Supporting information

for

The 1-Naphthylpropargyl Ether Group: A Readily Cleaved and Sterically Minimal Protecting System for Stereoselective Glycosylation

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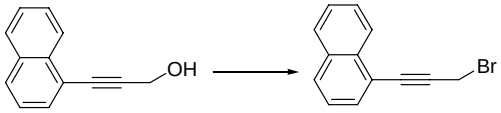
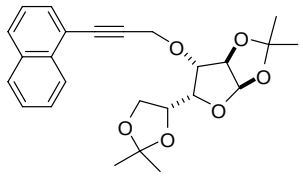
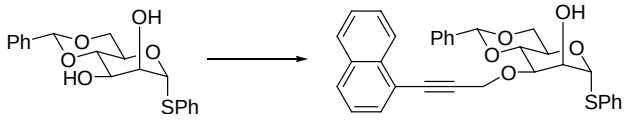


1-(3-Bromo-prop-1-ynyl)-naphthalene[1] To a stirred solution of 3-naphthalen-1-yl-prop-2-yn-1-ol[2] (1.82 g, 10 mmol) in DCM (30 mL), cooled to 0 °C under ice bath, was added triphenylphosphine (3.93 g, 15 mmol), followed by tetrabromocarbon (4.97 g, 15 mmol). The resulting mixture was stirred at this temperature for 20 minutes, after which the reaction was over as monitored by TLC. Then the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography (hexane) to give title compound as a colorless oil (2.26 g, 93%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (s, 2H), 7.42-7.45 (t, *J* = 8.0 Hz, 1H), 7.53-7.62 (m, 2H), 7.70 (d, *J* = 7.0 Hz, 1H), 7.86(dd, *J* = 3.5, 8.0 Hz, 2H), 8.33(d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.5, 85.1, 89.1, 119.8, 125.2, 126.0, 126.6, 127.1, 128.4, 129.4, 131.0, 133.1, 133.4.

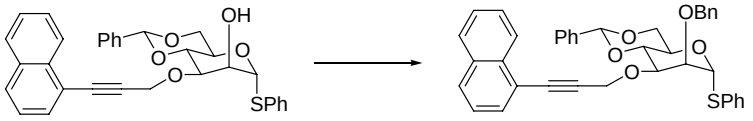


3-*O*-(3-Naphthalen-1-yl-prop-2-ynyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (5).
To a stirred solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (0.36 g, 1.38 mmol) in DMF (10 mL), cooled down to 0 °C under ice bath, was added NaH (0.11 g, 2.76 mmol). After 30 minutes of stirring at 0 °C, 1-naphtylpropargyl bromide **4** (0.37 g, 1.51 mmol) was added. The resulting mixture was stirred at 0 °C for another 30 minutes. The reaction mixture was then quenched carefully by addition of aq NH_4Cl, concentrated under vacuum. The residue was redissolved in DCM, washed with water, brine, dried, concentrated, and purified by column chromatography (hexane/ ethyl acetate, 5/1) to give **5** (0.44 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.36 (s, 3H), 1.43 (s, 3H), 1.53 (s, 3H), 4.06 (dd, *J* = 5.5, 8.5 Hz, 1H), 4.15 (dd, *J* = 6.5, 9.0 Hz, 1H), 4.22 (dd, *J* = 3.0, 7.5 Hz, 1H), 4.31 (d, *J* = 3.0 Hz, 1H), 4.38-4.42 (m, 1H), 4.67 (s, 2H), 4.79 (d, *J* = 3.5 Hz, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 7.42-7.43 (m, 1H), 7.45-7.58 (m, 2H), 7.70-7.71 (m, 1H), 7.84-7.86 (m, 2H), 8.34 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.4, 26.3, 26.9, 59.1, 67.3, 72.7, 81.2, 81.6, 82.9, 84.8, 89.5, 105.4, 109.1, 111.9, 120.1, 125.2, 126.1, 126.5, 126.9, 128.3, 129.1, 130.8, 133.1, 133.3. ESIHRMS Calcd for $C_{25}H_{28}O_6$ $[M+Na]^+$: 447.1784. Found 447.1768.



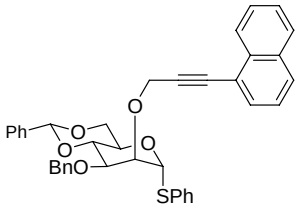
Phenyl 4,6-*O*-benzylidene-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-1-thio-α-D-mannopyranoside (7)
To a stirred solution of phenyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (0.30 g, 0.8 mmol)

in toluene (20 mL), Bu_2SnO (0.42 g, 1.6 mmol) was added. The resulting fine suspension was heated at refluxed for 3 hours, during which time the reaction mixture become clear. This mixture was then concentrated under vacuum, yielding the residue that was redissolved in DMF (20 mL), followed by addition of CsF (0.25g, 1.6mmol) and 1-(3-bromo-prop-1-ynyl)-naphthalene (0.25 g, 0.96 mmol). The resulting mixture was stirred at room temperature overnight, diluted with DCM (50 mL), filtered through Celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography(hexane/ethyl acetate, 3/1) to give the title compound **7** (0.408 g, 93%): $[\alpha]^{23}_D$ +260.6 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.00 (s, 1H), 3.90 (t, *J* = 10.5 Hz, 1H), 4.24-4.31 (m, 3H), 4.45 (dt, *J* = 5, 10 Hz, 1H), 4.56 (s, 1H), 4.79-4.90 (m, 2H), 5.65 (s, 1H), 5.66 (s, 1H), 7.27-7.61 (m, 13H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.87 (dd, *J* = 3.0, 8.0 Hz, 2H), 8.37 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 59.8, 64.8, 68.6, 71.9, 75.5, 79.0, 85.1, 88.1, 89.6, 101.9, 120.0, 125.2, 126.1, 126.2, 126.6, 127.1, 127.8, 128.3, 129.1, 129.2, 131.0, 131.8, 133.2, 133.3, 137.4. ESIHRMS Calcd for $C_{32}H_{28}O_5S$ $[M+Na]^+$: 547.1550. Found 547.1550.



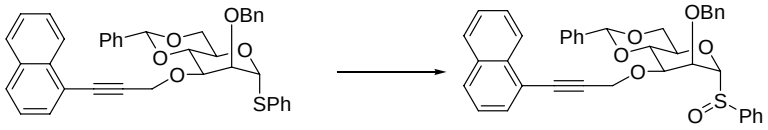
Phenyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-1-thio-α-D-manno-pyranoside (9).

To a stirred solution of **7** (0.308 g, 0.6 mmol) in DMF (20 mL), cooled down to 0 °C under ice bath, was added NaH (38 mg, 1.2 mmol, 60% in oil).. The resulting mixture was stirred at this temperature for 30 minutes, and then benzyl bromide (0.068 mL, 0.72 mmol) was added. After another 30 minutes of stirring at 0 °C, the reaction mixture was quenched by aqueous NH_4Cl, diluted with DCM (50 mL). The organic layer was separated, washed with water, brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate, 6/1) to give **9** (0.35 g, 97%): $[\alpha]^{23}_D$ +121.5 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (t, *J* = 10.0 Hz, 1H), 4.30 (dd, *J* = 4.5, 10.5 Hz, 1H), 4.34-4.35 (m, 1H), 4.38-4.46 (m, 3H), 4.78-4.90 (m, 4H), 5.59 (s, 1H), 5.71 (s, 1H), 7.27-7.60 (m, 18H), 7.76 (d, 7.5 Hz, 1H), 7.87-7.90 (m, 2H), 8.44 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 59.8, 65.5, 68.6, 73.4, 75.7, 78.7, 79.2, 84.8, 87.4, 90.2, 101.8, 120.3, 125.3, 126.3, 126.4, 126.5, 127.0, 127.7, 127.9, 128.2, 128.3, 128.5, 129.1, 129.2, 130.9, 131.7, 133.2, 133.4, 133.8, 137.6, 137.8. ESIHRMS Calcd for $C_{39}H_{34}O_5S$ $[M+Na]^+$: 637.2020. Found 637.2021.



Phenyl 4,6-*O*-benzylidene-2-*O*-(3-naphthalen-1-yl-prop-2-ynyl) -3-*O*-benzyl-1-thio -α-D-mannopyranoside (10).

To a stirred solution of **8** (3.38 g, 7.5 mmol) in DMF (40 mL) was added NaH (600 mg, 15.0 mmol, 60% in oil) portionwise at 0 °C. The resulting mixture was stirred at 0 °C for 30 minutes, then 1-(3-Bromo-prop-1-ynyl)-Naphthalene (2.0 g, 8.25 mmol) was added. The reaction mixture was kept stirring for another 30 minutes at 0 °C, then quenched by aqueous NH_4Cl, diluted with DCM (50 mL). The organic layer was separated, washed with water, brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate, 6/1) to give title compound **10** (4.2 g, 90%): $[\alpha]^{20}_D$ +105.4 (c, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (t, *J* = 10.0 Hz, 1H), 4.04 (dd, *J* = 3.0, 9.0 Hz, 1H), 4.24-4.34 (m, 3H), 4.48-4.49 (m, 1H), 4.80 (s, 2H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.92 (d, *J* = 12.0 Hz, 1H), 5.67 (s, 1H), 5.79 (s, 1H), 7.15-7.54 (m, 18H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.84-7.87 (m, 2H), 8.29 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 59.8, 65.3, 68.6, 73.4, 76.1, 77.9, 79.3, 85.2, 87.8, 89.6, 101.6, 120.0, 125.2, 126.1, 126.5, 127.0, 127.6, 127.7, 128.3, 128.4, 128.9, 129.1, 129.2, 130.9, 131.6, 133.1, 133.3, 133.6, 137.6, 138.2. ESIHRMS Calcd for $C_{39}H_{34}O_5S_1$ $[M+Na]^+$: 637.2025. Found 637.2001.



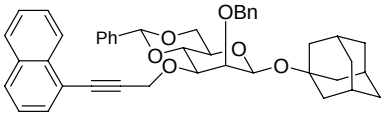
Phenyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-1-deoxy-1-thio-α-D-mannopyranoside *S*-oxide (11).

To a stirred solution of **9** (0.30 g, 0.49 mmol) in DCM (16 mL) was added MCPBA (77%, 0.11 g, 0.49 mmol) at -78°C. The reaction temperature was then allowed to warm to -20 °C naturely, at which point the reaction was quenched with saturated aqueous $NaHCO_3$. The organic layer was separated, washed with brine, dried, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 4/1) to give **11** as a single diastereomer (0.28 g, 90%): $[\alpha]^{23}_D$ – 28.8 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (t, *J* = 10.0 Hz, 1H), 4.18-4.27 (m, 2H), 4.35 (t, *J* = 9.0 Hz, 1H), 4.54 (s, 1H), 4,57-4.63 (m, 3H), 4,71-4.80 (m, 3H), 5.65 (s, 1H), 7.25-7.27 (m, 5H), 7.34-7.56 (m, 13H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.85-7.87 (m, 2H), 8.39 (dd, *J* = 0.5, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 59.8, 68.3, 70.0, 73.2, 73.8, 76.0, 78.1, 84.7, 90.1, 97.9, 101.9, 120.3, 124.3, 125.3, 126.2, 126.3, 126.5, 127.0, 127.9, 128.1, 128.2, 128.3, 128.4, 129.0, 129.1, 129.4, 131.0, 131.6, 133.1, 133.4, 137.2, 137.4, 141.4. ESIHRMS Calcd for $C_{39}H_{34}O_6S$ $[M+Na]^+$: 653.1969. Found 653.1971.

General procedure for the coupling of mannosyl donor 11 with acceptors using TTBP/Tf_2O

system.

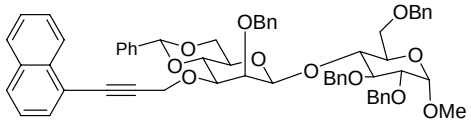
To a stirred solution of donor **11** (0.10 g, 1eq), TTBP(1.6 eq), and 4 Å molecular sieves in 4 mL of mixed solvent (DCM/octene, 3/1), at -78 °C under Ar atmosphere, was added Tf_2O (1.2 eq) slowly. The resulting mixture was stirred at this low temperatue for 30 minutes, and then a solution of the glycosyl acceptor (2.0 eq) in DCM (1 mL) was added. The stirring was continued for another 30 minutes, then the rection mixture was poured into saturated aqueous $NaHCO_3$ solution, diluted with DCM, filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$. Organic layer was separated, dried, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate) on silica gel to give the corresponding coupled products.



1-Adamantanyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-β-D-mannopyranoside (12a)

Eluent for purification: hexane/ethyl acetate, 10/1.

$[\alpha]^{21.8}_D$ – 72.2 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58-1.66 (m, 6H), 1.73-1.85 (m, 6H), 2.14 (s, 3H), 3.40(dt, *J* = 5.0, 10.0 Hz, 1H), 3.91-3.99 (m, 3H), 4.23 (t, *J* = 9.5Hz, 1H), 4.29 (dd, *J* = 5.0, 10.5Hz, 1H), 4.59-4.67(m, 2H), 4.84 (s, 1H), 4.95-5.09 (m, 2H), 5.63 (s, 1H), 7.25-7.34 (m, 6H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.46-7.56 (m, 6H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.85 (t, *J* = 7.5 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6, 36.2, 42.4, 59.0, 67.3, 68.9, 74.9, 75.2, 77.8, 78.5, 84.5, 90.3, 94.8, 101.6, 120.3, 125.2, 126.1, 126.2, 126.5, 126.9, 127.5, 128.1, 128.2, 128.3, 128.8, 128.9, 129.0, 130.6, 133.1, 133.4, 137.6, 138.6. ESIHRMS Calcd for $C_{43}H_{44}O_6$ $[M+Na]^+$: 679.3030. Found 679.3028.

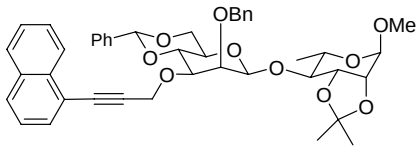


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl) -β-D-mannopyranosyl]-(1→4)- α-D-glucopyranoside (12b).

Eluent for purification: hexane/ethyl acetate, 2.5/1.

$[\alpha]^{23}_D$ – 36.7 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.11 (dt, *J* = 4.5, 9.0 Hz, 1H), 3.36-3.43 (m, 5H), 3.51 (dd, *J* = 4.0, 9.5 Hz, 1H), 3.55-3.59 (m, 2H), 3.67 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.83-3.91 (m, 3H), 4.05-4.15 (m, 3H), 4.12-4.45 (m, 2H), 4.58-4.92 (m, 8H), 5.07 (d, *J* = 10.5 Hz, 1H), 5.54 (s, 1H), 7.13-7.14 (m, 1H), 7.23-7.53 (m, 27H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.83-7.87 (m, 2H), 8.33 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 59.4, 67.3, 68.3, 68.6, 69.6, 73.4, 73.7, 75.1, 75.3, 77.9, 78.7, 79.0, 80.3, 84.4, 90.6, 98.4, 101.5, 101.6, 120.2, 125.2, 126.1, 126.2, 126.5, 127.0, 127.3, 127.5, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4, 128.5, 128.9,

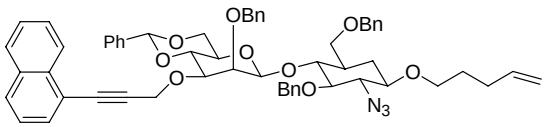
129.1, 130.7, 133.2, 133.4, 137.5, 137.6, 138.4, 138.6, 139.4. ESIHRMS Calcd for $C_{61}H_{60}O_{11}$ $[M+Na]^+$: 991.4028. Found 991.4039.



Methyl 4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-β-D-mann opyranosyl]-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (12c).

Eluent for purification: hexane/ethyl acetate, 6/1→3/1, then the mixture of α and β isomers was subject to preparative HPLC to give pure β **12c**.

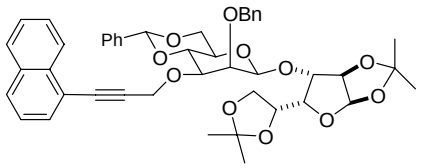
$[\alpha]^{21}_D$ – 34.9 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 3H), 1.34 (d, *J* = 6.0Hz, 3H), 1.50 (s, 3H), 3.39 (s, 3H), 3.39-3.43 (m, 1H), 3.61-3.71 (m, 2H), 3.96-4.01 (m, 2H), 4.07-4.13 (m, 3H), 4.22 (t, *J* = 10.0 Hz, 1H), 4.29 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.6-4.65 (m, 2H), 4.85-4.97 (m, 2H), 5.11 (s, 1H), 5.63 (s, 1H), 7.24-7.28 (m, 1H), 7.31-7.34 (m, 5H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.47-7.52 (m, 6H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.83-7.86 (m, 2H), 8.29-8.31 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.7, 26.4, 27.8, 54.9, 58.9, 64.2, 67.7, 68.7, 75.1, 76.1, 77.7, 77.8, 78.4, 78.6, 84.4, 90.3, 97.9, 100.0, 101.5, 109.4, 120.3, 125.2, 126.1, 126.4, 126.9, 127.5, 128.1, 128.2, 128.28, 128.32, 128.9, 129.0, 130.7, 133.1, 133.4, 137.5, 138.6. ESIHRMS Calcd for $C_{30}H_{38}O_{10}$ $[M+Na]^+$: 581.2357. Found 581.2354.



4-*O*-[4,6-*O*-Benzylidene-2-*O*-benzyl-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-β-D-mannopyranosy l]-(1→4)-pent-4-enyl-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (12d).

Eluent for purification: hexane/ethyl acetate, 7/1 →5/1.

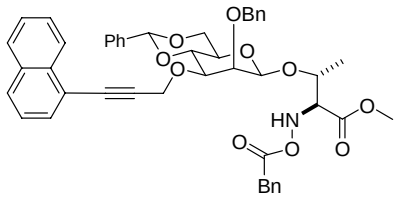
$[\alpha]^{24}_D$ – 18.1(c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70-1.82 (m, 2H), 2.15-2.23 (m, 2H), 3.15 (dt, *J* = 5.0, 9.5 Hz , 1H), 3.24-3.26 (m, 1H), 3.31-3.57 (m, 6H), 3.73-3.75 (m, 1H), 3.89-3.97 (m, 3H), 4.07-4.14 (m, 2H), 4.20-4.27 (m, 2H), 4.45-4.73 (m, 5H), 4.85-5.09 (m, 5H), 5,54 (s, 1H), 5.79-5.87 (m, 1H), 7.16-7.53 (m, 23H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.84-7.87 (m, 2H), 8.34 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.7, 30.1, 59.5, 65.9, 67.3, 68.3, 68.5, 69.4, 73.4, 74.7, 75.2, 75.3, 77.5, 77.9, 78.7, 81.4, 84.4, 90.5, 101.5, 102.1, 115.1, 120.2, 125.2, 126.0, 126.2, 126.5, 127.0, 127.57, 127.61, 127.6, 127.7, 127.96, 128.0, 128.18, 128.24, 128.3, 128.4, 128.5, 129.0, 129.1, 130.7, 133.2, 133.4, 137.5, 137.6, 138.0, 138.6. ESIHRMS Calcd for $C_{43}H_{46}O_{10}$ $[M+Na]^+$: 745.2984. Found 745.2985.



3-*O*-[4,6-*O*-Benzylidene-2-*O*-benzyl-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-β-D-mannopyranosyl]-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (12e).

Eluent for purification: hexane/ethyl acetate, 4/1.

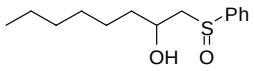
$[\alpha]^{23}_{D}$ – 38.3 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.42 (dt, *J* = 4.5, 9.5 Hz, 1H), 3.95 (t, *J* = 10.0 Hz, 1H), 4.00-4.15 (m, 4H), 4.25 (t, *J* = 9.0 Hz, 1H), 4.31-4.44 (m, 5H), 4.66 (s, 1H), 4.71 (s, 2H), 4.87-4.94 (m, 2H), 5.65 (s, 1H), 5.86 (d, *J* = 3.5 Hz, 1H), 7.26-7.54 (m, 13H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.85-7.87 (m, 2H), 8.31 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.5, 26.3, 26.7, 26.8, 59.4, 66.2, 67.8, 68.5, 73.1, 75.0, 76.6, 78.5, 80.5, 81.0, 82.8, 84.6, 90.2, 100.2, 101.6, 105.0, 108.7, 112.0, 120.1, 125.2, 126.0, 126.1, 126.5, 126.9, 127.8, 128.3, 128.4, 128.5, 129.0, 129.1, 130.7, 133.2, 133.4, 137.4, 138.2. ESIHRMS Calcd for $C_{45}H_{48}O_{11}$ $[M+Na]^+$: 787.3089. Found 787.3101.



***O*-[4,6-*O*-Benzylidene-2-*O*-benzyl-3-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-β-D-mannopyranosyl]-N-carbobenzyloxy-L-threonine methyl ester (12f)**

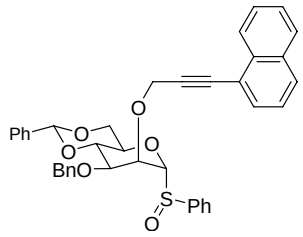
Eluent for purification: hexane/ethyl acetate, 4/1

$[\alpha]^{22}_{D}$ – 33.8(c, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (d, *J* = 6.5 Hz, 3H), 3.33 (dt, *J* = 5.0, 9.5 Hz), 3.74 (s, 3H), 3.89 (t, *J* = 10.0 Hz, 1H), 3.96 (dd, *J* = 3.0, 10.0 Hz, 1H), 4.00-4.01 (m, 1H), 4.19 (t, *J* = 9.5 Hz, 1H), 4.28 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.38 (dd, *J* = 2.0, 9.0 Hz, 1H), 4.47-4.50 (m, 1H), 4.56 (s, 1H), 4.69 (s, 2H), 4.83-4.93 (m, 2H), 5.16 (s, 2H), 5.55 (d, *J* = 9.5 Hz, 1H), 5.61 (s, 1H), 7.22-7.52 (m, 18H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.85 (dd, *J* = 5.0, 7.5 Hz, 2H), 8.30 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.46, 52.6, 58.5, 59.2, 67.2, 67.5, 68.5, 74.3, 74.9, 76.7, 78.5, 84.6, 90.1, 99.8, 101.6, 120.2, 125.2, 126.0, 126.2, 126.5, 126.9, 127.6, 128.1, 128.25, 128.29, 128.4, 128.6, 129.0, 129.1, 130.7, 133.1, 133.4, 136.3, 137.4, 138.5, 156.8, 170.8. ESIHRMS Calcd for $C_{46}H_{45}O_{10}N_1$ $[M+Na]^+$: 794.2936. Found 794.2946.



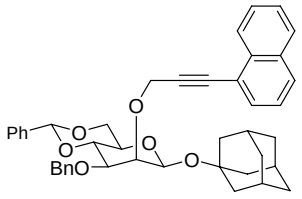
1-Phenylsulfinyl-octan-2-ol (13).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85-0.89 (m, 3H), 1.20-1.35 (m, 8H), 1.47-1.54 (m, 2H), 2.40 (d, *J* = 2.7 Hz, 1H), 2.83 (dd, *J* = 8.7, 13.5 Hz, 1H), 3.15 (dd, *J* = 3.3, 13.5 Hz, 1H), 3.60-3.66 (m, 1H), 7.20-7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.7, 29.3, 31.8, 36.2, 42.3, 69.4, 124.4, 126.6, 129.1, 129.3, 130.1, 135.4. ESIHRMS Calcd for $C_{14}H_{22}O_2S$ $[M+Na]^+$: 277.1233. Found 277.1232.



Phenyl 4,6-*O*-benzylidene-2-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-2-*O*-benzyl-1-deo xy-1-thio-α-D-mannopyranoside *S*-Oxide (14).

To a stirred solution of **5** (3.72 g, 6.06 mmol) in DCM (200 mL) was added MCPBA (77%, 1.36 g, 6.06 mmol) in DCM (25 mL) at -78 °C, then the reaction temperature was allowed to warm to-20 °C naturely. The reaction was then quenched with saturated aqueous $NaHCO_3$，the organic layer was sperated, washed with brine, dried over Na_2SO_4, and concentrated. the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 6/1→4/1) to give **14** as a single diastereomer (3.27 g, 94%), and recovered starting material (0.41 g, conv: 89%): $[\alpha]^{21}_D$ –22.0 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (t, *J* = 10.0 Hz, 1H), 4.19 (dt, *J* = 5.0, 9.5 Hz, 1H), 4.28 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.34-4.42 (m, 2H), 4.72 (s, 2H), 4.79-4.80 (m, 1H), 4.82 (s, 1H), 4.85 (d, *J* = 12.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 5.67 (s, 1H), 7.24-7.59 (m, 18H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.87-7.88 (m, 2H), 8.27 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 60.3, 68.3, 70.0, 72.9, 73.6, 76.4, 78.3, 85.1, 89.2, 98.0, 101.7, 120.0, 124.2, 125.2, 126.1, 126.3, 126.5, 127.0, 127.75, 127.84, 128.28, 128.32, 128.4, 129.1, 129.2, 129.3, 131.1, 131.5, 133.1, 133.4, 137.3, 138.2, 141.5. ESIHRMS Calcd for $C_{39}H_{34}O_6S_1$ $[M+Na]^+$: 653.1974. Found 653.1943.

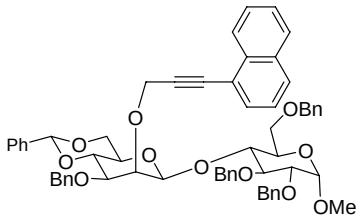


1-Adamantanyl 4,6-*O*-benzylidene-2-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranoside (16a).

Eluent for purification: hexane/ethyl acetate, 10/1.

$[\alpha]^{22}_D$ –31.9 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.56-1.65 (m, 6H), 1.79-1.88 (m, 6H), 2.14 (s, 3H), 3.35 (dt, *J* = 5.0, 10.0 Hz, 1H), 3.69 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.95 (t, *J* = 10.0 Hz,

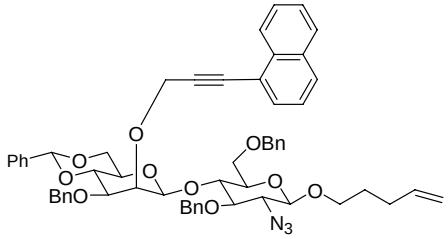
1H), 4.20 (t, *J* = 9.5 Hz, 1H), 4.27-4.31 (m, 2H), 4.83 (s, 2H), 4.80-4.86 (m, 1H), 4.99-5.13 (m, 2H), 5.62 (s, 1H), 7.07-7.56 (m, 13H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.85-7.87 (m, 2H), 8.42 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6, 36.2, 42.4, 61.0, 67.2, 68.9, 72.2, 75.5, 76.5, 78.5, 84.5, 90.8, 94.9, 101.4, 120.6, 125.2, 126.1, 126.4, 126.5, 126.8, 127.4, 127.5, 128.20, 128.23, 128.3, 128.9, 129.0, 131.0, 133.2, 133.6, 137.7, 138.4. ESIHRMS Calcd for $C_{43}H_{44}O_6$ $[M+Na]^+$: 679.3030. Found 679.303.



Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)- α-D-glucopyranoside (16b).

Eluent for purification: hexane/THF, 6/1→4/1.

$[\alpha]^{23}_D$ –3.6 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.06 (dt, *J* = 4.5, 9.5 Hz, 1H), 3.29 (s, 3H), 3.38 (dd, *J* = 3.5, 10.0 Hz, 1H), 3.47-3.52 (m, 2H), 3.57 (t, *J* = 10.0 Hz, 1H), 3.69 (d, *J* = 9.5 Hz, 1H), 3.76 (dd, *J* = 3.0, 10.5 Hz, 1H), 3.92 (p, *J* = 8.5 Hz, 2H), 4.01 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.07-4.11 (m, 2H), 4.26 (d, *J* = 12.0 Hz, 1H), 4.47 (s, 1H), 4.56-4.92 (m, 9H), 5.09 (d, *J* = 12.0 Hz, 1H), 5.54 (s, 1H), 7.15-7.53 (m, 28H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.84-7.87 (m, 2H), 8.35-8.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 60.7, 67.3, 68.4, 68.6, 69.6, 72.6, 73.55, 73.61, 75.3, 75.6, 77.7, 77.9, 78.7, 79.2, 80.2, 84.6, 90.6, 98.4, 101.4, 101.9, 120.4, 125.2, 126.1, 126.2, 126.5, 126.9, 127.3, 127.5, 127.75, 127.83, 127.96, 128.04, 128.1, 128.19, 128.23, 128.29, 128.33, 128.4, 128.5, 128.9, 129.0, 130.9, 133.2, 133.5, 137.6, 137.7, 138.4, 138.5, 139.4. ESIHRMS Calcd for $C_{61}H_{60}O_{11}[M+H]^+$: 969.4208. Found 969.4212.

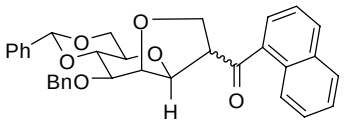


4-*O*-[4,6-*O*-Benzylidene-2-*O*-(3-naphthalen-1-yl-prop-2-ynyl)-3-*O*-benzyl -β-D-mannopyranosyl]-(1→4)-pent-4-enyl-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (16 c).

Eluent for purification: hexane/ethyl acetate, 5/1→2/1**.**

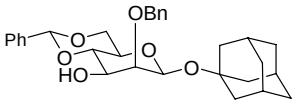
$[\alpha]^{23}_D$ –24.6 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70-1.73 (m, 2H), 2.15-2.18 (m, 2H), 3.06-3.14 (m, 2H), 3.33-3.37 (m, 2H), 3.42-3.46 (m, 2H), 3.52-3.58 (m, 2H), 3.70 (dd, *J* = 3.0, 11.0 Hz, 1H), 3.81-3.84 (m, 1H), 3.91-3.98 (m, 2H), 4.06 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.10-4.13 (m, 2H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.55-5.14 (m, 10H), 5.55 (s, 1H), 5.78-5.87 (m, 1H), 7.20-7.54 (m, 23H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.85-7.88 (m, 2H), 8.34 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 28.7, 30.0, 60.9, 65.8, 67.3, 68.3, 68.5, 69.3, 72.8, 73.5, 74.6, 75.2, 75.9, 77.9, 78.8, 81.2, 84.5, 90.7, 101.29, 101.4, 102.0, 115.1, 120.4, 125.3, 126.1, 126.2, 126.6, 127.0, 127.4, 127.6, 127.7, 127.8, 128.0, 128.26, 128.34, 128.4, 128.5, 128.9, 129.1, 130.9, 133.2, 133.4, 137.6, 137.7, 138.0, 138.4, 138.5. ESIHRMS Calcd for $C_{58}H_{59}O_{10}N_3$[M+Na]$^+$: 980.4093. Found 980.4100.

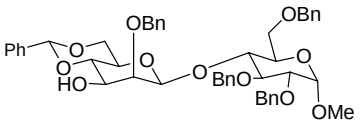


$[\alpha]^{23}_D$ –60.1 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.41 (dt, *J* = 5.0, 9.5 Hz, 1H), 3.80 (t, *J* = 10..5 Hz, 1H), 3.91 (dd, *J* = 4.0, 9.5 Hz, 1H), 4.11 (dd, *J* = 5.0, 9.0 Hz, 1H), 4.17 (t, 9.0 Hz, 1H), 4.22 (dd, 5.0, 8.5 Hz, 1H), 4.28-4.31 (m, 2H), 4.87-4.93 (m, 2H), 5.65 (s, 1H), 7.28-7.65 (m, 13H), 7.89-7.91 (m, 2H), 8.04 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.3, 68.6, 69.3, 70.1, 72.6, 75.1, 78.7, 79.5, 80.7, 101.4, 124.4, 125.6, 126.1, 126.9, 127.7, 128.1, 128.3, 128.4, 128.6, 128.7, 129.0, 130.5, 133.9, 134.1, 137.6, 138.2, 201.5. IR(neat) 698.1, 738.6, 781.0, 1099.2, 1214.9, 1384.6, 1454.1, 1496.5, 1675.8, 2879.2. ESIHRMS Calcd for $C_{33}H_{30}O_6$[M+Na]$^+$: 545.1935. Found 545.1936.

General procedure for oxidative removal of Naphthylpropargyl protecting group using DDQ.
To a stirred solution of coupled products (0.15-0.20 g, 1 eq) in a mixed solvent of DCM (0.06 M in coupled products) and water (water/DCM, 1/20) was added DDQ (1.5 eq), then the reaction mixture was vigorously stirred at rt for 2-3 hours, after which the reaction was over as monitored by TLC. Then the reaction was quenched by aqueous $NaHCO_3$ solution, diluted with DCM (20 mL). The organic layer was separated, washed with aqueous $NaHCO_3$ solution, brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate) on silica gel to give corresponding deprotected products.



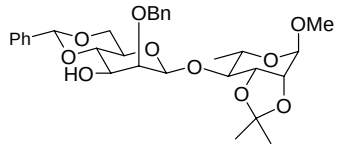
1-Adamantanyl 4,6-*O*-benzylidene-2-*O*-benzyl-β-D-mannopyranoside (17a).
Eluent for purification:hexane/ethyl acetate, 7/1.
$[\alpha]^{22}_D$ – 72.2 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62-1.70 (m, 6H**),** 1.80-1.90 (m, 6H), 2.20 (s, 3H), 2.42 (br s, 1H), 3.34 (dt, *J* = 5.0, 9.5 Hz, 1H), 3.77 (s, 1H), 3.77-3.83 (m, 2H), 3.88 (t, *J* = 10.0 Hz, 1H), 4.27 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.89 (s, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 5.53 (s, 1H), 7.29-7.49 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.7, 36.2, 42.4, 66.9, 68.8, 71.0, 75.5, 75.9, 79.3, 80.1, 94.9, 102.0, 126.3, 127.9, 128.3, 128.45, 128.51, 129.1, 137.4, 138.4. ESIHRMS Calcd for $C_{30}H_{36}O_6$ [M+Na]$^+$: 515.2404. Found 515.2402.



Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (17b).

Eluent for purification: ethyl acetate/toluene, 5/95.

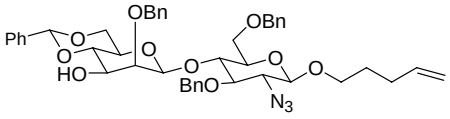
$[\alpha]^{21}_{D}$ – 103.5 (c, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (br s, 1H), 3.05 (dt, *J* = 5.0, 9.5 Hz, 1H), 3.41 (s, 3H), 3.44-3.60 (m, 7H), 3.68 (t, *J* = 9.5 Hz, 2H), 3.85 (t, *J* = 9.5 Hz, 1H), 3.94 (t, *J* = 9.5 Hz, 1H), 4.07 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.45 (s, 1H), 4.57-4.65 (m, 3H), 4.72-4.82 (m, 3H), 4.94 (d, *J* = 11.5 Hz, 1H), 5.03 (d, *J* = 10.5 Hz, 1H), 5.44 (s, 1H), 7.28-7.40 (m, 23H), 7.46-7.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 66.9, 68.2, 68.6, 69.6, 70.9, 73.7, 73.8, 75.4, 75.8, 77.9, 79.0, 79.2, 80.3, 98.5, 101.8, 102.0, 126.3, 127.3, 127.7, 127.85, 127.93, 128.1, 128.3, 128.4, 128.5, 128.7, 129.1, 137.3, 137.4, 138.1, 138.3, 139.4. ESIHRMS Calcd for $C_{48}H_{52}O_{11}$ $[M+Na]^+$: 827.3402 . Found 827.3400.



Methyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (17c).

Eluent for purification: hexane/ethyl acetate, 5/1.

$[\alpha]^{21}_{D}$ – 103.5 (c, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (d, *J* = 5.5 Hz, 3H), 1.36 (s, 3H), 1.54 (s, 3H), 2.38 (d, *J* = 9.0 Hz, 1H), 3.33 (dt, *J* = 5.0, 9.5 Hz, 1H), 3.39 (d, *J* = 2.0 Hz, 3H), 3.62-3.73 (m, 2H), 3.81-3.84 (m, 2H), 3.90 (t, *J* = 10.5 Hz, 1H), 3.96 (s, 1H), 4.12 (d, *J* = 5.0 Hz, 1H), 4.18-4.20 (m, 1H), 4.28 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.88 (s, 1H), 5.03 (d, *J* = 11.5 Hz, 1H), 5.12 (s, 1H), 5.55 (s, 1H), 7.30-7.40 (m, 8H), 7.48-7.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.7, 26.4, 27.9, 55.0, 64.1, 67.2, 68.6, 70.8, 75.7, 76.1, 78.1, 78.4, 78.8, 79.5, 97.9, 100.3, 102.0, 109.5, 126.3, 128.0, 128.1, 128.3, 128.6, 129.1, 137.2, 138.2. ESIHRMS Calcd for $C_{30}H_{38}O_{10}$ $[M+Na]^+$: 581.2357. Found 581.2354.

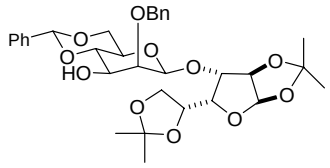


4-*O*-[4,6-*O*-Benzylidene-2-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-pent-4-enyl-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (17d).

Eluent for purification: hexane/ethyl acetate, 3/1→2/1.

$[\alpha]^{21}_{D}$ – 64.5 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.73-1.84 (m, 2H), 2.18-2.20 (m, 2H), 2.35 (br s, 1H), 3.09 (dt, *J* = 5.0, 10.0 Hz**,** 1H), 3.32-3.36 (m, 2H), 3.43 (dd, *J* = 8.0, 10.0 Hz, 1H),

3.49 (t, *J* = 10.0 Hz, 1H), 3.54-3.58 (m, 2H), 3.64-3.69 (m, 3H), 3.73 (t, *J* = 9.5 Hz, 1H), 3.93-3.97 (m, 1H), 4.00 (t, *J* = 9.0 Hz, 1H), 4.09 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.24 (d, *J* = 8.0 Hz, 1H), 4.47 (d, *J* = 12.5 Hz, 1H), 4.59 (s, 1H), 4.63-4.74 (m, 3H), 4.94 (d, *J* = 11.0 Hz, 1H), 5.00 (d, *J* = 10.5 Hz, 1H), 5.05-5.09 (m, 2H), 5.46 (s, 1H), 5.80-5.88 (m, 1H), 7.29-7.41 (m, 18H), 7.46-7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.7, 30.1, 65.9, 67.0, 68.3, 68.5, 69.4, 71.0, 73.8, 74.8, 75.2, 75.9, 77.7, 78.9, 79.1, 81.5, 101.7, 102.0, 102.1, 115.1, 126.3, 127.6, 127.9, 128.00, 128.04, 128.1, 128.2, 128.3, 128.5, 128.7, 129.2, 137.2, 137.6, 138.0, 138.1, 138.5. ESIHRMS Calcd for $C_{45}H_{51}N_3O_{10}$ $[M+Na]^+$: 816.3467. Found 816.3463.

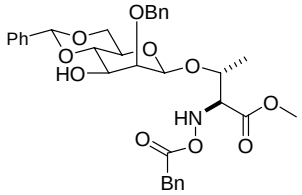


3-*O*-[4,6-*O*-Benzylidene-2-*O*-benzyl-β-D-mannopyranosyl]-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (17e).

Eluent for purification: hexane/ethyl acetate, 3/1→2/1.

$[\alpha]^{22}_D$ – 53.0 (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 3H), 1.35 (s, 3H), 1.45 (s, 3H), 1.52 (s, 3H), 2.45 (br s, 1H), 3.35 (dt, *J* = 5.0, 9.5 Hz, 1H), 3.79-3.90 (m, 4H), 4.06 (dd, *J* = 6.0, 8.5 Hz, 1H), 4.13 (dd, *J* = 6.5, 8.0 Hz, 1H), 4.27-4.35 (m, 3H), 4.39-4.43 (m, 1H), 4.41 (q, *J* = 6.0 Hz, 1H), 4.50 (d, *J* = 4.0 Hz, 1H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.68 (s, 1H), 4.94 (d, *J* = 11.5 Hz, 1H), 5.54 (s, 1H), 5.92 (d, *J* = 3.5 Hz, 1H), 7.31-7.48 (m, 8H), 7.48-7.50 (m**,** 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.5, 26.3, 26.7, 26.8, 66.4, 67.2, 68.5, 70.7, 72.9, 75.4, 78.0, 79.2, 80.5, 80.8, 82.8, 100.1, 102.0, 105.0, 108.8, 112.1, 126.3, 128.16, 128.22, 128.3, 128.6, 129.2, 137.2, 137.8.

ESIHRMS Calcd for $C_{32}H_{40}O_{11}$ $[M+Na]^+$: 623.2463 . Found 623.2461.

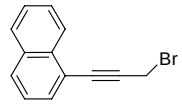


***O*-[4,6-*O*-Benzylidene-2-*O*-benzyl-β-D-mannopyranosyl]-N-carbobenzyloxy-L-threonine methyl ester (17f)**

Eluent for purification: hexane/ethyl acetate, 1.5/1.

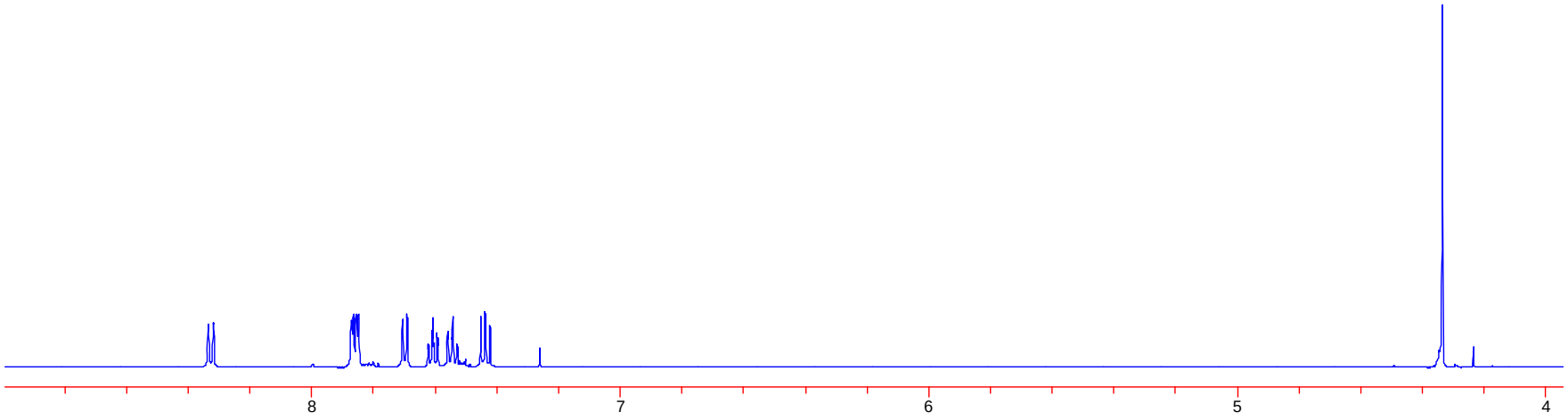
$[\alpha]^{22}_D$ – 33.8 (c, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (d, 6.5 Hz, 3H), 2.42 (br s, 1H), 3.26 (dt, *J* = 5.0, 10.0 Hz**,** 1H), 3.73 (s, 3H), 3.76-3.88 (m, 4H), 4.26 (dd, *J* = 5.0, 10.5 Hz**,** 1H), 4.41 (dd, *J* = 2.0, 9.0 Hz**,** 1H), 4.51 (dq, *J* = 2.0, 9.0 Hz**,** 1H), 4.58-4.61 (m, 2H), 4.95 (d, *J* = 11.5 Hz, 1H), 5.12-5.18 (m, 2H), 5.51 (s, 1H), 5.52 (d, *J* = 11.5 Hz**,** 1H), 7.27-7.38 (m, 13H), 7.46-7.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.2, 52.6, 58.5, 67.1, 67.3, 68.4, 70.8, 74.2, 75.6, 78.6, 79.1, 99.7, 102.1, 126.3, 128.0, 128.2, 128.3, 128.56, 128.59, 129.2, 136.5, 137.1, 138.1, 156.7, 170.8. ESIHRMS Calcd for $C_{33}H_{37}N_1O_{10}$ $[M+Na]^+$: 630.2310. Found 630.2309.

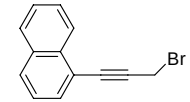
[1] Bromide **4** was prepared according to：Banerjee, M.; Roy, S. *Org. Lett.* **2004,** *6*, 2137-2140.
[2] See: Banerjee, M.; Roy, S. *Org. Lett.* **2004,** *6,* 2137-2140.



4

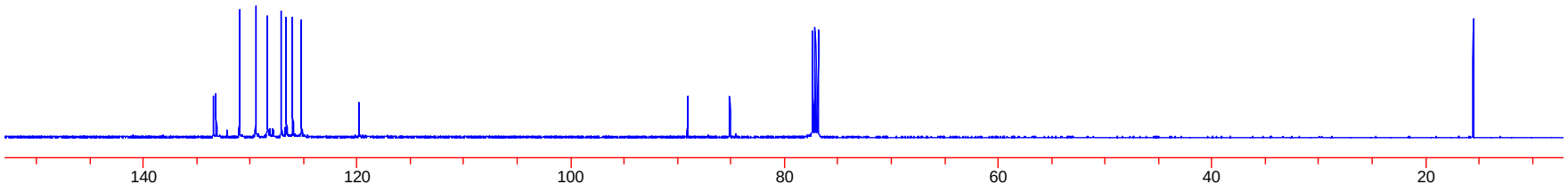
^{1}H-NMR ($CDCl_3$, 500MHz)

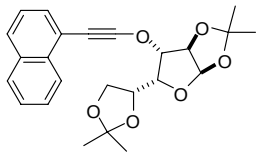




4

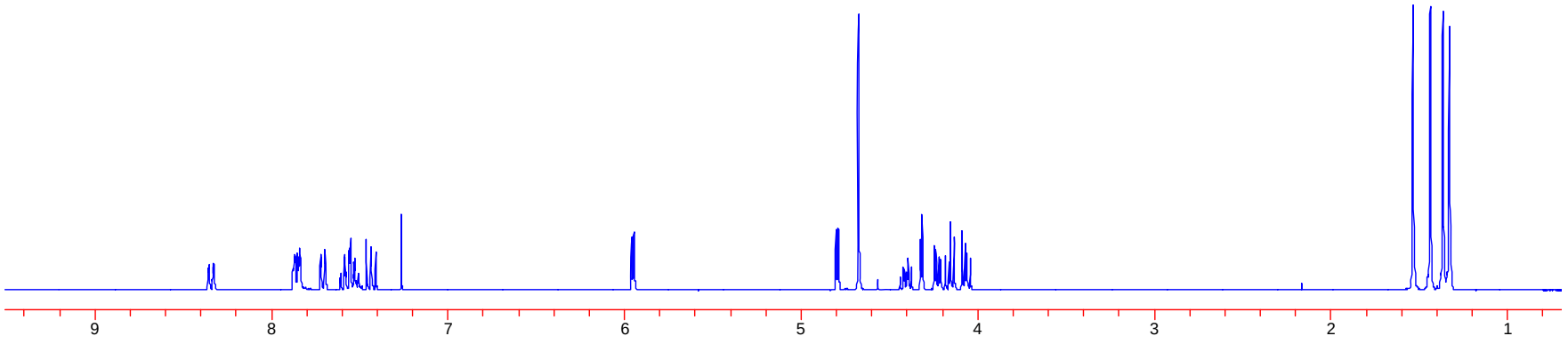
^{13}C-NMR ($CDCl_3$, 125MHz)

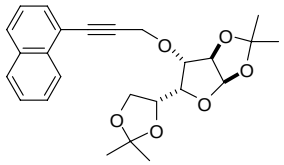




5

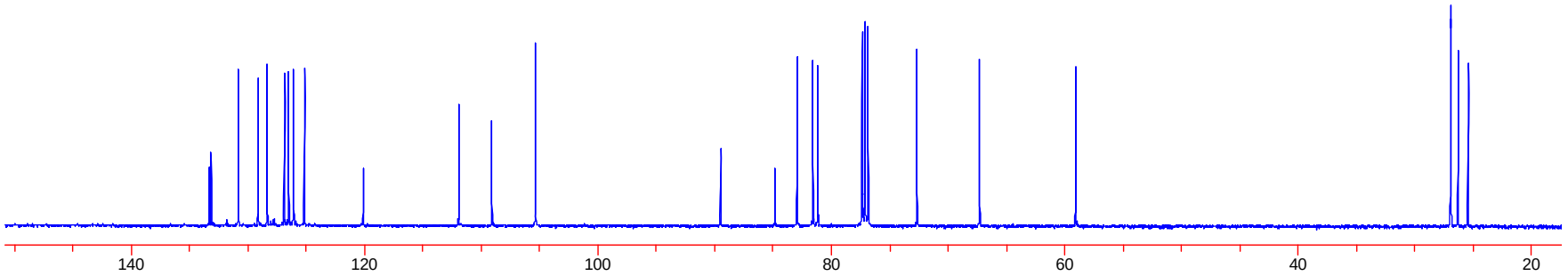
^{1}H-NMR ($CDCl_3$, 300MHz)

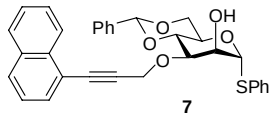




5

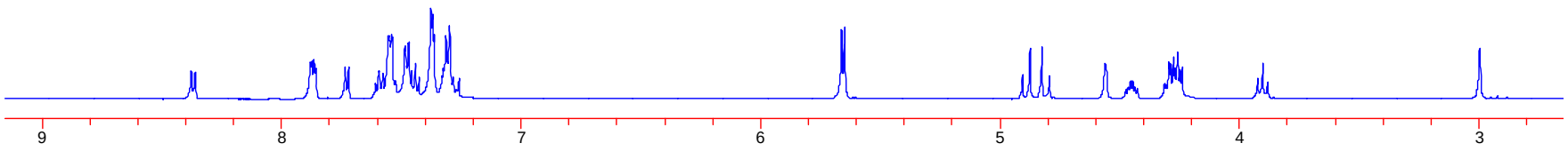
^{13}C-NMR ($CDCl_3$, 125MHz)

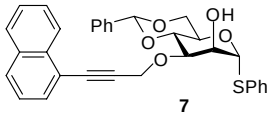




7

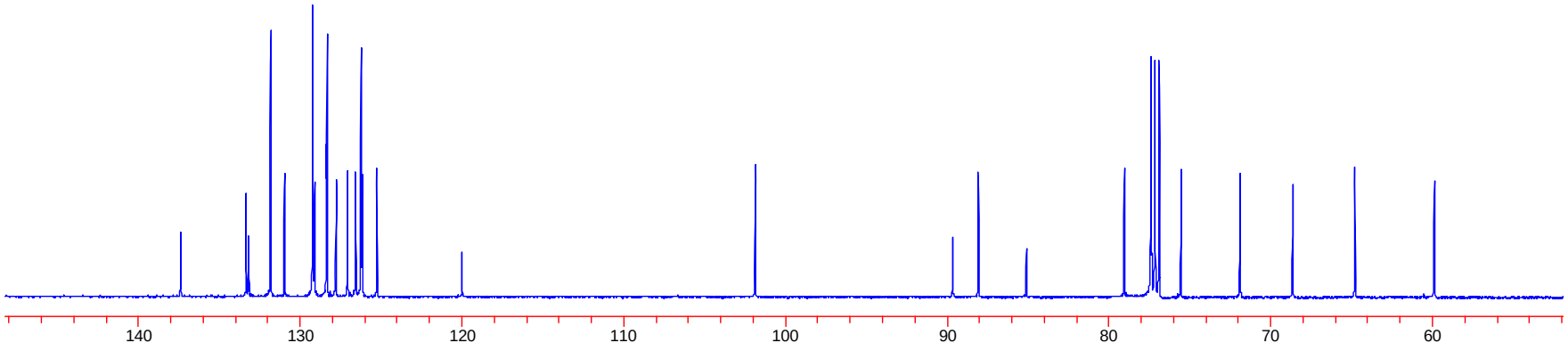
^{1}H-NMR ($CDCl_3$, 500MHz)

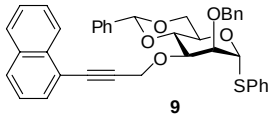




7

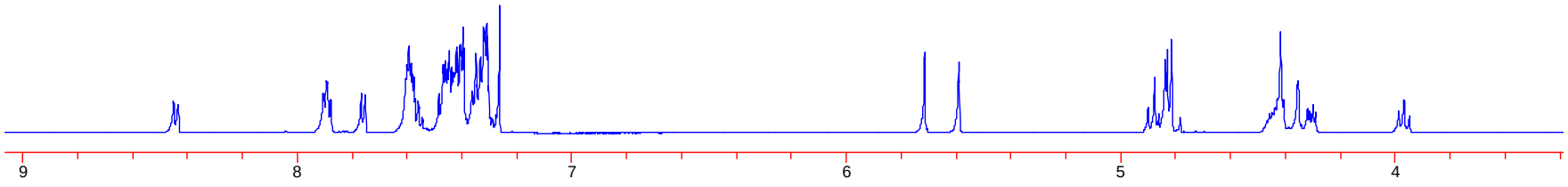
^{13}C-NMR ($CDCl_3$, 125MHz)

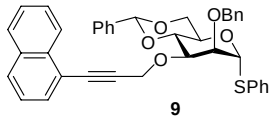




9

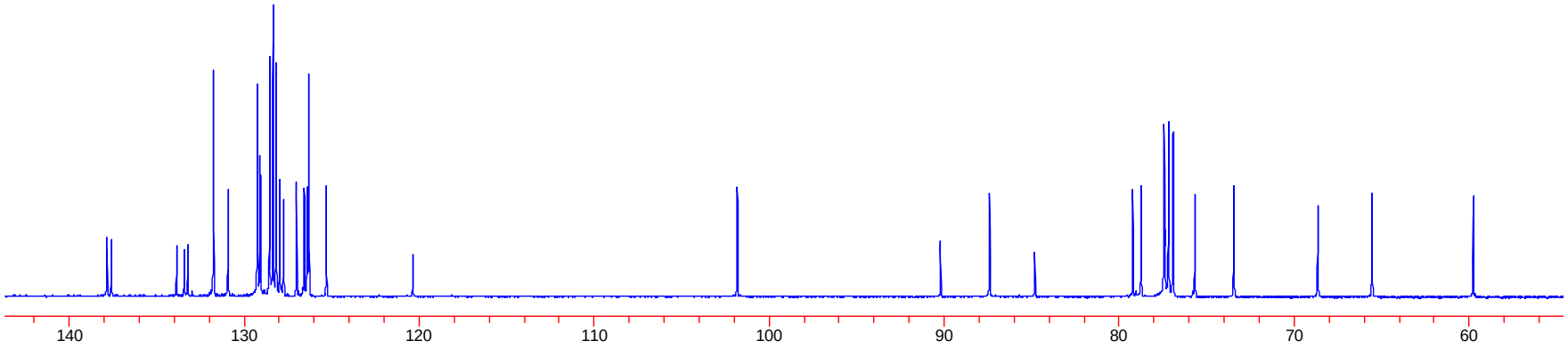
^{1}H-NMR ($CDCl_3$, 500MHz)

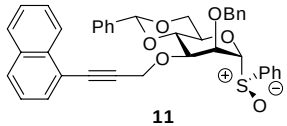




9

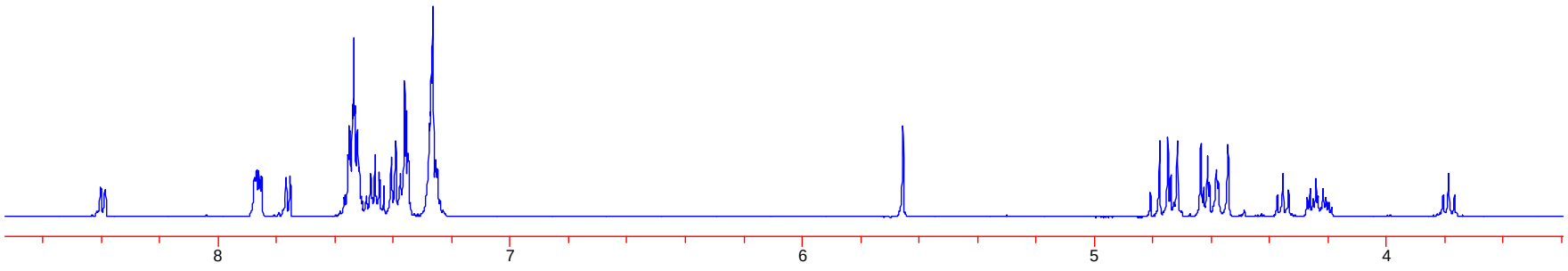
^{13}C-NMR ($CDCl_3$, 125MHz)

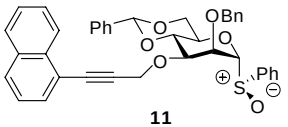




11

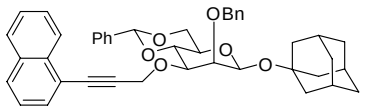
^{1}H-NMR ($CDCl_3$, 500MHz)





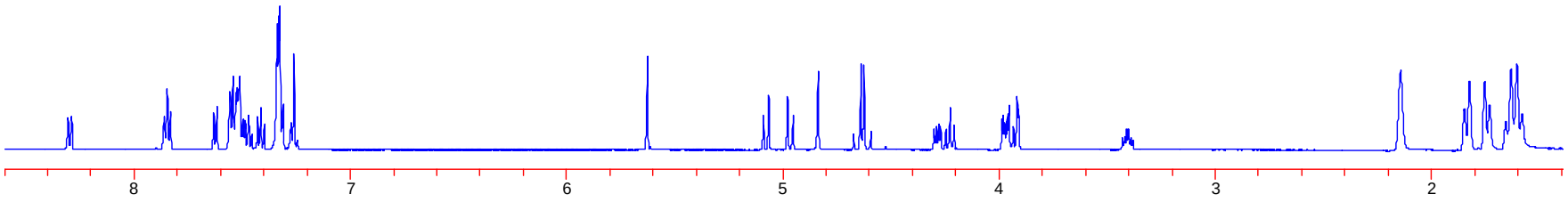
11

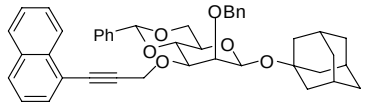
^{13}C-NMR ($CDCl_3$, 125MHz)



12a

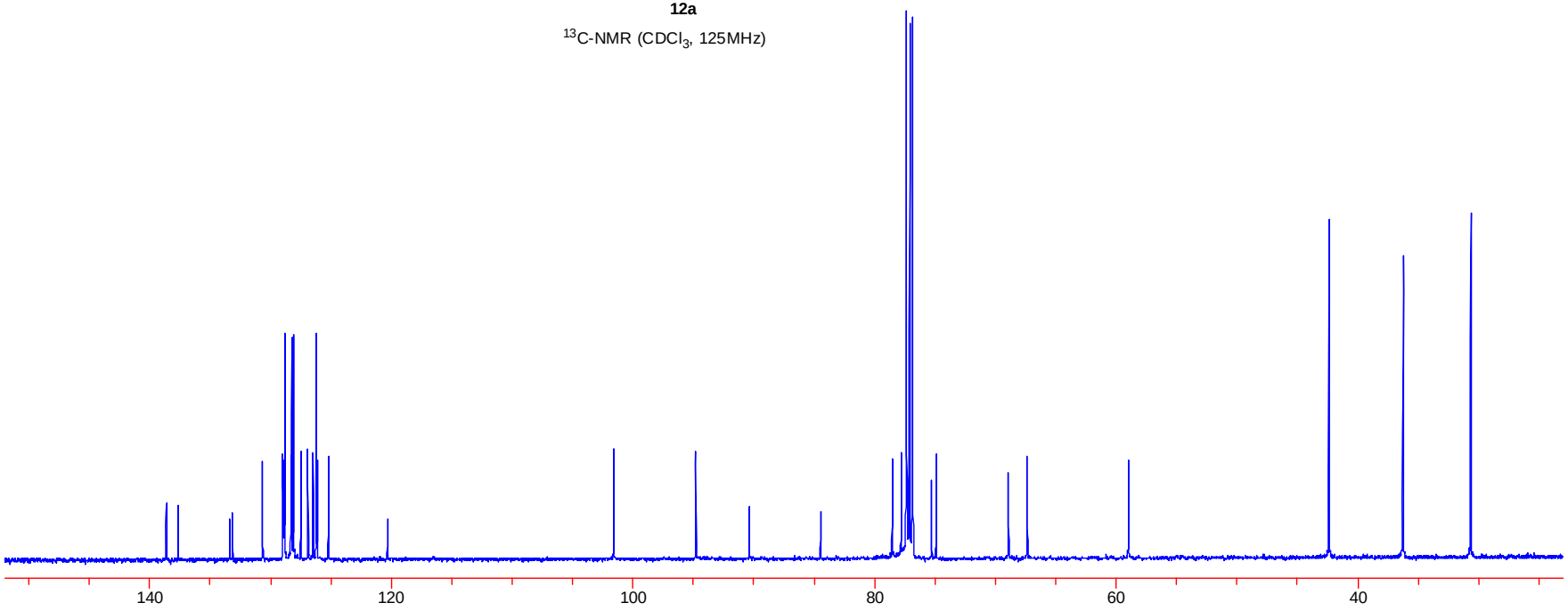
^{1}H-NMR ($CDCl_3$, 500MHz)

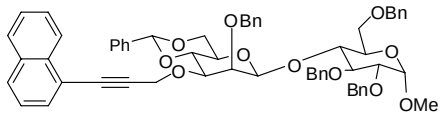




12a

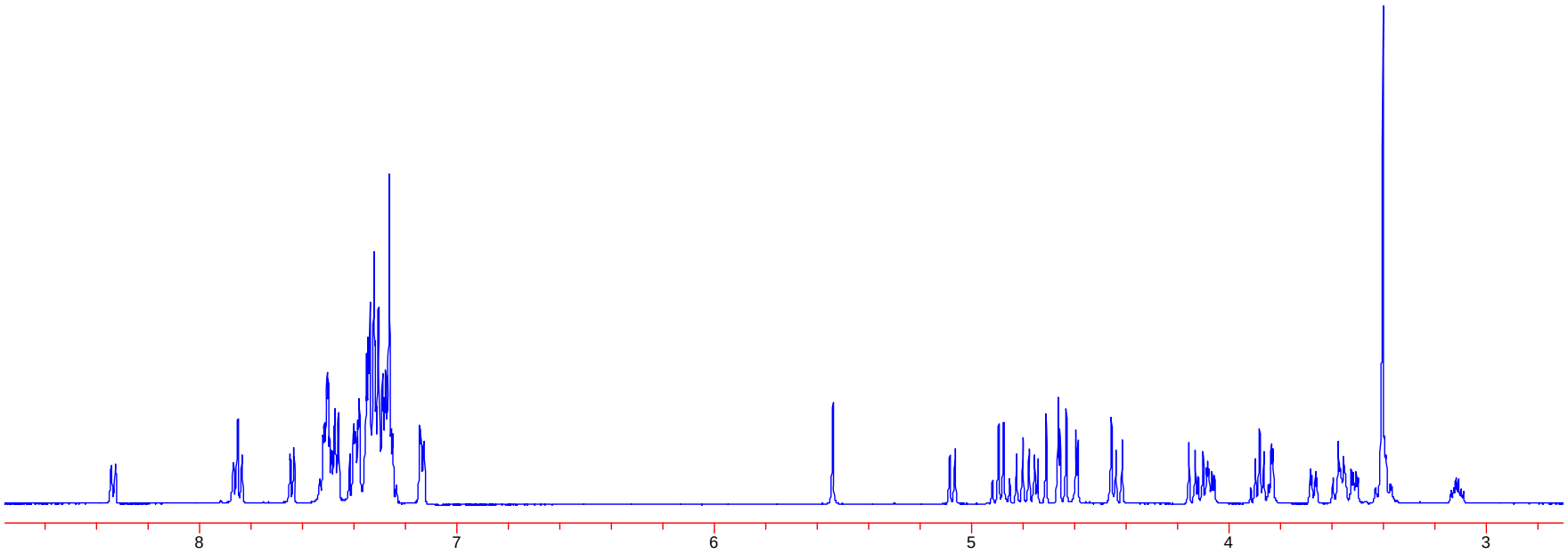
^{13}C-NMR ($CDCl_3$, 125MHz)

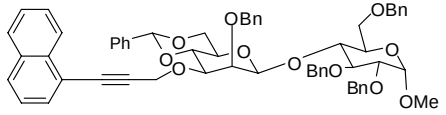




12b

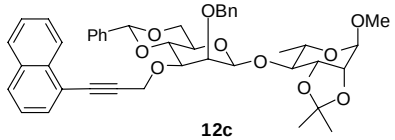
^{1}H-NMR ($CDCl_3$, 500MHz)





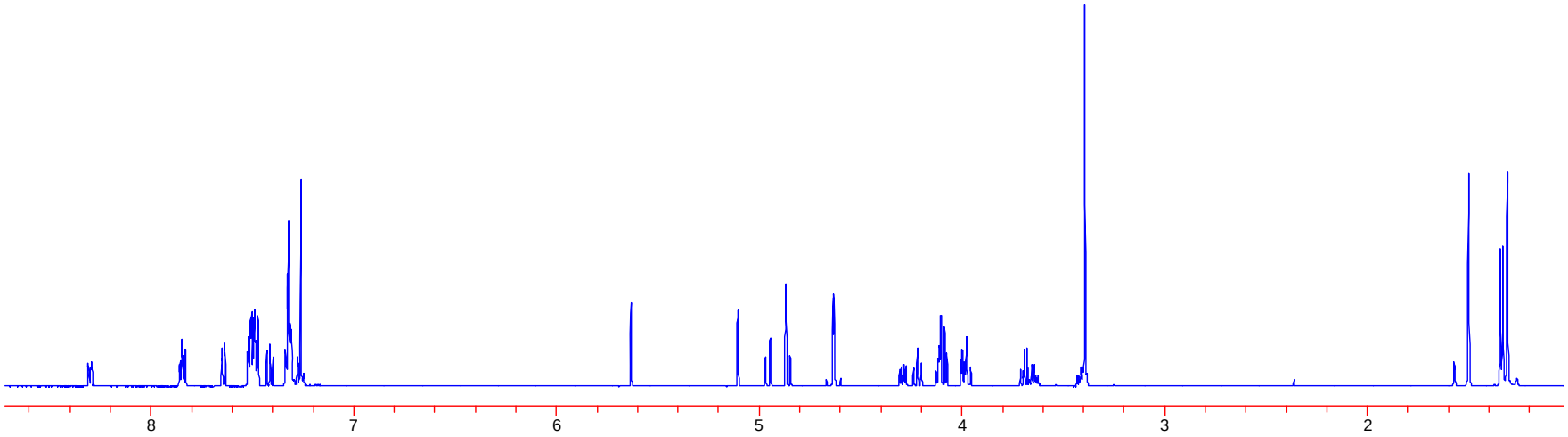
12b

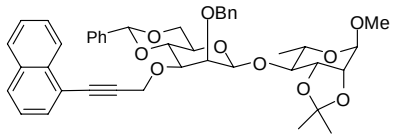
^{13}C-NMR ($CDCl_3$, 125MHz)



12c

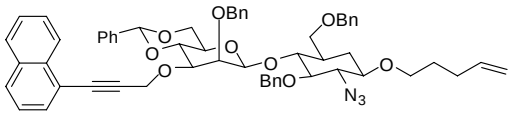
^{1}H-NMR ($CDCl_3$, 500MHz)





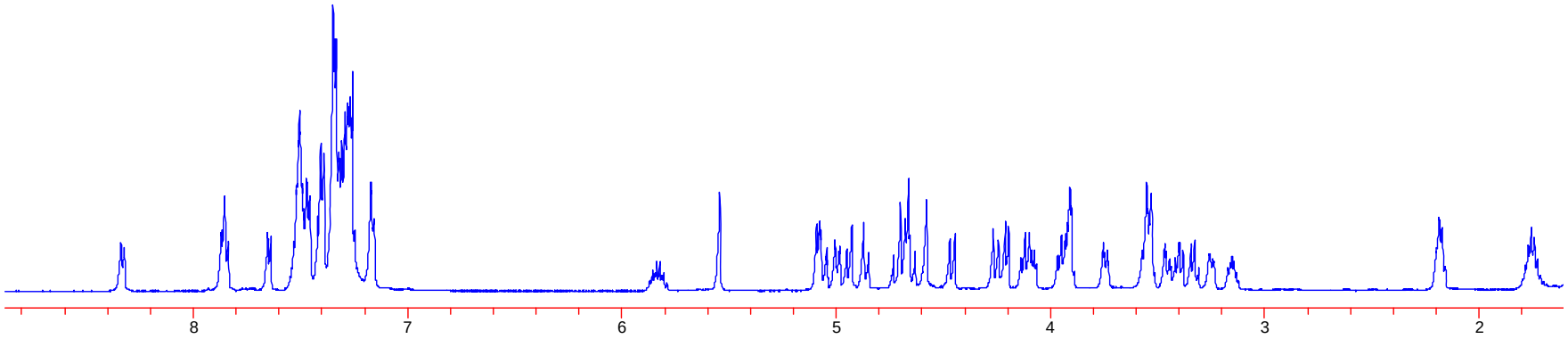
12c

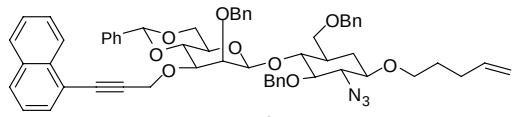
^{13}C-NMR ($CDCl_3$, 125MHz)



12d

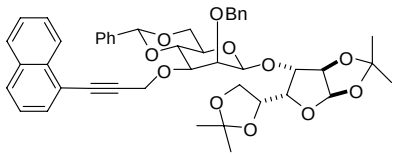
^{1}H-NMR ($CDCl_3$, 500MHz)





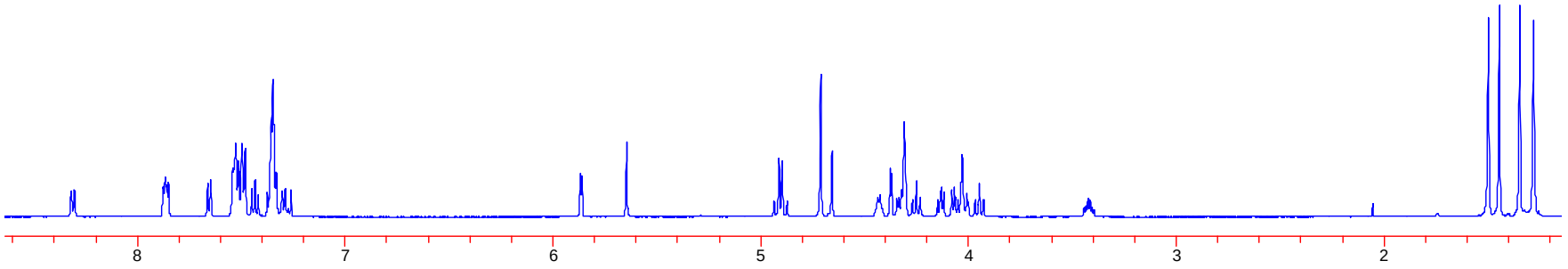
12d

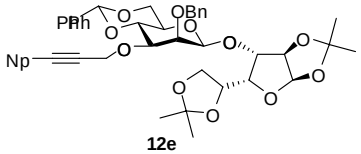
^{13}C-NMR ($CDCl_3$, 125MHz)



12e

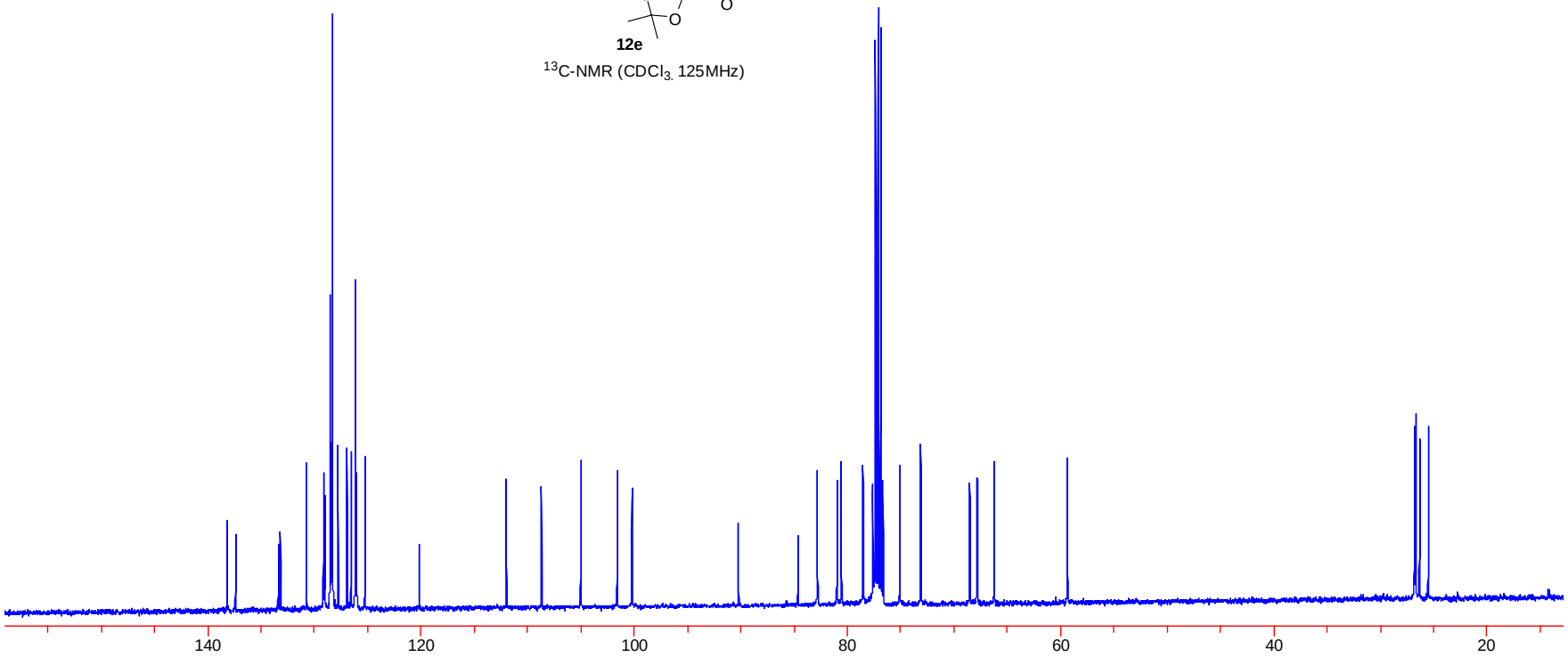
^{1}H-NMR ($CDCl_3$, 500MHz)

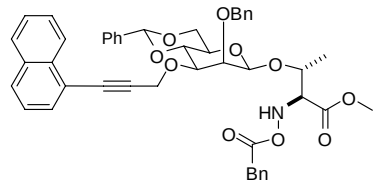




12e

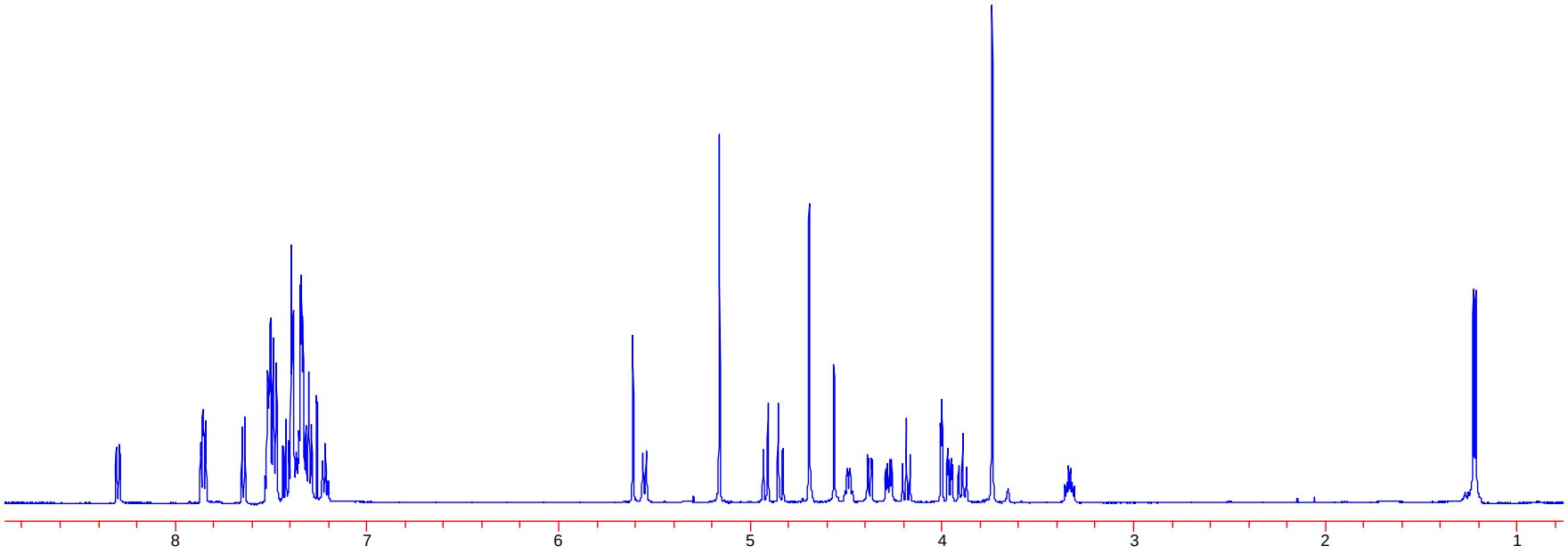
^{13}C-NMR ($CDCl_3$, 125MHz)

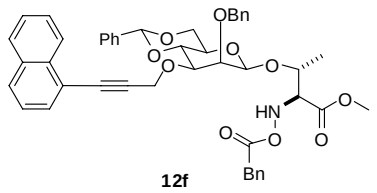




12f

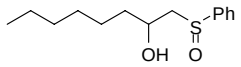
^{1}H-NMR ($CDCl_3$, 500MHz)





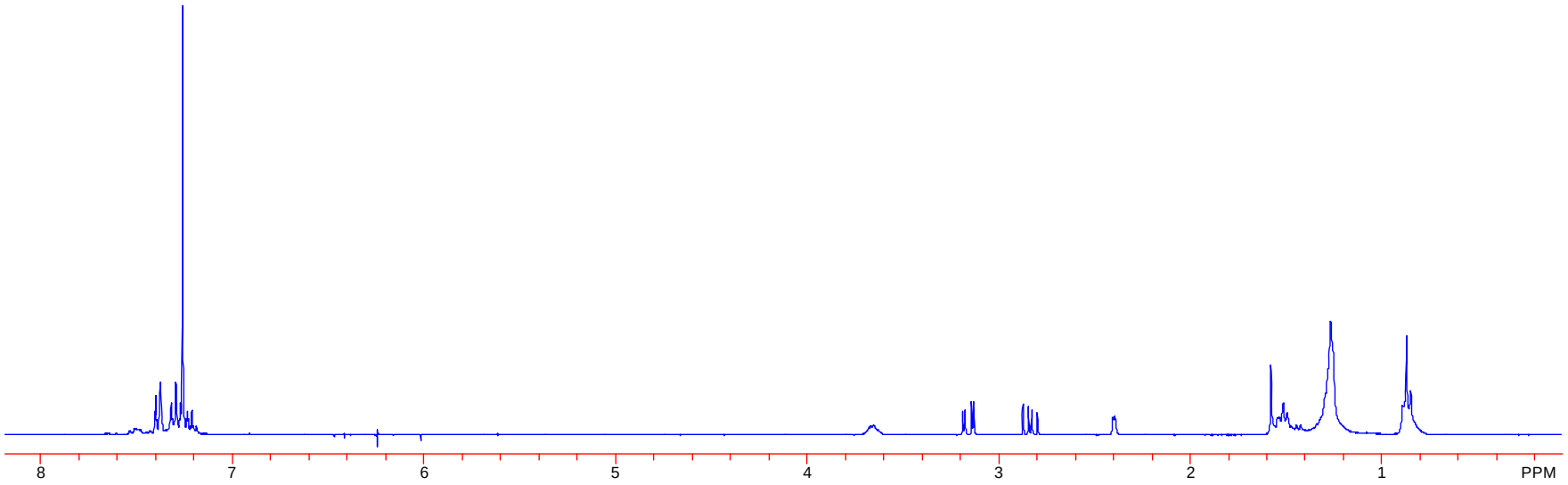
12f

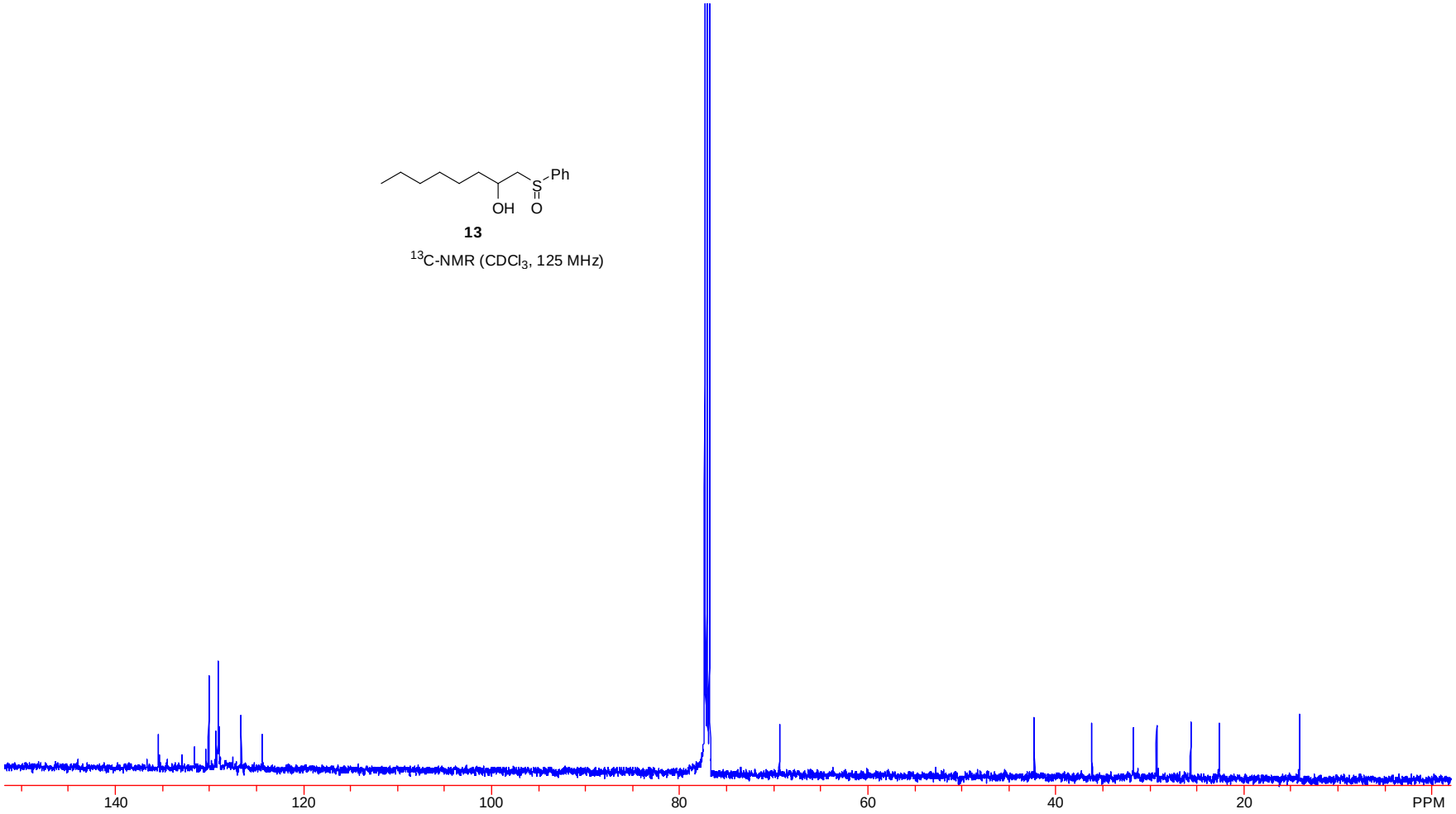
^{13}C-NMR ($CDCl_3$, 125MHz)



13

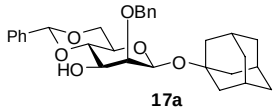
^{1}H-NMR ($CDCl_3$, 300 MHz)





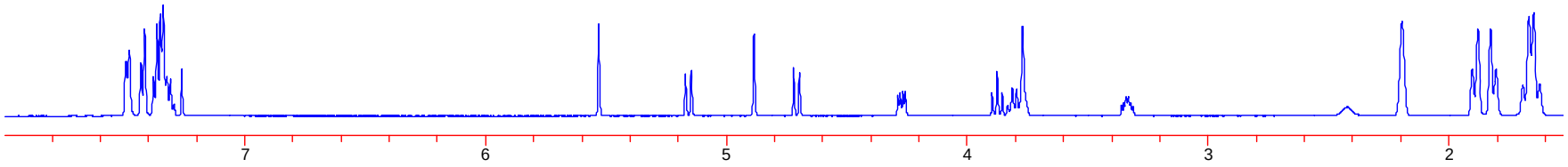
13

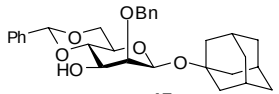
^{13}C-NMR ($CDCl_3$, 125 MHz)



17a

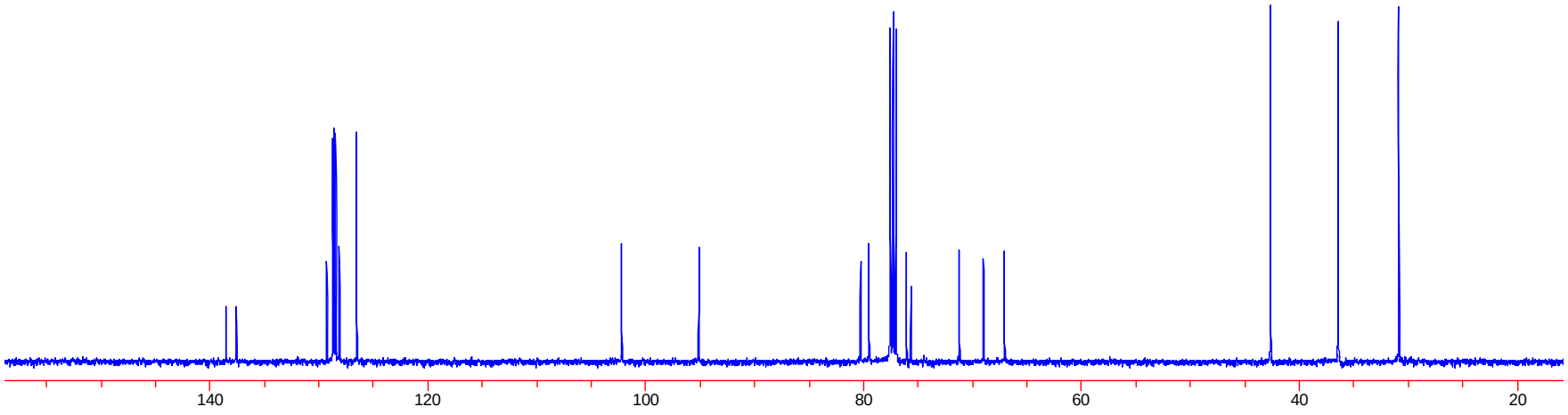
^{1}H-NMR ($CDCl_3$, 500MHz)

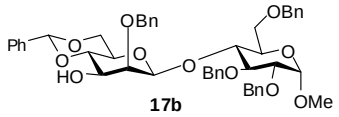




17a

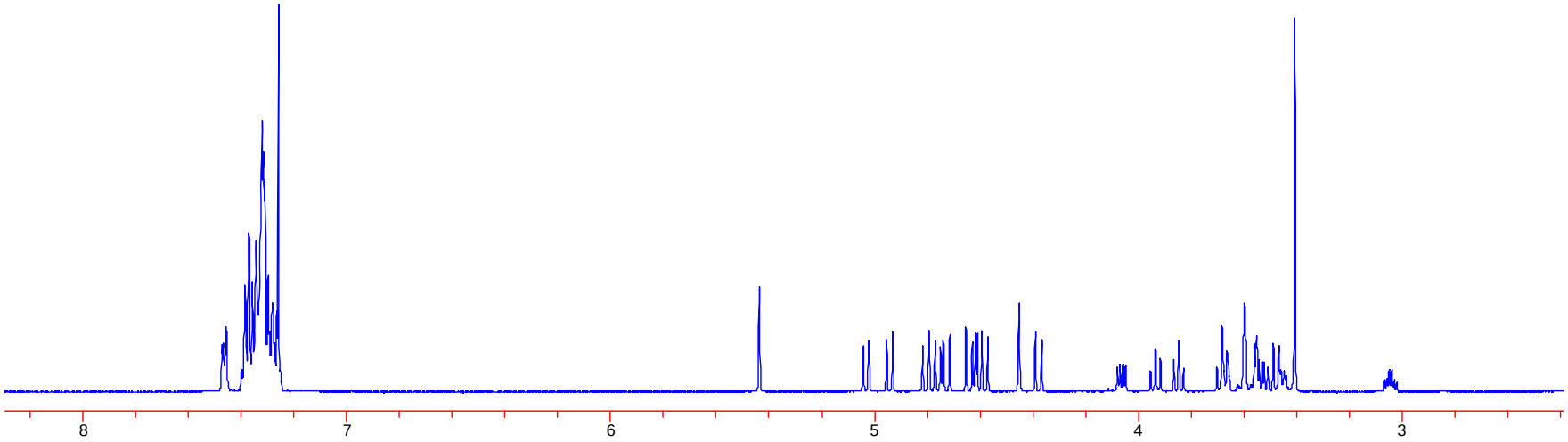
^{13}C-NMR ($CDCl_3$, 125MHz)

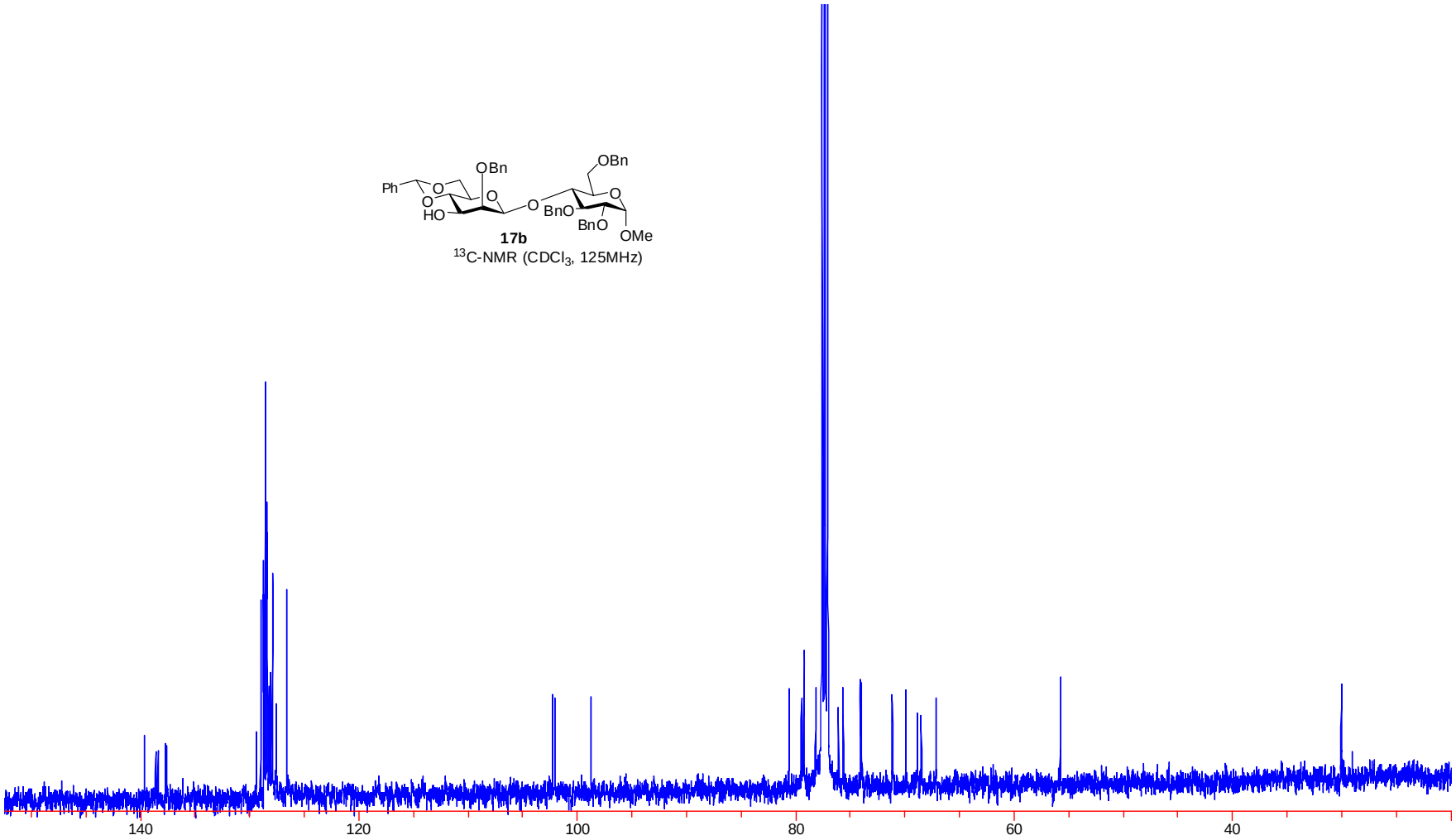




17b

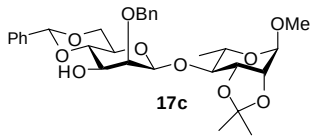
^{1}H-NMR ($CDCl_3$, 500MHz)





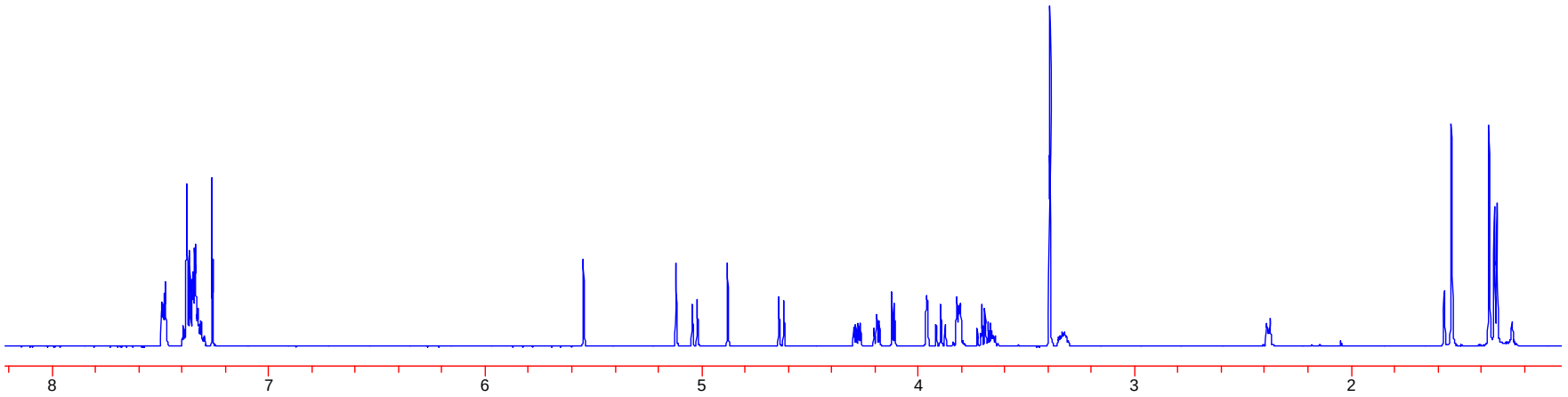
17b

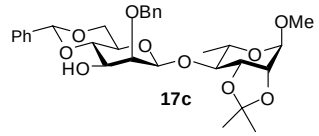
^{13}C-NMR ($CDCl_3$, 125MHz)



17c

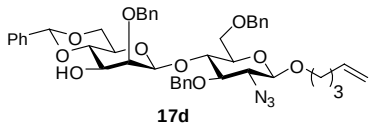
^{1}H-NMR ($CDCl_3$, 500MHz)





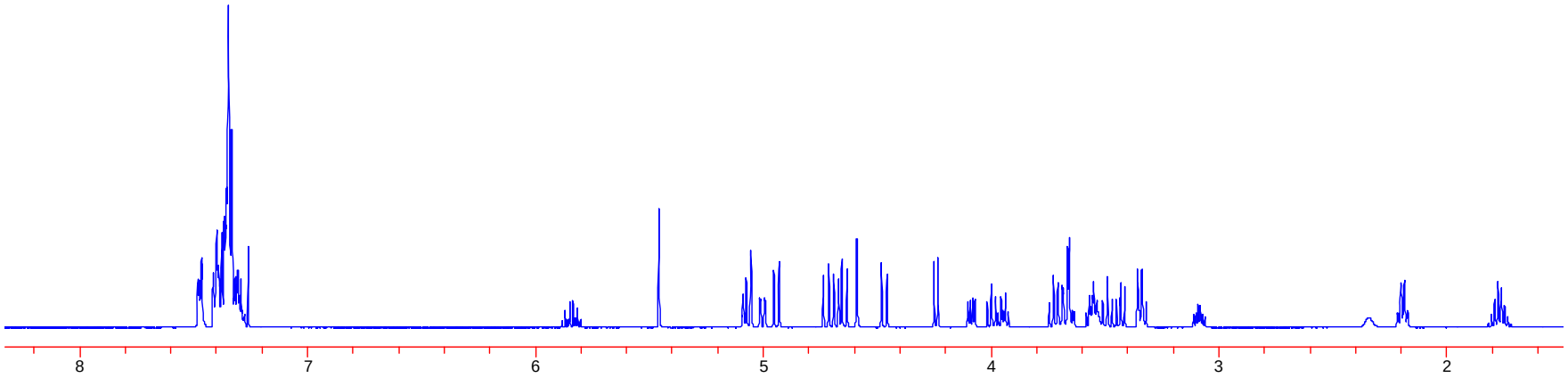
17c

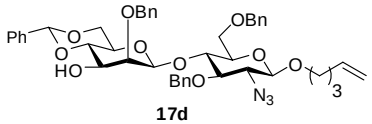
^{13}C-NMR ($CDCl_3$, 125MHz)



17d

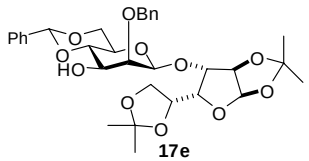
^{1}H-NMR ($CDCl_3$, 500MHz)





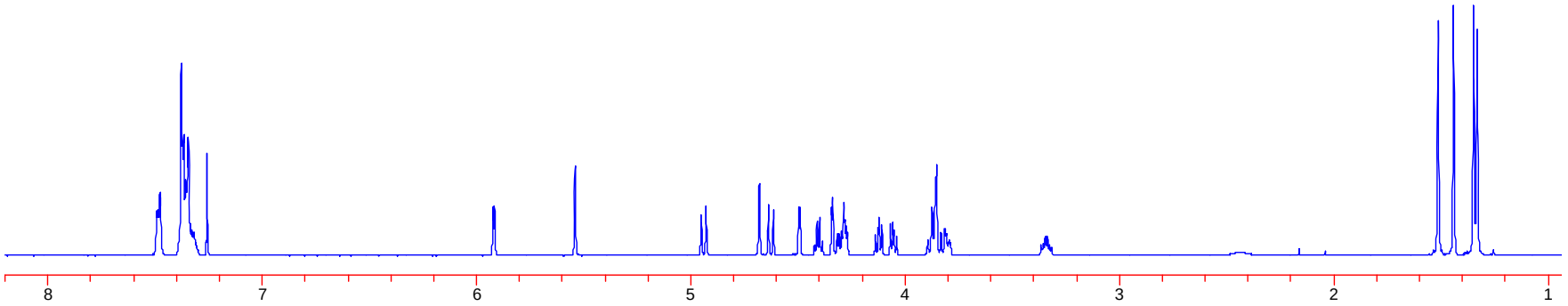
17d

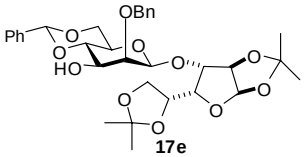
^{13}C-NMR ($CDCl_3$, 125MHz)



17e

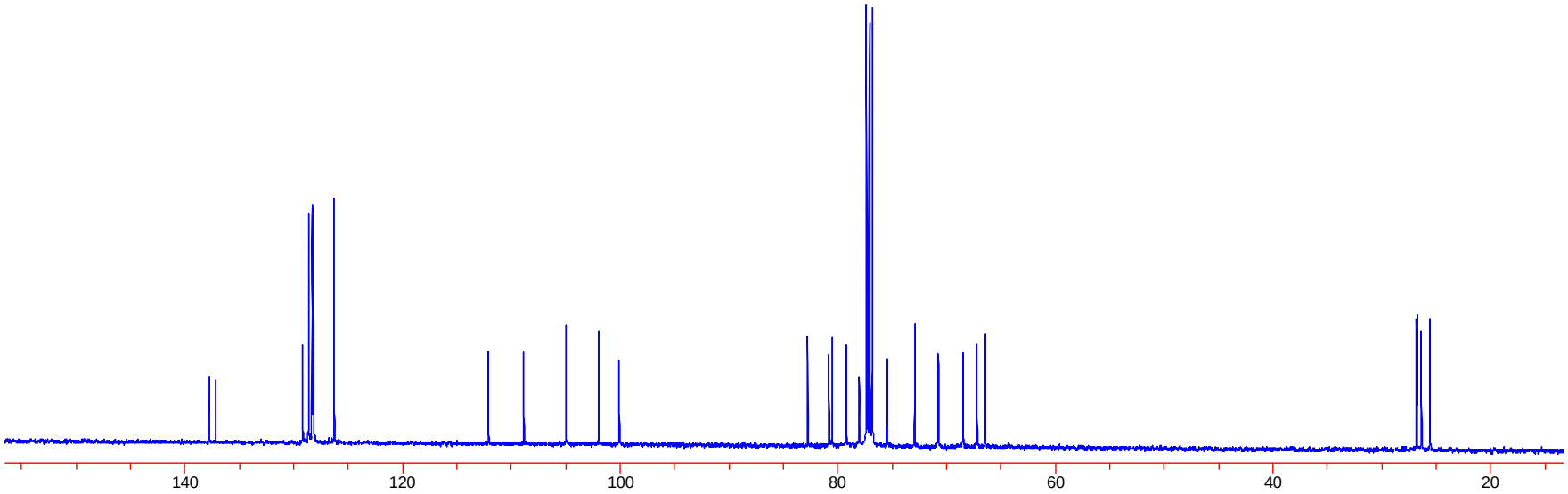
^{1}H-NMR ($CDCl_3$, 500MHz)

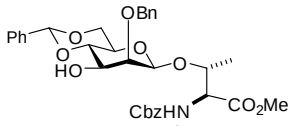




17e

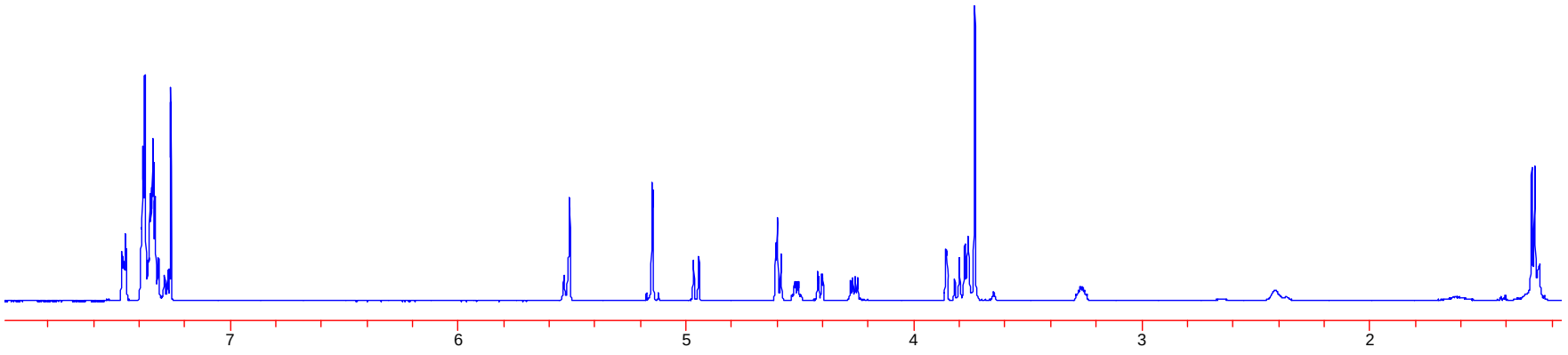
^{13}C-NMR ($CDCl_3$, 125MHz)

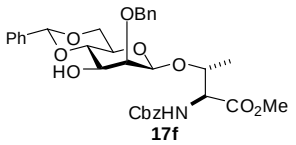




17f

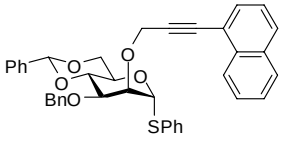
^{1}H-NMR ($CDCl_3$, 500MHz)





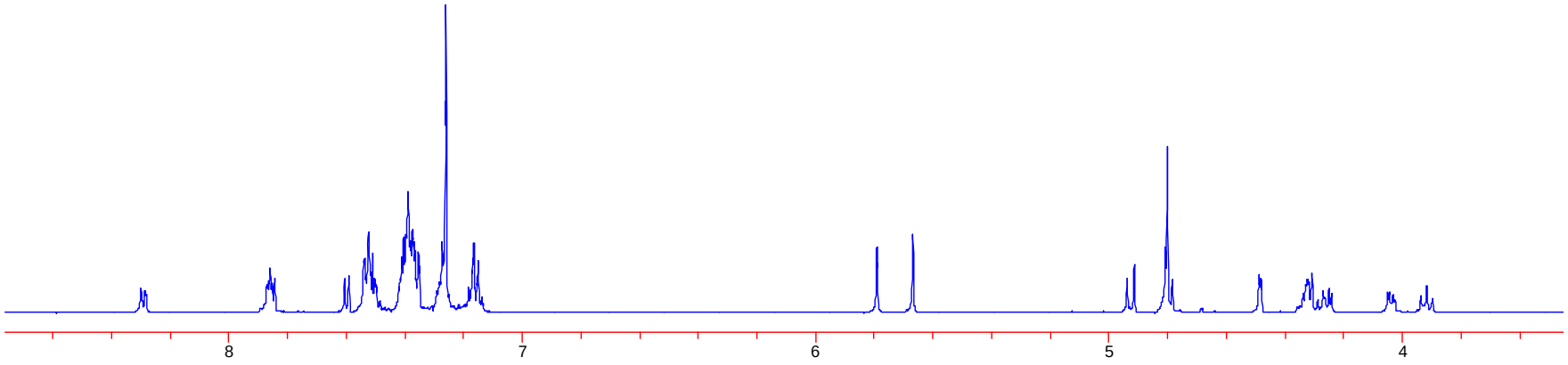
17f

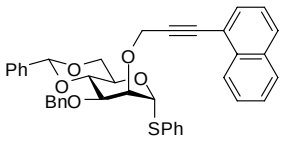
^{13}C-NMR ($CDCl_3$, 125MHz)



10

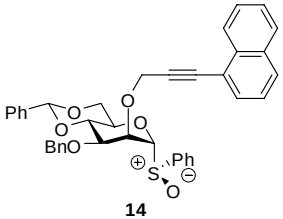
^{1}H-NMR ($CDCl_3$, 500MHz)





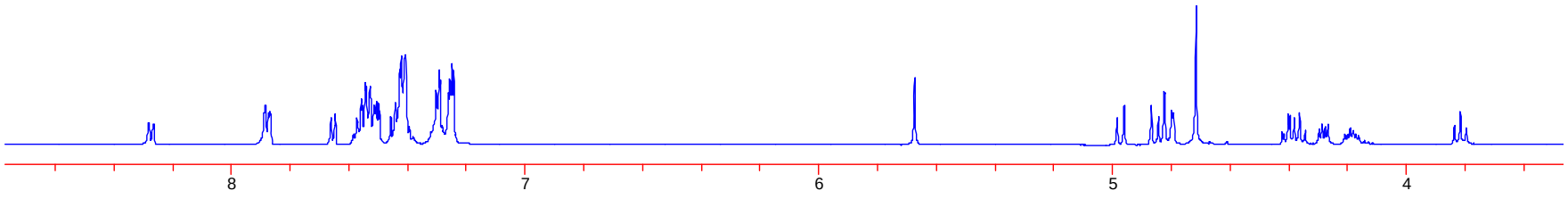
10

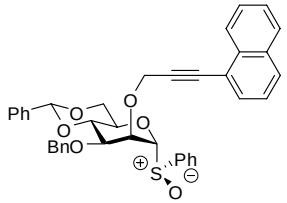
^{13}C-NMR ($CDCl_3$, 125MHz)



14

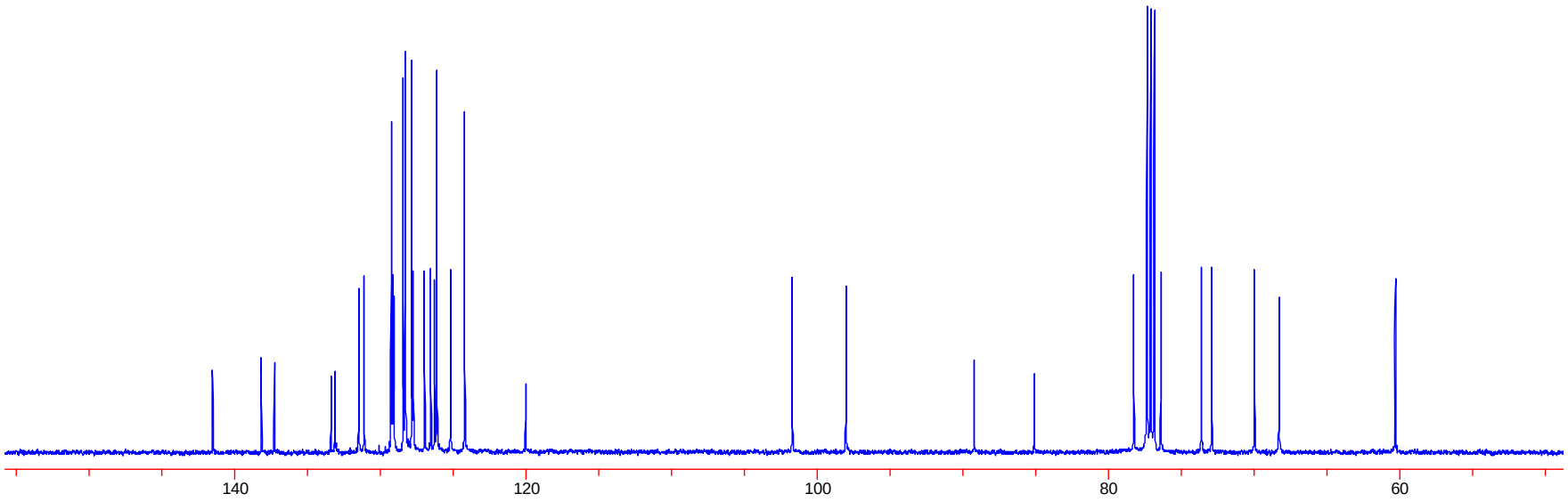
^{1}H-NMR ($CDCl_3$, 500MHz)

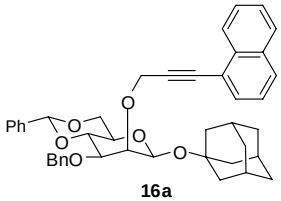




14

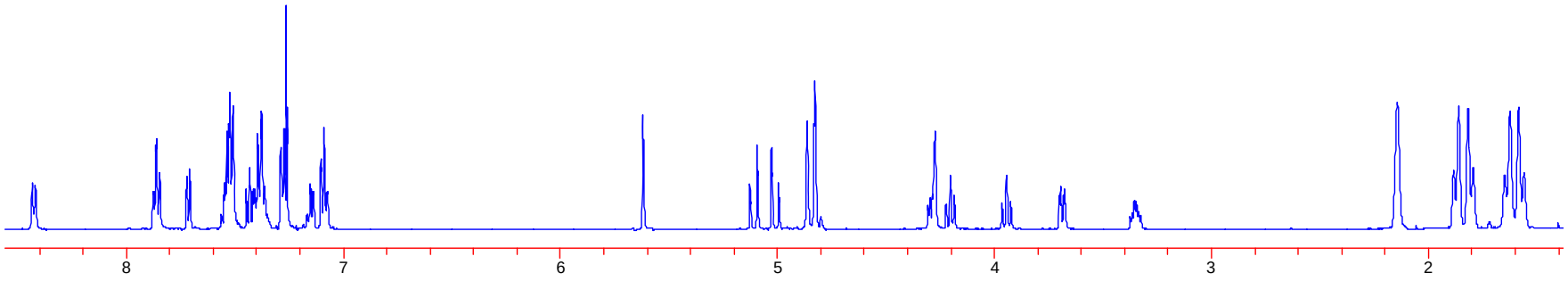
^{13}C-NMR ($CDCl_3$, 125MHz)

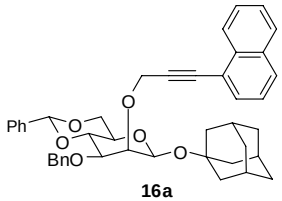




16a

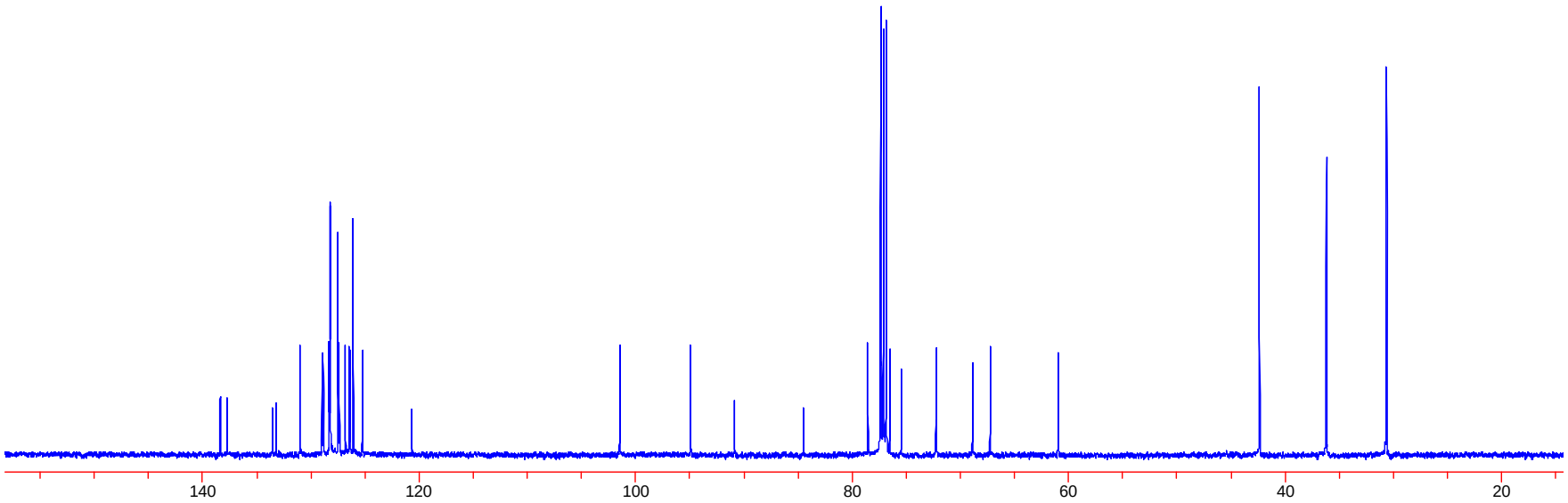
^{1}H-NMR ($CDCl_3$, 500MHz)

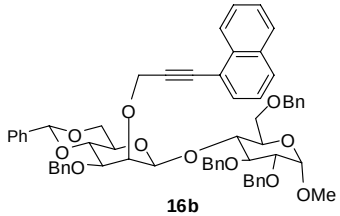




16a

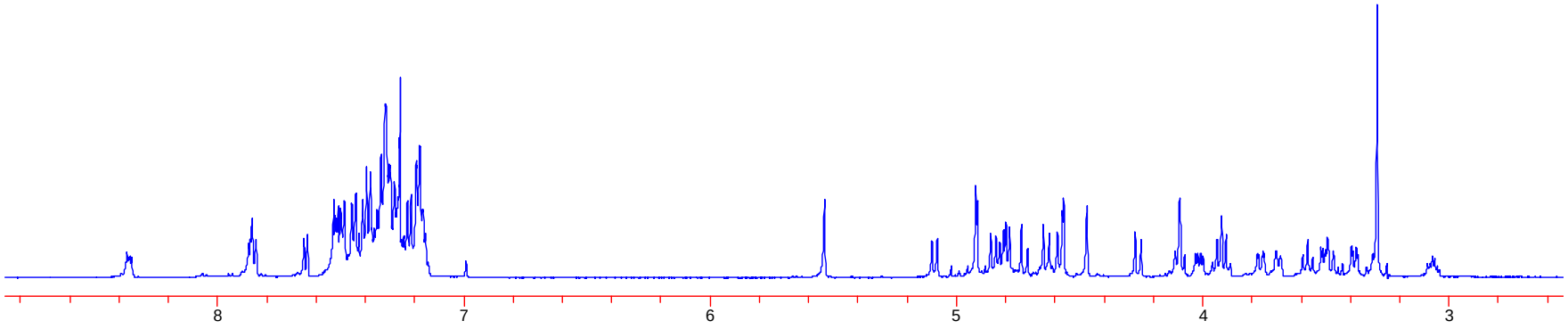
^{13}C-NMR ($CDCl_3$, 125MHz)

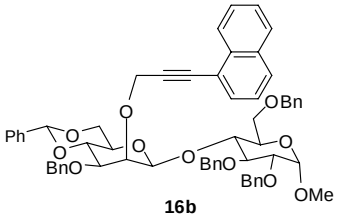




16b

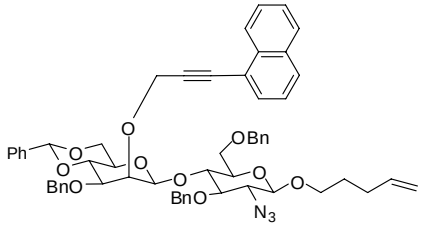
^{1}H-NMR ($CDCl_3$, 500MHz)





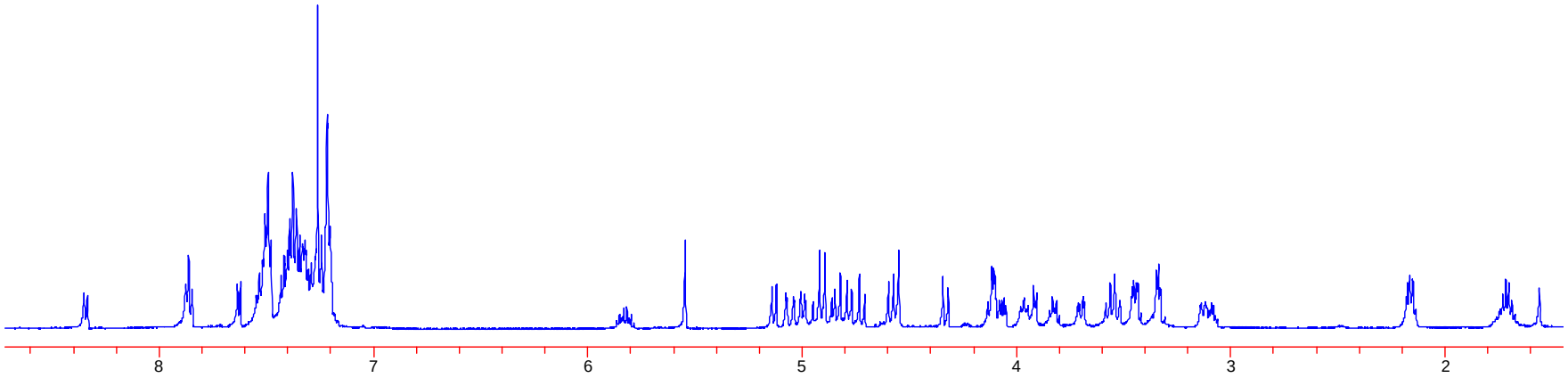
16b

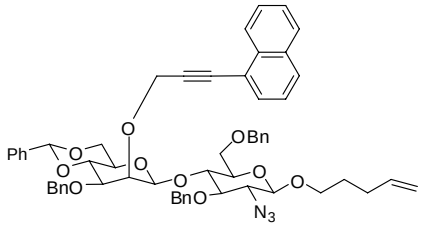
^{13}C-NMR ($CDCl_3$, 125MHz)



16c

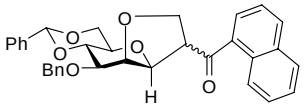
^{1}H-NMR ($CDCl_3$, 500MHz)





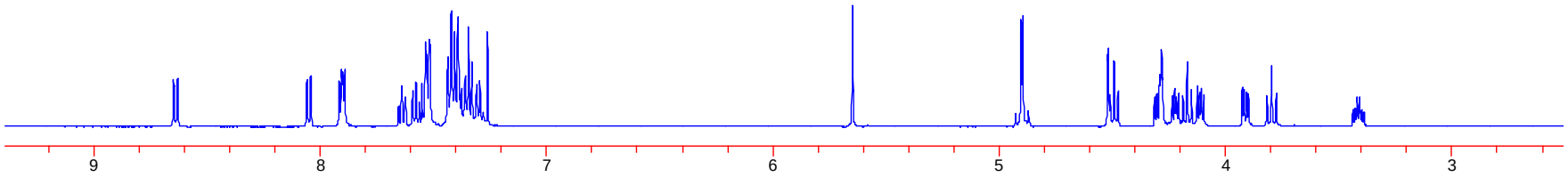
16c

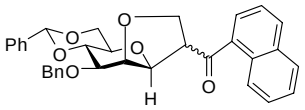
^{13}C-NMR ($CDCl_3$, 125MHz)



15

^{1}H-NMR ($CDCl_3$, 500MHz)





15

^{13}C-NMR ($CDCl_3$, 125MHz)