Electronic Supplementary Material (ESI) for Chemical Communications


# Harnessing a diacetylene unit: a molecular design for porous two-dimensional network formation by self-assembly of alkoxy dehydrobenzo[12]annulene derivatives at the liquid/solid interface

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**Contents**

**1. Details of STM Investigations.**

All STM investigations were performed at 22–26 °C using a Nanoscope IIIa (Digital Instruments Inc.) with an external pulse/function generator (model Agilent 33220A) and PicoSTM (Agilent) with negative sample bias. All STM images were acquired in the constant current mode. Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.20 or 0.25 mm).

Prior to imaging, a compound under investigation was dissolved in commercially available 1,2,4-trichlorobenzene (Aldrich) at various solute concentrations, and a drop of DBA solution was applied on a freshly cleaved surface of HOPG (grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH or Advanced Ceramics Inc., Cleveland, USA). The STM investigations were then performed at the liquid/solid interface. By changing the tunneling parameters during the STM imaging, namely, the voltage applied to the substrate and the average tunneling current, it was possible to switch from the visualization of the adsorbate layer to that of the underlying HOPG substrate. This enabled us to correct for drift effects by the use of SPIP software (Image Metrology A/S).

AFM experiments were performed using a Veeco Multimode Nanoscope IV (Veeco Instruments, Inc. Santa Barbara, USA) equipped with an E-scanner in tapping mode. Samples were prepared and imaged in air using minimal force and optimized feedback parameters. Silicon tips (AC160TS, drive frequency of 300-350 kHz, Olympus) were used. Dry film was prepared by blowing hot air from a heat-gun. The heat-gun was placed at 5 cm from the sample and after 4 minutes more than 96% of the solvent (estimated by weight change) was evaporated. This drying method was found to remove solvent molecules to the level sufficient to conduct tapping mode AFM experiments. Drying the film using a heating plate instead of a heat-gun results in patches of molecular multilayers as compared to a porous monolayer network.

## 2. Details of Molecular Modeling by DFT Calculations.

Optimal chain orientation of alkoxylated DBAs was evaluated by quantum chemical calculations using **DBA-OC4** as a model. Three geometries in which the two butoxy chains attached to a benzene ring orient in a synclinal arrangement (a), to the same direction (b) and in an anticlinal arrangement (c) were optimized using the B3LYP/6-31g(d) levels of theory (Fig. S1, ESI). As a result, the model (a) adopting the synclinal arrangement of alkoxy chains appeared to be more stable than the other two models by 8.8 (b) and 56.8 kcal/mol (c), respectively.

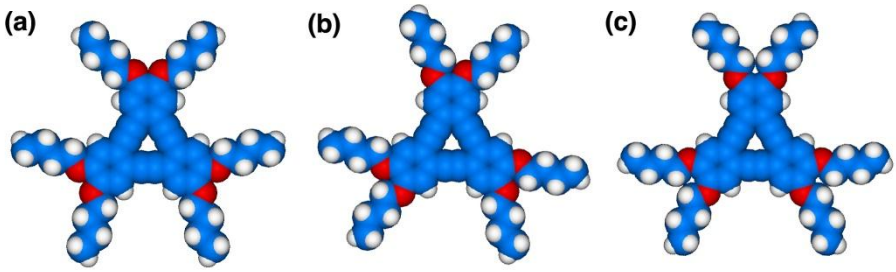



**Fig. S1**. Optimized geometries of **DBA-OC4** having differently-orientated alkoxy chains The optimizations were performed at the B3LYP/6-31g(d) level of theory under vacuum. (a) A model in which the two alkoxy chains attached to a benzene ring orient in a synclinal arrangement ($D_{3h}$ symmetric constraints). (b) A model in which the two alkoxy chains orient to the same direction ($C_{3h}$ symmetric constraints). (c) A model in which the two alkoxy chains orient in an anticlinal arrangement ($D_{3h}$ symmetric constraint).

## 3. Molecular Models of Dimers of DBA-DA12.12.

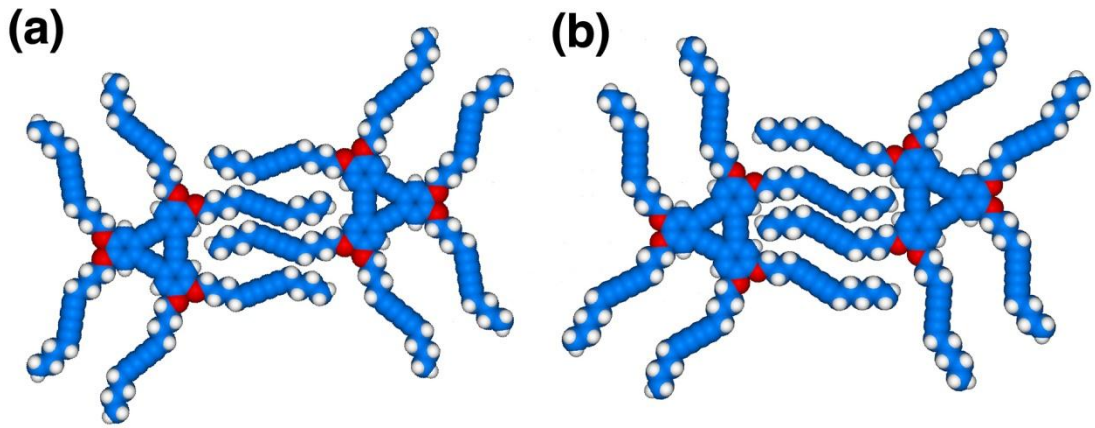



**Fig. S2**. (a) A chain-mismatched dimer of **DBA-DA12.12** with all 4-DA-4 chains. (b) A chain-interdigitated dimer of a hypothetical **DBA-DA** with alternating 3-DA-5 and 4-DA-4 chains.

**4. Details of Molecular Mechanics Simulations.**

The Tinker 4.2 software package[1] was used with the MM3 force field.[2] Threshold values were 20.0 Å for van der Waals interactions (Lennard-Jones type) and less than 0.01 kcal/mol$^{-1}$ for optimization. As the substrate, a monolayer piece of HOPG (i.e. single layer graphene) was used and it was fixed during the simulations. The DBA molecules were placed 0.35 nm above the substrate and the alkyl chains were adjusted to align parallel to the directions of the graphite symmetry axes. The relative stability of the hexamers was difference of total potentials between the two structures.

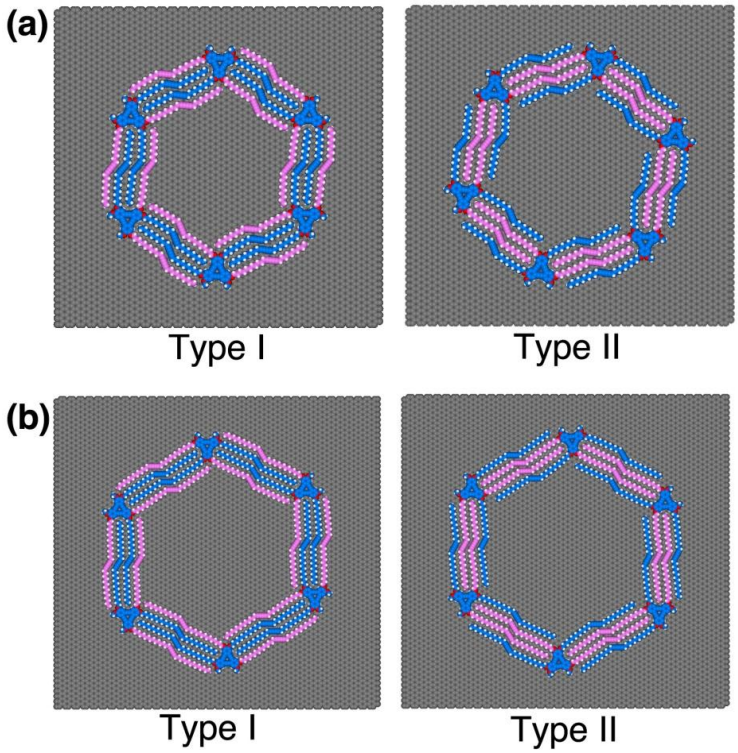



**Fig. S3**. (a) Optimized structures by the MM simulations of the hexamer models by **DBA-DA24.25** with high and low molecular densities, type I structure; a = b = 7.1 nm and γ = 60º, *d* = 0.069 molecules/nm$^2$ and type II structure; a = b = 7.4 nm, γ = 60º and *d* = 0.063 molecule/nm$^2$, respectively. Side chains R$^1$ (10-DA-10) and R$^2$ (10-DA-11) are colored in blue and pink, respectively. (b) Optimized structures by the MM simulations of the hexamer models by **DBA-DA32.33** with high and low molecular densities, type I structure; a = b = 8.9 nm, γ = 60º and *d* = 0.045 molecule/nm$^2$ and type II structure; a = b = 9.1 nm, γ = 60º and *d* = 0.041 molecule/nm$^2$, respectively. Side chains R$^1$ (14-DA-14) and R$^2$ (14-DA-15) are colored in blue and pink, respectively. Optimizations were performed on a single layered graphite sheet (gray) by using MM3 parameters.

## 5. Structural Parameters of Monolayer Structure of DBA-DAs.

**Table S1**. Structural Parameters of Monolayer Structure of **DBA-DA**s.

| Compound | unit cell parameters[a] | | $Z^b$ | *area* ($nm^2$)[c] | *d* ($nm^{-2}$)[d] | *pore size* (nm)[e] |
|---|---|---|---|---|---|---|
| | $a = b$ (nm) | $\gamma$ (°) | | | | |
| **DBA-DA 17.17** | 5.3 ± 0.1 | 61 ± 3 | 2 | 16.3 | 0.123 | 4.9 |
| **DBA-DA 24.25** | 7.0 ± 0.1 | 60 ± 2 | 2 | 28.4 | 0.070 | 6.0 |
| **DBA-DA 32.33** | 8.3 ± 0.1 | 60 ± 2 | 2 | 40.0 | 0.050 | 7.0 |

[a]Unit cells are shown in the respective STM images. [b]Number of molecules per unit cell. [c]Unit cell area. [d]Network density (molecule/$nm^2$). [e]The distance between the closest edges of the diacetylene units facing across a pair.

## 6. Additional STM Images of DBA-DAs and Details of Concentration Dependency.

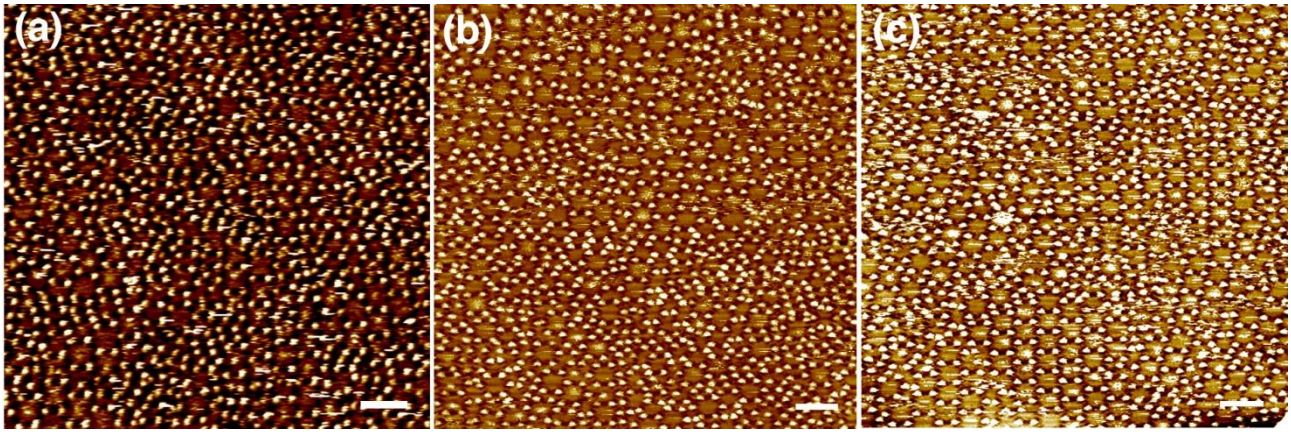



**Fig. S4**. A set of typical STM images for **DBA-DA24.25**. Images were collected at a concentration of (a) $5.0 \times 10^{-6}$ M, (b) $3.2 \times 10^{-6}$ M, and (c) $2.1 \times 10^{-6}$ M. All scale bars are 10 nm. STM imaging parameters, set point: 0.1 nA, tip voltage: –0.9 V.

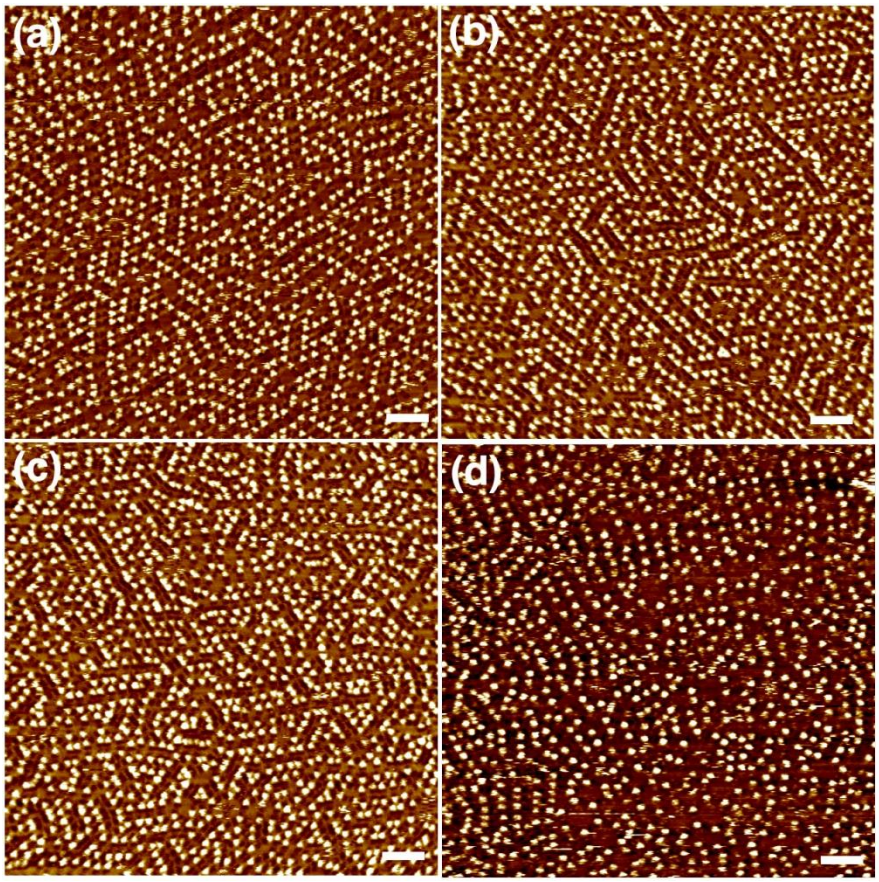



**Fig. S5**. A set of typical STM images for **DBA-DA32.33**. Images were collected at concentration of (a) 5.0 $\times 10^{-6}$ M, (b) 3.1 $\times 10^{-6}$ M, (c) 2.6 $\times 10^{-6}$ M, and (d) 2.3 $\times 10^{-6}$ M. All scale bars are 10 nm. STM imaging parameters, set point: 0.1 nA, tip voltage: –0.9 V.

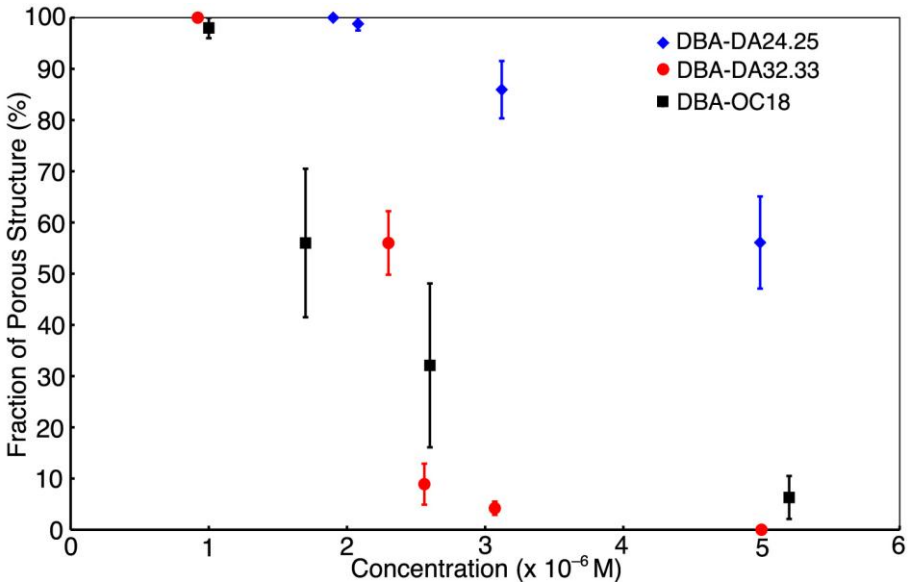



**Fig. S6**. Concentration dependent change of ratio of the porous networks of **DBA-DA24.25** (blue), **DBA-DA32.33** (red) and **DBA-OC18** (black) at the TCB/graphite interface. Typical STM images at each concentration are shown in Figs. S4 and S5, ESI.

## 7. AFM Images of a Dry Film of DBA-DA24.25.

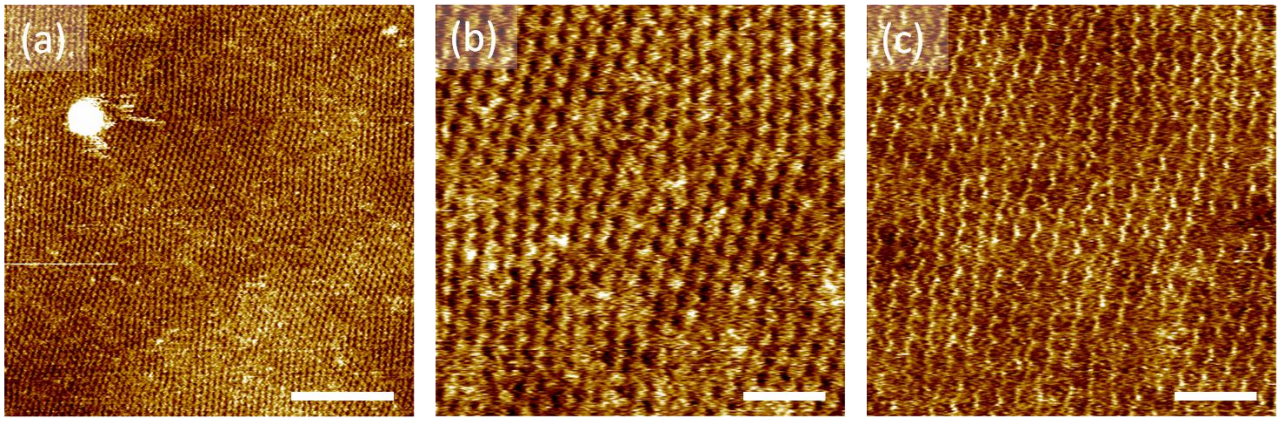



**Fig. S7.** AFM images of a dry film prepared from a TCB solution of **DBA-DA24.25** (initial concentration: $6.0 \times 10^{-6}$ M) through evaporation of the solvent using a heat-gun. a) phase image of the monolayer, showing the existence of large regular domains of the porous structure, b-c) respective height and phase image of a smaller area. In the height image (b) the pores show up as bright (higher) and the rims less bright (lower) due to contrast inversion. In the phase (c) image, the contrast is reversed. Figure (a) scale bar: 100 nm, scan rate: 1.969 Hz; fig (b-c) scale bar: 25 nm, scan rate: 5.086 Hz.

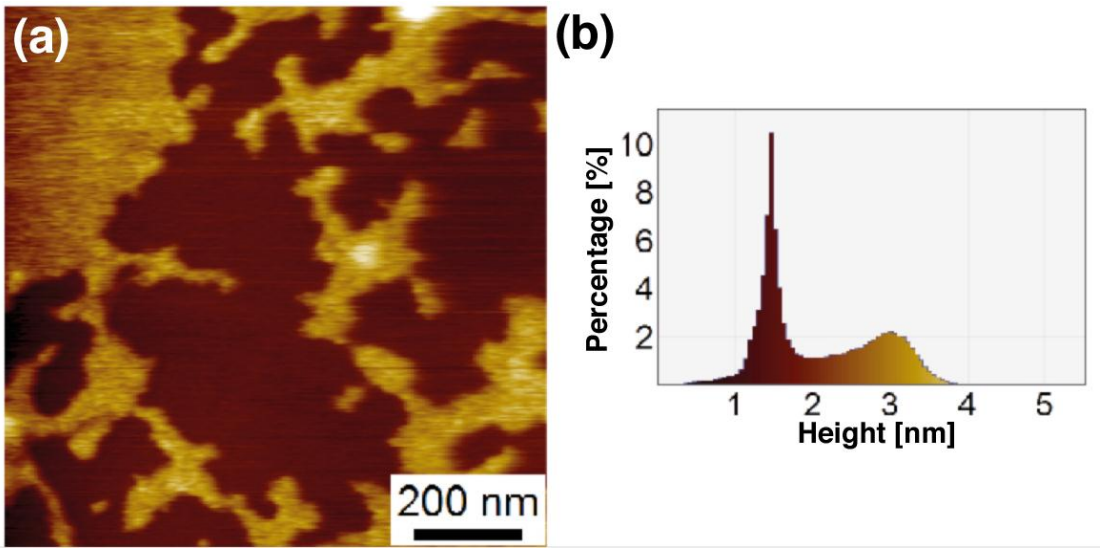


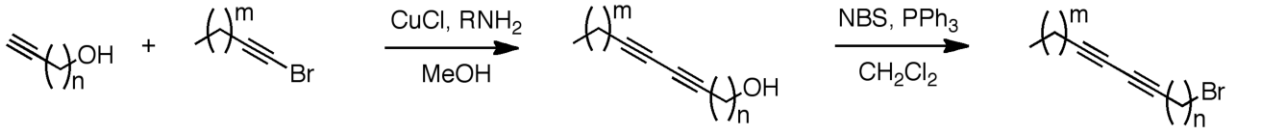

**Fig. S8**. (a) AFM image of a dry film prepared from a TCB solution of **DBA-DA24.25** (initial concentration $6.0 \times 10^{-6}$ M) using a heat plate. This drying method induces patches of molecular multilayers on the surface instead of domains of porous structures as observed when using a heat-gun (see Fig. S7). Scan rate: 2.959 Hz. (b) The corresponding height distribution histogram of (a) indicating the ≈2.5 nm height of the multilayers.

**8. Synthesis of DBA-DAs**.

**8-1. General**. All solvents were distilled or passed through activated alumina and copper catalyst in a Glass Contour solvent purification system prior use. All commercially available reagents were used as received. $Pd(PPh_3)_4$ was prepared following literature procedures.[3]

$^1H$ (400 MHz, 300 MHz and 270 MHz) and $^{13}C$ (100 MHz, 75 MHz and 67.5 MHz) NMR spectra were measured on a JEOL JNM AL-400, a Varian Mercury 300 or a JEOL JNM-GSX-270 spectrometer. When chloroform-*d* or acetone-$d_6$ was used as a solvent, the spectra were referenced to residual solvent proton signals in the $^1H$ NMR spectra (7.26 ppm for chloroform-*d* and 2.05 ppm for acetone-$d_6$) and to the solvent carbons in the $^{13}C$ NMR spectra (77.0 ppm for chloroform-*d* and 29.8 ppm for acetone-$d_6$). Preparative HPLC was undertaken with JAI LC-908 and JAI LC-908-C60 chromatographs using 600 mm × 20 mm JAIGEL-1H and 2H or JAIGEL-2H and 2.5H GPC columns with $CHCl_3$ as the eluent. Other spectra were recorded by the use of the following instruments: IR spectra, JACSCO FT/IR-410; mass spectra, JEOL JMS-700 for EI or FAB ionization mode, JEOL JMS-100LC for ESI ionization mode and Bruker Daltonics, Autoflex II for LD ionization mode.

**8-2. Syntheses of 1-Hydroxyalkadiynes.**




**1a**: n = 4
**1b**: n = 6
**1c**: n = 7
**1d**: n = 10
**1e**: n = 11
**1f**: n = 14
**1g**: n = 15

**2a**: m = 3
**2b**: m = 6
**2c**: m = 5
**2d**: m = 9
**2e**: m = 9
**2f**: m = 13
**2g**: m = 13

**3a**: m = 3, n = 4, 5%
**3b**: m = 6, n = 6, 91%
**3c**: m = 5, n = 7, 68%
**3d**: m = 9, n = 10, 68%
**3e**: m = 9, n = 11, 48%
**3f**: m = 13, n = 14, 73%
**3g**: m = 13, n = 15, 60%

**4a**: m = 3, n = 4, 38%
**4b**: m = 6, n = 6, 96%
**4c**: m = 5, n = 7, 86%
**4d**: m = 9, n = 10, 90%
**4e**: m = 9, n = 11, 90%
**4f**: m = 13, n = 14, 94%
**4g**: m = 13, n = 15, 96%

**Synthesis of Heptadeca-7,9-diyn-1-ol (3b)**. Under an argon atmosphere, CuCl (322 mg, 3.25 mmol) was dissolved in an aqueous solution of $EtNH_2$ (30wt%, 200 mL). $NH_2OH \cdot HCl$ (899 mg, 12.9 mmol) was added to the mixture. A solution of **1b** (8.17 g, 64.7 mmol) in MeOH (15 mL) was added dropwise to the mixture at 0 °C. Subsequently, a solution of **2b** (15.8 g, 77.6 mmol) in MeOH (20 mL)

was added dropwise to the mixture. After stirring at room temperature for 21 h, the reaction was quenched by addition of saturated aqueous solution of $NH_4Cl$. The products were extracted with ether, the extract was washed with aqueous solution of HCl (ca. 1 N) and brine, and the organic phase was dried over $MgSO_4$. After evaporation of the solvents, purification was performed by the use of silica gel column chromatography (hexane/AcOEt, from 1/0 to 4/1) to give **3b** (58.8 mmol, 91%) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.64 (t, $J$ = 6.6 Hz, 2H), 2.29–2.20 (m, 4H), 1.64–1.20 (m, 19H), 0.89 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 77.6, 77.4, 65.4, 65.2, 63.0, 32.7, 31.3, 28.8, 28.7, 28.5, 28.3, 28.2, 25.6, 22.5, 19.20, 19.18, 14.0; IR (neat) 3363, 2931, 2858, 2256, 2163, 1464, 1427, 1058, 725 cm$^{-1}$; HRMS (EI) *m/z* calcd for $C_{17}H_{28}O$: 248.2140, found: 248.2130 ($M^+$).

**Synthesis of Dodeca-5,7-diyn-1-ol (3a)**. Following the procedure for the synthesis of **3b**, we obtained **3a** (186 mg, 5%) as a pale yellow oil from **1a** (2.1 mL, 19 mmol) and **2a** (3.08 g, 19.2 mmol). $^1$H NMR (400 MHz, $CDCl_3$, 30 °C) δ 3.67 (dt, $J$ = 4.9 Hz, 4.9 Hz, 2H), 2.31 (t, $J$ = 6.8 Hz, 2H), 2.25 (t, $J$ = 6.8 Hz, 2H), 1.74–1.36 (m, 8H), 1.28 (br, 1H), 0.88 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 30 °C) δ 77.8, 76.9, 65.7, 65.2, 62.4, 31.8, 30.4, 24.7, 22.0, 19.1, 18.9, 13.6; IR (neat) 3363, 2934, 2870, 2256, 2165, 1456, 1429, 1322, 1061 cm$^{-1}$; HRMS (EI) *m/z* calcd for $C_{12}H_{18}O$: 178.1358, found: 178.1354 ($M^+$).

**Synthesis of Heptadeca-8,10-diyn-1-ol (3c)**. Following the procedure for the synthesis of **3b**, we obtained **3c** (8.75 g, 68%) as a pale yellow oil from **1c** (7.31 g, 52.1 mmol) and **2c** (10.1 g, 53.4 mmol). $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.64 (br, 2H), 2.29–2.20 (m, 4H), 1.63–1.23 (m, 18H), 1.19 (br, 1H), 0.88 (t, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 77.7, 77.3, 65.4, 65.2, 62.9, 32.6, 31.7, 28.8, 28.7, 28.6, 28.4, 28.3, 25.2, 22.6, 19.2, 19.1, 14.0; IR (neat) 3360, 2931, 2856, 2256, 2160, 1456, 1427, 1055, 724 cm$^{-1}$; HRMS (EI) *m/z* calcd for $C_{17}H_{28}O$: 248.2140, found: 248.2141 ($M^+$).

**Synthesis of Tetracosa-11,13-diyn-1-ol (3d)**. Following the procedure for the synthesis of **3b**, we obtained **3d** (14.8 g, 68%) as a white solid from **1d** (11.5 g, 63.3 mmol) and **2d** (16.8 g, 68.5 mmol). mp 49–50 °C; $^{1}$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.63 (t, $J$ = 6.3 Hz, 2H), 2.27–2.18 (m, 4H), 1.61–1.12 (m, 33H), 0.88 (t, $J$ = 5.7 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 30 °C) δ 77.6, 77.5, 65.29, 65.26, 63.1, 32.8, 31.9, 29.54, 29.50, 29.46, 29.37, 29.28, 29.1, 29.0, 28.84, 28.81, 28.4, 28.3, 25.7, 22.7, 19.2, 14.1; IR (KBr) 3434, 3383, 2920, 2850, 2181, 2140, 1470, 1061, 718 cm$^{-1}$; Anal. calcd for $C_{24}H_{42}O$: C, 83.17; H, 12.21; found: C, 83.60; H, 12.62.

**Synthesis of Pentacosa-12,14-diyn-1-ol (3e)**. Following the procedure for the synthesis of **3b**, compound **3e** (5.72 g, 48%) was obtained as a white solid from **1e** (6.52 g, 33.2 mmol) and **2e** (8.96 g, 36.5 mmol). mp 58–59 °C; $^{1}$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.63 (t, $J$ = 6.6 Hz, 2H), 2.27–2.18 (m, 4H), 1.61–1.18 (m, 35H), 0.87 (t, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 77.53, 77.49, 65.27, 65.26, 63.1, 32.8, 31.9, 29.53, 29.48, 29.45, 29.41, 29.38, 29.28, 29.07, 29.05, 28.83, 28.82, 28.34, 25.7, 22.6, 19.2, 14.1; IR (KBr) 3417, 3352, 2956, 2918, 2849, 2176, 2141, 1469, 1064, 720 cm$^{-1}$; Anal. calcd for $C_{25}H_{25}O$: C, 83.27; H, 12.30; found: C, 83.28; H, 12.76.

**Synthesis of Dotriaconta-15,17-diyn-1-ol (3f)**. Following the procedure for the synthesis of **3b**, we obtained **3f** (335 mg, 73%) as a white solid from **1f** (238 mg, 1.00 mmol) and **2f** (362 mg, 1.20 mmol). mp 69.2–70.5 °C; $^{1}$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 3.62 (t, $J$ = 6.6 Hz, 2H), 2.22 (t, $J$ = 6.6 Hz, 4H), 1.60–1.14 (m, 49H), 0.87 (t, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 77.5, 65.3, 32.9, 32.0, 29.74, 29.72, 29.70, 29.67, 29.53, 29.49, 29.40, 29.2, 28.9, 28.4, 25.8, 22.8, 19.3, 14.2; IR (KBr) 3437, 3391, 2919, 2850, 2179, 2142, 1471, 1057, 717 cm$^{-1}$; HRMS (FAB) *m/z* calcd for $C_{32}H_{58}O$:458.4488, found: 458.4468 ($M^+$).

**Synthesis of Tritriaconta-16,18-diyn-1-ol (3g)**. Following the procedure for the synthesis of **3b**, we obtained **3g** (454 mg, 60%) as a white solid from **1g** (407 mg, 1.61 mmol) and **2g** (583 mg, 1.93 mmol). mp 73.9–75.0 °C; $^{1}$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 3.63 (t, $J$ = 6.6 Hz, 2H), 2.23 (t, $J$ =

6.6 Hz, 4H), 1.64–1.14 (m, 51H), 0.89 (t, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 77.5, 65.5, 63.1, 33.0, 29.74, 29.72, 29.70, 29.67, 29.66, 29.5, 29.4, 29.2, 28.9, 28.5, 22.7, 19.3, 14.1; IR (KBr) 3418, 3350, 2954, 2918, 2849, 2176, 2141, 1470, 1061, 718 cm$^{-1}$; HRMS (EI) *m/z* calcd for $C_{33}H_{60}O$: 472.4644, found: 472.4664 ($M^+$).

**8-3. Syntheses of 1-Bromoalkadiynes.**

**Synthesis of 1-Bromoheptadeca-7,9-diyne (4b)**. Under an argon atmosphere, $PPh_3$ (11.0 g, 41.9 mmol) and *N*-bromosuccinimide (NBS, 6.84 g, 38.4 mmol) were added to a solution of **3b** (8.68 g, 34.9 mmol) in THF (70 mL) at –20 °C. The mixture was stirred at 0 °C for 2 h and then at room temperature for 2 h. To complete the reaction, additional amounts of $PPh_3$ (920 mg, 3.51 mmol) and NBS (1.25 g, 7.02 mmol) were added. After 20 min, MeOH was added to the mixture to terminate the reaction. The solvents were removed under vacuum. The residue was subjected to silica gel column chromatography (hexanes) to afford **4b** (10.5 g, 96%) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.40 (t, $J$ = 6.6 Hz, 2H), 2.31–2.18 (m, 4H), 1.87 (quint, $J$ = 6.9 Hz, 2H), 1.62–1.28 (m, 16H), 0.88 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 77.7, 77.1, 65.5, 65.2, 33.7, 32.6, 31.7, 28.8, 28.7, 28.3, 28.1, 27.9, 27.7, 22.6, 19.2, 19.1, 14.0; IR (neat) 2931, 2857, 2256, 2159, 1463, 1428, 1258, 725 cm$^{-1}$; HRMS (EI) *m/z* calcd for $C_{17}H_{27}{}^{79}Br$: 310.1296, found: 310.1283 ($M^+$).

**Synthesis of 1-Bromododeca-5,7-diyne** (**4a**). Following the procedure for the synthesis of **4b**, compound **9a** (78.0 mg, 38%) was obtained as a colorless oil from **3a** (153 mg, 0.856 mmol). $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.43 (t, $J$ = 6.6 Hz, 2H), 2.34–2.24 (m, 4H), 1.99 (quint, $J$ = 6.6 Hz, 2H), 1.69 (quint, $J$ = 6.6 Hz, 2H), 1.64–1.36 (m, 4H), 0.92 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 78.0, 76.2, 66.1, 65.1, 33.1, 31.7, 30.5, 26.9, 22.1, 19.1, 18.6, 13.7; IR (neat) 2957, 2934, 2863, 2268, 2168, 1456, 1428, 1251, 738 cm$^{-1;}$ HRMS (EI) *m/z* calcd for $C_{12}H_{17}{}^{79}Br$ 240.0514 found 240.0513 ($M^+$).

**Synthesis of 1-Bromoheptadeca-8,10-diyne** (**4c**). Following the procedure for the synthesis of **4b**, we obtained **4c** (15.8 g, 86%) as a yellow oil from **3c** (14.6 g, 58.8 mmol). $^{1}$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.40 (t, $J$ = 6.6 Hz, 2H), 2.28–2.20 (m, 4H), 1.86 (quint, $J$ = 6.6 Hz, 2H), 1.56–1.21 (m, 16H), 0.89 (t, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 77.7, 77.3, 65.4, 65.2, 33.8, 32.7, 31.3 28.6, 28.5, 28.3, 28.2, 28.1, 28.0, 22.5, 19.21, 19.15, 14.0; IR (neat) 2932, 2857, 2256, 2169, 1464, 1427, 1249, 724 cm$^{-1}$; HRMS (EI) *m/z* calcd for $C_{17}H_{27}{}^{81}Br$: 312.1277, found: 312.1268 ($M^+$).

**Synthesis of 1-Bromotetracosa-11,13-diyne (4d)**. Following the procedure for the synthesis of **4b**, compound **4d** (13.5 g, 90%) was obtained as a white solid from **3d** (12.7 g, 36.6 mmol). $^{1}$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.40 (t, $J$ = 6.9 Hz, 2H), 2.28–2.20 (m, 4H), 1.85 (quint, $J$ = 6.6 Hz, 2H), 1.77–1.21 (m, 30H), 0.88 (t, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 30 °C) δ 77.5, 77.4, 65.4, 65.3, 33.9, 32.9, 31.9, 29.6, 29.5, 29.38, 29.36, 29.33, 29.13, 29.05, 28.9, 28.83, 28.76, 28.42, 28.38, 28.2, 19.3; IR (neat) 2929, 2853, 2256, 2160, 1464, 1254, 722 cm$^{-1}$; Anal. calcd. for $C_{24}H_{41}Br$: C, 70.39; H, 10.09; found: C, 70.66; H, 10.46.

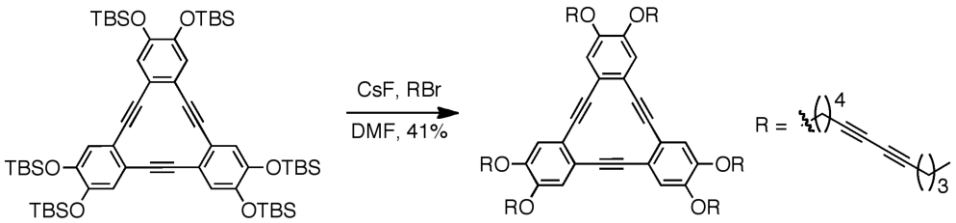
**Synthesis of 1-Bromopentacosa-12,14-diyne (4e)**. Following the procedure for the synthesis of **4b**, we obtained **4e** (5.80 g, 90%) as a white solid from **3e** (5.50 g, 13.2 mmol). $^{1}$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 3.41 (t, $J$ = 6.9 Hz, 2H), 2.28–2.20 (m, 4H), 1.86 (quint, $J$ = 6.6 Hz, 2H), 1.64–1.18 (m, 32H), 0.88 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 30 °C) δ 77.5, 77.4, 65.34, 65.31, 39.9, 32.9, 31.9, 29.6, 29.52, 29.49, 29.43, 29.3, 29.14, 29.10, 28.90, 28.86, 28.79, 28.43, 28.40, 28.2, 22.7, 19.3, 14.1; IR (neat) 2925, 2854, 2680, 2257, 2160, 1464, 1252, 721 cm$^{-1}$; Anal. calcd. for $C_{25}H_{43}{}^{79}Br$: C, 70.90; H, 10.23; found: C, 70.75; H, 10.48.

**Synthesis of 1-Bromodotriaconta-15,17-diyne (4f)**. Following the procedure for the synthesis of **4b**, we obtained compound **4f** (255 mg, 94%) as a white solid from **3f** (238 mg, 519 μmol). mp 50.0–50.4 °C; $^{1}$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 3.40 (t, $J$ = 6.9 Hz, 2H), 2.24 (t, $J$ = 6.9 Hz, 4H),

1.85 (quint, $J$ = 6.6 Hz, 2H), 1.58–1.14 (m, 46H), 0.88 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ77.5, 65.3, 33.9, 32.9, 32.0, 29.8, 29.74, 29.72, 29.65, 29.60, 29.55, 29.53, 29.51, 29.4, 29.2, 28.9, 28.8, 28.5, 28.3, 22.8, 19.3, 14.2; IR (KBr) 2956, 2920, 2849, 1469, 720 $cm^{-1}$; HRMS (EI) *m/z* calcd for $C_{32}H_{57}{}^{79}Br$: 520.3644, found: 520.3657 ($M^+$).

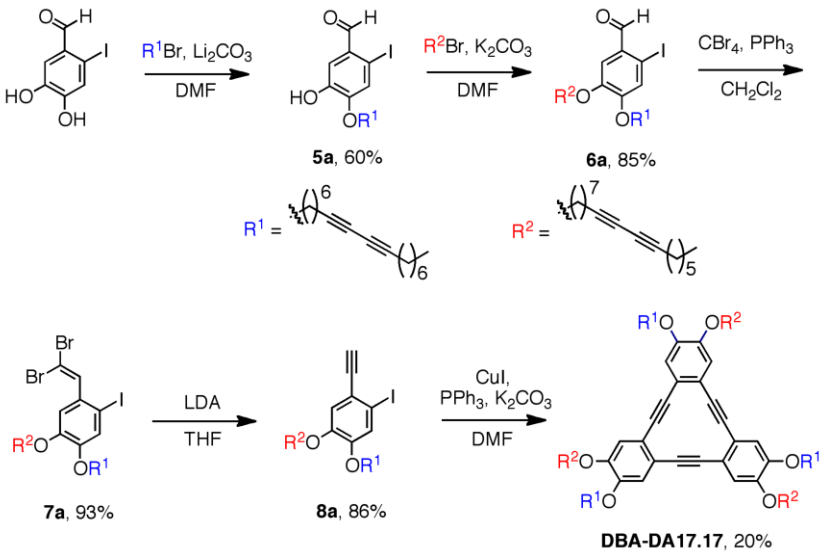
**Synthesis of 1-Bromotritriaconta-16,18-diyne (4g)**. Following the procedure for the synthesis of **4b**, compound **4g** (129 mg, 96%) was obtained as white solid from **3g** (118 mg, 250 μmol). mp 50.6–51.8 °C; $^1$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 3.40 (t, $J$ = 6.9 Hz, 2H), 2.24 (t, $J$ = 6.9 Hz, 4H), 1.85 (quint, $J$ = 6.6 Hz, 2H), 1.57–1.19 (m, 48H), 0.88 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 77.5, 65.3, 33.9, 32.9, 32.0, 29.8, 29.74, 29.72, 29.69, 29.67, 29.61, 29.54, 29.51, 29.4, 29.2, 28.93, 28.85, 28.5, 28.3, 22.8, 19.3, 14.2; IR (KBr) 2918, 2849, 2173, 2141, 1470, 1219, 718 $cm^{-1}$; HRMS (EI) *m/z* calcd for $C_{33}H_{59}{}^{79}Br$: 534.3800, found: 534.3813 ($M^+$).

**8-4. Synthesis of DBA-DA12.12.**




**Synthesis of Hexakis(dodeca-5,7-diynyloxy)hexadehydrotribenzo[12]annulene (DBA-DA12,12)**. Under a nitrogen atmosphere, CsF (28.5 mg, 188 μmol) and hexakis(*tert*-butyldimethylsilyloxy)hexadehydrotribenzo[12]annulene (23.2 mg, 21.4 μmol)[4] and DMF (1.0 mL) were added to a Schlenk flask. After stirring for 10 min at room temperature, a solution of **4a** (41.2 mg, 171 μmol) in DMF (1.5 mL) was added to the mixture. After stirring for 21 h, water was added to the mixture. The products were extracted with $CH_2Cl_2$, the extract was washed with water and brine, and the organic phase was dried over $MgSO_4$. Purification was performed by the use of silica gel column chromatography (hexane/$CH_2Cl_2$ = 4/1) and recycling HPLC to give **DBA-DA12,12** (11.6 mg, 8.54 μmol, 41%) as a yellow solid. mp 94–95 ºC; $^1$H NMR (300 MHz, $CDCl_3$, 30 ºC) δ 6.71 (s, 6H), 3.98 (t, *J* = 6.2 Hz, 12H), 2.37 (t, *J* = 11.3 Hz, 12H), 2.26 (t, *J* = 11.3 Hz, 12H), 1.94–1.91 (m, 12H), 1.73–1.71 (m, 12H), 0.91 (t, *J* = 7.27 Hz, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 148.9, 120.0, 115.8, 91.9, 77.8, 76.8, 68.4, 65.9, 65.2, 30.5, 28.2, 25.1, 22.0, 19.1, 19.0, 13.6; IR (KBr) 2954, 2934, 2871, 2255, 2206, 2170, 1592, 1513, 1355, 1233, 1069, 859 cm$^{-1}$; MS (LDI): *m/z* = 1356 ($M^+$). HRMS (FAB) *m/z* calcd for $C_{96}H_{109}O_6$: 1357.8224, found: 1357.8202 ($[M+H]^+$).

## 8-5. Synthesis of DBA-DA17.17.




**Synthesis of 4-(Heptadeca-8,10-diynyloxy)-5-hydroxy-2-iodobenzaldehyde (5a)**. 4,5-Dihydroxy-2-iodobenzaldehyde (3.00 g, 10.8 mmol)[5] and $Li_2CO_3$ (1.59 g, 21.5 mmol) were suspended in DMF (50 mL) at 45 °C for 30 min under an argon atmosphere. To this mixture, compound **4b** (5.05 g, 16.2 mmol) was added dropwise. After stirring at 60 °C for 21 h, the reaction was quenched by addition of an aqueous solution of HCl (1 N). The products were extracted with $CH_2Cl_2$, the organic phase was washed with water and brine, and the organic phase was dried over $MgSO_4$. After evaporation of the solvents, the residue was subjected to silica gel column chromatography (hexane/$CHCl_3$/acetone, from 1/0/0 to 6/3.5/0.5) to give **5a** (3.20 g, 6.48 mmol) as a white solid. mp 84–85 ºC; $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 9.86 (s, 1H), 7.48 (s, 1H), 7.30 (s, 1H), 5.63 (s, 1H), 4.12 (t, $J$ = 6.5 Hz, 2H), 2.31–2.22 (m, 4H), 1.87 (m, 2H), 1.48–1.34 (m, 16H), 0.88 (t, 6.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 194.6, 151.5, 146.4, 128.9, 122.1, 115.3, 90.3, 77.87, 76.93, 69.6, 65.7, 65.1, 31.7, 28.82, 28.79, 28.75, 28.4, 28.3, 28.1, 25.4, 22.6, 19.2, 19.1, 14.1; IR (KBr) 3230, 2932, 2853, 2254, 2175, 1666, 1598, 1497, 1469, 1278, 1156, 1007 cm$^{-1}$; Anal. calcd. for $C_{24}H_{31}O_3I$: C, 58.30; H, 6.32; found: C, 57.97; H, 6.19.

**Synthesis of 5-(Heptadeca-7,9-diynyloxy)-4-(heptadeca-8,10-diynyloxy)-2-iodobenzaldehyde (6a)**. To a suspension of **5a** (3.06 g, 6.19 mmol) and $K_2CO_3$ (1.28 g, 9.28 mmol) in DMF (10 mL), compound **4d** (2.89 g, 9.28 mmol) was added dropwise under an argon atmosphere. The mixture was stirred at 60 °C for 1 d. To this mixture, water was added to terminate the reaction. The products were extracted with ether, the extract was washed with water and brine. The organic phase was dried over $MgSO_4$. After evaporation of the solvents under vacuum, the product was separated by silica gel column chromatography (hexane/$CHCl_3$, from 1/0 to 1/1) to afford **6a** (3.80 g, 85%) as a white solid. mp 37–38 ºC; $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 9.84 (s, 1H), 7.34 (s, 1H), 7.23 (s, 1H), 4.00–3.96 (m, 4H), 2.21–2.18 (m, 8H), 1.78–1.75 (m, 4H), 1.48–1.34 (m, 32H), 0.84–0.82 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 194.9, 154.6, 149.5, 128.2, 123.0, 112.7, 92.5, 77.69, 77.56, 77.31, 77.08, 69.3, 69.0, 65.5, 65.4, 65.3, 65.2, 31.7, 31.3, 28.9, 28.80, 28.76, 28.73, 28.70, 28.5, 28.4, 28.34, 28.31, 28.25, 28.17, 25.8, 25.4, 22.6, 22.5, 19.19, 19.18, 19.09, 14.03, 14.00; IR (KBr) 3065, 2932, 2852, 2754, 2258, 2180, 2143, 1678, 1581, 1494, 1460, 1269, 1148 $cm^{-1}$; Anal. calcd for $C_{41}H_{58}O_3I$: C, 67.94; H, 7.93; found: C, 68.00; H, 7.75.

**Synthesis of 1-(2,2-Dibromoethenyl)-5-(heptadeca-7,9-diynyloxy)-4-(heptadeca-8,10-diynyloxy)-2-iodobenzene (7a)**. Under an argon atmosphere, a solution of $PPh_3$ (4.69 g, 17.9 mmol) in $CH_2Cl_2$ (10 mL) was added to a solution of $CBr_4$ (2.07 g, 8.94 mmol) in $CH_2Cl_2$ (20 mL) at 0 °C. After stirring at 0 °C for 15 min, a solution of **6a** (3.24 g, 4.47 mmol) in $CH_2Cl_2$ (10 mL) was added to the mixture. The mixture was stirred for 3 h. Water was added to the reaction mixture, the products were extracted with $CH_2Cl_2$, and the extract was dried over $MgSO_4$. After evaporation of the solvents under vacuum, the residue was subjected to silica gel column chromatography (hexane/$CH_2Cl_2$, from 4/1 to 2/1) to afford **7a** (3.65 g, 4.14 mmol) as a white solid. mp 27–28 ºC; $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 7.35 (s, 1H), 7.24 (s, 1H), 7.10 (s, 1H), 3.97 (m, 4H), 2.29–2.22 (m, 8H), 1.79 (m, 4H), 1.48–1.34 (m, 32H), 0.88 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 149.8,

148.8, 140.6, 131.9, 123.1, 114.9, 91.7, 87.4, 77.67, 77.59, 77.32, 77.17, 69.3, 69.2, 65.5, 65.4, 65.3, 65.2, 31.7, 31.3, 29.0, 28.9, 28.8, 28.7, 28.52, 28.46, 28.35, 28.32, 28.25, 28.23, 25.8, 25.5, 22.6, 22.5, 19.20, 19.18, 19.12, 14.04, 14.01, 14.00, 13.99; IR (KBr) 3013, 2930, 2856, 2577, 2255, 2142, 1589, 1499, 1466, 1259, 1203, 1175, 869 $cm^{-1}$; Anal. calcd for $C_{42}H_{57}O_2Br_2I$: C, 57.28; H, 6.52; found: C, 57.66; H, 6.52.

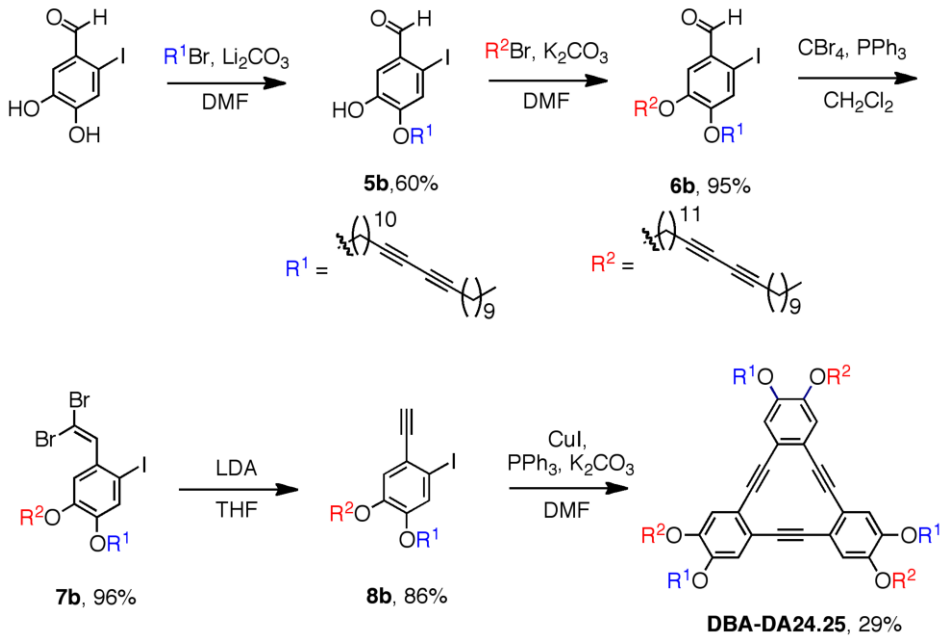
**Synthesis of 1-Ethynyl-5-(heptadeca-7,9-diynyloxy)-4-(heptadeca-8,10-diynyloxy)-2-iodobenzene (8a)**. Under an argon atmosphere, *n*-BuLi (1.65 M in hexane, 12.9 mL, 21.3 mmol) was added dropwise to a solution of $^{i}Pr_2NH$ (3.0 mL, 21.4 mmol) in THF (56 mL) at –78 °C. The mixture was stirred at 0 °C for 40 min, and then it was used as a solution of lithium diisopropylamide (LDA, 0.30 M in THF/hexane).

To a solution of **7a** (2.64 g, 3.00 mmol) in THF (60 mL) at –78 °C, LDA (0.30 M, 30 mL, 9.0 mmol) was added dropwise. After stirring for 1 h, reaction was quenched by addition of saturated aqueous solution of $NH_4Cl$. The products were extracted with $CHCl_3$, and the organic phase was dried over $MgSO_4$. After evaporation of the solvents under vacuum, purification was performed by the use of silica gel column chromatography (hexane/$CHCl_3$, from 2.5/1 to 2/1) to give **8a** (1.87 g, 86%) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 7.21 (s, 1H), 6.98 (s, 1H), 3.98–3.92 (m, 4H), 3.28 (s, 1H), 2.29–2.22 (m, 8H), 1.83–1.75 (m, 4H), 1.55–1.28 (m, 32H), 0.91–0.86 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 150.3, 148.8, 122.9, 120.7, 117.7, 89.6, 85.4, 77.6, 77.5, 77.2, 77.1, 69.2, 69.1, 65.5, 65.4, 65.24, 65.19, 31.6, 31.2, 29.0, 28.82, 28.76, 28.73, 28.70, 28.5, 28.4, 28.31, 28.28, 28.21, 28.17, 25.8, 25.4, 22.5, 22.4, 19.2, 19.1, 14.00, 13.97; IR (KBr) 3013, 2930, 2856, 2577, 2256, 2161, 2142, 1587, 1504, 1469, 1253, 1211, 1166, 1021, 856 $cm^{-1}$; Anal. calcd for $C_{42}H_{57}O_2I$: C, 69.98; H, 7.97; found: C, 69.63; H, 8.43.

**Synthesis of Hexakis(heptadiynyloxy)hexadehydrotribenzo[12]annulene (DBA-DA17.17)**. To a solution of **8a** (105 mg, 146 μmol) in DMF (2.0 mL), $PPh_3$ (11.3 mg, 43 μmol), CuI (8.3 mg, 44

μmol), and $K_2CO_3$ (60.5 mg, 438 μmol) were added under an argon atmosphere. After stirring at 150 °C for 20 h, saturated aqueous solution of $NH_4Cl$ was added to terminate the reaction. The products were extracted with $CHCl_3$, and the organic phase was dried over $MgSO_4$. After evaporation of the solvents under vacuum, the residue was subjected to silica gel column chromatography (hexane/$CH_2Cl_2$, 1/1) and recycling HPLC to afford **DBA-DA17.17** (17 mg, 20%) as a yellow solid. mp 60–61 °C; $^1$H NMR (400 MHz, $CDCl_3$, 30 °C) δ 6.72 (s, 6H), 3.96 (m, 12H), 2.25 (m, 24H), 1.81 (m, 12H), 1.56–1.26 (m, 96H), 0.88 (m, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$, 30 °C) δ 149.12, 149.07, 119.84, 119.80, 115.86, 115.82, 91.9, 77.7, 77.6, 77.4, 77.2, 69.0, 68.9, 65.5, 65.4, 65.26, 65.22, 31.7, 31.3, 29.1, 29.0, 28.83, 28.79, 28.76, 28.54, 28.49, 28.37, 28.34, 28.29, 28.25, 25.9, 25.5, 22.6, 22.5, 19.2, 19.1, 14.05, 14.02; IR (KBr) 3084, 2934, 2858, 2258, 2206, 2157, 1591, 1510, 1471, 1354, 1229, 1070, 1007, 863 cm$^{-1}$; MS (LDI): *m/z* = 1778 ($M^+$). HRMS (ESI) *m/z* calcd for $C_{126}H_{168}O_6Na_1$: 1800.2739, found: 1800.2757 ($[M+Na]^+$).

**8-6. Synthesis of DBA-DA24,25.**




**Synthesis of 5-Hydroxy-2-iodo-4-(tetracosa-11,13-diynyloxy)benzaldehyde (5b)**. Under an argon atmosphere, a mixture of 4,5-dihydroxy-2-iodobenzaldehyde (110 mg, 396 μmol),[5] $Li_2CO_3$ (43.9 mg,

594 μmol) and DMF (2 mL) was stirred at 45 °C for 1 h. A solution of **4d** (243 mg, 594 μmol) in DMF (0.5 mL) was added to the mixture. After stirring for 1 d, the reaction was quenched by addition of saturated aqueous solution of $NH_4Cl$. The products were extracted with $CHCl_3$, and the organic phase was dried over $MgSO_4$. The solvents were removed under vacuum. Purification was performed by silica gel column chromatography (hexane/$CHCl_3$/acetone, 15/4/1) to afford **5b** (141 mg, 60%) as a white solid. mp 81–82 ºC; $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 9.86 (s, 1H), 7.47 (s, 1H), 7.29 (s, 1H), 5.68 (s, 1H), 4.11 (t, $J$ = 6.6 Hz, 2H), 2.28–2.20 (m, 4H), 1.85 (quint, $J$ = 6.6 Hz, 2H), 1.60–1.18 (m, 30H), 0.88 (t, 6.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 194.6, 151.6, 146.4, 128.9, 122.1, 115.2, 90.3, 77.6, 69.7, 65.33, 65.25, 31.9, 29.53, 29.45, 29.37, 29.31, 29.2, 29.07, 29.00, 28.9, 28.83, 28.81, 28.76, 28.34, 28.30, 25.8, 22.6, 19.2, 14.1; IR (KBr) 3384, 3068, 2921, 2849, 2181, 2141, 1686, 1496, 1464, 1268, 1147 cm$^{-1}$; Anal. calcd. for $C_{31}H_{45}O_3I$: C, 62.83; H, 7.65; found: C, 62.82; H, 8.00.

**Synthesis of 2-Iodo-5-(pentacosa-12,14-diynyloxy)-4-(tetracosa-11,13-diynyloxy)benzaldehyde (6b)**. Under an argon atmosphere, compound **4e** (4.06 g, 9.59 mmol) was added to a mixture of **5b** (3.79 g, 6.40 mmol), $K_2CO_3$ (1.77 g, 12.8 mmol), and DMF (35 mL). After stirring at 60 °C for 20 h, the reaction was quenched by addition of saturated aqueous solution of $NH_4Cl$. The products were extracted with $CHCl_3$, and the organic phase was dried over $MgSO_4$. Purification was performed by the use of silica gel column chromatography (hexane/$CHCl_3$, from 1/0 to 0/1) to afford **6b** (5.70 g, 95%) as a white solid. mp 52–53 ºC; $^1$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 9.84 (s, 1H), 7.39 (s, 1H), 7.28 (s, 1H), 4.08–3.98 (m, 4H), 2.27–2.18 (m, 8H), 1.89–1.76 (m, 4H), 1.59–1.12 (m, 62H), 0.92–0.82 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 194.9, 154.7, 149.6, 128.1, 123.0, 112.8, 92.5, 77.53, 77.50, 77.46, 77.42, 69.4, 69.1, 65.33, 65.28, 65.26, 31.9, 29.53, 29.50, 29.45, 29.34, 29.28, 29.27, 29.21, 29.08, 29.06, 28.9, 28.83, 28.81, 28.3, 25.9, 25.8, 22.6, 19.2, 14.1; IR (KBr)

2918, 2850, 2257, 2143, 1677, 1582, 1503, 1469, 1270, 1166, 1013 $cm^{-1}$; Anal. calcd for $C_{56}H_{87}O_3I$: C, 71.92; H, 9.38; found: C, 68.00; H, 7.75.

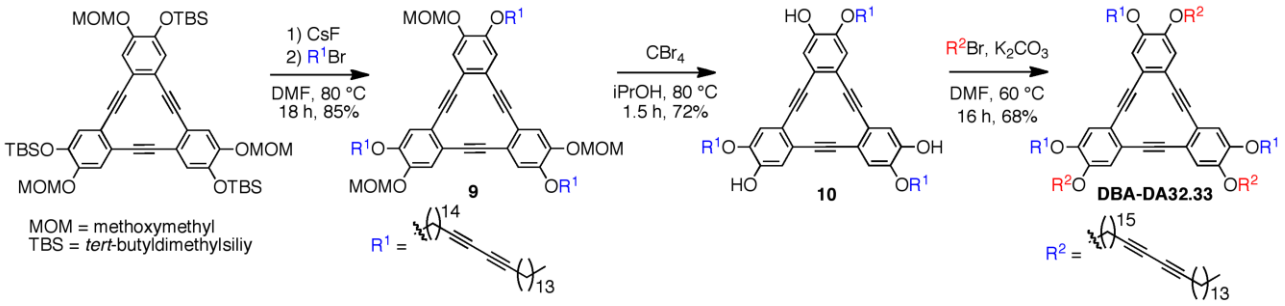
**Synthesis of 1-(2,2-Dibromoethenyl)-2-iodo-5-(pentacosa-12,14-diynyloxy)-4-(tetracosa-11,13-diynyloxy)benzene (7b)**. To a solution of $CBr_4$ (3.55 g, 10.7 mmol) in $CH_2Cl_2$ (23 mL) at 0 °C, a solution of $PPh_3$ (5.61 g, 21.4 mmol) in $CH_2Cl_2$ (14 mL) was added dropwise under an argon atmosphere. After stirring at room temperature for 15 min, the mixture was cooled down to 0 °C. A solution of **6b** (4.55 g, 4.87 mmol) in $CH_2Cl_2$ was added to the mixture. After stirring at room temperature for 3 h, the reaction was terminated by addition of saturated aqueous solution of $NaHCO_3$. The products were extracted with $CHCl_3$, and the organic phase was dried over $MgSO_4$. After evaporation of the solvents, the residue was subjected to silica gel column chromatography (hexane/$CH_2Cl_2$, from 11/2 to 2/1) to give **7b** (5.12 g, 96%) as a white solid. mp 55–56 ºC; $^1$H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.35 (s, 1H), 7.25 (s, 1H), 7.10 (s, 1H), 4.02–3.93 (m, 4H), 2.29–2.20 (m, 8H), 1.87–1.74 (m, 4H), 1.61–1.20 (m, 62H), 0.93–0.84 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 149.9, 148.9, 140.6, 131.9, 123.1, 115.0, 91.7, 87.4, 77.56, 77.55, 77.50, 77.47, 69.5, 69.4, 65.32 65.30, 65.28, 31.9, 29.55, 29.53, 29.50, 29.47, 29.39, 29.36, 29.29, 29.11, 29.08, 28.9, 28.4, 26.0, 25.9, 22.7, 19.2, 14.1; IR (KBr) 3014, 2951, 2918, 2848, 2176, 2144, 1500, 1468, 1200, 1173, 867 $cm^{-1}$; Anal. calcd for $C_{57}H_{87}Br_2IO_2$: C, 71.92; H, 9.38; found: C, 72.42; H, 9.66.

**Synthesis of 1-Ethynyl-2-iodo-5-(pentacosa-12,14-diynyloxy)-4-(tetracosa-11,13-diynyloxy)benzene (8b)**. To a solution of **7b** (4.48 g, 4.11 mmol) in THF (40 mL), LDA (0.30 M in THF/hexane, 41.1 mL, 12.3 mmol) was added dropwise at –78 °C under an argon atmosphere. After stirring for 40 min, the reaction was quenched by addition of saturated aqueous solution of $NH_4Cl$. The products were extracted with $CHCl_3$, and organic phase was washed with brine and dried over $MgSO_4$. The solvents were removed under vacuum. Purification was performed by the use of silica gel column chromatography (hexane/$CHCl_3$, from 5/1 to 3/1) to give **8b** (3.3 g, 86%) as a white solid.

mp 56–57 °C; $^{1}$H NMR (300 MHz, $CDCl_3$, 30 °C) δ 7.21 (s, 1H), 6.98 (s, 1H), 3.99–3.91 (m, 4H), 3.27 (s, 1H), 2.28–2.16 (m, 8H), 1.85–1.73 (m, 4H), 1.58–1.07 (m, 62H), 0.93–0.82 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, 30 °C) δ 150.4, 148.9, 123.0, 120.7, 117.9, 89.6, 85.5, 79.0, 77.49, 77.45, 69.40, 65.35, 65.33, 31.9, 29.59, 29.56, 29.53, 29.51, 29.43, 29.36, 29.33, 29.13, 29.10, 28.9, 28.4, 25.98, 25.95, 22.7, 19.3, 14.1; IR (KBr) 3284, 2918, 2850, 2255, 2142, 2103, 1586, 1497, 1483, 1254, 1209, 1167, 1016 cm$^{-1}$; Anal. calcd for $C_{57}H_{87}O_2I$: C, 73.52; H, 9.42; found: C, 73.46; H, 9.53.

**Synthesis of Tris(pentacosa-12,14-diynyloxy)tris(tetracosa-11,13-diynyloxy)-hexadehydrotribenzo[12]annulene (DBA-DA24,25)**. Under an argon atmosphere, a mixture of **8b** (500 mg, 549 μmol), $PPh_3$ (44.7 mg, 170 μmol), CuI (31.8 mg, 167 μmol), $K_2CO_3$ (237 mg, 17.1 mmol), and DMF (5 mL) were stirred at 160 °C for 22 h. Saturated aqueous solution of $NH_4Cl$ was added. The products were extracted with $CHCl_3$, and the extract was dried over $MgSO_4$. After evaporation of the solvents, the residue was subjected to silica gel column chromatography (hexane/$CH_2Cl_2$, 1/1) and recycling HPLC to afford **DBA-DA24,25** (127 mg, 29%) as a yellow solid. mp 52–53 °C; $^{1}$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 6.72 (s, 6H), 4.01–3.89 (m, 12H), 2.29–2.20 (m, 24H), 1.87–1.73 (m, 12H), 1.61–1.14 (m, 186H), 0.95–0.82 (m, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$, 30 °C) δ 149.1, 119.8, 115.8, 91.8, 77.5, 77.40, 69.0, 65.32, 65.29, 65.27, 31.9, 29.53, 29.50, 29.44, 29.38, 29.34, 29.31, 29.27, 29.12, 29.09, 29.06, 28.8, 28.3, 26.0, 22.6, 19.2, 14.1; IR (KBr) 2921, 2851, 2256, 2206, 2162, 1591, 1511, 1447, 1350, 1229, 1073, 856 cm$^{-1}$; MS (LDI): *m/z* = 2409.2 ($[M+H]^+$).

## 8-7. Synthesis of DBA-DA32.33.




**Synthesis of Tris(dotriaconta-15,17-diynloxy)tris(methoxymethoxy)hexadehydrotribenzo-[12]annulene (9).** Under a nitrogen atmosphere, tris(*tert*-butyldimethylsilyloxy)-tris(methoxymethoxy)dehydrobenzo[12]annulene (10.4 mg, 11.9 μmol)[5] and CsF (10.9 mg, 71.6 μmol) were suspended in DMF (1.0 mL) for 30 min. Compound 4f (37.4 μL, 71.6 μmol) was added to the mixture. After stirring at 60 °C for 4 h, water was added to the reaction mixture. The product was extracted with ether, and the extract was dried over $MgSO_4$. After evaporation of the solvents, the mixture was subjected to silica gel column chromatography (hexane/$CH_2Cl_2$, 1/1) to afford 9 (20.7 mg, 94%) as a yellow solid. mp 53.5–54.0 °C; $^1$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 7.02 (s, 3H), 6.77 (s, 3H), 5.19 (s, 6H), 3.99 (t, $J$ = 6.6 Hz, 6H), 3.52 (s, 9H), 2.24 (t, $J$ = 6.6 Hz, 12H), 1.83 (quint, $J$ = 6.6 Hz, 6H), 1.58–1.19 (m, 138H), 0.88 (t, $J$ = 6.3 Hz, 9H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ149.5, 146.7, 121.6, 119.5, 119.4, 115.8, 95.5, 92.0, 91.6, 77.5, 69.1, 65.9, 56.4, 32.0, 29.76, 29.72, 29.68, 29.65, 29.55, 29.4, 29.2, 28.9, 28.5, 26.0, 22.8, 19.3, 14.2; IR (KBr) 2921, 2849, 1593, 1509, 1345, 1228, 1153, 983 cm$^{-1}$; MS (LDI) $m/z$ = 1408 ([M–$C_{32}H_{57}$]$^-$).

**Synthesis of Tris(dotriaconta-15,17-diynloxy)trihydroxyhexadehydrotribenzo[12]annulene (10)**. Under a nitrogen atmosphere, a mixture of **9** (17.8 mg, 9.62 μmol), $CBr_4$ (1.3 mg, 3.9 μmol), and $^i$PrOH (0.5 mL) was stirred at 80 °C for 2 h. The solvent was removed under vacuum, and the residue was subjected to silica gel column chromatography (hexane/$CH_2Cl_2$, 1/1) to give **10** (15.8 mg, 96%) as a yellow solid. mp 85.8–87.8 °C; $^1$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 6.79 (s, 3H), 6.72 (s, 3H),

5.63 (s, 3H), 4.03 (t, $J$ = 6.6 Hz, 6H), 2.24 (t, $J$ = 6.6 Hz, 12H), 1.81 (quint, $J$ = 6.3 Hz, 6H), 1.59–1.15 (m, 138H) 0.88 (t, $J$ = 6.0 Hz, 9H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 145.91, 145.86, 120.3, 119.2, 119.2, 117.1, 114.4, 91.8, 91.2, 77.5, 69.2, 65.3, 32.0, 29.77, 29.75, 29.72, 29.69, 29.64, 29.61, 29.55, 29.49, 29.43, 29.2, 29.0, 28.5, 26.0, 22.8, 19.3, 14.2; IR (KBr) 3494, 2921, 2851, 1509, 1289, 1164, 1061, 875 cm$^{-1}$; MS (LDI): $m/z$ = 1277 ([M–$C_{32}H_{57}$]$^-$).

**Synthesis of Tris(dotriaconta-15,17-diynloxy)tris(tritriaconta-16,18-diynloxy) hexadehydrotribenzo[12]annulene (DBA-DA32.33)**. Under a nitrogen atmosphere, a mixture of **10** (14.3 mg, 8.32 μmol), $K_2CO_3$ (6.9 mg, 50 μmol), **4g** (26.8 mg, 50.0 μmol), and DMF (0.5 mL) was stirred at 80 °C for 5 h. The solvent was removed under vacuum. Purification was performed by the use of silica gel column chromatography (hexane/$CH_2Cl_2$, 2/1) to afford **DBA-DA32.33** (16.0 mg, 62%) as a yellow solid. mp 62.2–62.9 °C; $^1$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 6.71 (s, 6H), 3.95 (t, $J$ = 6.6 Hz, 12H), 2.24 (t, $J$ = 6.6 Hz, 24H), 1.80 (quint, $J$ = 6.3 Hz, 12H), 1.61–1.16 (m, 284H) 0.88 (t, $J$ = 6.0 Hz, 18H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 149.1, 120.0, 115.9, 91.8, 77.5, 69.2, 65.3, 32.0, 29.77, 29.75, 29.73, 29.69, 29.59, 29.56, 29.49, 29.44, 29.3, 29.21, 29.19, 28.98, 28.95, 28.49, 28.47, 26.1, 22.8, 19.3, 14.2; IR (KBr) 2921, 2851, 1509, 1468, 1348, 1227 cm$^{-1}$. MS (LDI): $m/z$ = 3081.7 ([M+H]$^+$).

## 9. $^{1}$H and $^{13}$C NMR Spectra of DBA-DAs.

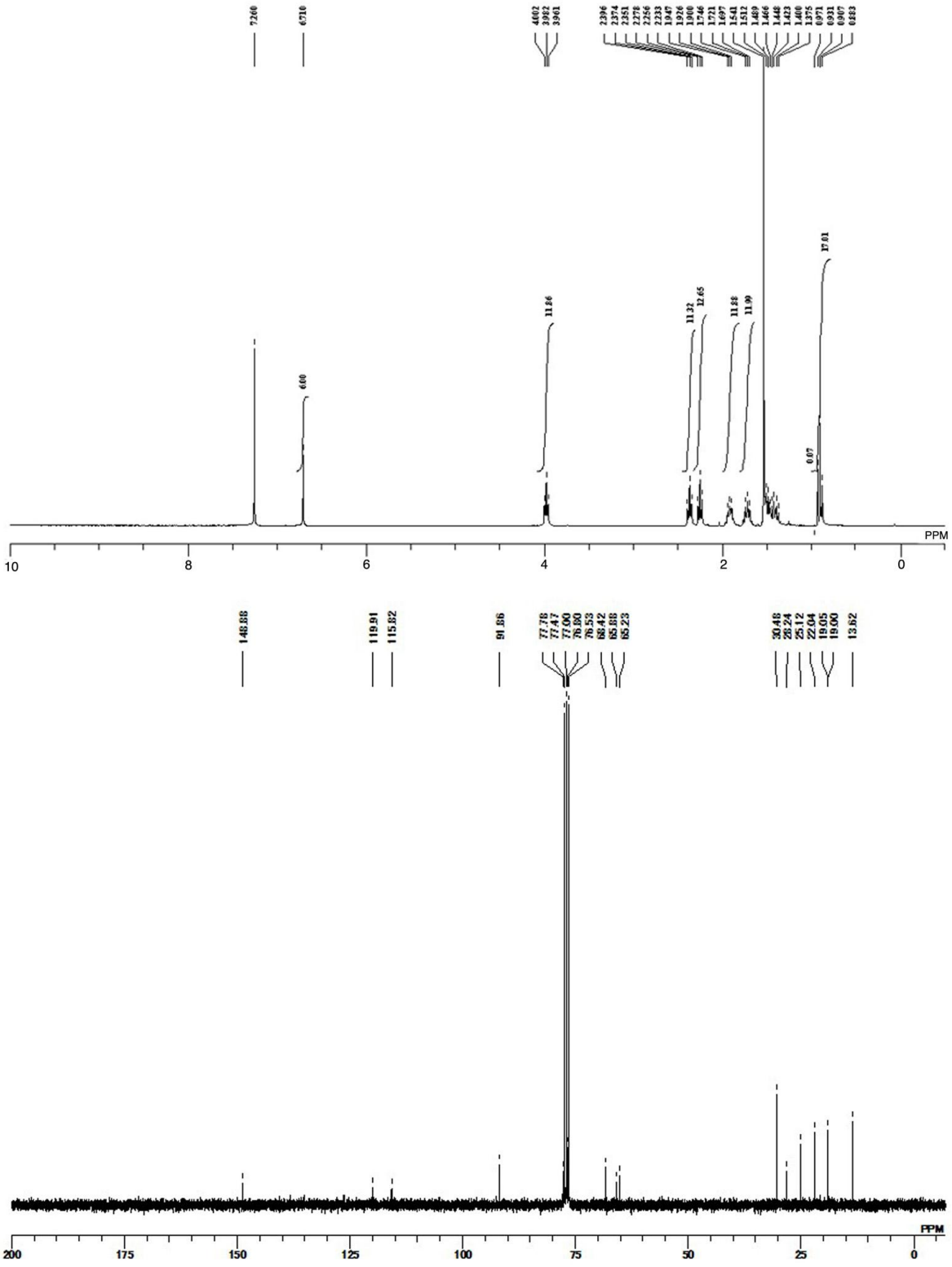



**Fig. S9**. $^{1}$H and $^{13}$C NMR spectra of **DBA-DA12.12** in $CDCl_3$ at 30 °C.

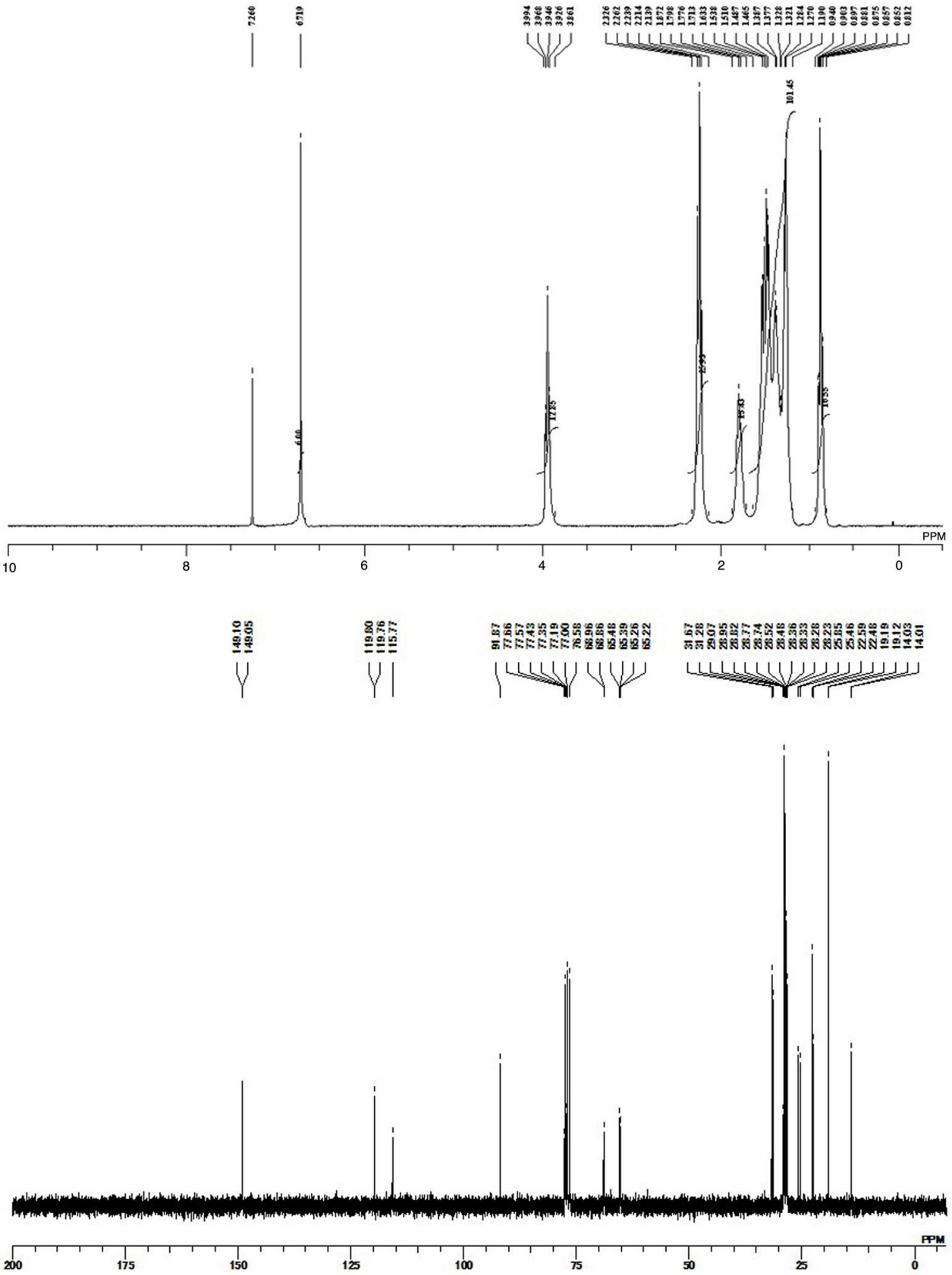



**Fig. S10**. $^{1}H$ and $^{13}C$ NMR spectra of **DBA-DA17.17** in $CDCl_3$ at 30 °C.

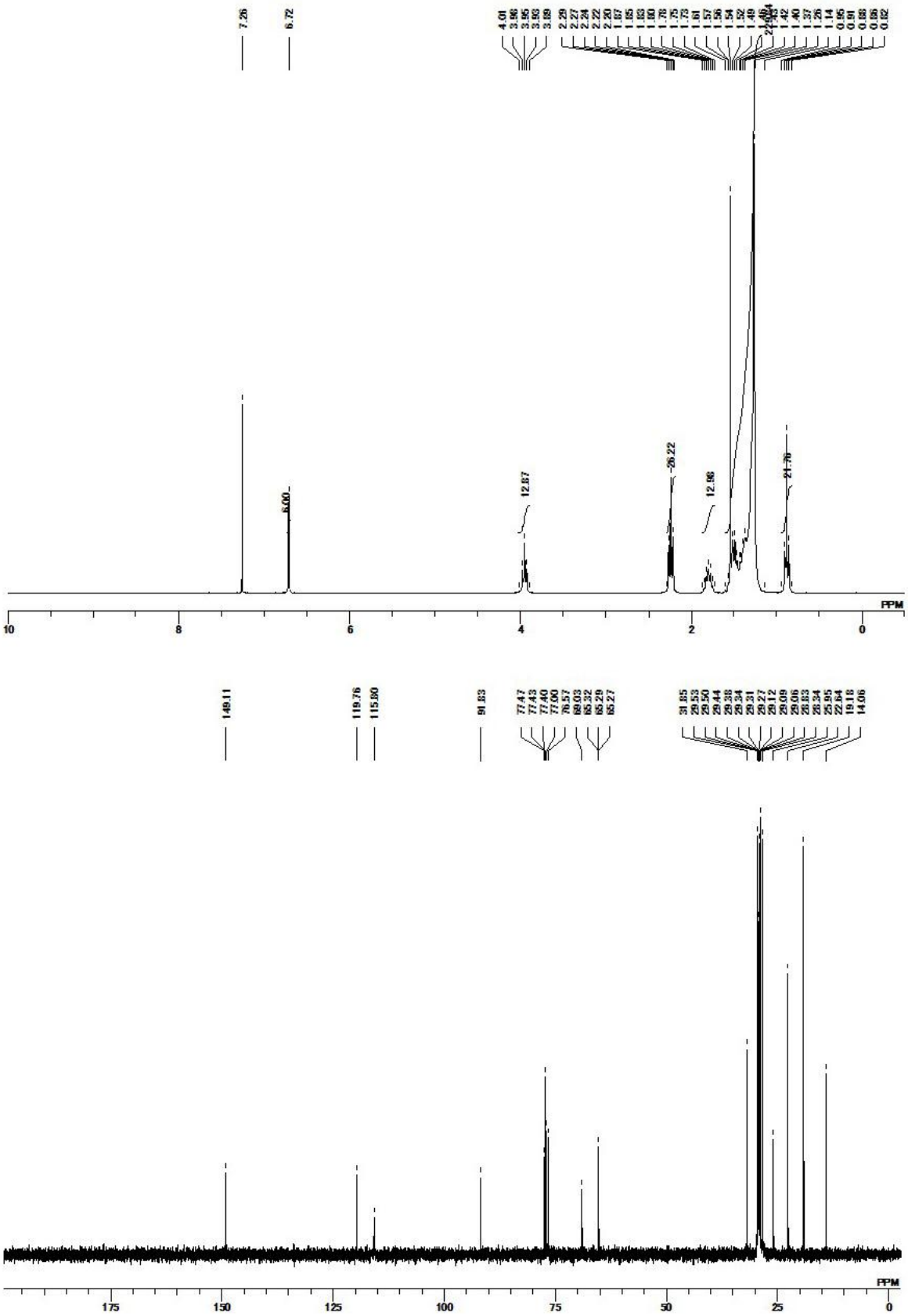



**Fig. S11**. $^{1}H$ and $^{13}C$ NMR spectra of **DBA-DA24.25** in $CDCl_3$ at 30 °C.

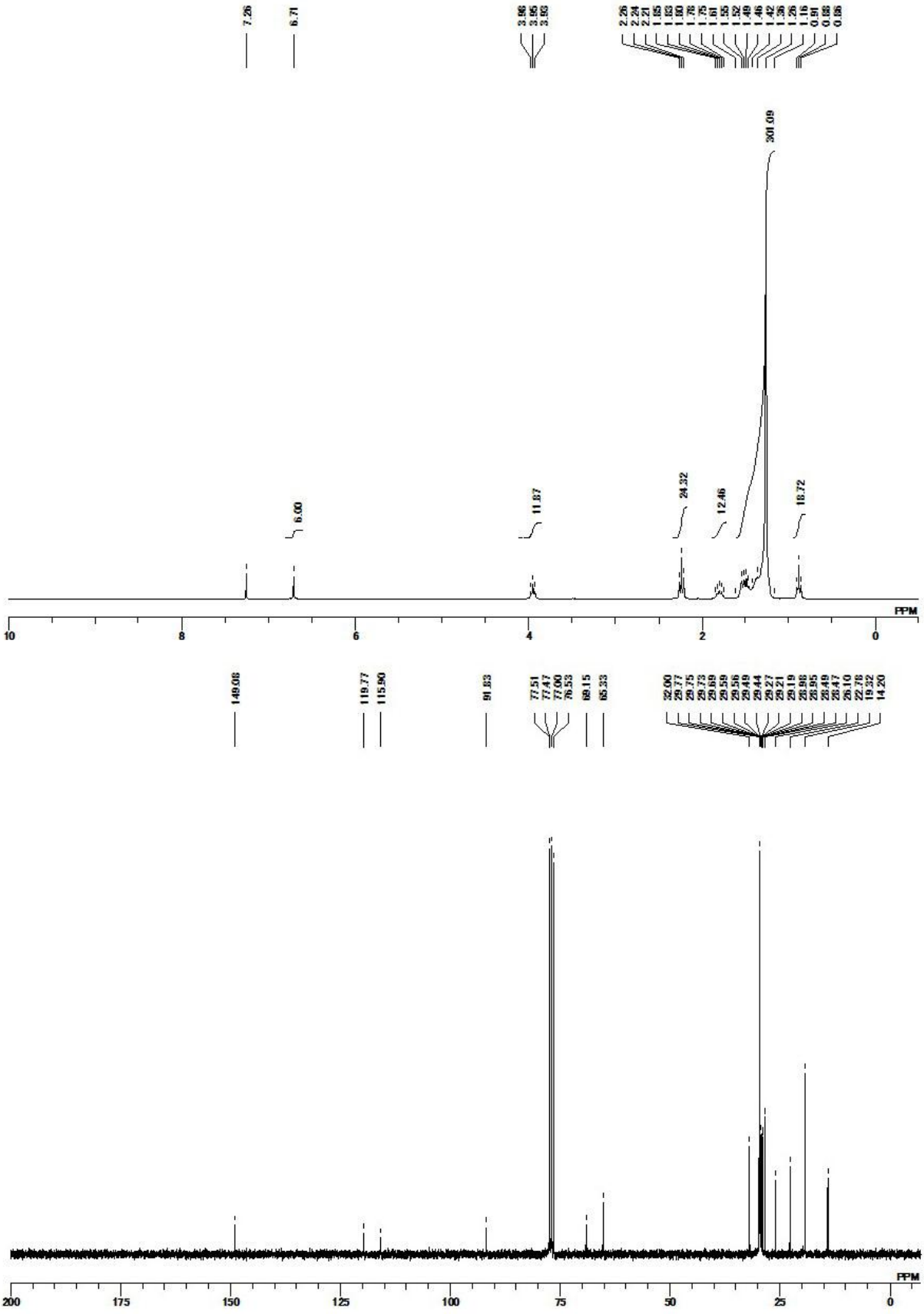



**Fig. S12**. $^{1}H$ and $^{13}C$ NMR spectra of **DBA-DA32.33** in $CDCl_3$ at 30 °C.

## 10. LDI-TOF Mass Spectra of DBA-DAs.

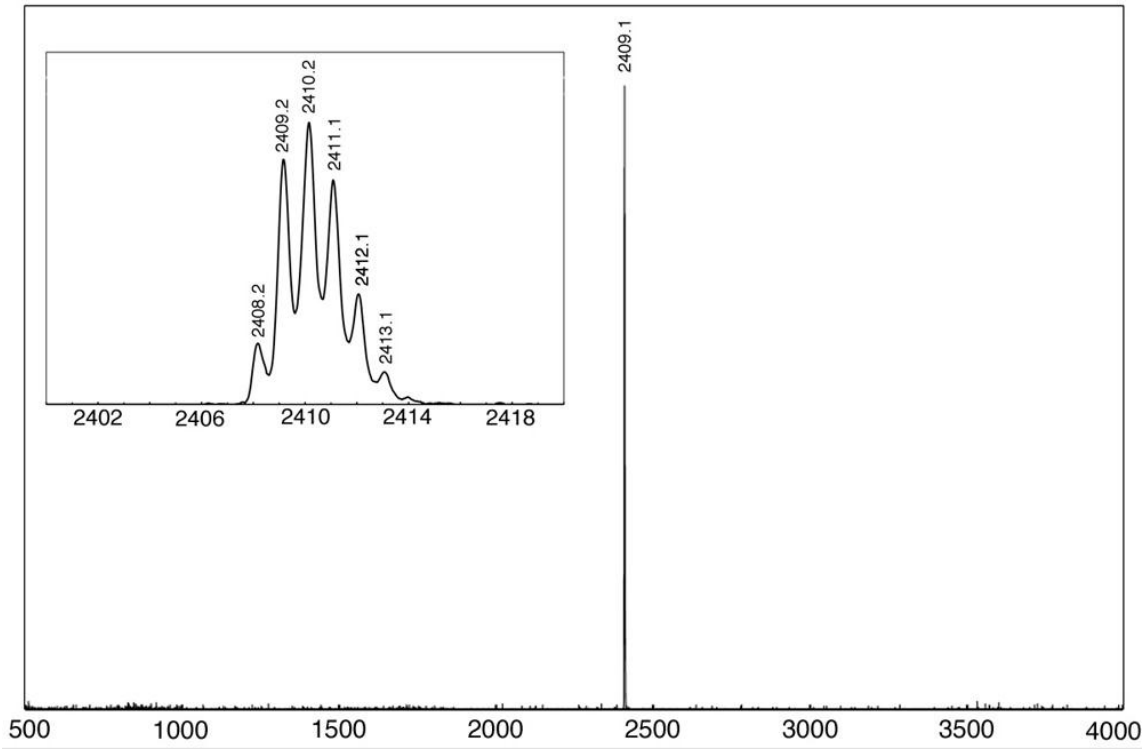



**Fig. S13**. LDI-TOF mass spectrum of **DBA-DA24.25**.

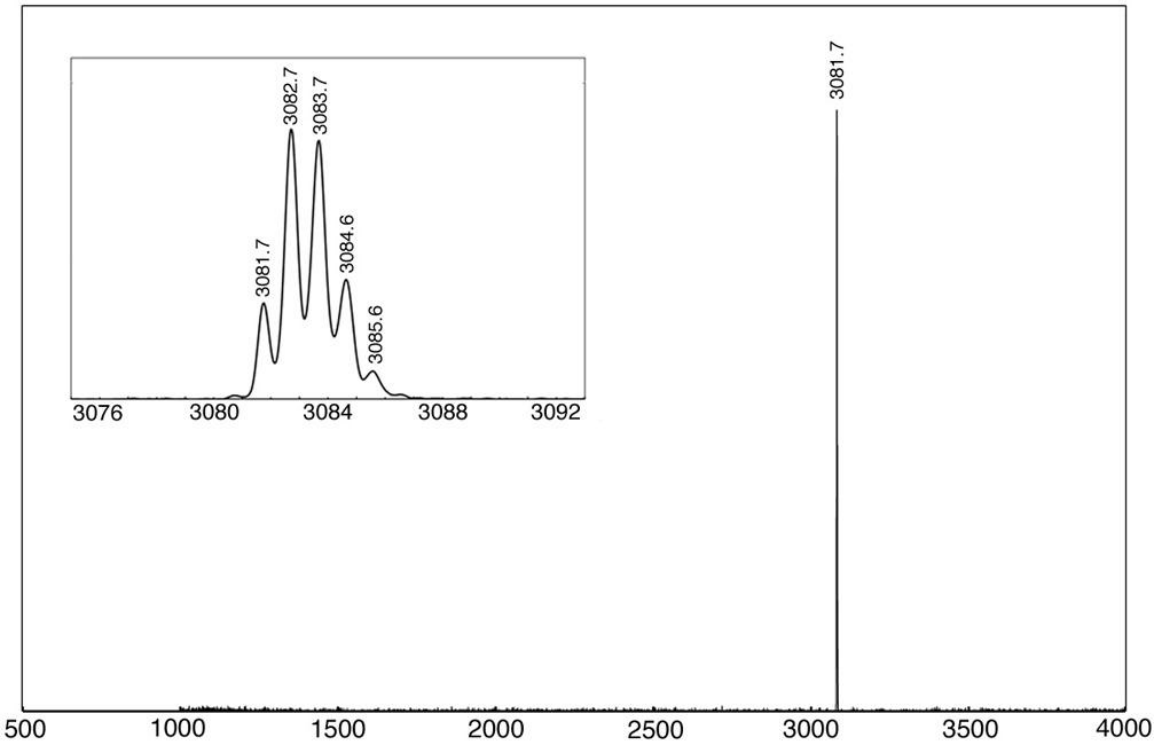



**Fig. S14**. LDI-TOF mass spectrum of **DBA-DA32.33**.

## 11. References

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