Supplementary Materials

Synthesis of unsymmetrically substituted pyrene derivatives through (6-bromo-3,8-dibutylpyren-1-yl)trimethylsilane

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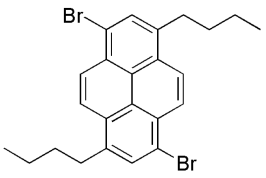
Contents

a) **General**: ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER-SPECTROSPIN-400 with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shift values, reported in parts per million (ppm), were indirectly referenced to external tetramethylsilane employing resonances due to trace monoprotio-solvent as an internal reference. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Elemental analyses were performed with Yanaco MT-5 CHN-Corder. Mass spectra were reported on a JEOL GC-mate II (for FAB). Column chromatography was carried out with silica gel, Silica Gel 60N (Kanto Chemical Co.). Thin-layer chromategraphy analyses were performed on Merck silica gel 60 F_{254}. Reactions were performed under an argon atmosphere unless otherwise noted. Materials were purchased from Kanto Chemicals, Co., Inc., and Wako Pure Chemicals, and Tokyo Chemical Industry Co., LTD., and Acros Organics. All the chemical materials were used without further purification.

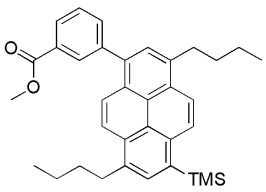
b) **Materials**: In the starting materials for the cross-coupling reactions, arylboronic acid compounds were purchased from Tokyo Chemical Industry Co., LTD. and used without further purification. The dehydrated toluene, DMF, and potassium carbonate were purchased from Wako Chemicals, Co., Inc., and used without further purification. Other bases were purchased and used without further purification. $Pd_2(dba)_3{\cdot}CHCl_3$ (dba; dibenzylideneacetone) (Strem Chemicals), $Pd(PPh_3)_4$ (Nacalai tesque, INC.), and PCy_3 (Strem Chemicals) were used as received.

c) **Preparation of 1,6-dibromo-3,8-dibutylpyrene**

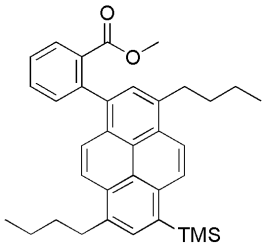


1,6-dibromo-3,8-dibutylpyrene: To the suspension of 1,6-dibromopyrene (24 g, 66 mmol) in anhydrous THF (320 mL) was cooled to -78 °C, and added *n*-BuLi (160 mmol, 1.62 M in hexane) dropwise over 15 min. The suspension was stirred for 15 min, and 1-bromobutane (17 mL, 160 mmol) was slowly added over 10 min. The reaction was allowed to warm to room temperature in 2.5 h, and quenched with methanol at 0 °C. The resultant precipitates were filtered off, and washed with water, and dissolved in chloroform. The organic phases were washed with brine, and dried over Na_2SO_4, and concentrated to give the crude. The crude product was purified by short-plug column chromatography (chloroform only), and the resultant yellow materials were provided to next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 9.2 Hz, 2H), 8.08 (d, J = 7.7 Hz, 2H), 8.05 (d, J = 9.2 Hz, 2H), 7.85 (d, J = 7.7 Hz, 2H), 3.34 (t, J = 7.7 Hz, 4H), 1.84 (tt, J = 7.7 Hz, 7.7 Hz, 4H), 1.51 (tq, J = 7.3 Hz, 7.7 Hz, 4H), 1.00 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 137.2, 129.7, 129.1, 125.7, 127.4 (two peaks are overlapped), 124.6, 122.7, 34.3, 33.7, 23.1, 14.3. EI-MS *m/z*: 314 (M^+). Anal. Calcd For $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.44; H, 8.30. To the 2 L flask charged with 1,6-dibutylpyrene (40 g, 128 mmol) was added CCl_4 (800 mL), and to the pale yellow cloudy was added bromine (14 mL, 269 mmol) dropwise over 1.5 min. After stirring at room temperature for 30 min, the reaction mixture of orange suspension was quenched with methanol. The precipitates were washed with methanol, and filtered to give crude product as pale yellow solid. The crude product was recrystallized from toluene to afford 39 g of 1,6-dibromo-3,8-dibutylpyrene in 65% yield as pale yellow solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 9.5 Hz, 2H), 8.23 (d, J = 9.5 Hz, 2H), 8.12 (s, 2H), 3.28 (t, J = 7.8 Hz, 4H), 1.82 (tt, J = 7.8 Hz, 7.8 Hz, 4H), 1.51 (tq, J = 7.8 Hz, 7.3 Hz, 4H), 1.00 (t, J = 7.3 Hz, 6H). EI-MS *m/z*: 472 (M^+). Anal. Calcd For $C_{24}H_{24}Br_2$: C, 61.04; H, 5.12. Found: C, 60.97; H, 5.06.

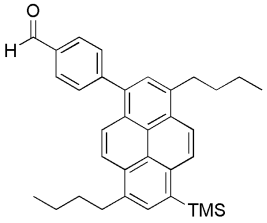
d) **Characterization data for compounds 3-13 in Table 1**



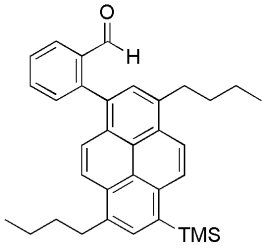
methyl 3-(3,8-dibutyl-6-(trimethylsilyl)pyren-1-yl)benzoate (Table 1, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 9.4 Hz, 1H), 8.32-8.29 (m, 2H), 8.17-8.15 (m, 2H), 8.06 (d, J = 9.4 Hz, 1H), 8.02 (s, 1H), 7.83-7.82 (m, 2H), 7.63 (t, J = 7.7 Hz, 7.7 Hz, 1H), 3.97 (s, 3H), 3.37 (t, J = 7.8 Hz, 7.8 Hz, 2H), 3.30 (t, J = 7.8 Hz, 7.8 Hz, 2H), 1.92-1.78 (m, 4H), 1.59-1.46 (m, 4H), 1.04-0.97 (m, 6H), 0.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 142.2, 137.1, 136.1, 135.9, 135.5, 135.4, 134.5, 134.1, 131.9, 130.6, 129.9, 129.0, 128.61, 128.57, 128.0, 127.2, 126.5, 126.0, 125.3, 123.4, 122.4, 52.4, 34.5, 34.4, 34.0, 33.8, 23.31, 23.26, 14.4, 1.0. MS (FAB) *m/z*: 520 (M^+). Anal. Calcd for $C_{35}H_{40}O_2Si$: C, 80.72; H, 7.74. Found: C, 80.47; H, 7.56.



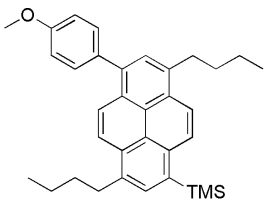
methyl 2-(3,8-dibutyl-6-(trimethylsilyl)pyren-1-yl)benzoate (Table 1, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 9.4 Hz, 1H), 8.30 (d, J = 9.4 Hz, 1H), 8.10-8.06 (m, 1H), 8.00 (s, 1H), 7.76 (d, J = 9.4 Hz, 1H), 7.70 (s, 1H), 7.65 (dt, J = 1.4 Hz, 7.5 Hz, 9.0 Hz, 1H), 7.56 (dt, J = 1.4 Hz, 7.5 Hz, 9.0 Hz, 1H), 7.50 (dd, J = 1.1 Hz, 7.6 Hz, 1H), 3.38-3.26 (m, 8H), 1.90-1.75 (m, 4H), 1.54-1.44 (m, 4H), 1.01-0.97 (m, 6H), 0.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 142.3, 136.7, 136.6, 135.9, 135.1, 134.6, 133.9, 132.7, 132.3, 131.6, 130.4, 129.9, 128.4, 128.2, 127.7, 127.5, 126.1, 126.0, 125.5, 123.0, 122.6, 52.1, 34.5, 34.4, 34.0, 33.7, 23.3, 23.2, 14.5, 14.4, 1.0. MS (FAB) m/z: 520 (M^+). Anal. Calcd for $C_{35}H_{40}O_2Si$: C, 80.72; H, 7.74. Found: C, 80.74; H, 7.48.



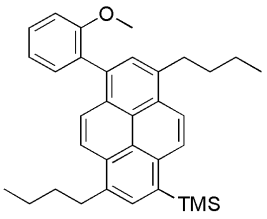
4-(3,8-dibutyl-6-(trimethylsilyl)pyren-1-yl)benzaldehyde (Table 1, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.2 (s, 1H), 8.40 (d, J = 9.5 Hz, 1H), 8.30 (d, J = 9.5 Hz, 1H), 8.18 (d, J = 9.5 Hz, 1H), 8.10-8.06 (m, 3H), 8.03 (s, 1H), 7.83-7.81 (m, 3H), 3.37 (t, J = 7.7 Hz, 2 H), 3.30 (t, J = 7.7 Hz, 2 H), 1.93-1.78 (m, 4H), 1.59-1.46 (m, 4H), 1.04-0.98 (m, 6H), 0.62 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 148.2, 137.1, 136.1, 135.7, 135.6, 135.3, 134.5, 134.2, 131.5, 129.84, 129.76, 128.8, 128.7, 128.3, 127.0, 126.5, 125.9, 125.0, 123.5, 122.4, 34.5, 34.3, 33.9, 33.8, 23.3, 23.2, 14.34, 14.33, 1.0. MS (FAB) m/z: 490 (M^+). Anal. Calcd for $C_{34}H_{38}OSi$: C, 83.21; H, 7.80. Found: C, 83.21; H, 7.76.



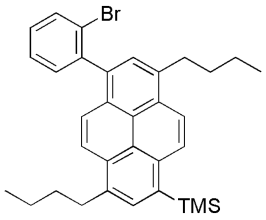
2-(3,8-dibutyl-6-(trimethylsilyl)pyren-1-yl)benzaldehyde (Table 1, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.43 (d, J = 9.4 Hz, 1H), 8.32 (d, J = 9.4 Hz, 1H), 8.19-8.13 (m, 2H), 8.04 (s, 1H), 7.79 (s, 1H), 7.78-7.73 (m, 2H), 7.65-7.58 (m, 2H), 3.37 (t, J = 7.7, 7.7 Hz, 2 H), 3.28 (t, J = 7.7, 7.7 Hz, 2 H), 1.92-1.75 (m, 4H), 1.57-1.44 (m, 4H), 1.03-0.96 (m, 6H), 0.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 145.5, 136.8, 136.4, 136.0, 135.4, 134.5, 134.3, 133.7, 132.5, 132.2, 129.7, 129.0, 128.7, 128.4, 128.3, 127.3, 126.2, 125.7, 125.2, 124.0, 122.4, 34.5, 34.3, 34.0, 33.7, 23.22, 14.35, 14.32, 1.0. MS (FAB) m/z: 490 (M^+). Anal. Calcd for $C_{34}H_{38}OSi$: C, 83.21; H, 7.80. Found: C, 83.24; H, 7.70.



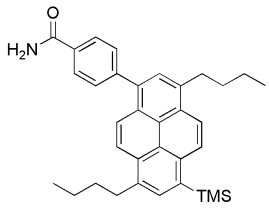
(3,8-dibutyl-6-(4-methoxyphenyl)pyren-1-yl)trimethylsilane (Table 1, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 9.5 Hz, 1H), 8.28 (d, J = 9.5 Hz, 1H), 8.17 (d, J = 9.5 Hz, 1H), 8.13 (d, J = 9.5 Hz, 1H), 8.00 (s, 1H), 7.81 (s, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 3.94 (s, 3H), 3.36 (t, J = 7.8, 7.8 Hz, 2 H), 3.29 (t, J = 7.8, 7.8 Hz, 2 H), 1.91-1.77 (m, 4H), 1.58-1.46 (m, 4H), 1.03-0.96 (m, 6H), 0.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 137.2, 137.0, 135.7, 135.0, 134.7, 134.2, 134.0, 132.0, 130.0, 129.3, 128.1, 127.7, 127.4, 126.6, 126.2, 126.0, 122.9, 122.5, 114.1, 55.5, 34.5, 34.4, 34.0, 33.8, 23.34, 23.29, 14.42, 14.41, 1.1. MS (FAB) m/z: 492 (M^+). Anal. Calcd for $C_{34}H_{40}OSi$: C, 82.87; H, 8.18. Found: C, 82.88; H, 8.20.



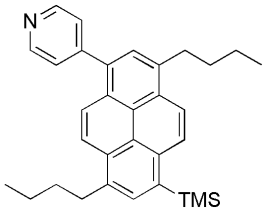
(3,8-dibutyl-6-(2-methoxyphenyl)pyren-1-yl)trimethylsilane (Table 1, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 9.4 Hz, 1H), 8.29 (d, J = 9.4 Hz, 1H), 8.09 (d, J = 9.4 Hz, 1H), 7.99 (m, 1H), 7.83 (d, J = 9.4 Hz, 1H), 7.80 (s, 1H), 7.50-7.39 (m, 2H), 7.16-7.10 (m, 2H), 3.71 (s, 3H), 3.40-3.24 (m, 4H), 1.92-1.76 (m, 4H), 1.58-1.45 (m, 4H), 1.03-0.97 (m, 6H), 0.60 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 136.8, 135.7, 134.9, 134.6, 134.1, 133.9, 132.8, 130.7, 130.1, 129.7, 129.3, 128.4, 128.1, 127.7, 126.5, 126.4, 126.1, 122.6, 120.9, 111.5, 55.8, 34.5, 34.3, 34.1, 33.8, 23.3, 23.30, 14.5, 14.4, 1.1. MS (FAB) *m*/*z*: 492 (M^+). Anal. Calcd for $C_{34}H_{40}OSi$: C, 82.87; H, 8.18. Found: C, 82.87; H, 8.20.



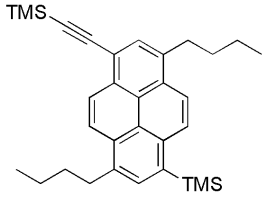
(6-(2-bromophenyl)-3,8-dibutylpyren-1-yl)trimethylsilane (Table 1, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 9.5 Hz, 1H), 8.31 (d, J = 9.5 Hz, 1H), 8.14 (d, J = 9.5 Hz, 1H), 8.01 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.70 (d, J = 9.5 Hz, 1H), 7.48-7.47 (m, 2H), 7.37-7.33 (m, 1H), 3.41-3.25 (m, 4H), 1.92-1.76 (m, 4H), 1.57-1.45 (m, 4H), 1.02-0.96 (m, 6H), 0.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 136.8, 136.14, 136.13, 136.12, 135.4, 134.5, 134.1, 133.1, 132.7, 129.9, 129.3, 128.9, 128.7, 128.1, 127.6, 127.4, 126.2, 125.9, 125.7, 125.1, 123.2, 122.5, 34.5, 34.3, 34.1, 33.8, 23.3, 23.2, 14.44, 14.39, 1.1. MS (FAB) *m*/*z*: 542 (M^+). Anal. Calcd for $C_{38}H_{37}BrSi$: C, 73.18; H, 6.89. Found: C, 73.22; H, 6.81.



4-(3,8-dibutyl-6-(trimethylsilyl)pyren-1-yl)benzamide (Table 1, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 9.5 Hz, 1H), 8.30 (d, J = 9.5 Hz, 1H), 8.16 (d, J = 9.5 Hz, 1H), 8.09 (d, J = 9.5 Hz, 1H), 8.03 (s, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.80 (s, 1H), 7.73 (d, J = 8.3 Hz, 2H), 3.37 (t, J = 7.3 Hz, 7.3 Hz, 2H), 3.37 (t, J = 7.8 Hz, 7.8 Hz, 2H), 3.30 (t, J = 7.8 Hz, 7.8 Hz, 2H), 1.92-1.77 (m, 4H), 1.60-1.46 (m, 4H), 1.03-0.97 (m, 6H), 0.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 145.7, 137.1, 136.0, 135.5, 134.5, 134.1, 132.4, 131.2, 129.79, 129.77, 128.9, 128.8, 128.6, 128.1, 127.8, 127.1, 126.4, 125.9, 125.2, 123.3, 122.4, 34.4, 34.2, 33.9, 33.7, 23.22, 23.19, 14.3, 1.0. MS (FAB) *m*/*z*: 505 (M^+). Anal. Calcd for $C_{34}H_{39}NOSi$: C, 80.74; H, 7.77; N, 2.77. Found: C, 80.71; H, 7.65; N, 2.94.

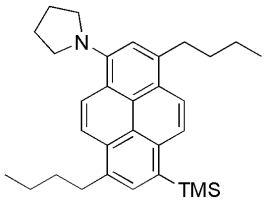


4-(3,8-dibutyl-6-(trimethylsilyl)pyren-1-yl)pyridine (Table 1, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 4.2 Hz, 2H), 8.41 (d, J = 9.4 Hz, 1H), 8.30 (d, J = 9.4 Hz, 1H), 8.20 (d, J = 9.5 Hz, 1H), 8.09 (d, J = 9.5 Hz, 1H), 8.04 (s, 1H), 7.79 (s, 1H), 7.59-7.58 (m, 2H), 3.37 (t, J = 7.7, 77 Hz, 2 H), 3.31 (t, J = 7.7, 7.7 Hz, 2 H), 1.92-1.78 (m, 4H), 1.59-1.47 (m, 4H), 1.04-0.98 (m, 6H), 0.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.6, 137.1, 136.2, 135.8, 134.4, 134.1, 133.9, 129.6, 128.9, 128.4, 128.2, 126.7, 126.3, 125.8, 124.6, 123.6, 122.2, 34.4, 34.1, 33.8, 33.6, 23.2, 23.1, 14.2, 0.9. MS (FAB) *m*/*z*: 463 (M^+). Anal. Calcd for $C_{32}H_{37}NSi$: C, 82.88; H, 8.04; N, 3.02. Found: C, 82.90; H, 8.00; N, 3.11.



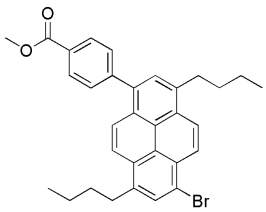
(3,8-dibutyl-6-((trimethylsilyl)ethynyl)pyren-1-yl)trimethylsilane (Table 1, entry 11): (6-bromo-3,8-dibutylpyren-1-yl)trimethylsilane **1** (116 mg, 0.25 mmol) was dried *in vacuo* in a Schelenk tube with heating, then CuI (4.8 mg, 0.025 mmol), $PdCl_2(PPh_3)_2$ (8.8 mg, 0.0125 mmol), and PPh_3 (6.6 mg 0.025 mmol) were added. The whole system was evacuated and backfilled with argon three times, then toluene and Et_3N (each 1.5 mL) were added. The reaction mixture was stirred at room temperature for 15 min, and followed by additional stirring at 70 ºC for 1 h. The solution was filtered through a pad of celite and florisil, and the crude product was purified with column chromatography (Hexane only) to yield **12** in 91% (110 mg) as yellow solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 9.4 Hz, 1H), 8.37 (d, J = 9.4 Hz, 1H), 8.31 (d, J = 9.4 Hz, 1H), 8.23 (d, J = 9.4 Hz, 1H), 8.02 (s, 1H), 8.00 (s, 1H), 3.35-3.27 (m, 4H), 1.87-1.80 (m, 4H), 1.52-1.48 (m, 4H), 1.03-0.99 (m, 6H), 0.59 (s, 9H), 0.39 (s, 9H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 136.8, 136.7, 135.9, 134.21, 134.15, 131.1, 131.0, 129.9, 129.3, 128.6, 126.0, 125.8, 125.3, 123.9, 122.3, 117.1, 104.9, 99.9, 34.6, 34.1, 33.5, 23.3, 23.2, 14.3, 1.0, 0.5. MS (FAB) *m/z*: 482 (M^+). Anal. Calcd for $C_{32}H_{42}Si_2$: C, 79.60; H, 8.77. Found: C, 79.66; H, 8.77.

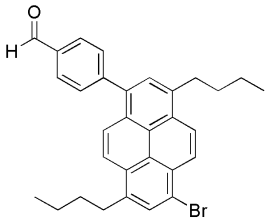


1-(3,8-dibutyl-6-(trimethylsilyl)pyren-1-yl)pyrrolidine (Table 1, entry 12): NaO^{t}Bu (72 mg, 0.75 mmol) was dried *in vacuo* in a Schelenk tube with heating, then $Pd_2(dba)_3 \cdot CHCl_3$ (13 mg, 0.0125 mmol), and BINAP (16 mg, 0.025 mmol) were added. The vessel was purged with argon. Toluene (2.0 mL) was added to the vessel, and stirred for 15 min. Then, (6-bromo-3,8-dibutylpyren-1-yl)trimethylsilane **1** (116 mg, 0.25 mmol) was added, and stirred for 15 min. Pyrrolidine (0.06 mL, 0.75 mmol) was added, and the vessel was sealed. The mixture was slowly heated to 90 °C over 1.5 h. After stirring for a further 15 h at 90 °C, the mixture was filtered through a pad of Celite and florisil. The crude product was purified with column chromatography (Hexane/CH_2Cl_2 = 9/1) to yield **13** in 70% (80 mg) as brown solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.4 Hz, 1H), 8.13-7.93 (m, 3H), 7.49 (brs, 1H), 7.26 (s, 1H), 3.58 (brs, 4H), 3.29 (t, J = 7.7 Hz, 7.7 Hz, 4H), 2.11 (brs, 4H), 1.88-1.79 (m, 4H), 1.56-1.49 (m, 4H), 1.03-0.99 (m, 6H), 0.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 137.8, 135.0, 134.4, 133.7, 133.4, 130.3, 127.8, 126.3, 125.1, 124.4, 123.5, 122.4, 121.2, 120.7, 116.1, 53.6, 34.4, 34.2, 34.1, 33.9, 25.4, 23.24, 23.23, 14.3, 0.8. MS (FAB) *m/z*: 455 (M^+). Anal. Calcd for $C_{31}H_{41}NSi$: C, 81.70; H, 9.07; N, 3.07. Found: C, 81.70; H, 9.07; N, 3.22.

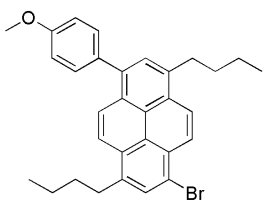
e) Characterization data for compounds 14, 15, and 16



methyl 4-(6-bromo-3,8-dibutylpyren-1-yl)benzoate 14: To the suspension of 4-(3,8-dibutyl-6-(trimethylsilyl)pyren-1-yl)benzoate **2** (1.0 g, 2 mmol) in anhydrous CCl_4 (4 mL) was cooled to 0 °C. The mixture was added 3 mL of bromine (1 M of CCl_4 stock solution) dropwise over 20 min, and stirred for 15 min. The reaction was allowed to warm to room temperature. After stirring for 1 h at ambient temperature, the reaction was quenched with water. The crude product was purified with column chromatography (Hexane/$CHCl_3$ = 1/3) to yield **14** in 91% (903 mg) as yellow solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 9.5 Hz, 1H), 8.30-8.23 (m, 3H), 8.11-8.04 (3H), 7.83 (s, 1H), 7.71 (d, J = 8.8 Hz, 2H), 4.02 (s, 1H), 3.22 (t. J = 7.5, 7.5 Hz, 2H), 3.19 (t. J = 7.5, 7.5 Hz, 2H), 1.89-1.74 (m, 4H), 1.56-1.43 (m, 4H), 1.01-0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 146.2, 138.1, 137.5, 136.6, 131.5, 130.9, 129.8, 129.4, 129.2, 128.8, 128.4, 128.3, 127.1, 127.0, 126.2, 125.4, 125.0, 124.2, 122.9, 120.1, 52.5, 34.3, 34.0, 33.7, 33.3, 31.8, 23.2, 23.0, 22.9, 14.4, 14.3, 14.2. MS (FAB) *m/z*: 526 (M^+). Anal. Calcd for $C_{32}H_{31}BrO_2$: C, 72.86; H, 5.92. Found: C, 72.86; H, 5.81.

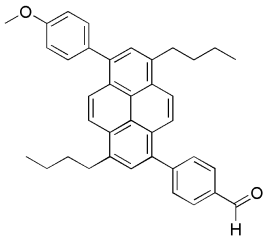


4-(6-bromo-3,8-dibutylpyren-1-yl)benzaldehyde 15: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.1 (s, 1H), 8.41 (d, J = 9.5 Hz, 1H), 8.26 (d, J = 9.5 Hz, 1H), 8.06-8.04 (m, 5H), 7.82 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 3.30 (t. J = 7.5, 7.5 Hz, 2H), 3.16 (t. J = 7.5, 7.5 Hz, 2H), 1.85-1.56 (m, 4H), 1.54-1.44 (m, 4H), 1.04-0.97 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 147.8, 138.2, 137.5, 136.2, 135.4, 131.48, 131.45, 129.9, 129.2, 128.9, 128.3, 128.2, 127.0, 126.9, 126.3, 125.4, 124.8, 124.1, 123.1, 120.2, 34.2, 33.9, 33.6, 33.2, 23.1, 23.0, 14.25, 14.19. MS (FAB) *m/z*: 496 (M^+). Anal. Calcd for $C_{31}H_{29}BrO$: C, 74.85; H, 5.88. Found: C, 74.81; H, 5.94.

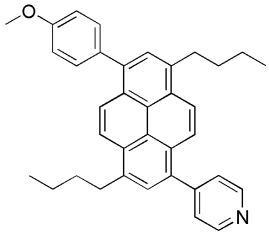


1-bromo-3,8-dibutyl-6-(4-methoxyphenyl)pyrene 16: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 9.5 Hz, 1H), 8.34 (d, J = 9.5 Hz, 1H), 8.19(d, J = 9.5 Hz, 1H), 82.1-8.08 (m, 2H), 7.85 (s, 1H), 7.55 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 3.94 (s, 3H), 3.36 (t. J = 7.8, 7.8 Hz, 2H), 3.26 (t. J = 7.8, 7.8 Hz, 2H), 1.88-1.79 (m, 4H), 1.53-1.46 (m, 4H), 1.02-0.96 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 137.8, 137.7, 137.4, 133.8, 131.9, 131.3, 129.8, 128.6, 128.4, 128.2, 127.30, 127.28, 125.7, 125.6, 124.3, 122.4, 119.7, 114.0, 55.6, 34.3, 34.0, 33.7, 33.3, 23.2, 23.1, 14.3, 14.2. MS (FAB) *m/z*: 498 (M^+). Anal. Calcd for $C_{31}H_{31}BrO$: C, 74.54; H, 6.26. Found: C, 74.58; H, 6.35.

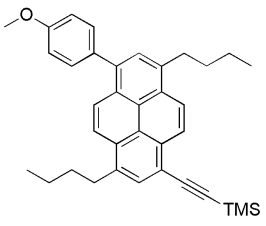
f) Characterization data for compounds 18-26 in Table 2



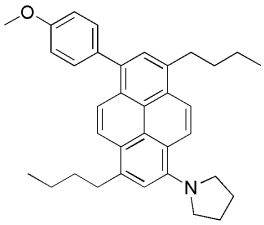
4-(3,8-dibutyl-6-(4-methoxyphenyl)pyren-1-yl)benzaldehyde (Table 2, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.25-8.18 (m, 3H), 8.11-8.07 (m, 3H), 7.84-7.82 (m, 4H), 7.58 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 3.95 (s, 3H), 3.56-3.31 (m, 4H), 1.88-1.81 (m, 4H), 1.54-1.46 (m, 4H), 1.01-0.96 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 159.2, 148.3, 138.0, 137.5, 137.0, 136.6, 135.5, 135.3, 133.9, 131.9, 131.5, 129.9, 129.6, 129.1, 128.9, 128.1, 127.5, 127.2, 126.4, 126.3, 125.9, 124.4, 123.4, 122.6, 114.1, 55.58, 55.57, 55.56, 34.3, 34.2, 33.7, 23.3, 23.2, 14.4, 14.3. MS (FAB) *m/z*: 524 (M^+). Anal. Calcd for $C_{38}H_{36}O_2$: C, 86.99; H, 6.92. Found: C, 86.97; H, 6.95.



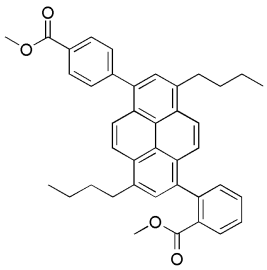
4-(3,8-dibutyl-6-(4-methoxyphenyl)pyren-1-yl)pyridine (Table 2, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 5.8 Hz, 2H), 8.25-8.17 (m, 3H), 8.10 (d, J = 9.5 Hz, 1H), 7.85 (s, 1H). 7.79 (s, 1H), 7.61 (d, J = 5.8 Hz, 2H), 7.57, (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 3.95 (s, 3H), 3.34 (t, J = 7.7, 7.7 Hz, 4H), 1.88-1.80 (m, 4H), 1.55-1.46 (m, 4H), 1.01-0.97 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 150.0, 149.8, 137.7, 137.2, 136.7, 134.0, 133.9, 131.9, 129.7, 129.3, 128.6, 128.1, 127.4, 127.1, 126.4, 126.3, 126.1, 125.9, 124.1, 123.6, 122.5, 114.1, 55.7, 34.3, 34.2, 33.71, 33.70, 23.2, 14.33, 14.32. MS (FAB) *m/z*: 497 (M^+). Anal. Calcd for $C_{36}H_{35}NO$: C, 86.88; H, 7.09; N, 2.81. Found: C, 86.93; H, 7.06; N, 2.85.



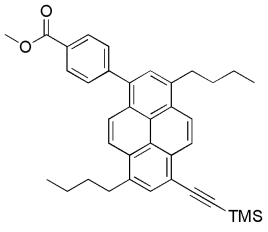
((3,8-dibutyl-6-(4-methoxyphenyl)pyren-1-yl)ethynyl)trimethylsilane (Table 2, entry 4): 1-bromo-3,8-dibutyl-6-(4-methoxyphenyl)pyrene **16** (125 mg, 0.25 mmol) was dried *in vacuo* in a Schelenk tube with heating, then CuI (4.8 mg, 0.025 mmol), $PdCl_2(PPh_3)_2$ (8.8 mg, 0.0125 mmol), and PPh_3 (6.6 mg 0.025 mmol) were added. The whole system was evacuated and backfilled with argon three times, then toluene and Et_3N (each 1.5 mL) were added. The reaction mixture was stirred at room temperature for 15 min, and followed by additional stirringat 70 ºC for 21 h. The solution was filtered through a pad of celite and florisil, and the crude product was purified with column chromatography (Hexane/$CHCl_3$ = 9/1) to yield **20** in 71% (92 mg) as pale yellow solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 9.3 Hz, 1H), 8.35 (d, J = 9.3 Hz, 1H), 8.19 (d, J = 9.5 Hz, 1H), 8.11 (d, J = 9.5 Hz, 1H), 8.01 (s, 1H), 7.83 (s, 1H), 7.56 (d, J = 6.6 Hz, 2H), 7.10 (d, J = 6.6 Hz, 2H), 3.94 (s, 3H), 3.36 (t, J = 7.7, 7.7 Hz, 2H), 3.25 (t, J = 7.7, 7.7 Hz, 2H), 1.90-1.76 (m, 4H), 1.52-1.43 (m, 4H), 1.02-0.95 (m, 6H), 0.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 137.7, 136.4, 133.9, 132.0, 131.4, 131.3, 129.69, 129.67, 128.4, 127.4, 126.4, 125.87, 125.86, 125.84, 125.4, 123.9, 122.6, 117.1, 114.1, 105.0, 99.9, 55.7, 34.5, 34.1, 33.9, 33.5, 23.3, 23.2, 14.41, 14.38, 0.6. MS (FAB) *m/z*: 516 (M^+). Anal. Calcd for $C_{36}H_{40}OSi$: C, 83.67; H, 7.80. Found: C, 83.65; H, 7.86.



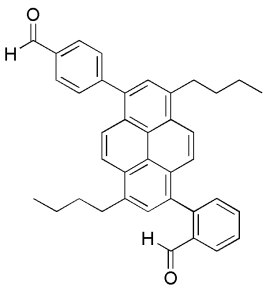
1-(3,8-dibutyl-6-(4-methoxyphenyl)pyren-1-yl)pyrrolidine (Table 2, entry 5): NaO^{t}Bu (72 mg, 0.75 mmol) was dried *in vacuo* in a Schelenk tube with heating, then $Pd_2(dba)_3 \cdot CHCl_3$ (13 mg, 0.0125 mmol), and BINAP (16 mg, 0.025 mmol) were added. The vessel was purged with argon. Toluene (2.0 mL) was added to the vessel, and stirred for 15 min. Then, 1-bromo-3,8-dibutyl-6-(4-methoxyphenyl)pyrene **16** (125 mg, 0.25 mmol) was added, and stirred for 15 min. Pyrrolidine (0.06 mL, 0.75 mmol) was added, and the vessel was sealed. The mixture was slowly heated to 90 °C over 1.5 h. After stirring for a further 25 h at 90 °C, the mixture was filtered through a pad of celite and florisil. The crude product was purified with column chromatography (Hexane/CH_2Cl_2 = 2/1) to yield **21** in 80% (98 mg) as brown solid materials. ^{1}H NMR (400 MHz, C_6D_6) δ 8.66 (d, J = 9.6 Hz, 1H), 8.29 (d, J = 9.4 Hz, 1H), 8.25 (d, J = 9.6 Hz, 1H), 8.11 (d, J = 9.4 Hz, 1H), 7.88 (s, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.54 (s, 1H), 7.00 (d, J = 8.7 Hz, 2H), 3.42-3.19 (m, 11H), 1.82-1.72 (m, 8H), 1.46-1.39 (m, 4H), 0.94-0.90 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 144.6, 137.4, 136.0, 135.5, 134.5, 131.9, 129.3, 128.7, 127.9, 127.8, 126.8, 124.2, 124.1, 123.7, 122.8, 121.7, 120.9, 116.5, 114.0, 55.6, 53.9, 34.3, 34.2, 34.1, 25.4, 23.3, 23.2, 14.3. MS (FAB) *m*/*z*: 489 (M^+). Anal. Calcd for $C_{35}H_{39}NO$: C, 85.84; H, 80.3; N, 2.86. Found: C, 85.82; H, 7.89; N, 2.99.



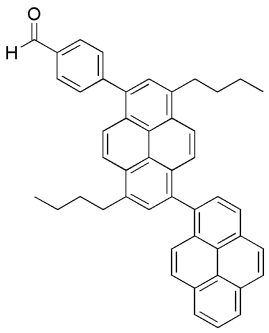
dimethyl 2,4'-(3,8-dibutylpyrene-1,6-diyl)dibenzoate (Table 2, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.20 (m, 3H), 8.15-8.08 (m, 3H), 7.81-7.79 (m, 2H), 7.74-7.72 (m, 3H), 7.68-7.65 (m, 1H), 7.59-7.51 (m, 2H), 4.01 (s, 3H), 3.31 (s, 7H), 1.87-1.79 (m, 4H), 1.53-1.42 (m, 4H), 0.99-0.95 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 167.4, 146.7, 142.2, 137.1, 136.9, 136.6, 136.1, 132.7, 132.2, 131.7, 131.0, 130.4, 129.9, 129.1, 129.0, 128.9, 128.7, 128.4, 127.8, 127.7, 127.3, 126.4, 126.0, 125.4, 124.7, 123.4, 122.8, 52.5, 52.1, 34.31, 34.30, 33.8, 33.7, 23.2, 23.1, 14.4, 14.3. MS (FAB) *m*/*z*: 582 (M^+). Anal. Calcd for $C_{40}H_{38}O_4$: C, 82.44; H, 6.57. Found: C, 82.45; H, 6.59.



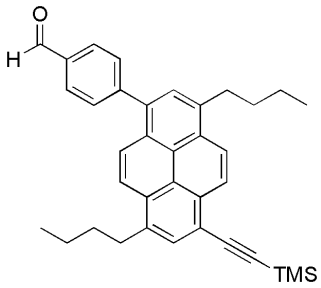
methyl 4-(3,8-dibutyl-6-((trimethylsilyl)ethynyl)pyren-1-yl) benzoate (Table 2, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 9.4 Hz, 1H), 8.36 (d, J = 9.4 Hz, 1H), 8.23 (d, J = 8.2 Hz, 2H), 8.15-8.09 (m, 2H), 8.03 (s, 1H), 7.83 (s, 1H), 7.71 (d, J = 8.2 Hz, 2H), 4.01 (s, 3H), 3.37 (t, J = 7.7 Hz, 7.7 Hz, 2H), 3.25 (t, J = 7.7 Hz, 7.7 Hz, 2H), 189-1.77 (m, 4H), 1.57-1.45 (m, 4H), 1.03-0.96 (m, 6H), 0.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 146.4, 137.8, 136.8, 136.6, 131.5, 131.3, 131.0, 129.9, 129.5, 129.3, 129.2, 129.0, 127.1, 125.9, 125.75, 125.74, 123.8, 123.2, 117.5, 104.7, 100.2, 52.5, 34.5, 34.1, 33.9, 33.5, 23.3, 23.2, 14.4, 14.3, 0.5. MS (FAB) *m*/*z*: 544 (M^+). Anal. Calcd for $C_{37}H_{40}O_2Si$: C, 81.57; H, 7.40. Found: C, 81.58; H, 7.48.



2,4'-(3,8-dibutylpyrene-1,6-diyl)dibenzaldehyde (Table 2, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 9.66 (s, 1H), 8.25 (d, J = 9.6 Hz, 1H), 8.21-8.15 (m, 3H), 8.10 (d, J = 8.2 Hz, 2H), 7.86-7.76 (m, 6H), 7.67-7.59 (m, 2H), 3.37-3.31 (m, 4H), 1.89-1.79 (m, 4H), 1.52-1.44 (m, 4H), 1.0-0.96 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 192.2, 148.0, 145.2, 137.5, 136.9, 136.3, 135.4, 135.3, 133.9, 132.7, 132.5, 131.6, 130.1, 130.0, 129.3, 129.1, 128.9, 128.8, 128.5, 127.5, 127.2, 126.1, 125.9, 125.3, 125.2, 123.7, 123.4, 34.3, 34.2, 33.7, 33.6, 23.2, 23.1, 14.29, 14.27. MS (FAB) *m*/*z*: 522 (M^+). Anal. Calcd for $C_{38}H_{34}O_2$: C, 87.32; H, 6.56. Found: C, 87.35; H, 6.68.

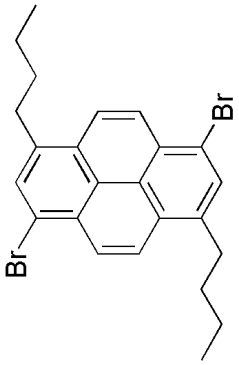


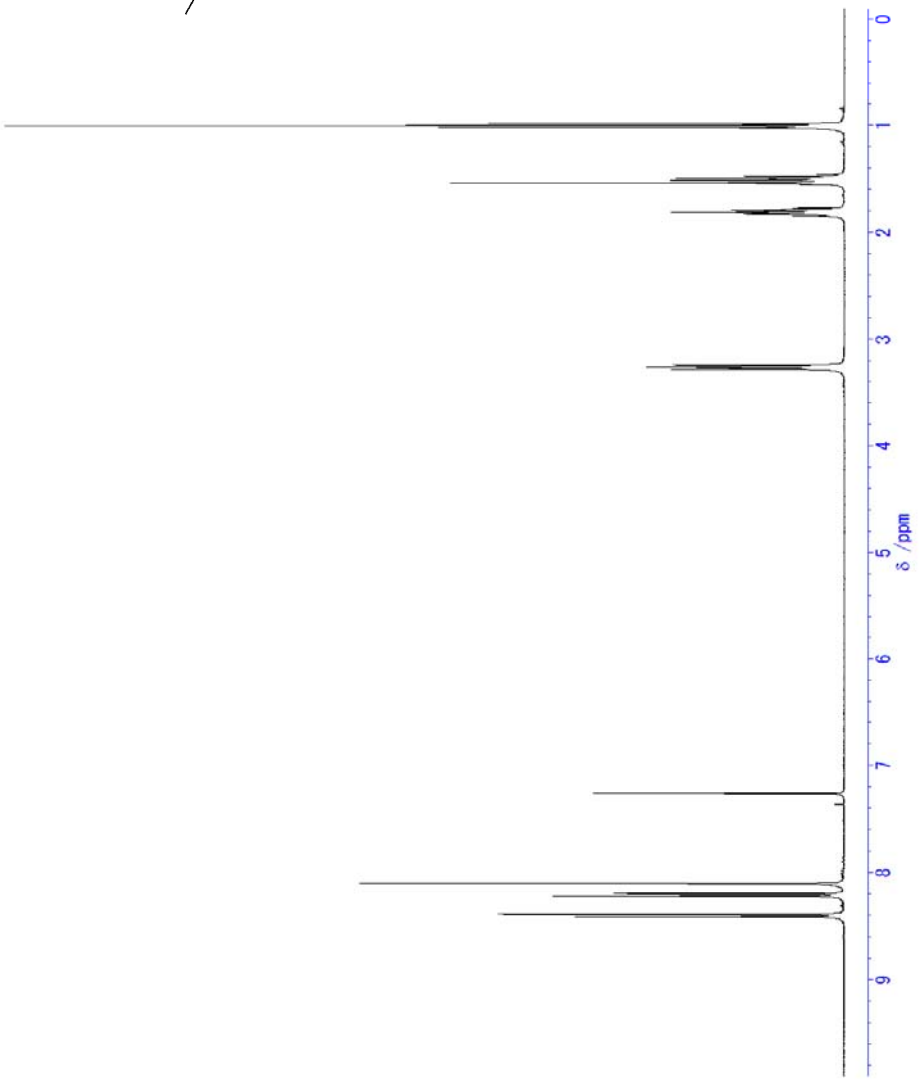
4-(3,8-dibutyl-1,11-bipyren-6-yl)benzaldehyde (Table 2, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.2 (s, 1H), 8.37-8.32 (m, 2H), 8.27-8.02 (m, 11H), 7.91-7.85 (m, 4H), 7.70 (d, J = 9.5, 9.5 Hz, 1H), 7.68 (d, J = 9.5, 9.5 Hz, 1H). 3.41 (t, J = 7.6, 7.9 Hz, 2H), 3.28 (t, J = 7.6, 7.9 Hz, 2H), 1.95-1.76 (m, 4H), 1.54-1.40 (m, 4H), 0.99 (t, J = 7.4, 7.4 Hz, 2H), 0.93 (t, J = 7.4, 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 148.3, 137.1, 136.9, 136.7, 136.4, 135.9, 135.4, 131.7, 131.6, 131.2, 131.1, 130.8, 130.3, 130.0, 129.14, 129.11, 129.05, 128.89, 128.7, 127.8, 127.7, 127.3, 126.4, 126.3, 126.2, 126.1, 125.5, 125.3, 125.08, 125.06, 124.83, 124.77, 123.6, 122.9, 34.3, 34.2, 33.7, 33.6, 23.2, 23.1, 14.4, 14.3. MS (FAB) m/z: 618 (M^+). Anal. Calcd for $C_{47}H_{38}O$: C, 91.22; H, 6.19. Found: C, 91.23; H, 6.20.



4-(3,8-dibutyl-6-((trimethylsilyl)ethynyl)pyren-1-yl)benzaldehyde (Table 2, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.63 (d, J = 9.4 Hz, 1H), 8.37 (d, J = 9.4 Hz, 1H), 8.17-8.03 (m, 5H), 7.84-7.80 (m, 3H), 3.38 (t, J = 7.7, 7.7 Hz, 2H), 3.32 (t, J = 7.7, 7.7 Hz, 2H), 1.89-1.78 (m, 4H), 1.53-1.45 (m, 4H), 1.03-0.97 (m, 6H), 0.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 148.1, 137.8, 136.9, 136.2, 135.5, 131.6, 131.5, 131.2, 130.0, 129.4, 129.20, 129.17, 127.0, 126.1, 125.74, 125.69, 125.5, 123.7, 123.3, 117.7, 104.7, 100.35, 34.4, 34.1, 33.9, 33.5, 23.3, 23.2, 14.4, 14.3, 0.6. MS (FAB) m/z: 514 (M^+). Anal. Calcd for $C_{36}H_{38}OSi$: C, 84.00; H, 7.44. Found: C, 84.02; H, 7.38.

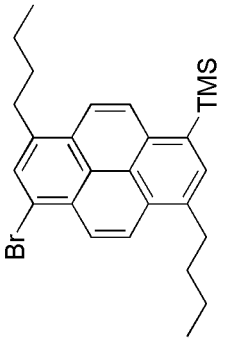
g) ^{1}H NMR Spectra for 1,6-dibromo-3,8-dibutylpyrene

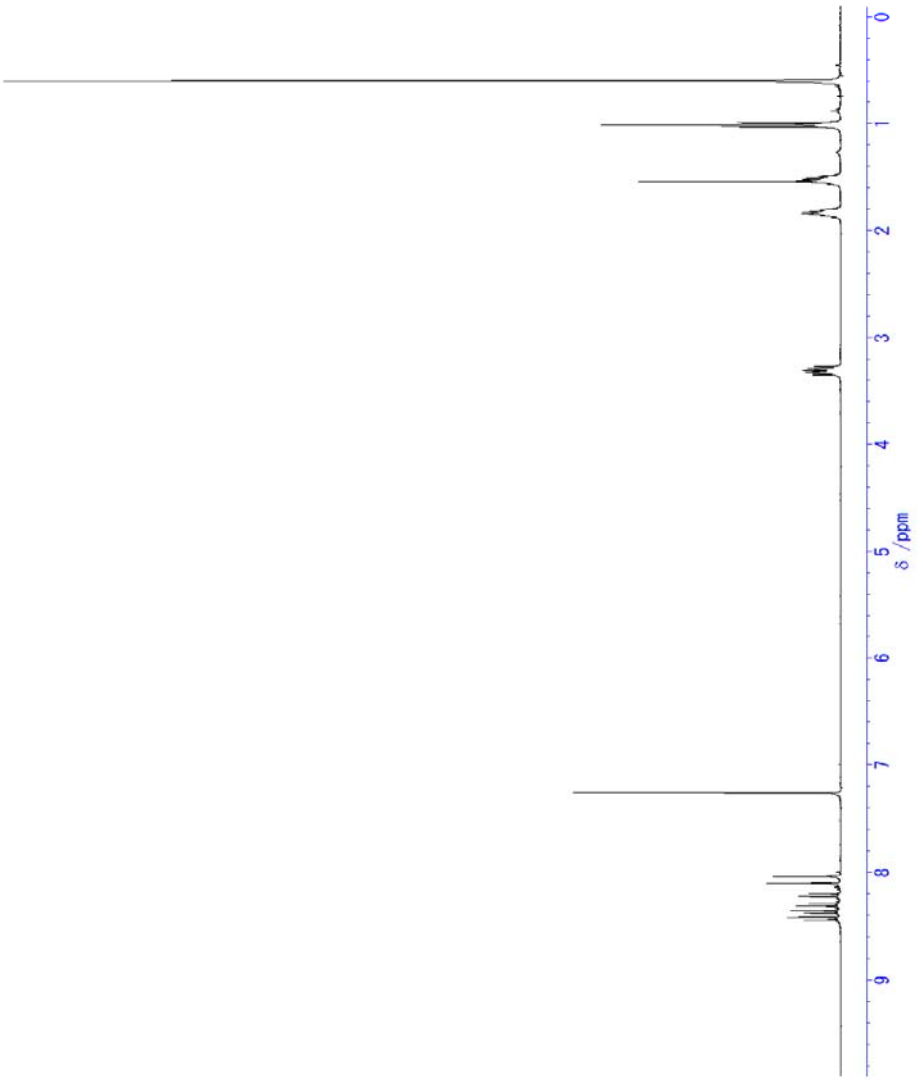




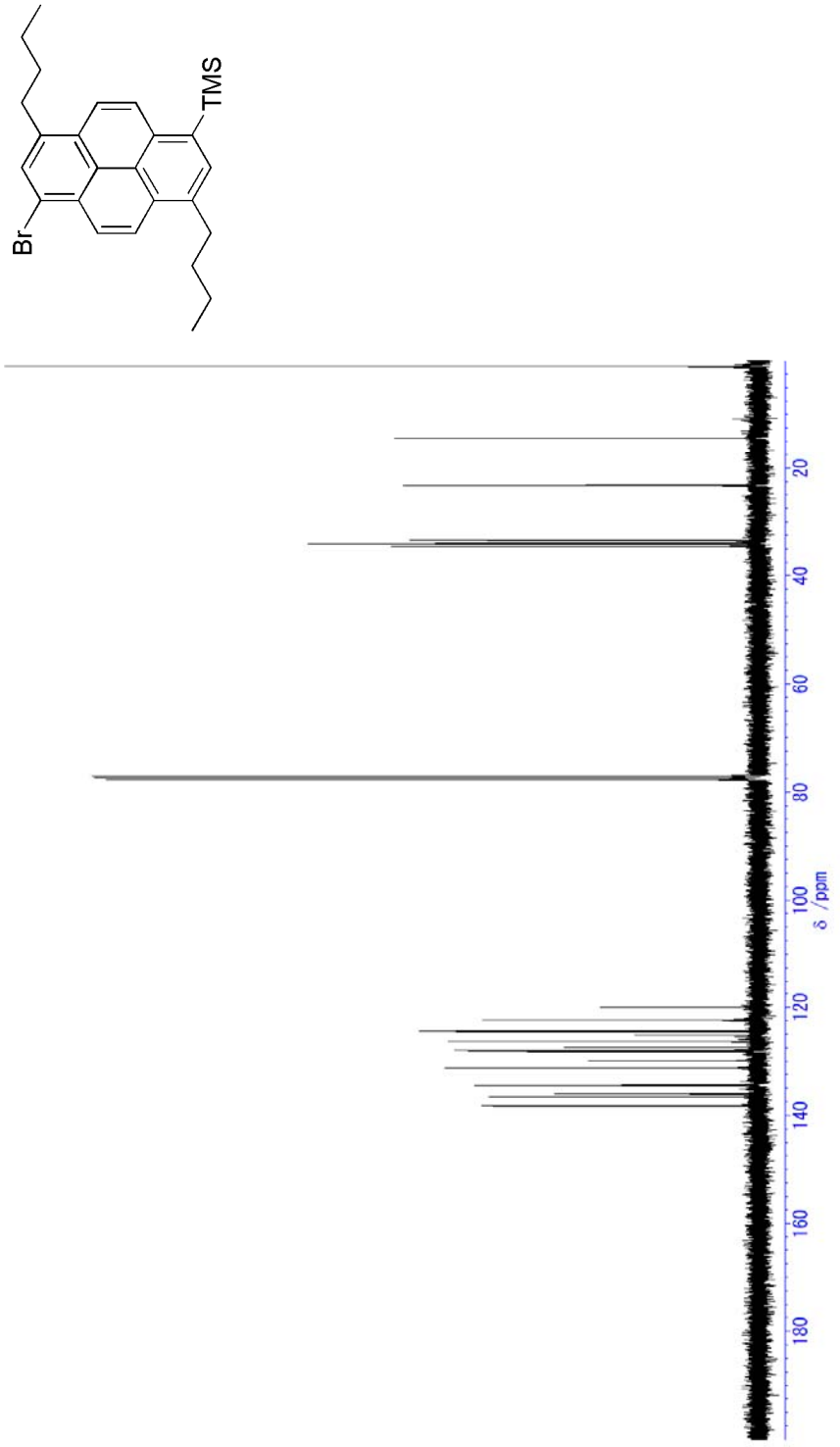
h) ^{1}H and ^{13}C NMR Spectra for (6-bromo-3,8-dibutylpyren-1-yl) trimethylsilane 1

^{1}H NMR spectrum: (6-bromo-3,8-dibutylpyren-1-yl) trimethylsilane **1**





^{13}C NMR spectrum: (6-bromo-3,8-dibutylpyren-1-yl) trimethylsilane **1**



i) ^{1}H and ^{13}C NMR Spectra for Compounds 2-13 Table 1

Table 1, entry 1: ^{1}H NMR spectrum

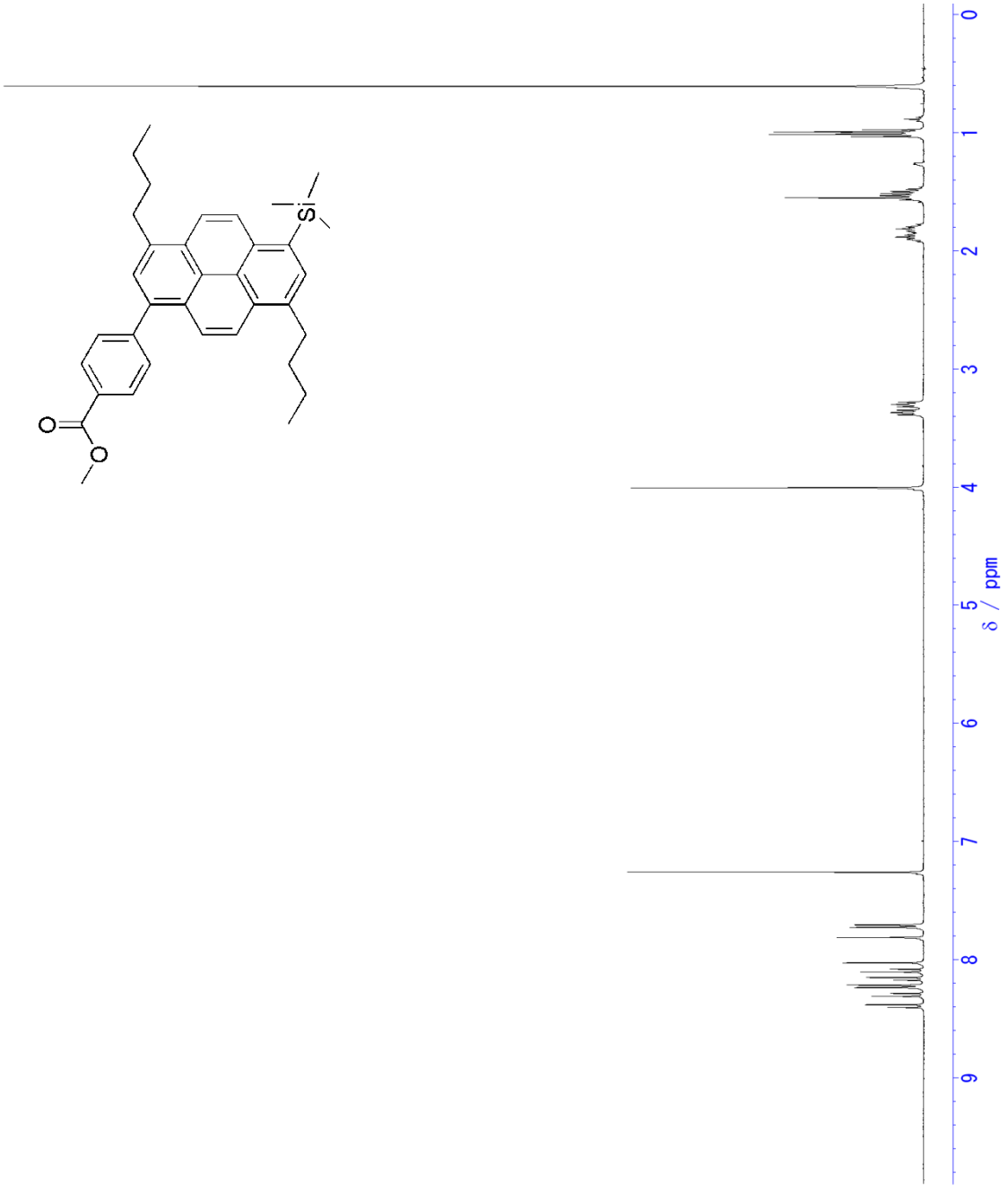


Table 1, entry 1: ^{13}C NMR spectrum

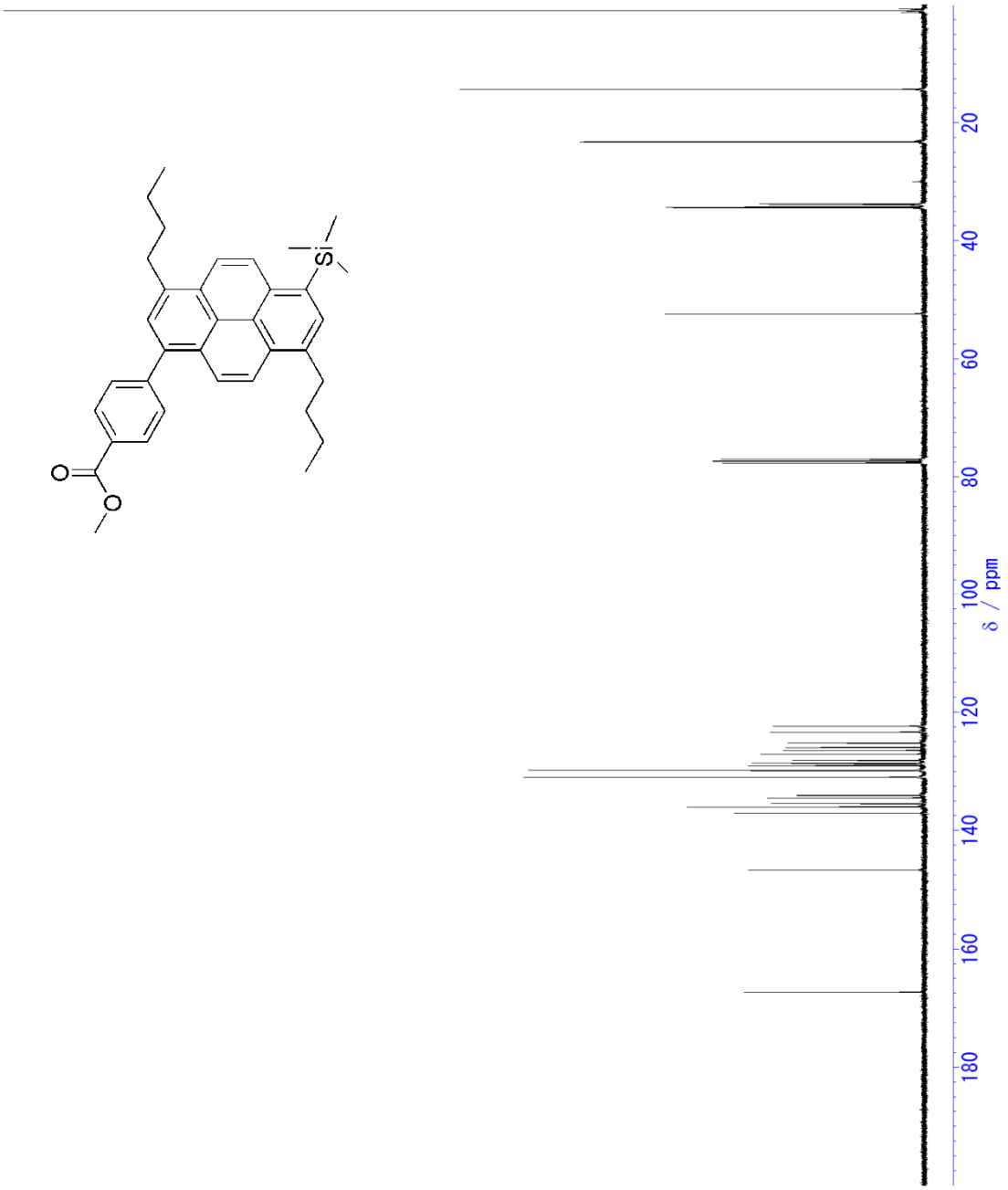


Table 1, entry 2: ^{1}H NMR spectrum

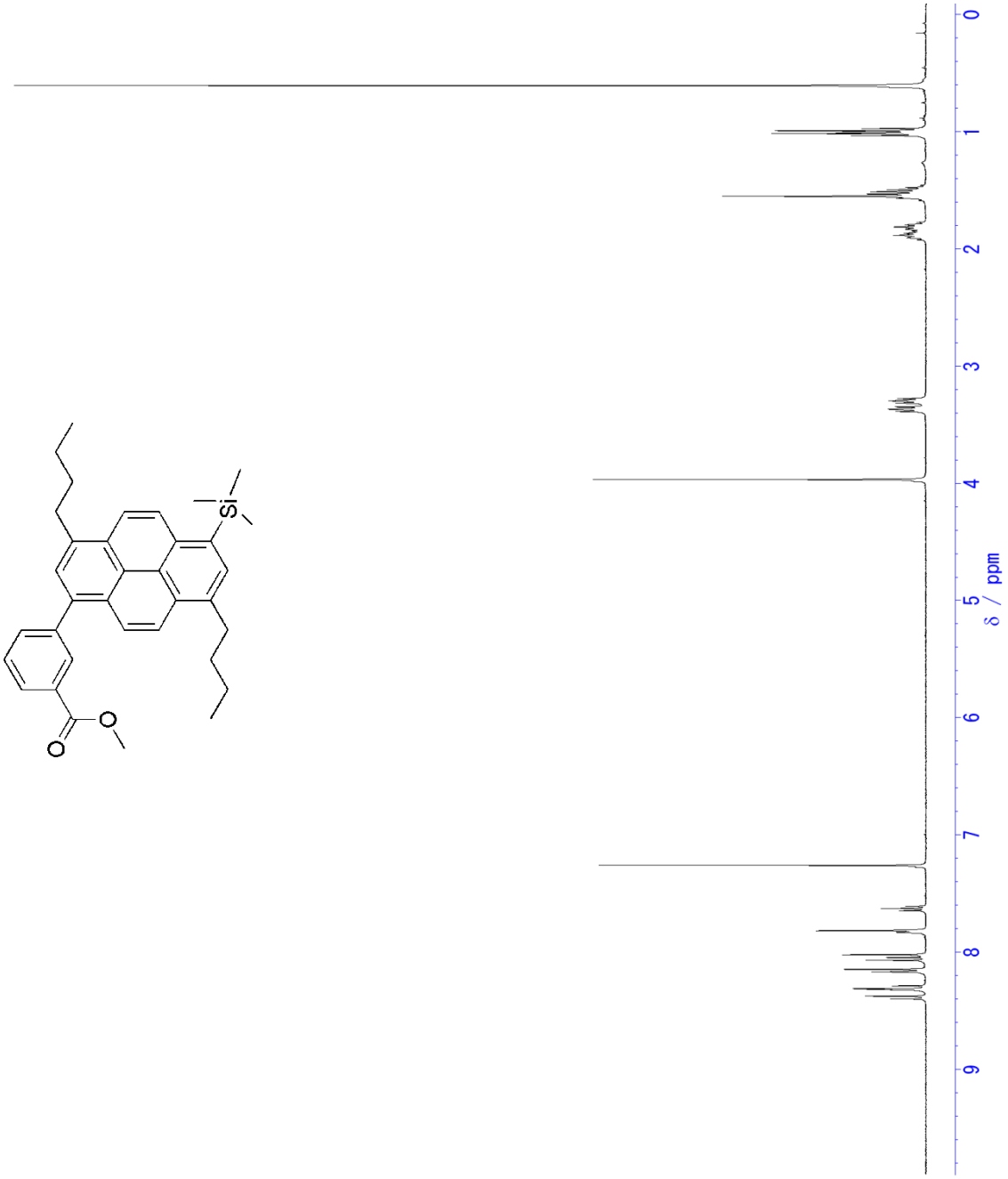


Table 1, entry 2: ^{13}C NMR spectrum

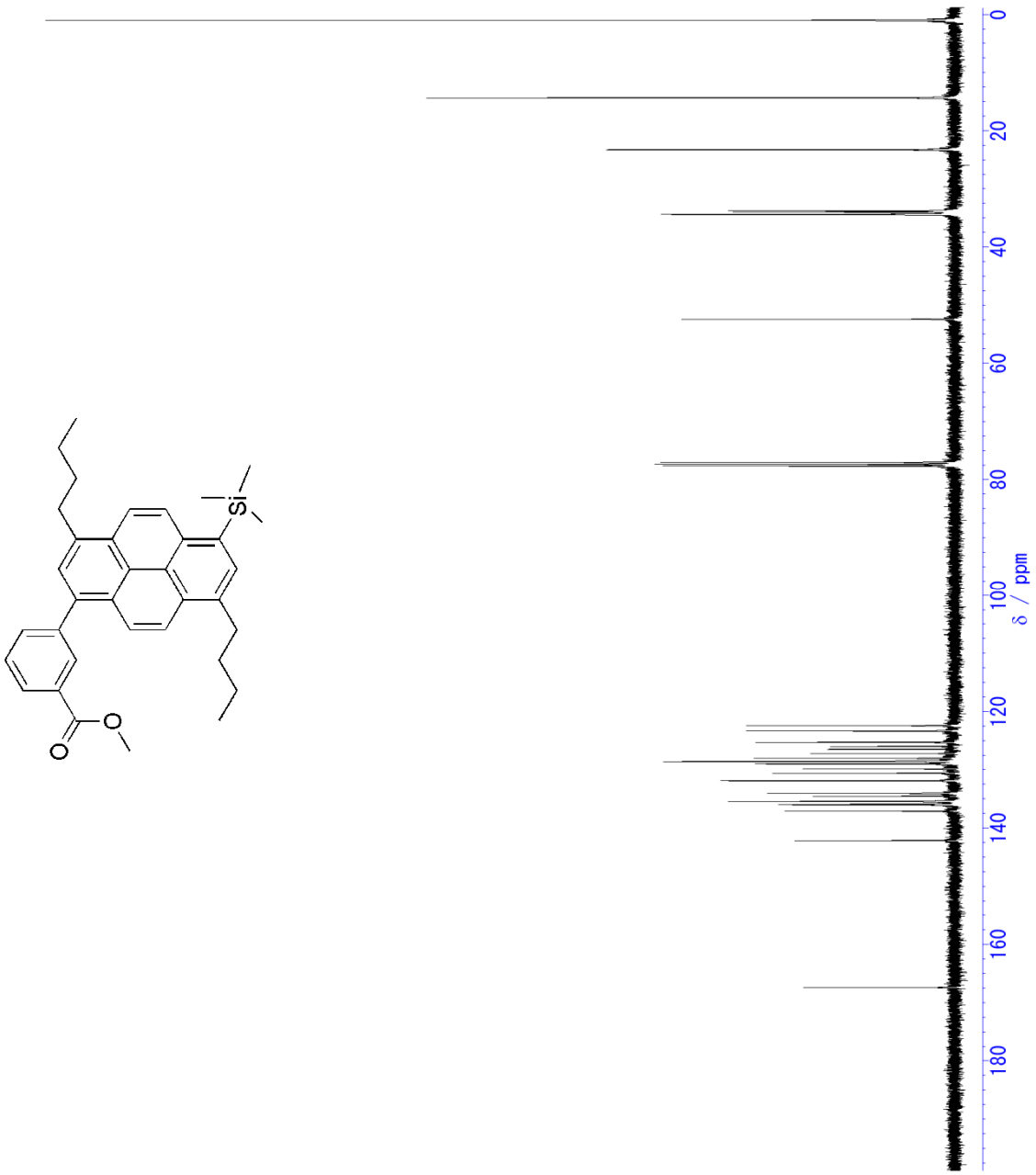


Table 1, entry 3: ^{1}H NMR spectrum

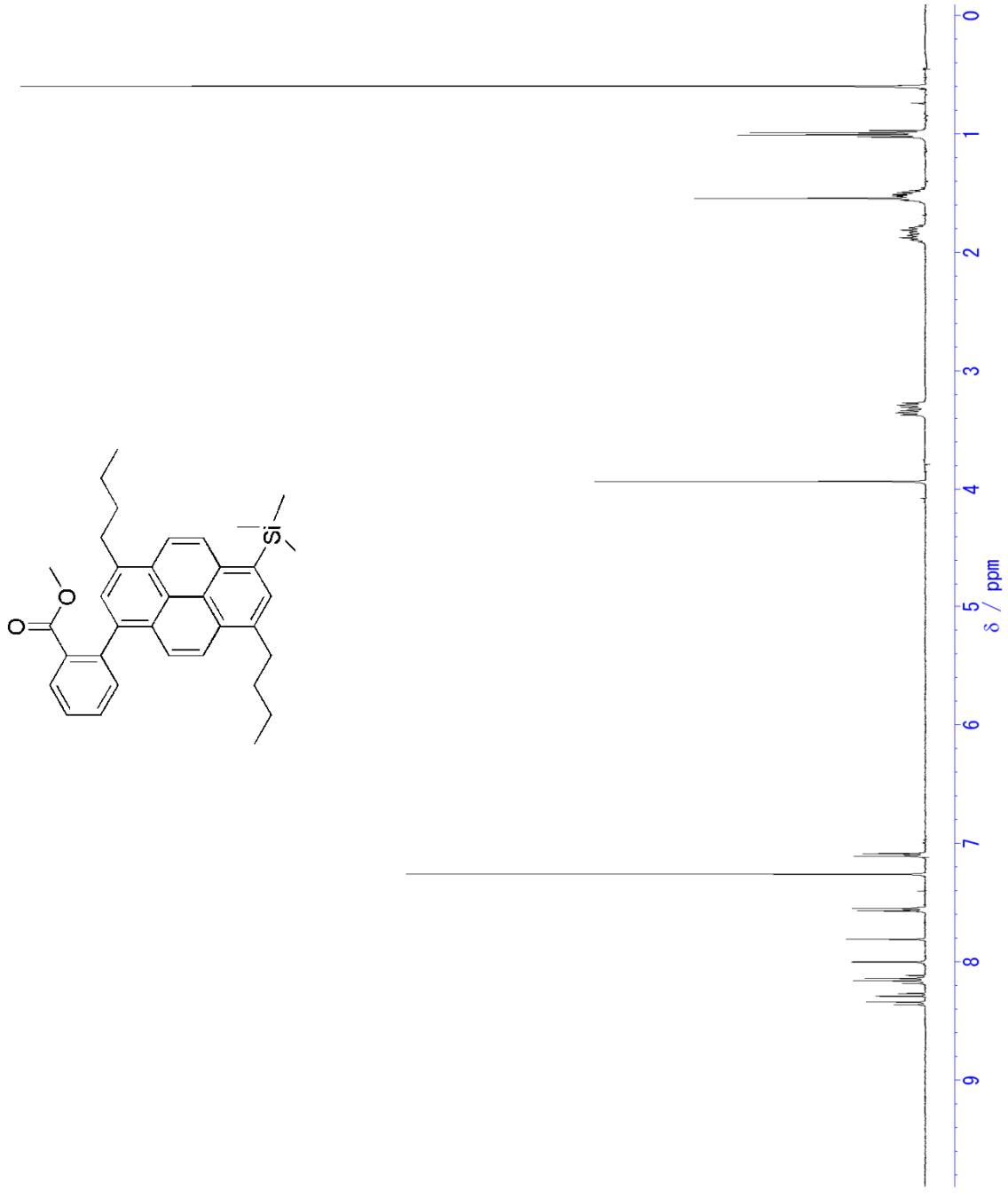


Table 1, entry 3: ^{13}C NMR spectrum

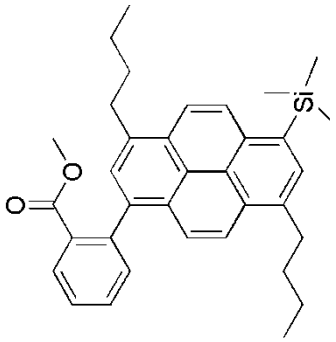


Table 1, entry 4: ^{1}H NMR spectrum

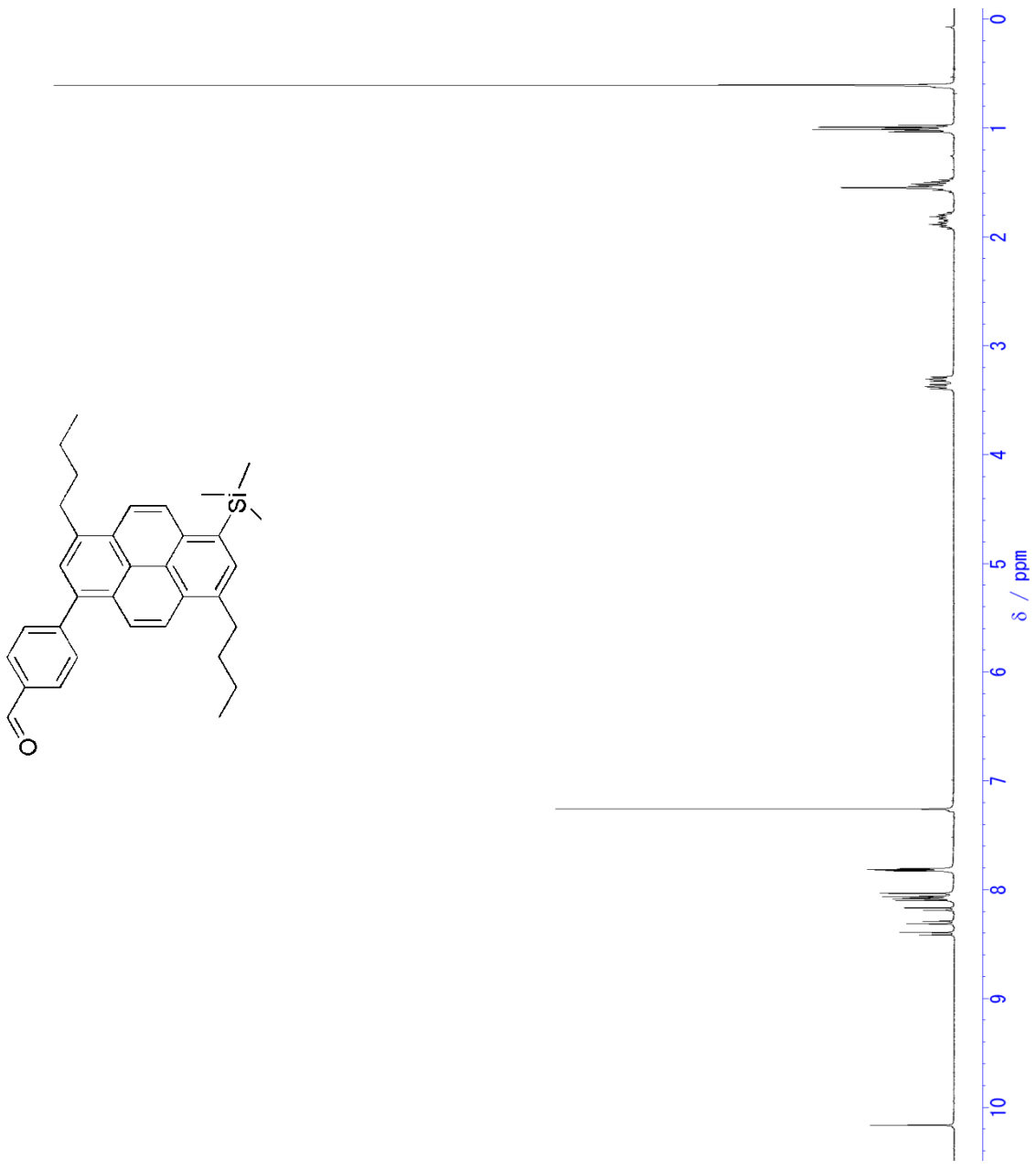


Table 1, entry 4: ^{13}C NMR spectrum

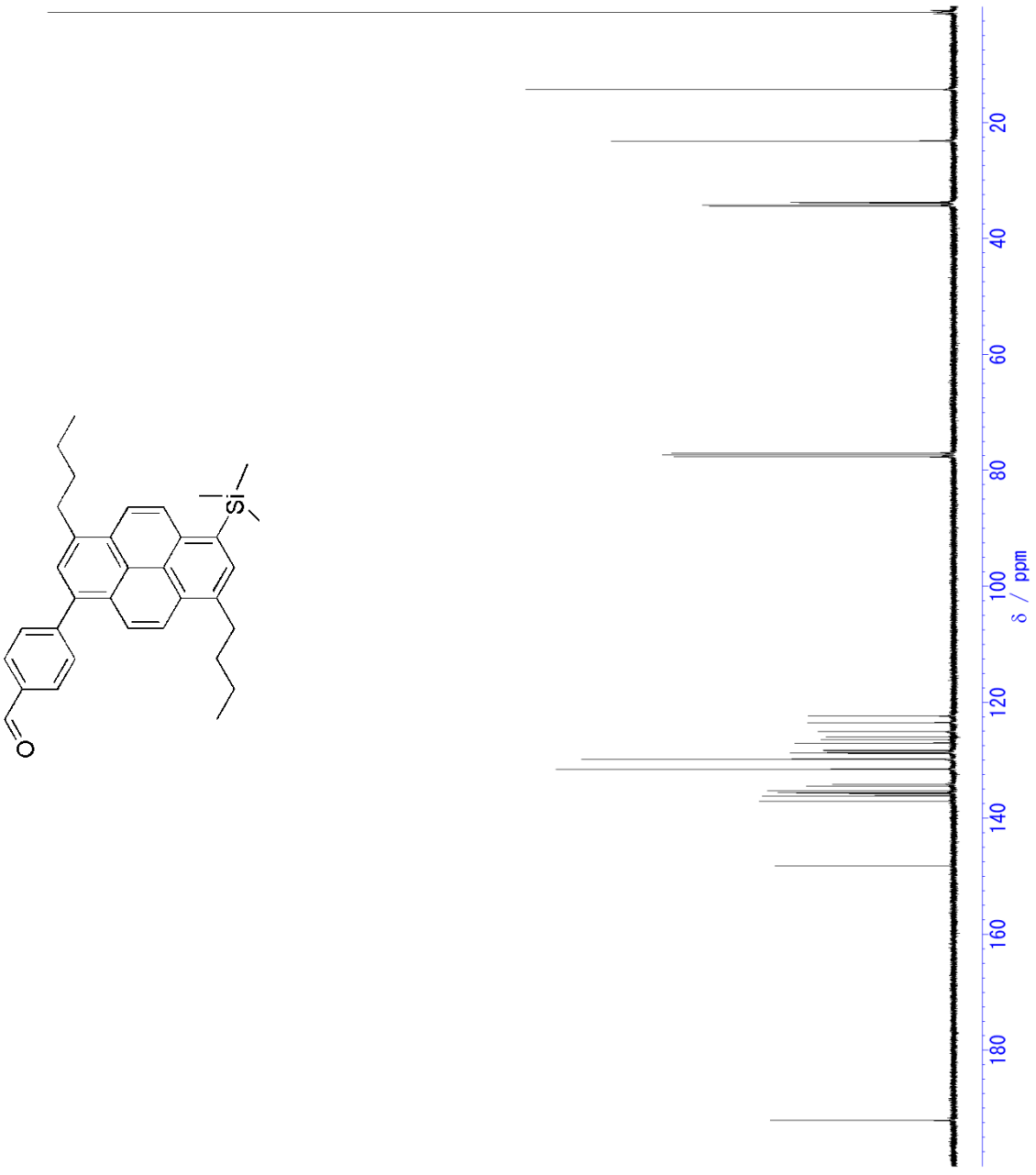


Table 1, entry 5: ^{1}H NMR spectrum

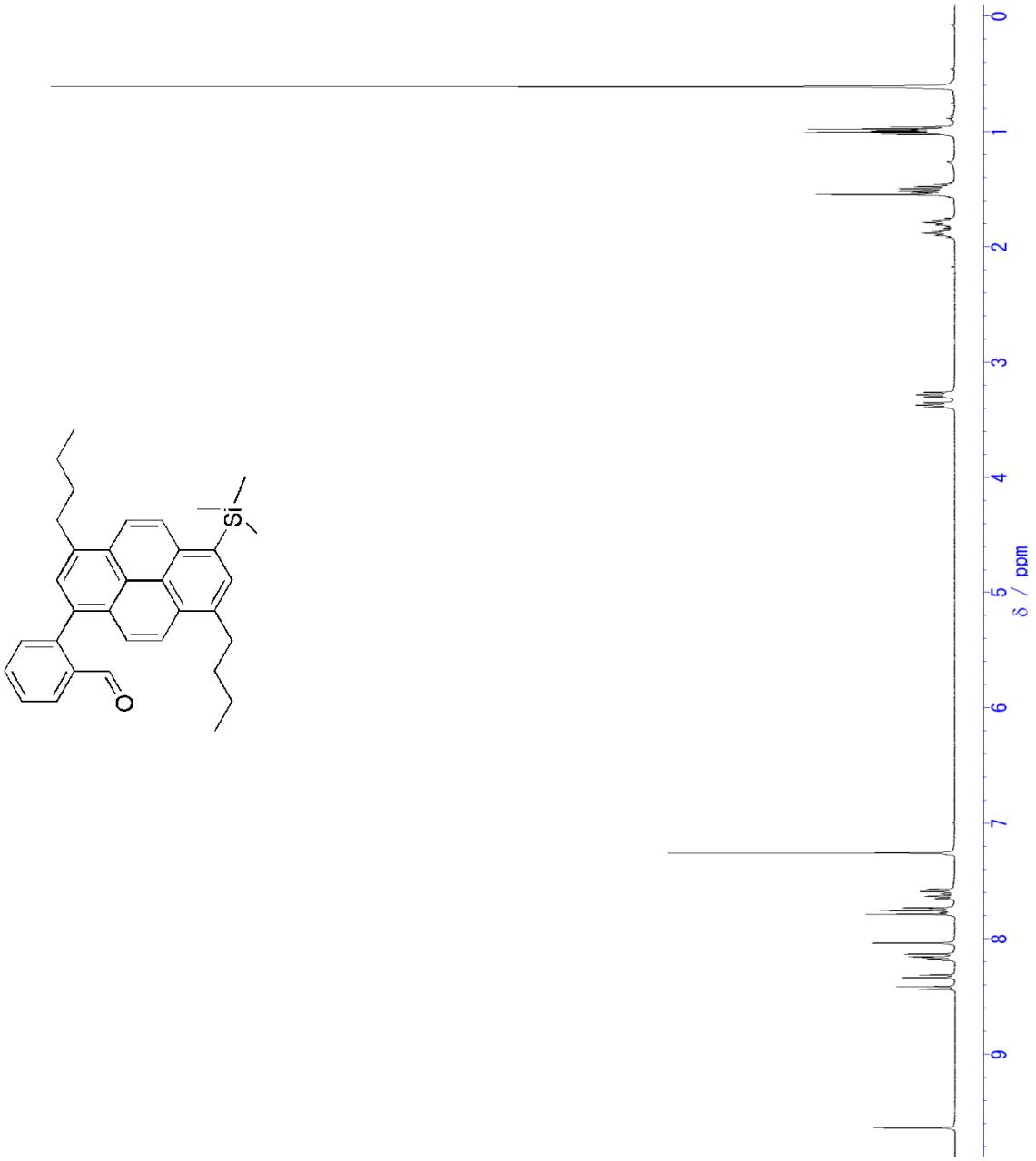


Table 1, entry 5: ^{13}C NMR spectrum

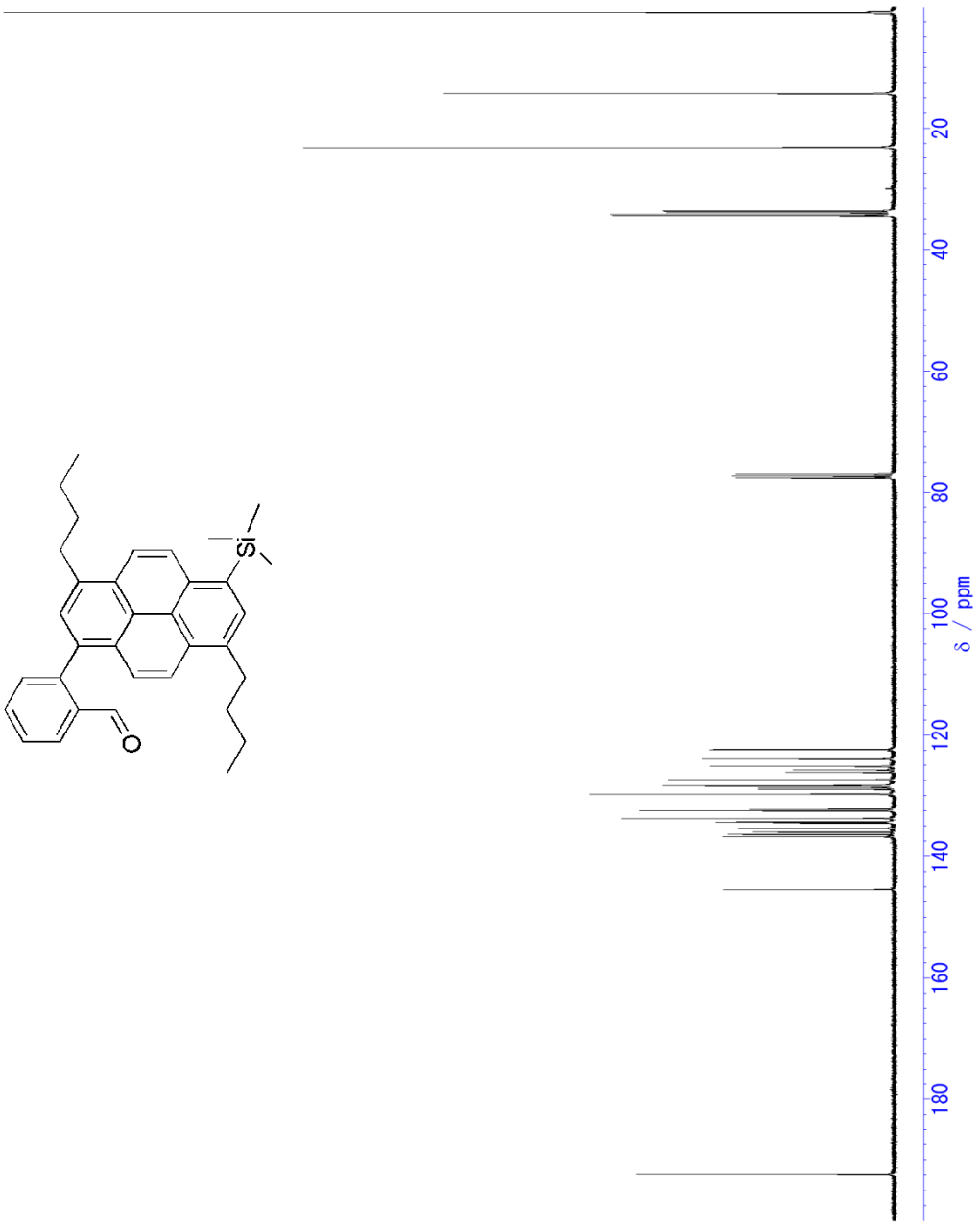


Table 1, entry 6: ^{1}H NMR spectrum

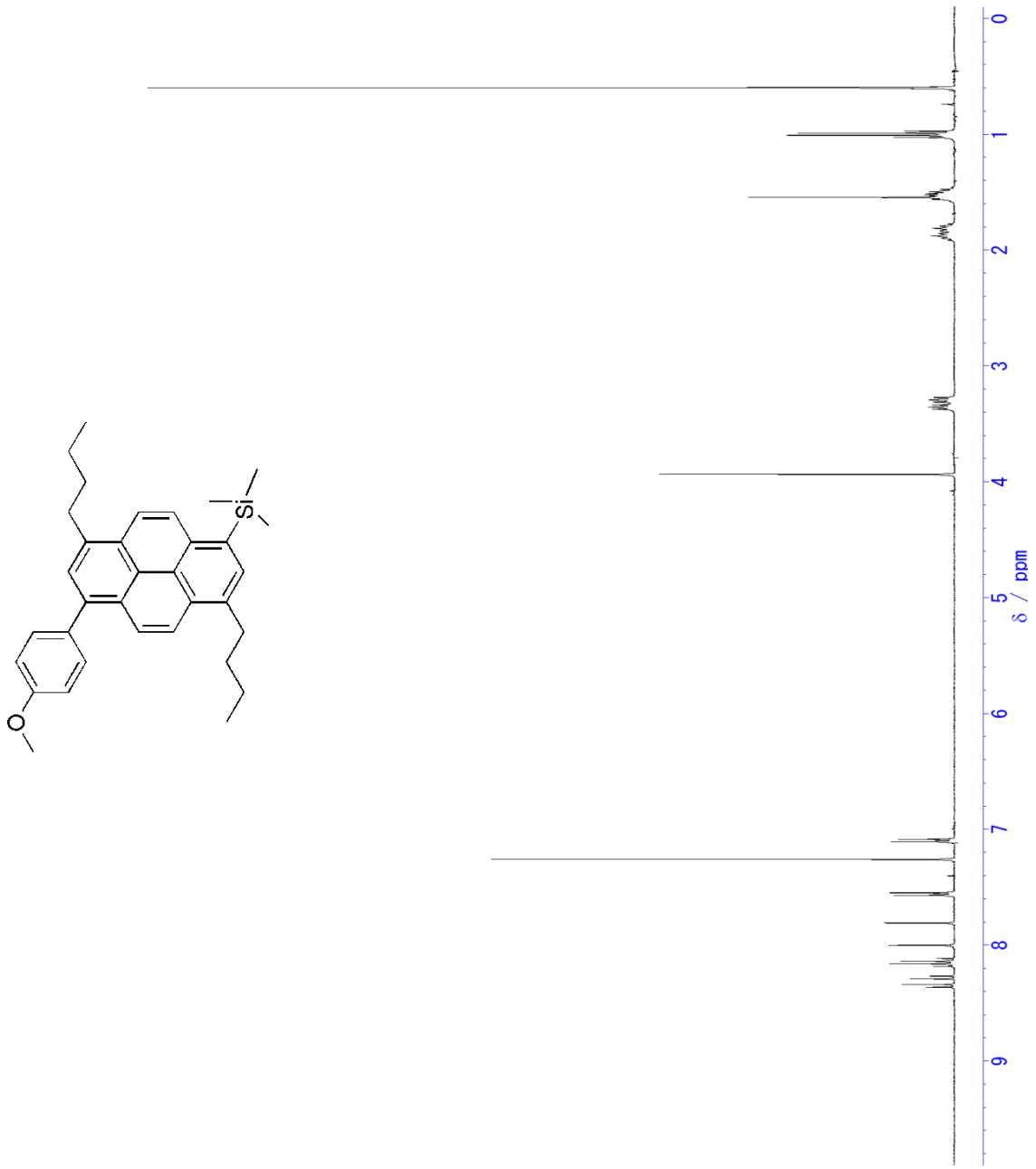


Table 1, entry 6: ^{13}C NMR spectrum

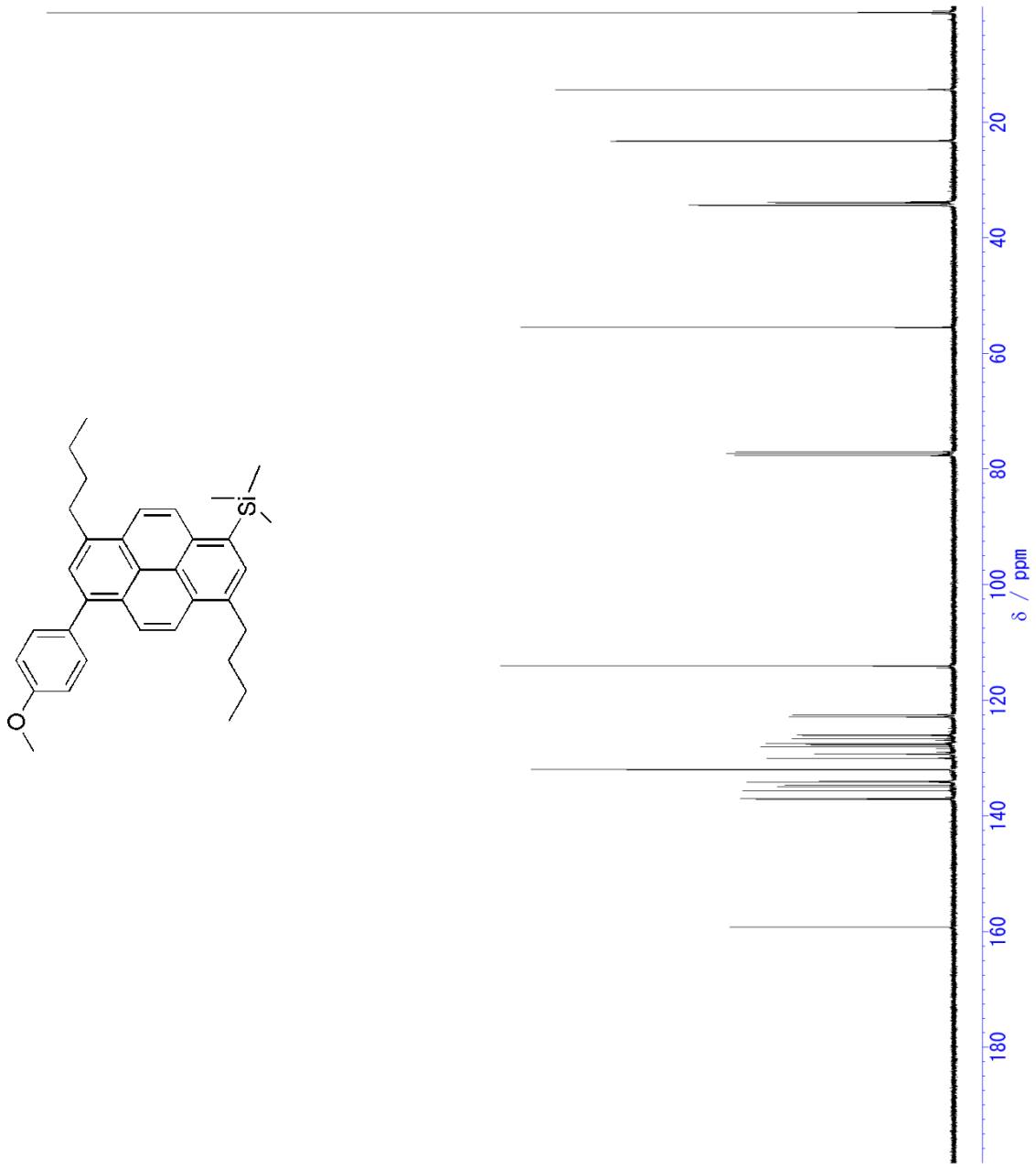


Table 1 entry 7: ^{1}H NMR spectrum

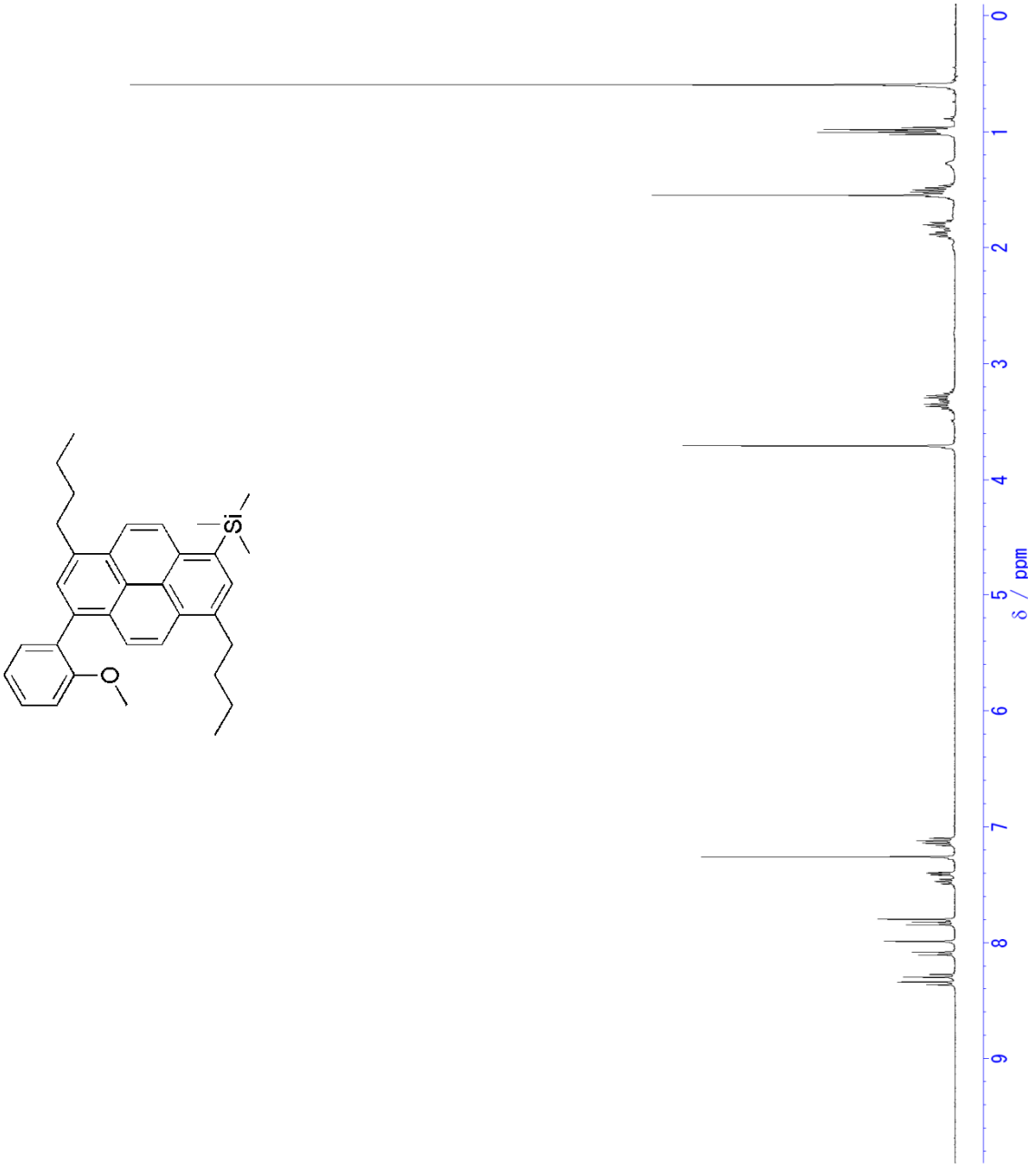


Table 1 entry 7: ^{13}C NMR spectrum

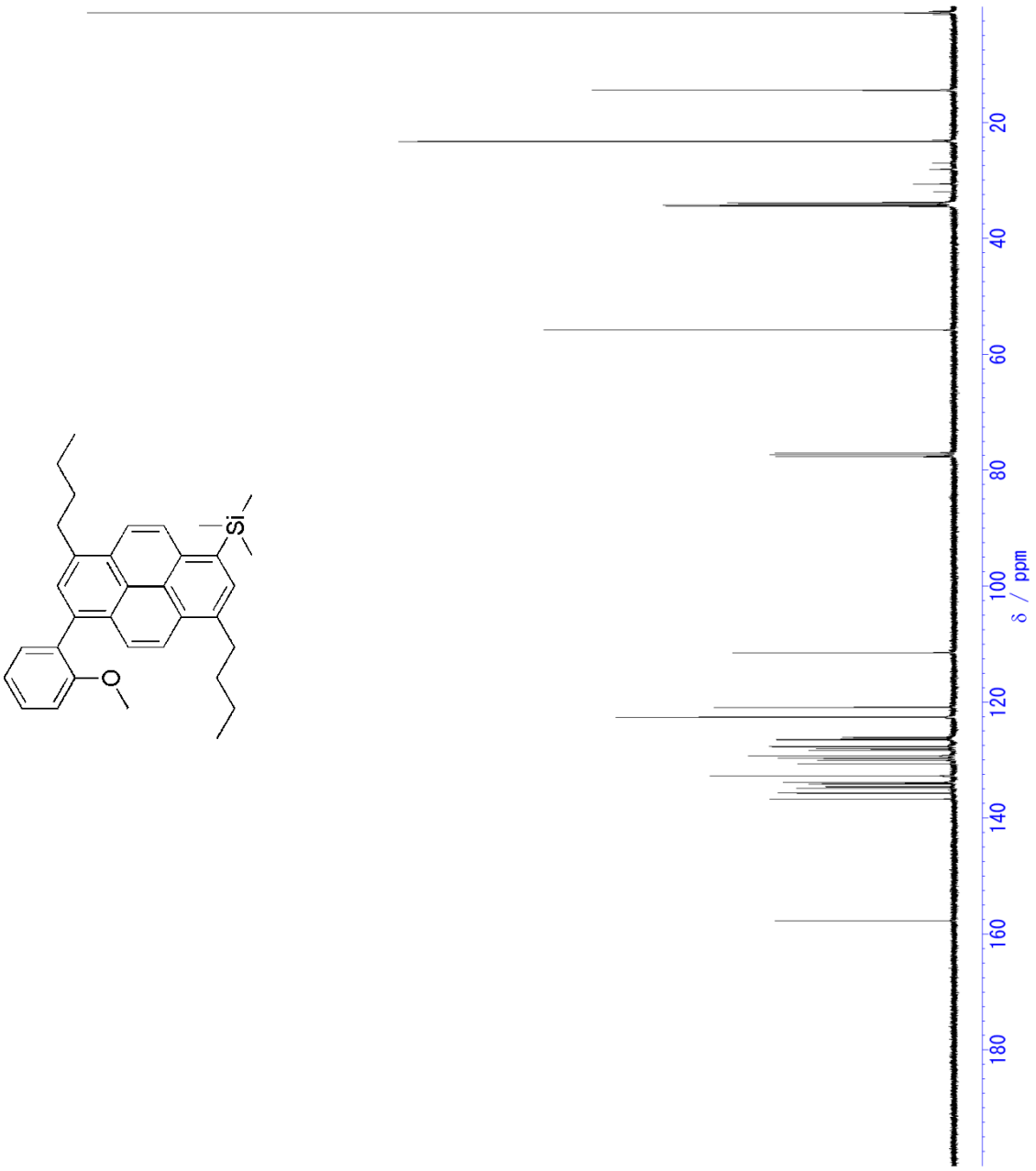


Table 1 entry 8: ^{1}H NMR spectrum

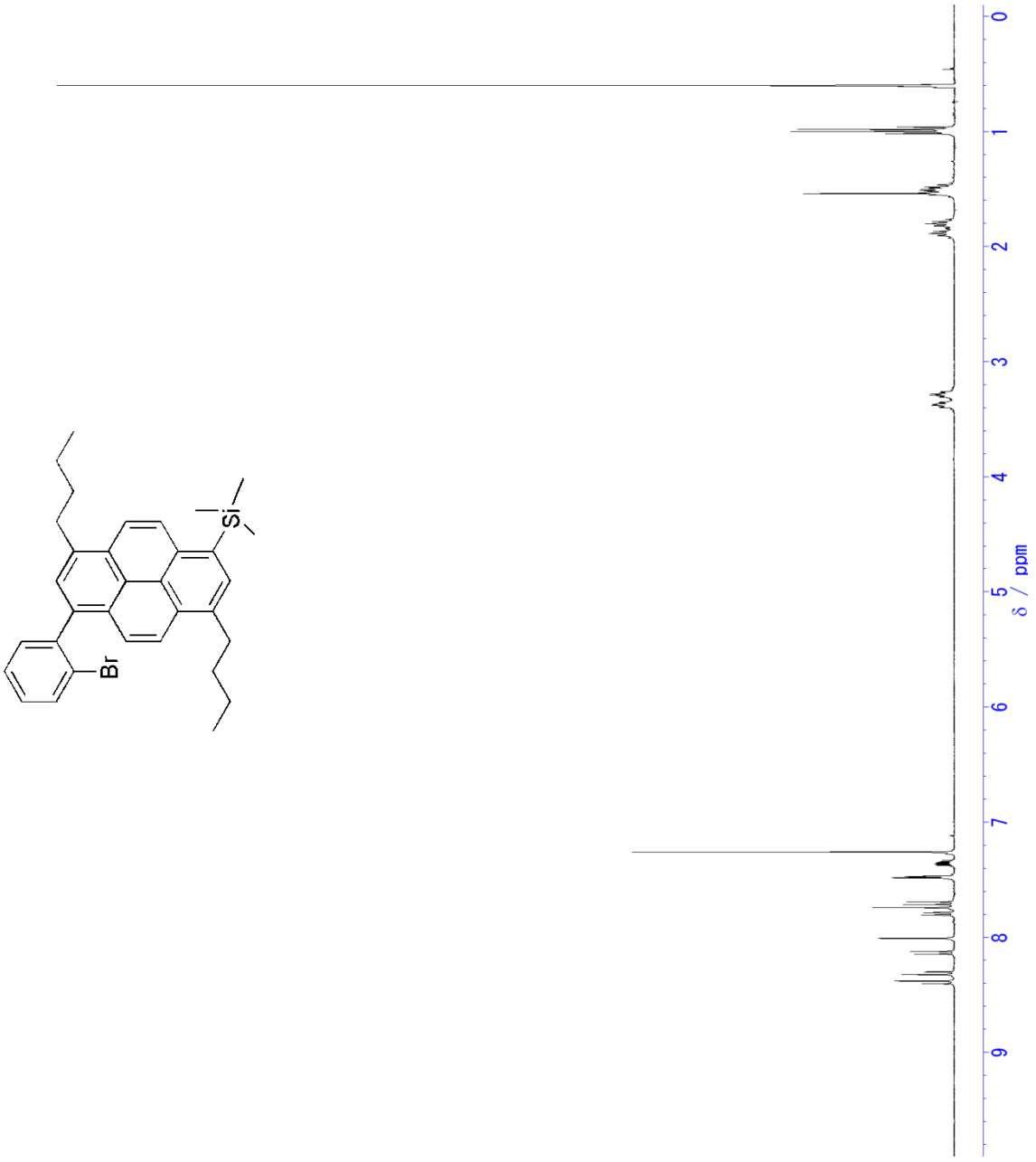


Table 1 entry 8: ^{13}C NMR spectrum

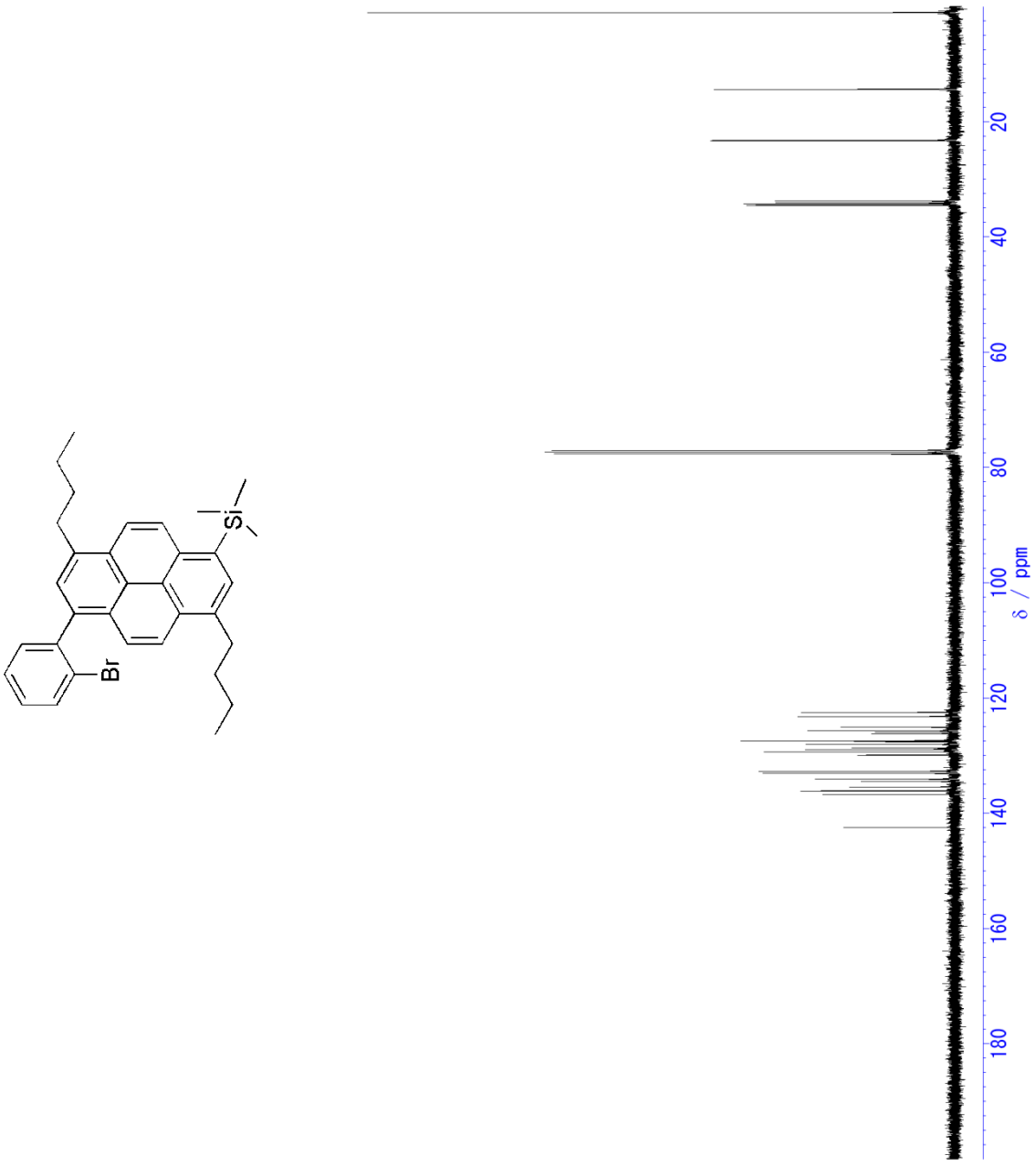


Table 1 entry 9: ^{1}H NMR spectrum

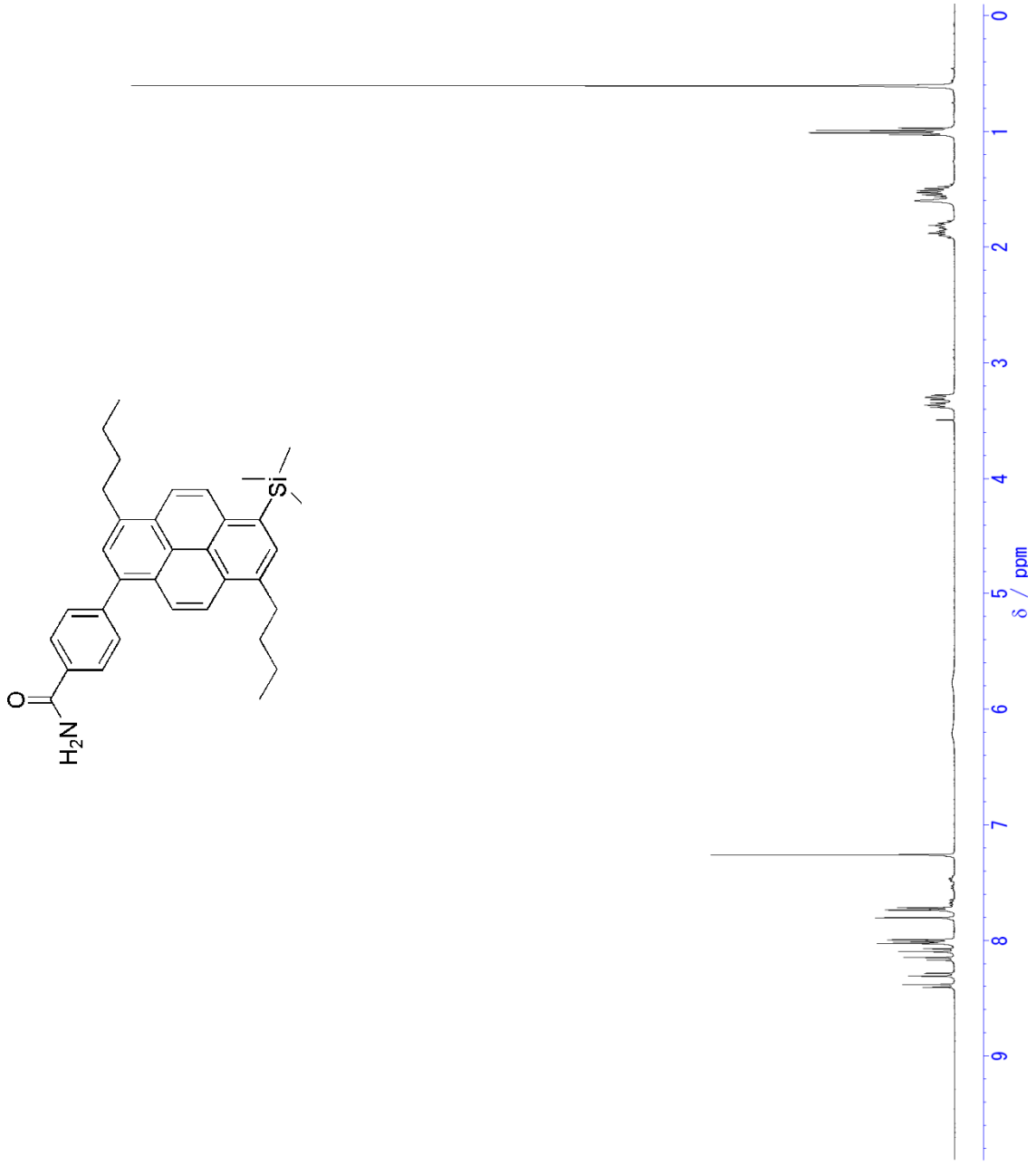


Table 1 entry 9: ^{13}C NMR spectrum

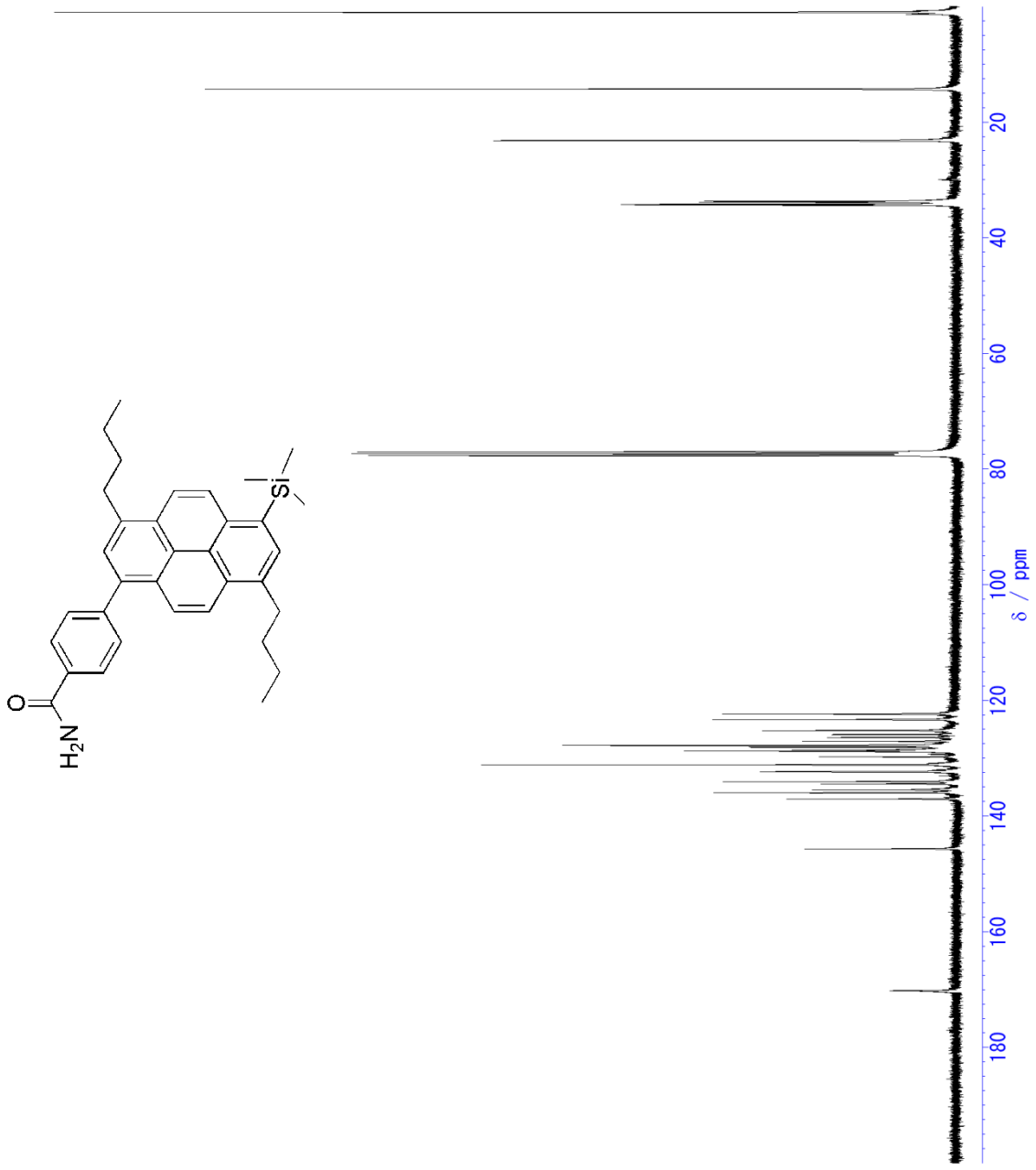


Table 1 entry 10: ^{1}H NMR spectrum

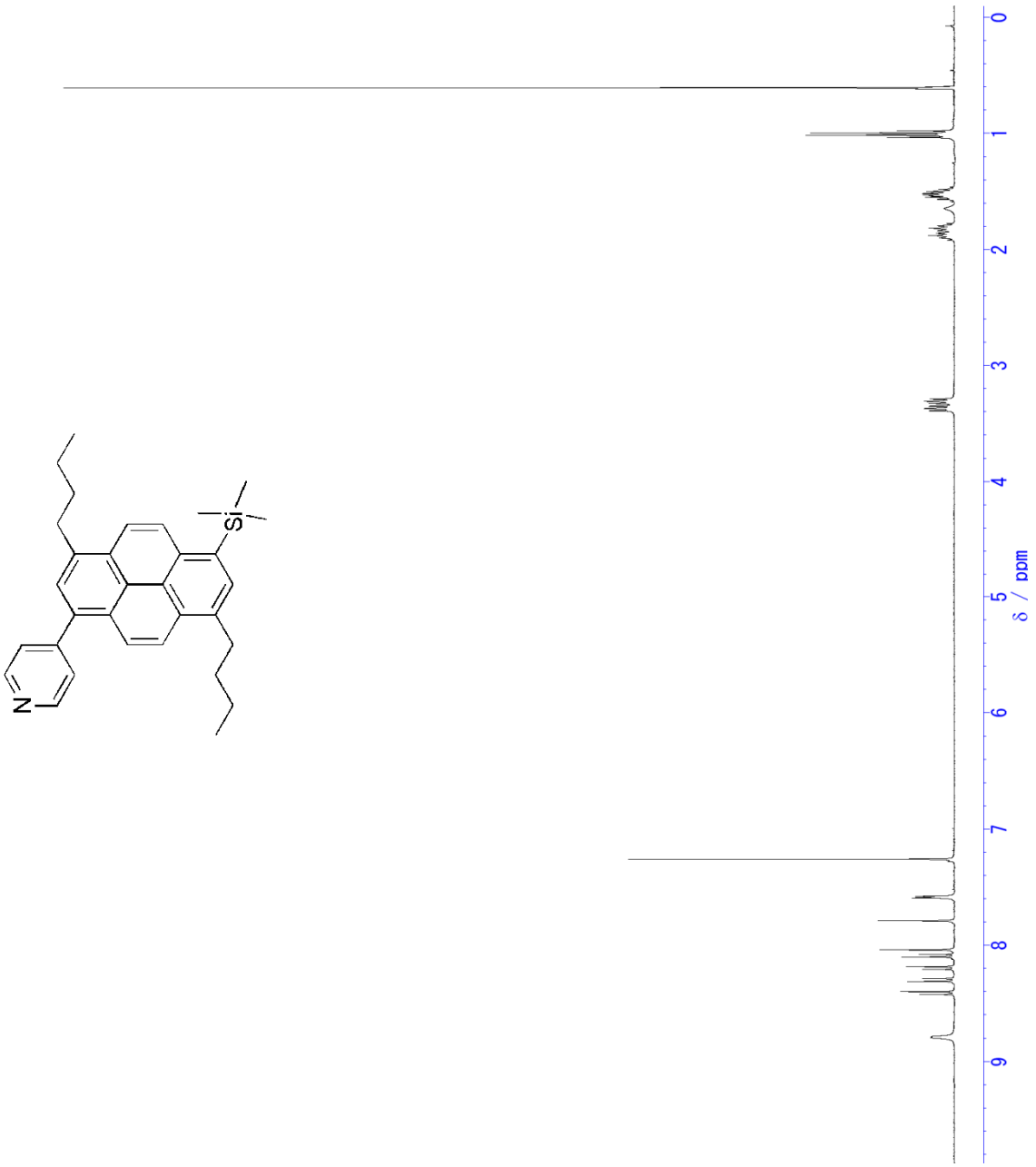


Table 1 entry 10: ^{13}C NMR spectrum

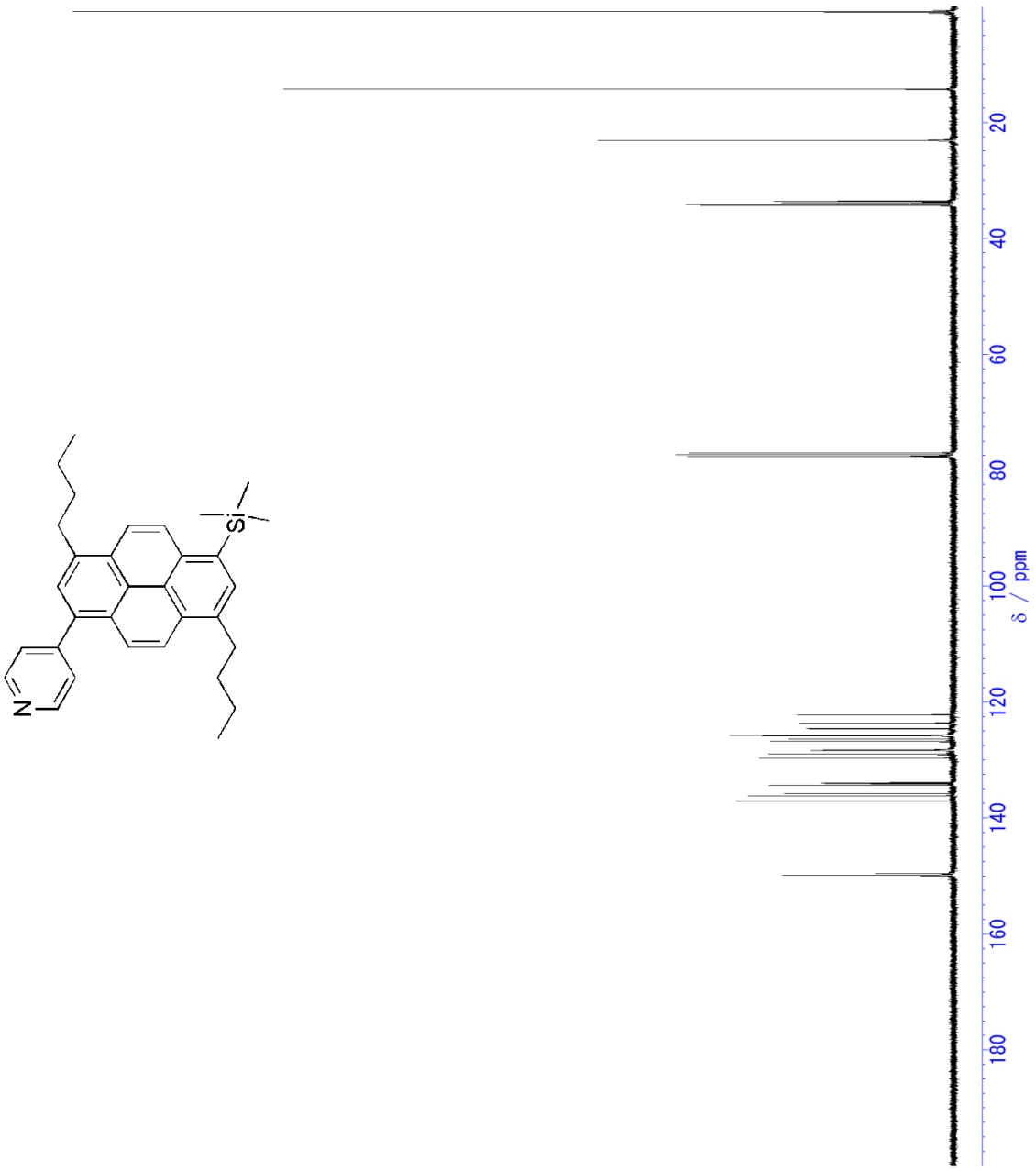


Table 1 entry 11: ^{1}H NMR spectrum

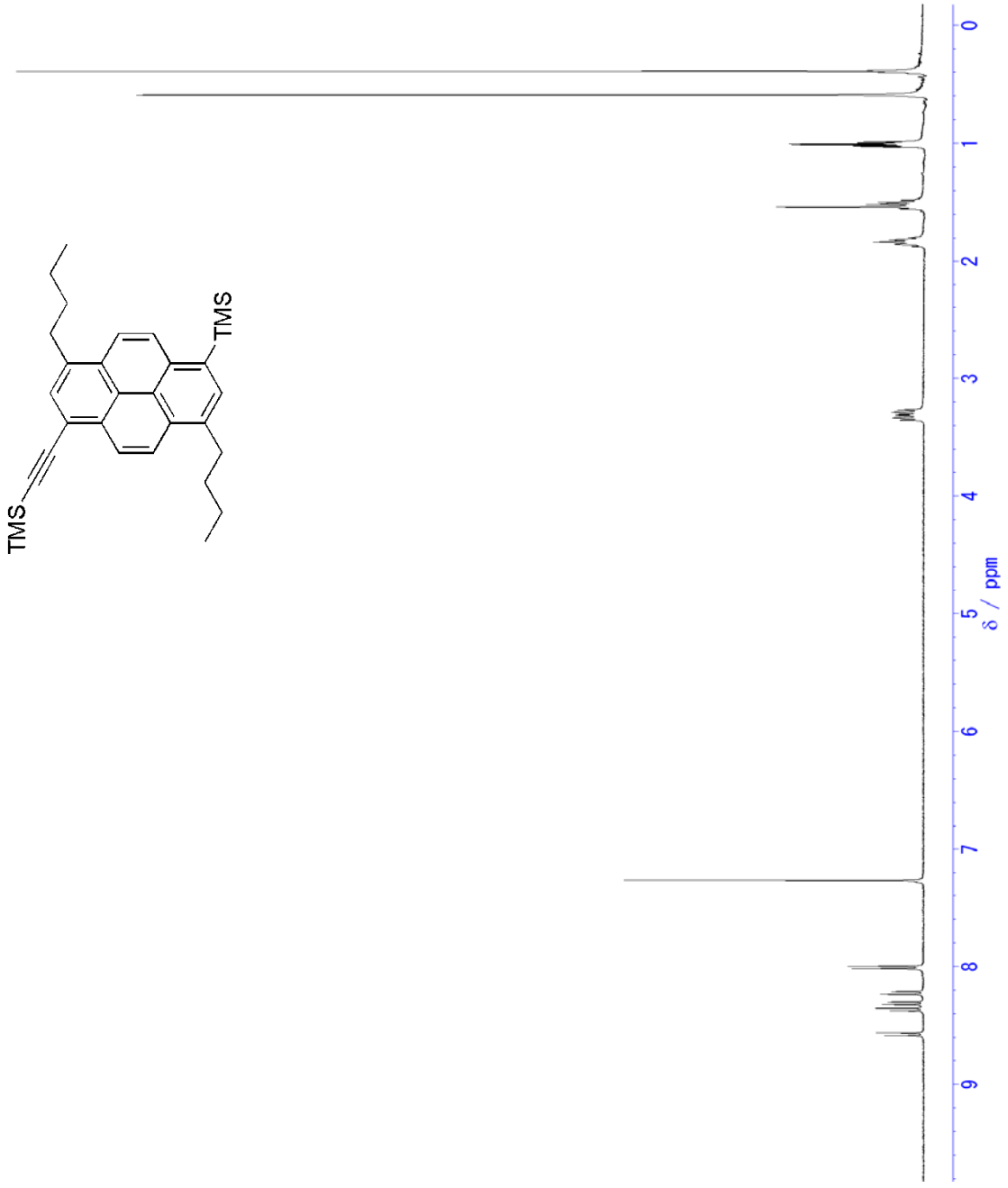


Table 1 entry 11: ^{13}C NMR spectrum

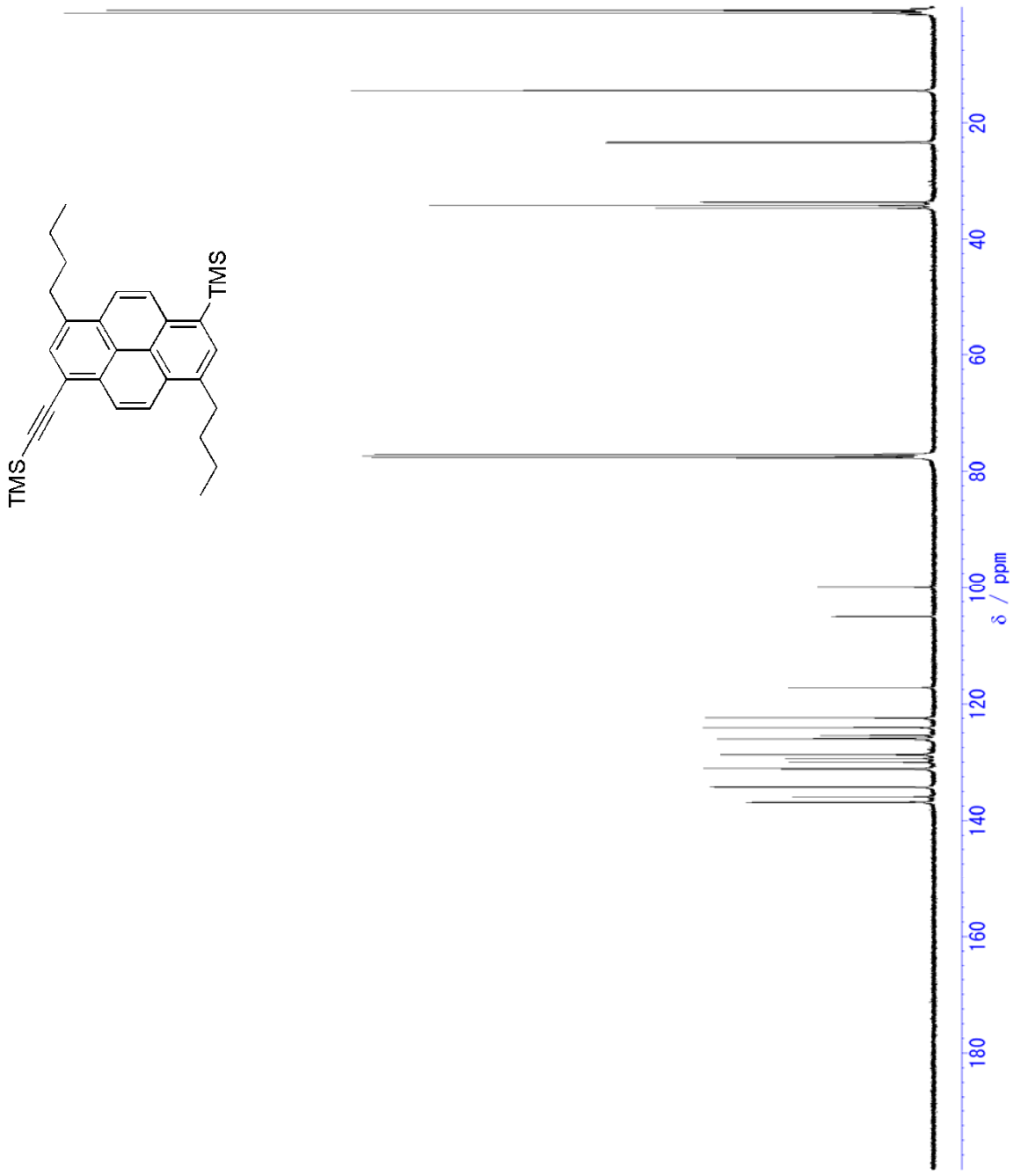


Table 1 entry 12: ^{1}H NMR spectrum

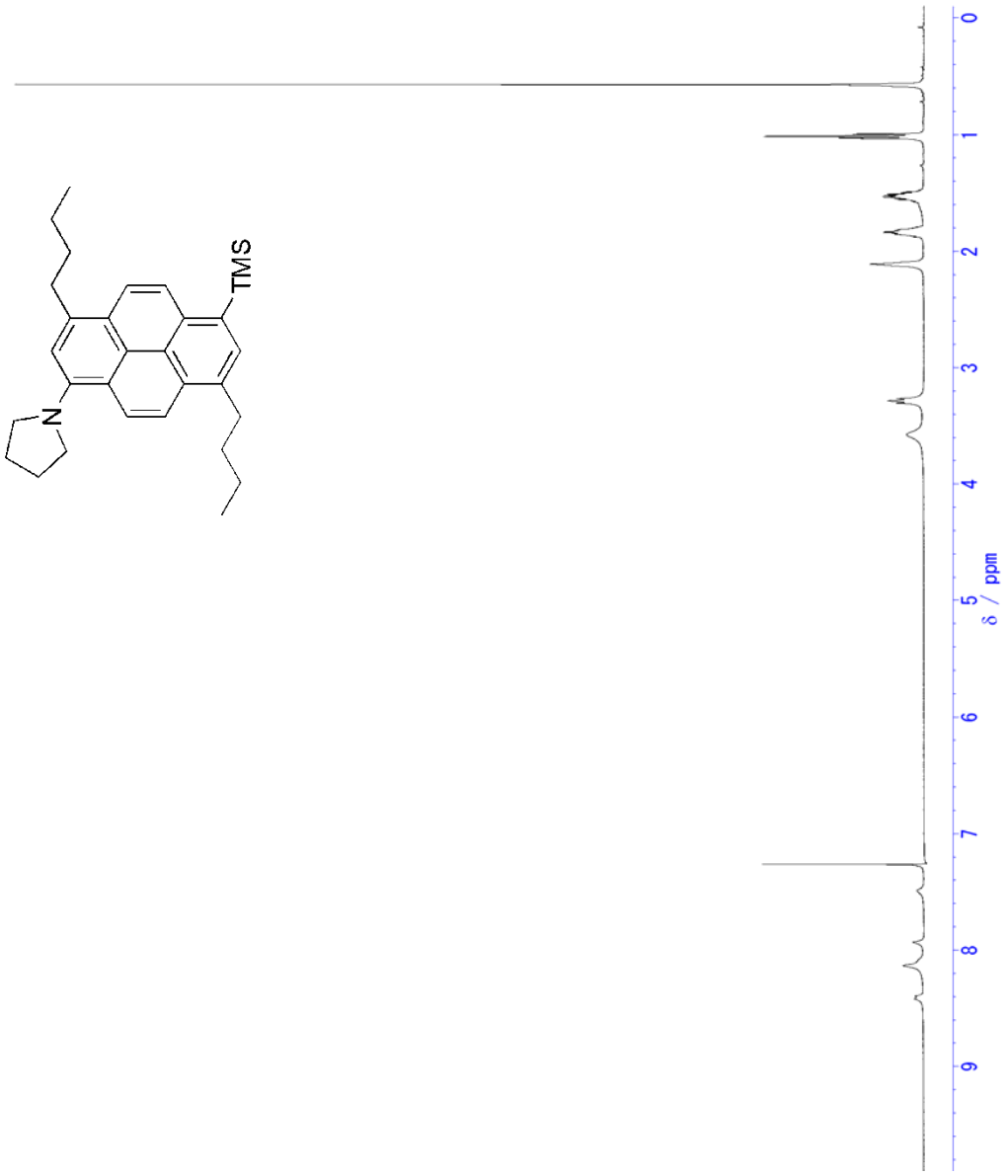
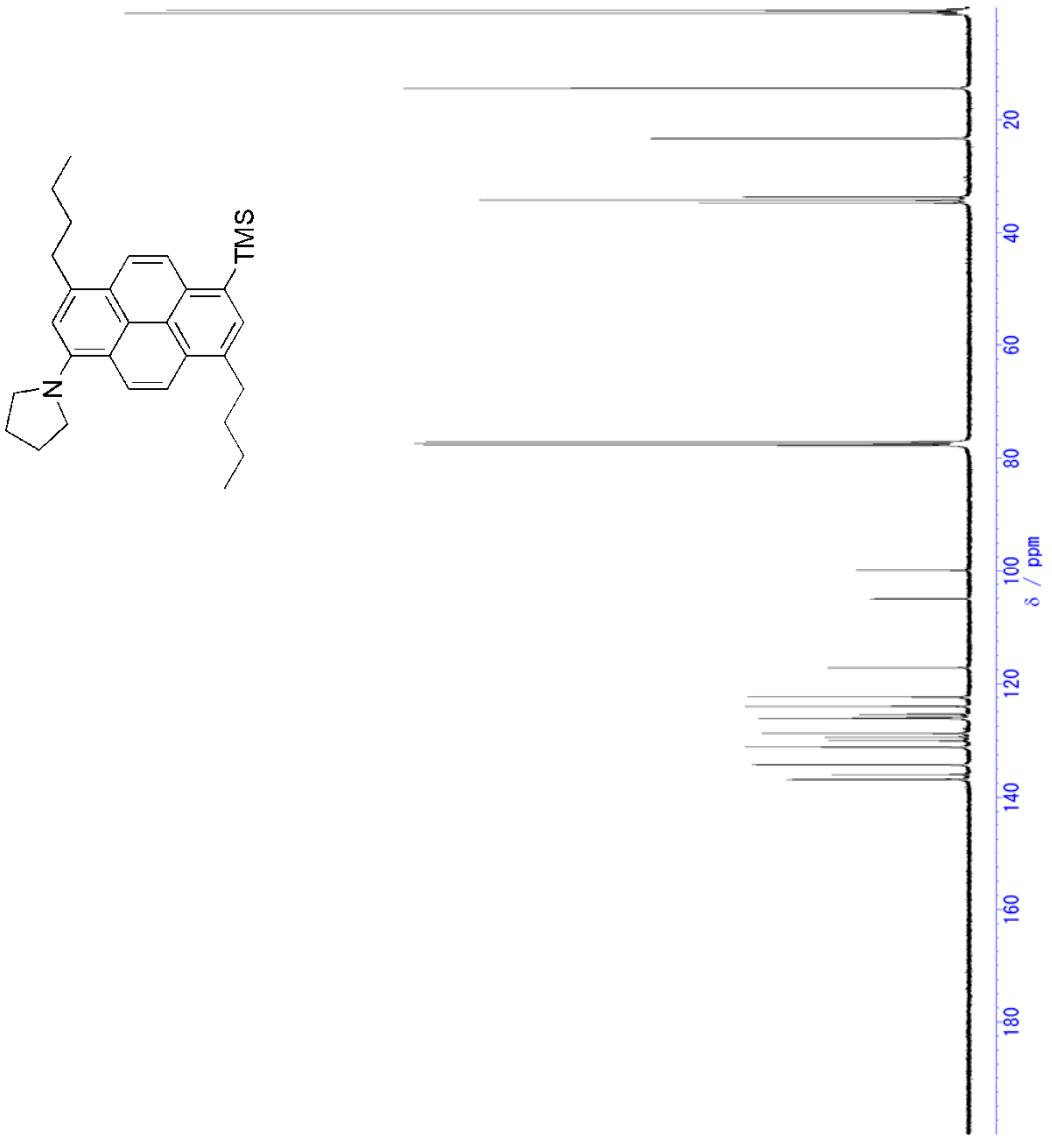
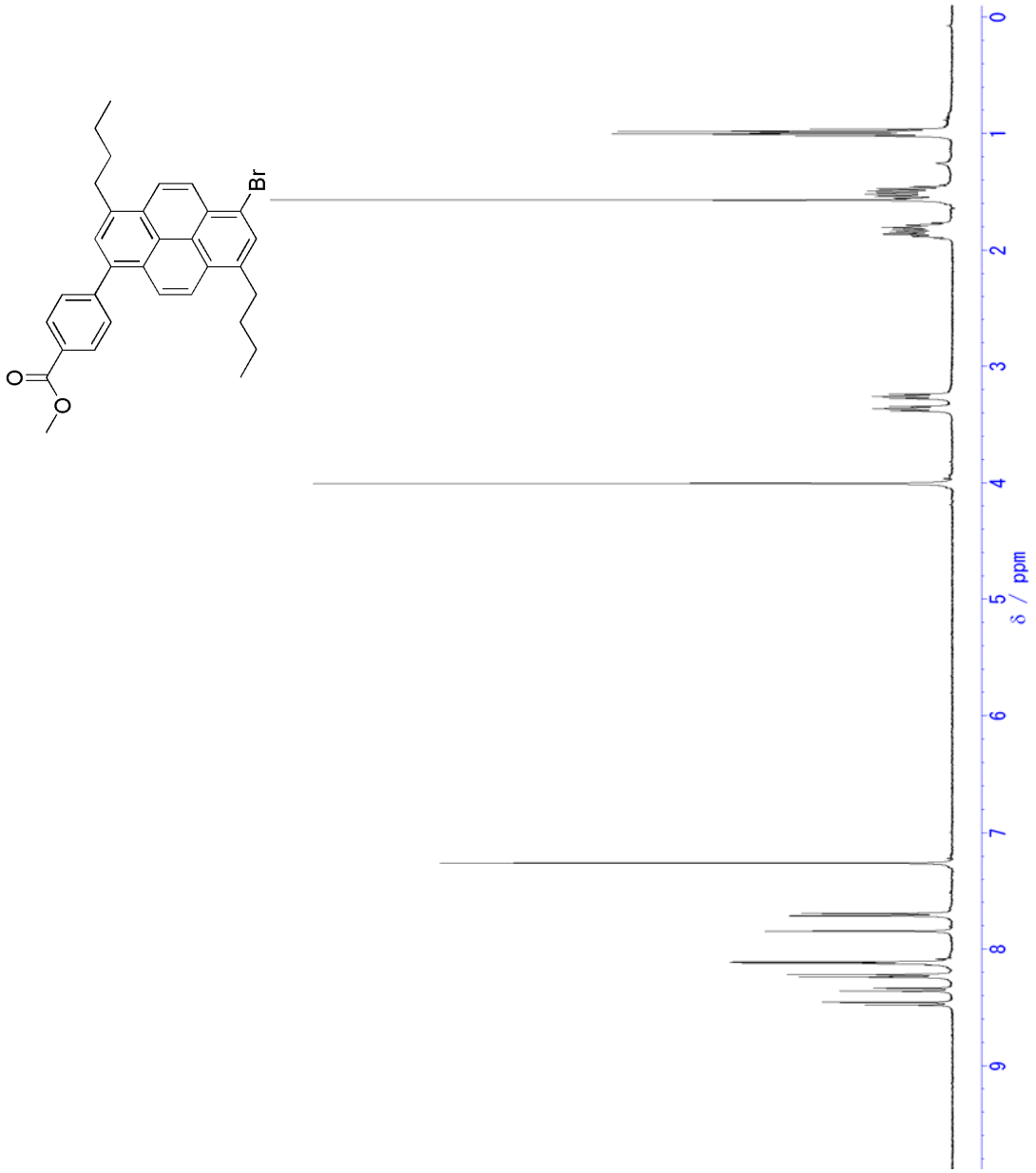


Table 1 entry 12: ^{13}C NMR spectrum

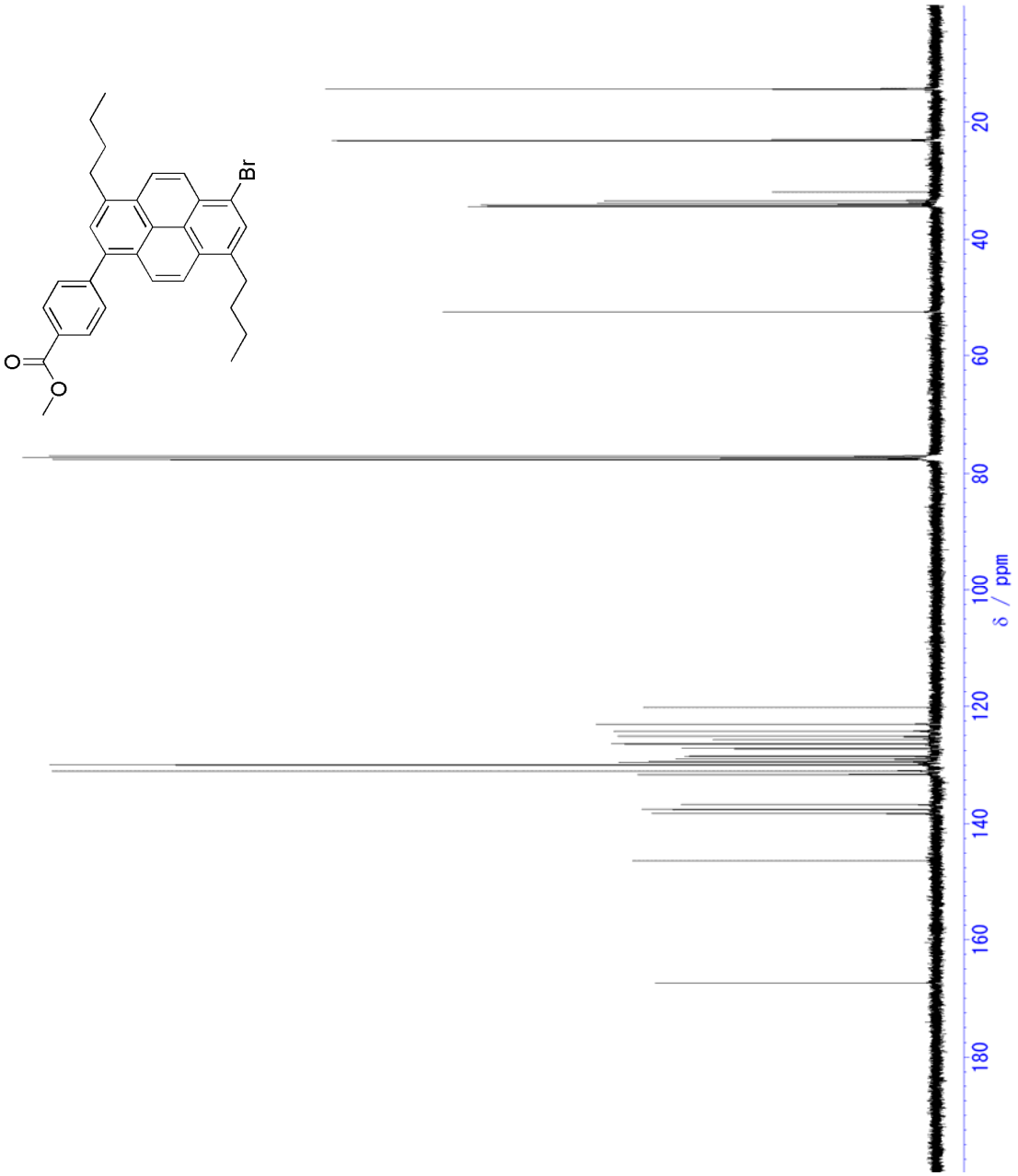


j) ^{1}H and ^{13}C NMR Spectra for Compounds 14, 15, and 16

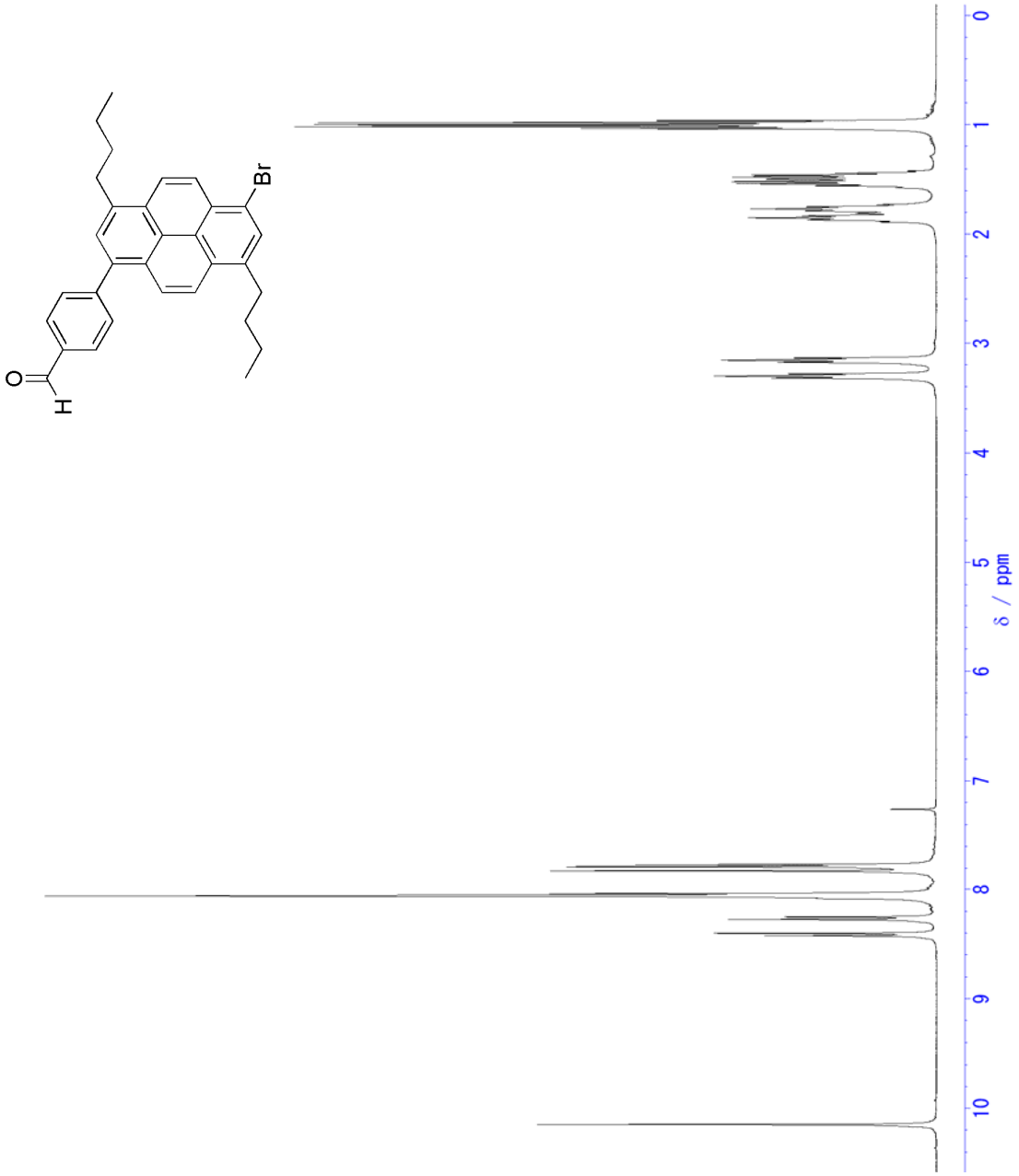
^{1}H NMR spectrum: methyl 4-(6-bromo-3,8-dibutylpyren-1-yl)benzoate **14**



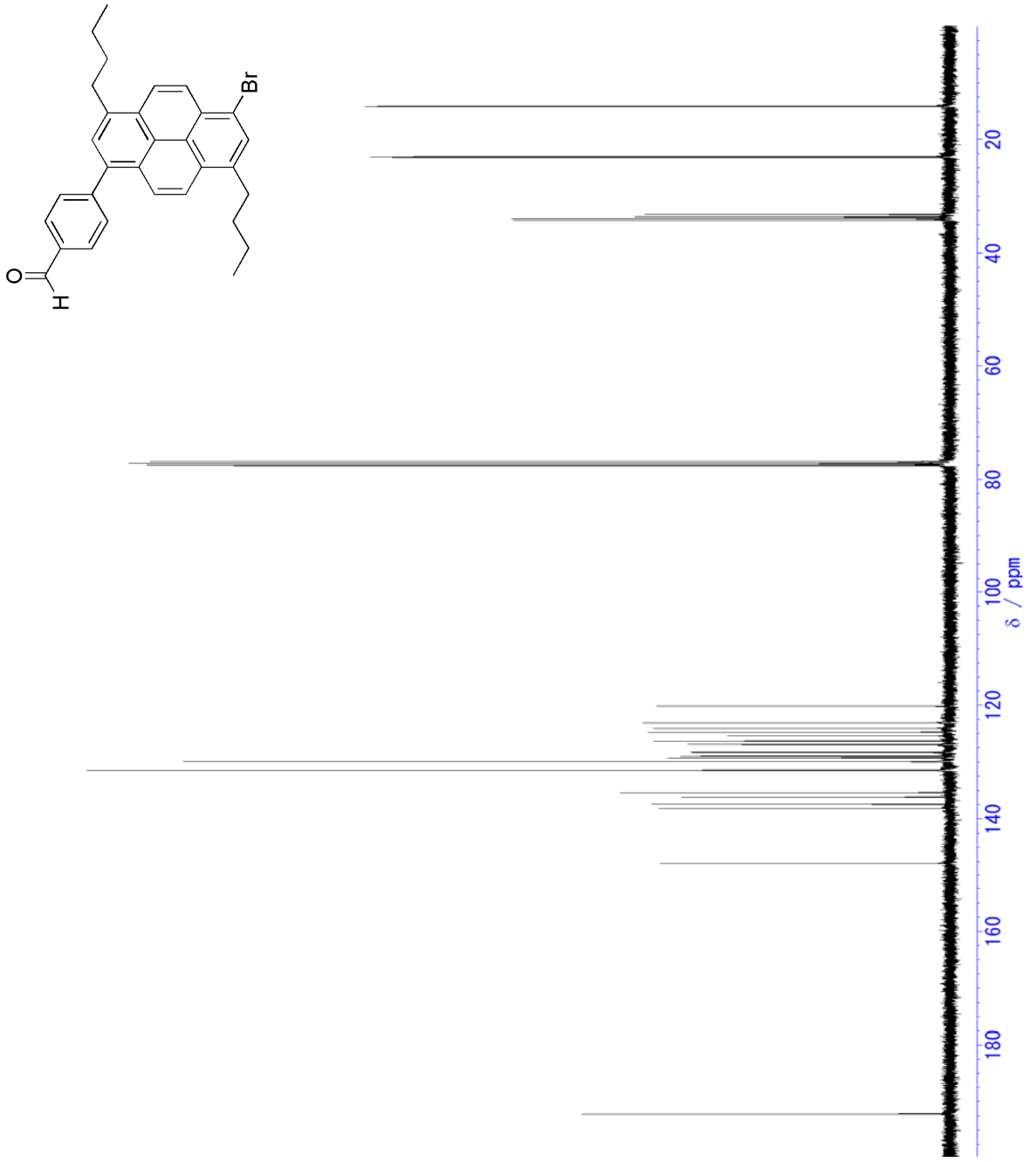
^{13} C NMR spectrum: methyl 4-(6-bromo-3,8-dibutylpyren-1-yl)benzoate **14**



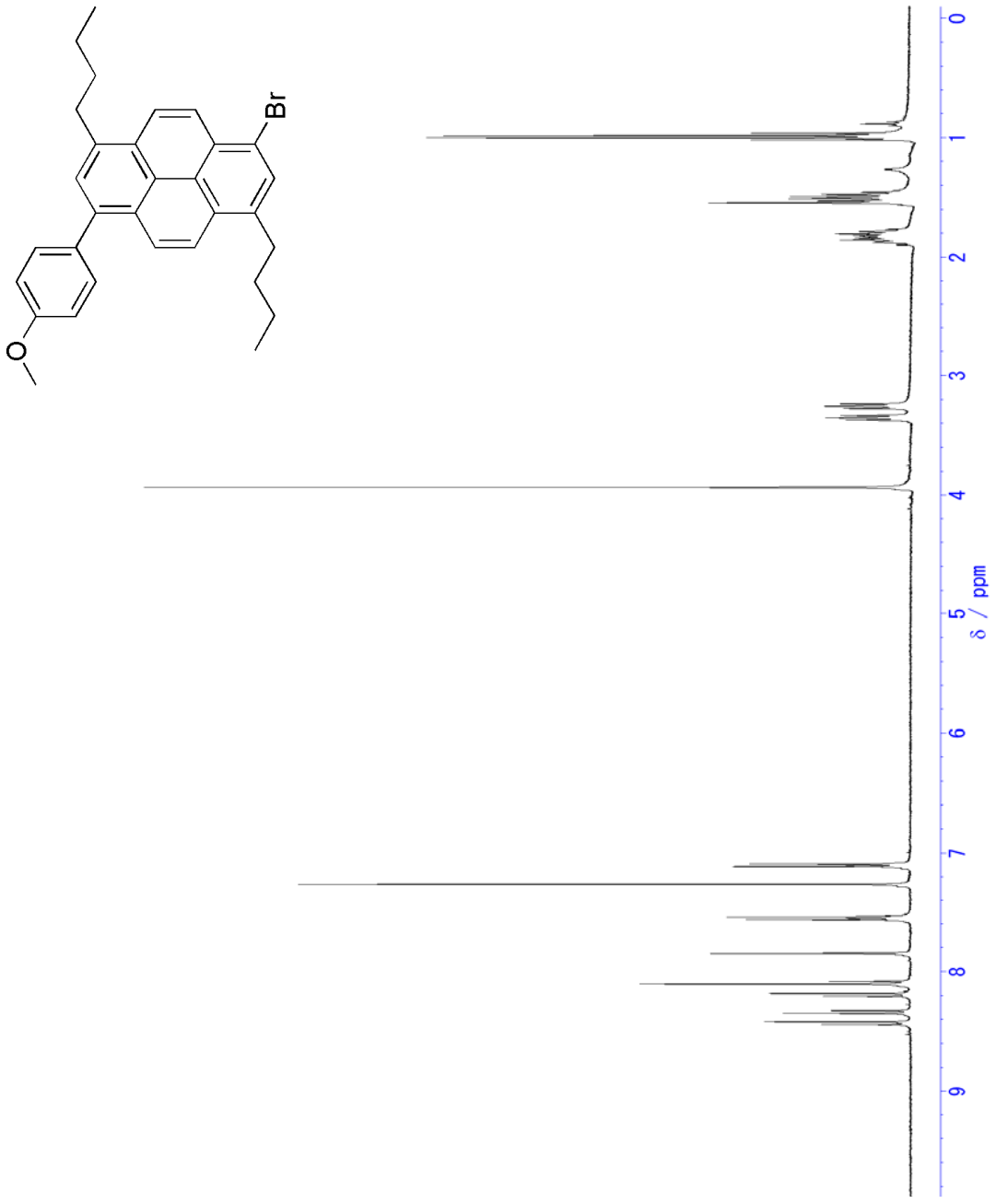
^{1}H NMR spectrum: 4-(6-bromo-3,8-dibutylpyren-1-yl)benzaldehyde **15**



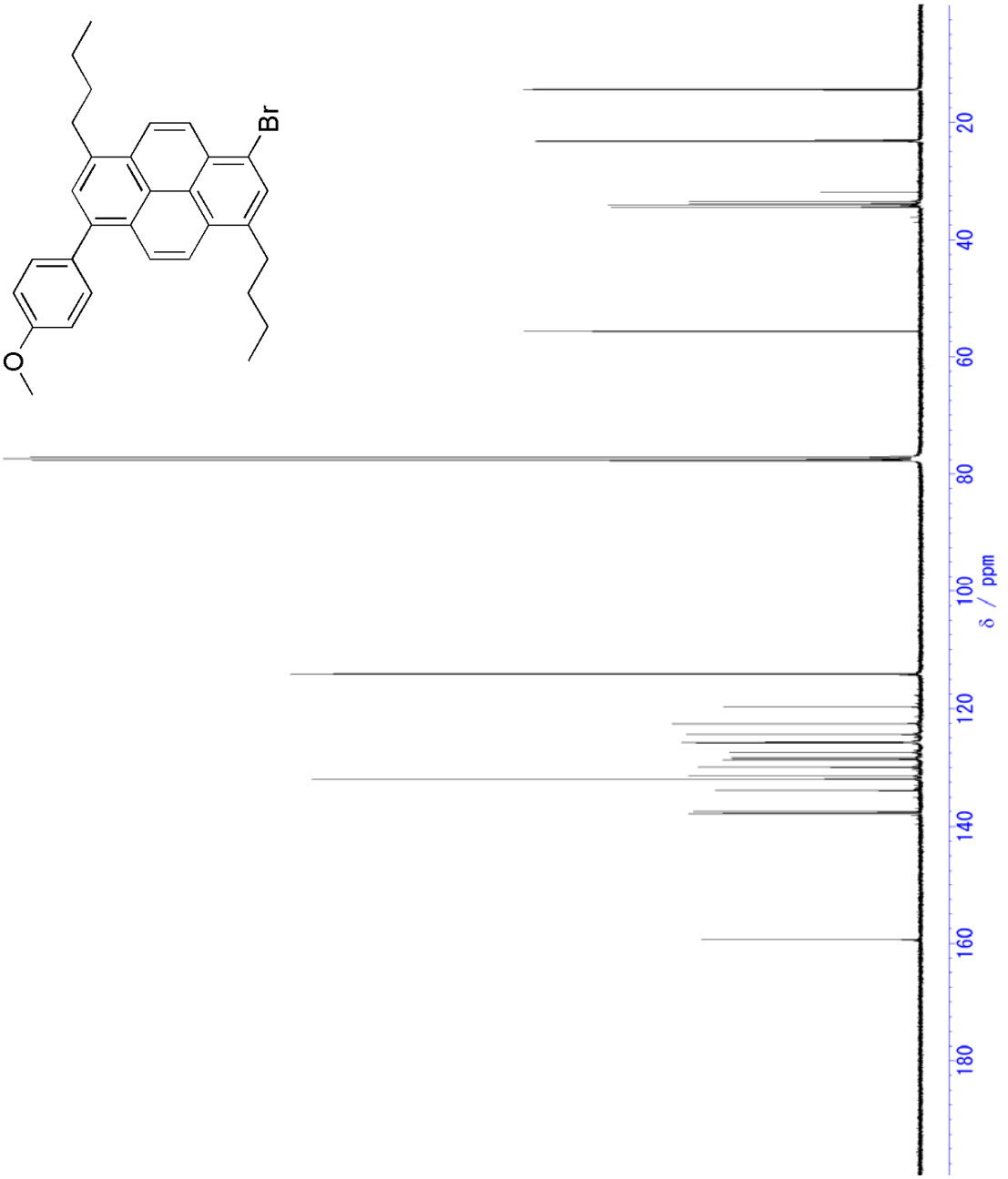
^{13}C NMR spectrum: 4-(6-bromo-3,8-dibutylpyren-1-yl)benzaldehyde **15**



^{1}H NMR spectrum: 1-bromo-3,8-dibutyl-6-(4-methoxyphenyl)pyrene **16**



^{13}C NMR spectrum: 1-bromo-3,8-dibutyl-6-(4-methoxyphenyl)pyrene **16**



k) H and ^{13}C NMR Spectra for Compounds 17-26 in Table 2

Table 2, entry 1: ^{1}H NMR spectrum

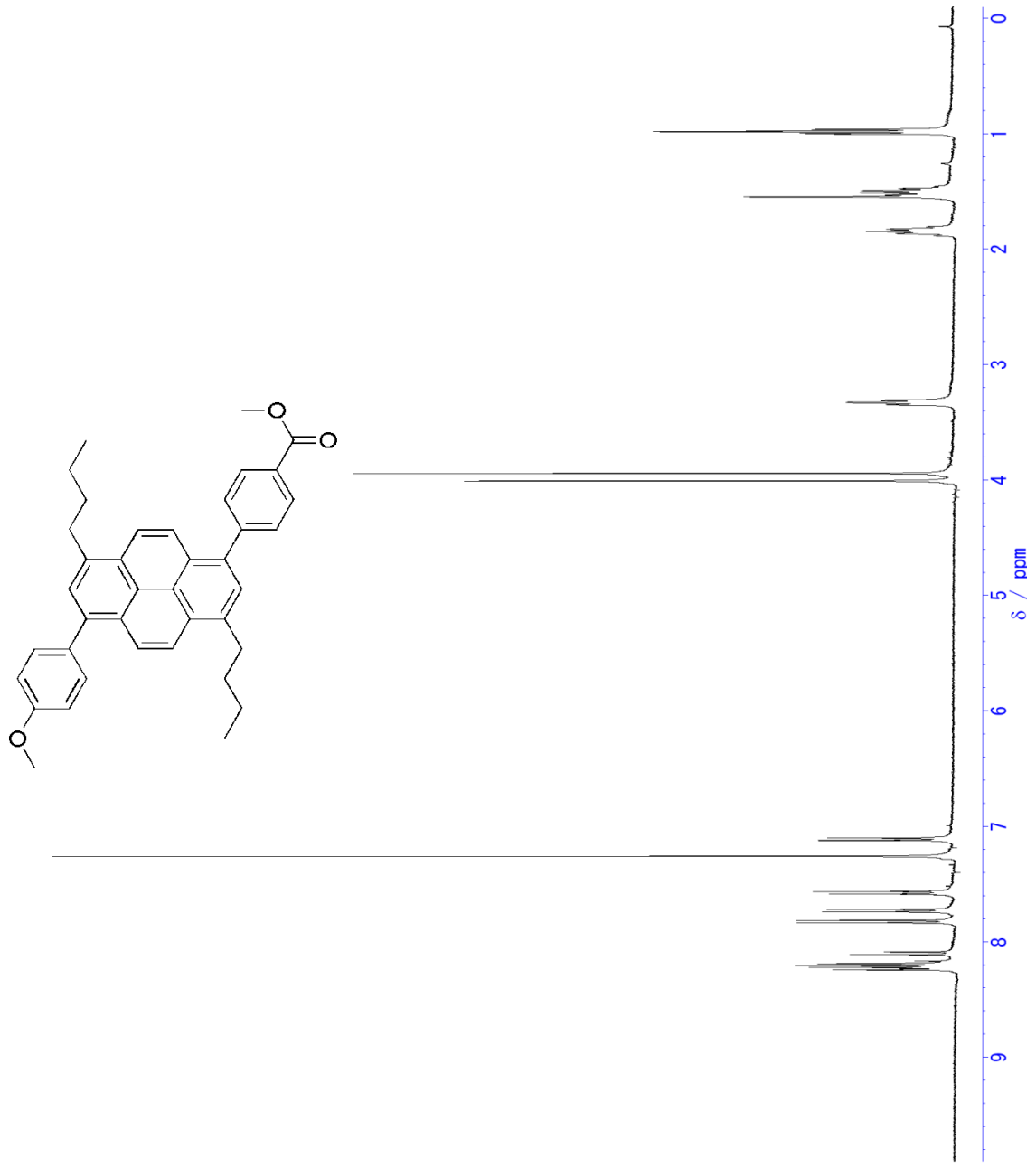


Table 2, entry 1: ^{13}C NMR spectrum

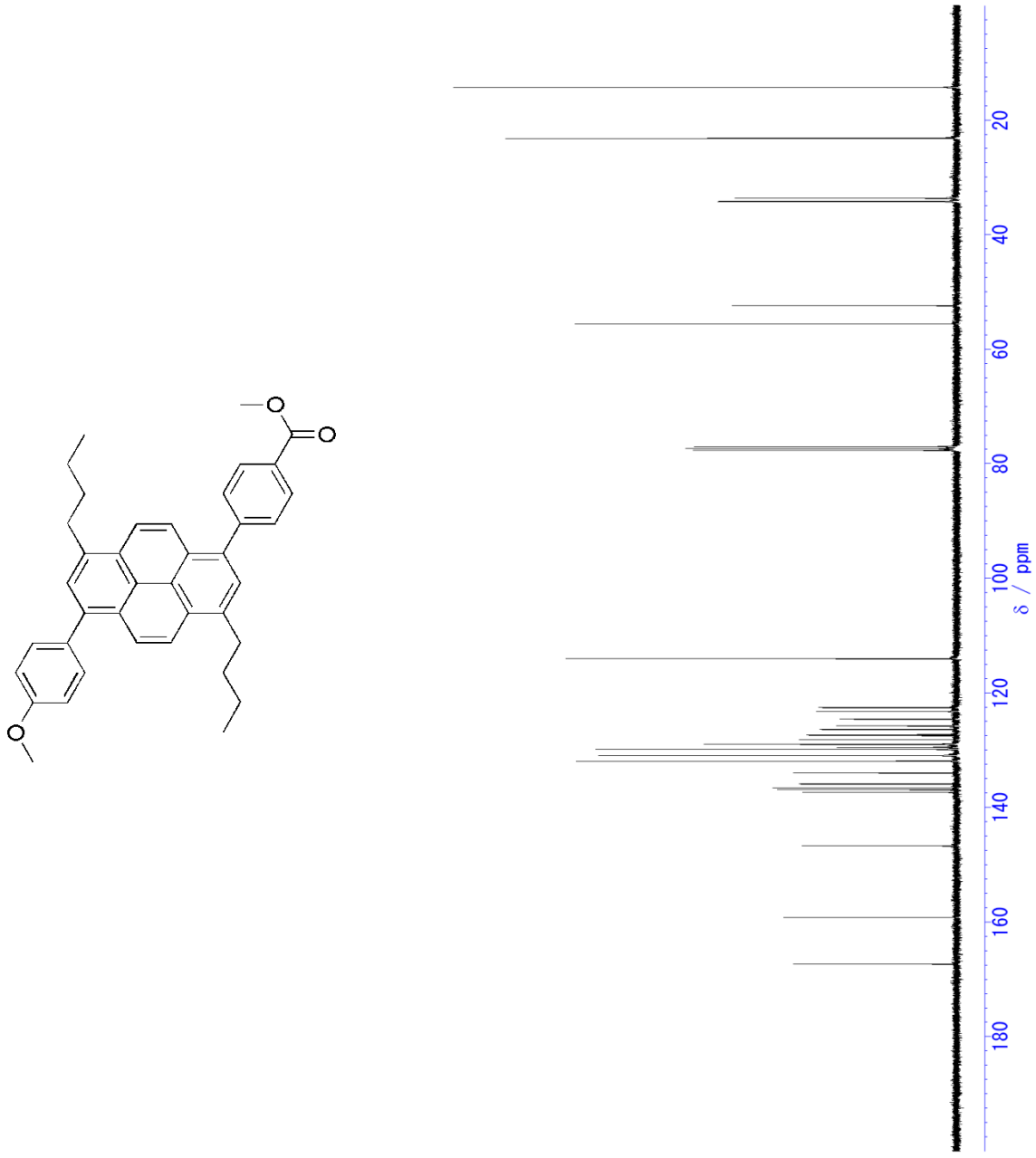


Table 2, entry 2: ^{1}H NMR spectrum

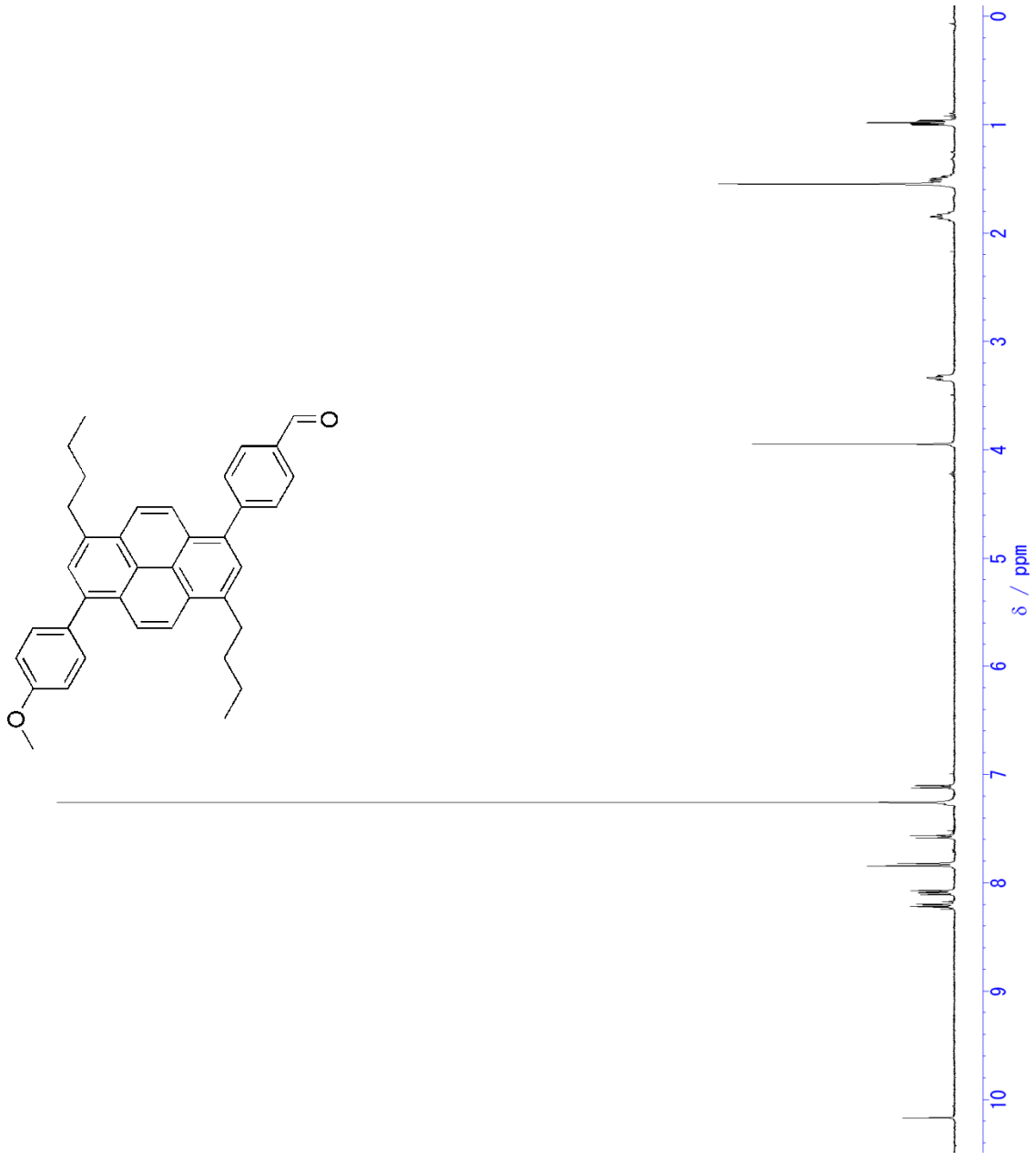


Table 2, entry 2: ^{13}C NMR spectrum

Table 2, entry 3: ^{1}H NMR spectrum

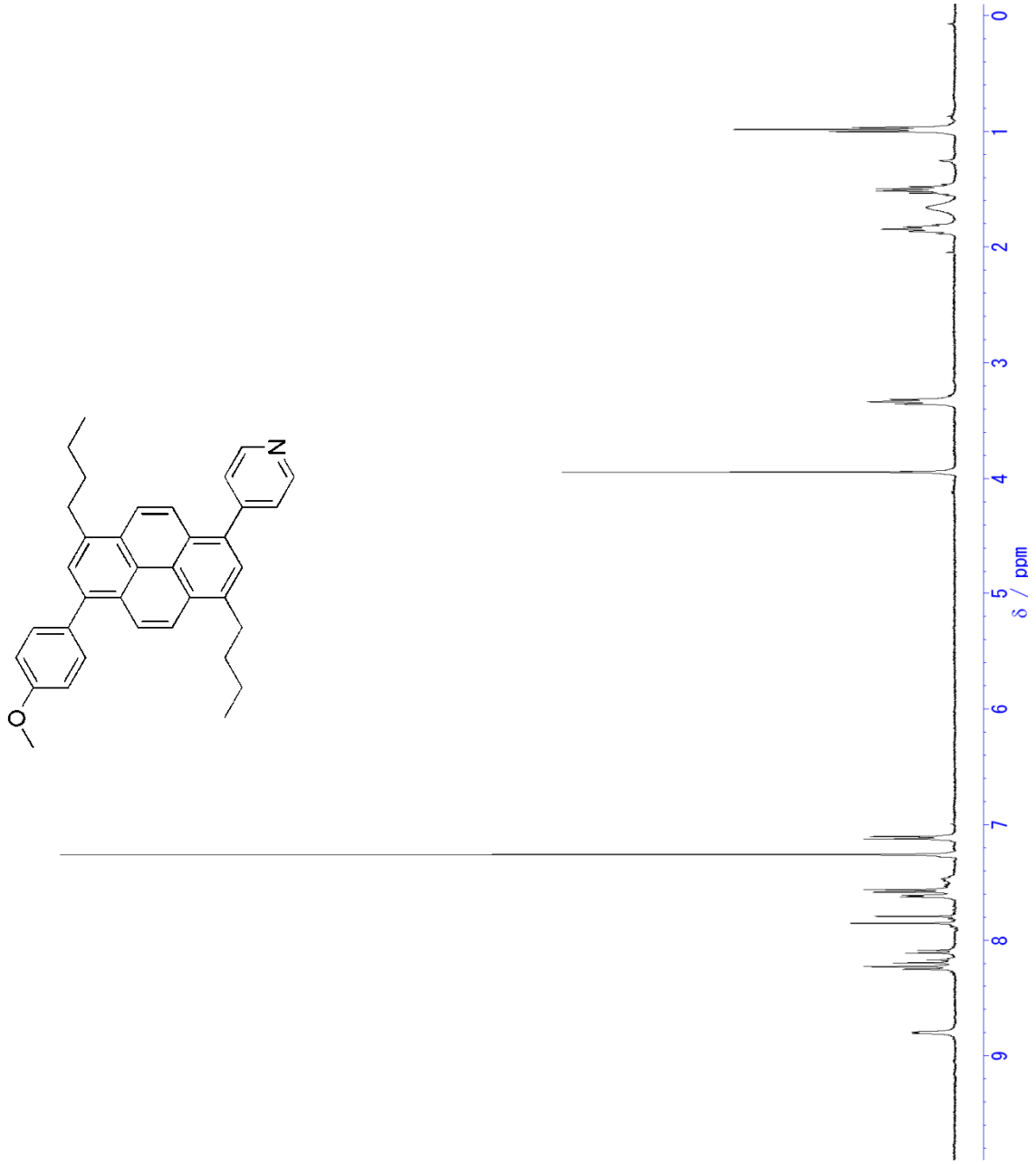


Table 2, entry 3: ^{13}C NMR spectrum

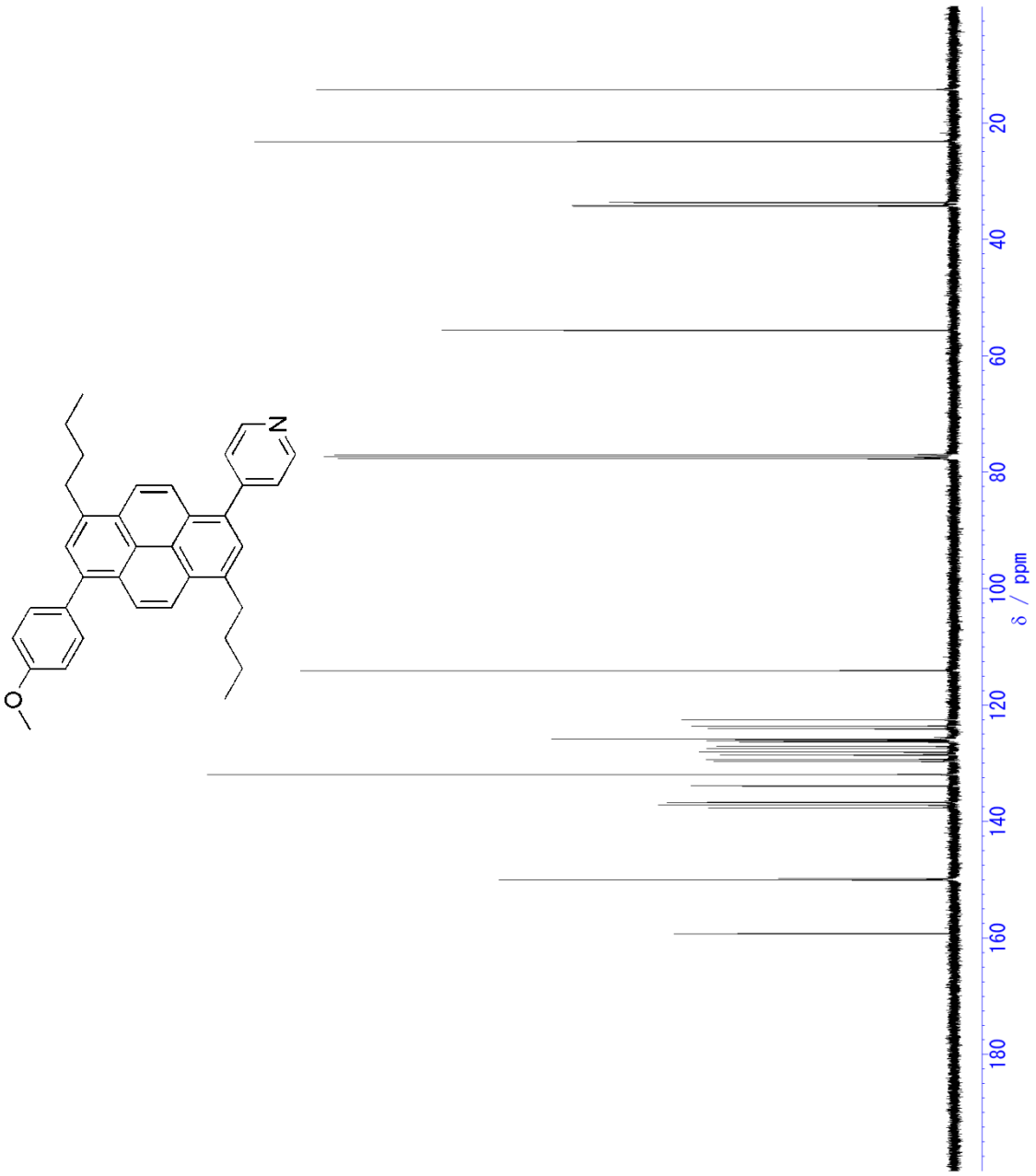


Table 2, entry 4: ^{1}H NMR spectrum

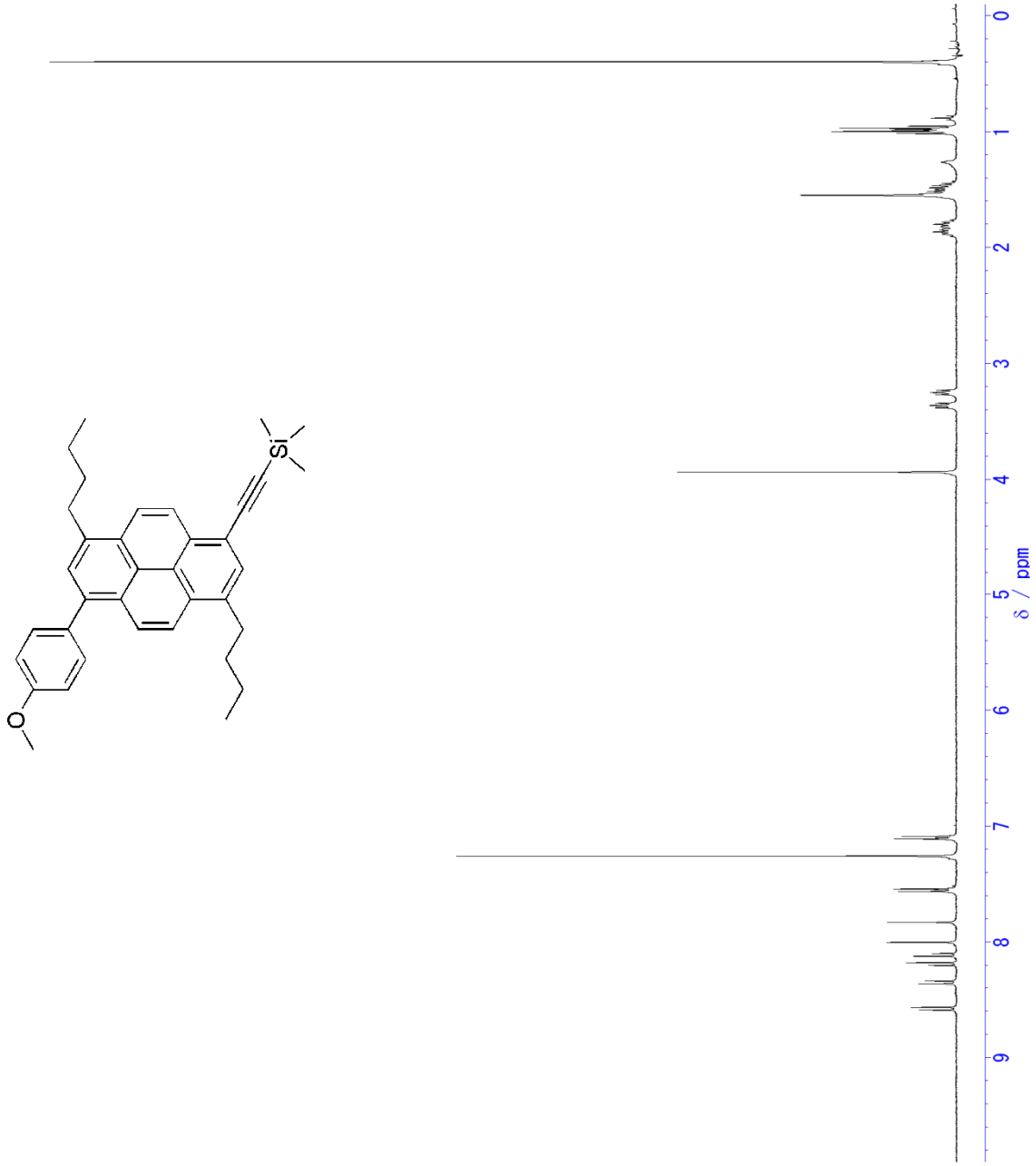


Table 2, entry 4: ^{13}C NMR spectrum

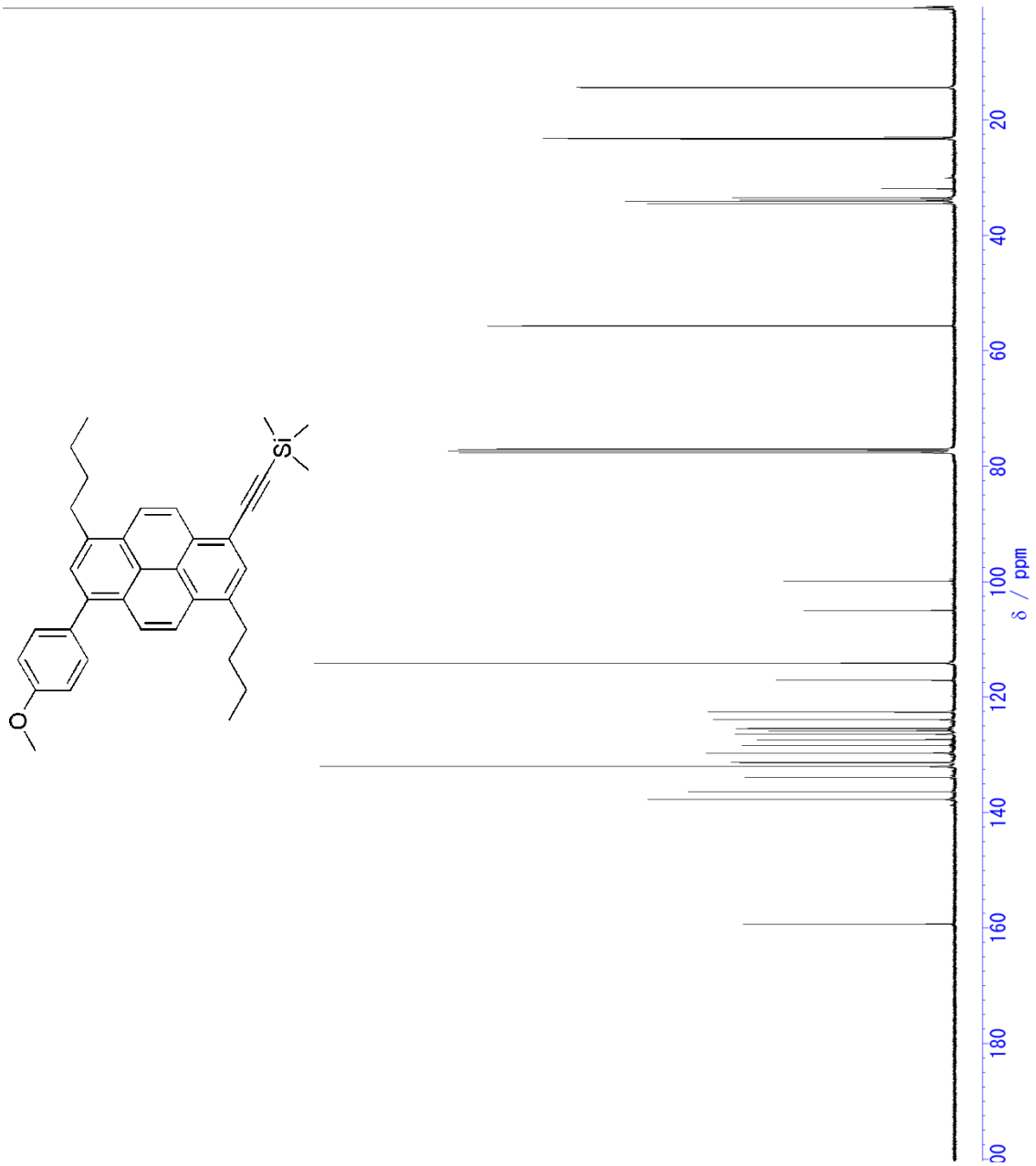


Table 2, entry 5: ^{1}H NMR spectrum

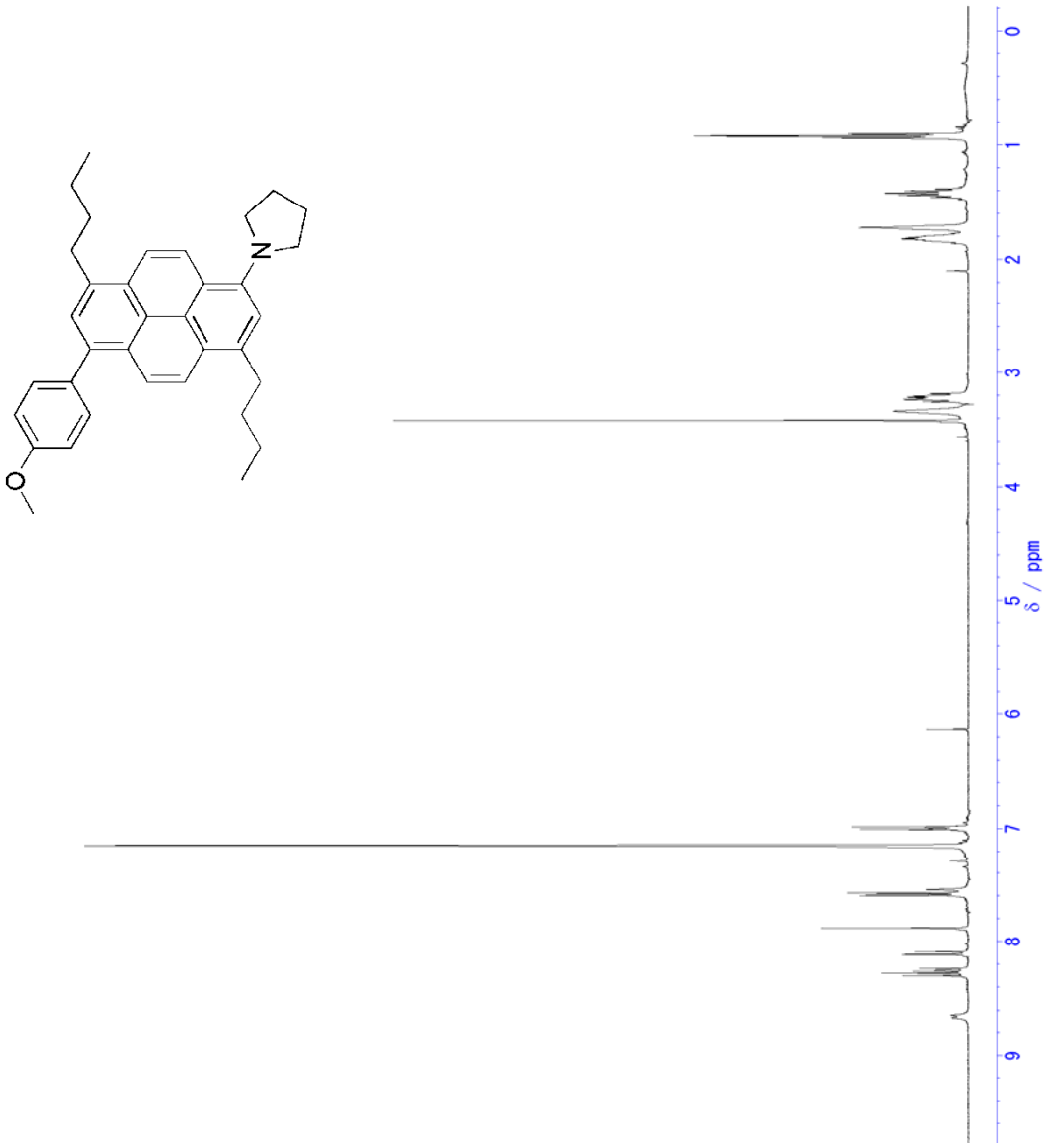


Table 2, entry 5: ^{13}C NMR spectrum

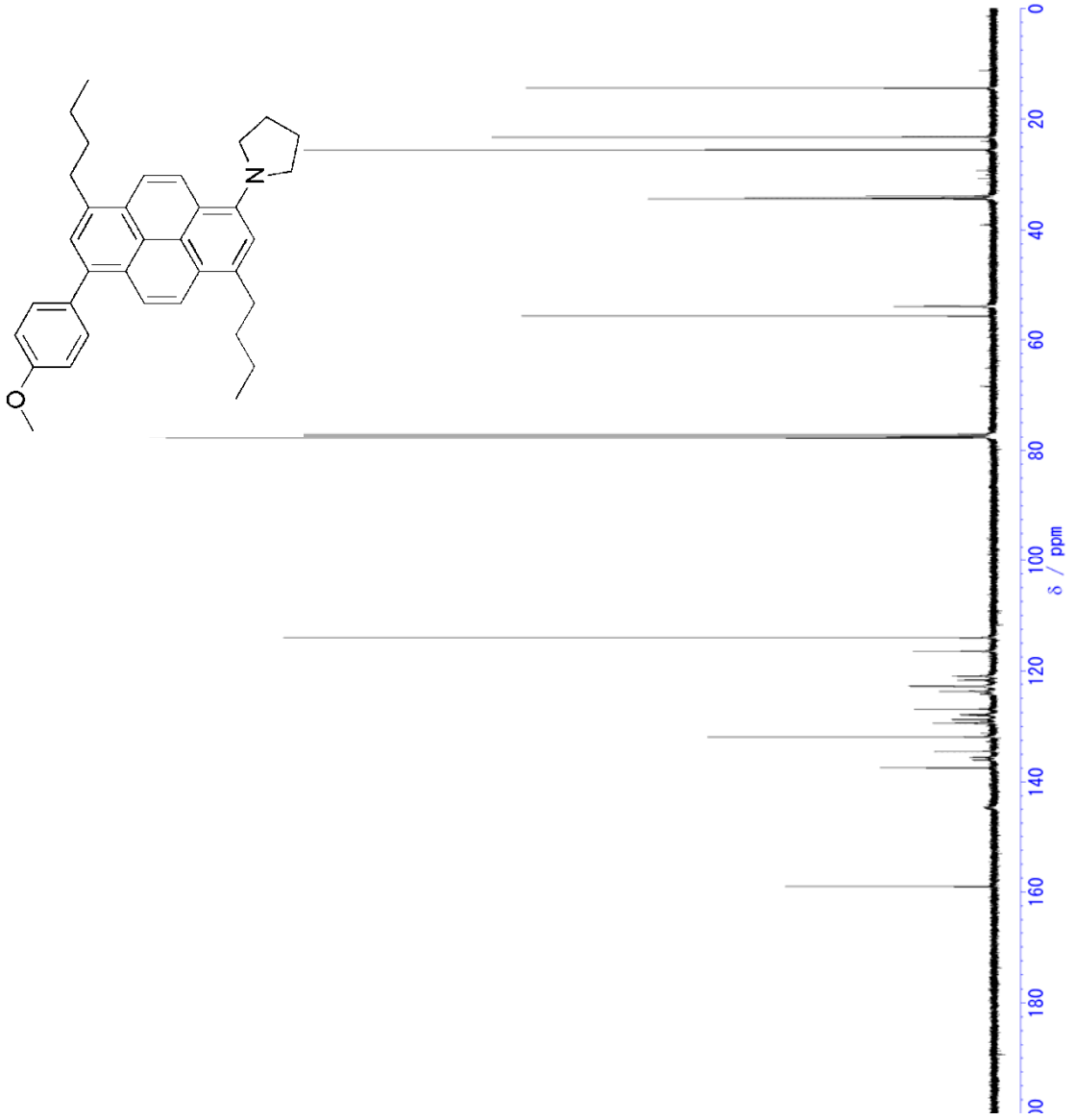


Table 2, entry 6: ^{1}H NMR spectrum

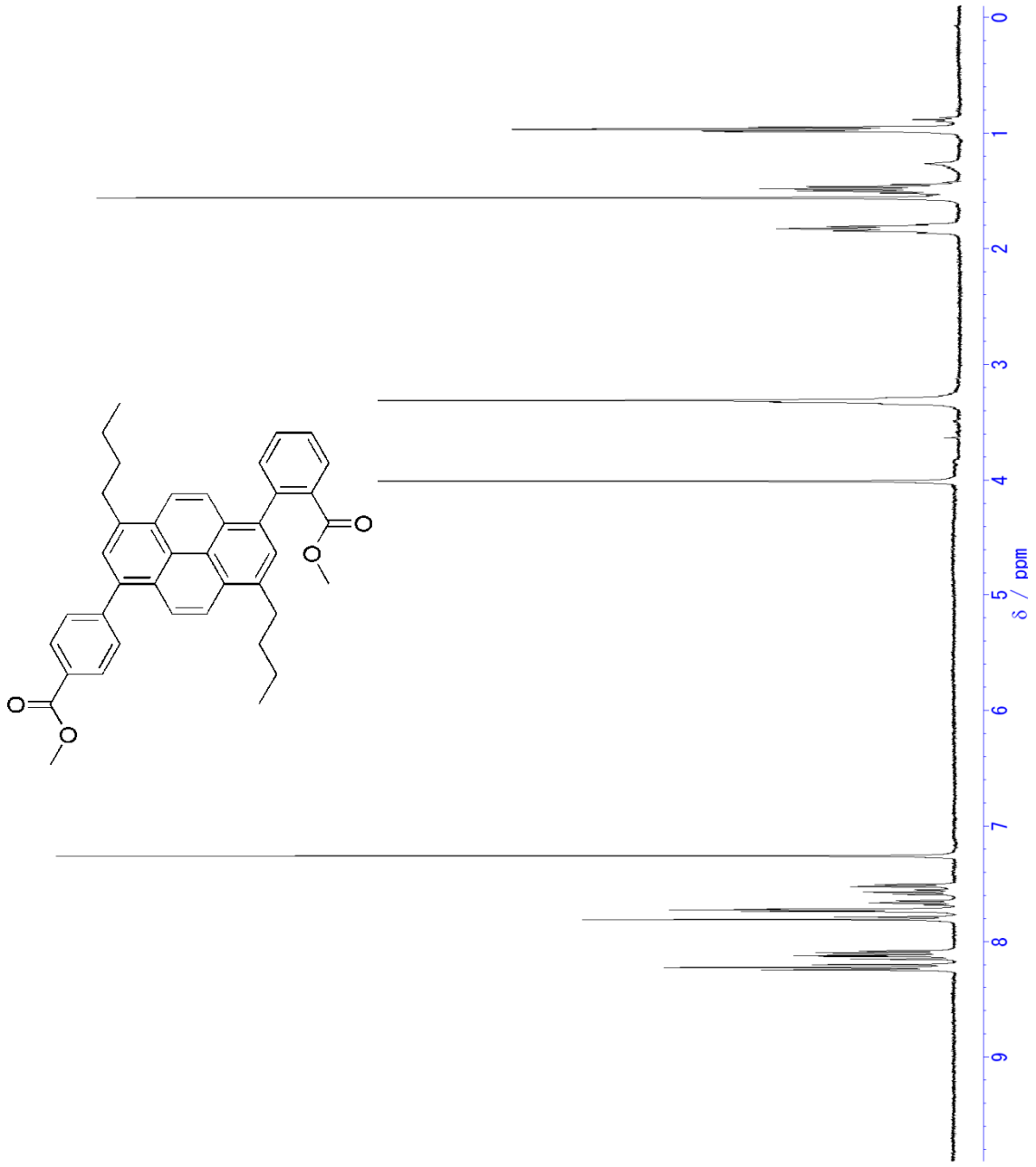


Table 2, entry 6: ^{13}C NMR spectrum

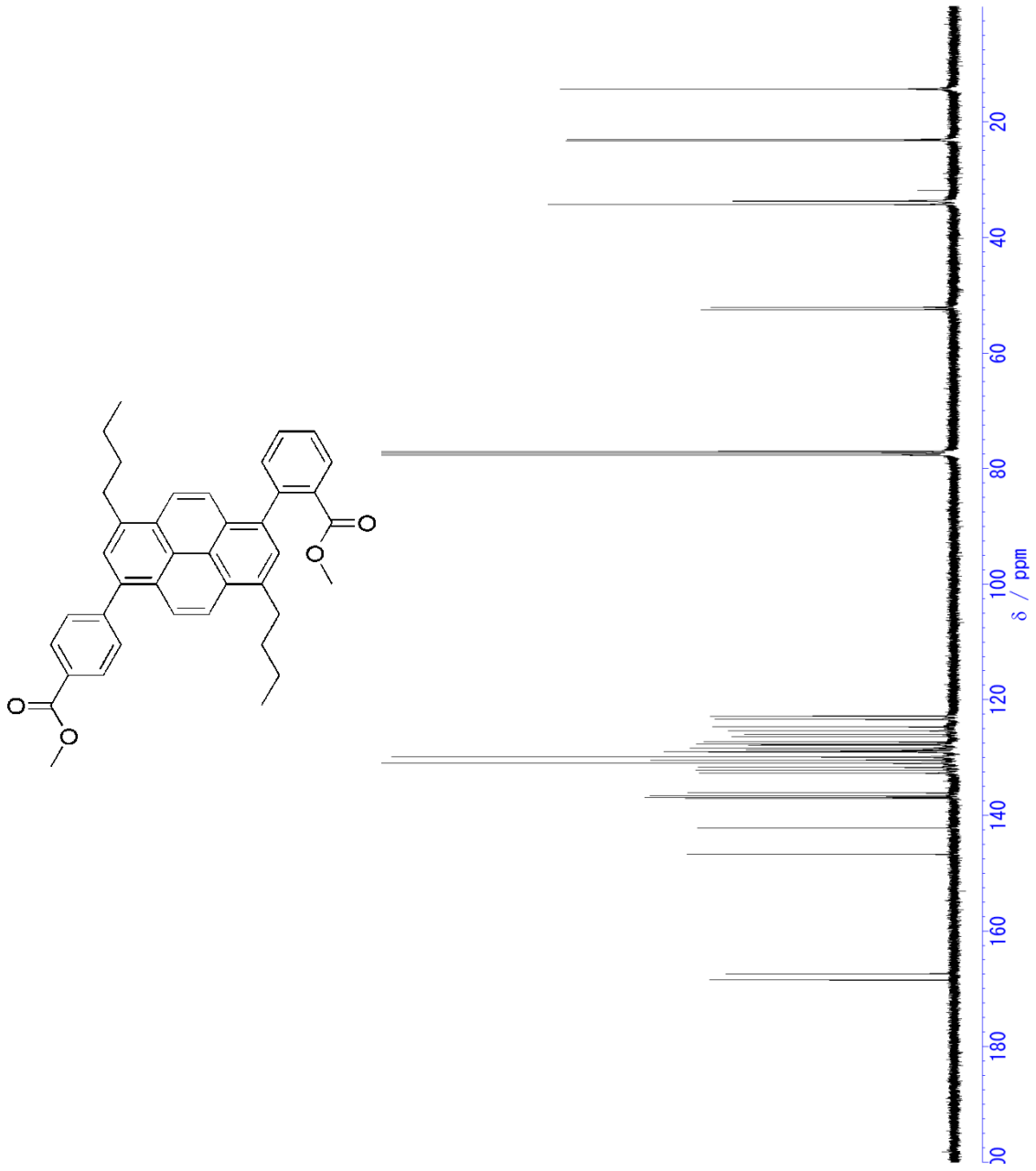


Table 2, entry 7: ^{1}H NMR spectrum

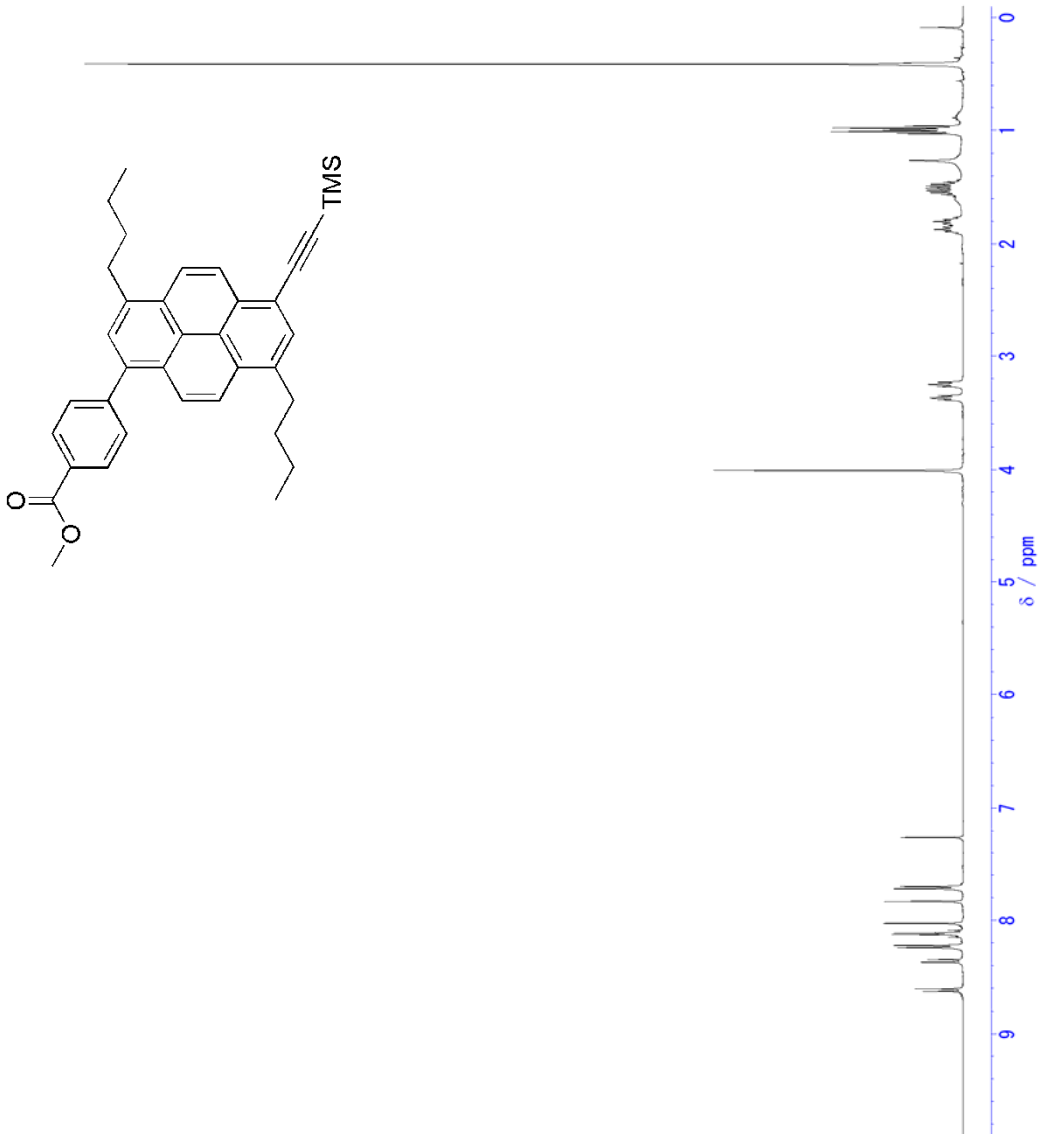


Table 2, entry 7: ^{13}C NMR spectrum

Table 2, entry 8: ^{1}H NMR spectrum

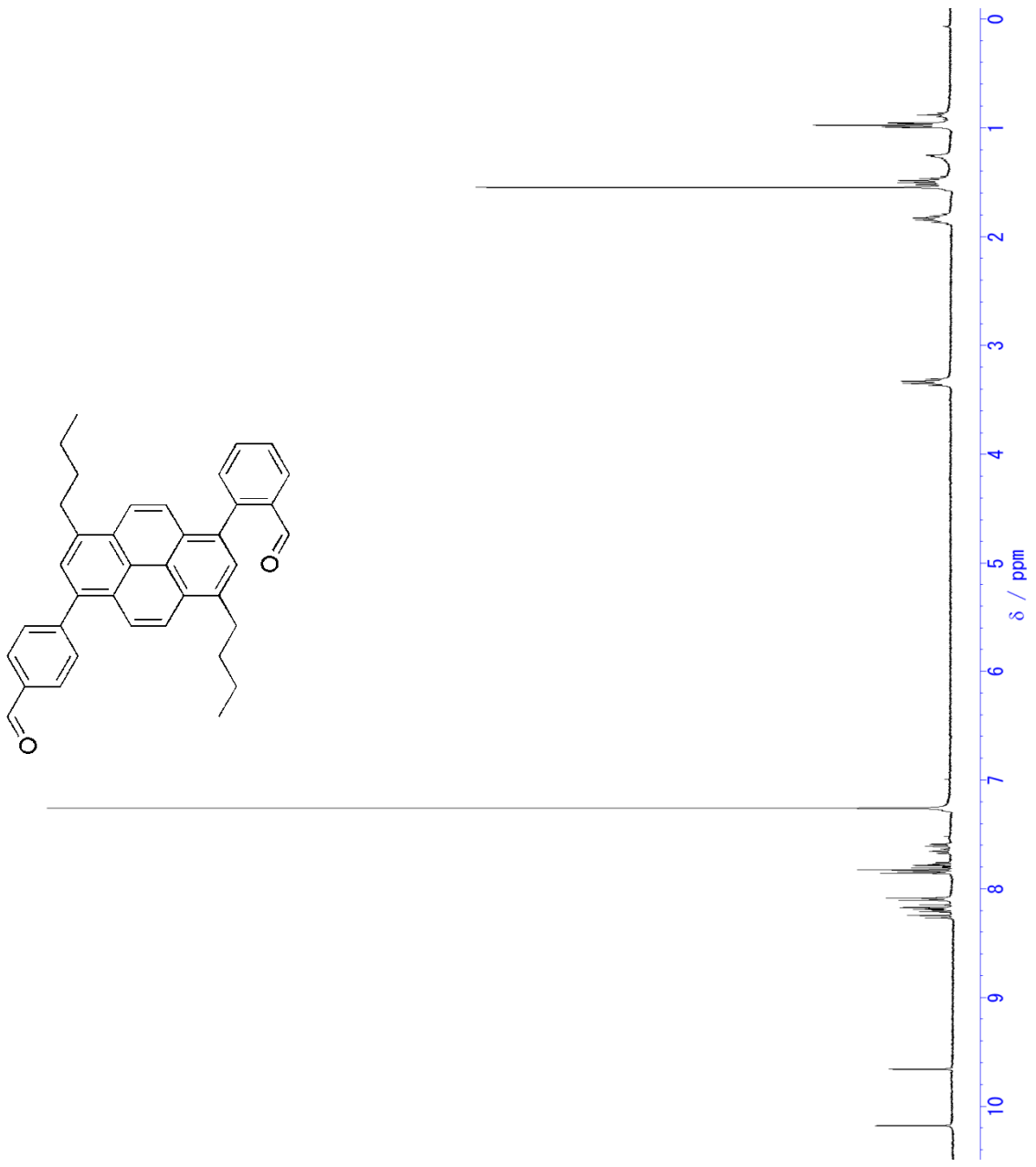


Table 2, entry 8: ^{13}C NMR spectrum

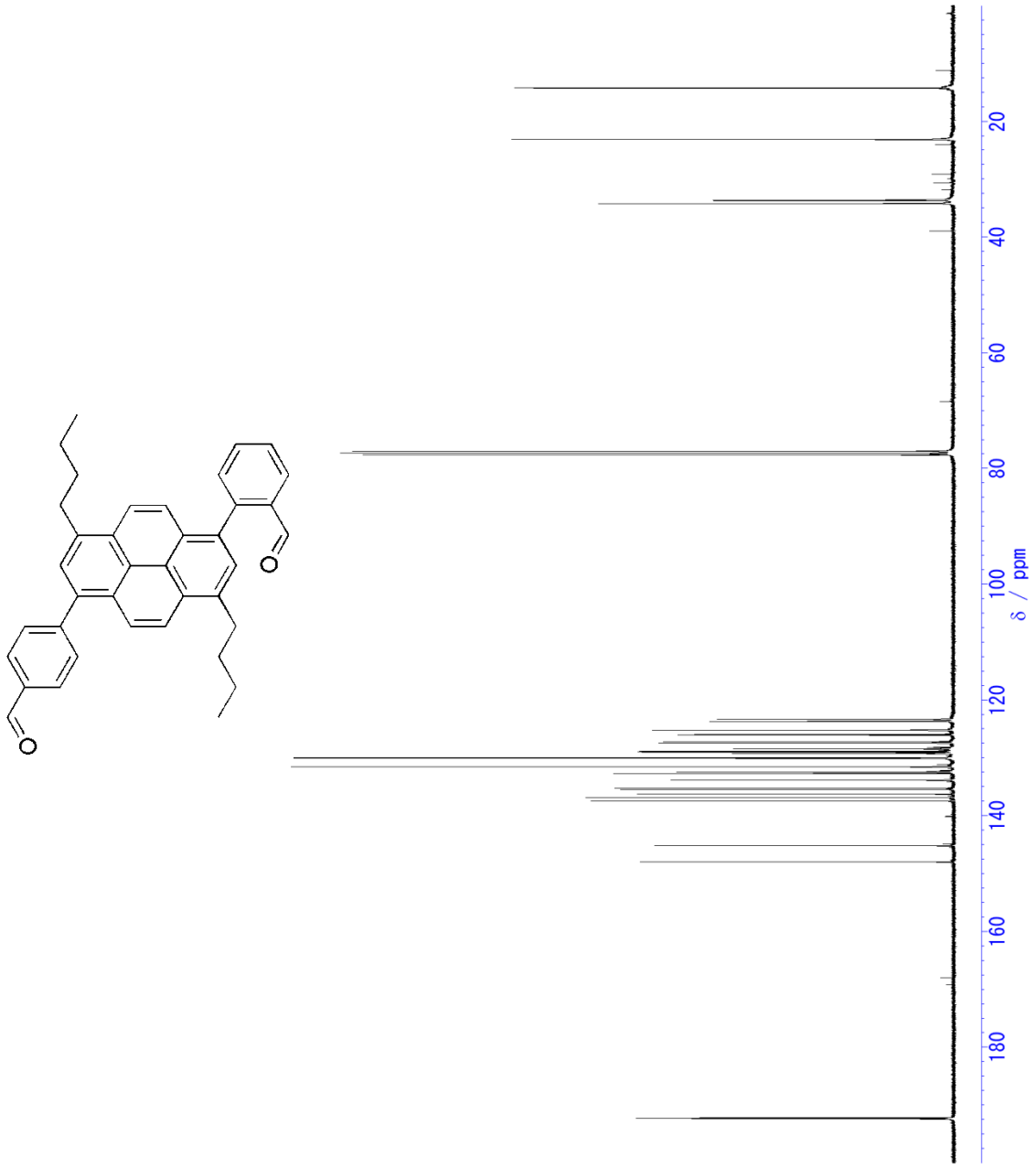


Table 2, entry 9: ^{1}H NMR spectrum

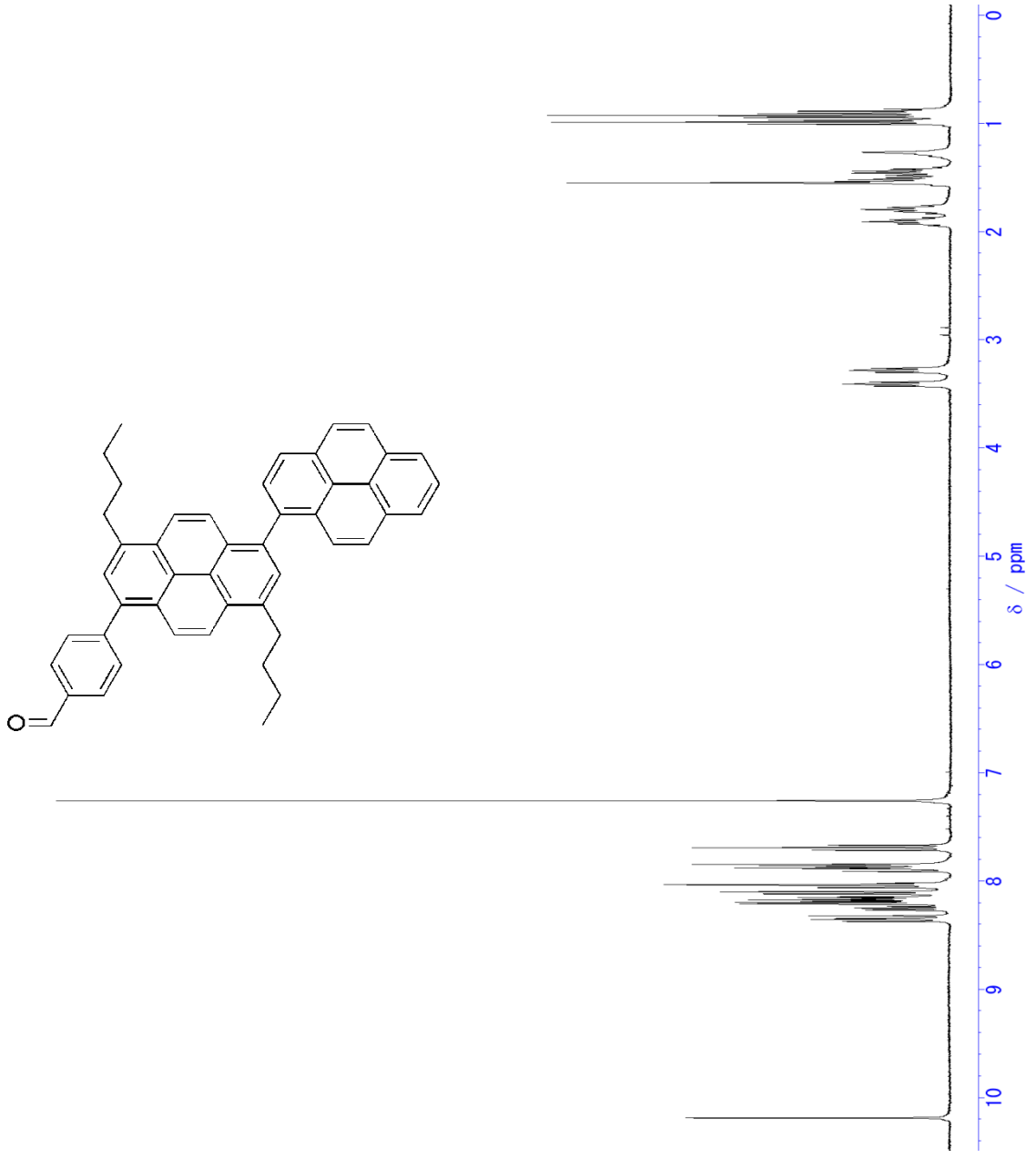


Table 2, entry 9: ^{13}C NMR spectrum

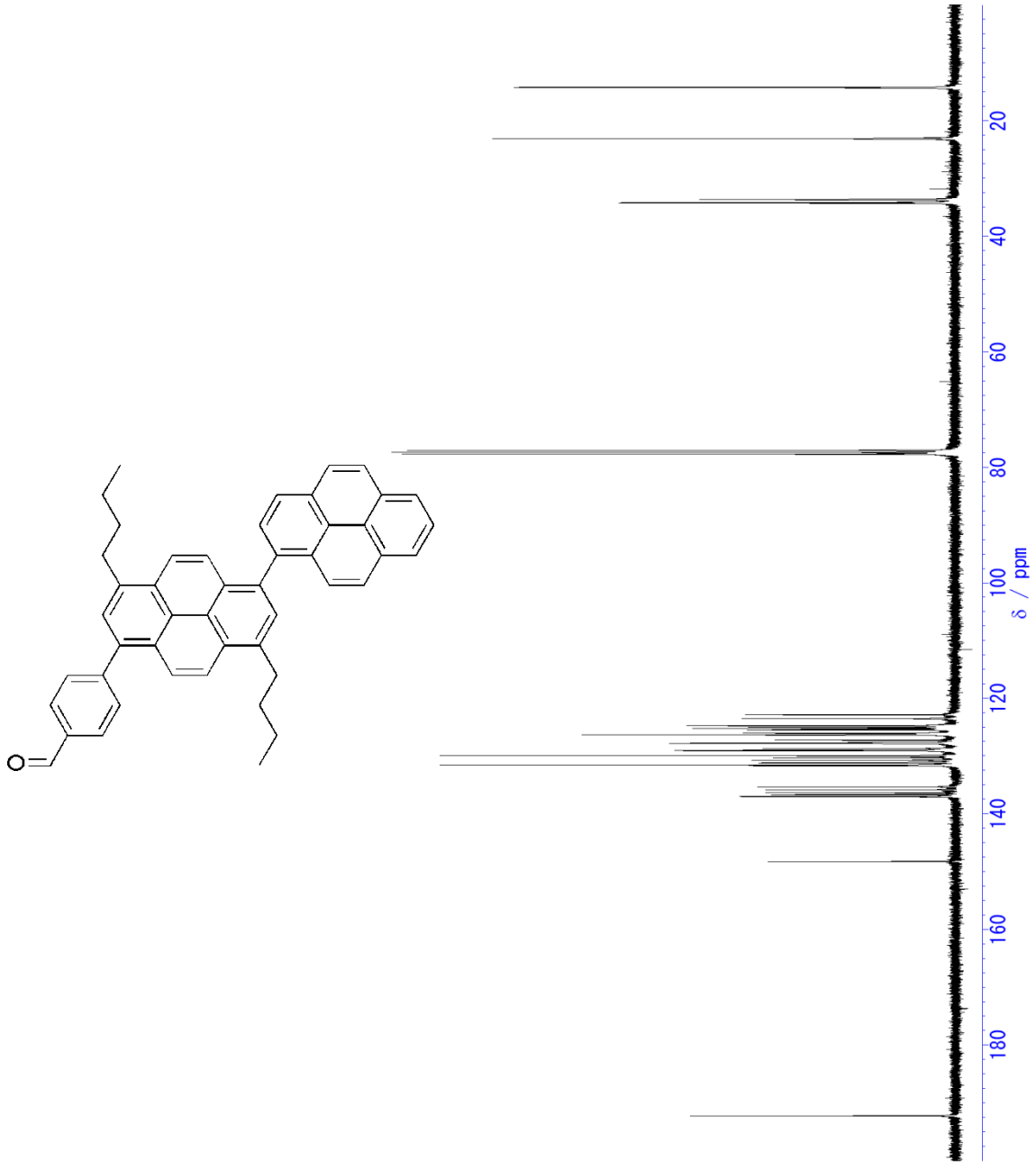
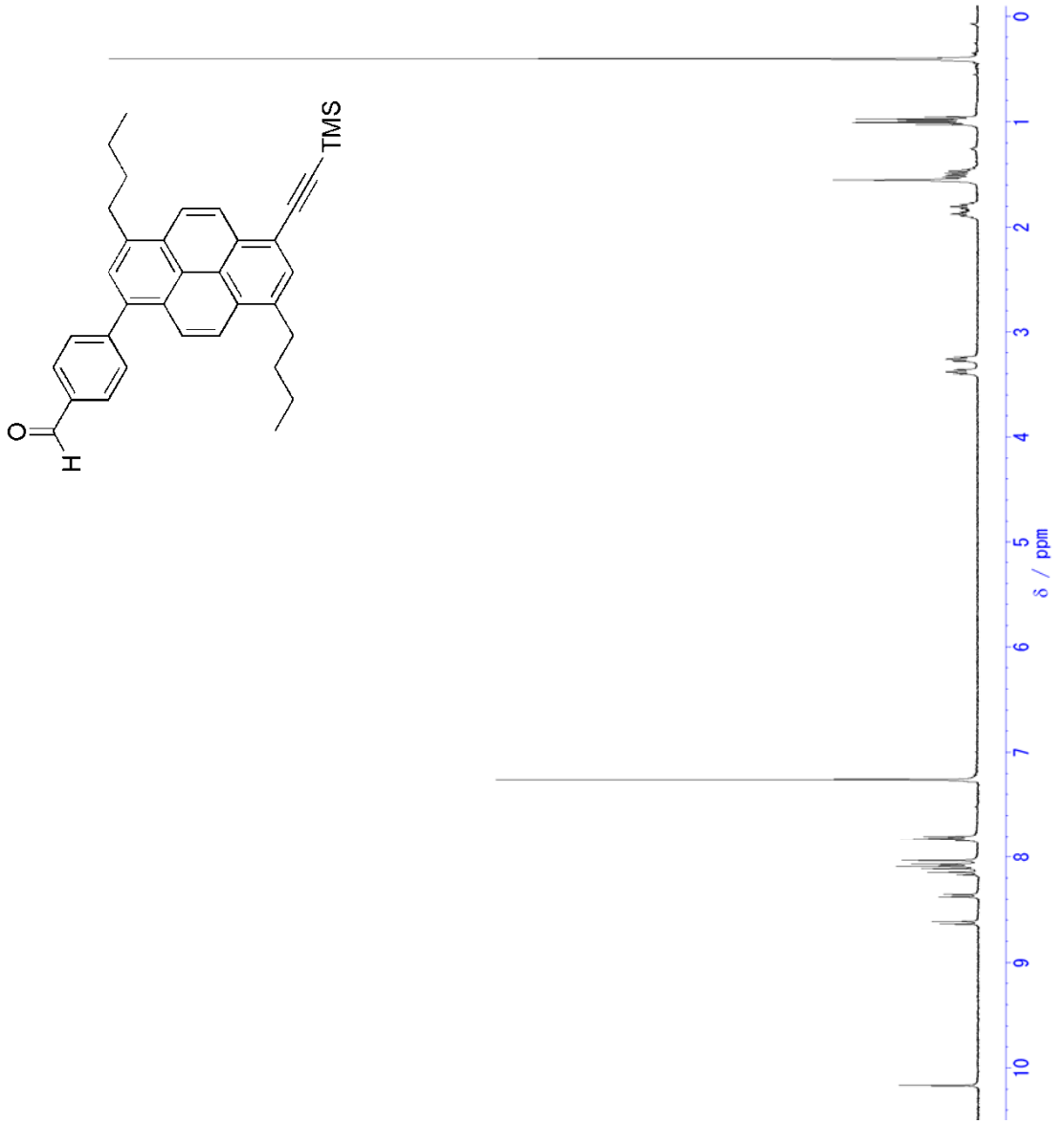


Table 2, entry 10: ^{1}H NMR spectrum



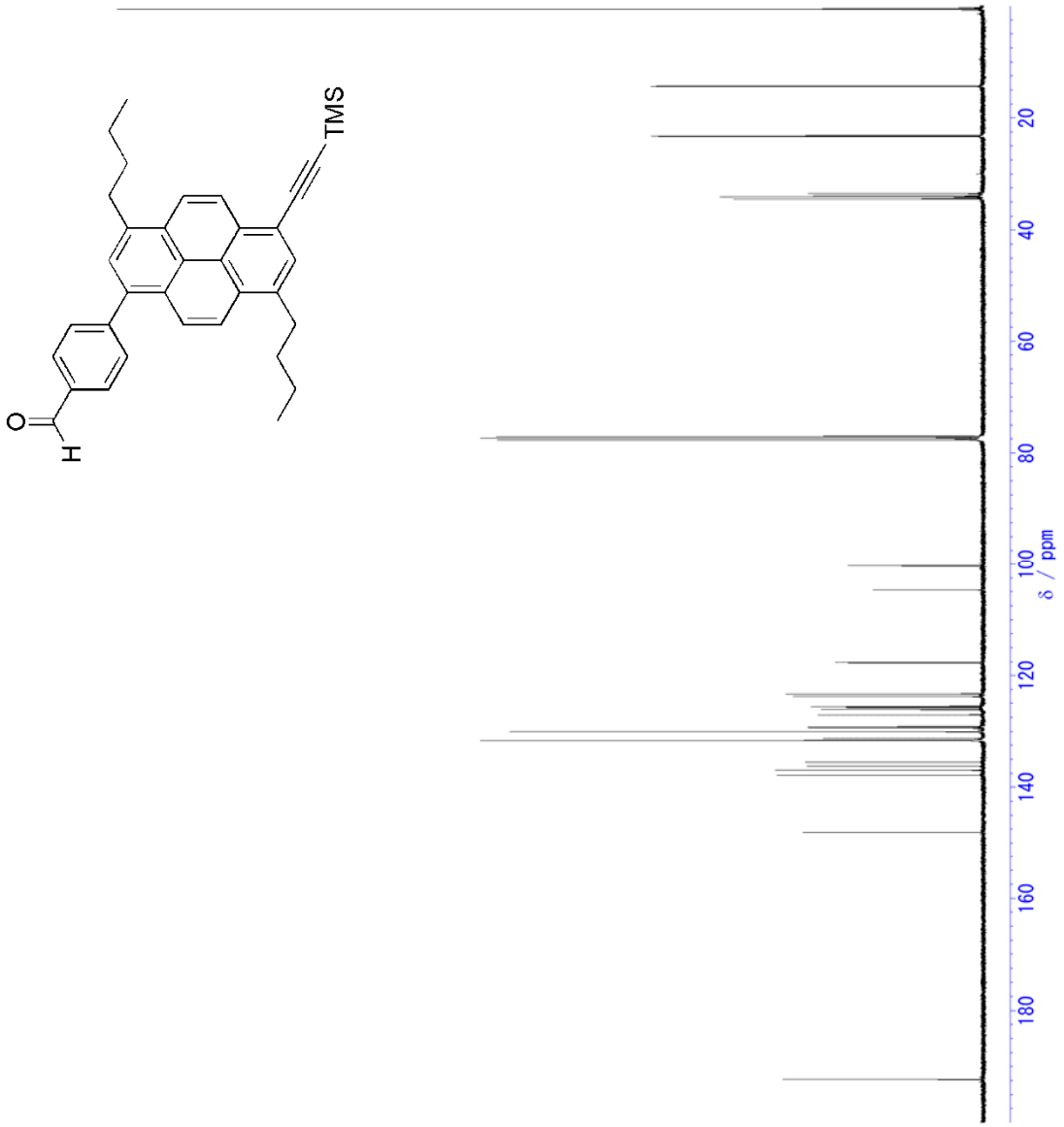


Table 2, entry 10: ^{13}C NMR spectrum