ELECTRONIC SUPPLEMENTARY INFORMATION

Phenylene Segment of Zigzag Carbon Nanotube Synthesized by Metal-mediated Dimerization

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Abbreviations table

CPP	Cycloparaphenylenes
CNT	Carbon nanotube
CPP[n]	Cycloparaphenylene with n para-phenylene units
CM2P[n]P	CycloMeta(2)Para(n)Phenylene
CN2P[n]P	CycloNaphthyl-2,7-ene(2)Para(n)Phenylene
SCXRD	Single Crystal X-Ray Diffraction
PLQY	Photoluminescence quantum yield
dcpm	Bis(dicyclohexylphosphino)methane
dppf	1,1'-Bis(diphenylphosphino)ferrocene
dba	Dibenzylideneacetone
Sphos	2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl

Experimental procedures and characterization data

General information

All the reactions were carried out under the Argon atmosphere. NMR spectra were acquired on a Bruker AVANCE III HD 500 MHz and Ascend 600 MHz spectrometer in the solvents indicated. Chemical shifts are expressed inn ppm units relatives to TMS (0.00 ppm, 1H). Mass spectra were recorded using a Bruker time of flight mass spectrometer coupled with matrix-assisted laser desorption/ionization source (MALDI-TOF). Silica gel (300-400 mesh) was used for column chromatography. UV/visible absorption spectra were recorded using a Shimadzu UV-2550 Spectrometer. Fluorescence measurements were carried out on FLS-980 Fluorescence Spectrophotometer.

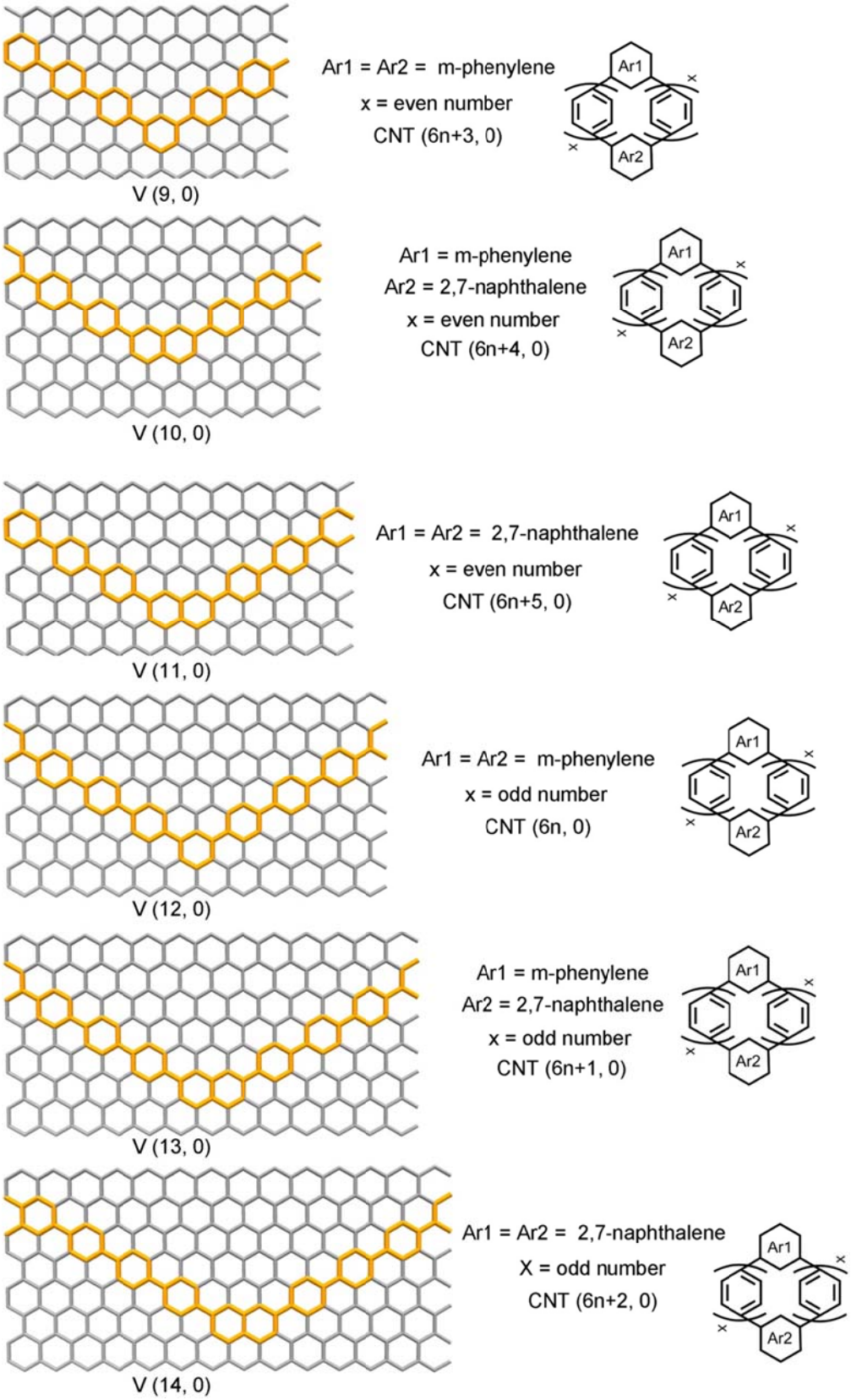


Figure S1. The phenylene macrocyclic segments of zigzag CNTs. Zigzag CNTs (N, 0) can be unzipped into a graphene sheet with a vector (N, 0). The phenylene macrocycles for zigzag CNTs can be summarized as macrocycles composed of two meta-arene **u**nits at opposite positions linked by two *para*-phenylene chains. The phenylene macrocycles of zigzag CNT(n,

0) are summarized as a molecular rosary with a general nomenclature, Cyclo-naphthyl-2,7-ene(h)-meta(k)-para(2x)-phenylene (CM[h]N[k]P[2x]P), with x = [[n/3]]-1, h = 2 – k, k = n – 3[[n/3]]. [[n/3]] denotes the integer part of n/3 and x denotes the number of *para*-phenylene beads "P" that is separated and connected by h (= 0, 1 or 2) m-phenylene beads "M" and k (= 2, 1 or 0) naphthyl-2,7-ene beads "N".

Mass Spectra

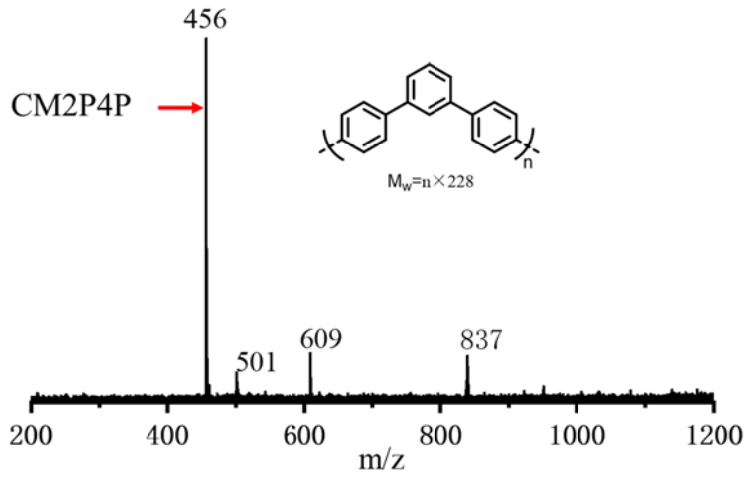


Figure S2. MALDI-TOF-MS spectrum of crude product of **CM2P4P**.

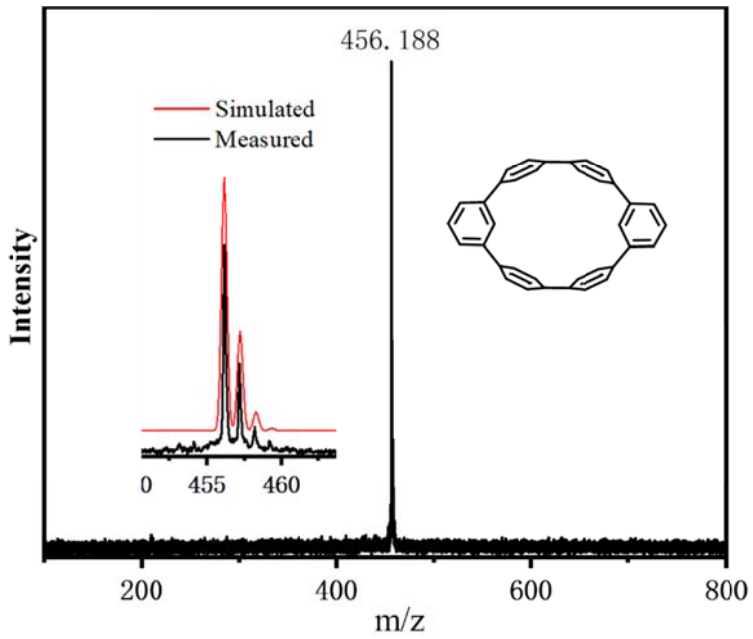


Figure S3. MALDI-TOF-MS spectrum of **CM2P4P**.

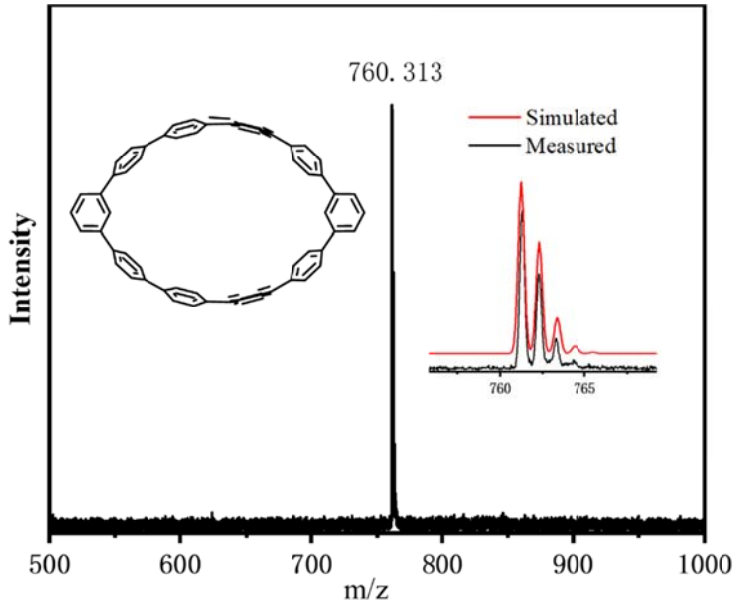


Figure S4. MALDI-TOF-MS spectrum of **CM2P8P**.

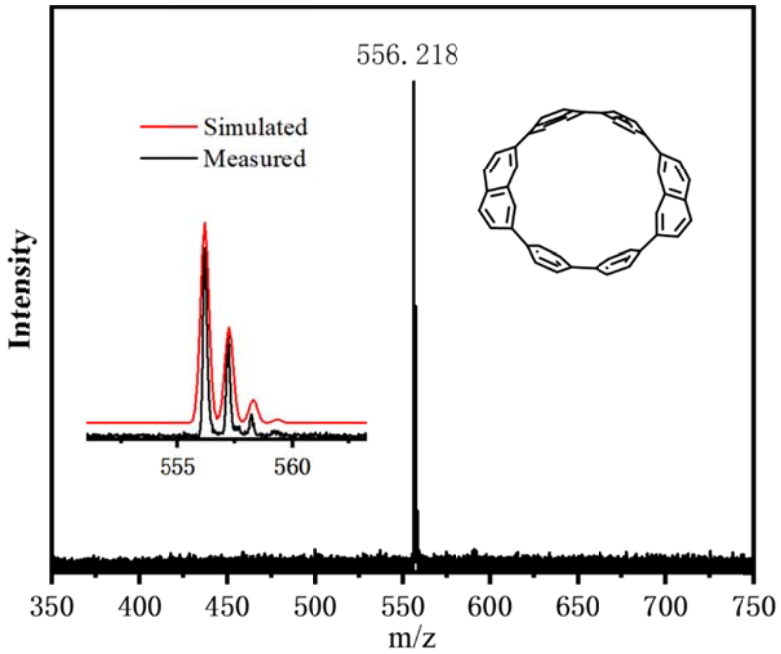


Figure S5. MALDI-TOF-MS spectrum of **CN2P4P**.

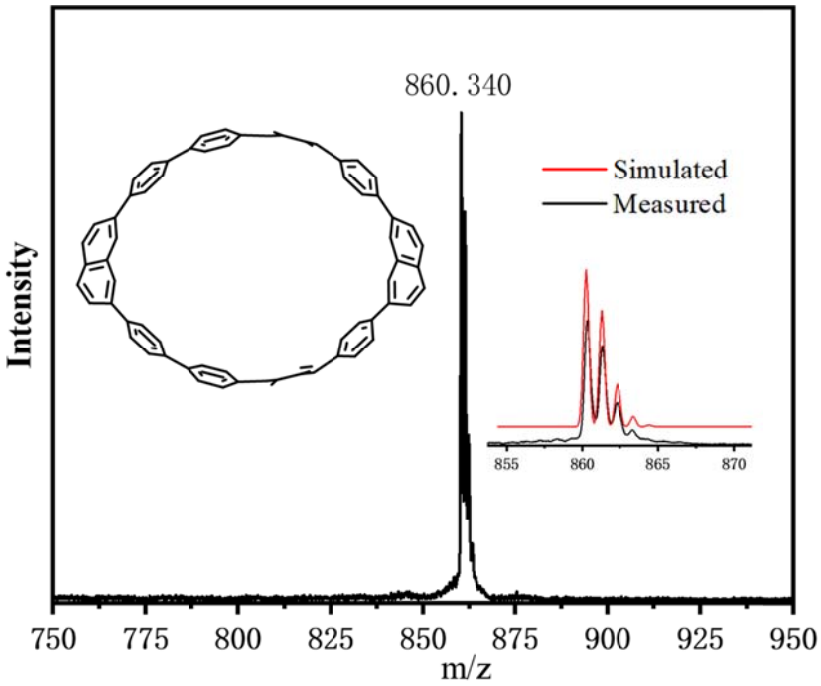
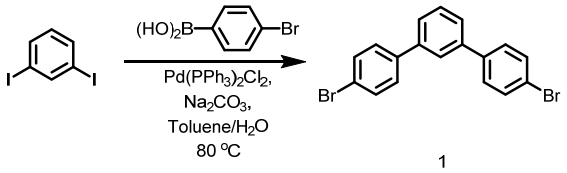


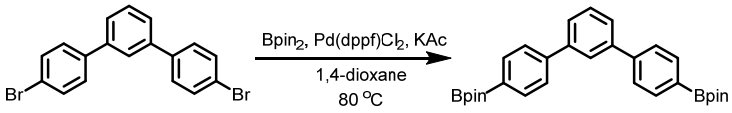
Figure S6. MALDI-TOF-MS spectrum of **CN2P8P**.

Synthetic details



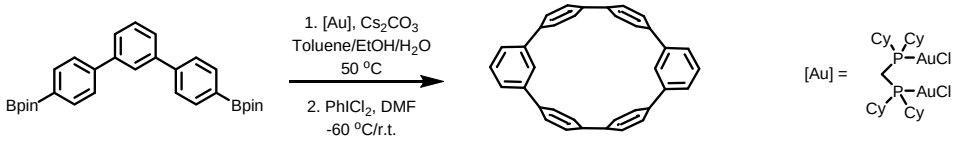
1

Compound 1. 1,3-Diiodobenzene (1.65 g, 5mmol, 1 equiv), 4-Bromophenylboronic acid (2.21 g, 11 mmol, 2.2 equiv), Na_2CO_3 (1.86 g, 17.5 mmol, 3.5 equiv), $Pd(PPh_3)_2Cl_2$ (175 mg, 0.25 mmol, 0.05 equiv), Toluene/H_2O (66 mL/22 mL) were added to a 200 mL Schlenk flask. Then the mixture was stirred at 80 °C for 12 h under argon. After cooling down to room temperature, water was added and the mixture was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane) to afford the product **1** as white solid (1.57 g, 81% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.67 (s, 1H), 7.47 (dd, *J* = 21.5, 10.9 Hz, 11H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.61, 139.86, 131.90, 129.50, 128.83, 126.23, 125.53, 121.67.



1 2

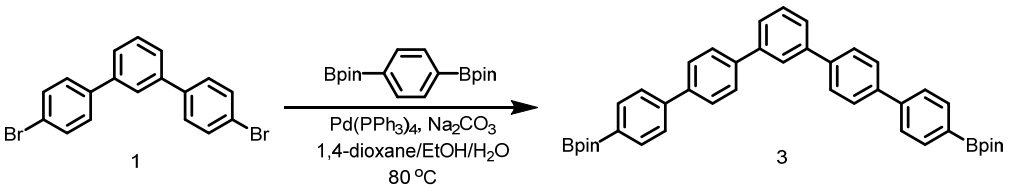
Compound 2. 1 (1.0 g, 2.58mmol, 1 equiv), bis(pinacolate)diboron (1.96 g, 7.73 mmol, 3 equiv), KOAc (1.06 g, 12.88 mmol, 5 equiv), $Pd(dppf)Cl_2$ (95 mg, 0.13 mmol, 0.05 equiv) and 1,4-dioxane (26 mL) were added to a 100 mL Schlenk flask. The mixture was stirred at 80 °C for 12 h under argon. After cooling down to room temperature, the mixture was filtered through a short pad of silica gel and washed with CH_2Cl_2. After evaporation of the filtrate, the residue was recrystallized from CH_2Cl_2/CH_3OH to afford the product **2** as white solid (0.86 g, 69% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.81–7.75 (m, 5H), 7.60 (d, *J* = 8.1 Hz, 4H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 15.3 Hz, 1H), 1.27 (s, 24H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.82, 141.67, 135.32, 129.23, 127.64, 126.58, 126.51, 126.25, 83.86, 24.90.



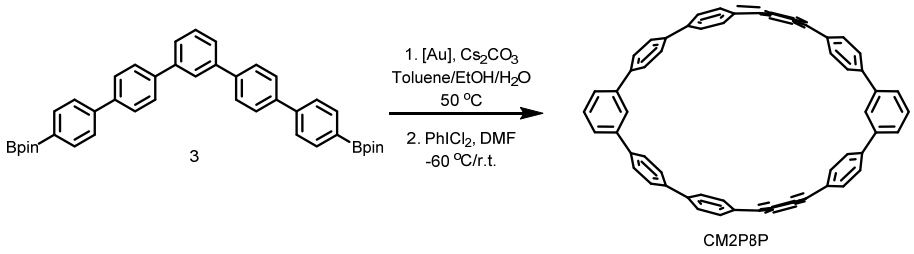
2 CM2P4P

CM2P4P. 2 (200 mg, 0.41 mmol, 1 equiv), $[Au_2Cl_2(dcpm)]$ (358 mg, 0.41 mmol, 1 equiv), Cs_2CO_3 (800 mg, 2.46 mmol, 6 equiv) and degassed toluene/EtOH/H_2O (16 mL /4 mL /4 mL) were added to a 100 mL Schlenk flask. The mixture was stirred at 50 °C for 24 h under argon. After cooling down to room temperature, the mixture was poured into MeOH (100mL) and the precipitates was collected and washed with water and methanol, then dried in vacuum. The off-white solid containing Au-intermediate (386 mg) was transferred to a 500 mL Schlenk flask. Degassed DMF (180 mL) as added under argon. The suspension was stirred at

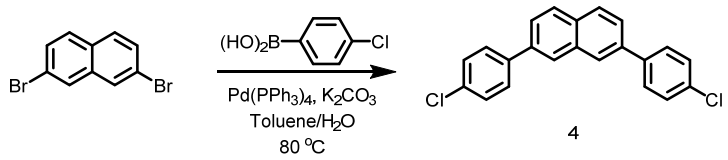
-60 °C for 10 minutes. Then the solution of $PhICl_2$ (103 mg, 0.38 mmol) in degassed DMF (63 mL) was added dropwise. The reaction mixture was stirred at the same temperature for 30 min, then it was allowed to warm to room temperature and stirred for 25 h. Solvent were removed under vacuum. The mixture was washed with water and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (Hexane/CH_2Cl_2 = 2:1) followed by recycle preparative HPLC (eluent: $CHCl_3$). **CM2P4P** was collected as white solid (30 mg, 31% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.49 (dd, *J* = 6.8, 1.6 Hz, 4H), 7.44 (dd, *J* = 12.1, 5.2 Hz, 10H), 7.17 (d, *J* = 8.5 Hz, 8H), 5.50 (s, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 142.84, 141.48, 141.37, 139.40, 129.51, 129.31, 127.48, 122.24. MALDI-TOF-MS m/z calcd. for $C_{36}H_{24}$, 456.1872; found 456.188.



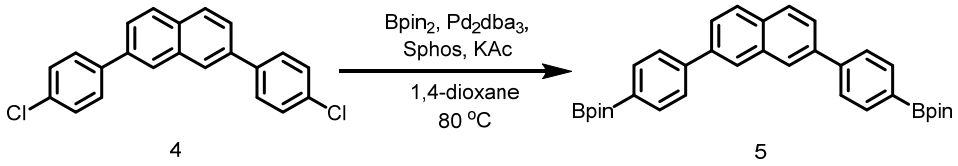
Compound 3. 1 (1.44 g, 3.72 mmol, 1 equiv), 1,4-Benzenediboronic acid bis(pinacol) ester (12.27 g, 37.2 mmol, 10 equiv), Na_2CO_3 (5.91 g, 55.8 mmol, 15 equiv), $Pd(PPh_3)_4$ (427 mg, 0.37 mmol, 0.1 equiv) and 1,4-dioxane/EtOH/H_2O (40 mL/28 mL/28 mL) were added to a 200 mL Schlenk flask. Then the mixture was stirred at 80 °C for 12 h under argon. After cooling down to room temperature, the mixture was washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/CH_2Cl_2 = 2:1) to afford crude product. The crude product was washed by a large amount of MeOH to removed extra 1,4-Benzenediboronic acid bis(pinacol) ester. After filtering and drying, product **3** (0.99 g, 42% yield) was collected as white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.93 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 4H), 7.76 (q, *J* = 8.5 Hz, 8H), 7.70–7.63 (m, 6H), 7.57–7.53 (m, 1H), 1.34 (s, 24H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 144.80, 143.04, 141.17, 140.26, 139.92, 135.19, 129.36, 127.56, 127.51, 126.19, 126.09, 125.68, 83.84, 24.67.



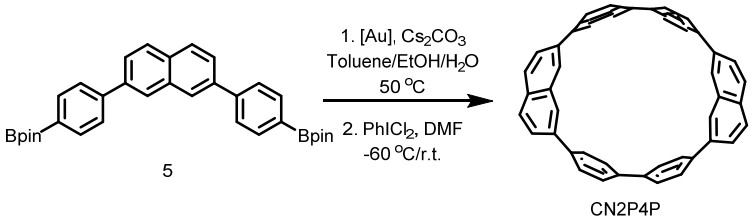
CM2P8P. The general procedure from the synthesis of **CM2P4P** was followed, delivering 70 mg (16 %) of **CM2P8P** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 8H), 7.62–7.59 (m, 4H), 7.54 (dd, *J* = 8.2, 1.7 Hz, 18H), 7.42 (d, *J* = 8.3 Hz, 8H), 6.66 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.54, 141.42, 139.51, 139.33, 138.31, 135.28, 130.04, 128.75, 127.68, 127.31, 127.11, 123.84. MALDI-TOF-MS m/z calcd. for $C_{60}H_{40}$, 760.3124; found 760.313.



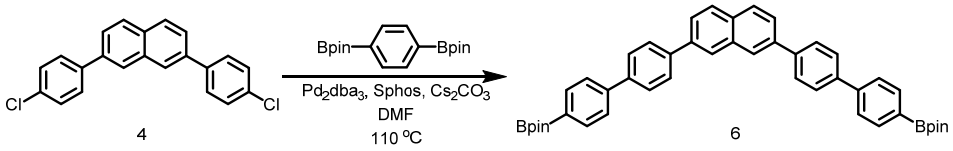
Compound 4. 2,7-Dibromonaphthalene (2.86 g, 10 mmol, 1 equiv), 4-Chlorophenylboronic acid (4.68 g, 30 mmol, 3 equiv), K_2CO_3 (5.52g, 40 mmol, 4 equiv), $Pd(PPh_3)_4$ (577 mg, 0.5mmol, 0.05 equiv) and Toluene/H_2O (100 mL/20 mL) were added to a 200 mL Schlenk flask. Then the mixture was stirred at 90 °C for 7 h under argon. After cooling down to room temperature, water was added and the mixture was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane) to afford the product **4** as white solid (3.24 g, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.71 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 4H), 7.47 (d, *J* = 8.5 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.44, 137.96, 133.85, 133.65, 131.96, 129.07, 128.63, 128.39, 126.01, 125.55.



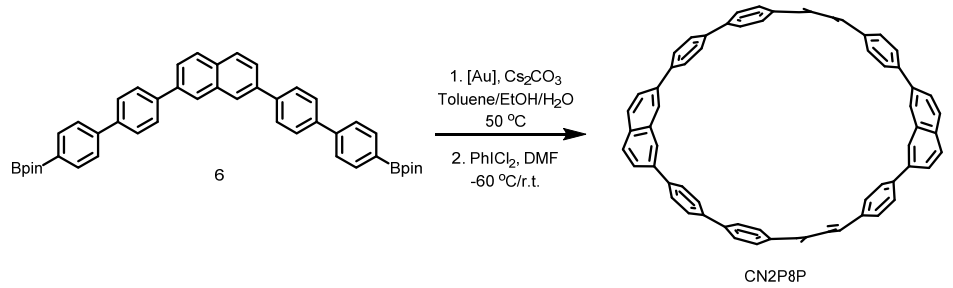
Compound 5. 4 (525 mg, 1.5mmol, 1 equiv), bis(pinacolate)diboron (1.53 g, 6 mmol, 4 equiv), KOAc (735 g, 7.5 mmol, 5 equiv), Pd_2dba_3 (70 mg, 0.075 mmol, 0.05 equiv), Sphos (62 mg, 0.15mmol, 0.1 equiv) and 1,4-dioxane (15 mL) were added to a 100 mL Schlenk flask. The mixture was stirred at 80 °C for 12 h under argon. After cooling down to room temperature, the mixture was filtered through a short pad of silica gel and washed with CH_2Cl_2. After evaporation of the filtrate, the residue was recrystallized from CH_2Cl_2/CH_3OH to afford the product **3** as white solid (585 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.94 (d, *J* = 8.1 Hz, 6H), 7.77 (t, *J* = 8.1 Hz, 6H), 1.38 (s, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.69, 138.80, 135.38, 133.90, 132.11, 128.20, 126.70, 126.38, 125.76, 83.89, 24.91.



CN2P4P. The general procedure from the synthesis of **CM2P4P** was followed, delivering 20 mg (19%) of **CN2P4P** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 4H), 7.72 (d, *J* = 8.5 Hz, 4H), 7.58 (d, *J* = 8.5 Hz, 8H), 7.36 (d, *J* = 8.4 Hz, 8H), 6.97 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.90, 139.65, 138.44, 134.28, 134.01, 130.69, 128.53, 128.19, 127.06, 123.08. MALDI-TOF-MS m/z calcd. for $C_{44}H_{28}$, 556.2186; found 556.218.



Compound 6. 4 (696 mg, 2 mmol, 1 equiv), 1,4-Benzenediboronic acid bis(pinacol) ester (6.6 g, 20 mmol, 10 equiv), Cs_2CO_3 (7.8 g, 24 mmol, 12 equiv), Pd_2dba_3 (183 mg, 0.2 mmol, 0.1 equiv), Sphos (164 mg, 0.4 mmol, 0.2 equiv) and DMF (20 mL) were added to a 50 mL Schlenk flask. Then the mixture was stirred at 110 °C for 12 h under argon. After cooling down to room temperature, the mixture was washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/CH_2Cl_2 = 2:1) to afford crude product. The crude product was washed by a large amount of MeOH to removed extra 1,4-Benzenediboronic acid bis(pinacol) ester. After filtering and drying, product **6** (747 mg, 55% yield) was collected as white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 4H), 7.84 (d, *J* = 8.3 Hz, 4H), 7.81 (d, *J* = 7.1 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 4H), 7.69 (d, *J* = 8.0 Hz, 4H), 1.38 (s, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.32, 140.27, 140.07, 138.50, 135.36, 134.01, 131.94, 128.29, 127.79, 127.72, 126.37, 126.04, 125.63, 83.88, 24.91.



CN2P8P. The general procedure from the synthesis of **CM2P8P** was followed, delivering 33 mg (12%) of **CN2P8P** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 4H), 7.78 (d, *J* = 8.5 Hz, 4H), 7.69 (d, *J* = 8.4 Hz, 8H), 7.65 (dd, *J* = 8.2, 4.2 Hz, 16H), 7.55 (d, *J* = 8.3 Hz, 8H), 7.44 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.22, 139.64, 139.34, 139.18, 138.49, 133.63, 131.25, 130.77, 128.48, 127.93, 127.59, 127.33, 127.26, 124.10. MALDI-TOF-MS m/z calcd. for $C_{68}H_{44}$, 860.3437; found 860.340.

NMR Spectra

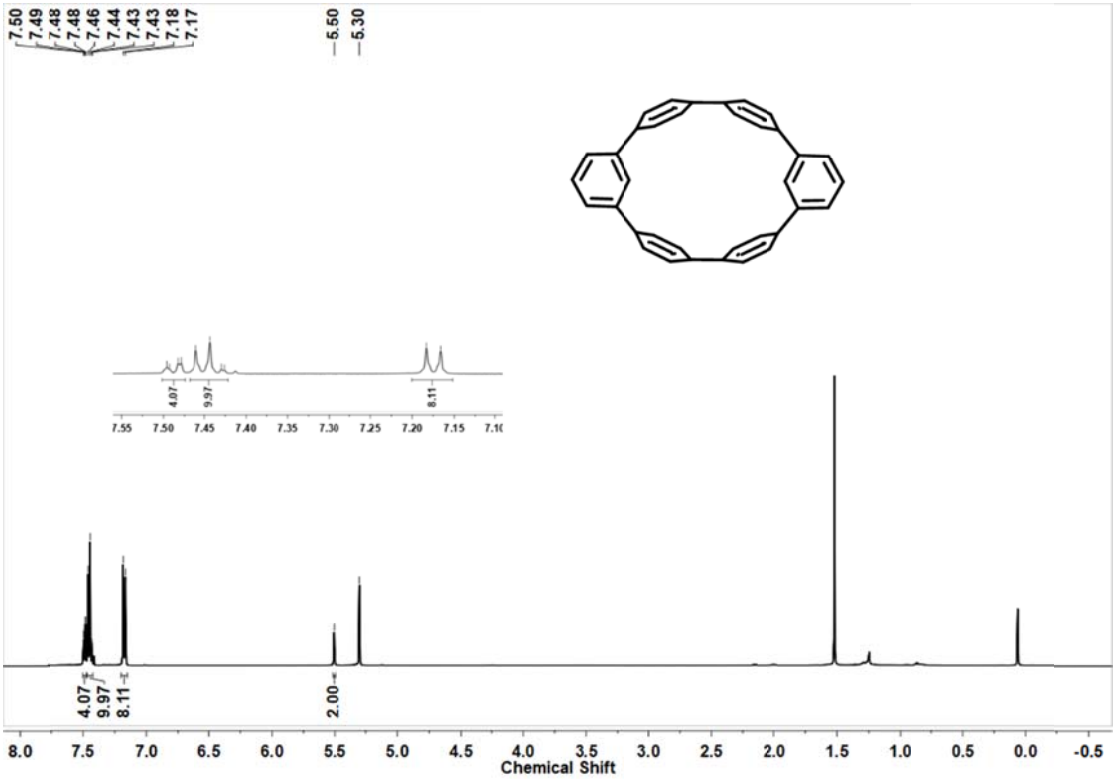


Figure S7. ^{1}H NMR spectrum of **CM2P4P** in CD_2Cl_2.

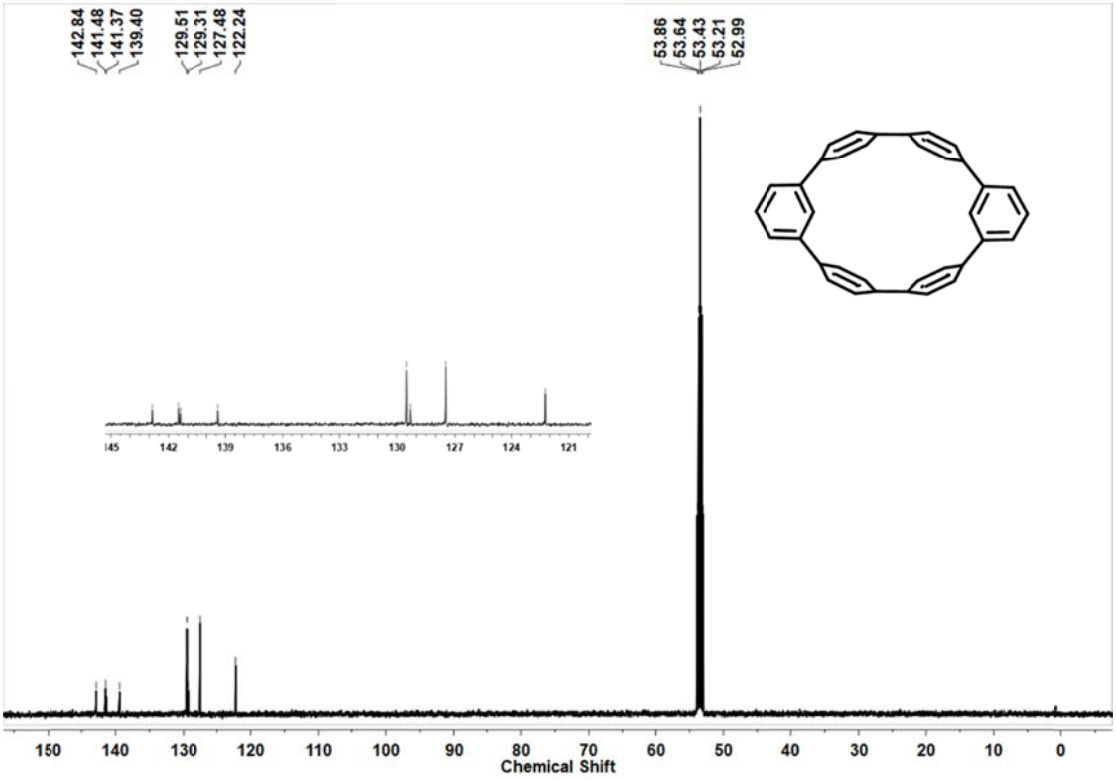


Figure S8. ^{13}C NMR spectrum of **CM2P4P** in CD_2Cl_2.

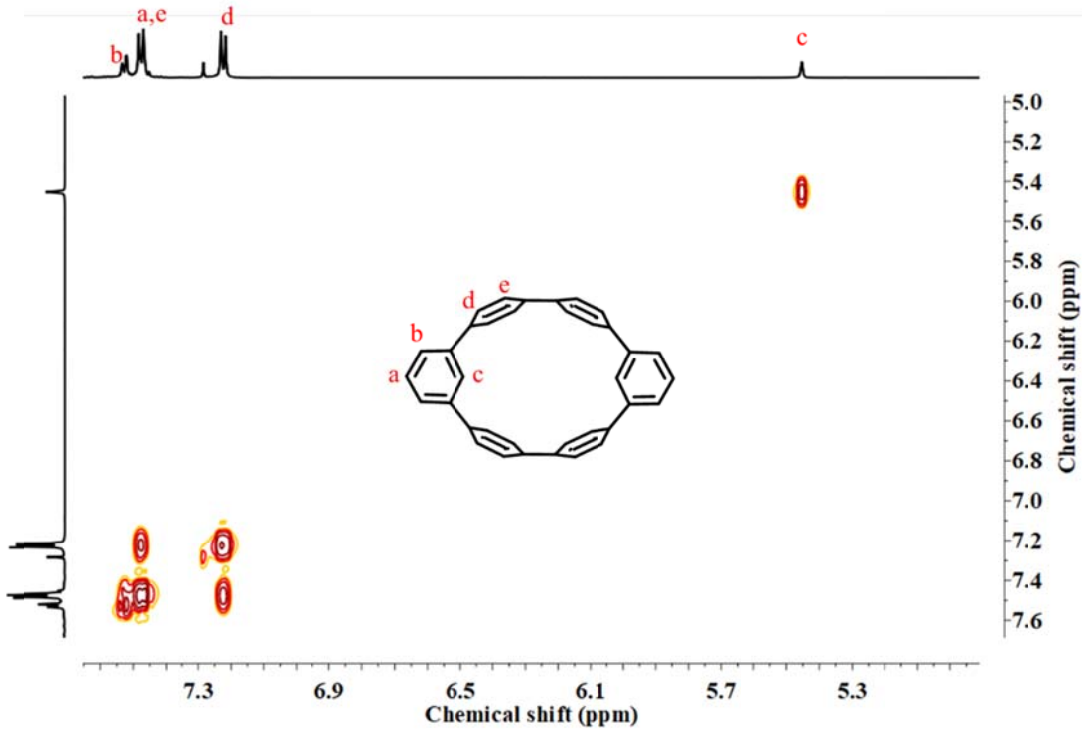


Figure S9. ^{1}H-^{1}H COSY NMR spectrum of **CM2P4P** in $CDCl_3$.

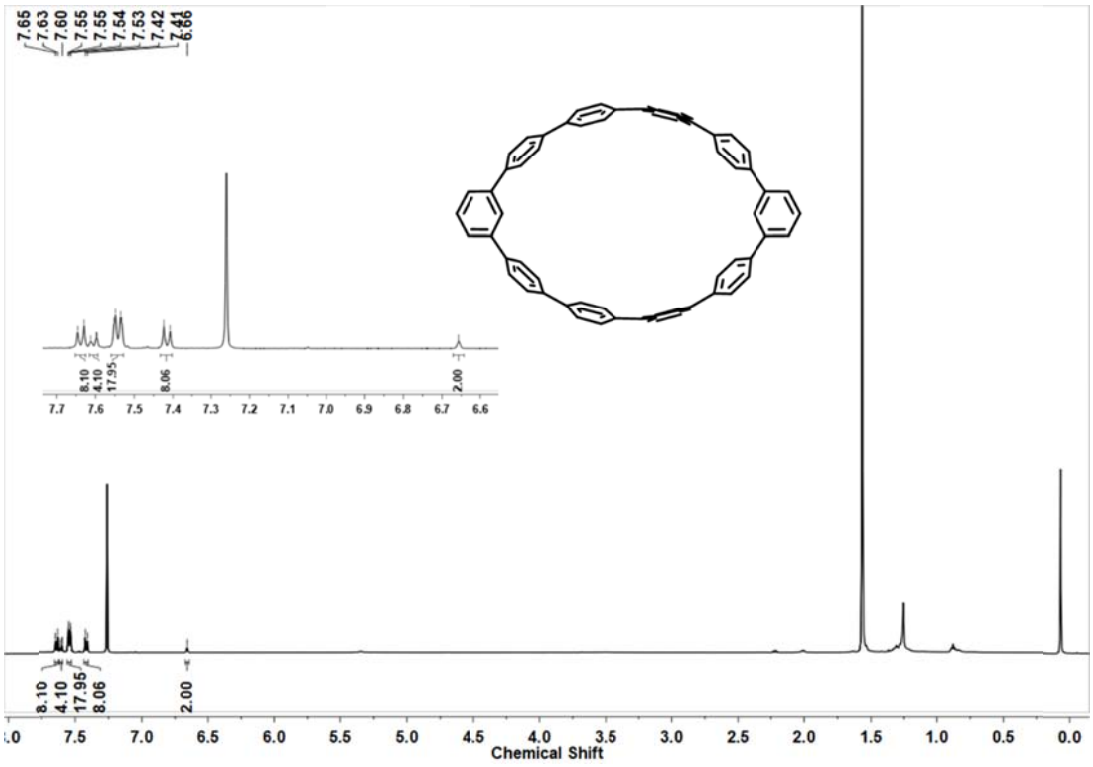


Figure S10. ^{1}H NMR spectrum of **CM2P8P** in $CDCl_3$.

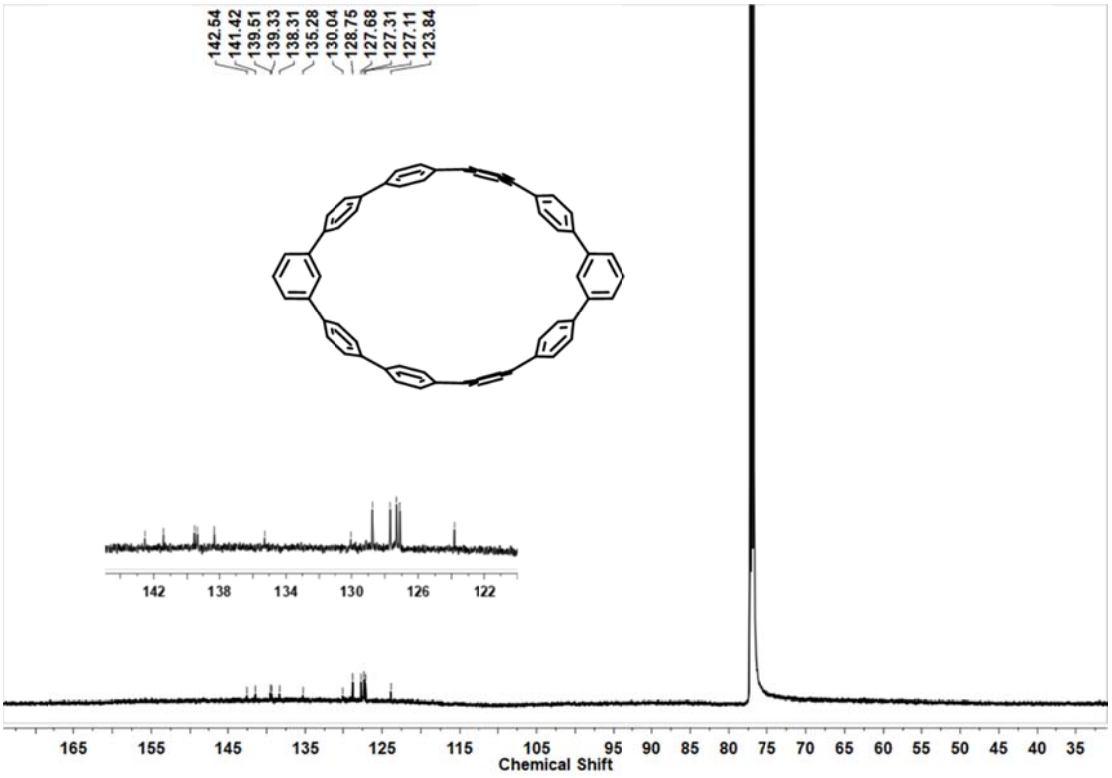


Figure S11. ^{13}C NMR spectrum of **CM2P8P** in $CDCl_3$.

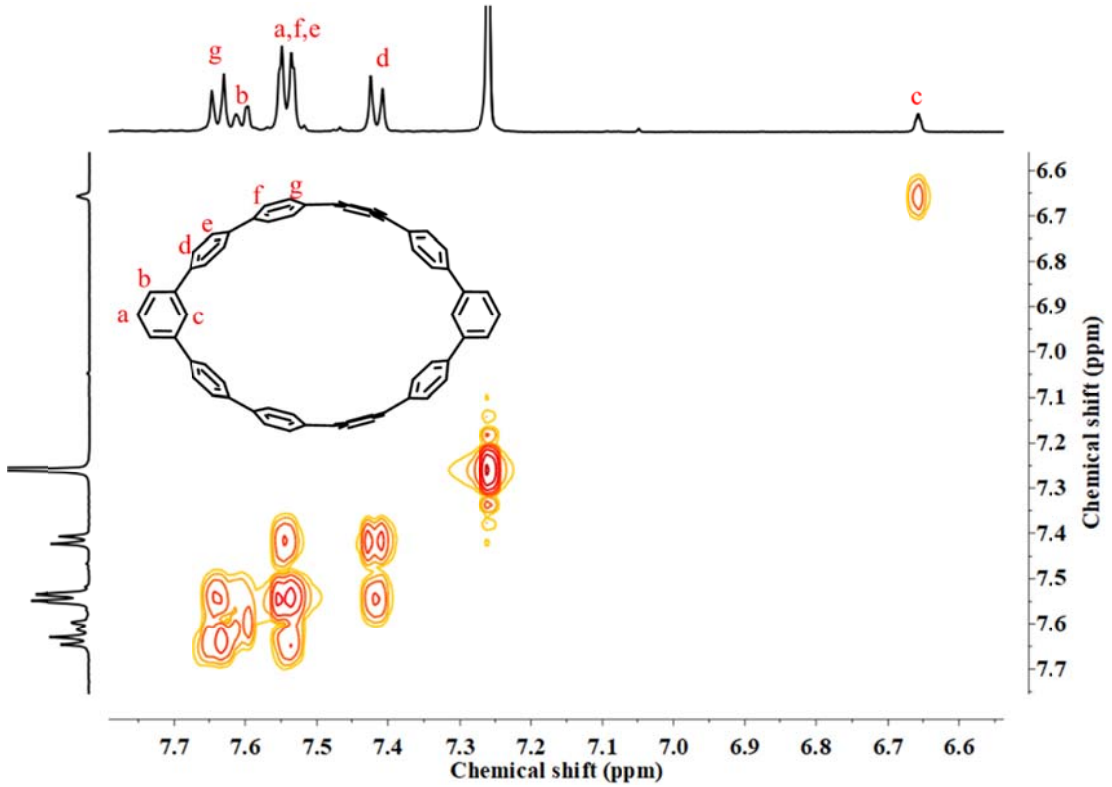


Figure S12. ^{1}H-^{1}H COSY NMR spectrum of **CM2P8P** in $CDCl_3$.

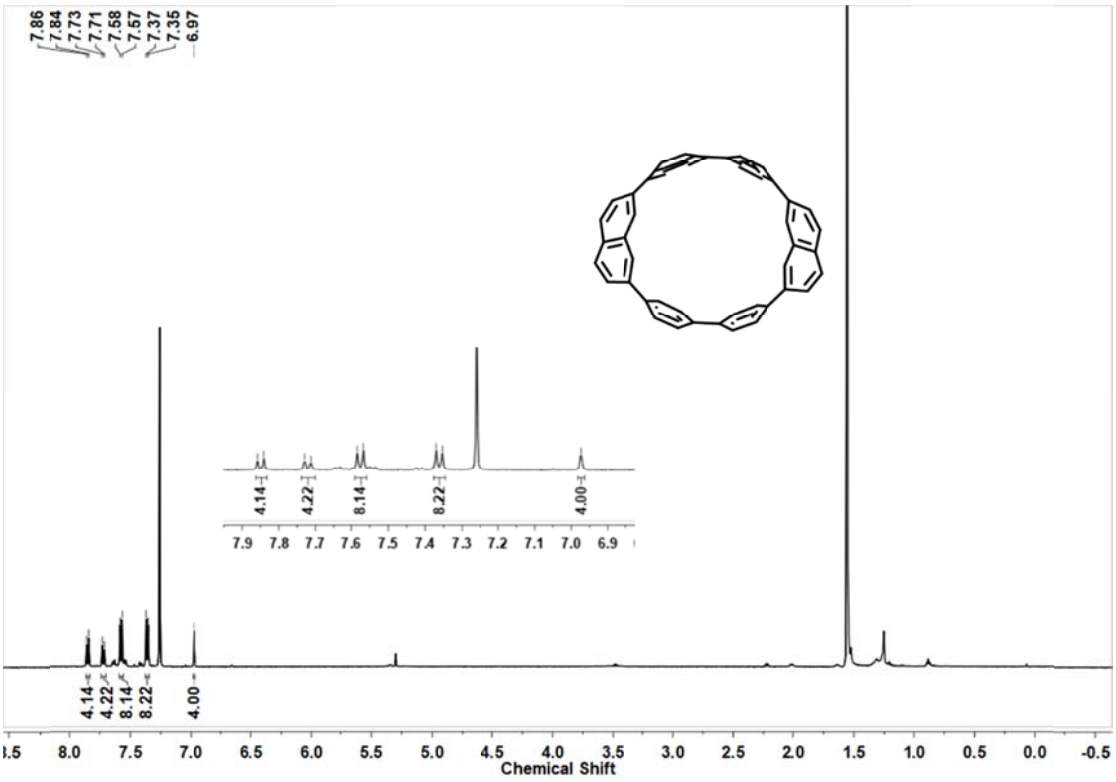


Figure S13. ^{1}H NMR spectrum of **CN2P4P** in $CDCl_3$.

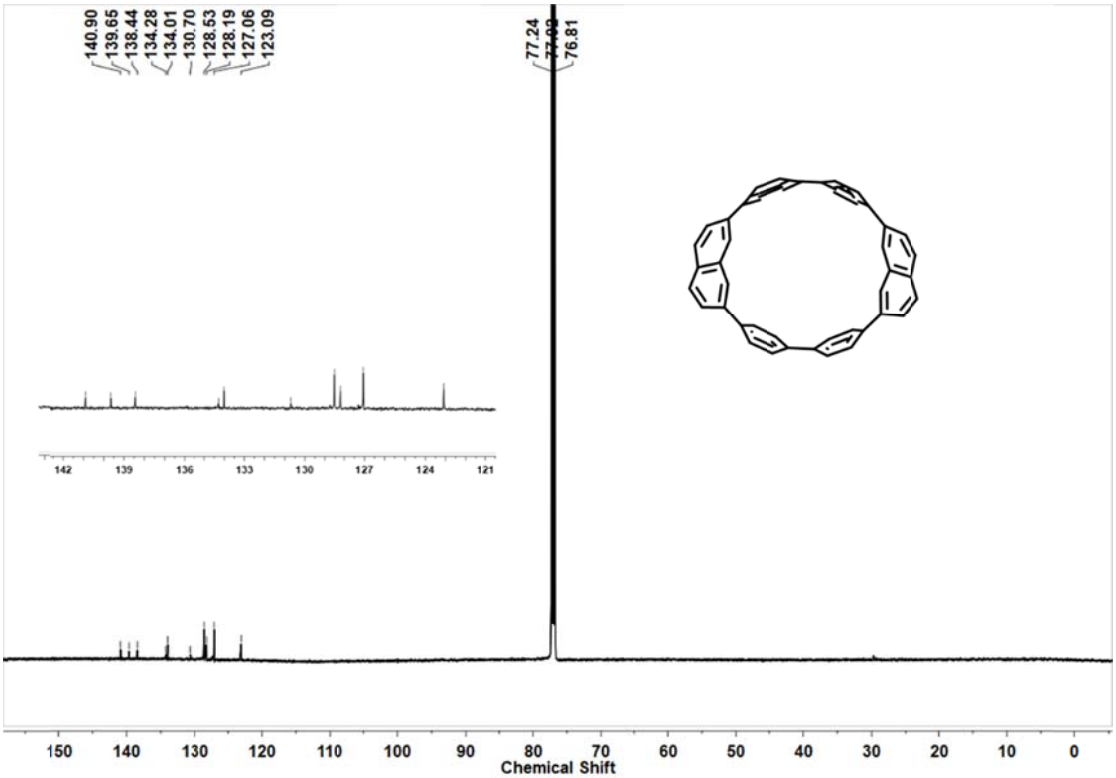


Figure S14. ^{13}C NMR spectrum of **CN2P4P** in $CDCl_3$.

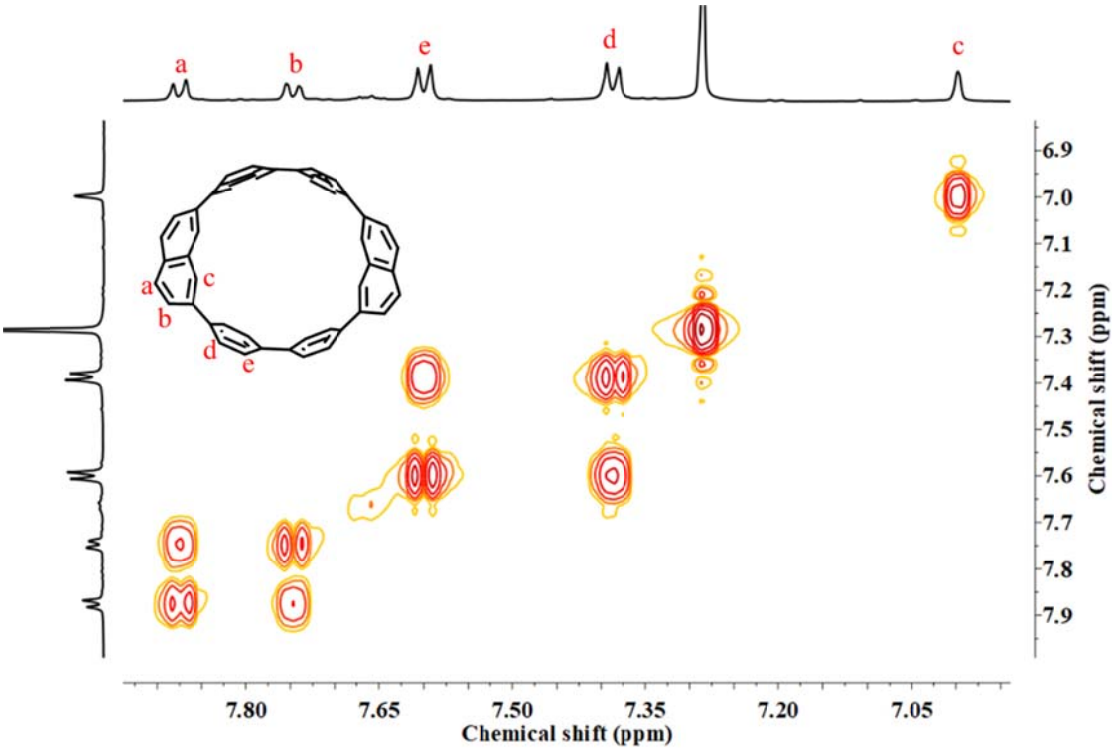


Figure S15. ^{1}H-^{1}H COSY NMR spectrum of **CN2P4P** in $CDCl_3$.

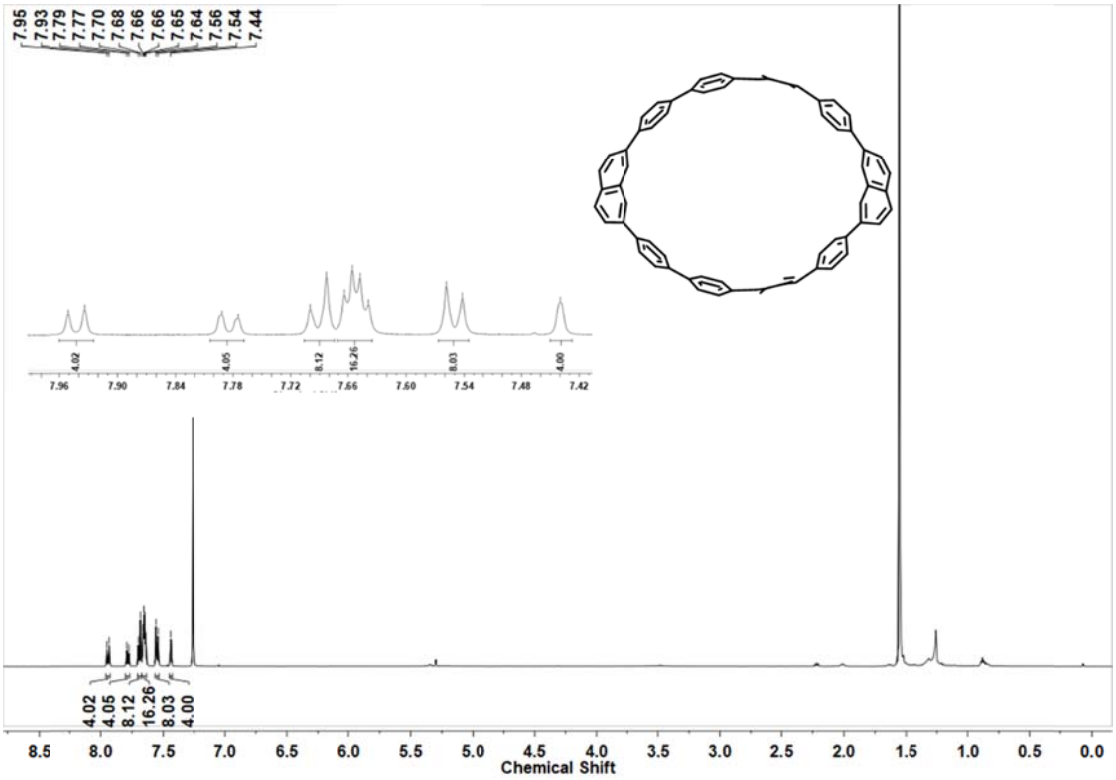


Figure S16. ^{1}H NMR spectrum of **CN2P8P** in $CDCl_3$.

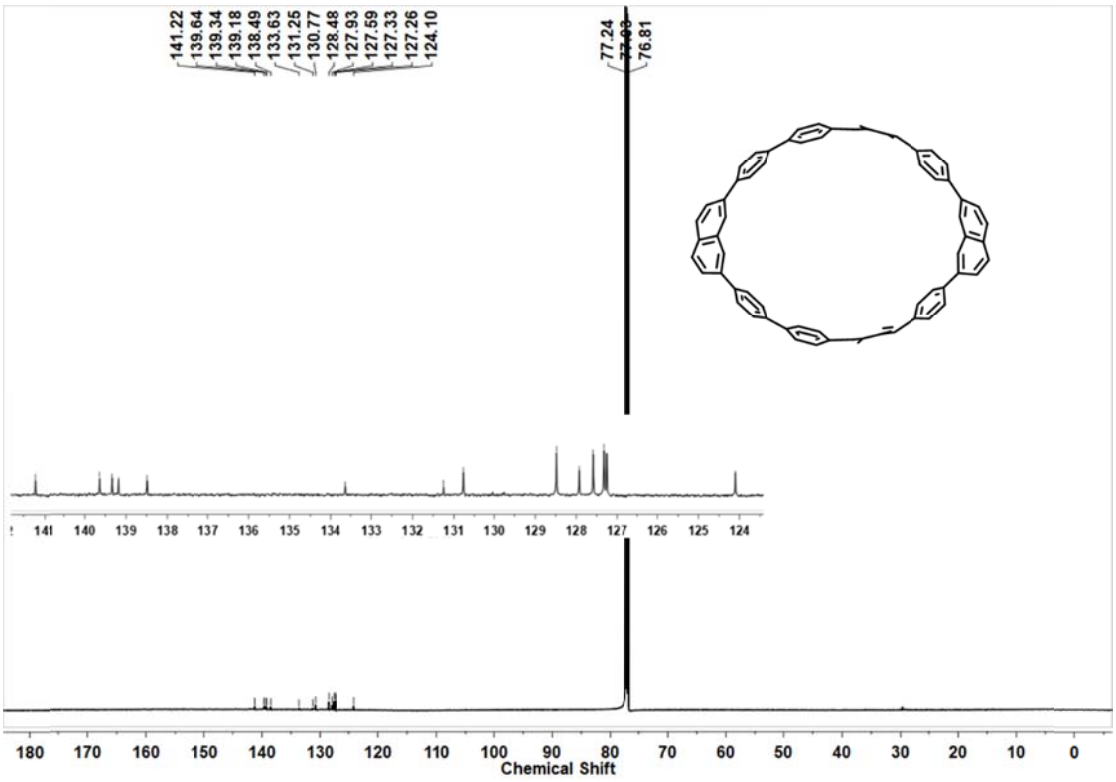


Figure S17 ^{13}C NMR spectrum of **CN2P8P** in $CDCl_3$.

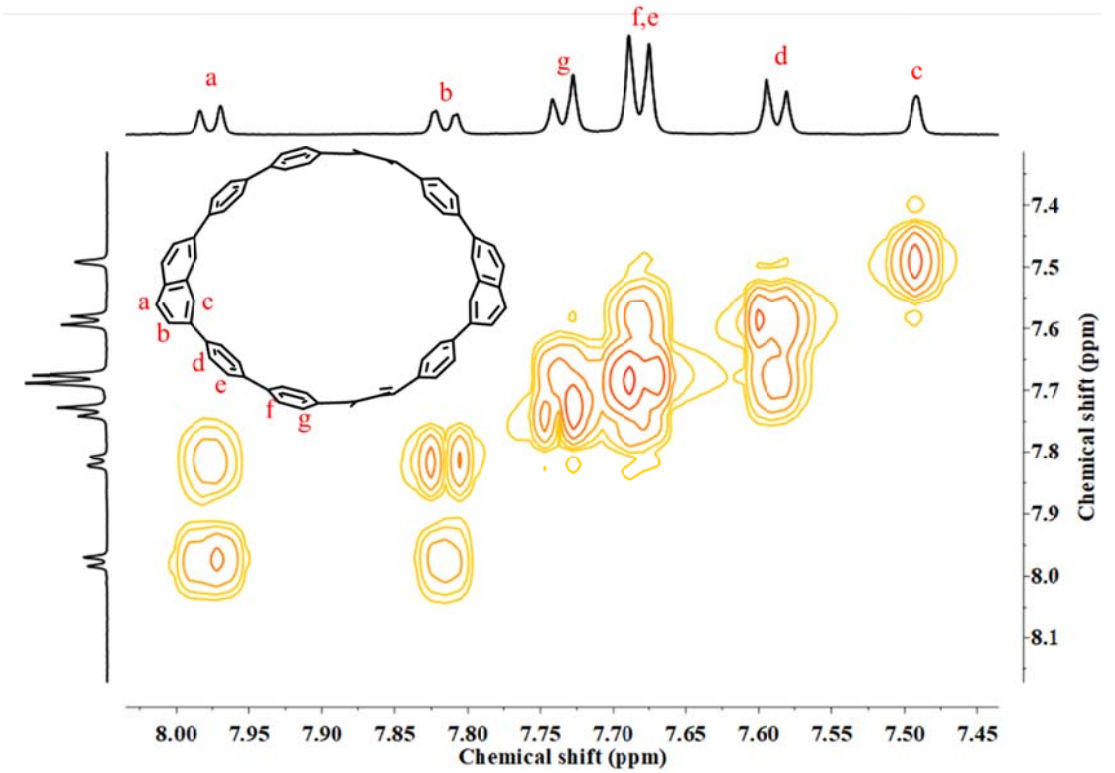


Figure S18. ^{1}H-^{1}H COSY NMR spectrum of **CN2P8P** in 1,1,2,2-tetrachloroethane-d2.

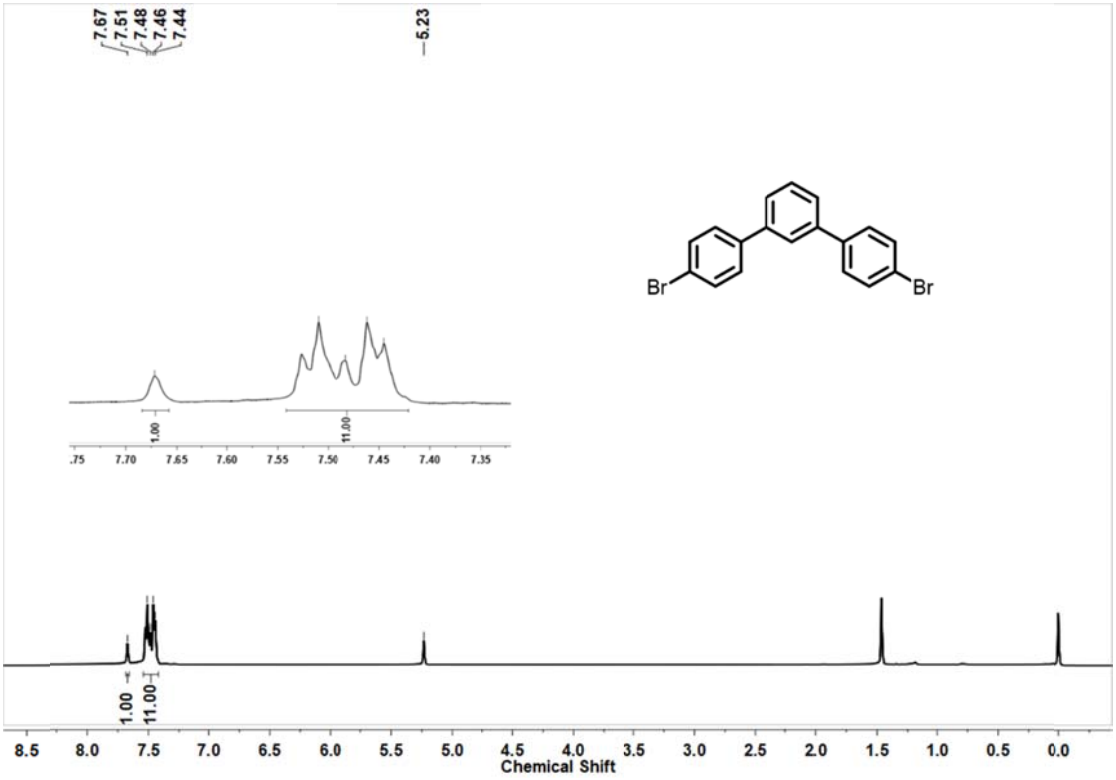


Figure S19. ^{1}H NMR spectrum of compound **1** in CD_2Cl_2.

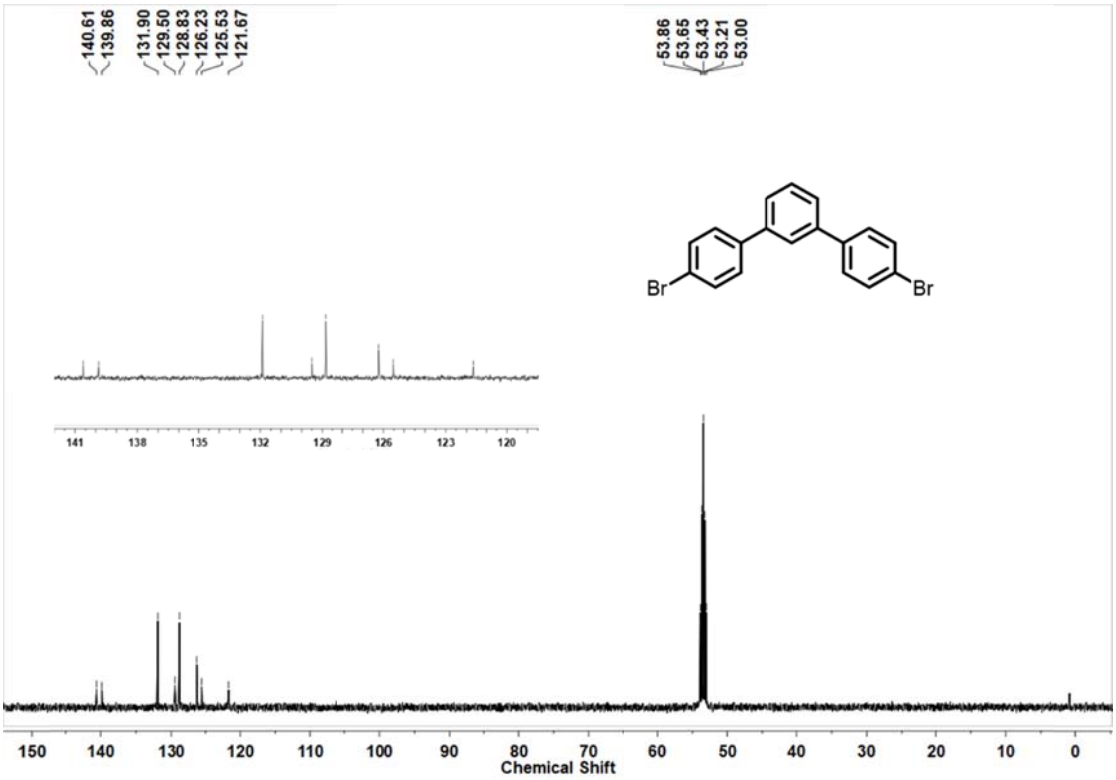


Figure S20. ^{13}C NMR spectrum of compound **1** in CD_2Cl_2.

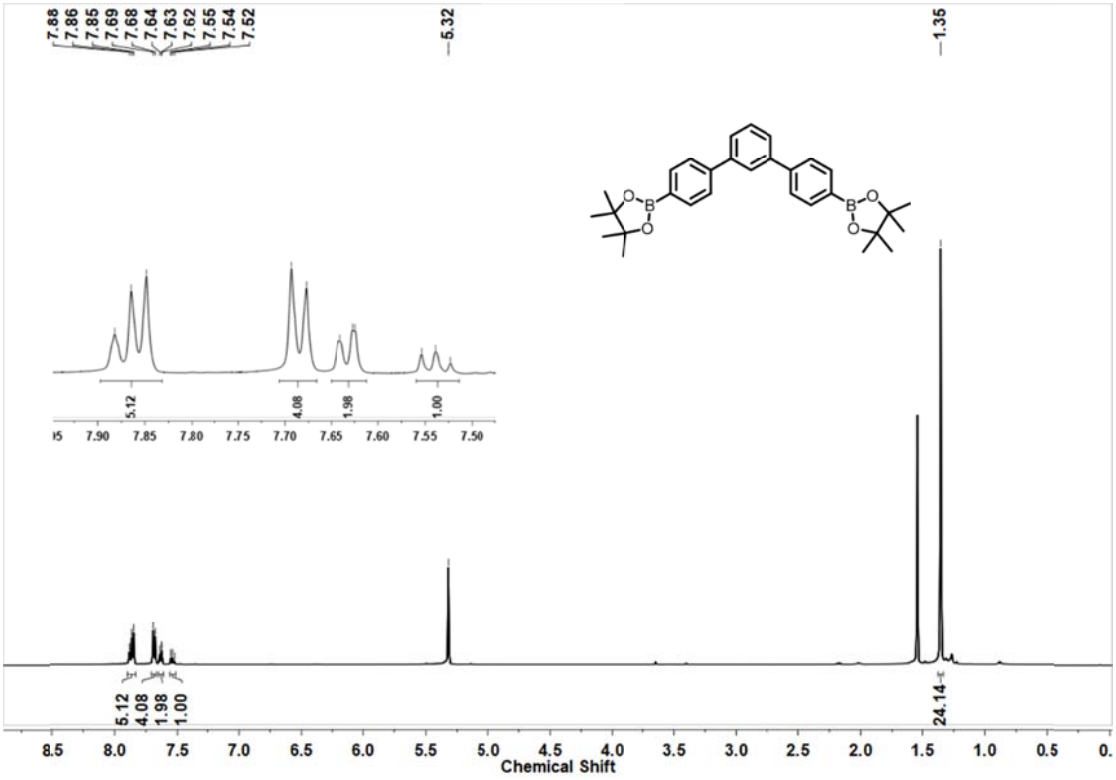


Figure S21. ^{1}H NMR spectrum of compound **2** in CD_2Cl_2.

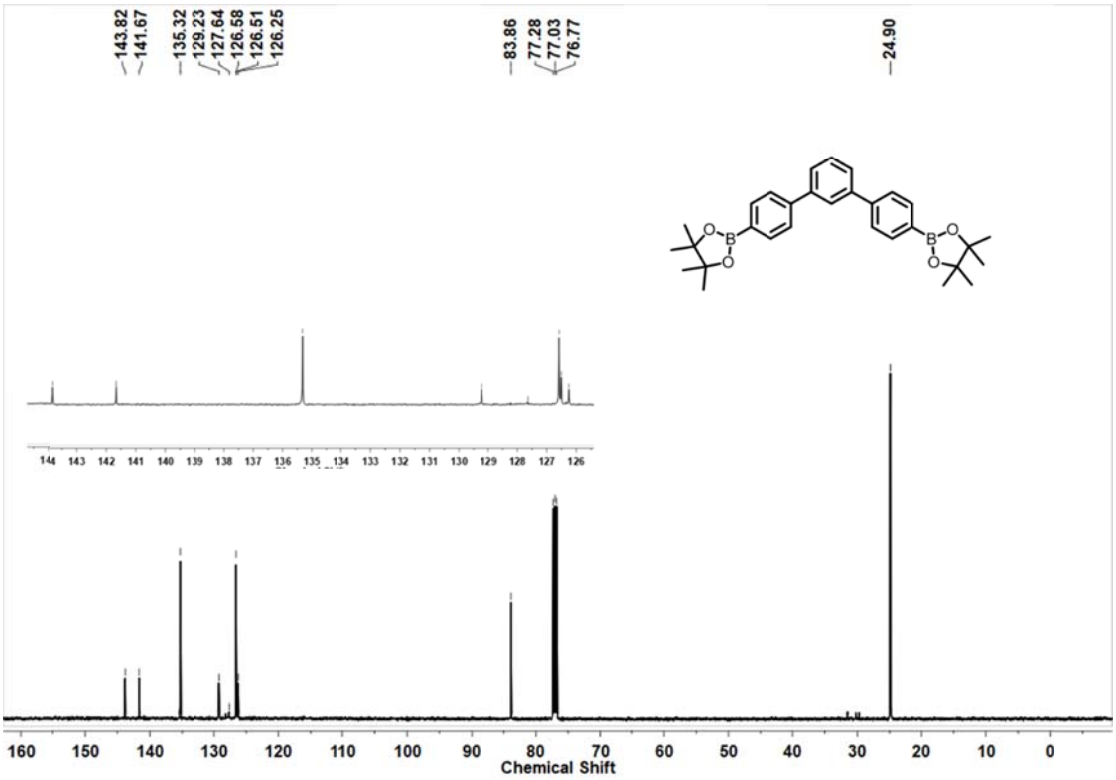


Figure S22. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

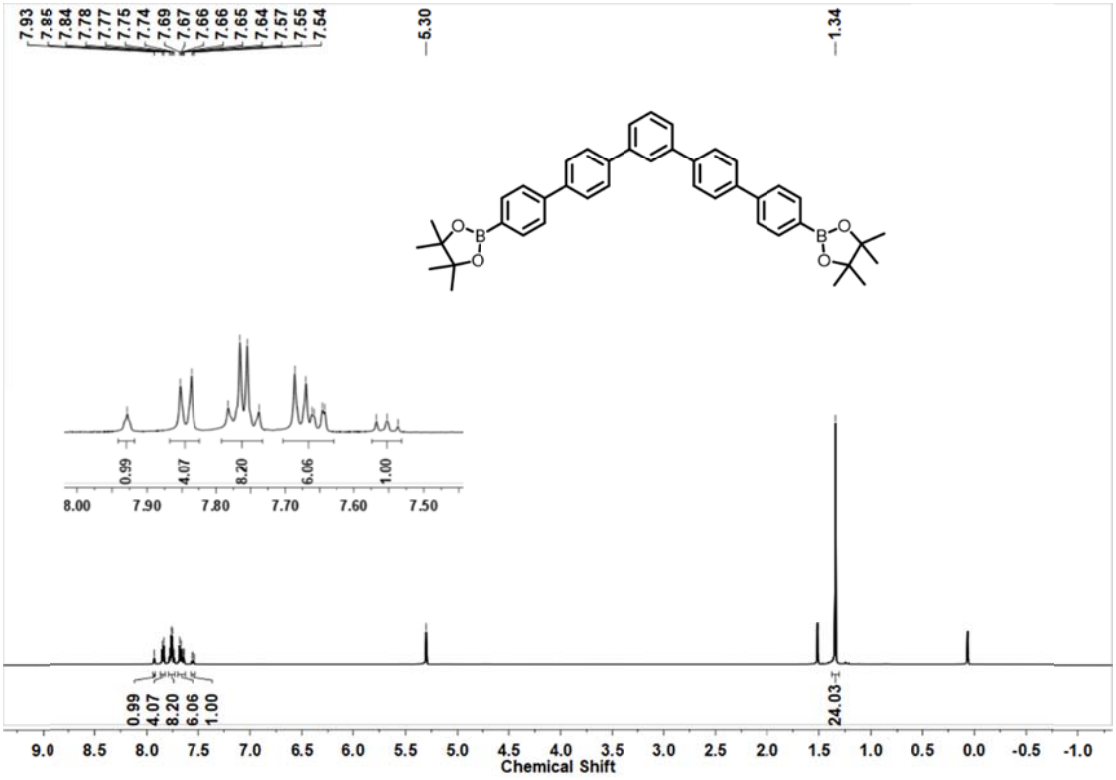


Figure S23. ^{1}H NMR spectrum of compound **3** in CD_2Cl_2.

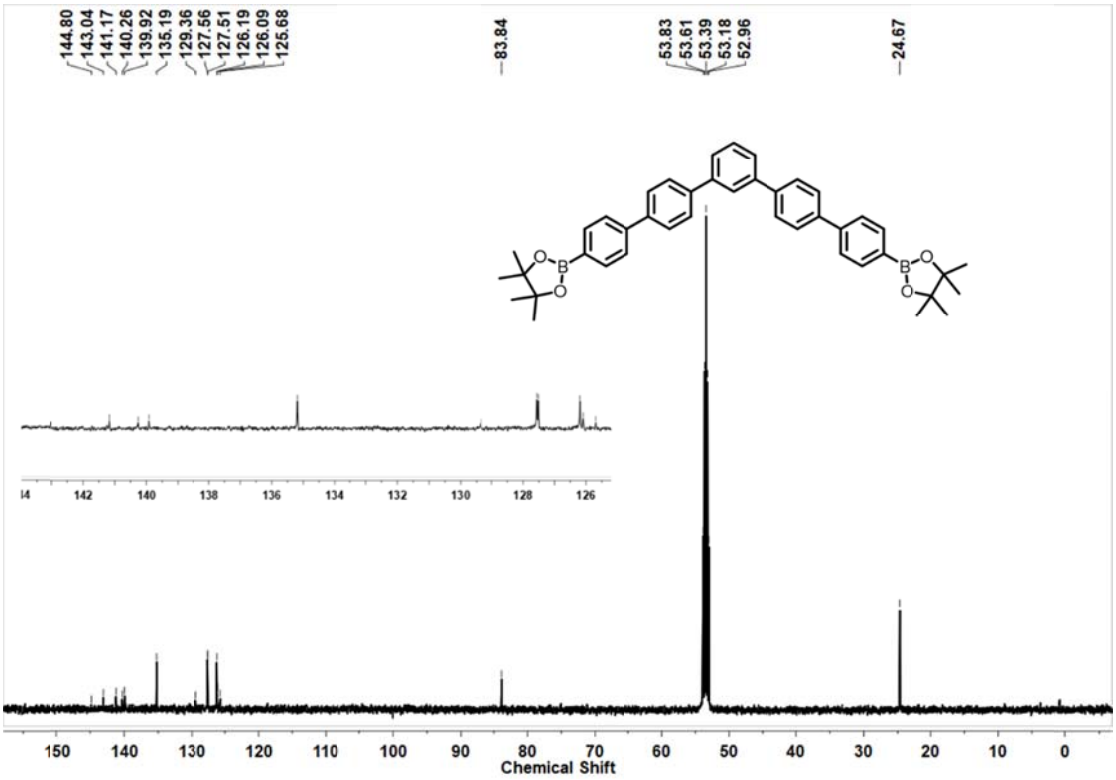


Figure S24. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

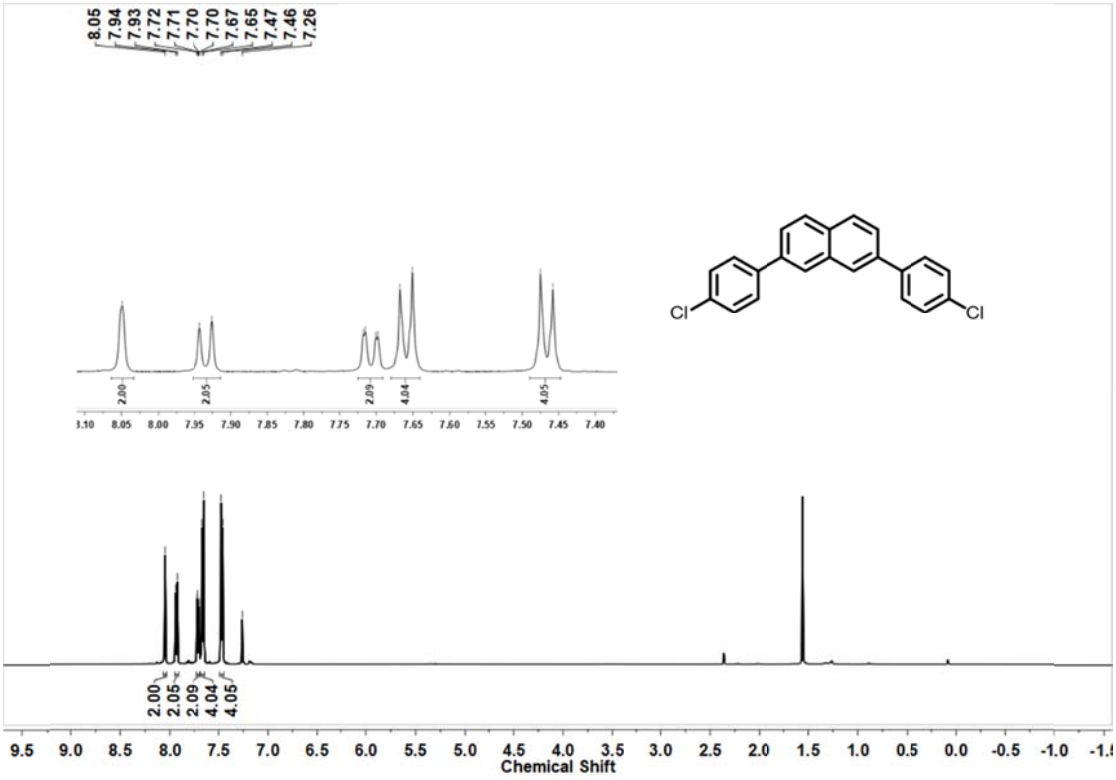


Figure S25. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

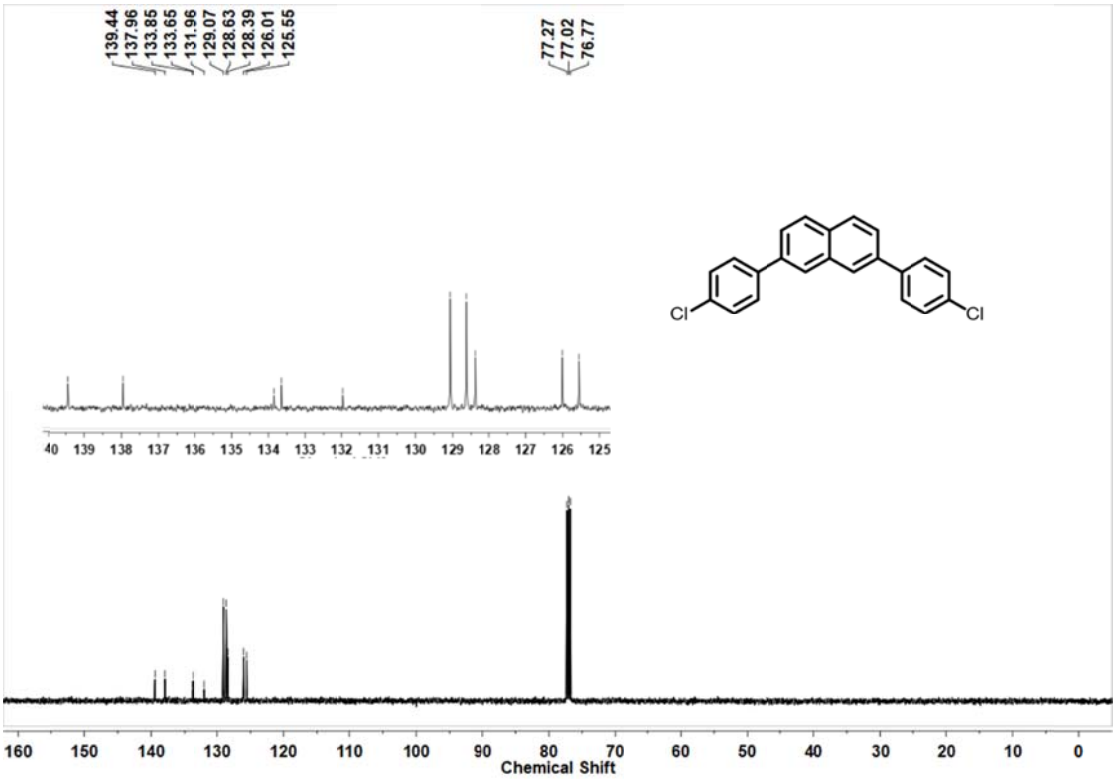


Figure S26. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

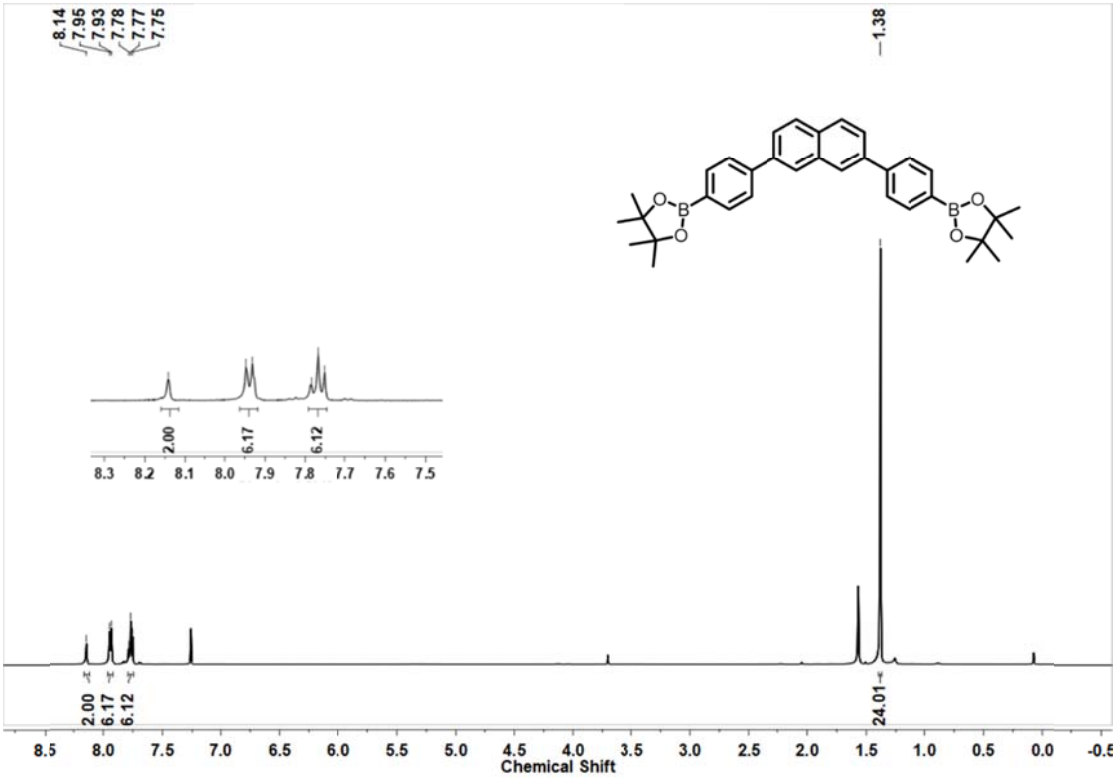


Figure S27. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

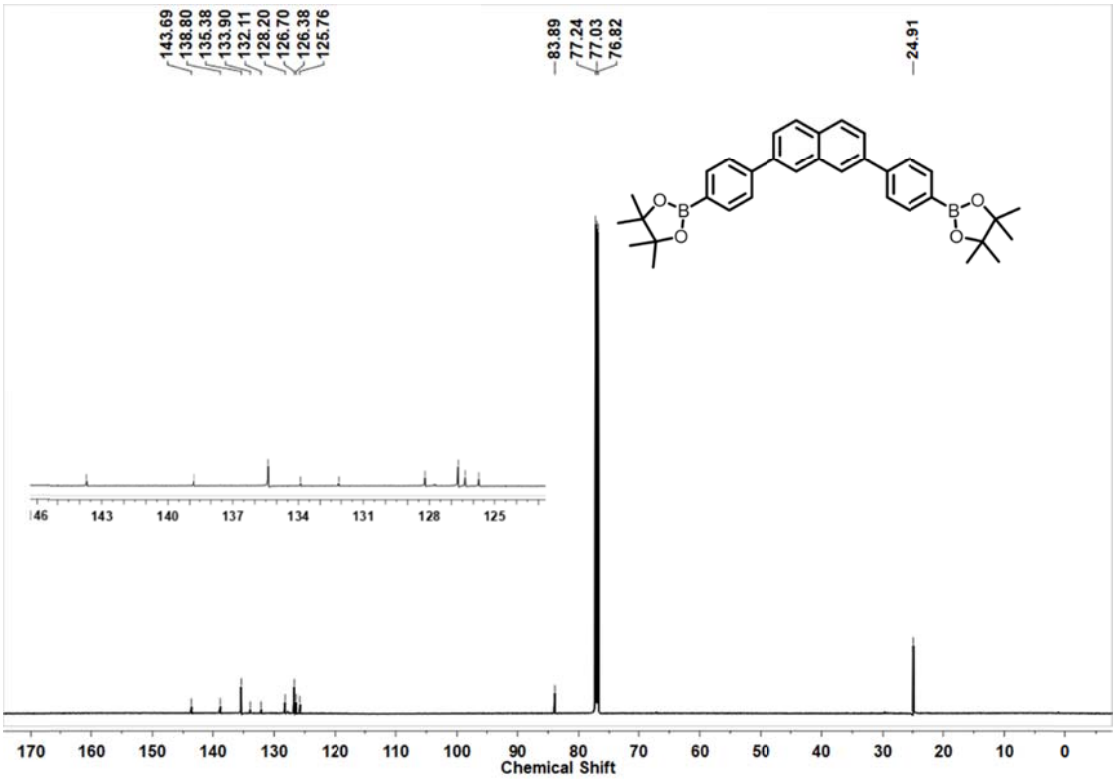


Figure S28. ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

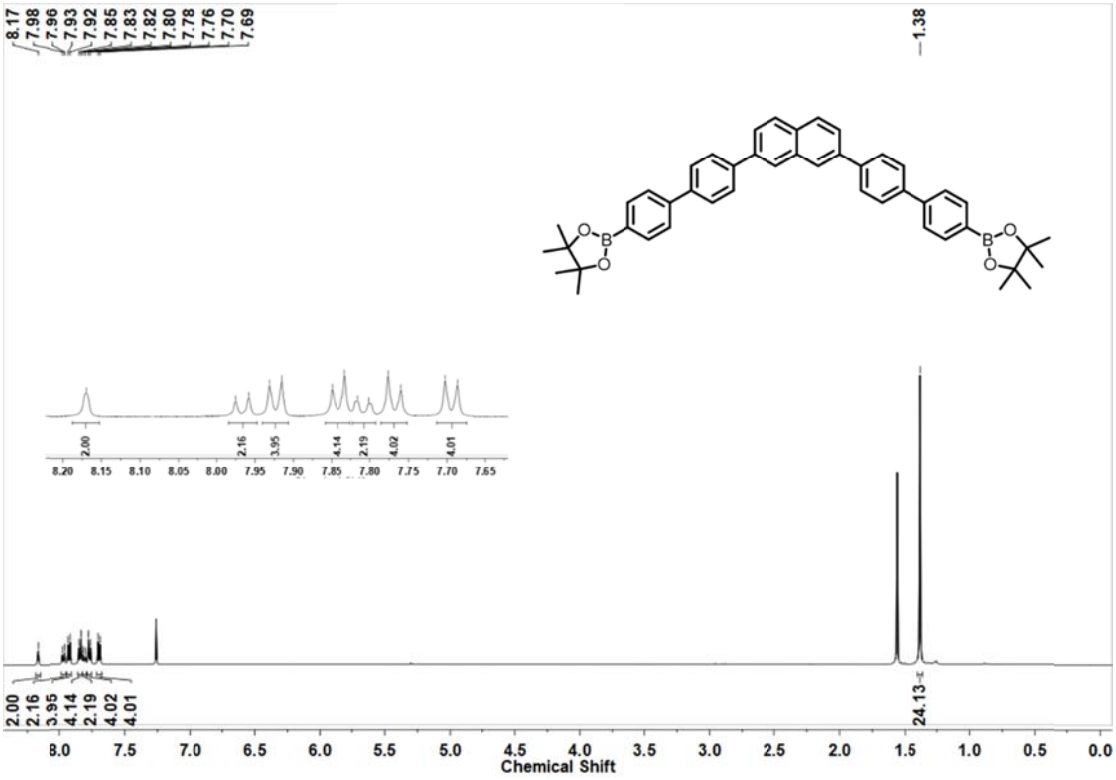


Figure S29. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

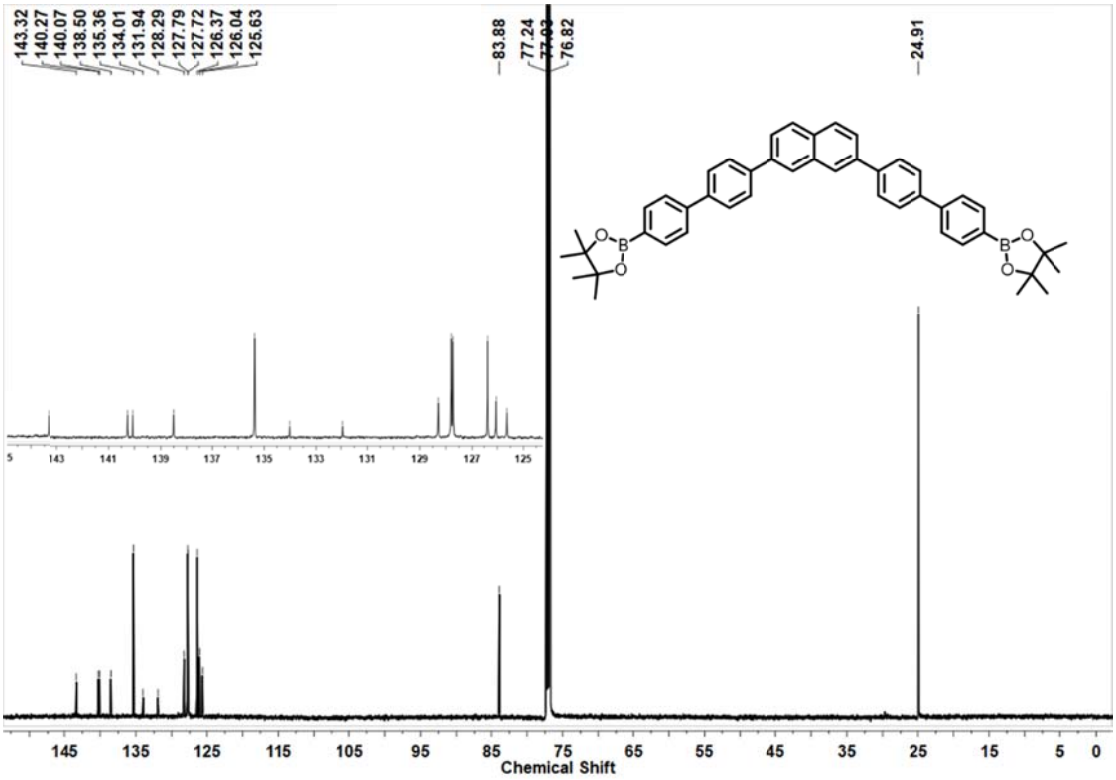


Figure S30. ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

Crystallographic information

All the crystals were measured on a Rigaku Oxford SuperNova Diffractometer and the temperature of the crystal was controlled by Oxford Cryostream 700. Using Olex2[1], all the initial structures were solved with the SHELX-XT structure solution program using direct method and refined with the XL refinement package using Least Squares minimization.

Crystallographic data were deposited in the Cambridge Crystallographic Data Centre (CCDC 2106515-2106519, 2124873). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Structure Refinement for intermediate **Au-complex of CM2P4P.**

CCDC	2124873
Empirical formula	$C_{86}H_{116}Au_4P_4$
Formula weight	2060.67
Temperature/K	100.1(6)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.7069(4)
b/Å	15.0274(3)
c/Å	16.9838(3)
α/°	90
β/°	90.962(2)
γ/°	90
Volume/Å^3	4263.37(15)
Z	2
ρ_{calc}g/cm^3	1.737
F(000)	2180.0
Crystal size/mm^3	0.02 × 0.02 × 0.01
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.36 to 131.998
Index ranges	$-19 \leq h \leq 17$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$
Data/restraints/parameters	7392/1/448
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	$R_1 = 0.0539$, $wR_2 = 0.1410$
Final R indexes [all data]	$R_1 = 0.0672$, $wR_2 = 0.1507$
Largest diff. peak/hole / e Å^{-3}	2.61/-2.02

Table S2. Crystal Data and Structure Refinement for **CM2P4P.**

CCDC	2106516
Empirical formula	$C_{36}H_{24}$
Formula weight	456.19
Temperature/K	100.0(5)
Crystal system	orthorhombic
Space group	Pnma
a/Å	21.2609(8)
b/Å	17.4543(8)
c/Å	7.0890(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2630.69(19)
Z	1
ρ_{calc} g/cm^3	1.345
F(000)	1112.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.04 to 62.368
Index ranges	$-28 \leq h \leq 27$, $-22 \leq k \leq 20$, $-9 \leq l \leq 7$
Data/restraints/parameters	3608/0/187
Goodness-of-fit on F^2	1.101
Final R indexes [I>=2σ (I)]	$R_1 = 0.0424$, $wR_2 = 0.1139$
Final R indexes [all data]	$R_1 = 0.0631$, $wR_2 = 0.1265$
Largest diff. peak/hole / e Å^{-3}	0.29/-0.30

Table S3. Crystal Data and Structure Refinement for **CM2P8P.**

CCDC	2106518
Empirical formula	$C_{60}H_{40}$
Formula weight	760.31
Temperature/K	100.0(6)
Crystal system	triclinic
Space group	P-1
a/Å	10.8159(2)
b/Å	18.1529(4)
c/Å	25.9016(5)
α/°	74.817(2)
β/°	83.098(2)
γ/°	82.344(2)
Volume/Å^3	4844.88(18)
Z	2
ρ_{calc}g/cm^3	1.200
F(000)	1828.0
Crystal size/mm^3	0.12 × 0.03 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.882 to 131.238
Index ranges	$-11 \leq h \leq 12$, $-21 \leq k \leq 21$, $-30 \leq l \leq 29$
Data/restraints/parameters	16337/0/1162
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	$R_1 = 0.0623$, $wR_2 = 0.1688$
Final R indexes [all data]	$R_1 = 0.0753$, $wR_2 = 0.1800$
Largest diff. peak/hole / e Å^{-3}	0.90/-1.02

Table S4. Crystal Data and Structure Refinement for **CN2P4P.**

CCDC	2106515
Empirical formula	$C_{44}H_{28}$
Formula weight	556.22
Temperature/K	99.8(6)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	22.7656(10)
b/Å	5.8183(2)
c/Å	26.2196(12)
α/°	90
β/°	111.135(5)
γ/°	90
Volume/Å^3	3239.4(3)
Z	2
ρ_{calc}g/cm^3	1.298
F(000)	1320.0
Crystal size/mm^3	0.2 × 0.09 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.42 to 130.98
Index ranges	$-26 \le h \le 24$, $0 \le k \le 6$, $0 \le l \le 30$
Data/restraints/parameters	5306/0/428
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	$R_1 = 0.0813$, $wR_2 = 0.1978$
Final R indexes [all data]	$R_1 = 0.0937$, $wR_2 = 0.2039$
Largest diff. peak/hole / e Å^{-3}	0.46/-0.36

Table S5. Crystal Data and Structure Refinement for **CN2P8P.**

CCDC	2106519
Empirical formula	$C_{68}H_{44}$
Formula weight	861.03
Temperature/K	99.9(5)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.1646(4)
b/Å	6.47980(10)
c/Å	25.8994(5)
α/°	90
β/°	107.360(2)
γ/°	90
Volume/Å^3	2909.58(10)
Z	2
ρ_{calc}g/cm^3	0.983
F(000)	904.0
Crystal size/mm^3	0.15 × 0.12 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.204 to 150.672
Index ranges	$-17 \le h \le 22$, $-8 \le k \le 7$, $-32 \le l \le 27$
Data/restraints/parameters	5708/0/307
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	$R_1 = 0.0458$, $wR_2 = 0.1237$
Final R indexes [all data]	$R_1 = 0.0517$, $wR_2 = 0.1285$
Largest diff. peak/hole / e Å^{-3}	0.21/-0.22

Table S6. Crystal Data and Structure Refinement for **C_{60}@CN2P8P.**

CCDC	2106516
Empirical formula	$C_{128}H_{44}$
Formula weight	1580.34
Temperature/K	99.8(7)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.9720(2)
b/Å	21.5606(4)
c/Å	15.2604(3)
α/°	90
β/°	100.313(2)
γ/°	90
Volume/Å^3	3875.43(13)
Z	2
ρ_{calc}g/cm^3	1.486
F(000)	1776.0
Crystal size/mm^3	0.05 × 0.02 × 0.01
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.174 to 134.954
Index ranges	$-13 \leq h \leq 14$, $-25 \leq k \leq 22$, $-18 \leq l \leq 18$
Data/restraints/parameters	6934/0/604
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	$R_1 = 0.0485$, $wR_2 = 0.1184$
Final R indexes [all data]	$R_1 = 0.0617$, $wR_2 = 0.1261$
Largest diff. peak/hole / e Å^{-3}	0.62/-0.62

Titration experiment of CN2P8P with C_{60} Fullerene

NMR Titration of CN2P8P with C_{60} Fullerene

The initial spectrum of CN2P8P was measured in 1,1,2,2-tetrachloroethane-d2. Then a solution of C_{60} in 1,1,2,2-tetrachloroethane-d2 was added.

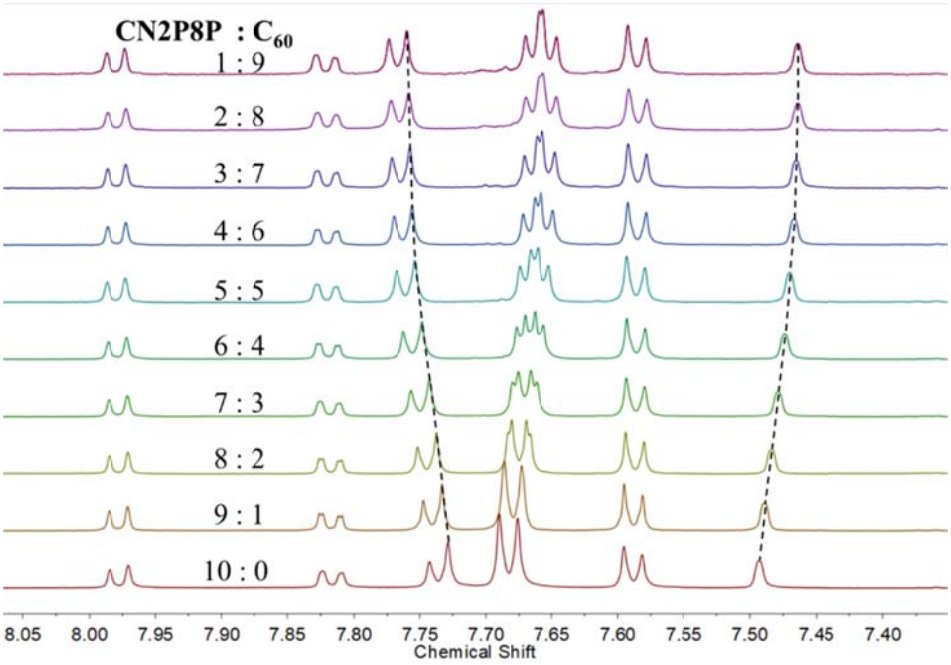


Figure S31. Selected region of the aromatic protons of the ^{1}H NMR spectra (600 MHz, 298 K) during titration of CN2P8P with C_{60} in 1,1,2,2-tetrachloroethane-d2.

A solution of C_{60} in 1,1,2,2-tetrachloroethane-d2 (6.45×10^{-4} mol·L^{-1}) and solutions of CN2P8P (6.45×10^{-4} mol·L^{-1}) were mixed in different ratios to prepare 10 samples. ^{1}H-NMR was recorded for each sample, and the chemical shift of hydrogen was monitored for Job's plot analysis[2].

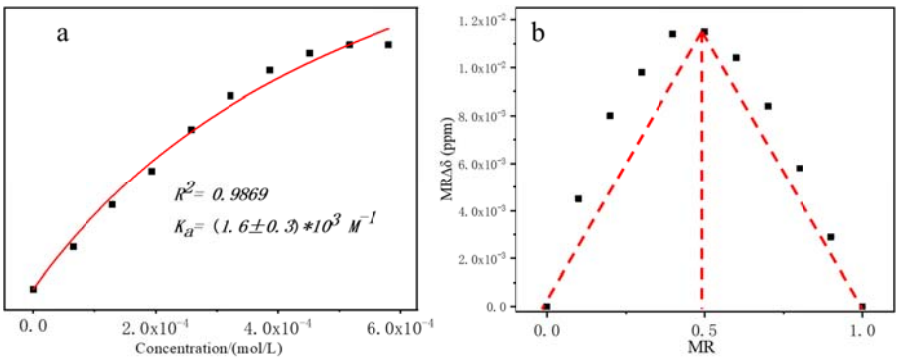


Figure S32. (a). Binding curve of [C60] for supramolecular assembly between CN2P8Pand C_{60} in 1,1,2,2-tetrachloroethane-d2 at 298 K. **(b)**. Job plot showing the 1:1 stoichiometry of CN2P8P⊃C_{60} complex. MR = Molar ratio of CN2P8P and C_{60}.

UV-Vis absorption spectra of CN2P8P with C_{60} Fullerene

Three samples, C_{60} (3.6×10^{-5} mol·L^{-1}), CN2P8P (3.6×10^{-5}mol·L^{-1}) and mixture of CN2P8P and C_{60} in 1:1 ratio (C_{CN2P8P}= C_{C60}= 3.6×10^{-5} mol·L^{-1}), were prepared. UV-Vis absorption spectra were recorded for each sample at 298K.

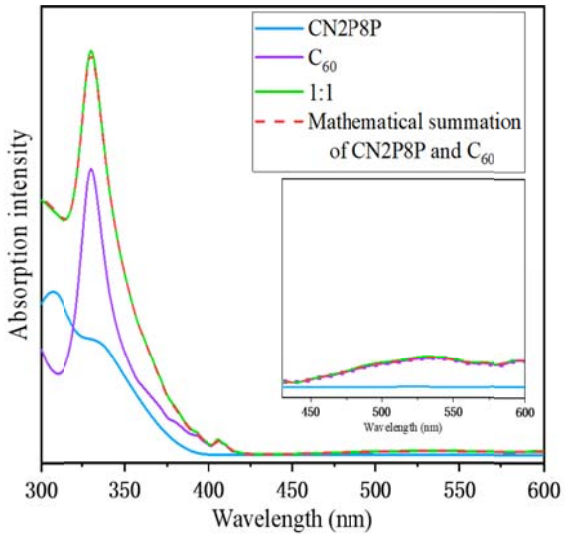


Figure S33. UV-Vis absorption spectra of CN2P8P (blue line), C_{60} (purple line), and their 1:1 mixture (green line) in 1,1,2,2-tetrachloroethane. Mathematical summation of the spectra of CN2P8P and C_{60} is shown in red dash line. There is no difference between mixture and mathematical summation in spectra.

Fluorescence-quenching of CN2P8P with C_{60} Fullerene

To a solution of CN2P8P in toluene (3.29×10^{-5} mol L^{-1}, λ_{exc}=305 nm) was added a solution of C_{60} in toluene by pipette (3.29×10^{-3} mol L^{-1}) at 298 K (Figure 5b). The change of fluorescence intensity of CN2P8P at 415 nm was measured for binding curve.

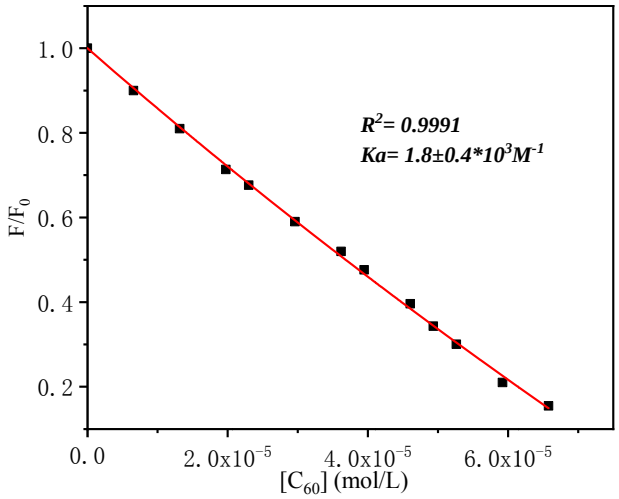


Figure S34. Binding curve of [C_{60}] for supramolecular assembly between CN2P8P and C_{60} in toluene at 298 K in terms of fluorescence-quenching.

Computation details

All the calculations were performed with the Gaussian 16 software package. The B3LYP/6-31G(d,p) level of density functional theory was used to optimize all of the structures[3].

According to the literature[4], the strain calculated by comparing the energy of optimized geometries of the molecules in the theoretical homodesmotic reaction shown below.

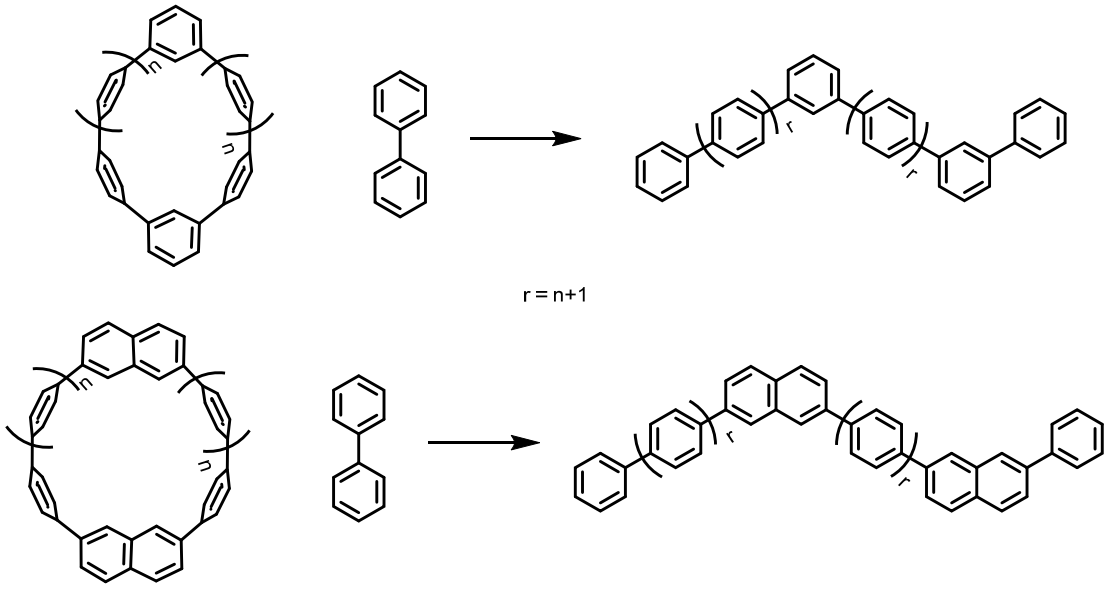


Figure S35. Theoretical homodesmotic reaction from the macrocycle to strain-free molecular pieces

Table S7. Single point energies of compounds used in homodesmotic reactions and calculated strain.

Compound	n	r	Total Energy (Hartree)	Linear Product Total Energy (Hartree)	Strain Energy (Hartree)	Strain Energy (kcal/mol)
Biphenyl	-	-	-463.1748	-	-	-
CM2P4P	1	2	-1385.8556	-1849.1137	0.0833	52.3
CM2P8P	3	4	-2309.8519	-2773.0736	0.0469	29.4
CN2P4P	1	2	-1693.0636	-2156.3220	0.0836	52.5
CN2P8P	3	4	-2617.0598	-3080.2818	0.0472	29.6

Cartesian coordinates (in Å) of **CM2P4P**

C	-0.3229	4.0597	0.3395	H	-4.2162	-0.9862	-1.6102
C	-0.6943	5.0323	-0.513	H	-3.6705	1.9371	-1.8595
C	-1.9348	5.0624	-1.0231	H	0.6519	2.8753	2.5367
C	-2.7885	4.0557	-0.7828	H	2.489	1.5078	2.5074
C	-2.4667	3.0667	0.0708	H	3.5113	3.0154	-1.3563
C	-1.2697	3.1598	0.6943	H	1.7063	4.4461	-1.2805
C	-3.0889	1.8613	0.1298	H	3.2617	-1.2774	-2.1748
C	0.9658	3.7232	0.605	H	3.3972	0.9881	-1.8512
C	-3.0504	1.0673	1.201	H	4.1949	0.3115	2.2926
C	-3.2102	-0.226	0.9238	H	4.1546	-1.9704	1.9314
C	-3.4196	-0.6425	-0.3489	H	-0.1634	-2.4918	-2.5367
C	-3.9616	0.0618	-1.4311	H	-2.0215	-1.1304	-2.4616
C	-3.5884	1.2765	-0.975	H	-3.115	-2.8626	1.2746
C	1.3322	2.991	1.6741	H	-1.2801	-4.2647	1.1718
C	2.4252	2.2105	1.6608	H	1.4617	-2.0739	-1.2672
C	3.1369	2.0696	0.5232	H	0.362	-5.6367	0.6961
C	2.9368	3.0176	-0.4145	H	2.5991	-5.8501	1.5321
C	1.8954	3.8678	-0.3605	H	4.2162	-4.0999	1.1892
C	3.5732	-0.9426	-1.1688				
C	3.6754	0.382	-0.9739				
C	3.7294	0.8703	0.283	Cartesian coordinates (in Å) of **CM2P8P**			
C	4.0788	-0.0096	1.2436				
C	4.0784	-1.3383	1.0302	C	-0.3627	-0.1164	5.6287
C	-0.8472	-2.6488	-1.684	C	0.4111	0.0768	6.7136
C	-1.9438	-1.8747	-1.6489	C	1.2577	-0.8725	7.1378
C	-2.7108	-1.8095	-0.5387	C	1.4017	-2.0188	6.4572
C	-2.4984	-2.7914	0.3617	C	0.6658	-2.2773	5.3588
C	-1.4463	-3.6271	0.2875	C	-0.2264	-1.3177	5.0219
C	3.6254	-1.8156	-0.1457	C	0.8841	-3.3384	4.5364
C	-0.5024	-3.4524	-0.6591	C	-1.1212	0.8576	5.0597
C	1.7607	-3.003	-0.7597	C	-0.0079	-3.7556	3.6161
C	0.7716	-3.8639	-0.4272	C	0.2911	-4.64	2.6516
C	1.1096	-4.8955	0.3684	C	1.5243	-5.1646	2.5016
C	2.3567	-5.0172	0.8499	C	2.368	-4.8607	3.5092
C	3.2599	-4.0469	0.6424	C	2.0556	-4.0053	4.5002
C	2.9733	-3.0059	-0.1591	C	-2.1242	0.599	4.1979
H	0.0213	5.7955	-0.8612	C	-2.7199	1.5498	3.4612
H	-2.2091	5.8501	-1.7457	C	-2.3317	2.841	3.49
H	-3.74	4.0461	-1.34	C	-1.4328	3.1165	4.4575
H	-0.9391	2.2744	1.2579	C	-0.8707	2.1709	5.2329
H	-2.6802	1.3877	2.1888	C	1.8918	-5.8182	1.3677
H	-2.8564	-0.8579	1.7551	C	3.1689	-6.0378	1.0341

C	3.3576	-6.1542	-0.2834	H	-1.0322	-3.3493	3.5736
C	2.3124	-6.2256	-1.1401	H	-0.5183	-4.7944	1.9215
C	1.0676	-6.7758	-0.8262	H	3.3996	-5.2464	3.5307
C	1.0434	-6.2453	0.4127	H	2.877	-3.7721	5.1968
C	-2.7313	3.7223	2.5349	H	-2.4813	-0.4288	4.0172
C	-2.1533	5.5717	-3.4611	H	-3.4525	1.1602	2.738
C	0.7536	5.2186	-5.606	H	-1.0573	4.1397	4.618
C	-0.1572	5.7757	-4.7861	H	-0.0791	2.5238	5.9138
C	-1.3269	5.1828	-4.4683	H	4.0368	-5.7963	1.6654
C	-1.5654	4.0483	-5.1576	H	4.3943	-5.9337	-0.5761
C	-0.6385	3.465	-5.9328	H	1.315	-7.1794	-1.812
C	1.5244	-0.8612	-6.3381	H	-0.0282	-6.2452	0.6797
C	1.518	-2.0711	-5.7572	H	1.7102	5.7588	-5.6972
C	2.6423	-2.7008	-5.3589	H	0.153	6.7262	-4.324
C	3.7692	-2.091	-5.784	H	-2.4779	3.4469	-5.0266
C	3.7784	-0.8919	-6.3963	H	-0.9299	2.4949	-6.3701
C	0.589	3.9854	-6.1247	H	0.5264	-0.4383	-6.541
C	2.6543	-0.1763	-6.6017	H	0.5074	-2.4438	-5.535
C	1.6187	1.9376	-6.6298	H	4.7672	-2.5036	-5.5698
C	2.6639	1.1395	-6.9465	H	4.777	-0.4645	-6.5819
C	3.7343	1.7742	-7.4624	H	0.7916	1.474	-6.0801
C	3.7482	3.1069	-7.6139	H	4.6458	1.238	-7.7695
C	2.7133	3.8568	-7.208	H	4.6439	3.5982	-8.0324
C	1.6048	3.2883	-6.6979	H	2.8164	4.9484	-7.3137
C	2.4966	-5.5929	-2.3537	H	4.6316	-5.3521	-2.4205
C	3.6529	-5.1248	-2.8693	H	4.723	-3.9016	-4.139
C	3.7109	-4.2667	-3.9051	H	0.4912	-4.1078	-4.5306
C	2.6158	-3.771	-4.5178	H	0.391	-5.5134	-2.7995
C	1.4758	-4.3655	-4.113	H	-3.8923	4.3759	-3.9611
C	1.4197	-5.2292	-3.0868	H	-4.6385	4.4475	-1.8298
C	-3.3697	5.0524	-3.2692	H	-2.8648	7.1794	-0.419
C	-3.8113	5.1457	-2.0156	H	-0.8752	6.9886	-2.6281
C	-3.1158	5.8166	-1.0689	H	-4.418	2.625	1.8007
C	-2.3083	6.9312	-1.3243	H	-4.777	3.8231	-0.0456
C	-1.8291	6.4495	-2.4914	H	-1.5278	6.3837	0.9963
C	-3.74	3.4841	1.675	H	-1.2105	5.1922	2.8823
C	-3.9519	4.2136	0.567				
C	-3.1663	5.2456	0.1905				
C	-2.2678	5.5772	1.1485	Cartesian coordinates (in Å) of **CN2P4P**			
C	-2.0688	4.8666	2.2735				
H	0.3847	1.0112	7.2961	C	1.0217	2.3626	-3.0583
H	1.8778	-0.6883	8.0324	C	0.8471	3.5815	-2.5269
H	2.1542	-2.7245	6.8426	C	-0.3834	4.1226	-2.5599
H	-0.7382	-1.4374	4.0602	C	-1.4414	3.3829	-2.9395

C	-1.3028	2.1245	-3.4024	H	-2.5102	-1.9724	-4.3127
C	-0.0324	1.6923	-3.5623	H	-4.6779	0.2716	-1.3946
C	-2.2885	1.1901	-3.4528	H	-3.579	2.1561	-2.039
C	4.0527	1.2892	-1.5947	H	4.1429	-0.0056	-3.2956
C	-2.17	0.0345	-4.1324	H	4.7886	-1.8592	-2.1723
C	-2.8374	-1.0725	-3.7722	H	4.9644	0.4182	1.4377
C	-3.6288	-1.0959	-2.6793	H	4.3435	2.2785	0.2853
C	-3.9933	0.1308	-2.2453	H	3.2705	-5.0647	-0.112
C	-3.356	1.2537	-2.6322	H	4.5053	-3.4814	-1.1515
C	4.3529	0.1367	-2.2214	H	4.6776	-1.2569	2.4913
C	4.7461	-0.9552	-1.5479	H	3.4596	-2.8746	3.5276
C	4.8165	-0.9662	-0.2002	H	-2.278	-5.1562	-1.7401
C	4.856	0.2662	0.3528	H	-2.7927	-3.5964	-3.2945
C	4.5023	1.3751	-0.3269	H	-4.9644	-1.4034	-0.3409
C	3.6008	-4.2248	0.5233	H	-4.4622	-2.998	1.2015
C	4.3428	-3.2848	-0.082	H	-0.7798	-4.8927	-0.3737
C	4.6194	-2.1082	0.5183	H	-3.8791	-4.5996	2.5159
C	4.4444	-2.1268	1.8581	H	-2.2886	-4.9834	4.2341
C	3.7352	-3.0886	2.4815	H	2.2184	0.6846	-3.2604
C	-2.9208	-4.3294	-1.3913	H	3.7424	3.9206	-0.9697
C	-3.2399	-3.4036	-2.3087	H	1.7717	5.1562	-1.4374
C	-3.8256	-2.2384	-1.9616	H	0.0471	-4.9455	4.9197
C	-4.4045	-2.2627	-0.7408	H	2.3014	-4.4999	4.3304
C	-4.1224	-3.2113	0.1743	H	1.2659	-4.8593	0.2268
C	3.1322	-4.0653	1.7748				
C	-3.2079	-4.1666	-0.0866				
C	-1.1788	-5.0013	0.6464	Cartesian coordinates (in Å) of **CN2P8P**			
C	-2.4772	-4.7337	0.9091				
C	-2.8402	-4.7992	2.2056	C	-6.3817	-3.8962	1.544
C	-1.9435	-5.012	3.1861	C	-6.7709	-4.3353	2.7499
C	-0.629	-5.0552	2.9067	C	-6.3363	-5.5365	3.1648
C	-0.2509	-5.0748	1.6201	C	-5.4436	-6.2319	2.4393
C	2.2003	1.7276	-2.909	C	-4.9933	-5.8014	1.2426
C	3.1706	2.1953	-2.0928	C	-5.5477	-4.6502	0.8019
C	3.0014	3.4531	-1.6388	C	-0.2332	-6.9995	-1.1345
C	1.8848	4.1585	-1.8959	C	0.0709	-6.651	-2.4004
C	0.3241	-4.9751	3.8517	C	1.3144	-6.3302	-2.7939
C	1.6016	-4.7271	3.5094	C	2.367	-6.31	-1.9507
C	1.9953	-4.661	2.2219	C	2.0972	-6.8771	-0.7562
C	1.0533	-4.9646	1.3017	C	0.8543	-7.2168	-0.3667
H	-0.5644	5.1192	-2.1215	C	5.4349	-4.4724	-1.4739
H	-2.4393	3.8234	-2.7801	C	4.4983	-5.4281	-1.3279
H	0.1722	0.6523	-3.8595	C	3.5197	-5.6414	-2.2325
H	-1.4072	-0.0944	-4.9197	C	3.727	-4.9926	-3.3965

C	4.6559	-4.0332	-3.5405	C	0.3466	7.2562	-0.8543
C	5.4655	-3.6416	-2.5363	C	6.137	-0.1946	-3.2195
C	-6.7304	-2.6572	1.1459	C	5.8489	-1.488	-3.4328
C	-7.3821	-1.7763	1.9372	C	6.1159	-2.4458	-2.5213
C	-7.7953	-2.2697	3.1229	C	1.2466	7.5332	0.113
C	-7.528	-3.5285	3.5113	C	2.5465	7.1935	0.0259
C	-1.5004	-6.9943	-0.6387	C	6.9358	-2.0347	-1.5307
C	-2.5182	-6.4165	-1.3095	C	7.2637	-0.7433	-1.3367
C	-3.6829	-6.0965	-0.7238	H	-6.6389	-5.9262	4.1522
C	-3.9519	-6.3593	0.5698	H	-5.0775	-7.1666	2.8931
C	-3.0258	-7.1323	1.1724	H	-5.1995	-4.1836	-0.1315
C	-1.8413	-7.4137	0.5977	H	-0.702	-6.5091	-3.1717
C	-7.4518	-0.4644	1.587	H	1.366	-5.9526	-3.8258
C	-6.4448	3.446	0.6674	H	2.8618	-6.975	0.0296
C	-5.9904	4.2887	1.6176	H	0.7734	-7.5298	0.686
C	-5.1539	5.3073	1.3446	H	6.0596	-4.3072	-0.5824
C	-4.7131	5.5869	0.1001	H	4.499	-5.9138	-0.3401
C	-5.3654	4.897	-0.858	H	3.0653	-5.1054	-4.2682
C	-6.1852	3.8684	-0.5859	H	4.6196	-3.5106	-4.5086
C	-1.8816	6.954	-1.6502	H	-6.2976	-2.3337	0.1876
C	-3.1368	6.54	-1.4105	H	-8.3518	-1.651	3.8449
C	-3.6214	6.3568	-0.1655	H	-7.8648	-3.8608	4.5086
C	-2.8283	6.8814	0.7922	H	-2.4211	-6.0327	-2.3361
C	-1.5729	7.304	0.5528	H	-4.3886	-5.539	-1.3614
C	-1.0014	7.2284	-0.6668	H	-3.121	-7.4337	2.2281
C	-7.285	-0.0274	0.3236	H	-1.1224	-7.9375	1.2473
C	-7.0793	1.263	0.0159	H	-6.1428	4.0958	2.691
C	-6.9821	2.2287	0.9525	H	-4.7511	5.8149	2.2344
C	-7.3254	1.8134	2.1897	H	-5.1686	5.0309	-1.9319
C	-7.5755	0.526	2.4936	H	-6.5521	3.331	-1.474
C	4.1855	5.7937	-0.9436	H	-1.5939	6.9335	-2.7124
C	4.3725	4.659	-1.6425	H	-3.6853	6.2366	-2.3147
C	5.0165	3.5025	-1.8811	H	-3.0983	6.8496	1.8589
C	5.9738	3.8968	-0.8637	H	-0.9943	7.5472	1.4574
C	6.0283	5.018	-0.0765	H	-7.2437	-0.7232	-0.5304
C	5.1344	6.0003	-0.0448	H	-6.8538	1.4317	-1.0478
C	3.0277	6.5014	-1.0263	H	-7.3301	2.503	3.0485
C	7.08	3.2471	-0.3801	H	-7.7254	0.3153	3.5649
C	7.4911	2.0318	-0.725	H	3.5467	4.4786	-2.3573
C	6.7167	1.5312	-1.6741	H	6.7965	5.2512	0.6884
C	5.7301	2.3728	-2.0344	H	5.1939	6.8481	0.6532
C	6.7468	0.2405	-2.1	H	7.7692	3.6134	0.4075
C	2.1908	6.4497	-2.0804	H	8.3518	1.531	-0.2582
C	0.9057	6.8292	-2.0053	H	5.0657	1.9212	-2.7959

H	2.4925	5.9982	-3.0404	H	7.2806	-2.721	-0.7415
H	0.3264	6.5948	-2.9106	H	7.8085	-0.5267	-0.4032
H	5.7527	0.5043	-3.9813				
H	5.2306	-1.6571	-4.3268				
H	0.9408	7.9375	1.0906				
H	3.1366	7.3329	0.9466				

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