Supplementary Information:

A Design Concept of Planar Conjugated Ladder Oligomers of Perylene Bisimides and the Efficient Synthetic Strategy via Regioselective Photocyclization

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INDEX

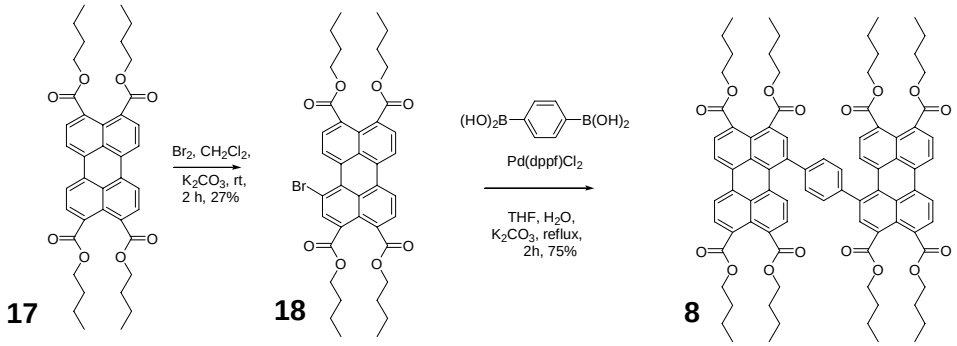
1 Material and methods

Compound **8** was synthesized according to Scheme S1. Compound **13** and **15** were synthesized according to Scheme S2. Compound **1,**[S1] **17**, [S2] and **19**[S3] were synthesized by literature methods. All other reactants were purchased from commercial sources.

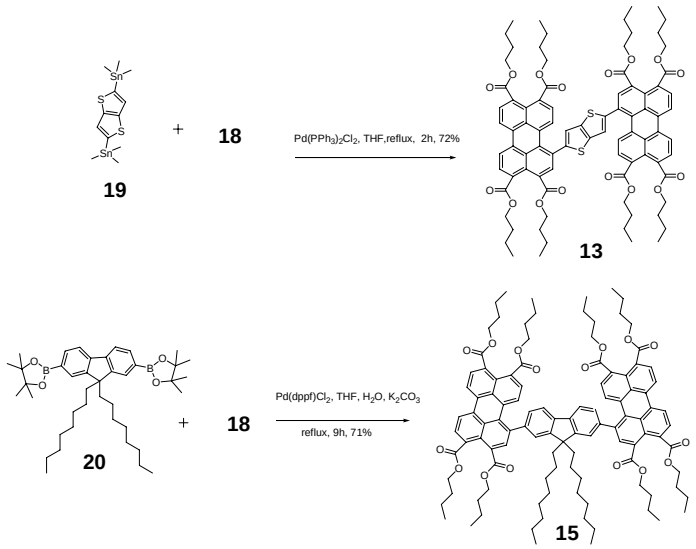
NMR spectra were measured with a Bruker spectrometer using **DSS** as reference for potassium salt of **10** and **12**, and for the other NMR spectra, **TMS** was reference.

Cyclic voltammetry (CV) was performed with a standard commercial electrochemical analyzer in a three electrode single-component cell under argon. The measurements were carried out at a concentration of 5×10^{-4} M with ferrocene as internal standard for the calibration of potential. Working electrode: glassy carbon; reference electrode: $Ag/AgNO_3$; auxiliary electrode: Pt wire. Samples were measured in 0.05 M solution of Bu_4NPF_6 in THF with a scan rate of 100 mV/s.

Atomic structure of compound 6 was optimized with density functional theory (DFT) calculations using the B3LYP hybrid functional with the basis set 6-31G. The quantum-chemical calculations were performed with the Gaussian03 package.[S4] Absorption spectra were determined on a HP-8453 UV-Vis spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6500 fluorescence. The fluorescence quantum yields were determined with Rhodamine 6G as reference.[S5]



Scheme S1 Synthesis of Intermediate **8**



Scheme S2 Synthesis of **13** and **15**

Reference

S1: M. J. Tauber, R. F. Kelley, J. M. Giaimo, B. Rybtchinski and M. R. Wasielewski, *J. Am. Chem. Soc.* 2006**, 128**, 1782.
S2: X. Mo, H. Chen, M. Shi and M. Wang, *Chem. Phys. Lett.* 2006**, 417**, 457.
S3: M. Sato, A. Asami, G. Maruyama, M. Kosuge, J. Nakayama, S. Kumakura, T. Fujihara and K. Unoura, *J. Organomet. Chem.* 2002, **654**, 56.
S4: M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Jr. Vreven, K.N. Kudin,

J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J.A. Pople. Gaussian 03, revision E.01; Gaussian, Inc.: Wallingford CT, **2004**.

S5: M. Fischer and J. Georges, *Chem. Phy. Lett.* 1996, **260**, 115.

2 Synthesis of intermediates and target compounds

Synthesis of 18

A mixture of 3 g compound **17** (4.6 mmol), 3 g K_2CO_3 (21.7 mmol), 50 mL CH_2Cl_2 and 3 mL Br_2 (59 mmol) was stirred at 20 ^oC for 100 min. The excess bromine was removed by adding aqueous Na_2SO_3. Then, the crude product was purified through silica gel column chromatography with CH_2Cl_2 as eluent. The second band was collected, and removal of the solvent yielded compound **18** as a brown solid (0.9 g, 27%). HRMS（API-ES）: Calcd for $C_{40}H_{43}BrO_8Na$ 753.2039, found: 753.2017 ($[M+Na]^+$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (m, 12H), 1.50 (m, 8H), 1.79 (m, 8H), 4.36 (m, 8H), 7.97 (d, 1H, *J* = 8 Hz), 8.02 (d, 2H, *J* = 7.6 Hz), 8.10 (m, 2H), 8.26 (s, 1H), 8.98 ppm (d, 1H, *J* = 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 13.8, 19.2, 19.3, 30.6, 30.7, 65.4, 65.5, 121.4, 122.4, 127.8, 128.6, 128.8, 129.6, 129.7, 129.9, 130.2, 130.3, 130.5, 130.6, 130.8, 131.4, 132.8, 133.2, 133.5, 134.9, 138.5, 142.8, 168.3, 168.4, 168.5, 168.6 ppm.

Synthesis of 8

A mixture of 220 mg Compound **18** (0.3 mmol), 25 mg 1,4-phenylenebisboronic acid (0.15 mmol), 510 mg K_2CO_3, 10 mg $Pd(dppf)Cl_2$, 3.5 mL THF, and 1.5 mL H_2O were stirred at reflux for 6 h. Then, the crude product was purified through silica gel column chromatography with mixture of CH_2Cl_2 and THF as eluent. The second band was collected, and removal of the solvent yielded compound **8** as a brown solid (155 mg, 75%). HRMS（API-ES）: Calcd for $C_{86}H_{90}O_{16}Na$ 1401.6127, found: 1401.6178 ($[M+Na]^+$); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (m, 24H), 1.48 (m, 16H), 1.79 (m, 16H), 4.37 (m, 16H), 8.50 (s, 4H), 7.65 (m, 4H), 8.12 (m, 6H), 8.31 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 19.2, 30.6, 65.4, 118.6, 121.6, 122.6, 127.3, 128.0, 129.2, 129.5, 130.0, 130.1, 130.2, 130.4, 130.8, 130.9, 131.6, 132.2, 132.4, 132.5, 137.4, 167.1, 168.2, 168.3, 168.4 ppm.

Synthesis of 9

A mixture of 65 mg compound **8** (0.047 mmol), 5 mL toluene, and 1 mg I_2 was illuminated by sunlight under reflux for 3 h. Then, the reaction mixture was reflux for another 3 h after 35 mg (0.16 mmol) DDQ was added. The crude product was purified through silica gel column chromatography CH_2Cl_2 and compound **9** was yielded as red solid（49 mg, 76%). HRMS（API-ES）: Calcd for $C_{86}H_{86}O_{16}Na$ 1397.5814, found: 1397.5857 ($[M+Na]^+$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (m, 24H), 1.57 (m, 16H), 1.88 (m, 16H), 4.47 (t, 8H), 4.56 (t, 8H), 8.50 (d, 4H, *J* = 8 Hz), 9.02 (d, 4H, *J* = 8.4 Hz), 10.00 (s, 4H), 10.84 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 13.9, 19.3, 19.4, 30.8, 65.6, 65.8, 119.4, 122.1, 125.3, 127.0, 127.4, 127.5, 127.8, 127.9, 129.8, 130.4, 130.8, 132.9, 168.7 ppm.

Synthesis of 10

Compound **9** (42 mg, 0.030 mmol) was added to 4 mL Chlorosulfonic acid gradually and the mixture was stirred for 3 h at room temperature. Then the mixture was added to ice. After filtration compound **10** was yielded as dark solid (27 mg, 100%). MALDI-TOF-MS: Calcd for $C_{54}H_{14}O_{12}$ 854.0, found: 854.9. ^1H NMR of potassium salt of compound **10** (400 MHz, D_2O) : δ = 8.08 (d, 4H, *J* = 8 Hz), 8.92 (d, 4H, *J* = 8 Hz), 9.78 (s, 4H), 10.88 ppm (s, 2H); ^{13}C NMR of potassium salt of compound 12 (125 MHz, D_2O) : δ = 120.0 122.3, 124.6, 124.7, 127.0, 127.4, 128.0, 128.3, 128.5, 131.9, 138.7, 139.0, 163.5, 163.8, 177.8, 177.9 ppm.

Synthesis of 6

Mixture of compound **10** (12 mg, 0.014 mmol), tricosan-12-amine (54 mg, 0.16 mmol) and 1.2 g imidazole was stirred for 6 h at 200 ^oC. The crude product was purified through silica gel column chromatography with CH_2Cl_2 as eluent and compound **6** was obtained as a black solid (30 mg, 100%). MALDI-TOF-MS: Calcd for $C_{146}H_{202}N_4O_8$ 2140.6, found: 2140.6. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.7-1.6 (m, 168H), 2.12 (m, 8H), 2.49 (m, 8H), 5.41 (m, 4H), 8.94 (m, 8H), 10.70 ppm (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.6, 22.7, 27.2, 27.7, 29.4, 29.5, 29.7, 29.8, 31.9, 32.7, 55.7, 56.0, 119.4, 122.7, 123.5, 124.1, 124.4, 125.2, 127.8, 128.2, 129.9, 133.0, 133.3, 163.8, 164.1, 164.7, 165.1 ppm.

Synthesis of 11

A mixture of 100 mg compound **8** (0.072 mmol), 50 mL CH_2Cl_2, and catalytic amount I_2 was illuminated by sunlight at room temperature for 6 h. The crude product was purified by recrystallization in a mixture of xylene and propanoic acid (1:1, v/v) and compound **11** was yielded as a red solid（91 mg, 91%). HRMS（API-ES）: Calcd for $C_{86}H_{86}O_{16}Na$ 1397.5814, found: 1397.5842 ($[M+Na]^+$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (m, 24H), 1.57-1.88 (m, 32H), 3.93 (m, 4H), 4.47 (m, 12H), 8.57 (m, 4H), 8.95 (s, 2H), 9.20 (m, 4H), 9.47 (s, 2H), 9.78 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.2, 13.8, 13.9, 14.1, 18.6, 19.3, 19.4, 22.7, 29.8, 30.8, 31.6, 64.8, 65.4, 65.6, 65.8, 122.0, 122.1, 123.6, 123.9, 124.6, 125.1, 125.7, 127.0, 127.1, 127.2, 127.5, 127.8, 128.6, 129.1, 129.5, 129.6, 129.9, 130.6, 131.0, 132.5, 132.8, 133.1, 167.8, 168.5, 168.8, 168.9 ppm.

Synthesis of 12

Compound **11** (103 mg, 0.075 mmol) was added to 7 mL chlorosulfonic acid gradually and the mixture was stirred for 3 h at room temperature. Then the mixture was added to ice. After filtration compound **12** was yielded as dark solid (65 mg, 100%). MALDI-TOF-MS: Calcd for $C_{54}H_{14}O_{12}$ 854.0, found: 854.9. ^1H NMR of potassium salt of compound **12** (400 MHz, D_2O) : δ = 8.18 (m, 4H), 8.51 (s, 2H), 9.08 (m, 4H), 9.34 ppm (m, 4H); ^{13}C NMR of potassium salt of compound 14 (125 MHz, D_2O) : δ = 122.3, 122.4, 123.8, 124.0, 124.3, 124.8, 125.2, 125.8, 126.8, 127.1, 127.2, 128.1, 128.4, 128.6, 129.1, 130.1, 131.7, 132.0, 137.1, 138.3, 138.5, 138.5, 139.0, 177.1, 177.8, 178.0 ppm.

Synthesis of 7

Mixture of compound **12** (7 mg, 0.0082 mmol), tricosan-12-amine (50 mg, 0.15 mmol) and 1.2 g imidazole was stirred for 6 h at 200 ^oC. The crude product was purified through silica gel column chromatography with CH_2Cl_2 as eluent and compound **7** was obtained as red solid (16 mg, 90%). MALDI-TOF-MS: Calcd for $C_{146}H_{202}N_4O_8$ 2140.6, found: 2140.4. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.5-2.6 (m, 184H), 5.39 (m, 4H), 9.08 (m, 4H), 9.36 (m, 4H), 9.65 (s, 2H), 9.73 (s, 2H), 10.38 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.6, 22.7, 27.1, 29.3, 29.4, 29.6, 29.7, 31.9, 32.0, 123.5, 123.8, 124.4, 124.5, 124.7, 124.9, 125.5, 125.9, 127.2, 127.4, 127.6, 129.0, 130.1, 134.0, 134.1, 164.3, 165.4 ppm.

Synthesis of 13

A mixture of 73 mg Compound **18** (0.1 mmol), 24 mg compound **19** (0.052 mmol), 2 mg $Pd(PPh_3)Cl_2$, and 5 mL THF were stirred at reflux for 2 h. Then, the crude product was purified through silica gel column chromatography with mixture of CH_2Cl_2 and THF as eluent. The second band was collected, and removal of the solvent yielded compound **13** as a red solid (52 mg, 72%). HRMS（API-ES）: Calcd for $C_{86}H_{88}O_{16}S_2$, found: ($[M+Na]^+$); ^1H NMR (500 MHz, $CDCl_3$): δ = 0.93–1.02 (m, 24H), 1.50 (m, 16H), 1.79 (m, 16H), 4.37 (m, 16H), 7.40 (s, 2H), 7.60 (d, 2H, *J* = 9 Hz), 7.95 (d, 2H, *J* = 9 Hz), 8.01 (d, 2H, *J* = 7.5 Hz), 8.06 (d, 2H, *J* = 9 Hz), 8.20 ppm (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 19.2, 19.3, 29.7, 30.6, 30.7, 65.4, 65.5, 65.6, 119.5, 121.4, 122.5, 128.1, 128.4, 129.0, 129.3, 129.5, 130.0, 130.1, 130.2, 130.3, 130.4, 130.5, 131.0, 132.1, 132.2, 132.8, 133.3, 135.2, 140.9, 147.1, 168.0, 168.4, 168.5, 168.6 ppm.

Synthesis of 14

A mixture of 49 mg compound **13** (0.034 mmol), 25 mL THF, and catalytic amount I_2 was illuminated by sunlight at room temperature for 3 h. The crude product was purified through silica gel column chromatography with mixture of CH_2Cl_2 and THF as eluent and compound **14** was yielded as a yellow solid（36 mg, 80%). HRMS（API-ES）: Calcd for $C_{86}H_{84}O_{16}S_2$, found: ($[M+Na]^+$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03–1.20 (m, 24H), 1.57 (m, 16H), 1.81-2.08 (m, 16H), 4.48 (m, 8H), 4.59 (t, 4H), 4.68 (t, 4H), 8.44 (m, 4H), 9.00 (d, 4H, *J* = 8 Hz), 9.06 (s, 2H), 9.43 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 14.0, 19.4, 29.7, 30.8, 30.9, 65.5, 65.6, 66.0, 122.1, 122.2, 122.8, 123.4, 123.6, 125.1, 126.2, 126.8, 127.0, 127.8, 128.4, 128.9, 129.0, 130.2, 130.4, 130.7, 131.4, 132.0, 132.2, 134.1, 141.2, 168.3, 168.4, 168.7 ppm.

Synthesis of 15

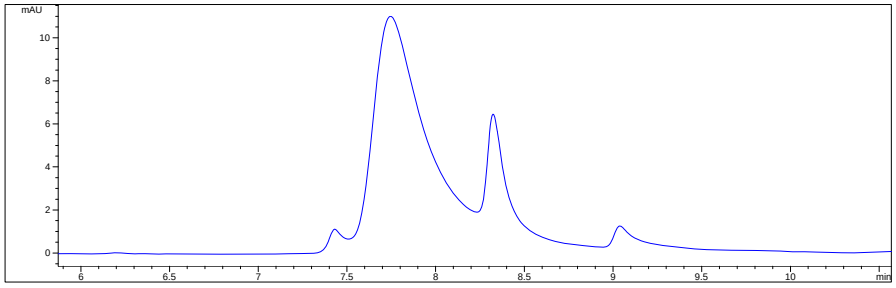
A mixture of 88 mg compound **20** (0.137 mmol), 2.1 g K_2CO_3, 14 mL THF, and 6 mL H_2O were stirred at reflux for 5 h. Then, 200 mg Compound **18** (0.274 mmol) and 28 mg $Pd(dppf)Cl_2$ were added and reflux for another 4 h. The crude product was purified through silica gel column chromatography with mixture of CH_2Cl_2 and THF as eluent. The second band was collected, and removal of the solvent yielded compound **15** as a yellow solid (163 mg, 71%). HRMS (API-ES): Calcd for $C_{86}H_{88}O_{16}S_2Na$ 1463.5412, found: 1463.5369 ($[M+Na]^+$); ^1H NMR (500 MHz, $CDCl_3$): δ = 0.75–1.10 (m, 54H), 1.49 (m, 16H), 1.79 (m, 16H), 1.91 (m, 4H) , 4.37 (m, 16H), 7.43 (m, 6H), 7.70-7.80 (m, 4H), 8.10 (m, 6H), 8.29 ppm (d, 4H, *J* = 9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 14.0, 19.2, 19.3, 22.6, 24.0, 29.2, 29.3, 30.6, 30.7, 31.7, 40.1, 55.8, 65.3, 65.4, 65.5, 121.3, 121.4, 121.6, 122.3, 123.4, 127.7, 128.3, 128.5, 128.9, 129.4, 129.6, 130.1, 130.2, 130.3, 130.5, 131.2, 133.0, 133.3, 133.5, 135.1, 139.7, 140.4, 142.4, 152.9, 168.3, 168.6, 168.7 ppm.

Synthesis of 16

A mixture of 99 mg compound **15** (0.058 mmol), 50 mL THF, and catalytic amount I_2 was illuminated by sunlight at room temperature for 3 h. The crude product was purified through silica gel column chromatography with toluene as eluent and compound **16** was yielded as a yellow solid（64 mg, 65%). HRMS (API-ES): Calcd for $C_{86}H_{84}O_{16}S_2Na$ 1459.5099, found: 1459.5164 ($[M+Na]^+$); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.65–1.19 (m, 54H), 1.58 (m, 16H), 1.90 (m, 16H), 2.62 (m, 4H), 4.50 (m, 16H), 8.51 (m, 4H), 9.05 (m, 4H), 9.20 (s, 2H), 9.73 (s, 2H), 9.93 ppm (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 19.4, 19.5,

22.4, 24.3, 29.1, 29.2, 30.1, 30.7, 30.8, 31.6, 42.1, 56.2, 65.6, 65.7, 115.7, 117.8, 121.9, 122.0, 124.1, 124.4, 127.0, 127.4, 127.6, 127.7, 127.8, 129.1, 129.4, 129.7, 129.9, 130.1, 130.4, 132.7, 132.8, 141.2, 151.9, 168.8, 168.9, 169.1 ppm.

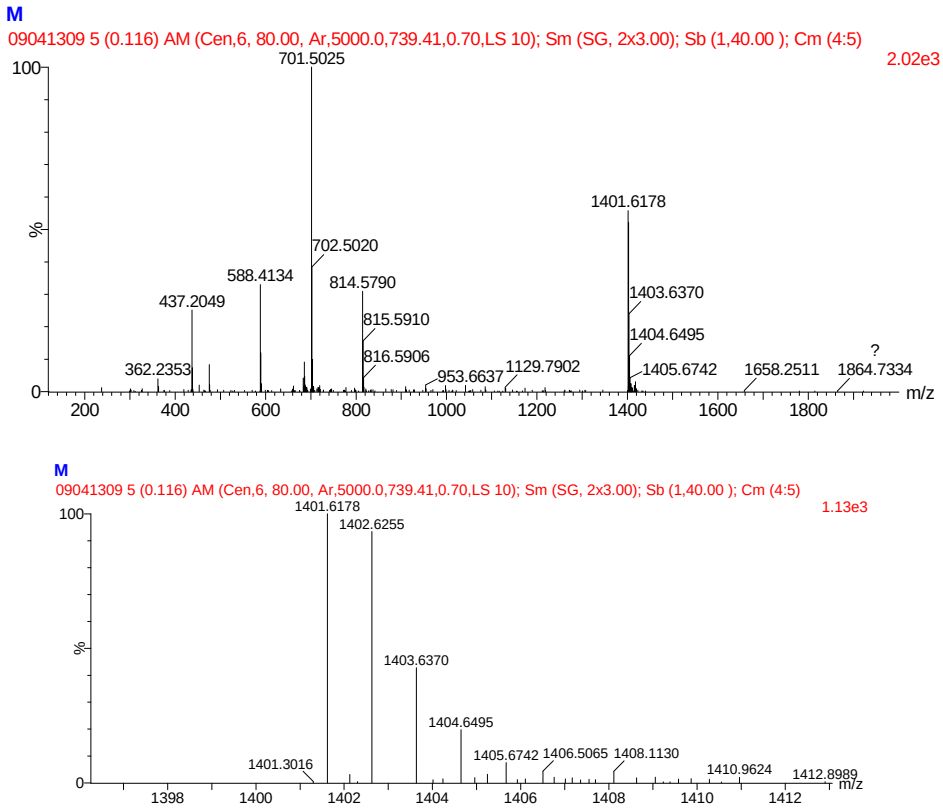
3 HPLC spectrum of M9



C-18 Column, $CHCl_3$: THF (49: 1 v/v) as mobile phase

Figure S1 HPLC spectrum of **M9**

4 Mass spectrum of 8 and M9



Molecular ion peak: 1401.6178

Figure S2 Mass spectrum of **8**

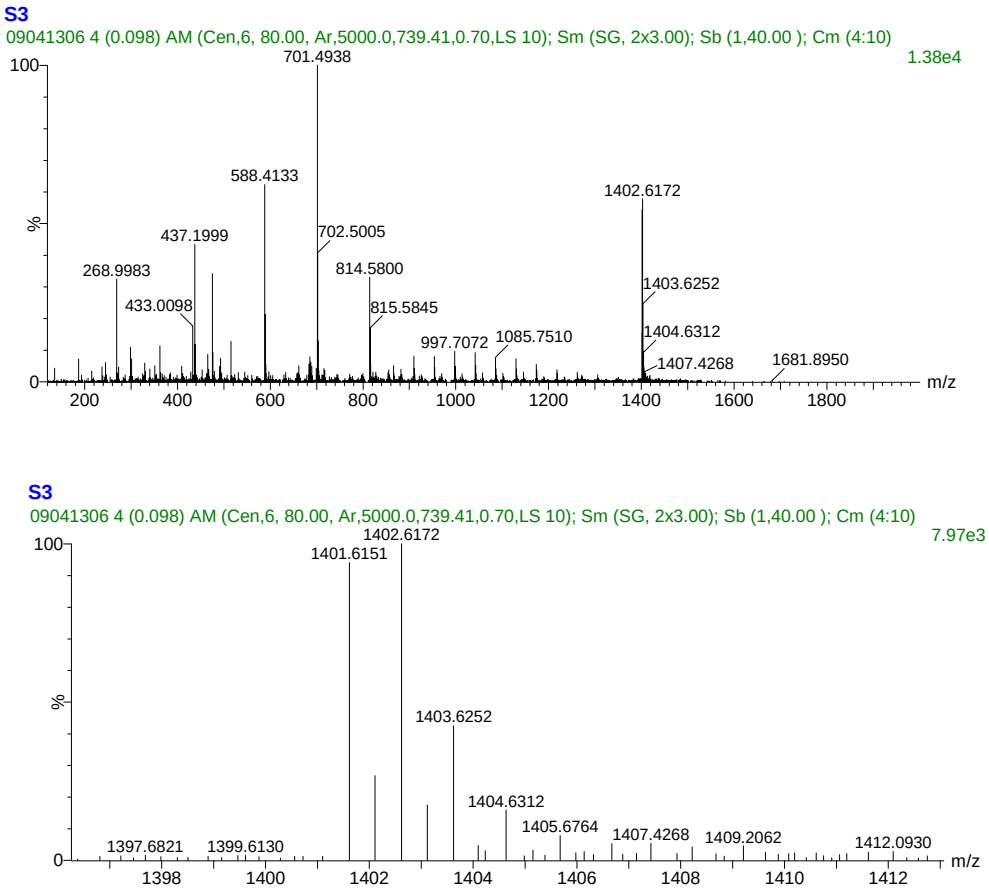


Figure S3 Mass spectrum of **M9**

5 Computed structure of conjugated core of 6 and 7

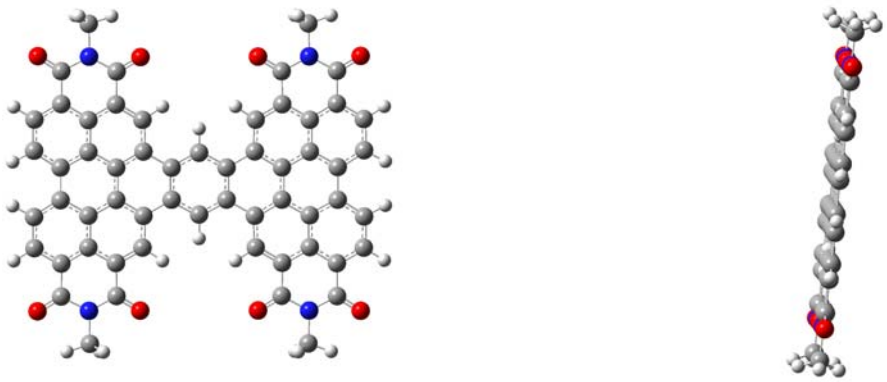


Figure S4 The B3LYP/6-31G computed structure of conjugated core of **6**

Figure S5 The B3LYP/6-31G computed structure of conjugated core of **7**

6 Cyclic voltammograms of compound 1, 6 and 7

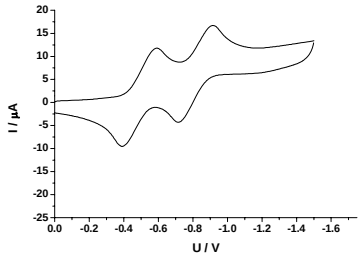


Figure S6 Reductive cyclic voltammograms of **1**

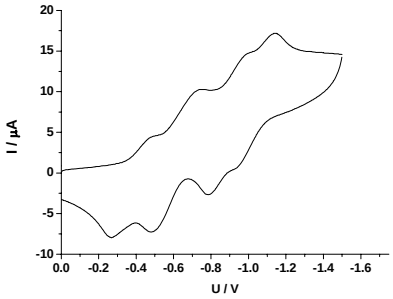


Figure S7 Reductive cyclic voltammograms of **6**

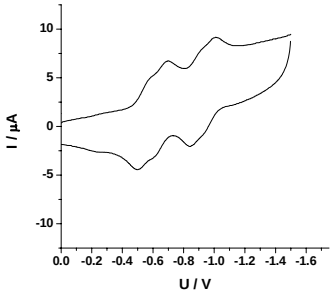
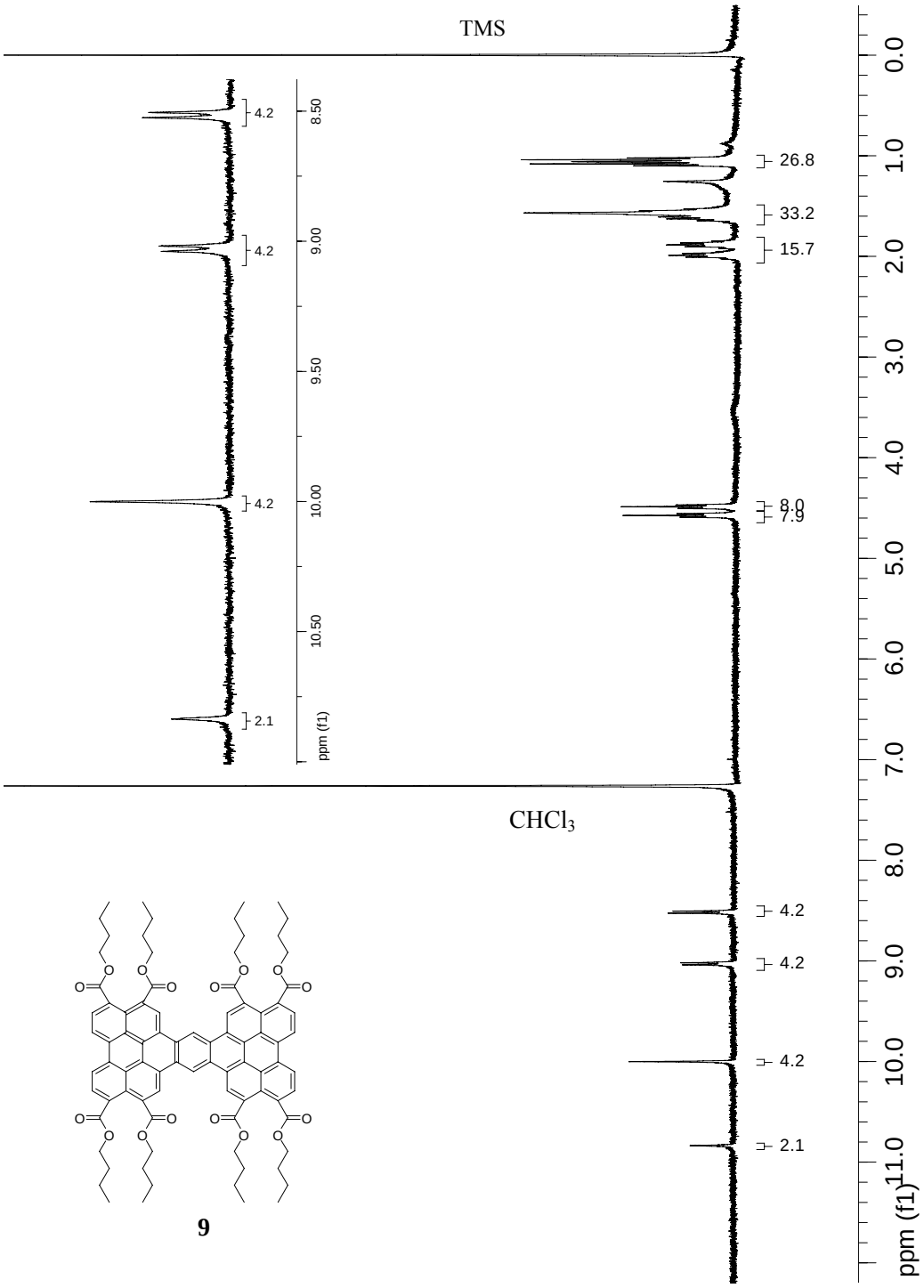


Figure S8 Reductive cyclic voltammograms of **7**

7 Copy of NMR spectrum

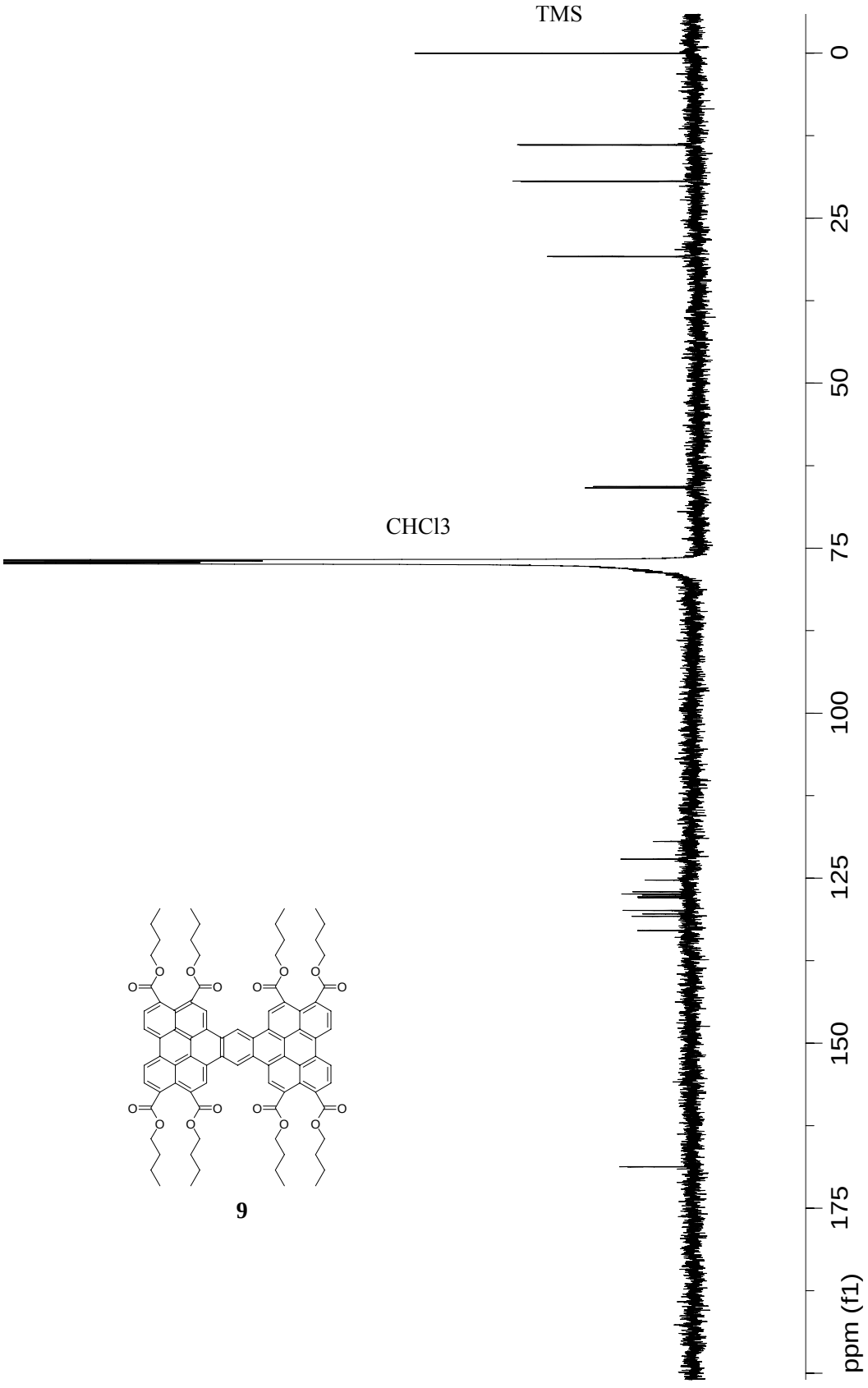
7.1 ^{1}H ^{13}C NMR spectrum of 9

^{1}H NMR (400 MHz) spectrum of **9** in $CDCl_3$ and its enlarged low-field section (inserted figure)



9

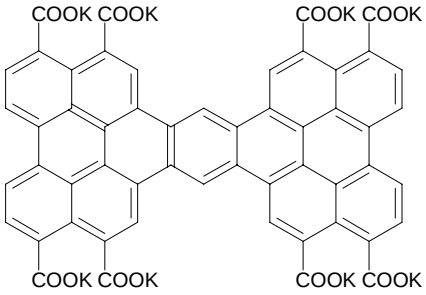
^{13}C NMR (125 MHz) spectrum of **9** in $CDCl_3$



9

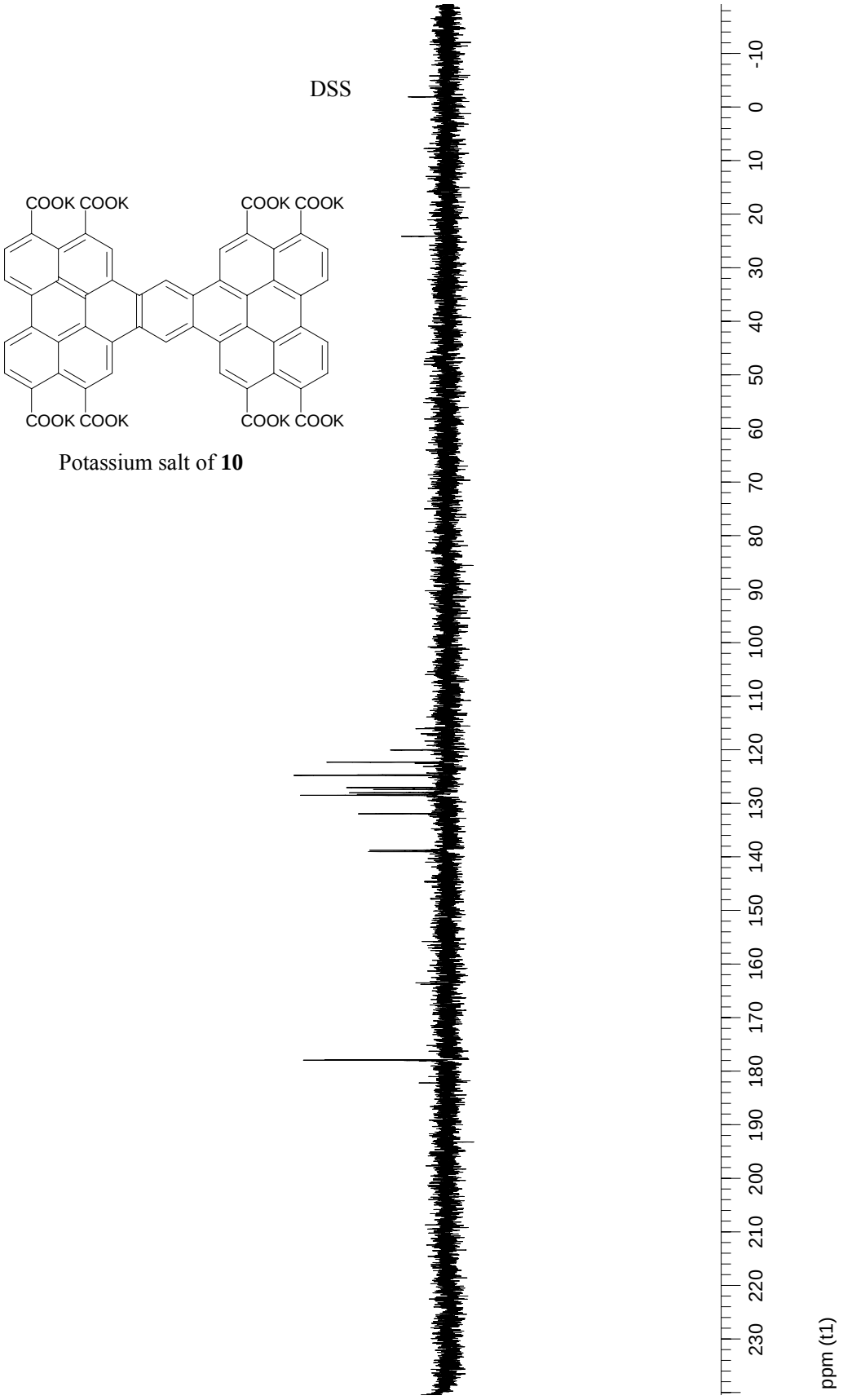
7.2 ^{1}H ^{13}C NMR spectrum of potassium salt of 10

^{1}H NMR (400 MHz) spectrum of potassium salt of **10** in D_2O and its enlarged low-field section (inserted figure)



Potassium salt of **10**

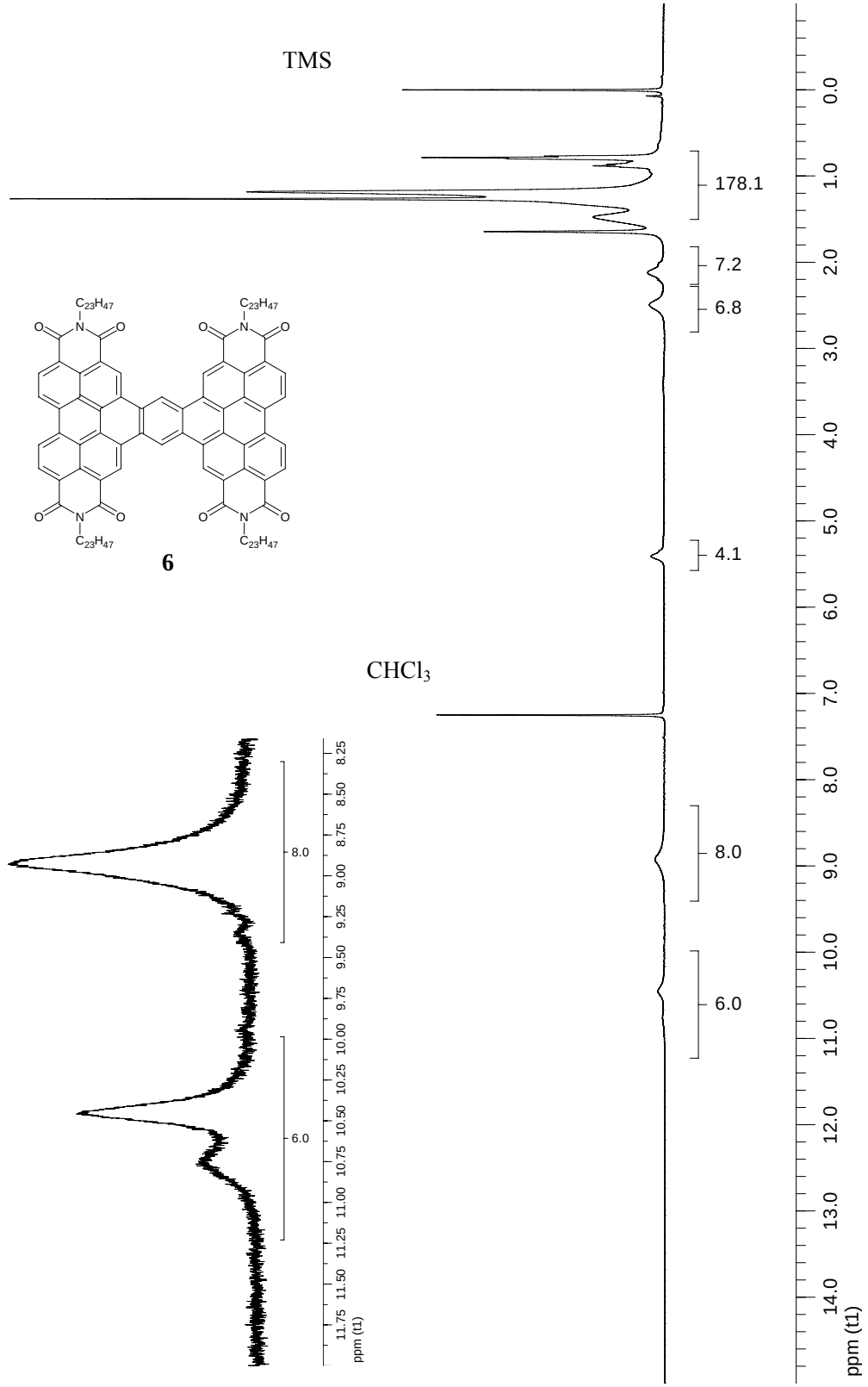
^{13}C NMR (125 MHz) spectrum of potassium salt of **10** in D_2O



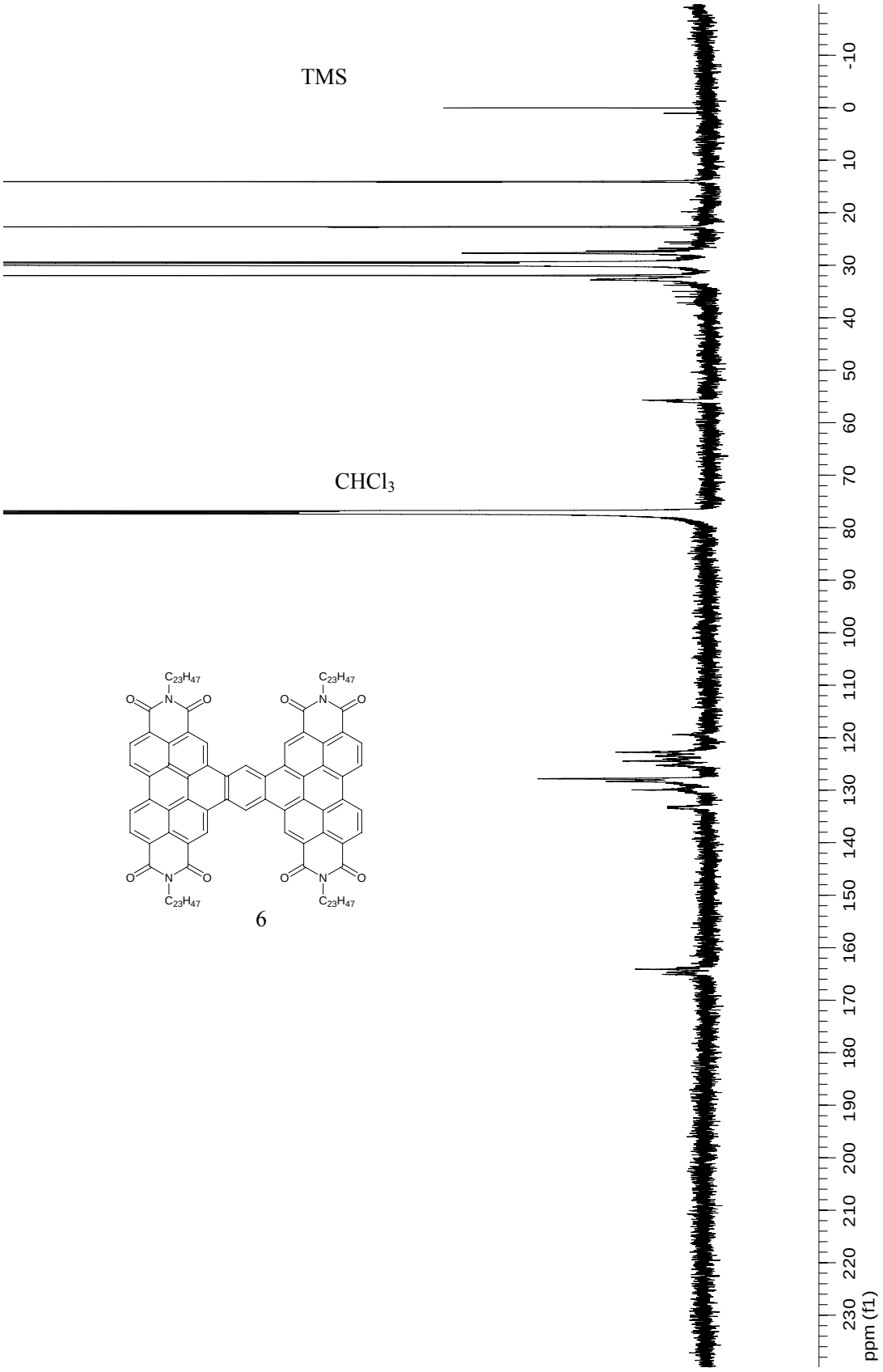
Potassium salt of **10**

7.3 ^{1}H ^{13}C NMR spectrum of 6

^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$ and its enlarged low-field section (inserted figure)



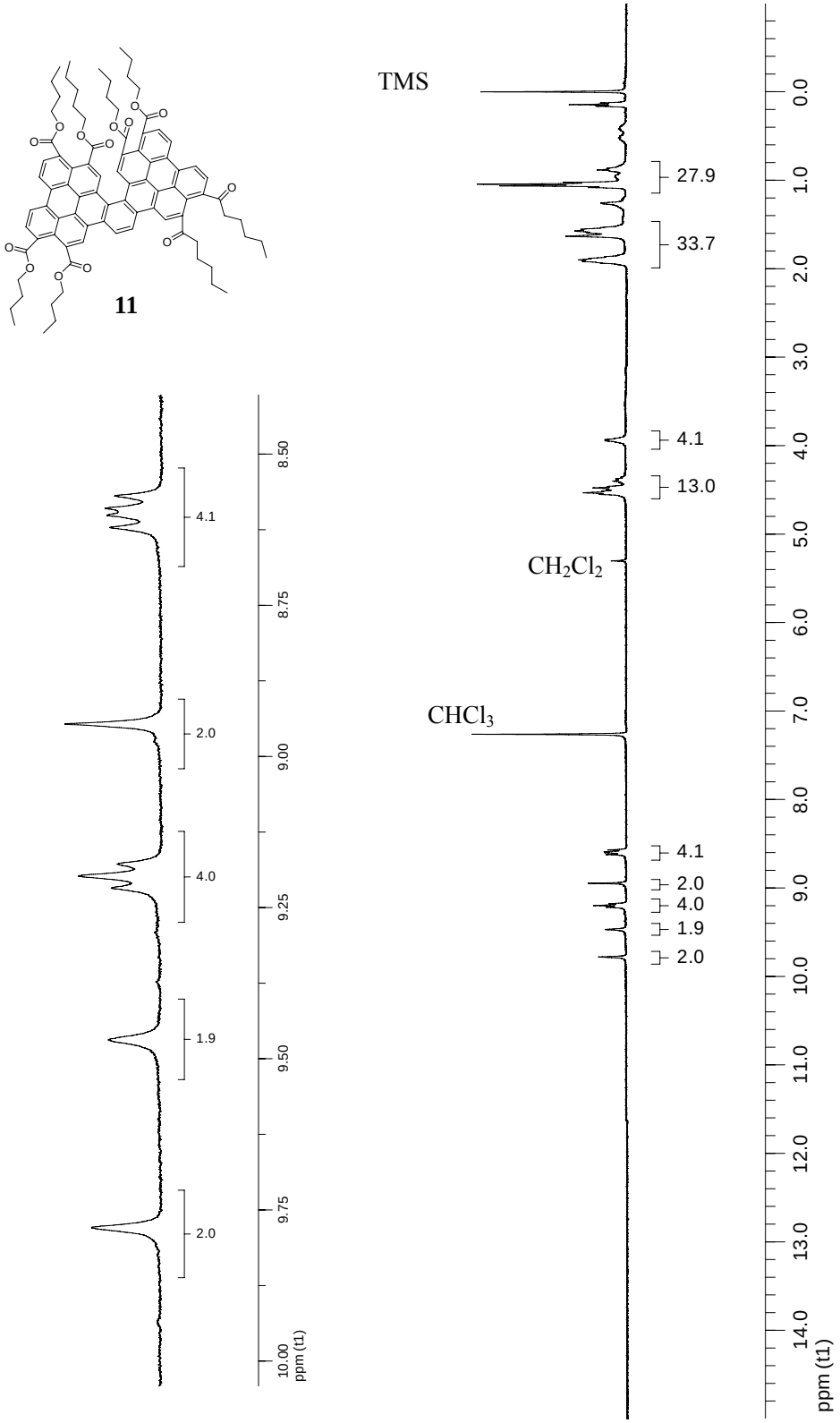
^{13}C NMR (125 MHz) spectrum of **6** in $CDCl_3$



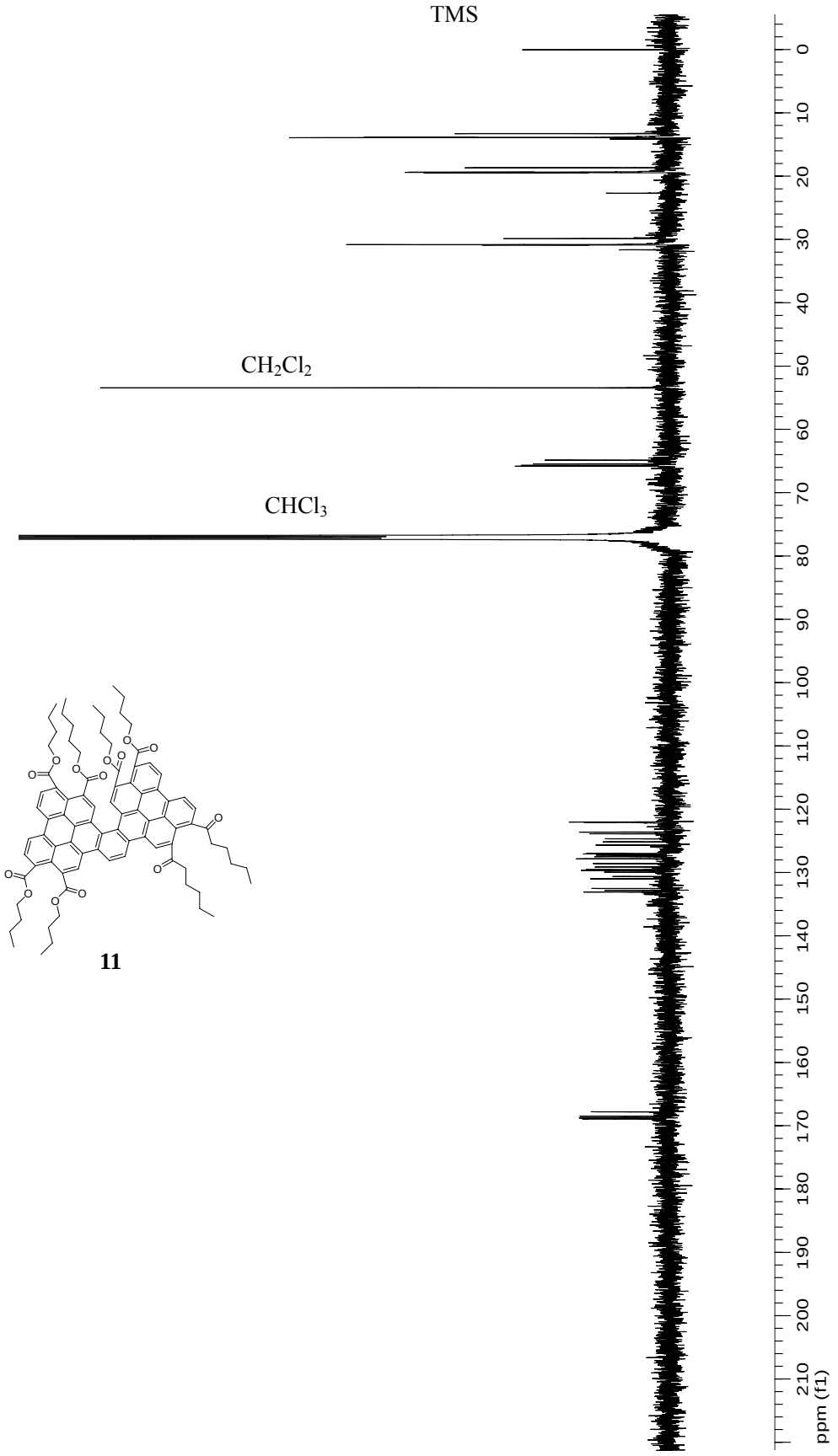
6

7.4 ^{1}H ^{13}C NMR spectrum of 11

^{1}H NMR (400 MHz) spectrum of **11** in $CDCl_3$ and its enlarged low-field section (inserted figure)



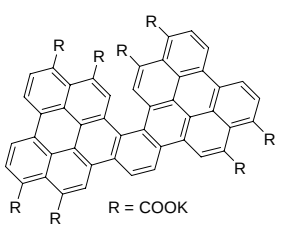
^{13}C NMR (125 MHz) spectrum of **11** in $CDCl_3$



11

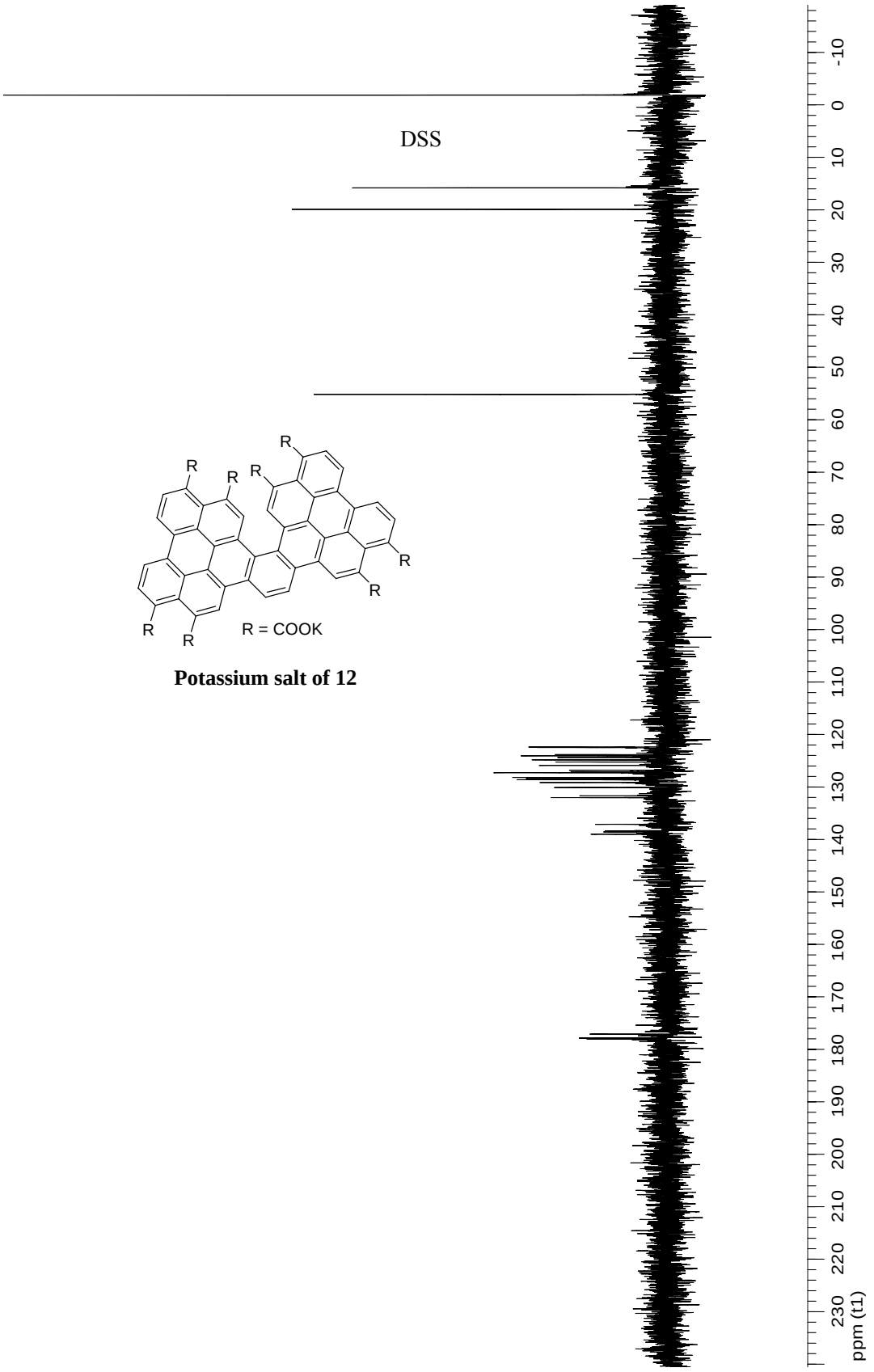
7.5 ^{1}H ^{13}C NMR spectrum of potassium salt of 12

^{1}H NMR (400 MHz) spectrum of potassium salt of **12** in D_2O and its enlarged low-field section (inserted figure)



Potassium salt of 12

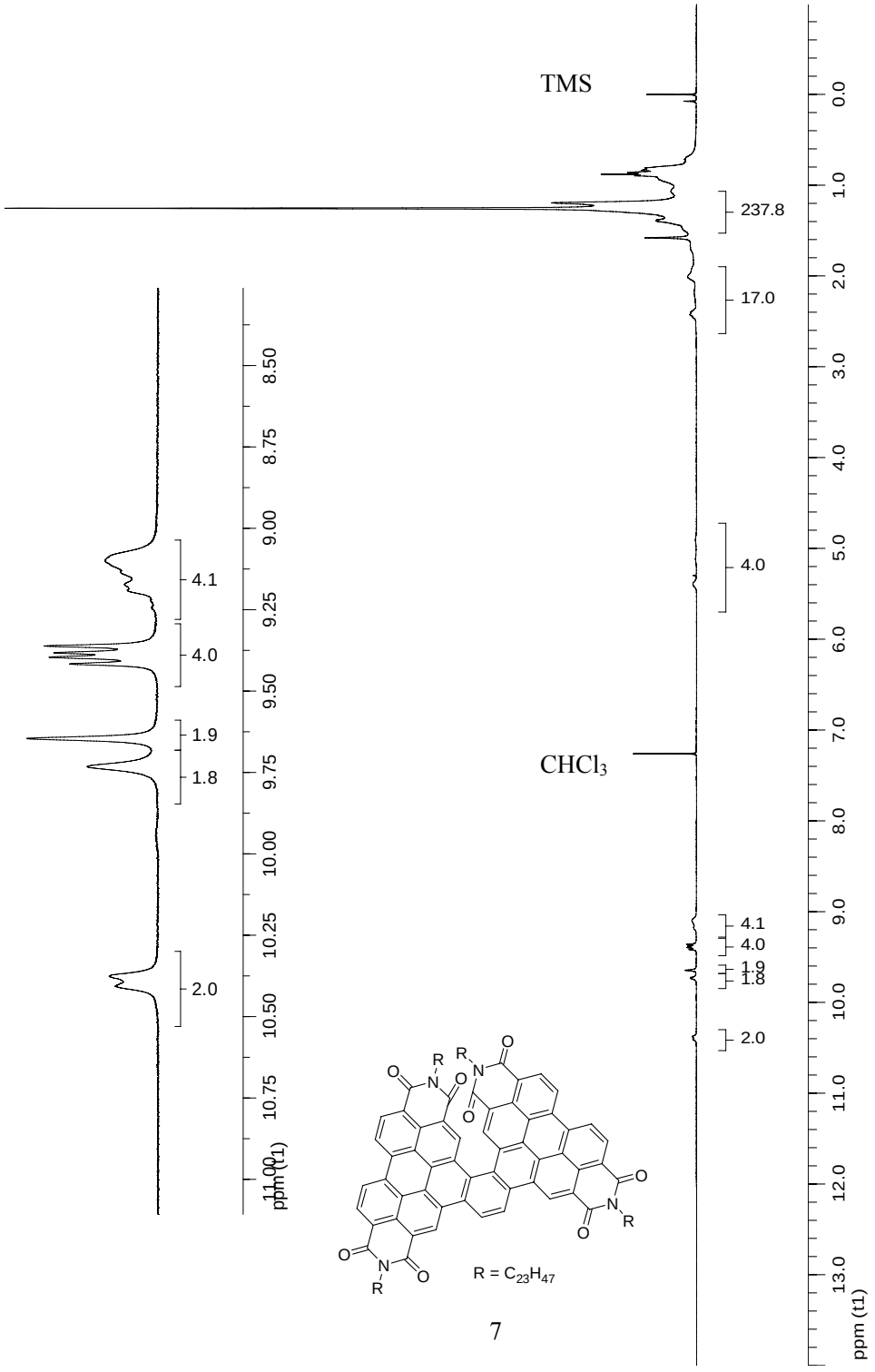
^{13}C NMR (125 MHz) spectrum of potassium salt of **12** in D_2O



Potassium salt of 12

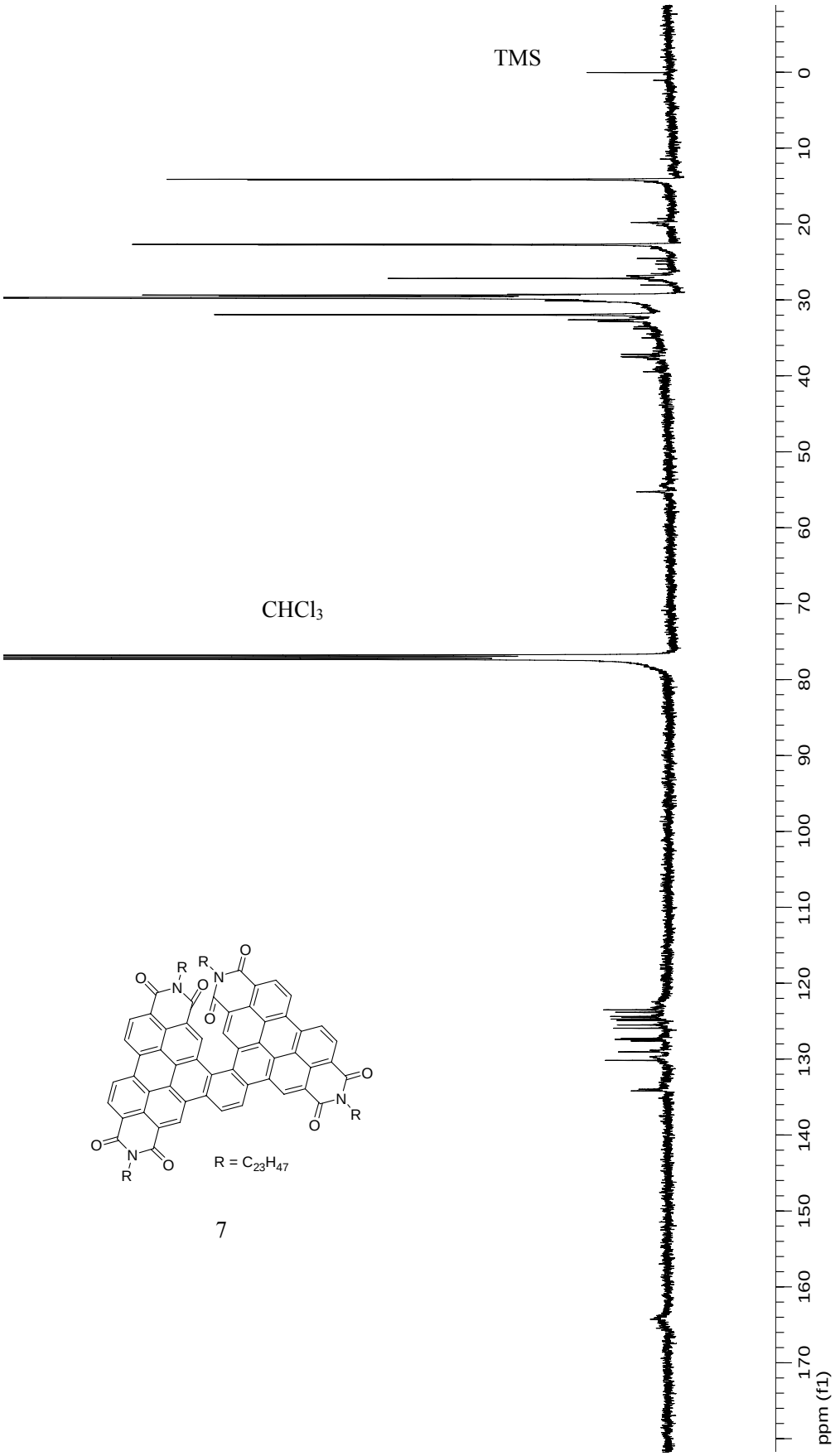
7.6 ^{1}H ^{13}C NMR spectrum of 7

^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$ and its enlarged low-field section (inserted figure)



7

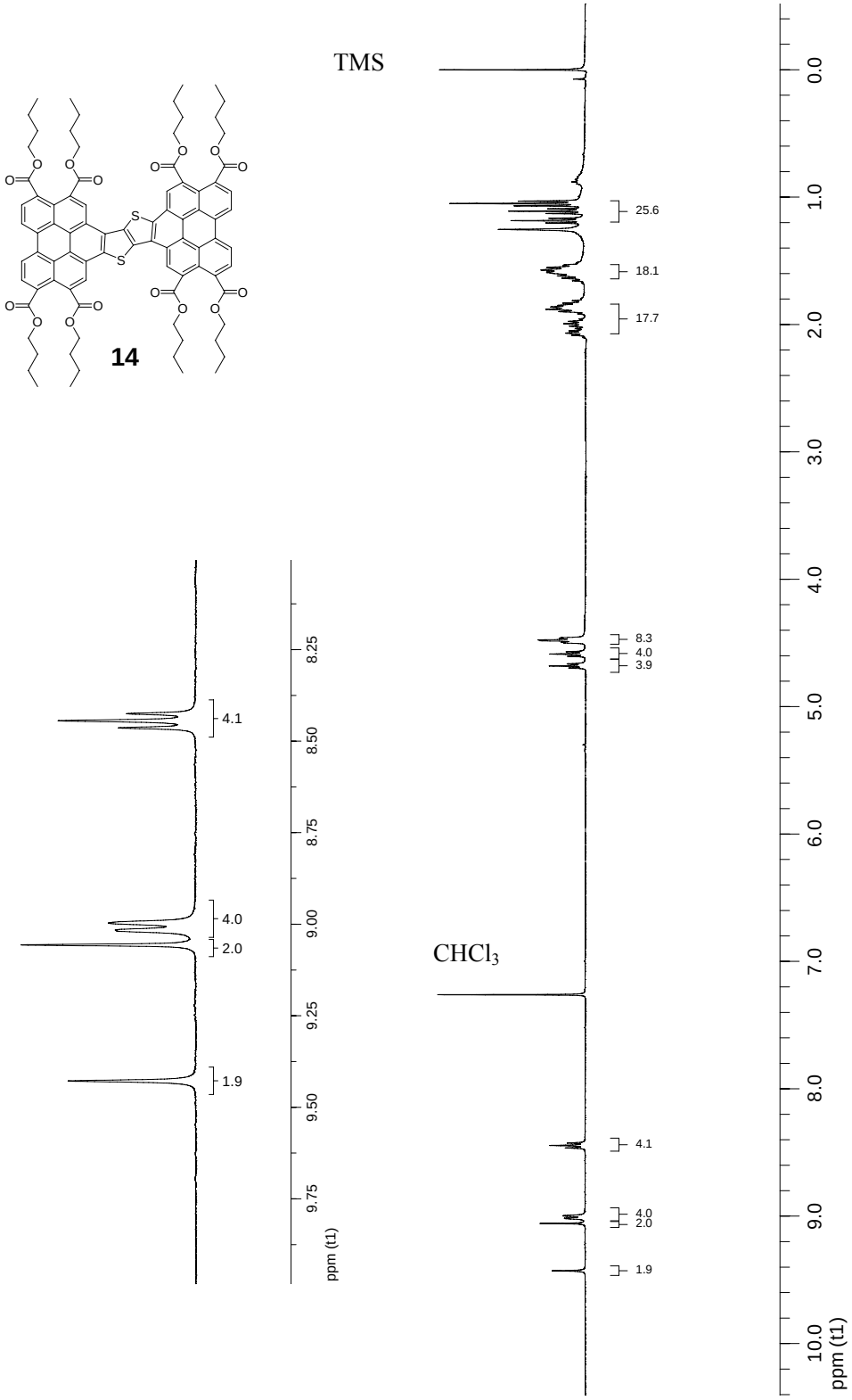
^{13}C NMR (125 MHz) spectrum of **7** in $CDCl_3$



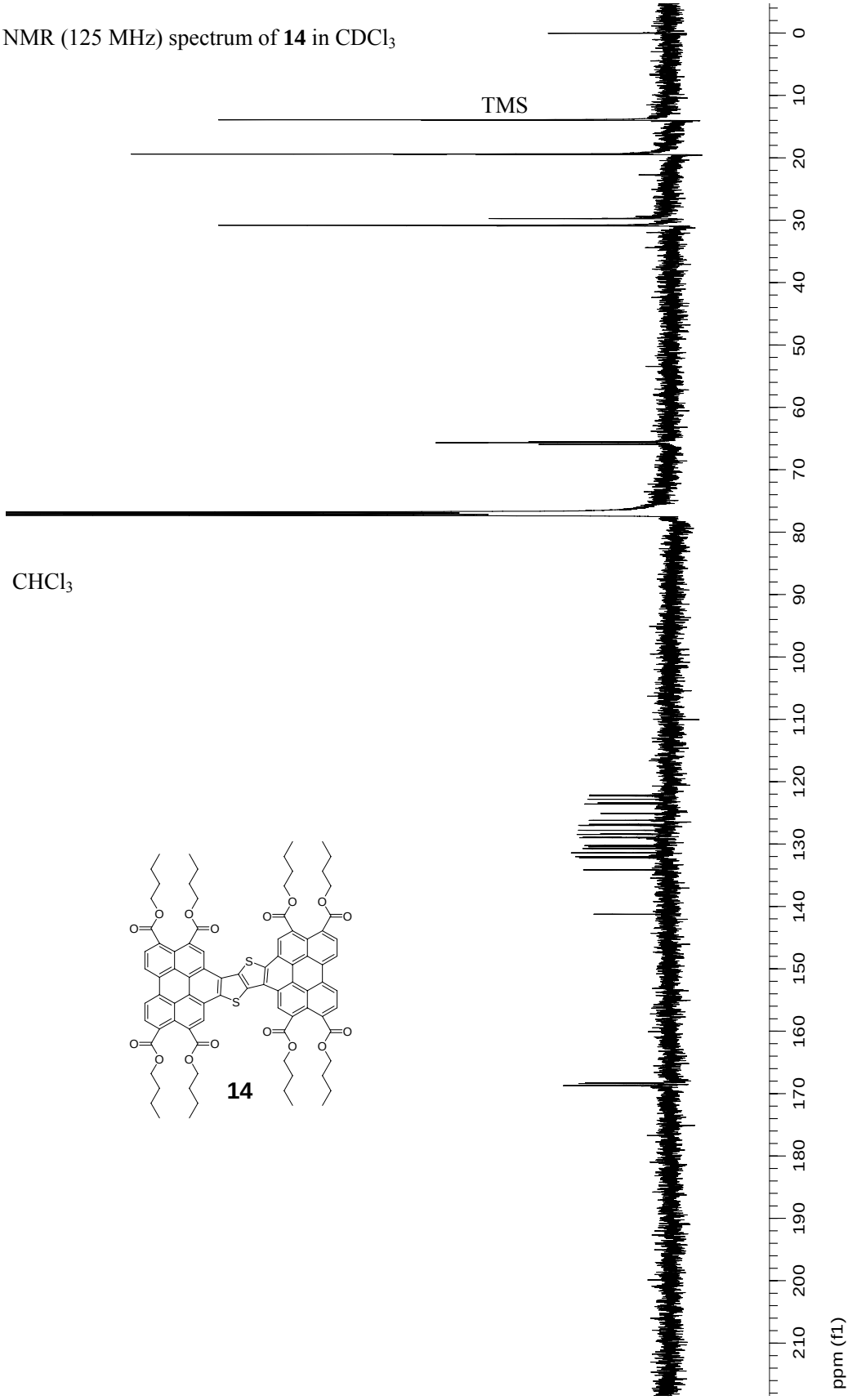
7

7.7 ^{1}H ^{13}C NMR spectrum of 14

^{1}H NMR (400 MHz) spectrum of **14** in $CDCl_3$ and its enlarged low-field section (inserted figure)

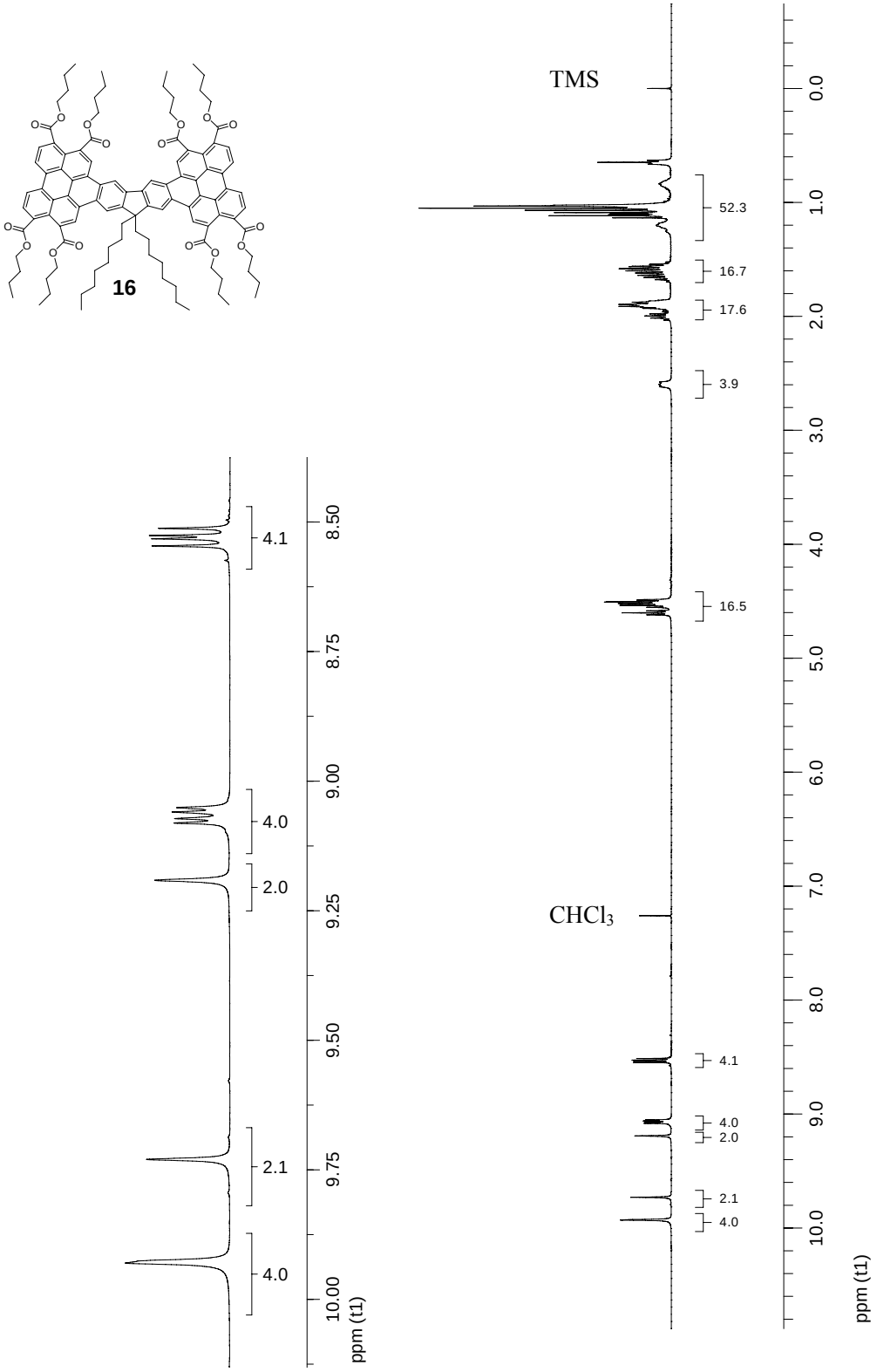


^{13}C NMR (125 MHz) spectrum of **14** in $CDCl_3$

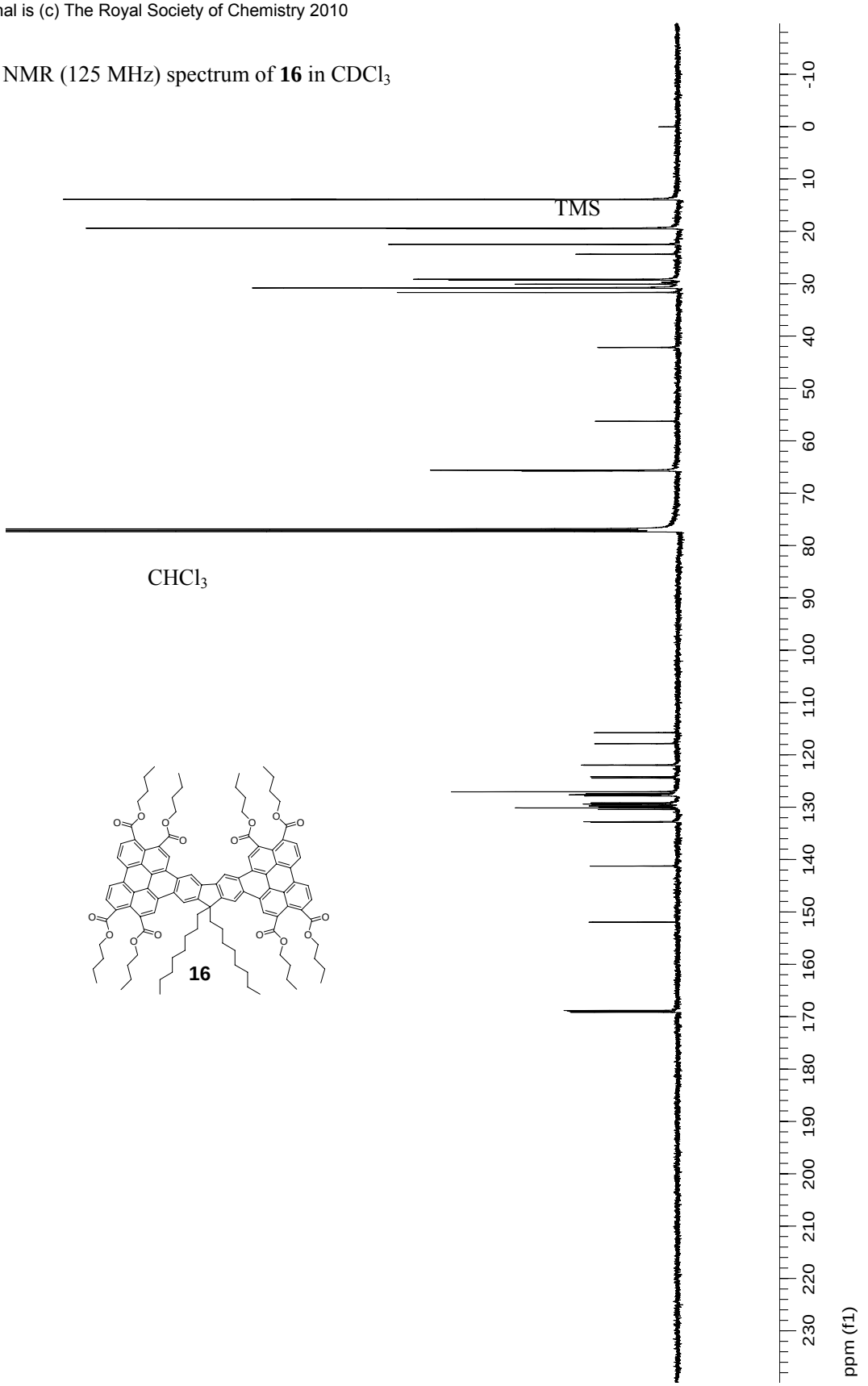


7.8 ^{1}H ^{13}C NMR spectrum of 16

^{1}H NMR (400 MHz) spectrum of **16** in $CDCl_3$ and its enlarged low-field section (inserted figure)



^{13}C NMR (125 MHz) spectrum of **16** in $CDCl_3$



16