**Electronic Supplementary Materials** *Mendeleev Commun.*, 2019, **29**, 680–682

# Synthesis of *N*-acetyllactosamine based branched hexasaccharide

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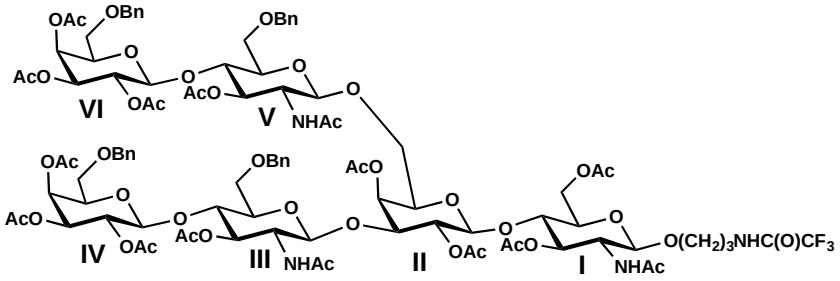
$^1$H and $^{13}$C NMR spectra were registered on a Bruker AVANCE spectrometer (Bruker BioSpin MRI GmbH) at 303K. Chemical shifts $\delta$ for characteristic protons are given in ppm using the internal standards DMSO-$d_5$ ($\delta$ 2.50) or $CHCl_3$ ($\delta$ 7.27) as references, and the coupling constants $J$ are given in Hz. The signals in $^1$H NMR and $^{13}$C NMR spectra were assigned by 2D-$^1$H,$^1$H-COSY and 2D-$^1$H,$^{13}$C-HSQC experiments. The values of optical rotation were measured on a Perkin Elmer 341 digital polarimeter at 25°C. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). TLC was carried out on silica gel 60 precoated aluminum sheets (Merck, Germany).

*Compound* **7**: white foam, $R_f$ 0.30 (*n*-$C_6H_{14}$–$Et_2O$–acetone, 1 : 2 : 4), $[\alpha]_D$ -18 (*c* 1, $CHCl_3$). $^1$H NMR (700 MHz, $CDCl_3$) $\delta$: 1.77–1.83 (m, 1H, $OCH_2CHHCH_2N$), 1.86–1.92 (m, 1H, $OCH_2CHHCH_2N$), 1.97, 2.08, 2.11, 2.15, 2.20 [5s, 15H, 5C(O)Me], 3.24–3.29 (m, 1H, $OCH_2CH_2CHHN$), 3.48 (dd, 1H, $J_{6a,6b}$ 11.4 Hz, $J_{5,6a}$ 6.3 Hz, H-6'a), 3.55–3.59 (m, 1H, $OCHHCH_2CH_2N$), 3.60–3.65 (m, 3H, H-5, H-5', $OCH_2CH_2CHHN$), 3.67 (dd, 1H, $J_{6a,6b}$ 11.4 Hz, $J_{5,6b}$ 6.7 Hz, H-6'b), 3.79 (dd, 1H, $J_{3,4}$ 9.0 Hz, $J_{4,5}$ 9.0 Hz, H-4), 3.82 (dd, 1H, $J_{2,3}$ 2.9 Hz, $J_{3,4}$ 10.2 Hz, H-3'), 3.89–3.93 (m, 1H, $OCHHCH_2CH_2N$), 4.01 (ddd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.2 Hz, $J_{2,NH}$ 9.1 Hz, H-2), 4.14 (dd, 1H, $J_{6a,6b}$ 11.8 Hz, $J_{5,6a}$ 5.6 Hz, H-6a), 4.45 (d, 1H $J_{1,2}$ 7.8 Hz, H-1), 4.50 (d, $J_{1,2}$ 7.8 Hz, H-1'), 4.55 (dd, 1H, $J_{6a,6b}$ 11.9 Hz, $J_{5,6b}$ 2.8 Hz, H-6b), 4.91 (dd, 1H, $J_{2,3}$ 10.1 Hz, $J_{1,2}$ 7.8 Hz, H-2'), 5.10 (dd, 1H, $J_{2,3}$ 9.2 Hz, $J_{3,4}$ 9.2 Hz, H-3), 5.25 (d, 1H, $J_{3,4}$ 2.9 Hz, H-4'), 5.90 (d, 1H, $J_{2,NH}$ 9.1 Hz, N*H*Ac), 7.33–7.35 [m, 1H, $NHC(O)CF_3$]. $^{13}$C NMR (DEPT, 176 MHz, $CDCl_3$) $\delta$: 20.80, 20.84, 20.9, 21.0 [4OC(O)*Me*], 23.3 [NC(O)*Me*], 28.6 ($OCH_2CH_2CH_2N$), 37.3 ($OCH_2CH_2CH_2N$), 53.6 (C-2), 60.6 (C-6'), 62.3 (C-6), 66.9 ($OCH_2CH_2CH_2N$), 70.4 (C-4'), 71.4 (C-3'), 72.9 (C-3), 73.1 (C-5), 73.3 (C-2'), 74.2 (C-5'), 75.7 (C-4), 100.9 (C-1'), 101.3 (C-1). HRMS (ESI), *m*/*z*: 727.2144 $[M+Na]^+$ (calc. for $C_{27}H_{39}F_3N_2O_{16}Na$, *m*/*z*: 727.2144).

*Compound* **13**: white foam, $R_f$ 0.44 (PhMe–acetone, 6 : 1), $[\alpha]_D$ +30 (*c* 1, $CHCl_3$). $^1$H NMR (700 MHz, $CDCl_3$) $\delta$: 1.91, 1.97, 1.99, 2.04 [4s, 12H, 4C(O)Me], 3.41 (dd, 1H, $J_{6a,6b}$ 9.3 Hz, $J_{5,6a}$ 7.5 Hz, H-6'a), 3.52 (dd, 1H, $J_{6a,6b}$ 9.3 Hz, $J_{5,6b}$ 5.6 Hz, H-6'b), 3.63–3.67 (m, 2H, H-6a, H-5'), 3.79

(dd, 1H, $J_{6a,6b}$ 11.3 Hz, $J_{5,6b}$ 2.7 Hz, H-6b), 3.86–3.89 (m, 1H, H-5), 4.11 (dd, 1H, $J_{3,4}$ 9.7 Hz, $J_{4,5}$ 9.7 Hz, H-4), 4.17 (ddd, 1H, $J_{2,3}$ 11.0 Hz, $J_{2,NH}$ 9.1 Hz, $J_{1,2}$ 3.6, H-2), 4.41–4.44 (m, 2H, 2PhC*H*H), 4.45 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1'), 4.54 (d, 1H, *J* 12.0 Hz, PhCH*H*), 4.69–4.74 (m, 2H, $OCH_2CCl_3$), 4.75 (d, 1H, *J* 11.9 Hz, PHCH*H*), 4.83 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.5 Hz, H-3'), 4.99 (dd, 1H, $J_{2,3}$ 10.3 Hz, $J_{1,2}$ 8.0 Hz, H-2'), 5.22 (d, 1H, $J_{2,NH}$ 9.1 Hz, N*H*Troc), 5.27 (dd, 1H, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 9.7 Hz, H-3), 5.40 (dd, 1H, $J_{3,4}$ 3.5 Hz, H-4'), 6.41 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 7.25–7.43 (m, 10H, Ar*H*), 8.73 [s, 1H, $OC(NH)CCl_3$]. $^{13}$C NMR (DEPT, 176 MHz, $CDCl_3$) $\delta$: 20.61, 20.64, 20.8 [4 C(O)*Me*], 54.2 (C-2), 66.9 (C-6'), 67.2 (C-6), 67.4 (C-4'), 69.5 (C-2'), 70.5 (C-3), 71.4 (C-3'), 71.9 (C-5'), 73.1 (C-5), 73.6 (Ph*C*$H_2$), 73.9 (Ph*C*$H_2$), 74.1 (C-4), 74.7 (O*C*$H_2CCl_3$), 95.1 (C-1), 100.6 (C-1'), 127.8–129.0 (12C-Ar). HRMS (ESI), *m*/*z*: 1031.0685 $[M+Na]^+$ (calc. for $C_{39}H_{44}Cl_6N_2O_{16}Na$, *m*/*z*: 1031.0690).

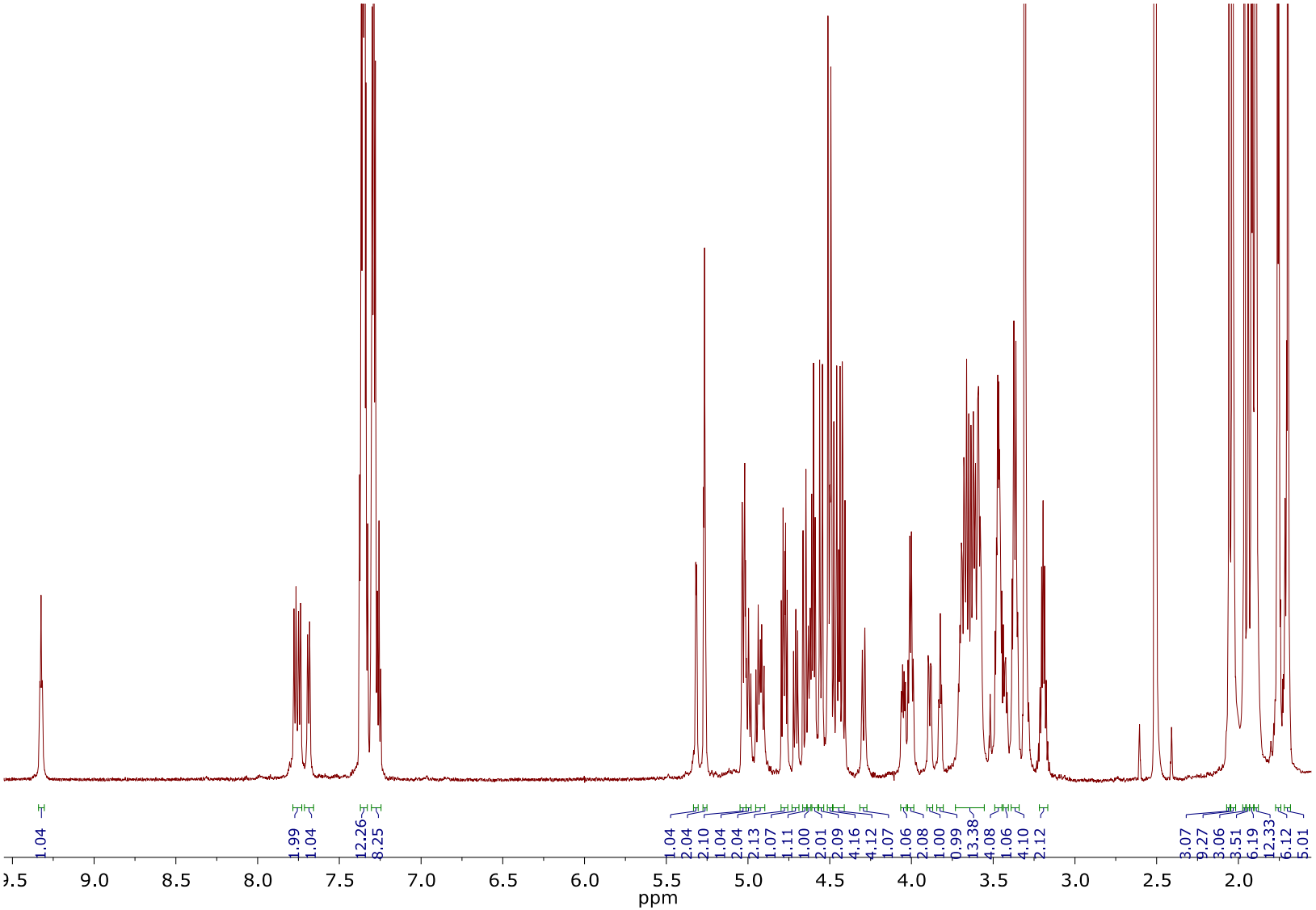



**1**

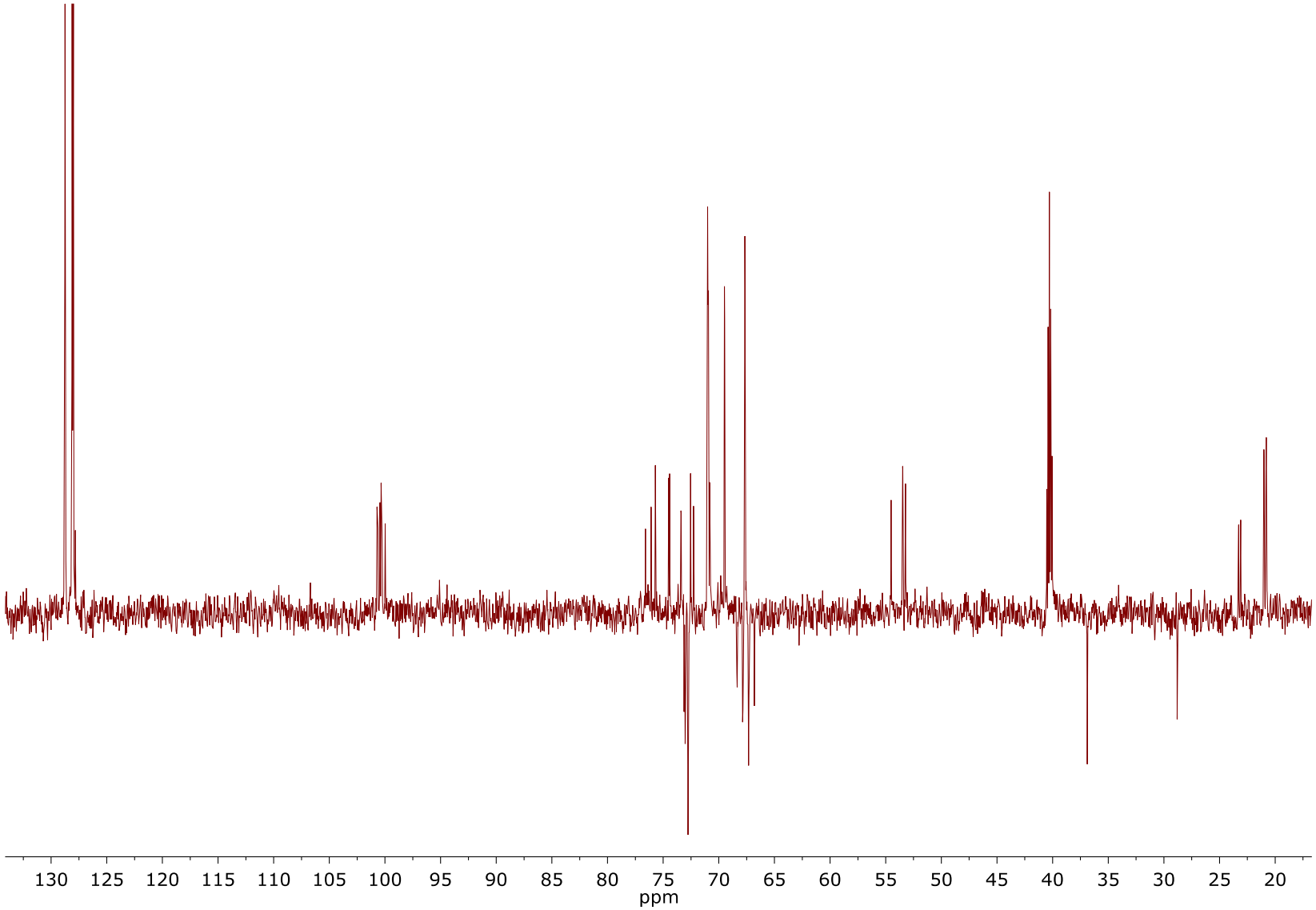
Numeration of monosaccharide residues in compound **1**.

*Compound* **1**: white foam, $R_f$ 0.22 (PhMe–acetone, 2 : 3), $[\alpha]_D$ -35 (*c* 0.25, $CHCl_3$). $^1$H NMR (700 MHz, DMSO-$d_6$) $\delta$: 1.68–1.73 [m, 5H, NC(O)Me, $OCH_2CH_2CH_2N$], 1.75, 1.76 [2s, 6H, 2NC(O)Me], 1.890, 1.894, 1.895, 1.896, 1.91, 1.92, 1.94, 1.96, 2.03, 2.042, 2.044, 2.06 [12s, 36H, 12OC(O)Me], 3.15–3.23 (m, 2H, $OCH_2CH_2CH_2N$), 3.34–3.39 (m, 3H, H-2 I, H-6a IV, H-6a VI), 3.43 (dd, 1H, $J_{6a,6b}$ 10.1 Hz, $J_{5,6a}$ 6.1 Hz, H-6a II), 3.44–3.49 (m, 3H, H-6b IV, H-6b VI, $OCHCH_2CH_2N$), 3.56–3.70 (m, 11H, H-4 I, H-5 I, H-4 III, H-5 III, H-6a III, H-6b III, H-4 V, H-5 V, H-6a V, H-6b V, $OCHCH_2CH_2N$), 3.70–3.73 (m, 1H, H-6b II), 3.82 (dd, 1H, $J_{5,6a}$ 6.0 Hz, $J_{5,6b}$ 6.0 Hz, H-5 II), 3.89 (dd, 1H, $J_{2,3}$ 10.1 Hz, $J_{3,4}$ 3.5 Hz, H-3 II), 3.98–4.03 (m, 2H, H-5 IV, H-5 VI), 4.05 (dd, 1H, $J_{6a,6b}$ 11.8 Hz, $J_{5,6a}$ 5.7 Hz, H-6a I), 4.29 (dd, 1H, $J_{6a,6b}$ 11.8 Hz, $J_{5,6a}$ < 1 Hz, H-6b I), 4.40–4.44 (m, 2H, 2 PHC*H*H), 4.45 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1 II), 4.47 (d, 1H, *J* 12.4 Hz, PhC*H*H), 4.47–4.50 (m, 3H, 2PhC*H*H), 4.51 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1 V), 4.54 (d, 1H, *J* 11.8 Hz, PhC*H*H), 4.56 (d, 1H, $J_{1,2}$ 9.0 Hz, H-1 III), 4.59 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1 IV), 4.61 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1 VI), 4.63 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1 I), 4.56 (d, 1H, *J* 12.4 Hz, PhC*H*H), 4.71 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.0 Hz, H-2 II), 4.76–4.80 (m, 2H, H-2 IV, H-2 VI), 4.90–4.96 (m, 2H, H-3 III, H-3 V), 5.00 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 9.8 Hz, H-3 I), 5.01–5.05 (m, 2H, H-3 IV, H-3 VI), 5.25–

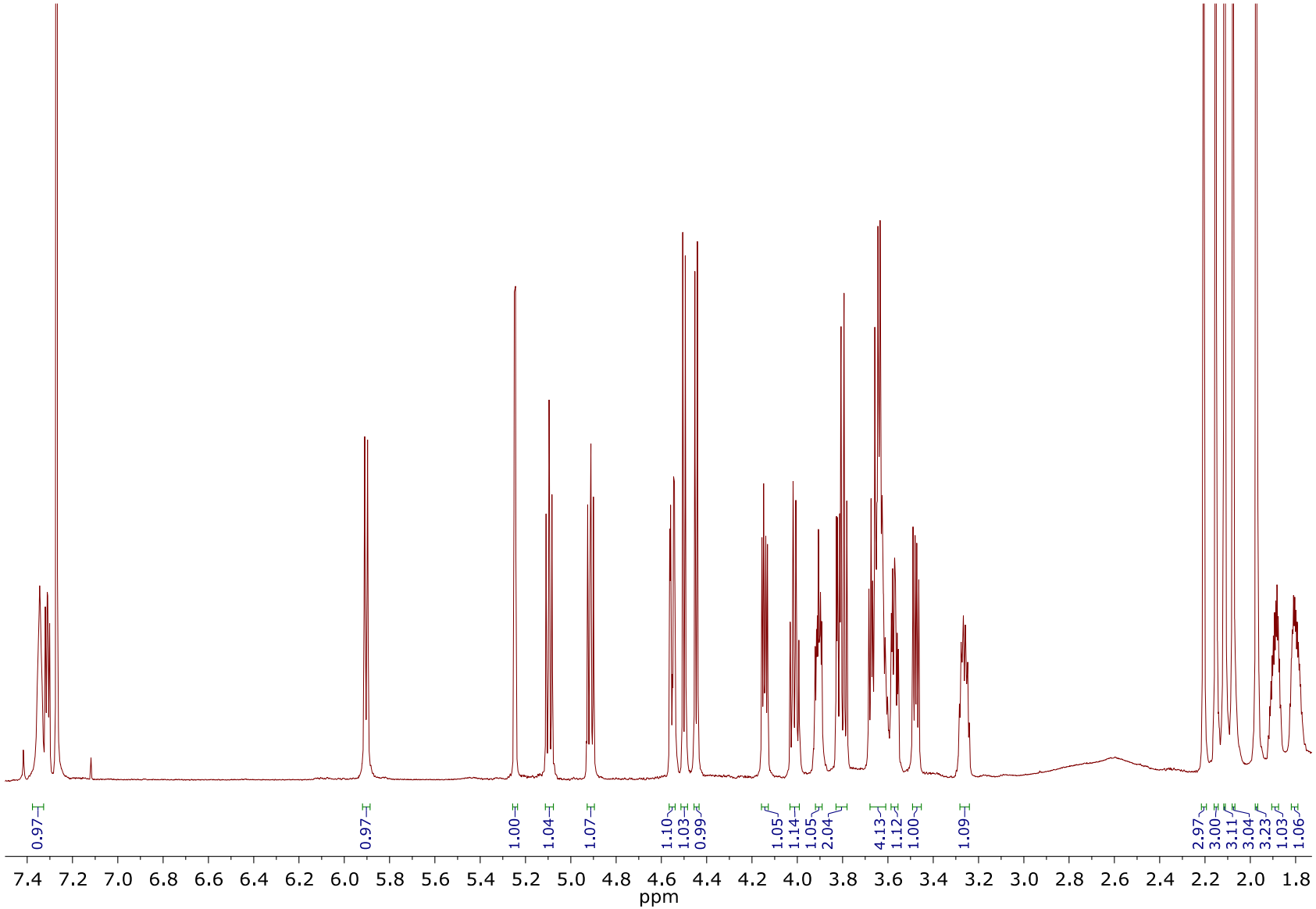
5.28 (m, 2H, H-4 IV, H-4 VI), 5.32 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ < 1 Hz, H-4 II), 7.24–7.39 (m, 20H, Ar*H*), 7.69 (d, 1H, $J_{2,NH}$ 8.8 Hz, N*H*Ac I), 7.74 (d, 1H, $J_{2,NH}$ 9.2 Hz, N*H*Ac III), 7.77 (d, 1H, $J_{2,NH}$ 9.2 Hz, N*H*Ac V), 9.30–9.35 [m, 1H, NHC(O)$CF_3$]. $^{13}$C NMR (DEPT, 176 MHz, DMSO-$d_6$) $\delta$: 20.7, 20.80, 20.83, 20.86, 20.91, 20.96, 21.01, 21.07 [8s, 12OC(O)*Me*], 23.7 [3NC(O)*Me*], 28.8 ($OCH_2$*C*$H_2CH_2N$), 36.9 ($OCH_2CH_2$*C*$H_2N$), 53.2, 53.5 (C-2 III, C-2 V), 54.5 (C-2 I), 62.8 (C-6 I), 66.3 (O*C*$H_2CH_2CH_2N$), 66.8 (C-6 II), 67.3 (C-6 IV, C-6 VI), 67.6 (C-4 IV, C-4 VI), 67.9, 68.4 (C-6 III, C-6 V), 69.5 (C-2 IV, C-2 VI), 69.8 (C-4 II), 70.77, 70.83, 70.93, 70.95, 71.0 (C-2 II, C-3 IV, C-5 IV, C-3 VI, C-5 VI), 72.3 (C-5 II), 72.5 (C-5 I), 72.8, 73.0, 73.1 (4 Ph*C*$H_2$), 73.2 (C-3 I), 73.7 (C-3 III, C-3 V), 74.47, 74.52 (C-5 III , C-5 V), 75.7, 76.1 (C-4 I, C-4 III, C-4 V), 76.6 (C-3 II), 99.97 (C-1 III), 100.26, 100.33 (C-1 IV, C-1 VI), 100.5 (C-1 II), 100.6 (C-1 I), 100.8 (C-1 V), 127.7–128.9 (24C-Ar). HRMS (ESI), *m*/*z*: 2154.7497 $[M+Na]^+$ (calc. for $C_{99}H_{125}F_3N_4O_{44}Na$, *m*/*z*: 2154.7544).



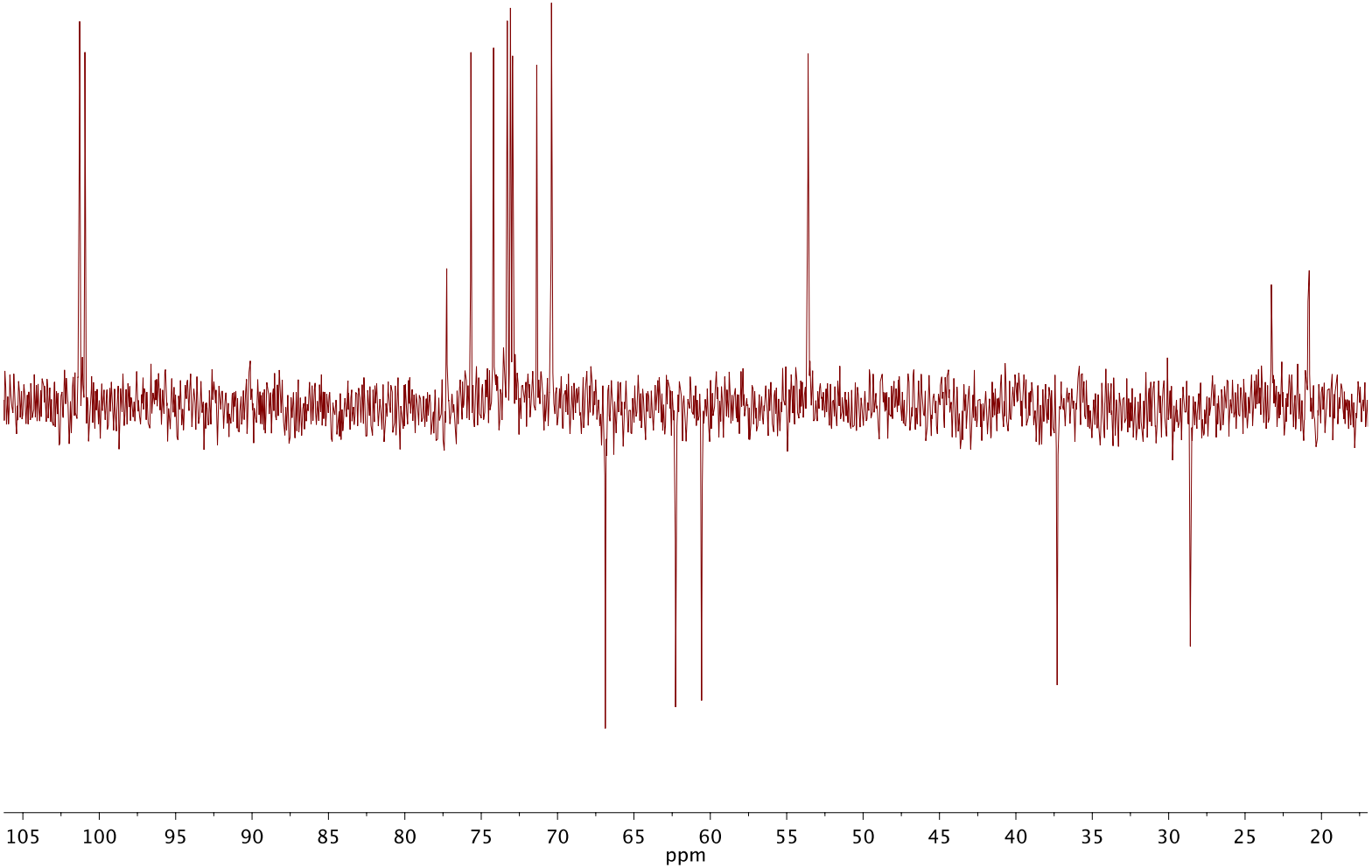

$^{1}$H NMR spectrum of compound **1**



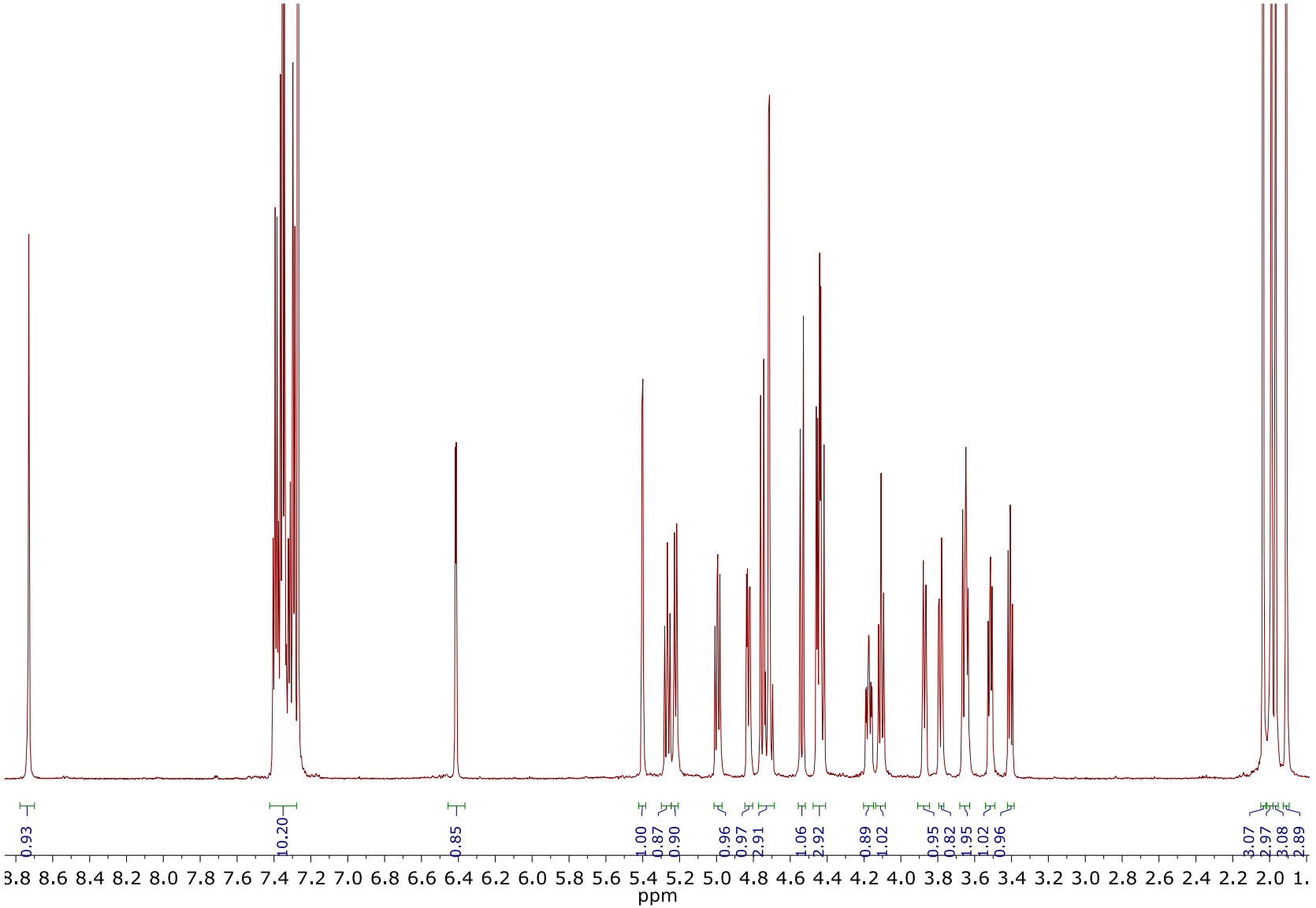

$^{13}$C NMR spectrum of compound **1** (DEPT)



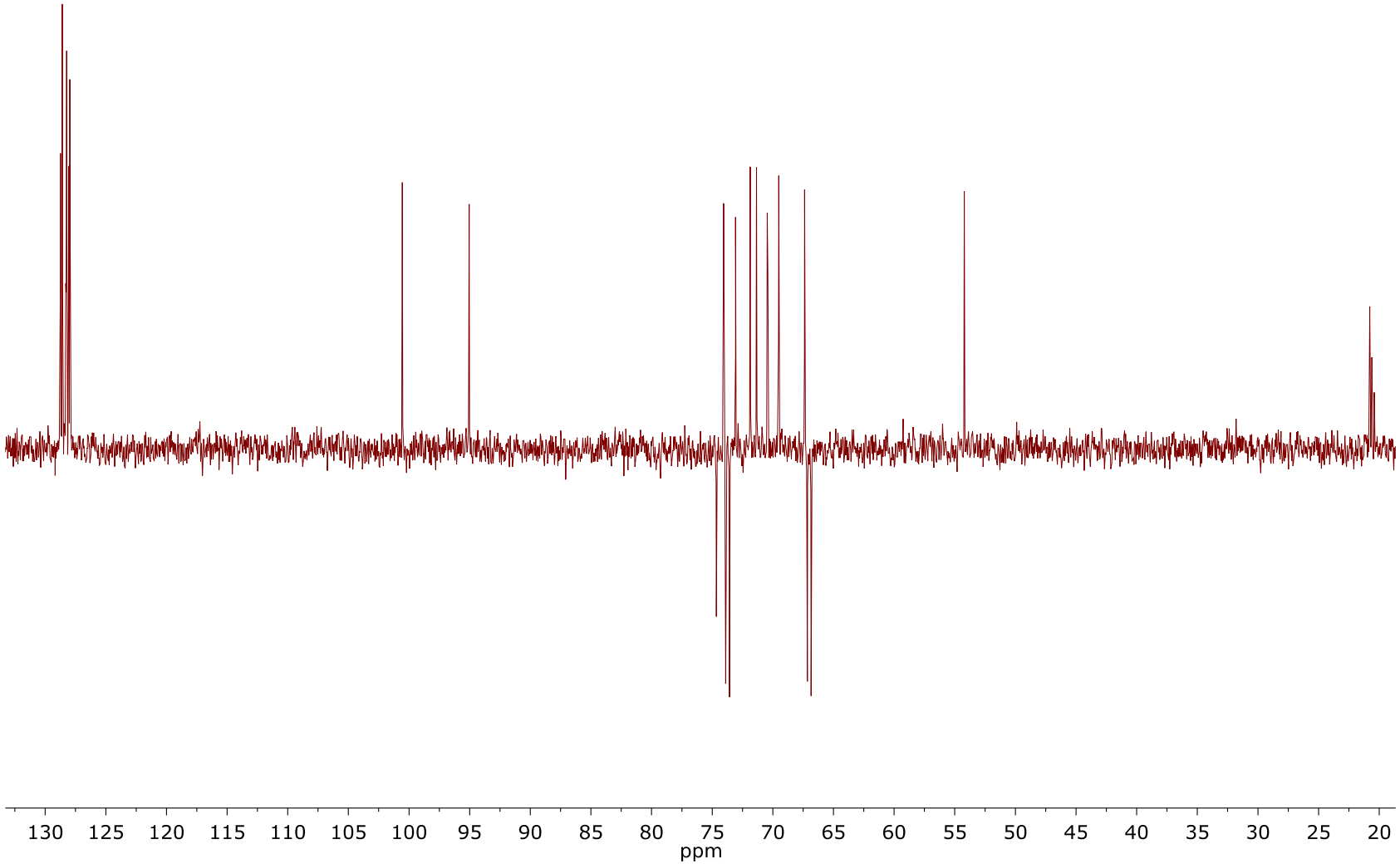

$^{1}$H NMR spectrum of compound **7**




$^{13}$C NMR spectrum of compound **7** (DEPT)




$^{1}$H NMR spectrum of compound **13**




$^{13}$C NMR spectrum of compound **13** (DEPT)