Supplementary Material for:

Chiral crystallization of aromatic helical foldamers via complementarities in shape and end functionalities**

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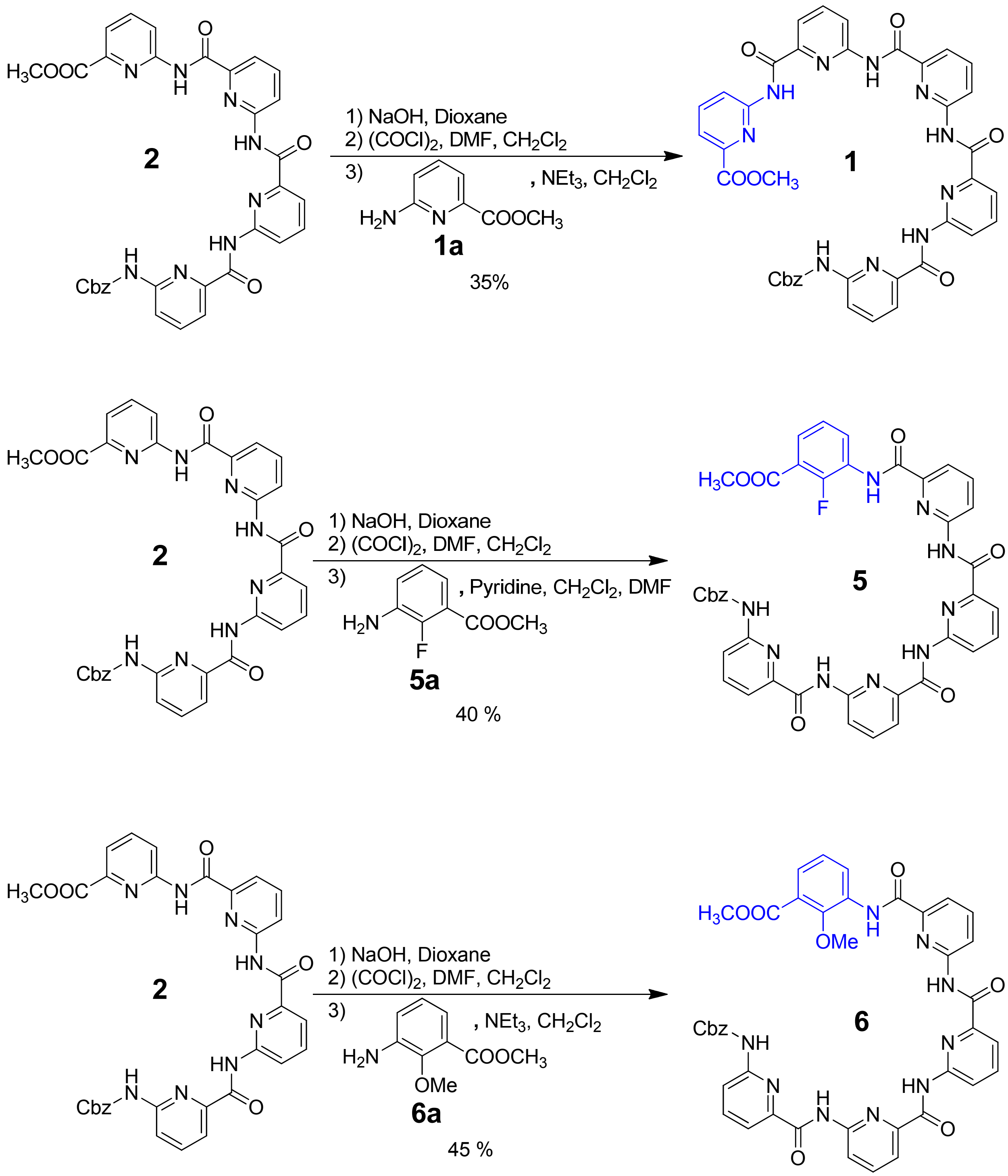
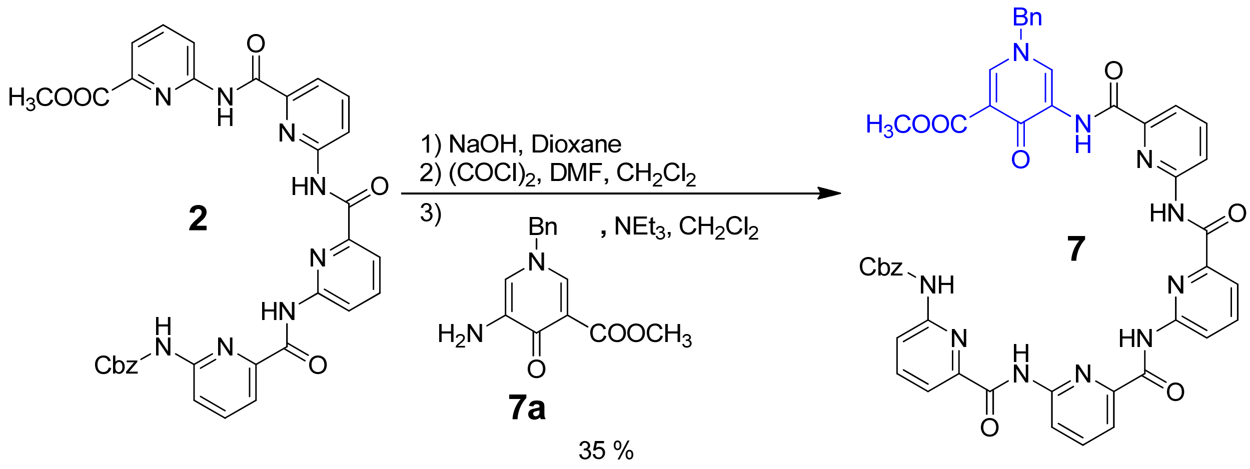
1. General Remarks

All the reagents were obtained from commercial suppliers and used as received unless otherwise stated. Aqueous solutions were prepared from distilled water. The organic solutions from all liquid extractions were dried over anhydrous sodium sulphate for a minimum of 15 minutes before filtration. Reactions were monitored by thin-layer chromatography (TLC) on silica gel pre-coated glass plates (0.25 mm thickness, 60F-254, E., Merck). Chemical yields refer to pure isolated substances. Mass spectra were obtained using instrumentation which includes Finnigan MAT95XL-T and Micromass VG7035. Single crystal X-ray diffraction study was recorded on Bruker-AXS Smart Apex CCD single crystal diffractometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX500 (500 MHz) spectrometer. The solvent signal of $CDCl_3$ in ^{1}H NMR was referenced at $\delta = 7.26$ 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), coupling constant and number of protons that gave rise to the signal, where applicable. ^{13}C NMR spectra are proton-decoupled and the solvent peaks of $CDCl_3$ was referenced at $\delta = 77.0$ ppm. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, Inc. and used without further purification unless otherwise stated.

2. Scheme S1. Synthetic Route that Affords Pentamer 1, 5, 6 and 7




2
1) NaOH, Dioxane
2) $(COCl)_2$, DMF, CH_2Cl_2
3)
, NEt_3, CH_2Cl_2
7a
35 %
7

3. Synthetic Procedures & Characterization

The synthesis of monomer **1a**,[1] **5a**,[2] **6a**[3] and **7a**,[4] tetramer **2**,[1] and **pentamer 3**[1] and **4**,[5] had been reported in the following journal article:

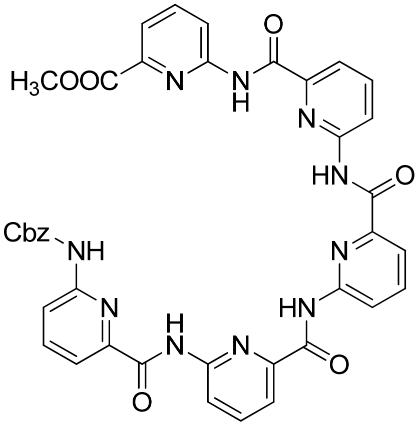
(1) Ong, W. Q.; Zhao, H.; Du, Z.; Yeh, J. Z. Y.; Ren, C.; Tan, L. Z. W.; Zhang, K.; Zeng, H. *Chem. Commun.* **2011**, *47*, 6416.

(2) Ren C.; Zhou, F.; Qin, B.; Ye, R.; Shen, S.; Su, H; Zeng, H. *Angew. Chem. Int. Ed.* **2011**, *50*, 10612.

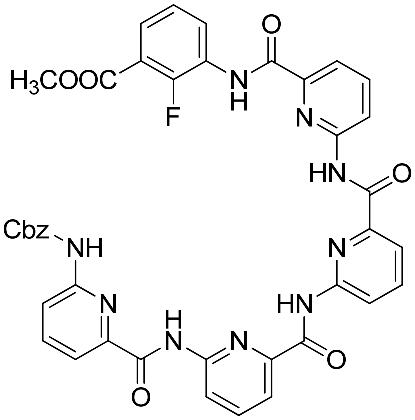
(3) Qin, B.; Chen, X.; Fang, X.; Shu, Y.; Yip Y. K.; Yan, Y.; Pan., S.; Ong, W. Q.; Ren C.; Su, H.; Zeng, H. *Org. Lett.*. **2008**, *10*, 5127.

(4) Ren, C.; Maurizot, V.; Zhao, H.; Shen, J.; Zhou, F.; Ong, W. Q.; Du, Z.; Zhang, K.; Su, H.; Zeng, H. *J. Am. Chem. Soc.* **2011**, *133*, 13920.

(5) Zhao, H.; Ong, W. Q.; Fang, X.; Zhou, F.; Hii, M. N.; Li, F. Y. S.; Su, H.; Zeng, H. *Org. Biomol. Chem.* **2012**, *10*, 1172.

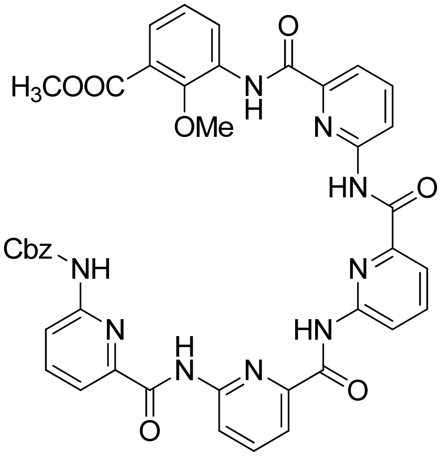


Pentamer **1**: Solid NaOH (0.16 g, 4.0 mmol) was dissolved in minimal amount of deionized water and was then added into the round bottom flask containing tetramer **2** (1.29 g, 2.0 mmol) in dioxane (20 ml). The mixture was stirred at room temperature overnight and the solvent was then removed *in vacuo*. Water (20 ml), MeOH (20 ml) and solid $KHSO_4$ (0.54 g, 4.0 mmol) was then added. The suspension was then filtered, washed and the residue obtained was dried to give the acid intermediate. The acid intermediate (0.63 g, 1.0 mmol) was dissolved in dry dichloromethane (10ml) in a round bottom flask. DMF (0.1 ml) was added, followed by the dropwise addition of oxalyl chloride (0.3 ml, 2.0 mmol) into the round bottom flask. The reaction mixture was stirred for 2 hrs and thereafter the solvent and excess oxalyl chloride were removed *in vacuo* and dry dichloromethane (10 ml) was added to the acid chloride in nitrogen atmosphere. Minimal amount of dry dichloromethane was added to a mixture containing compound **1a** (0.15 g, 1.0 mmol) and triethylamine (0.1 ml, 0.3 mmol) and the mixture was injected into the acid chloride. The mixture was allowed to stir for 1 hr at room temperature and after the reaction, the product was washed with water (2 x 10ml), 1M HCl (2 x 10ml) and 1M NaOH (2 x 10ml). The solvent was removed *in vacuo* to give the crude product and the flash column chromatography was used to afford the pure product as a white solid (0.27 g, 35 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.63 (s, 1H), 10.57 (s, 1H), 10.47 (s, 1H), 10.38 (s, 1H), 8.80 (d, 1H, *J* = 8.1 Hz), 8.72–8.76 (m, 3H), 8.15 (d, 1H, *J* = 7.7 Hz), 8.12 (d, 1H, *J* = 6.9 Hz), 8.00–8.07 (m, 2H), 7.97 (d, 1H, *J* = 7.0 Hz), 7.88–7.91 (m, 2H), 7.81 (t, 1H, *J* = 7.9 Hz), 7.67–7.72 (m, 2H), 7.54 (d, 1H, *J* = 7.4 Hz), 7.41 (br, 1H), 7.14–7.19 (m, 3H), 7.04–7.06 (m, 2H), 5.01 (s, 2H), 3.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.61, 162.58, 162.56, 162.52, 162.34, 152.31, 152.29, 151.13, 150.22, 150.17, 150.10, 150.01, 147.29, 146.86, 140.16, 140.13, 140.08, 139.96, 139.51, 135.19, 128.32, 128.02, 127.41, 120.93, 118.72, 118.69, 118.65, 118.57, 117.85, 117.47, 117.36, 117.23, 117.13, 114.94, 67.27, 52.90. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{39}H_{30}N_{10}O_8{}^{23}Na$): *m/z* 789.2140, found: *m/z* 789.2148.



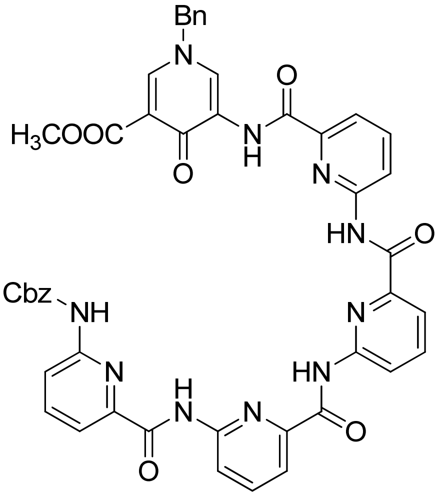
Pentamer 5: Solid NaOH (0.16 g, 4.0 mmol) was dissolved in minimal amount of deionized water and was then added into the round bottom flask containing tetramer **2** (1.29 g, 2.0 mmol) in dioxane (20 ml). The mixture was stirred at room temperature overnight and the solvent was then removed *in vacuo*. Water (20 ml), MeOH (20 ml) and solid $KHSO_4$ (0.54 g, 4.0 mmol) was then added. The suspension was then filtered, washed and the residue obtained was dried to give the acid intermediate. The acid intermediate (0.63 g, 1.0 mmol) was dissolved in dry dichloromethane (10 ml) in a round bottom flask. DMF (0.1 ml) was added, followed by the dropwise addition of oxalyl chloride (0.3 ml, 2.0 mmol) into the round bottom flask. The reaction mixture was stirred for 4 hrs and thereafter the solvent and excess oxalyl chloride were removed *in vacuo* and dry dichloromethane (10 ml) was added to the acid chloride in nitrogen atmosphere. Minimal amount of dry dichloromethane was added to a mixture containing the amine **5a** (0.25 g, 1.5 mmol) and pyridine (0.24 ml, 3 mmol) and the mixture was injected into the acid chloride. The mixture was allowed to stir for 5 hrs at room temperature and after the reaction, the product was washed with water (2 x 10ml), 1M HCl (2 x 10 ml) and 1M NaOH (2 x 10 ml). The solvent was removed *in vacuo* to give the crude product and the flash column chromatography was used to afford the pure product as a white solid (0.31 g, 40%). ^1H NMR (500 MHz, $CDCl_3$): δ 10.56 (s, 1H), 10.52, (s, 1H), 10.34 (d, 1H, $J = 4.7$ Hz), 10.27 (s, 1H), 8.86

(t, 1H, J = 7.1 Hz), 8.82 (d, 1H, J = 8.3 Hz), 8.77 (d, 1H, J = 7.9 Hz), 8.66 (d, 1H, J = 8.3 Hz), 8.14 (d, 1H, J = 3.6 Hz), 8.13 (d, 1H, J = 2.8 Hz), 8.02–8.07 (m, 2H), 7.94 (d, 1H, J = 7.1 Hz), 7.85–7.90 (m, 2H), 7.74 (d, 1H, J = 8.7 Hz), 7.64– 7.68 (m, 1H) 7.47 (s, 1H), 7.27–7.28 (m, 1H), 7.06–7.21 (m, 6H), 5.05 (s, 2H), 3.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.30, 162.24, 161.72, 150.44, 150.21, 149.94, 149.65, 147.61, 147.36, 147.23, 146.91, 140.48, 139.79, 128.15, 127.82, 125.13, 118.83, 118.60, 118.29, 117.56, 117.39, 115.89, 77.25, 77.00, 76.74, 65.03, 50.27. ^{19}F NMR (282 MHz, $CDCl_3$): δ -129.31 (s, 1F). HRMS-ESI: calculated for $[M+Na]^+$ ($C_{40}H_{30}FN_9O_8Na$): m/z 806.2099, found: m/z 806.2141.



Pentamer 6: Solid NaOH (0.16 g, 4.0 mmol) was dissolved in minimal amount of deionized water and was then added into the round bottom flask containing tetramer **2** (1.29 g, 2.0 mmol) in dioxane (20 ml). The mixture was stirred at room temperature overnight and the solvent was then removed *in vacuo*. Water (20 ml), MeOH (20 ml) and solid $KHSO_4$ (0.54 g, 4.0 mmol) was then added. The suspension was then filtered, washed and the residue obtained was dried to give the acid intermediate. The acid intermediate (0.63 g, 1.0 mmol) was dissolved in dry dichloromethane (10 ml) in a round bottom flask. DMF (0.1 ml) was added, followed by the

dropwise addition of oxalyl chloride (0.3 ml, 2.0 mmol) into the round bottom flask. The reaction mixture was stirred for 4 hrs and thereafter the solvent and excess oxalyl chloride were removed *in vacuo* and dry dichloromethane (10 ml) was added to the acid chloride in nitrogen atmosphere. Minimal amount of dry dichloromethane was added to a mixture containing the amine **6a** (0.27 g, 1.5 mmol) and TEA (0.40 ml, 3 mmol) and the mixture was injected into the acid chloride. The mixture was allowed to stir for 5 hrs at room temperature and after the reaction, the product was washed with water (2 x 10 ml), 1M HCl (2 x 10 ml) and 1M NaOH (2 x 10 ml). The solvent was removed *in vacuo* to give the crude product and the flash column chromatography was used to afford the pure product as a white solid (0.36 g, 45 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.81 (s, 1H), 10.69 (s,1H), 10.50 (s, 1H), 10.25 (s, 1H), 8.85 (d, 1H, J = 8.2 Hz), 8.75–8.77 (m, 2H), 8.57 (d, 1H, J = 7.1 Hz), 8.13–8.17 (m, 2H), 8.03–8.08 (m, 2H), 7.79–7.93 (m, 4H), 7.65–7.68 (m, 1H), 7.40 (s, 1H), 7.14–7.20 (m, 4H), 7.03–7.07 (m, 3H), 5.06 (s, 2H), 4.02 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.60, 162.69, 162.44, 161.89, 161.31, 152.13, 150.66, 150.04, 149.80, 149.45, 148.64, 148.12, 147.23, 147.19, 146.82, 140.57, 140.36, 140.23, 139.38, 135.49, 132.72, 128.34, 128.03, 127.54, 125.93, 124.46, 123.21, 118.93, 118.72, 118.22, 117.89, 117.79, 117.63, 116.48, 115.30, 67.24, 62.32, 51.92. HRMS-ESI: calculated for $[M+Na]^+$ ($C_{41}H_{33}N_9O_9Na$): m/z 818.2293, found: m/z 818.2277.



Pentamer 7: Solid NaOH (0.16 g, 4.0 mmol) was dissolved in minimal amount of deionized water and was then added into the round bottom flask containing tetramer **2** (1.29 g, 2.0 mmol) in dioxane (20 ml). The mixture was stirred at room temperature overnight and the solvent was then removed *in vacuo*. Water (20 ml), MeOH (20 ml) and solid $KHSO_4$ (0.54 g, 4.0 mmol) was then added. The suspension was then filtered, washed and the residue obtained was dried to give the acid intermediate. The acid intermediate (0.63 g, 1.0 mmol) was dissolved in dry dichloromethane (10 ml) in a round bottom flask. DMF (0.1 ml) was added, followed by the dropwise addition of oxalyl chloride (0.3 ml, 2.0 mmol) into the round bottom flask. The reaction mixture was stirred for 4 hrs and thereafter the solvent and excess oxalyl chloride were removed *in vacuo* and dry dichloromethane (10 ml) was added to the acid chloride in nitrogen atmosphere. Minimal amount of dry dichloromethane was added to a mixture containing the amine **7a** (0.39 g, 1.5 mmol) and TEA (0.40 ml, 3 mmol) and the mixture was injected into the acid chloride. The mixture was allowed to stir for 5 hr at room temperature and after the reaction, the product was washed with water (2 x 10 ml), 1M HCl (2 x 10 ml) and 1M NaOH (2 x 10 ml). The solvent was removed *in vacuo* to give the crude product and the flash column chromatography was used to afford the pure product as a white solid (0.31 g, 35 %). ^{1}H NMR

(500 MHz, $CDCl_3$): δ 11.07 (s, 1H), 10.69 (s, 1H), 10.62 (s, 1H), 10.46 (s, 1H), 9.02 (d, 1H, *J* = 1.9 Hz), 8.83 (d, 1H, *J* = 8.5 Hz), 8.78 (d, 1H, *J* = 8.1 Hz), 8.62 (d, 1H, *J* = 8.0 Hz), 8.10–8.13 (m, 2H), 8.00–8.06 (s, 2H), 7.73–7.89 (m, 6H), 7.46–7.53 (m, 4H), 7.38 (d, 2H, *J* = 7.7 Hz), 7.12–7.18 (m, 3H), 7.03–7.05 (d, 2H, *J* = 7.5 Hz), 5.006–5.013 (m, 4H), 3.56 (s, 3H). HRMS-ESI: calculated for $[M+Na]^+$ ($C_{46}H_{36}N_{10}O_9Na$): m/z 895.2559, found: m/z 895.2559. Please note here due to very bad solubility of pentamer **7** in $CDCl_3$, DMSO-d6 or their mixed solvents, the ^{13}C NMR cannot be obtained within a reasonable period of time. Its identity can be confidently established by ^1H NMR, HRMS and X-ray crystal structure.

4. X-Ray Crystal Data

(a) Crystal data of M1•MeOH for pentamer 1

CCDC Number	**838391**	
Empirical formula	$C_{40} H_{34} N_{10} O_9$	
Formula weight	798.77	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.3551(9) Å	α= 90°.
	b = 13.6824(11) Å	β= 90°.
	c = 25.595(2) Å	γ = 90°.
Volume	3626.3(5) $Å^3$	
Z	4	
Density (calculated)	1.463 Mg/m^3	
Absorption coefficient	0.107 mm^{-1}	
F(000)	1664	
Crystal size	0.36 x 0.16 x 0.14 mm^3	
Theta range for data collection	1.69 to 27.50°.	
Index ranges	-13<=h<=13, -15<=k<=17, -33<=l<=33	
Reflections collected	26021	
Independent reflections	8326 [R(int) = 0.0582]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9852 and 0.9625	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8326 / 31 / 571	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0621, wR2 = 0.1338	
R indices (all data)	R1 = 0.0815, wR2 = 0.1426	
Absolute structure parameter	0.0(11)	
Largest diff. peak and hole	0.590 and -0.266 e.$Å^{-3}$	

(b) Crystal data of M1•CH_2Cl_2 for pentamer 1

CCDC Number	**838392**	
Empirical formula	$C_{40} H_{32} Cl_2 N_{10} O_8$	
Formula weight	851.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.5103(13) Å	α= 90°.
	b = 13.6620(16) Å	β= 90°.
	c = 25.537(3) Å	γ = 90°.
Volume	3666.9(8) $Å^3$	
Z	4	
Density (calculated)	1.543 Mg/m^3	
Absorption coefficient	0.250 mm^{-1}	
F(000)	1760	
Crystal size	0.60 x 0.20 x 0.18 mm^3	
Theta range for data collection	1.59 to 27.49°.	
Index ranges	-13<=h<=13, -16<=k<=17, -32<=l<=33	
Reflections collected	26068	
Independent reflections	8409 [R(int) = 0.0848]	
Completeness to theta = 27.49°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9611 and 0.9066	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8409 / 35 / 572	
Goodness-of-fit on F^2	1.101	
Final R indices [I>2sigma(I)]	R1 = 0.0866, wR2 = 0.1850	
R indices (all data)	R1 = 0.1167, wR2 = 0.2012	
Absolute structure parameter	0.0(2)	
Largest diff. peak and hole	0.458 and -0.901 e.$Å^{-3}$	

(c) Crystal data of P1•CH_2Cl_2 for pentamer 1

CCDC Number	**838393**	
Empirical formula	$C_{40} H_{32} Cl_2 N_{10} O_8$	
Formula weight	851.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.5003(13) Å	α= 90°.
	b = 13.6695(17) Å	β= 90°.
	c = 25.510(3) Å	γ = 90°.
Volume	3661.5(8) $Å^3$	
Z	4	
Density (calculated)	1.545 Mg/m^3	
Absorption coefficient	0.250 mm^{-1}	
F(000)	1760	
Crystal size	0.40 x 0.18 x 0.16 mm^3	
Theta range for data collection	1.60 to 27.50°.	
Index ranges	-13<=h<=13, -17<=k<=16, -33<=l<=30	
Reflections collected	25780	
Independent reflections	8402 [R(int) = 0.0407]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9610 and 0.9065	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8402 / 35 / 572	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1579	
R indices (all data)	R1 = 0.0764, wR2 = 0.1665	
Absolute structure parameter	-0.08(18)	
Largest diff. peak and hole	0.555 and -0.866 e.$Å^{-3}$	

(d) Crystal data of pentamer 5

CCDC Number	**865971**	
Empirical formula	$C_{41}H_{33.25}Cl_{0.25}FN_9O_{8.75}$	
Formula weight	819.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.4183(10) Å	α= 90°.
	b = 13.6836(13) Å	β= 90°.
	c = 25.671(2) Å	γ = 90°.
Volume	3659.7(6) $Å^3$	
Z	4	
Density (calculated)	1.488 Mg/m^3	
Absorption coefficient	0.128 mm^{-1}	
F(000)	1702	
Crystal size	0.24 x 0.12 x 0.10 mm^3	
Theta range for data collection	2.11 to 27.49°.	
Index ranges	-13<=h<=13, -17<=k<=16, -29<=l<=33	
Reflections collected	26354	
Independent reflections	8395 [R(int) = 0.0665]	
Completeness to theta = 27.49°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9873 and 0.9699	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8395 / 75 / 589	
Goodness-of-fit on F^2	1.101	
Final R indices [I>2sigma(I)]	R1 = 0.0719, wR2 = 0.1385	
R indices (all data)	R1 = 0.0921, wR2 = 0.1469	
Absolute structure parameter	0.3(4)	
Largest diff. peak and hole	0.331 and -0.317 e.$Å^{-3}$	

(e) Crystal data of pentamer 6

CCDC Number	**865972**	
Empirical formula	$C_{41} H_{33} N_9 O_9$	
Formula weight	795.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.8466(7) Å	α= 90°.
	b = 33.387(3) Å	β= 94.602(2)°.
	c = 14.0698(14) Å	γ = 90°.
Volume	3674.1(6) Å^3	
Z	4	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	1656	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.90 to 27.50°.	
Index ranges	-10<=h<=10, -42<=k<=43, -18<=l<=14	
Reflections collected	26161	
Independent reflections	8421 [R(int) = 0.0606]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9896 and 0.9794	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8421 / 5 / 549	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1222	
R indices (all data)	R1 = 0.0925, wR2 = 0.1333	
Largest diff. peak and hole	0.376 and -0.234 e.Å^{-3}	

(f) Crystal data of pentamer 7

CCDC Number	**865973**	
Empirical formula	$C_{46} H_{36} N_{10} O_9$	
Formula weight	872.85	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.6110(10) Å	α= 73.499(2)°.
	b = 12.9590(12) Å	β= 77.989(3)°.
	c = 16.4525(16) Å	γ = 72.668(3)°.
Volume	2051.8(3) Å^3	
Z	2	
Density (calculated)	1.413 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	908	
Crystal size	0.36 x 0.30 x 0.16 mm^3	
Theta range for data collection	1.69 to 27.50°.	
Index ranges	-13<=h<=13, -16<=k<=16, -21<=l<=21	
Reflections collected	27469	
Independent reflections	9399 [R(int) = 0.0483]	
Completeness to theta = 27.50°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9840 and 0.9644	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9399 / 0 / 617	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1240	
R indices (all data)	R1 = 0.0764, wR2 = 0.1335	
Largest diff. peak and hole	0.389 and -0.282 e.Å^{-3}	

(g) Tetramer 2: CCDC# 817349 and **(h) Pentamer 3:** CCDC# 817350

Both **(g)** and **(g)** can be found from *Chem. Commun.* **2011**, *47*, 6416.

5. *Ab Initio* Molecular Modeling

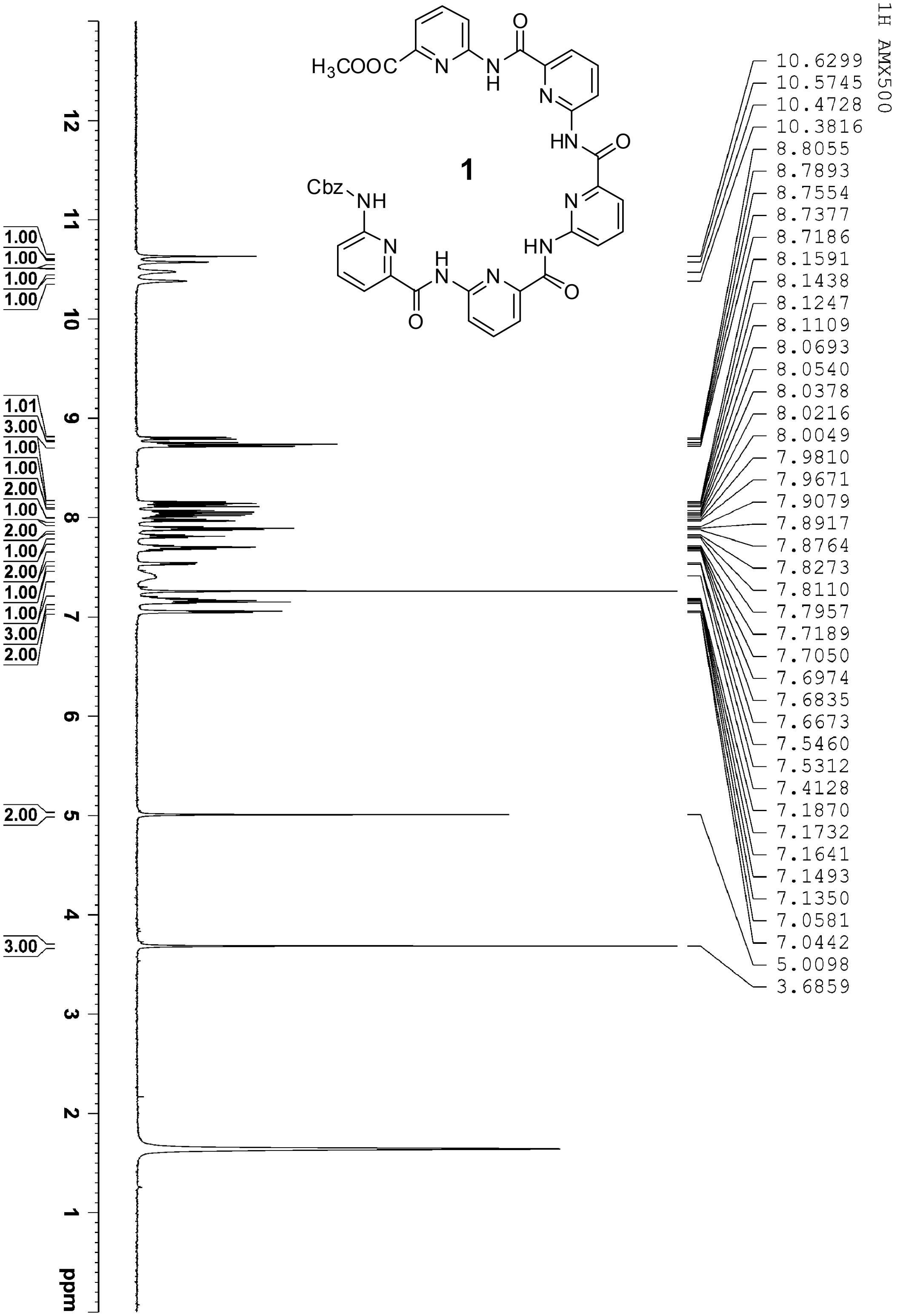
All the calculations were carried out by utilizing the either the Gaussian 03[1] or Gaussian 09[2] program package. The geometry optimizations were performed at the density functional theory (DFT) level, and the Becke's three parameter hybrid functional with the Lee-Yang-Parr correlation functional (B3LYP)[3] method was employed to do the calculations. Unless otherwise stated, the 6-311+G(2d, p)[4] basic from the Gaussian basis set library has been used in all the structural optimization and single point energy calculations. The harmonic vibrational frequencies and zero-point energy corrections were calculated at the same level of theory.

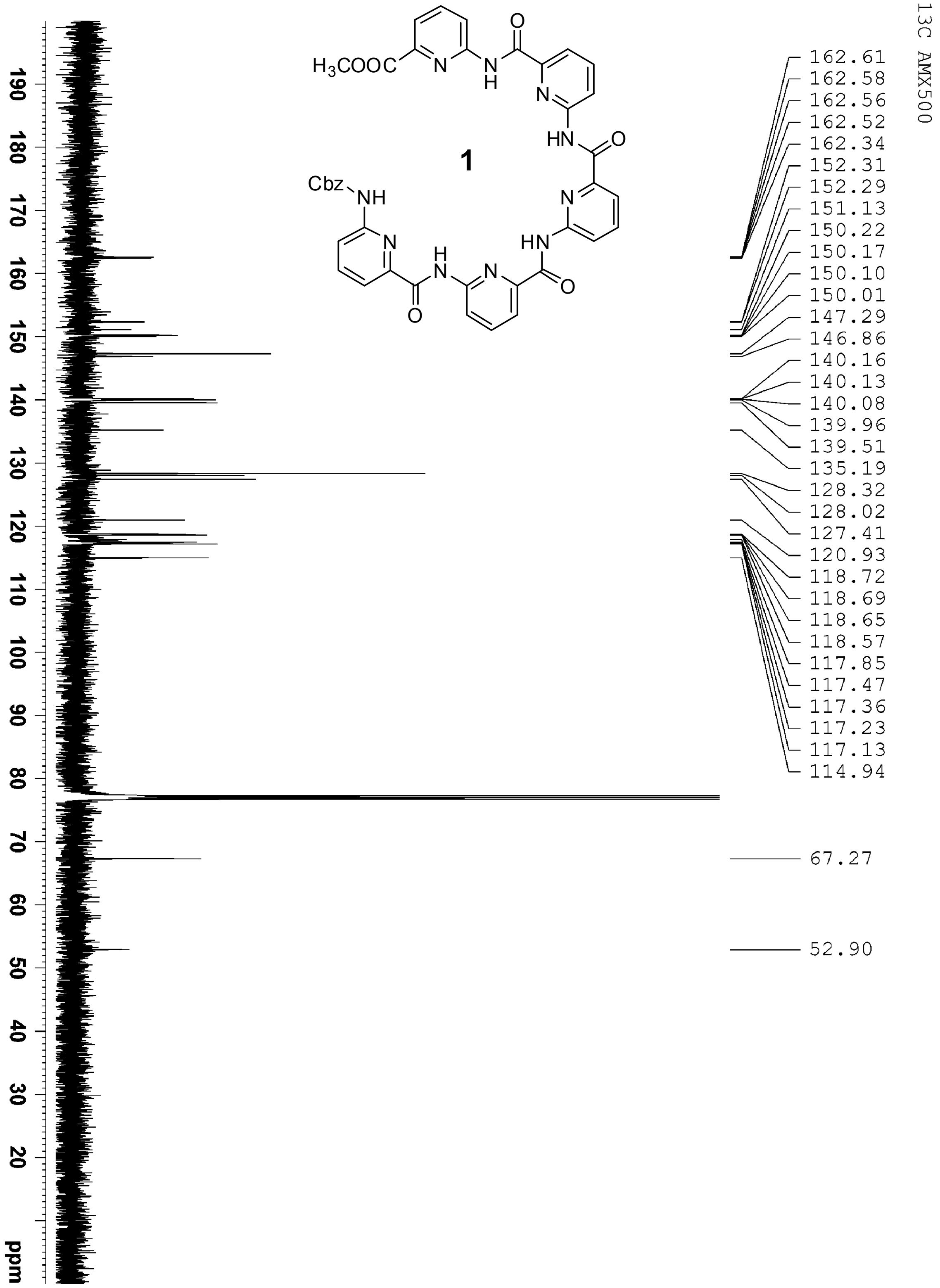
6. Theoretical Computations by dreiding force field[5]

In this paper, the dreiding force field [1] is used to optimize the geometry and calculate the energy of all the structural motifs taken from the respective crystal structures as tabulated in Table 1. The convergence tolerance is $2X10^{-5}$ kcal/mol for the energy, 0.001 kcal/mol/A for the force, 0.001 GPa for the stress and 10^{-5} A for the displacement. The Ewald method is used for calculating the electrostatic and the van der Waals terms. The accuracy is 10^{-5} kcal/mol. The repulsive cutoff is 6 Å for the van der Waals term. For the hydrogen bond term, the summation method is atom based and the truncation method is cubic spline with cutoff distance of 4.5 Å. For the isolated helical pentamer or dimer made up of two pentamers, these molecules are put in a three dimensional cubic box with every lattice length to be 100 Å to avoid the interaction of the molecules with their mirror counterparts. During the optimization the box is fixed and only the molecules are optimized for the isolated case. For the 1D or 2D cases, where the molecules repeat periodically in one or two directions, the box vectors are also optimized together with the molecules.

1. Frisch, M. J.; et al. *Gaussian 03*; Gaussian , Inc.: Wallingford CT, 2004.
2. Frisch, M. J.; et al. *Gaussian 09*; Gaussian , Inc.: Wallingford CT, 2009.
3. Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
4. Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, 94, 6081; Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, 89, 2193.
5. Mayo, S. L., Olafson, B. D. & Goddard III, W. A. "Dreiding - A generic force-field for molecular simulations," *J. Phys. Chem.*, **94**, 8897-909 (1990).

7. ^{1}H and ^{13}C NMR spectra of Oligomers 1–7

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O
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162.52
162.34
152.31
152.29
151.13
150.22
150.17
150.10
150.01
147.29
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140.16
140.13
140.08
139.96
139.51
135.19
128.32
128.02
127.41
120.93
118.72
118.69
118.65
118.57
117.85
117.47
117.36
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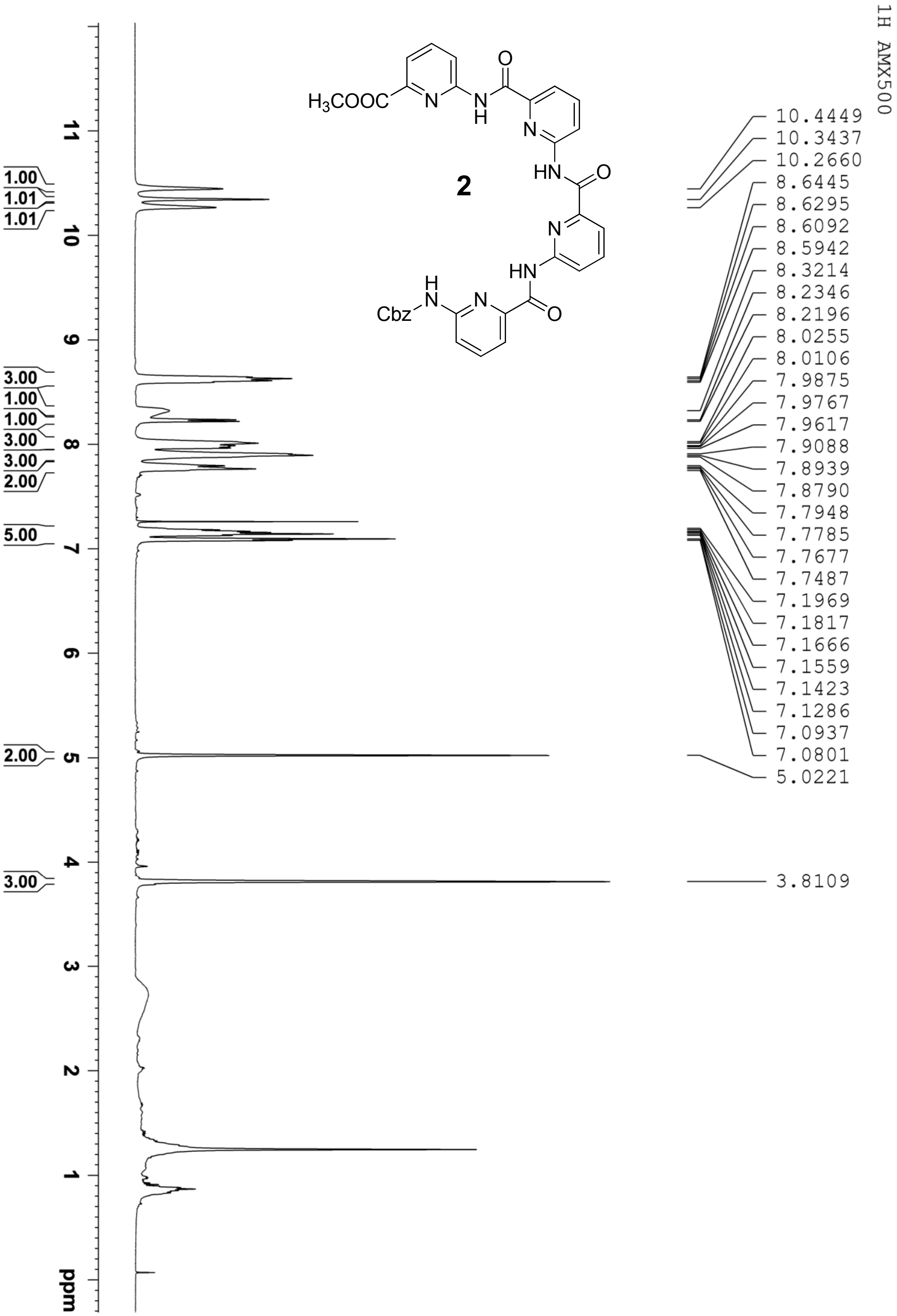
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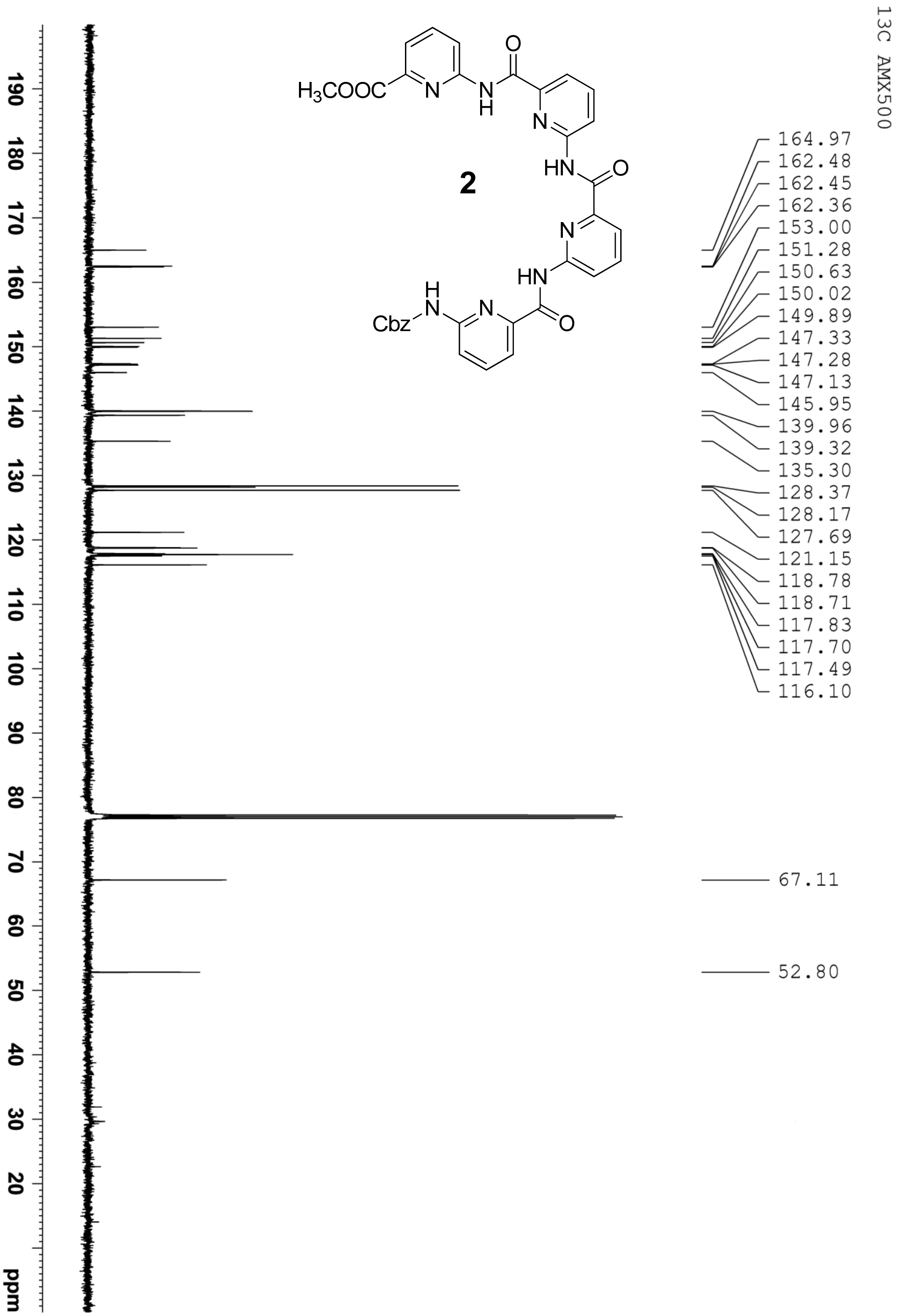
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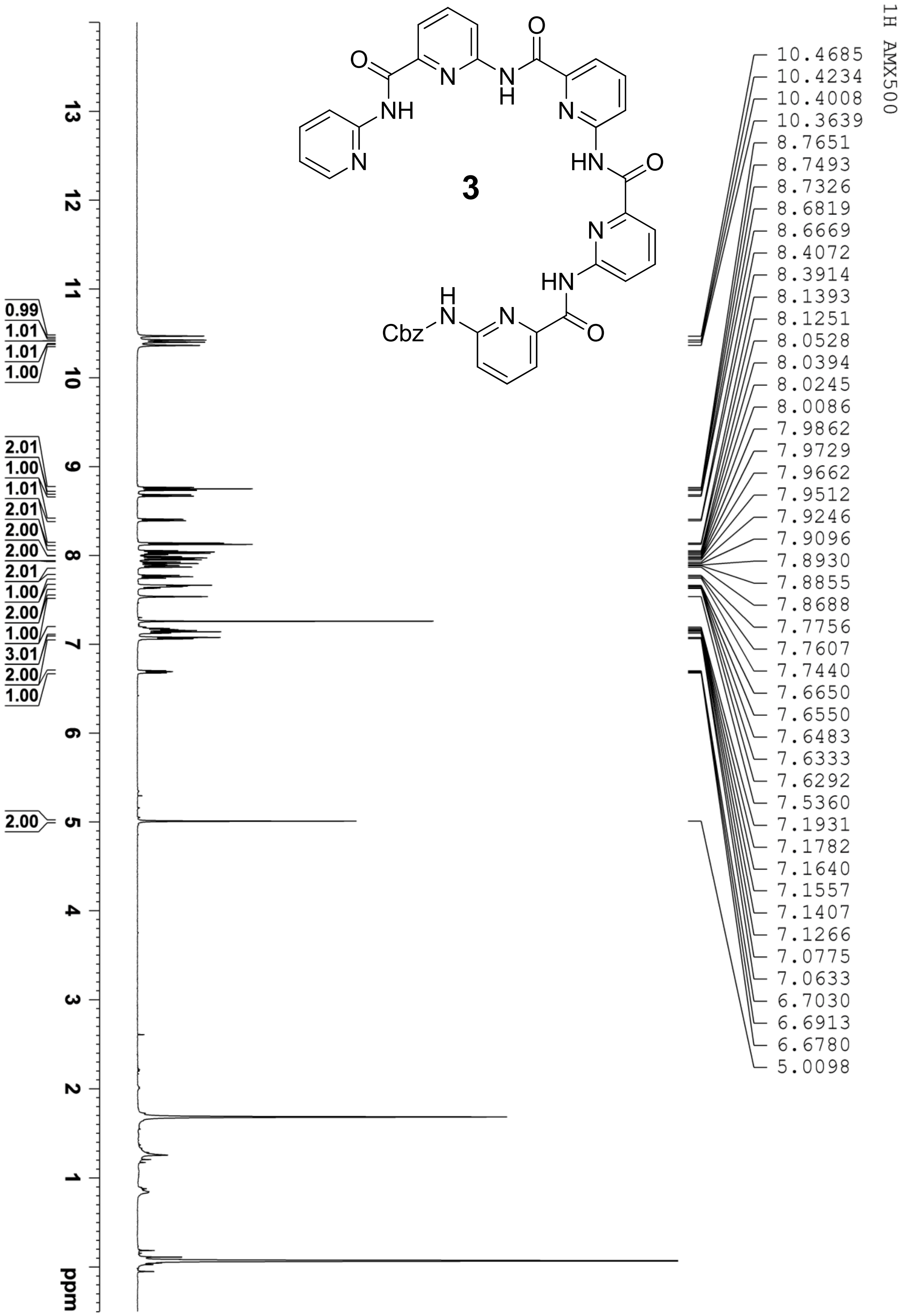
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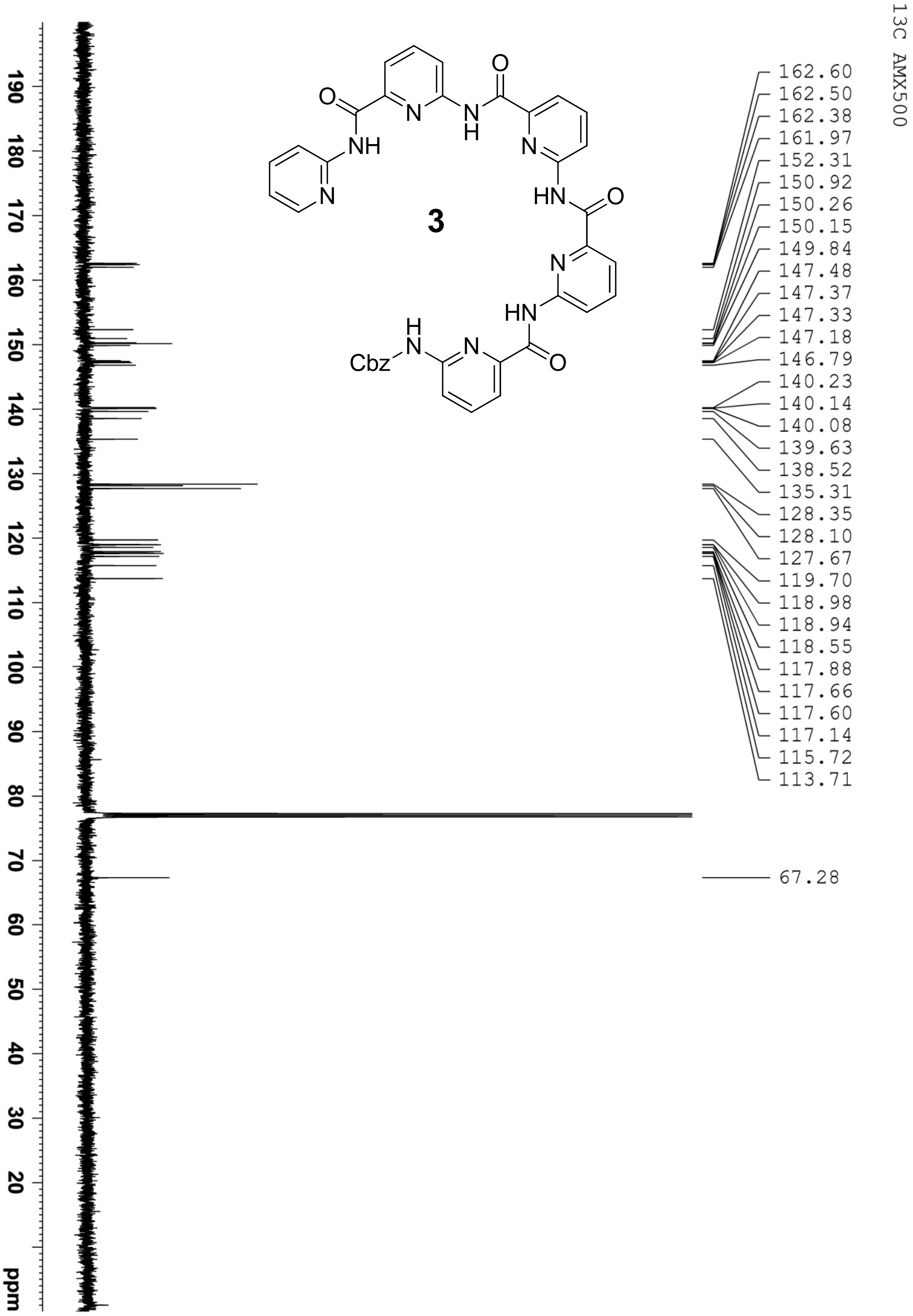
O

3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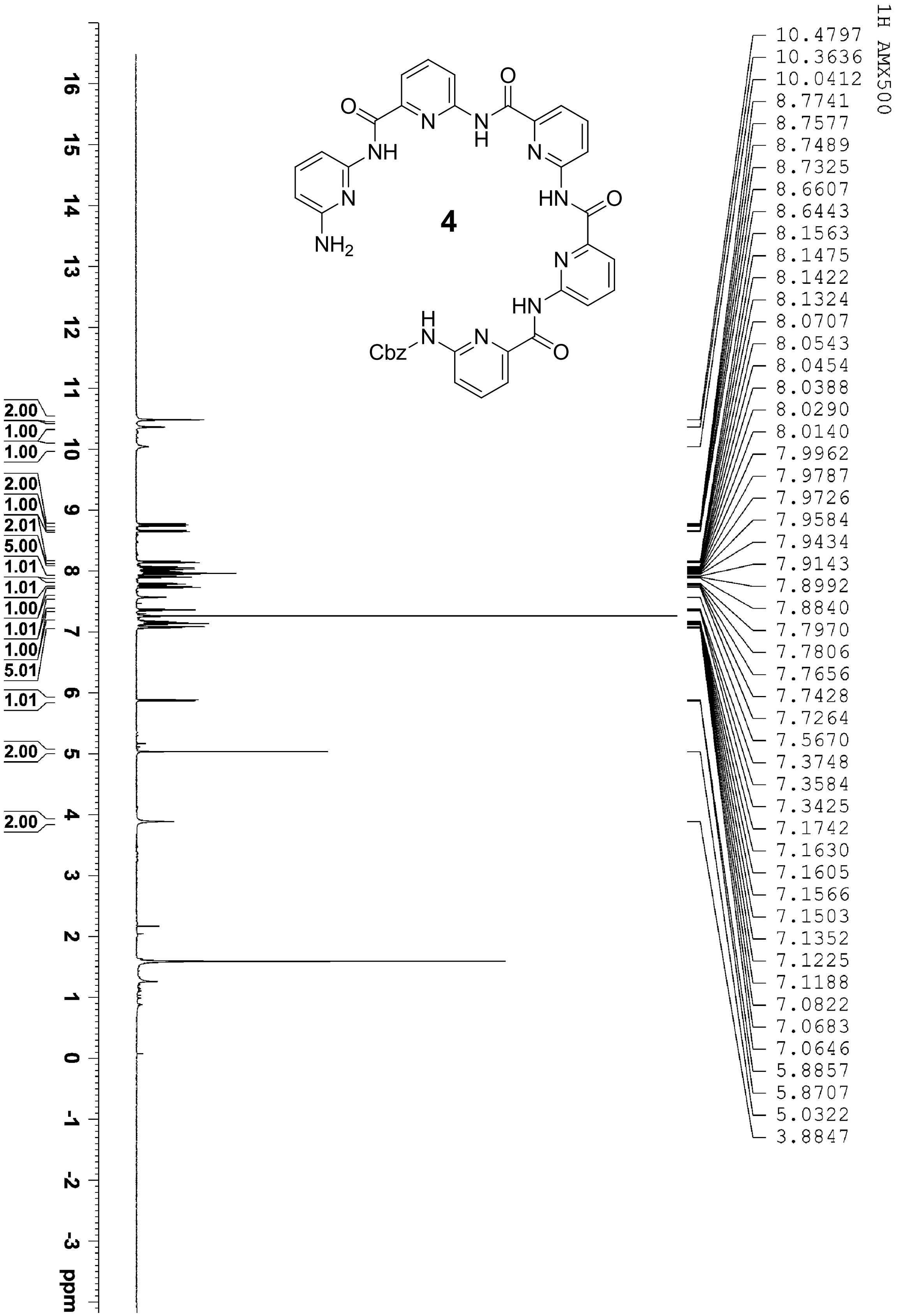
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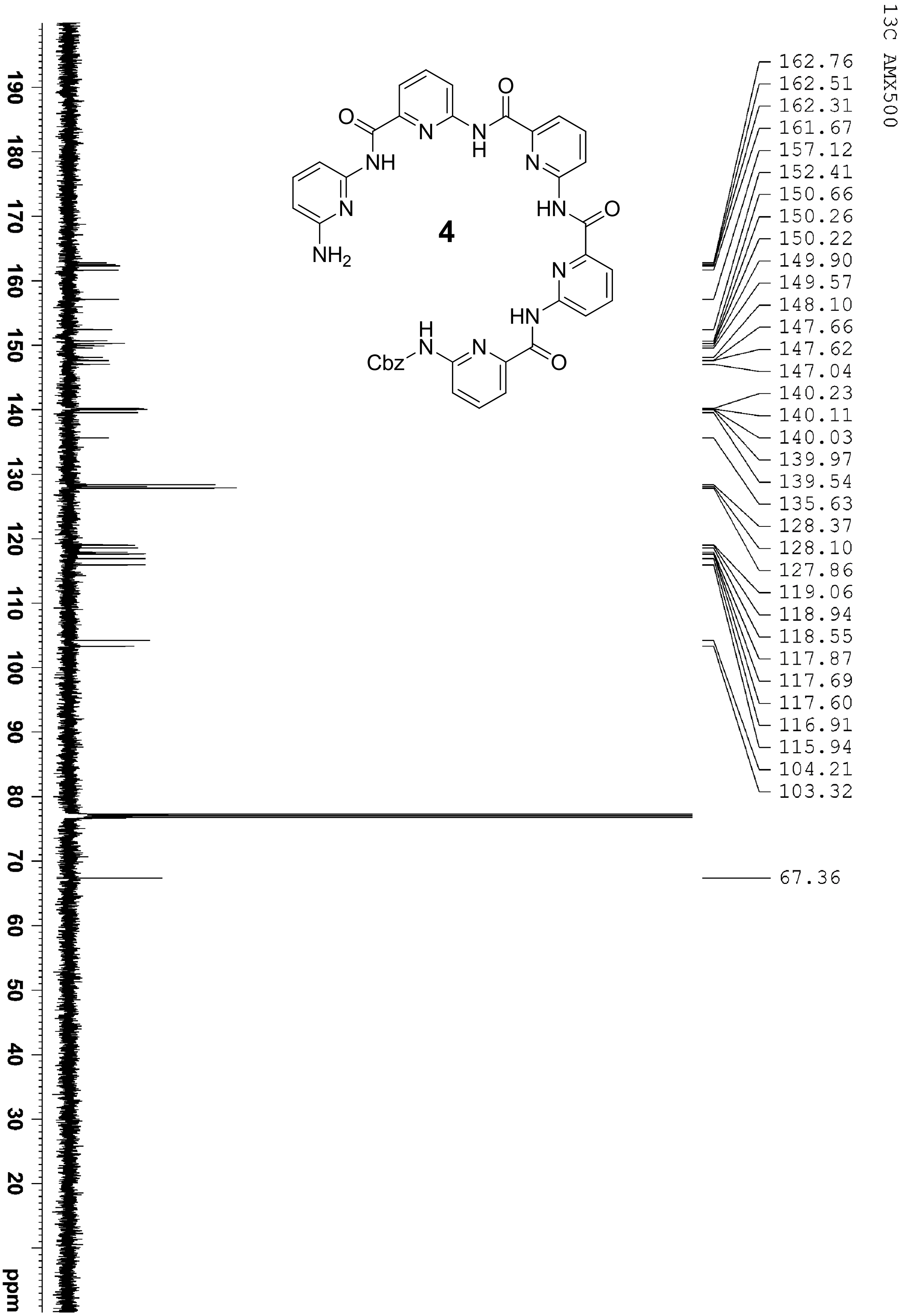
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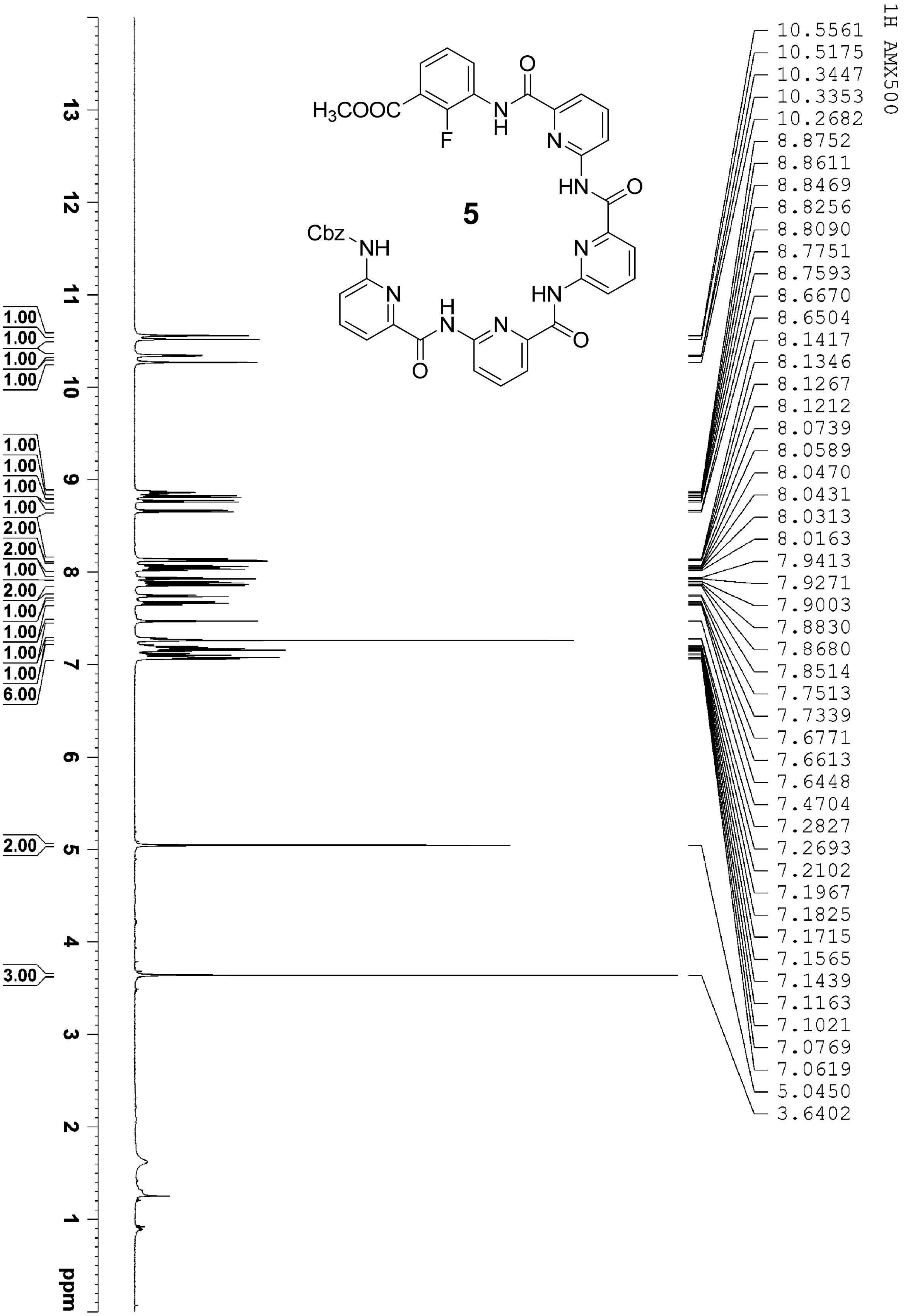
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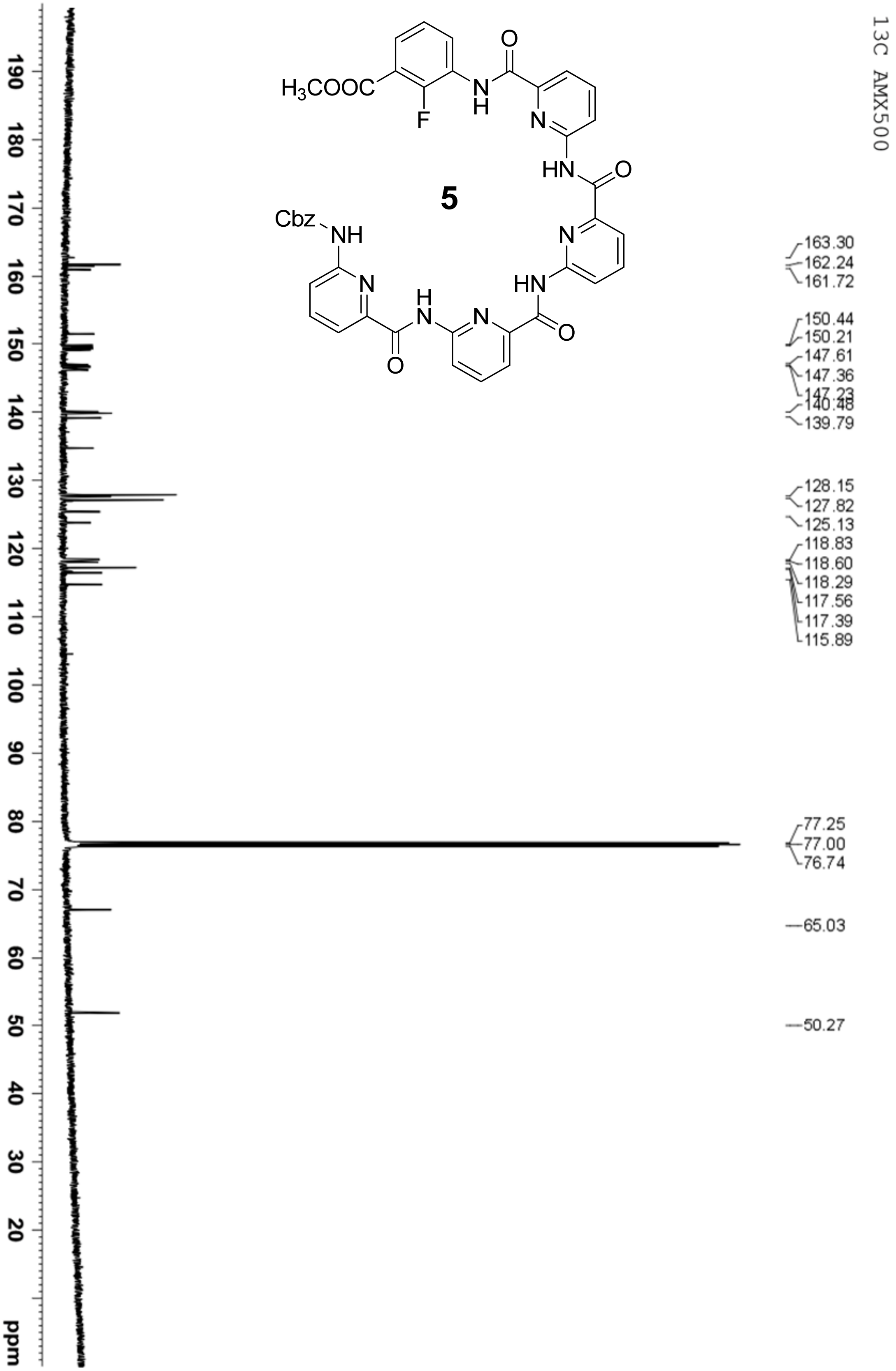
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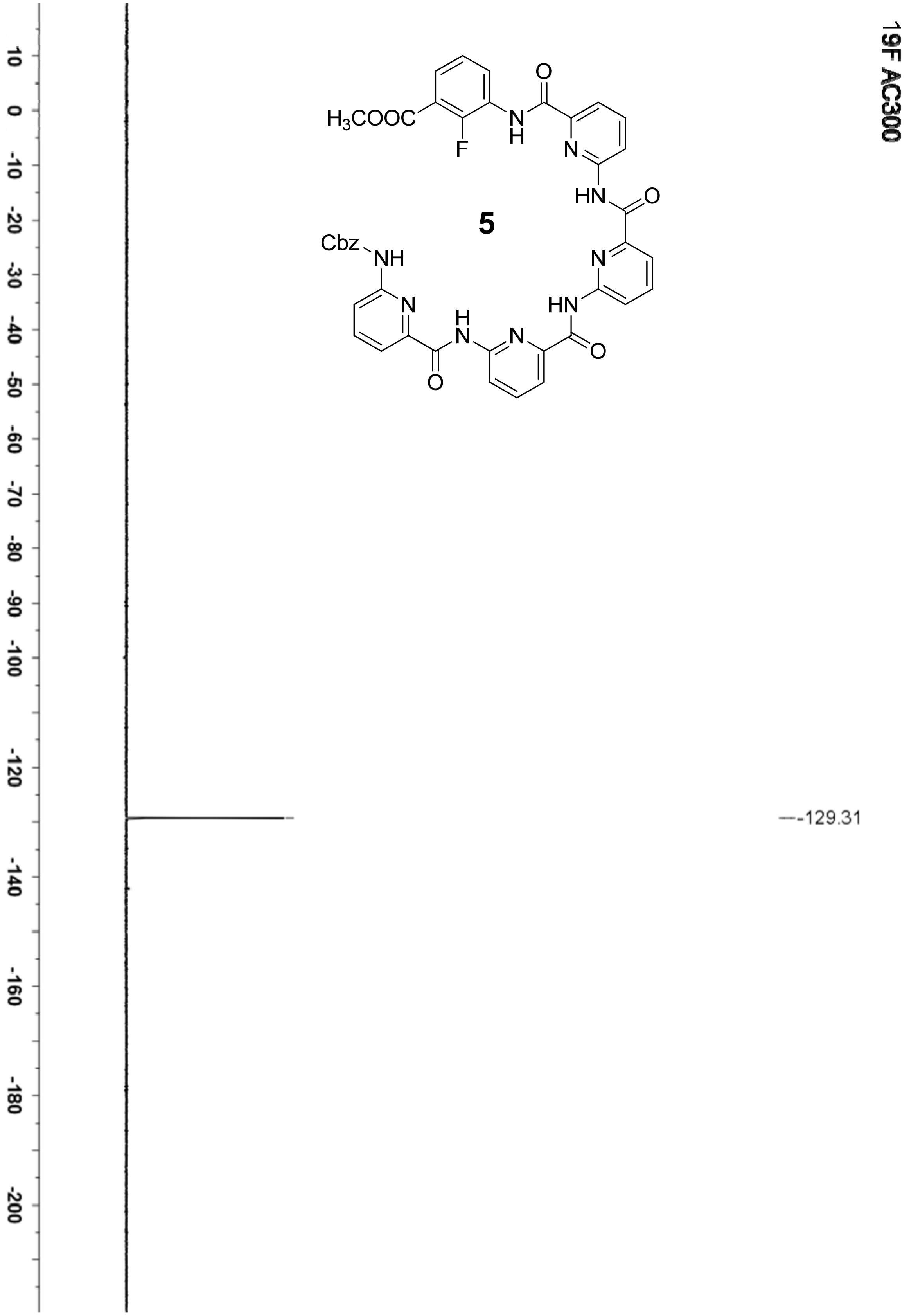
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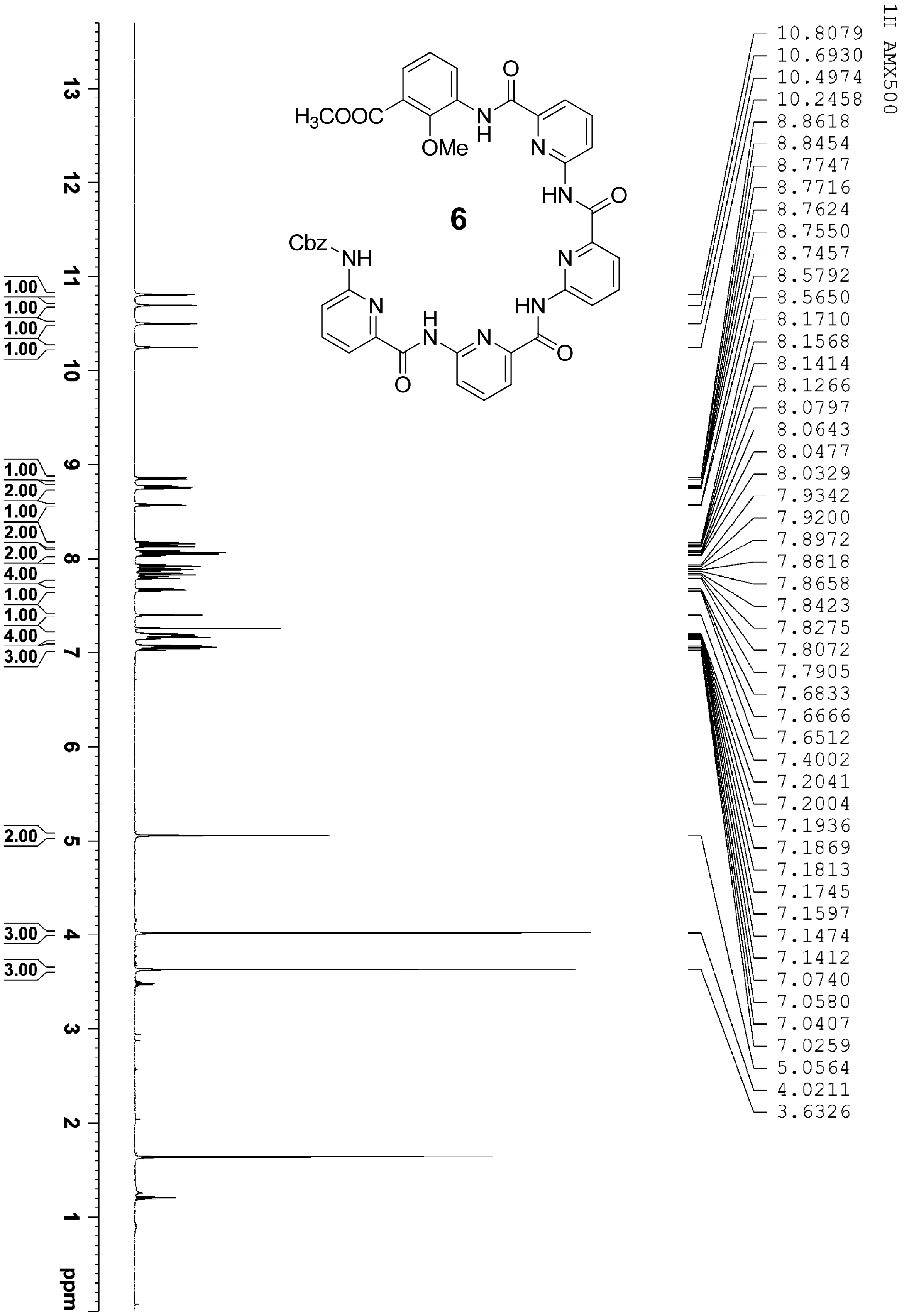

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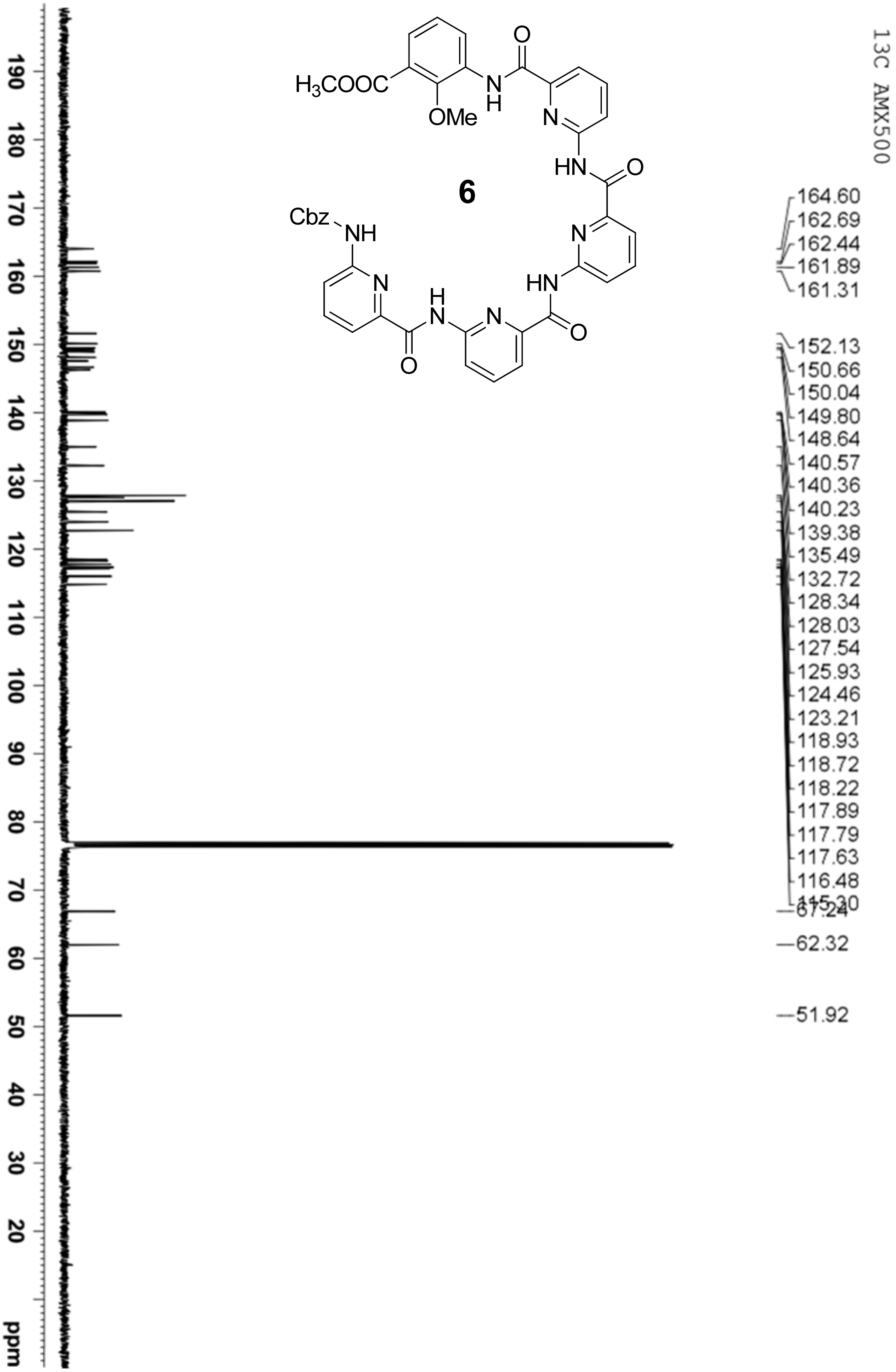

6

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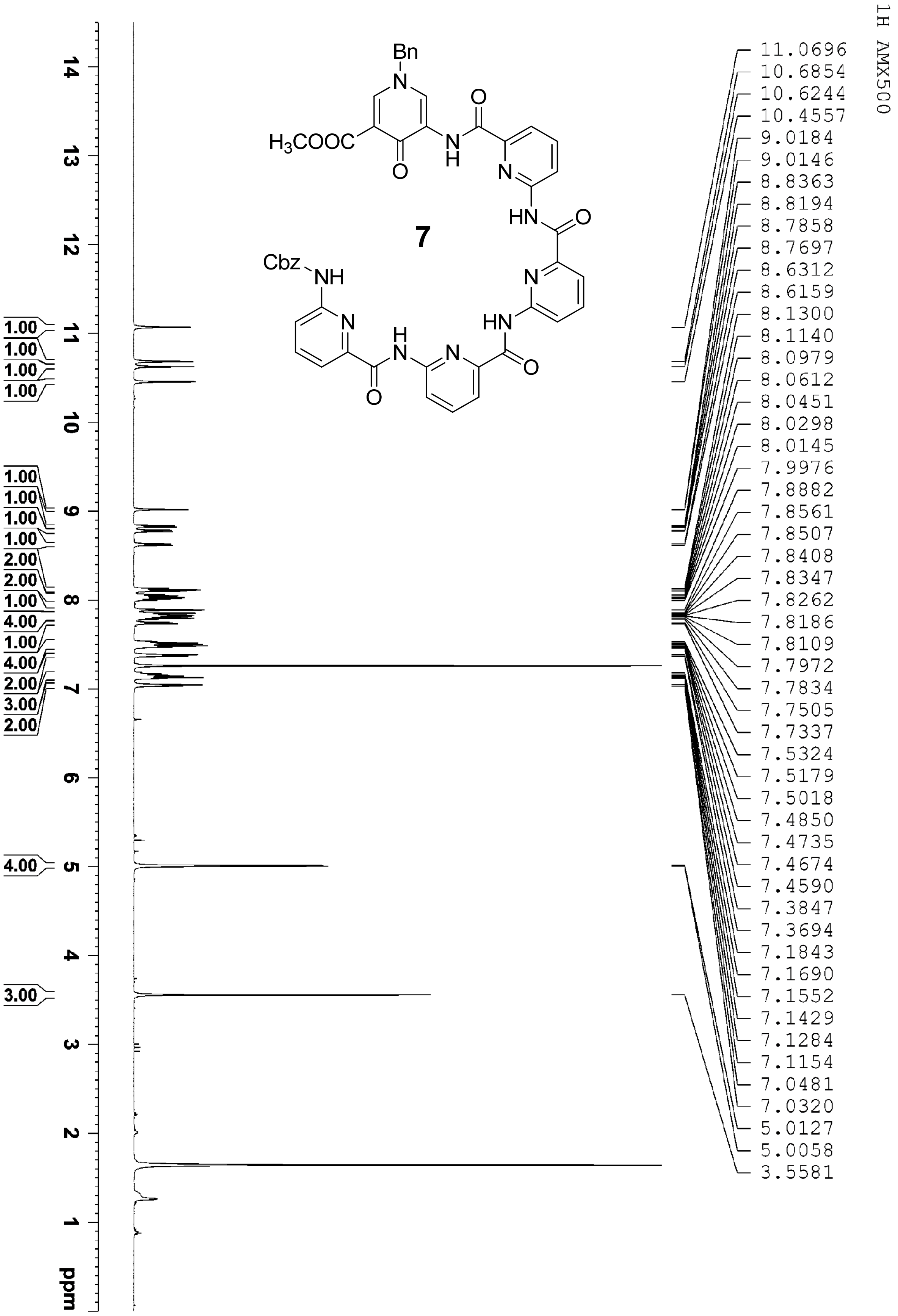
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