

## Construction of cyclic arrays of Zn-porphyrin units and their guest binding at the solid-liquid interface

*Kohei Iritani,<sup>a</sup> Kazukuni Tahara,<sup>a,b</sup> Keiji Hirose,<sup>a</sup> Steven De Feyter<sup>c</sup> and Yoshito Tobe<sup>\*a</sup>*

<sup>a</sup> Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan. <sup>b</sup> Department of Applied Chemistry, School of Science and Technology, Meiji University, Kawasaki, Kanagawa 214-8571, Japan. <sup>c</sup> Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven – University of Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.

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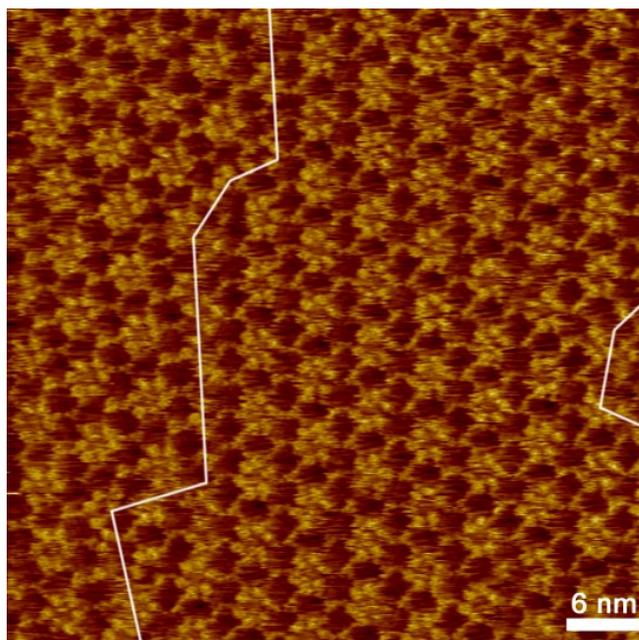
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## 1. Details of STM observations

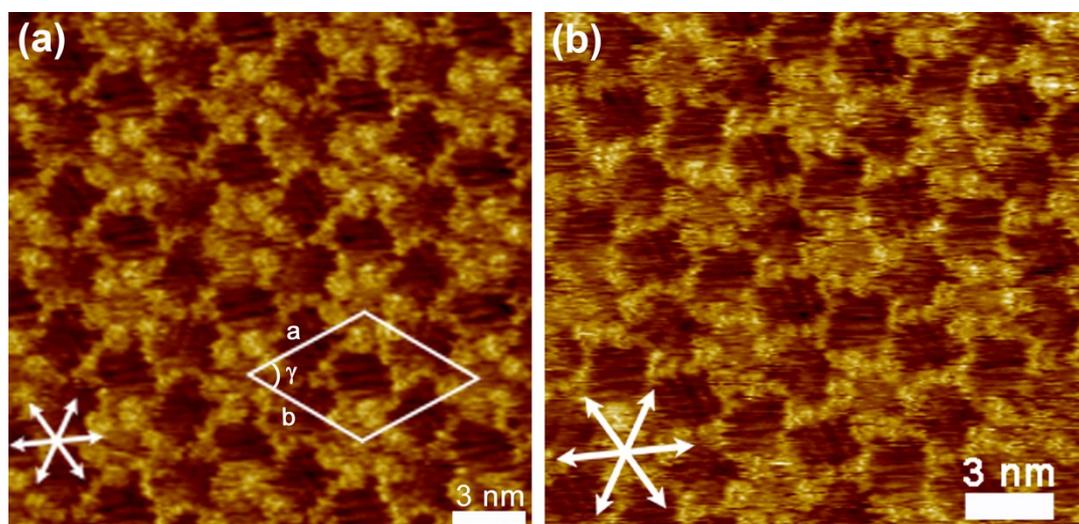
All experiments were performed at 22–27 °C using a Nanoscope IIIa (Digital Instruments Inc.) and a Nanoscope V (Bruker AXS) Multimode microscopes with an external pulse/function generator (Agilent 33220A) at negative sample bias. All STM images were acquired in the constant current mode. Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.25 nm). Prior to imaging, DBA **1** or its mixture of with C<sub>60</sub> was dissolved in commercially available 1,2,4-trichlorobenzene (Aldrich, ≥99%). Concentrations are described in each caption. A drop of this solution (ca. 5 μL) was applied on a freshly cleaved surface of HOPG (grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH). For annealing treatment of a mixture of **1** and a guest molecule, a homemade liquid cell placed on the HOPG substrate was employed to minimize the effect of solvent evaporation using a sample solution of ca. 25–30 μL. The liquid cell was wrapped with an aluminum foil during annealing in an oven. 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 (scanning probe image processor, version 5.0.7. or 6.2.4. (Image Metrology A/S, Hørsholm). The white double headed arrows shown in the figures indicate the directions of the main symmetry axes of graphite underneath the molecular layers.

Statistical analyses of adsorbed/desorbed ZnP units and those complexed/uncomplexed ZnP units with C<sub>60</sub> were performed by using 5 images (typically 30 × 30 nm<sup>2</sup>) at the bias voltage ranging from –100 to –125 mV. Irregular hexagonal structures typically found at domain boundaries were excluded from the analyses. The height profiles, the individual width of which corresponds to one pixel, were measured using the SPIP software. The maximum apparent heights of representative cross sections are shown in Figs. S4, S7b and S8b by blue arrows. The histograms obtained from statistical analyses of the maximum apparent heights were fitted to normal distribution curves, red and green curves in Fig. 3 and Fig. S5b, and orange and gray curves in Fig. 5. Average apparent heights and standard deviations of the normal distribution curve were summarized in Table S1 for Fig. 3, Table S2 for Fig. S5b and Table S3 for Fig. 5, together with the area ratios of the two fitting curves in each histogram.

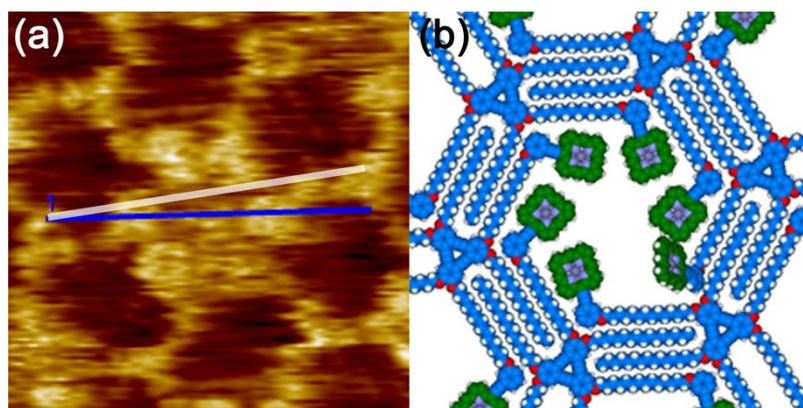
## 2. Additional STM images and height analyses



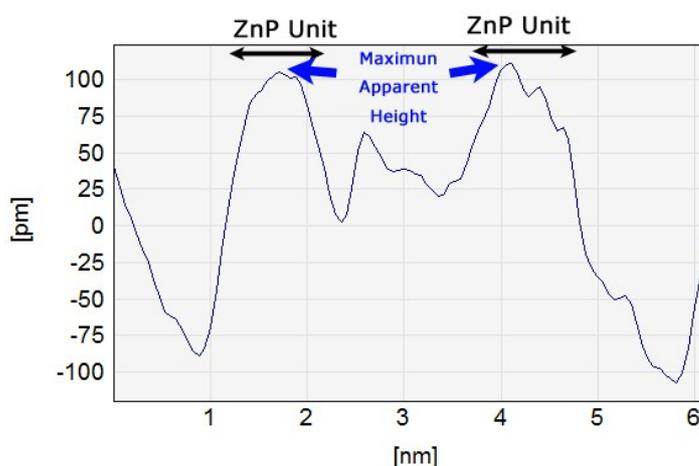
**Fig. S1** STM image of a monolayer formed by **1** at 1,2,4-trichlorobenzene (TCB)/graphite interface ( $5.8 \times 10^{-6}$  M,  $I_{set} = 180$  pA,  $V_{bias} = -120$  mV). The white lines indicate domain boundaries between clockwise (left domain) and anticlockwise (center domain) honeycomb structures.



**Fig. S2** STM images of enantiomeric honeycomb structures of **1** at TCB/graphite interface ( $5.8 \times 10^{-6}$  M,  $I_{set} = 180$  pA,  $V_{bias} = -120$  mV). (a) A domain with anticlockwise structure (the same image as that of Fig. 1) and (b) a clockwise domain.



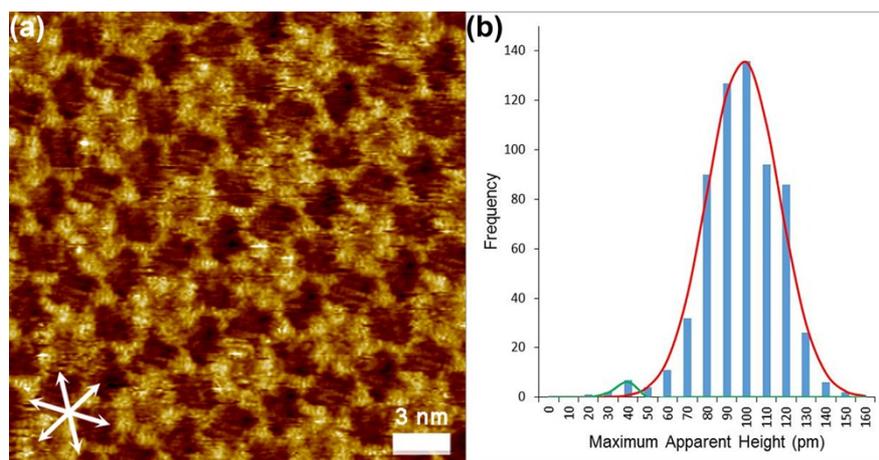
**Fig. S3** (a) Enlarged STM image of the monolayer of **1** at the TCB/graphite interface. The white line indicates the directions of one of the main symmetry axes of graphite underneath the molecular layer. The blue line indicates a representative line for the height profile measurement which is rotated by  $+7^\circ$  with respect to the white line. (b) A tentative molecular model of the honeycomb structure formed by **1**: note that one of the ZnP units is not adsorbed on the surface.



**Fig. S4** A representative apparent height profile along the blue line in Fig. S3.

**Table S1** Average apparent heights and standard deviations of red and green curves in Fig. 3 and their area ratio.

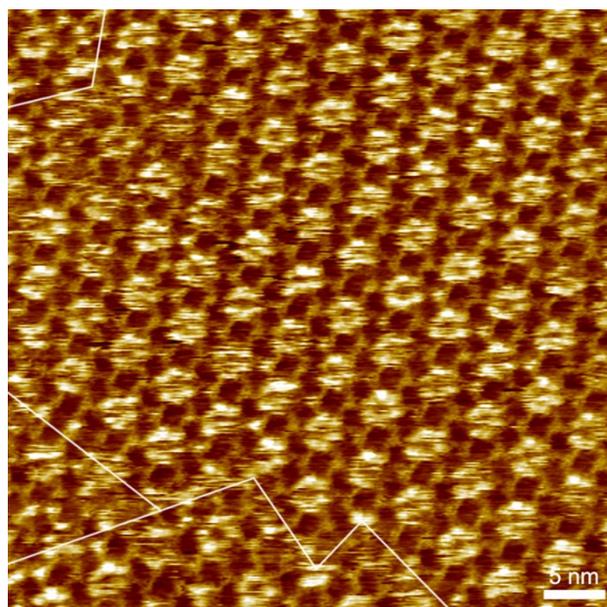
	Average apparent height (pm)	Standard deviation (pm)	Area ratio (Red curve : Green curve)
Red curve	106	19	98 : 2
Green curve	38	17	



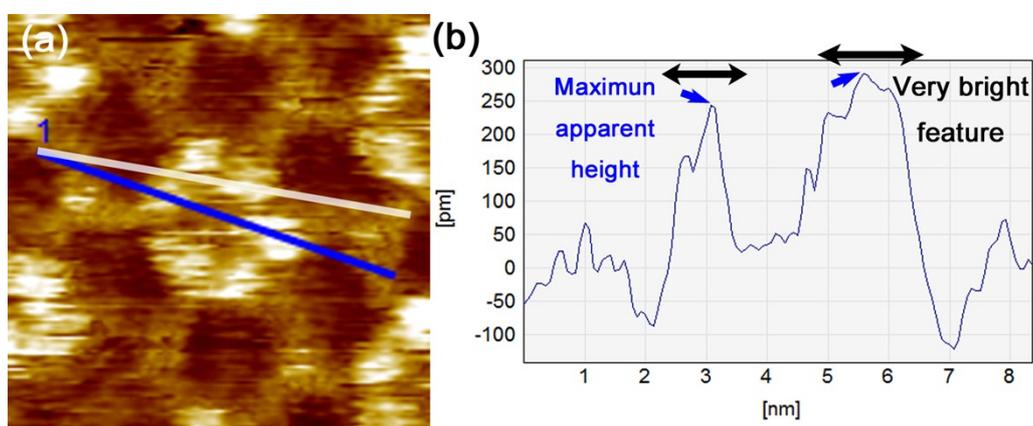
**Fig. S5** (a) STM image of a monolayer formed by a sample of **1** from another batch at TCB/graphite interface ( $5.8 \times 10^{-6}$  M,  $I_{set} = 180$  pA,  $V_{bias} = -120$  mV), (b) A histogram obtained from a statistical analysis for adsorbed/desorbed ZnP units. Comparison with the data in Fig.3 showed consistency of the results, i.e. 1-2% ZnP units desorbed, irrespective of the sample batch.

**Table S2** Average apparent heights and standard deviations of red and green curves in Fig. S5b and their area ratio.

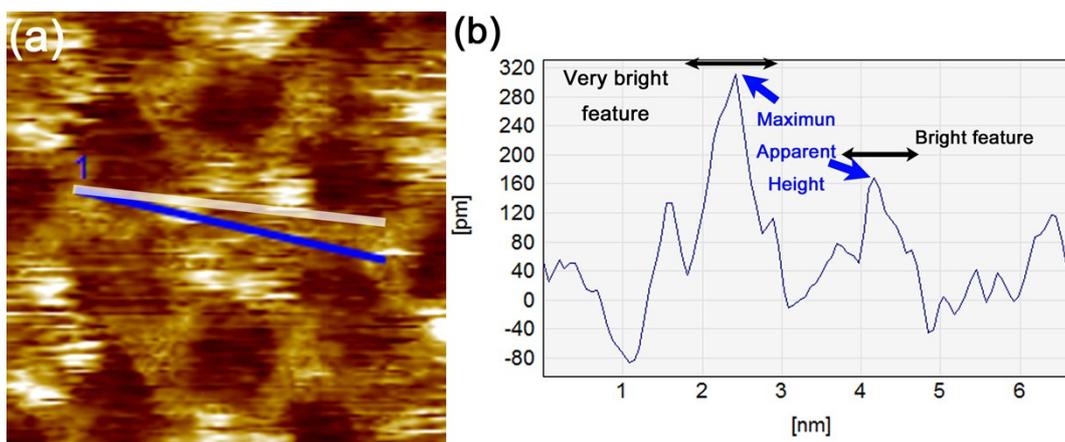
	Average apparent height (pm)	Standard deviation (pm)	Area ratio (Red curve : Green curve)
Red curve	98	18	99 : 1
Green curve	37	4	



**Fig. S6** STM image of a monolayer formed by a mixture of **1** and  $C_{60}$  at TCB/graphite interface ( $2.9 \times 10^{-6}$  M for DBA **1**,  $1.4 \times 10^{-5}$  M for  $C_{60}$ ,  $I_{set} = 250$  pA,  $V_{bias} = -110$  mV). The white lines indicate domain boundaries.



**Fig. S7** (a) Enlarged STM image of a monolayer formed by a mixture of **1** and  $C_{60}$  at the TCB/graphite interface. The white line indicates the direction of one of the main symmetry axes of graphite underneath the molecular layers. The blue line indicates a representative line for the height profile measurement which is rotated by  $+7^\circ$  with respect to the white line. (b) A representative apparent height profile along the blue line in (a).



**Fig. S8** (a) Enlarged STM image of a monolayer formed by a mixture of **1** and C<sub>60</sub> at the TCB/graphite interface. The white line indicates the direction of one of the main symmetry axes of graphite underneath the molecular layers. The blue line indicates a representative line for the height profile measurement which is rotated by +7° with respect to the white line. (b) A representative apparent height profile along the blue line in (a).

**Table S3** Average apparent heights and standard deviation of orange and gray curves in Fig. 5 and their area ratio.

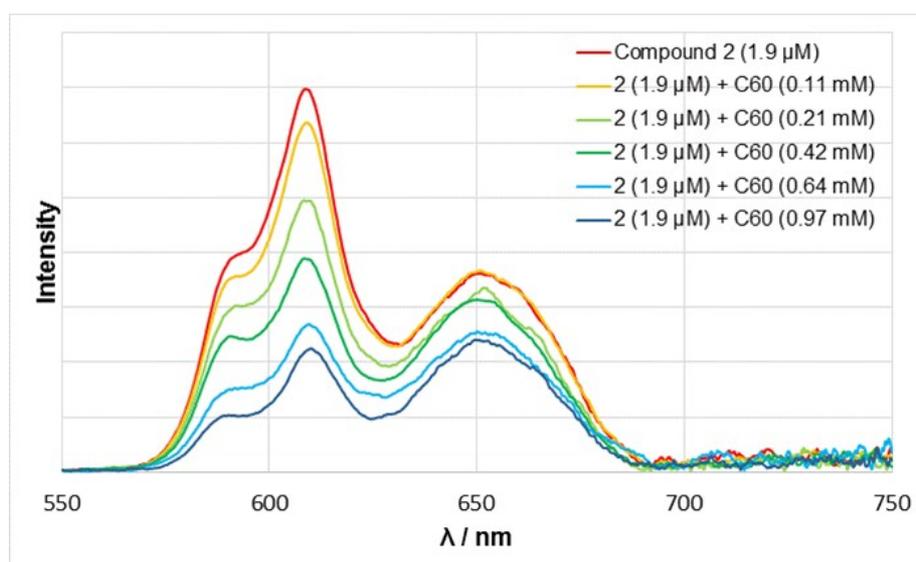
	Average apparent height (pm)	Standard deviation (pm)	Area ratio (Orange curve : Gray curve)
Orange curve	260	47	96 : 4
Gray curve	117	18	

### 3. Details of measurement of binding constant of C<sub>60</sub> with reference compound 2

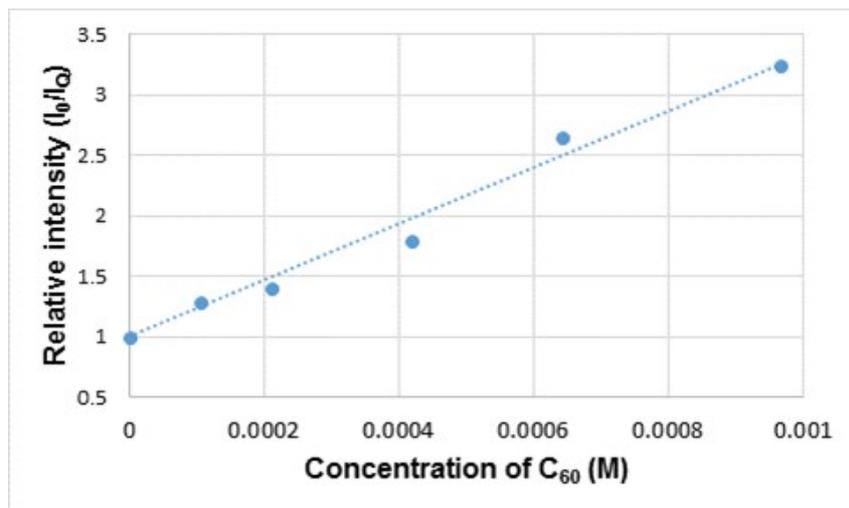
In order to estimate the binding constant between the reference compound **2** and C<sub>60</sub> in TCB, fluorescence quenching titration was performed.<sup>1</sup> Fig. S9 shows the fluorescence quenching of **2** in TCB ( $1.9 \times 10^{-6}$  M) upon addition of increasing concentration of C<sub>60</sub> ( $1.1 \times 10^{-4}$  M (56 eq.),  $2.1 \times 10^{-4}$  M (110 eq.),  $4.2 \times 10^{-4}$  M (220 eq.),  $6.4 \times 10^{-4}$  M (340 eq.) and  $9.7 \times 10^{-4}$  M (510 eq.)) when excited at 430 nm. The binding constant of **2** with C<sub>60</sub> in TCB was determined by Stern-Volmer equation:

$$I_0/I_Q = 1 + K_a[Q]$$

where  $I_0$  is the initial fluorescence intensity,  $I_Q$  is the intensity in the presence of C<sub>60</sub> at concentration [Q] and  $K_a$  is the binding constant. A Stern-Volmer plot is shown in Fig. S10. The binding constant ( $K_a$ ) at 25 °C was determined to be  $(1.9 \pm 0.6) \times 10^3 \text{ M}^{-1}$  (emission monitored at 608 nm).



**Fig. S9** Fluorescence quenching spectra of **2** with C<sub>60</sub> in TCB at 25 °C (excitation wavelength 430 nm).



**Fig. S10** A Stern-Volmer plot from Fig. S9 monitored at 608 nm.

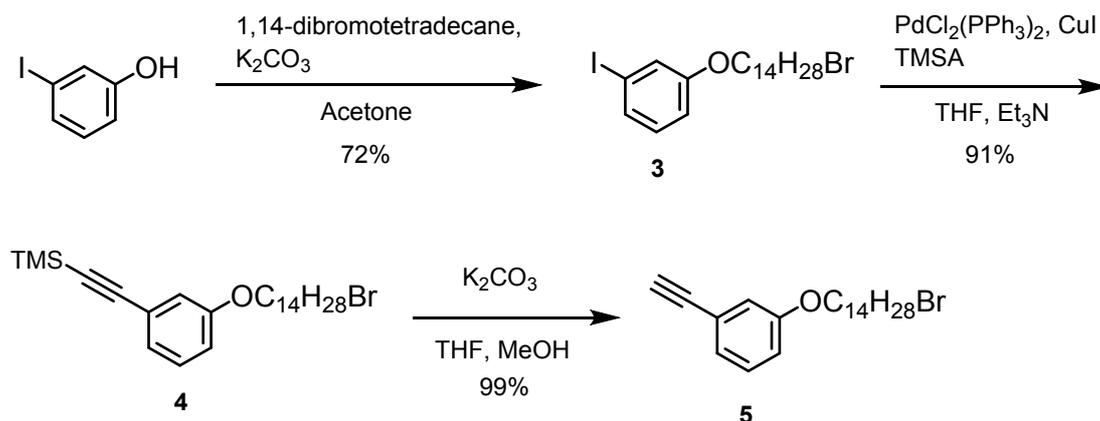
## 4. Details of syntheses of compounds under investigation.

### 4-1. General.

All manipulations except for the syntheses of **5** were performed under an inert gas (nitrogen or argon) atmosphere. All solvents were distilled or passed through active alumina and copper catalyst in a Glass Contour solvent purification system before use. C<sub>60</sub> was purchased from TCI. All commercially available reagents were used as received.

<sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were measured on a Bruker UltraShield Plus 400 spectrometer. When chloroform-*d*, dichloromethane-*d*<sub>2</sub> and THF-*d*<sub>8</sub> were used as a solvent, the spectra were referenced to residual solvent proton signals in the <sup>1</sup>H NMR spectra (7.26 ppm for chloroform-*d*, 5.32 ppm for dichloromethane-*d*<sub>2</sub> and 3.58 ppm for THF-*d*<sub>8</sub>) and to the solvent carbon signals in the <sup>13</sup>C NMR spectra (77.0 ppm for chloroform-*d*, 53.8 ppm for dichloromethane-*d*<sub>2</sub> and 67.3 ppm for THF-*d*<sub>8</sub>). Preparative GPC separation was undertaken with a JAI LC-908 and JAI LC-9204 recycling chromatographs using 600 mm × 20 mm JAIGEL-1H and 2H (for JAI LC-908) or 600 mm × 40 mm JAIGEL-1H-40 and 2H-40 (for JAI LC-9204) GPC columns with CHCl<sub>3</sub> as the eluent. Analytical HPLC was undertaken with a SHIMADZU SCL-10A $\nu$ P using a 4.6 mm × 150 mm COSMOSIL 5C<sub>18</sub>-AR-II column with CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> 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 and JEOL JMS-S3000 for LDI ionization mode. Elemental analyses were carried out with a Perkin-Elmer 2400II analyzer.

#### 4-2. Syntheses of 1-(14-bromotetradecyloxy)-3-ethynylbenzene (5).



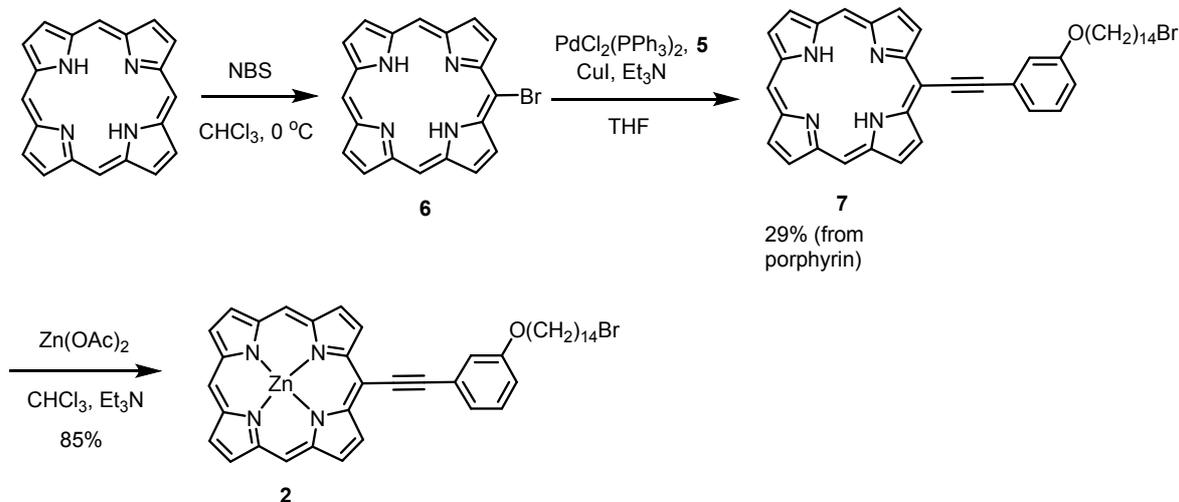
**Synthesis of 1-(14-bromotetradecyloxy)-3-iodobenzene (3).** A solution of 1,14-dibromotetradecane (1.57 g 4.41 mmol)<sup>2</sup> and 3-iodophenol (540 mg, 2.45 mmol) in acetone (60.0 mL) was heated under reflux in the presence of  $K_2CO_3$  (601 mg, 4.35 mmol) for 14 h. After the mixture was filtered, the solvent was evaporated under vacuum. The residue was subjected to silica gel column chromatography (hexanes) to give **3** (4.95 g, 72%) as a white solid. mp 52.3–53.0 °C;  $^1H$  NMR (400 MHz,  $CD_2Cl_2$ , 30 °C)  $\delta$  7.27–7.26 (m, 2H), 7.00 (t,  $J = 8.0$  Hz, 1H), 6.87 (dd,  $J = 7.5$  Hz,  $J = 1.5$  Hz, 1H), 3.92 (t,  $J = 6.7$  Hz, 2H), 3.42 (t,  $J = 6.9$  Hz, 2H), 1.85 (quint,  $J = 7.2$  Hz, 2H), 1.76 (quint,  $J = 7.2$  Hz, 2H), 1.44–1.29 (m, 20H);  $^{13}C$  NMR (100 MHz,  $CD_2Cl_2$ , 30 °C)  $\delta$  160.3, 131.2, 129.9, 124.1, 114.7, 94.6, 68.8, 34.6, 33.4, 30.04, 30.01, 29.98, 29.87, 29.77, 29.6, 29.2, 28.6, 26.4; IR (KBr) 3101, 3006, 2922, 2850, 1592, 1578, 1562, 1469, 1245, 1037, 1017, 988, 851, 786, 678, 648  $cm^{-1}$ ; HRMS (FAB)  $m/z$  calcd for  $C_{20}H_{32}O^{79}BrI$  ( $M^+$ ): 494.0681, found: 494.0676; Anal. Calcd for  $C_{20}H_{32}OBrI$ : C, 48.50; H, 6.51. Found: C, 48.80; H, 6.90.

**Synthesis of {[3-(14-bromotetradecyloxy)phenyl]ethynyl}trimethylsilane (4).** Compound **3** (4.95 g, 10.0 mmol),  $PdCl_2(PPh_3)_2$  (172 mg, 245  $\mu$ mol) and  $CuI$  (105 mg, 1.07 mmol) were stirred in a mixture of  $Et_3N$  (58.0 mL) and THF (60.0 mL). A solution of (trimethylsilyl)acetylene (4.70 mL, 33.2 mmol) in THF (20.0 mL) was added to the mixture via a syringe. After stirring at room temperature for 3 h, the solvents were removed under vacuum. The residue was dissolved in  $CH_2Cl_2$  and washed with water and brine, and the organic phase was dried over  $MgSO_4$ . After removal of the solvents under vacuum, the crude mixture was subjected to silica gel column chromatography (hexanes) followed by preparative HPLC to give **4** (4.25 g, 91%) as an orange solid. mp 44.2–44.9 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ , 30 °C)  $\delta$  7.18 (t,  $J = 8.0$  Hz, 1H), 7.04 (d,  $J = 7.6$  Hz, 1H), 6.98 (s, 1H),

6.86 (d,  $J = 6.8$  Hz, 1 H), 3.94 (t,  $J = 6.4$  Hz, 2H), 3.41 (t,  $J = 7.0$  Hz, 2H), 1.86 (quint,  $J = 7.2$  Hz, 2H), 1.76 (quint,  $J = 6.9$  Hz, 2H), 1.44–1.27 (m, 20 H), 0.25 (s, 9 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 30 °C)  $\delta$  159.1, 129.4, 124.5, 124.3, 117.5, 116.0, 105.4, 93.9, 68.2, 34.0, 33.1, 29.87, 29.85, 29.82, 29.78, 29.69, 29.61, 29.5, 29.0, 28.4, 26.3, 0.3; IR (KBr) 3071, 2921, 2852, 2154, 1602, 1573, 1473, 1288, 1251, 1159, 1038, 1030, 847, 783, 646  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{41}\text{O}^{79}\text{BrSi}$  ( $\text{M}^+$ ): 464.2110, found: 464.2111. Anal. Calcd for  $\text{C}_{25}\text{H}_{41}\text{OBrSi}$ : C, 64.49; H, 8.88. Found: C, 64.09; H, 9.03.

**Synthesis of 1-(14-bromotetradecyloxy)-3-ethynylbenzene (5).** To a solution of **4** (4.25 g, 9.13 mmol) in THF (130 mL) and methanol (130 mL),  $\text{K}_2\text{CO}_3$  (1.68 g, 12.1 mmol) was added. After stirring the mixture at room temperature for 1.5 h, water was added. The product was extracted by  $\text{CH}_2\text{Cl}_2$ . The extract was washed with water and brine, and organic phase was dried over  $\text{MgSO}_4$ . The solvent was removed under vacuum to give **5** (3.57 g, 99%) as a pale yellow solid. mp 35.3–36.0 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 30 °C)  $\delta$  7.21 (t,  $J = 7.8$  Hz, 1H), 7.07 (d,  $J = 7.6$  Hz, 1H), 7.01 (s, 1H), 6.90 (d,  $J = 8.0$  Hz, 1 H), 3.94 (t,  $J = 6.4$  Hz, 2H), 3.41 (t,  $J = 6.8$  Hz, 2H), 3.04 (s, 1 H), 1.86 (quint,  $J = 7.0$  Hz, 2H), 1.77 (quint,  $J = 6.9$  Hz, 2H), 1.43–1.24 (m, 20 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 30 °C)  $\delta$  158.9, 129.3, 124.4, 123.0, 117.6, 116.0, 83.7, 76.8, 68.1, 34.0, 32.8, 29.6, 29.5, 29.4, 29.3, 29.2, 28.8, 28.2, 26.0; IR (KBr) 3296, 3071, 2924, 2853, 2367, 1575, 1469, 1317, 1284, 1257, 1145, 1041, 687, 645  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{33}\text{O}^{79}\text{Br}$  ( $\text{M}^+$ ): 392.1715, found: 392.1711.

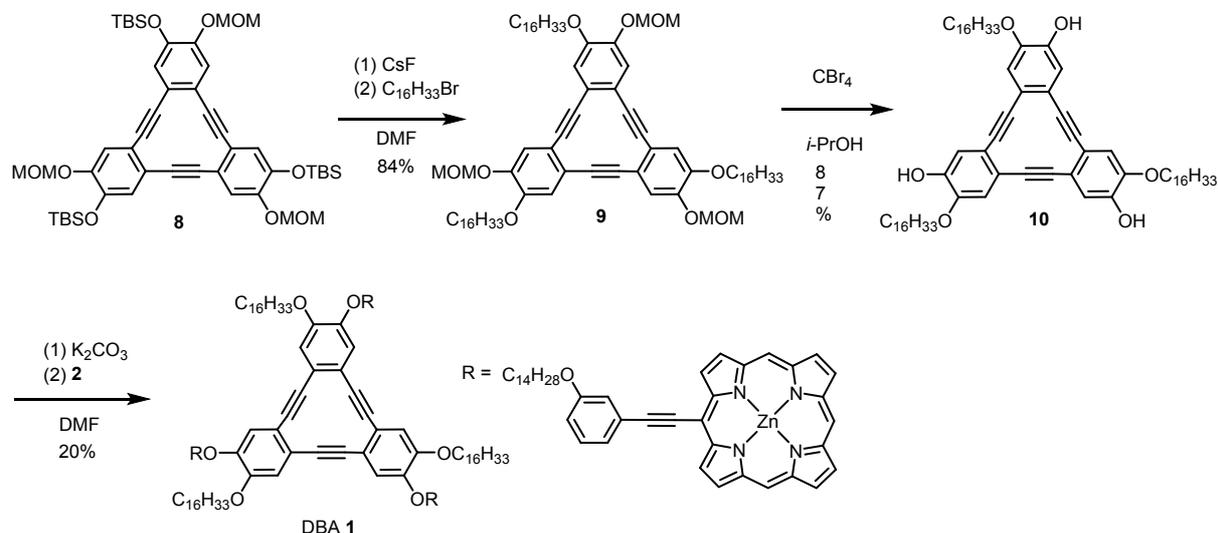
### 4-3. Syntheses of 2.



**Synthesis of 7.**<sup>3,4</sup> To a solution of porphyrin (265 mg, 868  $\mu\text{mol}$ ) in  $\text{CHCl}_3$  (1.0 L) cooled in an ice bath was added a solution of *N*-bromosuccinimide (163 mg, 915  $\mu\text{mol}$ ) in  $\text{CHCl}_3$  (100 mL) via a Pasteur pipet. After stirring for 4 min, acetone (300 mL) and water were added. The organic phase was washed by water and brine, and dried over  $\text{MgSO}_4$ . After removal of solvents under vacuum, the residue was subjected to silica gel column chromatography (hexanes/toluene = 1/2) to give a purple solid (195 mg) containing 6. The resulting mixture was used for the next step without further purification. Compound 5 (2.57 g, 6.52 mmol) was added to a mixture of the above solid containing 6 (195 mg),  $\text{PdCl}_2(\text{PPh}_3)_2$  (98.0 mg, 140  $\mu\text{mol}$ ), and  $\text{CuI}$  (34.9 mg, 183  $\mu\text{mol}$ ) in a mixture of THF (150 mL) and  $\text{Et}_3\text{N}$  (400 mL). After stirring the mixture at room temperature for 2.5 h, most of the solvents were removed under vacuum to afford a mixture of products which was passed through a short column chromatograph (silica gel,  $\text{CH}_2\text{Cl}_2$ ). The products were subjected to silica gel column chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  = 3/1). Further purification was performed by preparative HPLC to give 7 (178 mg, 29% (from porphyrin)) as a purple solid. mp  $131.7\text{--}132.5\text{ }^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $30\text{ }^\circ\text{C}$ )  $\delta$  10.26 (s, 2H), 10.21 (s, 1H), 9.92–9.91 (m, 2 H), 9.46–9.42 (m, 6 H), 7.68 (d,  $J = 6.8\text{ Hz}$ , 1H), 7.61 (s, 1 H), 7.51 (t,  $J = 7.8\text{ Hz}$ , 1H), 7.09 (d,  $J = 8.8\text{ Hz}$ , 1H), 4.18 (t,  $J = 6.4\text{ Hz}$ , 2 H), 3.38 (t,  $J = 6.8\text{ Hz}$ , 2H), 1.92 (quint,  $J = 6.4\text{ Hz}$ , 2H), 1.83 (quint,  $J = 6.8\text{ Hz}$ , 2H), 1.47–1.23 (m, 20H),  $-3.19$  (s, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $30\text{ }^\circ\text{C}$ )  $\delta$  159.4, 131.8, 131.6, 131.4, 130.4, 130.3, 129.8, 124.9, 124.2, 117.3, 115.7, 105.5, 105.1, 98.9, 96.7, 91.3, 68.3, 34.0, 32.8, 29.7, 29.64, 29.56, 29.47, 29.45, 29.39, 28.8, 28.2, 26.2; IR (KBr) 3420, 3304, 3118, 2919, 2850, 2198, 1593, 1572, 1409, 1235, 1203, 1157, 1045, 856, 772, 691  $\text{cm}^{-1}$ ; HRMS (FAB)  $m/z$  calcd for  $\text{C}_{42}\text{H}_{45}\text{ON}_4^{79}\text{Br}$  ( $\text{M}^+$ ): 702.2756, found: 702.2768.

**Synthesis of 2.** A solution of **7** (49.3 mg, 70.3  $\mu\text{mol}$ ) in  $\text{CHCl}_3$  (45.0 mL) and  $\text{Et}_3\text{N}$  (300  $\mu\text{L}$ ) was stirred at 65  $^\circ\text{C}$  for 10 min.  $\text{Zn}(\text{OAc})_2$  (158 mg, 860  $\mu\text{mol}$ ) was then added to the mixture. After string the mixture at 65  $^\circ\text{C}$  for 1.5 h, saturated aqueous solution of  $\text{NH}_4\text{Cl}$  was added. The product was extracted with  $\text{CHCl}_3$  and the extract was washed with water and brine. The organic phase was dried over  $\text{MgSO}_4$ . After removal of solvent under vacuum, the product was purified by reprecipitation from  $\text{CH}_2\text{Cl}_2$ /hexanes to give **2** (44.7 mg, 85%) as a purple solid. mp 162.2–163.0  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_8$ , 30  $^\circ\text{C}$ )  $\delta$  10.25–10.23 (m, 3H), 9.97–9.96 (m, 2H), 9.48–9.44 (m, 6H), 7.69–7.67 (m, 2H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.07 (d,  $J = 8.0$  Hz, 2H), 4.19 (t,  $J = 6.4$  Hz, 2H), 3.39 (t,  $J = 6.8$  Hz, 2H), 1.91 (quint,  $J = 6.4$  Hz, 2H), 1.81 (quint,  $J = 6.8$  Hz, 2H), 1.61–1.32 (m, 20H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF}-d_8$ , 30  $^\circ\text{C}$ )  $\delta$  160.6, 152.7, 150.8, 150.7, 150.2, 133.0, 132.9, 132.6, 131.6, 130.5, 126.5, 124.6, 117.9, 116.0, 106.8, 106.7, 99.1, 96.2, 93.7, 68.9, 34.2, 33.8, 30.63, 30.62, 30.60, 30.52, 30.45, 30.43, 30.40, 29.7, 29.1, 27.1; IR (KBr) 3448, 3105, 2922, 2850, 2195, 1593, 1509, 1222, 1053, 994, 849  $\text{cm}^{-1}$ ; HRMS (FAB)  $m/z$  calcd for  $\text{C}_{42}\text{H}_{43}\text{ON}_4^{81}\text{Br}^{64}\text{Zn}$  ( $\text{M}^+$ ): 764.1891, found: 764.1871.

#### 4-4. Syntheses of Dehydrobenzo[12]annulene (DBA) 1.



**Synthesis of DBA derivative 9.** CsF (25.9 mg, 17.1  $\mu\text{mol}$ ) and 1-bromohexadecane (50  $\mu\text{L}$ ) were added to a solution of **8** (19.5 mg, 22.4  $\mu\text{mol}$ )<sup>5</sup> in DMF (1.00 mg). After stirring at 70  $^\circ\text{C}$  for 16 h, the solvent was removed under vacuum. The products were separated by silica gel column chromatography (hexanes/ $\text{CHCl}_3$  = from 1/0 to 0/1) and purified by precipitation from  $\text{CH}_2\text{Cl}_2$ / $\text{CH}_3\text{OH}$  to afford **9** (22.5 mg, 84%) as a yellow solid. mp 62.0–63.2  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 30  $^\circ\text{C}$ )  $\delta$  7.02 (s, 3H), 6.77 (s, 3H), 5.19 (s, 6H), 4.00 (t,  $J = 6.6$  Hz,

6H), 3.52 (s, 9H), 1.82 (quint,  $J = 6.8$  Hz, 6H), 1.51–1.17 (m, 78H), 0.88 (t,  $J = 6.4$  Hz, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 30 °C)  $\delta$  149.8, 147.0, 121.8, 119.7, 119.6, 115.9, 95.6, 92.2, 91.8, 69.2, 56.5, 32.1, 29.9, 29.82, 29.75, 29.73, 29.5, 29.2, 26.1, 22.8, 14.2; IR (KBr) 2921, 2851, 2364, 1594, 1510, 1470, 1346, 1228, 1153, 1054  $\text{cm}^{-1}$ ; HRMS (FAB)  $m/z$  calcd for  $\text{C}_{78}\text{H}_{120}\text{O}_9$  ( $\text{M}^+$ ): 1200.8932, found: 1200.8933.

**Synthesis of DBA derivative 10.** A mixture of **9** (19.2 mg, 16.0  $\mu\text{mol}$ ),  $\text{CBr}_4$  (1.28 mg, 3.86  $\mu\text{mol}$ ) and 2-propanol (280  $\mu\text{L}$ ) was stirred at 80 °C. After 2 h, the solvent was removed under vacuum. The residue was subject to silica gel column chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  = from 1/0 to 1/1). Precipitation of the products from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  gave **10** (12.7 mg, 87%) as a yellow solid. mp 121.8–122.8 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 30 °C)  $\delta$  6.79 (s, 3H), 6.72 (s, 3H), 5.63 (s, 3H), 4.03 (t,  $J = 6.8$  Hz, 6H), 1.81 (quint,  $J = 6.8$  Hz, 6H), 1.50–1.19 (m, 78H), 0.88 (t,  $J = 6.4$  Hz, 9H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 30 °C)  $\delta$  146.2, 146.1, 123.0, 120.5, 119.4, 117.4, 114.6, 92.0, 91.4, 69.3, 32.1, 29.9, 29.8, 29.74, 29.69, 29.51, 29.49, 29.2, 26.1, 22.8, 14.3; IR (KBr) 3543, 3437, 2923, 2852, 2367, 1509, 1469, 1365, 1294, 1064, 872  $\text{cm}^{-1}$ ; HRMS (FAB)  $m/z$  calcd for  $\text{C}_{72}\text{H}_{109}\text{O}_6$  ( $[\text{M}+\text{H}]^+$ ): 1069.8224, found: 1069.8192.

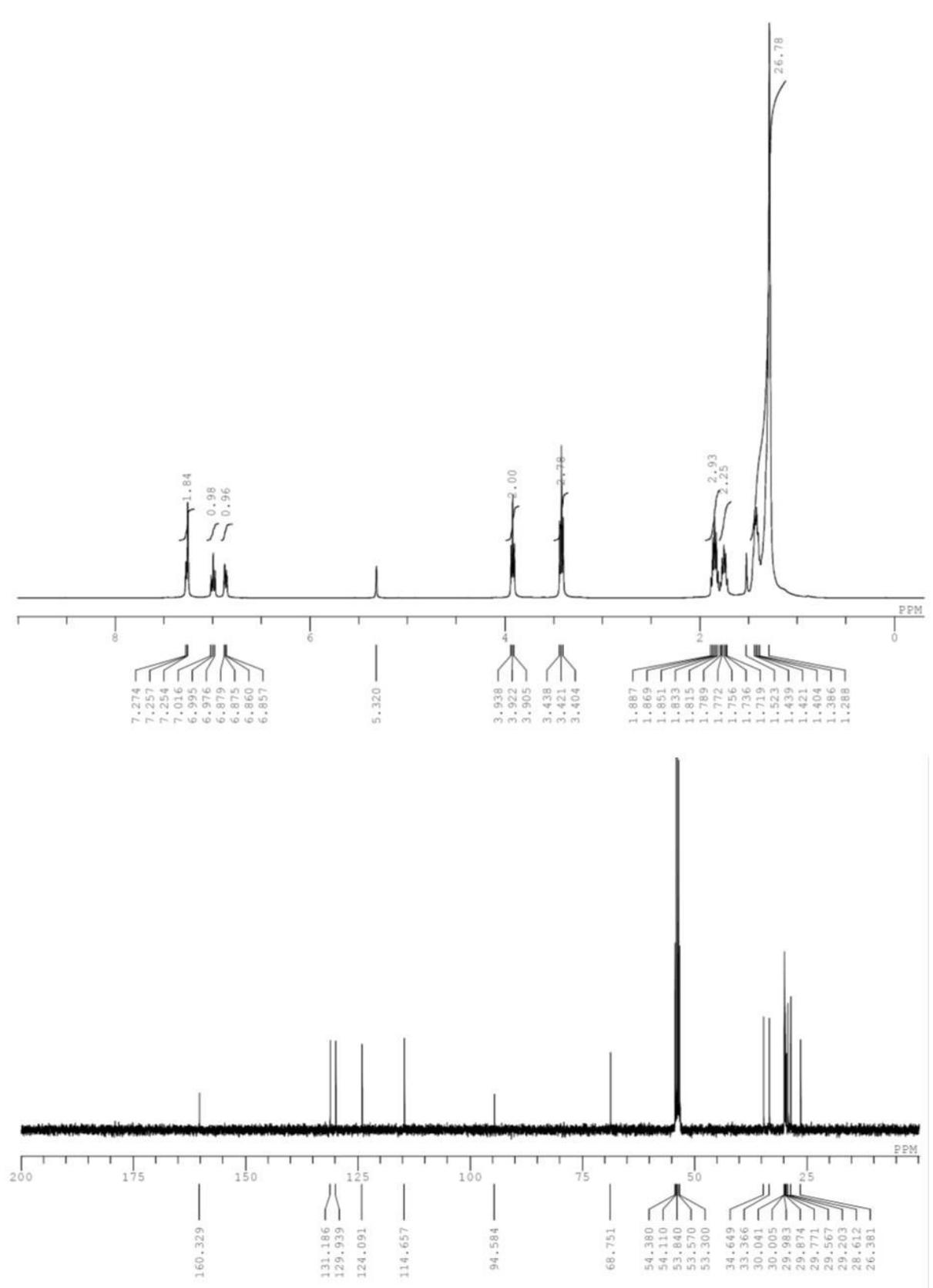
**Synthesis of DBA 1.** To a solution of **10** (5.0 mg, 4.6  $\mu\text{mol}$ ) and **7** (19.4 mg, 25.5  $\mu\text{mol}$ ) in DMF (420  $\mu\text{L}$ ),  $\text{K}_2\text{CO}_3$  (2.7 mg, 20  $\mu\text{mol}$ ) was added. The mixture was heated at 70 °C for 63 h. The solvent was evaporated under reduced pressure and the solid residue was separated by silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexanes} = 2/1$ ). The product was purified by precipitation from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  to afford DBA **1** (8.3 mg, 59%) as a purple solid.

In another run of the reaction, to a solution of **10** (4.8 mg, 4.4  $\mu\text{mol}$ ) and **7** (17.7 mg, 23.3  $\mu\text{mol}$ ) in DMF (800  $\mu\text{L}$ ),  $\text{K}_2\text{CO}_3$  (2.7 mg, 20  $\mu\text{mol}$ ) was added. The mixture was heated at 70 °C for 36 h. The solvent was evaporated under reduced pressure and the solid residue was separated by silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexanes}/\text{THF} = 2/1/0.1$ ). Further purification was performed by recycling GPC followed by precipitation from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  to afford DBA **1** (2.6 mg, 20%) as a purple solid. mp 152.0–152.8 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_8$ , 30 °C)  $\delta$  10.24–10.22 (m, 9H), 9.96–9.95 (m, 6H), 9.48–9.43 (m, 18H), 7.68–7.66 (m, 6H), 7.47 (t,  $J = 8.0$  Hz, 3H), 7.08–7.05 (m, 3H), 6.71 (s, 6H), 4.18 (t,  $J = 6.4$  Hz, 6H), 3.90 (t,  $J = 6.2$  Hz, 12H), 1.94–1.87 (m, 6H), 1.62–1.56 (m, 12H), 1.45–1.27 (m, 138H), 0.87 (t,  $J = 6.8$  Hz, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 30 °C)  $\delta$  160.4, 152.5, 150.6, 150.5, 150.3, 150.0, 132.8, 132.7, 132.4, 131.5, 130.3, 126.4, 124.4, 120.8, 117.7, 116.6, 115.8, 106.6,

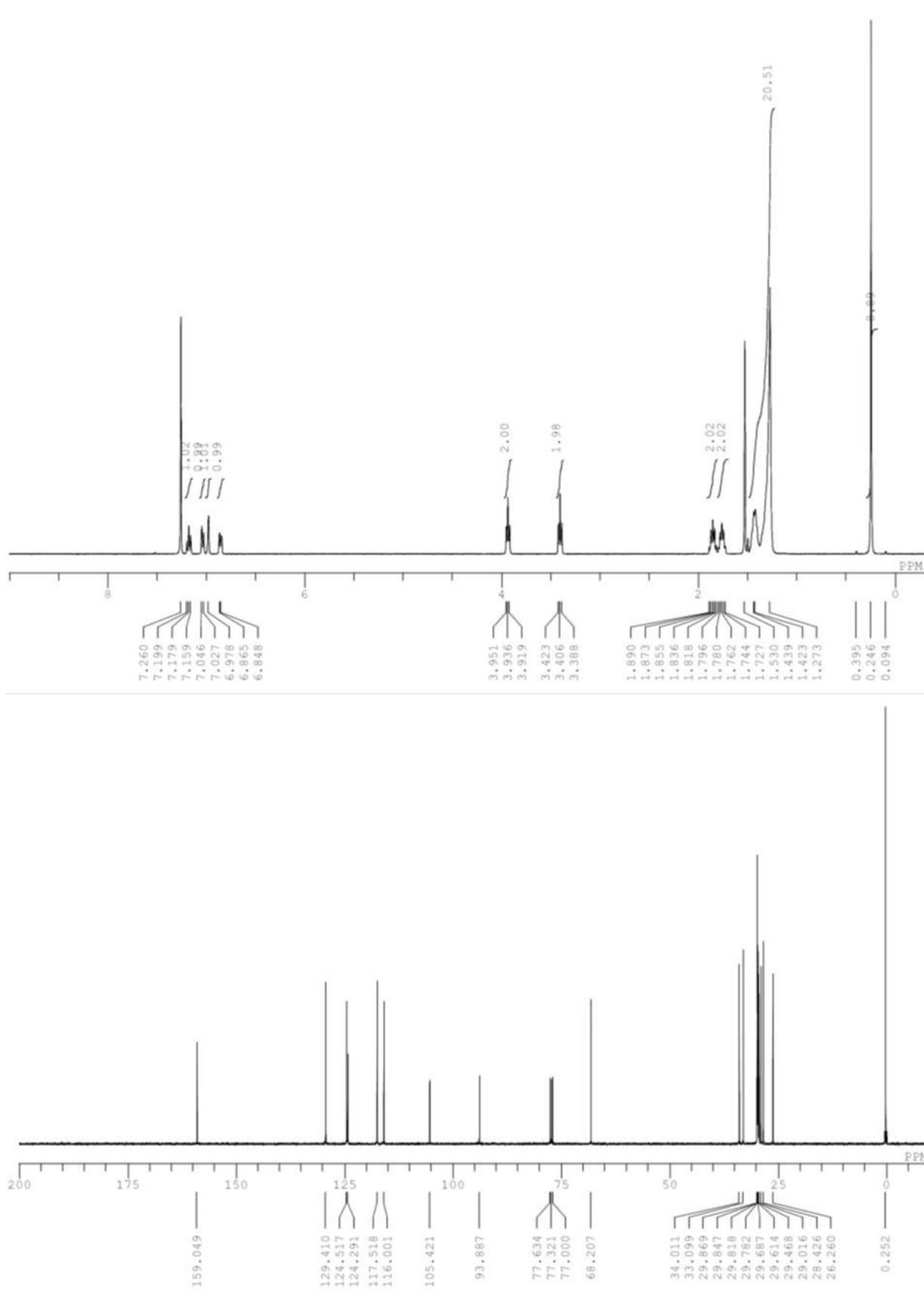
106.5, 99.0, 96.1, 93.6, 92.5, 71.4, 69.5, 68.7, 32.7, 30.5, 30.4, 30.3, 30.2, 30.14, 30.11, 30.0, 27.2, 27.0, 26.8, 23.4, 14.2; IR (KBr) 3324, 3101, 2921, 2850, 2359, 2195, 1593, 1509, 1467, 1349, 1226, 1053, 993, 852  $\text{cm}^{-1}$ ; HRMS (MALDI):  $m/z$  calcd for  $\text{C}_{198}\text{H}_{234}\text{O}_9\text{N}_{12}^{64}\text{Zn}_3$  ( $\text{M}^+$ ): 3115.6091, found: 3115.6039.

The integrity of the structure of **1** was confirmed by the symmetrical  $^1\text{H}$  NMR spectrum (Fig S19), which shows one signal at 6.71 ppm for the aromatic protons of the DBA core, unlike in trialkoxy compound **10** which exhibits two signals at 6.74 and 6.60 ppm (Fig S18 in the same solvent), and HRMS which does not exhibit peaks due to products of incomplete functionalization to the DBA core (Fig. S20). Moreover, reversed phase HPLC exhibited single peak, confirming its purity (Fig. S21). STM experiments were performed by using samples from different batches to furnish virtually the same results which are shown in Figs. 3 (main text) and S5 (ESI).

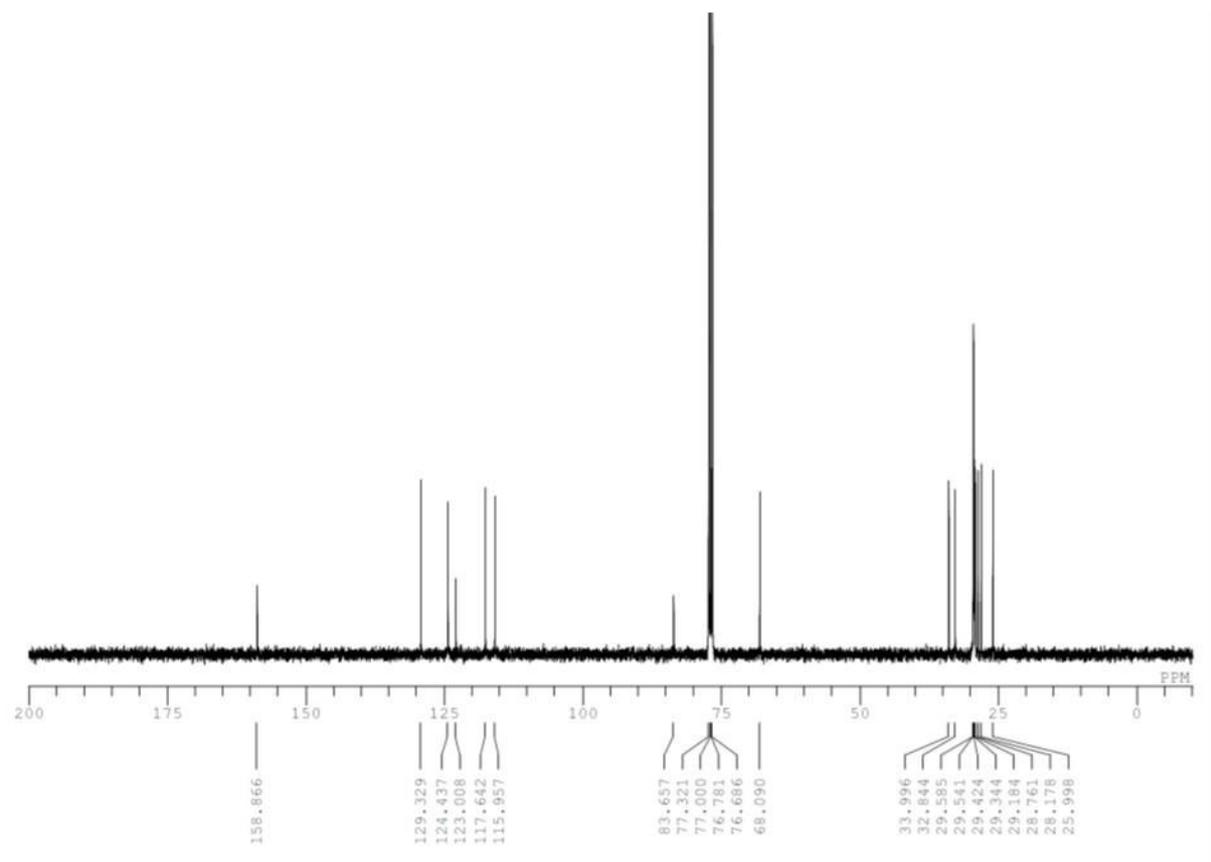
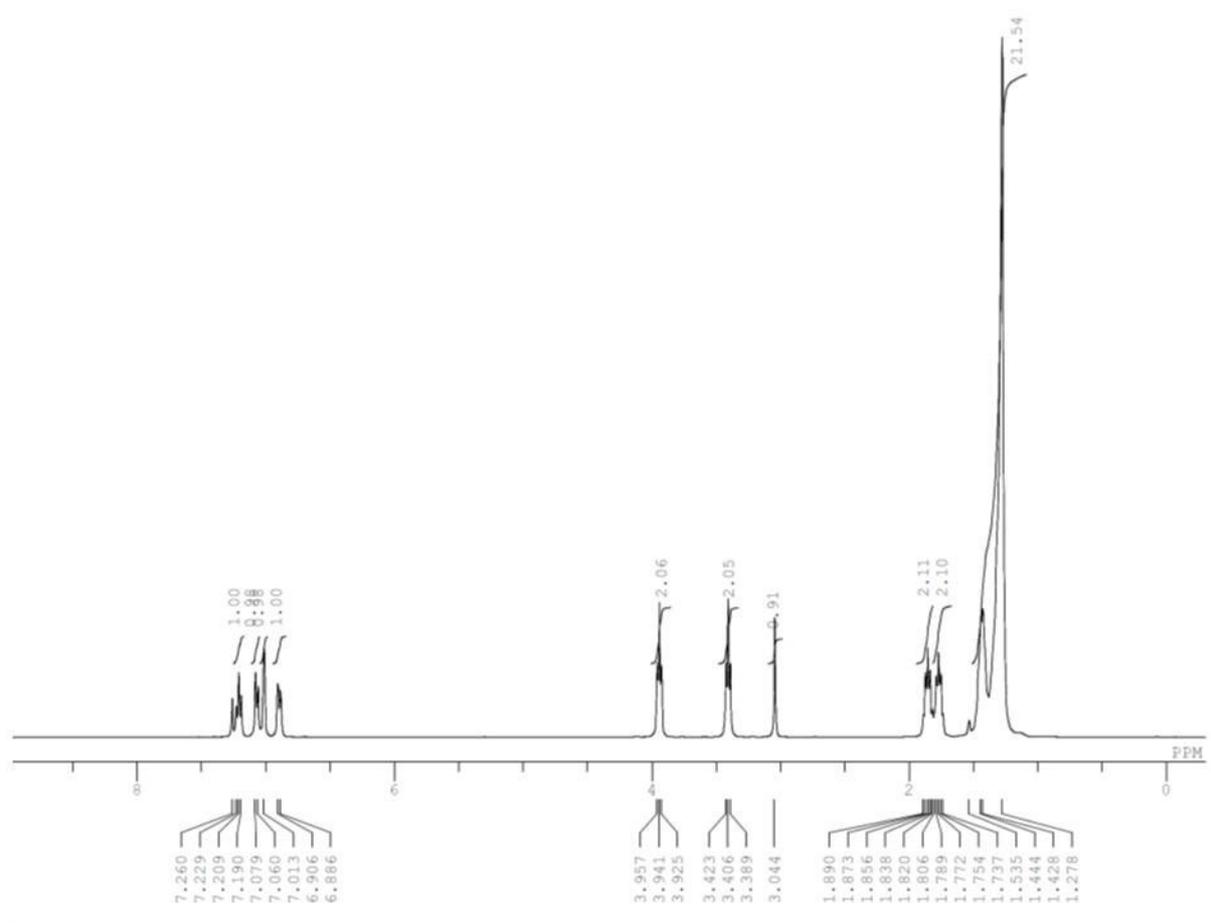
## 5. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Synthetic Compounds.



**Fig. S11**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** in  $\text{CD}_2\text{Cl}_2$  at  $30\text{ }^\circ\text{C}$ .



**Fig. S12** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4** in CDCl<sub>3</sub> at 30 °C.



**Fig. S13** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5** in CDCl<sub>3</sub> at 30 °C.

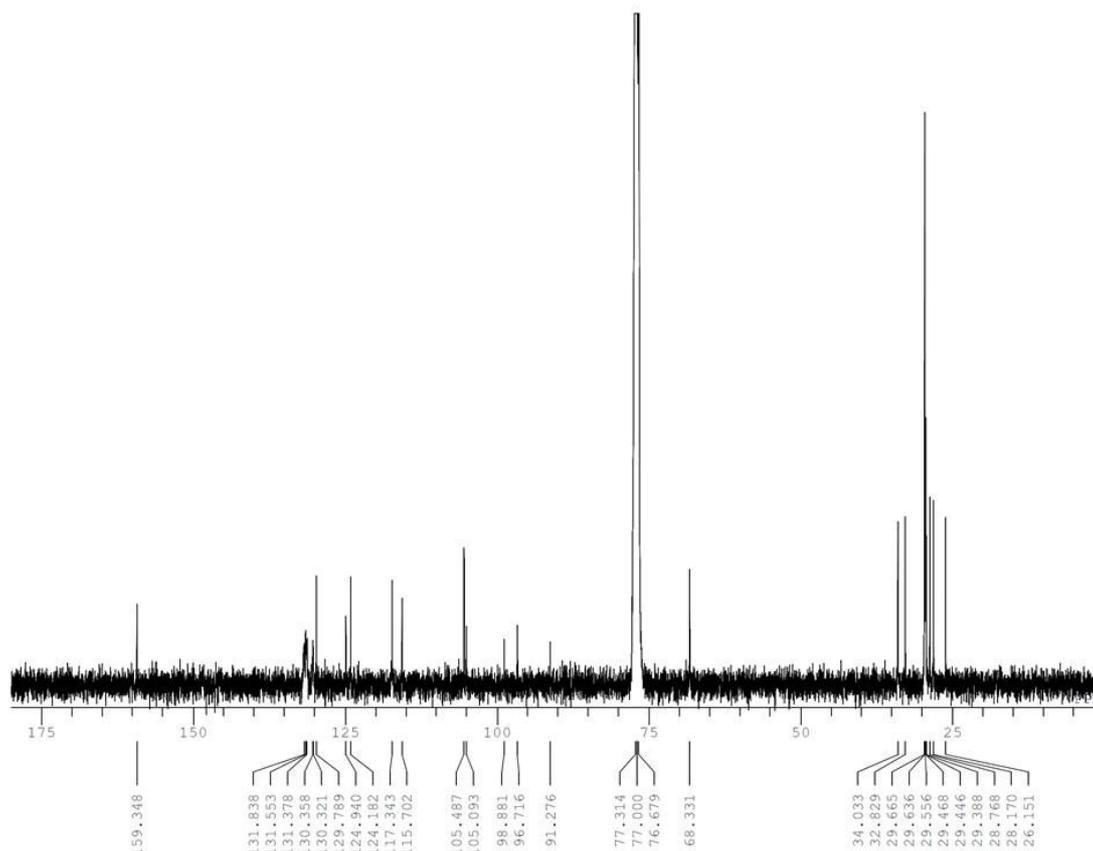
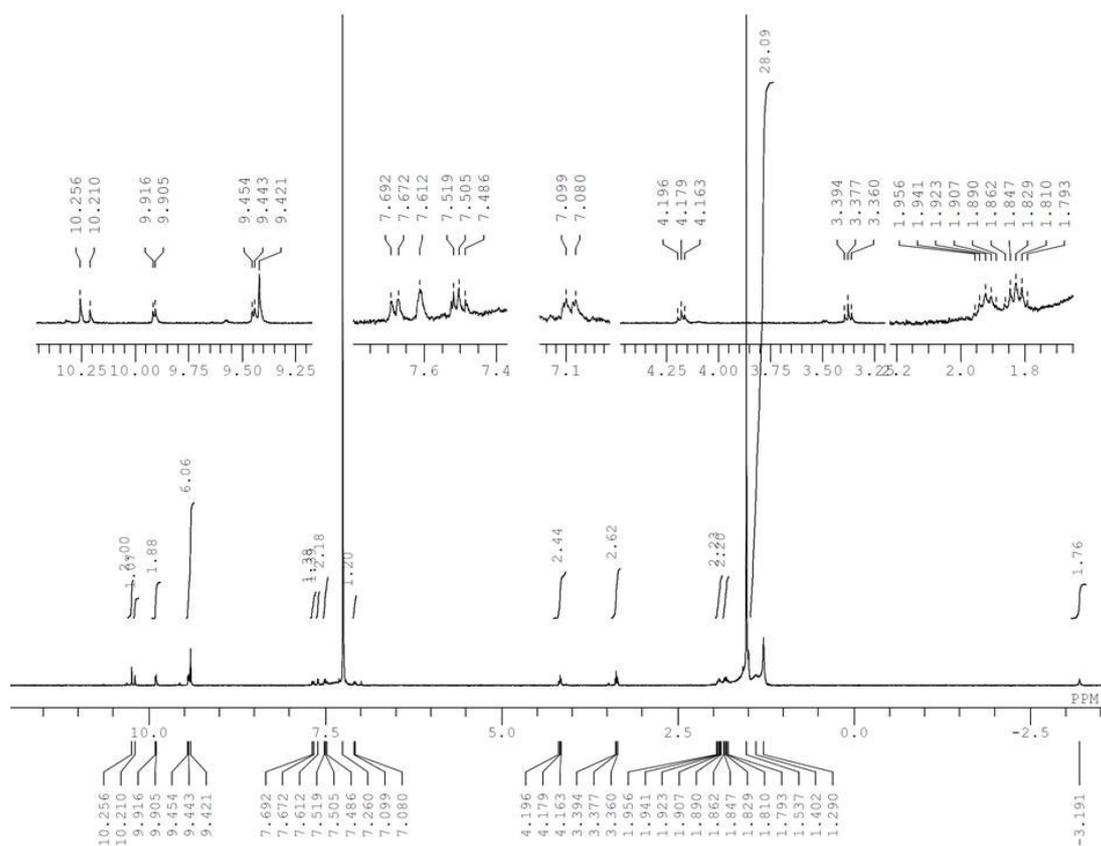
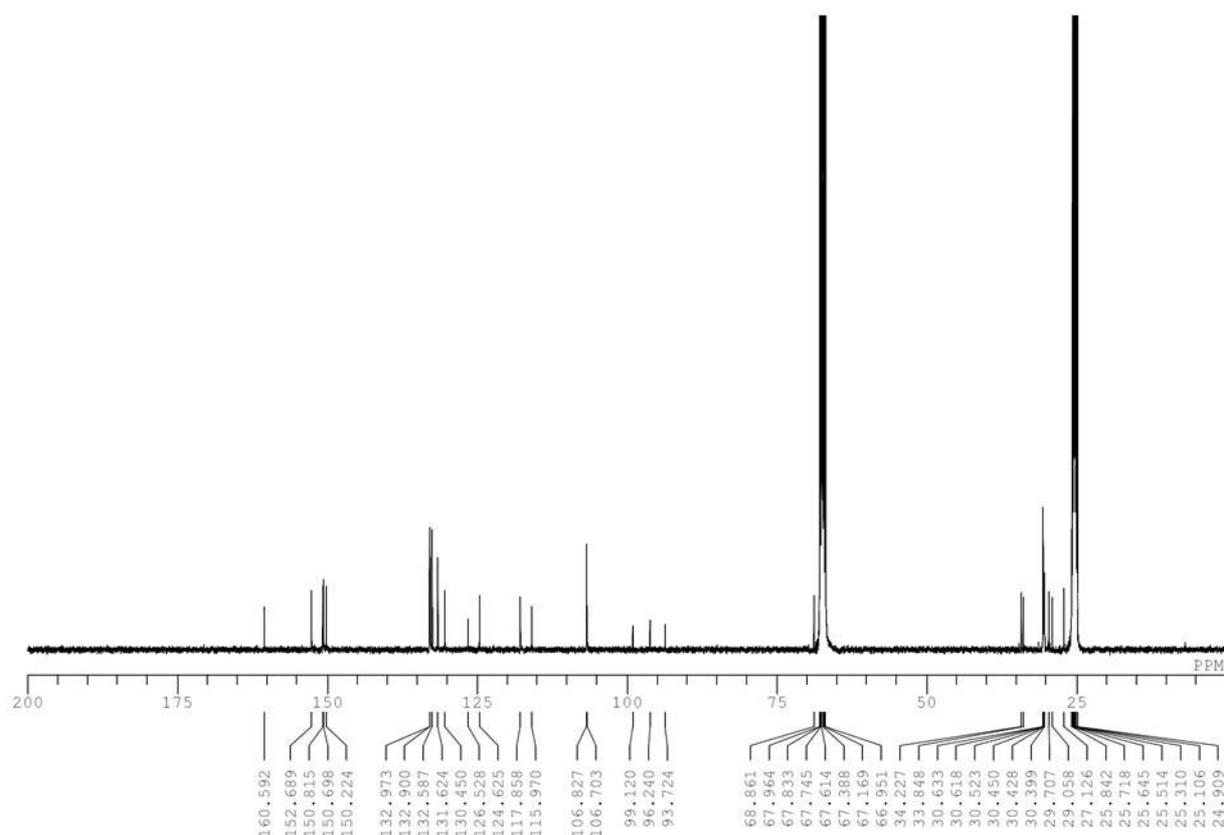
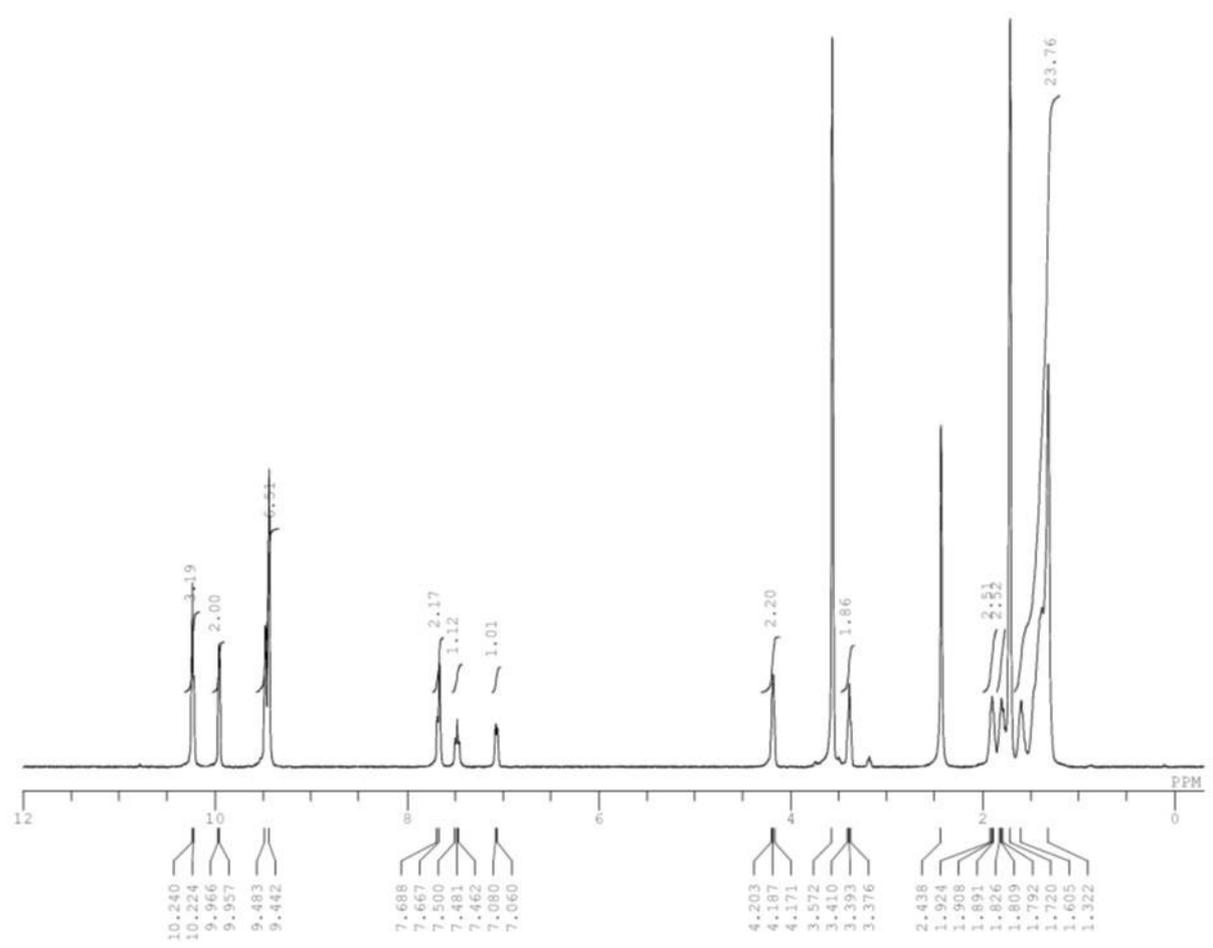
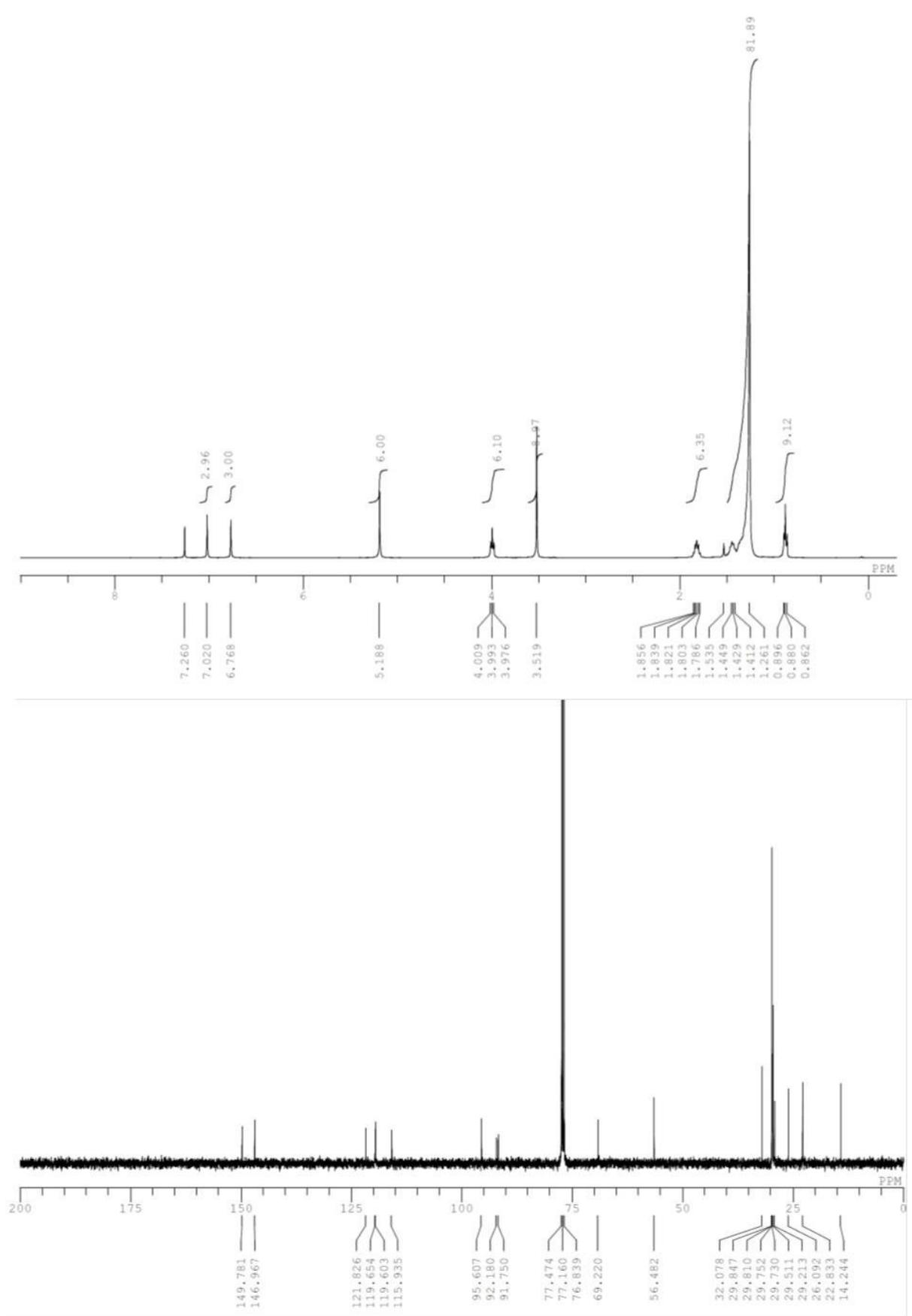


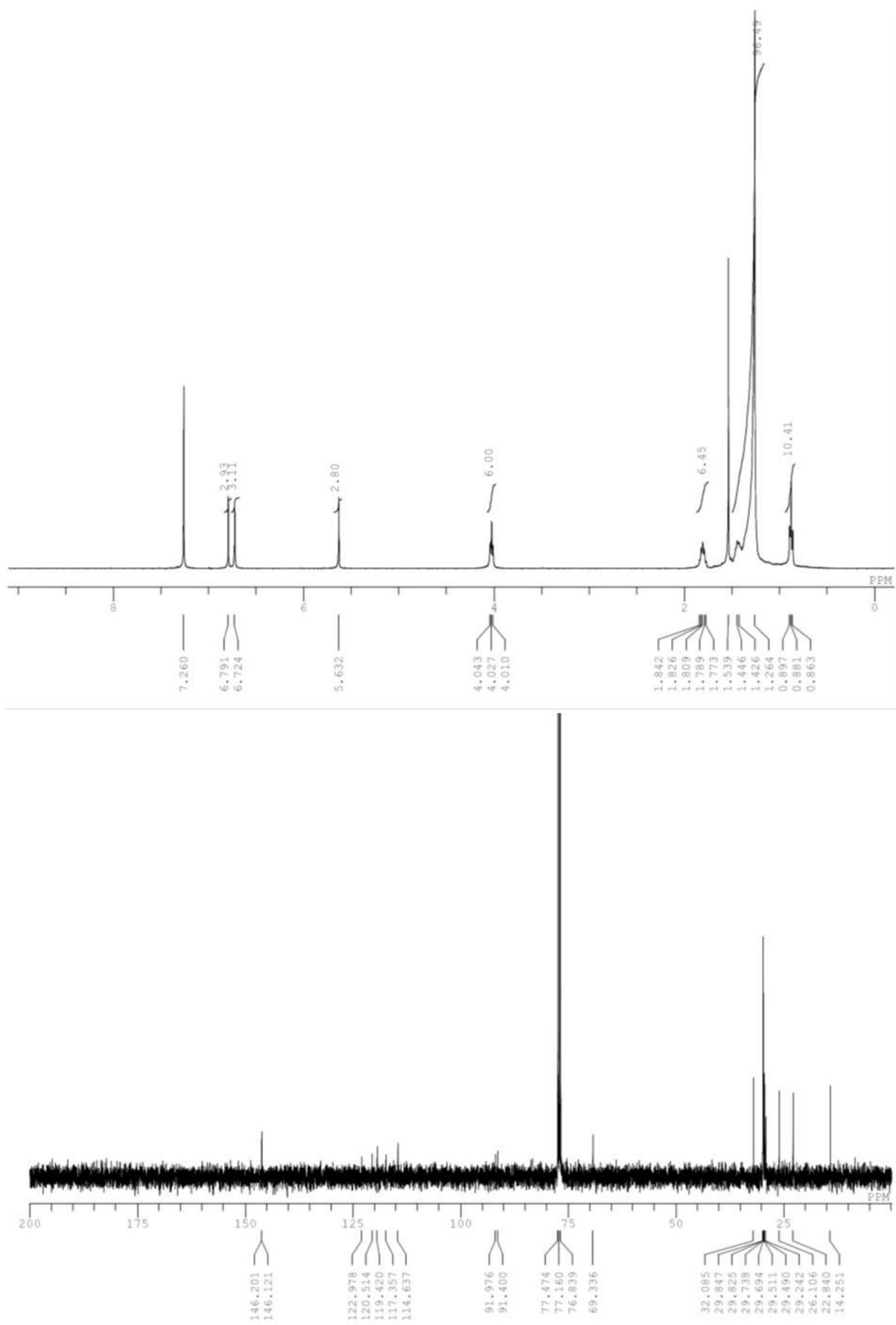
Fig. S14 <sup>1</sup>H and <sup>13</sup>C NMR spectra of 7 in CDCl<sub>3</sub> at 30 °C.



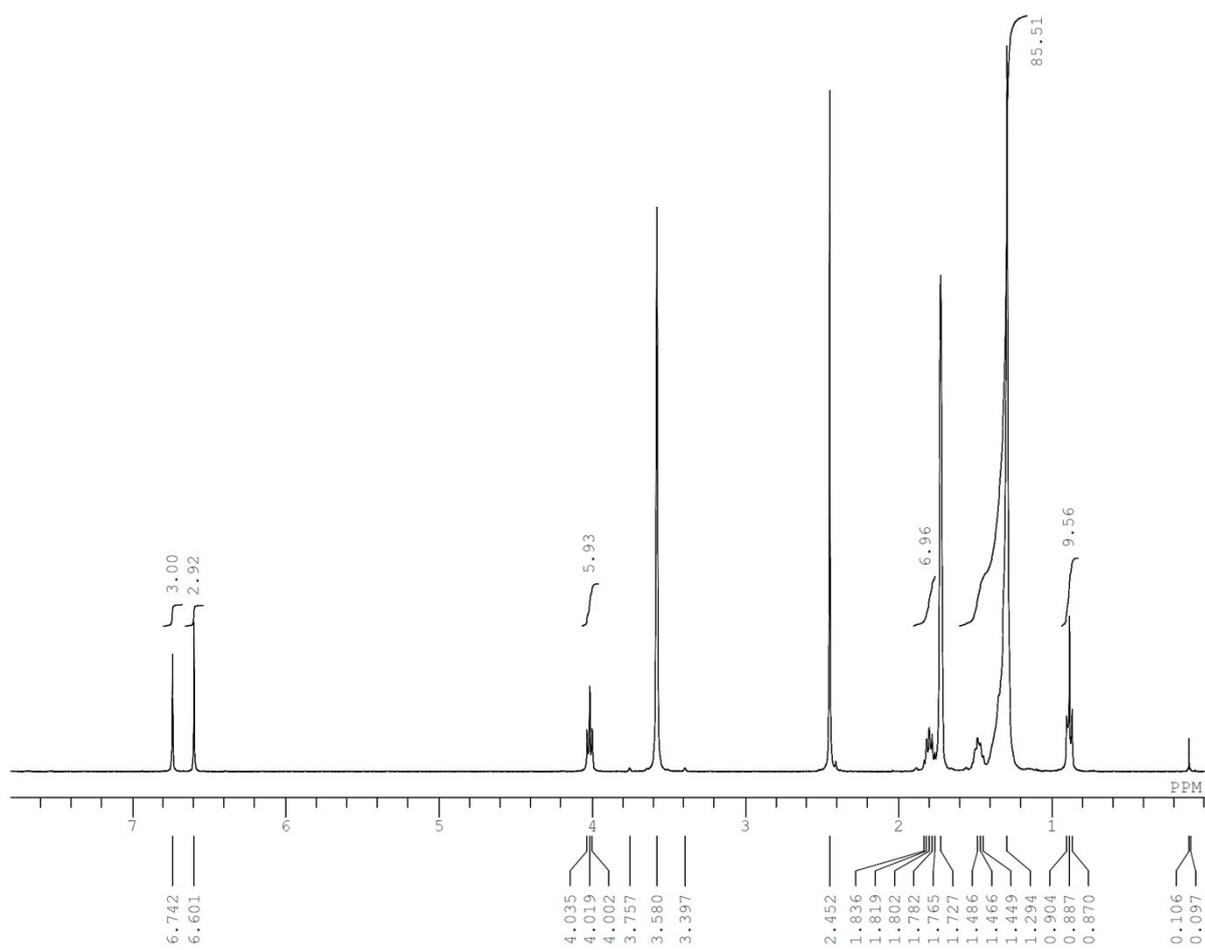
**Fig. S15** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2** in THF-*d*<sub>8</sub> at 30 °C.



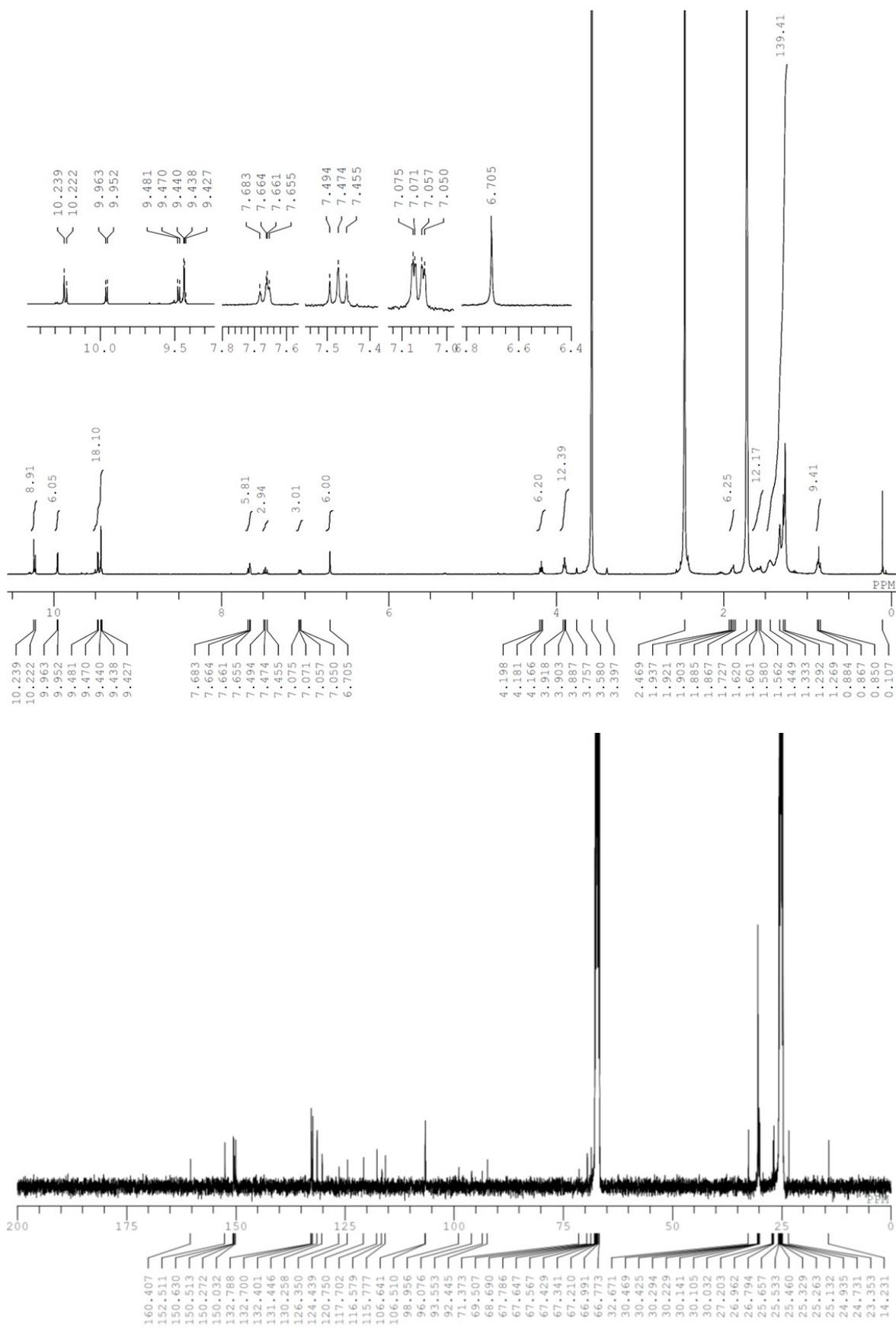
**Fig. S16**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **9** in  $\text{CDCl}_3$  at  $30^\circ\text{C}$ .



**Fig. S17**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **10** in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$ .

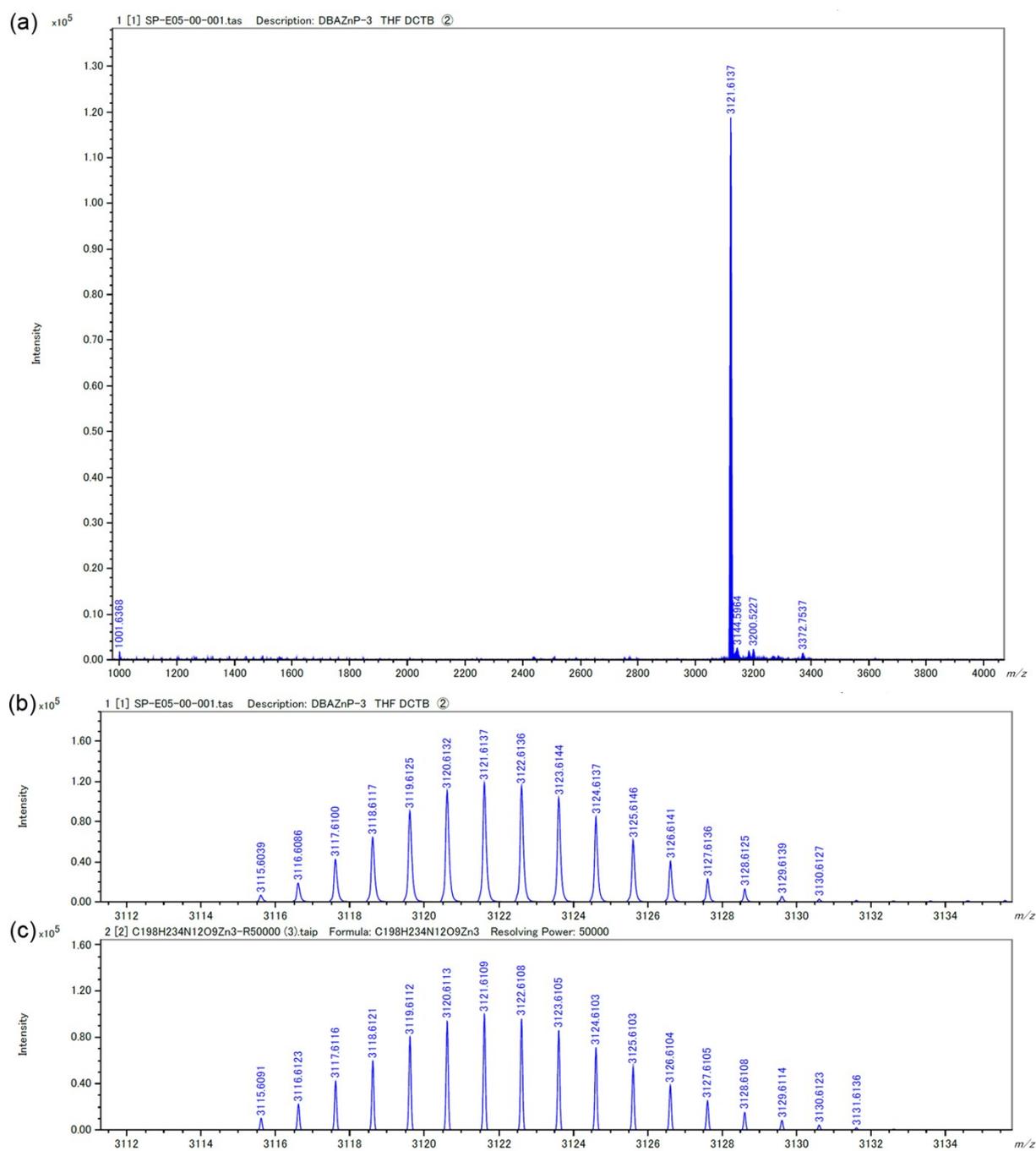


**Fig. S18**  $^1\text{H}$  NMR spectrum of **10** in  $\text{THF-}d_8$  at  $30\text{ }^\circ\text{C}$ .



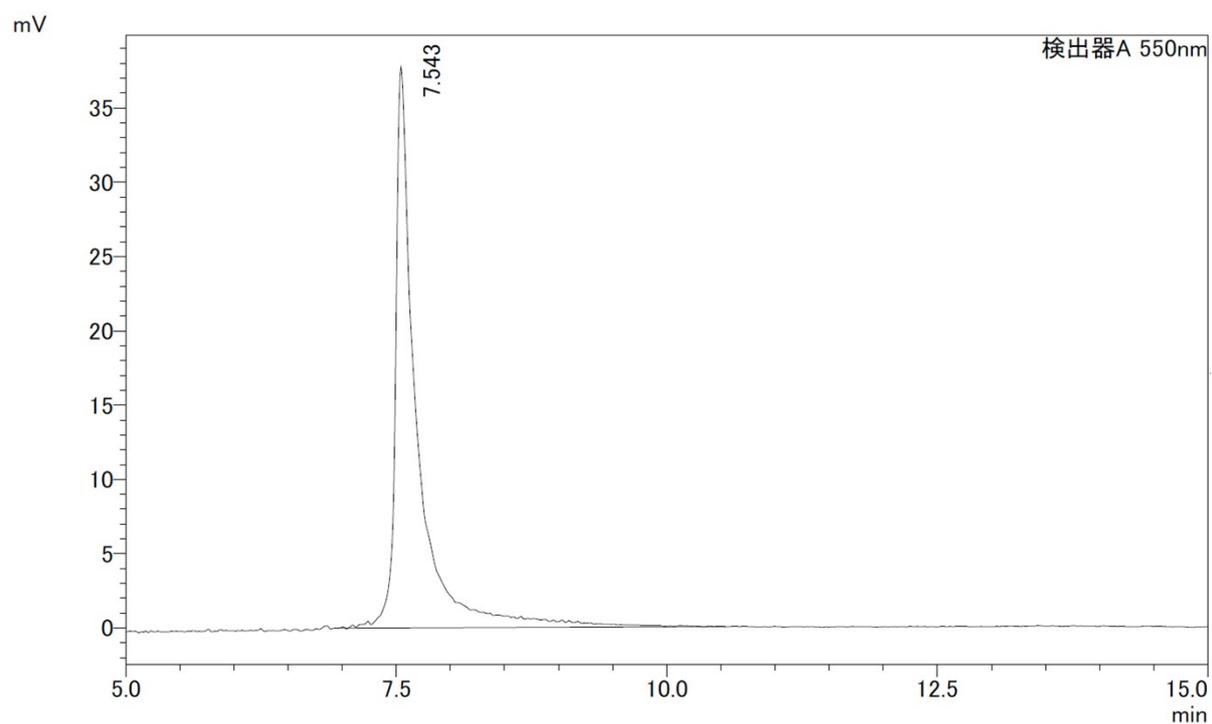
**Fig. S19**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1** in  $\text{THF-}d_8$  at  $30\text{ }^\circ\text{C}$ .

## 6. High resolution mass spectrum of 1.



**Fig. S20** (a) High resolution mass spectrum of **1**, (b) expanded spectrum for the molecular ion and (c) its simulation.

## 7. HPLC chromatogram of 1.



**Fig. S21** HPLC chromatogram of **1** using a reversed phase column (ODS) and  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  as the eluent mixed in a gradient mode from 100/0 (v/v) to 0/100 (v/v) (0–8 min) with a detection wavelength of 550 nm.

## 8. References

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