Supporting Information

Synthesis of Oligo(thienylene-vinylene) by Regiocontrolled Deprotonative Cross Coupling

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Experimental Section

General

All the reactions were carried out under nitrogen atmosphere. ^{1}H NMR (300, 400 or 500 MHz) and ^{13}C NMR (100 or 125 MHz) spectra were measured on Varian Gemini 300, JEOL ECZ400 and BRUKER Avance-500. Unless noted, NMR spectra were measured at room temperature. The chemical shift was expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C), $C_2D_5HSO_6$ (2.50 ppm for ^{1}H), DMSO-d_6 (39.52 ppm for ^{13}C) or C_6D_5H (7.16 ppm for ^{1}H) as internal standards. High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254) were used. Purification by HPLC with preparative SEC column (JAI-GEL-2H) was performed by JAI LC-9201. Nickel catalysts, $NiCl_2$(dppp),[1] and palladium catalyst, $PdCl_2(PPh_3)_2$,[2] were prepared according to the literature procedures. For the solvent of the palladium-catalyzed reaction anhydrous THF and toluene were employed. Other chemicals were purchased and used without further purification.

Fluorine-doped SnO_2-coated glass (FTO-glass), which is commonly used as a transparent conductive glass for photoelectrodes and counter electrodes, was purchased from Nippon Sheet Glass Co., Ltd. (TEC™ A9X, sheet resistance ≤ 10 Ω/sq). A TiO_2 paste consisting of nanocrystalline particles (DSL-18NRT) to enable the deposition of a transparent TiO_2 layer and another TiO_2 paste with large ca. 400 nm TiO_2 particles for light scattering (PST-400C) were purchased from Dysol and JGC C&C, Ltd., respectively. Cobalt(II)/(III) bipyridyl BCN_4 was purchased from Dynamo, Inc. Dye solutions with concentrations of 0.3 mM in toluene were used for dye adsorption process.

Synthesis of (*E*)-2-(2-bromoethenyl)-3-hexylthiophene (2a);

2-Formyl-3-hexylthiophene (1a-CHO)[3]: To a 500 mL of two necked reactor equipped with a magnetic stirring bar was added 0.93 M ethylmagnesium chloride in THF (18.0 mmol, 19.4 mL). To the solution was added 2-bromo-3-hexylthiophene (**1a-Br**, 15.0 mmol, 3.708 g) at 0 °C. The reaction was allowed to warm to 60 ºC and stirred for 3 h. The reaction mixture was cooled to 0 °C and then DMF (225 mmol, 17.4 mL) was added dropwise. The reaction mixture was stirred at room temperature for 24 h and then was quenched with 1.0 M hydrochloric acid. The mixture was poured into diethyl ether/water and two phases were separated. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel (hexane/MeOAc = 50/1) to afford 2.68 g of 2-formyl-3-hexylthiophene (**1a-CHO**, pale yellow oil, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.04 (d, *J* = 1.0 Hz, 1H), 7.64 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.01 (d, *J* = 5.0 Hz, 1H), 2.96 (t, *J* = 7.7 Hz, 2H), 1.74-1.56 (m, 2H), 1.48-1.18 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H).

2-(1,1-Dibromoethenyl)-3-hexylthiophene (1a-C=CBr$_2$): To a 500 mL of two necked reactor equipped with a magnetic stirring bar was added **1a-CHO** (10.7 mmol, 2.10 g) and 107 mL of CH_2Cl_2 under nitrogen atomosphere. To the solution was added tetrabromomethane (13.4 mmol, 4.44 g) and triphenylphosphine (26.8 mmol, 7.03 g) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 4 h. The reaction mixture concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel (hexane) to afford 3.39 g of 2-(1,1-dibromoethenyl)-3-hexylthiophene (**1a-C=CBr$_2$**, colorless oil, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.32 (d, *J* = 5.2 Hz, 1H), 6.88 (d, *J* = 5.2 Hz, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.62-1.47 (m, 2H), 1.42-1.19 (m, 6H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.33, 131.36, 129.33, 128.51, 1265.96, 86.38, 31.61, 30.78, 29.02, 28.98, 22.58, 14.08; IR (ATR) 3063, 2928, 2857, 1694, 1598, 1525, 1465, 1377, 1286, 1238, 1207, 1086, 924, 836, 807, 773, 748, 720, 704, 676, 660, 633 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{12}H_{17}Br_2S$ $[M+H]^+$:350.9418; found: m/z 350.9420.

(*E*)-2-(2-bromoethenyl)-3-hexylthiophene (2a): To a 50 mL of two necked tube equipped with a magnetic stirring bar was added **1a-C=CBr$_2$** (9.22 mmol, 3.24 g) and 7.37 mL of DMF under nitrogen atomosphere. To the solution was added triethylamine (46.08 mmol, 6.42 mL) and dimethyl phosphonate (36.9 mmol, 3.38 mL). The reaction mixture stirred overnight. The reaction mixture was quenched with 1.0 M hydrochloric acid. The mixture was poured into diethyl ether/water and two phases were separated. Aqueous was extracted with dichloromethane twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel (hexane) to afford 1.58 g of 2-((*E*)-2-bromoethenyl)-3-hexylthiophene (**2a**, colorless oil, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 13.7 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 1H), 6.83 (d, *J* = 5.2 Hz, 1H), 6.54 (d, *J* = 13.7 Hz, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.65-1.45 (m, 2H), 1.38-1.21 (m, 6H), 0.89 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.94, 133.31, 129.37, 128.87, 123.53, 104.32, 31.60, 30.75, 28.96, 28.31, 22.57, 14.06; IR (ATR) 3063, 2955, 2928, 2857, 2345, 1698, 1524, 1465, 1377, 1237, 1207, 1086, 924, 836, 773, 748, 719, 702, 676, 659, 633 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{12}H_{18}BrS$ [M+H]$^+$:273.0313; found: m/z 273.0302.

General procedure for the reaction of 3-hexylthiophene (1a) with 2-((*E*)-2-bromoethen-1-yl)-3-hexylthiophene (2a): To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added a THF solution of EtMgCl (6.45 mL, 6.0 mmol) and TMP-H (0.08 mL, 0.50 mmol). To the solution was added 3-hexylthiophene (**1a**, 0.90 mL, 5.0 mmol) and stirring was continued under reflux for 24 h. Then, 6.50 mL of THF, (*E*)-2-(2-bromoethenyl)-3-hexylthiophene (**2a**, 1.639 g, 6.0 mmol) and Pd-PEPPSI-IPr (68.0 mg, 0.1 mmol) were added successively. The mixture was allowed to stir at 120 ºC for 24 h. After cooling to room temperature the mixture was quenched by saturated aqueous solution of ammonium chloride (1.0 mL). The solution was poured into the mixture of diethyl ether/water and two phases were separated. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel using hexane as an eluent to afford 1.645g of 3-hexyl-2-(2-(3-hexylthiophen-2-yl)ethen-1-yl)thiophene **3aa** (light yellow oil, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 5.1 Hz, 1H), 7.02 (d, *J* = 15.7 Hz, 1H), 6.93 (d, *J* = 15.7 Hz, 1H), 6.86 (s, 1H), 6.84 (d, *J* = 5.1 Hz, 1H), 6.76 (s, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.68-1.50 (m, 4H), 1.45-1.14 (m, 12H), 0.89 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.75, 142.38, 140.83, 135.88, 129.68, 127.00, 122.65, 121.05, 119.46, 118.62, 31.66, 31.64, 30.85, 30.42, 30.30, 28.97, 28.95, 28.34, 22.59x2, 14.08x2; IR (ATR) 3017, 2955, 2926, 2855, 1525, 1458, 1377, 1303, 1272, 1215, 1085, 934, 843, 814, 724, 694, 670, 659, 646, 627, 614 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{22}H_{33}S_2$ [M+H]$^+$: 361.2024; found: m/z 361.2035.

3-Hexyl-4-((*E*)-2-thienyl)ethen-1-yl)thiophene (3ab): Synthesis of **3ab** was carried out in a similar manner to the synthesis of **3aa** with **1a** (0.090 mL, 0.5 mmol), EtMgCl (0.60 mmol, 0.93 M in THF), TMP-H (0.008 mL, 0.05 mmol), (*E*)-2-(2-bromoethenyl) thiophene **2b**[4] (113.4 mg, 0.6 mmol) and Pd-PEPPSI-IPr (6.80 mg, 0.01 mmol) in toluene (0.65 mL) at 120 ºC for 24 h (light yellow oil, 62.4 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.1 Hz, 1H), 7.03-6.96 (m, 4H), 6.88 (d, *J* = 1.3 Hz, 1H), 6.77 (s, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.63-1.57 (m, 2H), 1.38-1.25 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.85, 142.50, 141.91, 127.61, 127.43, 125.81, 124.11, 121.72, 120.96, 119.04, 31.67, 30.42, 30.32, 28.96, 22.60, 14.10; IR (ATR) 2952, 2917, 2855, 1508, 1471, 1265, 1181, 938, 857, 831, 773, 745, 729, 698, 650 cm^{-1}; HRMS

(DART-ESI+) Calcd for $C_{16}H_{21}S_2$ $[M+H]^+$: 277.1085; found: m/z 277.1083.

3-Hexyl-2-((*E*)-2-thienyl)ethen-1-yl)thiophene (3ba): Synthesis of **3ba** was carried out in a similar manner to the synthesis of **3aa** with thiophene (**1b**, 0.040 mL, 0.50 mmol), EtMgCl (0.60 mmol, 0.93 M in THF), TMP-H (0.008 mL, 0.05 mmol), **2a** (163.9 mg, 0.60 mmol) and Pd-PEPPSI-IPr (6.80 mg, 0.01 mmol) in toluene (0.65 mL) at 120 ºC for 24 h (light yellow oil, 99.5 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 4.5 Hz, 1H), 7.08 (d, *J* = 6.9 Hz, 1H), 7.05-6.95 (m, 4H), 6.85 (d, *J* = 5.1 Hz, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 1.65-1.47 (m, 2H), 1.42-1.19 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.81, 141.06, 135.74, 129.74, 127.58, 125.58, 123.86, 122.83, 120.75, 119.95, 31.63, 30.86, 28.97, 28.35, 22.58, 14.08; IR (ATR) 3018, 2955, 2928, 2856, 1509, 1456, 1441, 1377, 1277, 1240, 1208, 1043, 935, 853, 837, 806, 692, 650 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{22}H_{33}S_2$ $[M+H]^+$: 277.1085; found: m/z 277.1082.

3-Hexyl-2-((*E*)-2-(4-methylthiophen-2-yl)ethen-1-yl)thiophene (3ca): Synthesis of **3ca** was carried out in a similar manner to the synthesis of **3aa** with 3-methylthiophene (**1c**, 0.048 mL, 0.5 mmol), EtMgCl (0.60 mmol, 0.93 M in THF), TMP-H (0.008 mL, 0.05 mmol), **2a** (163.9 mg, 0.6 mmol) and Pd-PEPPSI-IPr (6.80 mg, 0.01 mmol) in toluene (0.65 mL) at 120 ºC for 24 h (light yellow oil, 125.3 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 5.2 Hz, 1H), 7.02 (d, *J* = 15.7 Hz, 1H), 6.92 (d, *J* = 15.7 Hz, 1H), 6.84 (s, 1H), 6.86-6.82 (m, 2H), 6.75 (s, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.23 (s, 3H), 1.64-1.56 (m, 2H), 1.39-1.23 (m, 6H), 0.89 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.49, 140.92, 138.14, 135.83, 129.72, 127.88, 122.71, 120.90, 119.57, 119.29, 31.63, 30.85, 28.98, 28.34, 22.58, 15.63, 14.08; IR (ATR) 3017, 2954, 2927, 2857, 1750, 1527, 1463, 1387, 1270, 1216, 1086, 935, 850, 813, 758, 726, 658 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{17}H_{24}S_2$ $[M+H]^+$: 291.1241; found: m/z 291.1244.

Bis(2,3-(4-hexylthiophen-2-yl)-5-((*E*)-2-(3-hexylthiophen-2-yl)ethen)-1-yl)thiophene (3da): Synthesis of **3da** was carried out in a similar manner to the synthesis of **3aa** with branched terthiophene **1d**[5] (0.21 g, 0.5 mmol), EtMgCl (0.60 mmol, 0.93 M in THF), TMP-H (0.008 mL, 0.05 mmol), **2a** (163.9 mg, 0.6 mmol) and Pd-PEPPSI-IPr (6.80 mg, 0.01 mmol) in toluene (0.65 mL) at 120 ºC for 24 h (light yellow viscous oil, 226.3 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 4.9 Hz, 1H), 7.10 (d, *J* = 16.1 Hz, 1H), 7.07 (s, 1H), 7.04 (s, 1H), 6.98 (s, 1H), 6.96 (d, *J* = 16.1 Hz 1H), 6.91 (s, 1H), 6.90 (s, 1H), 6.89 (t, *J* = 4.9 Hz, 1H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 6.2 Hz, 2H), 1.70-1.60 (m, 6H), 1.45-1.32 (m, 18H), 1.01-0.89 (m, 9H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 143.29, 143.24, 141.41, 140.56, 136.74, 135.63, 134.86, 132.12, 130.44, 129.75, 128.60, 128.57, 128.07, 123.17, 121.10, 120.46, 120.12, 120.03, 31.67, 31.65x2, 30.87, 30.43, 30.41, 30.37, 30.35, 29.00, 28.92x2, 28.38, 22.59x3, 14.09x3; IR (ATR) 2955, 2927, 2855, 1519, 1465, 1377, 1201, 1092, 932, 840, 727, 656 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{36}H_{49}S_4$ $[M+H]^+$: 609.2717; found: m/z 609.2690.

4-(4-Methoxybenzen-1-yl)-2-((*E*)-2-(3-hexylthiophen-2-yl)ethen-1-yl)thiophene (3ea): Synthesis of **3ea** was carried out in a similar manner to the synthesis of **3aa** with 3-(*p*-methoxyphenyl)thiophene[6] (**1e**, 95.1 mg, 0.5 mmol), EtMgCl (0.60 mmol, 0.95 M in THF), TMP-H (0.008 mL, 0.05 mmol), **2a** (163.9 mg, 0.6 mmol) and Pd-PEPPSI-IPr (6.80 mg, 0.01 mmol) in toluene (0.65 mL) at 120 ºC for 24 h (light yellow solid, 134.0 mg, 70%). ^1H NMR (400 MHz, DMSO-d_6) δ 7.65 (s, 2H), 7.63 (s, 2H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.14 (d, *J* = 16.0 Hz, 1H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.99 (s, 1H), 6.97 (s, 1H), 6.94 (d, J = 5.0 Hz, 1H), 3.78 (s, 3H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.54 (quint, *J* = 7.1 Hz, 2H), 1.34-1.22 (m, 6H), 0.85 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.94, 143.26, 142.34, 141.27, 135.70, 129.82, 128.48, 127.34, 124.60, 123.00, 120.75, 120.13, 117.48, 114.16, 55.33, 31.66, 30.90, 29.01, 28.40, 22.60, 14.10; IR (ATR) 3750, 3736, 3649, 2928, 2856, 1751, 1716, 1699, 1652, 1610, 1542, 1526, 1505, 1457, 1438, 1291, 1250, 1179, 1049, 1032, 935, 831, 814, 749, 714 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{23}H_{27}OS_2$ $[M+H]^+$: 383.1503; found: m/z 383.1496; Anal. Calcd for $C_{23}H_{26}OS_2$: C, 72.21; H, 6.85. Found: C, 71.91; H, 6.79

4-Hexyl-2-((*E*)-2-(furan-2-yl)ethen-1-yl)thiophene (3af): Synthesis of **3ag** was carried out in a similar manner to the synthesis of **3aa** with **1a** (0.090 mL, 0.50 mmol), EtMgCl (0.60 mmol, 0.93 M in THF), TMP-H (0.008 mL, 0.05 mmol), (*E*)-2-(2-bromoethenyl)furan[4] (**2f**, 130.0 mg, 0.75 mmol) and Pd-PEPPSI-IPr (6.80 mg, 0.01 mmol) in toluene (0.65 mL) at 60 ºC for 24 h (yellow oil, 48.5 mg, 37%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.8 Hz, 1H), 7.09 (d, *J* = 16.0 Hz, 1H), 6.88 (s, 1H), 6.77 (s, 1H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.40 (dd, *J* = 1.8, 3.3 Hz, 1H), 6.30 (d, *J* = 3.3 Hz, 1H), 2.55 (t, *J* = 7.7 Hz, 1H), 1.60 (m, 2H), 1.31 (m, 6H), 0.89 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.81, 143.85, 142.08, 142.00, 127.52, 120.57, 118.99, 115.62, 111.63, 108.31, 31.66, 30.40, 30.30, 28.96, 22.59, 14.08; IR (ATR) 3902, 3852, 3840, 3804, 3748, 3736, 3672, 3649, 3628, 3610, 2927, 2855, 1751, 1733, 1716, 1698, 1652, 1556, 1512, 1457, 1013, 944, 731 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{16}H_{21}OS$ $[M+H]^+$: 261.1313; found: m/z 261.1317.

(*E*)-2-(2-bromoethenyl)-1,4-dihexyloxybenzene (2g): To a 50 mL of two necked flask equipped with a magnetic stirring bar were added tetrabromomethane (9.13 mmol, 3.02 g) and 14 mL of CH_2Cl_2 under nitrogen atomosphere followed by addition of triphenylphospine (18.3 mmol, 4.79 g) at 0 ºC. After stirring for 30 min, 2-formyl-1,3-dihexyloxybenzene[7] (8.3 mmol, 2.54 g) was added and the mixture was stirred for 3 h at 0 ºC. The reaction mixture was quenched with saturated aqueous solution of sodium chloride and poured into CH_2Cl_2/water to separate into two phases. Aqueous was extracted with CH_2Cl_2 twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was used for the next reaction without further purification.

To a 100 mL of round bottomed flask equipped with a magnetic stirring bar were added the crude oil (8.3 mmol, 3.83 g) and 7.0 mL of DMF. Triethylamine (41.5 mmol, 5.75 mL) and dimethyl phosphonate (33.2 mmol, 3.04 mL) were added to the solution. The reaction mixture stirred at room tempereture overnight. The reaction mixture was quenched with 1.0 M hydrochloric acid and poured into diethyl ether/water to separate into two phases. Aqueous was extracted with dichloromethane twice and the combined organic layer was dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel (hexane/MeOAc = 100/1) to afford 2.65 g of (*E*)-2-(2-bromoethenyl)-1,4-dihexyloxybenzene (**2g**, yellow oil, 83%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.56 (d, *J* = 13.7 Hz, 1H), 6.91 (d, *J* = 13.7 Hz, 1H), 6.82-6.75 (m, 2H), 6.53 (d, *J* = 8.7 Hz, 1H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.55 (t, *J* = 6.4 Hz, 2H), 1.70-1.62 (m, 2H), 1.53-1.45 (m, 2H), 1.44-1.35 (m, 2H), 1.30-1.14 (m, 10H), 0.90 (t, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.04, 150.45, 133.08, 125.58, 115.02, 113.90, 113.41, 107.97, 69.24, 68.71, 31.64, 31.60, 29.37, 29.33, 25.85, 25.76, 22.63x2, 14.07x2; IR (ATR) 2954, 2931, 2859, 1601, 1576, 1495, 1468, 1432, 1389, 1312, 1280, 1222, 1173, 1120, 1031, 942, 869, 851, 801, 726 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{20}H_{32}BrO_2$ $[M+H]^+$:383.1580; found: m/z 383.1568.

2-((*E*)-2-(4-Hexylthiophen-2-yl)ethen-1-yl)-1,4-dihexyloxybenzene (3ag): Synthesis of **3ag** was carried out in a similar manner to the synthesis of **3aa** with **1a** (0.048 mL, 0.50 mmol), EtMgCl (0.60 mmol, 0.93 M in THF), TMP-H (0.008 mL, 0.05 mmol), (*E*)-2-(2-bromoethenyl)-1,4-dihexyloxybenzene (**2g**, 230 mg, 0.6 mmol) and Pd-PEPPSI-IPr (6.80 mg, 0.01 mmol) in toluene (0.65 mL) at 120 ºC for 24 h (yellow green oil, 166.5 mg, 71 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (s, 2H), 7.05 (d, *J* = 2.8 Hz, 1H), 6.89 (d, *J* = 1.3 Hz, 1H), 6.84-6.74 (m, 3H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 2.56

(t, *J* = 7.3 Hz, 2H), 1.87-1.72 (m, 4H), 1.66-1.24 (m, 20H), 0.94-0.84 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.16, 150.78, 143.53, 143.23, 127.03, 126.97, 122.91, 122.46, 118.74, 114.16, 113.66, 112.16, 69.32, 68.39, 31.65, 31.60, 30.40, 30.29, 29.46, 29.38, 29.37, 28.94, 25.89, 25.73, 22.60, 22.59, 22.57, 14.04, 13.99x2; IR (ATR) 3749, 2956, 2929, 2858, 1604, 1542, 1496, 1468, 1379, 1286, 1261, 1223, 1043, 956, 846, 799, 730 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{30}H_{47}O_2S$ $[M+H]^+$: 471.3297; found: m/z 471.3297.

2-((*E*)-2-(3-Hexylthiophen-2-yl)ethene-1-yl)-5-((*E*)-2-(4-hexylthiophen-2-yl)ethen-1-yl)thiophene (4): Synthesis of **4** was carried out in a similar manner to the synthesis of **3aa** from **3aa** (180 mg, 0.50 mmol), EtMgCl (0.60 mmol, 0.93 M in THF), TMP-H (0.008 mL, 0.05 mmol), **2a** (163.9 mg, 0.60 mmol) and Pd-PEPPSI-IPr (6.80 mg, 0.01 mmol) in toluene (0.65 mL) at 120 ºC for 24 h (yellow viscous oil, 215.5 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 5.1 Hz, 1H), 7.00 (d, *J* = 15.7 Hz, 1H), 6.99 (d, *J* = 15.7 Hz, 1H), 6.91 (d, *J* = 15.7 Hz, 1H), 6.89 (d, *J* = 15.7 Hz, 1H), 6.87 (s, 1H), 6.85 (d, *J* = 5.2 Hz, 1H), 6.77 (s, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.74-1.48 (m, 6H), 1.45-1.17 (m, 18H), 1.02-0.77 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.92, 142.50, 141.84, 141.18, 139.89, 136.01, 134.93, 129.82, 129.02, 127.09, 122.93, 121.00, 120.82, 119.91, 119.28, 118.85, 31.69, 31.67, 31.66, 30.91, 30.73, 30.44, 30.32, 29.03, 28.98, 28.97, 28.41, 28.30, 22.62, 22.61, 22.59, 14.12, 14.10, 14.09; IR (ATR) 3016, 2953, 2926, 2855, 1537, 1519, 1462, 1454, 1433, 1415, 1377, 1266, 1217, 930, 843, 812, 724, 698, 671, 659, 648 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{39}H_{49}S_3$ $[M+H]^+$: 553.2996; found: m/z 553.29993.

(*E*)-1-(3-Hexyl-5-((*E*)-(2-hexylthiophen-2-yl)ethen-1-yl)thiophen-2-yl)-2-((*E*)-(4-hexyl-5-(4-hexylthiophen-2-yl)ethen-1-yl)ethen-1-yl)-thiophen-2-yl)ethene (5): Synthesis of **5** was carried out in a similar manner to the synthesis of **3aa** from **4** (259.5 mg, 0.469 mmol), EtMgCl (0.563 mmol, 0.93 M in THF), TMP-H (0.00791 mL, 0.0469 mmol), **2a** (153.8 mg, 0.563 mmol) and Pd-PEPPSI-IPr (6.37 mg, 0.00938 mmol) at 120 ºC for 24 h (dark red solid, 203.7 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 5.1 Hz, 1H), 7.00 (d, *J* = 15.5 Hz, 1H), 6.99 (d, *J* = 15.5 Hz, 1H), 6.96 (d, *J* = 15.5 Hz, 1H), 6.94-6.86 (m, 3H), 6.87 (s, 1H), 6.85 (d, *J* = 5.1 Hz, 1H), 6.80-6.74 (brs, 3H), 2.74-2.51 (m, 8H), 1.73-1.49 (brs, 8H), 1.46-1.18 (br, 24H), 1.08-0.75 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.95, 142.51, 142.17, 141.97, 141.25, 140.15, 140.01, 136.02, 135.16, 135.08, 129.84, 129.11, 129.09, 127.13, 123.00, 121.05, 120.78, 120.72, 120.01, 119.67, 119.26, 118.89, 31.70, 31.69, 31.68, 31.67, 30.91, 30.76, 30.73, 30.44, 30.33, 29.04, 29.02, 28.98, 28.97, 28.42, 28.34, 28.30, 22.62x2, 22.61, 22.60, 14.13, 14.12, 14.10, 14.09; IR (ATR) 3016, 2956, 2924, 2853, 1563, 1554, 1546, 1536, 1513, 1502, 1493, 1478, 1462, 1453, 1433, 1423, 1415, 1377, 1265, 1239, 1220, 1158, 1091, 1025, 924, 893, 865, 842, 807, 725, 698, 678, 669, 653, 629, 614 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{46}H_{65}S_4$ [M+H]$^+$: 745.3969; found: m/z 745.3944; Anal. Calcd for $C_{46}H_{64}S_4$: C, 74.13; H, 8.66. Found: C, 73.92; H, 8.58.

Procedure for the reaction of 3aa or 4 with 3-bromo-9-ethylcarbazole: The cross coupling of **3aa** or **4** was performed according to literature procedure.[8] To 20 mL Schlenk tube equipped with a magnetic stirring bar was added **3aa** (721.2 mg, 2.0 mmol) at room temperature. To the resulting mixture TMPMgCl·LiCl (2.4 mmol, 0.7 M in THF) was added and stirring was continued for 3 h. Then, THF (1.4 mL), 3-bromo-9-ethylcarbazole (657.9 mg, 2.4 mmol) and Pd-PEPPSI-SIPr (27.2 mg, 0.04 mmol) were added successively. The mixture was allowed to stir at 60 ºC for 24 h. After cooling to room temperature the mixture was quenched by saturated aqueous solution of ammonium chloride (1.0 M, 1.0 mL). The solution was poured into the mixture of diethyl ether/water and two phases were separated. The aqueous phase was extracted with diethyl ether twice and the combined organic phase was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by chromatography on silica gel (hexanes/EtOAc = 50/1) and preparative HPLC to afford 778.3 mg of **3aa-Cz** (light brown solid, 70%). ^{1}H NMR (400 MHz, DMSO-d_6, 100 ºC) δ 8.40 (s, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.61 (d, J =7.8 Hz, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.31 (s, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 16.0 Hz, 1H), 7.08 (s, 1H), 6.99 (s, 1H), 6.97 (d, J = 16.0 Hz, 1H), 4.45 (q, J = 7.2 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 1.71-1.59 (m, 4H), 1.45-1.29 (m, 15H), 0.93-0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.84, 142.70, 142.58, 142.34, 140.34, 139.44, 134.34, 126.78, 125.93, 125.44, 124.54, 123.79, 123.30, 122.84, 120.52, 120.14, 119.58, 119.03, 118.46, 117.41, 108.65, 108.61, 37.56, 31.70, 31.68, 30.92, 30.45, 30.32, 29.09, 28.98, 28.58, 22.62, 22.61, 14.13, 14.10, 13.79; IR (ATR) 2954, 2927, 2855, 1599, 1491, 1456, 1379, 1346, 1299, 1274, 1232, 1153, 1124, 1088, 931, 841, 800, 745, 727 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{36}H_{44}NS_2$ [M+H]$^+$: 554.2915; found: m/z 554.2921.

4-Cz: To 20 mL Schlenk tube equipped with a magnetic stirring bar was added **4** (331.8 mg, 0.60 mmol) at room temperature. To the resulting mixture TMPMgCl·LiCl (0.72 mmol, 1.0 M in THF) was added and stirring was continued for 3 h. Then, THF (1.06 mL), 3-bromo-9-ethylcarbazole (197.4 mg, 0.72 mmol) and Pd-PEPPSI-SIPr (8.15 mg, 0.012 mmol) were added successively. The mixture was allowed to stir at 60 ºC for 16.5 h. After cooling to room temperature the mixture was quenched by hydrochloric acid (1.0 M, 1.0 mL). The solution was poured into the mixture of chloroform/water and two phases were separated. The aqueous phase was extracted with chloroform twice and the combined organic phase was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by chromatography on silica gel (hexanes/EtOAc = 50/1) and preparative HPLC to afford 192.8 mg of **4-Cz** (dark red viscous oil, 43%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 100 ºC) δ 8.41 (d, *J* = 1.8 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.74 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* =8.2 Hz, 1H), 7.48 (t, *J* = 8.2 Hz, 1H), 7.33 (s, 1H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* =15.6 Hz, 1H), 7.08 (s, 1H), 7.04 (d, *J* = 16.0 Hz, 1H), 7.02 (brs, 1H), 7.00 (brs, 1H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.94 (d, *J* =15.6 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.73-1.57 (m, 6H), 1.41-1.30 (m, 18H), 0.93-0.86 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.91, 142.86, 142.68, 142.57, 141.94, 140.37, 140.26, 139.49, 134.74, 134.48, 128.73, 127.03, 125.96, 125.42, 124.63, 123.81, 123.32, 122.85, 120.82, 120.54, 120.01, 119.86, 119.32, 119.06, 118.77, 117.44, 108.67 108.64, 37.60, 31.74, 31.67x2, 30.96, 30.74, 30.43, 30.31, 29.14, 29.00, 28.97, 28.63, 28.30, 22.65, 22.61x2, 14.16, 14.12, 14.10, 13.81; IR (ATR) 3015, 2954, 2927, 2855, 1597, 1491, 1466, 1379, 1346, 1299, 1232, 1153, 1124, 929, 842, 800, 746, 728 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{48}H_{60}NS_3$ $[M+H]^+$: 746.3888; found: m/z 746.3886.

Procedure for the reaction of TMFN-1 and TMFN-2: To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added $POCl_3$ (89.8 μL, 0.963 mmol) and *N*, *N*-dimethylformamide (DMF, 0.186 mL, 2.41 mmol) at room temperature. To the solution was cooled to 0 ºC and then **3aa-Cz** (444.6 mg, 0.803 mmol) and chloroform (0.784 mL) were added. The reaction was allowed to warm to 65 ºC and stirred for 5.5 h. After cooling to room temperature the mixture was quenched by water. The solution was poured into the mixture of chloroform/water and two phases were separated. The aqueous was extracted with chloroform twice and the combined organic layer was dried over anhydrous sodium sulfate. Removal of the gsolvent left a crude oil, which was used to the next reaction without further purification.

To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added above oil (207.2 mg, 0.356 mmol), acetic acid (1.39 mL), cyanoacetic acid (91.4 mg, 1.06 mmol), acetic ammonium (13.7 mg, 0.178 mmol) and toluene (2.5 mL) at room temperature. The reaction was allowed to warm to 115 ºC and stireed for 14.5 h. After cooling to room temperature the mixture was quenched by saturated aqueous solution of sodium hydrogen carbonate (1.0 mL). The solution was poured into the mixture of chloroform/water and two phases were separated. The aqueous was extracted with chloroform twice and the combined organic layer was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by column chromatography on silica gel (hexane/^{i}PrOAc = 1/1) to afford 218.9 mg of **TMFN-1** (dark purple solid, 93%). ^{1}H NMR (400 MHz, DMSO-d_6, 100 ºC) δ 8.48 (brs, 1H), 8.28 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.64 (dd, *J* = 12.6, 8.2 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.44 (s, 1H), 7.42 (d, *J* = 15.9 Hz, 1H), 7.41 (s, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 15.9 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 1.73-1.57 (m, 4H), 1.43-1.27 (m, 15H), 0.92-0.84 (m, 6H); ^{13}C NMR (100 MHz, DMSO-d_6, 100 ºC) δ 163.29, 154.71, 149.53, 144.74, 144.04, 141.76, 139.87, 139.17, 132.74, 127.79, 127.61, 125.62, 124.81, 124.11, 123.72, 123.21, 122.50, 121.85, 119.96, 118.60, 117.97, 116.75, 116.16, 109.06, 108.77, 96.64, 36.73, 30.42, 30.28, 29.80, 29.70, 27.78, 27.74, 27.65, 27.52, 21.34, 21.27, 13.08, 13.04, 12.94; IR (ATR) 2954, 2927, 2855, 2215, 1676, 1593, 1558, 1497, 1469, 1448, 1409, 1335, 1247, 1232, 1214, 1155, 1124, 1089, 925, 796, 743, 729 cm^{-1}; HRMS (ESI-) Calcd for $C_{40}H_{43}N_2O_2S_2$ [M-H]$^{-}$: 647.2765; found: m/z 647.2744.

TMFN-2: To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added $POCl_3$ (28.9 μL, 0.310 mmol) and DMF (0.60 μL, 0.775 mmol) at room temperature. To the solution was cooled to 0 ºC and then **4-Cz** (192.8 mg, 0.258 mmol) and chloroform (0.34 mL) were added. The reaction was allowed to warm to 70 ºC and stireed for 19 h. After cooling to room temperature the mixture was quenched by water. The solution was poured into the mixture of chloroform/water and two phases were separated. The aqueous was extracted with chloroform twice and the combined organic layer was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was used to the next reaction without further purification.

To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added above oil (125.9 mg, 0.163 mmol), acetic acid (0.64 mL), cyanoacetic acid (41.5 mg, 0.488 mmol), acetic ammonium (6.3 mg, 0.0813 mmol) and toluene (1.5 mL) at room temperature. The reaction was allowed to warm to 115 ºC and stireed for 17.5 h. After cooling to room temperature the mixture was quenched by saturated aqueous solution of sodium hydrogen carbonate (1.0 mL). The solution was poured into the mixture of chloroform/water and two phases were separated. The aqueous was extracted with chloroform twice and the combined organic layer was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by column chromatography on silica gel (hexane/^{i}PrOAc = 1/1) to afford 132.0 mg of **TMFN-2** (black solid, 60%). ^{1}H NMR (400

MHz, DMSO-d_6, 100 ºC) δ 8.44 (s, 1H), 8.28 (s, 1H), 8.23 (d, *J* = 7.3 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.66-7.57 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.39 (m, 3H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.18-6.93 (m, 4H), 4.50-4.40 (m, 2H), 2.82-2.64 (m, 6H), 1.72-1.55 (m, 6H), 1.42-1.25 (m, 21H), 0.92-0.83 (m, 9H); ^{13}C NMR (100 MHz, DMSO-d_6, 100 ºC) δ 163.31, 154.93, 149.56, 144.36, 142.83, 142.51, 142.00, 141.50, 139.85, 139.00, 133.40, 133.15, 128.54, 127.92, 127.75, 125.55, 124.57, 124.33, 123.47, 123.12, 122.48, 121.87, 120.41, 119.94, 119.01, 118.59, 118.53, 116.55, 115.97, 108.97, 108.72, 96.07, 36.70, 30.48, 30.40, 30.27, 29.77, 29.72, 29.57, 27.81, 27.77, 27.68, 27.64, 27.49, 27.26, 21.39, 21.33, 21.26, 13.12, 13.06, 13.02, 12.93; IR (ATR) 2954, 2927, 2854, 2215, 1681, 1599, 1557, 1521, 1494, 1469, 1454, 1406, 1345, 1332, 1248, 1231, 1154, 1124, 1088, 921, 842, 799, 772, 744, 727 cm^{-1}; HRMS (ESI-) Calcd for $C_{52}H_{59}N_2O_2S_3$ [M-H]$^-$: 839.3738; found: m/z 839.3702.

Formation and characterization of DSSC device composed of TMFN-1 and TMFN-2: A FTO-glass was immersed in 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min. The TiO_2 mesoporous layers were prepared on the $TiCl_4$-treated FTO-glass by the screen-printing method. The TiO_2 paste was coated onto the substrate over a 5 mm × 5 mm square area and sintered at 500 °C for 30 min. The optimum TiO_2 layers for the high-efficiency cells were a bilayer composed of a transparent layer and a light-scattering layer with thicknesses of 5 μm and 3 μm, respectively. For optimum TiO_2 layers, a post-$TiCl_4$ treatment was performed, in which the TiO_2 electrodes were immersed in 10 mM aqueous $TiCl_4$ solution for 30 min at 70 °C. After the TiO_2 layers were reheated at 450 °C for 30 min, the layers were immersed into the dye solution for 18 h at 30 °C. The dye-adsorbed TiO_2 electrodes were subsequently used as photoelectrodes. The counter electrodes were prepared by drilling two holes into the FTO-glass substrates for electrolyte injection, followed by the DC sputtering deposition of platinum as a catalyst and heating at 450 °C for 30 min. A 30-μm-thick layer of thermobonding polymer (Surlyn®, DuPont™) was sandwiched between the photoelectrode and counter electrode, and the sandwiched electrodes were sealed by heating. After sealing, the electrolyte was injected between the two electrodes through the hole in the counter electrode; the hole was then sealed with Surlyn® and a cover glass.

The photocurrent–voltage (*I*–*V*) characteristics were measured using an Advantest R6246 DC source/meter combined with a solar simulator (YSS-150A, Yamashita Denso Co.) with AM 1.5G filters. The light intensity of 100 mW cm^{-2} was calibrated with a standard amorphous silicon PV. The aperture cell area was fixed at 0.16 cm^2 by using a photomask on top of the cells. Incident photon-to-electron conversion efficiency (IPCE) spectra were measured with an apparatus composed of a source meter, a light-intensity-controllable monochrometer, and a xenon arc lamp (Bunkokeiki, CEP-99W).

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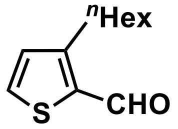
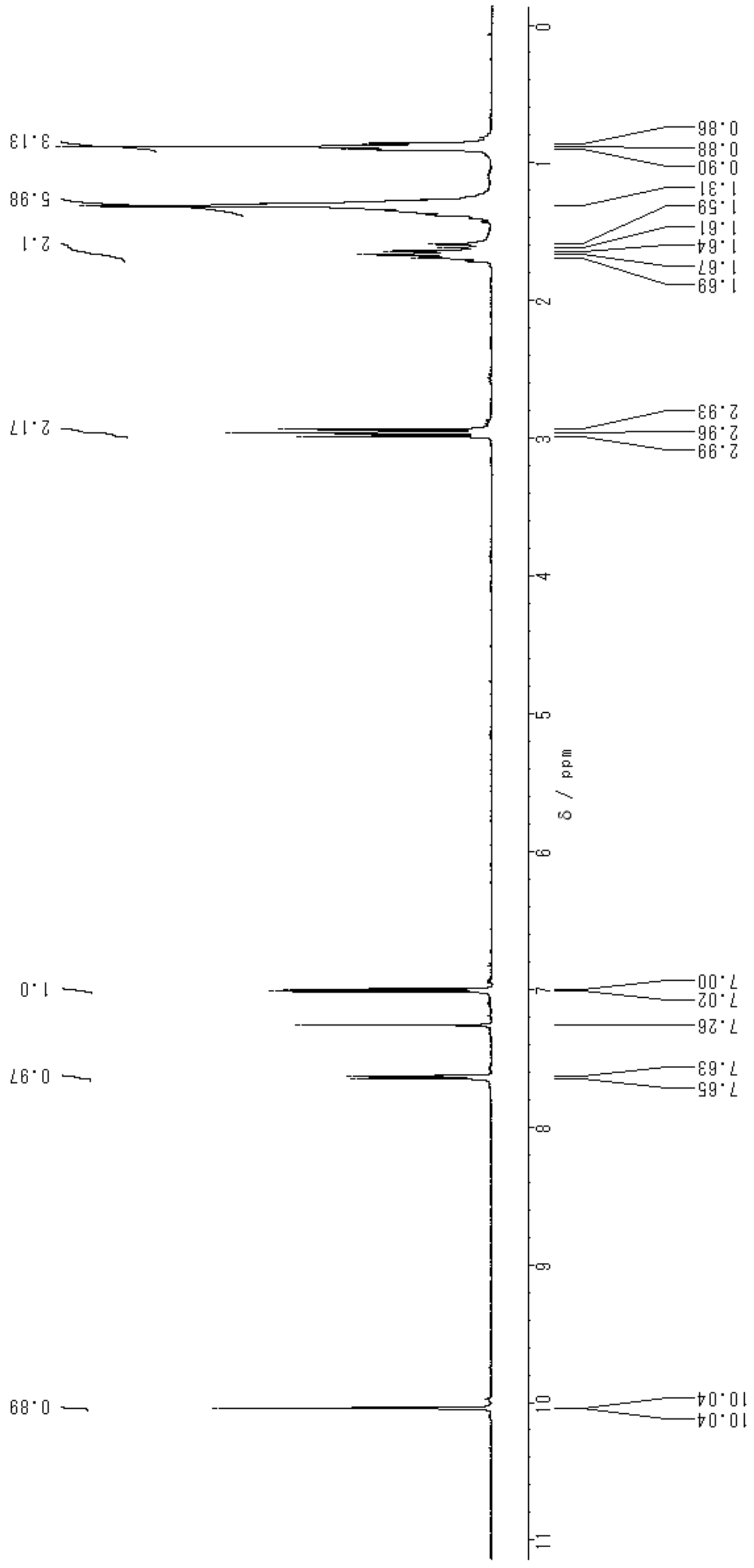
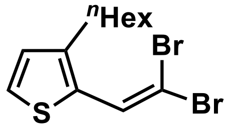
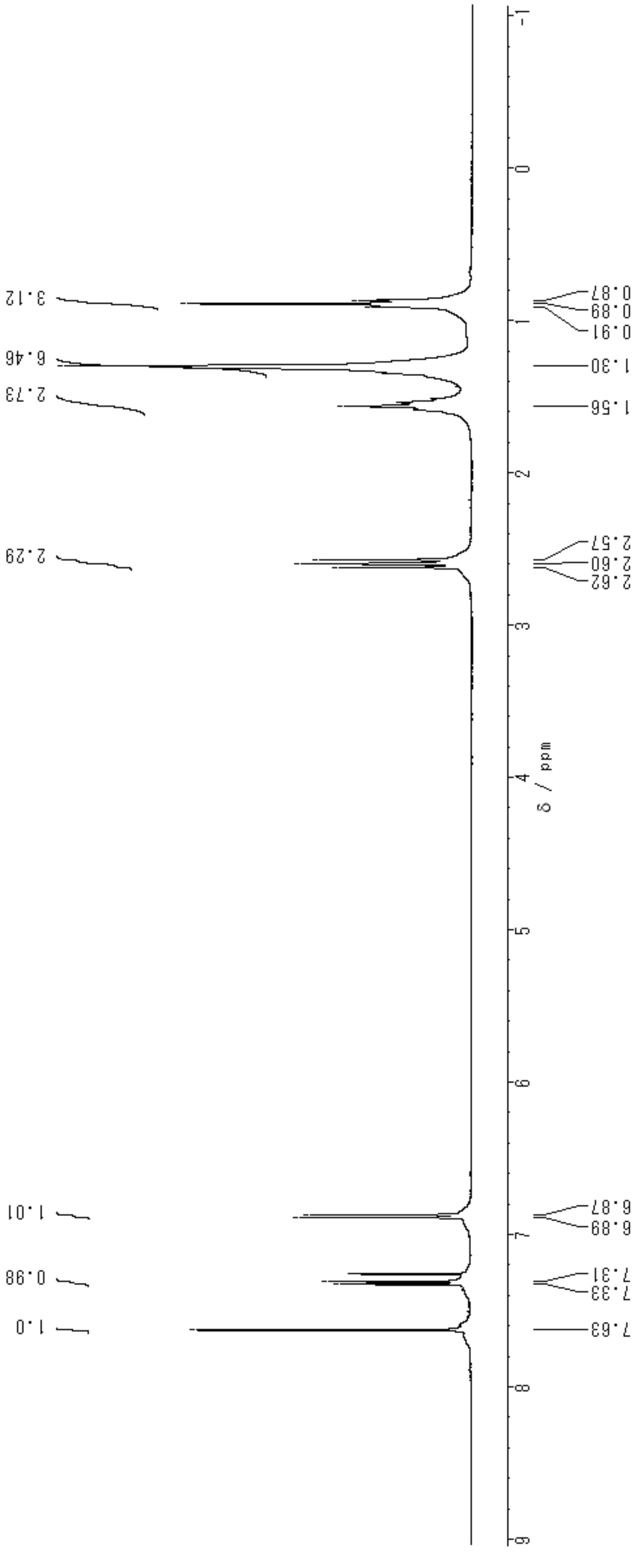
^{1}H NMR spectrum of **1a-CHO**



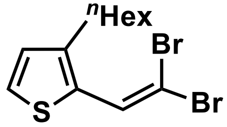


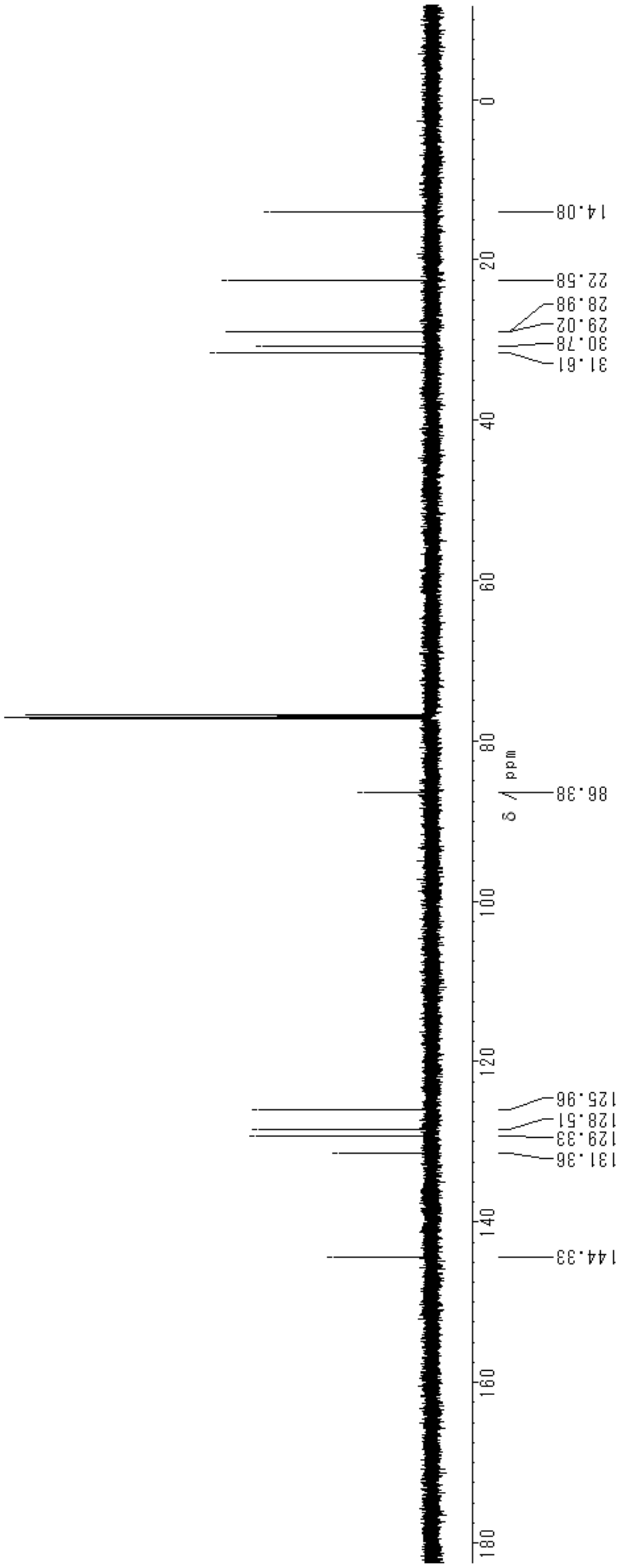
^{1}H NMR spectrum of **1a-C=CBr$_2$**



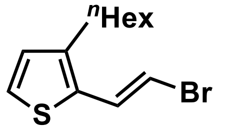


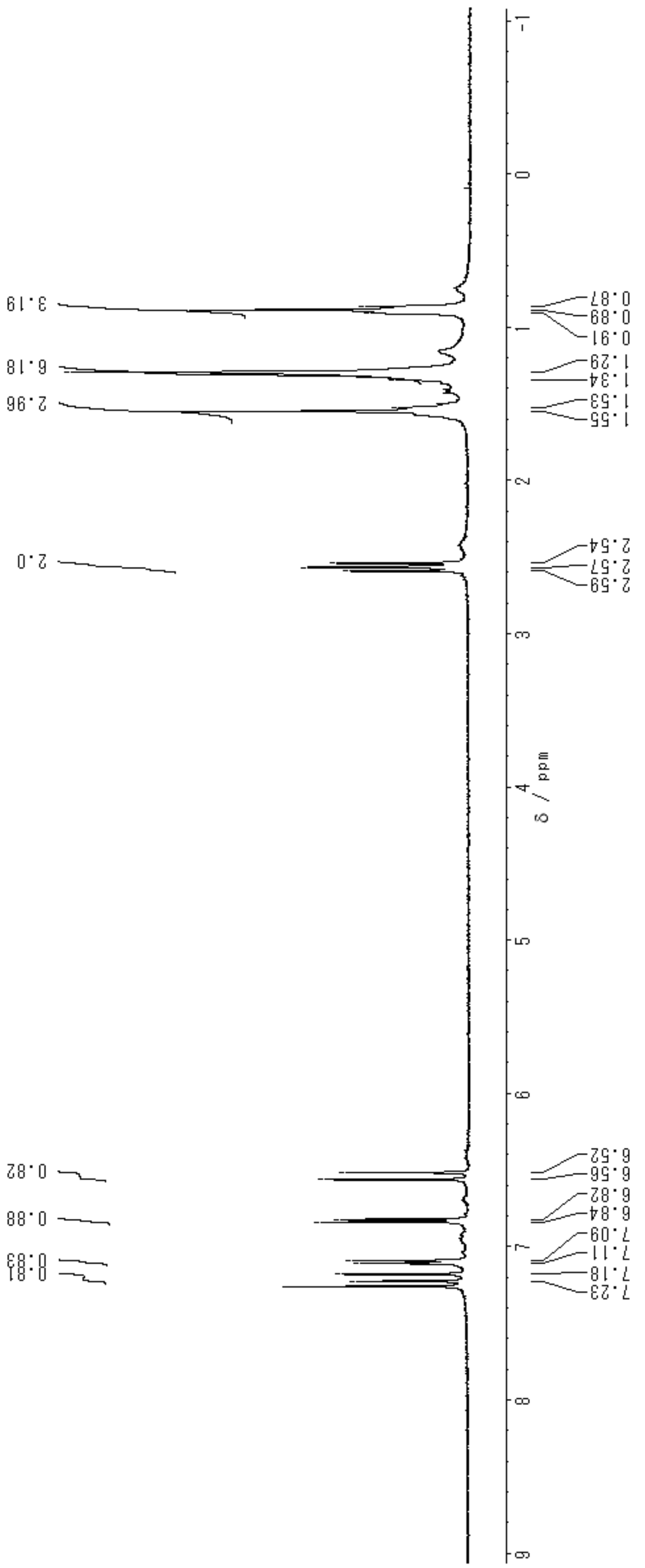
^{13}C NMR spectrum of **1a-C=CBr$_2$**



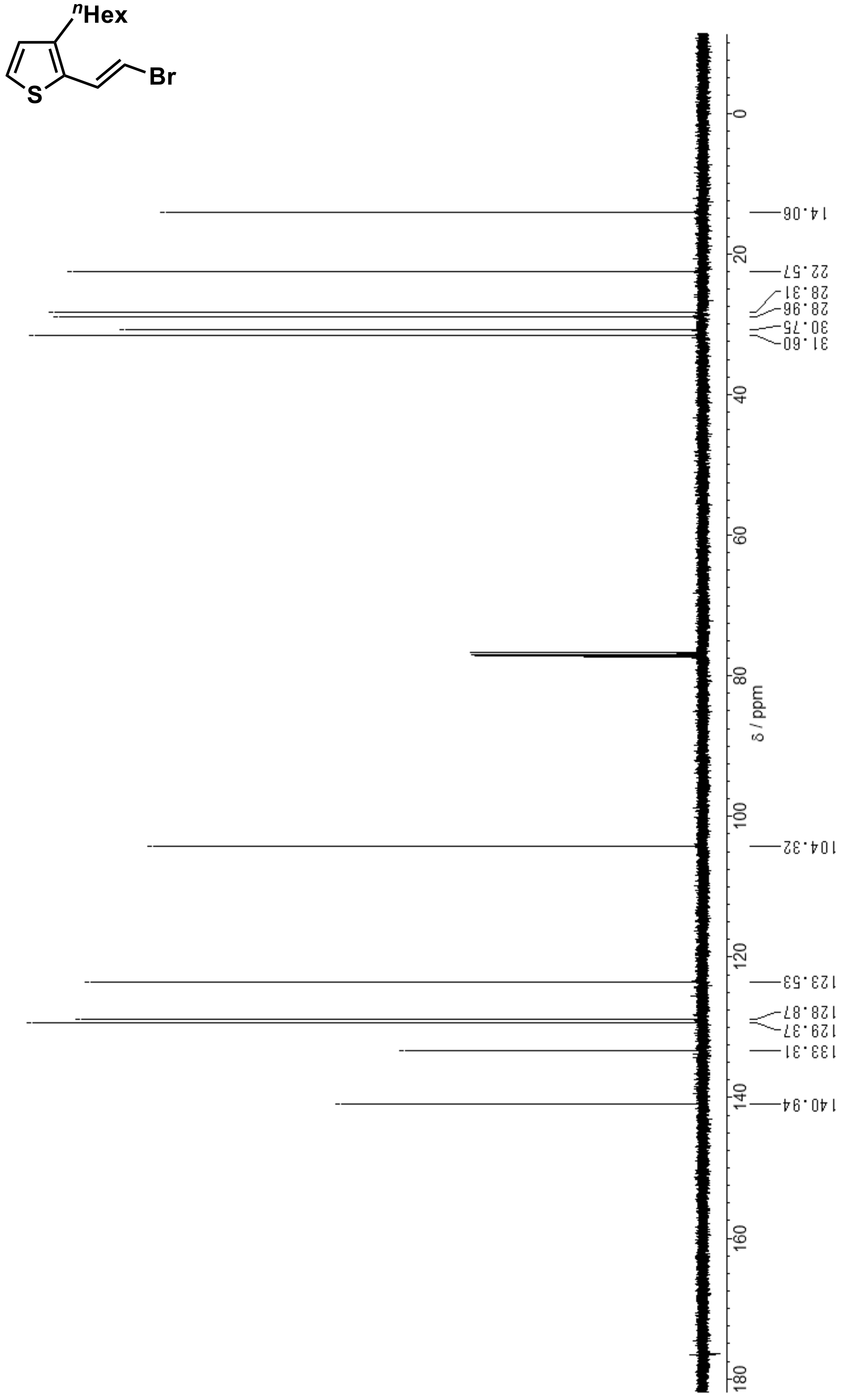


^{1}H NMR spectrum of **2a**

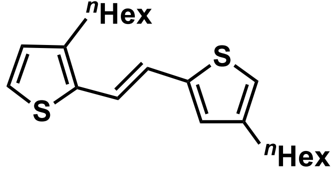


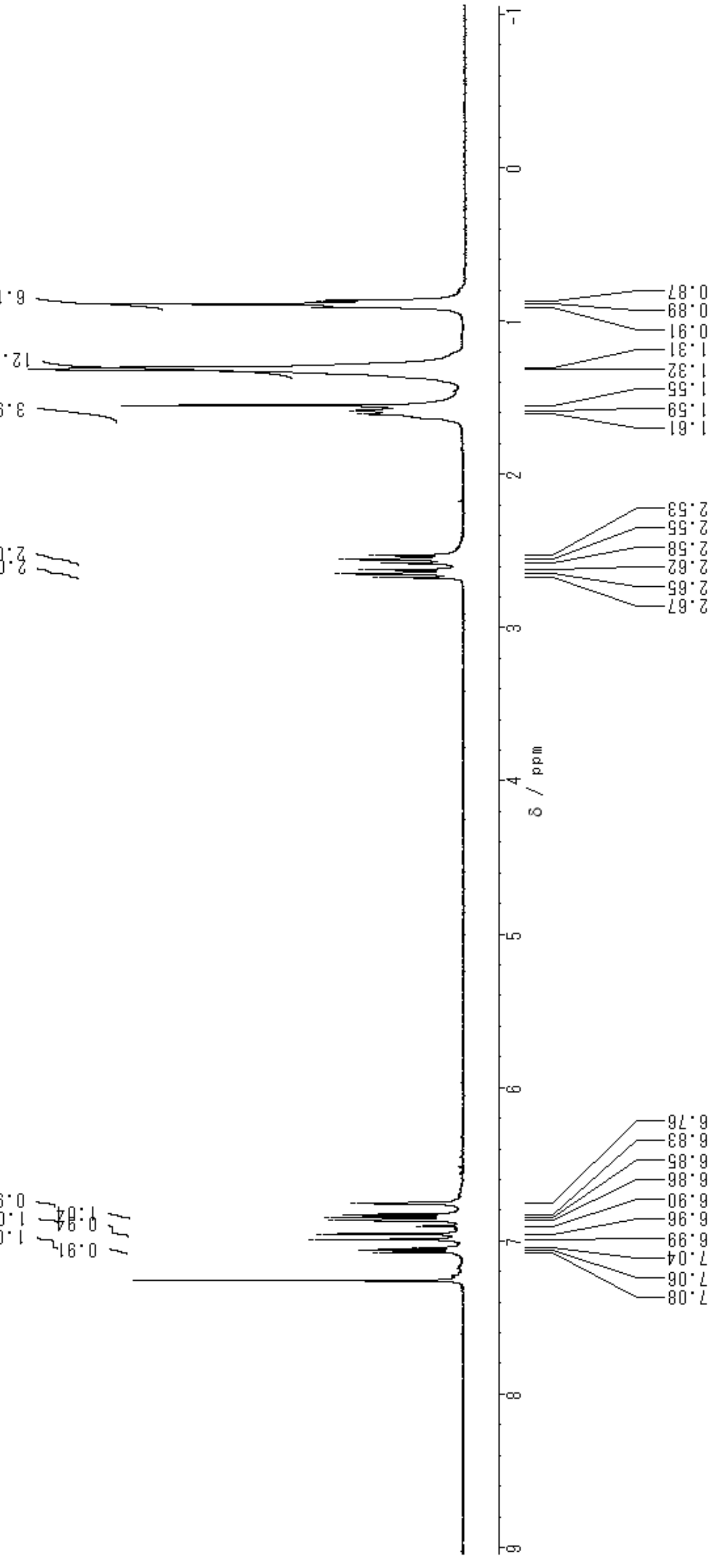


^{13}C NMR spectrum of **2a**

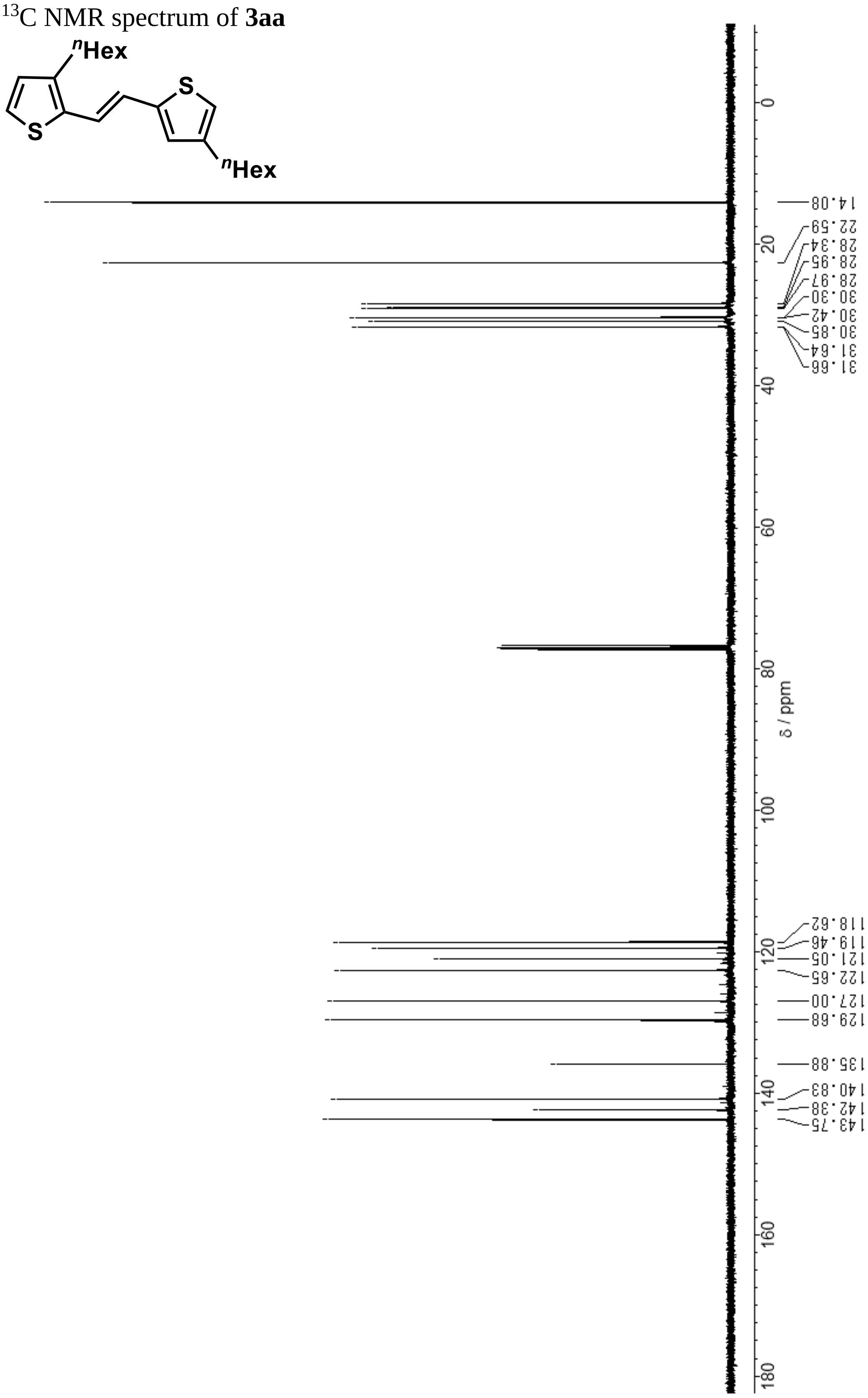


^{1}H NMR spectrum of **3aa**

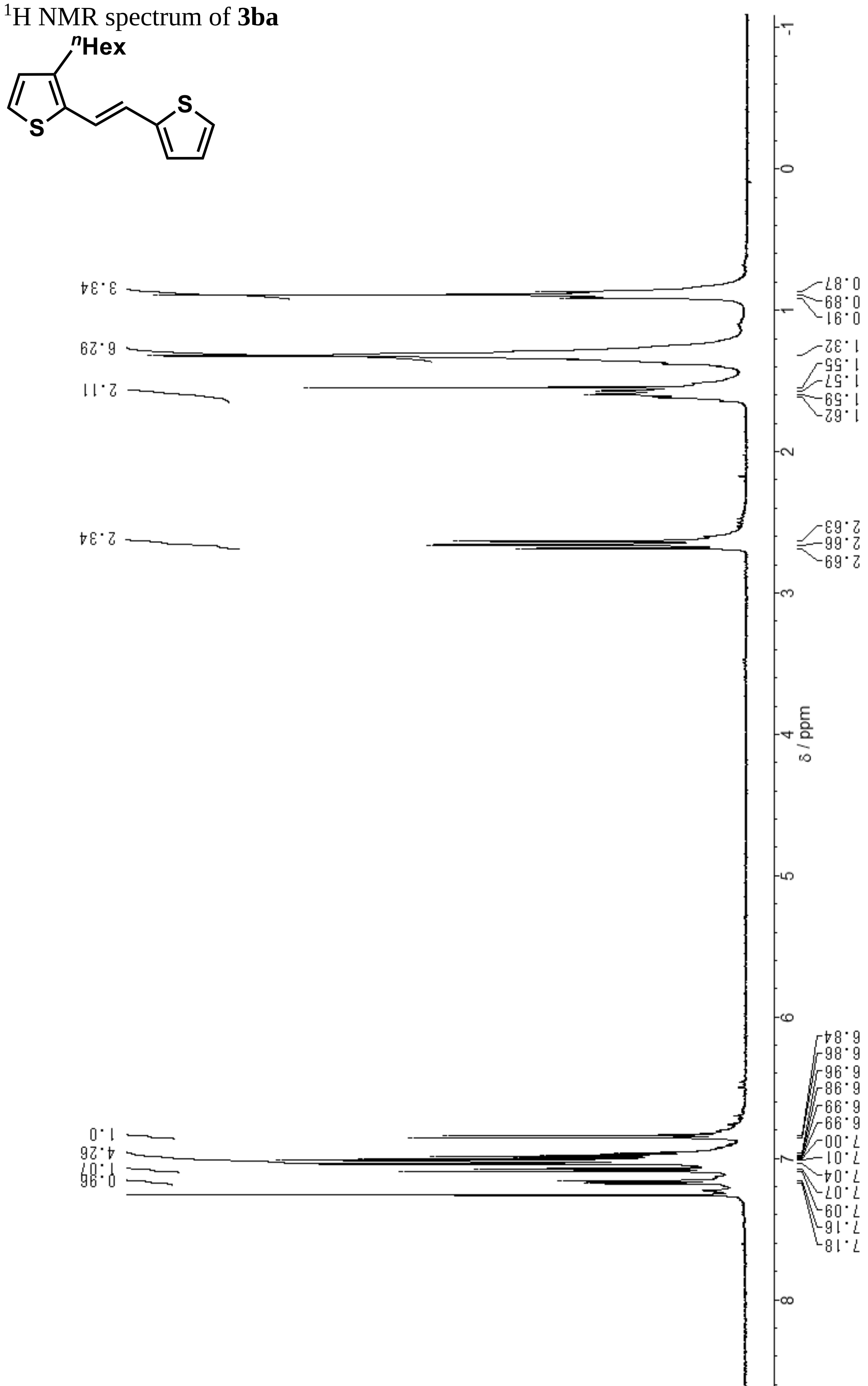




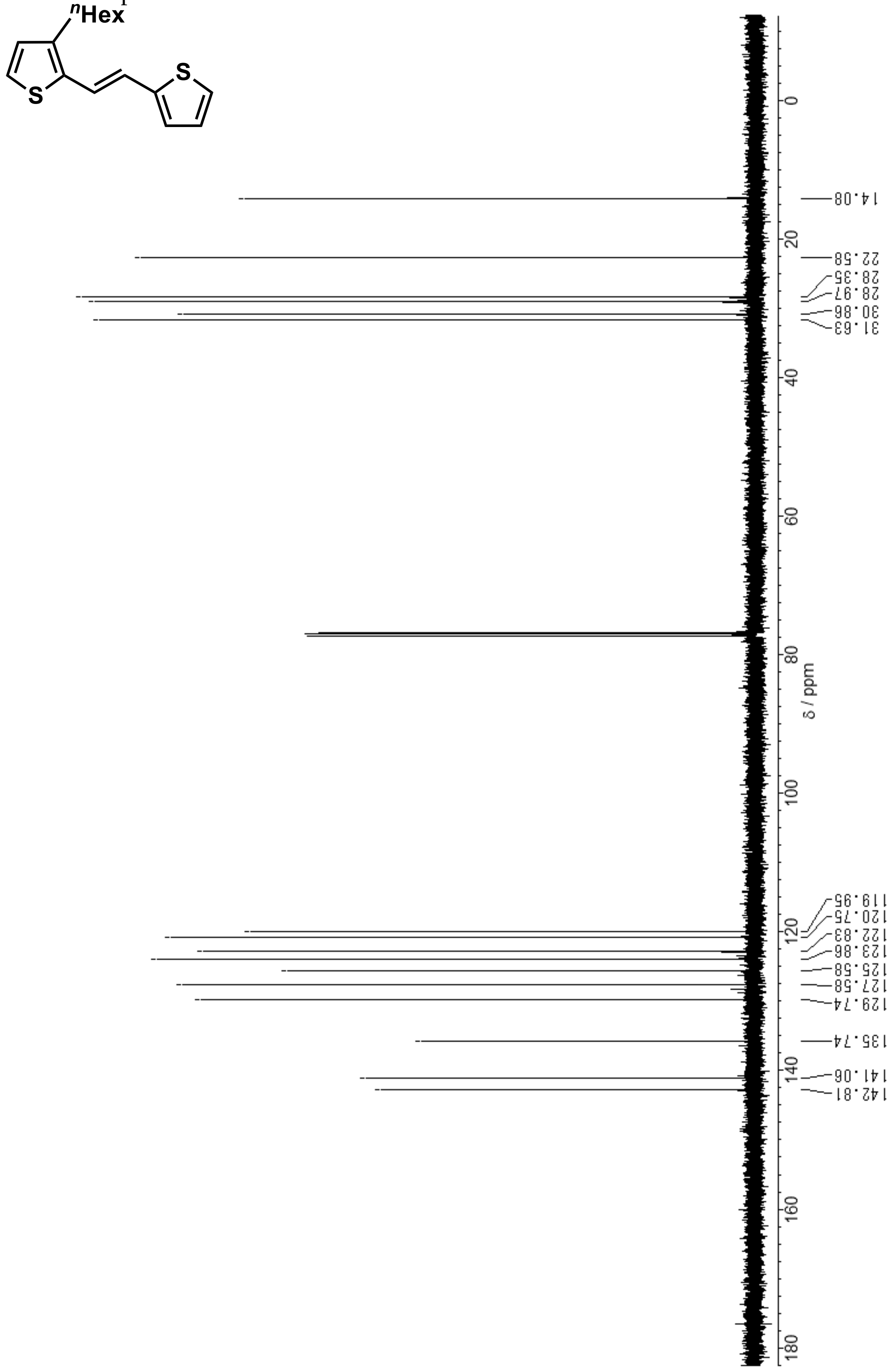
^{13}C NMR spectrum of **3aa**



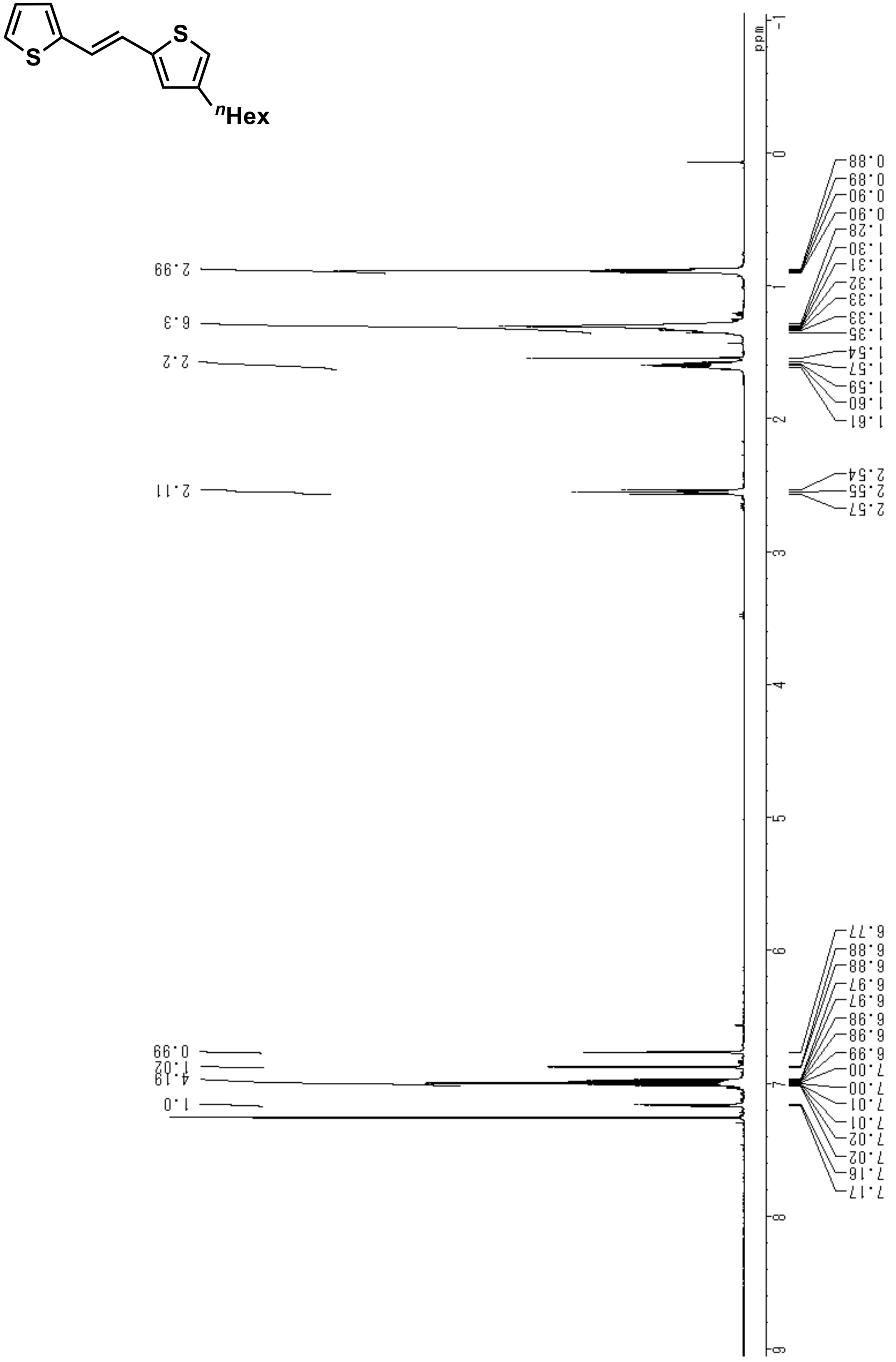
^{1}H NMR spectrum of **3ba**



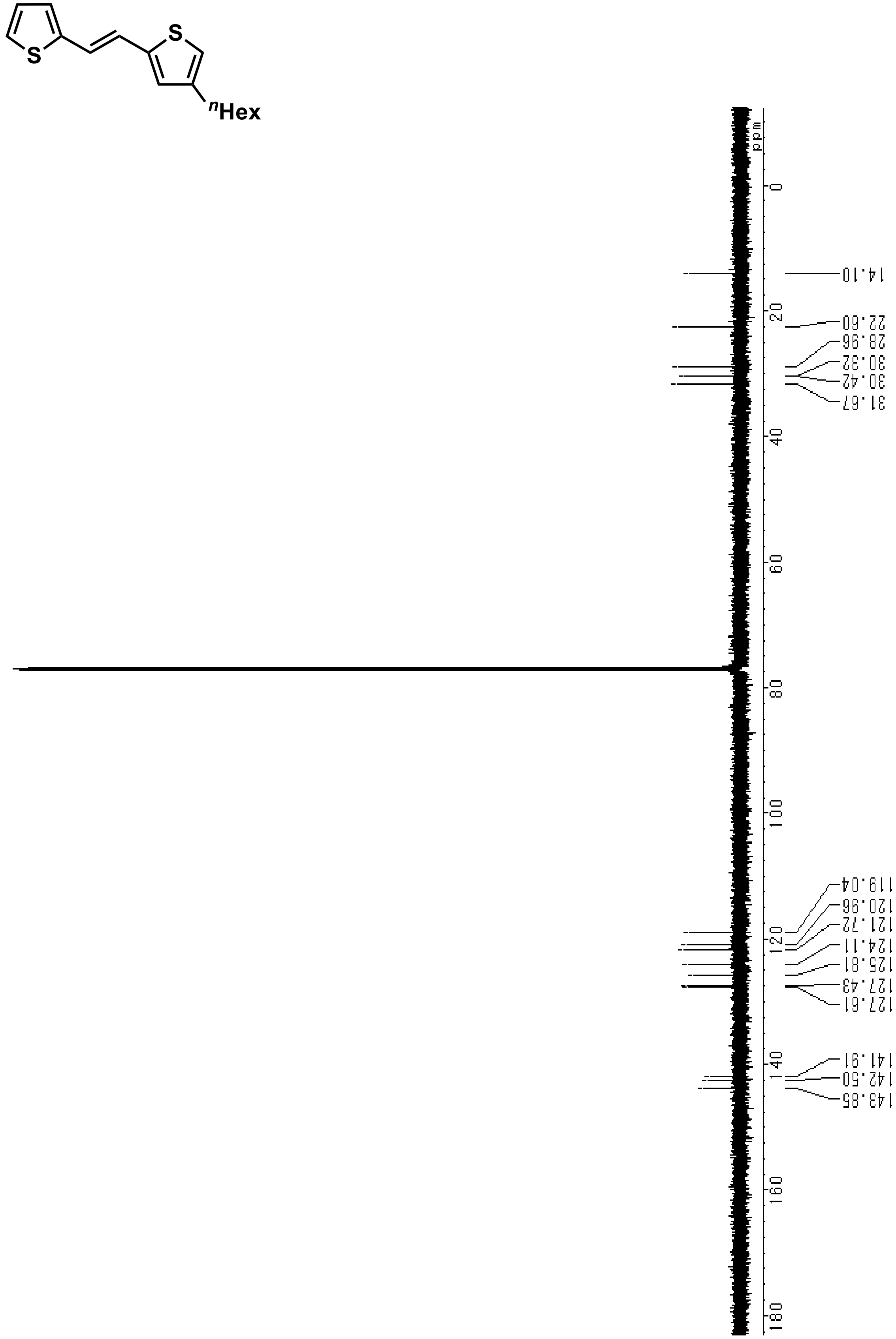
^{13}C NMR spectrum of **3ba**



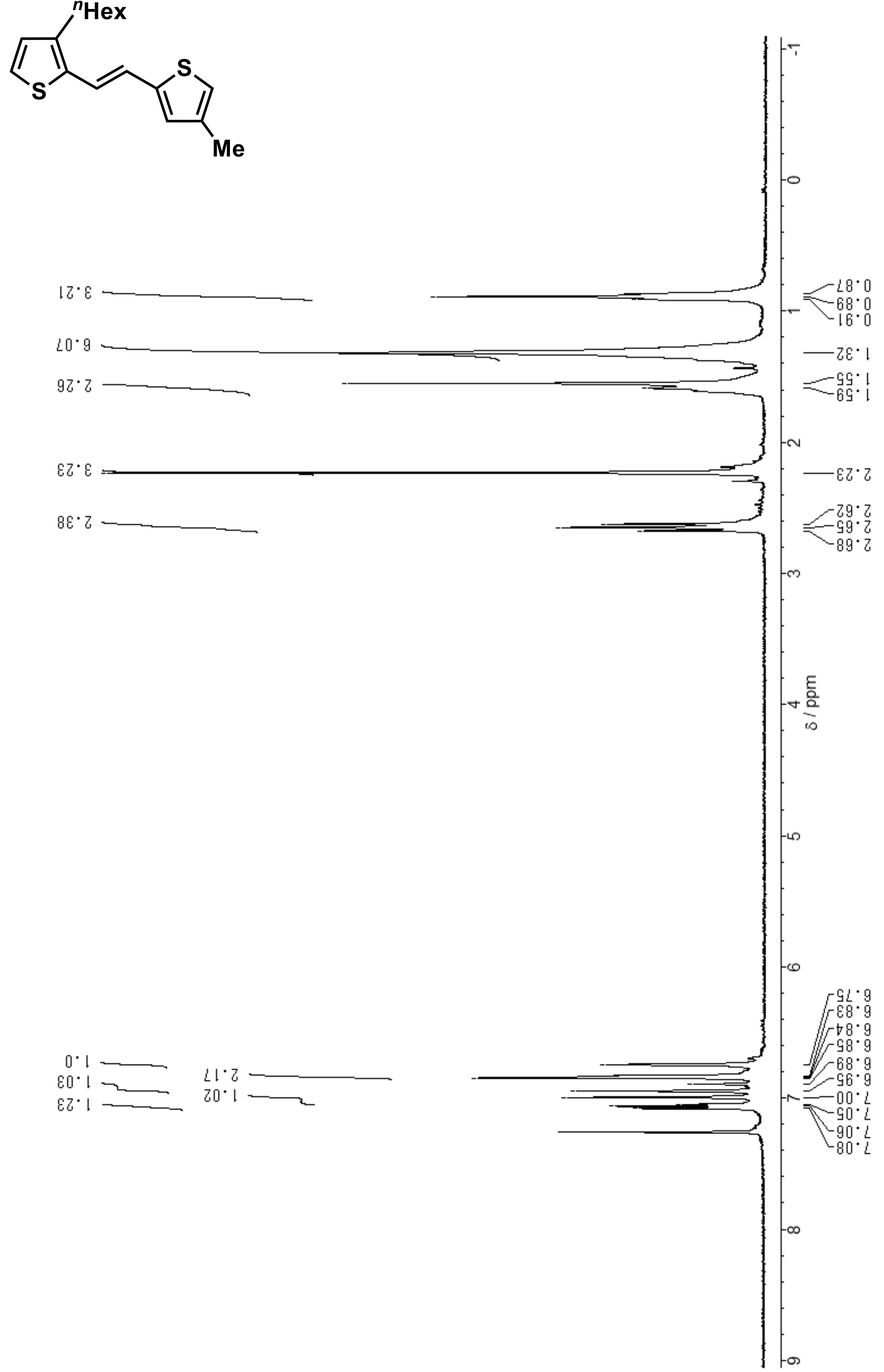
^{1}H NMR spectrum of **3ab**



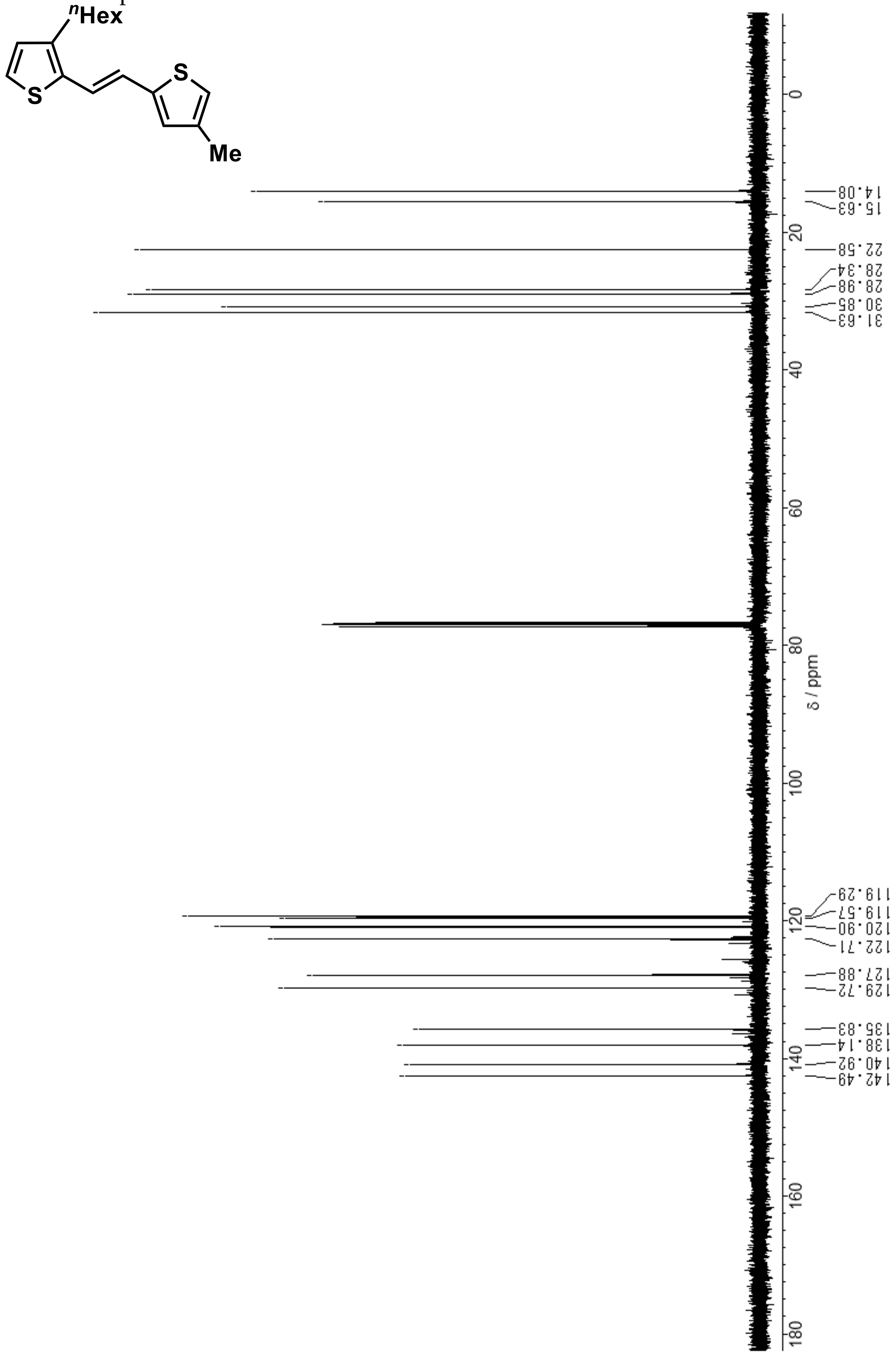
^{13}C NMR spectrum of **3ab**



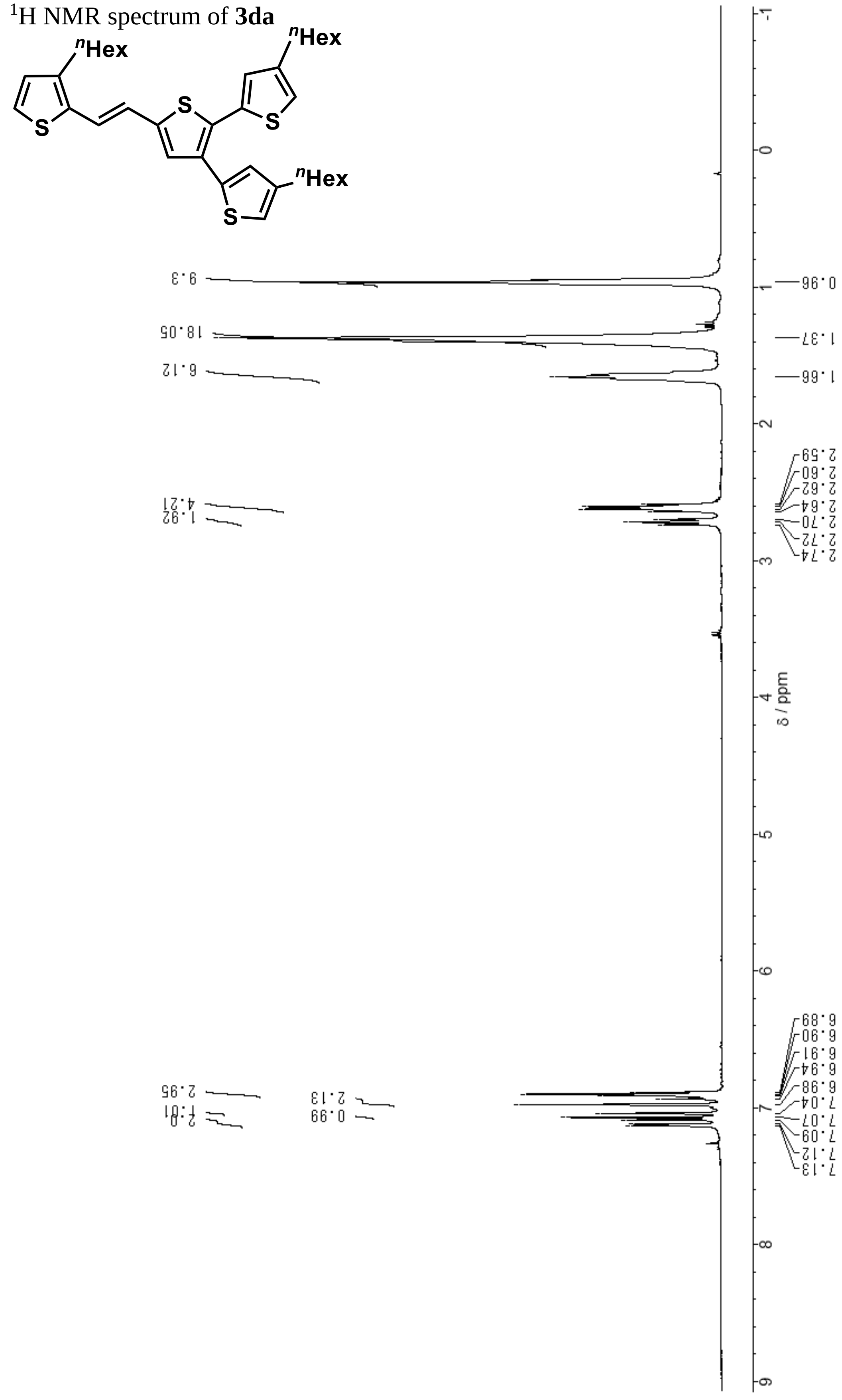
^{1}H NMR spectrum of **3ca**



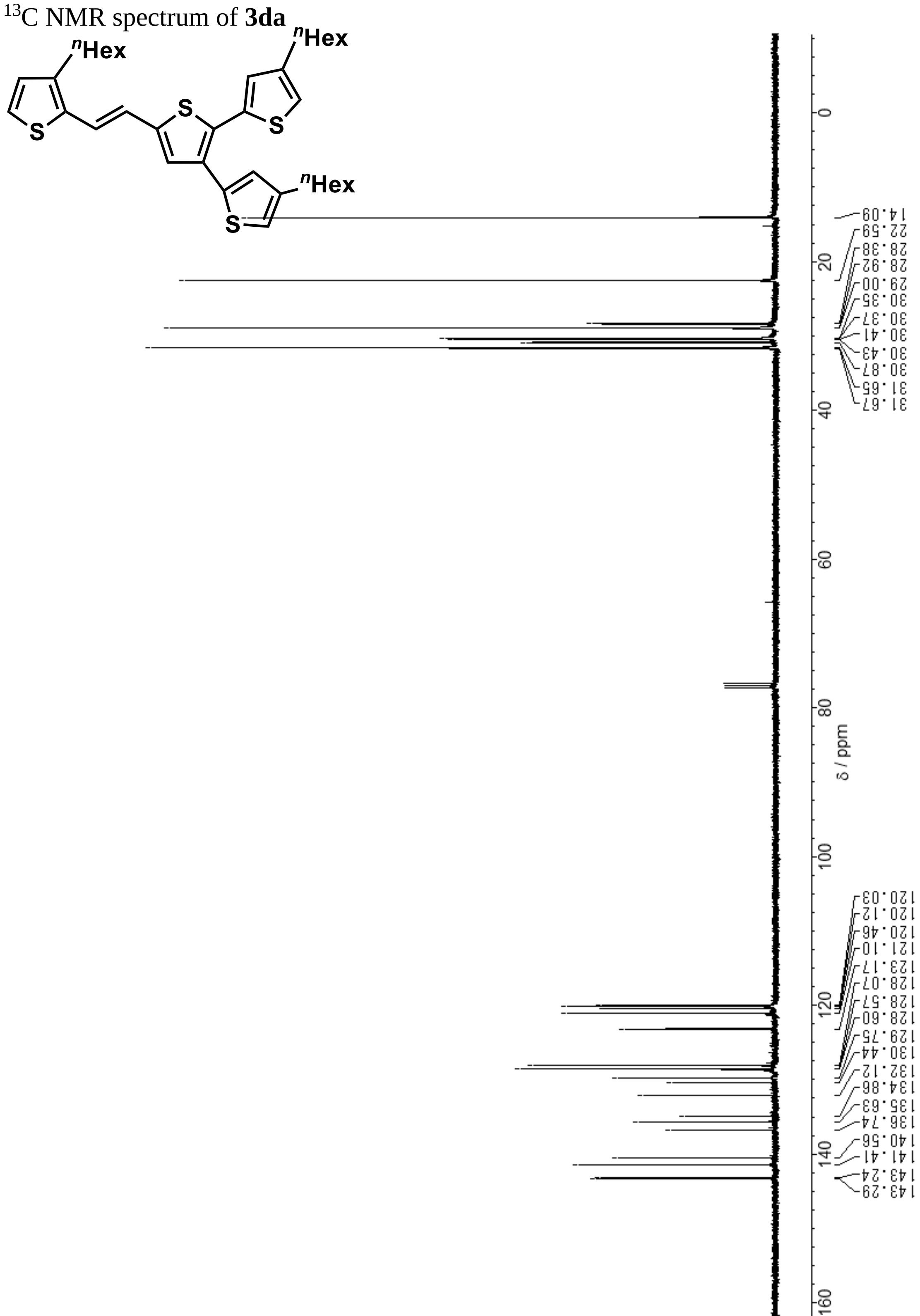
^{13}C NMR spectrum of **3ca**



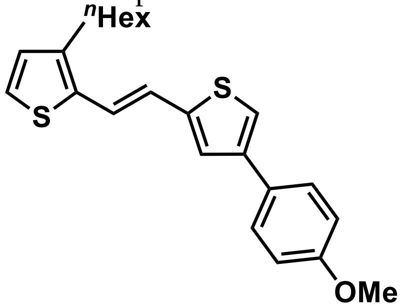
^{1}H NMR spectrum of **3da**

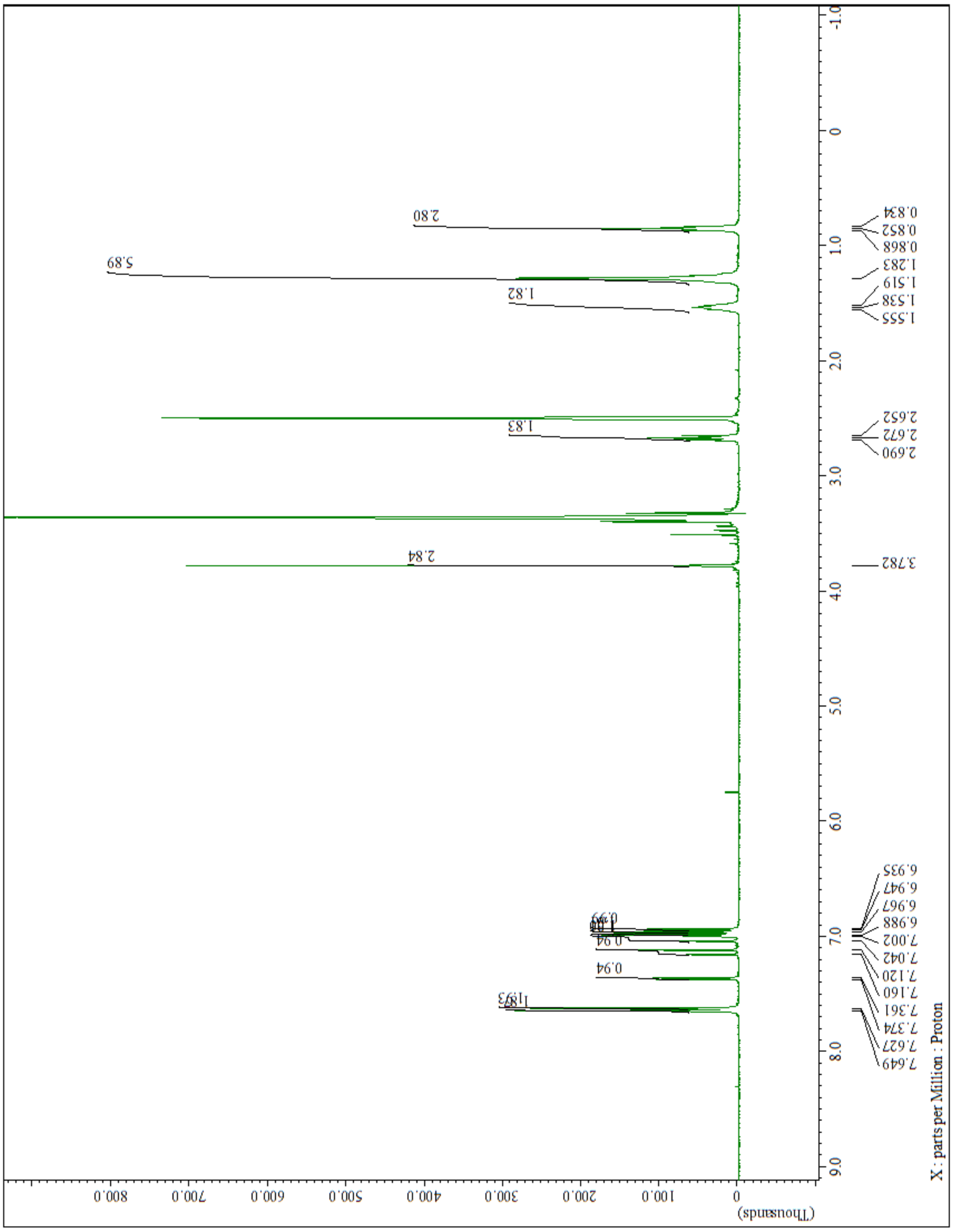


^{13}C NMR spectrum of **3da**

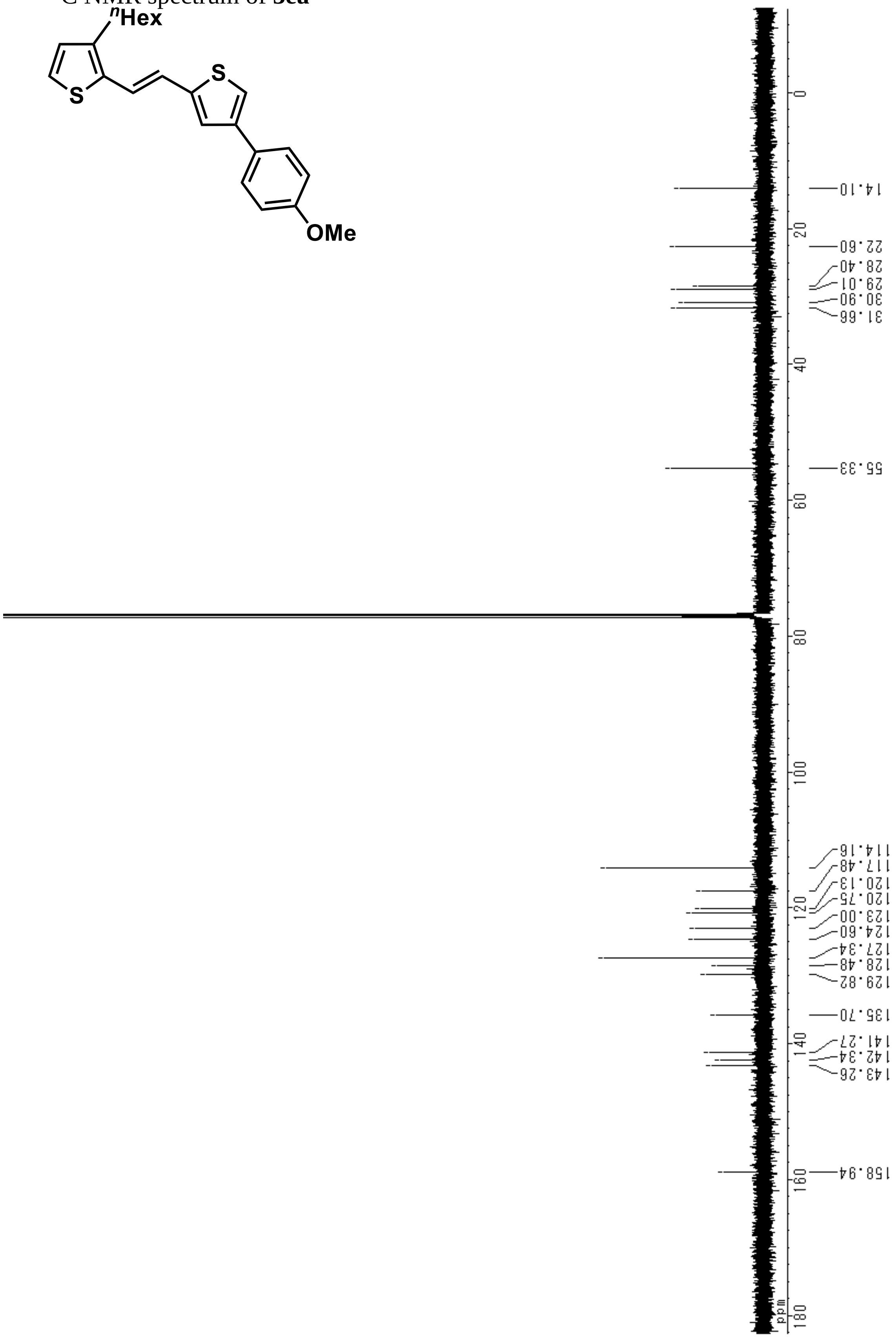


^{1}H NMR spectrum of **3ea**

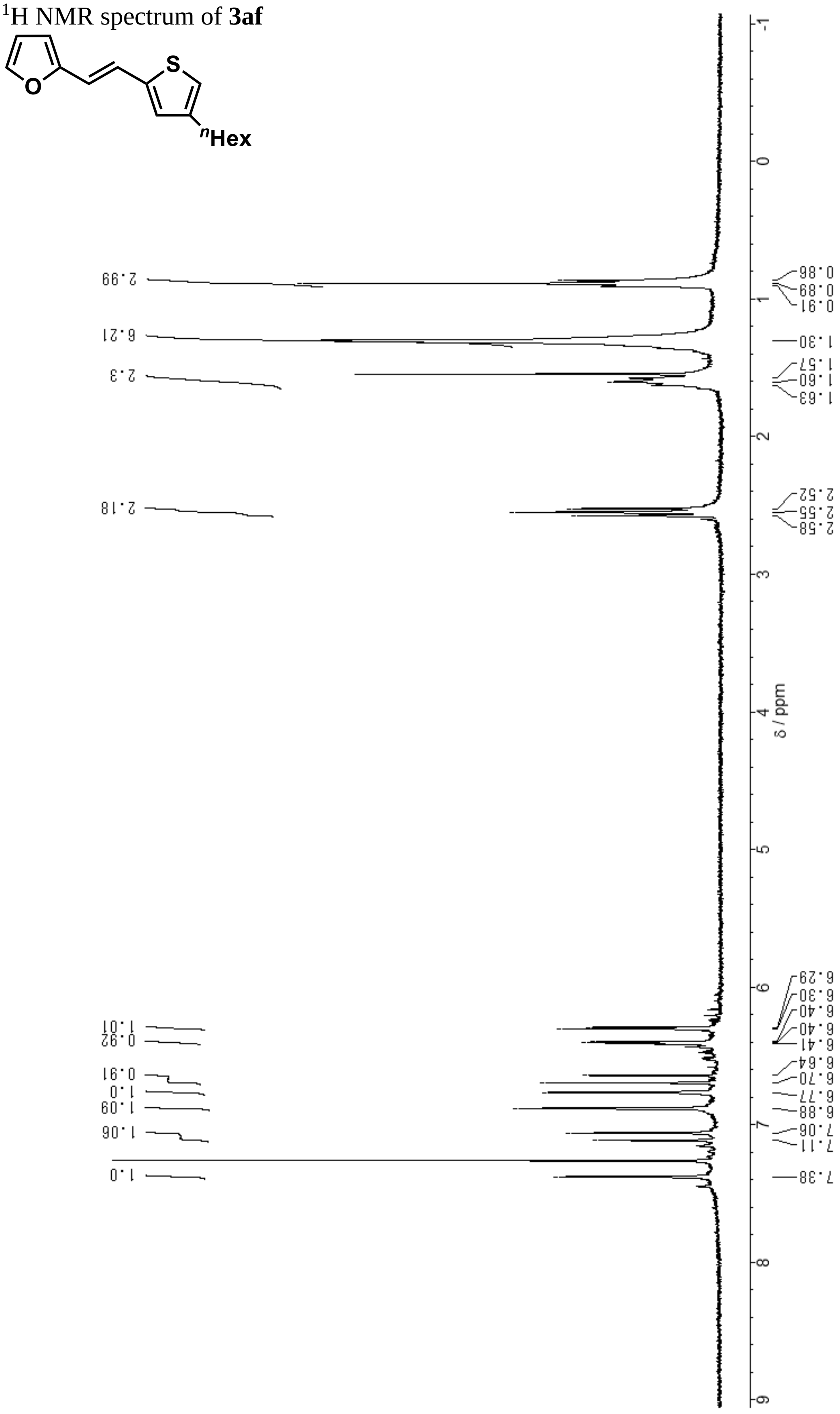




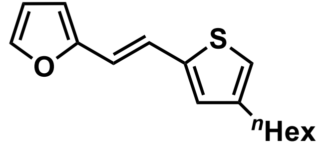
^{13}C NMR spectrum of **3ea**

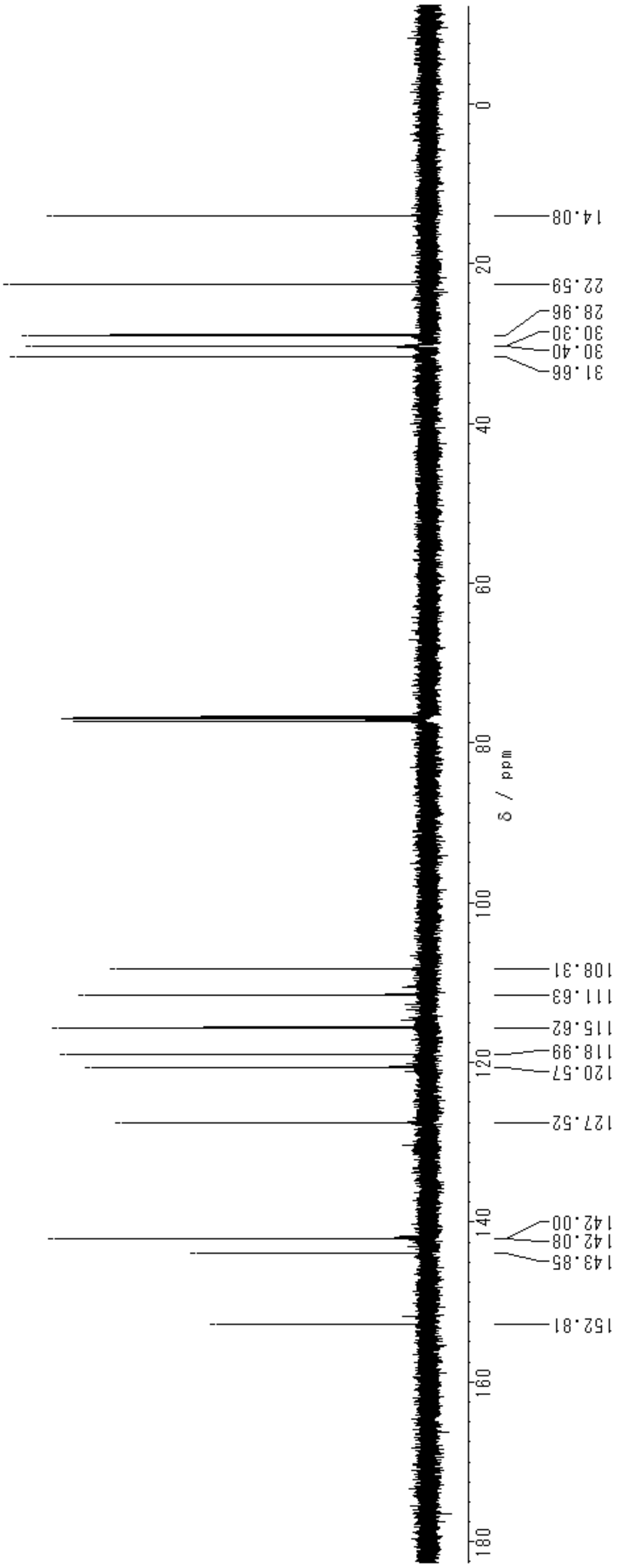


^{1}H NMR spectrum of **3af**

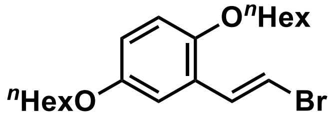


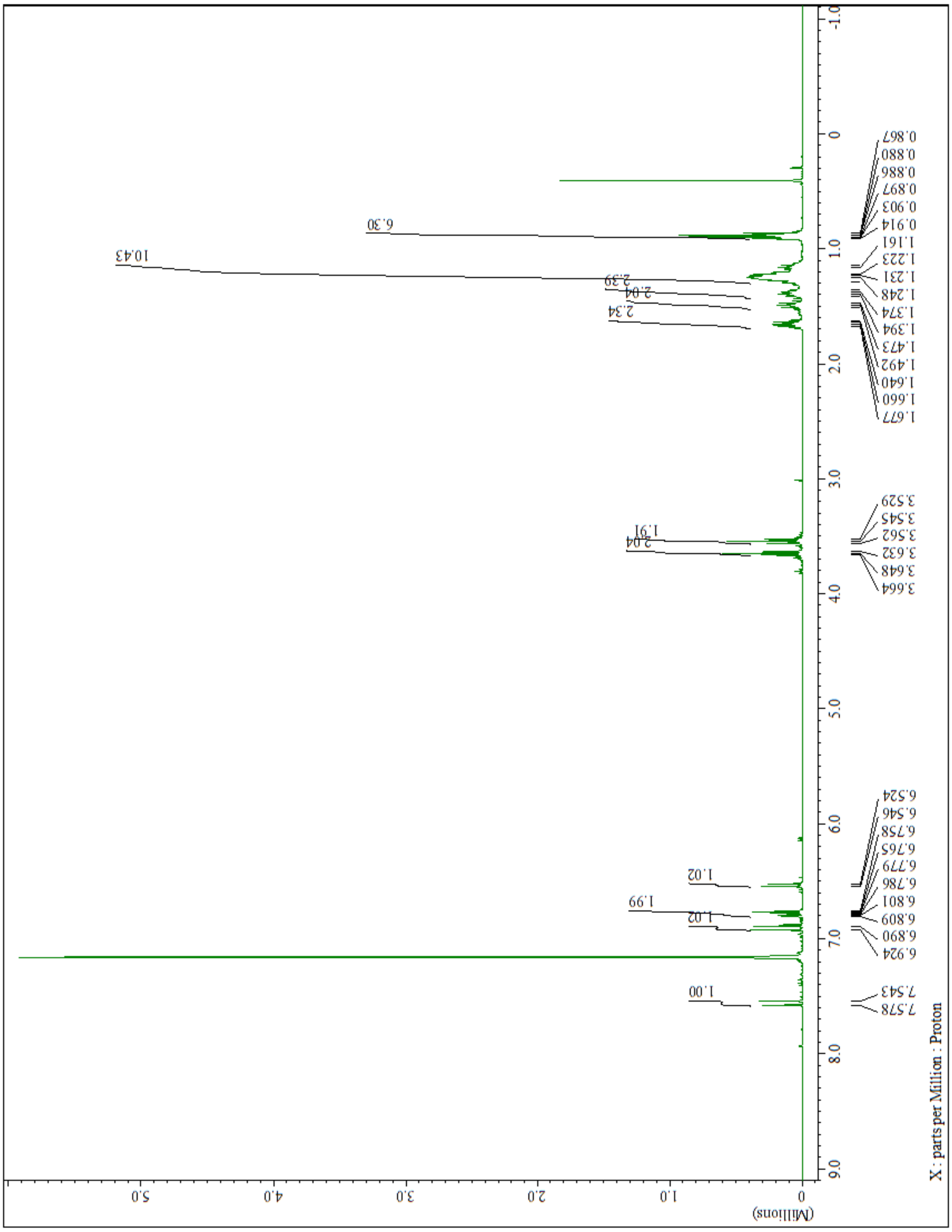
^{13}C NMR spectrum of **3af**



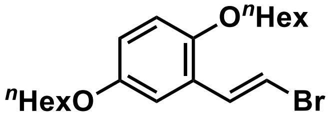


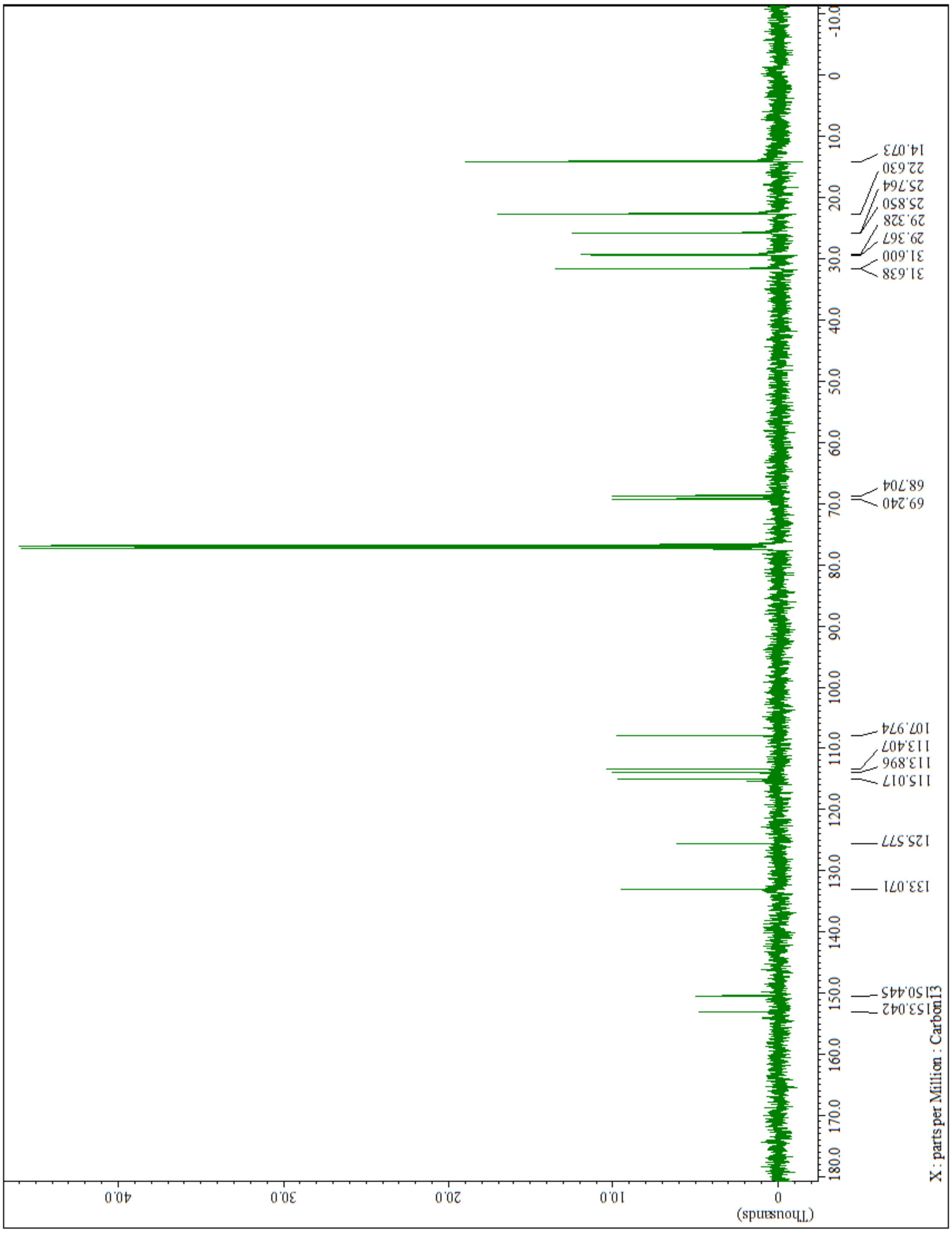
^{1}H NMR spectrum of **2g**



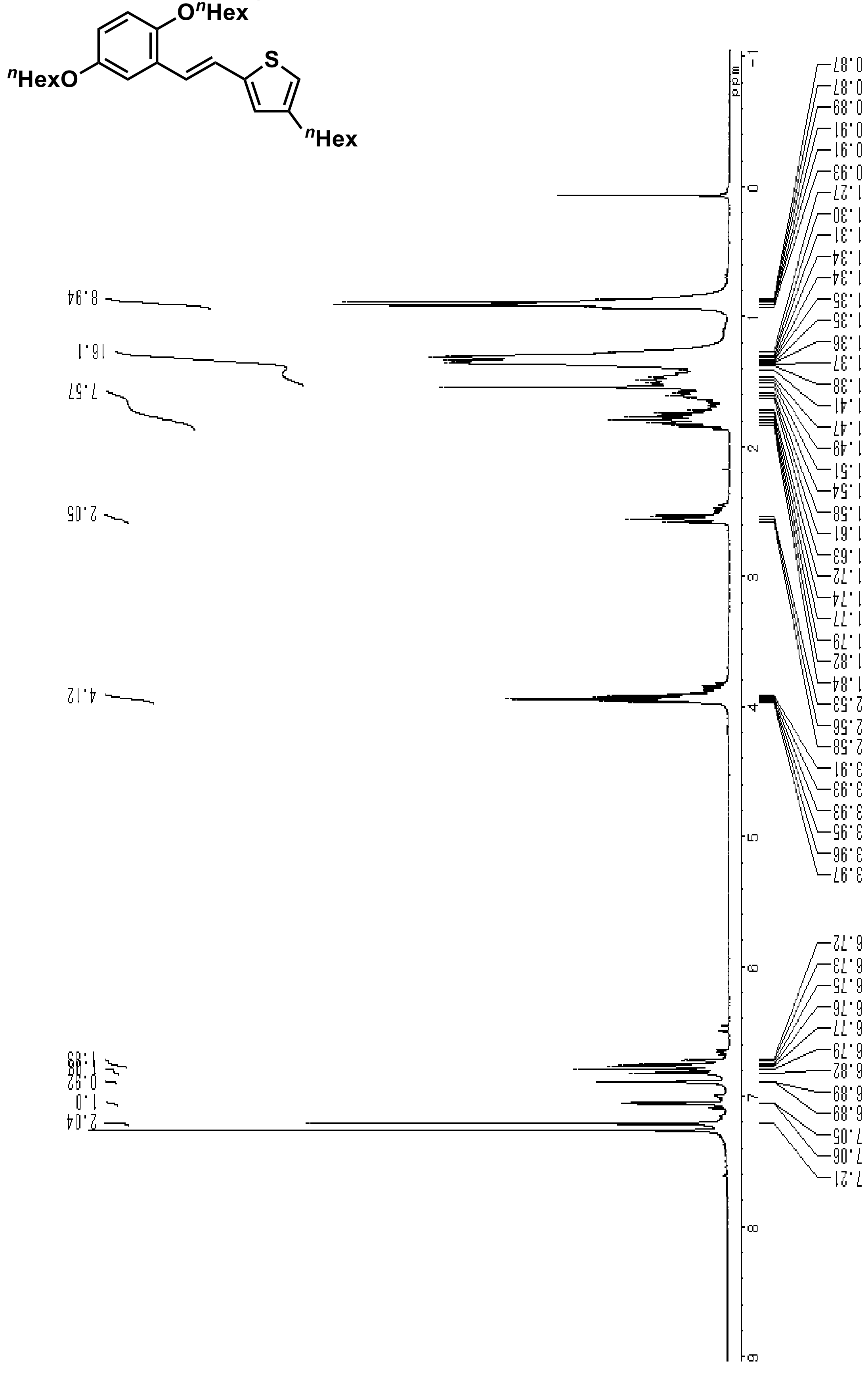


^{13}C NMR spectrum of **2g**

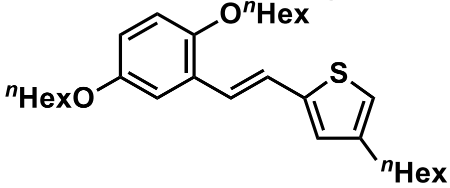


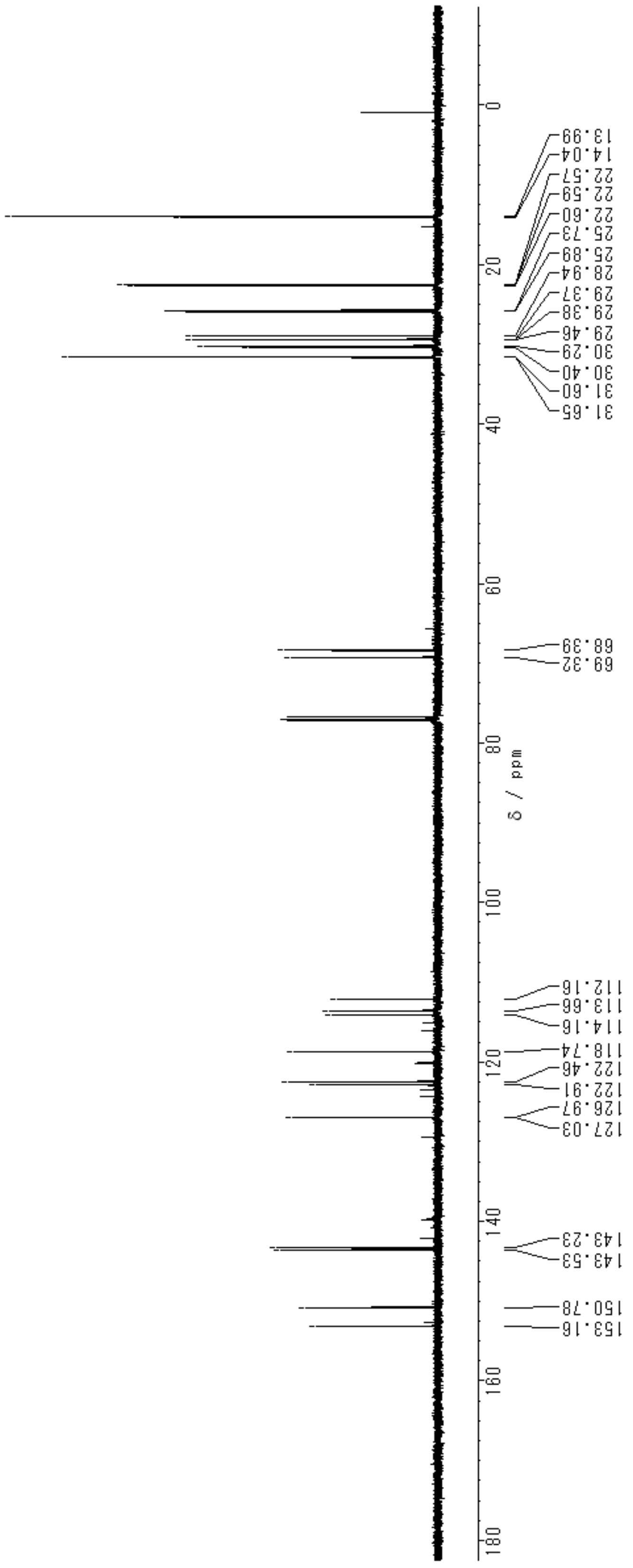


^{1}H NMR spectrum of **3ag**

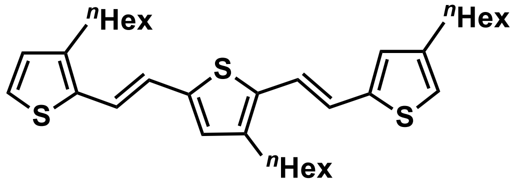


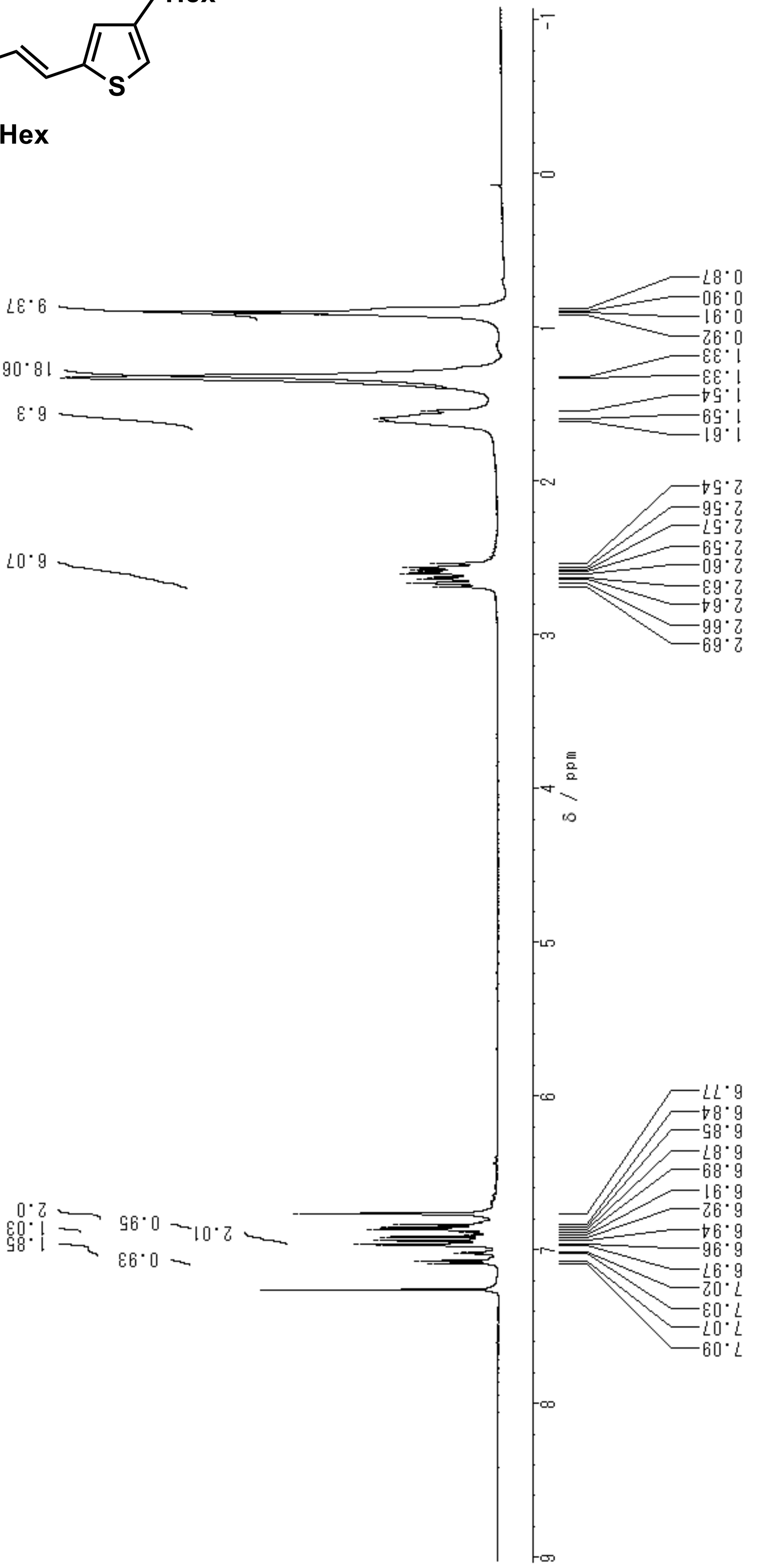
^{13}C NMR spectrum of **3ag**



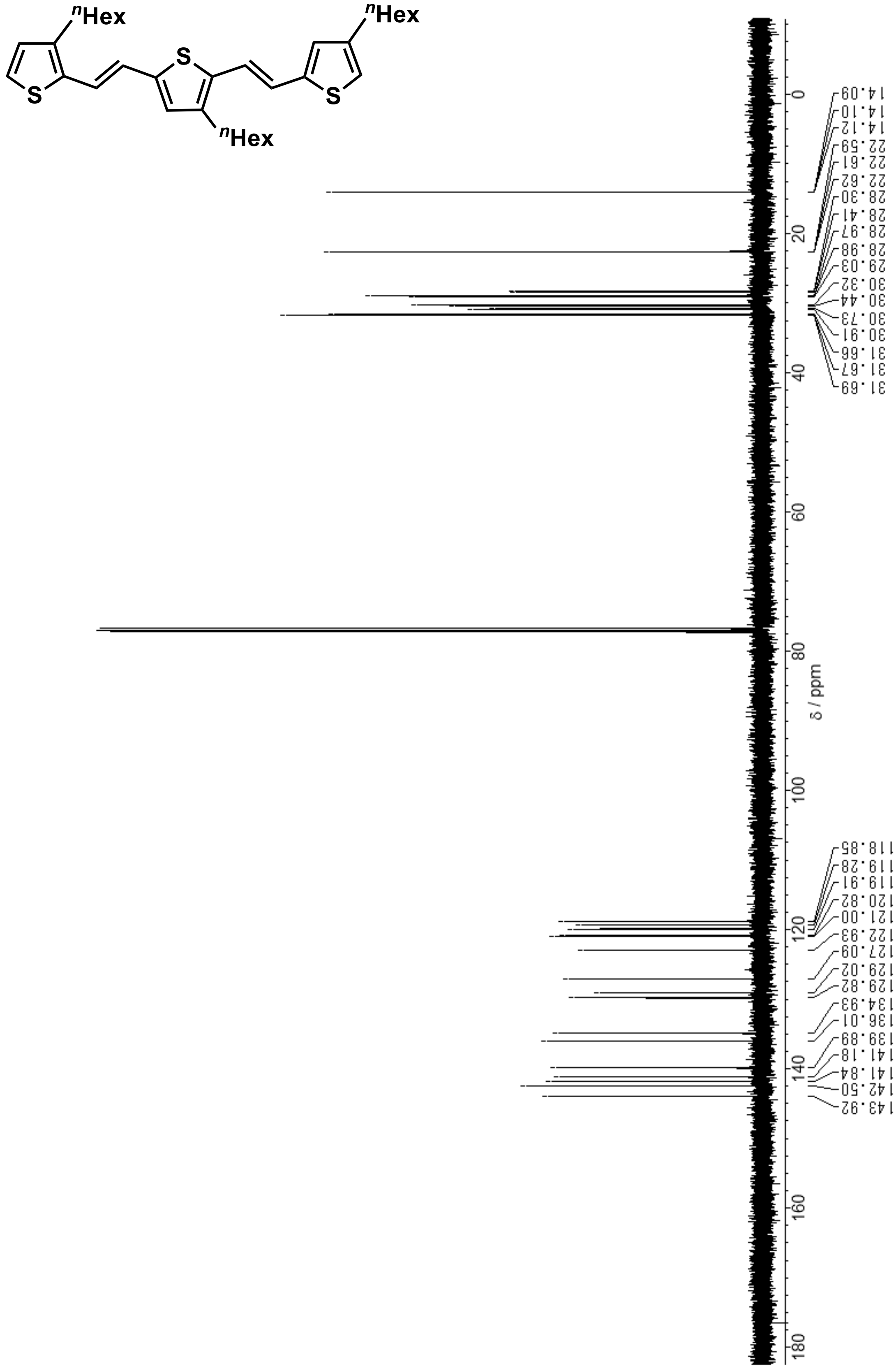


^{1}H NMR spectrum of **4**

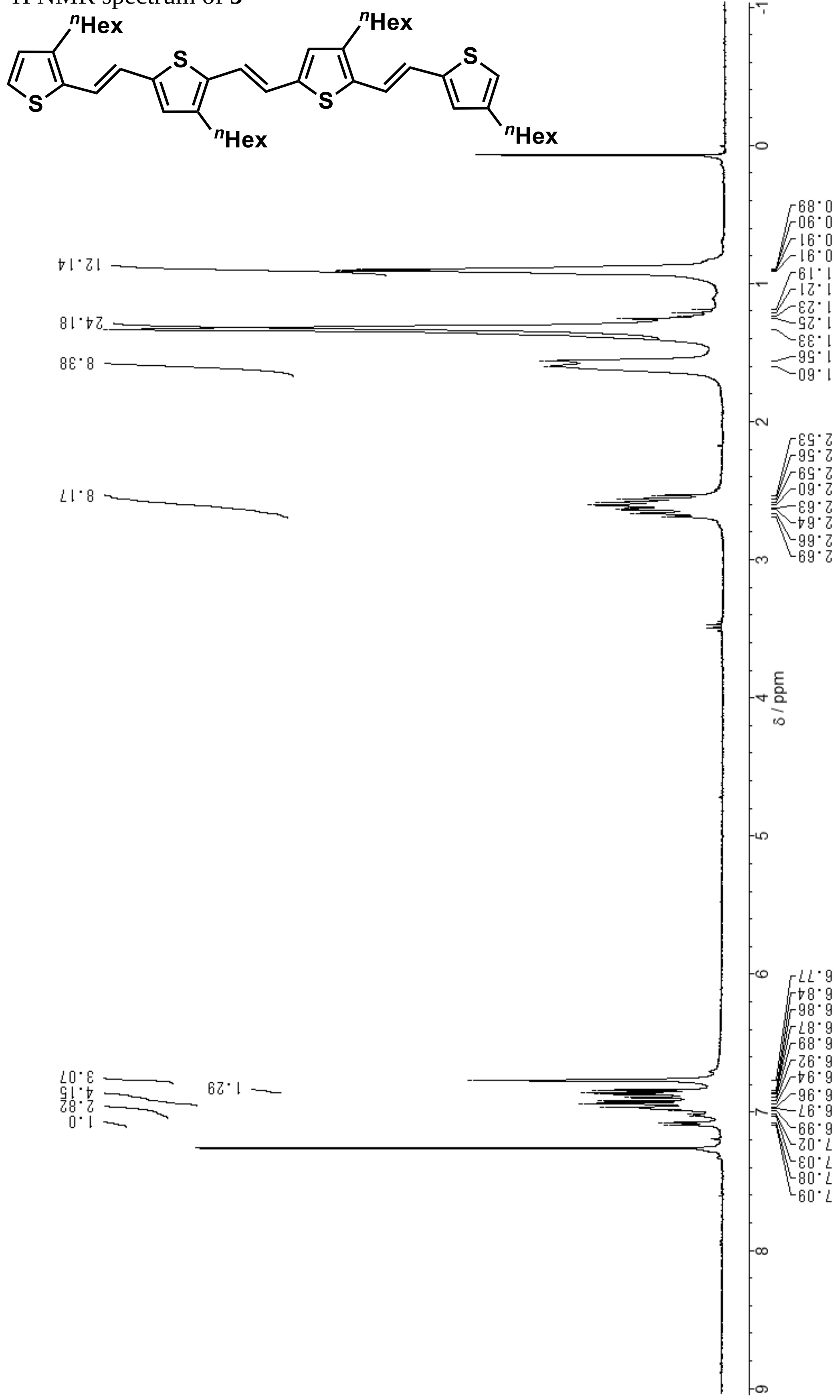




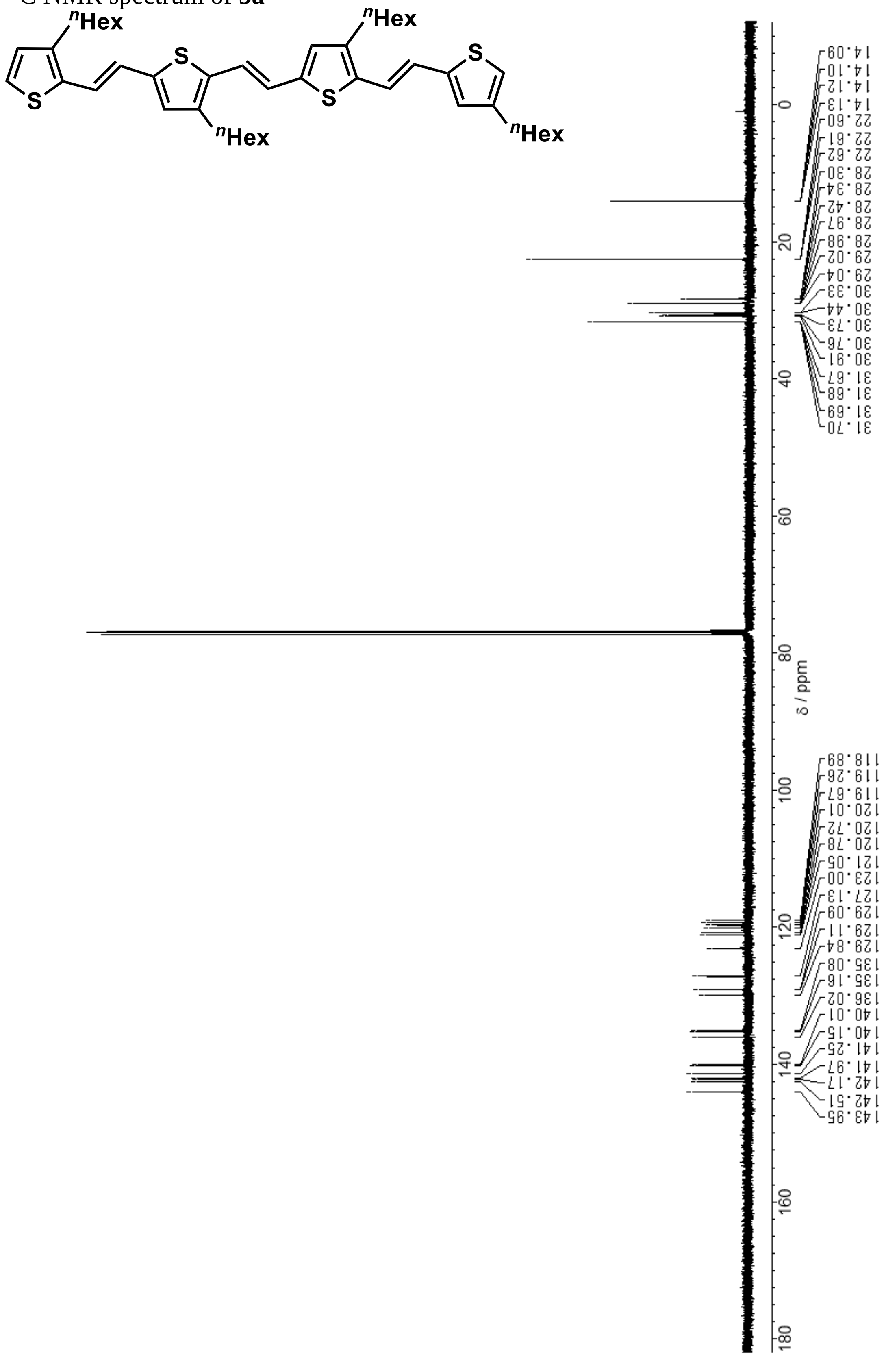
^{13}C NMR spectrum of **4**



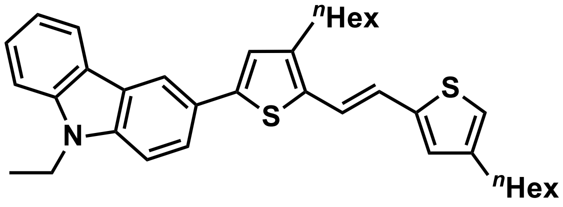
^{1}H NMR spectrum of **5**

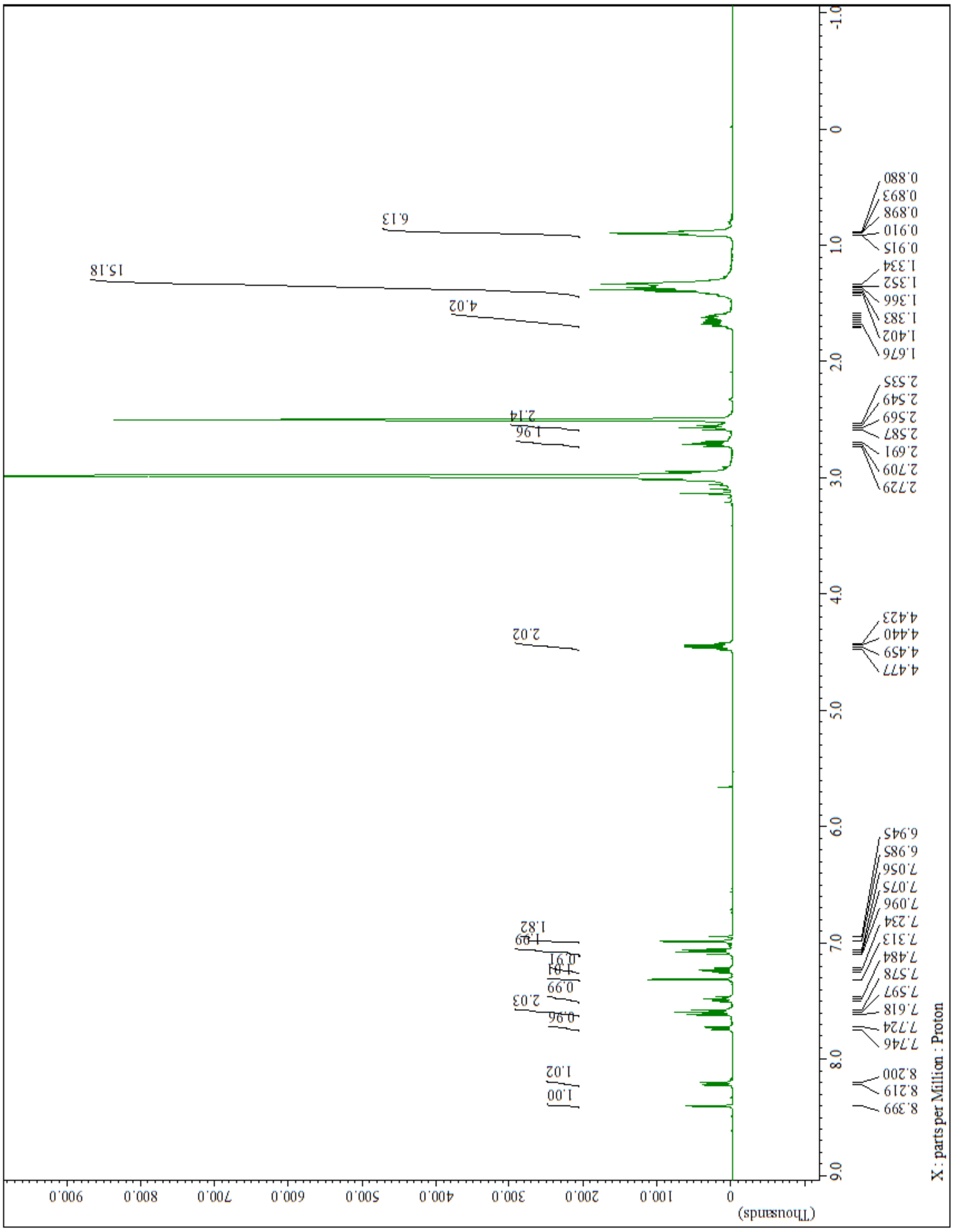


^{13}C NMR spectrum of **5a**

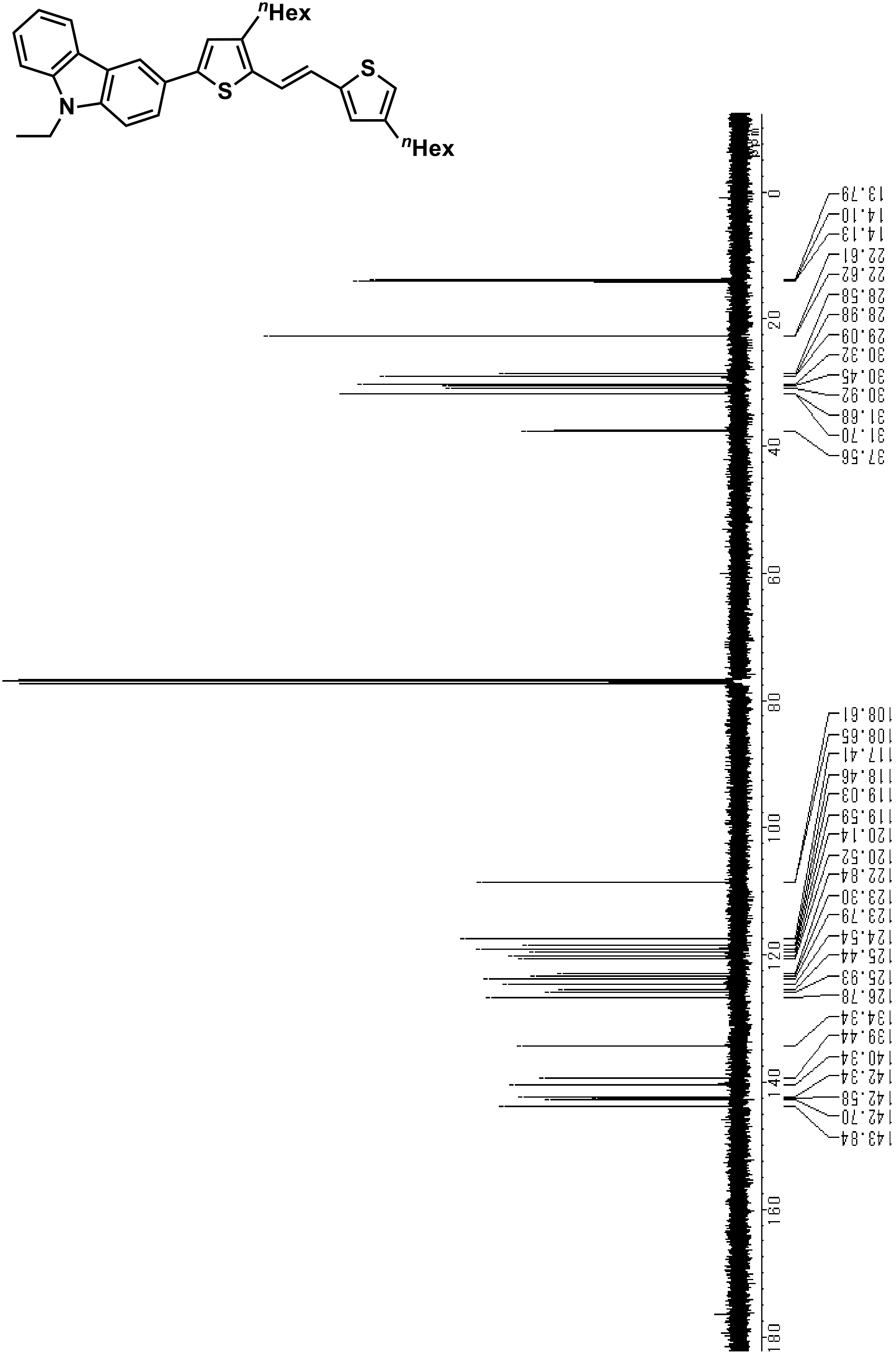


^{1}H NMR spectrum of **3aa-Cz**

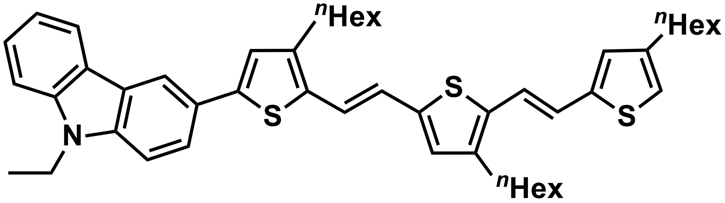


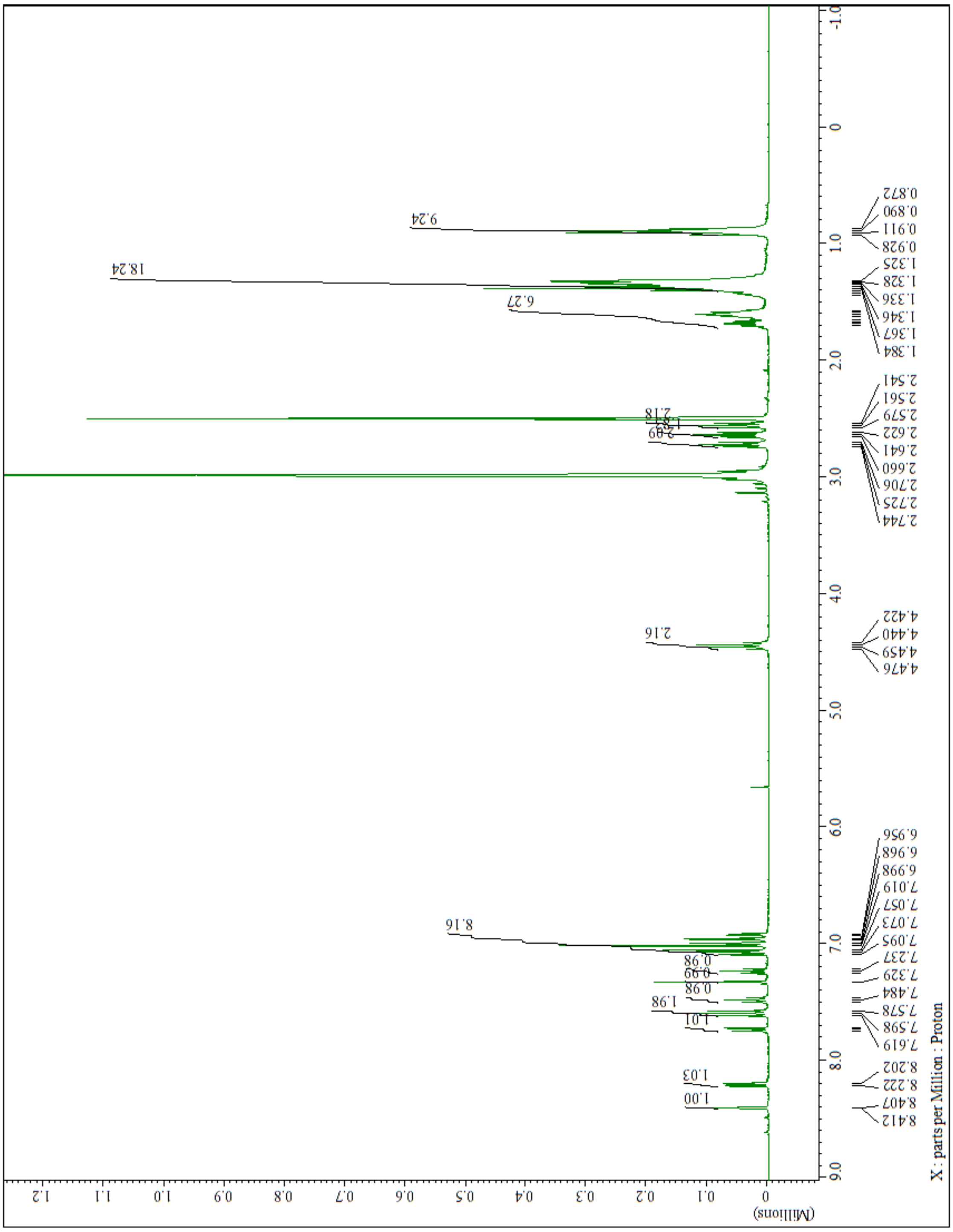


^{13}C NMR spectrum of **3aa-Cz**

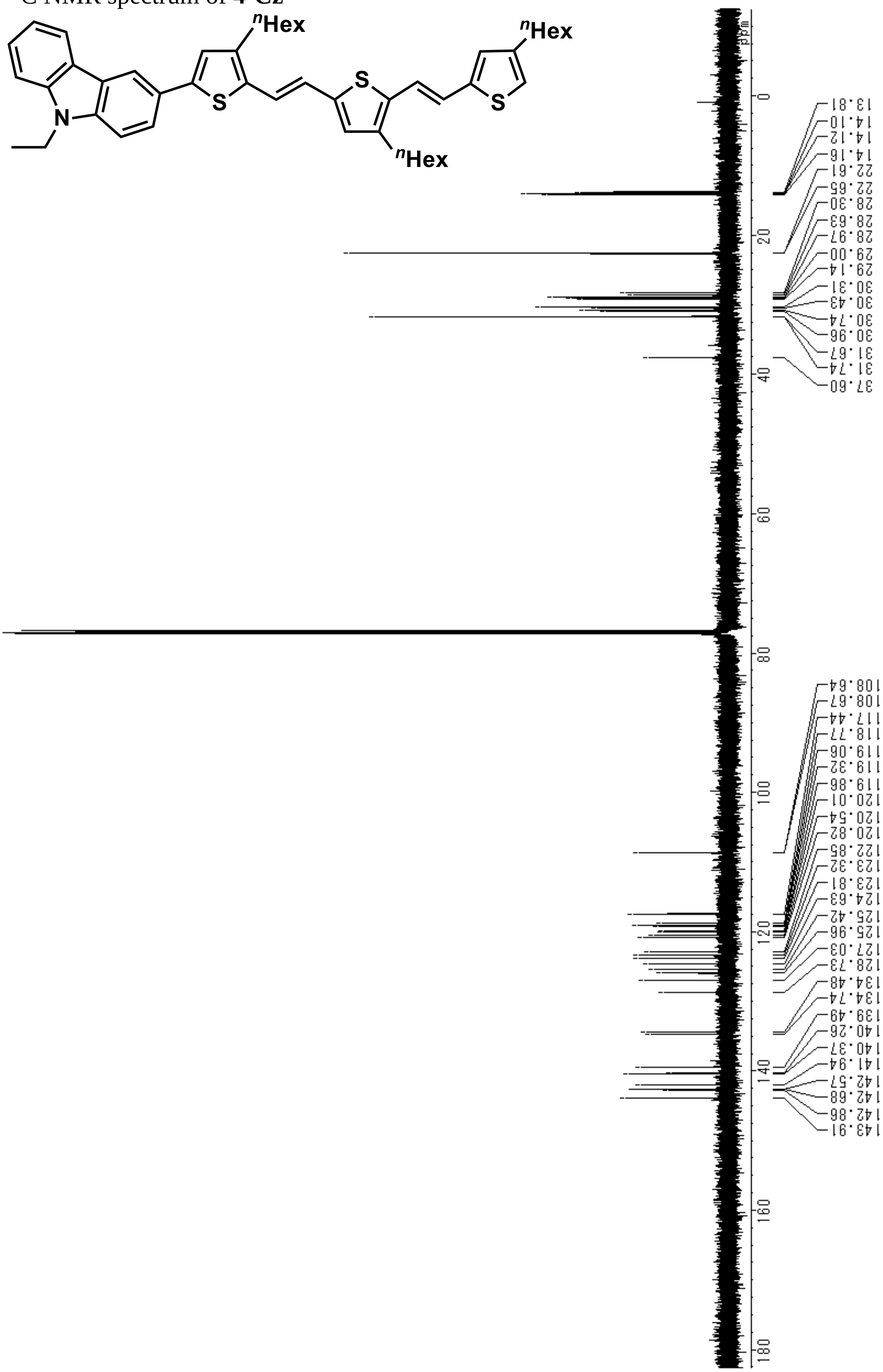


^{1}H NMR spectrum of **4-Cz**

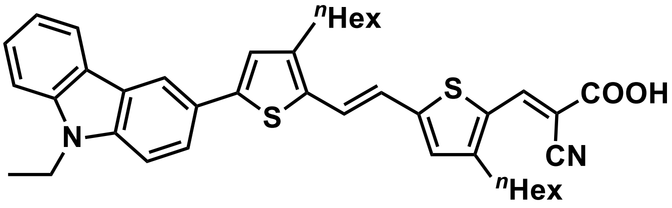


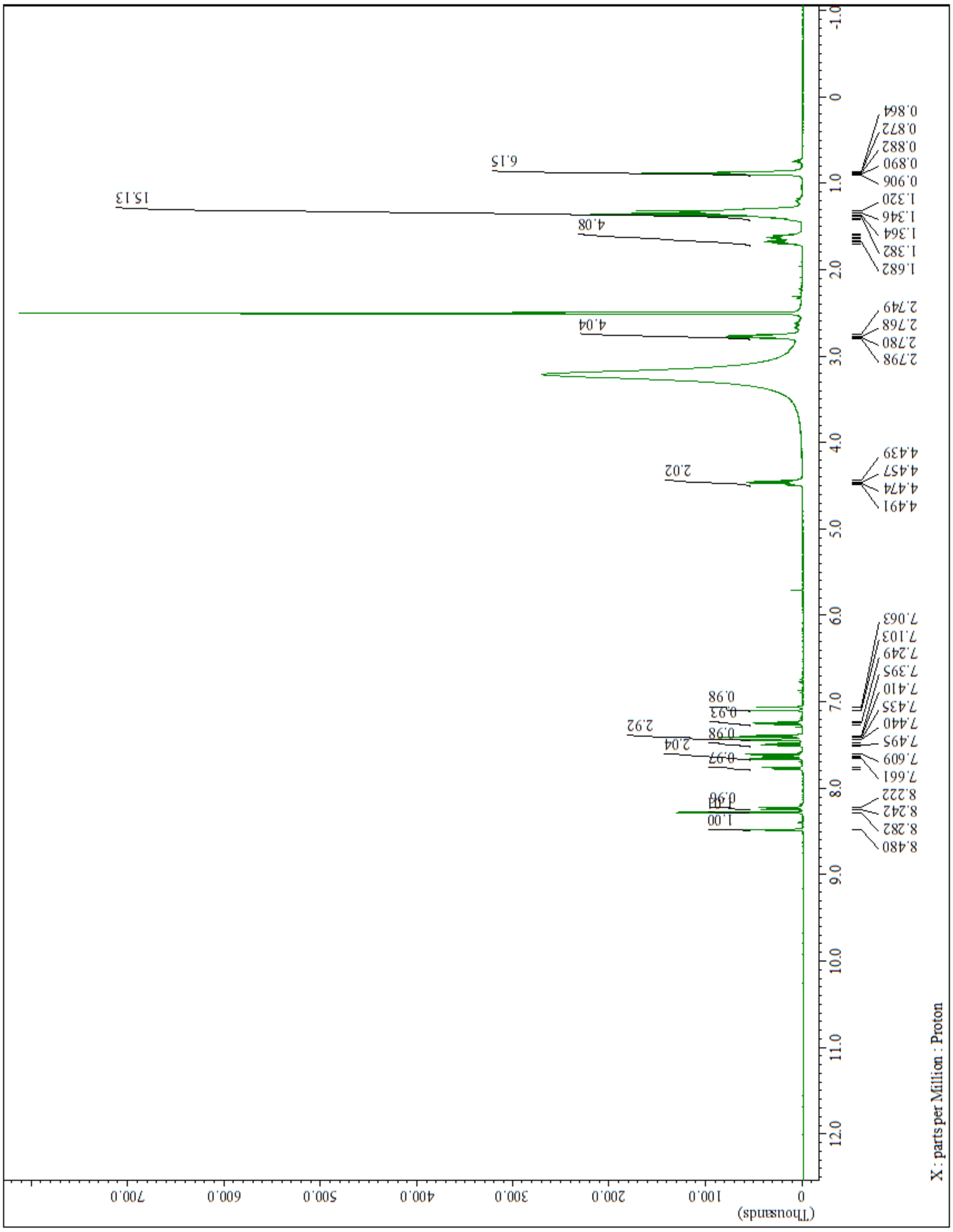


^{13}C NMR spectrum of **4-Cz**

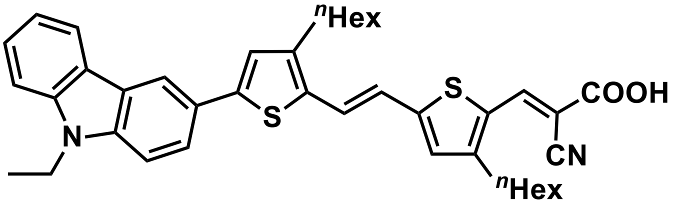


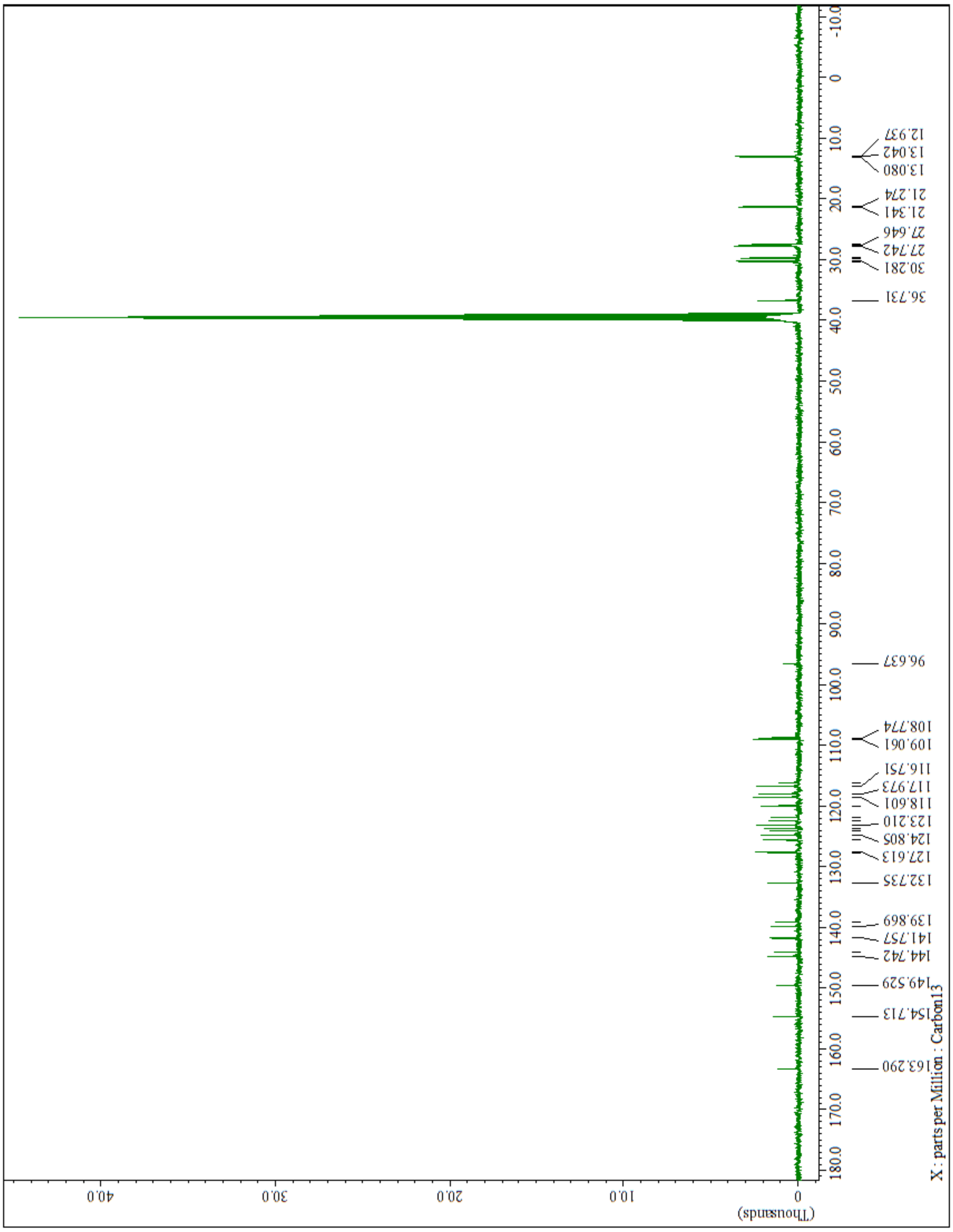
^{1}H NMR spectrum of **TMFN-1**



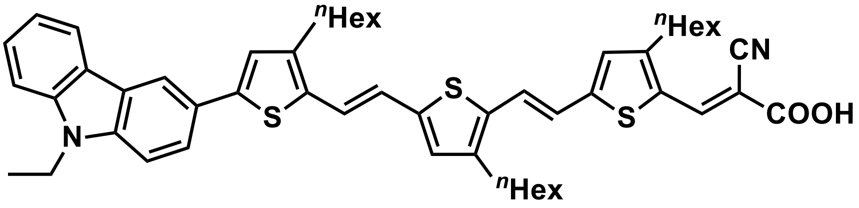


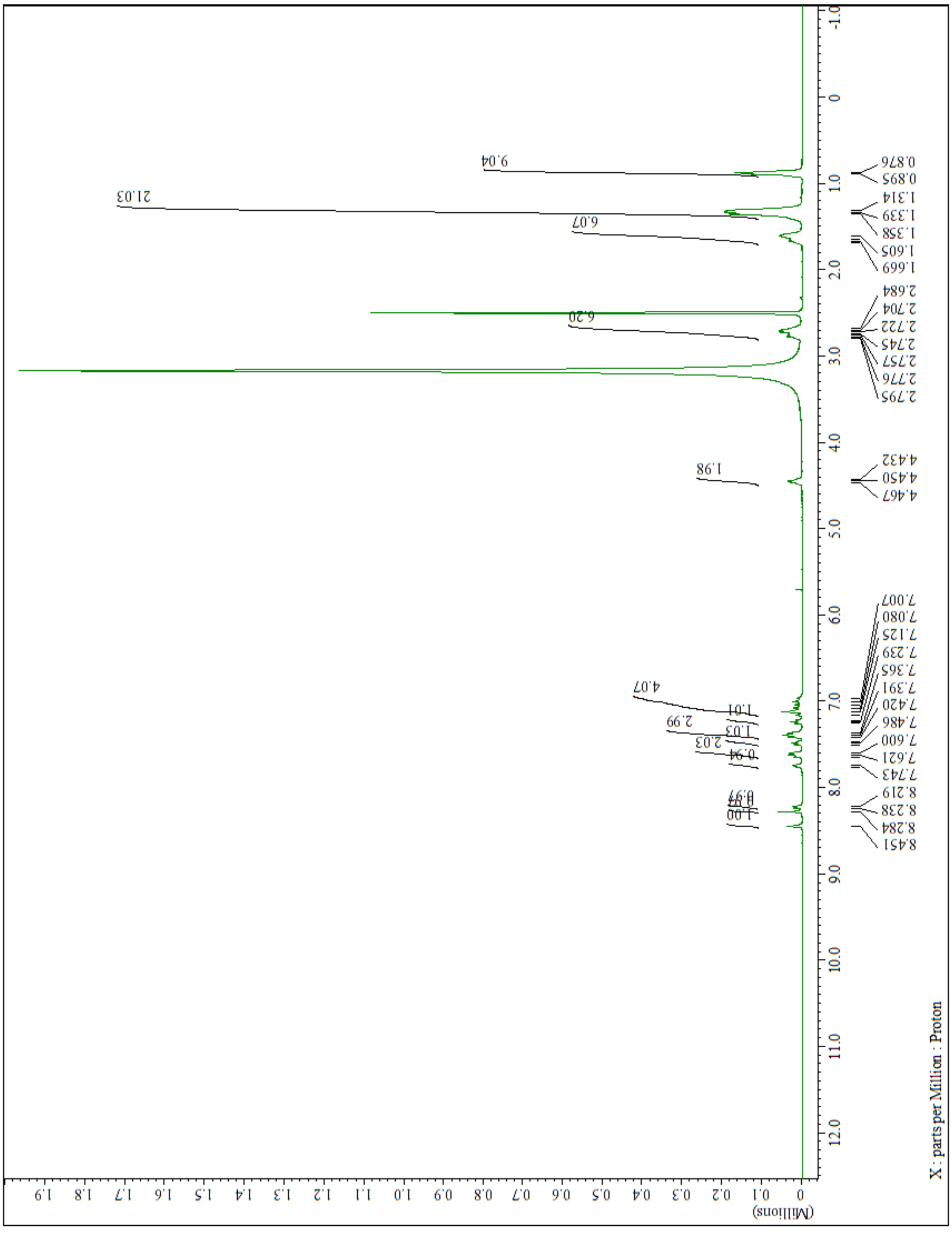
^{13}C NMR spectrum of **TMFN-1**



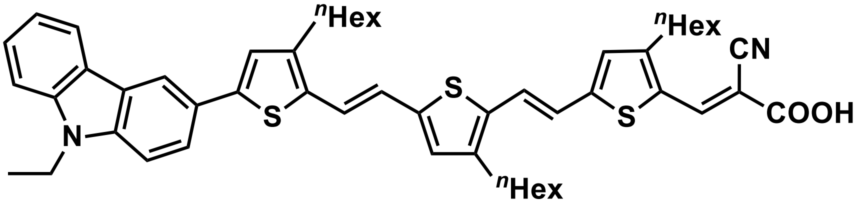


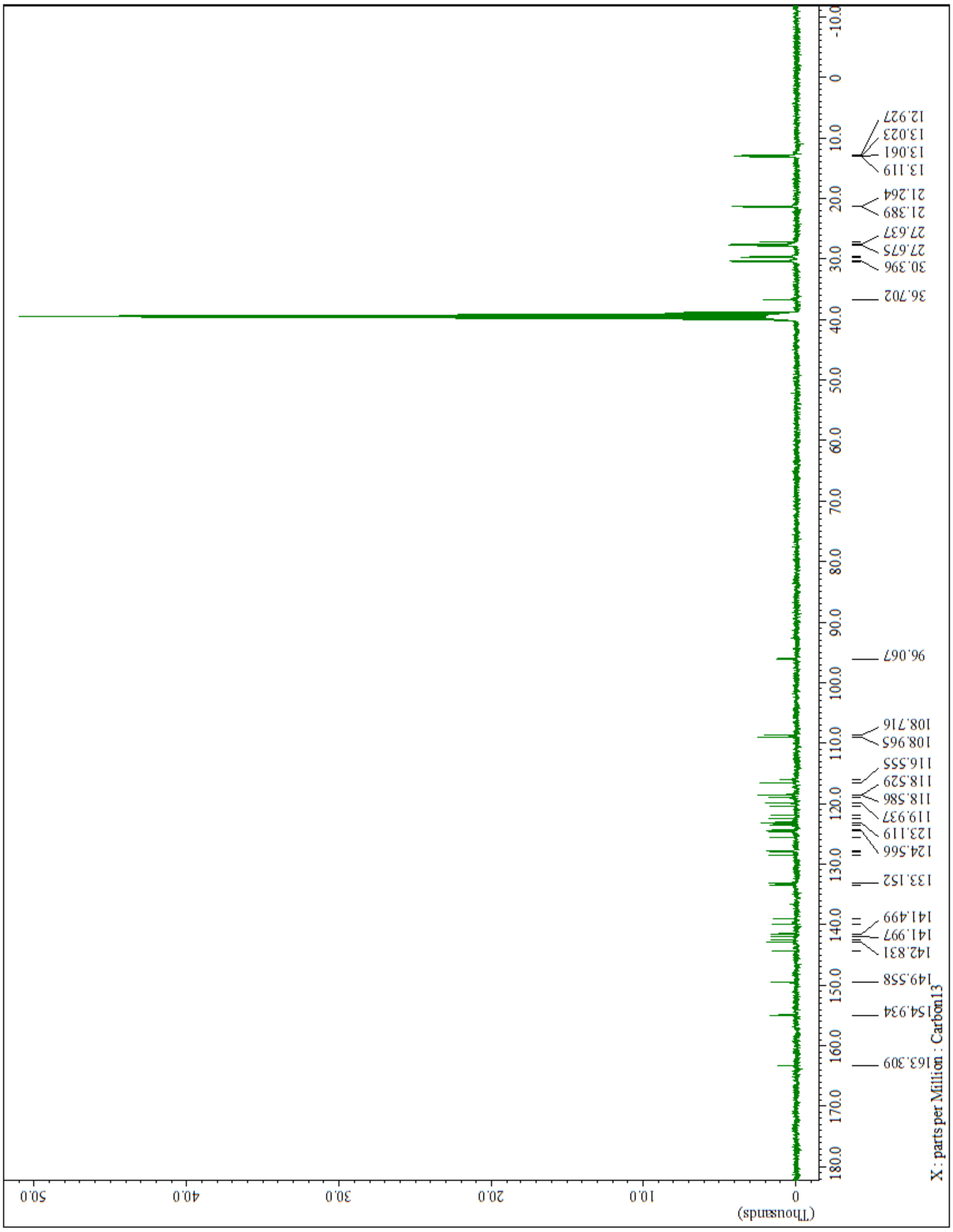
^{1}H NMR spectrum of **TMFN-2**

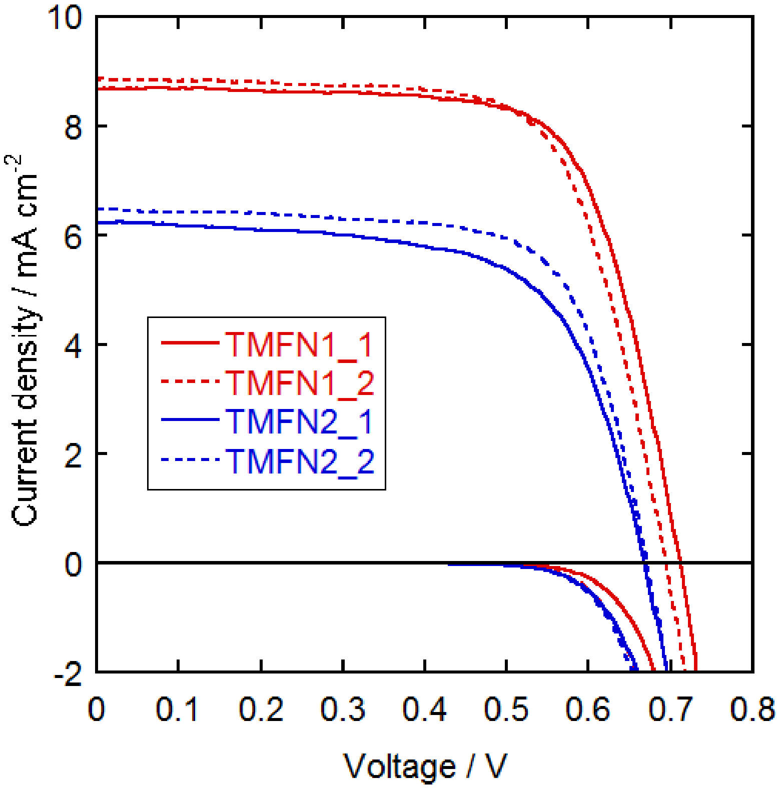




^{13}C NMR spectrum of **TMFN-2**

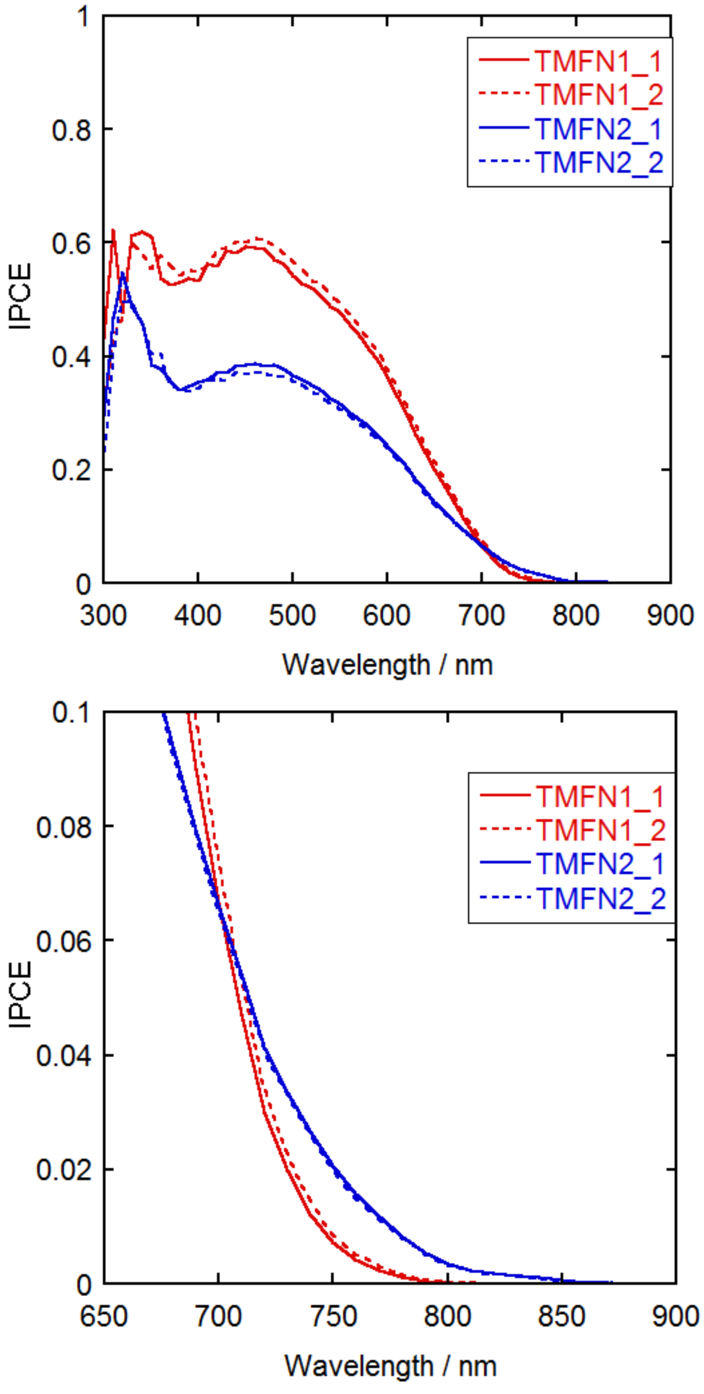






IV characteristics and cell performance of TMFN1 and TMFN-2 (after 4 h)

No.	**Dye**	**Adsorption period**	J_{sc} **/ mA cm^{-2}**	V_{oc} **/ V**	***FF***	**Efficiency / %**
1	**TMFN-1**	**18h**	**8.69**	**0.710**	**0.707**	**4.37**
2	**TMFN-1**	**18h**	**8.86**	**0.694**	**0.695**	**4.27**
1	**TMFN-2**	**18h**	**6.23**	**0.667**	**0.649**	**2.70**
2	**TMFN-2**	**18h**	**6.47**	**0.671**	**0.695**	**3.02**



External quantum yield spectra of TMFN1 and TMFN-2