Electronic Supplementary Information

Synthesis and *in vitro* phantom NMR and MRI studies of fully organic free radicals, TEEPO-glucose and TEMPO-glucose. Potential tumor targeting contrast agents for MRI

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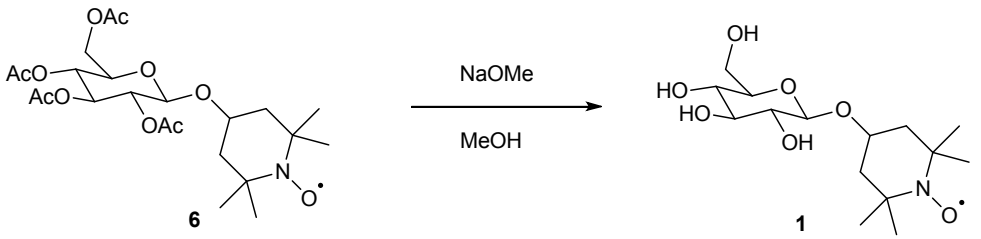
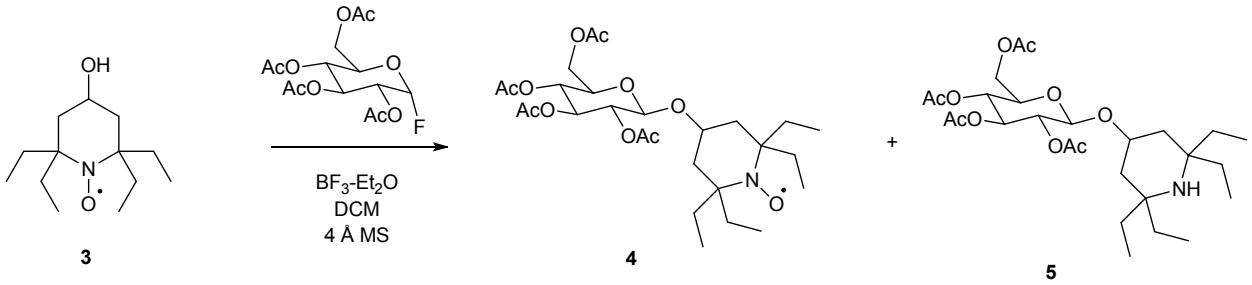
1. Synthesis of the contrast agents

General methods. The reagents were obtained from commercial sources and were used without further purification. The blood plasma was purchased from the Finnish Red Cross Blood Service. The NMR-spectra were recorded at 27 °C with Varian Unity Inova 500 NMR-spectrometer (^{1}H-frequency 500 MHz, 11.7 T magnetic field strength) equipped with 5 mm pulsed field gradient inverse detection dual ^{1}H-X probehead (X-coil tuned to ^{13}C-frequency) capable of delivering z-axis gradient amplitudes up to 20 G/cm. The spectrometer operating software was Vnmr 6.1C. For the NMR-analysis of the radical species, the nitroxides had to be pretreated by a rapid method of reduction by hydrazobenzene directly in the NMR sample tube to enable detection of NMR signals. The IR-spectra were recorded using Bruker Alpha ATR-FTIR spectrometer. High resolution mass spectra for exact mass were measured using Bruker Micro TOF with electron spray ionization (ESI). The conformations of the final products were determined based on the chemical shifts and coupling constants of the anomeric protons and their comparison to literature values.[1]



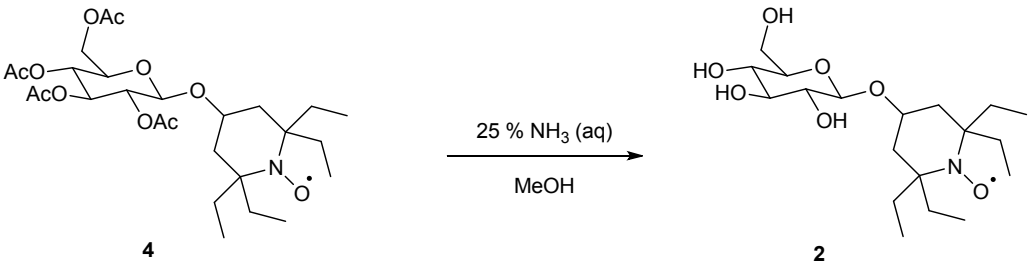
2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl-β-*D*-glucopyranoside (1). To a mixture of small amount of sodium and 100 ml of MeOH was added 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy-TEMPO **6** (1.0 g), and the mixture was stirred under argon atmosphere at room temperature for 3 h. NH_4Cl in small amount of water was added and the reaction mixture was stirred vigorously for 5 min. The mixture was filtrated and the solvent of the filtrate was evaporated to obtain the crude product, which was then dried in high vacuum. The crude product was purified by silica gel column chromatography (first 2:1 DCM–MeOH, then 20:1 CHCl3–MeOH and 10:1 CHCl3–MeOH) to give the product **1** (270 mg, 43 %) as an orange solid. ^{1}H NMR (500 MHz, CD_3OD + hydrazobenzene): δ (ppm): 4.36 (d, ^3J=7.8 Hz, 1 H, *H*-1'), 4.05-4.09 (m, 1 H, *H*-4), 3,79-3,88 (m, 1 H, *H*-6a'), 3.59-3.68 (m, 1 H, *H*-6b'), 3,58-3,62 (m, 1 H, *H*-3'), 3.28-3.29 (m, 1 H, *H*-4'), 3.27-3.28 (m, 1 H, *H*-5'), 3.11-3,15 (t, ^3J=8.5 Hz, 1 H, *H*-2'), 1.96-2,01 (m, 2 H, CH_2), 1.44-1.60 (m, 2 H, CH_2), 1.18 (s, 3 H, CH_3), 1,17 (s, 3 H, CH_3), 1,15 (s, 3 H, CH_3), 1,15 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$ + hydrazobenzene): δ (ppm): 102,66 (*C*-1'), 78,07 (*C*-3'), 77,87 (*C*-5'), 75,12 (*C*-2'), 72.01 (C), 71.81 (C-4), 71,69 (*C*-4'), 62,79 (*C*-6'), 60.16 (C), 46,98 (CH_2), 45,43 (CH_2), 32,74 (CH_3), 20,85 (CH_3); IR: *v* (cm^{-1}): 3211 (OH), 2933, 1662, 1567, 1400, 1305 (N-O•), 1021 (N-O•); HRMS (ESI) $C_{15}H_{28}NO_7^{\bullet}$: calc: 357.1758 $[M+Na]^+$, found: 357.1762 $[M+Na]^+$



4-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-2,2,6,6-tetraethylpiperidin-1-oxyl (4). 4-hydroxy-TEEPO **3** (103.7 mg, 0.45 mmol), Glc *α*-F (193.7 mg, 0.55 mmol) and crushed 4 Å molecular sieves (50 mg) were dissolved in dichloromethane (1 ml). The reaction mixture was cooled to 0 °C and $BF_3{\cdot}Et_2O$ (0.11 ml, 0.89 mmol) was added slowly. The reaction mixture was stirred at room temperature under argon atmosphere for six hours. The reaction was quenched with cold water and filtered through Celite®. The Celite® pad was washed with ethyl acetate and the organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under vacuo and the crude product was separated by silica gel column chromatography using *n*-hexane/ethyl acetate 1:1, then 10 % methanol/dichloromethane as eluent yielding 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy-TEEPO **4** (57.1 mg, 23 %) as light orange solid and 4-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-2,2,6,6-tetraethylpiperidine **5** (152.2 mg, 62 %) as yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$ + hydrazobenzene): δ (ppm): 5.21 (t, ^3J=9.5 Hz, 1 H, *H*-3'), 5.06 (t, ^3J=9.5 Hz, 1 H, *H*-4'), 4.95 (t, ^3J=9.5 Hz, 1 H, *H*-2'), 4.57 (d, ^3J=8.0 Hz, 1 H, *H*-1'), 4.24 (dd, ^3J=5.0 Hz, ^2J=12.0 Hz, 1 H, *H*-6b'), 4.14 (dd, ^3J=2.0 Hz, ^2J=12.0 Hz, 1 H, *H*-6a'), 3.81-3.88 (m, 1 *H*-4), 3.68-3.73 (m, 1 H, *H*-5'), 2.07 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 1.88-1.97 (m, 2 H, CH_2), 1.83-1.85 (m, 1 H, CH_2), 1.68-1.71 (m, 1 H, CH_2), 1.58-

1.67 (m, 4 H, CH_2), 1.48-1.48 (m, 1 H, CH_2), 1.27-1.37 (m, 2 H, CH_2), 1.23-1.25 (m, 1 H, CH_2), 0.86 (t, ^3J=7.5 Hz, 6 H, CH_3), 0.84 (t, ^3J=7.5 Hz, 6 H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$ + hydrazobenzene): δ (ppm): 170.66 (C=O), 170.32 (C=O), 169.41 (C=O), 169.23 (C=O), 100.05 (*C*-1'), 72.83 (*C*-3'), 72.54 (*C*-4), 71.90 (*C*-5'), 71.48 (*C*-2'), 68.57 (*C*-4'), 63.30 (C), 62,31 (*C*-6'), 36.86 (CH_2), 35.79 (CH_2), 29.97 (CH_2), 26.72 (CH_2), 20.70 (OAc), 20.67 (OAc), 20.62 (OAc), 20.60 (OAc), 9.67 (CH_3), 8.13 (CH_3); IR: ν (cm^{-1}): 2966, 1747 (C=O), 1464 (N-O•), 1364 (N-O•), 1217 (N-O•), 1166, 1036; HRMS (ESI) $C_{27}H_{44}NO_{11}^{\bullet}$: calc: 581.2807 $[M+Na]^+$, found: 581.2815 $[M+Na]^+$.

4-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-2,2,6,6-tetraethylpiperidine 5: ^{1}H NMR (500 MHz, CD_3OD): δ (ppm) 5.32 (d, ^3J=8.0 Hz, 1 H, *H*-1'), 5.23-5.29 (m, 1 H, *H*-3'), 4.99-5.06 (m, 1 H, *H*-4'), 4.88 (m, 1 H, *H*-2'), 4.22-4.27 (m, 1 H, *H*-6a'), 4.16-4.22 (m, 1 H, *H*-4), 4.07-4.16 (m, 1 H, *H*-6b'), 3.89-3.93 (m, 1 H, *H*-5'), 2.88-3.01 (m, 2 H, CH_2), 2.64-2.76 (m, 2 H, CH_2), 2.47-2.59 (m, 4 H, CH_2), 2.11-2.25 (m, 1 H, CH_2), 1.97-2.06 (m, 1 H, CH_2), 2.05 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), 1.97 (s, 3 H, OAc), 1.76-1.86 (m, 1 H, CH_2), 1.62-1.71 (m, 1 H, CH_2), 1.29 (bs, 1 H, NH), 1.14 (t, ^3J=7.5 Hz, 6 H, CH_3), 0.90 (t, ^3J=7.5 Hz, 3 H, CH_3), 0.80 (t, ^3J=7.5 Hz, 3 H, CH_3); ^{13}C NMR (126 MHz, CD_3OD): δ (ppm): 172.17 (C=O), 171.64 (C=O), 171.59 (C=O), 171.22 (C=O), 95.88 (C-1), 74.22 (C-3'), 73.02 (C-2'), 71.49 (C-5'), 69.77 (C-4'), 63.47 (C-6'), 63.14 (C-4), 35.98 (CH_2) 35.01 (CH_2), 32.64 (CH_2), 31.74 (CH_2), 26.74 (CH_2), 20.53 (OAc), 9.18 (C), 8.29 (CH_3), 8.23 (CH_3), 8.13 (CH_3); IR: ν (cm^{-1}): 2925, 1743 (C=O), 1366, 1213, 1030, 599; HRMS (ESI) $C_{27}H_{45}NO_{10}$: calc: 544.3116 $[M+H]^+$, found: 544.3119 $[M+H]^+$.



4 **2**

2,2,6,6-tetraethylpiperidin-1-oxyl-4-yl-β-*D*-glucopyranoside (2). To a solution of 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy-TEEPO **4** (50 mg) in 1 ml of methanol was added 1 ml of 25 % NH_3 solution. The reaction mixture was stirred at room temperature for two hours. The excess solvent and NH_3 were removed in vacuo. The product **2** was separated by silica gel column chromatography using 5 % MeOH/DCM as eluent and collected as an orange solid with 96 % yield. ^{1}H NMR (500 MHz, $(CD_3)_2O$ + D_2O + hydrazobenzene): δ (ppm): 4.41 (d, ^3J=8.0 Hz, 1 H, *H*-1'), 3.96-4.01 (m, 1 H, *H*-4), 3.78-3.81 (dd, ^3J=2.0 Hz, ^2J=11.8 Hz, 1 H, *H*-6a'), 3.66-3.69 (dd, ^3J=5.0 Hz, ^2J=11.9 Hz, 1 H, *H*-6b'), 3.42 (t, ^3J=8.8 Hz, 1 H, *H*-3'), 3.37 (t, ^3J=9.0 Hz, 1 H, *H*-4'), 3.29-3.31 (m, 1 H, *H*-5'), 3.17 (t, ^3J=8.2 Hz, 1 H, *H*-2'), 1.89-1.95 (m, 2 H, CH_2), 1.84-1.89 (m, 2 H, CH_2), 1.62-1.67 (m, 2 H, CH_2), 1.57-1.61 (m, 2 H, CH_2), 1.31-1.40 (m, 2 H, CH_2), 1.23-1.30 (m, 2 H, CH_2), 0.85 (t, ^3J=7.2 Hz, 6 H, CH_3), 0.82 (t, ^3J=7.4 Hz, 6 H, CH_3). ^{13}C NMR (126 MHz, $(CD_3)_2O$ + hydrazobenzene): δ (ppm): 102.88 (*C*-1), 78.05 (*C*-3'), 77.20 (*C*-5'), 74.99 (*C*-2'), 71.86 (*C*-4), 71.19 (*C*-4'), 63.79 (C), 63.69 (C), 63.06 (*C*-6'), 38.13 (CH_2), 36.43 (CH_2), 30.81 (CH_2), 30.78 (CH_2), 27.31 (CH_2), 10.09 (CH_3), 8.34 (CH_3); IR: ν (cm^{-1}): 3346 (OH), 2964, 1664, 1381 (N-O•), 1019 (N-O•); MS (ESI) $C_{19}H_{36}NO_7^{\bullet}$: calc: 389.2419 $[M-H]^-$, found: 389.2408 $[M-H]^-$.

2. Radical stability and relaxivity studies

Blood plasma NMR experiments were performed at 37 °C using Varian Unity Inova 500 NMR-spectrometer. Longitudinal relaxation times, T_1, of blood plasma water were determined using saturation-recovery method utilizing pulsed field gradients to destroy the transverse magnetization prior to recovery delay. Recovery delay durations were 0.003, 0.01, 0.02, 0.04, 0.1, 0.15, 0.2, 0.3, 0.4, 0.8, 1, 2, 4 and 6 s. Acquisition time was 2 s and relaxation delay was 4 s. Relaxation times were calculated using vendor provided fitting algorithms incorporated into the spectrometer operating software Vnmr 6.1C.

The NMR samples for stability and relaxitivity studies were prepared by adding 540 µl of blood plasma and 60 µl of D_2O into a NMR test tube. The initial stability tests for both radicals were conducted by preparing 0.6 mM radical solution in blood plasma. The samples were kept at 37 °C for one week and during that time several relaxation measurements were conducted to monitor the stability.

Table S1. The 11.7 T water T_1-relaxation times of the nitroxide samples (2.5 mM) measured in blood plasma at 37 °C as a function of time elapsed from sample preparation.

time	T_1 (s)	
	TEMPO-Glc	TEEPO-Glc
20 min	1.30	1.51
60 min	1.30	1.50
100 min	1.31	1.49
140 min	1.31	1.49
180 min	1.31	1.49
220 min	1.32	1.49
280 min	1.32	1.49
340 min	1.32	1.48
460 min	1.33	1.48
22 h	1.36	1.46
week	1.46	1.43
month	1.47	1.45

For radical stability measurements in presence of ascorbic acid, a rapid T_1 measurement, Driven Equilibrium Single Pulse Observation of T_1 (DESPOT) was used. In DESPOT, two different flip angles are utilized (approximately 45° and 90°). The pulse widths were calibrated with sample without ascorbic acid. After the addition of ascorbic acid, the measurements had to be started quickly, and thus pulse width determination was not possible, only probe tuning and shimming were performed. After the dataset was acquired, the actual flip angles were determined and those were used to calculate the T_1-values. Number of steady state scans before each measurement was 16. The repetition delay for DESPOT measurements was 1.6 s (relaxation delay of 0.6 s and acquisition time of 1.0 s). The signal integrals from the two acquisitions with aforementioned two different pulse widths were measured and T_1 was calculated using integral and flip angle values.

The samples for radical stability in the presence of reductant were prepared by mixing 10 µl H_2O in 600 µl D_2O and adding the radical (TEMPO-Glc or TEEPO-Glc) up to concentration of 5 mM. Appropriate amount of ascorbic acid (10-fold excess) was added just before the start of relaxation time measurements.

Table S2. The 11.7 T T_1 relaxation times of the nitroxide samples (5 mM) measured in D_2O and H_2O at 37 °C as a function of time elapsed from the addition of the reductant.

time (min)	T_1 (s)	
	TEMPO-Glc	TEEPO-Glc
0	0.81	0.61
5	9.85	0.62
6	10.51	0.63
7	10.86	0.64
8	11.10	0.65
9	11.41	0.65
10	11.60	0.66
11	11.89	0.66
12	12.21	0.67
13	12.74	0.67
14	12.61	0.67
15	12.51	0.68
16	12.66	0.68
17	12.73	0.69
18	12.85	0.69
19	12.78	0.69
20	12.81	0.87
21	12.86	0.70
22	12.87	0.70
23	12.77	0.71
24	12.76	0.71
120	-	1.02
180	-	1.33
240	-	1.81
360	-	3.49
600	-	9.81
840	-	12.80
1140	12.61	12.74

Based on the observed extreme stability (Table S2), it is possible to prepare a stock solution directly in blood plasma, that can be subsequently used to prepare samples with varying radical concentrations. A 19 mM stock solution of radical was prepared by dissolving suitable amount of radical in blood plasma. Appropriate volume of the stock solution was added to the NMR-sample so that concentrations of 0, 0.5, 1.0, 2.0, 3.0, 5.0, 7.50 mM were achieved.

Table S3. The concentrations of the TEMPO-Glc and TEEPO-Glc samples and corresponding T_1 and $1/T_1$ measured at 11.7 T.

c (mM)	T_1 (s)		$1/T_1$ (1/s)	
	TEMPO-Glc	TEEPO-Glc	TEMPO-Glc	TEEPO-Glc
0	3.08	3.03	0.32	0.33
0.5	2.55	2.57	0.39	0.39
1.0	2.17	2.20	0.46	0.46
2.0	1.67	1.69	0.60	0.59
3.0	1.35	1.38	0.74	0.73
5.0	0.99	1.03	1.01	0.97
7.5	0.75	0.82	1.34	1.23

3. MRI studies

Radical was weighed into a 30 ml flat bottom screw cap glass vial. Blood plasma (25 ml) was added just prior to MRI-session. The vials were placed into a round plastic holder (200 mm diameter, 50 mm depth), which was filled with 0.1 mM $MnCl_2$ solution containing 0.4 wt-% NaCl.

MRI was performed with a 1.5 T Siemens Avantofit (Siemens Medical Solutions, Erlangen, Germany) clinical MRI scanner using 20-channel head/neck receiving coil for signal detection. The T_1-weighted MRI was obtained using gradient echo sequence. Phantom relaxation times T_1 and T_2 were determined using inversion-recovery and multi-spin-echo imaging sequences, respectively. In-house written scripts running on Matlab-platform (MathWorks, Natick, MA) were used to calculate phantom T_1- and T_2-maps. For gradient echo MRI, single 5 mm axial slice was imaged using field-of-view (FOV) of 200x200 mm and the matrix size of 512x512. Repetition time (TR) was 400 ms, the echo time (TE) was 4.76 ms and flip angle was 90°. For inversion-recovery, single 5 mm axial slice was imaged using FOV of 250x250 mm and the matrix size of 128x128. TR was 2000 ms, the TE was 30 ms and inversion times were 150, 300, 450, 750, 900 and 1300 ms. For multi-echo imaging, single 5 mm axial slice was imaged using one repetition, FOV of 250x250 mm and the matrix size of 256x256. TR was 1000 ms and 32 images were recorded using TE increment of 25 ms (TE 25 ms-800 ms). For multi-echo imaging, single 5 mm axial slice was imaged using one repetition, FOV of 250x250 mm and the matrix size of 256x256. TR was 1000 ms and 32 images were recorded using TE increment of 25 ms (TE 25 ms-800 ms).

Table S4. The concentrations and corresponding T_1 and T_2 relaxation times for 1.5 T MRI.

c (mM)	T_1 (s)		T_2 (s)	
	TEMPO-Glc	TEEPO-Glc	TEMPO-Glc	TEEPO-Glc
0	1.05	1.06	0.62	0.66
0.2	1.01	1.03	0.60	0.61
0.5	0.97	0.80	0.56	0.58
1	0.92	0.91	0.55	0.51
2	0.80	0.79	0.45	0.43
5	0.62	0.53	0.35	0.28
10	0.37	0.33	0.23	0.19
16	0.26	0.213	0.18	0.13
	Gadopentetate dimeglumine / Gd (III)			
0.001	0.99	1.02	0.62	0.58
0.01	0.69	0.71	0.41	0.40
0.1	0.20	0.21	0.15	0.14

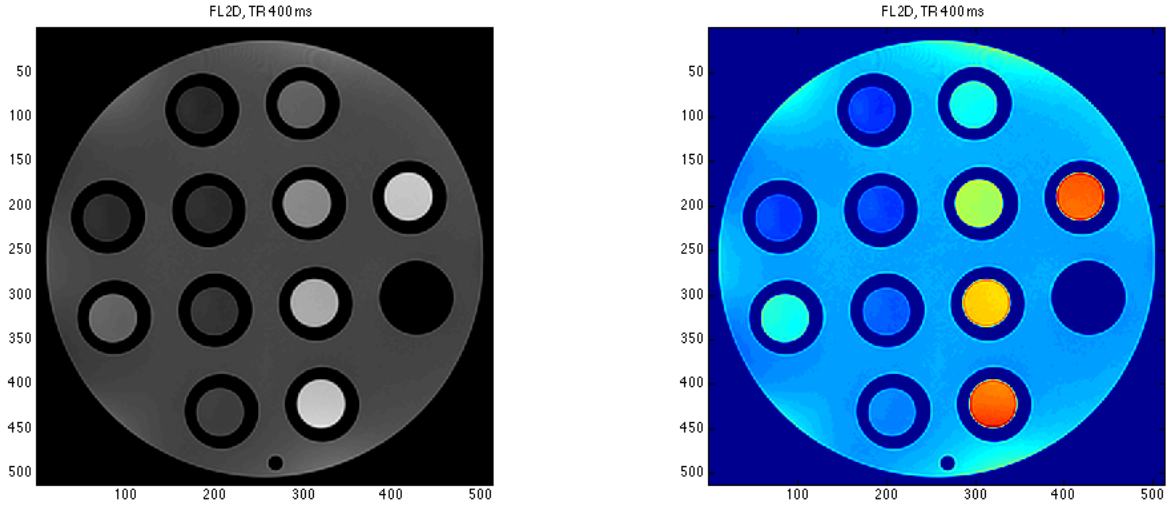


Figure S1. 1.5 T T_1-weighted gradient echo MRI (TE=4.76 ms, TR=400 ms, flip angle=90°) of TEEPO-Glc phantom presented in both gray and color scale.

4. Cell viability study

Cell culture

HeLa cells were cultured in complete cell culture medium composed of Dulbecco´s modified Eagle´s medium (DMEM, Sigma), 10% heat-inactivated fetal bovine serum (Gibco, Life Technologies), 100 U/ml penicillin and 100 µg/ml streptomycin (Gibco, Life Technologies).

HeLa cells were maintained under standard conditions cell culture conditions (37 °C, 5% CO_2 and 95% humidity) in a Sanyo MCO-18AIC CO_2 incubator (Sanyo Electric, Osaka, Japan).

CellTiter-Glo® assay

HeLa cells (10 000 cells per well) were seeded on white 96-well tissue culture plates (Thermo Scientific TM Nunc TM, Denmark) and allowed to attach for 24 h. After two washings with PBS (200 µl per well) cells were then treated with TEEPO-Glc (0,2, 1 and 10 mM in complete cell culture medium) for 1, 6 and 24 h. The cell viability was measured using CellTiter-Glo® reagent (Promega) according to the manufacturer's instructions by using a Fluoroskan Ascent FL (Thermo Labsystems).

Statistical analysis

Statistical analysis was performed by Kruskal-Wallis with Dunnett's test. Differences were considered significant when $p<0.05$.

5. The NMR and IR spectra of TEMPO-Glc and TEEPO-Glc

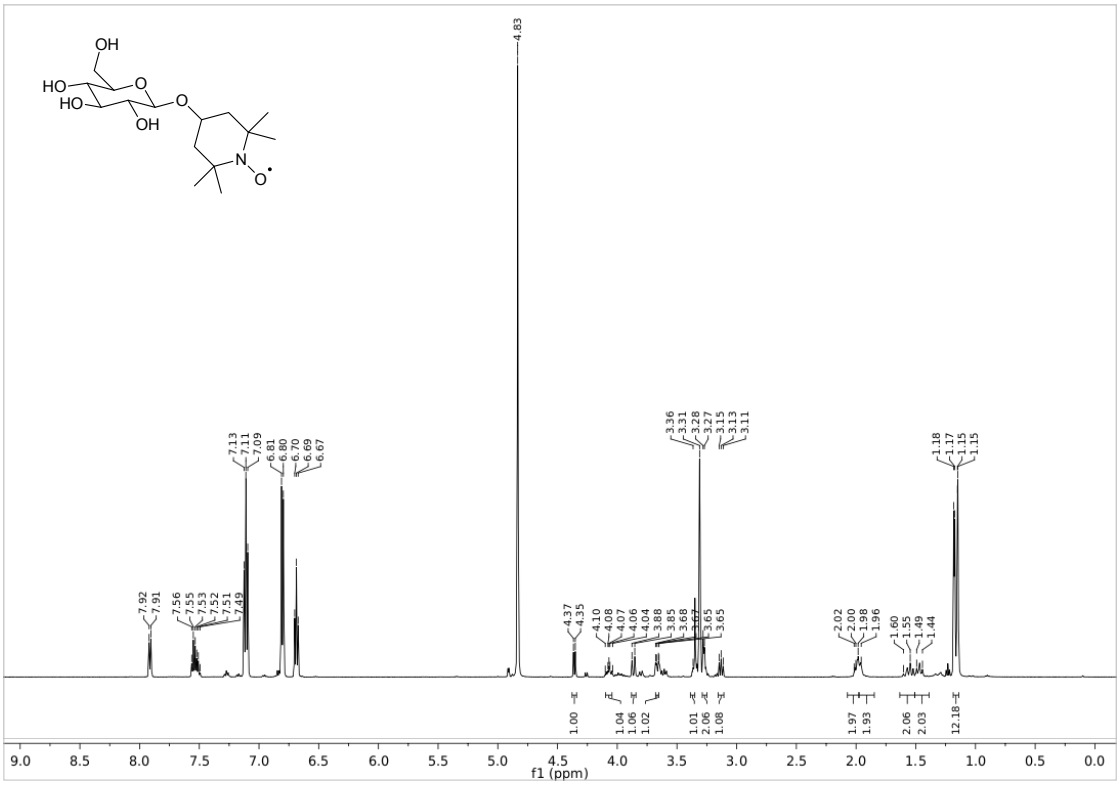


Figure S2. ^{1}H-spectrum of 2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl-β-D-glucopyranoside (**1**) in CD_3OD. The spectrum contains hydrazobenzene and its oxidized form.

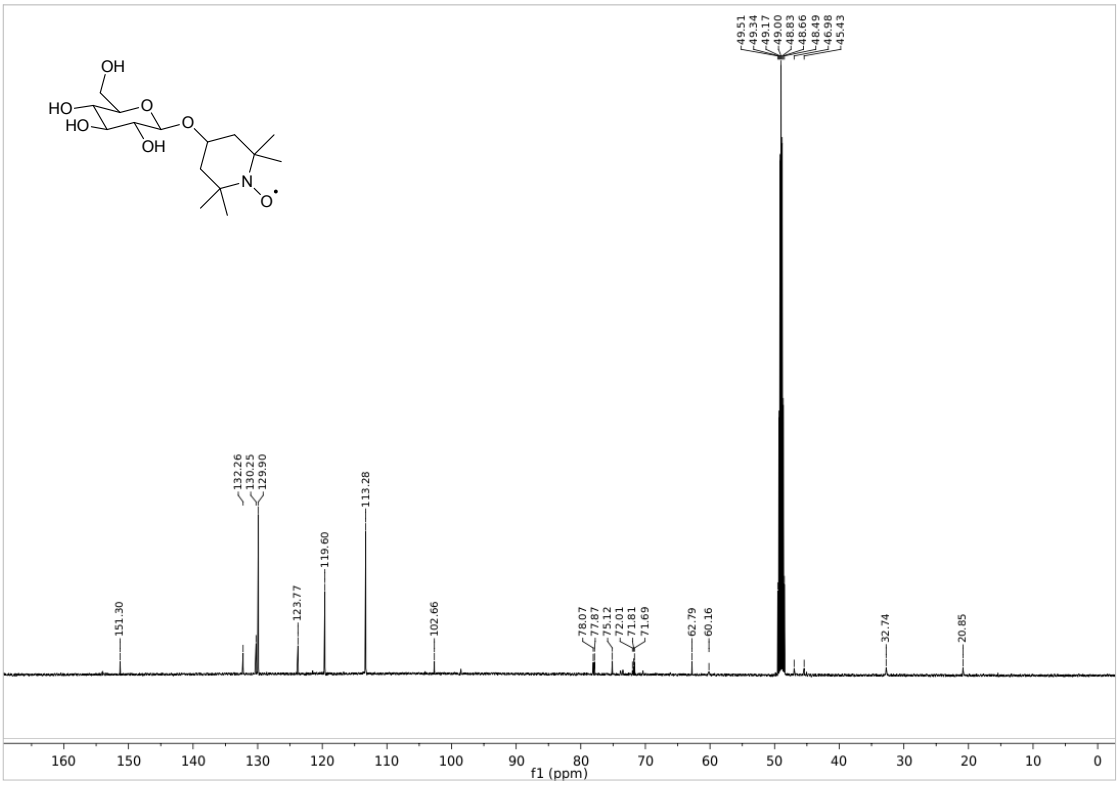


Figure S3. ^{13}C-spectrum of 2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl-β-D-glucopyranoside (**1**) in CD_3OD. The spectrum contains hydrazobenzene and its oxidized form.

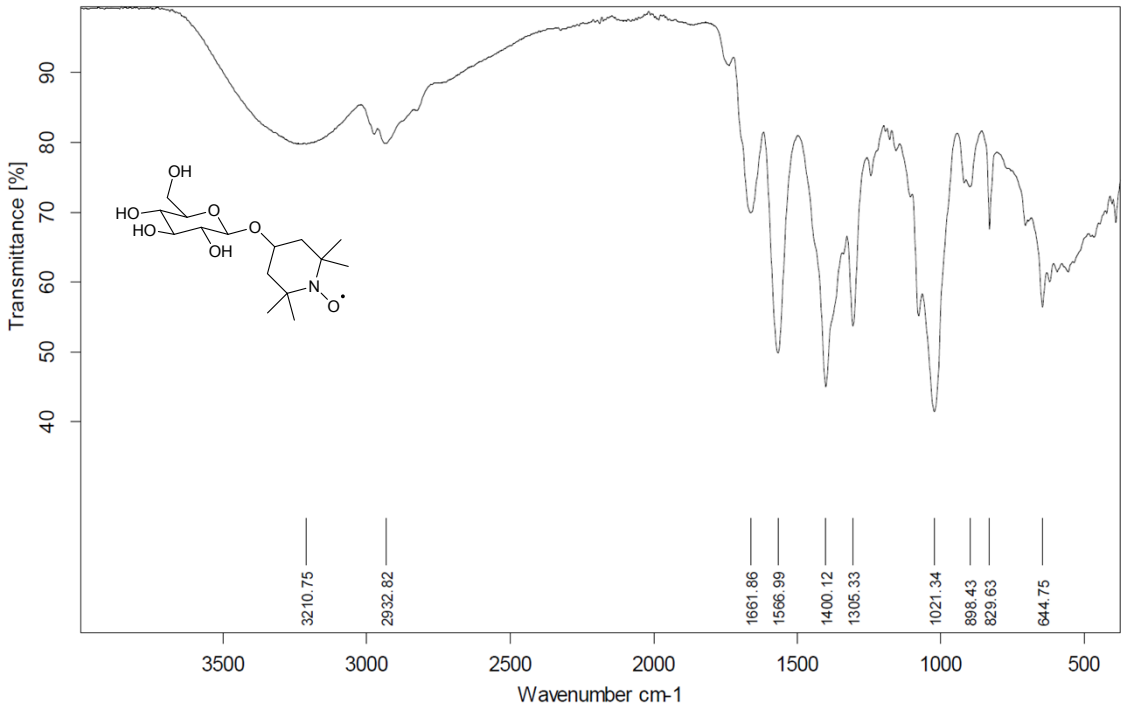


Figure S4. ATR-FTIR-spectrum of 2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl-β-D-glucopyranoside (**1**).

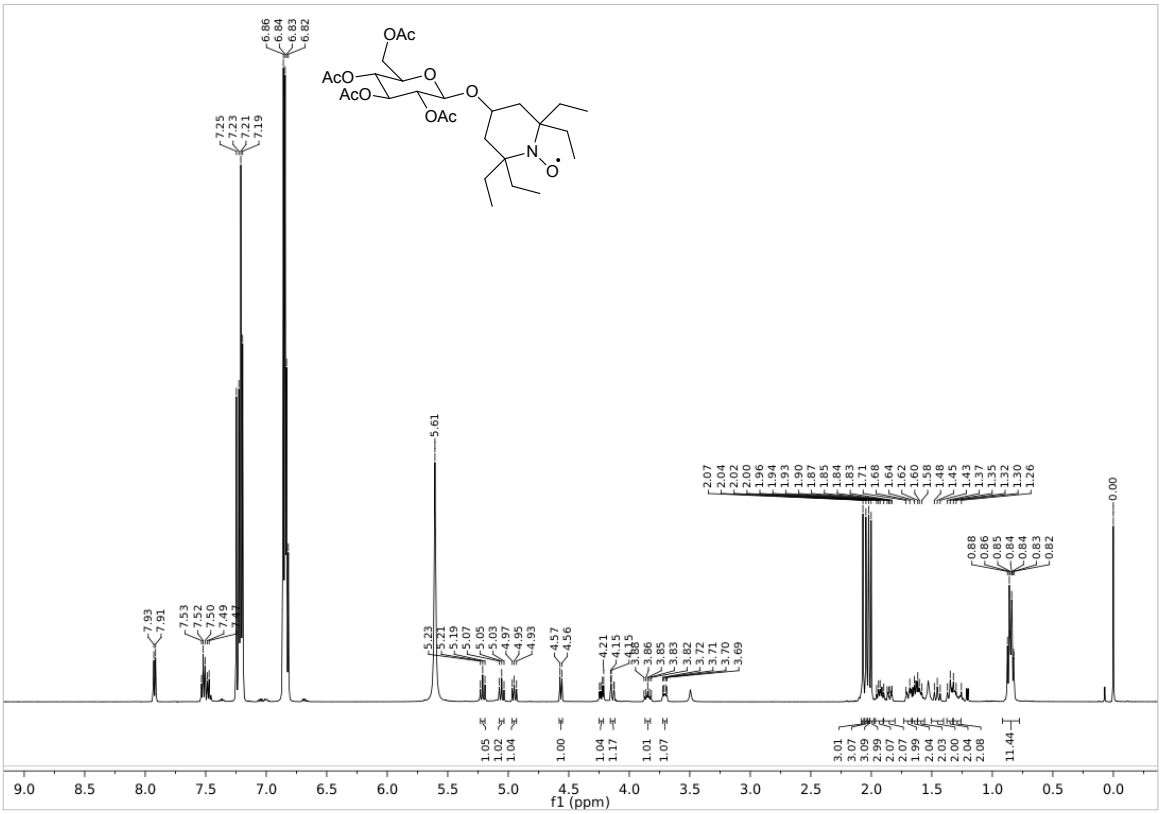


Figure S5. ^{1}H-spectrum of 4-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-2,2,6,6-tetraethylpiperidin-1-oxyl (**4**) in $CDCl_3$. The spectrum contains hydrazobenzene and its oxidized form.

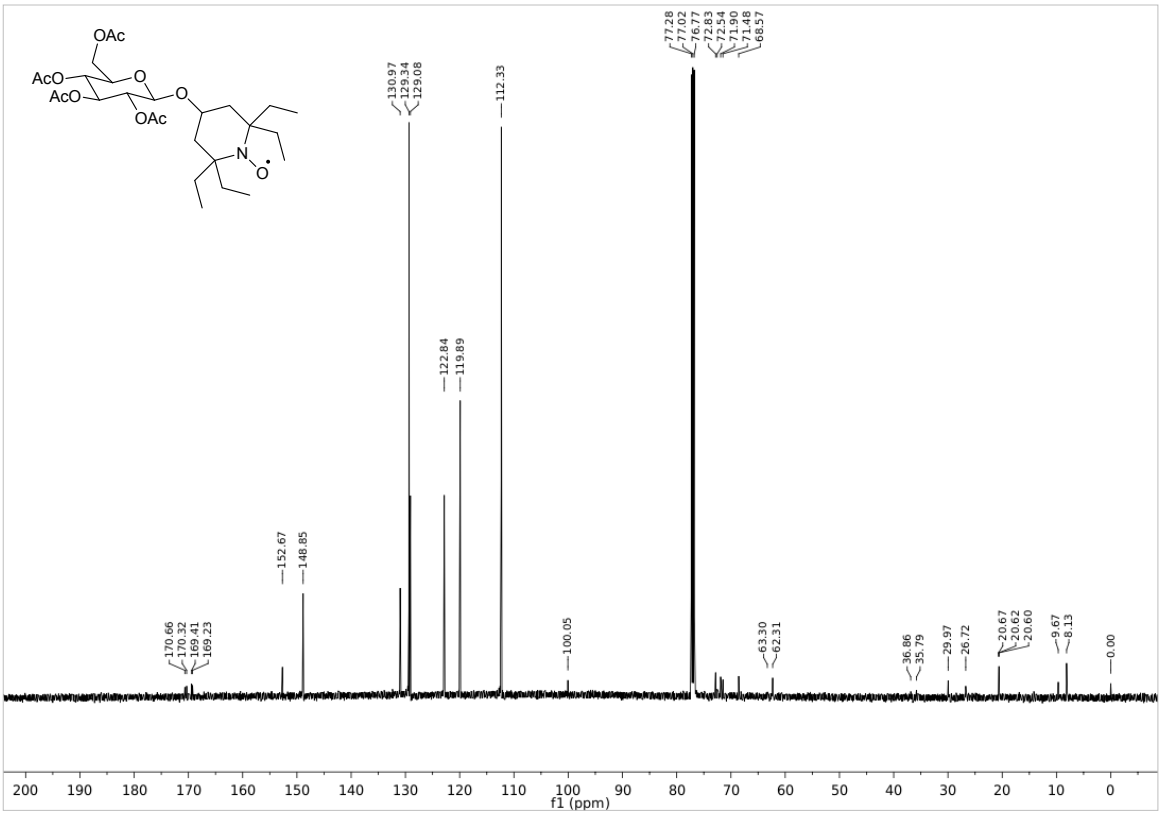


Figure S6. ^{13}C-spectrum of 4-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-2,2,6,6-tetraethylpiperidin-1-oxyl (**4**) in $CDCl_3$. The spectrum contains hydrazobenzene and its oxidized form.

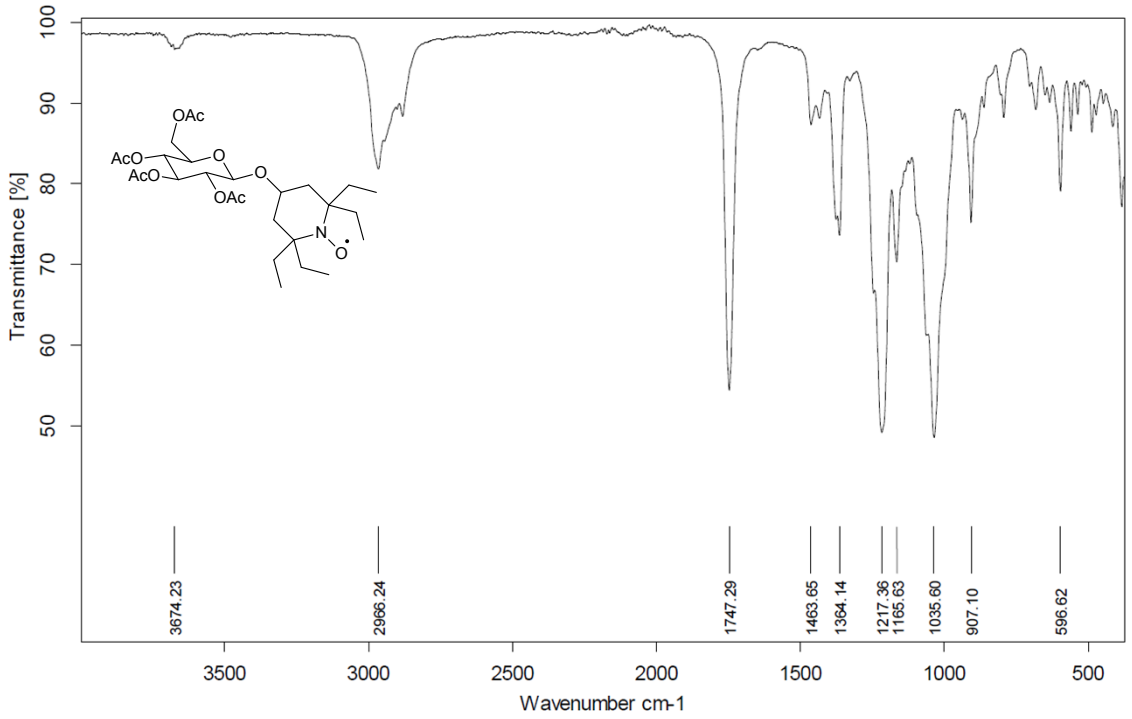


Figure S7. ATR-FTIR-spectrum of 4-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyloxy)-2,2,6,6-tetraethyl-piperidin-1-oxyl (**4**).

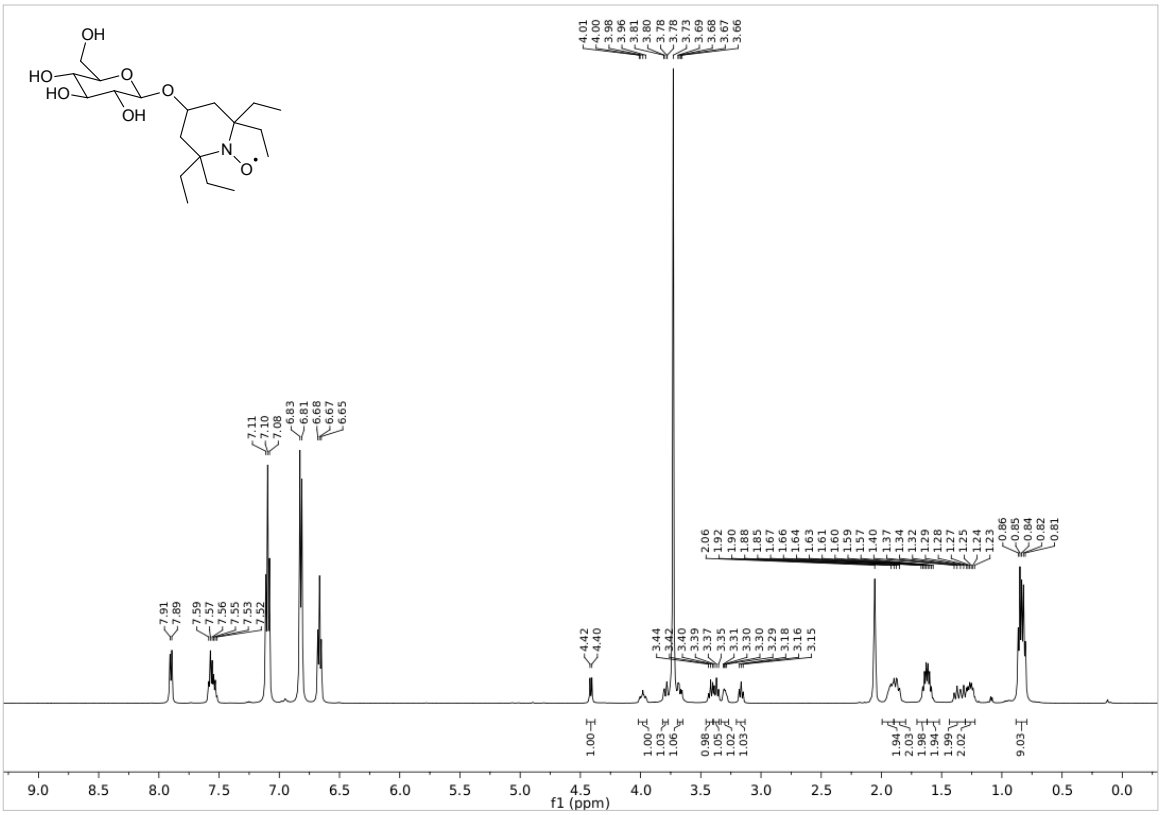


Figure S8. ^{1}H-spectrum of 2,2,6,6-tetraethylpiperidin-1-oxyl-4-yl-β-D-glucopyranoside (**2**) in $(CD_3)_2CO/D_2O$. The spectrum contains hydrazobenzene and its oxidized form.

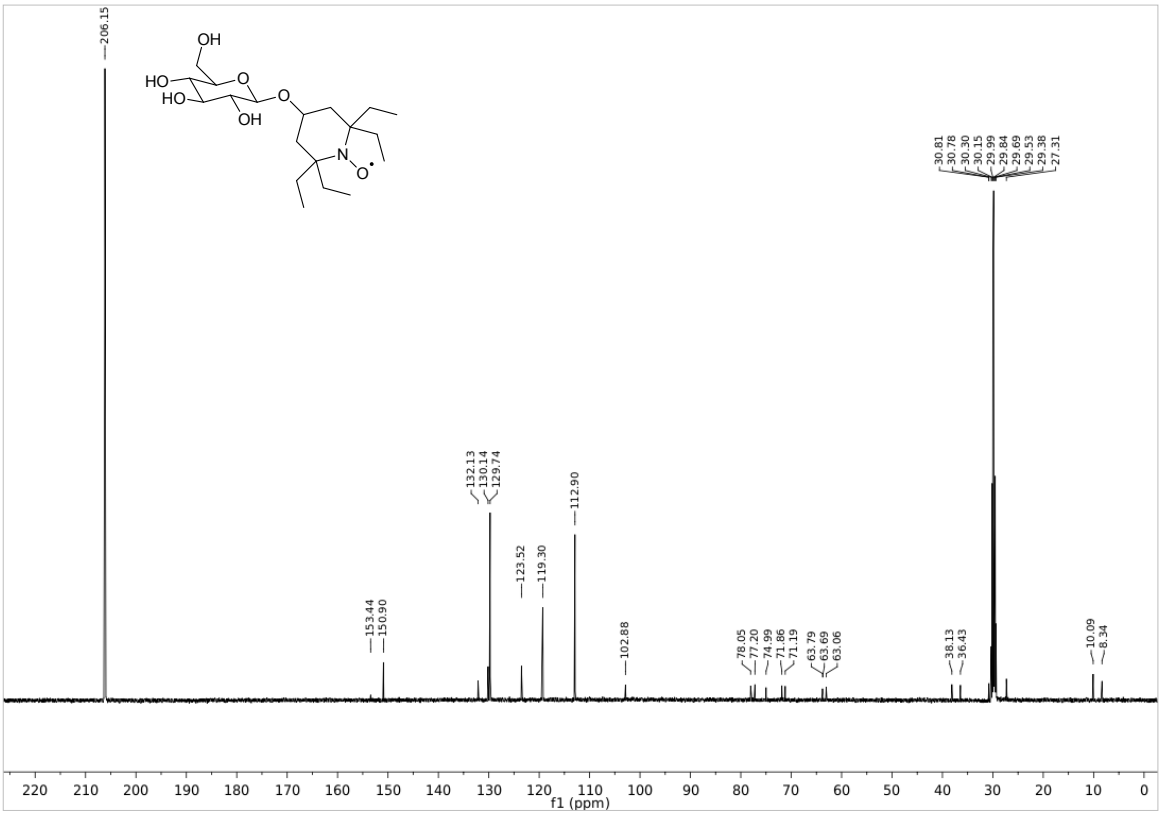


Figure S9. ^{13}C-spectrum of 2,2,6,6-tetraethylpiperidin-1-oxyl-4-yl-β-D-glucopyranoside (**2**) in $(CD_3)_2CO$. The spectrum contains hydrazobenzene and its oxidized form.

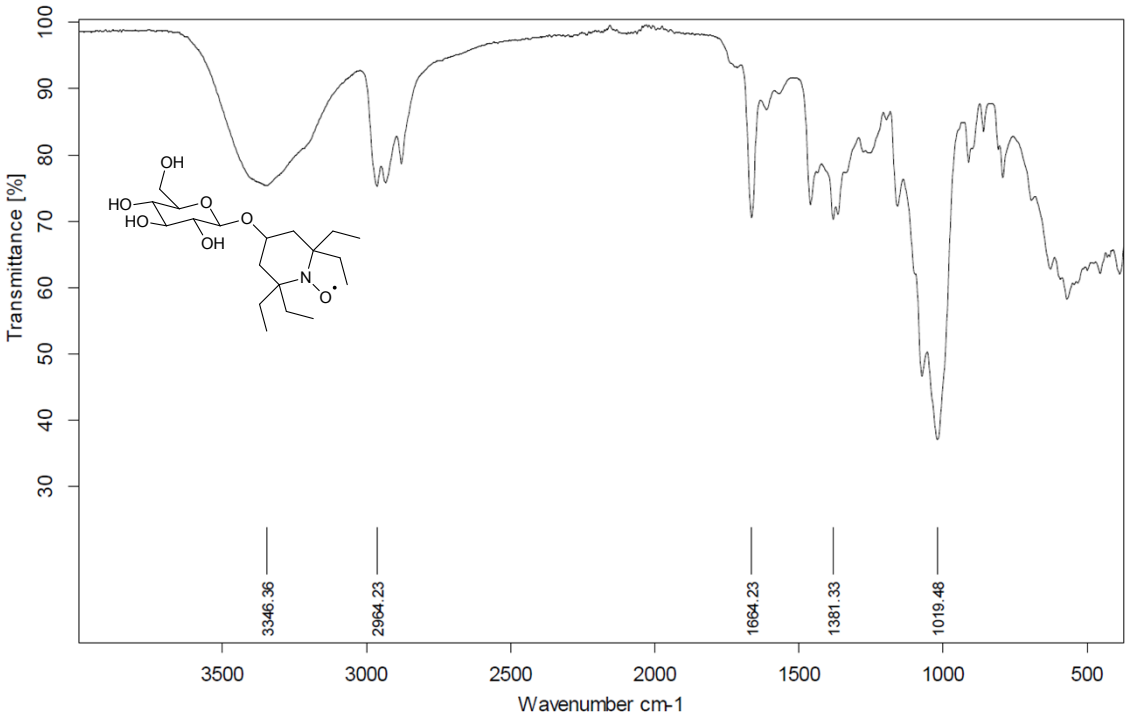


Figure S10. ATR-FTIR-spectrum of 2,2,6,6-tetraethylpiperidin-1-oxyl-4-yl-β-D-glucopyranoside (**2**).

5. References

1. S. Sato, T. Kumazawa, S. Matsuba, J.-i. Onodera, M. Aoyama, H. Obara and H. Kamada, *Carbohydrate Research*, 2001, **334**, 215-222.