Supplementary Material for:

BOP-Mediated One-Pot Synthesis of C_5-Symmetric Macrocyclic Pyridone Pentamers with High Cation-Binding Affinities†

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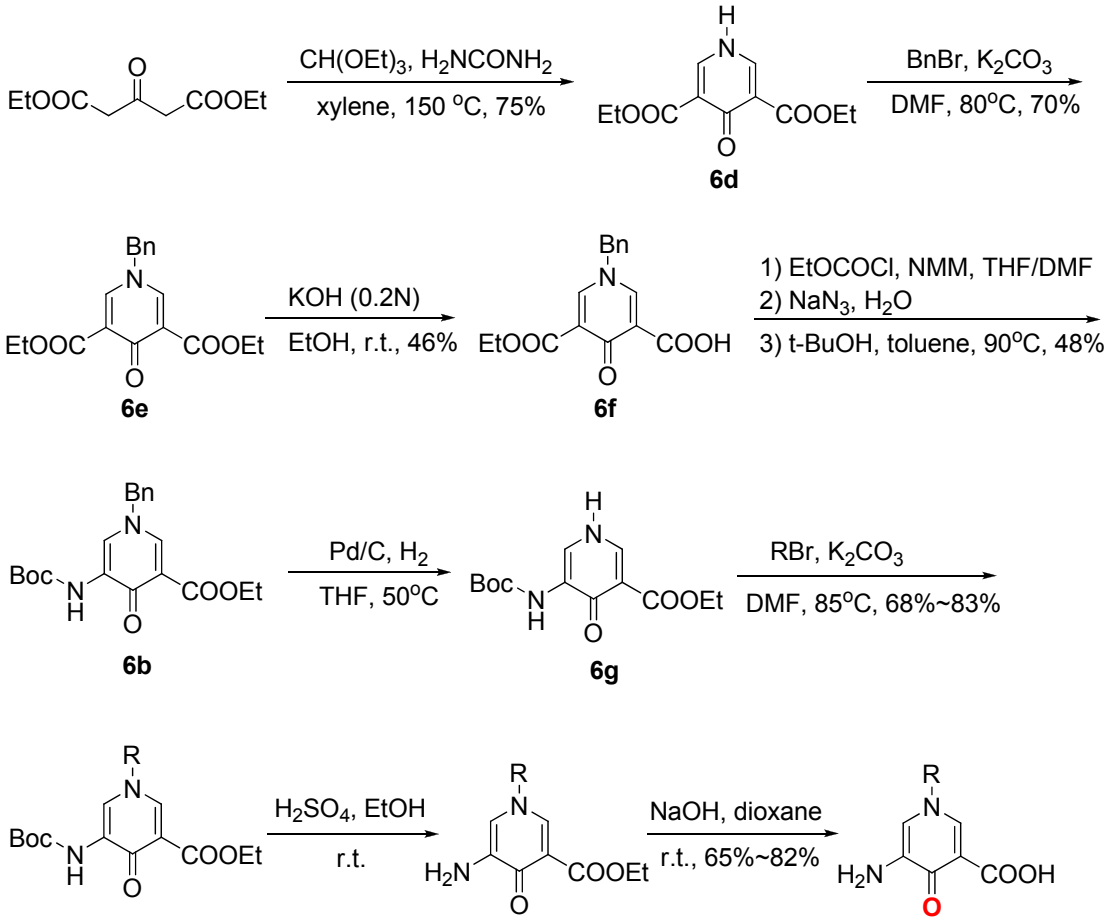
General Remarks

All the reagents were obtained from commercial suppliers and used as received unless otherwise noted. Aqueous solutions were prepared from distilled water. The organic solutions from all liquid extractions were dried over anhydrous Na_2SO_4 for a minimum of 15 minutes before filtration. Reactions were monitored by thin-layer chromatography (TLC) on silica gel pre-coated glass plate (0.225 mm thickness, 60F-254, E. Merck). Flash column chromatography was performed using pre-coated 0.2 mm silica plates from Selecto Scientific. Chemical yields refer to pure isolated substances. Mass spectra were obtained using the Instrumentation includes Finnigan MAT95XL-T and Micromass VG7035. ^{1}H NMR spectra were recorded on Bruker ACF300 (300 MHz) and ACF500 (500 MHz) spectrometers. In addition, key compounds were characterized by X-ray Diffraction. The solvent signal of $CDCl_3$ was referenced at δ = 7.26 ppm, and DMSO-d_6 at 2.50 ppm. Coupling constants (J values) are reported in Hertz (Hz). ^{1}H NMR data are recorded in the order: chemical shift value, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), number of protons that gave rise to the signal and coupling constant, where applicable. ^{13}C spectra were proton-decoupled and recorded on Bruker ACF300 (300 MHz) and ACF500 spectrometers (500 MHz). The solvent, $CDCl_3$ was referenced at 77 ppm and DMS0-d_6 at 39.5 ppm. $CDCl_3$ (99.8% deuterated) was purchased from Aldrich and used without further purification.

Scheme S1: Synthetic route that affords monomeric building blocks **1a**-**6a**



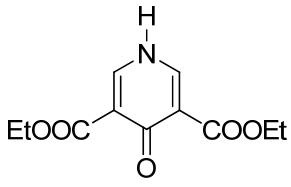
1b: R= *iso*-butyl
2b: R= C_8H_{17}
3b: R= $CH_2CH_2OCH_2CH_3$
4b: R= $(CH_2CH_2O)_2CH_3$
5b: R= $(CH_2CH_2O)_3CH_3$
6b: R= Bn= $CH_2C_6H_5$

1c: R= *iso*-butyl
2c: R= C_8H_{17}
3c: R= $CH_2CH_2OCH_2CH_3$
4c: R= $(CH_2CH_2O)_2CH_3$
5c: R= $(CH_2CH_2O)_3CH_3$
6c: R= Bn= $CH_2C_6H_5$

1a: R= *iso*-butyl
2a: R= C_8H_{17}
3a: R= $CH_2CH_2OCH_2CH_3$
4a: R= $(CH_2CH_2O)_2CH_3$
5a: R= $(CH_2CH_2O)_3CH_3$
6a: R= Bn= $CH_2C_6H_5$

Experimental Procedures and Compound Characterizations for Scheme S1
Preparation of monomeric building blocks 1a-6a

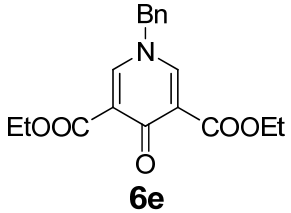
For synthesis of **6d**, see: Zheng, S. J.; Thompson, J. D.; Tontcheva, A.; Khan, S. I.; Rubin, Y. *Org. Lett.*, **2005**, 7, 1861.



6d

A mixture of diethyl 1,3-acetonedicarboxylate (0.2 mol, 40 mL), triethyl orthoformate (0.4 mol, 60 mL) and urea (0.3 mol, 18.00 g) in 100 mL of xylene was heated to reflux for 4 hours. After all the urea was dissolved and light yellow precipitate formed, the formed ethanol was removed *in vacuo*, and then the reaction mixture was allowed to reflux for another 1 hour. After cooling, the precipitate was filtered and washed with CH_2Cl_2 (3×50 mL), dried under vacuum to give the pure compound **6d**. Yield: 35.85 g, 75%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.18 (s, 1H), 8.19 (s, 2H), 4.18 (q, *J*=7.3Hz, 4H), 1.25 (t, *J*=7.3Hz, 6H).

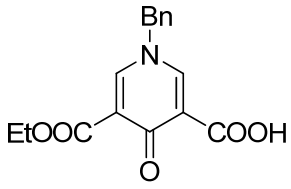
Diethyl 1-benzyl-4-oxo-1,4-dihydropyridine-3,5-dicarboxylate (6e)



6e

Compound **6d** (23.90 g, 100.0 mmol) was dissolved in DMF (350 mL), to which anhydrous K_2CO_3 (20.85 g, 150.0 mmol) and benzyl bromide (14.25 mL, 120.0 mmol) were added. The mixture was heated at 80℃ for 10 hours. The reaction mixture was then filtered and the solvent was removed in *vacuo*. The residue was dissolved in CH_2Cl_2 (350 mL), washed with water (3 x 400 mL), and dried over anhydrous Na_2SO_4. Removal of CH_2Cl_2 in *vacuo* gave the crude product, which was then washed with ethyl acetate (50 mL) to give the pure product **6e** as a pale yellow solid. Yield: 26.27 g, 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.39 – 7.35 (m, 3H), 7.21 (dd, *J* = 7.6, 1.7 Hz, 2H), 5.03 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.05, 164.54, 144.72, 133.59, 129.38, 129.18, 127.53, 123.04, 61.13, 60.79, 14.08. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{18}H_{19}O_5N_1Na$): *m/z* 352.1155, found: *m/z* 352.1154.

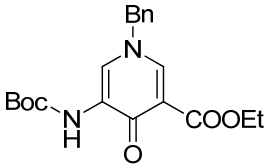
1-benzyl-5-(ethoxycarbonyl)-4-oxo-1,4-dihydropyridine-3-carboxylic acid (6f)



6f

Compound **6e** (13.16 g, 40.0 mmol) was dissolved in ethanol (200 mL), to which 0.2M KOH (200 mL, 40.0 mmol) was added dropwise using a dropping funnel at room temperature. The mixture was allowed to stir at room temperature for overnight. Then ethanol was removed in *vacuo* and the aqueous layer was neutralized by addition of 1M HCl (60 mL). The precipitated crude product was collected by filtration and dried in the oven, which was subjected to column purification (MeOH/CH_2Cl_2=1/50) to yield the pure product **6f** as a white solid. Yield: 5.54 g, 46%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.37 (s, 1H), 8.66 (d, *J* = 2.4 Hz, 1H), 8.39 (d, *J* = 2.4 Hz, 1H), 7.47– 7.43 (m, 3H), 7.32– 7.27 (m, 2H), 5.25 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 176.33, 165.52, 162.95, 146.62, 145.95, 132.67, 129.85, 129.75, 127.95, 121.36, 119.49, 61.99, 61.93, 14.15. ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.97, 166.13, 153.65, 152.37, 140.68, 133.22, 131.95, 129.64, 127.76, 126.05, 113.01, 81.95, 67.08, 62.80, 28.16. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{16}H_{15}O_5N_1Na$): *m/z* 324.0842, found: *m/z* 324.0845.

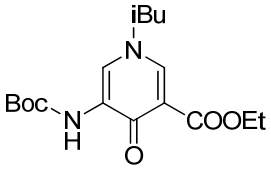
Ethyl 1-benzyl-5-(tert-butoxycarbonylamino)-4-oxo-1,4-dihydropyridine-3-carboxylate (6b)



6b

Compound **6f** (7.53 g, 25.0 mmol) was dissolved in THF/DMF (75 mL/50 mL) with an installation of balloon on top of the round bottom flask. This solution was cooled to 0ºC using an ice bath. 4-methylmorpholin (3.00 mL, 30.0 mmol) and ethyl chloroformate (3.00 mL, 30.0 mmol) was injected to the cooled solution. The mixture was allowed to stir for 25 minutes. Then sodium azide (2.44 g, 37.5 mmol) dissolved in minimal amount of water was injected into the cooled solution. 30 minutes later, THF was removed in *vacuo* at 28℃. The mixture was then dissolved in 200 mL CH_2Cl_2, washed with water (3 x 300 mL) and dried over anhydrous Na_2SO_4. Then CH_2Cl_2 was removed in *vacuo* and the residue was dissolved in toluene (150 mL), to which t-butanol (3.45 mL, 37.5 mmol) was added. The reaction was allowed to stirat 90℃ for 30 hours. The yellow precipitate was removed by filtration and removal of toluene in *vacuo* gave the crude product, which was subjected to column purification ($MeOH/CH_2Cl_2$=1/100) to yield the pure product **6b** as a pale yellow solid. Yield: 4.34 g, 47%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.15 (d, *J* = 2.1 Hz, 1H), 7.92 (s, 1H), 7.47 – 7.33 (m, 3H), 7.24-7.18 (m, 2H), 5.02 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 9H), 1.37 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 167.23, 165.11, 152.77, 141.87, 134.12, 133.32, 129.40, 129.13, 127.39, 123.50, 113.82, 81.03, 61.84, 61.02, 28.20, 14.29. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{20}H_{24}O_5N_2Na$)： *m/z* 395.1577, found: *m/z* 395.1575.

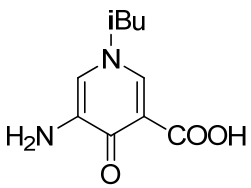
Ethyl 5-(tert-butoxycarbonylamino)-1-isobutyl-4-oxo-1,4-dihydropyridine-3-carboxylate (1b)



1b

Compound **6b** (1.86 g, 5.00 mmol) was reduced by catalytic hydrogenation in THF (20 mL) at 50 ^{0}C, using Pd/C (186 mg, 10%) as the catalyst for 6 hours. The reaction solvent was then removed in *vacuo* to give a white product **6g** mixed with Pd/C, which was directly used in the next step without further purification. DMF (20 mL), anhydrous K_2CO_3 (1.38 g, 10.00 mmol) and *iso*-butylbromide (0.65 mL, 6.00 mmol) was added to **6g** (5.00 mmol). The mixture was heated under 80℃ for 18hrs. The reaction mixture was then filtered and the solvent was removed in *vacuo*. The residue was dissolved in CH_2Cl_2 (100 mL), washed with water (3 x 100 mL), and dried over anhydrous Na_2SO_4. Removal of CH_2Cl_2 in *vacuo* gave the crude product, which was subjected to column purification ($MeOH/CH_2Cl_2$=1/100) to yield the pure product **1b** as a pale yellow oil. Yield: 1.15 g, 68%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.03 (d, *J* = 2.3 Hz, 1H), 7.92 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 3H), 3.65 (d, *J* = 7.5 Hz, 3H), 2.15 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.49 (s, 9H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.11, 165.12, 152.78, 141.85, 133.03, 123.13, 113.24, 80.89, 65.81, 60.83, 29.57, 28.16, 19.38, 14.24. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{17}H_{26}O_5N_2Na$)： *m/z* 361.1734, found: *m/z* 361.1731.

5-amino-1-isobutyl-4-oxo-1,4-dihydropyridine-3-carboxylic acid (1a)



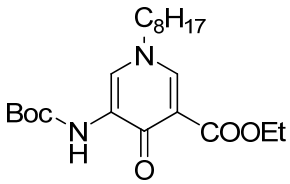
1a

Compound **1b** (1.01 g, 3.00 mmol) was dissolved in ethanol (30 mL), to which concentrated H_2SO_4 (3.0 mL) was slowly added to the solution. The reaction was allowed to stir at room temperature for 12 hours. Then the reaction mixture was neutralized using saturated aquous solution of $NaHCO_3$. The product was extracted with CH_2Cl_2 (5 x 50 mL). Combination of the organic layer and dried over anhydrous Na_2SO_4 to give the pure product **1c**, which was directly used in the next step without further purification.

Compound **1c** (3.00 mmol) was dissolved in dioxane/H_2O (30 mL/10 mL) to which 1.0 M NaOH (6.00 mL, 6.00 mmol) was added. The mixture was heated under 65℃ for 6 hours. Then H_2O (100 mL) was added to the solution, which was then neutralized by addition of 1M AcOH (6.50 mL). Dioxane was removed in *vacuo* and the precipitate was collected by filtration and dried in the oven to give the crude product which was then recrystallized from diethyl ether to give the pure product **1a** as a pink solid. Yield: 517 mg, 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.60 (br, 1H), 8.12 (d, J = 2.0 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 3.70 (d, J = 7.0 Hz, 2H), 3.45 (br, 2H), 2.13 (td, J = 13.8, 6.9 Hz, 1H), 0.97 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.51, 167.36, 139.47, 138.43, 119.34, 111.58, 66.30, 29.85, 19.49. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{10}H_{14}O_3N_2Na$)： *m/z* 233.0897, found: *m/z* 233.0892.

Monomers **2a**, **3a** and **6a** were prepared from **2c**, **3c** and **6c** via intermediates **2b**, **3b** and **6b** that were prepared from **6g** by alkylation in the same way as **1a** described above.

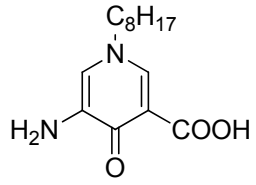
Ethyl 5-(tert-butoxycarbonylamino)-1-octyl-4-oxo-1,4-dihydropyridine-3-carboxylate (2b)



2b

Yield: 1.50 g, 76%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.07 (d, J = 2.3 Hz, 1H), 7.94 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.84 (t, J = 7.4 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.50 (s, 9H), 1.38 (t, J = 7.1 Hz, 3H), 1.33 – 1.23 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.16, 165.28, 152.90, 141.59, 133.25, 123.01, 113.45, 81.01, 60.98, 58.85, 31.61, 30.63, 28.98, 28.93, 28.23, 26.15, 22.53, 14.33, 14.00. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{21}H_{34}O_5N_2Na$)： *m/z* 417.2360, found: *m/z* 417.2353.

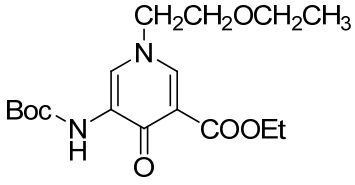
5-amino-1-octyl-4-oxo-1,4-dihydropyridine-3-carboxylic acid (2a)



2a

Yield: 519 mg, 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.17 (s, 1H), 3.95 (t, J = 7.3 Hz, 2H), 1.89 -1.83 (m, 2H), 1.36 -1.25 (m, 10H), 0.90 (t, J = 6.9 Hz, 3H), 0.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.34, 167.37, 143.02, 129.43, 114.22, 111.88, 59.33, 31.63, 30.66, 28.96, 28.94, 26.17, 22.55, 14.01. HRMS-ESI: calculated for $[M-H]^-$ ($C_{14}H_{21}O_3N_2$)**:** *m/z* 265.1558, found: *m/z* 265.1565.

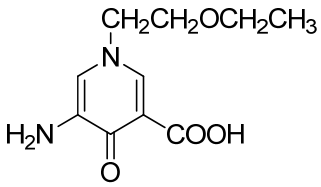
Ethyl 5-(tert-butoxycarbonylamino)-1-(2-ethoxyethyl)-4-oxo-1,4-dihydropyridine-3-carboxylate (3b)



3b

Yield: 1.40 g, 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.08 (d, J = 2.2 Hz, 1H), 7.79 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.94 (t, J = 4.8 Hz, 2H), 3.63 (t, J = 4.8 Hz, 2H), 3.37 (q, J = 7.0 Hz, 2H), 1.39 (s, 9H), 1.25 (t, J = 7.1 Hz, 3H), 1.04 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.25, 164.66, 152.65, 142.51, 132.70, 123.46, 113.17, 80.77, 68.49, 66.77, 60.56, 58.25, 28.10, 14.76, 14.21. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{17}H_{26}O_6N_2Na$)： *m/z* 377.1683, found: *m/z* 377.1698.

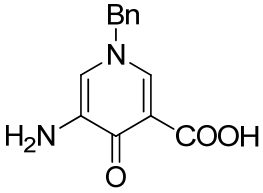
5-amino-1-(2-ethoxyethyl)-4-oxo-1,4-dihydropyridine-3-carboxylic acid (3a)



3a

Yield: 461 mg, 68%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.55 (s, 1H), 8.23 (d, *J* = 1.9 Hz, 1H), 7.18 (d, *J* = 1.8 Hz, 1H), 4.31 (s, 2H), 4.08 (t, *J* = 4.8 Hz, 2H), 3.75 (t, *J* = 4.8 Hz, 2H), 3.51 (q, *J* = 7.0 Hz, 1H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.71, 167.43, 139.17, 138.85, 120.06, 111.89, 68.66, 67.09, 58.94, 14.88. HRMS-ESI: calculated for $[M+H]^+$ ($C_{10}H_{13}O_4N_2$)：*m/z* 225.0881, found: *m/z* 225.0875.

5-amino-1-benzyl-4-oxo-1,4-dihydropyridine-3-carboxylic acid (6a)

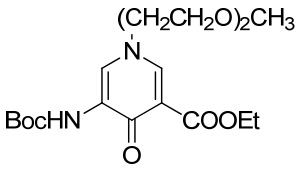


6a

Yield: 520 mg, 71%. ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6 = 4/1) δ 16.00 (br, 1H), 8.29 (d, *J* = 1.8 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.21 (d, *J* = 6.4 Hz, 2H), 5.11 (s, 2H), 4.92 (br, 2H). ^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6=4/1) δ 165.21, 162.47, 135.34, 132.50, 129.49, 124.19, 124.00, 122.92, 114.62, 106.17, 56.71. HRMS-ESI: calculated for $[M-H]^-$ ($C_{13}H_{11}O_3N_2$)：*m/z* 243.0775, found: *m/z* 243.0787.

4b and **5b** was prepares from **6g** in the same way as **1b** was prepared from **6g**.

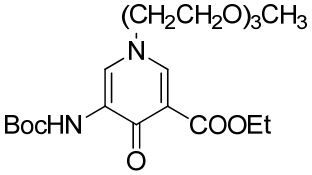
Ethyl-5-(tert-butoxycarbonylamino)-1-(2-(2-methoxyethoxy)ethyl)-4-oxo-1,4-dihydropyridine-3-carboxylate (4b)



4b

Yield: 1.59 g, 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.04 (d, *J* = 2.3 Hz, 1H), 7.73 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.94 (t, *J* = 4.9 Hz, 2H), 3.68 (t, *J* = 4.9 Hz, 2H), 3.44 (t, *J* = 4.9 Hz, 2H), 3.34 (t, *J* = 4.9 Hz, 2H), 3.17 (s, 3H), 1.34 (s, 9H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.88, 164.20, 152.21, 142.20, 132.25, 123.18, 112.75, 80.40, 71.36, 70.36, 69.08, 60.16, 58.50, 57.78, 27.72, 13.85. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{18}H_{28}O_7N_2Na$)：*m/z* 407.1789, found: *m/z* 407.1801.

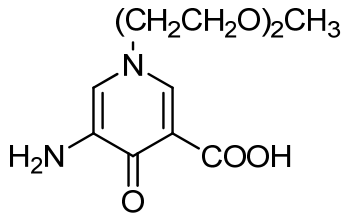
Ethyl 5-(tert-butoxycarbonylamino)-1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-4-oxo-1,4-dihydro pyridine-3-carboxylate (5b)



5b

Yield: 1.61 g, 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.08 (d, *J* = 2.3 Hz, 1H), 7.79 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 4.9 Hz, 2H), 3.72 (t, *J* = 4.9 Hz, 2H), 3.53 -3.47 (m, 6H), 3.39 (t, *J* = 4.9 Hz, 2H), 3.24 (s, 3H), 1.39 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.97, 164.48, 152.40, 142.31, 132.47, 123.20, 112.94, 80.56, 71.49, 70.68, 70.25, 70.22, 69.19, 60.39, 58.56, 57.98, 27.87, 13.99. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{18}H_{28}O_7N_2Na$)：*m/z* 451.2051, found: *m/z* 451.2071.

5-amino-1-(2-(2-methoxyethoxy)ethyl)-4-oxo-1,4-dihydropyridine-3-carboxylic acid (4a)

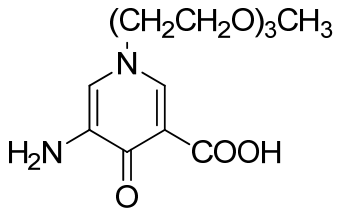


4a

Compound **4b** (1.15 g, 3.00 mmol) was dissolved in ethanol (30 mL), to which concentrated H_2SO_4 (3.0 mL) was slowly added to the solution. The reaction was allowed to stir at room temperature for 18 hours. Then the reaction mixture was neutralized using saturated aquous solution of $NaHCO_3$. The product was extracted with CH_2Cl_2 (10 x 50 mL). Combination of the organic layer and dried over anhydrous Na_2SO_4 to give the pure product **4c**, which was directly used in the next step without further purification. Compound **4c** was dissolved in dioxane/H_2O (30 mL/10 mL) to which 1.0 M NaOH (6.00 mL, 6.00 mmol) was added. The reaction was allowed to stir for 12 hours, which was then neutralized by addition of AcOH (1.00 mL). All of the solvent was removed in *vacuo* and CH_2Cl_2 (200 mL) was added. Collecting the solution by filtration and removal of the solvent in *vacuo* gave the crude product which was crystallized in diethyl ether to give the pure product **4a** as a pink solid. Yield: 361 mg, 47%. ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6=4/1) δ 8.15 (d, J = 1.9 Hz, 1H), 7.27 (d, J = 1.8 Hz, 1H), 4.06 (t, J = 4.9 Hz, 2H), 3.74 (t, J = 4.9 Hz, 2H), 3.51 (t, J = 4.9 Hz, 2H), 3.40 (t, J = 4.9 Hz, 2H), 3.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6=4/1) δ 169.66, 166.93, 139.05, 137.55, 119.84, 110.73, 71.13, 70.02, 68.95, 58.31, 57.92. HRMS-ESI: calculated for $[M-H]^-$ ($C_{11}H_{15}O_5N_2$)： *m/z* 255.0986, found: *m/z* 255.0984.

5a was prepared from **5b** in the same way as **4a** was prepared from **4b** described above.

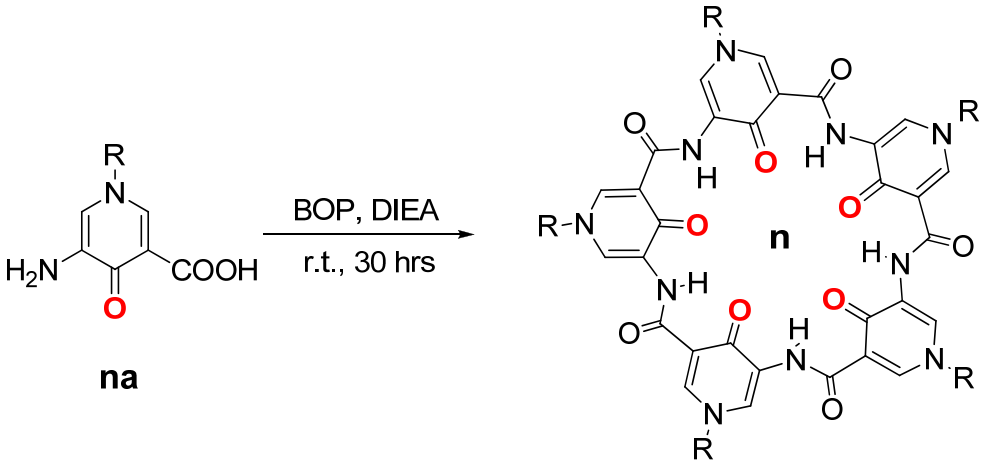
5-amino-1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-4-oxo-1,4-dihydropyridine-3-carboxylic acid(5a)



5a

Yield: 477 mg, 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.74 (s, 1H), 8.17 (d, J = 2.3 Hz, 1H), 7.36 (s, 1H), 4.52 (br, 2H), 4.07 (t, J = 4.9 Hz, 2H), 3.83 (t, J = 4.9 Hz, 2H), 3.65 – 3.54 (m, 8H), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.57, 167.49, 139.45, 138.35, 120.47, 111.78, 71.92, 70.67, 70.59, 70.46, 69.64, 58.82, 58.55. HRMS-ESI: calculated for $[M-H]^-$ ($C_{11}H_{15}O_5N_2$)： *m/z* 299.1249, found: *m/z* 299.1256.

Scheme S2: Synthetic route that affords pentamers **1-6**



na

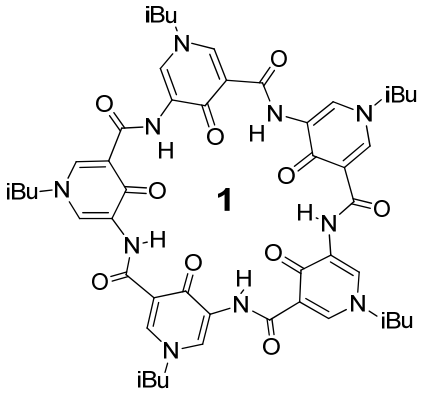
1a: R= *iso*-butyl
2a: R= C_8H_{17}
3a: R= $CH_2CH_2OCH_2CH_3$
4a: R= $(CH_2CH_2O)_2CH_3$
5a: R= $(CH_2CH_2O)_3CH_3$
6a: R= Bn= $CH_2C_6H_5$

1: R= *iso*-butyl
2: R= C_8H_{17}
3: R= $CH_2CH_2OCH_2CH_3$
4: R= $(CH_2CH_2O)_2CH_3$
5: R= $(CH_2CH_2O)_3CH_3$
6: R= Bn= $CH_2C_6H_5$

Experimental Procedures and Compound Characterizations for Scheme S2

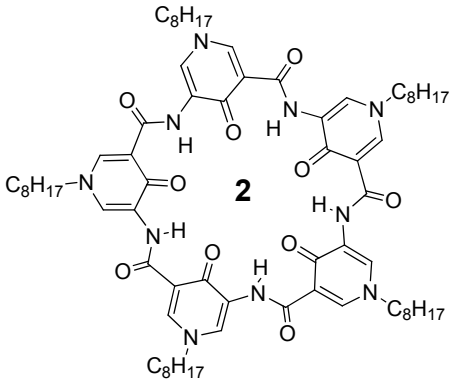
One-pot preparation of Pentamers 1-6:

Pentamer 1



Compound **1a** (42.0 mg, 0.20 mmol) and BOP (176.8 mg, 0.4 mmol) were dissolved in anhydrous CH_2Cl_2 (3.0 mL) to which DIEA (0.14 ml, 0.80 mmol) was added and the reaction mixture was allowed to stirred continuously for 30 hours at room temperature. Removal of the solvent in *vacuo* gave the crude product, which was then washed with MeOH (3 x 3 mL) and CH_2Cl_2 (3 x 3 mL) to yield the pure product **1** as a white solid. Yield: 9.6 mg, 25%. ^{1}H NMR (500 MHz, DMSO-d_6, 110℃) δ 13.42 (s, 5H), 8.97 (s, 5H), 8.47 (s, 5H), 4.03 (d, J = 7.0 Hz, 10H), 2.18 (td, J = 13.8, 6.9 Hz, 5H), 1.01 (d, J = 6.6 Hz, 30H). ^{13}C NMR (125 MHz, DMSO-d_6, 110℃) δ167.83, 161.94, 140.75, 131.45, 126.39, 113.92, 64.25, 28.46, 18.37. HRMS-ESI: calculated for $[M+K]^+$ ($C_{50}H_{60}O_{10}N_{10}K$)：*m/z* 999.4125, found: *m/z* 999.4138.

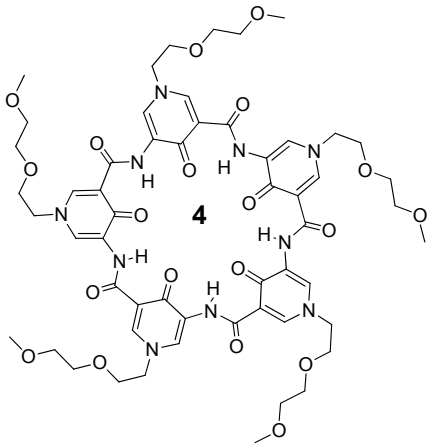
Pentamer 2



Compound **2a** (53.2 mg, 0.2 mmol) and BOP (176.8 mg, 0.4 mmol) were dissolved in anhydrous CH_2Cl_2 (6.0 mL) to which DIEA (0.14 ml, 0.80 mmol) was added and the reaction mixture was allowed to stirred continuously for 30 hours at room temperature. Removal of the solvent in *vacuo* gave the crude product, which was recrystallized from MeOH (20 mL) to yield the pure product **2** as a white solid. Yield: 8.9 mg, 18%. ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6=1/5, 110℃) δ 13.39 (s, 5H), 8.93 (s, 5H), 8.41 (s, 5H), 4.13 (t, J = 7.4 Hz, 10H), 1.97 – 1.86 (m, 10H), 1.49 – 1.27 (m, 50H), 0.89 (t, J = 7.0 Hz, 15H). ^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6=1/2, 110 ℃) δ 167.31, 160.92, 139.27, 131.22, 125.25, 113.88, 57.67, 30.44, 29.10, 27.89, 27.74, 25.19, 21.14, 12.61. HRMS-ESI: calculated for $[M+K]^+$ ($C_{70}H_{100}O_{10}N_{10}K$)：*m/z* 1279.7255, found: *m/z* 1279.7275.

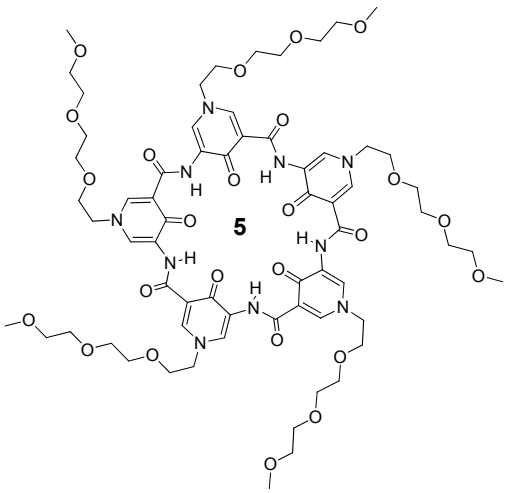
Pentamers **4, 5** and were prepared in the same way as **2** described above.

Pentamer 4



Yield: 4.8 mg, 10%. ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6=1/9, 110℃) δ 13.29 (s, 5H), 8.94 (s, 5H), 8.42 (s, 5H), 4.37 (t, *J* = 4.7 Hz, 10H), 3.90 (t, *J* = 4.8 Hz, 10H), 3.62 (t, *J* = 4.8 Hz, 10H), 3.48 (t, *J* = 4.8 Hz, 10H), 3.27 (s, 15H). ^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6=1/9, 110℃) δ 167.95, 161.76, 140.80, 131.50, 126.41, 114.19, 70.73, 69.39, 68.71, 57.36, 57.32. HRMS-ESI: calculated for $[M+K]^+$ ($C_{55}H_{70}O_{20}N_{10}K$)：*m/z* 1229.4399, found: *m/z* 1229.4388.

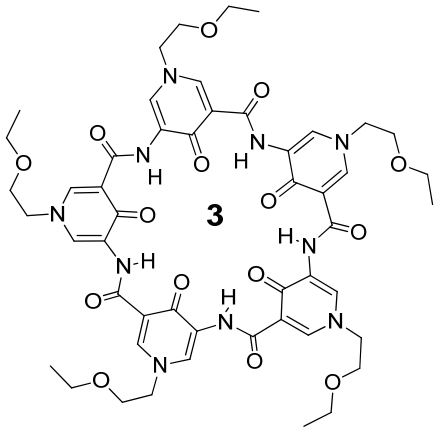
Pentamer 5



Yield: 9.0 mg, 16%. ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6=1/9, 110℃) δ 13.09 (s, 5H), 8.77 (s, 5H), 8.26 (s, 5H), 4.32 (t, *J* = 4.7 Hz, 10H), 3.98 (t, *J* = 4.8 Hz, 10H), 3.71 (t, *J* = 4.8 Hz, 10H), 3.64 (t, *J* = 4.8 Hz, 10H), 3.58 (t, *J* = 4.8 Hz, 10H), 3.47 (t, *J* = 4.8 Hz, 10H),3.28 (s, 15H). ^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6=1/9, 110℃) δ 167.67, 161.22, 140.33, 131.25, 126.22, 113.98, 70.86, 69.67, 69.33, 69.25, 68.75, 57.39, 57.31. HRMS-ESI: calculated for $[M+K]^+$ ($C_{65}H_{90}O_{25}N_{10}K$)：*m/z* 1449.5710, found: *m/z* 1449.5750.

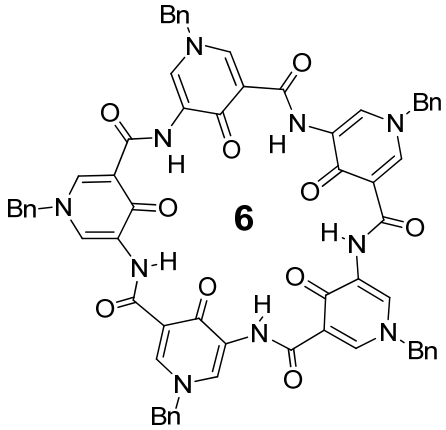
Pentamers **3** and **6** were prepared in the same way as **1** described above.

Pentamer 3



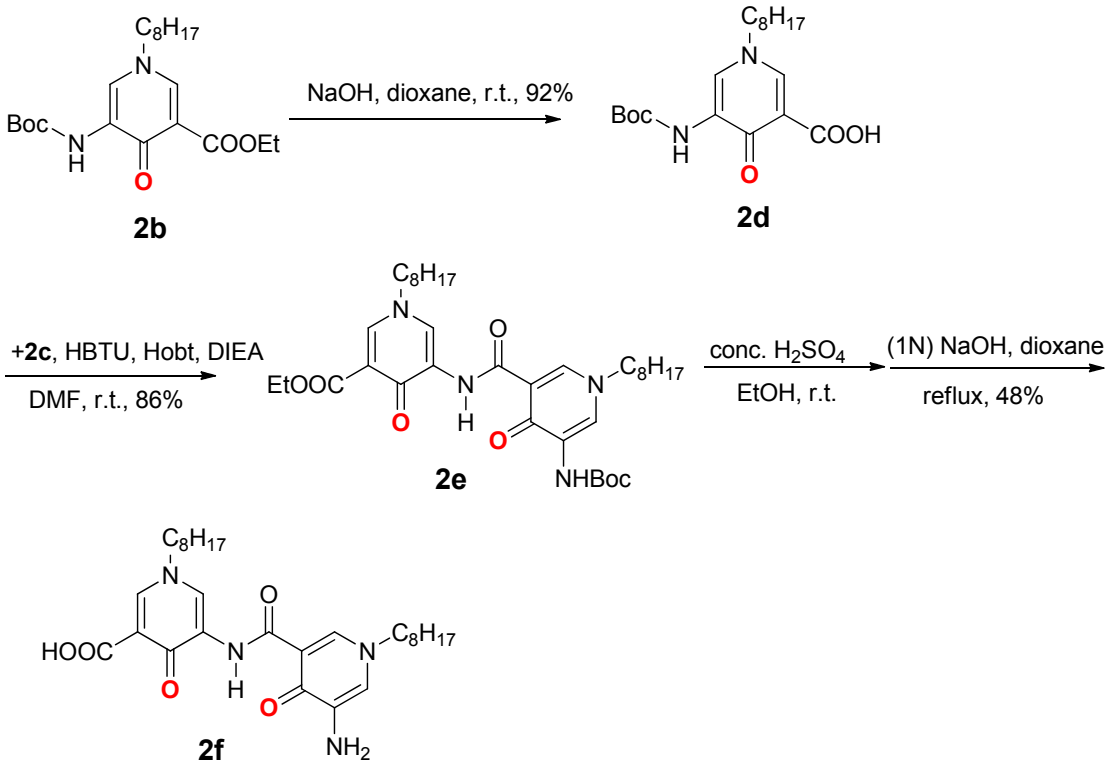
Yield: 5.0 mg, 12%. ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6=1/9, 110℃) δ 13.21 (s, 5H), 8.91 (d, J = 1.5 Hz, 5H), 8.39 (d, J = 1.8 Hz, 5H), 4.35 (t, J = 4.8 Hz, 10H), 3.86 (t, J = 4.8 Hz, 10H), 3.56 (q, J = 6.9 Hz, 10H), 1.17 (t, J = 6.9 Hz, 15H). ^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6=1/9, 110℃) δ 167.82, 161.63, 140.68, 131.39, 126.36, 114.06, 67.81, 65.21, 57.33, 13.84. HRMS-ESI: calculated for $[M+K]^+$ ($C_{50}H_{60}O_{15}N_{10}K$)：*m/z* 1079.3871, found: *m/z* 1079.3912.

Pentamer 6



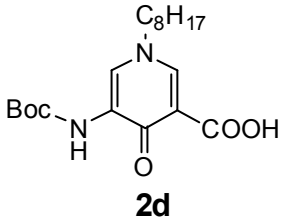
Yield: 4.3 mg, 10%. ^{1}H NMR (500 MHz, DMSO-d_6, 110℃) δ 13.43 (s, 5H), 8.99 (s, 5H), 8.70 (s, 5H), 7.46 – 7.38 (m, 25H), 5.43 (s, 10H). ^{13}C NMR (125 MHz, DMSO-d_6, 110℃) δ 167.81, 161.59, 140.60, 134.57, 131.56, 128.24, 127.80, 127.48, 126.00, 114.10, 60.25. HRMS-ESI: calculated for $[M+K]^+$ ($C_{65}H_{50}O_{10}$ $N_{10}K$)：*m/z* 1169.3343, found: *m/z* 1169.3350.

Scheme S3: Synthetic route that affords dimer **2f**



Experimental Procedures and Compound Characterizations for Scheme S4
Preparation of Dimer 2f

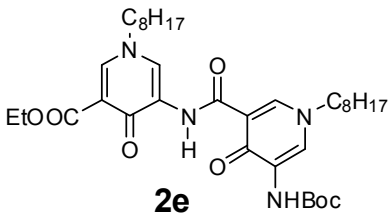
5-(tert-butoxycarbonylamino)-1-octyl-4-oxo-1,4-dihydropyridine-3-carboxylic acid (2d)



2d

Compound **2b** (3.15 g, 8.0 mmol) was dissolved in dioxane/H_2O (40 mL/10 mL), to which 1.0M NaOH (16.0 mL, 16.0 mmol) was added. The mixture was allowed to stir at room temperature for 10 hours. Then H_2O (100 mL) was added to the solution, which was then neutralized by addition of 1M AcOH (20.0 mL). Dioxane was removed in *vacuo* and the crude product was dissolved in 150 mL CH_2Cl_2, washed with water (3 x 200 mL) and dried over anhydrous Na_2SO_4 to give a pure product **2d** as a brown solid. Yield: 2.69 g, 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.94 (s, 1H), 8.56 (s, 1H), 8.32 (d, J = 2.2 Hz, 1H), 7.65 (s, 1H), 7.26 (s, 1H), 3.97 (t, J = 7.4 Hz, 2H), 2.00 – 1.80 (m, 2H), 1.56 (s, 9H), 1.39 – 1.20 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.77, 166.30, 152.48, 140.42, 131.82, 125.70, 112.76, 81.91, 59.72, 31.59, 30.74, 28.93, 28.88, 28.16, 26.12, 22.52, 13.99. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{19}H_{30}O_5N_2Na$)：*m/z* 389.2074, found: *m/z* 389.2032.

ethyl 5-(5-(tert-butoxycarbonylamino)-1-octyl-4-oxo-1,4-dihydropyridine-3-carboxamido)-1-octyl-4-oxo-1,4-dihydropyridine-3-carboxylate (2e)

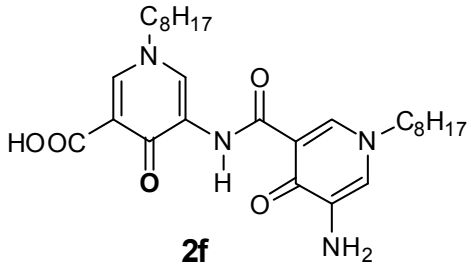


2e

Compound **2b** (1.97 g, 5.0 mmol) was dissolved in ethanol (70 mL), to which concentrated H_2SO_4 (5.0 mL) was slowly added to the solution. The reaction was allowed to stir at room temperature for 12 hours. Then the reaction mixture was neutralized using saturated aqueous solution of $NaHCO_3$. The product was extracted with CH_2Cl_2 (4 x 60 mL). Combination of the organic layer and dried over anhydrous Na_2SO_4 to give the pure product **2c**, which was directly used in the next step without further purification. Compound **2d** (1.83 g, 5.0 mmol), compound **2c** (5.0 mmol), HBTU (2.13 g, 5.5 mmol) and HoBt (0.73 g, 5.5 mmol) were dissolved in DMF (30 mL), to which DIEA (1.75 mL, 10.0 mmol) was added to the solution. The reaction was allowed to stir at room temperature for 24 hours. Then DMF was removed in *vacuo* and the residue was dissolved in CH_2Cl_2 (200 mL), washed with water (3 x 300 mL) and dried over Na_2SO_4 to give the crude product, which was subjected to column purification (MeOH/CH_2Cl_2=1/100) to yield the pure product **2e** as a colorless oil.. Yield: 2.76 g, 86%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.90 (s, 1H), 8.85 (d, J = 2.3 Hz, 1H), 8.33 (s, 1H), 8.25 (d, J = 2.2 Hz, 1H), 8.07 (d, J = 2.3 Hz, 1H), 8.03 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.89 (t, J = 7.3 Hz, 2H), 3.83 (t, J = 7.3 Hz, 2H), 1.85 – 1.75 (m, 4H), 1.47 (d, J = 3.6 Hz, 11H), 1.35 (t, J = 7.1 Hz, 3H), 1.31 – 1.19 (m, 20H), 0.83 (t, J = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.92, 167.60, 165.86, 163.22, 152.78, 142.28, 139.72, 133.68, 132.50, 126.05, 123.59, 114.82, 114.61, 80.94, 60.82, 59.09, 58.51, 38.47, 31.52, 31.51, 30.57, 30.46, 28.87, 28.84, 28.83, 28.12, 28.07, 26.07, 22.42, 14.28, 13.86. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{35}H_{54}O_7N_4Na$)：*m/z* 665.3885, found: *m/z* 665.3869.

5-(5-amino-1-octyl-4-oxo-1,4-dihydropyridine-3-carboxamido)-1-octyl-4-oxo-1,4-dihydropyridine -3-carboxylic acid (2f)

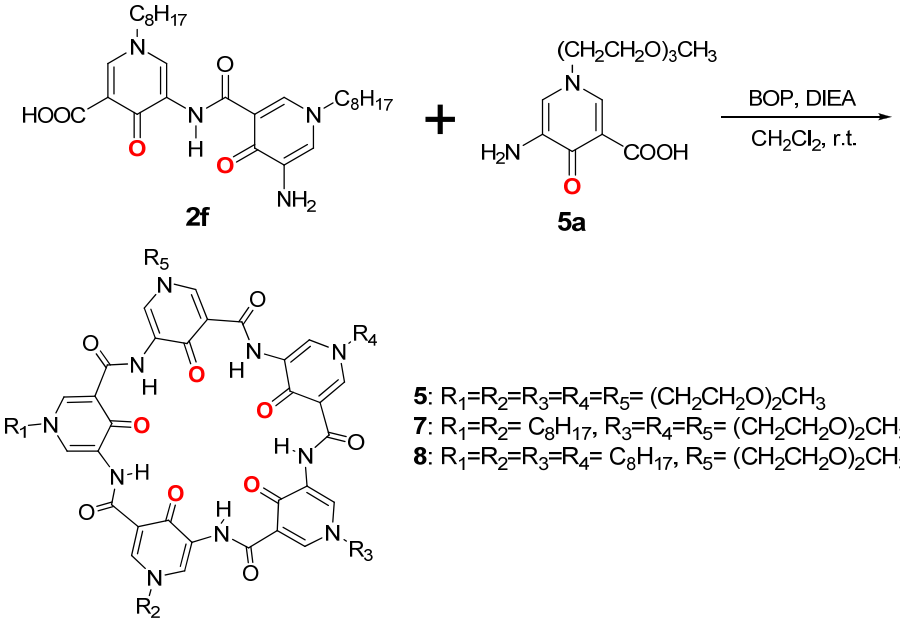
Compound **2e** (1.29 g, 2.00 mmol) was dissolved in ethanol (25 mL), to which concentrated H_2SO_4



2f

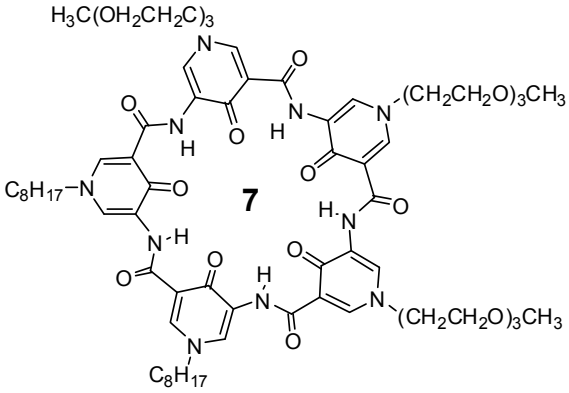
(3.0 mL) was slowly added to the solution. The reaction was allowed to stir at room temperature for 12 hours. Then the reaction mixture was neutralized using saturated aquous solution of $NaHCO_3$. The product was extracted with CH_2Cl_2 (4 x 50 mL). Combination of the organic layer and dried over anhydrous Na_2SO_4 to give the pure product **2g**, which was directly used in the next step without further purification. Compound **2g** (2.00 mmol) was dissolved in dioxane/H_2O (30 mL/10 mL) to which 1.0 M NaOH (4.0 mL, 4.00 mmol) was added. The mixture was heated under 65℃ for 6 hours. Then H_2O (100 mL) was added to the solution, which was then neutralized by addition of 1M AcOH (4.5 mL). Dioxane was removed in *vacuo* and the precipitate was collected by filtration and dried in the oven to give the crude product which was subjected to column purification (MeOH/CH_2Cl_2=1/40) to yield the pure product 2f as a pale yellow solid. Yield: 494 mg, 48%.^{1}H NMR (500 MHz, $CDCl_3$) δ 15.46 (s, 1H), 13.35 (s, 1H), 9.13 (s, 1H), 8.31 (s, 1H), 8.12 (s, 1H), 7.06 (s, 1H), 4.39 (br, 2H), 3.99 (t, J = 7.3 Hz, 2H), 3.88 (s, 3H), 1.86 (s, 2H), 1.80 (s, 2H), 1.32-1.20 (m, 20H), 0.88-0.81 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.71, 168.99, 166.68, 164.40, 140.72, 137.54, 132.18, 128.47, 117.86, 113.34, 112.83, 104.95, 59.54, 58.90, 31.56, 31.54, 30.65, 30.49, 28.91, 28.90, 28.88, 28.87, 26.11, 26.08, 22.47, 22.46, 13.95. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{28}H_{42}O_5N_4Na$)：*m/z* 537.3047, found: *m/z* 537.3034.

Scheme S4: One-pot reaction of **2f** and **5a** that affords pentamers **5**, **7** and **8**



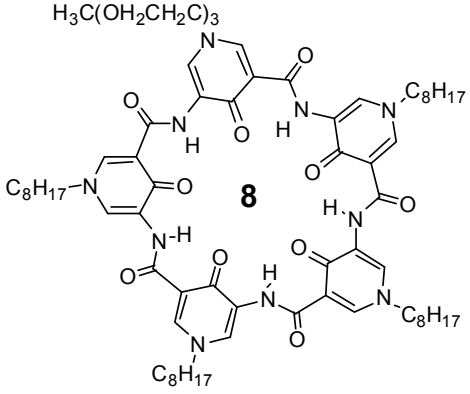
5: $R_1=R_2=R_3=R_4=R_5=(CH_2CH_2O)_2CH_3$
7: $R_1=R_2=C_8H_{17}$, $R_3=R_4=R_5=(CH_2CH_2O)_2CH_3$
8: $R_1=R_2=R_3=R_4=C_8H_{17}$, $R_5=(CH_2CH_2O)_2CH_3$

Compound **2f** (51.5 mg, 0.1 mmol), **5a** (90.1 mg, 0.3 mmol) and BOP (353.6 mg, 0.8 mmol) were dissolved in anhydrous CH_2Cl_2 (20.0 mL), to which DIEA (0.28 ml, 1.60 mmol) was added and the reaction mixture was allowed to stir for 30 hours at room temperature. Removal of the solvent in *vacuo* gave the crude product, which was recrystallized from MeOH (30 mL) to yield the mixture of pentamer **5**, **7** and **8**, which were separated by the preparative TLC plate to give the pure pentamer **5** (2.8 mg, 1.98 x 10^{-3} mmol), pentamer **7** (10.3 mg, 7.67 x 10^{-3} mmol) and pentamer **8** (6.7 mg, 5.25 x 10^{-3} mmol) as white solids. The molar ratio of produced pentamers **5**:**7**:**8** = 2:8:5



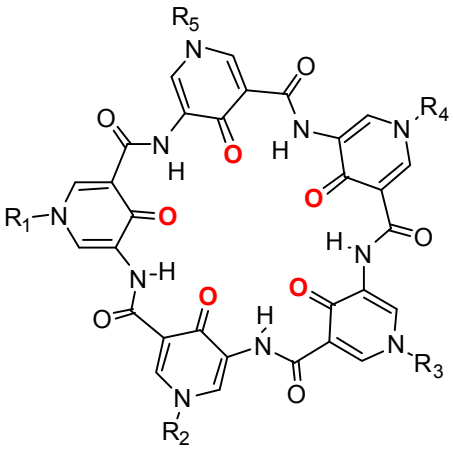
Pentamer 7

^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6=3/7, 85℃) δ 12.85 (s, 5H), 8.85=4 – 8.69 (m, 5H), 8.36 – 8.24 (m, 5H), 4.38 (s, 6H), 4.18 (s, 4H), 3.97 (s, 6H), 3.70 (s, 6H), 3.63 (s, 6H), 3.56 (s, 6H), 3.45 (t, J = 4.2 Hz, 6H), 3.25 (s, 9H), 1.95 (s, 4H), 1.52 – 1.35 (m, 20H), 0.92 – 0.89 (m, 6H). HRMS-ESI: calculated for $[M+K]^+$ ($C_{67}H_{94}O_{19}N_{10}K$): *m/z* 1381.6328, found: *m/z* 1381.6315.



Pentamer 8

^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6=3/7, 85℃) δ 12.88 (s, 5H), 8.77 – 8.66 (m, 5H), 8.29 – 8.18 (m, 5H), 4.36 (s, 2H), 4.16 (s, 8H), 3.98 (s, 2H), 3.72 (t, J = 4.2 Hz, 2H), 3.64 (t, J = 4.2 Hz, 2H), 3.56 (t, J = 4.2 Hz, 2H), 3.45 (t, J = 4.2 Hz, 2H), 3.25 (s, 3H), 1.97 – 1.92 (m, 8H), 1.51 – 1.34 (m, 40H), 0.91 (t, J = 6.2 Hz, 12H). HRMS-ESI: calculated for $[M+K]^+$ ($C_{69}H_{98}O_{12}N_{10}K$): *m/z* 1313.6946, found: *m/z* 1313.6977.



2: R_1=R_2=R_3=R_4=R_5= C_8H_{17}
5: R_1=R_2=R_3=R_4=R_5= $(CH_2CH_2O)_2CH_3$
7: R_1=R_2= C_8H_{17}, R_3=R_4=R_5= $(CH_2CH_2O)_2CH_3$
8: R_1=R_2=R_3=R_4= C_8H_{17}, R_5= $(CH_2CH_2O)_2CH_3$

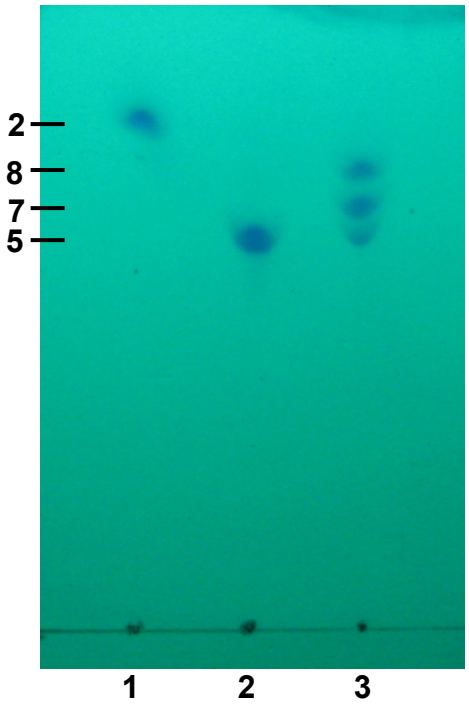


Figure S1. Structures of pentamers **2**, **5**, **7** and **8** containing monomeric units of **2a** and **5a** in varying ratios. Using MeOH/CH_2Cl_2 (1:10, v/v) as the eluent, pentamers **5**, **7** and **8** can be well separated in TLC plate. Lane 3 = macrocylization reaction products obtained by reacting **2f** and **5a** in a molar ratio of 1:3 and after recrystallizing the reaction mixture from MeOH.

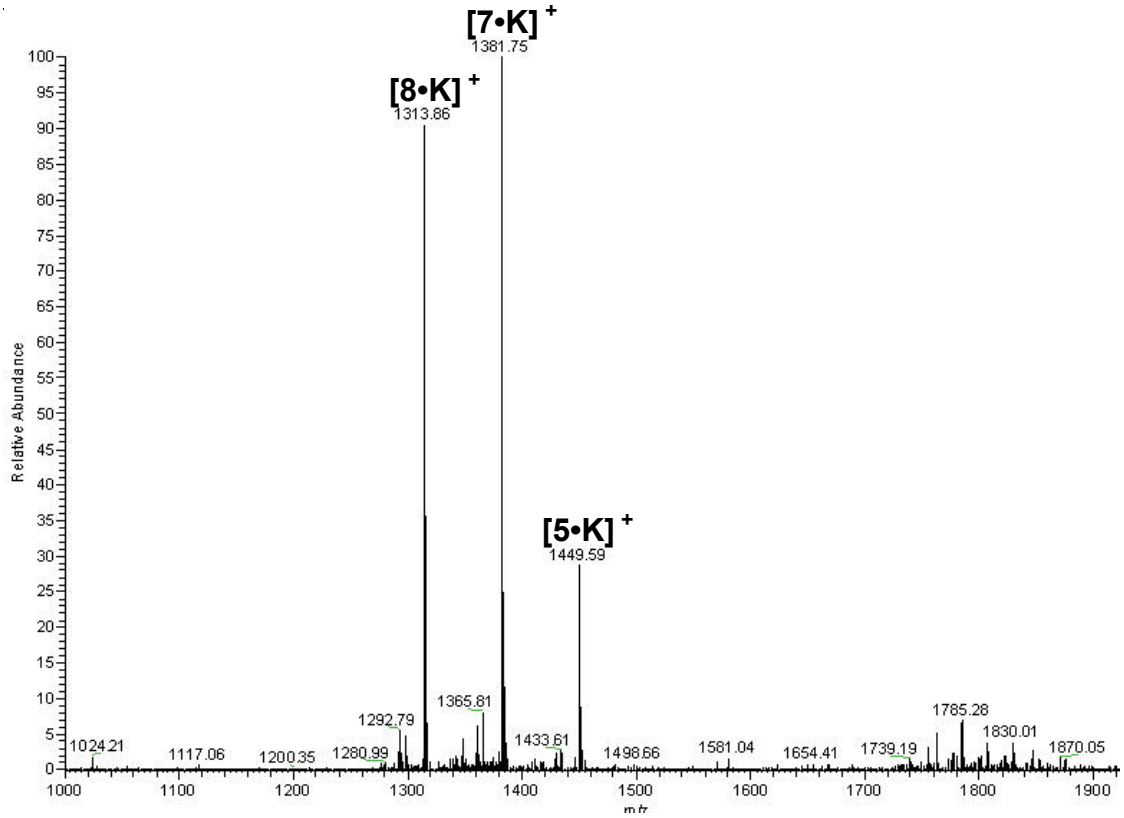
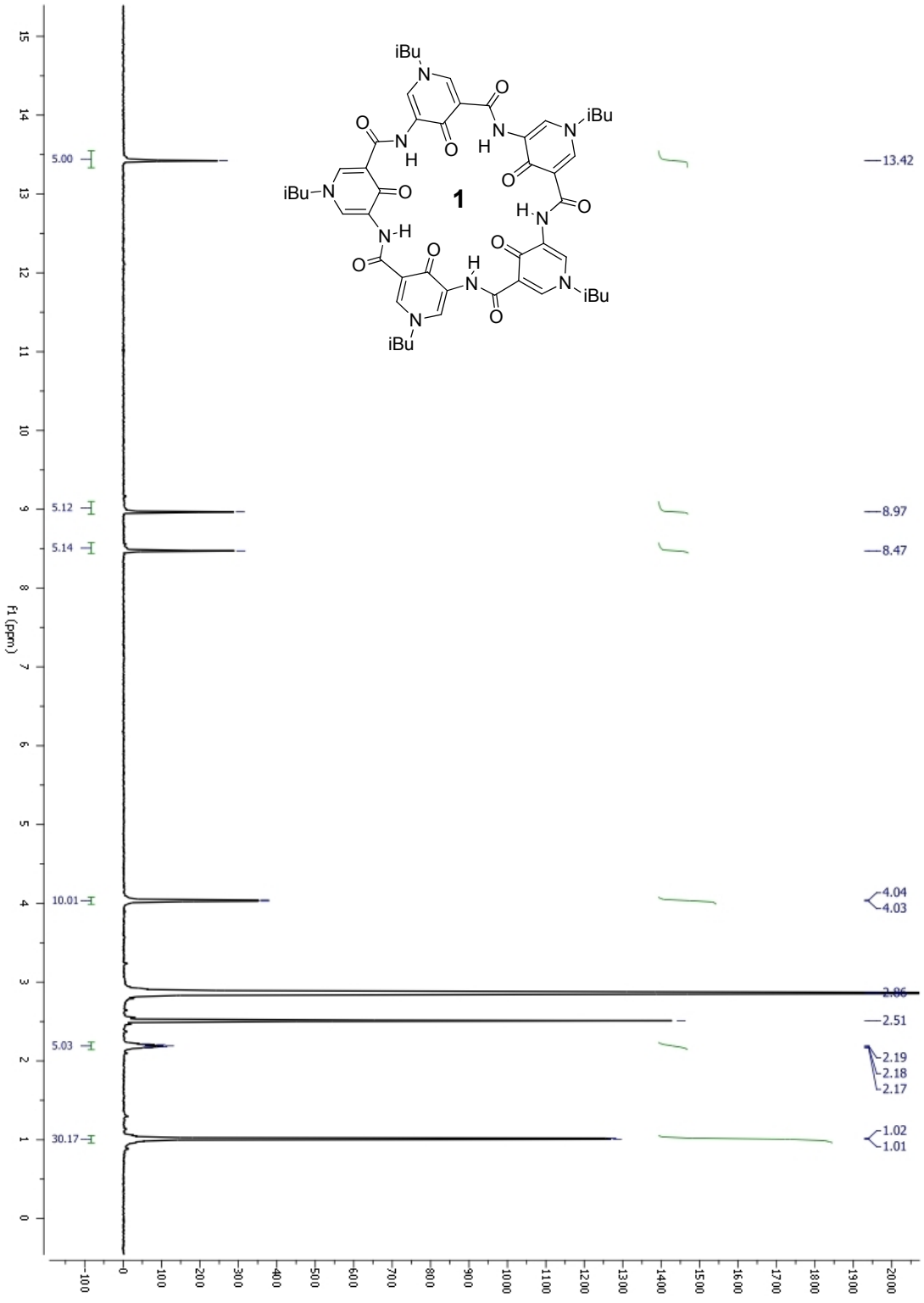
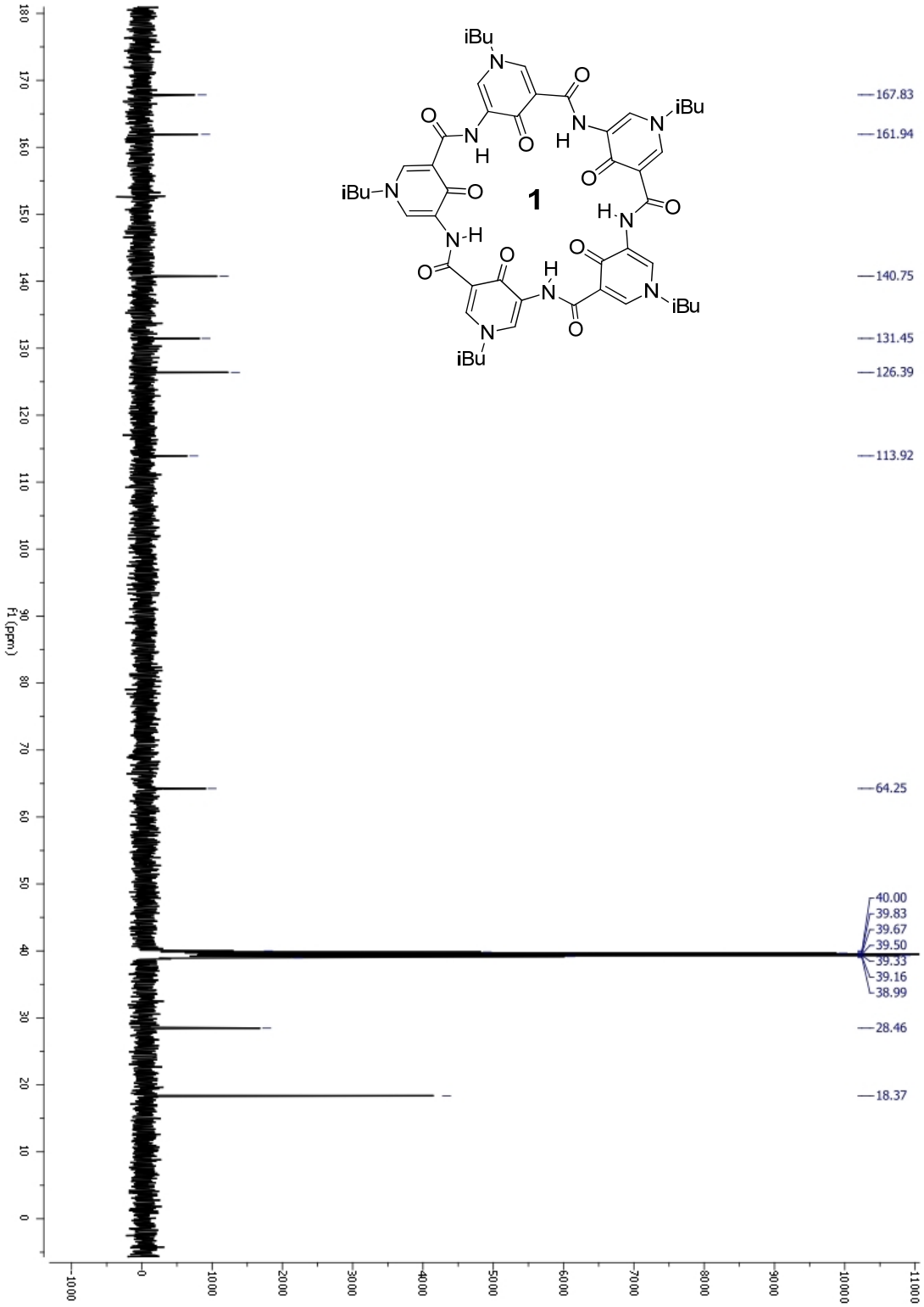
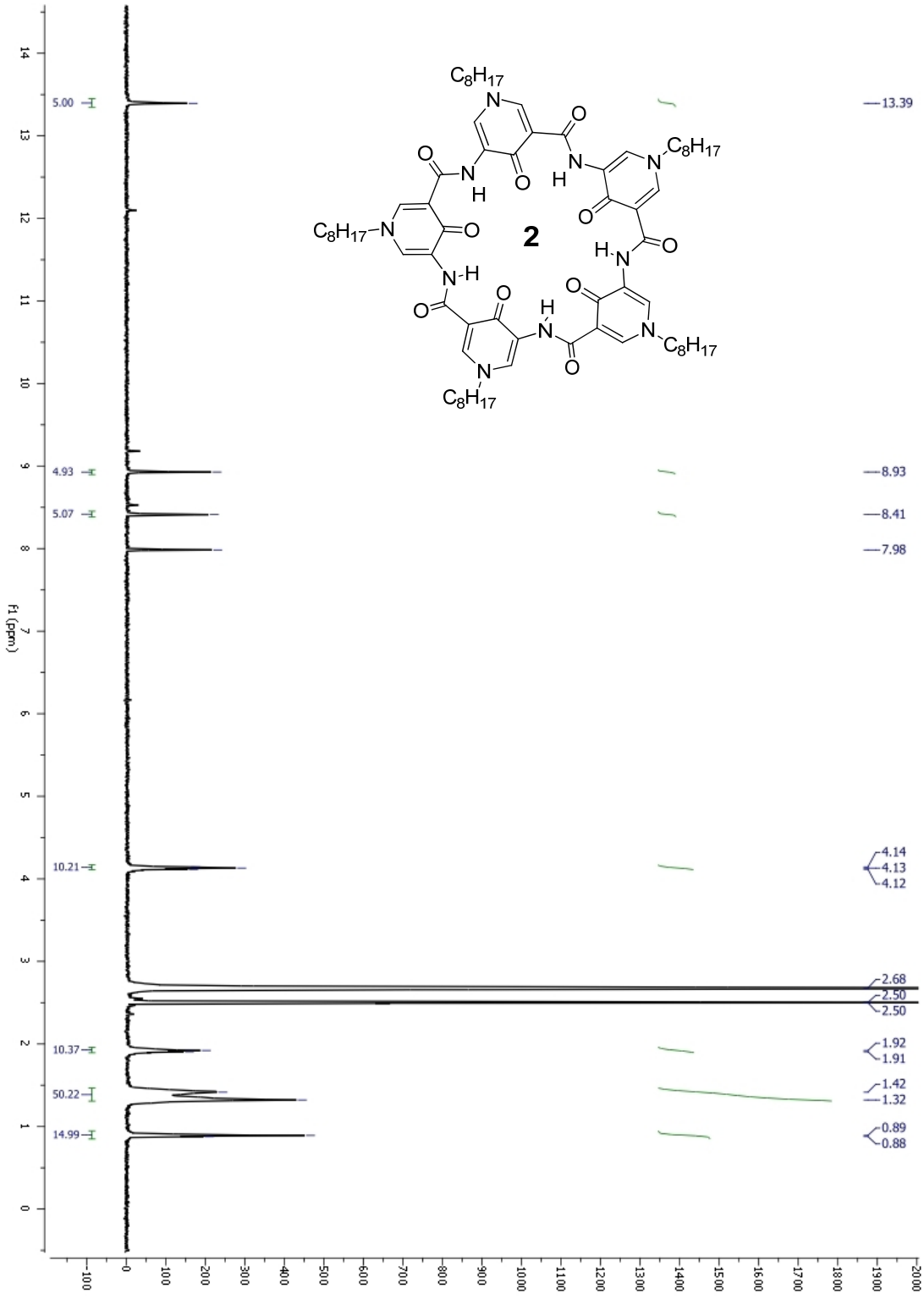


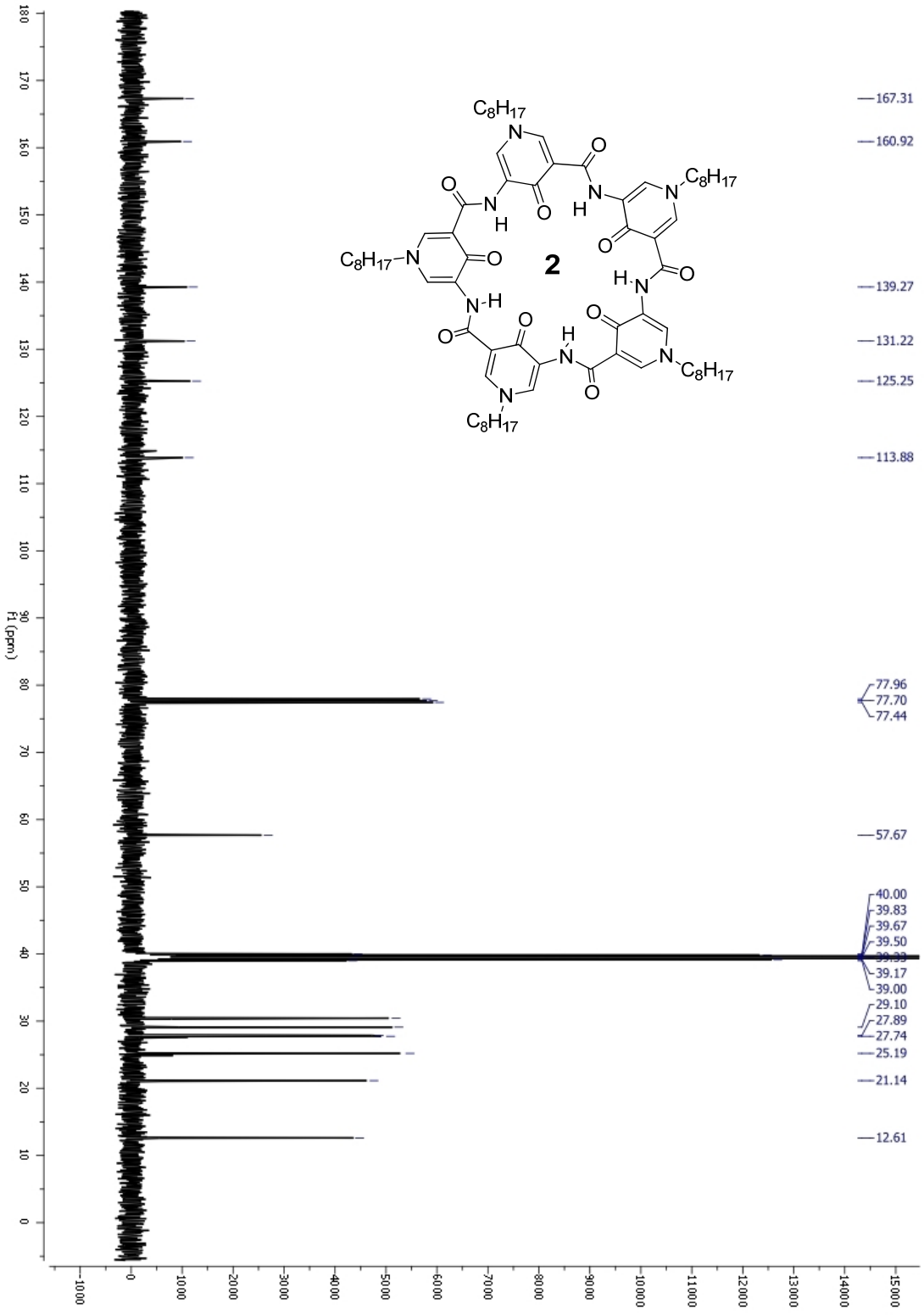
Figure S2. ESI spectrum of macrocylization reaction mixture containing pentamers **5**, **7** and **8** produced by reacting **2f** and **5a** in a molar ratio of 1:3 (Scheme S5). The crude product was recrystallized from MeOH before subjecting to ESI analysis.

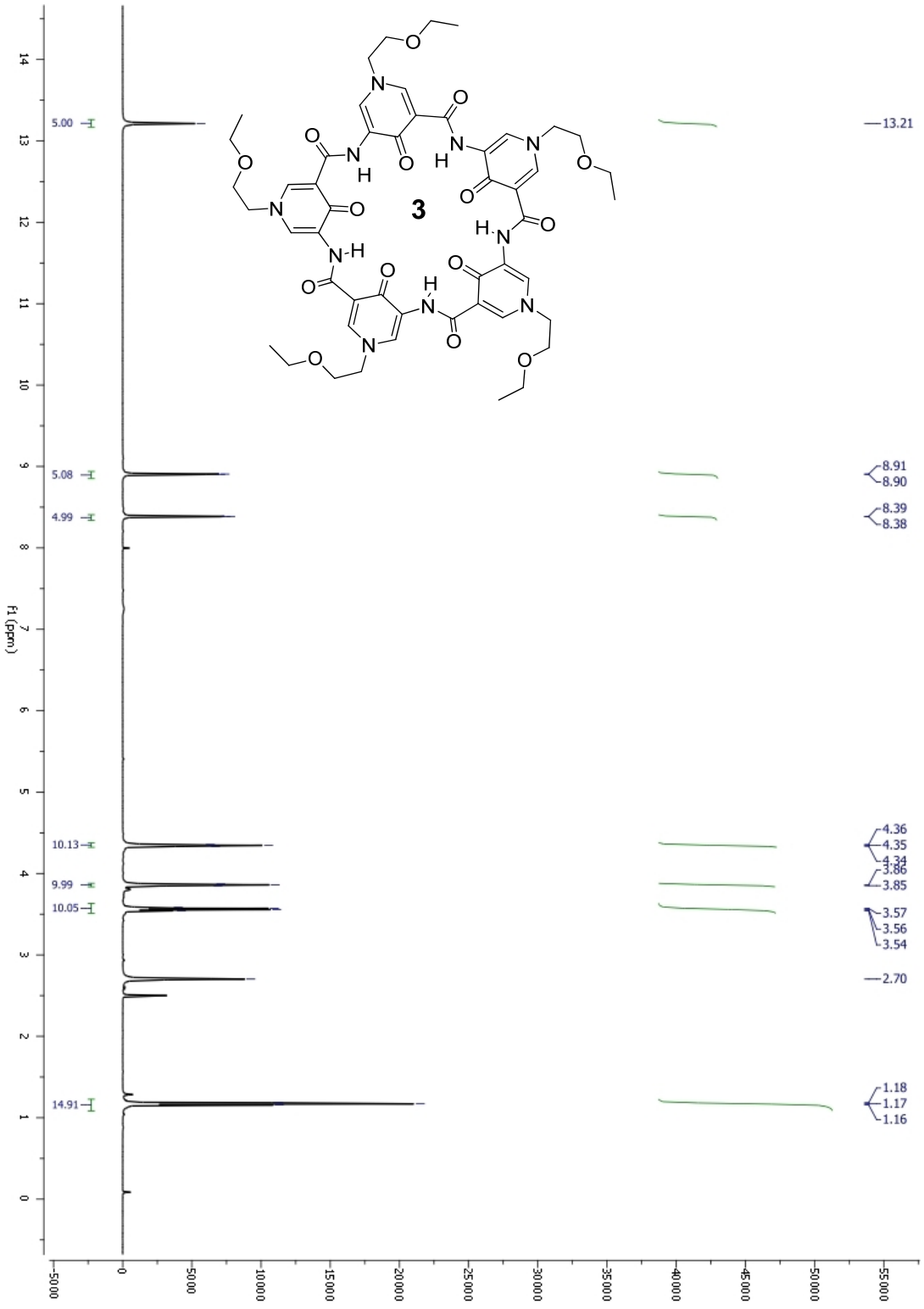
^{1}H NMR and ^{13}C NMR Spectra of Major Compounds

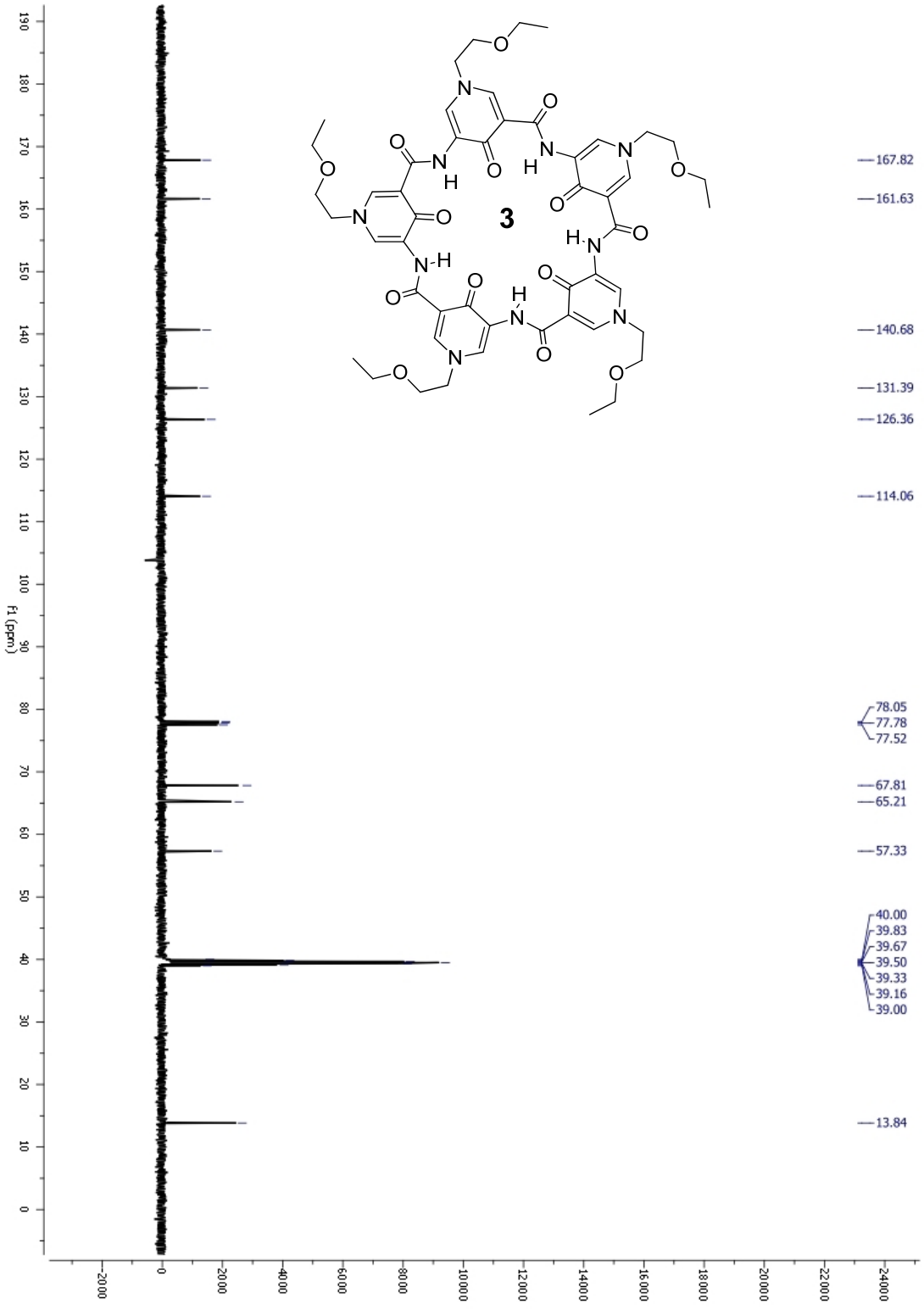


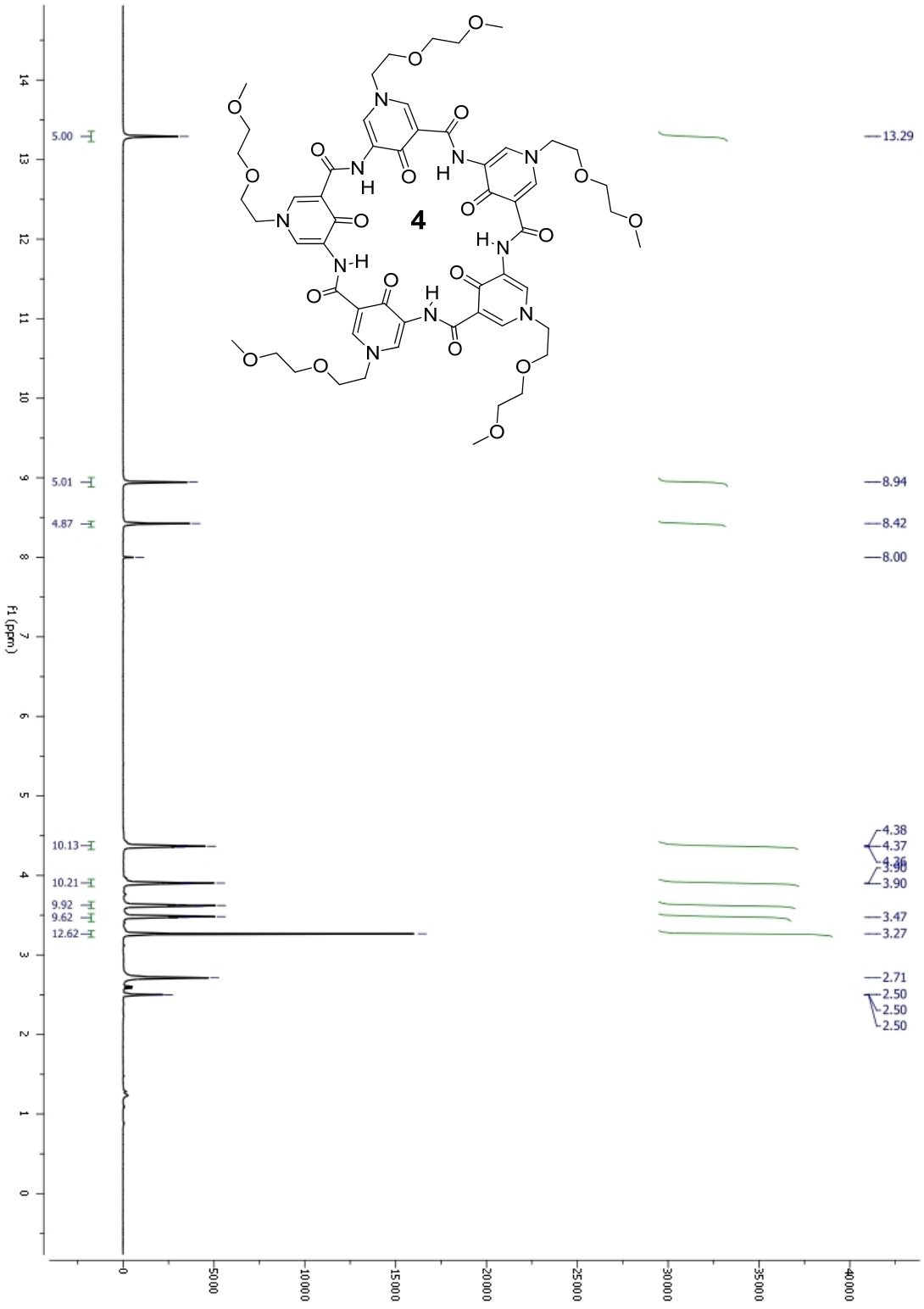

iBu
N
O
N
H
O
iBu
N
O
iBu–N
O
1
H
N
O
N-H
O
O
H
N
N
iBu
O
N
iBu
167.83
161.94
140.75
131.45
126.39
113.92
64.25
40.00
39.83
39.67
39.50
39.33
39.16
38.99
28.46
18.37
f1 (ppm)

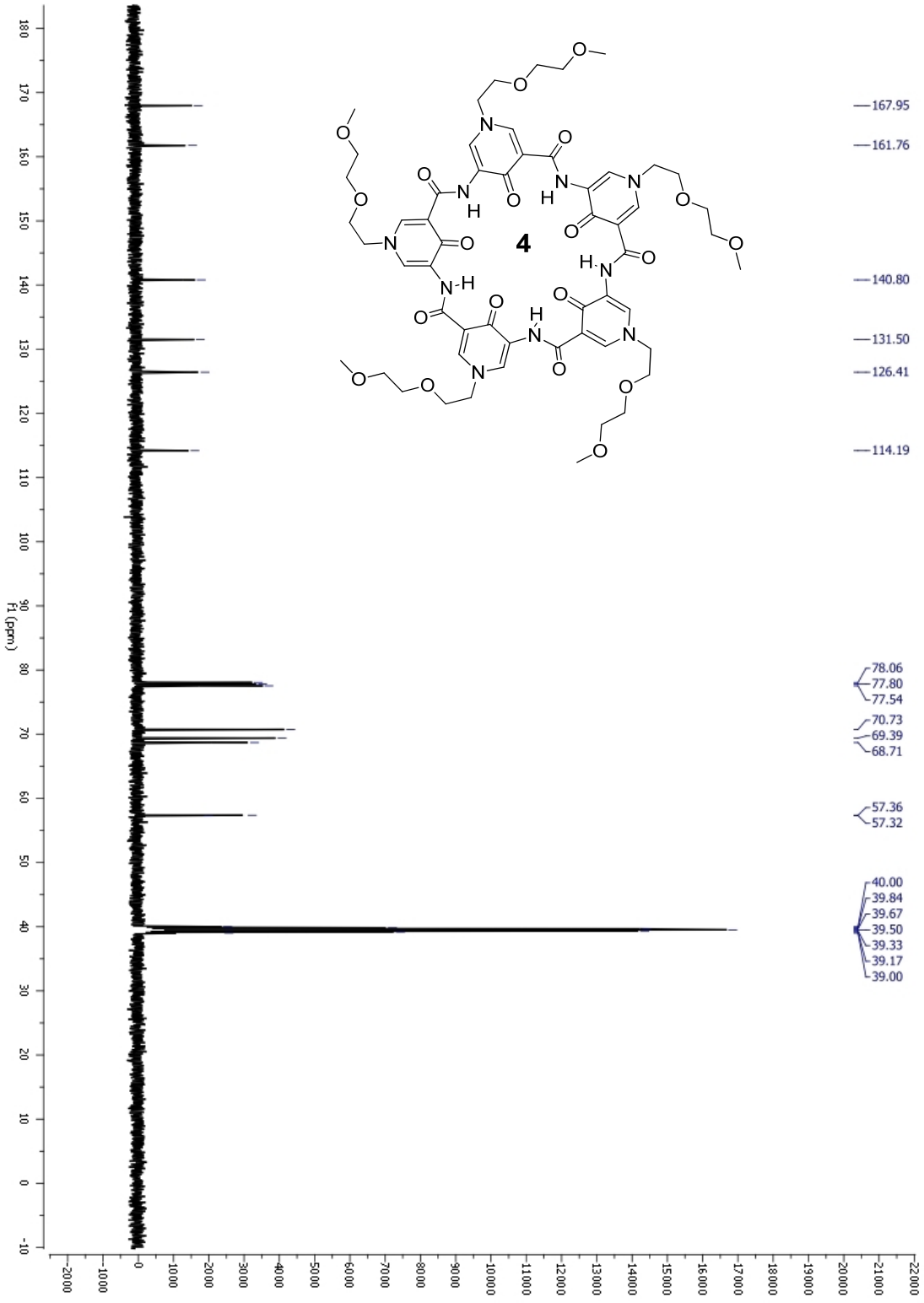

2
5.00
4.93
5.07
10.21
10.37
50.22
14.99
13.39
8.93
8.41
7.98
4.14
4.13
4.12
2.68
2.50
2.50
1.92
1.91
1.42
1.32
0.89
0.88
f1 (ppm)

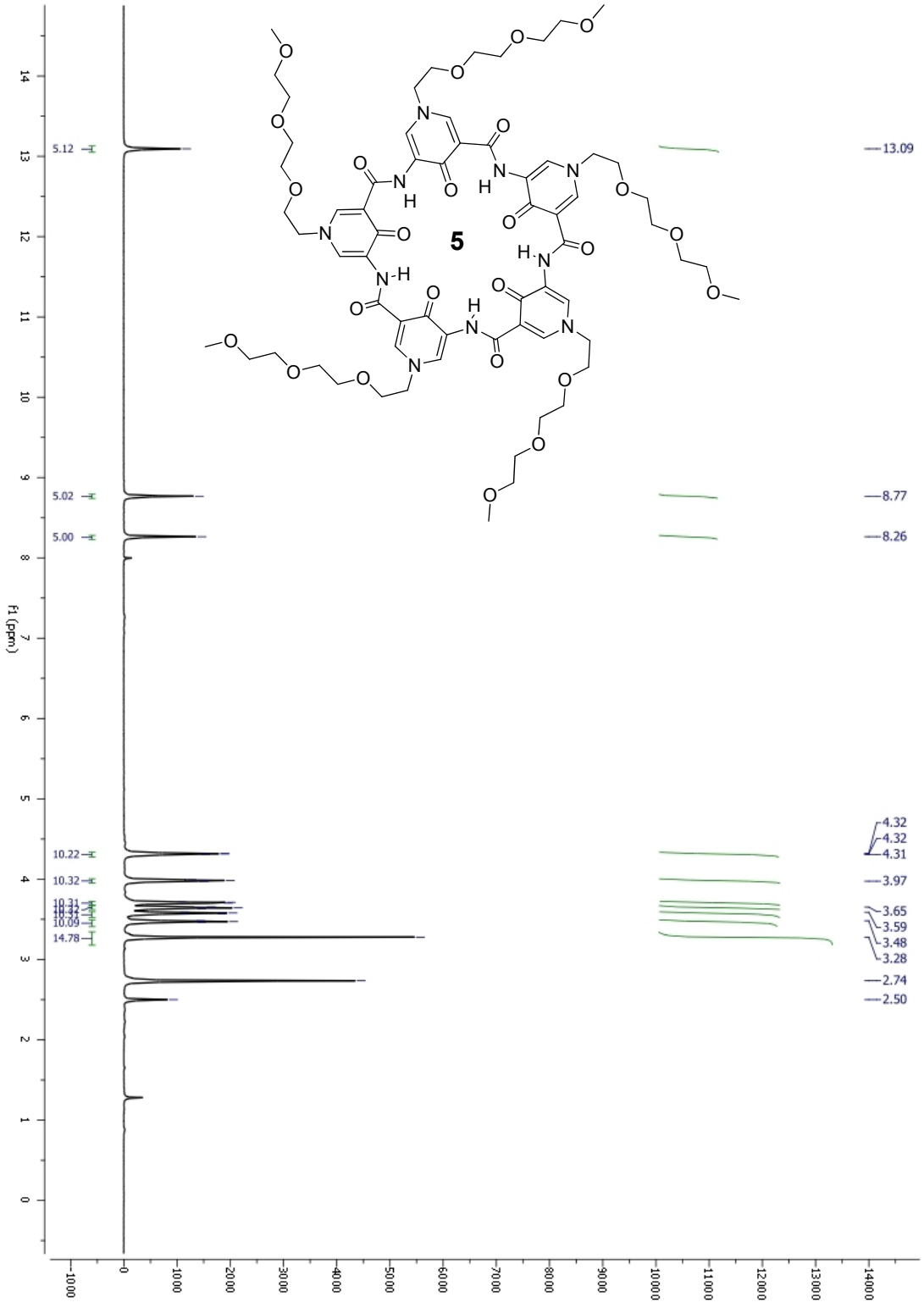

2
167.31
160.92
139.27
131.22
125.25
113.88
77.96
77.70
77.44
57.67
40.00
39.83
39.67
39.50
39.33
39.17
39.00
29.10
27.89
27.74
25.19
21.14
12.61
f1 (ppm)

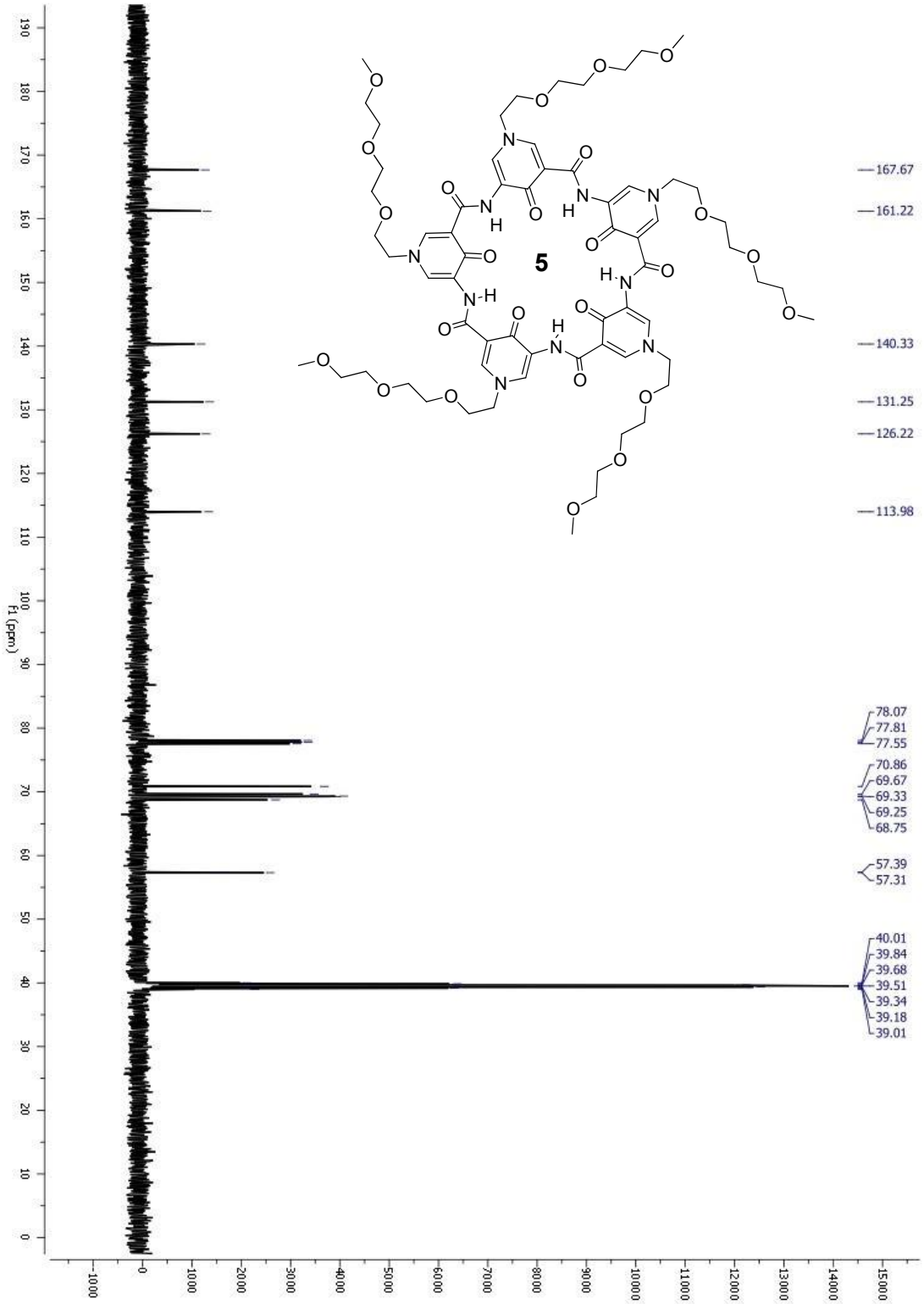

3
5.00
5.08
4.99
10.13
9.99
10.05
14.91
13.21
8.91
8.90
8.39
8.38
4.36
4.35
4.34
3.86
3.85
3.57
3.56
3.54
2.70
1.18
1.17
1.16
f1 (ppm)

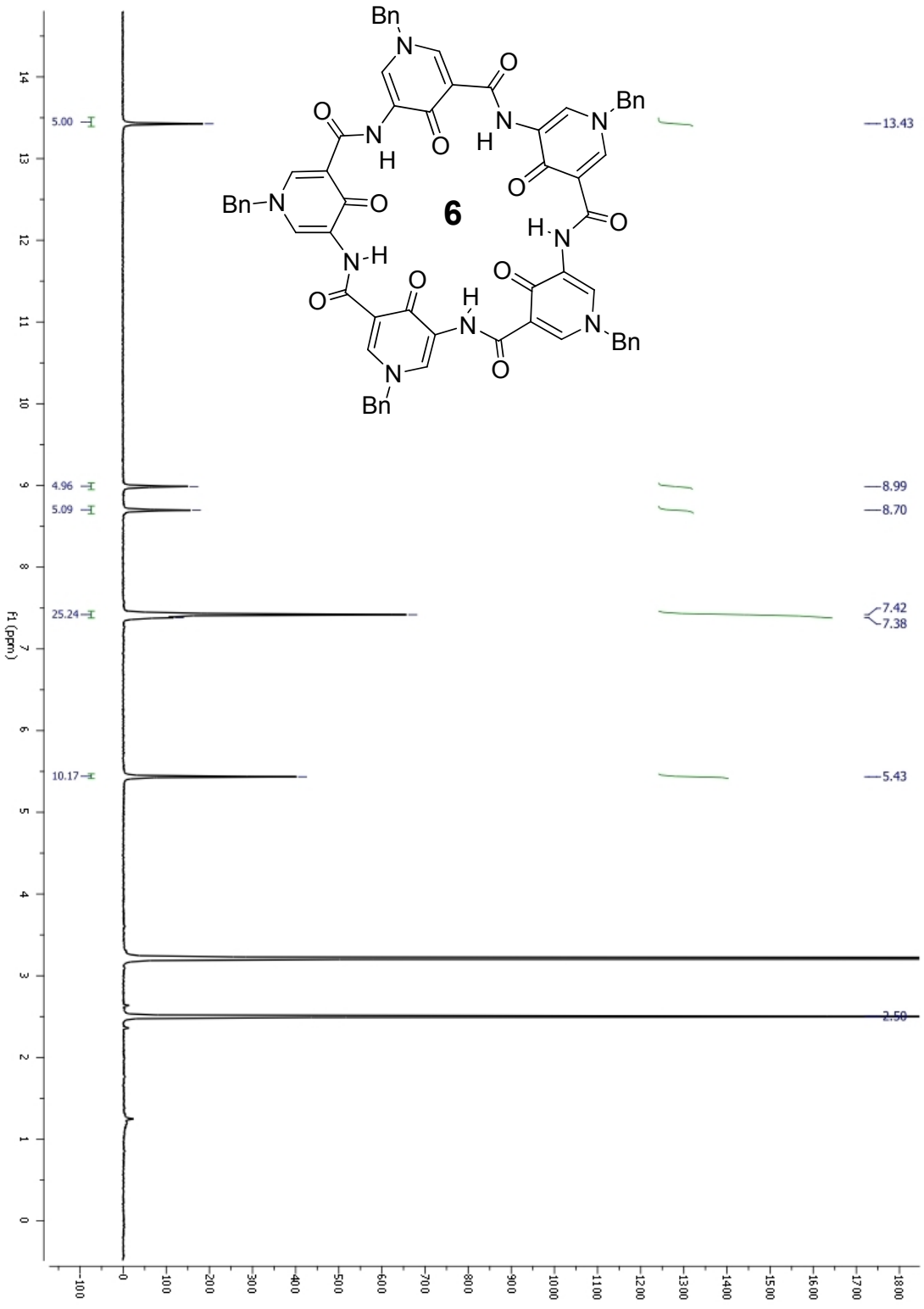

3
167.82
161.63
140.68
131.39
126.36
114.06
78.05
77.78
77.52
67.81
65.21
57.33
40.00
39.83
39.67
39.50
39.33
39.16
39.00
13.84
f1 (ppm)

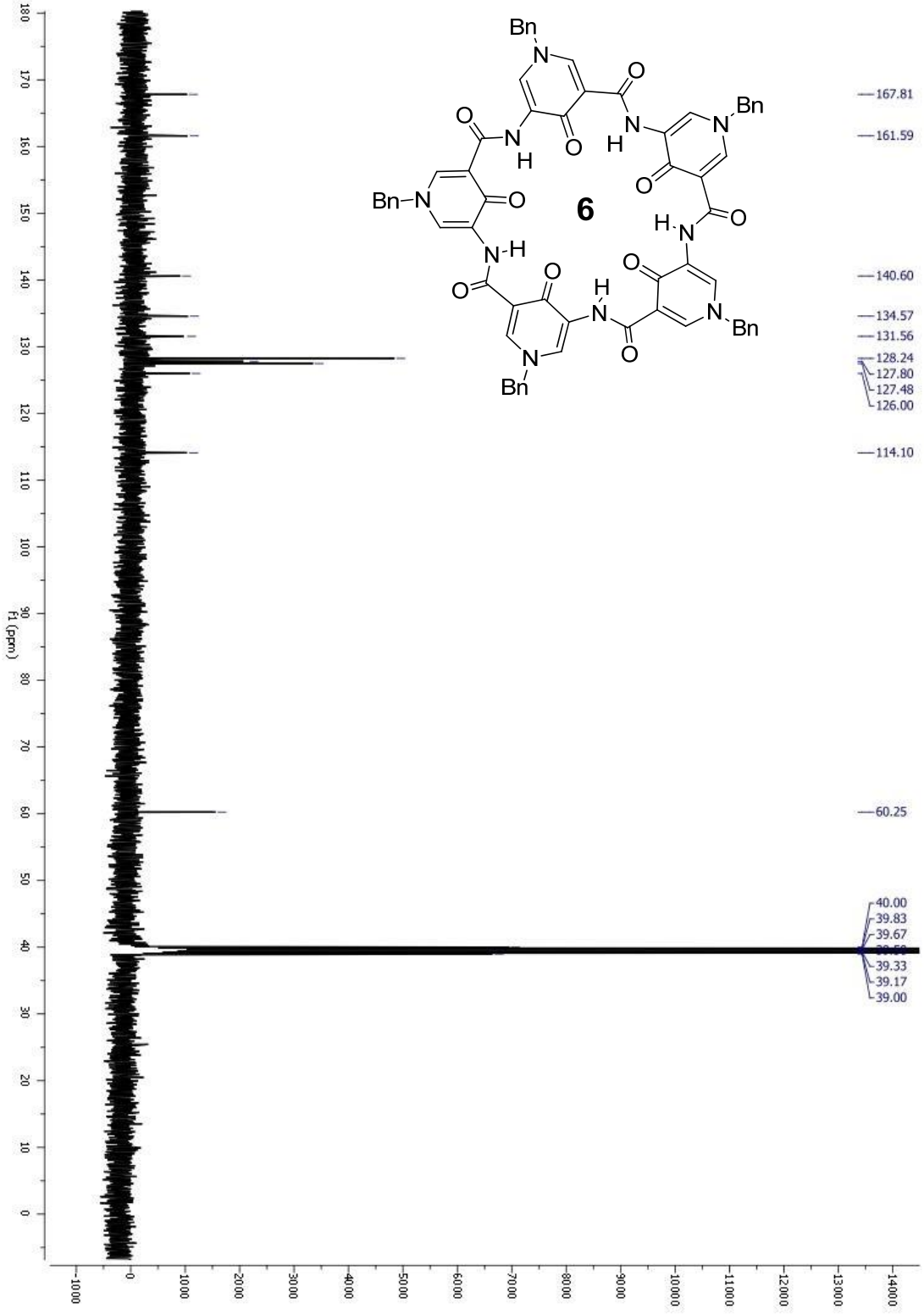

4
5.00
5.01
4.87
10.13
10.21
9.92
9.62
12.62
13.29
8.94
8.42
8.00
4.38
4.37
3.90
3.47
3.27
2.71
2.50
f1 (ppm)

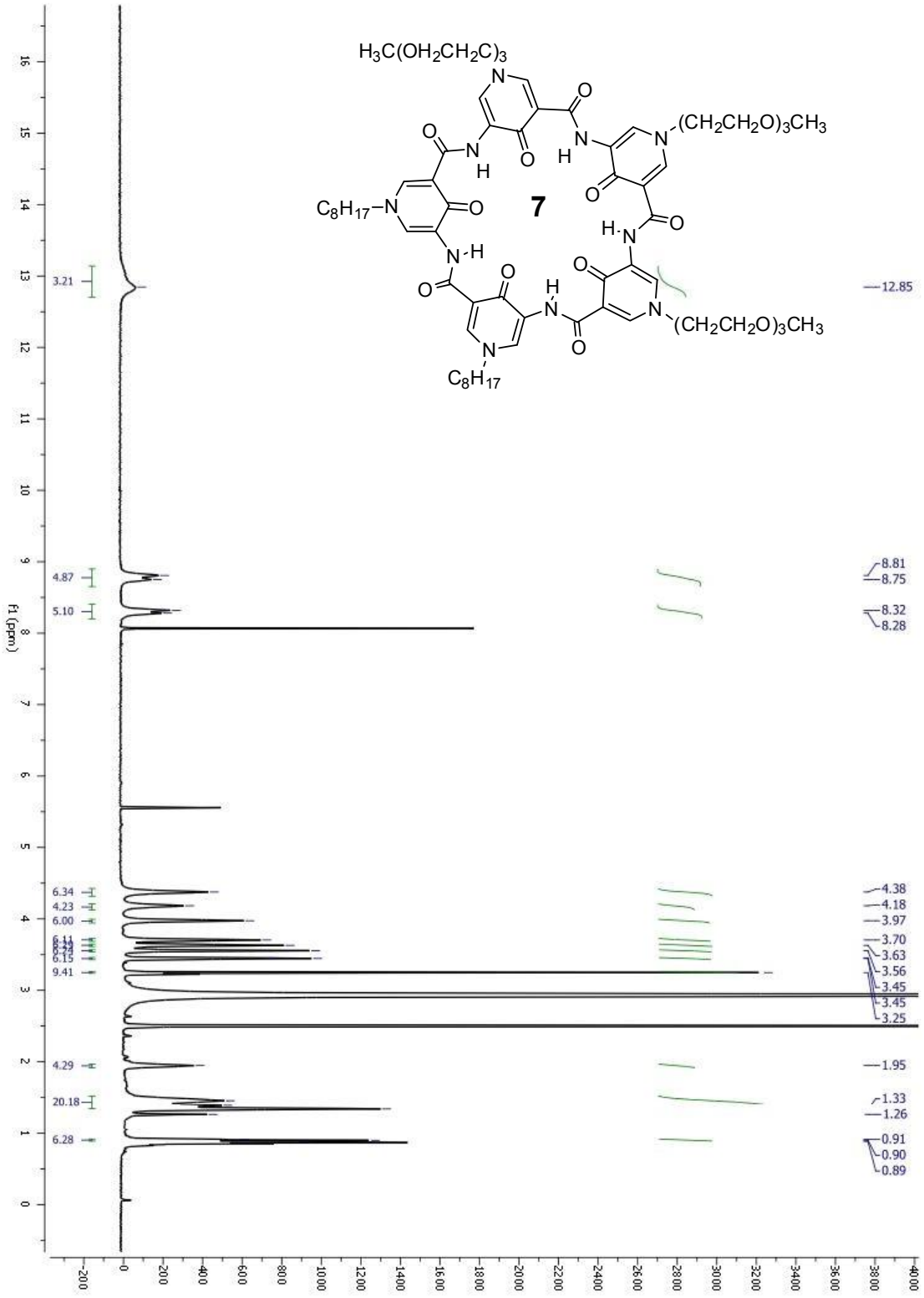

4
167.95
161.76
140.80
131.50
126.41
114.19
78.06
77.80
77.54
70.73
69.39
68.71
57.36
57.32
40.00
39.84
39.67
39.50
39.33
39.17
39.00
f1 (ppm)

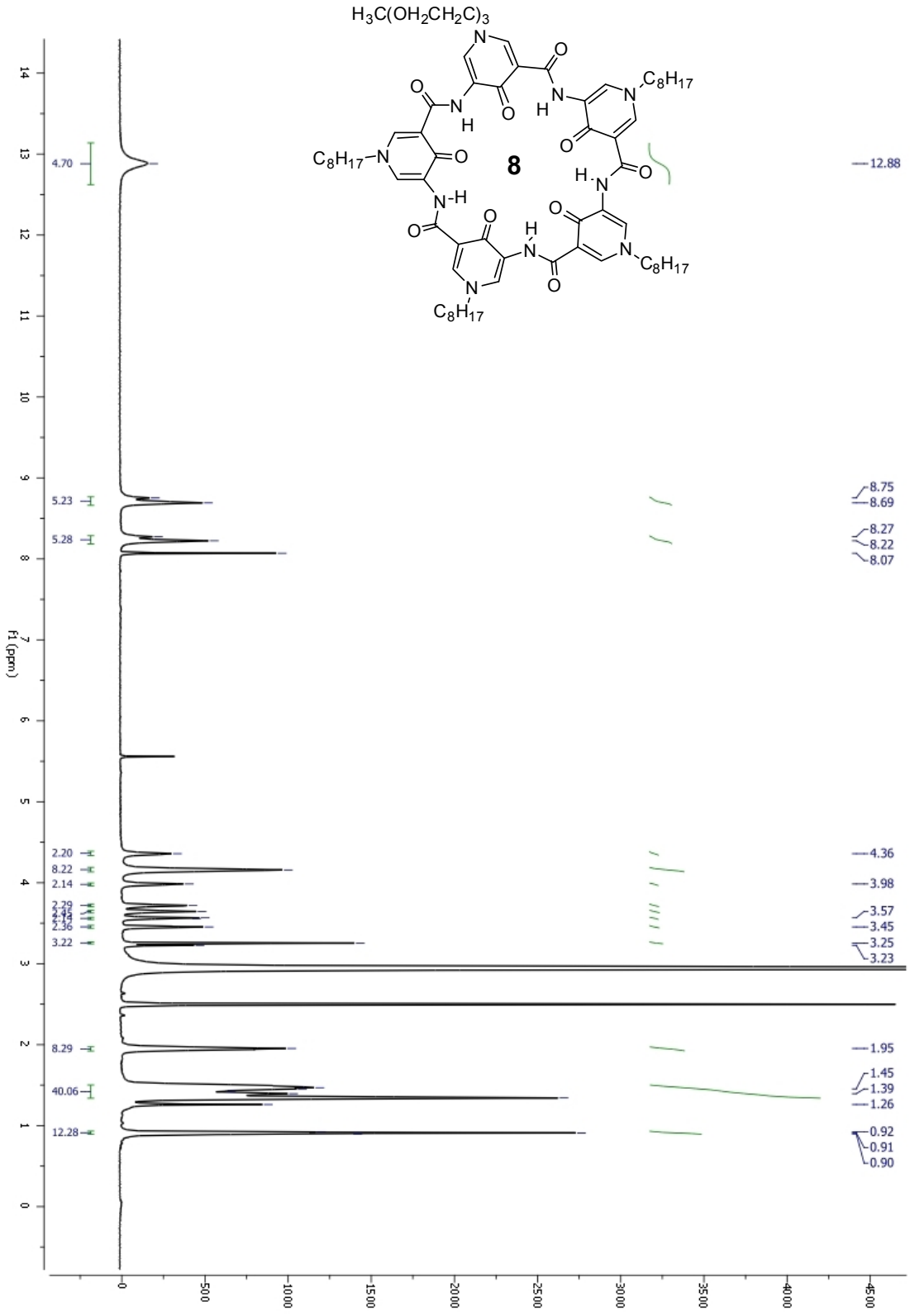

5
5.12
5.02
5.00
10.22
10.32
10.31
10.09
14.78
13.09
8.77
8.26
4.32
4.32
4.31
3.97
3.65
3.59
3.48
3.28
2.74
2.50
f1 (ppm)

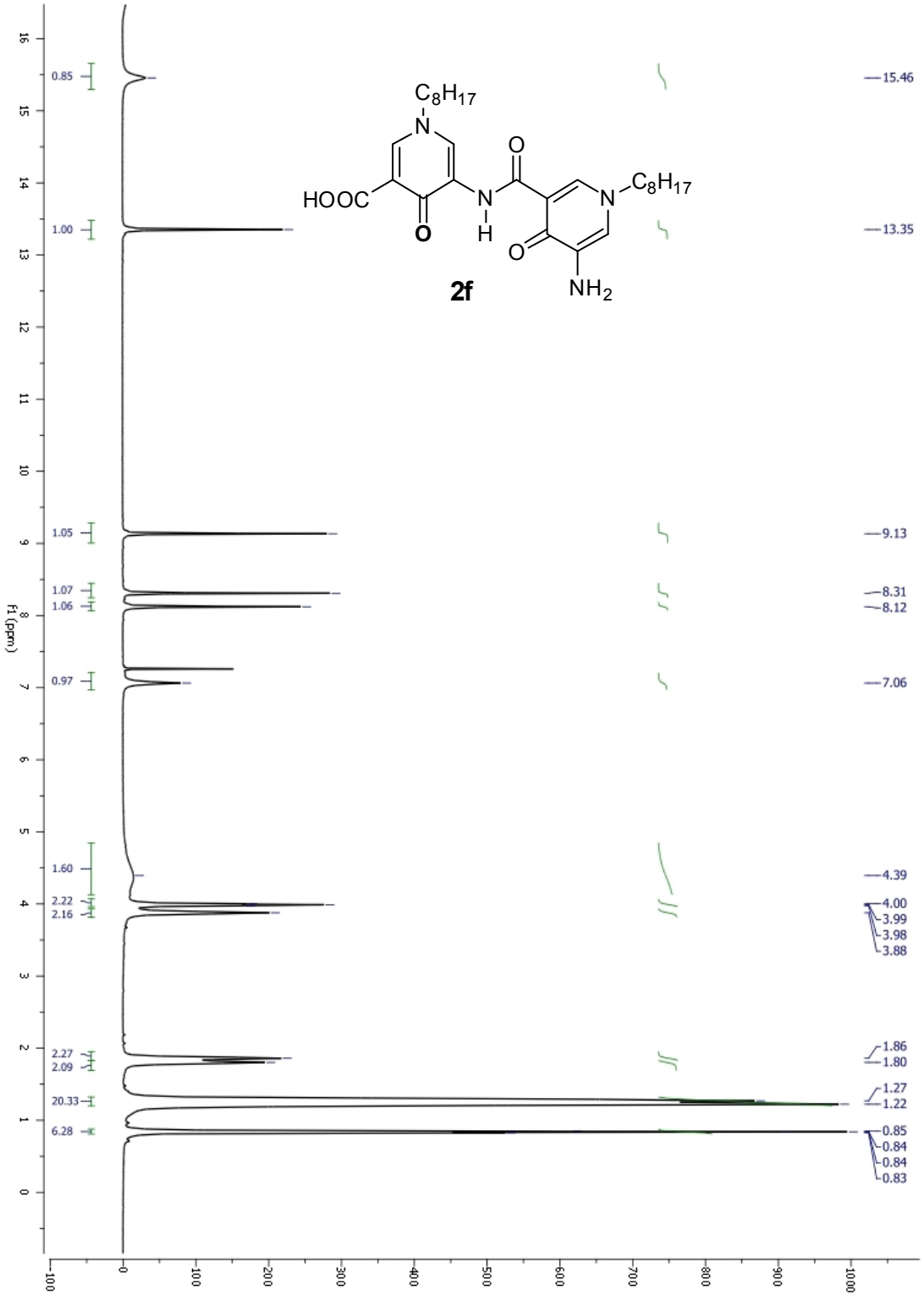

5
167.67
161.22
140.33
131.25
126.22
113.98
78.07
77.81
77.55
70.86
69.67
69.33
69.25
68.75
57.39
57.31
40.01
39.84
39.68
39.51
39.34
39.18
39.01
f1 (ppm)

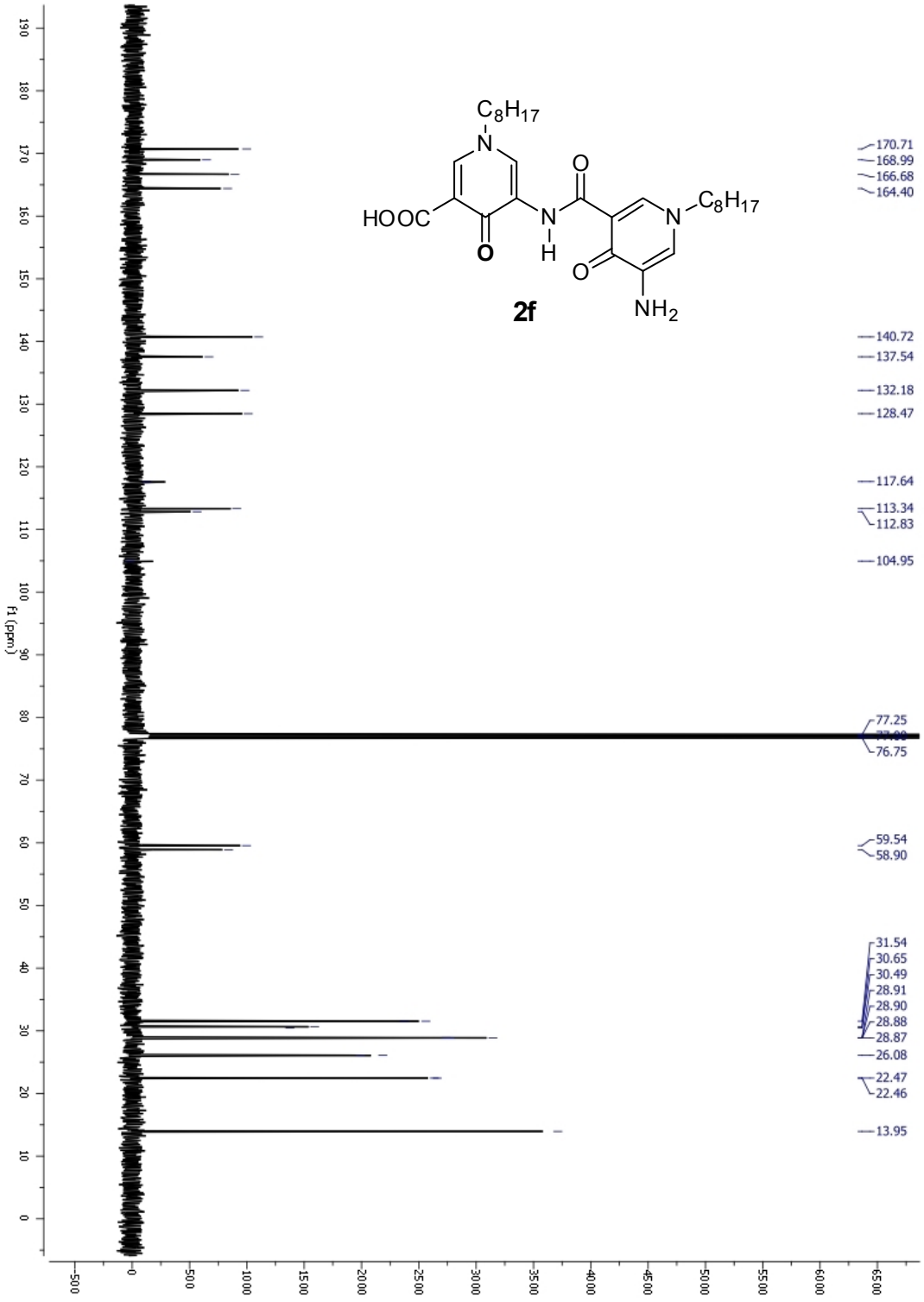

6
5.00
4.96
5.09
25.24
10.17
13.43
8.99
8.70
7.42
7.38
5.43
2.50
f1 (ppm)

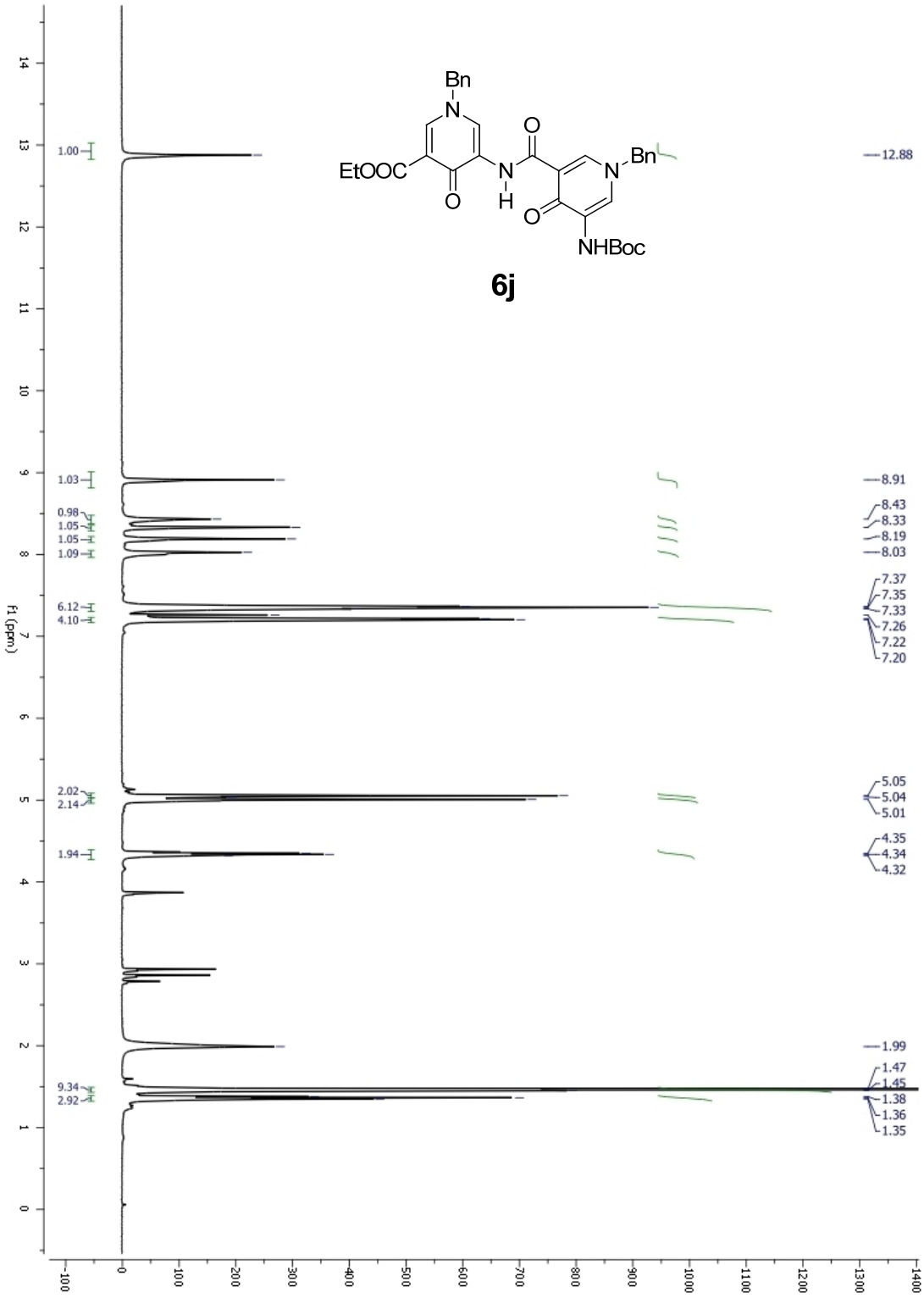

6
167.81
161.59
140.60
134.57
131.56
128.24
127.80
127.48
126.00
114.10
60.25
40.00
39.83
39.67
39.33
39.17
39.00
f1 (ppm)

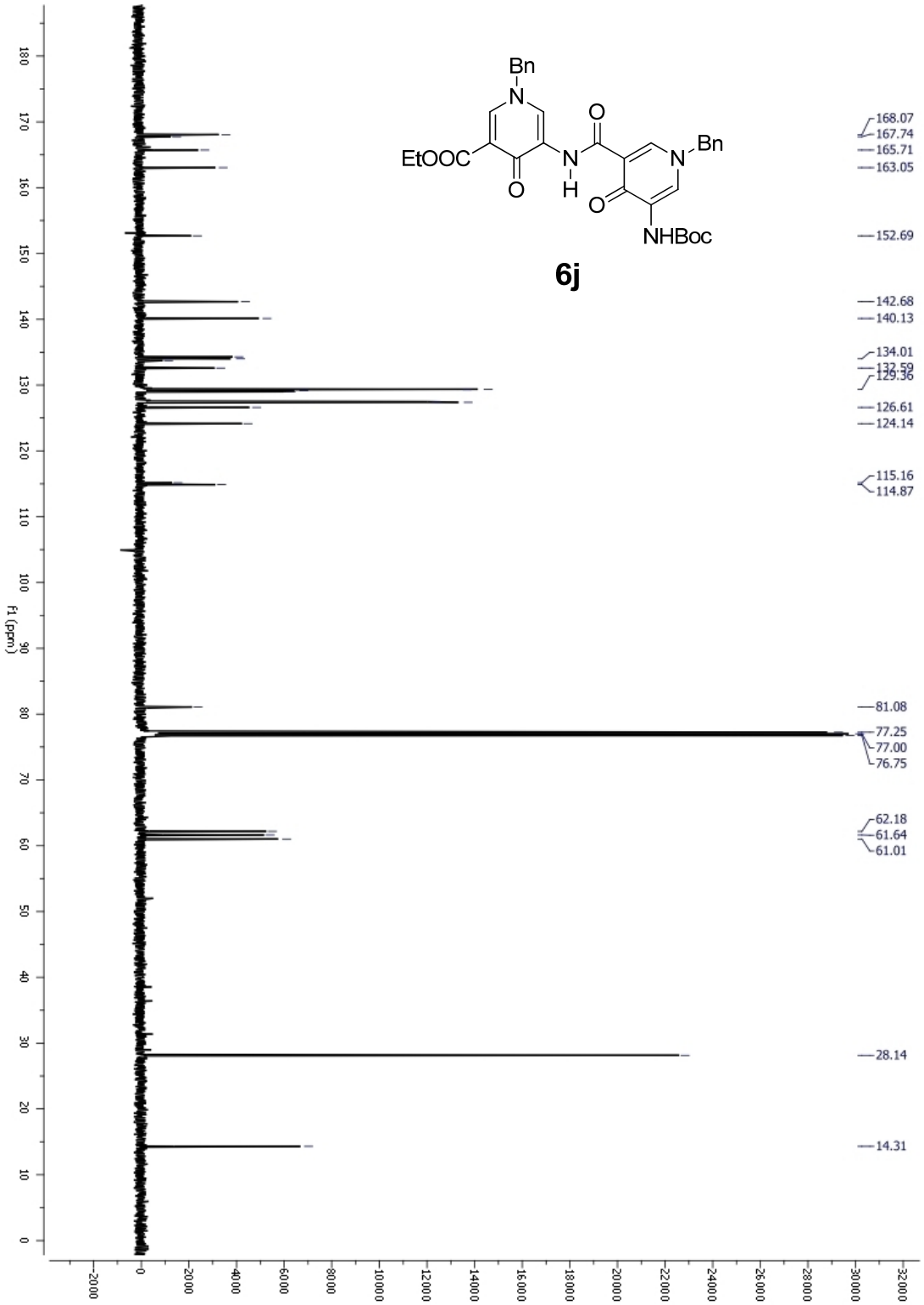

H3C(OH2CH2C)3
(CH2CH2O)3CH3
C8H17–N
7
(CH2CH2O)3CH3
C8H17
f1 (ppm)
3.21
4.87
5.10
6.34
4.23
6.00
9.41
4.29
20.18
6.28
12.85
8.81
8.75
8.32
8.28
4.38
4.18
3.97
3.70
3.63
3.56
3.45
3.45
3.25
1.95
1.33
1.26
0.91
0.90
0.89

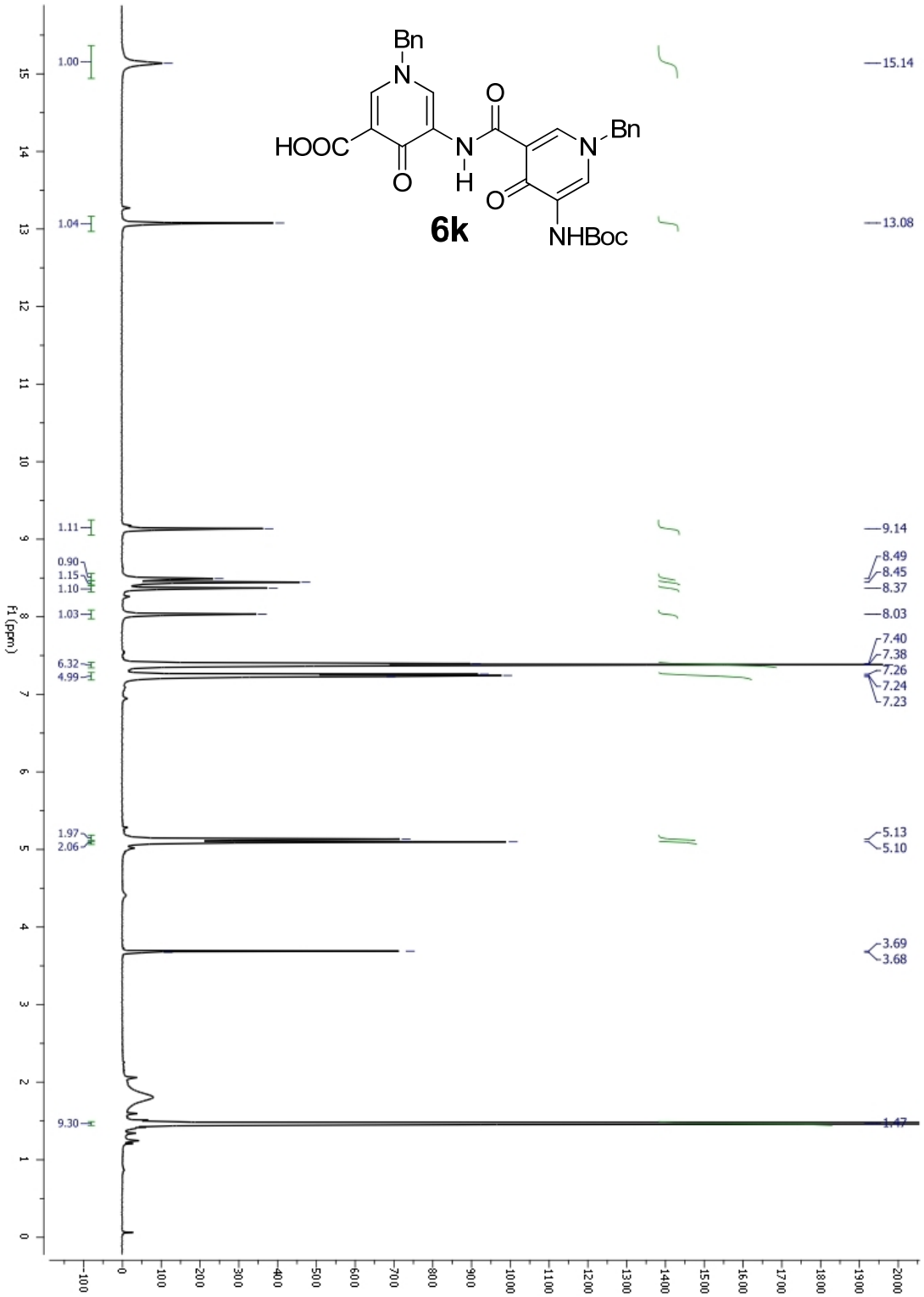

H3C(OH2CH2C)3
C8H17
8
4.70
5.23
5.28
2.20
8.22
2.14
2.29
2.36
3.22
8.29
40.06
12.28
12.88
8.75
8.69
8.27
8.22
8.07
4.36
3.98
3.57
3.45
3.25
3.23
1.95
1.45
1.39
1.26
0.92
0.91
0.90
f1 (ppm)

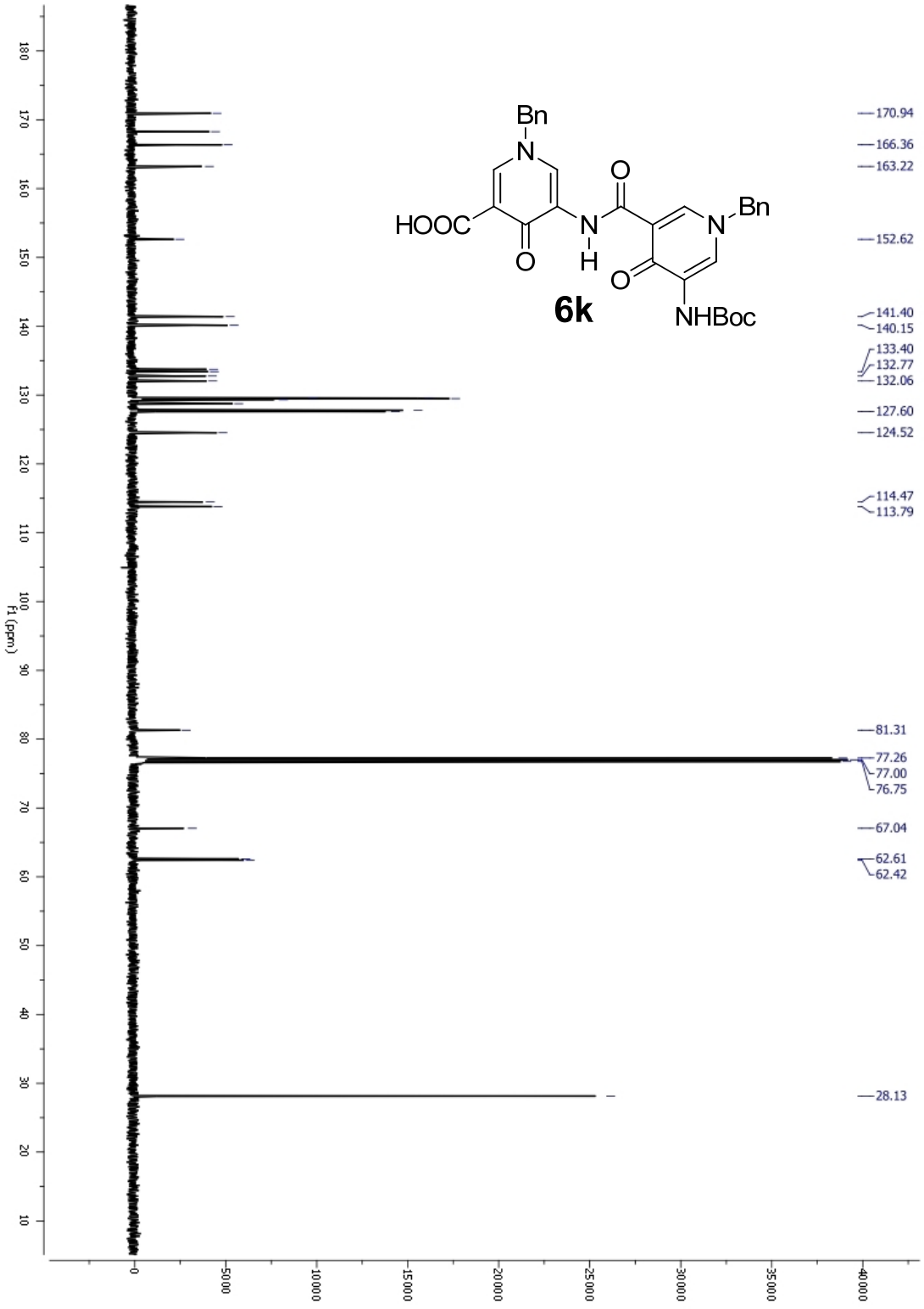

HOOC
C_8H_{17}
N
O
O
N
H
O
N
C_8H_{17}
NH_2
2f
f1 (ppm)
0.85
1.00
1.05
1.07
1.06
0.97
1.60
2.22
2.16
2.27
2.09
20.33
6.28
15.46
13.35
9.13
8.31
8.12
7.06
4.39
4.00
3.99
3.98
3.88
1.86
1.80
1.27
1.22
0.85
0.84
0.84
0.83

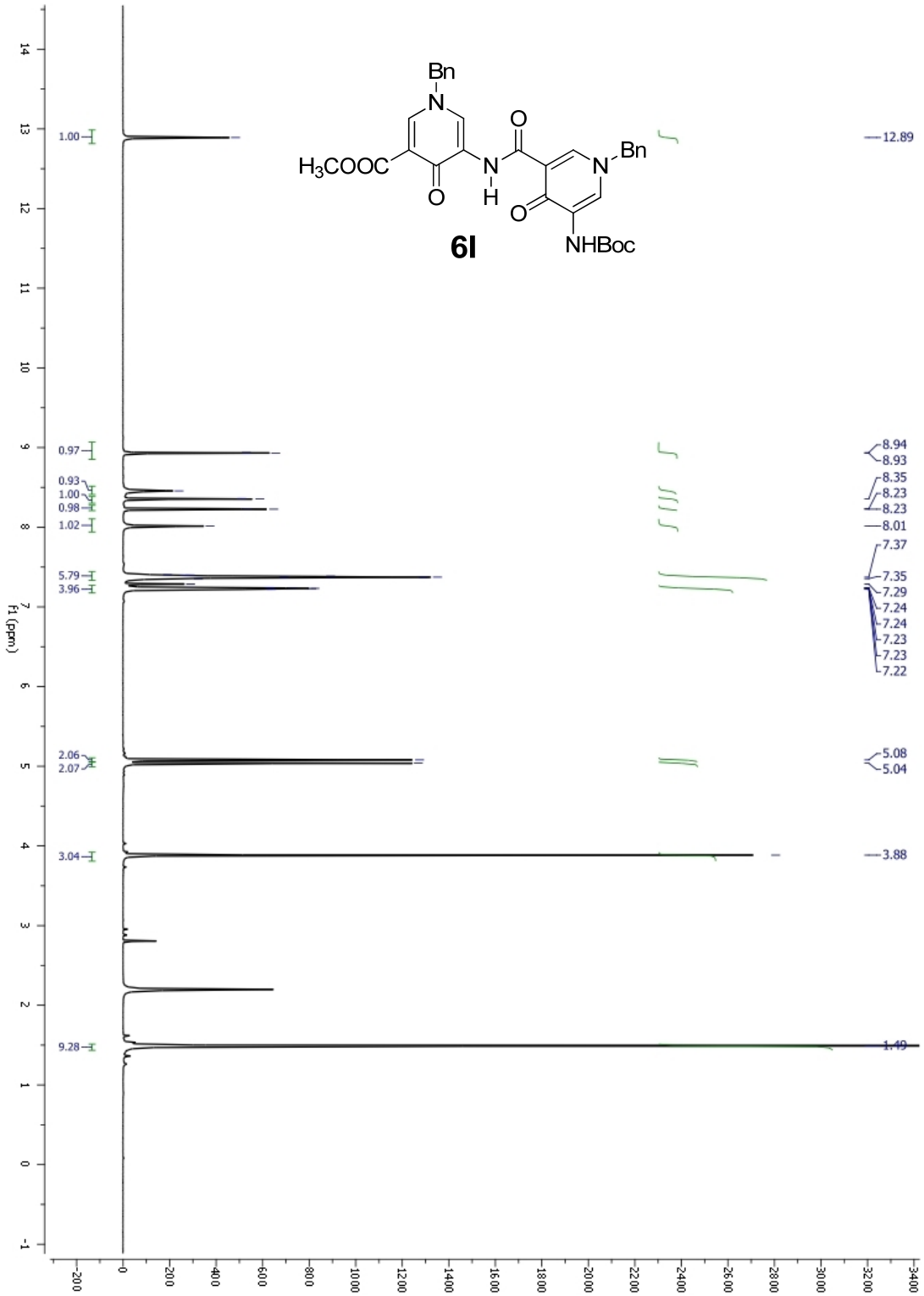


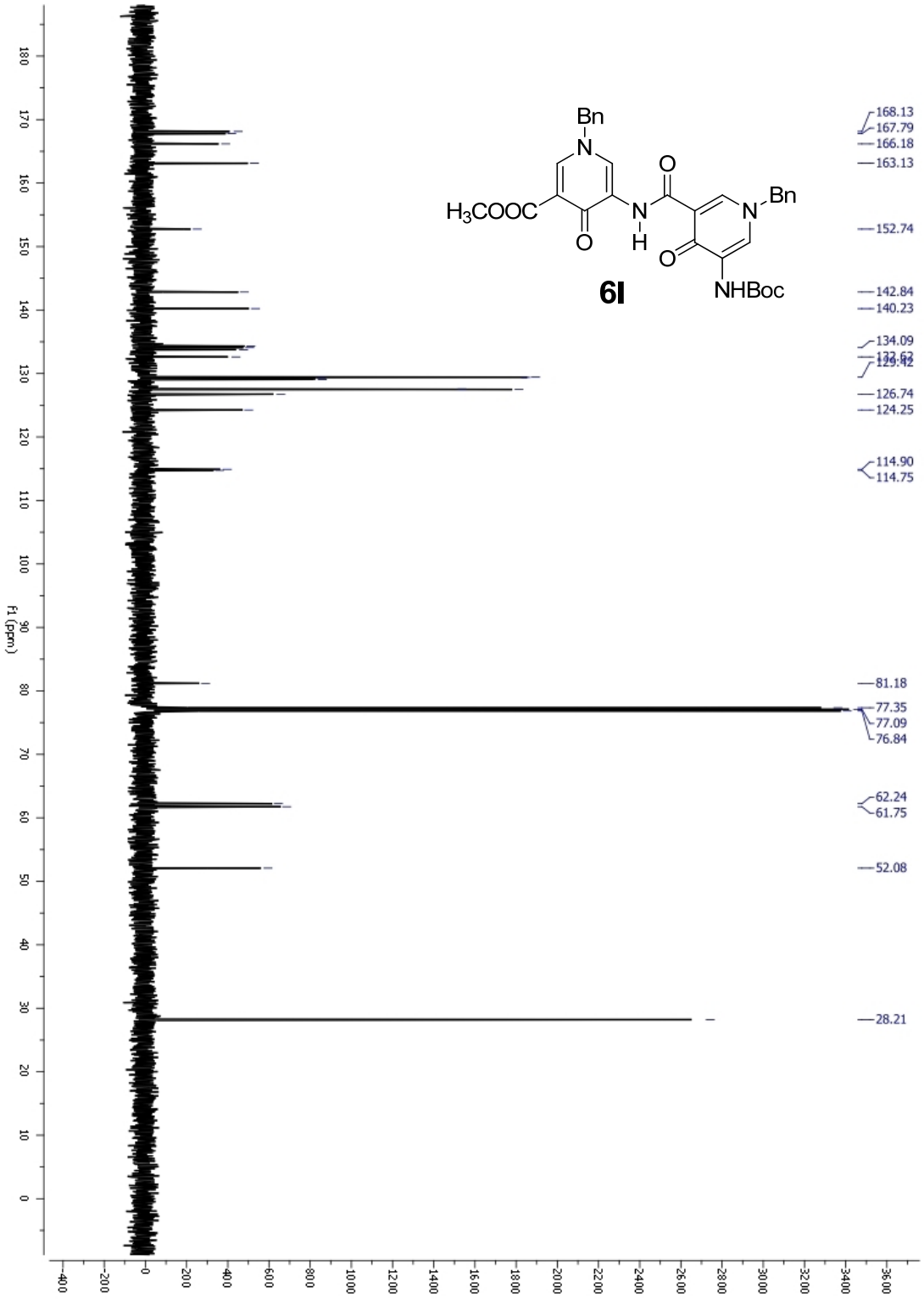

Bn
N
O
EtOOC
N
H
O
N
Bn
O
NHBoc
6j
f1 (ppm)
1.00
1.03
0.98
1.05
1.05
1.09
6.12
4.10
2.02
2.14
1.94
9.34
2.92
12.88
8.91
8.43
8.33
8.19
8.03
7.37
7.35
7.33
7.26
7.22
7.20
5.05
5.04
5.01
4.35
4.34
4.32
1.99
1.47
1.45
1.38
1.36
1.35

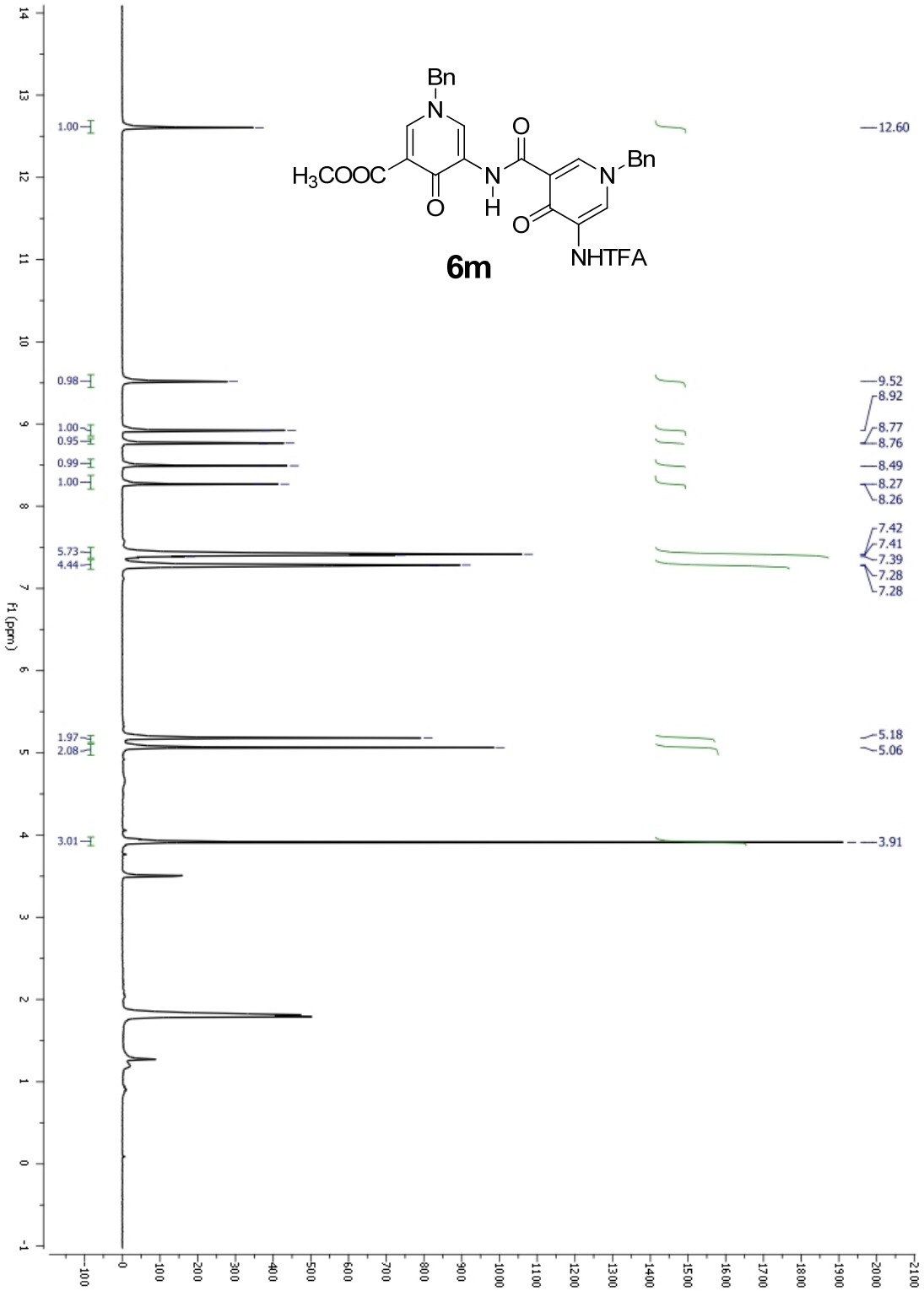

Bn
N
EtOOC
O
N
H
O
O
N
Bn
NHBoc
6j
168.07
167.74
165.71
163.05
152.69
142.68
140.13
134.01
132.59
129.36
126.61
124.14
115.16
114.87
81.08
77.25
77.00
76.75
62.18
61.64
61.01
28.14
14.31
f1 (ppm)

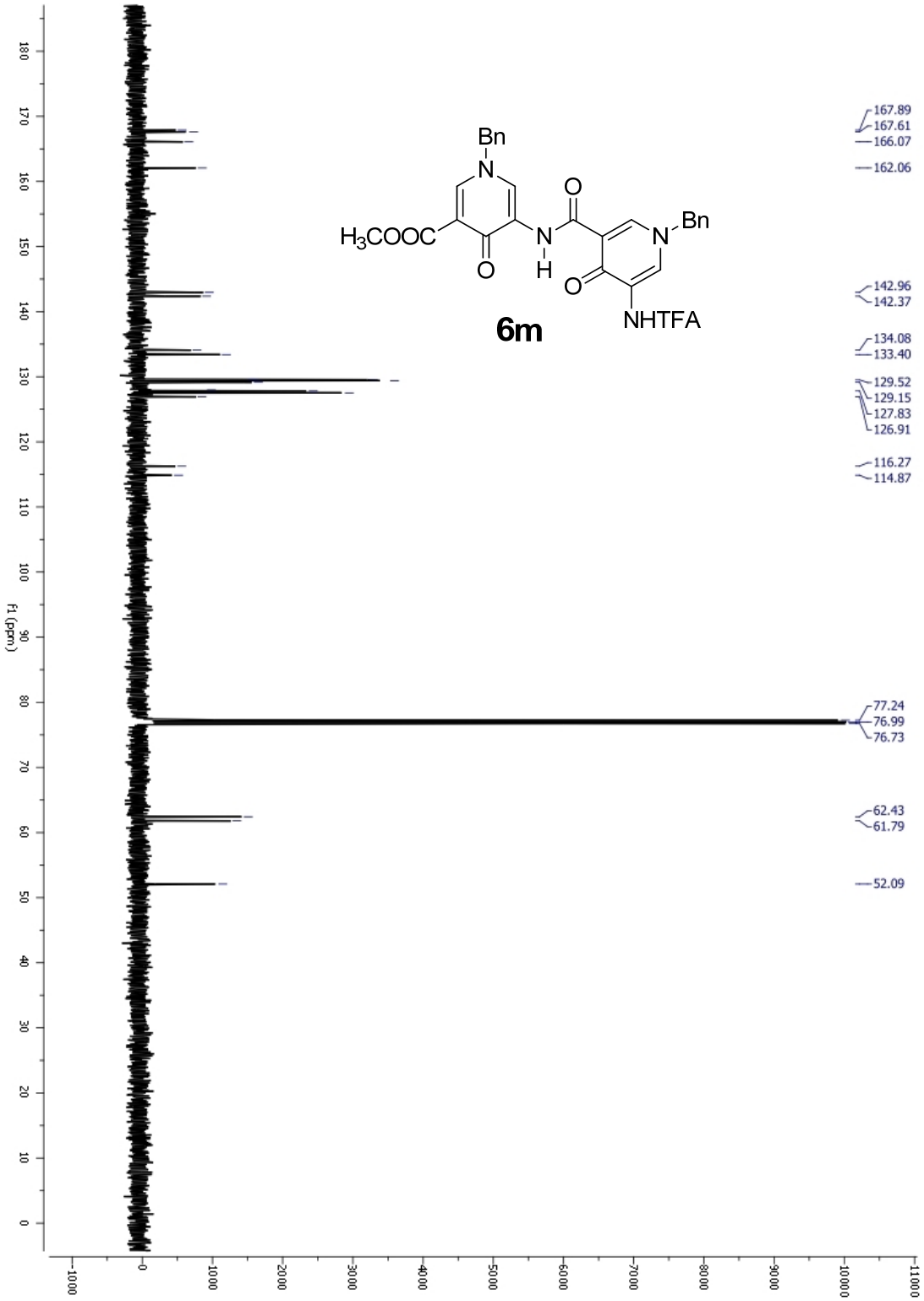

Bn
N
HOOC
O
N
H
O
O
N
Bn
NHBoc
6k
1.00
1.04
1.11
0.90
1.15
1.10
1.03
6.32
4.99
1.97
2.06
9.30
15.14
13.08
9.14
8.49
8.45
8.37
8.03
7.40
7.38
7.26
7.24
7.23
5.13
5.10
3.69
3.68
1.47
f1 (ppm)


Bn
N
HOOC
O
N
H
O
O
N
Bn
NHBoc
6k
170.94
166.36
163.22
152.62
141.40
140.15
133.40
132.77
132.06
127.60
124.52
114.47
113.79
81.31
77.26
77.00
76.75
67.04
62.61
62.42
28.13
f1 (ppm)


Bn
N
O
H3COOC
N
H
O
N
Bn
O
NHBoc
6l
F1 (ppm)
1.00
0.97
0.93
1.00
0.98
1.02
5.79
3.96
2.06
2.07
3.04
9.28
12.89
8.94
8.93
8.35
8.23
8.23
8.01
7.37
7.35
7.29
7.24
7.24
7.23
7.23
7.22
5.08
5.04
3.88
1.49


Bn
N
O
H3COOC
N
H
O
N
Bn
O
NHBoc
6l
168.13
167.79
166.18
163.13
152.74
142.84
140.23
134.09
132.62
129.42
126.74
124.25
114.90
114.75
81.18
77.35
77.09
76.84
62.24
61.75
52.08
28.21
f1 (ppm)


Bn
N
O
H3COOC
N
H
N
Bn
O
O
NHTFA
6m
f1 (ppm)
1.00
0.98
1.00
0.95
0.99
1.00
5.73
4.44
1.97
2.08
3.01
12.60
9.52
8.92
8.77
8.76
8.49
8.27
8.26
7.42
7.41
7.39
7.28
7.28
5.18
5.06
3.91


Bn
N
O
H3COOC
N
H
N
Bn
O
O
NHTFA
6m
167.89
167.61
166.07
162.06
142.96
142.37
134.08
133.40
129.52
129.15
127.83
126.91
116.27
114.87
77.24
76.99
76.73
62.43
61.79
52.09
f1 (ppm)