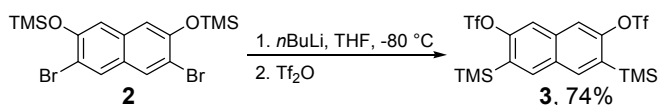


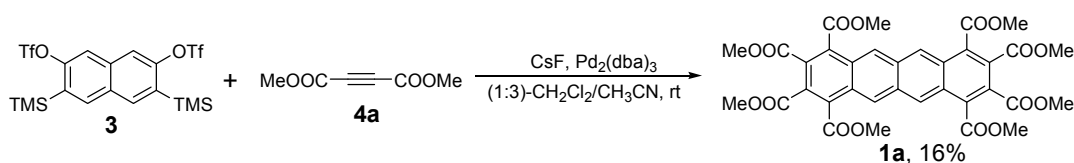
**General:** All reagents were commercially available and used without further purification. 3,6-Dibromo-2,7-bis(trimethylsilyloxy)naphthalene (**2**)<sup>1</sup> and dipropyl acetylenedicarboxylate (**4c**)<sup>2</sup> were prepared according to published literature procedures. Solvents for syntheses were purified by standard methods. All reactions were performed under nitrogen atmosphere. Column chromatography was performed on a Wako C-300 silica-gel column (45–75  $\mu\text{m}$ ). Melting points were measured on a Yanaco melting-point apparatus. <sup>1</sup>H and <sup>13</sup>C spectra were measured on a Bruker–Biospin DRX500 FT spectrometer. IR spectra of KBr pressed pellet samples were measured with a Shimadzu FTIR-8400 spectrometer. Elemental analyses were performed on a Yanaco MT-5 CHN corder. Absorption and fluorescence spectra in solution were measured on Hitachi U3500 and F2500 spectrophotometers, respectively. Fluorescence yields ( $\Phi_{\text{F}}$ ) in solution were determined using fluorescein ( $\Phi_{\text{F}} = 0.9$ ) in 0.1 M NaOH as the standard. Kubelka–Munk spectra were measured on a Hitachi U3010 spectrophotometer equipped with a  $\Phi 60$  integrating sphere attachment. Fluorescence spectra of solid-state samples were measured on a Hamamatsu Photonics PMA11 calibrated optical multichannel analyzer ( $\lambda_{\text{ex}} = 377 \text{ nm}$ ). Absolute quantum yields ( $\Phi_{\text{F}}$ ) were determined with a Labsphere IS-040-SF integrating sphere.

### Improved synthesis of 2,6-naphthodiyne precursor **3**:



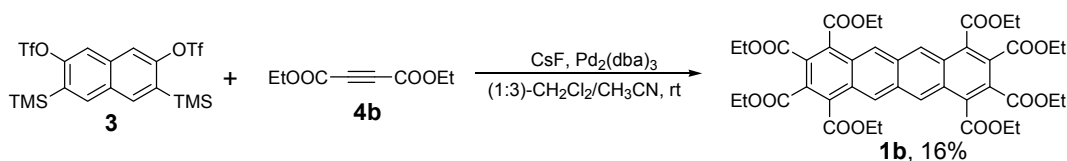
To a solution of **2** (6.00 g, 13.0 mmol) in THF (20 mL), 1.6 M *n*BuLi in hexane (19.4 mL, 31.0 mmol) was added dropwise at -80 °C, and the mixture was stirred for 30 min at -80 °C. Tf<sub>2</sub>O (3.8 mL, 42.8 mmol) was added dropwise, and the mixture was stirred for an additional 30 min, still at -80 °C. The mixture was then allowed to warm to room temperature. A saturated solution of Na<sub>2</sub>CO<sub>3</sub> in water was cautiously added, and the mixture was extracted with Et<sub>2</sub>O. The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvents were removed, and the residue was purified by column chromatography (hexane) on silica gel to give **3** (5.44 g, 74%) as a pale yellow solid (m.p. 55–56 °C; lit.<sup>1</sup> 70–72 °C). When purified **3** was kept at room temperature, it slowly decomposed over a period of 30 days. We therefore recommend that **3** be stored in a refrigerator to avoid decomposition. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.44 (s, 18H), 7.80 (s, 2H), 8.04 (s, 2H).

### Preparation of octamethyl tetracene-1,2,3,4,7,8,9,10-octacarboxylate **1a**:



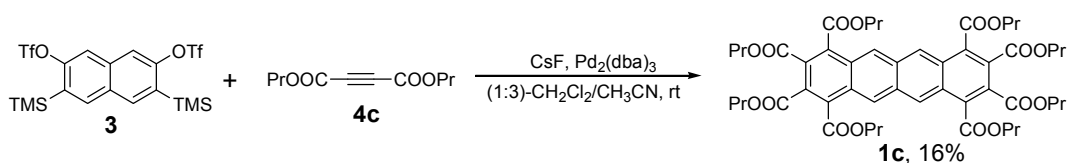
To a mixture of **3** (284 mg, 0.50 mmol), **4a** (0.60 mL, 4.88 mmol), and Pd<sub>2</sub>(dba)<sub>3</sub> (92 mg, 10 mol%) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and CH<sub>3</sub>CN (9 mL), CsF (612 mg, 4.04 mmol) was added, and the mixture was stirred at room temperature for 24 h in the dark. Insoluble substances were removed by filtration, the reaction mixture was evaporated, and the residue was roughly purified by column chromatography (toluene:AcOEt = 3:1). The product was dissolved in a small volume of CH<sub>2</sub>Cl<sub>2</sub>, and then Et<sub>2</sub>O was added. The resulting precipitate was collected on a membrane filter and dried under vacuum to give **1a** as a red solid (56 mg, 16%). M.p > 300 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.95 (s, 12H), 4.13 (s, 12H), 8.99 (s, 4H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 53.26, 53.49, 127.27, 127.30, 128.11, 131.33, 134.79, 166.32, 166.94; FT-IR (KBr): ν 1735.8, 1440.7, 1280.6, 1215.1, 1166.9, 1134.1, 1078.1 cm<sup>-1</sup>; MALDI-TOF-MS (negative mode) *m/z* 692.0 [M<sup>-</sup>]; elemental analysis: calcd (%) for C<sub>34</sub>H<sub>28</sub>O<sub>16</sub>: C 58.96, H 4.07; found C 59.00, H 4.25.

#### Preparation of octaethyl tetracene-1,2,3,4,7,8,9,10-octacarboxylate **1b**:



To a mixture of **3** (573 mg, 1.00 mmol), **4b** (1.6 mL, 10.0 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (92 mg, 10 mol%) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL) and CH<sub>3</sub>CN (18 mL), CsF (1.20 g, 7.92 mmol) was added. The mixture was stirred at room temperature for 96 h in the dark. Insoluble substances were removed by filtration, the reaction mixture was evaporated, and the residue was roughly purified by column chromatography (toluene:AcOEt = 10:1). The product was dissolved in a small volume of toluene, and then hexane was added. The resulting precipitate was collected by filtration and dried under vacuum to give **1b** as an orange solid (128 mg, 16%). M.p. 245–246.5 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.41 (t, *J* = 7.2 Hz, 12H), 1.48 (t, *J* = 7.2 Hz, 12H), 4.40 (q, *J* = 7.2 Hz, 8H), 4.60 (q, *J* = 7.2 Hz, 8H), 8.98 (s, 4H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 14.00, 14.04, 62.39, 62.67, 127.33, 127.38, 127.89, 131.29, 134.72, 165.98, 166.58; FT-IR (KBr): ν 1735.8, 1373.2, 1211.2, 1215.1, 1095.1, 1024.1 cm<sup>-1</sup>; MALDI-TOF-MS (negative mode) *m/z* 804.1 [M<sup>-</sup>]; elemental analysis: calcd (%) for C<sub>42</sub>H<sub>44</sub>O<sub>16</sub>: C 62.68, H 5.51; found C 62.48, H 5.54.

#### Preparation of octapropyl tetracene-1,2,3,4,7,8,9,10-octacarboxylate **1c**:



To a mixture of **3** (569 mg, 1.00 mmol), **4c** (2.00 g, 10.0 mmol), and  $\text{Pd}_2(\text{dba})_3$  (92 mg, 10 mol%) in  $\text{CH}_2\text{Cl}_2$  (6 mL) and  $\text{CH}_3\text{CN}$  (18 mL),  $\text{CsF}$  (631 mg, 8.06 mmol) was added. The mixture was stirred at room temperature for 96 h in the dark. Insoluble substances were removed by filtration, the reaction mixture was evaporated, and the residue was roughly purified by column chromatography (toluene:AcOEt = 20:1). The product was washed with hexane to remove impurities and dried under vacuum to give **1c** as an orange–yellow solid (148 mg, 16%). M.p. 155–157 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.02 (t,  $J = 7.4$  Hz, 12H), 1.05 (t,  $J = 7.4$  Hz, 12H), 1.74–1.81 (m, 8H), 1.82–1.89 (m, 8H), 4.28 (t,  $J = 6.8$  Hz, 8H), 4.49 (t,  $J = 6.8$  Hz, 8H), 8.97 (s, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.01, 10.51, 21.81, 21.83, 68.13, 68.31, 127.41, 127.48, 127.85, 131.31, 134.77, 166.11, 166.71; FT-IR (KBr):  $\nu$  1732.0, 1305.7, 1274.9, 1244.0, 1213.1, 1134.1  $\text{cm}^{-1}$ ; MALDI-TOF-MS (positive mode)  $m/z$ : 916.1 [ $\text{M}^+$ ]; elemental analysis calcd (%) for  $\text{C}_{50}\text{H}_{60}\text{O}_{16}$ : C 65.49, H 6.60; found C 65.56, H 6.69.

**X-ray crystallography:** Single crystals suitable for X-ray analysis were obtained by recrystallization from  $\text{CH}_3\text{CN}$  for **1a**, from  $\text{Et}_2\text{O}$  for **1b**, and from toluene for **1c**. X-ray data were collected using a Rigaku R-Axis RAPID 191R/FR-E with graphite-monochromated  $\text{Cu-K}\alpha$  ( $\lambda = 1.54178$  Å) radiation for **1a** and **1b**, and a Rigaku RAXIS RAPID with graphite-monochromated  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073$  Å) radiation for **1c**. The structures were solved by a direct method using SIR2004.<sup>[3]</sup> All non-H atoms were anisotropically refined by the full-matrix least-squares method on  $F^2$  using SHELXL97.<sup>4</sup> All H atoms were geometrically positioned and refined using a riding model with C–H = 0.95, 0.99, and 0.98 Å for aromatic, methylene, and methyl C, respectively;  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  except for methyl H [ $1.5U_{\text{eq}}(\text{C})$ ]. The refinement of **1c** was problematic, so "DELU" and "SIMU" restraints were applied to C18a and C18b. In addition, distance restraints were used to maintain sensible C18a–O5a, C18a–O6a, C18b–O5b, and C18b–O6b bonds. In **1c**, one ester moiety containing its inversion-symmetry part was disordered over two sites (O5a–C18a–O6a–C19a–C20a–C21a and O5b–C18b–O6b–C19b–C20b–C21b) with occupancies of 0.599(11) and 0.401(11), respectively. In addition, one propyl chain of the ester containing its inversion-symmetry part was disordered over two sites (C11–C12a–C13a and C11–C12b–C13b) with occupancies of 0.485(10) and 0.515(10), respectively. The values were determined by refining the site occupancies. All calculations were performed using the WinGX program package.<sup>5</sup> Crystallographic data have been deposited at Cambridge Crystallographic Data Centre:

deposition numbers are CCDC 812527 for **1a**, CCDC 812528 for **1b**, and CCDC 812529 for **1c**. Molecular structures are shown in Fig. S8–S10.

X-ray data for **1a**: C<sub>34</sub>H<sub>28</sub>O<sub>16</sub>,  $M_r = 692.56$ ,  $0.40 \times 0.04 \times 0.01 \text{ mm}^3$ , triclinic, space group  $P\bar{1}$ ,  $a = 5.9021(2)$ ,  $b = 12.0619(3)$ ,  $c = 12.1167(9) \text{ \AA}$ ,  $\alpha = 114.388(8)$ ,  $\beta = 95.781(7)$ ,  $\gamma = 95.404(7)^\circ$ ,  $V = 772.81(7) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.488 \text{ g cm}^{-3}$ ,  $\mu = 1.027 \text{ mm}^{-1}$ ,  $\lambda = 1.54178 \text{ \AA}$ ,  $T = 200 \text{ K}$ , 9625 reflections measured, 2764 unique, GOF = 1.065,  $R_1 = 0.0598$  and  $wR = 0.1593$  ( $I > 2\sigma(I)$ ).

X-ray data for **1b**: C<sub>42</sub>H<sub>44</sub>O<sub>16</sub>,  $M_r = 804.77$ ,  $0.40 \times 0.15 \times 0.10 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ ,  $a = 9.8822(7)$ ,  $b = 27.2631(5)$ ,  $c = 8.2149(6) \text{ \AA}$ ,  $\beta = 65.161(8)^\circ$ ,  $V = 2008.5(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.331 \text{ g cm}^{-3}$ ,  $\mu = 0.863 \text{ mm}^{-1}$ ,  $\lambda = 1.54178 \text{ \AA}$ ,  $T = 200 \text{ K}$ , 24742 reflections measured, 3662 unique, GOF = 1.074,  $R_1 = 0.0526$  and  $wR = 0.1498$  ( $I > 2\sigma(I)$ ).

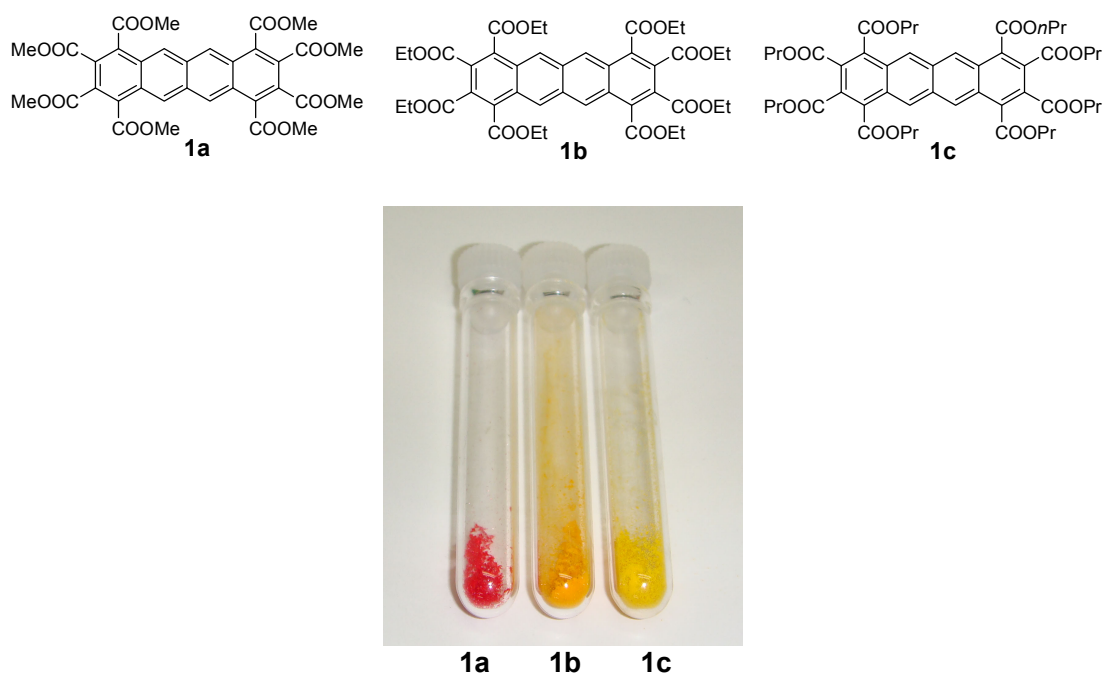
X-ray data for **1c**: C<sub>50</sub>H<sub>60</sub>O<sub>16</sub>,  $M_r = 916.98$ ,  $0.35 \times 0.19 \times 0.13 \text{ mm}^3$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.570(2)$ ,  $b = 10.081(2)$ ,  $c = 13.754(2) \text{ \AA}$ ,  $\alpha = 72.313(4)$ ,  $\beta = 73.227(4)$ ,  $\gamma = 73.558(4)^\circ$ ,  $V = 1182.3(4) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.288 \text{ g cm}^{-3}$ ,  $\mu = 0.096 \text{ mm}^{-1}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $T = 173 \text{ K}$ , 19549 reflections measured, 5390 unique, GOF = 0.969,  $R_1 = 0.0800$  and  $wR = 0.2080$  ( $I > 2\sigma(I)$ ).

**MO Calculations:** The lowest-energy absorption band of the tetracene molecule was calculated, based on the geometry obtained by X-ray analysis, by the TD-DFT B3LYP/6-31G\* method with the Gaussian 03 program package.<sup>6</sup>

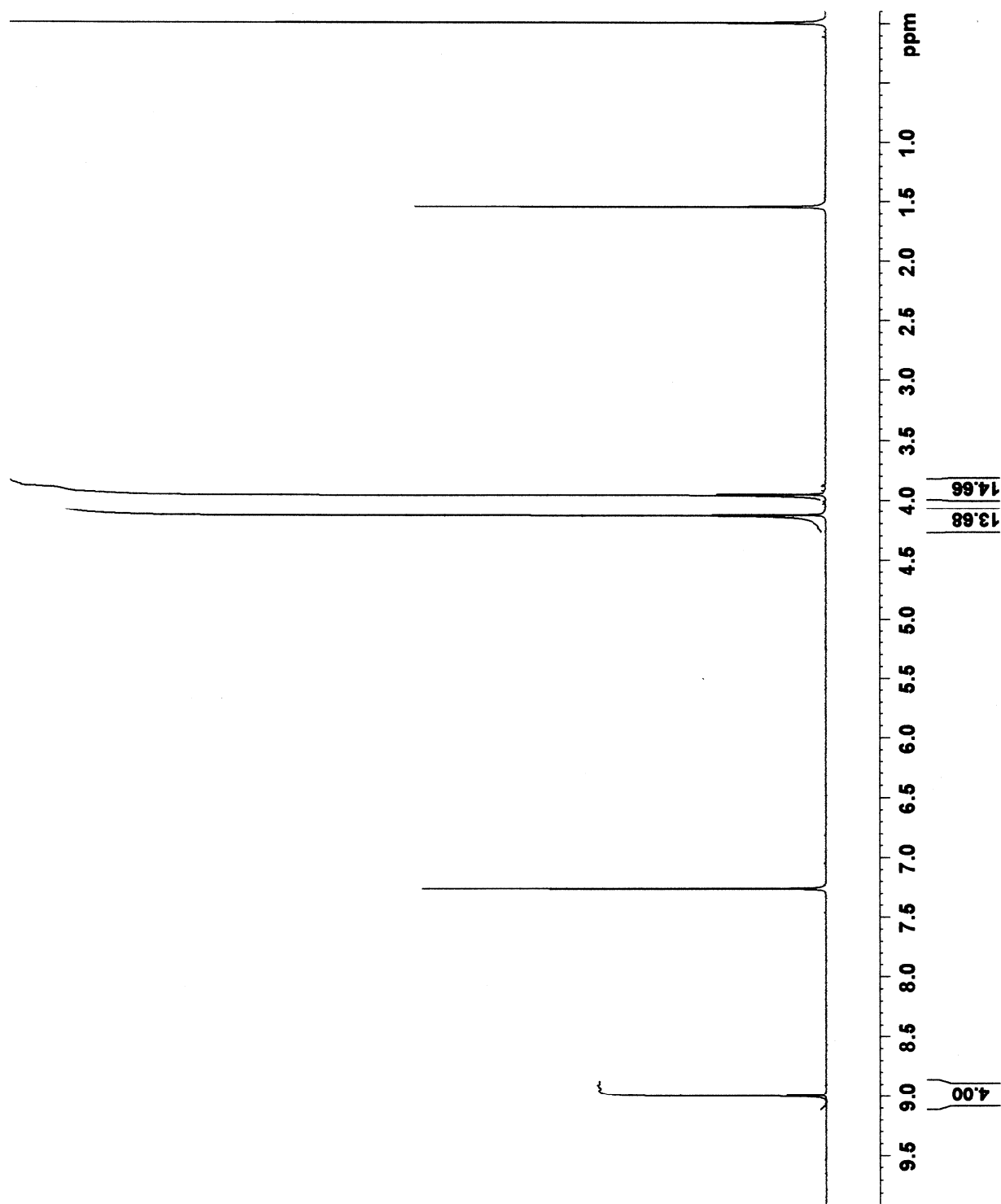
## References:

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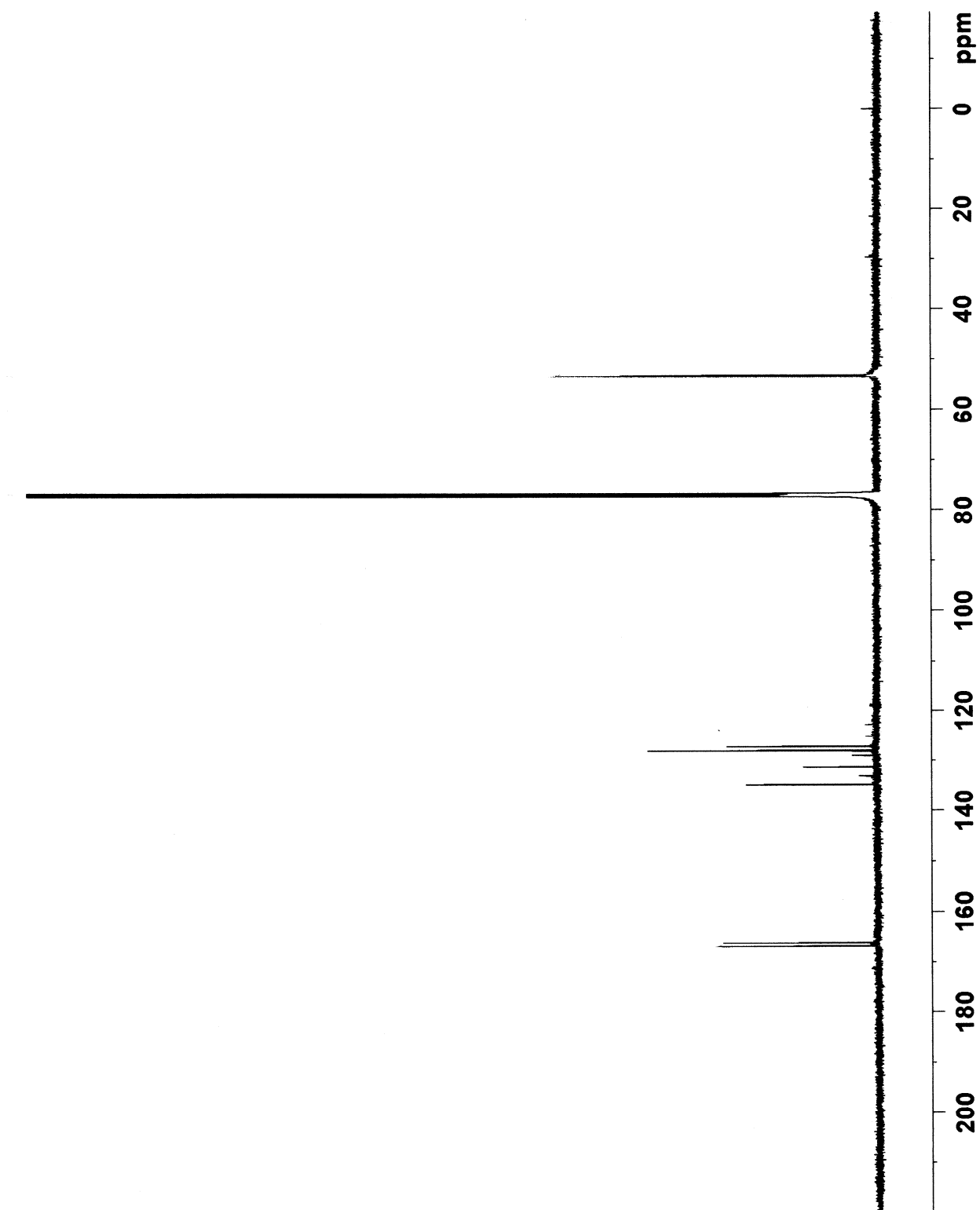
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**Fig. S1** Photograph of tetracenes **1a–c** in powder form.



**Fig. S2**  $^1\text{H}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ .



**Fig. S3**  $^{13}\text{C}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ .



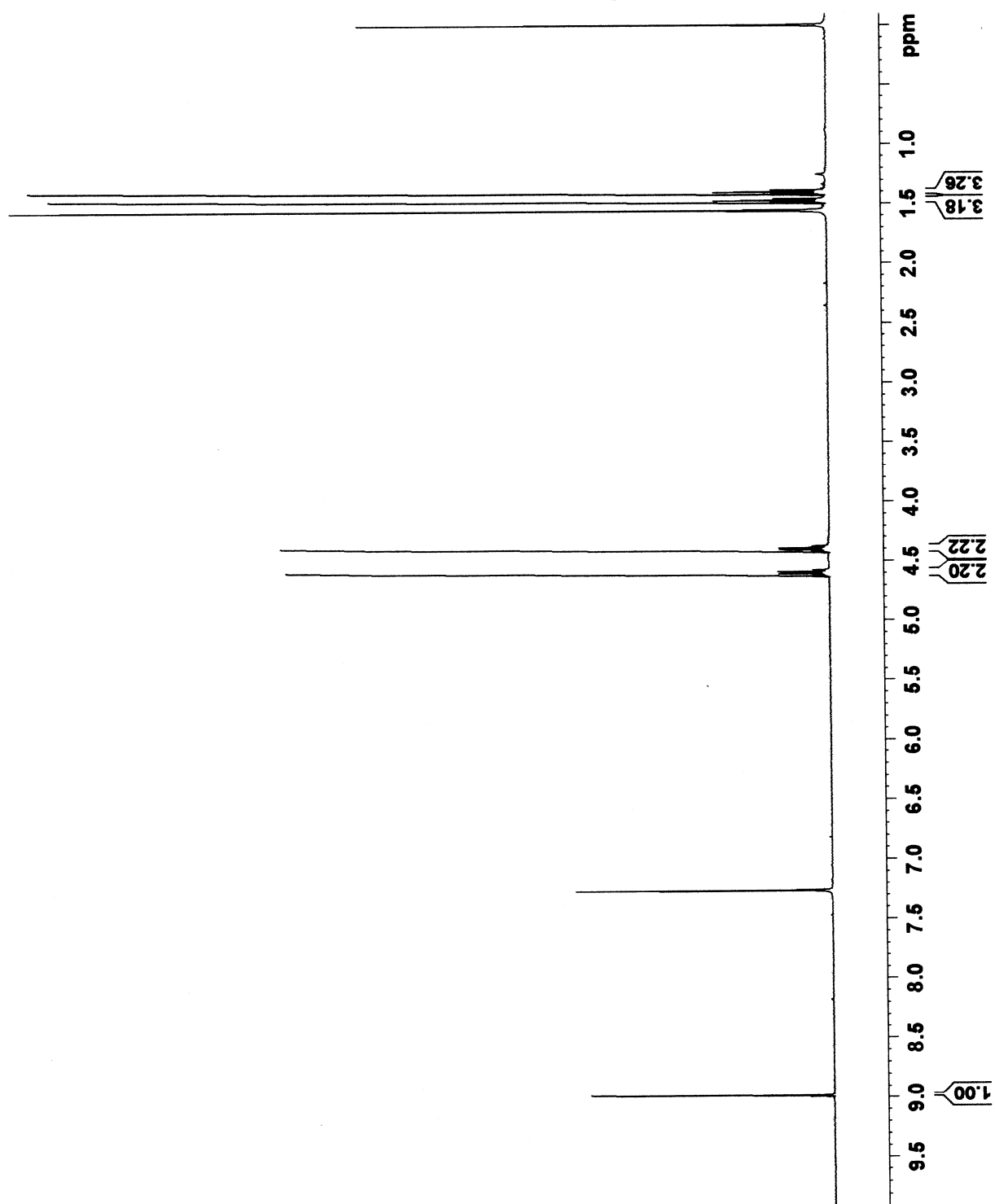
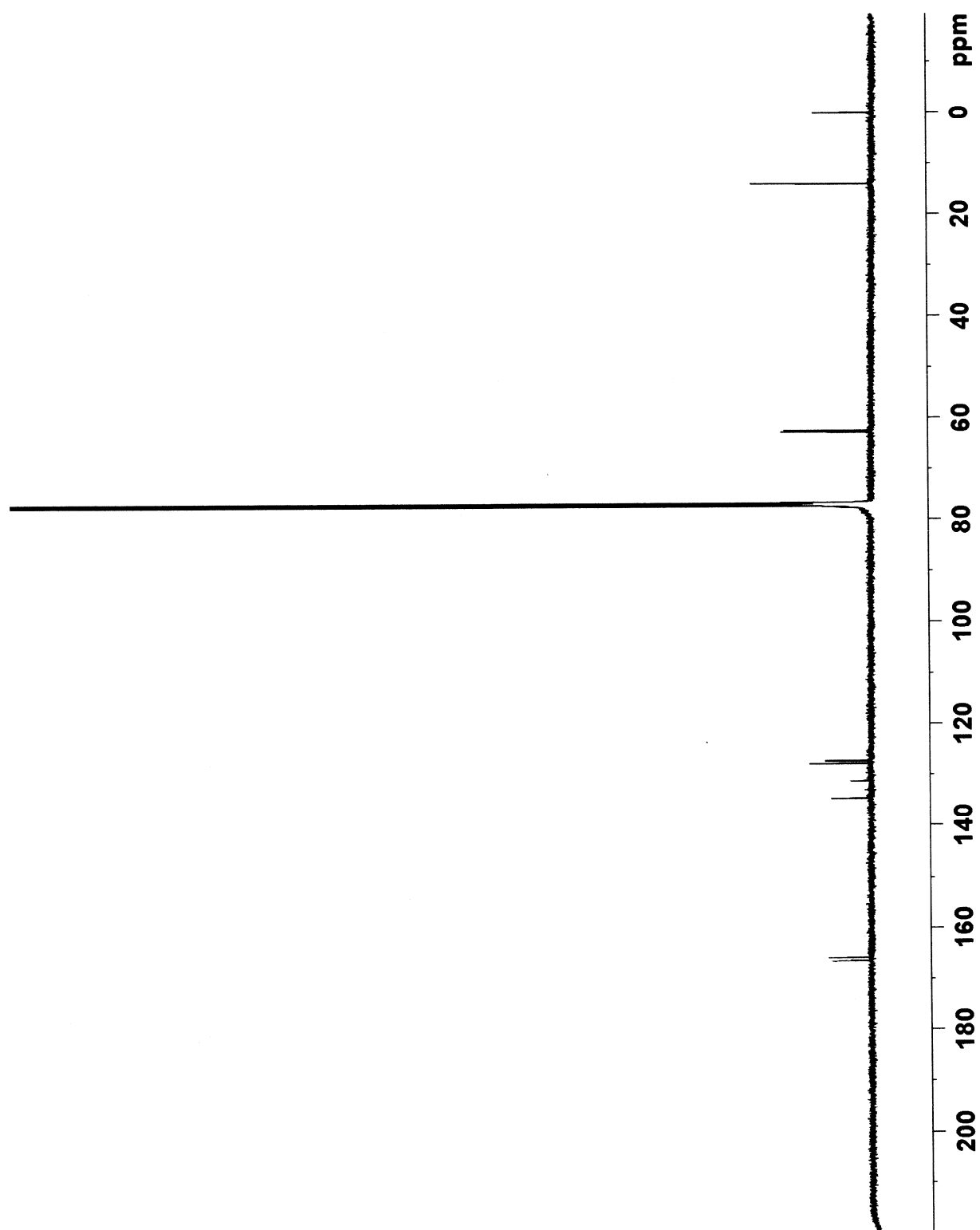
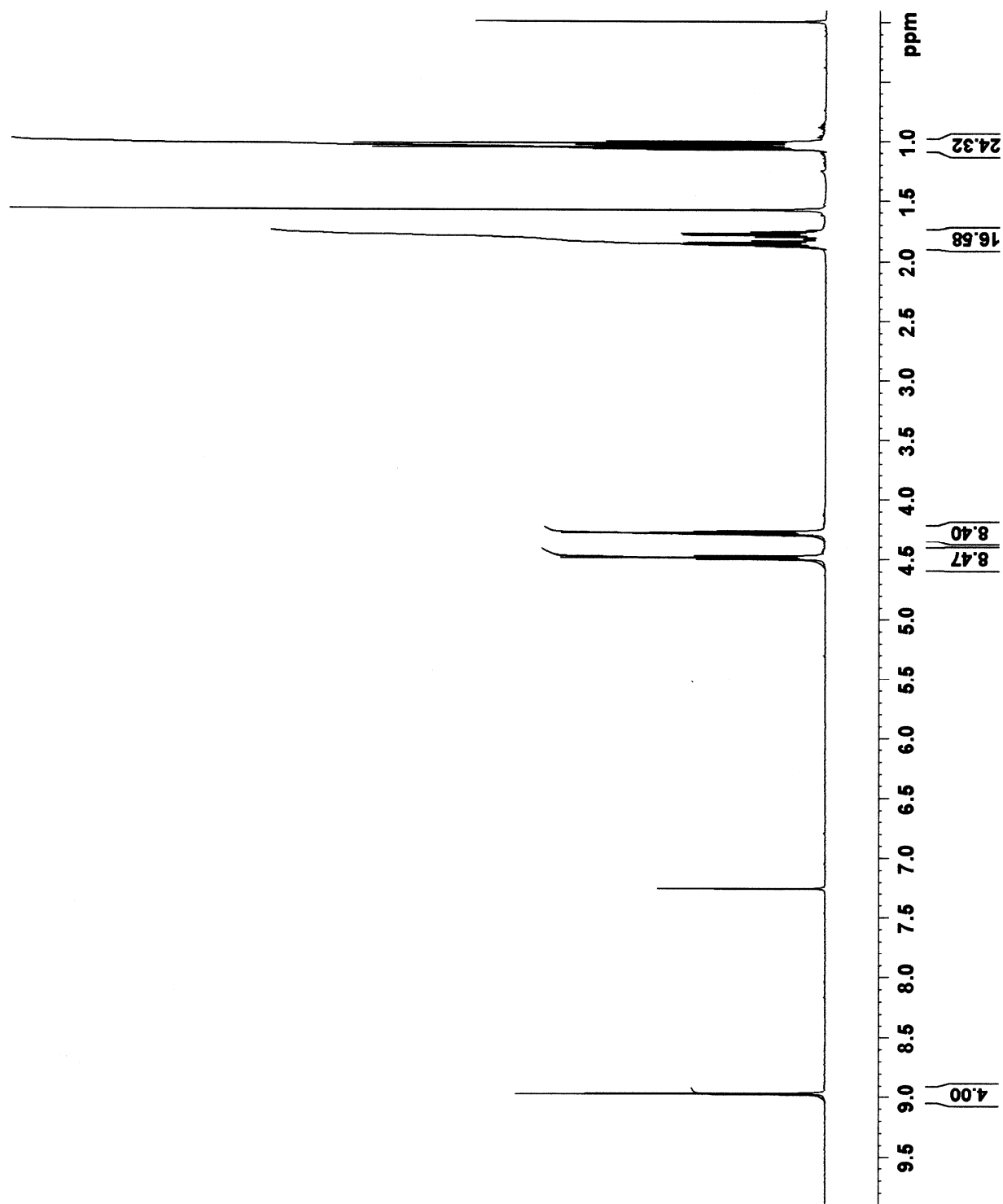


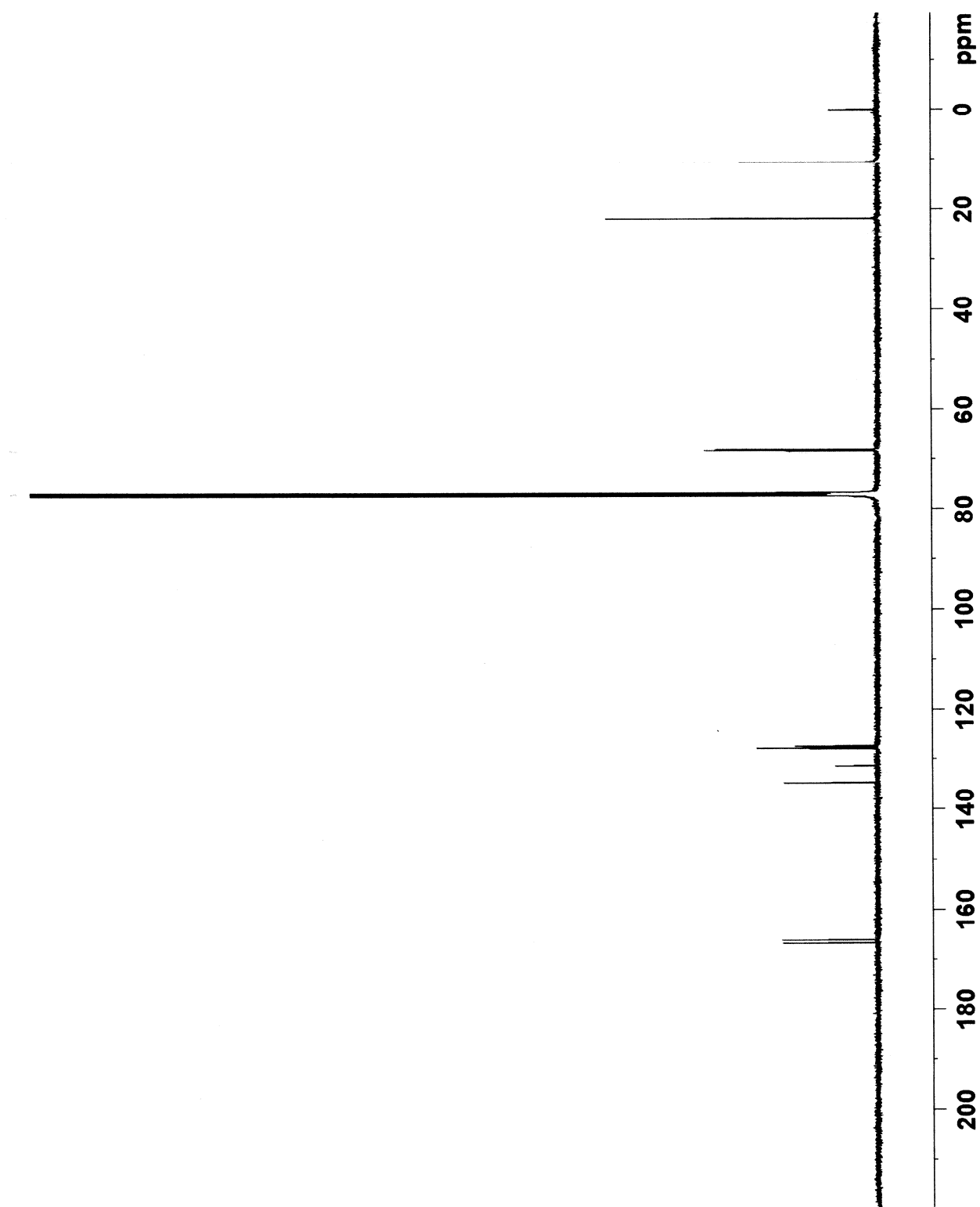
Fig. S4 <sup>1</sup>H NMR spectrum of **1b** in CDCl<sub>3</sub>.



**Fig. S5**  $^{13}\text{C}$  NMR spectrum of **1b** in  $\text{CDCl}_3$ .



**Fig. S6**  $^1\text{H}$  NMR spectrum of **1c** in  $\text{CDCl}_3$ .



**Fig. S7**  $^{13}\text{C}$  NMR spectrum of **1c** in  $\text{CDCl}_3$ .

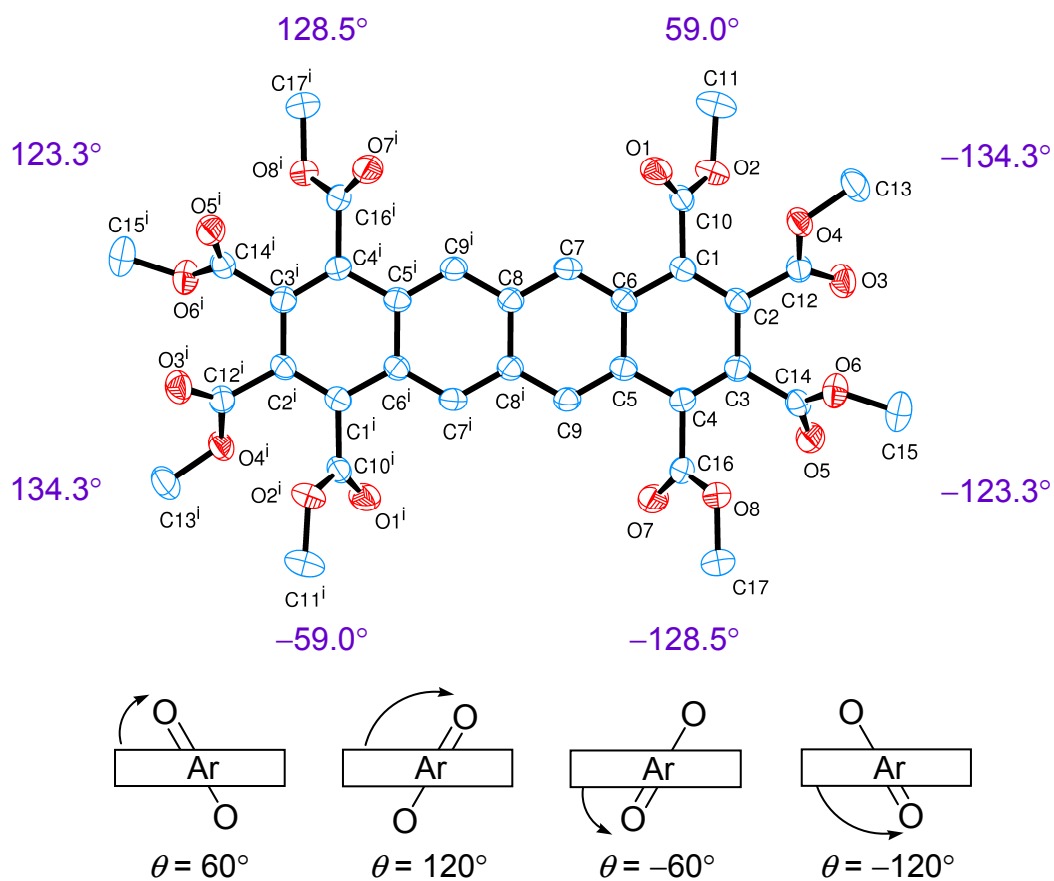
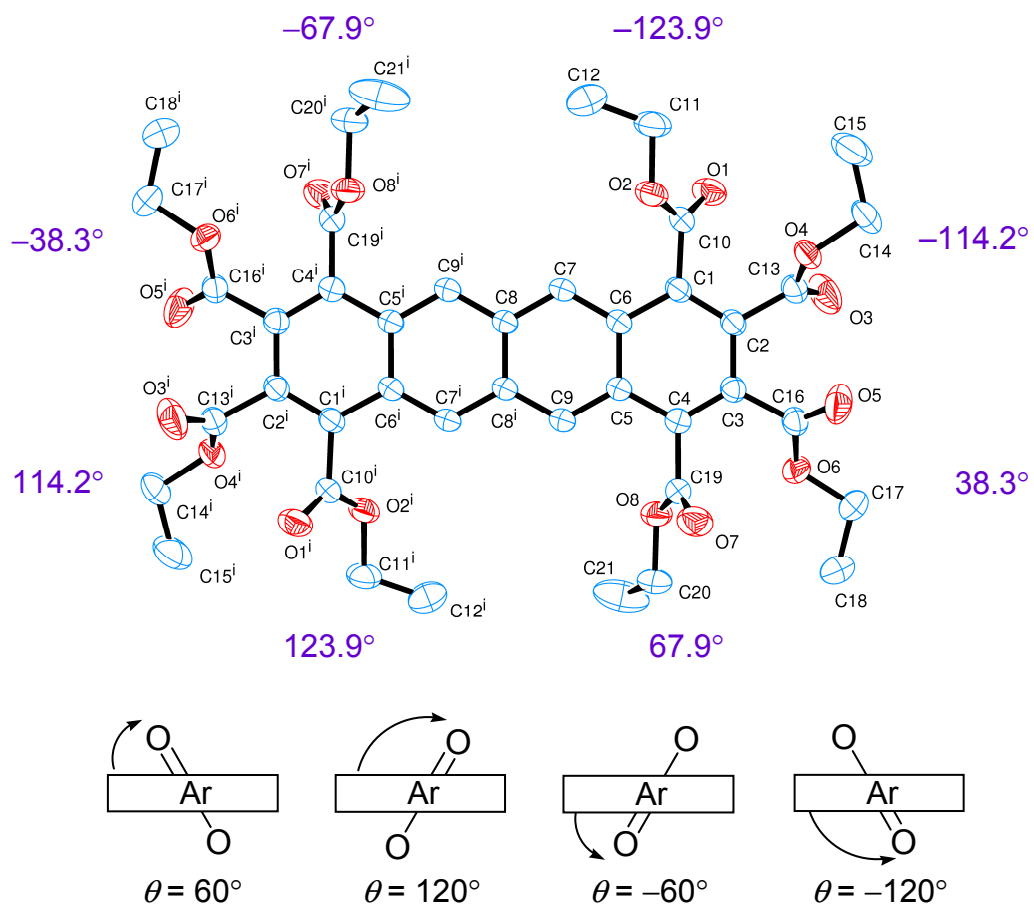


Fig. S8 Molecular structure of 1a.



**Fig. S9** Molecular structure of **1b**.

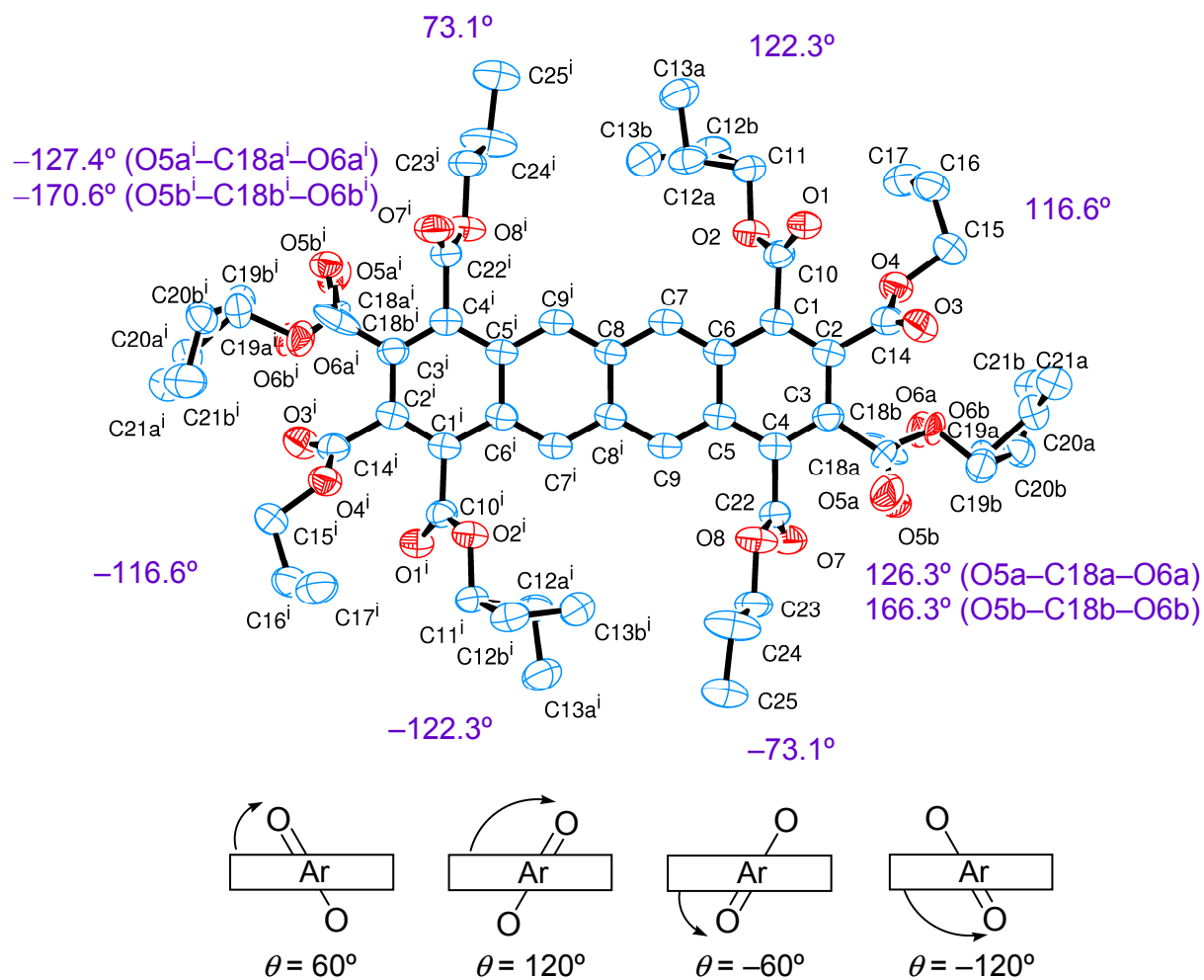


Fig. S10 Molecular structure of **1c**.

**Table S1** UV/Vis absorption and fluorescence properties of **1a–c** in CH<sub>3</sub>CN

Compd	Absorption	Fluorescence	
	$\lambda_{\max}^a/\text{nm}$ ( $\log \epsilon$ )	$\lambda_{\text{em}}^b/\text{nm}$	$\Phi_{\text{F}}^c$
<b>1a</b>	441 (3.44), 468 (3.64), 500 (3.57)	535	0.07
<b>1b</b>	439 (3.54), 467 (3.72), 498 (3.65)	532	0.07
<b>1c</b>	439 (3.54), 467 (3.72), 498 (3.65)	532	0.07

<sup>a</sup> Peaks based on the 0–0, 0–1, and 0–2 transitions. <sup>b</sup> Excited at 460 nm. <sup>c</sup> Fluorescence quantum yields were determined using fluorescein as the standard.

**Table S2** UV/Vis absorption and fluorescence properties of **1a–c** in the solid state

Compd	Absorption <sup>a</sup>		Fluorescence	
	$\lambda_{\max}/\text{nm}$	$\lambda_{\text{edge}}/\text{nm}$	$\lambda_{\text{em}}^b/\text{nm}$	$\Phi_{\text{F}}^c$
<b>1a</b>	— <sup>d</sup>	605	625	0.06
<b>1b</b>	508	582	580, 603	0.05
<b>1c</b>	503	554	563, 601	0.13

<sup>a</sup> Kubelka–Munk spectra of a diluted pellet. <sup>b</sup> Excited at 377 nm. <sup>c</sup> Absolute quantum yield in the solid state. <sup>d</sup> Maximum peak was not observed.



**Table S3** TD-DFT computational values

Compd	Energy/Hartree	Excitation energy/eV	Wavelength/nm	Oscillator strength
<b>1a</b>	-2515.80640971	2.3070	537.43	0.0432
		3.2266	384.26	0
		3.2571	380.66	0.0004
		3.5746	346.85	0
<b>1b</b>	-2830.17255812	2.3811	520.71	0.0525
		3.2911	376.73	0.0126
		3.3874	366.02	0
		3.5581	348.45	0
<b>1c</b>	-3144.47523993	2.2939	540.50	0.0812
		3.1522	393.33	0.0187
		3.2571	380.65	0
		3.3711	367.78	0

TD-DFT calculations were performed at the B3LYP/6-31G\* level based on the geometry obtained by X-ray analysis using Gaussian 03.