Supporting Information for:

# A Tetraazapentacene-Pyrene Belt: Toward Synthesis of N-Doped Zigzag Carbon Nanobelts

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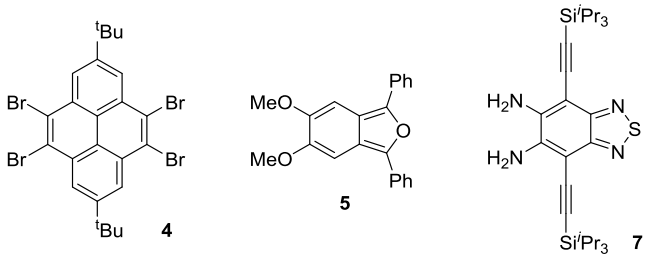
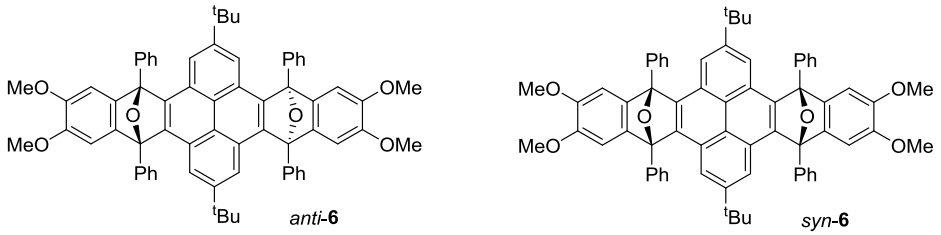
## 1. Synthesis

**General:** The reagents and starting materials employed were commercially available and used without any further purification or made following reported methods as indicated. Anhydrous and $O_2$-free diethyl ether, THF and dichloromethane were purified by an Advanced Technology Pure-Solv PS-MD-4 system. NMR spectra were recorded on Brucker 400MHz spectrometer ($^1$H NMR: 400 MHz, $^{13}$C NMR: 100 MHz) and Bruker 500MHz spectrometer ($^1$H NMR: 500 MHz, $^{13}$C NMR:126 MHz). Chemical shift values (δ) are expressed in parts per million using residual solvent protons ($^1$H NMR, δH = 7.26 for $CDCl_3$, δH = 2.05 for $CD_3COCD_3$, $^{13}$C NMR, δC = 77.16 for $CDCl_3$, δC = 29.84, 206.26 for $CD_3COCD_3$) as internal standard. Mass spectra were recorded on Therno Finnigan MAT 95 XL spectrometer or a Bruker Autoflex speed MALDI-TOF spectrometer. X-ray crystallography data were collected on a Bruker AXS Kappa ApexII Duo Diffractometer. UV-vis absorption spectra were recorded on a Varian CARY 1E UV-vis spectrophotometer. Fluorescence spectra were taken on a Hitachi F-45 spectrofluorometer. Melting points, without correction, were measured using a Nikon Polarized Light Microscope ECLIPSE 50i POL equipped with an INTEC HCS302 heating stage. FTIR spectra were recorded on a Thermo Nicolet iS10 mid-FTIR spectrometer.




4,5,9,10-tetrabromo-2,7-di(t-butyl)pyrene (**4**),[1] 5,6-dimethoxy-1,3-diphenylisobenzofuran (**5**) [2] and 4,7-bis[2-[tris(1-methylethyl)silyl]ethynyl]-2,1,3-benzothiadiazole-5,6-diamine (**7**) [3] were synthesized following the reported procedures.

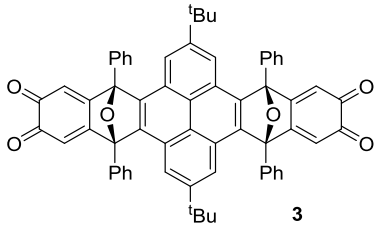



Compounds *anti*-**6** and *syn*-**6**: *n*-BuLi (1.8 mL of a 1.6 M solution in hexane, 2.8 mmol) was added to a stirred solution of **4** (700 mg, 1.12 mmol) and **5** (1.11 g, 3.35 mmol) in anhydrous THF (20 mL), which was cooled with a liquid nitrogen-ethyl acetate bath, under an atmosphere of $N_2$. The reaction mixture was stirred when slowly warmed from −80 ℃ to room temperature overnight, then quenched with $H_2O$, extracted with $CH_2Cl_2$. The extracts were combined, washed with brine, dried over $MgSO_4$, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate 5/1 (V/V) as eluent to afford *anti*-**6** (35%) and *syn*-**6** (50%) as light yellow solids separately.

*anti*-**6**: Melting point: not melt when heated up to 350 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ = 8.18−7.96 (m, 8H), 7.79 (s, 4H), 7.58−7.47 (m, 12H), 7.36 (s, 4H), 3.85 (s, 12H), 1.01 (s, 18H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ = 149.9, 147.6, 146.4, 144.7, 135.8, 129.4, 128.9,

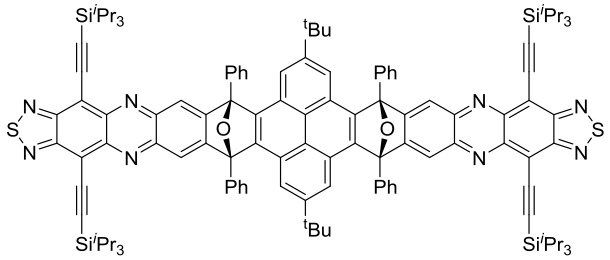
126.0, 122.0, 119.0, 108.6, 93.4, 56.8, 35.0, 31.3. HRMS ($ESI^+$): calcd. for $C_{68}H_{59}O_6$ ($[M+H]^+$): 971.4306, found: 971.4276.

*syn*-**6**: Melting point: not melt when heated up to 350 ℃. $^1H$ NMR (500 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 6.0 Hz, 8H), 7.83 (s, 4H), 7.68−7.56 (m, 12H), 7.29 (s, 4H), 3.79 (s, 12H), 1.08 (s, 18H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ = 150.3, 147.3, 146.3, 144.6, 135.2, 130.4, 129.5, 128.9, 126.6, 122.1, 118.9, 108.2, 93.7, 56.6, 34.9, 31.3. HRMS ($ESI^+$): calcd. for $C_{68}H_{58}O_6Na$ ($[M+Na]^+$): 993.4126, found: 993.4116.



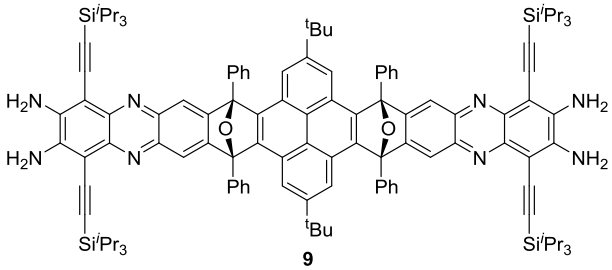
**3**

Compound **3**: To a stirred solution of *syn*-**6** (120 mg, 0.12 mmol) in acetonitrile (10 mL) under $N_2$ was added $Ce(NH_4)_2(NO_3)_6$ (678 mg, 1.2 mmol in 1.0 mL $H_2O$) at 0 ℃. The reaction mixture was stirred when slowly warmed from 0 ℃ to room temperature overnight, then quenched with $H_2O$, and extracted with $CH_2Cl_2$. The extracts were combined, washed with brine and dried over $MgSO_4$, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane/diethyl ether 30/1 (V/V) as eluent to afford **3** as red solid in a yield of 70%. Melting point: decomposed when heated up to 350 ℃. $^1H$ NMR (500 MHz, $CDCl_3$) δ = 8.04−7.96 (m, 8H), 7.88 (s, 4H), 7.65−7.58 (m, 12H), 6.72 (s, 4H), 0.99 (s, 18H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ = 178.2, 155.7, 149.6, 142.5, 131.2, 130.8, 130.0, 129.3, 125.9, 125.3, 121.9, 120.0, 90.1, 35.2, 31.1. HRMS ($ESI^+$): calcd. for $C_{64}H_{47}O_6$ ($[M+H]^+$): 911.3367, found: 911.3372.



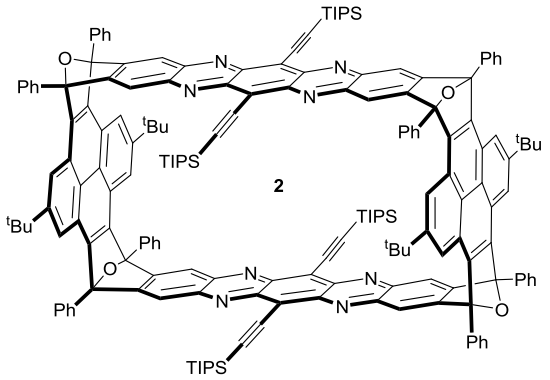
**8**

Compound **8**: A solution of **3** (285 mg, 0.3 mmol) and **7** (395 mg, 0.75 mmol) in 10 mL of acetic acid was stirred at 80 ℃ for 24 hours, and cooled to room temperature, then quenched with saturated $NaHCO_3$(aq), extracted with $CH_2Cl_2$. The extracts were combined, washed with brine, dried over $MgSO_4$, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with hexane/dichloromethane/diethyl ether 10/2/1 (V/V/V) as eluent to afford **8** as dark purple solid in a yield of 80%. Melting point: not melt when heated up to 350 ℃. $^1H$ NMR (500 MHz, $CDCl_3$) δ = 8.30−8.17 (m, 8H), 7.98 (s, 4H), 7.91 (s, 4H), 7.71−7.61 (m, 12H), 1.23−1.15 (m, 84H), 1.08 (s, 18H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 154.0, 151.5, 148.5, 146.5, 145.3, 142.6, 133.4, 130.3, 129.2, 126.0, 124.1, 121.0, 120.5, 114.0, 110.9, 101.8, 91.9, 35.2, 31.2, 18.9, 11.6. HRMS (MALDI-TOF): calcd. for $C_{120}H_{131}N_8O_2S_2Si_4$ ($[M+H]^+$): 1892.8935, found: 1892.8936.




**9**

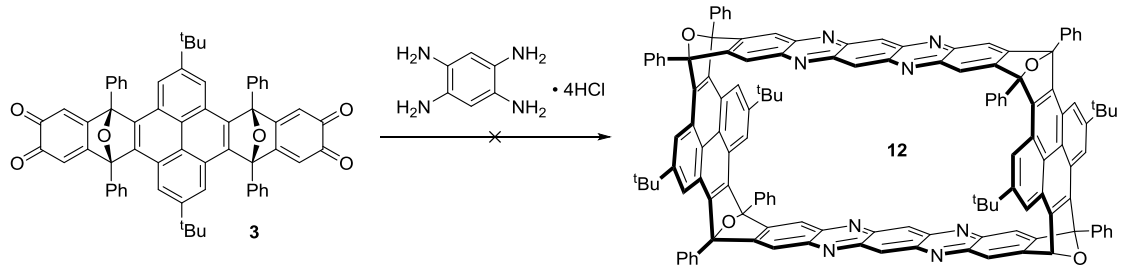
Compound **9**: To a stirred solution of **8** (240 mg, 0.13 mmol) in 20 mL of diethyl ether under an atmosphere of $N_2$ was added $LiAlH_4$ (97 mg, 2.6 mmol) at 0 ℃. The reaction mixture was stirred under ultrasonication at room temperature for 4 hours, then quenched with $H_2O$, extracted with diethyl ether. The extracts were combined, washed with brine and dried over $MgSO_4$, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ $CH_2Cl_2$/ diethyl ether 4/2/1 (V/V/V) as eluent to afford **9** as red solid in a yield of 75%. Melting point: not melt when heated up to 350 ℃. $^1$H NMR (500 MHz, $CD_3COCD_3$) δ = 8.31−8.24 (m, 8H), 8.00 (s, 4H), 7.90 (s, 4H), 7.76−7.69 (m, 12H), 5.75−5.71 (m, 4H), 1.21 – 1.15 (m, 84H), 1.08 (s, 18H). $^{13}$C NMR (126 MHz, $CD_3COCD_3$) δ = 149.3, 149.0, 148.7, 144.1, 141.6, 140.6, 135.8, 131.0, 130.6, 129.8, 127.1, 123.9, 121.6, 120.4, 102.9, 102.7, 100.1, 93.1, 35.6, 31.6, 19.2, 12.2. HRMS (MALDI-TOF): calcd. for $C_{120}H_{139}N_8O_2Si_4$ ($[M+H]^+$): 1836.0042, found: 1835.9999.



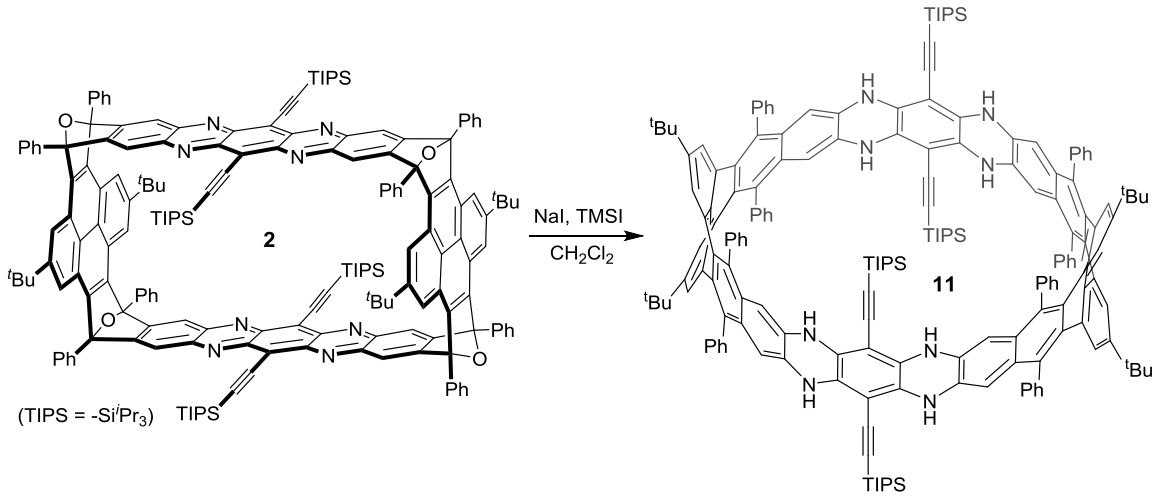

**2**

Compound **2**: A solution of **9** (97 mg, 0.053 mmol) and **3** (48 mg, 0.053 mmol) in 53 mL of acetic acid was stirred at 80 ℃ for 24 hours, and cooled to room temperature, then quenched with saturated $NaHCO_3$(aq), extracted with $CH_2Cl_2$. The extracts were combined, washed with brine, dried over $MgSO_4$, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with hexane / dichloromethane / acetone / triethylamine 60/20/4/1 (V/V/V/V) as eluent to afford **2** as dark purple solid in a yield of 30%. Melting point: not melt when heated up to 350 ℃. $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.29−8.16 (m, 16H), 7.93 (s, 8H), 7.85 (s, 8H), 7.66−7.61 (m, 24H), 1.18−1.11 (m, 84H), 1.03 (s, 36H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ = 151.2, 148.3, 146.7, 144.9, 142.2, 133.4, 130.2, 129.1, 125.9, 123.9, 121.8, 121.1, 120.5, 110.6, 102.4, 92.1, 35.0, 31.2, 18.9, 11.7. HRMS (MALDI−TOF): calcd. for $C_{184}H_{177}N_8O_4Si_4$ ($[M+H]^+$): 2676.3019, found: 2676.2950.

**Scheme S1.** Attempted synthesis of macrocycle **12**.




**Scheme S2.** Aromatization of **2**




To a stirred solution of **2** (10 mg, 0.004 mmol) and NaI (22.5 mg, 0.15 mmol) in 2 mL of $CH_2Cl_2$ under an atmosphere of $N_2$ was added TMSI (21 uL, 0.15 mmol). The reaction mixture was stirred at room temperature for 4 hours, then quenched with $NaHCO_3$ (aq), extracted with $CH_2Cl_2$. The extracts were combined, washed with an aqueous solution of $Na_2S_2O_3$ and brine subsequently, dried over $MgSO_4$, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ ethyl acetate 5/1 (V/V) as eluent to afford crude brown solid, from which compound **11** was identified with HRMS.

HRMS (MALDI-TOF) of **11**: calcd. for $C_{184}H_{185}N_8Si_4$ ($[M+H]^+$): 2619.3770, found: 2619.3766.

## 2. UV-vis absorption and fluorescence spectra

UV-vis spectra were recorded with a Varian CARY 5G UV-vis spectrophotometer. Fluorescence spectra were recorded with a Hitachi F-7000 fluorescence spectrometer.

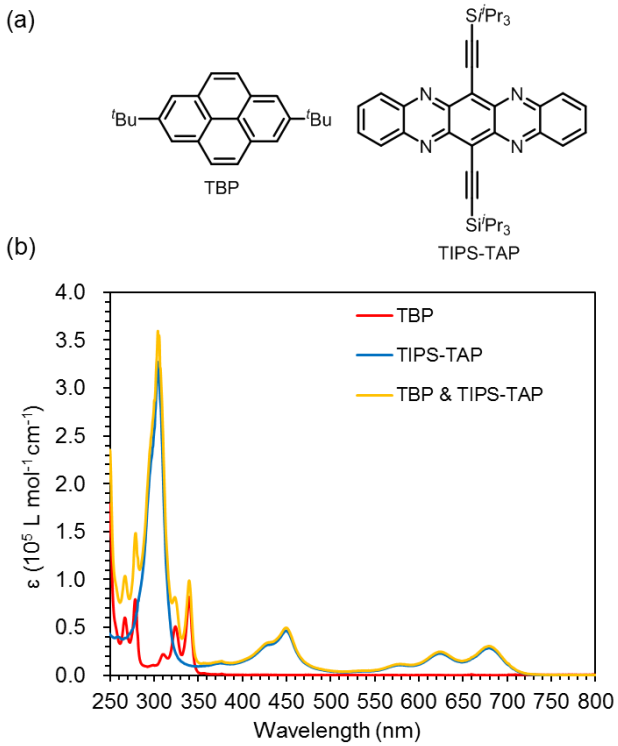



**Figure S1.** (a) Structures of TBP and TIPS−TAP; (b) absorption spectra of TBP, TIPS−TAP, 1:1 mixture of TBP and TIPS−TAP ($2\times10^{-5}$ mol/L in $CH_2Cl_2$).

## 3. Study of stability with UV-vis absorption spectroscopy

Two solutions of **2** in dichloromethane ($1 \times 10^{-5}$ mol/L) in two 100 ml volumetric flasks were prepared, one of the flasks was protected from light and both flasks were stored under ambient conditions. The change of absorbance of **2** was then monitored by UV-visible absorption spectroscopy.

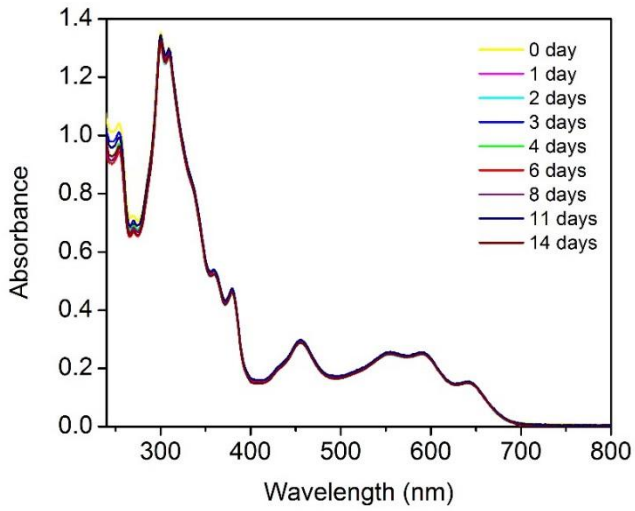



**Figure S2.** UV-visible spectra of **2** exposed to ambient light and air.

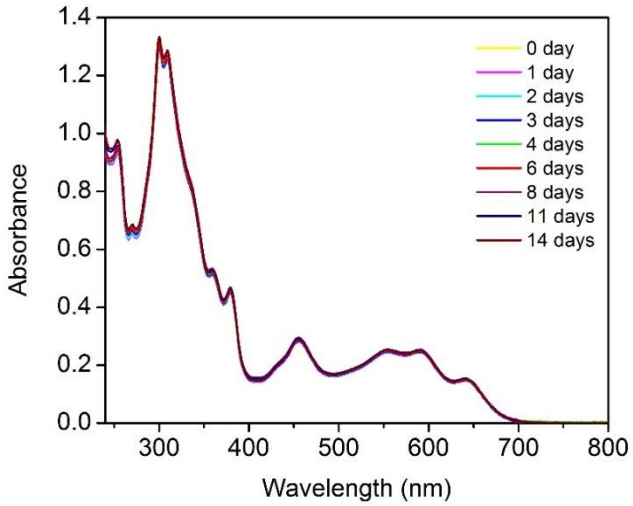



**Figure S3.** UV−visible spectra of **2** stored in dark and ambient air.

## 4. FT-IR spectra

FTIR spectra were recorded on a Thermo Nicolet iS10 mid−FTIR spectrometer using KBr pellet.

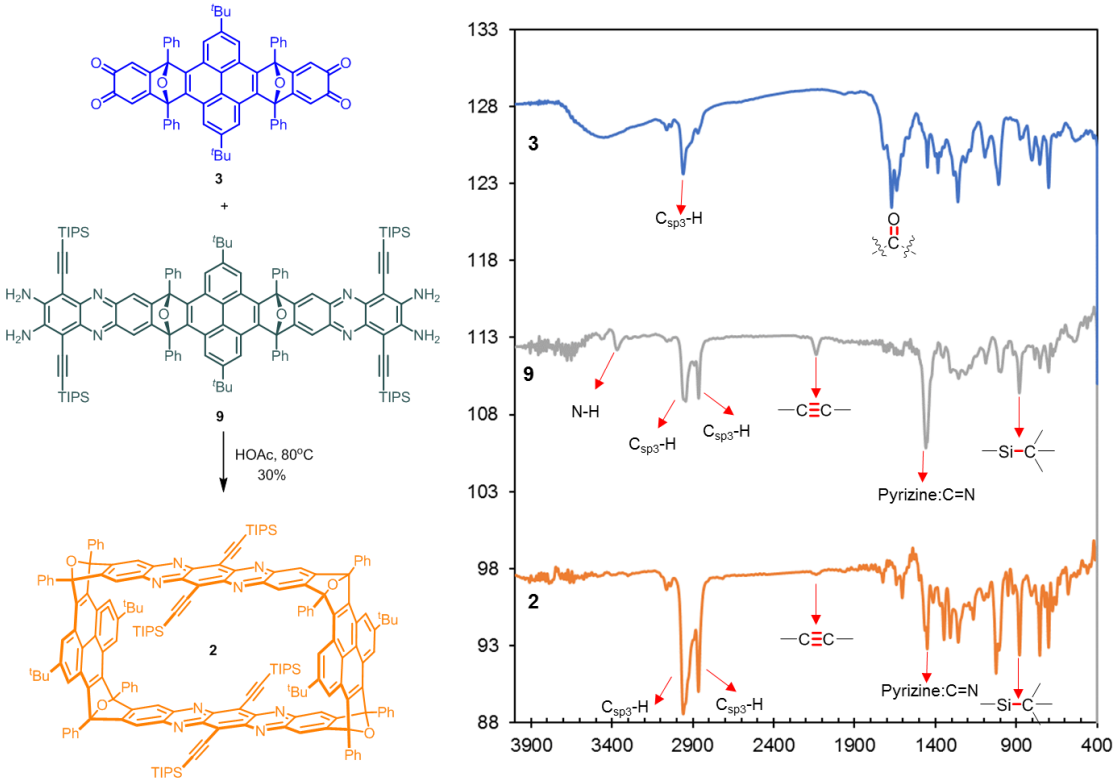



**Figure S4.** FTIR spectra of compouds **3**, **9** and **2**.

## 5. High−resolution mass spectra

High−resolution mass spectra of compounds **2** and **11** were recorded on Bruker Autoflex speed MALDI−TOF spectrometer.

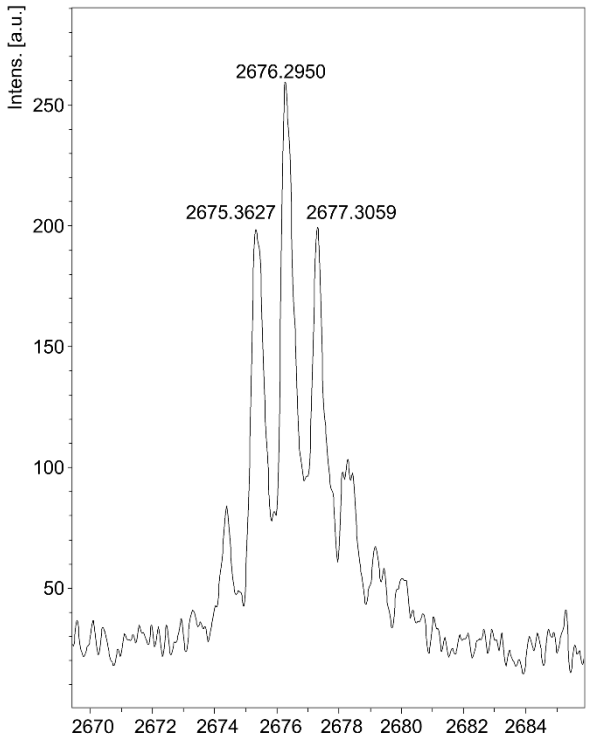



**Figure S5.** HRMS of the macrocycle **2** ($[M+H]^+$).

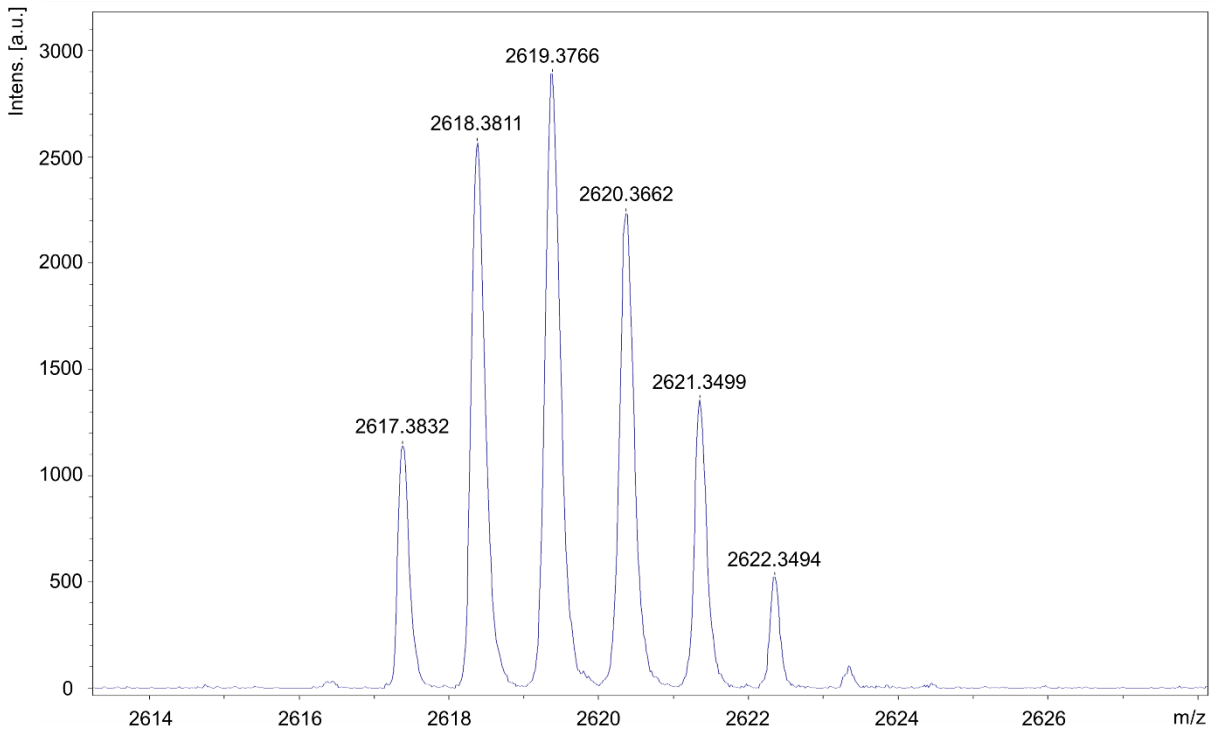



**Figure S6.** HRMS of N-heterocyclacene **11** ($[M+H]^+$).

## 6. X-ray crystallography

X−ray crystallography data were collected on a Bruker AXS Kappa ApexII Duo Diffractometer.

**Table S1.** Summary of crystal structure of **2**.

| | |
|---|---|
| Formula | $C_{184}H_{176}N_8O_4Si_4$ |
| Space group | $P\bar{1}(\underline{2})$ |
| Unit Cell Lengths (Å) | a = 19.104(2) |
| | b = 24.425(3) |
| | c = 24.731(3) |
| Unit Cell Angles ( °) | α = 69.871(3) |
| | β = 75.302(3) |
| | γ = 78.691(3) |
| Cell Volume ($Å^3$) | 10405 |
| R factor | 14.92 |

## 7. DFT calculations

The frontier molecular orbitals of **2**, 2,7-di(t-butyl)pyrene (TBP) and 6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacene (TIPS-TAP) were calculated using simplified model molecules **2'**, TBP' and TIPS-TAP', which have smaller methyl or trimethylsilyl groups replacing larger *t*-butyl or triisopropylsilyl (TIPS) groups to reduce computational cost. Energy−minimized models of **2'**, TBP' and TIPS-TAP' were calculated using Gaussian 09W program at the B3LYP/6−31G(d, p) level of Density Functional Theory (DFT), and their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were then calculated at the B3LYP/6−31++G(d, p) level of DFT.

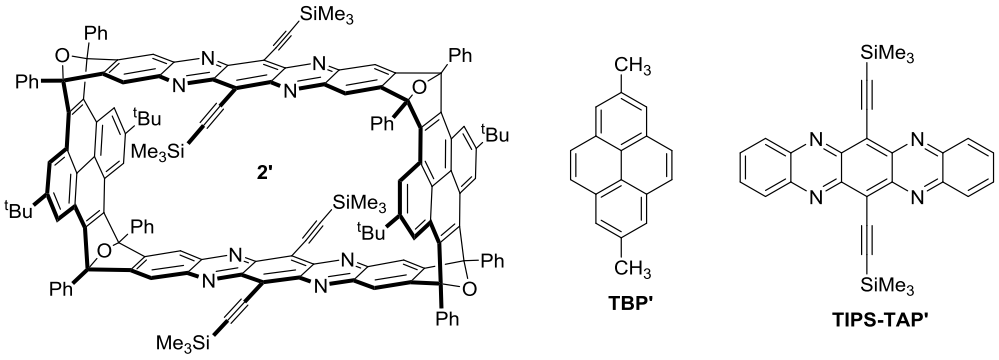
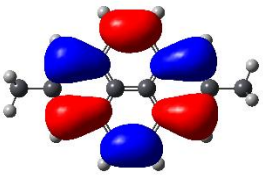
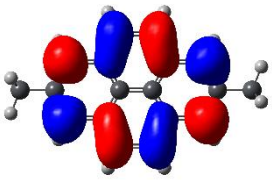



**Figure S7** Structures of simplified model molecules **2'**, TBP' and TIPS-TAP'.

**TBP'**

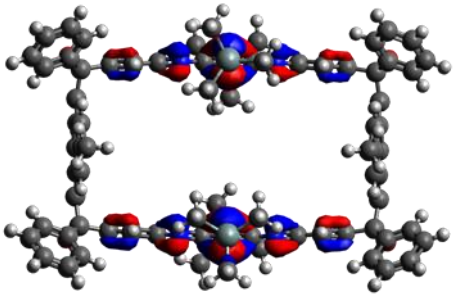


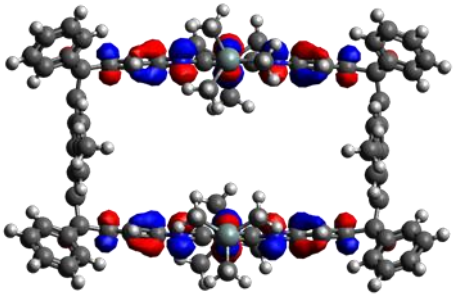


HOMO: −5.565 eV

LUMO: −1.791 eV

**2'**

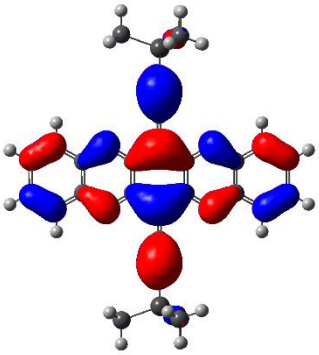


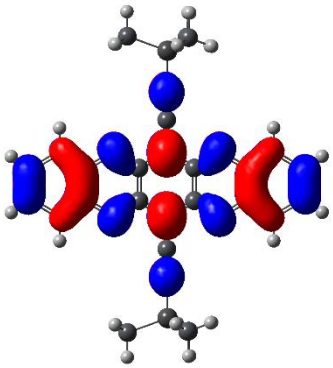


HOMO: −5.177 eV

LUMO: −3.144 eV

**TIP-TAP'**





HOMO: −5.635 eV

LUMO: −3.810 eV

**Figure S8** Calculated frontier molecular orbitals of **2'**, TBP' and TIPS-TAP'.

**Optimized Cartesian coordinates at B3LYP/6−31G(d,p) level of theory**

**2'**

| | | | |
|---|---|---|---|
| C | 7.398699 | −1.210507 | 2.838402 |
| C | 7.543099 | −1.237700 | 1.441202 |
| C | 7.585599 | −0.020700 | 0.714200 |
| C | 7.543300 | 1.231393 | 1.450602 |
| C | 7.399000 | 1.194593 | 2.847202 |
| C | 7.310199 | −0.010707 | 3.546602 |
| C | 7.606399 | −2.446407 | 0.675302 |
| C | 7.605799 | −2.441307 | −0.696298 |
| C | 7.542499 | −1.226307 | −1.453198 |
| C | 7.585299 | 0.519300 | −0.716798 |
| C | 7.543100 | 1.242193 | −1.443898 |
| C | 7.606700 | 2.451593 | −0.677998 |
| C | 7.606700 | 2.446393 | 0.693502 |
| C | 7.398099 | −1.189407 | −2.849998 |
| C | 7.309799 | 0.015793 | −3.549198 |
| C | 7.398600 | 1.215693 | −2.840998 |
| C | 7.395800 | 3.931193 | −1.091698 |
| C | 5.920300 | 4.158694 | −0.711498 |
| C | 5.919900 | 4.152694 | 0.739602 |
| C | 7.395400 | 3.922593 | 1.118502 |
| C | 7.395899 | −3.925807 | 1.089302 |
| C | 5.920299 | −4.153606 | 0.709702 |
| C | 5.919399 | −4.148306 | −0.741398 |
| C | 7.394699 | −3.917707 | −1.120998 |
| C | 4.768300 | 4.222194 | −1.425698 |
| C | 3.516500 | 4.301194 | −0.714998 |
| C | 3.516100 | 4.293794 | 0.742802 |
| C | 4.767400 | 4.209094 | 1.453702 |
| C | 4.768599 | −4.216506 | 1.424502 |
| C | 3.516599 | −4.296406 | 0.714402 |
| C | 3.515599 | −4.291606 | −0.743498 |
| C | 4.766599 | −4.206306 | −1.454898 |
| O | 8.045900 | 4.603393 | 0.016102 |
| O | 8.045699 | −4.598107 | −0.018798 |
| N | 2.384800 | 4.353094 | −1.403798 |
| C | 1.221100 | 4.378694 | −0.710798 |
| C | 1.220600 | 4.369794 | 0.737802 |
| N | 2.383800 | 4.337294 | 1.431402 |
| N | 2.385099 | −4.346806 | 1.403702 |
| C | 1.221199 | −4.374206 | 0.711102 |
| C | 1.220199 | −4.370306 | −0.737498 |
| N | 2.383199 | −4.338106 | −1.431498 |
| C | −0.260000 | 4.397694 | −1.435198 |
| C | −1.226700 | 4.377995 | −0.711598 |
| C | −1.227200 | 4.369695 | 0.737200 |
| C | −0.360000 | 4.378894 | 1.461602 |
| C | −0.240100 | −4.391600 | 1.436200 |
| C | −1.226601 | −4.374305 | 0.712802 |

| | | | |
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| C | 0.990000 | −4.404206 | 2.851502 |
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| C | 0.350000 | 4.436294 | −4.072398 |
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| C | −7.549500 | 1.232396 | 1.450702 |
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| C | −7.316100 | −0.640000 | 3.548802 |
| C | −7.613000 | 2.446196 | 0.691502 |
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| C | −7.549300 | 1.238296 | −1.443998 |
| C | −7.591701 | 0.249600 | −0.714498 |
| C | −7.549501 | −1.230304 | −1.448798 |
| C | −7.612601 | −2.443904 | −0.689798 |
| C | −7.612100 | −2.446604 | 0.681802 |
| C | −7.405300 | 1.209396 | −2.840898 |
| C | −7.317101 | 0.799600 | −3.547098 |
| C | −7.405501 | −1.195804 | −2.845898 |
| C | −7.402101 | −3.921400 | −1.112098 |
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| C | −5.925701 | −4.153805 | 0.717502 |
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| C | −7.402000 | 3.923096 | 1.114200 |
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| C | −4.773300 | 4.218795 | −1.429098 |
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| O | −8.051900 | 4.601996 | 0.010102 |
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| N | −2.389601 | −4.346305 | 1.407200 |
| N | −2.391401 | −4.340500 | −1.428398 |
| C | 7.102599 | −0.015207 | 5.042802 |
| H | 7.578500 | 0.849793 | 5.513902 |

| | | | |
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| H | 7.530500 | 0.916893 | −5.504298 |
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| C | 7.333600 | 5.446693 | 3.153102 |
| C | 7.935900 | 5.970393 | 4.298902 |
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| C | 9.241899 | −4.023807 | 2.783702 |
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| C | 7.940198 | −6.030700 | 4.251602 |
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| C | 7.934198 | −5.964700 | −4.302698 |
| C | 7.332299 | −5.440907 | −3.156398 |
| Si | 0.041799 | −4.440106 | 5.909302 |
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| C | 0.878298 | −6.035606 | 6.482102 |
| C | −1.730501 | −4.365505 | 6.559902 |
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| H | 0.556899 | −2.610600 | 6.183202 |
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| C | −0.129201 | −2.630606 | −6.551298 |
| C | −1.485901 | −5.415505 | −6.541798 |
| H | 2.475799 | −4.643306 | −6.178398 |
| H | 1.644199 | −5.215806 | −7.634298 |
| H | −1.050601 | −2.155305 | −6.219800 |
| H | −0.129501 | −2.598406 | −7.646898 |
| H | −1.431202 | −6.452205 | −6.194398 |
| H | −1.525201 | −5.429405 | −7.637098 |

| | | | |
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| C | −0.018200 | 6.146594 | 6.555200 |
| C | 1.553700 | 3.477394 | 6.539502 |
| C | −1.546600 | 3.452795 | 6.540202 |
| H | −0.017400 | 6.176494 | 7.650602 |
| H | −0.907400 | 6.689500 | 6.204602 |
| H | 1.589700 | 3.453994 | 7.634802 |
| H | 2.456400 | 3.983694 | 6.183102 |
| H | −2.457400 | 3.944395 | 6.183702 |
| H | −1.582000 | 3.429395 | 7.635502 |
| Si | 0.022100 | 4.458994 | −5.908698 |
| C | 1.287300 | 5.737894 | −6.488398 |
| C | −1.770000 | 4.920595 | −6.532998 |
| C | 0.504200 | 2.741094 | −6.531598 |
| H | 1.331200 | 5.774094 | −7.582998 |
| H | 2.289000 | 5.497094 | −6.118698 |
| H | −2.451500 | 4.204095 | −6.185198 |
| H | −1.728800 | 4.934095 | −7.628598 |
| H | 1.495500 | 2.454094 | −6.166898 |
| H | 0.527600 | 2.717194 | −7.627198 |
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| H | −6.041201 | 0.042595 | 5.294102 |
| H | −7.507901 | −0.917204 | 5.502202 |
| C | −7.110201 | 0.011796 | −5.043398 |
| H | −7.576300 | 0.885496 | −5.508198 |
| H | −7.529101 | −0.886304 | −5.506198 |
| H | −6.042401 | 0.040595 | −5.292898 |
| C | −7.978100 | −4.458904 | 2.385202 |
| C | −9.246801 | −4.021604 | 2.792702 |
| C | −9.849601 | −4.553400 | 3.930102 |
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| C | −7.980100 | −4.449504 | −2.479800 |
| C | −9.248801 | −4.010104 | −2.806098 |
| C | −9.852301 | −4.537400 | −3.945298 |
| C | −9.198301 | −5.518104 | −4.694298 |
| C | −7.945202 | −5.974704 | −4.288298 |
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| C | −7.979600 | 4.451696 | 2.402702 |
| C | −9.248500 | 4.012496 | 2.808202 |
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| C | −9.197600 | 5.520696 | 4.696202 |
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| C | −7.978400 | 4.461496 | −2.383198 |
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| C | −9.195500 | 5.538696 | −4.673298 |

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| H | 4.730499 | −4.185600 | 2.507702 |
| H | 4.726599 | −4.167206 | −2.537798 |
| H | −7.353100 | 2.130796 | 3.396302 |
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| H | −7.353000 | 2.144196 | −3.386098 |
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| H | −4.736401 | −4.172205 | −2.531598 |
| H | −4.733301 | −4.182305 | 2.513902 |
| H | −4.736000 | 4.170995 | 2.533202 |
| H | −4.733600 | 4.186795 | −2.512298 |
| H | 6.371700 | 5.829194 | 2.832202 |
| H | 7.425200 | 6.741393 | 4.868202 |
| H | 9.657000 | 5.921993 | 5.595602 |
| H | 10.826100 | 4.181993 | 4.255202 |
| H | 9.753400 | 3.253193 | 2.227402 |
| H | 9.752200 | 3.266993 | −2.207798 |
| H | 10.825500 | 4.211893 | −4.227798 |
| H | 9.658900 | 5.965893 | −5.552098 |
| H | 7.428900 | 6.782693 | −4.816398 |
| H | 6.374700 | 5.854394 | −2.788098 |
| H | 9.752599 | −3.261207 | 2.204502 |
| H | 10.826899 | −4.205907 | 4.224200 |
| H | 9.661198 | −5.960107 | 5.548802 |
| H | 7.430998 | −6.777307 | 4.813902 |
| H | 6.375799 | −5.849106 | 2.786102 |
| H | 9.752799 | −3.248607 | −2.229498 |
| H | 10.824999 | −4.176407 | −4.257998 |
| H | 9.655198 | −5.915207 | −5.599598 |
| H | 7.423198 | −6.734407 | −4.872498 |
| H | 6.370299 | −5.823506 | −2.835798 |
| H | 2.045599 | −2.958406 | 6.132402 |
| H | 1.899898 | −6.106206 | 6.095202 |
| H | −2.233701 | −3.451505 | 6.229200 |
| H | 1.697798 | −6.231600 | −6.184198 |
| H | 0.712799 | −2.027806 | −6.196698 |
| H | −2.425901 | −4.990405 | −6.176098 |
| H | 0.861000 | 6.695494 | 6.202902 |
| H | 1.587100 | 2.444194 | 6.179502 |
| H | −1.563400 | 2.418995 | 6.180702 |
| H | 1.031100 | 6.739694 | −6.129298 |
| H | −1.996200 | 5.912595 | −6.176598 |
| H | −0.207900 | 1.981794 | −6.193498 |

| | | | |
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| H | −10.831501 | −4.201704 | 4.233602 |
| H | −9.662802 | −5.949704 | 5.564200 |
| H | −7.431102 | −6.765404 | 4.831902 |
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| H | −9.760101 | −3.252104 | −2.221398 |
| H | −10.834101 | −4.184104 | −4.246998 |
| H | −9.666802 | −5.927604 | −5.584398 |
| H | −7.435202 | −6.747104 | −4.856198 |
| H | −6.380401 | −5.831805 | −2.822498 |
| H | −9.760000 | 3.254496 | 2.223602 |
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| H | −9.759500 | 3.264896 | −2.207998 |
| H | −10.832600 | 4.204596 | −4.230598 |
| H | −9.663600 | 5.951496 | −5.562198 |
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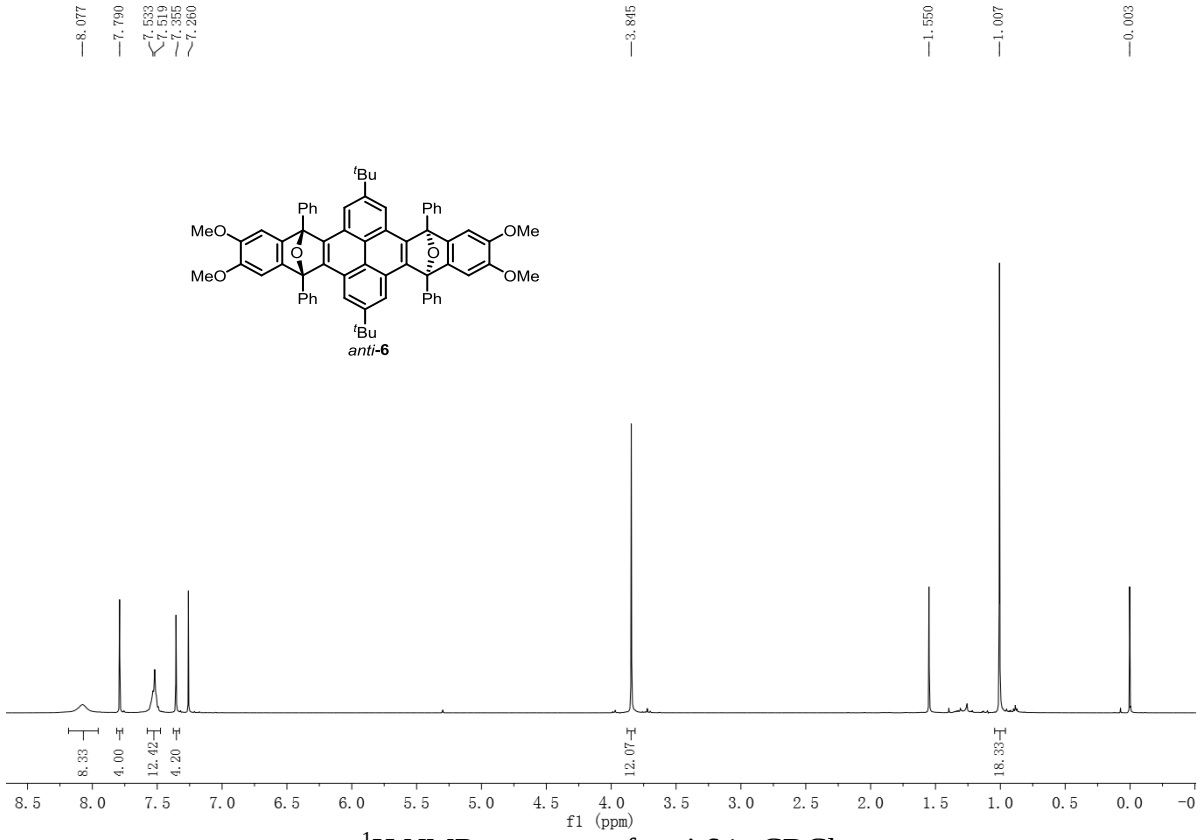
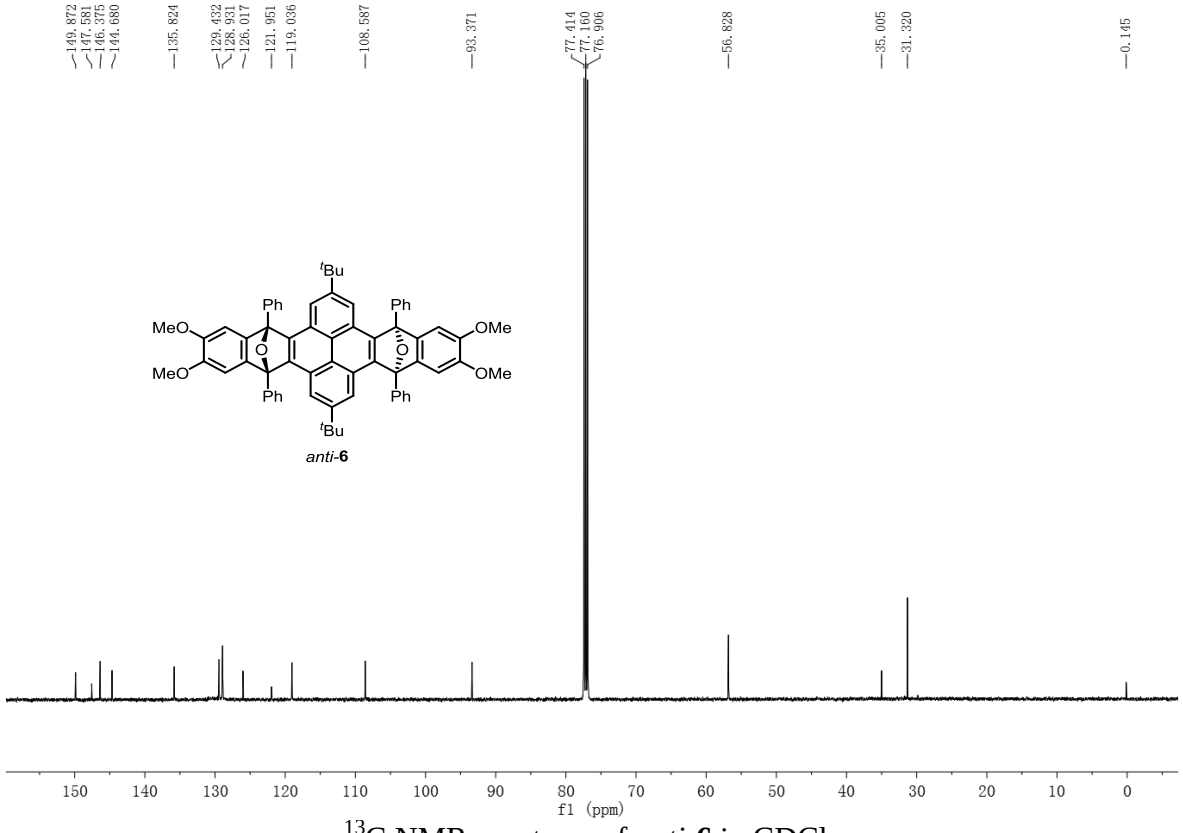
| H | −6.377600 | 5.843795 | −2.819800 |

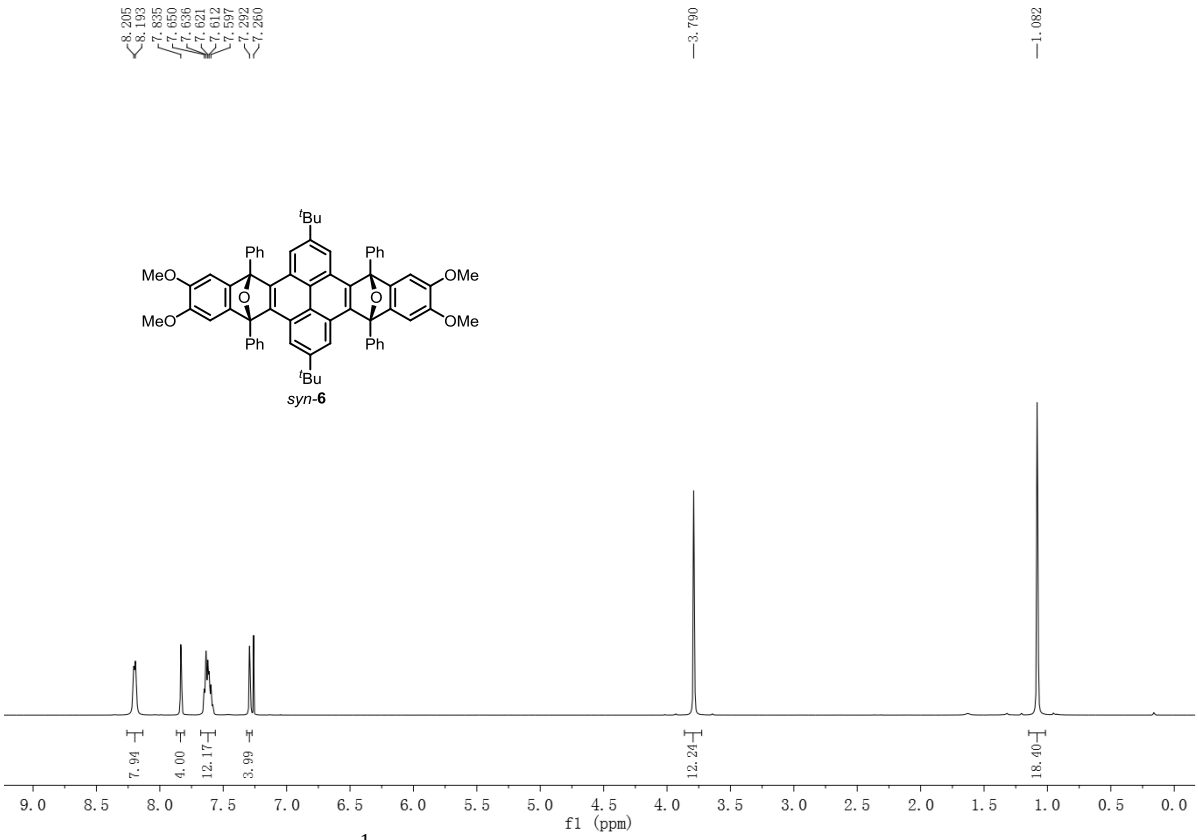
## 8. NMR spectra



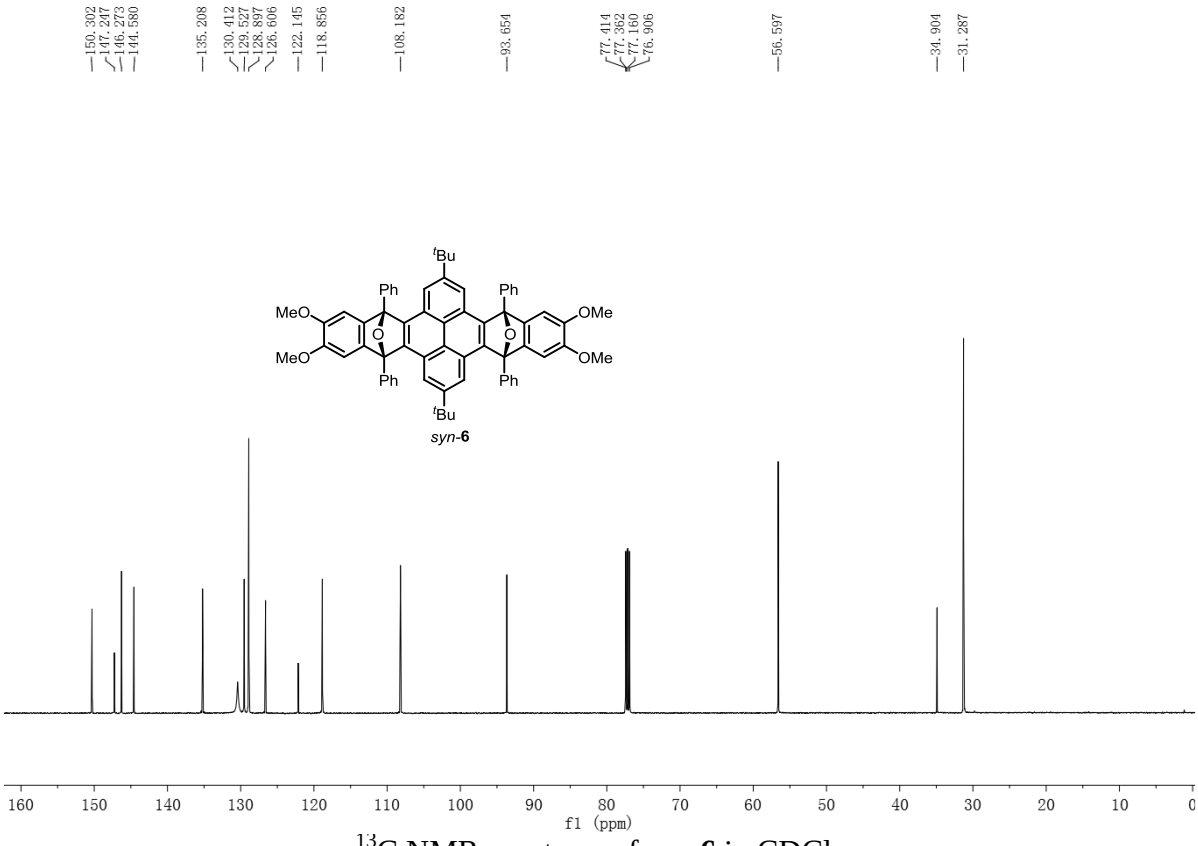

$^{1}$H NMR spectrum of *anti*-**6** in $CDCl_3$



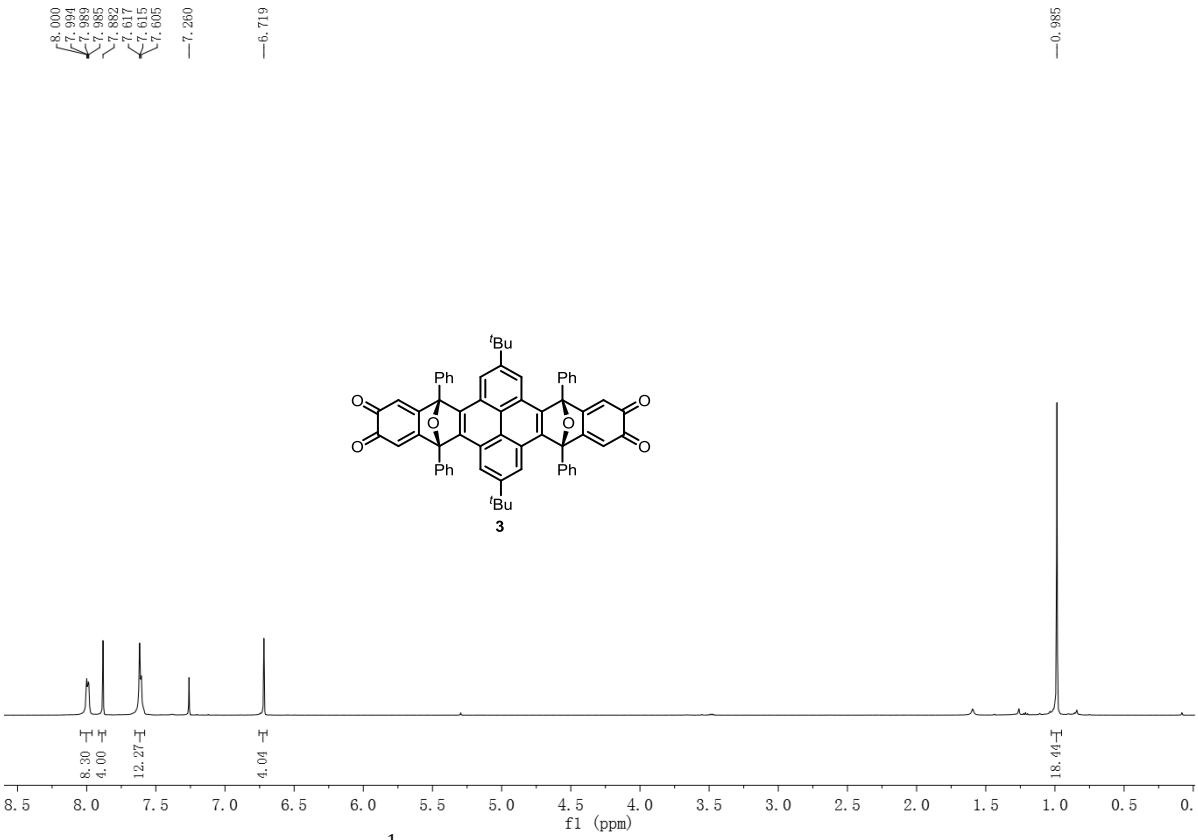

$^{13}$C NMR spectrum of *anti*-**6** in $CDCl_3$



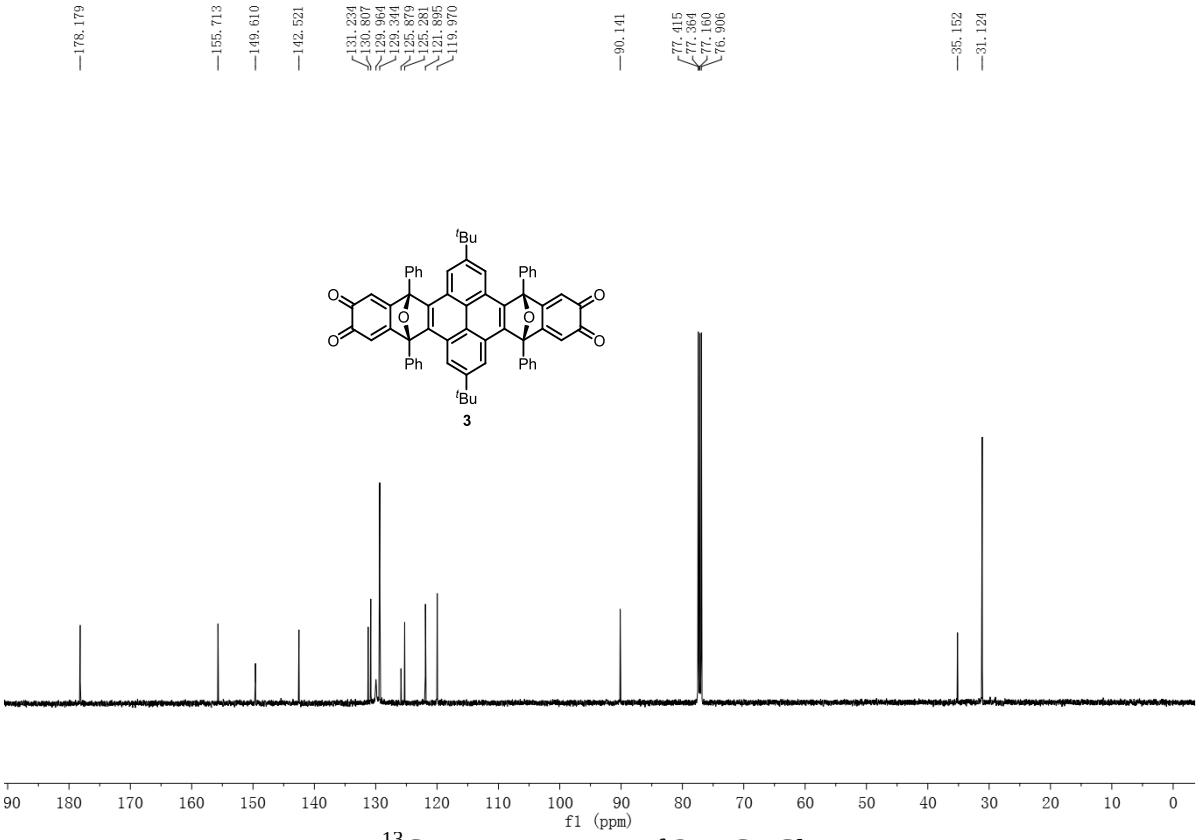

$^{1}$H NMR spectrum of *syn*-**6** in $CDCl_3$



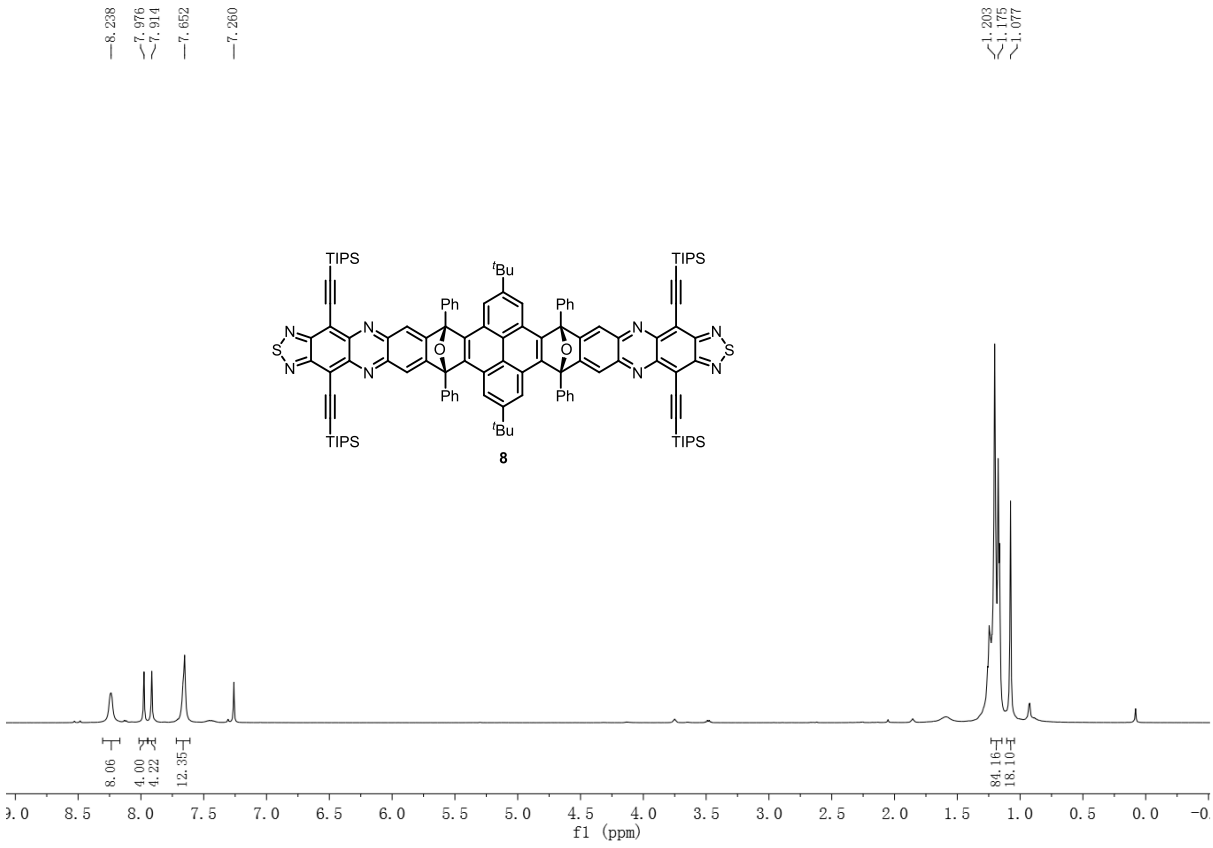

$^{13}$C NMR spectrum of *syn*-**6** in $CDCl_3$



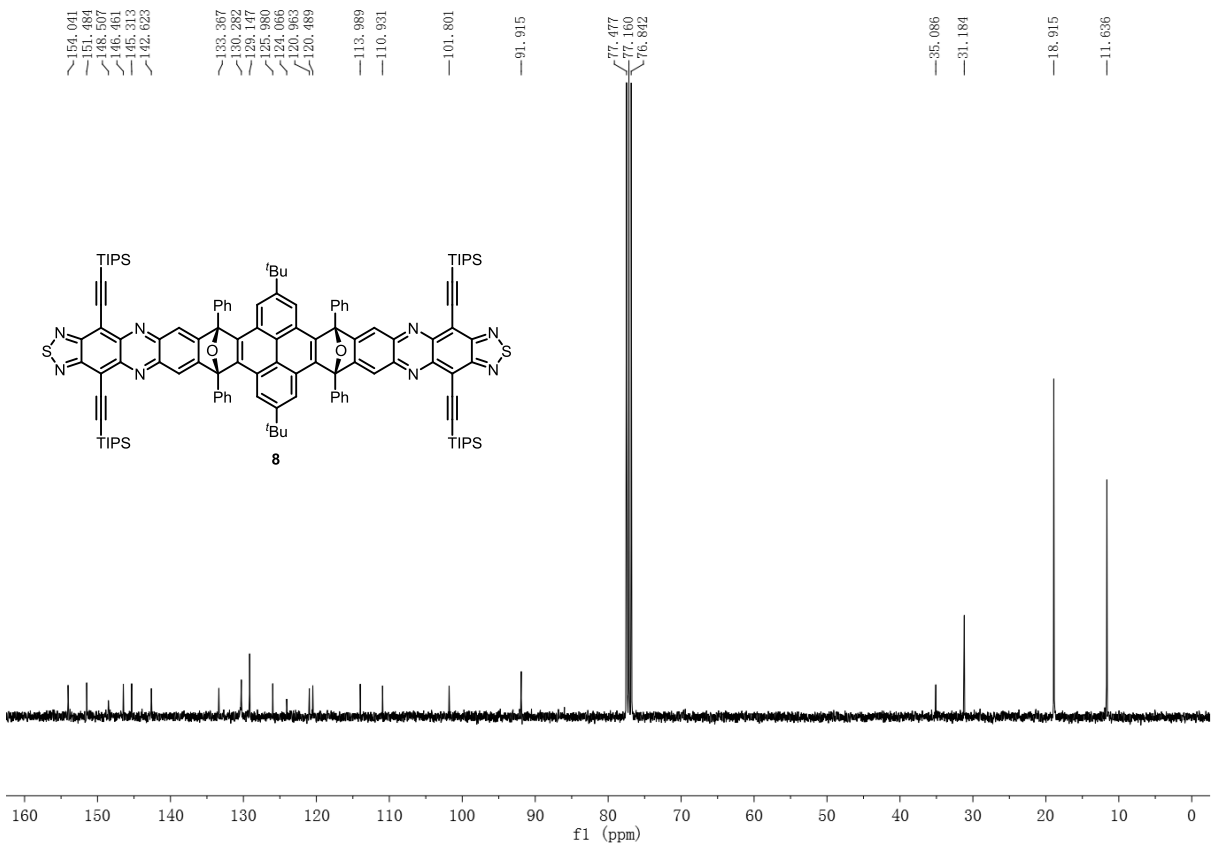

$^{1}$H NMR spectrum of **3** in $CDCl_3$



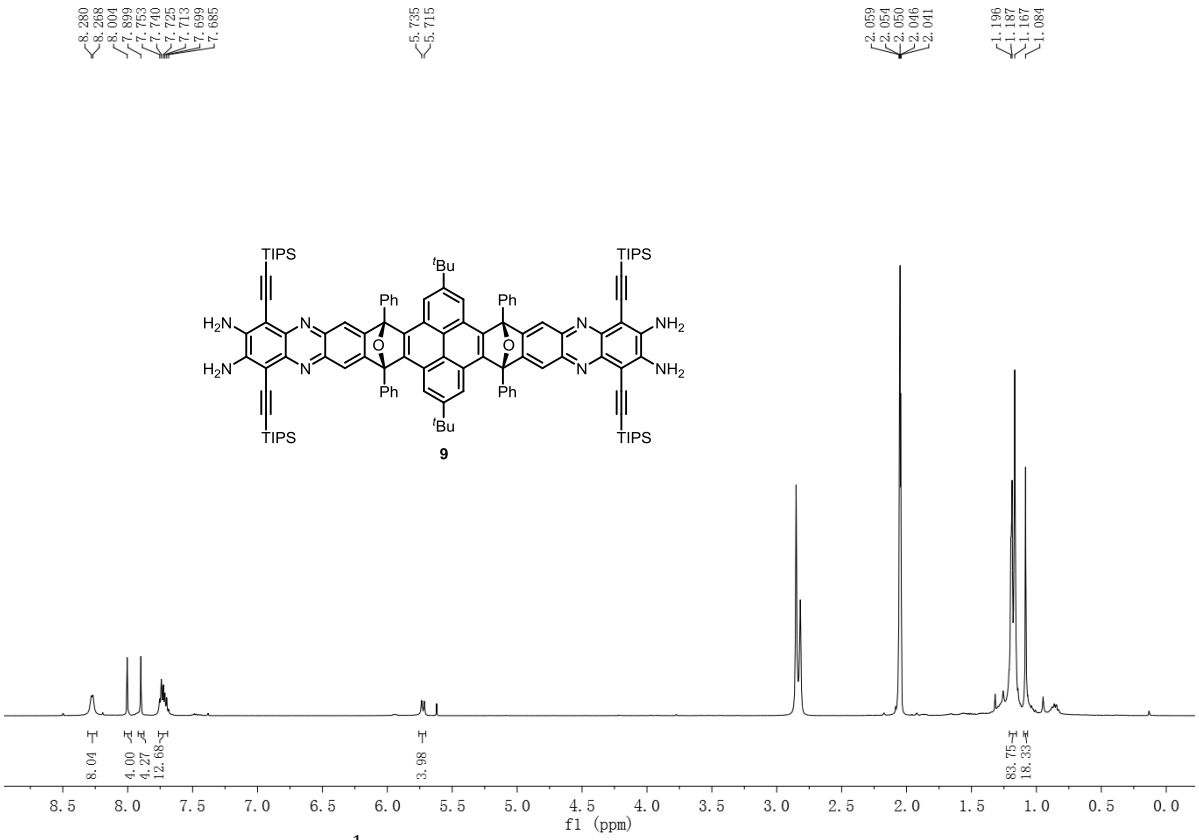

$^{13}$C NMR spectrum of **3** in $CDCl_3$



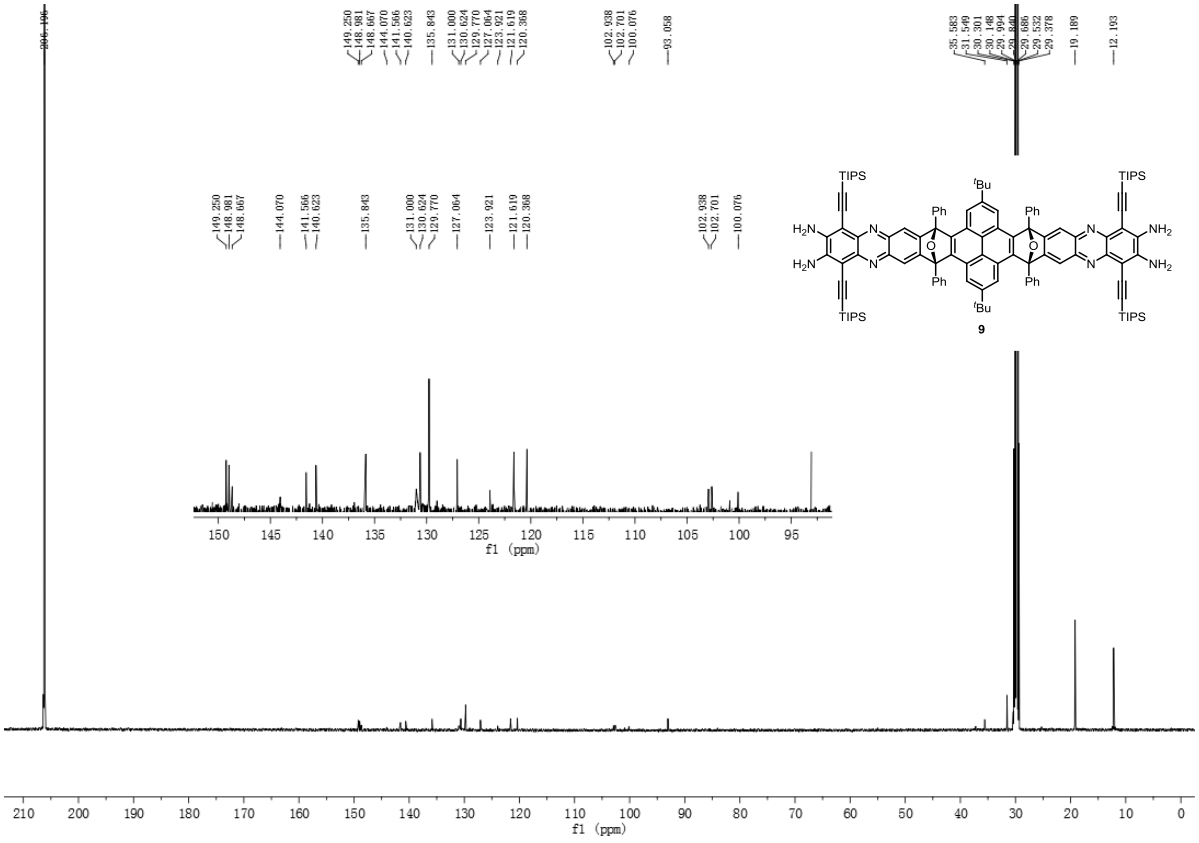

$^{1}$H NMR spectrum of **8** in $CDCl_3$



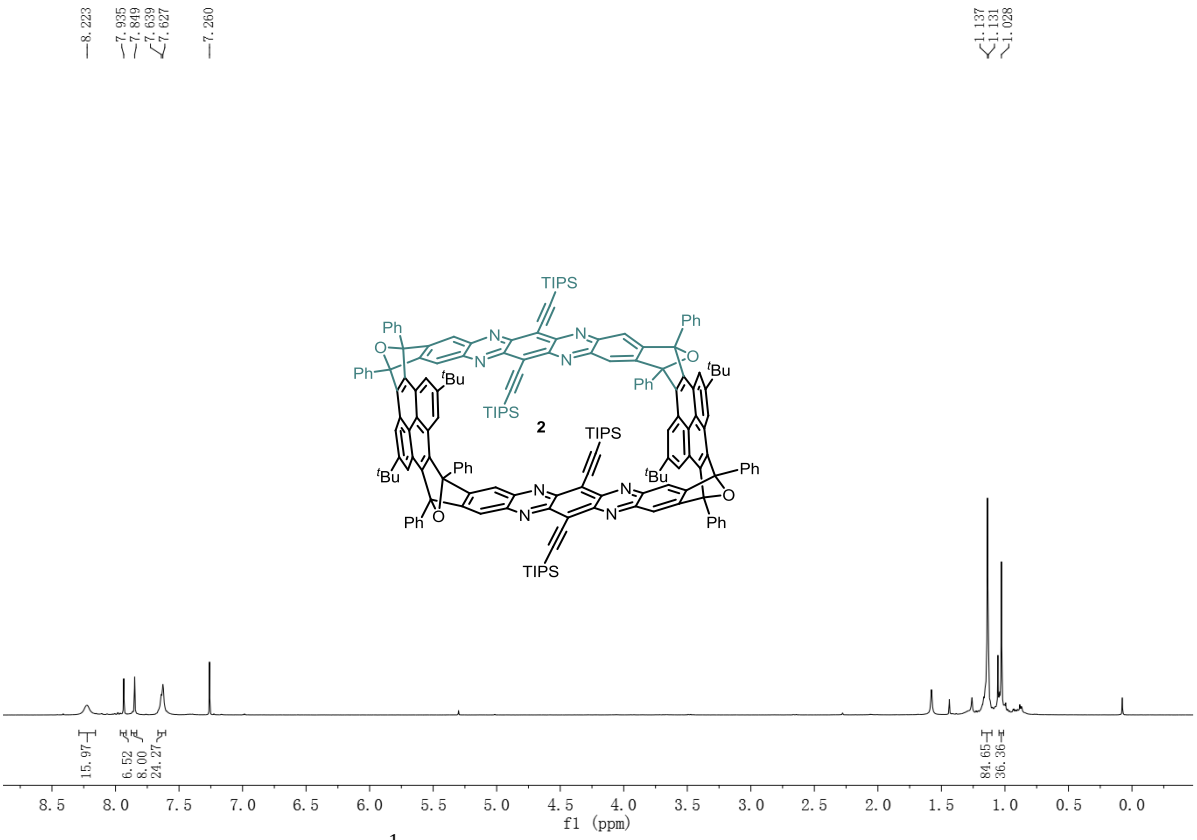

$^{13}$C NMR spectrum of **8** in $CDCl_3$



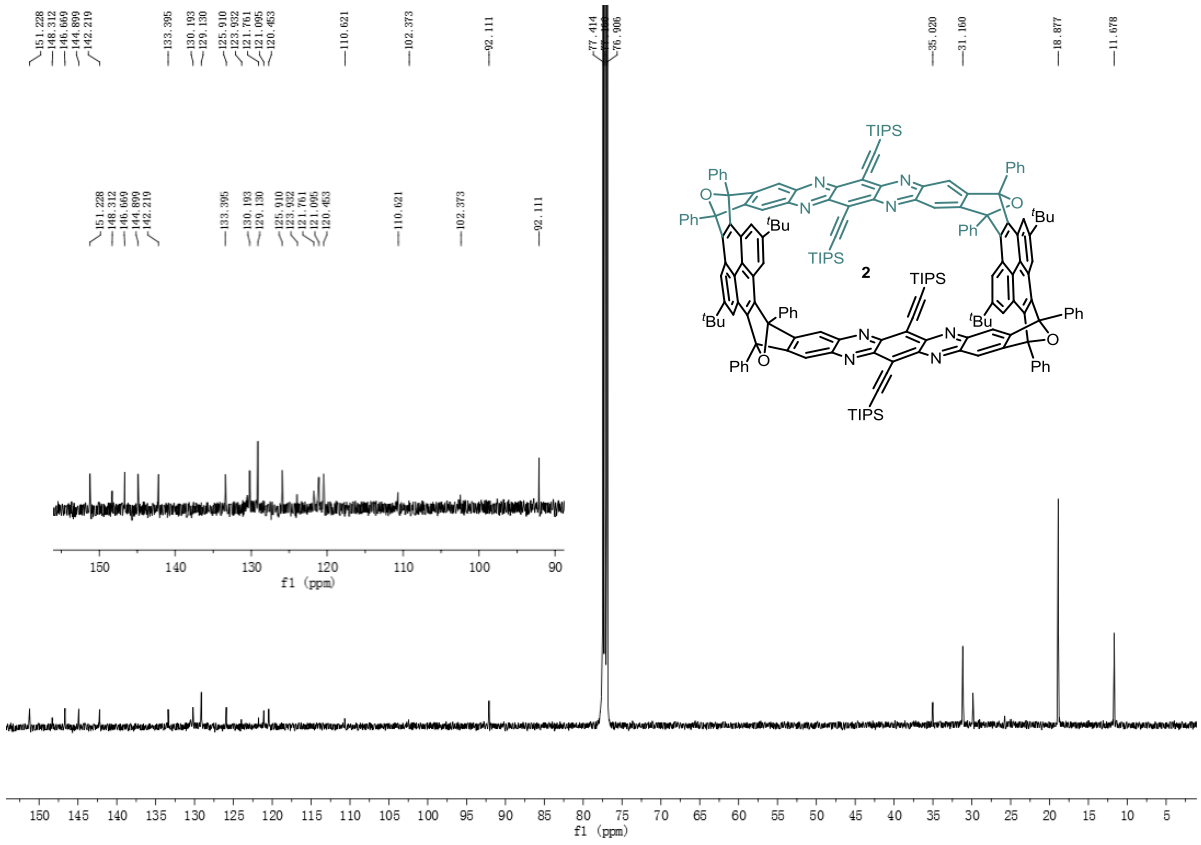

$^{1}$H NMR spectrum of **9** in $CD_3COCD_3$




$^{13}$C NMR spectrum of **9** in $CD_3COCD_3$




$^{1}$H NMR spectrum of **2** in $CDCl_3$




$^{13}$C NMR spectrum of **2** in $CDCl_3$

## 9. References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(2) T. Hamura, R. Nakayama, *Chem. Lett.* **2013**, *42*, 1013−1015.

(3) C. An, S. Zhou, M. Baumgarten, *Cryst. Growth Des.* **2015**, *15*, 1934−1938.