

Supplementary Information for

**Open-circuit-voltage shift of over 0.5 V in organic photovoltaic cells  
induced by a minor structural difference in alkyl substituents**

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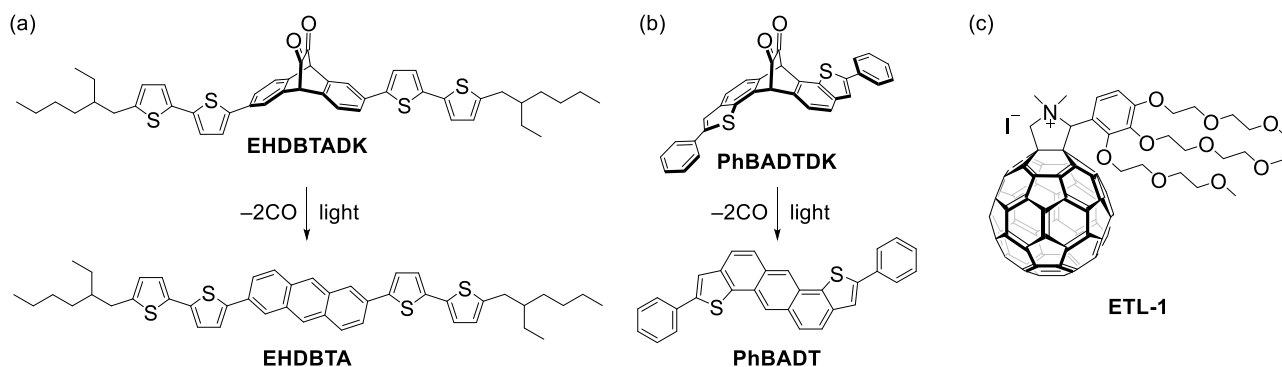
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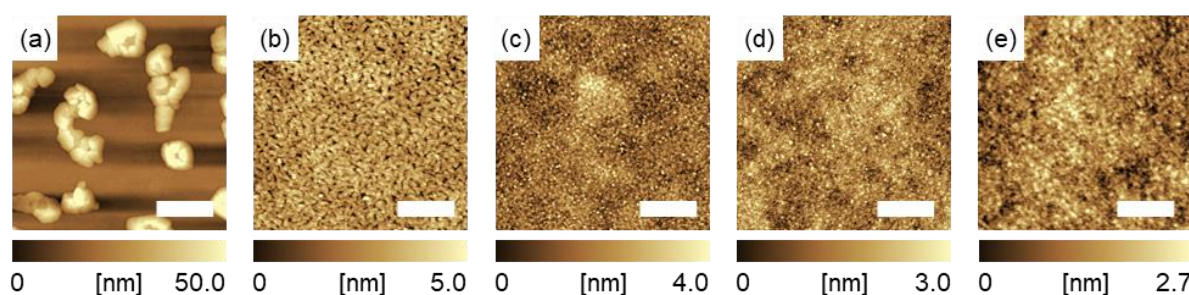
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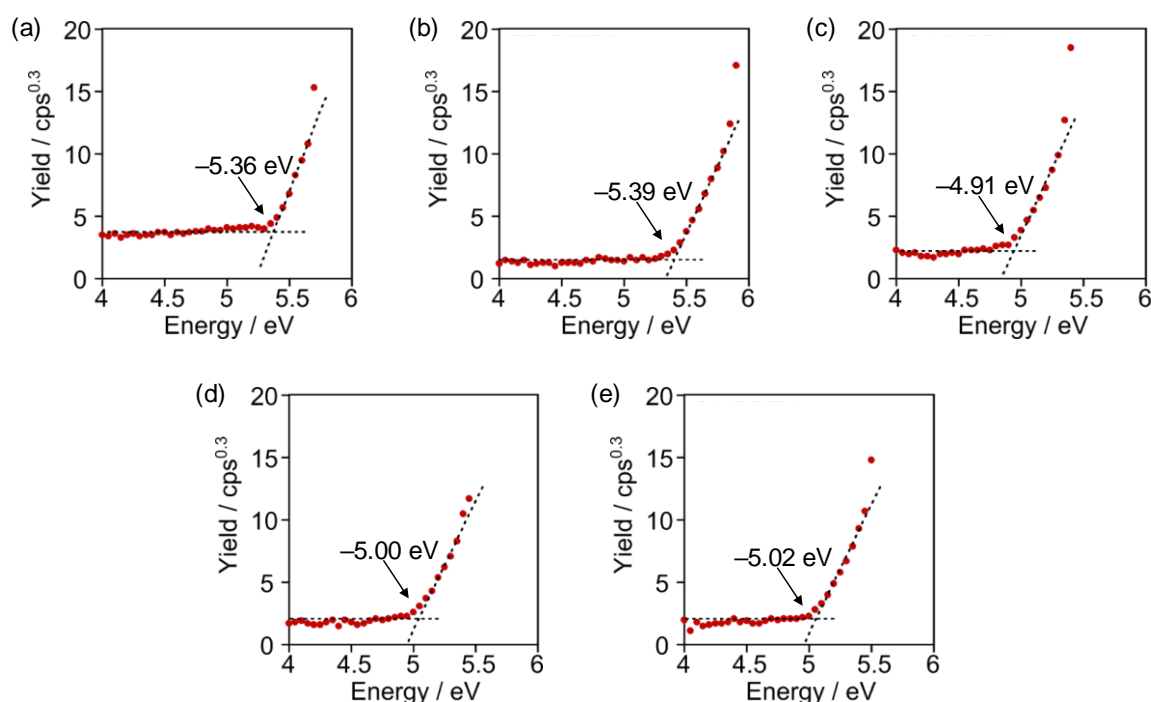
## 1. Supplementary Figures and Tables



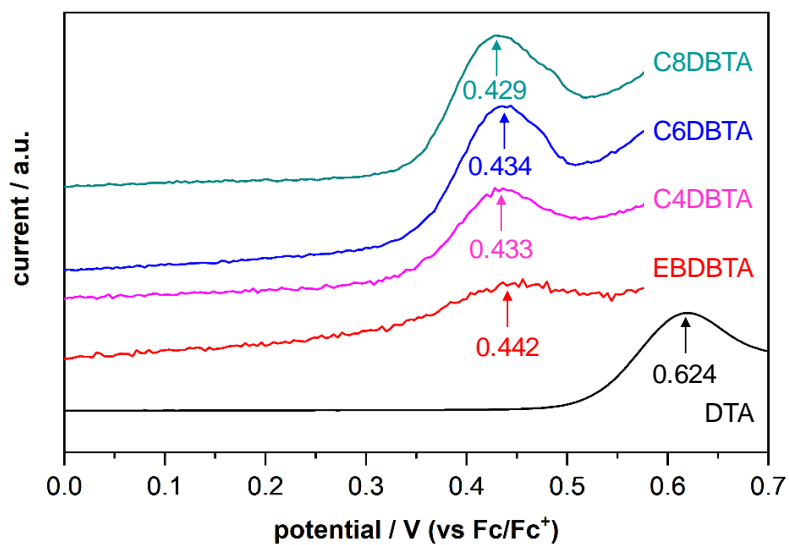
**Fig. S1** Chemical structures: (a) EHTBTA and its photoprecursor EHTBTADK (b) PhBADT and its photoprecursor PhBADTDK, (c) ETL-1.<sup>S1-3</sup>



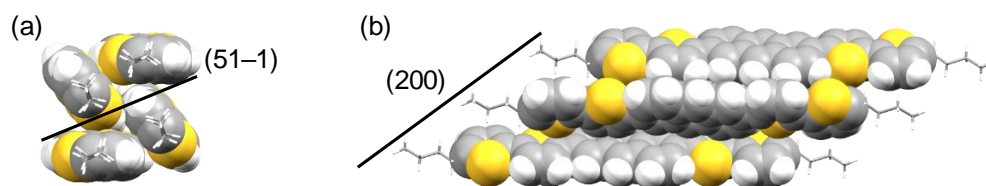
**Fig. S2** Surface topology of the i-layers probed by AFM. (a) DTA:PC<sub>71</sub>BM ( $R_{\text{RMS}} = 10.83$  nm); (b) EBDBTA:PC<sub>71</sub>BM ( $R_{\text{RMS}} = 0.87$  nm); (c) C4DBTA:PC<sub>71</sub>BM ( $R_{\text{RMS}} = 0.65$  nm); (d) C6DBTA:PC<sub>71</sub>BM ( $R_{\text{RMS}} = 0.53$  nm); (e) C8DBTA:PC<sub>71</sub>BM ( $R_{\text{RMS}} = 0.49$  nm). The scale bars correspond to 0.5  $\mu\text{m}$ . Samples were prepared by the same method and conditions as device preparation with the general configuration of [Glass/ITO/PEDOT:PSS/PhBADT/(DTA or RDBTA):PC<sub>71</sub>BM (2:1 w/w)].



**Fig. S3** PESA data of thin films prepared via the photoprecursor approach on glass/ITO substrates: (a) DTA, (b) EBDBTA, (c) C4DBTA, (d) C6DBTA, (e) C8DBTA.



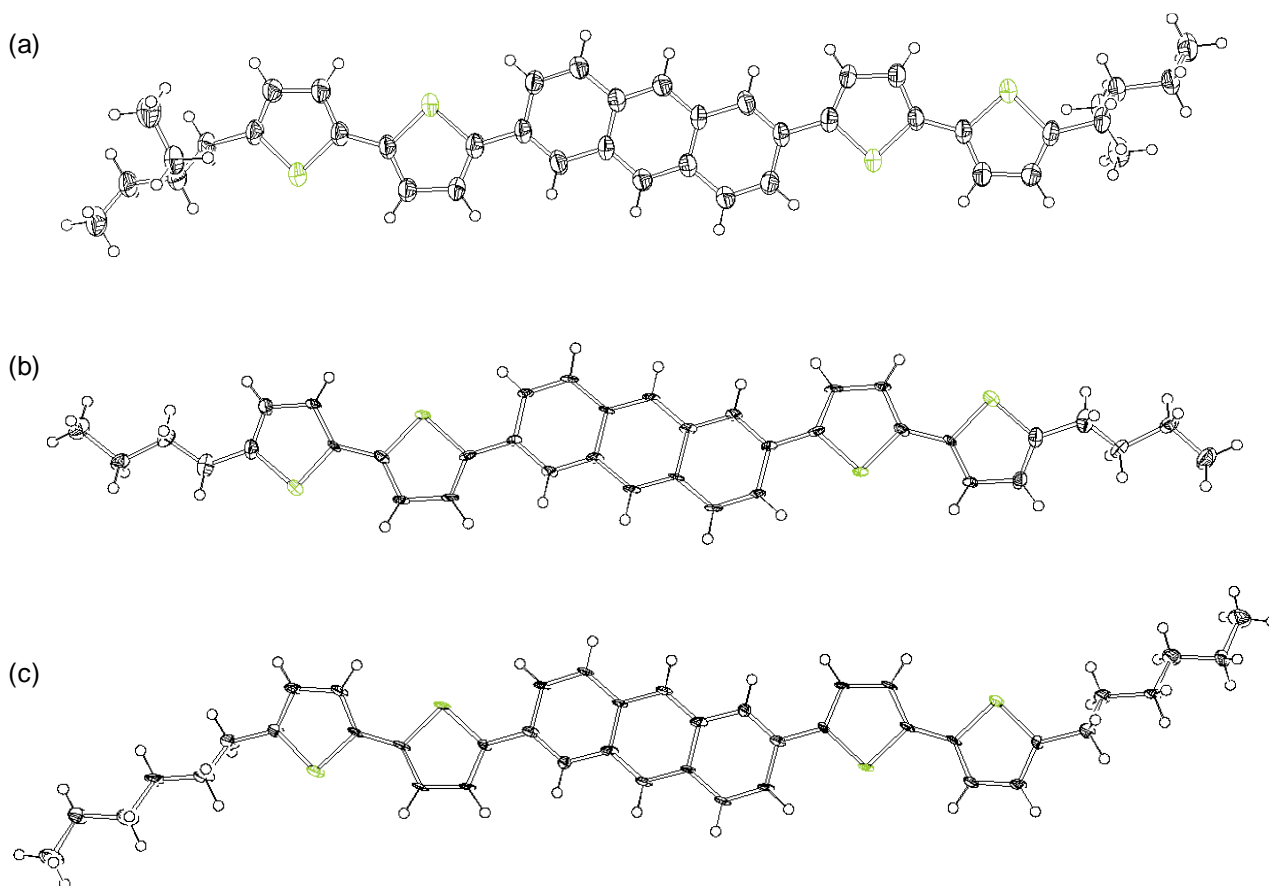
**Fig. S4** Differential pulse voltammograms of DTA, EBDBTA, C4DBTA, C6DBTA, and C8DBTA saturated in degassed *o*-dichlorobenzene/benzonitrile (9:1 v/v) containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>. Pulse amplitude: 50 mV, scan rate: 10 mV s<sup>-1</sup>, W.E.: glassy carbon (φ 1 mm), C.E.: Pt, R.E.: Ag/AgCl.



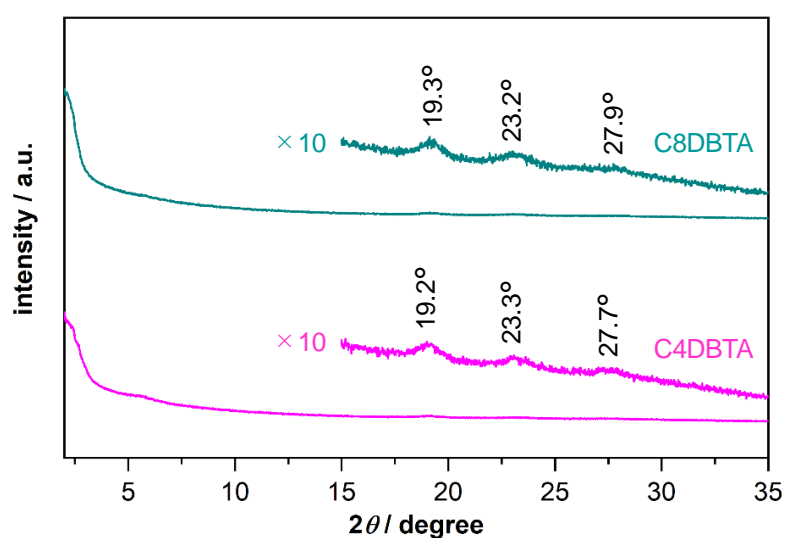
**Fig. S5** Molecular packing of C4DBTA in the single crystalline state. Black lines indicate approximate positions of the crystal planes relevant to the slipped herringbone motifs.

**Table S1** Single-crystal X-ray diffraction parameters and crystal data.

	EBDBTA	C4DBTA	C6DBTA
formula	C <sub>42</sub> H <sub>42</sub> S <sub>4</sub>	C <sub>38</sub> H <sub>34</sub> S <sub>4</sub>	C <sub>42</sub> H <sub>42</sub> S <sub>4</sub>
formula weight	675.03	618.89	674.99
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	22.150(3)	41.708(10)	23.82(3)
<i>b</i> (Å)	5.7413(7)	5.7563(10)	5.837(6)
<i>c</i> (Å)	13.1188(16)	12.670(3)	12.500(14)
$\alpha$ (deg.)	90	90	90
$\beta$ (deg.)	95.850(7)	98.46(2)	104.133(18)
$\gamma$ (deg.)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1659.6(4)	3008.7(11)	1685(3)
<i>Z</i>	2	4	2
<i>T</i> (K)	150	293	90
crystal size (mm <sup>3</sup> )	0.11 × 0.11 × 0.01	0.20 × 0.05 × 0.01	0.15 × 0.10 × 0.01
2 $\theta$ <sub>min</sub> , 2 $\theta$ <sub>max</sub> (deg.)	6.24, 50.70	3.95, 46.99	3.53, 47.00
reflections collected	20577	6462	6554
independent reflections	3019 ( <i>R</i> <sub>int</sub> = 0.1552)	2237 ( <i>R</i> <sub>int</sub> = 0.1835)	2474 ( <i>R</i> <sub>int</sub> = 0.1576)
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1411, 0.2772	0.1902, 0.2208	0.1864, 0.2799
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0965, 0.2486	0.1043, 0.1784	0.1165, 0.2407
GOF on <i>F</i> <sup>2</sup>	1.118	1.089	1.089
largest diff. peak and hole (e Å <sup>-3</sup> )	0.46, -0.53	0.408, -0.424	1.145, -0.535
CCDC number	1956923	1956921	1956922



**Fig. S6** Thermal ellipsoid plots of the molecular structures determined by single-crystal X-ray diffraction analysis: (a) EBDBTA, (b) C4DBTA, (c) C6DBTA. One of the two disordered conformations of the butyl groups are shown for C4DBTA. Thermal ellipsoids are scaled at 50% probability.



**Fig. S7** Thin-film XRD profiles of C4DBTA and C8DBTA. For C4DBTA, the 200 diffraction corresponding to the packing along the long molecular axis in the single-crystal structure was expected at  $2\theta = 4.3^\circ$ , but not detected. On the other hand, higher-angle peaks assignable to the herringbone motif were observed at  $2\theta = 19.2^\circ$  (51–1),  $23.3^\circ$  (100–2), and  $27.7^\circ$  (91–2).

## 2. Experimental

### 2.1. General

All reactions were carried out under argon unless otherwise noted. “Room temperature” (rt) means 15–25 °C. Flash column chromatography was performed on silica gel purchased from Kanto Chemical (Silica Gel 60N, 60 Å, 40–50 µm). Analytical thin-layer chromatography (TLC) was conducted on Merck 200-µm thickness silica-gel plates with a fluorescent indicator (1.05554.0001). Visualization of TLC was accomplished with UV light at 254 nm. <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a JEOL JNM-ECX 400P (400 MHz), JNM-ECX 500 (500 MHz), or JNM-ECA 600 (600 MHz) at 294 K using tetramethylsilane as internal standard. High-resolution electrospray ionization (ESI) mass spectra were measured on a JEOL AccuTOF/JMS-T100LC mass spectrometer.

### 2.2. Materials

Solvents and chemical reagents for synthesis were reagent grade obtained from commercial sources and used without further purification unless otherwise noted. Dibromide **1** (Scheme S1),<sup>S1</sup> 2-(tri-*n*-butylstannyl)-5-hexylthiophene,<sup>S4</sup> and ETL-1<sup>S3</sup> were prepared as described in literature. [6,6]-Phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) was purchased from Luminescence Technology Crop. and used as received.

### 2.3. Fabrication and evaluation of photovoltaic cells

Indium–tin oxide (ITO)-patterned glass substrates (20 × 20 mm<sup>2</sup>, 15 Ω per square) were cleaned by gentle rubbing with an acetone-soaked wipe for about 5 s, sequential sonication in Semicoclean 56 (Furuuchi Chemical Co.), distilled water, and isopropanol for 10 min each, and then drying with a flow of N<sub>2</sub> gas. The cleaned substrates were further treated in a UV–O<sub>3</sub> cleaner (BioForce Nanosciences TC-003) for 20 min, and then poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS, Clevious P VP AI4083) was spin-coated on the substrates at 3000 rpm for 30 s before thermally annealed at 130 °C for 10 min in air. The thickness of the resulting PEDOT:PSS layer was about 25 nm. The substrates were then transferred to a N<sub>2</sub>-filled glovebox (<5 ppm of O<sub>2</sub> and H<sub>2</sub>O) for preparation of p–i–n-type active layers. The p-sublayer was prepared by spin-coating of PhBADTDK (1 mg mL<sup>-1</sup> in CHCl<sub>3</sub>, 800 rpm, 30 s) followed by irradiation with a

blue LED (470 nm, 400 mW cm<sup>-2</sup>, 10 min). The i-sublayer was prepared by spin-coating of DTADK:PC<sub>71</sub>BM or RDBTADK:PC<sub>71</sub>BM (2:1 by weight) (10 mg mL<sup>-1</sup> in CHCl<sub>3</sub>, 800 rpm, 30 s) followed by irradiation with a blue LED (470 nm, 400 mW cm<sup>-2</sup>, 30 min). At this point, organic layers were exposed to the vapor of tetrahydrofuran for 60 s at rt in a covered Petri dish for annealing. The n-sublayer was then prepared by spin-coating of PC<sub>71</sub>BM (5 mg mL<sup>-1</sup> in CHCl<sub>3</sub>, 800 rpm, 30 s). The cathode buffer, ETL-1<sup>S3</sup> (see Fig. S1 for structure), was spin-coated from a 0.5 mg mL<sup>-1</sup> solution in MeOH (800 rpm, 30 s). Finally, each substrate was transferred to a vacuum-evaporation equipment without exposing to air, and Al (80 nm) was vapor-deposited at ~10<sup>-4</sup> Pa (10 Å s<sup>-1</sup>) through a shadow mask that defined an active area of 2 × 2 mm<sup>2</sup>. Thus fabricated devices were encapsulated with a glass plate and UV-cure resin in a glove box before measurements for evaluation.

Current-density–voltage (*J–V*) curves were measured using a Keithley 2400 source measurement unit under simulated AM 1.5G illumination at an intensity of 100 mW cm<sup>-2</sup> using a solar simulator (Bunkoukeiki CEP-2000RF). The external quantum efficiency (EQE) spectra were obtained under illumination of monochromatic light using the same system.

#### 2.4. Measurements of optoelectronic properties of thin films

Thin-film samples for the photoelectron spectrometry measurements were prepared on glass/ITO substrates by spin-coating of the photoprecursors from a 10 mg mL<sup>-1</sup> solution in CHCl<sub>3</sub> at 800 rpm for 30 s, followed by irradiation with a blue LED at 400 mW cm<sup>-2</sup> for 30 min. Samples for photoabsorption measurements were prepared similarly, but on glass plates without ITO coating. Ionization energies were determined from the onset of photoelectron spectra obtained with a Riken Keiki AC-3 photoelectron spectrometer. UV–vis absorption spectra were measured on a JASCO V-650 spectrophotometer.

#### 2.5. Computation

Energy calculations on single-crystal X-ray structures were performed at the PBEPBE/6-31G(d) level of theory using the Gaussian 09 program suite. The full citation of this software is:

*Gaussian 09, Revision E.01*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li,



X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

## 2.6. Single-crystal X-ray crystallography

Single crystals of EB, C4, and C6DBTA were obtained by leaving a solution of the corresponding DK-type photoprecursor in a closed amber ampoule under room fluorescent light. The solvent was *o*-dichlorobenzene, and the solutions were deoxygenized by bubbling with argon before the ampoules were flame-sealed. In this way, the photoreactions to form the target compounds progressed slowly enough to form crystals suitable for the single-crystal X-ray diffraction analysis. Diffraction data of EBDBTA were collected on a Rigaku VariMax X-ray structure analyzer with RAPID using Mo-K $\alpha$  radiation, whereas those of C4 and C6DBTA were recorded with a BRUKER APEXII X-ray diffractometer using Mo-K $\alpha$  radiation equipped with a large-area CCD detector. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares using the CrystalClear and SHELXS-2000 program. CCDC 1956921–1956923 contain these crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Visualization and analysis of the crystal structures were performed using Mercury of Cambridge Crystallographic Data Centre. The thermal-ellipsoid plots were generated using ORTEP-3 for Windows. The citations of these software are:

*Mercury*. Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453–457.

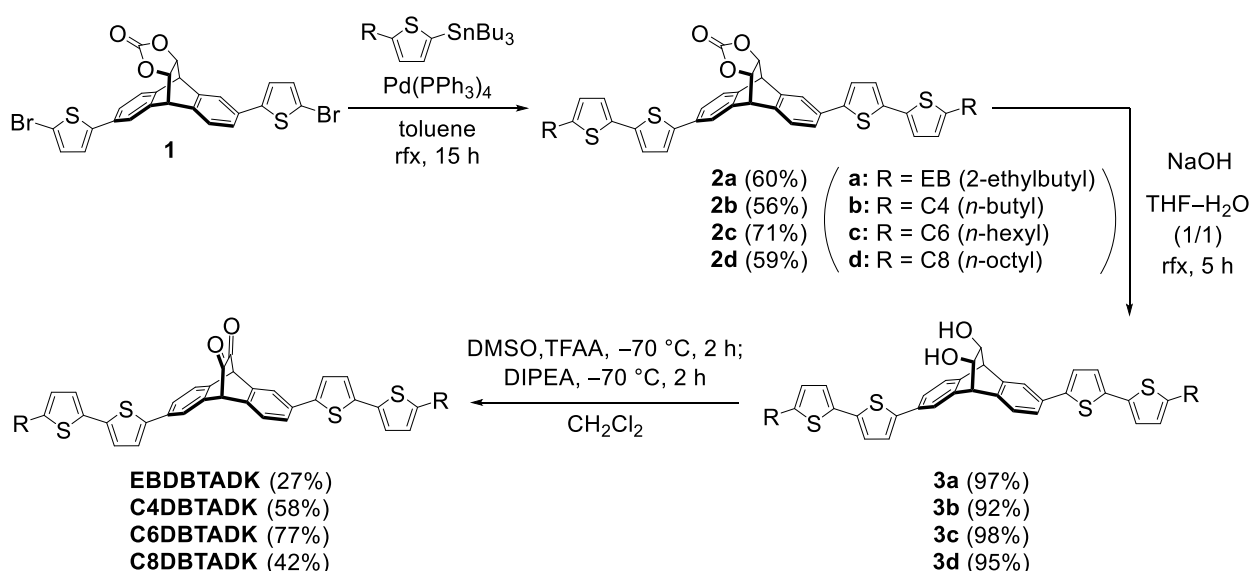
*ORTEP-3 for Windows*. Farrugia, L. J. *J. Appl. Cryst.* **2012**, *45*, 849–854.

## 2.7. X-ray diffraction analysis of thin films

Out-of-plane X-ray diffraction profiles were recorded on a Rigaku RINT-TTR III diffractometer equipped with a rotating anode (Cu-K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) operated at 15 kW and a Rigaku D/teX Ultra 1D silicon strip detector. Measurements were performed in the  $\theta$ - $2\theta$  mode with a scan range of  $2\theta = 2$ – $35^\circ$ . Sample films were prepared on glass plates by spin-coating of a corresponding DK-type photoprecursor from a solution in  $\text{CHCl}_3$  ( $10 \text{ mg mL}^{-1}$ , 800 rpm, 30 s) followed by irradiation with a blue LED ( $400 \text{ mW cm}^{-2}$ , 30 min).

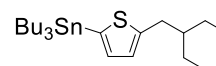
## 2.8. Synthetic procedures and spectroscopic data

The DK-type photoprecursors EB, C4, C6, and C8DBTADK were synthesized similarly to the previously reported synthesis of EHDBTADK (Scheme S1).<sup>S1</sup> The Diels–Alder adduct of 2,6-di(5-bromo-2-thienyl)anthracene and vinylene carbonate **1**<sup>S1</sup> was subjected to the Stille coupling with the corresponding stannylated alkylthiophene to afford compound **2** in 56–60% yield. After hydrolysis of the carbonate moiety to form  $\alpha$ -diols **3** in 92–97% yield, the target compounds were obtained by oxidation of **3** under Swern conditions in 42–59%.

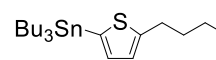


**Scheme S1** Synthesis of the DK-type photoprecursors. DMSO: dimethyl sulfoxide, TFAA: trifluoroacetic anhydride, DIPEA: *N,N*-diisopropylethylamine.

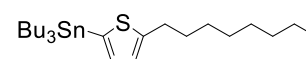
**2-(Tri-*n*-butylstannyl)-5-(2-ethylbutyl)thiophene.** To a 300 mL three-necked round-bottomed flask were added 2-(2-ethylbutyl)thiophene (8.23 g, 48.9 mmol) and THF (80 mL) under argon. *n*-BuLi solution in hexanes (2.6 M, 20.5 mL, 53 mmol) was added dropwise to the solution at  $-70\text{ }^{\circ}\text{C}$ . After stirring for 1 h, tri(*n*-butyl)tin chloride (18.5 mL, 68.5 mmol) was added to the reaction in one portion, and the resulting mixture was allowed to warm up to rt then stirred for 18 h. The mixture was poured into H<sub>2</sub>O (80 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 80 mL). The combined organic phase was washed with brine (100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated to give a brown oil (28.7 g). This crude product was directly used in the next reaction without further purification.



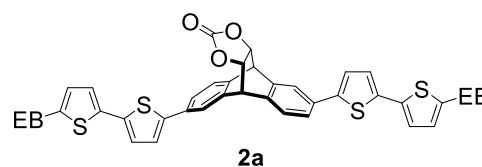
**2-(Tri-*n*-butylstannyl)-5-butylthiophene.** To a 200 mL three-necked round-bottomed flask were added 2-*n*-butylthiophene (6.06 g, 43.3 mmol) and THF (80 mL) under argon. *n*-BuLi solution in hexanes (2.6 M, 20.0 mL, 52 mmol) was added dropwise to the solution at  $-70\text{ }^{\circ}\text{C}$ . After stirring for 1 h, tri(*n*-butyl)tin chloride (20.0 mL, 52.0 mmol) was added to the reaction in one portion, and the resulting mixture was allowed to warm up to rt then stirred for 19 h. The mixture was poured into H<sub>2</sub>O (80 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 80 mL). The combined organic phase was washed with brine (160 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated to give a brown oil (27.5 g). This crude product was directly used in the next reaction without further purification.



**2-(Tri-*n*-butylstannyl)-5-octylthiophene.** To a 200 mL three-necked round-bottomed flask were added 2-*n*-octylthiophene (6.50 g, 38.6 mmol) and THF (60 mL) under argon. *n*-BuLi solution in hexanes (2.6 M, 15.5 mL, 40 mmol) was added dropwise to the solution at  $-70\text{ }^{\circ}\text{C}$ . After stirring for 1 h, tri(*n*-butyl)tin chloride (12.5 mL, 46.3 mmol) was added to the reaction in one portion, and the resulting mixture was allowed to warm up to rt then stirred for 15 h. The mixture was poured into H<sub>2</sub>O (60 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 60 mL). The combined organic phase was washed with brine (120 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated to give a brown oil (26.8 g). This crude product was directly used in the next reaction without further purification.

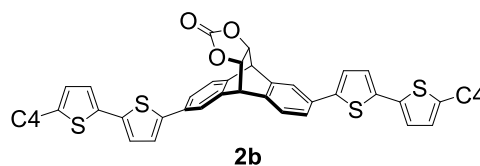


**Compound 2a.** Dibromide **1** (1.03 g, 1.76 mmol) and 2-(tri-*n*-butylstannyl)-5-(2-ethylbutyl)thiophene (2.52 g, 5.39 mmol) were added to a 50-mL round-bottomed flask. After the inner



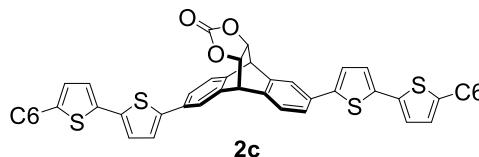
atmosphere was replaced with argon, Pd(PPh<sub>3</sub>)<sub>4</sub> (212 mg, 0.184 mmol) and toluene (23 mL) were sequentially added. The solution was partially evacuated and refilled with argon (three cycles) for deoxygenation, then stirred at 110 °C for 10 h before cooled down to rt. The resulting mixture was directly subjected to flash silica-gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes, 6:1) to afford **2a** as a yellow amorphous solid (800 mg, 1.05 mmol, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.90 (t, *J* = 7.3 Hz, 12H), 1.33–1.40 (m, 8H), 1.49–1.59 (m, partially overlapping with H<sub>2</sub>O), 2.73 (d, *J* = 6.9 Hz, 4H), 4.74 (d, *J* = 2.8 Hz, 2H), 4.94 (m, 2H), 6.68 (two overlapping d, *J* = 3.5 and 3.5 Hz, 2H), 7.00 (two overlapping d, *J* = 3.5 and 3.5 Hz, 2H), 7.05 (two overlapping d, *J* = 3.9 Hz, 2H), 7.17 and 7.18 (two d, *J* = 2.3 and 2.3 Hz, 2H in total), 7.38–7.41 (m, 2H), 7.45–7.50 (m, 2H), 7.60 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ: 10.9, 25.0, 33.7, 42.9, 47.5, 47.5, 76.1, 76.1, 122.7, 123.3, 123.4, 123.6, 123.7, 123.8, 124.1, 124.1, 124.9, 124.9, 125.9, 125.9, 126.2, 127.1, 133.9, 134.2, 134.7, 134.9, 135.0, 136.3, 136.9, 137.5, 137.9, 138.3, 141.1, 141.6, 144.1, 144.4, 154.0. LRMS (ESI) *m/z*: 760.2 ([M + Na]<sup>+</sup>). HRMS (ESI) *m/z*: calcd for C<sub>49</sub>H<sub>52</sub>O<sub>3</sub>S<sub>4</sub>Na ([M + Na]<sup>+</sup>) 760.2173, found 760.2184.

**Compound 2b.** Dibromide **1** (500 mg, 85.3 μmol) and 2-(tri-*n*-butylstannyl)-5-butylthiophene (1.46 g, 3.41 mmol) were added to a 50-mL round-bottomed flask. After the inner atmosphere was



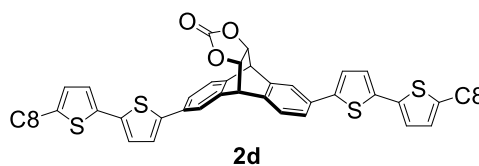
replaced with argon, Pd(PPh<sub>3</sub>)<sub>4</sub> (99.6 mg, 86.2 μmol) and toluene (20 mL) were sequentially added. The solution was partially evacuated and refilled with argon (three cycles) for deoxygenation, then refluxed for 15 h before cooled down to rt. The resulting mixture was directly subjected to flash silica-gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes, 3:2 then 3:1) to afford **2b** as a yellow amorphous solid (339 mg, 481 μmol, 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.95 (t, *J* = 7.3 Hz, 6H), 1.36–1.46 (m, 4H), 1.63–1.71 (m, 4H), 2.80 (t, *J* = 7.6 Hz, 4H), 4.74 (s, 2H), 4.94 (m, 2H), 6.69 (two overlapping d, *J* = 3.5 and 3.5 Hz, 2H), 7.00 (two overlapping d, *J* = 3.5 and 3.5 Hz, 2H), 7.05 (two overlapping d, *J* = 3.9 Hz, 2H), 7.17 and 7.18 (two d, *J* = 2.3 and 2.3 Hz, 2H in total), 7.38–7.40 (m, 2H), 7.44–7.49 (m, 2H), 7.60 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ: 13.8, 22.1, 29.9, 33.7, 47.5, 47.5, 76.1, 76.1, 122.7, 123.3, 123.5, 123.6, 123.8, 123.8, 124.1, 124.2, 124.8, 124.9, 124.9, 126.2, 127.1, 133.9, 134.1, 134.4, 134.7, 135.1, 136.4, 136.9, 137.5, 137.9, 138.3, 141.2, 141.6, 145.5, 145.8, 154.0. LRMS (ESI) *m/z*: 727.1 (rel intensity 100, [M + Na]<sup>+</sup>), 743.1 (11, [M + K]<sup>+</sup>), 759.2 (46, [M + MeOH + Na]<sup>+</sup>). HRMS (ESI) *m/z*: calcd for C<sub>41</sub>H<sub>36</sub>O<sub>3</sub>S<sub>4</sub>Na ([M + Na]<sup>+</sup>) 727.1445, found 727.1447.

**Compound 2c.** Dibromide **1** (1.16 g, 1.99 mmol) and 2-(tri-*n*-butylstannyl)-5-hexylthiophene (2.74 g, 6.00 mmol) were added to a 50-mL two-necked round-bottomed flask. After the inner



atmosphere was replaced with argon, Pd(PPh<sub>3</sub>)<sub>4</sub> (237 mg, 200 μmol) and toluene (20 mL) were sequentially added. The solution was partially evacuated and refilled with argon (10 cycles) for deoxygenation, then refluxed for 11 h before cooled down to rt. The resulting mixture was directly subjected to flash silica-gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes, 2:1 then 3:1). The resulting solid was dissolved in 2.5 mL of dichloromethane and precipitated by adding 20 mL of methanol. The precipitate was collected by filtration, rinsed with 10 mL of methanol, and dried under vacuum to afford **2c** as a pale yellow powder (0.927 g, 1.22 mmol, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.89 (t, *J* = 7.3 Hz, 6H), 1.26–1.42 (m, 12H), 1.64–1.72 (quint, *J* = 7.6 Hz, 4H), 2.79 (t, *J* = 7.6 Hz, 4H), 4.73 (s, 2H), 4.93 (m, 2H), 6.68–6.69 (m, 2H), 7.00 (two overlapping d, *J* = 3.7 Hz, 2H), 7.04 (two overlapping d, *J* = 3.9 Hz, 2H), 7.17 and 7.18 (two d, *J* = 3.7 Hz, 2H in total), 7.38 and 7.39 (two d, *J* = 7.8 Hz, 2H in total), 7.45 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.48 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.59–7.60 (m, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.1, 22.7, 29.1, 29.2, 29.3, 30.2, 31.6, 31.9, 47.48, 47.53, 76.07, 76.13, 122.7, 123.3, 123.5, 123.6, 123.79, 123.84, 124.1, 124.2, 124.8, 124.87, 124.92, 126.2, 127.1, 133.9, 134.1, 134.4, 134.7, 135.0, 136.4, 136.9, 137.5, 137.9, 138.3, 141.2, 141.6, 145.6, 145.8, 154.0. LRMS (ESI) *m/z*: 783.2 (rel intensity 100, [M + Na]<sup>+</sup>), 815.2 (40, [M + MeOH + Na]<sup>+</sup>). HRMS (ESI) *m/z*: calcd for C<sub>44</sub>H<sub>46</sub>O<sub>3</sub>S<sub>4</sub>Na [M + Na]<sup>+</sup> 783.2071, found 783.2071.

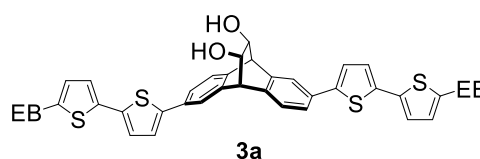
**Compound 2d.** Dibromide **1** (500 mg, 85.3 μmol) and 2-(tri-*n*-butylstannyl)-5-octylthiophene (1.66, 3.41 mmol) were added to a 50-mL round-bottomed flask. After the inner atmosphere was



replaced with argon, Pd(PPh<sub>3</sub>)<sub>4</sub> (99.3 mg, 85.9 μmol) and toluene (20 mL) were sequentially added. The solution was partially evacuated and refilled with argon (three cycles) for deoxygenation, then refluxed for 15 h before cooled down to rt. The resulting mixture was directly subjected to flash silica-gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes, 3:2 then 3:1) to afford **2d** as a yellow amorphous solid (411 mg, 503 μmol, 59%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.88 (t, *J* = 6.9 Hz, 6H), 1.28–1.39 (m, 20H), 1.64–1.72 (m, 4H), 2.79 (t, *J* = 7.6 Hz, 4H), 4.73 (s, 2H), 4.93 (m, 2H), 6.69 (two overlapping d, *J* = 3.5 and 3.5 Hz, 2H), 7.00 (two

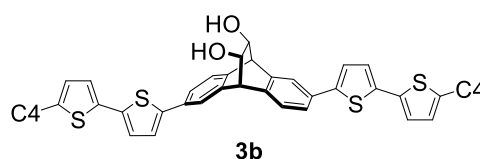
overlapping d,  $J = 3.5$  and  $3.5$  Hz, 2H), 7.05 (two overlapping d,  $J = 3.9$  Hz, 2H), 7.17 and 7.18 (two d,  $J = 2.3$  and  $2.3$  Hz, 2H in total), 7.38–7.40 (m, 2H), 7.44–7.49 (m, 2H), 7.60 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.1, 22.7, 29.1, 29.2, 29.3, 30.2, 31.6, 31.9, 47.5, 47.5, 76.1, 76.1, 122.7, 123.3, 123.5, 123.6, 123.8, 123.8, 124.1, 124.1, 124.8, 124.9, 124.9, 126.2, 127.1, 133.9, 134.1, 134.4, 134.7, 135.0, 136.4, 136.9, 137.5, 137.9, 138.3, 141.2, 141.6, 145.6, 145.8, 154.0. LRMS (ESI)  $m/z$ : 839.3 (rel intensity 100,  $[\text{M} + \text{Na}]^+$ ), 855.2 (11,  $[\text{M} + \text{K}]^+$ ), 871.3 (24,  $[\text{M} + \text{MeOH} + \text{Na}]^+$ ). HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{49}\text{H}_{52}\text{O}_3\text{S}_4\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ) 839.2697, found 839.2694.

**Compound 3a.** Carbonate **2a** (800 mg, 1.05 mmol) was dissolved in THF (11 mL) in a 50 mL round-bottomed flask, to which NaOH (220 mg, 5.50 mmol) was added with  $\text{H}_2\text{O}$  (11 mL).



The two-layer solution was refluxed for 5 h before cooled down to rt and acidified with 2 M HCl aq (10 mL). The resulting mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL), and the combined organic phase was washed with brine (80 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtrated, and evaporated. The crude product was purified by flash silica-gel chromatography ( $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ , 100:1 then 10:1) to afford **3a** as a yellow powder (749 mg, 1.02 mmol, 97%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.90 (t,  $J = 7.3$  Hz, 6H), 1.33–1.40 (m, 8H), 1.49–1.59 (m, partially overlapping with  $\text{H}_2\text{O}$ ), 2.24 (two overlapping d, 6.0 Hz, 2H), 2.74 (d,  $J = 6.9$  Hz, 4H), 4.12 (m, 2H), 4.46 (d,  $J = 2.3$  Hz, 2H), 6.67 (d,  $J = 3.7$  Hz, 2H), 7.00 (d,  $J = 3.7$  Hz, 2H), 7.04 (d,  $J = 3.7$  Hz, 2H), 7.16 and 7.17 (two d,  $J = 3.7$  and  $3.7$  Hz, 2H in total), 7.33 (d,  $J = 7.8$  Hz, 1H), 7.38–7.40 (m, 2H), 7.45 (dd,  $J = 7.8$  and  $1.8$  Hz, 1H), 7.54 (d,  $J = 1.4$  Hz, 1H) 7.60 (d,  $J = 1.4$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 10.9, 25.0, 33.7, 42.9, 51.1, 68.1, 122.0, 123.1, 123.2, 123.7, 123.7, 124.0, 124.1, 125.3, 125.9, 127.0, 133.0, 133.1, 134.9, 135.0, 137.2, 137.3, 137.7, 138.9, 139.1, 140.4, 142.0, 142.1, 144.0, 144.1. LRMS (ESI)  $m/z$ : 757.2 (rel intensity 100,  $[\text{M} + \text{Na}]^+$ ). HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{44}\text{H}_{46}\text{O}_2\text{S}_4\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ) 757.2278, found 757.2273.

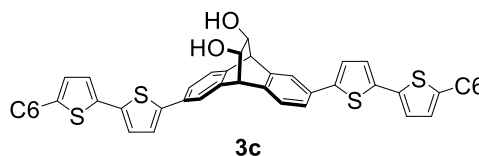
**Compound 3b.** Carbonate **2b** (220 mg, 312  $\mu\text{mol}$ ) was dissolved in THF (5 mL) in a 50 mL round-bottomed flask, to which NaOH (62.4 mg, 1.56 mmol) was added with  $\text{H}_2\text{O}$  (5 mL).



The two-layer solution was refluxed for 5 h before cooled down to rt and acidified with 2 M HCl aq (5 mL). The resulting mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL), and the combined organic phase was washed

with brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated. The crude product was purified by flash silica-gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>/AcOEt, 100:1 then 50:1) to afford **3b** as a yellow powder (194 mg, 0.286 mmol, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.95 (t, *J* = 7.3 Hz, 6H), 1.36–1.46 (m, 4H), 1.63–1.71(m, 4H), 2.25 (two overlapping d, *J* = 6.0 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 4H), 4.12 (m, 2H), 4.46 (d, *J* = 2.3 Hz, 2H), 6.68 (d, *J* = 3.7 Hz, 2H), 6.99 (d, *J* = 3.7 Hz, 2H), 7.04 (d, *J* = 3.7 Hz, 2H), 7.16 and 7.17 (two d, *J* = 3.7 and 3.7 Hz, 2H in total), 7.33 (d, *J* = 7.8 Hz, 1H), 7.38–7.40 (m, 2H), 7.45 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 1.8 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ: 13.8, 22.2, 29.9, 33.7, 51.1, 68.1, 122.0, 123.2, 123.3, 123.7, 123.7, 123.8, 123.1, 124.1, 124.8, 125.3, 127.0, 133.0, 133.1, 134.7, 134.8, 137.2, 137.3, 137.7, 137.9, 139.1, 140.4, 142.0, 142.2, 145.4, 145.5. LRMS (ESI) *m/z*: 701.2 (rel intensity 100, [M + Na]<sup>+</sup>), 733.2 (23, [M + MeOH + Na]<sup>+</sup>), HRMS (ESI) *m/z* calcd for C<sub>40</sub>H<sub>38</sub>O<sub>2</sub>S<sub>4</sub>Na ([M + Na]<sup>+</sup>) 701.1652, found 701.1652.

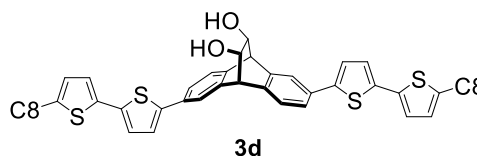
**Compound 3c.** Carbonate **2c** (0.901 g, 1.19 mmol) was dissolved in THF (5 mL) in a 25-mL two-necked round-bottomed flask, to which NaOH (482 mg, 12.5 mmol) was added with H<sub>2</sub>O



(5 mL). The two-layer solution was refluxed for 2 h before cooled down to rt and acidified with 2 M HCl aq (10 mL). The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL), and the combined organic phase was washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated. The crude product was purified by flash silica-gel chromatography (CH<sub>2</sub>Cl<sub>2</sub> then CH<sub>2</sub>Cl<sub>2</sub>/AcOEt, 20:1) to afford **3c** as a yellow powder (0.851 g, 1.16 mmol, 98%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 0.89 (t, *J* = 6.9 Hz, 6H), 1.29–1.41 (m, 12H), 1.68 (quint, *J* = 7.6 Hz, 4H), 2.20 (d, *J* = 6.3 Hz, 1H), 2.22 (d, *J* = 6.3 Hz, 1H), 2.79 (t, *J* = 7.4 Hz, 4H), 4.10–4.16 (m, 2H), 4.47 (d, *J* = 1.2 Hz, 2H), 6.69 (d, *J* = 3.4 Hz, 2H), 6.99 (d, *J* = 3.4 Hz, 2H), 7.05 (d, *J* = 4.6 Hz, 2H), 7.16 (d, *J* = 4.0 Hz, 1H), 7.18 (d, *J* = 3.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.46 (dd, *J* = 7.3 and 1.6 Hz, 1H), 7.55 (d, *J* = 1.1 Hz, 1H), 7.60 (d, *J* = 1.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ: 14.1, 22.6, 28.8, 30.2, 31.6, 51.1, 68.1, 122.0, 123.2, 123.3, 123.7, 123.8, 124.06, 124.10, 124.8, 125.3, 127.0, 133.0, 133.1, 134.7, 134.8, 137.2, 137.3, 137.7, 138.9, 139.1, 140.4, 142.0, 142.1, 145.5, 145.6. LRMS (ESI) *m/z*: 757.2 (rel intensity 100, [M + Na]<sup>+</sup>), 789.2 (13, [M + MeOH + Na]<sup>+</sup>), HRMS (ESI) *m/z* calcd for C<sub>44</sub>H<sub>46</sub>O<sub>2</sub>S<sub>4</sub>Na [M + Na]<sup>+</sup> 757.2278, found 757.2279.

**Compound 3d.** Carbonate **2d** (305 mg, 373  $\mu\text{mol}$ ) was

dissolved in THF (7 mL) in a 50 mL round-bottomed flask, to which NaOH (73.4 mg, 1.84 mmol) was added with H<sub>2</sub>O (7 mL).



The two-layer solution was refluxed for 5 h before cooled down to rt and acidified with 2 M HCl aq (7 mL).

The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  10 mL), and the combined organic phase was washed with brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated. The crude product was purified by flash

silica-gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>/AcOEt, 100:1 then 50:1) to afford **3d** as a yellow powder (280 mg, 354

$\mu\text{mol}$ , 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.88 (t, *J* = 6.9 Hz, 6H), 1.28–1.39 (m, 20H), 1.64–1.72 (m, 4H),

2.23 (two overlapping d, *J* = 6.0 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 4H), 4.12 (m, 2H), 4.46 (d, *J* = 2.3 Hz, 2H), 6.68

(d, *J* = 3.7 Hz, 2H), 6.99 (d, *J* = 3.7 Hz, 2H), 7.04 (d, *J* = 3.7 Hz, 2H), 7.16 and 7.17 (two d, *J* = 3.7 and 3.7

Hz, 2H in total), 7.33 (d, *J* = 7.8 Hz, 1H), 7.38–7.40 (m, 2H), 7.45 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.54 (d, *J* =

1.8 Hz, 1H) 7.60 (d, *J* = 1.8 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.1, 22.7, 29.1, 29.2, 29.3, 30.2,

31.6, 31.9, 51.1, 68.1, 122.0, 123.2, 123.3, 123.7, 123.8, 124.1, 124.1, 124.8, 125.3, 127.0, 133.0, 133.1, 134.7,

134.8, 137.2, 137.3, 137.7, 138.9, 139.1, 140.4, 142.0, 142.2, 145.5, 145.6. LRMS (ESI) *m/z*: 813.3 (rel

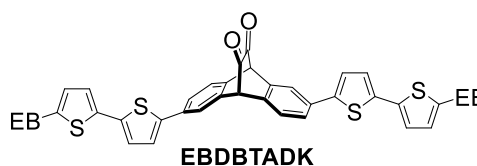
intensity 100, [M + Na]<sup>+</sup>), 845.3 (11, [M + MeOH + Na]<sup>+</sup>). HRMS (ESI) *m/z*: calcd for C<sub>48</sub>H<sub>54</sub>O<sub>2</sub>S<sub>4</sub>Na ([M +

Na]<sup>+</sup>) 813.2904, found 813.2905.

**EBDBTADK.** A 30 mL three-necked round-bottomed flask

containing CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and DMSO (1 mL) was immersed in a

cooling bath at –70 °C. TFAA (1.7 mL, 12 mmol) was added



dropwise, and the mixture was stirred at the same temperature for 30 min to form the Swern reagent. A solution

of diol **3a** (600 mg, 816  $\mu\text{mol}$ ) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was prepared in a different flask, and added dropwise to the

Swern reagent. The reaction mixture was stirred at –70 °C for 2 h before the dropwise addition of DIPEA (4.4

mL, 25 mmol). The reaction was further stirred at –70 °C for 2 h then allowed to warm up to rt, and quenched

by being poured into 2 M HCl aq (25 mL). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  25 mL), and the

combined organic phase was washed with H<sub>2</sub>O (3  $\times$  50 mL) and brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated,

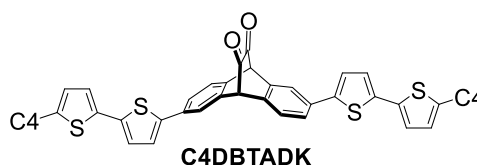
and evaporated. The crude product was purified by repetitive flash silica-gel column chromatography (gradient,

CH<sub>2</sub>Cl<sub>2</sub>/hexanes, 2:3 to CH<sub>2</sub>Cl<sub>2</sub>) to afford EBDBTADK as an orange solid (160 mg, 219  $\mu\text{mol}$ , 27%). <sup>1</sup>H NMR



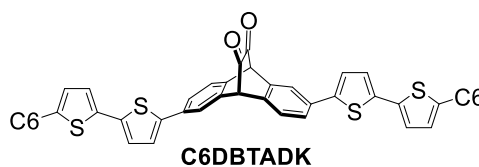
(400 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.90 (t,  $J$  = 7.3 Hz, 6H), 1.33–1.40 (m, 8H), 1.49–1.59 (m, partially overlapping with H<sub>2</sub>O), 2.74 (d,  $J$  = 6.9 Hz, 4H), 5.00 (s, 2H), 6.69 (d,  $J$  = 3.7 Hz, 2H), 7.02 (d,  $J$  = 3.7 Hz, 2H), 7.07 (d,  $J$  = 3.7 Hz, 2H), 7.23 (d,  $J$  = 3.7 Hz, 2H), 7.49 (d,  $J$  = 7.8 Hz, 2H), 7.60 (dd,  $J$  = 7.8 and 1.4 Hz, 2H), 7.60 (d,  $J$  = 1.4 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 10.9, 25.0, 33.8, 43.0, 59.6, 123.0, 123.6, 123.9, 124.6, 126.0, 126.0, 126.6, 126.9, 133.3, 134.6, 135.5, 135.8, 138.4, 140.1, 144.6, 183.2. LRMS (ESI)  $m/z$ : 727.1 (rel intensity 93, M<sup>+</sup>), 753.2 (48, [M + Na]<sup>+</sup>), 785.2 (100, [M + MeOH + Na]<sup>+</sup>). HRMS (ESI)  $m/z$ : calcd for C<sub>44</sub>H<sub>42</sub>O<sub>2</sub>S<sub>4</sub>Na ([M + Na]<sup>+</sup>) 753.1988, found 753.1965.

**C4DBTADK.** A 30 mL three-necked round-bottomed flask containing CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and DMSO (0.35 mL) was immersed in a cooling bath at –70 °C. TFAA (0.53 mL, 3.78 mmol) was added



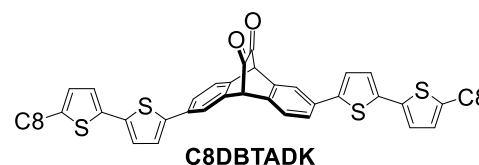
dropwise, and the mixture was stirred at the same temperature for 30 min to form the Swern reagent. A solution of diol **3b** (180 mg, 265  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and DMSO (0.5 mL) was prepared in a different flask, and added dropwise to the Swern reagent. The reaction mixture was stirred at –70 °C for 2 h before the dropwise addition of DIPEA (1.4 mL, 8.0 mmol). The reaction was further stirred at –70 °C for 2 h then allowed to warm up to rt, and quenched by being poured into 2 M HCl aq (10 mL). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  10 mL), and the combined organic phase was washed with H<sub>2</sub>O (3  $\times$  30 mL) and brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated. The crude product was purified by flash silica-gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes, 1:1 then 3:2) to afford C4DBTADK as an orange solid (103 mg, 153  $\mu$ mol, 58 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.95 (t,  $J$  = 7.3 Hz, 6H), 1.36–1.46 (m, 4H), 1.63–1.71 (m, 4H), 2.80 (t,  $J$  = 7.6 Hz, 4H), 5.03 (s, 2H), 6.70 (d,  $J$  = 3.7 Hz, 2H), 7.02 (d,  $J$  = 3.7 Hz, 2H), 7.06 (d,  $J$  = 3.7 Hz, 2H), 7.22 (d,  $J$  = 3.7 Hz, 2H), 7.48 (d,  $J$  = 7.8 Hz, 2H), 7.60 (dd,  $J$  = 7.8 and 1.8 Hz, 2H), 7.60 (d,  $J$  = 1.8 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 13.8, 22.2, 29.9, 33.7, 59.6, 123.0, 123.7, 123.9, 124.6, 124.9, 126.6, 126.9, 133.3, 134.3, 135.5, 135.8, 138.4, 140.6, 145.9, 183.2. LRMS (ESI)  $m/z$ : 697.1 (rel intensity 43, [M + Na]<sup>+</sup>), 729.2 (100, [M + MeOH + Na]<sup>+</sup>), 761.2 (18, [M + 2MeOH + Na]<sup>+</sup>). HRMS (ESI)  $m/z$ : calcd for C<sub>40</sub>H<sub>34</sub>O<sub>2</sub>S<sub>4</sub>Na ([M + Na]<sup>+</sup>) 697.1339, found 697.1338.

**C6DBTADK.** A 30 mL three-necked round-bottomed flask containing CH<sub>2</sub>Cl<sub>2</sub> (18.0 mL) and DMSO (2.40 mL) was immersed in a cooling bath at -65 °C. TFAA (2.35 mL, 16.7 mmol) was



added dropwise, and the mixture was stirred at the same temperature for 30 min to form the Swern reagent. A solution of diol **3c** (819 mg, 1.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (22 mL) and DMSO (11 mL) was prepared in a different flask, and added dropwise to the Swern reagent. The reaction mixture was stirred at -65 °C for 2 h before the dropwise addition of DIPEA (6.50 mL, 37.3 mmol). The reaction was further stirred at -65 °C for 2 h then allowed to warm up to rt and quenched by being poured to 2 M HCl aq (30 mL). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL), and the combined organic phase was washed with H<sub>2</sub>O (3 × 30 mL) then brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated. The crude product was mostly dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) with gentle warming and precipitated by adding CH<sub>3</sub>CN (50 mL). The precipitate was collected by filtration and filtered through a pad of silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent, then the filtrate was evaporated under vacuum to give a yellow powder. The powder was re-dissolved in hot toluene (20 mL), and the slowly cooled to 0 °C. The resulting precipitate was collected by filtration, rinsed with cold toluene (10 mL), and dried at 100 °C under vacuum to afford C6DBTADK as a yellow powder (627 mg, 857 μmol, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.89 (t, *J* = 7.1 Hz, 6H), 1.29–1.42 (m, 12H), 1.68 (quint, *J* = 7.5 Hz, 4H), 2.80 (t, *J* = 7.4 Hz, 4H), 5.03 (s, 2H), 6.70 (d, *J* = 3.7 Hz, 2H), 7.02 (d, *J* = 3.7 Hz, 2H), 7.07 (d, *J* = 4.0 Hz, 2H), 7.23 (d, *J* = 4.0 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.60 (dd, *J* = 8.1 and 1.8 Hz, 2H), 7.67 (d, *J* = 1.5 Hz, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (150.9 MHz, CDCl<sub>3</sub>) δ: 14.1, 22.6, 28.7, 30.2, 31.6, 59.7, 123.0, 123.7, 123.9, 124.6, 124.9, 126.6, 126.9, 133.3, 134.3, 135.5, 135.8, 138.4, 140.6, 146.0, 183.2. LRMS (FAB) *m/z*: 674.1 (rel intensity 100, [M - 2CO]<sup>+</sup>), 702.2 (30, [M - CO]<sup>+</sup>), 730.1 (45, M<sup>+</sup>). HRMS (FAB) *m/z*: calcd for C<sub>44</sub>H<sub>42</sub>O<sub>2</sub>S<sub>4</sub> (M<sup>+</sup>) 730.2068, found 730.2056.

**C8DBTADK.** A 30 mL three-necked round-bottomed flask containing CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and DMSO (0.38 mL) was immersed in a cooling bath at -70 °C. TFAA (0.65 mL, 4.6 mmol) was added



dropwise, and the mixture was stirred at the same temperature for 30 min to form the Swern reagent. A solution of diol **3d** (240 mg, 303 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and DMSO (0.5 mL) was prepared in different flask, and added dropwise to the Swern reagent. The reaction mixture was stirred at -70 °C for 2 h before the dropwise

addition of DIPEA (1.5 mL, 8.8 mmol). The reaction was further stirred at  $-70\text{ }^{\circ}\text{C}$  for 2 h then allowed to warm up to rt and quenched by being poured to 2 M HCl aq (10 mL). The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL), and the combined organic phase was washed with  $\text{H}_2\text{O}$  ( $3 \times 30$  mL) and brine (30 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtrated, and evaporated. The crude product was purified by flash silica-gel column chromatography ( $\text{CH}_2\text{Cl}_2$ /hexanes, gradient from 1:1 to 3:2) to afford C8DBTADK as an orange solid (101 mg, 128  $\mu\text{mol}$ , 42%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.88 (t,  $J = 6.9$  Hz, 6H), 1.28–1.39 (m, 20H), 1.65–1.72 (m, 4H), 2.80 (t,  $J = 7.6$  Hz, 4H), 5.03 (s, 2H), 6.70 (d,  $J = 3.7$  Hz, 2H), 7.02 (d,  $J = 3.7$  Hz, 2H), 7.07 (d,  $J = 3.7$  Hz, 2H), 7.23 (d,  $J = 3.7$  Hz, 2H), 7.49 (d,  $J = 8.2$  Hz, 2H), 7.60 (dd,  $J = 8.2$  and 1.8 Hz, 2H), 7.67 (d,  $J = 1.8$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.1, 22.7, 29.1, 29.2, 29.3, 30.2, 31.6, 31.9, 59.6, 123.0, 123.7, 123.9, 124.6, 124.9, 126.6, 126.9, 133.3, 134.3, 135.5, 135.8, 138.4, 140.6, 146.0, 183.2. LRMS (ESI)  $m/z$ : 809.3 (rel intensity 43,  $[\text{M} + \text{Na}]^+$ ), 841.3 (100,  $[\text{M} + \text{MeOH} + \text{Na}]^+$ ). HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{48}\text{H}_{54}\text{O}_2\text{S}_4\text{Na}$  ( $[\text{M} + \text{Na}]^+$ ) 809.2591, found 809.2594.

### 3. NMR spectra

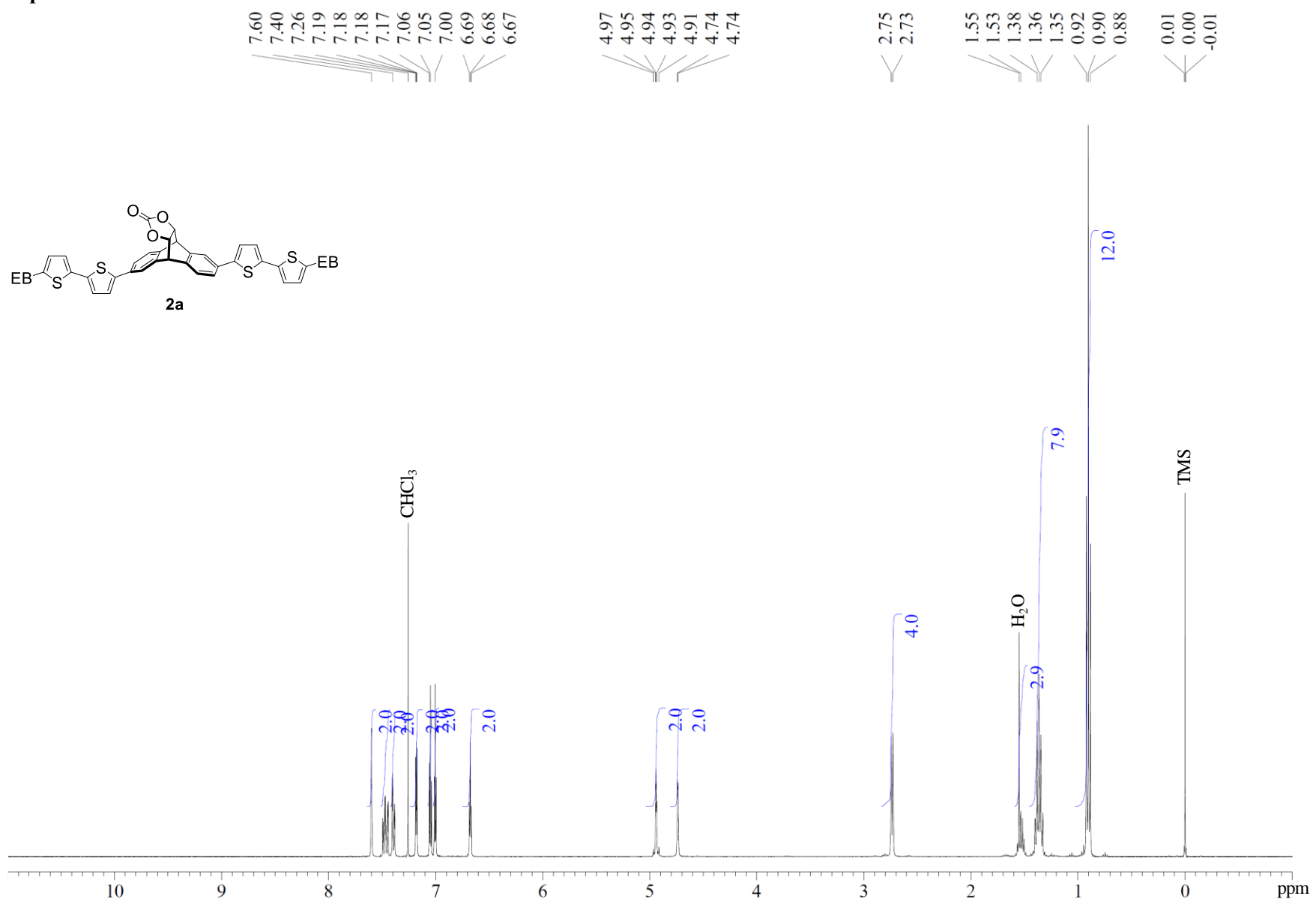
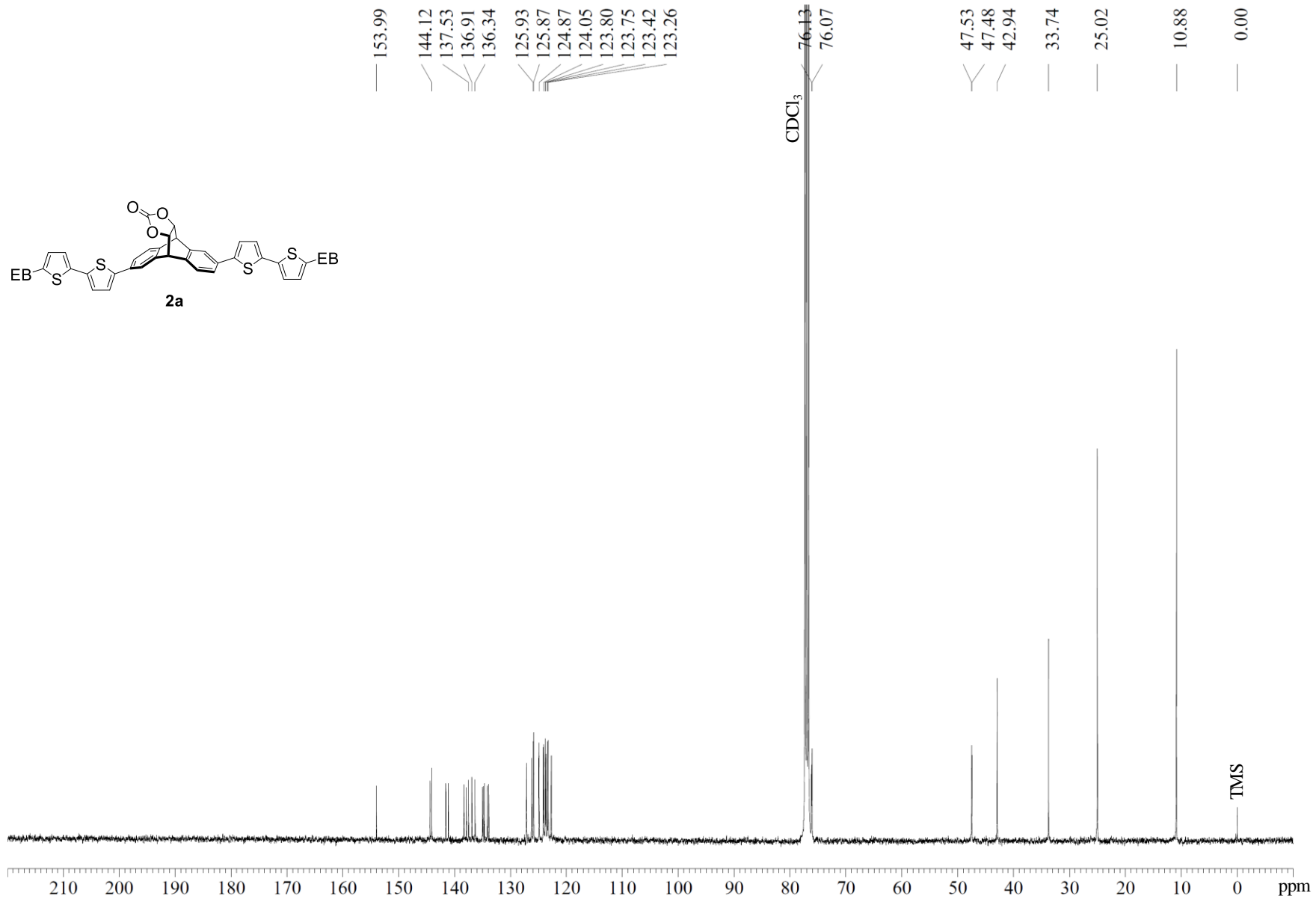


Fig. S8  $^1\text{H}$  NMR spectrum of compound **2a**.



**Fig. S9**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **2a**.

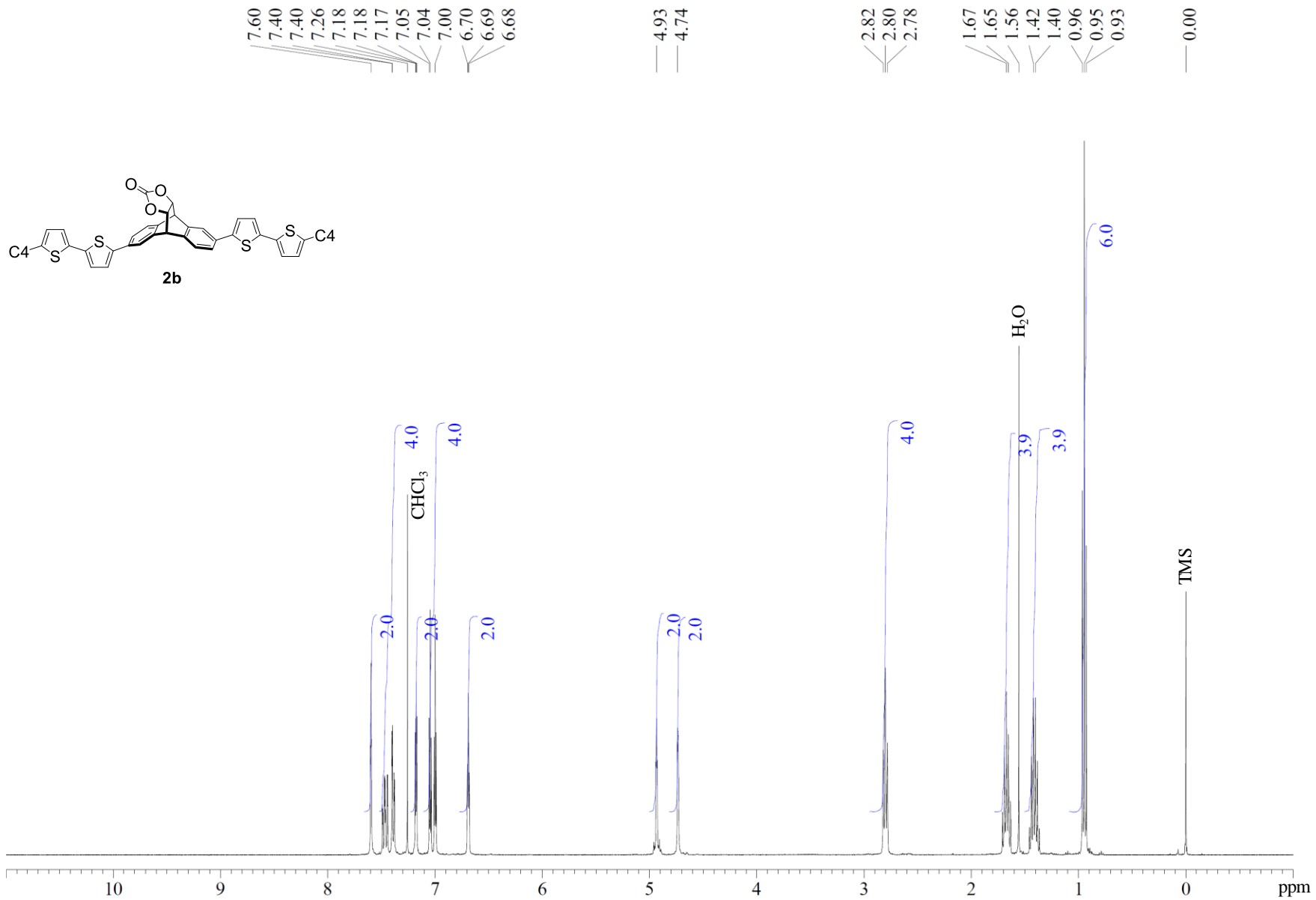


Fig. S10  $^1\text{H NMR}$  spectrum of compound **2b**.

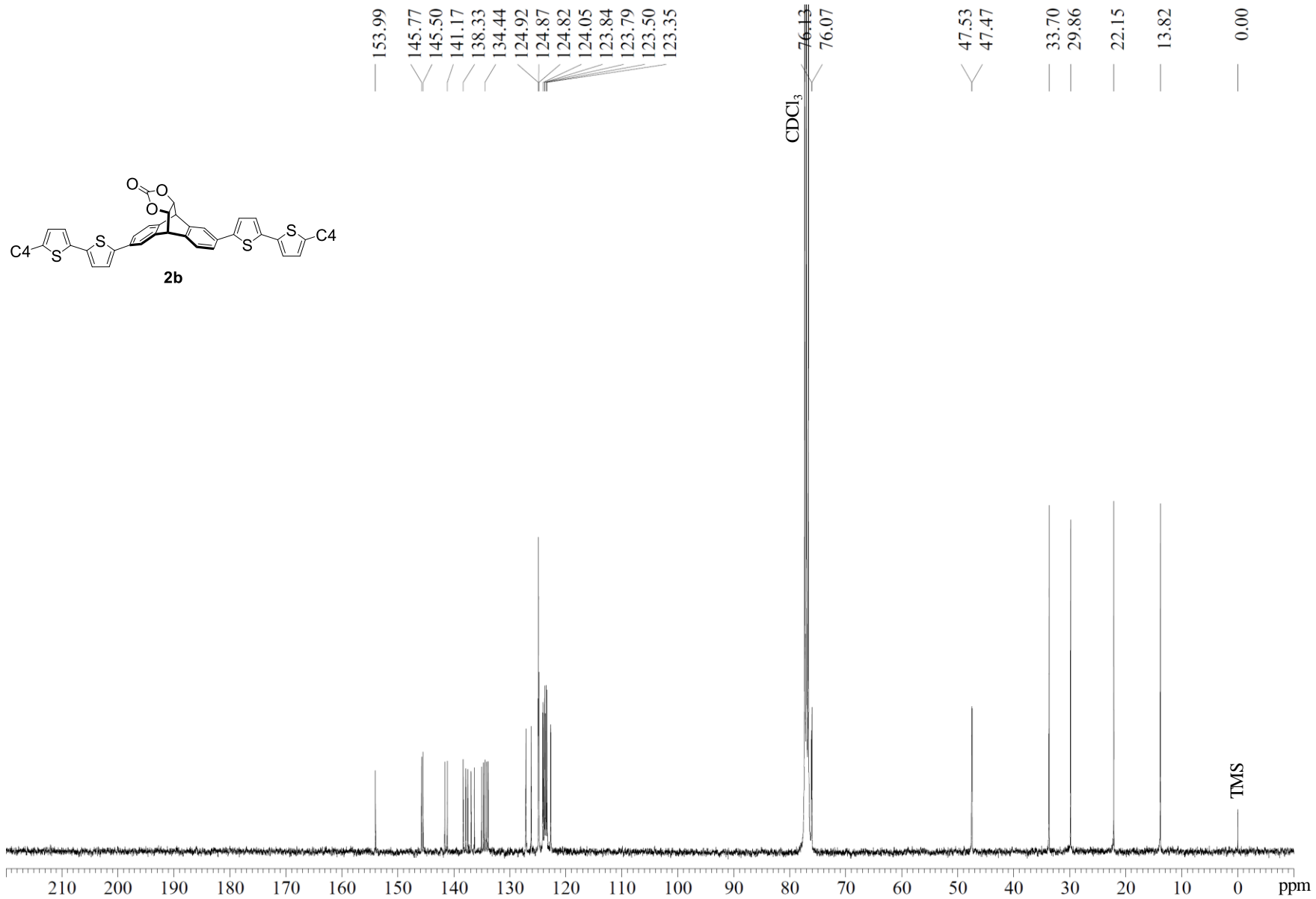


Fig. S11  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **2b**.

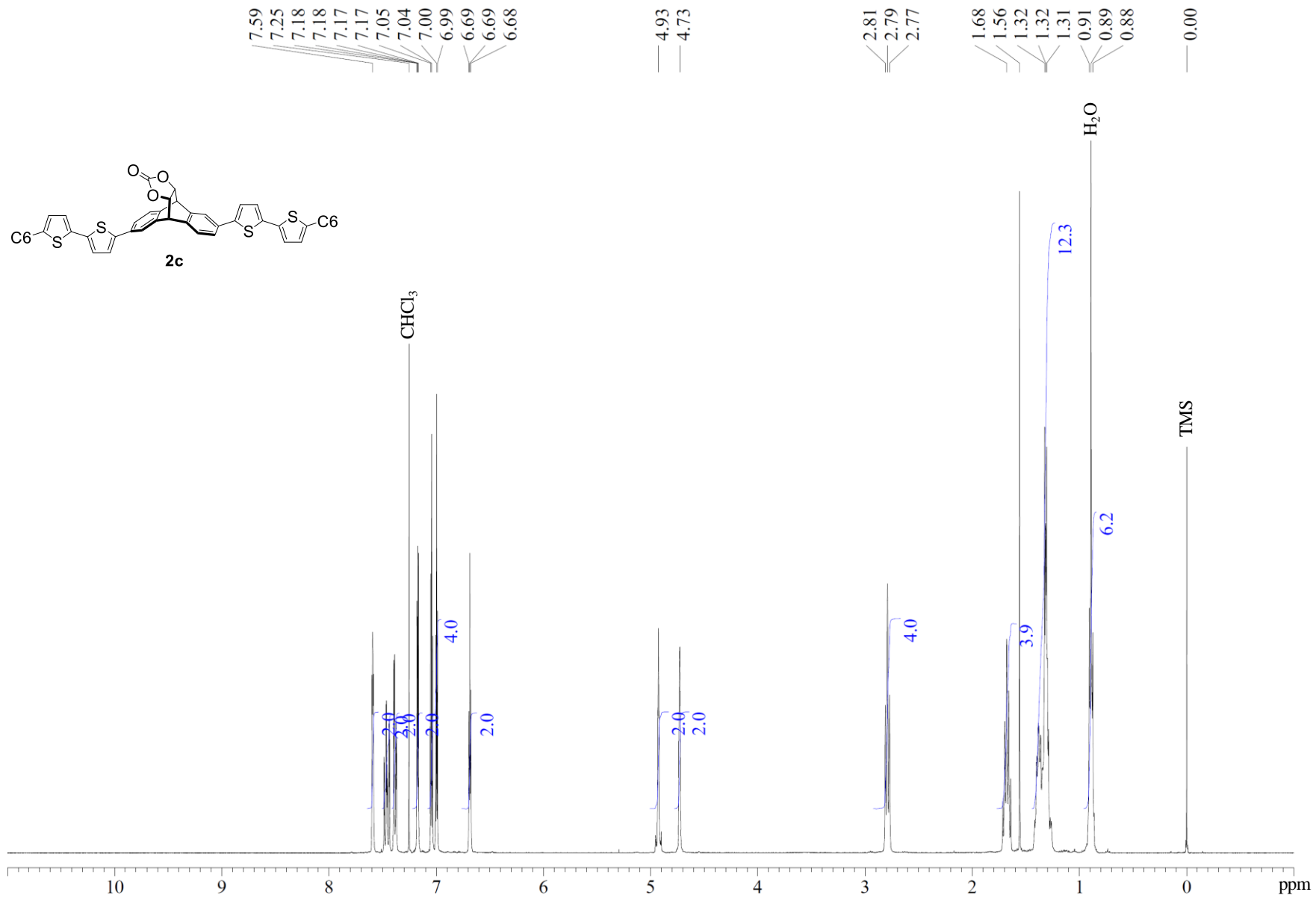


Fig. S12 <sup>1</sup>H NMR spectrum of compound **2c**.



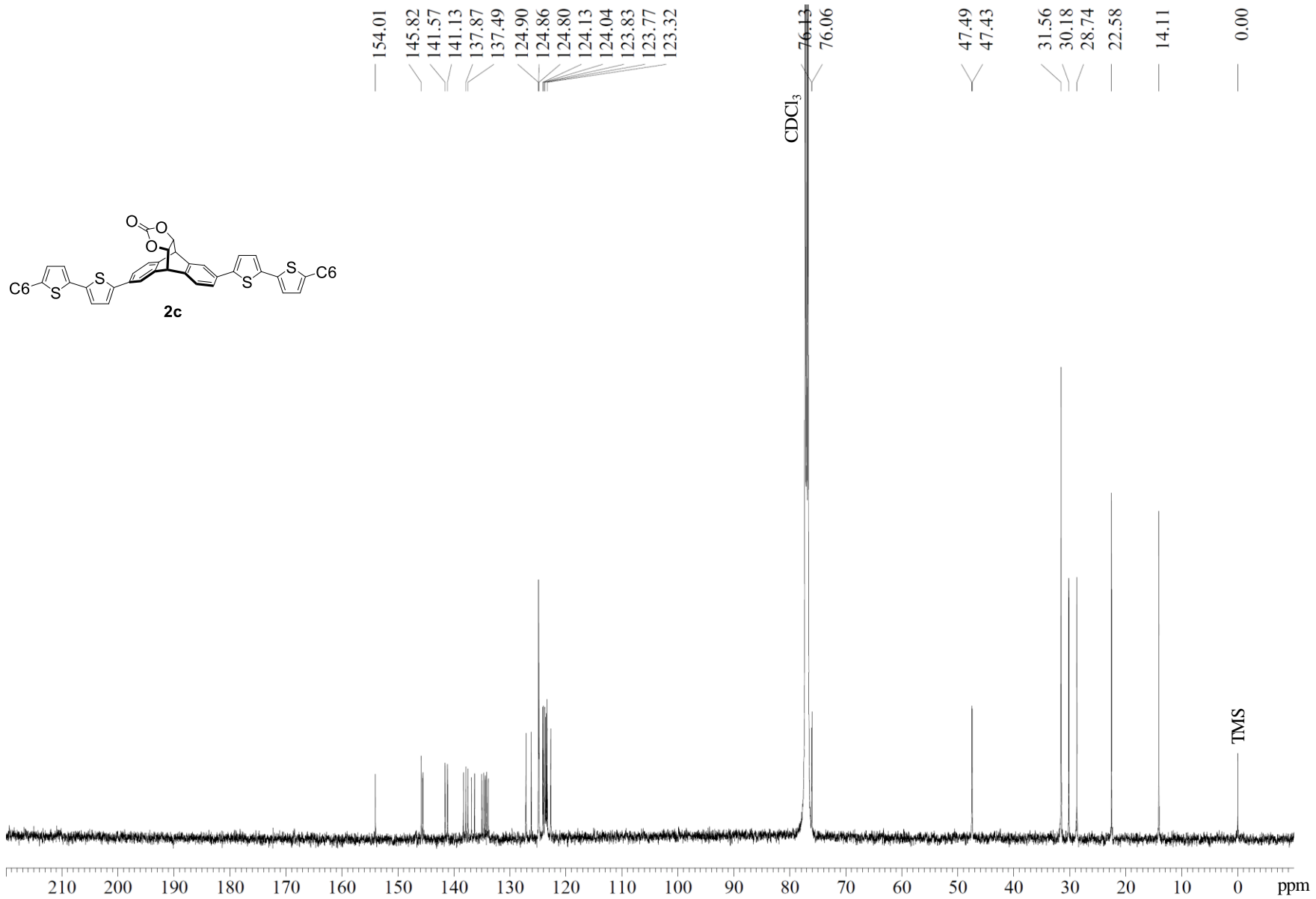


Fig. S13  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **2c**.

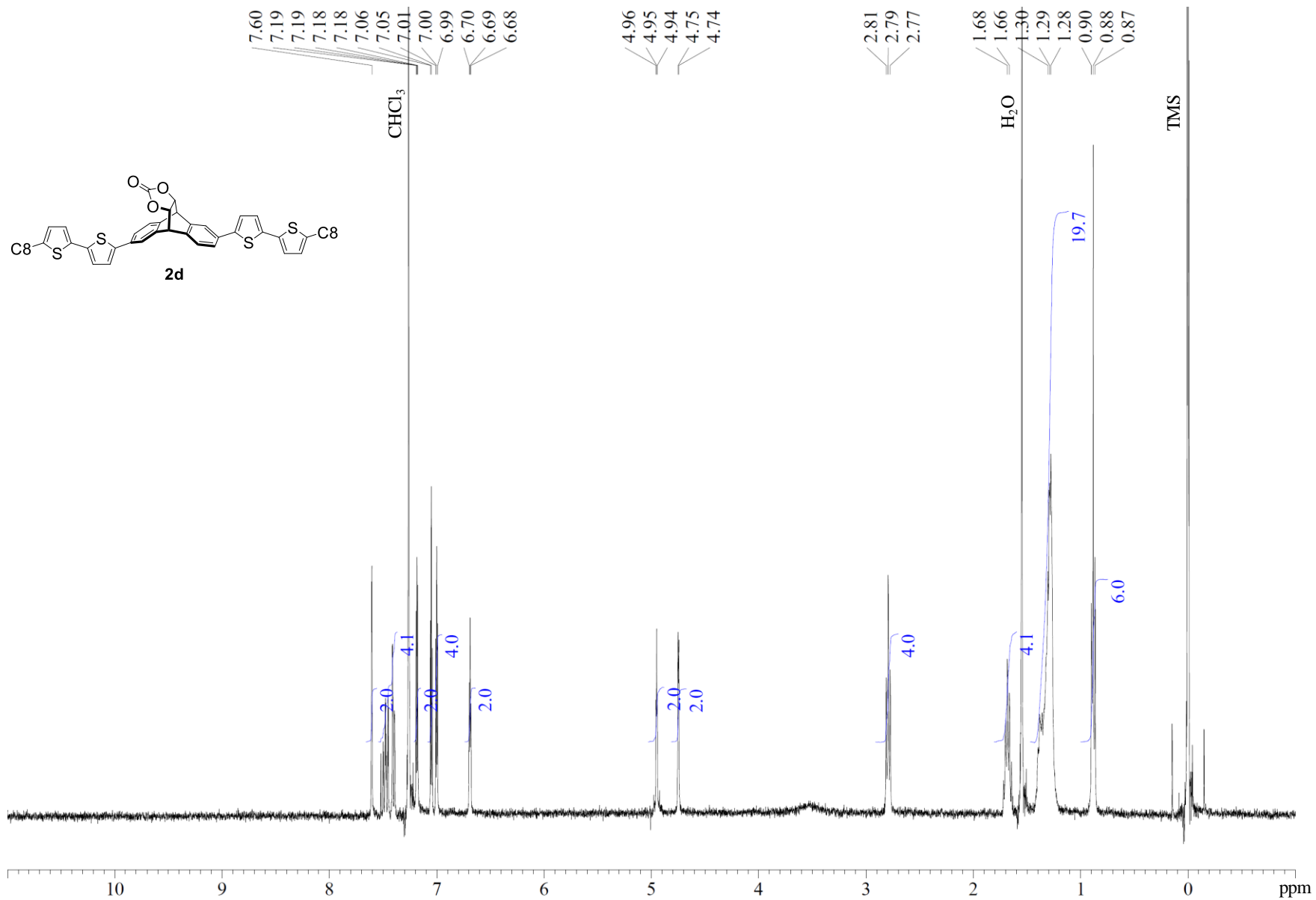
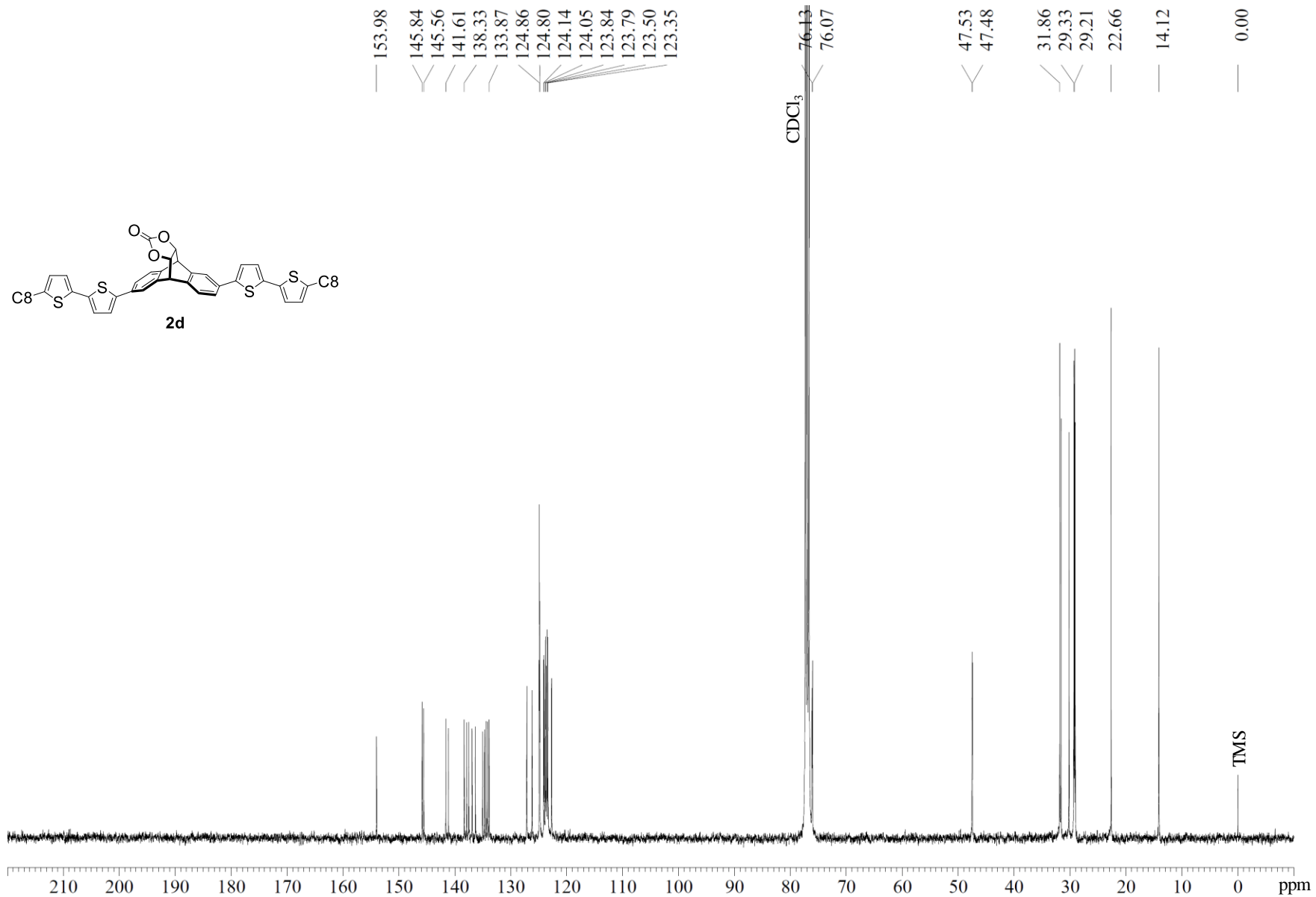


Fig. S14  $^1\text{H NMR}$  spectrum of compound **2d**.



**Fig. S15**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **2d**.

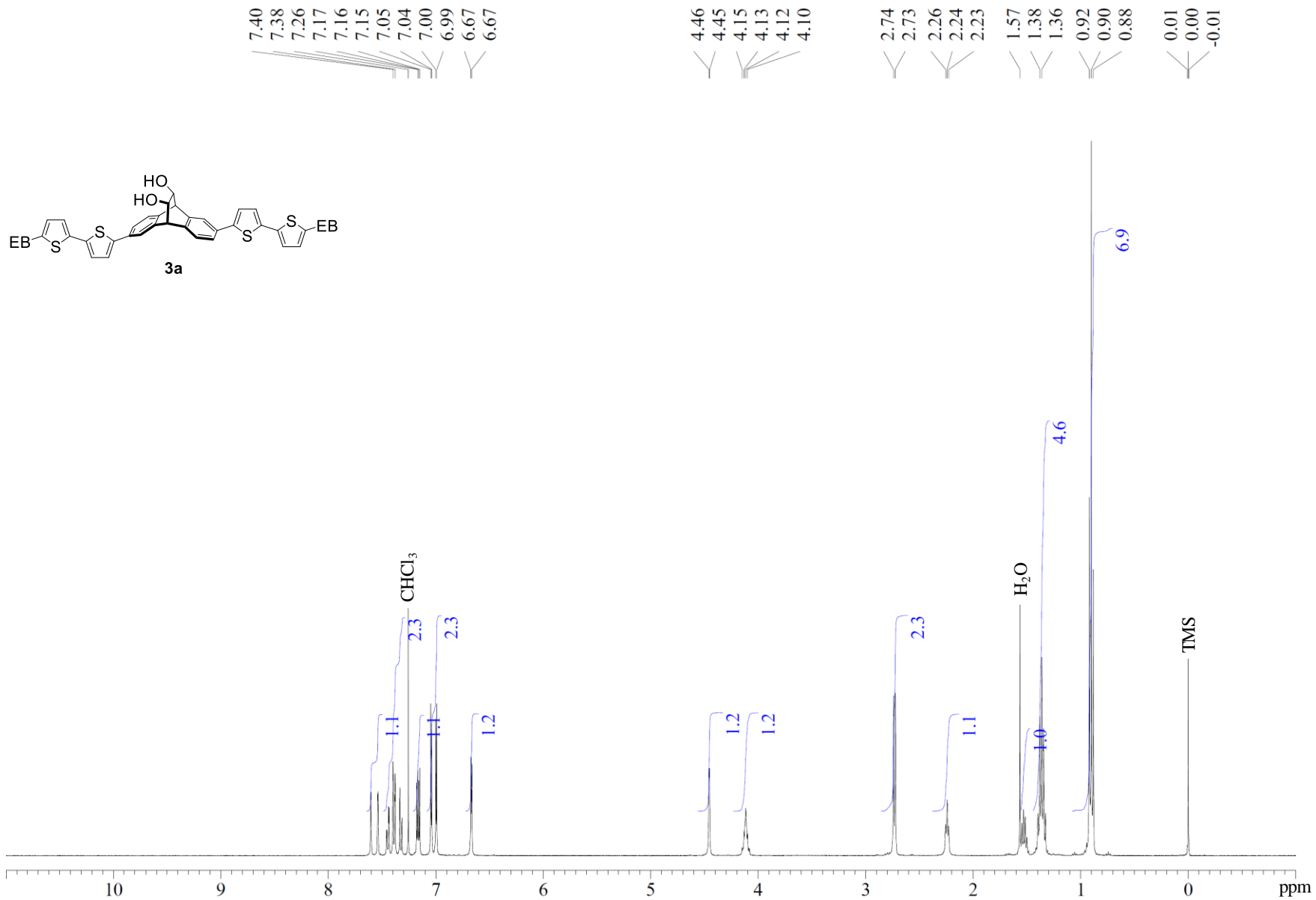
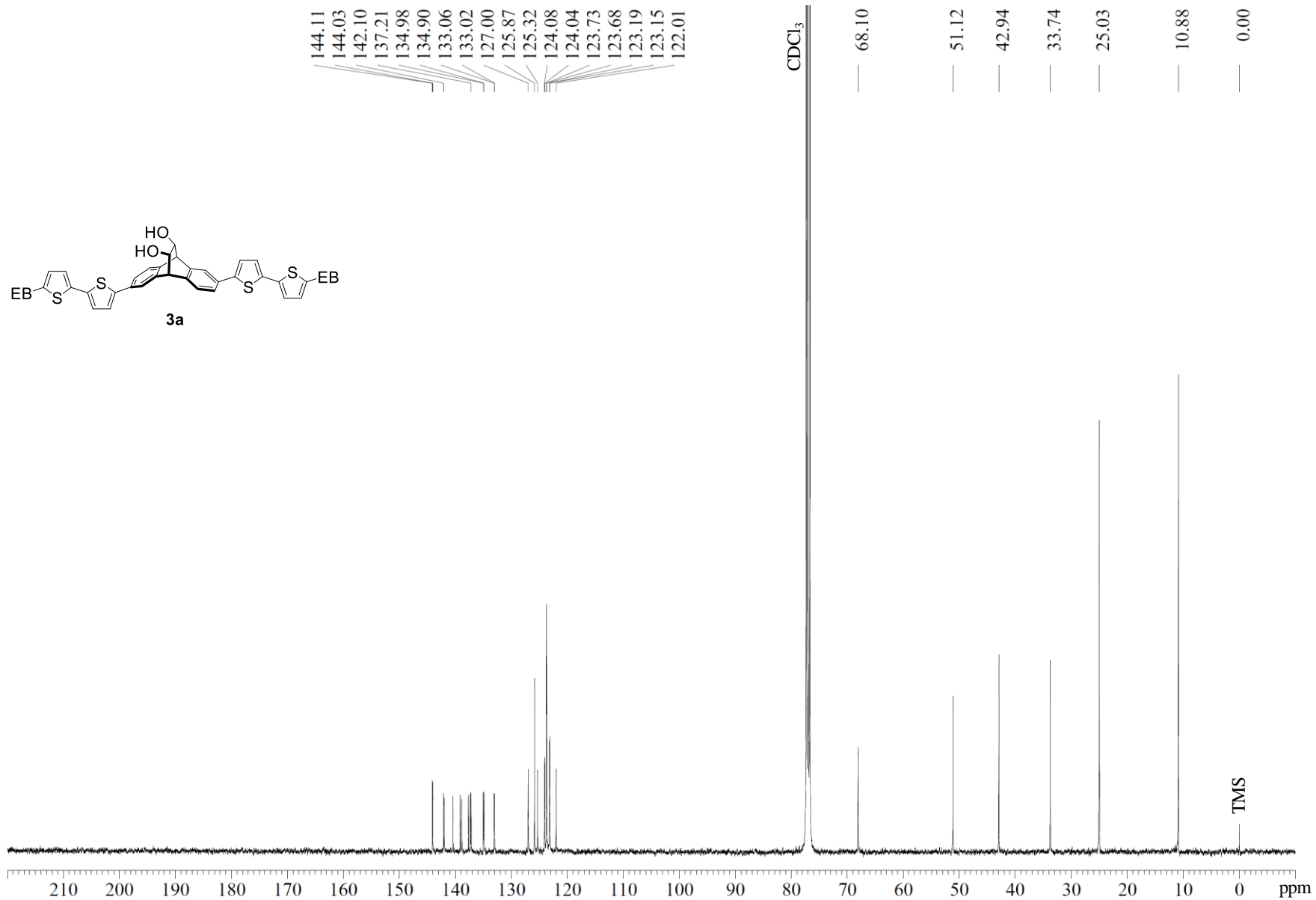
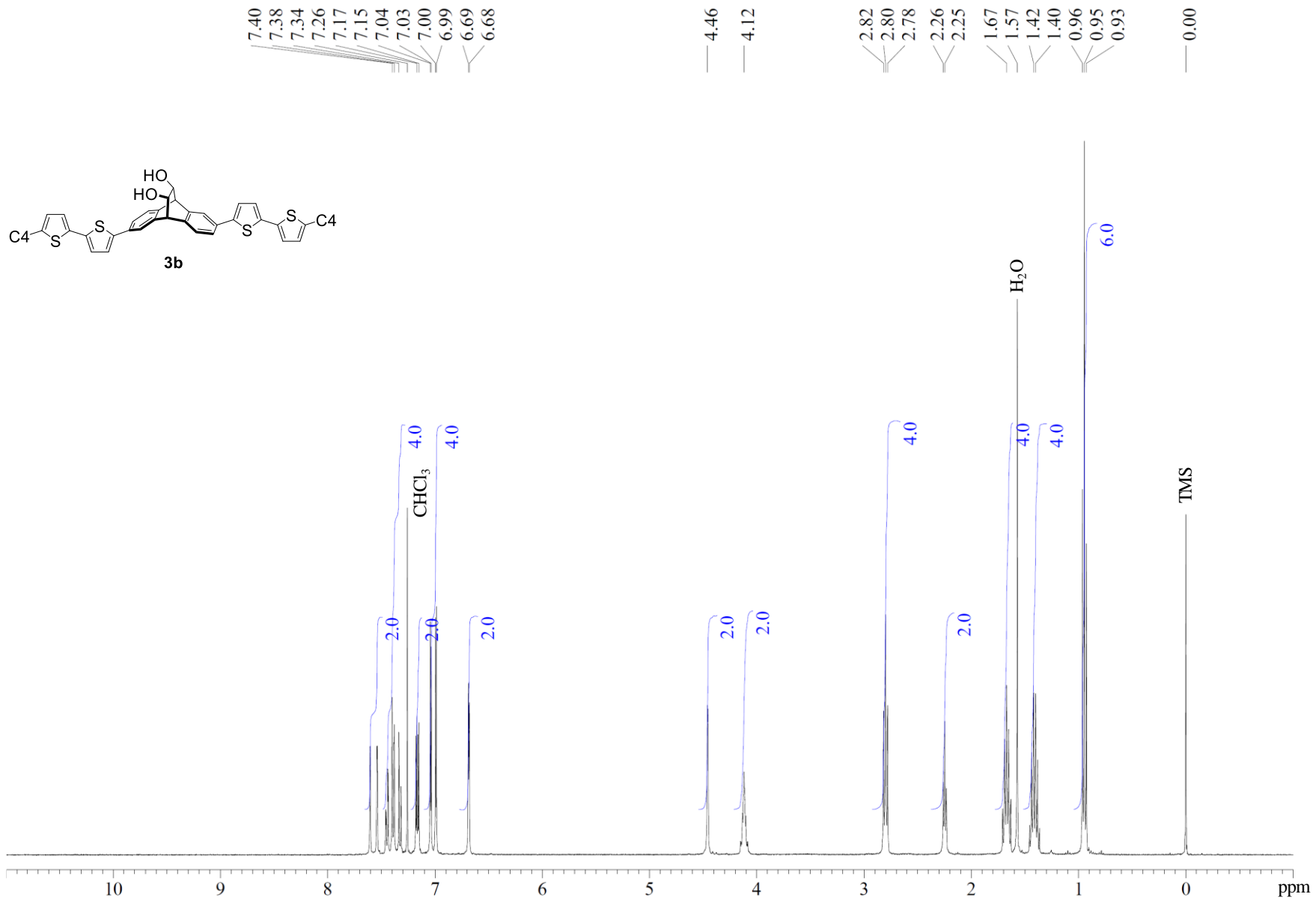


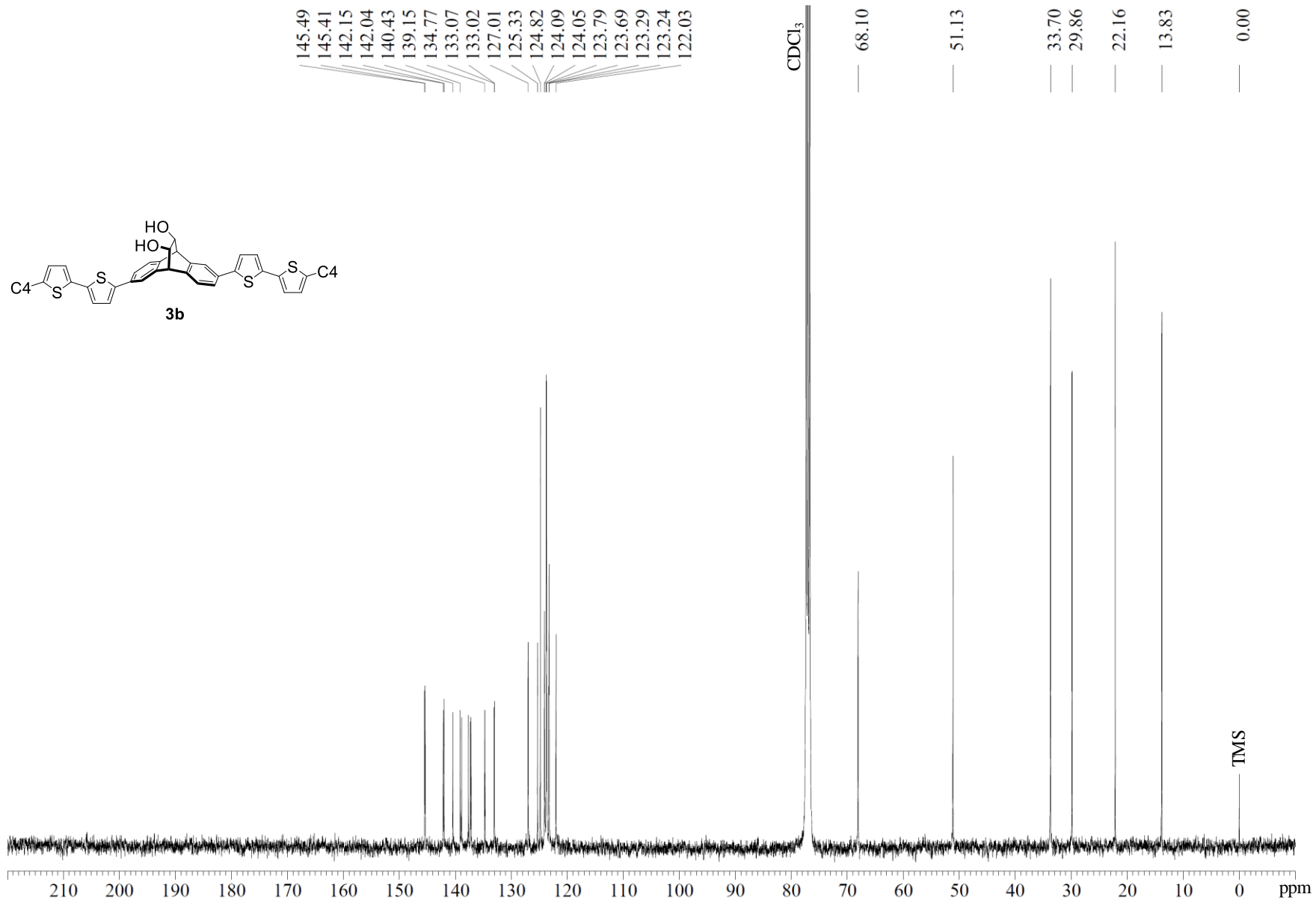
Fig. S16  $^1\text{H}$  NMR spectrum of compound **3a**.



**Fig. S17**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **3a**.



**Fig. S18** <sup>1</sup>H NMR spectrum of compound **3b**.



**Fig. S19**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **3b**.

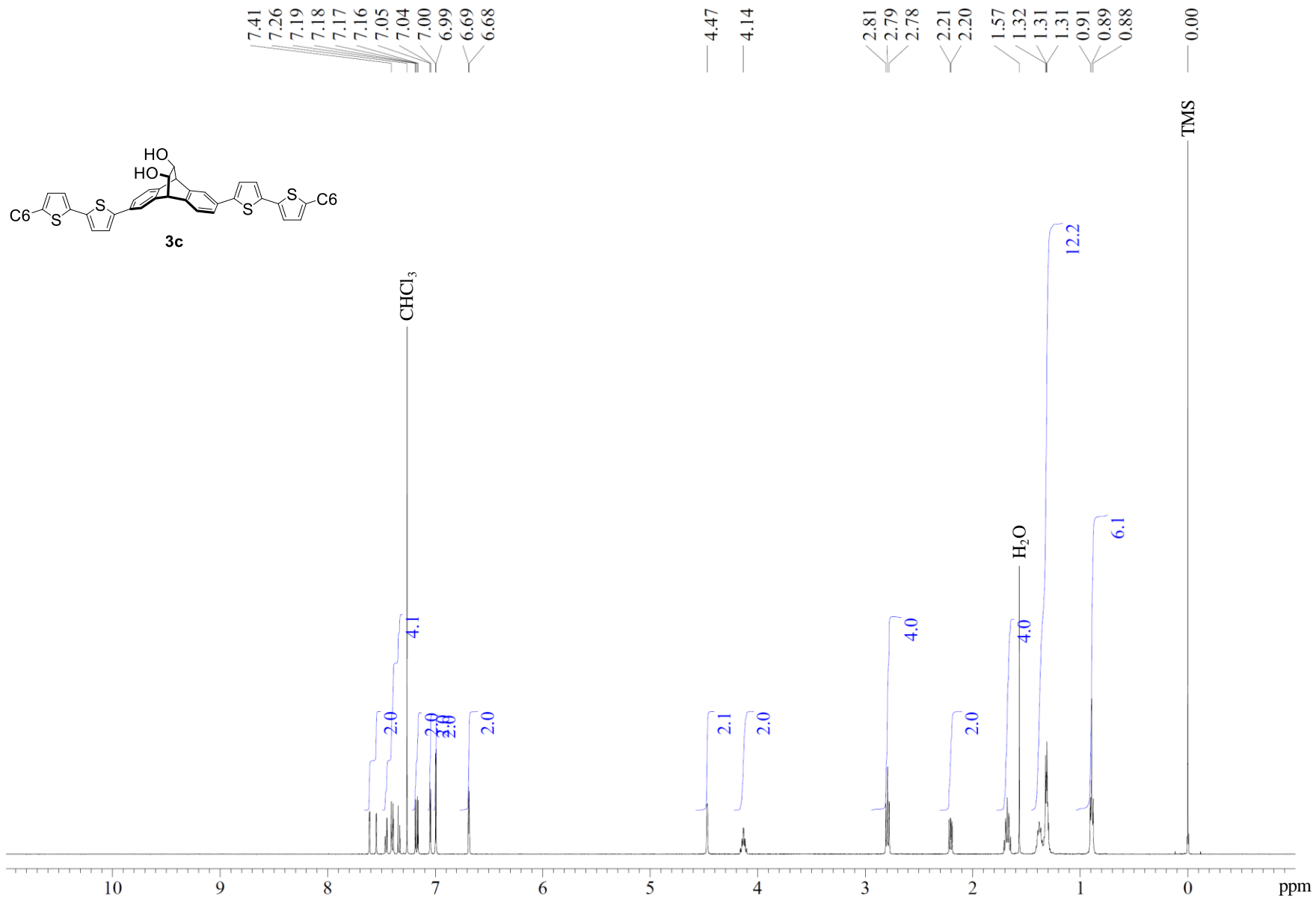
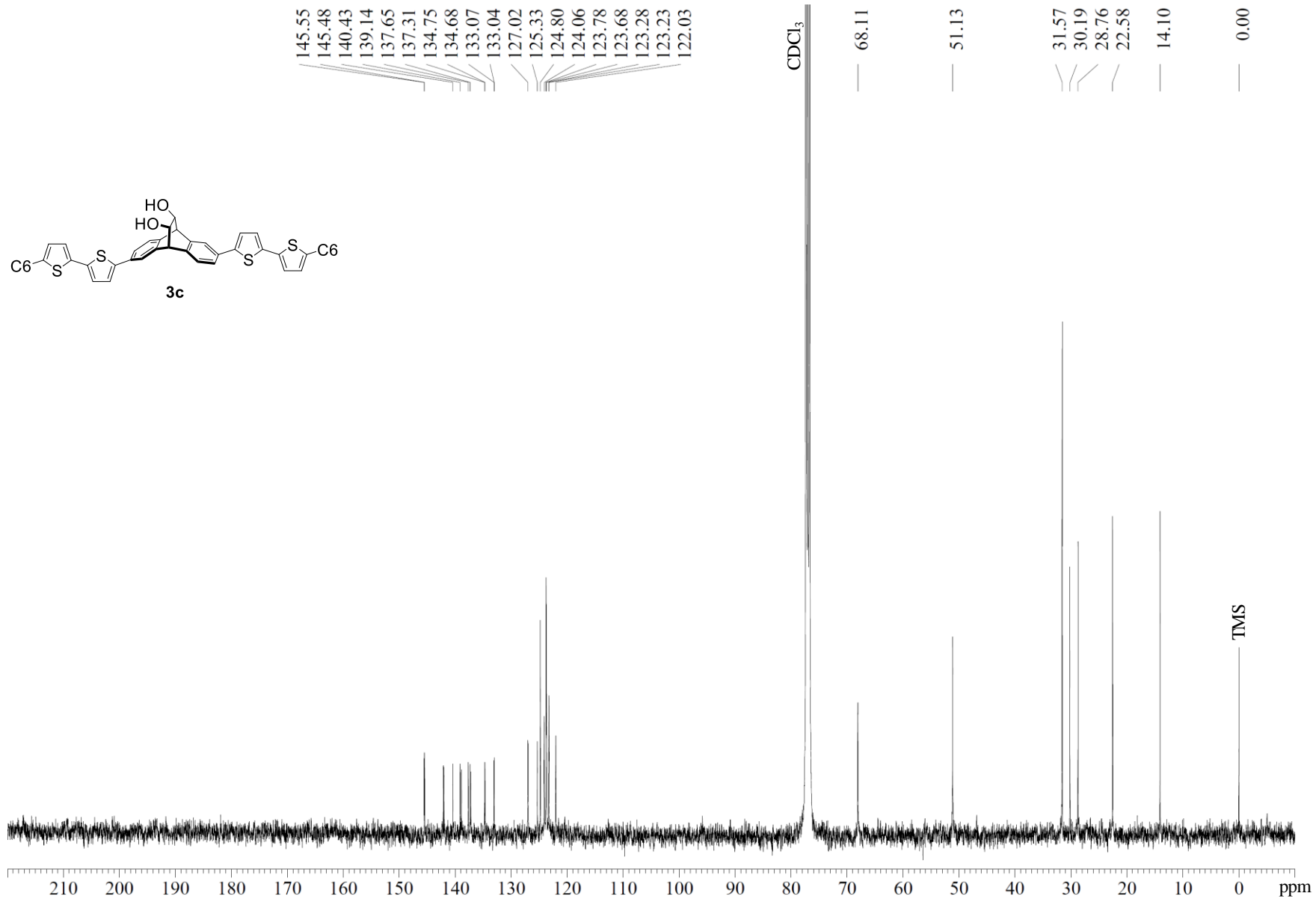


Fig. S20  $^1\text{H}$  NMR spectrum of compound **3c**.





**Fig. S21**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **3c**.

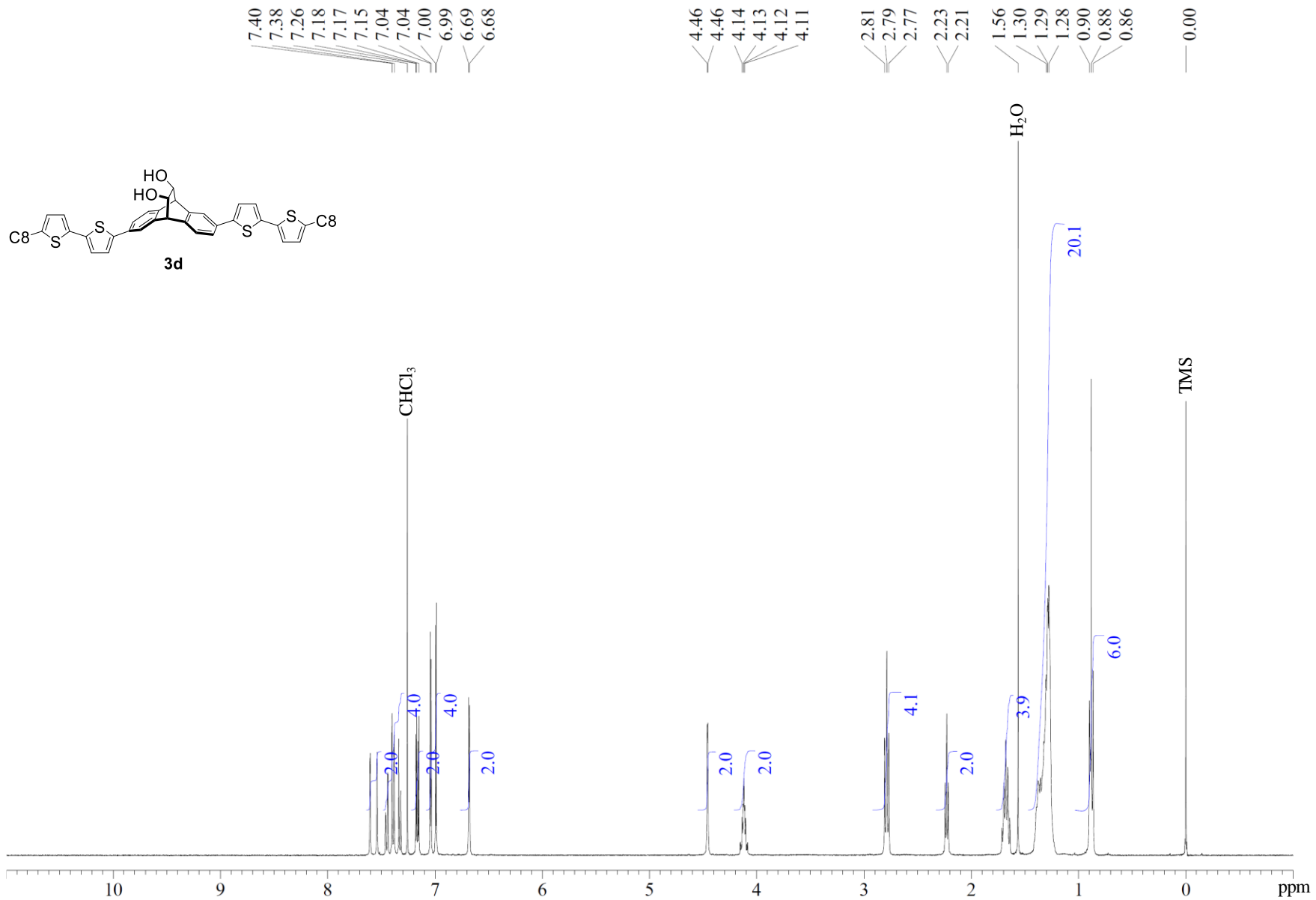
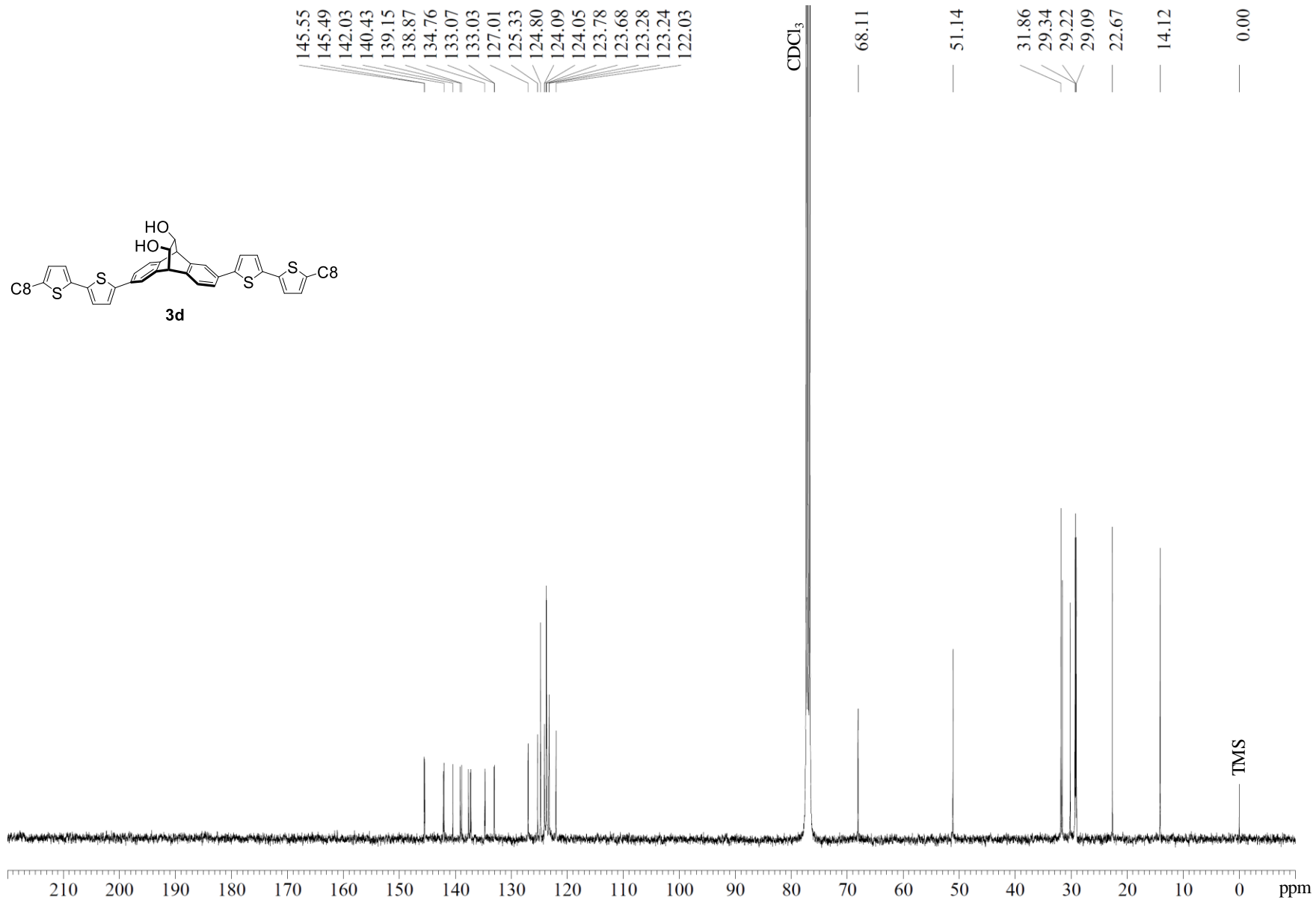


Fig. S22  $^1\text{H}$  NMR spectrum of compound **3d**.



**Fig. S23**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **3d**.

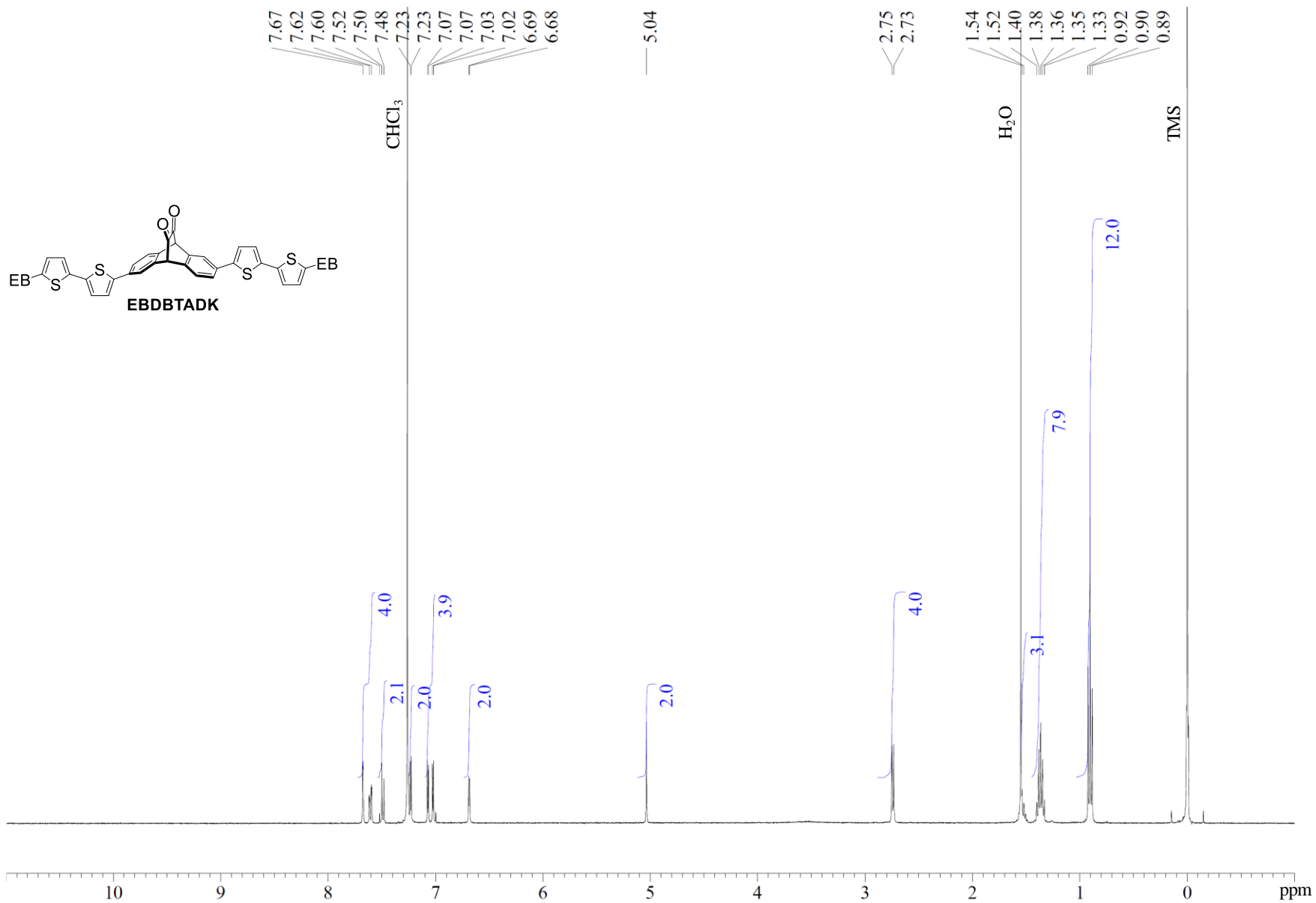
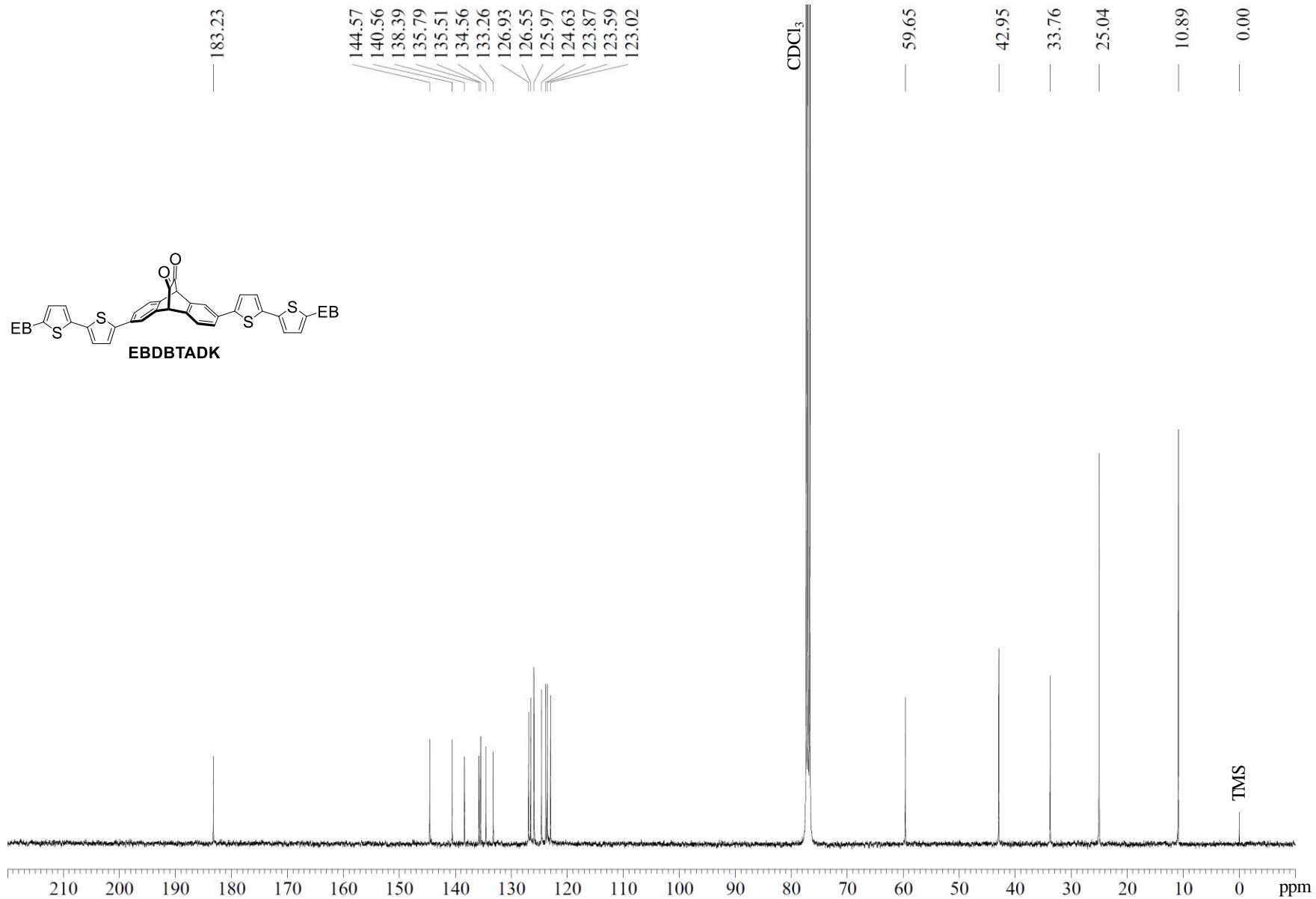


Fig. S24 <sup>1</sup>H NMR spectrum of EDBBTADK.



**Fig. S25**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of EDBBTADK.

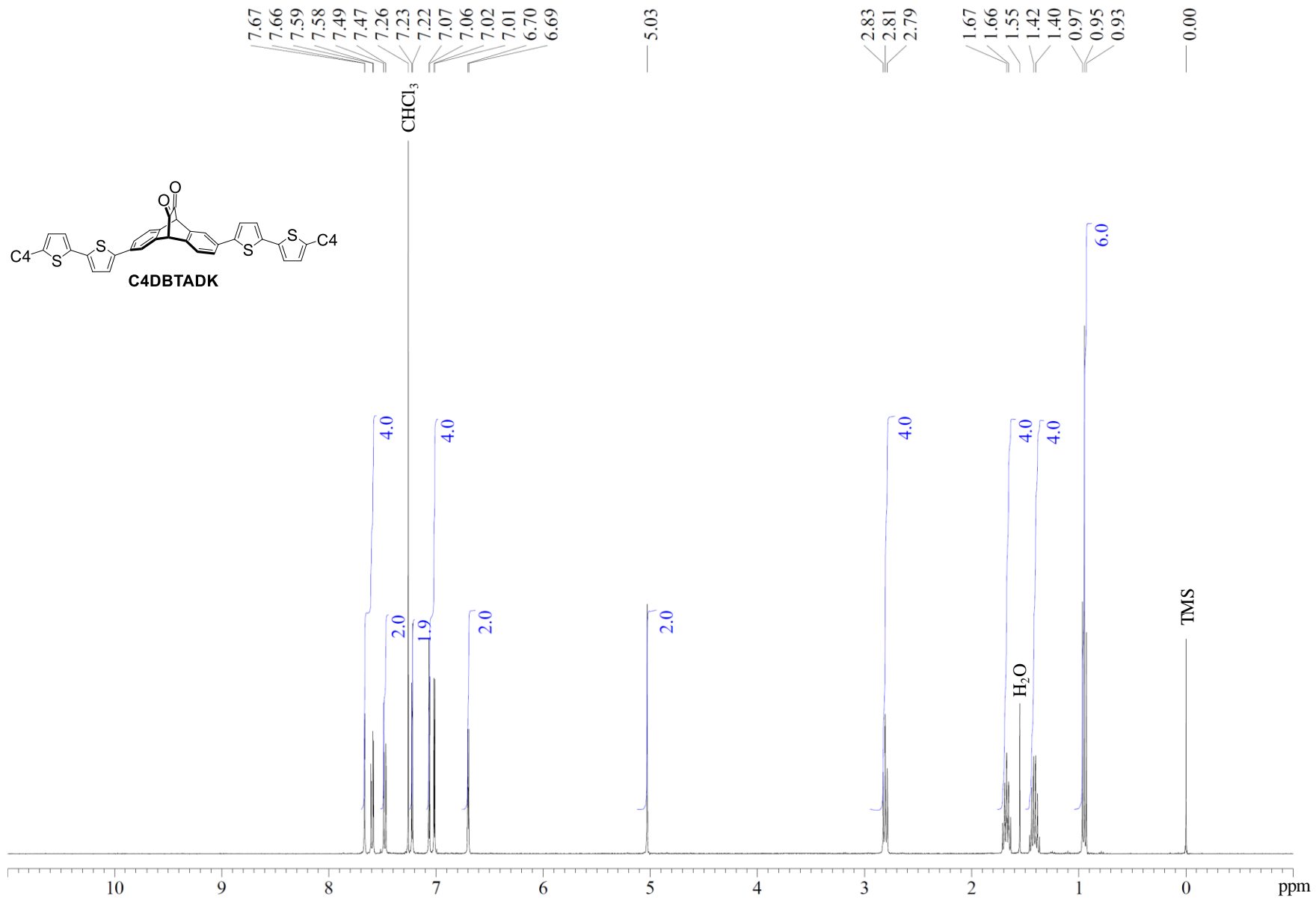
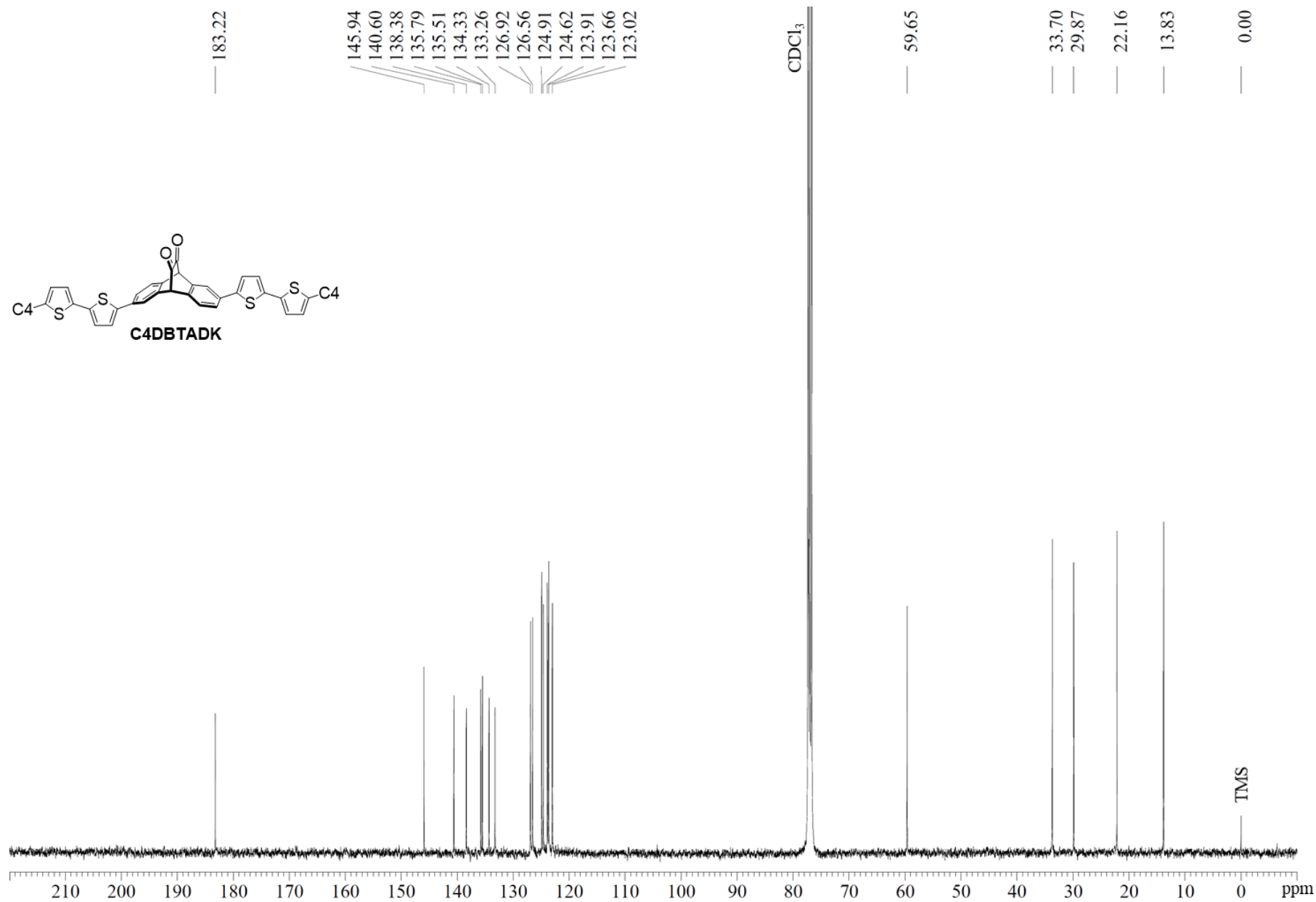
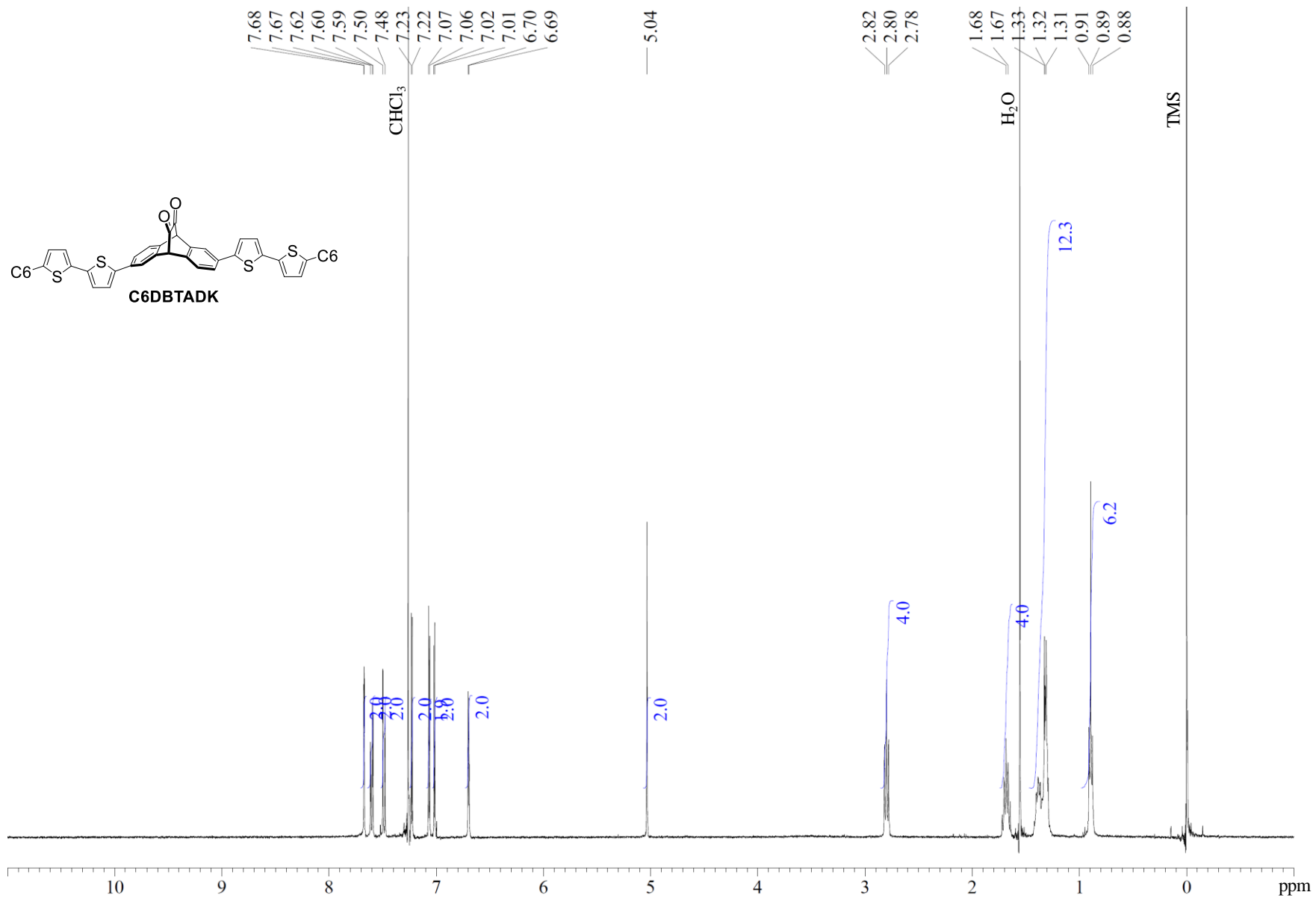


Fig. S26 <sup>1</sup>H NMR spectrum of C4DBTADK.

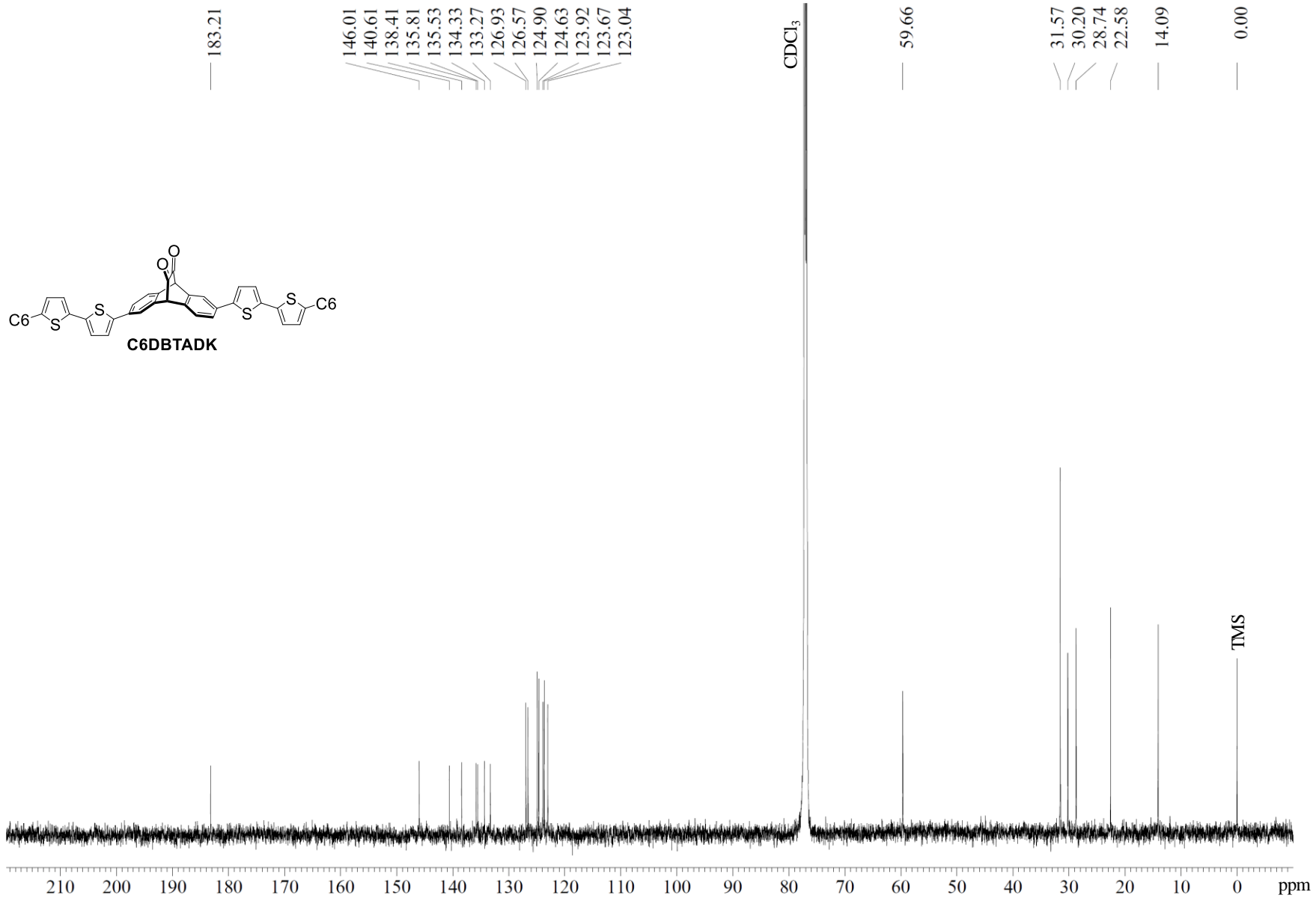


**Fig. S27**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of C4DBTADK.



**Fig. S28** <sup>1</sup>H NMR spectrum of C6DBTADK.





**Fig. S29**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of C6DBTADK.

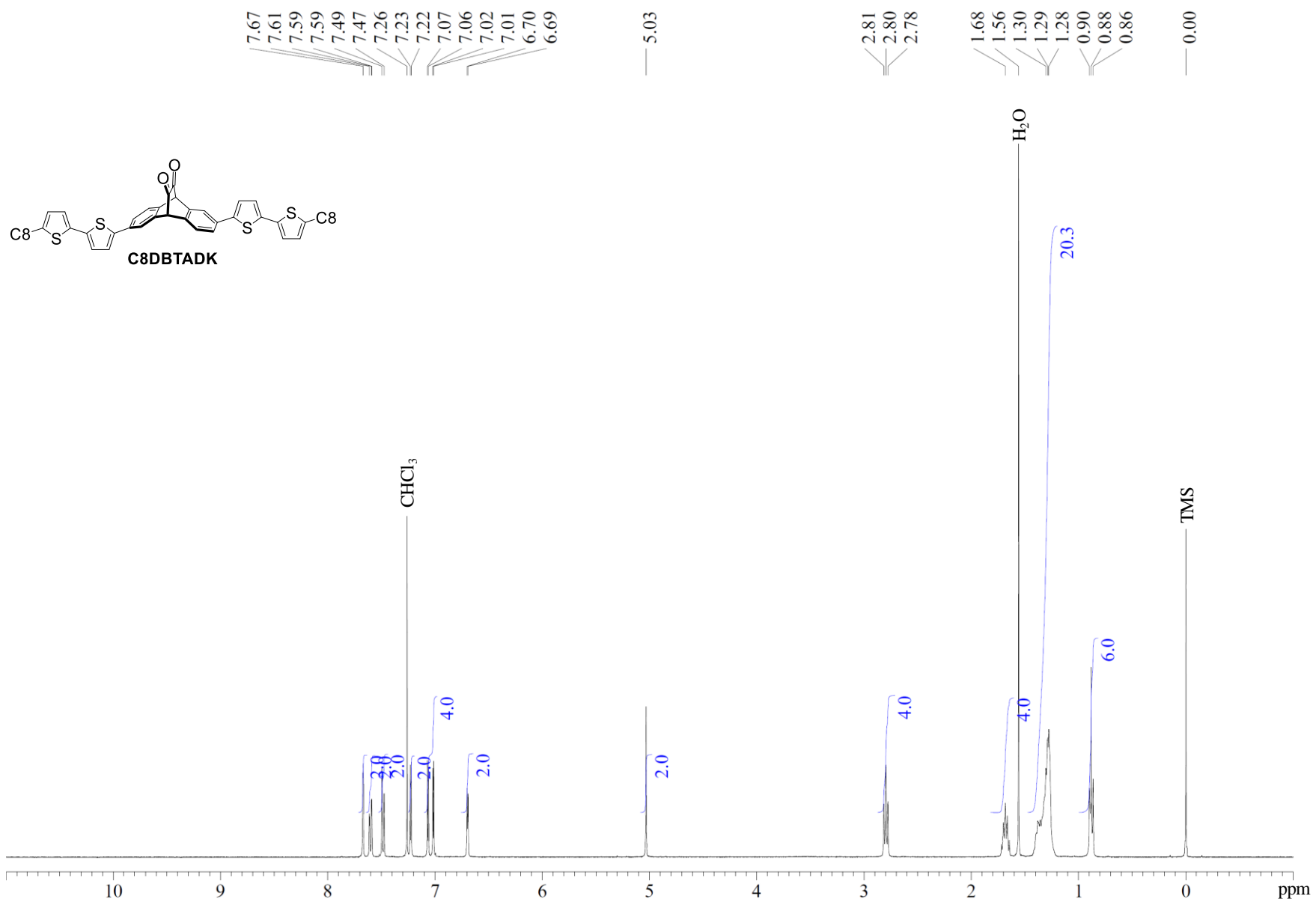
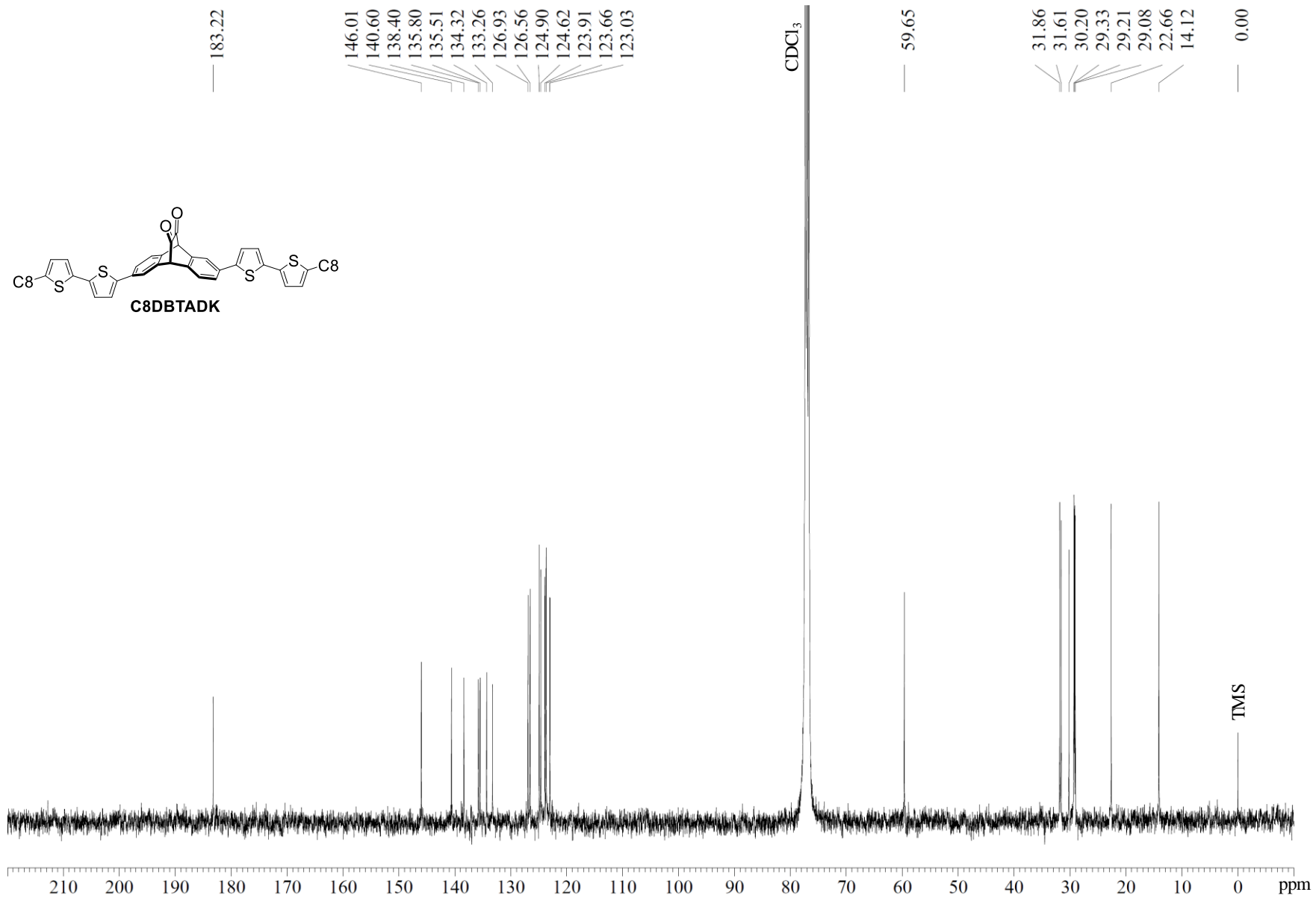


Fig. S30 <sup>1</sup>H NMR spectrum of C8DBTADK.



**Fig. S31**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of C8DBTADK.

### 3. References

- (S1) Yamaguchi, Y.; Suzuki, M.; Motoyama, T.; Sugii, S.; Katagiri, C.; Takahira, K.; Ikeda, S.; Yamada, H.; Nakayama, K. Photoprecursor Approach as an Effective Means for Preparing Multilayer Organic Semiconducting Thin Films by Solution Processes. *Sci. Rep.* **2014**, *4*, 7151.
- (S2) Suzuki, M.; Yamaguchi, Y.; Uchinaga, K.; Takahira, K.; Quinton, C.; Yamamoto, S.; Nagami, N.; Furukawa, M.; Nakayama, K.; Yamada, H. A Photochemical Layer-by-Layer Solution Process for Preparing Organic Semiconducting Thin Films Having the Right Material at the Right Place. *Chem. Sci.* **2018**, *9* (32), 6614–6621.
- (S3) Li, C.-Z.; Chueh, C.-C.; Yip, H.-L.; O'Malley, K. M.; Chen, W.-C.; Jen, A. K.-Y. Effective Interfacial Layer to Enhance Efficiency of Polymer Solar Cells via Solution-Processed Fullerene-Surfactants. *J. Mater. Chem.* **2012**, *22* (17), 8574–8578.
- (S4) Kuo, C.-Y.; Huang, Y.-C.; Hsiow, C.-Y.; Yang, Y.-W.; Huang, C.-I.; Rwei, S.-P.; Wang, H.-L.; Wang, L. Effect of Side-Chain Architecture on the Optical and Crystalline Properties of Two-Dimensional Polythiophenes. *Macromolecules* **2013**, *46* (15), 5985–5997.