Supporting Information

The synthesis and ring opening metathesis polymerization of glycomonomers

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13th April 2016

Note added after first publication: This Supplementary Information file replaces that originally published on 29th March 2015. Correct enantiomeric structures for compounds **15-20** are now shown.

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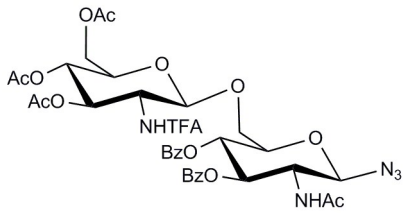
Experimental Procedures.

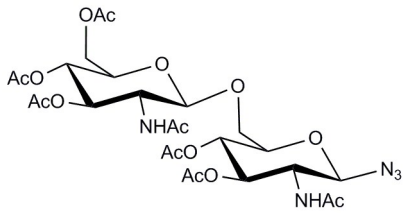
6-*O*-(2-Trifluoroacetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl]-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl azide (8)



N-Iodosuccinimide (74.0 mg, 3.29 x 10^{-4} mol) was added to a solution of ethyl 2-trifluoroacetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-D-glucopyranoside[1] (**12**, 0.10 g, 0.2 mmol) and 2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl azide[2] (**11**, 0.10 g, 0.2 mmol) in dry dichloromethane under anhydrous conditions. The red solution was stirred for 30 min before trimethylsilyl trifluoromethanesulfonate (4.0 μL, 0.02 mmol) was added. The reaction mixture was left to stir at room temperature for 22 h. Triethylamine (12.0 μL, 0.09 mmol) was added to quench the reaction mixture before the solvent was removed under reduced pressure. The crude product was purified using flash column chromatography over silica petroleum spirit (40-60 °C) with increasing quantities of diethyl ether as the eluent. The title compound **8** eluted in 100% diethyl ether and was dried to give an off white solid (0.16 g, 86%). R_f 0.32 (10% ethyl acetate/diethyl ether); mp. 118-120 °C (dec.); Elem. Anal.: Calc. for $C_{36}H_{38}F_3N_5O_{15}$: C, 51.62; H, 4.57; N, 8.36; found: C, 51.34; H, 4.49; N, 8.24; $[\alpha]_D^{21}$ -42.1° (*c* 0.19, CH_2Cl_2); λ_{abs} [CH_2Cl_2]/nm: 233 (log ε/$M^{-1}cm^{-1}$, 4.48), 276 (3.56), 283 (3.49); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.91 (s, 3H, NHCOC$\mathbf{H_3^I}$), 2.02 (s, 3H, OCOC$\mathbf{H_3}$), 2.05 (s, 3H, OCOC$\mathbf{H_3}$), 2.06 (s, 3H, OCOC$\mathbf{H_3}$), 3.51 (dd, 1H, $^2J_{6a,6b}$ 11.6, $J_{6a,5}$ 4.0 Hz, H-6_a^I), 3.65 (ddd, 1H, $J_{5,4}$ 9.6, $J_{5,6b}$ 4.8, $J_{5,6a}$ 2.4 Hz, H-5^{II}), 3.81 (q, 1H, $J_{2,3}$ 10.4, $J_{2,1}$ 8.8, $J_{2,NH}$ 8.8 Hz, H-2^I), 3.92 (ddd, 1H, $J_{5,4}$

10.0, $J_{5,6a}$ 4.0, $J_{5,6b}$ 2.0 Hz, H-5^{I}), 4.10 (dd, 1H, $^{2}J_{6a,6b}$ 12.4, $J_{6a,5}$ 2.4 Hz, H-6$_{a}^{II}$), 4.18-4.25 (m, 3H, H-2^{II}, H-6$_{b}^{I}$, H-6$_{b}^{II}$), 4.50 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1^{II}), 5.12 (t, 1H, $J_{4,5}$ 9.6, $J_{4,3}$ 9.2 Hz, H-4^{II}), 5.13 (d, 1H, $J_{1,2}$ 9.2 Hz, H-1^{I}), 5.19 (t, 1H, $J_{3,2}$ 10.4, $J_{3,4}$ 9.2 Hz, H-3^{II}), 5.44 (t, 1H, $J_{4,5}$ 9.6, $J_{4,3}$ 9.6 Hz, H-4^{I}), 5.68 (d, 1H, $J_{NH,2}$ 8.0 Hz, N**H**COCH$_3^{I}$), 5.86 (t, 1H, $J_{3,2}$ 9.6, $J_{3,4}$ 9.6 Hz, H-3^{I}), 7.30 (d, 1H, $J_{NH,2}$ 8.8 Hz, N**H**COCF$_3^{II}$), 7.34-7.41 (AA'BB'C, 4H, Ph-H), 7.49-7.57 (AA'BB'C, 2H, Ph-H), 7.87-7.93 (AA'BB'C, 4H, Ph-H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 20.5 (OCO**C**H$_3$), 20.6 (OCO**C**H$_3$), 20.7 (OCO**C**H$_3$), 23.3 (NHCO**C**H$_3$), 54.5 (C-2^{II}), 55.2 (C-2^{I}), 61.7 (C-6^{II}), 67.9 (C-6^{I}), 68.0 (C-4^{II}), 69.0 (C-4^{I}), 71.8 (C-3^{I}), 72.2 (C-5^{II}), 72.6 (C-3^{II}), 75.1 (C-5^{I}), 88.2 (C-1^{I}), 101.3 (C-1^{II}), 114.4, 117.3 (NHCO**C**F$_3$), 128.1 (Ph-C-), 128.4 (Ph-C-), 128.5 (Ph-CH), 128.6 (Ph-CH), 129.8 (Ph-CH), 130.0 (Ph-CH), 133.7 (Ph-CH), 134.1 (Ph-CH), 157.3, 157.7, (NH**C**OCF$_3$), 165.9 (O**C**OPh), 166.3 (O**C**OPh), 169.2 (O**C**OCH$_3$), 170.66 (NH**C**OCH$_3^{I}$), 170.70 (O**C**OCH$_3$), 170.8 (O**C**OCH$_3$); HRESIMS: Calc. for $C_{36}H_{38}F_3N_5NaO_{15}^{+}$ $[M+Na]^{+}$ *m/z* = 860.2209, found: 860.2228; IR (cm^{-1}): 3360, 2970, 2123, 1717, 1217, 1027, 711.

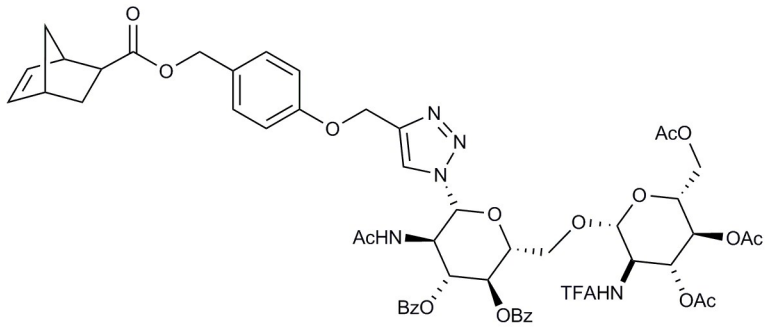
6-*O*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl azide (9)[3]



A solution of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride[4] (**14**, 27.9 mg, 0.08 mmol), 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl azide[3] (**13**, 25.2 mg, 0.08 mmol), and benzyltriethylammonium chloride (8.7 mg, 0.04 mmol) in dry chloroform (1 mL) was heated at reflux under anhydrous conditions for 18 h. After this time, the reaction

mixture was cooled to room temperature and diluted with chloroform (1 mL). This solution was filtered through a Strata-X-C solid phase extraction cartridge that was washed further with chloroform. The solvent was removed from the combined eluent under reduced pressure. The crude product was purified using preparative scale reverse-phase HPLC (t_R (1) = 20.1 min, low pressure gradient from 20% solvent B) and the fractions containing the title product **9**[3] were combined and dried to give a white solid (5.0 mg, 10%, isolated yield). R_f 0.11 (100% ethyl acetate); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.99 (s, 6H, 2 x NHCOC**H$_3$**), 2.04 (s, 3H, OCOC**H$_3$**), 2.05 (s, 3H, OCOC**H$_3$**), 2.06 (s, 3H, OCOC**H$_3$**), 2.08 (s, 3H, OCOC**H$_3$**), 2.12 (s, 3H, OCOC**H$_3$**), 3.53 (dd, 1H, $^2J_{6a,6b}$ 11.5, $J_{6a,5}$ 5.7 Hz, H-6$_a^{I}$), 3.69 (dq, 1H, $J_{5,4}$ 9.9, $J_{5,6b}$ 4.7, $J_{5,6a}$ 2.7 Hz, H-5^{II}), 3.75-3.78 (m, 1H, $J_{5,4}$ 10.1, $J_{5,6a}$ 5.5, $J_{5,6b}$ 1.9 Hz, H-5^{I}), 3.87 (q, 1H, $J_{2,3}$ 10.5, $J_{2,1}$ 9.2, $J_{2,NH}$ 8.7 Hz, H-2^{I}), 3.99 (q, 1H, $J_{2,3}$ 10.4, $J_{2,NH}$ 8.8, $J_{2,1}$ 8.4 Hz, H-2^{II}), 4.04 (dd, 1H, $^2J_{6b,6a}$ 11.5, $J_{6b,5}$ 1.9 Hz, H-6$_b^{I}$), 4.15 (dd, 1H, $^2J_{6a,6b}$ 12.3, $J_{6a,5}$ 2.4 Hz, H-6$_a^{II}$), 4.28 (dd, 1H, $^2J_{6b,6a}$ 12.3, $J_{6b,5}$ 4.7 Hz, H-6$_b^{II}$), 4.59 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1^{II}), 4.78 (d, $J_{1,2}$ 9.2 Hz, H-1^{I}), 5.06 (t, 1H, $J_{4,5}$ 9.7, $J_{4,3}$ 9.5 Hz, H-4^{I}), 5.10 (t, 1H, $J_{4,5}$ 9.8, $J_{4,3}$ 9.5 Hz, H-4^{II}), 5.20-5.28 (m, 2H, H-3^{I}, H-3^{II}), 5.61 (d, 1H, $J_{NH,2}$ 8.7 Hz, N**H**COCH$_3^{I}$), 5.77 (d, 1H, $J_{NH,2}$ 8.8 Hz, N**H**COCH$_3^{II}$); ^{13}C NMR 100 MHz; $CDCl_3$) δ 20.6 (OCO**C**H$_3$), 20.7 (OCO**C**H$_3$), 20.8 (OCO**C**H$_3$), 22.7 (OCO**C**H$_3$), 23.1 (NHCO**C**H$_3$), 23.2 (NHCO**C**H$_3$), 54.2 (C-2^{I}), 54.3 (C-2^{II}), 61.9 (C-6^{II}), 67.9 (C-6^{I}), 68.4 (C-4^{I}, C-4^{II}), 72.0 (C-3^{II}), 72.2 (C-3^{I}), 72.6 (C-5^{II}), 75.2 (C-5^{I}), 88.3 (C-1^{II}), 101.4 (C-1^{I}), 169.3 (NH**C**OCH$_3$), 169.8 (NH**C**OCH$_3$), 170.4 (O**C**OCH$_3$), 170.5 (O**C**OCH$_3$), 170.7 (O**C**OCH$_3$), 170.9 (O**C**OCH$_3$); HRESIMS: Calc. for $C_{26}H_{37}N_5NaO_{15}^+$ $[M+Na]^+$ *m/z* = 682.2178, found: 682.2199; IR (cm^{-1}): 3341, 2917, 2849, 2113, 1747, 1228. The data is in agreement with that previously reported.[3]

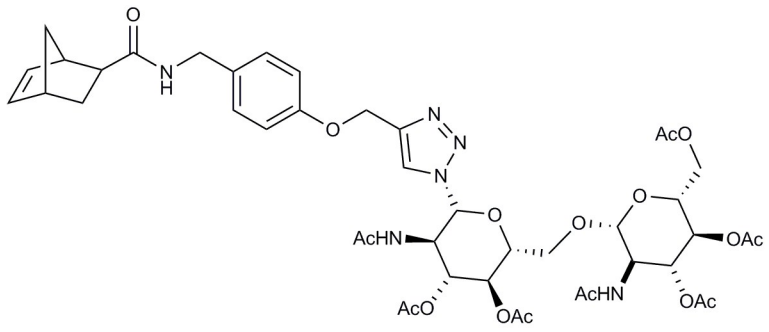
4-((1-[6-*O*-(2-Trifluoroacetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl]-1*H*-1,2,3-triazol-4-yl)methoxy)benzyl]-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylate (15)



A solution of 6-*O*-(2-trifluoroacetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl azide (**8**, 0.13 g, 0.2 mmol), compound **1** (53.6 mg, 0.2 mmol) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (36.3 μL, 0.2 mmol) in dry toluene (3 mL) was purged with argon for 20 min. Copper(I) bromide (23.8 mg, 0.2 mmol) was then added and the reaction mixture was purged with argon for a further 3 min before being sealed, and left to stir at room temperature for 4 d, protected from light. After this time, air was slowly bubbled through the dark green solution for 10 min and the solvent was removed under reduced pressure. The crude product was purified using flash silica gel column chromatography with petroleum spirit (40-60 °C) containing increasing quantities of ethyl acetate as the eluent. The title compound **15** eluted in 70% ethyl acetate/petroleum spirit (40-60 °C) and was dried to give a white solid (0.13 g, 88%). R_f 0.67 (80% ethyl acetate/petroleum spirit); mp. 182 °C (dec.); $[\alpha]_D^{23}$ -49.6° (*c* 0.43, CH_2Cl_2); λ_{abs} (CH_2Cl_2)/nm: 231 (log ε/$M^{-1}cm^{-1}$, 4.65), 274 (3.73), 282 (3.65); ^{1}H NMR (500 MHz; $CDCl_3$) δ 1.33-1.38 (m, 2H, CH_2), 1.52 (br d, 1H, CH_2), 1.67 (s, 3H, NHCOC$\mathbf{H_3^I}$), 1.93 (dt, 1H, $^2J_{CH,CH}$ 12.0, $J_{CH,CH}$ 3.5 Hz, CH_2), 2.01 (s, 3H, $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 2.04 (s, 3H, $OCOCH_3$), 2.25 (q, 1H,

$J_{CH,CH}$ 6.0, $J_{CH,CH2}$ 4.0 Hz, CH), 2.91 (s, 1H, CH), 3.04 (s, 1H, CH), 3.52 (dd, 1H, $^{2}J_{6a,6b}$ 12.0, $J_{6a,5}$ 4.0 Hz, H-6_a^{I}), 3.61 (dq, 1H, $J_{5,4}$ 10.0, $J_{5,6b}$ 4.5, $J_{5,6a}$ 2.5 Hz, H-5^{II}), 4.07 (dd, 1H, $^{2}J_{6a,6b}$ 12.5, $J_{6a,5}$ 2.5 Hz, H-6_a^{II}), 4.15 (dq, 1H, $J_{5,4}$ 10.0, $J_{5,6a}$ 3.5, $J_{5,6b}$ 1.5 Hz, H-5^{I}), 4.18-4.24 (m, 3H, H-2^{II}, H-6_b^{I}, H-6_b^{II}), 4.50 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1^{II}), 4.63 (q, 1H, $J_{2,3}$ 9.5, $J_{2,1}$ 9.5 Hz, H-2^{I}), 5.06 (s, 2H, O-C**H**$_2$-Ph), 5.18 (t, 1H, $J_{4,5}$ 9.5, $J_{4,3}$ 9.0 Hz, H-4^{II}), 5.10 (t, 1H, $J_{3,4}$ 9.5, $J_{3,2}$ 9.5 Hz, H-3^{II}), 5.20 (s, 2H, Ph-O-C**H**$_2$), 5.59 (t, 1H, $J_{4,5}$ 10.0, $J_{4,3}$ 9.5 Hz, H-4^{I}), 5.96-6.00 (m, 2H, N**H**$COCH_3^{I}$, H-3^{I}), 6.08 (dd, 1H, $J_{CH,CH}$ 5.5, $J_{CH,CH}$ 3.0 Hz, **H**C=CH), 6.13 (dd, 1H, $J_{CH,CH}$ 5.5, $J_{CH,CH}$ 2.5 Hz, HC=C**H**), 6.23 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1^{I}), 6.99 and 7.30 (AA'BB', 4H, Ph-H), 7.35-7.41 (AA'BB'C, 4H, Ph-H), 7.50-7.57 (AA'BB'C, 2H, Ph-H), 7.59 (d, 1H, $J_{NH,2}$ 8.5 Hz, N**H**$COCF_3^{II}$), 7.88-7.90 (AA'BB'C, 2H, Ph-H), 7.92-7.94 (AA'BB'C, 2H, Ph-H), 8.08 (s, 1H, triazole-**H**); ^{13}C NMR (100 MHz; $CDCl_3$) δ 20.46 (OCO**C**H_3), 20.54 (OCO**C**H_3), 20.7 (OCO**C**H_3), 22.9 (NHCO**C**H_3^{I}), 30.4 (CH_2), 41.6 (CH), 43.2 (CH), 46.3 (bridge CH_2), 46.6 (CH), 54.0 (C-2^{I}), 54.5 (C-2^{II}), 61.7 (Ph-O-**C**H_2, C-6^{II}), 66.0 (O-**C**H_2-Ph), 67.6 (C-6^{I}), 68.1 (C-4^{II}), 68.8 (C-4^{I}), 72.1 (C-5^{II}), 72.3 (C-3^{I}), 72.4 (C-3^{II}), 75.9 (C-5^{I}), 85.8 (C-1^{I}), 101.2 (C-1^{II}), 114.4, 117.3 (NHCO**C**F_3^{II}), 114.9 (Ph-CH), 122.5 (triazole-**C**H), 128.0 (Ph-C-), 128.3 (Ph-C-), 128.6 (Ph-CH), 128.7 (Ph-CH), 129.0 (Ph-C-), 129.8 (Ph-CH), 129.9 (Ph-CH), 130.0 (Ph-CH), 133.8 (Ph-CH), 134.2 (Ph-CH), 135.7 (HC=**C**H), 138.0 (HC=**C**H), 144.3 (triazole-**C**-), 157.5, 157.8 (NHCO**C**F_3^{II}), 158.2 (Ph-C-), 165.9 (O**C**OPh), 166.3 (O**C**OPh), 169.2 (O**C**OCH_3), 170.6 (O**C**OCH_3, N**H**$COCH_3^{I}$), 170.8 (O**C**OCH_3), 176.1 (C=O); HRESIMS: Calc. for $C_{54}H_{56}F_3N_5NaO_{18}^{+}$ $[M+Na]^{+}$ *m/z* = 1142.3465, found: 1142.3427; IR (cm^{-1}): 3249, 3071, 2955, 1723, 1215, 1068, 711.

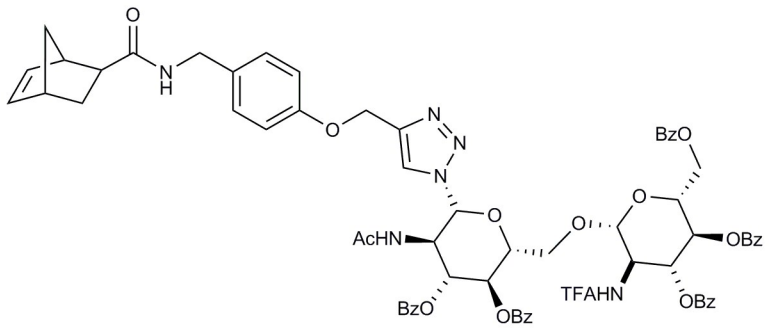
***N*-[4-((1-[6-*O*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl]-1*H*-1,2,3-triazol-4-yl)methoxy)benzyl]-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxamide (16)**



A solution of 6-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl azide[3] (**9**, 103.4 mg, 0.2 mmol), compound **2** (40.5 mg, 0.1 mmol) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (36.0 μL, 0.2 mmol) in dry toluene (3 mL) and dry *N,N*-dimethylformamide (0.5 mL) was purged with argon for 20 min. Copper(I) bromide (23.6 mg, 0.2 mmol) was then added and the reaction mixture was purged for a further 3 min, before being sealed, and left to stir at room temperature for 4 d, protected from light. After this time, air was slowly bubbled through the dark green solution for 10 min and the solvent was removed under reduced pressure. The crude product was purified using flash silica gel column chromatography, first with petroleum spirit (40-60 °C) containing increasing quantities of ethyl acetate, followed by ethyl acetate containing increasing quantities of methanol as the eluent. The title compound **16** eluted in 2% methanol/ethyl acetate and was dried to give a white solid (83.4 mg, 60%). R_f 0.69 (10% methanol/ethyl acetate); mp. 200 °C (dec.); $[\alpha]_D^{23}$ -15.4° (*c* 0.23, CH_2Cl_2); λ_{abs} (CH_2Cl_2)/nm: 228 (log ε/$M^{-1}cm^{-1}$, 4.22), 276 (3.32), 283 (3.25); ^{1}H NMR (400 MHz; $CDCl_3/CD_3OD$) δ 1.25-1.35 (m, 2H, CH_2), 1.65 (s, 3H, NHCOC**H$_3$**), 1.68 (br d, 1H,

CH_2), 1.80 (s, 3H, NHCOC**H$_3$**), 1.85-1.91 (m, 1H, CH_2), 1.96-2.01 (m, 10H, 3 x $OCOCH_3$, CH), 2.03 (s, 3H, $OCOCH_3$), 2.04 (s, 3H, $OCOCH_3$), 2.87-2.89 (br m, 2H, CH), 3.43 (dd, 1H, $^2J_{6a,6b}$ 11.4, $J_{6a,5}$ 5.6 Hz, H-6_a^I), 3.58 (dq, 1H, $J_{5,4}$ 9.9, $J_{5,6b}$ 4.5, $J_{5,6a}$ 2.3 Hz, H-5^{II}), 3.86-3.96 (m, 3H, H-2^{II}, H-5^I, H-6_b^I), 4.04 (dd, 1H, $^2J_{6a,6b}$ 12.3, $J_{6a,5}$ 2.3 Hz, H-6_a^{II}), 4.19 (dd, 1H, $^2J_{6b,6a}$ 12.3, $J_{6b,5}$ 4.6 Hz, H-6_b^{II}), 4.26-4.35 (m, 2H, NH-C**H$_2$**-Ph), 4.42-4.48 (m, 2H, H-1^{II}, H-2^I), 4.98 (t, 1H, $J_{4,5}$ 9.7, $J_{4,3}$ 9.5 Hz, H-4^{II}), 5.03-5.11 (m, 2H, H-3^{II}, H-4^I), 5.12 (s, 2H, Ph-O-C**H$_2$**), 5.31 (t, 1H, $J_{3,2}$ 10.1, $J_{3,4}$ 9.6 Hz, H-3^I), 5.87 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1^I), 6.08 (dd, 1H, $J_{CH,CH}$ 5.5, $J_{CH,CH}$ 2.6 Hz, **H**C=CH), 6.09 (dd, 1H, $J_{CH,CH}$ 5.5, $J_{CH,CH}$ 2.8 Hz, HC=C**H**), 6.88 and 7.15 (AA'BB', 4H, Ph-H), 7.98 (s, 1H, triazole-**H**); ^{13}C NMR (100 MHz; $CDCl_3/CD_3OD$) δ 20.39 (OCO**C**H_3), 20.44 (OCO**C**H_3), 20.47 (OCO**C**H_3), 20.54 (OCO**C**H_3), 20.58 (OCO**C**H_3), 22.2 (NHCO**C**H_3), 22.5 (NHCO**C**H_3), 30.4 (CH_2), 41.5 (CH), 42.9 (NH-**C**H_2-Ph), 44.4 (CH), 46.2 (bridge CH_2), 47.1 (CH), 52.7 (C-2^I), 53.8 (C-2^{II}), 61.4 (Ph-O-**C**H_2), 61.8 (C-6^{II}), 67.7 (C-6^I), 68.3 (C-4^I), 68.4 (C-4^{II}), 71.7 (C-5^{II}), 72.4 (C-3^{II}), 72.5 (C-3^I), 75.8 (C-5^I), 85.7 (C-1^I), 101.3 (C-1^{II}), 114.9 (Ph-CH), 122.2 (triazole-**C**H), 129.0 (Ph-CH), 131.1 (Ph-C-), 135.9 (H**C**=CH), 138.1 (HC=**C**H), 144.0 (triazole-**C**-), 157.3 (Ph-C-), 169.5 (O**C**OCH_3), 169.9 (O**C**OCH_3), 170.5 (O**C**OCH_3), 170.88 (O**C**OCH_3), 170.94 (O**C**OCH_3), 170.99 (NH**C**OCH_3), 171.5 (NH**C**OCH_3), 175.9 (C=O); HRESIMS: Calc. for $C_{44}H_{56}N_6NaO_{17}^+$ $[M+Na]^+$ *m/z* = 963.3594, found: 963.3572; IR (cm^{-1}): 3320, 2944, 1745, 1660, 1512, 1221, 1039.

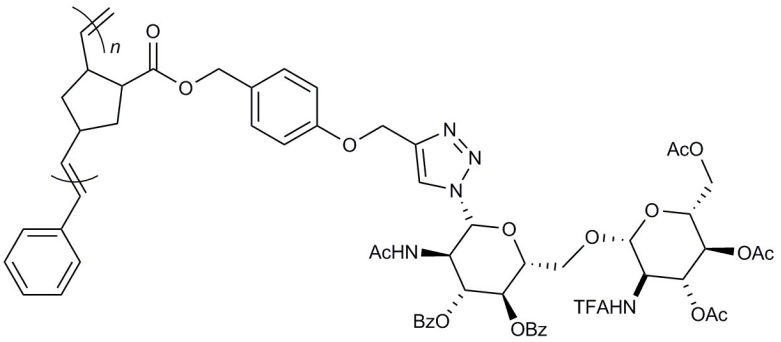
***N*-[4-((1-[6-*O*-(2-Trifluoroacetamido-3,4,6-tri-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl]-1*H*-1,2,3-triazol-4-yl)methoxy)benzyl]-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxamide (17)**



A solution of 6-*O*-(2-trifluroacetamido-3,4,6-tri-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl azide[5] (**10**, 178.6 mg, 0.2 mmol), compound **2** (48.3 mg, 0.2 mmol) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (35.9 μL, 0.2 mmol) in dry toluene (5 mL) was purged with argon for 20 min. Copper(I) bromide (23.5 mg, 0.2 mmol) was then added and the reaction mixture was purged for a further 5 min, before being sealed, and left to stir at room temperature for 4 d, protected from light. After this time, air was slowly bubbled through the dark green solution for 10 min and the solvent was removed under reduced pressure. The crude product was purified using flash silica gel column chromatography with diethyl ether containing increasing quantities of ethyl acetate as the eluent. The title compound **17** eluted in 20% ethyl acetate/diethyl ether and was dried to give a white solid (0.22 mg 99%). R_f 0.67 (50% ethyl acetate/diethyl ether); mp. 147-149 °C; $[\alpha]_D^{27}$ -38.0° (*c* 0.15, CH_2Cl_2); λ_{abs} (CH_2Cl_2)/nm: 237 (log ε/$M^{-1}cm^{-1}$, 4.79), 276 (3.93), 282 (3.92); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.18-1.26 (m, 2H, CH_2), 1.51 (s, 3H, NHCOC**H$_3$**), 1.60 (br d, 1H, CH_2), 1.79 (td, 1H, $J_{CH2,CH2}$ 11.6, $J_{CH2,CH}$ 4.0 Hz, CH_2), 1.94-1.97 (m, 1H, CH), 2.80-2.82 (br m, 2H,

CH), 3.60 (dd, 1H, $^{2}J_{6a,6b}$ 11.6, $J_{6a,5}$ 5.2 Hz, H-6_a^{I}), 3.93 (ddd, 1H, $J_{5,4}$ 10.0, $J_{5,6b}$ 4.8, $J_{5,6a}$ 1.6 Hz, H-5^{II}), 4.06 (dd, 1H, $^{2}J_{6b,6a}$ 11.6, $J_{6b,5}$ 1.6 Hz, H-6_b^{I}), 4.14 (ddd, 1H, $J_{5,4}$ 10.0, $J_{5,6a}$ 5.2, $J_{5,6b}$ 2.0 Hz, H-5^{I}), 4.20-4.30 (m, 4H, H-2^{II}, H-6_a^{II}, NH-C$\mathbf{H_2}$-Ph), 4.42 (dd, 1H, $^{2}J_{6b,6a}$ 12.4, $J_{6b,5}$ 3.2 Hz, H-6_b^{II}), 4.58 (t, 1H, $J_{2,3}$ 10.4, $J_{2,1}$ 10.0 Hz, H-2^{I}), 4.70 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1^{II}), 5.07 (s, 2H, Ph-O-C$\mathbf{H_2}$), 5.42-5.49 (m, 2H, H-4^{I}, H-4^{II}), 5.59 (dd, 1H, $J_{3,4}$ 9.6, $J_{3,2}$ 9.2 Hz, H-3^{II}), 5.78 (t, 1H, $J_{3,2}$ 10.0, $J_{3,4}$ 10.0 Hz, H-3^{I}), 5.95-5.98 (m, 1H, **H**C=CH), 6.00-6.03 (m, 1H, HC=C**H**), 6.05 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1^{I}), 6.84 and 7.10 (AA'BB', 4H, Ph-H), 7.20-7.30 (AA'BB'C, 10H, Ph-H), 7.36-7.46 (AA'BB'C, 5H, Ph-H), 7.74-7.85 (AA'BB'C, 10H, Ph-H), 7.98 (s, 1H, triazole-**H**); ^{13}C NMR (100 MHz; $CDCl_3$) δ 21.9 (NHCO**C**H_3), 30.2 (CH_2), 41.3 (CH), 42.7 (NH-**C**H_2-Ph), 44.2 (CH), 46.1 (bridge CH_2), 47.0 (CH), 53.2 (C-2^{I}), 54.3 (C-2^{II}), 61.3 (Ph-O-**C**H_2), 62.7 (C-6^{II}), 67.6 (C-6^{I}), 68.9 (C-4^{I}), 69.4 (C-4^{II}), 71.8 (C-5^{II}), 72.2 (C-3^{II}), 72.5 (C-3^{I}), 75.9 (C-5^{I}), 85.7 (C-1^{I}), 100.5 (C-1^{II}), 114.1, 117.0 (NHCO**C**F_3), 114.8 (Ph-CH), 122.2 (triazole-**C**H), 128.1 (Ph-C-), 128.21 (Ph-CH), 128.23 (Ph-CH), 128.27 (Ph-CH, Ph-C-), 128.31 (Ph-C-), 128.36 (Ph-CH, Ph-C-), 128.39 (Ph-C-), 128.8 (Ph-CH), 129.1 (Ph-C-), 129.45 (Ph-CH), 129.49 (Ph-CH), 129.52 (Ph-CH), 129.6 (Ph-CH), 131.0 (Ph-C-), 133.1 (Ph-CH), 133.37 (Ph-CH), 133.43 (Ph-CH), 133.7 (Ph-CH), 135.8 H**C**=CH), 137.9 (HC=**C**H), 144.0 (triazole-**C**-), 157.2 (Ph-C-), 157.7, 158.1 (NH**C**OCF_3), 165.1 (O**C**OPh), 165.5 (O**C**OPh), 166.0 (O**C**OPh), 166.1 (O**C**OPh), 166.2 (O**C**OPh), 171.3 (NH**C**OCH_3), 176.1 (C=O); HRESIMS: Calc. for $C_{69}H_{63}F_3N_6NaO_{17}^{+}$ $[M+Na]^{+}$ *m/z* = 1327.4094, found: 1327.4108; IR: 3324, 2949, 1726, 1267, 1068, 708.

Poly[4-((1-[6-*O*-(2-trifluoroacetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl]-1*H*-1,2,3-triazol-4-yl)methoxy)benzyl]-2,4-divinylcyclopentane-1-carboxamide] (18)



A solution of compound **15** (37.3 mg, 0.03 mmol) in dry tetrahydrofuran (0.8 mL) was treated with a solution of Grubbs' 3rd generation catalyst (**G3**, 25:1; 1.18 mg, 1.33 x 10^{-3} mmol in 0.2 mL of tetrahydrofuran) under anhydrous conditions. The reaction vessel was sealed and the mixture was stirred for 22 h at room temperature, protected from light. After this time, ethylvinyl ether (0.05 mL) was added and the stirring was continued for 5 min. The solvent was then removed under reduced pressure. The crude polymer was purified using flash silica gel column chromatography (Davisil® LC105Å 35-70 μm) with ethyl acetate containing increasing quantities of methanol as the eluent. The desired product eluted in 5% methanol/ethyl acetate and was dried to give a glassy solid. This solid was redissolved in dichloromethane (0.5 mL) and triturated with diethyl ether (40 mL). The precipitate was isolated by centrifugation (3000 rpm, 3 min) and the process was repeated twice more before the solid was dried under high vacuum to give the title compound **18** as a white solid (29.9 mg, 80%). λ_{abs} (THF)/nm: 228; ^{1}H NMR (500 MHz; $CDCl_3/CD_3OD$) δ (all signals are broad and referenced to CD_3OD) 1.07 (s, CH_2), 1.51 (s, NHCOC**H$_3$**, CH_2), 1.67-2.07 (m, $OCOCH_3$, CH), 2.48 (s, CH), 2.62 (s, CH), 2.94-3.12

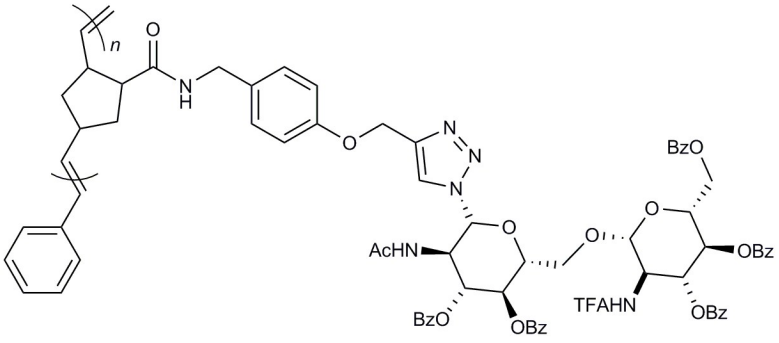
(m, CH), 3.61 (s, H-5^{II}, H-6$_a^{I}$), 3.96 (d, H-6$_a^{II}$), 3.99-4.16 (m, H-2^{II}, H-6$_b^{I}$, H-6$_b^{II}$), 4.20 (s, H-5^{I}), 4.52-4.74 (m, H-1^{II}, H-2^{I}), 4.75-5.38 (m, **H**C=C**H**, H-3^{II}, H-4^{II}, O-C**H$_2$**-Ph, Ph-O-C**H$_2$**), 5.48 (s, H-4^{I}), 5.93 (s, H-3^{I}), 6.22 (s, H-1^{I}), 6.74-6.93 (m, Ph-H), 7.07-7.37 (m, Ph-H), 7.42 (s, Ph-H), 7.82 (s, Ph-H), 8.02 (s, triazole-**H**); IR (cm^{-1}): 3347, 3075, 2950, 1723, 1218, 1027, 711; GPC (System 2): **Error!**: 18869; **Error!**: 23037; PDI: 1.22.

Poly[4-((1-[6-*O*-(2-trifluoroacetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl]-1*H*-1,2,3-triazol-4-yl)-methoxy)benzyl]-2,4-divinylcyclopentane-1-carboxamide] (19)

A solution of compound **15** (43.9 mg, 0.04 mmol) in dry tetrahydrofuran (1 mL) was treated with a solution of Grubbs' 3rd generation catalyst (**G3**, 100:1; 0.34 mg, 3.91 x 10^{-4} mmol in 0.5 mL of tetrahydrofuran) under anhydrous conditions. The reaction vessel was sealed and the mixture was stirred for 24 h at room temperature, protected from light. After this time, ethylvinyl ether (0.5 mL) was added and the stirring was continued for 5 min. The solvent was then removed under reduced pressure. The crude polymer was purified using flash silica gel column chromatography (Davisil® LC105Å 35-70 μm) with ethyl acetate containing increasing quantities of methanol as the eluent. The desired product eluted in 5% methanol/ethyl acetate and was dried to give a glassy solid. This solid was redissolved in dichloromethane (1 mL) and

triturated with diethyl ether (40 mL). The precipitate was isolated by centrifugation (3000 rpm, 3 min) and the process was repeated twice more before the solid was dried under high vacuum to give the title compound **19** as a white solid (16.1 mg, 37%). λ_{abs} (THF)/nm: 220; ^{1}H NMR (400 MHz; $CDCl_3/CD_3OD$) δ (all signals are broad and referenced to CD_3OD) 1.10 (s, CH_2), 1.53 (s, NHCOC**H$_3$**, CH_2), 1.82-2.05 (m, $OCOCH_3$, CH_2), 2.50 (s, CH), 2.63 (s, CH), 2.97 (s, CH), 3.63 (s, H-5^{II}, H-6$_a^I$), 3.91-4.27 (m, H-2^{II}, H-5^I, H-6$_b^I$, H-6^{II}), 4.55-4.75 (m, H-1^{II}, H-2^I), 4.82-5.40 (m, **H**C=C**H**, H-3^{II}, H-4^{II}, O-C**H$_2$**-Ph, Ph-O-C**H$_2$**), 5.48 (t, H-4^I), 5.92 (s, H-3^I), 6.21 (s, H-1^I), 6.87 (s, Ph-H), 7.10-7.53 (m, Ph-H), 7.77-7.92 (m, Ph-H), 8.04 (s, triazole-**H**); IR (cm^{-1}): 3260, 3072, 2919, 2850, 1725, 1219, 1027, 710; GPC (System 2): **Error!**: 43187; **Error!**: 63612; PDI: 1.47.

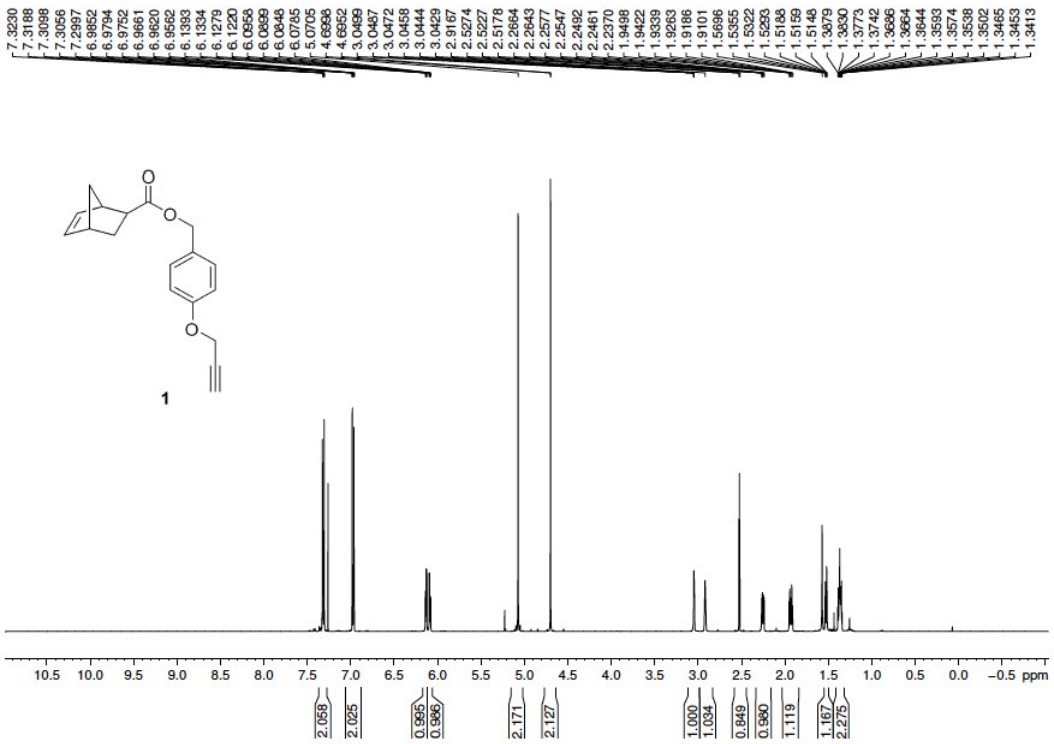
Poly(*N*-[4-((1-[6-*O*-(2-trifluoroacetamido-3,4,6-tri-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl]-1*H*-1,2,3-triazol-4-yl)methoxy)benzyl]-2,4-divinylcyclopentane-1-carboxamide) (20)



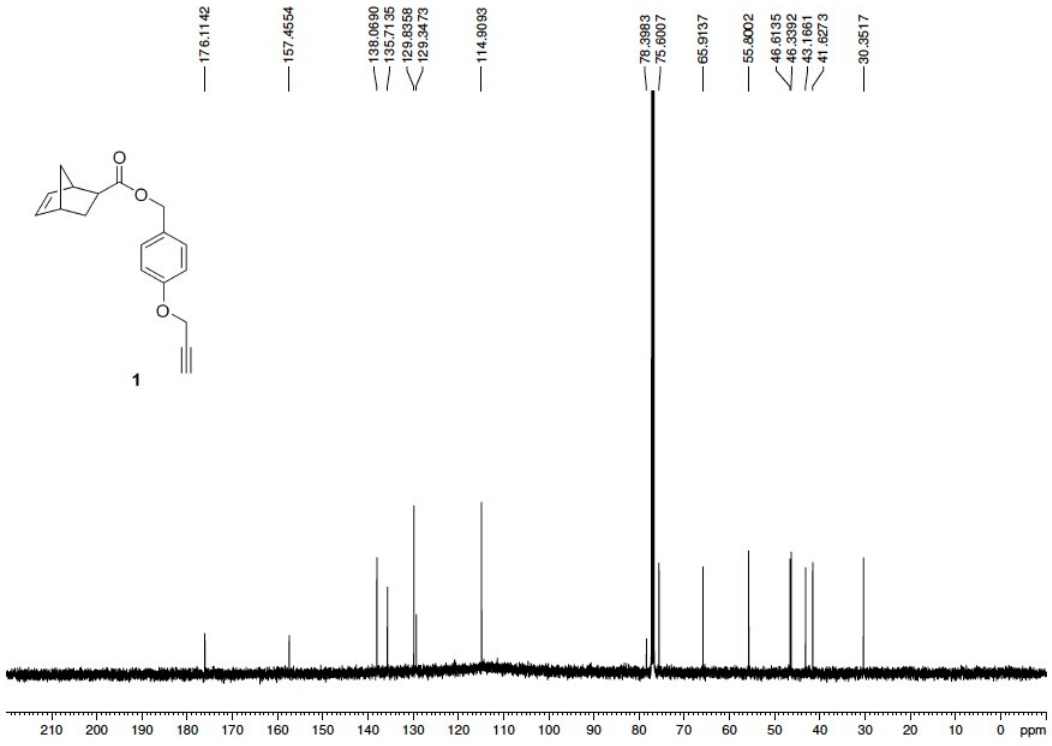
A solution of compound **17** (90.8 mg, 0.07 mmol) in dry tetrahydrofuran (0.8 mL) and benzene (1 mL) was treated with a solution of Grubbs' 3rd generation catalyst (**G3**, 25:1; 2.46 mg, 2.78 x 10^{-3} mmol in 1 mL benzene) under anhydrous conditions. The reaction vessel was sealed and the mixture was stirred at 60 °C for 4 d, protected from light. After this time, ethylvinyl ether (2 drops) was added and the stirring was continued for 1 h. The solvent was then removed under

reduced pressure. The crude polymer was purified using flash silica gel column chromatography (Davisil® LC150Å 35-70 μm) with dichloromethane containing increasing quantities of methanol as the eluent. The desired product eluted in 5% methanol/dichloromethane and was dried to give a glassy solid. This solid was redissolved in dichloromethane (1 mL) and triturated with diethyl ether (40 mL). The precipitate was isolated by centrifugation (3000 rpm, 3 min) and the process was repeated twice more before the solid was dried further under high vacuum to give the title compound **20** as a white solid (59.4 mg, 65%). λ_{abs} (THF)/nm: 224; ^{1}H NMR (500 MHz; $CDCl_3/CD_3OD$) δ (all signals are broad) 0.88-1.14 (m, CH_2), 1.27-1.59 (m, NHCOC**H$_3$**, CH_2), 1.68-1.97 (m, CH_2), 2.04-2.45 (m, CH), 2.57 (s, CH), 2.97 (s, CH), 3.71 (s, H-6$_a^I$), 3.93-4.63 (m, NH-C**H$_2$**-Ph, H-2^{II}, H-5^I, H-5^{II}, H-6$_b^I$, H-6^{II}), 4.64-5.42 (m, **H**C=C**H**, H-1^{II}, H-2^I, Ph-O-C**H$_2$**), 5.47-5.90 (m, H-3^{II}, H-4^I, H-4^{II}), 6.08 (s, H-3^I), 6.25 (s, H-1^I), 6.79 (s, Ph-H), 6.90-7.56 (m, Ph-H), 7.60-8.19 (m, triazole-**H**, Ph-H); IR (cm^{-1}): 3323, 2956, 1721, 1268, 1068, 709; GPC (System 2): **Error!**: 9796; **Error!**: 13297; PDI: 1.36.

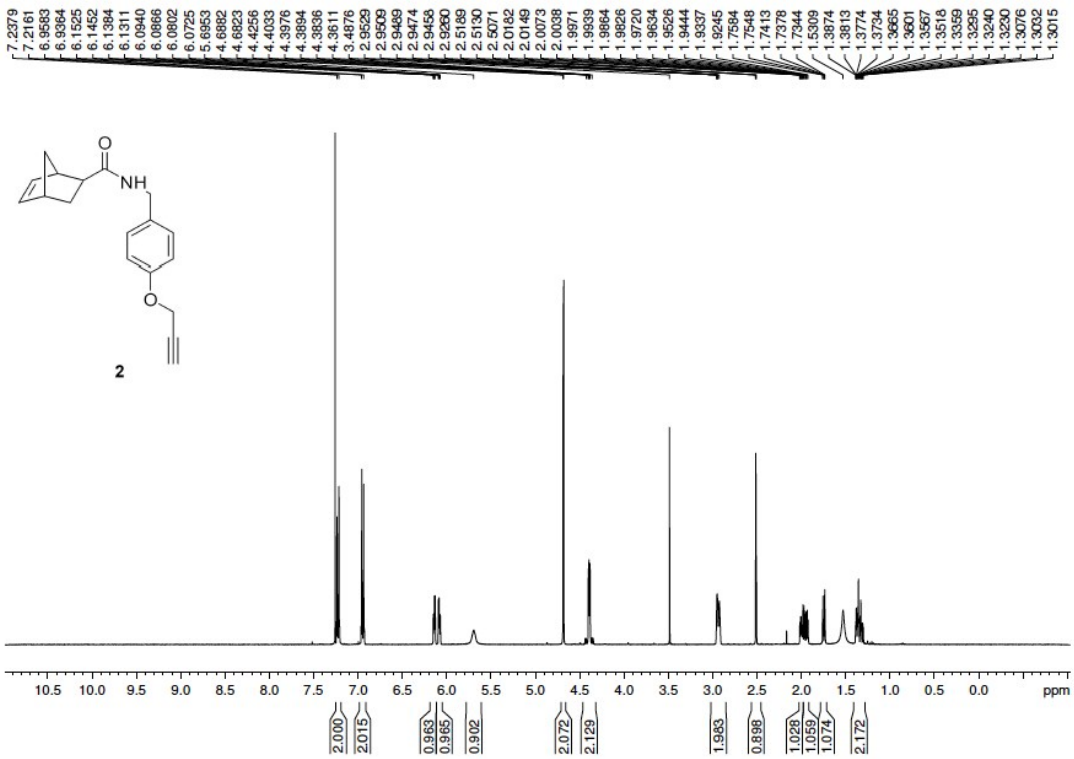
^{1}H NMR spectrum of compound **1** (500 MHz; $CDCl_3$)



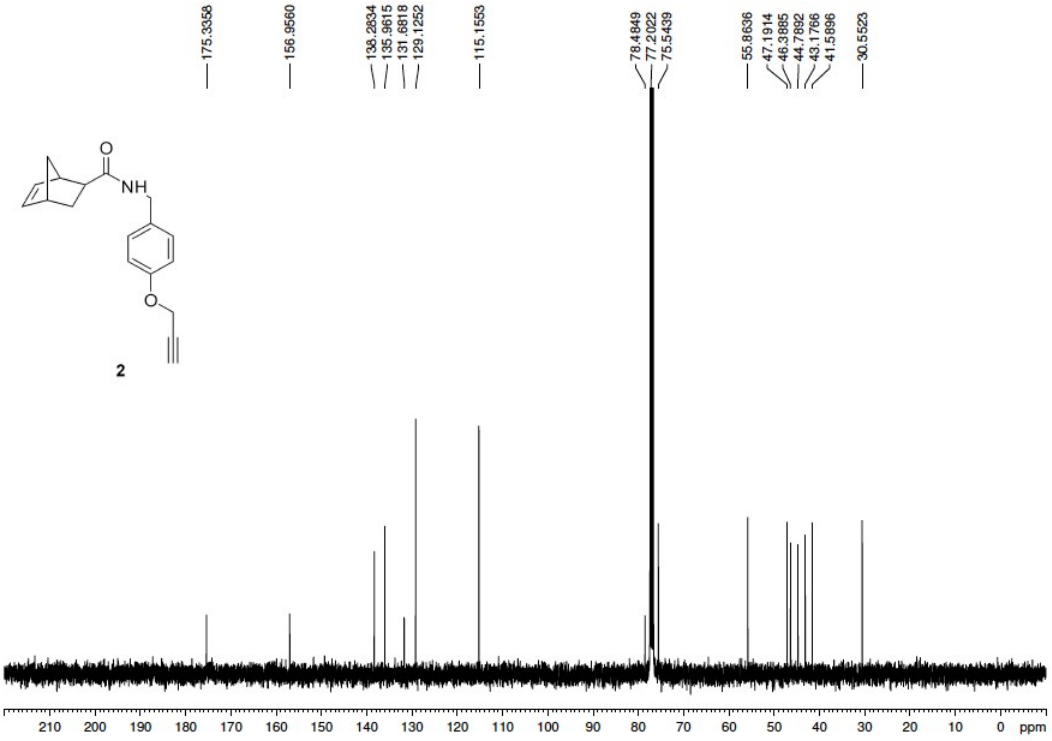
^{13}C NMR spectrum of compound **1** (125 MHz; $CDCl_3$)



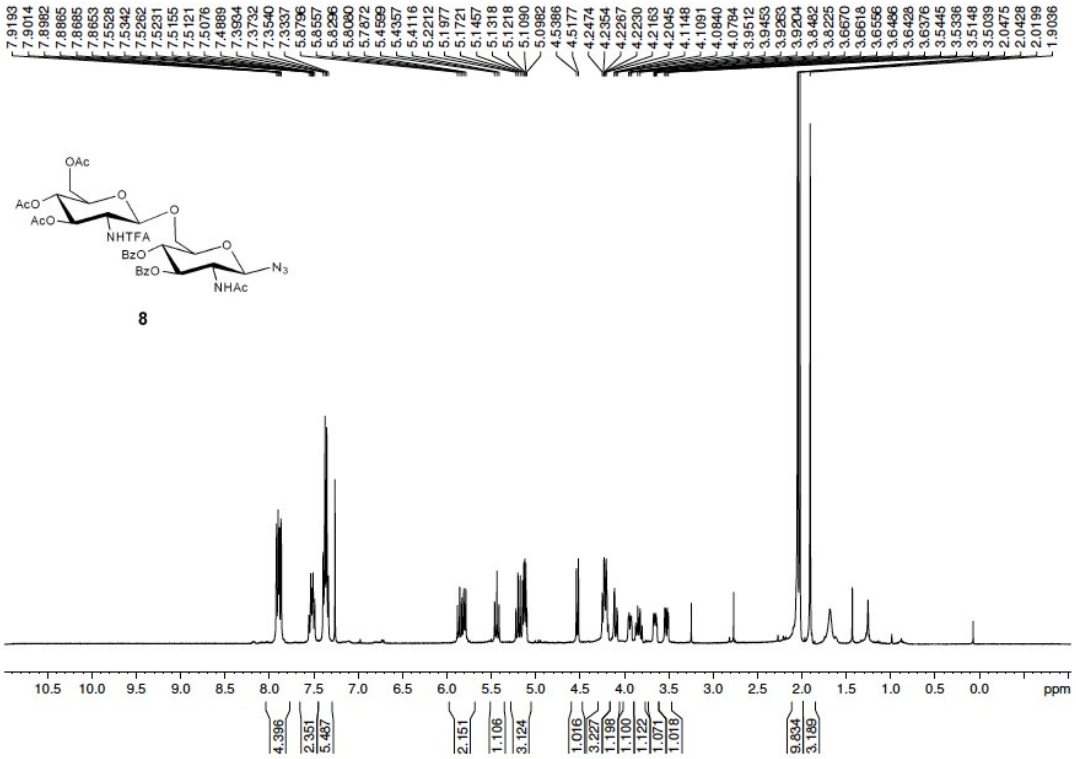
^{1}H NMR spectrum of compound **2** (500 MHz; $CDCl_3$)



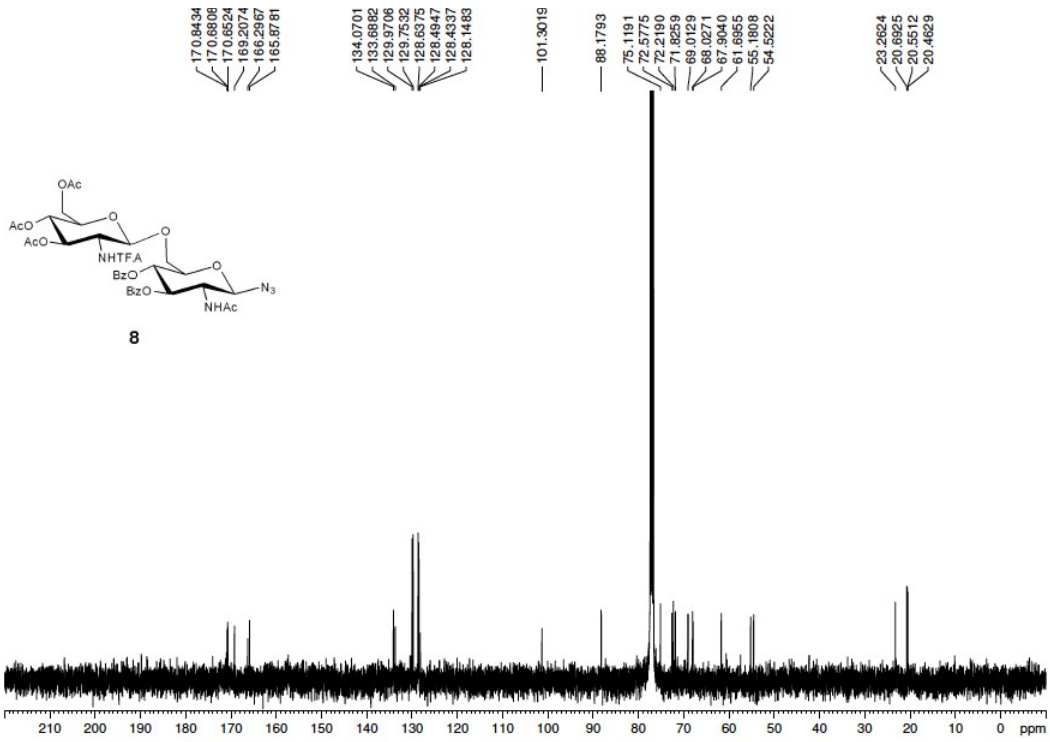
^{13}C NMR spectrum of compound **2** (100 MHz; $CDCl_3$)



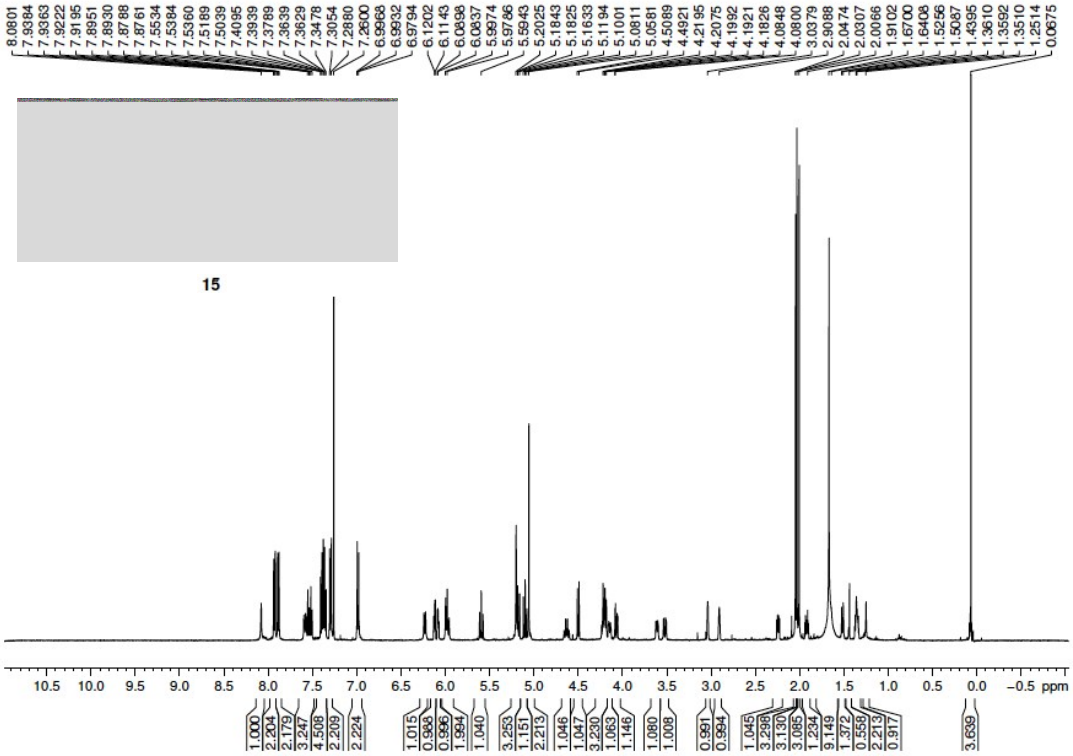
^{1}H NMR spectrum of compound **8** (500 MHz; $CDCl_3$)



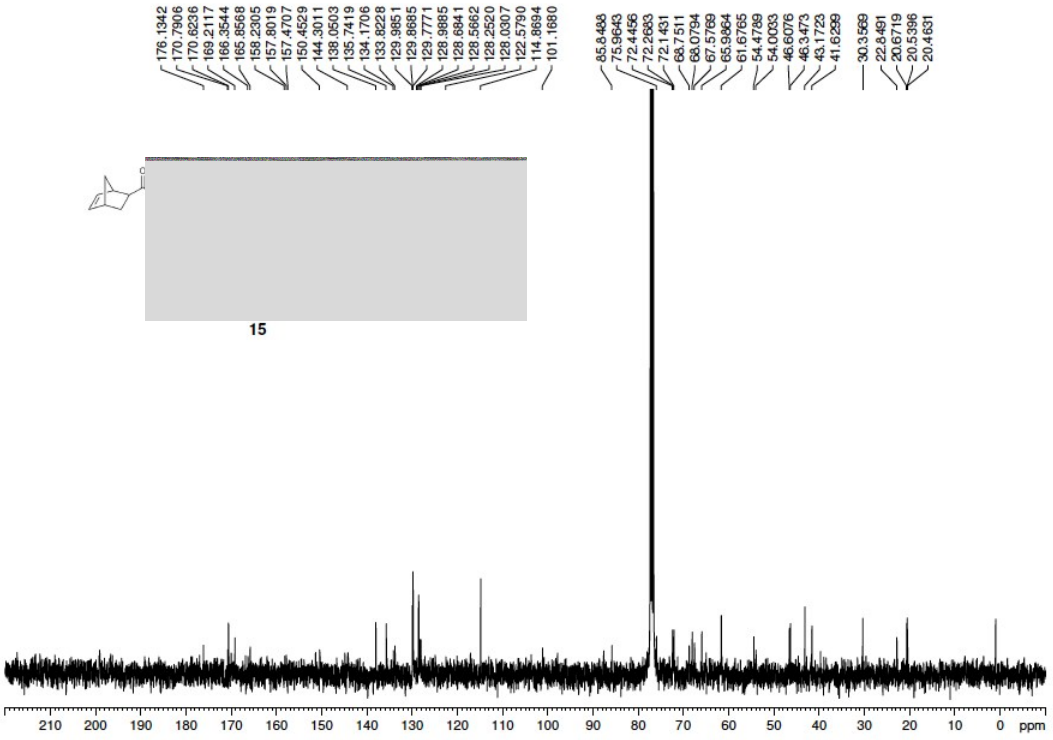
^{13}C NMR spectrum of compound **8** (100 MHz; $CDCl_3$)



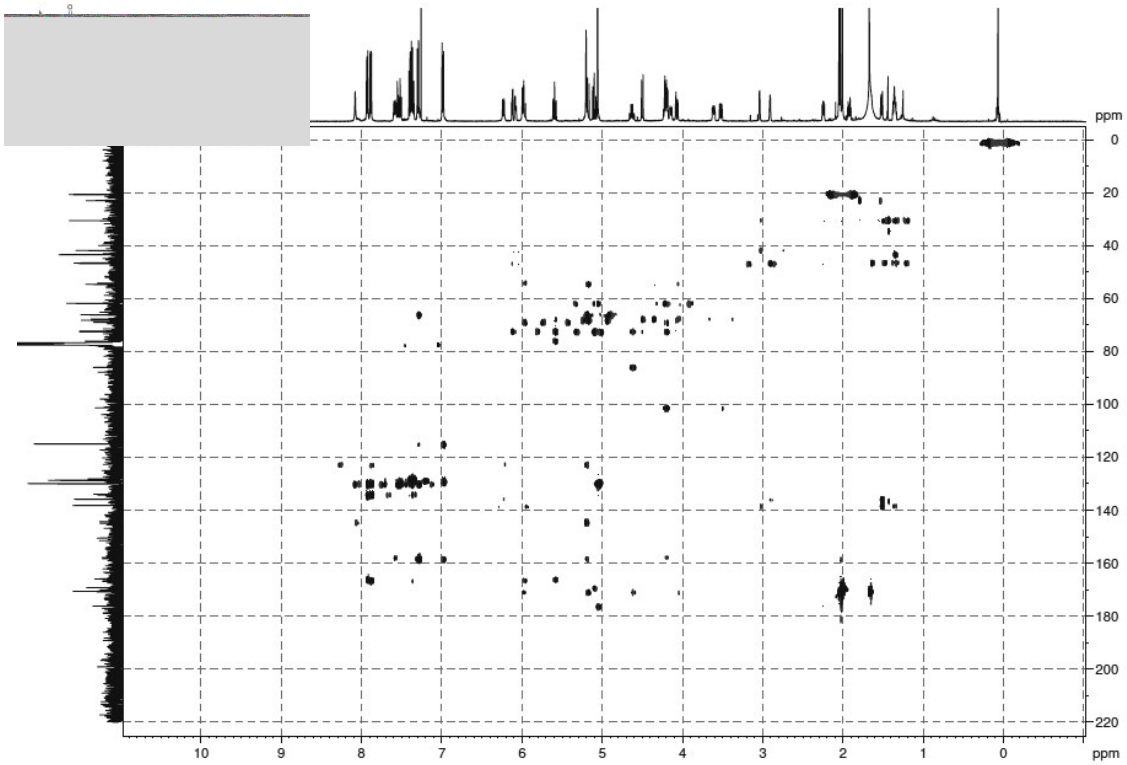
^{1}H NMR spectrum of compound **15** (500MHz; $CDCl_3$)



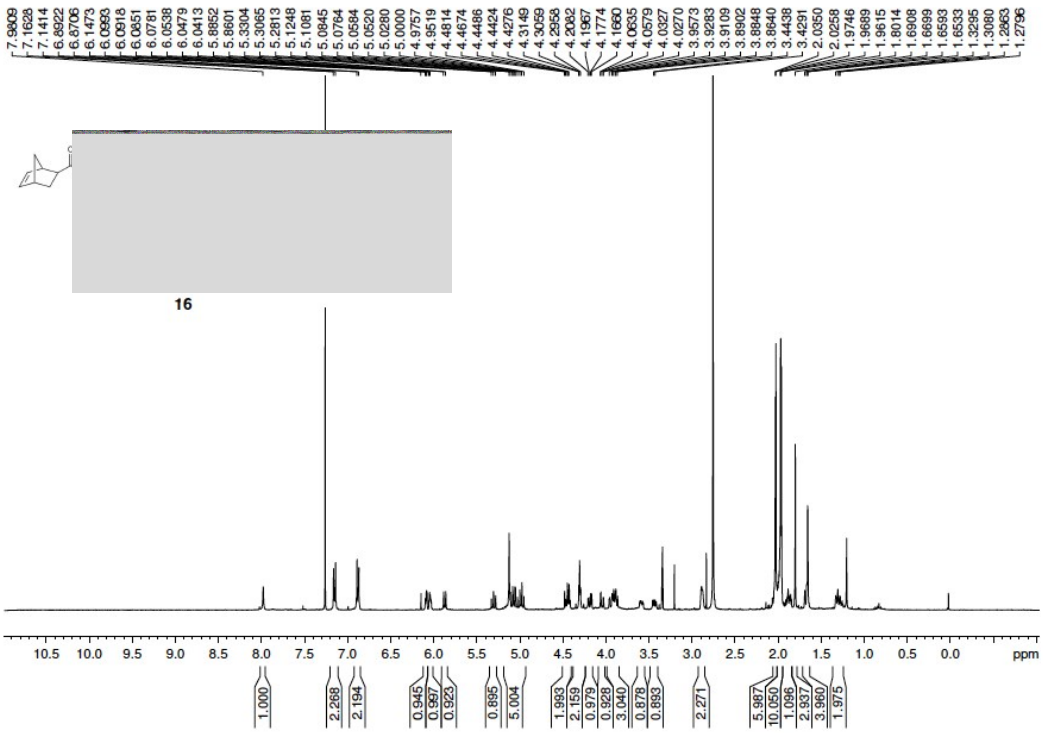
^{13}C NMR spectrum of compound **15** (100 MHz; $CDCl_3$)



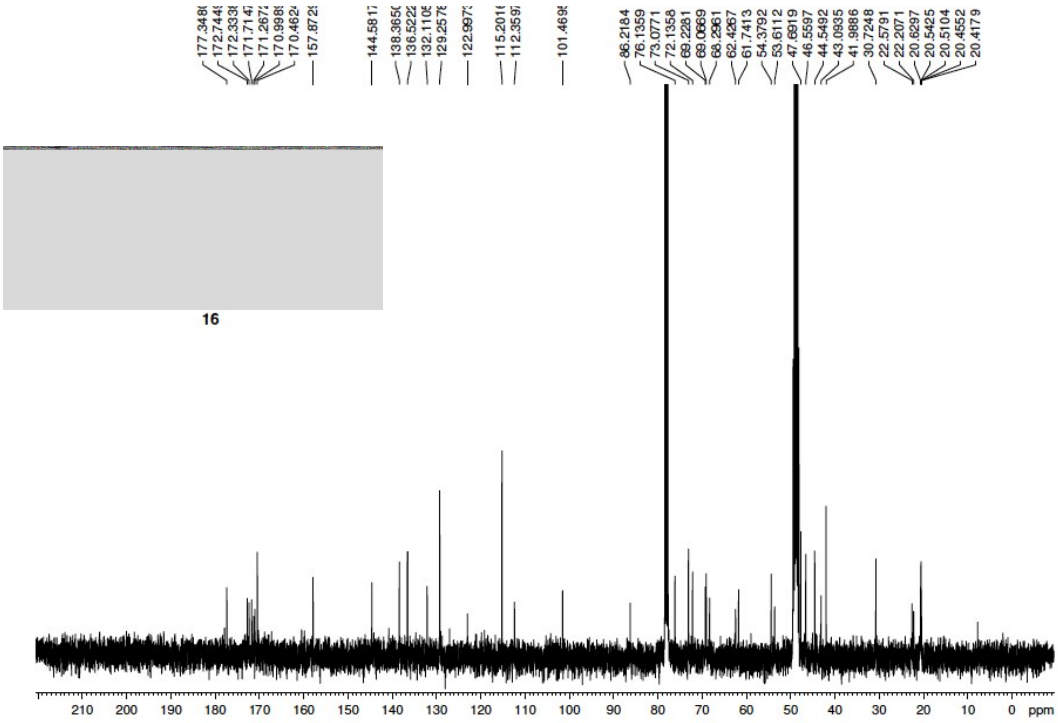
HMBC spectrum of compound **15** (500 MHz; $CDCl_3$)



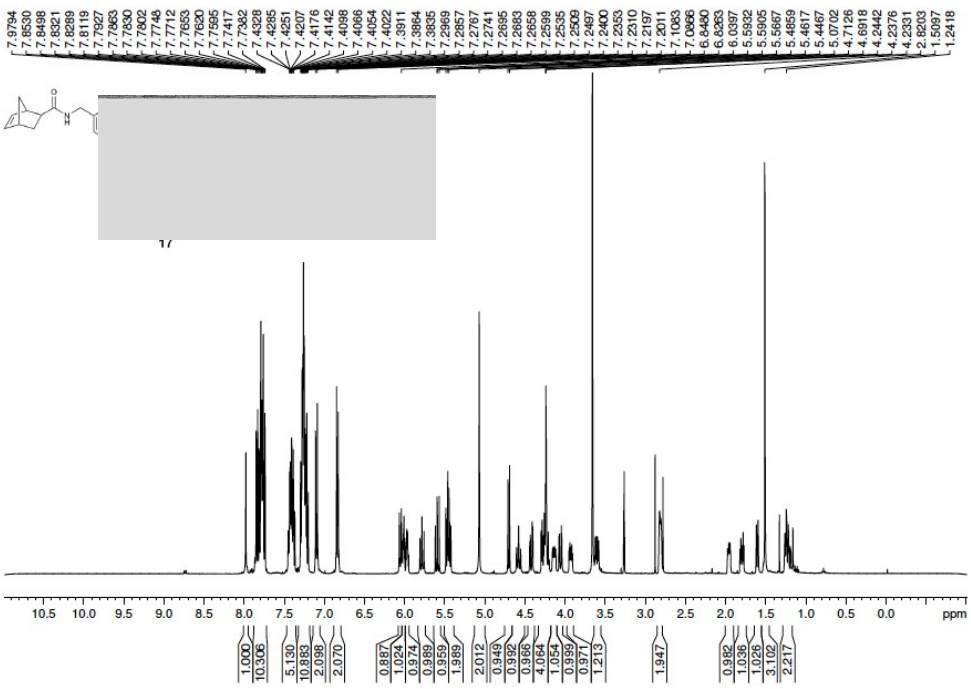
^{1}H NMR spectrum of compound **16** (500 MHz; $CDCl_3$/CD_3OD)



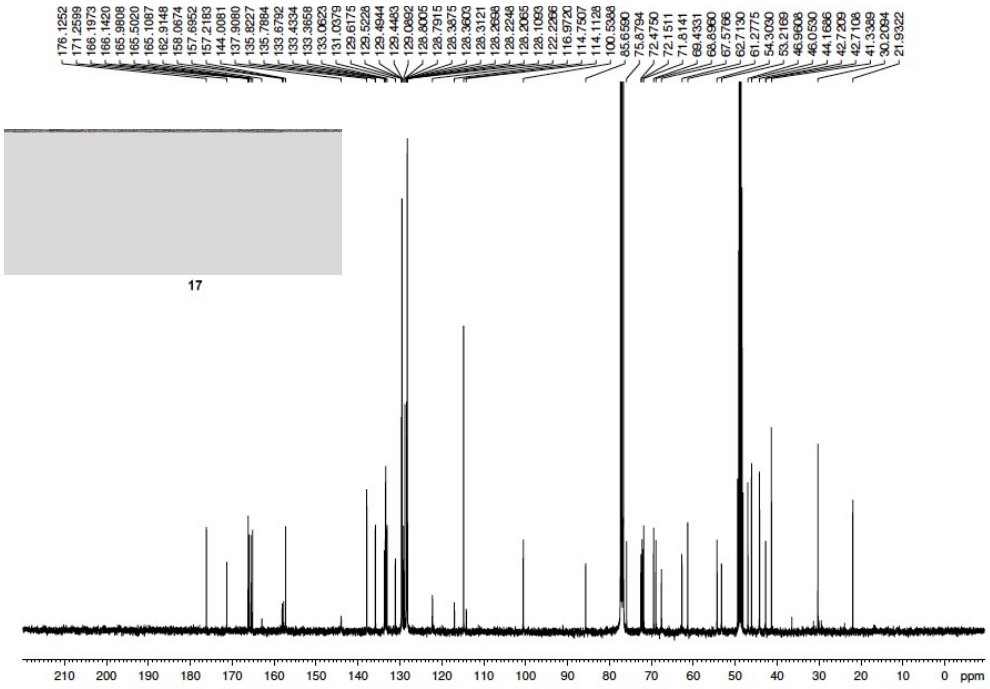
^{13}C NMR spectrum of compound **16** (100 MHz; $CDCl_3/CD_3OD$)



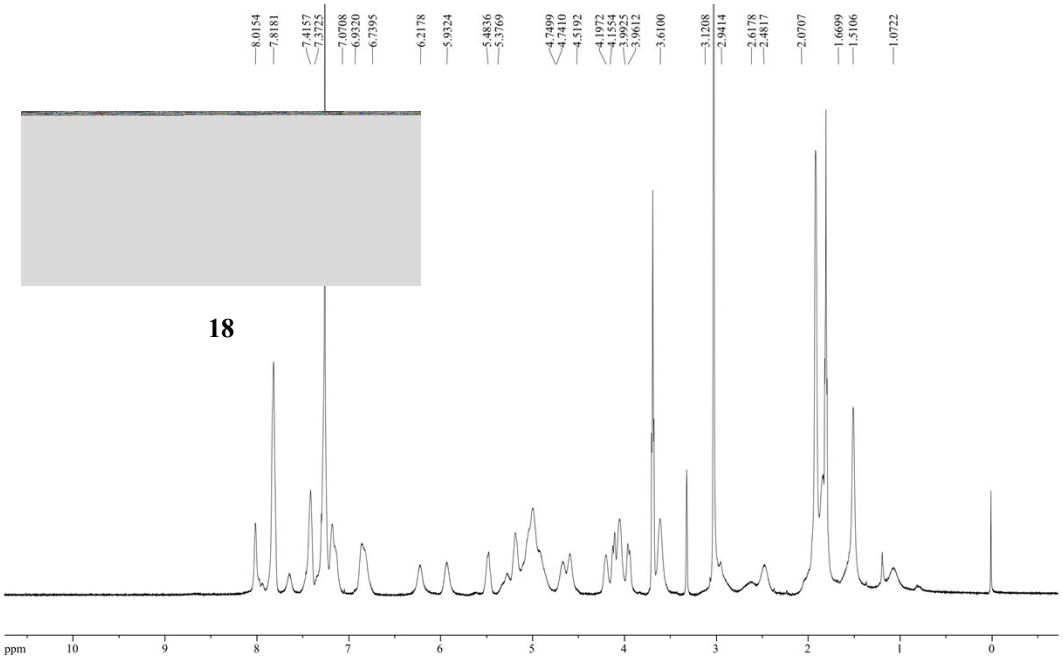
^{1}H NMR spectrum of compound **17** (500 MHz; $CDCl_3/CD_3OD$)



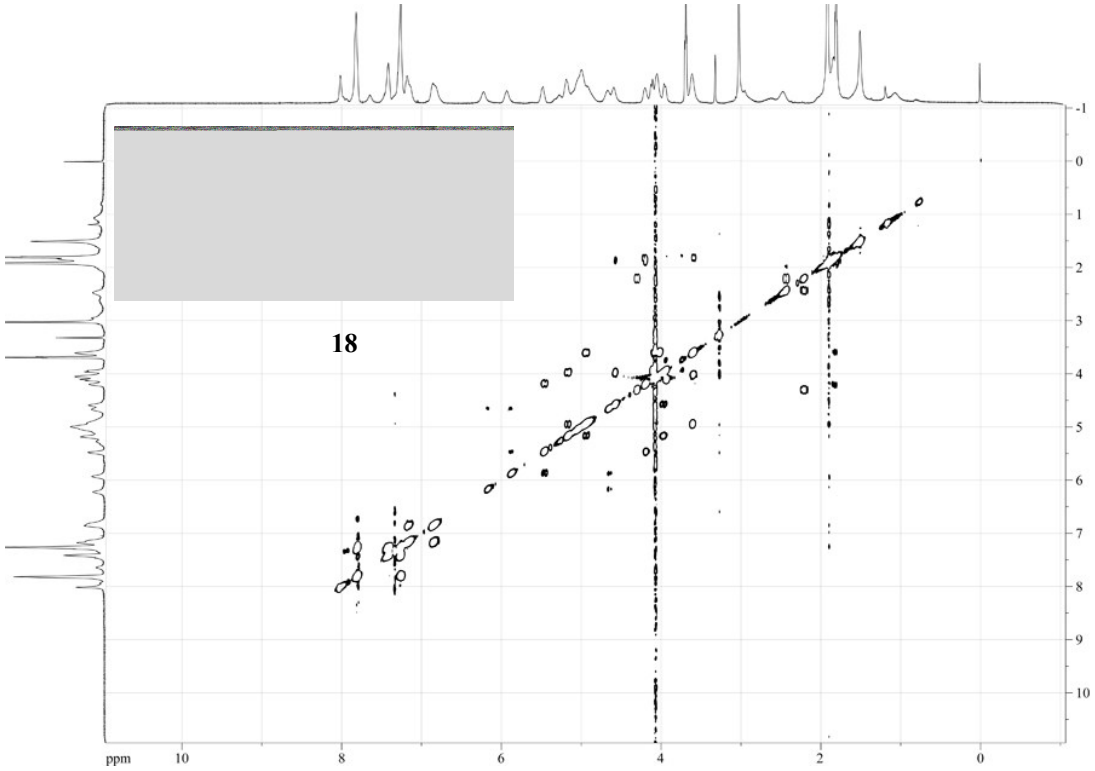
^{13}C NMR spectrum of compound **17** (100 MHz; $CDCl_3/CD_3OD$)



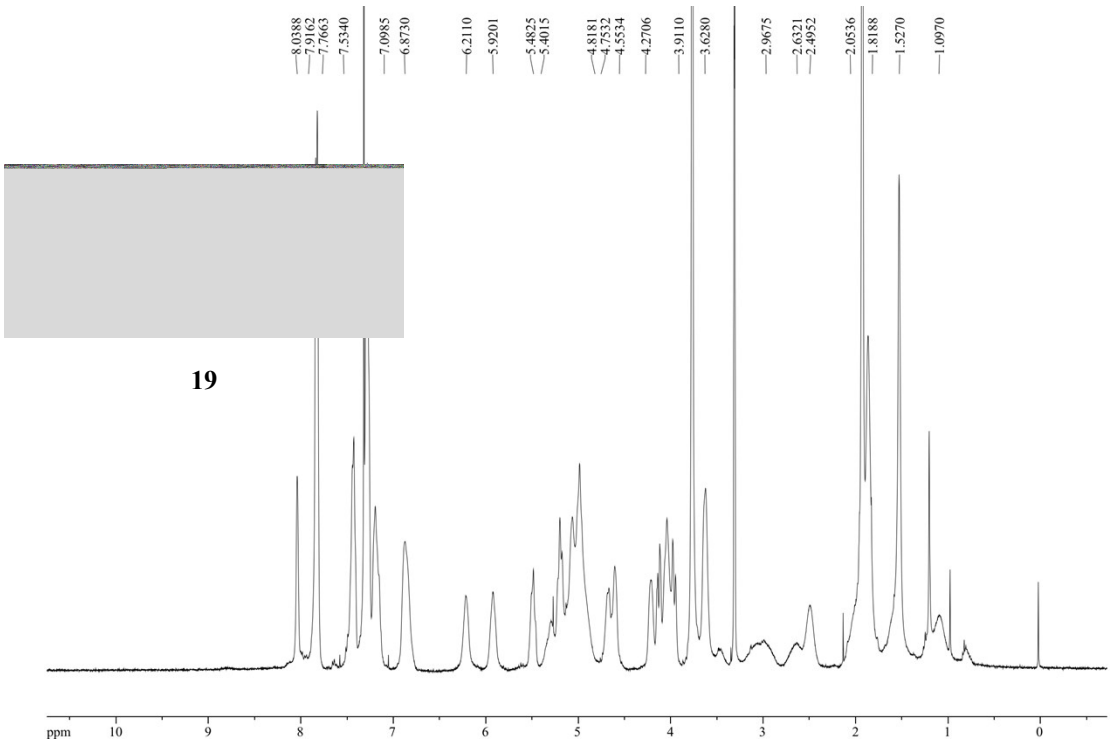
^{1}H NMR spectrum of compound **18** (500 MHz; $CDCl_3/CD_3OD$)



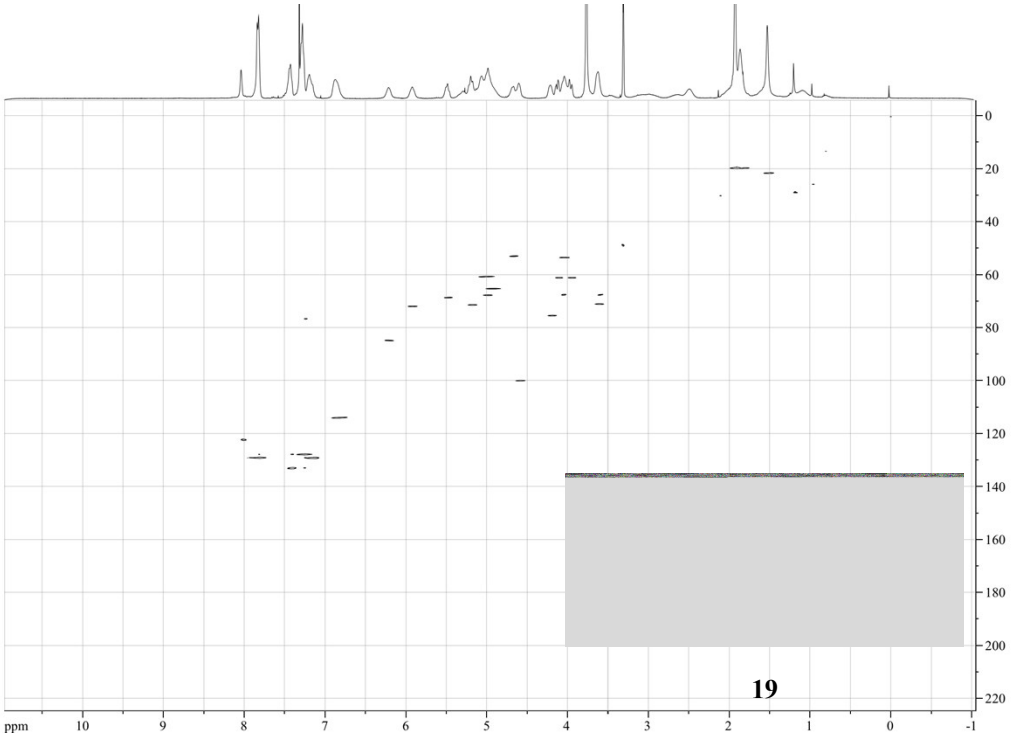
COSY NMR spectrum of compound **18** (500 MHz; $CDCl_3/CD_3OD$)



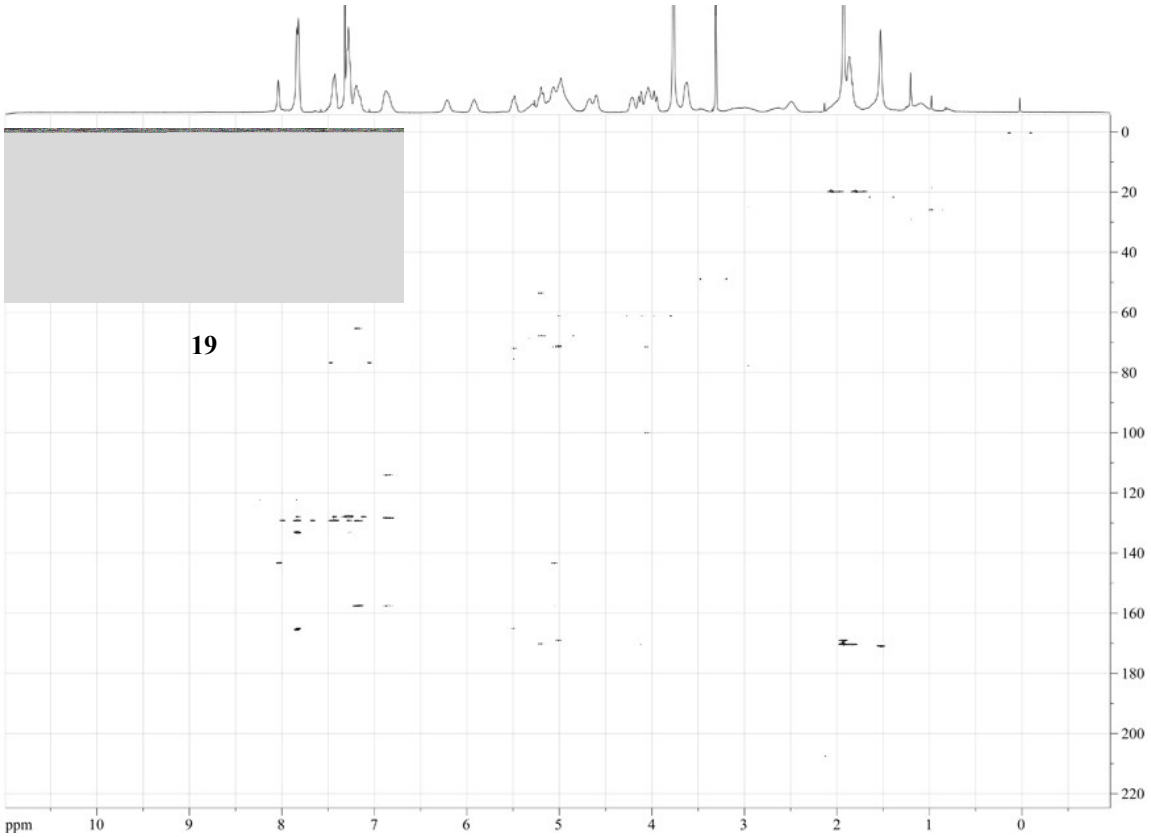
^1H NMR spectrum of compound **19** (500 MHz; $CDCl_3/CD_3OD$)



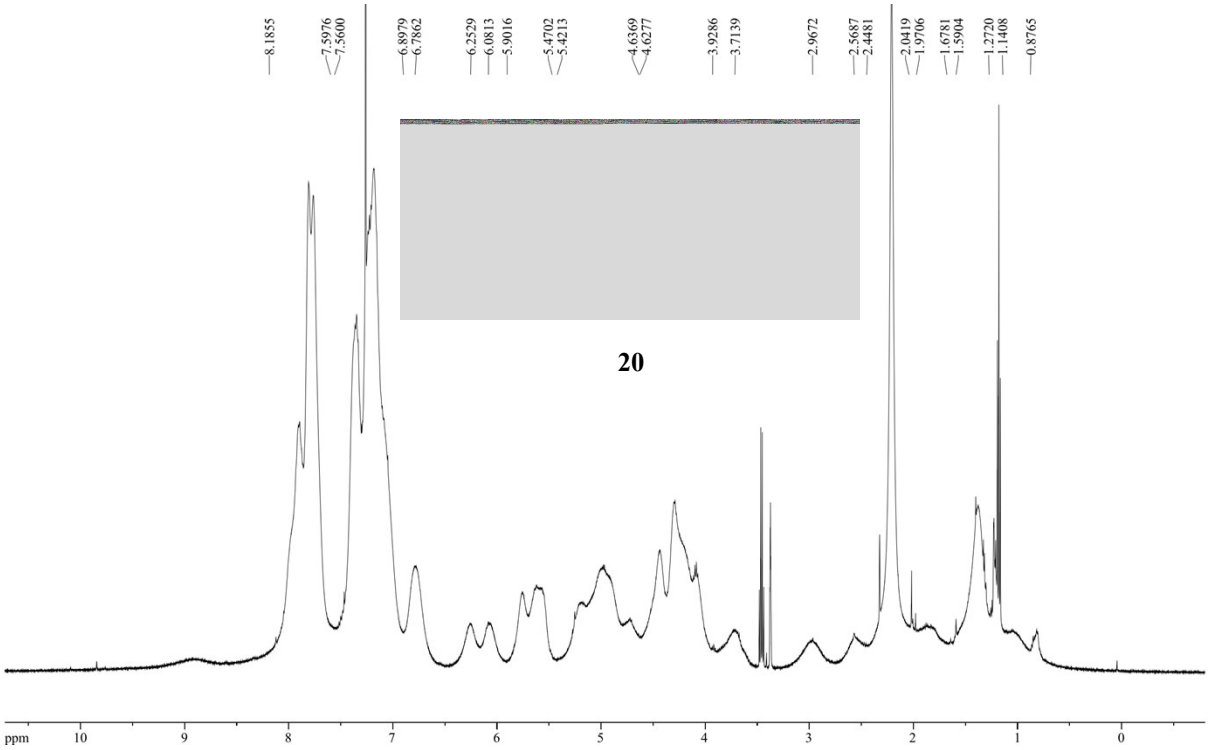
HSQC NMR spectrum of compound **19** (500 MHz; $CDCl_3/CD_3OD$)



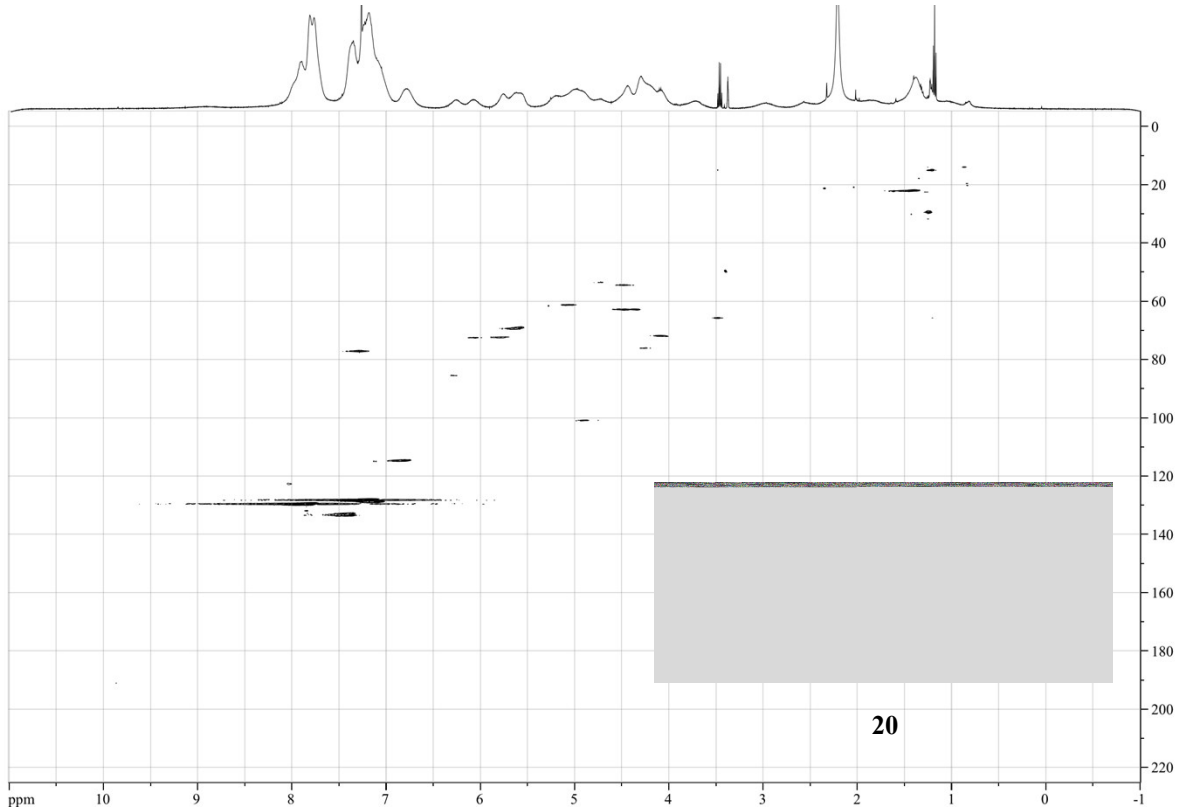
HMBC NMR spectrum of compound **19** (500 MHz; $CDCl_3/CD_3OD$)



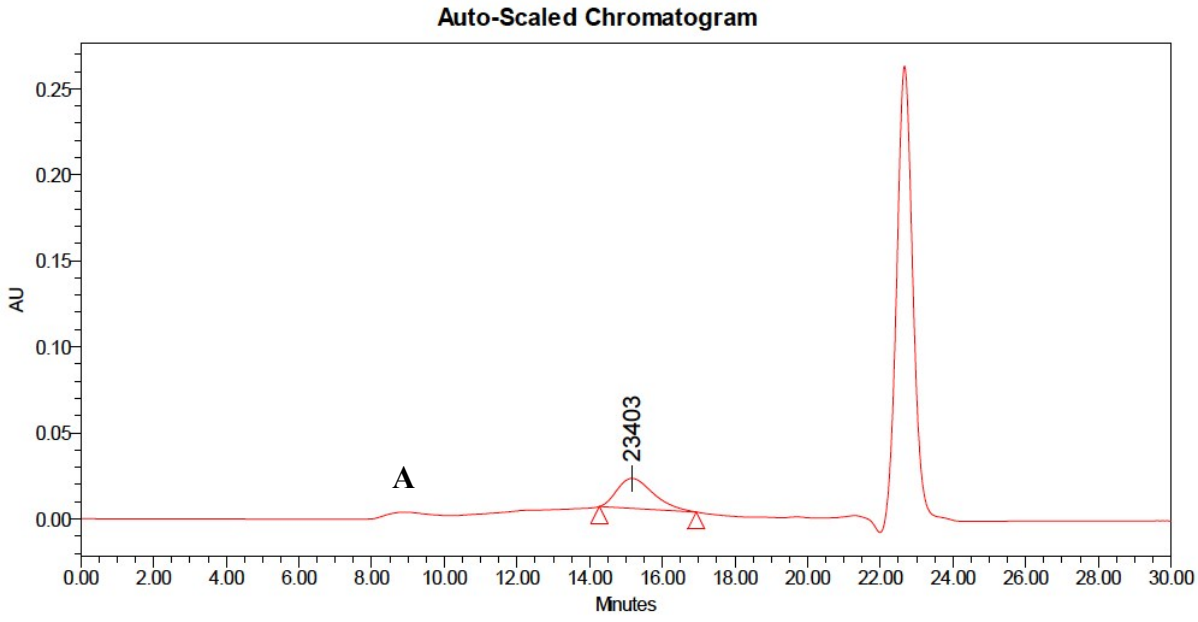
^{1}H NMR spectrum of compound **20** (500 MHz; $CDCl_3/CD_3OD$)



HSQC NMR spectrum of compound **20** (500 MHz; $CDCl_3/CD_3OD$)



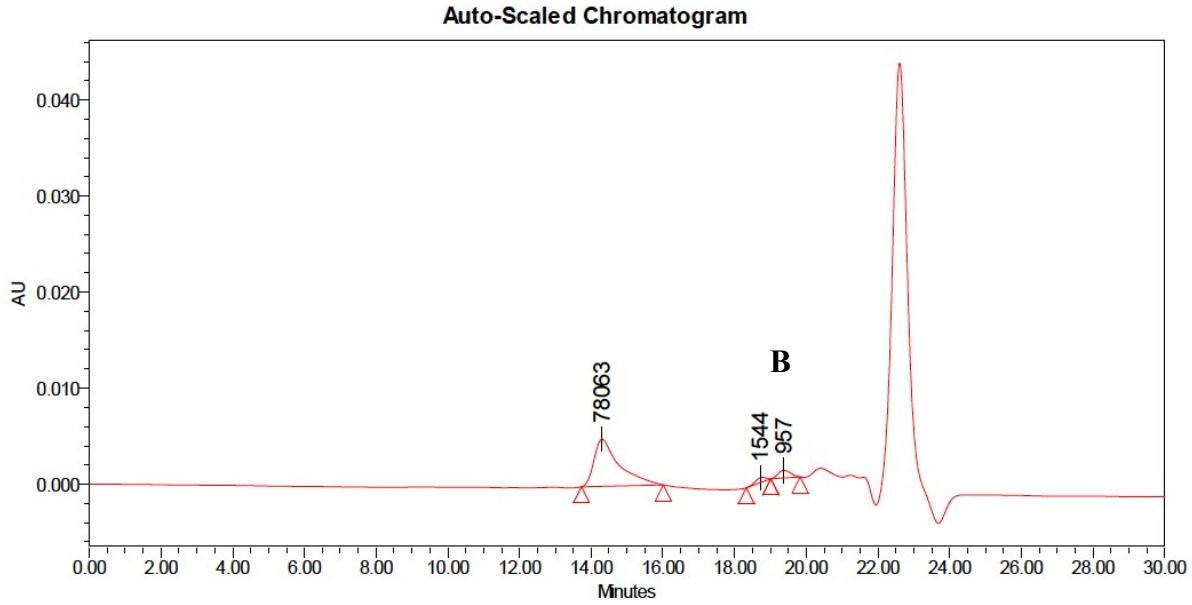
GPC trace of compound **18**



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		18869	23037	23403	28093	33686		1.220920		

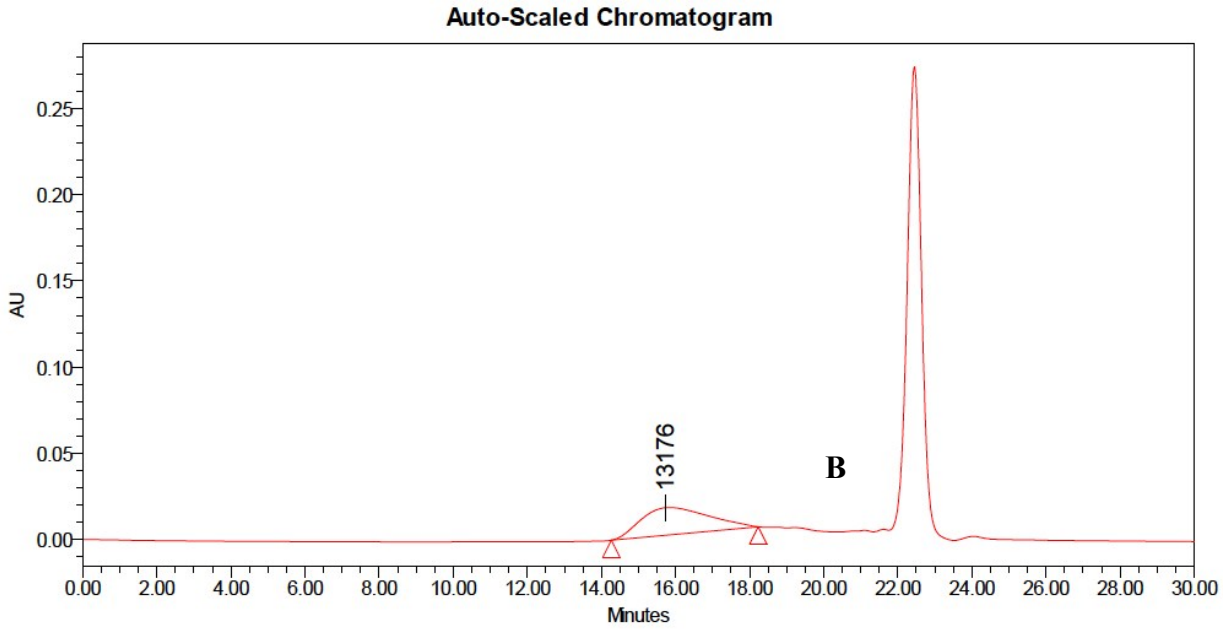
GPC trace of compound **19**



GPC Results

	Dist Name	Mn	Mw	Mv	MP	Mz	Mz+1	Polydispersity	K	alpha
1		43187	63612		78063	83223	99951	1.472928		

GPC trace of compound **20**



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		9796	13297	13176	18435	24922		1.357426		

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