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General Methods: All chemicals were purchased from Sigma-Aldrich unless stated otherwise. L-amino acid derivatives and resins were purchased from NovaBioChem and Biosystems. Methylene chloride (DCM) was dried over calcium hydride. Anhydrous tetrahydrofuran (THF), methanol and *N,N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich and EMD, respectively. All esterification, amidation, Staudinger reduction, $CuSO_4$ and CuI mediated reactions were carried out under an argon atmosphere. Reactions were performed at room temperature (20-22 °C), unless stated otherwise. Reactions were monitored by Thin Layer Chromatography (TLC) using aluminum backed silica gel 60 (F254) plates, visualized using UV254nm and potassium permanganate and cerium molybdate dips as appropriate. Flash chromatography was carried out using silica gel G60 (SiliCycle, 60-200μm 60 Å) as the stationary phase. Solid-Phase Peptide Synthesis (SPPS) was performed on a Applied Biosystems, ABI 433A peptide synthesizer equipped with UV-detector using L-N^{α}-Fmoc-protected amino acids and 2-(1H-benzotriazole-1-yl)-oxy-1,1,3,3-tertamethyl hexafluorophosphate (HBTU) / 1-hydroxybenzotriazole (HOBt) as the activating reagents. Reverse Phase HPLC was performed on an Agilent 1200 series system equipped with an automated injector, UV-detector, fraction-collector and Agilent Zorbax Eclipse XD8-C18 column (5 μm, 9.4 × 250 mm). The following gradient program was used for all purifications: water + 0.1% TFA over 5 min, then linear gradient 0-100% CH_3CN in water + 0.1% TFA 1.5 mL/min over 40 min.

The NMR spectra were recorded on Varian Mercury (300, 500 MHz) spectrometers at 25˚C. Chemical shifts are reported in δ units, parts per million (ppm) downfield from TMS, spectra are referenced by solvent signals. Coupling constants (*J*) are measured in Hertz (Hz) and are unadjusted. Splitting patterns are designed as follows: s – singlet, d – doublet, t – triplet, dd – doublet of doublets, dt – doublet of triplets, td – triplet of doublets, m – multiplet, br – broad. Various 2D NMR techniques (COSY, HSQC) were used to establish the structures and to assign the signals.

Mass spectra were obtained using MALDI-ToF instruments (Applied Biosystems 4700 Proteomics Analyzer, Bruker Microflex LT Mass Spectrometer) with 2,5-dihydroxybenzoic acid or α-cyano-4-hydroxycinnamic acid as a matrix. Positive reflector mode was used unless stated otherwise. Monoisotopic masses are provided unless stated otherwise. Fragmentation was often observed in spectra of surface modified dendrimers, proposed fragments are displayed on the spectra.

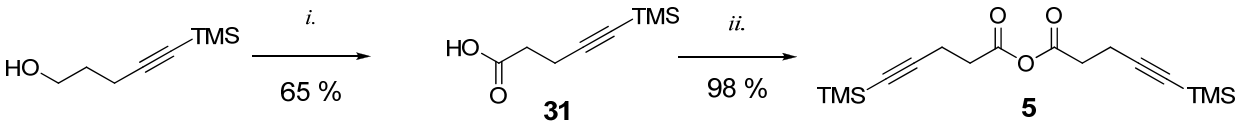
Sugar analysis was performed on DIONEX ICS-3000 HPAEC chromatograph using deionised water and 200 mM NaOH as an eluent. Sample preparation: 1-2 mg of sample and D-(+)-galactose were treated with 2M TFA in water (250 μl) for 4 h at 100˚C. Sample and standard were spin dried, redissolved in water (500 μl) and filtered. Sample concentration was then determined based on the

calibration curves of galactose standards (1, 3, 10, 30, 50 μM). Average (of two measurements) number of galactose residues per molecule of dendrimer is provided.

Fluorescein azide (7): 5(6)-Carboxyfluorescein (451 mg, 1.2 mmol) and 2-[2-(2-azidoethoxy)-ethoxy]-ethylamine [1] **(3)** (174 mg, 1.0 mmol) were suspended in DCM (10 mL). (Benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate (PyBop) (624 mg, 1.2 mmol), HOBt (202 mg, 1.5 mmol) and *N,N*-diisopropylethylamine (DIPEA) (340 μL, 2.0 mmol, 2 equiv) were added to the mixture. After stirring for 48 h, glacial acetic acid (3 mL) was added and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (MeOH:DCM:AcOH 6:93:1 v/v/v, product containing fractions were further purified by using 50% acetone in hexanes) yielding an orange solid **7** (240 mg, 45%) as a mixture of 5- and 6-isomers: ^{1}H NMR (300 MHz, CD_6CO) δ 2.93 (br s, 4H, 4×OH of both isomers), 3.28 (t, J = 4.9 Hz, 2H, CH_2N$_3$ of 6- isomer), 3.37 (t, J = 4.7 Hz, 2H, CH_2N$_3$ of 5- isomer), 3.48-3.71 (m, 20H, CH_2NH of both isomers, 4×CH_2O of both isomers), 6.61-6.70 (m, 8H, 4×CH-aryl of both isomers), 6.76 (d, J = 2.2 Hz, 4H, 2×CH-aryl of both isomers), 7.37 (d, J = 8.1 Hz, 1H, CH-aryl of 5-isomer), 7.73 (s, 1H, CH-aryl of 6-isomer), 8.00-8.06 (m, 3H, NH of both isomers, CH-aryl of 6-isomer), 8.22 (dd, J = 8.0, 1.3 Hz, 1H, CH-aryl of 6-isomer), 8.30 (dd, J = 7.9, 1.4 Hz, 1H, CH-aryl of 6-isomer), 8.43 (s, 1H, CH-aryl of 5-isomer); ^{13}C NMR (only peaks of 6-isomer listed) (75.5 MHz, CD_6CO) δ 41.58 (CH_2NH), 52.26 (CH_2N_3), 71.01 (CH_2O), 71.62 (CH_2O), 71.89 (CH_2O), 71.98 (CH_2O), 104.34 (2×CH-aryl), 112.15 (2×C-aryl), 114.40 (2×CH-aryl), 124.30 (CH-aryl), 126.55 (CH-aryl), 131.12 (2×C-aryl), 131.29 (2×CH-aryl), 143.12 (C-aryl), 154.29 (2×C-aryl), 155.18 (C-aryl), 161.41 (2×C-aryl), 166.93 (C=O), 169.83 (C=O); MS (MALDI-ToF) Calc. for $C_{27}H_{25}N_4O_8$ $[M+H]^+$ 533.2, Found $[M+H]^+$ 533.2.

Azido-RGD peptide (8): Solid phase peptide synthesis was performed on Rink amide AM resin (0.2 mmol) using Fmoc-Asp(O*t*-Bu)-OH (1.0 mmol), Fmoc-Gly-OH (1.0 mmol), Fmoc-Arg(Pbf)-OH (1.0 mmol). Azidoacetic acid [2] (60 mg, 0.6 mmol) was coupled manually using PyBop (310 mg, 0.6 mmol), HOBt (81 mg, 0.6 mmol), DIPEA (340 μL, 2 mmol). The resin was then thoroughly washed with DMF (10 mL), DCM (10 mL), and MeOH (10 mL) and dried *in vacuo*. The resin was then swelled in DCM (10 mL) for 1 h and treated with TFA:H_2O:TIS (95:2.5:2.5, v/v/v, 20 mL) for 2 h. The resin was filtered and washed with neat trifluoroacetic acid (TFA) (4 mL). The combined filtrates were concentrated *in vacuo* to approximately one third of the original volume. The crude peptide was precipitated by addition of Et_2O (0°C, 40 mL), recovered by centrifugation (5 °C, 3000

rpm, 20 min) and decanting of the solvent. The residue was purified by HPLC (t = 17.8 min). Lyophilisation of the appropriate fractions gave peptide **8** (52 mg, 54%) as a white foam: MS (MALDI-ToF) Calc. for $C_{16}H_{28}N_{11}O_7$ $[M+H]^+$ 486.2, Found $[M+H]^+$ 486.2.



Scheme S1. Synthesis of 5-(trimethylsilyl)pent-4-ynoic anhydride **5**. Reaction conditions: *i.* PDC, DMF, 24 h; *ii.* DCC, DCM, 3 h

5-(Trimethylsilyl)pent-4-ynoic acid (31): 5-(Trimethylsilyl)pent-4-yn-1-ol (5.0 g, 32 mmol) and pyridinium dichromate (30.0 g, 80 mmol) were dissolved in DMF (50 mL). The resulting black solution was stirred for 24 h. The reaction mixture was diluted with water (200 mL) and extracted with Et_2O (3×100 mL). The combined organic layers were washed with 1 M HCl (2×100 mL), brine (100 mL), dried ($MgSO_4$), filtered and the filtrate was concentrated under the reduced pressure. The residue was purified by silica gel column chromatography (20 then 30% ethyl acetate in hexanes) to give **25** (3.5 g, 65%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 9H, $Si(CH_3)_3$), 2.51-2.64 (m, 4H, CH_2CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ -0.01 ($Si(CH_3)_3$), 15.47 ($CH_2C{\equiv}C$), 33.33 ($CH_2CH_2C{\equiv}C$), 85.68 ($CH_2C{\equiv}C$), 104.51 ($CH_2C{\equiv}C$), 177.76 (C=O).

5-(Trimethylsilyl)pent-4-ynoic anhydride (5): 5-(Trimethylsilyl)pent-4-ynoic acid **(25)** (3.0 g, 17.6 mmol) and *N,N*'-dicyclohexylcarbodiimide (DCC) (1.8 g, 8.8 mmol) were dissolved in DCM (50 mL). The resulting solution was stirred vigorously for 3 h. The reaction mixture was filtered and the filtrate was concentrated to approximately 10 mL. The filtrate was cooled (-20˚C) and kept for 1 h at this temperature. The resulting cloudy solution was filtered, the solvent evaporated under reduced pressure to give **5** (2.8 g, 98%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 18H, 2×$Si(CH_3)_3$), 2.54-2.73 (m, 8H, 2×CH_2CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ -0.04 (2×$Si(CH_3)_3$), 15.22 (2×$CH_2C{\equiv}C$), 34.60 (2×$CH_2CH_2C{\equiv}C$), 86.13 (2×$CH_2C{\equiv}C$), 103.72 (2×$CH_2C{\equiv}C$), 167.27 (2×C=O).

Pent-4-ynoic anhydride (4): Compound **4** was prepared from pent-4-ynoic acid (3.8 g, 38.7mmol) as was described for compound **5**: **4** (3.1 g, 90%) colourless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (t, J = 2.6 Hz, 2H, 2×C≡CH), 2.52 (td, J = 7.3, 2.6 Hz, 4H, 2×$CH_2CH_2C{\equiv}CH$), 2.70 (t, J = 7.1

Hz, 4H, 2×C*H*$_2$CH$_2$C≡CH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.72 (2×*C*H$_2$C≡C), 34.27 (2×*C*H$_2$CH$_2$C≡C), 69.61 (2×C≡*C*H), 81.36 (2×CH$_2$*C*≡C), 167.10 (2×C=O).

G1 dendron (10): Prepared from 2-[2-(2-Azidoethoxy)-ethoxy]-ethylamine **(3)** (700 mg, 4.0 mmol) using: 4-dimethylaminopyridine (DMAP) (100 mg, 0.8 mmol), pyridine (1.6 mL, 20 mmol) and isopropylidene-2,2-bis(methoxy)propionic anhydride [3] **(1)** (2.64 g, 8.0 mmol) according to the general procedure for the synthesis of dendrons. The reaction mixture was stirred for 12 h. Flash chromatography on silica gel (30% acetone in hexanes) gave **10** (1.3 g, 99%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (s, 3H, CH_3), 1.40-1.44 (m, 6H, 2×CH_3), 3.35 (t, J =5.0 Hz, 2H, CH_2N_3), 3.46-3.74 (m, 12H, 5×OCH_2 , NHC*H*$_2$), 3.90 (d, J = 12.2 Hz, 2H, OCH_2), 7.37 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.73 (CH_3), 18.61 (CH_3), 28.42 (CH_3), 39.20 ($NHCH_2$), 40.14 (CH_2C), 50.58 (CH_2N_3), 67.05 (2×O*C*H$_2$C), 69.94 (CH_2O), 69.95 (CH_2O), 70.29 (CH_2O), 70.51 (CH_2O), 98.29 (C), 174.76 (C=O); MS (MALDI-ToF) Calc. for $C_{14}H_{27}N_4O_5$ $[M+H]^+$ 331.2, Found $[M+H]^+$ 331.2.

G2 dendron (11): G1 dendron **10** (1.25 g, 3.8 mmol) was unprotected using Dowex® 50WX8-200 H^+ resin (2 g, 2 h) to give hydroxyl terminated G1 dendron (1.1 g, 100%; MS (MALDI-ToF) Calc. for $C_{11}H_{23}N_4O_5$ $[M+H]^+$ 291.2, Found $[M+H]^+$ 291.2) as a colorless oil. G2 dendron **11** was prepared from hydroxyl terminated G1 dendron (1.05 g, 3.6 mmol) using: DMAP (170 mg, 1.4 mmol), pyridine (2.8 mL, 36.0 mmol) and anhydride **1** (5.0 g, 15.2 mmol) according to the general procedure for the synthesis of dendrons. The reaction mixture was stirred for 18 h. Column chromatography on silica gel (30% acetone in hexanes) gave **11** (2.1 g, 92%) as a transparent oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 6H, 2×CH_3), 1.26 (s, 3H, CH_3), 1.35-1.41 (m, 12H, 4×CH_3), 3.35-3.67 (m, 16H, CH_2N_3, 6×OCH_2, NHC*H*$_2$), 4.15 (d, J = 11.8 Hz, 4H, 2×OCH_2), 4.25-4.35 (m, 4H, 2×OCH_2), 6.54 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.58 (CH_3), 18.36 (2×CH_3), 21.66 (2×CH_3), 25.51 (2×CH_3), 39.38 ($NHCH_2$), 42.09 (2×CH_2C), 46.59 (CH_2C), 50.58 (CH_2N_3), 65.99 (2×O*C*H$_2$C), 66.01 (2×O*C*H$_2$C), 66.19 (2×O*C*H$_2$C), 69.54 (CH_2O), 69.99 (CH_2O), 70.17 (CH_2O), 70.48 (CH_2O), 98.14 (2×C), 172.23(C=O), 173.54 (2×C=O); MS (MALDI-ToF) Calc. for $C_{27}H_{46}N_4O_{11}Na$ $[M+Na]^+$ 625.4, Found $[M+Na]^+$ 625.4.

G3 dendron (12): G2 dendron **11** (2.06 g, 3.40 mmol) was unprotected using Dowex® 50WX8-200 H^+ resin (3 g, 3 h) to give hydroxyl terminated G2 dendron (1.62 g, 91%; MS (MALDI-ToF) Calc. for $C_{21}H_{38}N_4O_{11}Na$ $[M+Na]^+$ 545.2, Found $[M+Na]^+$ 545.3) as a colorless oil. G3 dendron **12** was prepared from hydroxyl terminated G2 dendron (960 mg, 1.84 mmol) using: DMAP (134 mg, 1.10

mmol), pyridine (2.96 mL, 36.80 mmol) and anhydride **1** (4.86 g, 14.72 mmol) according to the general procedure for the synthesis of dendrons. The reaction mixture was stirred for 18 h. Column chromatography on silica gel (20% acetone in hexanes) gave **12** (2.00 g, 95%) as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (s, 12H, 4×CH_3), 1.26-1.27 (m, 9H, 3×CH_3), 1.34 - 1.40 (m, 24H, 8×CH_3), 3.38 (t, J = 4.9 Hz, 2H, CH_2N_3), 3.46 (q, J = 5.1 Hz, 2H, NHCH_2), 3.56-3.68 (m, 16H, 8×OCH_2), 4.13 (d, J = 11.8 Hz, 8H, 4×OCH_2), 4.19 - 4.34 (m, 12H, 6×OCH_2), 6.39 (t, J = 5.3 Hz, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.55 (CH_3), 17.61 (2×CH_3), 18.48 (4×CH_3), 21.92 (2×CH_3), 21.94 (2×CH_3), 25.26 (4×CH_3), 39.45 ($NHCH_2$), 42.04 (4×CH_2C), 46.35 (CH_2C), 46.88 (2×CH_2C), 50.58 (CH_2N_3), 64.95 (4×OCH$_2$C), 65.91 (4×OCH$_2$C), 65.94 (4×OCH$_2$C), 67.12 (2×OCH$_2$C), 69.53 (CH_2O), 70.01 (CH_2O), 70.13 (CH_2O), 70.49 (CH_2O), 98.07 (4×C), 171.47 (C=O), 171.80 (2×C=O), 173.52 (4×C=O); MS (MALDI-ToF) Calc. for $C_{53}H_{86}N_4O_{23}Na$ $[M+Na]^+$ 1169.6, Found $[M+Na]^+$ 1169.8.

G4 dendron (13): G3 dendron **12** (1.20 g, 1.05 mmol) was unprotected using Dowex® 50WX8-200 H^+ ion-exchange resin (3 g, 12 h) to give hydroxyl terminated G3 dendron (1.04 g, 100%; MS (MALDI-ToF) Calc. for $C_{41}H_{70}N_4O_{23}Na$ $[M+Na]^+$ 1009.4, Found $[M+Na]^+$ 1009.7) as an amorphous solid. G4 dendron **13** was prepared from hydroxyl terminated G3 dendron (430 mg, 0.44 mmol) using: DMAP (54 mg, 0.44 mmol), pyridine (1.42 mL, 17.60 mmol) and anhydride **1** (2.32 g, 7.04 mmol) according to the general procedure for the synthesis of dendrons. The reaction mixture was stirred for 18 h. Column chromatography (30% acetone in hexanes) gave **13** (930 mg, 94%) as a yellowish oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (s, 24H, 8×CH_3), 1.24-1.27 (m, 21H, 7×CH_3), 1.32 - 1.39 (m, 48H, 16×CH_3), 3.37 (t, J = 5.2 Hz, 2H, CH_2N_3), 3.43 (q, J = 5.2 Hz, 2H, NHCH_2), 3.54-3.67 (m, 24H, 12×OCH_2), 4.12 (d, J = 11.9 Hz, 16H, 8×OCH_2), 4.17 - 4.32 (m, 28H, 14×OCH_2), 6.49 (t, J = 5.5 Hz, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.37 (CH_3), 17.41 (2×CH_3), 17.62 (4×CH_3), 18.44 (8×CH_3), 22.00 (8×CH_3), 25.12 (8×CH_3), 39.43 ($NHCH_2$), 41.97 (8×CH_2C), 46.31 (CH_2C), 46.66 (2×CH_2C), 46.76 (4×CH_2C), 50.52 (CH_2N_3), 64.74 (8×OCH$_2$C), 65.54 (4×OCH$_2$C), 65.84 (8×OCH$_2$C), 65.89 (8×OCH$_2$C), 67.34 (2×OCH$_2$C), 69.51 (CH_2O), 69.94 (CH_2O), 70.03 (CH_2O), 70.42 (CH_2O), 98.02 (8×C), 171.27 (C=O), 171.35 (2×C=O), 171.78 (4×C=O), 173.42 (8×C=O); MS (MALDI-ToF) Calc. for $C_{105}H_{166}N_4O_{47}Na$ $[M+Na]^+$ 2258.1, Found $[M+Na]^+$ 2258.7.

G3 dendron (14): G3 dendron **14** was prepared from hydroxyl terminated G3 dendron (500 mg, 0.50 mmol) using: DMAP (61 mg, 0.50 mmol), pyridine (1.45 mL, 18 mmol) and pent-4-ynoic

anhydride (**4**) (1.07 g, 6 mmol) according to the general procedure for the synthesis of dendrons. The reaction mixture was stirred for 15 h. Column chromatography (30% acetone in hexanes) gave **14** as a colorless oil (724 mg, 89%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23-1.27 (m, 21H, 7×CH_3), 1.98 (t, J = 2.4 Hz, 8H, 8×C≡CH), 2.46 (td, J = 6.4, 1.8 Hz, 16H, 8×CH_2C≡CH), 2.54 (t, J = 7.0 Hz, 16H, 8×CH_2CH_2C≡CH), 3.37 (t, J = 4.9 Hz, 2H, CH_2N_3), 3.44 (q, J = 4.9 Hz, 2H, NHCH_2), 3.55 (t, J = 5.0 Hz, 2H, CH_2CH_2N_3), 3.62-3.67 (m, 6H, 3×OCH_2), 4.19 - 4.25 (m, 28H, 14×OCH_2), 6.51 (t, J = 5.0 Hz, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.20 (8×*C*H_2C≡CH), 17.44 (3×CH_3), 17.72 (4×CH_3), 33.05 (8×*C*H_2CH_2C≡CH), 39.43 (NHCH_2), 46.24 (CH_2*C*), 46.29 (4×CH_2*C*), 46.66 (2×CH_2*C*), 50.50 (CH_2N_3), 65.18 (8×O*C*H_2C), 65.31 (4×O*C*H_2C), 67.14 (2×O*C*H_2C), 69.27 (8×C≡*C*H), 69.51 (CH_2O), 69.91 (CH_2O), 70.00 (CH_2O), 70.38 (CH_2O), 82.24 (8×*C*≡CH), 171.07 (8×C=O), 171.30 (C=O), 171.40 (2×C=O), 171.85 (4×C=O); MS (MALDI-ToF) Calc. for $C_{81}H_{102}N_4O_{31}Na$ $[M+Na]^+$ 1649.6, Found $[M+Na]^+$ 1649.9.

G4 dendron (18): G4 dendron **13** (930 mg, 0.42 mmol) was unprotected using Dowex® 50WX8-200 H^+ resin (4 g, 24 h) to give hydroxyl terminated G4 dendron (790 mg, 98%; MS (MALDI-ToF) Calc. for $C_{81}H_{134}N_4O_{47}Na$ $[M+Na]^+$ 1937.8, Found $[M+Na]^+$ 1938.1) as a white foam. G4 dendron **18** was prepared from hydroxyl terminated G4 dendron (785 mg, 0.41 mmol) using: DMAP (150 mg, 1.23 mmol), pyridine (2.64 mL, 32.8 mmol) and anhydride **4** (1.75 g, 9.84 mmol) according to the general procedure for the synthesis of dendrons. The reaction mixture was stirred for 18 h. Silica gel column chromatography (40% acetone in hexanes) gave **18** (965 mg, 74%) as a viscous colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25-1.32 (m, 45H, 15×CH_3), 2.00 (t, J = 2.5 Hz, 16H, 16×C≡CH), 2.47 (td, J = 6.8, 2.1 Hz, 32H, 16×CH_2C≡CH), 2.56 (t, J = 6.9 Hz, 32H, 16×CH_2CH_2C≡CH), 3.39 (t, J = 5.0 Hz, 2H, CH_2N_3), 3.44 (q, J = 5.1 Hz, 2H, NHCH_2), 3.57 (t, J = 5.2 Hz, 2H, CH_2CH_2N_3), 3.62-3.68 (m, 6H, 3×OCH_2), 4.18 - 4.30 (m, 60H, 30×OCH_2), 6.53 (t, J = 5.4 Hz, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.27 (16×*C*H_2C≡CH), 17.24 (CH_3), 17.40 (2×CH_3), 17.52 (4×CH_3), 17.80 (8×CH_3), 33.11 (16×*C*H_2CH_2C≡CH), 39.50 (NHCH_2), 46.34 (8×CH_2*C*), 46.40 (CH_2*C*), 46.64 (2×CH_2*C*), 46.67 (4×CH_2*C*), 50.55 (CH_2N_3), 65.23 (24×O*C*H_2C), 65.80 (4×O*C*H_2C), 67.69 (2×O*C*H_2C), 69.35 (16×C≡*C*H), 69.54 (CH_2O), 69.97 (CH_2O), 70.05 (CH_2O), 70.42 (CH_2O), 82.32 (16×*C*≡CH), 171.11 (16×C=O), 171.25 (C=O), 171.30 (2×C=O), 171.46 (4×C=O), 171.88 (8×C=O); MS (MALDI-ToF) Calc. for $C_{161}H_{198}N_4O_{63}Na$ $[M+Na]^+$ 3218.2g/mol, Found $[M+Na]^+$ 3219.5.

G2 dendron (21): G2 dendron **21** was prepared from hydroxyl terminated G2 dendron (637 mg, 1.22 mmol) using: DMAP (74 mg, 0.61 mmol), pyridine (1.97 mL, 24.40 mmol) and 5-(trimethylsilyl)pent-4-ynoic anhydride **(5)** (2.36 g, 7.32 mmol) according to the general procedure for the synthesis of dendrons. The reaction mixture was stirred for 18 h. Silica gel column chromatography (20% acetone in hexanes) gave **21** (1.26 g, 91%) as a pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 36H, 4×Si(CH_3)$_3$), 1.17 (s, 9H, 3×CH_3), 2.39-2.51 (m, 16H, 4×$CH_2CH_2C{\equiv}C$), 3.31 (t, J = 5.0 Hz, 2H, CH_2N_3), 3.38 (q, J = 4.9 Hz, 2H, NHCH_2), 3.50 (t, J = 4.9 Hz, 2H, C$H_2CH_2N_3$), 3.57-3.62 (m, 6H, 3×OCH_2), 4.16 (s, 12H, 6×OCH_2), 6.34 (t, J = 5.0 Hz, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ -0.16 (4×Si(CH_3)$_3$), 15.42 (4×$CH_2C{\equiv}C$), 17.44 (CH_3), 17.50 (2×CH_3), 33.14 (4×$CH_2CH_2C{\equiv}C$), 39.25 ($NHCH_2$), 46.12 (CH_2C), 46.34 (2×CH_2C), 50.39 (CH_2N_3), 65.02 (4×OCH_2C), 66.64 (2×OCH_2C), 69.33 (CH_2O), 69.83 (CH_2O), 69.93 (CH_2O), 70.29 (CH_2O), 85.23 (4×$CH_2C{\equiv}C$), 104.55 (4×$CH_2C{\equiv}C$), 170.93 (4×C=O), 171.29 (C=O), 171.65 (2×C=O); MS (MALDI-ToF) Calc. for $C_{53}H_{86}N_4O_{15}NaSi_4$ $[M+Na]^+$ 1153.5, Found $[M+Na]^+$ 1153.6.

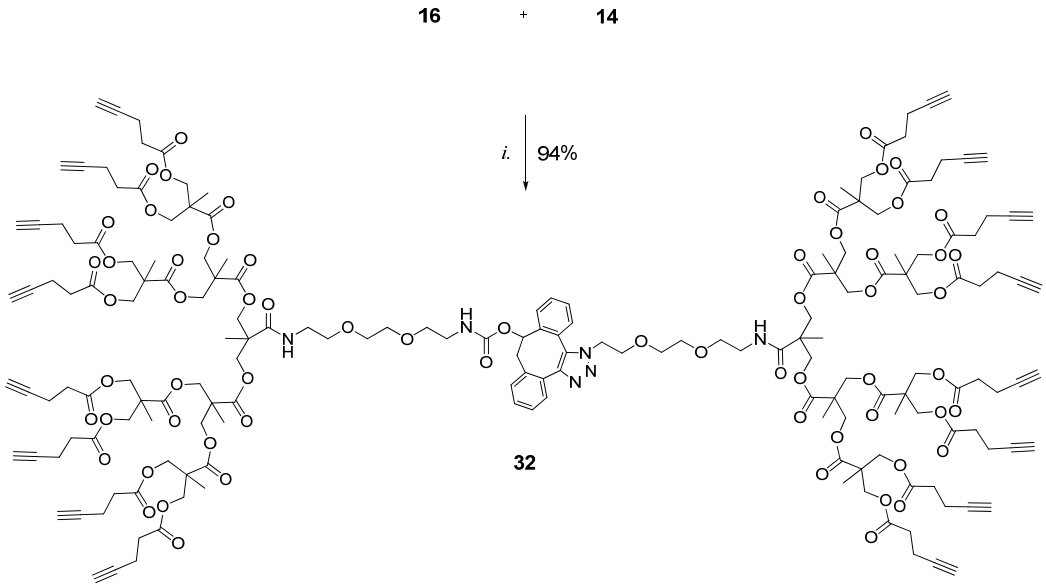
G3 dendron (16): Prepared from G3 azido-containing dendron **14** (100 mg, 0.06 mmol) according to the general procedure for the installation of a cyclooctynol moiety. Silica gel column chromatography (gradient 20 to 50% acetone in hexanes) gave **16** (101 mg, 89%) as a viscous colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27-1.27 (m, 21H, 7×CH_3), 1.98-1.99 (m, 8H, 8×C≡CH), 2.46-2.56 (m, 32H, 8×CH_2C≡CH, 8×C$H_2CH_2C{\equiv}CH$), 2.89 (dd, J = 15.1, 3.0 Hz, 1H, CH*H*CH), 3.16 (d, J = 15.1 Hz, 1H, C*H*HCH), 3.39-3.63 (m, 12H, 2×NHCH_2, 4×OCH_2), 4.20 - 4.26 (m, 28H, 14×OCH_2), 5.48-5.50 (m, 2H, CH_2CH, NHCOO) 6.49 (m, 1H, NHCO), 7.26-7.34 (m, 7H, 7 × CH-aryl), 7.49 (d, J = 7.4 Hz, 1H, CH-aryl); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.25 (8×$CH_2C{\equiv}CH$), 17.49 (3×CH_3), 17.78 (4×CH_3), 33.10 (8×$CH_2CH_2C{\equiv}CH$), 39.43 ($NHCH_2$), 40.86 ($NHCH_2$), 46.13 (CH_2CH), 46.27 (CH_2C), 46.34 (4×CH_2C), 46.69 (2×CH_2C), 65.22 (8×OCH_2C), 65.34 (4×OCH_2C), 67.11 (2×OCH_2C), 69.32 (8×C≡*C*H), 69.46 (CH_2O), 70.01 (CH_2O), 70.08 (CH_2O), 70.17 (CH_2O), 76.83 (CH_2CH), 82.27 (8×*C*≡CH), 109.88 (*C*≡C), 112.91 (C≡*C*), 121.28 (C-aryl), 123.62 (CH-aryl), 123.77 (C-aryl), 125.95 (CH-aryl), 126.25 (CH-aryl), 127.05 (CH-aryl), 127.07 (CH-aryl), 127. 86 (CH-aryl), 127.99 (CH-aryl), 129.85 (CH-aryl), 150.93 (C=O), 152.03 (C-aryl), 155.47 (C-aryl), 171.11 (8×C=O), 171.43 (3×C=O), 171.89 (4×C=O); MS (MALDI-ToF) Calc. for $C_{98}H_{114}N_2O_{33}Na$ $[M+Na]^+$ 1869.7, Found $[M+Na]^+$ 1870.2.

G4 dendron (20): Prepared from G4 azido-containing dendron **18** (200 mg, 0.06 mmol) according to the general procedure for the installation of a cyclooctynol moiety. Silica gel column chromatography (40 then 50% acetone in hexanes) gave **20** (198 mg, 93%) as a viscous colorless

oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22-1.29 (m, 45H, 15×CH_3), 1.96-2.00 (m, 16H, 16×C≡CH), 2.43 - 2.54 (m, 64H, 16×CH_2CH_2C≡CH), 2.86 (dd, J = 15.0, 3.0 Hz, 1H, CH*H*CH), 3.13 (d, J = 14.8 Hz, 1H, C*H*HCH), 3.36-3.42 (m, 4H, 2×NHCH_2), 3.54-3.61 (m, 8H, 4×OCH_2), 4.18 - 4.24 (m, 60H, 30×OCH_2), 5.45-5.53 (m, 2H, CH_2C*H*, NHCOO), 6.55-6.60 (m, 1H, NHCO), 7.24-7.32 (m, 7H, 7×CH-aryl), 7.46 (d, J = 7.5, 1H, CH-aryl); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.17 (16×*C*H_2C≡CH), 17.21 (CH_3), 17.32 (2×CH_3), 17.42 (4×CH_3), 17.70 (8×CH_3), 33.01 (16×*C*$H_2$$CH_2$C≡CH), 39.38 (NH$CH_2$), 40.76 (NH$CH_2$), 46.25 (*C*$H_2$CH, 8×$CH_2$*C*), 46.52 (3×$CH_2$*C*), 46.57 (4×$CH_2$*C*), 65.13 (24×O*C*$H_2$C), 65.67 (4×O*C*$H_2$C), 67.44 (2×O*C*$H_2$C), 68.03 ($CH_2$O), 69.30 (16×C≡*C*H), 69.95 (CH_2O), 70.06 (CH_2O), 70.55 (CH_2O), 76.71 (CH_2*C*H), 82.24 (16×*C*≡CH), 109.79 (*C*≡C), 112.83 (C≡*C*), 121.18 (C-aryl), 123.56 (CH-aryl), 123.67 (C-aryl), 125.87 (CH-aryl), 126.18 (CH-aryl), 126.99 (2×CH-aryl), 127. 78 (CH-aryl), 127.92 (CH-aryl), 129.79 (CH-aryl), 150.85 (C=O), 151.95 (C-aryl), 155.38 (C-aryl), 171.01 (16×C=O), 171.21 (3×C=O), 171.38 (4×C=O), 171.78 (8×C=O); MS (MALDI-ToF) Calc. for $C_{178}H_{210}N_2O_{65}Na$ $[M+Na]^+$ 3438.3, Found $[M+Na]^+$ 3439.5.

Fluorescein-labeled dendrimer 17 (isomers): Prepared from G3 dendron **16** (10.0 mg, 5.4 μmol) and fluorescein azide **7** (3.2 mg, 6.0 μmol) according to the general procedure for Cu-free ligation of dendrons. The reaction mixture was stirred for 2 h. Silica gel column chromatography (5% MeOH in DCM) gave dendrimer **17** (12.8 mg, 95%) as an orange oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20-1.38 (m, 21H, 7×CH_3), 1.63-1.99 (m, 10H, 8×C≡CH, 2×OH), 2.47-2.64 (m, 32H, 8×CH_2C≡CH, 8×C$H_2$$CH_2$C≡CH), 2.97-4.51 (m, 54H, CH_2CH, 6×OCH_2CH_2, 14×OCH_2), 5.50-5.68 (m, 1H, NH), 5.87-6.17 (m, 1H, CH_2C*H*), 6.32-8.44 (m, 19H, 17×CH-aryl, 2×NH); MS (most abundant mass) (MALDI-ToF) Calc. for $C_{125}H_{138}N_6O_{41}Na$ $[M+Na]^+$ 2402.9, Found $[M+Na]^+$ 2402.4.

Dendrimer 22 (isomers): Prepared from G4 dendron **20** (34.2 mg, 10.0 μmol) and G4 dendron **18** (35.2 mg, 11.0 μmol) according to the general procedure for Cu-free ligation of dendrons. The reaction mixture was stirred for 24 h. Silica gel column chromatography (3% MeOH in DCM) gave dendrimer **22** (61 mg, 93%) as a viscous oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30-1.41 (m, 90H, 30×CH_3), 2.36-2.82 (m, 160H, 32×C≡CH, 32×CH_2C≡CH, 32×C$H_2$$CH_2$C≡CH), 2.98-3.75 (m, 22H, CH_2CH, 2×OCH_2CH_2, 3×NHCH_2CH_2), 3.98-4.73 (m, 124H, 60×OCH_2, OCH_2CH_2-triazole), 5.96-6.46 (m, 2H, NHCOO, CH_2C*H* ,), 7.10-7.55 (m, 10H, 8×CH-aryl, 2×NHCO); MS (most abundant mass) (MALDI-ToF) Calc. for $C_{339}H_{408}N_6O_{128}Na$ $[M+Na]^+$ 6637.6, Found $[M+Na]^+$ 6643.2.



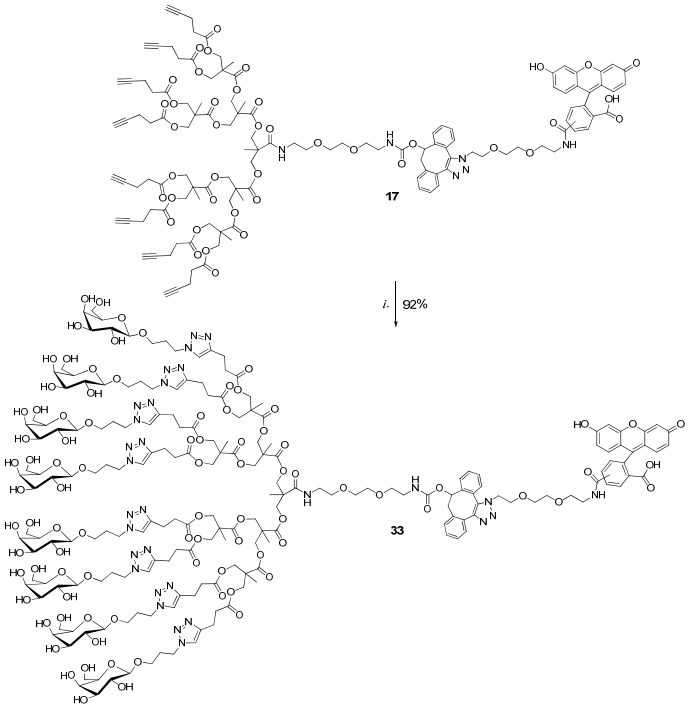
Scheme S2. Synthesis of glycodendrimer **34**. Reaction conditions: *i.* THF, 11 h

Dendrimer (32, isomers): Prepared from G3 dendron **16** (20.0 mg, 11 μmol) and G3 dendron **14** (19.7 mg, 12.0 μmol) according to the general procedure for Cu-free ligation of dendrons. The reaction mixture was stirred for 11 h. Silica gel column chromatography (50% acetone in hexanes) gave **32** (36.0 mg, 94%) as a viscous oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23-1.29 (m, 42H, 14×CH_3), 1.88-1.98 (m, 16H, 16×C≡CH), 2.46-2.55 (m, 64H, 16×CH_2C≡CH, 16×CH_2CH$_2$C≡CH), 2.98-3.71 (m, 22H, CH_2CH, 2×OCH_2CH_2, 3×NHCH_2CH_2), 3.97-4.59 (m, 60H, 28×OCH_2, OCH_2CH_2-triazole), 5.15-5.40 (m, 1H, NHCOO), 5.94-6.18 (m, 1H, CH_2C*H*), 6.46-6.76 (m, 2H, 2×NHCO), 7.10-7.55 (m, 8H, 8×CH-aryl); MS (MALDI-ToF) Calc. for $C_{179}H_{216}N_6O_{64}Na$ $[M+Na]^+$ 3496.4, Found $[M+Na]^+$ 3497.8.

Dendrimer 23 (isomers): Prepared from dendrimer **22** (10.0 mg, 1.5 μmol) using: 2-[2-[2-(2-azidoethoxy)ethoxy]ethoxy]-ethanol[27] (**6**) (21.2 mg, 96.6 μmol), TBTA (5.1 mg, 9.6 μmol), $CuSO_4$ (96 μL of 0.1 M solution in water, 9.6 μmol) and (+)-sodium L-ascorbate (240 μL of 0.1 M solution in water, 24.0 μmol) according to the general procedure for CuAAC reactions using $CuSO_4$ and Na ascorbate. HPLC purification (t = 32.5 min), followed by preparative SEC on Sephadex® LH-20 gel (MeOH:DCM, 1:1, v/v), gave **23** as a transparent glass (11 mg, 53%): ^{1}H NMR (500 MHz, D_2O) δ 1.09-1.35 (m, 90H, 30×CH_3), 2.68-2.79 (m, 64H, 32×CH_2CH$_2$-triazole), 2.90-3.01 (m, 64H, 32×CH$_2$CH_2-triazole), 3.45-3.76 (m, 406H, 98×OCH_2CH_2O, 3×NH CH_2CH_2, CH_2CH of cyclooctyne), 3.86-3.95 (m, 66H, 33×OCH_2CH$_2$-triazole), 4.05-4.39 (m, 120H, 60×CH_2O), 4.48-4.61 (m, 66H, 33×OCH$_2$CH_2 –triazole), 5.85-6.10 (m, 1H, CH_2C*H*), 7.14-7.61 (m, 8H, 8×CH-aryl of

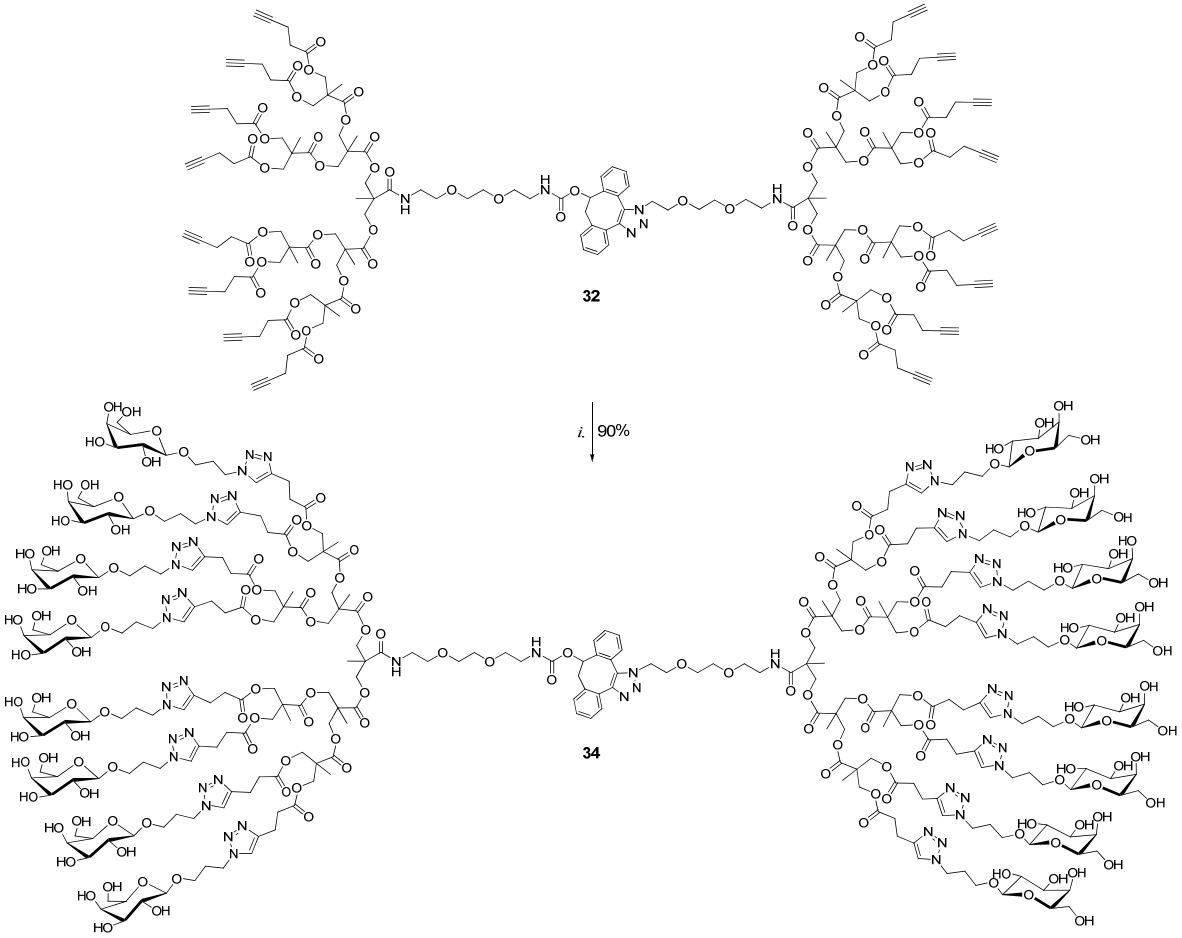
cyclooctyne), 7.81 (br s 32H, 32×CH of triazole); MS (MW, linear mode) (MALDI-ToF) Calc. for $C_{595}H_{953}N_{102}O_{256}$ $[M+H]^+$ 13631.5, Found $[M+H]^+$ 13643.7.

Glycodendrimer 24 (isomers): Prepared from dendrimer **22** (10.0 mg, 1.5 μmol) using: 3-azidopropyl β-D-galactopyranoside[28] (**9**) (25.4 mg, 96.6 μmol), TBTA (5.1 mg, 9.6 μmol), $CuSO_4$ (96 μL of 0.1 M solution in water, 9.6 μmol) and (+)-sodium L-ascorbate (240 μL of 0.1 M solution in water, 24.0 μmol) according to the general procedure for CuAAC reactions using $CuSO_4$ and Na ascorbate. HPLC purification (t = 24.0 min) gave **24** (19 mg, 84%) as a white powder: ^{1}H NMR (500 MHz, D_2O) δ 0.99-1.37 (m, 90H, 30×CH_3), 2.11-2.16 (m, 64H, 32×$CH_2CH_2CH_2$-triazole), 2.73 (br s, 64H, 32×CH_2CH_2–triazole), 2.97 (br. s, 64H, 32×CH_2CH_2–triazole), 3.48-3.76 (m, 216H, 32×$CHCH_2CH_2$-triazole, 32×CH_2 of galactose, 96×CHOH of galactose, 5×CH_2CH_2O, OCH_2CH_2-triazole, CH_2CH of cyclooctyne), 3.84-3.90 (m, 64H, 32×$CHHCH_2CH_2$-triazole, 32×CHOH of galactose), 4.00-4.33 (m, 152H, 32×CHO of galactose, 60×CH_2O), 4.47-4.62 (m, 66H, $CH_2CH_2CH_2$ –triazole, OCH_2CH_2-triazole) 5.79-6.05 (m, 1H, CH_2CH), 7.11-7.57 (m, 8H, 8×CH-aryl of cyclooctyne), 7.99(br. s 32H, 32×CH-triazole). Sugar analysis: 31.77 ± 0.18 (requires 32).



Scheme S3. Synthesis of glycodendrimer **33**. Reaction conditions: *i.* **9**, $CuSO_4$, Na ascorbate, TBTA, THF:H_2O, 18 h.

Glycodendrimer (33, isomers): Prepared from dendrimer **17** (10.0 mg, 4.2 μmol) using: 3-azidopropyl β-D-galactopyranoside [4] (**9**) (17.7 mg, 67.2 μmol), TBTA (3.6 mg, 6.7 μmol), $CuSO_4$ (67 μL of 0.1 M solution in water, 6.7 μmol) and (+)-sodium L-ascorbate (168 μL of 0.1 M solution in water, 16.8 μmol) according to the general procedure for CuAAC reactions using $CuSO_4$ and Na ascorbate. HPLC purification (t = 26.6 min) gave **33** (17.3 mg, 92%) as a yellow powder: ^{1}H NMR (500 MHz, D_2O) δ 1.03-1.25 (m, 21H, 7×CH_3), 2.04-2.21 (m, 16H, 8×$CH_2CH_2CH_2CH_2$-triazole), 2.60-2.99 (m, 32H, 8×CH_2CH_2-triazole), 3.09-4.45 (m, 142H, 8×$CH_2CH_2CH_2$, 40×CH of galactose, 8×CH_2 of galactose, CH_2CH, 6×CH_2CH_2O, 14×OCH_2), 5.65-5.93 (m, 1H, CH_2CH), 6.27-8.31 (m, 25H, 8×CH-aryl of cyclooctyne, 9×CH-aryl of fluorescein, 8×CH of triazole); Sugar analysis: Calc. 8, Found 10.38 ± 0.56; MS (most abundant mass) (MALDI-ToF) Calc. for $C_{197}H_{274}N_{30}O_{89}Na$ $[M+Na]^+$ 4508.8, Found $[M+Na]^+$ 4510.0.



Scheme S4. Synthesis of glycodendrimer **34**. Reaction conditions: *i.* **9**, $CuSO_4$, Na ascorbate, TBTA, THF:H_2O, 18 h.

Glycodendrimer (34, isomers): Prepared from dendrimer **32** (17.4 mg, 5.0 μmol) using: 3-azidopropyl β-D-galactopyranoside (**9**) (42.0 mg, 160.0 μmol), TBTA (8.6 mg, 16.0 μmol), $CuSO_4$ (160 μL of 0.1 M solution in water, 16.0 μmol) and (+)-sodium L-ascorbate (400 μL of 0.1 M solution in water, 40.0 μmol) according to the general procedure for CuAAC reactions using $CuSO_4$ and Na ascorbate. HPLC purification (t = 24.9 min) gave **34** (34.6 mg, 90%) as a white powder.^{1}H NMR (500 MHz, D_2O) δ 1.08-1.28 (m, 42H, 14×CH_3), 2.13-2.25 (m, 32H, 16×$CH_2CH_2CH_2$-triazole), 2.64-3.10 (m, 64H, 16×CH_2CH_2-triazole), 3.30-4.66 (m, 258H, 16×$CH_2CH_2CH_2$, 64×CH of galactose, 16×CH_2 of galactose, CH_2CH, 6×CH_2CH_2O, 28×OCH_2), 5.82-6.04 (m, 1H, CH_2CH), 7.11-7.59 (m, 8H, 8×CH-aryl of cyclooctyne), 7.88-8.04 (m, 16H, 16×CH of triazole); Sugar analysis: Calc. 16, Found 15.10 ± 0.83; MS (MW, linear mode), (MALDI-ToF) Calc. for $C_{323}H_{489}N_{54}O_{160}$ $[M+H]^+$ 7688.6, Found $[M+H]^+$ 7685.5.

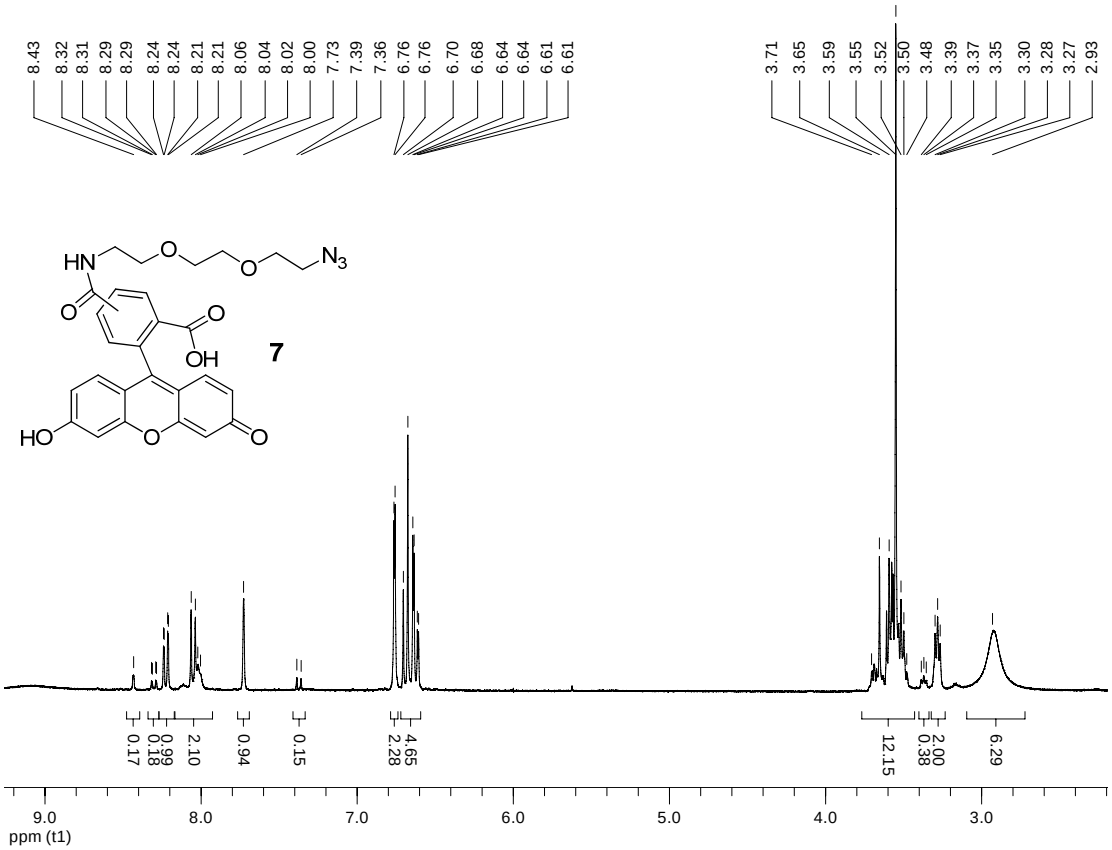
Dendrimer 26 (isomers): Prepared from dendrimer **25** (30.0 mg, 10 μmol) using: 2-[2-[2-(2-azidoethoxy)ethoxy]ethoxy]-ethanol (**6**) (26.3 mg, 120 μmol), CuI (1.5 mg, 8 μmol) and DIPEA (7 μL, 40 μmol) according to the general procedure for CuAAC reaction using CuI. The reaction mixture was stirred for 4 h. SEC purification gave **26** as transparent oil (41 mg, 87%): ^{1}H NMR (500 MHz, CD_6CO) δ 0.11 (s, 36H, 4×$Si(CH_3)_3$), 1.22-1.38 (m, 30H, 10×CH_3), 2.50-2.57 (m, 16H, 4×$CH_2CH_2C{\equiv}C$), 2.74 (t, J = 7.4 Hz, 16H, 8×CH_2CH_2-triazole), 2.97 (t, J = 7.4 Hz, 16H, 8×CH_2CH_2-triazole), 3.24-4.02 (m, 136H, CH_2CH, 26×OCH_2CH_2O, 9×OCH_2CH_2-triazole, 3×$NHCH_2CH_2O$), 4.19-4.37 (m, 40H, 20×OCH_2), 4.52 (t, J = 5.0 Hz, 18H, 9×OCH_2CH_2-triazole), 5.96-6.24 (m, 1H, CH_2CH), 6.31-6.70 (m, 1H, NH), 7.19-7.68 (m, 10H, 8×CH-aryl, 2×NH), 7.79 (s, 8H, 8×CH of triazole); MS (most abundant mass) (MALDI-ToF) Calc. for $C_{215}H_{336}N_{30}O_{80}Si_4Na$ $[M+Na]^+$ 4756.2, Found $[M+Na]^+$ 4759.2.

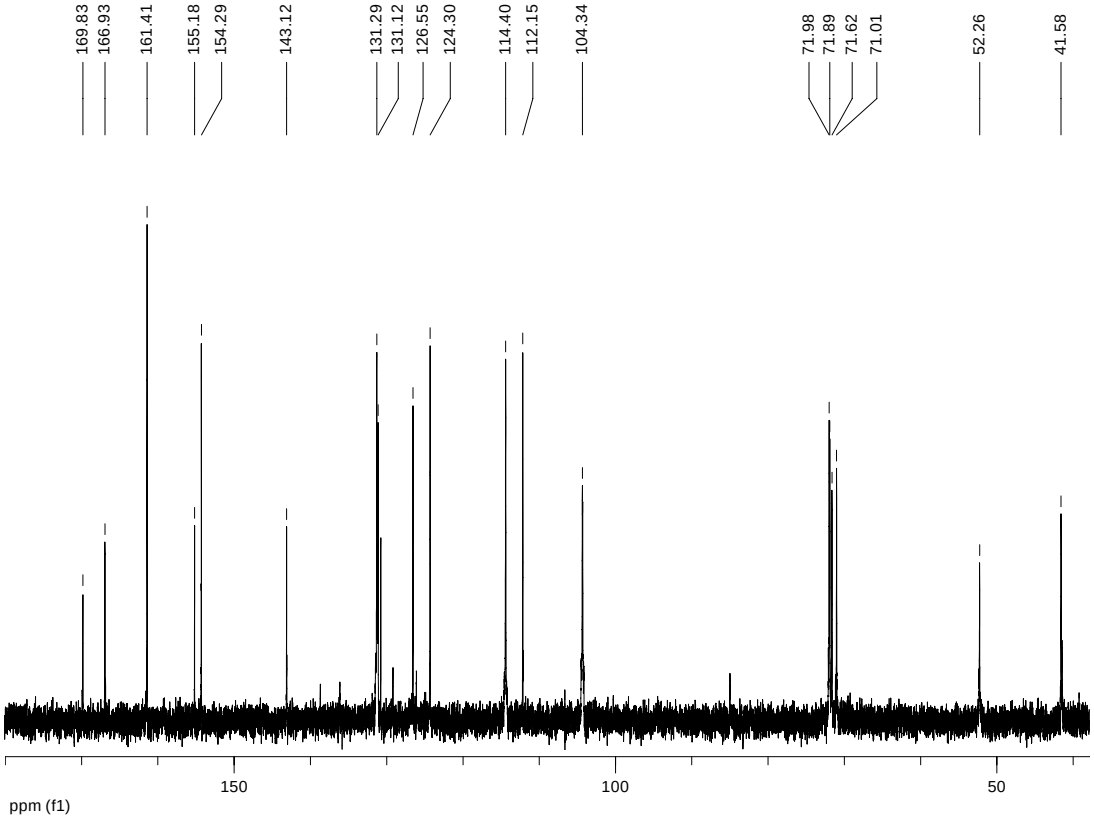
Dendrimer 28 (isomers): Prepared from dendrimer **26** (5.0 mg, 1.06 μmol) using 3-azidopropyl β-D-galactopyranoside **(9)** (2.2 mg, 8.4 μmol) and CuF_2 (0.8 mg, 8.4 μmol) according to the general procedure for CuF_2 mediated click reaction. The reaction mixture was stirred for 8 h. HPLC purification (t = 28.5 min) gave **28** (4.9 mg, 84%) as a white foam: ^{1}H NMR (500 MHz, D_2O) δ 1.04-1.35 (m, 30H, 10×CH_3), 2.09-2.23 (m, 8H, 4×$OCH_2CH_2CH_2$-triazole), 2.66-2.78 (m, 24H, 12×CH_2CH_2-triazole), 2.91-3.02 (m, 24H, 12×CH_2CH_2-triazole), 3.18-3.79 (m, 138H, CH_2CHO, 3×OCH_2CH_2NH, 26×OCH_2CH_2O, 12×CHOH of galactose, 4×CH_2 of galactose, 4×$OCHCH_2CH_2$-triazole), 3.84-3.99 (m, 30H, 4×$OCHCH_2CH_2$-triazole, 4×CHOH of galactose, 9×OCH_2CH_2-triazole), 4.02-4.39 (m, 44H, 4×CHO of galactose, 20×OCH_2), 4.47-4.66 (m, 26H, 13×CH_2-triazole), 5.80-6.13 (m, 1H, CH_2CH), 7.12-7.68 (m, 8H, 8×CH-aryl), 7.86-7.89 (m, 12H, 12×CH of

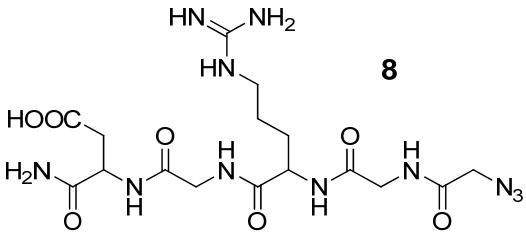
triazole); MS (most abundant mass) (MALDI-ToF) Calc. for $C_{239}H_{372}N_{42}O_{104}Na$ $[M+Na]^+$ 5519.5, Found $[M+Na]^+$ 5524.3.

Dendrimer 29 (isomers): Prepared from dendrimer **26** (10.0 mg, 2.1 μmol) using azido-RGD peptide **8** (6.1 mg, 12.6 μmol) and CuF_2 (1.7 mg, 16.8 μmol) according to the general procedure for CuF_2 mediated click reaction. The reaction mixture was stirred for 19 h. HPLC purification (t = 26.9 min) gave **29** (8.4 mg, 63%) as a white foam. ^{1}H NMR (500 MHz, D_2O) δ 1.05-1.32 (m, 30H, 10×CH_3), 1.57-1.69 (m, 8H, 4×α-$CHCH_2C\mathit{H}_2CH_2$), 1.73-1.80 (m, 4H, 4×α-$CHCH\mathit{H}CH_2CH_2$), 1.85-1.93 (m, 4H, 4×α-$CHCH\mathit{H}CH_2CH_2$), 2.68-2.76 (m, 24H, 12×$C\mathit{H}_2CH_2$-triazole), 2.83-2.99 (m, 32H, 12×$CH_2C\mathit{H}_2$-triazole, 4×$C\mathit{H}_2COOH$), 3.18 (t, J = 6.9 Hz, 8H, 4×α-$CHCH_2CH_2C\mathit{H}_2$), 3.24-3.75 (m, 118H, $C\mathit{H}_2CHO$, 3×$OC\mathit{H}_2C\mathit{H}_2NH$, 26×$OC\mathit{H}_2C\mathit{H}_2O$), 3.87-4.35 (m, 78H, 9×$OC\mathit{H}_2CH_2$-triazole, 8×$NHC\mathit{H}_2$ of Gly, 4×α-$C\mathit{H}CH_2CH_2CH_2$, 20×OCH_2), 4.51-4.56 (m, 18H, 9×$C\mathit{H}_2$-triazole), 4.73 (dd, J = 7.4, 5.3 Hz, 4H, 4×α-CH of Asp), 5.27 (s, 8H, 4×triazole-CH_2 of peptide), 5.83-6.09 (m, 1H, $CH_2C\mathit{H}$), 7.13-7.61 (m, 8H, 8×CH-aryl), 7.81(s, 12H, 12×CH of triazole); MS (MW, linear mode) (MALDI-ToF) Calc. for $C_{267}H_{413}N_{74}O_{108}$ $[M+H]^+$ 6387.6, Found $[M+H]^+$ 6372.6.

NMR and MALDI-ToF spectra



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NH2
HN
HOOC
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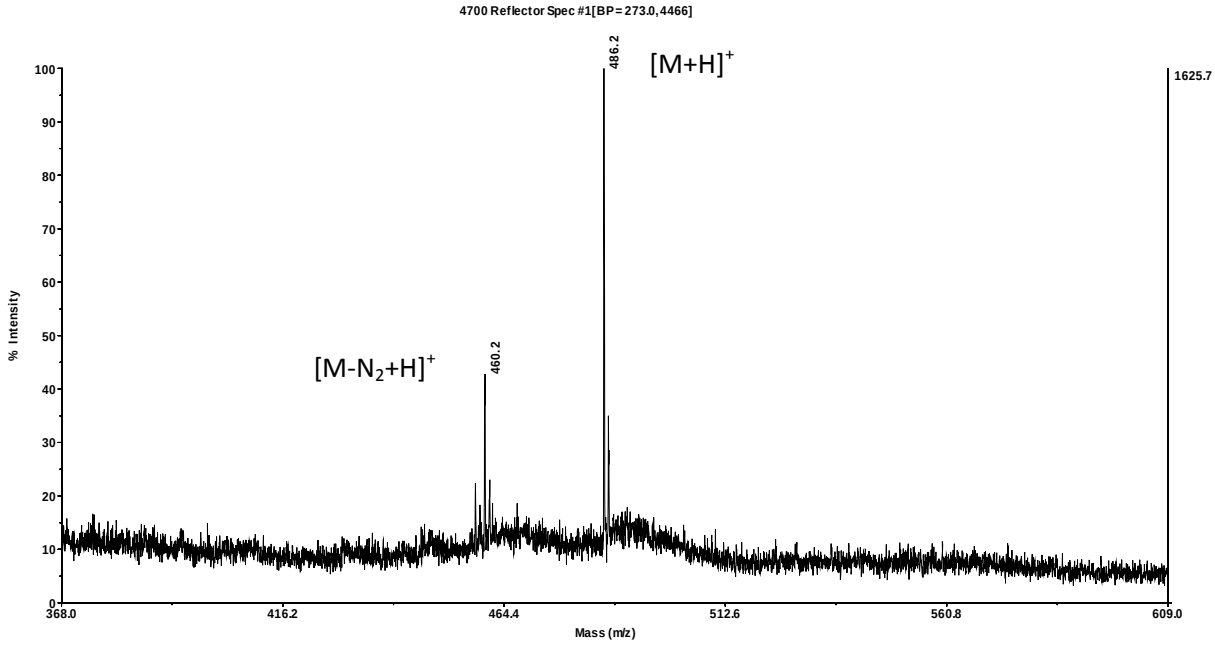
O
N
H
O
H
N
O
N
H
O
H
N
N3
O

8


4700 Reflector Spec #1[BP= 273.0,4466]
% Intensity
Mass (m/z)
[M+H]+
[M-N2+H]+
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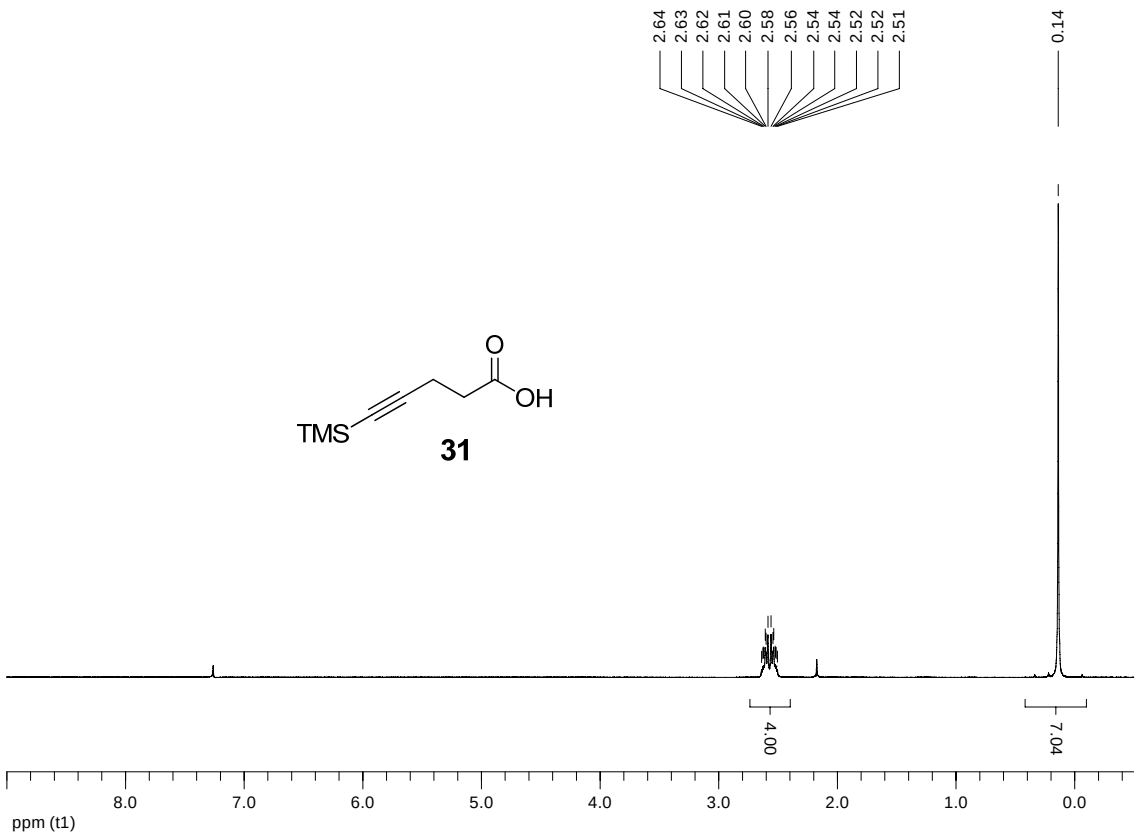
460.2
1625.7
100
90
80
70
60
50
40
30
20
10
0
368.0
416.2
464.4
512.6
560.8
609.0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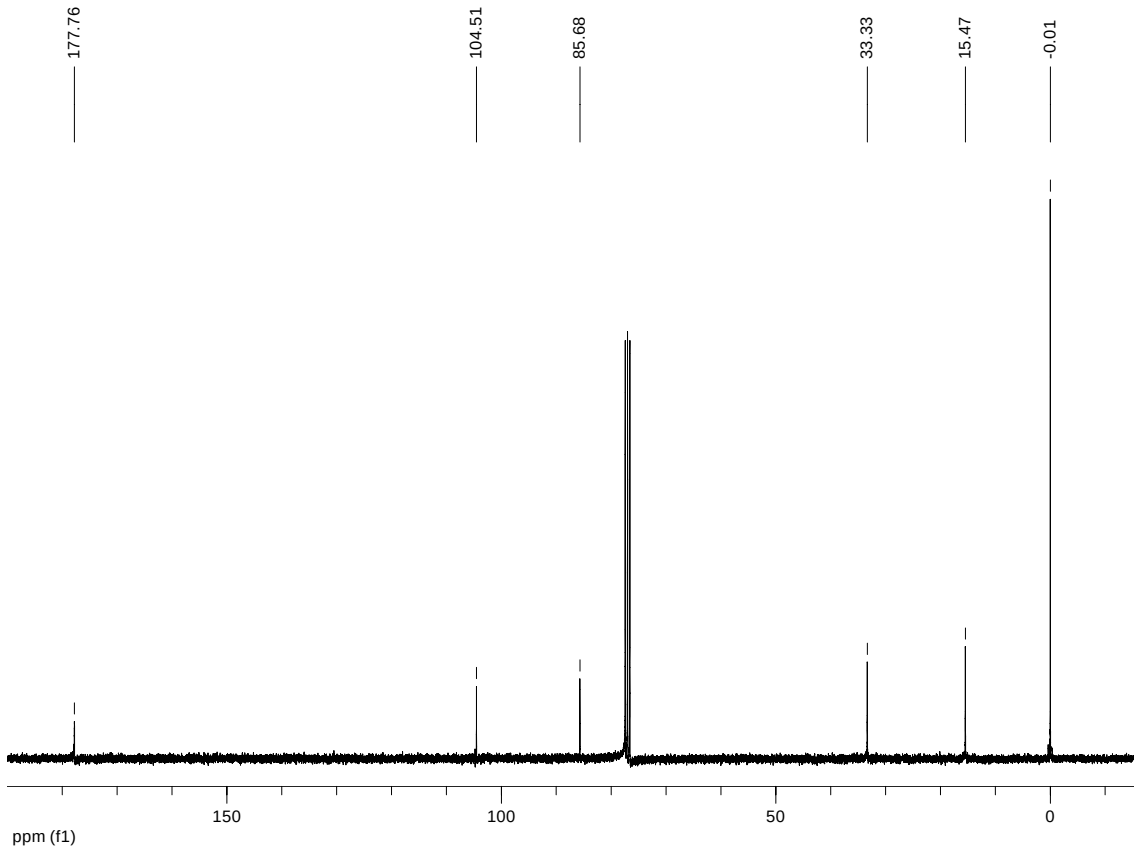
2.63
2.62
2.61
2.60
2.58
2.56
2.54
2.54
2.52
2.52
2.51
0.14
O
OH
TMS
4.00
7.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

31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104.51
85.68
33.33
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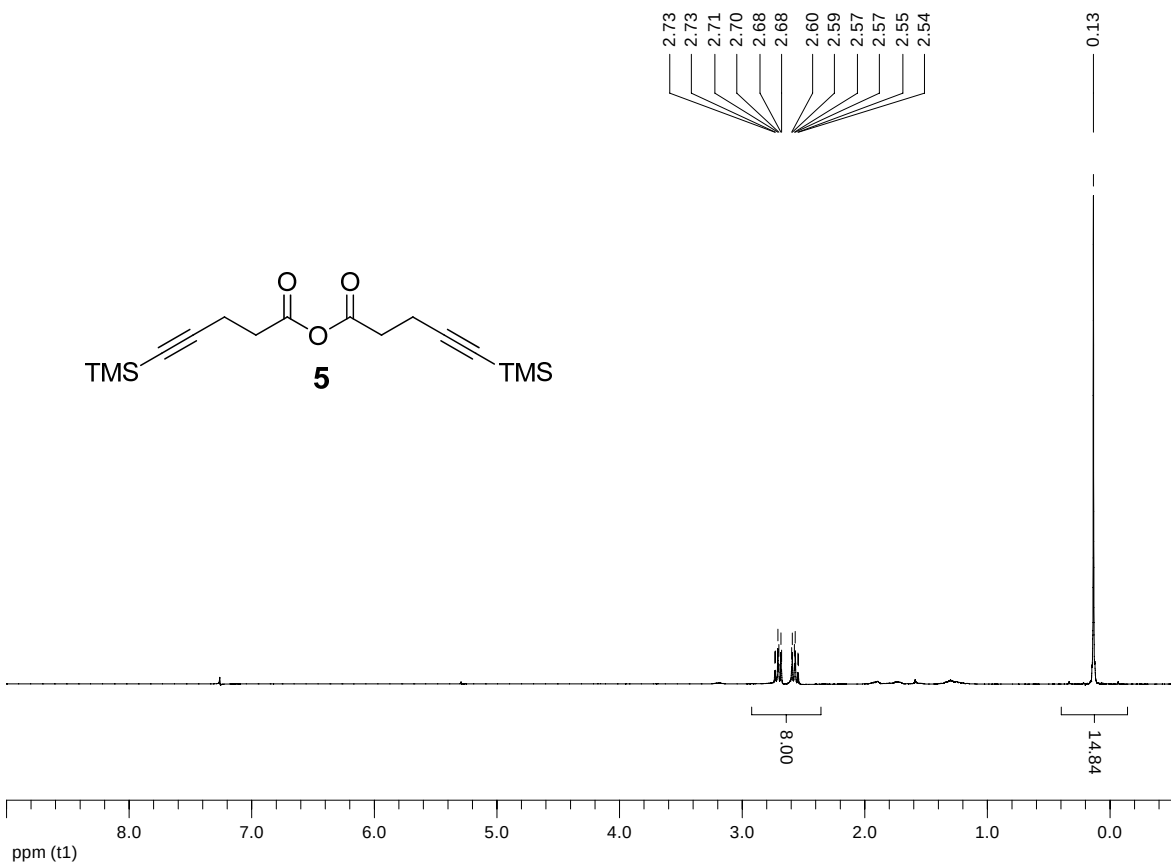
150
100
50
0
ppm (f1)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2.68
2.60
2.59
2.57
2.57
2.55
2.54
0.13
O
O
O
TMS
TMS
5
8.00
14.84
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7.0
6.0
5.0
4.0
3.0
2.0
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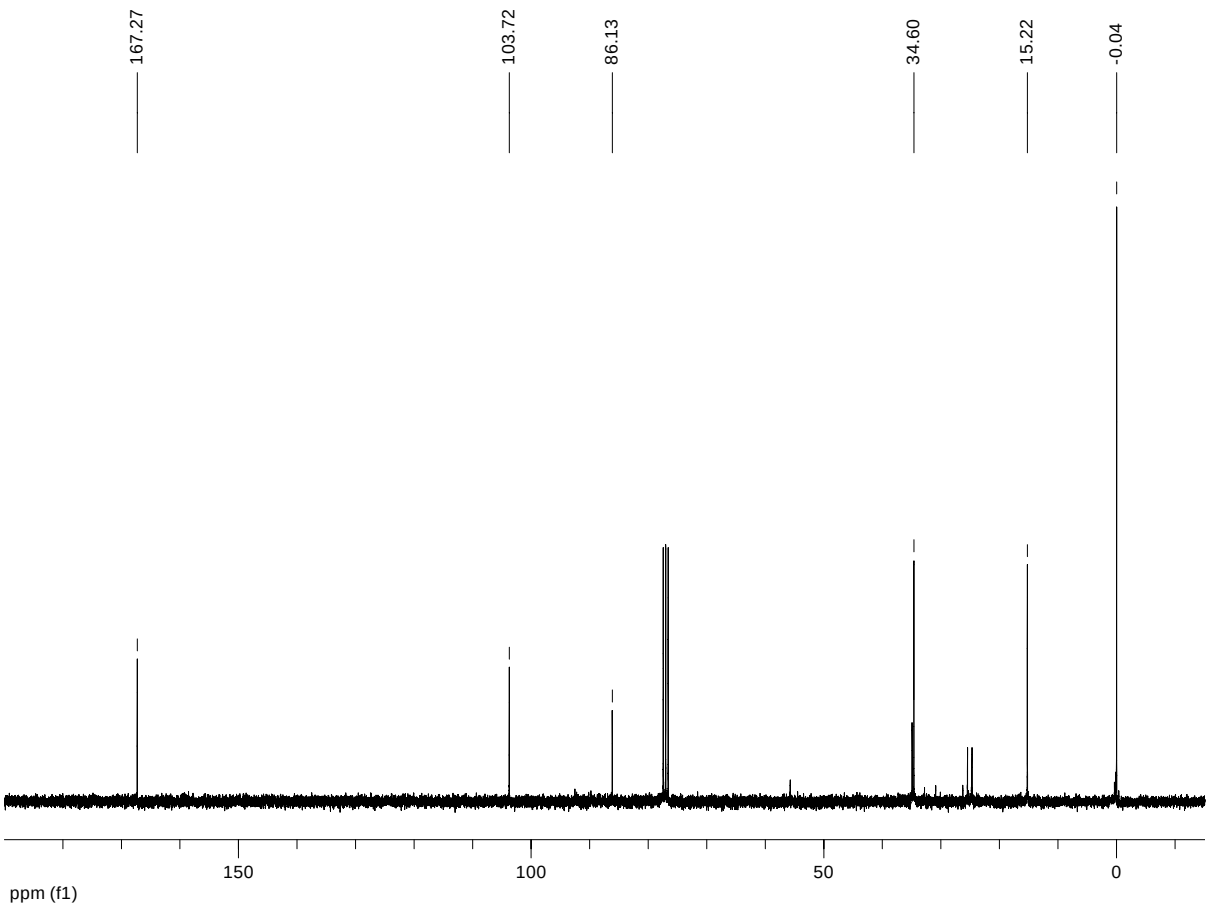
0.0
ppm (t1)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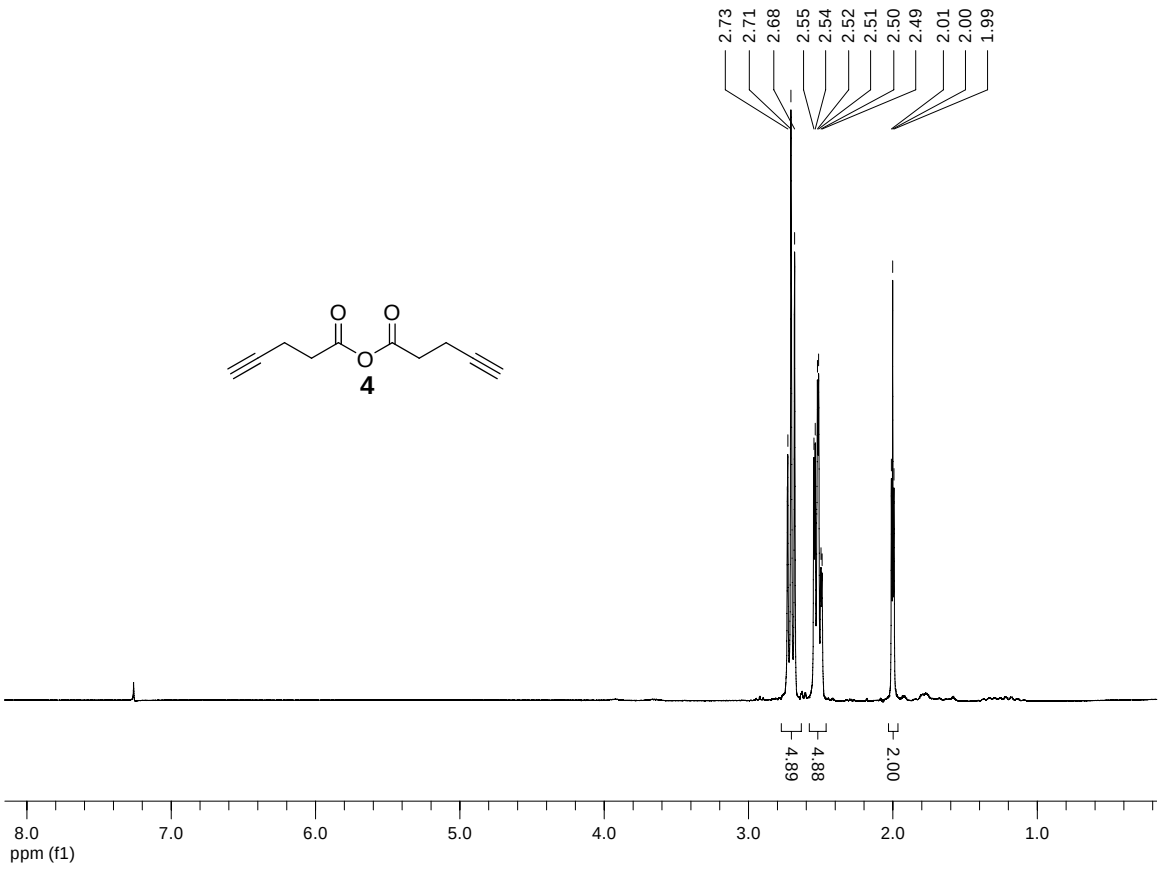
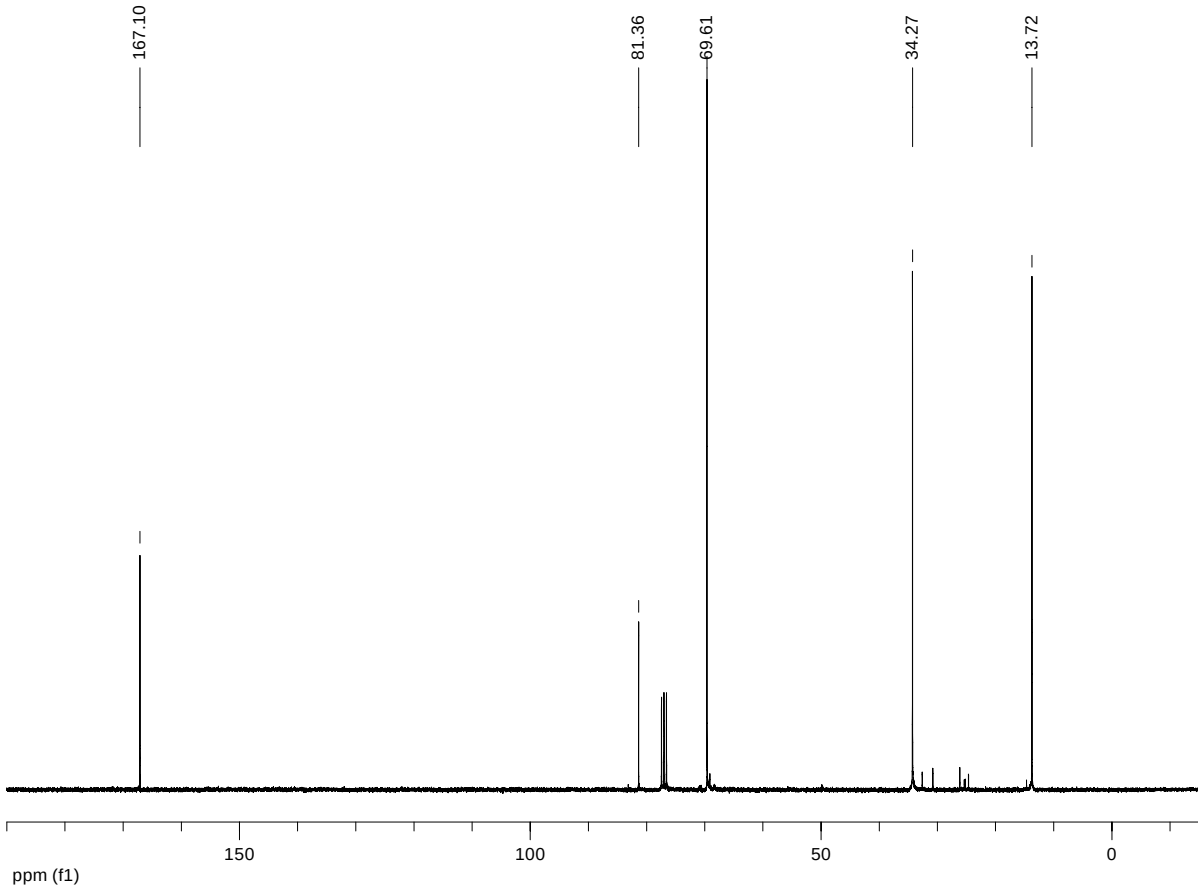
103.72
86.13
34.60
15.22
-0.04
150
100
50
0
ppm (f1)


2.73
2.71
2.68
2.55
2.54
2.52
2.51
2.50
2.49
2.01
2.00
1.99
4.89
4.88
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

4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69.61
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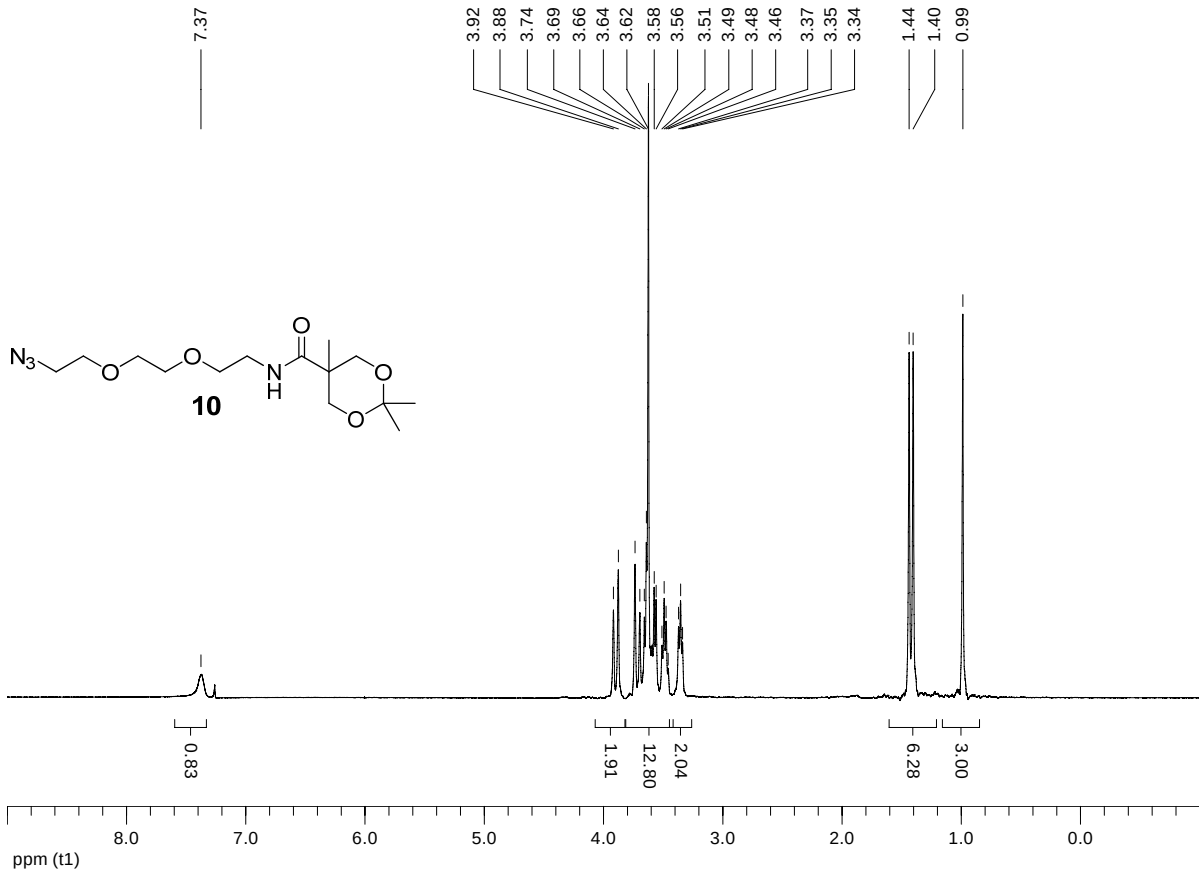
100
50
0
ppm (f1)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3.92
3.88
3.74
3.69
3.66
3.64
3.62
3.58
3.56
3.51
3.49
3.48
3.46
3.37
3.35
3.34
1.44
1.40
0.99
N3
O
O
O
N
H
O
O
O
10
0.83
1.91
12.80
2.04
6.28
3.00
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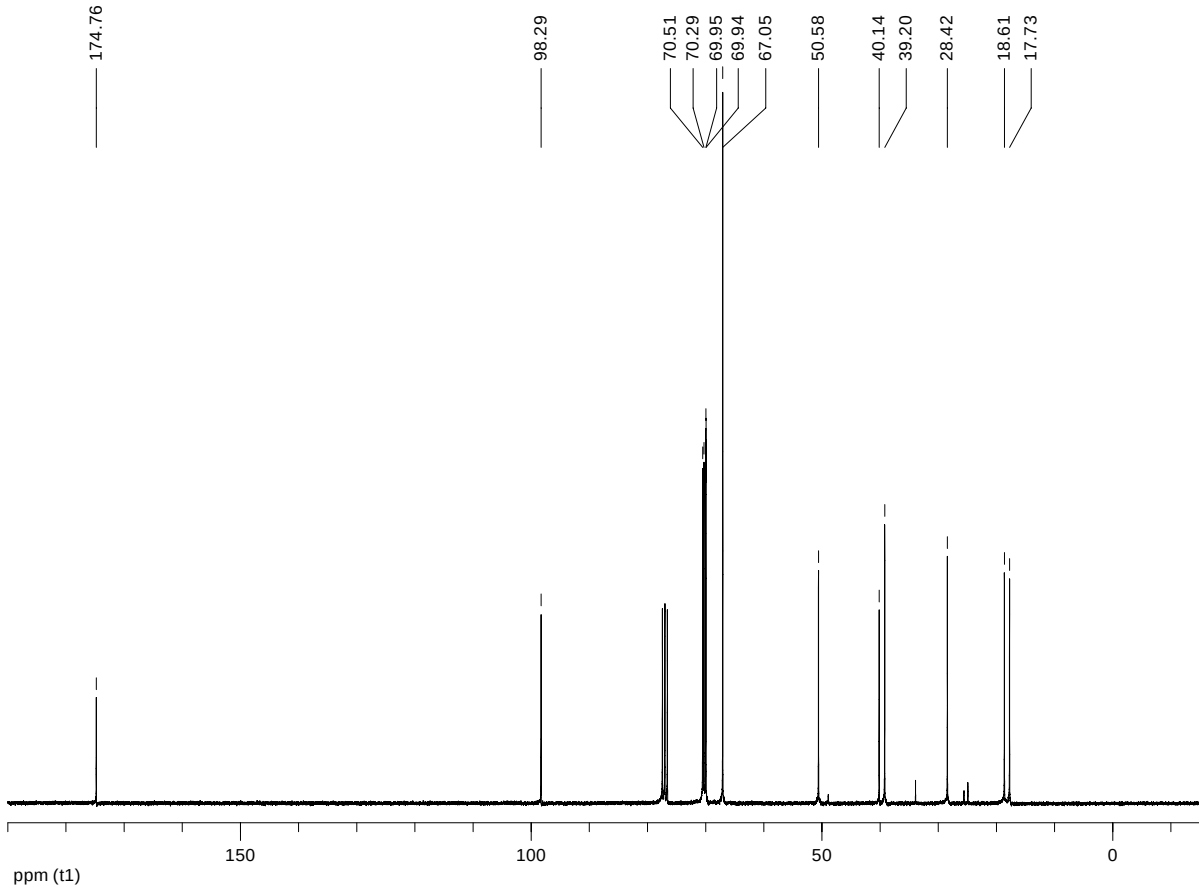
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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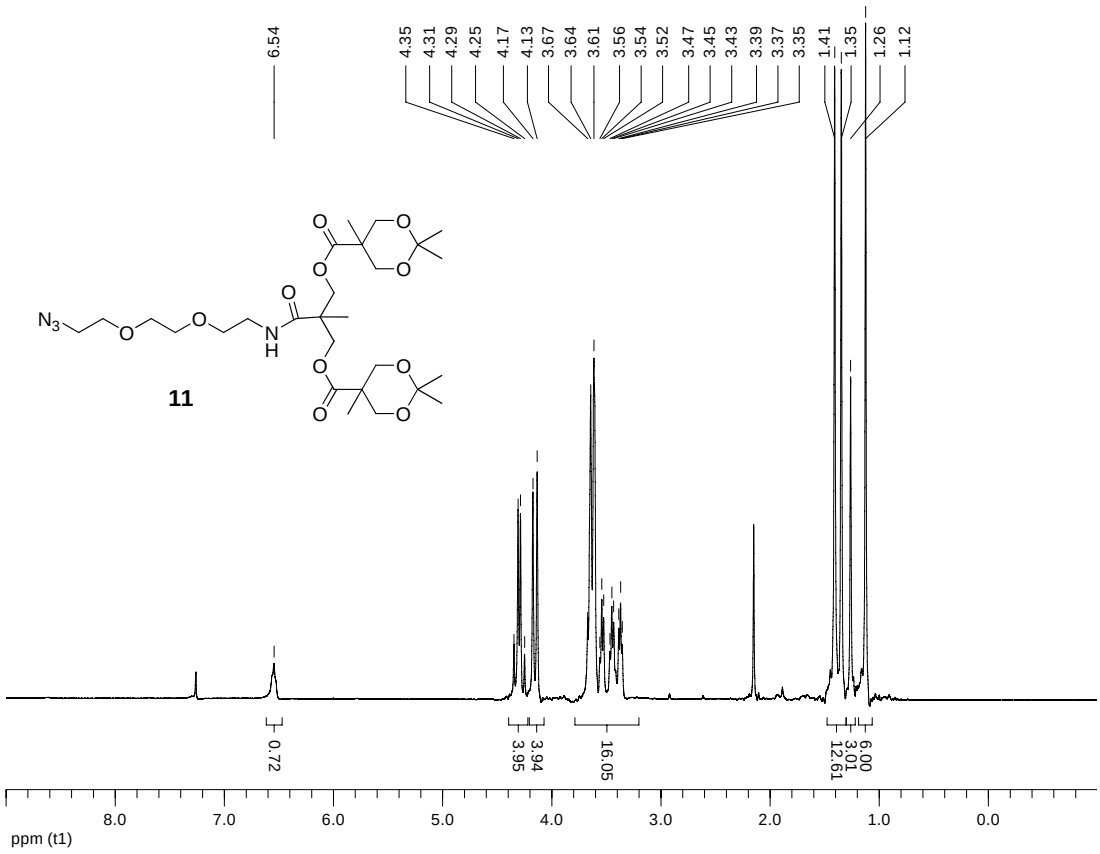
70.51
70.29
69.95
69.94
67.05
50.58
40.14
39.20
28.42
18.61
17.73
150
100
50
0
ppm (t1)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3.61
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3.54
3.52
3.47
3.45
3.43
3.39
3.37
3.35
1.41
1.35
1.26
1.12
11
0.72
3.95
3.44
16.05
12.61
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7.0
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4.0
3.0
2.0
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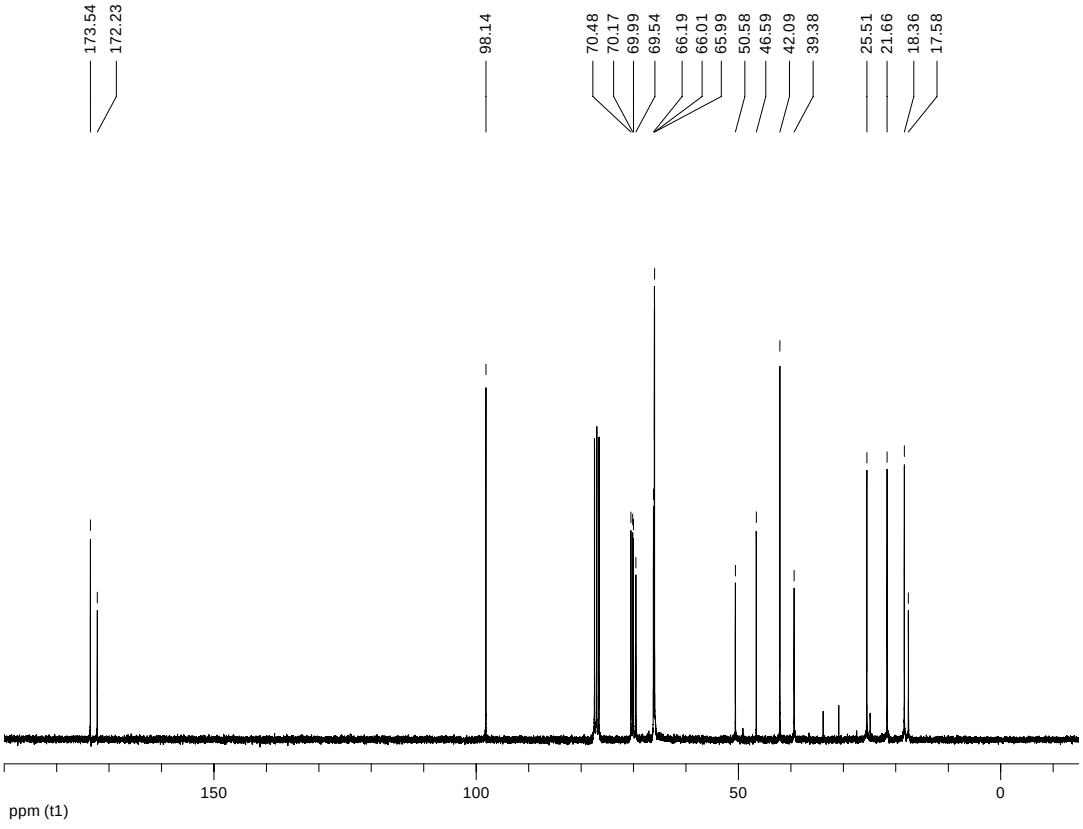
0.0
ppm (t1)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172.23
98.14
70.48
70.17
69.99
69.54
66.19
66.01
65.99
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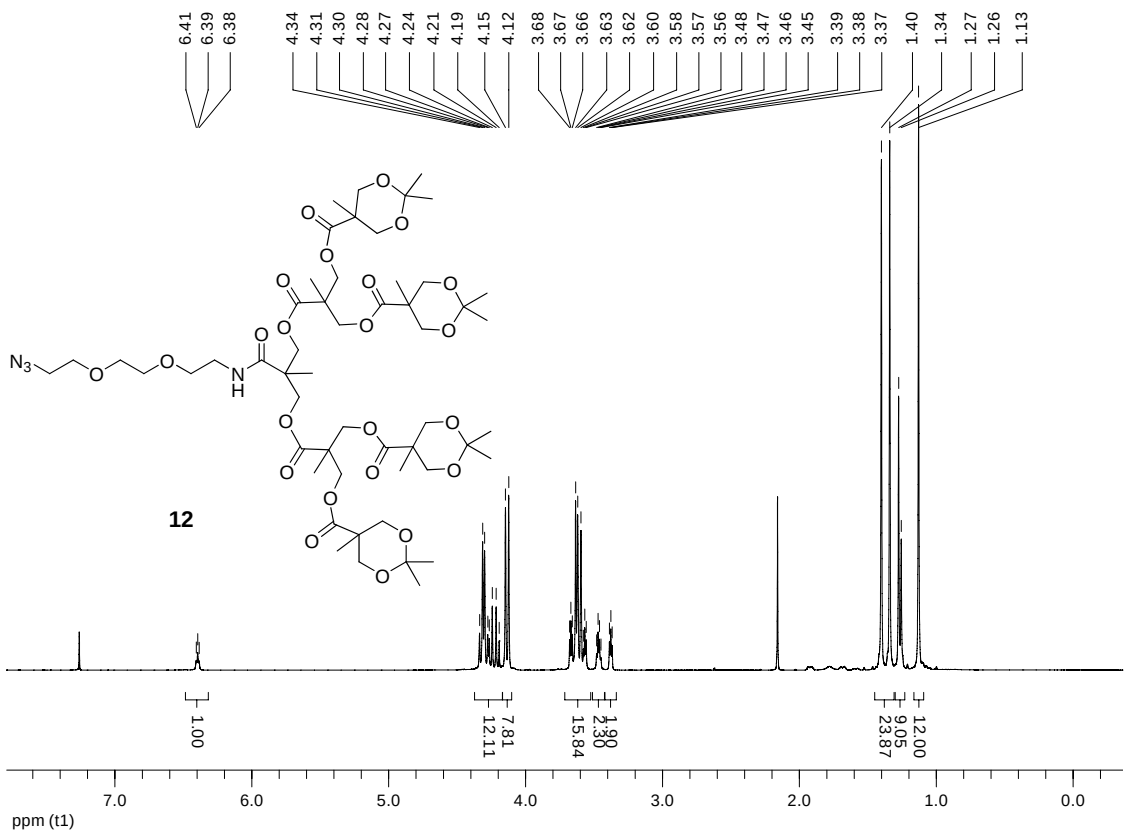
46.59
42.09
39.38
25.51
21.66
18.36
17.58
150
100
50
0
ppm (t1)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6.38
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4.30
4.28
4.27
4.24
4.21
4.19
4.15
4.12
3.68
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3.66
3.63
3.62
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3.58
3.57
3.56
3.48
3.47
3.46
3.45
3.39
3.38
3.37
1.40
1.34
1.27
1.26
1.13
12
1.00
12.11
7.81
15.84
1.90
1.30
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9.05
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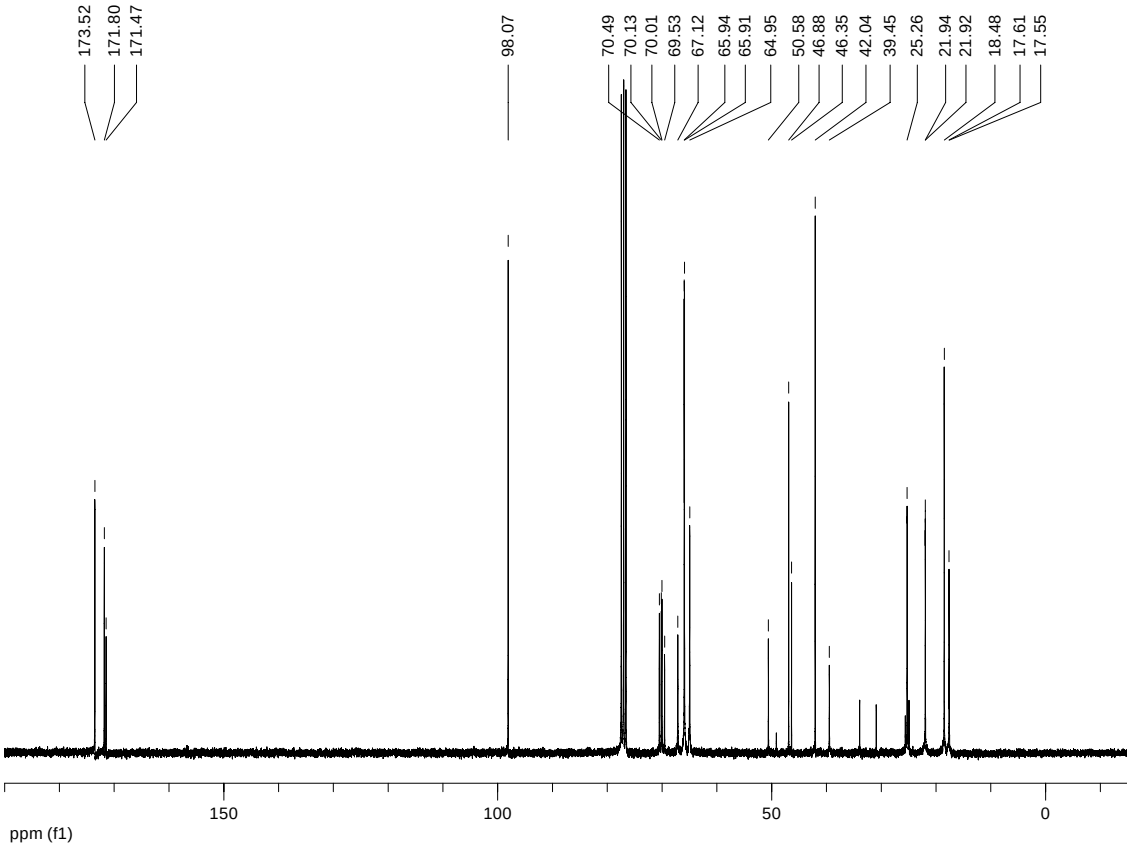
ppm (t1)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171.47
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70.13
70.01
69.53
67.12
65.94
65.91
64.95
50.58
46.88
46.35
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25.26
21.94
21.92
18.48
17.61
17.55
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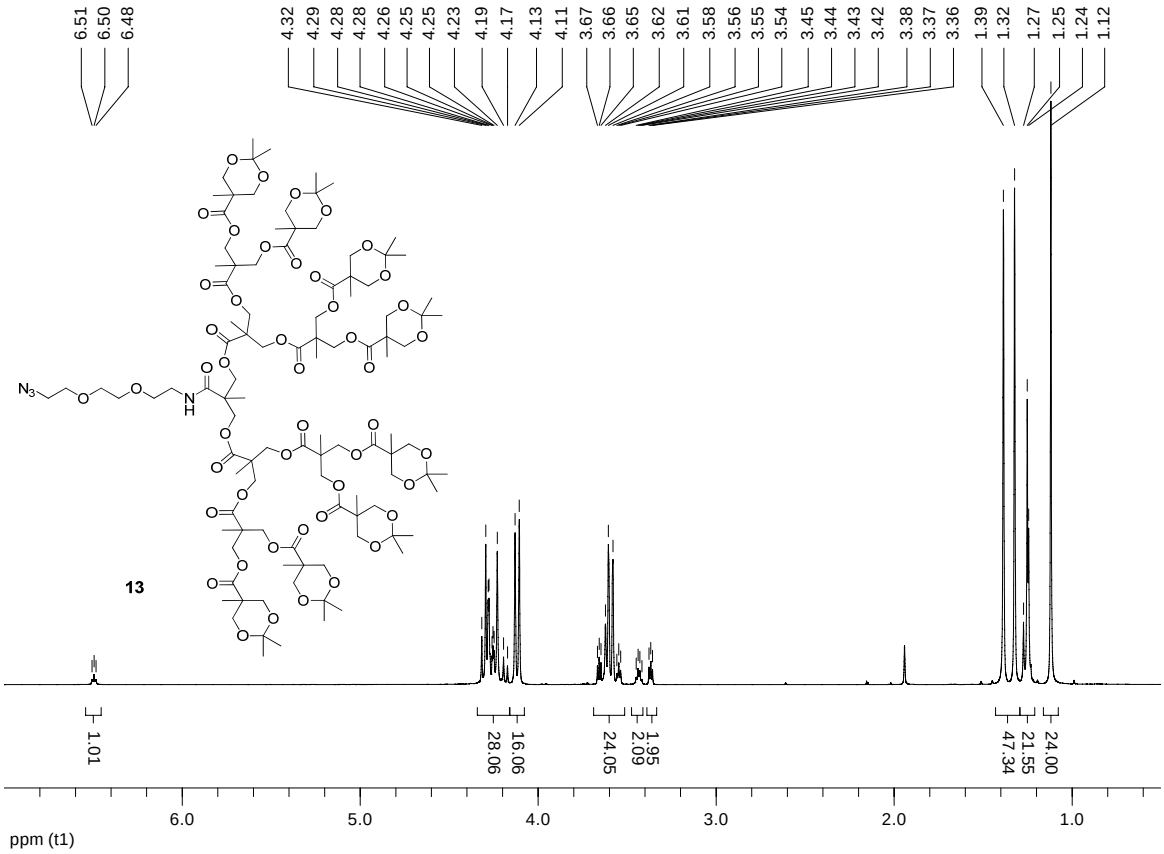
50
0
ppm (f1)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4.28
4.26
4.25
4.25
4.23
4.19
4.17
4.13
4.11
3.67
3.66
3.65
3.62
3.61
3.58
3.56
3.55
3.54
3.45
3.44
3.43
3.42
3.38
3.37
3.36
1.39
1.32
1.27
1.25
1.24
1.12
13
1.01
28.06
16.06
24.05
2.09
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21.55
24.00
6.0
5.0
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3.0
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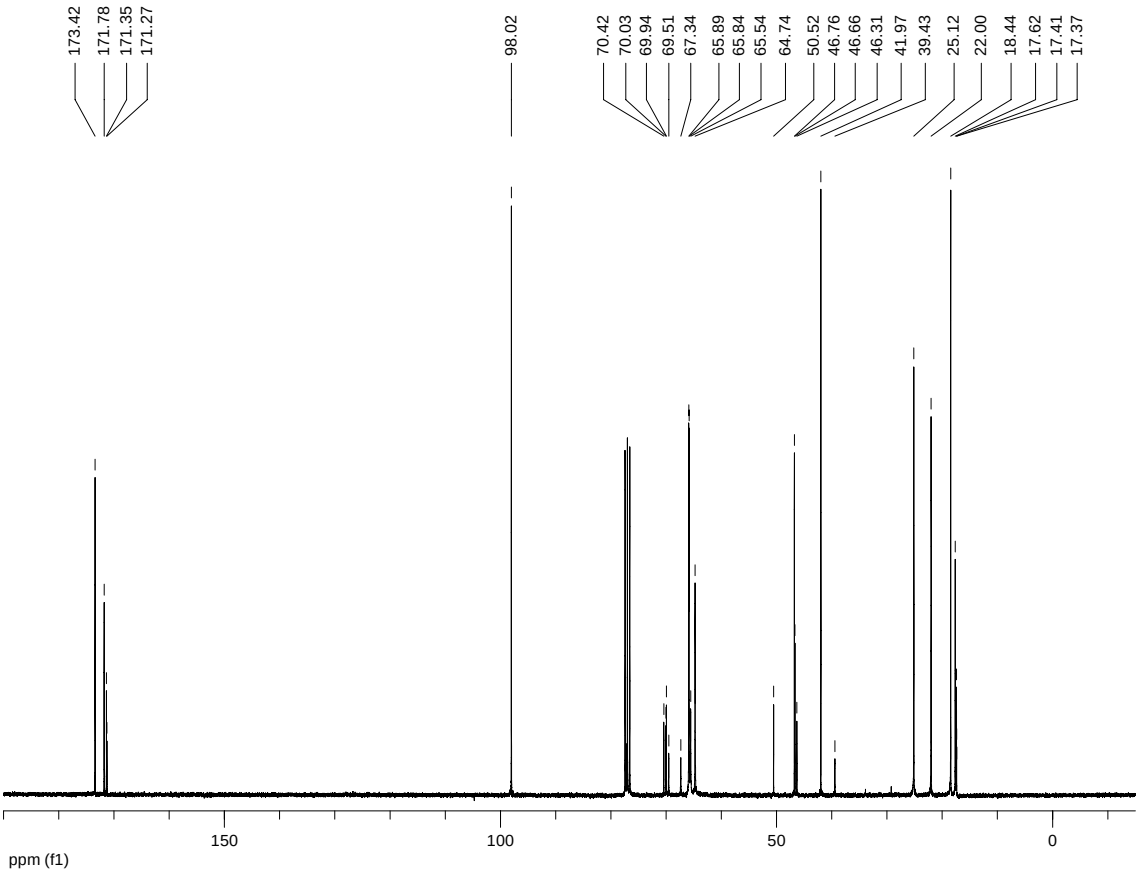
1.0
ppm (t1)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46.66
46.31
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22.00
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17.37
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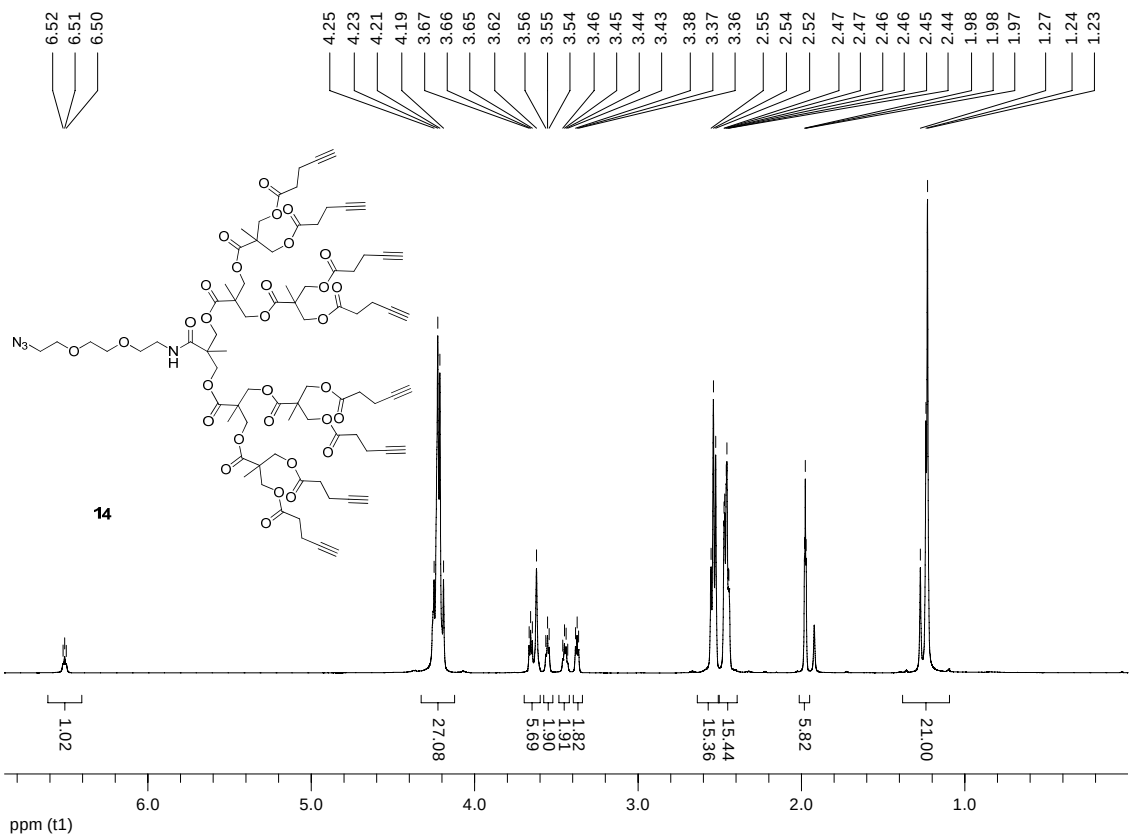
100
50
0
ppm (f1)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3.55
3.54
3.46
3.45
3.44
3.43
3.38
3.37
3.36
2.55
2.54
2.52
2.47
2.47
2.46
2.46
2.45
2.44
1.98
1.98
1.97
1.27
1.24
1.23
14
1.02
27.08
5.69
1.90
1.91
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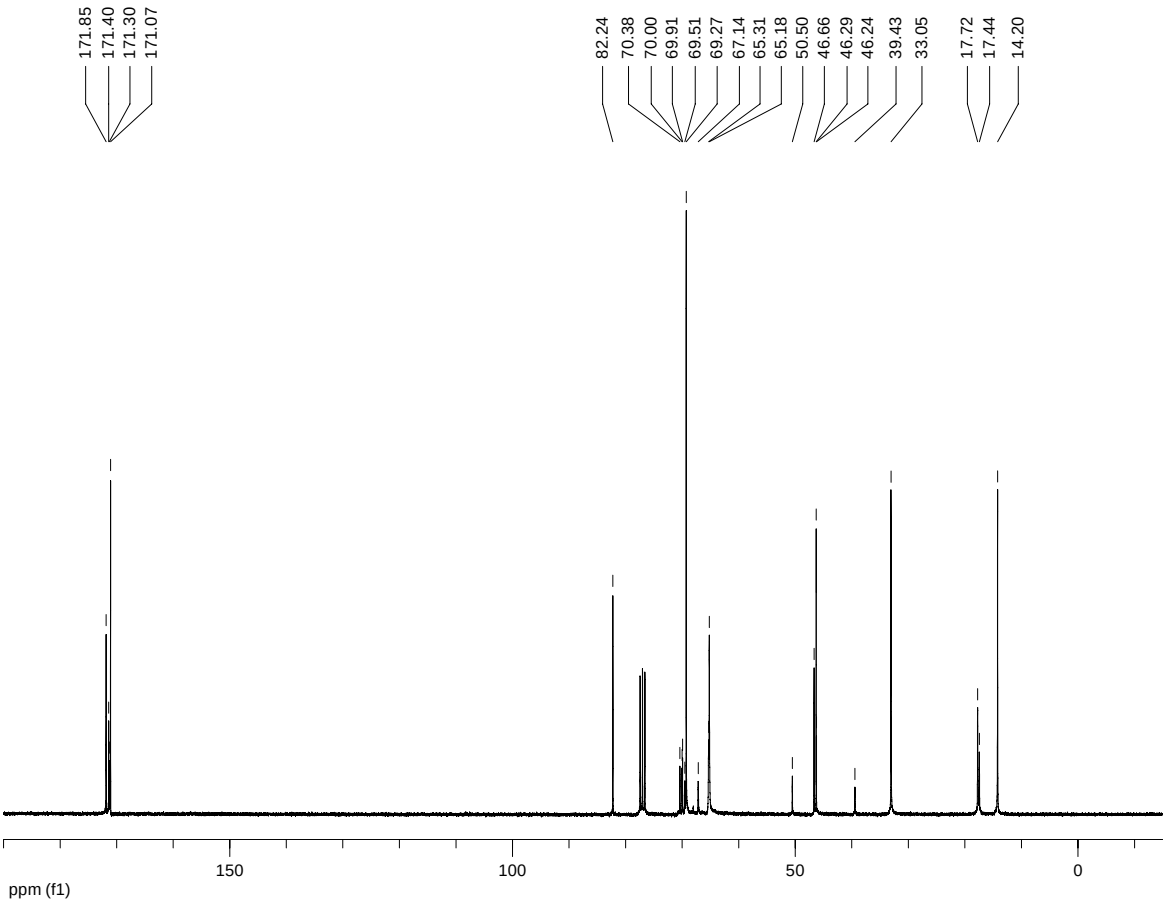
ppm (t1)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70.00
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69.51
69.27
67.14
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65.18
50.50
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46.24
39.43
33.05
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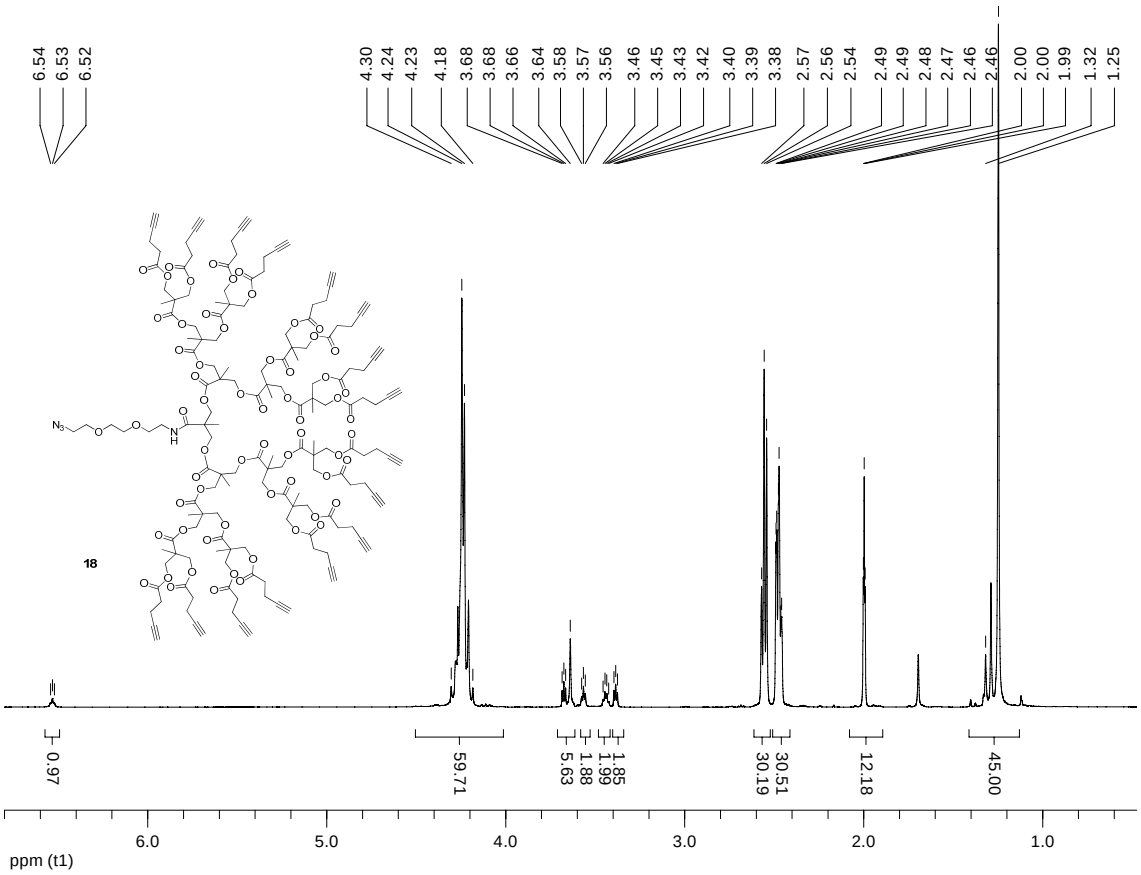
17.44
14.20
150
100
50
0
ppm (f1)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2.49
2.49
2.48
2.47
2.46
2.46
2.00
2.00
1.99
1.32
1.25
18
0.97
59.71
5.63
1.88
1.69
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12.18
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3.0
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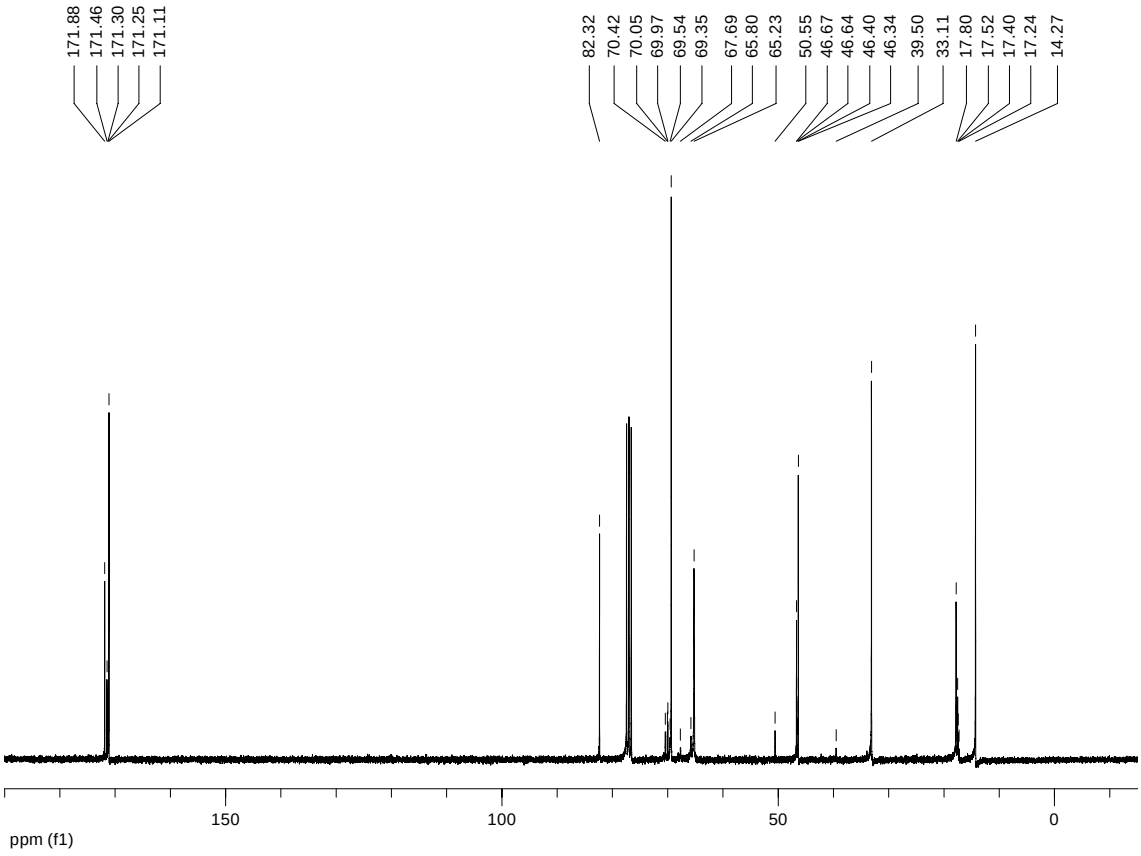
ppm (t1)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70.05
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69.35
67.69
65.80
65.23
50.55
46.67
46.64
46.40
46.34
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33.11
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17.52
17.40
17.24
14.27
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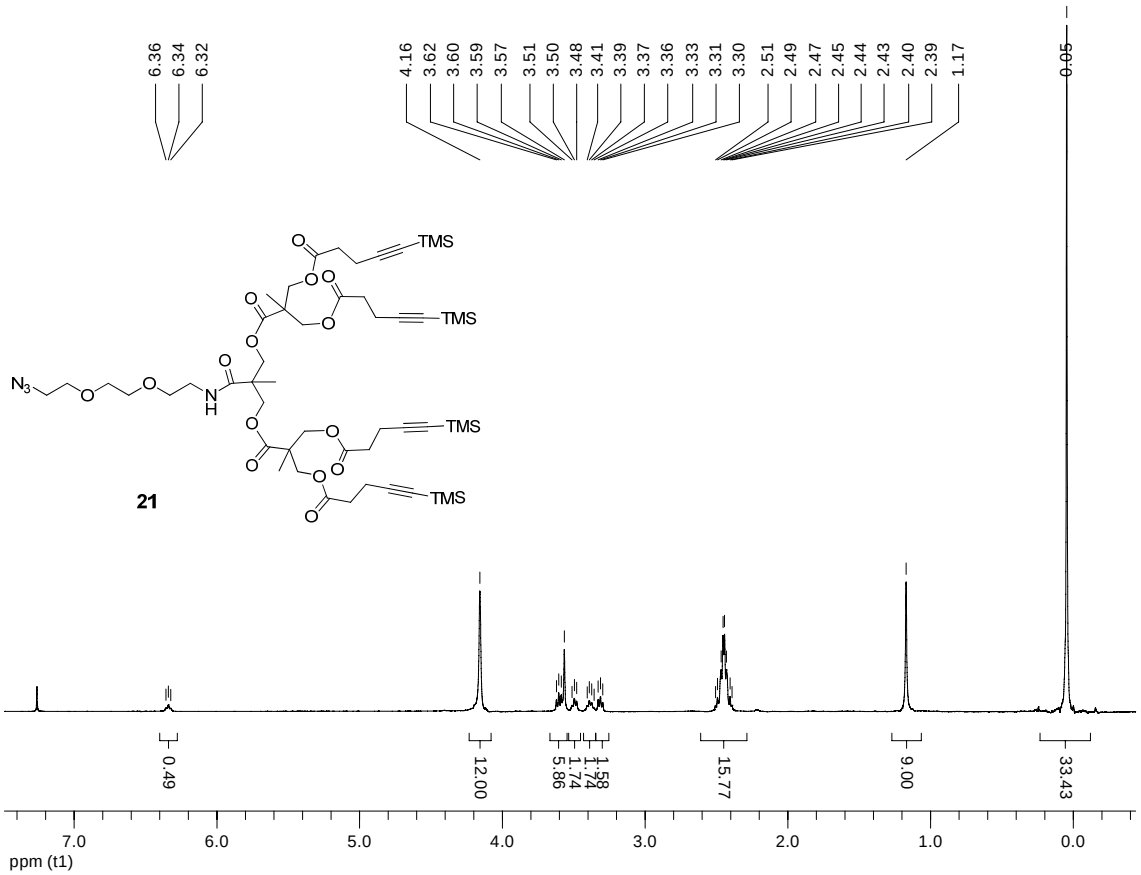
100
50
0
ppm (f1)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3.48
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3.37
3.36
3.33
3.31
3.30
2.51
2.49
2.47
2.45
2.44
2.43
2.40
2.39
1.17
0.05
TMS
TMS
TMS
TMS
N3
21
0.49
12.00
5.86
1.74
1.74
1.58
15.77
9.00
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2.0
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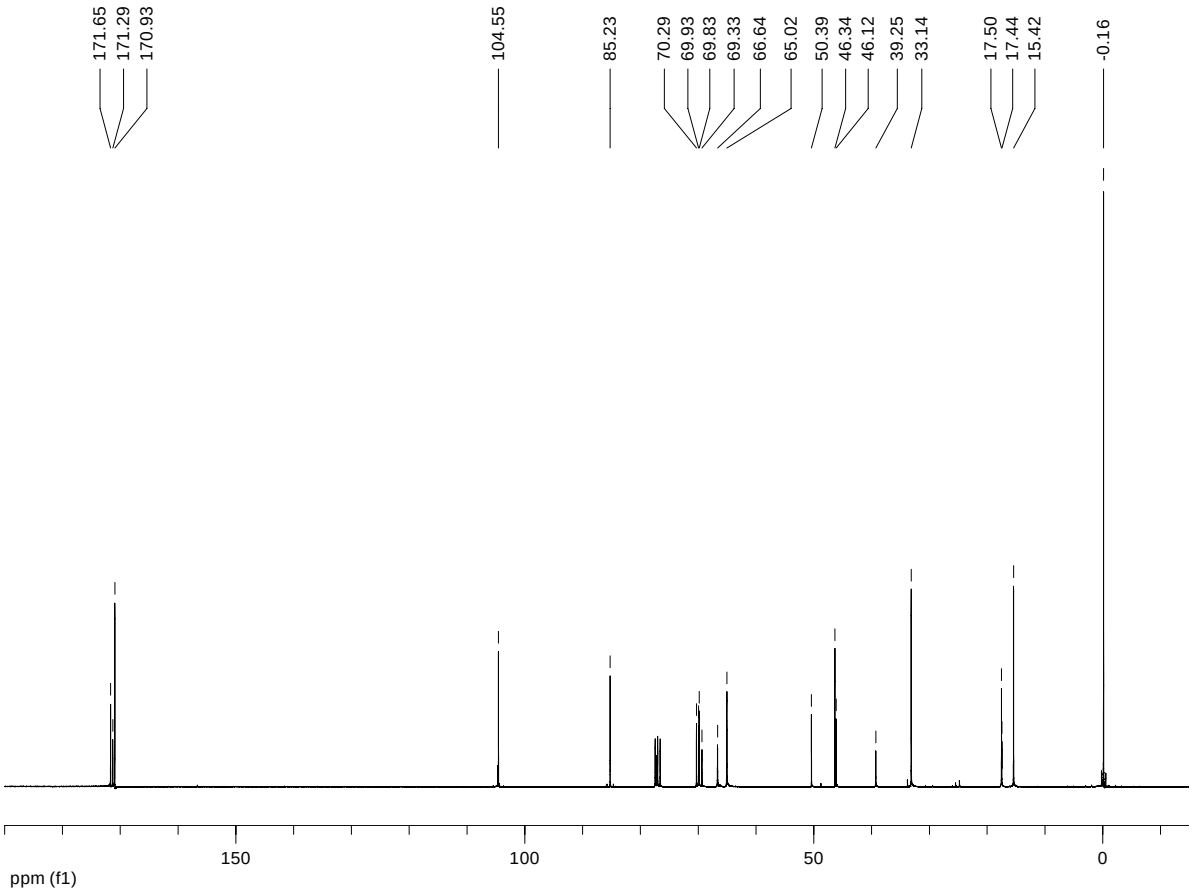
ppm (t1)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66.64
65.02
50.39
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33.14
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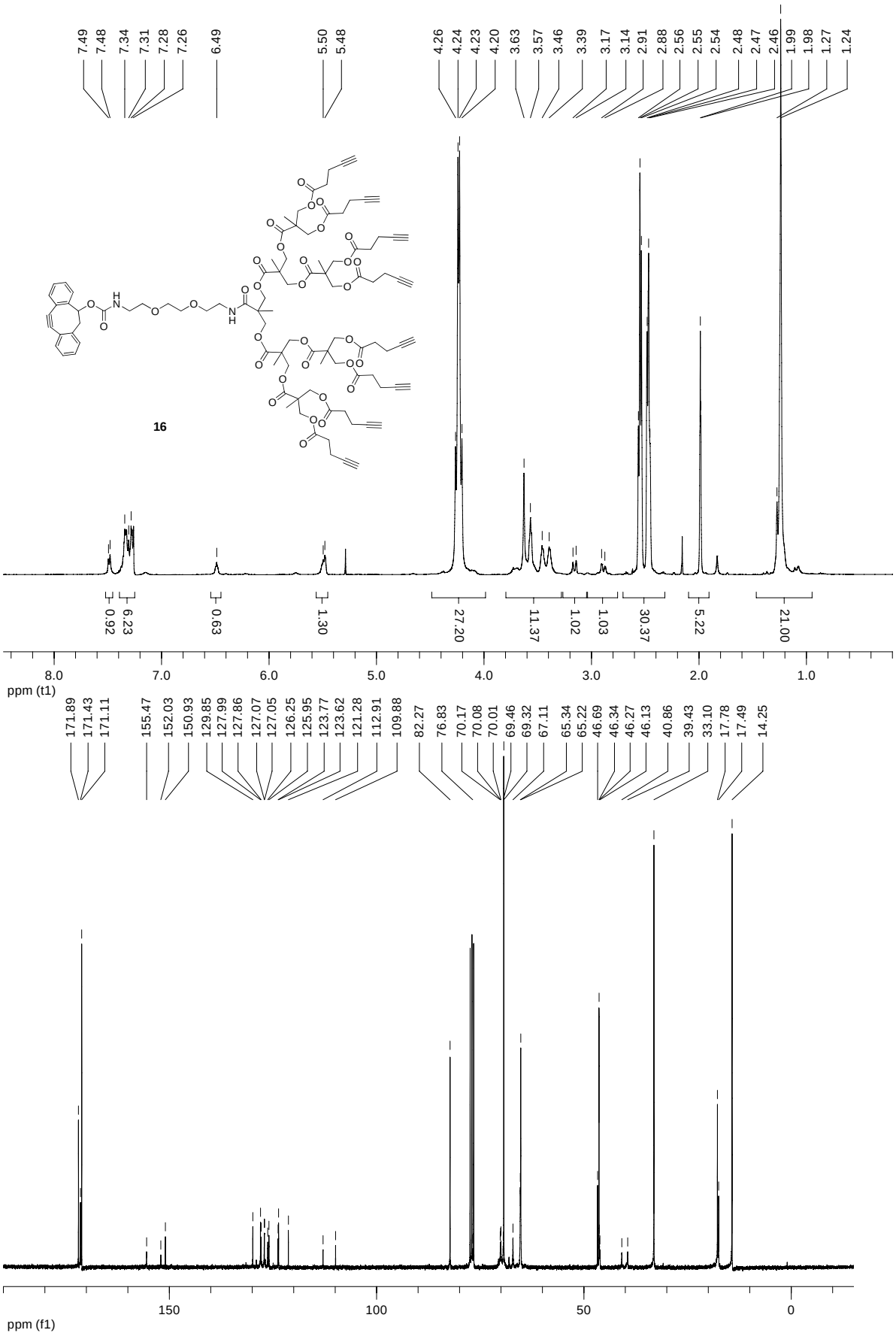
100
50
0
ppm (f1)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7.48
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7.26
6.49
5.50
5.48
4.26
4.24
4.23
4.20
3.63
3.57
3.46
3.39
3.17
3.14
2.91
2.88
2.56
2.55
2.54
2.48
2.47
2.46
1.99
1.98
1.27
1.24
16
0.92
6.23
0.63
1.30
27.20
11.37
1.02
1.03
30.37
5.22
21.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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ppm (t1)
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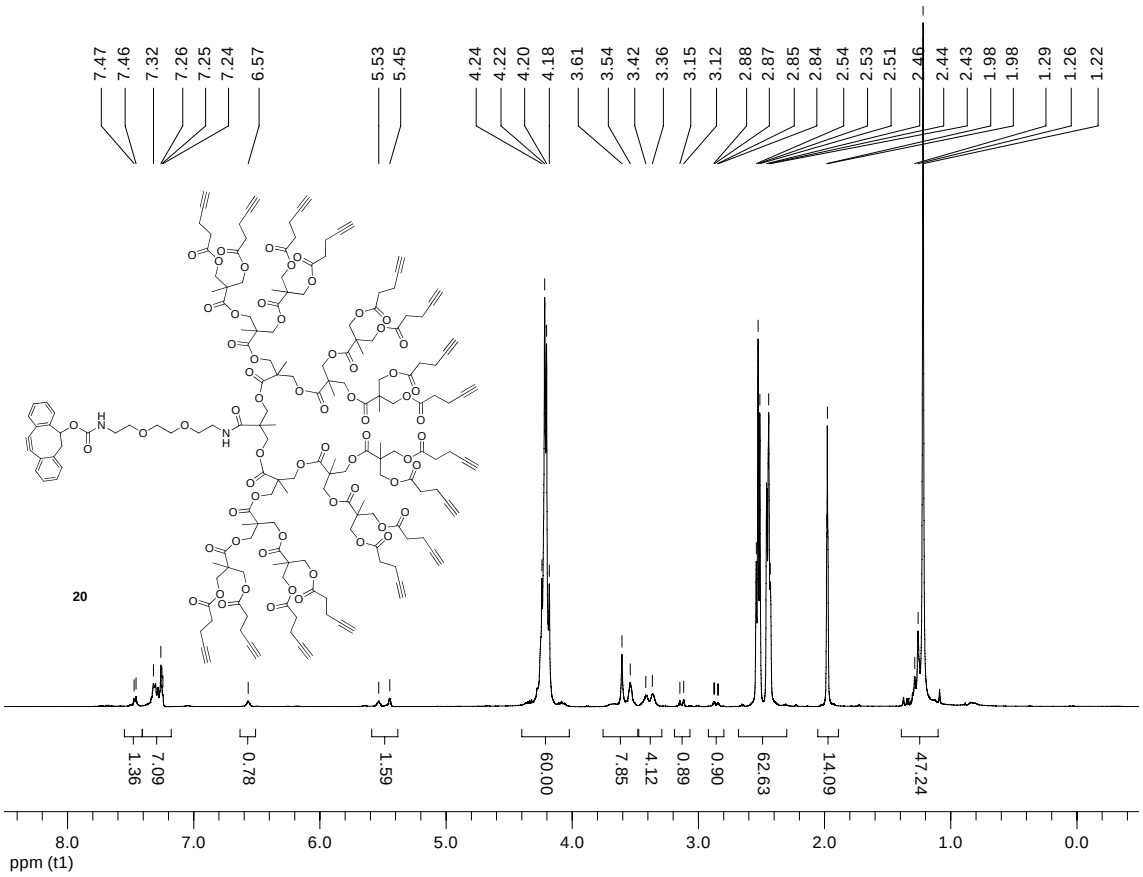
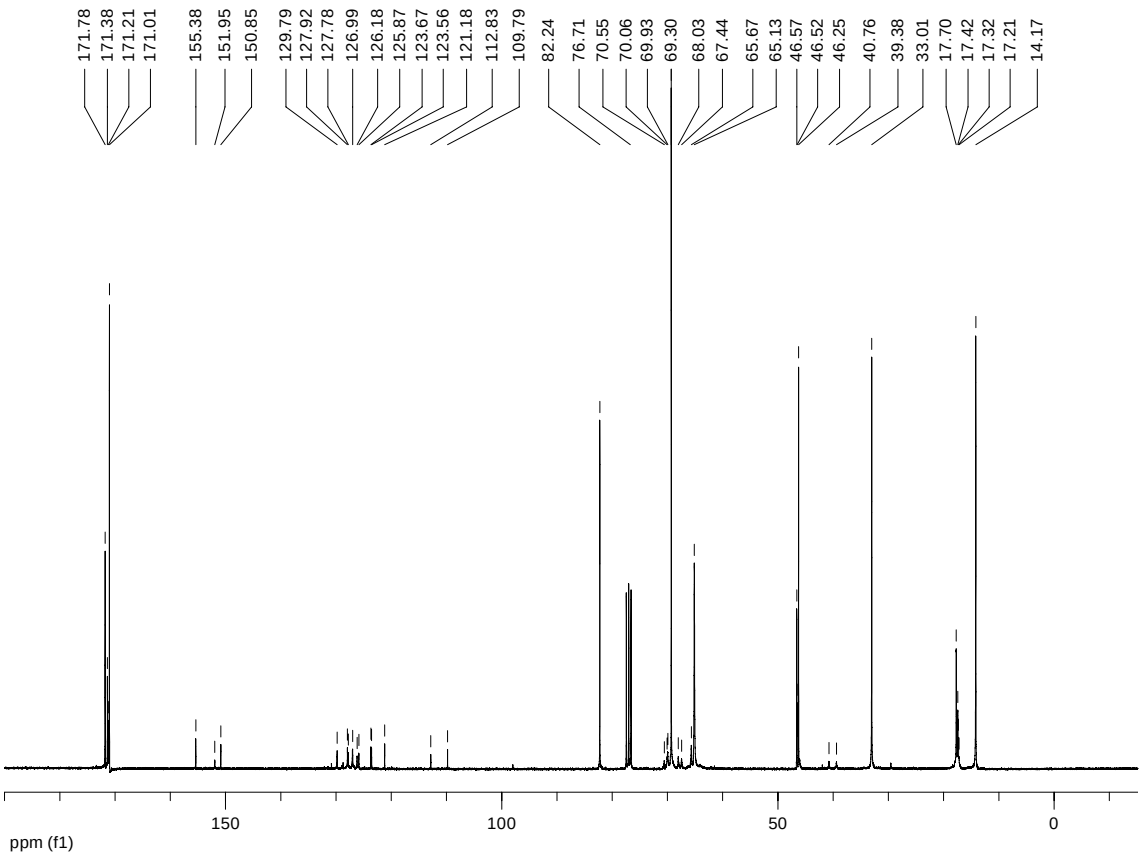
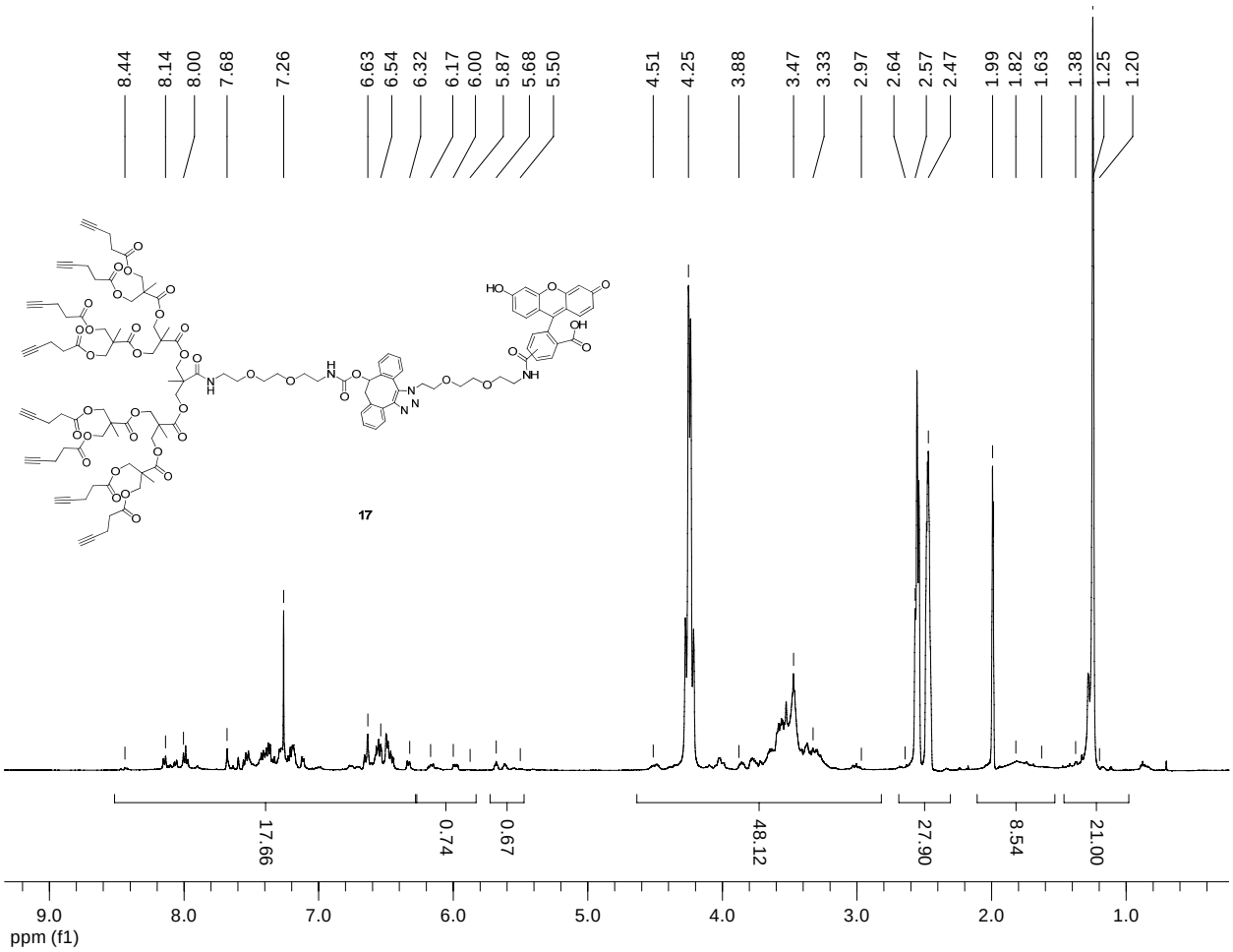
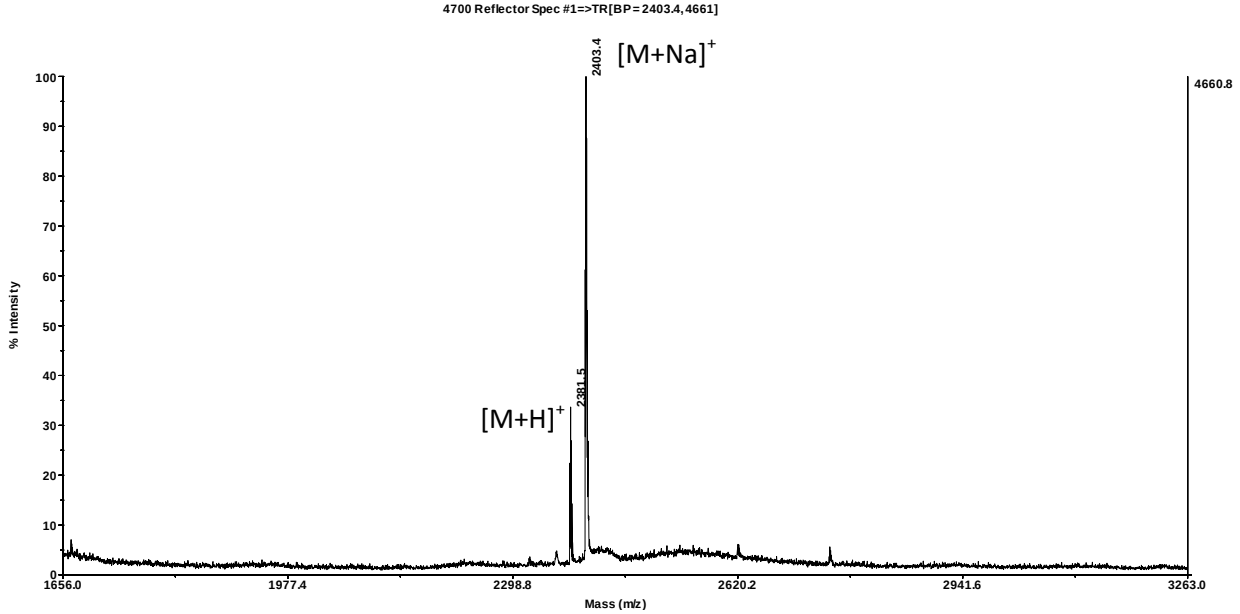
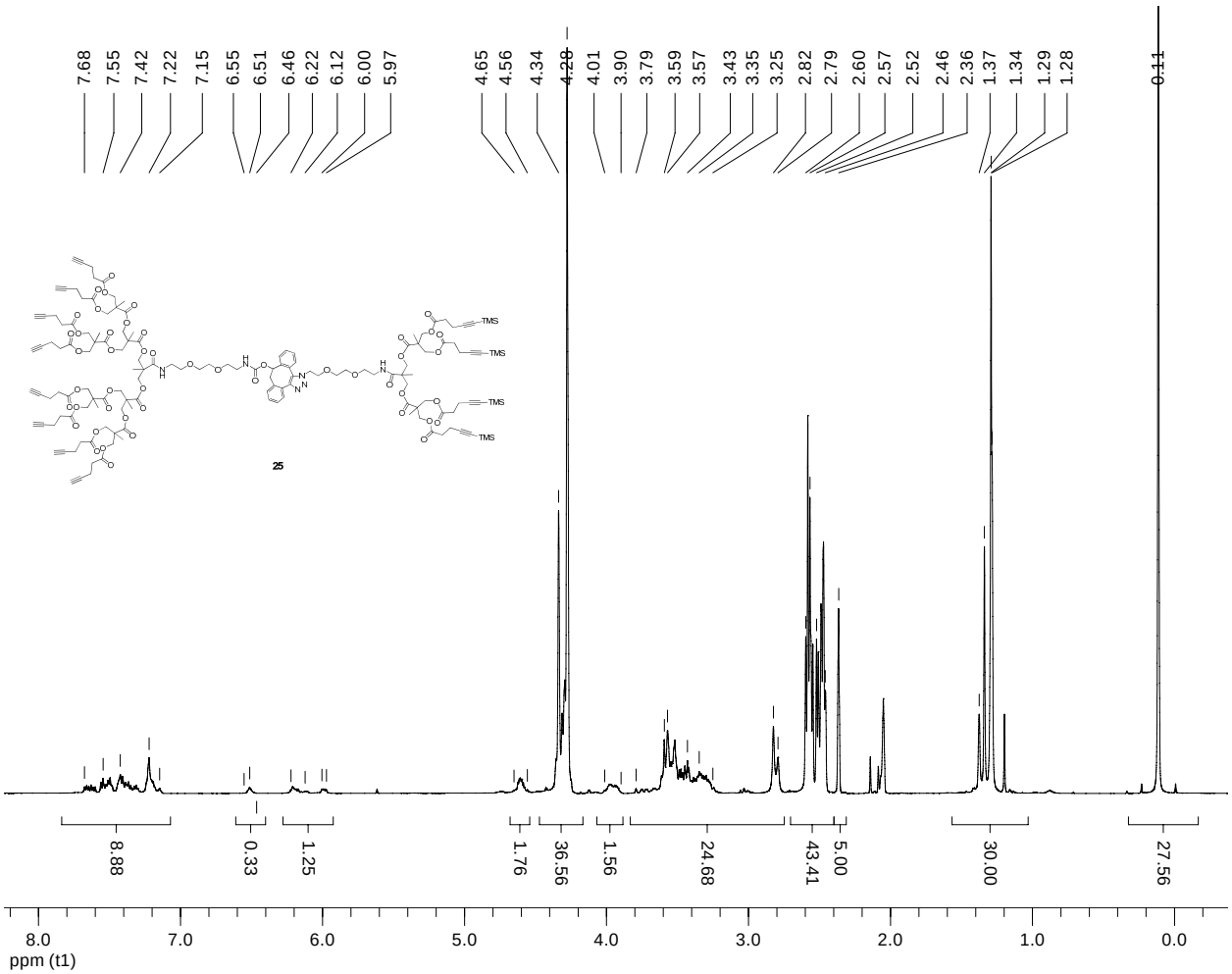
171.43
171.11
155.47
152.03
150.93
129.85
127.99
127.86
127.07
127.05
126.25
125.95
123.77
123.62
121.28
112.91
109.88
82.27
76.83
70.17
70.08
70.01
69.46
69.32
67.11
65.34
65.22
46.69
46.34
46.27
46.13
40.86
39.43
33.10
17.78
17.49
14.25
150
100
50
0
ppm (f1)

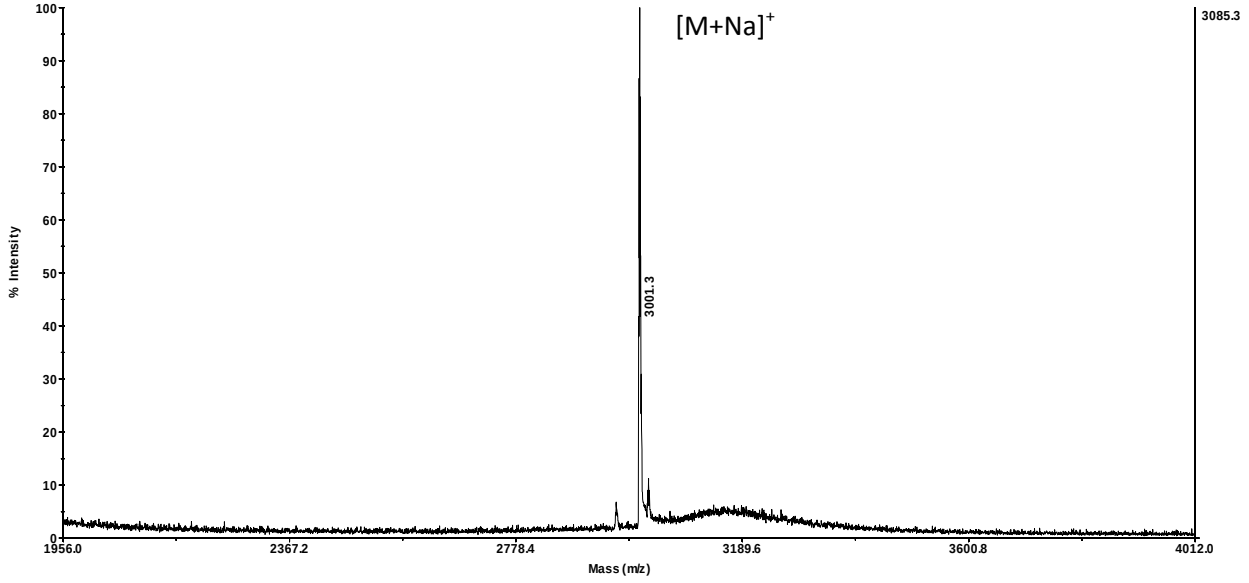

7.47
7.46
7.32
7.26
7.25
7.24
6.57
5.53
5.45
4.24
4.22
4.20
4.18
3.61
3.54
3.42
3.36
3.15
3.12
2.88
2.87
2.85
2.84
2.54
2.53
2.51
2.46
2.44
2.43
1.98
1.98
1.29
1.26
1.22
20
1.36
7.07
0.78
1.59
60.00
7.85
4.12
0.89
0.90
62.63
14.09
47.24
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

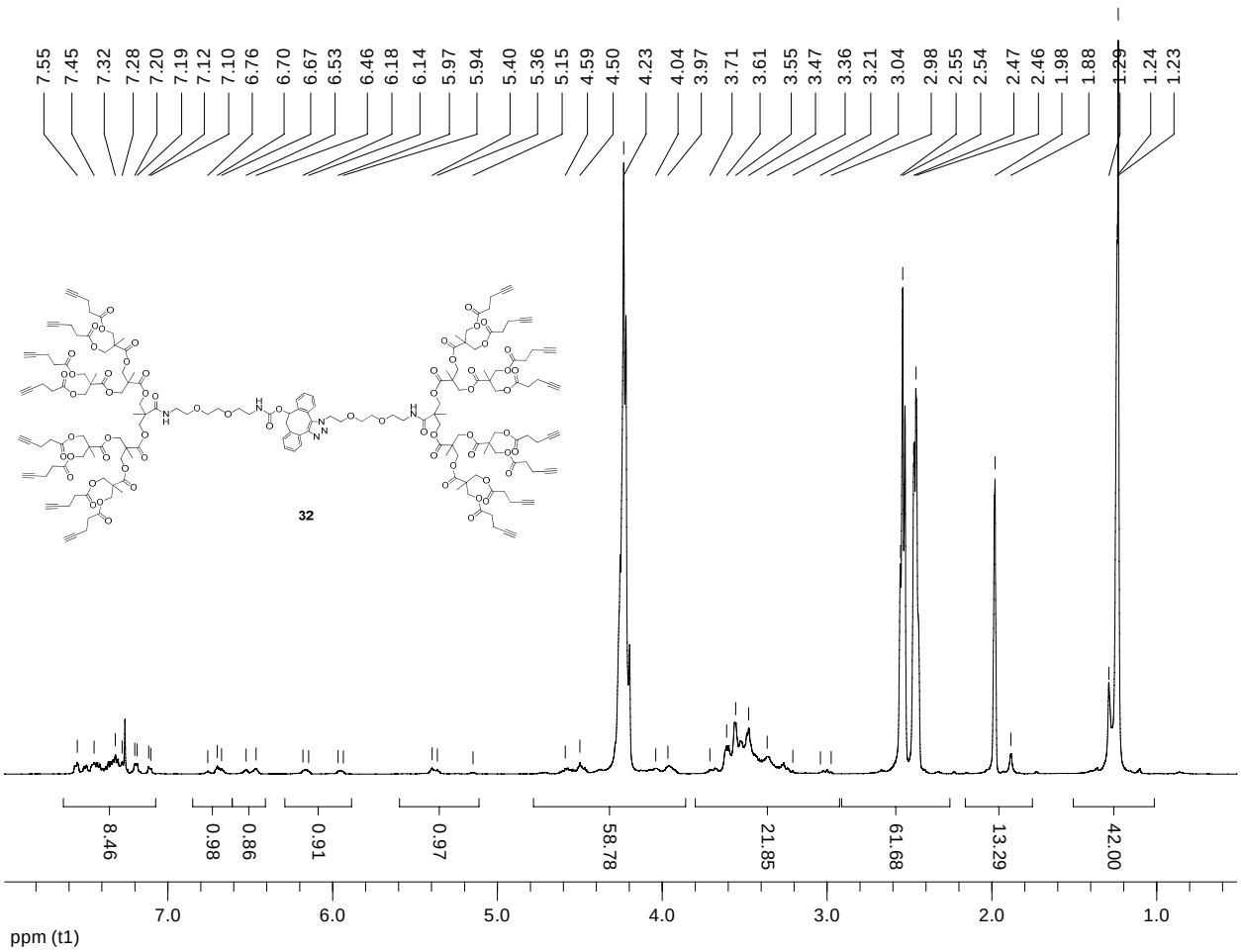

171.78
171.38
171.21
171.01
155.38
151.95
150.85
129.79
127.92
127.78
126.99
126.18
125.87
123.67
123.56
121.18
112.83
109.79
82.24
76.71
70.55
70.06
69.93
69.30
68.03
67.44
65.67
65.13
46.57
46.52
46.25
40.76
39.38
33.01
17.70
17.42
17.32
17.21
14.17
150
100
50
0
ppm (f1)

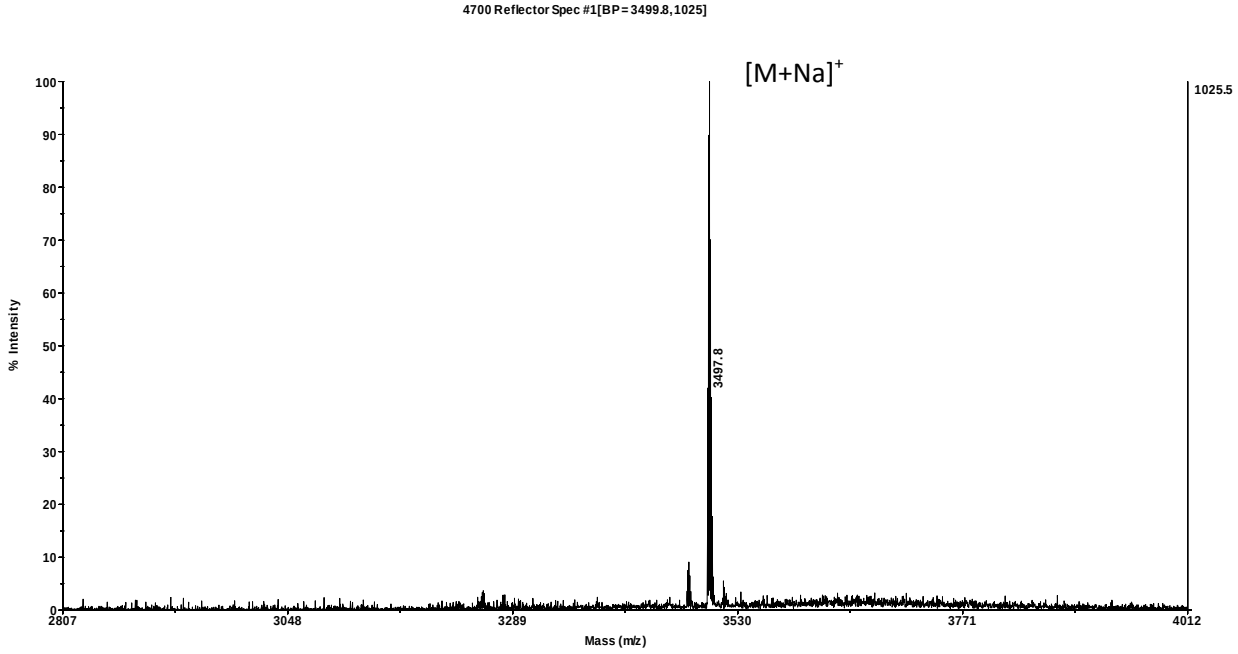

8.44
8.14
8.00
7.68
7.26
6.63
6.54
6.32
6.17
6.00
5.87
5.68
5.50
4.51
4.25
3.88
3.47
3.33
2.97
2.64
2.57
2.47
1.99
1.82
1.63
1.38
1.25
1.20
17
17.66
0.74
0.67
48.12
27.90
8.54
21.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

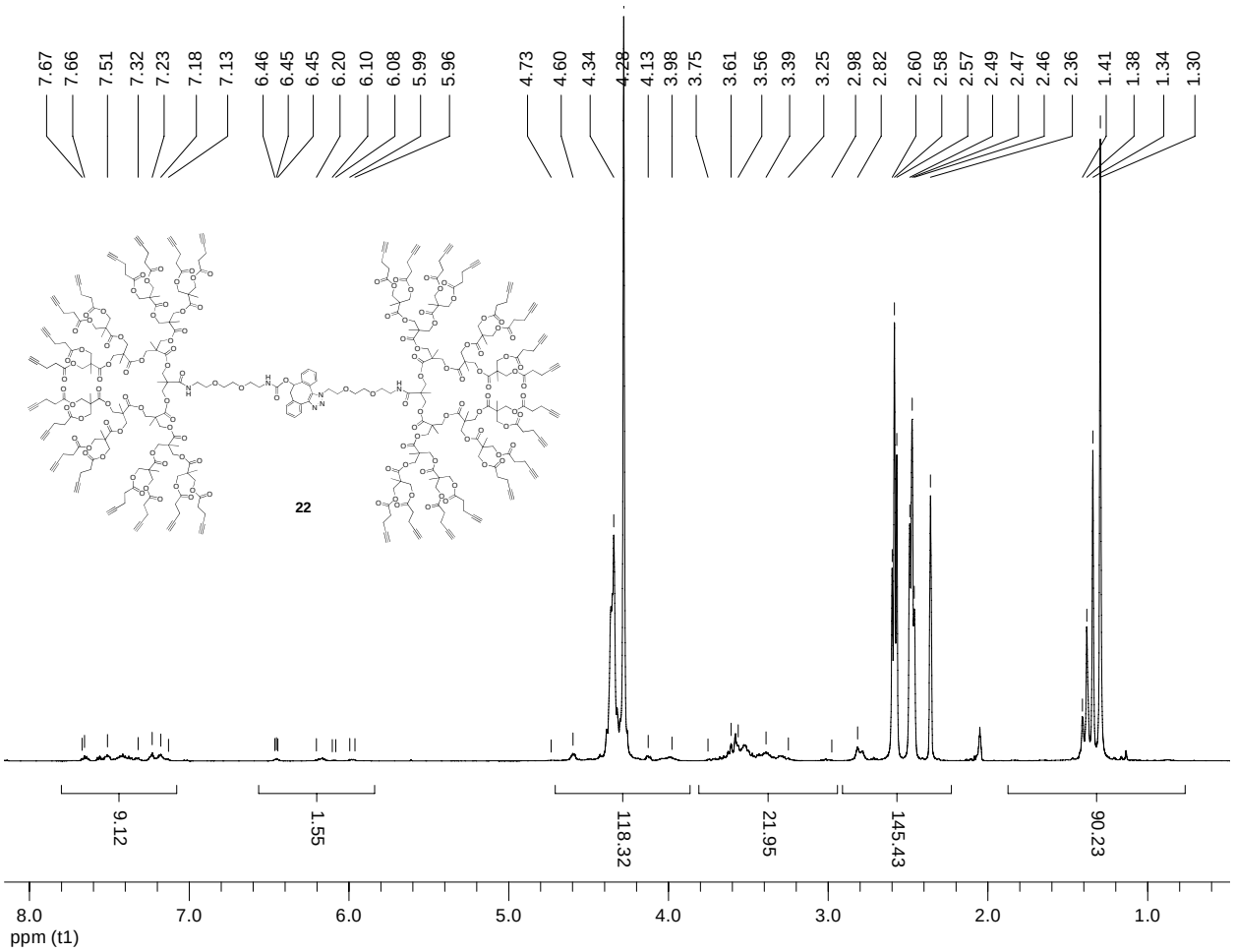

4700 Reflector Spec #1=>TR[BP = 2403.4, 4661]
[M+Na]+
[M+H]+
2403.4
2381.5
4660.8
% Intensity
Mass (m/z)
1656.0
1977.4
2298.8
2620.2
2941.6
3263.0

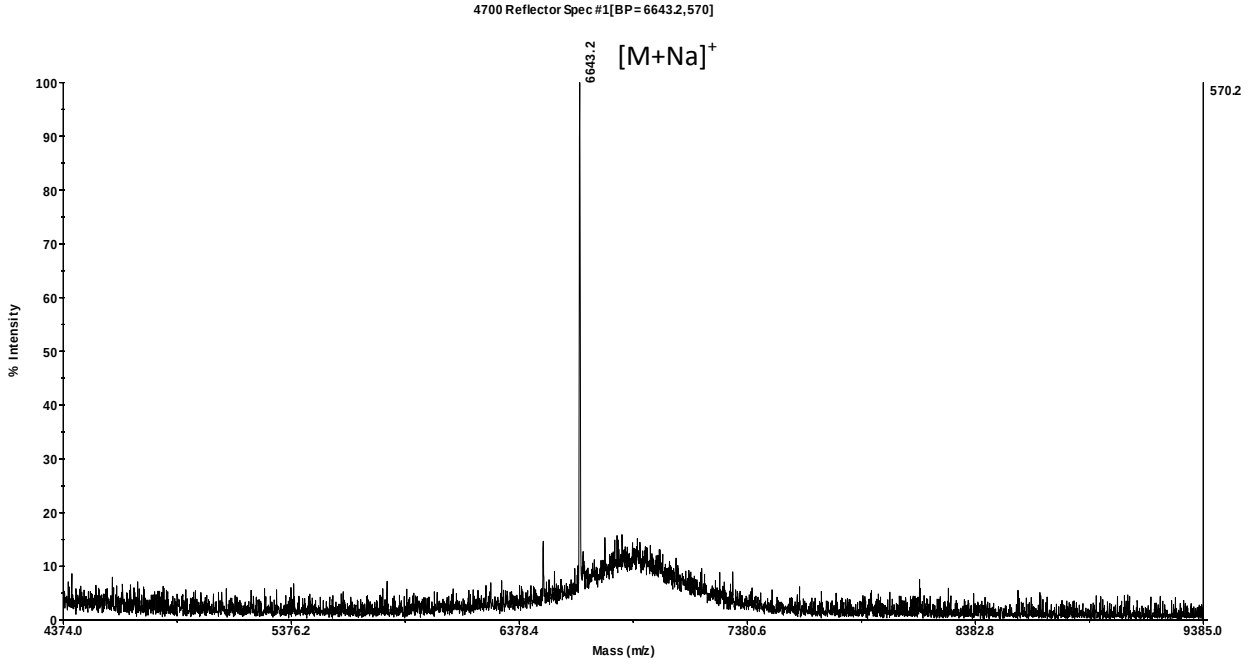

7.68
7.55
7.42
7.22
7.15
6.55
6.51
6.46
6.22
6.12
6.00
5.97
4.65
4.56
4.34
4.28
4.01
3.90
3.79
3.59
3.57
3.43
3.35
3.25
2.82
2.79
2.60
2.57
2.52
2.46
2.36
1.37
1.34
1.29
1.28
0.11
TMS
25
8.88
0.33
1.25
1.76
36.56
1.56
24.68
43.41
5.00
30.00
27.56
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

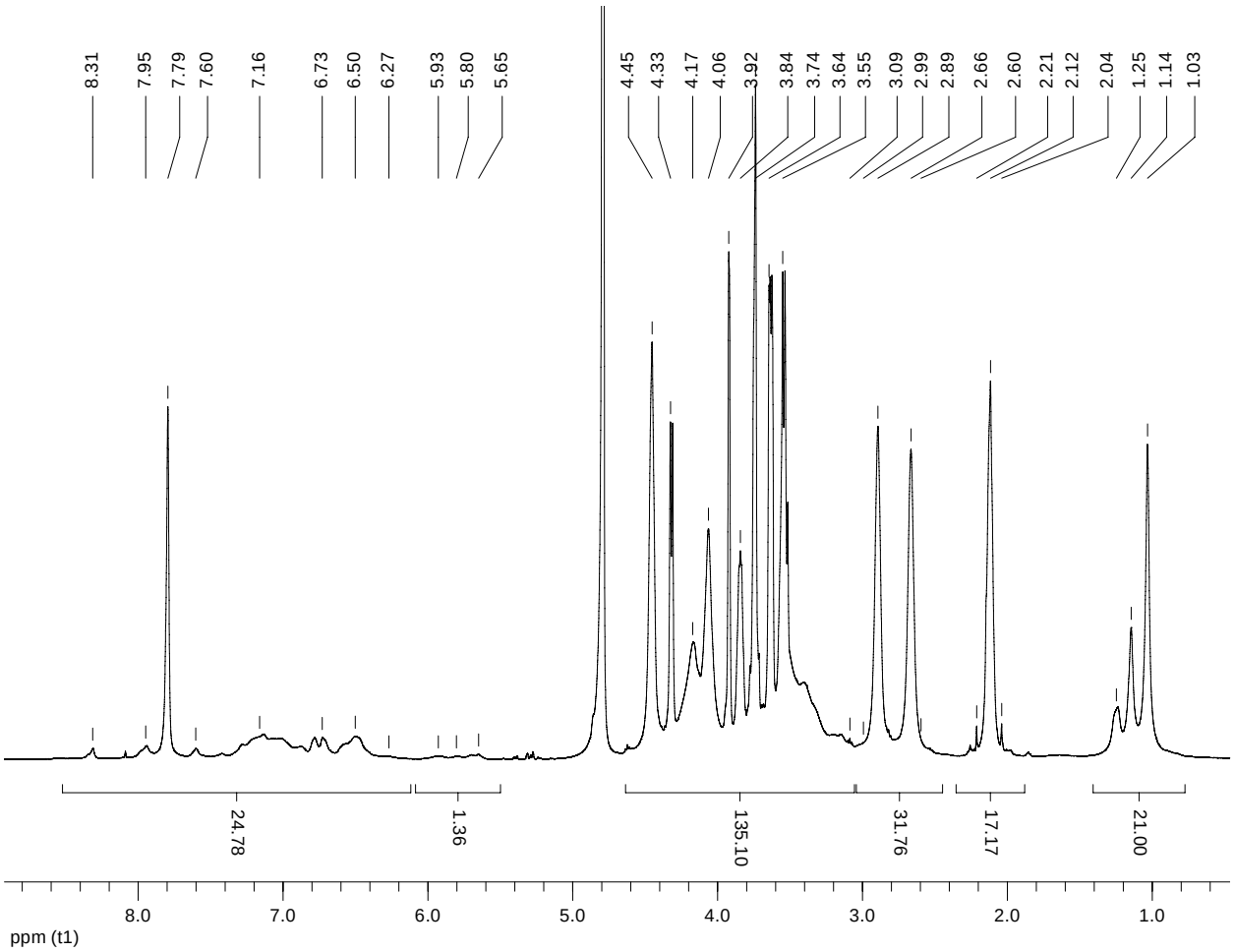

4700 Reflector Spec #1[BP = 3003.2, 3085]
[M+Na]+
3085.3
3001.3
% Intensity
Mass (m/z)
1956.0
2367.2
2778.4
3189.6
3600.8
4012.0

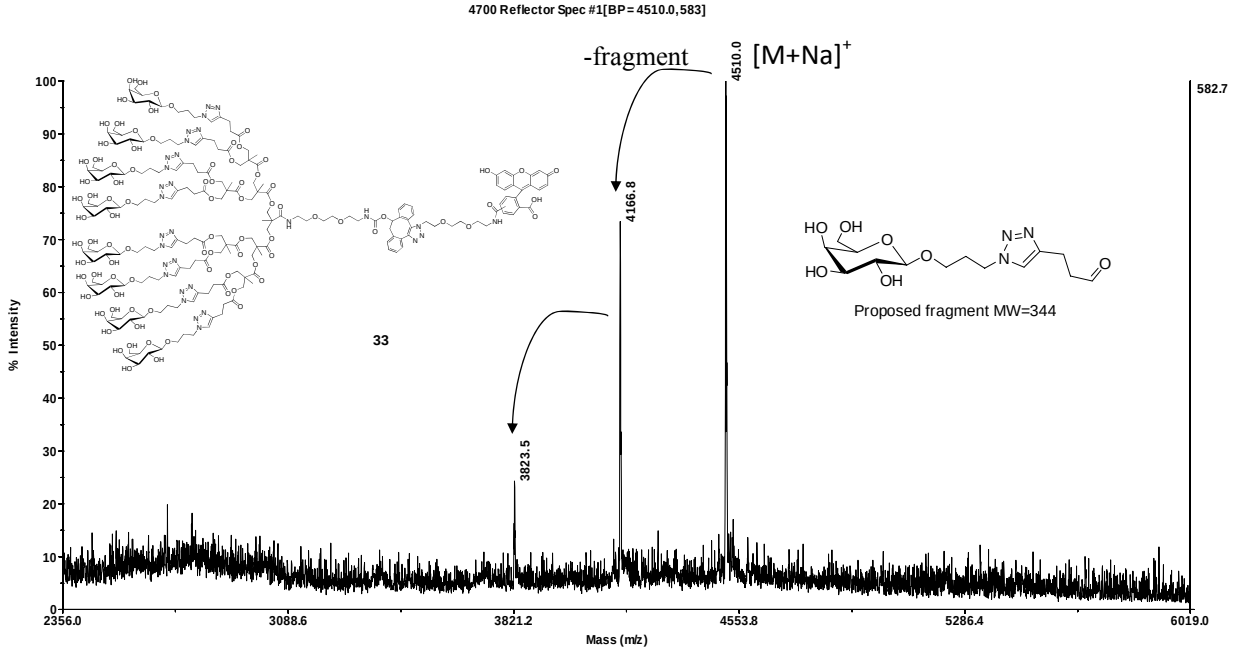

7.55
7.45
7.32
7.28
7.20
7.19
7.12
7.10
6.76
6.70
6.67
6.53
6.46
6.18
6.14
5.97
5.94
5.40
5.36
5.15
4.59
4.50
4.23
4.04
3.97
3.71
3.61
3.55
3.47
3.36
3.21
3.04
2.98
2.55
2.54
2.47
2.46
1.98
1.88
1.29
1.24
1.23
32
8.46
0.98
0.86
0.91
0.97
58.78
21.85
61.68
13.29
42.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

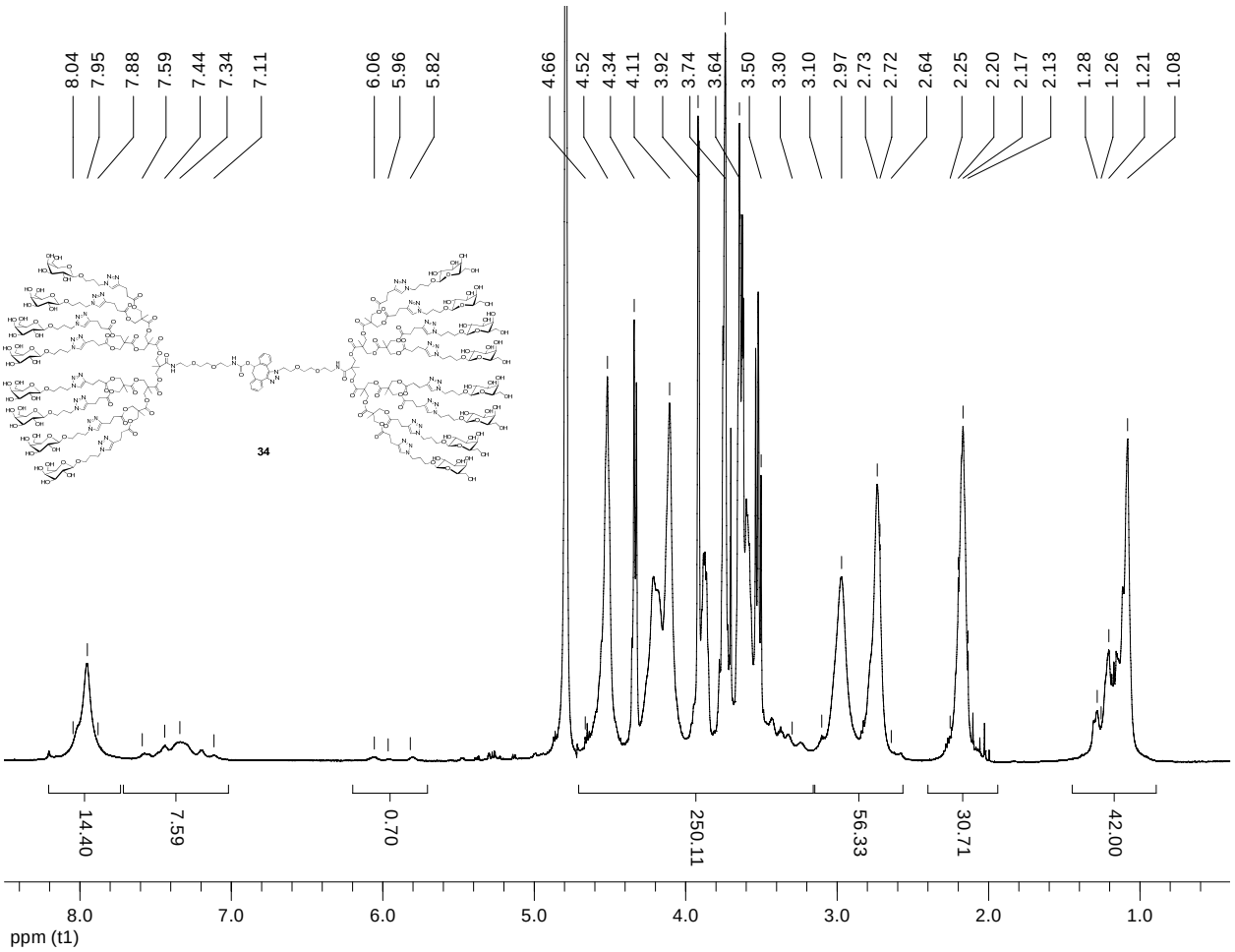

4700 Reflector Spec #1[BP = 3499.8, 1025]
[M+Na]+
1025.5
3497.8
% Intensity
Mass (m/z)
2807
3048
3289
3530
3771
4012

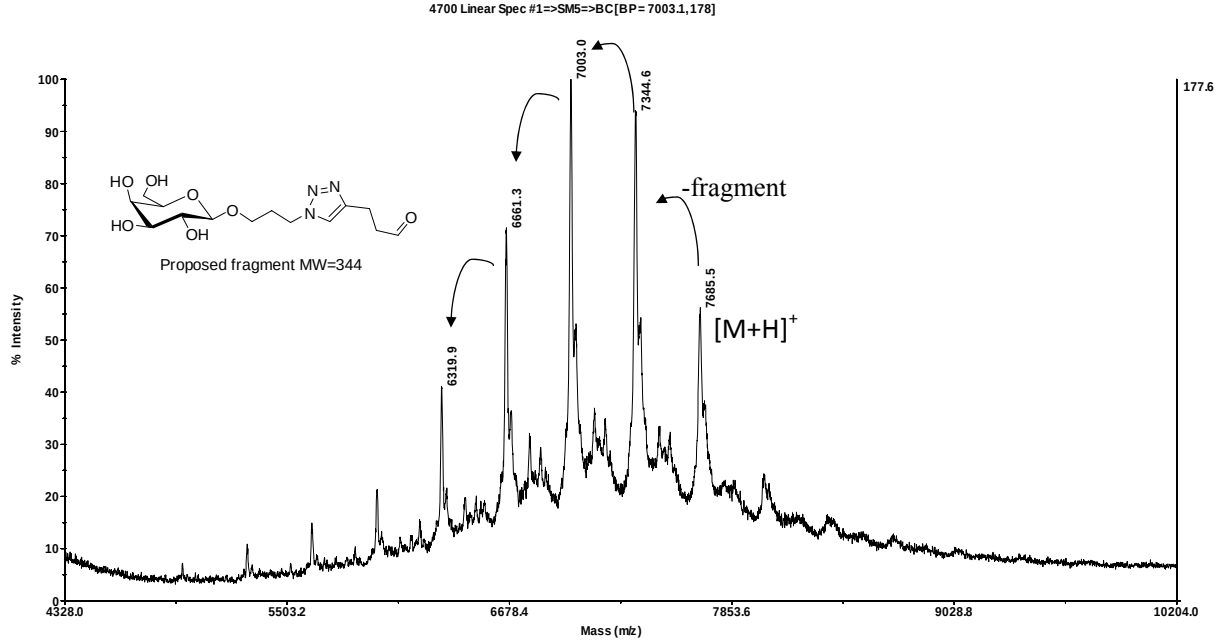

7.67
7.66
7.51
7.32
7.23
7.18
7.13
6.46
6.45
6.45
6.20
6.10
6.08
5.99
5.96
4.73
4.60
4.34
4.28
4.13
3.98
3.75
3.61
3.56
3.39
3.25
2.98
2.82
2.60
2.58
2.57
2.49
2.47
2.46
2.36
1.41
1.38
1.34
1.30
22
9.12
1.55
118.32
21.95
145.43
90.23
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

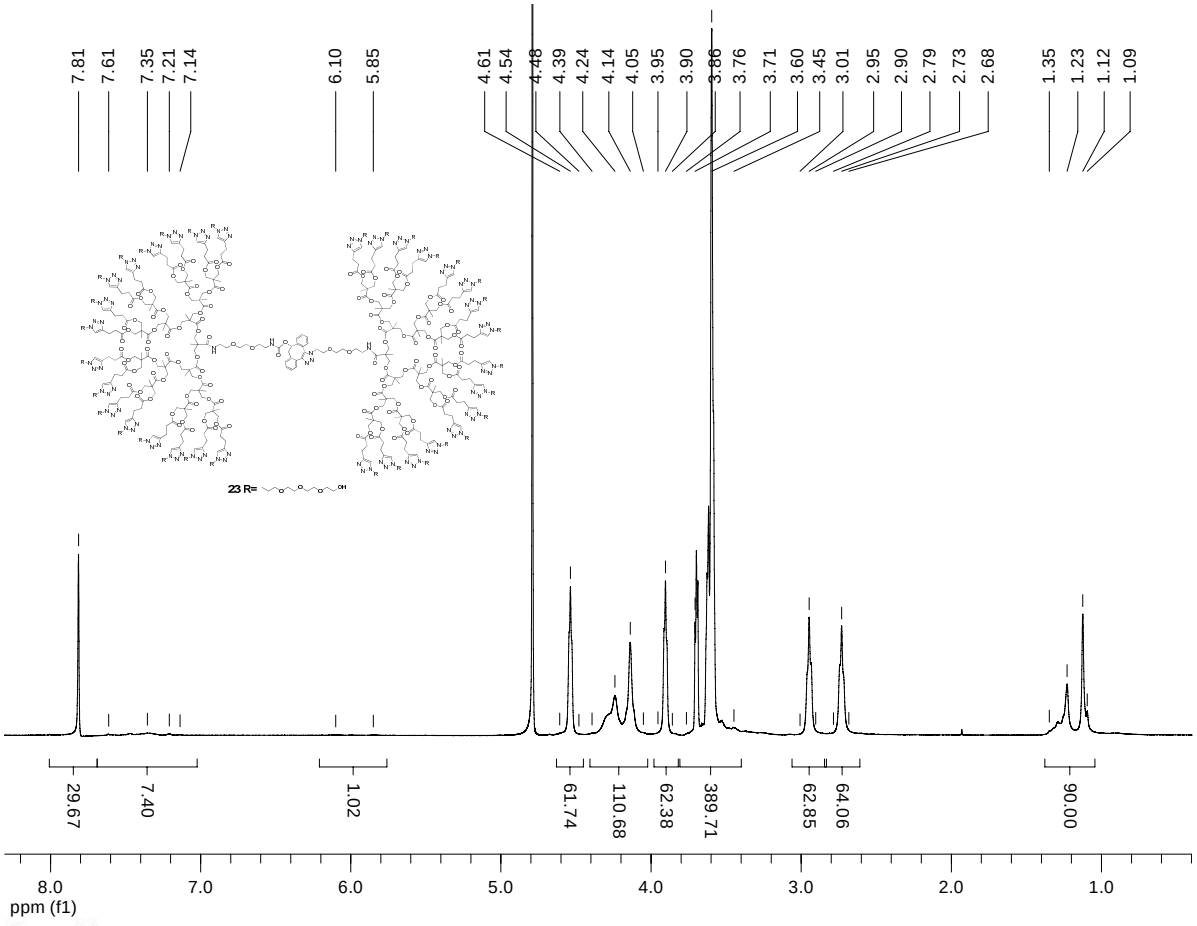

4700 Reflector Spec #1[BP = 6643.2, 570]
6643.2
[M+Na]+
570.2
% Intensity
100
90
80
70
60
50
40
30
20
10
0
4374.0
5376.2
6378.4
7380.6
8382.8
9385.0
Mass (m/z)

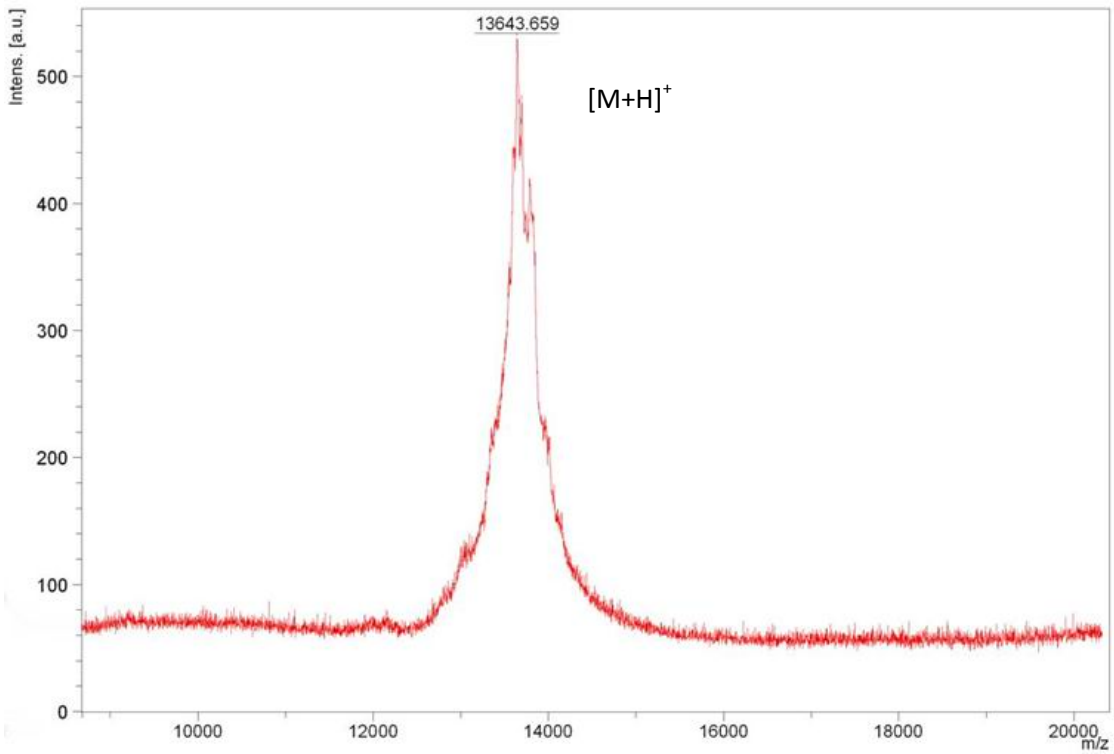

8.31
7.95
7.79
7.60
7.16
6.73
6.50
6.27
5.93
5.80
5.65
4.45
4.33
4.17
4.06
3.92
3.84
3.74
3.64
3.55
3.09
2.99
2.89
2.66
2.60
2.21
2.12
2.04
1.25
1.14
1.03
24.78
1.36
135.10
31.76
17.17
21.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

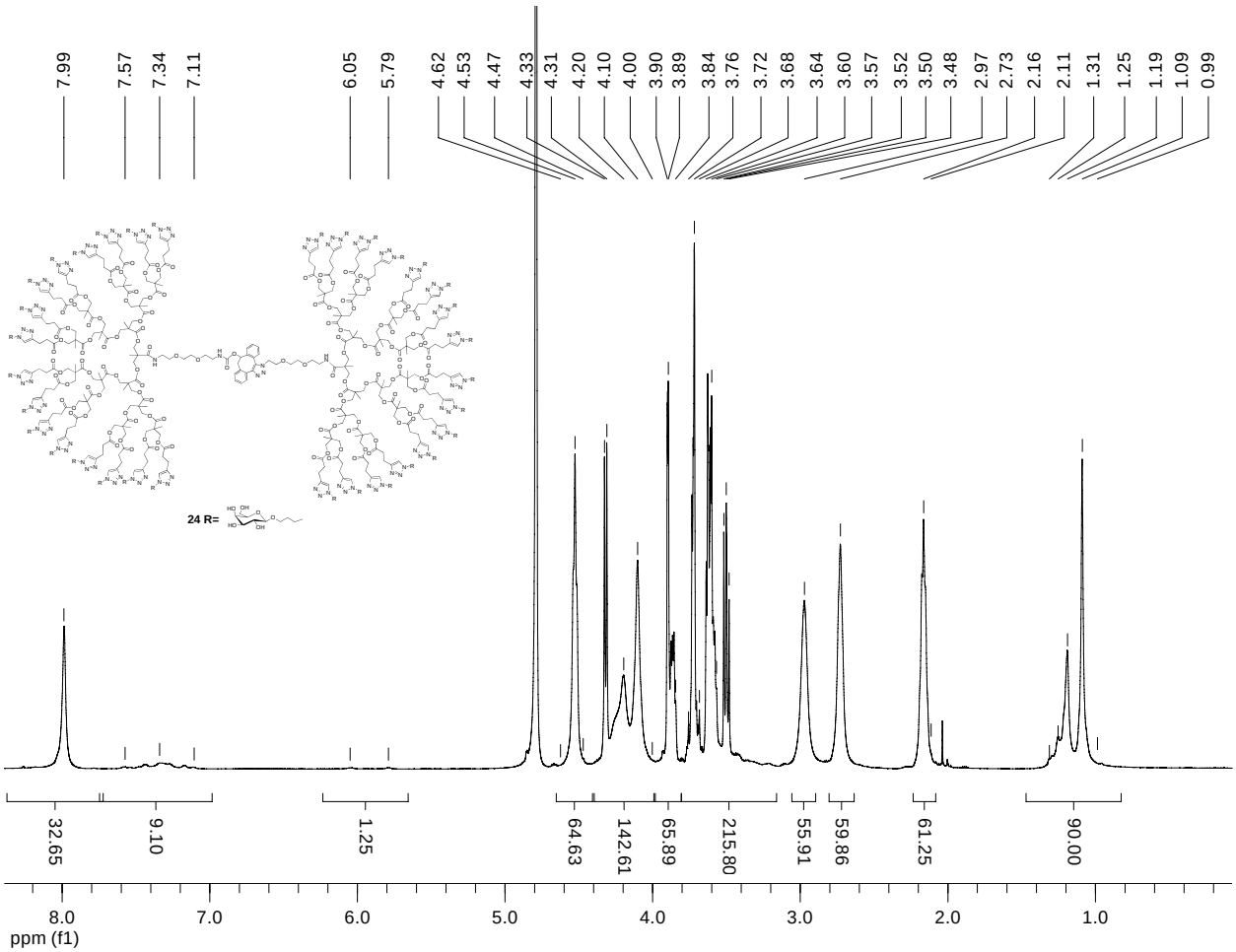

4700 Reflector Spec #1[BP = 4510.0, 583]
-fragment
[M+Na]+
4510.0
4166.8
3823.5
582.7
33
Proposed fragment MW=344
% Intensity
Mass (m/z)
2356.0
3088.6
3821.2
4553.8
5286.4
6019.0

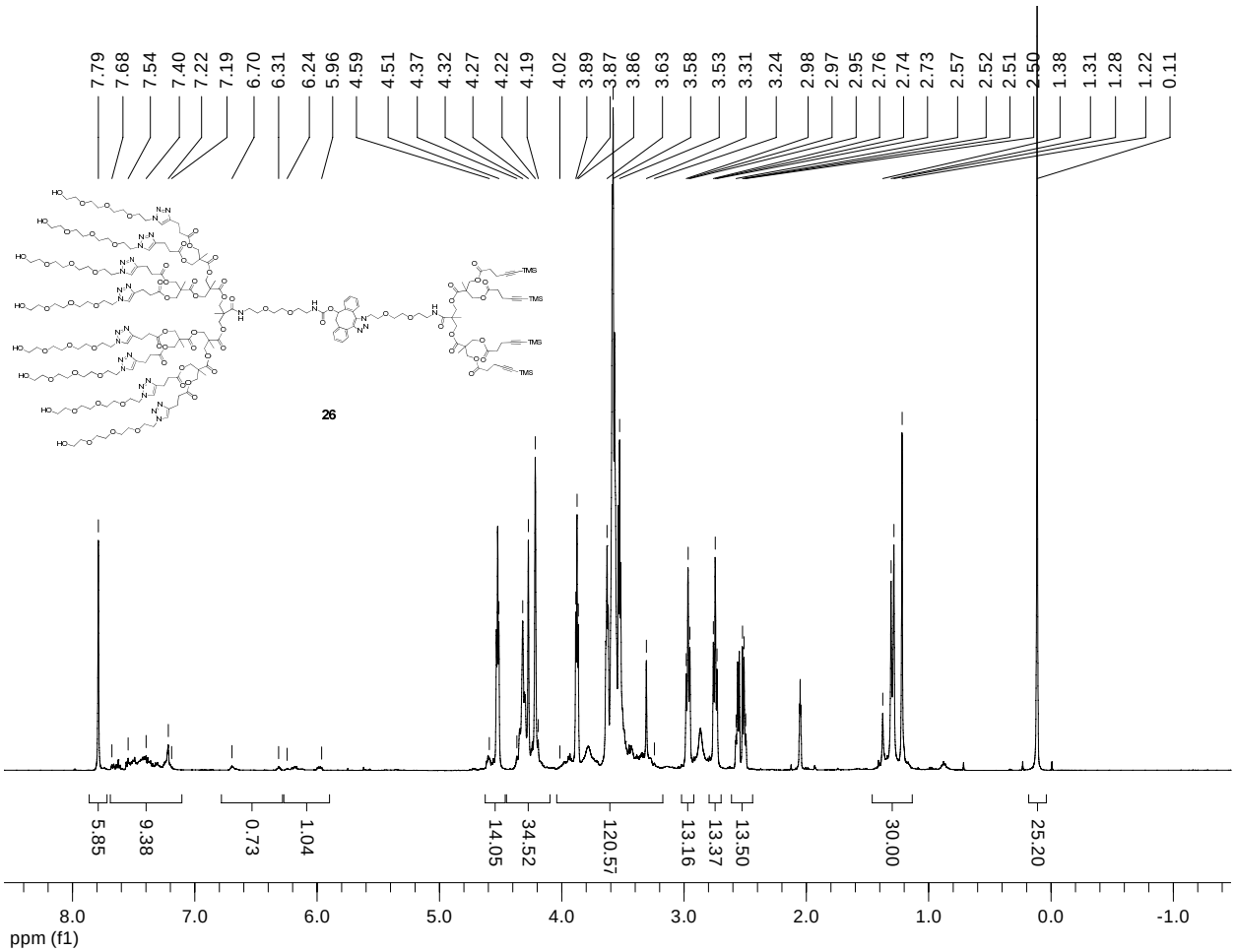

8.04
7.95
7.88
7.59
7.44
7.34
7.11
6.06
5.96
5.82
4.66
4.52
4.34
4.11
3.92
3.74
3.64
3.50
3.30
3.10
2.97
2.73
2.72
2.64
2.25
2.20
2.17
2.13
1.28
1.26
1.21
1.08
34
14.40
7.59
0.70
250.11
56.33
30.71
42.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

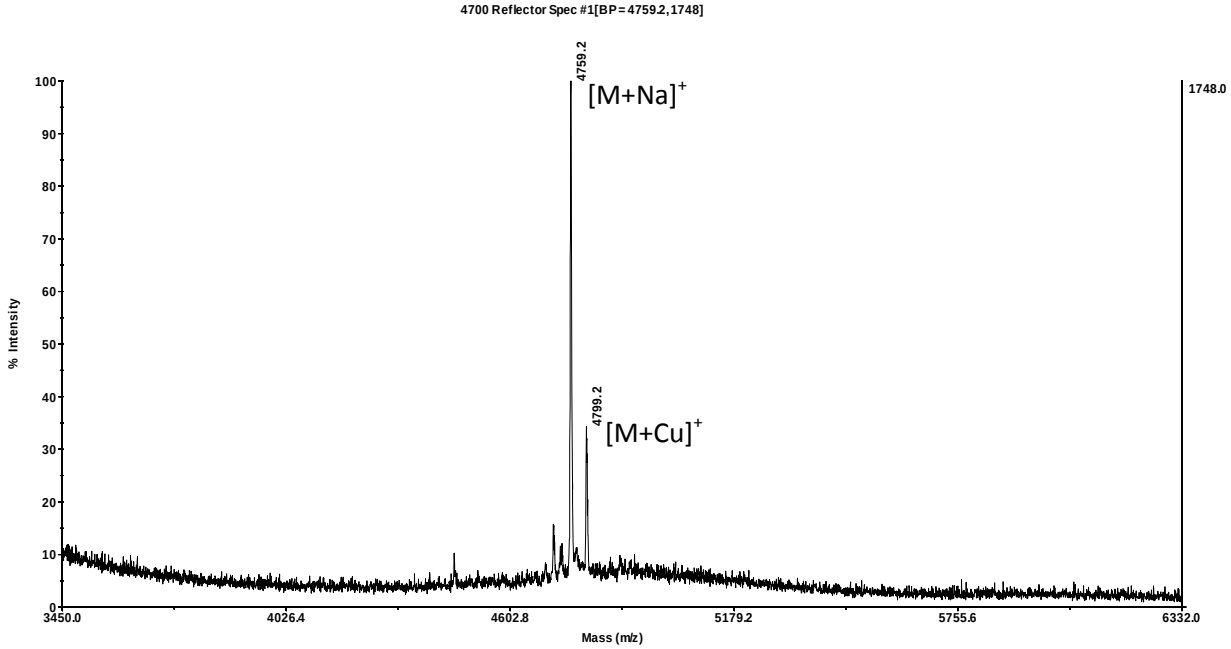

4700 Linear Spec #1=>SM5=>BC[BP = 7003.1,178]
7003.0
7344.6
6661.3
7685.5
6319.9
177.6
-fragment
[M+H]+
Proposed fragment MW=344
% Intensity
Mass (m/z)
4328.0
5503.2
6678.4
7853.6
9028.8
10204.0

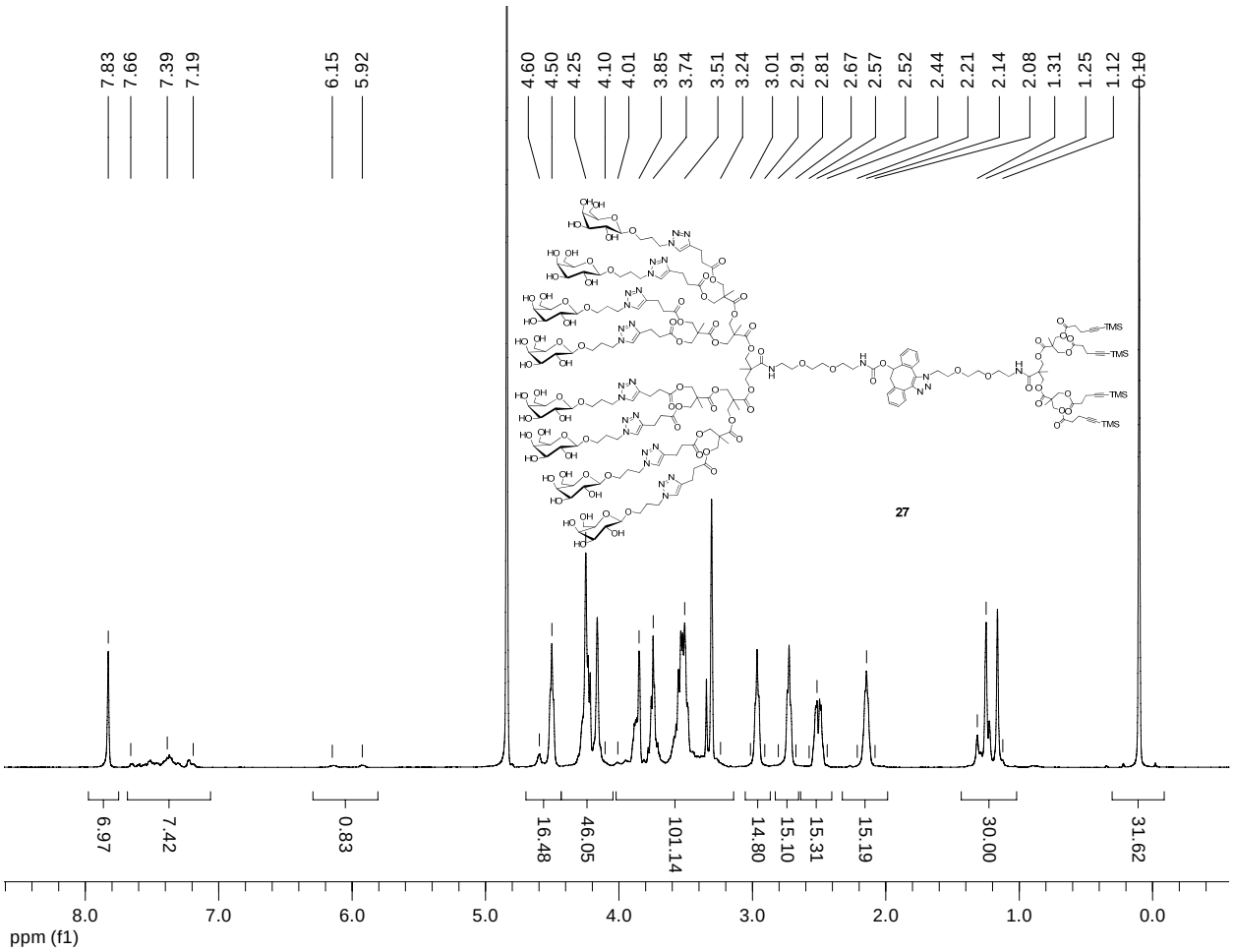

7.81
7.61
7.35
7.21
7.14
6.10
5.85
4.61
4.54
4.48
4.39
4.24
4.14
4.05
3.95
3.90
3.86
3.76
3.71
3.60
3.45
3.01
2.95
2.90
2.79
2.73
2.68
1.35
1.23
1.12
1.09
23 R=
29.67
7.40
1.02
61.74
110.68
62.38
389.71
62.85
64.06
90.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
Comment 1
Comment 2

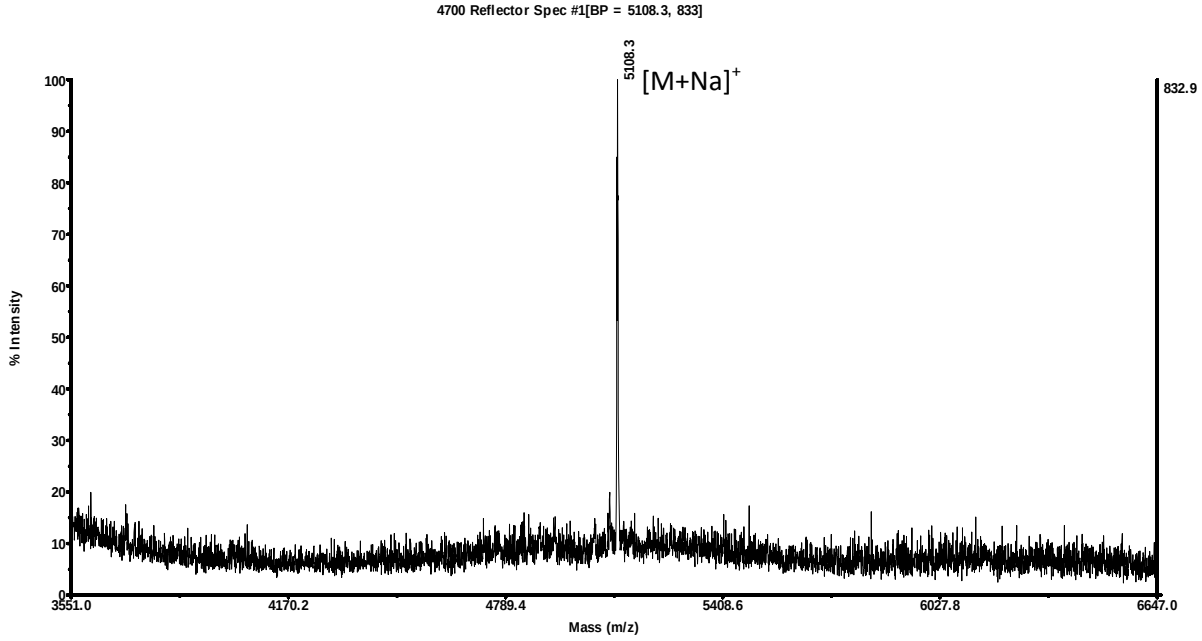

13643.659
[M+H]+
Intens. [a.u.]
500
400
300
200
100
0
10000
12000
14000
16000
18000
20000
m/z

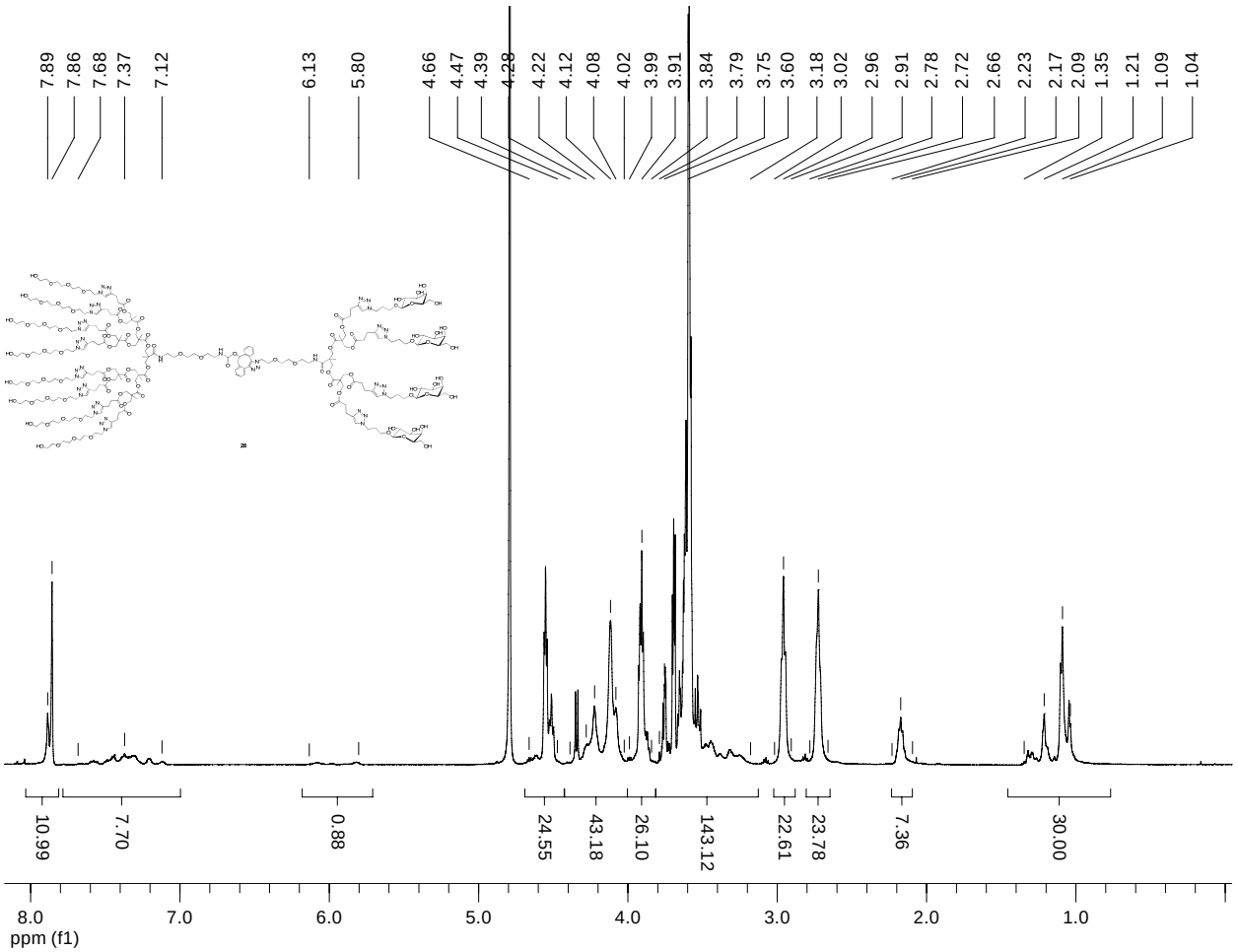

7.99
7.57
7.34
7.11
6.05
5.79
4.62
4.53
4.47
4.33
4.31
4.20
4.10
4.00
3.90
3.89
3.84
3.76
3.72
3.68
3.64
3.60
3.57
3.52
3.50
3.48
2.97
2.73
2.16
2.11
1.31
1.25
1.19
1.09
0.99
24 R=
32.65
9.10
1.25
64.63
142.61
65.89
215.80
55.91
59.86
61.25
90.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

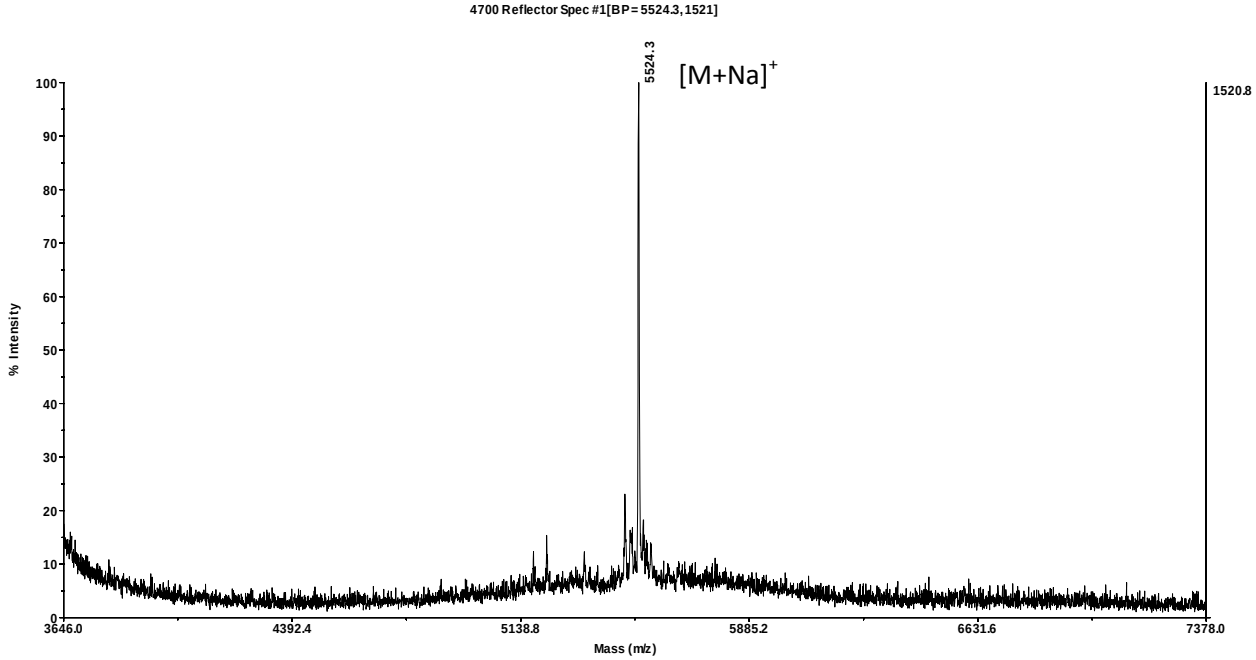

7.79
7.68
7.54
7.40
7.22
7.19
6.70
6.31
6.24
5.96
4.59
4.51
4.37
4.32
4.27
4.22
4.19
4.02
3.89
3.87
3.86
3.63
3.58
3.53
3.31
3.24
2.98
2.97
2.95
2.76
2.74
2.73
2.57
2.52
2.51
2.50
1.38
1.31
1.28
1.22
0.11
26
5.85
9.38
0.73
1.04
14.05
34.52
120.57
13.16
13.37
13.50
30.00
25.20
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

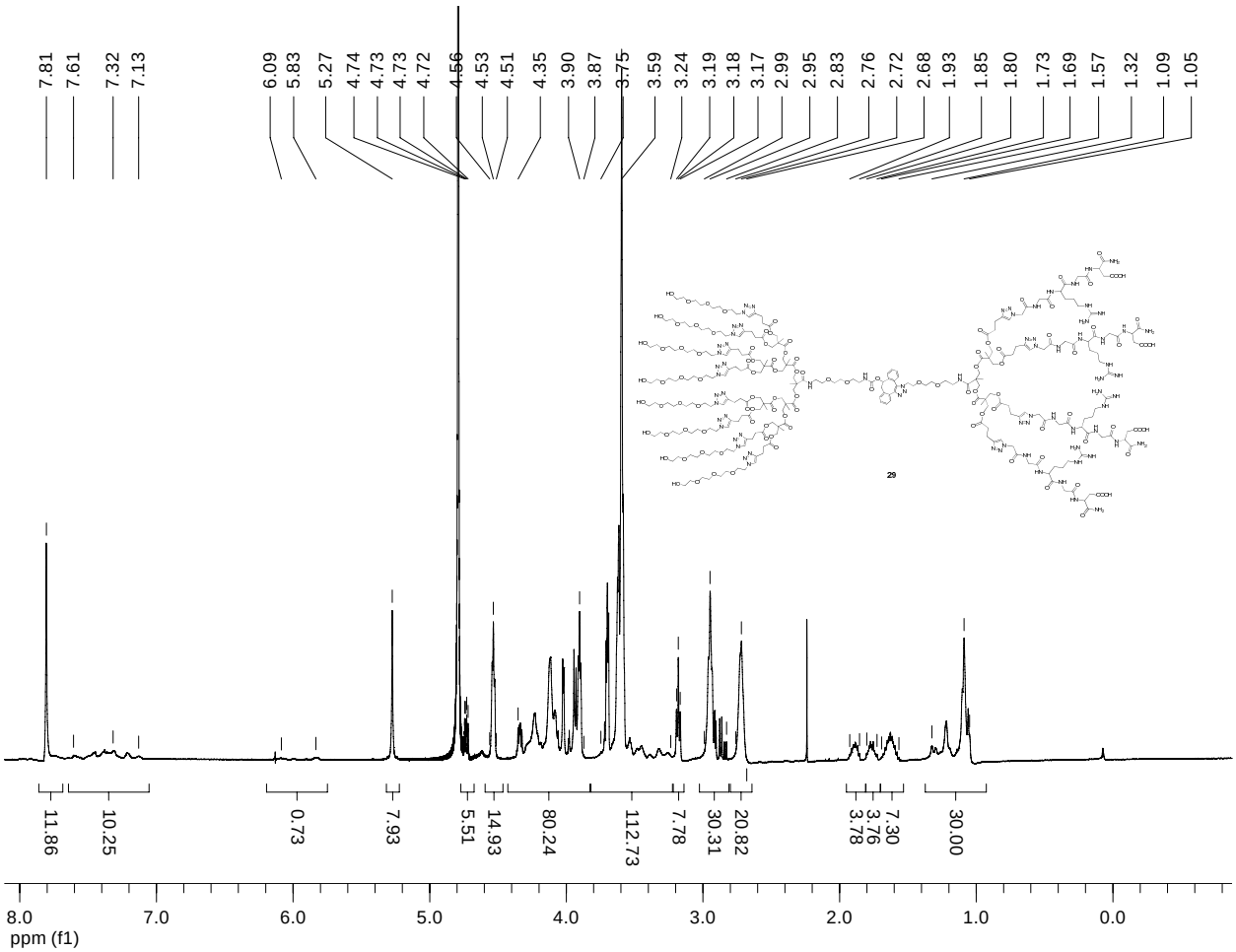

4700 Reflector Spec #1[BP = 4759.2, 1748]
4759.2
[M+Na]+
1748.0
4799.2
[M+Cu]+
% Intensity
Mass (m/z)
3450.0
4026.4
4602.8
5179.2
5755.6
6332.0

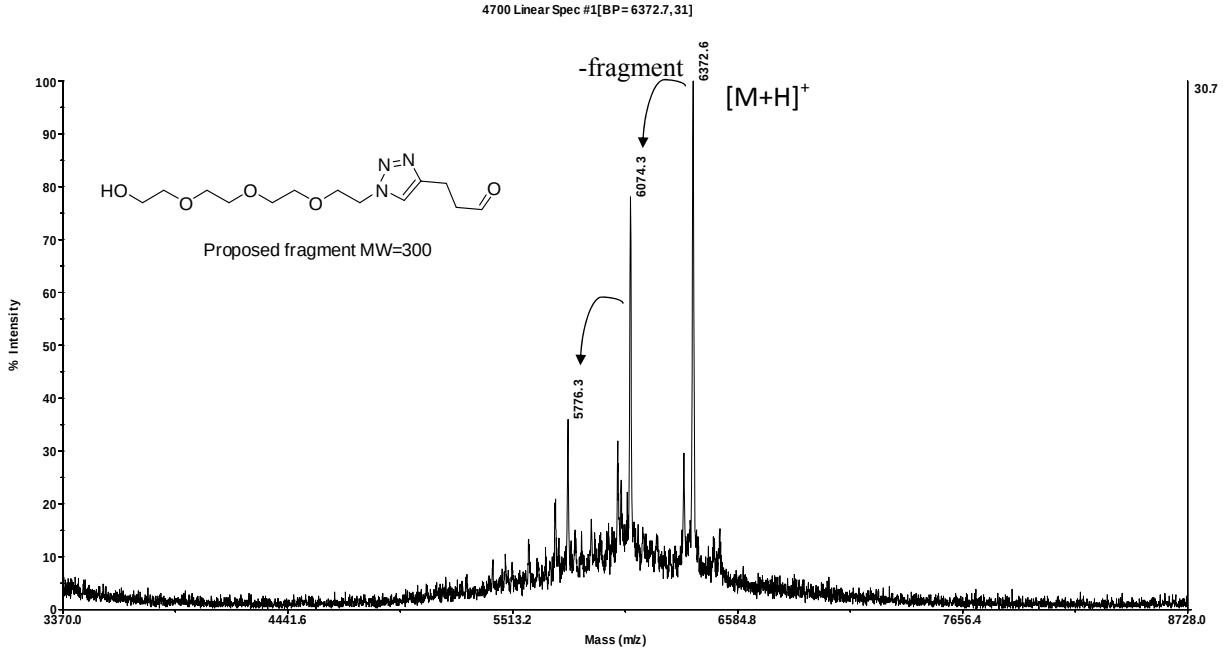

7.83
7.66
7.39
7.19
6.15
5.92
4.60
4.50
4.25
4.10
4.01
3.85
3.74
3.51
3.24
3.01
2.91
2.81
2.67
2.57
2.52
2.44
2.21
2.14
2.08
1.31
1.25
1.12
0.10
27
6.97
7.42
0.83
16.48
46.05
101.14
14.80
15.10
15.31
15.19
30.00
31.62
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

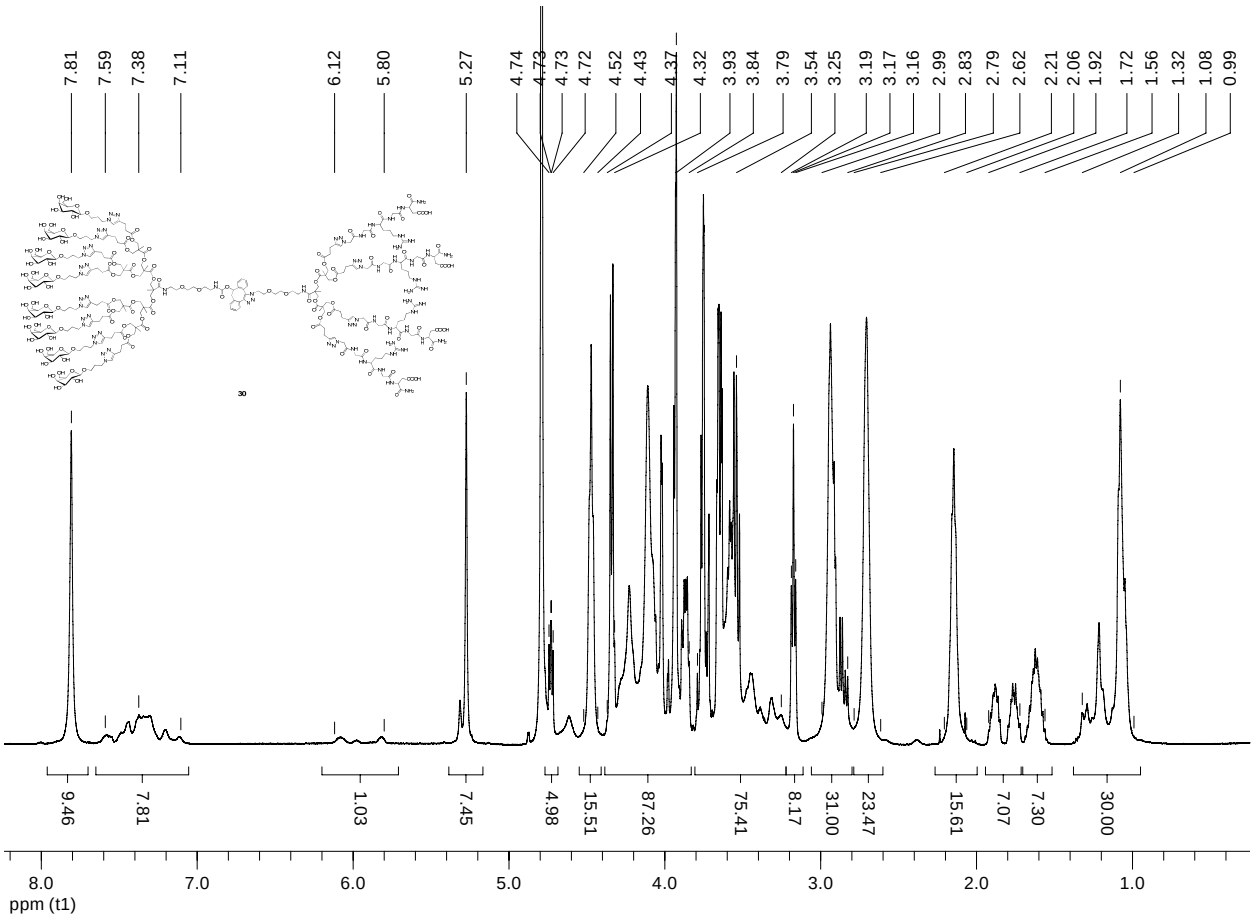

4700 Reflector Spec #1[BP = 5108.3, 833]
5108.3
[M+Na]+
832.9
% Intensity
100
90
80
70
60
50
40
30
20
10
0
3551.0
4170.2
4789.4
5408.6
6027.8
6647.0
Mass (m/z)

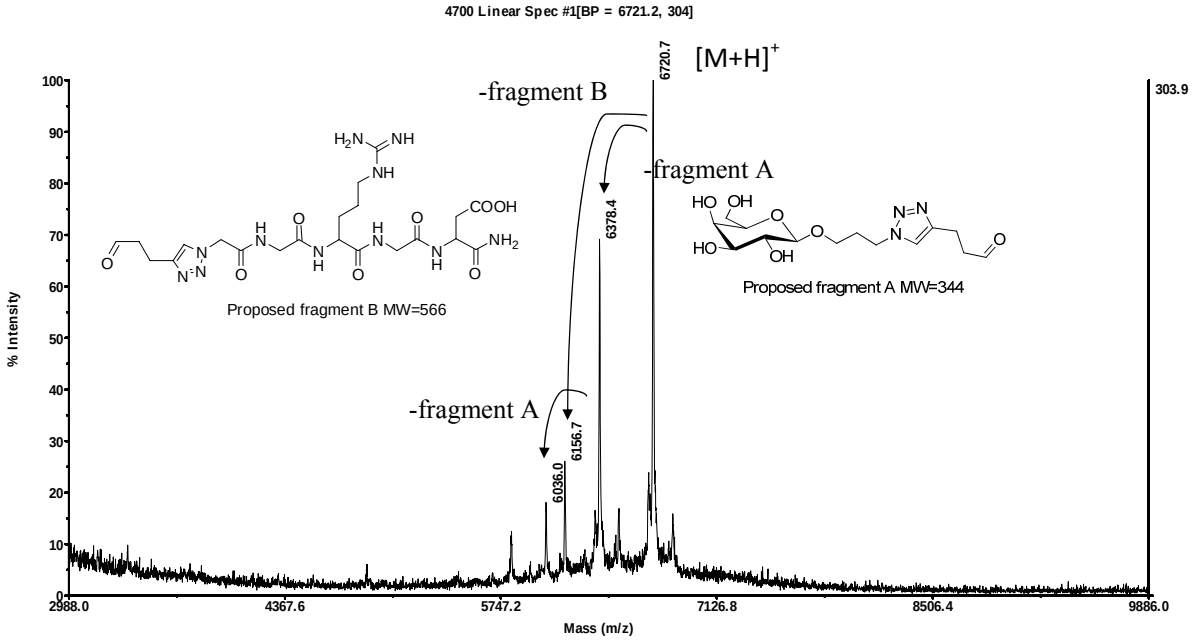

7.89
7.86
7.68
7.37
7.12
6.13
5.80
4.66
4.47
4.39
4.28
4.22
4.12
4.08
4.02
3.99
3.91
3.84
3.79
3.75
3.60
3.18
3.02
2.96
2.91
2.78
2.72
2.66
2.23
2.17
2.09
1.35
1.21
1.09
1.04
10.99
7.70
0.88
24.55
43.18
26.10
143.12
22.61
23.78
7.36
30.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


4700 Reflector Spec #1[BP= 5524.3, 1521]
5524.3
[M+Na]+
1520.8
% Intensity
100
90
80
70
60
50
40
30
20
10
0
3646.0
4392.4
5138.8
5885.2
6631.6
7378.0
Mass (m/z)


7.81
7.61
7.32
7.13
6.09
5.83
5.27
4.74
4.73
4.73
4.72
4.56
4.53
4.51
4.35
3.90
3.87
3.75
3.59
3.24
3.19
3.18
3.17
2.99
2.95
2.83
2.76
2.72
2.68
1.93
1.85
1.80
1.73
1.69
1.57
1.32
1.09
1.05
29
11.86
10.25
0.73
7.93
5.51
14.93
80.24
112.73
7.78
30.31
20.82
3.78
3.76
7.30
30.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

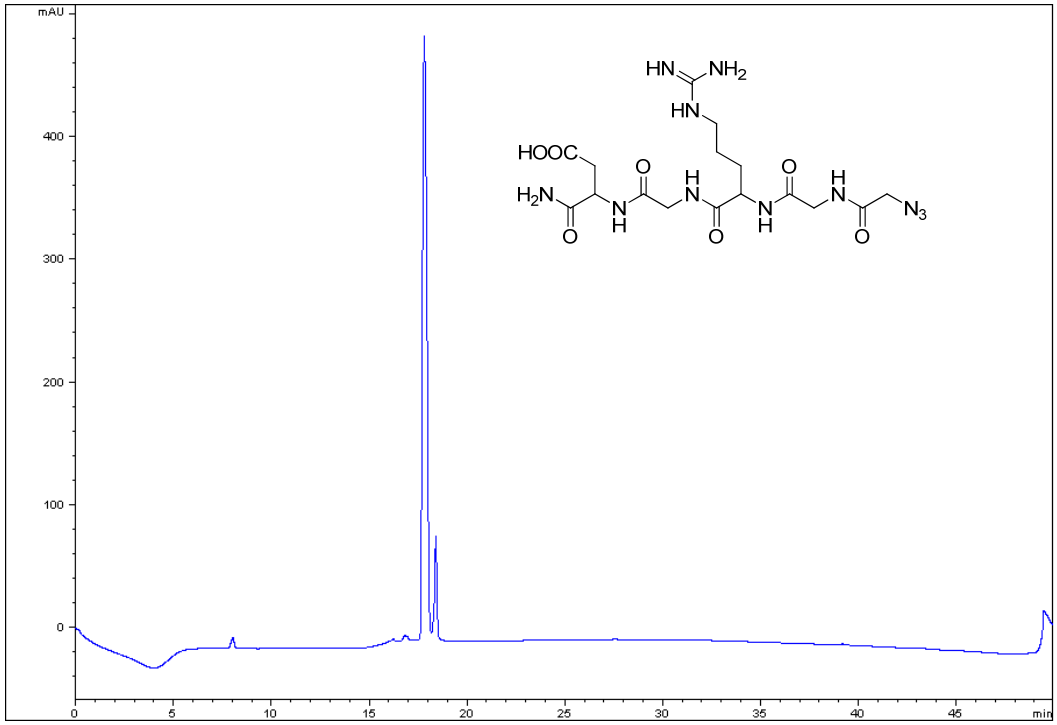

4700 Linear Spec #1[BP = 6372.7, 31]
-fragment
6372.6
[M+H]+
30.7
6074.3
5776.3
HO
O
O
O
N=N
N
O
Proposed fragment MW=300
% Intensity
100
90
80
70
60
50
40
30
20
10
0
3370.0
4441.6
5513.2
6584.8
7656.4
8728.0
Mass (m/z)


7.81
7.59
7.38
7.11
6.12
5.80
5.27
4.74
4.73
4.72
4.52
4.43
4.37
4.32
3.93
3.84
3.79
3.54
3.25
3.19
3.17
3.16
2.99
2.83
2.79
2.62
2.21
2.06
1.92
1.72
1.56
1.32
1.08
0.99
9.46
7.81
1.03
7.45
4.98
15.51
87.92
75.41
8.17
31.00
23.47
15.61
7.07
7.30
30.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

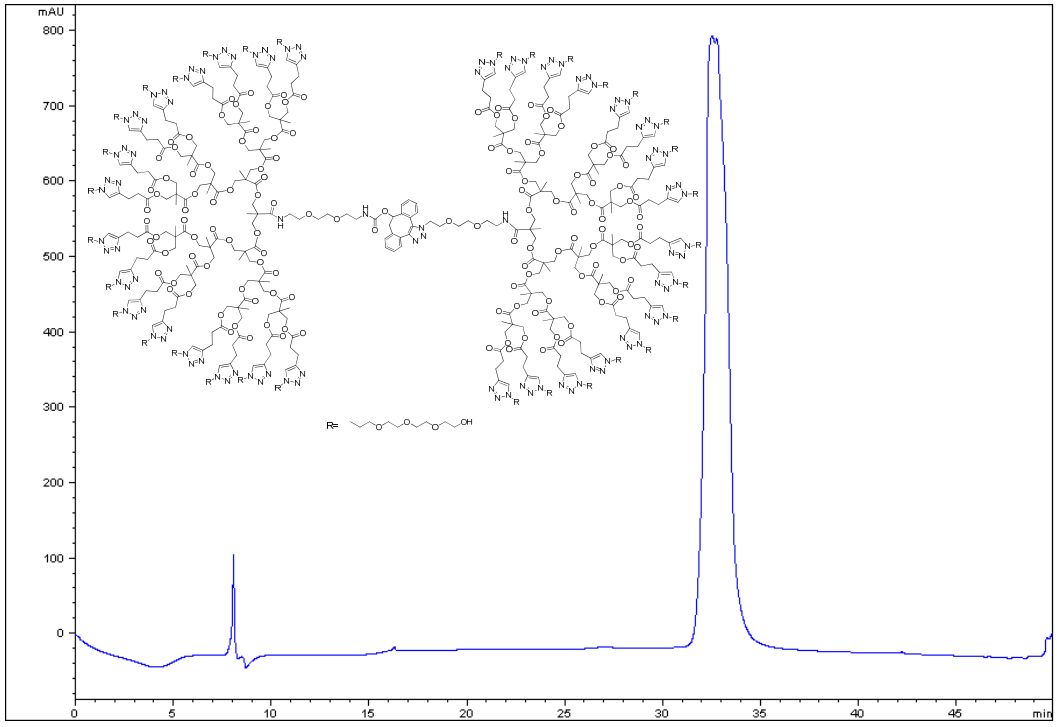

4700 Linear Spec #1[BP = 6721.2, 304]
[M+H]+
6720.7
303.9
-fragment B
-fragment A
-fragment A
6378.4
6156.7
6036.0
Proposed fragment B MW=566
Proposed fragment A MW=344
% Intensity
Mass (m/z)
2988.0
4367.6
5747.2
7126.8
8506.4
9886.0

HPLC Traces

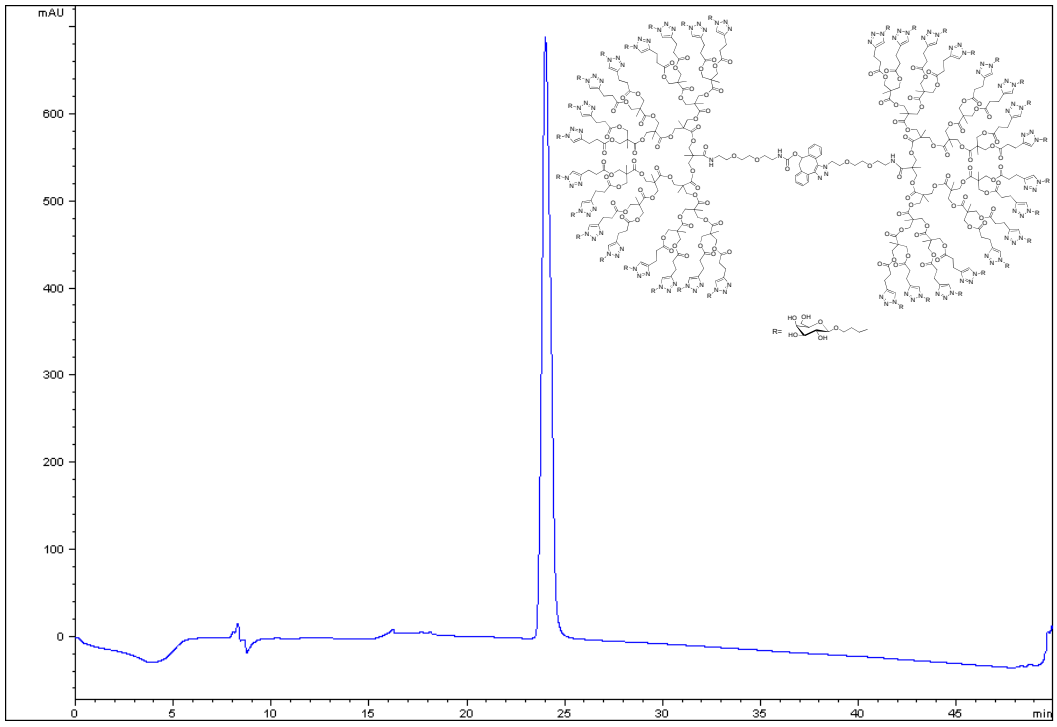
Compound 8



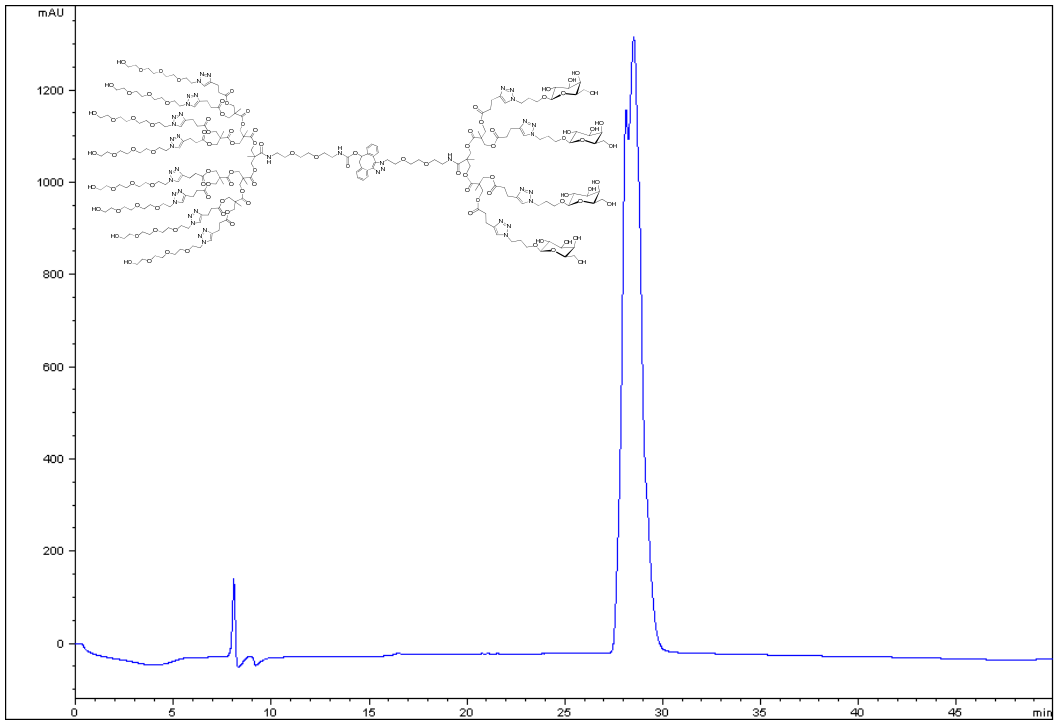
Compound 23



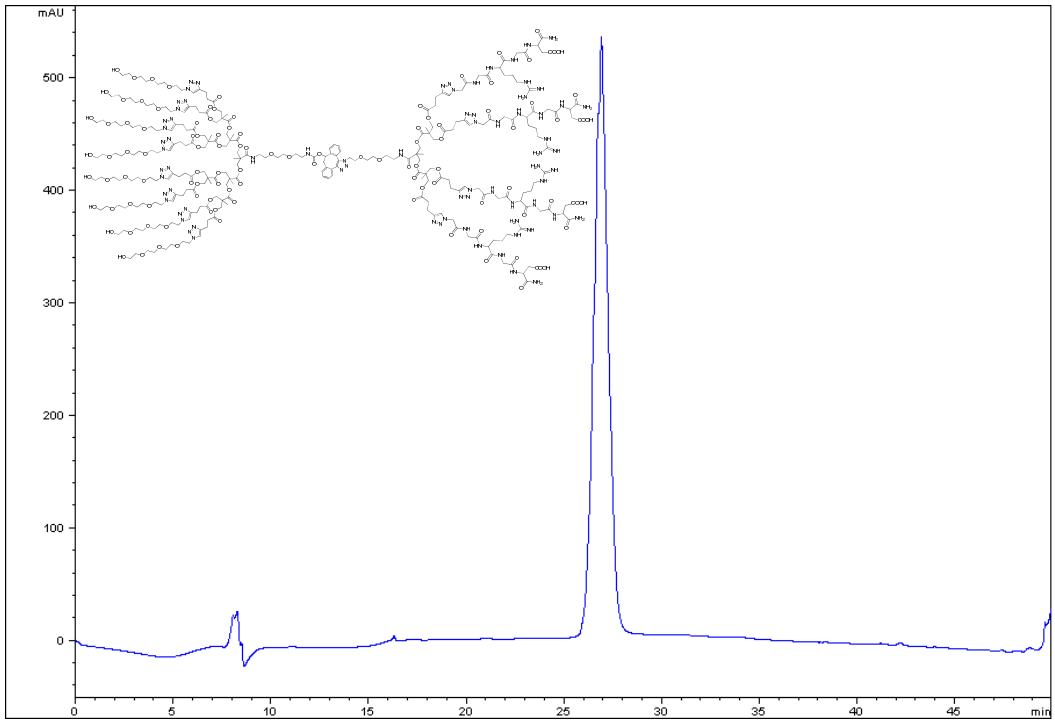
Compound 24



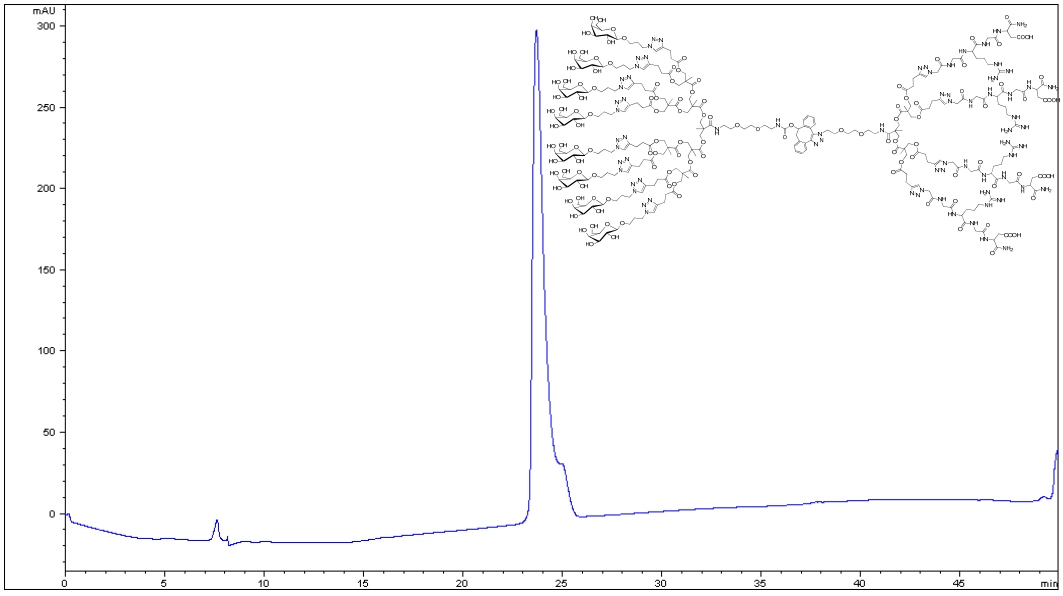
Compound 28



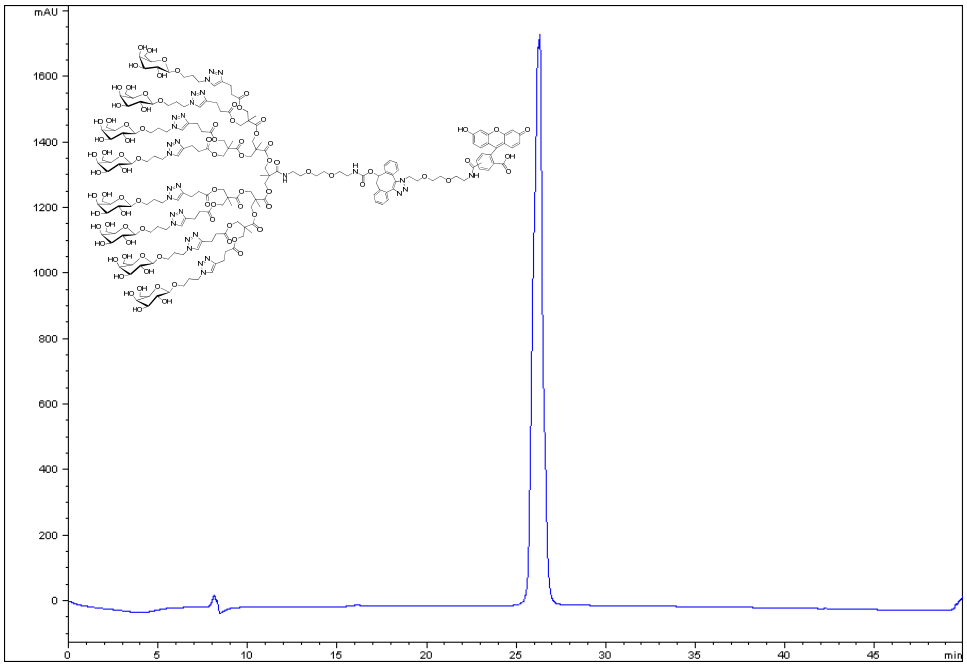
Compound 29



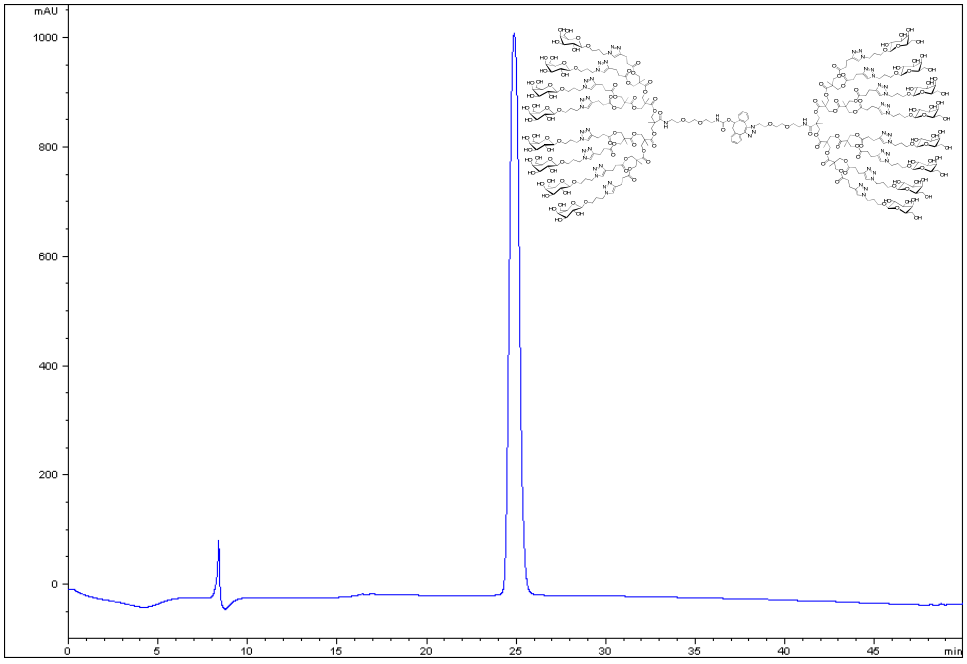
Compound 30



Compound 33



Compound 34



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[2] S. M. Parkhouse, M. C. Garnett, W. C. Chan, *Bioorg. Med. Chem.* **2008**, *16*, 6641–6650

[3] H. Ihre, A. Hult, J. M. J. Fréchet, I. Gitsov, *Macromolecules* **1998**, *31*, 4061-4068; M. Malkoch, E. Malmström, A. Hult, *Macromolecules* **2002**, *35*, 8307-8314.

[4] V. Ladmiral, G. Mantovani, G.J. Clarkson, S. Cauet, J. L. Irwin, D. M. Haddleton, *J. Am. Chem. Soc.* **2006**, *128*, 4823-4830