Supporting Information

For

Organic Semiconducting Materials from Sulfur-Hetero Benzo[*k*]fluoranthene Derivatives: Synthesis, Photophysical Properties and Thin Film Transistor Fabrication

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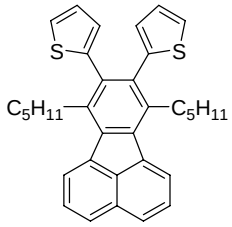
1. Experimental Section

General Methods. Chemicals were purchased and used as received. All air and water sensitive reactions were performed under nitrogen atmosphere. Toluene and tetrahydrofuran (THF) were distilled from sodium, dichloromethane (DCM) was distilled from CaH_2, methanol (MeOH) was dried over sieves, and nitromethane ($MeNO_2$) was dried over sieves then distilled prior to use. 2,2′-(ethyne-1,2-diyl)bisthiophene was obtained from 2-iodothiophene[128] and 7,9-dipentyl-8*H*-cyclopenta[α]acenaphthylen-8-one was obtained from acenaphthenequinone followed literature procedure.[111] ^{1}H and ^{13}C NMR spectra were recorded using $CDCl_3$ as solvent unless otherwise noted. All chemical shifts were reported in parts per million (ppm), ^{1}H NMR chemical shifts were referenced to TMS (0 ppm) or residual $CHCl_3$ (7.26 ppm), and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.23 ppm) or 1,1,2,2-tetrachloroethane-d_2 (73.70 ppm).

Fabrications of Organic Films and OFETs. Organic field-effect transistors based on fluoranthene derivatives **8-11** were fabricated in a "top contact" configuration. A heavily doped, *n*-type Si wafer was used as the gate electrode and substrate. A thermally grown SiO_2 layer (ca. 300 nm thick) acted as gate insulator with a unit capacitance of 11 nF cm^{-2}. Prior to the deposition of semiconductors, the Si/SiO_2 substrate was immersed in 10 mg/mL *n*-octadecyltrichlorosilane (OTS) in toluene at 60 ^{o}C for 20 min. Semiconductors **8-11** were vacuum-evaporated onto Si/SiO_2 substrate at 4×10^{-4} Pa at a rate of 0.1 nm s^{-1} to form thin films (ca. 50 nm thick) as active layers. Source and drain electrodes (ca. 100 nm thick) were prepared by

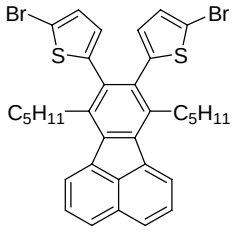
deposition of Au with a shadow mask. The defined channel width (W) and channel length (L) were 100 μm and 10 mm, respectively. Annealing procedure was done before the deposition of Au under nitrogen. Thin films of semiconductors **8-11** were thermally annealed at 240, 235, 230 and 270 ^{o}C for 20 min, respectively.

Characterization of Thin Film OFETs. The thin films of semiconductors were imaged with tapping mode. The organic transistors were tested under ambient condition at room temperature. Field-effect mobilities (μ_{FET}) were extracted from the saturation region of I_d using the equation $I_d = (WC_i/2L)\,\mu_{FET}(V_g - V_{th})^2$.



7,10-dipentyl-8,9-di(2′-thienyl)fluoranthene (**2**). A solution of 2,2′-(ethyne-1,2-diyl)bisthiophene (0.19 g, 1.0 mmol) in 1,2,4-trimethylbenzene (2 mL) was refluxed for 40 h while 7,9-dipentyl-8*H*-cyclopenta[*a*]acenaphthylen-8-one (0.34 g, 1.0 mmol) was added by portions. After the removal of the solvent under reduced pressure, the residue was purified by flash chromatography over silica gel (petroleum ether, and then petroleum ether/dichloromethane = 20/1 as eluent) to afford **2** (0.36 g, 69%) as a light yellow solid, while 0.048 g of 2,2′-(ethyne-1,2-diyl)bisthiophene was recovered. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 8.01 (d, 2H, *J* = 7.0 Hz), 7.87 (d, 2H, *J* = 8.0 Hz), 7.63-7.71 (m, 2H), 7.21 (dd, 2H, *J* = 5.2, 1.4 Hz), 6.89 (dd, 2H, *J* = 5.2, 3.5 Hz), 6.76 (dd, 2H, *J* = 3.5, 1.4 Hz), 2.91-3.00 (m, 4H), 1.72-1.78 (m, 4H), 1.26-1.42 (m, 8H), 0.86 (t, 6H, *J* = 7.0 Hz). ^{13}C

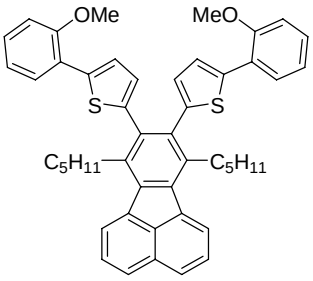
NMR (50 MHz, $CDCl_3$, ppm): δ 141.3, 137.9, 137.7, 137.2, 135.7, 133.6, 130.2, 128.6, 128.2, 126.9, 126.2, 125.5, 123.5, 32.5, 31.6, 29.8, 22.4, 14.2. MS (EI, *m/z*): 504 (M^+, 100%). Anal. Calcd. for $C_{34}H_{34}S_2$: C, 80.58; H, 6.76. Found: C, 80.39; H, 6.78.



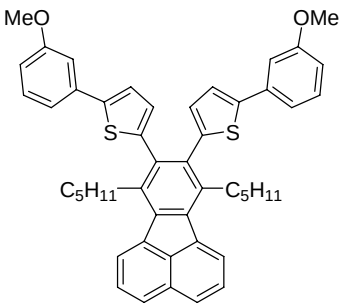
8,9-di(5-bromo-2-thienyl)-7,10-dipentylfluoranthene (**3**). To a solution of **2** (0.51 g, 1.0 mmol) in dichloromethane (15 mL) was added acetic acid (15 mL). The mixture was cooled to 0 ^oC, and then *N*-bromosuccinimide (NBS) (0.39 g, 2.2 mmol) was added by portions. The mixture was stirred overnight at room temperature. The organic phase was washed with brine, 2 M aqueous NaOH and NH_4Cl solutions, respectively, and then dried over $MgSO_4$. After the removal of solvents under reduced pressure, the residue was recrystallized with CH_2Cl_2/EtOH to afford **3** as a light yellow solid (0.57 g, 85%). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ 8.00 (d, 2H, J = 6.8 Hz), 7.87 (d, 2H, J = 8.2 Hz), 7.62-7.70 (m, 2H), 6.90 (d, 2H, J = 3.8 Hz), 6.54 (d, 2H, J = 3.8 Hz), 2.93-3.01 (m, 4H), 1.71-1.78 (m, 4H), 1.27-1.46 (m, 8H), 0.91 (t, 6H, J = 7.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 141.3, 137.9, 137.7, 137.2, 135.7, 133.6, 130.2, 128.6, 128.2, 126.9, 126.2, 125.5, 123.5, 32.5, 31.6, 29.8, 22.4, 14.2. MS (EI, *m/z*): 662 (M^+), 664 (M^+ + 2, 100%). Anal. Calcd. for $C_{34}H_{32}Br_2S_2$: C, 61.45; H, 4.85. Found: C, 61.28; H, 4.85.

General Procedure for 4-7. To a mixture of **3** (0.66 g, 1.0 mmol),

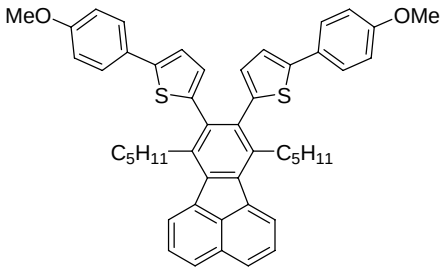
methoxyphenylboronic acid or phenylboronic acid (4.0 mmol), and $Pd(PPh_3)_4$ (70 mg, 0.060 mmol) in THF (40 mL) was added a solution of K_2CO_3 (2.8 g, 20 mmol) in H_2O (10 mL). The mixture was refluxed for overnight. The organic layer was washed with aqueous NH_4Cl solution, dried over $MgSO_4$. After the removal of solvents under reduced pressure, the residue was recrystallized from CH_2Cl_2/EtOH to afford the desired product as a light yellow solid.



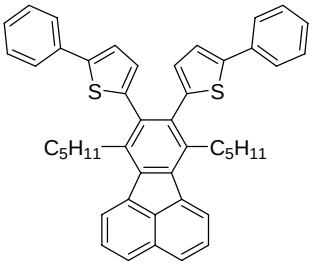
8,9-di(5′-(2″-methoxyphenyl)-2′-thienyl)-7,10-dipentylfluoranthene (**4**). (0.61 g, 85%). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 8.03 (d, 2H, *J* = 7.0 Hz), 7.88 (d, 2H, *J* = 8.0 Hz), 7.58-7.71 (m, 4H), 7.33 (d, 2H, *J* = 3.6 Hz), 7.15-7.20 (m, 2H), 6.91-6.99 (m, 4H), 6.76 (d, 2H, *J* = 3.6 Hz), 3.84 (s, 6H), 3.01-3.09 (m, 4H), 1.78-1.82 (m, 4H), 1.26-1.46 (m, 8H), 0.86 (t, 6H, *J* = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 155.6, 141.3, 139.2, 137.9, 137.6, 137.3, 135.8, 133.5, 130.1, 128.4, 128.1, 128.0, 126.8, 124.6, 123.9, 123.4, 121.1, 112.2, 55.7, 32.6, 31.7, 30.0, 22.6, 14.2. MS (EI, *m/z*): 718 (M^+, 100%). Anal. Calcd. for $C_{48}H_{46}O_2S_2$: C, 80.18; H, 6.45. Found: C, 80.00; H, 6.44.



8,9-di(5′-(3″-methoxyphenyl)-2′-thienyl)-7,10-dipentylfluoranthene (**5**). (0.66 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ: 8.02 (d, 2H, *J* = 6.9 Hz), 7.88 (d, 2H, *J* = 8.1 Hz), 7.65-7.70 (m, 2H), 7.22-7.27 (m, 2H), 7.07-7.16 (m, 6H), 6.76-6.80 (m, 2H), 6.74 (d, 2H, *J* = 3.6 Hz), 3.82 (s, 6H), 3.01-3.07 (m, 4H), 1.75-1.85 (m, 4H), 1.24-1.46 (m, 8H), 0.86 (t, 6H, *J* = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 160.0, 144.0, 140.9, 137.9, 137.8, 137.0, 136.0, 135.3, 133.5, 130.1, 130.0, 129.6, 128.2, 126.9, 123.5, 122.7, 118.3, 112.8, 111.3, 55.4, 32.5, 31.7, 29.9, 22.5, 14.2. MS (EI, *m/z*): 718 (M^+, 100%). Anal. Calcd. for $C_{48}H_{46}O_2S_2$: C, 80.18; H, 6.45. Found: C, 80.02; H, 6.49.

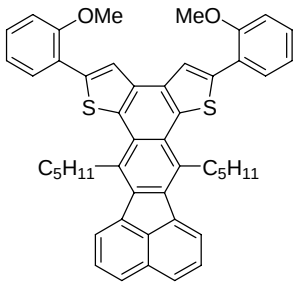


8,9-di(5′-(4″-methoxyphenyl)-2′-thienyl)-7,10-dipentylfluoranthene (6). (0.65 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.03 (d, 2H, *J* = 7.2 Hz), 7.89 (d, 2H, *J* = 8.1 Hz), 7.66-7.71 (m, 2H), 7.48 (d, 4H, *J* = 8.8 Hz), 7.01 (d, 2H, *J* = 3.4 Hz), 6.88 (d, 4H, *J* = 8.8 Hz), 6.73 (d, 2H, *J* = 3.4 Hz), 3.81 (s, 6H), 3.01-3.07 (m, 4H), 1.77-1.81 (m, 4H), 1.21-1.44 (m, 8H), 0.86 (t, 6H, *J* = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 159.1, 144.0, 139.8, 138.0, 137.7, 137.2, 135.6, 130.1, 129.5, 128.2, 127.7, 127.0, 126.9, 123.5, 121.4, 114.4, 55.6, 32.6, 31.7, 29.9, 22.5, 14.2. MS (EI, *m/z*): 718 (M^+, 100 %). Anal. Calcd. for $C_{48}H_{46}O_2S_2$: C, 80.18; H, 6.45. Found: C, 80.06; H, 6.42.

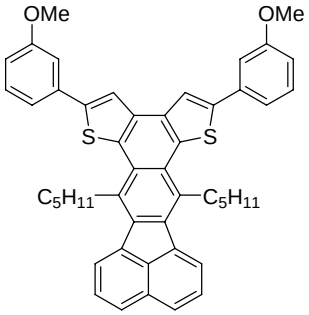


7,10-dipentyl-8,9-di(5′-phenyl-2′-thienyl)fluoranthene (**7**). (0.56 g, 85%). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 8.01 (d, 2H, *J* = 7.0 Hz), 7.86 (d, 2H, *J* = 7.8 Hz), 7.62-7.70 (m, 2H), 7.53-7.57 (m, 4H), 7.28-7.36 (m, 4H), 7.16-7.24 (m, 2H), 7.12 (d, 2H, *J* = 3.9 Hz), 6.76 (d, 2H, *J* = 3.9 Hz), 2.99-3.08 (m, 4H), 1.72-1.86 (m, 4H), 1.28-1.49 (m, 8H), 0.86 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 144.2, 140.9, 138.1, 137.9, 137.2, 135.5, 134.8, 133.6, 130.2, 129.7, 129.0, 128.3, 127.3, 127.0, 125.8, 123.6, 122.5, 32.5, 31.6, 29.9, 22.5, 14.2. MS (EI, *m/z*): 658 (M^+, 100%). Anal. Calcd. for $C_{46}H_{42}S_2$: C, 83.85; H, 6.42. Found: C, 83.86; H, 6.48.

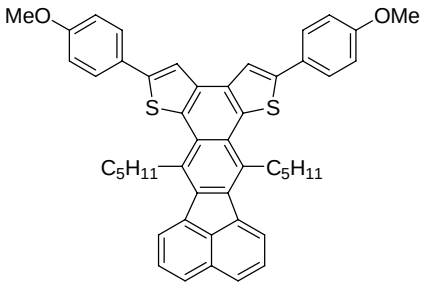
General Procedure for 8-12. To a vigorously stirred solution of **4-7** or **3** (0.20 mmol) in dicholormethane (100 mL) was added dropwise a solution of $FeCl_3$ (0.19 g, 1.2 mmol) in $MeNO_2$ (3 mL) at 0 ^{o}C. Anhydrous MeOH was added after 30 min and stirred for another 60 min. The mixture was washed with brine, 2 M aquoues NaOH, and NH_4Cl solution, respectively, and then pushed through a plug of silica gel. After the removal of solvents under reduced pressure, the residue was recrystallized from $CHCl_3$/EtOH to give the desired product as a yellow solid.



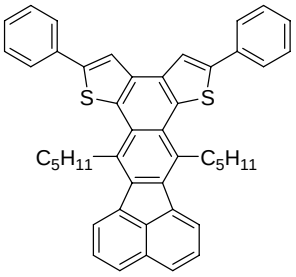
Compound 8. (0.11 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$, 55 ^{o}C, ppm): δ 8.27 (s, 2H), 8.20 (d, 2H, *J* = 6.9 Hz), 7.91-7.94 (m, 2H), 7.87 (d, 2H, *J* = 8.1 Hz), 7.70-7.75 (m, 2H), 7.34-7.40 (m, 2H), 7.09-7.15 (m, 4H), 3.80-4.40 (m, 4H), 4.06 (s, 6H), 1.80-2.30 (m, 8H), 1.59-1.66 (m, 4H), 1.06 (t, 6H, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $Cl_2DCCDCl_2$, 95 ^{o}C, ppm): δ 156.3, 139.8, 137.4, 135.5, 135.0, 134.6, 134.3, 130.3, 128.9, 128.5, 127.8, 125.9, 123.3, 122.7, 121.1, 119.9, 112.3, 55.7, 32.4, 32.2, 28.0, 22.4, 14.0. MS (EI, *m/z*): 716 (M^+, 100%). HR-MS (EI): Calcd. for $C_{48}H_{44}O_2S_2$: 716.2783; Found: 716.2789.



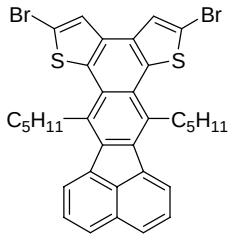
Compound 9. (0.12 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$, 55 ^{o}C, ppm): δ 8.14-8.16 (m, 2H), 8.01 (s, 2H), 7.87 (d, 2H, *J* = 8.1 Hz), 7.68-7.74 (m, 2H), 7.39-7.48 (m, 6H), 6.94-6.98 (m, 2H), 3.75-4.25 (m, 4H), 3.95 (s, 6H), 1.75-2.25 (m, 8H), 1.58-1.65 (m, 4H), 1.06 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $Cl_2DCCDCl_2$, 95 ^{o}C, ppm): δ 160.1, 143.8, 137.1, 135.8, 135.2, 134.4, 133.8, 130.3, 129.8, 128.3, 127.8, 126.1, 122.8, 118.9, 117.5, 113.9, 112.1, 55.3, 32.2, 32.1, 27.9, 22.3, 14.0. MS (EI, *m/z*): 716 (M^+, 100%). HR-MS (EI): Calcd. for $C_{48}H_{44}O_2S_2$: 716.2783; Found: 716.2783.



Compound 10. (0.14 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$, 55 ^{o}C, ppm): δ 8.18 (d, 2H, *J* = 7.5 Hz), 7.92 (s, 2H), 7.88 (d, 2H, *J* = 7.8 Hz), 7.80 (d, 4H, *J* = 9.0 Hz), 7.69-7.75 (m, 2H), 7.04 (d, 4H, *J* = 9.0 Hz), 3.80-4.28 (m, 4H), 3.91 (s, 6H), 1.80-2.30 (m, 8H), 1.58-1.66 (m, 4H), 1.07 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $Cl_2DCCDCl_2$, 95 ^{o}C, ppm): δ 159.8, 143.8, 137.3, 135.5, 135.4, 135.0, 134.3, 130.3, 128.2, 127.8, 127.5, 126.8, 125.9, 122.7, 122.6, 116.3, 114.6, 55.3, 32.2, 32.1, 28.0, 22.3, 14.0. MS (EI, *m/z*): 716 (M^+, 100%). HR-MS (EI): Calcd. for $C_{48}H_{44}O_2S_2$: 716.2783; Found: 716.2785.

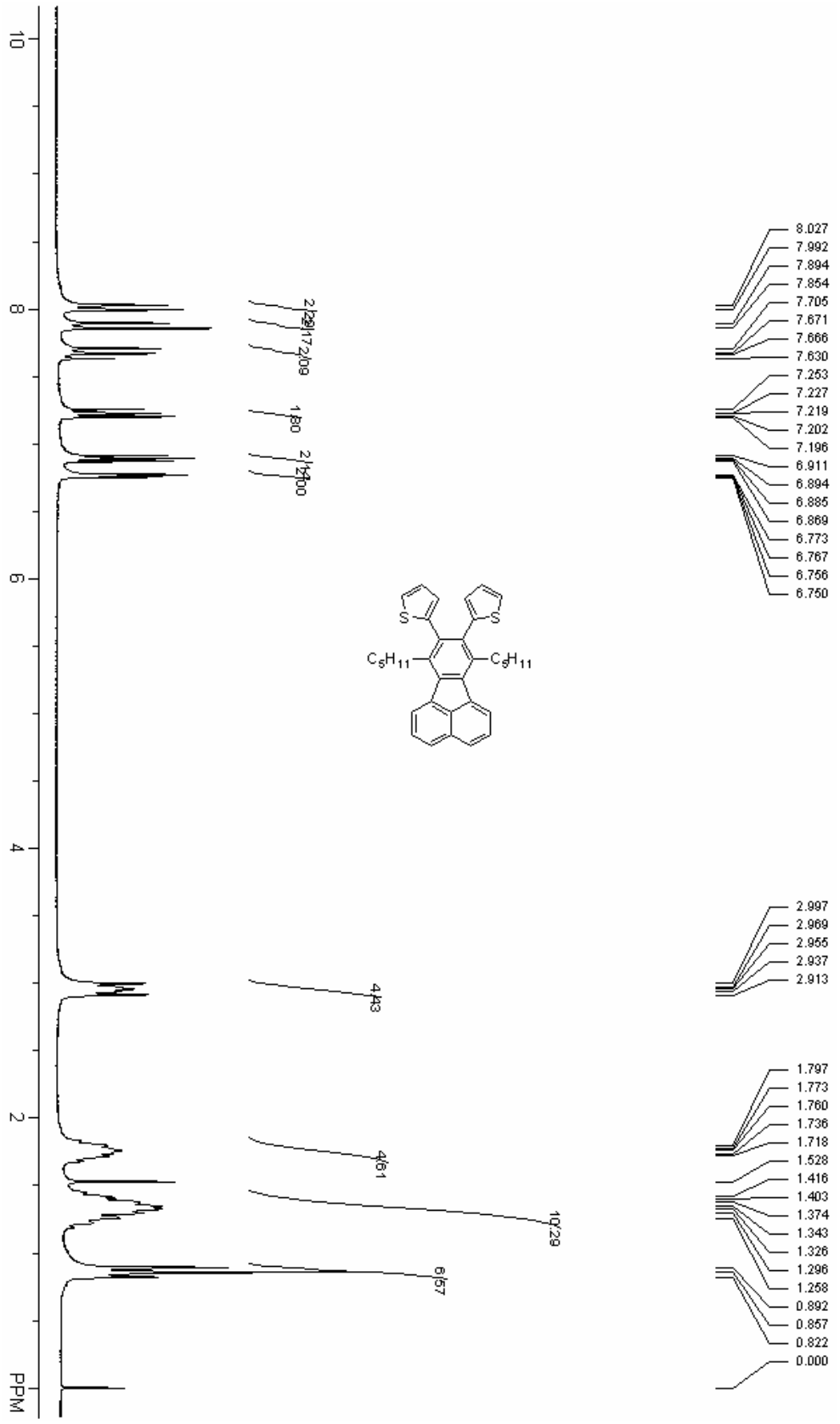


Compound 11. (0.12 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$, 55 ^{o}C, ppm): δ 8.18-8.21 (m, 2H), 8.06 (s, 2H), 7.88-7.90 (m, 6H), 7.71-7.76 (m, 2H), 7.49-7.54 (m, 4H), 7.38-7.43 (m, 2H), 3.76-4.17 (m, 4H), 1.71-2.18 (m, 8H), 1.48-1.62 (m, 4H), 1.07 (t, 6H, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $Cl_2DCCDCl_2$, 95 ^{o}C, ppm): δ 143.9, 137.2, 135.7, 135.3, 135.0, 134.4, 133.9, 133.8, 130.3, 128.8, 128.3, 127.9, 127.8, 126.2, 126.0, 122.8, 117.4, 32.2, 32.1, 27.9, 22.3, 14.0. MS (EI, *m/z*): 656 (M^+, 100%); HR-MS (EI): Calcd. for $C_{46}H_{40}S_2$: 656.2571; Found: 656.2564.

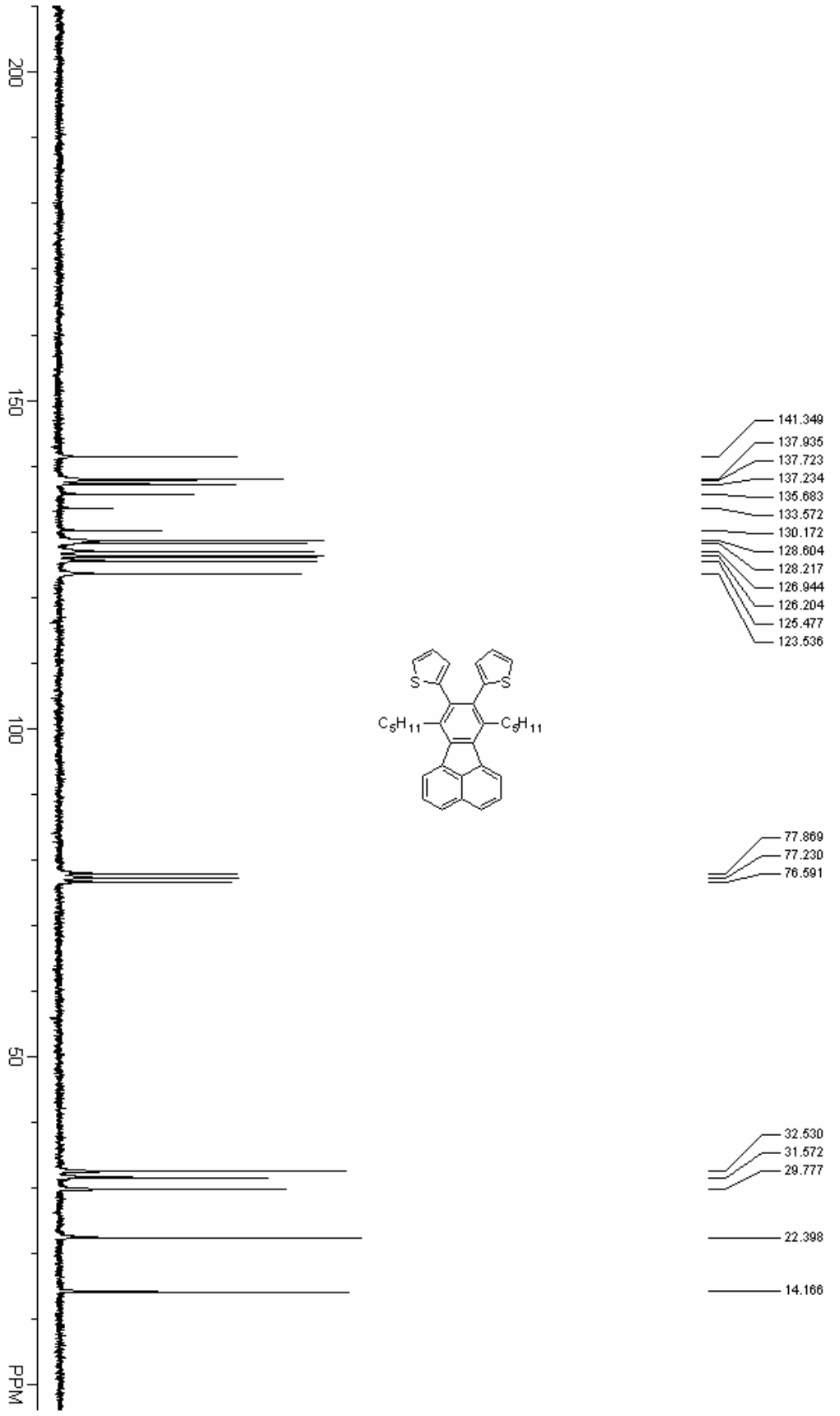


Compound 12. (0.11 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$, 50 ^{o}C, ppm): δ 8.08-8.10 (m, 2H), 7.88 (d, 2H, *J* = 8.1 Hz), 7.66-7.72 (m, 4H), 3.80 (m, 4H), 1.99-2.01 (m, 4H), 1.79 (m, 4H), 1.46-1.59 (m, 4H), 1.04 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 50 ^{o}C, ppm): δ 137.2, 136.4, 135.7, 134.2, 133.4, 130.7, 128.3, 126.7, 124.6, 123.3, 115.5, 32.5, 32.3, 28.2, 22.8, 14.4. MS (EI, *m/z*): 660 (M^+), 662 (M^++2, 100%). HR-MS (EI): Calcd. for $C_{34}H_{30}Br_2S_2$: 662.0135; Found: 662.0135.

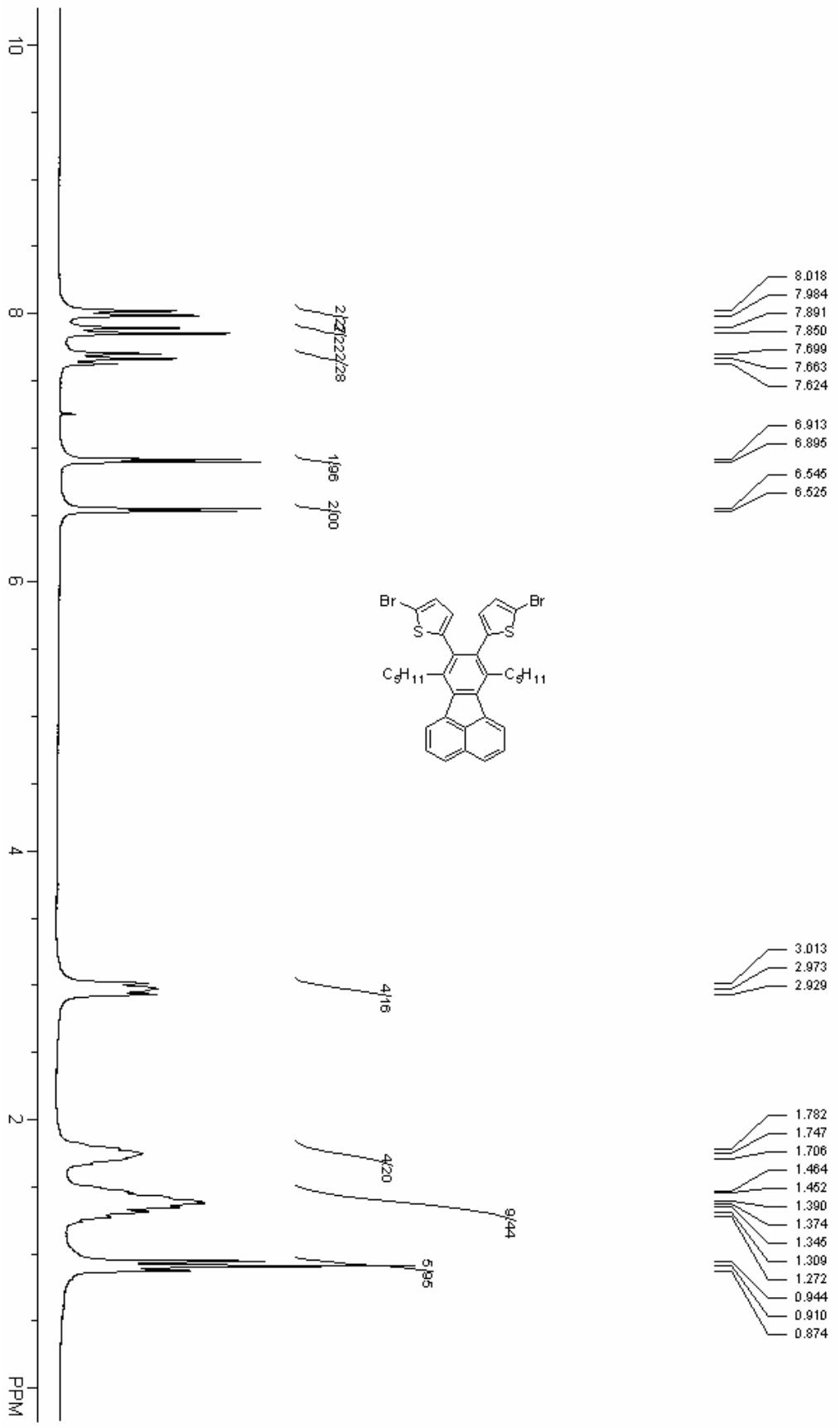
2. Copies of ^{1}H and ^{13}C NMR spectra.



^{1}H NMR spectrum for compound **2**



^{13}C NMR spectrum for compound **2**



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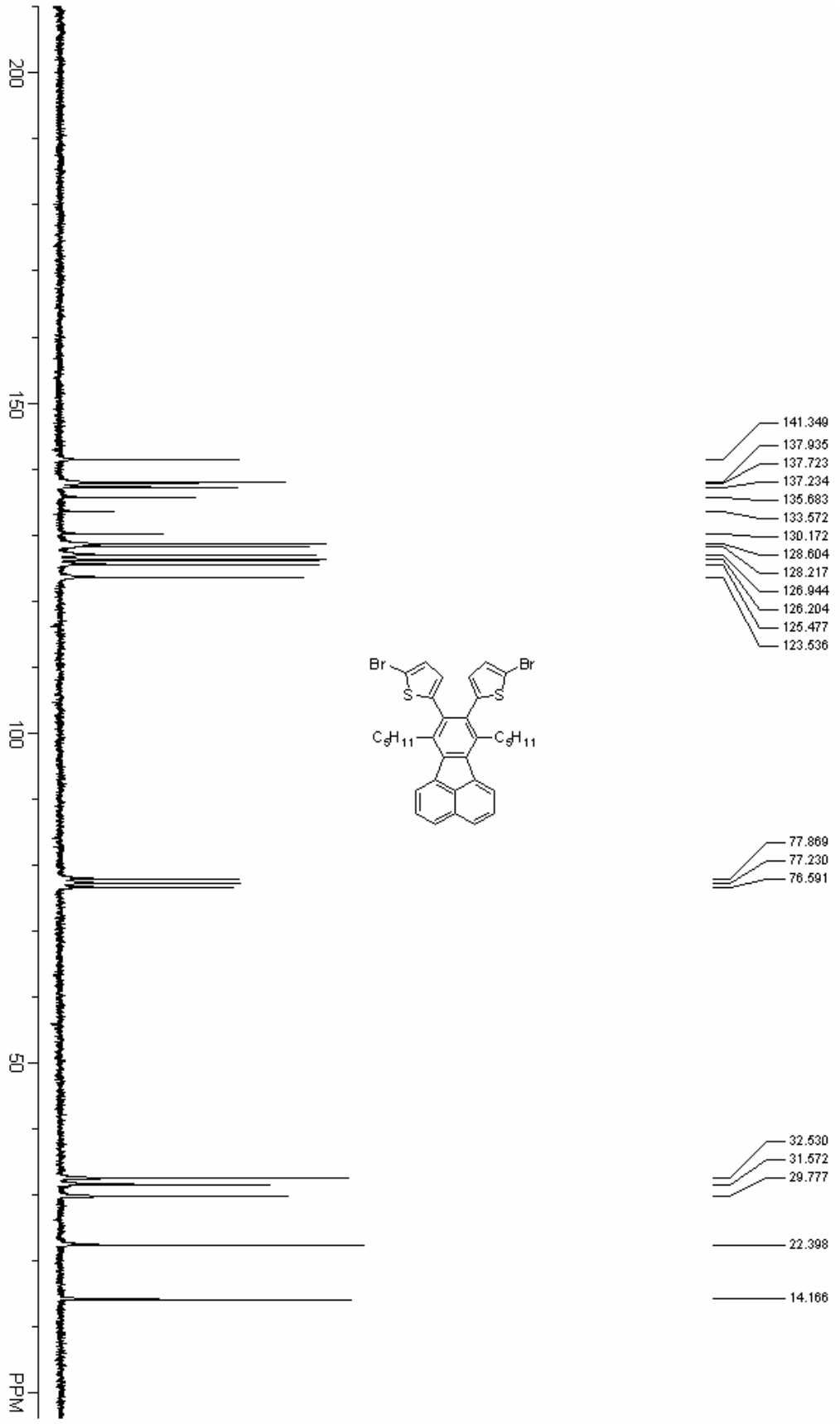
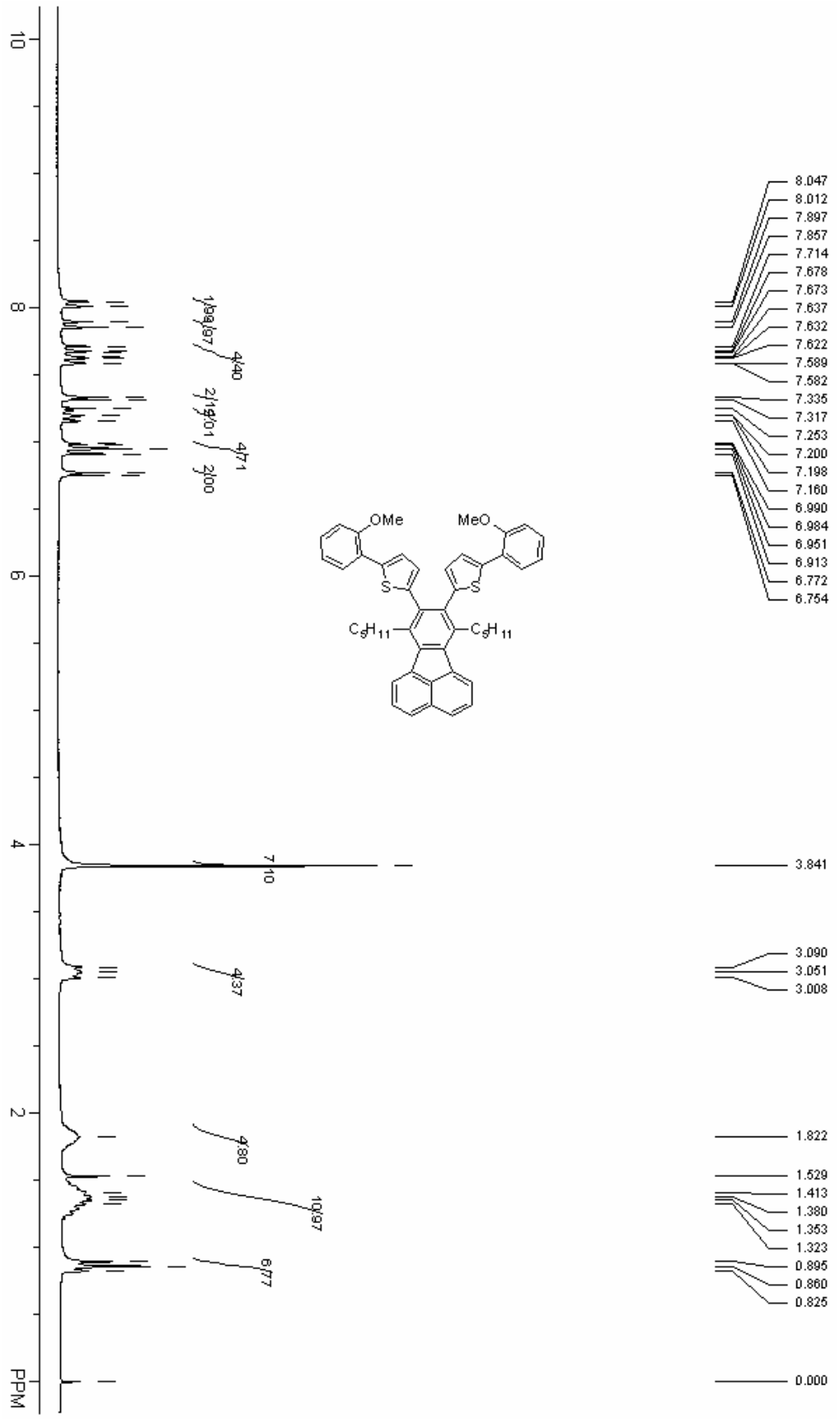
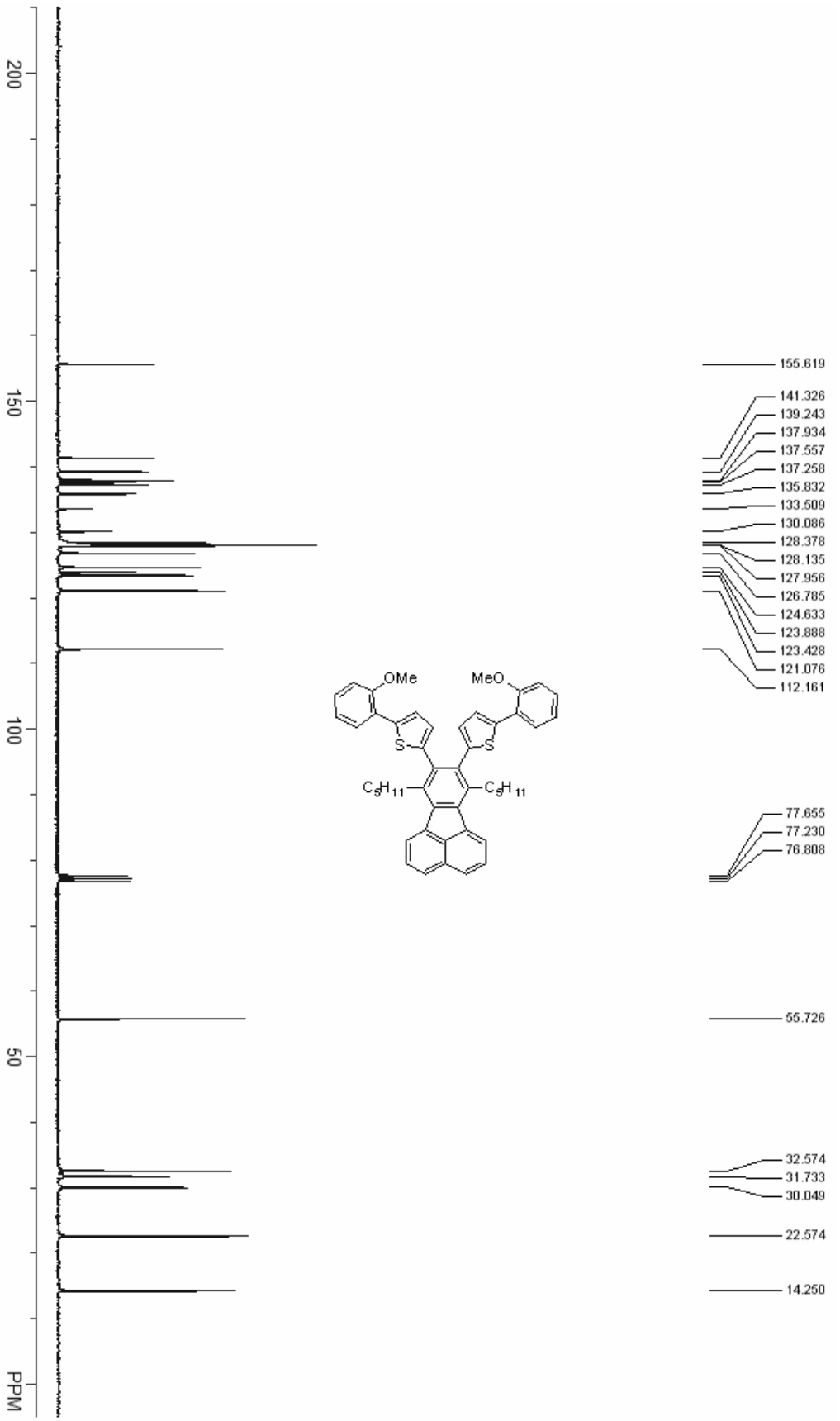


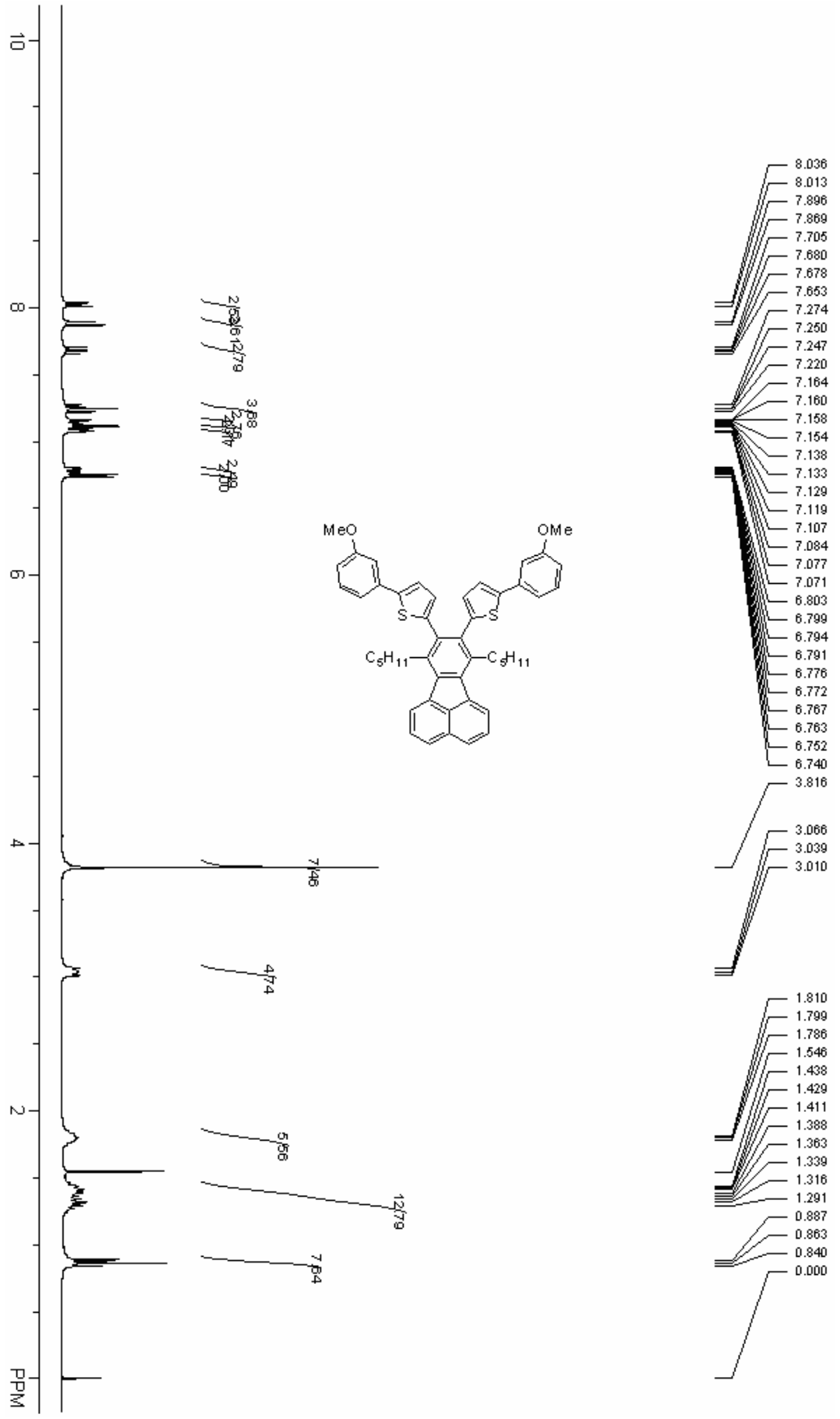
^{13}C NMR spectrum for compound **3**



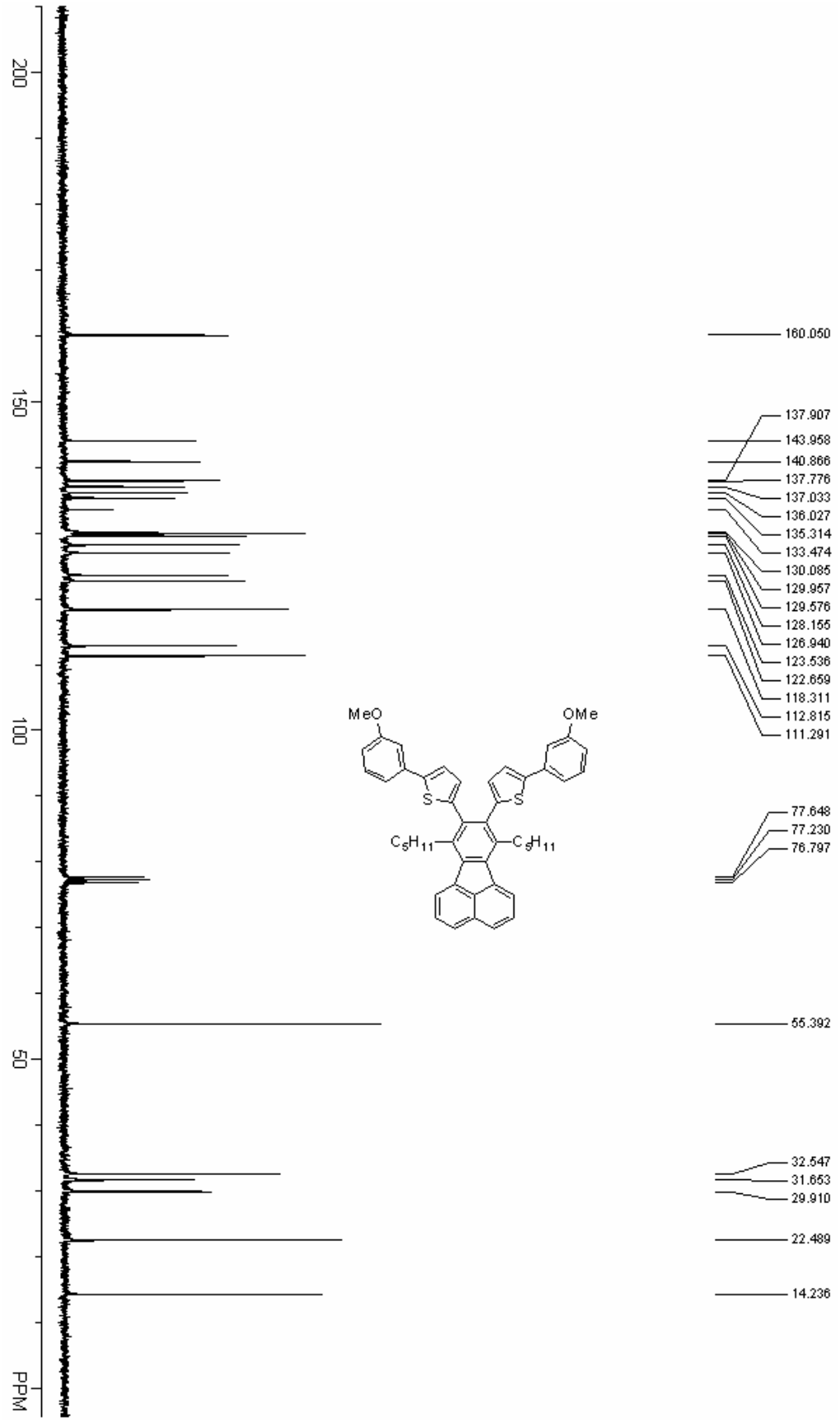
^{1}H NMR spectrum for compound **4**



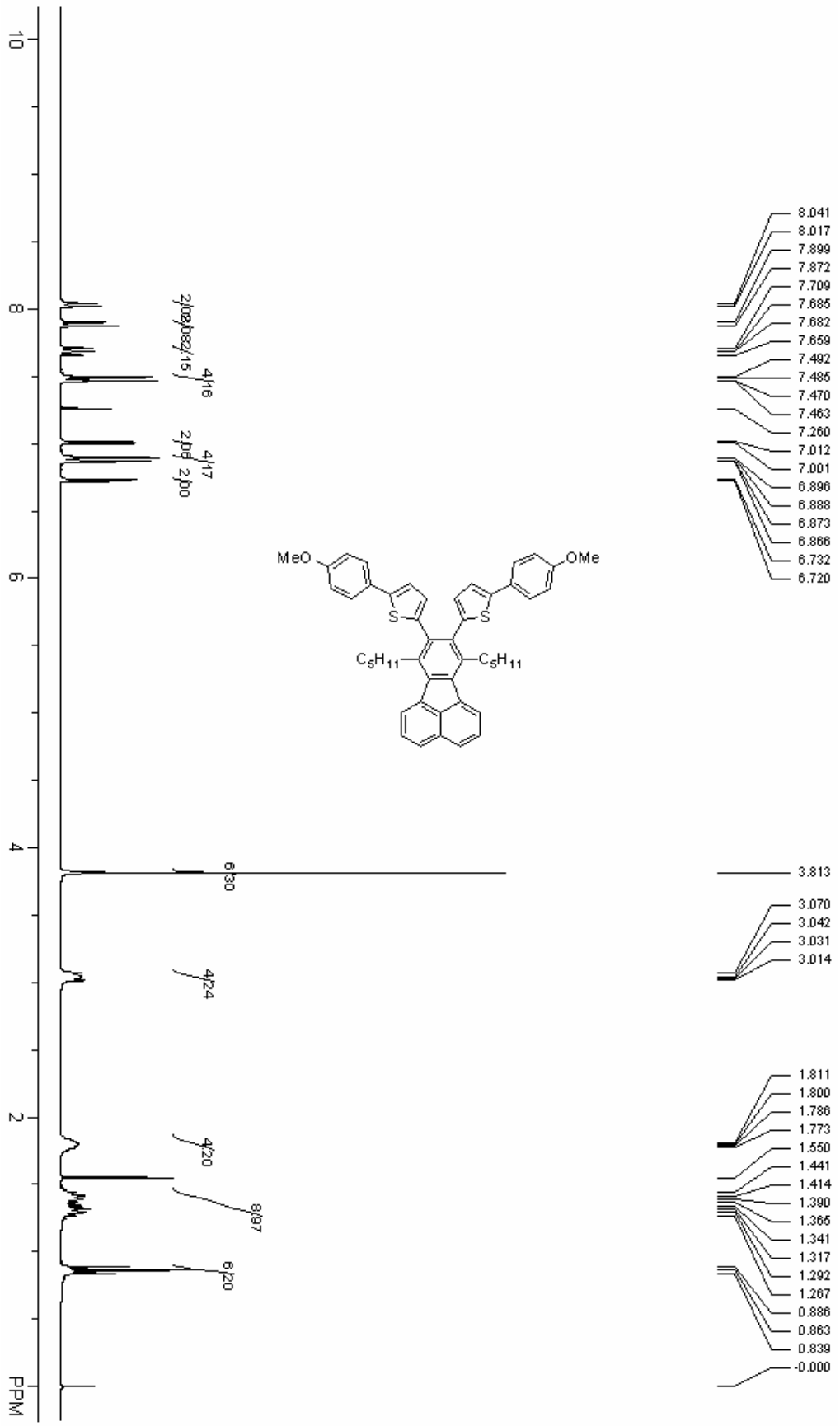
^{13}C NMR spectrum for compound **4**



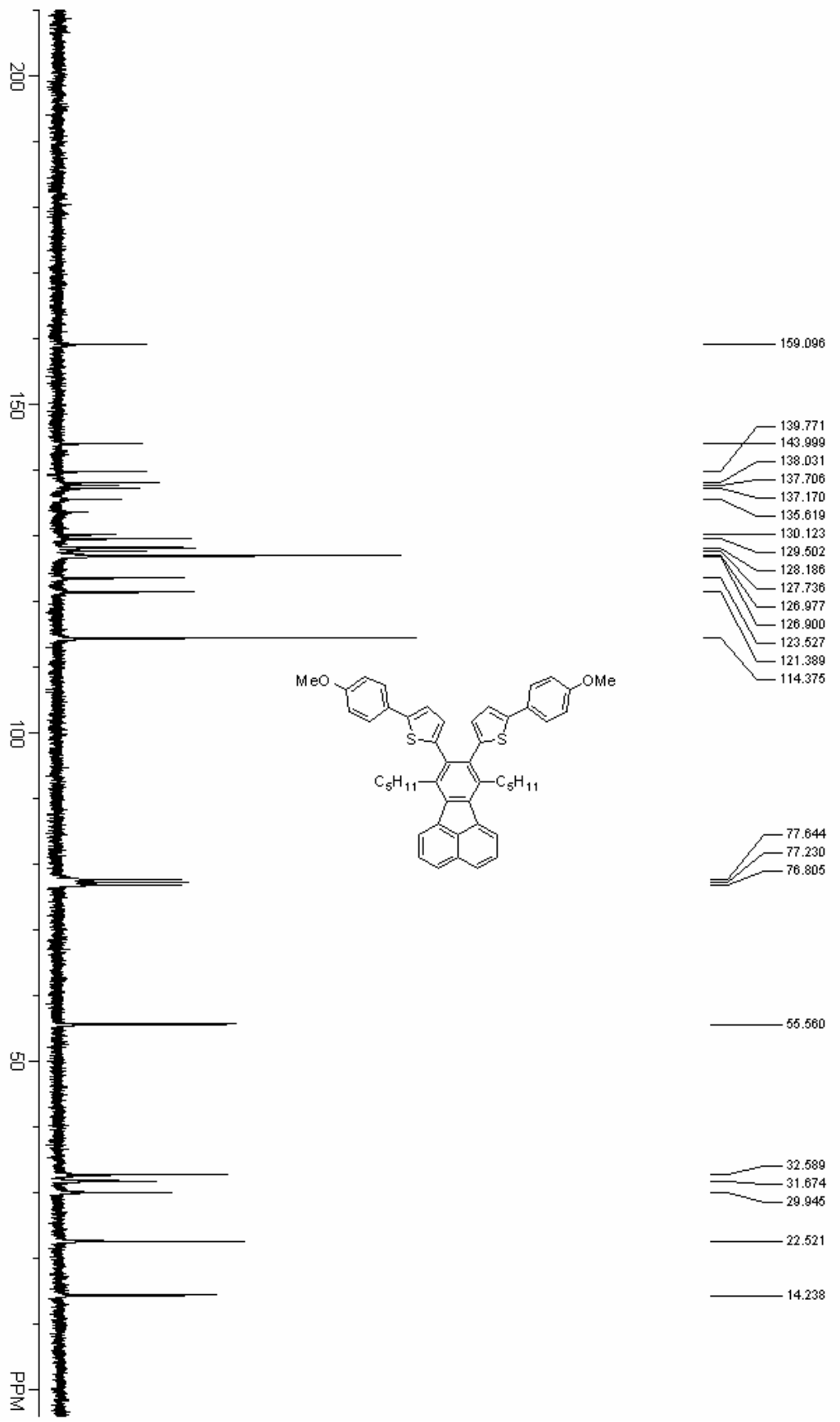
^{1}H NMR spectrum for compound **5**



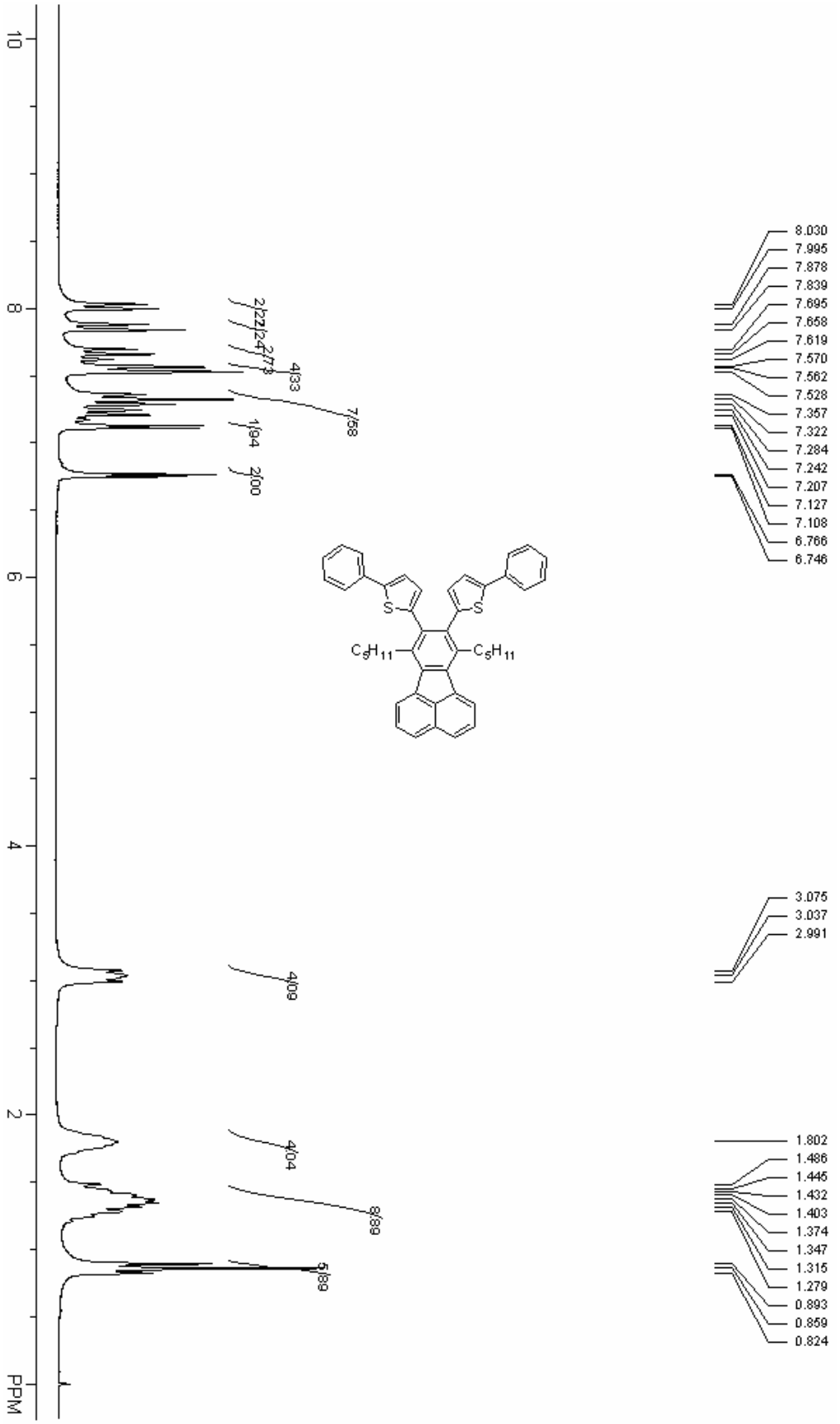
^{13}C NMR spectrum for compound **5**



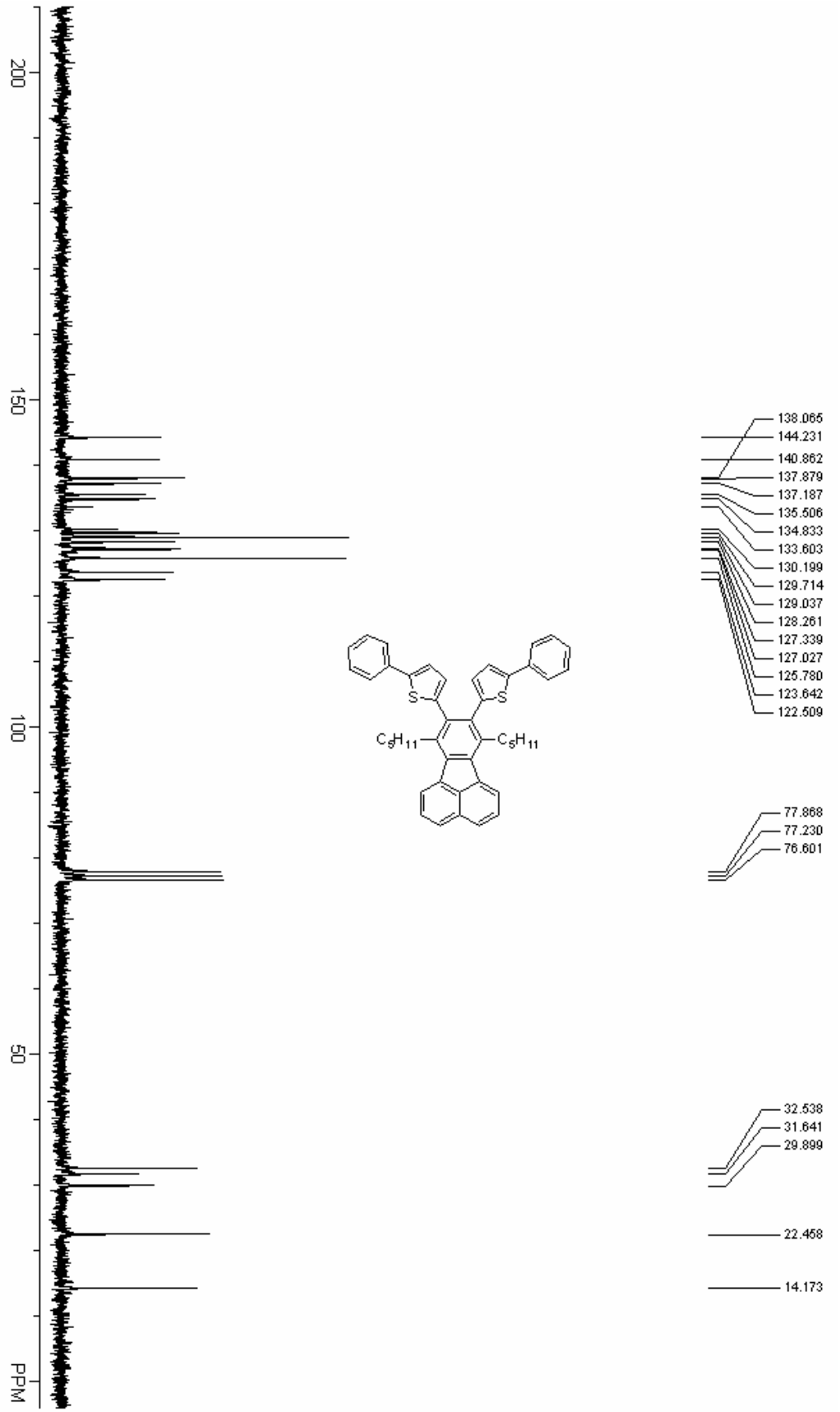
^{1}H NMR spectrum for compound **6**



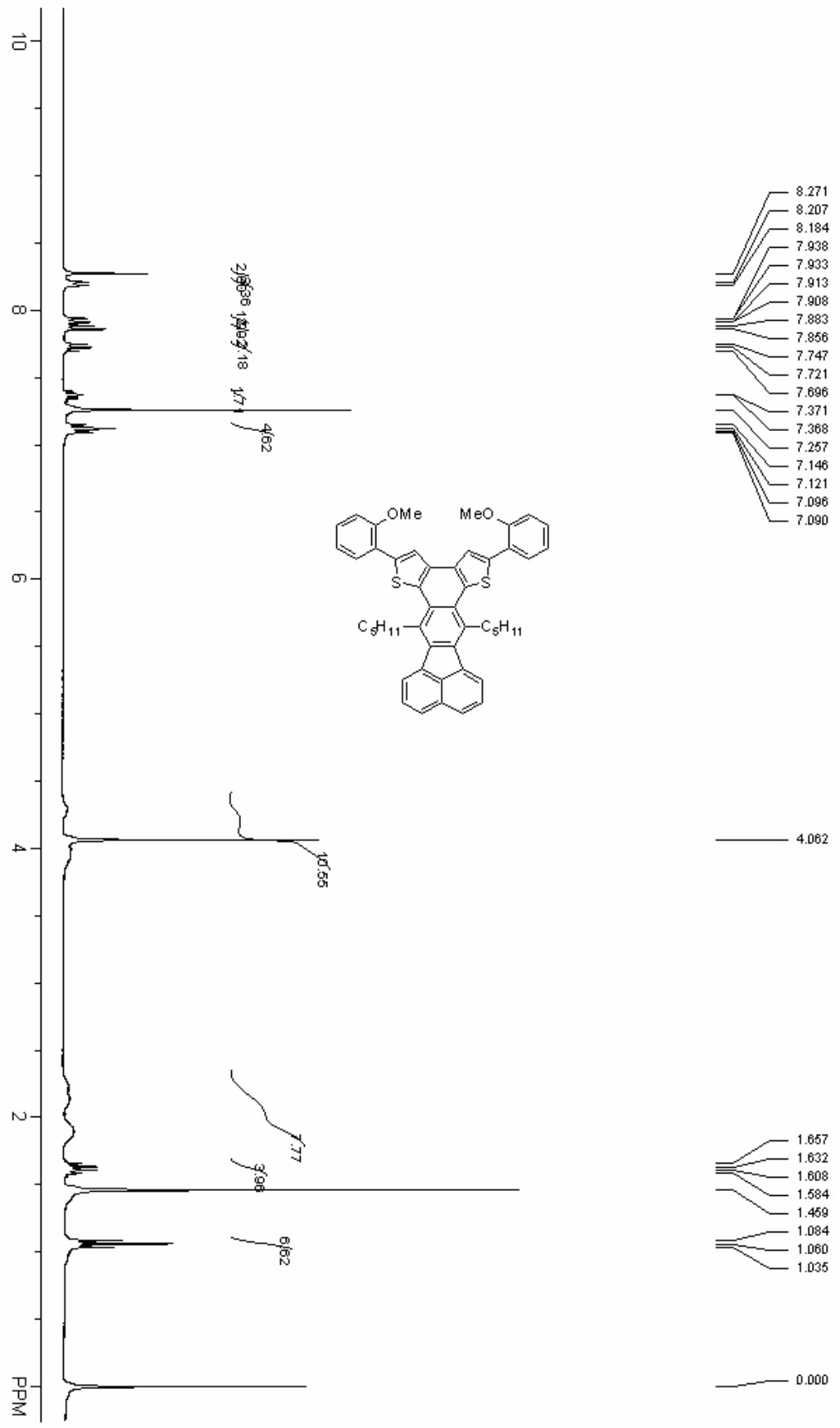
^{13}C NMR spectrum for compound **6**



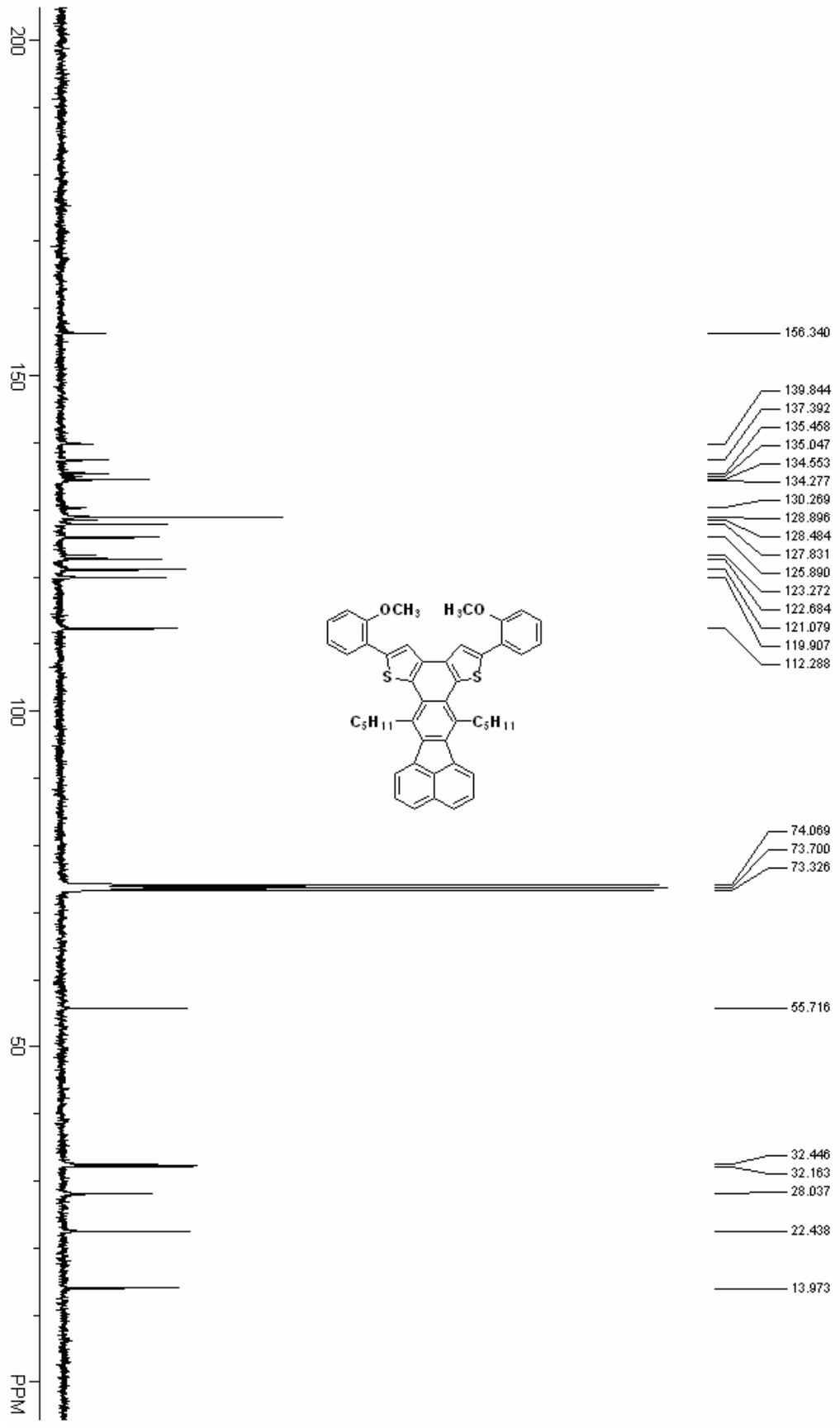
^{1}H NMR spectrum for compound **7**



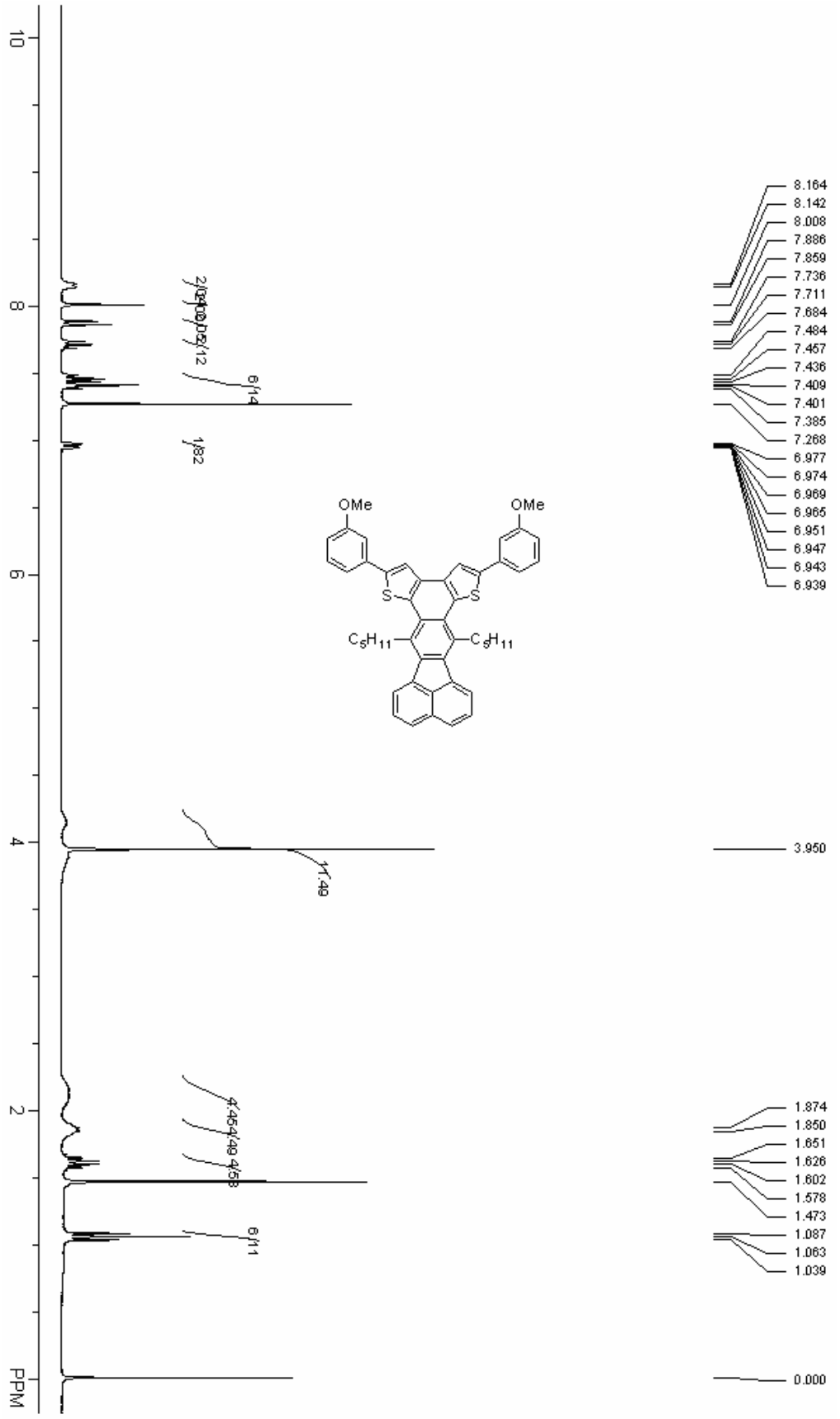
^{13}C NMR spectrum for compound **7**



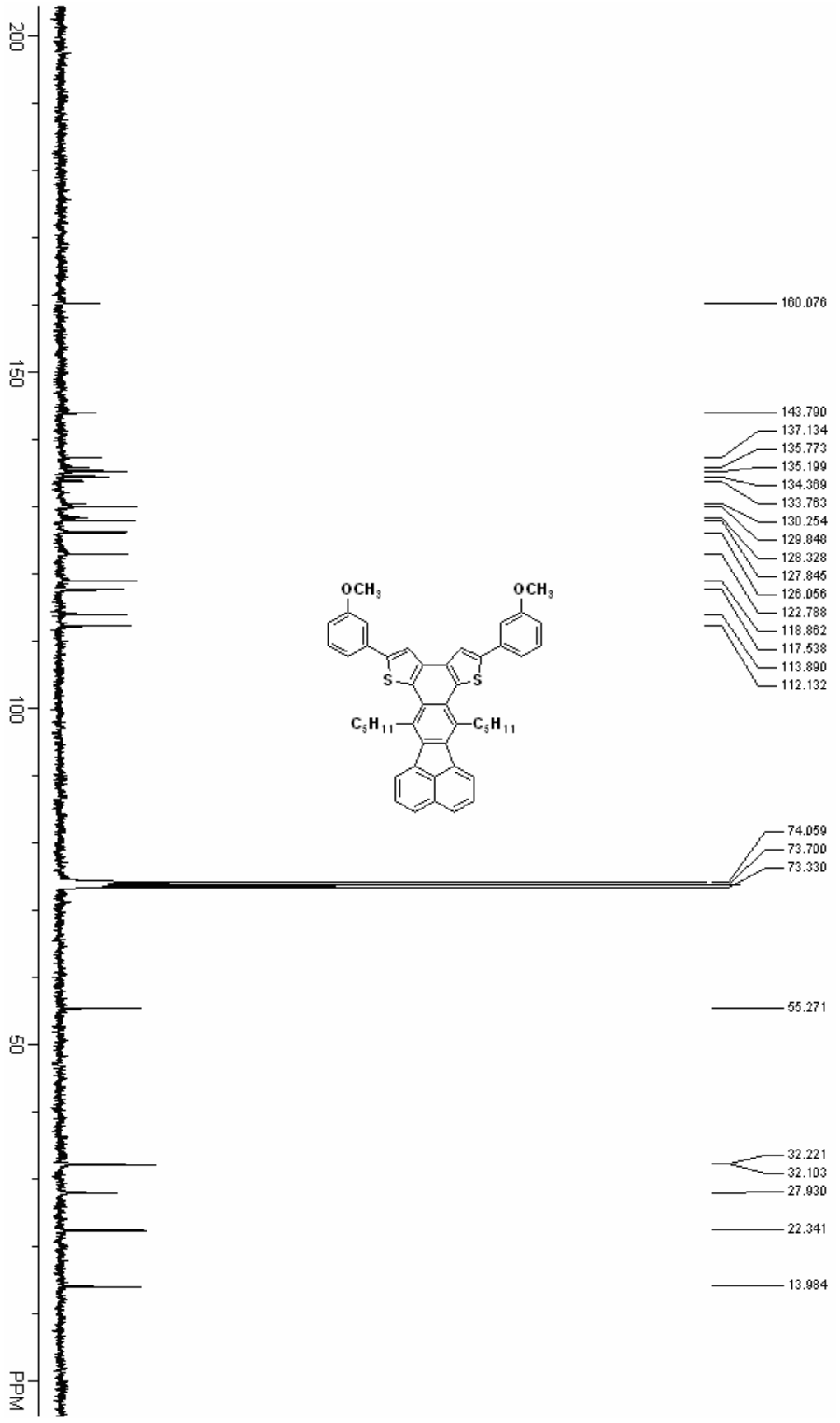
^{1}H NMR spectrum for compound **8**



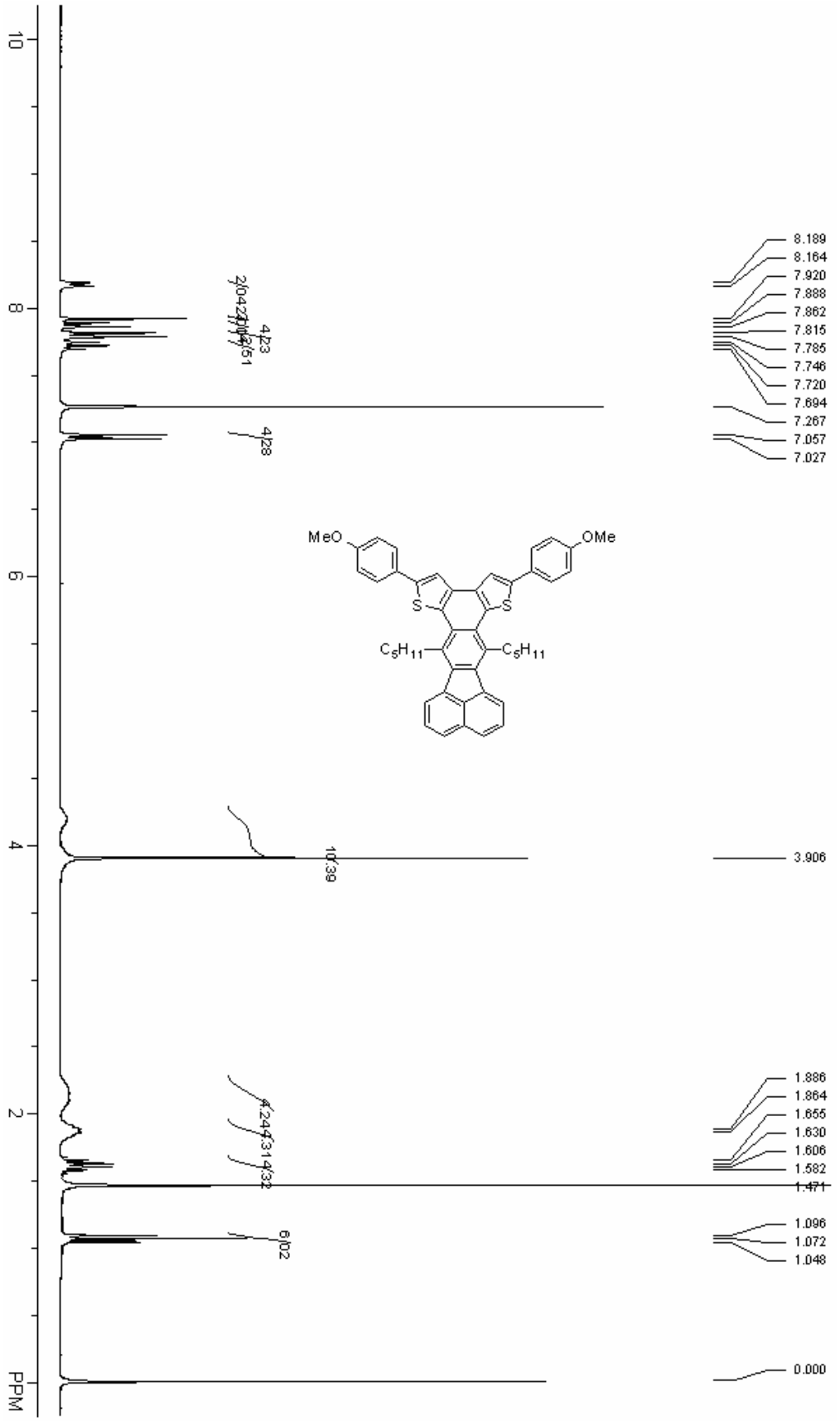
^{13}C NMR spectrum of compound **8**



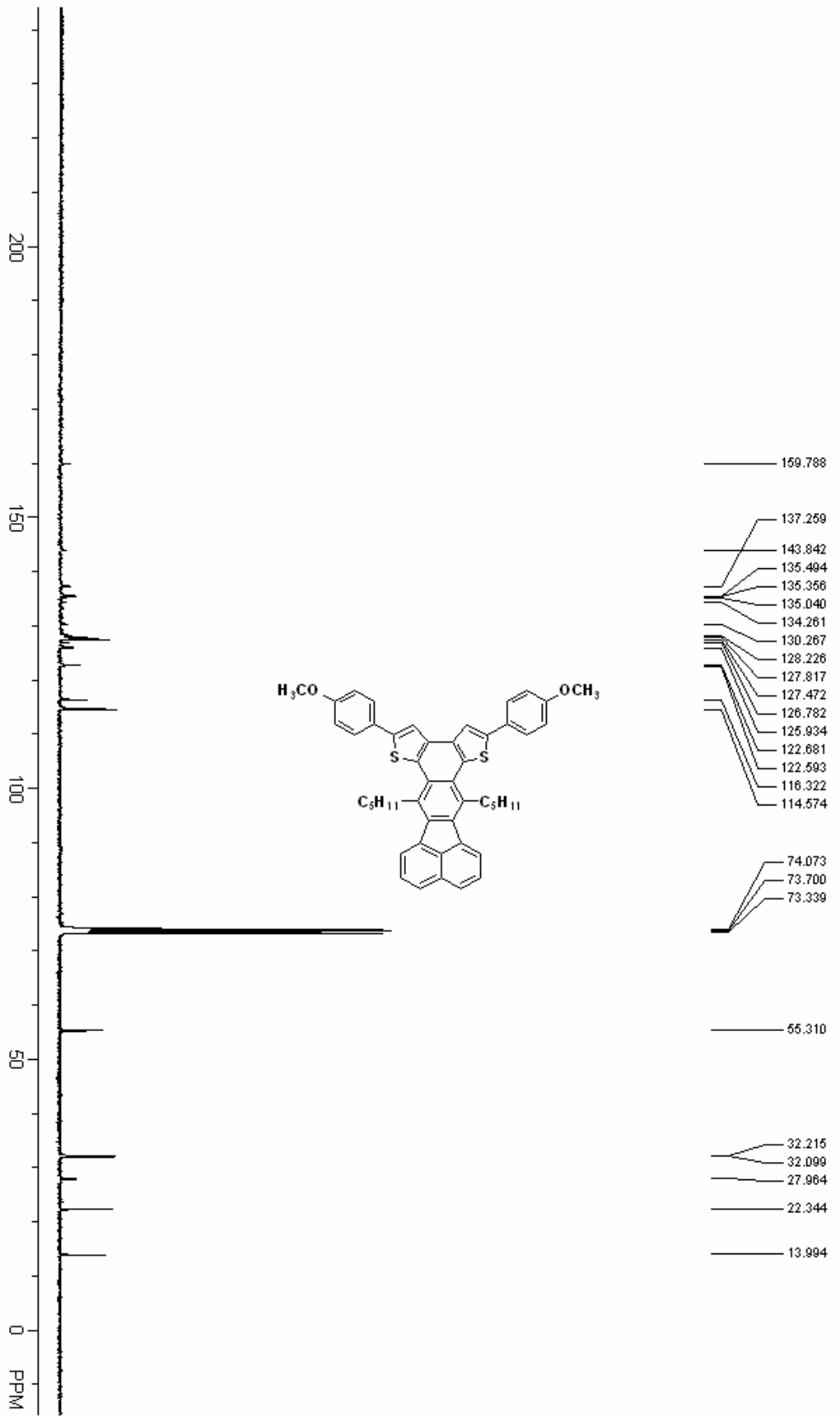
^{1}H NMR spectrum for compound **9**



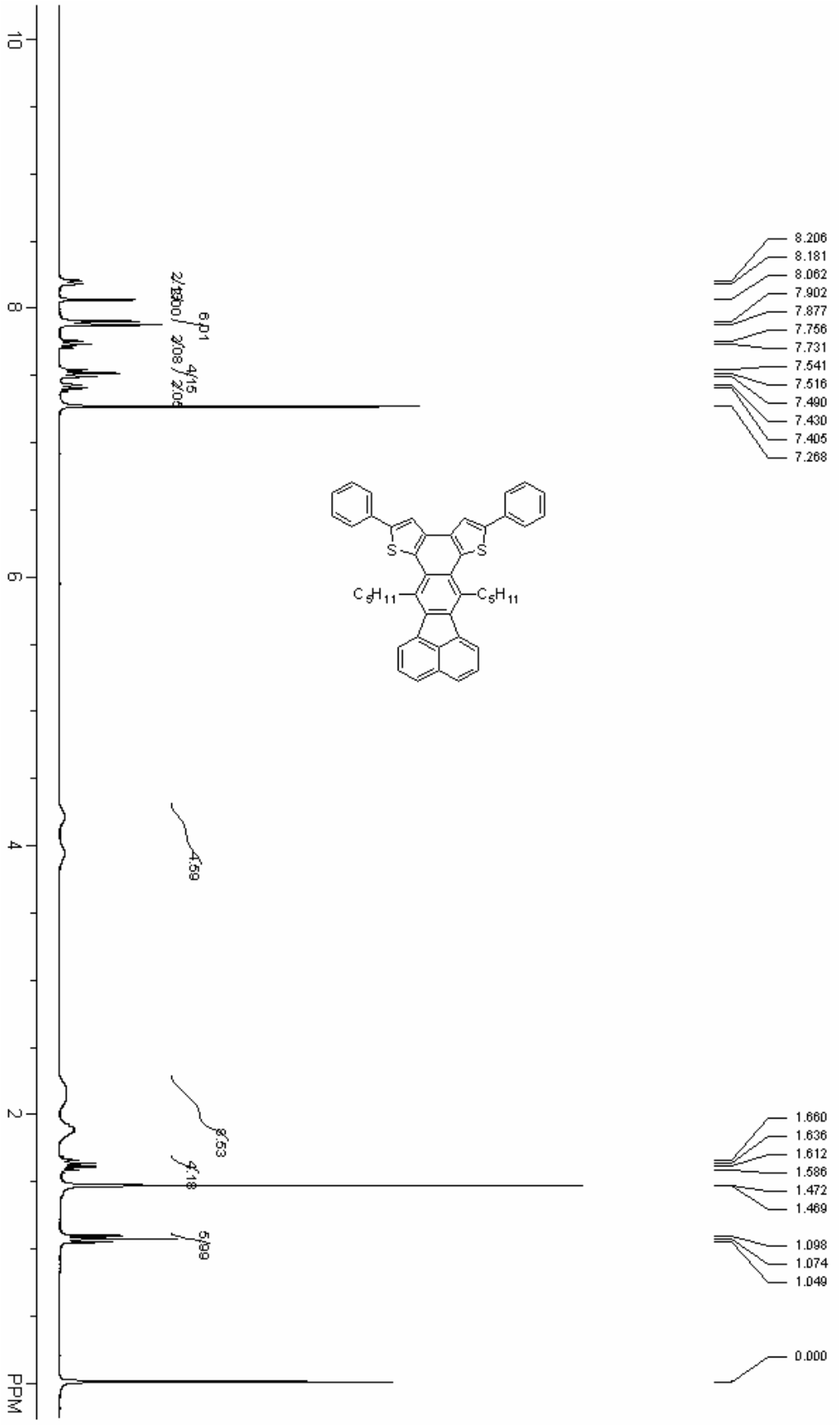
^{13}C NMR spectrum of compound **9**



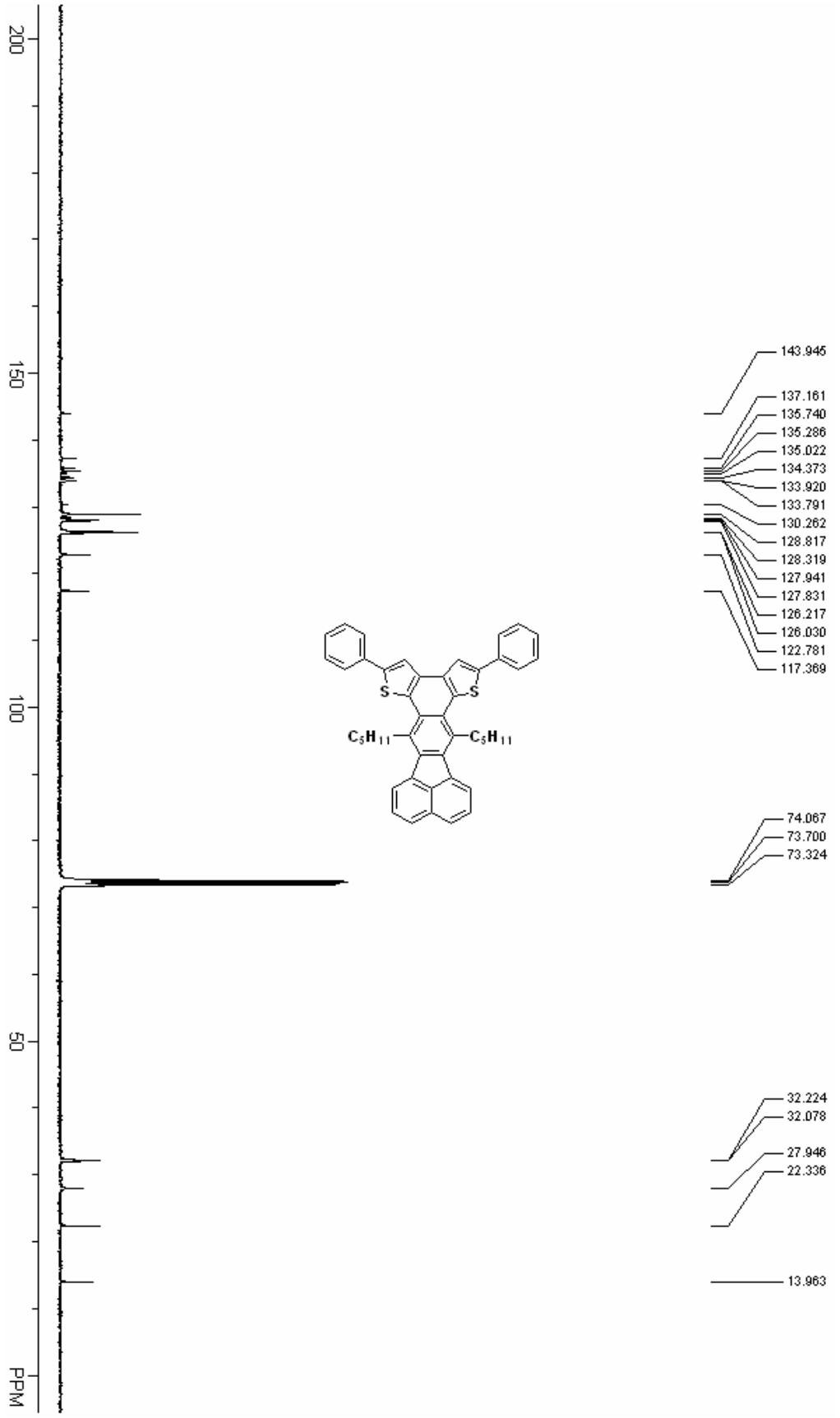
^{1}H NMR spectrum for compound **10**



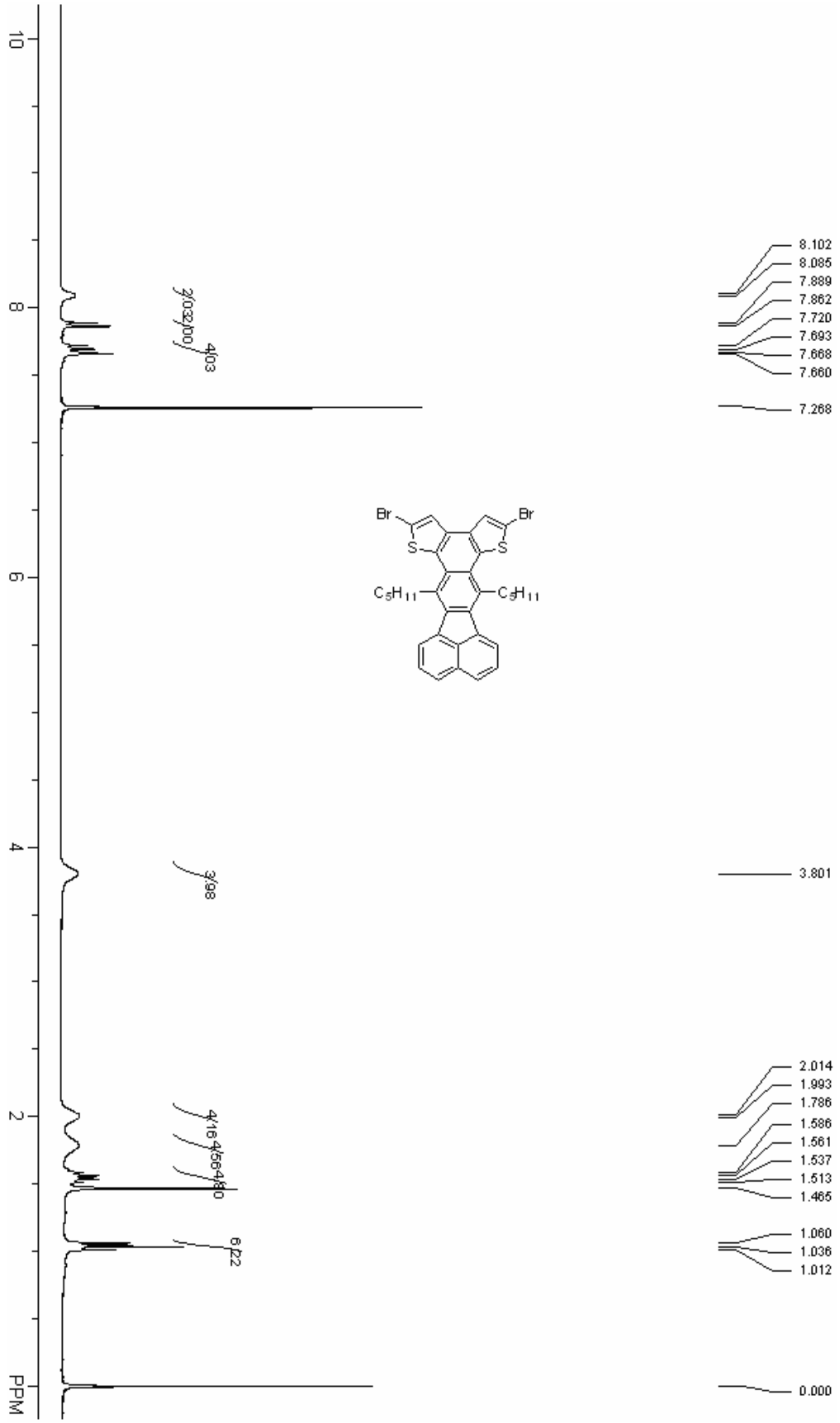
^{13}C NMR spectrum of compound **10**



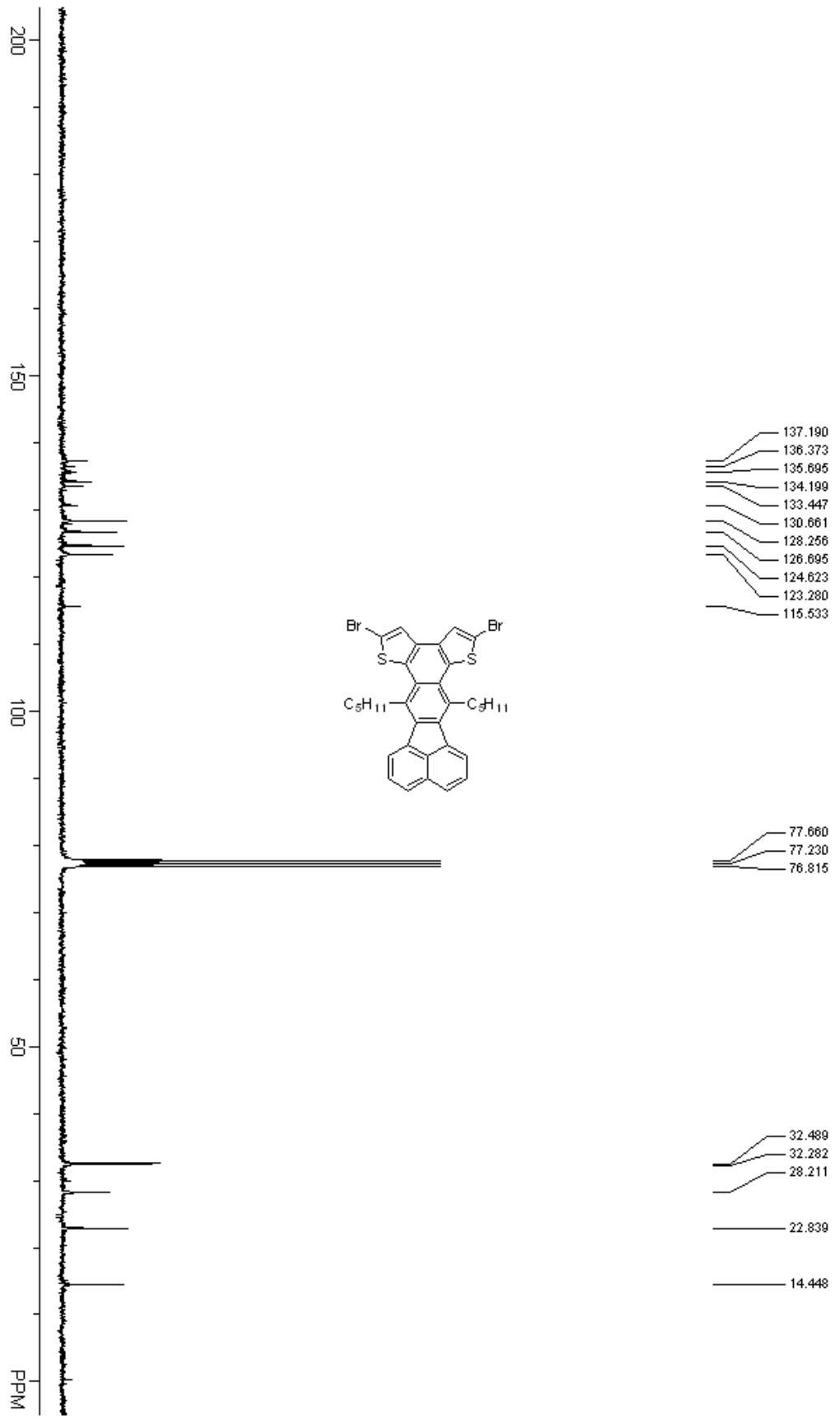
^{1}H NMR spectrum for compound **11**



^{13}C NMR spectrum for compound **11**



^{1}H NMR spectra for compound **12**



^{13}C NMR spectrum for compound **12**