< Supporting Information >

Anti-inflammatory effects of α-galactosylceramide derivatives in activated microglia; involvement of p38 MAPK signaling pathway

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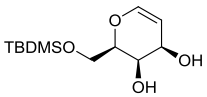
I. General Experimental Information

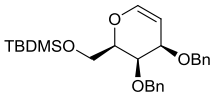
All reactions were performed either in oven-dried glassware or microwave vessel under dry argon atmosphere. Toluene and tetrahydrofuran (THF) was dried by distillation from sodium–benzophenone immediately prior to use. Dichloromethane (DCM) was dried by distillation from CaH_2. Other solvents and organic reagents were purchased from commercial venders and used without further purification unless otherwise mentioned. All reagents used for cell culture were purchased from Gibco BRL (Grand Island, NY, USA). LPS was obtained from Sigma-Aldrich (St. Louis, MO, USA). All reagents and enzymes for RT-PCR were purchased from Promega (Madison, WI, USA). Antibodies against phospho-/total form of MAP kinases were purchased form Cell Signaling Technology (Beverley, MA, USA).

^1H and ^{13}C NMR spectra were obtained on Varian Inova-500 (Varian Assoc., Palo Alto, USA) or Bruker DRX-300 (Bruker Biospin, Germany). Chemical shifts were reported in ppm relative to the residual solvent peak ($CDCl_3$, ^1H: 7.24; ^{13}C: 77.23). Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quin (quintet); m (multiplet); dd (doublet of doublet); dt (doublet triplet); br s (broad singlet), etc. Coupling constants were reported in Hz. Routine mass analyses were performed on LC/MS system using electron spray ionization (ESI) or atmospheric pressure chemical ionization (APCI). The high resolution mass spectrometric analyses were conducted at the Mass Spectrometry Laboratory of Seoul National University using mass spectrometer by direct injection for fast atomic bombardment (FAB). The products were purified by flash column chromatography on silica gel (230–400 mesh). The eluent used for purification is reported in parentheses. Thin-layer chromatography (TLC) was performed on pre-coated glass-backed plates (silica gel 60 F_{254} 0.25mm), and components were visualized by observation under UV light (254 and 365 nm) or by treating the plates with anisaldehyde, $KMnO_4$, phosphomolybdic acid, and vanillin followed by heating. Distilled water was polished by ion exchange and filtration.

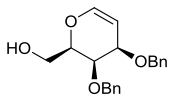
II. Synthetic Procedures and Spectroscopic Data



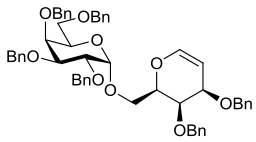
Compound 6. D-Galactal (1.0 g, 6.84 mmol), *tert*-butyldimethylsilyl chloride (1.13 g, 7.52 mmol) and imidazole (930 mg, 13.68 mmol) were stirred in anhydrous dimethylformamide (DMF, 10 mL) at room temperature for 12 h. After the completion of reaction monitored by TLC, DMF was evaporated under reduced pressure and the resulting mixture was diluted with ethyl acetate (EtOAc) and washed with saturated $NaHCO_3$(aq) and brine. The combined organic layer was dried over anhydrous Na_2SO_4 (s). The filtrate was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:1, v/v) to provide desired product **6** (1.35 g, 76%) as an amorphous white solid; $[\alpha]_D^{25}$ +4.8 (c = 2.55, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 (dd, *J* = 6.3, 1.3 Hz, 1H), 4.73 (dt, *J* = 6.3, 2.0 Hz, 1H), 4.33–4.30 (m, 1H), 4.13–4.10 (m, 1H), 4.00–3.88 (m, 3H), 3.20 (d, *J* = 5.0 Hz, 1H), 2.73 (d, *J* = 10.5 Hz, 1H), 0.91 (s, 9H), 0.11 (s, 6H); LRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{24}NaO_4Si$ [M + Na]$^+$: 283.13; Found: 283.23.



Compound 7. To a solution of compound **6** (1.21 g, 4.647 mmol) in anhydrous THF (25 mL) stirred at 0 ℃, was added sodium hydride (690 mg in 60% mineral oil, 17.19 mmol) over a 15 min period. The reaction mixture was stirred for 30 min and warm up to room temperature. Then, benzyl bromide (1.77 mL, 14.87 mmol) and tetra-*n*-butylammonium iodide (TBAI, 170 mg, 0.4647 mmol) were added carefully in dropwise. The mixture was stirred at room temperature for overnight under nitrogen atmosphere. After the completion of reaction monitored by TLC, the resultant was diluted with EtOAc and washed twice with brine. The combined organic layer was dried over anhydrous Na_2SO_4(s). The filtrate was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:3, v/v) to provide the desired product **7** (1.60 g, 78%) as an amorphous white solid; $[\alpha]_D^{25}$ –40.9 (c = 2.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.25 (m, 10H), 6.35 (dd, *J* = 6.5, 1.5 Hz, 1H), 4.91 (dd, *J* = 11.5 Hz, 1H), 4.85 (dq, *J* = 3.0, 1.3 Hz, 1H), 4.70–4.60 (m, 3H), 4.22–4.20 (m, 1H), 4.02–3.97 (m, 2H), 3.90–3.79 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H); LRMS (ESI$^+$) *m/z* calcd for $C_{26}H_{37}O_4Si$ [M + H]$^+$: 441.25; Found: 441.30.

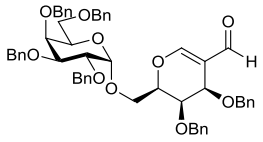


Compound 8. To a solution of compound **7** (800 mg, 1.815 mmol) in anhydrous tetrahydrofuran (THF, 15 mL) was added tetra-*n*-butylammonium fluoride (2.72 mL in 1.0 M THF solution, 2.72 mmol) over a 10 min period. The mixture was stirred at room temperature for 2 h under nitrogen atmosphere. After the completion of reaction monitored by TLC, the resultant was diluted with EtOAc and washed twice with brine. The combined organic layer was dried over anhydrous Na_2SO_4(s). The filtrate was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:2, v/v) to provide the desired products **8** (527 mg, 89%) as a colorless oil; $[\alpha]_D^{25}$ –101.9 (c = 2.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.24 (m, 10H), 6.40 (d, *J* = 6.0 Hz, 1H), 4.86–4.82 (m, 2H), 4.72–4.62 (m, 3H), 4.18–4.16 (m, 1H), 4.11–4.09 (m, 1H), 3.99–3.95 (m, 2H), 3.75–3.72 (m, 1H), 2.54 (br s, 1H); LRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{22}O_4$ $[M + H]^+$: 326.15; Found: 326.09.

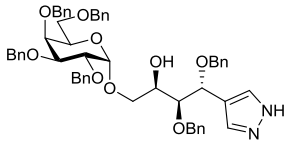


Compound 9. To a solution of 1-*O*-acetyl-2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (2.95 g, 5.055 mmol) in DCM (30 mL) at 0 °C was added trimethylsilyl iodide (TMSI, 719 μL, 5.055 mmol) and stirred for at 0 ℃ for 30 min. The reaction was stopped by adding 30 mL of anhydrous toluene and the residual TMSI was removed by azeotrope-evaporation with anhydrous toluene in three times. The slightly yellow residue was dissolved in anhydrous benzene (10 mL) and kept under argon atmosphere. In a separate round-bottom flask, molecular sieves (MS, 4 Å, 1 g), TBAI (5.6 g, 15.2 mmol), compound **8** (550 mg, 1.685 mmol), and diisopropylethylamine (880 μL, 5.055 mmol) were added into anhydrous benzene (10 mL). The reaction mixture was stirred under argon at 65 ℃ for 10 min. Upon the complete dissolution of TBAI, the glycosyl iodide in anhydrous benzene was added into this flask and the reaction mixture was stirred at 65 ℃ for 2 h. The reaction was stopped by adding EtOAc (100 mL) and cooled to 0 ℃. The white precipitate and MS were removed by filtration through Celite® -packed glass filter with EtOAc-washing. The filtrate was washed with sat. $Na_2S_2O_3$(aq) (2 × 100 mL) and brine, dried over anhydrous Na_2SO_4. The filtrate was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:5,

v/v) to provide the desired product **9** (1.26 g, 88%) as a colorless oil; $[\alpha]_D^{19}$ +8.6 (c = 2.25, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.22 (m, 30H), 6.24 (dd, *J* = 6.3, 1.2 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.83−4.66 (m, 5H), 4.65–4.54 (m, 5H), 4.44–4.37 (m, 2H), 4.28–4.26 (m, 1H), 4.14–4.11 (m, 1H), 4.04–3.95 (m, 5H), 3.91−3.90 (m, 1H), 3.71 (dd, *J* = 10.7, 4.7 Hz, 1H), 3.56–3.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 139.1, 138.9, 138.8, 138.8, 138.5, 138.2, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 99.9, 98.0, 79.3, 76.6, 75.2, 75.2, 75.0, 73.6, 73.2, 72.0, 71.0, 69.4, 69.0, 66.5, 53.6; LRMS (ESI^+) *m/z* calcd for $C_{54}H_{57}O_9$ $[M + H]^+$: 849.40; Found: 849.51.

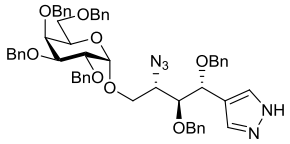


Compound 10. To a solution of compound **9** (1.2 g, 1.413 mmol) in DMF (14 mL) stirred at 0 ℃, was added $POCl_3$ (263 μL, 2.827 mmol) over a 30-min period. The reaction mixture was stirred for 1 h and warm up to room temperature. After 18 h, the resultant was diluted with EtOAc and washed with saturated $NaHCO_3$(aq) and brine. Then, the combined organic layer was dried over anhydrous Na_2SO_4(s). The filtrate was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:3, v/v) to provide the desired products **10** (556 mg, 45%) as a colorless oil; $[\alpha]_D^{25}$ +38.9 (c = 0.81, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.41–7.22 (m, 30H), 6.94 (s, 1H), 4.96 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 11.5 Hz, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.77–4.50 (m, 10H), 4.38–4.32 (m, 2H), 4.09–3.97 (m, 6H), 3.74 (dd, *J* = 5.2, 3.8 Hz, 1H), 3.47–3.42 (m, 2H); LRMS (ESI^+) *m/z* calcd for $C_{55}H_{57}O_{10}$ $[M + H]^+$: 877.40; Found: 877.59.



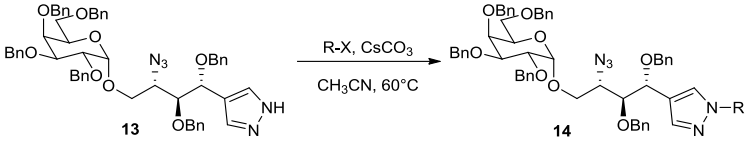
Compound 11. Compound **10** (552 mg, 0.629 mmol) and hydrazine monohydrate (61 μL, 1.259 mmol) were dissolved in MeOH (6 mL), and the mixture was stirred at room temperature for 2 h. After completion of reaction as indicated by TLC, the resulting mixture was condensed under reduced pressure without more purification to provide the desired product **11** (560 mg, quantitative yield) as a colorless oil; $[\alpha]_D^{19}$ +9.5 (c = 1.66, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$)

δ 7.52 (s, 2H), 7.51–7.10 (m, 30H), 4.92 (d, *J* = 11.5 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.66–4.64 (m, 2H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.46–4.43 (m, 2H), 4.37–4.35 (m, 2H), 4.31–4.27 (m, 2H), 4.10–4.03 (m, 2H), 3.99 (m, 1H), 3.93–3.91 (m, 2H), 3.72 (dd, *J* = 10.5, 6.5 Hz, 1H), 3.66 (dd, *J* = 6.5, 3.0 Hz, 1H), 3.53–3.48 (m, 3H); LRMS (ESI^+) *m/z* calcd for $C_{55}H_{59}N_2O_9$ $[M + H]^+$: 891.42; Found: 891.45.

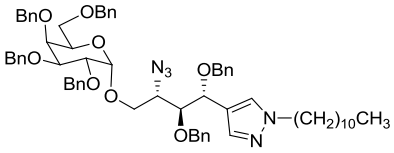


Compound 13. To a solution of compound **11** (560 mg, 0.628 mmol) and DIPEA (547 μL, 3.142 mmol) in dry DCM (5 mL) stirred at 0 ℃, was added MsCl (146 μL, 1.884 mmol) in dropwise. The reaction mixture was stirred for 3 h and the resultant was diluted with EtOAc and washed with saturated $NaHCO_3$(aq) and brine. Then, the combined organic layer was dried over anhydrous Na_2SO_4(s). The filtrate was condensed under reduced pressure to provide the desired crude product **12**. Crude compound **12** and NaN_3 (817 mg, 12.56 mmol) were dissolved in DMF (3 mL) and stirred at 120 ℃ for 2.5 days. After completion of reaction as indicated by TLC, the resulting mixture was diluted with EtOAc and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4(s). The filtrate was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:1, v/v) to provide the desired product **13** (328 mg, 57%) as a colorless oil; $[\alpha]_D^{25}$ +7.4 (c = 1.60, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.38–7.10 (m, 30H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 3.5 Hz, 1H), 4.83–4.78 (m, 2H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.68–4.55 (m, 5H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.31 (d, *J* = 11.5 Hz, 1H), 4.05 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.98 (dd, *J* = 10.0, 2.5 Hz, 1H), 3.94–3.90 (m, 4H), 3.69 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.48–3.42 (m, 3H); LRMS (ESI^+) *m/z* calcd for $C_{55}H_{58}N_5O_8$ $[M + H]^+$: 916.43; Found: 916.38.

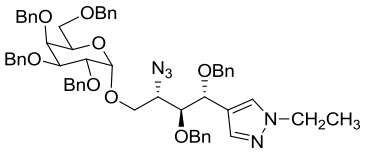
General Procedure for the *N*-alkylation of pyrazole 14



Compound **13**, alkylating agent (1.5 equiv.) and $CsCO_3$ (3 equiv.) were stirred in CH_3CN (0.05 M concentration) at 60℃ for 10 h. After the completion of reaction monitored by TLC, CH_3CN was evaporated under reduced pressure and the resulting mixture was diluted with EtOAc and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4(s). The filtrate was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:3, v/v) to provide desired product **14** (>90% yield) as a colorless oil.

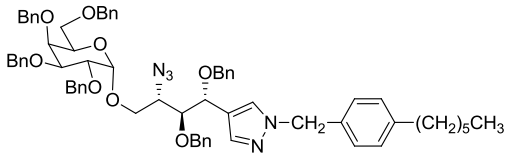


Compound **14a**; 92% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38–7.20 (m, 29H), 7.17–7.15 (m, 2H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 4.83–4.77 (m, 2H), 4.75–4.73 (m, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.61–4.54 (m, 4H), 4.48–4.43 (m, 2H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.08–4.06 (m, 3H), 3.98 (dd, *J* = 10.3 Hz, 2.5 Hz, 1H), 3.95–3.90 (m, 4H), 3.70 (dd, *J* = 11.0, 7.0 Hz, 1H), 3.51–3.45 (m, 3H), 1.82 (quin, *J* = 7.0 Hz, 2H), 1.30–1.24 (m, 18H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 139.5, 139.0, 138.9, 138.9, 138.5, 138.4, 138.2, 129.2, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 117.8, 98.8, 80.8, 79.1, 76.5, 75.3, 75.0, 74.9, 74.6, 73.6, 73.4, 73.3, 73.0, 70.5, 69.9, 69.2, 67.9, 62.3, 52.5, 32.1, 30.5, 29.8, 29.8, 29.7, 29.5, 29.3, 26.9, 22.9, 14.3.

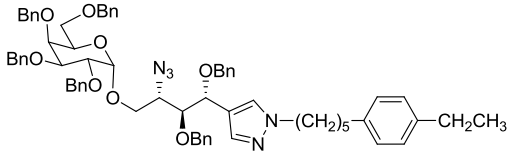


Compound **14b**; 91% yield; $[\alpha]_D^{25}$ +10.7 (c = 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.38–7.35 (m, 2H), 7.33–7.21 (m, 27H), 7.17–7.15 (m, 2H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.87 (d, *J* = 3.0 Hz, 1H), 4.83–4.78 (m, 2H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 1.5 Hz, 2H), 4.59 (d, *J* = 5.0 Hz, 1H), 4.56 (d, *J* = 11.0 Hz, 1H), 4.89–4.42 (m, 2H), 4.37–4.30 (m, 2H), 4.11 (q, *J* = 7.3 Hz, 2H), 4.05 (dd, *J* = 10.0, 4.0 Hz, 1H),

3.98 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.94–3.91 (m, 4H), 3.69 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.50–3.46 (m, 3H), 1.45 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 139.0, 138.9, 138.8, 138.5, 138.7, 138.2, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 117.9, 98.8, 80.7, 79.1, 76.5, 75.2, 74.9, 74.9, 74.7, 73.6, 73.4, 73.3, 70.5, 69.9, 69.2, 68.0, 62.2, 60.6, 47.2, 15.6.

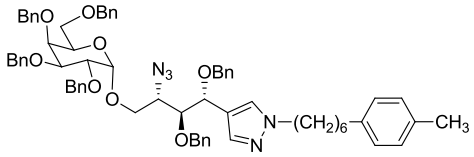


Compound **14c**; 93% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.38–7.36 (m, 2H), 7.33–7.21 (m, 29H), 7.13–7.09 (m, 4H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 3.5 Hz, 1H), 4.83–4.66 (m, 4H), 4.58–4.52 (m, 5H), 4.45–4.42 (m, 3H), 4.34 (d, *J* = 11.5 Hz, 1H), 4.27 (d, *J* = 11.5 Hz, 1H), 4.04 (dd, *J* = 3.5, 10.0 Hz, 1H), 3.97 (dd, *J* = 10.0, 2.5 Hz, 1H), 3.93–3.87 (m, 4H), 3.69 (dd, *J* = 10.8, 6.5 Hz, 1H), 3.54–3.52 (m, 1H), 3.47 (d, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 8.0 Hz, 2H), 1.57 (quin, *J* = 7.5 Hz, 2H), 1.34–1.27 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 139.8, 139.0, 138.9, 138.9, 138.4, 138.3, 138.2, 129.6, 129.1, 128.6, 128.5, 128.4, 128.0, 128.0, 127.9, 127.9, 127.7, 127.7, 127.6, 118.7, 98.8, 80.8, 79.1, 76.5, 75.2, 74.9, 74.8, 74.4, 73.6, 73.4, 73.2, 70.5, 69.9, 69.2, 67.9, 62.3, 56.1, 35.8, 31.9, 31.6, 29.9, 29.2, 22.8, 14.3; LRMS (ESI^+) *m/z* calcd for $C_{68}H_{75}N_5O_8$ $[M + H]^+$: 1090.56; Found: 1090.57.



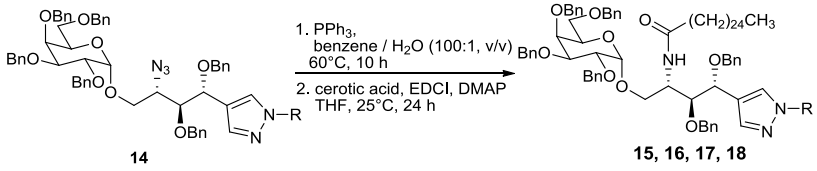
Compound **14d**; 92% yield; $[\alpha]_D^{25}$ +8.7 (c = 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38–7.21 (m, 29H), 7.17–7.15 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 4.83–4.78 (m, 2H), 4.72 (d, *J* = 11.5 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.61 (s, 2H), 4.58−4.54 (m, 2H), 4.47−4.42 (m, 2H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.29 (d, *J* = 11.5 Hz, 1H), 4.06−4.02 (m, 3H), 3.97 (dd, *J* = 10.0, 2.5 Hz, 1H), 3.94−3.90 (m, 4H), 3.69 (dd, *J* = 10.0, 6.5 Hz, 1H), 3.49−3.46 (m, 3H), 2.60 (q, *J* = 7.7 Hz, 2H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.85 (quin, *J* = 7.4 Hz, 2H), 1.61 (quin, *J* = 7.6 Hz, 2H), 1.31 (quin, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 139.6, 139.6, 139.0, 138.9, 138.5, 138.4, 138.2, 129.3, 128.6, 128.5, 128.5, 128.4, 128.4, 128.1,

128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 117.8, 98.8, 80.7, 79.1, 77.4, 76.5, 75.3, 75.0, 74.9, 74.6, 73.7, 73.4, 73.3, 70.5, 69.9, 69.2, 68.0, 62.3, 52.4, 35.5, 31.2, 30.4, 28.6, 26.5, 15.8; LRMS (ESI^+) *m/z* calcd for $C_{68}H_{76}N_5O_8$ $[M + H]^+$: 1090.57; Found: 1090.59.



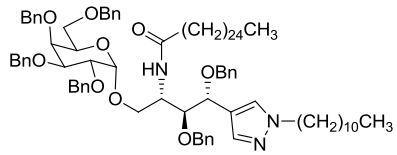
Compound **14e**; 91% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38–7.15 (m, 31H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 3.0 Hz, 1H), 4.82 (d, *J* = 11.5 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.61−4.54 (m, 3H), 4.47−4.42 (m, 2H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.06−4.02 (m, 2H), 3.97 (dd, *J* = 10.0, 2.5 Hz, 1H), 3.94−3.90 (m, 3H), 3.69 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.51−3.45 (m, 2H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.30 (s, 3H), 1.81 (quin, *J* = 7.3 Hz, 2H), 1.56 (quin, *J* = 7.5 Hz, 2H), 1.36−1.24 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 138.9, 138.9, 138.5, 138.4, 138.2, 129.1, 128.6, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 117.9, 98.8, 80.7, 79.1, 77.4, 76.8, 76.5, 75.2, 75.0, 74.9, 74.6, 73.6, 73.4, 73.3, 70.5, 70.0, 69.2, 68.0, 62.2, 52.5, 35.5, 31.6, 30.5, 28.9, 26.7, 21.2; LRMS (ESI^+) *m/z* calcd for $C_{68}H_{76}N_5O_8$ $[M + H]^+$: 1090.57; Found: 1090.77.

General Procedure for the *N*-acylation at sphingosine backbone for the preparation of 15-18

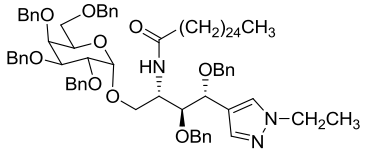


Compound **14** and PPh_3 (2 equiv.) were dissolved in benzene/H_2O co-solvent (100/1, 10 mM concentration). Then, the mixture was stirred at 60 ºC for 10 h. After completion of reaction monitored by TLC, the reaction mixture was condensed under reduced pressure and re-dissolved in anhydrous THF (10 mM concentration). Carboxylic acid (1.5 equiv.), EDCI (3 equiv.), and DMAP (catalytic amount) were added to the corresponding mixture and stirred at room temperature for 24 h. After reaction completion, the resulting mixture was diluted with EtOAc and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4(s). The filtrate was condensed under reduced pressure and purified by silica-gel flash

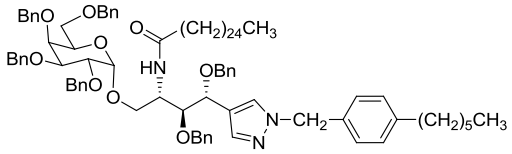
column chromatography (EtOAc:Hex = 1:3, v/v) to provide the desired product **15**–**18** as a colorless oil.



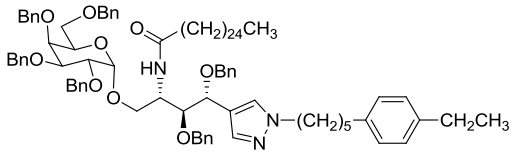
Compound **15a**; 55% yield; $[\alpha]_D^{25}$ -2.68 (c = 0.90, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.41 (s, 1H), 7.37−7.35 (m, 2H), 7.33−7.21 (m, 28H), 6.16 (d, *J* = 9.5 Hz, 1H), 4.91 (m, 3H), 4.72 (q, *J* = 6.0 Hz, 2H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.55 (d, *J* = 11.0 Hz, 2H), 4.49−4.45 (m, 3H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.10−4.06 (m, 1H), 4.05−4.01 (m, 3H), 3.95−3.91 (m, 2H), 3.89−3.86 (m, 3H), 3.55 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.35 (dd, *J* = 9.3, 6.3 Hz, 1H), 1.98−1.86 (m, 2H), 1.81 (quin, *J* = 7.0 Hz, 2H), 1.53−1.44 (m, 2H), 1.31−1.15 (m, 60H), 0.91−0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 139.7, 138.8, 138.7, 138.6, 137.9, 129.1, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 117.5, 99.7, 80.9, 79.0, 75.2, 74.9, 74.5, 73.7, 73.6, 73.1, 70.3, 70.1, 69.6, 69.4, 52.5, 50.2, 36.9, 32.1, 30.6, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 26.9, 25.9, 24.7, 22.9, 14.3



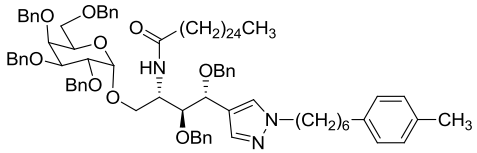
Compound **15b**; 80% yield; $[\alpha]_D^{25}$ -4.21 (c = 0.38, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.44 (s, 1H), 7.37–7.21 (m, 30H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.807–4.71 (m, 5H), 4.64–4.55 (m, 3H), 4.50–4.45 (m, 3H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 4.11 (q, *J* = 7.8 Hz, 2H), 4.08–4.01 (m, 2H), 3.99–3.92 (m, 2H), 3.90–3.86 (m, 3H), 3.53 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.49 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.34 (dd, *J* = 9.5, 6.0 Hz, 1H), 1.96–1.86 (m, 2H), 1.48 (quin, *J* = 7.0 Hz, 3H), 1.34–1.23 (m, 44H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 139.7, 138.8, 138.6, 138.6, 137.8, 129.1, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.6, 127.6, 117.6, 99.8, 80.8, 79.0, 75.3, 74.9, 74.9, 74.5, 73.7, 73.7, 73.1, 70.3, 70.2, 69.7, 69.4, 50.2, 47.1, 36.9, 32.1, 29.9, 29.9, 29.8, 29.7, 29.6, 29.6, 25.9, 22.9, 15.7, 14.3.



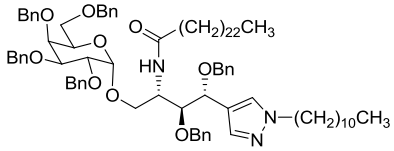
Compound **15c**; 78% yield; $[\alpha]_D^{25}$ –4.21 (c = 0.38, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.43 (s, 1H), 7.36–7.18 (m, 30H), 1.12–7.08 (m, 4H), 6.07 (d, *J* = 9.0 Hz, 1H), 5.21 (d, *J* = 3.0 Hz, 2H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.80–4.76 (m, 3H), 4.72–4.61 (m, 3H), 4.57–4.50 (m, 2H), 4.46–4.44 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.20 (d, *J* = 12.0 Hz, 1H), 4.13–4.08 (m, 1H), 4.02 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.94–3.85 (m, 5H), 3.55 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.3, 6.3 Hz, 1H), 2.55 (t, *J* = 7.8 Hz), 1.95–1.83 (m, 2H), 1.56 (quin, *J* = 7.5 Hz, 2H), 1.46 (quin, *J* = 7.3 Hz, 2H), 1.33–1.23 (m, 50H), 0.89–0.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ172.9, 142.9, 140.7, 138.8, 138.7, 138.6, 137.9, 134.1, 130.1, 129.0, 128.6, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.6, 118.4, 99.7, 81.0, 79.0, 75.0, 75.0, 74.9, 74.5, 73.7, 73.6, 73.1, 70.3, 70.2, 69.4, 56.0, 50.3, 36.9, 35.8, 32.1, 31.9, 31.6, 29.9, 29.9, 29.8, 29.7, 29.6, 29.2, 25.9, 22.9, 22.8, 14.3, 14.3.



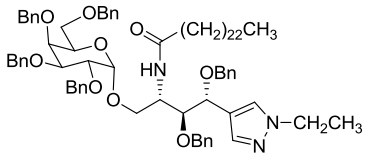
Compound **15d**; 65% yield; $[\alpha]_D^{25}$ –1.9 (c = 1.10, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (s, 1H), 7.37–7.23 (m, 30H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.16 (d, *J* = 9.0 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.80–4.71 (m, 5H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.58–4.55 (m, 2H), 4.49–4.45 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.09–3.87 (m, 9H), 3.54 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.48 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.3, 5.8 Hz, 1H), 2.60 (q, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.96–1.82 (m, 4H), 1.65–1.57 (m, 4H), 1.48 (quin, *J* = 7.0 Hz, 2H), 1.28–1.24 (m, 49H), 0.88 (t, *J* = 6.8 Hz, 3H); LRMS(ESI^+) *m/z* calcd for $C_{94}H_{128}N_3O_9$ $[M+H]^+$: 1442.97; Found: 1442.93.



Compound **15e**; 75% yield; $[\alpha]_D^{25}$ -16.1 (c = 1.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (s, 1H), 7.37–7.21 (m, 30H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.17 (d, *J* = 9.0 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.80–4.71 (m, 5H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.57–4.55 (m, 2H), 4.48–4.45 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.08–4.01 (m, 4H), 3.97–3.91 (m, 2H), 3.89–3.87 (m, 5H), 3.53 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.0, 7.0 Hz, 1H), 3.35 (dd, *J* = 9.0, 6.0 Hz, 1H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.30 (s, 3H), 1.96–1.88 (m, 2H), 1.81 (quin, *J* = 7.1 Hz, 2H), 1.55 (quin, *J* = 7.4 Hz, 2H), 1.48 (quin, *J* = 7.1 Hz, 2H), 1.31–1.25 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 139.7, 138.8, 138.7, 138.6, 137.9, 129.1, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 117.6, 99.7, 81.0, 79.0, 77.4, 75.0, 74.9, 74.5, 73.7, 73.7, 73.1, 70.3, 70.2, 69.4, 52.4, 36.9, 35.5, 32.1, 31.6, 30.6, 29.9, 29.8, 29.7, 29.6, 29.6, 29.0, 26.7, 25.9, 22.9, 21.2, 14.3; LRMS(ESI^+) *m/z* calcd for $C_{94}H_{128}N_3O_9$ $[M+H]^+$: 1442.97; Found: 1443.11.

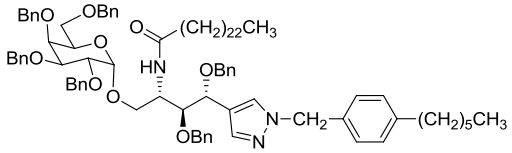


Compound **16a**; 58% yield; $[\alpha]_D^{25}$ -3.29 (c = 1.40, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (s, 1H), 7.37–7.22 (m, 30H), 6.13 (d, *J* = 9.0 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.80–4.76 (m, 3H), 6.72 (q, *J* = 5.5 Hz, 2H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.49–4.45 (m, 3H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.10–4.06 (m, 1H), 4.05–4.00 (m, 3H), 3.97–3.91 (m, 2H), 3.90–3.87 (m, 3H), 3.54 (dd, *J* = 10.8, 3.8 Hz, 1H), 3.47 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.3, 5.8 Hz, 1H), 1.97–1.86 (m, 2H), 1.81 (quin, *J* = 6.8 Hz, 2H), 1.48 (quin, *J* = 7.0 Hz, 2H), 1.30–1.1.16 (m, 56H), 0.89–0.86 (m, 6H).

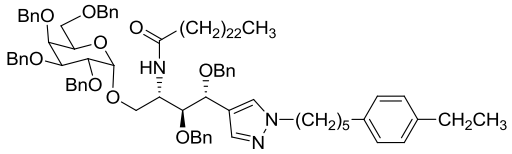


Compound **16b**; 59% yield; $[\alpha]_D^{25}$ -3.46 (c = 1.38, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.44 (s, 1H), 7.35–7.23 (m, 30H), 6.16 (d, *J* = 9.5 Hz, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.81–4.71 (m, 5H), 4.64–4.55 (m, 3H), 4,50–4.45 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 4.09 (q, *J* = 7.3 Hz, 2H), 4.07–3.98 (m, 2H), 3.97–3.12 (m, 2H), 3.89–

3.87 (m, 3H), 3.53 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.34 (dd, *J* = 9.3, 5.8 Hz, 1H), 1.98–1.86 (m, 2H), 1.48 (quin, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.5 Hz, 3H), 1.33–1.16 (m, 40H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 139.7, 138.8, 137.8, 129.2, 128.6, 128.6, 128.6, 128.5, 128.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 117.6, 99.8, 80.8, 79,0, 75.3, 74.9, 74.5, 73.7, 73.1, 70.4, 70.2, 69.7, 69.4, 50.2, 47.1, 37.5, 36.9, 32.1, 29.9, 29.9, 29.3, 29.7, 29.6, 25.9, 22.9, 15.7, 14.4.

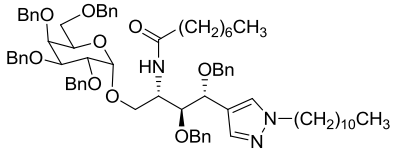


Compound **16c**; 82%; $[\alpha]_D^{25}$ -1.96 (c = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.43 (s, 1H), 7.34–7.35 (m, 2H), 7.33–7.18 (m, 28H), 7.12–7.09 (m, 4H), 5.21 (d, *J* = 3.0 Hz, 2H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.80–4.76 (m, 3H), 4.72–4.61 (m, 3H), 4.57–4.50 (m, 2H), 4.47–4.44 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.20 (d, *J* = 11.5 Hz, 1H), 4.14–4.09 (m, 1H), 4.02 (dd, *J* = 10.3, 3.8 Hz, 1H), 3.94–3.85 (m, 5H), 3.55 (dd, *J* = 10.8, 3.8 Hz, 1H), 3.48 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.3, 6.3 Hz, 1H), 2.55 (t, *J* = 7.8 Hz, 2H), 1.95–1.83 (m, 2H), 1.56 (quin, *J* = 7.5 Hz, 2H), 1.46 (quin, *J* = 7.3 Hz, 2H), 1.33–1.23 (m, 48H), 0.91–0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 142.9,141.7 138.8, 138.7, 138.6, 137.9, 134.1, 130.9, 129.0, 128.6, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.6, 118.4, 99.7, 81.0, 79.0, 75.0, 75.0, 74.9, 74.5, 73.7, 73.6, 73.1, 70.3, 70.2, 69.4, 55.9, 50.4, 35.8, 32.1, 31.9, 31.6, 29.9, 29.9, 29.7, 29.6, 29.6, 29.2, 25.9, 22.9, 22.8, 14.3, 14.3

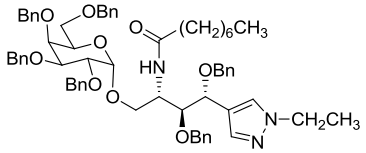


Compound **16d**; 81% yield; $[\alpha]_D^{25}$ -2.42 (c = 1.92, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (s, 1H), 7.37–7.35 (m, 2H), 7.33–7.22 (m, 28H), 7.10–7.04 (m, 4H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.80–4.75 (m, 3H), 4.72 (d, *J* = 12.5 Hz, 2H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.57 (d, *J* = 4.5 Hz, 1H), 4.55 (d, *J* = 3.0 Hz, 1H), 4.48–4.45 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 11.5 Hz, 1H), 4.08–4.01 (m, 4H), 3.97–3.92 (m, 2H), 3.89–3.86 (m, 3H), 3.53 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.0 Hz, 1H), 2.60 (q, *J* = 7.8 Hz, 2H), 2.53 (t, *J* = 8.0 Hz, 2H), 1.98–1.82 (m, 4H), 1.60 (quin, *J* = 7.8 Hz, 2H), 1.48 (quin, *J* = 7.0 Hz, 2H), 1.33–1.19 (m, 45H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz,

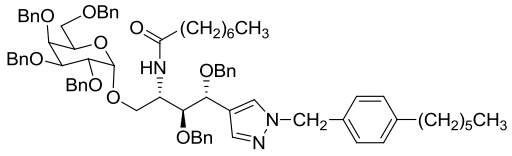
$CDCl_3$) δ 173.0, 141.7, 139.7, 138.8, 138.7, 138.6, 137.9, 129.8, 128.6, 128.6, 128.6, 128.5, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 117.6, 99.7, 81.0, 79.0, 75.2, 75.0, 74.9, 74.5, 73.7, 73.7, 73.1, 70.3, 70.2, 69.5, 69.4, 52.4, 50.3, 36.9, 35.5, 32.1, 31.2, 30.5, 29.9, 29.8, 29.7, 29.6, 29.6, 28.6, 26.6, 25.9, 22.9, 15.8, 14.3.



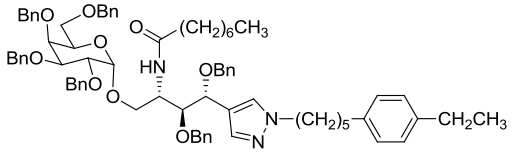
Compound **17a**; 69% yield; $[\alpha]_D^{25}$ -4.35 (c = 1.40, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (s, 1H), 7.37–7.22 (m, 30H), 6.13 (d, *J* = 9.5 Hz, 1H), 4.9. (d, *J* = 11.5 Hz, 1H), 4.80–4.77 (m, 3H), 4.73 (q, *J* = 5.8 Hz, 2H), 4.63 (*J* = 11.5 Hz, 1H), 4.56 (dd, *J* = 11.5, 1.5 Hz, 2H), 4.49–4.45 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.10–4.06 (m, 1H), 4.05–4.00 (m, 3H), 3.97–3.91 (m, 2H), 3.90–3.86 (m, 3H), 3.54 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.0 Hz, 1H), 1.98–1.86 (m, 2H), 1.81 (quin, *J* = 7.0 Hz, 2H), 1.48 (quin, *J* = 7.3 Hz, 2H), 1.28–1.23 (m, 24H), 0.88–0.85 (m, 6H).



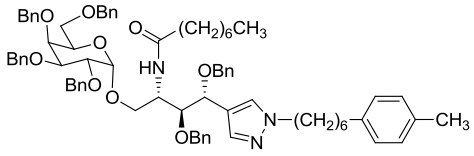
Compound **17b**; 84% yield; $[\alpha]_D^{25}$ -9.96 (c = 1.35, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.44 (s, 1H), 7.37–7.23 (m, 30H), 6.22 (d, *J* = 9.0 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.80–4.71 (m, 5H), 4.64–4.55 (m, 3H), 4.50–4.45 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 4.12 (q, *J* = 7.3 Hz, 2H), 4.03–4.01 (m, 2H), 3.97–3.92 (m, 2H), 3.89–3.87 (m, 3H), 3.53 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.48 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.34 (dd, *J* = 9.3, 5.8 Hz, 1H), 2.34 (t, H = 7.5 Hz, 2H), 1.98–1.89 (m, 2H), 1.63 (quin, *J* = 7.3 Hz, 2H), 1.49 (quin, *J* = 7.5 Hz, 2H), 1.44 (t, *J* = 7.5 Hz, 3H), 1.31–1.23 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1,139.7, 138.8, 138.8, 138.6, 138.6, 137.9, 128.6, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 117.6, 99.7, 80.9, 79.0, 75.3, 75.0, 74.5, 73.7, 73.1, 70.4, 70.2, 69.6, 69.4, 50.3, 47.1, 36.9, 32.0, 31.8, 29.9, 29.5, 29.3, 29.1, 25.9, 25.0, 22.9, 22.8, 15.7, 14.3.



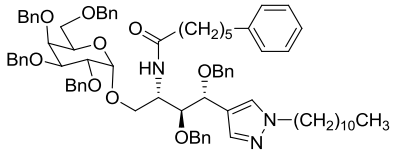
Compound **17c**; 85% yield; $[\alpha]_D^{25}$ –2.51 (c = 1.40, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.43 (s, 1H), 7.36–7.35 (m, 2H), 7.33–7.18 (m, 28H), 7.12–7.08 (m, 4H), 5.21 (d, *J* = 3.0 Hz, 2H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.78 (q, *J* = 5.8 Hz, 3H), 4.72–4.61 (m, 3H), 4.57–4.50 (m, 2H), 4.46–4.44 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.20 (d, *J* = 12.0 Hz, 1H), 4.12–4.08 (m, 1H), 4.02 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.94–3.85 (m, 5H), 3.55 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.0, 6.0 Hz, 1H), 2.55 (t, *J* = 7.8 Hz, 2H), 1.95–1.83 (m, 2H), 1.56 (quin, *J* = 7.5 Hz, 2H), 1.47 (quin, *J* = 7.3 Hz, 2H), 1.33–1.16 (m, 14H), 0.91–0.8 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 142.9, 138.8, 138.7, 137.9, 134.1, 130.1, 129.0, 128.6, 128.6, 128.6, 128.5, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.6, 118.5, 99.7, 81.0, 79.1, 75.0, 74.9, 74.5, 73.7, 73.6, 73.2, 70.3, 70.2, 69.4, 56.0, 50.3, 36.9, 35.8, 32.0, 31.9, 31.6, 29.9, 29.5, 29.3, 29.2, 25.9, 22.9, 22.8, 14.3.



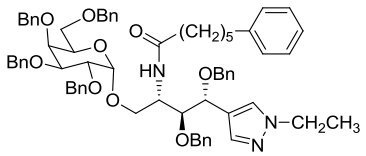
Compound **17d**; 91% yield; $[\alpha]_D^{25}$ +9.42 (c = 1.43, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.43 (s, 1H), 7.39–7.37 (m, 2H), 7.35 (m, 28H), 7.11–7.06 (m, 4H), 6.19 (d, *J* = 9.0 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.82–4.77 (m, 3H), 4.75–4.72 (m, 2H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 4.47 (d, *J* = 8.5 Hz, 1H), 4.50–4.46 (m, 3H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 11.5 Hz, 1H), 4.08–4.03 (m, 4H), 3.99–3.93 (m, 2H), 3.91–3.87 (m, 3H), 3.55 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.50 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.36 (dd, *J* = 9.0, 6.0 Hz, 1H), 2.61 (q, *J* = 7.8 Hz, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.00–1.84 (m, 4H), 1.62 (quin, *J* = 8.0 Hz, 2H), 1.50 (quin, *J* = 7.5 Hz, 2H), 1.36–1.19 (m, 13H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 141.7, 139.7, 138.8, 138.7, 138.6, 137.8, 129.8, 128.6, 128.6, 128.5, 128.5, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 117.5, 99.8, 80.9, 79.0, 75.2, 74.9, 74.5, 73.7, 73.7, 73.1, 70.3, 70.2, 69.6, 69.4, 52.4, 50.2, 36.9, 35.5, 32.0, 31.3, 30.5, 29.9, 29.5, 29.3, 28.6, 26.6, 25.9, 22.9, 15.9, 14.3.



Compound **17e**; 79% yield; $[\alpha]_D^{25}$ +4.62 (c = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.40–7.19 (m, 31H), 7.07–7.02 (m, 4H), 6.16 (d, *J* = 9.5 Hz, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.78–4.67 (m, 5H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.55 (dd, *J* = 11.3, 1.3 Hz, 2H), 4.48–4.45 (m, 3H), 4.37–4.32 (m, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.10–4.01 (m, 4H), 3.96–3.85 (m, 5H), 3.57 (dd, *J* = 10.8, 3.8 Hz, 1H), 3.48 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.36 (dd, *J* = 9.5, 6.0 Hz, 1H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.30 (s, 3H), 1.98–1.78 (m, 4H), 1.55 (quin, *J* = 7.5 H, 2H), 1.48 (quin, *J* = 7.5 Hz, 2H), 1.35–1.20 (m, 12H), 0.86 (t, *J* = 7.0 Hz, 3H).

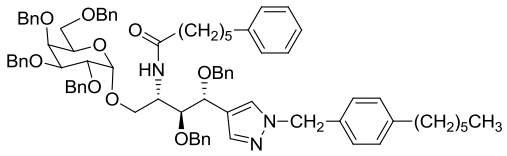


Compound **18a**; 61% yield; $[\alpha]_D^{25}$ -2.10 (c = 1.16, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.40 (s, 1H), 7.35–7.22 (m, 32H), 7.17–7.13 (m, 3H), 1.91 (d, *J* = 11.5 Hz, 1H), 4.78–4.76 (m, 3H), 4.70 (d, *J* = 11.0 Hz, 2H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.55 (dd, *J* = 11.3, 4.3 Hz, 2H), 4.48–4.53 (m, 3H), 4.34 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 11.5 Hz, 1H), 4.11–4.06 (m, 1H), 4.05–4.01 (m, 3H), 3.95–3.86 (m, 5H), 3.54 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.50–3.47 (m, 1H), 3.36 (dd, *J* = 8.8, 6.3 Hz, 1H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.95–1.86 (m, 2H), 1.57 (quin, *J* = 7.5 Hz, 2H), 1.51 (quin, *J* = 7.5 Hz, 2H), 1.29–1.23 (m, 18H), 0.87 (t, *J* = 6.5 Hz, 3H).

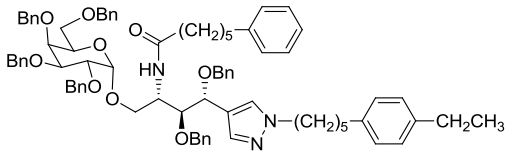


Compound **18b**; 75% yield; $[\alpha]_D^{25}$ +3.09 (c = 0.50, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.44 (s, 1H), 7.36–7.22 (m, 29H), 7.18–7.13 (m, 4H), 6.16 (d, *J* = 9.0 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.79–4.70 (m, 5H), 4.62 (d, 11.5 Hz, 1H), 4.56 (t, *J* = 10.5 Hz, 2H), 4.49–4.43 (m, 3H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.11 (q, *J* = 7.3 Hz, 2H), 4.06–4.00 (m, 2H), 3.97 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.92 (dd, *J* = 8.0, 3.5 Hz, 1H), 3.89–3.85 (m, 3H), 3.52 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.33 (dd, *J* = 9.3,

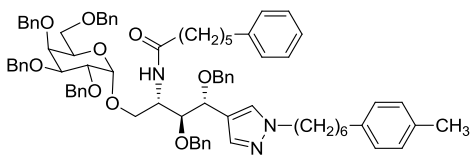
5.8 Hz, 1H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.97–1.84 (m, 2H), 1.70–1.48 (m, 6H), 1.44 (t, *J* = 7.3 Hz, 3H).



Compound **18c**; 82% yield; $[\alpha]_D^{25}$ -0.55 (c = 1.41, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.42 (s, 1H), 7.35–7.34 (m, 2H), 7.32–7.14 (m, 28H), 7.11–7.01 (m, 4H), 6.06 (d, *J* = 9.0 Hz, 1H), 5.21 (d, *J* = 3.0 Hz, 2H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.78–4.75 (m, 3H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.63 (t, *J* = 12.0 Hz, 2H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.0 Hz, 1H), 4.44 (dd, *J* = 11.0, 4.5 Hz, 3H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.20 (d, *J* = 12.0 Hz, 1H), 4.16–4.11 (m, 1H), 4.01 (dd, *J* = 10.3, 3.3 Hz, 1H), 3.92–3.84 (m, 5H), 3.55 (dd, *J* = 10.8, 3.8 Hz, 1H), 3.48 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.0 Hz, 1H), 2.55 (t, *J* = 8.0 Hz, 4H), 1.93–1.80 (m, 2H), 1.58–1.46 (m, 4H), 1.33–1.20 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H).

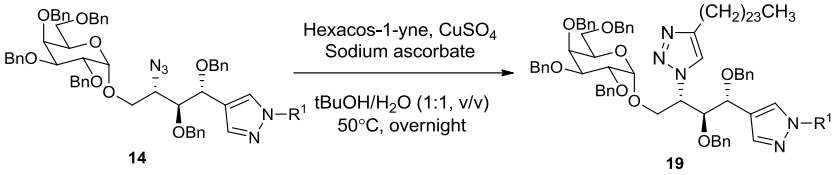


Compound **18d**; 82% yield; $[\alpha]_D^{25}$ -1.95 (c = 1.41, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.40 (s, 1H), 7.35–7.34 (m, 2H), 7.32–7.21 (m, 30H), 7.17–7.14 (m, 3H), 7.09–7.04 (m, 4H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.78–7.76 (m, 3H), 4.71 (t, *J* = 10.5 Hz, 2H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 2H), 4.48–4.43 (m, 3H), 4.34 (d, *J* = 12.0 Hz, 1H), 4.21 (d, *J* = 12.0, 1H), 4.09–3.96 (m, 4H), 3.95–3.85 (m, 5H), 3.53 (dd, *J* = 10.8, 3.8 Hz, 1H), 3.48 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.0 Hz, 1H), 2.62–2.51 (m, 6H), 1.96–1.82 (m, 4H), 1.63–1.48 (m, 6H), 1.34–1.24 (m, 4H), 1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 142.7, 141.7, 139.7, 138.8, 138.7, 138.6, 137.9, 129.8, 128.6, 128.6, 128.5, 128.5, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 125.9, 117.6, 99.8, 81.0, 89.0, 75.1, 74.9, 74.9, 74.5, 79.7, 73.1, 70.3, 70.2, 69.4, 50.4, 50.3, 36.7, 36.0, 35.5, 31.4, 31.3, 30.5, 29.9, 29.2, 28.6, 26.6, 25.7, 15.9.

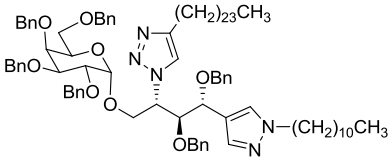


Compound **18e**; 76% yield; $[\alpha]_D^{25}$ -4.17 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.39 (s, 1H), 7.35–7.21 (m, 32H), 7.17–7.13 (m, 3H), 7.07–7.01 (m, 4H), 6.14 (d, *J* = 9.0 Hz, 1H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.78–4.76 (m, 3H), 4.73–4.69 (m, 2H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.54 (dd, *J* = 11.3, 2.8 Hz, 2H), 4.48–4.43 (m, 3H), 4.34 (d, *J* = 12.0 Hz, 1H), 4.21 (d, *J* = 12.0 Hz, 1H), 4.10–4.00 (m, 4H), 3.95–3.95 (m, 5H), 3.53 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.48 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.0 Hz, 1H), 2.57–2.50 (m, 4H), 2.30 (s, 3H), 1.96–1.78 (m, 4H), 1.67–1.48 (m, 6H), 1.39–1.21 (m, 6H).

General procedure of click reaction for the preparation of 19

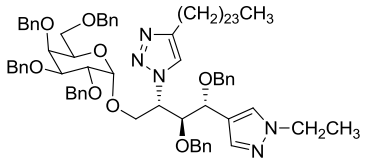


To a stirred solution of **19** (1.0 equiv.) in tBuOH/H_2O (1:1, v/v), hexacos-1-yne (1.5 equiv.), $CuSO_4$ (0.15 equiv.), and sodium ascorbate (0.6 equiv.) were added. The mixture was stirred at 50℃ for overnight. After completion of reaction monitored by TLC, solvent was evaporated under reduced pressure and the resulting mixture was diluted with EtOAc and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4(s). The filtrate was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:4, v/v) to provide the desired product **19**.

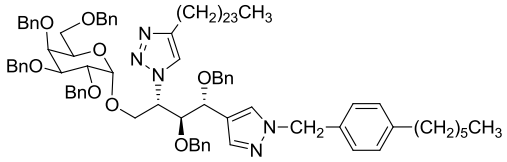


Compound **19a**; 75% yield; $[\alpha]_D^{25}$ -8.39 (c = 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.38–7.20 (m, 30H), 7.15–7.13 (m, 2H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.83–4.80 (m, 2H), 4.76 (d, 12.0 Hz, 1H), 4.69 (t, *J* = 11.5 Hz, 2H), 4.58 (d, *J* = 11.0 Hz, 1H), 4.53 (dd, *J* = 11.8, 4.8 Hz, 2H), 4.42–4.38 (m, 3H), 4.33–4.30 (m, 2H), 4.16 (d, *J* = 11.5 Hz, 1H), 4.11 (dd, *J* = 11.0, 6.5 Hz, 1H), 4.04 (t, *J* = 7.5 Hz, 2H), 4.01–3.98 (m, 2H), 3.95 (dd, *J* = 11.3, 2.8 Hz), 3.88 (d, *J* = 2.0 Hz, 1H), 3.81 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.61 (t, *J* = 6.3 Hz, 1H), 3.45–3.38 (m, 2H), 2.62–2.51 (m, 2H), 1.81 (quin, *J* = 7.0 Hz, 2H), 1.55 (quin, *J* = 7.5 Hz, 2H), 1.33–1.23 (m, 58H), 0.89–0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 139.6, 138.8, 138.7, 138.6, 138.3, 138.1, 129.5, 128.6, 128.5, 128.5, 128.4, 128.4, 128.0, 127.9,

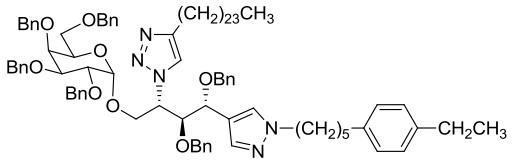
127.8, 127.7, 127.6, 121.4, 117.2, 98.8, 81.1, 79.1, 76.3, 75.0, 74.9, 74.1, 73.6, 73.4, 73.0, 70.3, 69.9, 68.9, 66.6, 61.9, 52.6, 32.1, 32.1, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.9, 26.0, 22.9, 14.4.



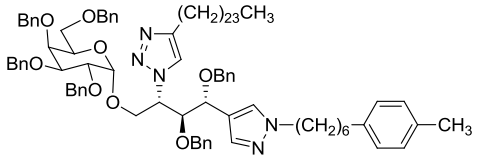
Compound **19b**; 88% yield; $[\alpha]_D^{25}$ +9.21 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.37 (s, 1H), 7.35–7.21 (m, 31H), 7.16–7.14 (m, 2H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.80–4.77 (m, 2H), 4.74–4.66 (m, 3H), 4.61 (d, *J* = 11.0 Hz, 1H), 4.53 (dd, *J* = 11.5, 5.0 Hz, 2H), 4.44–4.39 (m, 3H), 4.33–4.31 (m, 2H), 4.17 (d, *J* = 12.0 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 3H), 4.00–3.98 (m, 2H), 3.96 (dd, *J* = 11.3, 2.8 Hz, 1H), 3.88 (d, *J* = 2.0 Hz, 1H), 3.81 (dd, *J* = 10.0, 2.5 Hz, 1H), 3.62 (t, *J* = 6.5 Hz, 1H), 3.46–3.38 (m, 2H), 2.62–2.51 (m, 2H), 1.55 (quin, *J* = 7.5 Hz, 2H), 1.44 (t, *J* = 7.5 Hz, 3H), 1.30–1.23 (m, 42H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ148.5, 139.6, 138.8, 138.6, 138.3, 138.2, 128.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 121.4, 117.3, 98.8, 81.0, 79.2, 76.3, 75.0, 74.9, 74.2, 73.6, 73.4, 73.0, 70.4, 69.9, 68.9, 66.7, 61.8, 47.2, 32.1, 29.9, 29.8, 29.7, 29.6, 26.0, 22.9, 15.7, 14.3.



Compound **19c**; 60% yield; $[\alpha]_D^{25}$ +9.32 (c = 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.36–7.76 (m, 29H), 7.10–7.07 (m, 6H), 5.20 (s, 2H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.86–4.83 (m, 1H), 4.80 (d, *J* = 3.0 Hz, 1H), 4.76–7.65 (m, 3H), 4.53 (d, *J* = 11.5 Hz, 2H), 4.48 (d, *J* = 10.4 Hz, 1H), 4.41–4.26 (m, 5H), 4.16–4.09 (m, 2H), 4.00–4.39 (m, 3H), 3.87 (s, 1H), 3.80 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.61 (t, *J* = 6.3 Hz, 1H), 3.42 (m, 2H), 2.57–2.53 (m, 4H), 1.59–1.51 (m, 4H), 1.27–1.23 (m, 48H), 0.89–0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 148.4, 143.1, 139.9, 138.8, 138.6, 138.2, 138.0, 133.7, 129.8, 129.1, 128.6, 128.5, 128.4, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 121.4, 118.2, 98.8, 81.3, 79.1, 76.4, 75.0, 74.9, 74.0, 73.6, 73.4, 73.0, 70.4, 69.9, 69.0, 66.6, 61.9, 60.6, 56.1, 53.6, 35.8, 32.1, 31.9, 31.6, 29.9, 29.7, 29.7, 29.6, 29.2, 26.0, 22.9, 22.8, 21.3, 14.4, 14.3, 14.3.

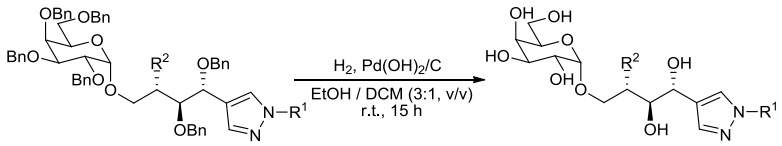


Compound **19d**; 72% yield; $[\alpha]_D^{25}$ +6.73 (c = 1.85, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.37–7.20 (m, 30H), 7.15–7.13 (m, 2H), 7.09–7.04 (m, 4H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.81–4.79 (m, 2H), 4.75 (d, *J* = 11.5 Hz, 1H), 4.71–4.66 (m, 2H), 4.59 (d, *J* = 11.0 Hz, 1H), 4.53 (dd, *J* = 1.5, 6.0 Hz, 2H), 4.42–4.38 (m, 3H), 4.33–4.30 (m, 2H), 4,16 (d, *J* = 12.0 Hz, 1H), 4.11 (dd, *J* = 11.3, 6.8 Hz, 1H), 4.04–3.98 (m, 4H), 3.95 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.87 (d, *J* = 1.5 Hz, 1H), 3.80 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.62 (t, *J* = 6.0 Hz, 1H), 3.46–3.38 (m, 2H), 2.62–2.51 (m, 6H), 1.85 (quin, *J* = 7.5 Hz, 2H), 1.64–1.52 (m, 4H), 1.34–1.19 (m, 47H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 148.5, 141.8, 139.6, 138.8, 138.6, 138.3, 138.2, 129.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 121.6, 117.3, 98.8, 81.1, 79.2, 76.4, 75.0, 74.9, 74.1, 73.6, 73.4, 73.0, 70.4, 69.9, 68.9, 66.6, 61.9, 61.9, 52.5, 35.5, 32.1, 31.2, 30.4, 29.9, 29.8, 29.7, 29.6, 28.6, 26.5, 26.0, 22.9, 15.9, 14.3.



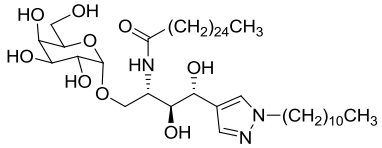
Compound **19e**; 56% yield; $[\alpha]_D^{25}$ +6.75 (c = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.38–7.20 (m, 30H), 7.14–7.13 (m, 2H), 7.07–7.01 (m, 4H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.81–4.79 (m, 2H), 4.77–4.66 (m, 3H), 4.58 (d, *J* = 11.0 Hz, 1H), 4.53 (dd, *J* = 11.8, 5.3 Hz, 2H), 4.42–4.38 (m, 3H), 4.31 (dd, *J* = 11.3, 3.8 Hz, 2H), 4.16 (d, *J* = 11.5 Hz, 1H), 4.11 (dd, *J* = 11.3, 6.8 Hz, 1H), 4.04–3.98 (m, 4H), 3.95 (dd, *J* = 11.0, 2.0 H, 1H), 3.61 (t, *J* = 6.5 Hz, 1H), 3.46–3.38 (m, 2H), 2.60–2.51 (m, 4H), 2.30 (s, 3H), 1.81 (quin, *J* = 7.3 Hz, 2H), 1.56–1.52 (m, 4H), 1.30–1.23 (m, 49H), 0.88 (t, *J* = 6.5 Hz, 3H).

General Procedure for the benzyl deprotection via hydrogenation for final compounds 1–5

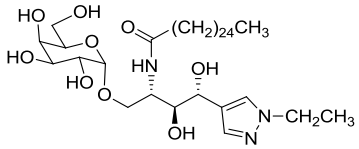


15, 16, 17, 18, 19 **1, 2, 3, 4, 5**

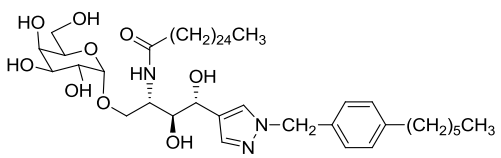
Compound **15**–**19** and $Pd(OH)_2/C$ (equal wt. quantity to starting material, 20 wt. % loading) were dissolved in EtOH/DCM co-solvent (1 mM concentration). Then, the mixture was stirred under H_2 environment at atmospheric pressure for 15 h. After completion of reaction monitored by TLC, the catalyst was removed by filtration through 0.45 μm PTFE syringe filter and washed with MeOH/DCM (1:1, v/v) solution. The filtrate was concentrated under reduced pressure to provide the desired product **1**–**5** as an amorphous white solid.



Compound **1a**; 54% yield; $[\alpha]_D^{25}$ +41.9 (c = 0.56, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, CD_3OD; reference peak : CD_3OD at 3.31 ppm) δ 7.61 (s, 1H), 7.59 (s, 1H), 4.93 (d, *J* = 4.0 Hz, 1H), 4.69 (d, *J* = 4.5 Hz, 1H), 4.11 (t, *J* = 7.2 Hz, 2H), 4.05 (m, 1H), 3.94 (d, *J* = 2.5 Hz, 1H), 3.88–3.81 (m, 4H), 3.78–3.72 (m, 4H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.86–1.82 (m, 2H), 1.65–1.59 (m, 2H), 1.35–1.22 (m, 60H), 0.85 (t, *J* = 7.0 Hz, 6H).

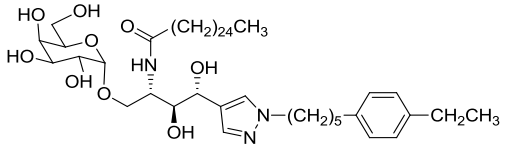


Compound **1b**; 59% yield; $[\alpha]_D^{25}$ +37.6 (c = 1.0, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.69 (d, *J* = 9.0 Hz, 1H), 7.51 (s, 1H), 7.48 (s, 1H), 4.89 (d, *J* = 3.5 Hz, 1H), 4.11 (q, *J* = 7.3 Hz, 2H), 4.04 (m, 1H), 3.91 (d, *J* = 1.5 Hz, 1H), 3.85–3.70 (m, 8H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.60–1.57 (m, 2H), 1.43 (t, *J* = 7.3 Hz, 3H), 1.31–1.24 (m, 44H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 138.7, 128.8, 122.3, 100.6, 78.5, 74.8, 71.7, 71.0, 70.5, 69.7, 67.9, 62.4, 51.3, 47.4, 37.1, 32.6, 30.4, 30.3, 30.1, 30.1, 26.6, 23.3, 20.7, 15.9, 14.5; HRMS (FAB+) *m/z* calcd for $C_{41}H_{78}N_3O_9$ $[M+H]^+$: 756.5738; Found: 756.5742.

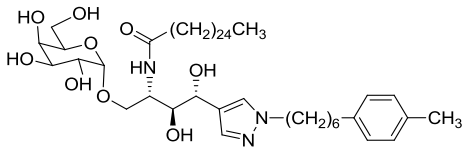


Compound **1c**; 78% yield; $[\alpha]_D^{25}$ +34.1 (c = 1.1, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.58 (d, *J* = 8.5 Hz, 1H), 7.52

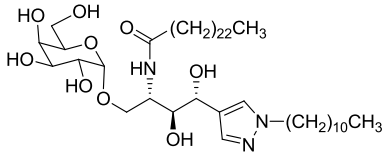
(s, 1H), 7.50 (s, 1H), 7.11 (s, 4H), 5.20 (s, 2H), 4.89 (d, *J* = 3.5 Hz, 1H), 4.64 (m, 1H), 4.06 (m, 1H), 3.90 (d, *J* = 2.5 Hz, 1H), 3.84-3.76 (m, 4H), 3.74–3.67 (m, 4H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.15 (m, 2H), 1.56-1.52 (m, 4H), 1.26–1.24 (m, 50H), 0.87–0.84 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 143.6, 139.0, 134.3, 129.6, 129.4, 128.4, 123.0, 100.5, 71.6, 70.9, 70.5, 69.7, 67.8, 62.4, 56.2, 51.2, 37.0, 36.2, 32.6, 32.4, 32.1, 30.3, 30.1, 29.6, 26.6, 23.3, 23.2, 14.5.



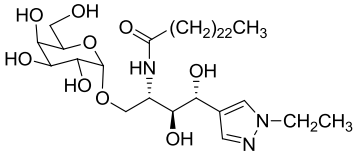
Compound **1d**; 95% yield; $[\alpha]_D^{25}$ +42.14 (c = 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.49 (s, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.66 (d, *J* = 6.0 Hz, 1H), 4.07–4.01 (m, 3H), 3.90 (d, *J* = 3.0 Hz, 1H), 3.84–3.67 (m, 8H), 2.60–2.52 (m, 4H), 2.18 (t, *J* = 7.7 Hz, 2H), 1.84 (quin, *J* = 7.5 Hz, 2H), 1.64–1.58 (m, 5H), 1.33–1.24 (m, 46H), 1.19 (t, *J* = 7.7 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H); HRMS (FAB+) *m/z* calcd for $C_{52}H_{92}N_3O_9$ $[M+H]^+$: 902.6834; Found: 902.6845.



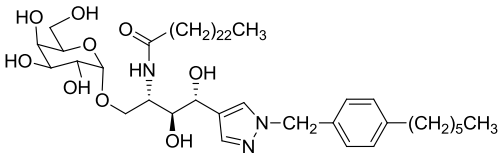
Compound **1e**; 96% yield; $[\alpha]_D^{25}$ +38.5 (c = 0.85, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.61 (s, 1H), 7.57 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.89 (d, *J* = 3.5 Hz, 1H), 4.13−4.09 (m, 2H), 4.00−3.98 (m, 1H), 3.90 (d, *J* = 3.5 Hz, 1H), 3.83−3.61(m, 8H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.60−1.57 (m, 2H), 2.28 (s, 3H), 2.24−2.17 (m, 2H), 1.82 (quin, *J* = 7.1 Hz, 2H), 1.60−1.54 (m, 4H), 1.32−1.24(m, 48H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 138.7, 128.8, 122.3, 100.6, 78.5, 74.8, 71.7, 71.0, 70.5, 69.7, 67.9, 62.4, 51.3, 47.4, 37.1, 32.6, 30.4, 30.3, 30.1, 30.1, 26.6, 23.3, 20.7, 15.9, 14.5; HRMS (FAB+) *m/z* calcd for $C_{52}H_{92}N_3O_9$ $[M+H]^+$: 902.6834; Found: 902.6827.



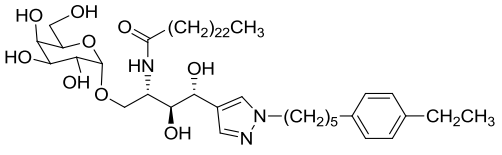
Compound **2a**; 95% yield; $[\alpha]_D^{25}$ +49.1 (c = 0.77, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, CD_3OD; reference peak : CD_3OD at 3.31 ppm) δ 7.71 (d, *J* = 9.0 Hz, 1H), 7.50 (s, 1H), 7.49 (s, 1H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.67 (d, *J* = 5.5 Hz, 1H), 4.06 (t, *J* = 7.3 Hz, 2H), 4.02 (m, 1H), 3.88 (d, *J* = 24.5 Hz, 1H), 3.84–3.75 (m, 4H), 3.74–3.68 (m, 4H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.84–1.78 (m, 2H), 1.62–1.57 (m, 2H), 1.30–1.12 (m, 56H), 0.87 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 138.8, 129.6, 122.5, 100.8, 75.0, 72.0, 71.2, 70.7, 70.0, 68.1, 62.5, 52.8, 51.6, 50.0, 37.2, 32.8, 31.3, 30.5, 30.4, 30.3, 30.2, 30.1, 27.5, 26.8, 23.5, 14.5.



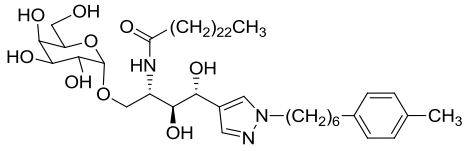
Compound **2b**; 87% yield; $[\alpha]_D^{25}$ +41.9 (c = 0.64, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.51 (s, 1H), 7.49 (s, 1H), 4.89 (d, *J* = 4 Hz, 1H), 4.66 (d, *J* = 6.0 Hz, 1H), 4.12 (q, *J* = 7.3 Hz, 2H), 4.05–4.02 (m, 1H), 3.91 (d, *J* = 2.5 Hz, 1H), 3.84–3.77 (m, 4H), 3.74-3.69 (m, 4H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.59 (m, 2H), 1.43 (t, *J* = 7.3 Hz, 3H), 1.29–1.24 (m, 40H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 138.7, 128.8, 122.4, 100.6, 78.5, 74.9, 71.7, 71.0, 70.5, 69.7, 67.9, 62.4, 51.3, 47.4, 37.1, 32.6, 30.4, 30.1, 30.1, 26.6, 23.4, 15.9, 14.5.



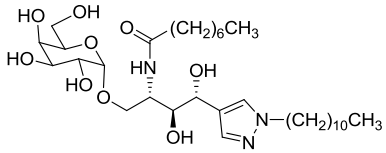
Compound **2c**; 88% yield; $[\alpha]_D^{25}$ +48.6 (c = 1.4, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.52 (s, 1H), 7.50 (s, 1H), 7.11 (s, 4H), 5.20 (s, 2H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.64 (m, 1H), 4.05 (m, 1H), 3.90 (d, *J* = 2.5 Hz, 1H), 3.84–3.77 (m, 4H), 3.74–3.67 (m, 4H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.14 (m, 2H), 1.55 (m, 4H), 1.26–1.23 (m, 46H), 0.86–0.84 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 143.6, 139.0, 134.3, 129.6, 129.4, 128.4, 123.0, 100.5, 74.9, 71.6, 70.9, 70.4, 69.7, 67.8, 62.4, 56.2, 51.2, 37.0, 36.2, 32.6, 32.4, 32.1, 31.1, 30.3, 30.2, 30.1, 30.0, 29.6, 26.6, 23.3, 23.2, 14.5.



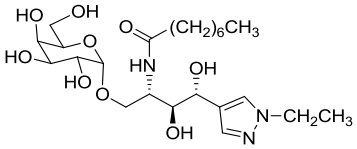
Compound **2d**; 99% yield; $[\alpha]_D^{25}$ +42.0 (c = 1.03, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.59 (s, 1H), 7.58 (s, 1H), 7.07–7.03 (m, 4H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.66 (d, *J* = 5.5 Hz, 1H), 4.09 (t, *J* = 7.3 Hz, 2H), 4.02–3.99 (m, 1H), 3.90 (d, *J* = 3.0 Hz, 1H), 3.84–3.77 (m, 4H), 3.74–3.67 (m, 4H), 2.60–2.53 (m, 4H), 2.18 (dt, *J* = 7.3, 2.0 Hz, 2H), 1.85 (quin, *J* = 7.5 Hz, 2H), 1.65–1.57 (m, 4H), 1.35–1.19 (m, 42H), 1.19 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H); δ 175.4, 142.4, 140.1, 138.0, 129.0, 128.4, 122.9, 100.6, 74.8, 71.8, 71.0, 70.5, 69.8, 67.8, 62.4, 52.7, 51.3, 37.1, 35.9, 32.6, 31.8, 30.9, 30.4, 30.1, 30.1, 29.9, 29.1, 26.8, 26.6, 23.4, 16.1, 14.5.



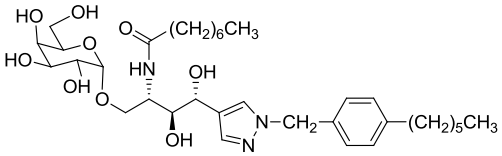
Compound **2e**; 94% yield; $[\alpha]_D^{25}$ +50.2 (c = 0.82, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.60 (s, 1H), 7.56 (s, 1H), 7.02 (q, *J* = 7.5 Hz, 4H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.66 (m, 1H), 4.07 (t, *J* = 7.3 Hz, 2H), 4.03–4.00 (m, 1H), 3.90 (d, *J* = 3.0 Hz, 1H), 3.84–3.76 (m, 4H), 3.74–3.67 (m, 4H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.27 (s, 3H), 2.18 (t, *J* = 8.0 Hz, 2H), 1.81 (quin, *J* = 6.5 Hz, 2H), 1.60–1.54 (m, 4H), 1.32–1.24 (m, 44H), 0.86 (t, *J* = 7.0 Hz, 3H).



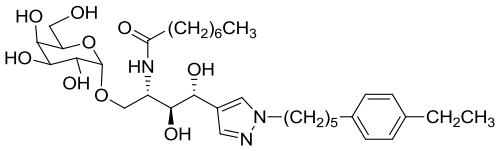
Compound **3a**; 93% yield; $[\alpha]_D^{25}$ +58.0 (c = 0.79, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.54 (d, *J* = 9.0 Hz, 1H), 7.47 (s, 1H), 7.47 (s, 1H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.65 (d, *J* = 6.0 Hz, 1H), 4.09–4.02 (m, 1H), 4.03 (t, *J* = 7.5 Hz, 2H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.84–3.77 (m, 4H), 3.74–3.67 (m, 4H), 2.16 (dt, *J* = 7.5, 2.5 Hz, 2H), 1.82–1.76 (m, 2H), 1.60–1.55 (m, 2H), 1.29–1.23 (m, 24H), 0.86–0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 138.4, 129.1, 122.2, 100.4, 74.9, 71.5, 70.8, 70.3, 69.6, 67.8, 62.3, 52.7, 51.1, 36.9, 32.5, 32.3, 31.0, 30.2, 30.1, 29.9, 29.8, 29.6, 27.2, 26.4, 23.2, 23.2, 14.4, 14.4.



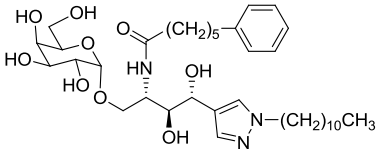
Compound **3b**; 96% yield; $[\alpha]_D^{25}$ +69.9 (c = 0.51, $CHCl_3$/MeOH = 1:1); ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.75 (d, *J* = 9.0 Hz, 1H), 7.52 (s, 1H), 7.49 (s, 1H), 4.89 (d, *J* = 3.5 Hz, 1H), 4.66 (d, *J* = 5.5 Hz, 1H), 4.12 (q, *J* = 7.3 Hz, 2H), 4.04 (m, 1H), 3.90 (d, *J* = 3 Hz, 1H), 3.81 (m, 4H), 3.72 (m, 4H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.60 (m, 2H), 1.43 (t, *J* = 7.3 Hz, 3H), 1.29 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H).



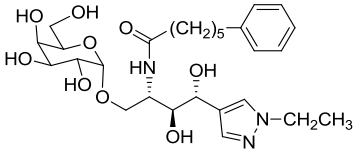
Compound **3c**; 72% yield; $[\alpha]_D^{25}$ +52.4 (c = 0.20, $CHCl_3$/MeOH = 1:1); ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.52 (s, 1H), 7.51 (s, 1H), 7.11 (s, 4H), 7.03 (d, *J* = 2.0 Hz, 1H), 5.20 (s, 2H), 4.89 (d, *J* = 3.5 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 4.07–4.04 (m, 1H), 3.90 (d, *J* = 2.5 Hz, 1H), 3.84–3.74 (m, 4H), 3.73–3.67 (m, 4H), 2.55 (t, *J* = 7.8 Hz, 2H), 2.16 (td, *J* = 7.5, 2.0 Hz, 2H), 1.58–1.52 (m, 4H), 1.32–1.24 (m, 14H), 0.88–0.82 (m, 6H).



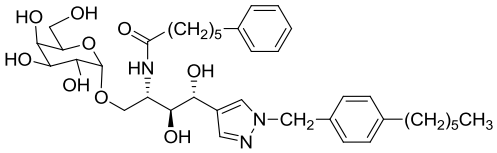
Compound **3d**; 98% yield; $[\alpha]_D^{25}$ +52.3 (c = 0.75, $CHCl_3$/MeOH = 1:1); ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.50 (s, 2H), 7.07–7.03 (m, 4H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.66 (d, *J* = 5.5 Hz, 1H), 4.06–4.02 (m, 3H), 3.90 (d, *J* = 3.0 Hz, 1H), 3.84–3.78 (m 4H), 3.74-3.68 (m, 4H), 2.60–2.52 (m, 4H), 2.18 (dt, *J* = 7.5, 1.5 Hz, 2H), 1.84 (quin, *J* = 7.5 Hz, 2H), 1.64–1.58 (m, 4H), 1.35–1.25 (m, 10H), 1.19 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H).



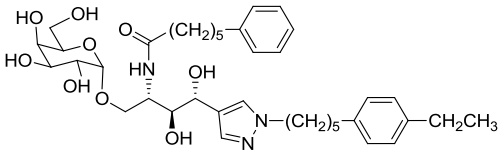
Compound **4a**; 95% yield; $[\alpha]_D^{25}$ +58.0 (c = 0.60, $CHCl_3$/MeOH = 1:1); ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.72 (d, *J* = 9.0 Hz, 1H), 7.49–7.47 (m, 2H), 7.23–7.20 (m, 2H), 7.15–7.10 (m, 3H), 4.88 (d, *J* = 3.5 Hz, 1H), 4.65 (d, *J* = 5.5 Hz, 1H), 4.07–4.02 (m, 3H), 3.89 (d, *J* = 3.5 Hz, 1H), 3.84–3.76 (m, 4H), 3.75–3.66 (m, 4H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.18 (dt, *J* = 6.3, 2.5 Hz, 2H), 1.83–1.70 (m, 2H), 1.66–1.60 (m, 4H), 1.38–1.32 (m, 2H), 1.27–1.24 (m, 16H), 0.86 (t, 3H).



Compound **4b**; 94% yield; $[\alpha]_D^{25}$ +65.2 (c = 0.75, $CHCl_3$/MeOH = 1:1); ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.70 (d, *J* = 9.0H, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.15–7.10 (m, 3H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.65 (d, *J* = 5.5 Hz, 1H), 4.12 (q, *J* = 6.5 Hz, 2H), 4.05–4.02 (m, 1H), 3.90 (d, *J* = 3.0 Hz, 1H), 3.83–3.76 (m, 4H), 3.75–3.66 (m, 4H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.18 (dt, *J* = 7.5, 2.0 Hz, 2H), 1.66–1.58 (m, 4H), 1.43 (t, 7.3 Hz, 3H), 1.38–1.32 (m, 2H).

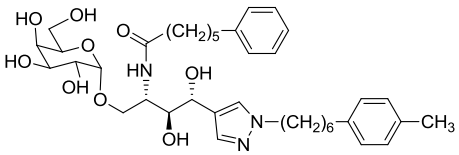


Compound **4c**; 95% yield; $[\alpha]_D^{25}$ +58.2 (c = 0.32, $CHCl_3$/MeOH = 1:1); ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.64 (d, *J* = 0.5 Hz, 1H), 7.53 (s, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.14–7.09 (m, 6H), 5.21 (s, 2H), 4.88 (d, *J* = 4.0 Hz, 1H), 4.65 (d, *J* = 5.5 Hz, 1H), 4.06–4.03 (m, 1H), 3.89 (d, *J* = 3.0 Hz, 1H), 3.85–3.77 (m, 4H), 3.74-3.66 (m, 4H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.16 (dt, *J* = 7.5, 3.0 Hz, 2H), 1.65–1.58 (m, 4H), 1.56–1.52 (m, 2H), 1.37–1.31 (m, 2H), 1.30–1.25 (m, 4H), 0.84 (t, *J* = 6.8, 3H).

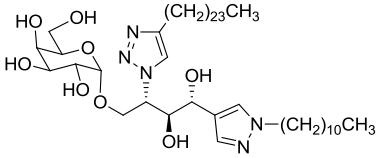


Compound **4d**; 97% yield; $[\alpha]_D^{25}$ +60.8 (c = 0.60, $CHCl_3$/MeOH = 1:1); ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.64 (d, *J* = 9.0 Hz, 1H), 7.48

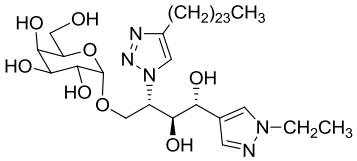
(d, *J* = 5.5 Hz, 2H), 7.21 (t, *J* = 6.8 Hz, 2H), 7.14–7.10 (m, 3H), 7.07–7.02 (m, 4H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.64 (d, *J* = 3.5 Hz, 1H), 4.07–4.02 (m, 3H), 3.90 (d, *J* = 3.0 Hz, 1H), 3.84–3.77 (m, 4H), 3.73–3.68 (m, 4H), 2.60–2.52 (m, 6H), 2.18 (dt, *J* = 7.5, 2.5 Hz, 2H), 1.83 (quin, *J* = 7.5 Hz, 2H), 1.65–1.57 (m, 6H), 1.38–1.28 (m, 4H), 1.18 (t, *J* = 7.8 Hz, 3H).



Compound **4e**; 97% yield; $[\alpha]_D^{25}$ +52.5 (c = 0.45, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.49 (s, 1H), 7.49 (s, 1H), 7.23–7.20 (m, 2H), 7.14–7.01 (m, 3H), 7.03–6,99 (m, 4H), 4.88 (d, *J* =4.0 Hz, 1H), 4.65 (d, *J* = 5.0 Hz, 1H), 4.07–4.00 (m, 3H), 3.89 (d, *J* = 3.0 Hz, 1H), 3.84–3.3.76 (m, 4H), 3.74–3.66 (m, 4H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.8 Hz, 2H), 2.26 (s, 3H), 2.18 (dt, *J* = 7.5, 1.8 Hz, 2H), 1.80 (quin, *J* = 6.0 Hz, 2H), 1.66–1.60 (m, 4H), 1.59–1.53 (m, 2H), 1.38–1.25 (m, 8H).

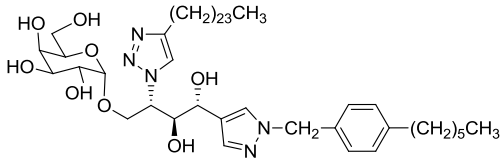


Compound **5a**; 59% yield; $[\alpha]_D^{25}$ +32.5 (c = 0.65, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 8.12 (s, 1H), 7.64 (s, 1H), 7.58 (s, 1H), 5.08 (m, 1H), 5.09–5.06 (m, 1H), 4.86 (d, *J* = 3.5 Hz, 1H), 4.52 (d, *J* = 6.5 Hz, 1H), 4.30-4.27 (m, 1H), 4.16–4.09 (m, 4H), 3.87 (d, *J* = 3.0 Hz, 1H), 3.79–3.73 (m, 1H), 3.73–3.62 (m, 4H), 2.75 (t, *J* = 7.8 Hz, 2H), 1.85–1.79 (m, 2H), 1.71–1.65 (m, 2H), 1.39–1.23 (m, 58H), 0.87–0.83 (m, 6H).

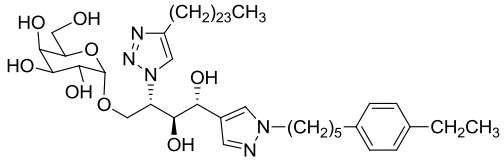


Compound **5b**; 88% yield; $[\alpha]_D^{25}$ +39.8 (c = 0.29, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 8.11 (s, 1H), 7.65 (s, 1H), 7.59 (s, 1H), 5.10–5.06 (m, 1H), 4.86 (d, *J* = 4.0 Hz, 1H), 4.52 (d, *J* = 6.5 Hz, 1H), 4.30–4.27 (m,

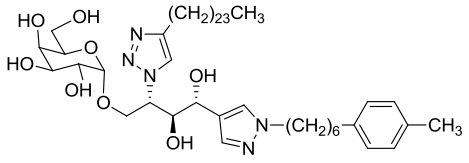
1H), 4.21–4.08 (m, 4H), 3.87 (d, *J* = 3 Hz, 1H), 3.79–3.62 (m, 5H), 2.74 (t, *J* = 7.8 Hz, 2H), 1.70–1.65 (m, 2H), 1.46 (t, *J* = 3.5 Hz, 3H), 1.35–1.22 (m, 42H), 0.85 (t, *J* = 6.8 Hz, 3H).



Compound **5c**; 79% yield; $[\alpha]_D^{25}$ +41.2 (c = 0.60, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 8.08 (s, 1H), 7.98 (s, 1H), 7.58 (s, 1H), 7.55 (s, 1H), 7.15–7.09 (m, 3H), 5.24 (s, 2H), 5.08 (m, 1H), 4.85 (d, *J* = 3.5 Hz, 1H), 4.52 (d, *J* = 7.0 Hz, 1H), 4.31–4.26 (m, 1H), 4.15–4.08 (m, 2H), 3.88–3.86 (m, 1H), 3.81–3.62 (m 5H), 2.75–2.71 (m, 2H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.69–1.63 (m 2H), 1.57–1.51 (m, 2H), 1.36–1.18 (m 48H), 0.86–0.83 (m, 3H).

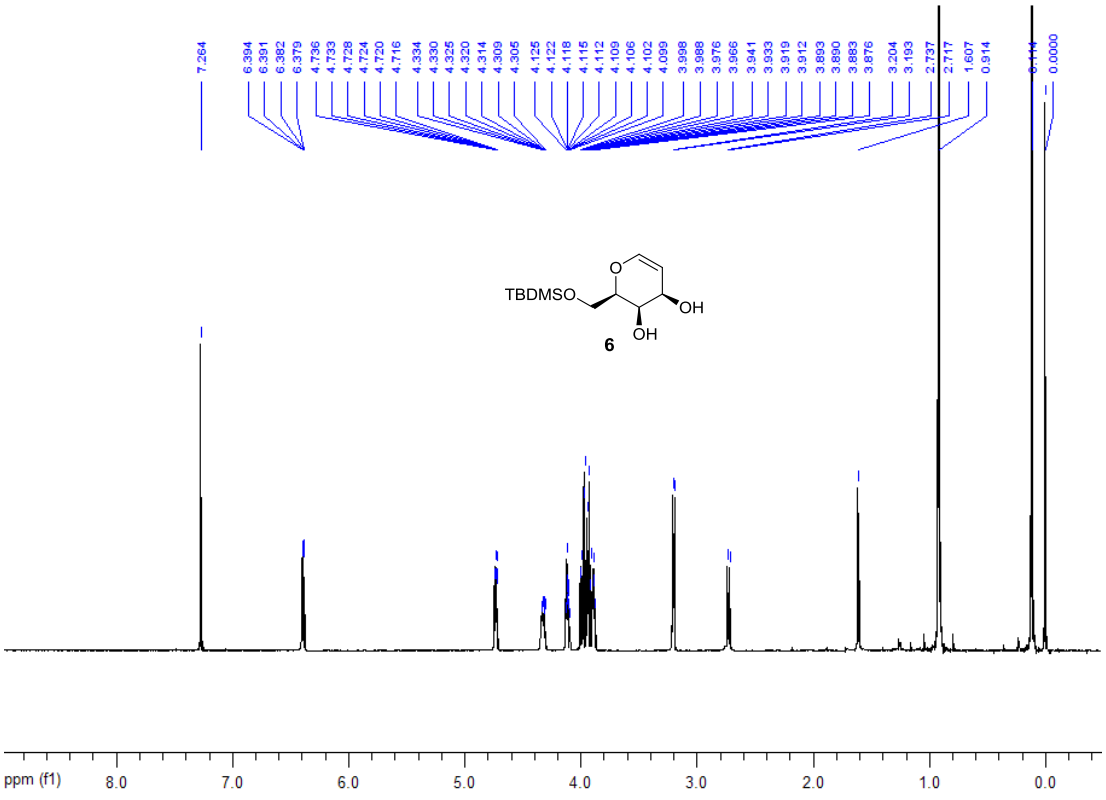


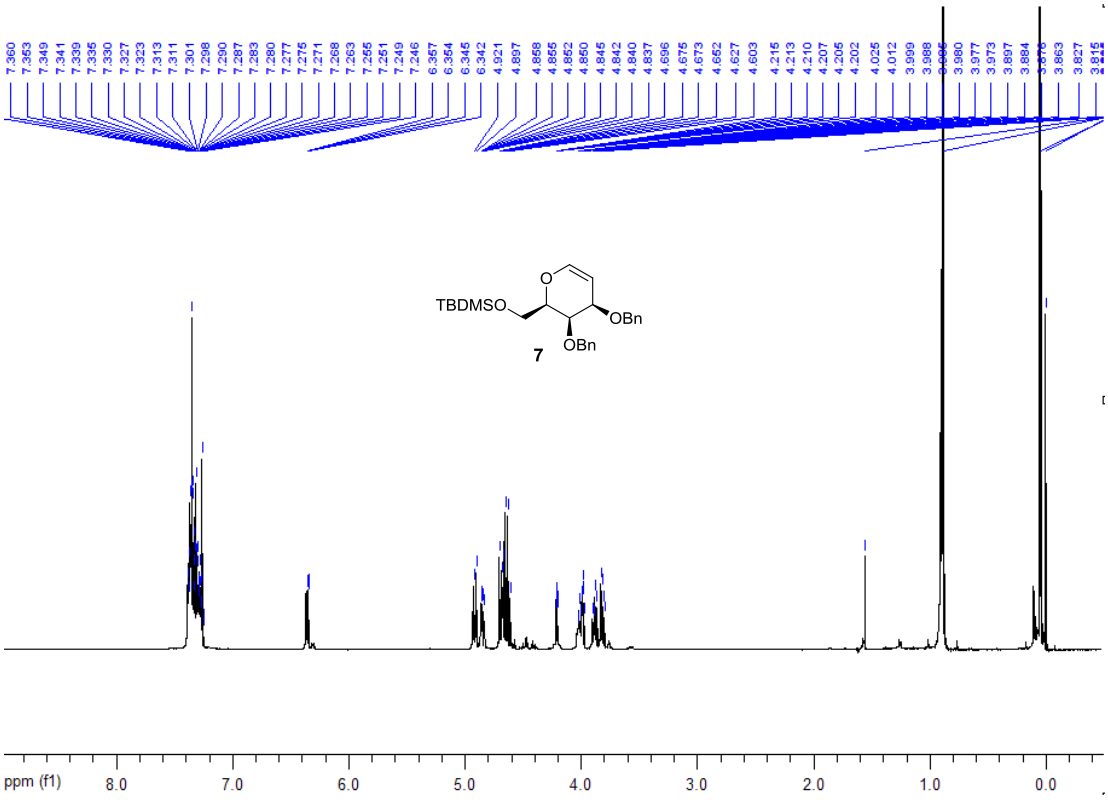
Compound **5d**; 88% yield; $[\alpha]_D^{25}$ +41.1 (c = 1.0, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.83 (s, 1H), 7.49 (s, 1H), 7.47 (s, 1H), 7.07–7.02 (m, 4H), 4.91 (m, 1H), 4.85 (d, *J* = 4.0 Hz, 1H), 4.43 (d, *J* = 6.0 Hz, 1H), 4.22–4.17 (m, 2H), 4.08–4.05 (m, 3H), 3.86 (d, *J* = 3.0 Hz, 1H), 3.77 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.71–3.63 (m, 3H), 3.60–3.57 (m, 1H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.59–2.52 (m, 4H), 1.83 (quin, *J* = 7.5 Hz, 2H), 1.66–1.58 (m, 4H), 1.36–1.21 (m, 44H), 1.18 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H).

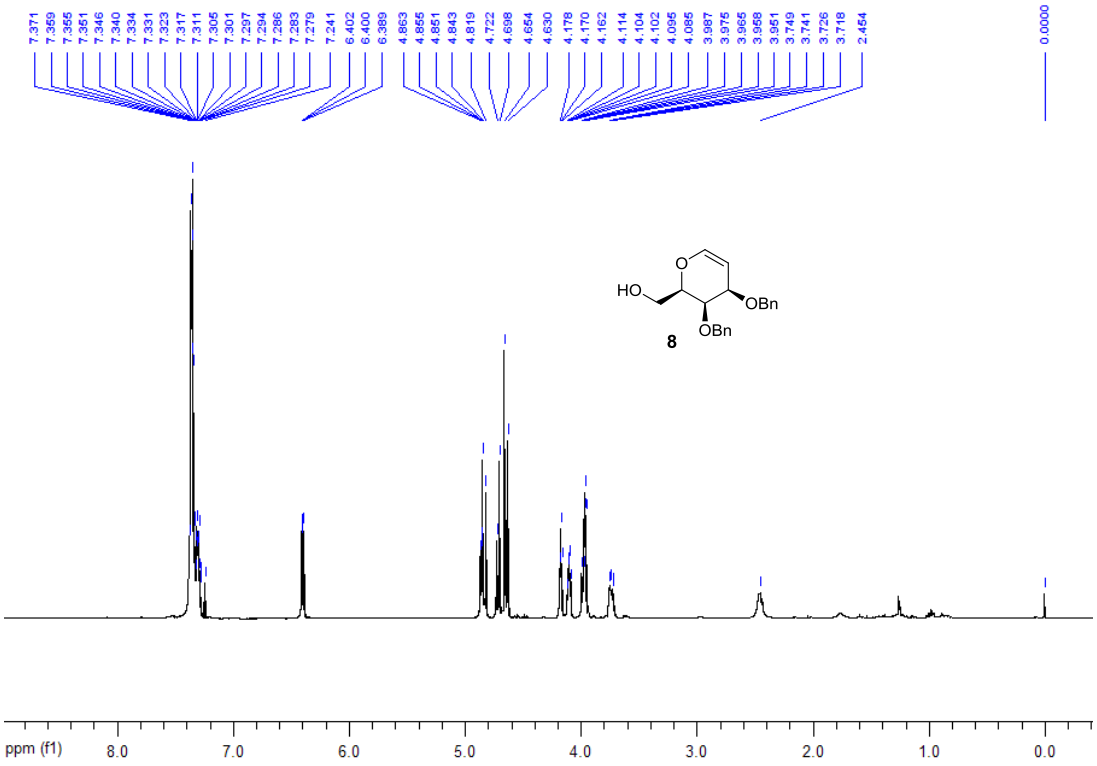


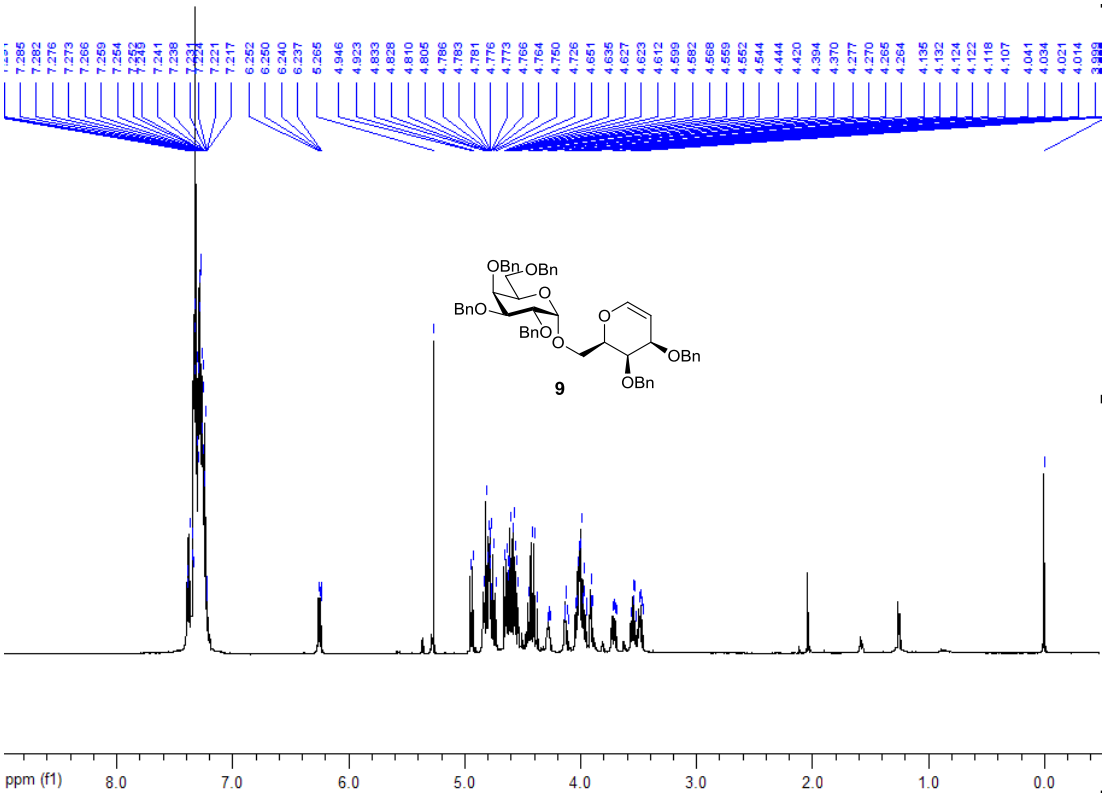
Compound **5e**; 93% yield; $[\alpha]_D^{25}$ +42.0 (c = 0.40, $CHCl_3$/MeOH = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD = 1:1; reference peak : CD_3OD at 3.31 ppm) δ 7.71 (s, 1H), 7.45 (s, 1H), 7.44 (s, 1H), 7.02 (q, *J* = 7.5 Hz, 4H), 4.85–4.82 (m, 2H), 4.39 (d, *J* = 5.0 Hz, 1H), 4.22–4.16 (m, 2H), 4.05–4.02 (m, 3H), 3.86 (d, *J* = 3.0 Hz, 1H), 3.77 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.70–3.62 (m, 3H), 3.58–3.55 (m, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.26 (s, 3H),

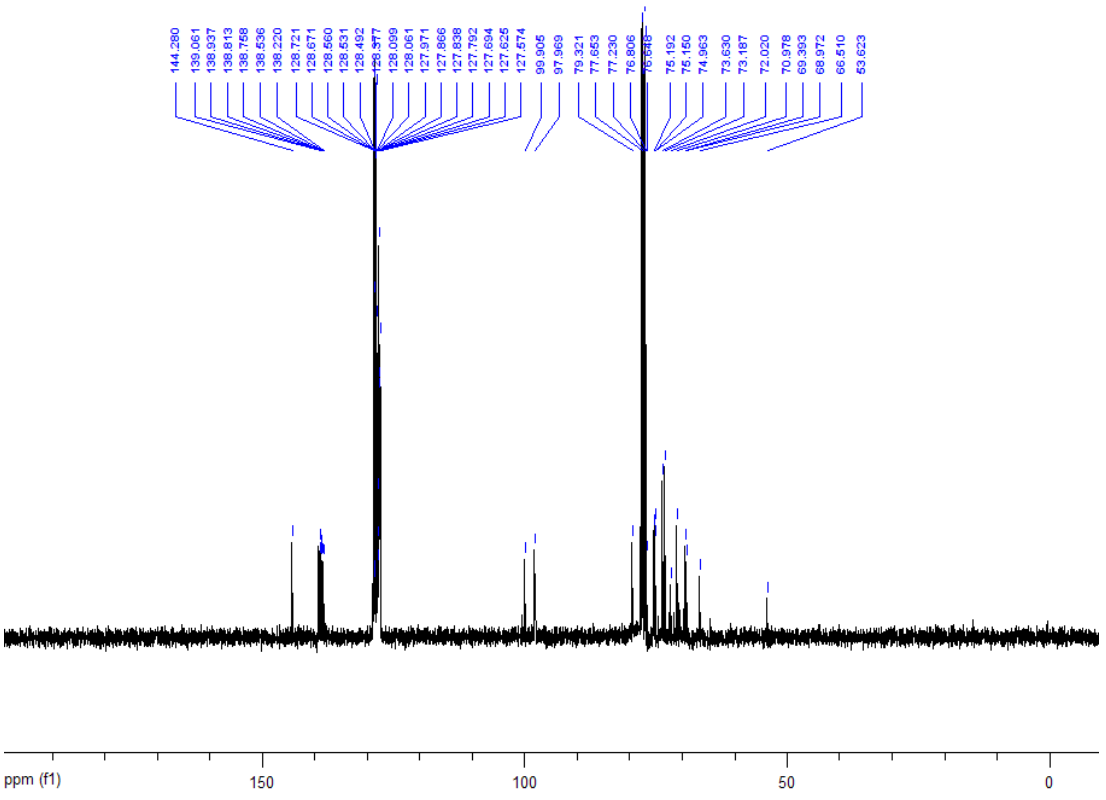
1.80 (quin, *J* = 7.5 Hz, 2H), 1.64 (quin, *J* = 7.5 Hz, 2H), 1.56 (quin, *J* = 7.5 Hz, 2H), 1.36–1.20 (m, 46H), 0.86 (t, *J* = 7.0 Hz, 3H).

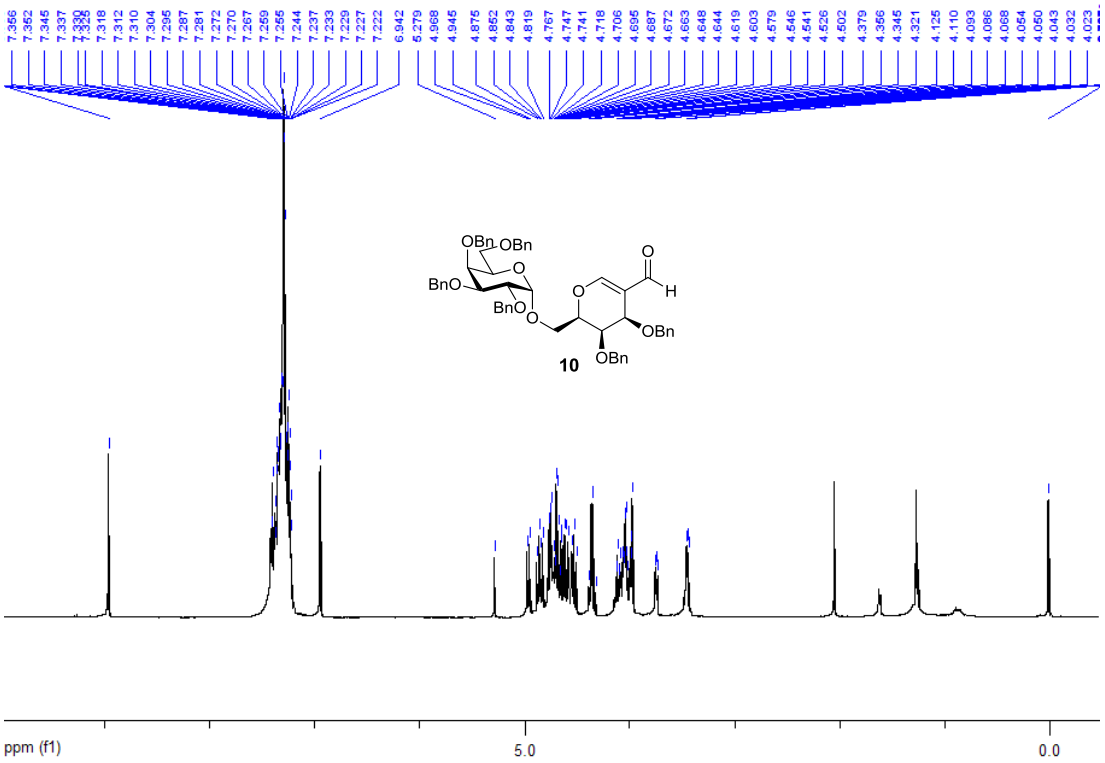


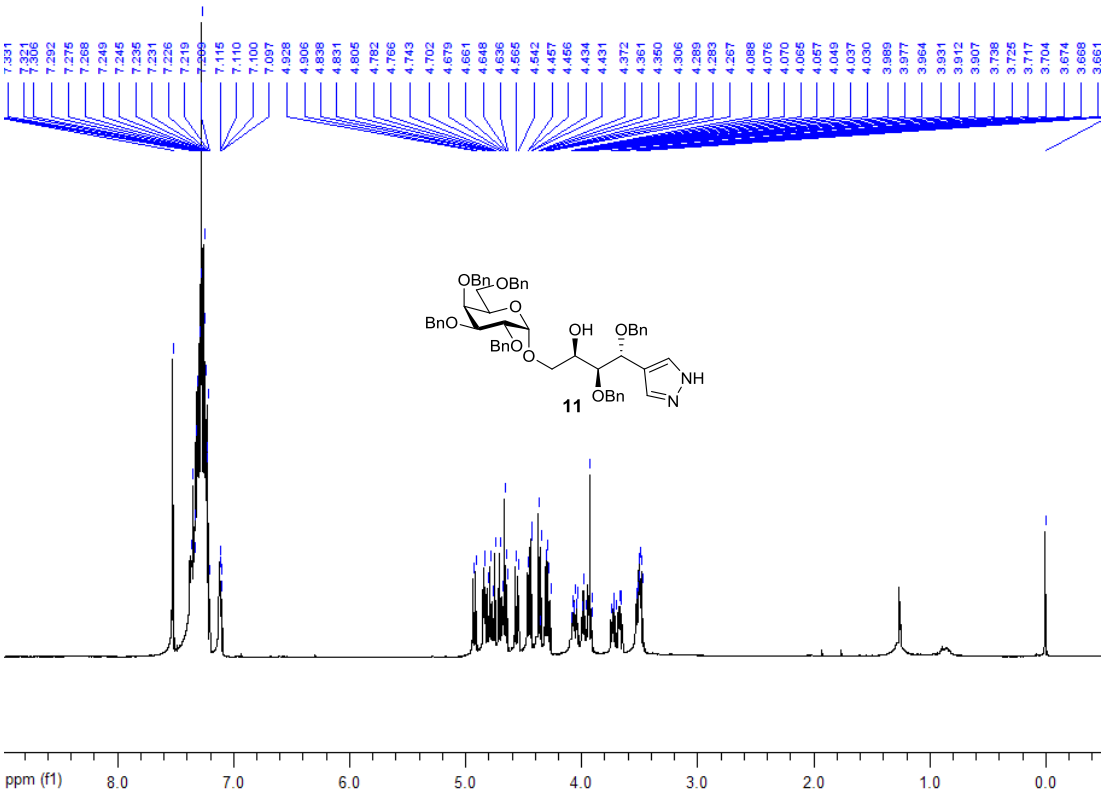

TBDMSO
OBn
OBn
O
7
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

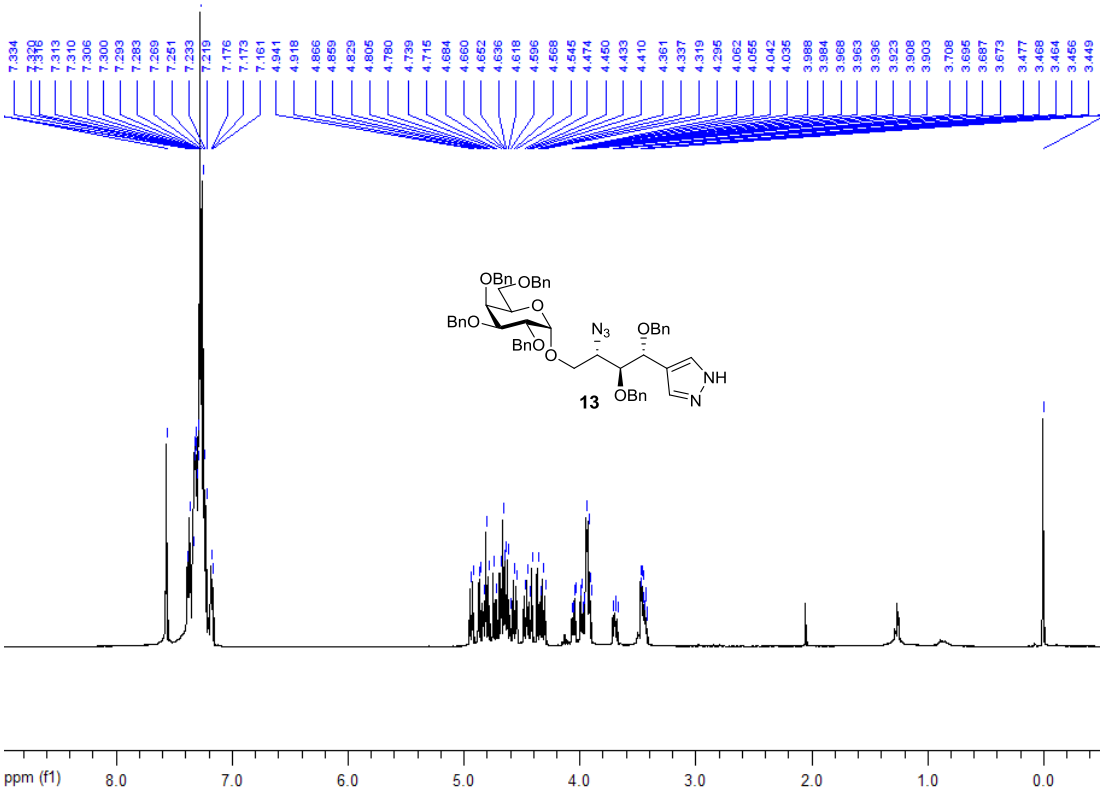

HO
OBn
OBn
O
8
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

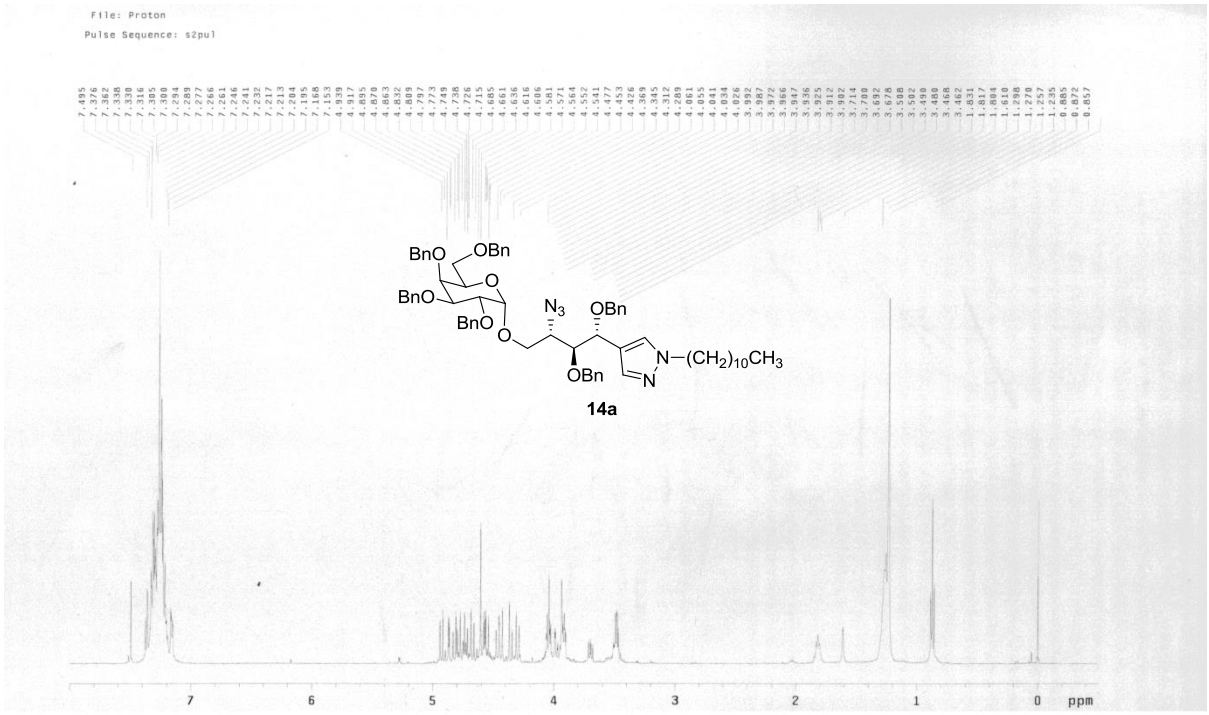

OBn
OBn
O
BnO
BnO
O
O
OBn
OBn
9
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

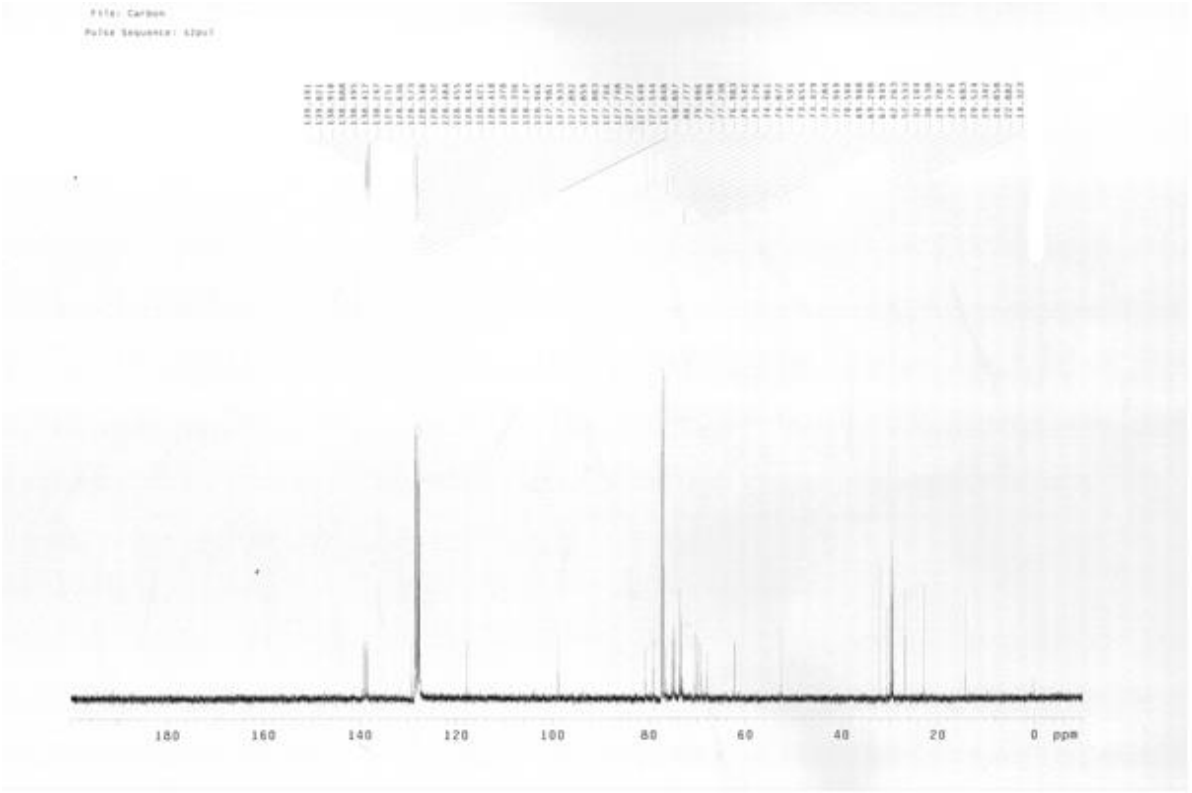

144.280
139.061
138.937
138.813
138.768
138.536
138.220
128.721
128.671
128.560
128.531
128.492
128.099
128.061
127.971
127.866
127.838
127.792
127.694
127.625
127.574
99.905
97.969
79.321
77.653
77.230
76.806
75.192
75.150
74.963
73.630
73.187
72.020
70.978
69.393
68.972
66.510
53.623
ppm (f1)
150
100
50
0

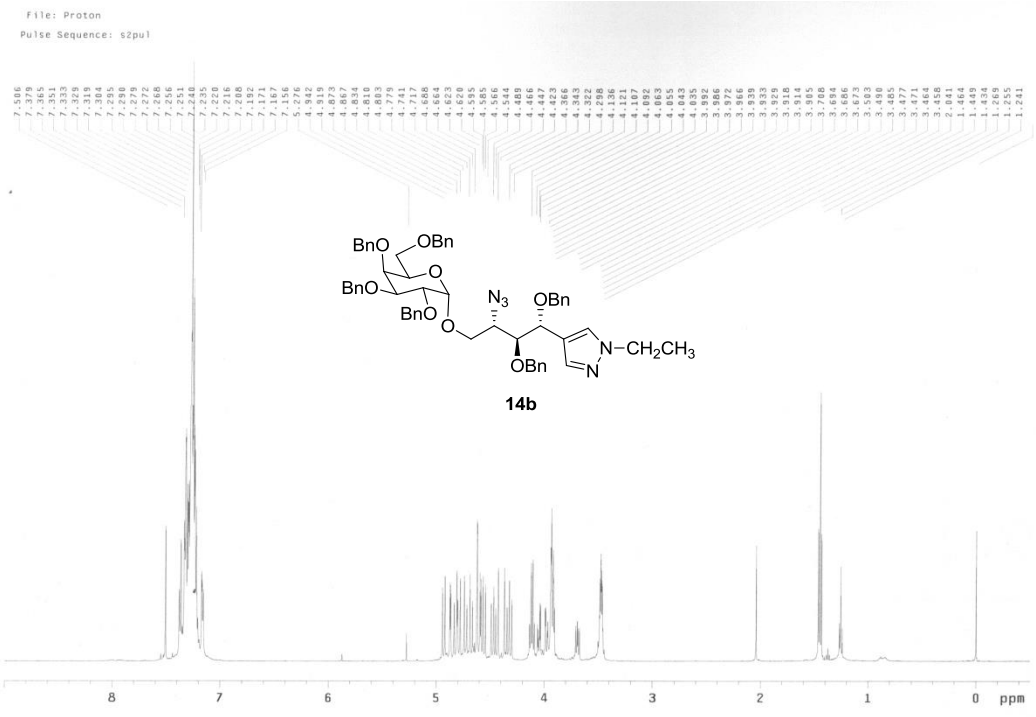

OBn
OBn
O
BnO
BnO
O
O
H
OBn
OBn
10
ppm (f1)
5.0
0.0


OBn
OBn
O
BnO
BnO
O
OH
OBn
OBn
NH
N
11
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

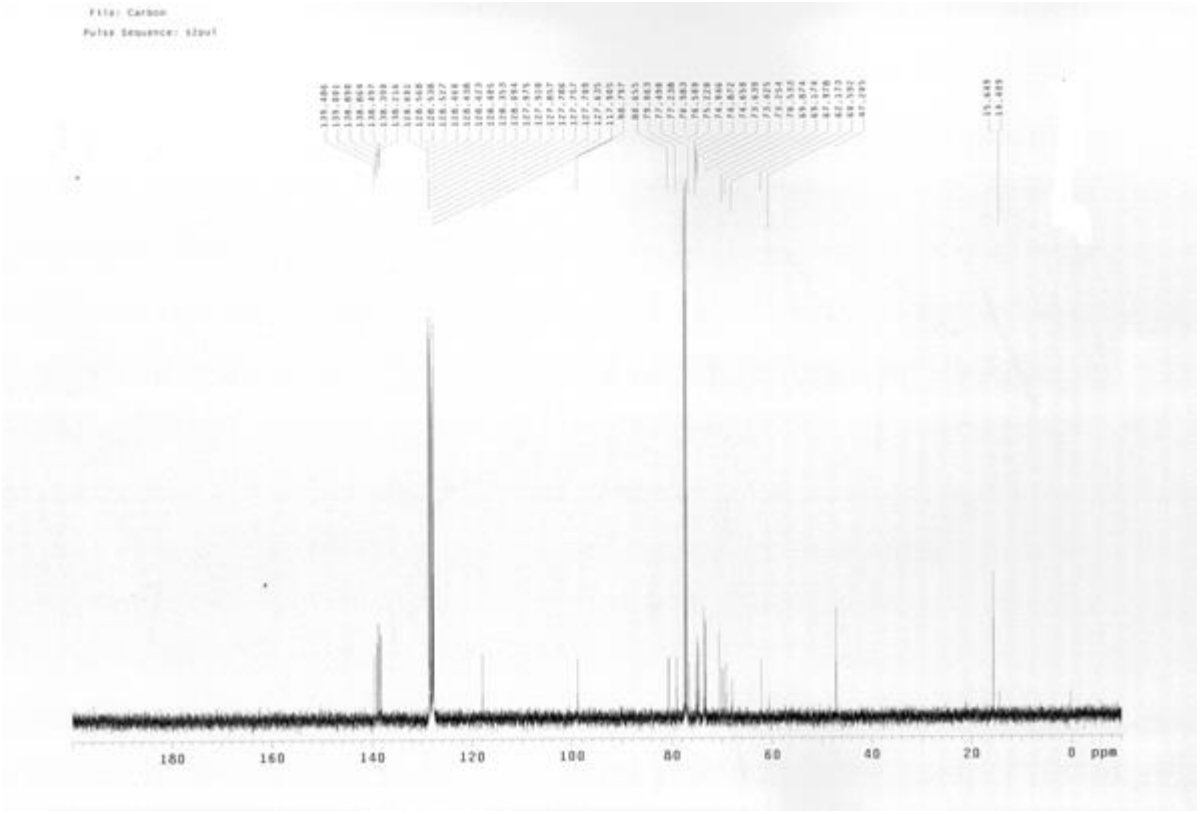

OBn
OBn
O
BnO
BnO
O
N3
OBn
OBn
NH
N
13
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

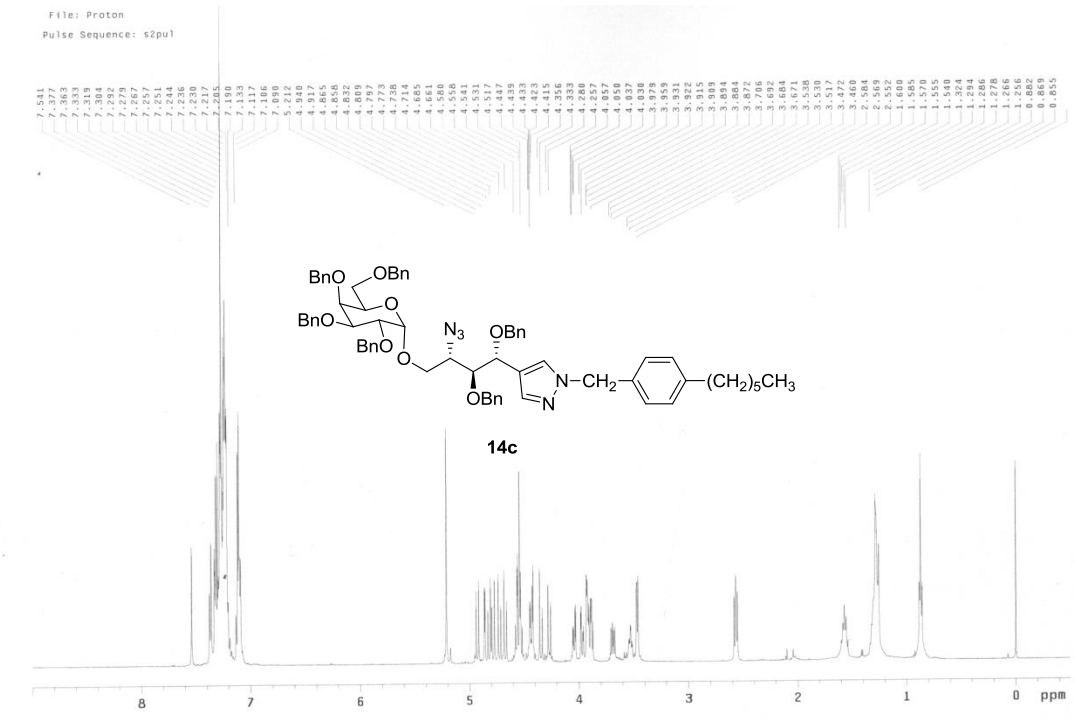

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
N3
OBn
OBn
N–(CH2)10CH3
N
14a
7
6
5
4
3
2
1
0
ppm


File: Carbon
Pulse Sequence: s2pul
180
160
140
120
100
80
60
40
20
0 ppm

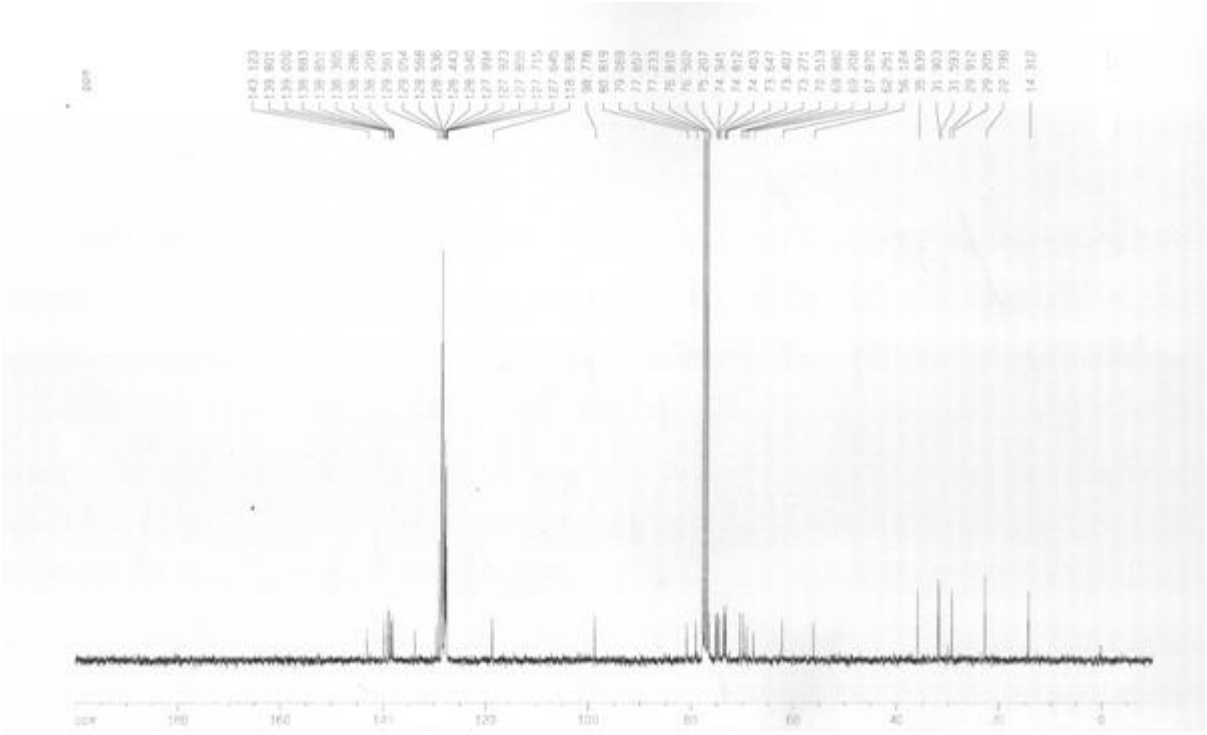

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
N3
OBn
OBn
N
N–CH2CH3
8
7
6
5
4
3
2
1
0 ppm

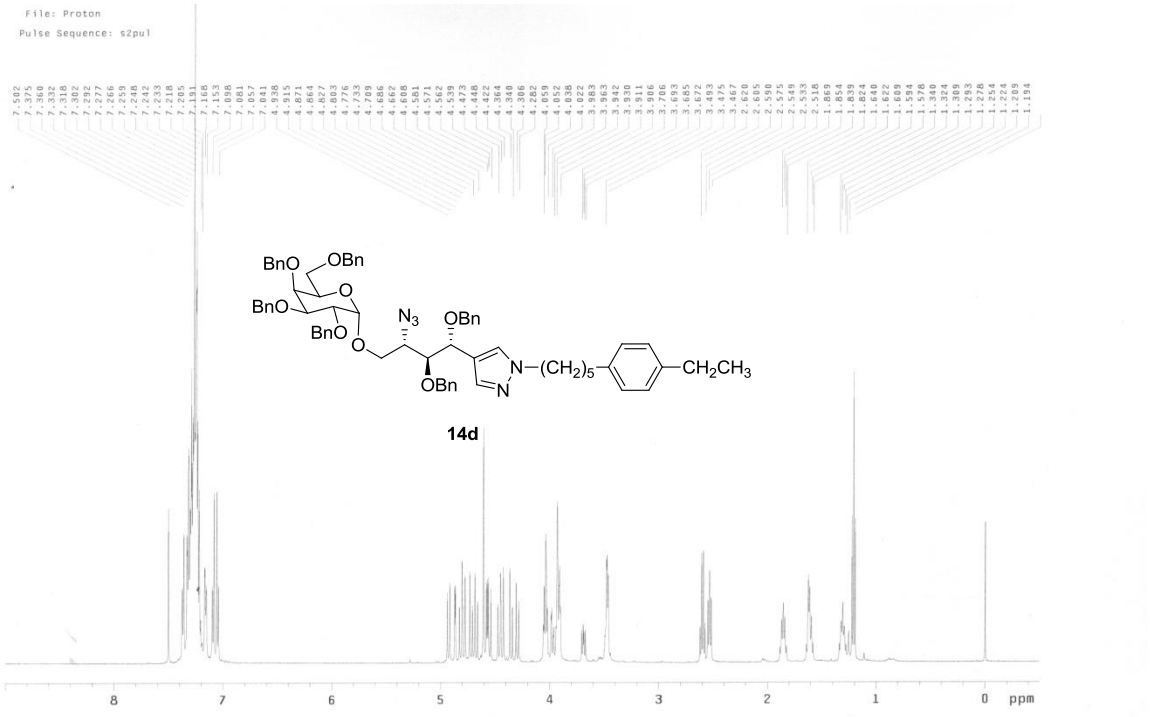
14b


File: Carbon
Pulse Sequence: s2pul
180
160
140
120
100
80
60
40
20
0 ppm

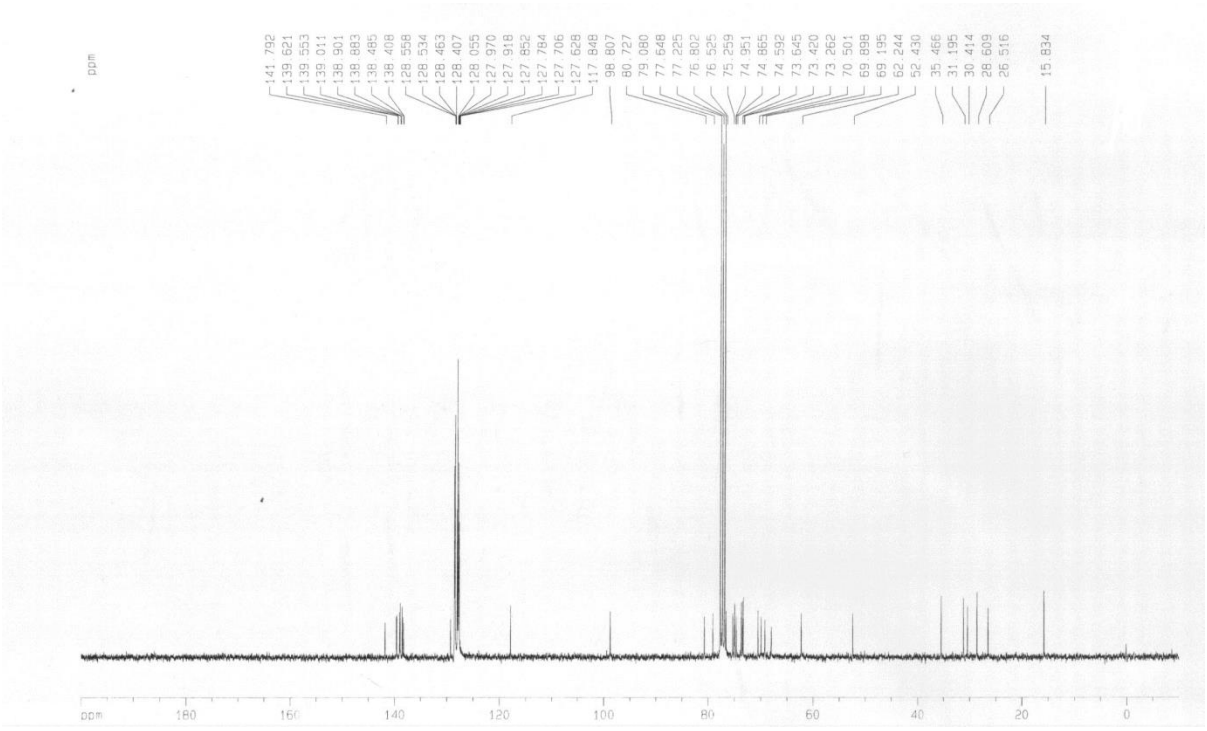

File: Proton
Pulse Sequence: s2pul
BnO
OBn
BnO
BnO
O
O
N3
OBn
OBn
N
N
CH2
(CH2)5CH3
8
7
6
5
4
3
2
1
0 ppm

14c




File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
N_3
OBn
OBn
N
N
$(CH_2)_5$
CH_2CH_3
8
7
6
5
4
3
2
1
0
ppm

14d


ppm
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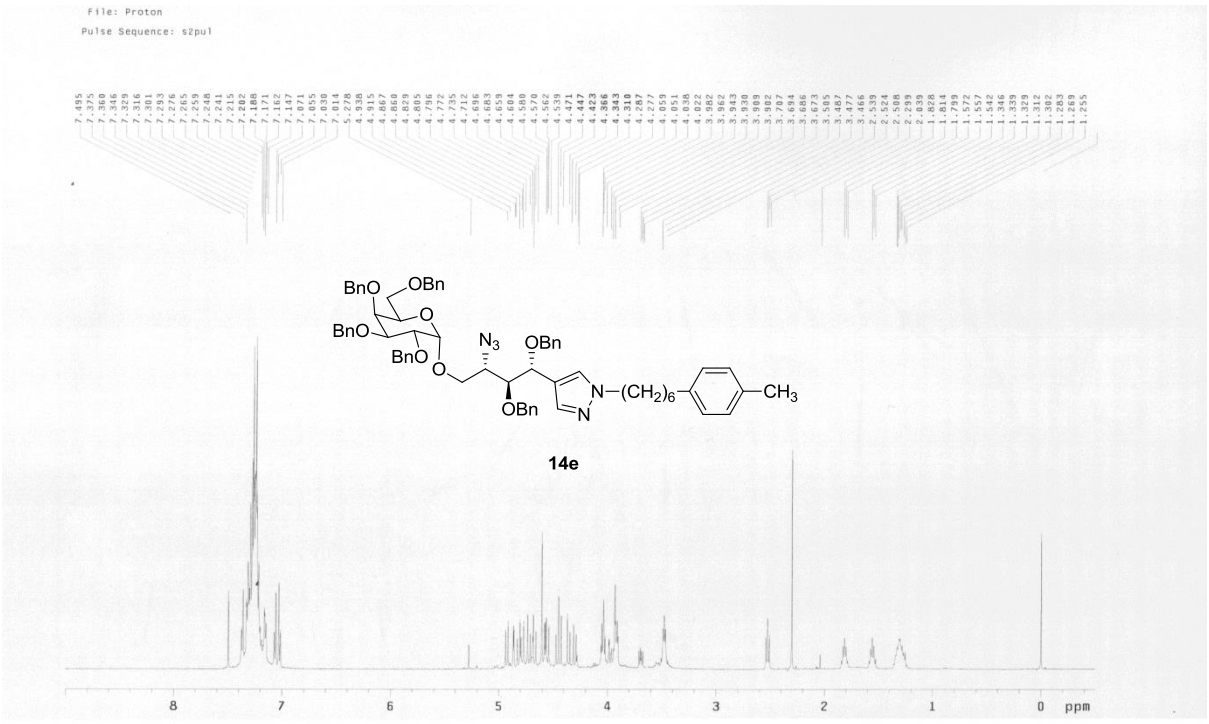
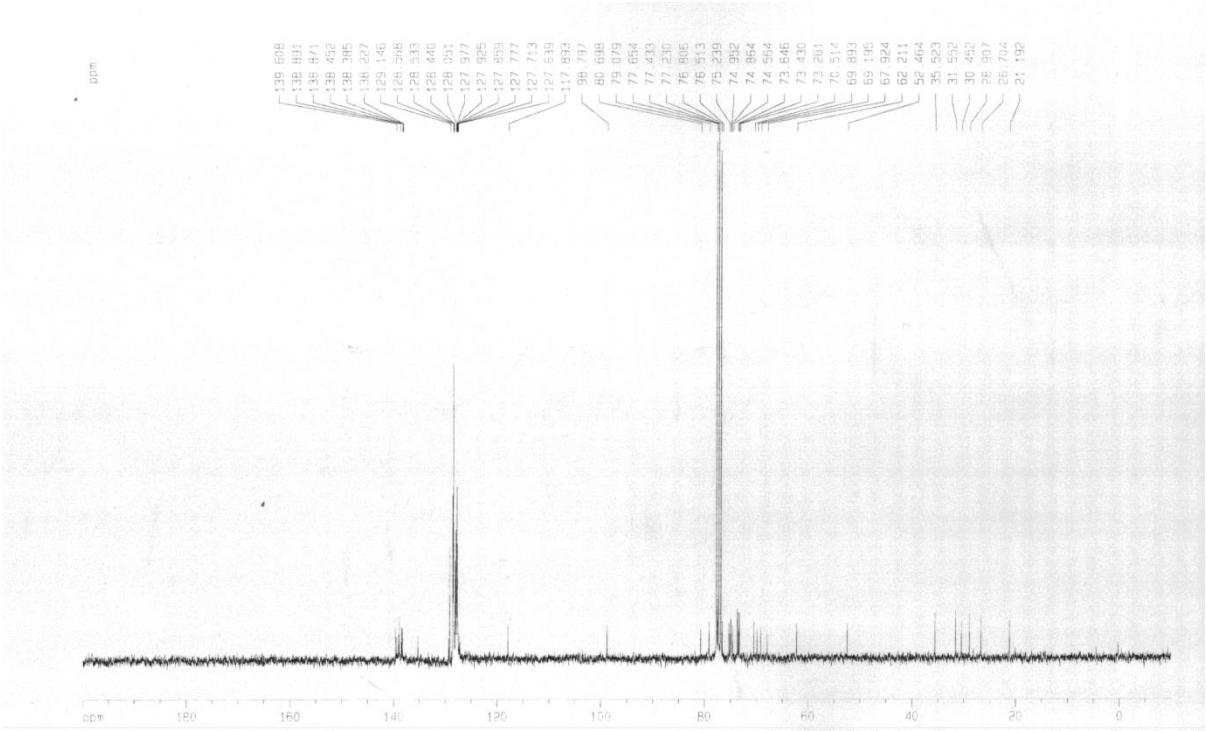
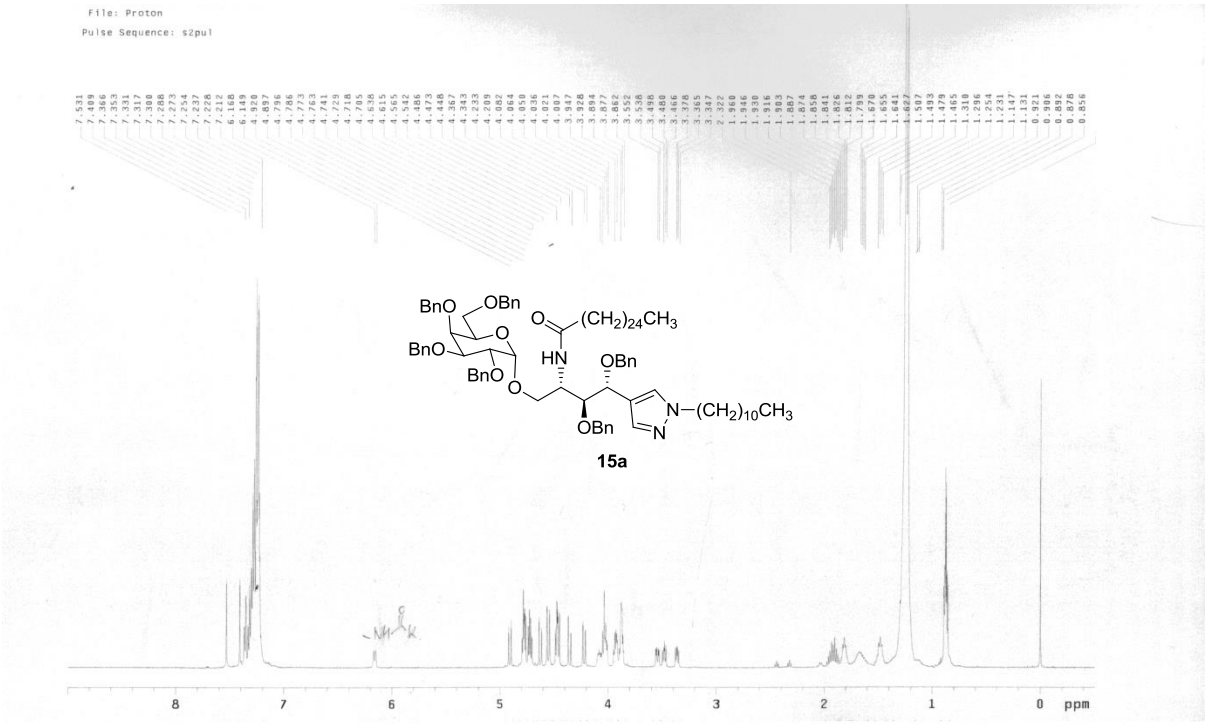
139.621
139.553
139.011
138.901
138.883
138.485
138.408
128.558
128.534
128.463
128.407
128.055
127.970
127.918
127.852
127.784
127.706
127.628
117.848
98.807
80.727
79.080
77.648
77.225
76.802
76.525
75.259
74.951
74.865
74.592
73.645
73.420
73.262
70.501
69.898
69.195
62.244
52.430
35.486
31.195
30.414
28.609
26.516
15.834
ppm
180
160
140
120
100
80
60
40
20
0

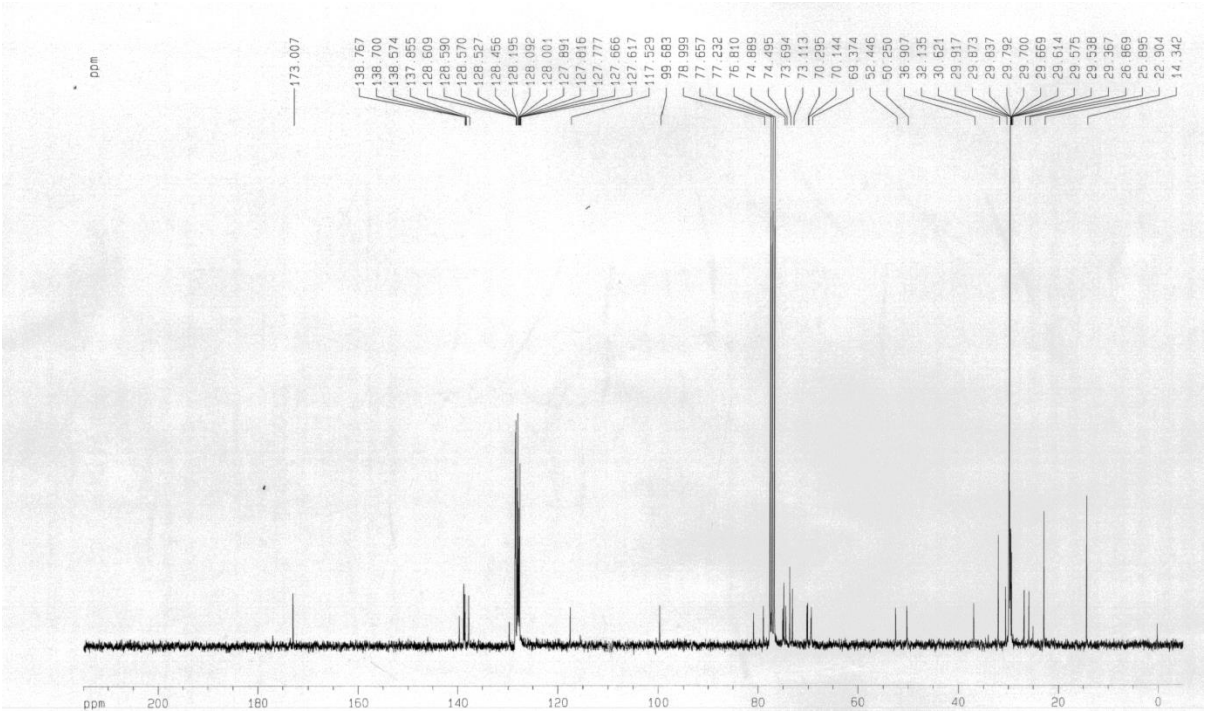

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
N3
OBn
OBn
N
N–(CH2)6
CH3
8
7
6
5
4
3
2
1
0
ppm

14e




File: Proton
Pulse Sequence: s2pul
BnO
OBn
BnO
BnO
O
HN
O
(CH2)24CH3
OBn
OBn
N
N
(CH2)10CH3
8
7
6
5
4
3
2
1
0
ppm

15a


ppm
173.007
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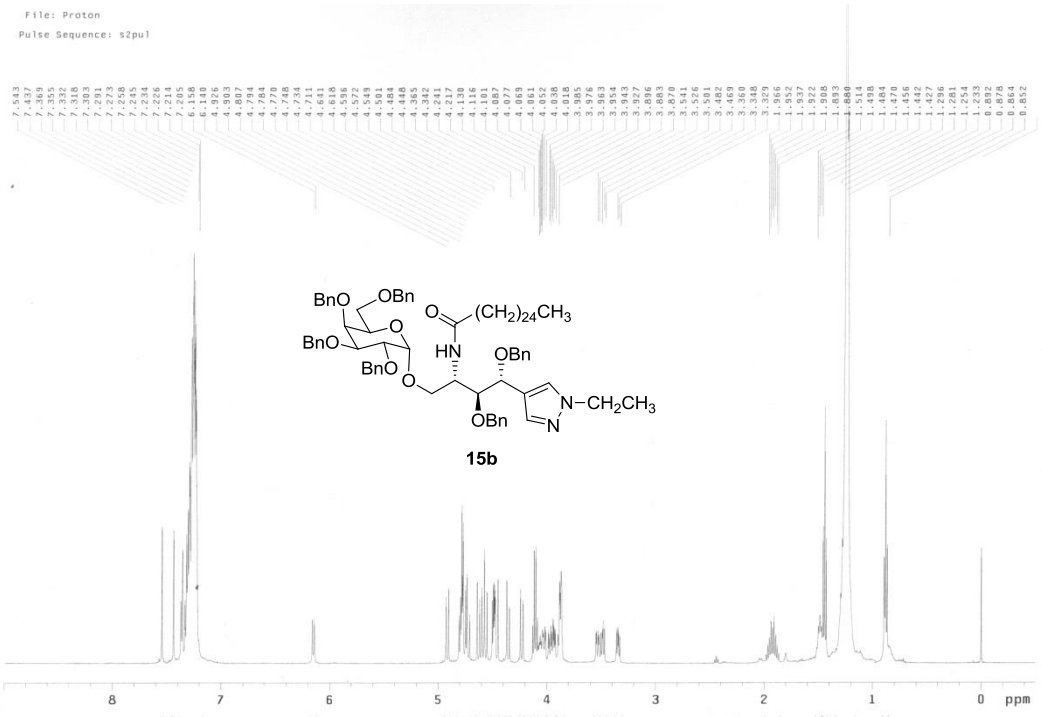
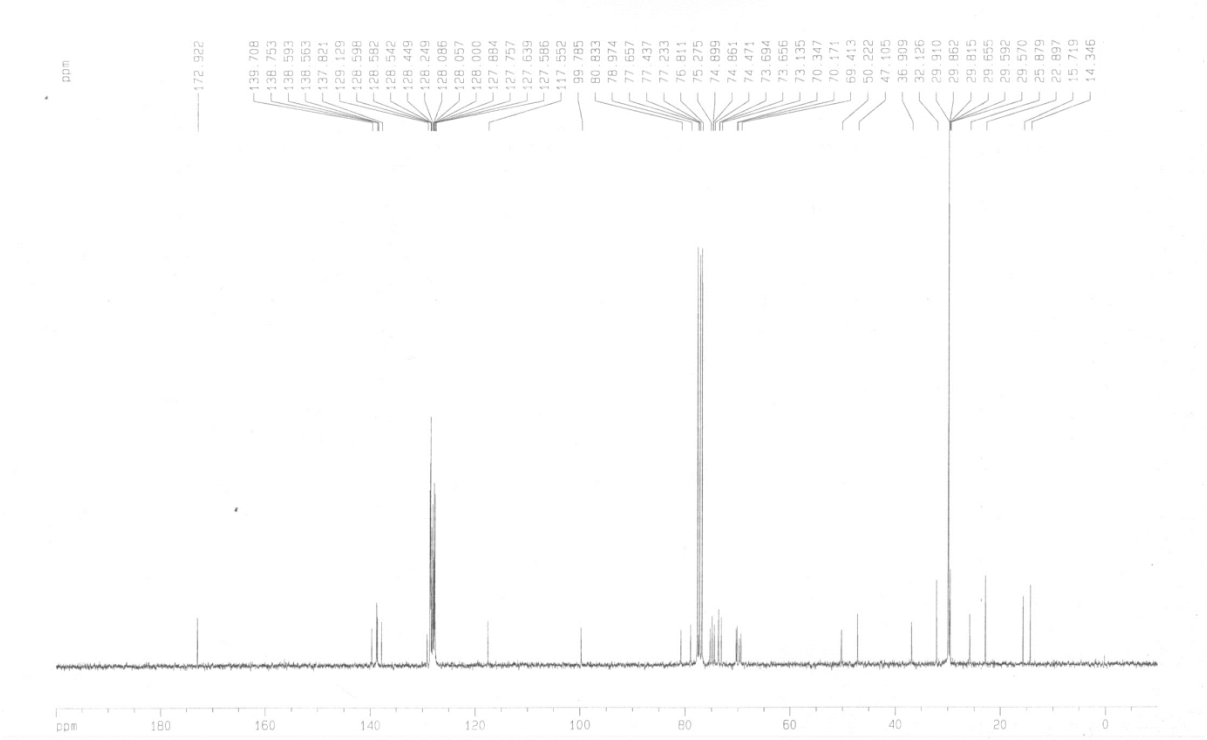
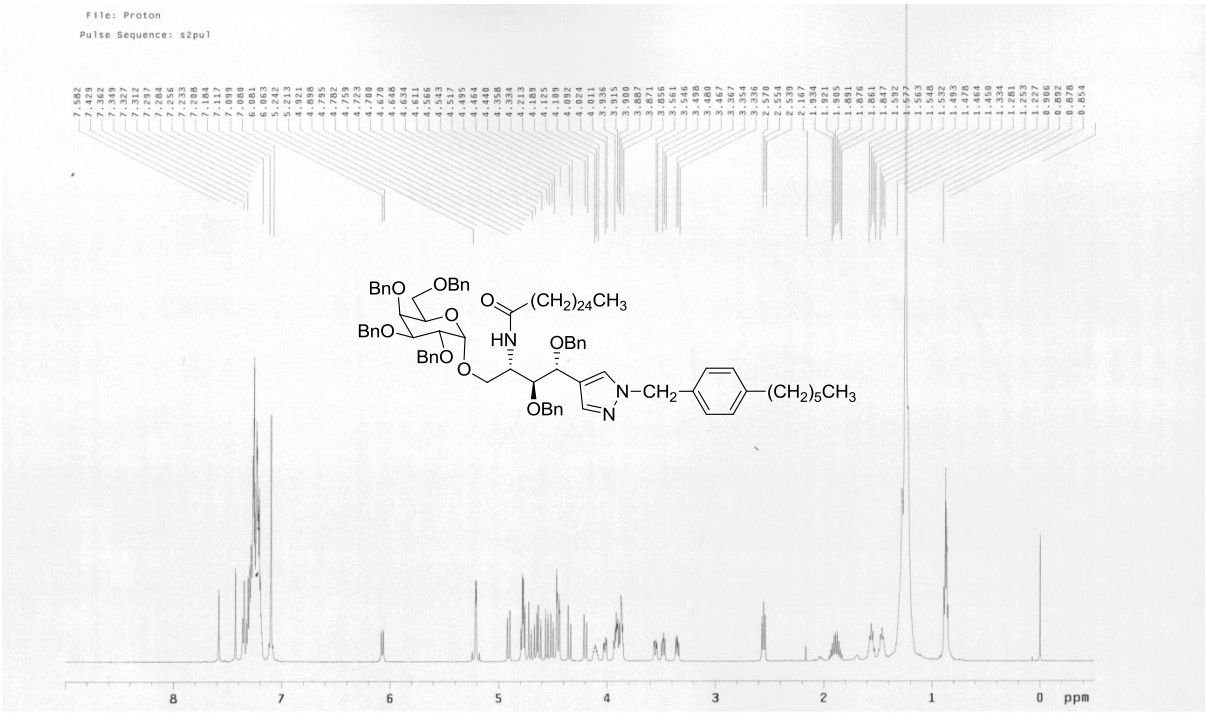
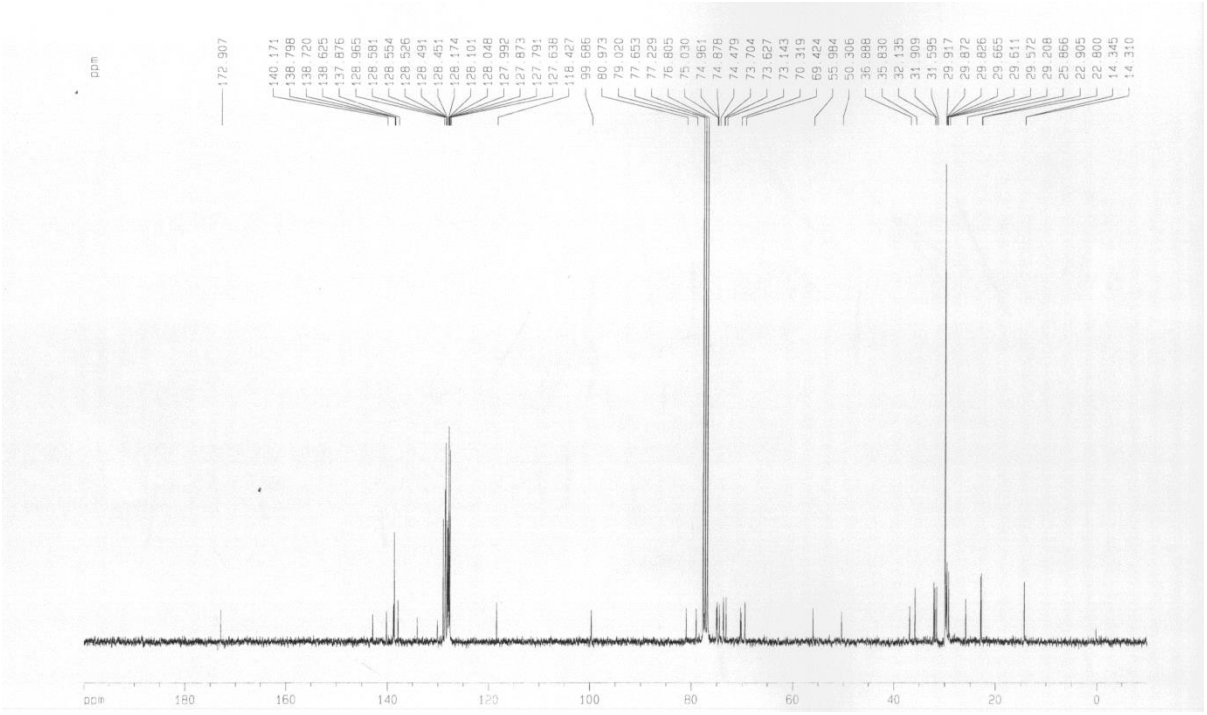
138.700
138.574
137.855
128.609
128.590
128.570
128.527
128.456
128.195
128.092
128.001
127.891
127.816
127.777
127.666
127.617
117.529
99.683
78.999
77.657
77.232
76.810
74.889
74.495
73.694
73.113
70.295
70.144
69.374
52.446
50.250
36.907
32.135
30.621
29.917
29.873
29.837
29.792
29.700
29.669
29.614
29.575
29.538
29.367
26.869
25.895
22.904
14.342
ppm 200 180 160 140 120 100 80 60 40 20 0

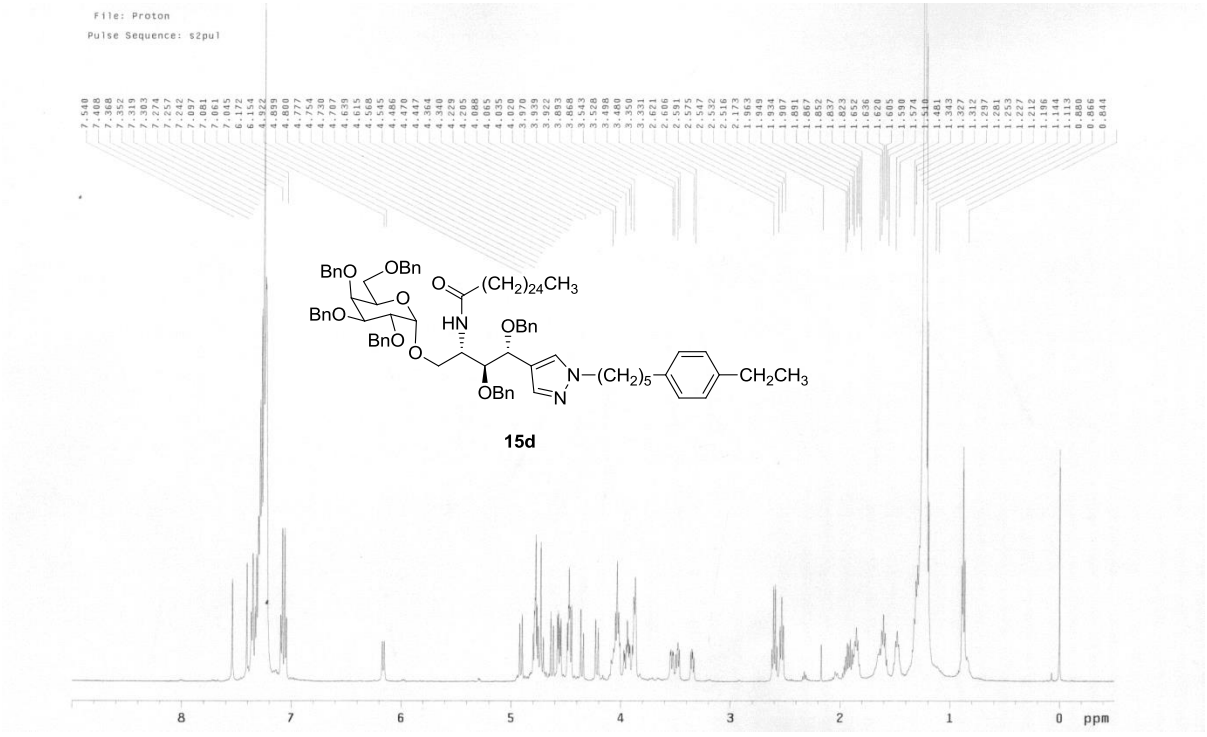

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
HN
O
(CH2)24CH3
OBn
OBn
N
N–CH2CH3
8 7 6 5 4 3 2 1 0 ppm

15b

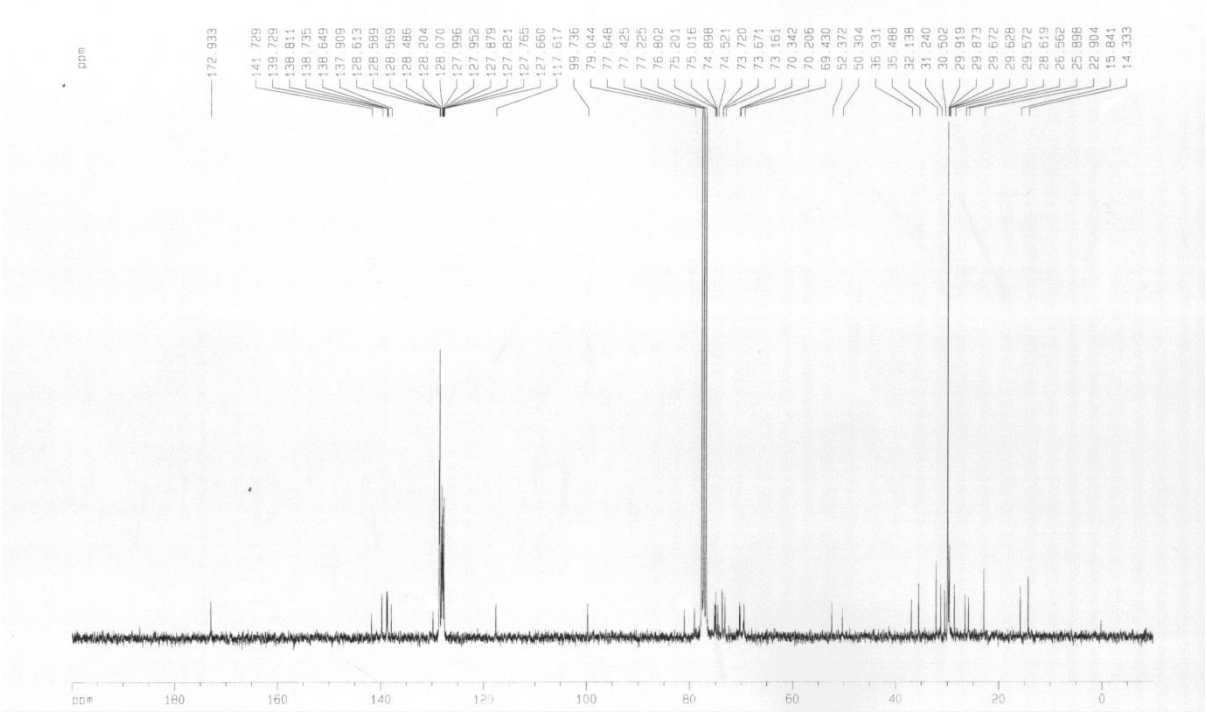

ppm
172.922
139.708
138.753
138.593
138.563
137.821
129.129
128.598
128.582
128.542
128.449
128.249
128.086
128.057
128.000
127.884
127.757
127.639
127.586
117.552
99.785
80.833
78.974
77.657
77.437
77.233
76.811
75.275
74.899
74.861
74.471
73.694
73.656
73.135
70.347
70.171
69.413
50.222
47.105
36.909
32.126
29.910
29.862
29.815
29.655
29.592
29.570
25.879
22.897
15.719
14.346
ppm
180
160
140
120
100
80
60
40
20
0

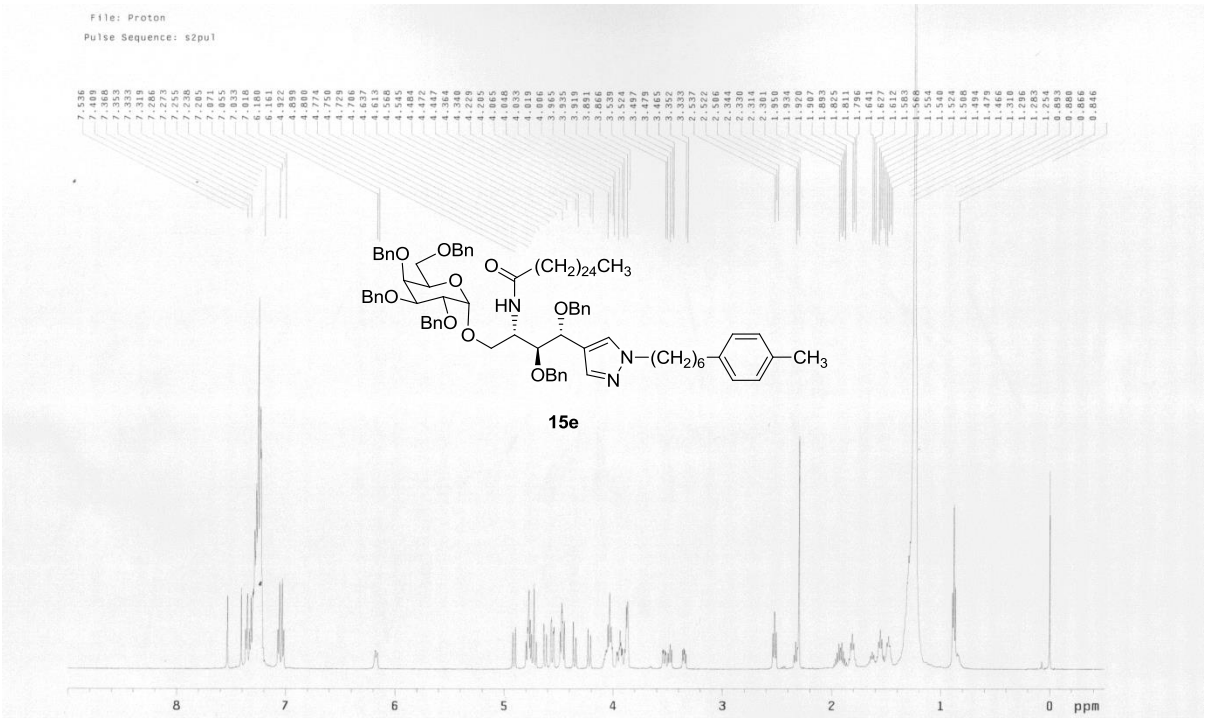

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
HN
O
(CH2)24CH3
OBn
OBn
N
N
CH2
(CH2)5CH3
8
7
6
5
4
3
2
1
0
ppm



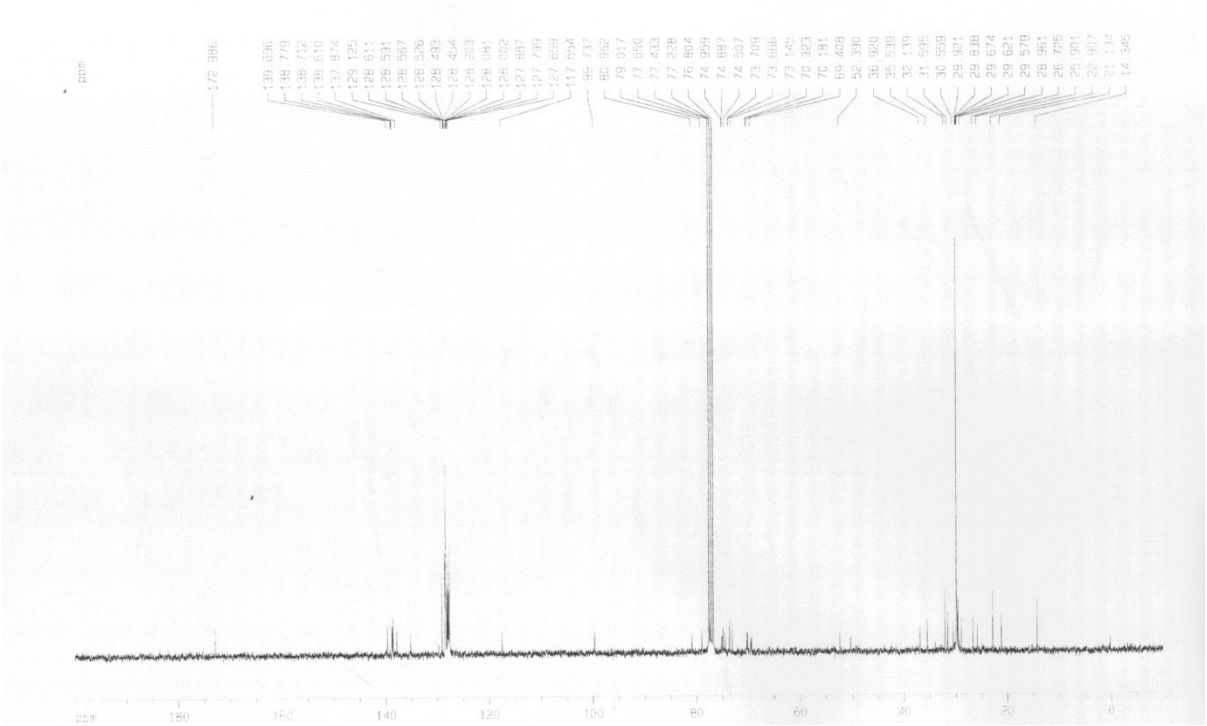

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
(CH2)24CH3
HN
OBn
N
(CH2)5
CH2CH3
ppm

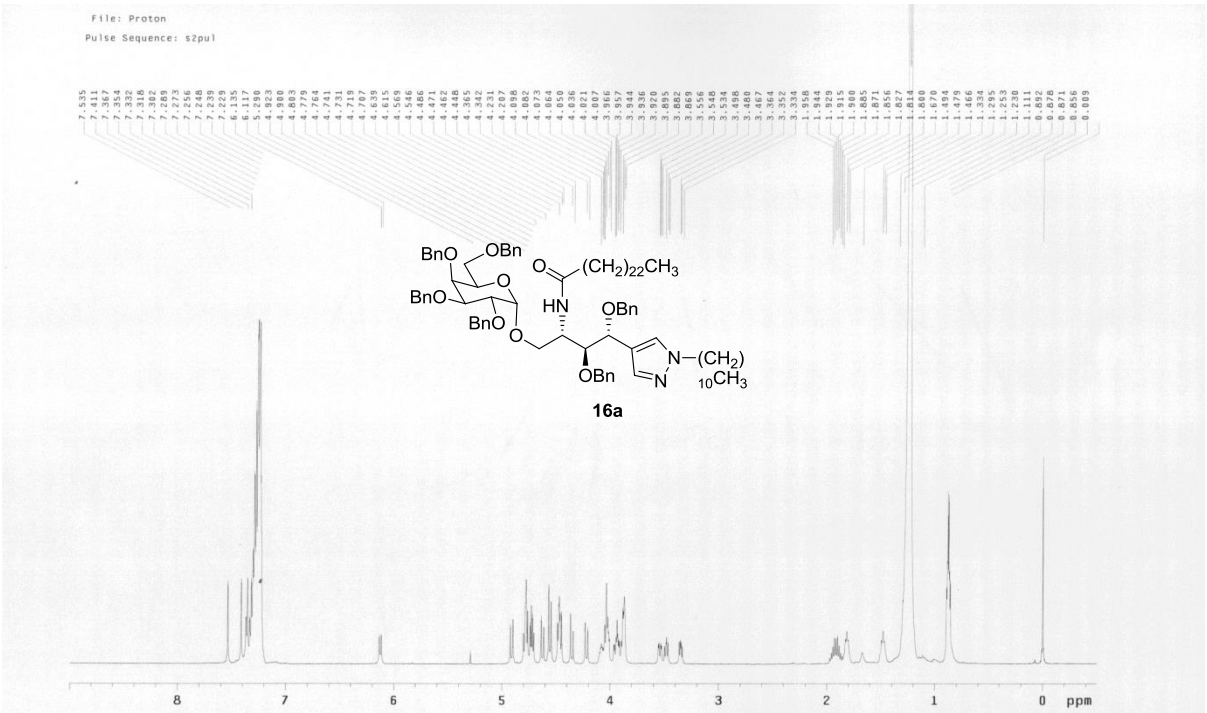
15d



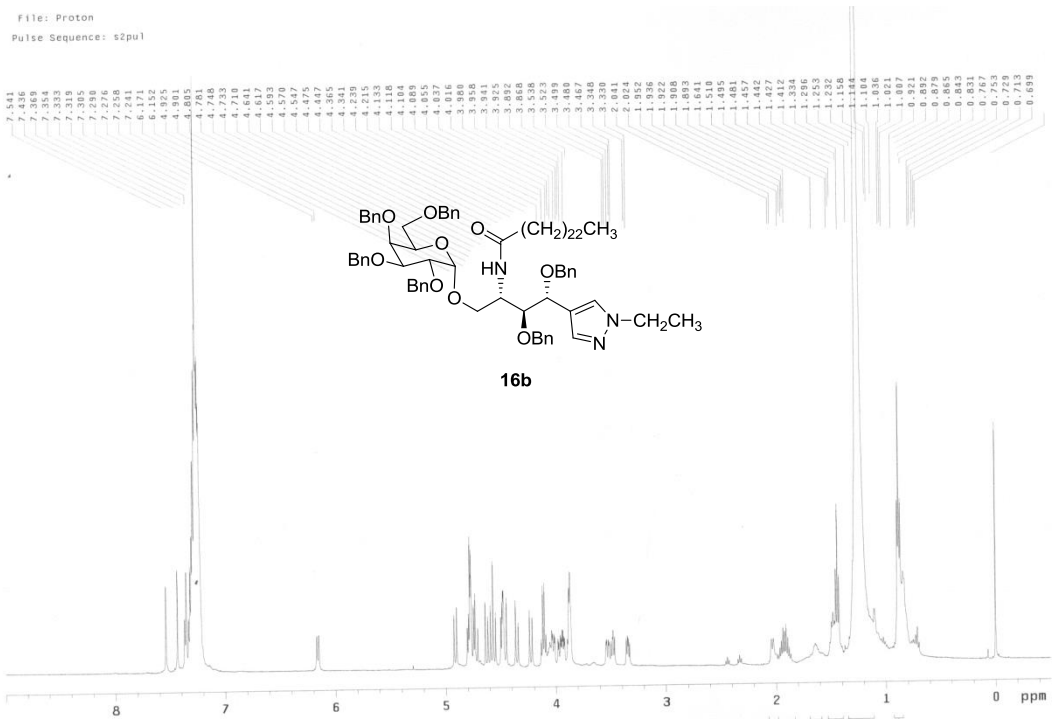

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
HN
O
(CH2)24CH3
OBn
OBn
N
N
(CH2)6
CH3
8
7
6
5
4
3
2
1
0
ppm

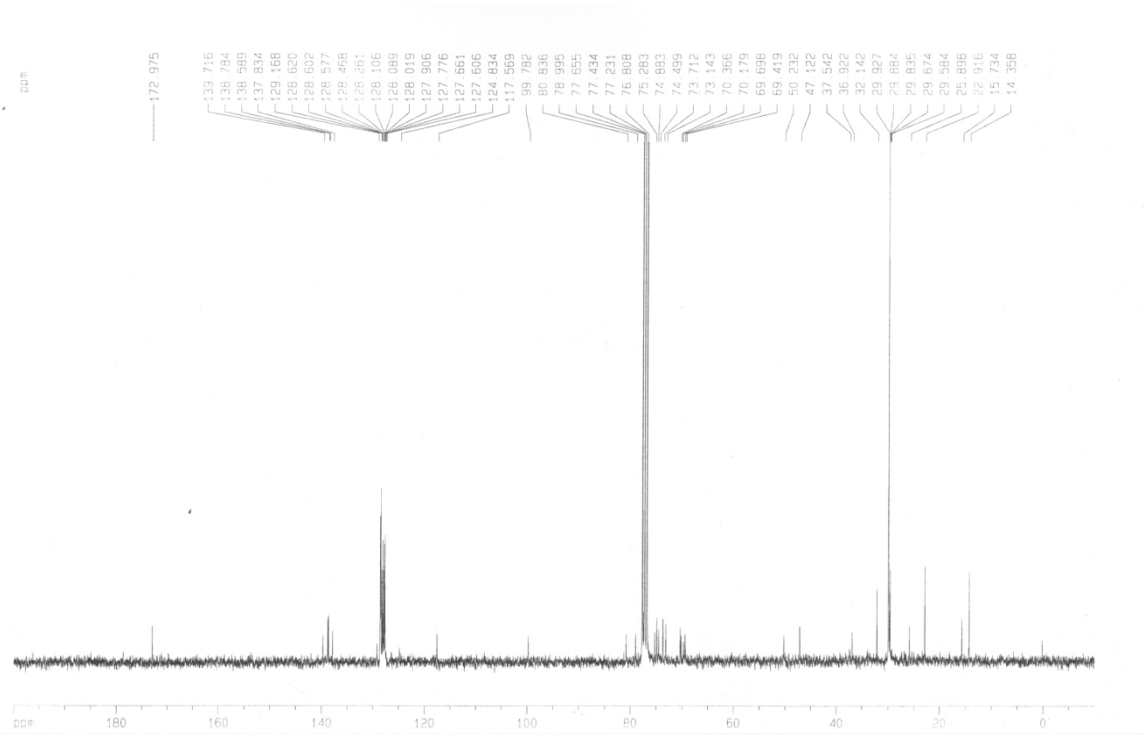
15e

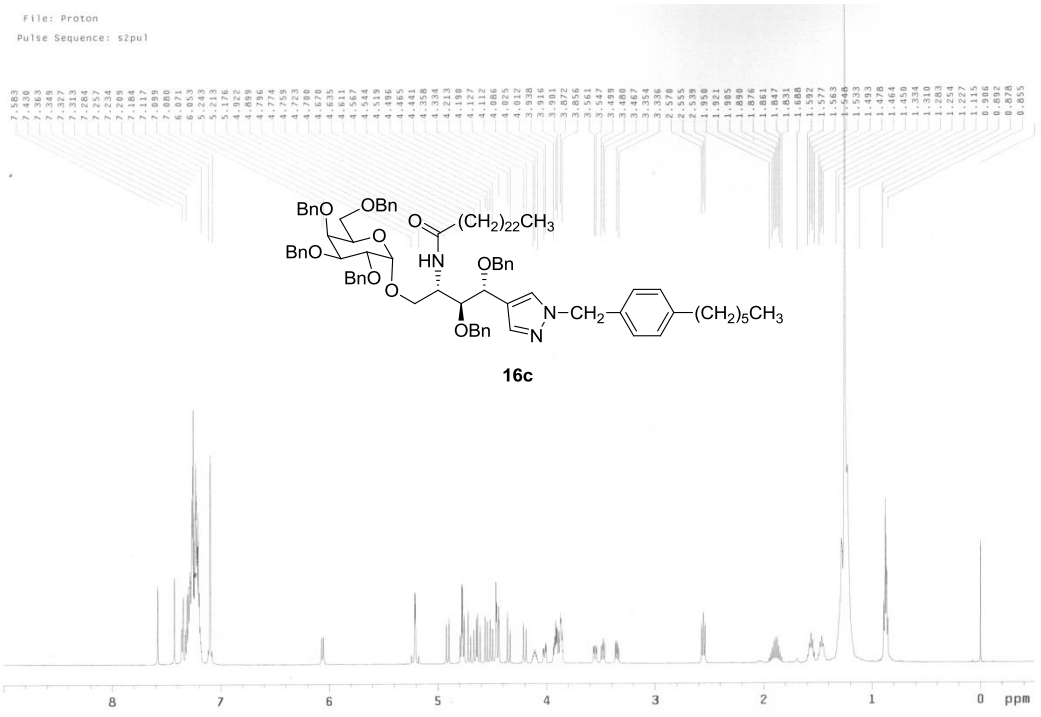



File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
HN
O
(CH2)22CH3
OBn
OBn
N
N
(CH2)
10CH3
8
7
6
5
4
3
2
1
0
ppm

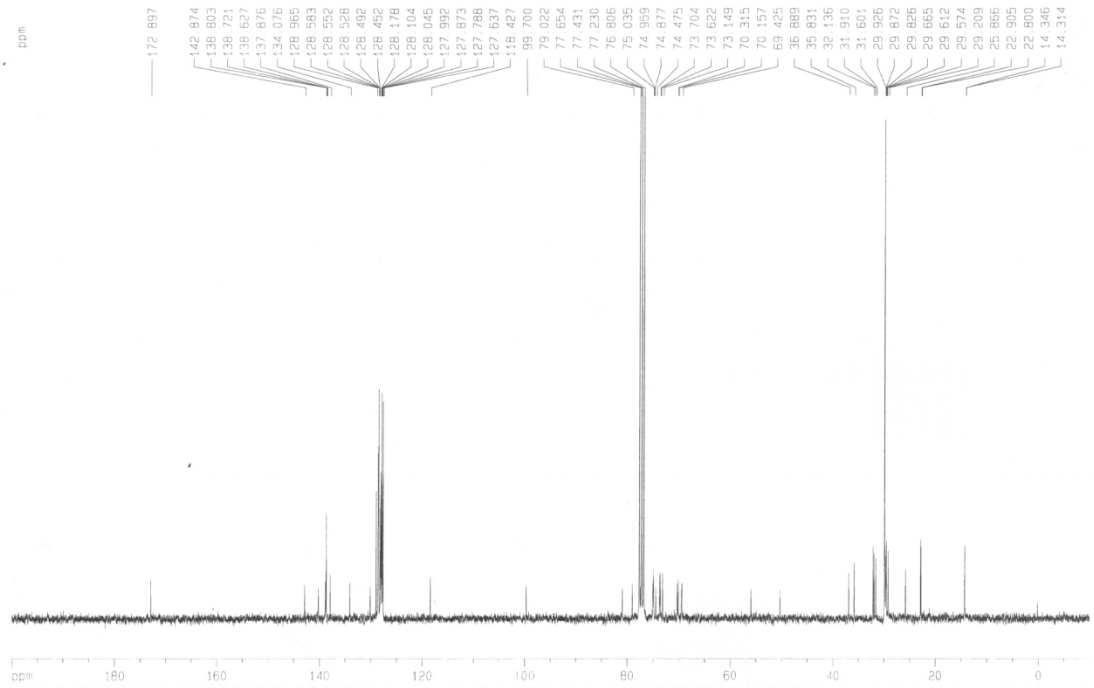
16a

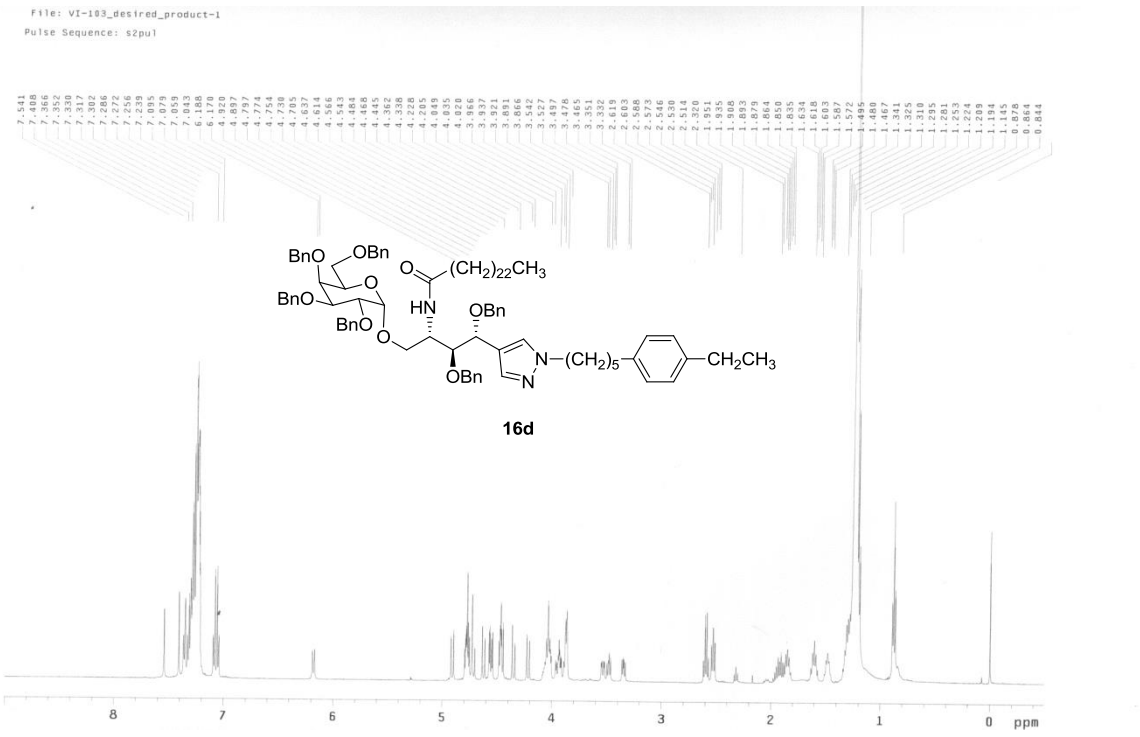

File: Proton
Pulse Sequence: s2pul
BnO
OBn
BnO
BnO
O
O
HN
O
(CH2)22CH3
OBn
OBn
N
N
CH2CH3
16b
8
7
6
5
4
3
2
1
0
ppm


ppm
172.975
139.716
138.784
138.589
137.834
129.168
128.620
128.602
128.577
128.468
128.361
128.106
128.089
128.019
127.906
127.776
127.661
127.606
124.834
117.569
99.782
80.836
78.995
77.655
77.434
77.231
76.808
75.283
74.883
74.499
73.712
73.143
70.366
70.179
69.698
69.419
50.232
47.122
37.542
36.922
32.142
29.927
29.884
29.835
29.674
29.584
25.898
22.916
15.734
14.358
ppm
180
160
140
120
100
80
60
40
20
0

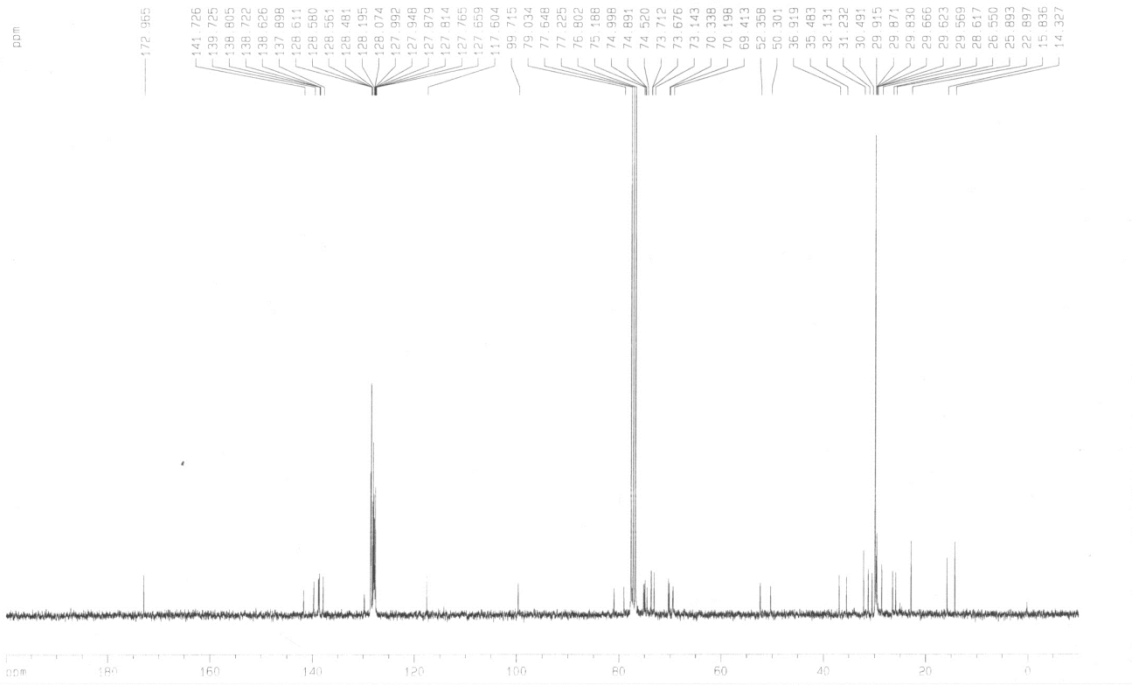

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
HN
O
(CH2)22CH3
OBn
OBn
N
N–CH2
(CH2)5CH3
8
7
6
5
4
3
2
1
0
ppm

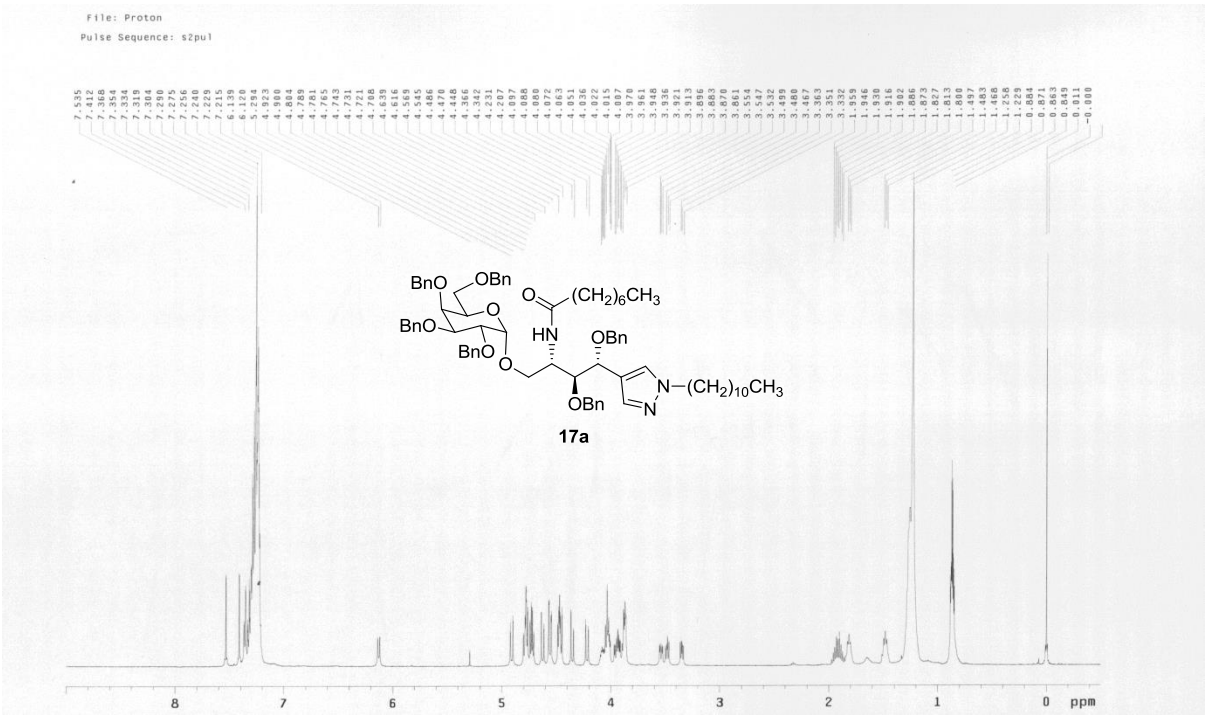
16c


ppm
172.897
142.874
138.803
138.721
138.627
137.876
134.076
128.965
128.583
128.552
128.528
128.492
128.452
128.178
128.104
128.045
127.992
127.873
127.788
127.637
118.427
99.700
79.022
77.654
77.431
77.230
76.806
75.035
74.959
74.877
74.475
73.704
73.622
73.149
70.315
70.157
69.425
36.889
35.831
32.136
31.910
31.601
29.926
29.872
29.826
29.665
29.612
29.574
29.209
25.866
22.905
22.800
14.346
14.314
ppm
180
160
140
120
100
80
60
40
20
0

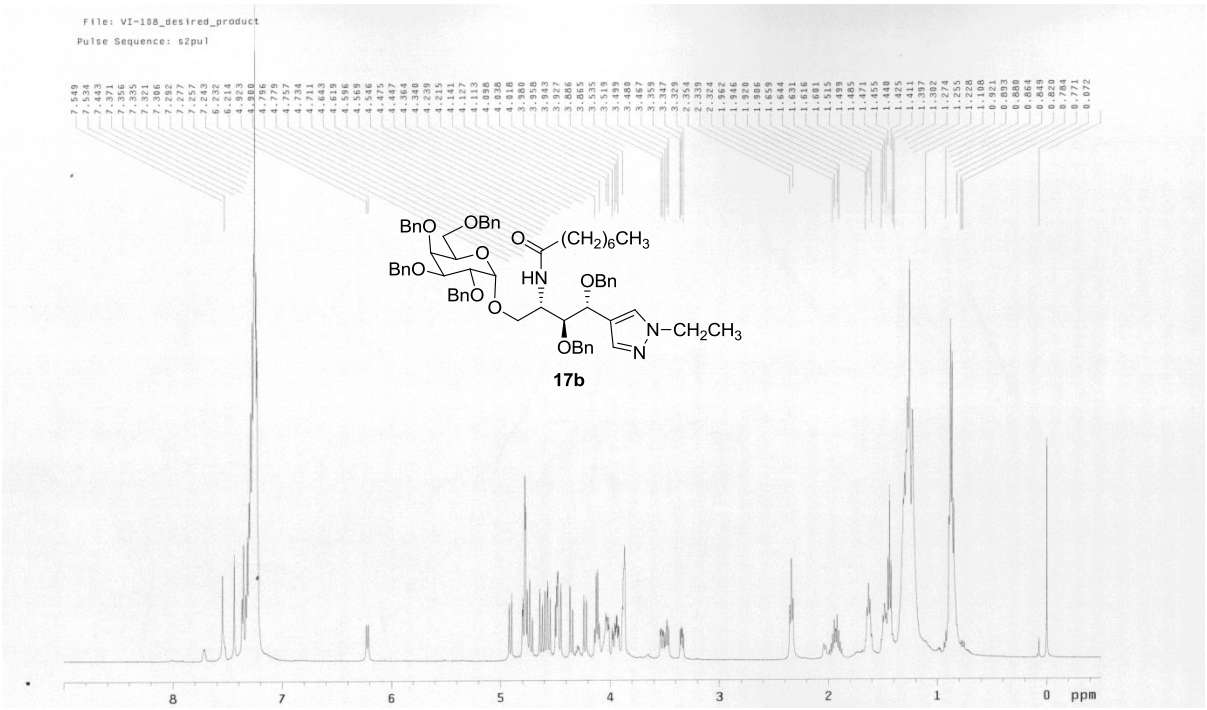

File: VI-103_desired_product-1
Pulse Sequence: s2pul
BnO
OBn
BnO
BnO
O
HN
O
(CH2)22CH3
OBn
OBn
N
N
(CH2)5
CH2CH3
8
7
6
5
4
3
2
1
0
ppm

16d

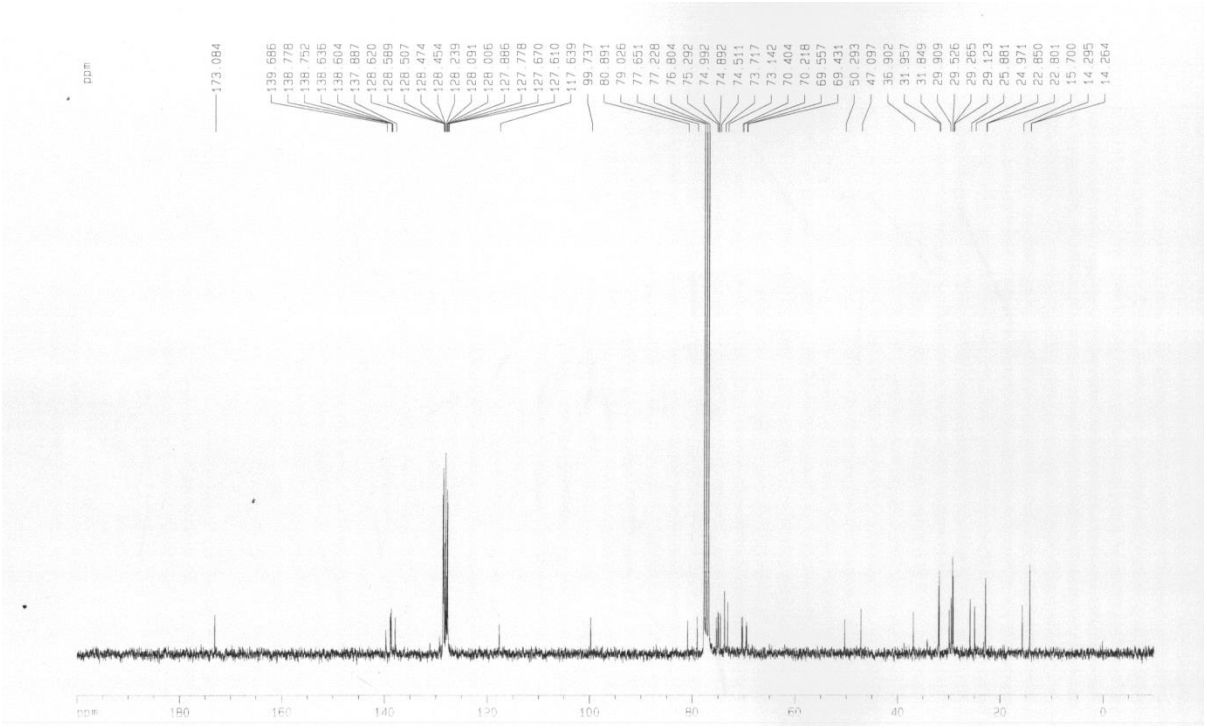

ppm
172.965
141.726
139.725
138.805
138.722
138.626
137.898
128.611
128.580
128.561
128.481
128.195
128.074
127.992
127.948
127.879
127.814
127.765
127.659
117.604
99.715
79.034
77.648
77.225
76.802
75.186
74.998
74.891
74.520
73.712
73.676
73.143
70.338
70.198
69.413
52.358
50.301
36.919
35.483
32.131
31.232
30.491
29.915
29.871
29.830
29.666
29.623
29.569
28.617
26.550
25.893
22.897
15.836
14.327
ppm
180
160
140
120
100
80
60
40
20
0

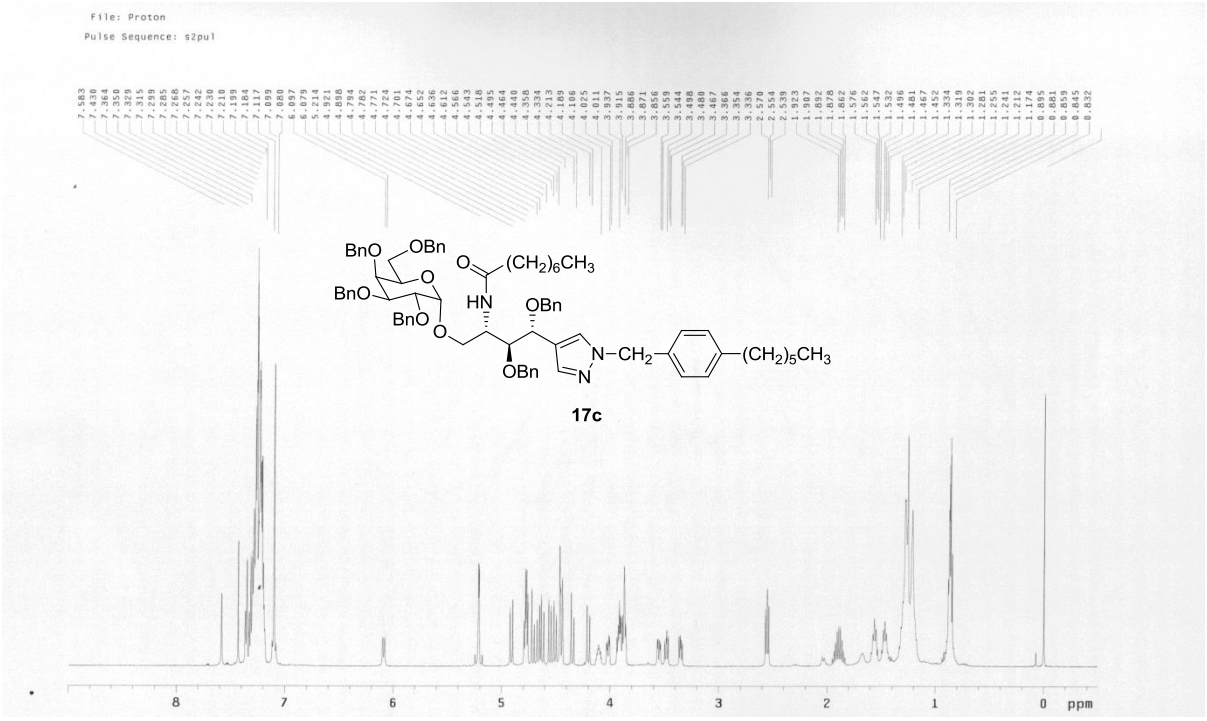

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
HN
O
(CH2)6CH3
OBn
OBn
N
N
(CH2)10CH3
8
7
6
5
4
3
2
1
0
ppm

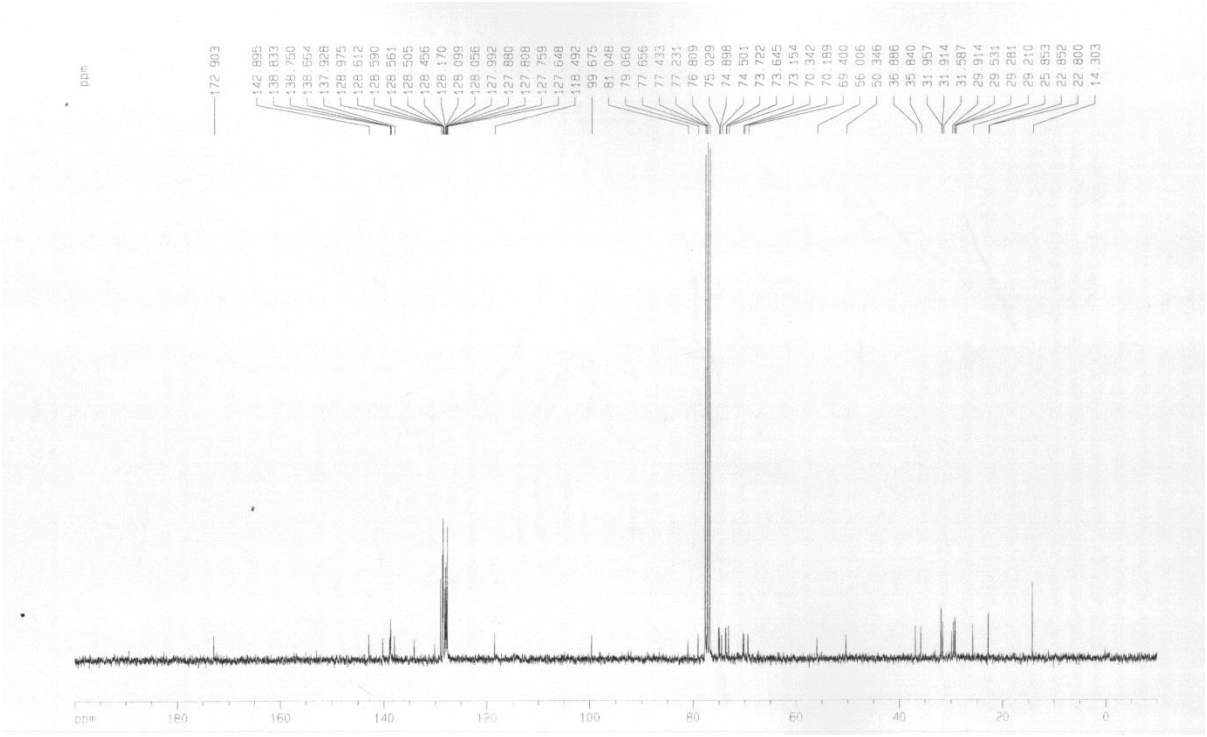
17a

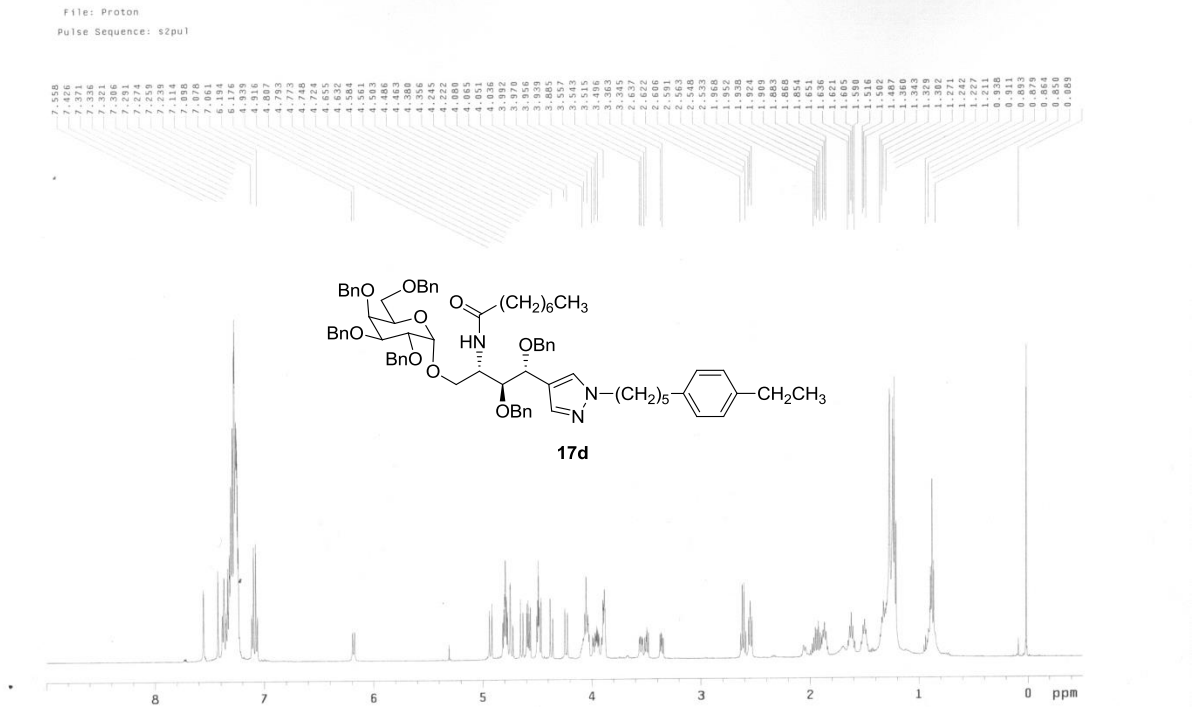

File: VI-108_desired_product
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
HN
O
(CH2)6CH3
OBn
OBn
N
N
CH2CH3
8
7
6
5
4
3
2
1
0
ppm

17b

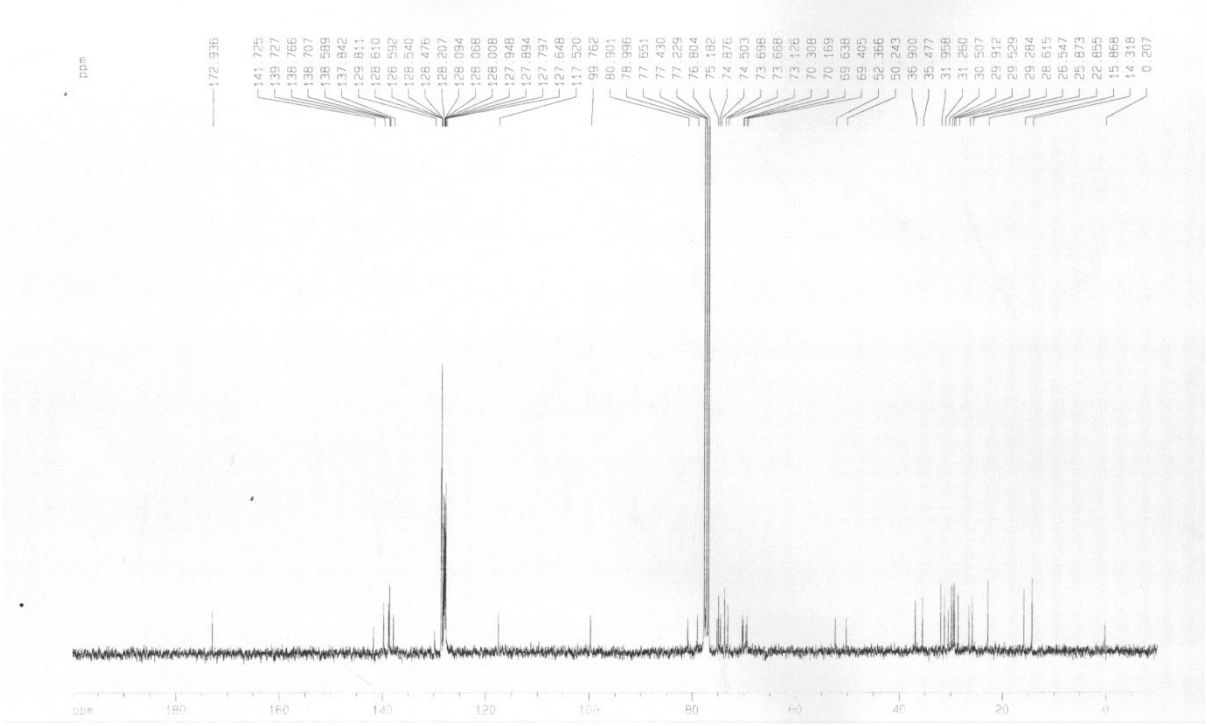

ppm
173.084
139.686
138.778
138.752
138.636
138.604
137.887
128.620
128.589
128.507
128.474
128.454
128.239
128.091
128.006
127.886
127.778
127.670
127.610
117.639
99.737
80.891
79.026
77.651
77.228
76.804
75.292
74.992
74.892
74.511
73.717
73.142
70.404
70.218
69.557
69.431
50.293
47.097
36.902
31.957
31.849
29.909
29.526
29.265
29.123
25.881
24.971
22.850
22.801
15.700
14.295
14.264
ppm
180
160
140
120
100
80
60
40
20
0

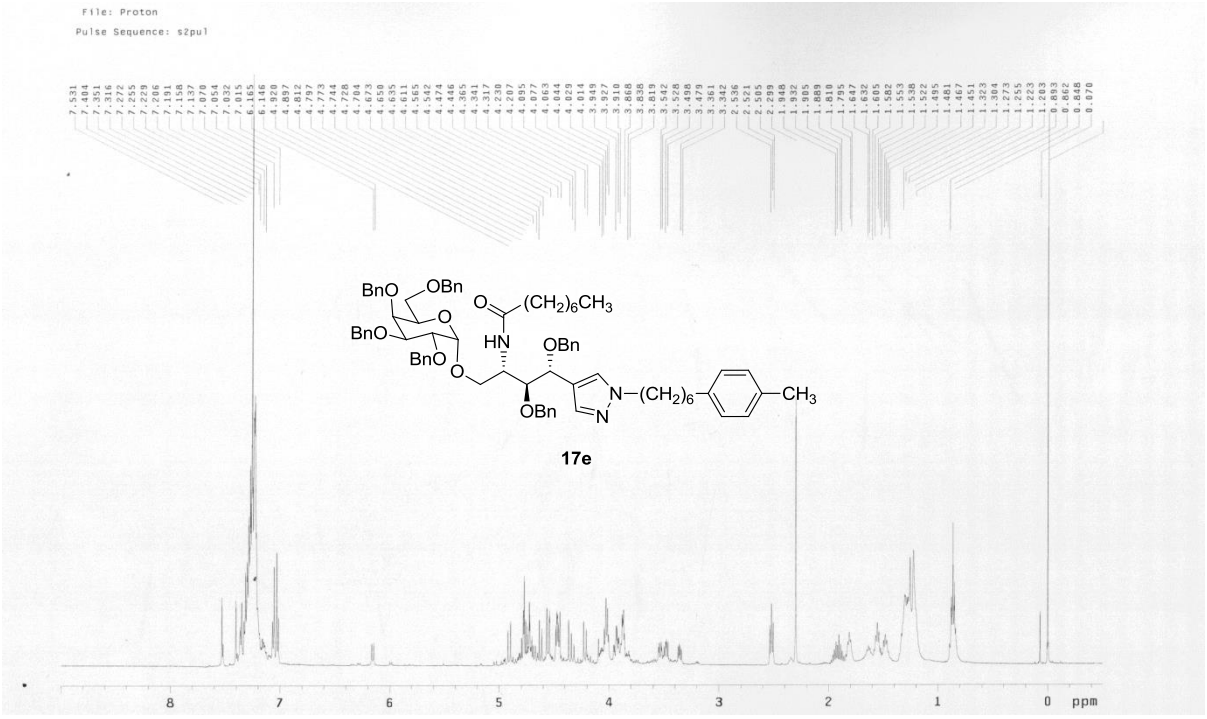

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
BnO
BnO
O
HN
O
(CH2)6CH3
OBn
OBn
N
N
CH2
(CH2)5CH3
17c
8
7
6
5
4
3
2
1
0
ppm

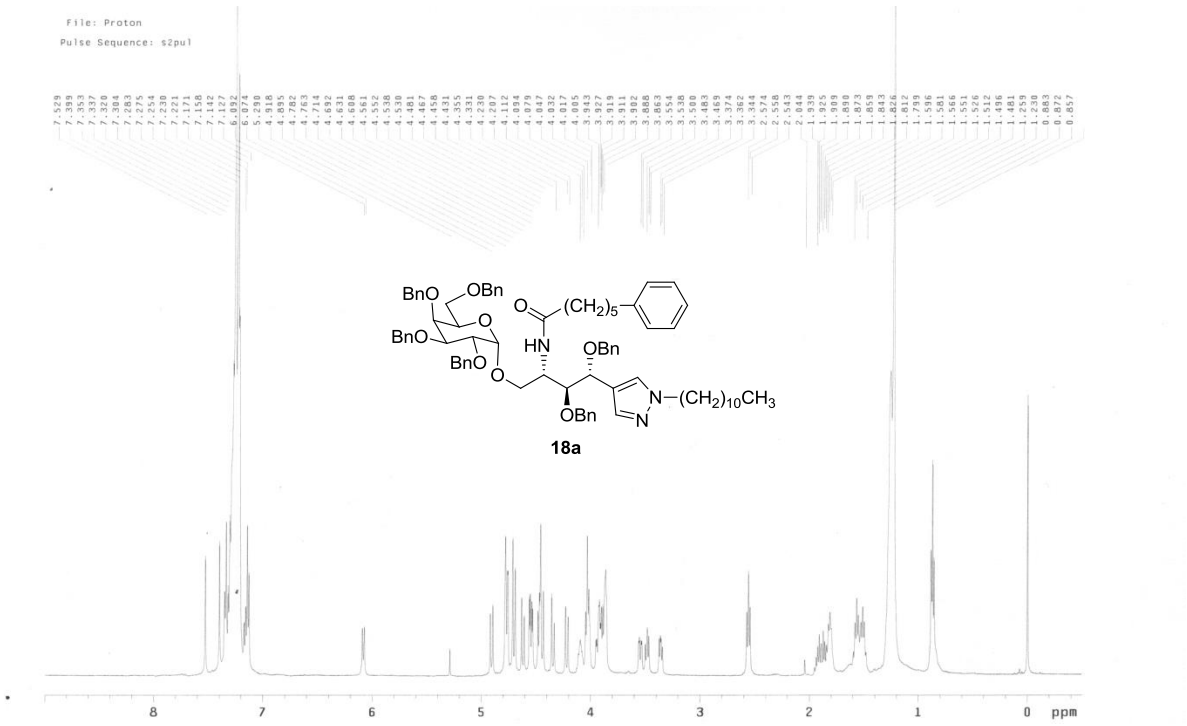




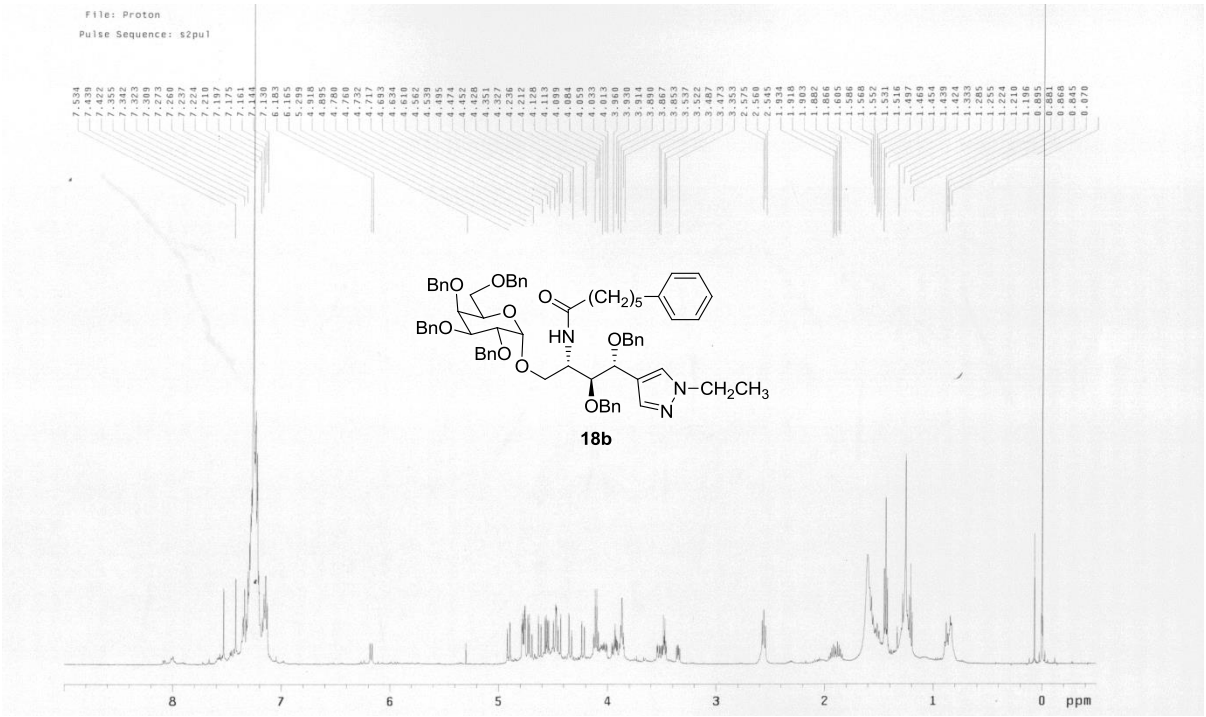
17d


ppm
172.936
141.725
139.727
138.766
138.707
138.589
137.842
129.811
128.610
128.592
128.540
128.476
128.207
128.094
128.068
128.008
127.948
127.894
127.797
127.648
127.520
99.762
80.901
78.996
77.651
77.430
77.229
76.804
75.182
74.876
74.503
73.698
73.668
73.126
70.308
70.169
69.638
69.405
52.366
50.243
36.900
35.477
31.958
31.260
30.507
29.912
29.539
29.284
28.615
26.547
25.873
22.855
15.868
14.318
0.207
ppm
180
160
140
120
100
80
60
40
20
0

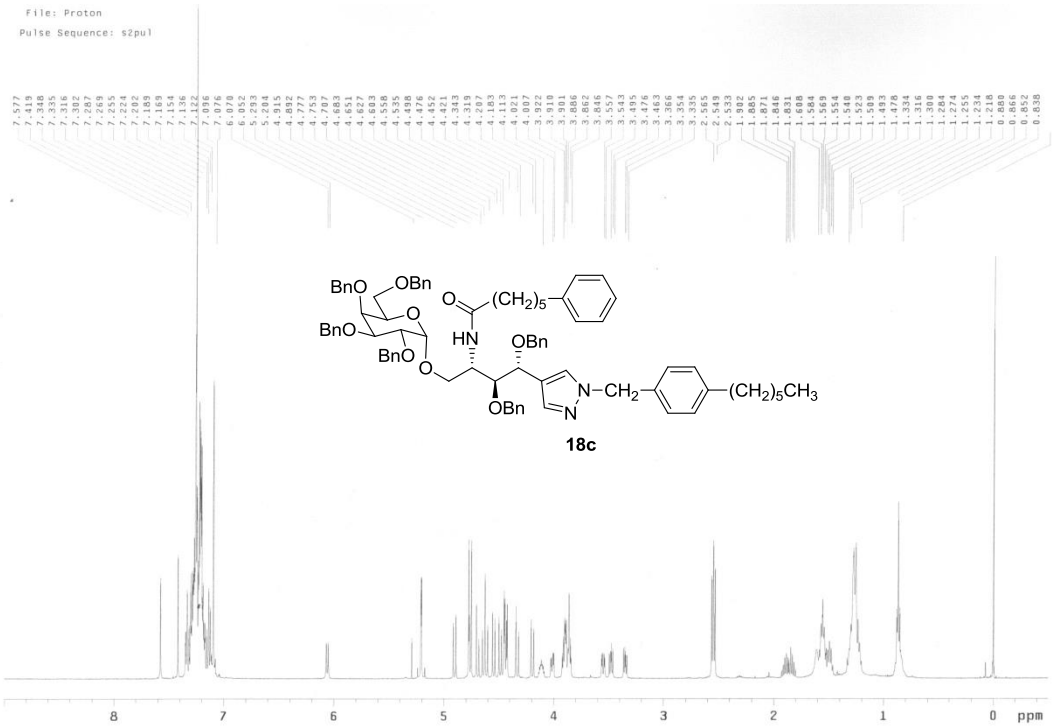

File: Proton
Pulse Sequence: s2pul
7.531
7.404
7.351
7.316
7.272
7.255
7.229
7.206
7.191
7.158
7.137
7.078
7.054
7.032
7.015
6.165
6.146
4.928
4.897
4.817
4.797
4.773
4.744
4.728
4.704
4.673
4.658
4.635
4.611
4.565
4.542
4.527
4.446
4.365
4.341
4.317
4.230
4.207
4.195
4.077
4.063
4.029
4.014
3.949
3.927
3.910
3.868
3.838
3.819
3.542
3.526
3.498
3.479
3.361
3.342
2.536
2.522
2.505
2.299
1.948
1.905
1.888
1.810
1.795
1.647
1.632
1.605
1.552
1.538
1.522
1.495
1.481
1.467
1.451
1.323
1.304
1.273
1.255
1.223
1.203
0.883
0.862
0.848
0.070
BnO
OBn
BnO
BnO
O
O
HN
O
(CH2)6CH3
OBn
OBn
N
N
(CH2)6
CH3
17e
8
7
6
5
4
3
2
1
0
ppm


File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
(CH2)5
HN
OBn
BnO
BnO
O
OBn
N
N–(CH2)10CH3
8
7
6
5
4
3
2
1
0
ppm

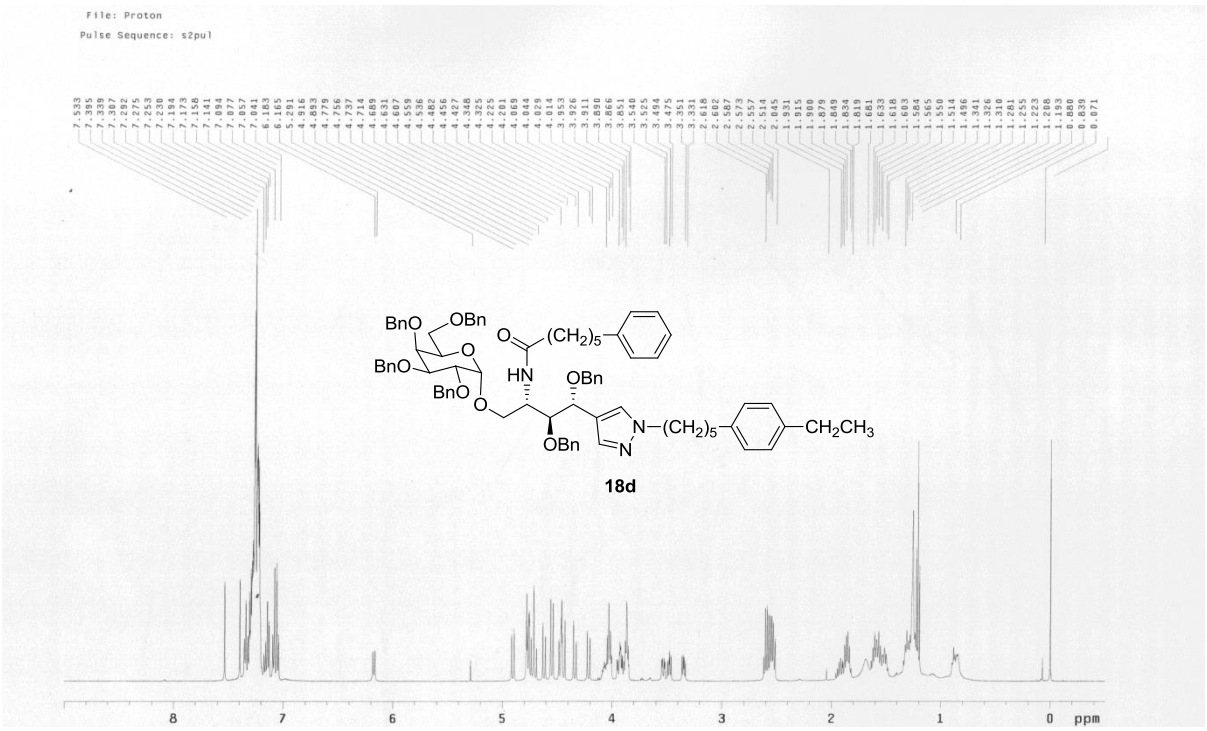
18a


File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
(CH2)5
HN
OBn
BnO
BnO
O
OBn
N
N–CH2CH3
8
7
6
5
4
3
2
1
0
ppm

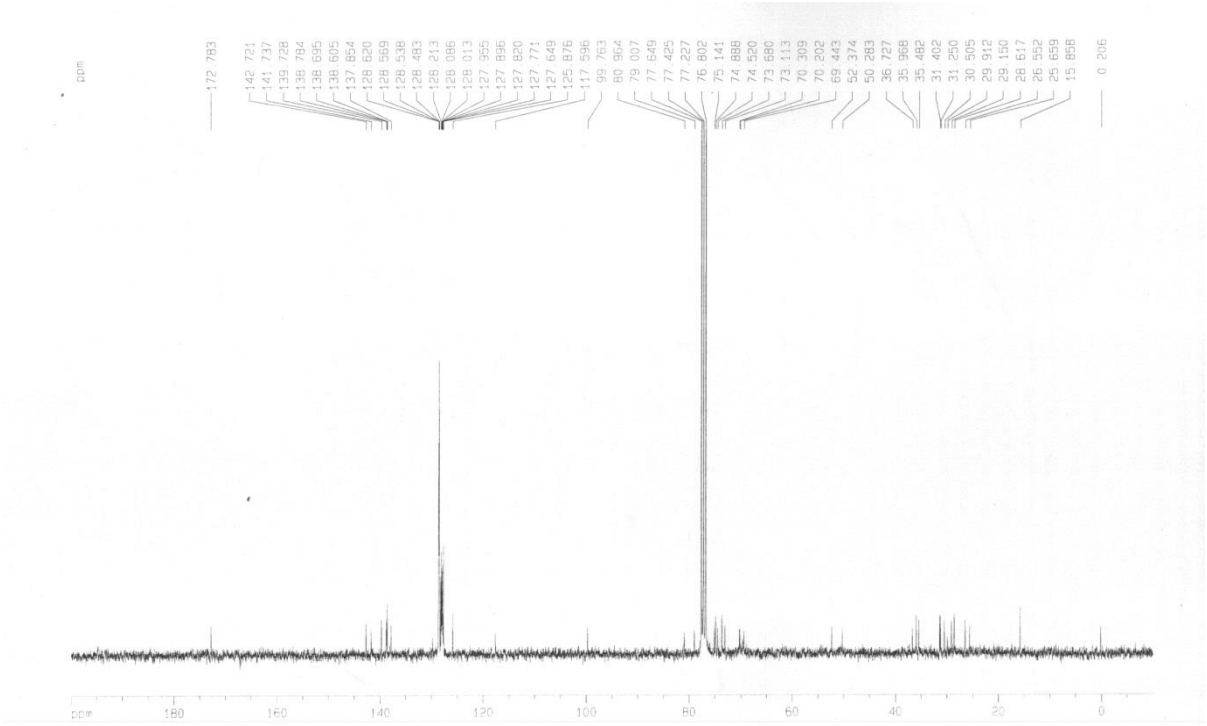
18b

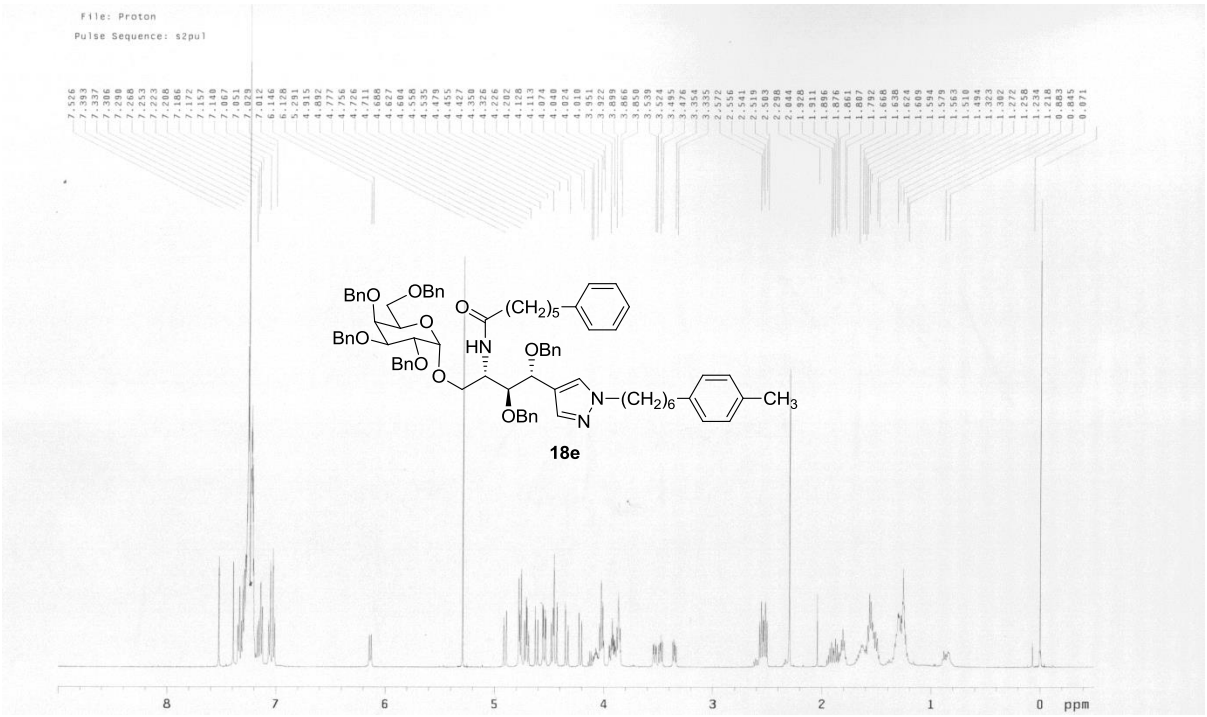

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
(CH2)5
HN
OBn
N–CH2
(CH2)5CH3
N
8
7
6
5
4
3
2
1
0
ppm

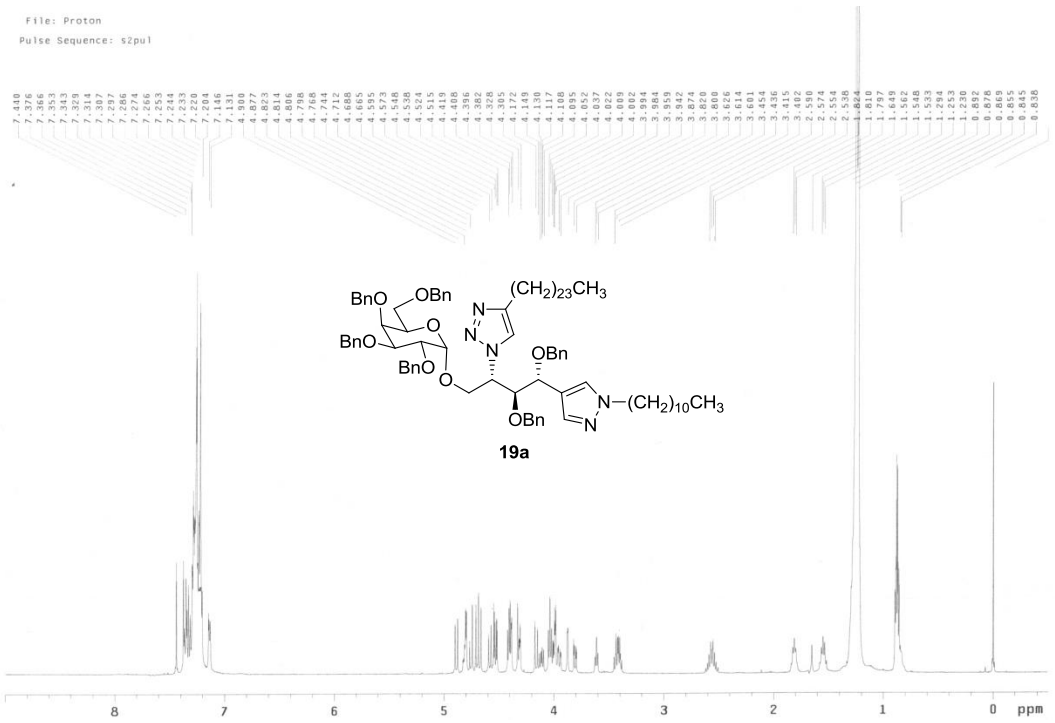
18c


File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
(CH2)5
HN
OBn
N–(CH2)5
CH2CH3
N
8
7
6
5
4
3
2
1
0
ppm

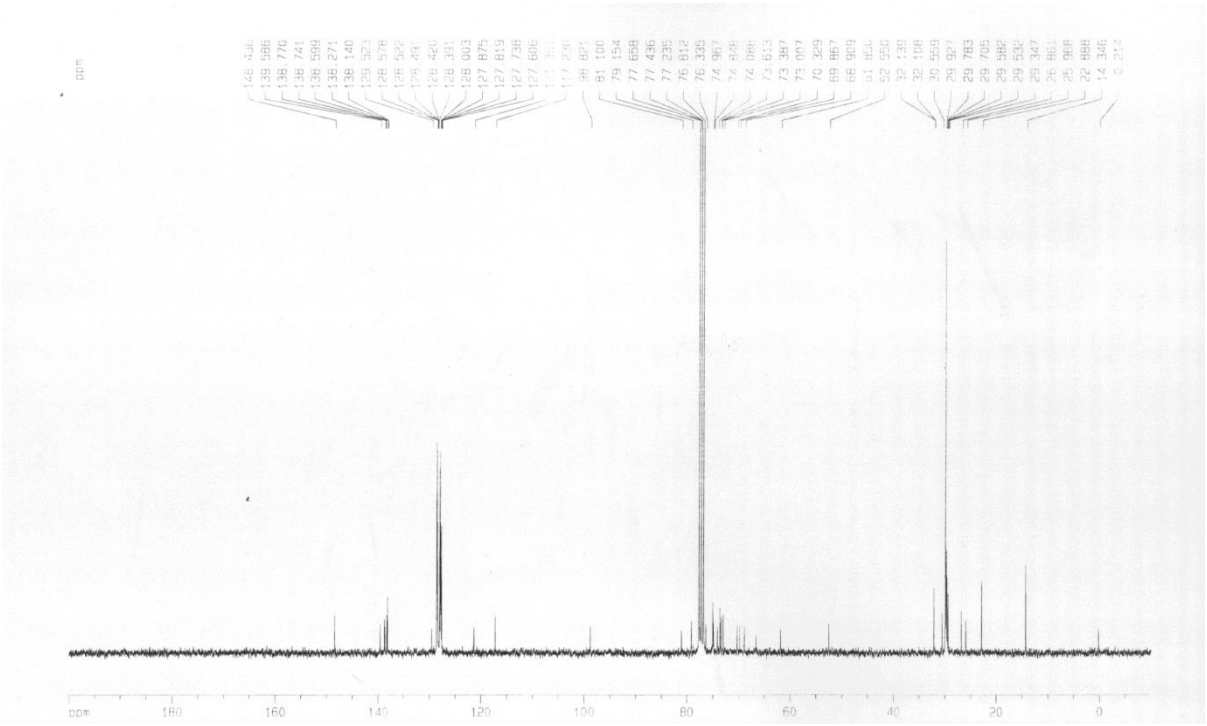
18d

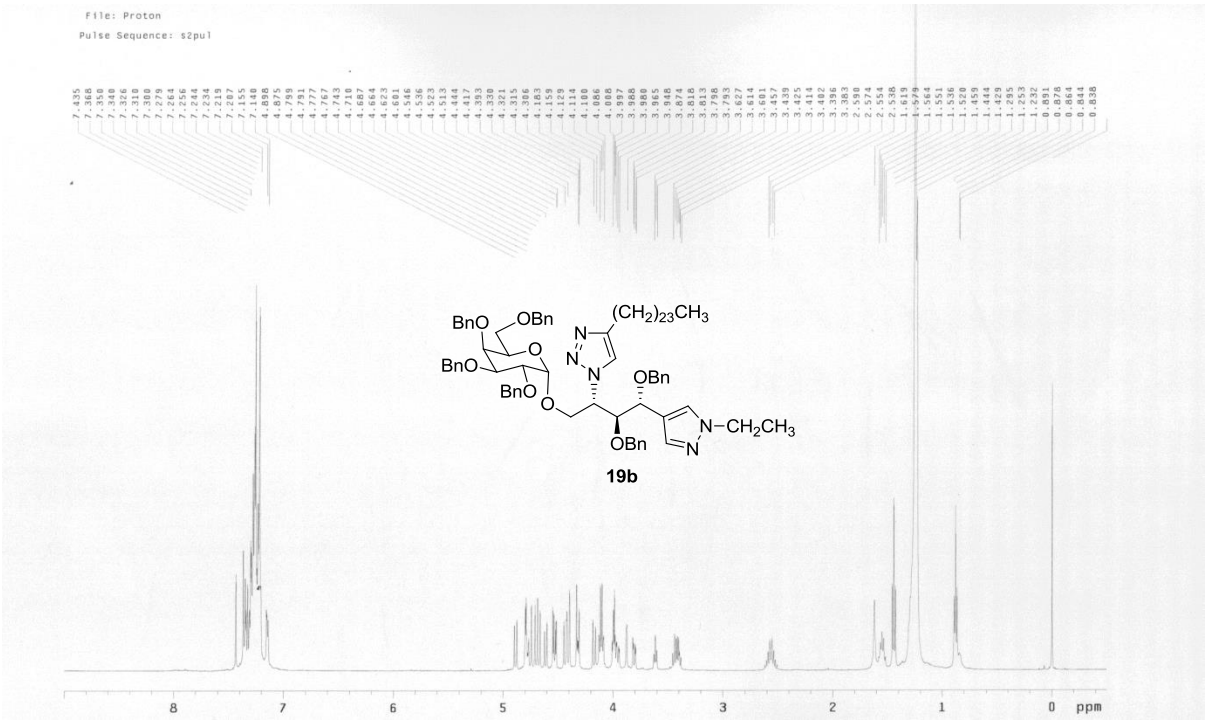


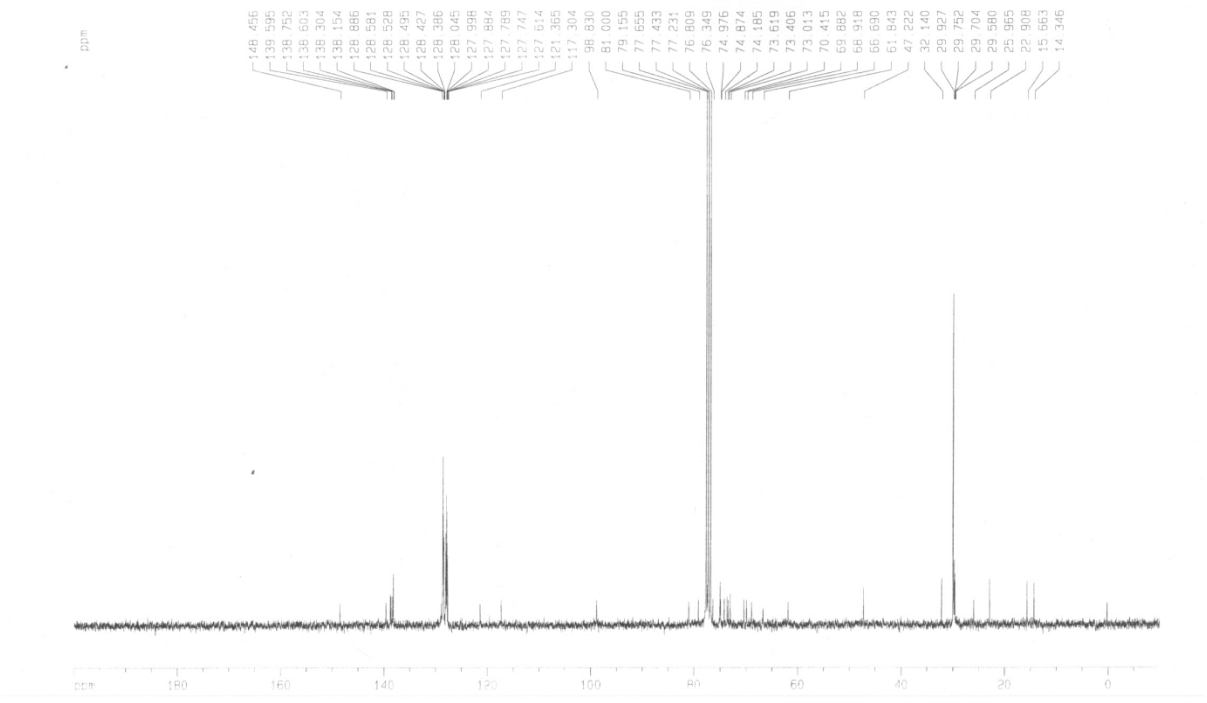

File: Proton
Pulse Sequence: s2pul
BnO
OBn
O
(CH2)5
HN
OBn
BnO
BnO
OBn
N
(CH2)6
CH3
N
18e

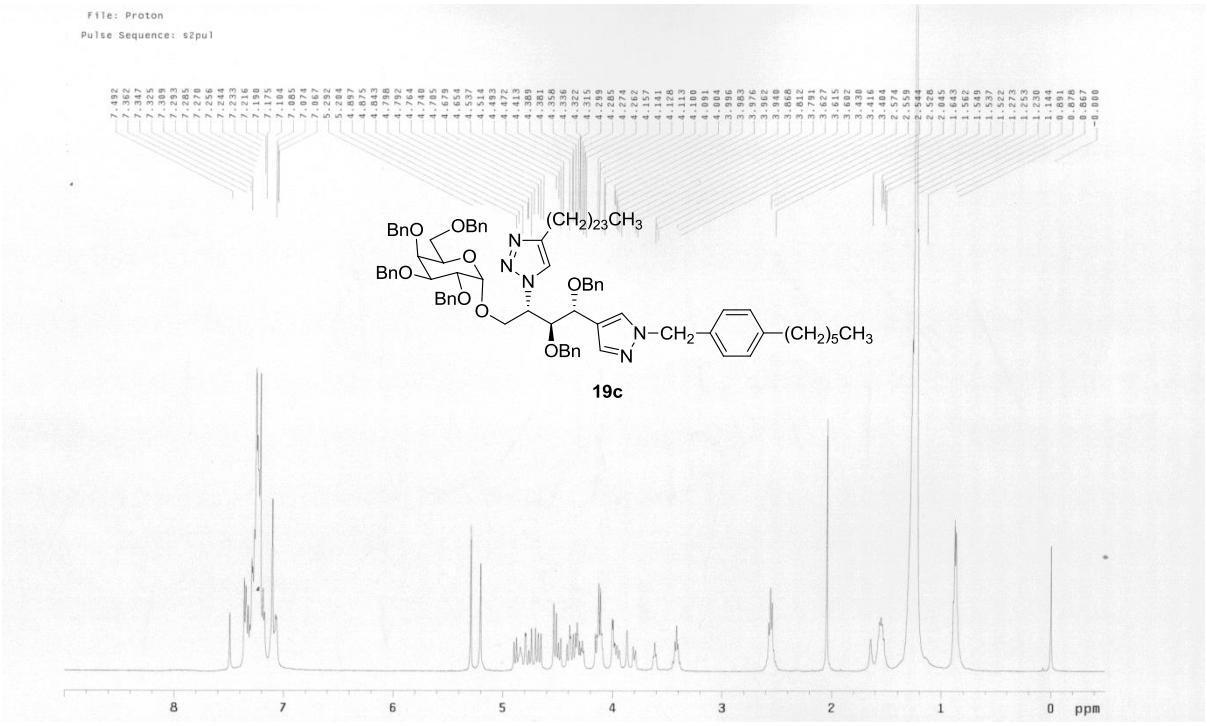

File: Proton
Pulse Sequence: s2pul
BnO
OBn
BnO
BnO
O
O
N
N
N
(CH2)23CH3
OBn
OBn
N
N
(CH2)10CH3
8
7
6
5
4
3
2
1
0
ppm

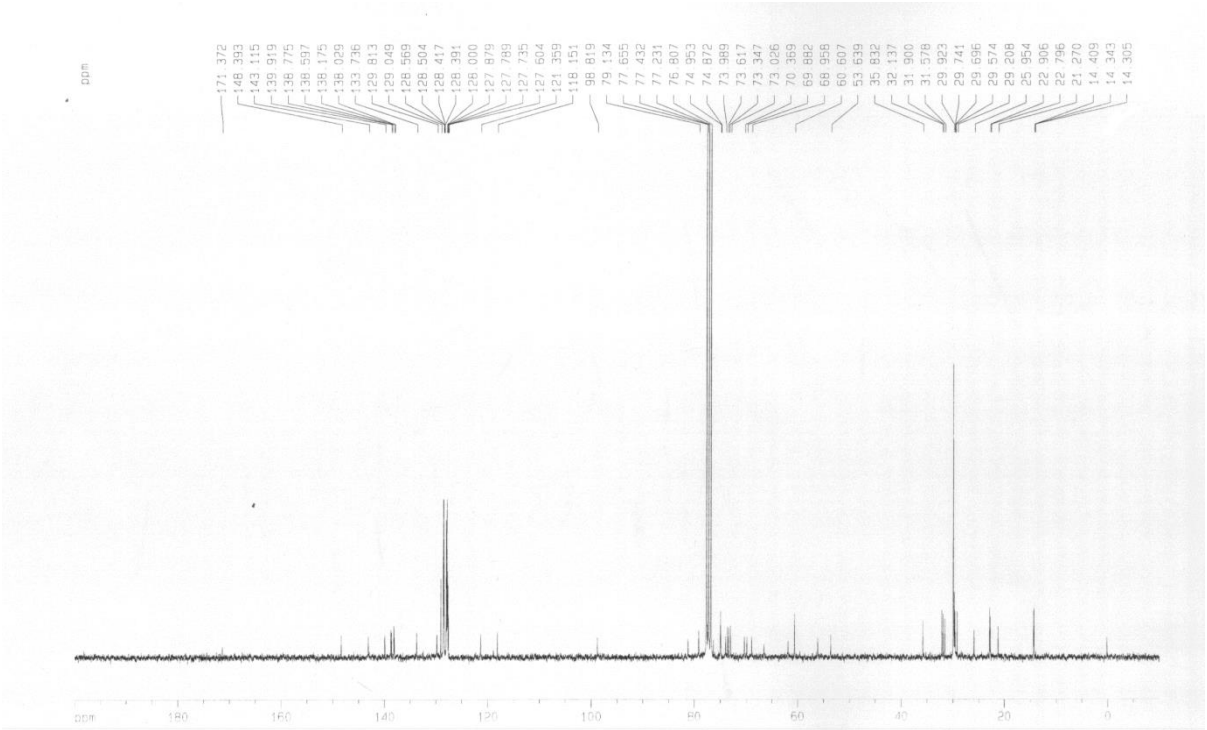
19a

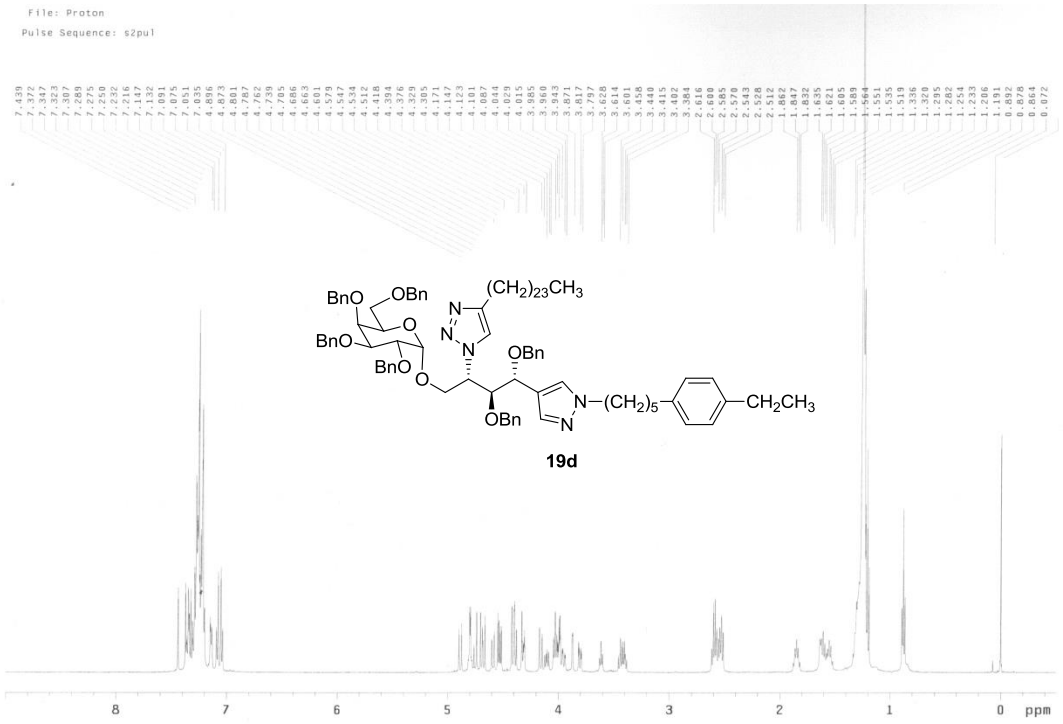

ppm
ppm
180
160
140
120
100
80
60
40
20
0


File: Proton
Pulse Sequence: s2pul
BnO
OBn
BnO
BnO
O
O
N
N
N
(CH2)23CH3
OBn
OBn
N−CH2CH3
N
19b
8
7
6
5
4
3
2
1
0
ppm

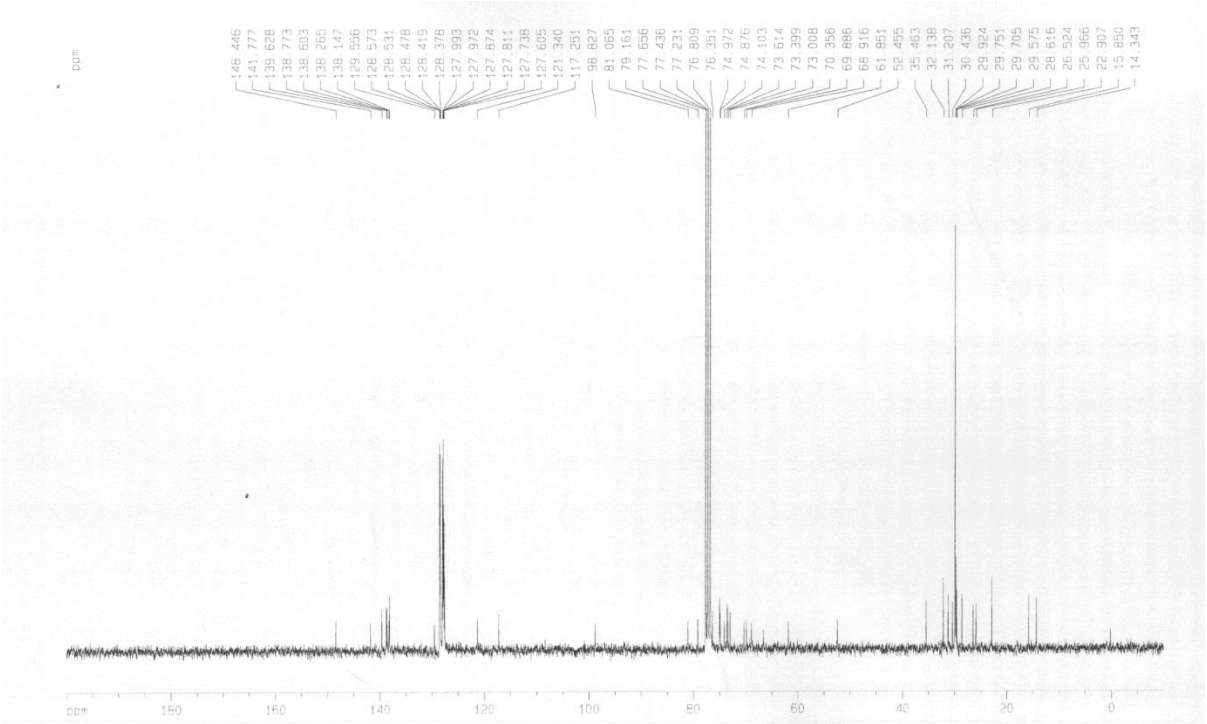

ppm
148.456
139.595
138.752
138.603
138.304
138.154
128.886
128.581
128.528
128.495
128.427
128.386
128.045
127.998
127.884
127.799
127.747
127.614
121.365
117.304
98.830
81.000
79.155
77.655
77.433
77.231
76.809
76.349
74.976
74.874
74.185
73.619
73.406
73.013
70.415
69.882
68.918
66.690
61.843
47.222
32.140
29.927
29.752
29.704
29.580
25.965
22.908
15.663
14.346
ppm
180
160
140
120
100
80
60
40
20
0

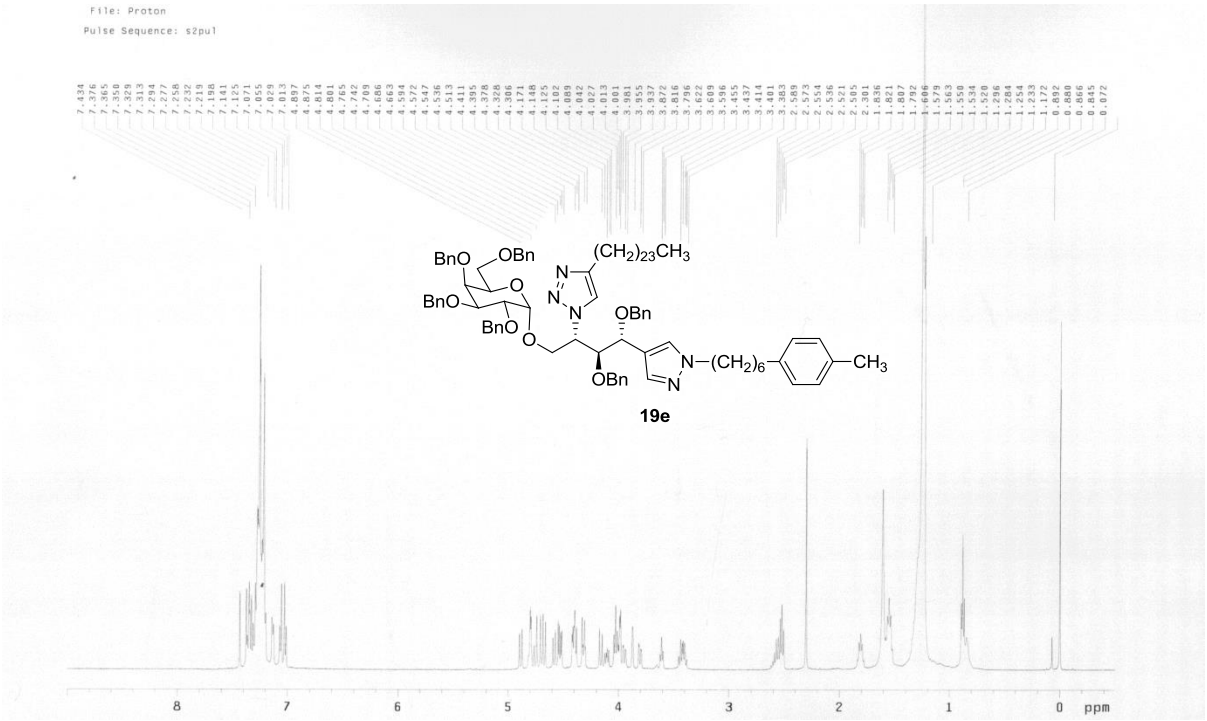

File: Proton
Pulse Sequence: s2pul
BnO
OBn
BnO
O
BnO
O
(CH2)23CH3
N
N
N
OBn
OBn
N
N–CH2
(CH2)5CH3
19c
8
7
6
5
4
3
2
1
0
ppm


ppm
171.372
148.393
143.115
139.919
138.775
138.597
138.175
138.029
133.736
129.813
129.049
128.569
128.504
128.417
128.391
128.000
127.879
127.789
127.735
127.604
121.359
118.151
98.819
79.134
77.655
77.432
77.231
76.807
74.953
74.872
73.989
73.617
73.347
73.026
70.369
69.882
68.958
60.607
53.639
35.832
32.137
31.900
31.578
29.923
29.741
29.696
29.574
29.208
25.954
22.906
22.796
21.270
14.409
14.343
14.305
ppm
180
160
140
120
100
80
60
40
20
0

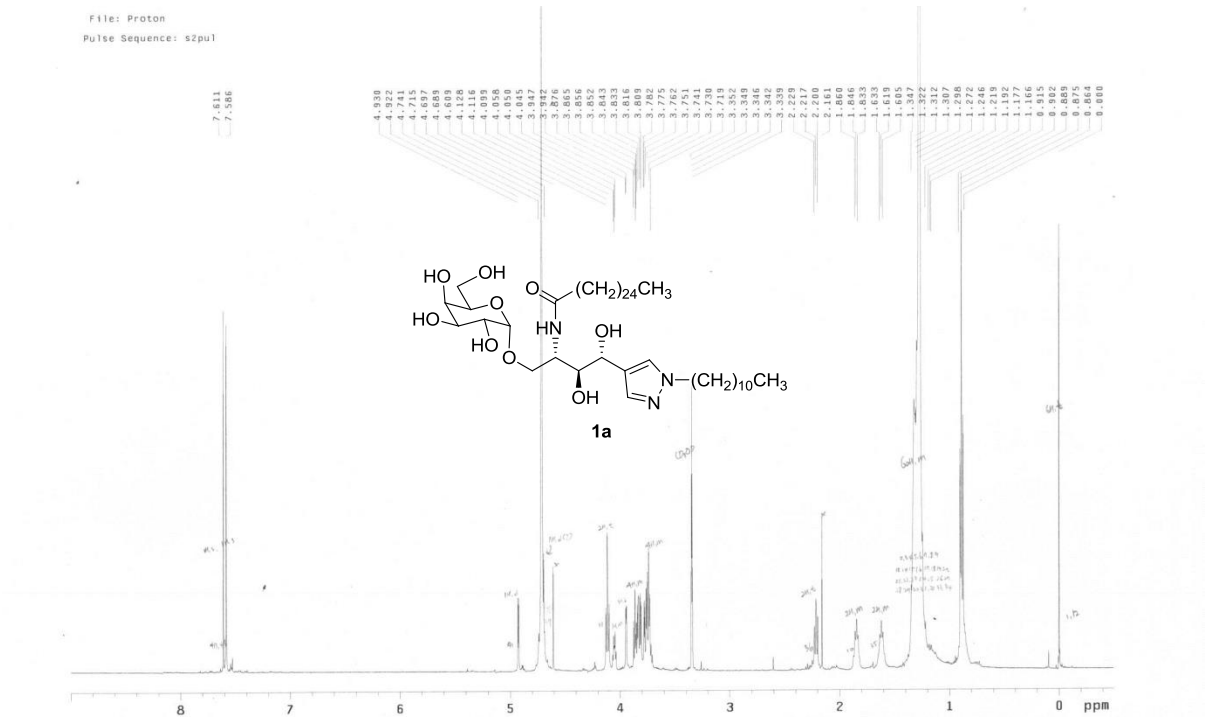

File: Proton
Pulse Sequence: s2pul
BnO
OBn
BnO
BnO
O
O
N
N
N
(CH2)23CH3
OBn
OBn
N
N
(CH2)5
CH2CH3
8
7
6
5
4
3
2
1
0
ppm

19d

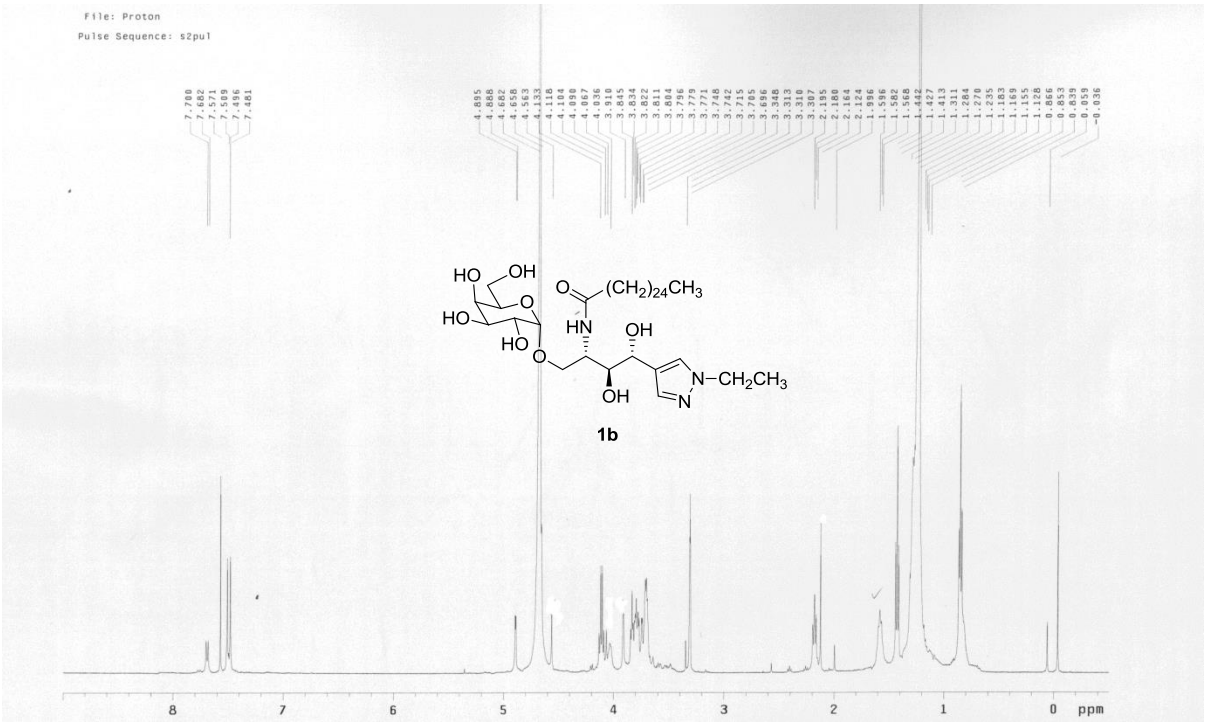

ppm
200
180
160
140
120
100
80
60
40
20
0


File: Proton
Pulse Sequence: s2pul
BnO
OBn
BnO
BnO
O
N
N
N
(CH2)23CH3
OBn
OBn
N
N
(CH2)6
CH3
8
7
6
5
4
3
2
1
0
ppm

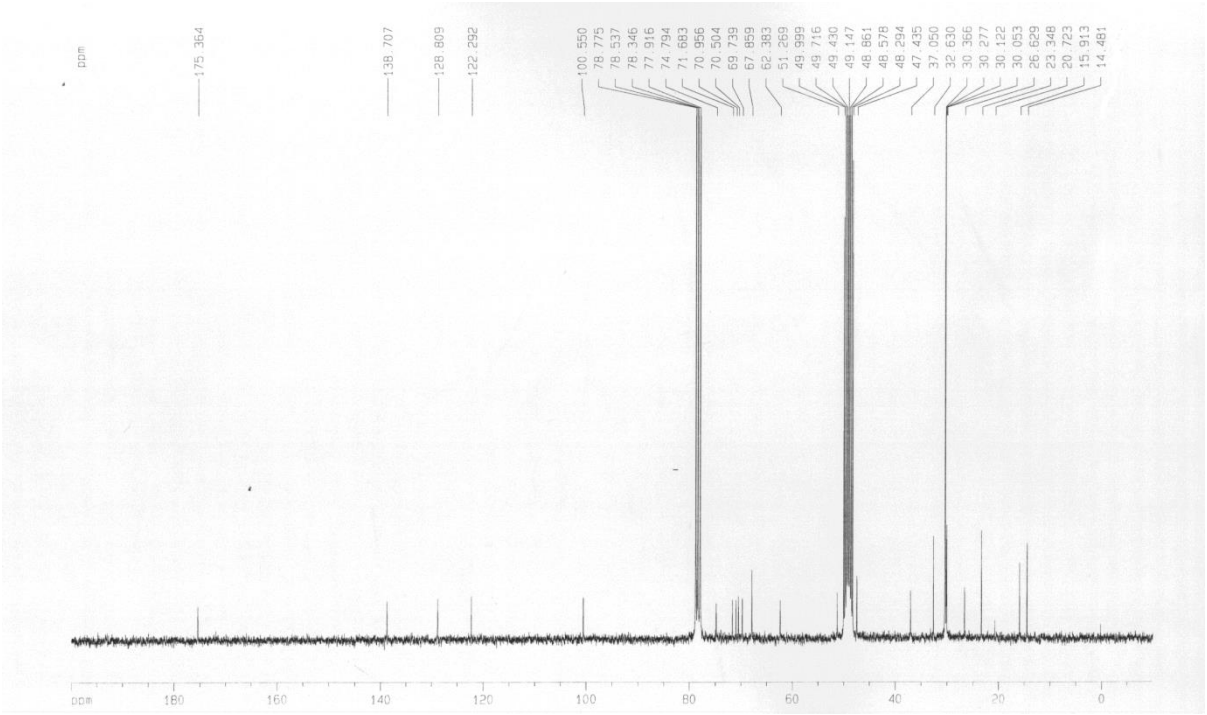
19e

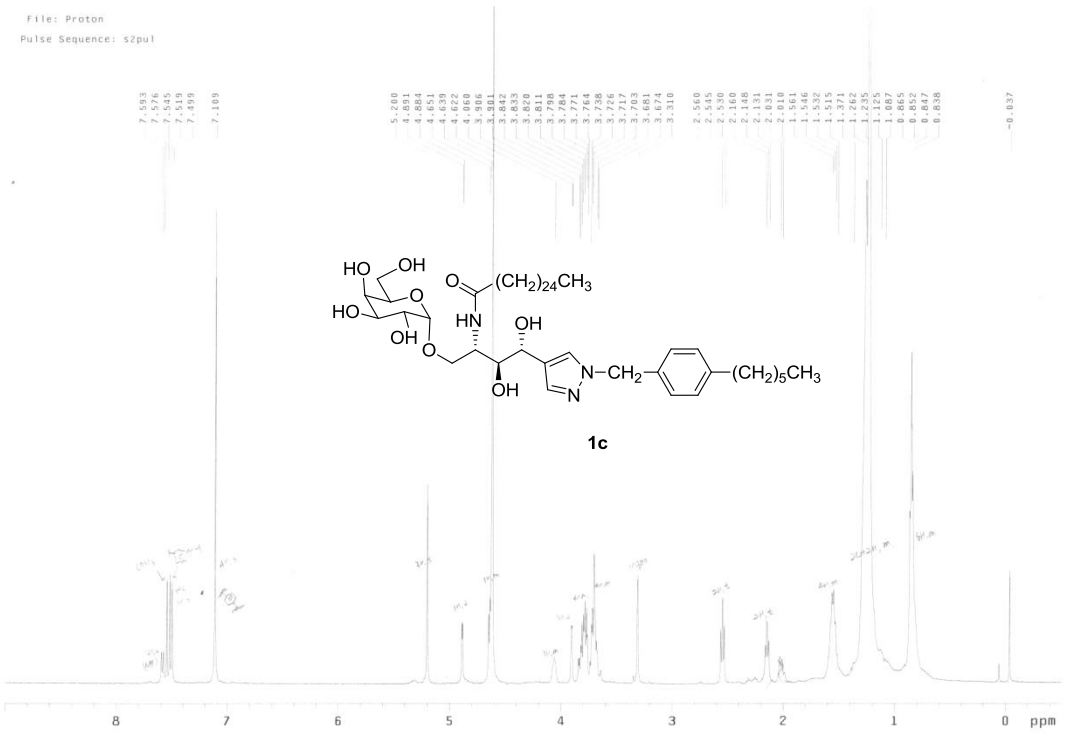

File: Proton
Pulse Sequence: s2pul
HO
OH
HO
O
HO
O
HN
O
(CH2)24CH3
OH
OH
N
N
(CH2)10CH3
8
7
6
5
4
3
2
1
0
ppm

1a

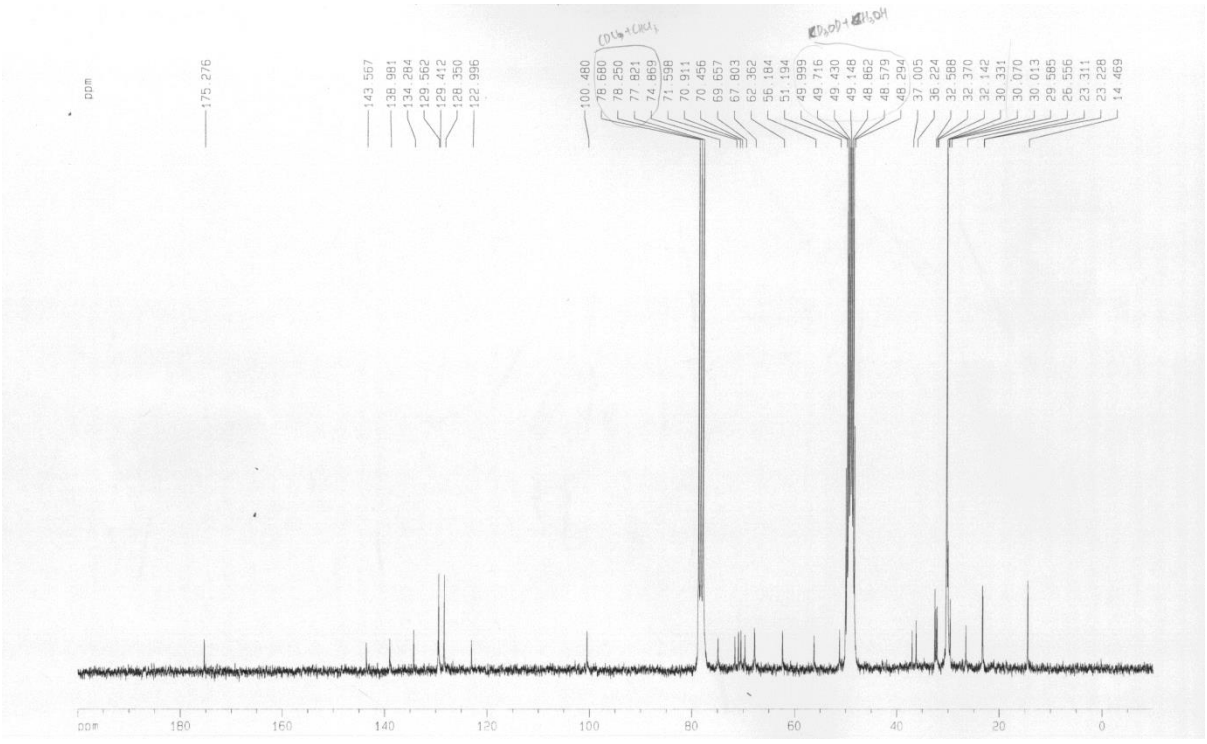

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
HO
O
HN
O
(CH2)24CH3
OH
OH
N
N–CH2CH3
8
7
6
5
4
3
2
1
0
ppm

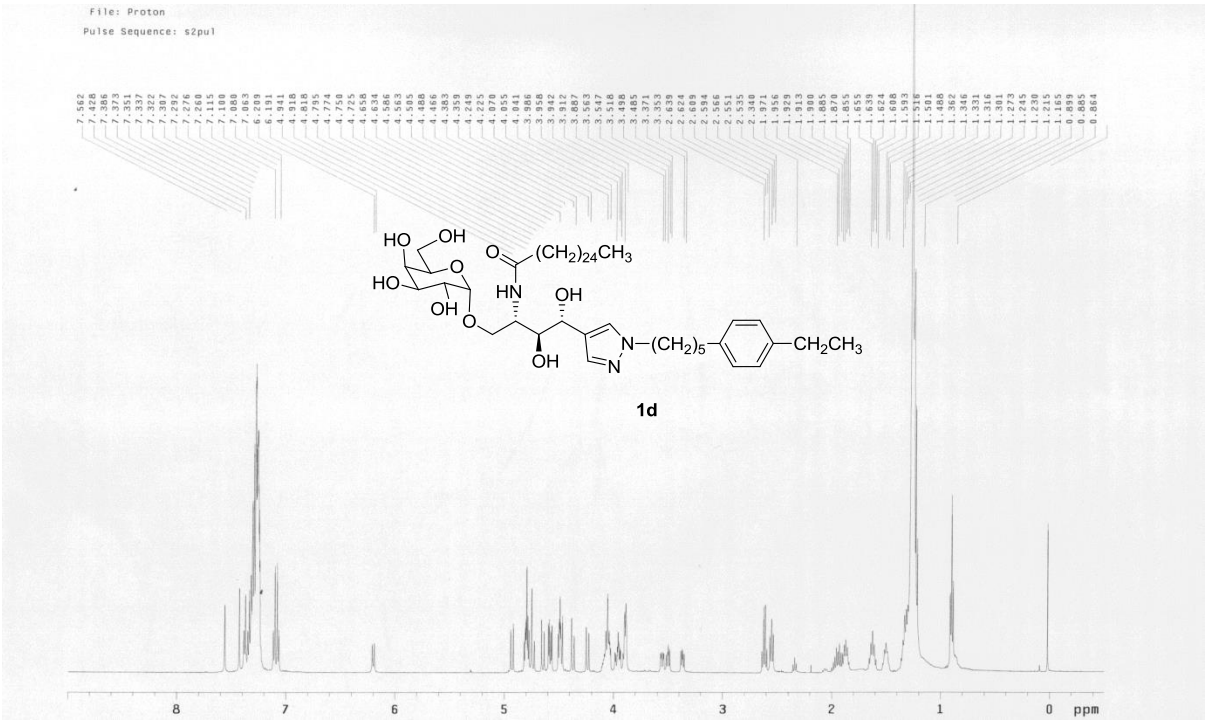
1b


ppm
175.364
138.707
128.809
122.292
100.550
78.775
78.537
78.346
77.916
74.794
71.683
70.956
70.504
69.739
67.859
62.383
51.269
49.999
49.716
49.430
49.147
48.861
48.578
48.294
47.435
37.050
32.630
30.366
30.277
30.122
30.053
26.629
23.348
20.723
15.913
14.481
ppm
180
160
140
120
100
80
60
40
20
0

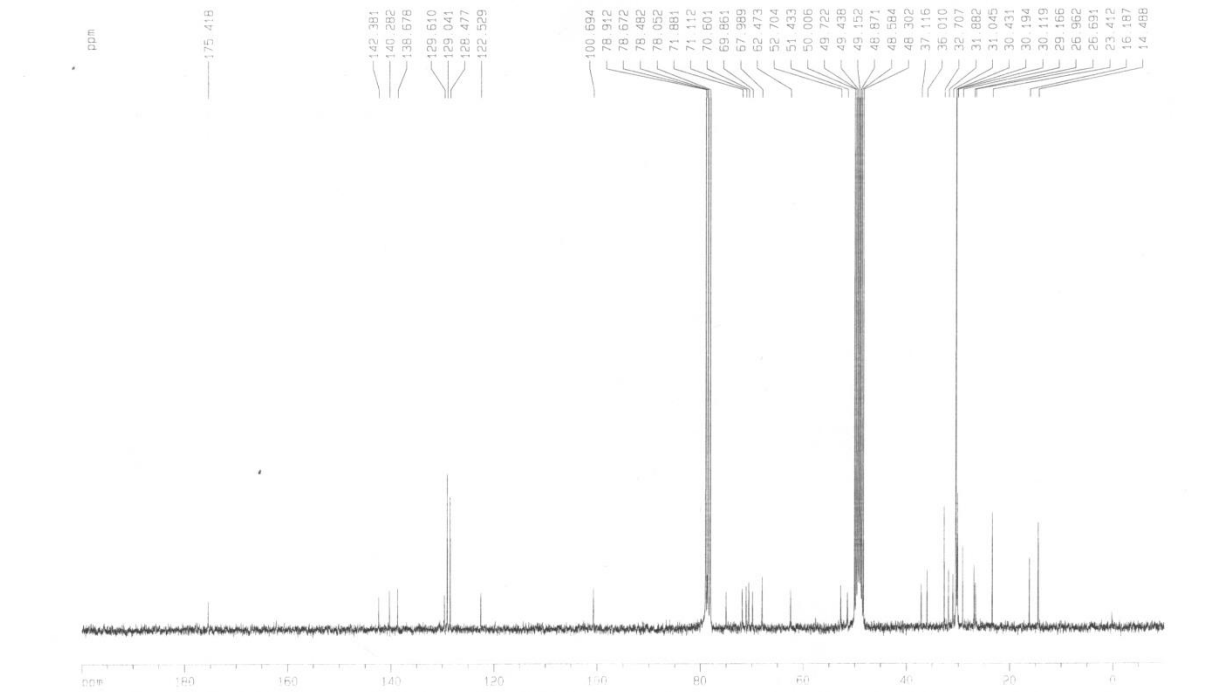

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
OH
O
HN
O
(CH2)24CH3
OH
OH
N
N
CH2
(CH2)5CH3
8
7
6
5
4
3
2
1
0
ppm

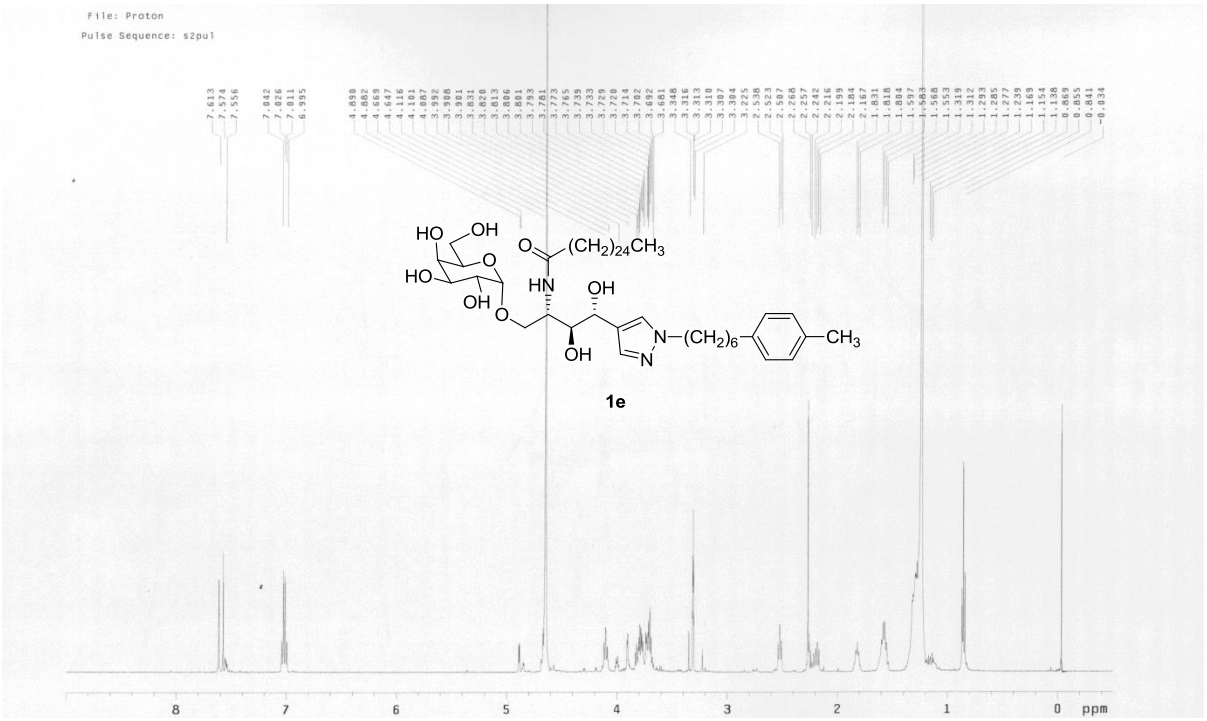
1c


ppm
175.276
143.567
138.981
134.284
129.562
129.412
128.350
122.996
100.480
76.680
78.250
77.821
74.869
71.598
70.911
70.456
69.657
67.803
62.362
56.184
51.194
49.999
49.716
49.430
49.148
48.862
48.579
48.294
37.005
36.224
32.588
32.370
32.142
30.331
30.070
30.013
29.585
26.556
23.311
23.228
14.469
ppm
180
160
140
120
100
80
60
40
20
0

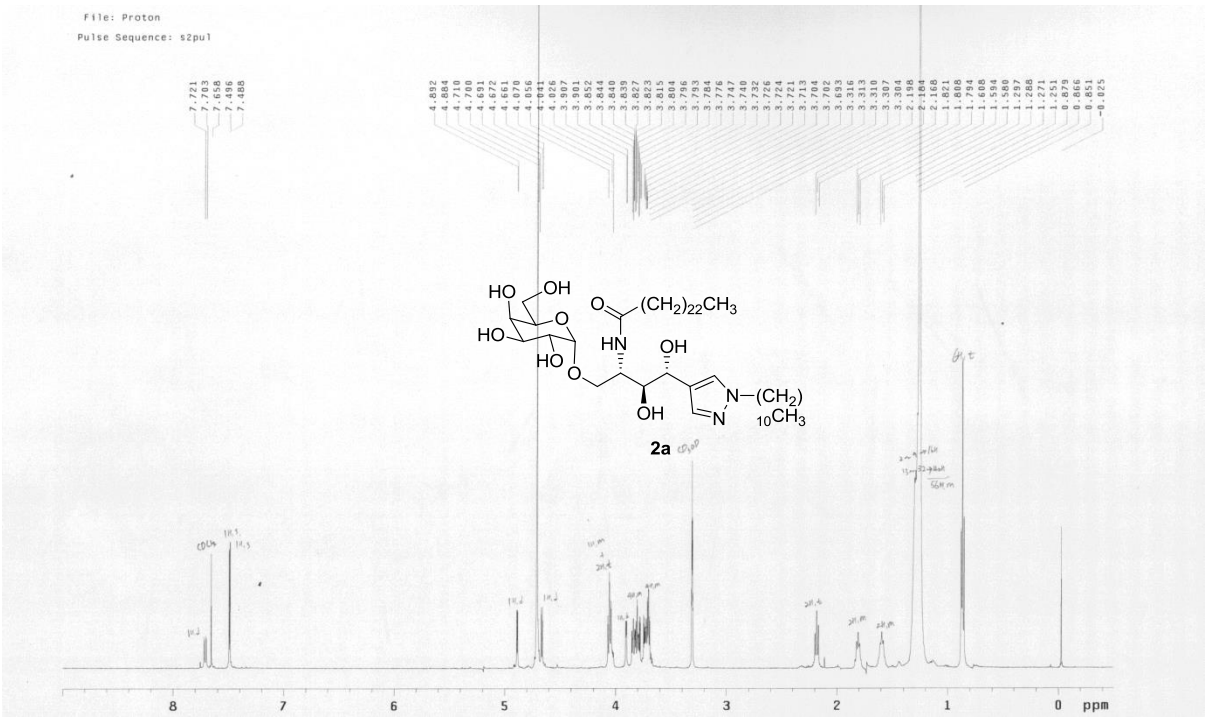

File: Proton
Pulse Sequence: s2pul
HO
OH
HO
O
OH
O
O
(CH2)24CH3
HN
OH
OH
N
N
(CH2)5
CH2CH3
8
7
6
5
4
3
2
1
0
ppm

1d

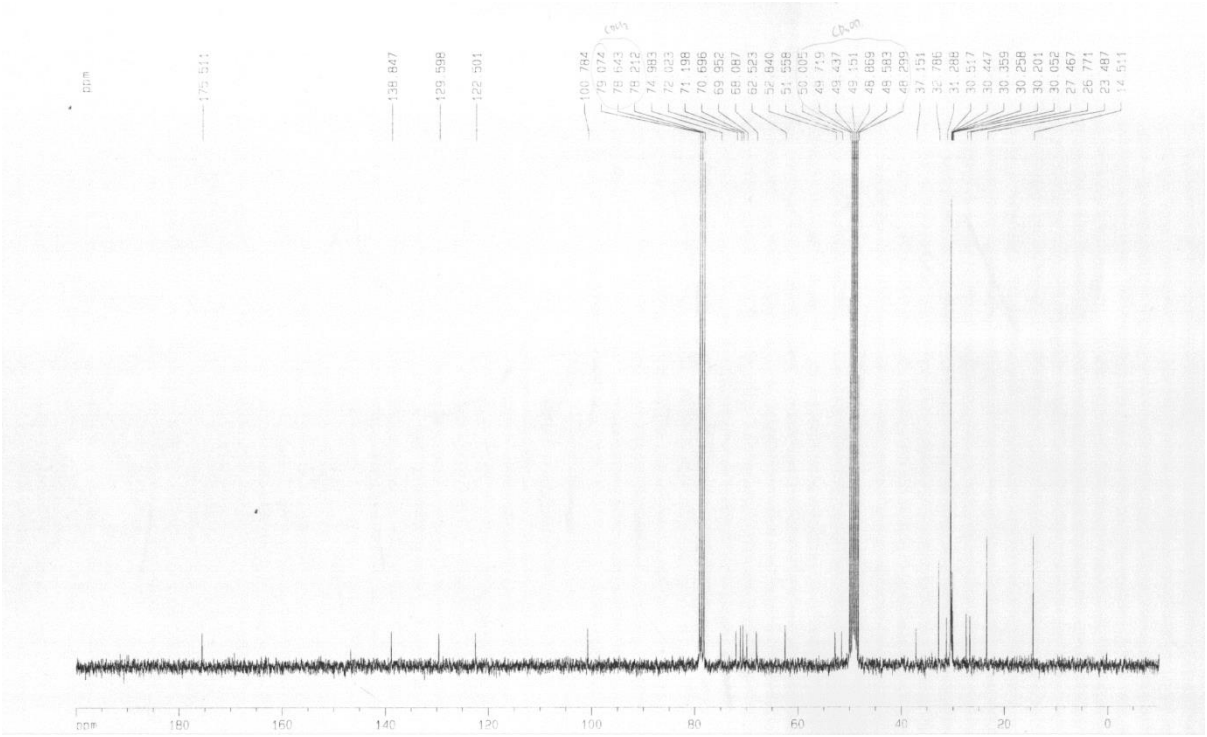

ppm
175.418
142.381
140.282
138.678
129.610
129.041
128.477
122.529
100.694
78.912
78.672
78.482
78.052
71.881
71.112
70.601
69.861
67.989
52.473
52.704
51.433
50.006
49.722
49.438
49.152
48.871
48.584
48.302
37.116
36.010
32.707
31.882
31.045
30.431
30.194
30.119
29.166
26.962
26.691
23.412
16.187
14.488
ppm
180
160
140
120
100
80
60
40
20
0

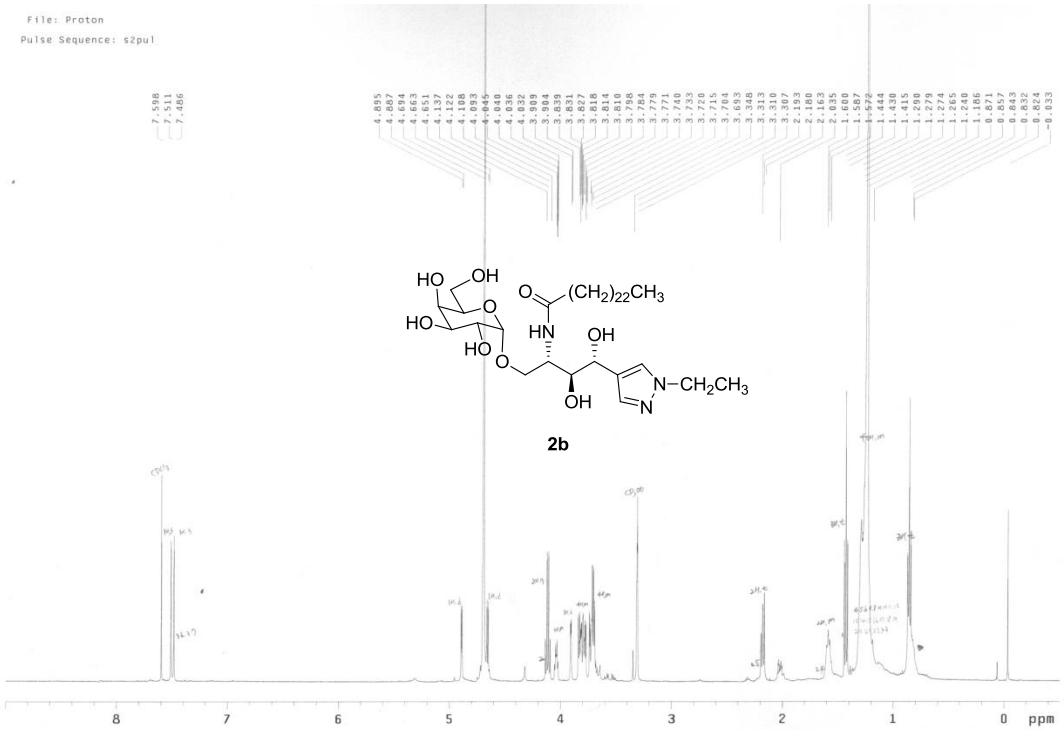

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
OH
O
HN
O
(CH2)24CH3
OH
OH
N
N
(CH2)6
CH3
8
7
6
5
4
3
2
1
0
ppm

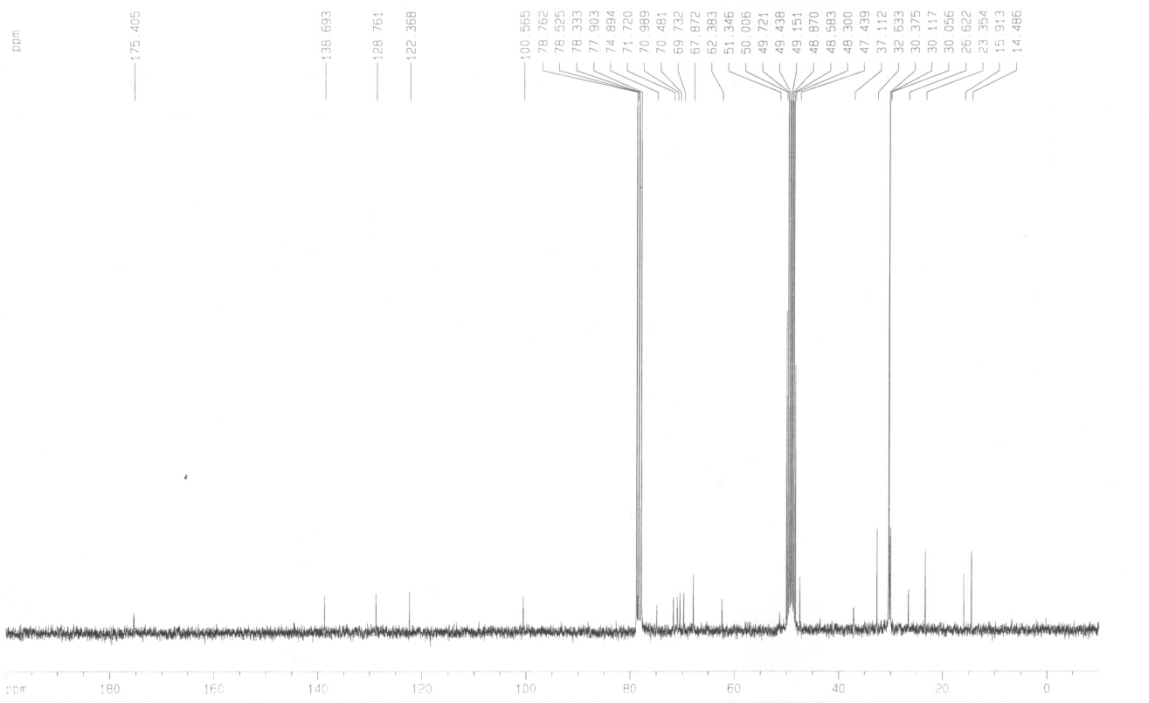
1e

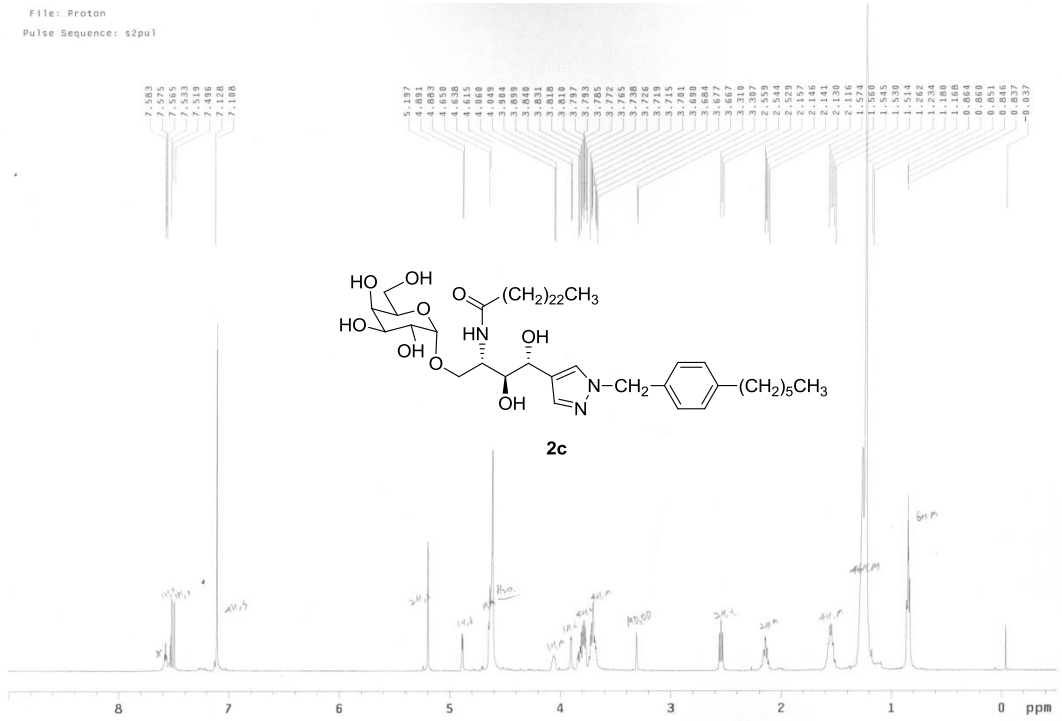

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
HO
O
HN
O
(CH2)22CH3
OH
OH
N
N
(CH2)
10CH3
8
7
6
5
4
3
2
1
0
ppm

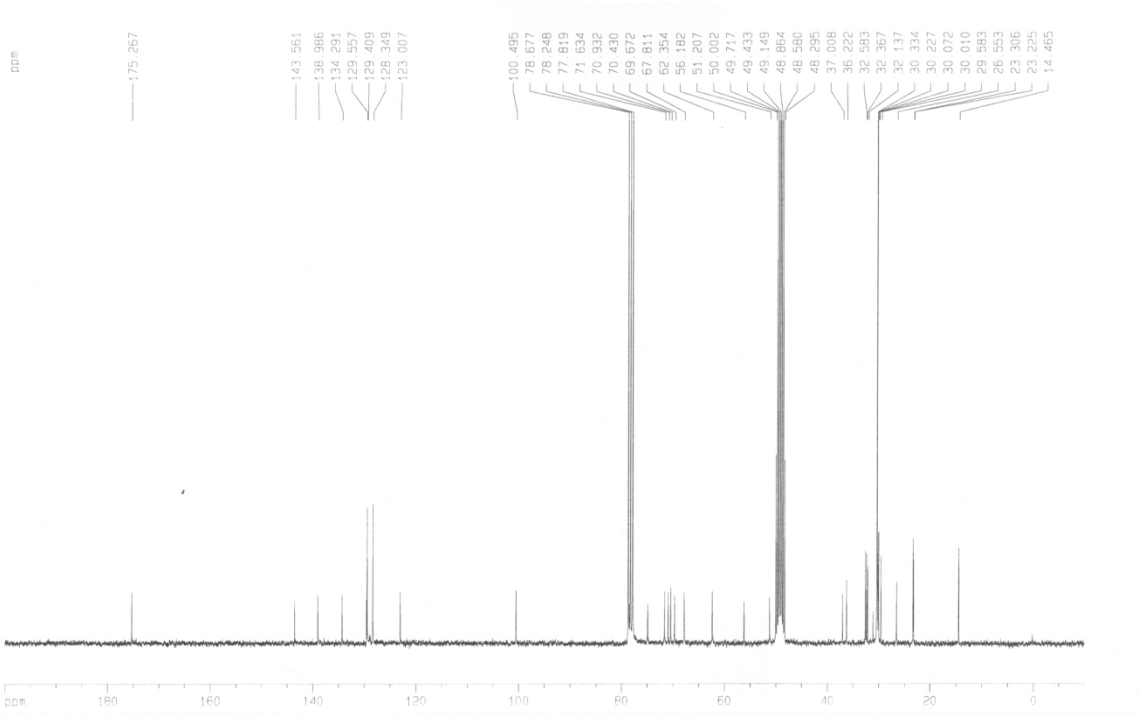
2a

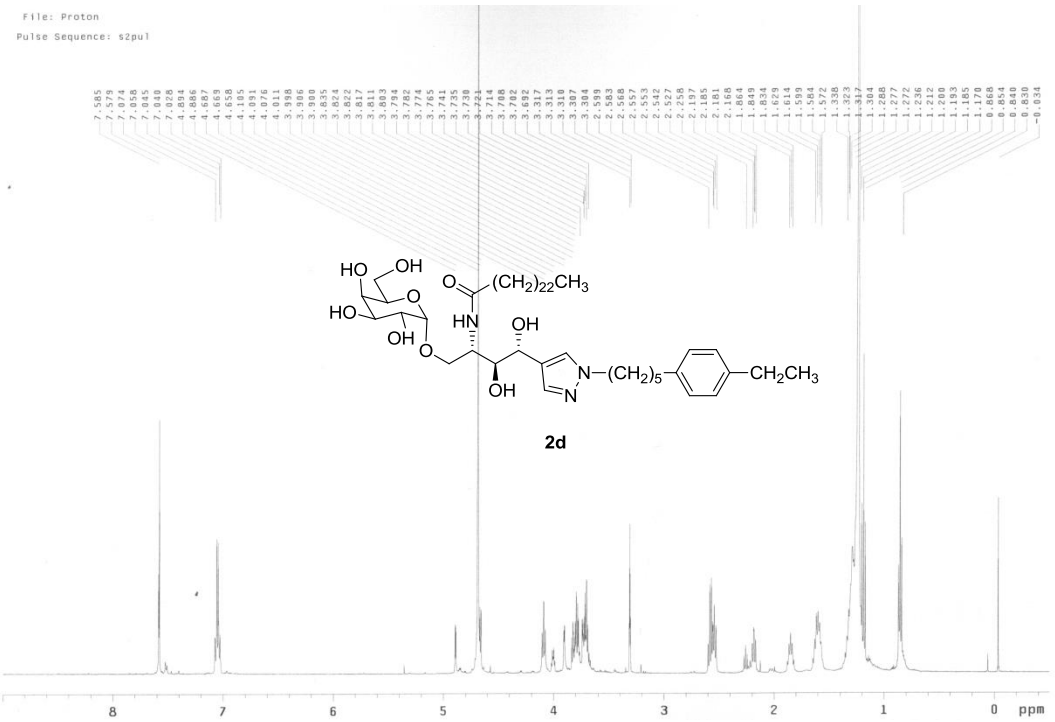



File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
HO
O
HN
O
(CH2)22CH3
OH
OH
N
N–CH2CH3
2b
8
7
6
5
4
3
2
1
0
ppm

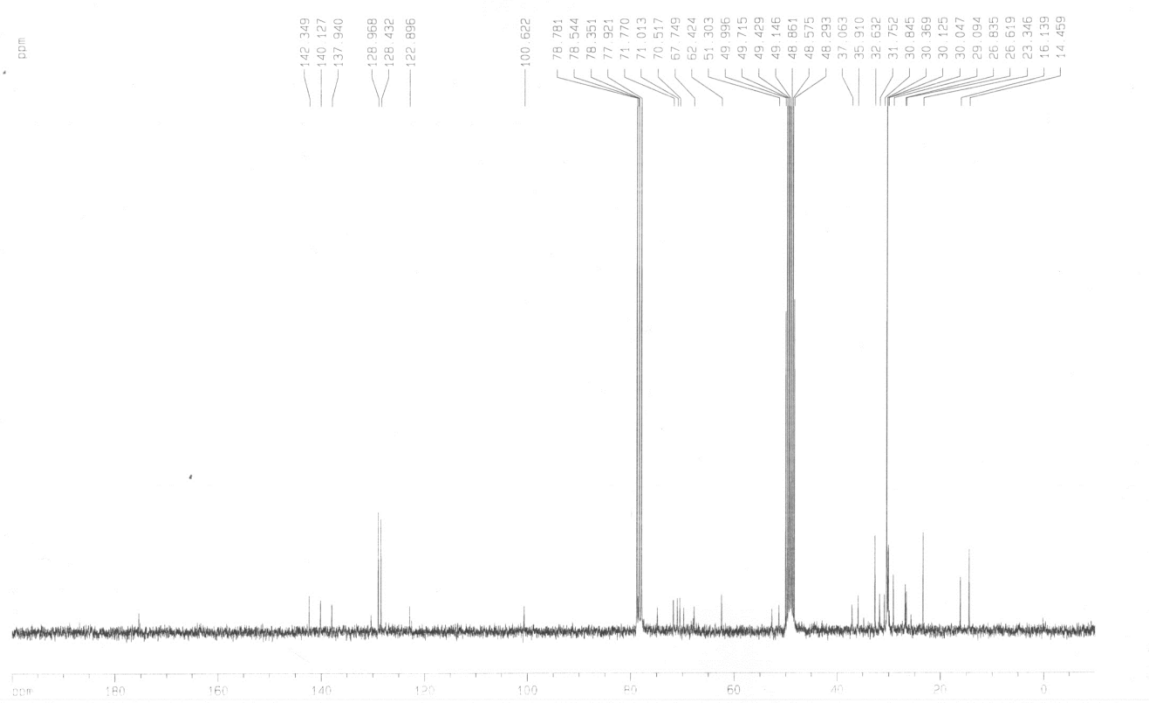

ppm
175.405
138.693
128.761
122.368
100.565
78.762
78.525
78.333
77.903
74.894
71.720
70.989
70.481
69.732
67.872
62.383
51.345
50.006
49.721
49.438
49.151
48.870
48.583
48.300
47.439
37.112
32.633
30.375
30.117
30.056
26.622
23.354
15.913
14.486
ppm
180
160
140
120
100
80
60
40
20
0

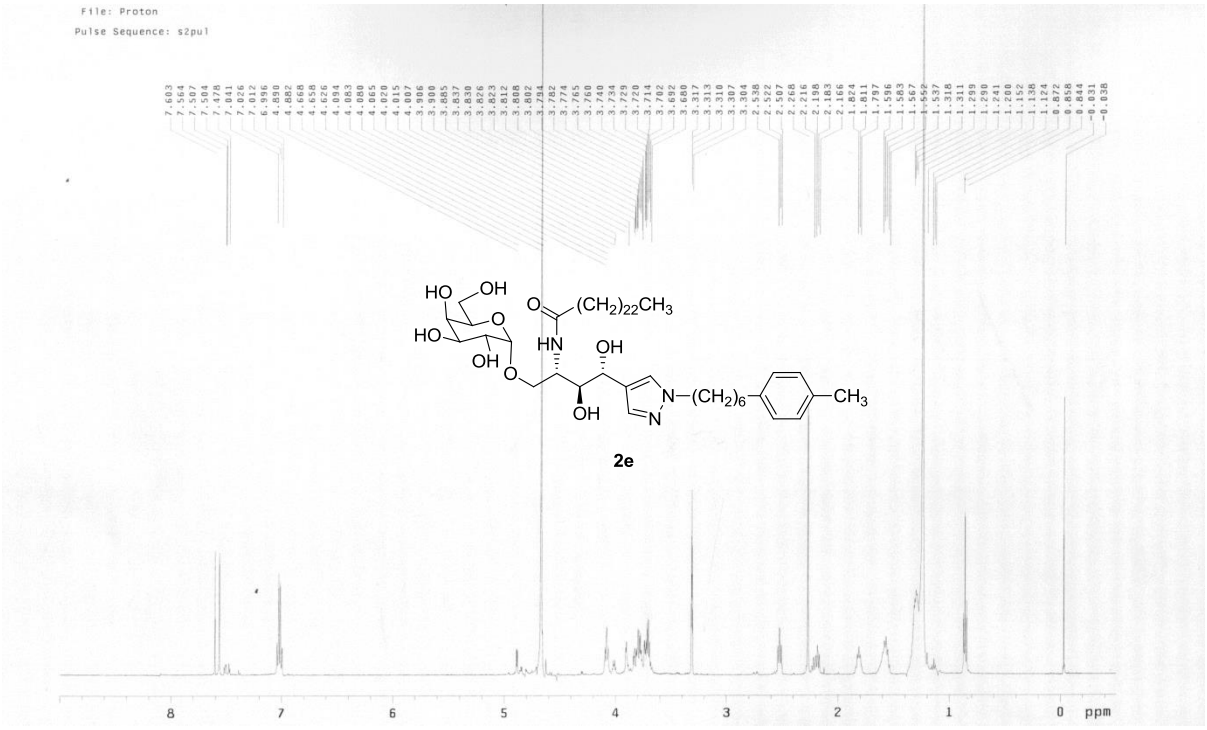

File: Proton
Pulse Sequence: s2pul
7.583
7.575
7.555
7.533
7.519
7.496
7.128
7.108
5.197
4.891
4.883
4.650
4.638
4.515
4.060
4.049
3.984
3.899
3.840
3.831
3.816
3.810
3.797
3.793
3.785
3.772
3.765
3.758
3.726
3.719
3.715
3.701
3.690
3.684
3.677
3.667
3.310
3.307
2.559
2.544
2.539
2.157
2.146
2.141
2.130
2.116
1.574
1.566
1.545
1.530
1.514
1.262
1.234
1.168
1.148
1.146
0.864
0.860
0.851
0.846
0.837
0.837
HO
OH
O
HO
OH
O
HN
O
(CH2)22CH3
OH
OH
N
N
CH2
(CH2)5CH3
2c
8
7
6
5
4
3
2
1
0
ppm


ppm
175.267
143.561
138.986
134.291
129.557
129.409
128.349
123.007
100.495
78.677
78.248
77.819
71.634
70.932
70.430
69.672
67.811
62.354
56.182
51.207
50.002
49.717
49.433
49.149
48.864
48.580
48.295
37.008
36.222
32.583
32.367
32.137
30.334
30.227
30.072
30.010
29.583
26.553
23.306
23.225
14.465
ppm
180
160
140
120
100
80
60
40
20
0

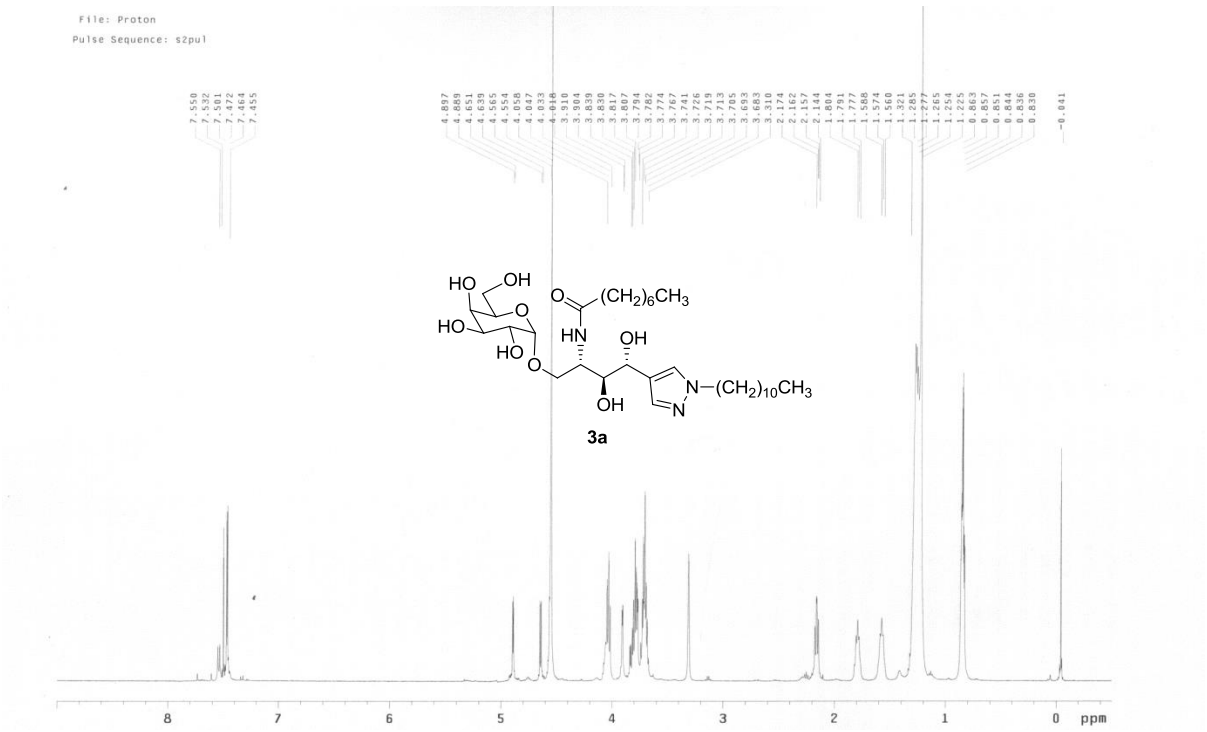

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
OH
O
HN
O
(CH2)22CH3
OH
OH
N
N
(CH2)5
CH2CH3
8
7
6
5
4
3
2
1
0
ppm

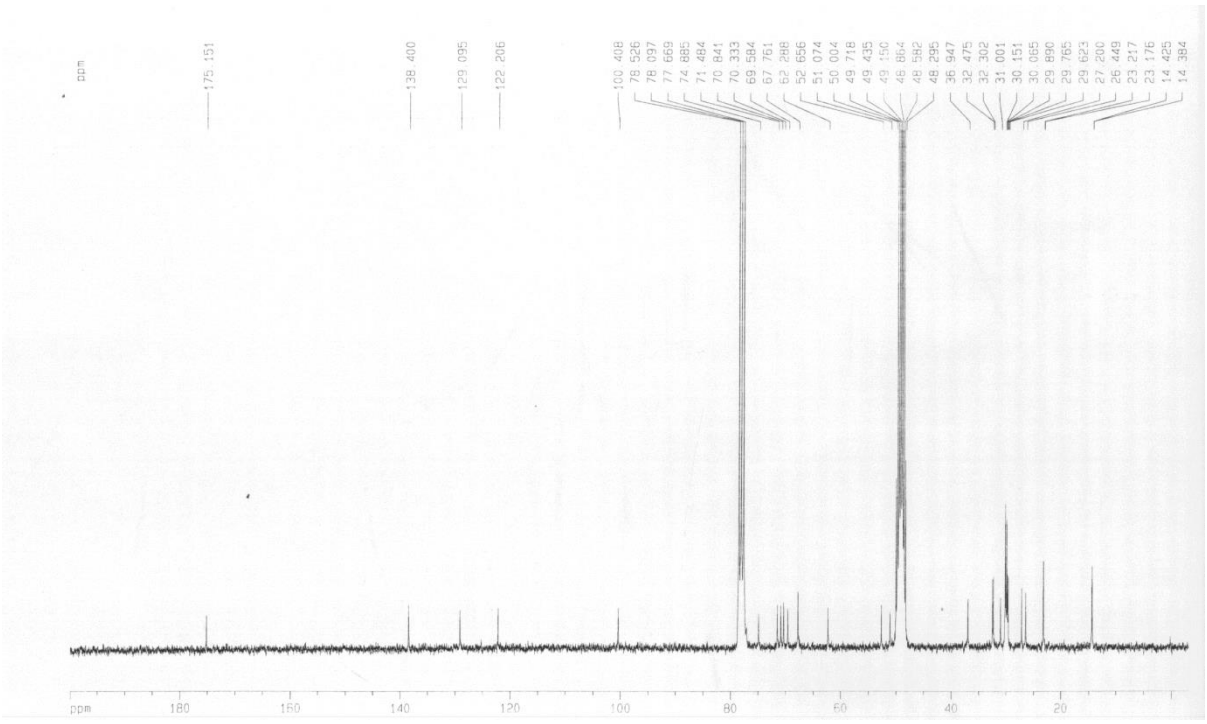
2d

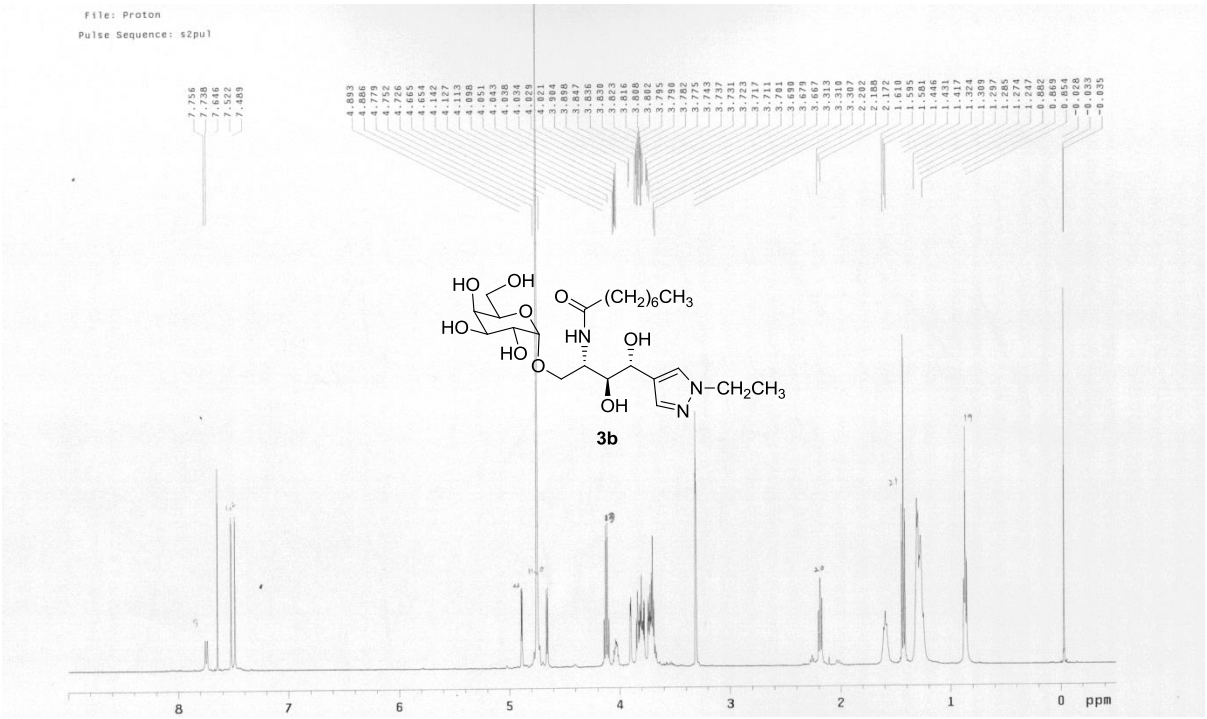

ppm
142.349
140.127
137.940
128.968
128.432
122.896
100.622
78.781
78.544
78.351
77.921
71.770
71.013
70.517
67.749
62.424
51.303
49.996
49.715
49.429
49.146
48.861
48.575
48.293
37.063
35.910
32.632
31.752
30.845
30.369
30.125
30.047
29.094
26.835
26.619
23.346
16.139
14.459
ppm
180
160
140
120
100
80
60
40
20
0

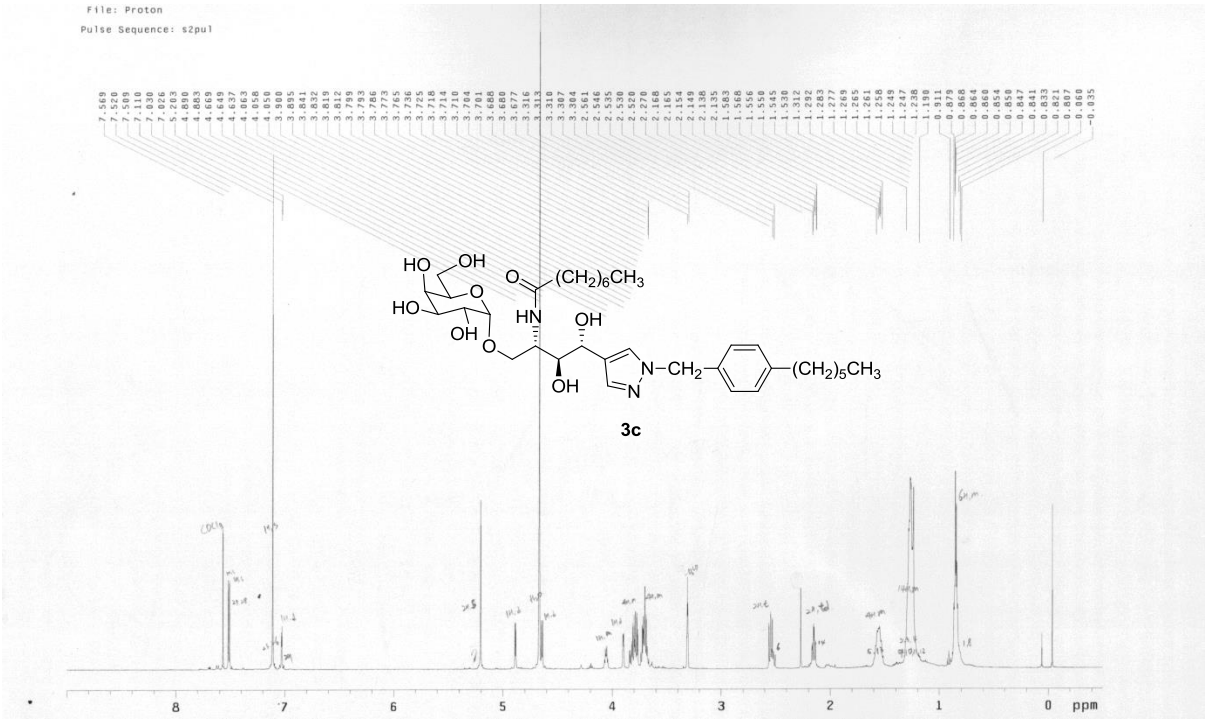

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
OH
O
HN
O
(CH2)22CH3
OH
OH
N
N
(CH2)6
CH3
8
7
6
5
4
3
2
1
0
ppm

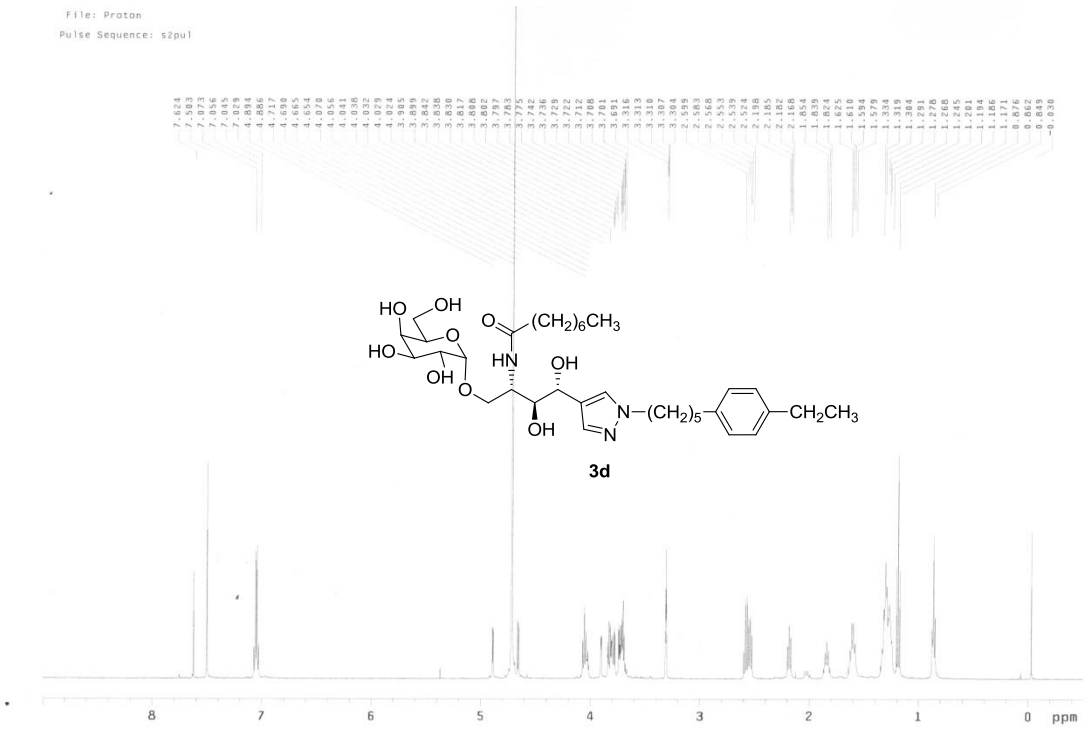
2e

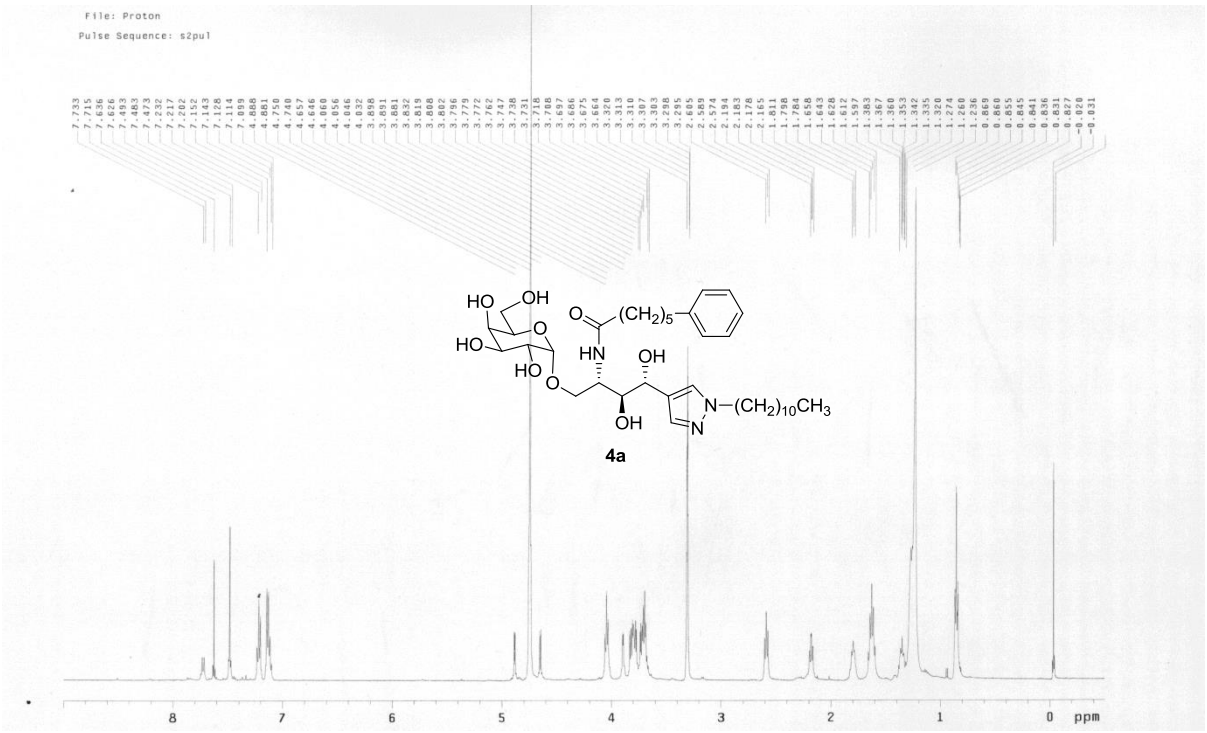

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
HO
O
HN
O
(CH2)6CH3
OH
OH
N
N
(CH2)10CH3
3a
8
7
6
5
4
3
2
1
0
ppm

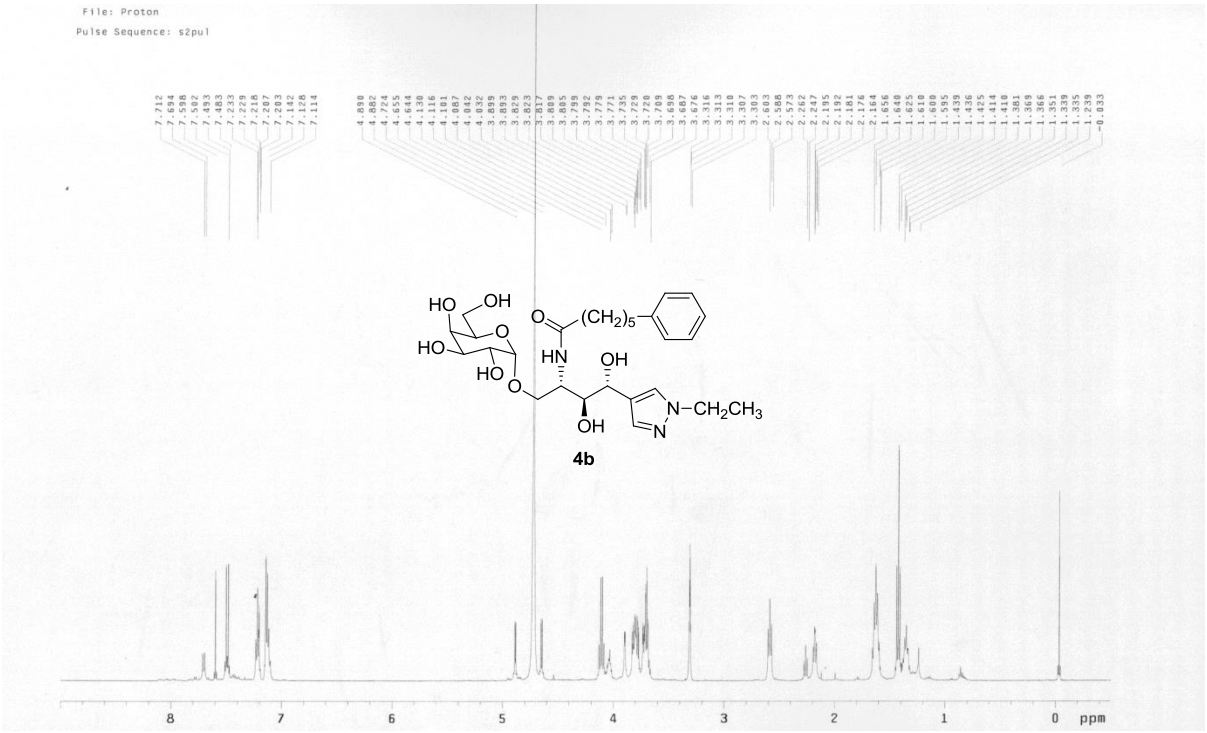

ppm
175.151
138.400
129.095
122.206
ppm
180
160
140
120
100
80
60
40
20


File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
HO
O
HN
O
(CH2)6CH3
OH
OH
N
N–CH2CH3
3b
8
7
6
5
4
3
2
1
0
ppm

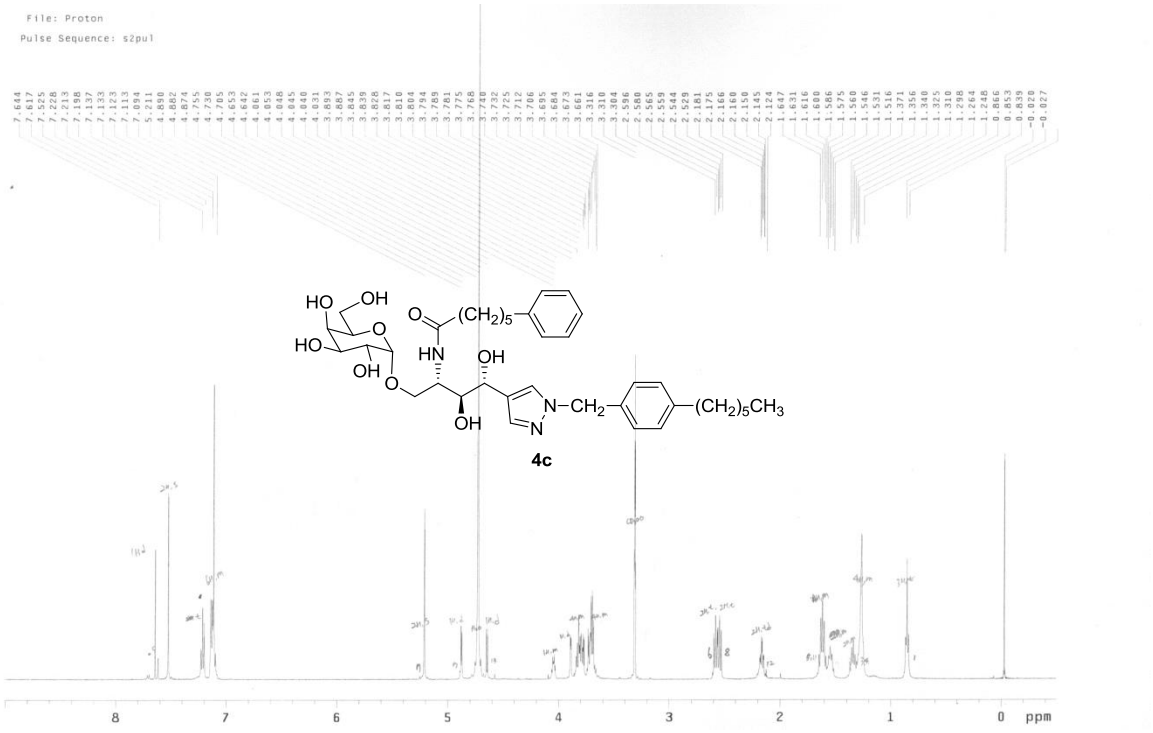

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
OH
O
HN
O
(CH2)6CH3
OH
OH
N
N–CH2
(CH2)5CH3
3c
8
7
6
5
4
3
2
1
0
ppm


File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
OH
O
HN
OH
OH
O
(CH2)6CH3
N
N
(CH2)5
CH2CH3
3d
8
7
6
5
4
3
2
1
0
ppm

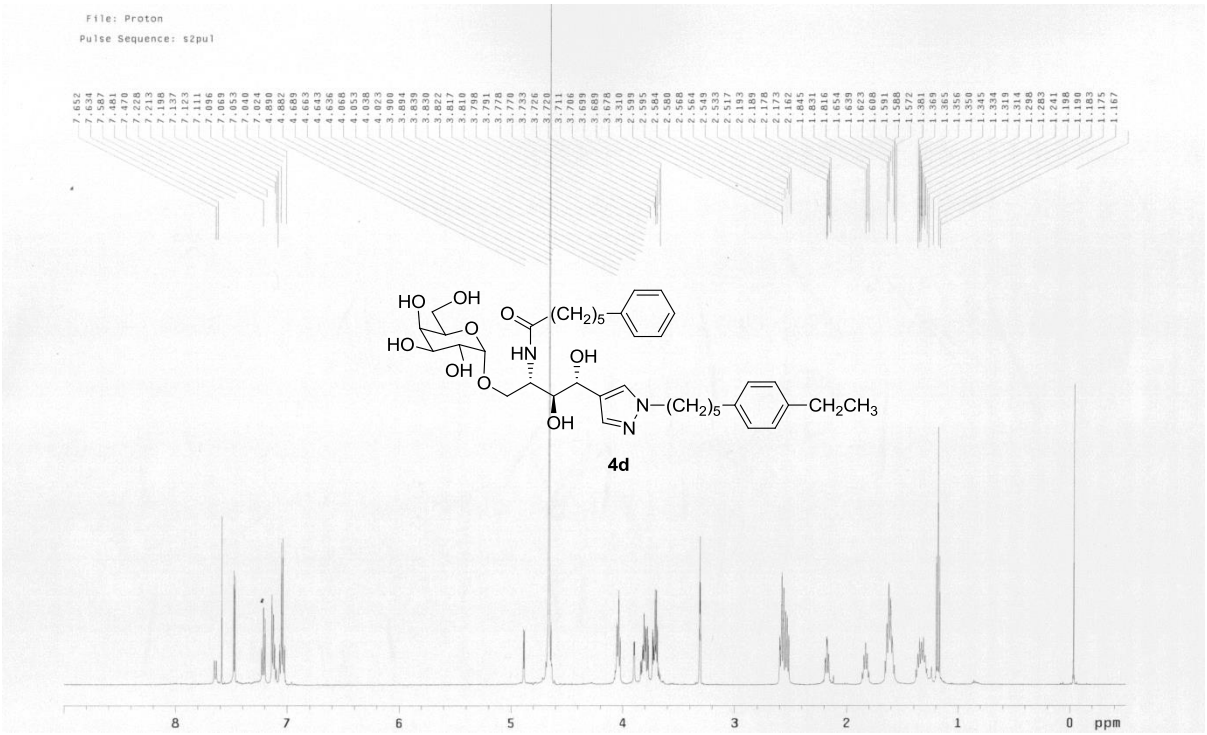

File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
HO
O
HN
OH
OH
O
(CH2)5
N
N
(CH2)10CH3
4a
8
7
6
5
4
3
2
1
0
ppm


File: Proton
Pulse Sequence: s2pul
HO
OH
HO
HO
O
O
HN
OH
OH
O
(CH2)5
N–CH2CH3
N
8
7
6
5
4
3
2
1
0
ppm

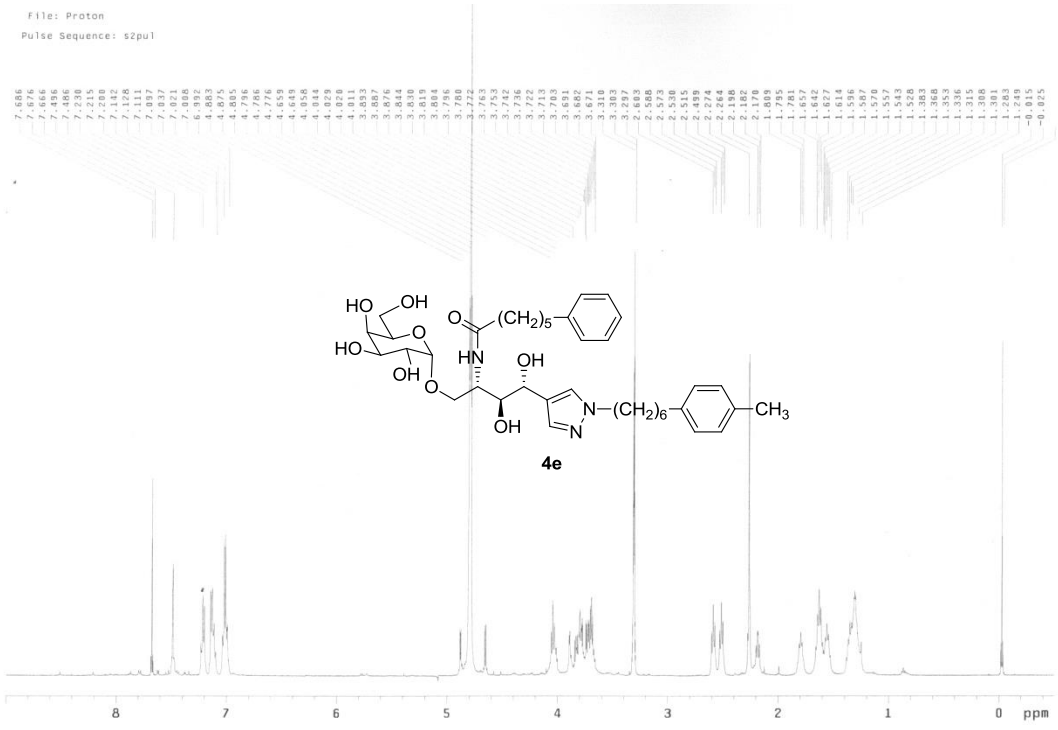
4b


File: Proton
Pulse Sequence: s2pul
HO
OH
HO
OH
O
O
HN
OH
OH
O
(CH2)5
N–CH2
(CH2)5CH3
N
8
7
6
5
4
3
2
1
0
ppm

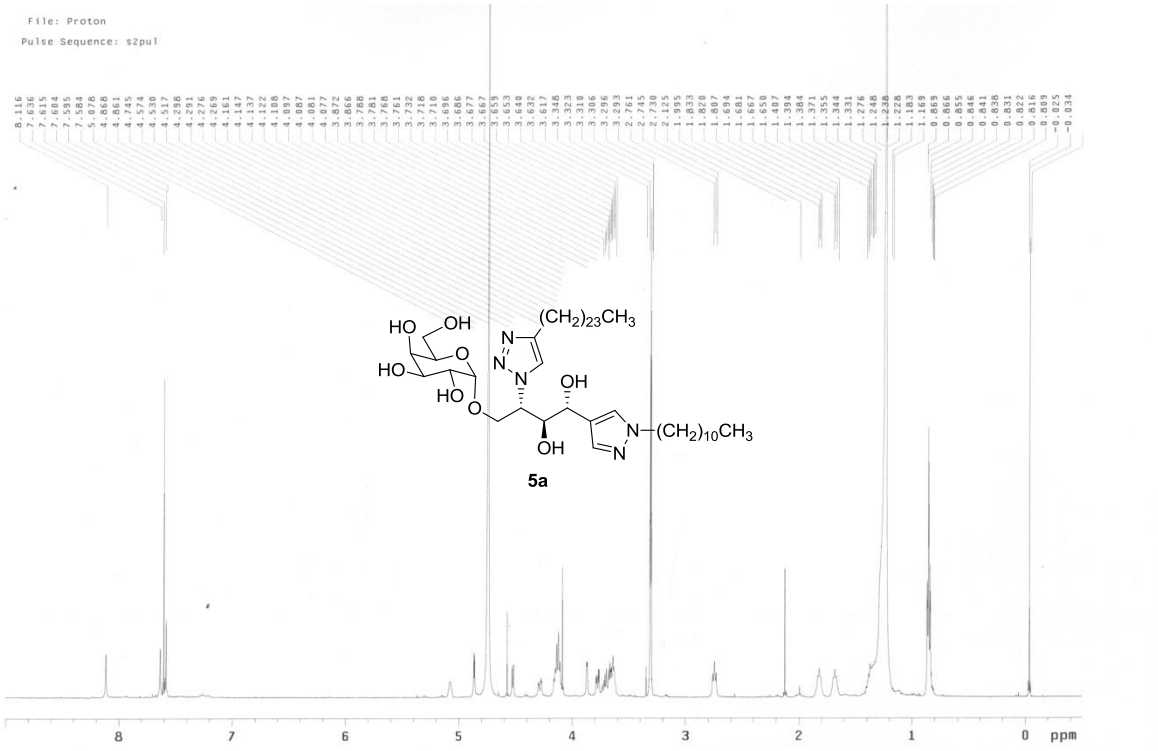
4c


File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
OH
O
HN
OH
OH
O
(CH2)5
N
N
(CH2)5
CH2CH3
8
7
6
5
4
3
2
1
0
ppm

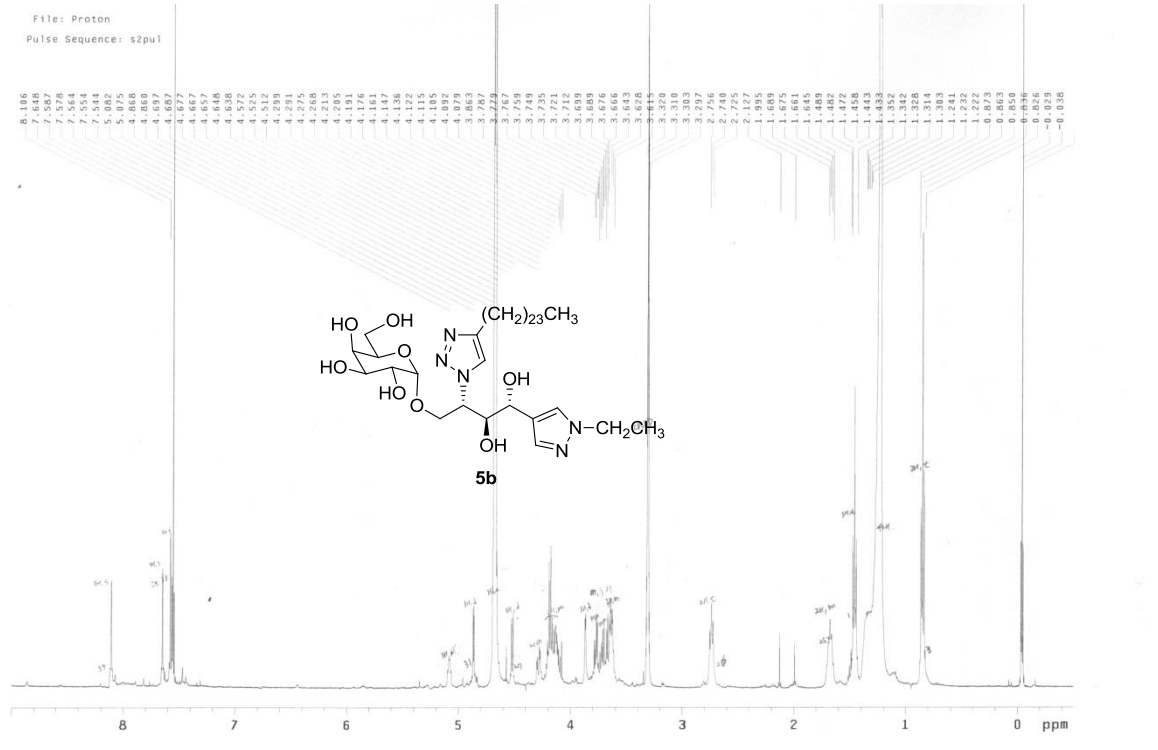
4d


File: Proton
Pulse Sequence: s2pul
HO
OH
O
HO
OH
O
HN
OH
OH
O
(CH2)5
N
N
(CH2)6
CH3
8
7
6
5
4
3
2
1
0
ppm

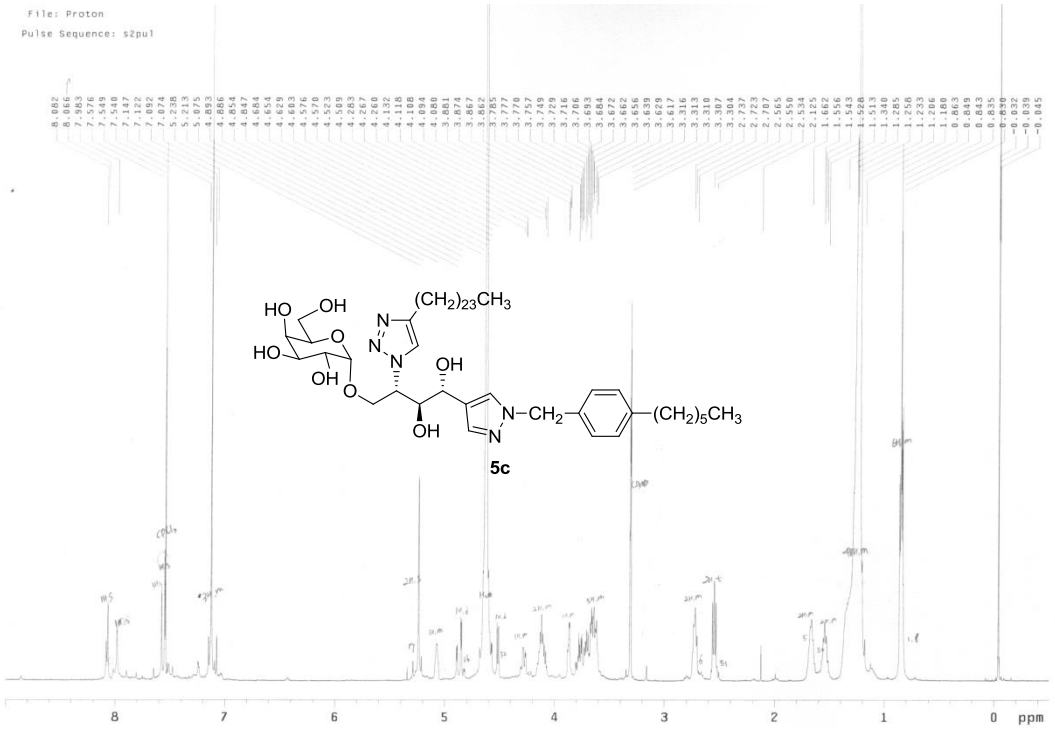
4e


File: Proton
Pulse Sequence: s2pul
HO
OH
HO
HO
O
O
N
N
N
(CH2)23CH3
OH
OH
N
N
(CH2)10CH3
8
7
6
5
4
3
2
1
0
ppm

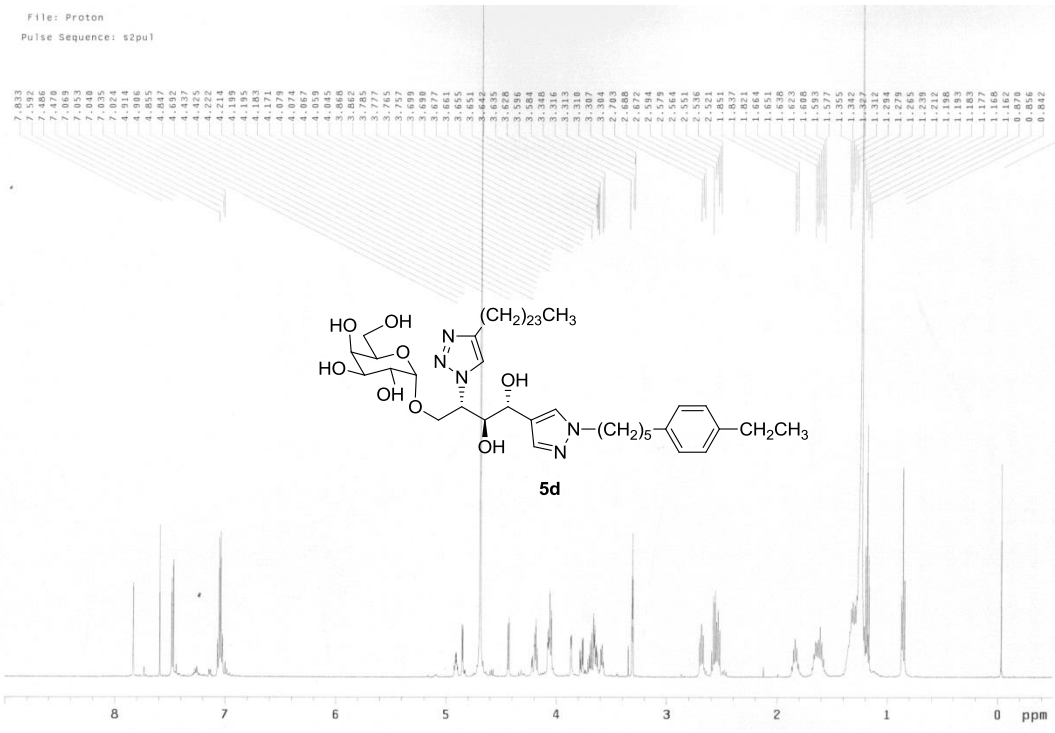
5a


File: Proton
Pulse Sequence: s2pul
HO
OH
HO
HO
O
O
N
N
N
(CH2)23CH3
OH
OH
N
N
CH2CH3
8
7
6
5
4
3
2
1
0
ppm

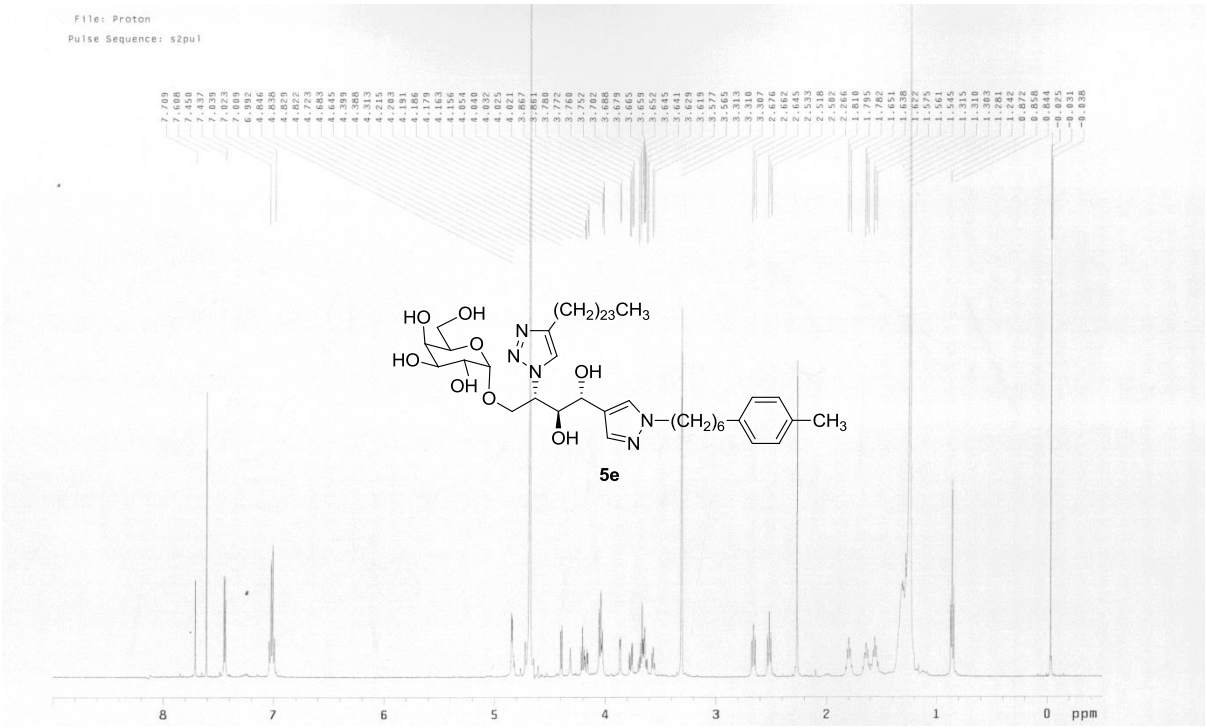
5b


File: Proton
Pulse Sequence: s2pul
HO
OH
HO
OH
O
N
N
N
(CH2)23CH3
OH
OH
N–CH2
(CH2)5CH3
8
7
6
5
4
3
2
1
0
ppm

5c


File: Proton
Pulse Sequence: s2pul
HO
OH
HO
OH
O
N
N
N
(CH2)23CH3
OH
OH
N–(CH2)5
CH2CH3
8
7
6
5
4
3
2
1
0
ppm

5d


File: Proton
Pulse Sequence: s2pul
HO
OH
HO
OH
O
O
N
N
N
(CH2)23CH3
OH
OH
N
N
(CH2)6
CH3
8
7
6
5
4
3
2
1
0
ppm

5e