Supporting Information

for

Branching out at *C*-2 of septanosides. Synthesis of 2-deoxy-2-*C*-alkyl/aryl septanosides from a bromo-oxepine

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Experimental procedures and spectroscopic data

Contents

General methods

Chemicals were purchased from commercial sources and used without further purification. Solvents were dried and distilled by following literature procedures. Bromo-oxepine was synthesized according to the reported procedure [1]. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm) with detection by fluorescence and/or charring following immersion in 5% H_2SO_4/EtOH. Silica gel (230–400 mesh) was used for column chromatography. Optical rotations were recorded on a

polarimeter at the sodium D line at 24 °C. High resolution mass spectra were obtained from a Micromass Q-TOF instrument by the electrospray ionization (ESI) technique. ^{1}H and ^{13}C NMR spectral analyses were performed on 400 and 100 MHz NMR spectrometers, respectively, with the residual solvent signal acting as the internal standard. Standard abbreviations s, d, t, dd, br, app., m and band refer to singlet, doublet, triplet, doublet of doublet, broad, apparent, multiplet and set of resonances.

Experimental

Methyl 2-deoxy-2-*C*-(2-(methoxycarbonyl)ethyl)-3,4,5,7-tetra-*O*-benzyl-α-D-*arabino*-hept-2-enoseptanoside (**3**). A solution of **2** (0.05 g, 0.07 mmol) in 1,4-dioxane (1 mL) was admixed with $Pd(OAc)_2$ (1 mg, 10 mol %) under a N_2 atmosphere, and was followed by addition of Cs_2CO_3 (0.03 g, 0.11 mmol) and methyl acrylate (8 µL, 0.13 mmol), in a sealed tube. The reaction mixture was stirred at 98 °C for 72 h, cooled, filtered, diluted with EtOAc (20 mL), washed with water (2 × 30 mL) and brine (2 × 10 mL), dried (Na_2SO_4) and concentrated in vacuo. The resulting residue was purified (hexane/EtOAc 8:2) to afford **3** (0.035 g, 70%), as an oil.

R_f 0.30 (hexane/EtOAc 8:2); $[\alpha]_D$ −21.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 16.0 Hz, 1 H, C*H*=CHCO$_2$Me), 7.37–7.24 (m, 18 H, aromatic), 7.10–7.08 (m, 2 H, aromatic), 5.97 (d, *J* = 16.0 Hz, 1 H, CH=C*H*CO$_2$Me), 5.36 (s, 1 H, H-1), 4.67 (d, *J* = 4.0 Hz, 1 H, PhCH_2), 4.65 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 4.59 (d, *J* = 12.0 Hz, 2 H, PhCH_2), 4.47 (d, *J* = 12.4 Hz, 1 H, PhCH_2), 4.43 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 4.29 (d, *J* = 11.6 Hz, 2 H, PhCH_2), 4.20–4.15 (band, 2 H, H-4 and H-6), 3.77–3.75 (dd, *J* = 8.4, 2.0 Hz, 1 H, H-5), 3.73 (s, 3 H, CO$_2$Me), 3.60 (dd, *J* = 10.8, 6.0 Hz, 1 H, H-7a), 3.52–3.49 (band, 4 H, H-7b, OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8 (C=O), 159.5 (C-3), 138.5–137.2 (aromatic), 136.3 (*C*H=CHCO$_2$Me), 128.5–127.5 (aromatic), 124.2 (C-2), 119.5

(CH=*C*HCO$_2$Me), 100.1 (C-1), 80.0 (C-5), 77.2 (C-4), 73.1 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.2 (Ph*C*H$_2$), 71.1 (C-6), 70.9 (C-7), 55.4 (OMe), 51.4 (CO$_2$Me); HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for 673.2777; found, 673.2776.

Methyl 2-deoxy-2-*C*-((3-((5-(acryloyloxy)pentyl)oxy)-3-oxoprop-1-en-1-yl)-3,4,5,7-*tetra*-*O*-benzyl-α-D-*arabino*-hept-2-enoseptanoside (5). A solution of **2** (0.05 g, 0.07 mmol) in 1,4-dioxane (1 mL) was admixed with Pd(OAc)$_2$ (1 mg, 10 mol %) under a N_2 atmosphere, and was followed by addition of Cs_2CO_3 (0.03 g, 0.11 mmol) and H_2C=CH-COO(CH$_2$)$_5$OCOCH=CH$_2$ (0.01 g, 0.04 mmol), in a sealed tube. The reaction mixture was stirred at 98 °C for 72 h, cooled, filtered, diluted with EtOAc (20 mL), washed with water (2 × 30 mL) and brine (2 × 10 mL), dried (Na_2SO_4) and concentrated in vacuo. The resulting residue was purified (hexane/EtOAc 5.7:1) to afford **5** (0.034 g, 60%, based on **2**), as an oil.

R_f 0.20 (hexane/EtOAc 9:1); $[\alpha]_D$ −124.3 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 16.4 Hz, 1 H, -C*H*=CHCOO(CH$_2$)$_5$-), 7.33–7.18 (m, 18 H, aromatic), 7.10–7.08 (m, 2 H, aromatic), 6.39 (dd, *J* = 17.2, 1.2 Hz, 1 H, -CH=C*H*$_2$), 6.10 (dd, *J* = 17.2, 10.4 Hz, 1 H, -C*H*=CH$_2$), 5.93 (d, *J* = 16.4 Hz, 1 H, -CH=C*H*COO(CH$_2$)$_5$-), 5.80 (dd, *J* = 10.4, 1.2 Hz, 1 H,-CH=C*H*$_2$), 5.36 (s, 1 H, H-1), 4.67 (d, *J* = 12.4 Hz, 2 H, PhC*H*$_2$), 4.57 (d, *J* = 11.6 Hz, 2 H, PhC*H*$_2$), 4.45 (m, 3 H, PhC*H*$_2$), 4.33 (d, *J* = 11.6 Hz, 1 H, PhC*H*$_2$), 4.20–4.10 (band, 6 H, H-4, H-6, -OC*H*$_2$(CH$_2$)$_3$C*H*$_2$O-), 3.76 (dd, *J* = 8.4, 2.0 Hz, 1 H, H-5), 3.58 (dd, *J* = 10.6, 6.2, 1 H, H-7a), 3.53–3.50 (band, 4 H, H-7b, OMe), 1.73–1.66 (m, 4 H, -COOCH$_2$(C*H*$_2$)$_3$CH$_2$OCO-), 1.48–1.41 (m, 2 H, -COOCH$_2$-(C*H*$_2$)$_3$CH$_2$OCO-); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3 (C=O), 166.2 (C=O), 159.3 (C-3), 138.3 (-*C*H=CHCOO(CH$_2$)$_5$-), 138.1–136.3 (aromatic), 130.4 (-COO(CH$_2$)$_5$OCO-CH=*C*H$_2$), 128.5 (-OCOCH=*C*H$_2$), 128.4–127.5 (aromatic), 124.2 (C-2), 119.8

(-CH=*C*HCOO$(CH_2)_5$-), 100.0 (C-1), 80.0 (C-5), 76.6 (C-4), 73.0 (*C*H_2Ph), 72.9 (*C*H_2Ph), 72.1 (*C*H_2Ph), 71.2 (*C*H_2Ph), 71.1 (C-6), 70.9 (C-7), 64.3 (-COO*C*$H_2(CH_2)_3CH_2$OCO-), 63.9 (-COO$CH_2(CH_2)_3$*C*H_2OCO-), 55.4 (OMe), 28.3 (-COOCH_2(*C*H_2)$_3CH_2$OCO-), 28.2 (-COOCH_2(*C*H_2)$_3CH_2$OCO-), 22.4 (-COOCH_2(*C*H_2)$_3CH_2$OCO-); HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for 799.92; found, 800.17.

Methyl 2-deoxy-2-*C*-(2-phenylethenyl)-3,4,5,7-*tetra*-*O*-benzyl-*α*-D-arabino-hept-2-enoseptanoside (**6**). A solution of **2** (0.05 g, 0.07 mmol) in 1,4-dioxane (1 mL) was admixed with $Pd(OAc)_2$ (1 mg, 10 mol %) under a N_2 atmosphere, and was followed by addition of Cs_2CO_3 (0.03 g, 0.11 mmol) and styrene (0.01 mL, 0.09 mmol), in a sealed tube. The reaction mixture was stirred at 98 °C for 72 h, cooled, filtered, diluted with EtOAc (20 mL), washed with water (2 × 30 mL) and brine (2 × 10 mL), dried (Na_2SO_4) and concentrated in vacuo. The resulting residue was purified (hexane/EtOAc 9:1) to afford **6** (0.043 g, 74%), as an oil.

R_f 0.29 (hexane/EtOAc 9:1); $[\alpha]_D$ −54.6 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 23 H, aromatic), 7.19 (d, *J* = 16.8 Hz, 1 H, -C*H*=CHPh), 7.12–7.09 (m, 2 H, aromatic), 6.66 (d, *J* = 16.8 Hz, 1 H, -CH=C*H*Ph), 5.48 (s, 1 H, H-1), 4.72 (d, *J* = 12.8 Hz, 1 H, PhC*H*$_2$), 4.67–4.57 (m, 3 H, PhC*H*$_2$), 4.50 (d, *J* = 12.8 Hz, 2 H, PhC*H*$_2$), 4.38 (d, *J* = 12.0 Hz, 1 H, PhC*H*$_2$), 4.29–4.22 (band, 3 H, H-4, H-6 and PhC*H*$_2$), 3.76 (dd, *J* = 8.4, 2.4 Hz, 1 H, H-5), 3.65 (dd, *J* = 10.4, 6.4 Hz, 1 H, H-7a), 3.58 (s, 3 H, OMe), 3.54 (dd, *J* = 10.4, 2.8 Hz, 1 H, H-7b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (C-3), 138.3–137.1 (aromatic), 130.6 (-*C*H=CHPh), 128.4–127.3 (aromatic), 126.4 (C-2), 122.9 (-CH=*C*HPh), 100.6 (C-1), 80.3 (C-5), 77.8 (C-4), 72.9 (Ph*C*H_2), 72.8 (2 × Ph*C*H_2), 71.9 (Ph*C*H_2), 71.1 (C-6), 71.0 (C-7), 55.4 (OMe); HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for 691.3036; found, 691.3047.

Methyl 2-deoxy-2-*C*-phenyl-3,4,5,7-*tetra*-*O*-benzyl-α-D-*arabino*-hept-2-enoseptanoside (**8**). A solution of **2** (0.05 g, 0.07 mmol) in 1,4-dioxane (1 mL) was admixed with $Pd(OAc)_2$ (1 mg, 10 mol %) under a N_2 atmosphere, and was followed by addition of Cs_2CO_3 (0.03 g, 0.11 mmol) and phenylboronic acid (0.02 g, 0.15 mmol), in a sealed tube. The reaction mixture was stirred at 98 °C for 72 h, cooled, filtered, diluted with EtOAc (20 mL), washed with water (2 × 30 mL) and brine (2 × 10 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude reaction mixture was purified (hexane/EtOAc 9:1) to afford **8** (0.038 g, 79 %), as a gum.

R_f 0.45 (hexane/EtOAc 9:1); $[\alpha]_D$ −14.2 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.12 (m, 23 H, aromatic), 6.83 (d, *J* = 6.0 Hz, 2 H, aromatic), 5.41 (s, 1 H, H-1), 4.82 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 4.63 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 4.57 (d, *J* = 12.4 Hz, 2 H, PhCH_2), 4.50 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 4.39 (d, *J* = 11.2 Hz, 2 H, PhCH_2), 4.34–4.31 (m, 1 H, H-6), 4.28 (app. d, *J* = 12.0 Hz, 1 H, H-4), 4.24 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 3.80 (dd, *J* = 8.4, 1.6 Hz, 1 H, H-5), 3.66 (dd, *J* = 10.4, 6.0 Hz, 1 H, H-7a), 3.58 (dd, *J* = 10.4, 2.4 Hz, 1 H, H-7b), 3.31 (s, 3 H, OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (C-3), 138.4–136.8 (aromatic), 129.6 (aromatic), 129.0 (C-2), 128.3–126.7 (aromatic), 102.0 (C-1), 80.6 (C-5), 77.9 (C-4), 73.0 (Ph*C*H_2), 72.6 (Ph*C*H_2), 72.0 (Ph*C*H_2), 71.2 (Ph*C*H_2), 71.1 (C-6), 71.0 (C-7), 55.9 (OMe); HRMS–ESI (*m/z)*: $[M + Na]^+$ calcd for 665.2879; found, 665.2878.

Methyl 2-deoxy-2-*C*-(*m*-tolyl)-3,4,5,7-tetra-*O*-benzyl-α-D-*arabino*-hept-2-enoseptano-side (**10**). A solution of **2** (0.05 g, 0.07 mmol) in 1,4-dioxane (1 mL) was admixed with $Pd(OAc)_2$ (1 mg, 10 mol %) under a N_2 atmosphere, and was followed by addition of Cs_2CO_3 (0.03 g, 0.11 mmol) and 3-methylphenylboronic acid (0.010 g, 0.07 mmol), in a sealed tube. The reaction mixture was stirred at 98 °C for 72 h, cooled, filtered, diluted

with EtOAc (20 mL), washed with water (2 × 30 mL) and brine (2 × 10 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude reaction mixture was purified (hexane/EtOAc 9:1) to afford **10** (0.032 g, 61%), as an oil.

R_f 0.40 (hexane/EtOAc 9:1); $[\alpha]_D$ +10.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.14 (m, 20 H, aromatic), 7.05–6.99 (m, 2 H, aromatic), 6.85 (d, *J* = 6.8 Hz, 2 H, aromatic), 5.41 (s, 1 H, H-1), 4.80 (d, *J* = 12.4 Hz, 1 H, PhC*H*$_2$), 4.62 (d, *J* = 12.4 Hz, 1 H, PhC*H*$_2$), 4.56 (d, *J* = 12.4 Hz, 1 H, PhC*H*$_2$), 4.50 (d, *J* = 12.4 Hz, 1 H, PhC*H*$_2$), 4.40 (d, *J* = 9.6 Hz, 2 H, PhC*H*$_2$), 4.32–4.27 (m, 2 H, H-4, H-6), 4.25 (d, *J* = 11.6 Hz, 2 H, PhC*H*$_2$), 3.80 (dd, *J* = 8.8, 2.0 Hz, 1 H, H-5), 3.66 (dd, *J* = 10.4, 6.0 Hz, 1 H, H-7a), 3.58 (dd, *J* = 10.4, 2.4 Hz, 1 H, H-7b), 3.31 (s, 3 H, OMe), 2.29 (s, 3 H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0 (C-3), 138.4–136.6 (aromatic), 130.2 (aromatic), 129.2 (C-2), 128.9–126.4 (aromatic), 102.1 (C-1), 80.6 (C-5), 78.0 (C-4), 73.0 (Ph*C*H$_2$), 72.6 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.2 (C-6), 71.1 (C-7), 55.8 (OMe), 21.4 (Me); ESI-MS *m*/*z* $[M + Na]^+$ calcd for 679.3036; found, 679.3016.

Methyl 2-deoxy-2-*C*-(2-phenylethynyl)-3,4,5,7-*tetra*-*O*-benzyl-α-D-*arabino*-hept-2-enoseptanoside (11). A solution of **2** (0.05 g, 0.07 mmol) in DMF/THF/Et_3N 5:3:2 (1 mL) was admixed with $Pd(PPh_3)_2Cl_2$ (0.01 g, 20 mol %) under N_2 atmosphere, and was followed by addition of CuI (0.012 g, 10 mol %) and phenylacetylene (0.017 mL, 0.15 mmol), in a sealed tube. The reaction mixture was stirred at 98 °C for 72 h, cooled, filtered, diluted with EtOAc (20 mL), washed with water (2 × 30 mL) and brine (2 × 10 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude reaction mixture was purified (hexane/EtOAc 9:1) to afford **11** (0.039 g, 77%), as a semi-solid.

R_f 0.45 (hexane/EtOAc 9:1); $[\alpha]_D$ +22.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.23 (m, 23 H, aromatic), 7.08–7.06 (m, 2 H, aromatic), 5.39 (s, 1 H, H-1), 5.19 (d,

J = 11.6 Hz, 1 H, PhC*H*$_2$), 4.93 (d, *J* = 11.6 Hz, 1 H, PhC*H*$_2$), 4.75 (d, *J* = 12.2 Hz, 1 H, PhC*H*$_2$), 4.61 (d, *J* = 12.2 Hz, 1 H, PhC*H*$_2$), 4.48 (d, *J* = 11.8, 2 H, PhC*H*$_2$), 4.37 (d, *J* = 11.8 Hz, 1 H, PhC*H*$_2$), 4.33–4.22 (m, 3 H, H-4, H-6 and PhC*H*$_2$), 3.73 (app. d, *J* = 9.2 Hz, 1 H, H-5), 3.62 (dd, *J* = 10.4, 6.0 Hz, 1 H, H-7a), 3.53–3.49 (band, 4 H, H-7b, OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (C-3), 138.3–137.2 (aromatic), 131.3 (aromatic), 128.3–123.6 (aromatic), 108.4 (C-2), 100.5 (C-1), 95.8 (-*C*≡CPh), 85.2 (-C≡*C*Ph), 80.3 (C-5), 78.5 (C-4), 73.6 (Ph*C*H$_2$), 72.8 (Ph*C*H$_2$), 71.9 (Ph*C*H$_2$), 71.2 (Ph*C*H$_2$), 71.1 (C-6), 70.6 (C-7), 55.9 (OMe); HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for 689.2879; found, 689.2877.

Methyl 2-deoxy-2-*C*-(2-(*tert*-butoxycarbonyl)ethyl)-α-D-*glycero*-D-*ido*-septanoside (14). To a solution of **13** (0.017 g, 0.05 mmol) in MeOH (2 mL) was added $NaBH_4$ (0.003 g, 0.07 mmol) at 0 °C and the mixture was stirred for 3 h at rt. The solvents were then removed in vacuo, and the resulting residue was dissolved in EtOAc (2 × 15 mL), washed with brine (10 mL), dried (Na_2SO_4), concentrated in vacuo and purified ($CHCl_3$/MeOH 8 :2) to afford **14** (0.016 g, 93%), as a colorless oil.

R_f 0.3 (MeOH/$CHCl_3$ 8:2); $[\alpha]_D$ +21.5 (*c* 0.5, MeOH); ^{1}H NMR (400 MHz, D_2O) δ 4.50 (d, *J* = 6.8 Hz, 1 H, H-1), 4.24 (band, 2 H, H-6, H-7a), 3.77 (dd, *J* = 12.4, 4.8 Hz, 1 H, H-7b), 3.73–3.63 (app. ddd, *J* = 12.4, 9.6, 4. 8 Hz, 2 H, H-3, H-4), 3.49 (s, 3 H, OMe), 3.47–3.44 (br, 1 H, H-5), 2.47–2.34 (br, 2 H, -CH_2C*H*$_2$$CO_2$*t*-Bu), 1.89–1.78 (m, 3 H, H-2, -C*H*$_2$$CH_2$$CO_2$*t*-Bu), 1.49 (s, 9 H, *t*-Bu); ^{13}C NMR (100 MHz, D_2O) δ 175.4 (C=O), 103.7 (C-1), 82.5 (*C*-*t*-Bu), 78.7 (C-5), 73.1 (C-6), 70.3 (C-4), 70.1 (C-3), 61.9 (C-7), 55.4 (OMe), 42.6 (C-2), 33.0 (-CH_2*C*$H_2$$CO_2$*t*-Bu), 27.2 (*t*-Bu), 25.7 (-*C*$H_2$$CH_2$$CO_2$*t*-Bu); HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for 359.1682; found, 359.1680.

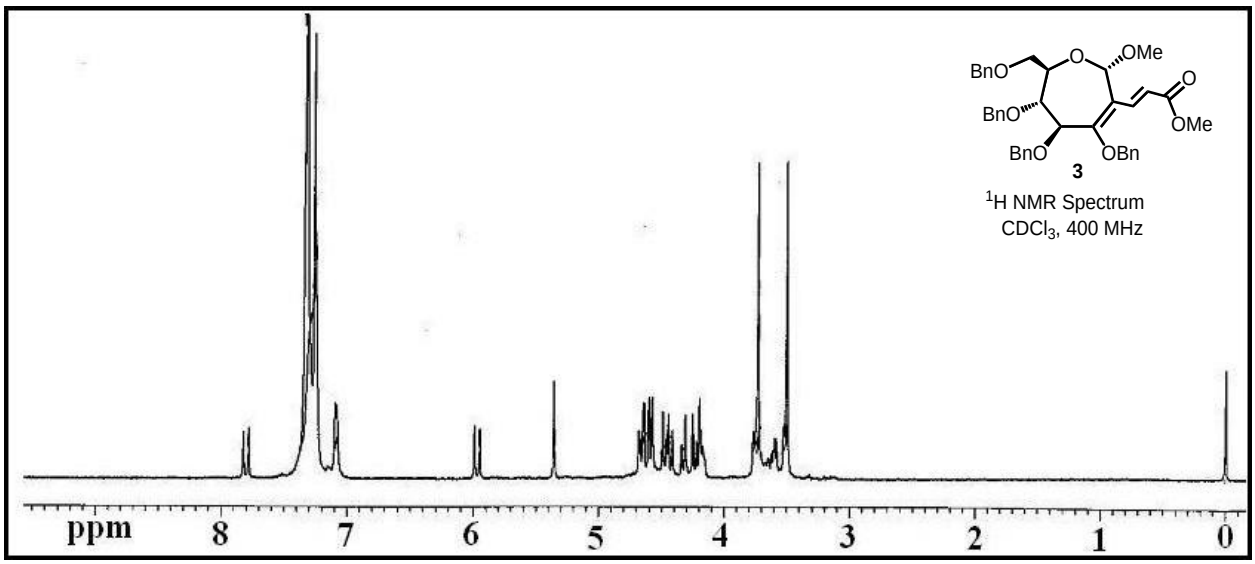

Figure 1: ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

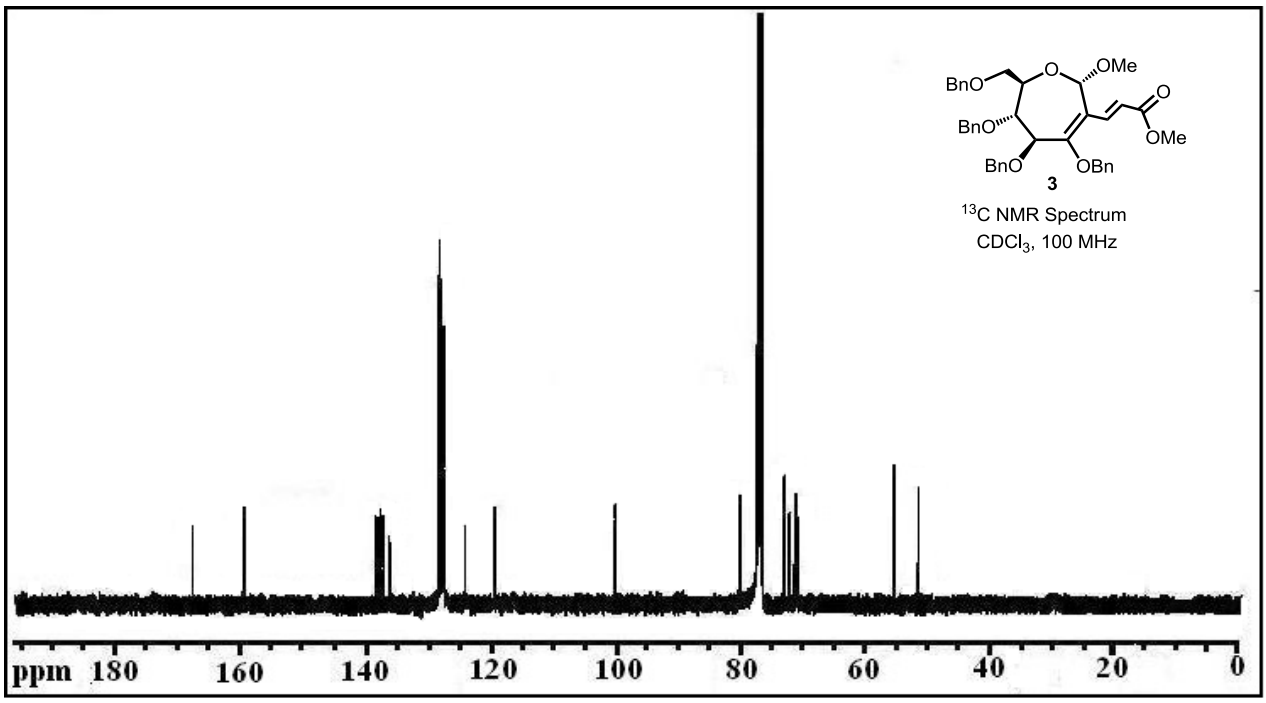

Figure 2: ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$).

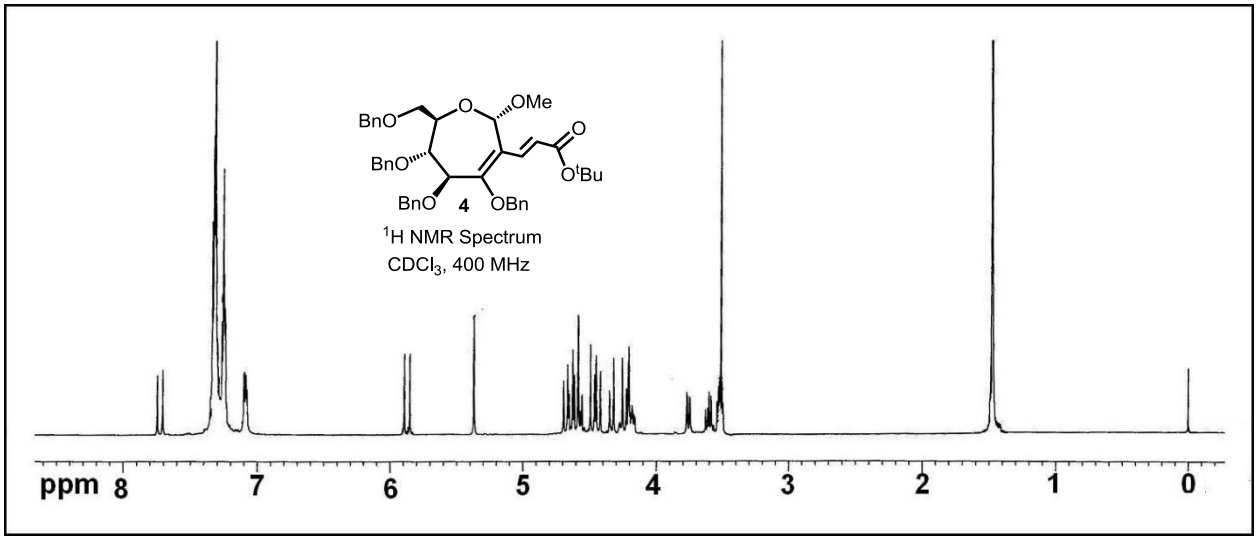

Figure 3: ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$).

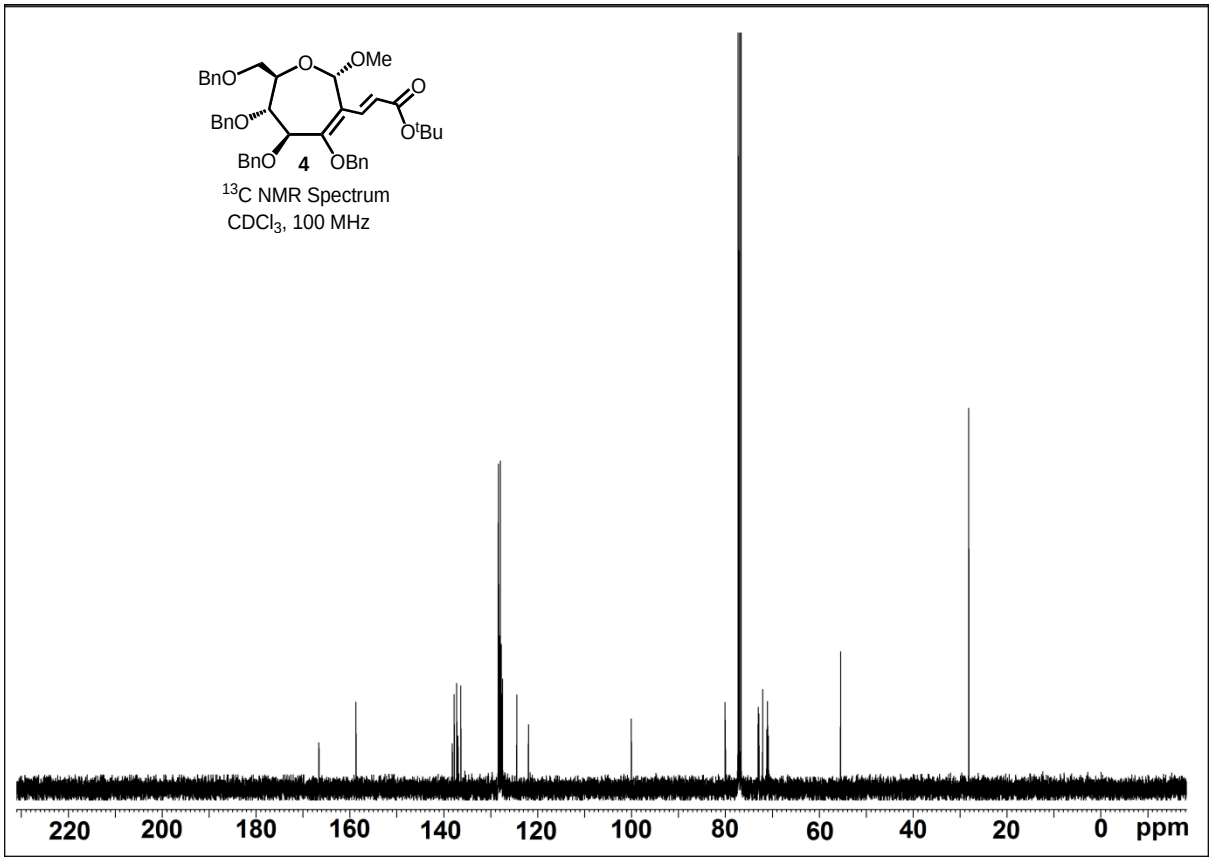

Figure 4: ^{13}C NMR spectrum of **4** (100 MHz, $CDCl_3$).

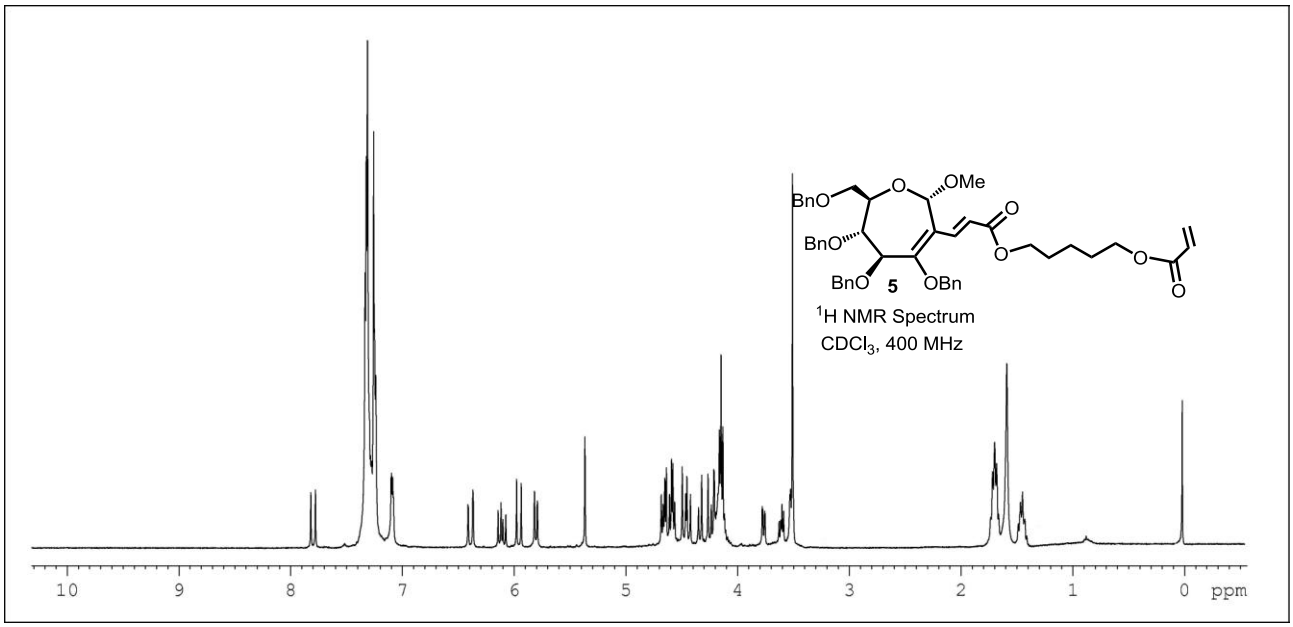

Figure 5: ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

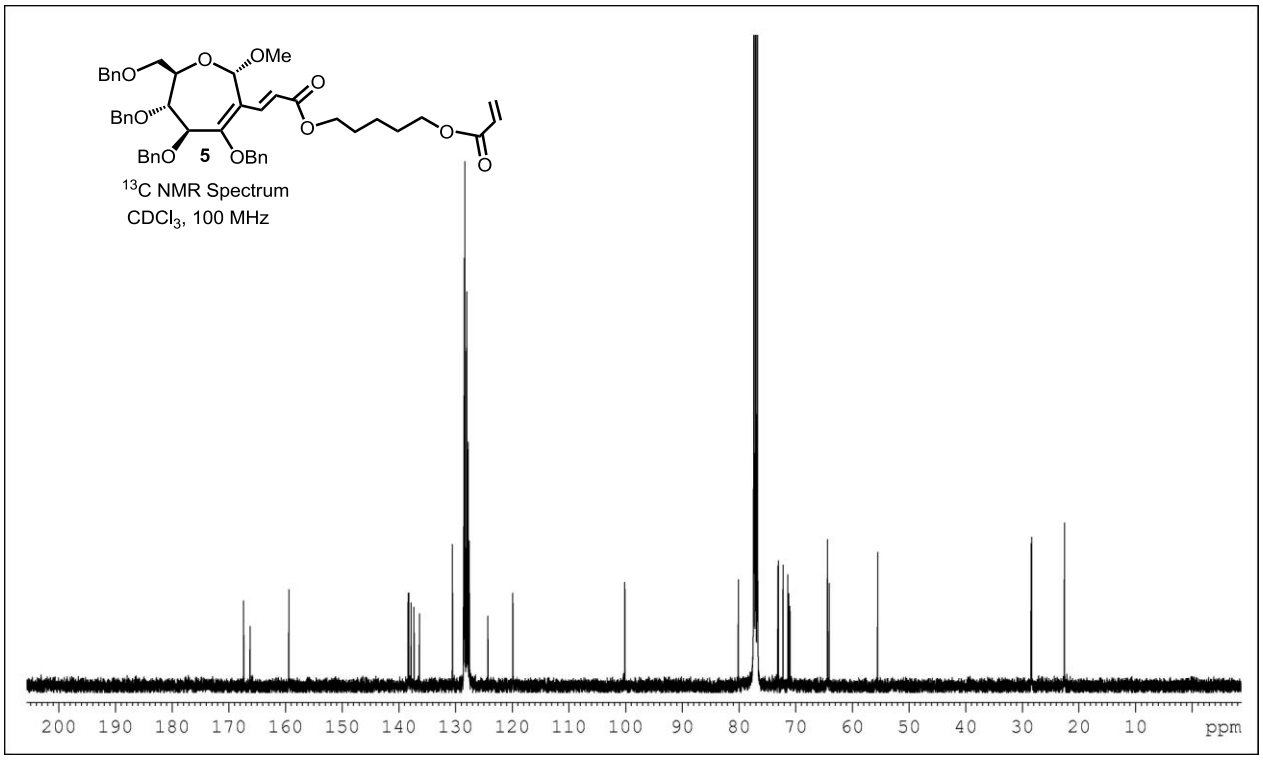

Figure 6: ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$).

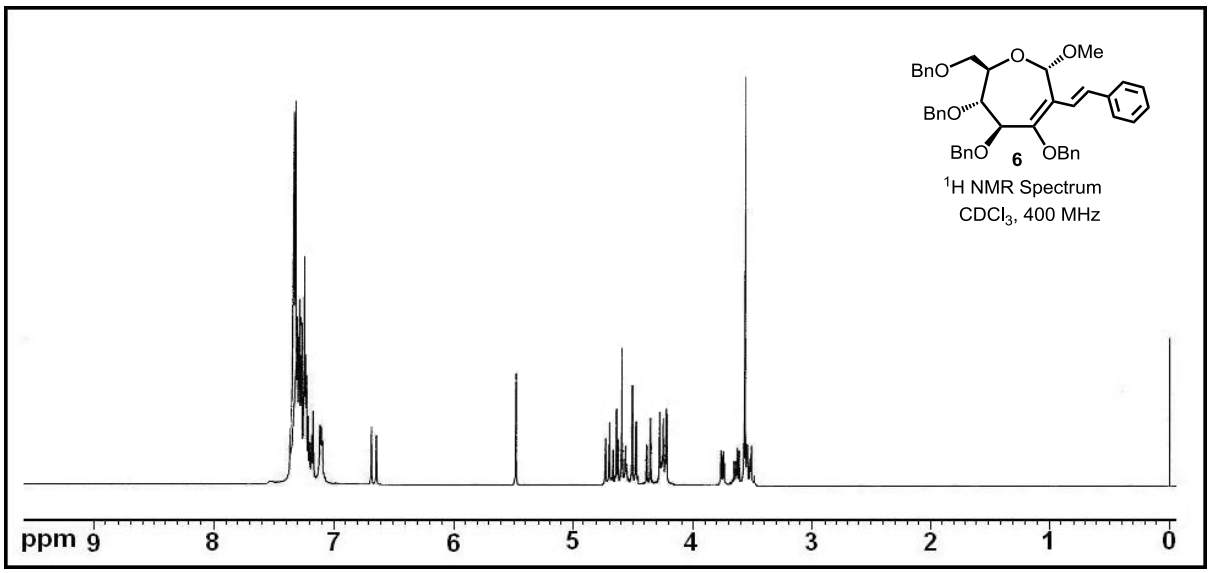

Figure 7: ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).

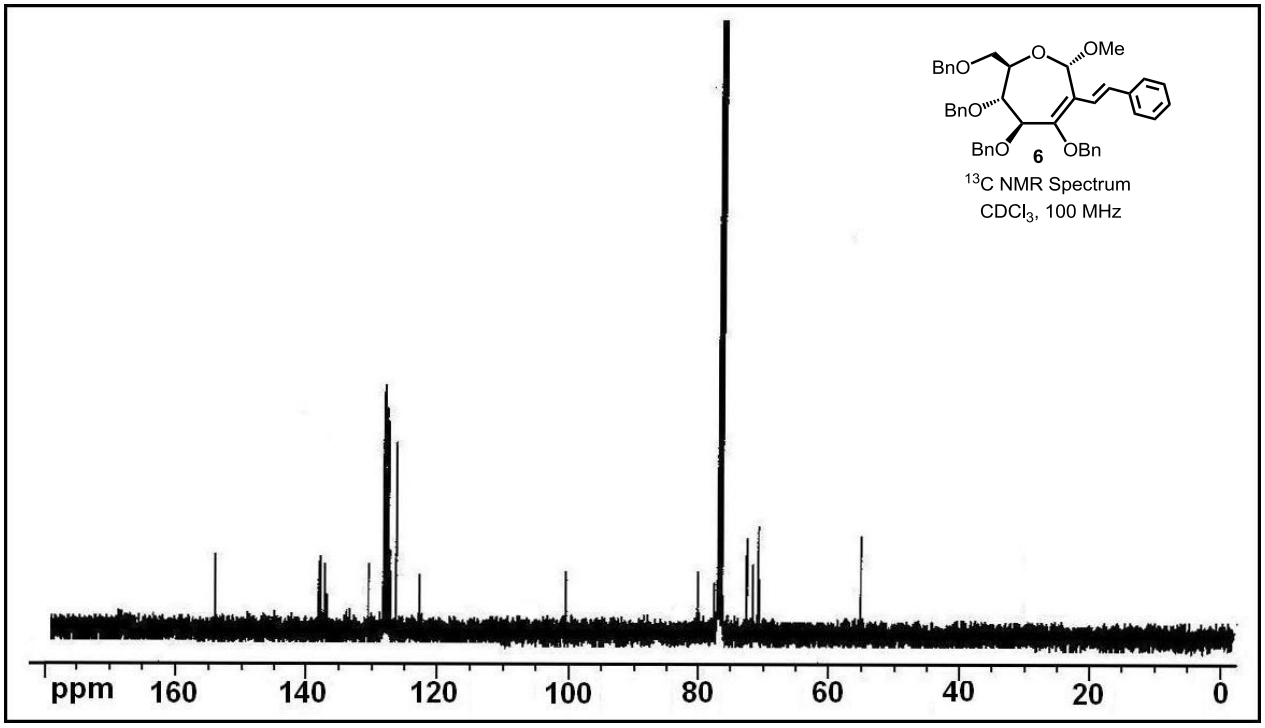

Figure 8: ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$).

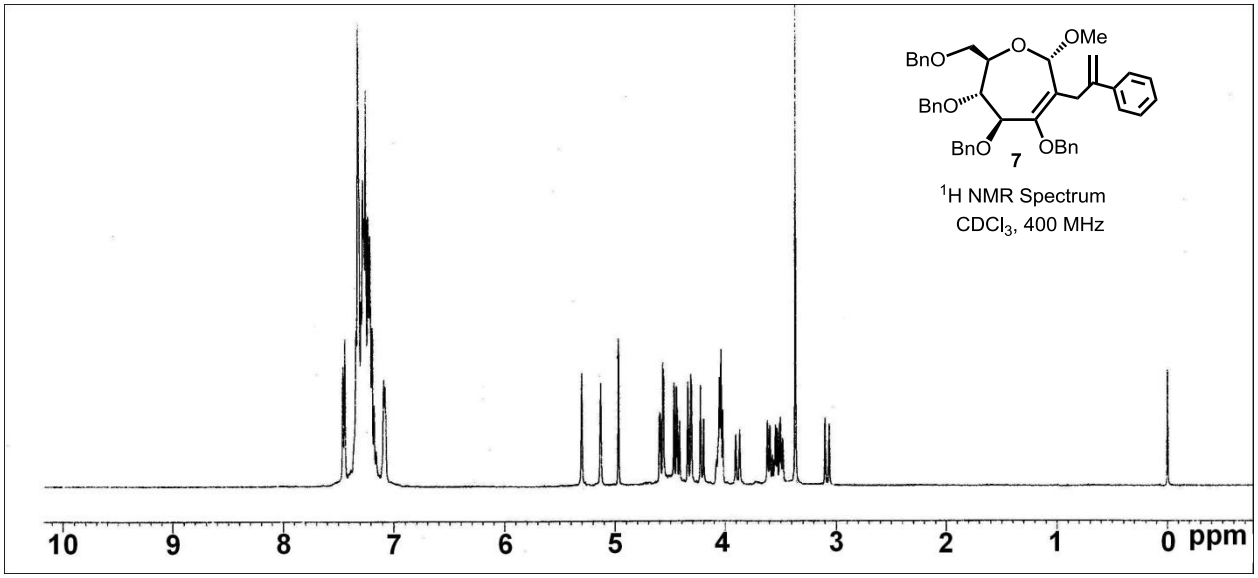

Figure 9: ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$).

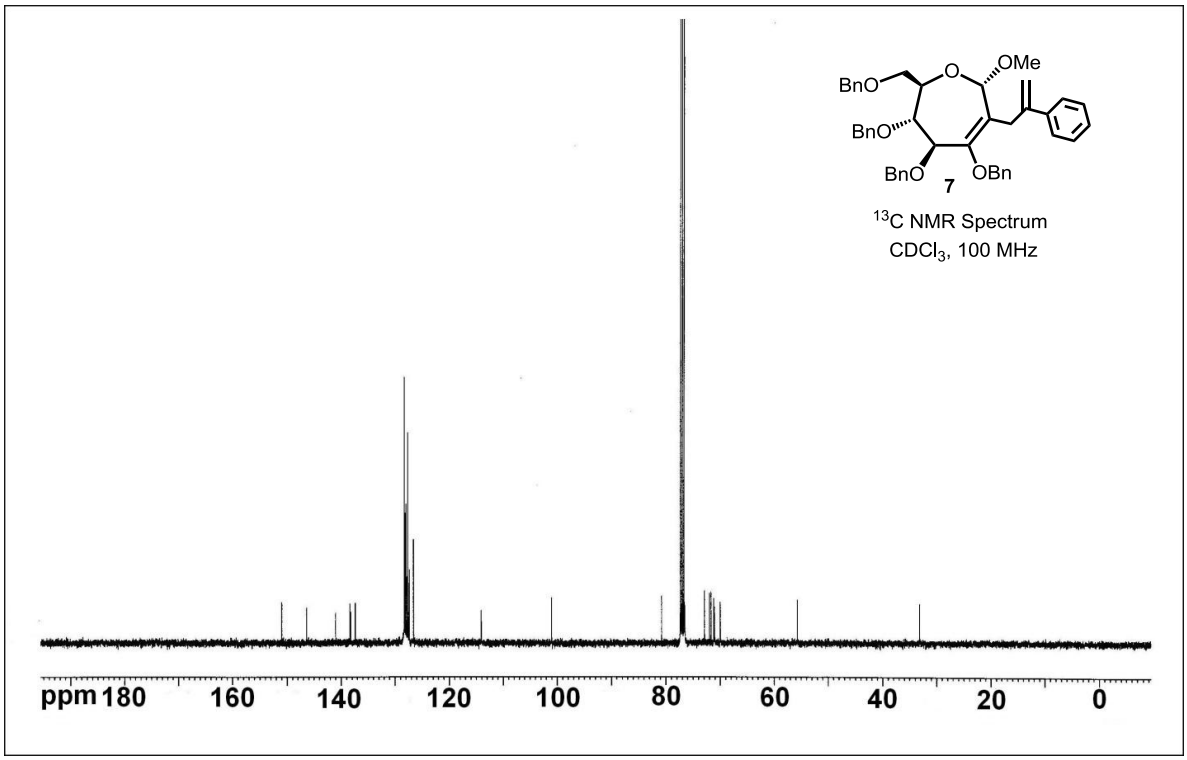

Figure 10: ^{13}C NMR spectrum of **7** (100 MHz, $CDCl_3$).

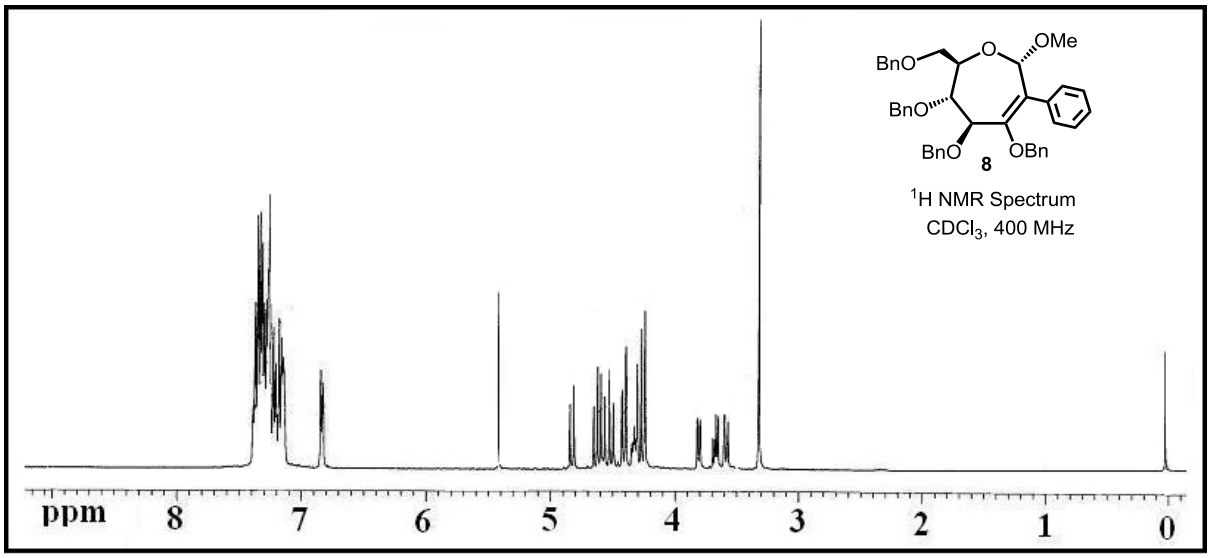

Figure 11: ^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$).

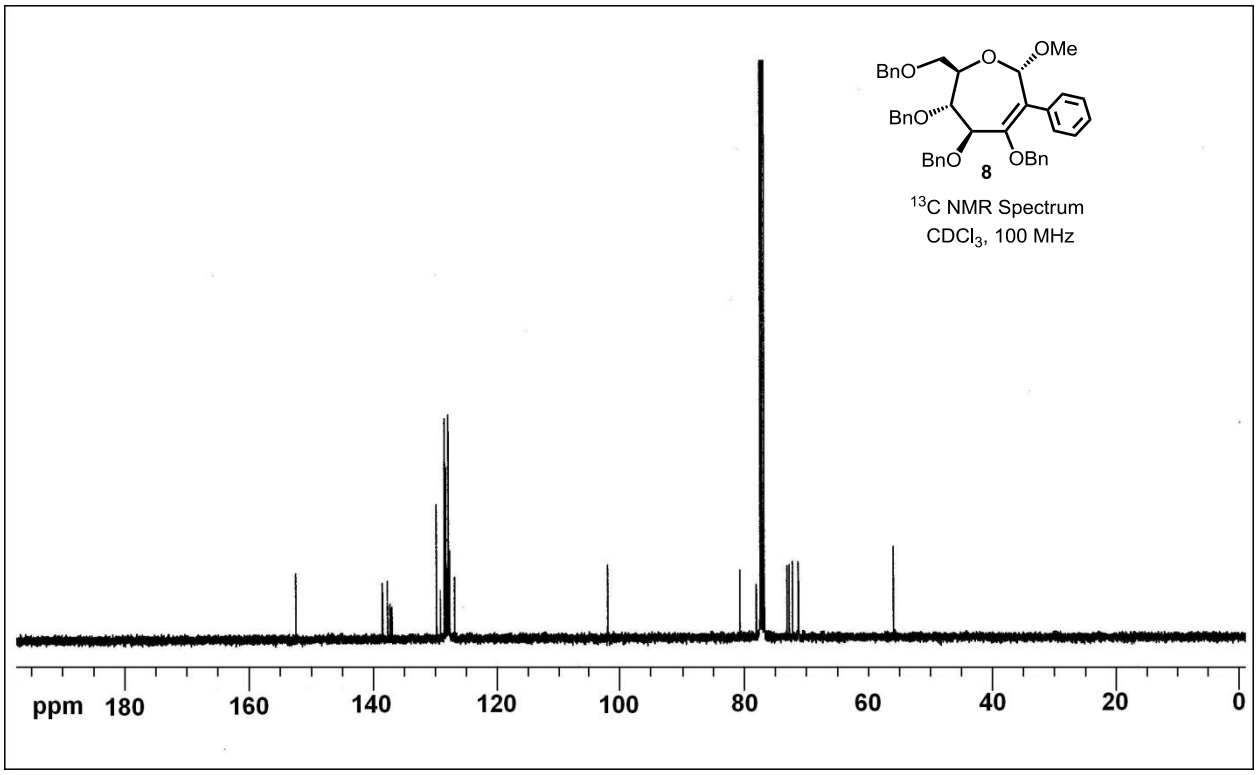

Figure 12: ^{13}C NMR spectrum of **8** (100 MHz, $CDCl_3$).

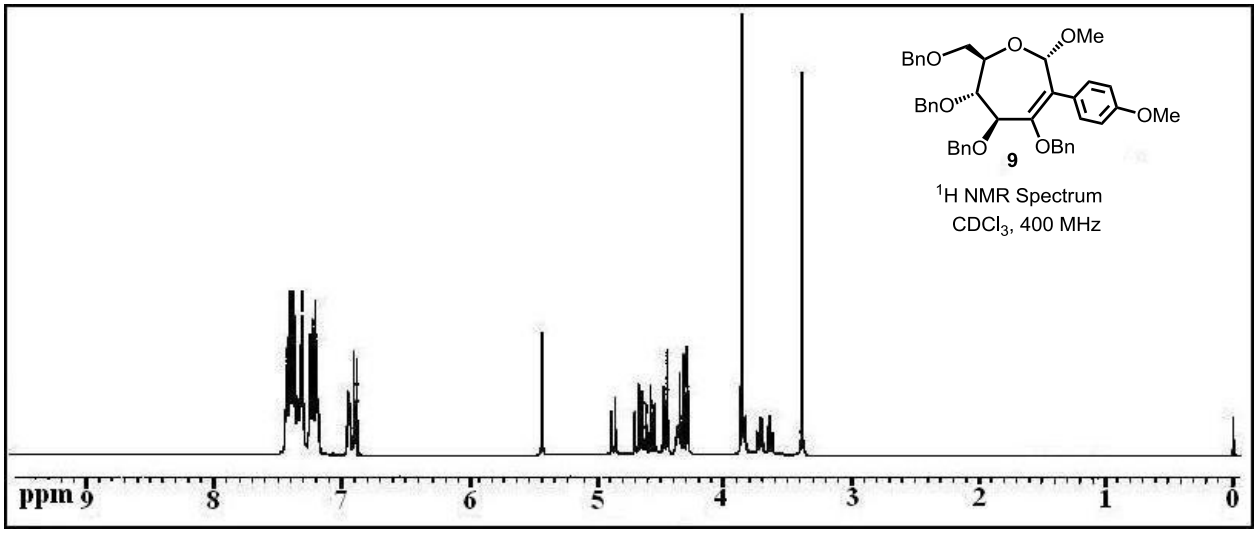

Figure 13: ^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$).

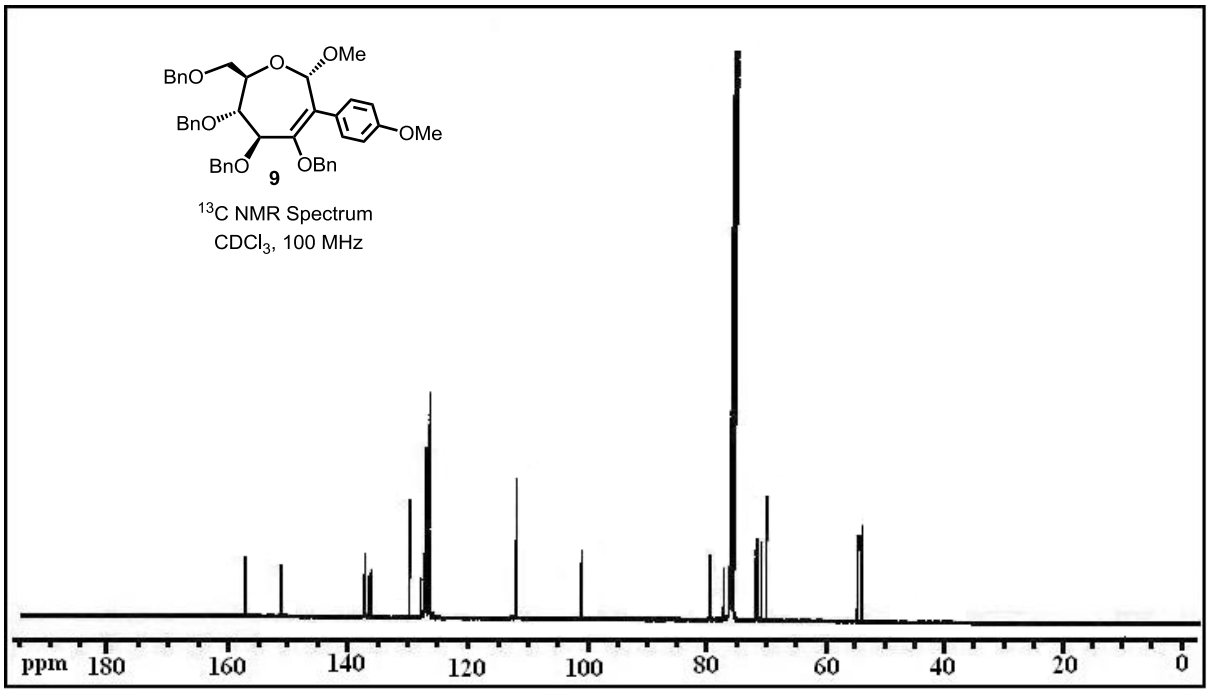

Figure 14: ^{13}C NMR spectrum of **9** (100 MHz, $CDCl_3$).

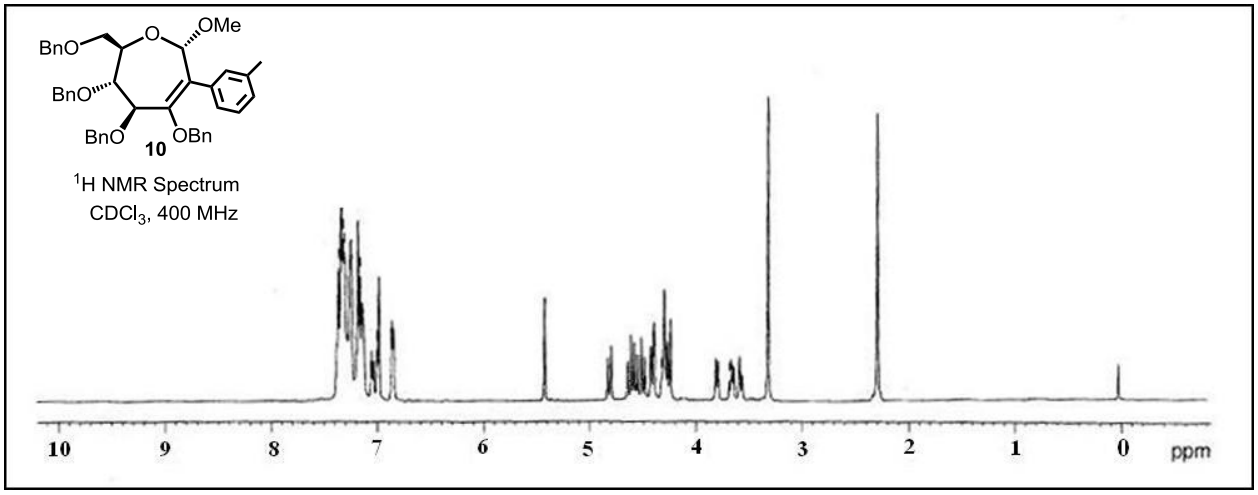

Figure 15: ^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$).

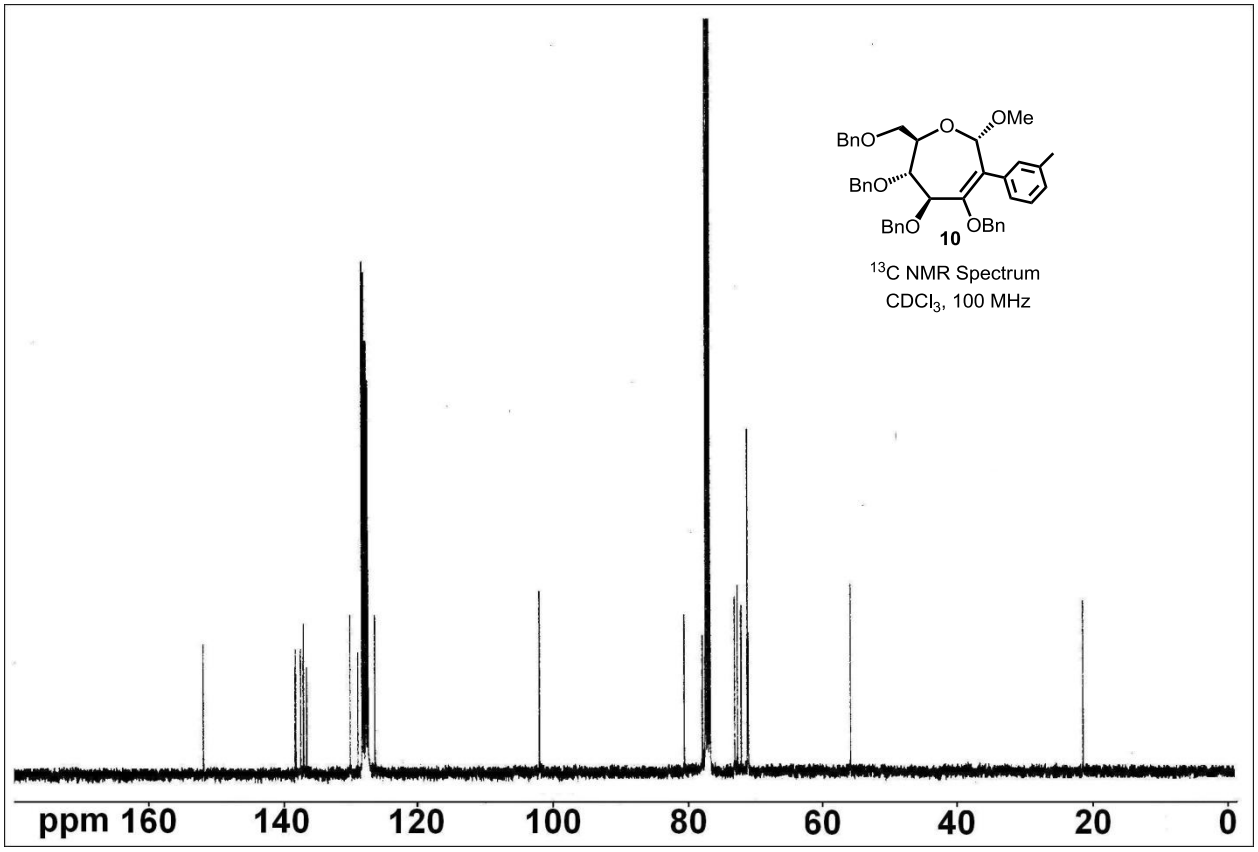

Figure 16: ^{13}C NMR spectrum of **10** (100 MHz, $CDCl_3$).

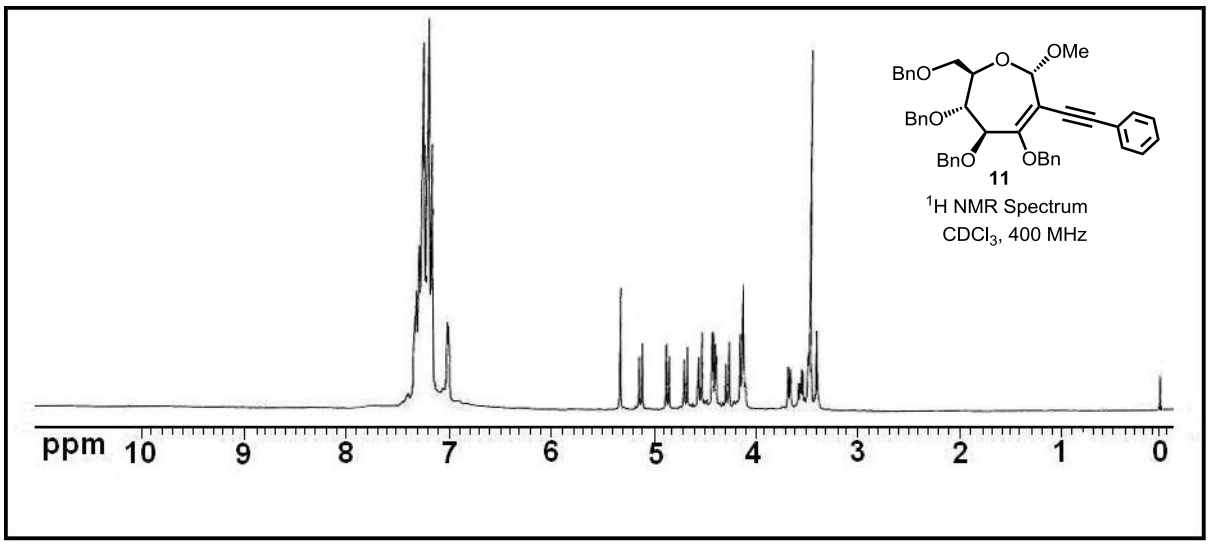

Figure 17: ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$).

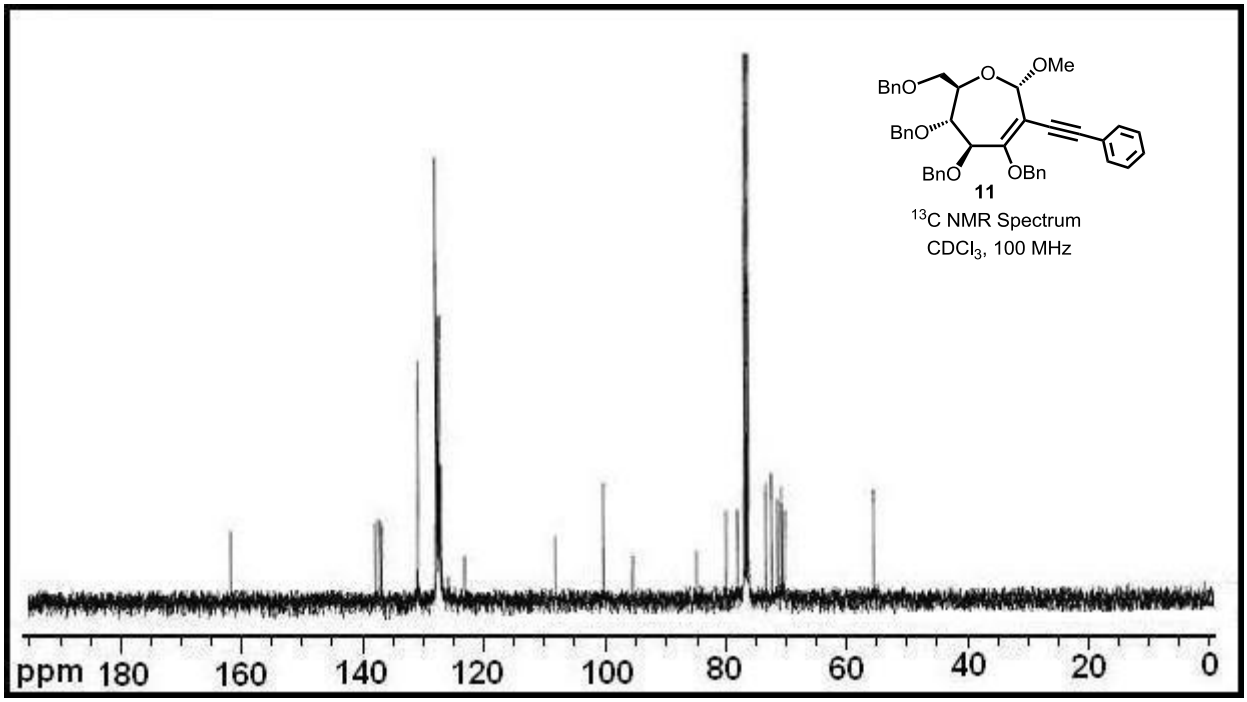

Figure 18: ^{13}C NMR spectrum of **11** (100 MHz, $CDCl_3$).

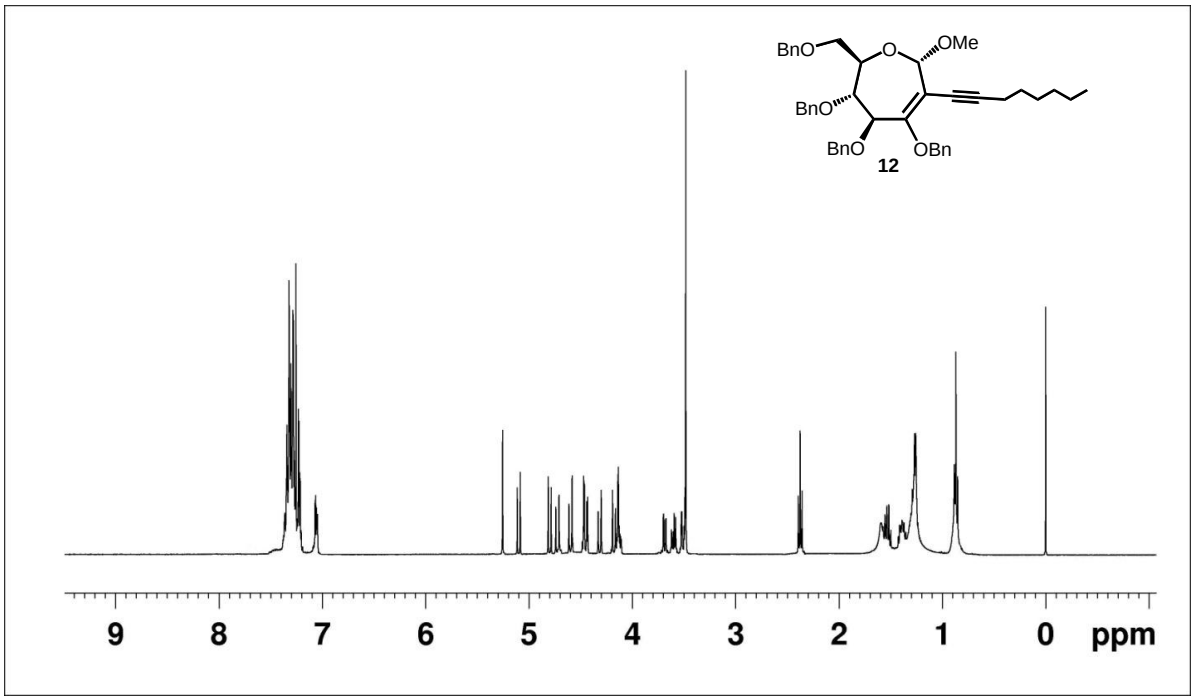

Figure 19: ^{1}H NMR spectrum of **12** (400 MHz, $CDCl_3$).

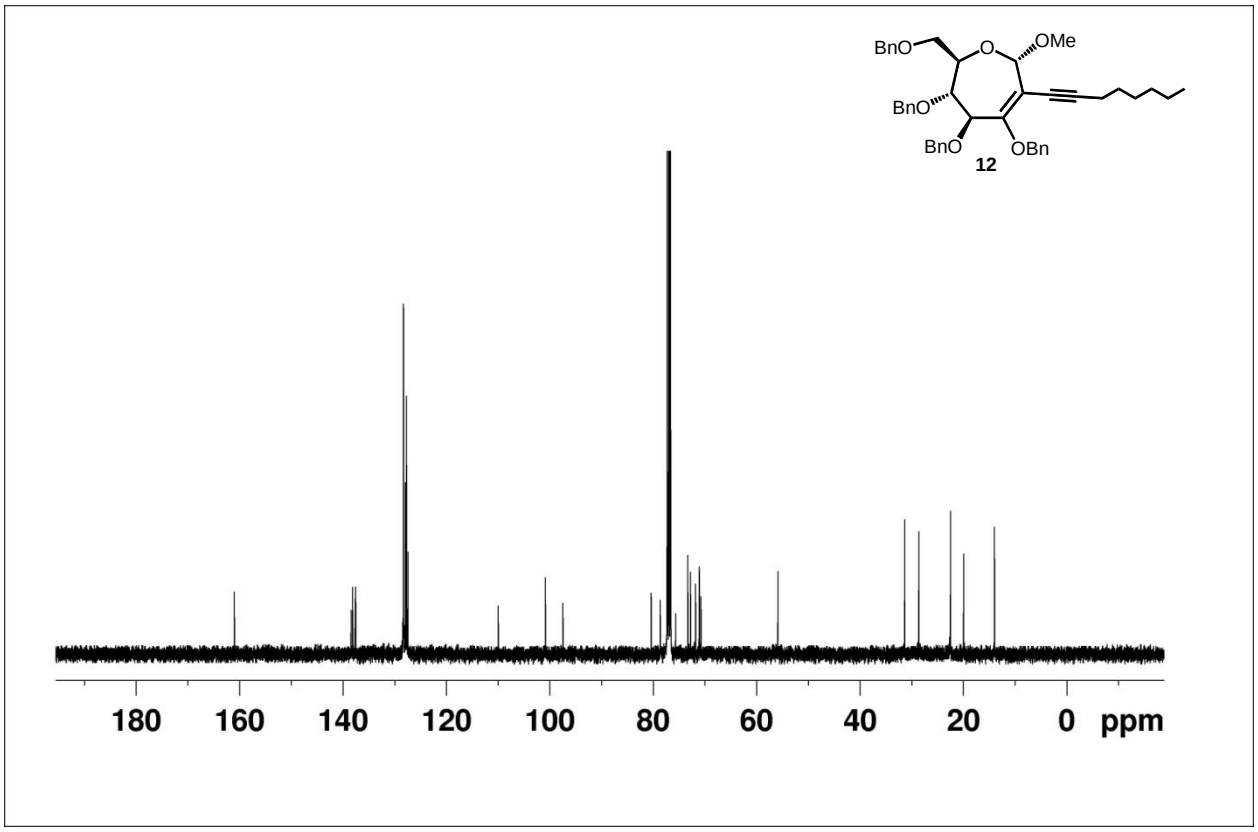

Figure 20: ^{13}C NMR spectrum of **12** (100 MHz, $CDCl_3$).

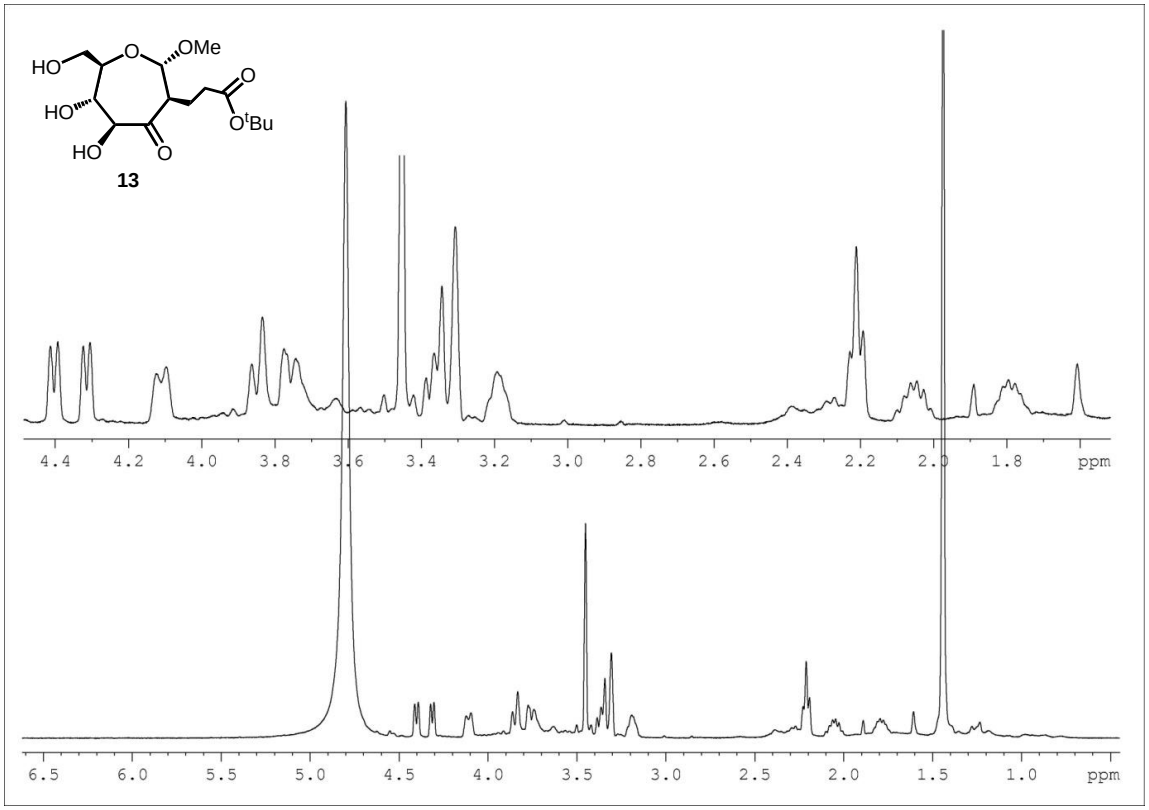

Figure 21: ^{1}H NMR spectrum of **13** (400 MHz, CD_3OD).

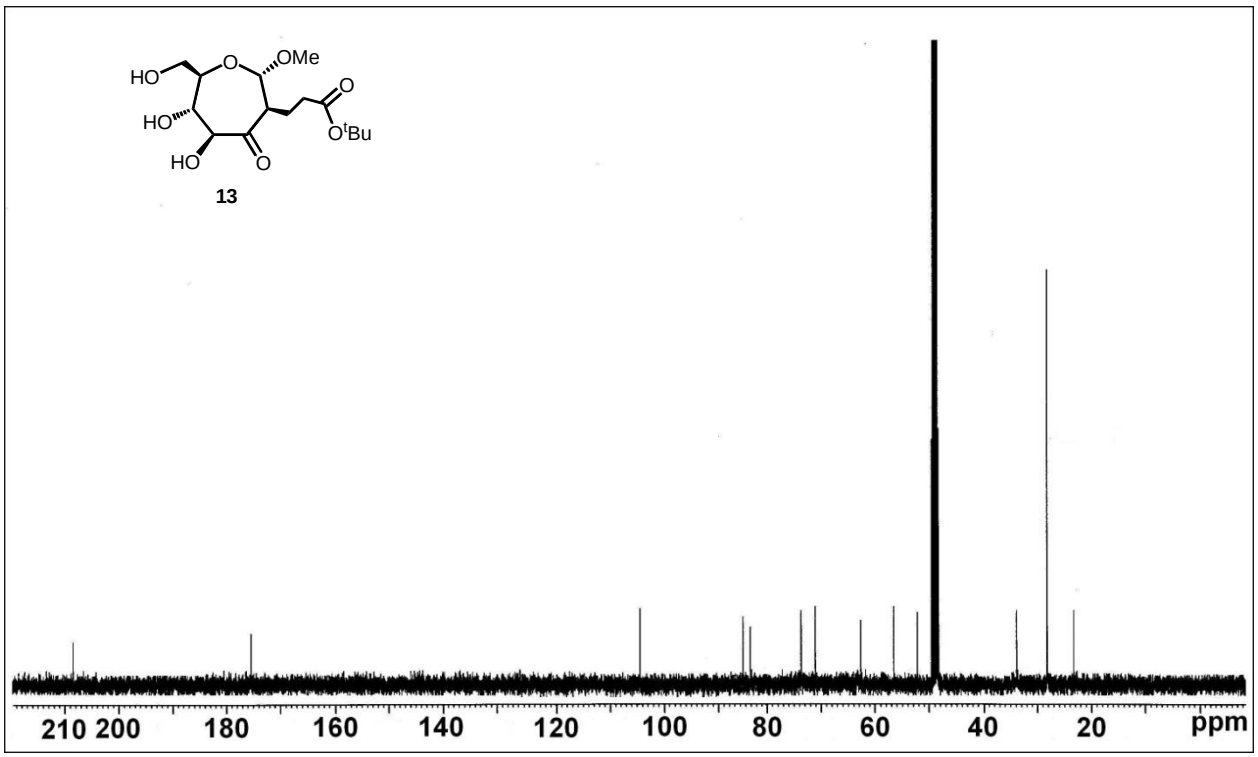

Figure 22: ^{13}C NMR spectrum of **13** (100 MHz, CD_3OD).

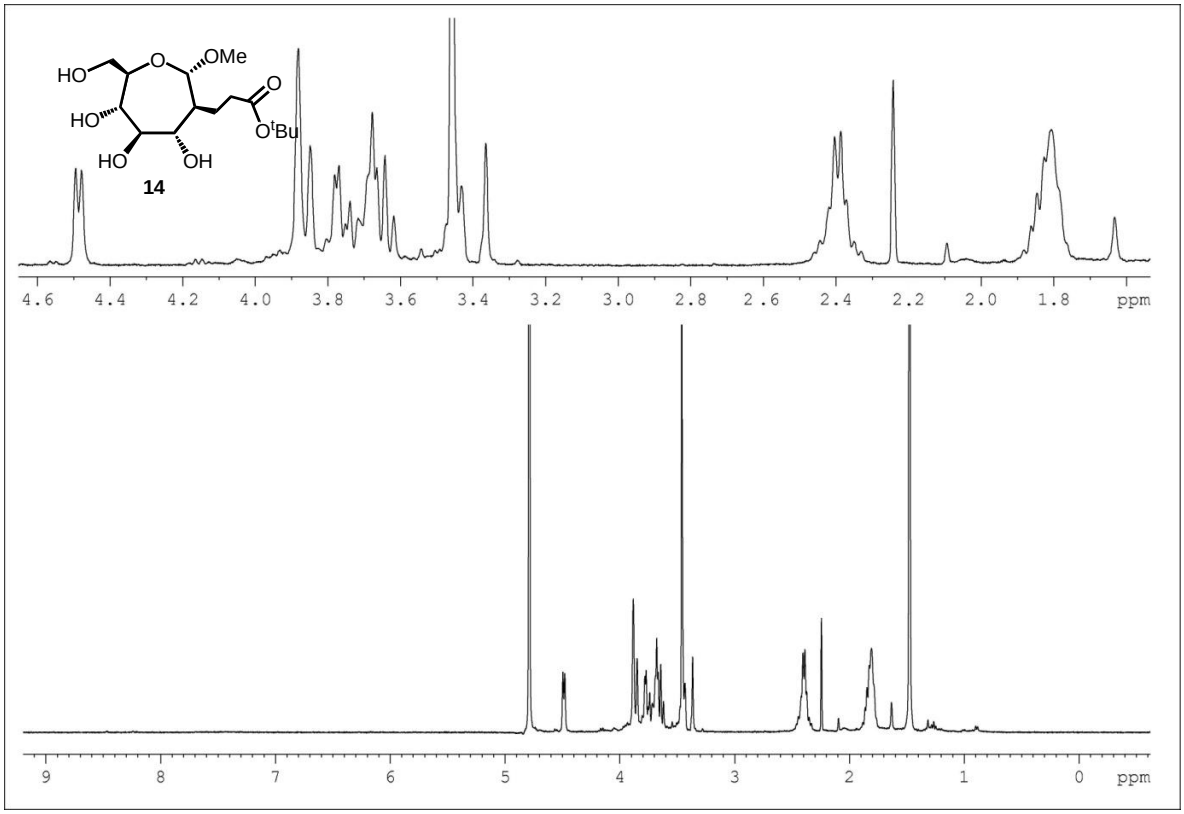

Figure 23: ^{1}H NMR spectrum of **14** (400 MHz, D_2O).

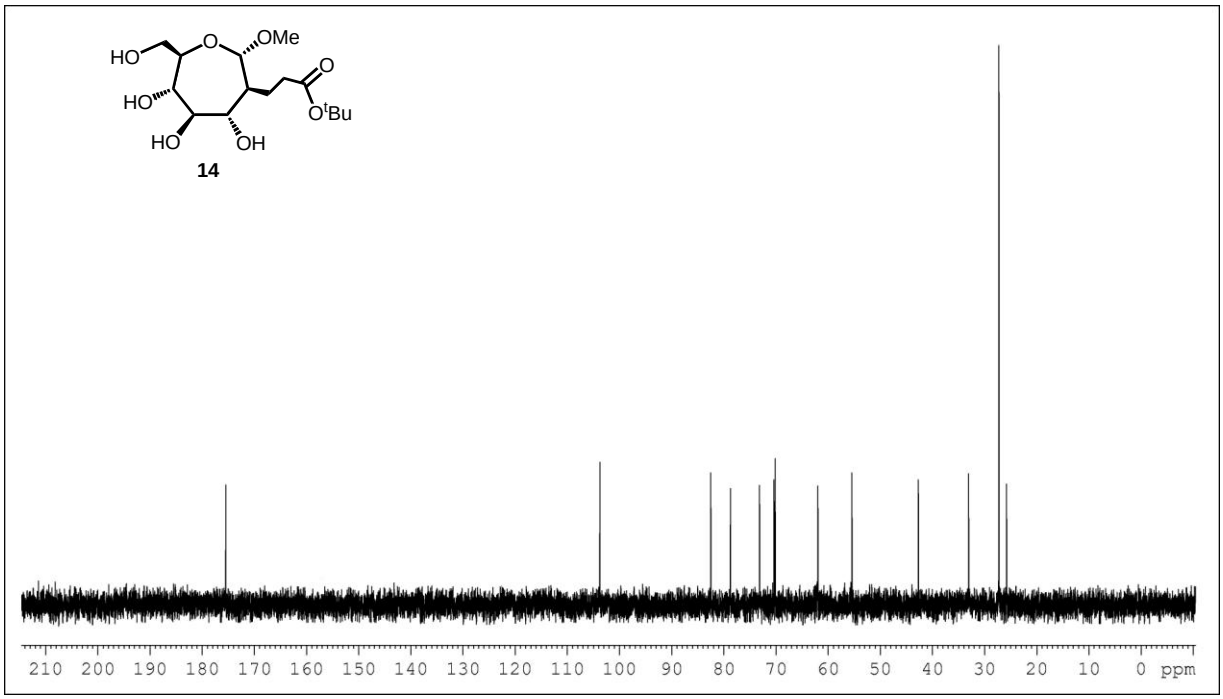

Figure 24: ^{13}C NMR spectrum of **14** (100 MHz, D_2O).

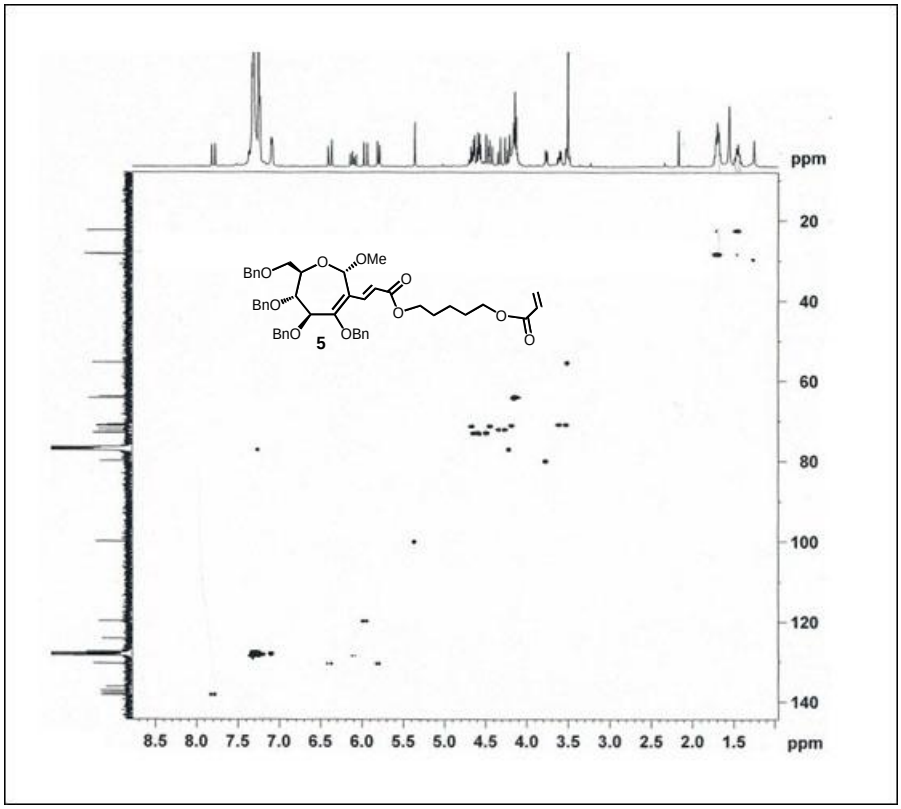

Figure 25: HSQC NMR spectrum of **5** (400 MHz, $CDCl_3$).

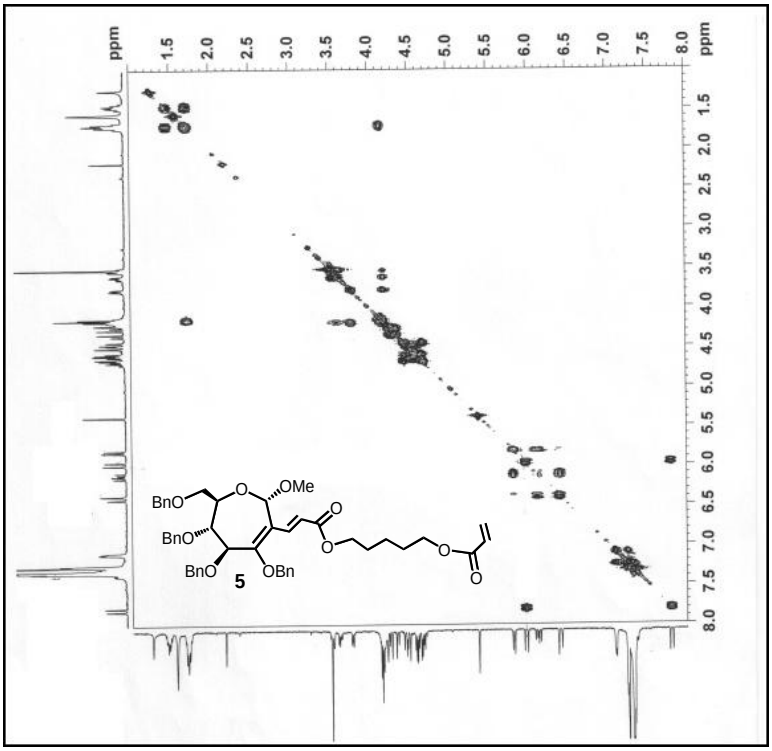

Figure 26: COSY NMR spectrum of **5** (400 MHz, $CDCl_3$).

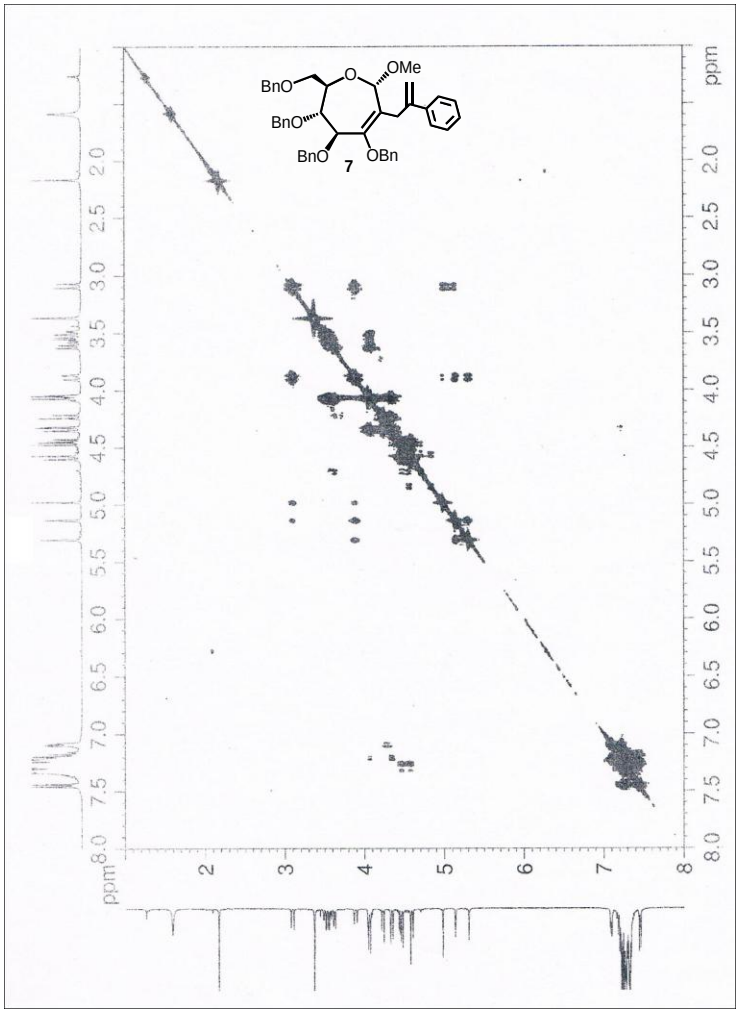

Figure 27: COSY NMR spectrum of **7** (400 MHz, $CDCl_3$).

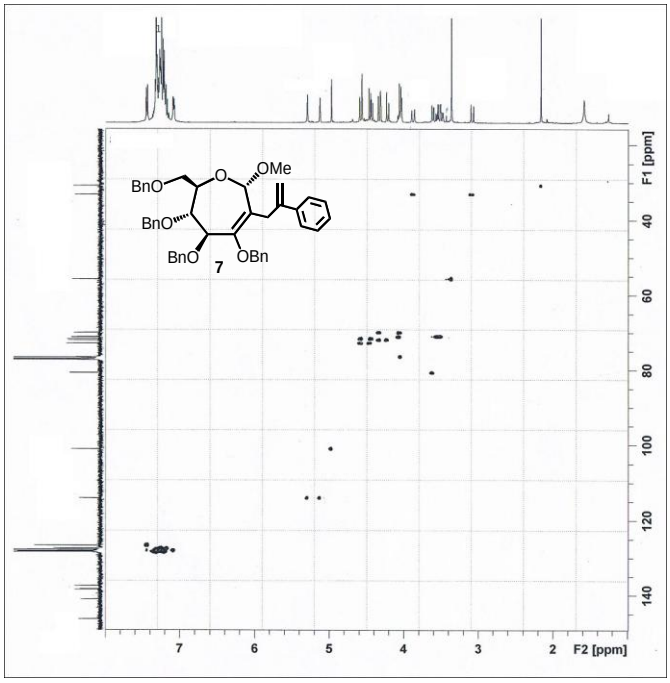

Figure 28: HSQC NMR spectrum of **7** (400 MHz, $CDCl_3$).

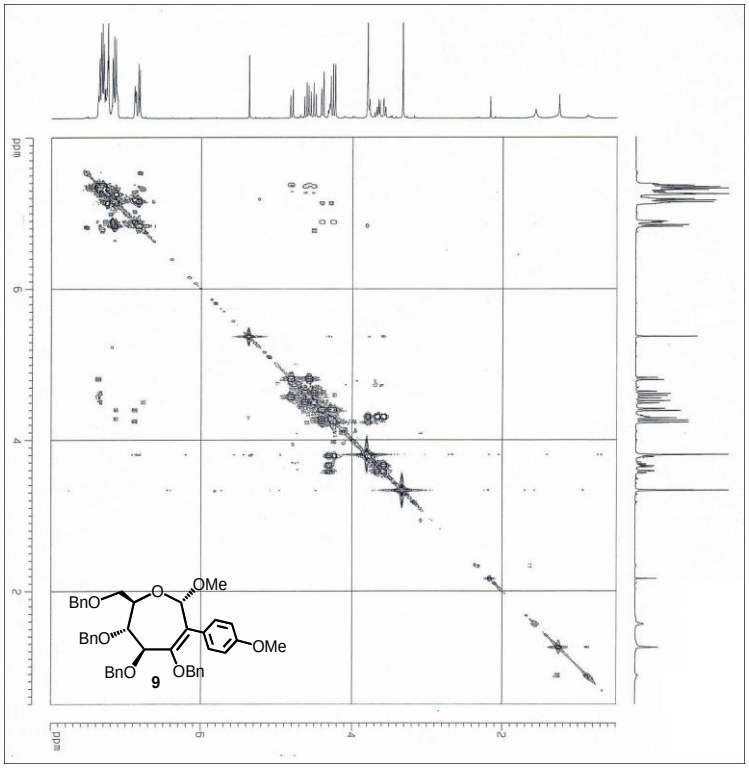

Figure 29: COSY NMR spectrum of **9** (400 MHz, $CDCl_3$).

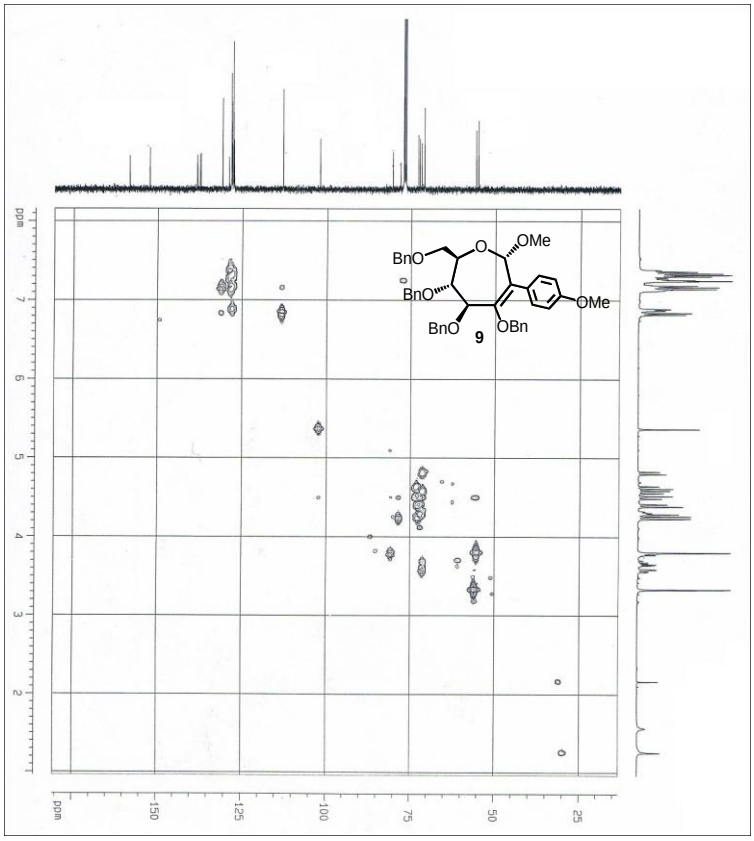

Figure 30: HSQC NMR spectrum of **9** (400 MHz, $CDCl_3$).

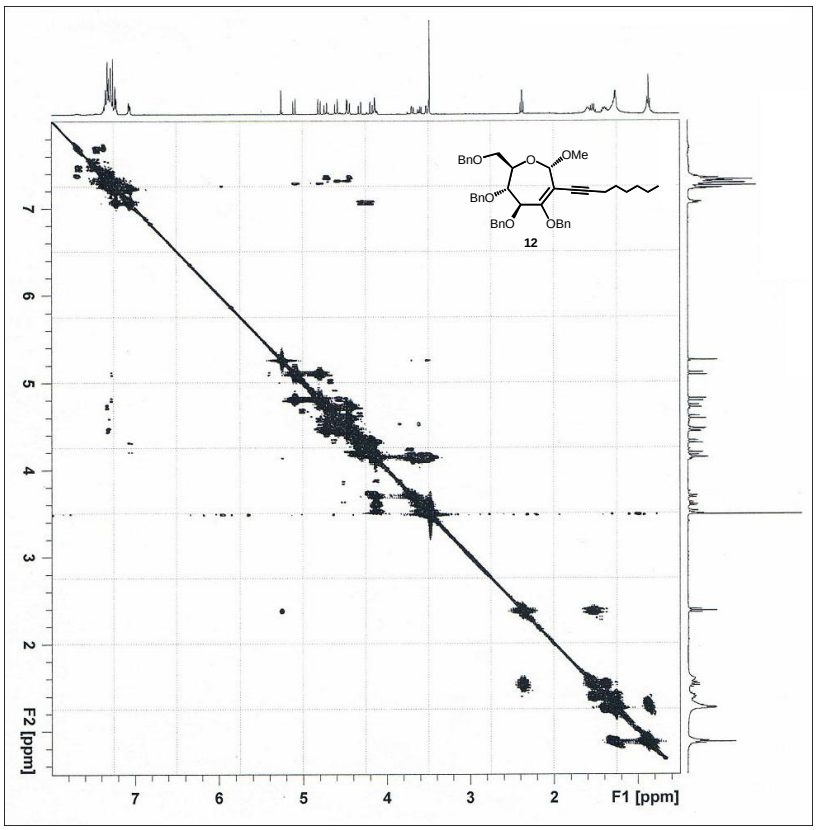

Figure 31: COSY NMR spectrum of **12** (400 MHz, $CDCl_3$).

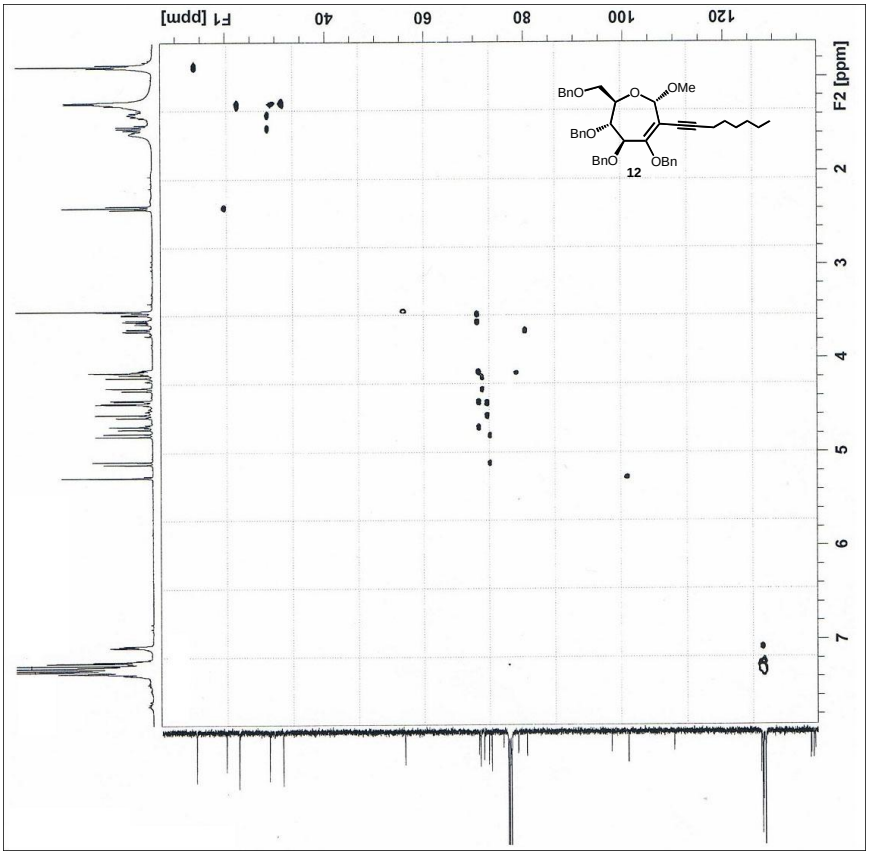

Figure 32: HSQC NMR spectrum of **12** (400 MHz, $CDCl_3$).

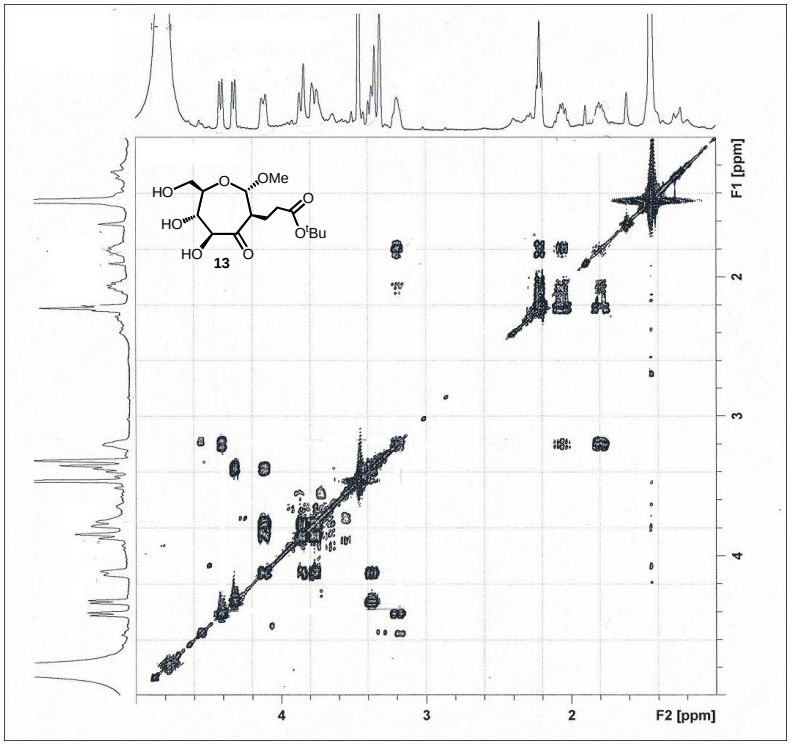

Figure 33: COSY NMR spectrum of **13** (400 MHz, CD_3OD).

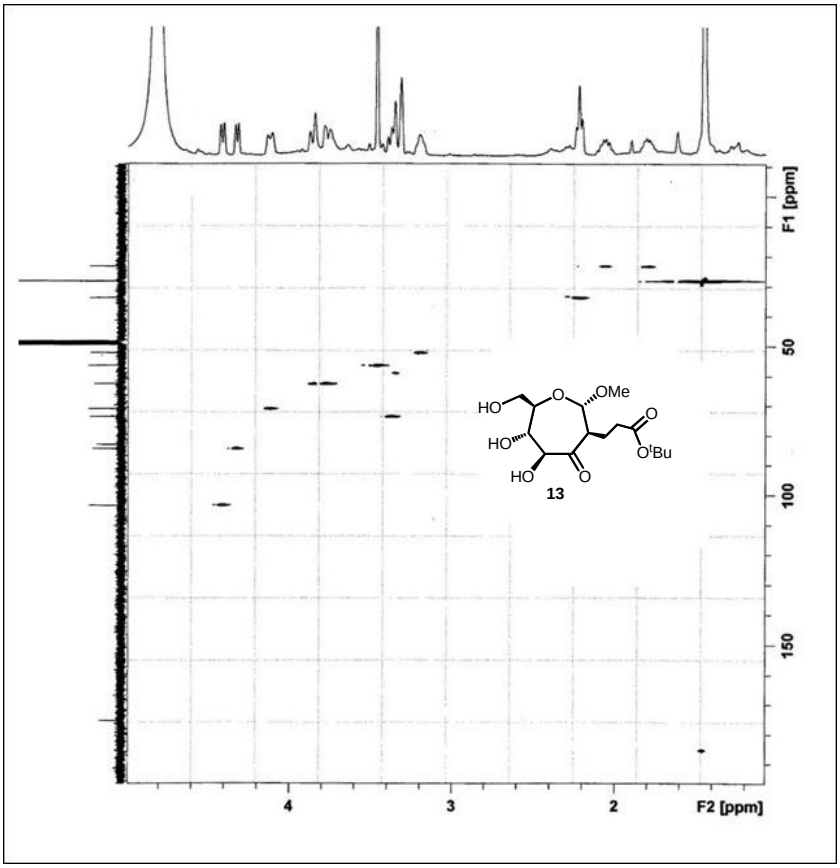

Figure 34: HSQC NMR spectrum of **13** (400 MHz, CD_3OD).

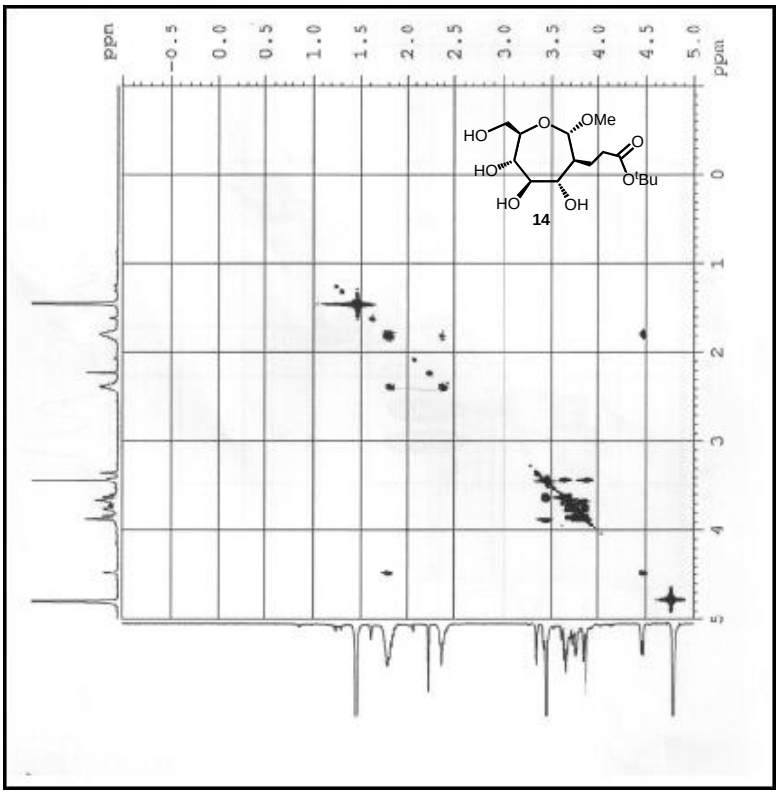

Figure 35: COSY NMR spectrum of **14** (400 MHz, D_2O).

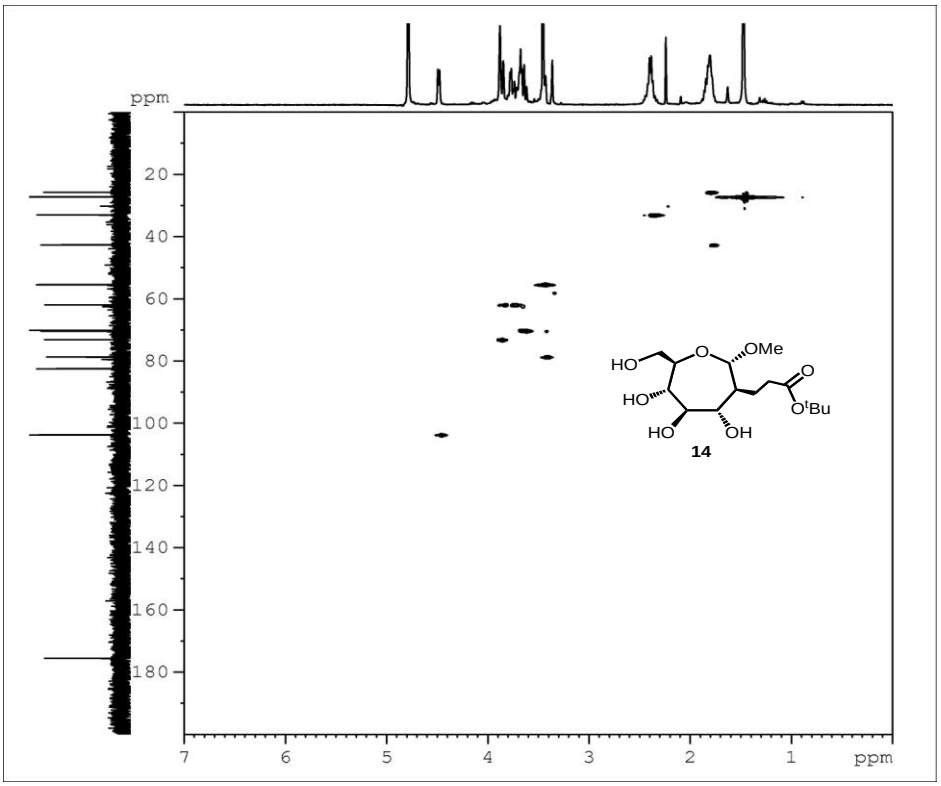

Figure 36: HSQC NMR spectrum of **14** (400 MHz, D_2O).

References

1. Ganesh, N. V.; Jayaraman, N. *J. Org. Chem.* **2007**, *72*, 5500–5504.