nature portfolio

https://doi.org/10.1038/s44160-022-00075-8

Supplementary information

Synthesis of a Möbius carbon nanobelt

In the format provided by the authors and unedited

Supplementary Information

Synthesis of a Möbius carbon nanobelt

Yasutomo Segawa,[1,2,3,4,*] Tsugunori Watanabe,[3] Kotono Yamanoue,[3] Motonobu Kuwayama,[3,5] Kosuke Watanabe,[1,4] Jenny Pirillo,[6] Yuh Hijikata,[6] and Kenichiro Itami[3,4,5,*]

[1] *Institute for Molecular Science, Myodaiji, Okazaki 444-8787, Japan*
[2] *Department of Structural Molecular Science, SOKENDAI (The Graduate University for Advanced Studies), Myodaiji, Okazaki 444-8787, Japan*
[3] *JST, ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Nagoya 464-8602, Japan*
[4] *Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan*
[5] *Institute of Transformative Bio-Molecules (WPI-ITbM) Nagoya University, Nagoya 464-8602, Japan*
[6] *Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 001-0021, Japan*

*E-mail: segawa@ims.ac.jp (Y.S.), itami@chem.nagoya-u.ac.jp (K.I.)

Table of Contents

1. Materials and methods

Synthesis and purification

Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in dried glassware with standard vacuum-line techniques. Materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF), dichloromethane, and toluene for reactions were purified by passing through a solvent purification system (Glass Contour). Work-up and purification procedures were carried out with reagent-grade solvents under air. 2,7-Dibromo-9,10-dibutoxyphenanthrene (**2**) and **5** were prepared according to reported procedures[1,2]. Analytical thin-layer chromatography (TLC) was performed using Wako silica gel 70 F_{254} coated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). Flash column chromatography was performed with E. Kanto silica gel 60 N (spherical, neutral, 40–100 μm). Preparative thin-layer chromatography (PTLC) was performed using Merck® PLC Silica gel 60 F_{254} 0.5 mm glass plates 20 × 20 cm with concentrating zone (20 × 4 cm). Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-9260II NEXT instrument equipped with JAIGEL-2HR columns (20 mm I.D. × 600 mm × 2) using $CHCl_3$ as an eluent. Chiral HPLC was performed with a Shimadzu Prominence 2000 instrument equipped with CHIRALPAK IE column (4.6 mm I.D. × 250 mm) eluted by THF/hexane (6:4).

Measurements

Melting points (mp) were measured on a MPA100 Optimelt automated melting point system or not measured. High-resolution mass spectra (HRMS) were determined on a JEOL JMS-S3000 SpiralTOF (MALDI-TOF MS) using polyethyleneglycol mixture (PEG) as internal standards and *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix with NaI as cationizing agent, a Bruker Daltonics Ultraflex III TOF/TOF (MALDI-TOF MS) with Peptide Calibration Standard II (Bruker) as internal standards, or a Bruker Daltonics microTOF-QII (ESI and APCI). Nuclear magnetic resonance (NMR) spectra were recorded on JEOL spectrometers (JNM-ECA-600: ^{1}H 600 MHz, ^{13}C 150 MHz). Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to the residual protons in $CDCl_3$ (δ 7.26 ppm) or $C_2D_2Cl_4$ (δ 5.98 ppm). ^{13}C NMR spectra were measured using a proton-decoupled pulse sequence. Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm) or $C_2D_2Cl_4$ (δ 73.78 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, dd = doublet of doublets, td = triplet of doublets, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

UV–Vis absorption spectra were recorded on a Shimadzu UV-3510 spectrometer with a resolution of 0.5 nm. Emission spectra were measured on Shimadzu RF-6000 spectrometer with a resolution of 0.4 nm. Absolute fluorescence quantum yields (Φ_F) were determined on a Shimadzu RF-6000 using a calibrated integrating sphere system upon excitation at 380 nm. For FL lifetime measurements of **1**, Hamamatsu Photonics Quantaurus-Tau® fluorescence lifetime spectrometer C11367-21 with LED as a light source was used (excitation: 340nm, emission: 505 nm, time range: 103 ns, frequency: 2 MHz). Circular dichroism spectra were measured with a JASCO FT/IR6100. Dilute solutions in spectral grade dichloromethane in a 1 cm square quartz cell were used for measurements.

Theoretical study

DFT: The Gaussian 16 program[3] running on a NEC LX 110Rh system was used for optimization (B3LYP/6-31G(d)[4,5]. Structures were optimized without any symmetry

assumptions. Structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency). Simulated CD spectra were visualized with GaussView 6.0.16 for Mac. The half-width at half-height was adjusted to fit the experimental spectra.

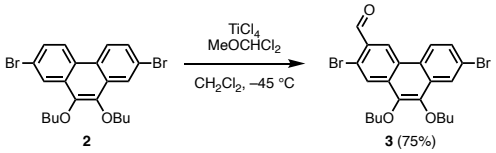
DFTB-MD: Optimization of (25,25)MCNB was performed using the self-consistent-charge density-functional tight-binding (SCC-DFTB) method[6] with the third-order expansion[7] as implemented in the DFTB+ package version 20.1[8]. The 3ob parameter set[9,10] with Hubbard parameters –0.1492 for C and –0.1857 for H were employed. After the optimization, the system was equilibrated at 500 K for 10 ps with a time step of 0.4 fs by DFTB with molecular dynamics (DFTB-MD) simulations. For the equilibration, NVT ensemble with the Nose–Hoover chain thermostat was employed[11,12]. After that, the thermostat was turned off and the DFTB-MD simulation with NVE ensemble was conducted for 100 ps with 0.4 fs time interval. Structures were extracted every 1 ps and the thus-obtained 100 structures were re-optimized by SCC-DFTB method to investigate essential dynamics of the (25,25)MCNB. Grimme's D3 type dispersion[13] was included in all calculations.

Movie S1

Animation of the 100 structures of (25,25)MCNB obtained by DFTB-MD calculations.

2. Experimental section

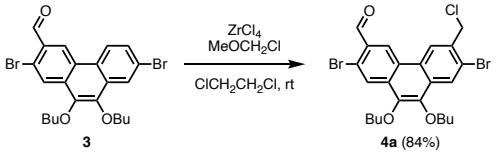
Synthesis of **3**



To a 1-L flask filled with argon gas were added **2** (20.2 g, 42.0 mmol) and dichloromethane (84 mL). A dichloromethane solution of $TiCl_4$ (1.0 M, 185 mL, 185 mmol, 4.4 equiv) was added to the solution at –45 °C and the mixture was stirred at –45 °C for 1 h. Dichloromethyl methyl ether (8.00 mL, 92.0 mmol, 2.2 equiv) was added to the reaction mixture at –45 °C and the mixture was stirred at –45 °C for 3 h. The reaction was quenched by the addition of the aq. NH_4Cl. The organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo*. The crude product was purified by column chromatography (hexane/chloroform = 4:1 to 1:1) to afford **3** as a white solid (2.00 g, 75%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 10.53 (s, 1H), 9.11 (s, 1H), 8.52 (d, *J* = 9.0 Hz, 1H), 8.45 (s, 1H), 8.38 (d, *J* = 1.8 Hz, 1H), 7.74 (dd, *J* = 9.0, 2.4 Hz, 1H), 4.26 (t, *J* = 6.0 Hz, 2H) 4.18 (t, *J* = 6.0 Hz, 2H), 1.89 (quint, *J* = 7.2 Hz, 4H), 1.64-1.56 (m, 4H), 1.044 (t, *J* = 7.2 Hz, 3H) , 1.035 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 191.77 (CH), 145.87 (4°), 142.26 (4°), 134.66 (4°), 131.40 (4°), 130.08 (CH), 130.01 (4°), 127.42 (4°), 127.22 (CH), 126.77 (4°), 125.39 (CH), 125.35 (CH), 124.61 (CH), 123.75 (4°), 122.52 (4°), 73.69 (CH_2), 32.55 (CH_2), 32.50 (CH_2), 19.50 (CH_2), 19.48 (CH_2), 14.08 (CH_3); HRMS (APCI MS) *m/z* calcd for $C_{23}H_{25}O_3Br_2$ $[M+H]^+$: 509.0146, found: 509.0123; mp: 91–93 ºC.

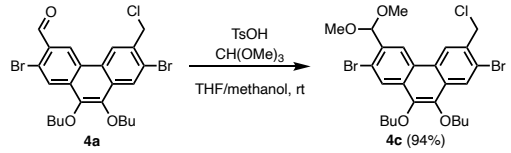
Synthesis of **4a**



To a 1-L flask filled with argon gas were added **3** (18.1 g, 35.7 mmol), 1,2-dichloroethane (71 mL), and $ZrCl_4$ (23.3 g, 99.8 mmol, 2.8 equiv). Chloromethyl methyl ether (13.0 mL, 178 mmol, 5.0 equiv) was added to the solution at 0 °C and the mixture was stirred at room temperature for 14 h. After the addition of chloroform (106 mL) and aq. NH_4Cl, the mixture was filtered through Celite® with chloroform. Water was added and the organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo*. The crude product was purified by column chromatography (hexane/chloroform = 7:1 to 1:2) to afford **4a** as a white solid (16.7 g, 84%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 10.55 (s, 1H), 9.12 (s, 1H), 8.74 (s, 1H), 8.46 (s, 2H), 4.95 (s, 2H), 4.26 (t, *J* = 8.1 Hz, 2H), 4.19 (t, *J* = 8.1 Hz, 2H) 1.92-1.86 (m, 4H), 1.64-1.55 (m, 4H), 1.04 (t, *J* = 9.0 Hz, 3H) , 1.03 (t, *J* = 9.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 191.91 (CH), 145.57 (4°), 142.75 (4°), 135.16 (4°), 135.04 (4°), 131.36 (4°), 130.24 (4°), 128.04 (4°), 127.48 (CH), 127.37 (CH), 126.67 (4°), 125.53 (CH), 125.44 (CH), 124.14 (4°), 123.98 (4°), 73.83 (CH_2), 46.64 (CH_2), 32.52 (CH_2), 32.49 (CH_2), 19.48 (CH_2), 14.08 (CH_3); HRMS (APCI MS) *m/z* calcd for $C_{24}H_{26}O_3Br_2Cl$ $[M+H]^+$: 556.9911, found: 556.9909; mp: 157–159 ºC.

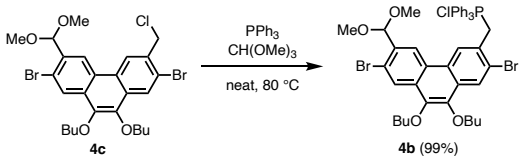
Synthesis of **4c**



To a 200-mL flask were added **4a** (1.82 g, 3.27 mmol), THF (24 mL), methanol (2.6 mL), $CH(OMe)_3$ (3.6 mL, 32.7 mmol, 10 equiv), and $TsOH \cdot H_2O$ (34.0 mg, 0.164 mmol, 0.05 equiv). The mixture was stirred at room temperature for 20 h. After the addition of aq. $NaHCO_3$ (1 mL), the mixture was evaporated *in vacuo*. The crude product was purified by column chromatography (hexane/chloroform = 7:3 to 3:7) to afford **4c** as a white solid (1.86 g, 94%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 8.77 (s, 1H), 8.69 (s, 1H), 8.44 (s, 1H), 8.42 (s, 1H), 5.76 (s, 1H), 4.96 (s, 2H), 4.20 (t, J = 6.9 Hz, 2H), 4.20 (t, J = 6.9 Hz, 2H), 3.49 (s, 6H), 1.88 (quint, J = 7.2 Hz, 2H), 1.87 (quint, J = 7.2 Hz, 2H), 1.59 (sext, J = 7.4 Hz, 4H), 1.031 (t, J = 7.5 Hz, 3H), 1.029 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 143.28 (4°), 142.99 (4°), 134.30 (4°), 134.09 (4°), 131.35 (4°), 131.33 (4°), 127.63 (4°), 127.04 (CH), 126.79 (CH), 126.71 (4°), 125.68 (CH), 123.29 (4°), 122.64 (CH), 122.28 (4°), 103.136 (CH) 73.61 (CH_2), 54.23 (CH_3), 46.95 (CH_2), 32.52 (CH_2), 19.49 (CH_2), 14.07 (CH_3); HRMS (APCI MS) *m/z* calcd for $C_{25}H_{28}O_3Br_2Cl$ $[M–OMe]^+$: 571.0068, found: 571.0079; mp: 116–118 ºC.

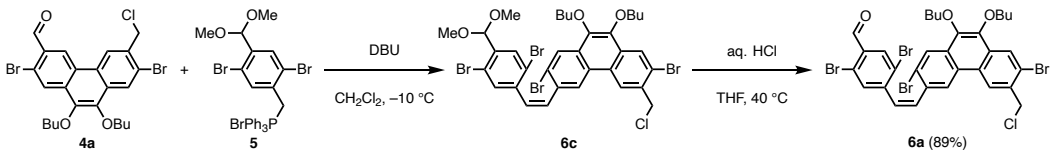
Synthesis of **4b**



To a 50-mL flask were added **4c** (641 mg, 1.06 mmol), PPh_3 (695 mg, 2.65 mmol, 2.5 equiv), and $CH(OMe)_3$ (1.5 mL, 13.6 mmol, 13 equiv). The mixture was stirred at 80 °C for 2 days. After the volatile was evaporated *in vacuo*, the crude product was purified by column chromatography (hexane/chloroform = 1:1, chloroform/methanol = 20:1 to 4:1) to afford **4b** as a pale brown powder (907 mg, 99%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 8.67 (d, $^4J_{PH}$ = 3.0 Hz 1H), 8.34 (s, 1H), 8.28 (s, 1H), 8.19 (s, 1H), 7.84-7.77 (m, 9H), 7.67-7.63 (m, 6H), 6.04 (d, J = 17.4 Hz, 2H), 5.68 (s, 1H), 4.16 (t, J = 8.1 Hz, 2H), 4.15 (t, J = 8.1 Hz, 2H), 3.50 (s, 6H), 1.89-1.79 (m, 4H), 1.58 (sext, J = 9.1 Hz, 2H), 1.54 (sext, J = 9.1 Hz, 2H), 1.02 (t, J = 9.0 Hz, 3H), 1.00 (t, J = 8.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 142.99 (4°), 142.15 (4°), 135.03 (CH, $^4J_{PC}$ = 1.2 Hz), 134.12 (CH, $^2J_{PC}$ = 45.6 Hz), 134.04 (4°), 130.80 (4°), 130.47(4°), 130.45 (4°), 130.06 (CH, $^3J_{PC}$ = 57.0 Hz), 127.50 (CH, $^3J_{PC}$ = 28.2 Hz), 127.02 (4°, J_{PC} = 17.4 Hz), 126.33 (CH), 125.90 (CH), 125.28 (4°, J_{PC} = 22.8 Hz), 124.26 (4°, J_{PC} = 39.6 Hz), 122.94 (CH), 122.12 (4°), 117.05 (4°, $^1J_{PC}$ = 406.8 Hz), 102.52 (CH), 73.22 (CH_2), 73.14 (CH_2), 53.65 (CH_3), 32.16 (CH_2), 32.08 (CH_2), 30.44 (CH_2, $^1J_{PC}$ = 228.6 Hz), 19.11 (CH_2), 19.08 (CH_2), 13.71 (CH_3), 13.67 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{44}H_{46}O_4Br_2P$ $[M–Cl]^+$: 827.1495, found: 827.1490; mp: 155–157 ºC.

Synthesis of **6a**

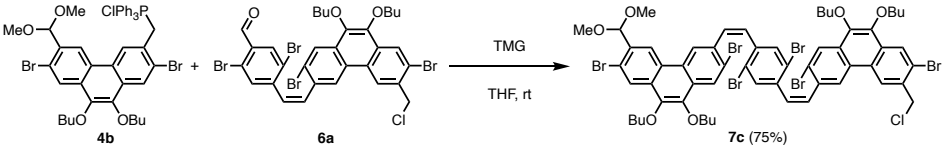


To a 1-L three-necked flask filled with argon gas were added dichloromethane (430 mL) and **4a** (31.1 g, 46.7 mmol, 1.3 equiv), and the mixture was stirred at –20 °C for 1 h. **5** (20.0 g, 35.9 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 6.71 mL, 44.9 mmol, 1.25 equiv) were added at –20 °C and the resulting mixture was stirred at –10 °C for 1 h. The reaction was quenched by the addition of silica gel (120 mL), and the mixture was filtered through Celite® with chloroform and hexane, and then evaporated *in vacuo* to afford the crude product containing **6c**, which was used in the next step without further purification.

To a 1-L flask were added the crude product containing **6c**, THF (400 mL), and aq. HCl (4 M, 53 mL). The mixture was stirred at 40 °C for 5 h. Water was added and the organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo*. The crude product was purified by column chromatography (hexane/chloroform = 9:1 to 2:3) to afford **6a** as a yellow solid (26.0 g, 89%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 10.13 (s, 1H), 8.42 (s, 1H), 8.35 (s, 1H), 8.15 (s, 1H), 8.14 (s, 1H), 7.95 (s, 1H), 7.41 (s, 1H), 7.16 (d, *J* = 12.0 Hz, 1H) 6.82 (d, *J* = 12.0 Hz, 1H), 4.78 (s, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 1.90-1.84 (m, 4H), 1.63-1.55 (m, 4H), 1.04 (t, *J* = 7.2 Hz, 3H) , 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 189.77 (CH), 145.00 (4°), 143.05 (4°), 135.26 (CH), 134.02 (4°), 133.92 (CH), 133.75 (CH), 133.33 (4°), 132.98 (4°), 131.10 (4°), 130.77 (4°), 129.28 (CH), 127.03 (4°), 126.84 (CH), 126.63 (CH), 126.43 (4°), 124.96 (4°), 124.66 (CH), 124.34 (CH), 123.81 (4°), 123.30 (4°), 122.96 (4°), 73.60 (CH_2), 46.65 (CH_2), 32.513 (CH_2), 19.49 (CH_2), 19.46 (CH_2), 14.09 (CH_3), 14.06 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{32}H_{29}O_3Br_4Cl$ [M·]$^+$: 815.8494, found: 815.8484.

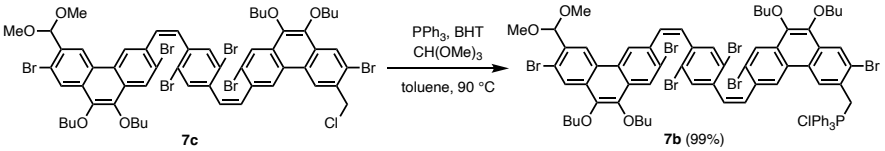
Synthesis of **7c**



To a 1-L flask filled with argon gas were added **4b** (27.0 g, 33.1 mmol), **6a** (36.0 g, 41.6 mmol, 1.2 equiv), and dichloromethane (330 mL), and the mixture was cooled to –78 °C. The 15 mL dichloromethane solution of 1,1,3,3-tetramethylguanidine (TMG) (5.0 mL, 39.7 mmol, 1.2 equiv) were added to the mixture at –78 °C, and the resulting mixture was stirred at room temperature for 1 h. After hexane (300 mL) and silica gel (150 mL) were added, the mixture was filtered, and the volatile was evaporated *in vacuo*. The crude product was purified by reprecipitation using ethyl acetate (1.10 L) to afford **7c** (33.7 g, 75%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 8.40 (s, 1H), 8.39 (s, 1H), 8.35 (s, 1H), 8.33 (s, 1H), 8.26 (s, 1H), 8.21 (s, 2H), 7.98 (s, 1H), 7.48 (s, 1H), 7.38 (s, 1H), 7.01 (d, *J* = 12.0 Hz, 1H), 6.99 (d, *J* = 12.0 Hz, 1H), 6.73 (d, *J* = 12.0 Hz, 1H), 6.65 (d, *J* = 12.0 Hz, 1H), 5.64 (s, 1H) 4.80 (s, 2H), 4.198 (t, *J* = 7.2 Hz, 2H), 4.195 (t, *J* = 6.6 Hz, 2H), 4.179 (t, *J* = 7.2 Hz, 2H), 4.175 (t, *J* = 6.6 Hz, 2H), 3.38 (s, 6H), 1.91-1.84 (m, 8H), 1.60 (sext, *J* = 7.8 Hz, 4H), 1.59 (sext, *J* = 7.8 Hz, 4H), 1.04 (t, *J* = 7.2 Hz, 6H), 1.03 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 143.15 (4°), 143.02 (4°), 142.90 (4°), 142.82 (4°), 138.68 (4°), 138.28 (4°), 134.06 (CH), 134.01 (CH), 133.92 (4°), 133.78 (4°), 133.35 (4°), 132.27 (CH), 131.97 (CH), 131.09 (4°), 130.45 (4°), 129.71 (CH), 129.66 (CH), 127.16 (4°), 127.07 (4°), 126.78 (CH), 126.59 (CH), 126.51 (4°), 126.42 (CH), 126.34 (CH), 125.14 (CH), 124.72 (CH), 124.69 (CH), 123.58 (4°), 123.29 (4°), 122.90 (4°), 122.73 (4°), 122.48 (CH), 121.99 (4°), 102.55 (CH), 73.56 (CH_2), 53.71 (CH_3), 46.81 (CH_2), 32.56 (CH_2), 19.50 (CH_2), 14.12 (CH_3), 14.10 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{58}H_{59}O_6Br_6Cl$ [M·]$^+$: 1365.9043, found: 1365.9033; mp: 199–201 ºC.

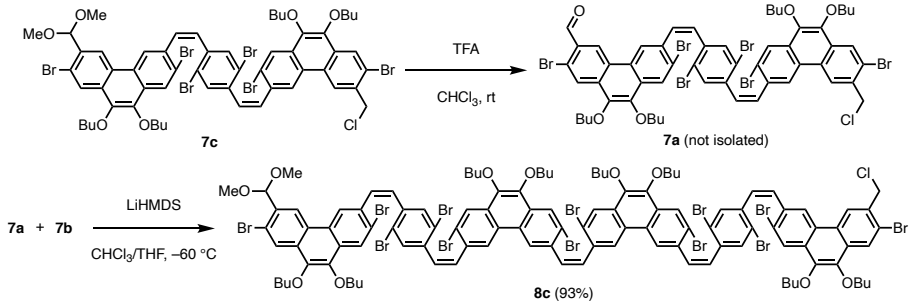
Synthesis of **7b**



To a 100-mL flask were added **7c** (10.0 g, 7.32 mmol), PPh_3 (5.77 g, 22.0 mmol, 3 equiv), 2,6-di-*t*-butyl-4-methylphenol (BHT) (16.1 mg, 0.00732 mmol, 0.01 equiv), $CH(OMe)_3$ (6 mL), and toluene (12.6 mL). The mixture was stirred at 90 °C for 15 h. After the volatile was evaporated *in vacuo*, the crude product was purified by column chromatography (hexane/chloroform/methanol = 4:1:0, 0:1:0, 0:97:3, then 0:17:3) to afford **7b** as yellow amorphous solid (12.4 g, 99%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 8.40 (s, 1H), 8.39 (d, $^4J_{PH}$ = 4.2 Hz, 1H), 8.354 (s, 1H), 8.349 (s, 1H), 8.31 (s, 1H), 8.30 (s, 1H), 8.20 (s, 1H), 7.82 (s, 1H), 7.79-7.70 (m, 9H), 7.61-7.58 (m, 6H), 7.33 (s, 1H), 6.99 (s, 1H), 6.96 (d, *J* = 14.4 Hz, 1H), 6.88 (d, *J* = 14.4 Hz, 1H), 6.75 (d, *J* = 14.4 Hz, 1H), 6.69 (d, *J* = 14.4 Hz, 1H), 5.97 (d, *J* = 18.0 Hz, 2H), 5.66 (s, 1H), 4.193 (t, *J* = 7.8 Hz, 2H), 4.189 (t, *J* = 7.8 Hz, 2H), 4.174 (t, *J* = 7.8 Hz, 2H), 4.170 (t, *J* = 7.8 Hz 2H), 3.39 (s, 6H), 1.90-1.81 (m, 8H), 1.61-1.53 (m, 8H), 1.05-1.00 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 143.17 (4°), 142.75 (4°), 142.67 (4°), 142.06 (4°), 137.63 (4°), 136.79 (4°), 135.17 (CH), 134.61 (4°), 134.14 (CH, $^2J_{PC}$ = 49.6 Hz), 133.89 (CH), 133.65 (4°), 133.43 (4°), 133.28 (CH), 132.03 (CH), 131.92 (CH), 131.84 (CH), 131.48 (CH), 130.88 (4°), 130.77 (4°), 130.75 (4°), 130.25 (4°), 130.16 (CH, $^3J_{PC}$ = 57 Hz) 129.76 (CH), 129.39 (CH), 128.43 (CH), 128.32 (CH), 127.35 (CH, J_{PC} = 28.8 Hz), 126.86 (4°), 126.75 (4°, J_{PC} = 18.0 Hz), 126.45 (CH), 126.42 (4°), 126.38 (CH), 126.36 (4°), 126.24 (CH), 126.14 (CH), 125.30 (4°, J_{PC} = 20.8 Hz), 124.67 (CH), 124.41 (CH), 124.24 (4°, J_{PC} = 40.2 Hz), 122.88 (4°), 122.66 (4°), 122.62 (4°), 122.20 (CH), 122.06 (4°), 121.82 (4°), 117.09 (4°, $^1J_{PC}$ = 412.2 Hz), 102.47 (CH), 73.35 (CH_2), 73.29 (CH_2), 53.73 (CH_3), 32.25 (CH_2), 32.22 (CH_2), 30.86 (CH_2, $^1J_{PC}$ = 234.6 Hz), 19.22 (CH_2), 13.84 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{76}H_{74}O_6Br_6P$ $[M–Cl]^+$: 1593.0276, found: 1593.0266; mp: 134–136 ºC.

Synthesis of **8c**



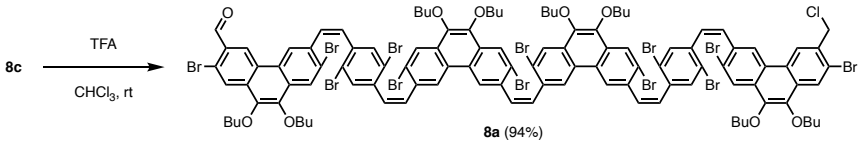
To a 500-mL flask were added **7c** (2.00 g, 1.46 mmol) and chloroform (240 mL). Trifluoroacetic acid (TFA) (1.12 mL, 14.6 mmol, 10 equiv) was added to the mixture at 0 °C, and the resulting mixture was stirred at room temperature for 15 h. The reaction was quenched by adding cold water (16 mL) and aq. $NaHCO_3$ (16 mL). The organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo* to afford **7a** (1.98 g), which was used without further purification.

To a 1-L flask filled with argon gas were added **7a** (3.50 g, 2.64 mmol), molecular sieves 4A (MS4A: 66.8 g), and chloroform (440 mL). The mixture was stirred at 40 °C to dissolve **7a**, then cooled to –60 °C. To a 200-mL flask filled with argon gas were added **7b** (5.59 g, 3.43 mmol, 1.3 equiv) and THF (55 mL). The 1.0 M THF solution of LiHMDS (3.30 mL, 3.30 mmol, 1.25 equiv) was added at –78 °C and the resulting mixture was stirred at –78 °C for 1 h,

then transferred to the 1-L flask by canular at –78 °C. The combined mixture was stirred at –60 °C for 3 h. The reaction was quenched by adding 1.0 mL THF solution of acetic acid (0.045 mL) and silica gel (40 mL). After hexane (200 mL) was added, the mixture was filtered and evaporated *in vacuo*. The crude product was purified by column chromatography (hexane/chloroform = 88:12 to 28:72) to afford **8c** as yellow amorphous solid (6.48 g, 93% in two steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.35-8.30 (m, 4H), 8.25-8.18 (m, 5H), 7.95 (s, 1H), 7.72-7.69 (m, 2H), 7.45-7.43 (m, 3H), 7.33 (s, 1H), 7.12-7.10 (m, 2H), 7.02-6.97 (m, 4H), 6.67-6.60 (m, 2H), 6.54-6.52 (m, 3H), 6.45-6.41 (m, 1H), 5.63 (s, 1H), 4.75 (s, 2H), 4.20-4.10 (m, 16H), 3.32 (s, 6H), 1.88-1.81 (m, 16H), 1.62-1.53 (m, 16H), 1.06-0.97 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.23 (4°), 143.09 (4°), 142.95 (4°), 142.91 (4°), 142.82 (4°), 142.72 (4°), 138.28 (4°), 138.19 (4°), 137.83 (4°), 137.54 (4°), 134.48 (4°), 134.34 (4°), 134.01 (CH), 133.92 (4°), 133.78 (4°), 133.74 (CH), 133.64 (CH), 133.53 (4°), 133.42 (4°), 132.11 (CH), 131.95 (CH), 131.56 (CH), 131.36 (CH), 131.28 (CH), 131.14 (4°), 130.50 (4°), 130.37 (4°), 130.32 (4°), 130.19 (4°), 130.15 (4°), 129.88 (CH), 129.69 (CH), 129.47 (CH), 129.45 (CH), 127.21 (4°), 127.14 (4°), 126.82 (CH), 126.78 (4°), 126.73 (4°), 126.71 (4°), 126.63 (CH), 126.59 (4°), 126.53 (CH), 126.40 (CH), 126.32 (CH), 126.25 (CH), 126.19 (CH), 125.20 (CH), 124.79 (4°), 124.63 (4°), 124.24 (4°), 124.18 (CH), 124.12 (4°), 124.65 (CH), 124.64 (CH), 124.24 (CH), 124.18 (CH), 124.12 (CH) 123.31 (4°), 123.02 (4°), 122.94 (4°), 122.92 (4°), 122.87 (4°), 122.77 (4°), 122.58 (CH), 122.54 (4°), 121.98 (4°), 102.41 (CH), 73.59 (CH_2), 73.53 (CH_2), 53.58 (CH_3), 46.78 (CH_2), 32.58 (CH_2), 32.50 (CH_2), 19.51 (CH_2), 19.47 (CH_2), 14.10 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{114}H_{111}O_{10}Br_{12}Cl$ $[M\cdot]^+$: 2635.7964, found: 2635.7942; mp: 120–122 ºC.

Synthesis of **8a**

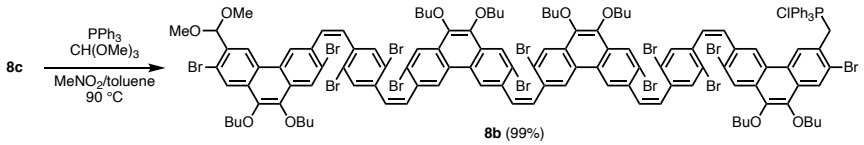


To a 200-mL flask were added **8c** (3.01 g, 1.14 mmol) and chloroform (60 mL). TFA (0.87 mL, 11.4 mmol, 10 equiv) was added to the mixture at 0 °C, and the resulting mixture was stirred at room temperature for 15 h. The reaction was quenched by adding ice and aq. $NaHCO_3$ (12 mL). The organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo* to afford **8a** (2.85 g, 94%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 10.29 (s, 1H), 8.43 (s, 1H), 8.41 (s, 1H), 8.35 (s, 1H), 8.34 (s, 2H), 8.28 (s, 1H), 8.262 (s, 1H), 8.261 (s, 1H), 8.19 (s, 2H), 8.17 (s, 1H), 7.97 (s, 1H), 7.72 (s, 1H), 7.64 (s, 1H), 7.56 (s, 1H), 7.45 (s, 1H), 7.38 (s, 1H), 7.37 (s, 1H), 7.27 (s, 1H), 7.03 (d, *J* = 12.0 Hz, 2H), 6.99 (d, *J* = 12.0 Hz, 1H), 6.92 (d, *J* = 12.0 Hz, 1H), 6.80 (d, *J* = 12.0 Hz, 1H), 6.73 (d, *J* = 12.0 Hz, 1H), 6.65 (d, *J* = 12.0 Hz, 1H), 6.54 (d, *J* = 12.0 Hz, 1H), 6.50 (d, *J* = 12.0 Hz, 1H), 6.47 (d, *J* = 12.0 Hz, 1H), 6.36 (d, *J* = 12.0 Hz, 1H), 4.76 (s, 2H), 4.28 (t, *J* = 6.9 Hz, 2H), 4.21 (t, *J* = 6.9 Hz, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 4.15 (t, *J* = 6.9 Hz, 2H), 4.10 (t, *J* = 6.0 Hz, 4H), 4.09 (t, *J* = 6.0 Hz, 4H), 1.95-1.78 (m, 16H), 1.66-1.50 (m, 16H), 1.08-0.97 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 190.93 (CH), 145.49 (4°), 143.22 (4°), 142.84 (4°), 142.82 (4°), 142.74 (4°), 142.68 (4°), 142.22 (4°), 138.50 (4°), 138.06 (4°), 137.90 (4°), 137.61 (4°), 134.52 (4°), 134.50 (4°), 134.13 (CH), 134.07 (4°), 134.00 (CH), 133.94 (CH), 133.82 (4°), 133.66 (CH), 133.60 (CH), 133.53 (4°), 133.36 (CH), 133.20 (CH), 131.95 (CH), 131.34 (CH), 131.24 (CH), 131.12 (4°), 130.90 (CH), 130.48 (4°), 130.29 (4°), 130.11 (4°), 129.98 (4°), 129.86 (CH), 129.73 (4°), 129.44 (4°), 127.41 (4°), 127.20 (4°), 127.00 (CH), 126.84 (CH), 126.81 (4°), 126.77 (CH), 126.73 (4°), 126.59 (4°), 126.54 (4°), 126.50 (CH), 126.77 (4°), 126.26 (CH), 126.16 (CH), 125.12 (CH), 124.83 (CH), 124.62 (CH),

124.54 (CH), 124.31 (4°), 124.27 (CH), 124.18 (CH), 124.05 (CH), 123.99 (CH), 123.78 (4°), 123.70 (4°), 123.63 (4°), 123.25 (4°), 123.11 (4°), 123.06 (4°), 122.97 (4°), 122.54 (4°), 122.48 (4°), 73.71 (CH_2), 73.60 (CH_2), 73.47 (CH_2), 73.35 (CH_2), 46.81 (CH_2), 32.67 (CH_2), 32.62 (CH_2), 32.57 (CH_2), 32.53 (CH_2), 32.50 (CH_2), 19.53 (CH_2), 14.16 (CH_3), 14.14 (CH_3), 14.10 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{112}H_{105}O_9Br_{12}Cl$ $[M\cdot]^+$: 2589.7544, found: 2589.7561; mp: 289 ºC (dec).

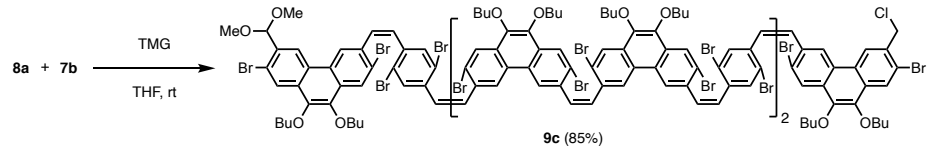
Synthesis of **8b**



To a 15-mL test tube were added **8c** (3.47 g, 1.32 mmol), PPh_3 (1.75 g, 6.60 mmol, 5.0 equiv), $CH(OMe)_3$ (1.0 mL), nitromethane (1.0 mL), and toluene (1.0 mL). The mixture was stirred at 90 °C for 20 h. After the volatile was evaporated *in vacuo*, the crude product was purified by column chromatography (hexane/chloroform = 4:1 to 0:1, chloroform/methanol = 50:1 to 4:1) to afford **8b** as an orange powder (3.79 g, 99%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, $^4J_{PH}$ = 3.0 Hz, 1H), 8.41 (s, 1H), 8.36 (s, 1H), 8.34 (s, 1H), 8.32 (s, 1H), 8.31 (s, 1H), 8.24-8.22 (m, 3H), 8.20 (s, 1H), 8.19 (s, 1H), 7.85 (s, 1H), 7.85 (s, 1H), 7.79-7.76 (m, 6H), 7.71-7.69 (m, 5H), 7.62-7.58 (m, 6H), 7.55 (s, 1H), 7.39 (s, 1H), 7.34 (s, 1H), 7.17 (s, 1H), 7.08 (d, *J* = 11.4 Hz, 1H), 6.99 (d, *J* = 11.4, 1H), 6.98 (d, *J* = 11.4 Hz, 1H), 6.95 (s, 1H), 6.89 (d, *J* = 11.4 Hz, 1H), 6.75 (d, *J* = 12.0 Hz, 1H), 6.61 (d, *J* = 11.4 Hz, 1H), 6.60 (d, *J* = 11.4 Hz, 1H), 6.48-6.41 (m, 3H), 5.97 (d, $^2J_{PH}$ = 14.4 Hz, 2H), 5.63 (s, 1H), 4.23-4.18 (m, 8H), 4.11-4.07 (m, 8H), 3.32 (s, 6H), 1.91-1.76 (m, 16H), 1.66-1.48 (m, 16H), 1.09-0.94 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.31 (4°), 142.81 (4°), 142.71 (4°), 142.66 (4°), 142.50 (4°), 142.07 (4°), 138.07 (4°), 137.58 (4°), 137.06 (4°), 136.89 (4°), 135.164 (CH), 134.67 (4°), 134.31 (CH, $^2J_{PC}$ = 40.2 Hz), 133.80 (4°), 133.76 (CH), 133.67 (CH), 133.58 (4°), 133,44 (CH), 133.18 (4°), 133.09 (CH), 131.90 (CH), 131.38 (CH), 131.29 (CH), 131.17 (CH, $^3J_{PC}$ = 74.4), 130.88 (4°), 130.74 (4°), 130.26 (4°), 130.19 (CH, $^3J_{PC}$ = 51.6 Hz), 129.97 (4°), 129.95 (4°), 129.53 (CH), 129.32 (CH), 129.29 (4°), 127.79 (CH), 126.87 (4°), 126.77 (CH), 126.61 (4°), 126.54 (4°), 126.47 (4°), 126.38 (CH), 126.15 (CH), 126.08 (CH), 126.03 (CH), 125.96 (CH), 125.25 (4°, J_{PC} = 16.8 Hz), 124.95 (CH), 124.76 (CH), 124.21 (4°), 124.15 (CH), 124.09 (CH), 123.99 (CH), 123.94 (CH), 123.49 (4°), 123.31 (4°), 123.10 (4°), 122.83 (4°), 122.65 (4°), 122.54 (4°), 122.40 (4°), 122.36 (4°), 122.29 (CH), 122.23 (4°), 121.79 (4°), 117.19 (4°, $^1J_{PC}$ = 345 Hz), 102.24 (CH), 73.42 (CH_2), 73.34 (CH_2), 73.28 (CH_2), 53.43 (CH_3), 32.32 (CH_2), 32.27 (CH_2), 32.23 (CH_2), 30.79 (CH_2, $^1J_{PC}$ = 192 Hz), 19.30 (CH_2), 19.28 (CH_2), 13.94 (CH_3), 13.90 (CH_3), 13.88 (CH_2); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{132}H_{125}O_{10}Br_{12}P$ $[M\cdot]^+$: 2861.9122, found: 2861.9140; mp: 140–142 ºC.

Synthesis of **9c**

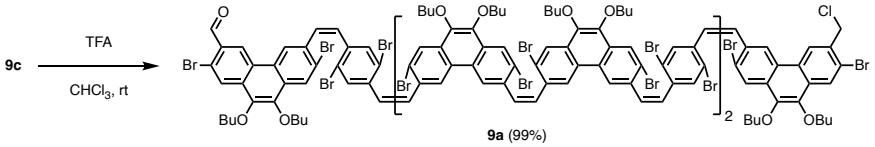


To a 100-mL flask filled with argon gas were added **8a** (2.76 g, 1.07 mmol), **7b** (2.26 g, 1.39 mmol, 1.3 equiv), and THF (12 mL), and the mixture was cooled to –78 °C. The 0.6 mL THF solution of TMG (0.173 mL, 1.38 mmol, 1.3 equiv) was added to the mixture at –78 °C, and the resulting mixture was stirred at room temperature for 4 h. After hexane (15 mL), acetic acid (0.018 mL), and silica gel (20 mL) were added, the mixture was filtered by hexane and

chloroform, and the volatile was evaporated *in vacuo*. The crude product was purified by reprecipitation using ethyl acetate (20 mL) to afford **9c** as a yellow powder (3.54 g, 85%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 8.414 (s, 1H), 8.411 (s, 1H), 8.34-8.29 (m, 6H), 8.25-8.20 (m, 7H), 7.93 (s, 1H), 7.75 (s, 1H), 7.74 (s, 1H), 7.70-7.67 (m, 3H), 7.47 (s, 2H), 7.44 (s, 1H), 7.39 (s, 1H), 7.38 (s, 1H), 7.34 (s, 1H), 7.14 (s, 2H), 7.04-6.97 (m, 5H), 6.93 (d, *J* = 12.0 Hz, 1H), 6.90 (d, *J* = 12.0 Hz, 1H), 6.65 (d, *J* = 12.0 Hz, 1H), 6.62 (d, *J* = 11.4 Hz, 1H), 6.56 (d, *J* = 12.0 Hz, 1H), 6.54 (s, 1H), 6.53 (s, 1H), 6.47-6.43 (m, 5H), 5.63 (s, 1H), 4.73 (s, 2H), 4.22-4.16 (m, 10H), 4.13-4.08 (m, 14H), 3.32 (s, 6H), 1.92-1.79 (m, 24H), 1.64-151 (m, 24H), 1.06-0.97 (m, 36H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 143.11 (4°), 143.00 (4°), 142.18 (4°), 142.84 (4°), 142.83 (4°), 142.74 (4°), 142.71 (4°), 142.63 (4°), 138.30 (4°), 138.20 (4°), 137.99 (4°), 137.62 (4°), 137.31 (4°), 134.68 (4°), 134.56 (4°), 134.08 (4°), 134.01 (4°), 133.95 (CH), 133.91 (CH), 133.80 (4°), 133.71 (4°), 133.66 (CH), 133.57(CH), 133.54 (4°), 133.42 (4°), 133.34 (4°), 133.27 (4°), 133.21 (4°), 132.98 (CH), 132.29 (4°), 132.18 (4°), 132.11 (CH), 132.07 (CH), 131.96 (CH), 131.88 (CH), 131.50 (CH), 131.47 (CH), 131.26 (CH), 131.20(CH), 131.17(CH), 131.13(CH), 131.03 (CH), 130.96 (4°), 130.40 (4°), 130.37 (4°), 130.28 (4°), 130.24 (4°), 130.09 (4°), 130.04 (4°), 129.79 (CH), 129.55 (CH), 129.50 (CH), 129.41 (CH), 128.58 (CH), 128.50 (CH), 127.08 (4°), 127.05 (4°), 126.74 (4°), 126.64 (CH), 126.54 (CH), 126.46 (4°), 126.44 (CH), 126.30 (CH), 126.23 (CH), 126.12 (CH), 125.14 (CH), 124.62 (CH), 124.53 (CH), 124.22 (CH), 124.14 (CH), 124.06 (CH), 123.97 (CH), 123.66 (4°), 123.60 (4°), 123.52 (4°), 123.31 (4°), 122.96 (4°), 122.85 (4°), 122.87 (4°), 122.84 (4°), 122.70 (4°), 122.58 (4°), 122.54 (CH), 121.94 (4°), 102.26 (CH), 73.47 (CH_2), 73.43 (CH_2), 53.47 (CH_3), 46.68 (CH_2), 32.56 (CH_2), 32.53 (CH_2), 32.49 (CH_2), 32.47 (CH_2), 19.48 (CH_2), 19.44 (CH_2), 14.10 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{170}H_{163}O_{14}Br_{18}Cl$ $[M\cdot]^+$: 3903.6898, found: 3903.6872; mp: 167–169 ºC.

Synthesis of **9a**

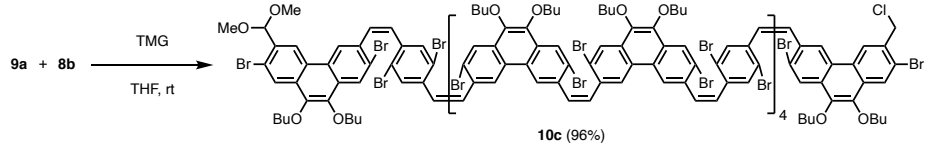


To a 200-mL flask were added **9c** (3.54 g, 0.907 mmol) and chloroform (60 mL). TFA (0.69 mL, 9.07 mmol, 10 equiv) was added to the mixture at 0 °C, and the resulting mixture was starred at room temperature for 15 h. The reaction was quenched by adding ice and aq. $NaHCO_3$ (10 mL). The organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo*. The crude product was purified by column chromatography (hexane/chloroform = 1:1) to afford **9a** (3.47 g, 99%).

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 10.27 (s, 1H), 8.42 (s, 1H), 8.41 (s, 1H), 8.35 (s, 1H), 8.34 (s, 1H), 8.33 (s, 1H), 8.31 (s, 1H), 8.29 (s, 2H), 8.24 (s, 1H), 8.234 (s, 1H), 8.230 (s, 1H), 8.21 (s, 2H), 8.20 (s, 2H), 7.93 (s, 1H), 7.77 (s, 1H), 7.76 (s, 1H), 7.70 (s, 1H), 7.64 (s, 1H), 7.63 (s, 1H), 7.49 (s, 1H), 7.48 (s, 1H), 7.44 (s, 1H), 7.42 (s, 1H), 7.36 (s, 1H), 7.22 (s, 1H), 7.15 (s, 1H), 7.06-6.99 (m, 4H), 6.96-6.88 (m, 3H), 6.76-6.72 (m, 2H), 6.65 (d, *J* = 13.8 Hz, 1H), 6.58-6.50 (m, 4H), 6.42 (s, 2H), 6.38 (d, *J* = 14.4 Hz, 1H), 6.29 (d, *J* = 14.4 Hz, 1H), 4.73 (s, 2H), 4.28 (t, *J* = 8.1 Hz, 2H), 4.23-4.08 (m, 22H), 1.96-1.79 (m, 24H), 1.66-152 (m, 24H), 1.07-0.96 (m, 36H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 190.94 (CH), 143.23 (4°), 142.90 (4°), 142.84 (4°), 142.81 (4°), 142.69 (4°), 142.23 (4°), 138.65 (4°), 138.25 (4°), 138.05 (4°), 137.94 (4°), 137.25 (4°), 137.16 (4°), 134.81 (4°), 134.71 (4°), 134.52 (4°), 134.18 (CH), 134.10 (4°), 134.00 (4°), 133.98 (CH), 133.91 (4°), 133.76 (4°), 133.74 (CH), 133.69 (4°), 133.66 (CH), 133.63 (4°), 133.57 (CH), 133.46 (4°), 133.34 (CH), 133.28 (4°), 133.14 (4°), 131.93 (CH), 131.60 (CH), 131.30 (CH), 131.18 (CH), 131.12 (4°), 131.05 (CH), 130.94 (CH), 130.49 (4°), 130.29 (4°), 130.15 (4°), 130.11 (4°), 129.97 (4°), 129.94 (CH), 129.85 (4°),

129.68 (CH), 129.62 (CH), 129.44 (CH), 127.40 (4°), 127.19 (4°), 126.98 (CH), 126.86 (CH), 126.83 (4°), 126.80 (4°), 126.77 (CH), 126.75 (4°), 126.70 (4°), 126.67 (4°), 126.56 (4°), 126.55 (4°), 126.51 (CH), 126.35 (CH), 126.28 (4°), 126.25 (CH), 126.12 (CH), 125.11 (CH), 124.77 (CH), 124.64 (CH), 124.54 (CH), 124.36 (CH), 124.21 (CH), 124.10 (CH), 124.05 (CH), 123.99 (CH), 123.84 (4°), 123.73 (4°), 123.70 (4°), 123.69 (4°), 123.57 (4°), 123.18 (4°), 123.16 (4°), 123.01 (4°), 122.99 (4°), 122.93 (4°), 122.91 (4°), 122.69 (4°), 122.65 (4°), 122.60 (4°), 122.50 (4°), 73.72 (CH_2), 73.62 (CH_2), 73.59 (CH_2), 73.52 (CH_2), 73.49 (CH_2), 73.47 (CH_2), 73.33 (CH_2), 46.79 (CH_2), 32.68 (CH_2), 32.62 (CH_2), 32.58 (CH_2), 32.54 (CH_2), 19.51 (CH_2), 14.14 (CH_3), 14.11 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{168}H_{157}O_{13}Br_{18}Cl$ $[M\cdot]^+$: 3857.6478, found: 3857.6503; mp: 191–193 ºC.

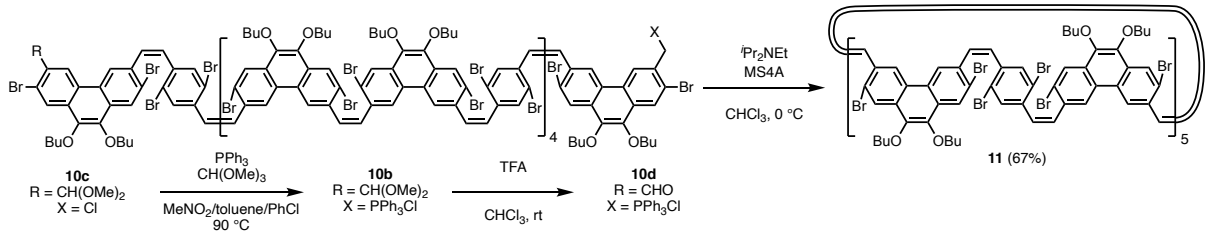
Synthesis of **10c**



To a 200-mL flask filled with argon gas were added **9a** (3.47 g, 0.899 mmol), **8b** (3.65 g, 1.26 mmol, 1.4 equiv), and THF (25 mL), and the mixture was cooled to –78 °C. The 0.6 mL THF solution of TMG (0.150 mL, 1.25 mmol, 1.39 equiv) were added to the mixture at –78 °C, and the resulting mixture was stirred at room temperature for 4 h. After hexane (25 mL) and silica gel (15 mL) were added, the mixture was filtered by hexane and chloroform, and the volatile was evaporated *in vacuo*. The crude product was purified by column chromatography (hexane/chloroform = 7:3 to 3:7) to afford **10c** (5.54 g, 96%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.409 (s, 1H), 8.407 (s, 1H), 8.34-8.29 (m, 9H), 8.24-8.19 (m, 10H), 7.93 (s, 1H), 7.74-7.68 (m, 8H), 7.47-7.40 (m, 9H), 7.33 (s, 1H), 7.130 (s, 1H), 7.127 (s, 1H), 7.07-6.89 (m, 16H), 6.64 (d, *J* = 14.4 Hz, 1H), 6.61 (d, *J* = 14.4 Hz, 1H), 6.56-6.41 (m, 18H), 5.63 (s, 1H), 4.73 (s, 2H), 4.22-4.08 (m, 40H), 3.32 (s, 6H), 1.91-1.78 (m, 40H), 1.63-1.49 (m, 40H), 1.06-0.94 (m, 60H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.13 (4°), 143.02 (4°), 142.89 (4°), 142.84 (4°), 142.72 (4°), 142.65 (4°), 138.32 (4°), 138.22 (4°), 137.97 (4°), 137.62 (4°), 137.56 (4°), 137.45 (4°), 137.38 (4°), 134.64 (4°), 134.51 (4°), 134.43 (4°), 134.27 (4°), 134.15 (4°), 134.09 (4°), 133.94 (CH), 133.82 (4°), 133.77 (4°), 133.58 (CH), 133.51 (4°), 133.44 (4°), 133.37 (4°), 133.25 (4°), 132.08 (CH), 131.89 (CH), 131.15 (4°), 131.47 (CH), 131.25 (CH), 131.05 (4°), 130.97 (4°), 130.86 (CH), 130.42 (4°), 130.39 (4°), 130.26 (4°), 130.09 (4°), 129.79 (CH), 129.52 (CH), 128.87 (CH), 127.07 (4°), 126.67 (CH), 126.56 (CH), 126.49 (CH), 126.26 (CH), 125.14 (CH), 124.61 (CH), 124.54 (CH), 124.18 (CH), 123.66 (4°), 126.58 (4°), 123.33 (4°), 122.98 (4°), 122.88 (4°), 122.85 (4°), 122.73 (4°), 122.68 (4°), 122.59 (CH), 121.97 (4°), 102.30 (CH), 73.47 (CH_2), 53.47 (CH_3), 46.66 (CH_2), 32.59 (CH_2), 32.51 (CH_2), 19.51 (CH_2), 19.48 (CH_2), 14.10 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{300}H_{282}Br_{30}O_{22}P$ $[M–Cl+PPh_3]^+$: 6667.5988, found: 6667.5785; mp: 144–146 ºC.

Synthesis of **11**



To a 50-mL flask were added **10c** (5.54 g, 0.860 mmol), PPh_3 (1.80 g, 6.88 mmol, 8.0 equiv), $CH(OMe)_3$ (2.1 mL), nitromethane (2.1 mL), toluene (7 mL), and chlorobenzene (1.0

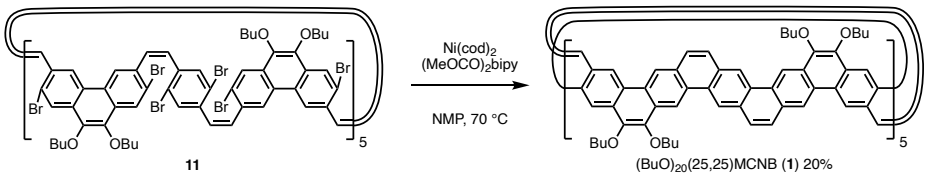
mL). The mixture was stirred at 90 °C for 20 h. After the volatile was evaporated *in vacuo*, the crude product was purified by column chromatography (hexane/chloroform = 4:1 to 0:1, then chloroform/methanol = 49:1 to 8:2) to afford **10b** as a yellow amorphous solid (5.72 g), which was used in the next step without complete purification.

To a 200-mL flask were added **10b** (5.72 g) and chloroform (50 mL). TFA (0.656 mL, 8.53 mmol, 10 equiv) was added to the mixture at 0 °C, and the resulting mixture was stirred at room temperature for 12 h. The reaction was quenched by adding pyridine (1.0 mL). The organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo* to afford the crude product of **10d** (5.17 g), which was used to the next step without further purification.

To a 2-L flask filled with argon gas were added the crude product of **10d** (5.07 g), MS4A (37.6 g), and chloroform (760 mL). Diisopropylethylamine (2.7 mL, 15.2 mmol, ca. 20 equiv) was added at 0 °C and the resulting mixture was starred at 0 °C for 14 h. The reaction was quenched by adding silica gel (50 mL). The mixture was filtered with chloroform and the volatile was evaporated *in vacuo*. The crude product was purified by column chromatography (hexane/chloroform = 90:10 to 40:60) to afford **11** as yellow solid (3.48 g, 67% in three steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (s, 10H), 8.59 (s, 10H), 8.31 (s, 10H), 7.90 (s, 10H), 7.47 (s, 10H), 7.31 (s, 10H), 6.61 (s, 20H), 4.06 (br, 40H), 1.73 (br, 40H), 1.50 (sext, J = 9.0 Hz, 40H), 0.98-0.95 (m, 60H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.88 (4°), 142.81 (4°), 137.58 (4°), 134.37 (4°), 133.58 (CH), 131.20 (CH), 130.28 (4°), 130.14 (4°), 129.65 (CH), 126.75 (4°), 126.68 (4°), 126.34 (CH), 124.23 (CH), 123.59 (4°), 122.78 (4°), 122.68 (4°), 73.56 (CH_2), 73.47 (CH_2), 32.59 (CH_2), 32.53 (CH_2), 19.50 (CH_2), 14.12 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{280}H_{260}Br_{30}O_{20}Ag$ $[M+Ag]^+$: 6450.3671, found: 6450.4084; mp: 174–176 ºC.

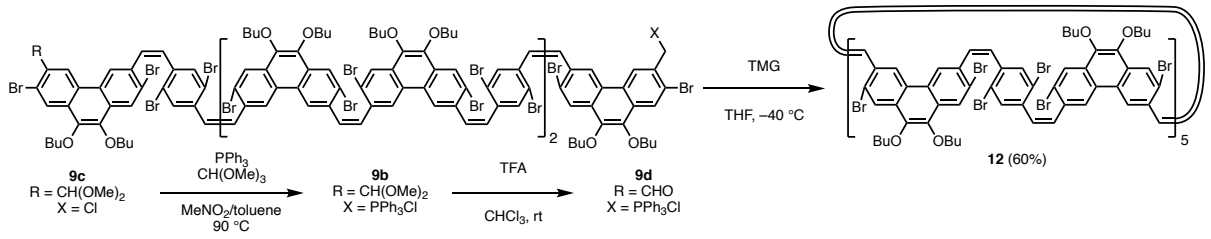
Synthesis of $(BuO)_{20}$(25,25)MCNB (**1**)



To a 50-mL flask filled with argon gas were added $Ni(cod)_2$ (130 mg, 0.473 mmol, 30 equiv), 4,4'-methoxycarbonyl-2,2'-bipyridyl (129 mg, 0.473 mmol, 30 equiv), and *N*-methylpyrrolidone (NMP: 9.6 mL). After the mixture was stirred at 70 °C for 1 h, the NMP (6.2 mL) solution of **11** (100 mg, 0.0157 mmol) was added and the resulting mixture was stirred at 70 °C for 20 min. The mixture was cooled at 0 °C and aq. NH_4Cl (12 mL) was added. The organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo*. The crude product was purified by column chromatography (chloroform) and PTLC (hexane/chloroform/ethanol = 15:85:0.5) to afford $(BuO)_{20}$(25,25)MCNB (**1**) (12.7 mg, 20%).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) δ 9.32 (s, 10H), 9.25 (s, 10H), 8.82 (s, 10H), 8.67 (s, 10H), 8.62 (s, 10H), 7.73 (s, 20H), 7.64 (s, 10H), 4.46 (br, 40H), 2.13 (br, 40H), 1.86 (sext, J = 7.8 Hz, 20H), 1.77 (sext, J = 7.8 Hz, 20H), 1.22 (t, J = 7.5 Hz, 30H), 1.16 (t, J = 7.5 Hz, 30H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) δ 142.87 (4°), 142.57 (4°), 130.67 (4°), 129.83 (4°), 129.62 (4°), 129.44 (4°), 129.34 (4°), 129.17 (4°), 128.57 (4°), 128.55 (4°), 127.56 (4°), 126.72 (CH), 126.64 (CH), 126.54 (CH), 122.26 (CH), 122.22 (CH), 122.04 (CH), 116.42(CH), 116.17 (CH), 73.29 (CH_2), 73.19 (CH_2), 32.70 (CH_2), 32.65 (CH_2), 29.35 (CH_2), 19.51 (CH_2), 19.33 (CH_2), 13.75 (CH_3) 13.62 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{280}H_{260}O_{20}$ $[M\cdot]^+$: 3944.9423, found: 3944.9449.

Synthesis of **12**



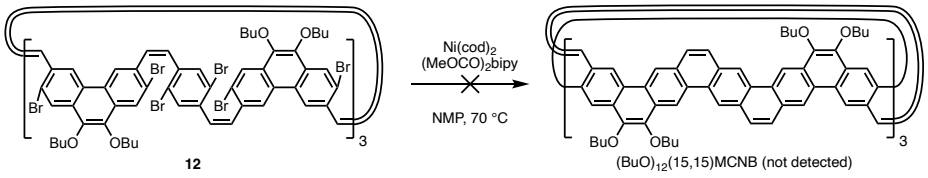
To a 10-mL flask were added **9c** (1.52 g, 0.384 mmol), PPh_3 (604 mg, 2.30 mmol, 6.0 equiv), $CH(OMe)_3$ (0.40 mL), nitromethane (0.40 mL), and toluene (0.80 mL). The mixture was stirred at 90 °C for 20 h. After the volatile was evaporated *in vacuo*, the crude product was purified by column chromatography (hexane/chloroform = 4:1 to 0:1, then chloroform/methanol = 49:1 to 44:6) to afford **9b** as a yellow amorphous solid (1.57 g), which was used in the next step without complete purification.

To a 100-mL flask were added **9b** (1.15 g) and chloroform (25 mL). TFA (0.210 mL, 2.76 mmol, 10 equiv) was added to the mixture at 0 °C, and the resulting mixture was stirred at room temperature for 15 h. The reaction was quenched by adding aq. $NaHCO_3$ (13 mL). The organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo* to afford the crude product of **9d** (1.12 g), which was used to the next step without further purification.

To a 300-mL flask were added TMG (0.410 mL, 3.28 mmol, 12 equiv) and THF (65 mL), and the mixture was starred at –40 °C. The crude product of **9d** (1.12 g) dissolved in THF (25 mL) was added dropwise by using syringe pump for 40 min at –40 °C, and the resulting mixture was starred at –40 °C for 2 h. After acetic acid (0.02 mL), THF (1 mL), and silica gel (10 mL) were added to the mixture, the mixture was filtered, and the volatile was evaporated *in vacuo*. The crude product was purified by GPC (chloroform) to afford **12** (619 mg, 60% in three steps).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ 8.35 (s, 6H), 8.33 (s, 6H), 8.07 (s, 6H), 7.90 (s, 6H), 7.19 (s, 6H), 7.00 (s, 6H), 6.57 (s, 12H), 4.21-4.17 (m, 24H), 1.89-1.84 (m, 24H), 1.61-1.54 (m, 24H), 1.04 (t, J = 7.2 Hz, 18H), 1.00 (t, J = 7.5 Hz, 18H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$) δ 142.74 (4°), 142.52 (4°), 137.23 (4°), 134.82 (4°), 133.68 (4°), 133.42 (CH), 131.48 (CH), 131.10 (CH), 130.37 (4°), 130.19 (4°), 129.32 (CH), 126.76 (4°), 126.69 (4°), 126.33 (CH), 126.06 (CH), 124.31 (CH), 124.00 (CH), 123.17 (4°), 122.67 (4°), 122.54 (4°), 73.49 (CH_2), 73.43 (CH_2), 32.20 (CH_2), 19.07 (CH_2), 13.46 (CH_3); HRMS (MALDI-TOF MS) *m/z* calcd for $C_{168}H_{156}Br_{18}O_{12}Na$ $[M+Na]^+$: 3828.6664, found: 3828.6675; mp: 177–179 ºC.

Attempt for the synthesis of $(BuO)_{12}$(15,15)MCNB



To a 20-mL flask filled with argon gas were added $Ni(cod)_2$ (26.8 mg, 97.4 μmol, 18 equiv), 4,4'-methoxycarbonyl-2,2'-bipyridyl (26.5 mg, 97.4 μmol, 18 equiv), and NMP (3.3 mL). After the mixture was stirred at 70 °C for 1 h, the NMP (2.1 mL) solution of **12** (20.6 mg, 5.41 μmol) was added and the resulting mixture was stirred at 70 °C for 20 min and 16 h. The mixture was cooled at 0 °C and aq. NH_4Cl (12 mL) was added. The organic layer was extracted with chloroform, washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo*. The crude product (28.4 mg) was analyzed by MALDI-TOF MS.

3. Supplementary figures and tables

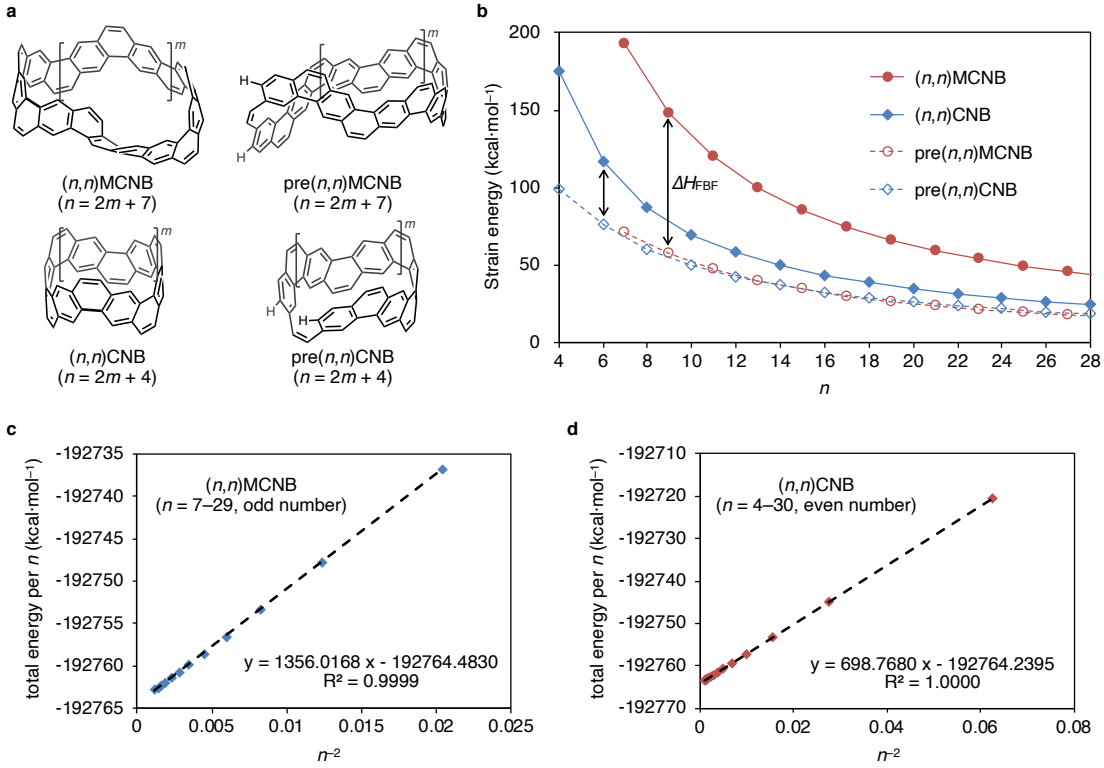


Fig. S1. (a) Structures of MCNBs, CNBs, and their corresponding precursors. (b) Stain energies of (*n*,*n*)MCNBs, (*n*,*n*)CNBs, pre(*n*,*n*)MCNBs, and pre(*n*,*n*)CNBs. Arrows represent the the strain induced in the final bond-formation step (ΔH_{FBF}). (c) Linear regression analysis[14] of (*n*,*n*)MCNBs. (d) Linear regression analysis[14] of (*n*,*n*)CNBs.

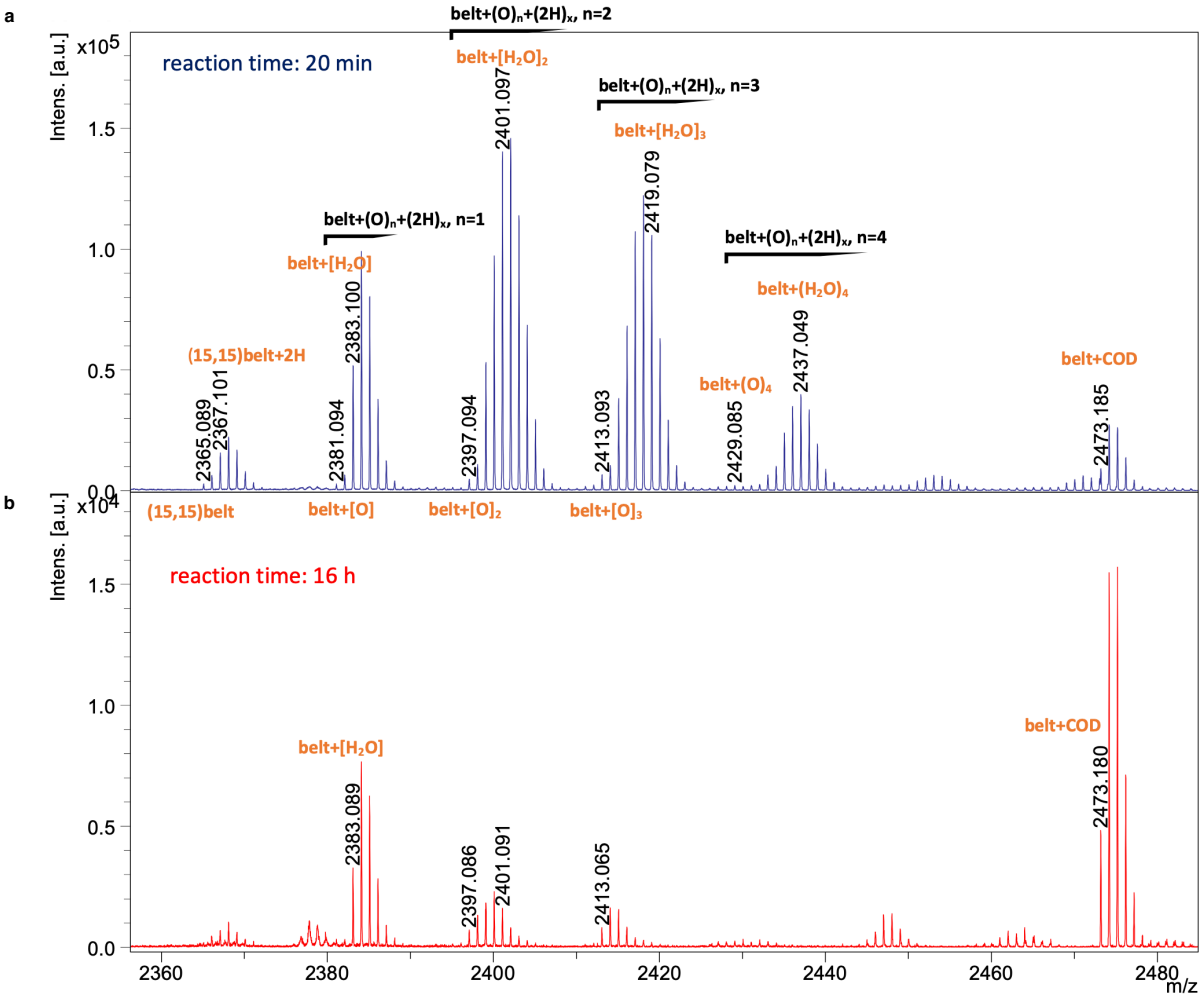


Fig. S2. (**a**,**b**) MALDI-TOF MS spectra of the mixture generated from **12** (reaction time: 20 min (**a**), 16 h (**b**)). Trace amount of the signal corresponding to $(BuO)_{12}$(15,15)MCNB with unidentified adducts were observed.

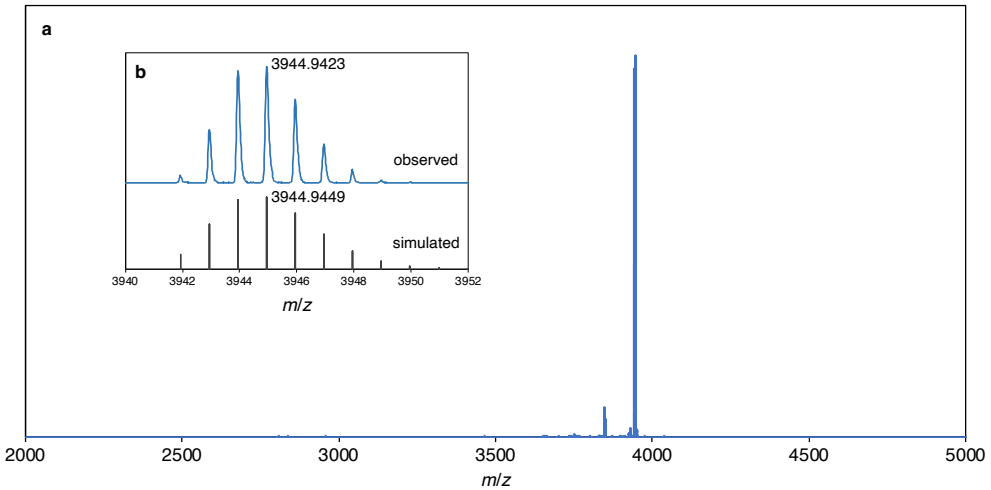


Fig. S3. (**a**) MALDI-TOF MS spectrum of **1**. (**b**) Magnified MALDI-TOF MS spectrum of **1** (top) with a simulated isotope pattern for $C_{280}H_{260}O_{20}$ (bottom).

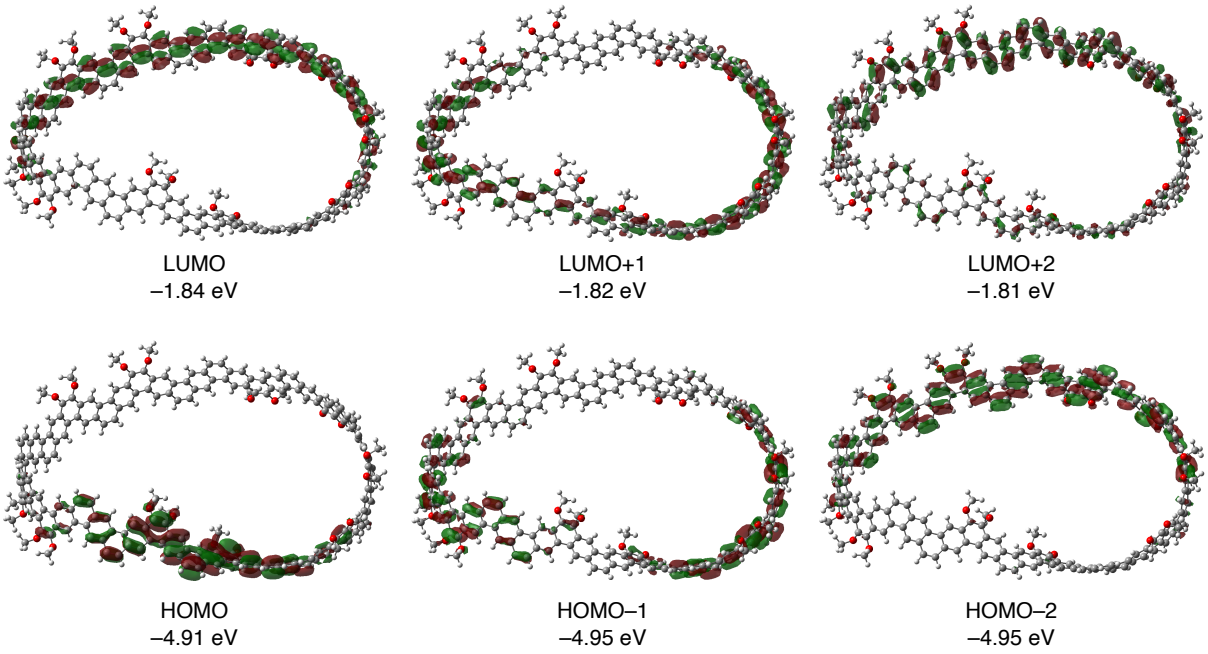


Fig. S4. Frontier molecular orbitals of $(MeO)_{20}$(25,25)MCNB (**1′**) calculated at the B3LYP/6-31G(d) level of theory (isovalue = 0.04). HOMO: the highest occupied molecular orbital, LUMO: the lowest unoccupied molecular orbital.

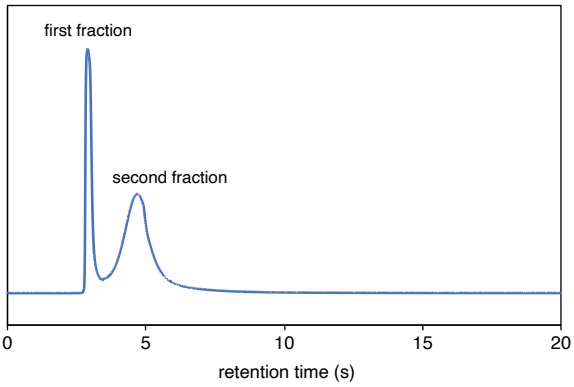


Fig. S5. HPLC chart of racemic **1** equipped with CHIRALPAK IE column (4.6 mm I.D. × 250 mm) eluted by THF/hexane (6:4) monitored with the absorption at 388 nm.

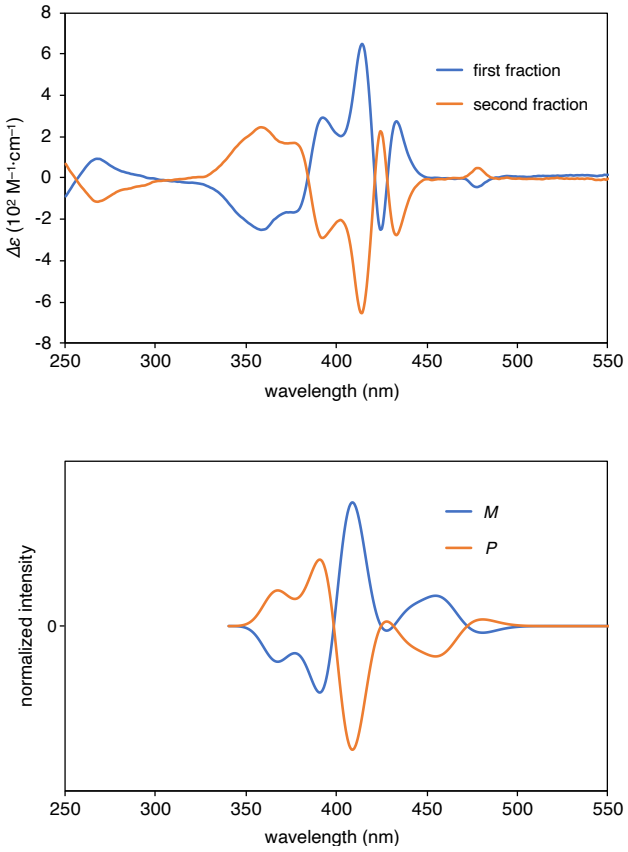
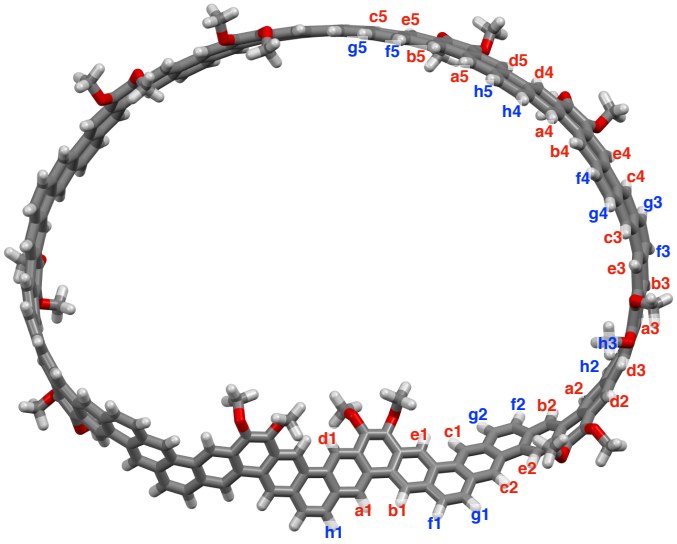
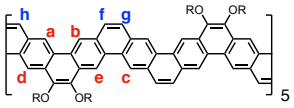


Fig. S6. (top) CD spectra of **1** in CH_2Cl_2 separated by chiral HPLC. (bottom) Simulated CD spectrum of **1** by TD-DFT calculation using B3LYP/6-31G(d) level of theory where 100 excited states (S_1–S_{100}) were used (Half-width at half-height: 0.08 eV).





	a	b	c	d	e	f	g	h
1	8.34	8.30	8.40	8.77	8.76	7.36	7.36	7.34
2	8.44	8.36	8.54	9.15	8.89	7.29	7.25	7.35
3	8.53	8.53	8.65	9.10	9.20	7.43	7.47	7.39
4	8.62	8.57	8.77	9.42	9.34	7.39	7.44	7.41
5	8.63	8.68	8.82	9.43	9.35	7.46	7.53	7.45
average	8.51	8.49	8.64	9.17	9.11	7.39	7.41	7.39
observed	[8.67, 8.62]		8.82	[9.32, 9.25]		[7.73]		7.64

Fig. S7. The ^{1}H NMR chemical shift (ppm) of $(MeO)_{20}$(25,25)MCNB calculated by using GIAO B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). Reference: $SiMe_4$ (0.00 ppm).

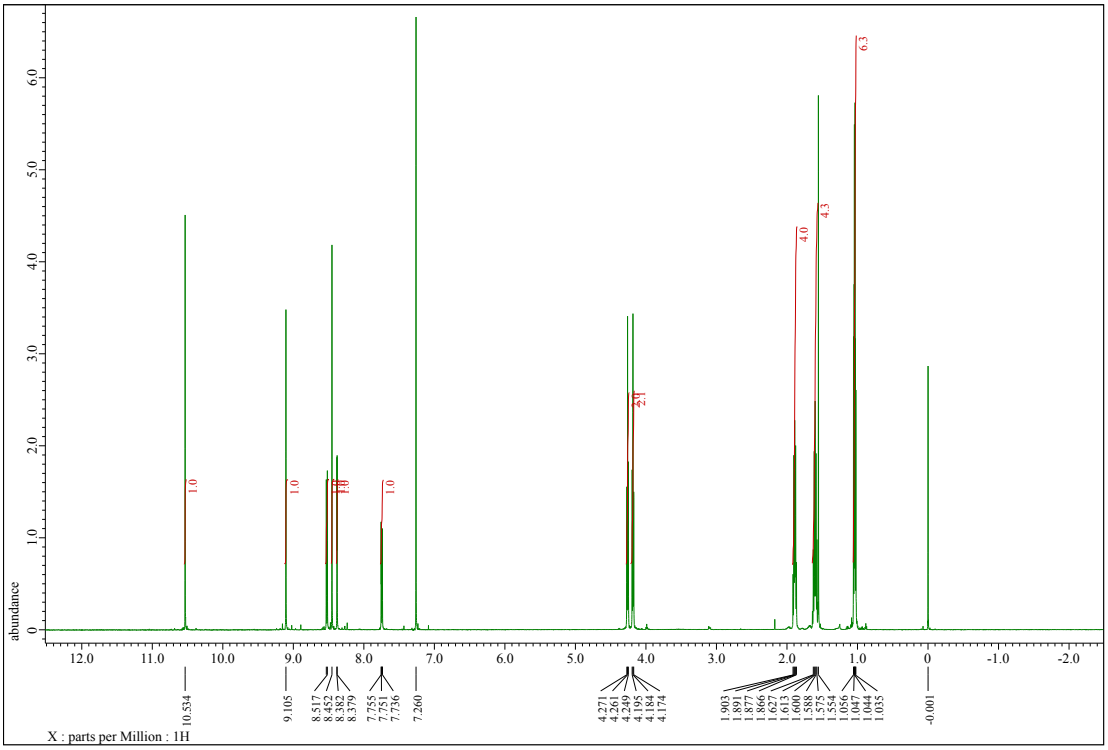
Table S1. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).[a]

	E	*E* + *ZPE*	*H*	*G*
(7,7)MCNB	-2150.704607	-2150.054954	-2150.018700	-2150.117575
(9,9)MCNB	-2765.353003	-2764.514920	-2764.467926	-2764.589922
(11,11)MCNB	-3379.975796	-3378.949584	-3378.891791	-3379.036623
(13,13)MCNB	-3994.584875	-3993.370667	-3993.302030	-3993.470682
(15,15)MCNB	-4609.185351	-4607.783379	-4607.703845	-4607.896700
(17,17)MCNB	-5223.779949	-5222.190439	-5222.099968	-5222.317411
(19,19)MCNB	-5838.370670	-5836.593586	-5836.492178	-5836.733850
(21,21)MCNB	-6452.958610	-6450.994036	-6450.881681	-6451.146868
(23,23)MCNB	-7067.544502	-7065.392504	-7065.269186	-7065.558890
(25,25)MCNB	-7682.128872	-7679.789449	-7679.655173	-7679.968874
(27,27)MCNB	-8296.712057	-8294.185274	-8294.040027	-8294.377686
(29,29)MCNB	-8911.294313	-8908.580184	-8908.423966	-8908.788222
pre(7,7)MCNB	-2152.064849	-2151.390221	-2151.352606	-2151.455442
pre(9,9)MCNB	-2766.664042	-2765.801882	-2765.753370	-2765.879981
pre(11,11)MCNB	-3381.257283	-3380.207676	-3380.148277	-3380.298222
pre(13,13)MCNB	-3995.846117	-3994.608934	-3994.538599	-3994.712833
pre(15,15)MCNB	-4610.432154	-4609.007460	-4608.926218	-4609.123799
pre(17,17)MCNB	-5225.015980	-5223.404075	-5223.311874	-5223.533822
pre(19,19)MCNB	-5839.598415	-5837.799193	-5837.696029	-5837.942280
pre(21,21)MCNB	-6454.179789	-6452.193267	-6452.079132	-6452.349236
pre(23,23)MCNB	-7068.760382	-7066.586595	-7066.461490	-7066.756627
pre(25,25)MCNB	-7683.340384	-7680.979254	-7680.843191	-7681.162059
pre(27,27)MCNB	-8297.919900	-8295.371510	-8295.224475	-8295.567879
pre(29,29)MCNB	-8912.499032	-8909.763425	-8909.605415	-8909.974133
(4,4)CNB	-1228.868118	-1228.499167	-1228.479042	-1228.541668
(6,6)CNB	-1843.539737	-1842.981260	-1842.950677	-1843.034569
(8,8)CNB	-2458.163591	-2457.417136	-2457.375675	-2457.482378
(10,10)CNB	-3072.768958	-3071.834558	-3071.782219	-3071.914202
(12,12)CNB	-3687.364704	-3686.242575	-3686.179277	-3686.333825
(14,14)CNB	-4301.955113	-4300.645798	-4300.571513	-4300.748884
(16,16)CNB	-4916.542174	-4915.045445	-4914.960185	-4915.162219
(18,18)CNB	-5531.126933	-5529.442881	-5529.346628	-5529.575049
(20,20)CNB	-6145.710139	-6143.838762	-6143.731532	-6143.984284
(22,22)CNB	-6760.292187	-6758.233492	-6758.115281	-6758.392450
(24,24)CNB	-7374.873370	-7372.627366	-7372.498178	-7372.799750
(26,26)CNB	-7989.453870	-7987.020596	-7986.880431	-7987.206536
(28,28)CNB	-8604.033856	-8601.413300	-8601.262165	-8601.612700
(30,30)CNB	-9218.613369	-9215.805589	-9215.643451	-9216.016789
pre(4,4)CNB	-1230.153724	-1229.762098	-1229.740490	-1229.808729
pre(6,6)CNB	-1844.767676	-1844.187659	-1844.155433	-1844.246255
pre(8,8)CNB	-2459.370652	-2458.602656	-2458.559625	-2458.673870
pre(10,10)CNB	-3073.964483	-3073.008851	-3072.954914	-3073.093364
pre(12,12)CNB	-3688.553279	-3687.410114	-3687.345264	-3687.507380
pre(14,14)CNB	-4303.139195	-4301.808613	-4301.732845	-4301.918790
pre(16,16)CNB	-4917.723271	-4916.205272	-4916.118584	-4916.328263
pre(18,18)CNB	-5532.305930	-5530.600547	-5530.502917	-5530.736689
pre(20,20)CNB	-6146.887544	-6144.994818	-6144.886241	-6145.144181

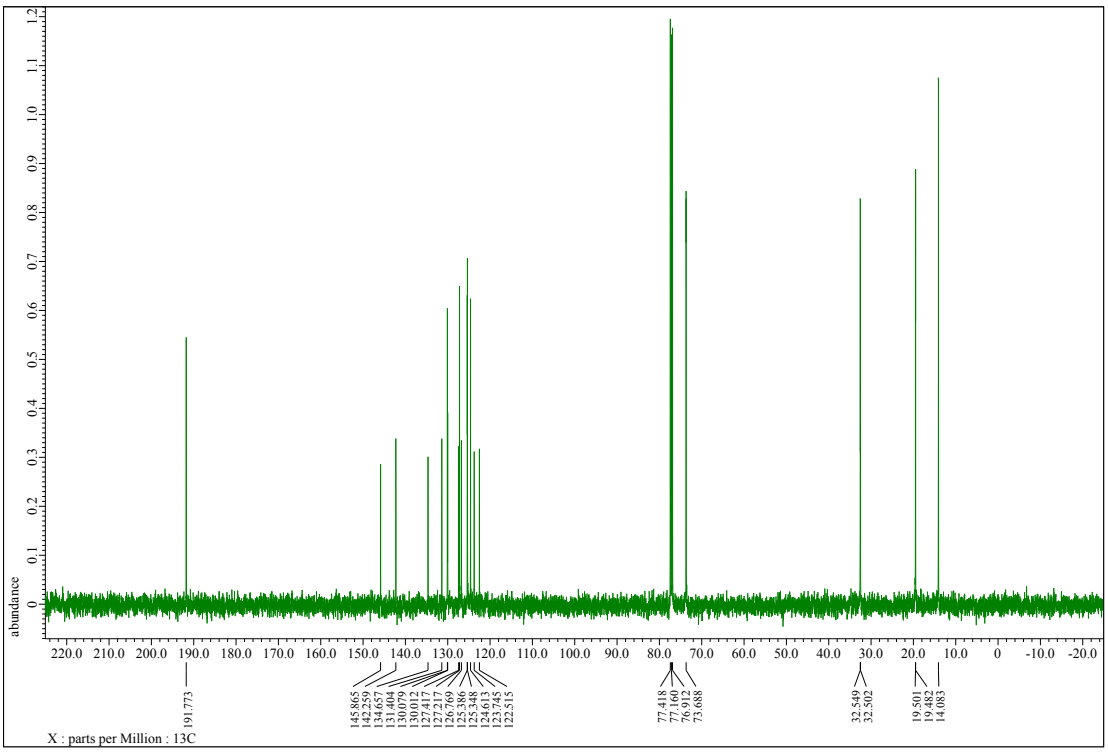
pre(22,22)CNB	-6761.468340	-6759.388296	-6759.268760	-6759.551060
pre(24,24)CNB	-7376.048515	-7373.781166	-7373.650666	-7373.957408
pre(26,26)CNB	-7990.628198	-7988.173575	-7988.032106	-7988.363405
pre(28,28)CNB	-8605.207499	-8602.565605	-8602.413167	-8602.768994
pre(30,30)CNB	-9219.786488	-9216.957313	-9216.793910	-9217.174250
cis-stilbene	-540.701967	-540.486257	-540.474298	-540.524593
phenanthrene	-540.524593	-539.343809	-539.333432	-539.378639
$(MeO)_{20}$(25,25)MCNB (**1′**)	-9972.485819	-9969.497301	-9969.305328	-9969.748433

a) *E*: electronic energy; *ZPE*: zero-point energy; *H* (= $E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT$): sum of electronic and thermal enthalpies; *G* (= $H - TS$): sum of electronic and thermal free energies.

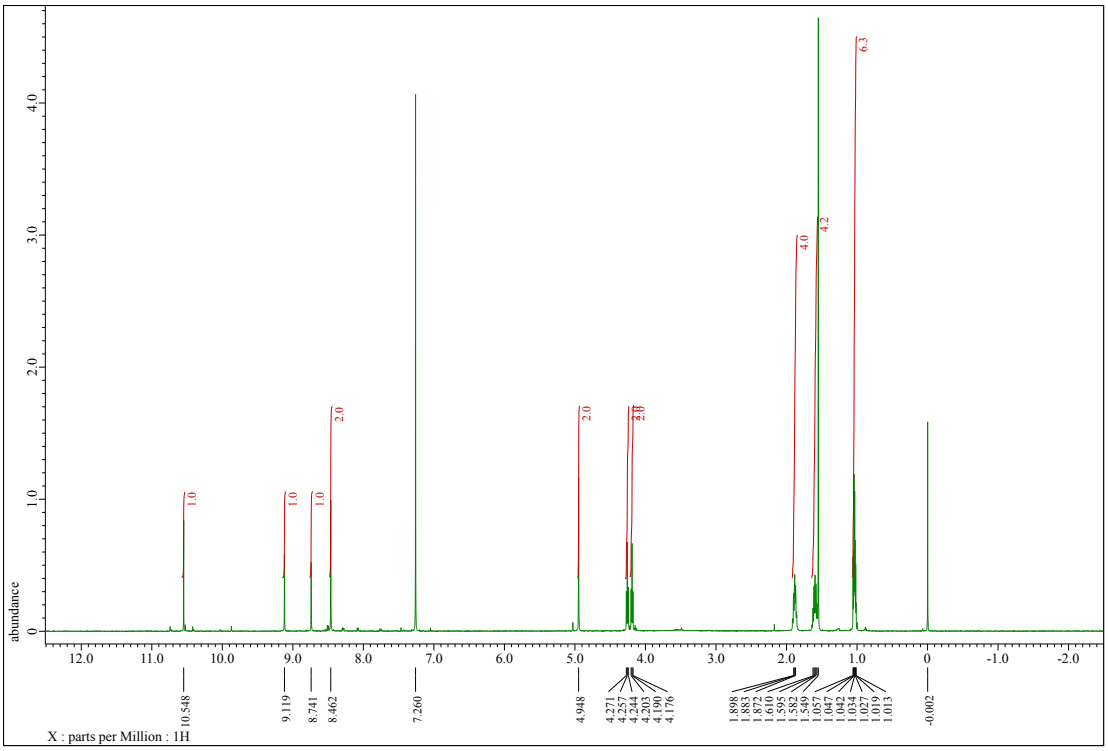
4. NMR spectra



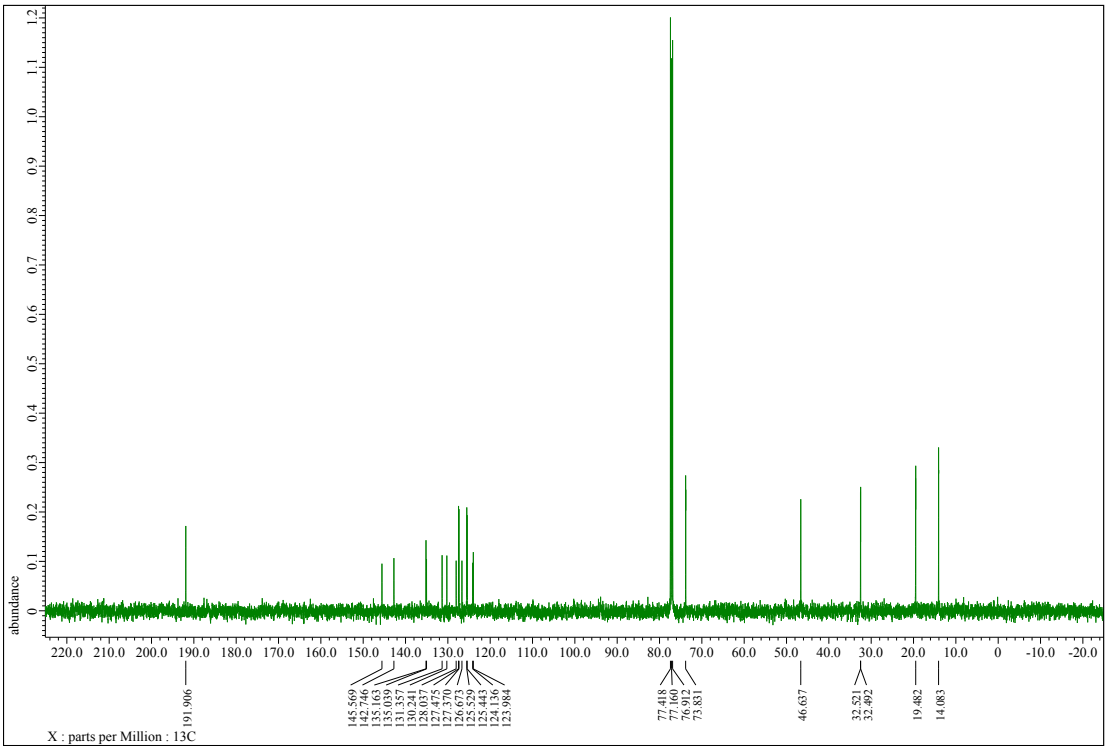
^{1}H NMR spectrum of **3** (600 MHz, $CDCl_3$)



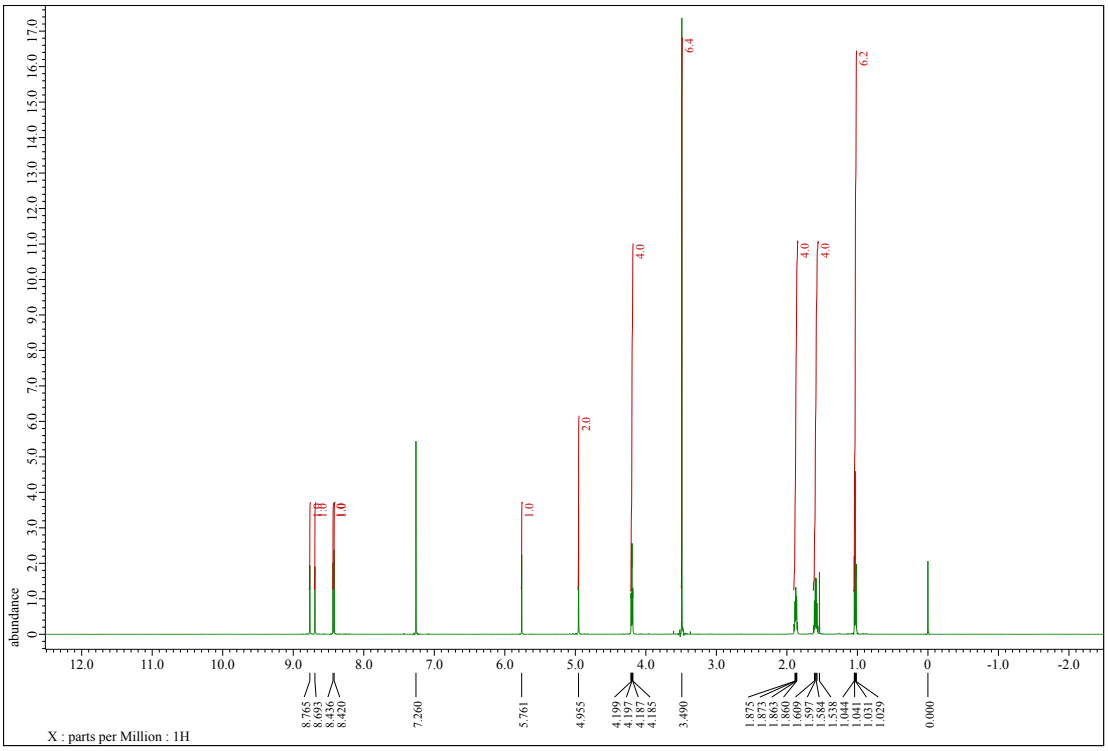
^{13}C NMR spectrum of **3** (150 MHz, $CDCl_3$)



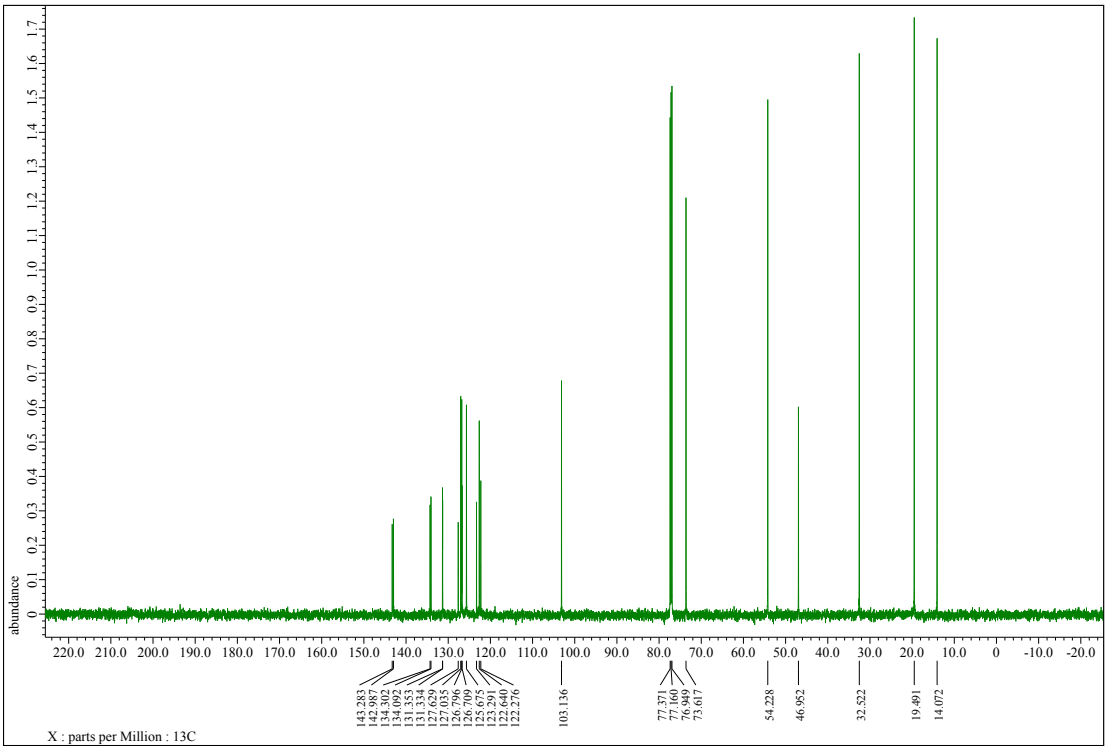
^{1}H NMR spectrum of **4a** (600 MHz, $CDCl_3$)



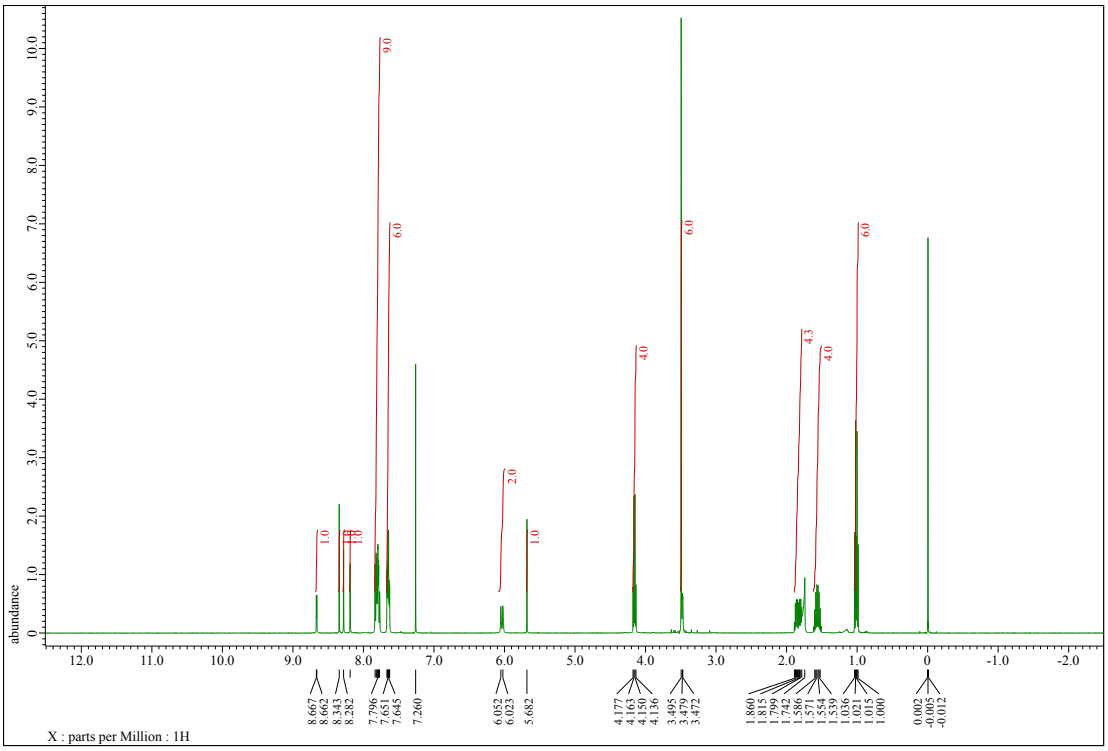
^{13}C NMR spectrum of **4a** (150 MHz, $CDCl_3$)



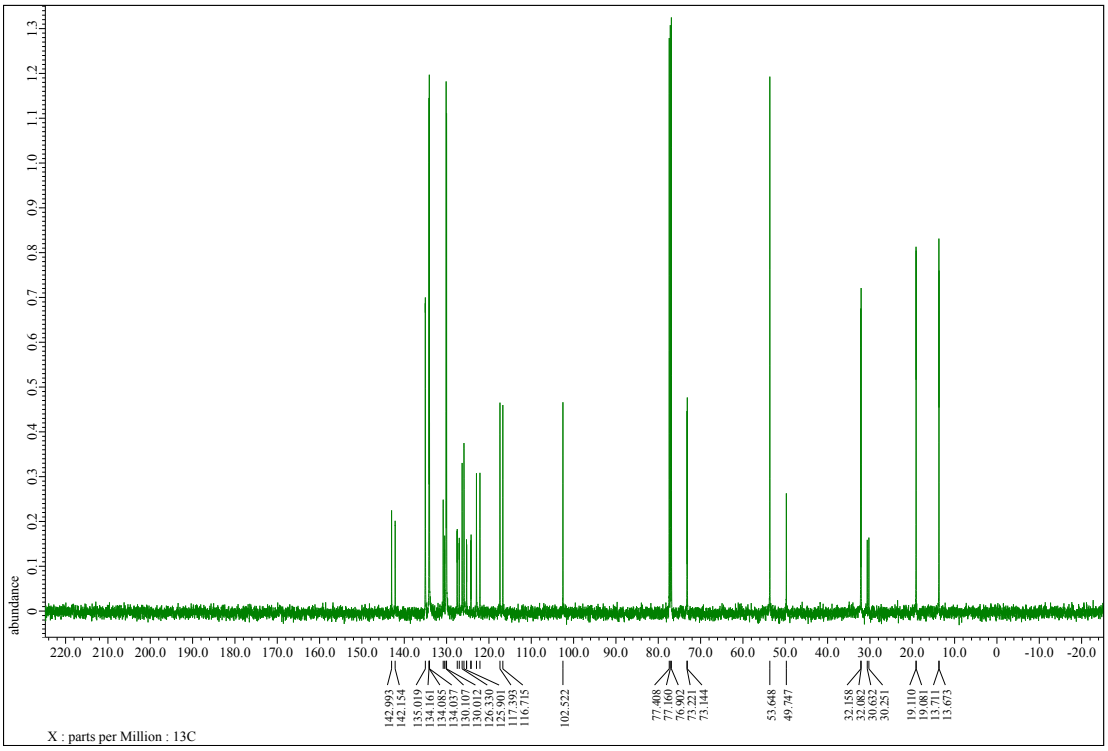
^{1}H NMR spectrum of **4c** (600 MHz, $CDCl_3$)



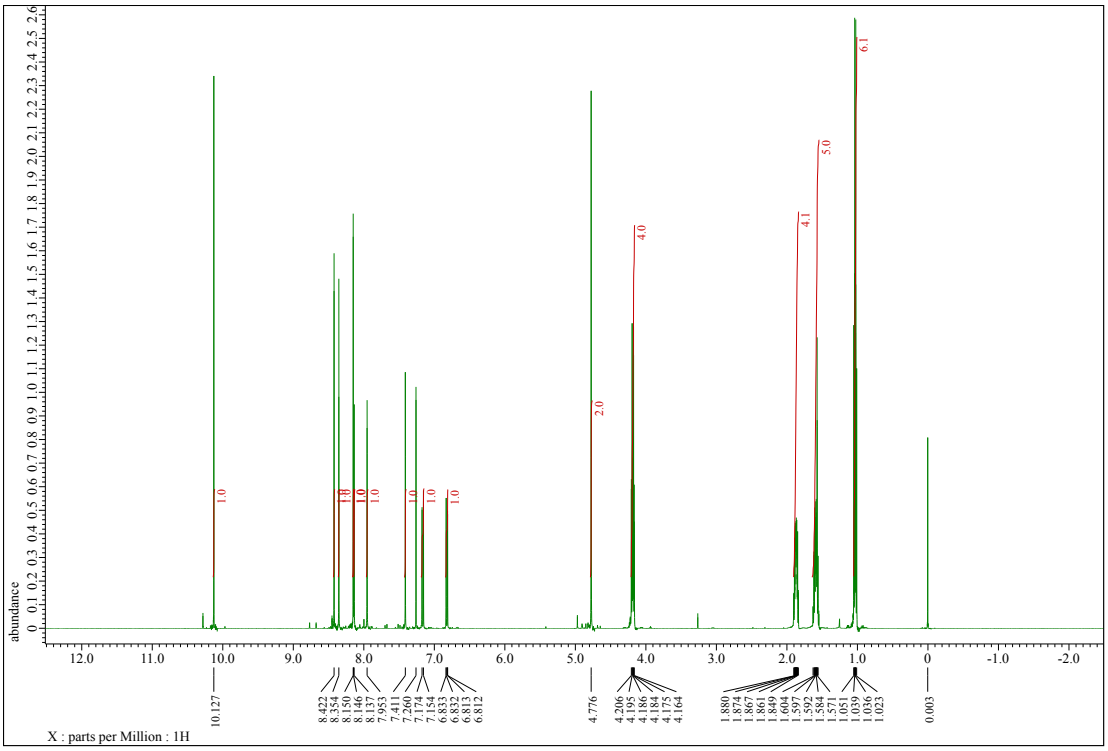
^{13}C NMR spectrum of **4c** (150 MHz, $CDCl_3$)



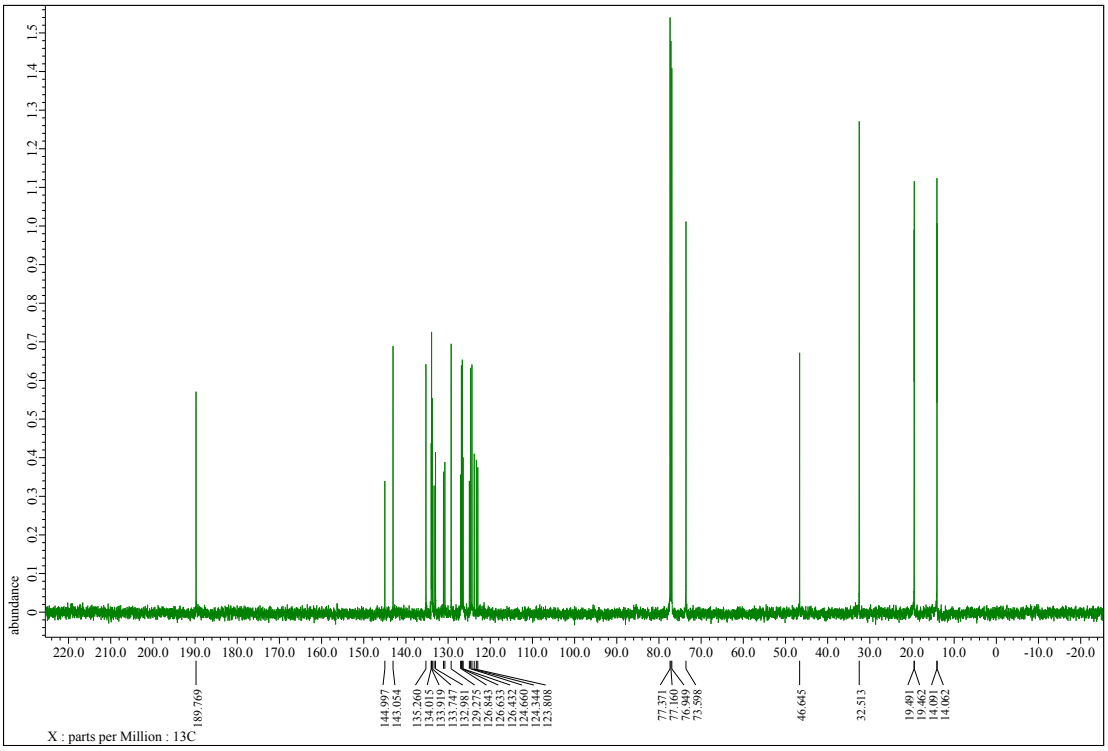
^{1}H NMR spectrum of **4b** (600 MHz, $CDCl_3$)



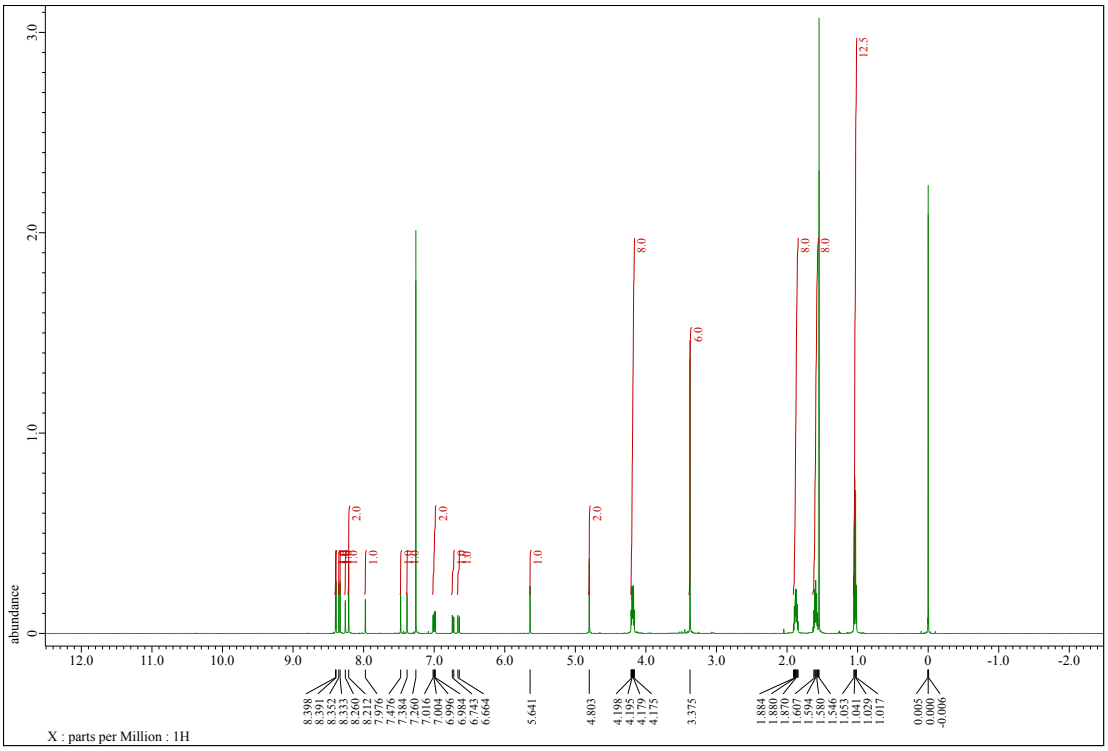
^{13}C NMR spectrum of **4b** (150 MHz, $CDCl_3$)



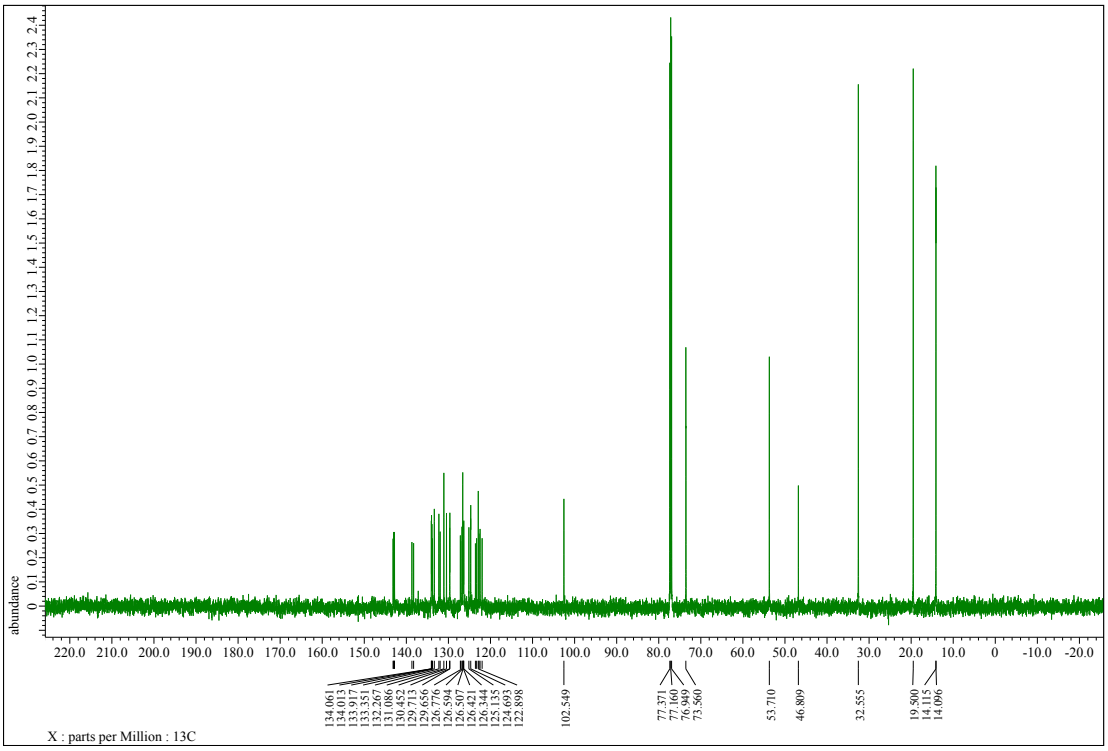
^{1}H NMR spectrum of **6a** (600 MHz, $CDCl_3$)



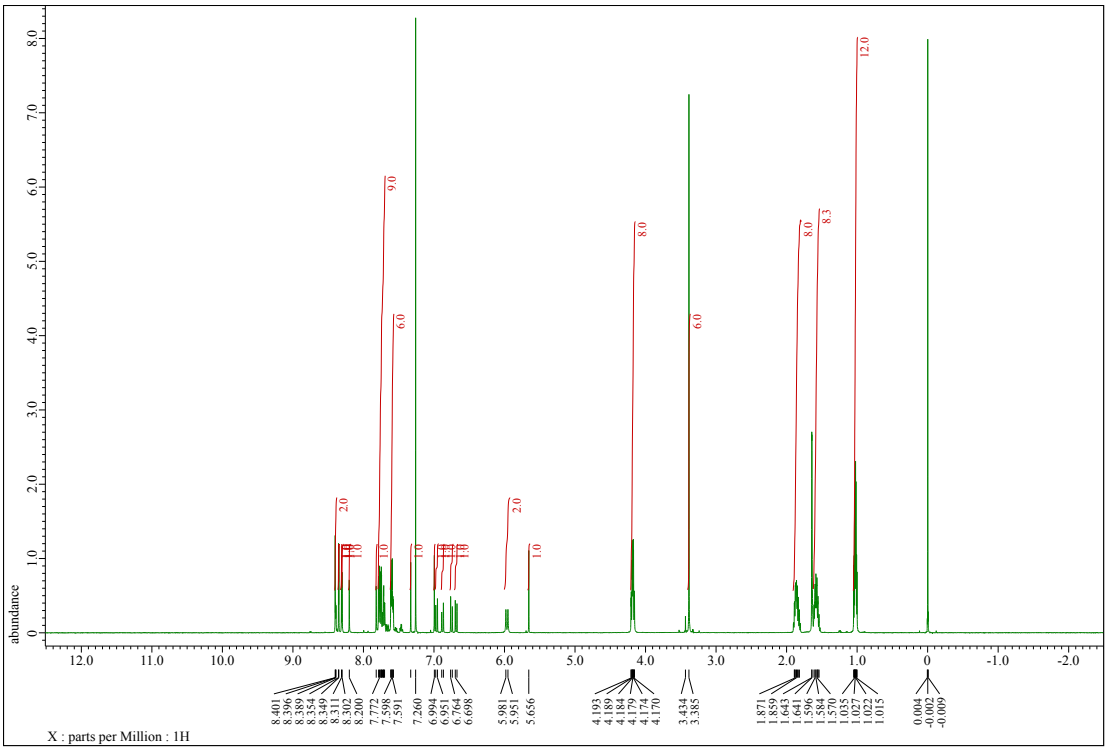
^{13}C NMR spectrum of **6a** (150 MHz, $CDCl_3$)



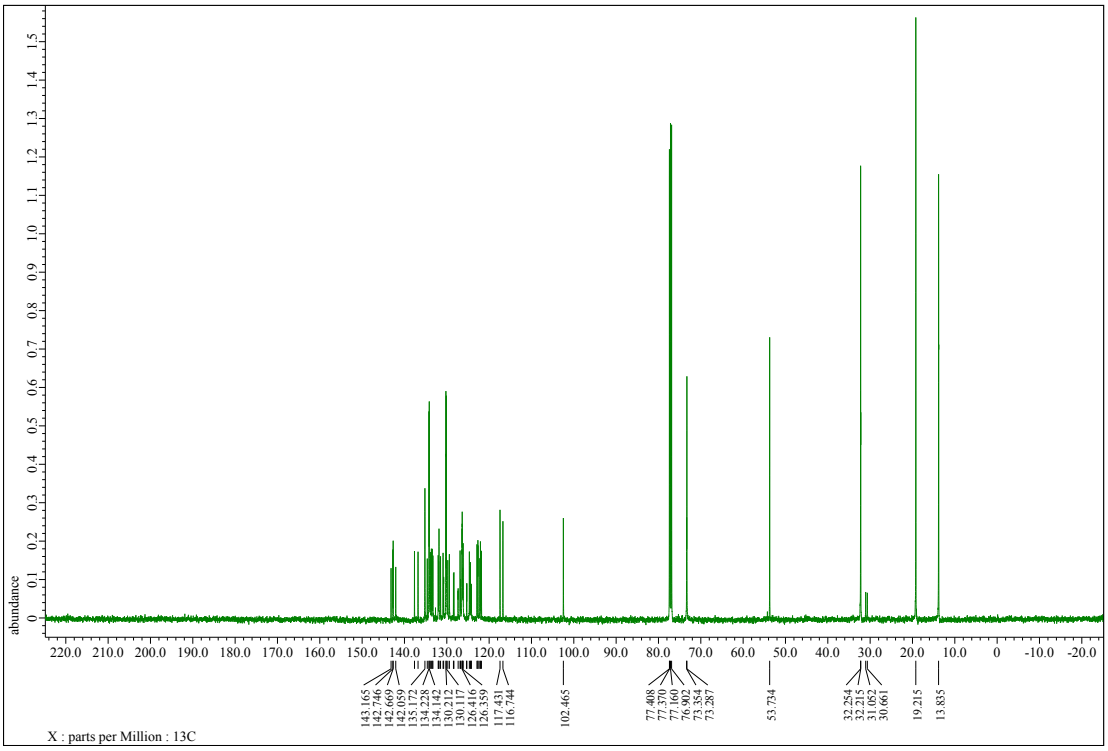
^{1}H NMR spectrum of **7c** (600 MHz, $CDCl_3$)



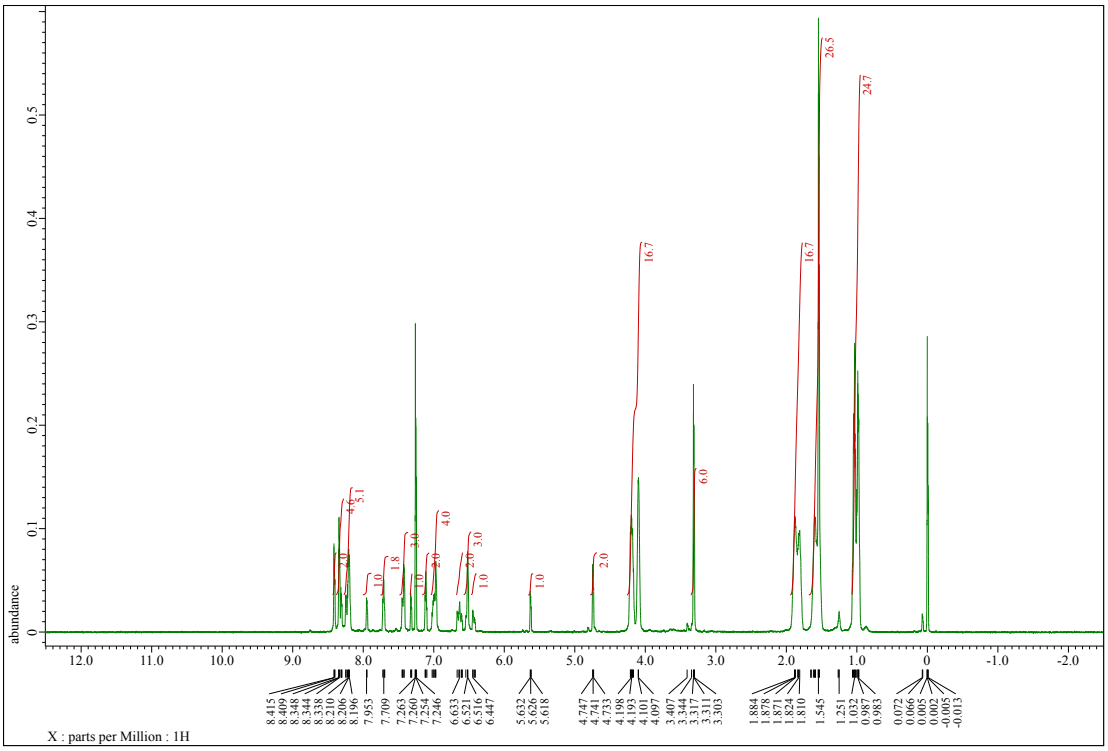
^{13}C NMR spectrum of **7c** (150 MHz, $CDCl_3$)



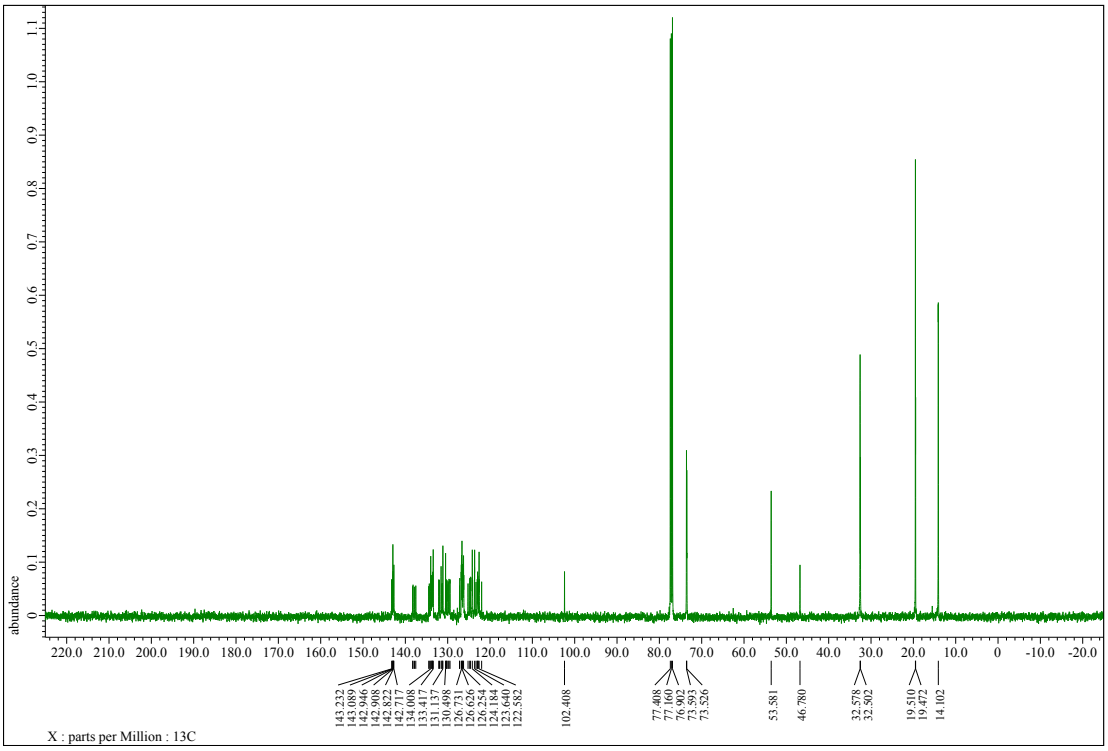
^{1}H NMR spectrum of **7b** (600 MHz, $CDCl_3$)



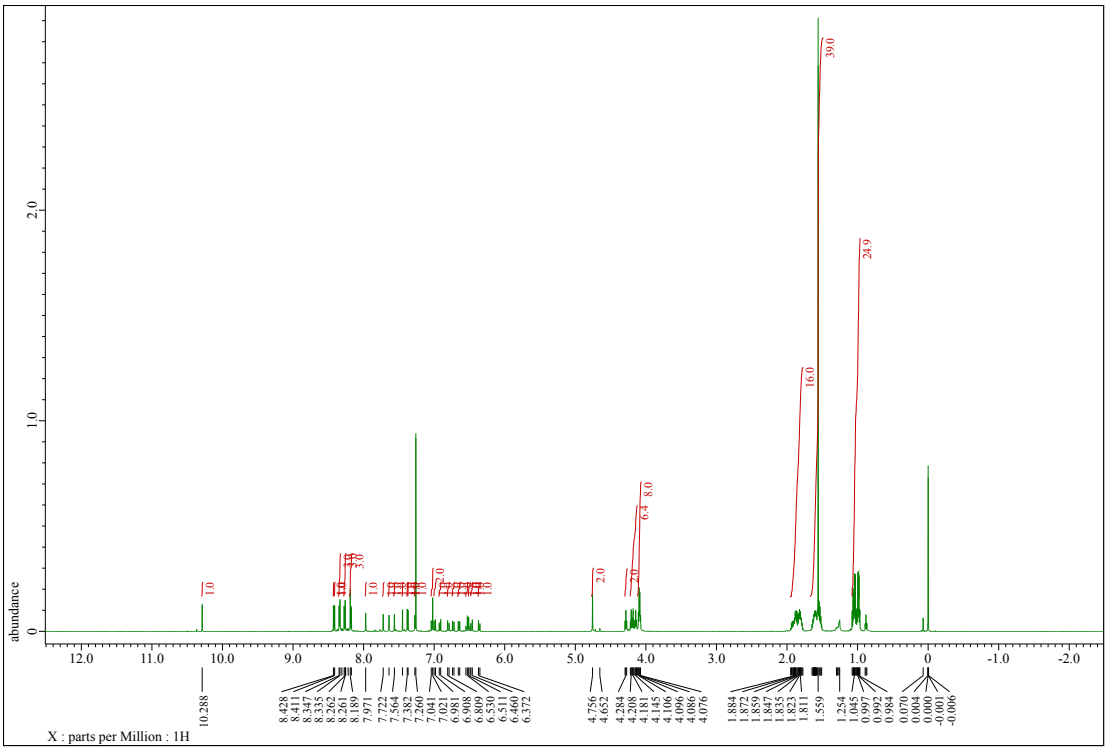
^{13}C NMR spectrum of **7b** (150 MHz, $CDCl_3$)



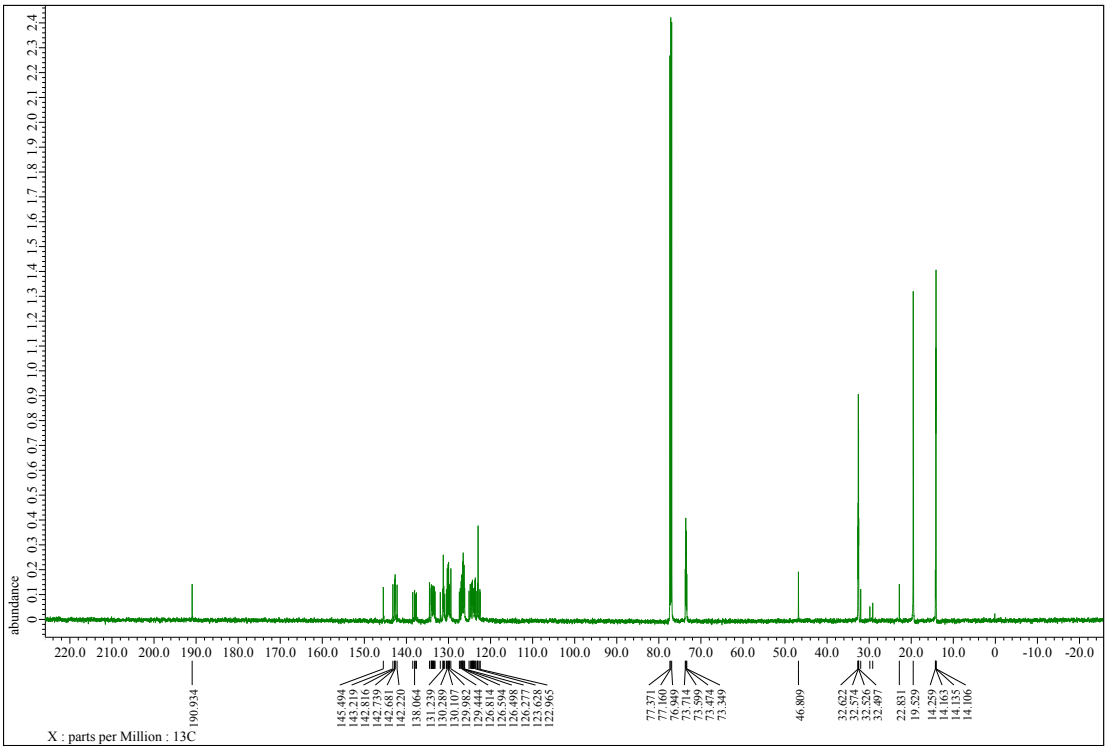
^{1}H NMR spectrum of **8c** (600 MHz, $CDCl_3$)



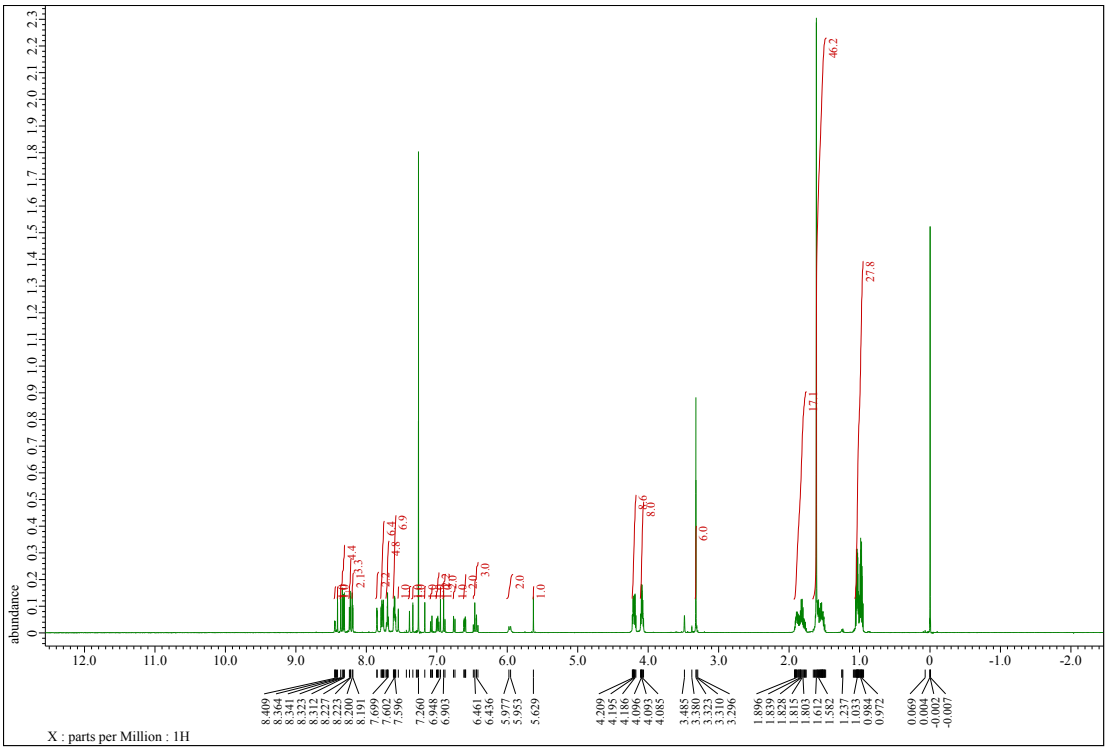
^{13}C NMR spectrum of **8c** (150 MHz, $CDCl_3$)



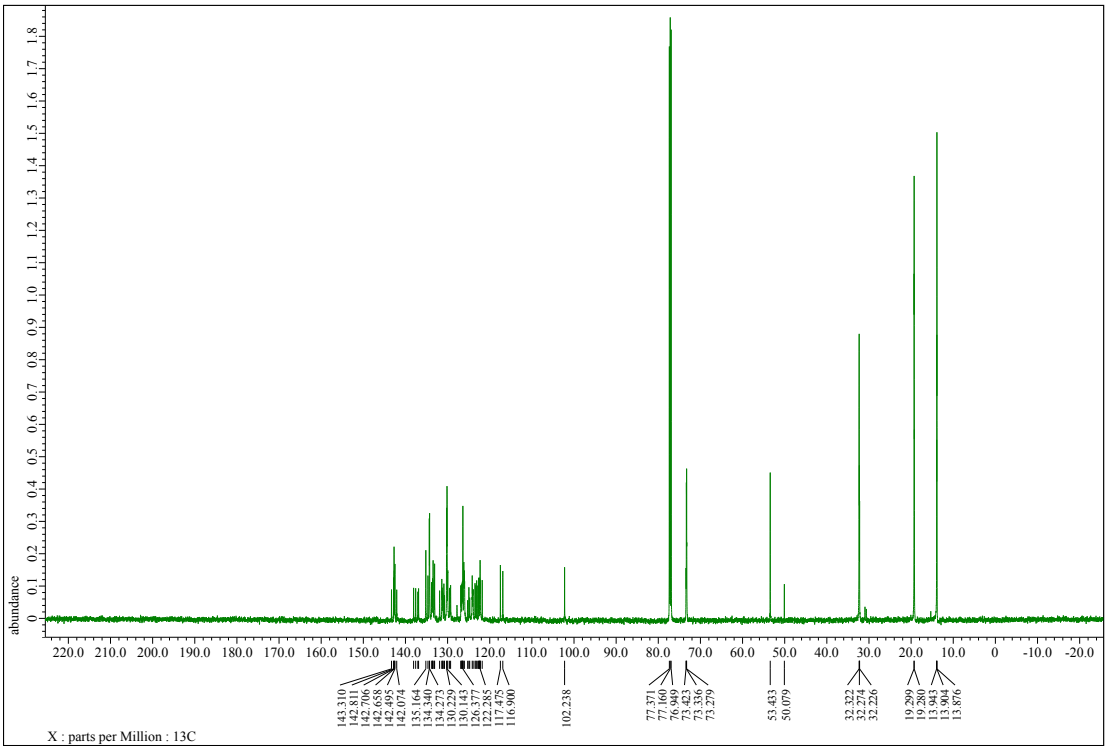
^{1}H NMR spectrum of **8a** (600 MHz, $CDCl_3$)



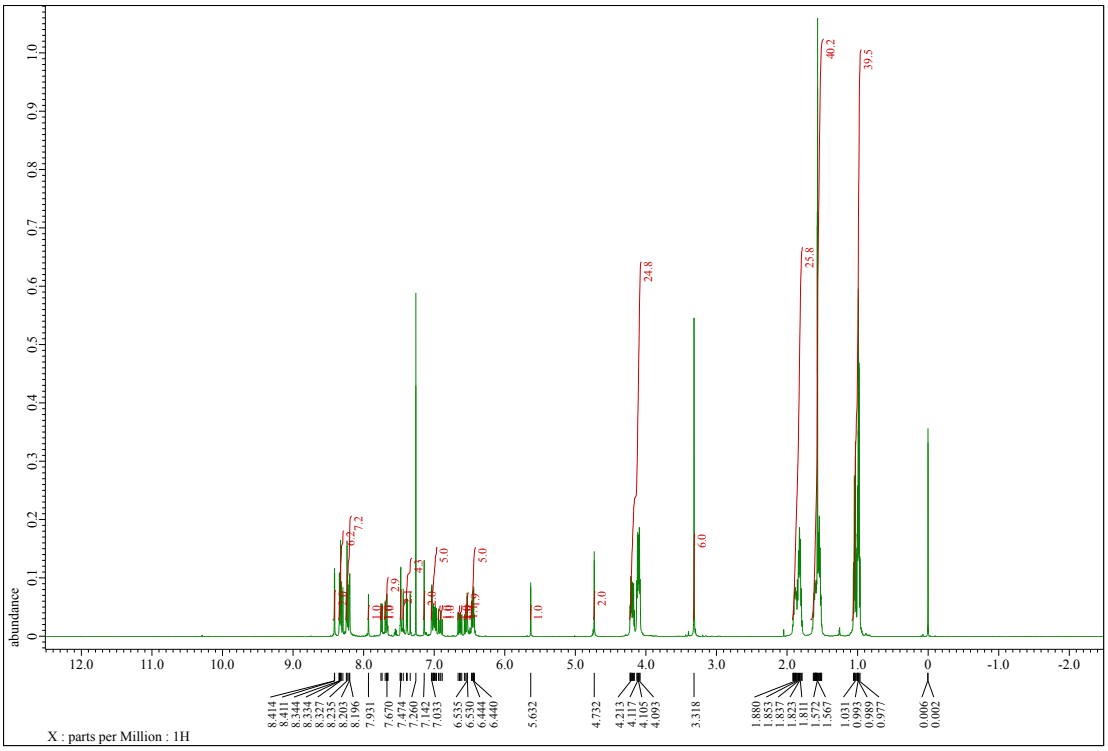
^{13}C NMR spectrum of **8a** (150 MHz, $CDCl_3$)



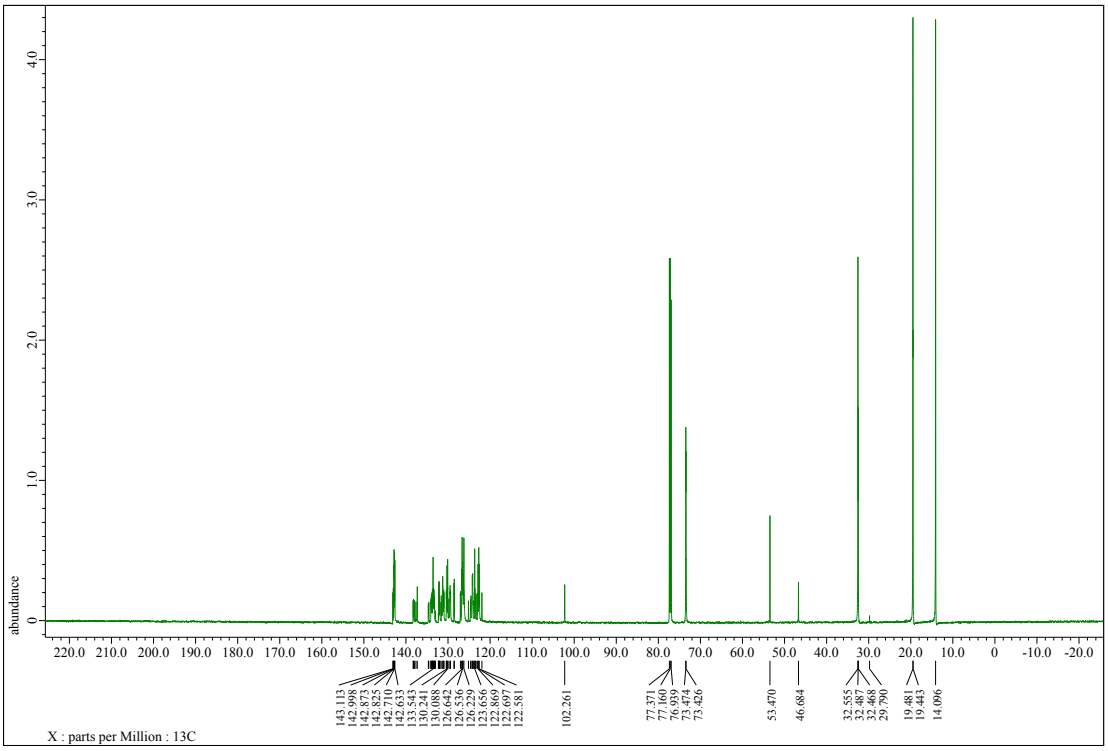
^{1}H NMR spectrum of **8b** (600 MHz, $CDCl_3$)



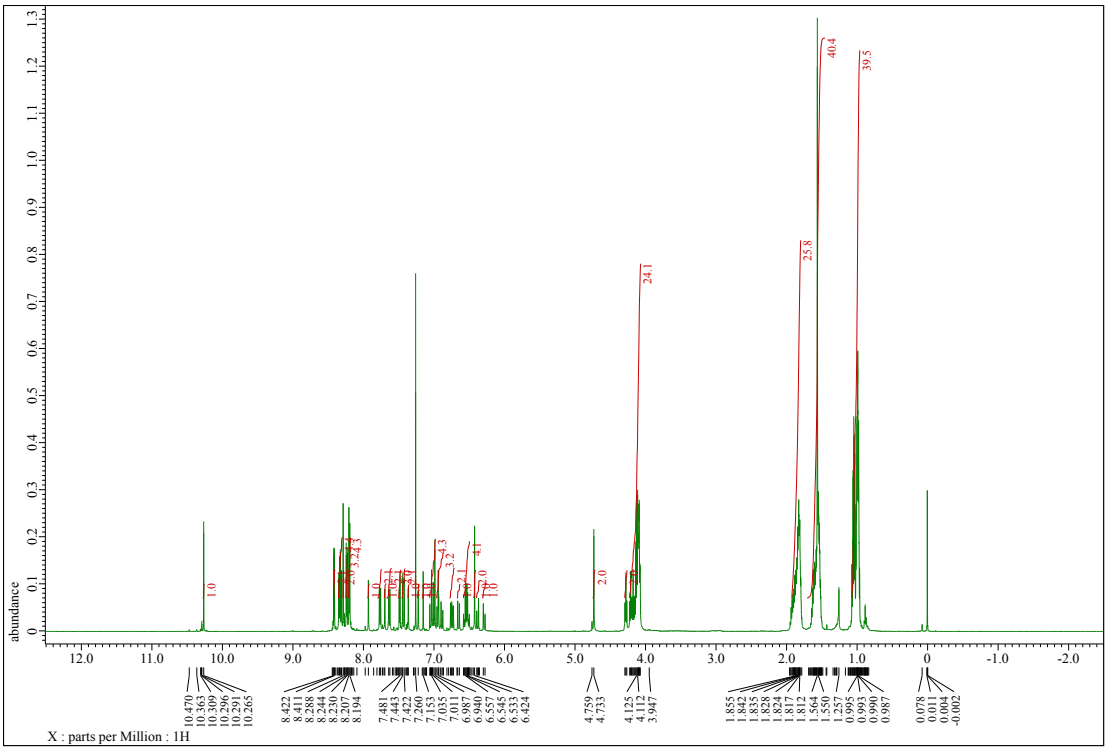
^{13}C NMR spectrum of **8b** (150 MHz, $CDCl_3$)



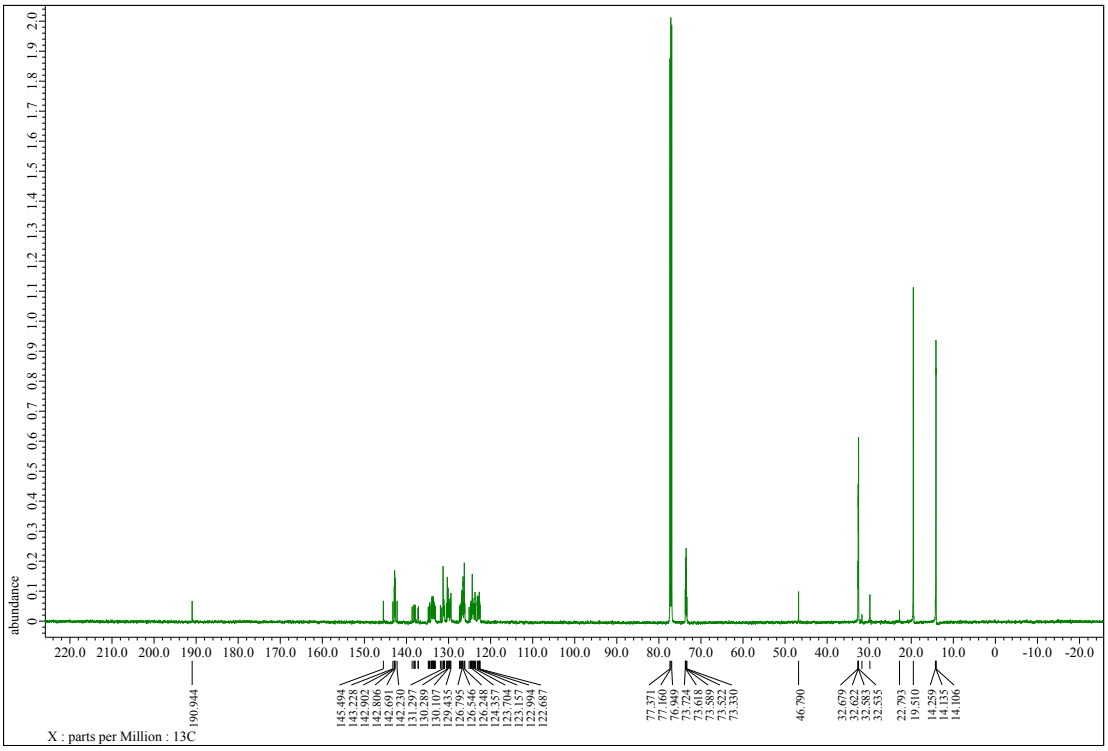
^{1}H NMR spectrum of **9c** (600 MHz, $CDCl_3$)



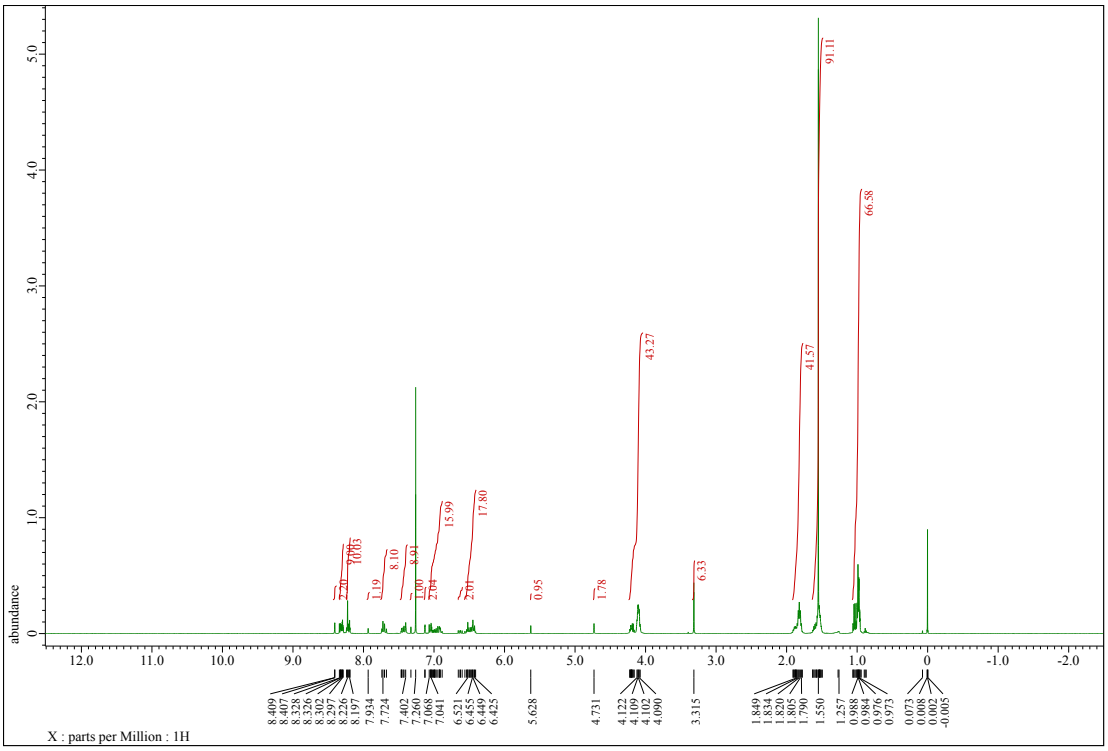
^{13}C NMR spectrum of **9c** (150 MHz, $CDCl_3$)



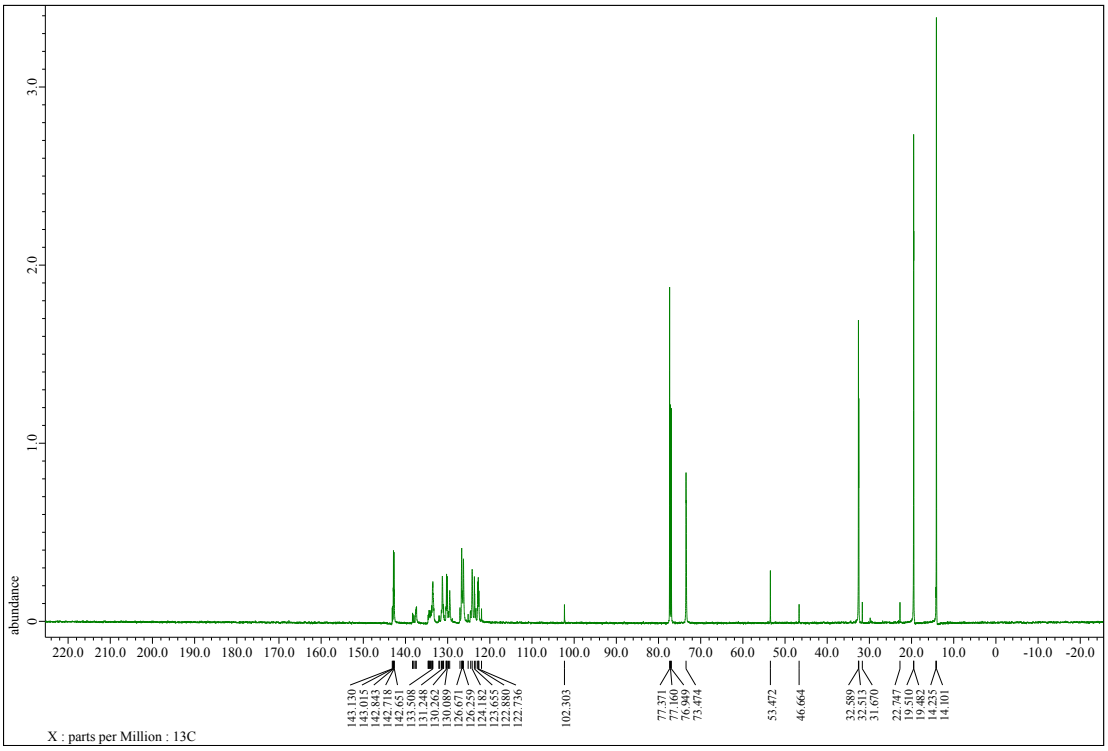
^{1}H NMR spectrum of **9a** (600 MHz, $CDCl_3$)



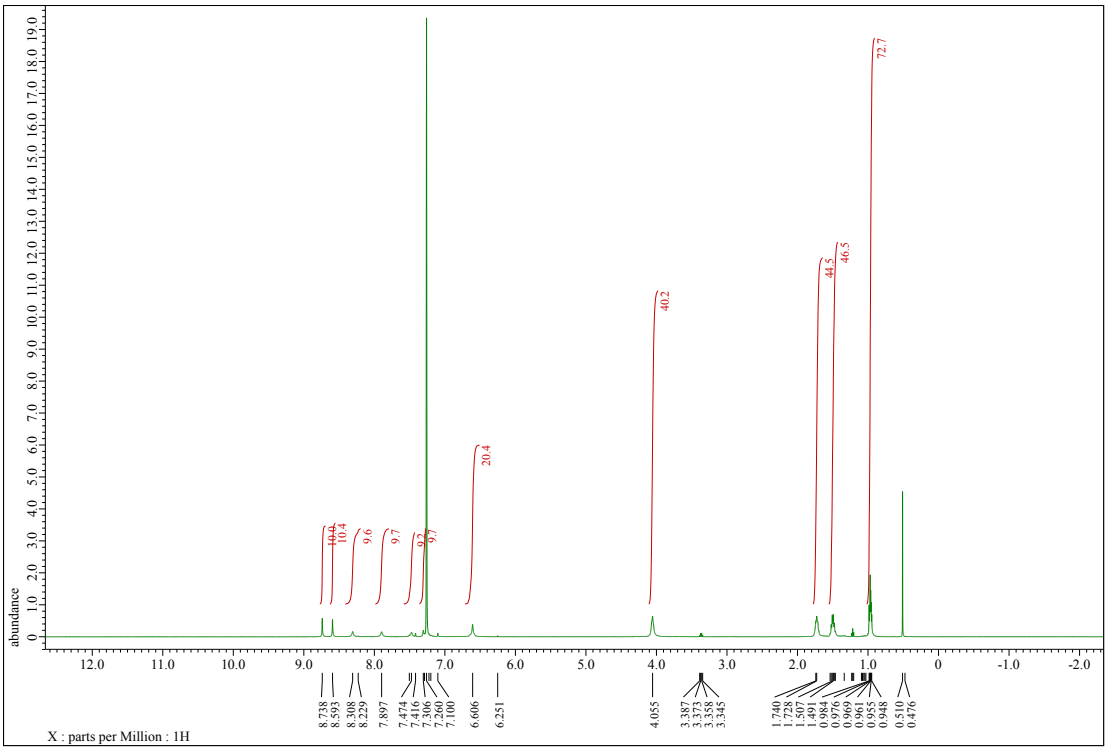
^{13}C NMR spectrum of **9a** (150 MHz, $CDCl_3$)



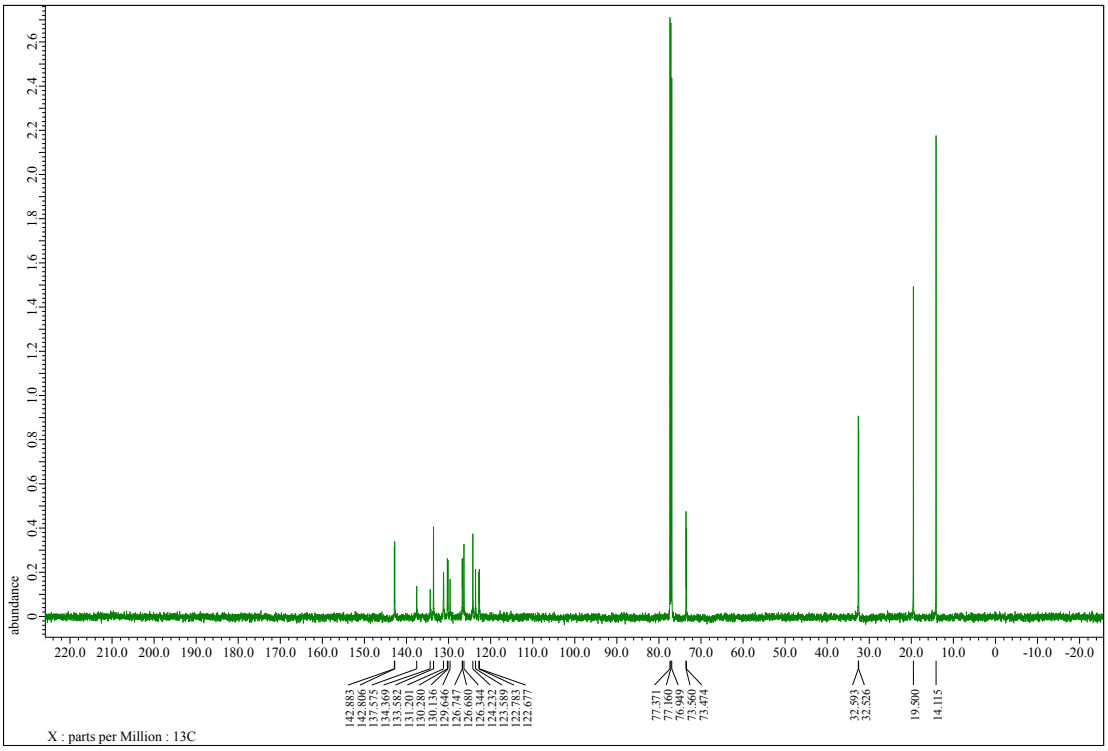
^{1}H NMR spectrum of **10c** (600 MHz, $CDCl_3$)



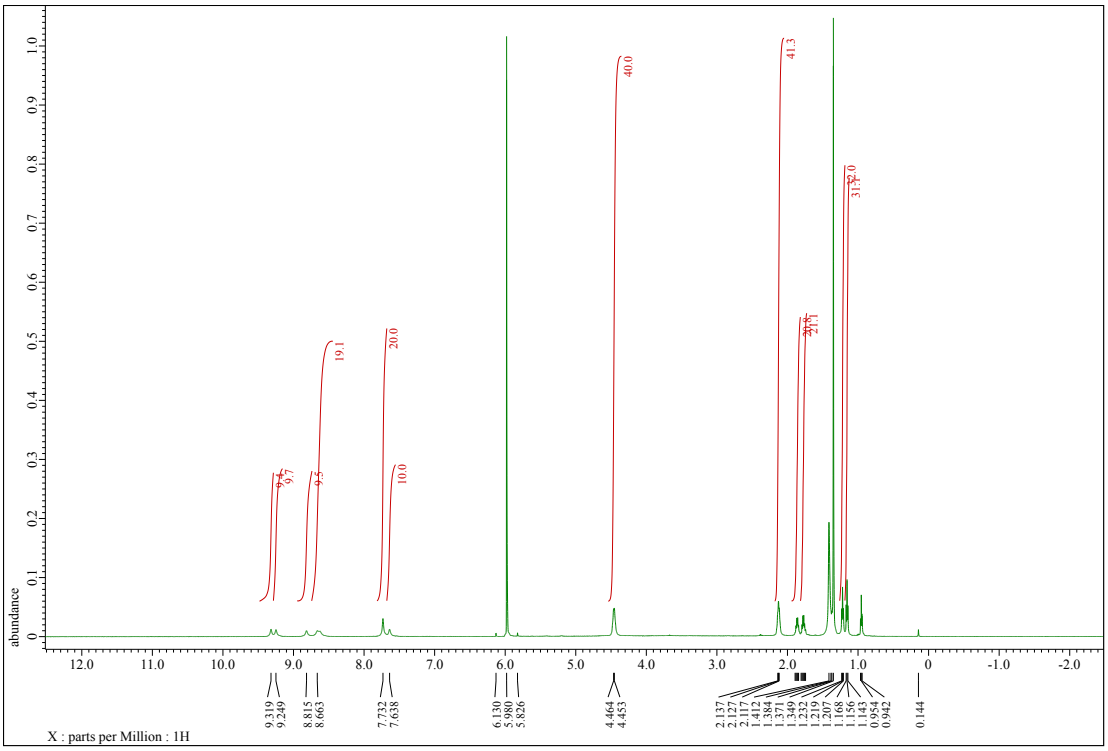
^{13}C NMR spectrum of **10c** (150 MHz, $CDCl_3$)



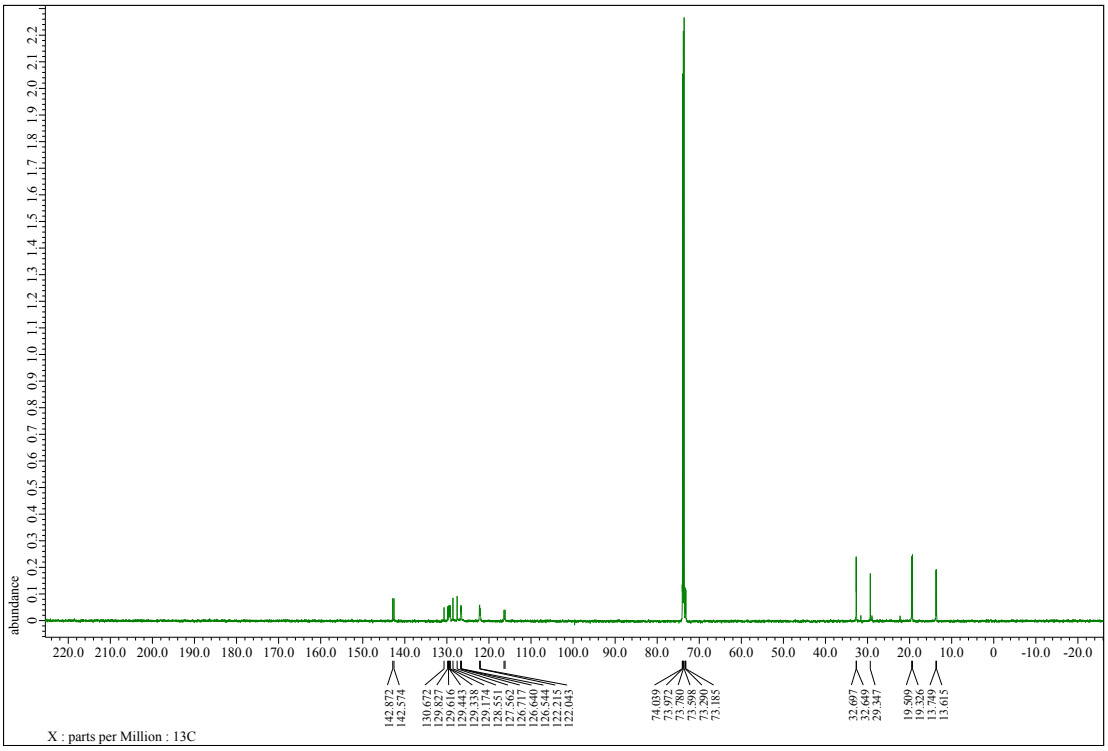
^{1}H NMR spectrum of **11** (600 MHz, $CDCl_3$)



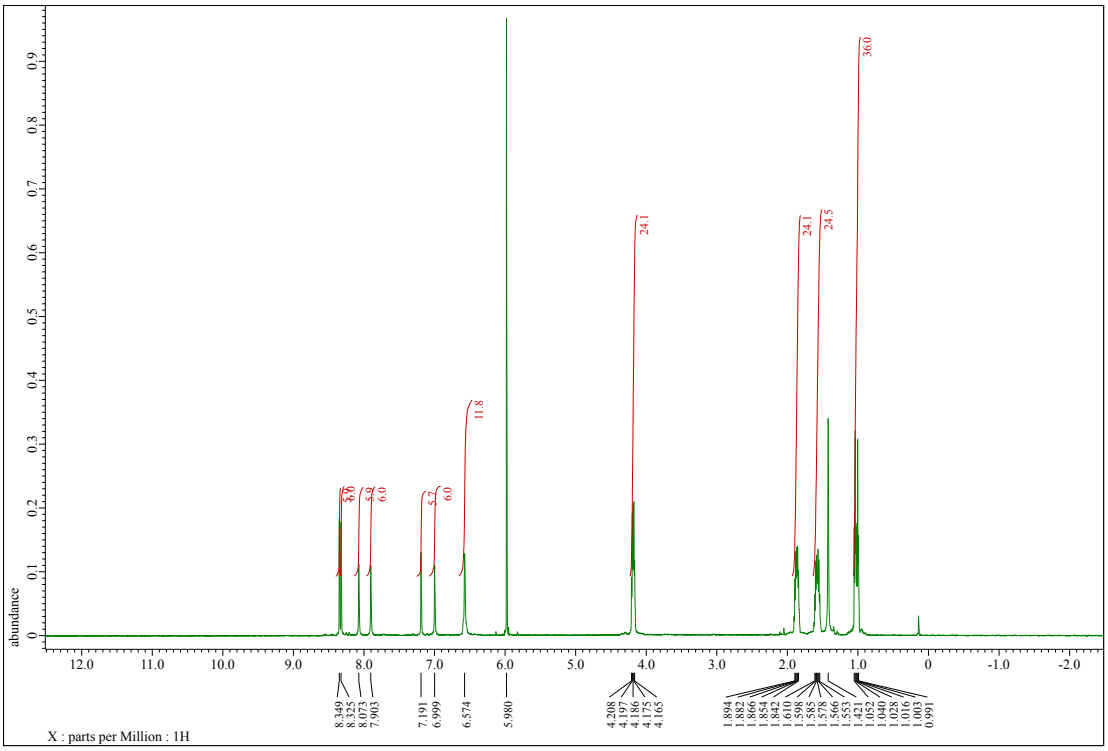
^{13}C NMR spectrum of **11** (150 MHz, $CDCl_3$)



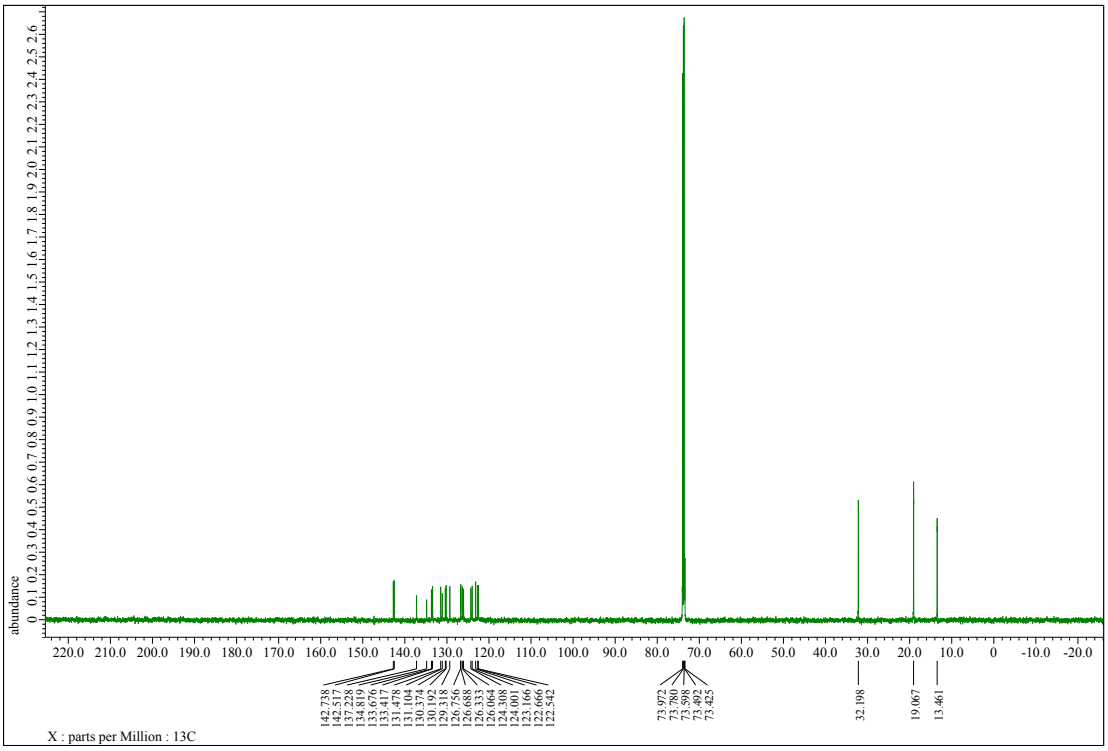
^{1}H NMR spectrum of **1** (600 MHz, $C_2D_2Cl_4$, 140 °C)



^{13}C NMR spectrum of **1** (150 MHz, $C_2D_2Cl_4$, 140 °C)



^{1}H NMR spectrum of **12** (600 MHz, $C_2D_2Cl_4$, 140 °C)



^{13}C NMR spectrum of **12** (150 MHz, $C_2D_2Cl_4$, 140 °C)

5. Supplementary references

1 Li, G. *et al.* Planar Conjugated Polymers Containing 9,10-Disubstituted Phenanthrene Units for Efficient Polymer Solar Cells. *Macromol. Rapid Commun.* **35**, 1142–1147 (2014).

2 Povie, G., Segawa, Y., Nishihara, T., Miyauchi, Y. & Itami, K. Synthesis of a Carbon Nanobelt. *Science* **356**, 172–175 (2017).

3 Frisch, M. J. *et al.* Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT, 2016.

4 Becke, A. D. Density functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.***98**, 5648–5652 (1993).

5 Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785–789 (1988).

6 Elstner, M. *et al.* Self-consistent-charge density-functional tight-binding method for simulationsof complex materials properties. *Phys. Rev. B* **58**, 7260–7268 (1998).

7 Yang, Yu, H., York, D., Cui, Q. & Elstner, M. Extension of the self-consistent-charge density-functional tight-binding method: third-order expansion of the density functional theory total energy and introduction of a modified effective coulomb interaction. *J. Phys. Chem. A* **111**, 10861–10873 (2007).

8 Aradi, B., Hourahine, B. & Frauenheim, T. DFTB+, a sparse matrix-based implementation of the DFTB method. *J. Phys. Chem. A* **111**, 5678–5684 (2007).

9 Gaus, M., Goez, A. & Elstner, M. Parametrization and benchmark of DFTB3 for organic molecules. *J. Chem. Theory Comput.* **9**, 338–354 (2013).

10 Kubillus, M., Kubař, T., Gaus, M., Řezáč, J. & Elstner, M. Parameterization of the DFTB3 method for Br, Ca, Cl, F, I, K, and Na in organic and biological systems. *J. Chem. Theory Comput.* **11**, 332–342 (2015).

11 Nosé, S. A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.* **81**, 511–519 (1984).

12 Hoover, W. G. Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A* **31**, 1695–1697 (1985).

13 Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010).

14 Segawa, Y., Yagi, A., Ito, H. & Itami, K. A Theoretical Study on the Strain Energy of Carbon Nanobelts. *Org. Lett.* **18**, 1430–1433 (2016).