Electronic Supplementary Material (ESI) for Chemical Communications

β-Rhamnosides from 6-thio mannosides

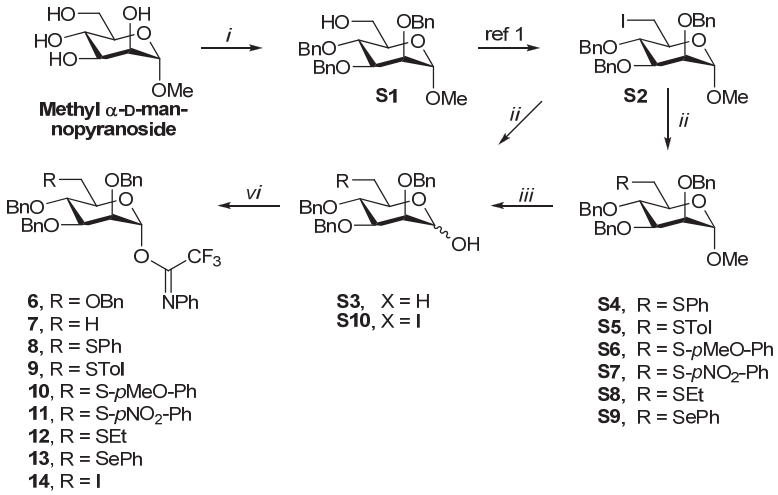
Alphert E. Christina, Daan van der Es, Jasper Dinkelaar, Hermen S. Overkleeft, Gijsbert A. van der Marel,* and Jeroen D. C. Codée*

Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

E-mail: marel_g@chem.leidenuniv.nl; jcodee@chem.leidenuniv.nl

Supporting Information

Contents



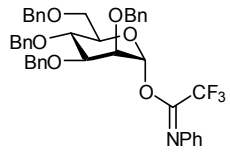
Reagents and conditions: (*i*) 1) TrCl, pyridine, 50 °C 2) BnBr, NaH, DMF 3) *p*-TsOH, MeOH (75% over 3 steps) (*ii*) DiPEA, RH, DMF (*iii*) 1) cat. H_2SO_4, Ac_2O 2) piperidine, THF (*iv*) $CF_3C(=NPh)Cl$, Cs_2CO_3, acetone, H_2O.

General experimental procedure for the preparation of 6-deoxy-6-thio/selenomannosides (S4-S7, S9): To a 0.1 M solution of the starting 6-deoxy-6-iodo-mannoside in DMF were added DiPEA (1.2 equiv) and thiol/selenol (1.2 equiv). After stirring overnight the reaction mixture was diluted with Et_2O, washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. Flash column chromatography afforded the pure products.

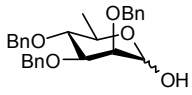
General experimental procedure for the preparation of (*N*-phenyl)trifluoroacetimidates (8-13): To the subject methyl glycoside was added 3 mL of a H_2SO_4/Ac_2O (1/999, v/v) solution and the reaction was stirred for 90 minutes. The solution was neutralized with triethylamine, concentrated and coevaporated with toluene. To the crude acetate was added 3 mL of a piperidine/THF (1/19, v/v) solution and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with EtOAc, washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude hemiacetal was dissolved in 2.85 mL acetone and 0.15 mL H_2O, 224 mg Cs_2CO_3 and 114 µL $ClC(C=NPh)CF_3$ were added. After stirring for 3 days, the mixture was filtered over celite and the filtrate was evaporated. Purification of the crude product by flash column chromatography (silica was pretreated with triethylamine/PE (1/19 → 0/1)) using toluene/PE (1/1 → 1/0) as eluent yielded the desired imidates.

General glycosylation procedure: The donor (0.22 mmol, 1 equiv) and acceptor (0.33 mmol, 1.5 equiv) were dissolved in 4.4 mL DCM and stirred over 3Å molecular sieves for 30 minutes. The mixture was then cooled to -80 °C after which TfOH (0.044 mmol) in DCM (0.1 mL) was added and the reaction was stirred overnight at -80 °C. The reaction was quenched by the addition of 1mL Et_3N at -80 °C. After filtration over celite, the mixture was washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification by size exclusion chromatography (DCM/MeOH, 1/1, v/v) yielded the coupled products.

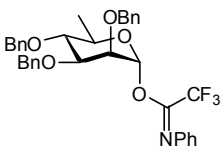
1. Mukherjee, C.; Ghosh, S.; Nandi, P.; Sen, P. C.; Misra, A. K. *Eur. J. Med. Chem.* **2010**, *45*, 6012-6019.



2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidates (6): Acetyl 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose[2] (956 mg, 1.64 mmol) was stirred in a 5% piperidine in THF solution (8 mL) for 3 days. The reaction mixture was diluted with EtOAc, washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude hemiacetal was dissolved in 8 mL acetone and 0.4 mL H_2O, 339 mg K_2CO_3 (2.45 mmol, 1.5 equiv.) and 0.37 mL ClC(C=NPh)CF_3 (2.44 mmol, 1.5 equiv.) were added. After stirring overnight the mixture was partitioned between EtOAc and sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification of the crude product by flash column chromatography (silica was pretreated with triethylamine/PE (1/19 → 0/1)) using toluene/PE (1/1 → 1/0) as eluent yielded 617 mg of the title imidate (0.87 mmol, 53%). Rf 0.39 (toluene); $[\alpha]_D^{22}$ +9 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3032, 2870, 1714, 1598, 1497, 1490, 1454, 1118, 732, 694; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.37 – 7.14 (m, 22H, H_{arom}), 7.06 (t, *J* = 7.5 Hz, 1H, H_{arom}), 6.73 (d, *J* = 7.7 Hz, 2H, H_{arom}), 6.21 (br s, 1H, H-1), 4.87 (d, *J* = 11.0 Hz, 1H, CH_2 benzyl), 4.71 – 4.48 (m, 7H, CH_2 benzyl), 4.08 (t, *J* = 9.5 Hz, 1H, H-4), 3.97 – 3.85 (m, 2H, H-5, H-3), 3.84 – 3.75 (m, 2H, H-2, H-6), 3.72 (dd, *J* = 11.2, 1.8 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 143.6, 138.5, 138.3, 137.9 (C_q), 128.7, 128.4, 128.3, 127.9, 127.7, 127.6, 127.4, 124.3, 119.5 (CH_{arom}), 96.0 (C-1), 79.1 (C-3), 75.1 (CH_2 benzyl), 75.0 (C-5), 74.5 (C-4), 73.9 (C-2), 73.5, 72.8 (CH_2 benzyl), 69.2 (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 96.0 ($J_{C1\text{-}H1}$ = 178.1 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{42}H_{40}F_3NO_6Na$ 734.26999, found 734.26983.



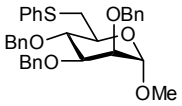
2,3,4-tri-*O*-benzyl-6-deoxy-D-mannopyranose (S3): To a solution of 4.04 g iodine **S2** (7.04 mmol, 1 equiv) in 35 mL DMSO was added 1.60 g $NaBH_4$ (42.23 mmol, 6 equiv) and the reaction was stirred overnight at 100 °C. The mixture was then allowed to cool to room temperature followed by the addition of 35 mL acetone. After refluxing for 1 hour, the mixture was concentrated and partitioned between EtOAc and water and the organic layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, evaporated and coevaporated with toluene. The crude product was dissolved in 35 mL Ac_2O and the pH was adjusted to approximately 1 by the addition of H_2SO_4. After stirring at 80°C for 2 nights, the mixture was neutralized by the addition of triethylamine and concentrated *in vacuo*. The residue was taken up in EtOAc, washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The crude acetate was dissolved in 35 mL THF and 2.09 mL piperidine (21.12 mmol, 3 equiv) was added. After stirring for 3 nights, the mixture was partitioned between EtOAc and water and the organic layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography using EtOAc/PE (3/17 → 7/13) gave the title compound **S3** (2.49 g, 5.74 mmol, 81% over 3 steps). Spectroscopic data were in accordance with known literature data.[3]



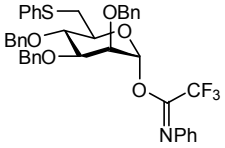
2,3,4-tri-*O*-benzyl-6-deoxy-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (7): To a solution of 872 mg hemiacetal **S3** (2.01 mmol, 1 equiv.) in 9.5 mL acetone and 0.5 mL H_2O were added 981 mg Cs_2CO_3 (3.01 mmol, 1.5 equiv.) and 912 µL ClC(C=NPh)CF_3 (6.02 mmol, 3 equiv.). When TLC analysis showed complete consumption of the starting material, the mixture was filtered over celite and the filtrate was evaporated. Purification of the crude product by flash column chromatography using EtOAc/PE (1/44 → 1/19) yielded 886 mg of the title imidate (1.46 mmol, 73%). Rf 0.80 (EtOAc/PE, 1/4, v/v); $[\alpha]_D^{22}$ -2 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3036, 1710, 1599, 1498, 1490, 1454, 1116, 730, 693; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.36 – 7.10 (m, 17H,

2. Tamura, J.-i.; Horito, S.; Yoshimura, J.; Hashimoto, H. *Carbohydr. Res.* **1990**, *207*, 153-165.
3. Hirooka, M.; Yoshimura, A.; Saito, L.; Ikawa, F.; Uemoto, Y.; Koto, S.; Takabatake, A.; Taniguchi, A.; Shinoda, Y.; Morinaga, A. Bull. *Chem. Soc. Jpn.* **2003**, *76*, 1409-1421.

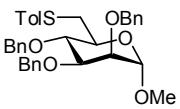
H_{arom}), 7.06 (t, *J* = 7.4 Hz, 1H, H_{arom}), 6.74 (d, *J* = 7.8 Hz, 2H, H_{arom}), 6.10 (br s, 1H, H-1), 4.91 (d, *J* = 11.0 Hz, 1H, CH_2 benzyl), 4.73 – 4.50 (m, 5H, CH_2 benzyl), 3.94 – 3.76 (m, 3H, H-5, H-3, H-2), 3.68 (t, *J* = 9.2 Hz, 1H, H-4), 1.33 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 143.7, 138.5, 138.3, 137.9 (C_q), 129.2, 128.7, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 126.3, 124.3, 120.7, 119.5 (CH_{arom}), 96.0 (C-1), 79.8 (C-4), 79.1 (C-3), 75.3 (CH_2 benzyl), 74.1 (C-2), 72.9, 72.7 (CH_2 benzyl), 71.1 (C-5), 18.0 (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 96.0 (J_{C1-H1} = 175.1 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{35}H_{34}F_3NO_5Na$ 628.22813, found 628.22764.



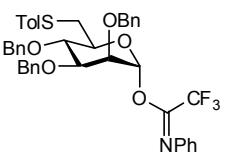
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-α-D-mannopyranoside (S4): Iodine **S2** (287 mg, 500 µmol) was treated with thiophenol according to the general procedure delivering 6-phenylmannoside **S4** (248 mg, 445 µmol, 89%). Flash column chromatography eluent: EtOAc/PE (0/1 → 1/4). R_f 0.49 (EtOAc/PE, 1/9, v/v); $[\alpha]_D^{22}$ +17 (c 2.0, CH_2Cl_2); IR (neat, cm^{-1}) 3030, 2912, 1584, 1497, 1482, 1454, 1439, 1065, 732, 695; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.50 – 6.95 (m, 20H, H_{arom}), 4.97 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.76 – 4.64 (m, 3H, CH_2 benzyl, H-1), 4.64 – 4.53 (m, 3H, CH_2 benzyl), 3.91 – 3.71 (m, 4H, H-3, H-4, H-2, H-5), 3.42 (dd, *J* = 13.4, 1.7 Hz, 1H, H-6), 3.27 (s, 3H, CH_3 OMe), 3.02 (dd, *J* = 13.4, 8.6 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.3, 138.2, 138.1 (C_q), 137.0, 128.7, 128.4, 128.3, 128.2, 127.8, 127.7, 127.5, 125.4 (CH_{arom}), 98.7 (C-1), 80.1 (C-3), 77.7 (C-4), 75.0 (CH_2 benzyl), 74.4 (C-2), 72.6, 71.9 (CH_2 benzyl), 70.9 (C-5), 54.6 (CH_3 OMe), 35.6 (C-6); HRMS $[M+Na]^+$ calcd for $C_{34}H_{36}O_5SNa$ 579.21757, found 579.21688.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (8): 6-*S*-phenyl-6-thio-α-D-mannopyranoside **S4** (248 mg, 445 µmol) was converted according to the general procedure to the title imidate (299 mg, 419 µmol, 94% over 3 steps) with trace amounts of its β configured epimer. R_f 0.46 (toluene); IR (neat, cm^{-1}) 3033, 2872, 1718, 1598, 1490, 1454, 1116, 736, 693; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 7.39 – 6.99 (m, 23H, H_{arom}), 6.77 (d, *J* = 7.7 Hz, 2H, H_{arom}), 6.15 (br s, 1H, H-1), 4.92 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.70 – 4.54 (m, 5H, CH_2 benzyl), 4.00 – 3.90 (m, 2H, H-4, H-5), 388 – 3.80 (m, 2H, H-3, H-2), 3.37 (d, *J* = 13.1 Hz, 1H, H-6), 3.11 – 2.99 (m, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 143.6, 138.3, 138.1, 137.8, 136.8 (C_q), 129.8, 129.5, 128.8, 128.7, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 126.1, 124.3, 119.5 (CH_{arom}), 95.4 (C-1), 79.3 (C-3), 77.1 (C-4), 75.2 (CH_2 benzyl), 74.1 (C-5), 73.9 (C-2), 72.9, 72.7 (CH_2 benzyl), 36.5 (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 95.4 (J_{C1-H1} = 176.1 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{42}H_{38}F_3NO_5SNa$ 736.23150, found 736.23161.

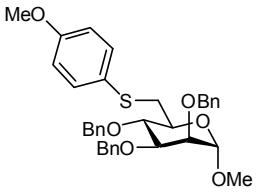


Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-α-D-mannopyranoside (S5): Iodine **S2** (287 mg, 500 µmol) was treated with thiocresol according to the general procedure delivering 6-tolylmannoside **S5** (267 mg, 468 µmol, 94%). Flash column chromatography eluent: EtOAc/PE (0/1 → 1/4). R_f 0.52 (EtOAc/PE, 1/9, v/v); $[\alpha]_D^{22}$ +17 (c 2.0, CH_2Cl_2); IR (neat, cm^{-1}) 2913, 1495, 1454, 1067, 735, 697; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.39 – 7.18 (m, 17H, H_{arom}), 7.01 (d, *J* = 8.0 Hz, 2H, H_{arom}), 4.96 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.75 – 4.66 (m, 3H, CH_2 benzyl, H-1), 4.62 – 4.53 (m, 3H, CH_2 benzyl), 3.88 – 3.71 (m, 4H, H-3, H-4, H-2, H-5), 3.39 (dd, *J* = 13.4, 1.9 Hz, 1H, H-6), 3.29 (s, 3H, CH_3 OMe), 3.01 (dd, *J* = 13.4, 8.7 Hz, 1H, H-6), 2.26 (s, 3H, CH_3 Tol); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.6, 138.5, 138.4, 135.8, 133.5 (C_q), 129.7, 129.5, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 99.0 (C-1), 80.4 (C-3), 78.0 (C-4), 75.3 (CH_2 benzyl), 74.7 (C-2), 72.9, 72.2 (CH_2 benzyl), 71.2 (C-5), 54.8 (CH_3 OMe), 36.7 (C-6), 21.1 (CH_3 Tol); HRMS $[M+Na]^+$ calcd for $C_{35}H_{38}O_5SNa$ 593.23322, found 593.23261.

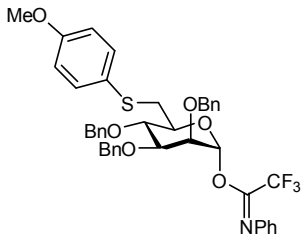


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (9): 6-*S*-*p*-tolyl-6-thio-α-D-mannopyranoside **S5** (267 mg, 468 µmol) was converted according to the general procedure to the title imidate **9** (333 mg, 458 µmol, 98% over 3 steps) with trace amounts of its β

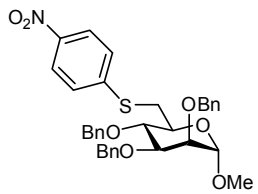
configured epimer. R_f 0.51 (toluene); IR (neat, cm^{-1}) 3031, 2920, 1714, 1598, 1490, 1454, 1118, 735, 694; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 7.36 – 7.16 (m, 19H, H_{arom}), 7.07 (t, *J* = 7.4 Hz, 1H, H_{arom}), 7.02 (d, *J* = 8.0 Hz, 2H, H_{arom}), 6.77 (d, *J* = 7.7 Hz, 2H, H_{arom}), 6.16 (br s, 1H, H-1), 4.91 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.68 – 4.53 (m, 5H, CH_2 benzyl), 3.96 – 3.88 (m, 2H, H-4, H-5), 3.88 – 3.80 (m, 2H, H-3, H-2), 3.33 (d, *J* = 13.1 Hz, 1H, H-6), 3.02 (dd, *J* = 13.6, 7.0 Hz, 1H, H-6), 2.27 (s, 3H, CH_3 Tol); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 143.7, 138.3, 138.2, 137.8, 136.3, 133.0 (C_q), 130.7, 130.4, 129.6, 129.5, 129.1, 128.7, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 124.3, 119.5 (CH_{arom}), 95.4 (C-1), 79.3 (C-3), 77.1 (C-4), 75.2 (CH_2 benzyl), 74.1 (C-5), 74.0 (C-2), 72.9, 72.7 (CH_2 benzyl), 37.2 (C-6), 20.9 (CH_3 Tol); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 95.4 ($J_{C1\text{-}H1}$ = 178.1 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{42}H_{40}F_3NO_5SNa$ 750.24715, found 750.24723.



Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-α-D-mannopyranoside (S6): Iodine **S2** (287 mg, 500 µmol) was treated with *p*-methoxythiophenol according to the general procedure delivering 6-*p*-methoxymannoside **S6** (271 mg, 462 µmol, 92%). Flash column chromatography eluent: EtOAc/PE (0/1 → 1/4). R_f 0.31 (EtOAc/PE, 1/9, v/v); $[\alpha]_D^{22}$ +17 (c 2.0, CH_2Cl_2); IR (neat, cm^{-1}) 3030, 2910, 1593, 1494, 1454, 1243, 1066, 735, 697; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.39 – 7.20 (m, 17H, H_{arom}), 6.80 – 6.73 (m, 2H, H_{arom}), 4.94 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.75 – 4.66 (m, 3H, CH_2 benzyl, H-1), 4.59 – 4.54 (m, 3H, CH_2 benzyl), 3.87 – 3.72 (m, 4H, H-3, H-4, H-2, H-5), 3.71 (s, 3H, CH_3 PhOMe), 3.35 – 3.25 (m, 4H, H-6, CH_3 OMe), 3.00 (dd, *J* = 13.4, 8.6 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 158.7, 138.6, 138.5, 138.4 (C_q), 132.5, 128.5, 128.0, 127.8, 127.7 (CH_{arom}), 127.4 (C_q), 114.7 (CH_{arom}), 98.9 (C-1), 80.4 (C-3), 78.0 (C-4), 75.2 (CH_2 benzyl), 74.7 (C-2), 72.8, 72.2 (CH_2 benzyl), 71.3 (C-5), 55.4 (CH_3 PhOMe), 54.9 (CH_3 OMe), 38.1 (C-6); HRMS $[M+Na]^+$ calcd for $C_{35}H_{38}ClO_6SNa$ 609.22813, found 609.22768.

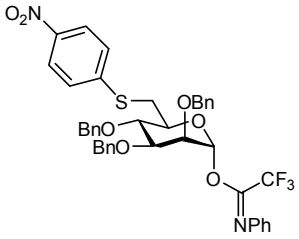


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (10): 6-*S*-*p*-methoxyphenyl-6-thio-α-D-mannopyranoside **S6** (271 mg, 462 µmol) was converted according to the general procedure to the title imidate **10** (325 mg, 437 µmol, 95% over 3 steps) with trace amounts of its β configured epimer. R_f 0.37 (toluene); IR (neat, cm^{-1}) 3034, 2930, 1714, 1596, 1494, 1454, 1118, 736, 695; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 7.38 – 7.18 (m, 19H, H_{arom}), 7.08 (t, *J* = 7.5 Hz, 1H, H_{arom}), 6.81 – 6.73 (m, 4H, H_{arom}), 6.16 (br s, 1H, H-1), 4.90 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.68 – 4.54 (m, 5H, CH_2 benzyl), 3.94 – 3.88 (m, 2H, H-4, H-5), 3.87 – 3.80 (m, 2H, H-3, H-4), 3.73 (s, 3H, CH_3 OMe), 3.26 (dd, *J* = 13.8, 1.9 Hz, 1H, H-6), 2.98 (dd, *J* = 13.7, 7.2 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 159.2, 143.7, 138.3, 138.1, 137.8 (C_q), 133.6, 133.4, 128.7, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 127.0 (C_q), 124.3, 119.5, 114.7 (CH_{arom}), 95.5 (C-1), 79.2 (C-3), 77.1 (C-4), 75.1 (CH_2 benzyl), 74.1 (C-5), 73.9 (C-2), 72.9, 72.7 (CH_2 benzyl), 55.3 (CH_3 OMe), 38.4 (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 95.5 ($J_{C1\text{-}H1}$ = 176.1 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{42}H_{40}F_3NO_6SNa$ 766.24206, found 766.24223.

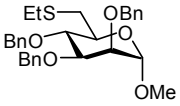


Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-α-D-mannopyranoside (S7): Iodine **S2** (5.00 g, 8.70 mmol) was treated with *p*-nitrothiophenol according to the general procedure delivering 6-thiomannoside **11** (3.75 g, 6.23 mmol, 72%). Flash column chromatography eluent: EtOAc/PE (0/1 → 3/7). R_f 0.30 (EtOAc/PE, 1/9, v/v); $[\alpha]_D^{22}$ +12 (c 2.0, CH_2Cl_2); IR (neat, cm^{-1}) 3031, 2911, 1579, 1508, 1480, 1454, 1335, 1065, 737, 697; ^{1}H NMR (300 MHz, $CDCl_3$, HH-COSY, HSQC) δ 8.01 – 7.97 (m, 2H, H_{arom}), 7.49 – 7.12 (m, 17H, H_{arom}), 5.05 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.78 – 4.63 (m, 5H, CH_2 benzyl, H-1), 4.61 (s, 2H, CH_2 benzyl), 3.91 – 3.81 (m, 2H, H-3, H-4), 3.81 – 3.78 (m, 1H, H-2), 3.78 – 3.70 (m, 1H, H-5), 3.42 (dd, *J* =

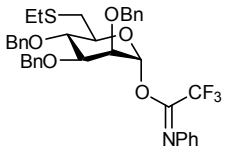
13.5, 1.7 Hz, 1H, H-6), 3.25 (s, 3H, CH_3 OMe), 3.02 (dd, *J* = 13.6, 8.8 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$, HH-COSY, HSQC) δ 147.7, 144.7, 138.1, 138.0 (C_q), 128.5, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 126.0, 124.3, 123.7 (CH_{arom}), 98.9 (C-1), 80.1 (C-3), 77.5 (C-4), 75.2 (CH_2 benzyl), 74.3 (C-2), 72.8, 71.9 (CH_2 benzyl), 70.9 (C-5), 54.7 (CH_3 OMe), 34.0 (C-6); HRMS $[M+Na]^+$ calcd for $C_{34}H_{35}NO_7SNa$ 624.20264, found 624.20243.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (11): 6-*S*-*p*-nitrophenyl-6-thio-α-D-mannopyranoside **S7** (188 mg, 312 µmol) was converted according to the general procedure to the title imidate **11** (192 mg, 253 µmol, 81% over 3 steps) with trace amounts of its β configured epimer. Rf 0.43 (toluene); IR (neat, cm^{-1}) 3031, 2926, 1714, 1596, 1581, 1512, 1455, 1336, 1116, 741, 694; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 7.99 (d, *J* = 8.8 Hz, 2H, H_{arom}), 7.40 – 7.19 (m, 19H, H_{arom}), 7.09 (t, *J* = 7.3 Hz, 1H, H_{arom}), 6.72 (d, *J* = 7.7 Hz, 2H, H_{arom}), 6.09 (br s, 1H, H-1), 5.00 (d, *J* = 11.3 Hz, 1H, CH_2 benzyl), 4.72 – 4.54 (m, 5H, CH_2 benzyl), 4.00 – 3.85 (m, 3H, H-4, H-5, H-3), 3.83 (br s, 1H, H-2), 3.49 – 3.34 (m, 1H, H-6), 3.06 (dd, *J* = 13.8, 7.1 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 147.2, 143.4, 138.1, 137.9, 137.7 (C_q), 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.0, 124.5, 123.8, 119.4 (CH_{arom}), 95.2 (C-1), 79.3 (C-3), 76.9 (C-4), 75.4 (CH_2 benzyl), 74.0 (C-5), 73.9 (C-2), 73.1, 72.7 (CH_2 benzyl), 34.6. (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 95.2 ($J_{C1\text{-}H1}$ = 177.3 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{42}H_{40}F_3NO_6SNa$ 766.24206, found 766.24209.

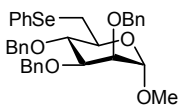


Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-α-D-mannopyranoside (S8): To a solution of 3.22 g iodine **S2** (5.61 mmol, 1 equiv) in 63 mL DMF was added 0.49 mL ethanethiol (6.55 mmol, 1.2 equiv) and 270 mg NaH (60% in mineral oil, 6.75 mmol, 1.2 equiv). The reaction was stirred for 1 hour at room temperature and quenched by the addition of acetic acid. The mixture was partitioned between Et_2O and water and the organic layer was washed with water, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography using EtOAc/PE (1/44 → 1/4) gave the title compound **S8** (2.66 g, 4.42 mmol, 79%). Rf 0.56 (EtOAc/PE, 1/9, v/v); $[\alpha]_D^{22}$ +27 (c 2.0, CH_2Cl_2); IR (neat, cm^{-1}) 2916, 1497, 1454, 1055, 732, 696; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.39 – 7.22 (m, 15H, H_{arom}), 4.96 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.76 – 4.66 (m, 3H, H-1, CH_2 benzyl), 4.64 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.59 (s, 2H, CH_2 benzyl), 3.87 (dd, *J* = 9.1, 2.9 Hz, 1H, H-3), 3.82 (t, *J* = 9.1 Hz, 1H, H-4), 3.77 (dd, *J* = 2.8, 1.9 Hz, 1H, H-2), 3.72 (td, *J* = 8.8, 2.0 Hz, 1H, H-5), 3.33 (s, 3H, CH_3 OMe), 2.95 (dd, *J* = 13.5, 2.1 Hz, 1H, H-6), 2.70 (dd, *J* = 13.5, 8.6 Hz, 1H, H-6), 2.60 (q, *J* = 7.4 Hz, 2H, CH_2 ethyl), 1.23 (t, *J* = 7.4 Hz, 3H, CH_2 ethyl); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.4, 138.3, 138.1 (C_q), 128.2, 127.8, 127.7, 127.5, 127.4 (CH_{arom}), 98.6 (C-1), 80.1 (C-3), 77.7 (C-4), 75.1 (C-2), 74.5 (C-2), 72.5 (CH_2 benzyl), 72.2 (C-5), 71.9 (CH_2 benzyl), 54.5 (CH_3 OMe), 33.4 (C-6), 26.7 (CH_2 ethyl), 14.7 (CH_3 ethyl); HRMS $[M+Na]^+$ calcd for $C_{30}H_{36}O_5SNa$ 531.21757, found 531.21699.

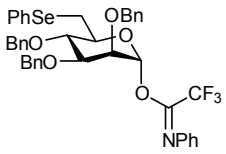


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (12): 6-*S*-ethyl-6-thio-α-D-mannopyranoside **S8** (244 mg, 480 µmol) was converted according to the general procedure to the title imidate **12** (288 mg, 432 µmol, 90% over 3 steps) with trace amounts of its β configured epimer. Rf 0.47 (toluene); IR (neat, cm^{-1}) 2926, 1714, 1598, 1490, 1454, 1117, 735, 694; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 7.37 – 7.18 (m, 17H, H_{arom}), 7.08 (t, *J* = 7.5 Hz, 1H, H_{arom}), 6.77 (d, *J* = 7.6 Hz, 2H, H_{arom}), 6.14 (br s, 1H, H-1), 4.93 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.73 – 4.56 (m, 5H, CH_2 benzyl), 4.00 – 3.85 (m, 3H, H-4, H-5, H-3), 3.82 (t, *J* = 2.5 Hz, 1H, H-2), 2.94 (dd, *J* = 14.1, 2.2 Hz, 1H, H-6), 2.71 (dd, *J* = 14.1, 7.1 Hz, 1H, H-6), 2.59 (q, *J* = 7.4 Hz, 2H, CH_2 ethyl), 1.21 (t, *J* = 7.4 Hz, 3H, , CH_3 ethyl); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 143.7, 138.4, 138.2, 137.9 (C_q), 128.7, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 124.3, 119.5 (CHa_{rom}), 95.5 (C-1), 79.2 (C-3), 77.1 (C-4), 75.5 (C-5), 75.2 (CH_2 benzyl), 74.1 (C-2), 72.9, 72.7

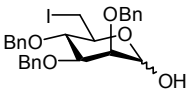
(CH_2 benzyl), 33.5 (C-6), 26.9 (CH_2 ethyl), 14.7 (CH_3 ethyl); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 95.5 ($J_{C1\text{-}H1}$ = 179.1 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{37}H_{38}F_3NO_5SNa$ 688.23150, found 688.23146.



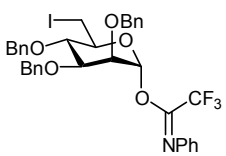
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*Se*-phenyl-6-seleno-α-D-mannopyranoside (S9): Iodine **S2** (287mg, 500 µmol) was treated with phenylselenol according to the general procedure delivering 6-selenomannoside **S9** (301 mg, 499 µmol, quant). Flash column chromatography eluent: EtOAc/PE (0/1 → 3/17). Rf 0.56 (EtOAc/PE, 1/9, v/v); $[\alpha]_D^{22}$ +21 (c 2.0, CH_2Cl_2); IR (neat, cm^{-1}) 3030, 2908, 1579, 1497, 1479, 1438, 1454, 1062, 732, 696; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.50 – 7.11 (m, 20H, H_{arom}), 4.95 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.76 – 4.66 (m, 3H, H-1, CH_2 benzyl), 4.61 – 4.56 (m, 3H, CH_2 benzyl), 3.88 – 3.79 (m, 3H, H-3, H-4, H-5), 3.78 (dd, *J* = 2.8, 1.9 Hz, 1H, H-2), 3.36 (dd, *J* = 12.3, 1.6 Hz, 1H, H-6), 3.31 (s, 3H, CH_3 OMe), 3.11 – 3.01 (m, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.6, 138.5, 138.6 (C_q), 132.0 (CH_{arom}), 131.4 (C_q), 129.1, 128.5, 128.1, 128.0, 127.8, 127.7, 126.6 (CH_{arom}), 99.0 (C-1), 80.4 (C-3), 78.8 (C-4), 75.32 (CH_2 benzyl), 74.8 (C-2), 72.9 (CH_2 benzyl), 72.2 (CH_2 benzyl), 71.9 (C-5), 54.9 (CH_3 OMe), 30.2 (C-6); HRMS $[M+Na]^+$ calcd for $C_{34}H_{36}O_5SeNa$ 627.16202, found 627.16156.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-*Se*-phenyl-6-seleno-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (13): 6-Se-phenyl-6-seleno-α-D-mannopyranoside **S9** (302 mg, 500 µmol) was converted according to the general procedure to the title imidate **13** (292 mg, 384 µmol, 77% over 3 steps) with trace amounts of its β configured epimer. Rf 0.57 (toluene); IR (neat, cm^{-1}) 3030, 2870, 1714, 1598, 1490, 1454, 1117, 732, 692; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 7.56 – 7.42 (m, 2H, H_{arom}), 7.39 – 7.11 (m, 20H, H_{arom}), 7.08 (t, *J* = 7.4 Hz, 1H, H_{arom}), 6.79 (d, *J* = 7.4 Hz, 2H, H_{arom}), 6.15 (br s, 1H, H-1), 4.90 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.72 – 4.53 (m, 5H, CH_2 benzyl), 4.02 – 3.95 (m, 1H, H-5), 3.92 (t, *J* = 8.8 Hz, 1H, H-4), 3.86 (dd, *J* = 8.5, 3.0 Hz, 1H, H-3), 3.84 – 3.78 (m, 1H, H-2), 3.33 (dd, *J* = 12.6, 2.6 Hz, 1H, H-6), 3.06 (dd, *J* = 12.6, 7.6 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 143.7, 138.3, 138.2, 137.9 (C_q), 132.8 (CH_{arom}), 130.9 (C_q), 129.0, 128.7, 128.4, 128.0, 127.9, 127.8, 127.7, 126.8, 124.3, 119.5 (CH_{arom}), 95.4 (C-1), 79.2 (C-3), 77.9 (C-4), 75.2 (CH_2 benzyl), 74.6 (C-5), 74.1 (C-2), 72.9, 72.7 (CH_2 benzyl), 30.1 (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 95.4 ($J_{C1\text{-}H1}$ = 177.1 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{41}H_{38}F_3NO_5SeNa$ 784.17595, found 784.17586.

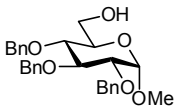


2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranose (S10): The pH of a solution of 3.00 g iodine **S2** (5.23 mmol, 1 equiv) in 25 mL Ac_2O was adjusted to approximately 1 by the addition of H_2SO_4 at 0°C. After stirring at ambient temperature for 7 hours, the mixture was neutralized by the addition of triethylamine, concentrated *in vacuo* and coevaporated with toluene. The crude acetate was dissolved in 30 mL THF and 1.55 mL piperidine (15.69 mmol, 3 equiv) was added. After stirring overnight at room temperature, the mixture was partitioned between EtOAc and water and the organic layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography using EtOAc/PE (1/9 → 1/2) gave the title compound **S10** (2.37 g, 4.24 mmol, 81% over 2 steps). Rf 0.29 (EtOAc/PE, 1/4, v/v); IR (neat, cm^{-1}) 3404, 3031, 2862, 1497, 1454, 1100, 736, 697; NMR data of the major anomer: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.42 – 7.22 (m, 15H, H_{arom}), 5.24 (br s, 1H, H-1), 4.98 (d, *J* = 10.9 Hz, 1H, CH_2 benzyl), 4.79 – 4.66 (m, 3H, CH_2 benzyl), 4.62 (s, 2H, CH_2 benzyl), 3.97 (dd, *J* = 9.2, 3.0 Hz, 1H, H-3), 3.85 – 3.79 (m, 2H, H-4, H-2), 3.72 – 3.67 (m, 1H, H-5), 3.52 (dd, *J* = 10.6, 2.5 Hz, 1H, H-6), 3.36 (dd, *J* = 10.6, 6.8 Hz, 1H, H-6), 2.85 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.2 (C_q), 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8 , 127.6 (CH_{arom}), 92.7 (C-1), 79.2 (C-3), 78.5 (C-4), 75.4 (CH_2 benzyl), 74.8 (C-2), 72.7, 72.1 (CH_2 benzyl), 71.3 (C-5), 7.8 (C-6); HRMS $[M+Na]^+$ calcd for $C_{27}H_{29}IO_5Na$ 583.09519, found 583.09522.

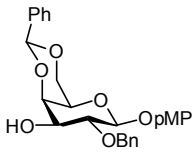


2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (14): To a solution of 1.04 g hemiacetal **S10** (1.85

mmol, 1 equiv.) in 8.55 mL acetone and 0.45 mL H_2O were added 904 mg Cs_2CO_3 (2.78 mmol, 1.5 equiv) and 841 µL $ClC(C=NPh)CF_3$ (5.55 mmol, 3 equiv). When TLC analysis showed complete consumption of the starting material, the mixture was filtered over celite and the filtrate was evaporated. Purification of the crude product by flash column chromatography using EtOAc/PE (1/44 → 1/19) yielded 1.17 mg of imidate **14** (1.60 mmol, 86%) with trace amounts of its β configured epimer. Rf 0.83 (EtOAc/PE, 1/4, v/v); IR (neat, cm^{-1}) 3031, 2920, 1714, 1598, 1489, 1454, 1117, 737, 695; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 7.40 – 7.17 (m, 17H, H_{arom}), 7.08 (t, *J* = 7.5 Hz, 1H, H_{arom}), 6.79 (d, *J* = 7.6 Hz, 2H, H_{arom}), 6.18 (br s, 1H, H-1), 4.95 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.74 – 4.55 (m, 5H, CH_2 benzyl), 3.94 – 3.83 (m, 2H, H-3, H-4), 3.82 (br s, 1H, H-2), 3.63 – 3.55 (m, 1H, H-5), 3.49 (dd, *J* = 10.7, 2.6 Hz, 1H, H-6), 3.33 (dd, *J* = 10.7, 6.5 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 143.5, 138.2, 138.0, 137.8 (C_q), 128.8, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 124.4, 119.5 (CH_{arom}), 95.3 (C-1), 78.9 (C-3), 78.1 (C-4), 75.4 (CH_2 benzyl), 74.0 (C-2), 73.9 (C-5), 72.9, 72.7 (CH_2 benzyl), 6.0 (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$, T = 333 K) δ 95.3 ($J_{C1\text{-}H1}$ = 175.8 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{35}H_{33}F_3INO_5Na$ 754.12477, found 754.12482.



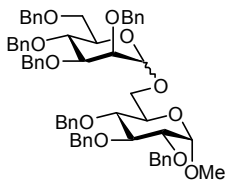
Methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (15a): A solution of methyl α-D-mannopyranoside (9.71 g, 50.0 mmol) and TrCl (15.33 g, 55.0 mmol) in pyridine (250 mL) was heated to 50 °C and stirred overnight. The mixture was quenched by the addition of MeOH (10 mL) and concentrated *in vacuo*. The product was dissolved in EtOAc and washed with H_2O three times. The organic layer was dried over $MgSO_4$ and concentrated. The now obtained yellow oil was dissolved in DMF (250 mL) and BnBr (20 mL, 165 mmol) was added. The mixture was cooled to 0 °C, NaH (60 % in mineral oil, 6.6 g, 165 mmol) was added portion wise and the reaction was left to stir for 24 hours. The mixture was then quenched by addition of MeOH (20 mL). DMF was removed by diluting the mixture with Et_2O and washing it three times with H_2O. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The remaining brown oil was dissolved in a mixture of DCM (50 mL) and MeOH (200 mL). To this solution a catalytic amount of *p*-toluenesulfonic acid monohydrate was added until the pH was approximately 1 and the reaction was left to stir at room temperature over the weekend. After neutralization with Et_3N the solvents were removed. The remaining oil was purified by column chromatography using EtOAc/PE (1/4 → 2/3) as the eluent to give 17.33 g of the title compound **15a** (37.3 mmol, 75 % over 3 steps) as a yellow oil. Spectroscopic data were in accordance with known literature data.[4]



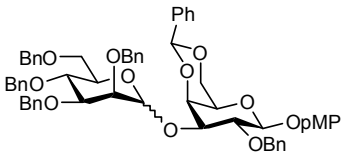
4-Methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (15b): 4-Methoxyphenyl β-D-galactopyranoside[5] (5.47g, 19.1 mmol, 1 equiv) was stirred under argon for 48 hours at room temperature in 100 mL 2,2-dimethoxypropane with a catalytic amount of (±)-10-camphorsulphonic acid. The mixture was neutralized by the addition of triethylamine and the volatile material was evaporated. The residue was dissolved in 100 mL dry tetrahydrofuran and 9.1 mL benzyl bromide (76 mmol, 4 equiv) and 1.53 g sodium hydride (60% dispersion in oil, 38.2 mmol, 2 equiv) were added and the mixture was stirred at 45 °C under argon until TLC analysis showed complete conversion of the starting material. Methanol and then water were added at 0 °C to destroy the excess of sodium hydride. The mixture was extracted twice with ether, and the combined extracts were dried over $MgSO_4$ and concentrated. A solution of the residue in 100 mL methanol was treated with a catalytic amount of (±)-10-camphorsulphonic acid and the reaction was monitored by TLC. Next, triethylamine was used to neutralize the mixture and the solvent was evaporated. The crude product was filtered through a plug of silica gel using EtOAc/PE (9/1) as the eluent. Rf 0.24 (EtOAc/PE, 17/3, v/v) ^1H NMR (400 MHz, $CDCl_3$/MeOD) δ 7.44 – 7.25 (m, 5H, H_{arom}), 7.02 (d, *J* = 9.1 Hz, 2H, H_{arom}), 6.84 (d, *J* = 9.1 Hz, 2H, H_{arom}), 5.02 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.88 (d, *J* = 7.7 Hz, 1H, H-1), 4.82 (d, *J* =

4. El-Badri, M. H.; Willenbring, D.; Tantillo, D. J.; Gervay-Hague, J. *J. Org. Chem.* **2007**, *72*, 4663-4672.
5. McGill, N. W.; Williams, S. J. *J. Org. Chem.* **2009**, *74*, 9388-9398.

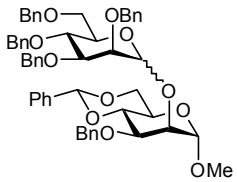
11.1 Hz, 1H, CH_2 benzyl), 3.96 (d, *J* = 3.3 Hz, 1H, H-4), 3.88 – 3.73 (m, 6H, H-6, CH_3 OMe, H-2), 3.67 (dd, *J* = 9.6, 3.4 Hz, 1H, H-3), 3.59 (t, *J* = 6.0 Hz, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$/MeOD) δ 154.9, 151.2, 138.0 (C_q), 128.1, 127.9, 127.5, 117.8, 114.3 (CH_{arom}), 102.5 (C-1), 79.0 (C-2), 74.8 (CH_2 benzyl), 74.6 (C-5), 72.8 (C-3), 68.5 (C-4), 60.9 (C-6), 55.3 (CH_3 OMe). After evaporation of the solvent, the crude product was dissolved in 45 mL acetonitrile and was treated with 1.93 mL benzaldehyde dimethylacetal (12.82 mmol, 0.67 equiv) and 325 mg *p*-toluenesulfonic acid monohydrate (1.71 mmol, 0.09 equiv). Upon complete conversion the mixture was neutralized by the addition of triethylamine and the solvent was removed. Crystallization from EtOAc/PE yielded 3.31 g of the title compound (7.13 mmol 37% over 4 steps). Rf 0.39 (EtOAc/PE, 1/1, v/v); mp = 161.1 °C; $[\alpha]_D^{22}$ -38 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3454, 2878, 2361, 2342, 1507, 1455, 1216, 1004, 826, 730; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.59 – 7.23 (m, 10H), 7.06 (d, *J* = 9.0 Hz, 2H, H_{arom}), 6.83 (d, *J* = 9.0 Hz, 2H, H_{arom}), 5.58 (s, 1H, CH benzylidene), 5.05 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.89 (d, *J* = 7.5 Hz, 1H, H-1), 4.82 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.36 (d, *J* = 12.3 Hz, 1H, H-6), 4.26 (d, *J* = 3.2 Hz, 1H, H-4), 4.09 (d, *J* = 11.5 Hz, 1H, H-6), 3.94 – 3.81 (m, 2H, H-2, H-3), 3.78 (s, 3H, CH_3 OMe), 3.53 (s, 1H, H-5), 2.56 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 155.4, 151.5, 138.3, 137.5 (Cq), 129.2, 128.4, 128.2, 128.0, 127.8, 126.5, 118.9, 114.5, 103.0 (C-1), 101.5 (CH benzylidene), 79.0 (C-2), 75.3 (CH_2 benzyl), 75.1 (C-4), 72.5 (C-3), 69.1 (C-6), 66.6 (C-5), 55.6 (C-6); HRMS $[M+Na]^+$ calcd for $C_{27}H_{28}O_7Na$ 487.17272, found 487.17223.



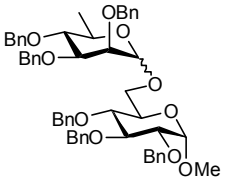
2,3,4,6-Tetra-*O*-benzyl-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (16a): Donor **6** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 204 mg (207 µmol, 94%) of the title compound **16a** as an epimeric mixture (α/β 1/3.5). Spectroscopic data were in accordance with previously published data.[6]



2,3,4,6-Tetra-*O*-benzyl-D-mannopyranosyl-(1→3)-(*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (16b): Donor **6** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 191 mg (194 µmol, 88%) of the title compound **16b** as an epimeric mixture (α/β 1/1). Spectroscopic data were in accordance with previously published data.[6]

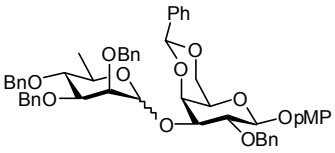


2,3,4,6-Tetra-*O*-benzyl-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (16c): Donor **6** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 195 mg (218 µmol, 99%) of the title compound **16c** as an epimeric mixture (α/β 1/4). Spectroscopic data were in accordance with known literature data.[7]

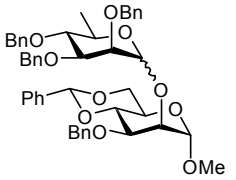


2,3,4-Tri-*O*-benzyl-6-deoxy-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (17a): Donor **7** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 176 mg (200 µmol, 91%) of the title compound **17a** as an epimeric mixture (α/β 1/2.5).
Spectroscopic data were in accordance with previously published data.[6]

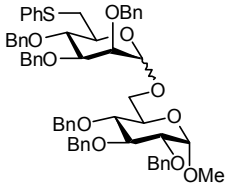
6. Dinkelaar, J.; de Jong, A. R.; van Meer, R.; Somers, M.; Lodder, G.; Overkleeft, H. S.; Codée, J. D. C.; van der Marel, G. A. *J. Org. Chem.* **2009**, *74*, 4982-4991.
7. Baek, J. Y.; Lee, B.-Y.; Jo, M. G.; Kim, K. S. *J. Am. Chem. Soc.* **2009**, *131*, 17705-17713.



2,3,4-Tri-*O*-benzyl-6-deoxy-D-mannopyranosyl-(1→3)-(*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (17b): Donor **7** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 169 mg (191 µmol, 87%) of the title compound as an epimeric mixture (α/β 1/1.5). Spectroscopic data were in accordance with previously published data.[6]



2,3,4-Tri-*O*-benzyl-6-deoxy-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (17c): Donor **7** and acceptor **15c** were coupled according to the general glycosylation procedure to yield 156 mg (198 µmol, 90%) of the title compound **17c** as an epimeric mixture (α/β 1/1). R*f* 0.47, 0.71 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3030, 2912, 1497, 1454, 1071, 733, 695; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC)[8] δ 7.55 – 7.20 (m, 50H), 5.61 (s, 1H), 5.53 (s, 1H), 5.16 (s, 1H), 5.08 – 4.92 (m, 4H), 4.84 (d, *J* = 12.2 Hz, 1H), 4.77 (d, *J* = 11.8 Hz, 1H), 4.74 – 4.68 (m, 2H), 4.67 – 4.56 (m, 6H), 4.55 – 4.48 (m, 4H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.31 – 4.20 (m, 3H), 4.13 – 4.03 (m, 2H), 4.00 – 3.87 (m, 6H), 3.84 – 3.71 (m, 5H), 3.71 – 3.59 (m, 2H), 3.46 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.39 – 3.30 (m, 7H), 1.38 (d, *J* = 6.1 Hz, 3H), 1.35 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC)[8] δ 138.8, 138.7, 138.6, 138.4, 138.3, 138.1, 137.6, 137.5, 128.8, 128.8, 128.6, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 126.1, 126.0, 101.6, 101.4, 101.0, 99.8, 99.7, 99.2, 81.8, 80.4, 79.9, 79.2, 79.1, 78.5, 76.0, 75.7, 75.5, 75.4, 75.1, 73.8, 73.5, 73.2, 72.3, 72.1, 71.9, 71.0, 70.7, 68.9, 68.8, 68.5, 63.9, 63.6, 54.9, 54.8, 18.0, 17.9; ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.0 ($J_{C\text{-}H}$ = 171 Hz), 99.8 ($J_{C\text{-}H}$ = 171 Hz), 99.7 ($J_{C\text{-}H}$ = 153 Hz), 99.2 ($J_{C\text{-}H}$ = 168 Hz); HRMS $[M+Na]^+$ calcd for $C_{48}H_{52}O_{10}Na$ 811.34527, found 811.34492.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (18a): Donor **8** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 196 mg (198 µmol, 90%) of the title compound **18a** as an epimeric mixture (α/β 1/7). R*f* 0.47 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3029, 2918, 1584, 1497, 1482, 1454, 1069, 735, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.50 – 6.95 (m, 35H, H_{arom}), 5.06 – 4.89 (m, 3H, CH_2 benzyl), 4.89 – 4.72 (m, 4H, CH_2 benzyl), 4.72 – 4.41 (m, 6H, H-1, CH_2 benzyl), 4.16 (dd, *J* = 10.2, 1.4 Hz, 1H, H-6), 4.08 (s, 1H, H-1'), 4.03 (t, *J* = 9.2 Hz, 1H, H-3), 3.85 – 3.72 (m, 2H, H-5, H-4'), 3.70 (d, *J* = 2.7 Hz, 1H, H-2'), 3.51 (dd, *J* = 9.7, 3.5 Hz, 1H, H-2), 3.49 – 3.30 (m, 8H, H-4, H-6, H-3', H-6', H-5', CH_3 OMe), 3.04 (dd, *J* = 13.7, 9.1 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.8, 138.5, 138.2, 138.1, 138.0, 137.9, 137.3 (C_q), 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 125.3 (CH_{arom}), 101.2 (C-1'), 97.7 (C-1), 82.1 (C3, C3'), 79.8 (C-2), 77.6, 77.5 (C-4, C-4'), 75.6 (CH_2 benzyl), 75.2 (C-5', CH_2 benzyl), 74.7, 73.7 (CH_2 benzyl), 73.5 (C-2'), 73.2, 71.4 (CH_2 benzyl), 69.5 (C-5), 68.0 (C-6), 55.0 (CH_3 OMe), 35.3 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.2 ($J_{C1'\text{-}H1'}$ = 158.1 Hz, C-1'), 97.7 ($J_{C1\text{-}H1}$ = 166.2 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 3.95 (t, *J* = 9.2 Hz, 0.14H, H-3), 3.27 (s, 0.42H, CH_3 OMe). HRMS $[M+Na]^+$ calcd for $C_{61}H_{64}O_{10}SNa$ 1011.41124, found 1011.41158.

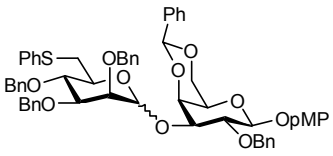
Pre-activation experiment with donor 8 at room temperature: Donor **8** (157 mg, 0.22 mmol, 1 equiv) was coevaporated with toluene, dissolved in 3.0 mL DCM and stirred over 3Å molecular sieves for 30 minutes. The mixture was then cooled to -80 °C after which 21.4 µL TfOH (242 µmol, 1.1 equiv) was added. The mixture was allowed to warm up to room temperature in 15 minutes. Next 153 mg acceptor **15a** (0.33 mmol, 1.5 equiv) and 88 mg 2,6-di-*tert*-butyl-4-methylpyridine (429 µmol, 2 equiv) were added in 1.4 mL DCM and the reaction was stirred overnight at room temperature. The reaction was quenched by the addition of 1mL Et_3N. After filtration over celite, the mixture was washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and

8. Complete assignment of the peaks is omitted due to a 1:1 mixture of anomers.

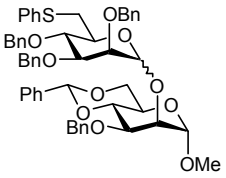
concentrated. Purification by size exclusion chromatography (DCM/MeOH, 1/1, v/v) yielded 169 mg of the coupled product **18a** (171 µmol, 78%, α/β 1/1). NMR data for the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$,HH-COSY, HSQC) δ 7.64 – 6.91 (m, 35H, H_{arom}), 5.00 – 4.94 (m, 2H, CH_2 benzyl), 4.91 (d, *J* = 1.3 Hz, 1H, H-1'), 4.84 – 4.64 (m, 6H, CH_2 benzyl), 4.61 – 4.57 (m, 3H, CH_2 benzyl), 4.51 – 4.45 (m, 2H, H-1, CH_2 benzyl), 3.95 (t, *J* = 9.2 Hz, 1H, H-3), 3.86 – 3.74 (m, 5H, H-2', H-4', H-5', H-3', H-6), 3.69 – 3.58 (m, 2H, H-5, H-6), 3.39 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.36 – 3.30 (m, 2H, H-6', H-4), 3.27 (s, 3H, CH_3 OMe), 2.99 (dd, *J* = 13.2, 7.5 Hz, 1H, H-6'). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.4, 138.2, 138.1, 138.0, 137.2 (C_q), 128.9, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 127.6, 125.3 (CH_{arom}), 97.8 (C-1'), 97.5 (C-1), 82.0 (C-3), 79.9 (C-2), 79.5 (C-2'), 77.7 (C-4, C-4'), 75.7, 75.1, 74.9 (CH_2 benzyl), 74.4 (C-3'), 73.1, 72.5, 71.8 (CH_2 benzyl), 71.0 (C-5'), 69.6 (C-5), 65.6 (C-6), 54.9 (CH_3 OMe), 35.6 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 97.8 ($J_{C1'\text{-}H1'}$ = 170 Hz, C-1'), 97.5 ($J_{C1\text{-}H1}$ = 170 Hz, C-1).

Pre-activation experiment with donor 8 at -80°C: Donor **8** (155 mg, 0.217 mmol, 1 equiv) was coevaporated with toluene, dissolved in 3.5 mL DCM and stirred over 3Å molecular sieves for 30 minutes. The mixture was then cooled to -80 °C after which 21 µL TfOH (239 µmol, 1.1 equiv) was added. The mixture was stirred at -80°C for 15 minutes. Next 303 mg acceptor **15a** (651 µmol, 1.5 equiv) and 90 mg 2,6-di-*tert*-butyl-4-methylpyridine (434 µmol, 2 equiv) were added in 1.0 mL DCM and the reaction was stirred overnight at -60 °C for 3 days. The reaction was quenched by the addition of 1mL Et_3N and the mixture was allowed to warm up to room temperature. After filtration over celite, the mixture was washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification by size exclusion chromatography (DCM/MeOH, 1/1, v/v) yielded 144 mg of the coupled product **18a** (146 µmol, 67%, α/β 1/4).

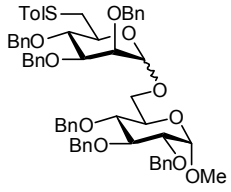
Pre-activation experiment with mannoside 27 at room temperature: Mannoside **27** (123 mg, 226 µmol, 1 equiv) and 4.5 mg Ph_2SO (23 µmol, 0.1 equiv) were coevaporated with toluene, dissolved in 3.0 mL DCM and stirred over 3Å molecular sieves for 30 minutes. Triflic anhydride (41 µL, 249 µmol, 1.1 equiv) was added and the mixture was stirred for 1 minute. Next 158 mg acceptor **15a** (0.34 mmol, 1.5 equiv) and 140 mg 2,6-di-*tert*-butyl-4-methylpyridine (680 µmol, 3 equiv) were added in 1.4 mL DCM and the reaction was stirred overnight at room temperature. The reaction was quenched by the addition of 1mL Et_3N. After filtration over celite, the mixture was washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification by size exclusion chromatography (DCM/MeOH, 1/1, v/v) yielded 94 mg of the coupled product **18a** (95 µmol, 42%, α/β 1/1).



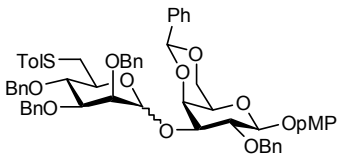
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranosyl-(1→3)-(*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (18b): Donor **8** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 194 mg (196 µmol, 89%) of the title compound **18b** as an epimeric mixture (α/β 1/11). Rf 0.26, 0.43 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3032, 2858, 1584, 1506, 1454, 1060, 732, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.74 – 6.65 (m, 34H, H_{arom}), 5.55 (s, 1H, CH benzylidene), 4.99 – 4.83 (m, 5H, H-1, CH_2 benzyl), 4.63 – 4.55 (m, 2H, H-1', CH_2 benzyl), 4.46 – 4.26 (m, 4H, H-6, CH_2 benzyl), 4.24 (d, *J* = 3.4 Hz, 1H, H-4), 4.08 – 3.97 (m, 2H, H-2, H-6), 3.80 – 3.70 (m, 5H, H-4', H-3, CH_3 OMe), 3.68 (d, *J* = 2.8 Hz, 1H, H-2'), 3.44 – 3.30 (m, 3H, H-5, H-5', H-6'), 3.24 (dd, *J* = 9.3, 2.9 Hz, 1H, H-3'), 3.07 (dd, *J* = 14.1, 9.8 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 155.2, 151.4, 138.5, 138.4, 138.0, 137.9, 137.4 (C_q), 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 126.2, 125.3, 118.7, 114.4 (CH_{arom}), 103.0 (C-1), 102.9 (C-1'), 100.5 (CH benzylidene), 82.5 (C-3'), 78.7 (C-2), 78.1 (C-3), 77.5 (C-4'), 75.8 (C-4), 75.5 (C-5'), 75.2, 73.3 (CH_2 benzyl), 72.4 (C-2'), 71.4 (CH_2 benzyl), 68.8 (C-6), 66.6 (C-5), 55.5 (CH_3 OMe), 35.2 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 103.0 ($J_{C1\text{-}H1}$ = 162 Hz, C-1), 102.9 ($J_{C1'\text{-}H1'}$ = 160 Hz, C-1'); Diagnostic peak from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.43 (s, 0.09H, CH benzylidene); HRMS $[M+Na]^+$ calcd for $C_{60}H_{60}O_{11}Na$ 1011.37485, found 1011.37543.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (18c): Donor **8** and acceptor **15c** were coupled according to the general glycosylation procedure to yield 172 mg (191 µmol, 87%) of the title compound **18c** as an epimeric mixture (α/β 1/5). R_f 0.54, 0.71 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3033, 2905, 1584, 1497, 1482, 1454, 1072, 736, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.66 – 6.87 (m, 30H, H_{arom}), 5.54 (s, 1H, CH benzylidene), 5.11 – 4.88 (m, 4H, CH_2 benzyl), 4.76 (s, 1H, H-1), 4.69 – 4.48 (m, 4H, H-1', CH_2 benzyl), 4.42 – 4.37 (m, 2H, H-2, CH_2 benzyl), 4.28 – 4.23 (m, 1H, H-6), 4.10 (t, *J* = 9.3 Hz, 1H, H-4), 4.01 – 3.93 (m, 2H, H-2', H-3), 3.86 – 3.76 (m, 3H, H-6, H-4', H-5), 3.49 (dd, *J* = 9.1, 2.9 Hz, 1H, H-3'), 3.46 – 3.37 (m, 2H, H-6', H-5'), 3.34 (s, 3H, CH_3 OMe), 2.95 (dd, *J* = 14.0, 9.5 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.8, 138.6, 138.1, 137.9, 137.5, 137.0 (C_q), 128.8, 128.5, 128.3, 128.1, 128.0, 127.9, 127.5, 127.4, 126.1, 125.3 (CH_{arom}), 101.6 (CH benzylidene), 99.1 (C-1'), 98.8 (C-1), 81.8 (C-3'), 78.3 (C-4), 77.5 (C-4'), 75.2 (C-5'), 75.1, 73.6 (CH_2 benzyl), 73.5 (C-3), 73.2 (C-2'), 72.6 (C-2), 71.0, 70.3 (CH_2 benzyl), 68.8 (C-6), 63.8 (C-5), 54.9 (CH_3 OMe), 35.2 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.1 ($J_{C1'-H1'}$ = 155 Hz, C-1'), 98.8 (J_{C1-H1} = 167 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.59 (s, 0.21H, CH benzylidene), 3.17 (s, 0.65H, CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{54}H_{56}O_{10}SNa$ 919.34864, found 919.34870.

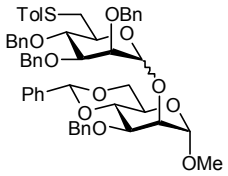


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (19a): Donor **9** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 190 mg (189 µmol, 86%) of the title compound **19a** as an epimeric mixture (α/β 1/5). R_f 0.60 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3030, 2911, 1497, 1489, 1454, 1070, 732, 694; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.61 – 6.73 (m, 34H, H_{arom}), 5.07 – 4.89 (m, 3H, CH_2 benzyl), 4.89 – 4.72 (m, 4H, CH_2 benzyl), 4.72 – 4.41 (m, 6H, H-1, CH_2 benzyl), 4.19 (dd, *J* = 10.3, 1.9 Hz, 1H, H-6), 4.08 (s, 1H, H-1'), 4.03 (t, *J* = 9.2 Hz, 1H, H-3), 3.85 – 3.71 (m, 2H, H-5, H-4'), 3.70 (d, *J* = 2.9 Hz, 1H, H-2'), 3.52 (dd, *J* = 9.7, 3.5 Hz, 1H, H-2), 3.49 – 3.42 (m, 2H, H-6, H-4), 3.42 – 3.25 (m, 6H, H-3', CH_3 OMe, H-6', H-5'), 3.02 (dd, *J* = 14.0, 9.6 Hz, 1H, H-6'), 2.27 (s, 3H, CH_3 Me); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.7, 138.5, 138.1, 137.9, 135.4, 133.4 (C_q), 129.5, 129.4, 129.2, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4 (CH_{arom}), 101.1, 97.7, 82.1, 82.0 (C-3, C-3'), 79.7 (C-2), 77.6, 77.4 (C-4, C-4'), 75.6, 75.1 (CH_2 benzyl), 75.1 (C-5'), 74.7, 73.6 (CH_2 benzyl), 73.4 (C-2'), 73.2, 71.4 (CH_2 benzyl), 69.5 (C-5), 67.9 (C-6), 55.0 (CH_3 OMe), 36.0 (C-6'), 20.9 (CH_3 Me); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.1 ($J_{C1'-H1'}$ = 154.6 Hz, C-1'), 97.7 (J_{C1-H1} = 167.1 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 3.96 (t, *J* = 9.3 Hz, 0.19H, H-3), 2.26 (s, 0.57H, CH_3 Me); HRMS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{10}SNa$ 1025.42689, found 1025.42706.

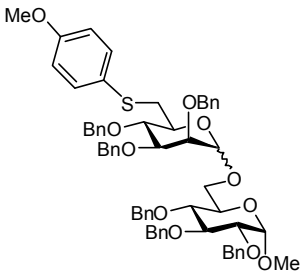


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-D-mannopyranosyl (1→3)-(*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (19b): Donor **9** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 124 mg (123 µmol, 56%) of the title compound **19b** as an epimeric mixture (α/β 1/8). R_f 0.59 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3030, 2866, 1505, 1454, 1060, 731, 697; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.74 – 6.70 (m, 33H, H_{arom}), 5.57 (s, 1H, CH benzylidene), 4.98 – 4.84 (m, 5H, CH_2 benzyl, H-1), 4.63 – 4.55 (m, 2H, H-1', CH_2 benzyl), 4.46 – 4.29 (m, 5H, CH_2 benzyl, H-6, H-4), 4.10 – 4.00 (m, 2H, H-2, H-6), 3.80 – 3.70 (m, 5H, H-4', CH_3 OMe, H-3), 3.67 (d, *J* = 2.9 Hz, 1H, H-2'), 3.45 (s, 1H, H-5), 3.37 – 3.27 (m, 2H, H-5', H-6'), 3.23 (dd, *J* = 9.3, 2.9 Hz, 1H, H-3'), 3.04 (dd, *J* = 14.0, 9.9 Hz, 1H, H-6'), 2.29 (s, 3H, CH_3 Me); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 155.3, 151.5, 138.5, 138.0, 135.5, 133.5 (C_q), 129.6, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.3, 118.8, 114.4

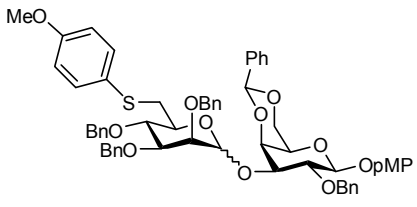
(CH_{arom}), 103.1 (C-1), 102.9 (C-1'), 100.6 (CH benzylidene), 82.5 (C-3'), 78.7 (C-2), 78.3 (C-3), 77.7 (C-4'), 75.9 (C-4), 75.3 (C-5'), 75.2, 73.3 (CH_2 benzyl), 72.4 (C-2'), 71.5 (CH_2 benzyl), 68.9 (C-6), 66.7 (C-5), 55.6 (CH_3 OMe), 36.0 (C-6'), 20.9 (CH_3 Me); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 103.1 ($J_{C1\text{-}H1}$ = 158 Hz, C-1), 102.9 ($J_{C1'\text{-}H1'}$ = 158 Hz, C-1'); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.46 (s, 0.13H, CH benzylidene), 2.08 (s, 0.38H, CH_3 Me); HRMS $[M+Na]^+$ calcd for $C_{61}H_{62}O_{11}SNa$ 1025.39050, found 1025.39141.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (19c): Donor **9** and acceptor **15c** were coupled according to the general glycosylation procedure to yield 178 mg (196 µmol, 89%) of the title compound **19c** as an epimeric mixture (α/β 1/3.5). Rf 0.55, 0.75 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3032, 2919, 1496, 1454, 1072, 735, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.67 – 7.07 (m, 29H, H_{arom}), 5.66 (s, 1H, CH benzylidene), 5.20 – 5.00 (m, 4H, CH_2 benzyl), 4.87 (s, 1H, H-1), 4.83 – 4.58 (m, 4H, H-1', CH_2 benzyl), 4.54 – 4.47 (m, 2H, CH_2 benzyl, C-2), 4.41 – 4.34 (m, 1H, H-6), 4.20 (t, *J* = 9.3 Hz, 1H, H-4), 4.12 – 4.06 (m, 2H, H-2', H-3'), 3.94 – 3.83 (m, 3H, H-6, H-5, H-4'), 3.58 (dd, *J* = 9.2, 2.9 Hz, 1H, H-3'), 3.53 – 3.44 (m, 5H, H-6', H-5', CH_3 OMe), 3.05 (dd, *J* = 13.9, 9.7 Hz, 1H, H-6'), 2.38 (s, 3H, CH_3 Me); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.8, 138.6, 138.1, 137.9, 137.5, 135.5, 133.1 (C_q), 129.6, 128.8, 128.6, 128.3, 128.1, 128.0, 127.6, 127.5, 126.1 (CH_{arom}), 101.6 (CH_{arom}), 99.1 (C-1'), 98.8 (C-1), 81.8 (C-3'), 78.3 (C-4), 77.6 (C-4'), 75.3 (CH2 benzyl, C-5'), 73.6 (CH_2 benzyl), 73.5 (C-3), 73.1 (C-2'), 72.5 (C-2), 71.0, 70.3 (CH_2 benzyl), 68.9 (C-6), 63.8 (C-5), 55.0 (CH_3 OMe), 36.0 (C-6'), 20.9 (CH_3 Me); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.1 ($J_{C1'\text{-}H1'}$ = 154 Hz, C-1'), 98.8 ($J_{C1\text{-}H1}$ = 168 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.71 (s, 0.29H, CH benzylidene), 3.32 (s, 0.88H, CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{55}H_{58}O_{10}SNa$ 933.36429, found 933.36435.

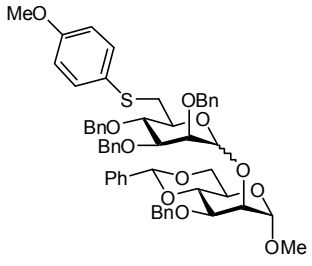


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (20a): Donor **10** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 191 mg (187 µmol, 85%) of the title compound **20a** as an epimeric mixture (α/β 1/5). Rf 0.52 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3031, 2908, 1593, 1496, 1454, 1070, 734, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.60 – 6.99 (m, 32H, H_{arom}), 6.86 – 6.59 (m, 2H, H_{arom}), 5.03 (d, *J* = 10.9 Hz, 1H, CH_2 benzyl), 4.97 – 4.88 (m, 2H, CH_2 benzyl), 4.88 – 4.73 (m, 4H, CH_2 benzyl), 4.66 (d, *J* = 12.1 Hz, 1H, CH_2 benzyl), 4.61 – 4.38 (m, 5H, CH_2 benzyl, H-1), 4.18 (dd, *J* = 10.3, 1.8 Hz, 1H, H-6), 4.08 (s, 1H, H-1'), 4.03 (t, *J* = 9.2 Hz, 1H, H-3), 3.87 – 3.69 (m, 6H, H-5, CH_3 OMe, H-4', H-2'), 3.52 (dd, *J* = 9.7, 3.5 Hz, 1H, H-2), 3.49 – 3.42 (m, 2H, H-6, H-4), 3.40 – 3.22 (m, 6H, H-3', CH_3 OMe, H-6', H-5'), 3.00 (dd, *J* = 13.5, 9.0 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 158.5, 138.8, 138.5, 138.1, 138.0, 137.9 (C_q), 132.2, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4 (CH_{arom}), 127.2 (C_q), 114.4 (CH_{arom}), 101.2 (C-1'), 97.7 (C-1), 82.1 (C-3, C-3'), 79.8 (C-2), 77.6, 77.5 (C-4, C-4'), 75.6 (CH_2 benzyl), 75.1 (C-5', CH_2 benzyl), 74.7, 73.6 (CH_2 benzyl), 73.4 (C-2'), 73.2, 71.4 (CH_2 benzyl), 69.5 (C-5), 68.0 (C-6), 55.2, 55.0 (CH_3 OMe), 37.6 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.2 ($J_{C1'\text{-}H1'}$ = 154.9 Hz, C-1'), 97.7 ($J_{C1\text{-}H1}$ = 171.7 Hz, C-1); Diagnostic peak from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 3.96 (t, *J* = 9.2 Hz, 0.20H, H-3); HRMS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}SNa$ 1041.42180, found 1041.42186.

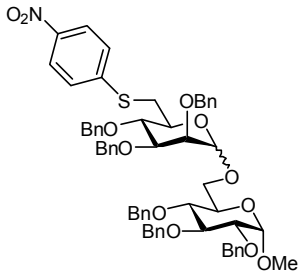


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-D-mannopyranosyl (1→3)(-*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (20b): Donor **10** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 130 mg (128 µmol, 58%) of the

title compound **20b** as an epimeric mixture (α/β 1/7). Rf 0.33 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3034, 2858, 1593, 1505, 1495, 1454, 1060, 730, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.81 – 6.69 (m, 33H, H_{arom}), 5.59 (s, 1H, CH benzylidene), 4.97 – 4.84 (m, 5H, H-1, CH_2 benzyl), 4.57 (d, *J* = 11.2 Hz, 2H, H-1', CH_2 benzyl), 4.44 – 4.27 (m, 5H, H-6, H-4, CH_2 benzyl), 4.10 – 4.01 (m, 2H, H-6, H-2), 3.78 – 3.70 (m, 8H, H-3, H-4', 2*CH_3 OMe), 3.67 (d, *J* = 2.9 Hz, 1H, H-2'), 3.48 (s, 1H, H-5), 3.35 – 3.27 (m, 1H, H-5'), 3.25 – 3.19 (m, 2H, H-3', H-6'), 3.03 (dd, *J* = 13.7, 9.4 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 158.5, 155.3, 151.5, 138.5, 138.1, 138.0, 132.06 (C_q), 132.0, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4 (CH_{arom}), 127.4 (C_q), 126.3, 119.0, 118.8, 114.5, 114.4 (CH_{arom}), 103.1 (C-1), 102.9 (C-1'), 100.7 (CH benzylidene), 82.5 (C-3'), 78.8 (C-2), 78.2 (C-3), 77.5 (C-4'), 75.9 (C-4), 75.5 (C-5'), 75.3, 73.3 (CH_2 benzyl), 72.4 (C-2'), 71.5 (CH_2 benzyl), 68.9 (C-6), 66.7 (C-5), 55.6, 55.3 (CH_3 OMe), 37.5 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 103.1 ($J_{C1\text{-}H1}$ = 159 Hz, C-1), 102.9 ($J_{C1'\text{-}H1'}$ = 158 Hz, C-1'); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.48 (s, 0.12H, CH_3 OMe), 3.58 (s, 0.38H); HRMS $[M+Na]^+$ calcd for $C_{61}H_{62}O_{12}SNa$ 1041.38542, found 1041.38571.

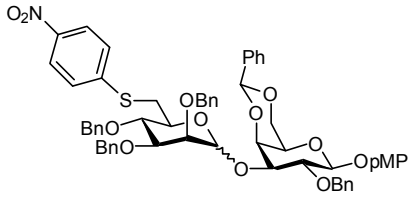


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (20c): Donor **10** and acceptor **15c** were coupled according to the general glycosylation procedure to yield 179 mg (194 μmol, 88%) of the title compound **20c** as an epimeric mixture (α/β 1/4.5). Rf 0.40, 0.60 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 2910, 1593, 1495, 1454, 1072, 730, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.57 – 7.17 (m, 27H, H_{arom}), 6.82 – 6.69 (m, 2H), 5.55 (s, 1H, CH benzylidene), 5.06 (d, *J* = 12.4 Hz, 1H, CH_2 benzyl), 5.01 – 4.90 (m, 3H, CH_2 benzyl), 4.78 (d, *J* = 0.9 Hz, 1H, H-1), 4.69 – 4.48 (m, 3H, H-1', CH_2 benzyl), 4.43 (dd, *J* = 3.3, 1.4 Hz, 1H, H-2), 4.39 (d, *J* = 11.8 Hz, 1H, CH_2 benzyl), 4.29 – 4.25 (m, 1H, H-6), 4.12 – 4.06 (m, 1H, H-4), 4.01 – 3.95 (m, 2H, H-2', H-3), 3.83 – 3.74 (m, 3H, H-6, H-4', H-5), 3.72 (s, 3H, CH_3 OMe), 3.47 (dd, *J* = 9.2, 3.0 Hz, 1H, H-3'), 3.41 – 3.34 (m, 4H, CH_3 OMe, H-5'), 3.30 (dd, *J* = 13.5, 1.7 Hz, 1H, H-6'), 2.94 (dd, *J* = 13.6, 9.2 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 158.5, 138.8, 138.6, 138.2, 137.9, 137.5 (C_q), 132.0, 128.5, 128.3, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 126.1, 114.5 (CH_{arom}), 101.6 (CH benzylidene), 99.1 (C1'), 98.8 C-1), 81.8 (C-3'), 78.3 (C-4), 77.6 (C-4'), 75.2 (C-5'), 75.1, 73.6 (CH_2 benzyl), 73.5 (C-3), 73.1 (C-2'), 72.5 (C-2), 71.0, 70.3 (CH_2 benzyl), 68.9 (C-6), 63.8 (C-5), 55.2, 55.0 (CH_3 OMe), 37.5 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.1 ($J_{C1'\text{-}H1'}$ = 154 Hz, C-1'), 98.8 ($J_{C1\text{-}H1}$ = 168 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.61 (s, 022H, CH benzylidene), 3.27 (s, 0.66H, CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{55}H_{58}O_{11}SNa$ 949.35920, found 949.35920.

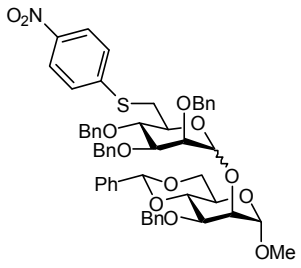


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (21a): Donor **11** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 180 mg (174 μmol, 79%) of the title compound as **21a** an epimeric mixture (α/β 1/7). Rf 0.59 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3032, 2903, 1578, 1512, 1497, 1454, 1336, 1067, 733, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 8.10 – 7.85 (m, 2H, H_{arom}), 7.50 – 7.09 (m, 32H, H_{arom}), 5.08 – 4.99 (m, 2H, CH_2 benzyl), 4.92 (d, *J* = 12.4 Hz, 1H, CH_2 benzyl), 4.87 – 4.75 (m, 4H, CH_2 benzyl), 4.69 – 4.46 (m, 6H, H-1, CH_2 benzyl), 4.12 – 4.06 (m, 2H, H-1', H-6), 4.02 (t, *J* = 9.2 Hz, 1H, H-3), 3.86 – 3.74 (m, 2H, H-4', H-5), 3.72 (d, *J* = 2.8 Hz, 1H, H-2'), 3.54 – 3.30 (m, 9H, H-2, H-6, H3', H-4, H-6', H-5', CH_3 OMe), 3.04 (dd, *J* = 14.1, 9.1 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ147.9, 144.7, 138.7, 138.4, 138.2, 137.9, 137.8 (C_q), 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 125.9, 123.7, 123.6 (CH_{arom}), 101.2 (C-1'), 97.7 (C-1), 82.0 (C-3, C-

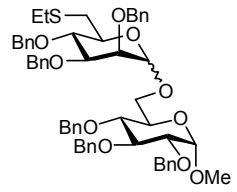
3'), 79.8 (C-2), 77.2 (C-4, C-4'), 75.6, 75.3 (CH_2 benzyl), 74.9 (C-5'), 74.6, 73.8 (CH_2 benzyl), 73.4 (C-2'), 73.2, 71.4 (CH_2 benzyl), 69.5 (C-5), 68.1 (C-6), 55.0 (CH_3 OMe), 33.9 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.2 ($J_{C1'\text{-}H1'}$ = 156.0 Hz, C-1'), 97.7 ($J_{C1\text{-}H1}$ = 168.1 Hz, C-1); Diagnostic peak from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 3.95 (t, *J* = 9.2 Hz, 0.14H, H-3); HRMS $[M+Na]^+$ calcd for $C_{61}H_{63}NO_{12}SNa$ 1056.39632, found 1056.39636.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-D-mannopyranosyl-(1→3)-(*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (21b): Donor **11** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 207 mg (200 µmol, 91%) of the title compound **21b** as an epimeric mixture (α/β 1/4). R_f 0.37 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 2870, 1579, 1506, 1454, 1336, 1060, 730, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 8.05 – 7.96 (m, 2H, H_{arom}), 7.62 – 6.75 (m, 31H, H_{arom}), 5.56 (s, 1H, CH benzylidene), 5.03 – 4.82 (m, 5H, H-1, CH_2 benzyl), 4.65 – 4.59 (m, 2H, H-1', CH_2 benzyl), 4.43 (d, *J* = 11.6 Hz, 1H, CH_2 benzyl), 4.38 – 4.28 (m, 3H, H-6, CH_2 benzyl), 4.26 (d, *J* = 3.4 Hz, 1H, H-4), 4.10 – 3.98 (m, 2H, H-2, H-6), 3.83 – 3.70 (m, 5H, H-4', H-3, CH_3 OMe), 3.69 (d, *J* = 2.8 Hz, 1H, H-2'), 3.43 (s, 1H, H-5), 3.39 – 3.28 (m, 2H, H-5', H-6'), 3.23 (dd, *J* = 9.2, 2.9 Hz, 1H, H-3'), 3.09 – 3.00 (m, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 155.3, 151.4, 147.9, 144.7, 138.4, 138.2, 137.9, 137.8 (C_q), 128.5, 128.4, 128.3, 128.0, 127.9, 127.6, 127.4, 126.2, 125.8, 123.7, 119.1, 118.7, 114.4 (CH_{arom}), 103.1 (C-1), 102.7 (C-1'), 100.7 (CH benzylidene), 82.4 (C-3'), 78.8 (C-2), 78.0 (C-3), 77.1 (C-4'), 75.9 (C-4), 75.3, 75.2 (CH_2 benzyl), 74.9 (C-5'), 73.4 (CH_2 benzyl), 72.3 (C-2'), 71.4 (CH_2 benzyl), 68.8 (C-6), 66.6 (C-5), 55.5 (CH_3 OMe), 33.9 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 103.1 ($J_{C1\text{-}H1}$ = 159 Hz, C-1), 102.7 ($J_{C1'\text{-}H1'}$ = 157 Hz, C-1'); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.45 (s, 0.24H, benzylidene), 2.93 (dd, *J* = 14.1, 9.2 Hz, 1H, H-6'); HRMS $[M+Na]^+$ calcd for $C_{60}H_{59}NO_{13}SNa$ 1056.35993, found 1056.36042.

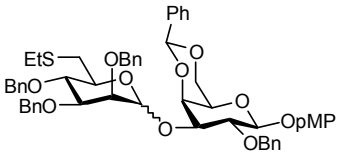


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (21c): Donor **11** and acceptor **15c** were coupled according to the general glycosylation procedure to yield 187 mg (198 µmol, 90%) of the title compound **21c** as an epimeric mixture (α/β 1/4). R_f 0.47 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 2908, 1579, 1512, 1598, 1454, 1336, 1072, 730, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.97 – 7.91 (m, 2H, H_{arom}), 7.56 – 7.14 (m, 27H, H_{arom}), 5.53 (s, 1H, CH benzylidene), 5.06 (dd, *J* = 11.7, 4.6 Hz, 2H, CH_2 benzyl), 4.97 (d, *J* = 12.3 Hz, 1H, CH_2 benzyl), 4.88 (d, *J* = 12.3 Hz, 1H, CH_2 benzyl), 4.73 (d, *J* = 1.1 Hz, 1H, H-1), 4.70 – 4.53 (m, 4H, CH_2 benzyl, H-1'), 4.43 (d, *J* = 11.8 Hz, 1H, CH_2 benzyl), 4.31 (dd, *J* = 3.3, 1.4 Hz, 1H, H-2), 4.29 – 4.24 (m, 1H, H-6), 4.11 – 4.06 (m, 1H, H-4), 4.02 (d, *J* = 2.9 Hz, 1H, H-2'), 3.96 (dd, *J* = 9.9, 3.4 Hz, 1H, H-3), 3.85 (t, *J* = 9.2 Hz, 1H, H-4'), 3.81 – 3.76 (m, 2H, H-5, H-6), 3.53 (dd, *J* = 9.1, 2.9 Hz, 1H, H-3'), 3.46 – 3.36 (m, 2H, H-6', H-5'), 3.34 (s, 3H, CH_3 OMe), 2.92 (dd, *J* = 13.9, 9.2 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 147.6, 144.7, 138.6, 138.4, 137.9, 137.7, 137.4 (C_q), 128.5, 128.3, 128.2, 128.1, 127.9, 127.5, 127.4, 126.0, 125.6, 123.7 (CH_{arom}), 101.6 (CH benzylidene), 99.4 (C-1'), 99.0 (C-1), 81.7 (C-3'), 78.4 (C-4), 77.2 (C-4'), 75.3 (CH_2 benzyl), 74.8 (C-5'), 73.8 (CH_2 benzyl), 73.7, 73.4, 73.2 (C-3, C-2', C-2), 71.0, 70.7 (CH_2 benzyl), 68.8 (C-6), 63.8 (C-5), 54.9 (CH_3 OMe), 33.8 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.4 ($J_{C1'\text{-}H1'}$ = 152 Hz, C-1'), 99.0 ($J_{C1\text{-}H1}$ = 168 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.60 (s, 0.25H, CH benzylidene), 3.15 (s, 0.75H, CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{54}H_{55}NO_{12}SNa$ 964.33372, found 964.33391.

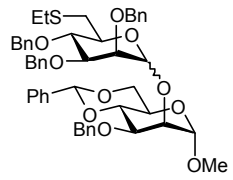


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (22a): Donor **12** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 166 mg

(176 µmol, 80%) of the title compound **22a** as an epimeric mixture (α/β 1/4). R_f 0.48, 0.53 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3030, 2924, 1497, 1454, 1067, 736, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.44 – 7.15 (m, 30H, H_{arom}), 5.07 – 4.89 (m, 3H, CH_2 benzyl), 4.86 – 4.73 (m, 4H, CH_2 benzyl), 4.70 – 4.43 (m, 6H, H-1, CH_2 benzyl), 4.16 (dd, *J* = 10.3, 1.8 Hz, 1H, H-6), 4.12 (s, 1H, H-1'), 4.02 (t, *J* = 9.2 Hz, 1H, H-3), 3.82 – 3.74 (m, 2H, H-5, H-4'), 3.72 (d, *J* = 2.8 Hz, 1H, H-2'), 3.54 – 3.42 (m, 3H, H-2, H-6, H-4), 3.40 (dd, *J* = 9.3, 2.9 Hz, 1H, H-3'), 3.34 – 3.27 (m, 4H, CH_3 OMe, H-5'), 2.89 (dd, *J* = 13.9, 2.0 Hz, 1H, H-6'), 2.71 (dd, *J* = 14.0, 8.6 Hz, 1H, H-6'), 2.58 (q, *J* = 7.4 Hz, 2H, CH_2 ethyl), 1.18 (t, *J* = 7.4 Hz, 3H, CH_3 ethyl); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.7, 138.6, 138.2, 138.0, 137.9 (C_q), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3 (CH_{arom}), 101.3 (C-1'), 97.7 (C-1), 82.1, 82.0 (C-3, C-3'), 79.7 (C-2), 77.5, 77.4 (C-4, C-4'), 77.1 (C-5'), 75.5 , 75.2, 74.6, 73.6 (CH_2 benzyl), 73.5 (C-2'), 73.2, 71.4 (CH_2 benzyl), 69.6 (C-5), 68.1 (C-6), 54.9 (CH_3 OMe), 33.1 (C-6'), 26.9 (CH_2 ethyl), 14.78 (CH_3 ethyl); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.3 ($J_{C1'-H1'}$ = 153.1 Hz, C-1'), 97.7 (J_{C1-H1} = 168.1 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 3.62 (dd, *J* = 11.5, 1.7 Hz, 0.22 H, H-6), 2.47 (q, *J* = 7.3 Hz, 0.44H, CH_2 ethyl); HRMS $[M+Na]^+$ calcd for $C_{57}H_{64}O_{10}SNa$ 963.41124, found 963.41153.

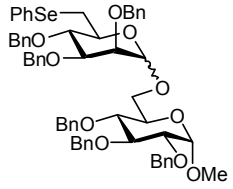


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-D-mannopyranosyl-(1→3)-(*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (22b): Donor **12** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 178 mg (189 µmol, 86%) of the title compound **22b** as an epimeric mixture (α/β 1/3.5). R_f 0.21, 0.29 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) IR (neat, cm^{-1}) 2867, 1506, 1454, 1062, 733, 697; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.62 – 6.78 (m, 29H), 5.62 (s, 1H, CH benzylidene), 4.97 – 4.88 (m, 4H, H-1, CH_2 benzyl), 4.64 – 4.57 (m, 3H, H-1', CH_2 benzyl), 4.44 – 4.30 (m, 5H, H-4, H-6, CH_2 benzyl), 4.10 – 4.02 (m, 2H, H-2, H-6), 3.82 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3), 3.76 – 3.70 (m, 4H, CH_3 OMe, H-4'), 3.68 (d, *J* = 2.9 Hz, 1H, H-2'), 3.51 (s, 1H, H-5), 3.32 – 3.25 (m, 1H, H-5'), 3.23 (dd, *J* = 9.3, 2.9 Hz, 1H, H-3'), 2.87 (dd, *J* = 13.7, 2.0 Hz, 1H, H-6'), 2.71 (dd, *J* = 13.7, 9.2 Hz, 1H, H-6'), 2.57 (q, *J* = 7.4 Hz, 2H, CH_2 ethyl), 1.21 (t, *J* = 7.4 Hz, 3H, CH_3 ethyl); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 155.3, 151.5, 138.5, 138.5, 138.1, 138.0 (C_q), 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.5, 126.3, 118.8, 114.4 (CH_{arom}), 103.1 (C-1), 102.9 (C-1'), 100.7 (CH benzylidene), 82.5 (C-3'), 78.7 (C-2), 78.4 (C-3), 77.5 (C-4'), 76.4 (C-4), 76.1 (C-5'), 75.2, 73.3 (CH_2 benzyl), 72.4 (C-2'), 71.5 (CH_2 benzyl), 68.9 (C-6), 66.7 (C-5), 55.6 (CH_3 OMe), 33.5 (C-6'), 26.8 (CH_2 ethyl), 14.9 (CH_3 ethyl); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 103.1 (J_{C1-H1} = 159 Hz, C-1), 102.9 ($J_{C1'-H1'}$ = 158 Hz, C-1'); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.46 (s, 0.29H, CH benzylidene), 2.32 (q, *J* = 7.4 Hz, 0.57H, CH_2 ethyl), 1.00 (t, *J* = 7.4 Hz, 0.86H, CH_3 ethyl); HRMS $[M+Na]^+$ calcd for $C_{56}H_{60}O_{11}SNa$ 963.37485, found 963.37521.

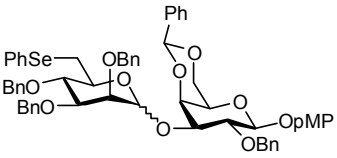


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (22c): Donor **12** and acceptor **15c** were coupled according to the general glycosylation procedure to yield 146 mg (172 µmol, 78%) of the title compound **22c** as an epimeric mixture (α/β 1/1.5). R_f 0.40, 0.59 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 2926, 1718, 1497, 1454, 1075, 738, 697; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ7.54 – 7.18 (m, 25H, H_{arom}), 5.54 (s, 1H, CH benzylidene), 5.09 – 4.85 (m, 2H, CH_2 benzyl), 4.79 (d, *J* = 0.8 Hz, 1H), 4.71 – 4.50 (m, 6H, H-1', CH_2 benzyl), 4.43 (d, *J* = 11.8 Hz, 1H, CH_2 benzyl), 4.39 (dd, *J* = 3.4, 1.5 Hz, 1H, H-2), 4.28 – 4.21 (m, 1H, H-6), 4.13 – 4.05 (m, 1H, H-4), 4.02 – 3.95 (m, 2H, H-2', H-3), 3.88 – 3.74 (m, 3H, H-4', H-5, H-6), 3.50 (dd, *J* = 9.3, 3.0 Hz, 1H, H-3'), 3.41 – 3.33 (m, 4H, H-5', CH_3 OMe), 2.99 – 2.89 (m, 1H, H-6'), 2.73 – 2.65 (m, 1H, H-6'), 2.55 (q, *J* = 7.4 Hz, 2H, CH_2 ethyl), 1.15 (t, *J* = 7.4 Hz, 3H, CH_3 ethyl); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.8, 138.7, 138.3, 137.5 (C_q), 128.5, 128.3, 128.1, 128.0, 127.6, 127.5, 126.1 (CH_{arom}), 101.6 (CH benzylidene), 99.0 (C-1'), 98.7 (C-1), 81.9 (C-3'), 78.5 (C-4), 77.4 (C-4'), 76.9 (C-5'), 75.2, 73.7 (CH_2

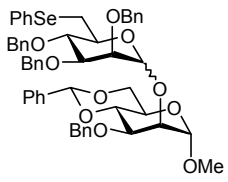
benzyl), 73.6, 73.5 (C-2', C-3), 72.8 (C-2), 71.1, 70.7 (CH_2 benzyl), 68.9 (C-6), 63.9 (C-5), 55.0 (CH_3 OMe), 33.5 (C-6'), 26.9 (CH_2 ethyl), 14.8 (CH_3 ethyl); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.0 ($J_{C1'-H1'}$ = 154 Hz, C-1'), 98.7 (J_{C1-H1} = 167 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.61 (s, 0.65H, CH benzylidene), 1.24 (t, *J* = 7.5 Hz, 1.95H, CH_3 ethyl); HRMS $[M+Na]^+$ calcd for $C_{50}H_{56}O_{10}SNa$ 871.34864, found 871.34859.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-*Se*-phenyl-6-seleno-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (23a): Donor **13** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 226 mg (218 μmol, 99%) of the title compound **23a** as an epimeric mixture (α/β 1/7). Rf 0.47 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3030, 2910, 1580, 1497, 1454, 1069, 731, 694; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.70 – 6.94 (m, 35H, H_{arom}), 5.03 (d, *J* = 10.9 Hz, 1H, CH_2 benzyl), 4.99 – 4.89 (m, 2H, CH_2 benzyl), 4.88 – 4.73 (m, 4H, CH_2 benzyl), 4.70 – 4.39 (m, 6H, H-1, CH_2 benzyl), 4.18 (br d, *J* = 9.9 Hz, 1H, H-6), 4.10 (s, 1H, H-1'), 4.04 (t, *J* = 9.2 Hz, 1H, H-3), 3.86 – 3.72 (m, 2H, H-5, H-4'), 3.71 (d, *J* = 2.3 Hz, 1H, H-2'), 3.52 (dd, *J* = 9.6, 3.4 Hz, 1H, H-2), 3.50 – 3.24 (m, 8H, H-6, H-4, H-5', H-3', CH_3 OMe, H-6'), 3.08 (dd, *J* = 12.5, 9.5 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.7, 138.4, 138.1, 138.0, 137.9, 137.8 (C_q), 131.6, 131.4 (CH_{arom}), 131.2 (C_q), 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.2 (CH_{arom}), 101.1 (C-1'), 97.6 (C-1), 82.0 (C-3, C-3'), 79.7 (C-2), 78.3 (C-4'), 77.4 (C-4), 75.7 (C-5'), 75.5, 75.1, 74.5, 73.6 (CH_2 benzyl), 73.4 (C-2'), 73.1, 71.4 (CH_2 benzyl), 69.4 (C-5), 67.9 (C-6), 54.9 (CH_3 OMe), 29.4 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.2 ($J_{C1'-H1'}$ = 154 Hz, C-1'), 97.6 (J_{C1-H1} = 169.0 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 3.97 (t, *J* = 9.2 Hz, 0.15H); HRMS $[M+Na]^+$ calcd for $C_{61}H_{64}O_{10}SeNa$ 1059.35569, found 1059.35680.

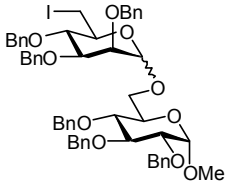


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*Se*-phenyl-6-seleno-D-mannopyranosyl-(1→3)-(*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (23b): Donor **13** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 210 mg (203 μmol, 96%) of the title compound **23b** as an epimeric mixture (α/β 1/10). Rf 0.24, 0.38 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3034, 2867, 1578, 1506, 1454, 1059, 731, 695; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.62 – 6.73 (m, 34H, H_{arom}), 5.55 (s, 1H, CH benzylidene), 4.99 – 4.82 (m, 5H, H-1, CH_2 benzyl), 4.59 (d, *J* = 13.5 Hz, 2H, H-1', CH_2 benzyl), 4.47 – 4.25 (m, 5H, H-4, H-6, CH_2 benzyl), 4.11 – 3.96 (m, 2H, H-6, H-2), 3.80 – 3.66 (m, 6H, H-4', H-3, CH_3 OMe, H-2'), 3.44 – 3.33 (m, 2H, H-5, H-5'), 3.30 (br d, *J* = 11.3 Hz, 1H, H-6'), 3.24 (dd, *J* = 9.2, 2.4 Hz, 1H, H-3'), 3.10 (dd, *J* = 12.2, 10.2 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 155.2, 151.4, 138.5, 138.4, 138.0, 137.9 (C_q), 131.6, 131.2, 128.9, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.4, 126.2, 118.7, 114.4 (CH_{arom}), 103.0 (C-1), 102.9 (C-1'), 100.5 (CH benzylidene), 82.4 (C-3'), 78.7 (C-2), 78.4, 78.3 (C-3, C-4'), 75.9 (C-4), 75.7 (C-5'), 75.2, 73.3 (CH_2 benzyl), 72.5 (C-2'), 71.4, 68.8 (CH_2 benzyl), 66.6 (C-6), 55.5 (CH_3 OMe), 29.6 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 103.0 (J_{C1-H1} = 160 Hz, C-1), 102.9 ($J_{C1'-H1'}$ = 159 Hz, C-1'); Diagnostic peak from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.43 (s, 0.10H, CH benzylidene); HRMS $[M+Na]^+$ calcd for $C_{60}H_{60}O_{11}SeNa$ 1059.31931, found 1059.32029.

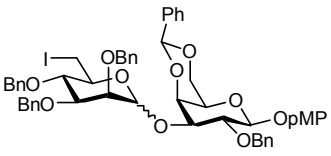


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*Se*-phenyl-6-seleno-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (23c): Donor **13** and acceptor **15c** were coupled according to the general glycosylation procedure to yield 191 mg (202 μmol, 92%) of the title compound **23c** as an epimeric mixture (α/β 1/3). Rf 0.45, 0.64 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3034, 2909, 1580, 1497, 1454, 1073, 735, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.56 – 7.12 (m, 30H, H_{arom}), 5.55 (s, 1H, CH benzylidene), 5.07 (d, *J* = 12.4 Hz, 1H, CH_2 benzyl), 5.01 – 4.88 (m, 3H, CH_2 benzyl), 4.78 (s, 1H, H-1),

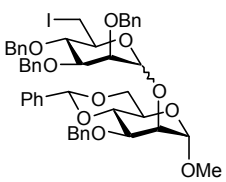
4.67 (d, *J* = 12.3 Hz, 1H, CH_2 benzyl), 4.63 – 4.48 (m, 3H, H-1', CH_2 benzyl), 4.44 – 4.38 (m, 2H, H-2, CH_2 benzyl), 4.28 – 4.23 (m, 1H, H-6), 4.13 – 4.07 (m, 1H, H-4), 4.01 – 3.95 (m, 2H, H-2', H-3), 3.85 – 3.77 (m, 3H, H-6, H-4', H-5), 3.51 – 3.43 (m, 2H, H-3', H-5'), 3.40 – 3.33 (m, 4H, CH_3 OMe, H-6'), 3.01 (dd, *J* = 12.4, 9.6 Hz, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.8, 138.6, 138.2, 137.9, 137.5 (C_q), 131.4 (CH_{arom}), 131.1 (C_q), 129.0, 128.5, 128.3, 128.1, 128.0, 127.9, 127.6, 127.4, 126.1 (CH_{arom}), 101.6 (CH benzylidene), 99.0 (C-1'), 98.7 (C-1), 81.8 (C-3'), 78.4 (C-4), 78.3 (C-4'), 75.9 (C-5'), 75.2, 73.7 (CH_2 benzyl), 73.6 (C-3), 73.4 (C-2'), 72.6 (C-2), 71.1, 70.5 (CH_2 benzyl), 68.8 (C-6), 63.8 (C-5), 55.0 (CH_3 OMe), 29.5 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.0 ($J_{C1'-H1'}$ = 154 Hz, C-1'), 98.7 (J_{C1-H1} = 168 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.60 (s, 0.33H, CH benzylidene), 3.24 (s, 1H, CH_3 OMe), 3.09 (dd, *J* = 12.4, 9.5 Hz, 0.33H, H-6'); HRMS $[M+Na]^+$ calcd for $C_{54}H_{56}O_{10}SeNa$ 967.29309, found 967.29351.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranosyl-(1→6)-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (24a): Donor **14** and acceptor **15a** were coupled according to the general glycosylation procedure to yield 186 mg (185 µmol, 84%) of the title compound **24a** as an epimeric mixture (α/β 1/7). Rf 0.49 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3032, 2872, 1497, 1454, 1066, 908, 728, 695; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.64 – 7.09 (m, 30H, H_{arom}), 5.03 (d, *J* = 10.9 Hz, 1H, CH_2 benzyl), 4.98 – 4.90 (m, 2H, CH_2 benzyl), 4.87 – 4.74 (m, 4H, CH_2 benzyl), 4.70 – 4.48 (m, 5H, H-1, CH_2 benzyl), 4.43 (d, *J* = 11.9 Hz, 1H, CH_2 benzyl), 4.27 (dd, *J* = 10.3, 1.7 Hz, 1H, H-6), 4.12 (s, 1H, H-1'), 4.04 (t, *J* = 9.2 Hz, 1H, H-3), 3.88 – 3.79 (m, 1H, H-5), 3.71 (d, *J* = 2.8 Hz, 1H, H-2'), 3.67 (t, *J* = 9.0 Hz, 1H, H-4'), 3.55 – 3.42 (m, 4H, H-2, H-6', H-6, H-4), 3.39 (dd, *J* = 9.2, 2.9 Hz, 1H, H-3'), 3.34 (s, 3H, CH_3 OMe), 3.20 (dd, *J* = 7.9, 4.5 Hz, 2H, H-5', H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.6, 138.3, 138.1, 137.9, 137.7 (C_q), 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4 (CH_{arom}), 101.2 (C-1'), 97.6 (C-1), 82.0 (C-3), 81.6 (C-3'), 79.6 (C-2), 78.0 (C-4'), 77.5 (C-4), 75.6 (C-5'), 75.5, 75.2, 74.6, 73.6 (CH_2 benzyl), 73.3 (C-2'), 73.2, 71.4 (CH_2 benzyl), 69.4 (C-5), 68.3 (C-6), 55.0 (CH_3 OMe), 5.5 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.2 ($J_{C1'-H1'}$ = 155.0 Hz, C-1'), 97.6 (J_{C1-H1} = 168.4 Hz, C-1); Diagnostic peak from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 3.30 (s, 0.43H, CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{55}H_{59}IO_{10}Na$ 1029.30451, found 1029.30480.

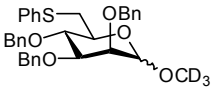


2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranosyl-(1→3)-(*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside) (24b): Donor **14** and acceptor **15b** were coupled according to the general glycosylation procedure to yield 210 mg (209 µmol, 95%) of the title compound **24b** as an epimeric mixture (α/β 1/6). Rf 0.24, 0.39 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3030, 2866, 1506, 1454, 1059, 732, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.66 – 6.73 (m, 29H, H_{arom}), 5.65 (s, 1H, CH benzylidene), 4.98 – 4.84 (m, 5H, H-1, CH_2 benzyl), 4.61 – 4.56 (m, 2H, H-1', CH_2 benzyl), 4.53 (d, *J* = 3.4 Hz, 1H, H-4), 4.49 – 4.30 (m, 4H, H-6, CH_2 benzyl), 4.13 – 4.04 (m, 2H, H-6, H-2), 3.85 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3), 3.75 (s, 3H, CH_3 OMe), 3.70 – 3.63 (m, 2H, H-2', H-4'), 3.57 – 3.50 (m, 2H, H-6', H-5), 3.25 (dd, *J* = 9.2, 3.0 Hz, 1H, H-3'), 3.23 – 3.14 (m, 2H, H-5', H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 155.3, 151.5, 138.5, 138.3, 138.0, 137.8 (C_q), 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.5, 126.3, 118.8, 114.4 (CH_{arom}), 103.1 (C-1, C-1'), 100.6 (CH benzylidene), 82.2 (C-3'), 78.7, 78.6 (C-2, C-3), 78.0 (C-4'), 76.0 (C-4), 75.6 (C-5'), 75.3 (2*CH_2 benzyl), 73.4 (CH_2 benzyl), 72.5 (C-2'), 71.5 (CH_2 benzyl), 68.9 (C-6), 66.7 (C-5), 55.6 (CH_3 OMe), 6.5 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 103.1 (J_{C1-H1} = 160 Hz, C-1, $J_{C1'-H1'}$ = 158 Hz, C-1'); Diagnostic peak from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.45 (s, 0.16H, CH benzylidene); HRMS $[M+Na]^+$ calcd for $C_{54}H_{55}IO_{11}Na$ 1029.26813, found 1029.26818.



2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranosyl-(1→2)-(methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside) (24c): Donor **14** and acceptor

15c were coupled according to the general glycosylation procedure to yield 175 mg (191 µmol, 87%) of the title compound **24c** as an epimeric mixture (α/β 1/3). R_f 0.45, 0.71 (EtOAc/PE, 1/3, v/v); IR (neat, cm^{-1}) 3032, 2916, 1497, 1454, 1073, 735, 696; NMR data of the major β-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.59 – 7.19 (m, 25H, H_{arom}), 5.55 (s, 1H, CH benzylidene), 5.06 (d, *J* = 12.4 Hz, 1H, CH_2 benzyl), 4.98 (dd, *J* = 11.3, 5.1 Hz, 3H, CH_2 benzyl), 4.81 (s, 1H, H-1), 4.73 – 4.57 (m, 3H, H-1', CH_2 benzyl), 4.55 – 4.48 (m, 2H, H-2, CH_2 benzyl), 4.40 (d, *J* = 11.9 Hz, 1H, CH_2 benzyl), 4.29 – 4.25 (m, 1H, H-6), 4.13 – 4.03 (m, 1H, H-4), 4.04 – 3.97 (m, 2H, H-2', H-3), 3.86 – 3.71 (m, 3H, H-5, H-6, H-4'), 3.55 (dd, *J* = 10.3, 1.6 Hz, 1H, H-6'), 3.50 (dd, *J* = 9.2, 2.9 Hz, 1H, H-3'), 3.37 (s, 3H, CH_3 OMe), 3.32 – 3.25 (m, 1H, H-5'), 3.23 – 3.16 (m, 1H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.77, 138.5, 137.9, 137.7, 137.5 (Cq), 128.5, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 126.1 (CH_{arom}), 101.6 (CH benzylidene), 98.8 (C-1'), 98.5 (C-1), 81.4 (C-3'), 78.3 (C-4), 78.0 (C-4'), 76.0 (C-5'), 75.3, 73.7 (CH_2 benzyl), 73.5 (C-3), 73.2 (C-2'), 72.4 (C-2), 71.0, 70.5 (CH_2 benzyl), 68.8 (C-6), 63.8 (C-5), 55.0 (CH_3 OMe), 5.7 (C-6'); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 98.8 ($J_{C1'-H1'}$ = 154 Hz, C-1'), 98.5 (J_{C1-H1} = 168 Hz, C-1); Diagnostic peaks from the α-linked product: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.62 (s, 0.32H, CH benzylidene), 3.34 (s, 1H, CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{48}H_{51}IO_{10}Na$ 937.24173, found 937.24191.



Methyl (*d*3) 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranoside (26) (NMR tube experiment)**:** Donor **8** (38 mg, 53 µmol, 1 equiv) was coevaporated with toluene and transferred with 0.6 mL CD_2Cl_2 to a dry NMR tube capped with a septum. The temperature was lowered to -80°C, 4.7 µL triflic acid (53 µmol, 1 equiv) was added, the tube was shaken thoroughly and NMR spectra were recorded (crude sulfonium species **25**: ^{1}H NMR (400 MHz, CD_2Cl_2, HH-COSY, HSQC, T = 193 K) δ 7.89 – 7.03 (m, 20H, H_{arom}), 5.87 (d, *J* = 2.3 Hz, 1H, H-1), 5.74 (d, *J* = 7.4 Hz, 1H, H-5), 4.82 (d, *J* = 11.7 Hz, 1H, CH_2 benzyl), 4.75 – 4.63 (m, 3H, CH_2 benzyl), 4.59 – 4.51 (m, 3H, CH_2 benzyl, H-6), 4.21 (t, *J* = 3.4 Hz, 1H, H-2), 3.94 (app s, 1H, H-3), 3.91 – 3.89 (m, 1H, H-4), 3.71 (dd, *J* = 13.0, 7.5 Hz, 1H, H-6); ^{13}C NMR (100 MHz, CD_2Cl_2, HH-COSY, HSQC, T = 193 K) δ 137.4, 137.3, 136.9 (C_q), 135.5, 131.7, 130.9, 129.7, 129.5, 129.4, 129.3, 129.1, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 128.2 (CH_{arom}), 127.0 (C_q), 126.7, 125.9, 121.2 (CH_{arom}), 105.2 (C-1), 82.4 (C-5), 75.6 (C-4), 75.2 (CH_2 benzyl), 74.6 (C-2), 74.0 (C-3), 73.2, 72.8 (CH_2 benzyl), 52.4 (C-6)). Next 25 µL MeOH-*d*4 was added, the tube was shaken thoroughly and was kept at room temperature overnight to give the crude title compound **26** as a mixture of anomers (α/β 3.5:1)[9]. NMR data of the major α-linked product: ^{1}H NMR (400 MHz, CD_2Cl_2, HH-COSY, HSQC) δ 7.50 – 6.95 (m, 20H, H_{arom}), 4.97 (d, *J* = 11.1 Hz, 1H, CH_2 benzyl), 4.76 – 4.64 (m, 3H, CH_2 benzyl, H-1), 4.64 – 4.53 (m, 3H, CH_2 benzyl), 3.91 – 3.71 (m, 4H, H-3, H-4, H-2, H-5), 3.42 (dd, *J* = 13.4, 1.7 Hz, 1H, H-6), 3.02 (dd, *J* = 13.4, 8.6 Hz, 1H, H-6); ^{13}C NMR (100 MHz, CD_2Cl_2, HH-COSY, HSQC) δ 139.1, 138.9, 138.8, 137.7 (C_q), 130.6, 129.7, 129.6, 129.5, 129.4, 129.1, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2 , 126.5, 126.2 (CH_{arom}), 99.4 (C-1), 80.6 (C-3), 78.3 (C-4), 75.7 (C-2, CH_2 benzyl), 73.5, 72.5 (CH_2 benzyl), 71.6 (C-5), 36.3 (C-6). Diagnostic peak from the β-linked product: ^{1}H NMR (400 MHz, CD_2Cl_2, HH-COSY, HSQC) δ 4.32 (s, H-1); ^{13}C NMR (150 MHz, CD_2Cl_2, HH-COSY, HSQC) δ 103.1 (0.29C, C-1).[9]

Synthesis of 18a by pre-activation of 8:

Donor **8** (155 mg, 0.21 mmol) was dissolved in DCM (3.5 mL) and the solution was cooled to -80 °C. TfOH (21 µL, 0.24 mmol, 1.1 eq) was added and the mixture was stirred at -80 °C for 15 min, after which a mixture of **15a** (303 mg, 0.61 mmol, 3 eq) and DTBMP (90 mg, 0.43 mmol, 2 eq) in DCM (1 mL) was added and the resulting mixture was stirred at -60 °C over weekend. The reaction was quenched by the addition of Et_3N (1 mL) at -60 °C. The mixture was filtered over celite, concentrated and purified by size-exclusion chromatography (DCM/MeOH, 1/1, v/v) to give product **18a** (144mg, 0.15 mmol, 67%).

9. Due to overlapping peaks in ^{1}H spectrum, the anomeric ratio was based on integration of the ^{13}C spectrum.

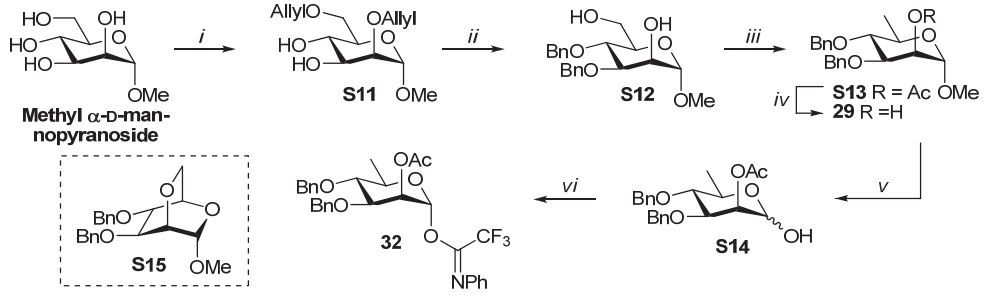
Control experiments to exclude acid catalyzed anomerisation:

1)

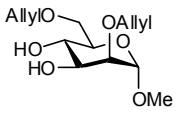
Compound **18a** (144 mg, 0.15 mmol) and TTBP (72 mg, 0.29 mmol, 2 eq) were dissolved in DCM-d_2 (1 mL). TfOH (13 µL, 0.15 mmol, 1 eq) was added and the mixture was stirred for a period of 5 days. NMR spectroscopy of the mixture did not indicate any change in the composition of the mixture.

2)

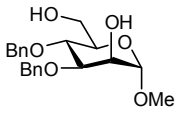
Dimer **18b** (126 mg, 0.13 mmol) was dissolved in 2.5 mL DCM and stirred over 3Å molecular sieves for 30 minutes. The mixture was then cooled to -80 °C after which TfOH (0.025 mmol) in DCM (0.1 ml) was added and the reaction was stirred overnight at -80 °C. The reaction was quenched by the addition of 0.6 mL Et_3N at -80 °C. After filtration over celite, the mixture was washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and evaporated. NMR spectroscopy of the mixture did not indicate any anomerisation.



Reagents and conditions: (*i*) 1) butadione, CSA 2) allylBr, NaH 3) TFA/H_2O (9:1), 53% over 3 steps (*ii*) 1. BnBr, NaH 2) KO*t*Bu, DMF, reflux 3) MeOH, cat *p*-TsOH, 80% (*iii*) 1) Ph_3P, imidazole, I_2, THF, 70°C 2) $NaBH_4$, 100 °C 3) Ac_2O, pyridine, 63% over 3 steps (*iv*) NaOMe, MeOH, 95% (v) 1) H_2O/TFA (5:2) 2) Ac_2O, pyridine 3) piperidine, THF, 86% over 3 steps (*vi*) $CF_3C(=NPh)Cl$, Cs_2CO_3, acetone, H_2O, 59%.

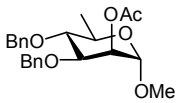


Methyl 2,6-di-*O*-allyl-α-D-mannopyranoside (S11): To a stirred solution of 5.0 g methyl α-D-mannopyranoside (25.75 mmol, 1 equiv) in 50 mL methanol were added 11.3 mL trimethyl orthoformate (103.0 mmol, 4 equiv), 2.46 mL butane-2,3-dione (28.32 mmol, 1.1 equiv) and 598 mg (±)-camphorsulfonic acid (2.57 mmol, 0.1 equiv). The reaction was stirred under refluxing conditions overnight, cooled to ambient temperature and quenched by the addition of 1.79 mL Et_3N (12.88 mmol, 0.5 equiv). After concentration of the mixture and coevaporation with toluene, the residue was dissolved in 50 mL *N*,*N*-dimethylformamide and 6.67 mL ally bromide (77.13 mmol, 3 equiv) and 3.09 g NaH (60% dispersion in mineral oil, 77.13 mmol, 3 equiv) were added. The reaction was stirred overnight and was subsequently quenched by the addition of 6.25 mL of MeOH. The mixture was partitioned between water and diethyl ether. The organic layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and water. Next, 100 mL TFA/H_2O (9/1, v/v) was added and the reaction was stirred for 30 min. Another 40 mL of water was added and the mixture was concentrated *in vacuo* and coevaporated with toluene. Flash column chromatography using EtOAc/PE (1/1 → 3/2) gave the title compound **S11** (3.73 g, 13.60 mmol, 53% over 3 steps). R_f 0.21 (EtOAc/PE, 3/2, v/v); $[\alpha]_D^{22}$ +21 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3372, 2912, 1136, 1051; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 6.01 – 5.82 (m, 2H, CH allyl), 5.34 – 5.22 (m, 2H, CH_2 allyl), 5.22 – 5.12 (m, 2H, CH_2 allyl), 4.76 (d, *J* = 1.2 Hz, 1H, H-1), 4.21 – 4.00 (m, 4H, CH_2 allyl), 3.82 – 3.57 (m, 8H, H-2, H-3, H-4, H-5, H-6, OH), 3.36 (s, 3H, CH_3 OMe); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 134.5, 134.2 (CH allyl), 117.4, 116.7 (CH_2 allyl), 98.1 (C-1), 77.2 (C-2), 72.2, 71.8 (CH_2 allyl), 71.1 (C-3), 70.7 (C-4), 69.7 (C-6), 68.6 (C-5), 54.5 (CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{13}H_{22}O_6Na$ 297.13086, found 297.13077.

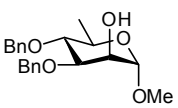


Methyl 3,4-di-*O*-benzyl-α-D-mannopyranoside (S12): To a solution of 4.22 g methyl 2,6-di-*O*-allyl-α-D-mannopyranoside **S11** (15.38 mmol, 1 equiv) in 60 mL DMF were added 5.52 mL benzyl bromide (46.15 mmol, 3 equiv) and 1.85 g NaH (60% in mineral oil, 46.15 mmol, 3 equiv). The reaction was stirred overnight at room temperature and quenched by the addition of 3.73 mL MeOH. The mixture was partitioned between Et_2O and water and the organic layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The residue was coevaporated with toluene and dissolved in 60 mL DMF. 3.55 g sodium tert-butoxide (36.93 mmol, 2.4 equiv) was added and the mixture was stirred overnight at 120 °C. After cooling to ambient temperature, the mixture was partitioned between Et_2O and water and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered and concentrated. The residue was dissolved in 60 mL MeOH and 293 mg *p*-toluenesulfonic acid monohydrate (1.54 mmol, 0.1 equiv) was added. When TLC analysis showed complete consumption of the starting material, the

reaction mixture was neutralized by the addition of 1.07 mL Et_3N and the solvent was removed under vacuum. Flash column chromatography using EtOAc/PE (3/7 → 1/0) gave the title compound **S12** (461 g, 12.31 mmol, 80% over 2 steps). R_f 0.20 (EtOAc/PE, 7/3, v/v); $[\alpha]_D^{22}$ +49 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3388, 2918, 1454, 1064, 737, 698; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.39 – 7.22 (m, 10H, H_{arom}), 4.88 (d, *J* = 10.9 Hz, 1H, CH_2 benzyl), 4.74 (d, *J* = 1.3 Hz, 1H, H-1), 4.72 – 4.63 (m, 3H, CH_2 benzyl), 4.00 (dd, *J* = 3.0, 1.7 Hz, 1H, H-2), 3.94 (t, *J* = 9.5 Hz, 1H, H-4), 3.85 (dd, *J* = 9.3, 3.2 Hz, 1H, H-3), 3.82 (d, *J* = 1.5 Hz, 2H, H-6), 3.60 (dt, *J* = 9.7, 2.8 Hz, 1H, H-5), 3.28 (s, 3H, CH_3 OMe), 3.22 (s, 2H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 138.3, 137.8 (C_q), 128.3, 128.2, 127.7, 127.6, 127.5 (CH_{arom}), 100.2 (C-1), 79.7 (C-3), 75.0 (CH_2 benzyl), 73.7 (C-4), 71.8 (CH_2 benzyl), 71.4 (C-5), 68.2 (C-2), 61.5 (C-6), 54.7 (CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{21}H_{26}O_6Na$ 397.16216, found 397.16153.

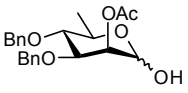


Methyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside (S13): 2.99 g Diol **S12** (7.97 mmol, 1 equiv) was dissolved in 40 mL toluene and argon was bubbled through the mixture for 15 minutes. To this solution 3.14 g Ph_3P (11.98 mmol, 1.5 equiv), 1.09 g imidazole (15.97 mmol, 2 equiv) and 2.84 g I_2 (11.18 mmol, 1.4 equiv) were added and the reaction was stirred at 70 °C for 90 minutes. The reaction was quenched by adding sat. aq. $Na_2S_2O_3$. The mixture was diluted with EtOAc and the organic phase was washed with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The residue was coevaporated with toluene and dissolved in 40 mL DMSO. To this solution 1.81 g $NaBH_4$ (47.82 mmol, 6 equiv) was added and the reaction was stirred at 100 °C overnight. 20 mL Acetone was added and the reaction was stirred at 100 °C for another 15 min. The flask was allowed to cool to room temperature and the mixture was partitioned between water and EtOAc. The organic layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The residue was filtered through a plug of silica gel using EtOAc/PE (1/3) as the eluent. After evaporation of the solvent, the crude mixture was dissolved in 30 mL pyridine and 10 mL acetic anhydride was added. The reaction was stirred overnight and quenched with MeOH. Removal of the solvents and coevaporation with toluene gave a crude mixture that was purified by flash column chromatography using EtOAc/toluene (1/19). This yielded the title compound **S13** (2.00 g, 4.99 mmol, 63% over 3 steps) as the major product. R_f 0.65 (EtOAc/PE, 3/7, v/v); $[\alpha]_D^{22}$ +7 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 2910, 1747, 1454, 1370, 1233, 1078, 698; ^1H NMR (300 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.46 – 7.06 (m, 10H, H_{arom}), 5.37 (dd, *J* = 3.4, 1.8 Hz, 1H, H-2), 4.91 (d, *J* = 10.9 Hz, 1H, CH_2 benzyl), 4.67 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.62 – 4.58 (m, 2H, H-1, CH_2 benzyl), 4.49 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 3.91 (dd, *J* = 9.3, 3.5 Hz, 1H, H-3), 3.80 – 3.65 (m, 1H, H-5), 3.43 (t, *J* = 9.4 Hz, 1H, H-4), 3.30 (s, 3H, CH_3 OMe), 2.11 (s, 3H, CH_3 Ac), 1.33 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$, HH-COSY, HSQC) δ 170.1 (C=O), 138.3, 137.9 (C_q), 128.2, 128.1, 127.8, 127.7, 127.5, 127.4 (CH_{arom}), 98.5 (C-1), 79.8 (C-4), 77.8 (C-3), 75.1 (CH_2 benzyl), 71.5 (CH_2 benzyl), 68.7 (C-2), 67.3 (C-5), 54.5 (CH_3 OMe), 20.8 (CH_3 Ac), 17.8 (C-6); HRMS $[M+Na]^+$ calcd for $C_{23}H_{28}O_6Na$ 423.17781, found 423.17768; Methyl 2,6-anhydro-3,4-di-*O*-benzyl-α-D-mannopyranoside **S15** was isolated as a side product (509 mg, 1.43 mmol, 18%). R_f 0.40 (EtOAc/PE, 1/3, v/v); $[\alpha]_D^{22}$ +3 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 2880, 1454, 1113, 737, 696; ^1H NMR (300 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.38 – 7.16 (m, 10H, H_{arom}), 5.04 (d, *J* = 2.7 Hz, 1H, H-1), 4.63 – 4.53 (m, 3H, CH_2 benzyl), 4.46 (d, *J* = 11.8 Hz, 1H, CH_2 benzyl), 4.09 – 4.03 (m, 2H, H-3, H-5), 3.99 – 3.89 (m, 2H, H-2, H-6), 3.70 (dd, *J* = 9.7, 0.7 Hz, 1H, H-6), 3.55 – 3.52 (m, 1H, H-4), 3.42 (s, 3H, CH_3 OMe); δ ^{13}C NMR (75 MHz, $CDCl_3$, HH-COSY, HSQC) δ 137.7, 137.7 (C_q), 128.1, 127.6, 127.5, 127.4 (CH_{arom}), 99.8 (C-1), 79.9 (C-4), 77.5 (C-3), 70.5, 69.9 (CH_2 benzyl), 68.3 (C-5), 67.8 (C-2), 65.8 (C-6), 55.2 (CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{21}H_{24}O_5Na$ 379.15160, found 379.15176.

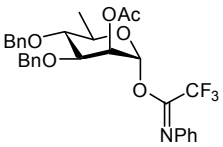


Methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside (29): A catalytic amount of NaOMe (54 mg, 1.00 mmol, 0.2 equiv) was added to a solution of 2.00 g mannopyranoside **S13** (4.99 mmol, 1 equiv) and the solution was stirred overnight at room temperature. 286 µL AcOH (4.99 mmol, 1 equiv) was added and the solvent

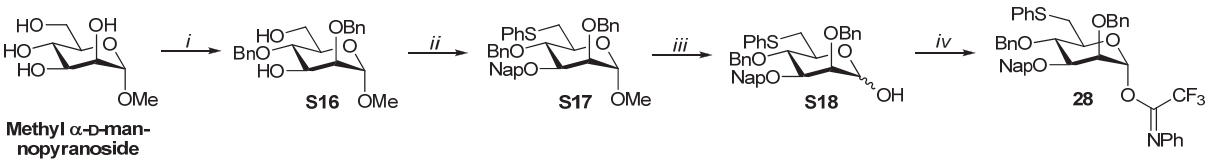
was removed *in vacuo*. The residue was partitioned between EtOAc and water and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated, yielding the title alcohol **29** as a colorless oil (1.70 g, 4.74 mmol, 95%). R_f 0.28 (EtOAc/PE, 3/7, v/v); $[\alpha]_D^{22}$ +44 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3462, 2908, 1454, 1056, 974, 735, 696; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.39 – 7.20 (m, 10H, H_{arom}), 4.87 (d, *J* = 11.0 Hz, 1H, CH_2 benzyl), 4.68 – 4.58 (m, 4H, H-1, CH_2 benzyl), 3.98 (d, *J* = 1.3 Hz, 1H, H-2), 3.80 (dd, *J* = 9.1, 3.2 Hz, 1H, H-3), 3.73 – 3.64 (m, 1H, H-5), 3.46 (t, *J* = 9.3 Hz, 1H, H-4), 3.28 (s, 3H, CH_3 OMe), 2.91 (s, 1H, OH), 1.31 (d, *J* = 6.3 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 138.2, 137.7 (C_q), 128.2, 128.1, 127.6, 127.6, 127.6, 127.4 (CH_{arom}), 99.9 (C-1), 79.7 (C-3, C-4), 75.0 (CH_2 benzyl), 71.6 (CH_2 benzyl), 68.1 (C-2), 67.0 (C-55), 54.4 (CH_3 OMe), 17.7 (C-6); HRMS $[M+Na]^+$ calcd for $C_{21}H_{26}O_5Na$ 381.16725, found 381.16720.



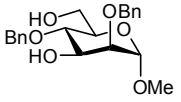
2-*O*-Acetyl-3,4-di-*O*-benzyl-6-deoxy-D-mannopyranose (S14): Methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside **29** (509 mg, 1.42 mmol, 1 equiv) was refluxed for 1 hour in 7 mL H_2O/TFA (5/2, v/v) and subsequently coevaporated with toluene. The crude product was stirred in 8 mL pyridine/Ac_2O (3/1, v/v) overnight. After quenching by the addition of MeOH, the mixture was evaporated and partitioned between EtOAc and water. The organic layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. Next, the residue was dissolved in 8 mL THF/piperidine (7/1, v/v) and was stirred overnight. The reaction mixture was diluted by the addition of EtOAc and washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography using EtOAc/PE (1/4 → 2/3) gave the title compound **S14** (474 mg, 1.23 mmol, 86% over 3 steps). R_f 0.24 (EtOAc/PE, 3/7, v/v); IR (neat, cm^{-1}) 3384, 2935, 1736, 1454, 1370, 1232, 1052, 736, 697; NMR data of the major anomer (α): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 5.36 (s, 1H, H-2), 5.09 (s, 1H, H-1), 4.91 (d, *J* = 10.8 Hz, 1H, CH_2 benzyl), 4.69 (d, *J* = 11.3 Hz, 1H, CH_2 benzyl), 4.61 (d, *J* = 10.9 Hz, 1H, CH_2 benzyl), 4.53 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.04 – 3.93 (m, 2H, H-3, H-5), 3.48 – 3.41 (m, 1H, H-4), 2.14 (s, 3H, CH_3 Ac), 1.30 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 170.5 (C=O Ac), 138.3, 137.9 (C_q), 128.3, 128.0, 127.9, 127.7, 127.6 (CH_{arom}), 92.3 (C-1), 78.8 (C-4), 77.4 (C-3), 75.3 (CH_2 benzyl), 71.7 (CH_2 benzyl), 69.4 (C-2), 67.7 (C-5), 21.1 (CH_3 Ac), 18.0 (C-6); HRMS $[M+Na]^+$ calcd for $C_{22}H_{26}O_6Na$ 409.16216, found 409.16195.



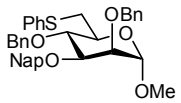
2-*O*-acetyl-3,4-di-*O*-benzyl-6-deoxy-D-mannopyranosyl *N*-phenyltrifluoroacetimidate (32): To a solution of 554 mg hemiacetal **S14** (1.43 mmol, 1 equiv) in 8 mL acetone/H_2O (19/1, v/v) were added 513 mg Cs_2CO_3 (1.58 mmol, 1.1 equiv) and 434 µL ClC(C=NPh)CF_3 (2.87 mmol, 2.0 equiv). The mixture was stirred for 2 days at ambient temperature, evaporated slightly and filtered over celite. After evaporation the crude product was purified by flash column chromatography using EtOAc/toluene (0/1→3/97) with 1% triethylamine to give 469 mg (841 µmol, 59%) of the title imidate as a mixture of epimers. R_f 0.51 (EtOAc/PE, 1/9, v/v); IR (neat, cm^{-1}) 3032, 1748, 1718, 1598, 1490, 1453, 1370, 1334, 1208, 1162, 1112, 751, 694; NMR data of the major anomer (α): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 7.63 – 6.60 (m, 15H, H_{arom}), 6.09 (s, 1H, H-1), 5.48 – 5.43 (m, 1H, H-2), 4.90 (d, *J* = 11.0 Hz, 1H, CH_2 benzyl), 4.70 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 4.63 (d, *J* = 11.0 Hz, 1H, CH_2 benzyl), 4.57 (d, *J* = 11.2 Hz, 1H, CH_2 benzyl), 3.95 (dd, *J* = 9.3, 3.4 Hz, 1H, H-3), 3.92 – 3.84 (m, 1H, H-5), 3.50 (t, *J* = 9.4 Hz, 1H, H-4), 2.10 (s, 3H, CH_3 Ac), 1.34 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333 K) δ 169.8 (C=O), 143.4, 138.4, 137.7 (C_q), 128.8, 128.4, 128.2, 128.0, 127.9, 127.7, 124.5, 119.5 (CH_{arom}), 94.7 (C-1), 79.4 (C-4), 77.5 (C-3), 75.4 (CH_2 benzyl), 72.3 (CH_2 benzyl), 70.7 (C-5), 67.9 (C-2), 20.7 (CH_3 Ac), 18.0 (C-6); HRMS $[M-(OC(N=Ph)CF_3)]^+$ calcd for $C_{22}H_{25}O_5$ 369.16965, found 369.16964.



Reagents and conditions: *i*) 1) TBSCl, imidazole, DMF 2) BnBr, NaH, DMF 3) TBAF, THF, 60% over 3 steps *ii*) 1) Ph_3P, imidazole, I_2, toluene, 70°C 2) PhSH, DiPEA. DMF 3) NapBr, NaH. DMF, 77% over 3 steps *iii*) 1) cat. H_2SO_4, Ac_2O 2) piperidine, THF (77% over 2 steps) *iv*) $CF_3C(=NPh)Cl$, Cs_2CO_3, acetone, H_2O, 94%.

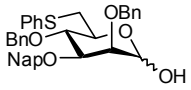


Methyl 2,4-di-*O*-benzyl-α-D-mannopyranoside (S16): To a mixture of 996 mg methyl α-D-mannopyranoside (5.13 mmol, 1 equiv) in 25 mL DMF were added 1.22 g imidazole (17.95 mmol, 3.5 equiv) and 2.32 g TBSCl (15.39 mmol, 3 equiv). After 2 hours of stirring, TLC analysis showed complete consumption of the starting material. The reaction was quenched by the addition of 375 µL MeOH. The mixture was partitioned between H_2O and Et_2O and the aqueous layer was extracted. The combined organic phases were washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The crude product was coevaporated with toluene and subsequently dissolved in 25 mL of DMF. To this solution 1.84 mL BnBr (15.39 mmol, 3 equiv) and 616 mg NaH (60% in mineral oil, 15.39 mmol, 3 equiv) were added. After stirring at ambient temperature overnight, the reaction was quenched with 2.08 mL MeOH, taken up in Et_2O and washed with 5% aq. LiCl and brine. After drying over $MgSO_4$, filtration and concentration under reduced pressure, the residue was dissolved in 5 mL THF and treated with 20.52 mL 1.0 M TBAF (in THF, 20.52 mmol, 4 equiv). The mixture was stirred for 2 hours and subsequently partitioned between EtOAc and H_2O. The water layer was further extracted with EtOAc and the combined organic layers were dried ($MgSO_4$), filtered and concentrated. Purification by flash column chromatography using EtOAc/PE (2/3 → 1/1) afforded the target compound **S16** (1.16 g, 3.10 mmol, 60% over 3 steps). R_f 0.33 (EtOAc/PE, 1/1, v/v); $[\alpha]_D^{22}$ +20 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3446, 2906, 1454, 1028, 698; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.38 – 7.22 (m, 10H, H_{arom}), 4.88 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 4.72 (d, *J* = 1.3 Hz, 1H, H-1), 4.69 (d, *J* = 11.8 Hz, 1H, CH_2 Bn), 4.64 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 4.58 (d, *J* = 11.8 Hz, 1H, CH_2 Bn), 4.02 – 3.93 (m, 1H, H-3), 3.84 (dd, *J* = 11.8, 2.5 Hz, 1H, H-6), 3.76 (dd, *J* = 11.8, 3.8 Hz, 1H, H-6), 3.73 – 3.63 (m, 2H, H-2, H-4), 3.60 – 3.54 (m, 1H, H-5), 3.29 (s, 3H, CH_3 OMe), 2.49 (d, *J* = 8.6 Hz, 1H, OH), 2.36 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ138.4, 137.7 (C_q Ph), 128.6, 128.5, 128.1, 128.0, 127.9, 127.8 (CH_{arom}), 98.3 (C-1), 78.4 (C-2), 76.4 (C-4), 74.9, 73.2 (CH_2 Bn), 71.7 (C-3), 71.3 (C-5), 62.2 (C-6), 54.9 (CH_3 OMe); HRMS $[M+Na]^+$ calcd for $C_{21}H_{26}O_6Na$ 397.16216, found 397.16050.

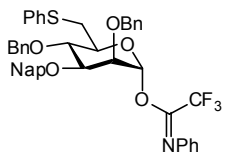


Methyl 2,4-di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-α-D-mannopyranoside (S17): Argon was bubbled through a solution of 1.16 g methyl 2,4-di-*O*-benzyl-α-D-mannopyranoside (3.10 mmol, 1 equiv) in 20 mL toluene. Next, 1.22 g triphenylphosphine (4.65 mmol, 1.5 equiv), 422 mg imidazole (6.20 mmol, 2.0 equiv) and 1.10 g iodine (4.34 mmol, 1.4 equiv) were added and the mixture was stirred for 3 hours at 70 °C. The reaction was quenched by the addition of sat. aq. $Na_2S_2O_3$ and the organic phase was diluted with EtOAc. Washing with H_2O and brine, drying ($MgSO_4$), filtration and evaporation afforded the crude product, which was dissolved in 15 mL of DMF. To this solution 1.10 mL DiPEA (6.20 mmol, 2 equiv) and 475 µL thiophenol (4.65 mmol, 1.5 equiv) were added. After stirring at ambient temperature for 1 hour, TLC-MS analysis showed complete consumption of the starting material and the emergence of the desired product. The reaction was diluted with Et_2O, washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The crude product was dissolved in 15 mL DMF and 1.37 g 2-(bromomethyl)naphthalene (6.20 mmol, 2 equiv) and 248 mg NaH (60% in mineral oil, 6.20 mmol, 2 equiv) were added. After stirring overnight, the mixture was partitioned between H_2O and Et_2O and the aqueous layer was extracted. The combined organic

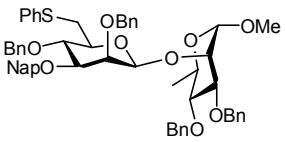
phases were washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. Purification by flash column chromatography using EtOAc/PE (1/19 → 1/9) afforded the title compound **S17** (1.46 g, 2.40 mmol, 77% over 3 steps). R_f 0.42 (EtOAc/PE, 1/6, v/v); $[\alpha]_D^{22}$ +6 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 2908, 1454, 1064, 733; ^1H NMR (300 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 7.83 – 7.65 (m, 4H, H_{arom}), 7.50 – 7.02 (m, 18H, H_{arom}), 5.01 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 4.73 – 4.72 (m, *J* = 2.4 Hz, 5H, CH_2 Bn, CH_2 Nap, H-1), 4.64 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 3.97 – 3.69 (m, 4H, H-3, H-4, H-2, H-5), 3.48 – 3.40 (m, 1H, H-6), 3.27 (s, 3H, CH_3 OMe), 3.05 (dd, *J* = 13.4, 8.6 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 138.3, 138.1, 137.0, 135.8, 133.2, 132.8 (C_q Ph), 128.7, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 126.1, 126.0, 125.7, 125.6, 125.5 (CH_{arom}), 98.7 (C-1), 80.1 (C-3), 77.8 (C-4), 75.1 (CH_2 Bn), 74.51 (C-2), 72.6 (CH_2 Bn), 71.9 (CH_2 Nap), 71.0 (C-5), 54.6 (CH_3 OMe), 35.7 (C-6); HRMS $[M+Na]^+$ calcd for $C_{38}H_{38}O_5SNa$ 629.23322, found 629.23180.



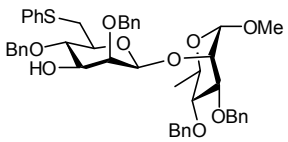
2,4-Di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-D-mannopyranose (S18): A catalytic amount of concentrated sulphuric acid was added to a solution of 1.21 g methyl 2,4-di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-α-D-mannopyranoside **S17** (1.99 mmol, 1 equiv) in 10 mL acetic anhydride at 0 °C. The reaction was quenched by the addition of triethylamine after 7 hours of stirring at 0 °C. The mixture was partitioned between H_2O and EtOAc and the organic layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The crude product was dissolved in 10 mL THF and 590 µL piperidine (5.97 mmol, 3 equiv) was added. After stirring overnight, the mixture was partitioned between H_2O and EtOAc and the aqueous layer was washed with aq. 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. Purification by flash column chromatography using EtOAc/toluene (0/1 → 1/19) gave the title compound **S18** (902 mg, 1.52 mmol, 77% over 2 steps). R_f 0.23 (EtOAc/PE, 1/4, v/v); IR (neat, cm^{-1}) 3403, 3060, 2926, 1454, 1069, 732; NMR data of the major anomer: ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 7.81 – 7.65 (m, 4H, H_{arom}), 7.45 – 7.04 (m, 18H, H_{arom}), 5.19 (dd, *J* = 3.1, 1.7 Hz, 1H, H-1), 5.00 (d, *J* = 11.1 Hz, 1H, CH_2 Bn), 4.70 (s, 2H, CH_2 Nap), 4.66 (s, 2H, CH_2 Bn), 4.62 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 4.11 – 4.03 (m, 1H, H-5), 4.00 (dd, *J* = 9.2, 2.8 Hz, 1H, H-3), 3.89 (t, *J* = 9.3 Hz, 1H, H-4), 3.80 – 3.76 (m, 1H, H-2), 3.58 (d, *J* = 3.6 Hz, 1H, OH), 3.42 (dd, *J* = 13.5, 1.9 Hz, 1H, H-6), 3.04 (dd, *J* = 13.6, 8.5 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 138.5, 138.4, 137.1, 136.0, 133.4, 133.1 (C_q), 129.1, 129.0, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 126.5, 126.3, 126.0, 125.8 (CH_{arom}), 92.6 (C-1), 79.8 (C-3), 78.0 (C-4), 75.4 (CH_2 Bn), 75.1 (C-2), 72.8 (CH_2 Bn), 72.3 (C-1), 71.3 (C-5), 35.9 (C-6); HRMS $[M+Na]^+$ calcd for $C_{37}H_{36}O_5SNa$ 615.21757 found 615.21714.



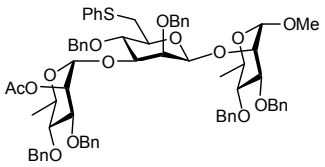
2,4-Di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-D-mannopyranosyl *N*-phenyltrifluoroacetimidate (28): To a solution of 902 mg hemiacetal **S18** (1.52 mmol, 1 equiv) in 8 mL acetone/H_2O (19/1, v/v) were added 545 mg Cs_2CO_3 (1.67 mmol, 1.1 equiv) and 632 mg $ClC(C=NPh)CF_3$ (3.04 mmol, 2.0 equiv). The mixture was stirred overnight at ambient temperature, evaporated slightly and filtered over Celite. After evaporation the crude product was purified by flash column chromatography using EtOAc/PE (1/19→1/9) with 1% triethyamine to give 1.10 g (1.43 mmol, 94%) of the title imidate **28** as a mixture of epimers. R_f 0.65 (EtOAc/PE, 3/17, v/v); IR (neat, cm^{-1}) 3063, 1718, 1117, 694; NMR data of the major anomer : ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, T = 333K) δ 7.84 – 7.68 (m, 4H, H_{arom}), 7.50 – 6.99 (m, 21H, H_{arom}), 6.67 (d, *J* = 7.5 Hz, 2H, H_{arom}), 6.15 (s, 1H, H-1), 4.95 (d, *J* = 11.2 Hz, 1H, CH_2 Bn/Nap), 4.80 (d, *J* = 11.9 Hz, 1H, CH_2 Bn/Nap), 4.72 (d, *J* = 11.9 Hz, 1H, CH_2 Bn/Nap), 4.67 – 4.58 (m, 3H, CH_2 Bn/Nap), 4.03 – 3.90 (m, 3H, H-5, H-4, H-3), 3.82 (t, *J* = 2.3 Hz, 1H, H-2), 3.42 – 3.34 (m, 1H, H-6), 3.06 (dd, *J* = 13.7, 7.1 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, T= 333K) δ 143.5, 138.3, 137.8, 136.8, 135.6, 133.4, 133.2 (C_q), 129.8, 129.3, 128.8, 128.7, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 126.7, 126.3, 126.2, 126.1, 126.0, 125.9, 124.3, 119.4 (CH_{arom}), 95.4 (C-1), 79.4 (C-3), 77.1 (C-4/C-5), 75.2 (CH_2 Bn/Nap) , 74.1 (C-4/C-5, C-2), 72.9 (CH_2 Bn/Nap), 36.4 (C-6); HRMS $[M-(OC(N=Ph)CF_3)]^+$ calcd for $C_{37}H_{35}O_4S$ 575.22506, found 575.22512.



2,4-Di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (30): Imidate donor **28** (367 mg, 481 µmol, 1 equiv) and 258 mg acceptor **29** (721 µmol, 1.5 equiv) were co-evaporated together with toluene. Freshly distilled DCM (7 mL) and 3Å activated molecular sieves were added and the mixture was stirred under argon for 30 min at room temperature. The mixture was cooled to -80 °C and 386 µL of a well-shaken 0.25 M solution of TfOH in DCM (0.2 equiv) was added. After stirring for 4 nights at -80 °C, 1 mL of Et_3N was added, the mixture was filtered over Celite and the solvent was removed under reduced pressure. The epimeric mixture could be separated by flash column chromatography using EtOAc/toluene (0/1 → 1/19) giving the title β-linked disaccharide **30** (341 mg, 366 µmol, 76%) R_f 0.30 (EtOAc/PE, 3/17, v/v); $[\alpha]_D^{22}$ -32 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3030, 2900, 1454, 1068, 732, 696; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) δ 7.84 – 7.67 (m, 4H, H_{arom}), 7.58 – 7.05 (m, 28H, H_{arom}), 5.12 (d, *J* = 12.0 Hz, 1H, CH_2 Bn/Nap), 5.06 (d, *J* = 11.1 Hz, 1H, CH_2 Bn/Nap), 5.02 (d, *J* = 11.6 Hz, 1H, CH_2 Bn/Nap), 4.95 (d, *J* = 12.1 Hz, 1H, CH_2 Bn/Nap), 4.91 (d, *J* = 11.0 Hz, 1H, CH_2 Bn/Nap), 4.71 – 4.62 (m, 3H, H-1, CH_2 Bn/Nap), 4.56 – 4.50 (m, 4H, H-1', CH_2 Bn/Nap), 4.38 (dd, *J* = 3.1, 2.0 Hz, 1H, H-2), 4.04 (d, *J* = 3.0 Hz, 1H, H-2'), 3.93 (dd, *J* = 9.0, 3.3 Hz, 1H, H-3), 3.82 (t, *J* = 9.2 Hz, 1H, H-4'), 3.74 – 3.65 (m, 1H, H-5), 3.53 (dd, *J* = 9.2, 3.0 Hz, 1H, H-3'), 3.48 (t, *J* = 9.2 Hz, 1H, H-4), 3.45 – 3.39 (m, 2H, H-5', H-6'), 3.33 (s, 3H, CH_3 OMe), 2.93 (dd, *J* = 13.9, 9.6 Hz, 1H, H-6'), 1.28 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 139.0, 138.6, 138.5, 138.2, 137.0, 135.4, 133.1, 132.9 (C_q), 128.8, 128.6, 128.4, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.6, 127.5, 127.4, 127.0, 126.2, 126.0, 125.8, 125.6, 125.4 (CH_{arom}), 99.3 (C-1'), 97.9 (C-1), 81.6 (C-3'), 79.7 (C-4), 77.7, 77.6 (C-3, C-4'), 75.2 (CH_2 Bn/Nap), 75.0 (C-5', CH_2 Bn/Nap), 73.8 (CH_2 Bn/Nap), 73.2 (C-2'), 71.8 (C-2), 70.8 (CH_2 Bn/Nap), 69.9 (CH_2 Bn/Nap), 67.4 (C-5), 54.7 (CH_3 OMe), 35.4 (C-6'), 18.2 (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.3 ($J_{C1'-H1'}$ = 153.9 Hz, C-1'), 97.9 (J_{C1-H1} = 166.1 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{58}H_{60}O_9SNa$ 955.38503, found 955.38453.

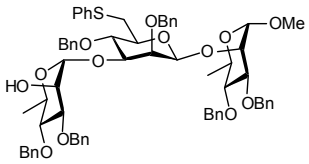


2,4-di-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (31): To a solution of 140 mg disaccharide **30** (150 µmol, 1 equiv) in 5 mL DCM was added 0.1 mL H_2O and 68 mg 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (300 µmol, 2 equiv). After 1 hour the reaction was quenched by the addition of sat. aq. $NaHCO_3$ and the layers were separated. The aqueous phase was extracted with DCM and the combined organic fractions were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography using EtOAc/toluene (1/9 → 1/4) gave alcohol **31** (71 mg, 89 µmol, 60%). R_f 0.25 (EtOAc/PE, 3/7, v/v); $[\alpha]_D^{22}$ +38 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3526, 3030, 2902, 1454, 1067, 736, 697; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC) 7.47 (dd, *J* = 7.6, 1.7 Hz, 2H, H_{arom}), 7.43 (dd, *J* = 6.6, 2.9 Hz, 2H, H_{arom}), 7.34 – 7.08 (m, 21H, H_{arom}), 5.20 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 5.02 – 4.96 (m, 2H, CH_2 Bn), 4.86 (d, *J* = 11.0 Hz, 1H, CH_2 Bn), 4.71 (d, *J* = 1.6 Hz, 1H, H-1), 4.68 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 4.63 (s, 1H, H-1'), 4.57 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 4.52 (d, *J* = 11.5 Hz, 1H, CH_2 Bn), 4.47 (d, *J* = 11.0 Hz, 1H, CH_2 Bn), 4.39 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 3.92 (dd, *J* = 9.1, 3.4 Hz, 1H, H-3), 3.88 (d, *J* = 3.8 Hz, 1H, H-2'), 3.73 – 3.63 (m, 2H, H-5, H-3'), 3.48 – 3.36 (m, 4H, H-4, H-4', H-5', H-6'), 3.35 (s, 3H, CH_3 OMe), 2.90 (dd, *J* = 13.3, 8.3 Hz, 1H, H-6'), 2.62 (s, 1H, OH), 1.25 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 139.0, 138.4, 138.2, 138.1, 136.9 (C_q), 128.8, 128.7, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.1, 125.5 (CH_{arom}), 99.3 (C-1'), 97.9 (C-1), 79.7 (C-4, C-4'), 77.8 (C-3), 77.5 (C-2'), 75.1, 74.9, 74.8 (CH_2 Bn), 74.4 (C-5'), 74.1 (C-3'), 71.9 (C-2), 70.1 (CH_2 Bn), 67.4 (C-5), 54.8 (CH_3 OMe), 35.4 (C-6'), 18.2; ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.3 ($J_{C1'-H1'}$ = 154.3 Hz, C-1'), 97.9 (J_{C1-H1} = 166.2 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{47}H_{52}O_9SNa$ 815.32243, found 815.32190.

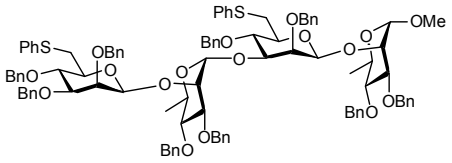


2-*O*-acetyl-3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (33): Imidate donor **32**

(173 mg, 311 µmol, 1.7 equiv) and 142 mg acceptor **31** (179 µmol, 1 equiv) were co-evaporated together with toluene. Freshly distilled DCM (3 mL) and 3Å activated molecular sieves were added and the mixture was stirred under argon atmosphere for 30 min at room temperature. The mixture was cooled to 0 °C and 100 µL of a well-shaken 0.62 M solution of TfOH in DCM (0.35 equiv) was added. After stirring for 15 min at 0 °C, 250 µL Et_3N was added and the solvent was removed under reduced pressure. Flash column chromatography using EtOAc/toluene (1/19 → 3/17) gave the title trisaccharide **33** (175 mg, 151 µmol, 84%). R_f 0.50 (EtOAc/PE, 3/7, v/v); $[\alpha]_D^{22}$ -5 (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 3032, 2908, 1743, 1454, 1233, 1070, 736, 697; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 7.51 – 7.09 (m, 35H, H_{arom}), 5.46 (apparent s, 1H, H-2''), 5.15 (d, *J* = 11.5 Hz, 1H, CH_2 Bn), 5.05 (app s, 1H, H-1''), 4.99 (d, *J* = 11.5 Hz, 1H, CH_2 Bn), 4.93 (d, *J* = 11.2 Hz, 1H, CH_2 Bn), 4.89 – 4.81 (m, 2H, CH_2 Bn), 4.75 – 4.69 (m, 2H, H-1, CH_2 Bn), 4.68 – 4.59 (m, 3H, H-1', CH_2 Bn), 4.56 – 4.45 (m, 4H, CH_2 Bn), 4.38 (app s, 1H, H-2), 3.98 – 3.86 (m, 3H, H-3'', H-3, H-2'), 3.81 – 3.74 (m, 2H, H-4', H-5''), 3.71 – 3.64 (m, 2H, H-5, H-3'), 3.45 – 3.33 (m, 6H, H-4'', H-4, H-5', CH_3 OMe), 3.30 (d, *J* = 13.5 Hz, 1H, H-6'), 2.82 (dd, *J* = 13.5, 9.4 Hz, 1H, H-6'), 2.08 (s, 3H, CH_3 Ac), 1.27 (t, *J* = 5.7 Hz, 6H, H-6'', H-6); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 170.1 (C=O Ac), 139.0, 138.7, 138.6, 137.9, 137.7, 136.8 (C_q), 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.1, 125.6 (CH_{arom}), 99.6 (C-1''), 99.2 (C-1'), 98.0 (C-1), 80.3 (C-3'), 79.9 (C-4), 79.7 (C-4''), 78.4 (C-4'), 77.8 (C-2', C-3''), 77.5 (C-3), 75.4, 75.1 (CH_2 Bn), 74.9 (C-5'), 74.4 (CH_2 Bn), 71.9 (CH_2 Bn), 71.7 (C-2), 70.0 (CH_2 Bn), 69.1 (C-2''), 68.4 (C-5''), 67.5 (C-5), 54.8 (CH_3 OMe), 35.3 (C-6'), 21.0 (CH_3 Ac), 18.1 (C-6, C-6''); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.6 ($J_{C1''\text{-}H1''}$ = 171.7 Hz, C-1''), 99.2 ($J_{C1'\text{-}H1'}$ = 154.5 Hz, C-1'), 98.0 ($J_{C1\text{-}H1}$ = 171.7 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{69}H_{76}O_{14}SNa$ 1183.48480, found 1183.48542.

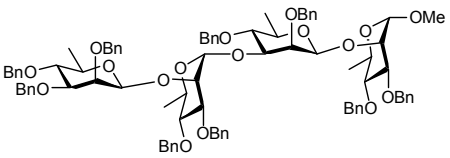


3,4-Di-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (34): To a solution of 175 mg (151 µmol, 1 equiv) trisaccharide **33** in 3 mL MeOH was added 20 mg NaOMe (377 µmol, 2.5 equiv) and the mixture was stirred overnight at ambient temperature. The reaction was quenched with 43 µL acetic acid (755 µmol, 5 equiv) and the solvent was evaporated. The crude mixture was partitioned between EtOAc and H_2O. The organic phase was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography using EtOAc/toluene (1/4 → 3/7) gave the title alcohol **34** (165 mg, 147 µmol, 98%). R_f 0.33 (EtOAc/PE, 2/3, v/v); $[\alpha]_D^{22}$ +27 (c 0.66, CH_2Cl_2); IR (neat, cm^{-1}) 2928, 1454, 1074, 697; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 7.53 – 7.06 (m, 35H, H_{arom}), 5.16 (d, *J* = 11.5 Hz, 1H, CH_2 benzyl), 5.11 (d, *J* = 1.6 Hz, 1H, H-1''), 5.00 (d, *J* = 11.5 Hz, 1H, CH_2 benzyl), 4.92 – 4.82 (m, 2H, CH_2 benzyl), 4.76 – 4.59 (m, 7H, H-1, H-1', CH_2 benzyl), 4.55 – 4.44 (m, 3H, CH_2 benzyl), 4.38 (dd, *J* = 3.0, 2.1 Hz, 1H, H-2), 4.03 – 3.97 (m, 1H, H-2''), 3.93 – 3.87 (m, 2H, H-3, H-3'), 3.85 (dd, *J* = 9.1, 3.2 Hz, 1H, H-3''), 3.82 – 3.72 (m, 2H, H-5'', H-4'), 3.72 – 3.63 (m, 2H, H-2', H-5), 3.49 – 3.28 (m, 7H, H-4'', H-4, H-5', CH_3 OMe, H-6'), 2.86 (dd, *J* = 13.4, 9.2 Hz, 1H, H-6'), 2.41 (d, *J* = 1.8 Hz, 1H, OH), 1.26 – 1.25 (d, *J* = 6.1 Hz, 6H, H-6, H-6''); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 139.1, 138.6, 138.5, 137.9, 137.7, 136.8 (C_q), 128.9, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.0, 125.6 (CH_{arom}), 101.2 (C-1''), 99.3 (C-1'), 98.0 (C-1), 80.6 (C-2'), 79.9, 79.8, 79.7 (C-3'', C-4'', C-4), 78.4 (C-4'), 77.9 (C-3), 77.6 (C-3'), 75.4 (CH_2 benzyl), 75.1 (CH_2 benzyl), 75.0 (CH_2 benzyl), 74.8 (C-5'), 74.3 (CH_2 benzyl), 72.3 (CH_2 benzyl), 71.8 (C-2), 70.0 (CH_2 benzyl), 69.0 (C-2''), 68.0 (C-5''), 67.5 (C-5), 54.8 (CH_3 OMe), 35.3 (C-6'), 18.1 (C-6, C-6''); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 101.2 ($J_{C1''\text{-}H1''}$ = 170.2 Hz, C-1''), 99.3 ($J_{C1'\text{-}H1'}$ = 154.1 Hz, C-1'), 98.0 ($J_{C1\text{-}H1}$ = 166.7 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{67}H_{74}O_{13}SNa$ 1141.47423, found 1141.47440.

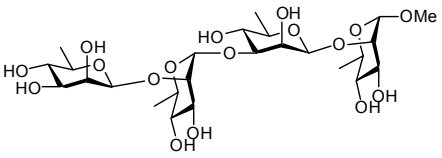


2,3,4-tri-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (35): Imidate donor

8 (70 mg, 98 µmol, 1.5 equiv) and 73 mg acceptor **34** (65 µmol, 1.0 equiv) were co-evaporated together with toluene. Freshly distilled DCM (1 mL) and 3Å activated molecular sieves were added and the mixture was stirred under argon for 30 min at room temperature. The mixture was cooled to -60 °C and a solution of 13 µmol of TfOH in 0.1 mL DCM (0.2 equiv) was added. After stirring for 3 nights at -60 °C, 0.5 mL of Et_3N was added, the mixture was filtered over celite and the solvent was removed under reduced pressure. The epimeric mixture (α/β 1:3) could be separated by flash column chromatography using EtOAc/toluene (1/99 → 3/97) giving the title tetrasaccharide **35** (60 mg, 36 µmol, 55%). Rf 0.26 (EtOAc/toluene, 1/19, v/v); $[\alpha]_D^{22}$ -12 (c 0.6, CH_2Cl_2); IR (neat, cm^{-1}) 2932, 1454, 1364, 1074, 1028, 737, 697; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 7.77 – 6.79 (m, 55H, H_{arom}), 5.12 (d, *J* = 1.1 Hz, 1H, H-1''), 5.08 – 4.97 (m, 5H, CH_2 benzyl), 4.93 – 4.84 (m, 2H, CH_2 benzyl), 4.84 – 4.74 (m, 3H, CH_2 benzyl), 4.71 (d, *J* = 1.5 Hz, 1H, H-1), 4.60 (s, 1H, H-1'), 4.59 – 4.43 (m, 7H, CH_2 benzyl), 4.39 (dd, *J* = 3.0, 2.0 Hz, 1H, H-2), 4.36 – 4.32 (m, 1H, H-2''), 4.30 (d, *J* = 12.2 Hz, 1H, CH_2 benzyl), 3.95 (dd, *J* = 9.1, 3.2 Hz, 1H, H-3''), 3.91 (dd, *J* = 9.0, 3.4 Hz, 1H, H-3), 3.85 (d, *J* = 1.5 Hz, 1H, H-2'), 3.81 (s, 1H, H-1'''), 3.79 – 3.72 (m, 3H, H-4', H-3', H-2'''), 3.71 – 3.61 (m, 2H, H-5, H-5''), 3.56 (t, *J* = 9.2 Hz, 1H, H-4'''), 3.46 – 3.33 (m, 6H, H-4, H-4'', H-5', CH_3 OMe), 3.31 – 3.19 (m, 2H, H-6''', H-6'), 2.89 (dd, *J* = 9.1, 3.0 Hz, 1H, H-3'''), 2.84 – 2.64 (m, 3H, H-6', H-5''', H-6'''), 1.27 (d, *J* = 6.3 Hz, 3H, H-6), 1.22 (d, *J* = 6.1 Hz, 3H, H-6''); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 139.0, 138.8, 138.7, 138.6, 138.5, 138.3, 138.1, 137.9, 137.2, 136.6 (C_q), 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.2, 127.0, 126.0, 125.5, 125.2 (CH_{arom}), 99.4 (C-1'''), 99.2 (C-1'), 99.0 (C-1''), 97.9 (C-1), 81.0 (C-3'''), 79.7 (C-4), 79.6 (C-4''), 78.5, 78.4 (C-3', C-4'), 77.8 (C-3), 77.5 (C-3'', C-4''), 77.14 (C-2'), 75.1, 74.9 (CH_2 benzyl, C-5'), 74.8 (CH_2 benzyl), 74.6 (C-5'''), 74.4, 73.8 (CH_2 benzyl), 73.3 (C-2'''), 72.3 (C-2''), 71.6 (C-2), 70.6, 70.0 (CH_2 benzyl), 68.4 (C-5''), 67.5 (C-5), 54.8 (CH_3 OMe), 34.9 (C-6'), 34.6 (C-6'''), 18.5 (C-6''), 18.2 (C-6); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.4 ($J_{C1'''\text{-}H1'''}$ = 155.0 Hz, C-1'''), 99.2 ($J_{C1'\text{-}H1'}$ = 154.6 Hz, C-1'), 99.0 ($J_{C1''\text{-}H1''}$ = 168.4 Hz, C-1''), 97.9 ($J_{C1\text{-}H1}$ = 165.8 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{100}H_{106}O_{17}S_2Na$ 1666.67972, found 1666.68036.

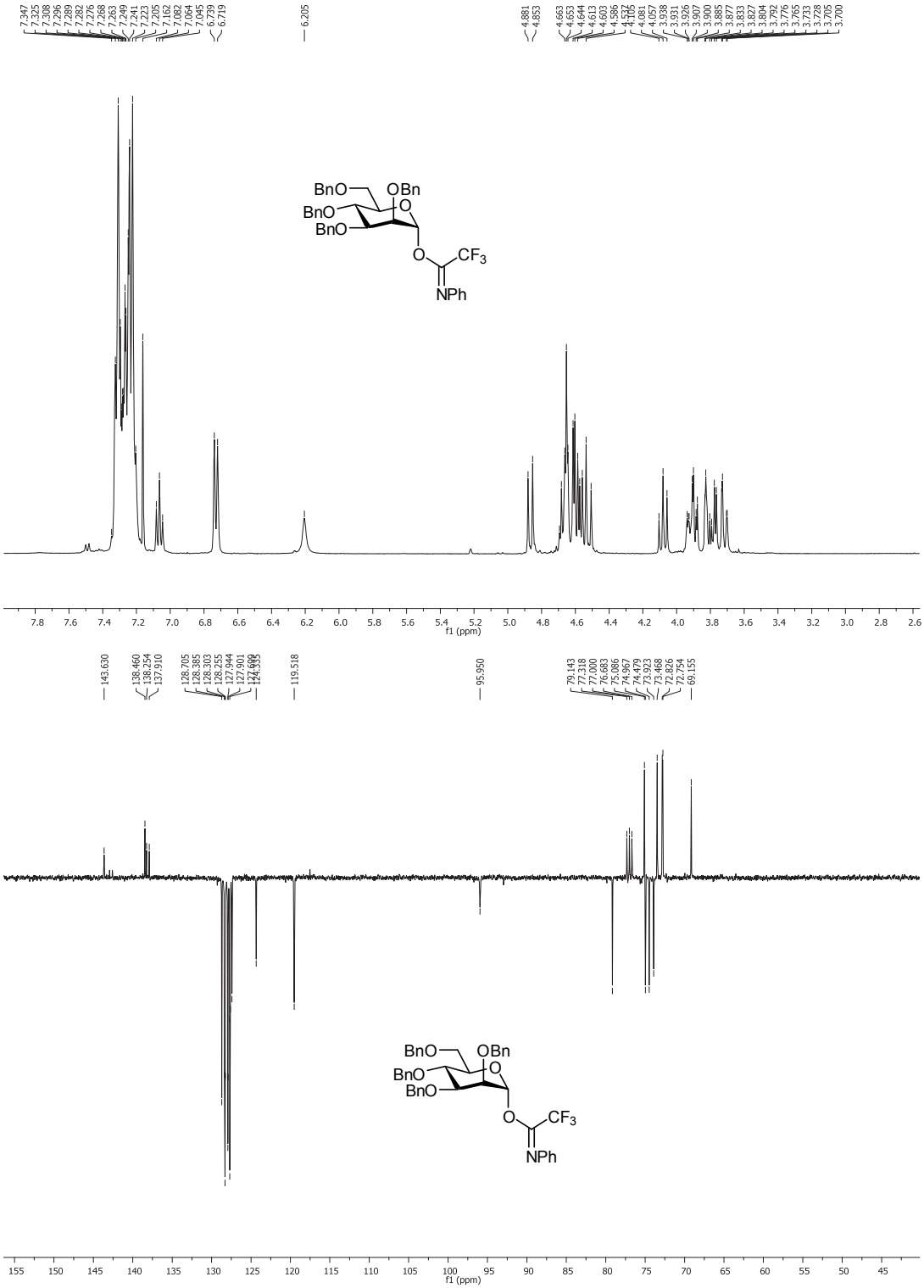


2,3,4-tri-*O*-benzyl-6-deoxy-β-D-mannopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (36): To a solution of tetrasaccharide **35** (9.2 mg, 5.6 µmol) were added 300 mg Raney nickel 2800 (slurry in H_2O) and 3 mL of MeOH. The mixture was allowed to reflux under H_2 atmosphere overnight. Filtration over celite gave the crude product, which was purified by flash column chromatography using EtOAc/toluene (1/9) giving the title tetrarhamnoside **36** (7.7 mg, 5.4 µmol, 96%). Rf 0.30 (EtOAc/toluene, 1/9, v/v); $[\alpha]_D^{22}$ -58 (c 0.15, CH_2Cl_2); IR (neat, cm^{-1}) 2934, 1454, 1364, 1074, 735, 697; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC) δ 7.50 – 7.02 (m, 45H, H_{arom}), 5.13 – 5.07 (m, 2H, H-1'', CH_2 benzyl), 5.00 (d, *J* = 12.1 Hz, 1H, CH_2 benzyl), 4.96 – 4.79 (m, 6H, CH_2 benzyl), 4.77 – 4.68 (m, 3H, H-1, CH_2 benzyl), 4.65 – 4.56 (m, 3H, H-1', CH_2 benzyl), 4.50 – 4.42 (m, 5H, CH_2 benzyl), 4.35 – 4.30 (m, 2H, H-2, CH_2 benzyl), 4.20 – 4.17 (m, 1H, H-2''), 4.02 (s, 1H, H-1'''), 3.92 (dd, *J* = 9.0, 3.2 Hz, 1H, H-3''), 3.90 – 3.84 (m, 2Hm H-2', H-3), 3.78 (d, *J* = 3.0 Hz, 1H, H-2'''), 3.76 – 3.59 (m, 4H, H-5'', H-3', H-5, H-4'), 3.53 – 3.38 (m, 3H, H-4''', H-4'', H-4), 3.38 – 3.29 (m, 4H, CH_3 OMe, H-5'), 3.05 (dd, *J* = 9.4, 3.1 Hz, 1H, H-3'''), 2.82 – 2.72 (m, 1H, H-5'''), 1.31 – 1.20 (m, 12H, H-6, H-6', H-6'', H-6'''); ^{13}C NMR (100 MHz, $CDCl_3$, HH-COSY, HSQC) δ 139.0, 138.9, 138.7, 138.5, 138.4, 138.3 (C_q), 128.5, 128.3, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 127.3, 127.2, 126.2 (CH_{arom}), 99.8 (C-1'''), 99.3 (C-1'', C-1'), 98.2 (C-1), 81.2 (C-3'''), 80.5 (C-4'), 79.9, 79.8, 79.7 (C-4'', C-4, C-4'''), 79.4 (C-3'), 78.0, 77.9, 77.8 (C-3, C-2', C-3''), 75.1, 74.9, 74.8, 74.5, 74.3 (CH_2 benzyl), 73.8 (CH_2 benzyl, C-2'''), 73.3 (C-2'''), 72.0 (C-2, C-5'), 71.6 (C-5'''), 70.7, 70.6, 70.4 (CH_2 benzyl), 68.4 (C-5''), 67.6 (C-5), 54.7 (CH_3 OMe), 18.5, 18.1, 17.9, 17.8 (C-6, C-6', C-6'', C-6'''); ^{13}C-HMBC NMR (100 MHz, $CDCl_3$) δ 99.8 ($J_{C1'''\text{-}H1'''}$ = 152.1 Hz, C-1'''), 99.3 ($J_{C1''\text{-}H1''}$ = 167.3 Hz, C-1''), 99.3 ($J_{C1'\text{-}H1'}$ = 153.6 Hz, C-1'), 98.2 ($J_{C1\text{-}H1}$ = 165.3 Hz, C-1); HRMS $[M+Na]^+$ calcd for $C_{88}H_{98}O_{17}Na$ 1449.66962, found 1449.67083.

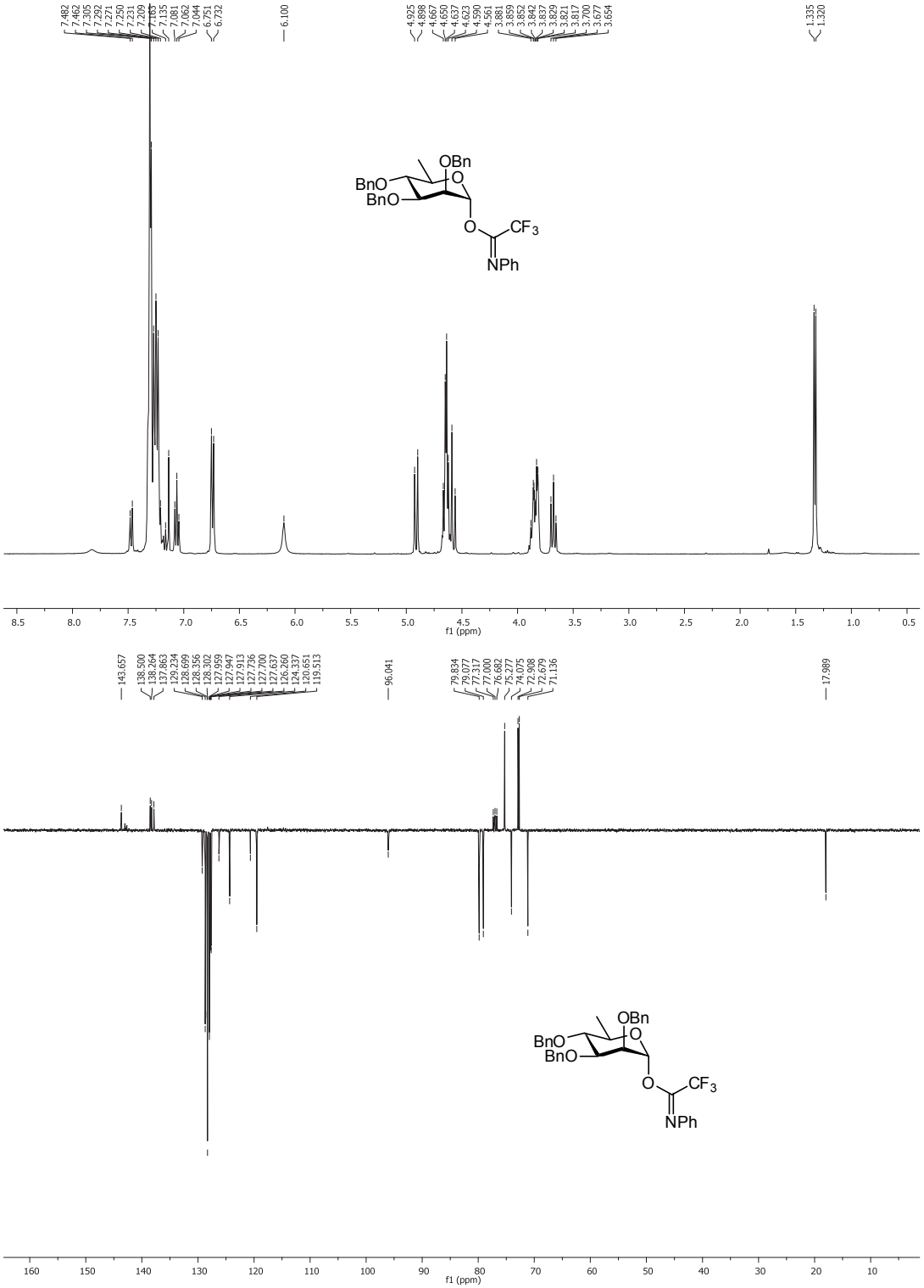


6-deoxy-β-D-mannopyranosyl-(1→2)-6-deoxy-α-D-mannopyranosyl-(1→3)-6-deoxy-β-D-mannopyranosyl-(1→2)-(methyl 6-deoxy-α-D-mannopyranoside) (37): A solution of 7.7 mg (5.4 µmol) tetramer **36** in 5 mL ^{t}BuOH/H_2O (7/3, v/v) was purged with argon for 15 minutes. Next half a teaspoon of palladium on activated charcoal was added and the mixture was stirred overnight under hydrogen atmosphere. Filtration over Celite and subsequent lyophilisation afforded 2.8 mg of the pure title compound **37** (4.6 µmol, 85%). ^{1}H NMR (600 MHz, D_2O, HH-COSY, HSQC, HMBC) δ 5.12 (d, *J* = 1.2 Hz, 1H, H-1''), 4.79 (d, *J* = 1.2 Hz, 1H, H-1), 4.72 (s, 1H, H-1'), 4.70 (s, 1H, H-1'''), 4.22 (dd, *J* = 3.2, 1.7 Hz, 1H, H-2''), 4.10 – 4.07 (m, 2H, H-2', H-2), 4.00 (d, *J* = 3.2 Hz, 1H, H-2'''), 3.87 – 3.83 (m, 2H, H-3'', H-5''), 3.71 (dd, *J* = 9.8, 3.4 Hz, 1H, H-3), 3.69 – 3.62 (m, 2H, H-5, H-3'), 3.59 – 3.56 (m, 1H, H-3'''), 3.50 – 3.36 (m, 9H, H-4', H-4'', H-4, H-5', CH_3 OMe, H-4''', H-5'''), 1.32 – 1.27 (m, 12H, H-6, H-6', H-6'', H-6'''); ^{13}C NMR (150 MHz, D_2O, HH-COSY, HSQC, HMBC) δ 101.1 (C-1''), 99.5 (C-1''', C-1), 99.2 (C-1'), 81.7 (C-3'), 78.3 (C-2''), 78.1 (C-2), 73.5 (C-3''', C-4, C-4''), 73.3 (C-5'''), 73.1 (C-5'), 72.9 (C-4'''), 72.2 (C-4'), 71.9 (C-2'''), 71.8 (C-2'), 70.6 (C-3), 70.5 (C-3''), 70.3 (C-5''), 69.6 (C-5), 55.8 (CH_3 OMe), 17.7, 17.6, 17.5 (C-6, C-6', C-6'', C-6'''); ^{13}C-HMBC NMR (150 MHz, D_2O) δ 101.1 ($J_{C1''\text{-}H1''}$ = 170.6 Hz, C-1''), 99.5 ($J_{C1'''\text{-}H1'''}$ = 159.8 Hz, C-1'''), 99.5 ($J_{C1\text{-}H1}$ = 170.6 Hz, C-1), 99.2 ($J_{C1'\text{-}H1'}$ = 160.0 Hz, C-1'); HRMS $[M+Na]^+$ calcd for $C_{25}H_{44}O_{17}Na$ 639.24707, found 639.24695.

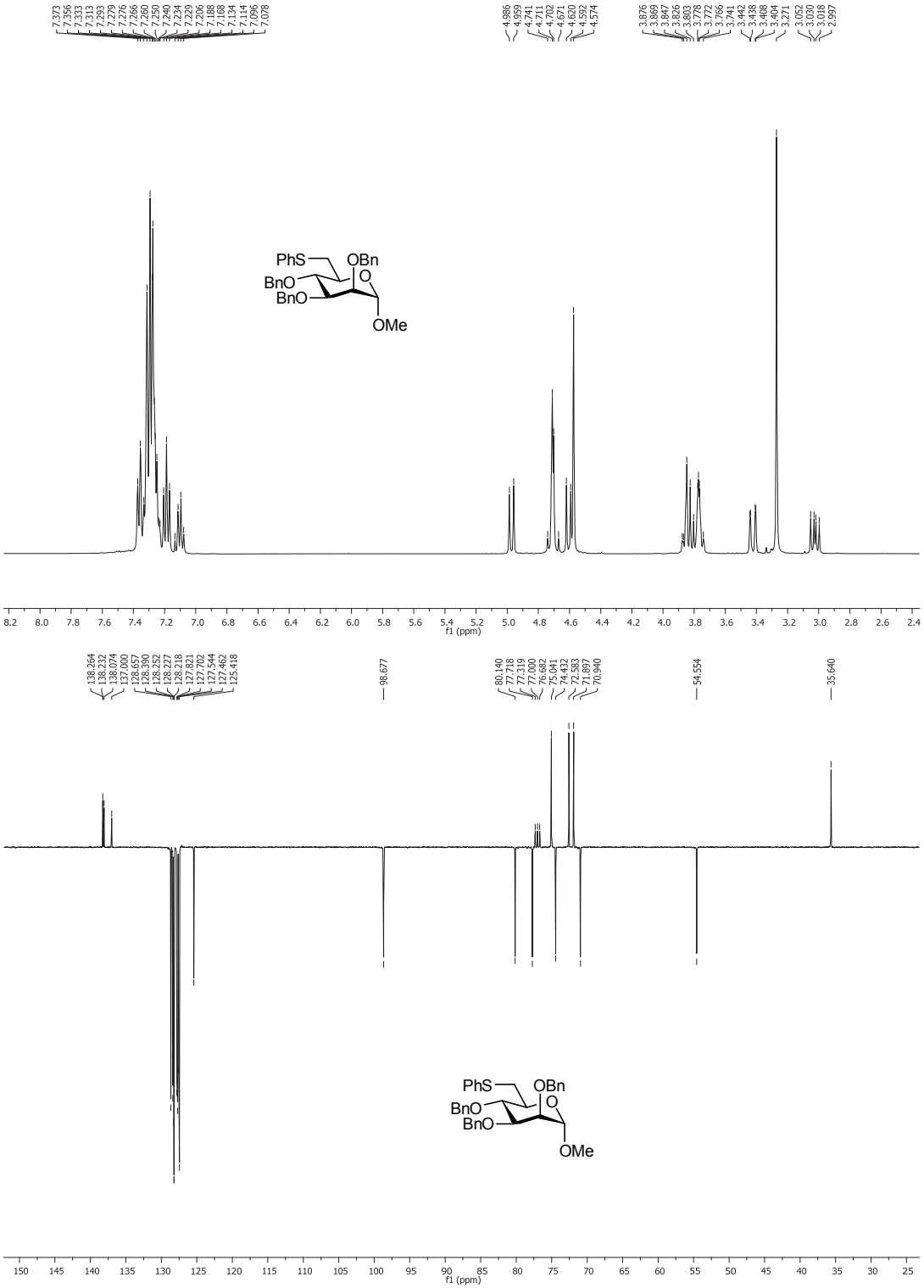
2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidates (6):



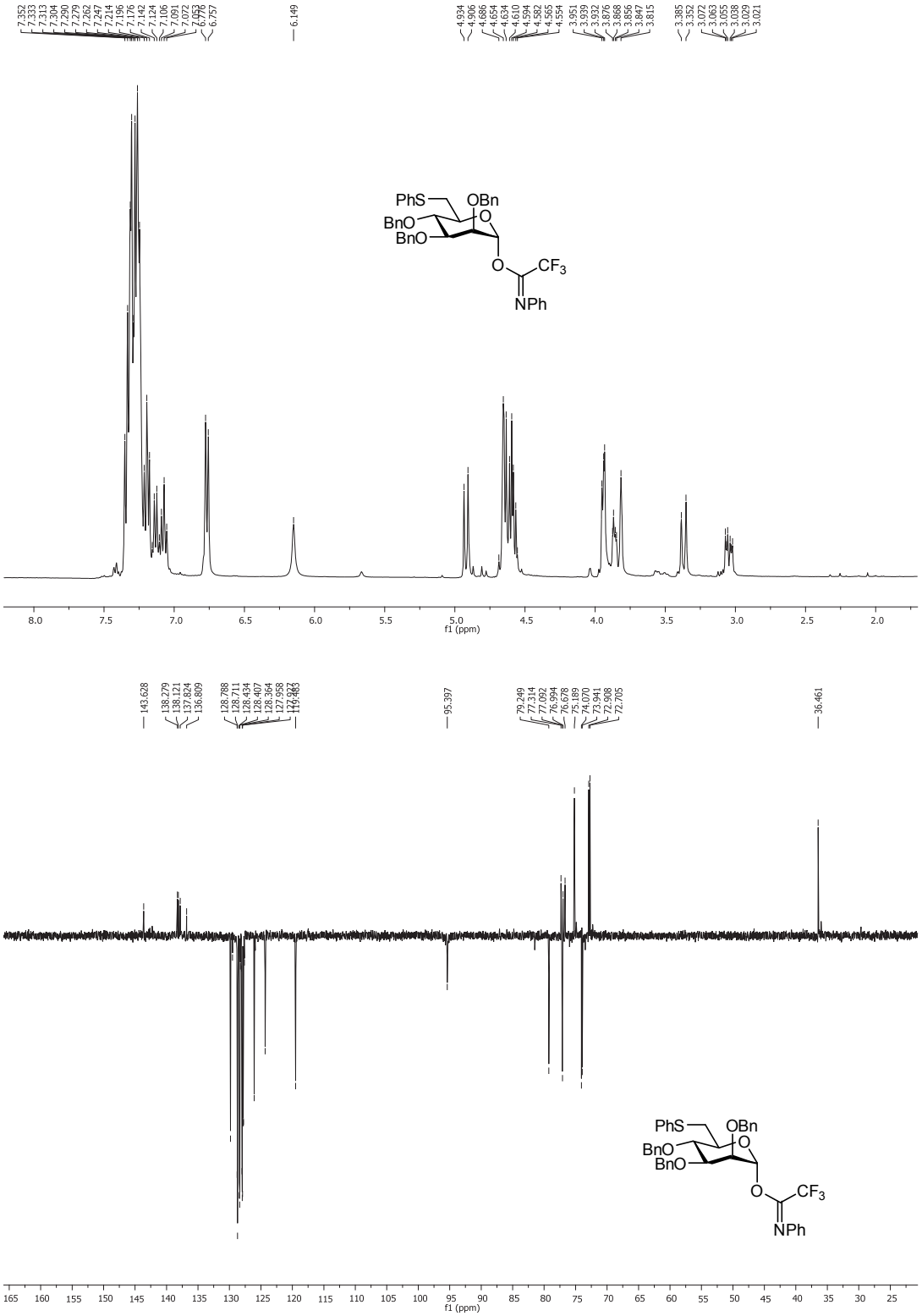
2,3,4-tri-*O*-benzyl-6-deoxy-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (7):



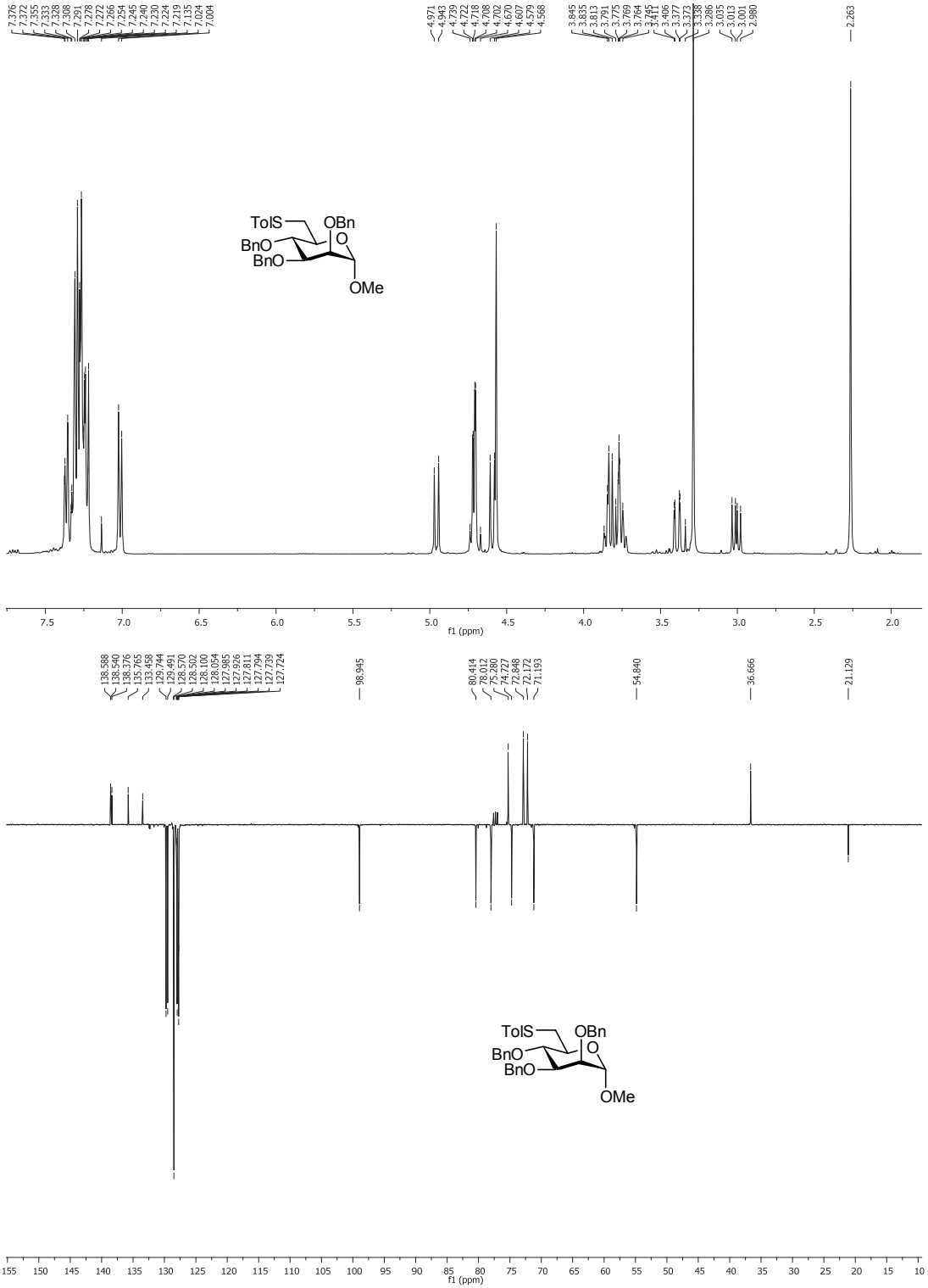
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-α-D-mannopyranoside (S4):



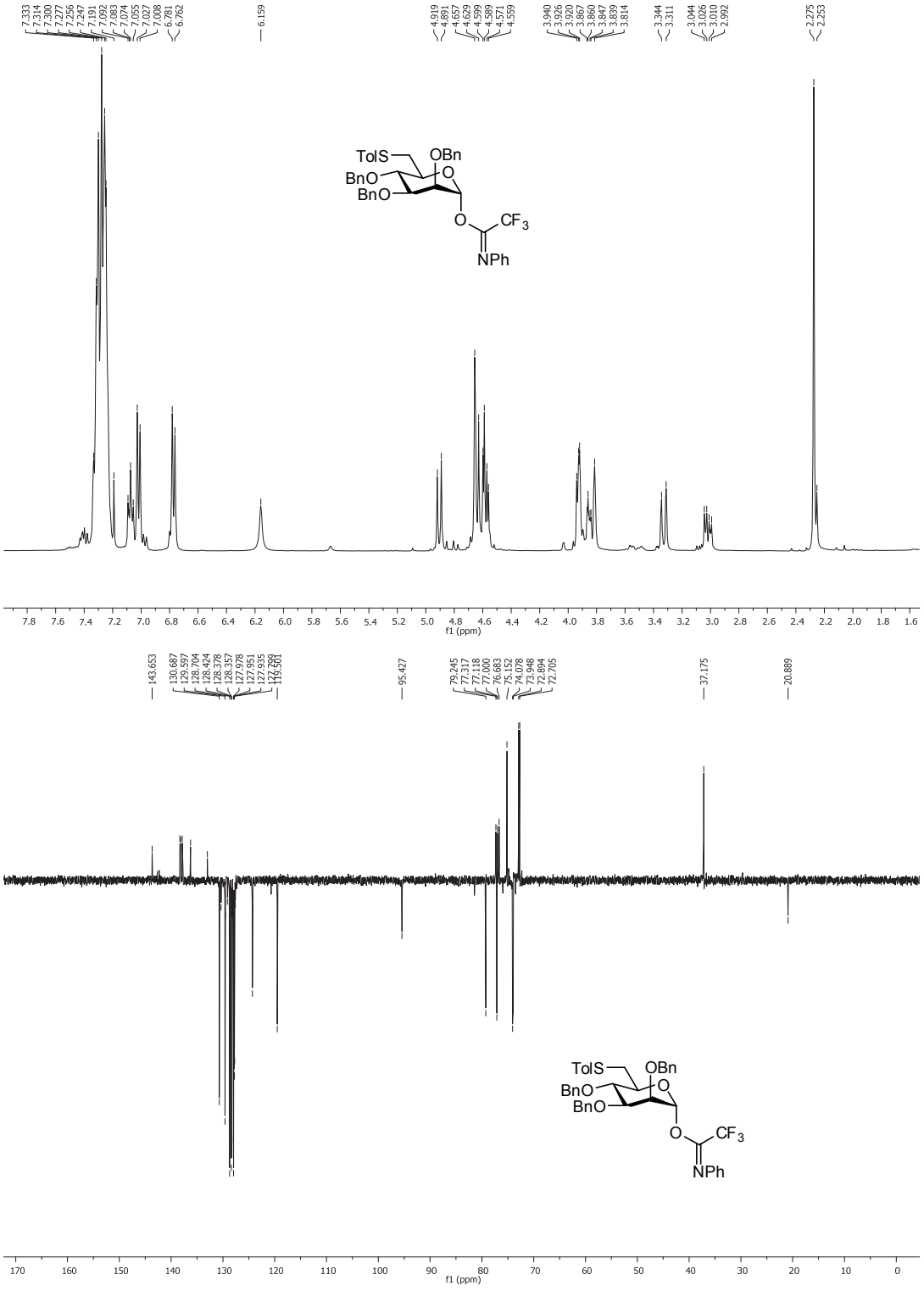
2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (8):



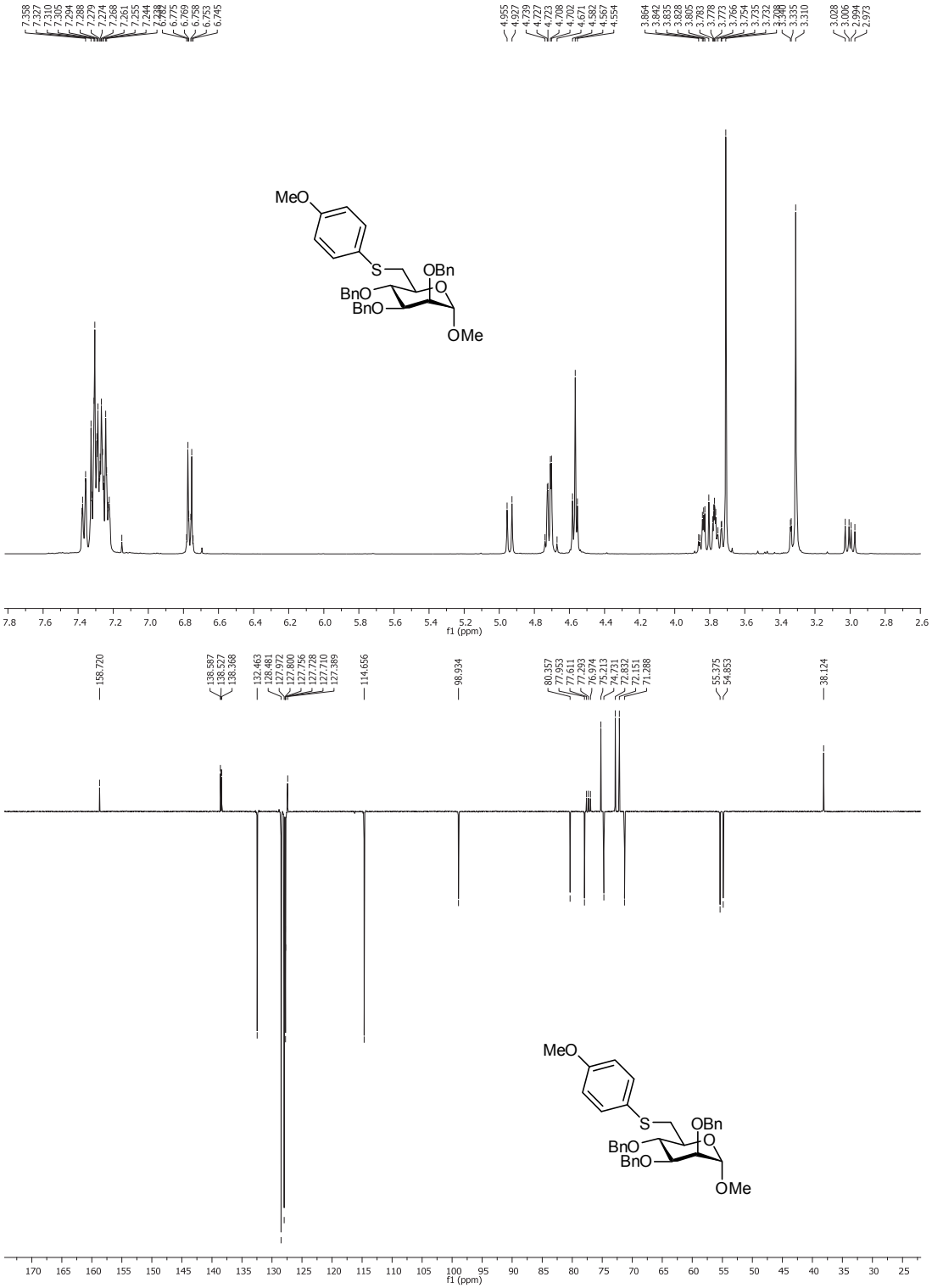
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-α-D-mannopyranoside (S5):



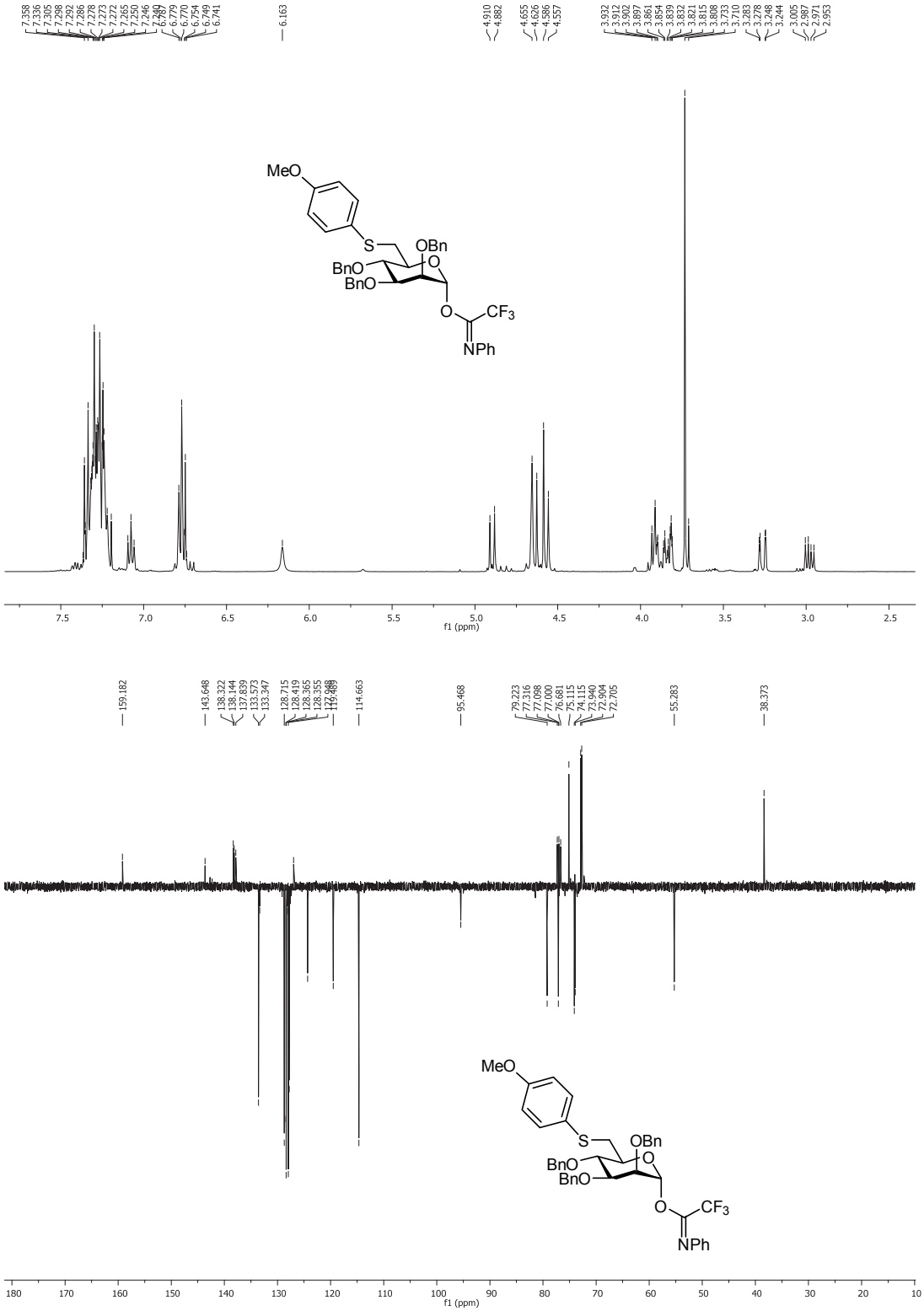
2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (9):



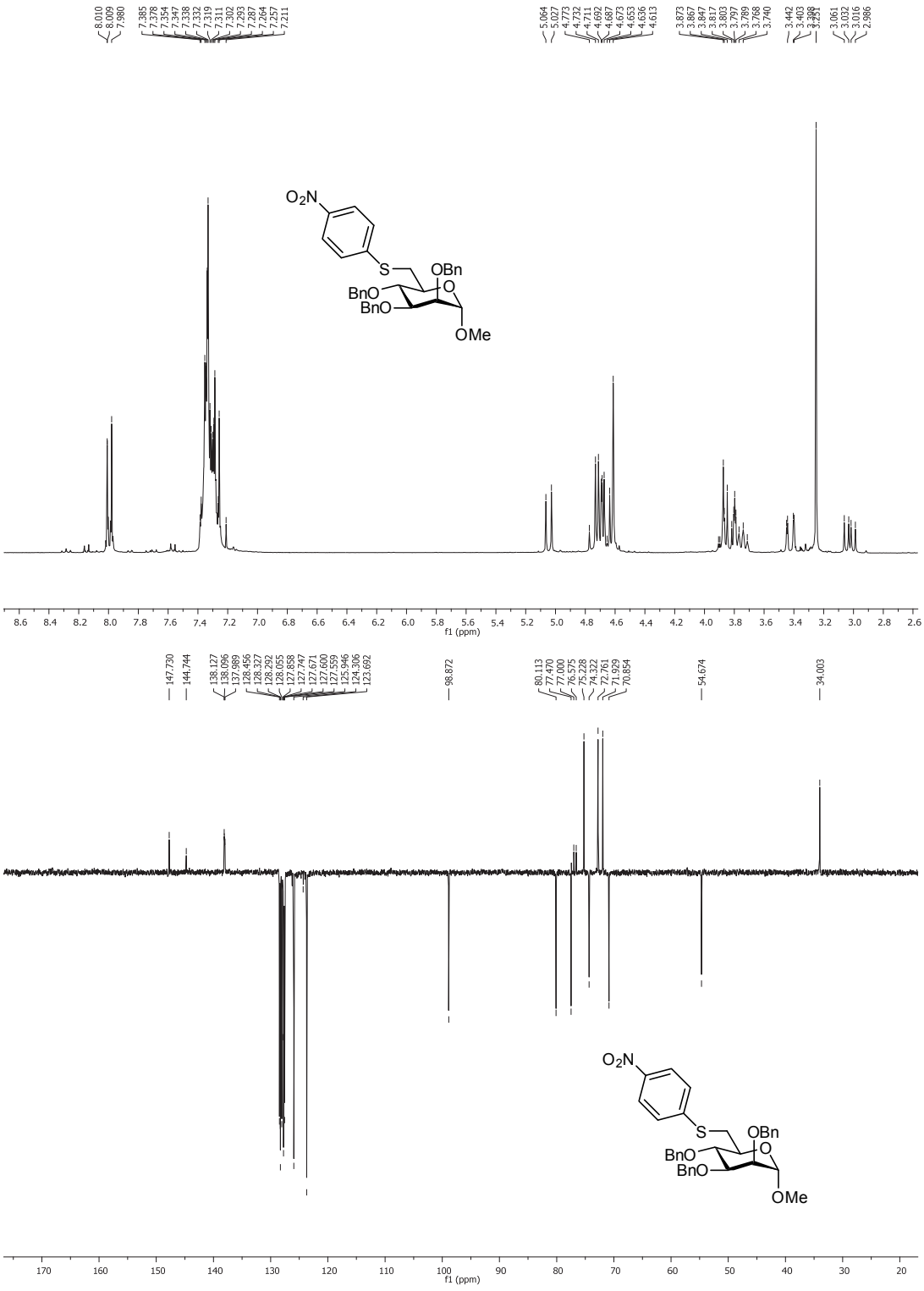
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-α-D-mannopyranoside (S6):



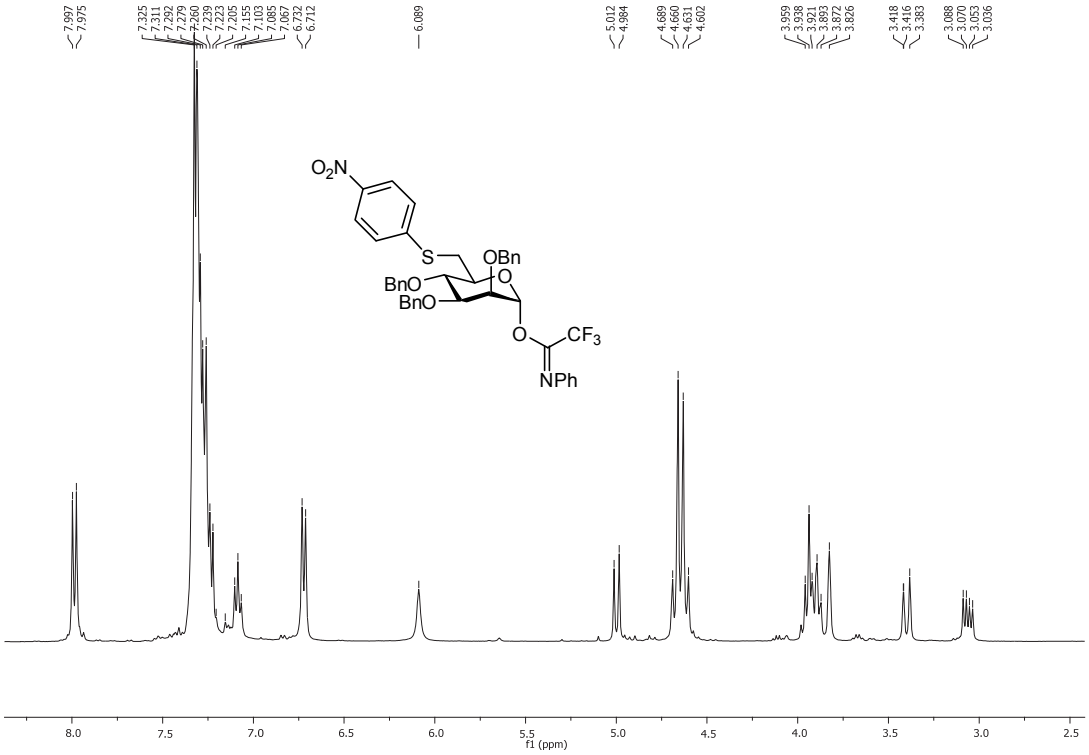
2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (10):

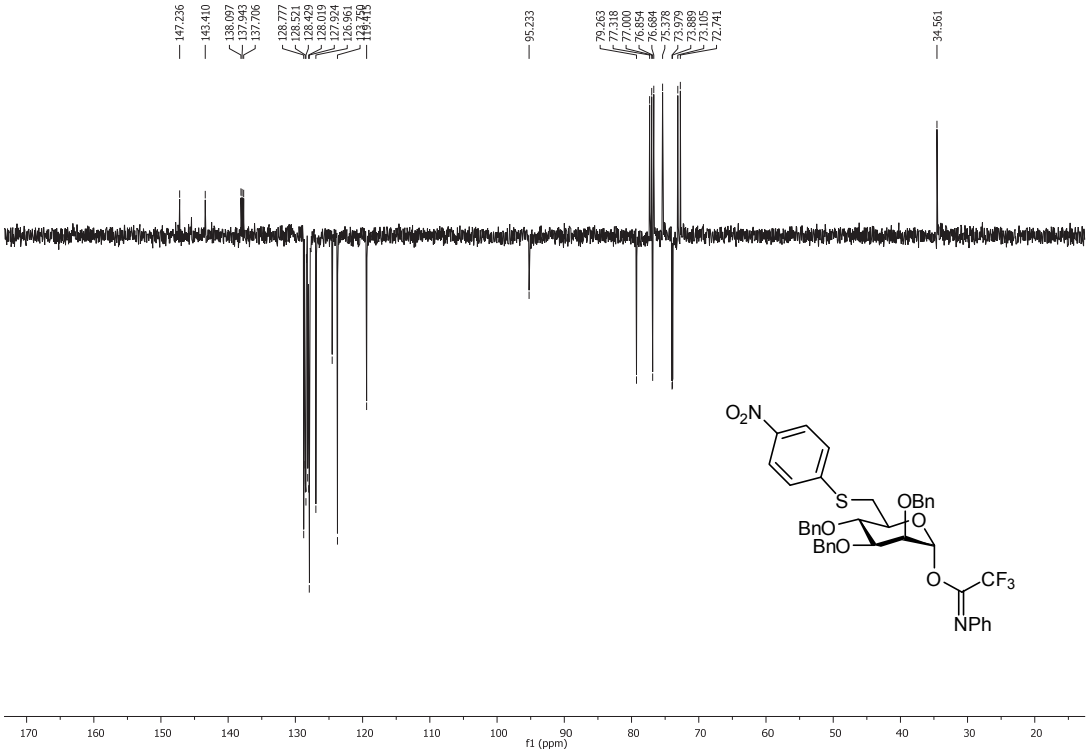


Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-α-D-mannopyranoside (S7):

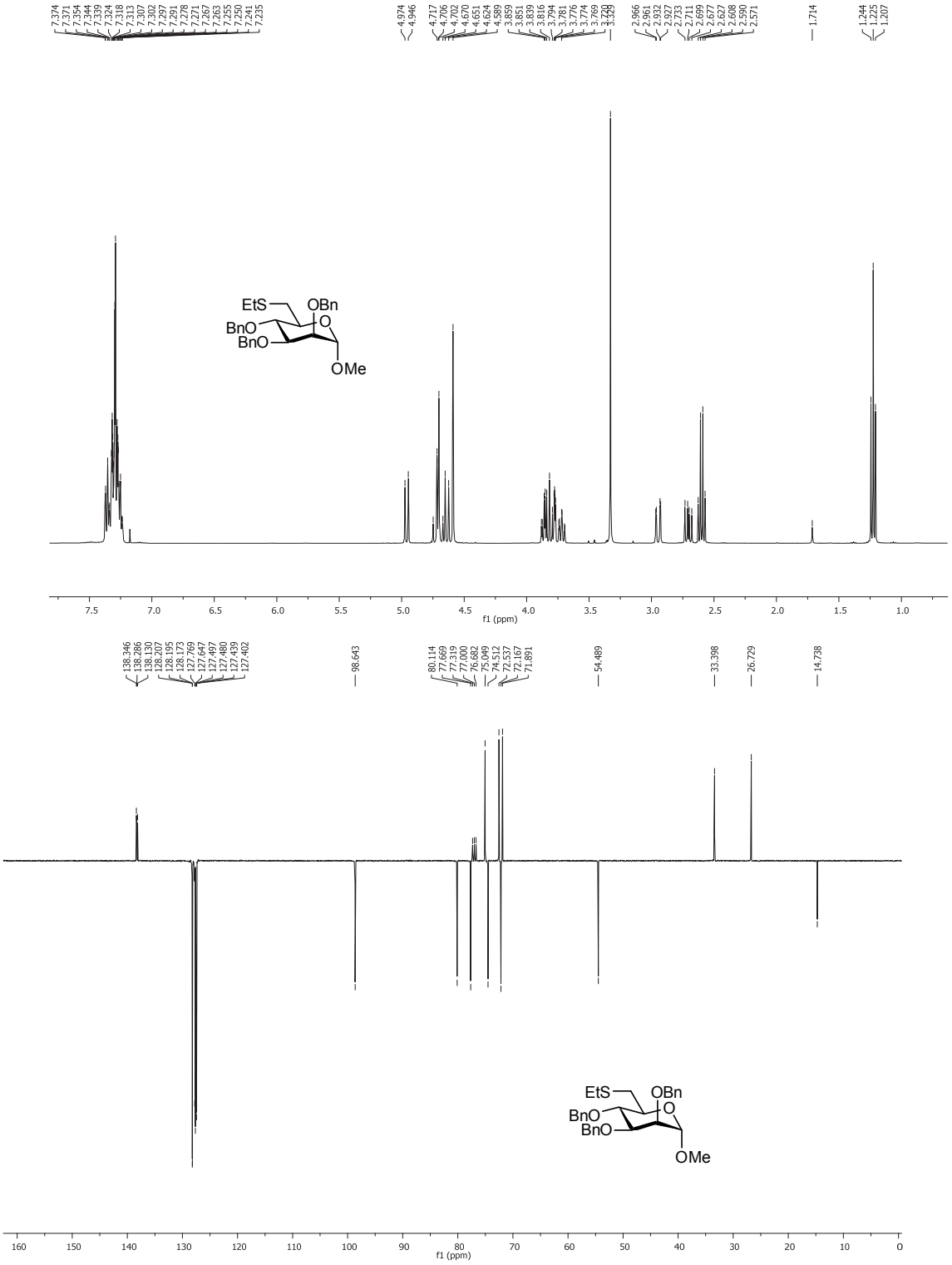


2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (11):

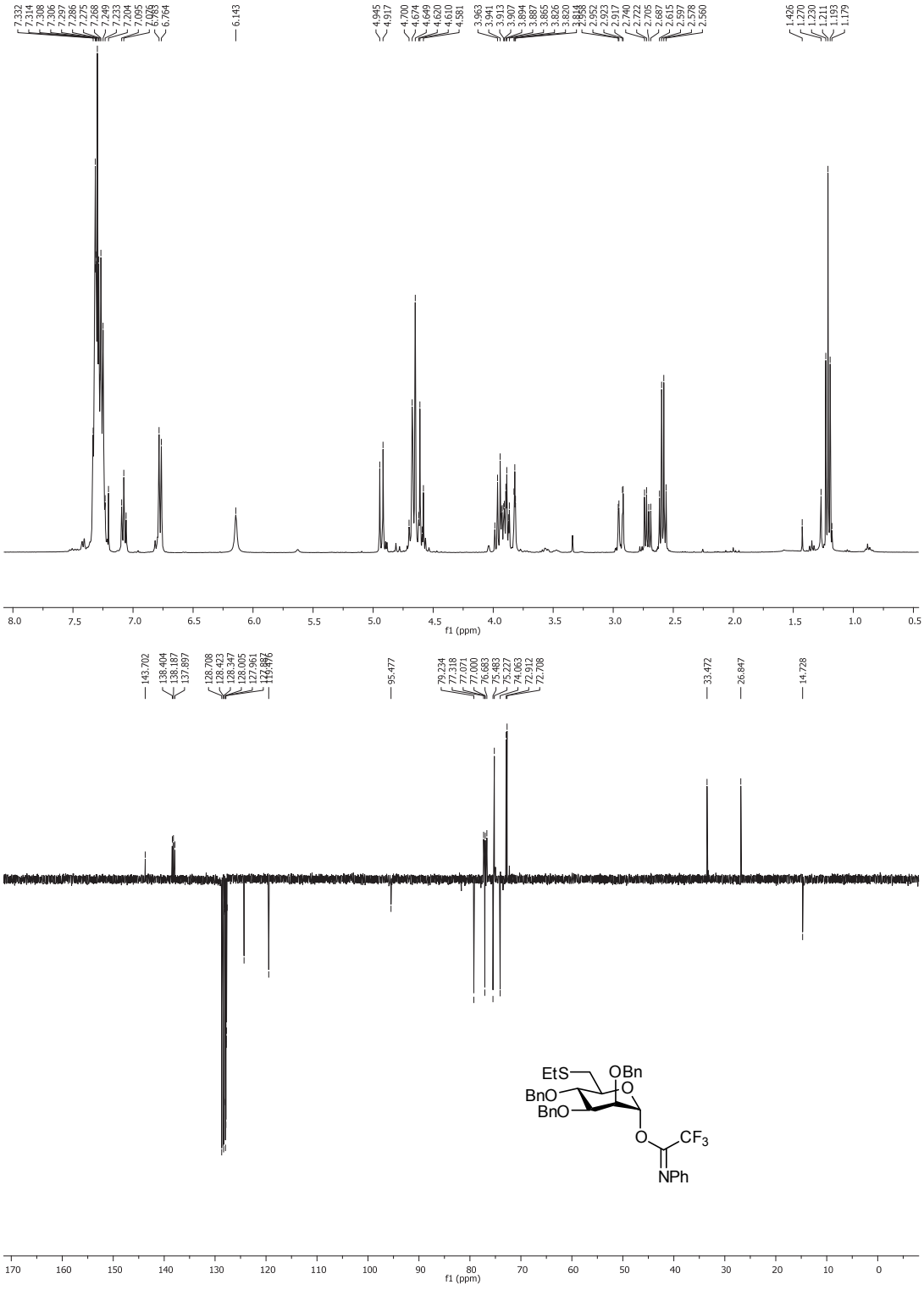




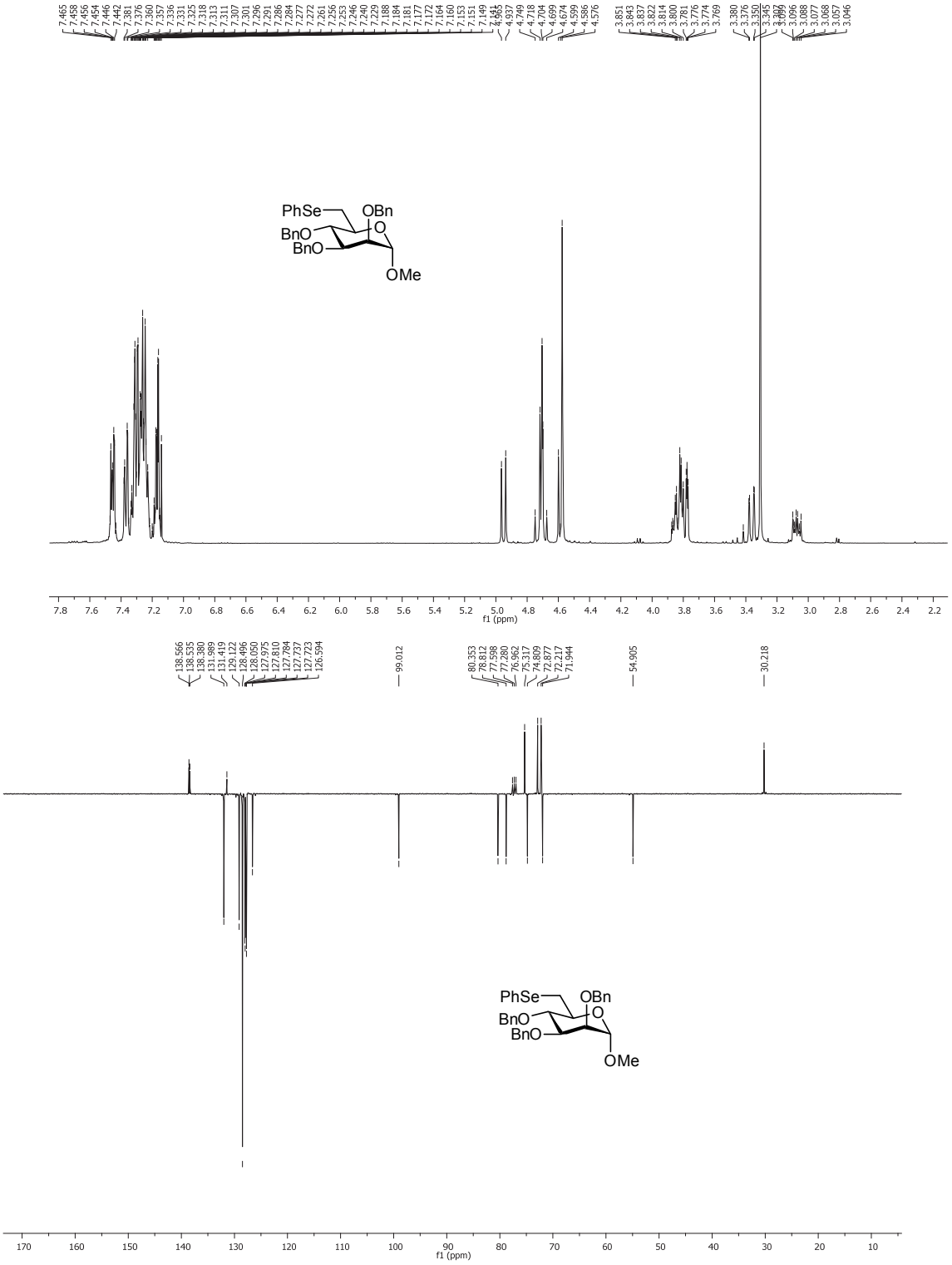
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-α-D-mannopyranoside (S8):



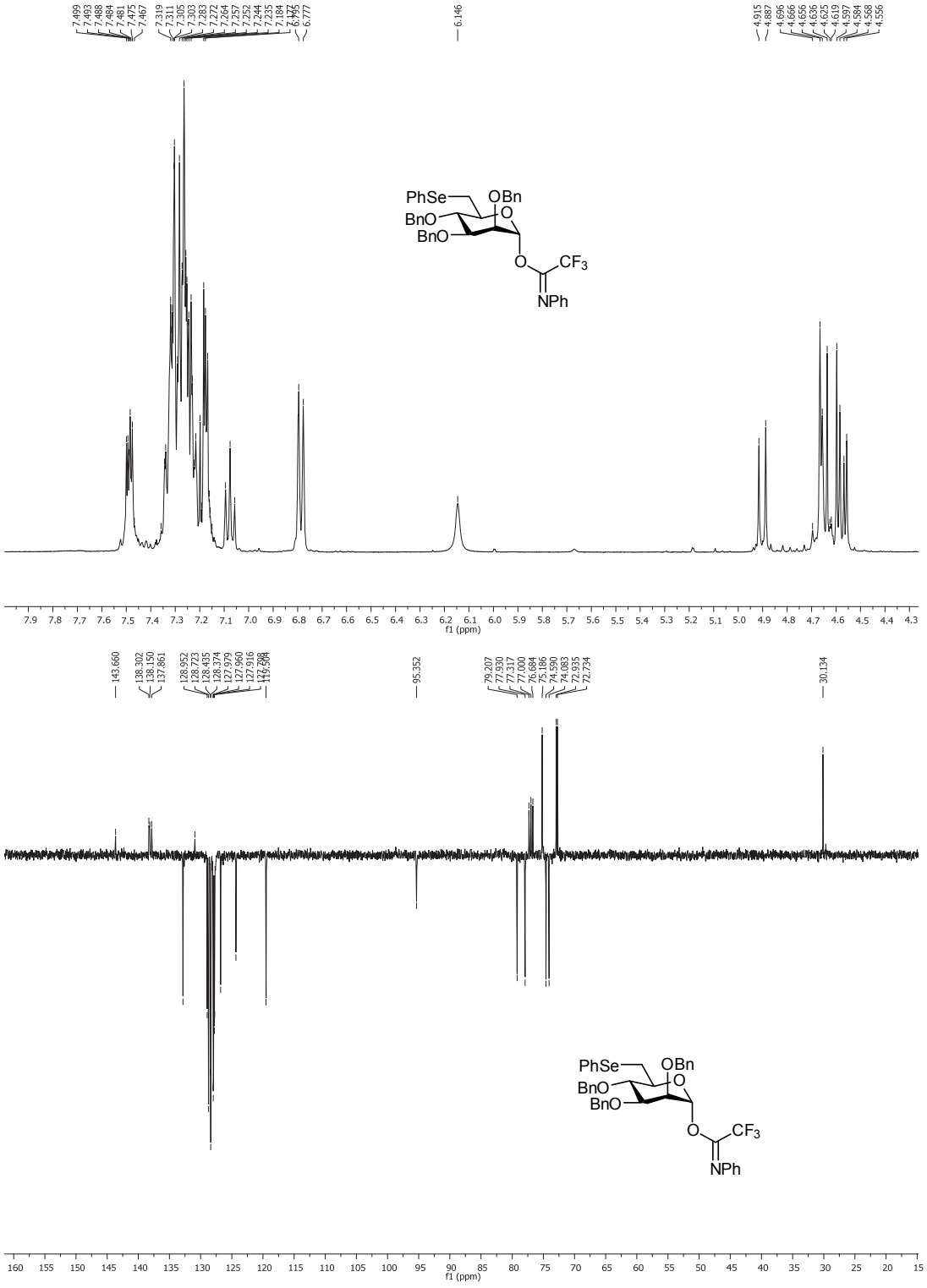
2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (12):



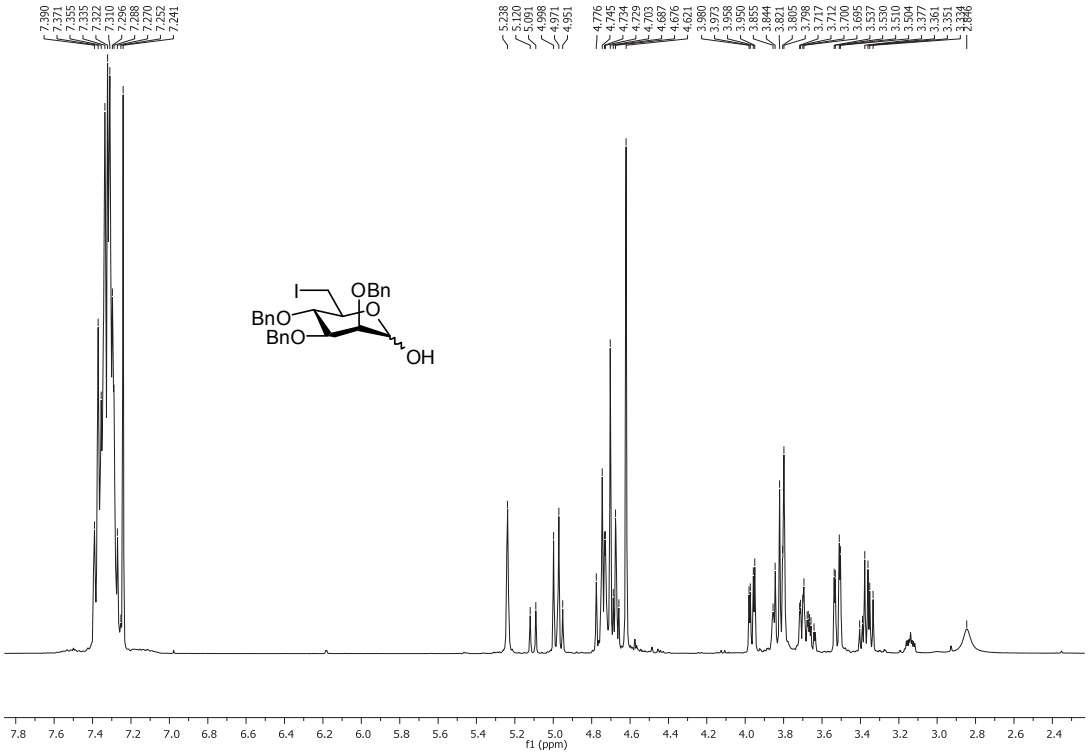
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-Se-phenyl-6-seleno-α-D-mannopyranoside (S9):

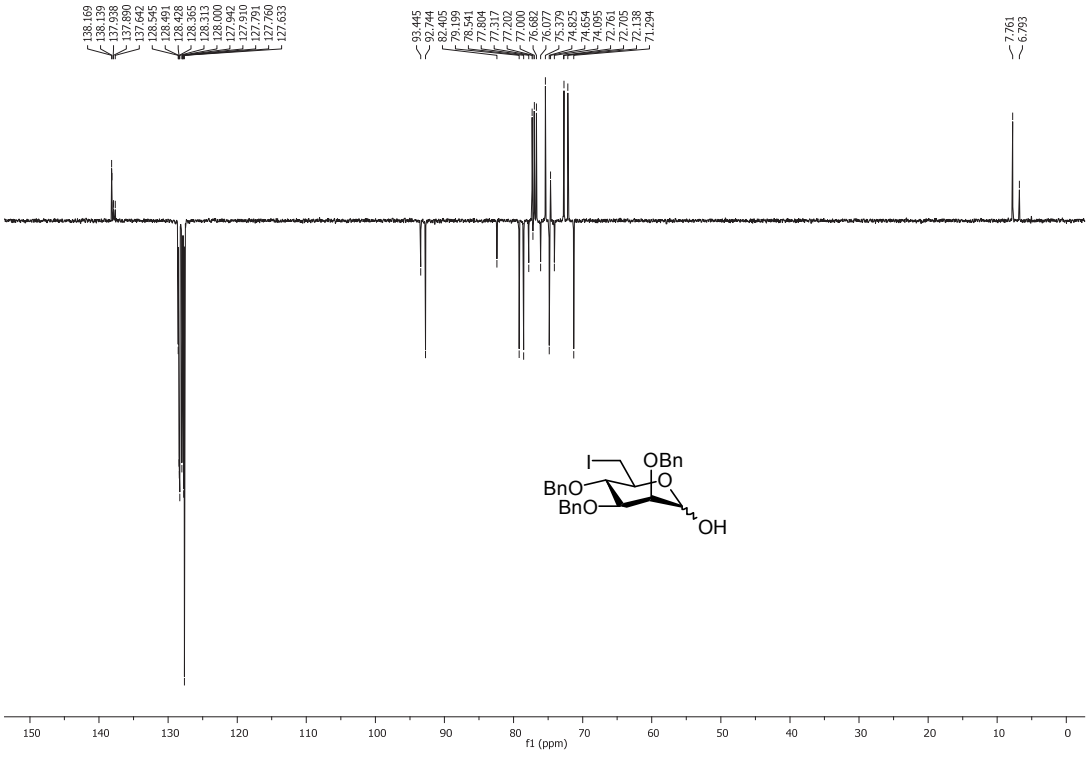


2,3,4-tri-*O*-benzyl-6-deoxy-6-Se-phenyl-6-seleno-α-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (13):

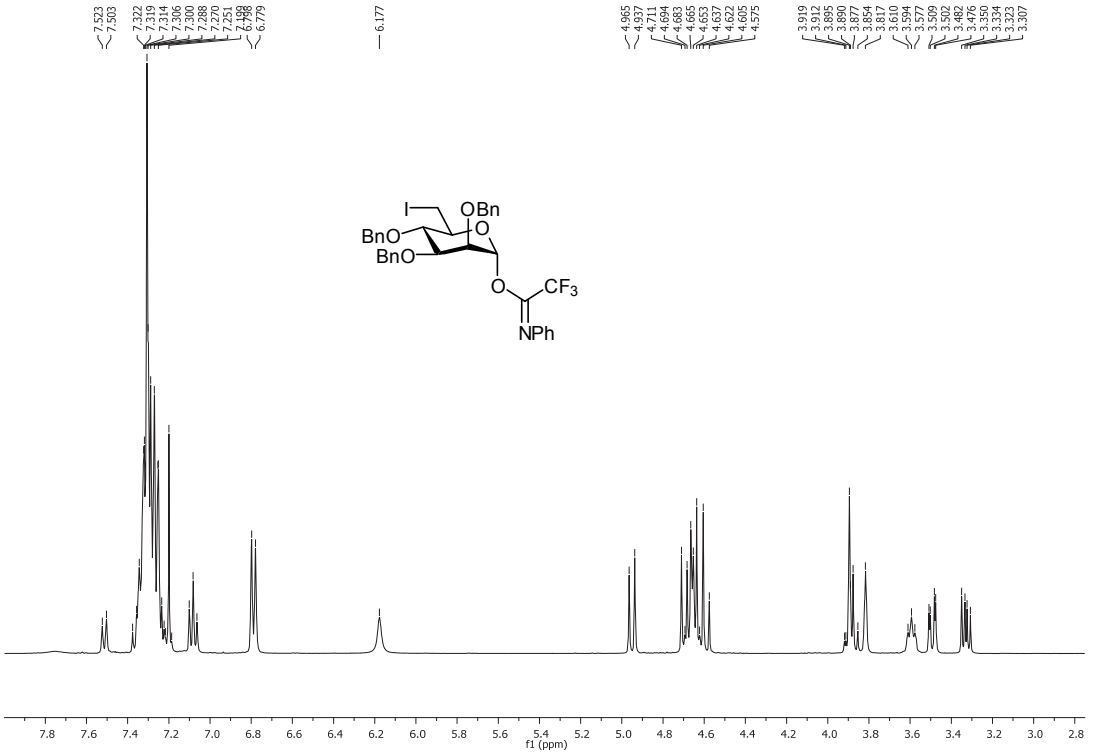


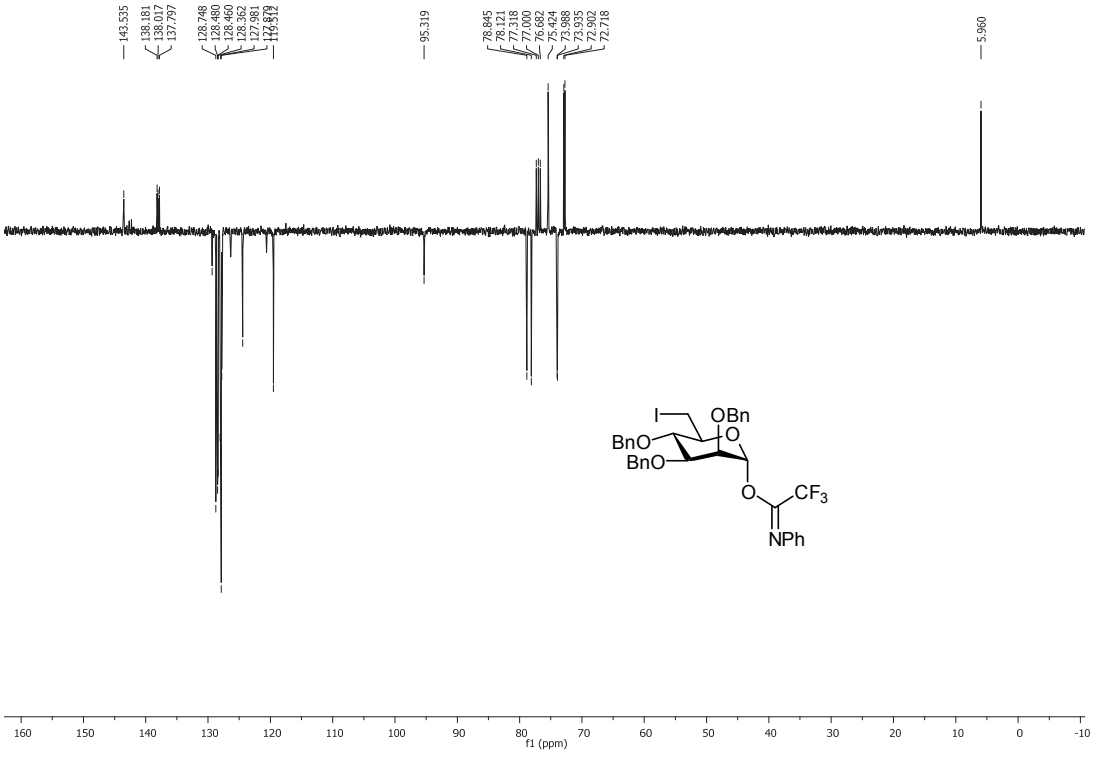
2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranose (S10):



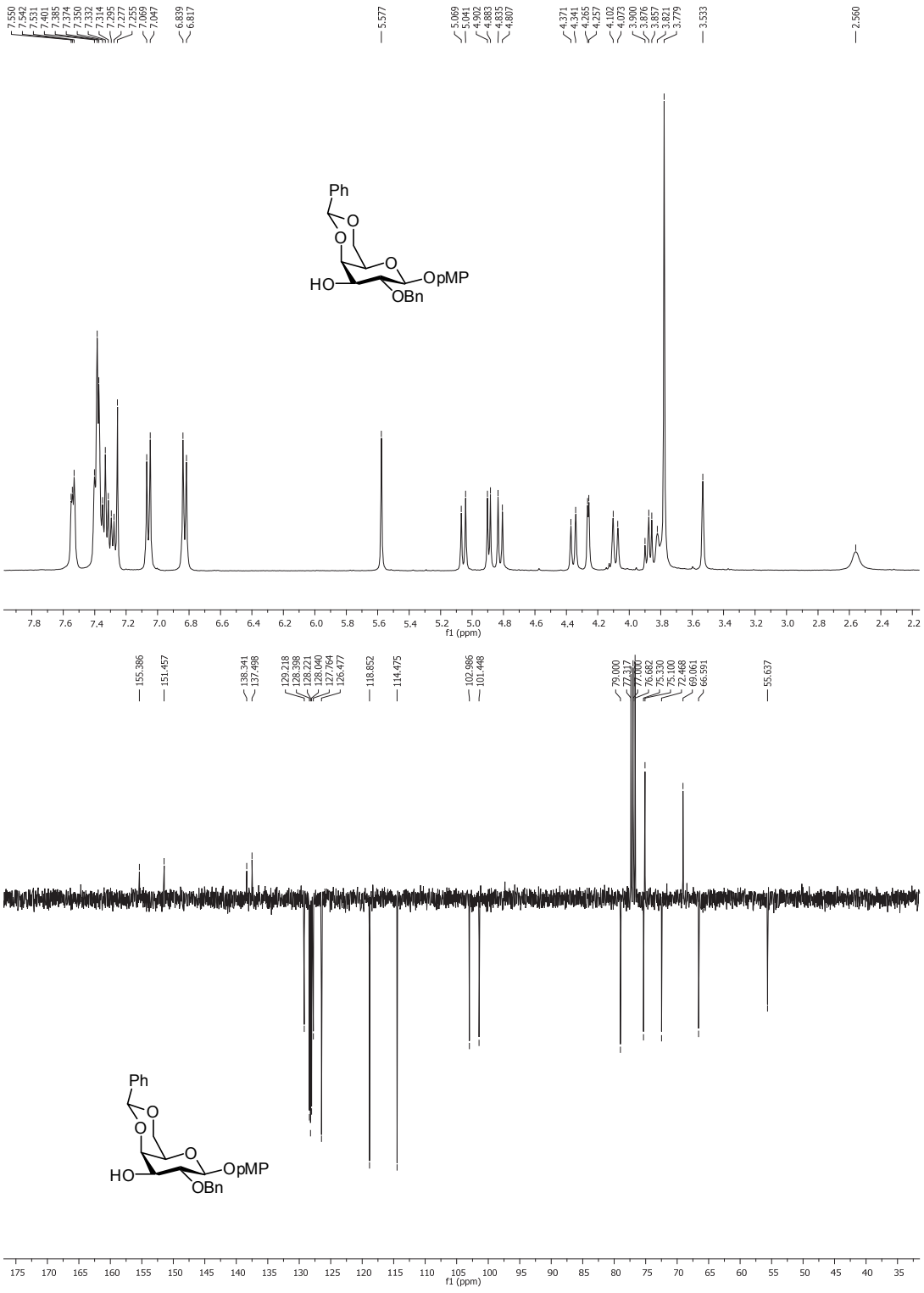


2,3,4-tri-*O*-benzyl-6-deoxy-6-iodo-α/β-D-mannopyranosyl (*N*-phenyl)trifluoroacetimidate (14):

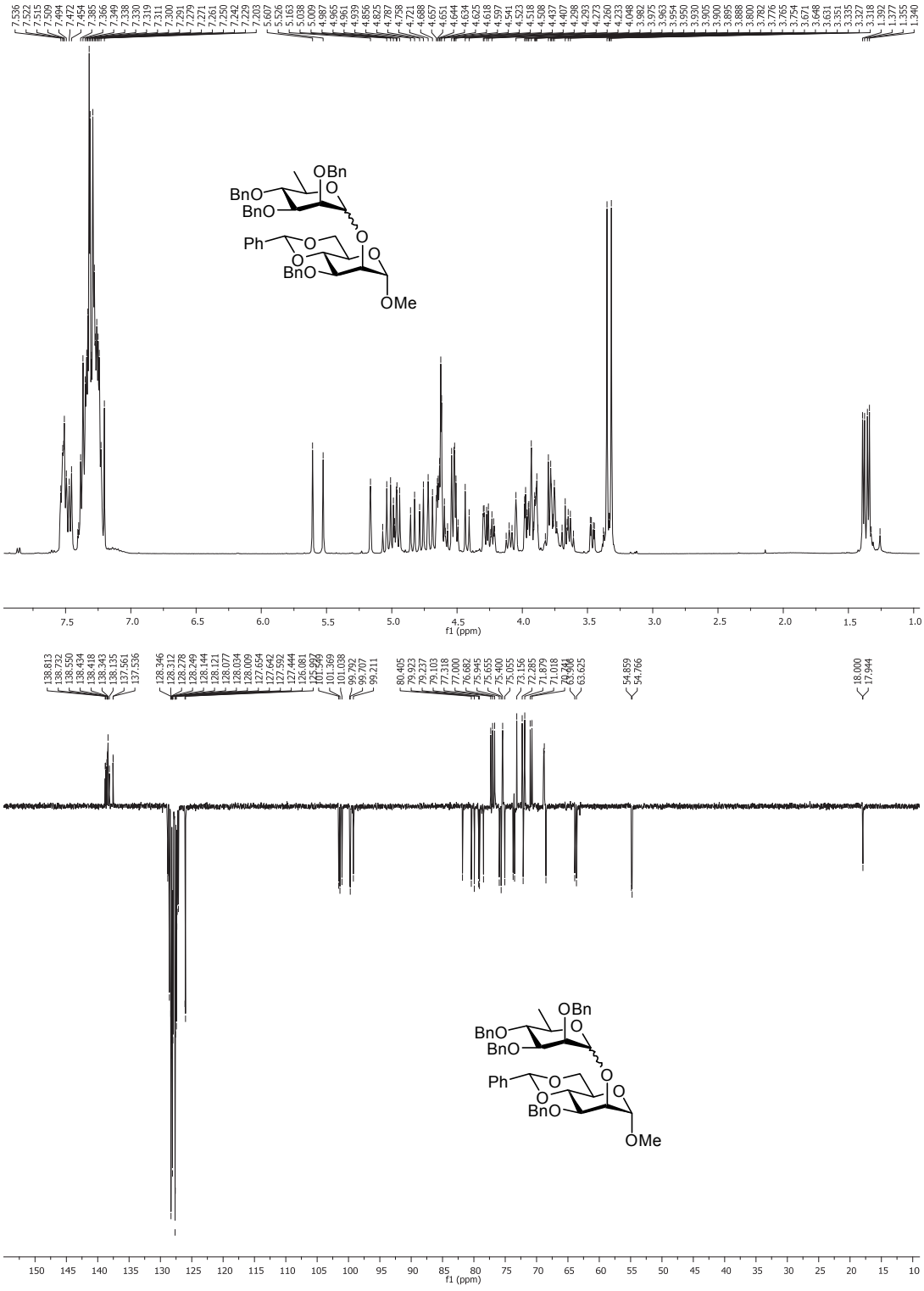




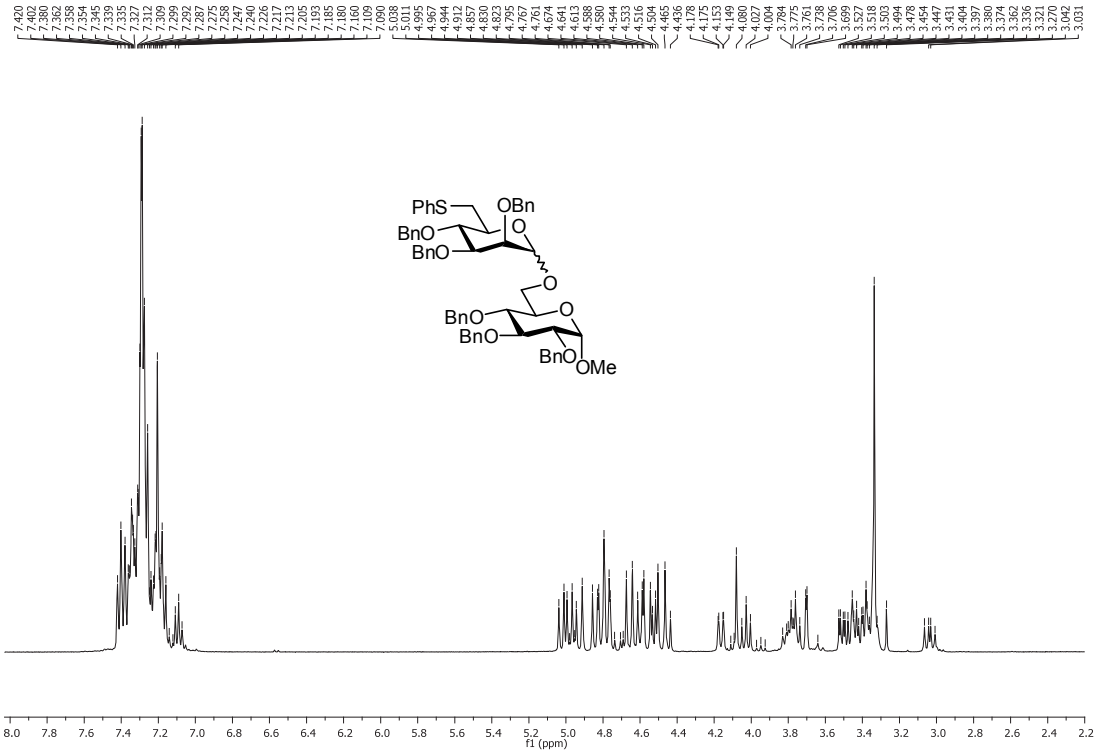
4-Methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (15b):

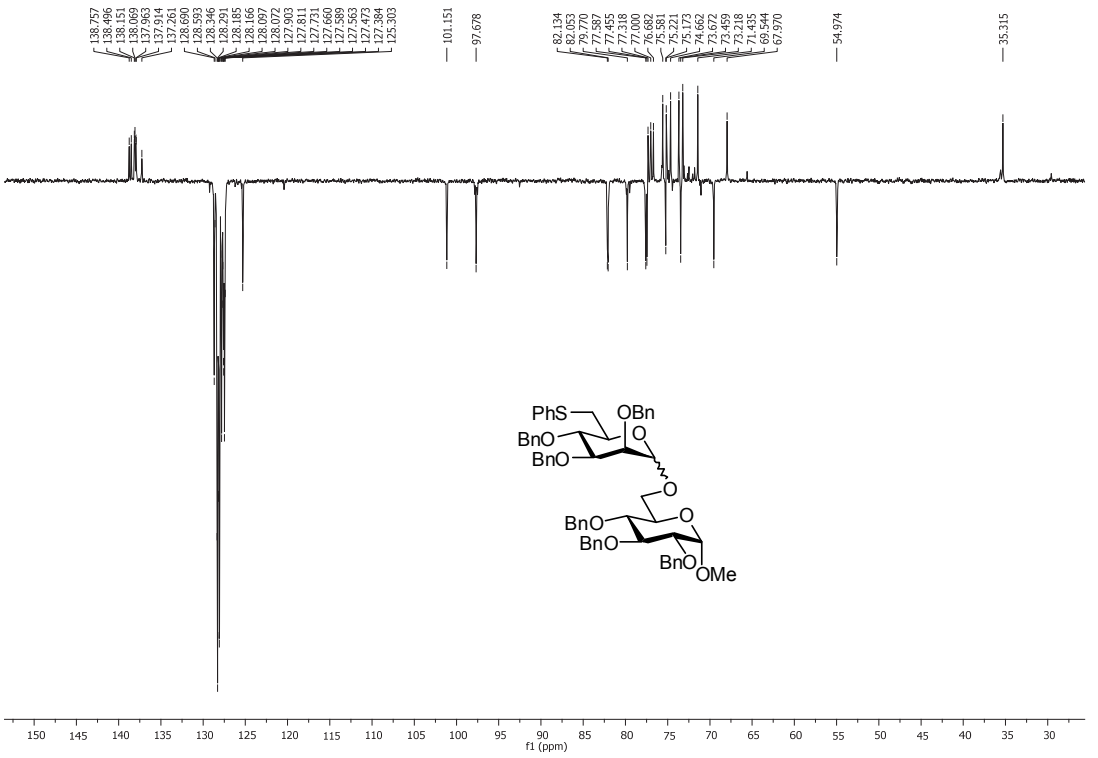


2,3,4-Tri-*O*-benzyl-6-deoxy-D-mannopyranosyl-(1→2)- methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (17c):

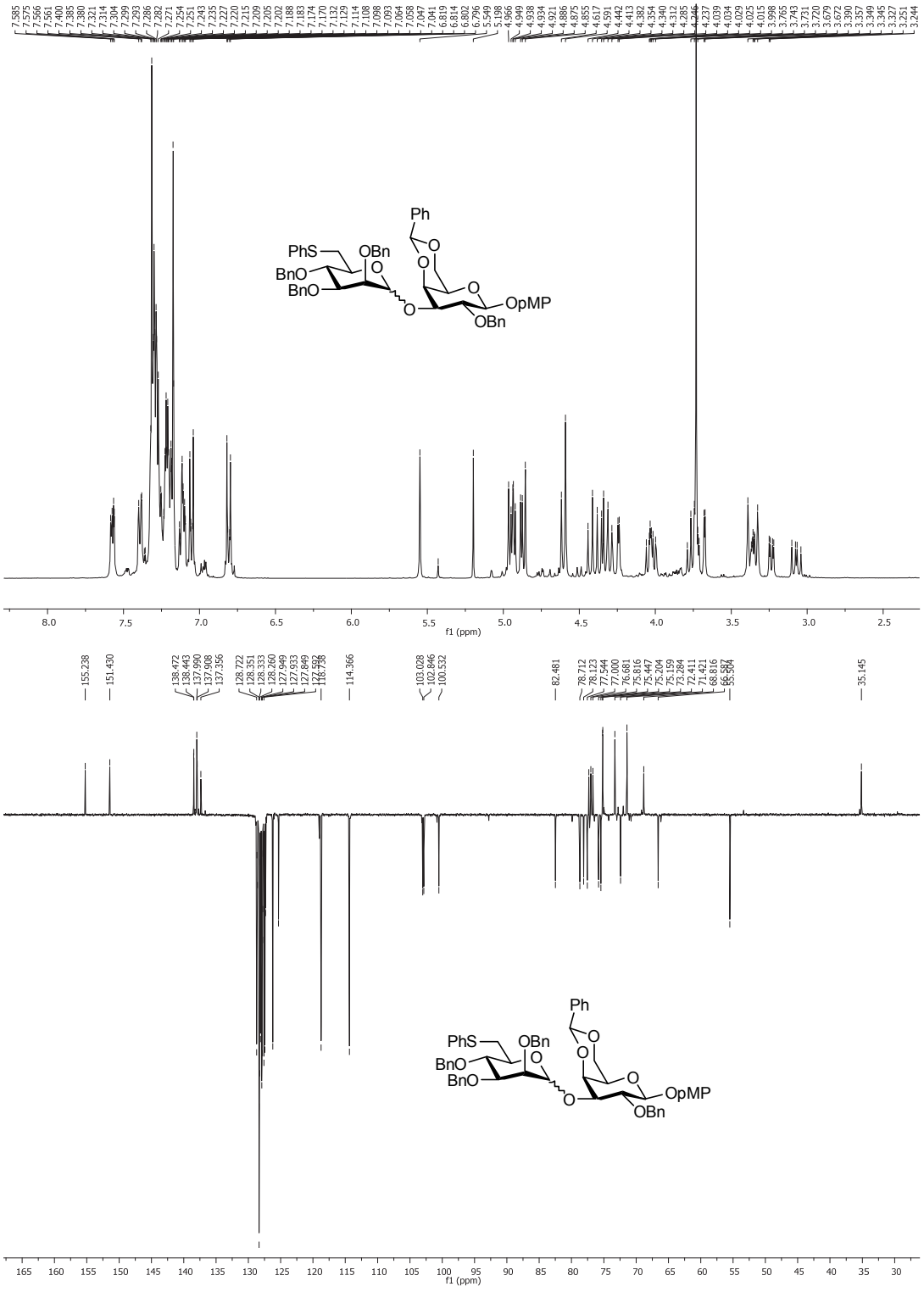


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranosyl-(1→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (18a) (α/β 1/7):

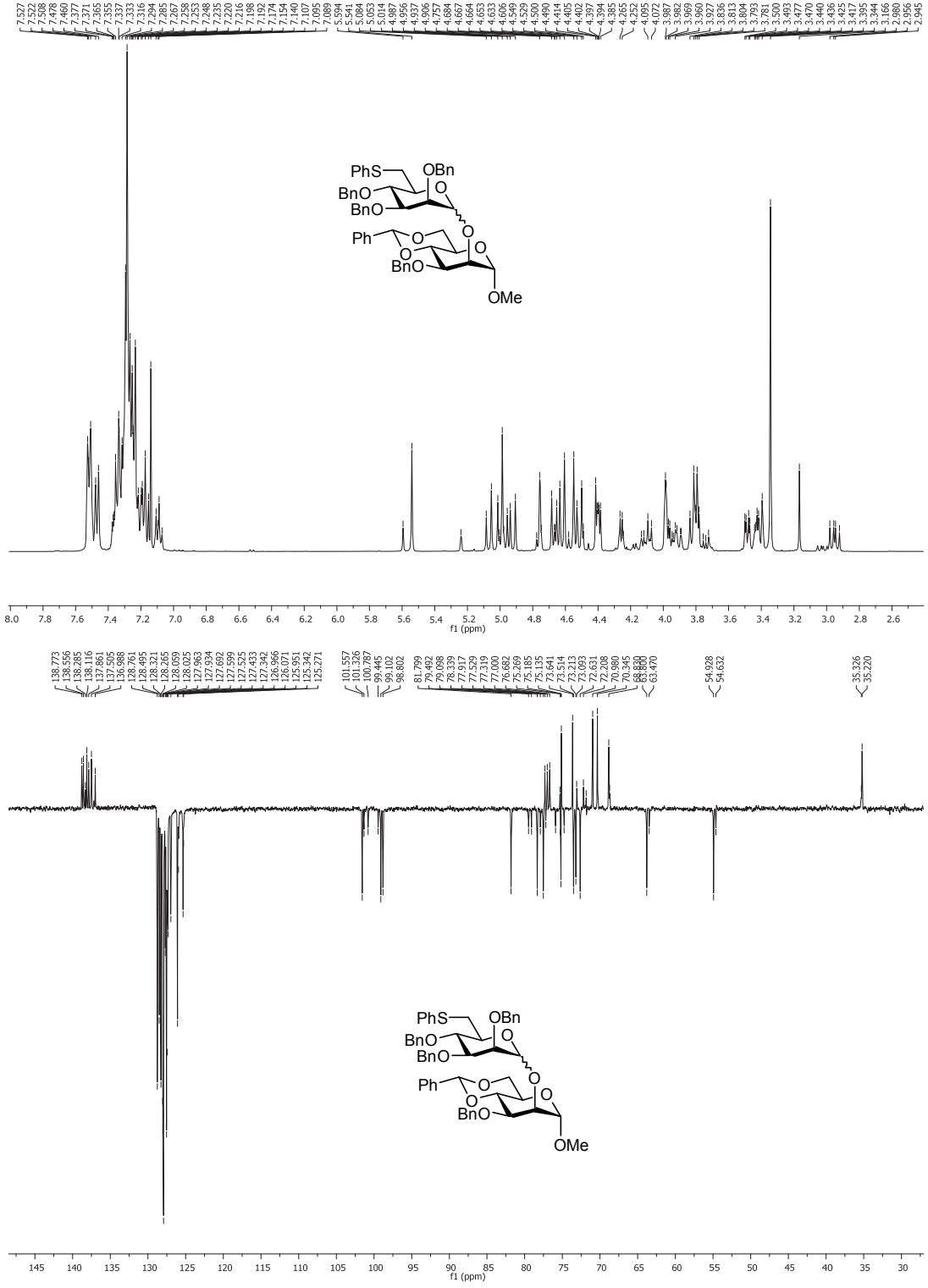




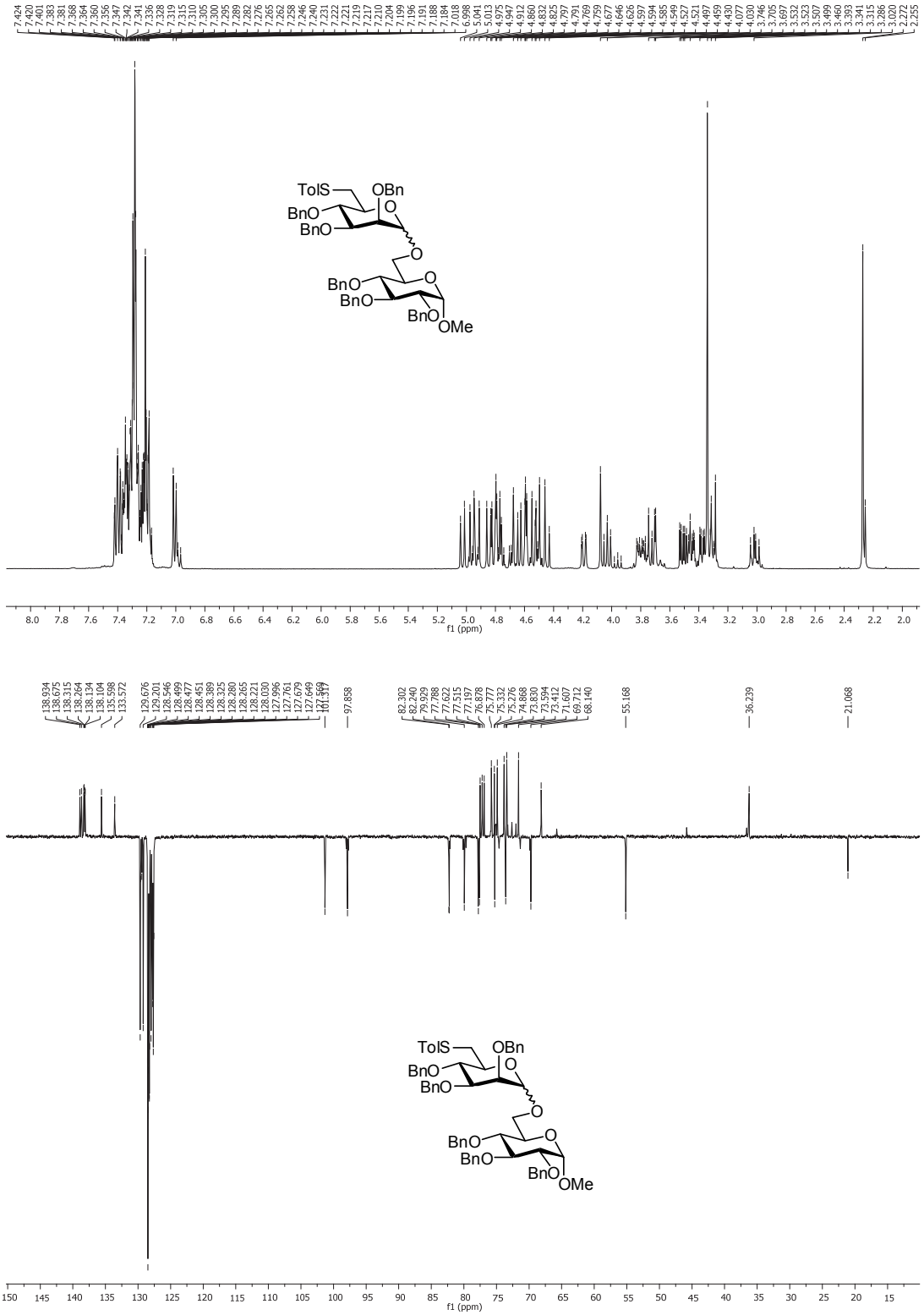
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranosyl-(1→3)-*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (18b):



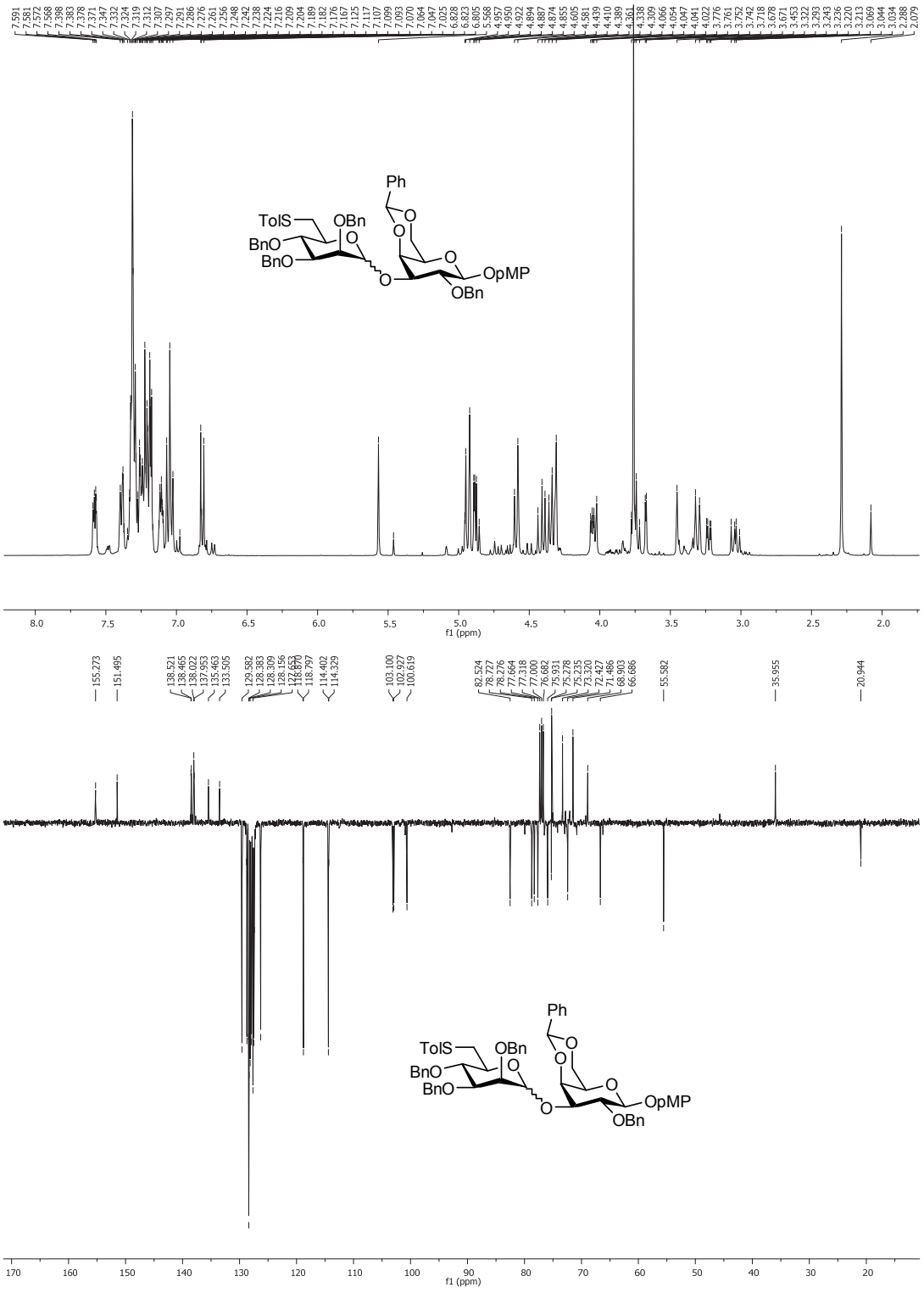
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranosyl-(1→2)- methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (18c):



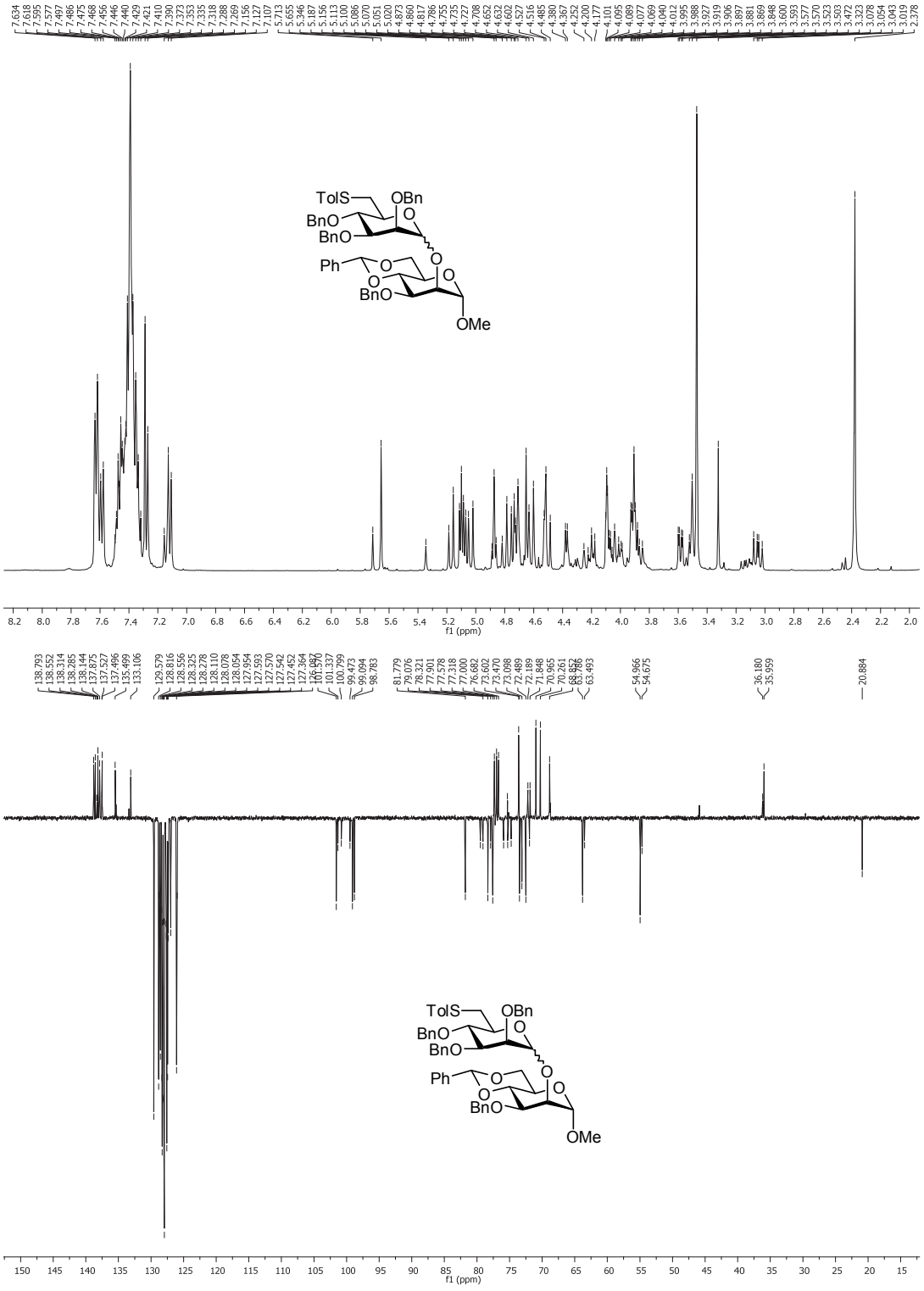
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-D-mannopyranosyl-(1→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (19a):



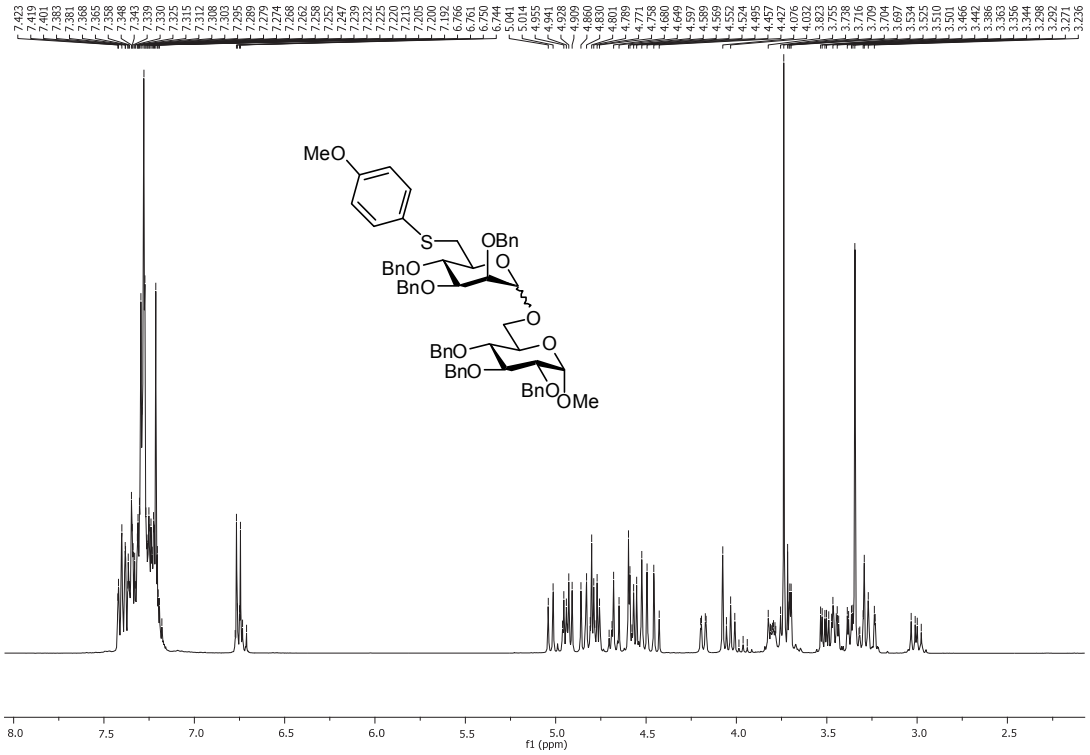
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-D-mannopyranosyl (1→3)-*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (19b):

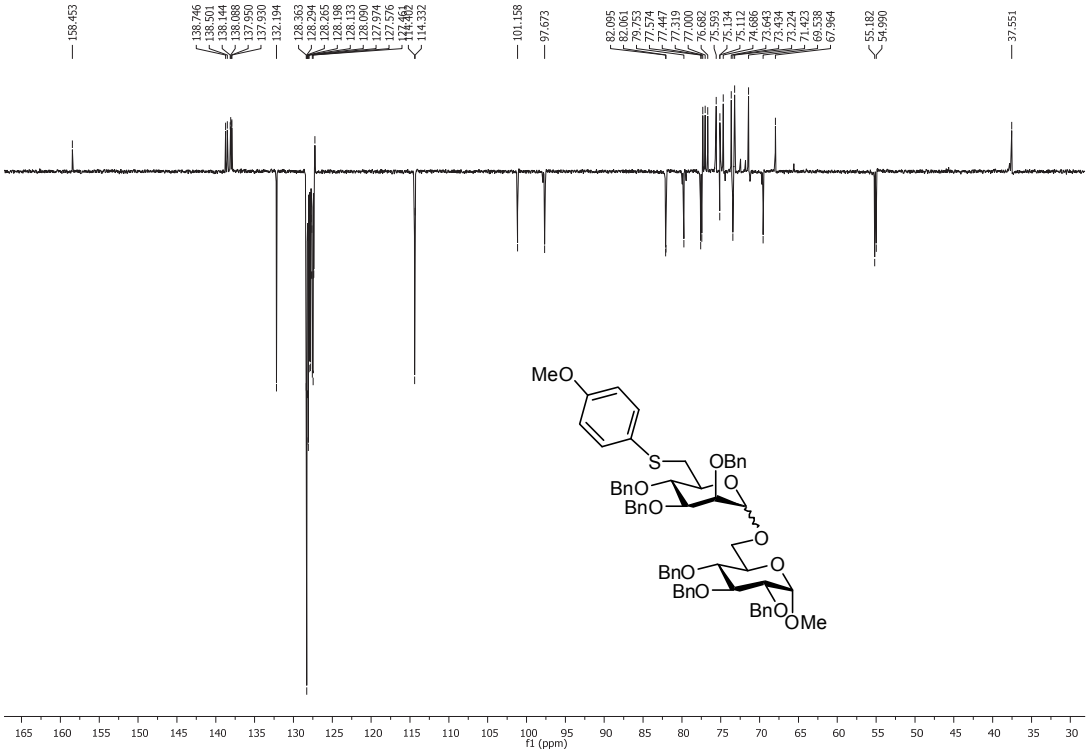


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-tolyl-6-thio-D-mannopyranosyl-(1→2)- methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (19c):

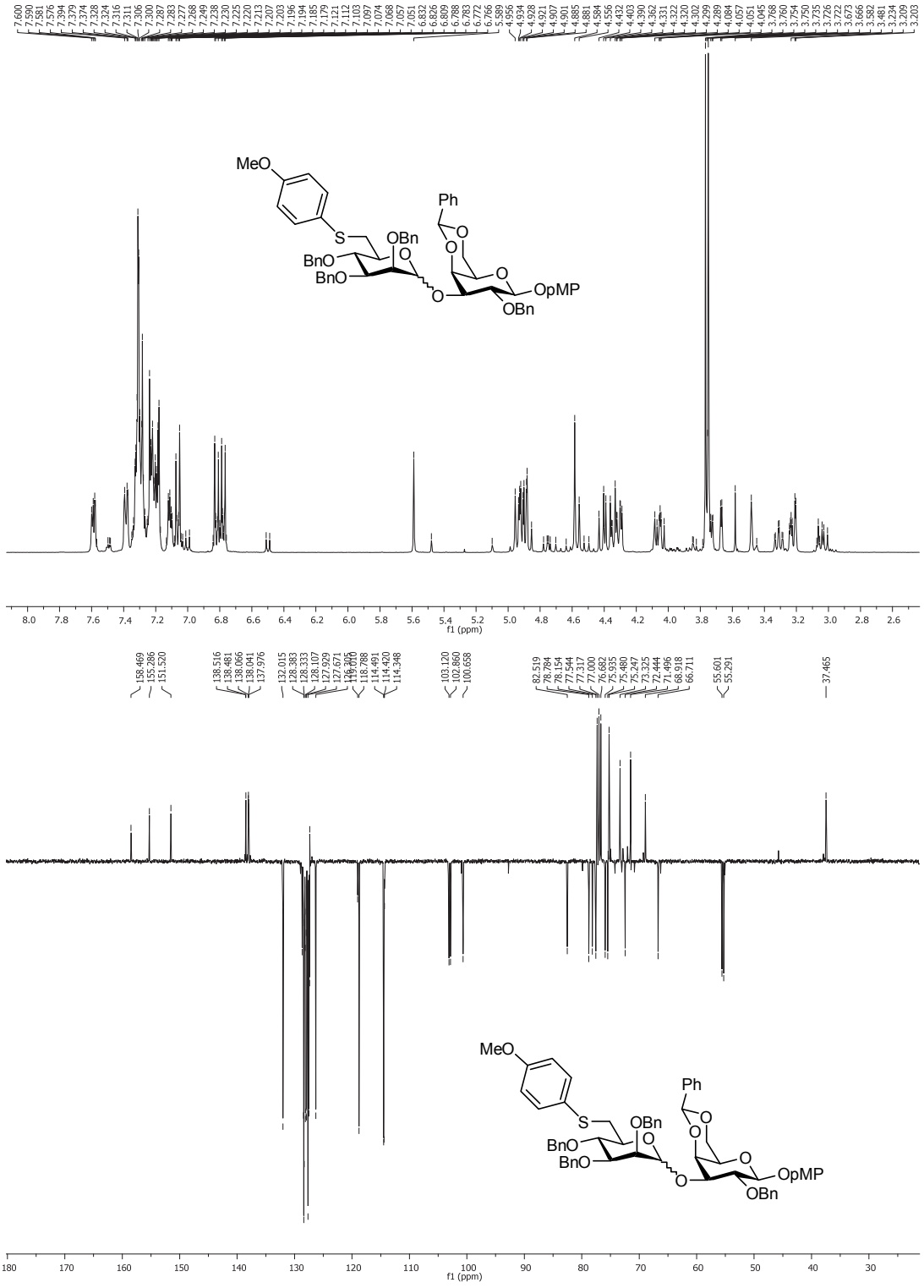


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-D-mannopyranosyl-(1→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (20a):

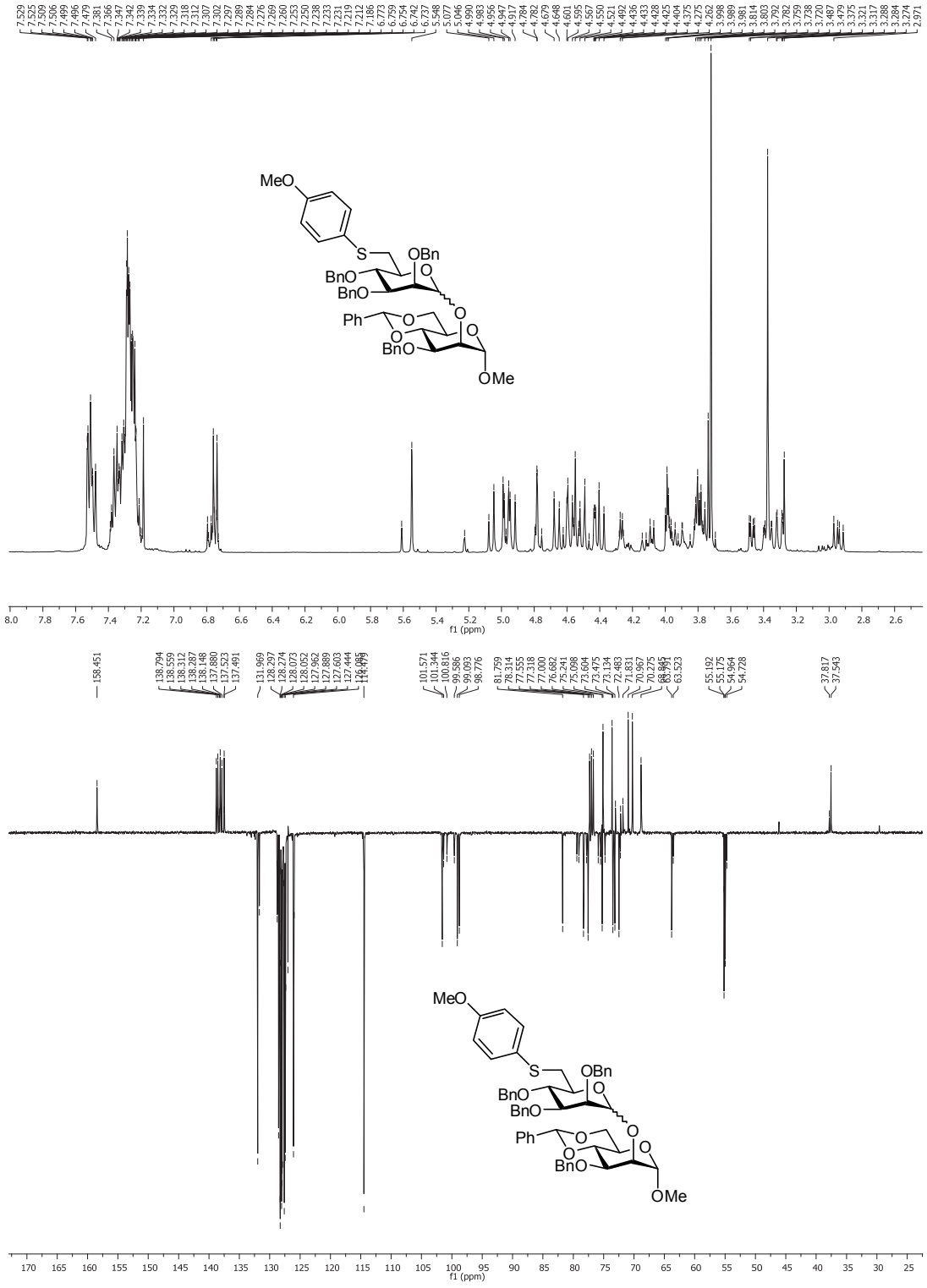




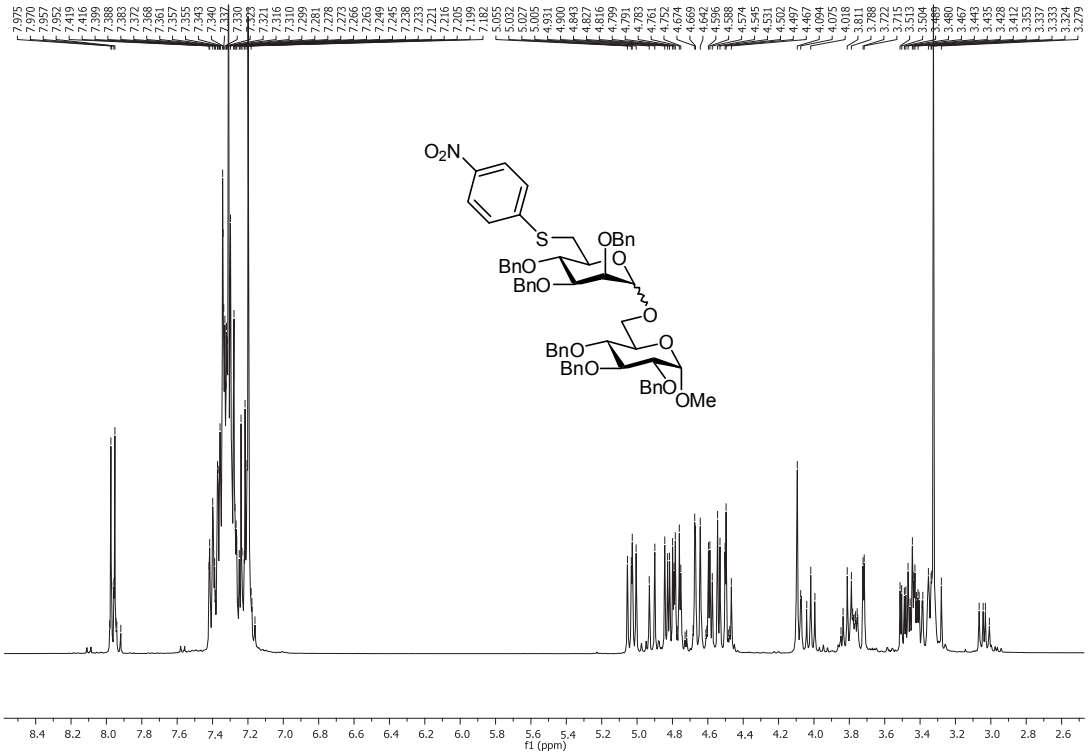
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-D-mannopyranosyl (1→3)-*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (20b):

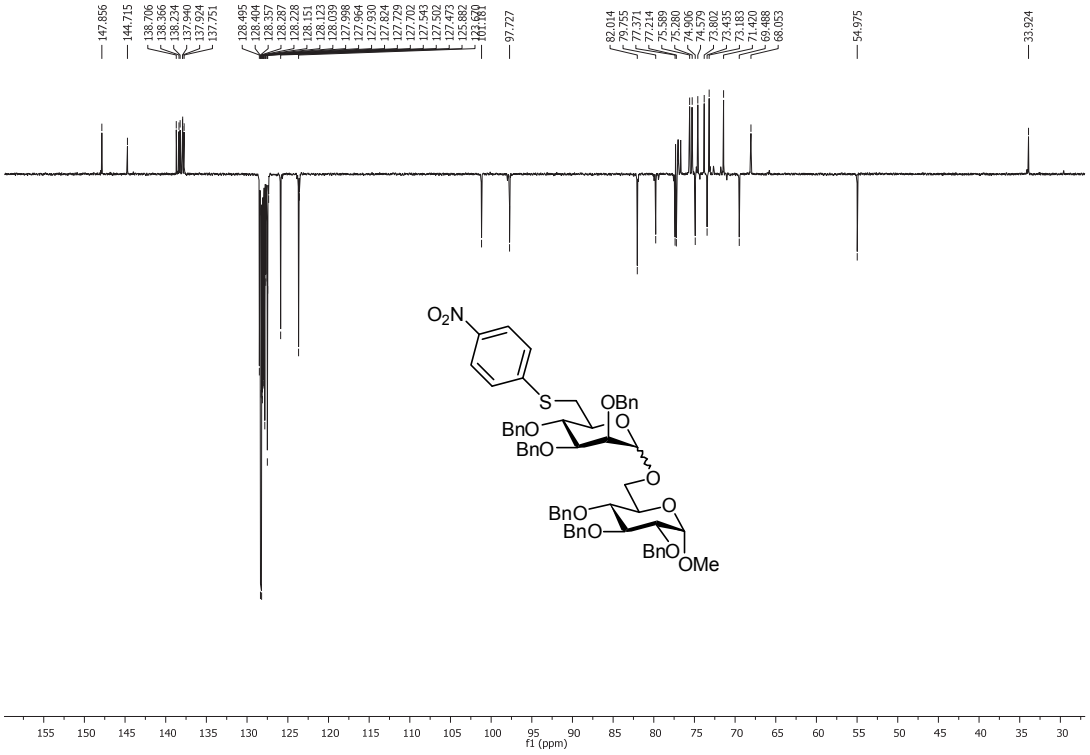


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-methoxyphenyl-6-thio-D-mannopyranosyl-(1→2)- methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (20c):

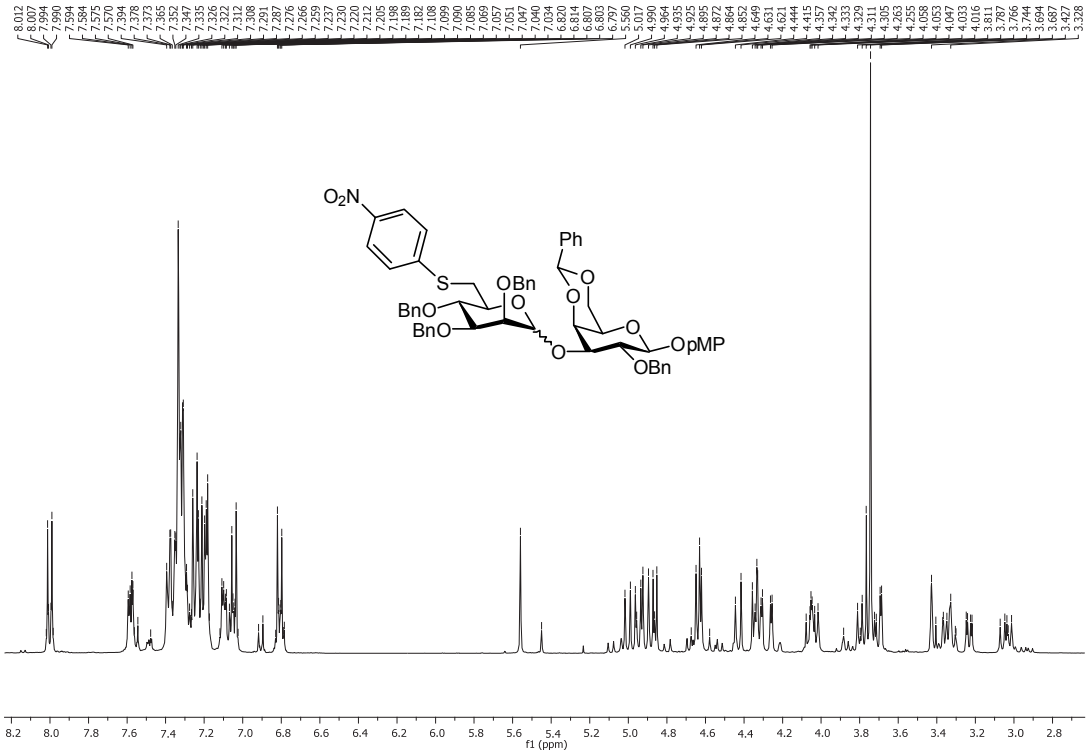


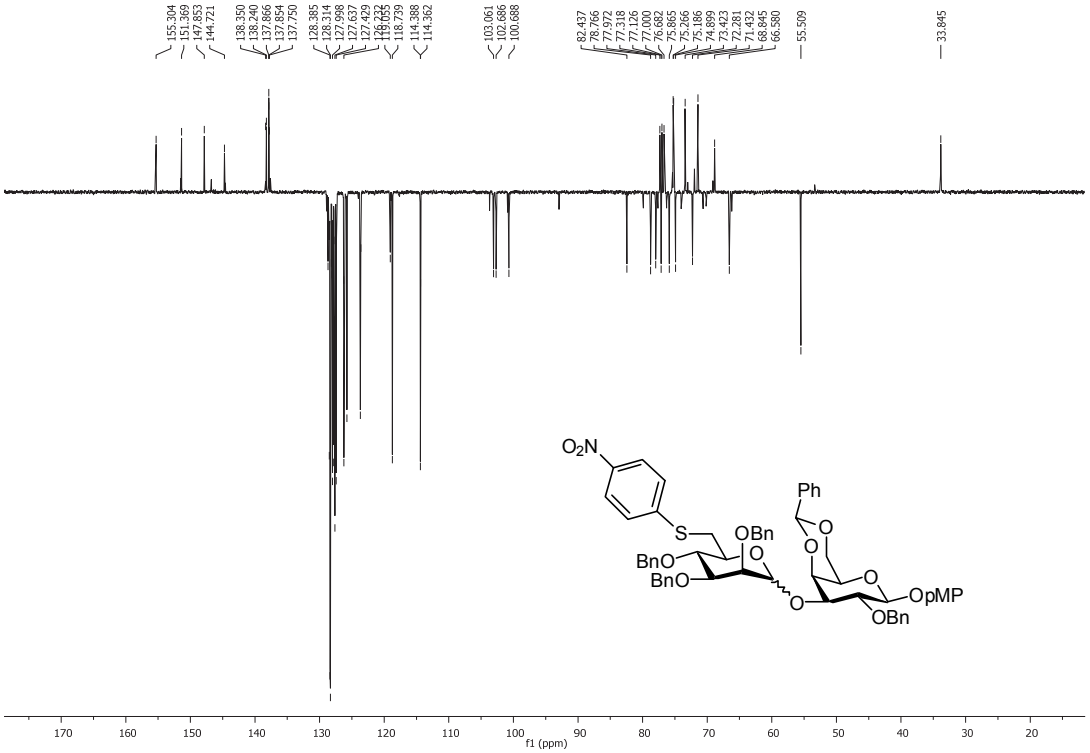
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-D-mannopyranosyl-(1→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (21a):



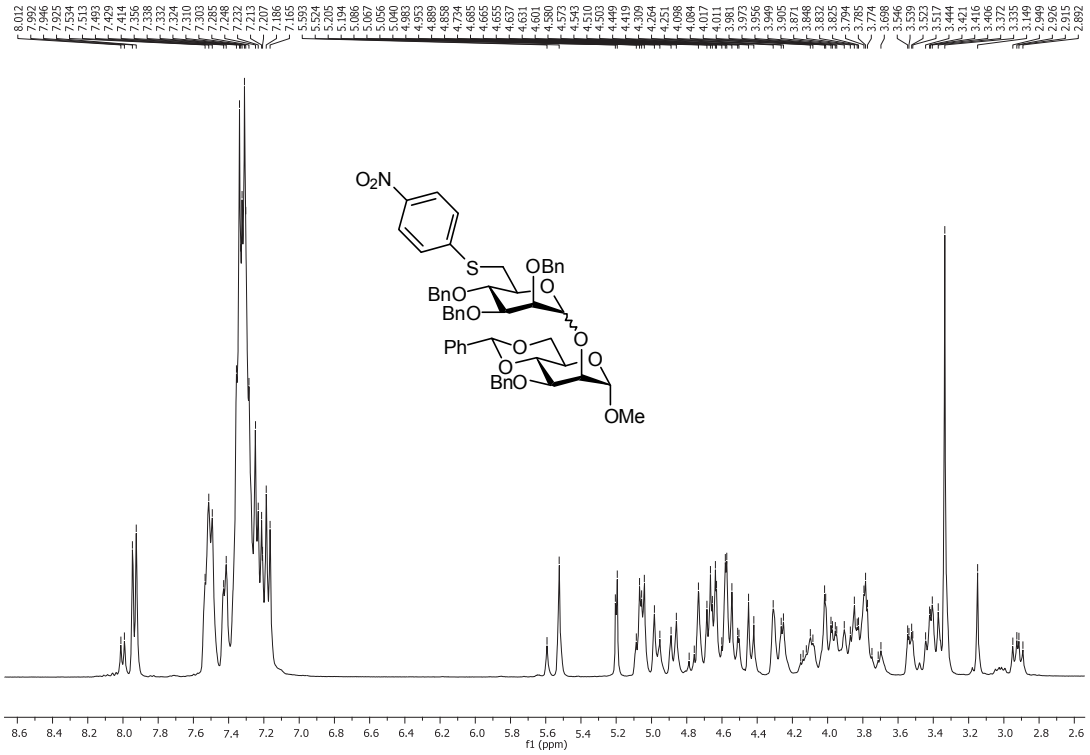


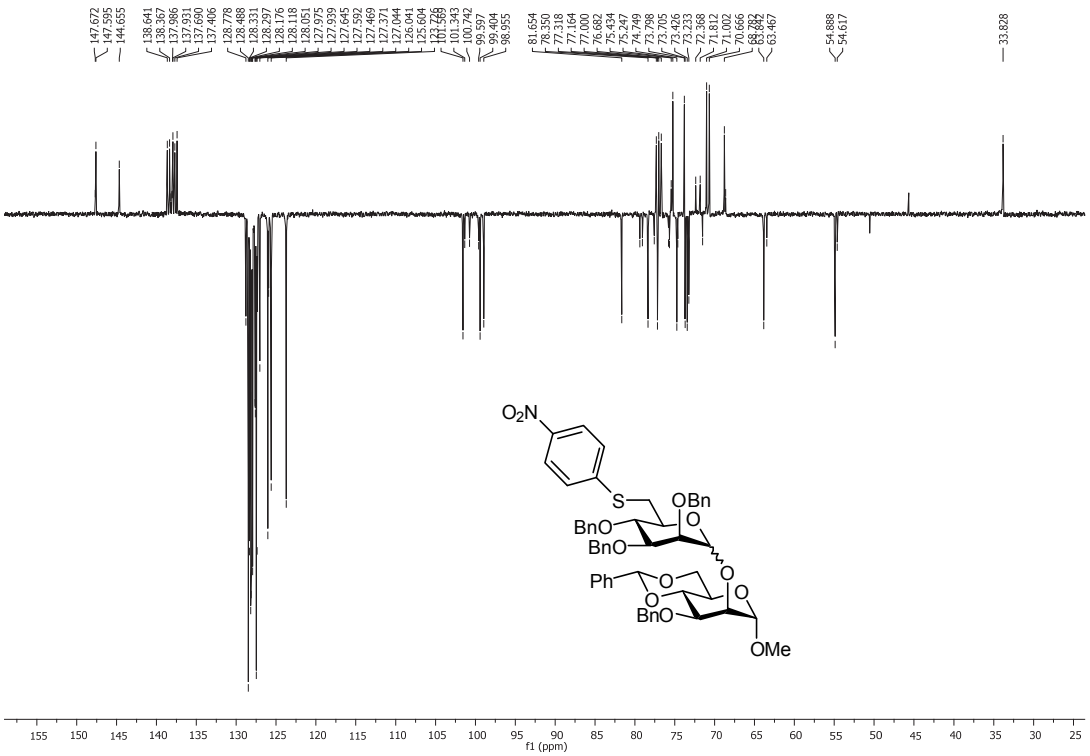
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-D-mannopyranosyl-(1→3)-*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (21b):



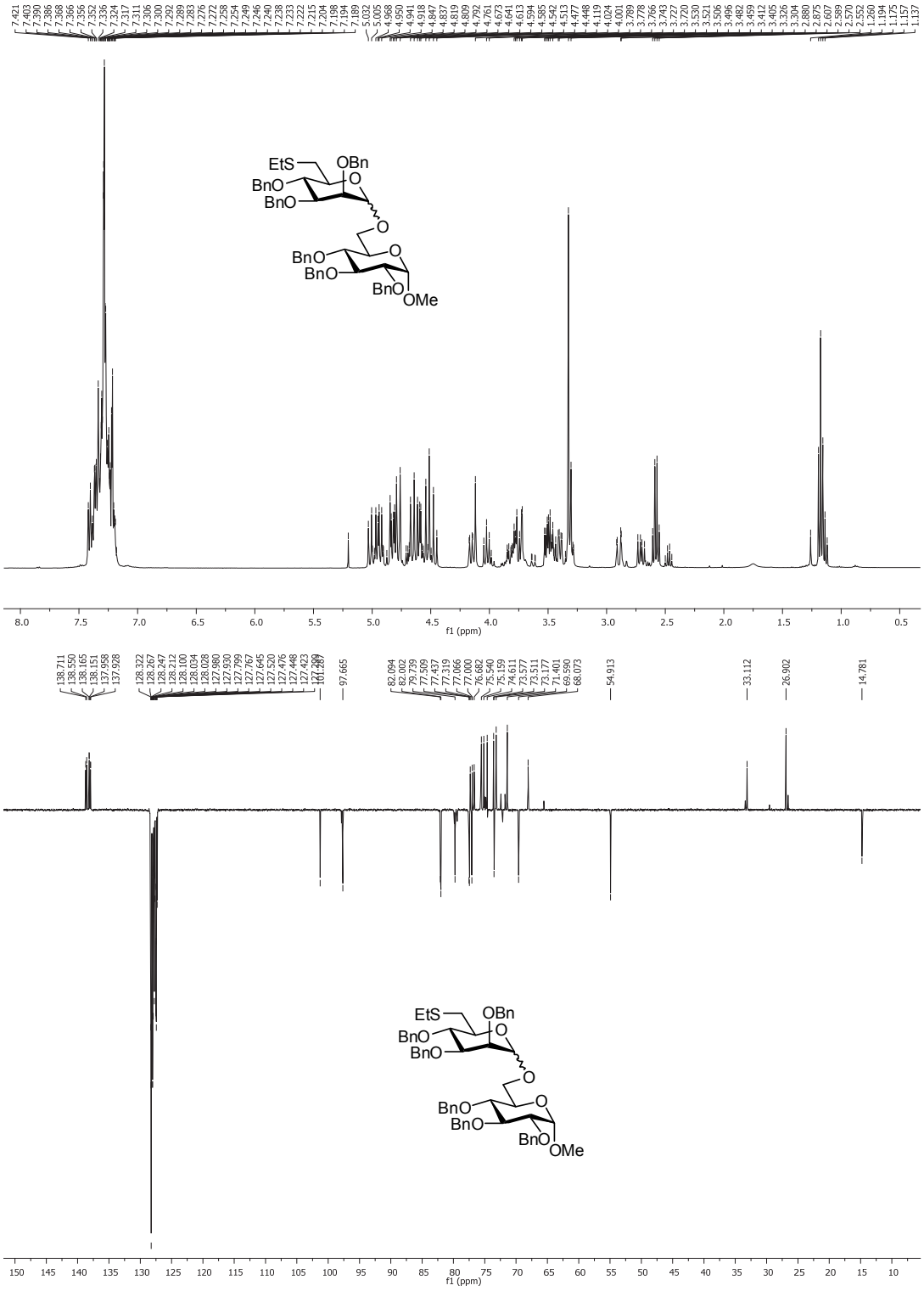


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-*p*-nitrophenyl-6-thio-D-mannopyranosyl-(1→2)- methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (21c):

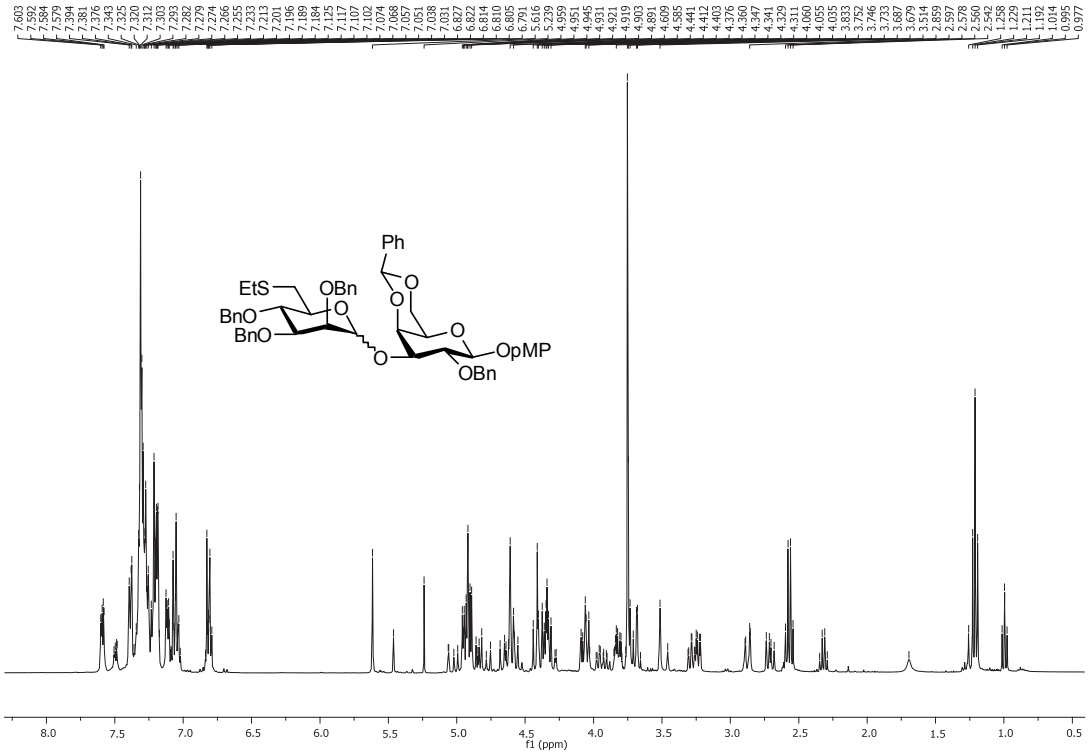


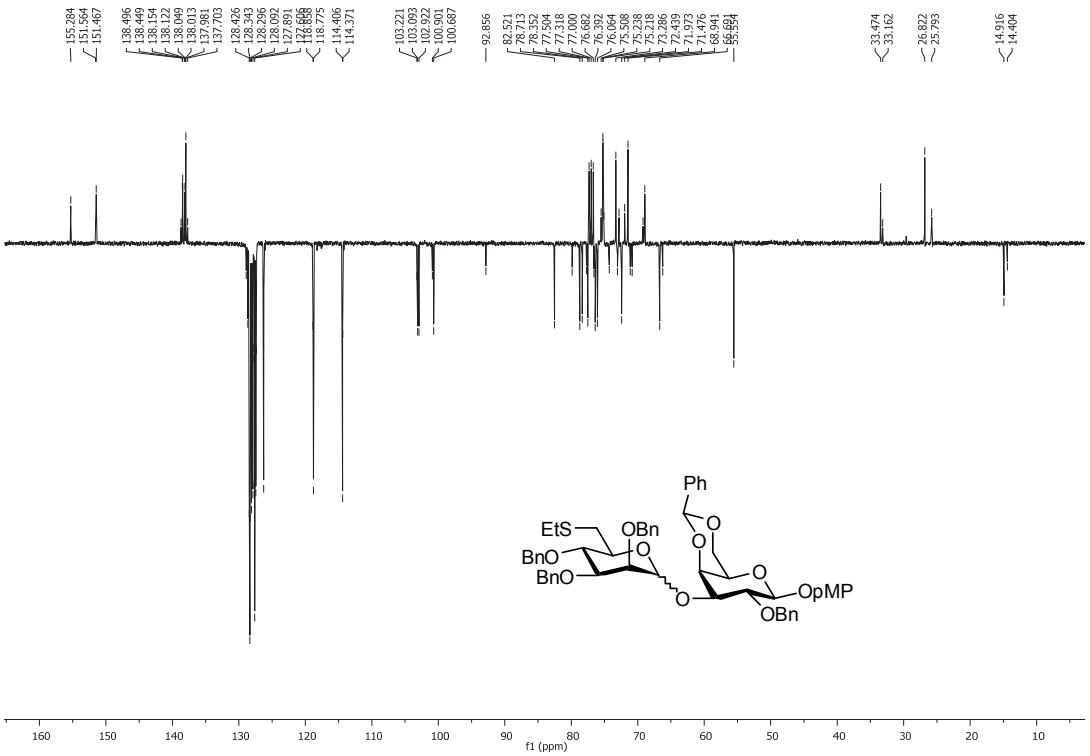


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-D-mannopyranosyl-(1→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (22a):

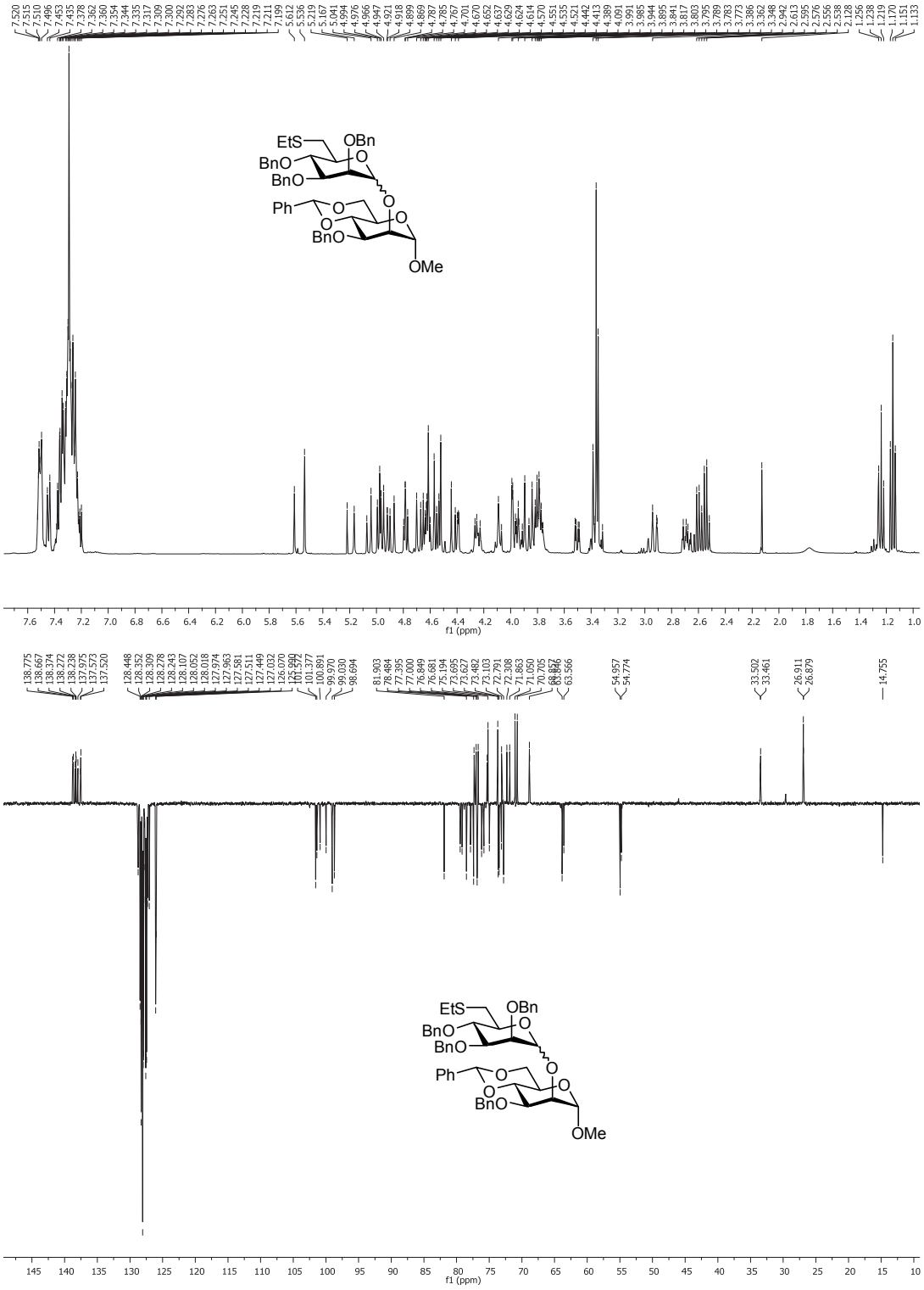


2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-D-mannopyranosyl-(1→3)-*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (22b):

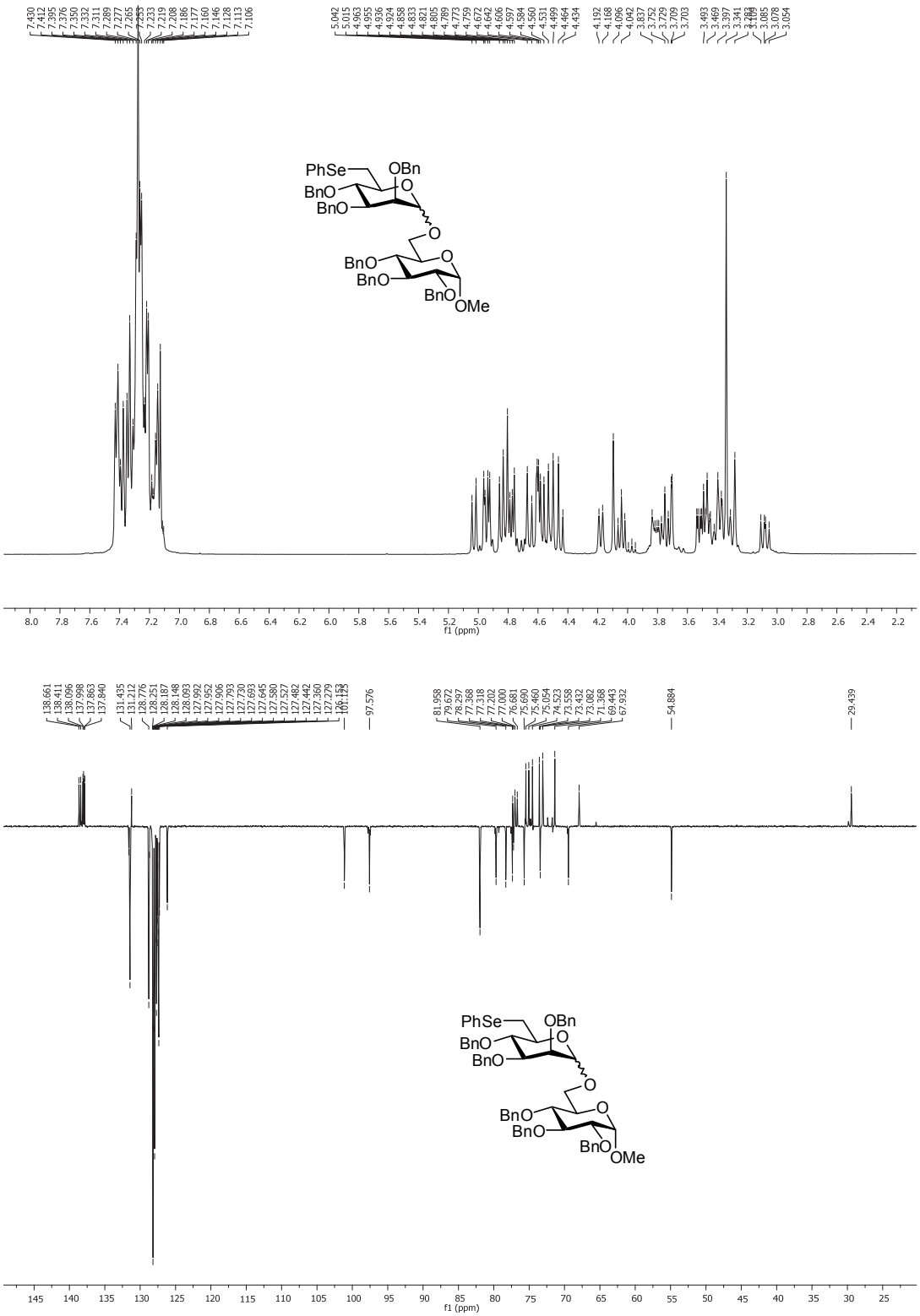




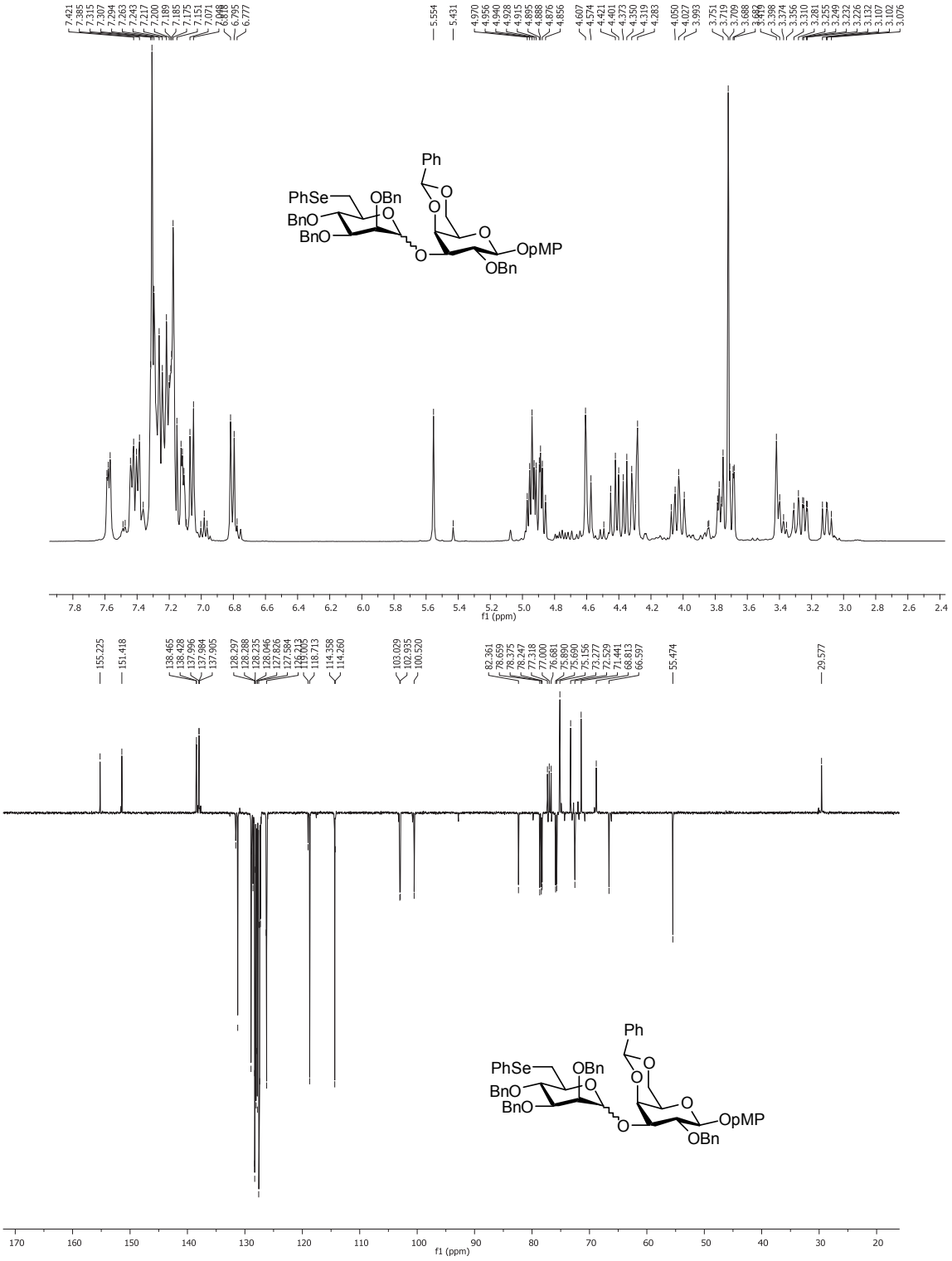
2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-ethyl-6-thio-D-mannopyranosyl-(1→2)-methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (22c):



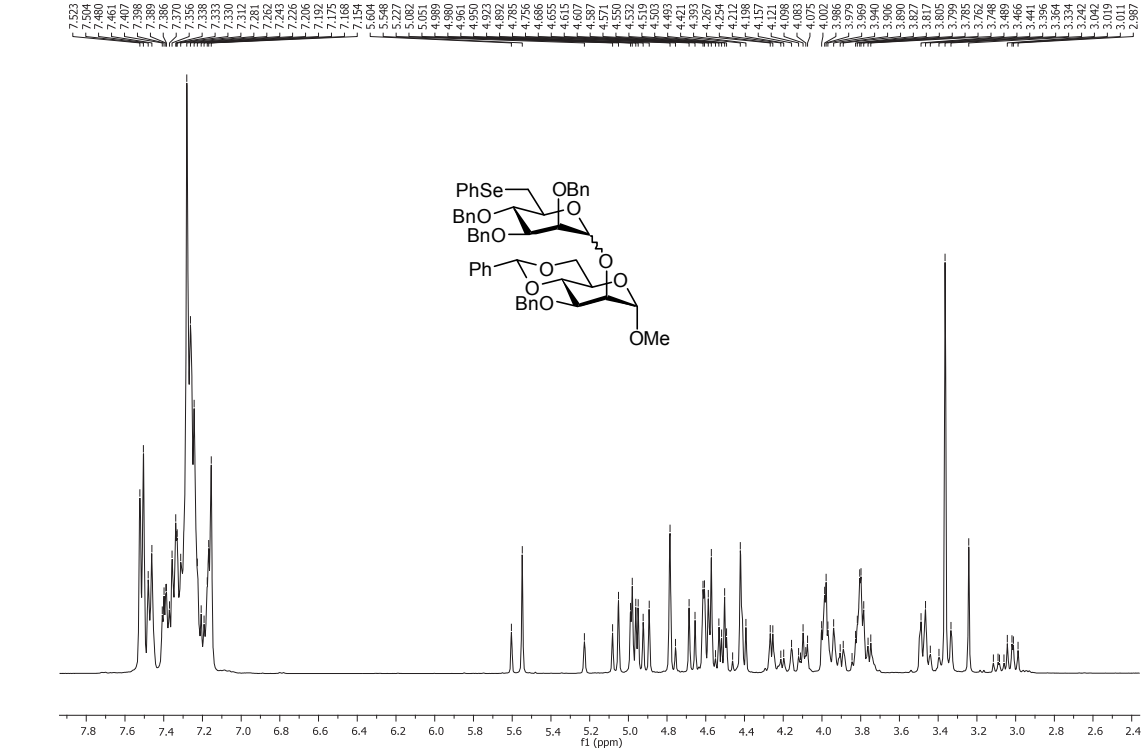
2,3,4-Tri-*O*-benzyl-6-deoxy-6-Se-phenyl-6-seleno-D-mannopyranosyl-(1→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (23a):

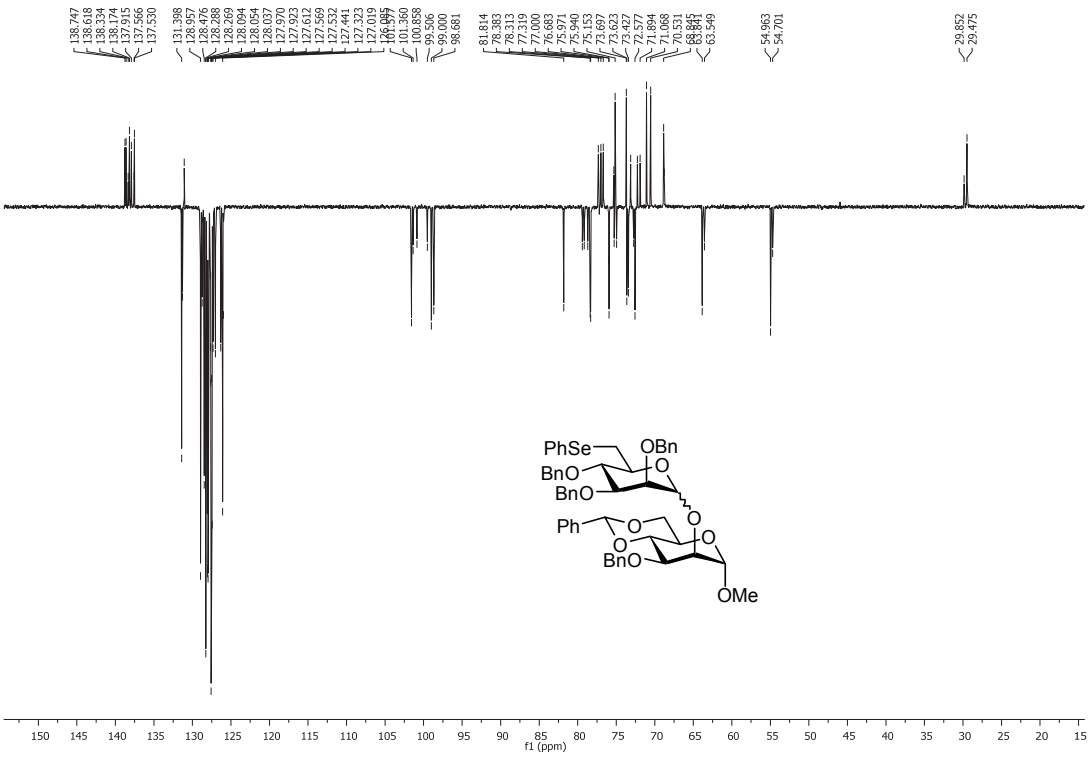


2,3,4-Tri-*O*-benzyl-6-deoxy-6-Se-phenyl-6-seleno-D-mannopyranosyl -(1→3)-*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (23b):

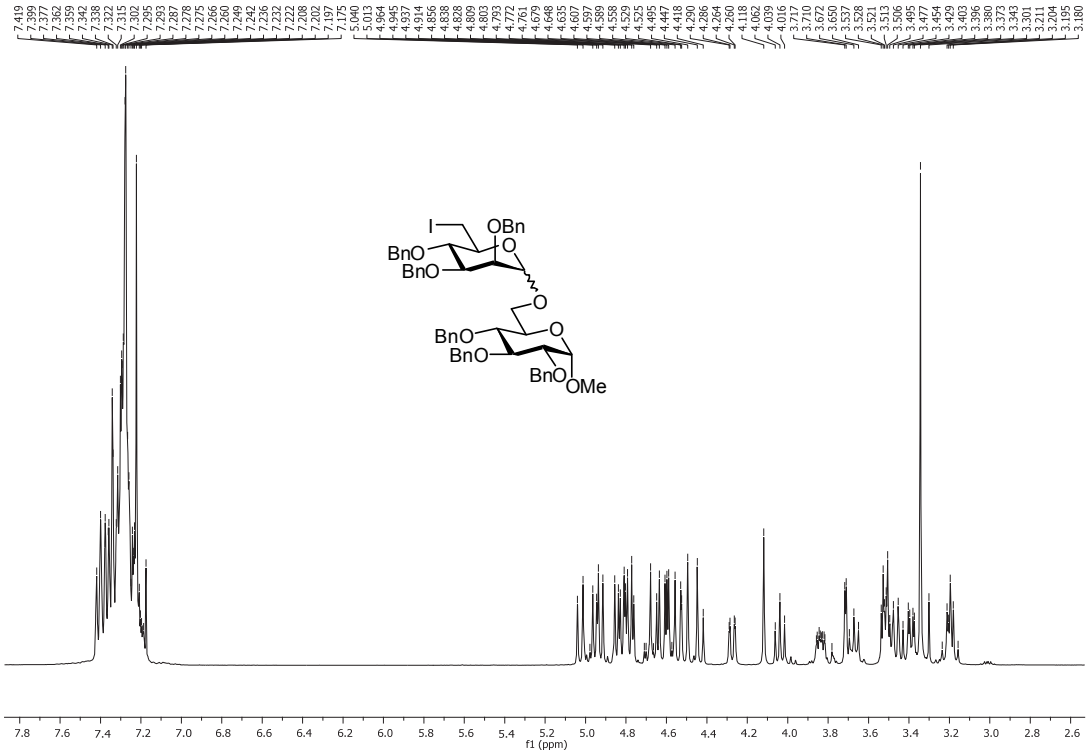


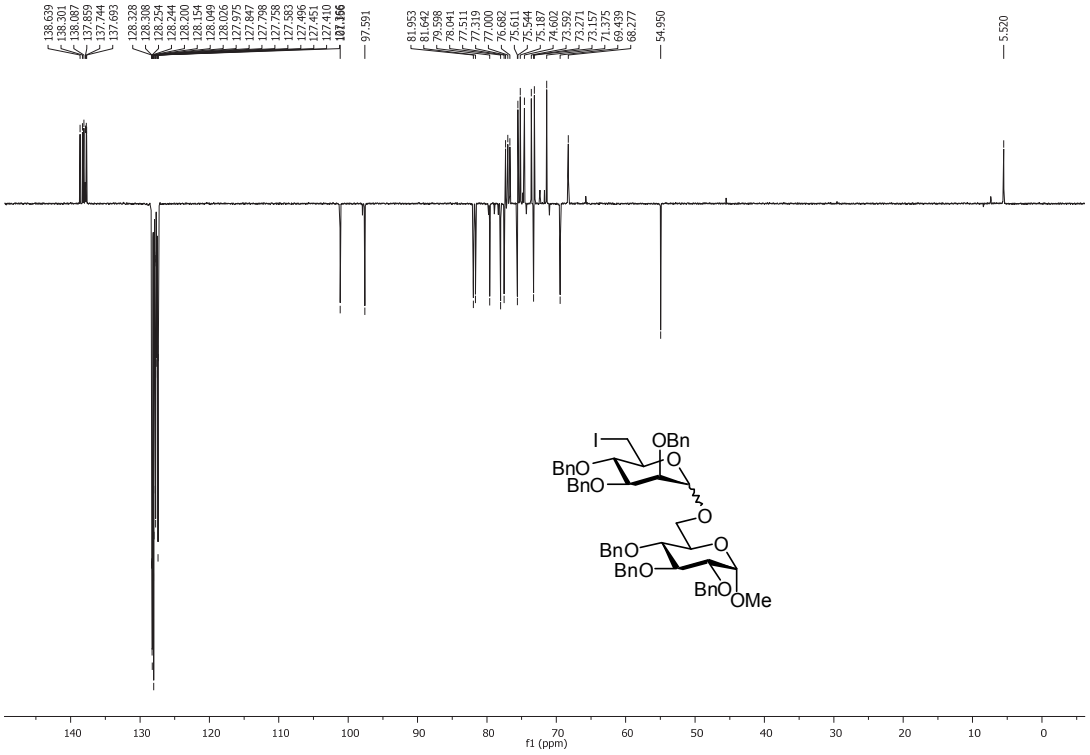
2,3,4-Tri-*O*-benzyl-6-deoxy-6-Se-phenyl-6-seleno-D-mannopyranosyl-(1→2)- methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (23c):



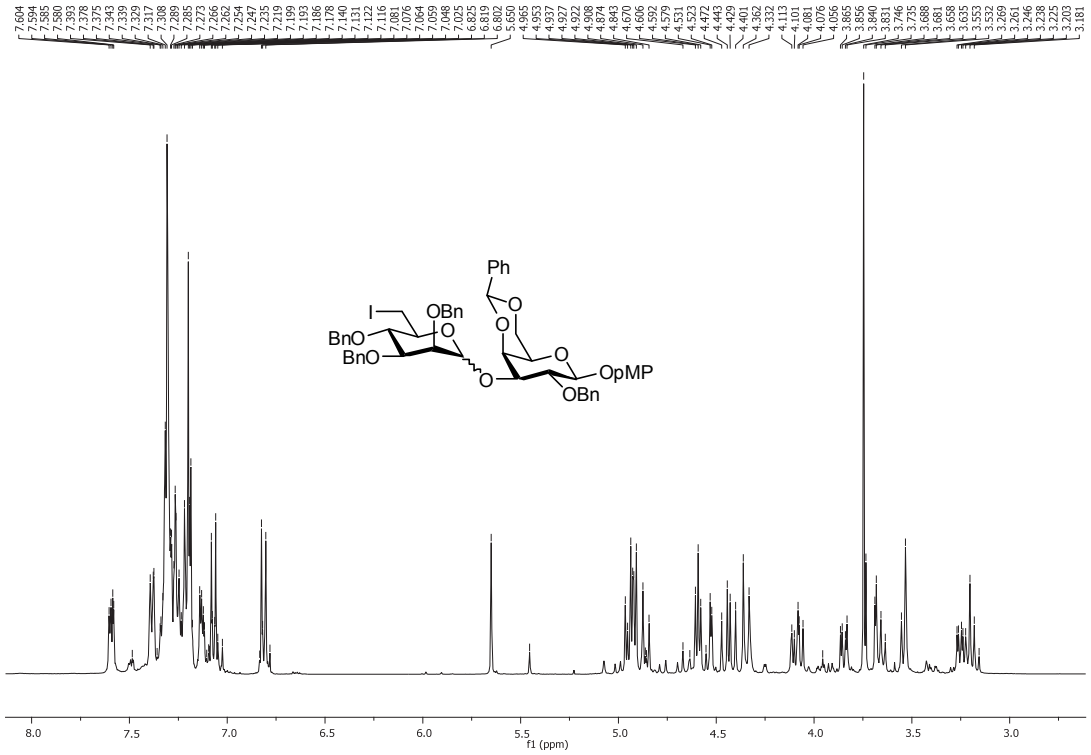


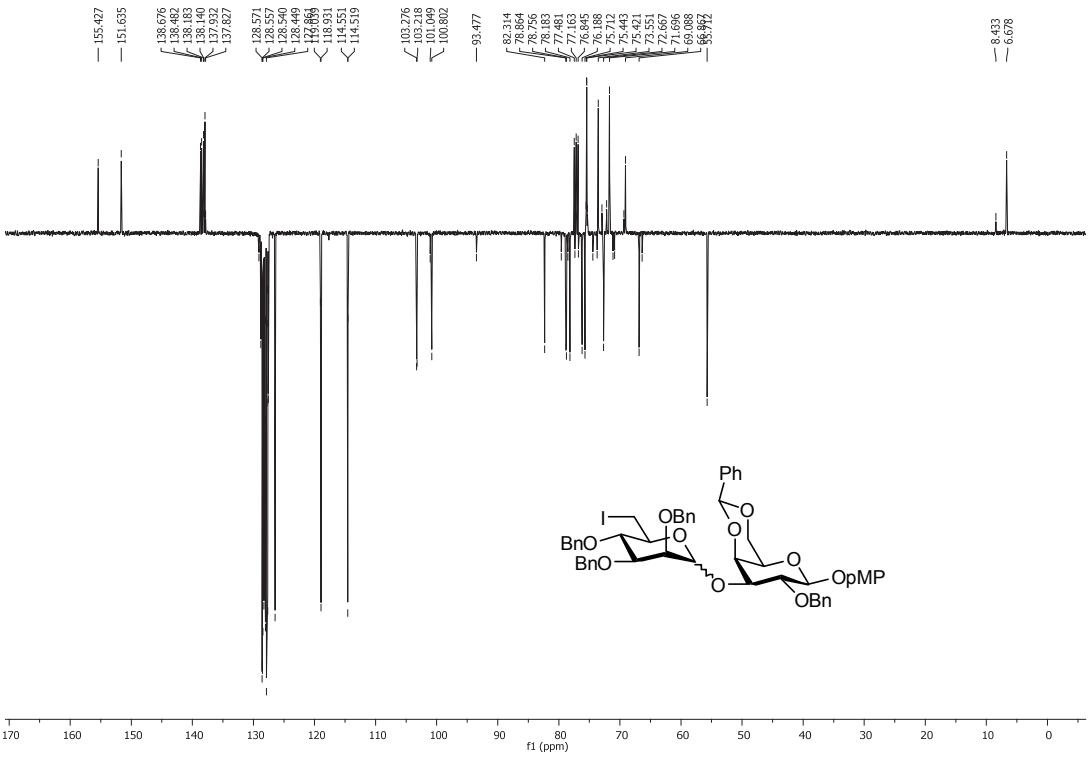
2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranosyl-(1→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (24a):



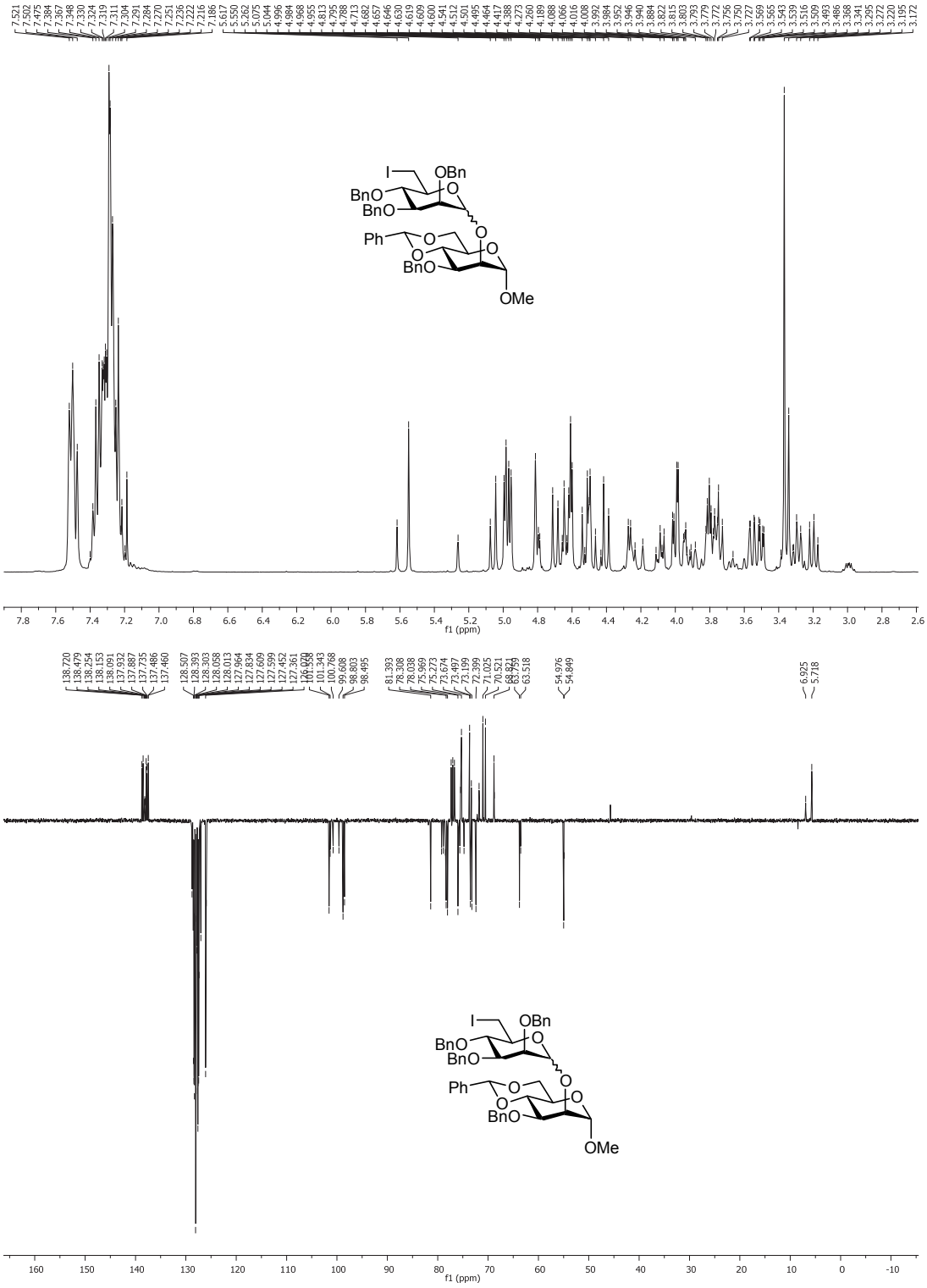


2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranosyl-(1→3)-*p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (24b):

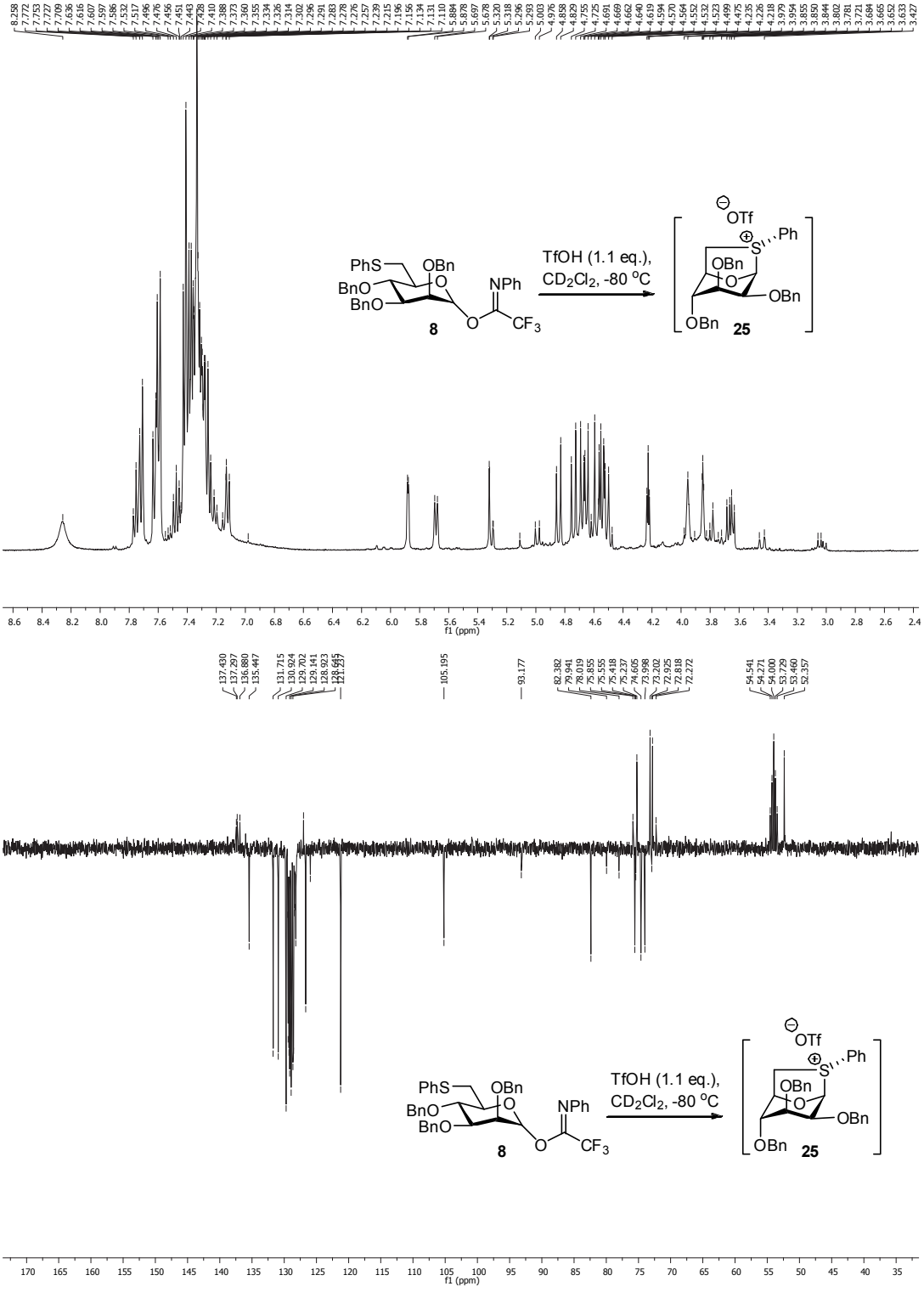




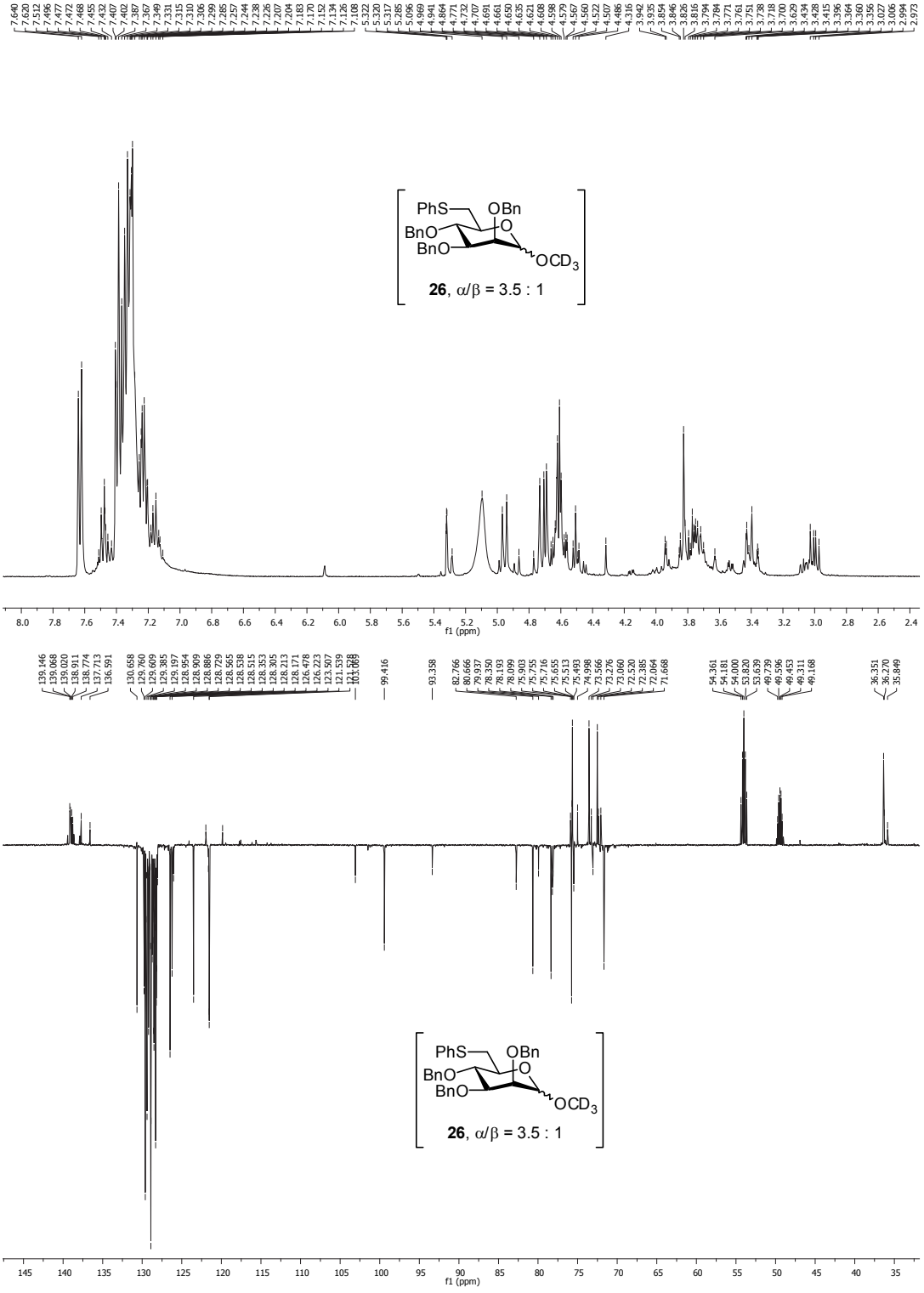
2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-D-mannopyranosyl-(1→2)- methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (24c):



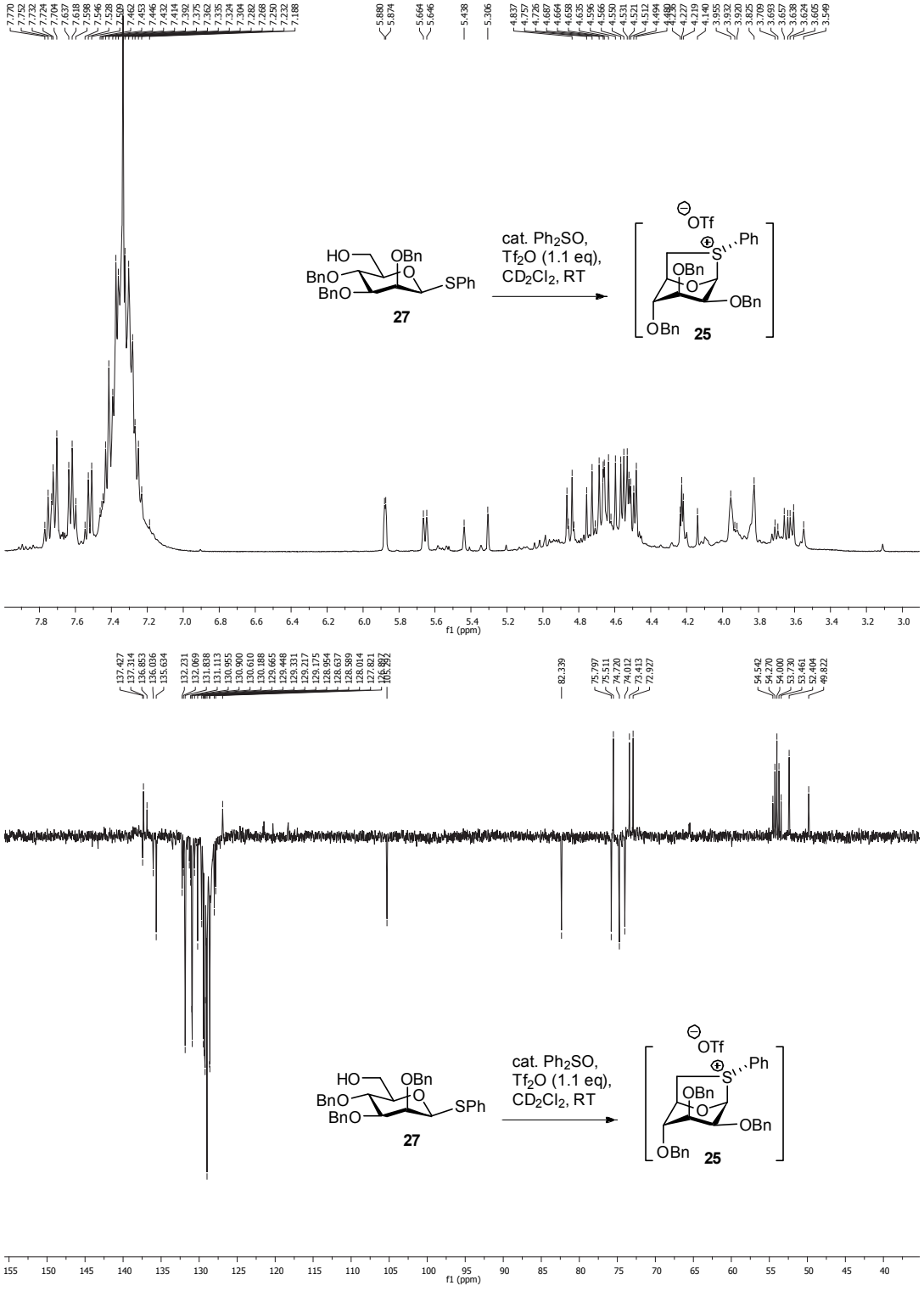
1,6-Anhydro-2,3,4-tri-*O*-benzyl-5-deoxy-5-S-phenyl-5-sulfonium-β-D-mannopyranose triflate (25)
(from imidate donor **8**, T = 193 K, NMR tube experiment):



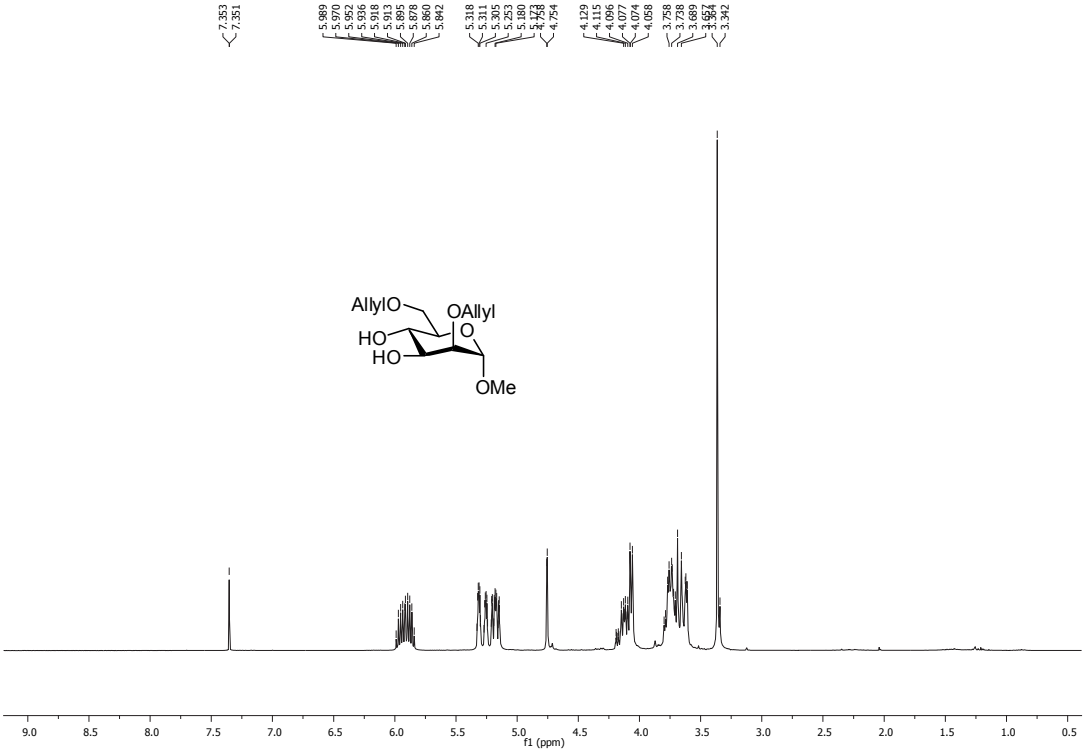
Methyl (*d*3) 2,3,4-tri-*O*-benzyl-6-deoxy-6-*S*-phenyl-6-thio-D-mannopyranoside (26) (NMR tube experiment)**:**

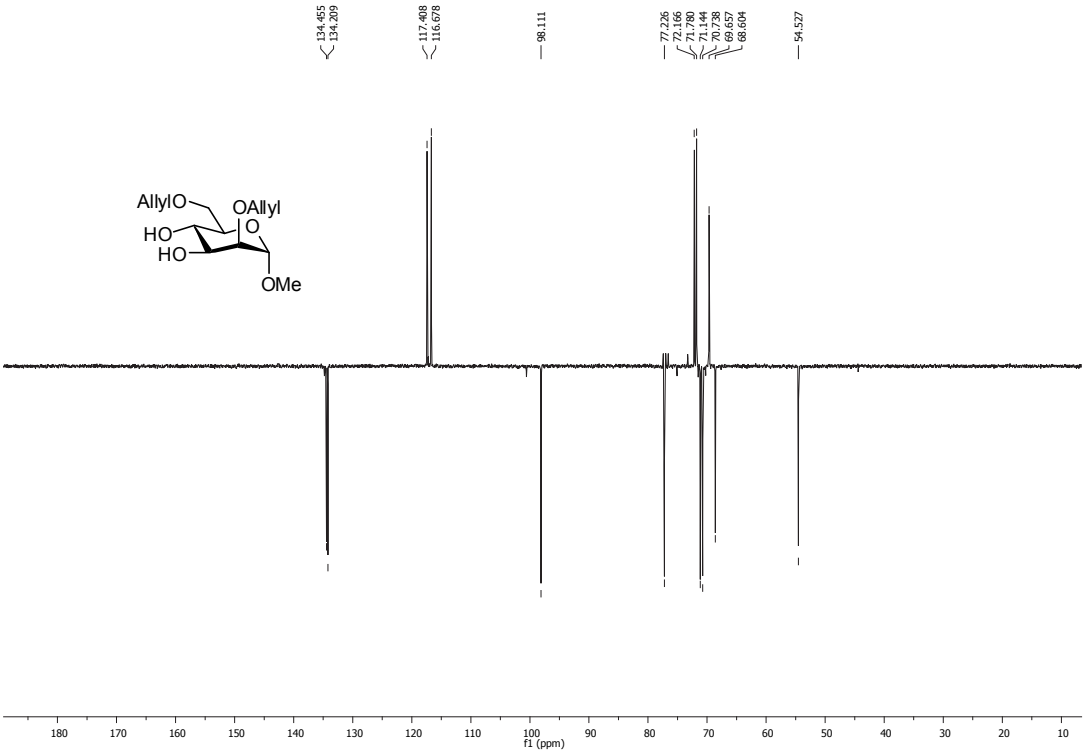


1,6-Anhydro-2,3,4-tri-*O*-benzyl-5-deoxy-5-S-phenyl-5-sulfonium-β-D-mannopyranose triflate (25)
(from mannoside **27**, NMR tube experiment):

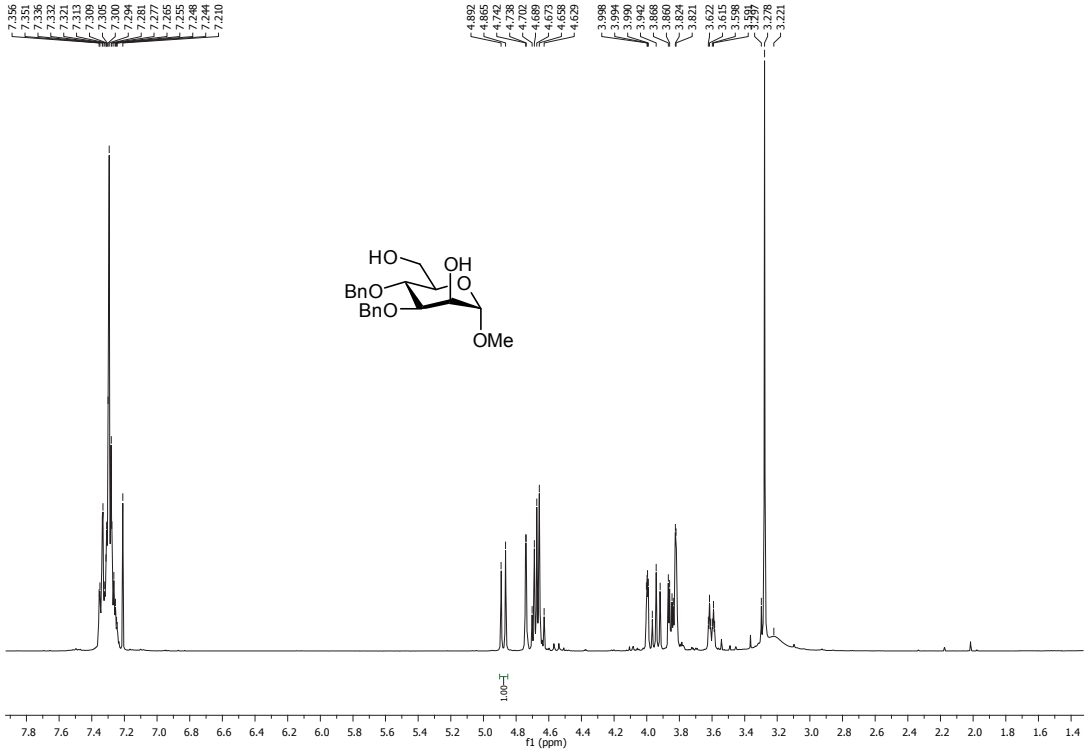


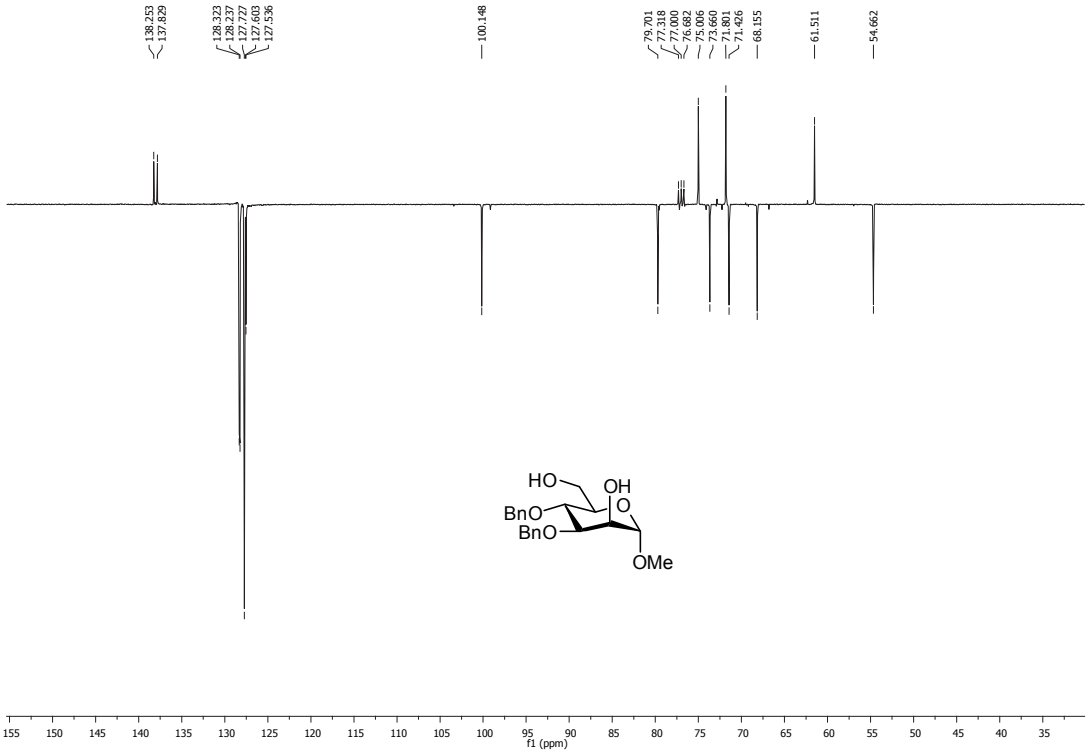
Methyl 2,6-di-*O*-allyl-α-D-mannopyranoside (S11):



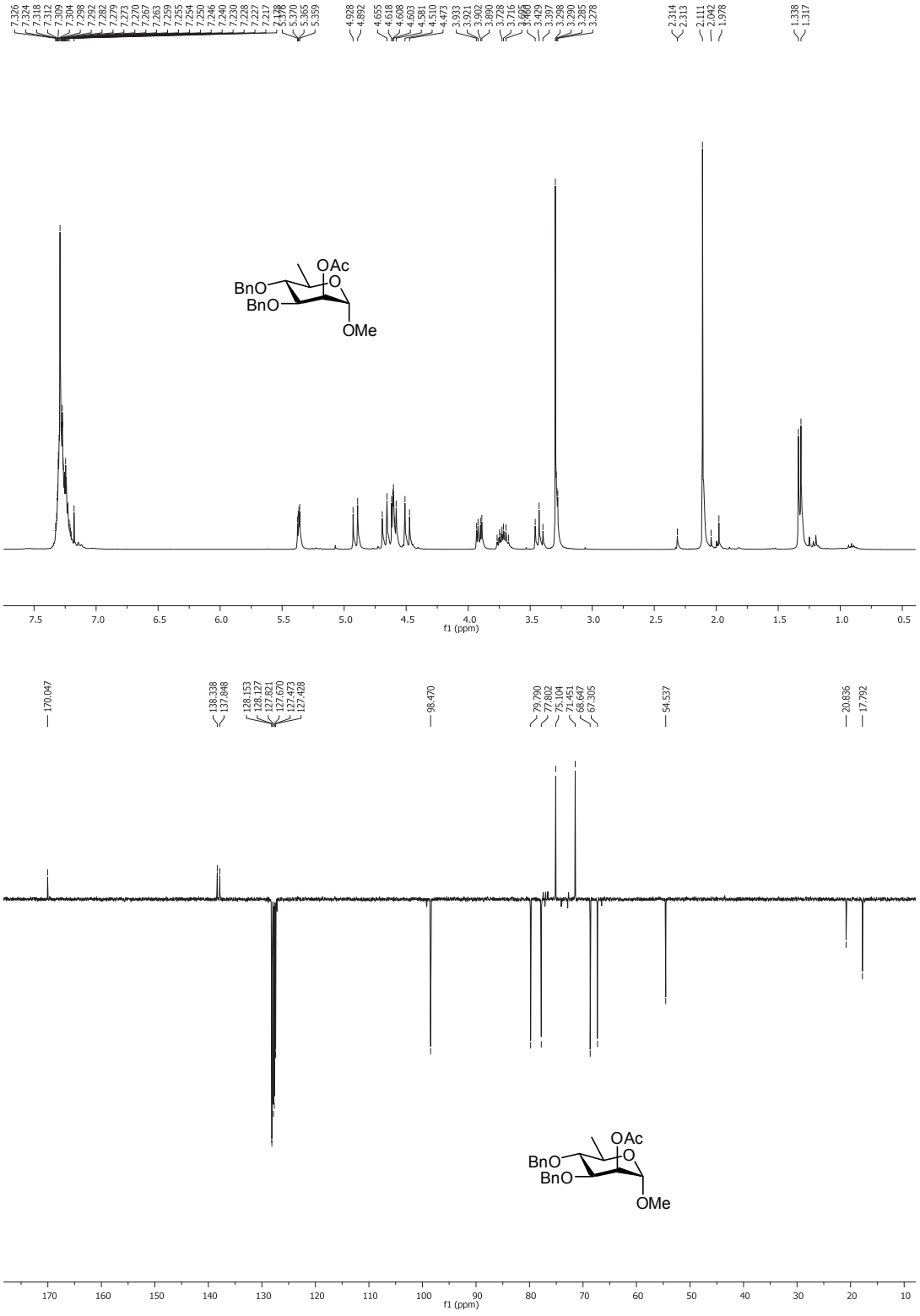


Methyl 3,4-di-*O*-benzyl-α-D-mannopyranoside (S12):

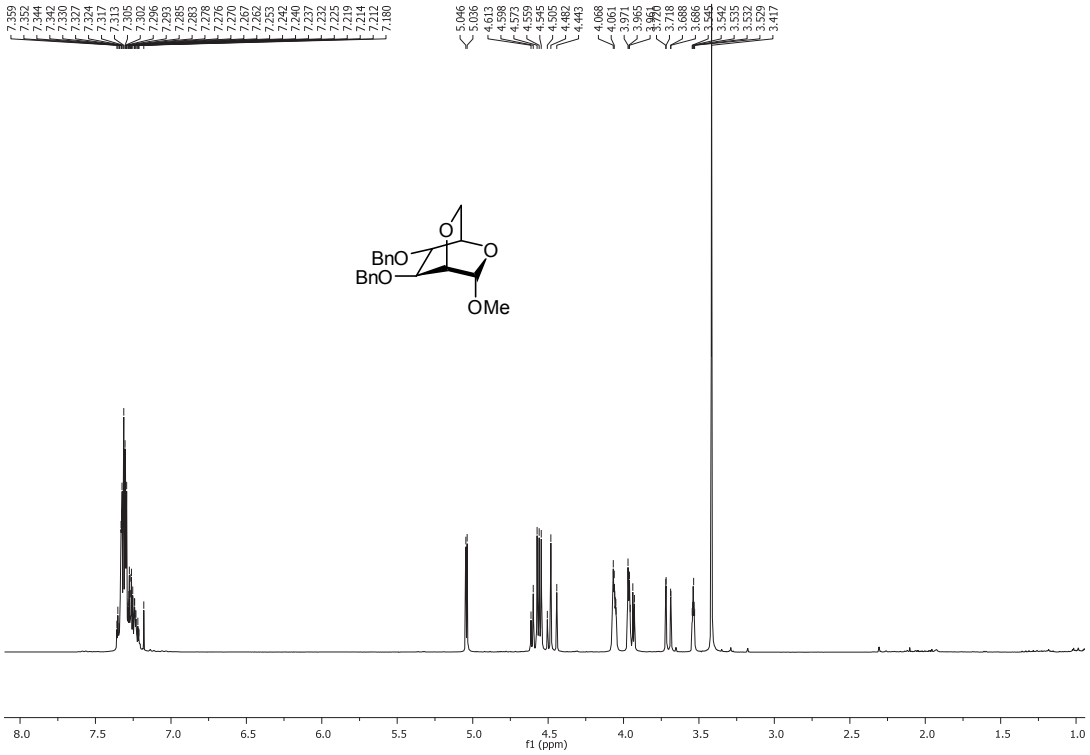


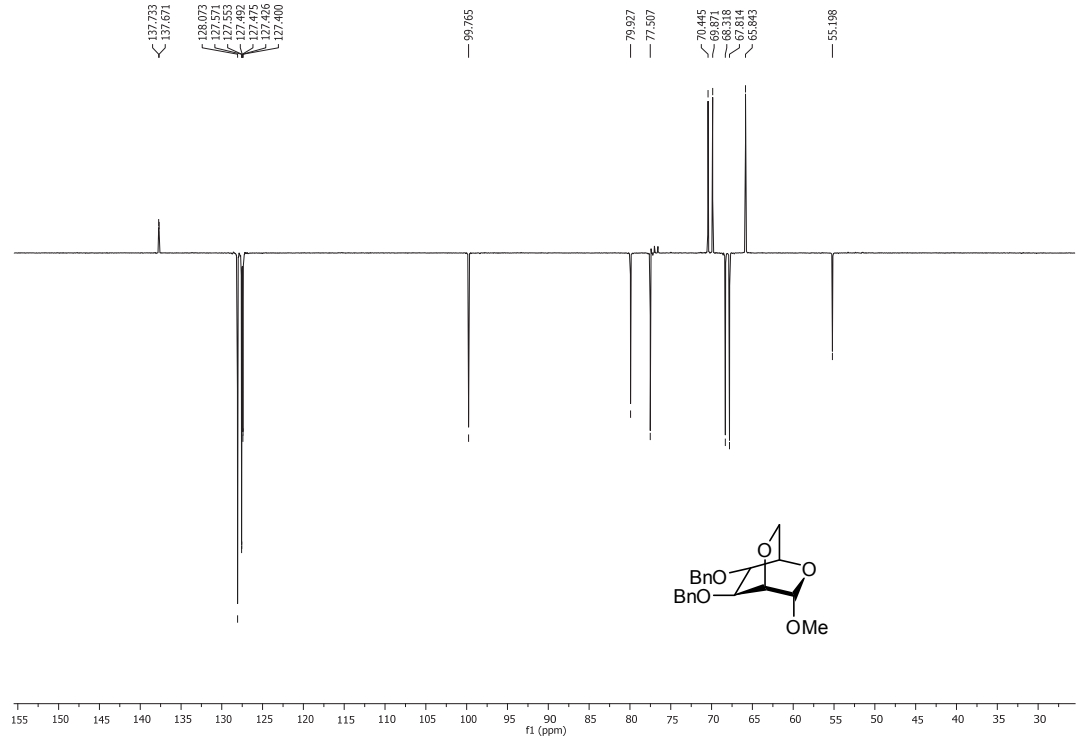


Methyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside (S13):

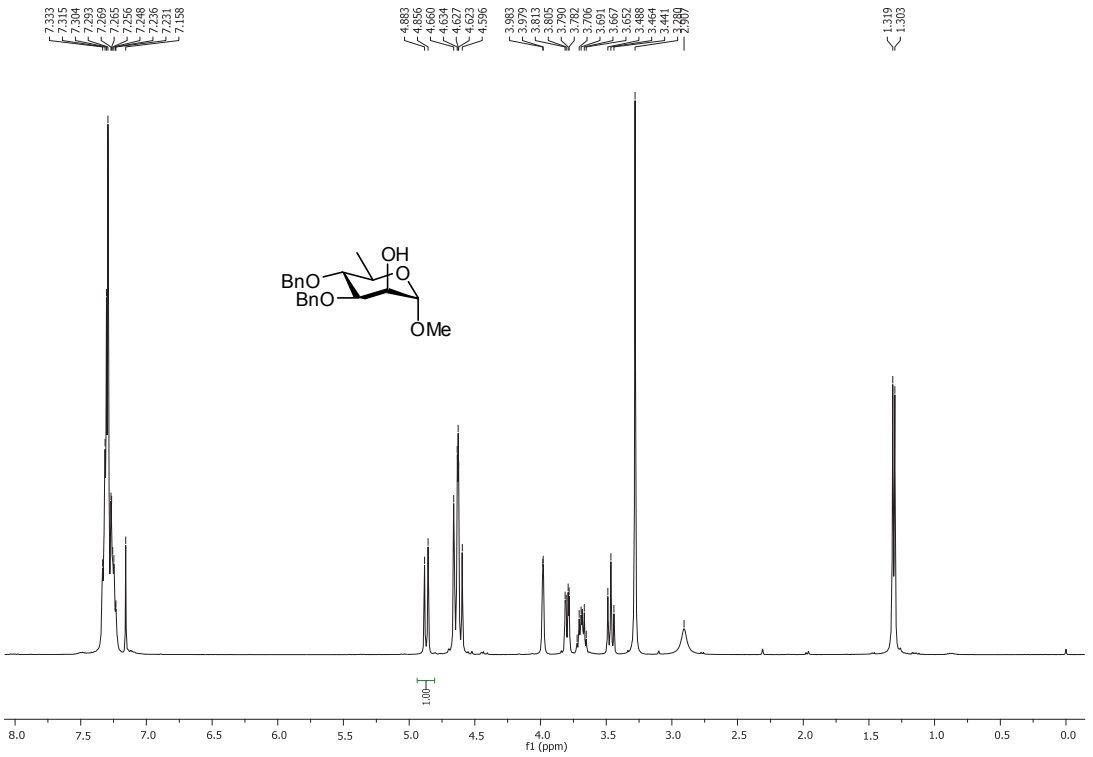


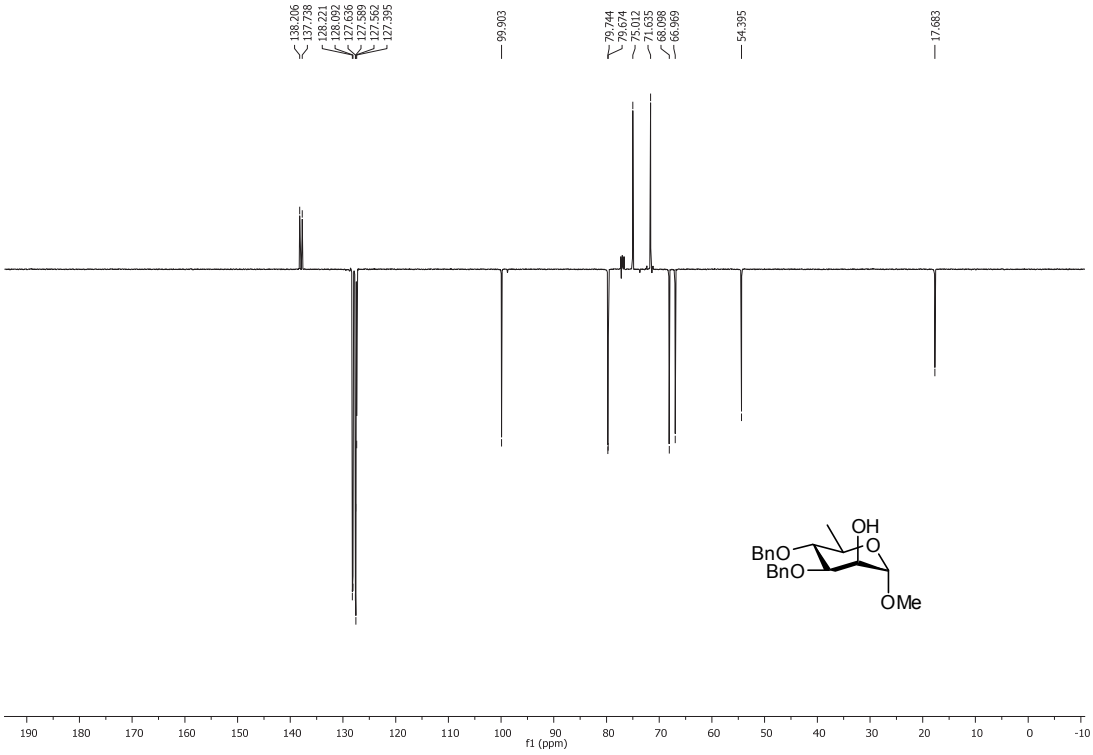
Methyl 2,6-anhydro-3,4-di-*O*-benzyl-α-D-mannopyranoside (S15):



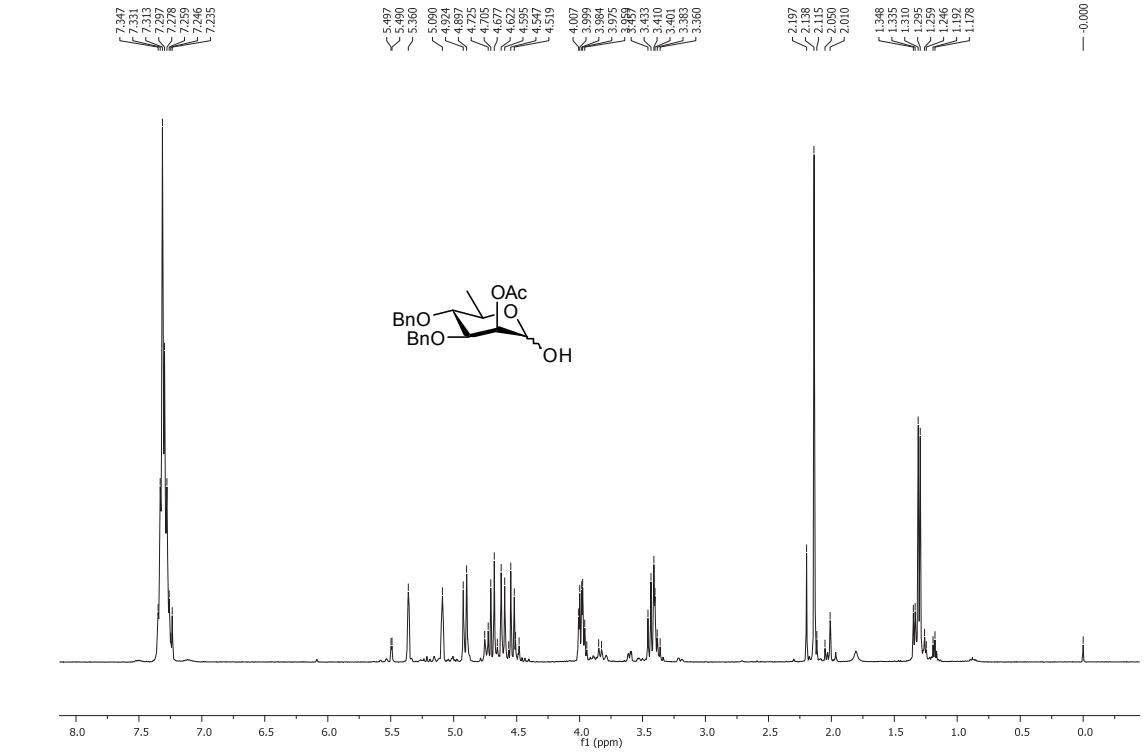


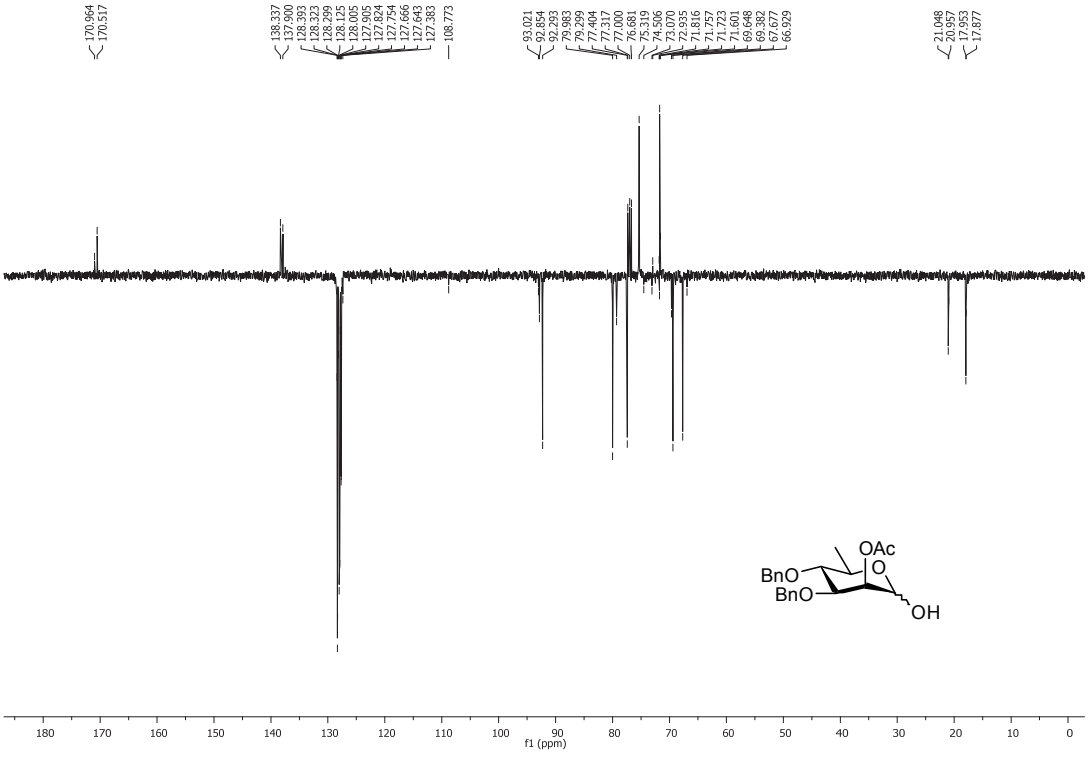
Methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside (29):



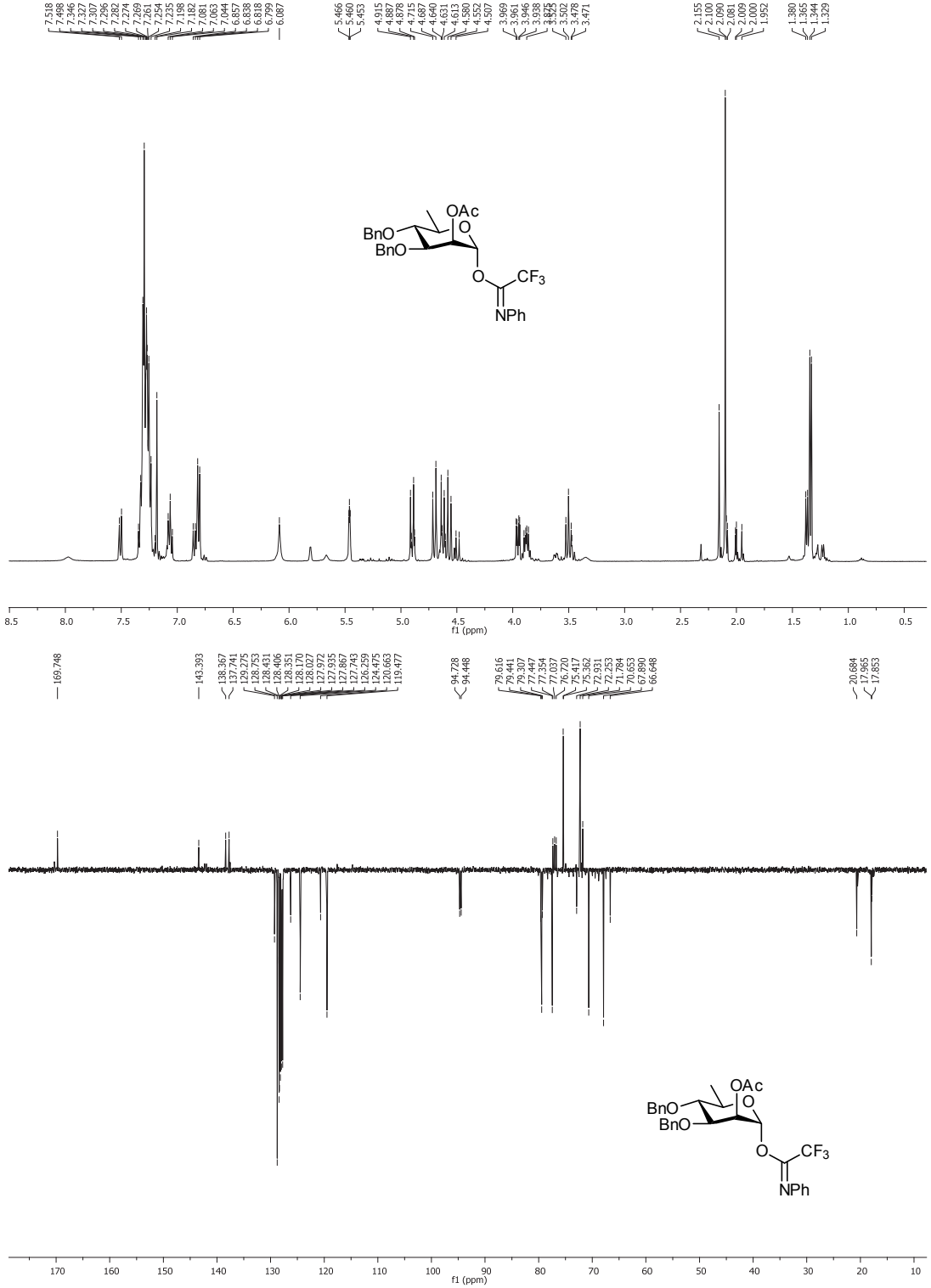


2-*O*-Acetyl-3,4-di-*O*-benzyl-6-deoxy-D-mannopyranose (S14):

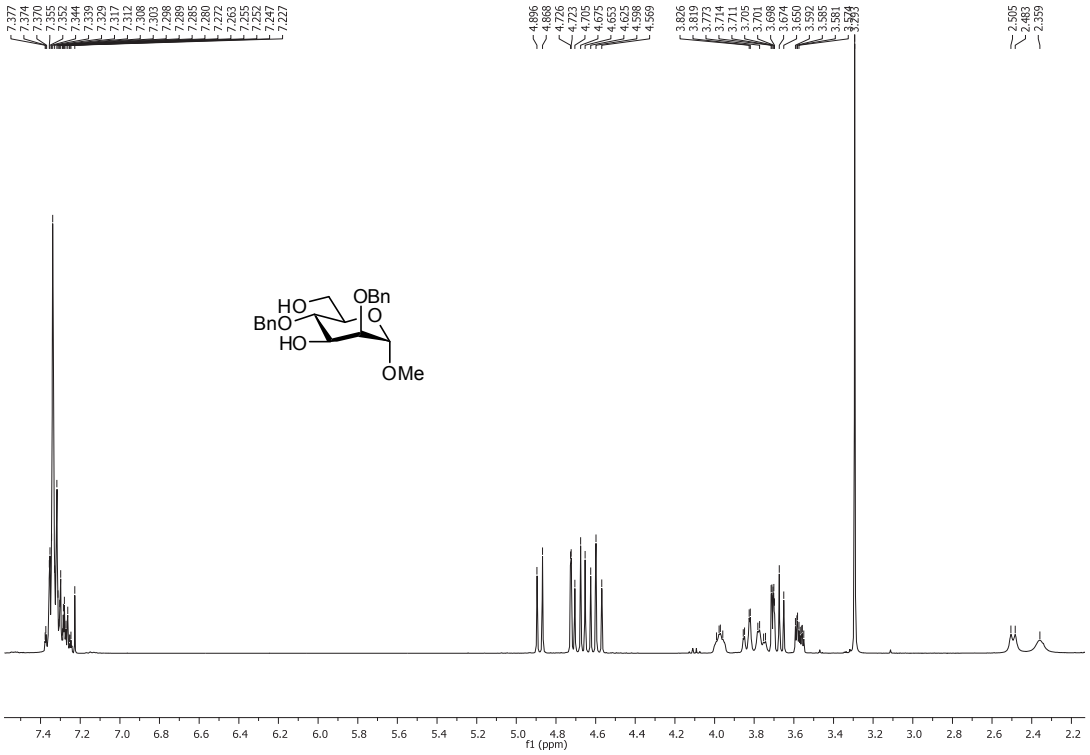


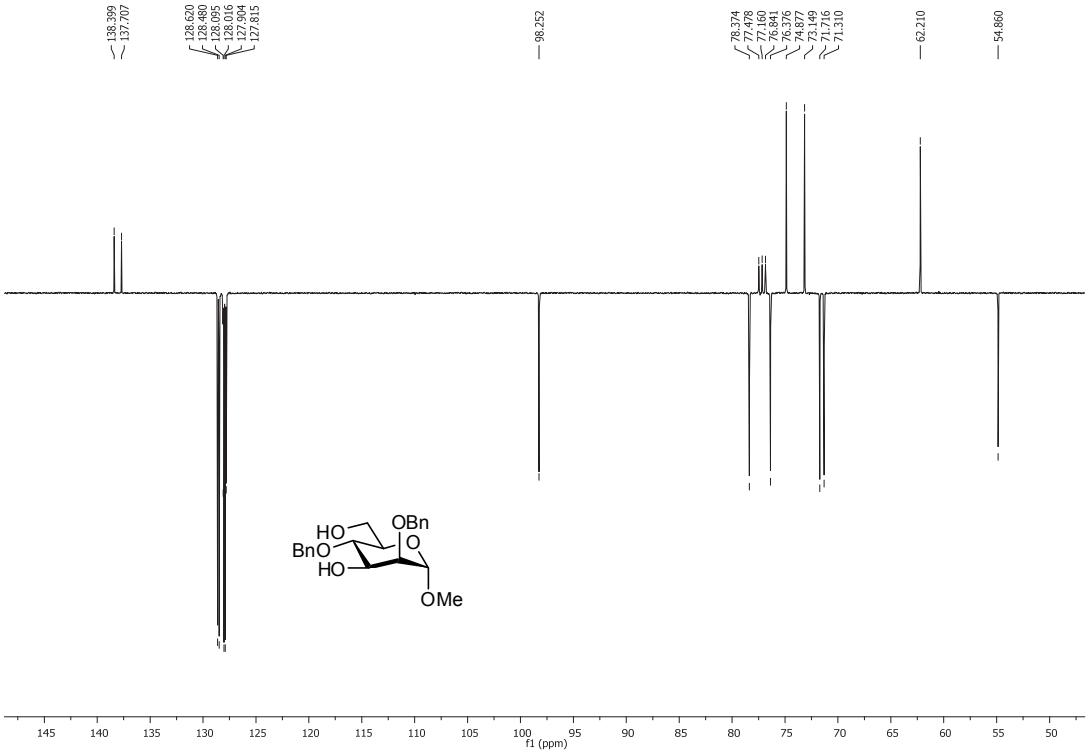


2-*O*-acetyl-3,4-di-*O*-benzyl-6-deoxy-D-mannopyranosyl *N*-phenyltrifluoroacetimidate (32):

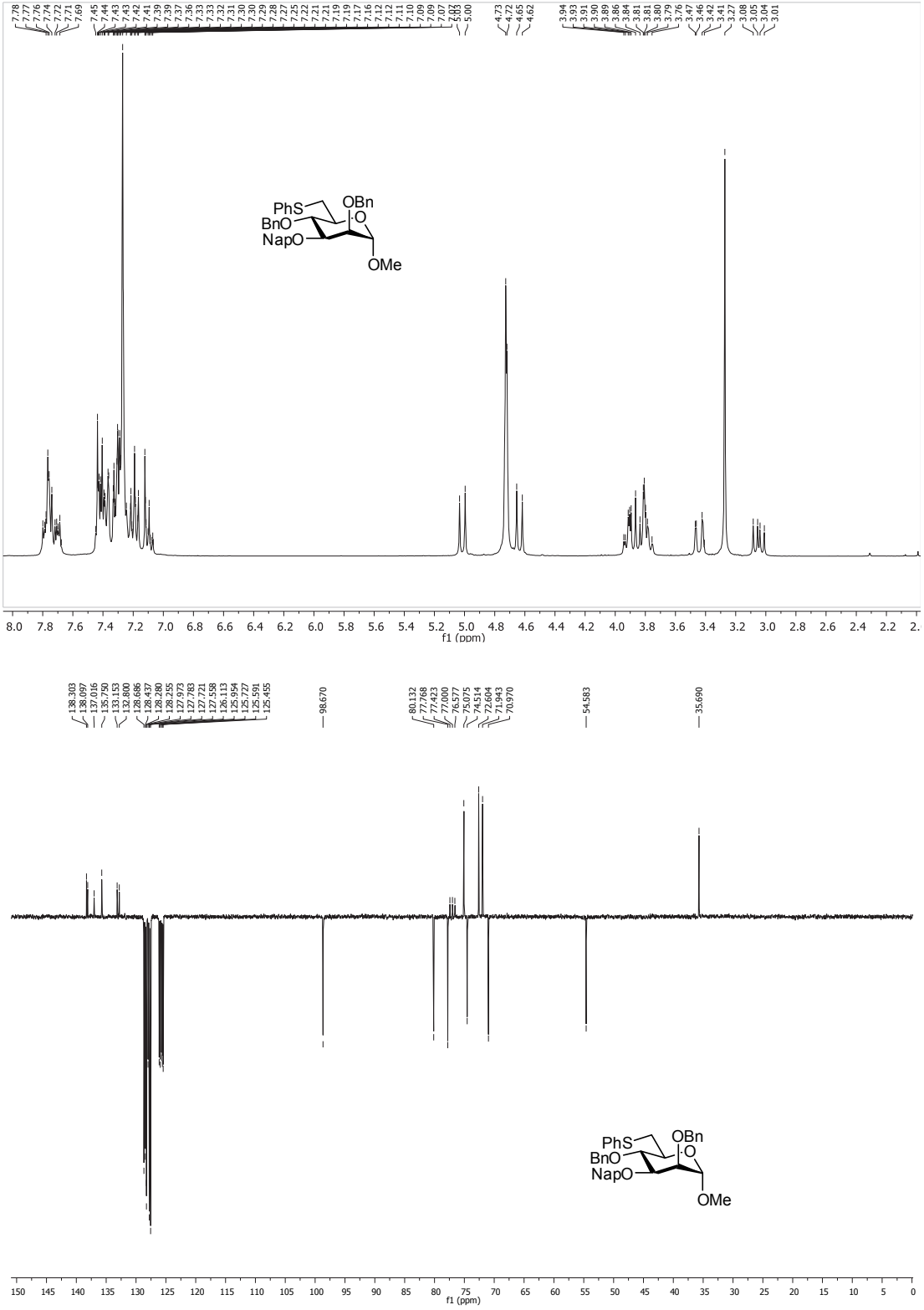


Methyl 2,4-di-*O*-benzyl-α-D-mannopyranoside (S16):

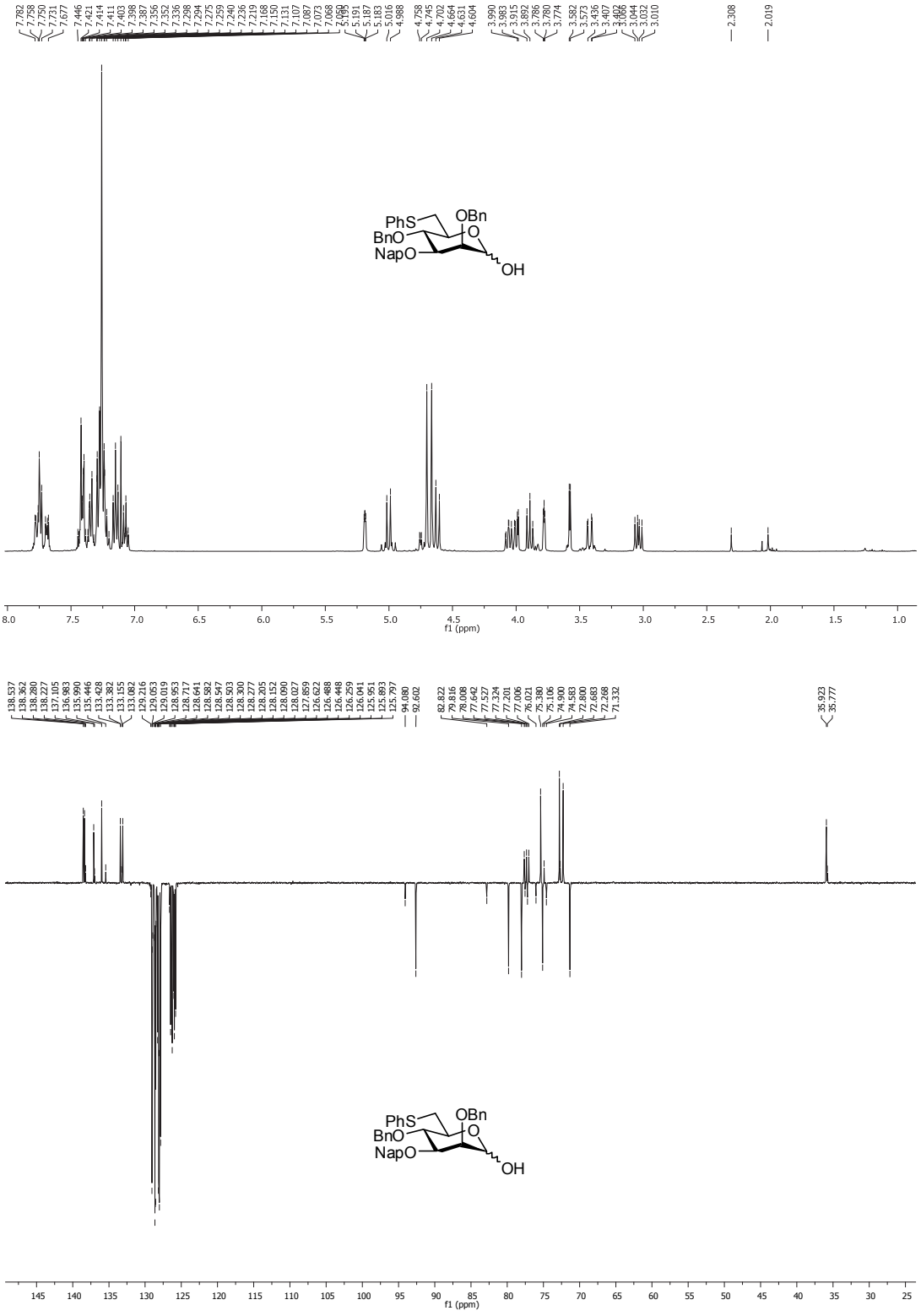




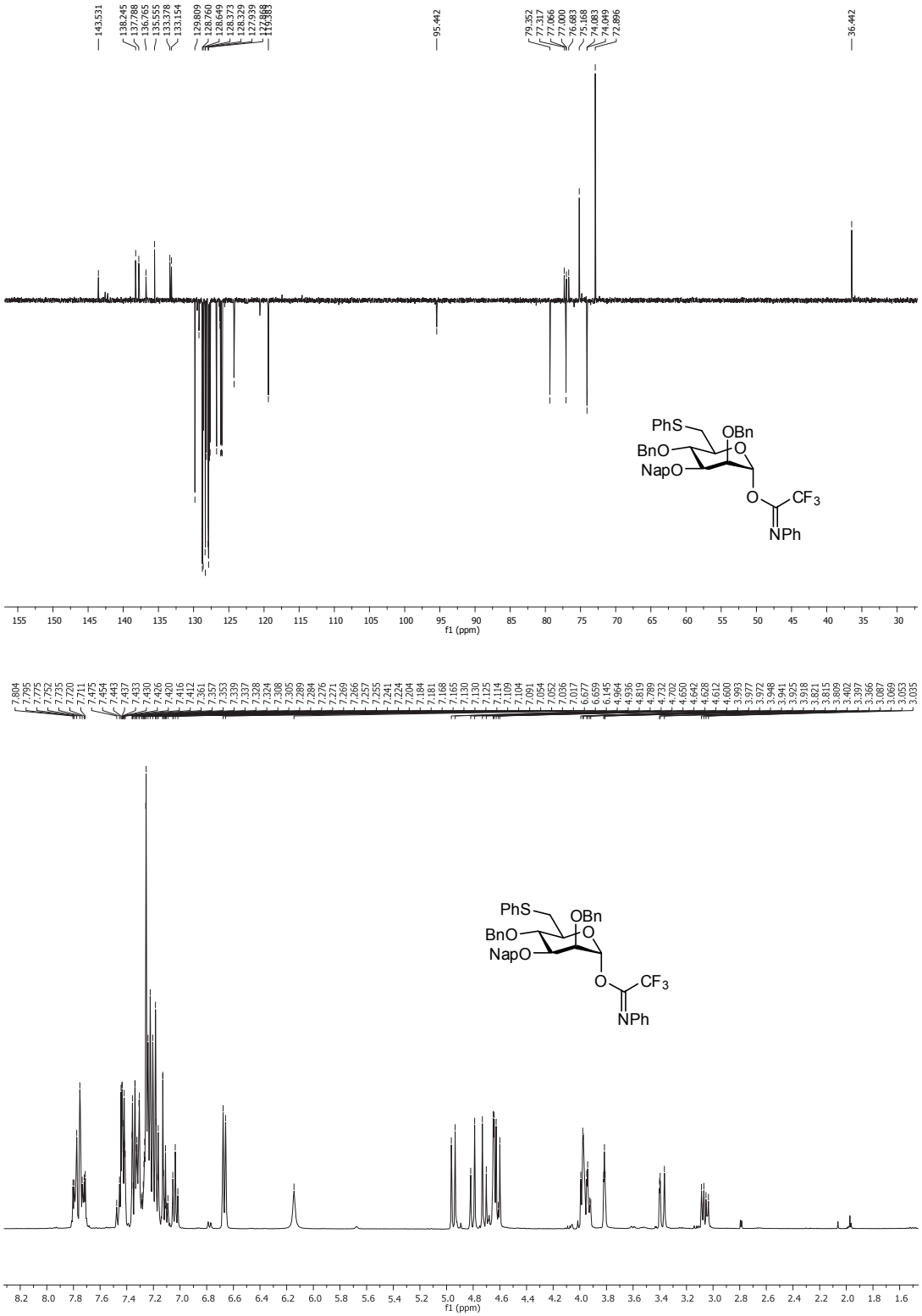
Methyl 2,4-di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-α-D-mannopyranoside (S17):



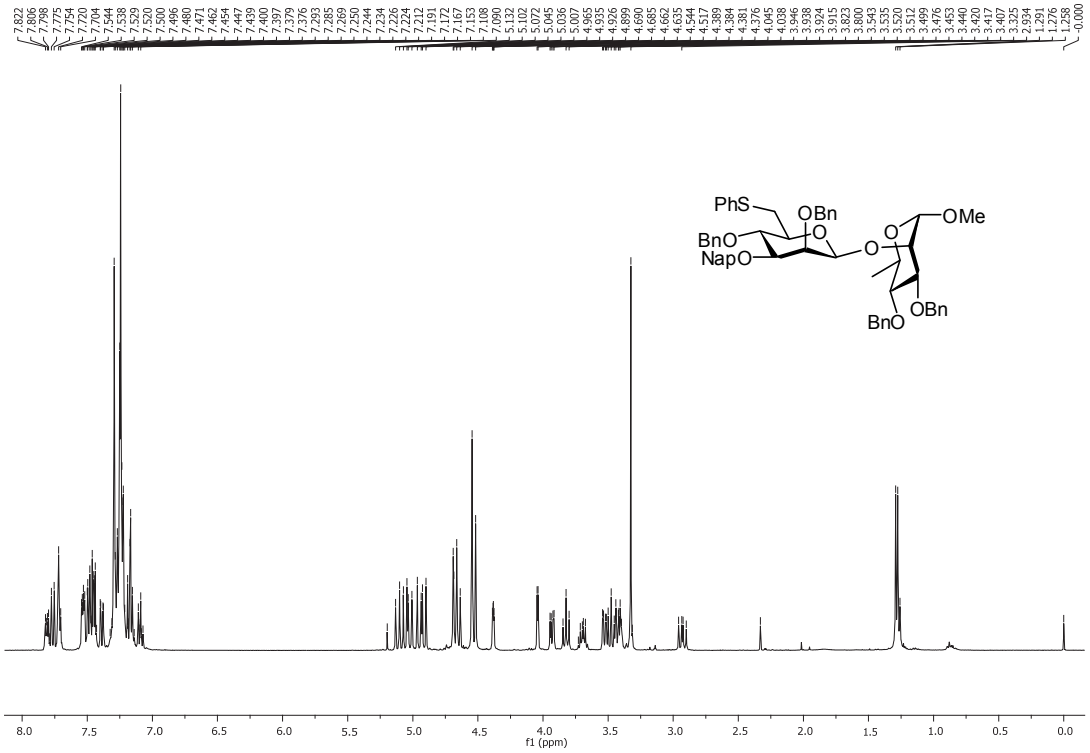
2,4-Di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-D-mannopyranose (S18):

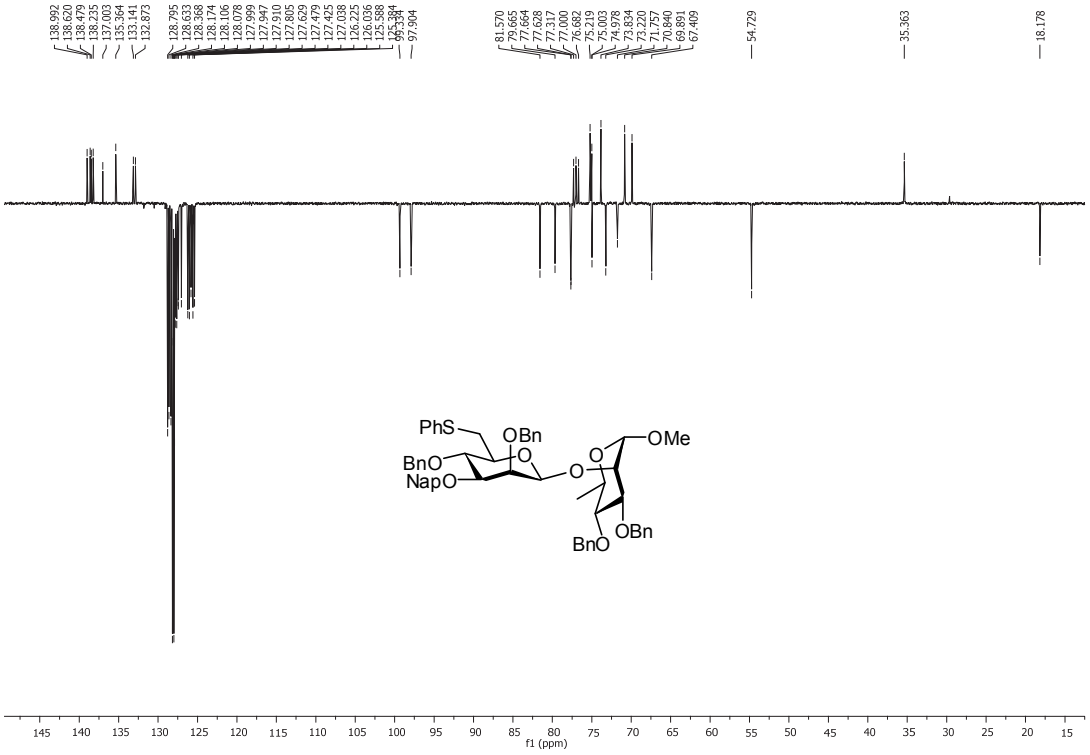


2,4-Di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-D-mannopyranosyl *N*-phenyltrifluoroacetimidate (28):

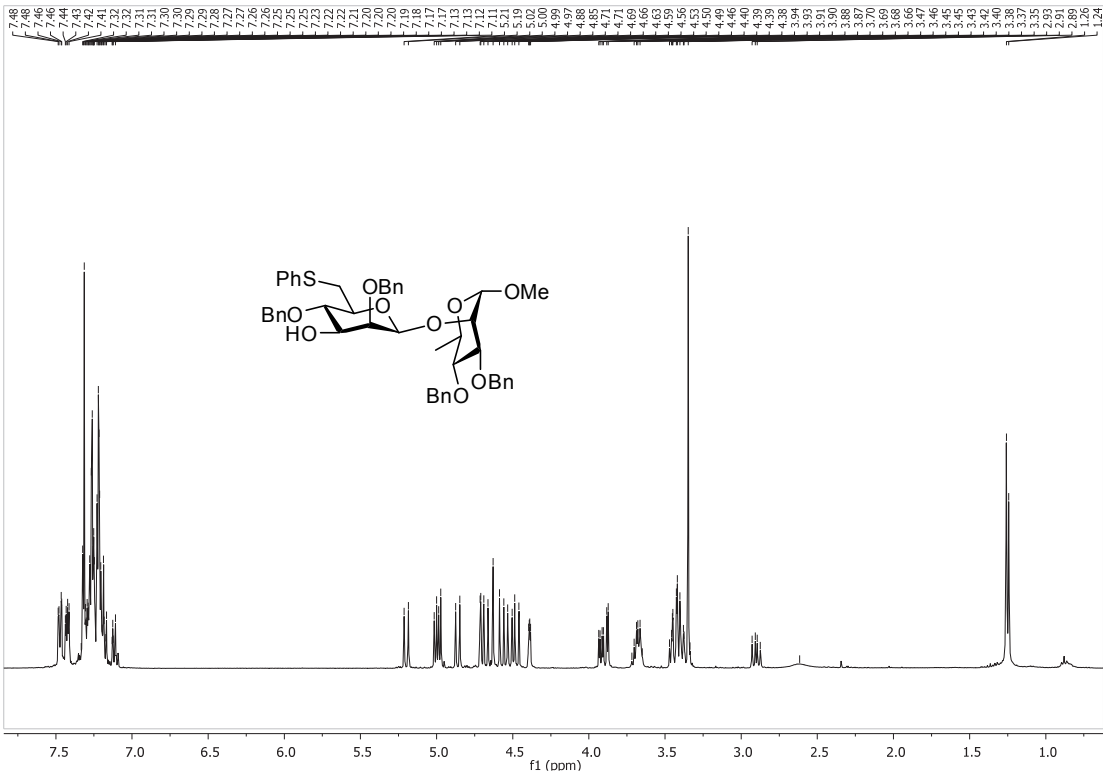


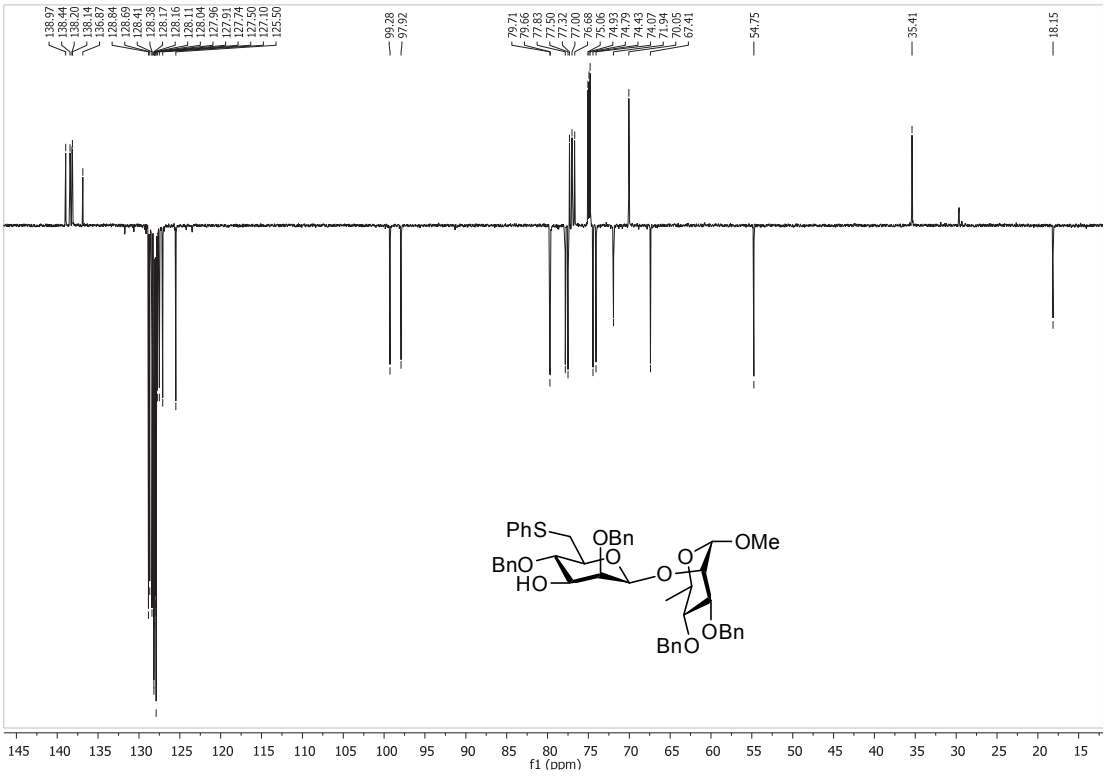
2,4-Di-*O*-benzyl-6-deoxy-3-(2-napthylmethyl)-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (30):



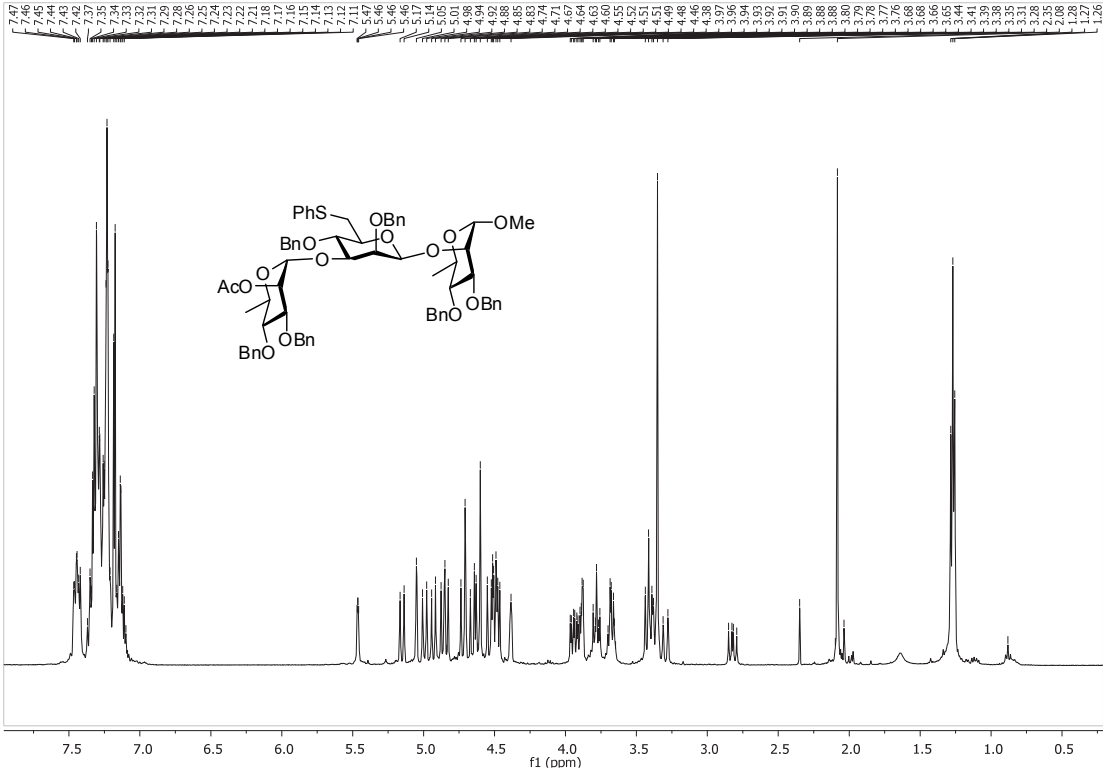


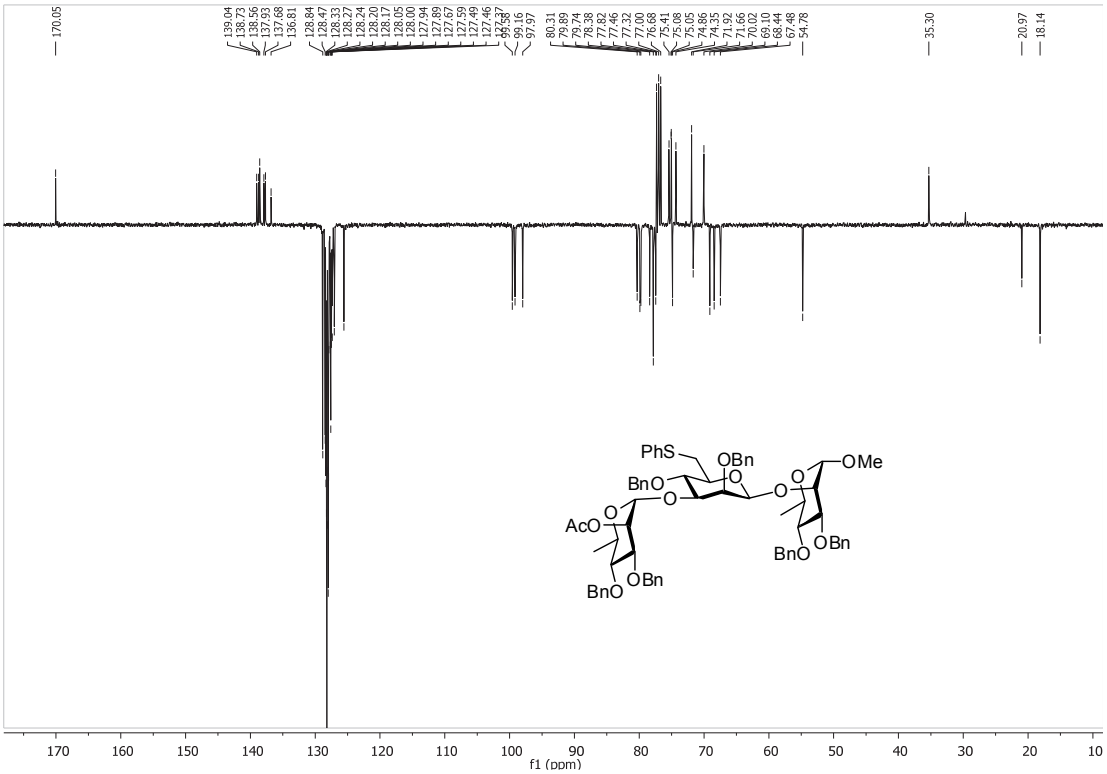
2,4-di-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (31):



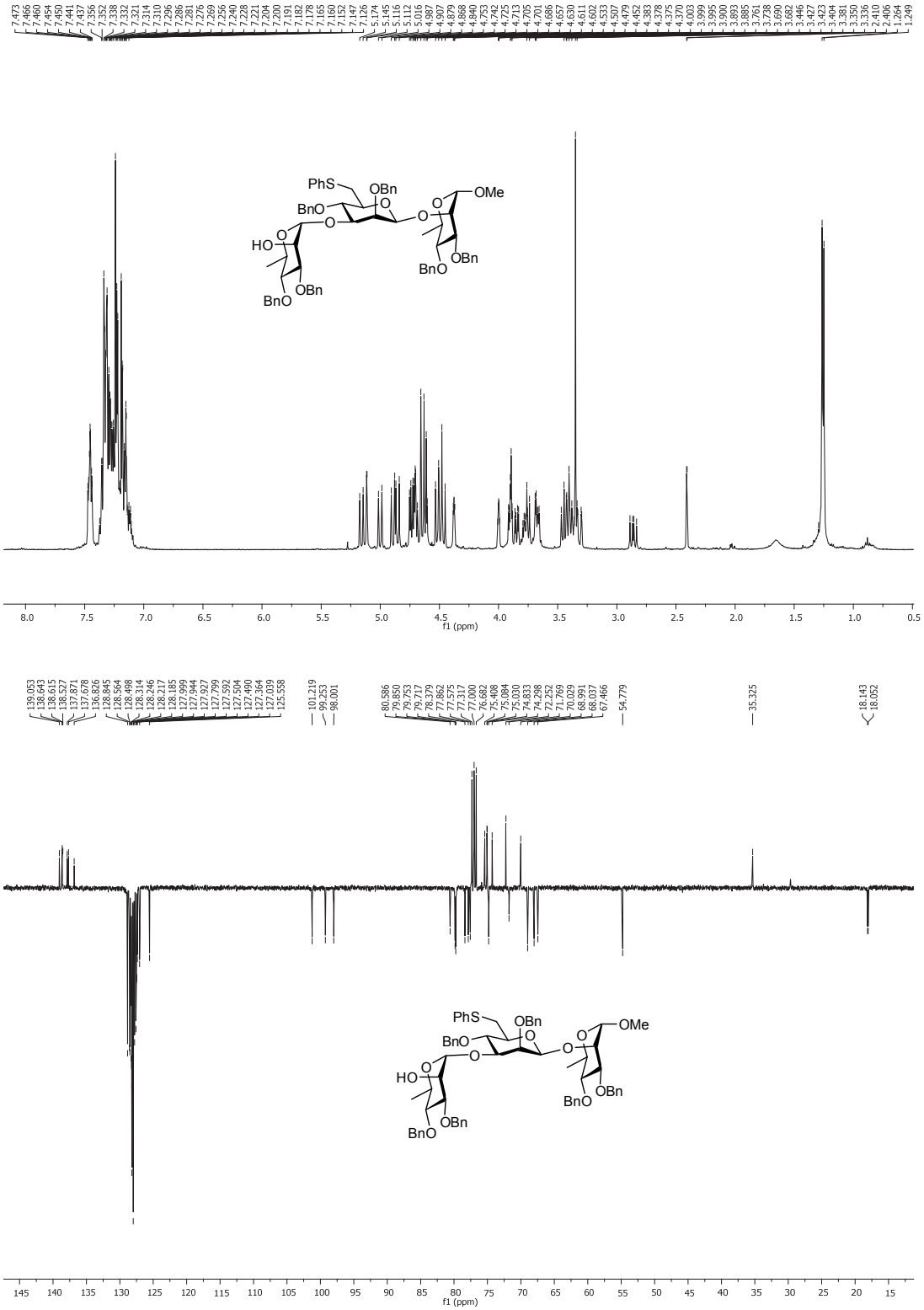


2-*O*-acetyl-3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (33):

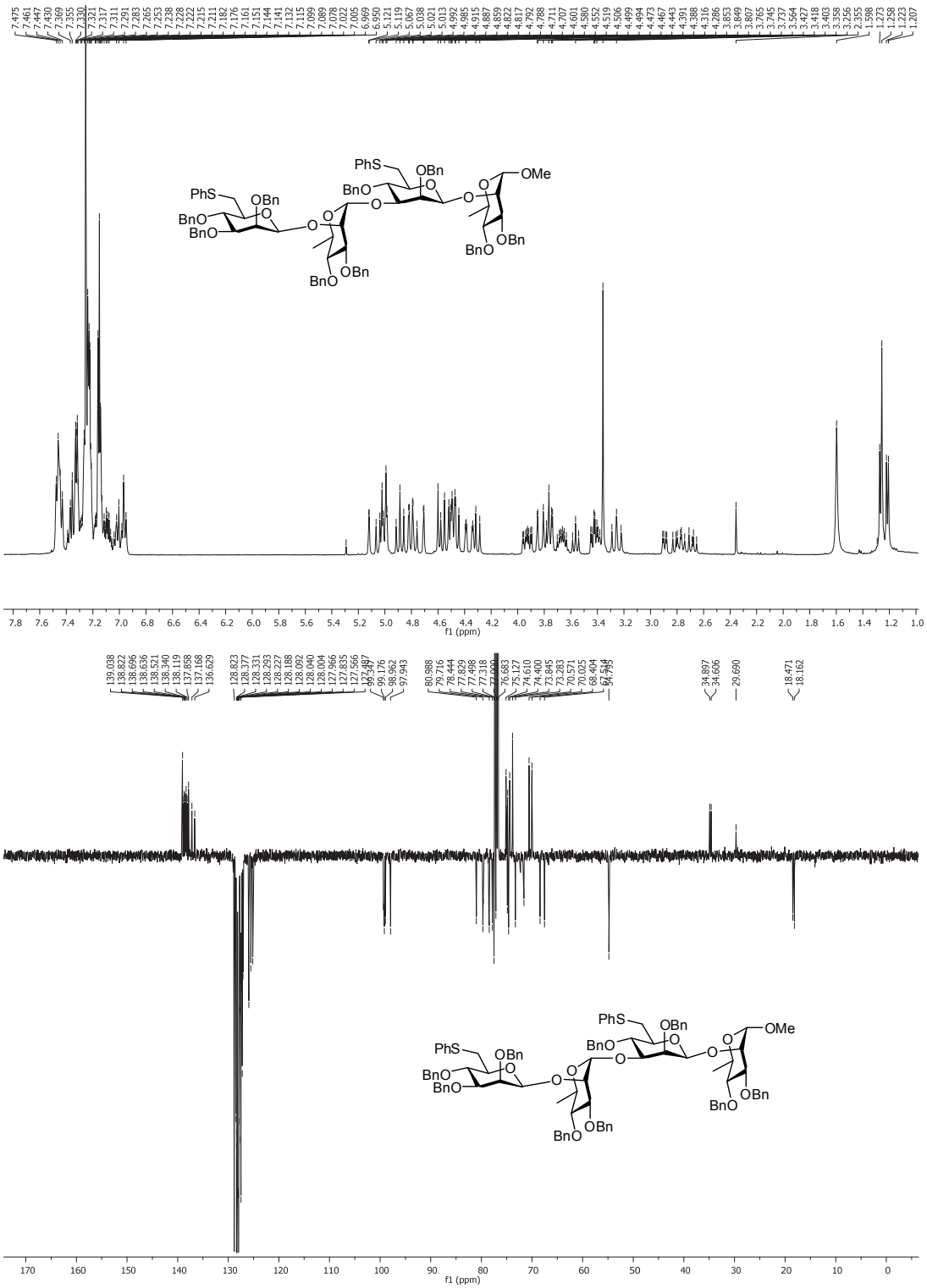




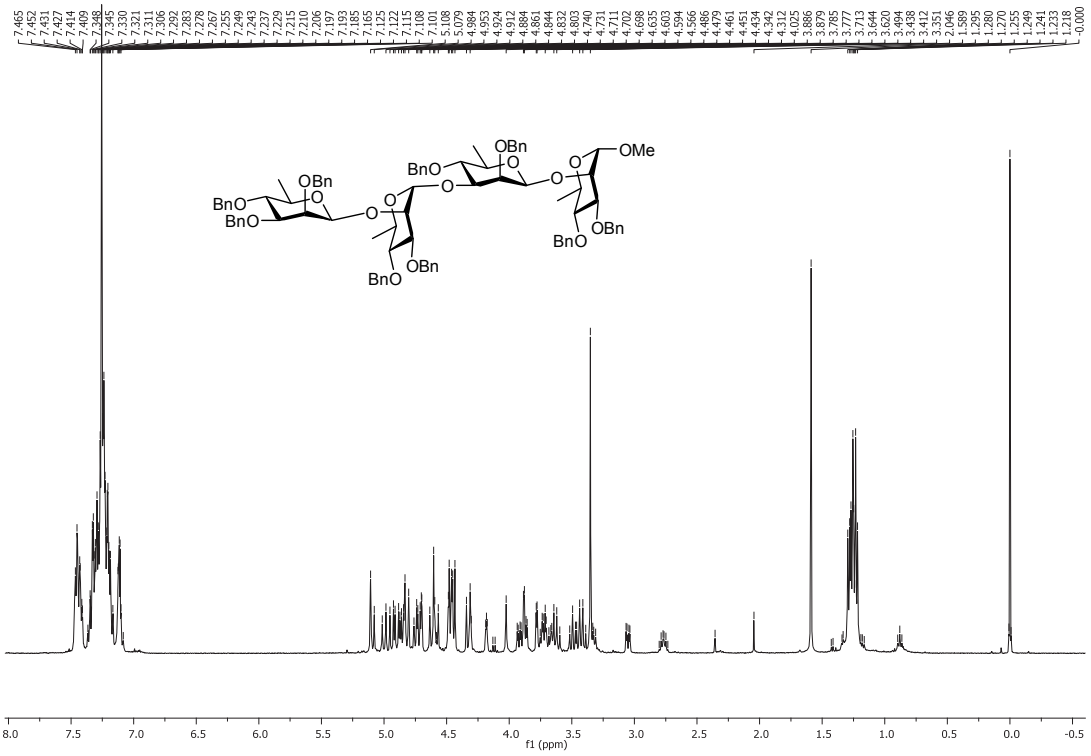
3,4-Di-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (34):

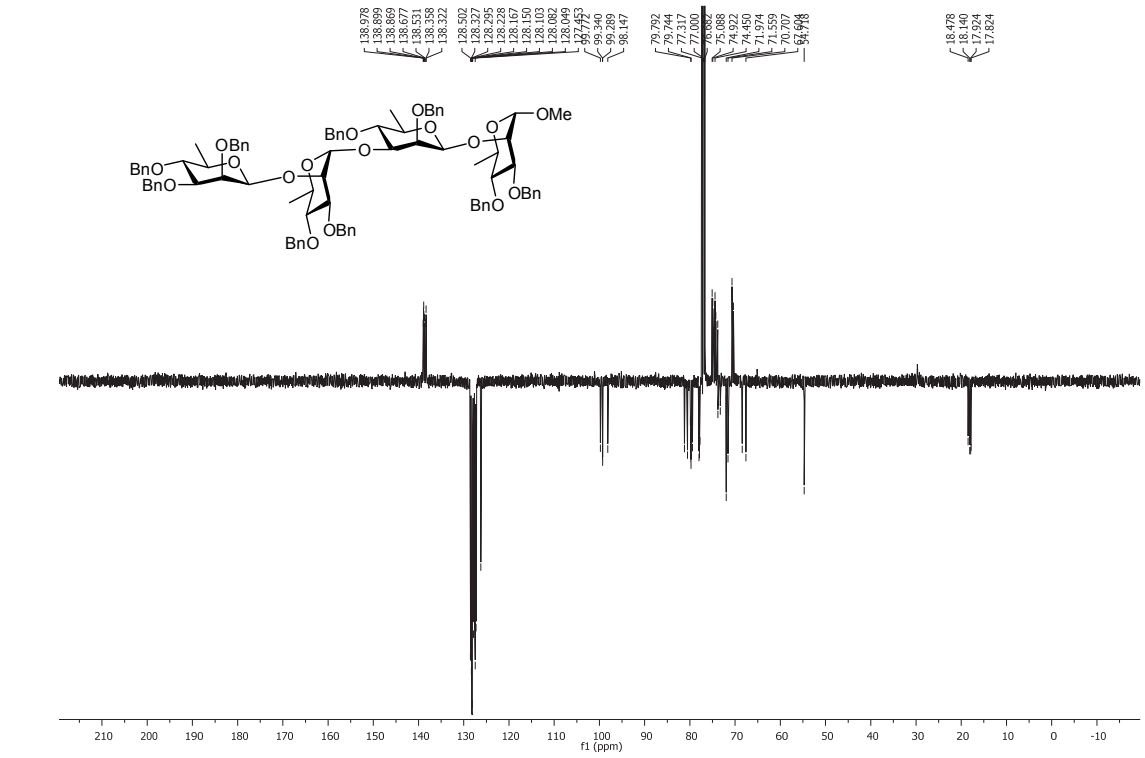


2,3,4-tri-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-6-thiophenyl-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (35):



2,3,4-tri-*O*-benzyl-6-deoxy-β-D-mannopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-β-D-mannopyranosyl-(1→2)-(methyl 3,4-di-*O*-benzyl-6-deoxy-α-D-mannopyranoside) (36):





6-deoxy-β-D-mannopyranosyl-(1→2)-6-deoxy-α-D-mannopyranosyl-(1→3)-6-deoxy-β-D-mannopyranosyl-(1→2)-(methyl 6-deoxy-α-D-mannopyranoside) (37):