Electronic Supplementary Material (ESI) for ChemComm.

ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

Amplifying Fluorescent Conjugated Polymer Sensor for Singlet Oxygen Detection

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I. Additional Figures

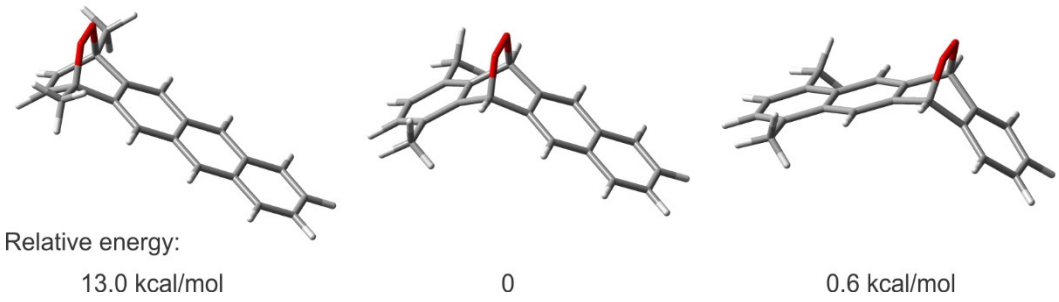


Figure S1. Energy difference between different endo-peroxides formed from 1,4-dimethyltetracene (calculated at B3LYP-6-31G* level of theory).

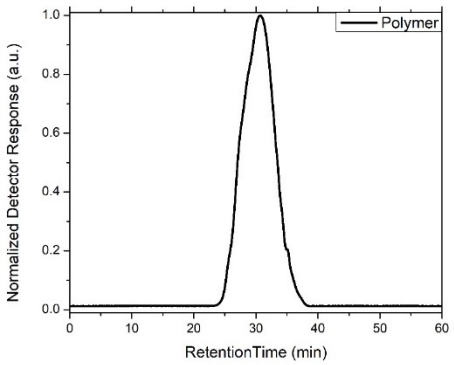


Figure S2. GPC elution trace for conjugated polymer **P1**. Experimental conditions: solvent THF, flow rate 0.7 ml/min, UV/vis absorbance detection at 450 nm.

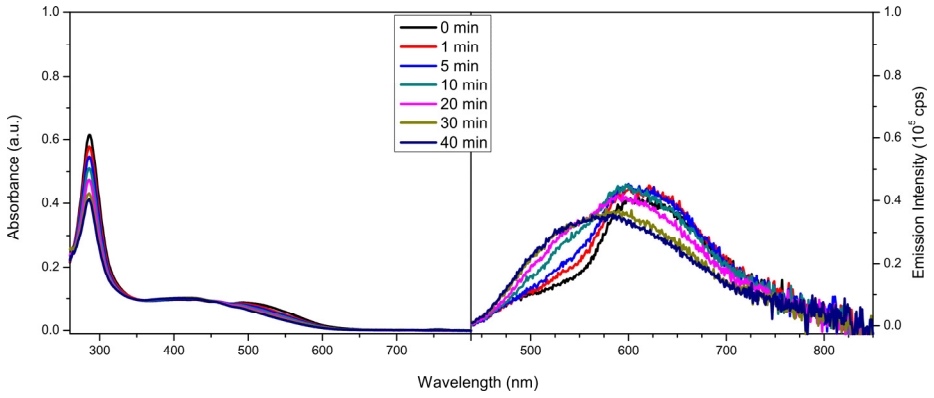


Figure S3. Change in UV/vis absorption (left) and fluorescence (right) spectra of a 17 μM solution of the polymer sensor **P1** with Rose Bengal polymer beads in DMSO upon photoirradiation without oxygen.

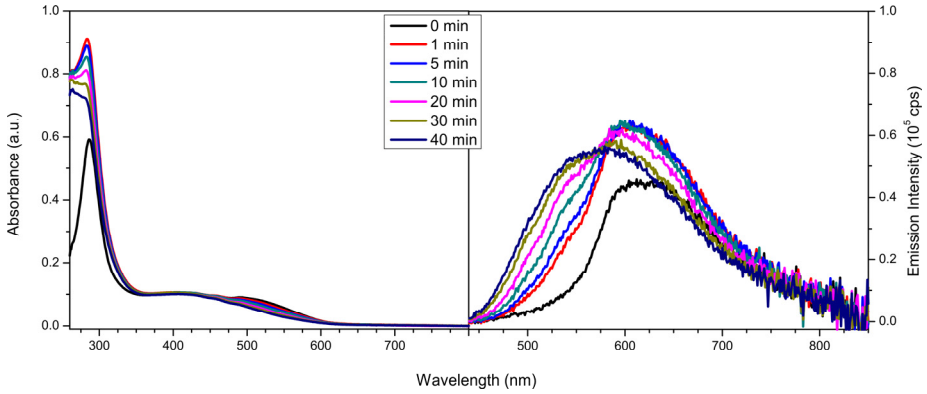


Figure S4. Change in UV/vis absorption (left) and fluorescence (right) spectra of a 17 μM solution of the polymer sensor **P1** in DMSO upon exposure to oxygen and photoirradiation (without Rose Bengal sensitizer).

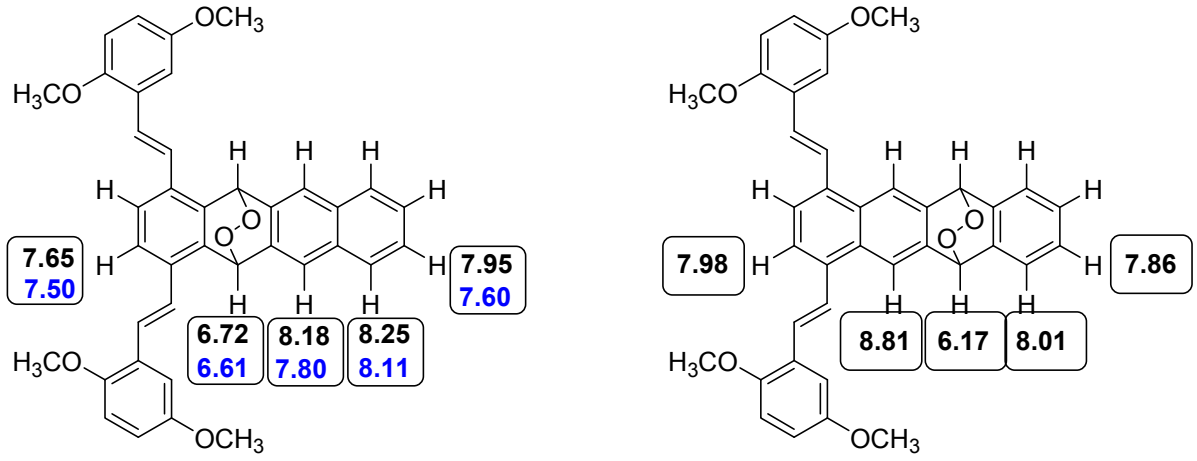


Figure S5. Computational prediction and experimental chemical shifts for two alternative endo-peroxides formed from small-molecule sensor **M1**. Calculated chemical shifts are shown in black, and experimental shifts (obtained in DMSO-D_6) are shown in blue. Computational structure was truncated by replacing OTEG substituents with OCH_3 substituents. Geometry optimizations were done at B3LYP/6-31G* level, and NMR chemical shifts were calculated on the geometry optimized structures using GIAO at HF/6-31G* level. All computations were done with CPCM solvent treatment (DMSO).

II. Experimental Section

General procedures

All the reactions were performed under an atmosphere of dry nitrogen (unless mentioned otherwise). Column chromatography was performed on silica gel (Sorbent Technologies, 60 Å, 40-63 μm) slurry packed into glass columns. Tetrahydrofuran (THF) and toluene were dried by

passing through activated alumina, and *N,N*-dimethylformamide (DMF) was dried by passing through molecular sieves, using a PS-400 Solvent Purification System from Innovative Technology, Inc. The water content of the solvents was periodically controlled by Karl Fischer titration (using a DL32 coulometric titrator from Mettler Toledo). All other reagents and solvents were obtained from Aldrich and Alfa Aesar and used without further purification. UV/vis absorption spectra were recorded on a Varian Cary 50 UV-Vis spectrometer. Fluorescence studies were carried out using a PTI QuantaMaster4/2006SE spectrofluorimeter. ^{1}H NMR spectra were recorded at 400 MHz and are reported in ppm downfield from tetramethylsilane. High-resolution mass spectra (HRMS) was obtained at the Louisiana State University Mass Spectrometry Facility using an Agilent 6210 instrument. GPC analysis of polymers was performed with an Agilent 1100 chromatograph equipped with two PLgel 5 μm MIXED-C and one PLgel 5 μm 1000 Å columns connected in series, using THF as a mobile phase, and calibrated against polystyrene standards. DFT and *ab initio* computations were carried out using *Gaussian 16* computational package running on a Windows-based computer.[1]

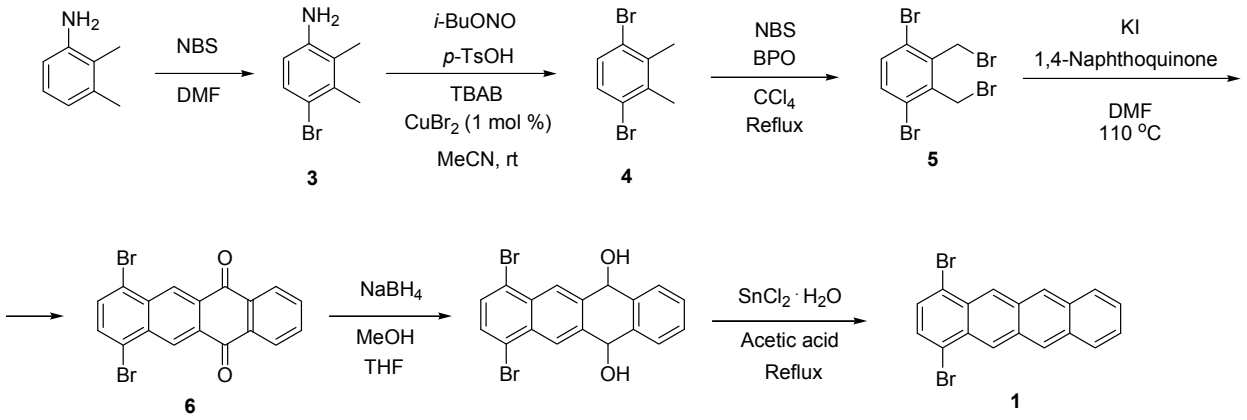
Photoirradiation experiments

Rose Bengal modified polystyrene beads (10 mg) were added in a solution of compound **P1** or **M1** in DMSO placed in a 1 cm path rectangular quartz cuvette. The mixture was stirred under flow of O_2 (50 ml/min) and irradiated for specified time periods using a 500 W tungsten-halogen lamp placed at a distance of 0.3 m from the sample.

Synthesis details

1,4-bis(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)-2,5-bis((4,4,5,5-tetramethyl)-1,3,2-dioxaborolan-1-yl)benzene (2) and **1,4-bis(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)-2-((4,4,5,5-tetramethyl)-1,3,2-dioxaborolan-1-yl)benzene (S1)** were prepared following previous literature procedures.[2]

4-Bromo-2,3-dimethylaniline (3). A solution of *N*-bromosuccinimide (44.06 g, 248 mmol) in 100 ml of dry DMF was added dropwise to a solution of 2,3-dimethylaniline (30 g, 248 mmol) in 50 ml of dry DMF, and the resulting mixture was stirred at room temperature for 24 h. The mixture was then poured into water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (eluent hexanes: CH_2Cl_2 1:1) to yield 33.94 g (42 %) of **3** as a viscous



purple oil, R_f 0.2. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, J = 4.0 Hz, 1H), 6.44 (d, J = 6.4 Hz, 1H), 3.56 (br s, 2H), 2.38 (s, 3H), 2.13 (s, 3H).

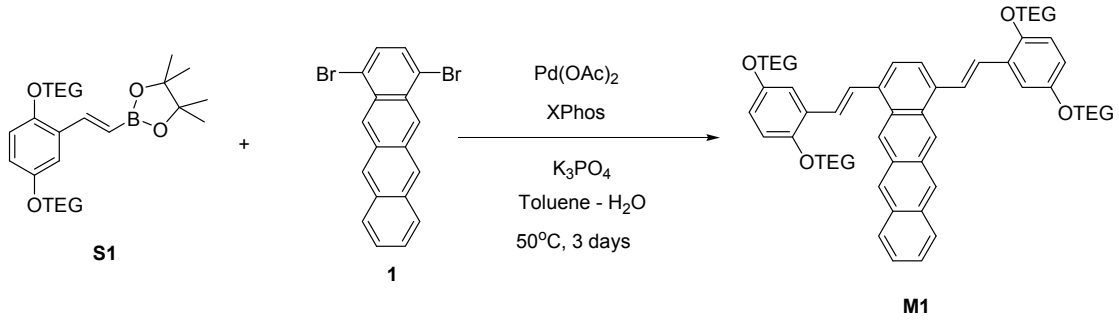
1,4-Dibromo-2,3-dimethylbenzene (4). A solution of isobutyl nitrite (3.17 g, 30.8 mmol) and *p*-TsOH (5.84 g, 30.8 mmol) in 20 ml of dry acetonitrile was added dropwise to a solution of compound **3** (5.13 g, 25.6 mmol) in 50 ml of dry acetonitrile and the mixture was stirred at room temperature for 10 min. This was followed by addition of tetra-*n*-butylammonium bromide (TBAB, 16.5 g, 51.2 mmol) and catalytic amount of copper(II) bromide (57.2 mg, 0.26 mmol), and the reaction mixture was stirred at room temperature for 50 min. After completion of the reaction (as confirmed by TLC) the reaction mixture was concentrated *in vacuo*. The solid was washed with water and extracted with dichloromethane. The organic solution was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (eluent hexane) to yield 5.33 g (79 %) of compound **4** as a white solid, R_f 0.55, mp. 44 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (s, 2H), 2.45 (s, 6H).

1,4-dibromo-2,3-bis(dibromomethyl)benzene (5).[3] A mixture of 1,4-dibromo-2,3-dimethylbenzene **4** (2.66 g, 10.1 mmol), NBS (4.31 g, 24.2 mmol) and benzoyl peroxide (244 mg, 1.01 mmol) was refluxed in CCl_4 overnight. After cooling to room temperature, water (100 ml) was added and the mixture was extracted with dichloromethane (3 × 75 ml). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Recrystallization from EtOH yielded 2.87 g (67 %) of compound **5** as a pale yellow crystalline solid, mp. 108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (s, 2H), 4.82 (s, 4H).

1,4-Dibromo-6,11-tetracenequinone (6). A solution of compound **5** (2.0 g, 4.74 mmol), 1,4-naphthoquinone (749 mg, 4.74 mmol) and potassium iodide (3.15 g, 19.0 mmol) in 150 ml of

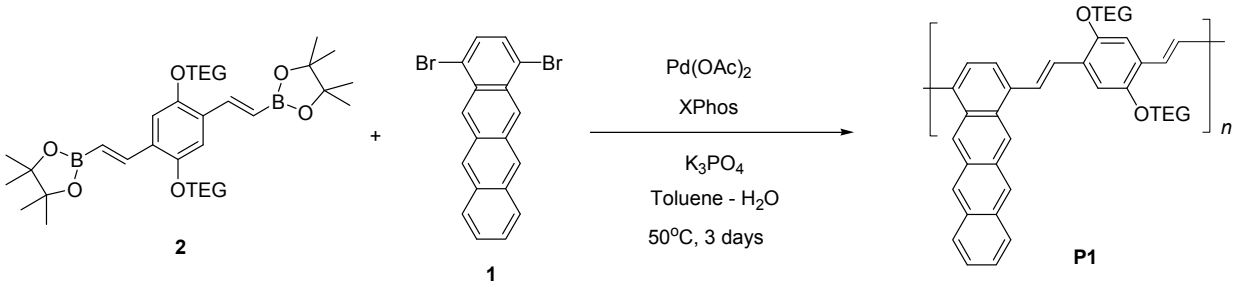
dry DMF was stirred at 110 °C for 18 h. After cooling to room temperature, the resulting mixture was poured into 500 ml of 4:1 methanol: water mixture. The solid was collected on a Büchner funnel, washed successively with methanol, water and small amount of dichloromethane to yield 1.18 g (60%) of compound **6** as a yellow solid, mp. 321 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.27 (s, 2H), 8.44 - 8.42 (m, 2H), 7.88 - 7.86 (m, 2H), 7.83 (s, 2H).

1,4-Dibromotetracene (1). A mixture of compound **6** (963 mg, 2.32 mmol), sodium borohydride (192 mg, 5.10 mmol) and 60 ml of dry THF and 60 ml of dry MeOH was stirred at room temperature for 1 h. The resulting mixture was then poured into 300 ml of water and a white solid precipitated and was collected without further purification. A mixture of the obtained solid (890 mg), $SnCl_2$ (1.05 g, 4.66 mmol) and acetic acid (150 ml) was refluxed for 4 hours. After cooling down to room temperature, the mixture was poured into 400 ml of water to yield an orange solid. This orange solid was collected and further purified by column chromatography on silica gel (eluent hexane: CH_2Cl_2 5:1) to yield 667 mg (82 %) of compound **1** as an orange solid, R_f 0.6, mp. 212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.09 (s, 2H), 8.80 (s, 2H), 8.07 - 8.04 (m, 2H), 7.57 (s, 2H), 7.49-7.46 (m, 2H). HRMS *m/e* 383.9149 M^+ (calcd for $C_{18}H_{10}Br_2$ 383.9143).

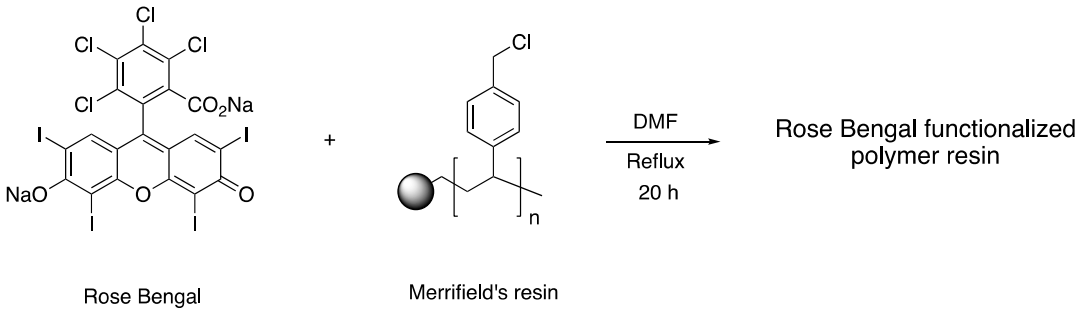


Small-molecule sensor M1. A mixture of compound **S1** (75.6 mg, 0.136 mmol), 1,4-dibromotetracene **1** (24.2 mg, 62 μmol), $Pd(OAc)_2$ (0.7 mg, 3.1 μmol), XPhos (2.95 mg, 6.2 μmol), K_3PO_4 (105 mg, 0.50 mmol) in 10 ml of toluene and 2 ml of ultrapure water was stirred in a sealed air-free flask at 50 °C for 72 h. After allowing to cool down to room temperature, the reaction mixture was filtered through a glass filter, and the filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (eluent ethyl acetate: MeOH 50:1) to afford 12 mg (18%) of **M1** as a red solid, R_f 0.2. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.12 (s, 2H), 8.77 (s, 2H), 8.17 (d, J = 16 Hz, 2H), 8.03 (m, 2H), 7.77 (s, 2H), 7.62 (d, J = 16 Hz, 2H), 7.42 (m,

4H), 6.97 (d, J = 8 Hz, 4H), 4.22 (m, 8H), 3.93-3.87 (m, 8H), 3.73-3.61 (m, 16H), 3.56-3.46 (m, 16H), 3.33 (d, J = 8 Hz, 12H). HRMS *m/e* 1079.5355 $[M–2+H]^+$ (calcd for $C_{62}H_{80}O_{16}$ 1079.5323).



Conjugated Polymer P1. A mixture of monomer **2** (81.2 mg, 0.109 mmol), 1,4-dibromotetracene **1** (42.7 mg, 0.109 mmol), $Pd(OAc)_2$ (1.23 mg, 5.4 μmol), XPhos (5.20 mg, 10.9 μmol), K_3PO_4 (185 mg, 0.87 mmol) in 10 ml of toluene and 2 ml of ultrapure water was stirred in a sealed air-free flask at 50 °C for 72 h. After cooling down to room temperature, the reaction mixture was added dropwise to acetone (100 ml), and the precipitate was collected by centrifugation and dried *in vacuo* to yield 32 mg (43%) of polymer **P1** as a dark red solid. GPC (THF vs. polystyrene standard): M_n 11.8 kDa, PDI 1.64. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.30-9.12 (broad m, 2H), 8.80-8.51 (broad m, 2H), 8.16-7.94 (broad m, 4H), 7.58-7.20 (broad m, 8H), 4.50-3.00 (broad m, 30H).



Rose Bengal functionalized polystyrene beads.[4] A mixture of 1.0 g (1.05 mmol) of Rose Bengal and 1 g of chloromethylated styrene-divinylbenzene copolymer beads (2.0-3.5 mmol/g Cl, 50-100 mesh) in 60 ml of dimethylformamide was refluxed for 20 h. After cooling down to room temperature, the polymer solid (now dark red) was filtered and washed successively with 150 ml portions of benzene, ethanol, ethanol-water (1:1), water, methanol-water (1:1), and methanol. Upon completing the washing, the final filtrate was colorless. The polymer beads were dried in a vacuum oven to a final weight of 1.12 g.

References

(1) Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

(2) C.-H. Chiang, D. Pangeni, and E. E. Nesterov, *Macromolecules* 2017**, 50**, 6961-6966.

(3) K. N. Plunkett, K. Godula, C. Nuckolls, N. Tremblay, A. C. Whitney, and S. Xiao, *Org. Lett.* 2009, **11**, 2225-2228.

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^{1}H NMR spectra of the key compounds

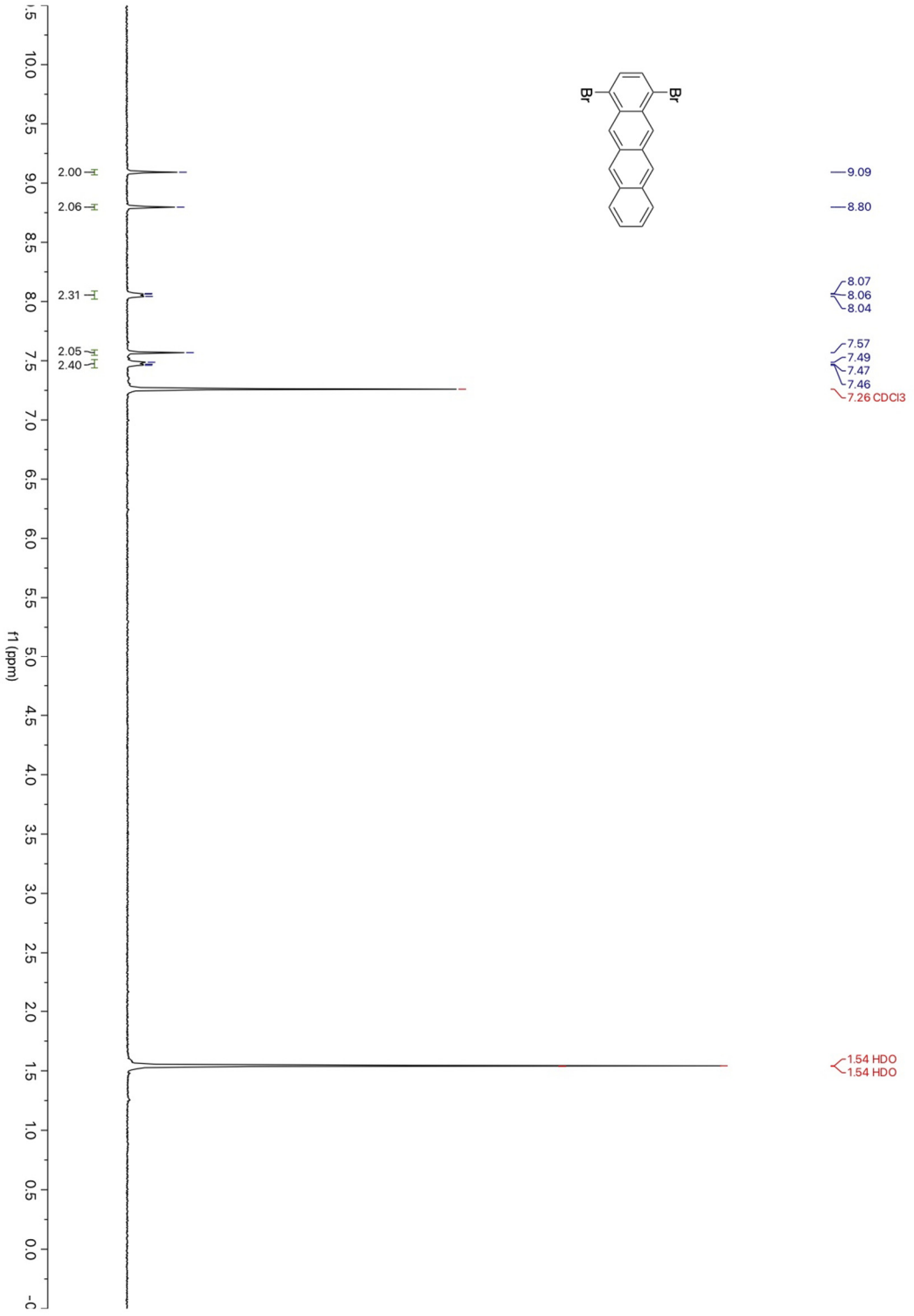

Figure S6. ^{1}H NMR spectrum of compound **1** ($CDCl_3$, 400 MHz).

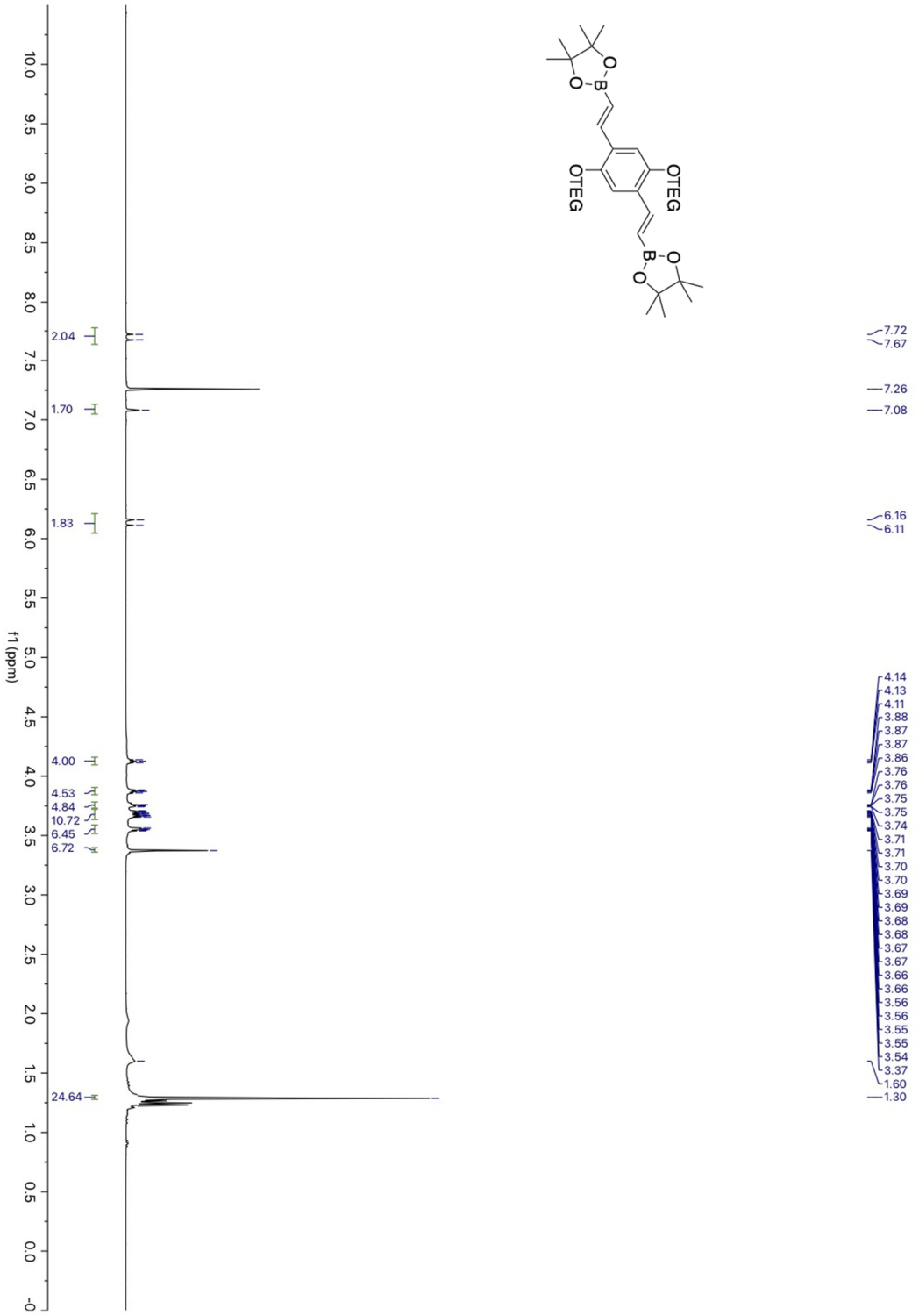

Figure S7. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 400 MHz).

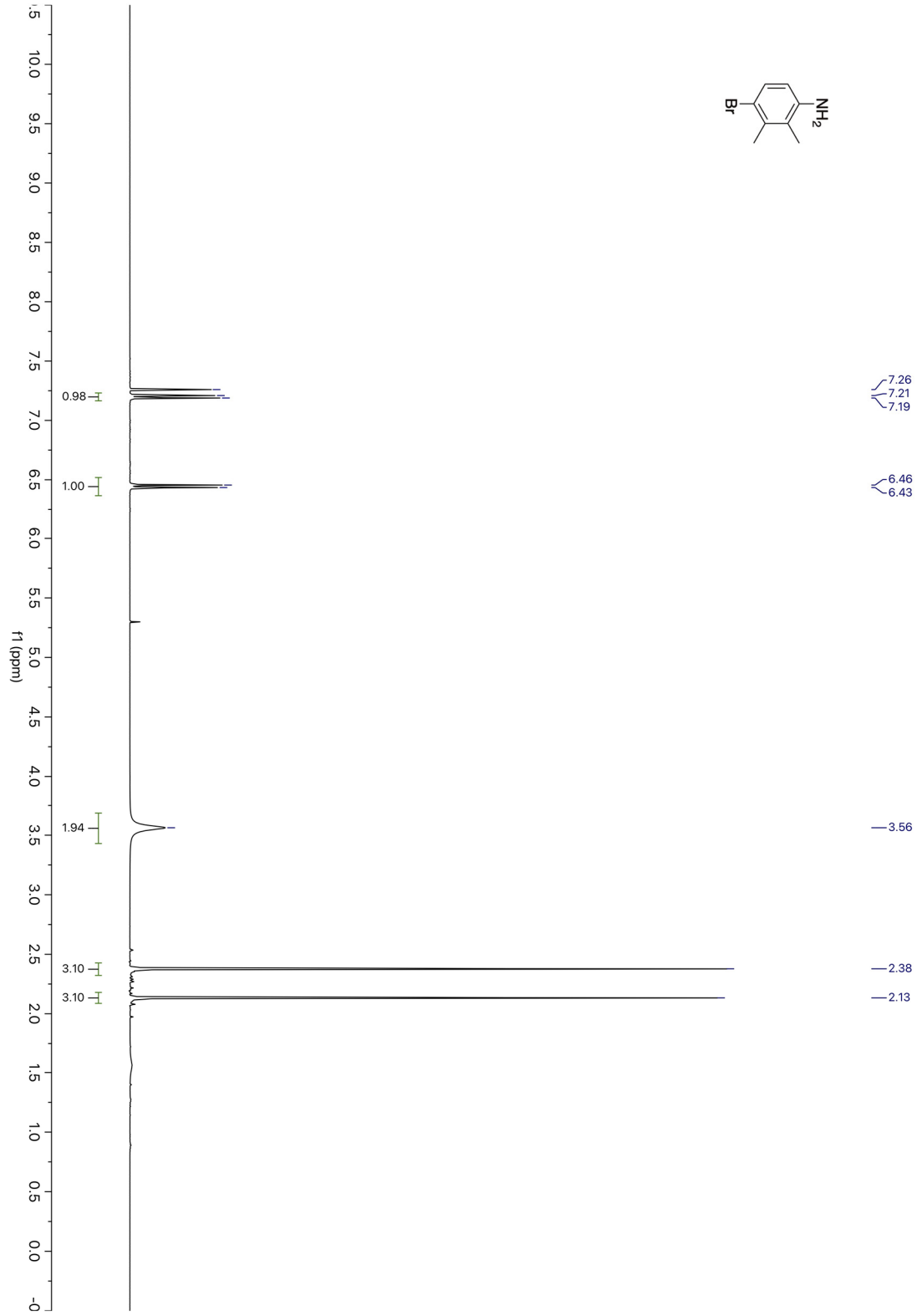

Figure S8. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 400 MHz).

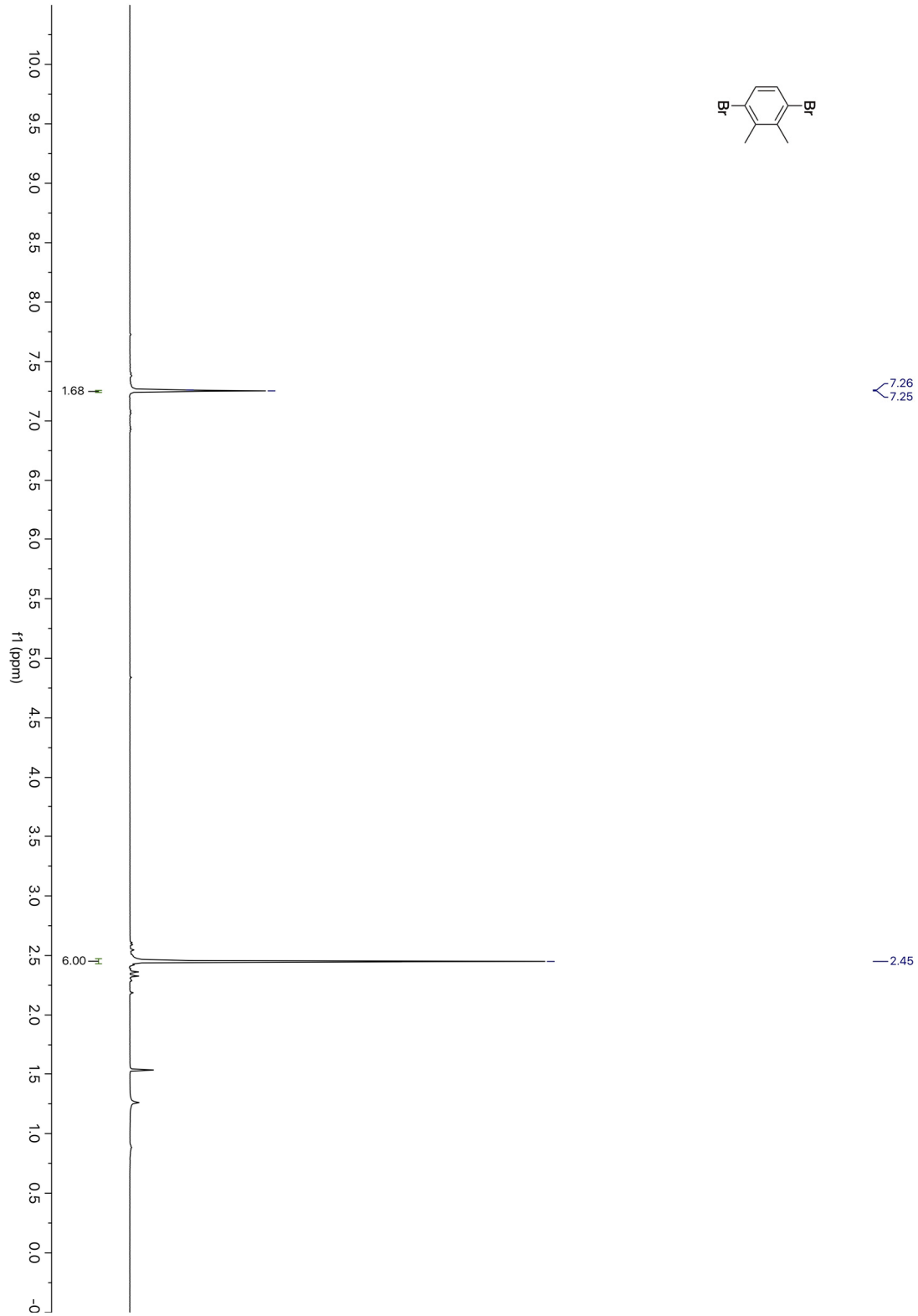

Figure S9. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 400 MHz).

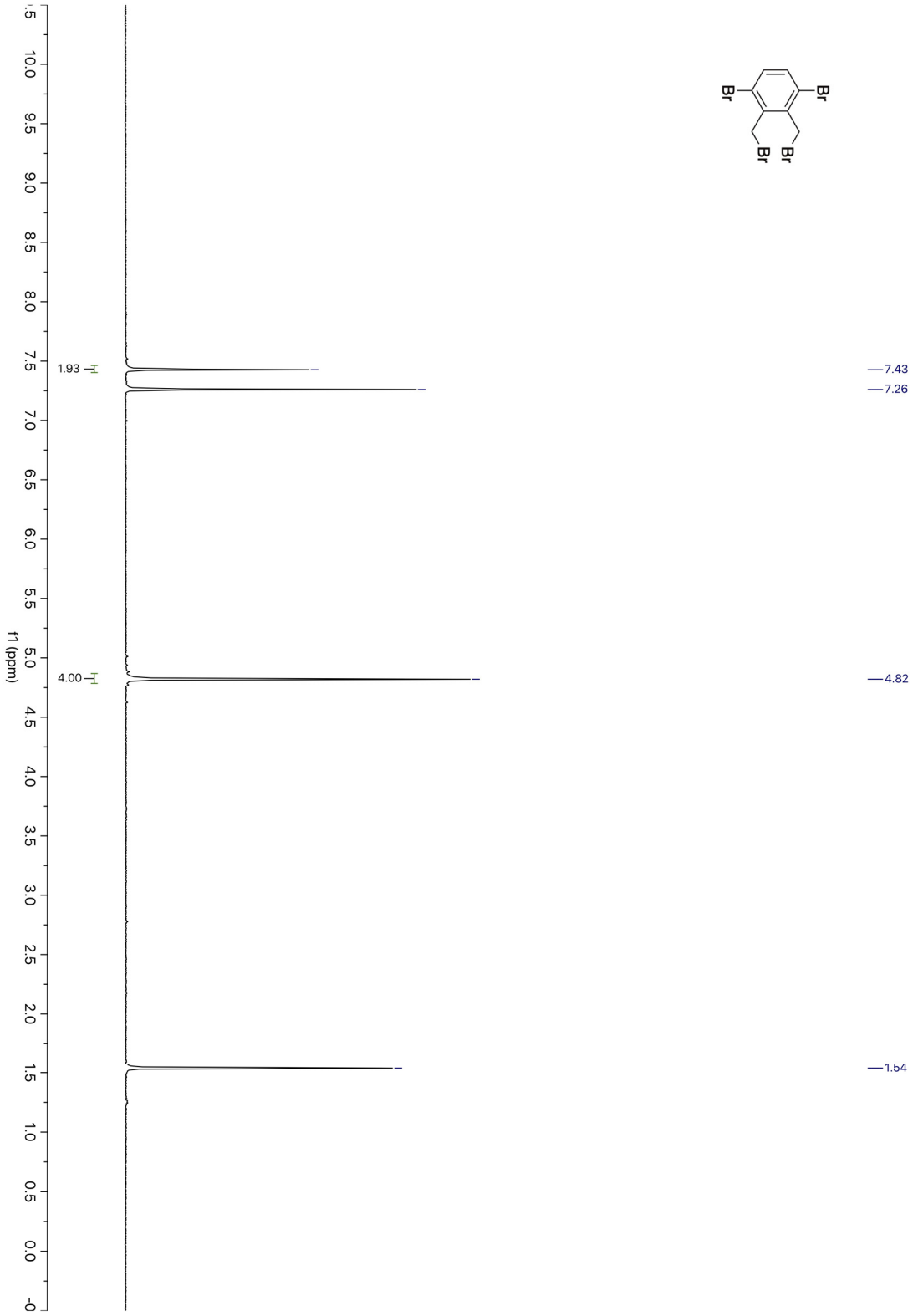

Figure S10. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400 MHz).

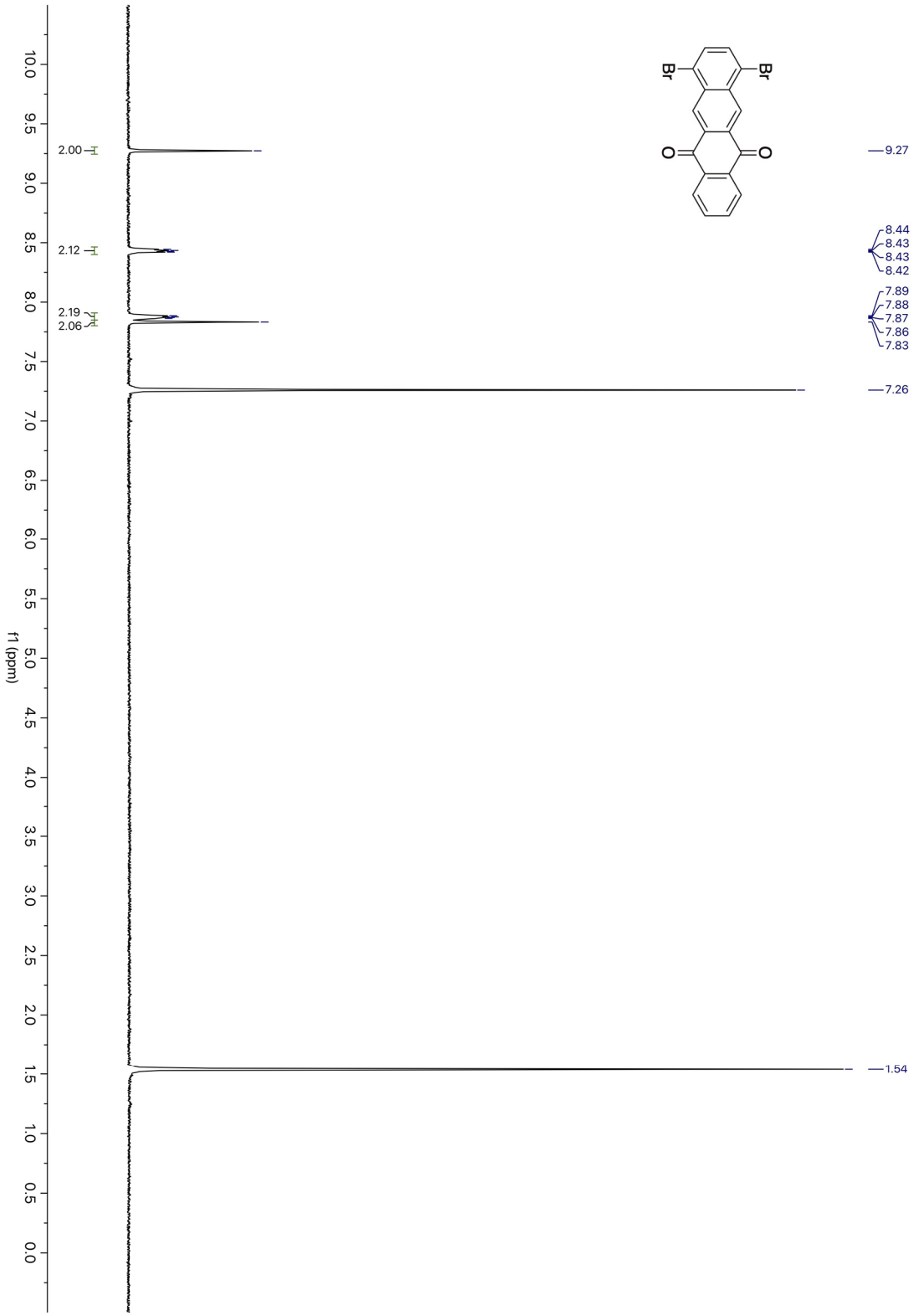

Figure S11. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400 MHz).

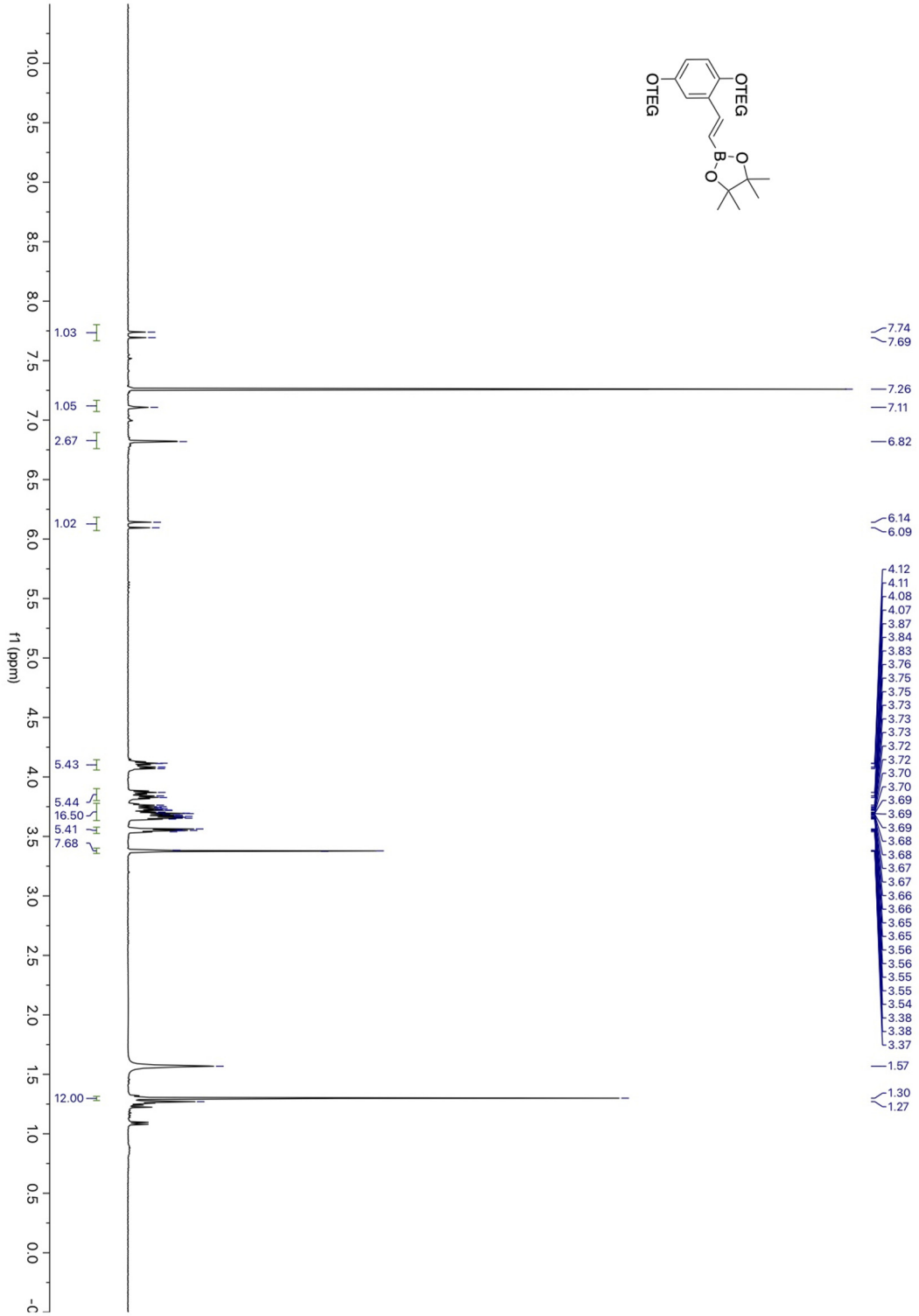

Figure S12. ^{1}H NMR spectrum of compound **S1** ($CDCl_3$, 400 MHz).

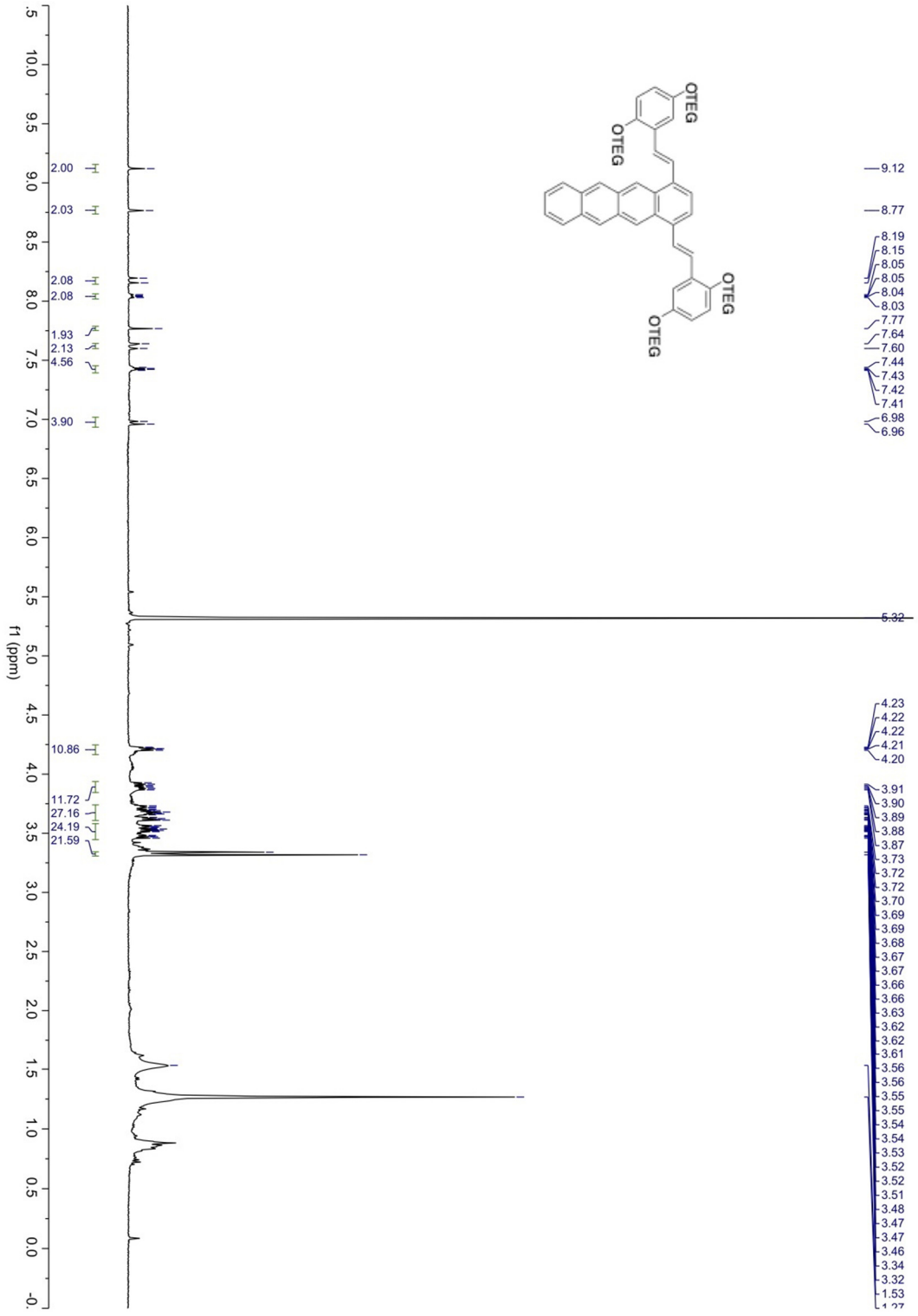

Figure S13. ^{1}H NMR spectrum of compound **M1** (CD_2Cl_2, 400 MHz).

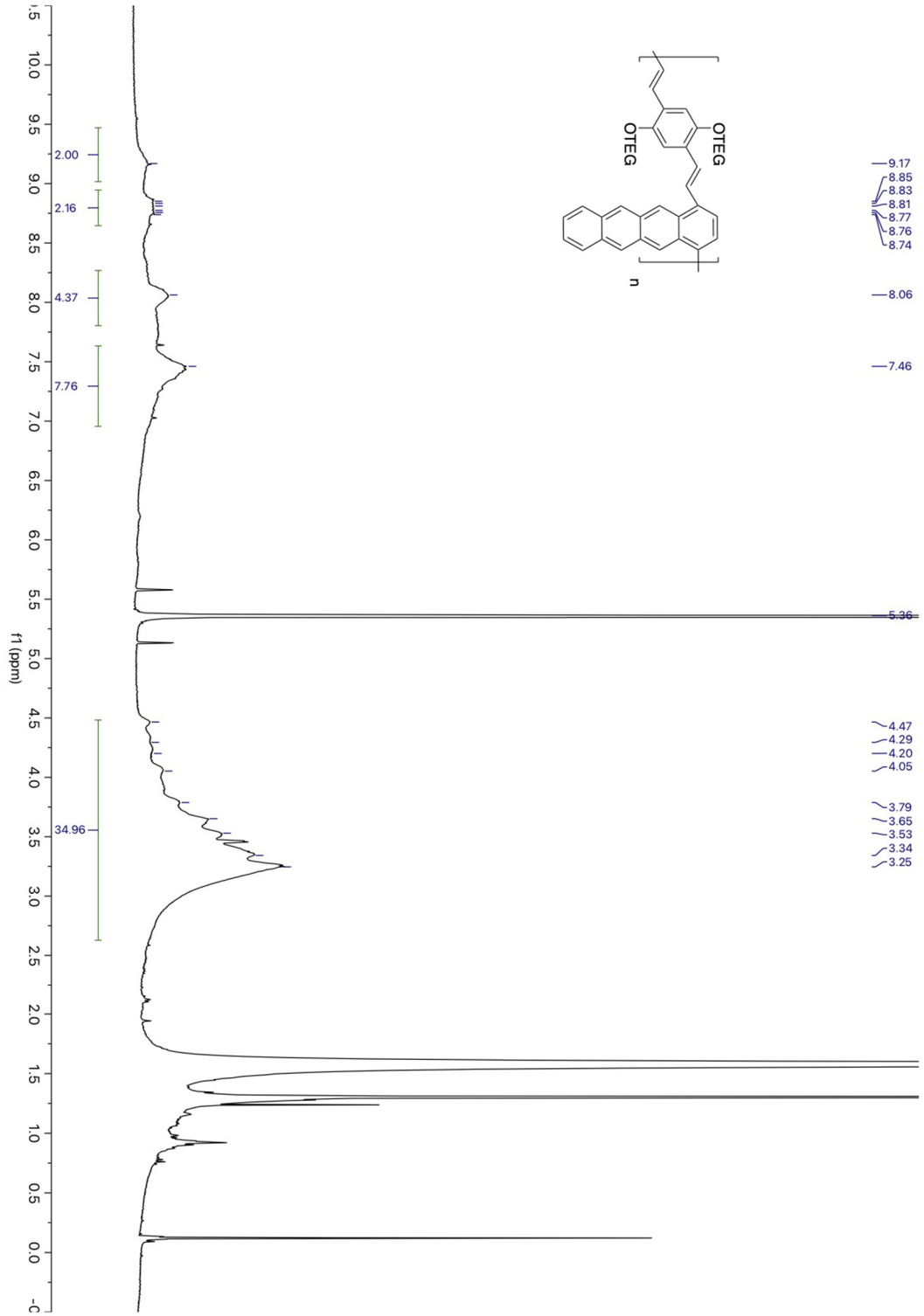

Figure S14. ^{1}H NMR spectrum of compound **P1** (CD_2Cl_2, 400 MHz).