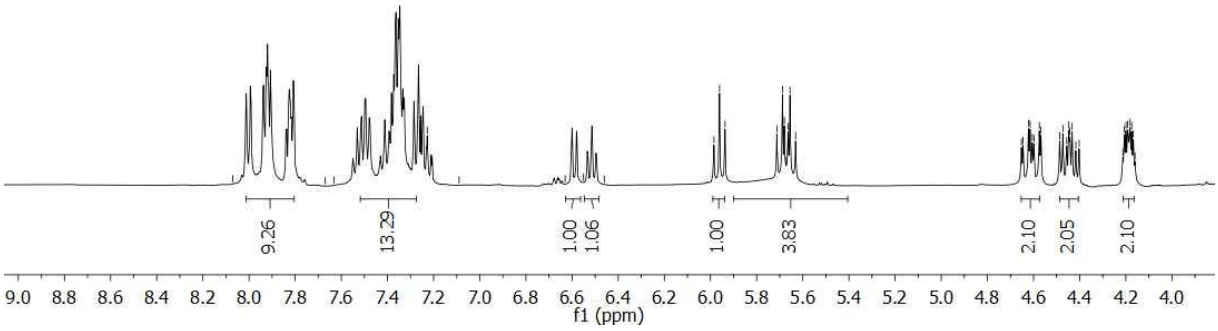


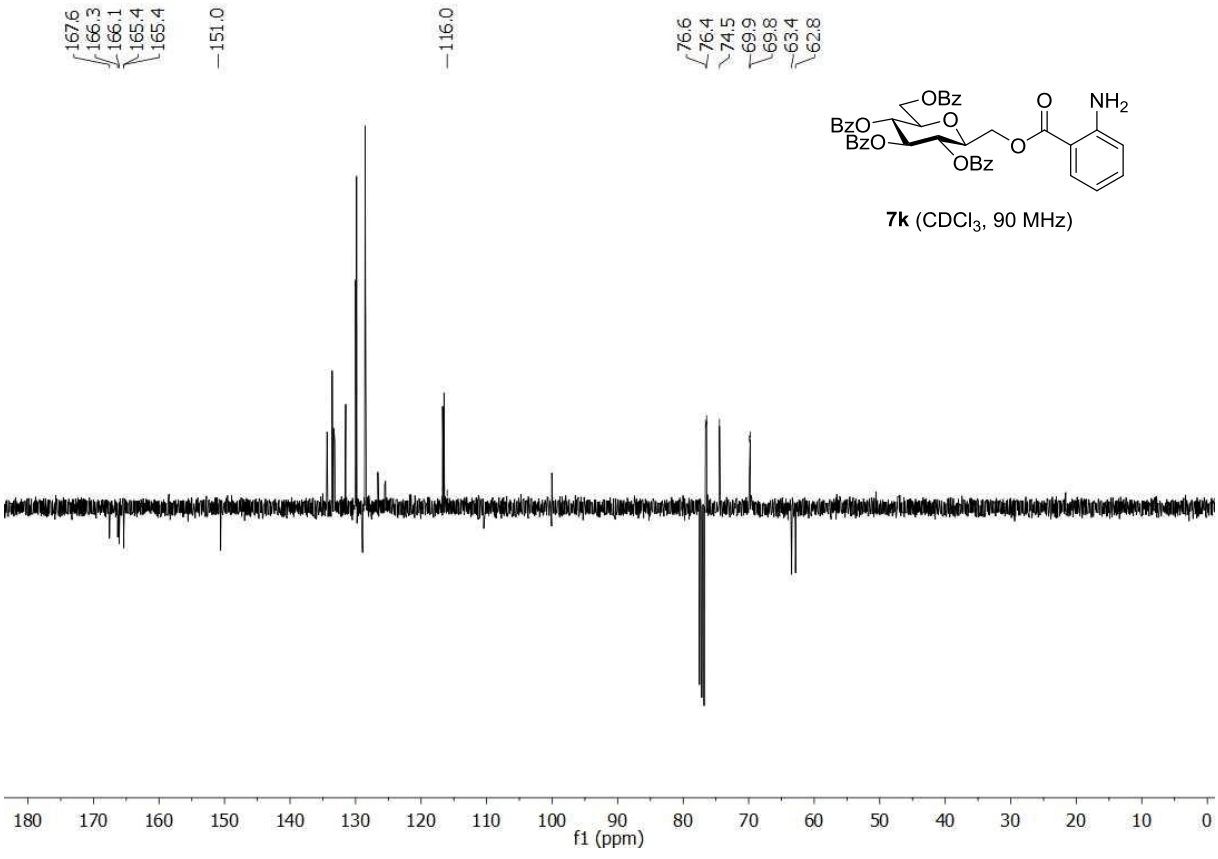
7j ($CDCl_3$, 400 MHz)



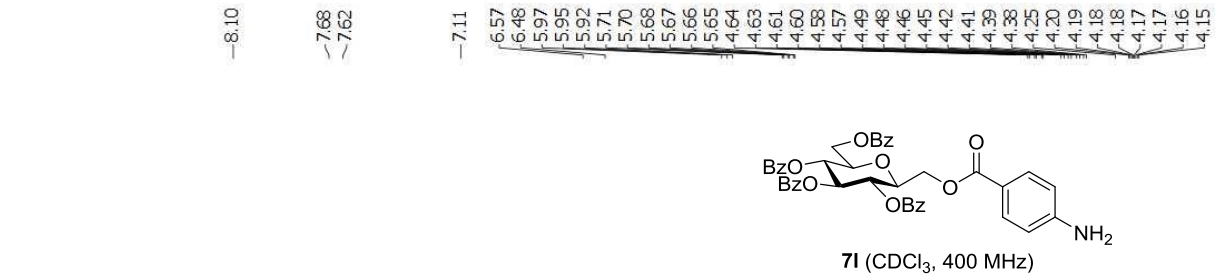
7j ($CDCl_3$, 100 MHz)

7k ($CDCl_3$, 400 MHz)

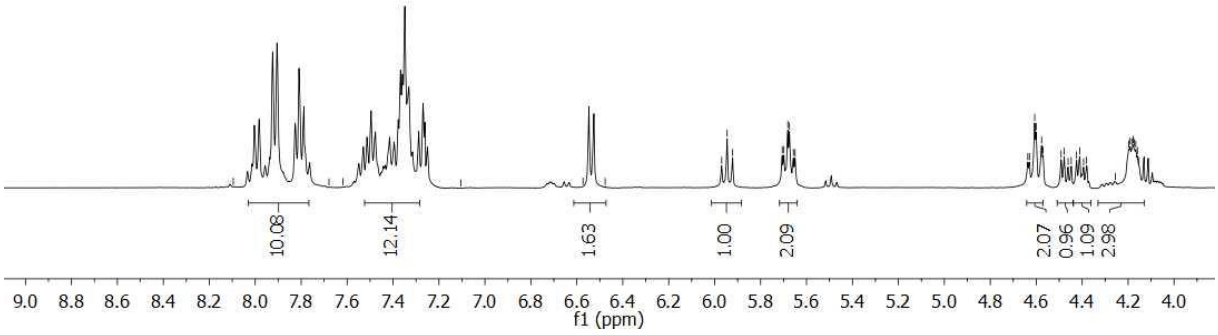


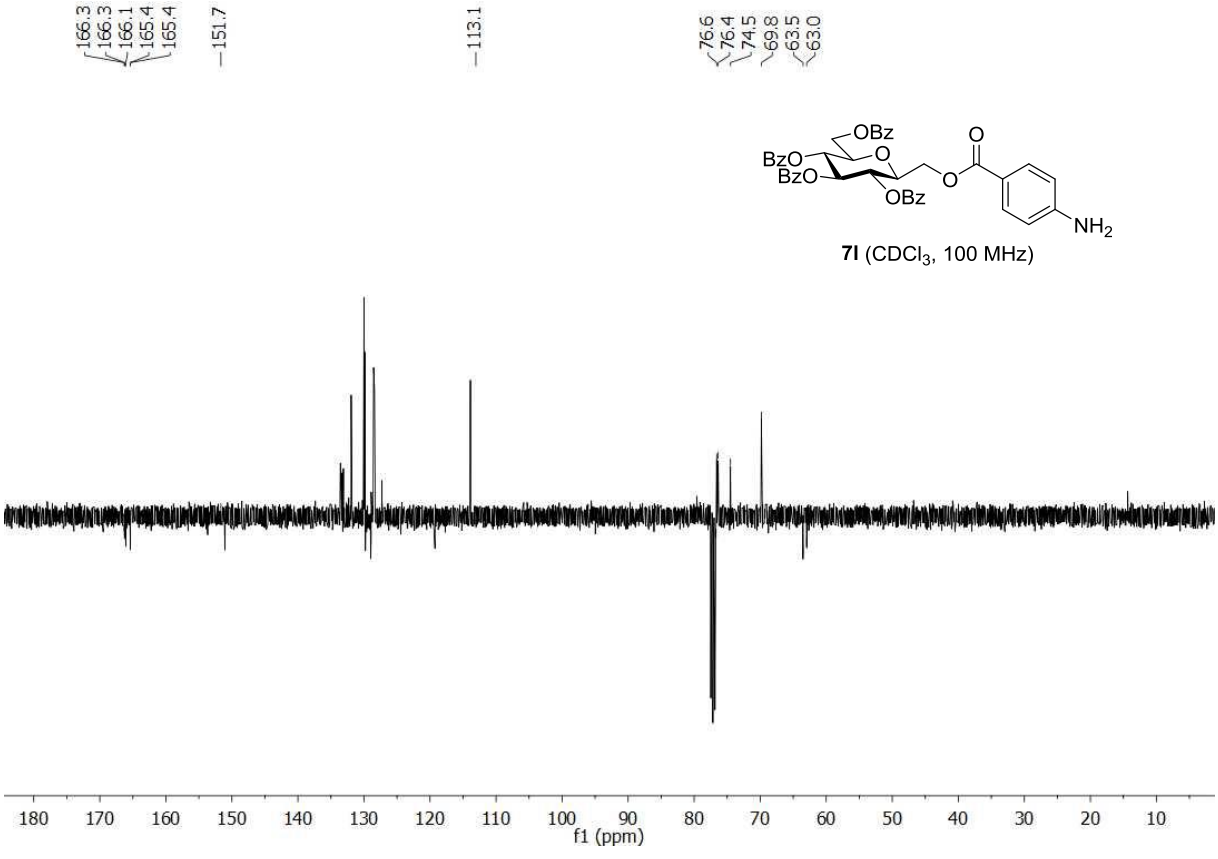


7k ($CDCl_3$, 90 MHz)

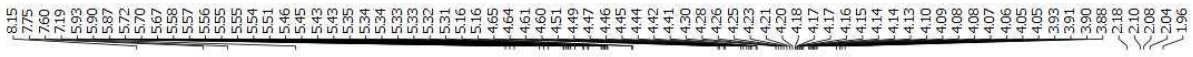


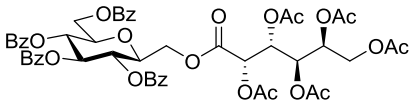
7l ($CDCl_3$, 400 MHz)



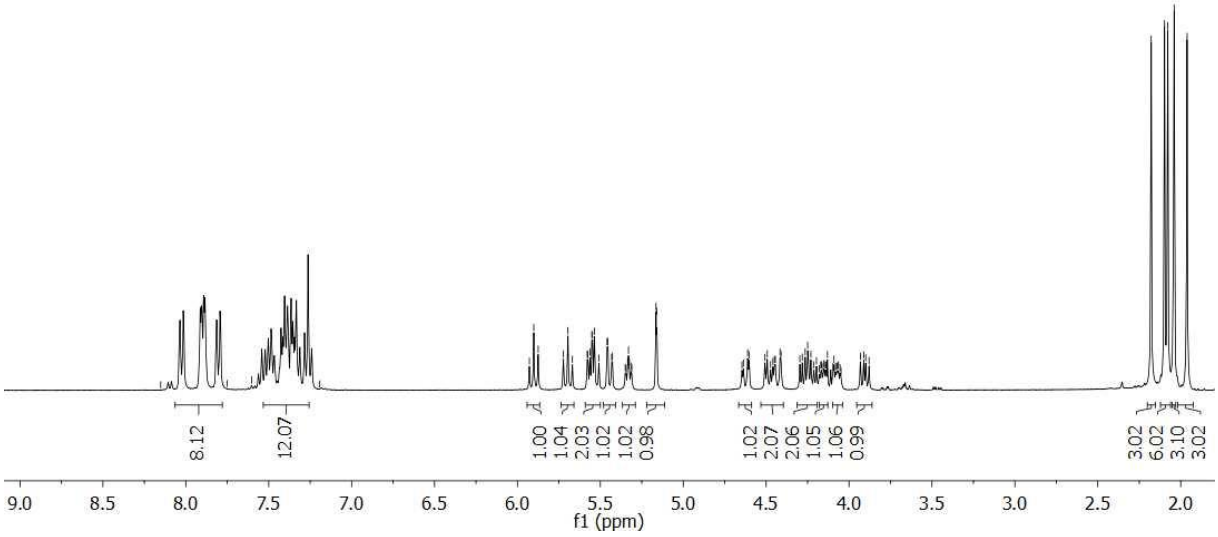


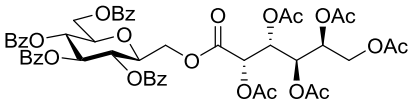
7l ($CDCl_3$, 100 MHz)



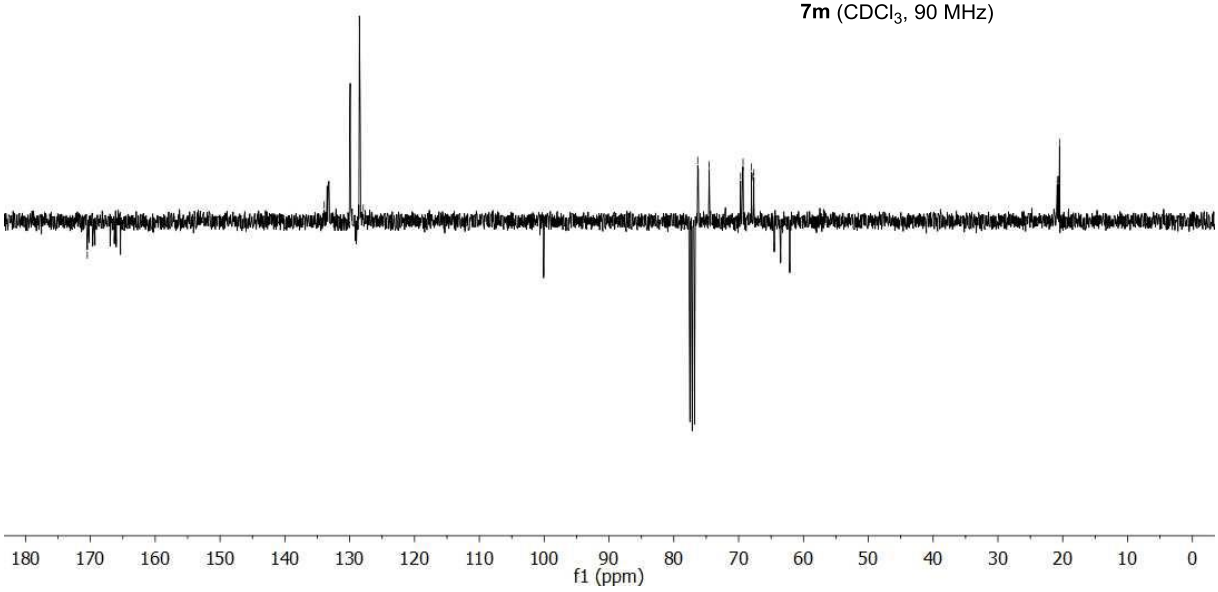


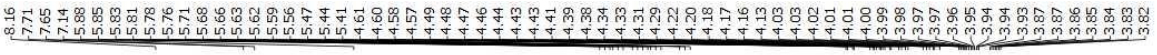
7m ($CDCl_3$, 360 MHz)

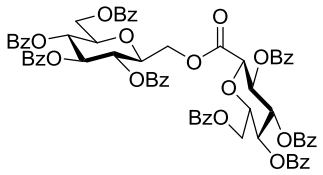




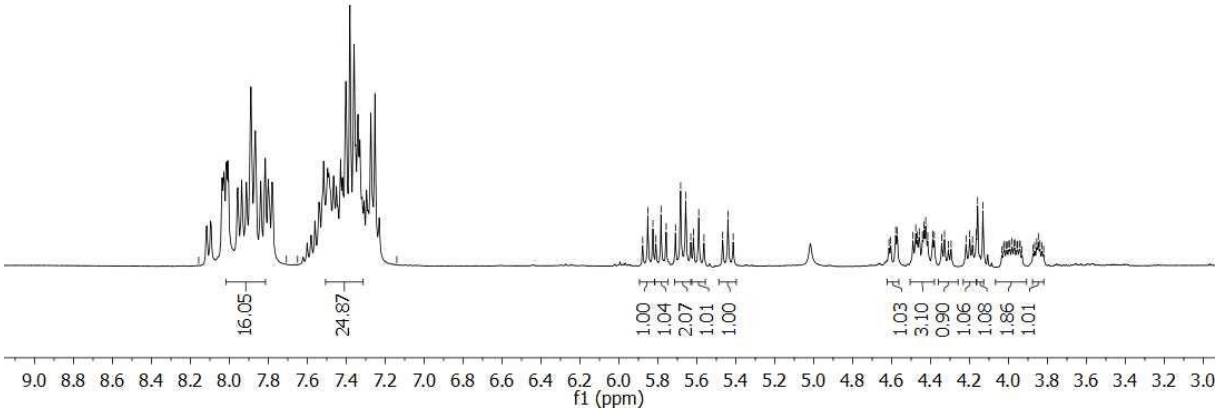
7m ($CDCl_3$, 90 MHz)

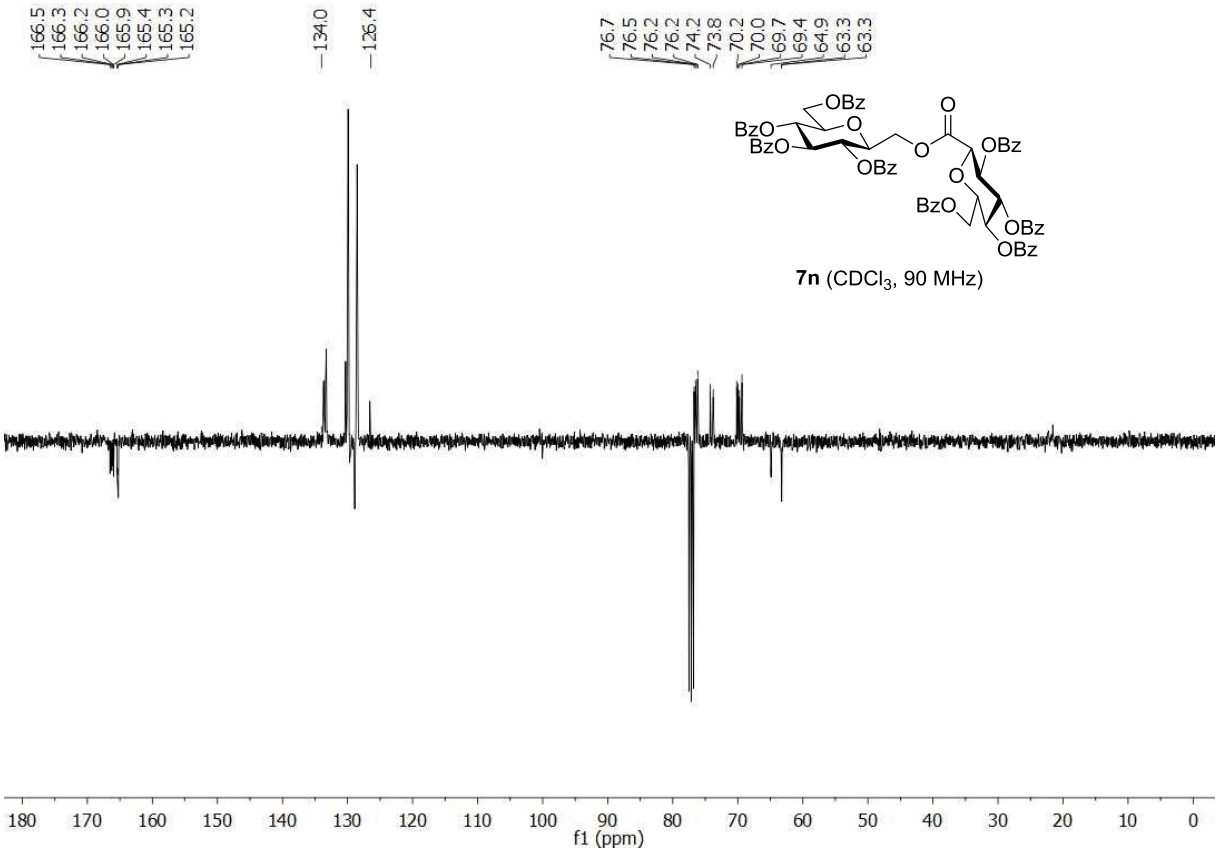




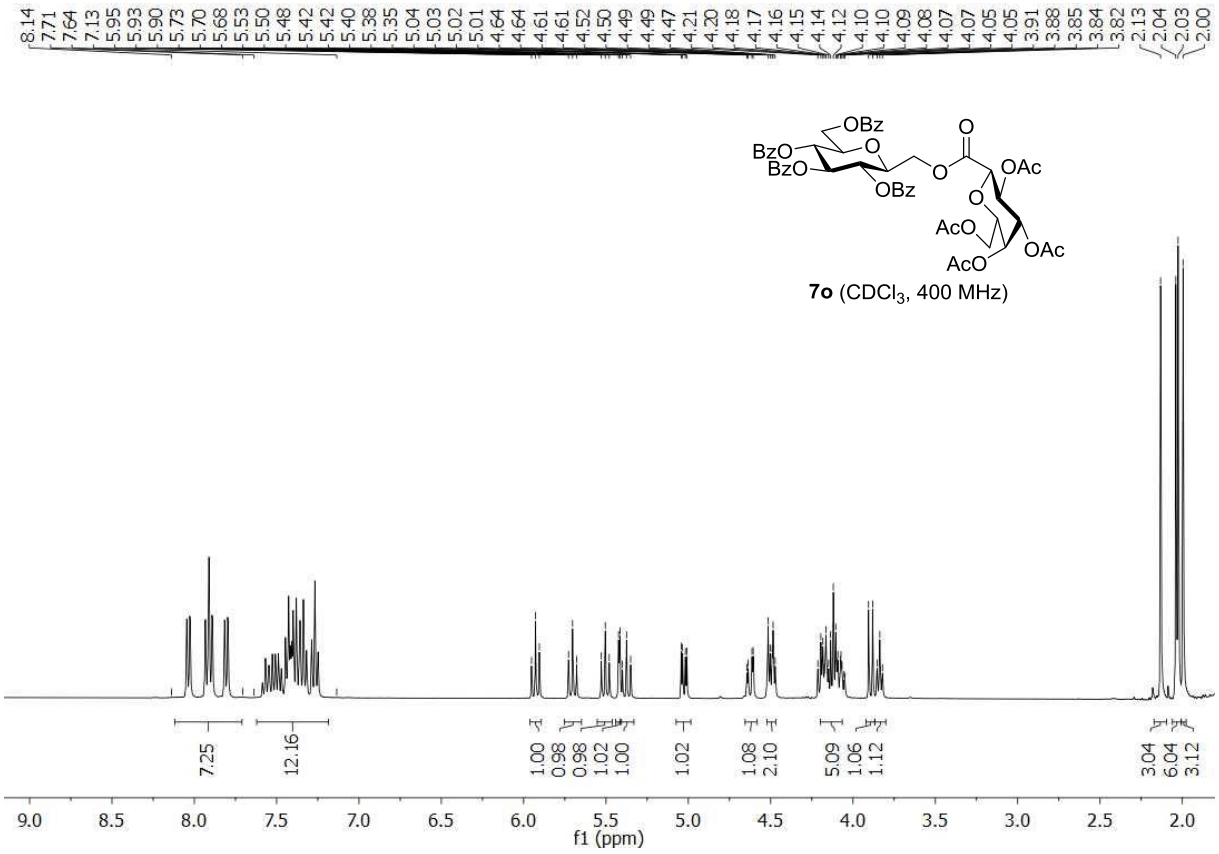


7n ($CDCl_3$, 360 MHz)

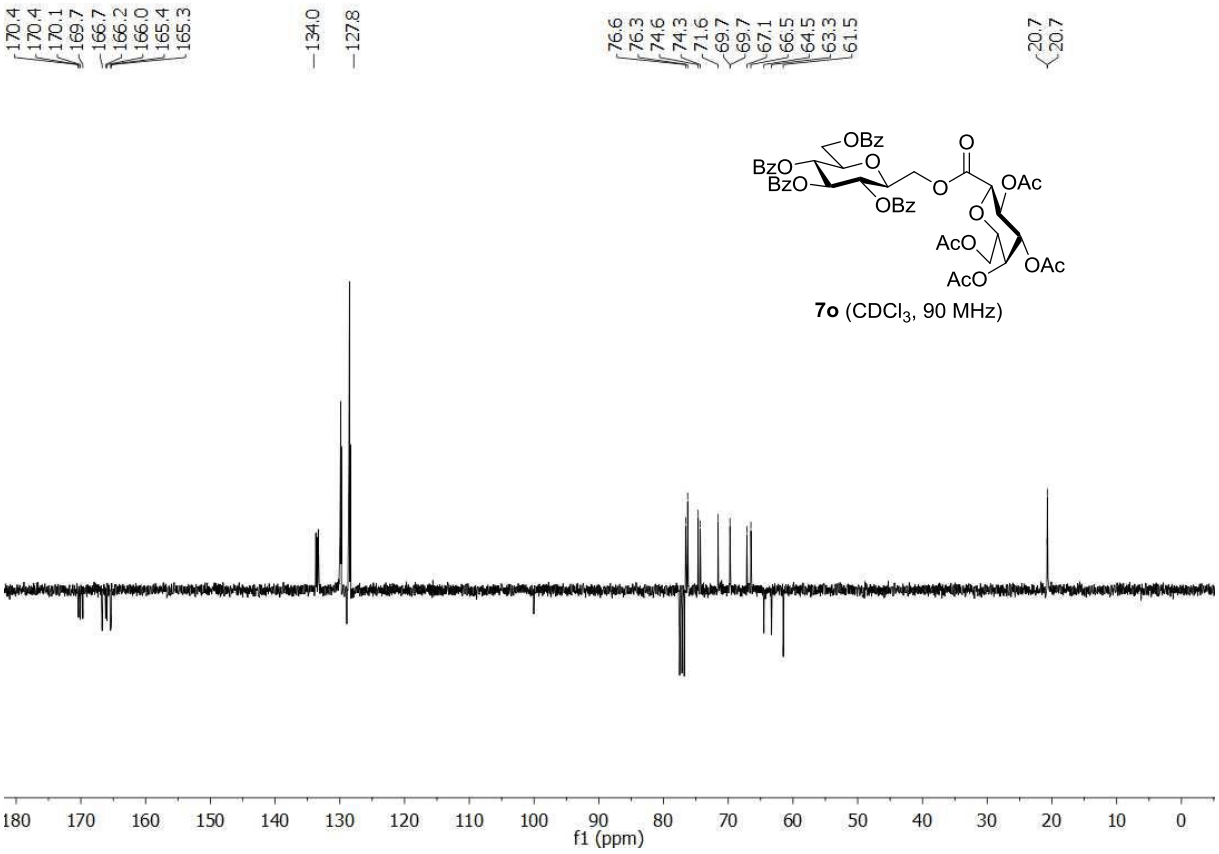




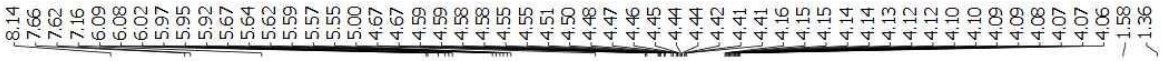
7n ($CDCl_3$, 90 MHz)

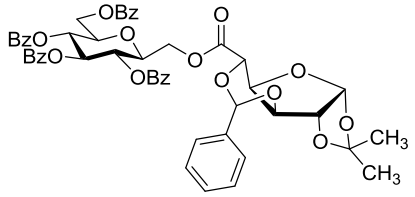


7o ($CDCl_3$, 400 MHz)

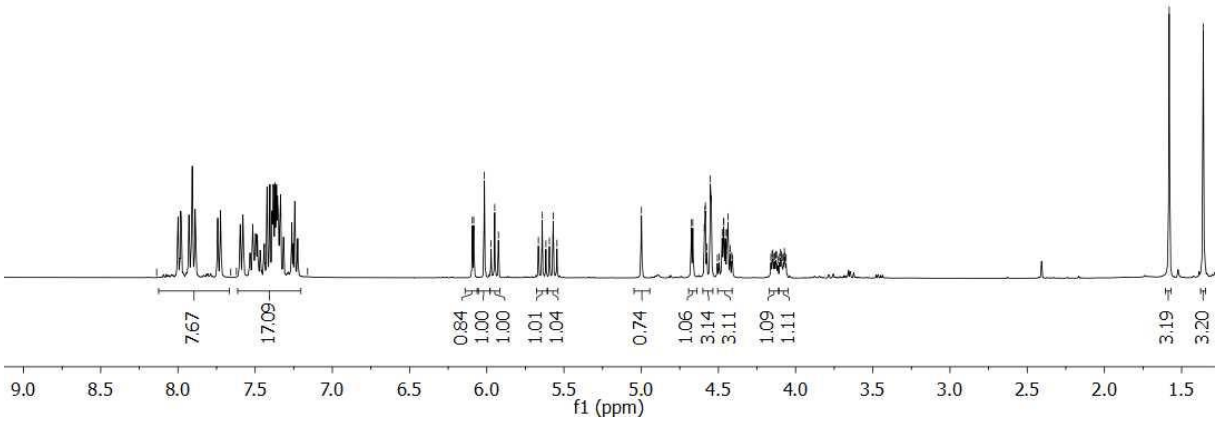


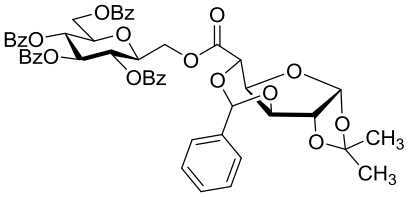
7o ($CDCl_3$, 90 MHz)



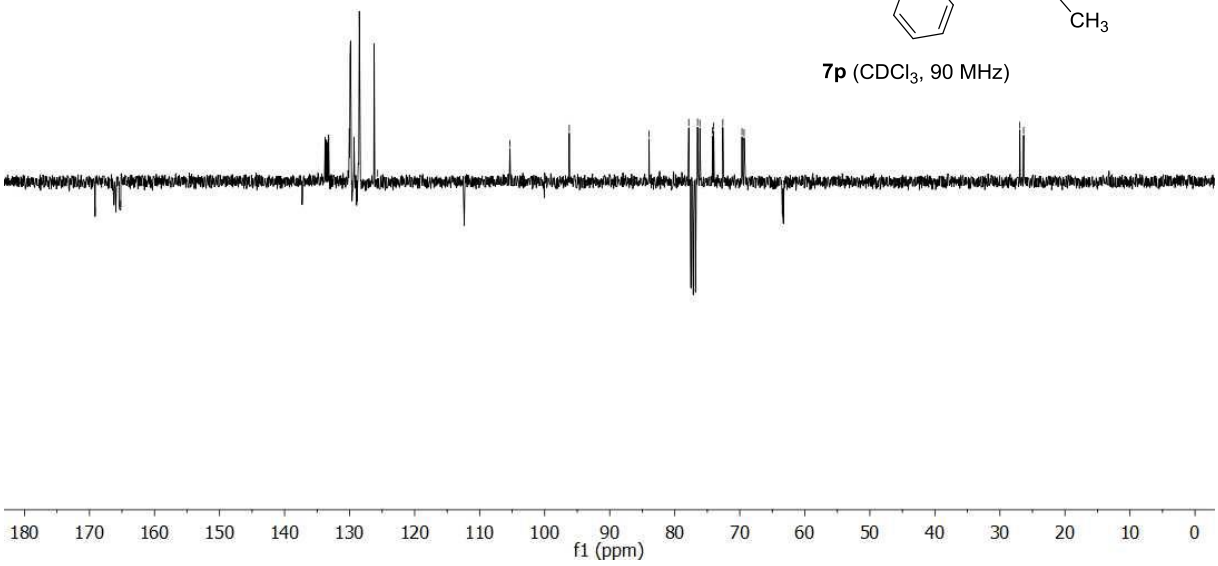


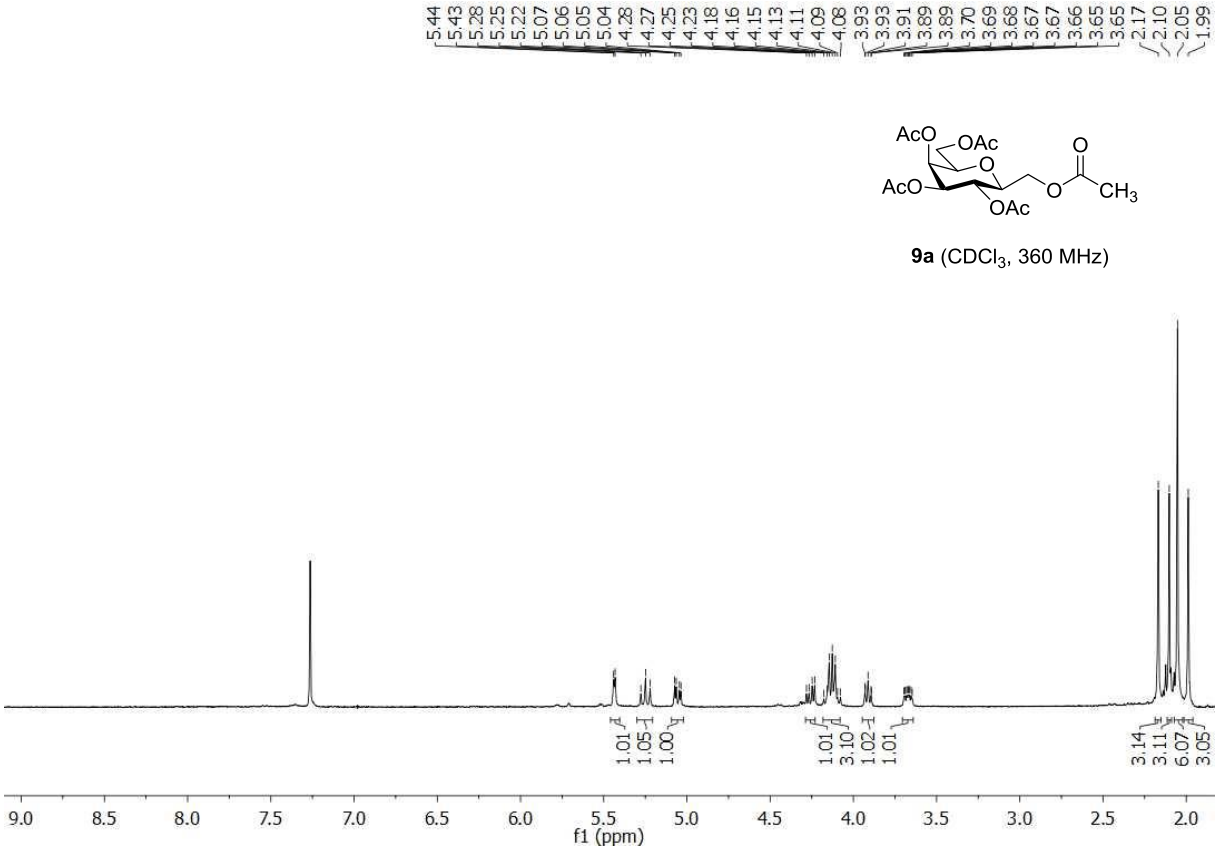
7p ($CDCl_3$, 400 MHz)



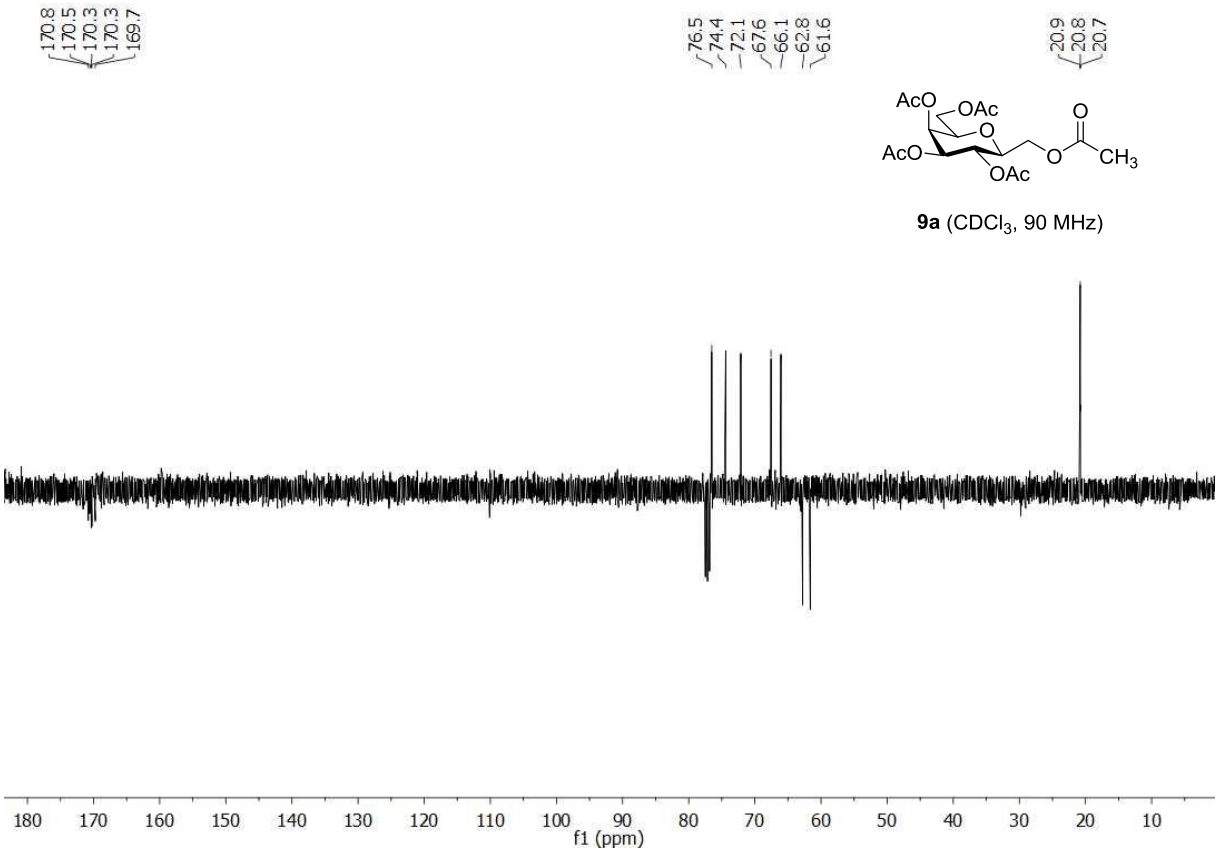


7p ($CDCl_3$, 90 MHz)

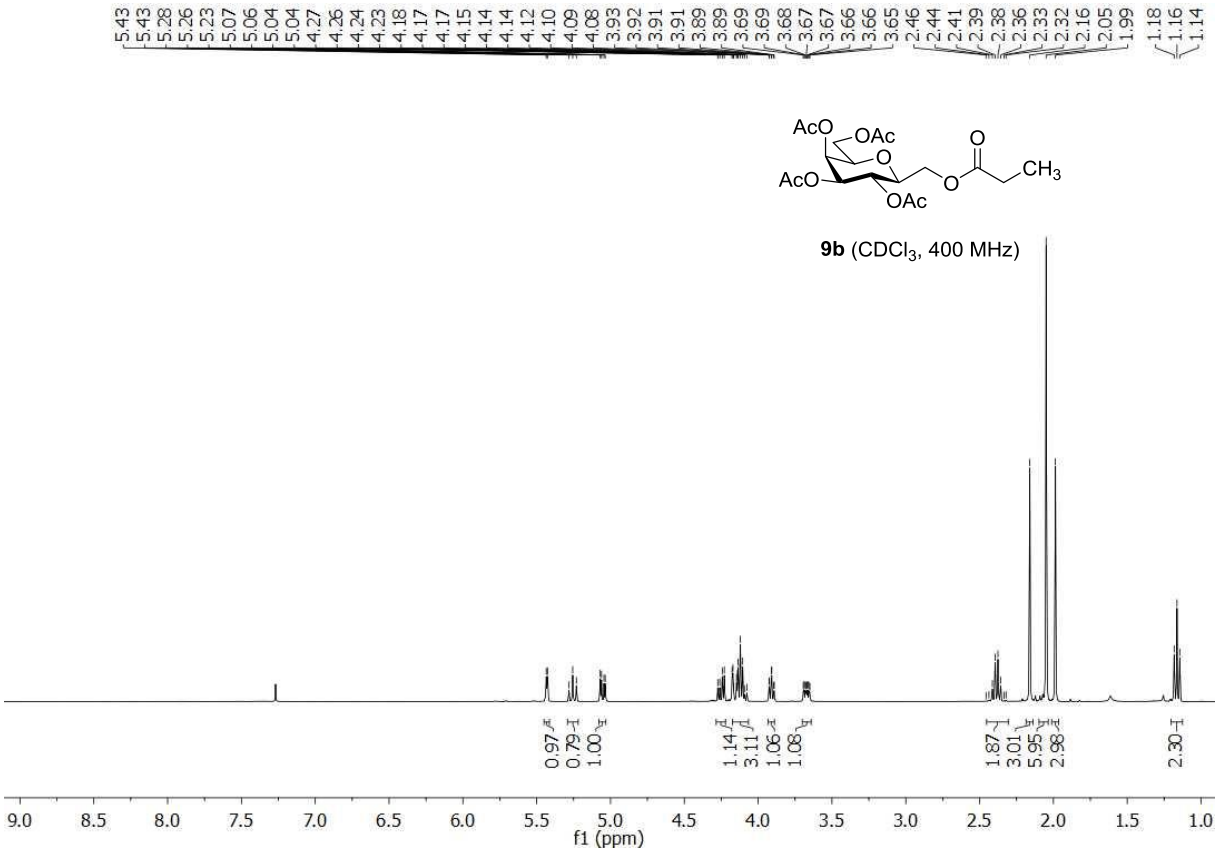




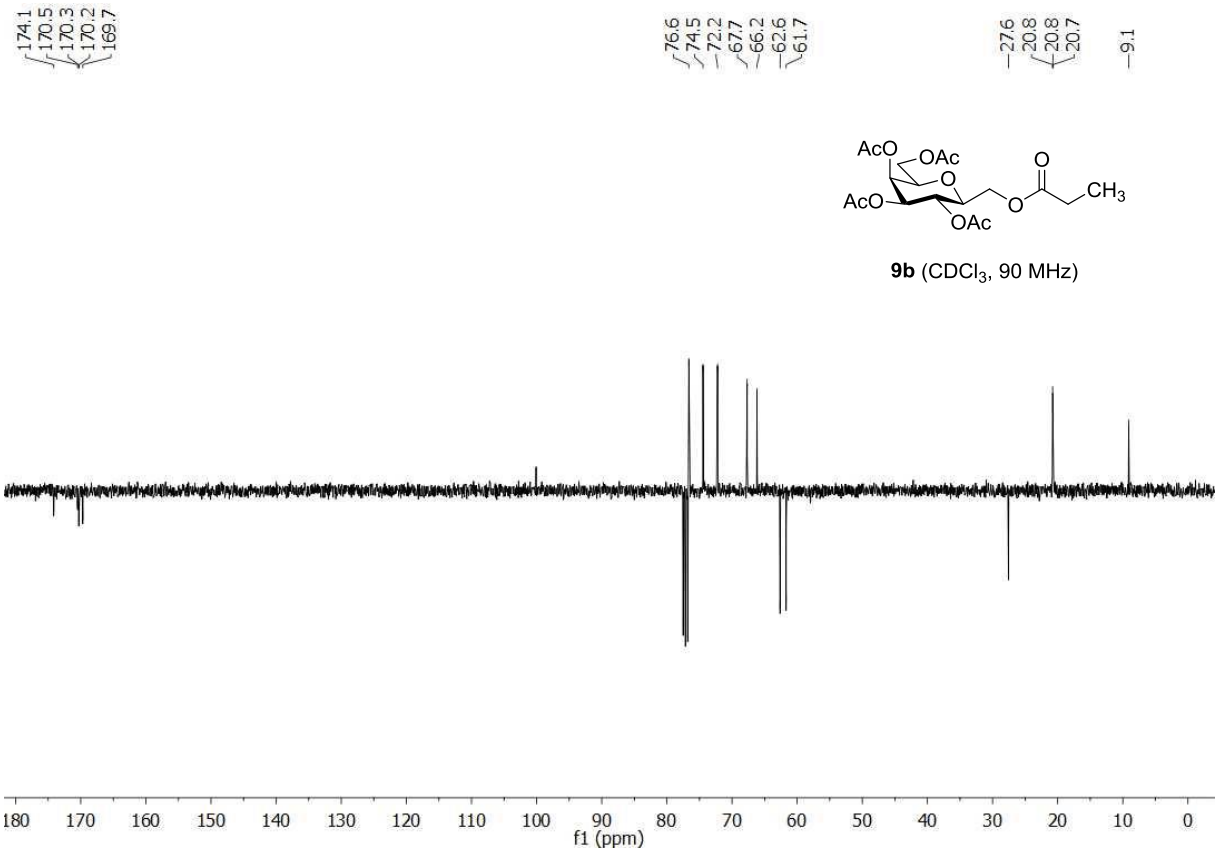
9a ($CDCl_3$, 360 MHz)



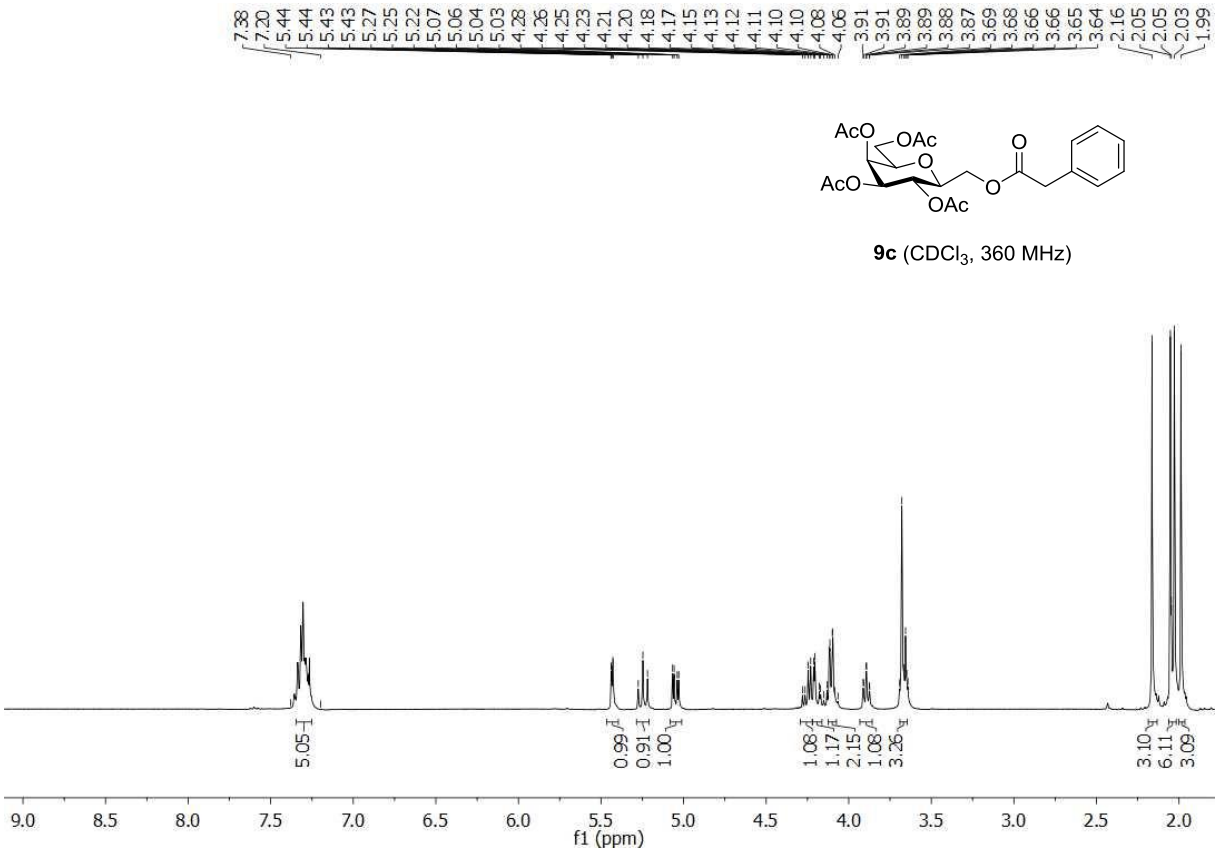
9a ($CDCl_3$, 90 MHz)



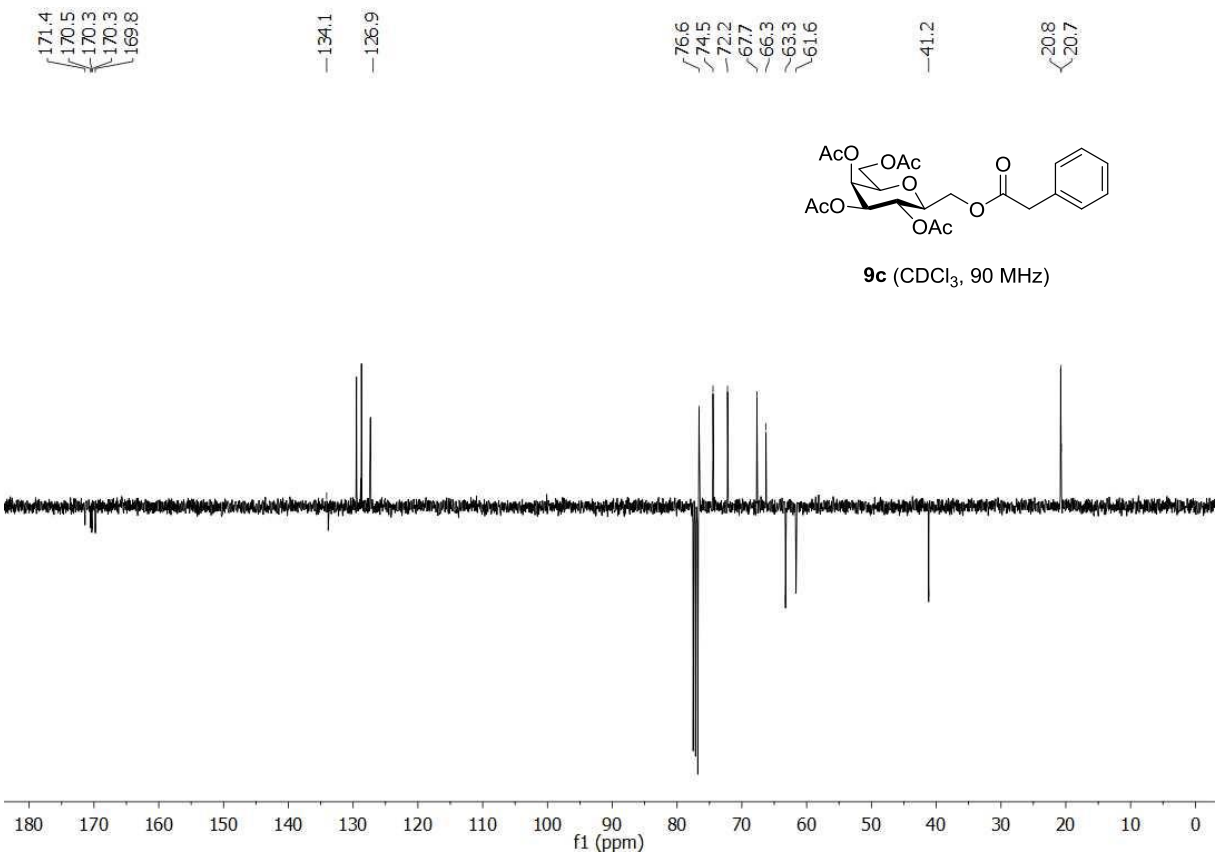
9b ($CDCl_3$, 400 MHz)



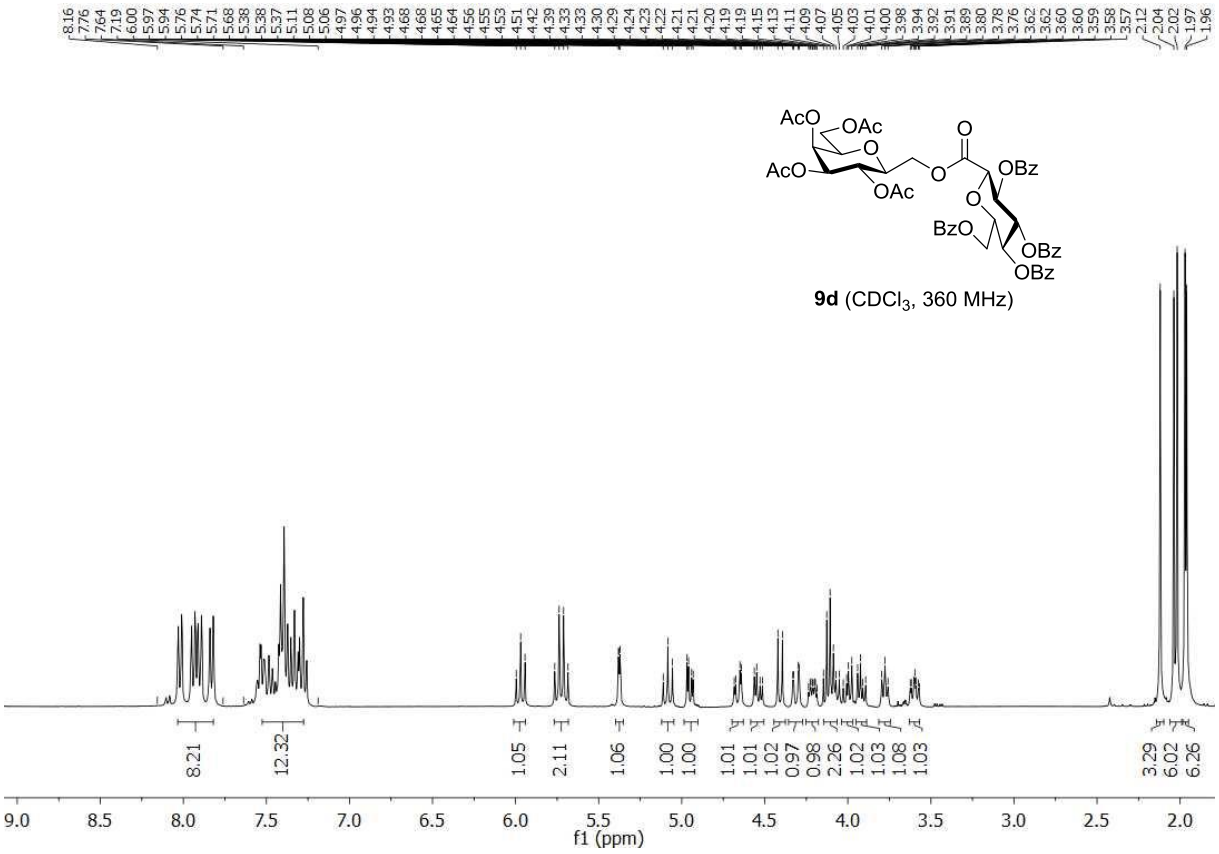
9b ($CDCl_3$, 90 MHz)

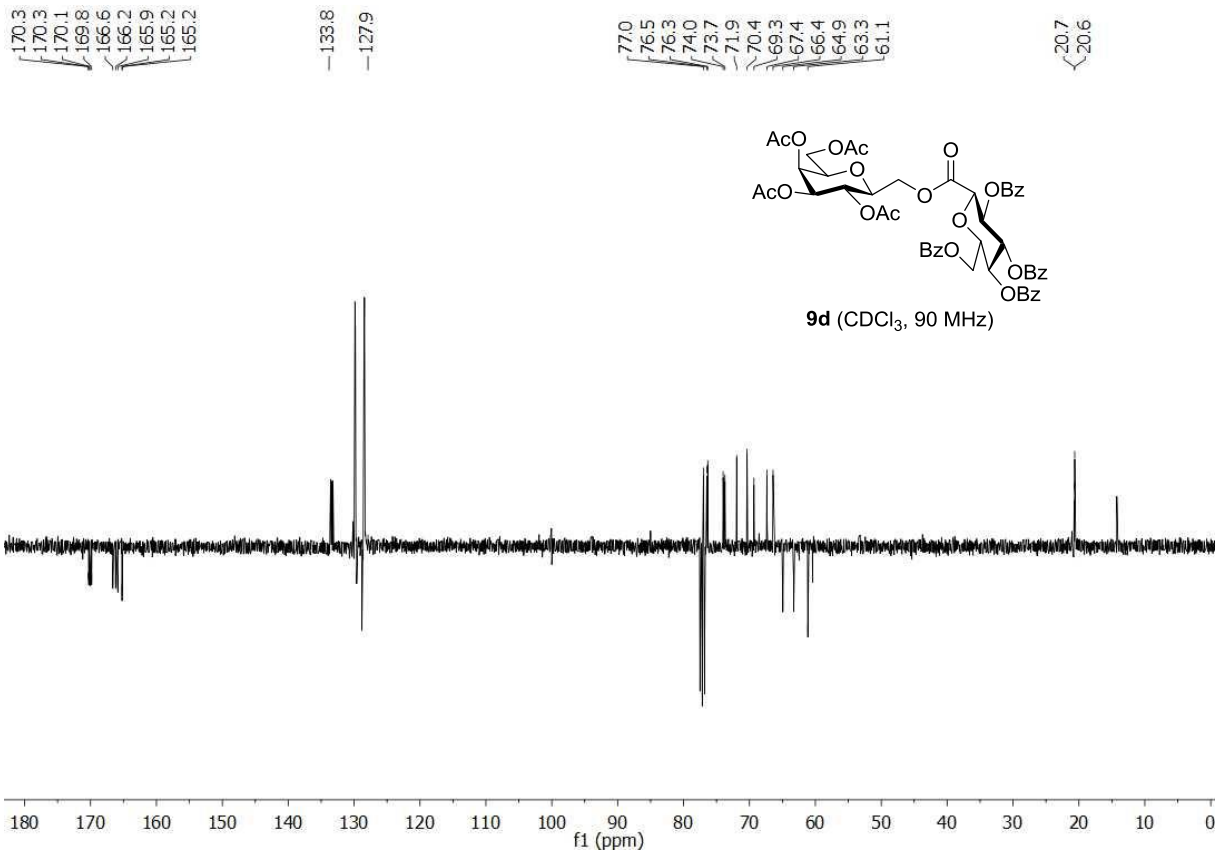


9c ($CDCl_3$, 360 MHz)



9c ($CDCl_3$, 90 MHz)


AcO
OAc
O
AcO
OAc
O
OBz
O
BzO
OBz
OBz
9d (CDCl3, 360 MHz)
8.21
12.32
1.05
2.11
1.06
1.00
1.00
1.01
1.01
1.02
0.97
0.98
2.26
1.02
1.03
1.08
1.03
3.29
6.02
6.26
f1 (ppm)


AcO
OAc
O
AcO
OAc
O
OBz
O
BzO
OBz
OBz
9d (CDCl3, 90 MHz)
f1 (ppm)