BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Introduction of peripheral nitrogen atoms to cyclo-*meta*-phenylenes

Koki Ikemoto and Hiroyuki Isobe

Beilstein J. Org. Chem. **2024,** *20,* 1207–1212. doi:10.3762/bjoc.20.103

Experimental and copies of spectra

Table of contents

Supplementary data

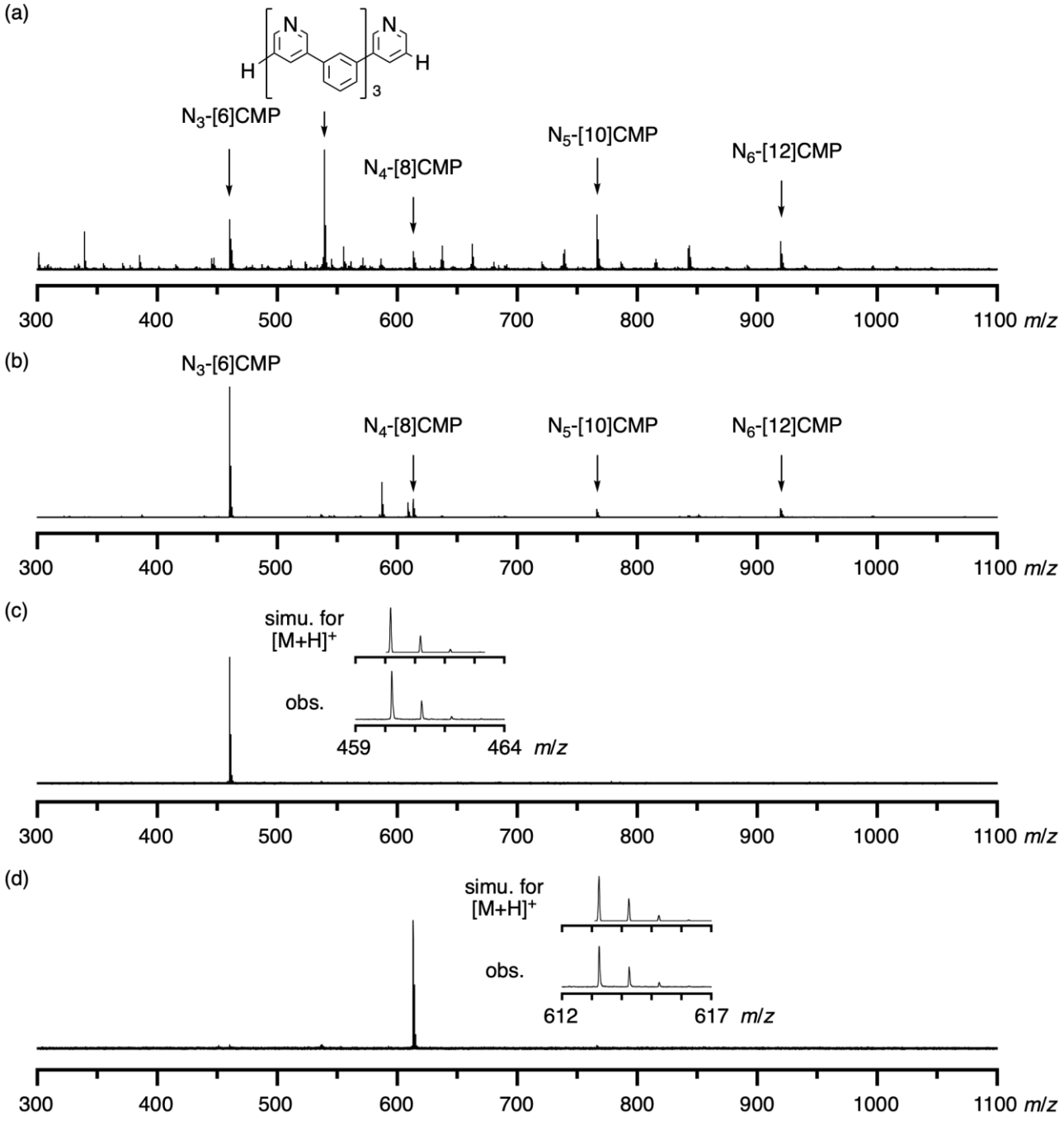

Figure S1: MALDI-TOF MS analyses (matrix: dithranol, ionization: reflector positive). Spectra of crude mixtures obtained by using (a) $Pd(PPh_3)_4$ and (b) $PdCl_2(dppf)•CH_2Cl_2$ as a catalyst. Spectra of (c) N_3-[6]CMP (**3a**) and (d) N_4-[8]CMP (**3b**) after the purification.

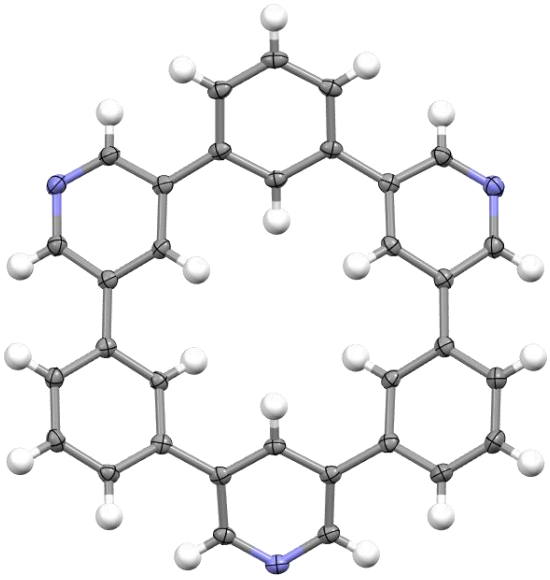

Figure S2: ORTEP diagram of a crystal structure of N_3-[6]CMP (**3a**). Thermal ellipsoids are shown at the 50% probability level.

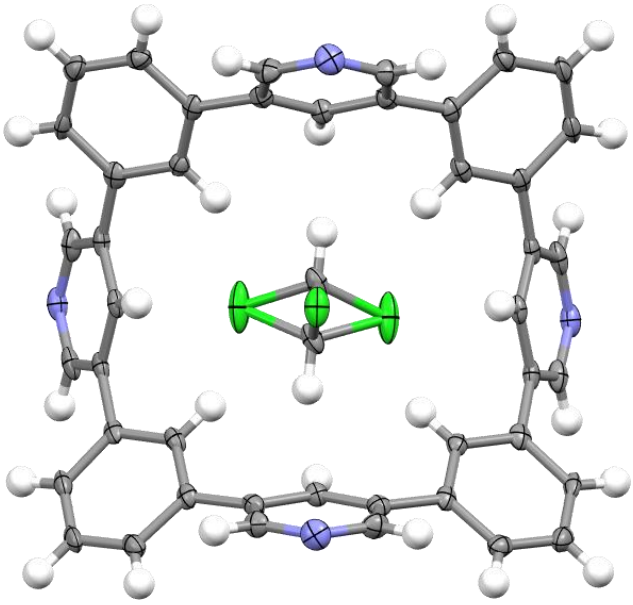

Figure S3: ORTEP diagram of a crystal structure of N_4-[8]CMP (**3b**). Thermal ellipsoids are shown at the 50% probability level.

Methods

General

Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral gel, 40–50 μm, Kanto). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL RESONANCE JNM-ECA II 600 equipped with an UltraCOOL probe. Chemical shift values are given relative to an internal tetramethylsilane. Data are reported as follows: chemical shift, multiplicity, coupling constant in Hz and the relative integration value. High-resolution mass spectra were performed on a Bruker Daltonics autoflex speed using matrix assisted laser desorption ionization (MALDI) method with dithranol as a matrix (ionization mode: reflector positive) or on a Bruker micrOTOF II spectrometer equipped with an APCI probe equipped with a DirectProbe (DIP). UV–vis spectra were recorded at 25 °C on a JASCO V670 spectrometer.

Materials

Anhydrous DMF was purified by a solvent purification system (GlassContour) equipped with columns of activated alumina and supported copper catalyst (Q-5) [1]. All other chemicals were of reagent grade and used without any further purification. Diborylbenzene **5** was prepared by the reported procedure [2].

Crystallography

Single crystals of N_3-[6]CMP (**3a**) and N_4-[8]CMP (**3b**) suitable for X-ray crystallographic analysis were obtained by slowly diffusing hexane vapor into a $CHCl_3$/MeOH (10:1) solution of **3a** and **3b** at 25 °C. A single crystal was mounted on a thin polymer tip with cryoprotectant oil and was subjected to the X-ray diffraction studies as follows. The X-ray diffraction experiment was performed on a Rigaku XtaLAB P200 diffractometer equipped with a PILATUS200K area detector using multi-layer mirror monochromated Cu Kα radiation.

IAM refinements by SHELX

The crystal structures of **3a** and **3b** were first solved by a conventional method adopting spherical, independent atom models (IAM) [3]. The initial structures were solved by the direct method with the SHELXT program [4] and refined by full-matrix least-squares on F^2 using the SHELXL program suite [5]. The non-hydrogen atoms were analyzed anisotropically, and hydrogen atoms were located at the calculated positions and refined with a riding model. The refinement data are summarized in Tables S1 and S2.

Table S1: Crystal data of N_3-[6]CMP (**3a**) with the IAM refinements by SHELX

CCDC	2335441	
Empirical formula	$C_{33}H_{21}N_3$	
Formula weight	459.53	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*–1	
Unit cell dimensions	*a* = 5.8332(12) Å	*α* = 79.684(13)°
	b = 9.0678(16) Å	*β* = 89.420(16)°
	c = 21.492(4) Å	*γ* = 83.71(2)°
Volume	1111.6(4) $Å^3$	
Z	2	
Density (calculated)	1.373 mg/m^3	
Absorption coefficient	0.630 mm^{-1}	
F(000)	480	
Crystal size	0.10 × 0.04 × 0.03 mm^3	
Theta range for data collection	2.090° to 68.218°	
Index ranges	–7<=*h*<=6, –10<=*k*<=10, –25<=*l*<=25	
Reflections collected	14564	
Independent reflections	3942 [*R*(int) = 0.0294]	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3942 / 0 / 325	
Goodness-of-fit on F^2	1.053	
Final *R* indices [*I* > 2sigma(*I*)]	R_1 = 0.0386, wR_2 = 0.1066	
R indices (all data)	R_1 = 0.0487, wR_2 = 0.1169	

Table S2. Crystal data of N_4-[8]CMP (**3b**) with the IAM refinements by SHELX

CCDC	2335442
Empirical formula	$C_{44}H_{28}N_4$•$CHCl_3$
Formula weight	732.07
Temperature	93(2) K
Wavelength	1.54184 Å

Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 23.783(15) Å	α = 90°
	b = 5.771(3) Å	β = 108.62(2)°
	c = 26.322(15) Å	γ = 90°
Volume	3424(3) Å^3	
Z	4	
Density (calculated)	1.420 mg/m^3	
Absorption coefficient	2.743 mm^{-1}	
F(000)	1512	
Crystal size	0.18 × 0.03 × 0.02 mm^3	
Theta range for data collection	3.923° to 70.629°	
Index ranges	–28<=h<=26, –7<=k<=6, –32<=l<=32	
Reflections collected	14509	
Independent reflections	3202 [R(int) = 0.0530]	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3202 / 0 / 243	
Goodness-of-fit on F^2	1.082	
Final R indices [I > 2sigma(I)]	R_1 = 0.0805, wR_2 = 0.1999	
R indices (all data)	R_1 = 0.0932, wR_2 = 0.2071	

X-ray charge density analysis by XD-2016

For elucidating the difference of the electronic properties by nitrogen doping, crystallographic data of N_3-[6]CMP (**3a**) and [6]CMP (CCDC 1015816) [6] were subjected to X-ray charge density analyses. The SHELXL-refined structures and the HKL data were transferred to the XD-2016 program [7]. The structures were first converged by the IAM refinement with the XDLSM module in XD-2016. The resultant *R* factors were as follows:

$R(F) = 0.0382$ and $Rw(F) = 0.0573$ for **3a**;

$R(F) = 0.0361$ and $Rw(F) = 0.0460$ for [6]CMP.

Then, the data were refined by the aspherical model by adopting the transferable aspherical atom model (TAAM) [8] with the parameters of the University at Buffalo Pseudoatom Databank (UBDB) [9,10]. The significant improvement of the refinement was found with the deformation map ($F_1 - F_2$) and *R* factors:

$R(F) = 0.0269$ and $Rw(F) = 0.0430$ for **3a**;

$R(F) = 0.0237$ and $Rw(F) = 0.0312$ for [6]CMP.

The refinement data of X-ray charge density analyses of **3a** and [6]CMP are summarized in Tables S3 and S4.

Table S3: Crystal data of N_3-[6]CMP (**3a**) with the TAAM/UBDB refinements by XD-2016

CCDC	2335443	
Empirical formula	$C_{33}H_{21}N_3$	
Formula weight	459.53	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*–1	
Unit cell dimensions	a = 5.8332(12) Å	α = 79.684(13)°
	b = 9.0678(16) Å	β = 89.420(16)°
	c = 21.492(4) Å	γ = 83.71(2)°
Volume	1111.6(4) Å^3	
Z	2	
Density (calculated)	1.373 mg/m^3	
Absorption coefficient	0.630 mm^{-1}	
F(000)	480	
Crystal size	0.10 × 0.04 × 0.03 mm^3	
Theta range for data collection	2.090° to 68.218°	

Index ranges	–7<=*h*<=6, –10<=*k*<=10, –25<=*l*<=25
Reflections collected	14568
Independent reflections	3945 [*R*(int) = 0.0294]
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on *F*
Data / restraints / parameters	3228 / 0 / 346
Goodness-of-fit	2.24
Final *R* indices [*I* > 2sigma(*I*)]	*R*(*F*) = 0.0269, *Rw*(*F*) = 0.0430
R indices (all data)	*R*(F^2) = 0.0391, *Rw*(F^2) = 0.1138

Table S4: Crystal data of [6]CMP with the TAAM/UBDB refinements by XD-2016

CCDC	2335444	
Empirical formula	$C_{36}H_{24}$	
Formula weight	465.55	
Temperature	90(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	*a* = 12.289(3) Å	*α* = 90°
	b = 15.382(3) Å	*β* = 99.35(3)°
	c = 6.0239(12) Å	*γ* = 90°
Volume	1123.6(4) $Å^3$	
Z	2	
Density (calculated)	1.394 mg/m^3	
Absorption coefficient	0.579 mm^{-1}	
F(000)	480	
Crystal size	0.20 × 0.05 × 0.05 mm^3	
Theta range for data collection	3.65° to 67.33°	
Index ranges	–12<=*h*<=14, –18<=*k*<=18, –7<=*l*<=7	
Reflections collected	8005	
Independent reflections	1755 [*R*(int) = 0.0371]	
Absorption correction	none	
Refinement method	Full-matrix least-squares on *F*	
Data / restraints / parameters	1755 / 0 / 175	
Goodness-of-fit	1.485	

Final *R* indices [*I* > 2sigma(*I*)]	$R(F) = 0.0237$, $Rw(F) = 0.0312$
R indices (all data)	$R(F^2) = 0.0417$, $Rw(F^2) = 0.0610$

Visualization and analyses

Molecular structures were visualized and analyzed by Mercury CSD 4.1.0 [11] and UCSF Chimera (ver. 1.13.1) [12]. The electron densities after the TAAM/XD2016 refinements were visualized by MoleCoolQt [13]. The contour map of the deformation density was obtained by the XDGRAPH module in the XD2016 package [7], and the ESP maps were generated by MolIso [14]. All the crystallographic data were deposited in the Cambridge Crystallographic Data Centre (CCDC 2335441-2335443). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spectra

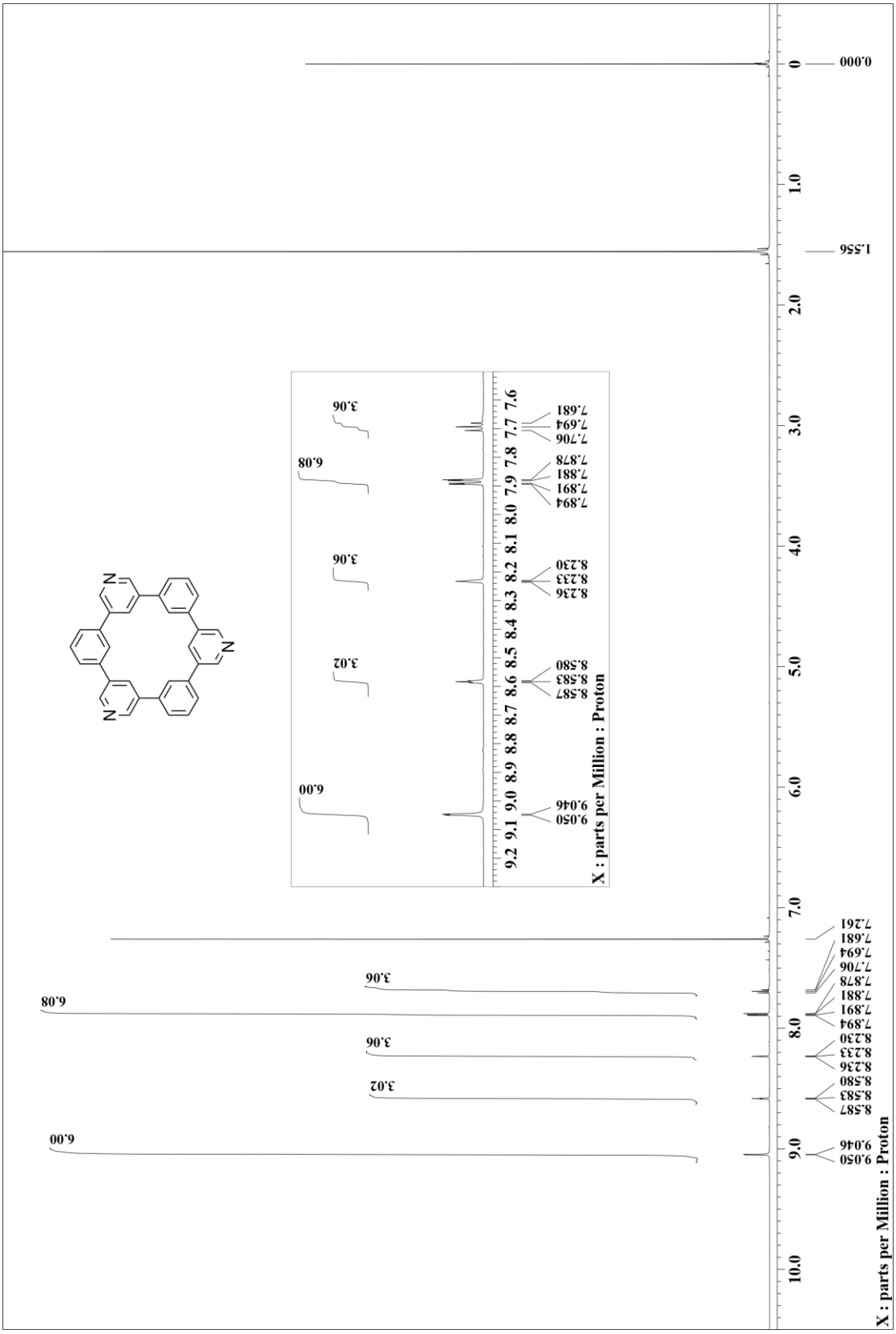

Figure S4: ^{1}H NMR spectrum of N_3-[6]CMP (**3a**) ($CDCl_3$, 25 °C, 600 MHz).

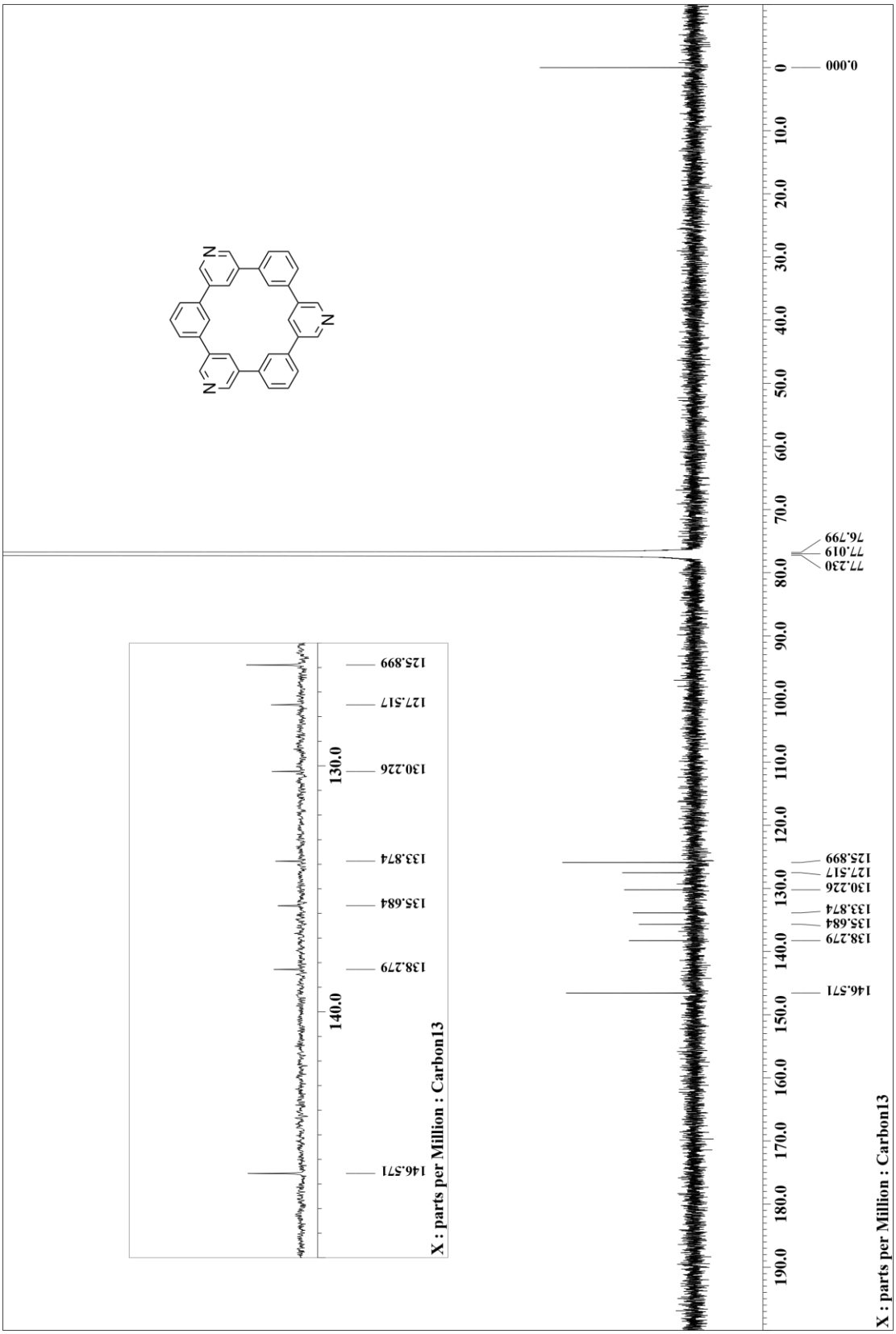

Figure S5: ^{13}C NMR spectrum of N_3-[6]CMP (**3a**) ($CDCl_3$, 25 °C, 151 MHz).

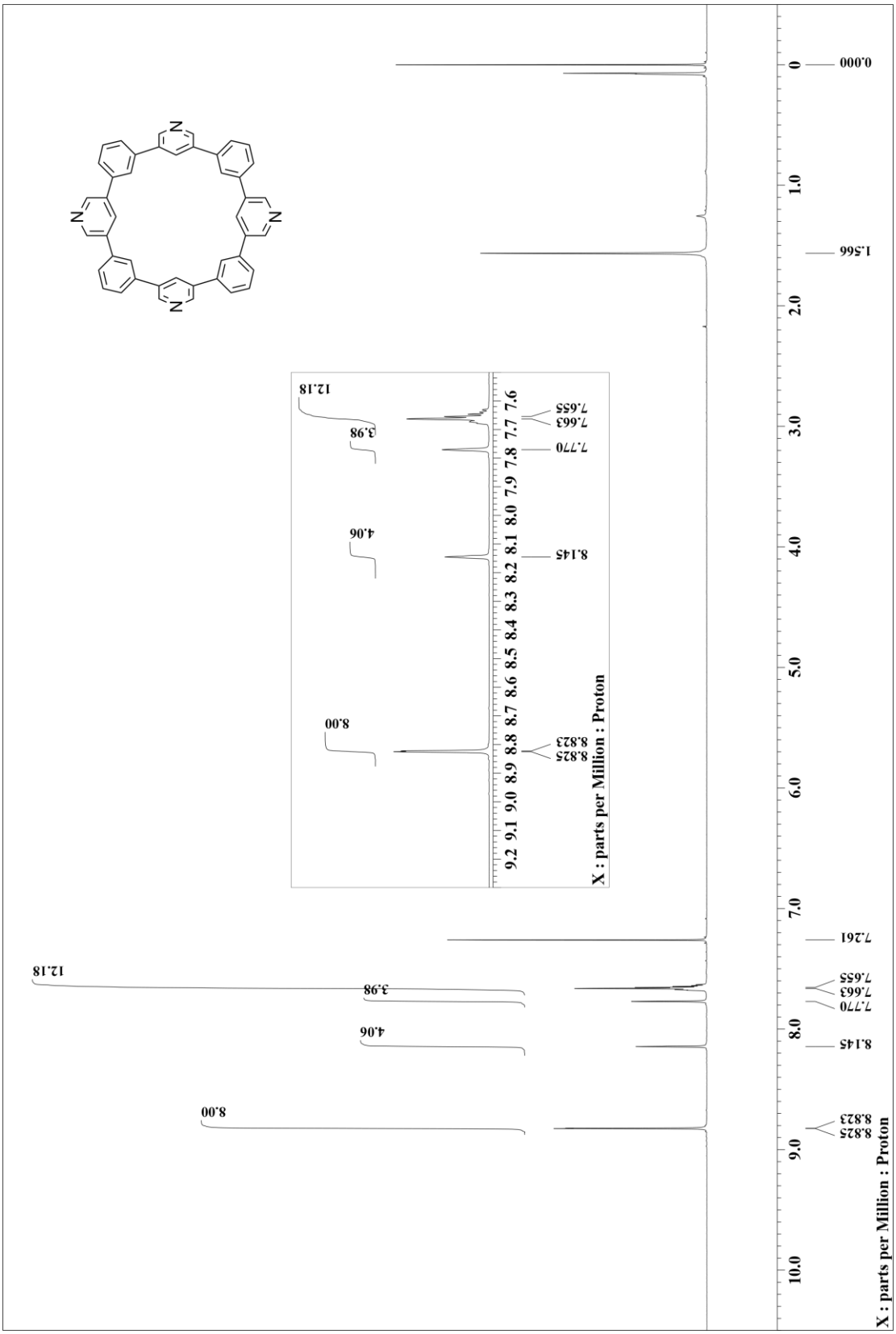

Figure S6: ^{1}H NMR spectrum of N_4-[8]CMP (**3b**) ($CDCl_3$, 25 °C, 600 MHz).

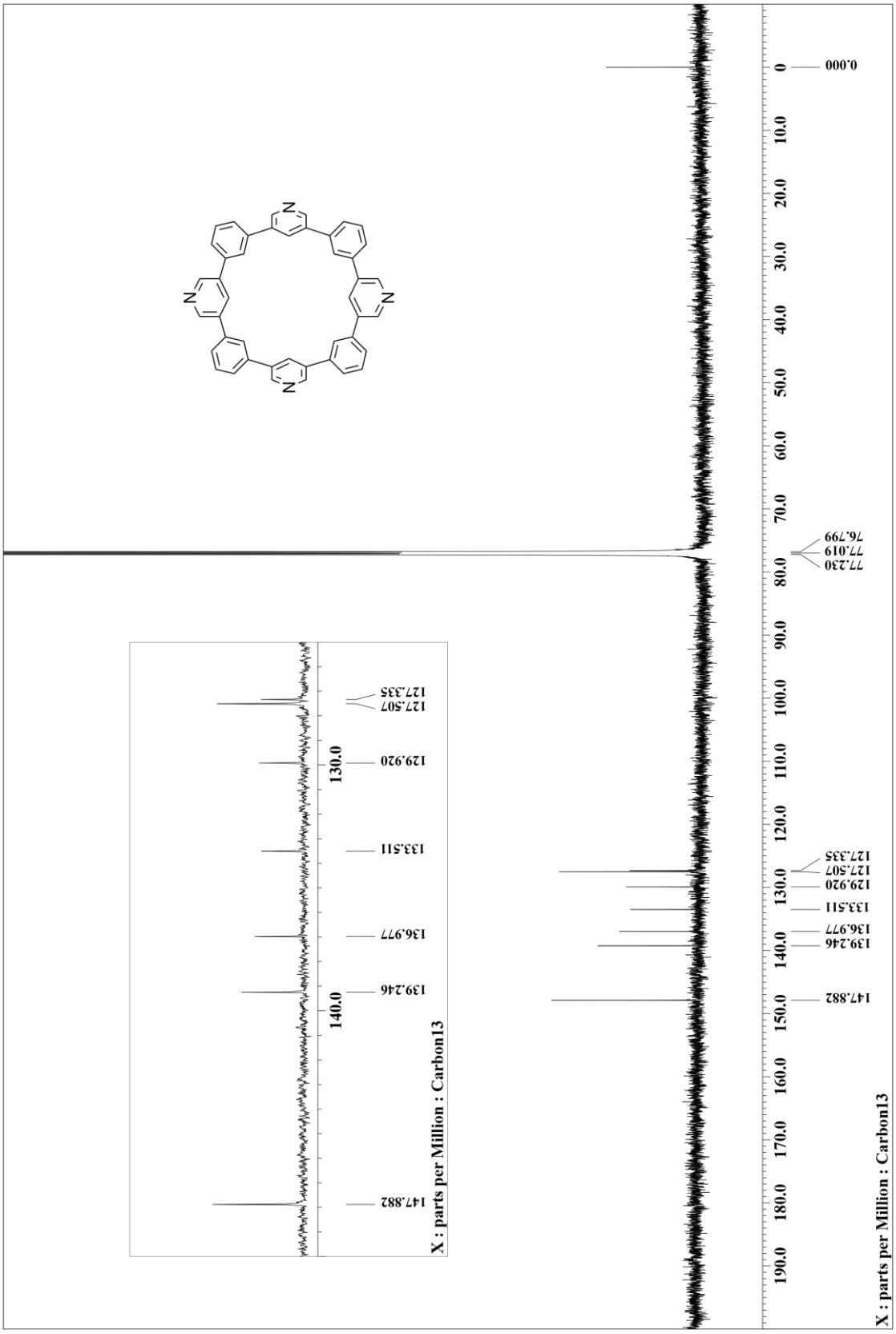

Figure S7: ^{13}C NMR spectrum of N_4-[8]CMP (**3b**) ($CDCl_3$, 25 °C, 151 MHz).

Supplementary references

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
2. Sun, Z.; Ikemoto, K.; Fukunaga, T. M.; Koretsune, T.; Arita, R.; Sato, S.; Isobe, H. *Science* **2019**, *363*, 151-155.
3. Doyle, P. A.; Turner, P. S. *Acta Crystallogr. A* **1968**, *24*, 390-397.
4. Sheldrick, G. M. *Acta Crystallogr. A* **2015**, *71*, 3-8.
5. Sheldrick, G. M. *Acta Crystallogr. C* **2015**, *71*, 3-8.
6. Xue, J. Y.; Ikemoto, K.; Takahashi, N.; Izumi, T.; Taka, H.; Kita, H.; Sato, S.; Isobe, H. *J. Org. Chem.* **2014**, *79*, 9735-9739.
7. Volkov, A.; Macchi, P.; Farrugia, L. J.; Gatti, C.; Mallinson, P.; Rihter, T.; Koritsánszky, T. *XD2016, a computer program package for multipole refinement, topological analysis of charge densities and evaluation of intermolecular energies from experimental and theoretical structure factors*; University at Buffalo; State University of New York; University of Milano; University of Glasgow; CNR-ISTM; Middle Tennessee State University, 2016.
8. Brock, C. P.; Dunitz, J. D.; Hirshfeld, F. L. *Acta Crystallogr. B* **1991**, *47*, 789-797.
9. Koritsanszky, T.; Volkov, A.; Coppens, P. *Acta Crystallogr. A* **2002**, *58*, 464-472.
10. Dominiak, P. M.; Volkov, A.; Li, X.; Messerschmidt, M.; Coppens, P. *J. Chem. Theory Comput.* **2007**, *3*, 232-247.
11. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Cryst.* **2008**, *41*, 466-470.
12. Pettersen, E. F.; Goddard, T. D.; Huang, C. C.; Couch, G. S.; Greenblatt, D. M.; Meng, E. C.; Ferrin, T. E. *J. Comput. Chem.* **2004**, *13*, 1605-1612.
13. Hübschle, C. B.; Dittrich, B. *J. Appl. Cryst.* **2011**, *44*, 238-240.
14. Hübschle, C. B.; Luger, P. *J. Appl. Cryst.* **2006**, *39*, 901-904.