Supporting Information

Synthesis and Properties of Cycloparaphenylene-2,5-pyridylidene: A Nitrogen-Containing Carbon Nanoring

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1. Experimental Section

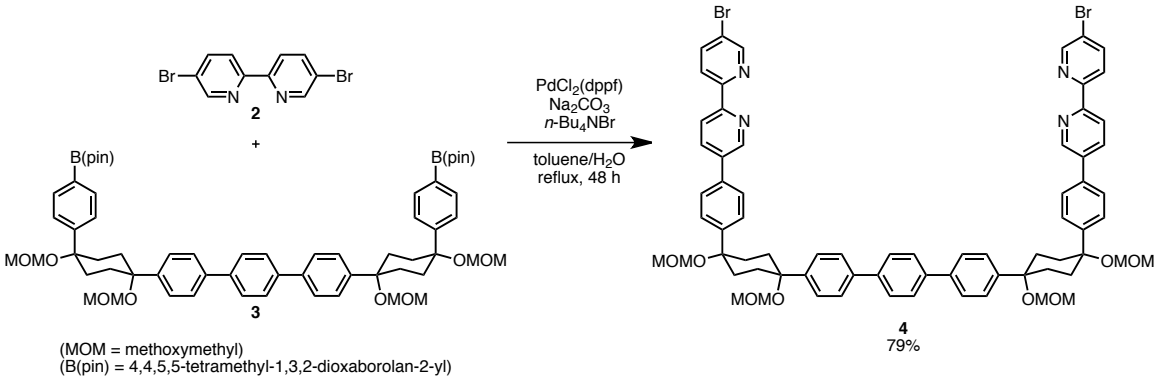
General

Unless otherwise noted, all materials including dry solvents (1,4-dioxane and dimethyl sulfoxide (DMSO)) were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF), dichloromethane, toluene, and *m*-xylene were purified by passing through a solvent purification system (Glass Contour). All reactions were performed using standard vacuum-line and Schlenk techniques. Work-up and purification procedures were carried out with reagent-grade solvents under air. L-shaped unit (**1**),[S1] 5,5'-dibromo-2,2'-bipyridine (**2**),[S2] and diborylated U-shaped unit (**3**)[S1] were synthesized following the reported procedures.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (PTLC) was performed using Wako-gel® B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. High-resolution mass spectra (HRMS) were obtained from JEOL JMS700 (fast atom bombardment mass spectrometry, FAB-MS) or Bruker Daltonics Ultraflex III TOF/TOF (MALDI-TOF-MS) with 9-nitroanthorathene as matrix. Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL A-400 (^{1}H 400 MHz, ^{13}C 100 MHz), or JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CHCl_3$ (δ 7.26 ppm), or DMSO-d_5 (δ 2.50 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm) or 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$, δ 73.8 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

S1) Omachi, H.; Matsuura, S.; Segawa, Y.; Itami, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 10202.
S2) Schwab, P. F. H.; Fleischer, F.; Michl, J. *J. Org. Chem.* **2002**, *67*, 443.

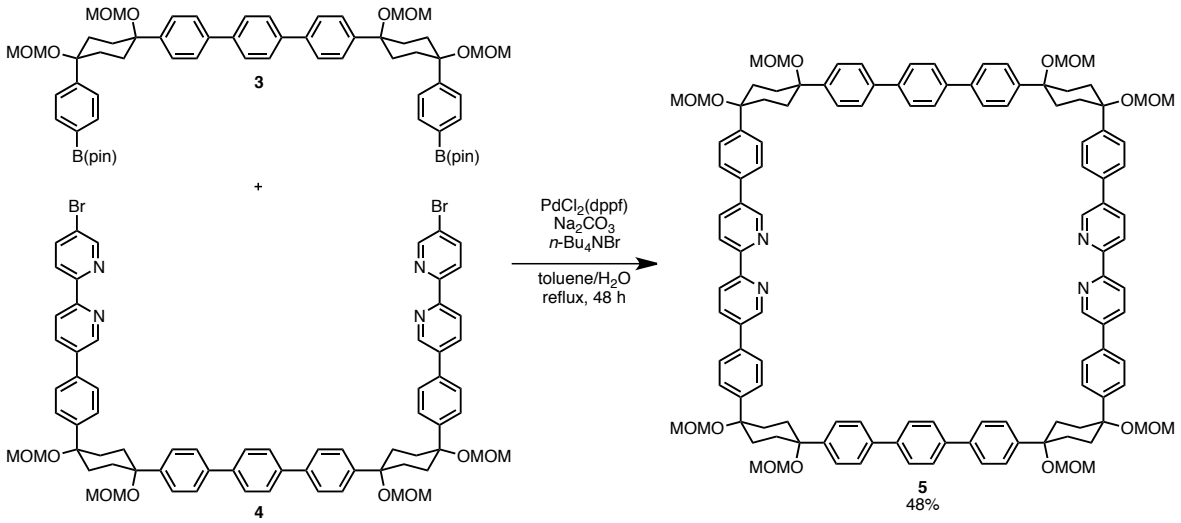
Synthesis of Bipyridine-containing U-shaped Unit 4



To a 50-mL round-bottom flask containing a magnetic stirring bar was added **3** (312 mg, 300 μmol), 5,5'-dibromo-2,2'-bipyridine **2** (942 mg, 3.00 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (7.4 mg, 9.1 μmol), Na_2CO_3 (159 mg, 1.50 mmol), and *n*-Bu_4NBr (96.9 mg, 300 μmol). The flask was purged under vacuum, and then backfilled with argon three times. After addition of dry toluene (23 mL) and degassed water (8 mL), the resulting reaction mixture was stirred and allowed to reflux over 48 h. The reaction was cooled to room temperature and then was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude material obtained was purified via silica gel chromatography ($CHCl_3$) to afforded **4** (295 mg, 79%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88–2.77 (br, 16H), 3.45 (s, 6H), 3.45 (s, 6H), 4.49 (s, 4H), 4.51 (s, 4H), 7.50–7.69 (m, 20H), 7.94 (dd, *J* = 8.6, 2.4 Hz, 2H), 7.99 (dd, *J* = 8.5, 2.4 Hz, 2H), 8.34 (dd, *J* = 8.6, 0.6 Hz, 2H), 8.43 (dd, *J* = 8.5, 0.6 Hz, 2H), 8.73 (dd, *J* = 2.4, 0.6 Hz, 2H), 8.88 (dd, *J* = 2.3, 0.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.0 (CH_2), 56.0 (CH_3), 56.0 (CH_3), 78.1 (4°), 78.1 (4°), 92.2 (CH_2), 120.9 (CH), 121.1 (4°), 122.2 (CH), 126.9 (CH), 127.0 (CH), 127.3 (CH), 127.7 (CH), 135.1 (CH), 136.1 (4°), 136.5 (4°), 139.4 (4°), 139.5 (CH), 139.7 (4°), 147.5 (CH), 150.2 (CH), 154.0 (4°), 154.3 (4°); HRMS (FAB) *m/z* calcd for $C_{70}H_{68}Br_2N_4O_8Na$ $[M+Na]^+$: 1273.3302, found 1273.3301; mp: 229.4–231.8 °C.

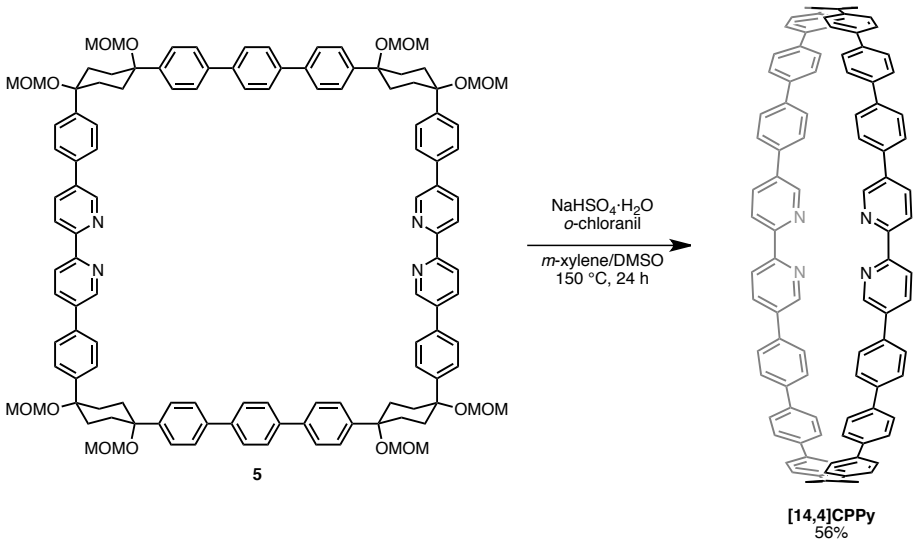
Synthesis of Macrocycle 5



To a 200-mL round-bottom flask containing a magnetic stirring bar was added **4** (125 mg, 100 μmol), **3** (125 mg, 120 μmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (2.5 mg, 3.1 μmol), Na_2CO_3 (52.6 mg, 49.6 μmol), and *n*-Bu_4NBr (32.9 mg, 102 μmol). The flask was purged under vacuum, and backfilled with argon three times. After addition of dry toluene (80 mL) and degassed water (8 mL), the resulting reaction mixture was stirred and was allowed to reflux over 48 h. The reaction was cooled to room temperature and then was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The crude material obtained was purified via GPC to afford **5** (91.1 mg, 48%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79–2.65 (br, 32H), 3.45 (s, 12H), 3.46 (s, 12H), 4.50 (s, 8H), 4.51 (s, 8H), 7.48–7.67 (m, 40H), 8.01 (dd, *J* = 8.4, 2.4 Hz, 4H), 8.48 (d, *J* = 8.4 Hz, 4H), 8.91 (d, *J* = 2.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.0 (CH_2), 56.0 (CH_3), 78.1 (4º), 92.2 (CH_2), 120.9 (CH), 126.9 (CH), 127.0 (CH), 127.3 (CH), 127.6 (CH), 135.1 (CH), 135.8 (4º), 136.7 (4º) 139.4 (4º), 139.7 (4º), 147.6 (CH) 154.7 (4º); HRMS (FAB) *m/z* calcd for $C_{120}H_{124}N_4O_{16}Na$ $[M+Na]^+$: 1899.8910, found 1899.8925; mp: 235.0–240.0 ºC (dec.).

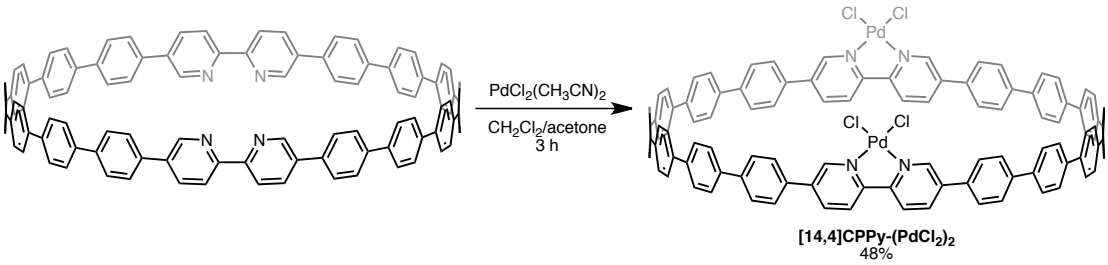
Synthesis of [14,4]CPPy



To a 20-mL Schlenk flask containing a magnetic stirring bar and a condenser were added **5** (48.5 mg, 25.8 μmol), $NaHSO_4 \cdot H_2O$ (72.2 mg, 523 μmol), *o*-chloranil (30.6 mg, 124 μmol), dry DMSO (1.2 mL), and *m*-xylene (4.0 mL). The resulting mixture was stirred at 150 °C for 24 h. After the reaction mixture was cooled to room temperature, 1 N $NaOH_{(aq)}$ was added to the reaction mixture. The mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified via PTLC ($CHCl_3$/MeOH = 20:1) to afford [14,4]CPPy (19.7 mg, 56%) as a light tan solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 56H), 8.05 (dd, J = 8.4, 1.6 Hz, 4H), 8.45 (d, J = 8.4 Hz, 4H), 8.97 (d, J = 1.6 Hz, 4H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 80 °C) δ 121.1 (CH), 127.2 (CH), 127.2 (CH), 127.5 (CH), 134.2 (CH), 134.5 (4º), 135.9 (4º), 138.6 (4º), 138.8 (4º), 138.9 (4º), 138.9 (4º), 139.1 (4º), 139.7 (4º), 147.1 (CH), 154.6 (4º); HRMS (MALDI-TOF) m/z calcd for $C_{84}H_{56}$ $[M]^+$: 1114.4543, found 1114.4539; mp: 260.0–270.0 ºC (dec.).

Synthesis of [14,4]CPPy-$(PdCl_2)_2$



To a 5-mL test-tube containing a magnetic stirring bar were added a solution of $PdCl_2(CH_3CN)_2$ (3.12 mg, 12.0 μmol) in 0.5 mL of acetone, and a solution of [14,4]CPPy (7.96 mg, 5.80 μmol) in 2 mL of CH_2Cl_2. The resulting mixture was stirred for 3 h, after which hexane was added. The solvents were removed by decantation, and the precipitate was washed with hexane. The product was dried under reduce pressure to afford **[14,4]CPPy-$(PdCl_2)_2$** (4.65 mg, 48%) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_5, 140 °C) δ 7.77–7.90 (m, 48H), 7.93 (d, J = 3.6 Hz, 8H), 8.53 (d, J = 8.8 Hz, 4H), 8.68 (d, J = 9.2 Hz, 4H), 9.42 (s, 4H). Unfortunately, it was not possible to observe the ^{13}C NMR and mass spectra of the complex.

2. Photophysical Study

UV/vis absorption spectra were recorded on a Shimadzu UV- 3510 spectrometer with a resolution of 0.5 nm. Emission spectra were measured with an F-4500 Hitachi spectrometer with a resolution of 0.2 nm. Dilute solutions in degassed spectral grade dichloromethane in a 1 cm square quartz cell were used for measurements. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system equipped with multichannel spectrometer (PMA- 11). Fluorescence lifetimes were measured with a Hamamatsu Picosecond Fluorescence Measurement System C4780 equipped with a USHO pulsed nitrogen laser (excitation wavelength 337 nm with a repetition rate of 10 Hz).

3. Computational Study

The Gaussian 03 program[S3] running on a SGI Altix4700 system was used for optimization and TD-DFT of [14,4]CPPy (B3LYP/6-31G(d)).[S4] Structure was optimized without any symmetry assumptions. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency). Visualization of the results was performed by use of GaussView 5.0.9 software.

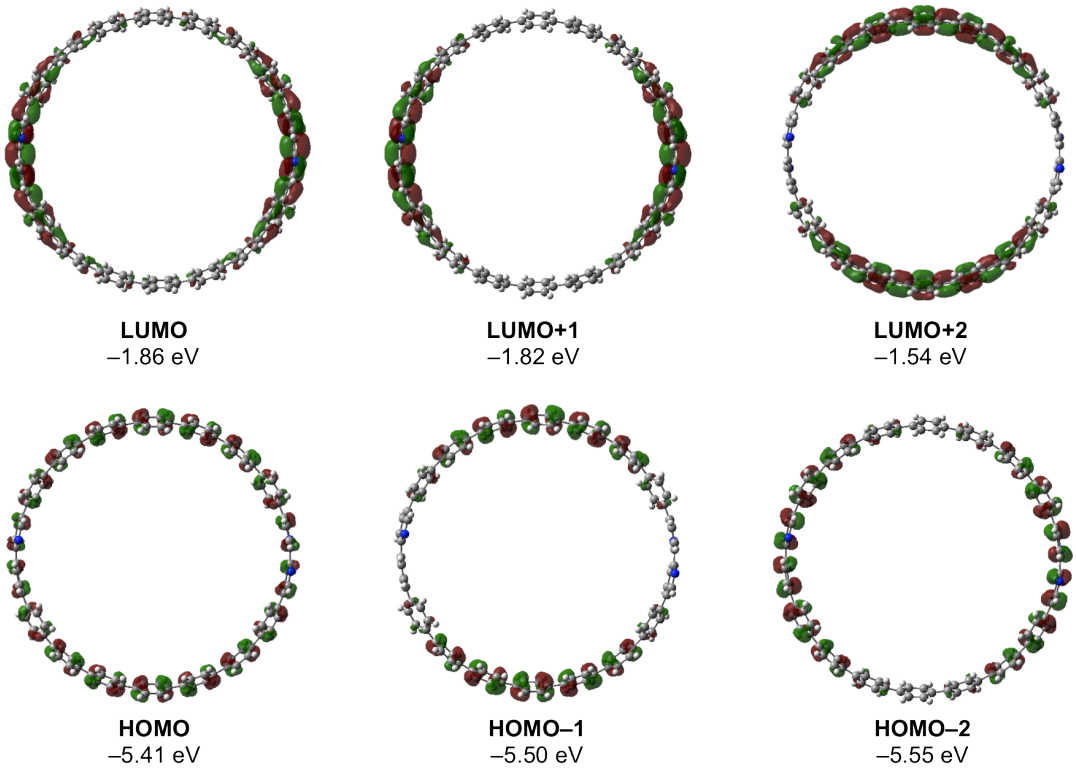


Figure S1. Frontier molecular orbitals of [14,4]CPPy.

S3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03, Revision E.01*; Gaussian, Inc.: Wallingford CT, 2004.

S4) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

Table S1. Cartesian coordinates of optimized structure of [14,4]CPPy.

C	-1.248539	2.765991	12.134775	C	0.008248	-8.406652	9.043978	H	1.988494	-12.550547	-3.370567
C	-1.256355	1.410023	12.431789	C	-1.136744	-9.143863	8.695231	H	-2.113817	-10.392985	-5.097367
C	-0.031250	0.741677	12.575679	C	1.192675	-8.677822	8.338636	H	1.932612	-11.724669	-5.678661
C	1.125809	2.714385	12.328282	C	-1.121573	-10.034922	7.627317	C	0.971961	-2.748259	-12.100264
C	-0.030530	3.456226	12.016862	H	-2.055425	-9.003610	9.258628	C	-1.402115	-2.724497	-12.310899
H	-2.185192	3.274227	11.923597	C	1.205152	-9.562857	7.265195	H	1.913115	-3.257961	-11.902343
H	-2.178221	0.842378	12.476900	H	2.094110	-8.119114	8.574530	C	-1.320220	-1.362995	-12.567597
H	2.095988	3.207817	12.354494	C	0.035912	-10.223762	6.850515	H	-2.370221	-3.217648	-12.320970
C	0.031250	-0.741677	12.575679	H	-2.028908	-10.578443	7.378813	C	-0.064345	-0.739471	-12.524700
C	1.256355	-1.410023	12.431789	H	2.116492	-9.672671	6.684605	H	-2.204839	-0.764978	-12.752008
C	-1.125809	-2.714385	12.328282	C	0.000649	-10.950852	5.557898	C	0.064345	0.739471	-12.524700
C	1.248539	-2.765991	12.134775	C	1.128057	-11.601850	5.025822	C	1.320220	1.362995	-12.567597
H	2.178221	-0.842378	12.476900	C	-1.144852	-10.880674	4.746283	C	-0.971961	2.748259	-12.100264
C	0.030530	-3.456226	12.016862	C	1.138825	-12.073640	3.715980	C	1.402115	2.724497	-12.310899
H	-2.095988	-3.207817	12.354494	H	2.014913	-11.728118	5.640963	H	2.204839	0.764978	-12.752008
H	2.185192	-3.274227	11.923597	C	-1.135625	-11.355145	3.440126	C	0.241651	3.455684	-12.004579
C	0.044068	4.824829	11.458289	H	-2.029316	-10.367985	5.112425	H	-1.913115	3.257961	-11.902343
C	1.146511	5.202183	10.670795	C	0.021074	-11.920847	2.876968	H	2.370221	3.217648	-12.320970
C	-1.017639	5.741859	11.563728	H	2.033819	-12.557059	3.333426	C	0.284310	4.830464	-11.455882
C	1.152825	6.397929	9.963256	H	-2.012943	-11.203652	2.818040	C	-0.791319	5.729404	-11.575720
H	1.976167	4.514055	10.541431	C	0.074201	-12.187210	1.418900	C	1.373081	5.229564	-10.660705
C	-1.016473	6.933713	10.844320	C	1.227975	-11.871386	0.681292	C	-0.816002	6.923819	-10.860486
H	-1.863879	5.514988	12.206434	C	-1.057967	-12.608333	0.699005	H	-1.627253	5.486929	-12.225799
C	0.052101	7.270819	9.995480	C	1.217515	-11.872636	-0.709898	C	1.353131	6.426863	-9.956478
H	1.987751	6.617001	9.304077	H	2.118494	-11.531108	1.202173	H	2.213663	4.555996	-10.523282
H	-1.863013	7.609435	10.933485	C	-1.068207	-12.610143	-0.691976	C	0.238245	7.281190	-10.002204
C	-0.044068	-4.824829	11.458289	H	-1.948873	-12.920624	1.237134	H	-1.672244	7.585541	-10.961094
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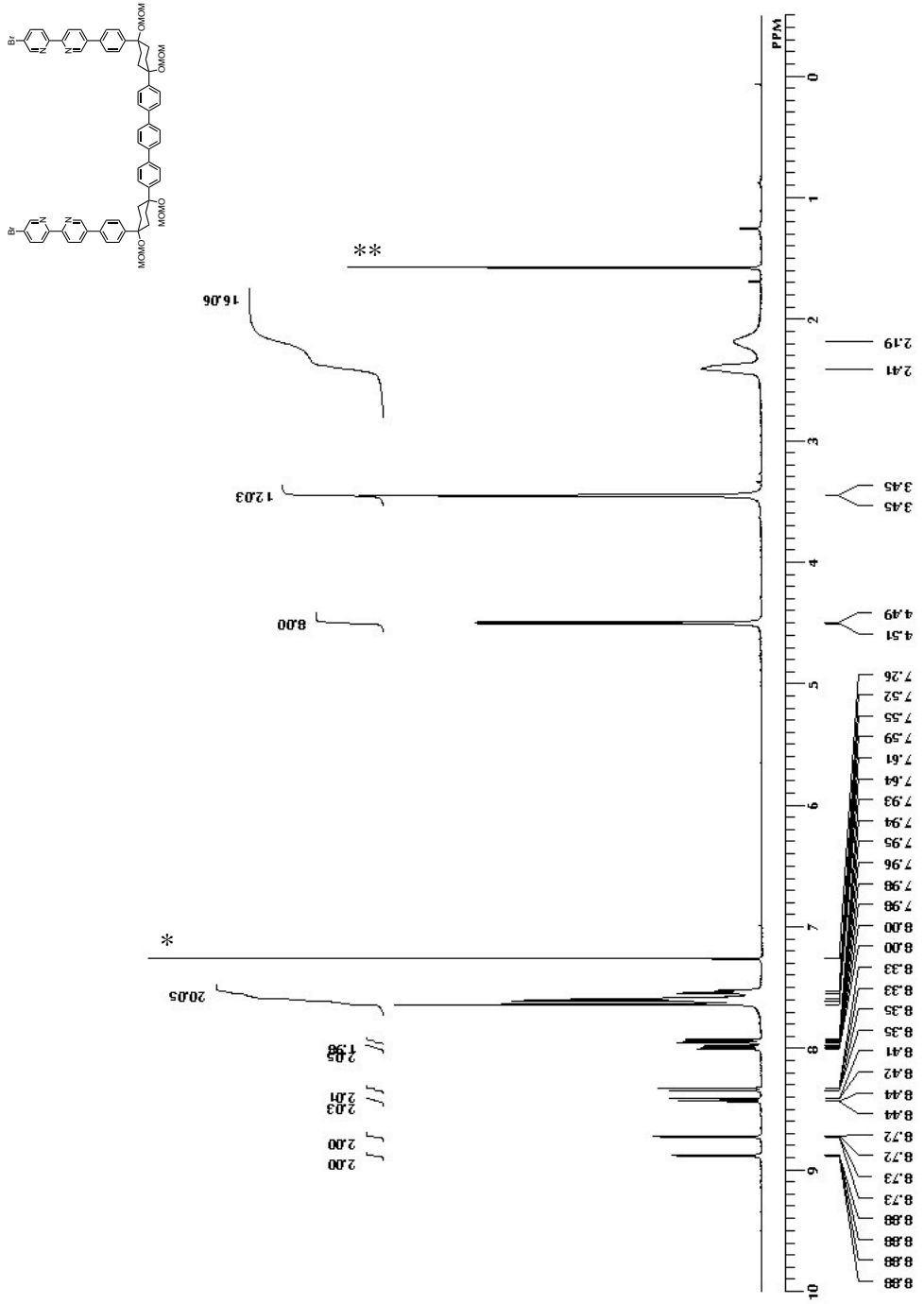
C	-1.146511	-5.202183	10.670795	H	2.100068	-11.533044	-1.244563	C	0.150726	8.418671	-9.054704
C	1.016473	-6.933713	10.844320	H	-1.966878	-12.924117	-1.215993	C	1.281720	9.171581	-8.693841
H	1.863879	-5.514988	12.206434	C	-0.022099	-11.927199	-2.887358	C	-1.045383	8.675274	-8.363776
C	-1.152825	-6.397929	9.963256	C	-1.190263	-11.370365	-3.435533	C	1.242827	10.062620	-7.626563
H	-1.976167	-4.514055	10.541431	C	1.085013	-12.073918	-3.741506	H	2.208511	9.043154	-9.246663
C	-0.052101	-7.270819	9.995480	C	-1.220842	-10.898741	-4.742351	C	-1.081769	9.560937	-7.291308
H	1.863013	-7.609435	10.933485	H	-2.059888	-11.223310	-2.801714	H	-1.936664	8.104676	-8.609531
H	-1.987751	-6.617001	9.304077	C	1.053216	-11.604111	-5.051746	C	0.074201	10.236336	-6.863102

H	2.140035	10.617964	-7.367663	C	1.135625	11.355145	3.440126	C	-1.373081	-5.229564	-10.660705
H	-2.001138	9.659626	-6.721448	C	-1.138825	12.073640	3.715980	C	0.816002	-6.923819	-10.860486
C	0.086019	10.962257	-5.569423	C	1.144852	10.880674	4.746283	H	1.627253	-5.486929	-12.225799
C	-1.053216	11.604111	-5.051746	H	2.012943	11.203652	2.818040	C	-1.353131	-6.426863	-9.956478
C	1.220842	10.898741	-4.742351	C	-1.128057	11.601850	5.025822	H	-2.213663	-4.555996	-10.523282
C	-1.085013	12.073918	-3.741506	H	-2.033819	12.557059	3.333426	C	-0.238245	-7.281190	-10.002204
H	-1.932612	11.724669	-5.678661	C	-0.000649	10.950852	5.557898	H	1.672244	-7.585541	-10.961094
C	1.190263	11.370365	-3.435533	H	2.029316	10.367985	5.112425	H	-2.178320	-6.662301	-9.290716
H	2.113817	10.392985	-5.097367	H	-2.014913	11.728118	5.640963	C	-0.074201	-10.236336	-6.863102
C	0.022099	11.927199	-2.887358	C	-0.035912	10.223762	6.850515	C	-1.242827	-10.062620	-7.626563
H	-1.988494	12.550547	-3.370567	C	1.121573	10.034922	7.627317	C	1.081769	-9.560937	-7.291308
H	2.059888	11.223310	-2.801714	C	-1.205152	9.562857	7.265195	C	-1.281720	-9.171581	-8.693841
C	-0.053000	12.190269	-1.429628	C	1.136744	9.143863	8.695231	H	-2.140035	-10.617964	-7.367663
C	1.068207	12.610143	-0.691976	H	2.028908	10.578443	7.378813	C	1.045383	-8.675274	-8.363776
C	-1.217515	11.872636	-0.709898	C	-1.192675	8.677822	8.338636	H	2.001138	-9.659626	-6.721448
C	1.057967	12.608333	0.699005	H	-2.116492	9.672671	6.684605	C	-0.150726	-8.418671	-9.054704
H	1.966878	12.924117	-1.215993	C	-0.008248	8.406652	9.043978	H	-2.208511	-9.043154	-9.246663
C	-1.227975	11.871386	0.681292	H	2.055425	9.003610	9.258628	H	1.936664	-8.104676	-8.609531
H	-2.100068	11.533044	-1.244563	H	-2.094110	8.119114	8.574530	N	1.138824	1.407206	12.576766
C	-0.074201	12.187210	1.418900	C	-0.241651	-3.455684	-12.004579	N	-1.138824	-1.407206	12.576766
H	1.948873	12.920624	1.237134	C	-0.086019	-10.962257	-5.569423	N	-1.069017	1.444415	-12.350456
H	-2.118494	11.531108	1.202173	C	-0.284310	-4.830464	-11.455882	N	1.069017	-1.444415	-12.350456
C	-0.021074	11.920847	2.876968	C	0.791319	-5.729404	-11.575720				

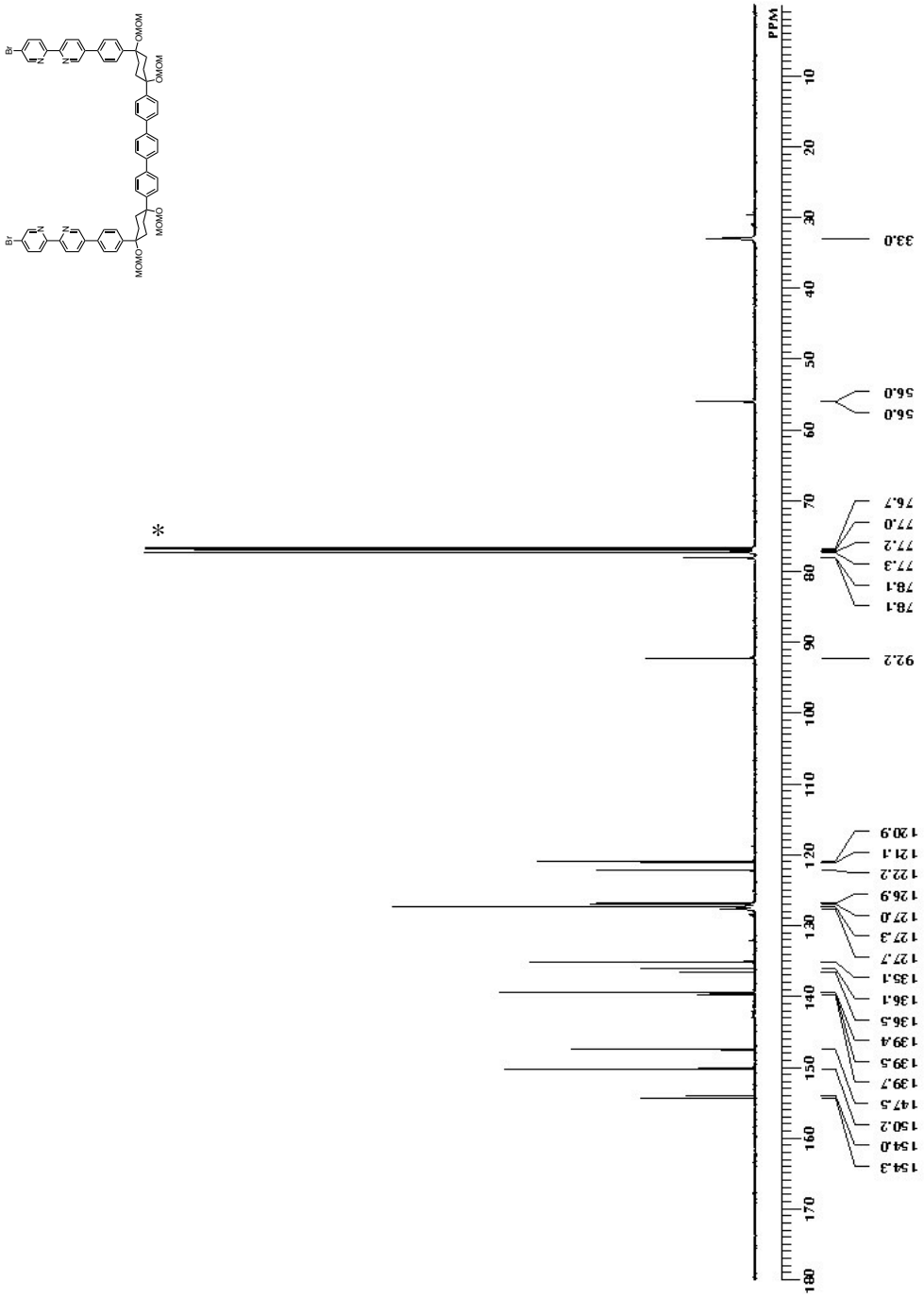
4. Spectra of New Products

^{1}H NMR spectrum of **4** ($CDCl_3$)



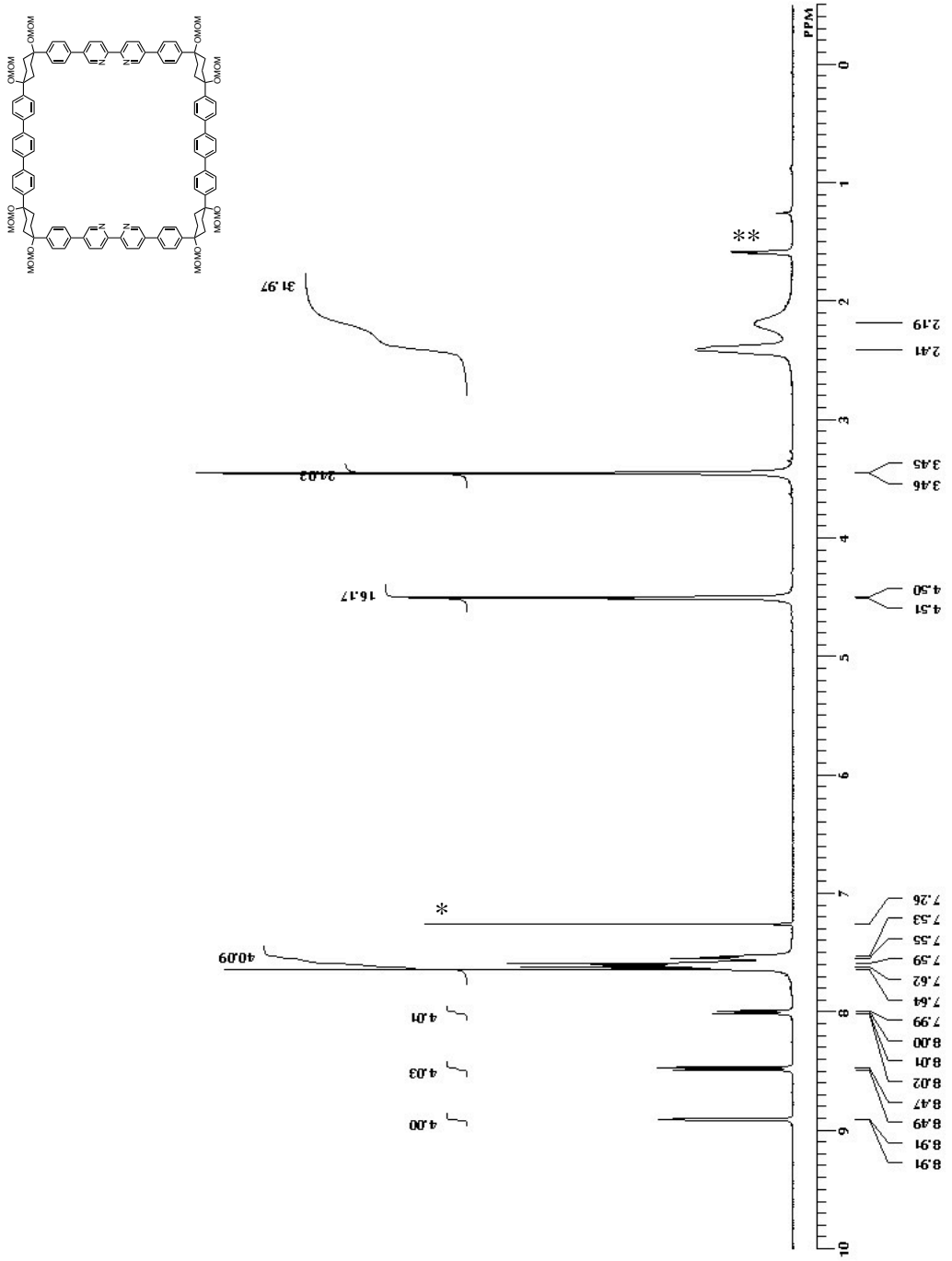
*: $CHCl_3$ **: H_2O

^{13}C NMR spectrum of **4** ($CDCl_3$)



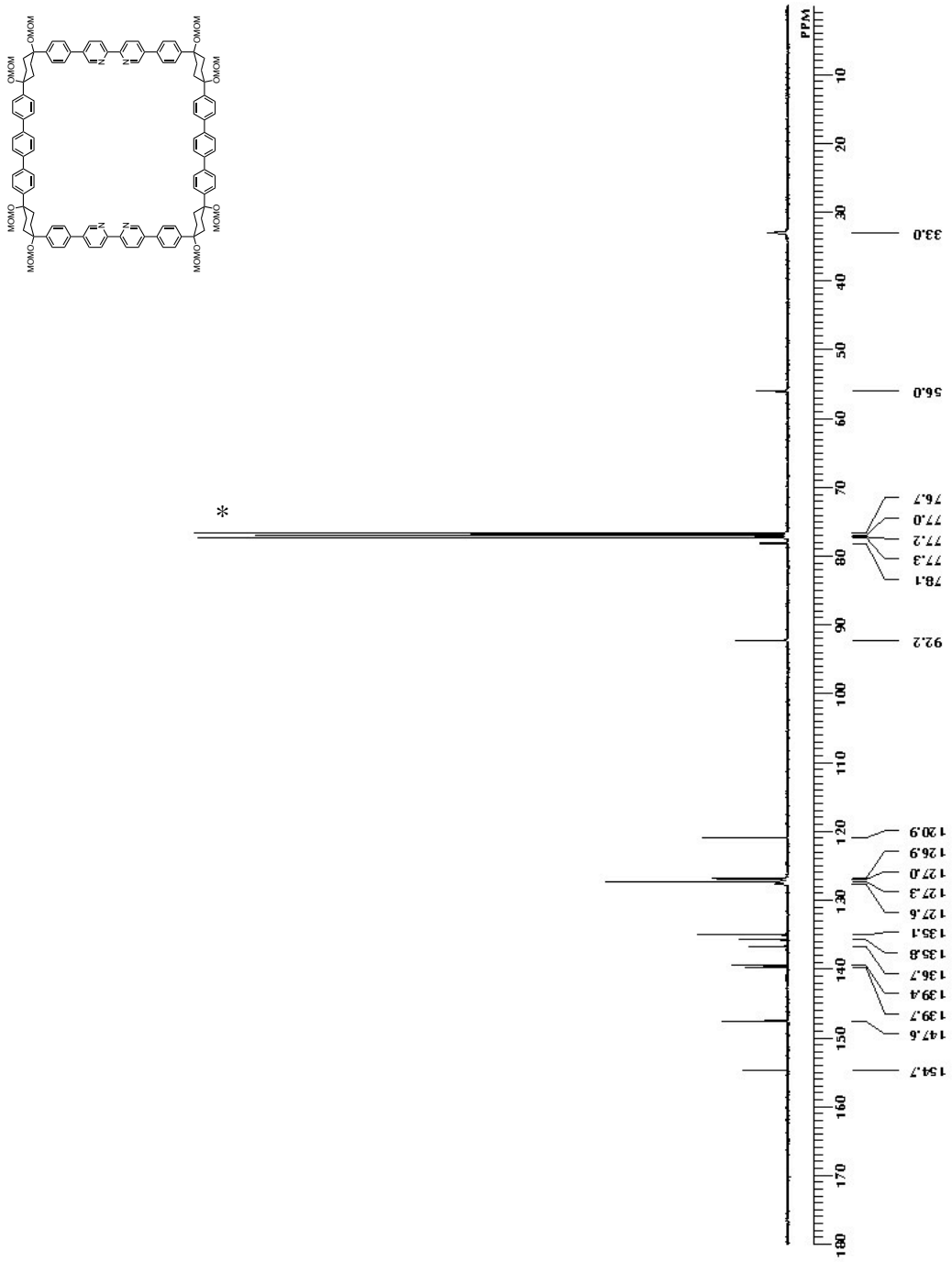
*: $CDCl_3$

^{1}H NMR spectrum of **5** ($CDCl_3$)



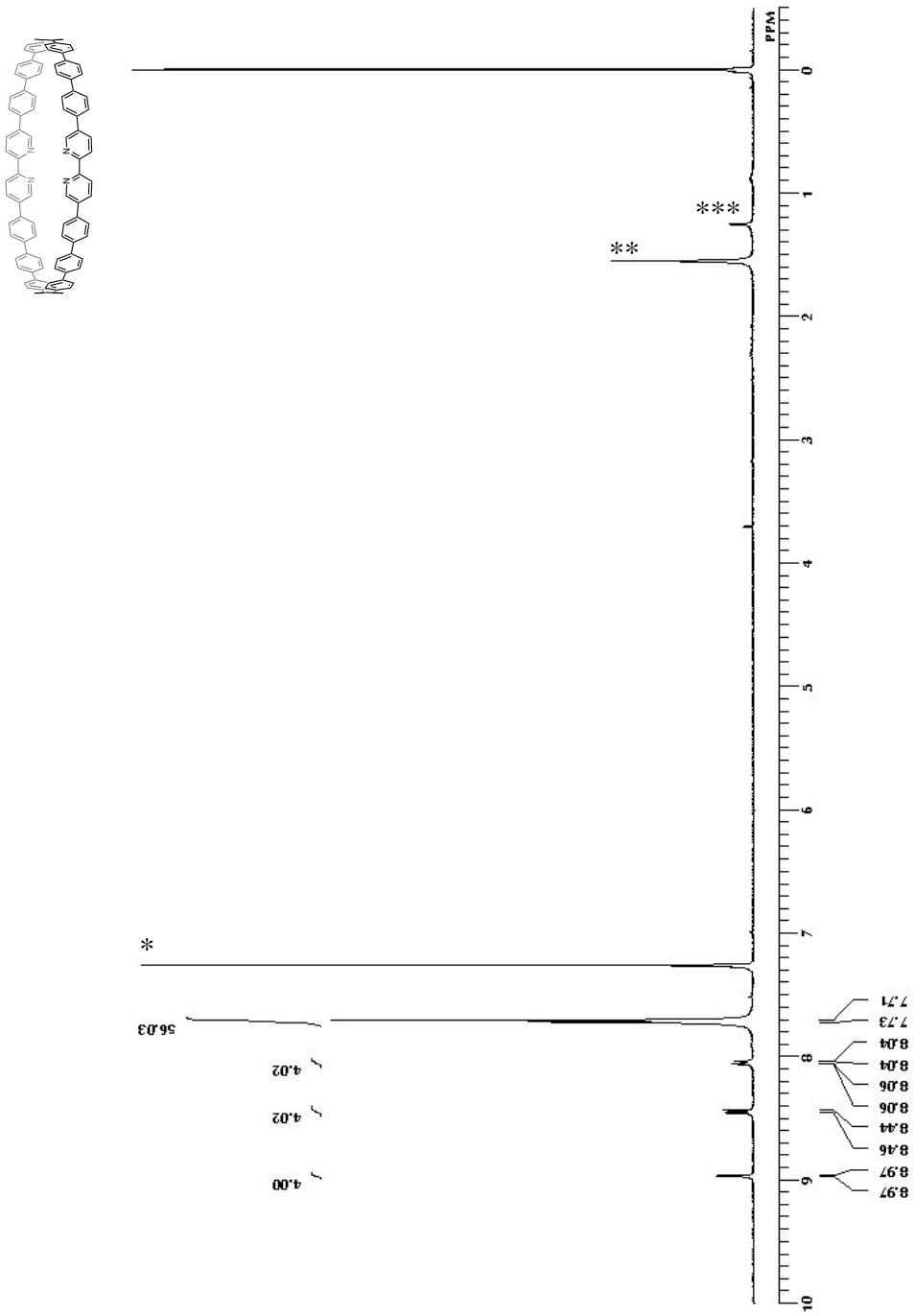
*: $CHCl_3$ **: H_2O

^{13}C NMR spectrum of **5** ($CDCl_3$)



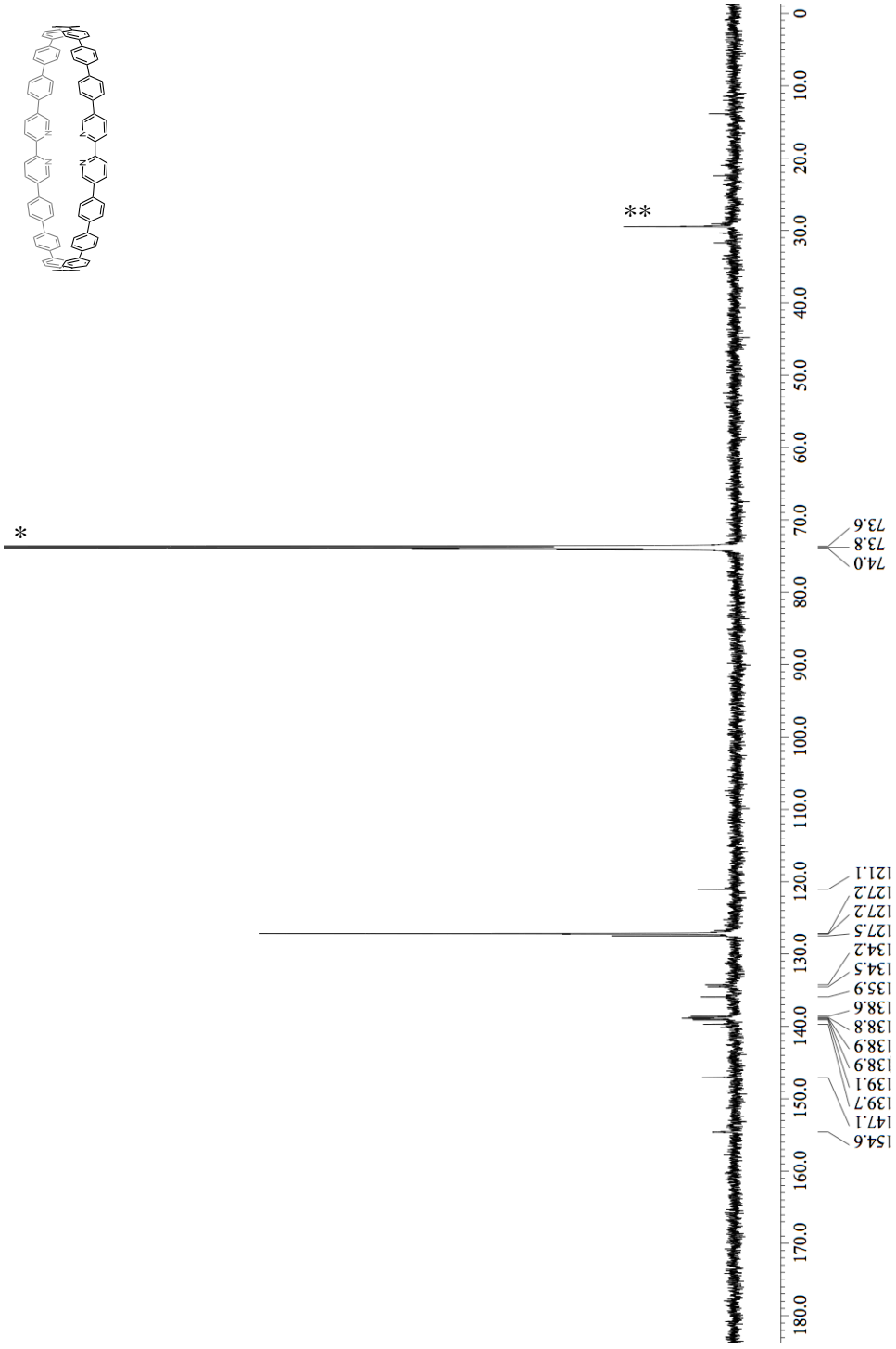
*: $CDCl_3$

^{1}H NMR spectrum of **[14,4]CPPy** ($CDCl_3$)



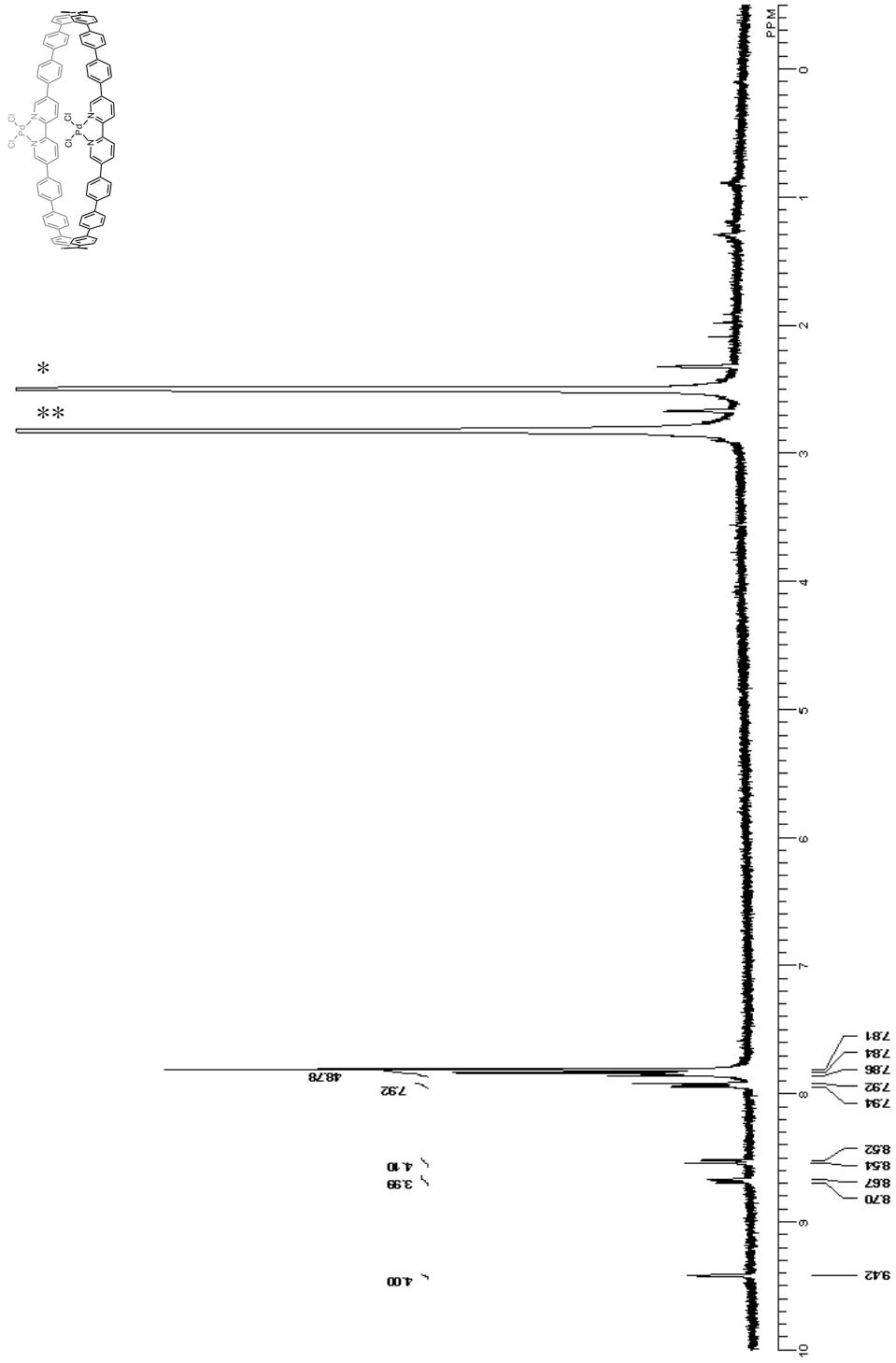
*: $CHCl_3$ **: H_2O ***: grease

^{13}C NMR spectrum of **[14,4]CPPy** ($C_2D_2Cl_4$, 80 °C)



*: $C_2D_2Cl_4$ **: grease

^{1}H NMR spectrum of **[14,4]CPPy-(PdCl)$_2$** (DMSO-d_5, 140 °C)



*: DMSO **: H_2O

^{1}H NMR spectra of [14,4]CPPy and its complexation with $PdCl_2(CH_3CN)_2$ (DMSO-d_5, 140 °C)