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First Synthesis of Dodeca-substituted Porphycenes

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Dedication ((optional))

Abstract: Synthesis of dodeca-substituted porphycenes has never been reported so far. In this paper, the preparation of tetramethyl-octaethylporphycene by McMurry-type coupling of 3,3',4,4'-ethyl-5,5'-formyl-2,2'-bipyrrole was attempted at first, but dodeca-substituted porphycene was not successfully obtained and only pyrrolocyclophene was obtained. The structure of the pyrrolocyclophene was decided by ^{1}H-NMR and TOF-MS spectra, and X-ray crystal structure analysis. The pyrrolocyclophene was not successfully oxidized to porphycene. Then the McMurry-type coupling of bicyclo[2.2.2]octadiene(BCOD)-fused 5,5'-diacyl-2,2'-bipyrroles was performed and tetra-*meso*-octa-β-substituted (dodeca-substituted) porphycenes were successfully obtained for the first time. The structures were decided by ^{1}H-NMR spectra and X-ray crystal structure. Their crystal structures and NMR spectra were compared carefully with octa-substituted porphycenes, and there was a good correlation between the position of the substituents, the N1-N2 and N1-N4 distances of the porphycene inner nitrogen atoms, and NMR chemical shifts of the inner NH protons which expressed the strength of N-H···N hydrogen bonding between N1 and N2. These results suggested that BCOD structure is relatively compact compared to common alkyl groups and that's why the dodeca-substituted porphycenes were available this time. UV-vis absorption and fluorescence properties are also discussed.

Keywords: Porphycene • McMurry coupling • crystal structure • retro-Diels-Alder reaction

Introduction

Dodeca-substituted porphyrins occupy an important position in porphyrin chemistry, since they are forced to take severely distorted conformations and hence have unique properties and reactivities.[1,2] Tetra-*meso*-aryl-tetrabenzoporphyrins have also been reported by us and others as soluble π-expanded porphyrins.[3] Forrest, Thompson and co-workers have reported organic solar cells using platinum tetraphenylbenzoporphyrins as donors with 1.9% solar-to-electronic energy conversion efficiency.[4]

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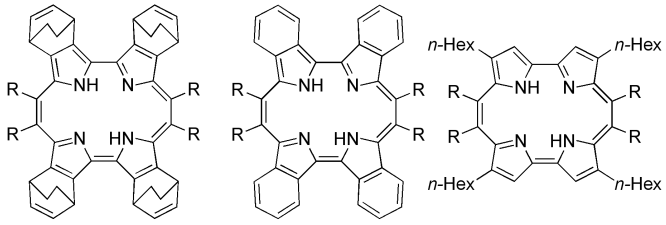


1a: R = Et **2a**: R = Et **3a**: R = Et
1b: Me **2b**: Me **3b**: Me
1c: H **2c**: H **3c**: H

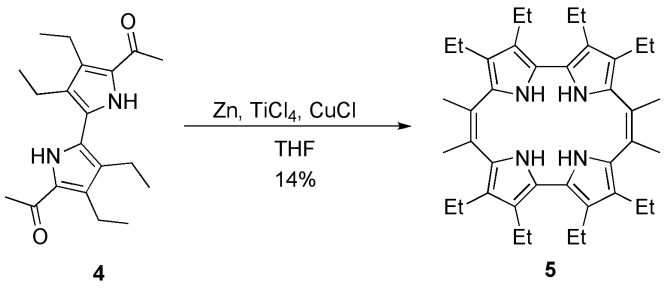
Porphycene, a constitutional isomer of porphyrin defined as [18]porphyrin(2.0.2.0), was first prepared by Vögel *et al.* in 1986[5] and has been extensively studied due to versatile possibilities in PDT-dye, catalyst, protein mimicry, and so on.[6] However dodeca-substituted porphycenes have never been reported so far, despite a keen interest to see the influences that such substitution will cause. Tuning of the electronic properties of porphycenes has been only attempted by introducing β-substituents,[7] *meso*-substituents,[8] p-expansion,[9,10] and core-modification.[11] This is mainly due to difficulty to introduce substituents both at *b* and *meso*-position of porphycene.[12] Here we report the first synthesis of dodeca-substituted porphycenes **1** by taking advantage of unique features of

bicyclo[2.2.2]octadiene(BCOD)-fused 2,2'-bipyrroles. Porphycenes **1** are converted, by retro-Diels-Alder reaction,[3c,13] to *meso*-substituted tetrabenzoporphycenes **2** that have expanded π-electronic network with absorption tails over 800 nm.

Results and Discussion

First we examined McMurry coupling of bipyrrole **4** (Scheme 1). After **4** was subjected to the typical McMurry coupling conditions, a colorless solid was obtained through column chromatography, which has been identified as pyrrolocyclophene **5** by ^{1}H-NMR and FAB-MS spectra (Figure 1 and S1), UV-bis absorption spectra (Figure 2), and single crystal X-ray diffraction analysis (Figure 3).[14] All pyrrole nitrogen atoms are amine-type and the N-H protons resonated at 6.46 ppm as 4H (Figure 1b), although the peaks of N-H protons of octaethylporphycene **6**[15] are shown in 0.65 ppm (Figure 1a; see Table 1 for the structure of porphycene **6**). For **5**, the methylene protons of peripheral ethyl groups are unsymmetrical and observed around 2.3-2.6 ppm. For **6**, those peaks are observed as two quartet peaks at 3.9 and 4.0 ppm. Thus non-aromatic character was elucidated by ^{1}H-NMR spectra.

UV-vis absorption spectra of **5** and **6** are shown in Figure 2. The spectra of **6** shows typical porphycene compound with Soret peaks at 384 nm and braod Q band at 550-700 nm. The spectum of **5** shows no peaks in visible region over 400 nm, which is in harmony with its macrocyclic 20π electronic system (Figure 2).



4 **5**

Scheme 1. Synthesis of pyrrolocyclophene **5**.

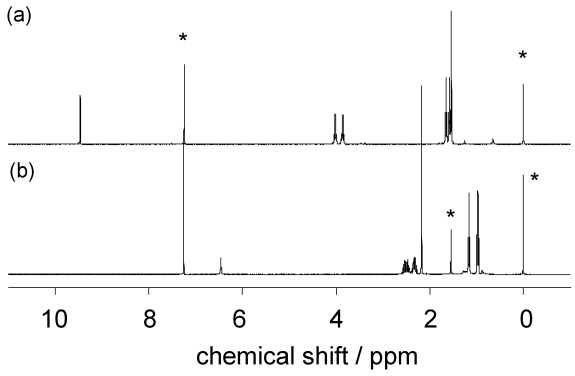


Figure 1. NMR Spectra of (a) **6** and (b) **5** in $CDCl_3$. See table 1 for the structure of **6**. *:$CHCl_3$, H_2O and TMS peaks.

The crystal structure of compound **5** is shown in Figure 2. There were two crystallographyically independent molecules in an asymmetric unit cell of **5**, where mutual angles between neighbouring pyrrole rings are different; 52.6˚ to 60.4˚ for directly connected pyrroles and 38.6˚ to 44.7˚ for the ethylene-linked pyrroles. The similar twisted structure was reported by Vögel and

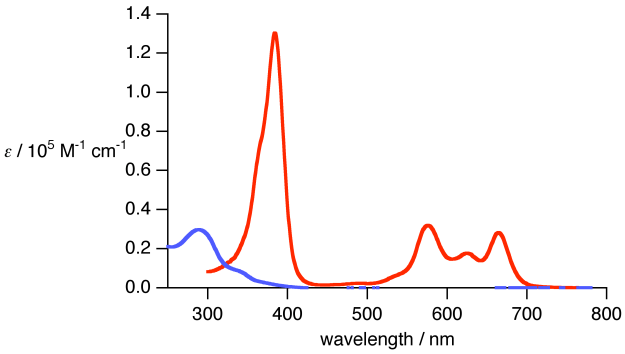


Figure 2. UV-vis absorption spectra of **5** (blue line) and **6** (red line) in CH_2Cl_2.

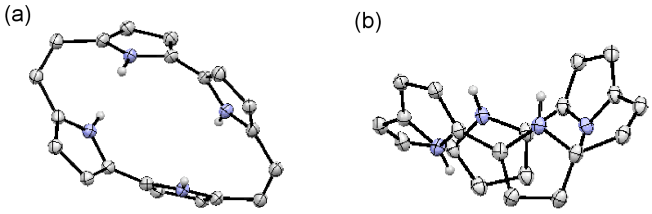


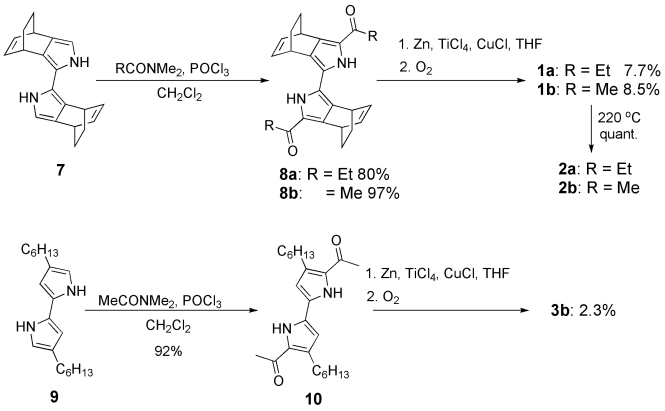
Figure 3. X-ray crystal structures of **5**. Two crystallographically independent molecules exist in the unit cell. One of the molecules is shown here. (a) top view and (b) side view. Peripheral ethyl groups and hydrogen atoms except for the inner hydrogen are omitted for clarity.

co-workers in 1989 as N,N'-dihydro-9,10,19,20-tetrapropylporphycene obtained by the reduction of 9,10,19,20-tetrapropylporphycene.[16] Hayashi and co-workers have also prepared tetraethyl-tetratrifluoromethyl-dihydroporphycene.[7f] These dihydroporphycenes were converted to porphycene by re-oxidation with air or DDQ. We have also tried to oxidize **5** in the similar conditions to get porphycene, but the dodeca-substituted porphycene was not obtained, probably because the repulsion between alkyl substituents is too severe to stabilize a planar conformation of porphycene macrocycle.

Next we examined McMurry coupling of bipyrrole **8a** and **8b** (Scheme 2). Bipyrrole **7**[10] was doubly acylated by Vilsmeyer-type acylation to give **8a** and **8b** in 80 and 97%, respectively. The obtained **8a** and **8b** were served to McMurry-type coupling to give dodeca-substituted porphycenes **1a** and **1b** in 7.7 and 8.5%, respectively. The BCOD moiety is relatively small compared to the common alkyl groups and dodeca-substitution is possible for **1a** and **1b**. From thermogravimetric analysis of **1a** and **1b** (Figure S2), retro-Diels-Alder reaction started around 150 ˚C and ended at 200 ˚C. The weight losses of **1a** and **1b** were 17.8% and 17.2 %, respectively, and were coincident with the calculated values, 16.5 % and 15.3 %, respectively. The porphycenes **1a** and **1b** were quantitatively converted to tetraalkyl-tetrabenzoporphycenes **2a** and **2b**, respectively, at 220 ˚C under vacuum. Tetrahexyl-tetramethylporphycene **3b** as the reference compound was also

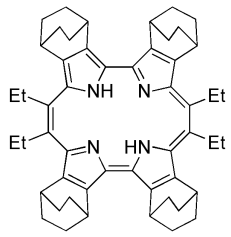
prepared from bipyrrole **7**[10] in two steps, but tetrahexyl-tetraethylporphycene **3a** was not successful to be prepared.

The ^{1}H-NMR spectra of porphycenes **1a** and **1c** are shown in Figure 4b and 4a, respectively. The meso-protons at 9.77 ppm of **1c** disappeared for **1a** and ethyl-proton peaks are appeared at at 4.4 and 1.8 ppm. The NH proton of **1c** appeared at 0.8 ppm. The peak of NH proton in **1a** was drastically changed and was observed at 5.5 ppm



Scheme 2. Synthesis of dodeca-substituted porphycenes **1** and **2**, and reference porphycene **3b**.

with those of bridgehead. To make sure the structure of dodecaalkyl-substituted porphycene, bicyclo[2.2.2] octene-fused porphycene **11**, where the double bonds of BCOD moieties were reduced, was prepared (See experimental section for the synthetic detail of **11**.). The ^{1}H-NMR spectrum of **11** is also shown in Figure 4c. NH inner proton was observed at 5.6 ppm and ethyl peaks were clearly observed at 4.4 and 1.8 ppm. For porphycene **3b**, NH proton was observed at 6.99 ppm, which was in a further lower field.



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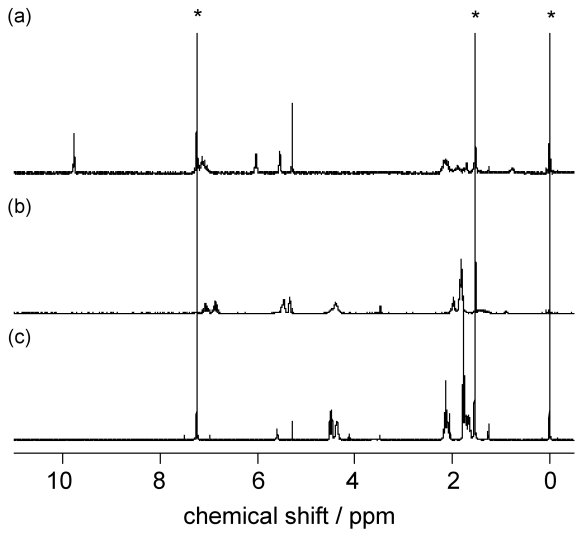


Figure 4 NMR Spectra of (a) **1c**, (b) **1a**, and (c) **11** in $CDCl_3$. *'s represent the $CHCl_3$, H_2O and TMS peaks.

Absorption spectra of dodeca-, octa-, and tetra-substituted porphycenes are summarized in Figure 5. Porphycene **1c** showed the B-band at 383 nm with a shoulder at 373 nm, and Q bands at 566, 611, and 646 nm (Figure 5a). B- and Q bands of **1a** were observed at 384 and 570-770 nm, respectively. B band is observed at the similar wavelength with **1c**, but Q-band was ca. 100-nm red-shifted compared to **1a** and oscillatory structure was not observed for **1a**. Porphycene **1b** also showed the similar spectrum with that of **1a**. Tetrahexyl-tetramethylporphycene **3b** showed broad peaks, as shown in Figure 5a, although tetrahexylporphycene **3c**[10] showed the similar spectrum as **1c** with a clear oscillatory structure[10]. The absorption spectra of benzoporphycenes are also shown in Figure 5a. B band was observed at 450 nm, and Q band reached to ca. 820 nm as a very broad band for **2a** and **2b**. Both of B and Q bands of **2a** and **2b** were red-shifted compared to those of **2c**. Fluorescence spectra were also measured. When alkyl substituents were introduced to *meso*-positions, porphycenes **1a**, **1b**, and **3b** were all non-fluorescent, although the fluorescence quantum yields of reference porphycenes **1c** and **3c** were 42 and 34%, respectively.[10] *Meso*-alkyltetrabenzoporphycenes were also non-fluorescent (ϕ_{em} was less than 0.01%), as were the *meso*-free tetrabenzoporphycenes.[10]

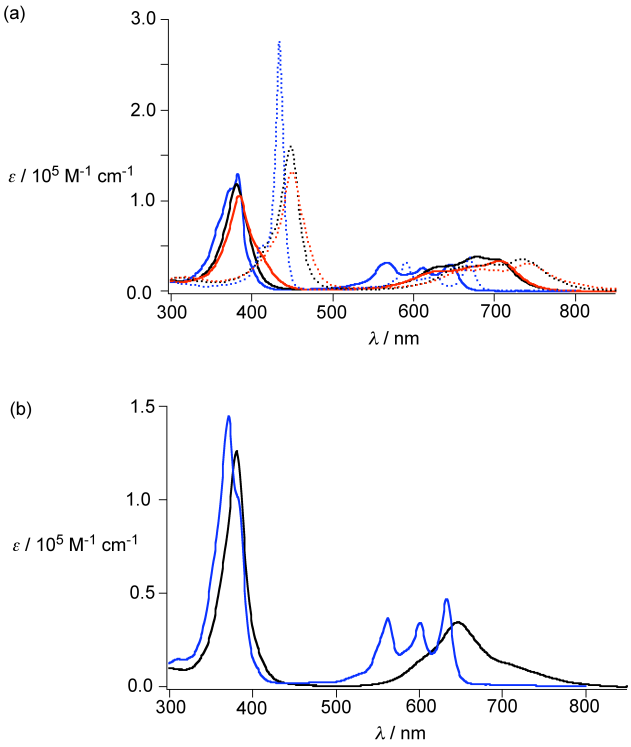


Figure 5. UV-vis absorption spectra of (a) **1a** (red solid line), **1b** (black solid line), **1c** (blue solid line), **2a** (red dotted line), **2b** (black dotted line) and **2c** (blue dotted line) in CH_2Cl_2, and (b) **3b** (black solid line) and **3c** (blue solid line) in CH_2Cl_2.

The crystal structures of **1a** and **1c** are shown in Figure 6. The molecule of **1a** occupied an inversion center and the N1-N2 and N1-N4 distances were 2.898(3) and 2.602(3) Å, respectively. N_4-cavity gave parallelogram shape: an acute angle at N1 was 86.26(8)° and an obtuse angle at N2 was 93.74(9)°. The side view of **1a** showed saddle-shaped structure (Figure 6b) and the dihedral angle between directly connected pyrroles were 26.87°. The molecule of **1c** also occupied an inversion center and the N1-N2 and N1-N4 distances were 2.805(2) and 2.694(3) Å, respectively. The difference between longer and shorter axes was smaller than that of **1a** and the interior angles were close to perpendicular angles: 88.77(7)° and 91.23(7)°

at N1 and N2, respectively. The porphycene plane is relatively flat and directly-connected pyrrole-pyrrole dihedral angle was 11.71˚(Figure 6d). The slippage of the core atoms from the mean porphycene plane is shown in Figure 7. The length of C5-C6 bonds were 1.402(4) and 1.385(3) Å for **1a** and **1c**, respectively. The interior angles at C5 and C6 positions of **1a** were smaller than those of **1c**, because of the repulsion between ethyl groups at *meso*-positions as shown in Figure 6. This repulsion also induced the shorter distances of C2 and C19 atoms and thereby the torsion of porphycene planes for **1a**.

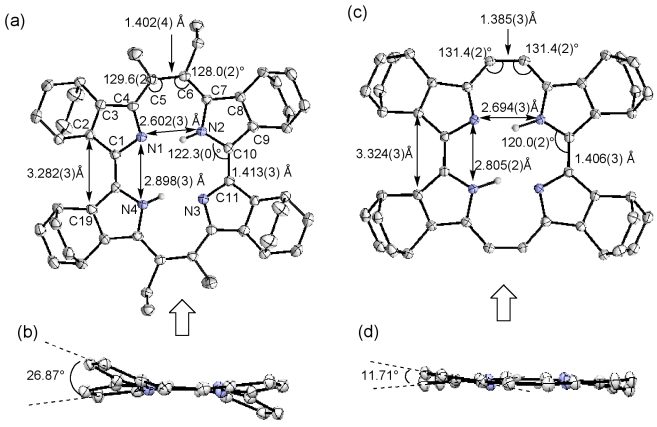


Figure 6. X-ray crystal structures of **1a**: (a) top view; (b) side view; and **1c**: (c) top view; (d) side view. Hydrogen atoms except for the inner hydrogen are omitted for clarity.Peripheral substituents in (b) and (d) are also omitted for clarity. Arrows in (a) and (c) show the direction of side views.

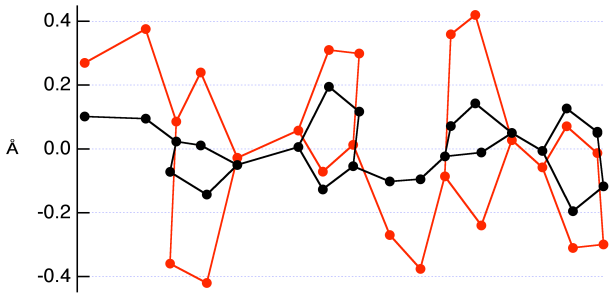


Figure 7. Skeletal deviations of the macrocycle atoms from the 24 atoms/4N mean plane for **1a** (red line) and **1c** (black line).

For porphycene **3b**, facing-*β*-substituents were removed, and the steric hindrance between directly-connected pyrroles is reduced. The crystal structure of **3b** is shown in Figure 8. There were one and a half crystallographically independent molecules of **3b** in an asymmetric unit cell, both of which showed sigmoidal shape. The dihedral angle of two mean planes of porphycene core 16 inner-atoms was 16.8˚. Molecule 1 in Figure 8 occupied the inversion center and slightly warped molecule 2 was found in a normal position. Here molecule 1 is discussed representatively. The longer and shorter N1-N2 distances were 2.960(3) and 2.519(3) Å, respectively, and the shape of N_4-cavity square was slender rectangle with the interior angles of 88.74(8)˚ and 91.26(8)˚, at N1 and N2, respectively. The C5-C6 length was 1.422(4) Å, which was longer than those of **1a** and **1c**. On the other hand, C2-C19 distance was 3.087(4) Å, which was *ca.* 0.2-Å shorter than those of **1a** and **1c**. These are because of the lack of substituents at C2 and C19 positions.

Vögel and co-workers have found that the peripheral alkyl substituents of porphycene effect the geometry of the ring skeleton and the shape and size of the N_4-coordination hole.[8a] The strength of N-H···N hydrogen bonding between N1 and N4 can be observed by chemical shift of NH protons and the N-N distances can be estimated by X-ray crystal structure analysis. Generally the chemical shifts of porphycene NH protons were observed at

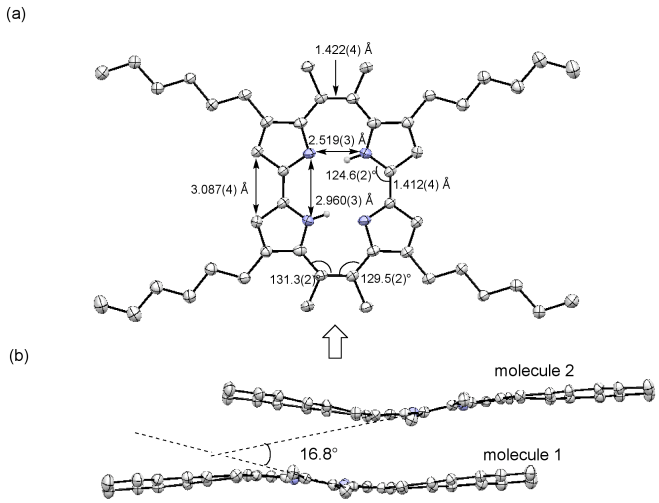
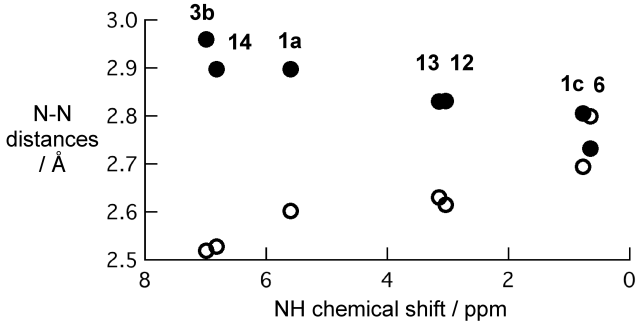
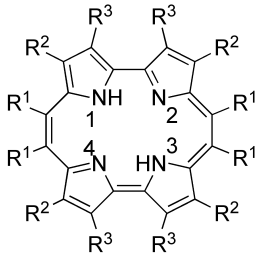


Figure 8. X-ray crystal structures of **3b**: (a) top view of molecule 1 and (b) side view of two independent molecules. Hydrogen atoms except for the pyrrolic hydrogen are omitted for clarity. A large arrow in (a) shows the direction of the side view.

relatively higher field because of the ring current of porphycene aromatic macrocycles. However, the N-H···N hydrogen bonding between N1 and N4 was stronger compared to porphyrin and the chemical shift of the proton showed the lower magnetic field shift.





Compounds	R^1	R^2	R^3
6[15]	H	Et	Et
1c	H	BCOD	
12[7b]	H	Pr	H
13[5]	H	H	H
1a	Et	BCOD	
14[8a]	Pr	H	H
3b	Me	Hex	H

Figure 9. Relationship between NH chemical shifts in $CDCl_3$ and N1-N2 (closed circles) or N1-N4 (open circles) distances obtained from X-ray single crystal structure. NH chemical shift for **1a** is used from porphycene **11**, because NH proton was not clearly observed for porphycene **1a**. For **3b**, two conformational isomers were included in a unit cell and the data of molecule 1 in Figure 8 is used here.

They have also reported the relationship between the position of substituents and the shape of the N_4-cavities. The 9,10,19,20-substituted porphycenes (R^1-positons in Figure 9) showed rectangular shape,[8a] 3,6,13,16-substituented ones (R^3-positions) showed nearly-square shape,[15] and 2,7,12,17-substituted ones (R^2-positions) was in between.[7b] Typical NH chemical shifts and N-N distances of our porphycenes, **1a**, **1c**, and **3b** are summarized in Figure 9 with the previously reported porphycenes, **6**,[15] **12**,[7b] **13**,[5] and **14**.[8a] With increasing the chemical shift values of NH, the difference of the longer and shorter N1-N2 linkages become larger, which means N_4-cavity become narrower rectangular.Octaethylporphycene **6**[15] and BCOD porphycene **1c** are both *b*-octaalkyl-porphycenes, but N_4-cavity of **6** is more close to square than that of BCOD-type **1c**. This is because BCOD-substituents are less bulky than octaethyl-substituents, and therefore repulsion between substituents at 3- and 6-positions is smaller. When R^1- and R^2- positions are both substituted (**3b**), the N_4-cavity is rectangular and NH chemical shift reached 6.99 ppm. The rectangular shape of **3b** was narrower than that of *meso*-propyl porphycene **14**, because of the repulsion between substituents. The porphycene **1a** positioned between non-substituted and *meso*-substituted porphycenes, because the close proximities at R^3-positions competed with the repulsion at R^1-position.

Conclusion

Finally, we have succeeded to prepare dodeca-substituted porphycenes for the first time by McMurry coupling of bipyrroles fused with BCOD-rings. Crystallographic analysis of **1a**, **1c**, **3b**, and **5** suggested the common alkyl substituents are too bulky to stabilize the dodeca-substituted porphycenes. *Meso*-tetraalkyl-tetrabenzoporphycenes were also prepared by retro-Diels-Alder reaction of BCOD-fused porphycenes.

Experimental Section

General Melting points were measured with a Yanaco M-500D melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 400 spectrometers using tetramethylsilane as an internal standard. VT NMR spectra were recorded on a JEOL JNM-EX-400. IR spectra were measured on a Hitachi 270-30 as KBr disks. MALDI-TOF mass spectra were measured on Voyager DE Pro (Applied Biosystems). Elemental analyses were performed on Yanaco MT-5 elemental analyzer. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. For spectral measurements, spectral grade of toluene and chloroform were purchased from Nakalai tesque co. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively.

X-ray Analysis. Single crystals of **1a** and **5** suitable for X-ray diffraction analysis were obtained by slow diffusion of MeOH into a $CHCl_3$, while Single crystals of **3b** suitable for X-ray diffraction analysis were obtained by slow diffusion of MeOH into a CS_2. The crystals were mounted in *LithoLoops* (purchased from Protein Wave Co.) The diffraction data were collected at -173 °C on a Rigaku VariMaxRAPID/α imaging plate diffractometer equipped graphite-monochromated CuKα radiation or on a Rigaku Mercury-8 diffractometer equipped graphite-monochromated MoKα radiation with a CCD detector. The diffraction data were processed with *CrystalStructure* on a Rigaku program, solved with SIR-97[17] and refined with SHELX-97.[18]

Synhtesis Bipyrrole 4 $POCl_3$ (3.1 ml, 34 mmol) was added to a solution of 3,3',4,4'-diethyl-2,2'-bipyrrole[15] (3.24 g, 13.2 mmol) and *N,N*-dimethylacetoamide (21 ml) in *dry*-CH_2Cl_2 (83 ml) under an Ar atmosphere. The reaction mixture was refluxed for 1 h. After cooling to rt, aqueous sodium acetate (8.4 g in 125 ml) was added and the reaction mixture was refluxed for another 1 h. After cooling to r.t, the mixture was extracted with $CHCl_3$. The combined organic layers were washed with sat. $NaHCO_3$ aq., water and brine, dried over Na_2SO_4. The solvent was concentrated to give the crude product. The crude product was crystallized from $CHCl_3$/MeOH to give 4 as white powder. Yield: 90% (03.89 g, 11.9 mmol). mp; 210 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.96 (br, 2H, N<u>H</u>), 2.79 (q, 4H, J = 7.5 Hz, -C<u>H</u>$_2$CH$_3$), 2.51, (s, 6H, CO<u>Me</u>), 2.49 (q, 4H, J = 7.5 Hz, -C<u>H</u>$_2$CH$_3$), 1.24 (t, 6H, J = 7.5 Hz, -CH$_2$C<u>H</u>$_3$), 1.10 (t, 6H, J = 7.5 Hz, -CH$_2$C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.17, 132.54, 128.98, 126.40, 125.30, 27.54, 18.90, 17.83, 16.58, 16.42; MS (FAB) m/z: 328 [M^+]; Anal. Calcd for $C_{20}H_{28}N_2O_2$+1/4H_2O: C, 72.15; H, 8.63; N, 8.41. Found: C, 72,14; H, 8.63; N, 8.37.

Bipyrrole 8a $POCl_3$ (0.75 ml, 8 mmol) was added to a solution of 7 (0.58 g, 2.0 mmol) and *N,N*-dimethylpropionamide (3.0 ml) in *dry*-CH_2Cl_2 (10 ml) under an Ar atmosphere. The reaction mixture was refluxed for 3 h. After cooling to rt, aqueous sodium acetate (2.0 g in 30 ml) was added and the reaction mixture was refluxed for another 1 h. After cooling to r.t, the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with sat. $NaHCO_3$ aq., water and brine, dried over Na_2SO_4, and the solvent was concentrated. The crude product was purified by recrystallization from CH_2Cl_2/MeOH to give 8a as a greenish yellow solid. Yield: 80% (0.64 g, 1.6 mmol). Decomp. Temp. > 215 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.12 (br, 2H, N<u>H</u>), 6.57 (m, 4H, olefin), 4.31 (m, 2H, bridge head), 4.05 (m, 2H, bridge head), 2.90 (q, 4H, J = 7 Hz, -C<u>H</u>$_2$CH$_3$), 1.61 (m, 8H, bridge), 1.25 (t, 6H, J = 7 Hz, -CH$_2$C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) [mixture of stereoisomers]: δ 190.81, 136.70, 136.66, 136.05, 135.91, 134.69, 134.60, 129.76, 129.68, 123.79, 123.78, 119.96, 119.93, 35.09, 35.07, 33.52, 33.47, 32.83, 26.73, 26.64, 26.46, 26.38, 9.17; MS (FAB) m/z: 400 [M^+], 372 [M^+-C_2H_4], 344 [M^+-2C_2H_4]; HRMS (FAB): *m/z* calcd for $C_{26}H_{29}N_2O_2^+$: 401.2229, found 401.2220.

Bipyrrole 8b $POCl_3$ (0.5 ml, 5.5 mmol) was added to a solution of 7 (0.43 g, 1.5 mmol) and *N,N*-dimethylacetoamide (3.0 ml) in *dry*-CH_2Cl_2 (5.0 ml) under an Ar atmosphere. The reaction mixture was refluxed for 3 h. After cooling to rt, aqueous sodium acetate (5.0 g in 50 ml) was added and the reaction mixture was refluxed for another 1 h. After cooling to r.t, the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with sat. $NaHCO_3$ aq., water and brine, dried over Na_2SO_4, and the solvent was concentrated. Triturated with MeOH gave crude target product. The crude product was purified by silica gel column chromatography (25% EtOAc in CH_2Cl_2) and crystallized from $CHCl_3$/MeOH to give 8b as off-white solid. Yield: 84% (0.47 g, 1.3 mmol). Decomp. Temp. > 212 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.67 (br, 2H, -N<u>H</u>), 6.64-6.52 (m, 4H, olefine), 4.33 (m, 2H, bridge head), 4.06 (m, 2H, bridge head), 2.59 (s, 6H, CO<u>Me</u>), 1.68-1.52 (m, 8H, bridge); ^{13}C NMR ($CDCl_3$, 100 MHz) [mixture of stereoisomers]: δ 187.31, 137.77, 136.03, 135.86, 134.82, 134.71, 130.10, 130.04, 124.42, 120.38, 35.02, 33.67, 33.59, 27.28, 26.74, 26.63, 26.46, 26.34; MS (FAB) m/z: 373 [M^++1]; Anal. Calcd for $C_{24}H_{24}N_2O_2$+1/2H_2O: C, 75.57; H, 6.61; N, 7.34. Found: C, 75.36; H, 6.39; N, 7.33.

Bipyrrole 10 $POCl_3$ (0.81 ml, 8.6 mmol) was added to a mixture of 9 (1.05 g, 3.5 mmol) and $MeCONMe_2$ (4.2 ml) in 1,2-dichloroetane (4 ml) via a syringe at 0 ºC under an Ar atmosphere. The mixture was then refluxed for 3 h. The mixture was poured into aqueous sodium acetate (100 ml) and refluxed for another 1 h. After cooling to rt, the mixture was extracted with $CHCl_3$. The combined organic layer was washed with a saturated solution of $NaHCO_3$, water, and brine. The solution was then dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (10% EtOAc in $CHCl_3$). Recrystallization from $CHCl_3$/MeOH provided 10 in 92% yield (1.13 g, 3.2 mmol) as a yellowish green powder. m.p. 187-189 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) *d* 11.41 (br, 2H, N<u>H</u>), 6.46 (d, 2H, J = 2.5 Hz, *b*-position), 2.78 (t, 4H, J = 7.8 Hz, -C<u>H</u>$_2$C$_5$H$_{11}$), 2.61 (s, 6H, -CO<u>Me</u>), 1.69 (m, 4H, -CH$_2$C<u>H</u>$_2$C$_4$H$_9$), 1.43 (m, 4H, -CH$_2$CH$_2$C<u>H</u>$_2$C$_3$H$_7$), 1.35 (m, 8H, -CH$_2$CH$_2$CH$_2$C<u>H</u>$_2$C$_2$H$_5$ + CH$_2$CH$_2$CH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 0.91 (t, 6H, J = 6.8 Hz, -CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): *d* 188.08, 135.00, 129.66, 129.29, 111.19, 31.79, 30.78, 29.44, 28.37, 28.06, 22.71, 14.18; MS (EI) m/z: 384 [M^+]; HRMS (FAB): *m/z* calcd for $C_{24}H_{37}N_2O_2^+$: 385.2855, found 385.2850.

General procedure of McMurry coupling reaction $TiCl_4$ (2.7 ml, 25 mmol) was added to a mixture of Zn dust (3.27 g / atom) and CuCl (0.2 g. 2 mmol) in THF (100 ml), and the mixture was refluxed for 2 h. A solution of 5,5'-diacyl-2,2'-bipyrrole (1.0 mmol) in THF (100 ml) was added dropwise to a reaction mixture, and refluxed for another 1 h. After coolig to rt, the reaction was quenched with 10% aqueous K_2CO_3 (100 ml). The precipitate was filtrated with Celite pad, and washed with $CHCl_3$, the organic layer was dried over Na_2SO_4, and the solvent was concentrated. The residue was chromatographed on alumina with $CHCl_3$ to give crude product. The crude product was purified by silica gel column chromatography and recrystallization to afford pure porphycenes.

Porphycene 5 According to the general procedure, 5 was prepared from 4 in 14% (41 mg, 69 μmol) after purification by silica gel column chromatography ($CHCl_3$) and recrystallization from $CHCl_3$/MeOH. Colorless crystal. m.p. 197 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.46 (s, 4H, -N<u>H</u>), 2.54 (m, 4H), 2.46 (m, 4H), 2.40-2.25 (m, 8H), 2.17 (s, 12H), 1.16 (t, 12H, J = 7.5 Hz), 0.97 (t, 12H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.96, 125.45, 123.11, 121.16, 120.89, 19.04, 18.04, 17.49, 17.22, 16.11; UV (CH_2Cl_2) λ_{max} (logε) 289 (4.47); MS (FAB) m/z: 593 [M^+]; HRMS (FAB): *m/z* calcd for $C_{40}H_{57}N_4^+$: 593.4583, found 593.4553.

Porphycene 1a According to the general procedure, 1a was prepared from 8a in 7.7% (28.2 mg, 38 μmol) after purification by silica gel column chromatography (20% EtOAc in CH_2Cl_2) and recrystallization from $CHCl_3$/MeOH. Greenish blue solid. Decomp. temp.>158 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.14-6.82 (m, 8H, olefin), 5.51-5.34 and 5.06 (m+br, 10H, bridge head+-N<u>H</u>), 4.54-4.31 (m, 8H, -C<u>H</u>$_2$CH$_3$), 2.04-1.24 (m, 28H, bridge+-COCH$_2$C<u>H</u>$_3$); ^{13}C NMR spectra were not recorded because of poor solubility; UV (CH_2Cl_2) λ_{max} (logε) 385 (5.02), 631 (4.34), 674 (4.23), 707 (4.52); MS (MALDI-TOF) m/z: 735 [M^+], 707 [M^+-C_2H_4], 679 [M^+-2C_2H_4], 651 [M^+-3C_2H_4], 623 [M^+-4C_2H_4]; Anal. Calcd for $C_{52}H_{54}N_4$+1/3H_2O+1/3$CHCl_3$: C, 80.50; H, 7.10; N, 7.18. Found: C, 80.68; H, 7.08; N, 7.19.

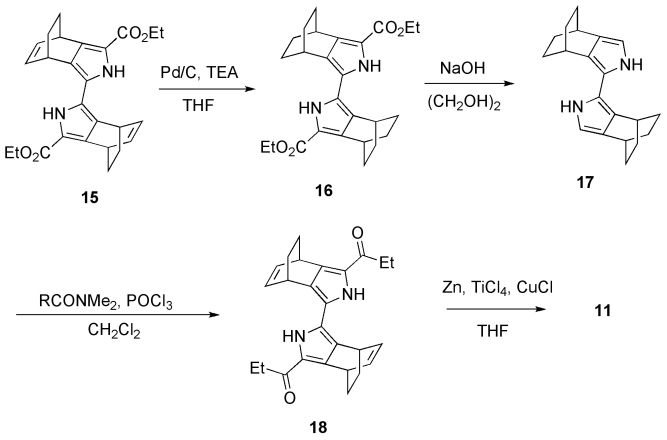
Porphycene 1b According to the general procedure, 1b was prepared from 8b in 8.5% (28.5 mg, 42 µmol) after purification by silica gel column chromatography (20% EtOAc in CH_2Cl_2) and recrystallization from $CHCl_3$/MeOH. Greenish blue solid. Decomp. temp.>155 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11-6.74 (m, 8H, olefin), 5.42-5.42 and 5.06 (m+br, 10H, bridge head+-NH), 3.93, 3.91, 3.90, 3.89 (s, 12H, -Me), 2.17-1.26 (m, 16H, bridge); ^{13}C NMR spectra were not recorded because of poor solubility; UV (CH_2Cl_2) λ_{max} (logε) 381 (5.07), 623 (4.38), 678 (4.58), 706 (4.53); MS (MALDI-TOF) m/z: 679 [M$^+$], 651 [M$^+$-C_2H_4], 623 [M$^+$-2C_2H_4], 595 [M$^+$-3C_2H_4], 567 [M$^+$-4C_2H_4]; Anal. Calcd for $C_{48}H_{46}N_4$+MeOH: C, 82.78; H, 7.09; N, 8.25. Found: C, 82.99; H, 7.04; N, 7.99.

Porphycene 3b According to the general procedure, 3b was prepared from 10 in 2.3% (8.0 mg, 11 µmol) after purification by silica gel column chromatography (CH_2Cl_2) and recrystallization from $CHCl_3$/MeOH. Blue solid. m.p. 196 ºC;^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (s, 4H, *b*-position), 6.81 (br, 2H, -NH), 3.72-3.69 (t+s, 8H+12H), 2.12 (m, 8H), 1.65-1.34 (m+m+m, 24H), 0.93 (t, 12H, J = 7.1 Hz); ^{13}C NMR spectra were not recorded because of poor solubility; UV (CH_2Cl_2) λ_{max} (logε) 381 (5.10), 647 (4.53); MS (FAB) m/z: 703 [M$^+$]; HRMS (FAB): *m/z* calcd for $C_{48}H_{71}N_4^+$: 703.5679, found 703.5658.

Porphycene 2a **1a** was heated to 200 ºC in the solid phase under vacuum for 30 min. After cooling to rt, 2a was obtained quantitatively. m.p. 298 ºC (decomp.); ^{1}H and ^{13}C NMR spectra were not recorded because of poor solubility; UV (CH_2Cl_2) λ_{max} (logε) 450 (5.12), 683 (4.37), 741 (4.48); MS (MALDI-TOF) m/z: 623 [M$^+$]; Anal. Calcd for $C_{44}H_{38}N_4$+1/2H_2O: C, 83.64; H, 6.22; N, 8.87. Found: C, 83.89; H, 6.01; N, 8.87.

Porphycene 2b **1b** was heated to 200 ºC in the solid phase under vacuum for 30 min. After cooling to rt, 2b was obtained quantitatively. m.p. > 300 ºC; ^{1}H and ^{13}C NMR spectra were not recorded because of poor solubility; UV (CH_2Cl_2) λ_{max} (logε) 448 (5.20), 694 (4.47), 733 (4.55); MS (MALDI-TOF) m/z: 567 [M$^+$]; Anal. Calcd for $C_{40}H_{30}N_4$: C, 84.78; H, 5.34; N, 9.89. Found: C, 84.48; H, 5.41; N, 9.83.

Porphycene 11 was prepared as shown in Scheme 3.



Scheme 3. Synthesis of porphycene **11.**

Bipyrrole 16 A mixture of Pd/C (0.5 g) and TEA (1 drop) in THF (30 ml) was stirred for 30 min under an H_2 atmosphere. A solution of **15** (1.3 g, 3.0 mmol) in THF (50 ml) was added. After stirring for 17 h, the precipitate was filtrated. The filtrate was concentrated under a reduced pressure. The crude product was recystallized from $CHCl_3$/MeOH to give **16** as colorless solid. Yield: quant. m.p. 261 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (br, 2H, NH), 4.32 (q, 4H, J = 7.1 Hz, -CH_2CH_3), 3.55 (s, 2H, bridge head), 3.11 (s, 2H, bridge head), 1.80 (m, 8H, bridge), 1.42 (m, 8H, bridge), 1.36 (t, 6H, J = 7.1 Hz-CH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.77, 136.45, 127.29, 119.99, 114.72, 60.05, 27.75, 27.61, 27.15, 26.49, 14.64; MS (FAB) m/z: 436 [M$^+$+1]; HRMS (FAB): *m/z* calcd for $C_{26}H_{33}N_4^+$: 437.2440, found 437.2404.

Bipyrrole 17 A mixture of **16** (1.3 g, 3.0 mmol) and NaOH (1.5 g) in ethylene glycol (30 ml) was heated for 90 min at 165 ºC under an Ar atmosphere. After cooling to rt, saturated $NaHCO_3$ aq. was added. The mixture was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4. After removal solvent, the residue was purified by silica gel column chromatography (CH_2Cl_2). Recrystallized from $CHCl_3$/hexane gave **17** (68%, 0.59g, 2.0 mmol) as white solid. m.p. 240 ºC (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (br, 2H, NH), 6.50 (d, 2H, J = 1.8 Hz, α-position), 3.09 (s, 2H), 2.99 (s, 2H), 1.83-1.74 (m, 4H), 1.49-1.40 (m, 4H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.79, 123.52, 116.86, 107.62, 27.75, 27.68, 27.58, 27.49; MS (FAB) m/z: 292 [M$^+$]; Anal. Calcd for $C_{20}H_{24}N_2$+1/9$CHCl_3$: C, 79.02; H, 7.95; N, 9.16. Found: C, 79.11; H, 7.86; N, 9.11.

Bipyrrole 18 $POCl_3$ (0.65 ml, 7 mmol) was added to a solution of **17** (0.51 g, 1.7 mmol) and *N,N*-dimethylpropionamide (2.0 ml) in *dry*-CH_2Cl_2 (20 ml) under an Ar atmosphere. The reaction mixture was refluxed for 3 h. After cooling to rt, aqueous sodium acetate (2.0 g in 30 ml) was added and the reaction mixture was refluxed for another 1 h. After cooling to r.t, the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with sat. $NaHCO_3$ aq., water and brine, dried over Na_2SO_4, and the solvent was concentrated. The crude product was purified by recrystallization from CH_2Cl_2/MeOH to give **18** as a yellow powder. m.p. 232 ºC; Yield: 80% (0.57 g, 1.4 mmol). m.p. 232-233 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.59 (br, 2H, -NH), 3.46 (m, 2H, bridge head), 3.16 (m, 2H, bridge head), 2.87 (q, 4H, J = 7.5 Hz, -CH_2CH_3), 1.89-1.78 (m, 8H, bridge), 1.51-1.39 (m, 8H, bridge), 1.23 (t, J = 7.5 Hz, -CH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ191.25, 135.68, 128.10, 124.57, 121.43, 33.01, 29.39, 27.61, 26.90, 26.61, 9.56; MS (FAB) m/z: 404 [M$^+$]; Anal. Calcd for $C_{26}H_{32}N_2O_2$: C, 77.19; H, 7.97; N, 6.92. Found: C, 77.06; H, 7.88; N, 6.99.

Porphycene 11 $TiCl_4$ (2.7 ml, 25 mmol) was added to a mixture of Zn dust (3.27 g) in THF (100 ml) under an Ar atmosphere. Then the mixture was refluxed for 2 h. A solution of **18** (0.40 g, 1.0 mmol) in THF (100 ml) was added dropwise to a reaction mixture, and refluxed for 1 h. The reaction was quenched with 10% aqueous K_2CO_3 (100 ml). After filtration, the precipitate was washed with $CHCl_3$, the organic layer was dried with Na_2SO_4, and the solvent was concentrated under a reduce pressure. The residue was purified by alumina column chromatography ($CHCl_3$) and silica gel column chromatography (10% EtOAc in CH_2Cl_2). Recrystallization from $CHCl_3$/MeOH gave **11** as blue solid. Yield: 5% (20 mg, 0.027mmol). m.p. 273 ºC (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.60 (br, 2H, -NH), 4.51 (m, 4H), 4.47 (m, 4H), 4.37 (m, 4H), 2.13 (m, 16H), 1.77 (t, 12H, J = 7.4 Hz), 1.69 (m, 16H). ^{13}C NMR spectra were not recorded because of poor solubility; MS (FAB) m/z: 743 [M$^+$+1]; HRMS (FAB): *m/z* calcd for $C_{52}H_{63}N_4^+$: 743.5053, found 743.5070.

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[14] Crystal data for **1a** ($C_{52}H_{54}N_4$):*M*w=735.03, monoclinic $P2_1/c$, *a*=14.163(7), *b*=10.751(5), *c*=13.171(7) Å, *β*=105.776(7)°, *V*=1930.0(17) Å^3, *T*=100(2) K, *Z*=2. 14888 reflections were measured, and R_1=0.0723 (2482, $I>2\sigma(I)$), wR_2(all)=0.1363 (4404), *GOF*=1.018. Crystal data for **1c** ($C_{44}H_{38}N_4 CH_2Cl_2$):*M*w=707.74, monoclinic $P2_1/c$, *a*=8.995(2), *b*=10.016(3), *c*=18.897(5) Å, *β*=102.398(3)°, *V*=1662.8(7) Å^3, *T*=100(2) K, *Z*=2. 8596 reflections were measured, and R_1=0.0625 (3021, $I>2\sigma(I)$), wR_2(all)=0.1740 (3776), *GOF*=1.094. Crystal data for **3b** ($C_{48}H_{70}N_4$):*M*w=703.11, triclinic *P*-1, *a*=8.56152(16), *b*=18.3223(4), *c*=20.0544(5) Å, *α*=81.5430 (10)°, *β*=86.0640(10)°, *γ*=79.7740(10)°, *V*=3059.30(11) Å^3, *T*=100(2) K, *Z*=3. 55505 reflections were measured, and R_1=0.0651 (5155, $I>2\sigma(I)$), wR_2(all)=0.0928 (11016), *GOF*=1.032. Crystal data for **5** ($C_{40}H_{56}N_4$):*M*w=592.91, triclinic *P*-1, *a*=12.837(3), *b*=16.501(4), *c*=17.554(4) Å, *α*=96.639(4)°, *β*=102.904(3)°, *γ*=99.679(2)°, *V*=3527.3(13) Å^3, *T*=100(2) K, *Z*=4. 44734 reflections were measured, and R_1=0.0546 (12307, $I>2\sigma(I)$), wR_2(all)=0.1279 (16091), *GOF*=1.085. CCDC-783114 (**1a**), CCDC-783113 (**1c**), CCDC-783115 (**3b**), and CCDC-783112 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[16] E. Vögel, I. Grigat, M. Köcher, J. Lex, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1655-1657.

[17] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115-118.

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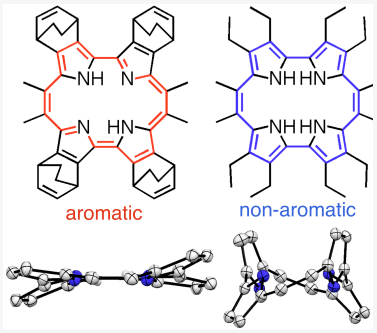
Entry for the Table of Contents (Please choose one layout only)

Layout 1:

Dodeca-substituted porphycenes!

Daiki Kuzuhara, Hiroko Yamada, Keiko Yano, Tetsuo Okujima, Shigeki Mori, and Hidemitsu Uno*……..…… Page – Page

First Synthesis of Dodeca-substituted Porphycenes



Dodeca-substituted porphycenes were prepared for the first time by taking advantage of unique features of bicyclo[2.2.2]octadiene (BCOD)-fused 2,2'-dipyrroles. The dihedral angle between directly connected pyrroles was 26.87°. The retro-Diels-Alder reaction of dodeca-substituted porphycenes gave *meso*-substituted tetrabenzoporphyrcenes. Octaethyl-tetramethylporphycene could not be obtained in the similar reaction condition and only pyrrolocyclophene was obtained.

Supporting Information

First Synthesis of Dodeca-substituted Porphycenes

Daiki Kuzuhara,[a] Hiroko Yamada,[a]* Keiko Yano,[a] Tetsuo Okujima,[a] Shigeki Mori,[b] and Hidemitsu Uno[a]

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E-mail: yamada@chem.sci.ehime-u.ac.jp
[b]Department of Molecular Science, Integrated Center for Sciences, Ehime University, Matsuyama 790-8577, Japan

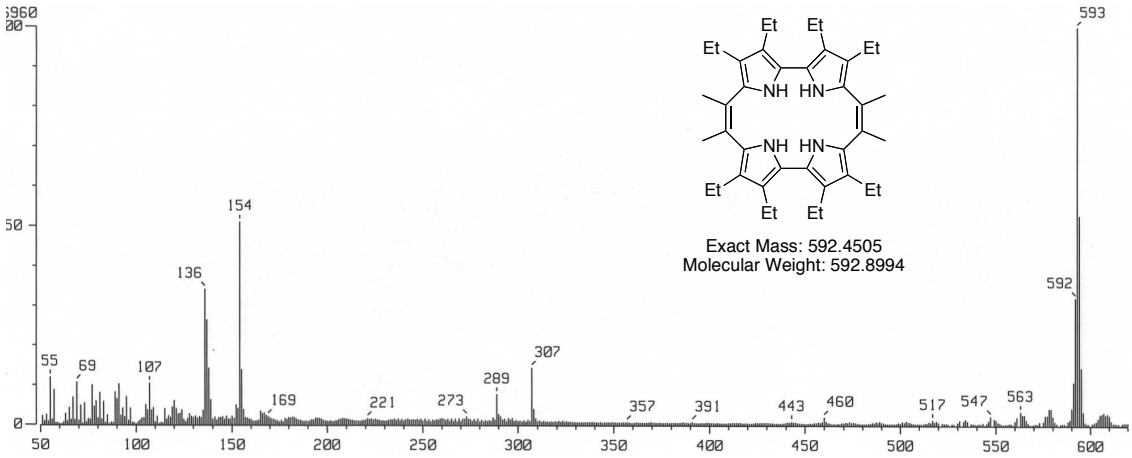


Figure S1. FAB-MS Spectrum of 5.

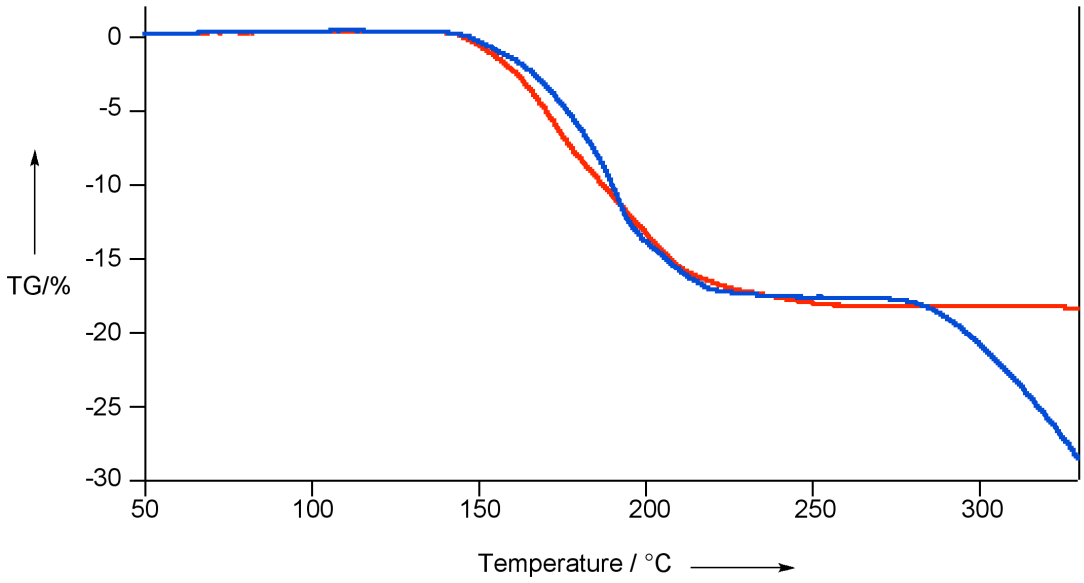
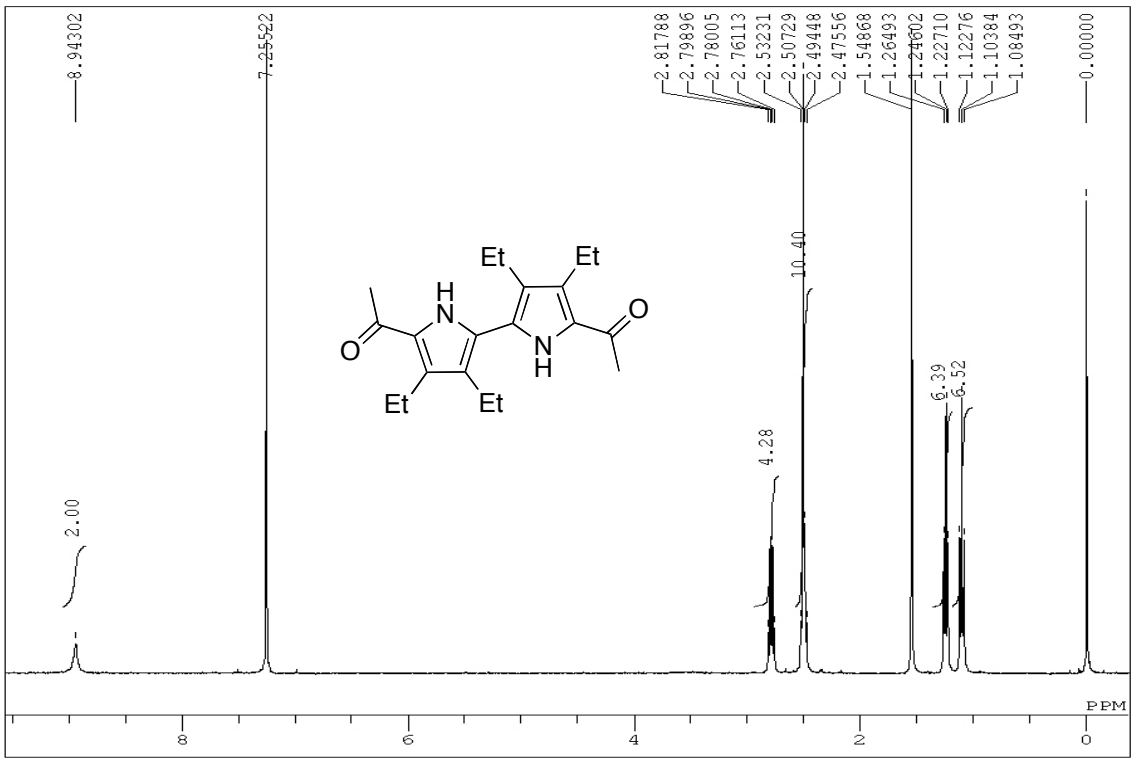


Figure S2. Thermogravimetric analysis of 1a(blue line) and 1b (red line).



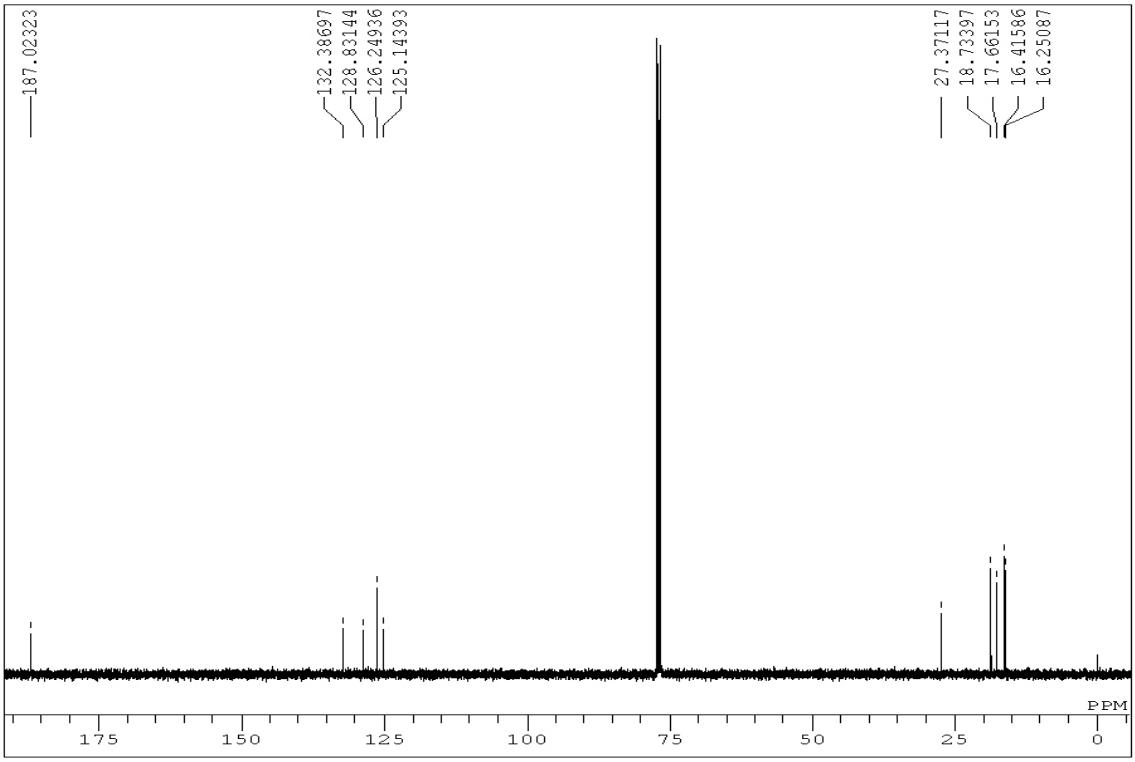


Figure S3. ^{1}H (upper) and ^{13}C (bottom) NMR spectra of 4 in $CDCl_3$

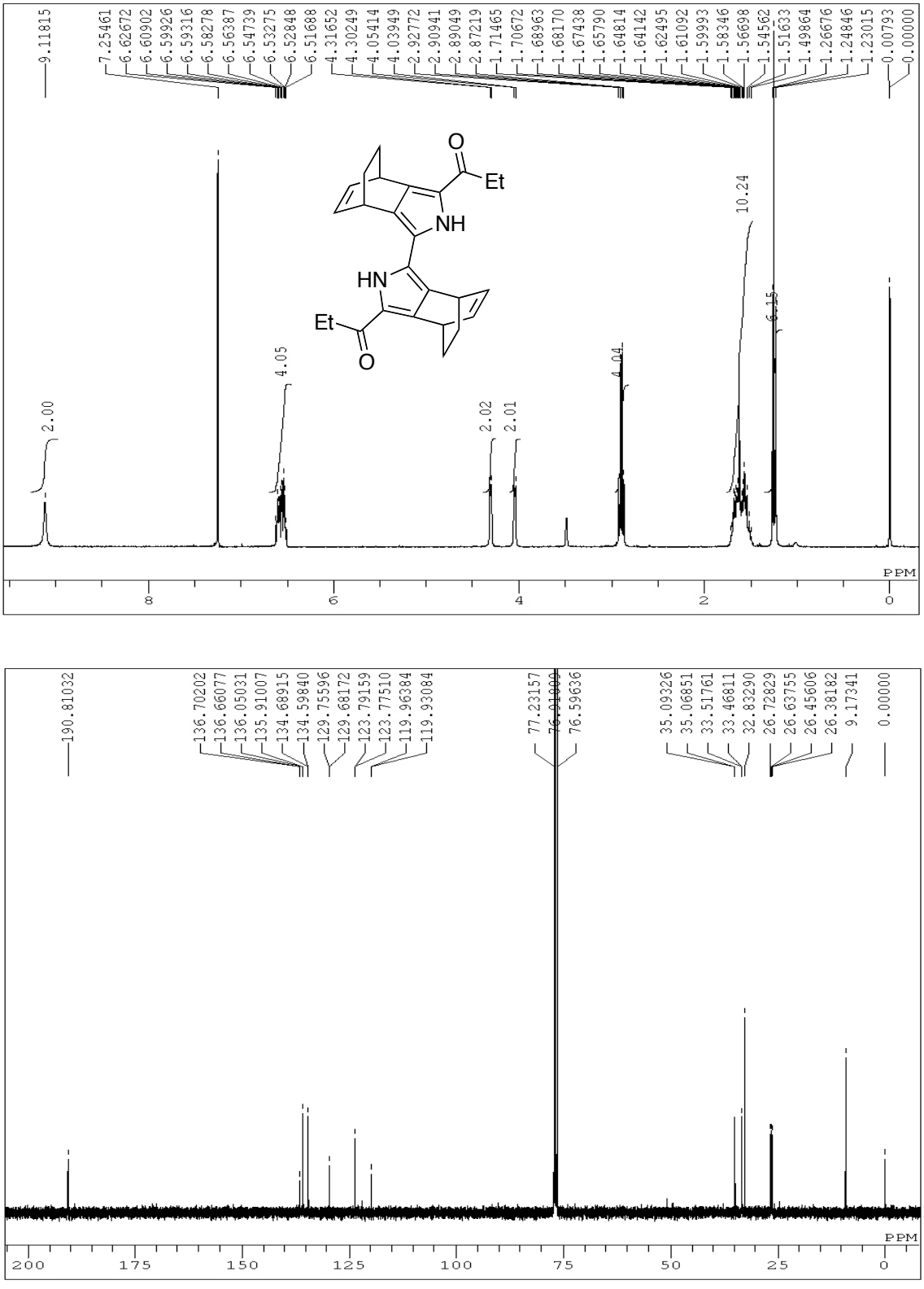


Figure S4. ^{1}H (upper) and ^{13}C (bottom) NMR spectra of 8a in $CDCl_3$.

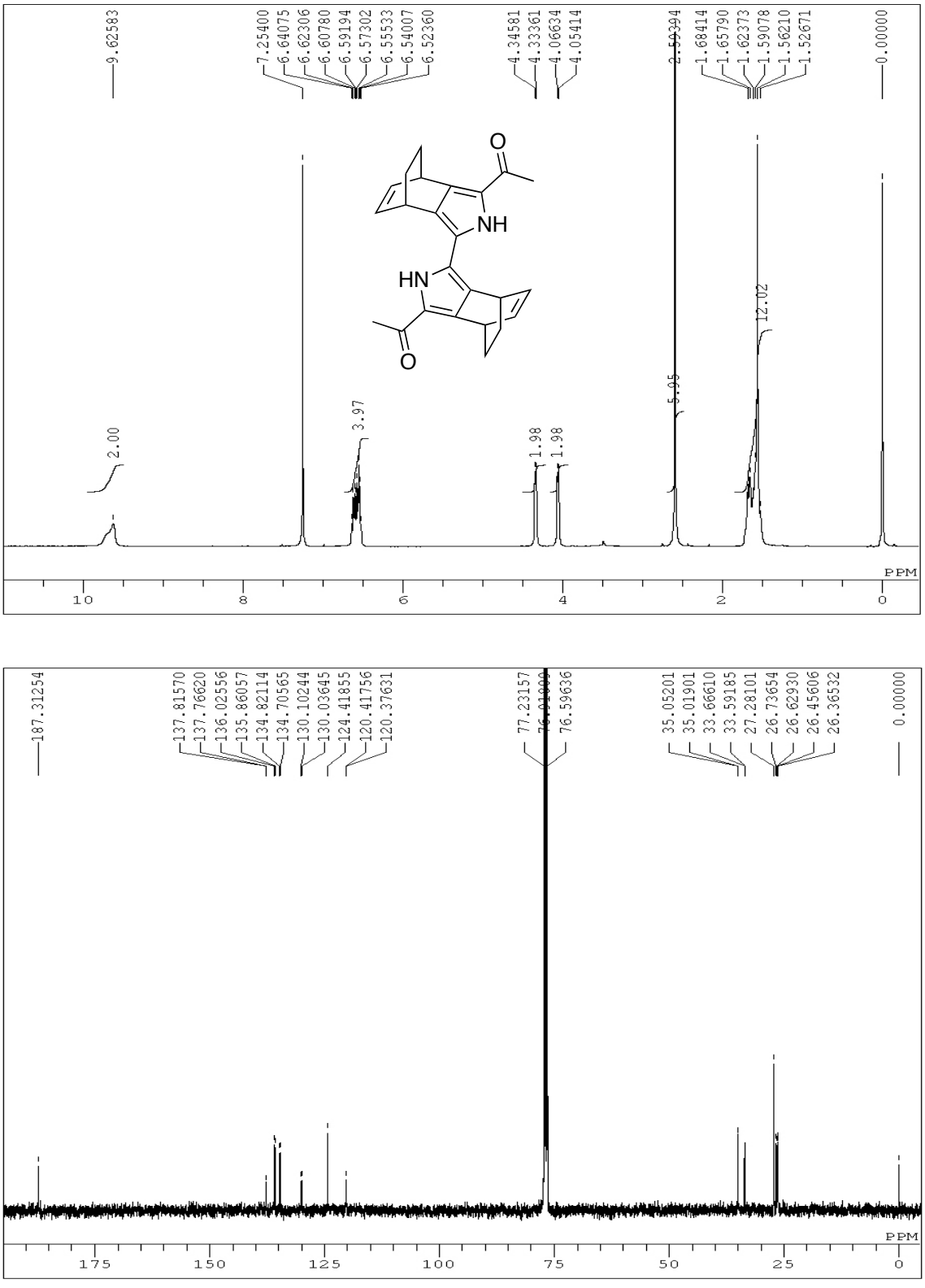


Figure S5. ^{1}H (upper) and ^{13}C (bottom) NMR spectra of 8b in $CDCl_3$.

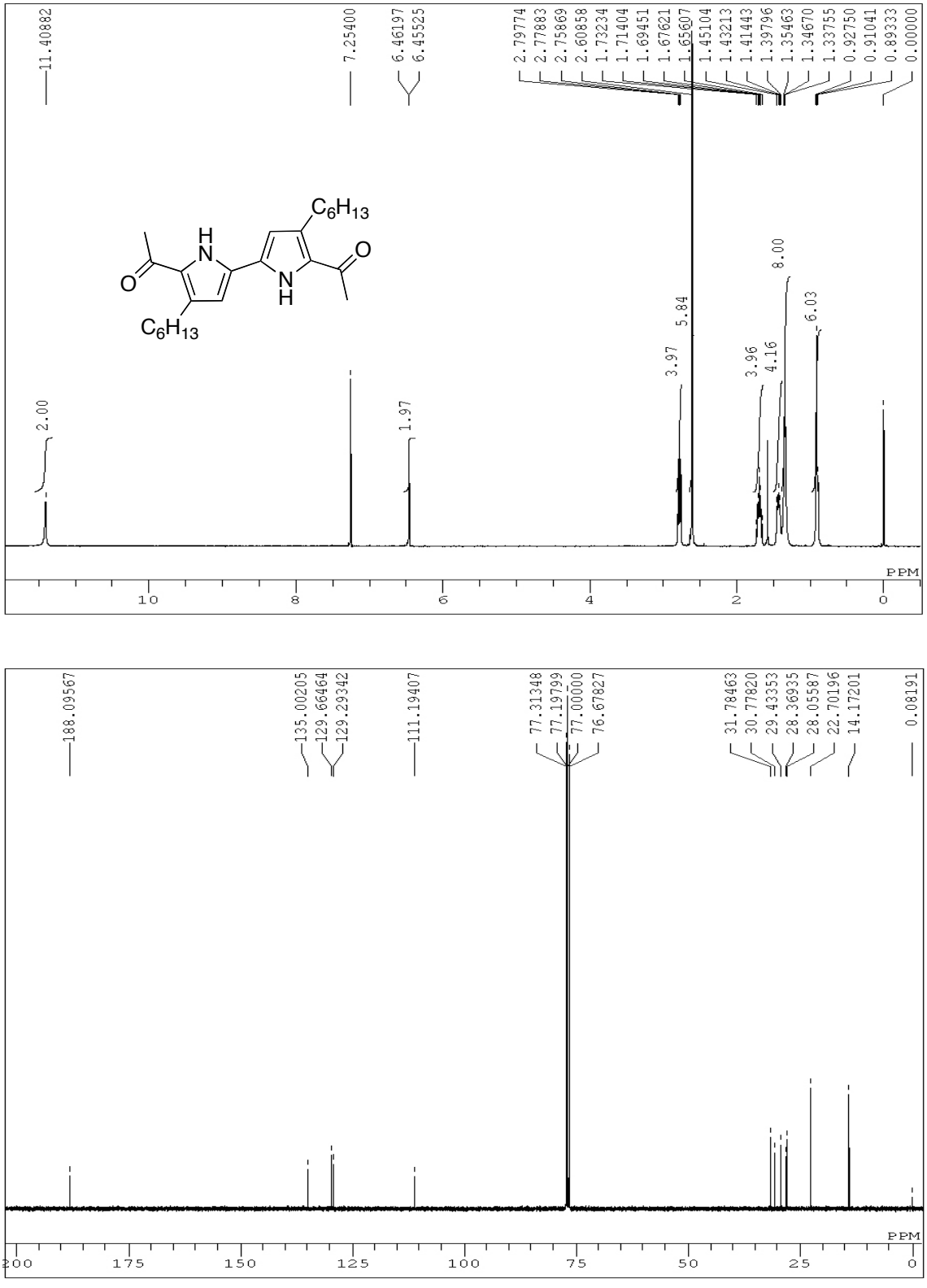


Figure S6. ^{1}H (upper) and ^{13}C (bottom) NMR spectra of 10 in $CDCl_3$.

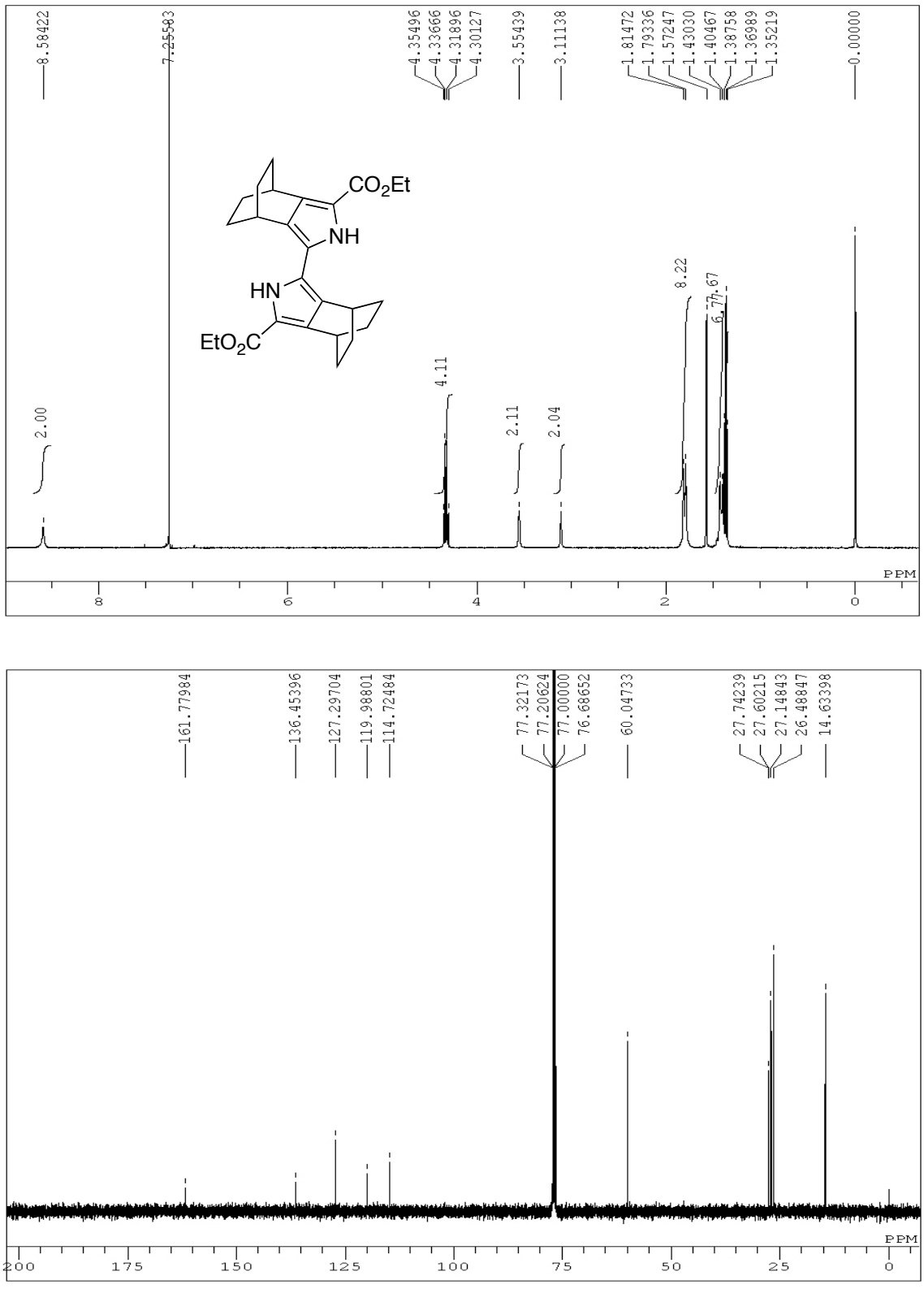


Figure S7. ^{1}H (upper) and ^{13}C (bottom) NMR spectra of 16 in $CDCl_3$.

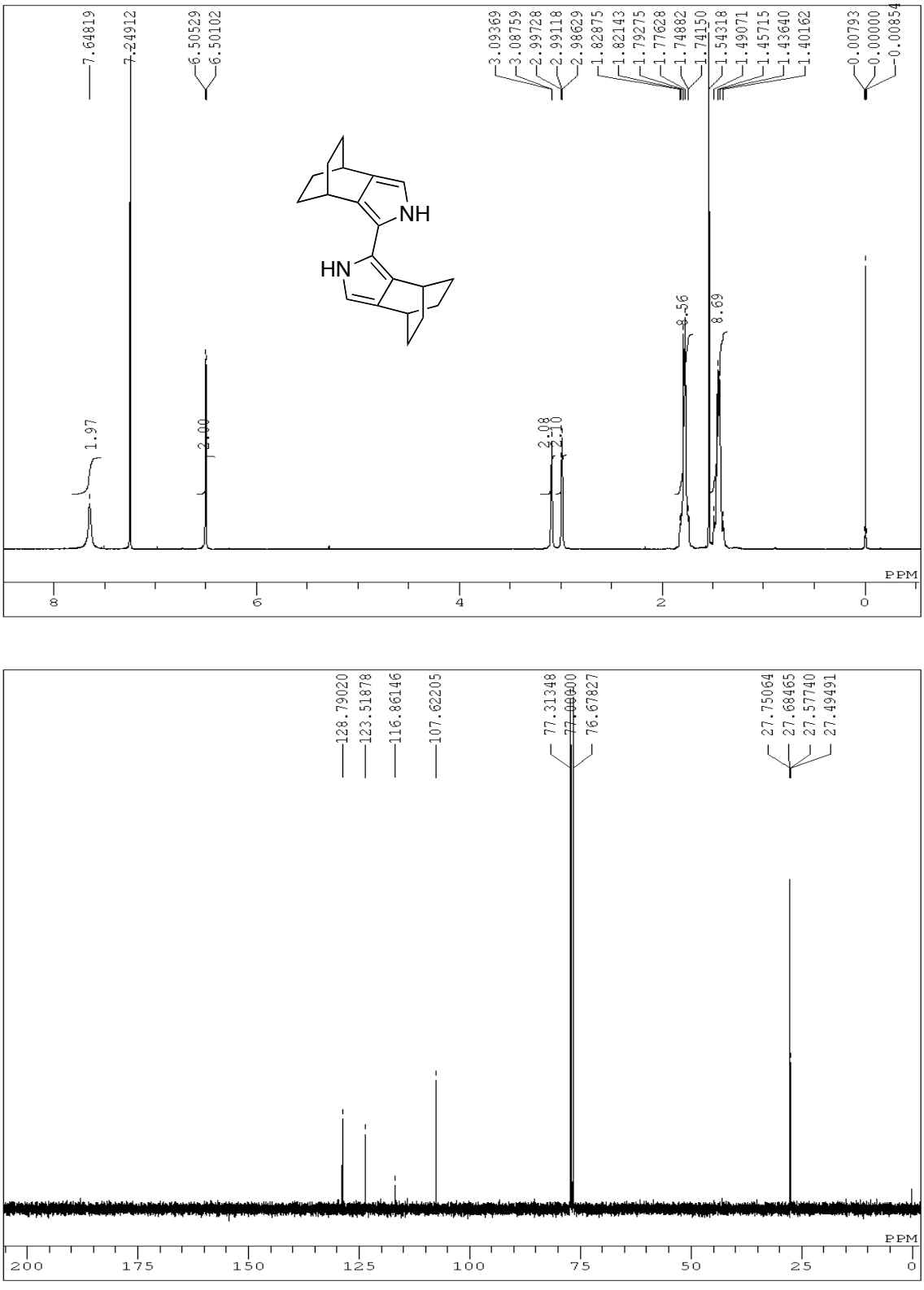


Figure S8. ^{1}H (upper) and ^{13}C (bottom) NMR spectra of 17 in $CDCl_3$.

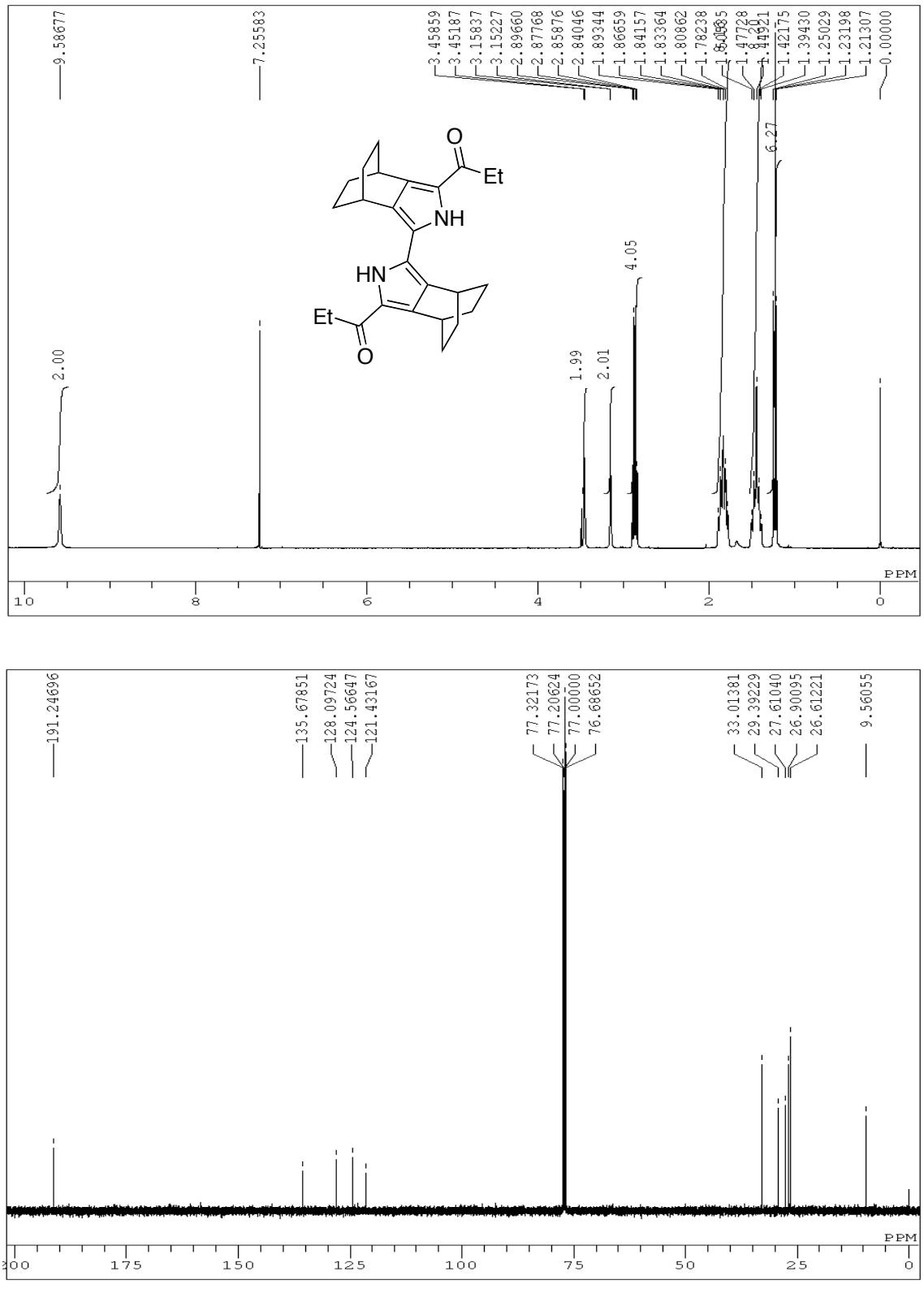


Figure S9. ^{1}H (upper) and ^{13}C (bottom) NMR spectra of 18 in $CDCl_3$.

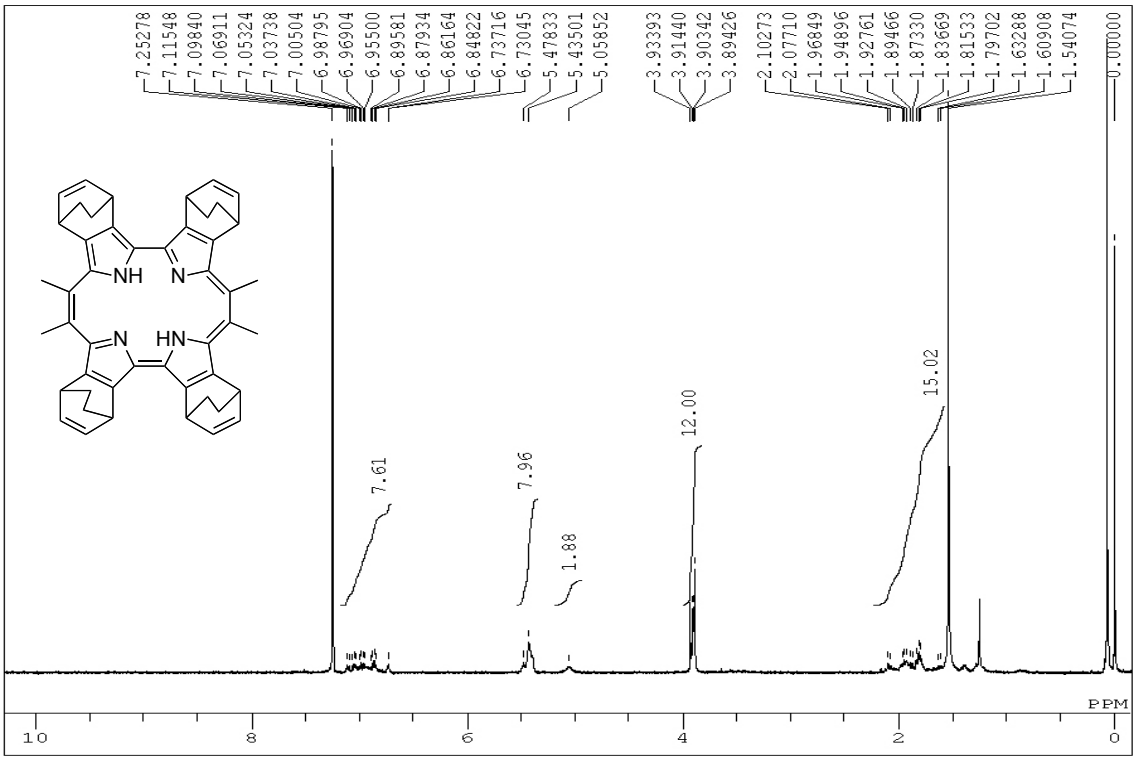


Figure S10. ^{1}H NMR spectrum of 1b in $CDCl_3$.

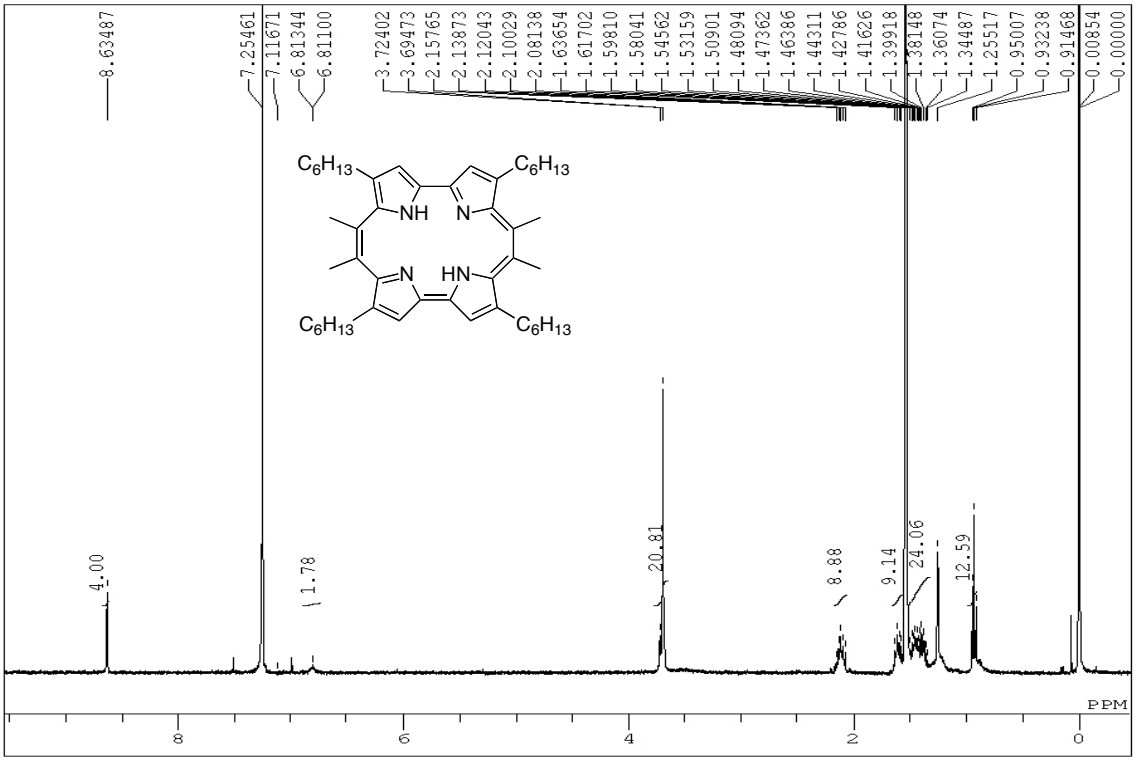


Figure S11. ^{1}H NMR spectrum of 3b in $CDCl_3$.

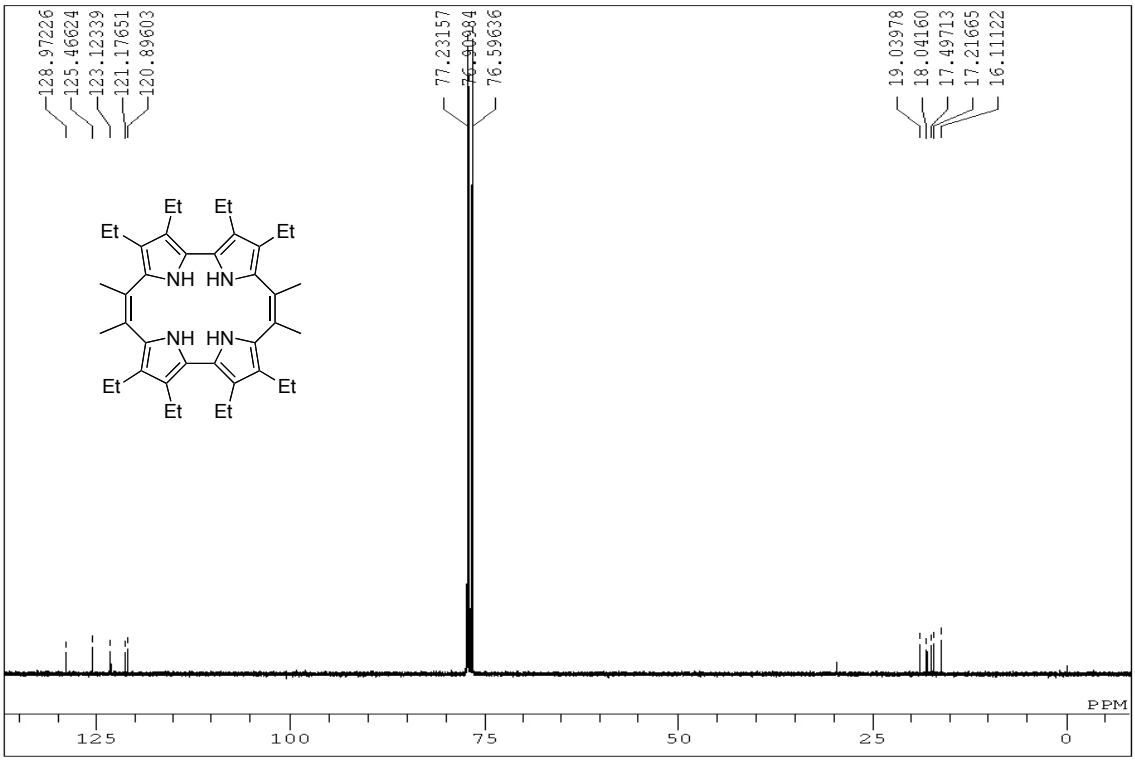


Figure S12. ^{13}C NMR spectrum of 5 in $CDCl_3$.