Thiophene-fused polyaromatics: synthesis, columnar liquid crystal, fluorescent and electrochemical properties

Yifan Li, Alberto Concellón, Che-jen Lin, Nathan A. Romero, Sibo Lin, Timothy, M. Swager*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, 02139, United States

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1. General Methods

All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography, technical grade solvents were used. THF, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 10 ppm, *Karl-Fischer* titration). The solvents were degassed by Freeze-Pump-Thaw method when mentioned. All chemicals were purchased from Acros, Aldrich, Fluka or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F_{254} TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, *o*-DCB-*d4*, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm or the internal *o*-DCB-*d4* signal at 7.17 ppm and 7.40 as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, p = pantaplet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation).^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a Bruker DPX-400 100 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm as standard. High resolution mass spectrometric measurements were recorded with a high-resolution JEOL AccuTOF 4G LC-plus equipped with an ionSense DART (Direct Analysis in Real Time) source, on a MICROMASS (ESI) Q-TOF Ultima API (CH3CN as eluant) or high-resolution Bruker Autoflex LRF Speed mass spectrometer with a measurable mass range of up to 450 kDa (*trans*-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix). For electrochemistry experiments, the solvents were dried over 3 Å MS and passed through activated alumina. Tetrabutylammonium hexafluorophosphate was recrystallized twice from ethanol prior to use. Absorption spectra were collected using Cary 60. Emission spectra were collected using Horiba Fluorolog-3. Fluorescence quantum yields were collected using Horiba Quanta-φ. Thermogravimetric analysis (TGA) was performed using a Q50 from TA instruments at heating rate of 10 ºC min^{-1} under a nitrogen atmosphere. Liquid crystal properties were investigated by polarized-light optical microscopy (POM) using a Leica DMRXP polarized-light microscope fitted with a Linkam TMS 94 hot stage. Thermal transitions were determined by differential scanning calorimetry (DSC) using a Discovery DSC from TA instruments with powdered samples (2−5 mg) sealed in aluminum pans. Glass

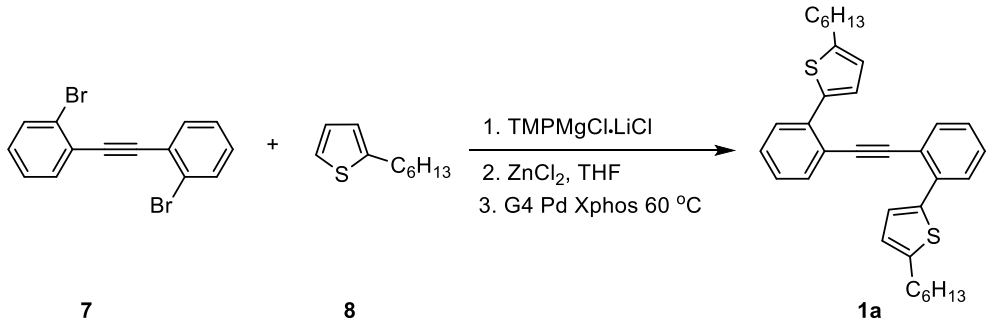
transition temperatures (T_g) were determined at the half height of the baseline jump, and first order transition temperatures were read at the maximum of the corresponding peak. X-ray diffraction (XRD) was performed with a SAXSLAB instrument equipped with a Rigaku 002 microfocus X-ray source ($CuK_{\alpha 1}$ = 1.5409 Å) and a Dectris Pilatus 300K detector. The beam center and the q range were calibrated using the diffraction peaks of silver behenate. Powdered samples were placed in Lindemann glass capillaries (1 mm diameter).

2. Experimental Section.

2.1 Preparation of starting materials

1,2-bis(2-bromophenyl)ethyne (**7**),[1] **2,2'-((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(bromobenzene)** (**9**),[2] **2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**11**),[3] **2,2'-((4,6-dibromo-1,3-phenylene)bis(ethyne-2,1-diyl))bis(bromobenzene)** (**12**),[4] **2,3-dibromo-1,4-diiodobenzene (14)**,[5] **2-(5-hexylthiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**18**),[6] were synthesized according to literature.

1,2-bis(2-(5-hexylthiophen-2-yl)phenyl)ethyne (1a)



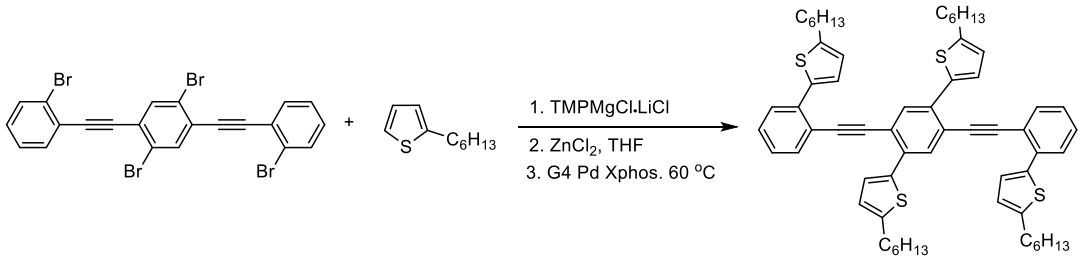
7 **8** **1a**

TMPMgCl·LiCl (18.8 mL, 1 M in THF/Toluene, 4.00 equiv.) was slowly added into **8** (3.40 mL, 18.8 mmol, 4.00 equiv.). The solution was kept stirring at room temperature during 20 mins. Then $ZnCl_2$ (0.5 M in THF, 37.6 mL, 4.00 equiv.) was added into the mixture. After 1 hour, **7** (1.53 g, 4.56 mmol, 1.00 equiv.) and G4 Pd Xphos (143 mg, 0.300 mol, 0.0400 equiv.) were added to the solution. The solution was kept stirring at 60 °C during 72 h before quenching with saturated NH_4Cl solution. The aqueous phase was extracted by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM: 30/1) to afford **1a** as pale solid (1.71 g, 3.36 mmol, 74%).

Melting point: 75-76 °C

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 7.7, 1.4 Hz, 2H, *benzene H*), 7.62 (dd, *J* = 7.9, 1.2 Hz, 2H, *benzene H*), 7.53 (d, *J* = 3.6 Hz, 2H, *thiophene H*), 7.38 (td, *J* = 7.6, 1.4 Hz, 2H, *benzene H*), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H, *benzene H*), 6.83 (d, *J* = 3.6 Hz, 1H,*thiophene H*). 2.95 (t, *J* = 7.7 Hz, 4H, *alkyl H*), 1.84 (p, *J* = 7.6 Hz, 4H. *alkyl H*), 1.69 – 1.31 (m, 16H, *alkyl H*), 1.16 – 0.93 (m, 6H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.6, 139.3, 136.2, 133.5, 128.5, 128.5, 126.5, 126.5, 124.4, 120.5, 93.6 31.64, 31.60, 30.21, 28.9 22.56, 14.08. HRMS (ESI-MeOH) calcd for $C_{34}H_{39}S_2^+$ $[M+H]^+$ 511.2488; found 511.2519.

5,5'-(2,5-bis((2-(5-hexylthiophen-2-yl)phenyl)ethynyl)-1,4-phenylene)bis(2-hexylthiophene) (10a)



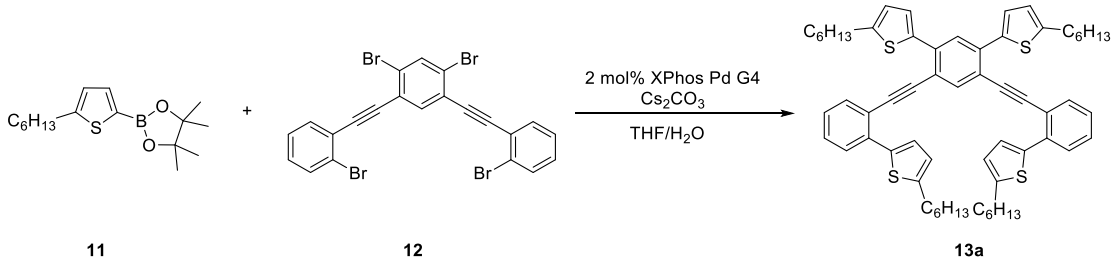
9 **8** **10a**

TMPMgCl·LiCl (7.85 mL, 1 M in THF/Toluene, 8.82 equiv.) was slowly added into **8** (1.42 mL, 7.85 mmol, 8.82 equiv.). The solution was kept stirring at room temperature during 20 mins. Then $ZnCl_2$ (0.5 M in THF, 15.6 mL, 8.82 equiv.) was added into the mixture. After 1 hour, **9** (0.53 g, 0.89 mmol, 1.00 equiv.) and G4 Pd Xphos (38 mg, 0.080 mol, 0.090 equiv.) were added to the solution. The solution was kept stirring at 60 °C during 72 h before quenching with saturated NH_4Cl solution. The aqueous phase was extracted by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM: 30/1) to afford **10a** as pale solid (0.27 g, 0.28 mmol, 44%).

Melting point: 136-137 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 2H, *benzene H*), 7.70 (dd, *J* = 7.6, 1.4 Hz, 2H, *benzene H*), 7.66 (dd, *J* = 7.9, 1.2 Hz, 2H, *benzene H*), 7.59 (d, *J* = 3.6 Hz, 2H, *thiophene H*), 7.53 (d, *J* = 3.6 Hz, 2H, *thiophene H*), 7.44 (td, *J* = 7.6, 1.5 Hz, 2H, *benzene H*), 7.34 (td, *J* = 7.6, 1.5 Hz, 2H, *benzene H*), 6.88 (d, *J* = 3.6 Hz, 2H, *thiophene H*), 6.85 (d, *J* = 3.6 Hz, 2H, *thiophene H*), 2.95 (t, *J* = 7.7 Hz, 8H, *alkyl H*), 1.68-1.58 (m, 8H, *alkyl H*), 1.57 – 1.31 (m, 24H, *alkyl H*), 1.09 – 0.91 (m, 12H, *alkyl H*). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.9, 146.8, 139.1, 138.2, 136.4, 133.9, 133.4, 133.2, 128.7, 128.5, 126.7, 126.5, 124.5, 124.4, 120.3, 120.6, 95.3, 93.3, 31.7, 31.6, 31.6, 30.3, 30.3, 28.9, 28.9, 22.6, 22.6, 14.1, 14.1. *One aromatic carbon is not resolved*. HRMS (ESI-MeOH) calcd for $C_{62}H_{71}S_4^+$ $[M+H]^+$ 943.4433; found 943.4519.

5,5'-(4,6-bis((2-(5-hexylthiophen-2-yl)phenyl)ethynyl)-1,3-phenylene)bis(2-hexylthiophene) (13a)

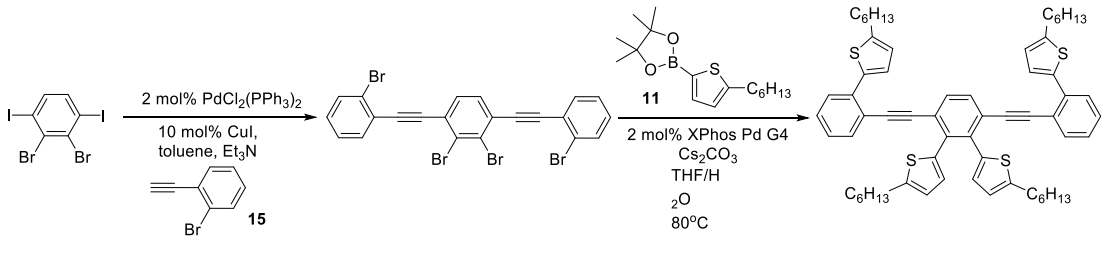


11 12 13a

A mixture of **11** (1.74 g, 4.92 mmol, 4.80 equiv.), **12** (733 mg, 1.23 mmol, 1.00 equiv.), G4 Pd Xphos (21 mg, 25 umol, 0.02 equiv.) and Cs_2CO_3 (7.70 g, 23.6 mmol, 19.2 equiv.) in THF (12 mL)/H_2O (5 mL) was degassed with liquid nitrogen. The mixture was kept stirring overnight in 80 °C before quenching with H_2O (30 mL). The aqueous phase was extracted by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM: 30/1-10/1) to afford **13a** as yellow oil (0.71 g, 0.75 mmol, 61%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (s, 1H, *benzene H*), 7.79 (s, 1H, *benzene H*), 7.65 (dd, *J* = 7.7, 1.4 Hz, 2H, *benzene H*), 7.61 (dd, *J* = 7.9, 1.2 Hz, 2H, *benzene H*), 7.57 (d, *J* = 3.6 Hz, 2H, *thiophene H*), 7.50 (d, *J* = 3.6 Hz, 2H, *thiophene H*), 7.38 (td, *J* = 7.7, 1.4 Hz, 2H, *benzene H*), 7.28 (ddd, *J* = 8.8, 6.9, 1.2 Hz, 2H, *benzene H*), 6.80 (d, *J* = 3.7 Hz, 2H, *thiophene H*), 6.76 (d, *J* = 3.6 Hz, 2H, *thiophene H*), 2.88 (t, *J* = 7.7 Hz, 4H, *alkyl H*), 2.80 (t, *J* = 7.8 Hz, 4H, *alkyl H*), 1.77 (p, *J* = 7.6 Hz, 4H, *alkyl H*), 1.69 (p, *J* = 7.6 Hz, 4H, *alkyl H*), 1.49 – 1.42 (m, 4H, *alkyl H*), 1.41 – 1.23 (m, 20H, *alkyl H*), 0.98 – 0.92 (m, 6H, *alkyl H*), 0.92 – 0.84 (m, 6H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.4, 146.9, 139.2, 138.7, 138.6, 136.3, 135.8, 133.5, 128.6, 128.5, 128.1, 127.1, 126.6, 126.5, 124.7, 124.4, 120.3, 118.6, 94.6, 92.9, 31.6, 31.5, 30.3, 30.2, 28.9, 28.8, 22.6, 14.1, 14.0. HRMS (Maldi) calcd for $C_{62}H_{70}S_4^+$ $[M]^+$ 942.4355; found 942.4351.

5,5'-(3,6-bis((2-(5-hexylthiophen-2-yl)phenyl)ethynyl)-1,2-phenylene)bis(2-hexylthiophene) (17a)



14 16 17a

16 (1.15 g, 6.30 mmol, 2.20 equiv.) was injected into a degassed solution of **14** (1.40 g, 2.86 mmol, 1.00 equiv.), $PdCl_2(PPh3)_2$ (40 mg, 57 umol, 0.02 equiv.) and CuI (54 mg, 0.29 mmol, 0.10 euqiv.) in toluene (10 mL)/Et_3N (4 mL) at room temperature. The reaction was quenched with H_2O (30 mL) after 4h. The aqueous phase was extracted

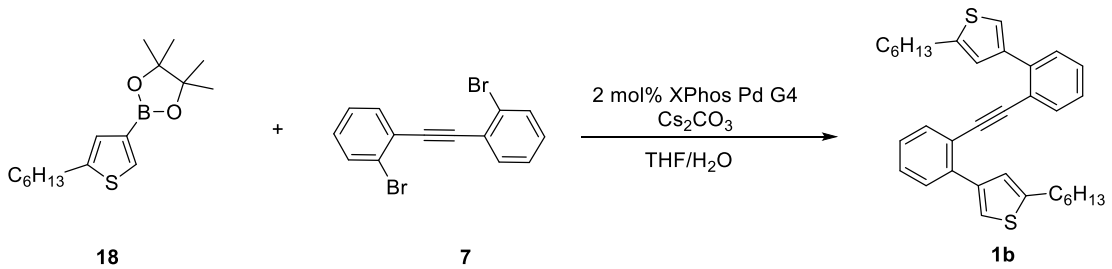
by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was recrystallized in acetone to afford **16** as yellow powder (1.57 g, 2.64 mmol, 93%, more than 90% purity from 1H NMR). **16** is used for reactions without further purification.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.63 (m, 2H, *benzene H*), 7.62 (dd, *J* = 7.7, 1.7 Hz, 2H, *benzene H*), 7.54 (s, 2H, *benzene H*), 7.33 (td, *J* = 7.6, 1.1 Hz, 2H, *benzene H*), 7.23 (td, *J* = 7.8, 1.7 Hz, 2H, *benzene H*).

A mixture of **11** (1.12 g, 3.80 mmol, 4.80 equiv.), **16** (0.47 g, 0.79 mmol, 1.00 equiv.), G4 Pd Xphos (14 mg, 25 umol, 0.02 equiv.) and Cs_2CO_3 (4.95 g, 15.2 mmol, 19.2 equiv.) in THF (10 mL)/H_2O (3 mL) was degassed with liquid nitrogen. The mixture was kept stirring overnight in 80 °C before quenching with H_2O (30 mL). The aqueous phase was extracted by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM: 30/1-10/1) to afford **17a** as brown oil (0.68 g, 0.75 mmol, 91%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.48 (m, 4H, *benzene H*), 7.36 (d, *J* = 3.6 Hz, 2H, *benzene H*), 7.34 – 7.24 (m, 4H, *benzene H* + *thiophene H*), 7.16 (td, *J* = 7.6, 1.3 Hz, 2H), 6.85 (d, *J* = 3.5 Hz, 2H, *thiophene H*), 6.77 (d, *J* = 3.5 Hz, 2H, *thiophene H*), 6.64 (d, *J* = 3.5 Hz, 2H, *thiophene H*), 2.87 (t, *J* = 7.6 Hz, 4H, *alkyl H*), 2.77 (t, *J* = 7.6 Hz, 4H, *alkyl H*), 1.76 (p, *J* = 7.6 Hz, 4H, *alkyl H*), 1.65 (p, *J* = 7.4 Hz, 4H, *alkyl H*), 1.51 – 1.24 (m, 24H, *alkyl H*), 1.04 – 0.80 (m, 12H, *alkyl H*). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.2, 146.6, 139.3, 137.9, 137.0, 135.9, 134.1, 131.2, 128.9, 128.6, 128.3, 126.6, 126.4, 124.7, 124.6, 123.2, 120.2, 94.8, 93.3, 31.8, 31.7, 31.6, 31.6 30.3, 30.1, 28.9, 28.7, 22.7, 14.2. HRMS (Maldi) calcd for $C_{62}H_{70}S_4^+$ $[M]^+$ 942.4355; found 942.4347.

1,2-Bis(2-(5-hexylthiophen-3-yl)phenyl)ethyne (1b)

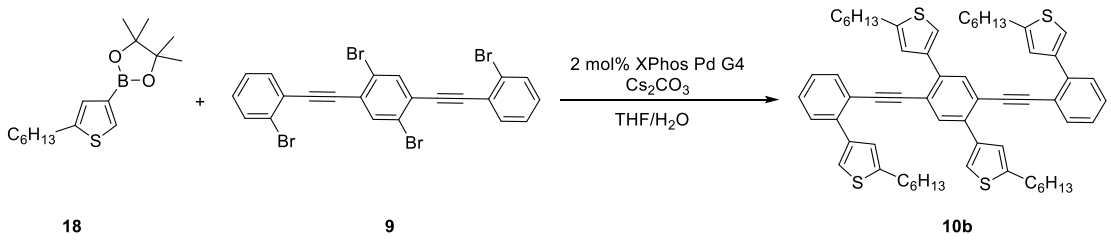


18 **7** **1b**

A mixture of **18** (0.76 g, 2.40 mmol, 2.4 equiv.), **7** (0.34 g, 1.00 mmol, 1.00 equiv.), G4 Pd Xphos (17 mg, 20 umol, 0.02 equiv.) and Cs_2CO_3 (2.9 g, 8.8 mmol, 19.2 equiv.) in THF (10 mL)/H_2O (3 mL) was degassed with liquid nitrogen. The mixture was kept stirring overnight in 80 °C before quenching with H_2O (30 mL). The aqueous phase was extracted by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM: 30/1) to afford **1b** as brown oil (0.45 g, 0.88 mmol, 88%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.8, 1.4 Hz, 2H, *benzene H*), 7.52 (dd, *J* = 7.8, 1.4 Hz, 2H, *benzene H*), 7.45 (d, *J* = 1.4 Hz, 2H, *thiophene H*), 7.38 (td, *J* = 7.6, 1.5 Hz, 2H, *benzene H*), 7.29 (ddd, *J* = 7.6, 6.8, 1.5 Hz, 2H, *benzene H*), 7.22 (d, *J* = 1.4 Hz, 2H. *thiophene H*), 2.88 (t, *J* = 7.7 Hz, 4H, *alkyl H*), 1.76 (p, *J* = 7.6 Hz, 4H, *alkyl H*), 1.53 – 1.26 (m, 12H, *alkyl H*), 0.99 – 0.86 (m, 6H, *alkyl H*). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.3, 140.3, 138.3, 133.3, 128.8, 128.5, 126.6, 125.6, 121.3, 121.2, 92.8, 31.7, 31.6, 30.3, 29.0, 22.6, 14.2. HRMS (AccuTof-dart) calcd for $C_{34}H_{39}S_2^+$ $[M]^+$ 511.2488; found 511.2473.

4,4'-(2,5-Bis((2-(5-hexylthiophen-3-yl)phenyl)ethynyl)-1,4-phenylene)bis(2-hexylthiophene) (10b)



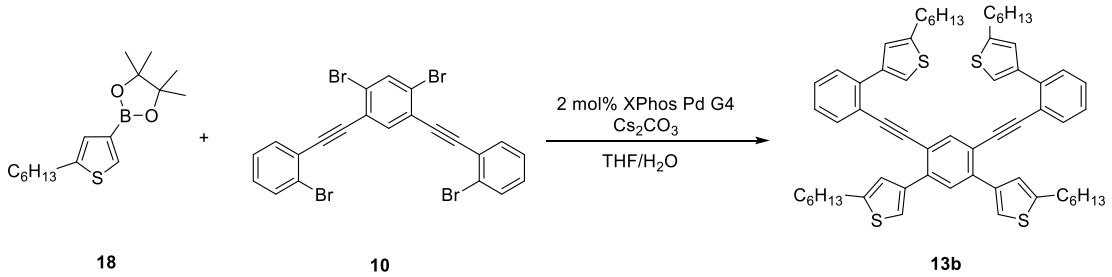
18 **9** **10b**

A mixture of **18** (1.56 g, 5.28 mmol, 4.80 equiv.), **9** (0.65 g, 1.10 mmol, 1.00 equiv.), G4 Pd Xphos (19 mg, 22 umol, 0.02 equiv.) and Cs_2CO_3 (6.9 g, 21 mmol, 19.2 equiv.) in THF (12 mL)/H_2O (4 mL) was degassed with liquid nitrogen. The mixture was kept stirring overnight in 80 °C before quenching with H_2O (30 mL). The aqueous phase was extracted by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM: 30/1) to afford **10b** as brown powder (0.76 g, 0.81 mmol, 73%).

Melting point: 82-83°C

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (s, 2H, *benzene H*), 7.56 (d, *J* = 7.7 Hz, 2H, *benzene H*), 7.50 (m, *J* = 8.3 Hz, 4H, *benzene H + thiohene H*), 7.43 (s, 2H, *thiophene H*), 7.38 (t, *J* = 7.6 Hz, 2H, *benzene H*), 7.29 (t, *J* = 7.6 Hz, 2H, *benzene H*), 7.22 (s, 2H, *thiohene H*), 7.20 (s, 2H, *thiohene H*), 2.89 (t, *J* = 7.8 Hz, 4H, *alkyl H*), 2.83 (t, *J* = 7.8 Hz, 4H, *alkyl H*), 1.77 (p, *J* = 7.7 Hz, 4H, *alkyl H*), 1.70 (p, *J* = 7.7 Hz, 4H, *alkyl H*), 1.49 – 1.23 (m, 24H, *alkyl H*), 0.97-0.90 (m, 12H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.5, 145.4, 140.3, 139.1, 138.6, 136.1, 133.5, 133.1, 128.9, 128.6, 126.7, 125.6, 125.3, 121.5, 121.3, 121.1, 121.1, 94.3, 92.6, 31.8, 31.7, 31.7, 31.6, 30.3, 30.2, 29.0, 28.9, 22.6, 14.2, 14.1. HRMS (Maldi) calcd for $C_{62}H_{70}S_4^+$ $[M]^+$ 942.4355; found 942.4326.

4,4'-(4,6-Bis((2-(5-hexylthiophen-3-yl)phenyl)ethynyl)-1,3-phenylene)bis(2-hexylthiophene) (13b)

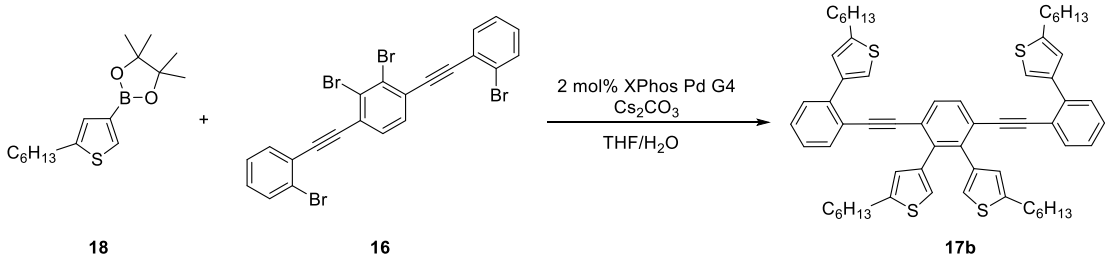


18 10 13b

A mixture of **18** (1.40 g, 4.80 mmol, 4.80 equiv.), **10** (594 mg, 1.00 mmol, 1.00 equiv.), G4 Pd Xphos (18 mg, 20 umol, 0.02 equiv.) and Cs_2CO_3 (6.26 g, 19.2 mmol, 19.2 equiv.) in THF (10 mL)/H_2O (3 mL) was degassed with liquid nitrogen. The mixture was kept stirring overnight in 80 °C before quenching with H_2O (30 mL). The aqueous phase was extracted by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM: 30/1-10/1) to afford **13b** as brown oil (0.72 g, 0.76 mmol, 76%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (s, 1H, *benzene H*), 7.58 (s, 1H, *benzene H*), 7.55 (dd, *J* = 7.7, 1.4 Hz, 2H, *benzene H*), 7.49 (dd, *J* = 7.7, 1.4 Hz, 2H, *benzene H*), 7.46 (d, *J* = 1.5 Hz, 2H, *thiophene H*), 7.40 (d, *J* = 1.5 Hz, 2H, *thiophene H*), 7.36 (td, *J* = 7.6, 1.4 Hz, 2H, *benzene H*), 7.28 (td, *J* = 7.6, 1.4 Hz, 2H, *benzene H*), 7.18 (m, 4H, *thiophene H*), 2.87-2.79 (m, 8H, *alkyl H*), 1.75-1.65 (m, 8H, *alkyl H*), 1.44 – 1.22 (m, 24H), 0.94-0.88 (m, 6H, *alkyl H*), 0.89 – 0.81 (m, 6H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.6, 145.5, 140.3, 139.6, 138.5, 138.1, 137.9, 133.3, 129.1, 128.9, 128.6, 126.6, 125.5, 125.3, 121.8, 121.3, 121.1, 119.6, 93.4, 91.9, 31.7, 31.7, 31.6, 31.6, 30.2, 29.0, 28.9, 22.6, 14.1, 14.1. HRMS (Maldi) calcd for $C_{62}H_{70}S_4^+$ $[M]^+$ 942.4355; found 942.4316.

4,4'-(3,6-Bis((2-(5-hexylthiophen-3-yl)phenyl)ethynyl)-1,2-phenylene)bis(2-hexylthiophene) (17b)



18 16 17b

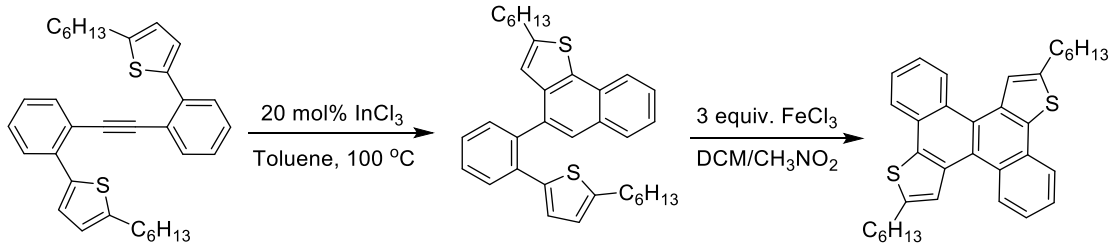
A mixture of **18** (1.56 g, 5.28 mmol, 4.80 equiv.), **16** (0.65 g, 1.10 mmol, 1.00 equiv.), G4 Pd Xphos (19 mg, 22 umol, 0.02 equiv.) and Cs_2CO_3 (6.9 g, 21 mmol, 19.2 equiv.) in THF (12 mL)/H_2O (4 mL) was degassed with liquid nitrogen. The mixture was kept stirring overnight in 80 °C before quenching with H_2O (30 mL). The aqueous phase was

extracted by DCM (3 x 30 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM: 30/1-10/1) to afford **17b** as brown powder (0.78 g, 0.83 mmol, 75%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.8 2H, *benzene H*), 7.47 (s, 2H, *thiophene H*), 7.41 (dd, *J* = 7.8, 1.4 Hz, 2H, *benzene H*), 7.37 – 7.33 (m, 4H, *benzene H* + *thiophene H*), 7.25 (t, *J* = 7.6, Hz, 2H, *benzene H*), 7.17 (s, 2H, *thiophene H*), 6.98 (d, *J* = 1.4 Hz, 2H, *thiophene H*), 6.59 (s, 2H, *thiophene H*), 2.91 (t, *J* = 7.7 Hz, 4H, *alkyl H*), 2.77 (t, *J* = 7.6 Hz, 4H, *alkyl H*), 1.80 (p, *J* = 7.7 Hz, 4H, *alkyl H*), 1.64 (p, *J* = 7.5 Hz, 4H, *alkyl H*), 1.52 – 1.31 (m, 24H, *alkyl H*), 1.00-0.94 (m, 12H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.2, 143.9, 140.1, 139.1, 138.6, 138.1, 133.6, 130.9, 128.7, 128.5, 126.9, 126.5, 125.5, 123.5, 122.7, 121.4, 121.0, 94.2, 92.6, 31.8, 31.8, 31.7, 30.3, 30.0, 29.0, 28.8, 22.7, 22.6, 14.2. HRMS (Maldi) calcd for $C_{62}H_{70}S_4^+$ $[M]^+$ 942.4355; found 942.4381.

2.2 Synthesis of thiophene-fused polyaromatic hydrocarbons.

2,9-dihexylchryseno[6,5-b:12,11-b']dithiophene (3a)



1a **2a** **3a**

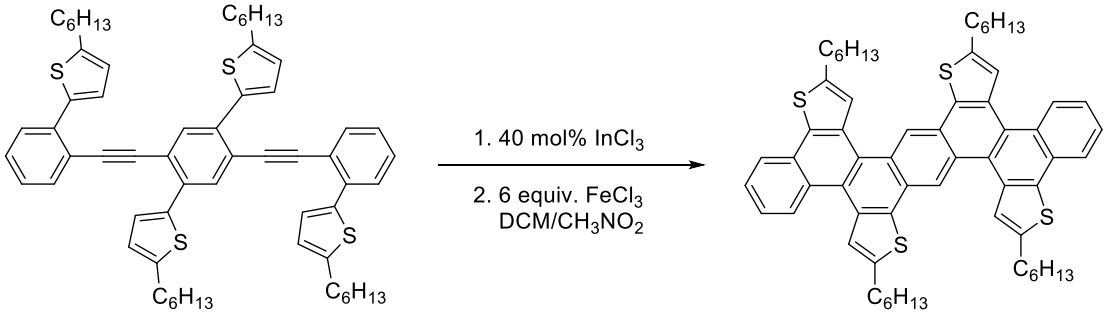
1a (76 mg, 0.15 mmol, 1 equiv.) wad added into a solution of $InCl_3$ (6 mg, 0.03 mmol, 0.2 equiv.) in toluene (3 mL). The mixture was kept stirring at 100 °C overnight. The mixture was concentrated and purified by a plug of silica gel to afford **2a** as transparent oil (67 mg, 0.13 mmol, 88%)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.2 Hz, 1H, *benzene H*), 7.88 (d, *J* = 8.0 Hz, 1H, *benzene H*), 7.69 – 7.66 (m, 1H, *benzene H*), 7.63 (s, 1H, *benzene H*), 7.58 – 7.52 (m, 1H, *benzene H*), 7.49 – 7.44 (m, 3H, *benzeneH*), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H, *benzene H*), 6.71 (s, 1H, *thiophene H*), 6.41 (d, *J* = 3.6 Hz, 1H, *thiophene H*), 6.33 (d, *J* = 3.6 Hz, 1H, *thiophene H*), 2.82 (t, *J* = 7.6 Hz, 2H, *alkyl H*), 2.60 (t, *J* = 7.6 Hz, 2H, *alkyl H*), 1.67 (p, *J* = 7.4 Hz, 2H,), 1.50 (h, *J* = 7.3, 6.0 Hz, 2H, *alkyl H*), 1.41 – 1.15 (m, 12H, *alkyl H*), 0.89 (dt, *J* = 18.1, 7.0 Hz, 6H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.9, 145.2, 140.1, 138.7, 137.7, 136.0, 135.6, 134.2, 131.6, 130.6, 129.6, 128.9, 128.5, 127.9, 127.0, 126.3, 126.2, 125.8, 125.1, 124.1, 123.3, 121.6, 31.6, 31.5, 31.5, 31.4, 30.7, 29.9, 28.7, 28.6, 22.6, 22.5, 14.1. HRMS (AccuTof-Dart) calcd for $C_{34}H_{39}S_2^+$ $[M+H]^+$ 511.2488; found 511.2513.

A solution of $FeCl_3$ (63 mg, 0.39 mmol, 3.0 equiv.) in dry CH_3NO_2 (1 mL) was added dropwise into a solution of **2a** (67 mg, 0.13 mmol, 1.0 equiv.) in dry DCM (65 mL) at 0 °C. Dry MeOH was used to quench the reaction after 5 mins. The organic phase was washed with 1.0 M HCl (20 mL). The aqueous was extracted with DCM (3 X 15 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane) to afford **3a** as white powder (62 mg, 0.12 mmol, 94%).

Melting point: 63 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 (d, *J* = 7.2 Hz, 2H, *benzene H*), 8.18 (dd, *J* = 7.2, 1.9 Hz, 2H, *benzene H*), 8.02 (s, 2H, *thiophene H*), 7.62 (m, 4H, *benzene H*), 3.05 (t, *J* = 7.6 Hz, 4H, *alkyl H*), 1.84 (p, *J* = 7.6 Hz, 4H, *alkyl H*), 1.65 – 1.19 (m, 12H, *alkyl H*), 0.91 (t, *J* = 6.9 Hz, 6H, *alkyl H*). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.4, 135.6, 134.4, 128.5, 128.1, 128.0, 126.6, 125.1, 125.0, 124.2, 123.8, 31.7, 31.6, 31.0, 28.8, 22.6, 14.1. HRMS (AccuTof-Dart) calcd for $C_{34}H_{37}S_2^+$ $[M+H]^+$ 509.2331; found 509.2343.



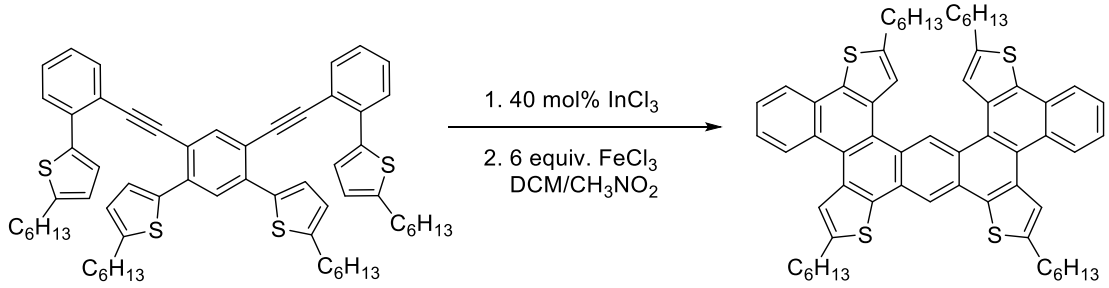
10a **4a**

$InCl_3$ (4 mg, 0.02 mmol, 0.4 equiv.) was added into a solution of **10a** (47 mg, 0.050 mmol, 1.0 equiv.) in toluene (1 mL). The solution was kept stirring at 100 °C overnight. The mixture was concentrated and purified by column chromatography (Hexane/DCM: 15/1) to afford a mixture of regioisomers a brown powder (37.0 mg, 0.0395 mmol, 79%).

A solution of $FeCl_3$ (97 mg, 0.60 mmol, 6.0 equiv.) in dry CH_3NO_2 (1.0 mL) was added dropwise into a solution of regioisomers (94 mg, 0.10 mmol, 1.0 equiv.) in dry DCM (50 mL) at 0 °C. Dry MeOH was added to quench the reaction after 10 mins. The organic phase was washed with 1.0 M HCl (20 mL). The aqueous was extracted with DCM (3 X 15 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM:5/1) to afford **4a** as brown powder (83 mg, 0.088 mmol, 70% over two steps).

Melting point: 72 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 2H, *benzene H*), 8.71 (d, *J* = 8.3 Hz, 2H, *benzene H*), 8.10 (m, 4H, *benzene H* + *thiophene H*), 7.85 (s, 2H, *thiophene H*), 7.58 (t, *J* = 7.4 Hz, 2H, *benzene H*), 7.51 (t, *J* = 7.6 Hz, 2H, *benzene H*), 3.05 (t, *J* = 7.5 Hz, 4H, *alkyl H*), 2.99 (t, *J* = 7.7 Hz, 4H, *alkyl H*), 1.94 (p, *J* = 7.6 Hz, 4H, *alkyl H*), 1.83 (p, *J* = 7.5 Hz, 4H, *alkyl H*), 1.58 – 1.21 (m, 24H, *alkyl H*), 0.94 (td, *J* = 7.0, 2.8 Hz, 12H, *alkyl H*). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.4, 144.9, 135.9, 135.7, 134.6, 134.0, 128.6, 128.0, 127.8, 127.0, 126.5, 126.0, 125.2, 124.88, 124.5, 124.4, 123.8, 123.7, 122.2, 31.8, 31.7, 31.7, 31.2, 31.0, 31.0, 29.0, 29.0, 22.7, 14.2, 14.1. HRMS (Maldi) calcd for $C_{62}H_{66}S_4^+$ $[M]^+$ 938.4042; found 938.4053.



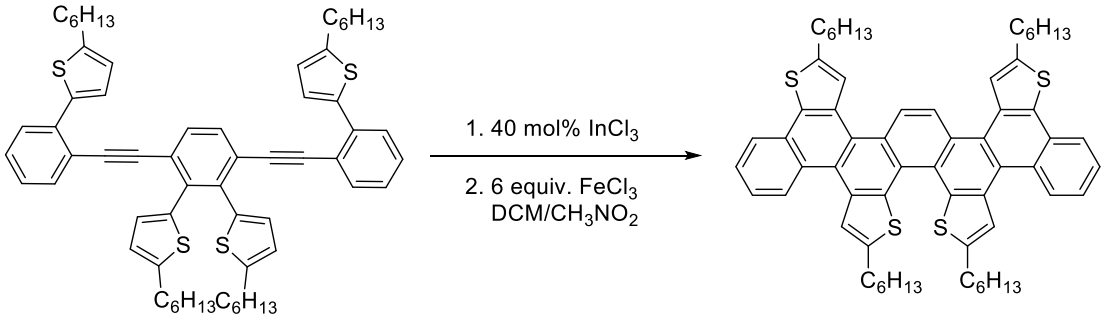
$InCl_3$ (9 mg, 0.040 mmol, 0.4 equiv.) was added into a solution of **13a** (94 mg, 0.10 mmol, 1.0 equiv.) in toluene (2 mL). The solution was kept stirring at 100 °C overnight. The mixture was concentrated and purified by column chromatography (Hexane/DCM: 15/1) to afford a mixture of regioisomers a brown powder (67 mg, 0.071 mmol, 71%).

A solution of $FeCl_3$ (97 mg, 0.60 mmol, 6.0 equiv.) in dry CH_3NO_2 (1.0 mL) was added dropwise into a solution of regioisomers (94 mg, 0.10 mmol, 1.0 equiv.) in dry DCM (50 mL) at 0 °C. Dry MeOH was added to quench the reaction after 10 mins. The organic phase was washed with 1.0 M HCl (20 mL). The aqueous was extracted with DCM (3 X 15 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM:5/1) to afford **5a** as brown powder (84 mg, 0.090 mmol, 64% over two steps).

Melting point: 135 °C

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.43 (s, 1H, *benzene H*), 8.71 (d, *J* = 8.3 Hz, 2H, *benzene H*), 8.47 (s, 1H, *benzene H*), 8.16 (dd, *J* = 7.9, 1.3 Hz, 2H, *benzene H*), 7.96 (s, 2H, *thiophene H*), 7.70 (s, 2H, *thiophene H*), 7.62 (t, *J* = 7.3 Hz, 2H, *thiophene H*), 7.56 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 2H, *benzene H*), 2.88 (t, *J* = 7.9 Hz, 4H, *alkyl H*), 2.83 (t, *J* = 7.8 Hz, 4H, *alkyl H*), 1.84-1.65 (m, 8H, *alkyl H*), 1.49 – 1.24 (m, 24H, *alkyl H*), 0.99 – 0.93 (m, 6H, *alkyl H*), 0.91 – 0.80 (m, 6H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-

d) δ 145.6, 145.4, 136.0, 134.7, 134.5, 134.2, 128.4, 128.1, 128.0, 126.7, 126.6, 126.4, 125.9, 125.3, 124.9, 124.8, 124.3, 123.8, 123.7, 116.0, 31.7, 31.7, 31.5, 31.0, 30.9, 29.1, 29.0, 22.7, 22.6, 14.2, 14.1. HRMS (Maldi) calcd for $C_{62}H_{66}S_4^+$ [M]+ 938.4042; found 938.3994.



17a **6a**

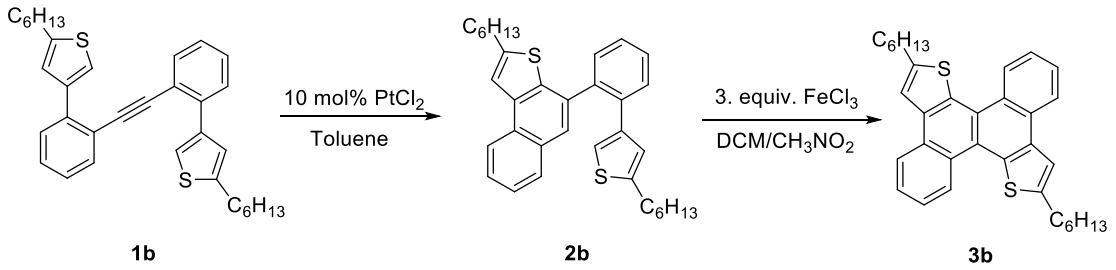
$InCl_3$ (15 mg, 0.068 mmol, 0.4 equiv.) was added into a solution of **17a** (160 mg, 0.17 mmol, 1.0 equiv.) in toluene (3.4 mL). The solution was kept stirring at 100 °C overnight. The mixture was concentrated and purified by column chromatography (Hexane/DCM: 15/1) to afford a mixture of regioisomers a brown powder (115 mg, 0.12 mmol, 72%).

A solution of $FeCl_3$ (92 mg, 0.57 mmol, 6.0 equiv.) in dry CH_3NO_2 (1.0 mL) was added dropwise into a solution of regioisomers (90 mg, 0.095 mmol, 1.0 equiv.) in dry DCM (50 mL) at 0 °C. Dry MeOH was added to quench the reaction after 10 mins. The organic phase was washed with 1.0 M HCl (20 mL). The aqueous was extracted with DCM (3 X 15 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM:5/1) to afford **6a** as brown powder (70 mg, 0.075 mmol, 57% over two steps).

Melting point: 75 °C

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.10 (dd, *J* = 6.2, 3.3 Hz, 2H, *benzene H*), 8.94 (s, 2H, *benzene H*), 8.32 (s, 2H, *thiophene H*), 8.24 (dd, *J* = 6.2, 3.3 Hz, 2H, *benzene H*), 8.03 (s, 2H, *thiophene H*), 7.71-7.67 (m, 4H, *benzene H*), 3.17 (t, *J* = 7.6 Hz, 4H, *alkyl H*), 3.01 (t, *J* = 7.6 Hz, 4H), 1.92 (p, *J* = 7.7 Hz, 4H), 1.76 (p, *J* = 7.6 Hz, 4H), 1.57 – 1.22 (m, 24H), 0.93 (t, *J* = 7.0 Hz, 6H), 0.86 (td, *J* = 5.8, 4.7, 2.3 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.7, 145.1, 137.1, 136.2, 134.6, 134.1, 129.2, 128.7, 128.3, 127.8, 127.0, 126.0, 125.3, 125.2, 124.6, 124.4, 124.1, 123.8, 123.7, 31.8, 31.7, 31.6, 31.5, 31.2, 30.7, 28.9, 28.8, 22.7, 22.6, 14.2, 14.1. HRMS (Maldi) calcd for $C_{62}H_{66}S_4^+$ [M]+ 938.4042; found 938.4017.

2,9-dihexylchryseno[5,6-b:11,12-b']dithiophene (3b)



1b **2b** **3b**

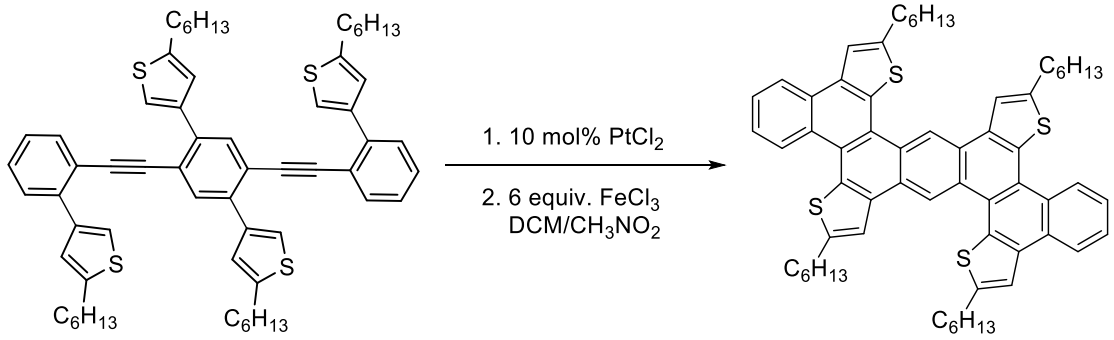
$PtCl_2$ (4.0 mg, 0.015 mmol, 0.1 equiv.) was added into a solution of **1b** (76 mg, 0.15 mmol, 1.0 equiv.) in toluene (3 mL). The solution was kept stirring at 100 °C overnight. The mixture was concentrated and purified by column chromatography (Hexane/DCM: 15/1) to afford **2b** as a brown oil (72 mg, 0.14 mmol, 95%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.2 Hz, 1H, *benzene H*), 7.85 (d, *J* = 8.0 Hz, 1H, *benzene H*), 7.67 (s, 1H, *benzene H*), 7.64 (dd, *J* = 7.8, 1.3 Hz, 1H, *benzene H*), 7.60 – 7.56 (m, 2H, *benzene H*), 7.54 – 7.47 (m, 3H, *benzene H* + *thiophene H*), 7.44 (td, *J* = 7.5, 1.3 Hz, 1H, *benzene H*), 6.76 (d, *J* = 1.3 Hz, 1H, *thiophene H*), 6.46 (s, 1H, *thiophene H*), 2.94 (t, *J* = 7.6 Hz, 2H, *alkyl H*), 2.51 (t, *J* = 7.5 Hz, 2H, *alkyl H*), 1.75 (p, *J* = 7.5 Hz, 2H, *alkyl H*), 1.44 – 1.26 (m, 8H, *alkyl H*), 1.25 – 1.02 (m, 6H, *alkyl H*), 0.95 – 0.90 (m, 3H, *alkyl H*), 0.87 (t, *J* = 7.2 Hz, 3H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.3, 144.5, 140.9, 138.6, 137.8, 136.1, 136.1, 134.9, 131.5, 130.7, 129.7, 128.6, 128.3, 128.1, 127.0, 125.8, 125.5, 125.1, 124.6, 123.5, 120.3, 118.7, 31.6, 31.4, 31.4, 31.3, 31.0, 29.7, 28.8, 28.3, 22.6, 22.4, 14.1. HRMS (AccuTof-Dart) calcd for $C_{34}H_{39}S_2^+$ $[M+H]^+$ 511.2488; found 511.2489.

Melting point: 97 °C

A solution of $FeCl_3$ (61 mg, 0.38 mmol, 3.0 equiv.) in dry CH_3NO_2 (1.0 mL) was added dropwise into a solution of **2b** (64 mg, 0.13 mmol, 1.0 equiv.) in dry DCM (63 mL) at 0 °C. Dry MeOH was added to quench the reaction after 10 mins. The organic phase was washed with 1.0 M HCl (20 mL). The aqueous was extracted with DCM (3 X 15 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM:5/1) to afford **3b** as brown powder (58 mg, 0.11 mmol, 86% over two steps).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.35 (dd, *J* = 8.1, 1.3 Hz, 2H, *benzene H*), 8.45 (dd, *J* = 7.7, 1.7 Hz, 2H, *benzene H*), 7.78 (s, 2H, *thiophene H*), 7.77-7.71 (m, 4H, *benzene H*), 3.06 (t, *J* = 7.7 Hz, 4H, *alkyl H*), 1.88 (p, *J* = 7.6 Hz, 4H, *alkyl H*), 1.51 – 1.24 (m, 12H, *alkyl H*), 0.92 (t, *J* = 7.0 Hz, 6H, *alkyl H*). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.4, 135.5, 133.6, 128.8, 128.5, 126.9, 126.7, 125.7, 124.3, 124.2, 119.2, 31.7,31.5, 30.5, 28.3, 22.6, 14.1. HRMS (AccuTof-Dart) calcd for $C_{34}H_{39}S_2^+$ $[M+H]^+$ 509.2331; found 511.2309.



10b **4b**

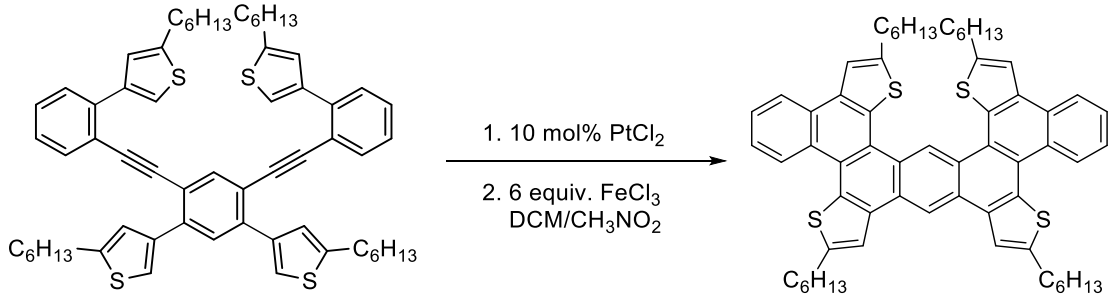
$PtCl_2$ (3.4 mg, 0.013 mmol, 0.1 equiv.) was added into a solution of **10b** (120 mg, 0.13 mmol, 1.0 equiv.) in toluene (3.5 mL). The solution was kept stirring at 100 °C overnight. The mixture was concentrated and purified by column chromatography (Hexane/DCM: 15/1) to afford a mixture of regioisomers a brown powder (102 mg, 0.11 mmol, 85%).

A solution of $FeCl_3$ (97 mg, 0.60 mmol, 6.0 equiv.) in dry CH_3NO_2 (1.0 mL) was added dropwise into a solution of regioisomers (94 mg, 0.10 mmol, 1.0 equiv.) in dry DCM (50 mL) at 0 °C. Dry MeOH was added to quench the reaction after 10 mins. The organic phase was washed with 1.0 M HCl (20 mL). The aqueous was extracted with DCM (3 X 15 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM:5/1) to afford **4b** as yellow powder (78 mg, 0.083 mmol, 71% over two steps).

Melting point: 110 °C

^{1}H NMR (600 MHz, dichlorobenzene-d_4) δ 10.44 (s, 2H, *benzene H*), 9.51 (d, J = 8.4 Hz, 2H, *benzene H*), 8.42 (d, J = 8.0 Hz, 2H, *benzene H*), 8.24 (s, 2H, *thiophene H*), 7.81-7.76 (m, 4H, *benzene H + thiophene H*), 7.70 (t, J = 7.4 Hz, 2H, *benzene H*), 3.11 (td, J = 7.8, 3.0 Hz, 8H, *alkyl H*), 1.92 (q, J = 7.8 Hz, 8H), 1.47 (q, J = 7.4 Hz, 8H, *alkyl H*), 1.36 – 1.15 (m, 24H, *alkyl H*), 0.89 (t, J = 6.8 Hz, 12H, *alkyl H*). HRMS (Maldi) calcd for $C_{62}H_{66}S_4^+$ [M]+ 938.4042; found 938.3997.

Due to low solubility of **4b** in common D-solvents, ^{13}C NMR spectra was not able to acquire.



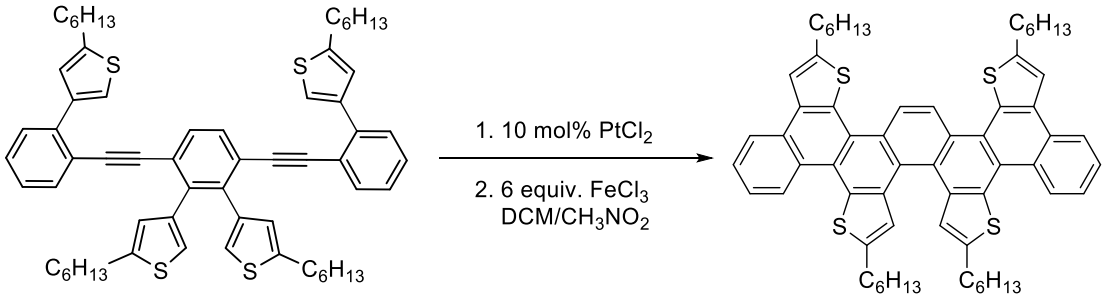
13b **5b**

$PtCl_2$ (3.4 mg, 0.013 mmol, 0.1 equiv.) was added into a solution of **13b** (120 mg, 0.13 mmol, 1.0 equiv.) in toluene (3.5 mL). The solution was kept stirring at 100 °C overnight. The mixture was concentrated and purified by column chromatography (Hexane/DCM: 15/1) to afford a mixture of regioisomers a brown powder (80 mg, 0.085 mmol, 67%).

A solution of $FeCl_3$ (64 mg, 0.39 mmol, 6.0 equiv.) in dry CH_3NO_2 (1.0 mL) was added dropwise into a solution of regioisomers (62 mg, 0.066 mmol, 1.0 equiv.) in dry DCM (33 mL) at 0 °C. Dry MeOH was added to quench the reaction after 10 mins. The organic phase was washed with 1.0 M HCl (20 mL). The aqueous was extracted with DCM (3 X 15 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM:5/1) to afford **5b** as yellow powder (59 mg, 0.063 mmol, 64% over two steps).

Melting point: 194 °C

^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.05 (s, 1H, *benzene H*), 9.08 (dd, *J* = 6.2, 3.3 Hz, 2H, *benzene H*), 8.43 – 8.31 (m, 4H, *benzene H*), 7.74 (dd, *J* = 6.2, 3.2 Hz, 4H, *benzene H*), 7.46 (s, 2H, *thiophene H*), 7.40 (s, 2H, *thiophene H*), 2.80 (dt, *J* = 16.1, 7.8 Hz, 8H, *alkyl H*), 1.87 – 1.75 (m, 4H, *alkyl H*), 1.75 – 1.68 (m, 4H, *alkyl H*), 1.50 – 1.23 (m, 22H, *alkyl H*), 1.02 – 0.95 (m, 6H), 0.94 – 0.80 (m, 6H, *alkyl H*). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.1, 145.2, 134.9, 134.4, 133.5, 133.2, 128.6, 128.6, 127.1, 126.4, 126.1, 125.9, 125.2, 124.2, 124.1 123.8, 123.4, 118.9, 118.4, 117.0, 31.8, 31.7, 31.5, 31.4, 30.4, 30.4, 29.4, 29.2, 22.8, 22.7, 14.2, 14.1.). HRMS (Maldi) calcd for $C_{62}H_{66}S_4^+$ [M]+ 938.4042; found 938.4034.



17b **6b**

$PtCl_2$ (3.4 mg, 0.013 mmol, 0.1 equiv.) was added into a solution of **17b** (120 mg, 0.13 mmol, 1.0 equiv.) in toluene (3.5 mL). The solution was kept stirring at 100 °C overnight. The mixture was concentrated and purified by column chromatography (Hexane/DCM: 15/1) to afford a mixture of regioisomers a brown powder (102 mg, 0.085 mmol, 85%).

A solution of $FeCl_3$ (165 mg, 1.02 mmol, 6.0 equiv.) in dry CH_3NO_2 (1.0 mL) was added dropwise into a solution of regioisomers (160 mg, 0.17 mmol, 1.0 equiv.) in dry DCM (85 mL) at 0 °C. Dry MeOH was added to quench the reaction after 10 mins. The

organic phase was washed with 1.0 M HCl (20 mL). The aqueous was extracted with DCM (3 X 15 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (Hexane/DCM:5/1) to afford **10** as yellow powder (110 mg, 0.12 mmol, 58% over two steps).

Melting point: 202 ºC

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.53 (dd, *J* = 8.3, 1.2 Hz, 2H, *benzene H*), 9.33 (s, 2H, *benzene H*), 8.42 (dd, *J* = 8.0, 1.5 Hz, 2H, *benzene H*), 7.78 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 2H, *benzene H*), 7.75 – 7.71 (m, 4H, *benzene H* +*thiophene H*), 7.68 (s, 2H, *thiophene H*), 3.06 (t, *J* = 7.7 Hz, 4H, *alkyl H*), 2.93 (td, *J* = 7.3, 2.0 Hz, 4H, *alkyl H*), 1.91 (p, *J* = 7.7 Hz, 4H, *alkyl H*), 1.79 (p, *J* = 7.7, Hz, 4H, *alkyl H*), 1.56 – 1.18 (m, 24H, *alkyl H*), 0.94 (t, *J* = 7.0 Hz, 6H, *alkyl H*), 0.92 – 0.83 (m, 6H, *alkyl H*). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.4, 144.4, 136.2, 135.9, 134.3, 133.3, 129.3, 128.3, 127.7, 126.9, 126.8, 125.7, 125.6, 125.1, 124.9, 124.2, 123.8, 123.7, 119.1, 31.8, 31.7, 31.5, 30.6, 30.4, 29.1, 29.0, 22.7, 22.6, 14.2, 14.2.). HRMS (Maldi) calcd for $C_{62}H_{66}S_4^+$ [M]+ 938.4042; found 938.4095.

3. Liquid crystal properties

Figure S1. POM microphotographs for: **a) 4a** taken at 125 ºC, **b) 5a** taken at room temperature, **c) 4b** taken at 200 ºC, and **d) 5b** taken at room temperature.

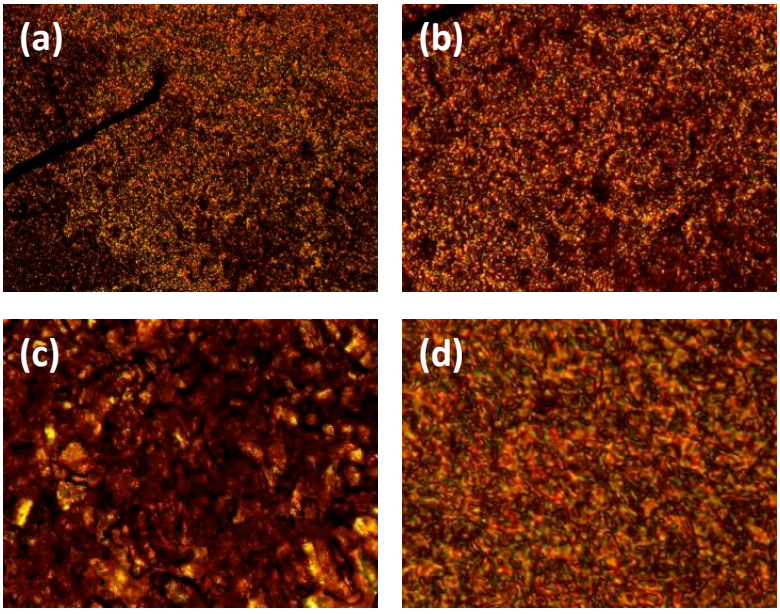


Figure S2. 1D XRD profiles of the hexagonal columnar mesophases.

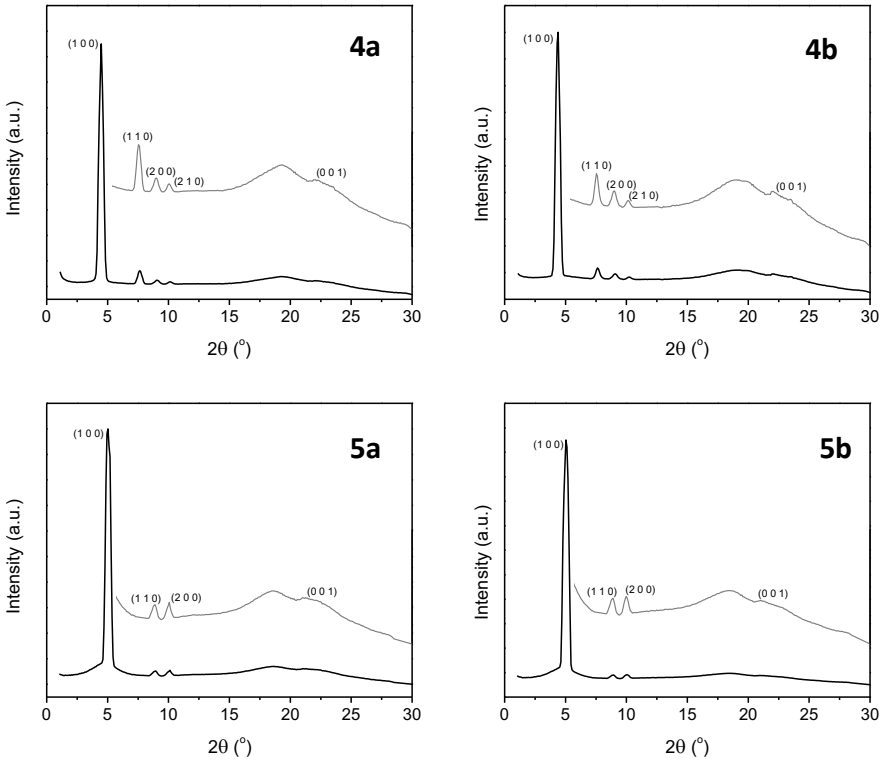


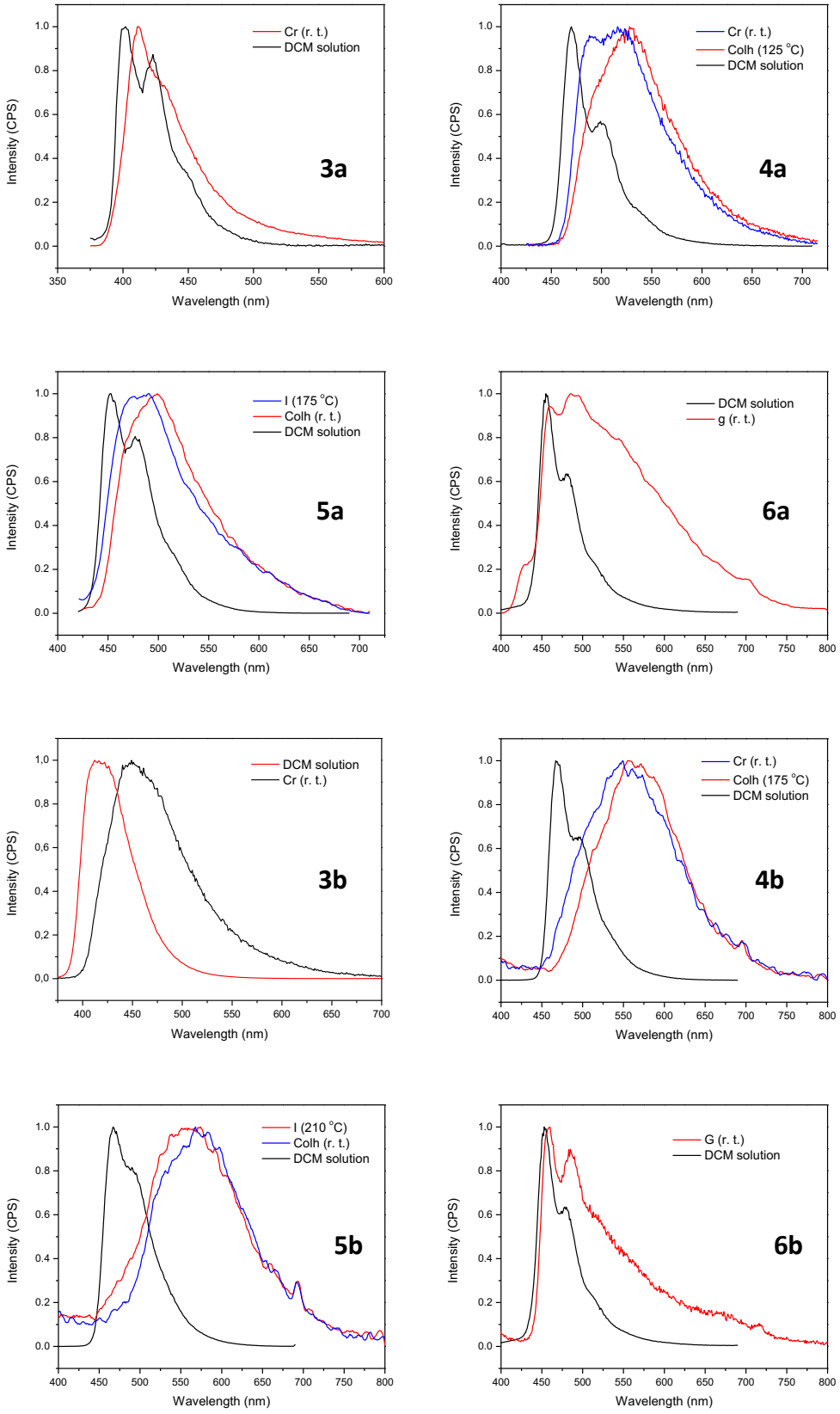
Table S1. XRD structural parameters.

Compound	d_{obs} [a] (Å)	d_{calc} [a] (Å)	*h k l* [b]	Structural parameters[c]
4a	19.6	19.5	1 0 0	a = 22.5 Å; c = 3.5 Å
	11.1	11.3	1 1 0	ρ = 1.01 g/cm^3
	9.8	9.8	2 0 0	
	7.4	7.4	2 1 0	
	4.4 (br)			
	3.5		0 0 1	
5a	18.0	17.8	1 0 0	a = 20.5 Å; c = 4.0 Å
	10.2	10.3	1 1 0	ρ = 1.04 g/cm^3
	8.8	8.9	2 0 0	
	4.6 (br)			
	4.0		0 0 1	
4b	19.4	19.5	1 0 0	a = 22.5 Å; c = 3.5 Å
	11.3	11.3	1 1 0	ρ = 1.02 g/cm^3
	9.7	9.7	2 0 0	
	7.4	7.4	2 1 0	
	4.4 (br)			
	3.5		0 0 1	
5b	17.7	17.6	1 0 0	a = 20.3 Å; c = 4.1 Å
	10.1	10.2	1 1 0	ρ = 1.06 g/cm^3
	8.8	8.8	2 0 0	
	4.7 (br)			
	4.1		0 0 1	

[a] d_{obs}: d value calculated according to Bragg's equation. d_{calc}: calculated d spacings. [b]Miller indices. [c] $a = (2/\sqrt{3})\cdot(d_{10}+\sqrt{3}\cdot d_{11}+\sqrt{4}\cdot d_{20}+\sqrt{7}\cdot d_{21}+\ldots)/n_{reflections}$; c: mean stacking distance; ρ: calculated density value.

4. Solid state photoluminescence

Figure S3. Comparison of the normalized fluorescence spectra of **3-10** in DCM and thin film at different temperatures (Cr: crystal, I: isotropic liquid, Col_h: hexagonal columnar mesophase, G: glass).



5. Calculation Details

DFT calculations were performed with *Orca version 4.0.1*,[7] using the *B3LYP* functional [8,9] and *def2-SVP* basis set [10] with the *RIJCOSX* approximation[11] and *D3BJ* dispersion correction[12], and the *TIGHTSCF* convergence criteria. Previous calculations on polycyclic aromatic hydrocarbons have accurately predicted structures, ionization energies, and optical absorption spectra using *B3LYP* and similar split valence basis sets.[13,14] After geometry optimizations, the structures were then submitted to TD-DFT calculations to calculate UV-Vis absorption spectra. These calculations used the same parameters as the geometry optimizations, along with a tighter integration grid (*FinalGrid6*) and the following TD-DFT-specific parameters: determine 50 roots (*nroots 50*), allow triplet excitations (*triplets true*), and allow up to 5 expansion vectors in the iterative solution of the CI equations (*maxdim 5*). Simulated UV-Vis absorption spectra were plotted with 2000 cm^{-1} broadening. Molecular orbital images were generated with *Jmol*.[15]

Figure S4: Frontier molecular orbitals of **3a'–6a'** and **3b' -6b**

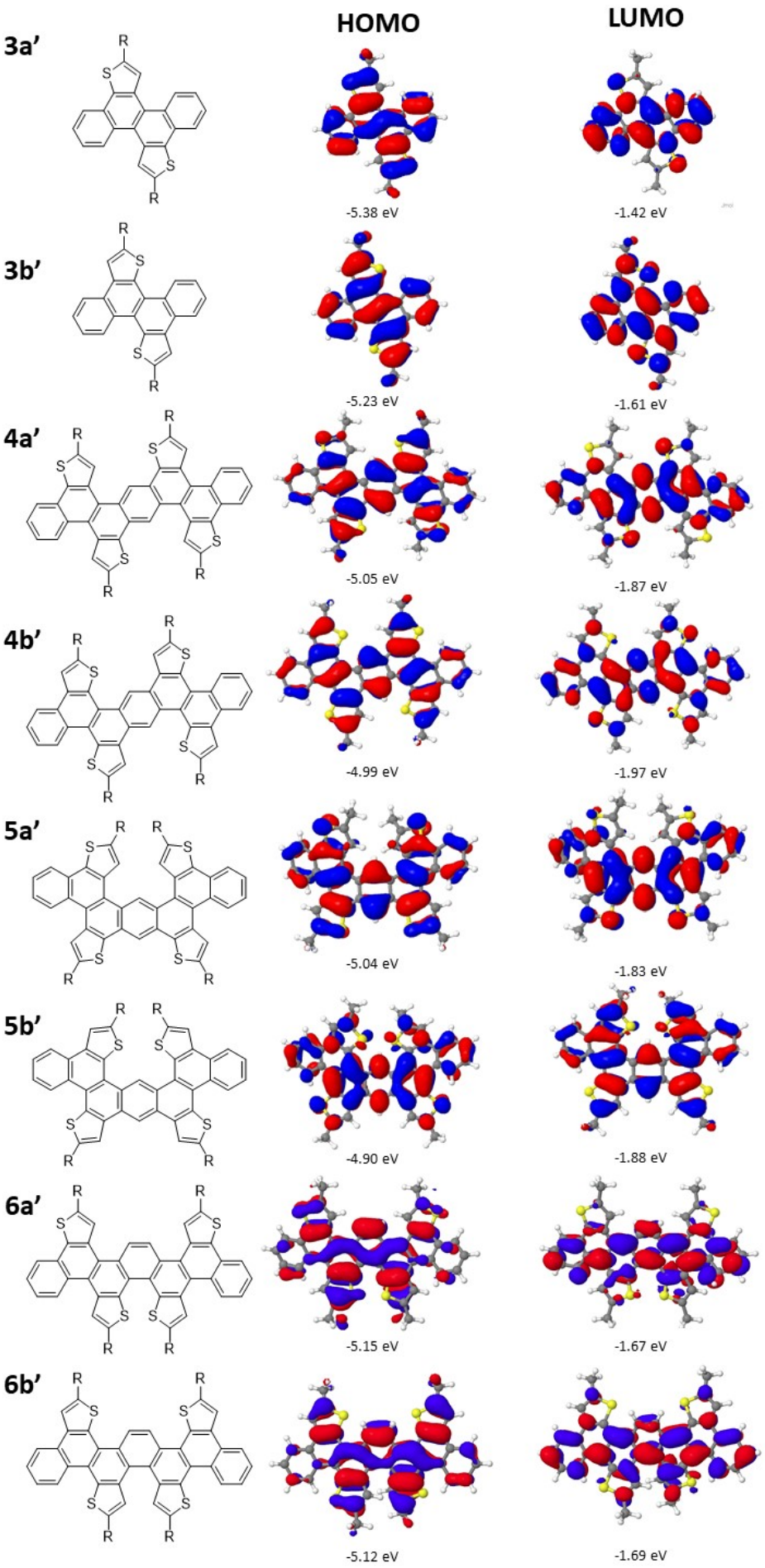


Table S2. TD-DFT-calculated electronic transition energy (ΔE), oscillator strength (*f*), and description and percentage of configuration interactions

Compd	Excited state	ΔE (nm)	*f*	description[a]	percentage[b]
3a'	S_1	363	0.012	H-1→L	28%
				H-1→H+1 H→L	7%
				H→L+1	31%
				H→L	33%
	S_2	344	0.034	H-1→L	17%
				H-1→L+1	11%
				H→L	48%
				H→L+1	21%
	S_5	299	0.298	H-3→L	6%
				H-2→L+2	22%
				H-1→L	38%
				H→L+1	29%
4a'	S_1	440	0.078	H-1→L	7%
				H→L	81%
	S_6	354	1.278	H-3→L	6%
				H-1→L	33%
				H→L+1	38%
				H->L+3	12%
5a'	S_1	430	0.039	H→L	91%
	S_5	363	0.573	H-1→L	18%
				H→L+1	20%
				H→L+2	55%
	S_6	346	0.980	H-4→L	6%
				H-2→L	18%
				H-1→L	18%
				H→L+1	25%
				H→L+2	19%
6a'	S_1	426	0.016	H-1→L+1	24%
				H→L	72%
	S_5	358	0.960	H-3→L+1	10%
				H-2→L+1	9%
				H-1→L	44%
				H→L+1	27%
3b'	S_1	368	0.287	H→L	93%
	S_4	298	0.349	H-4→L	7%
				H-2→L	48%
				H→L+2	29%
	S_6	279	0.420	H-4→L	34%

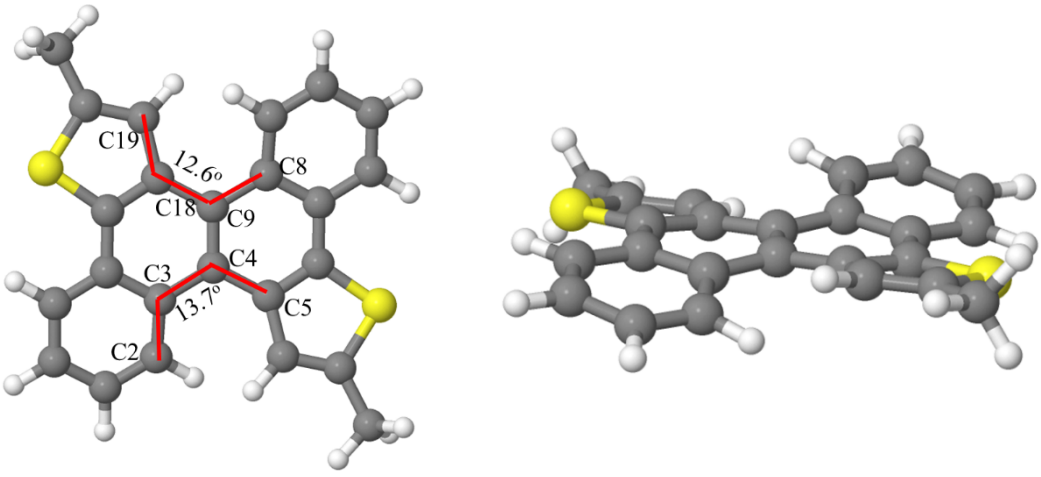
				H-2→L	14%
				H→L+4	28%
4b'	S_1	451	0.205	H→L	92%
	S_5	346	0.808	H-3→L	26%
				H-2→L	25%
				H→L+2	28%
				H→L+3	14%
5b'	S_1	451	0.179	H→L	93%
	S_6	341	1.280	H-2→L	42%
				H→L+2	36%
6b'	S_1	427	0.010	H-1→L+1	27%
				H→L	63%
	S_2	401	0.108	H-1→L	22%
				H→L+1	69%
	S_3	382	0.375	H-2→L	6%
				H-1→L	63%
				H→L+1	21%
	S_4	366	0.412	H-2→L+1	6%
				H-1→L+1	59%
				H→L	21%
	S_5	357	0.179	H-2→L	41%
				H-1→L+2	33%
				H→L+3	8%

[a] H and L denotes HOMO and LUMO, respectively. [b] Percentage listed if greater than 5%

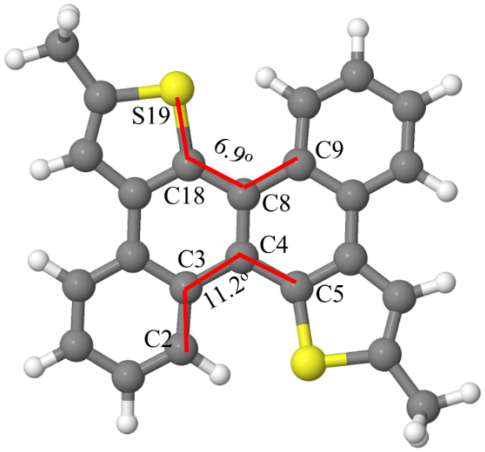
Figure S5: Optimized geometry of **3a'–6a'** and **3b' -6b**

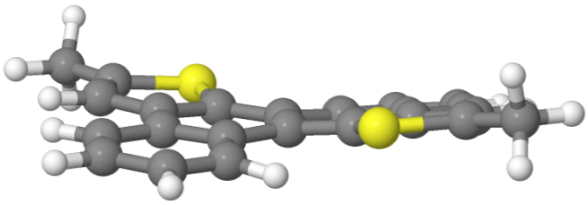
Top view Side view

3a'

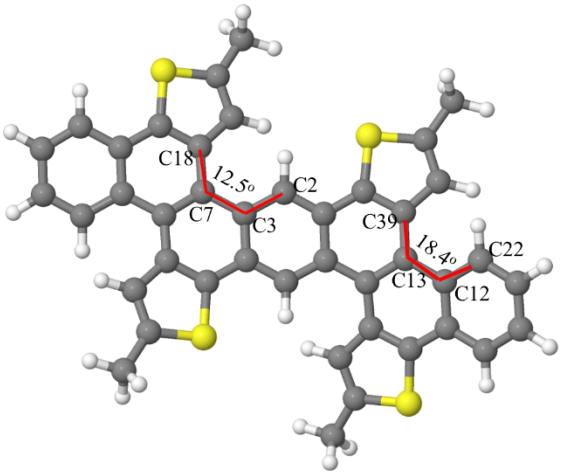


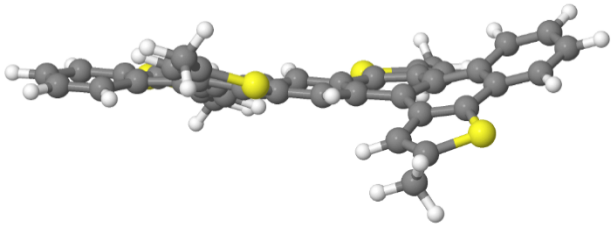
3b’


S19
6.9°
C9
C18
C8
C4
C3
11.2°
C5
C2

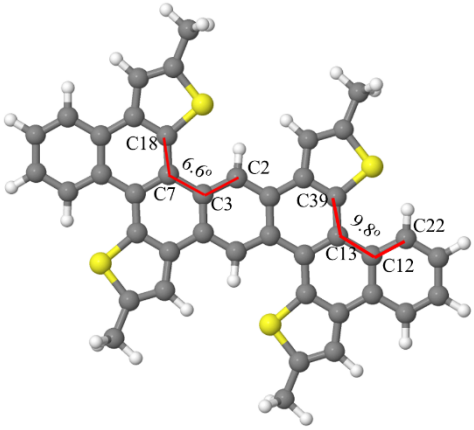


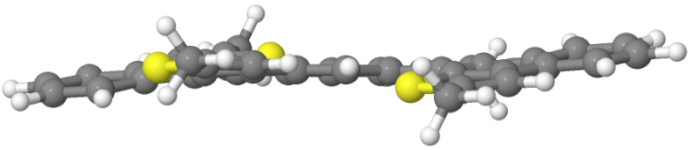
4a


C18
12.5°
C2
C7
C3
C39
18.4°
C22
C13
C12

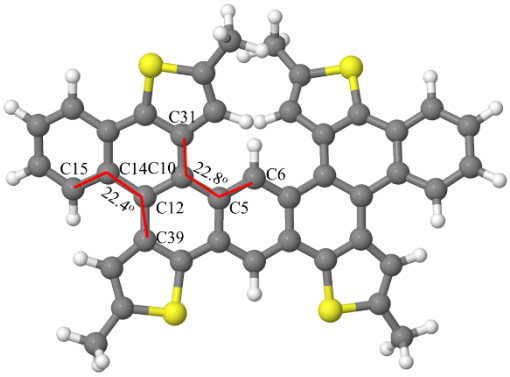


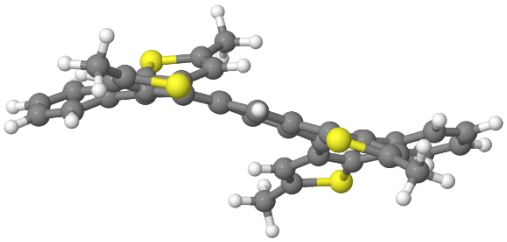
4b’


C18
6.6°
C2
C7
C3
C39
9.8°
C22
C13
C12

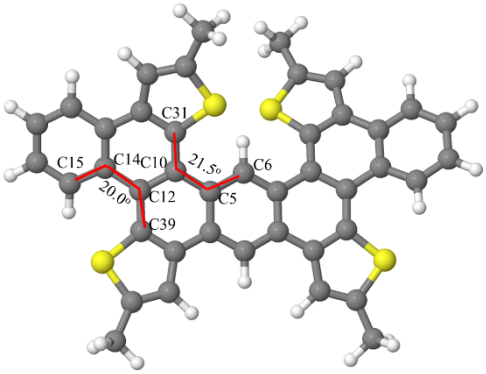


5a’


C31
C15
C14
C10
22.8°
C6
22.4°
C12
C5
C39



5b’


C31
C15
C14
C10
21.5°
C6
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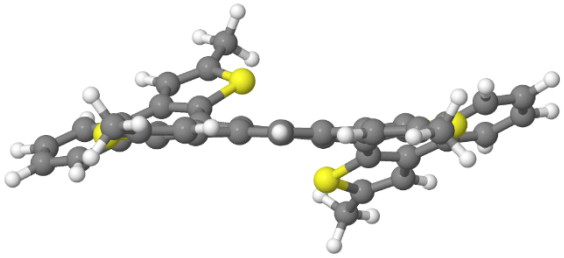
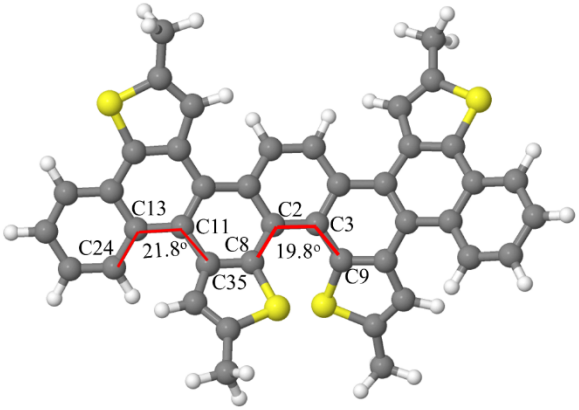
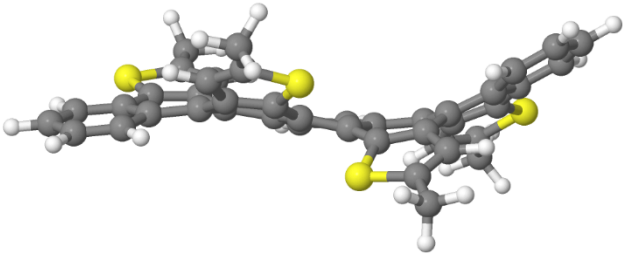
C12
C5
C39

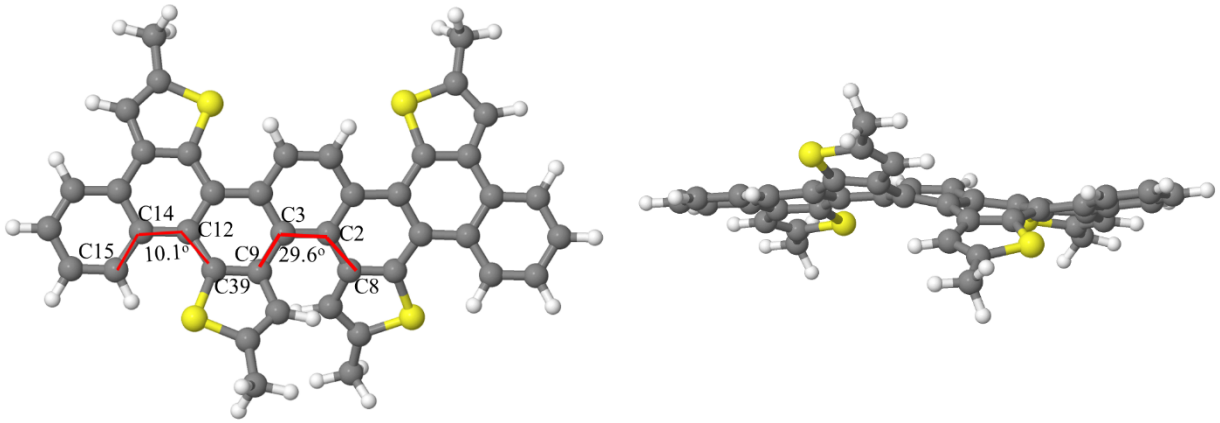


6a’


C13
C11
C2
C3
C24
21.8°
C8
19.8°
C9
C35



6b'



6. Electrochemical Methods

Cyclic voltammetry was performed using a Biologic VSP potentiostat, and the cell consisted of a glassy carbon working electrode, a platinum wire counter electrode, and a $Ag/AgNO_3$ pseudo-reference electrode contained in a solution of 0.1 M $[Bu_4N][PF_6]$ in DCM. Prior to each experiment, the glassy carbon electrode was polished with an aqueous suspension of alumina (0.3 μm) on a felt pad, and the platinum electrode was cleaned by heating to glowing with a propane torch. Voltammetric studies were conducted under Ar with Ar-sparged solutions. For compounds **3a, 3b, 4a, 5a, 5b, 6a**, and **6b** solutions of 5 mM analyte in DCM with 0.1 M $[Bu_4N][PF_6]$ as a supporting electrolyte were used. For compound **4b**, which was poorly soluble in DCM, studies were performed using a ca. 2 mM solution of **4b** in 1,2-dichlorobenzene (DCB) with 80 mM $[Bu_4N][PF_6]$ as a supporting electrolyte. All potentials were referenced versus the ferrocene/ferrocenium couple ($Fc^{+/0}$ = 0 V) using Fc as an external standard, measured as $E_{1/2}(Fc^{+/0})$ = +0.43 V in 0.1 M $[Bu_4N][PF_6]$/DCM and +0.49 V in 80 mM $[Bu_4N][PF_6]$/DCB versus the $Ag/AgNO_3$ pseudo-reference electrode. At least 3 scans were performed to confirm stability over repeated cycling in the potential range of –1 to +1.6 V. Scanning to more oxidizing potentials leads to large, irreversible oxidative events. Peak potentials were extracted from the forward (anodic) sweep using EC-Lab software, and half wave potentials ($E_{1/2}$) for pseudo-reversible couples were determined as the midpoint between peaks of forward and reverse waves.

Table S3. Redox potentials for compounds **3-6** determined by cyclic voltammetry

compound	E_{p1}[a]	E_{p2}[a]	E_{p3}[a]	E_{p4}[a]
3a	+0.84 (+0.80[b])	+1.38 (+1.32[b])		
3b	+0.79	+1.55		
4a	+0.49	+0.71	+1.06	
4b	+0.45	+0.61	+0.94	
5a	+0.57	+0.76	+1.12	
5b	+0.36	+0.59	+1.00	+1.55
6a	+0.74	+1.20		
6b	+0.71	+0.98	+1.33	

[a]Potentials in volts (V) referenced to Fc^+/Fc; reported values are peak potentials determined from the forward sweep using [b]Half wave potential ($E_{1/2}$) for a pseudo-reversible couple determined as the midpoint between peaks of forward and reverse waves

7. References:

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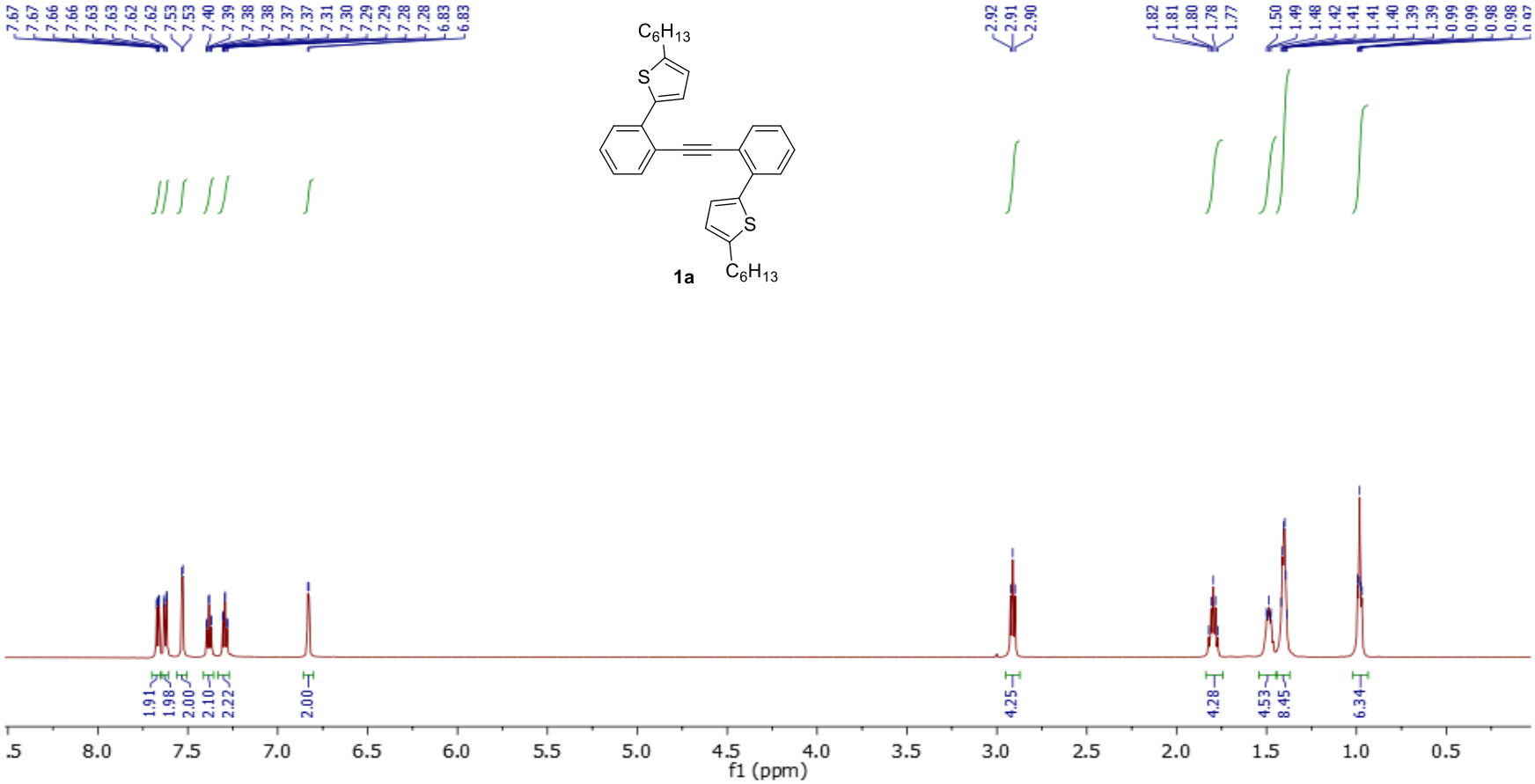
15. Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/

Spectra of New Compounds:

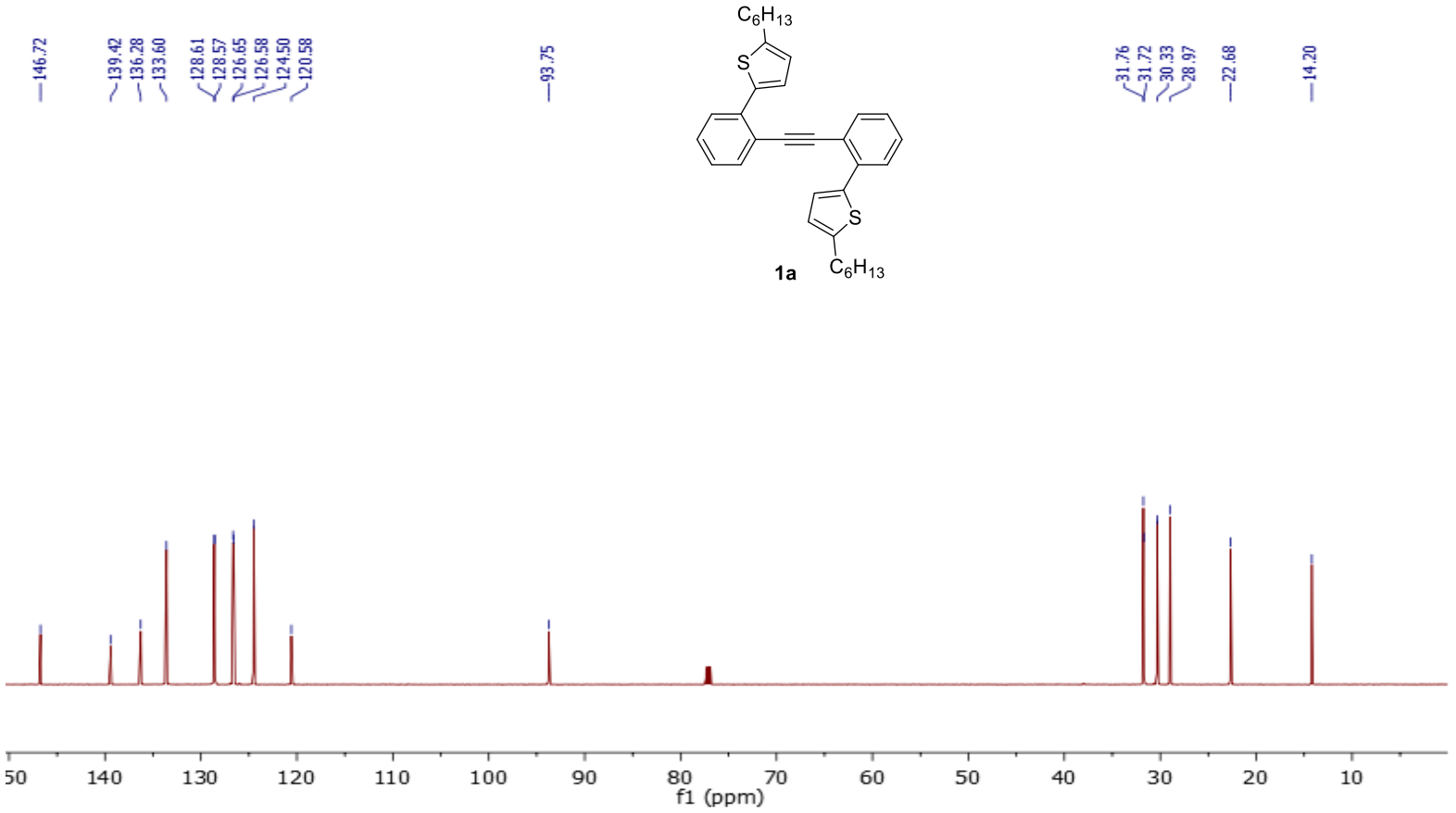
^{1}H NMR

(400 MHz, $CDCl_3$)



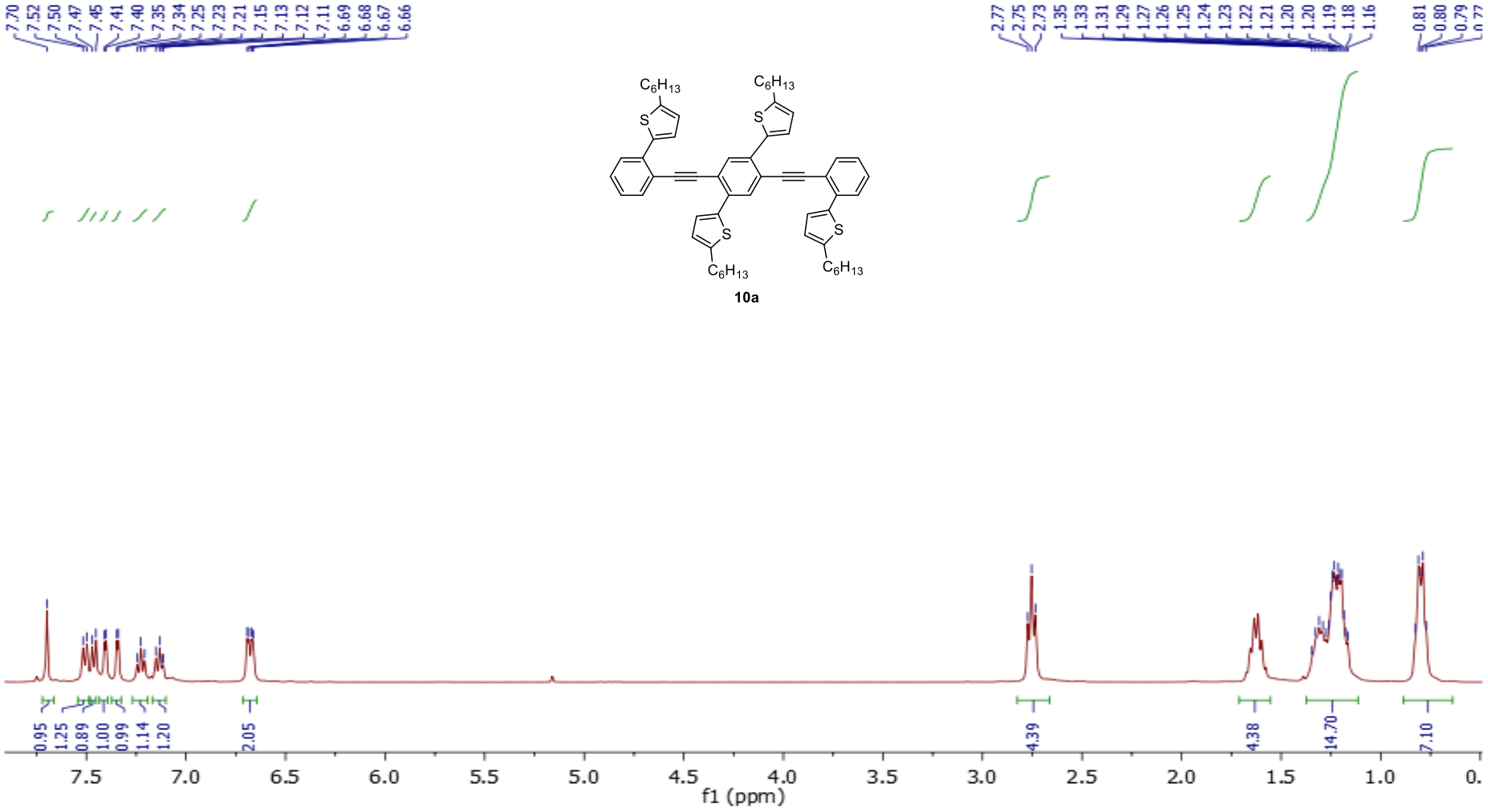
^{13}C NMR

(101 MHz, $CDCl_3$)



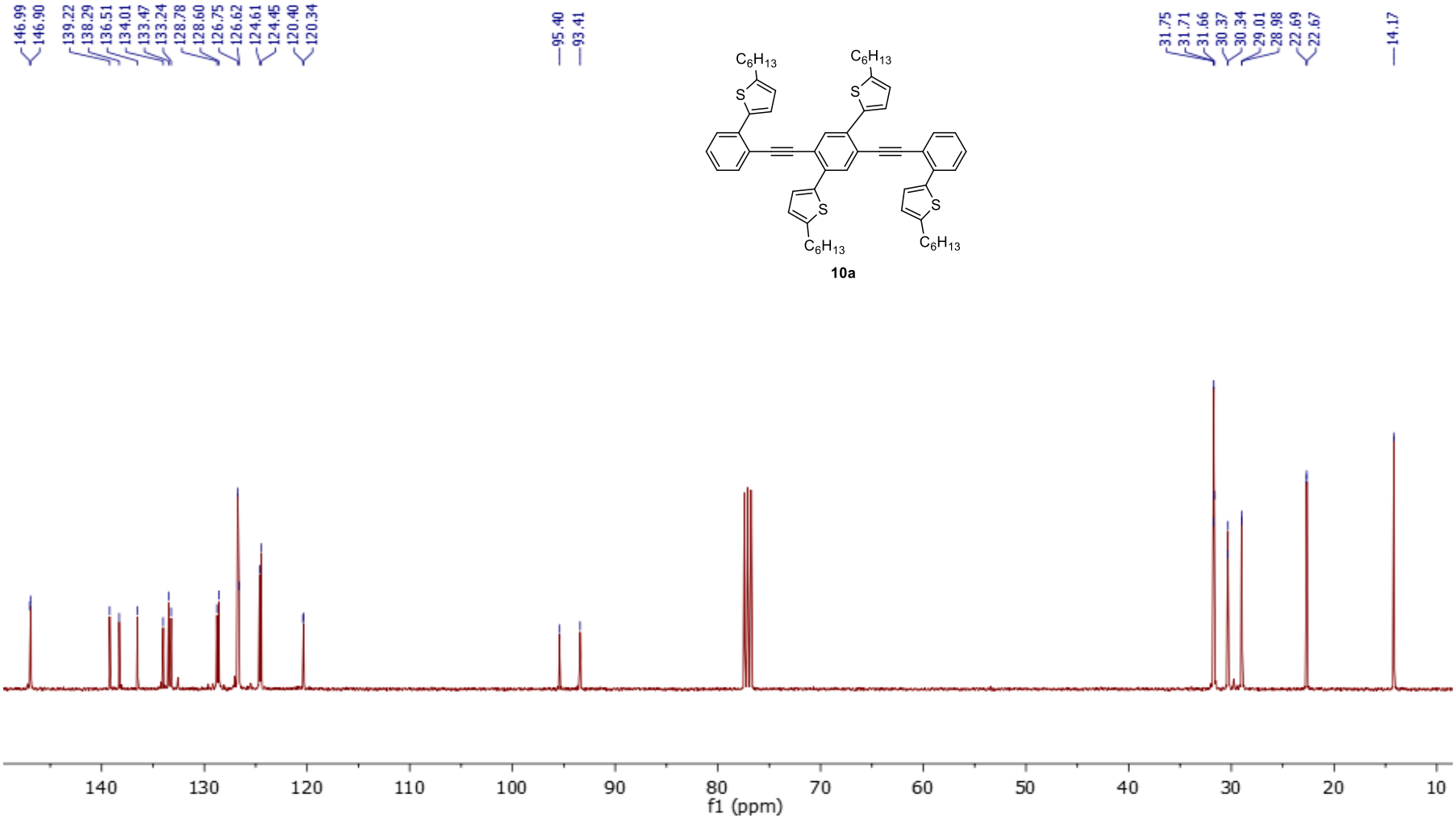
^{1}H NMR

(400 MHz, $CDCl_3$)



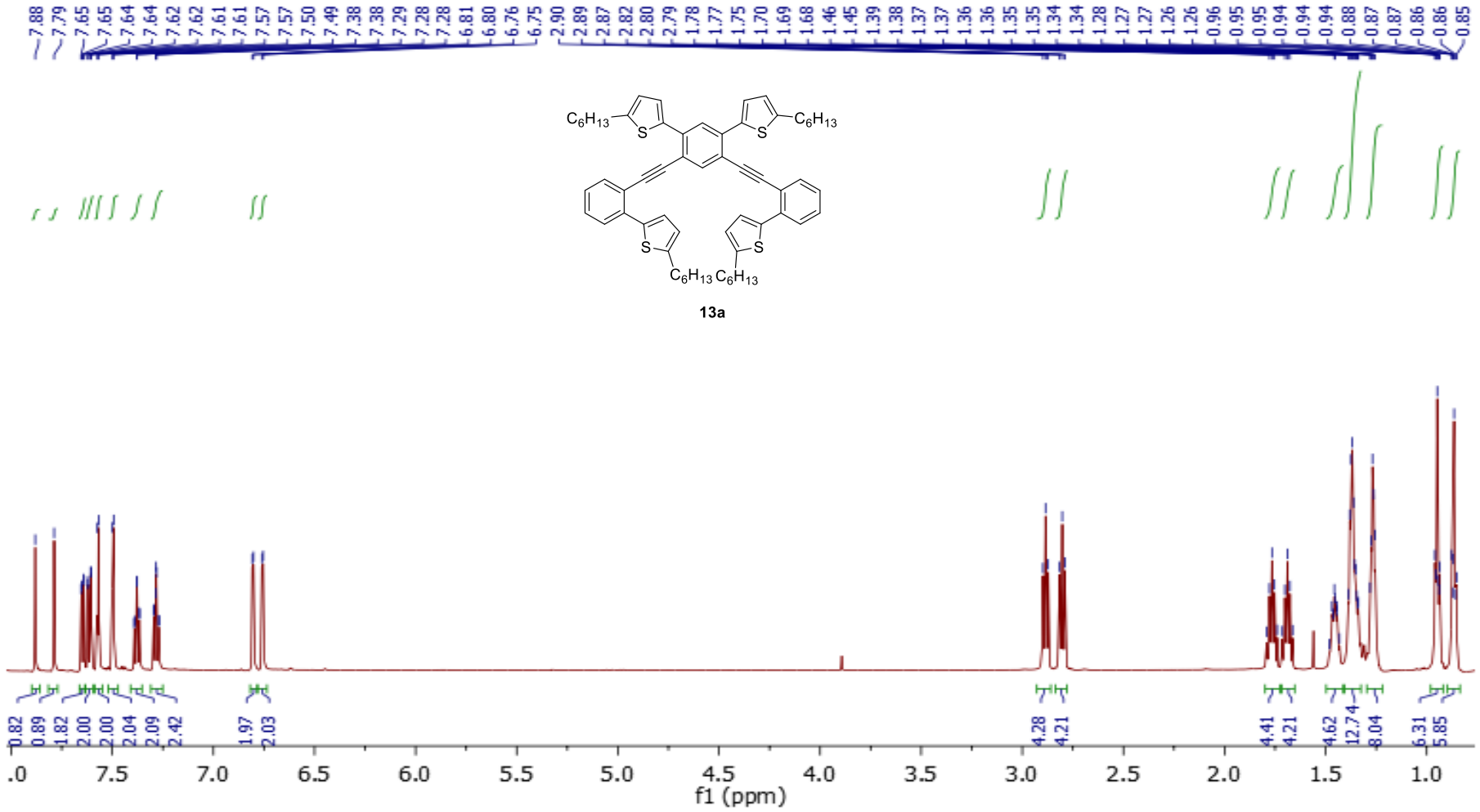
^{13}C NMR

(101 MHz, $CDCl_3$)



^{1}H NMR

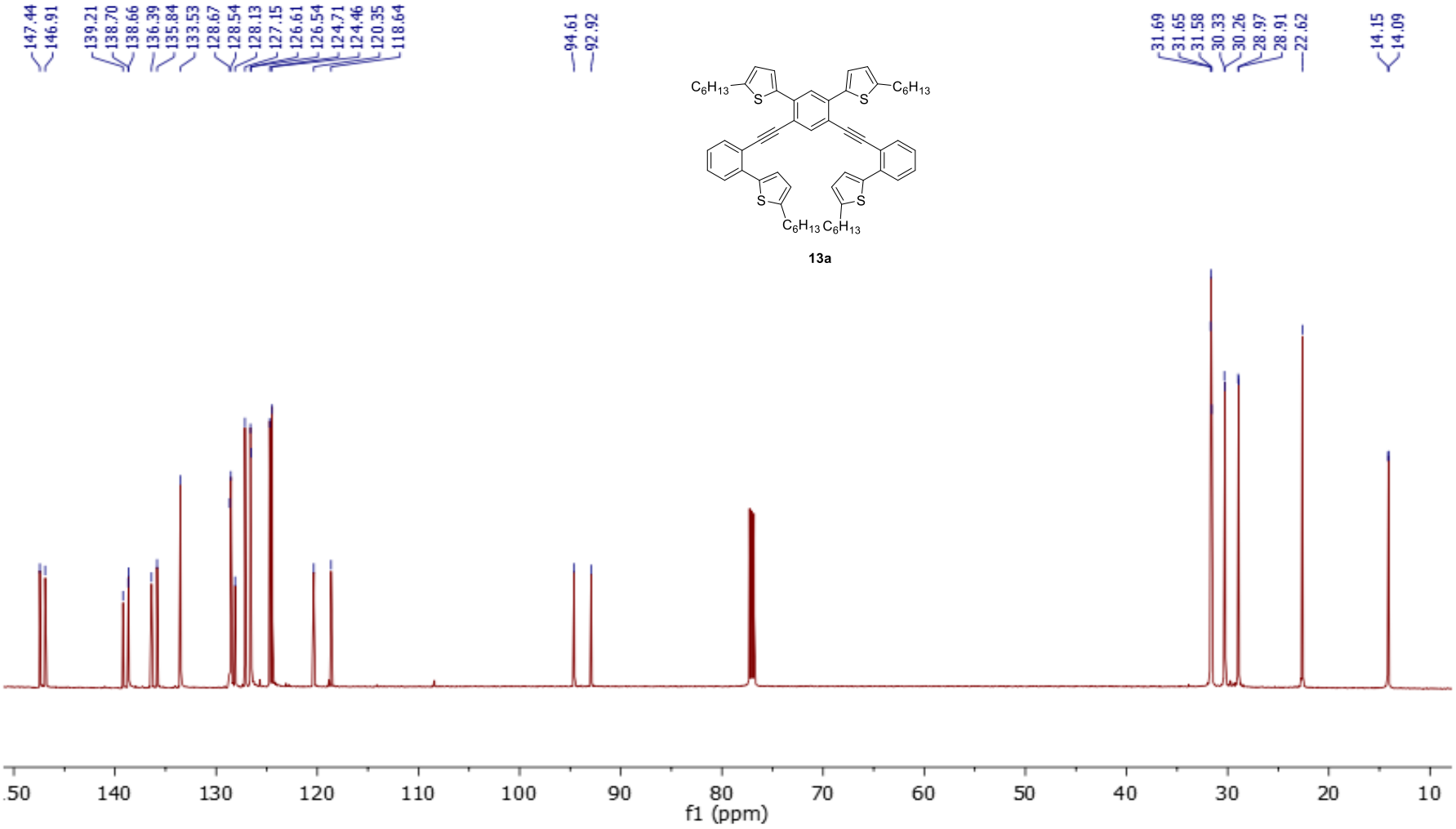
(400 MHz, $CDCl_3$)



13a

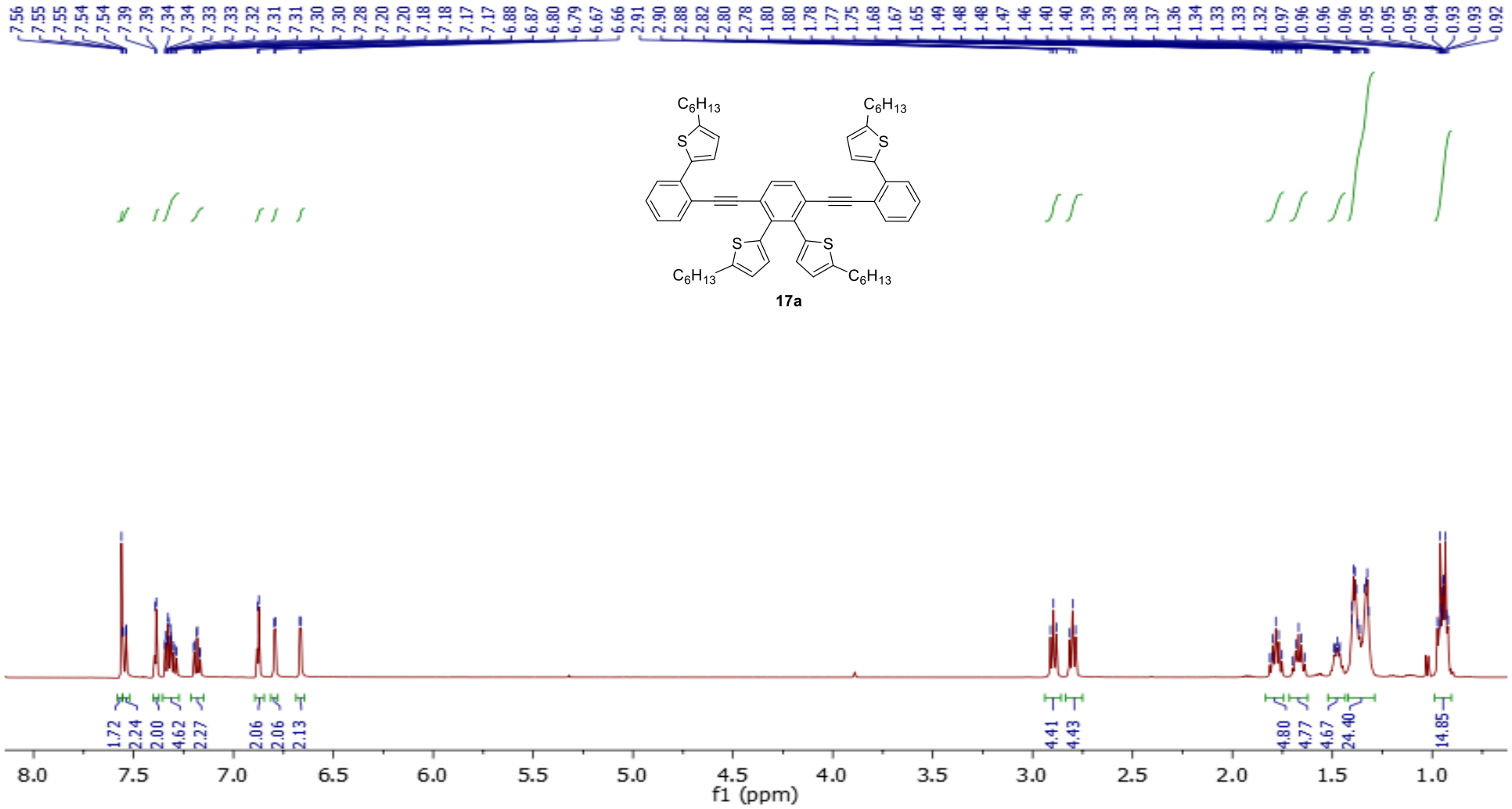
^{13}C NMR

(101 MHz, $CDCl_3$)



^{1}H NMR

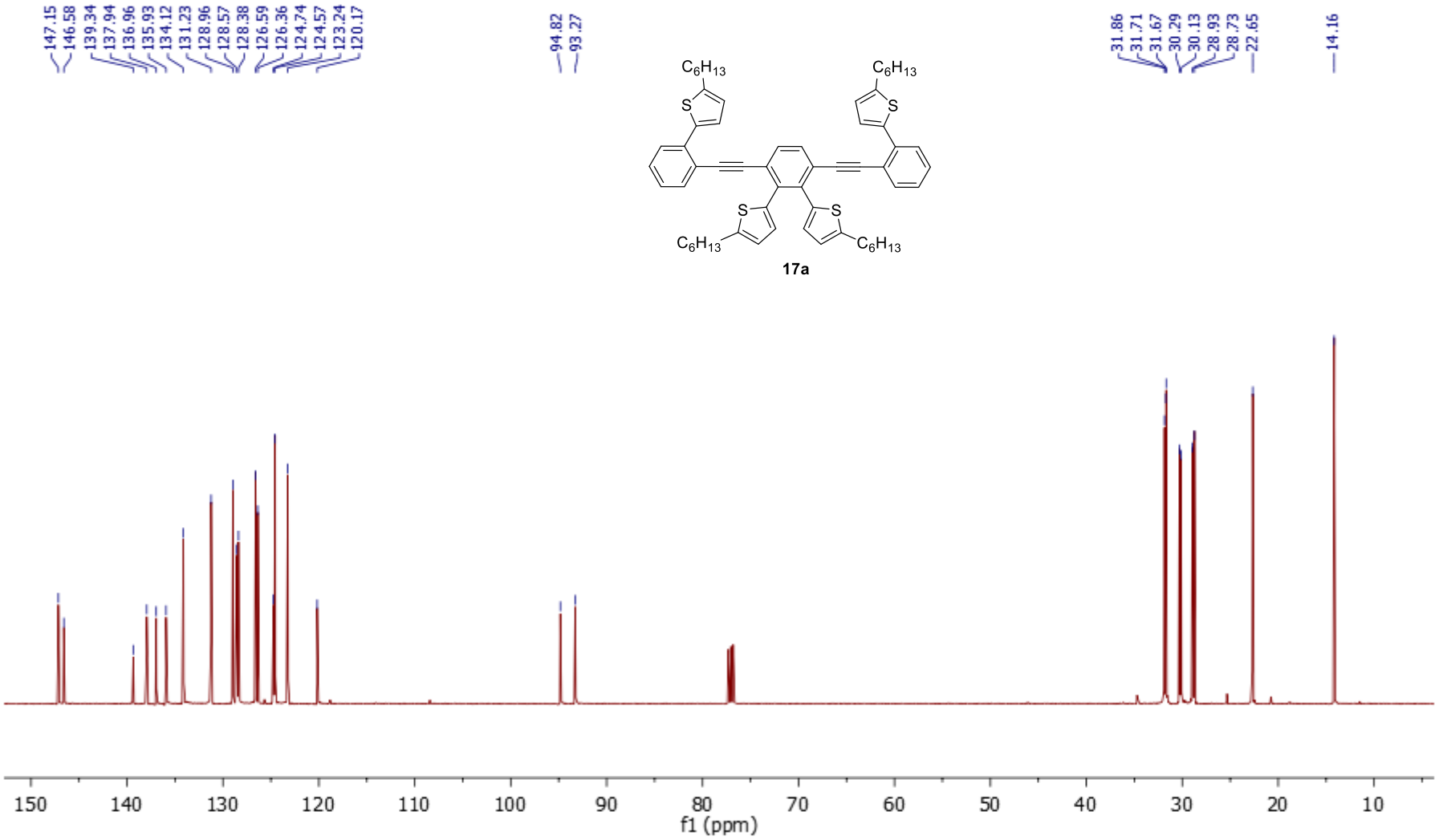
(400 MHz, $CDCl_3$)



17a

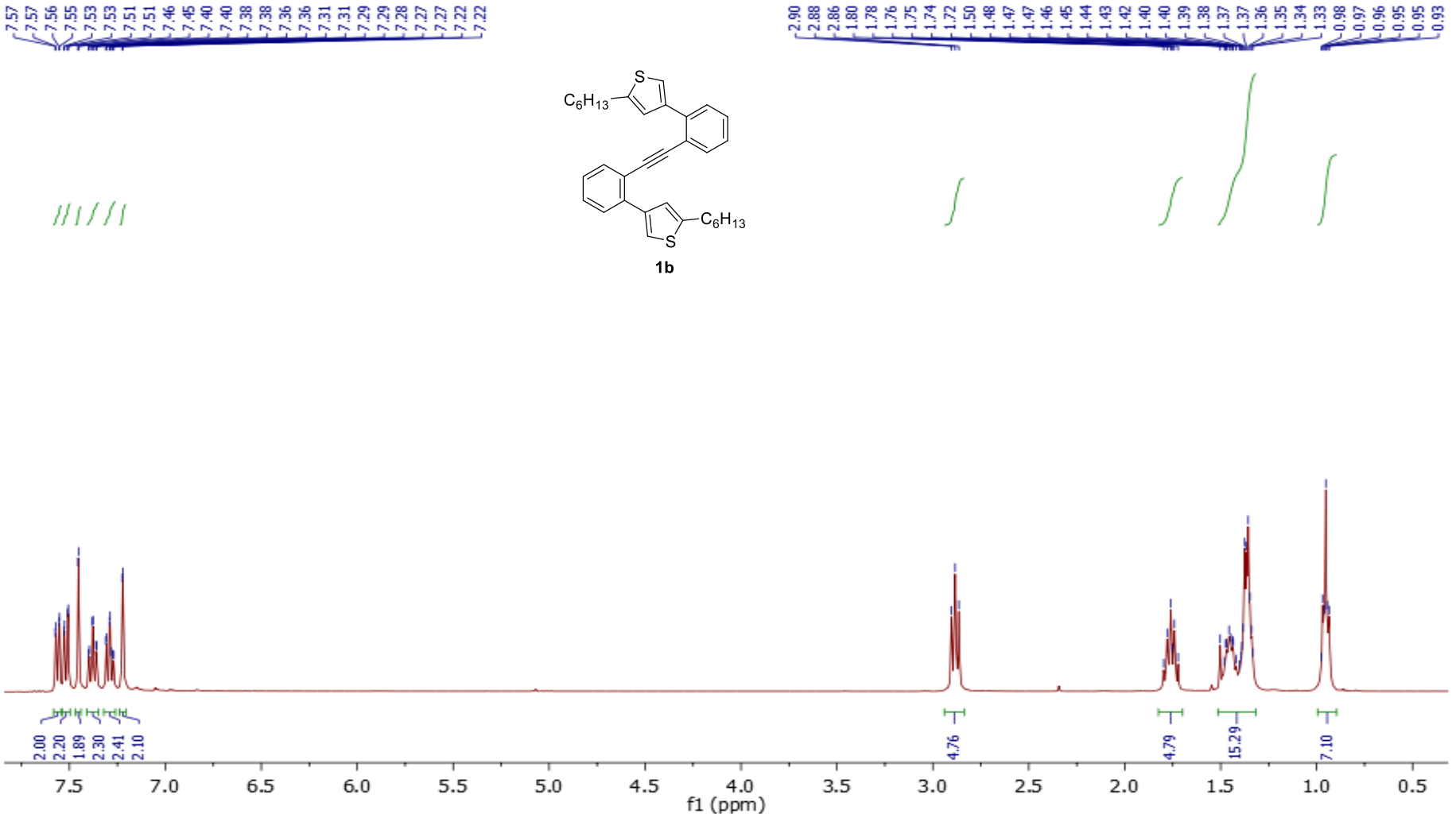
^{13}C NMR

(101 MHz, $CDCl_3$)



^{1}H NMR

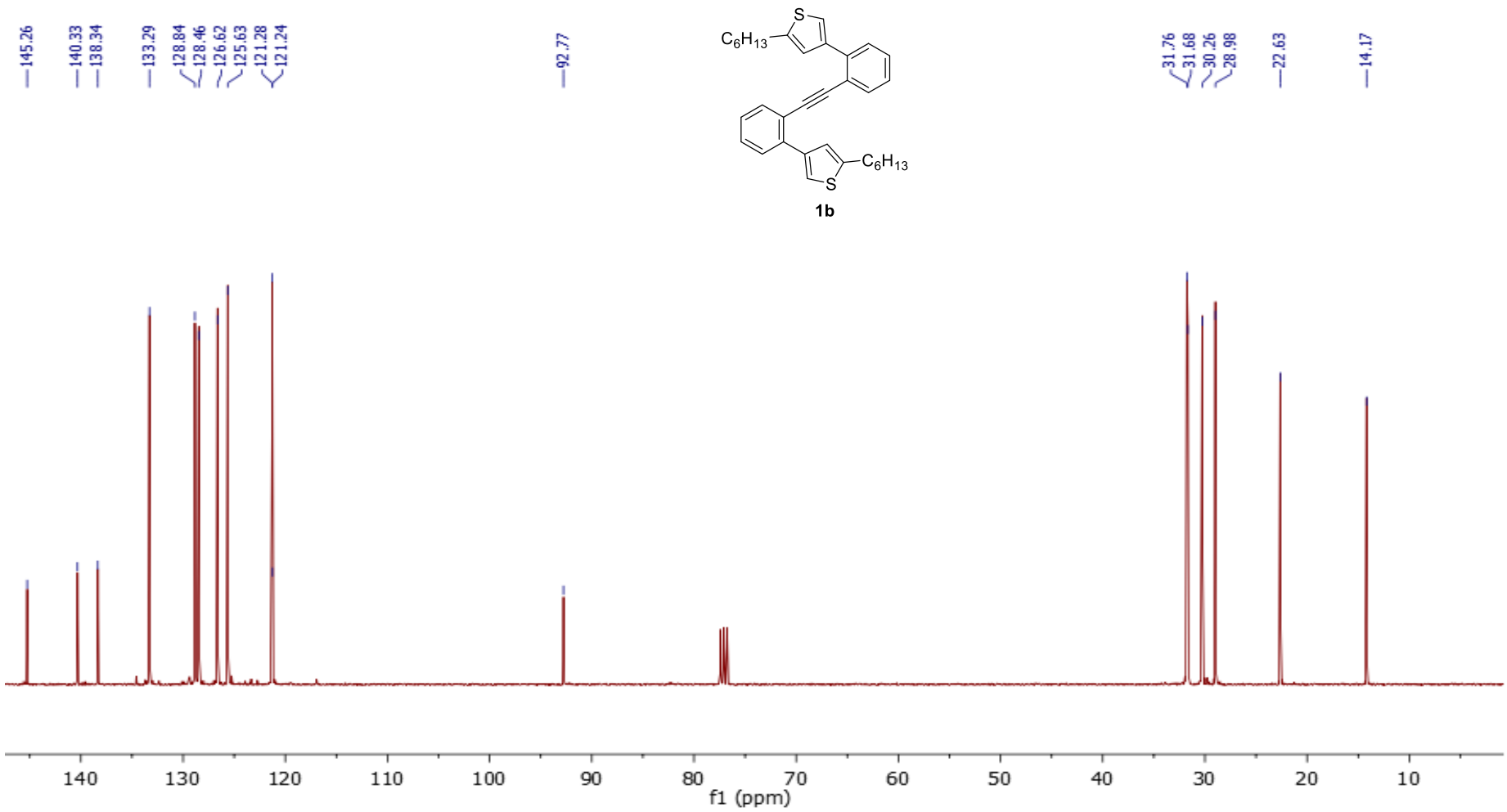
(400 MHz, $CDCl_3$)



1b

^{13}C NMR

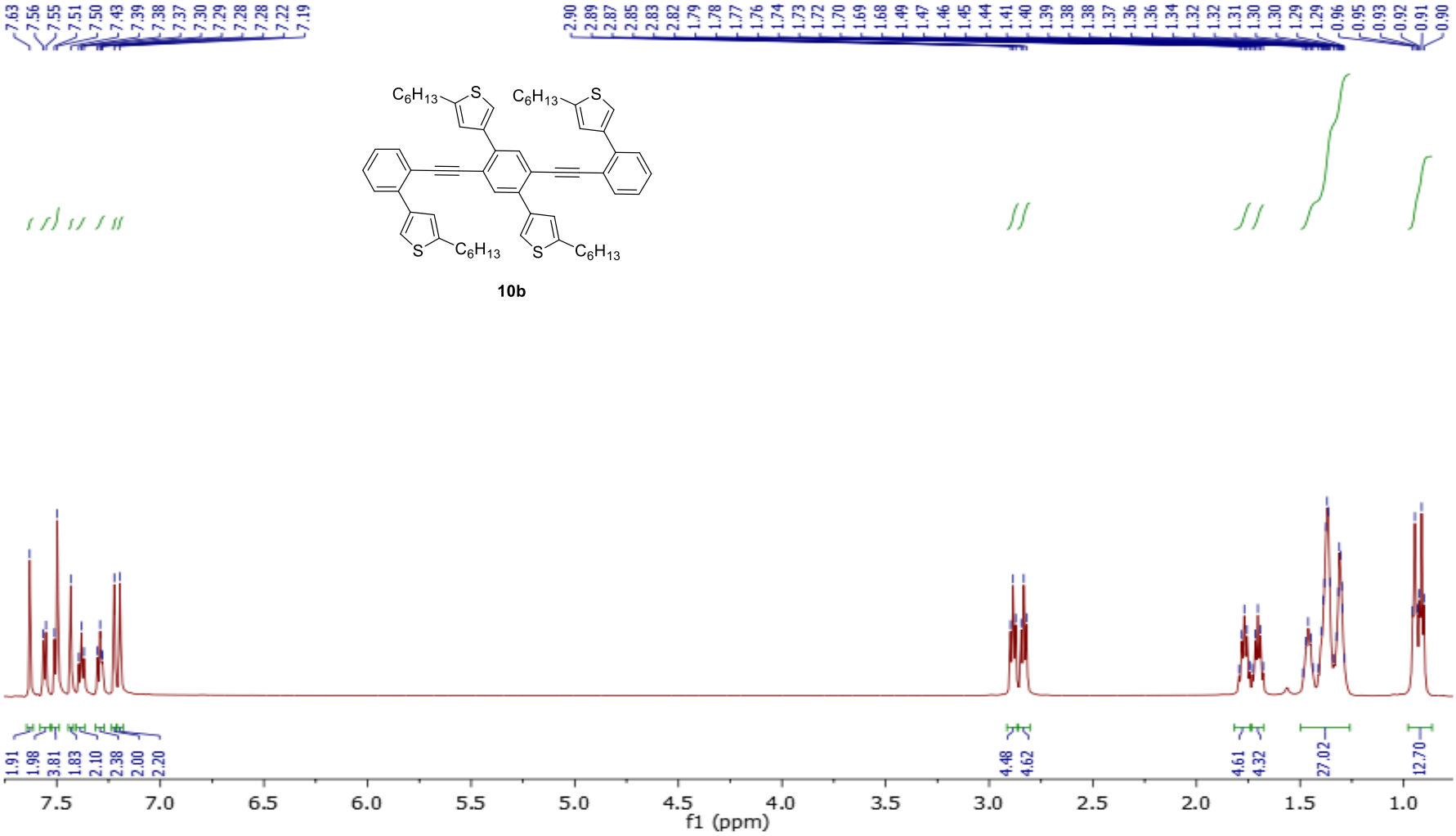
(101 MHz, $CDCl_3$)



1b

^{1}H NMR

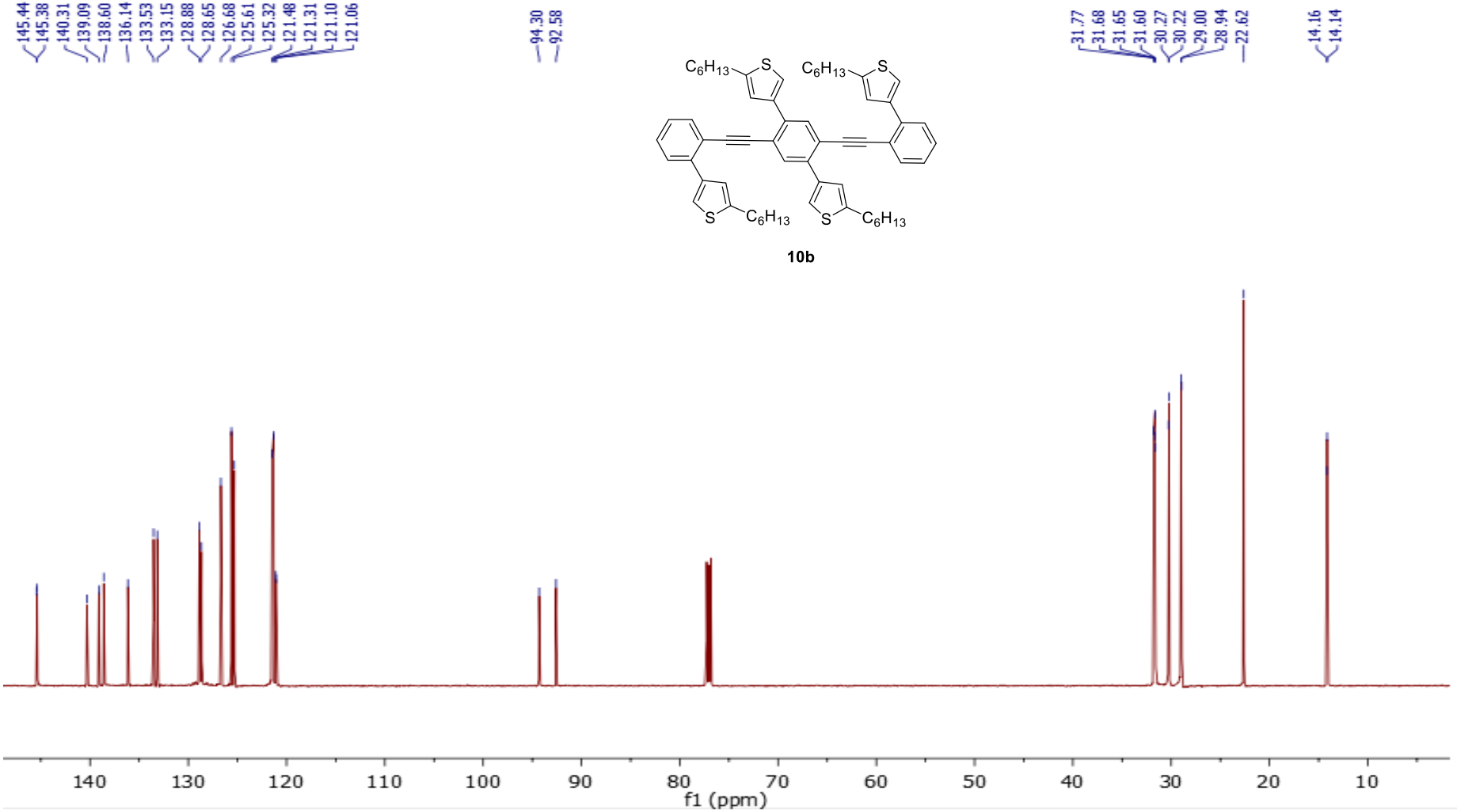
(400 MHz, $CDCl_3$)



10b

^{13}C NMR

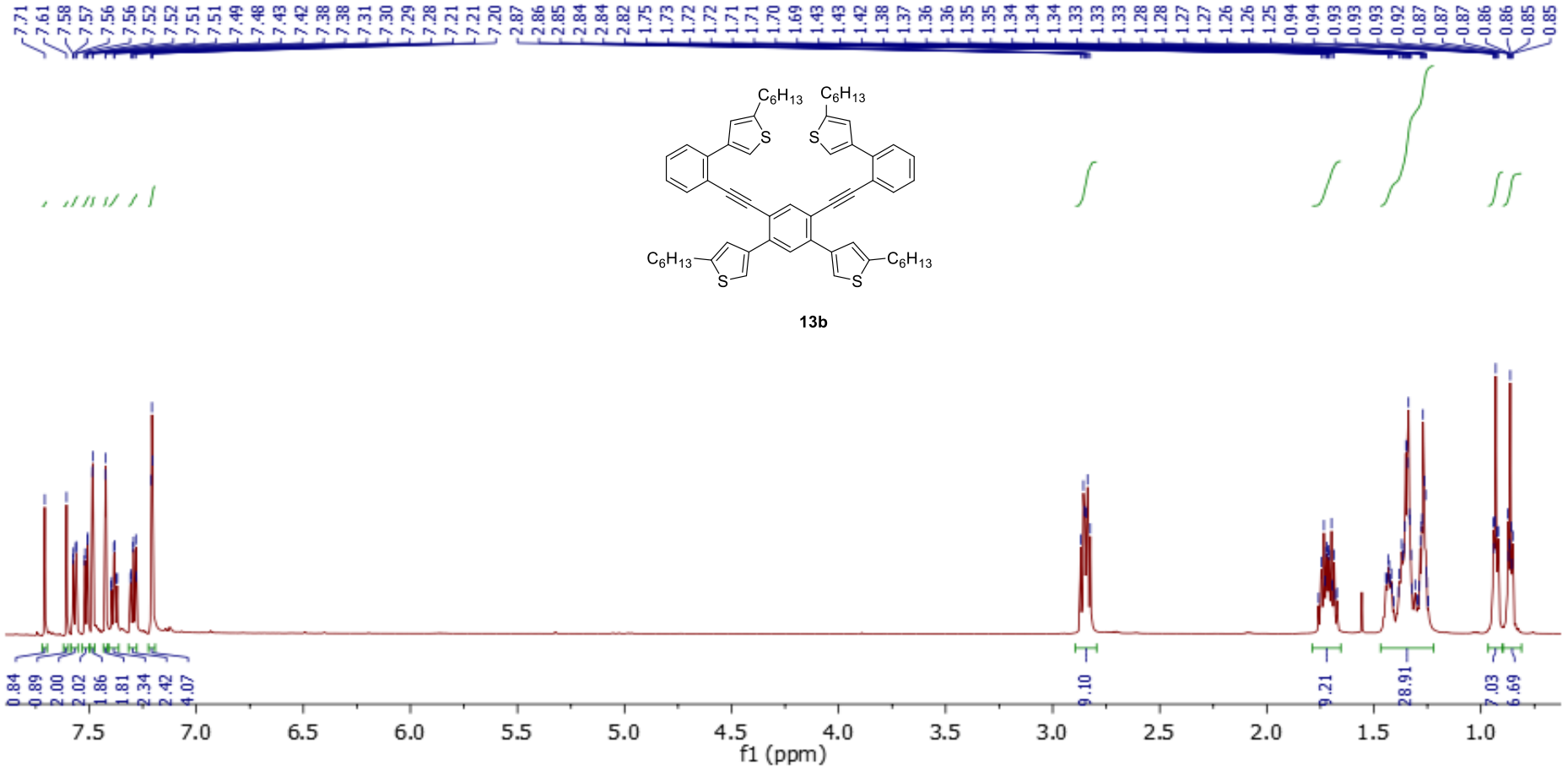
(101 MHz, $CDCl_3$)



10b

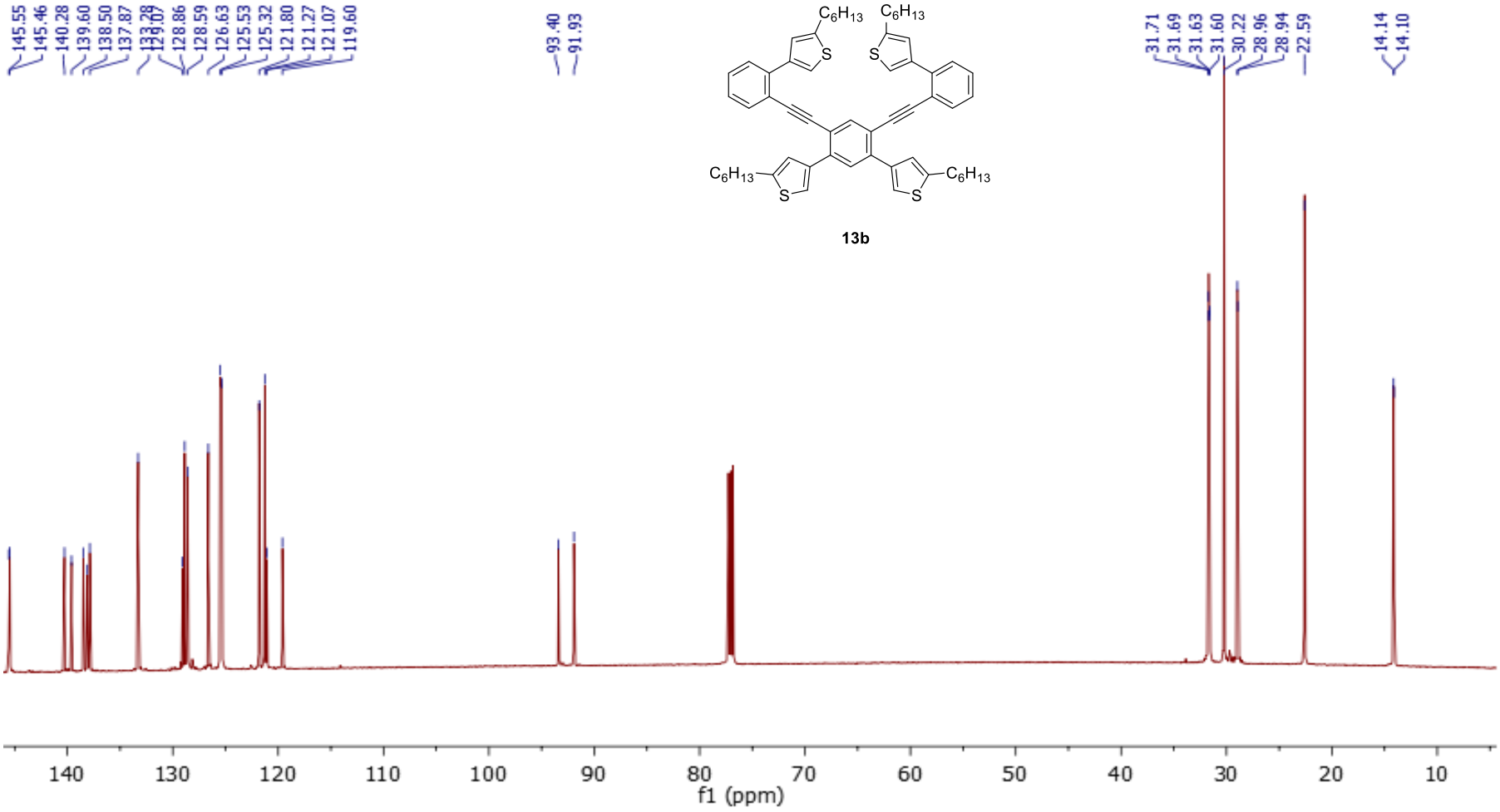
^{1}H NMR

(400 MHz, $CDCl_3$)



^{13}C NMR

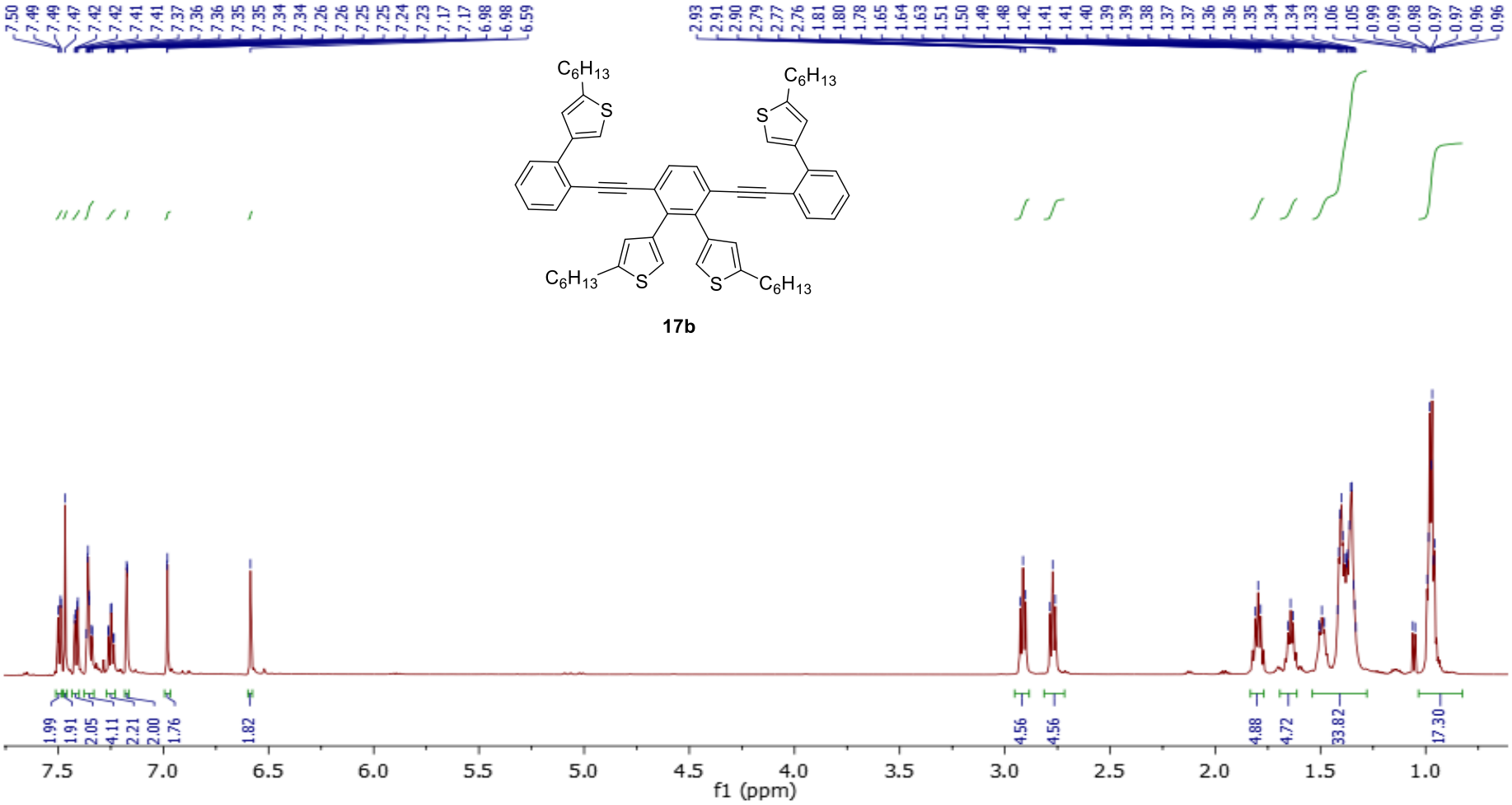
(101 MHz, $CDCl_3$)



13b

^{1}H NMR

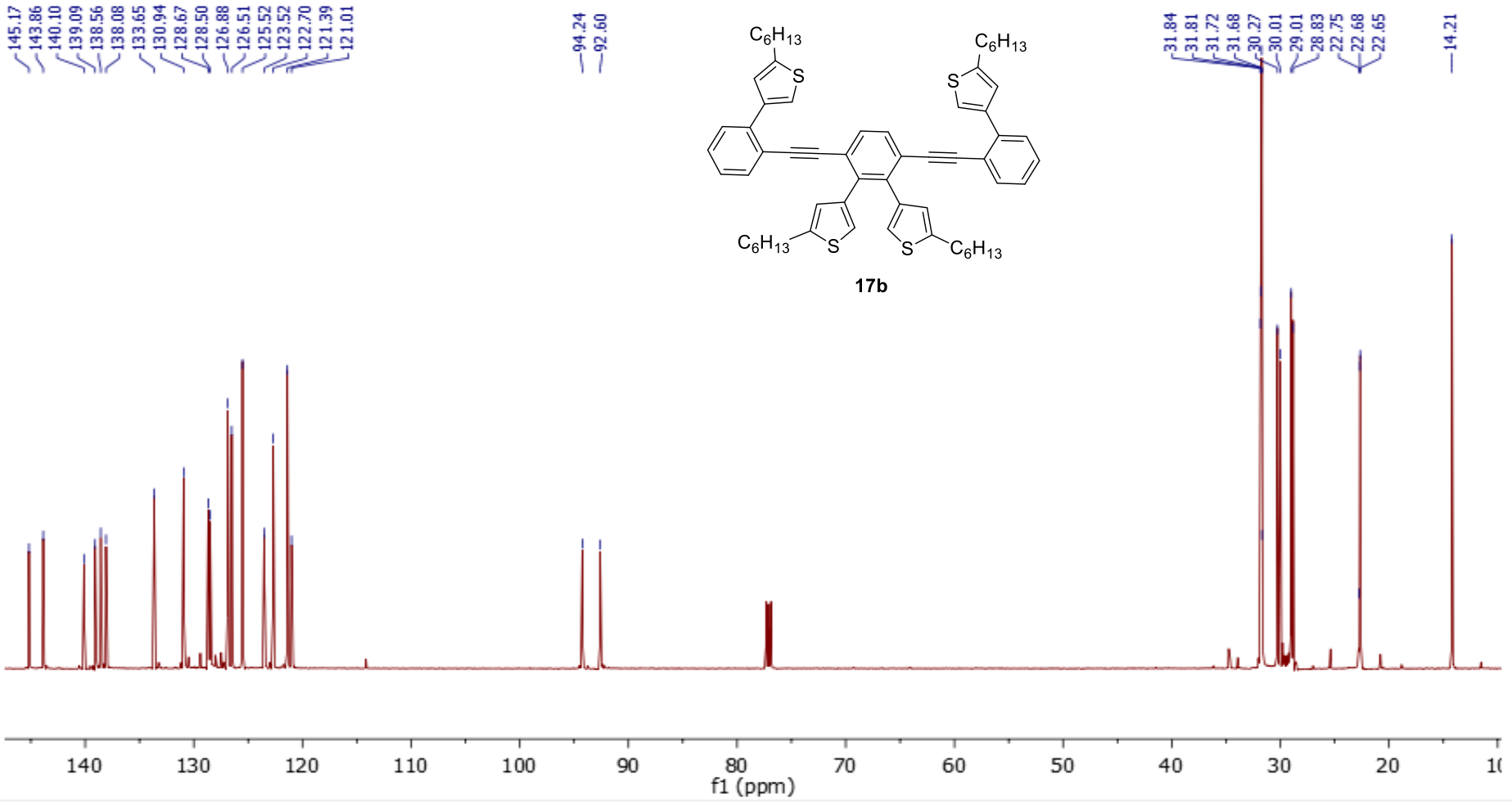
(400 MHz, $CDCl_3$)



17b

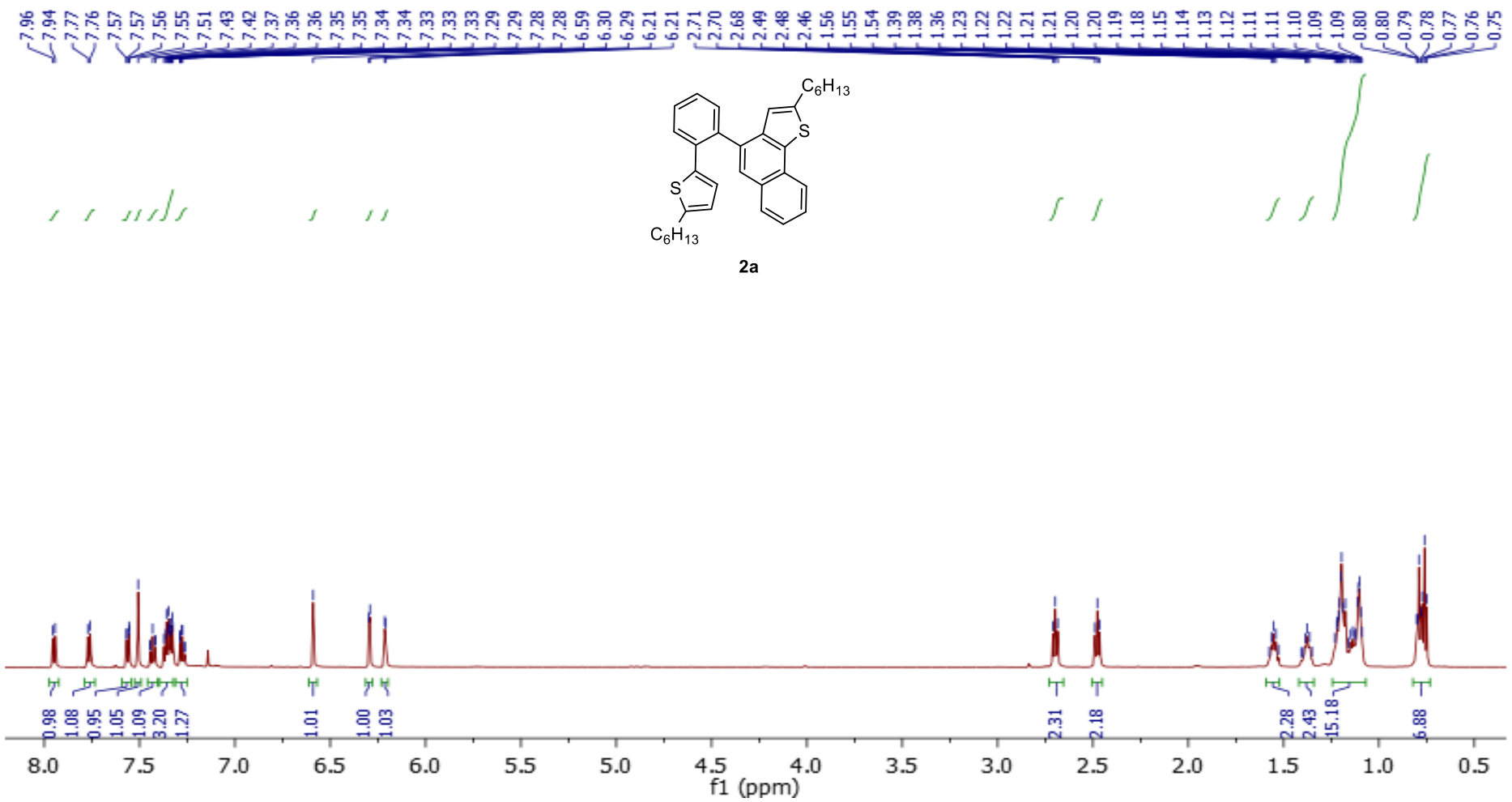
^{13}C NMR

(101 MHz, $CDCl_3$)



^{1}H NMR

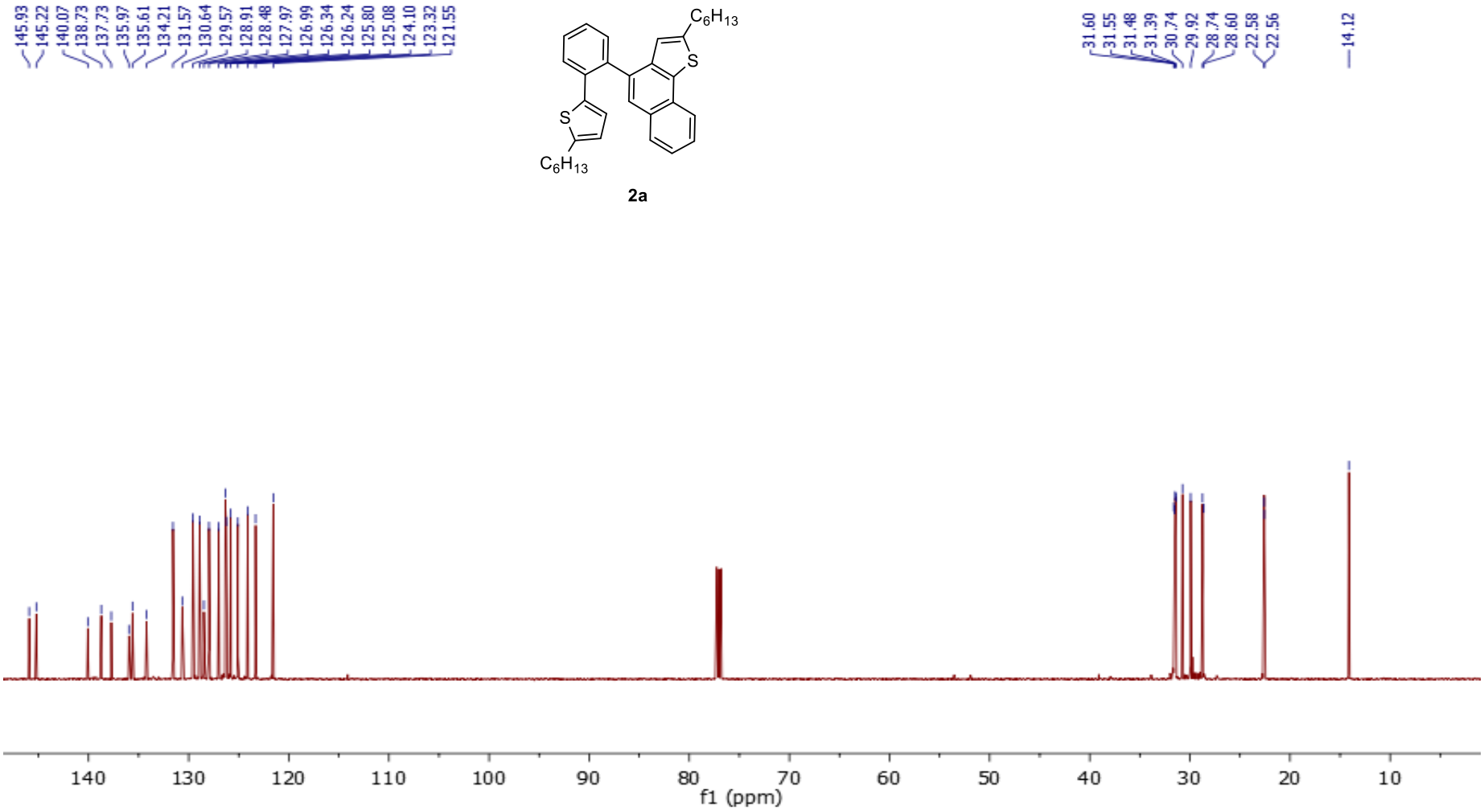
(400 MHz, $CDCl_3$)



2a

^{13}C NMR

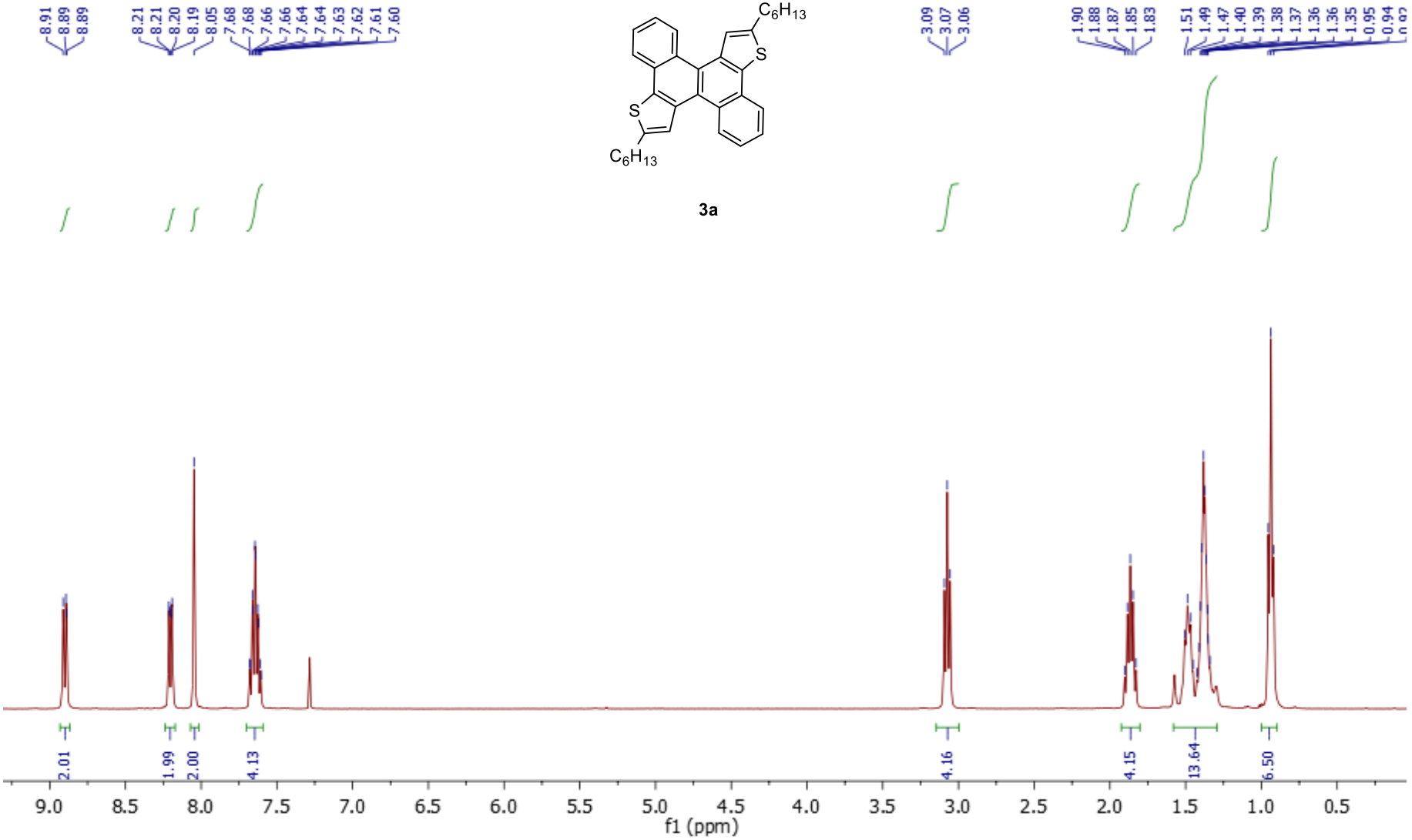
(101 MHz, $CDCl_3$)



2a

^{1}H NMR

(400 MHz, $CDCl_3$)

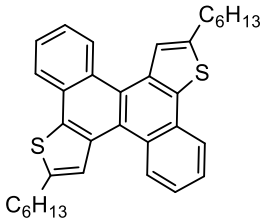


3a

^{13}C NMR

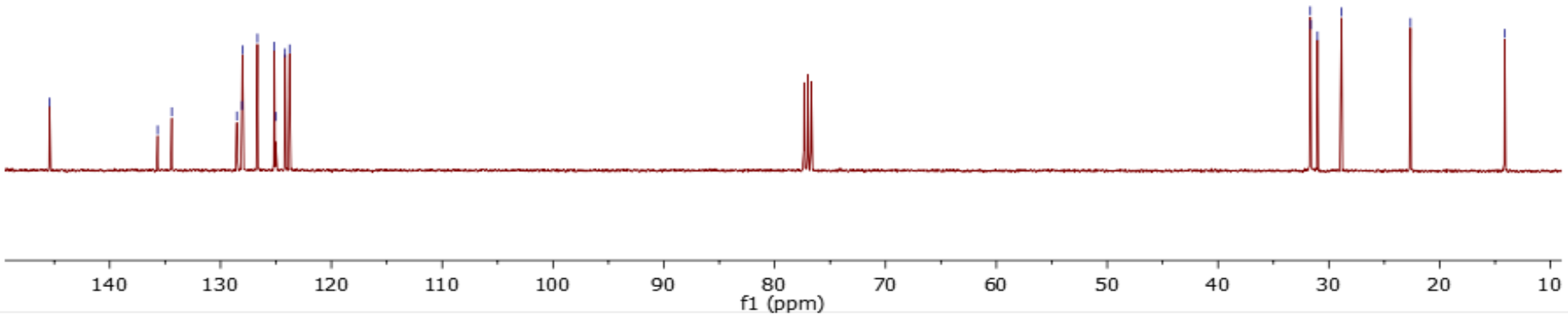
(101 MHz, $CDCl_3$)

145.43
135.68
134.40
128.53
128.07
128.02
126.67
125.15
125.04
124.18
123.77



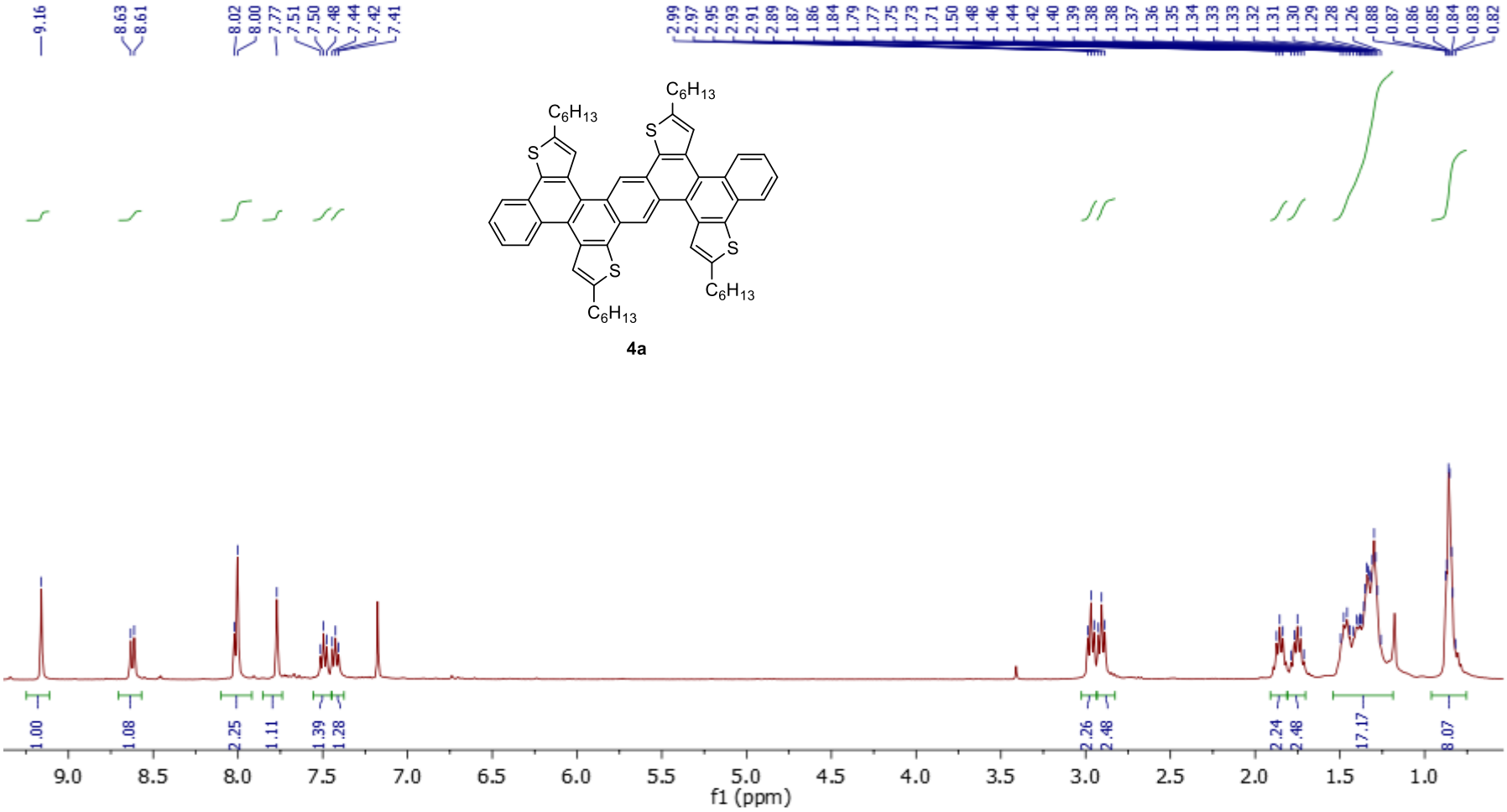
3a

31.68
31.64
31.03
28.85
22.63
14.13



^{1}H NMR

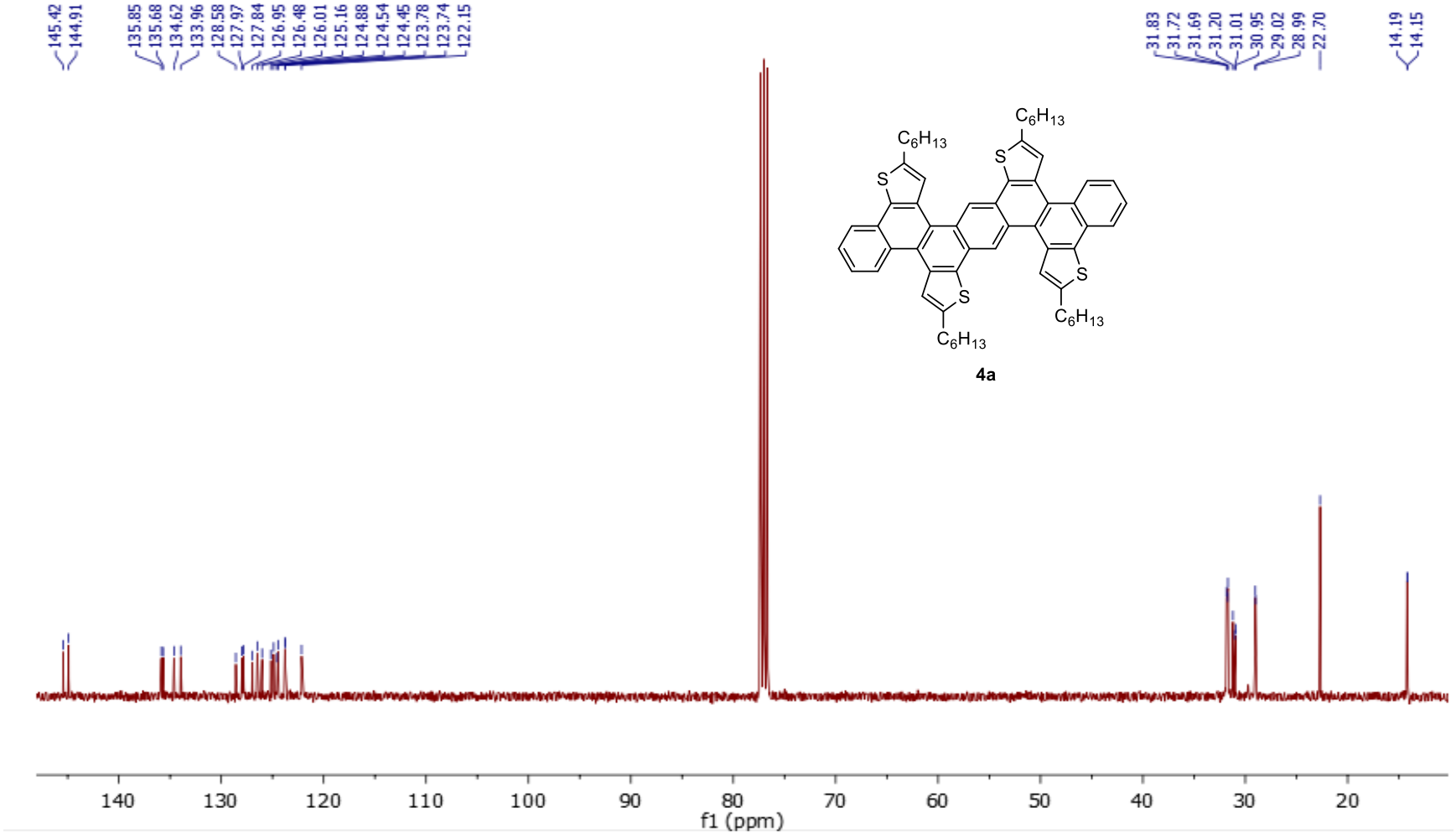
(400 MHz, $CDCl_3$)



4a

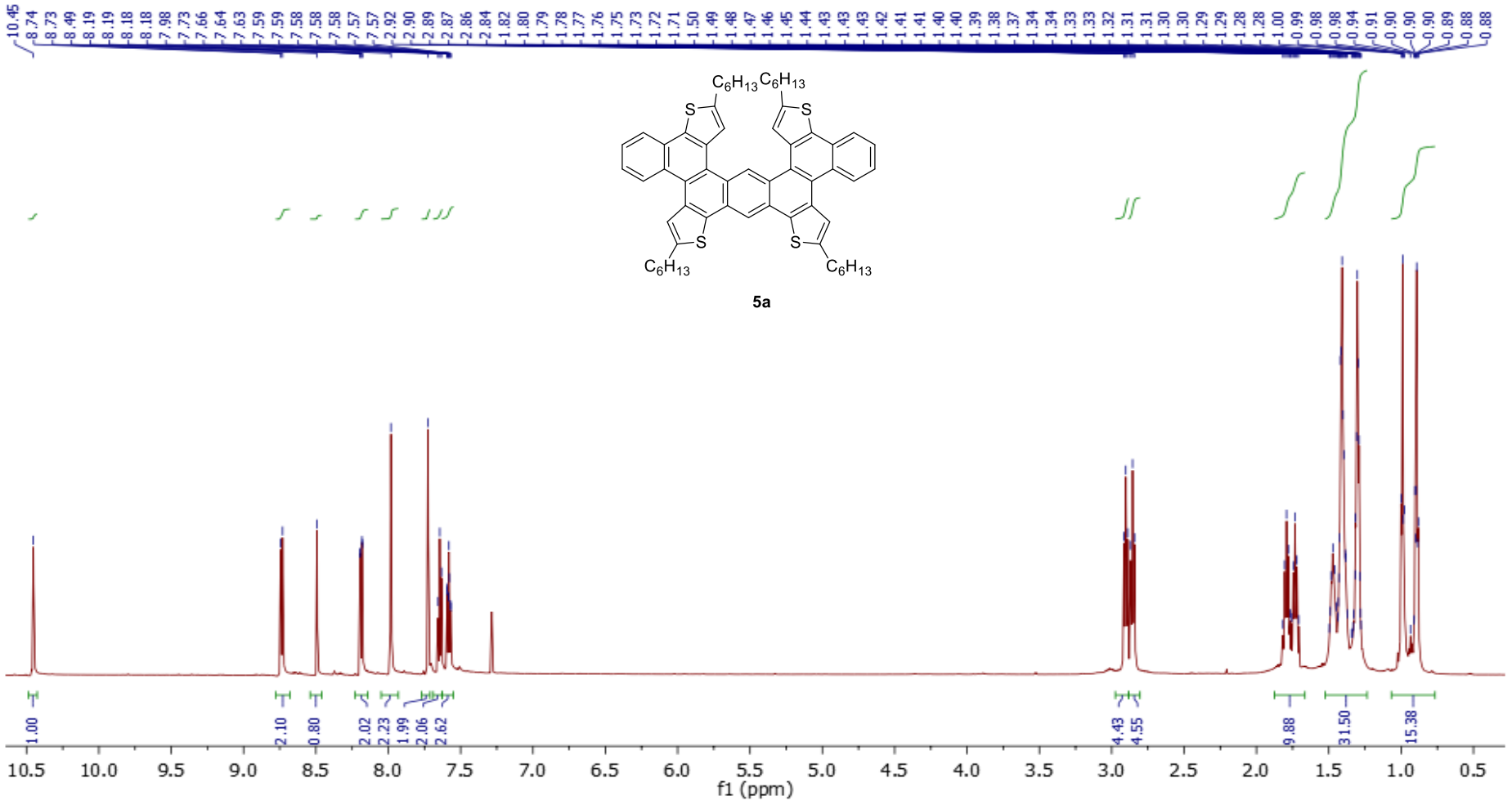
^{13}C NMR

(101 MHz, $CDCl_3$)



^{1}H NMR

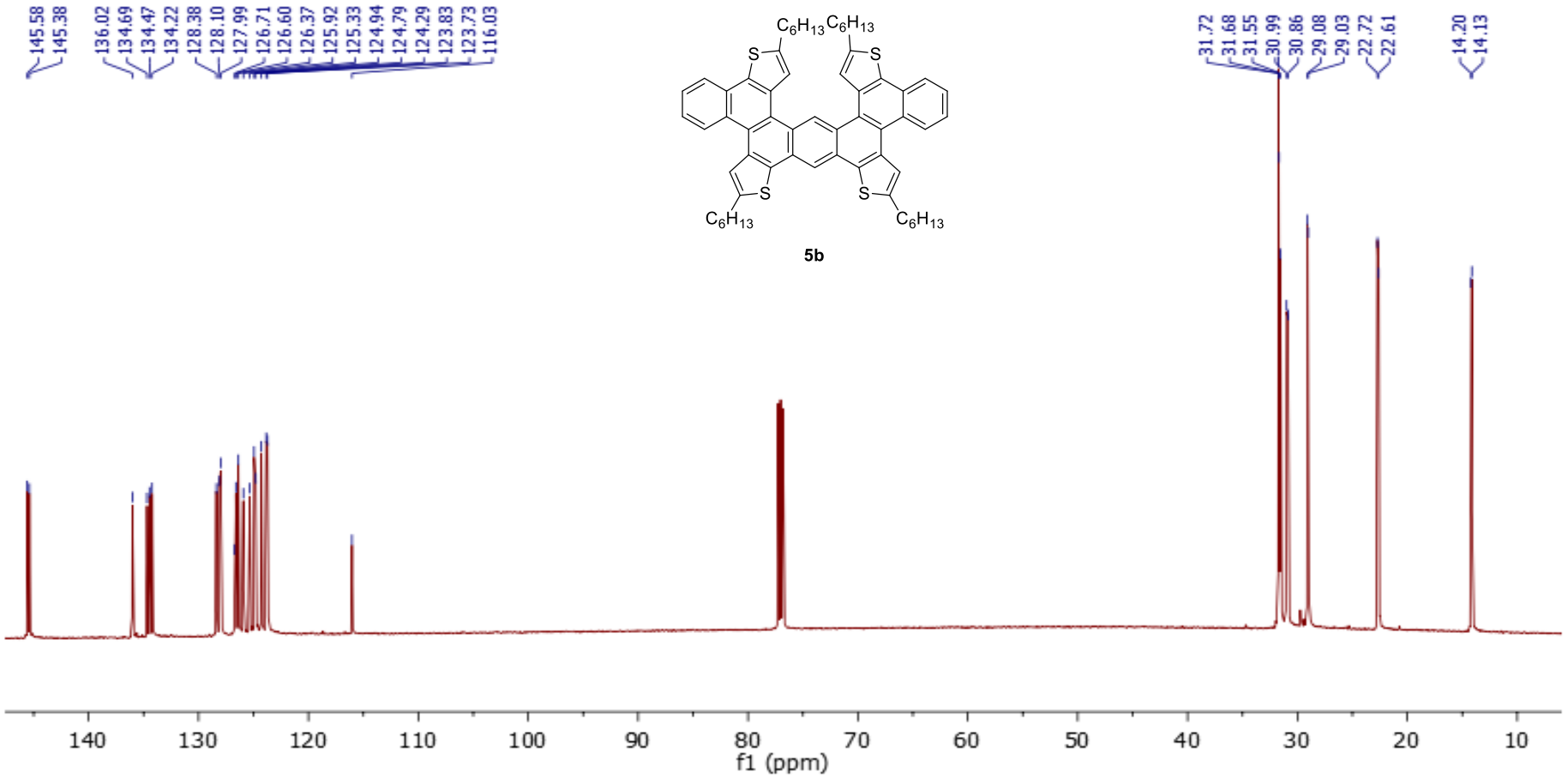
(400 MHz, $CDCl_3$)



5a

^{13}C NMR

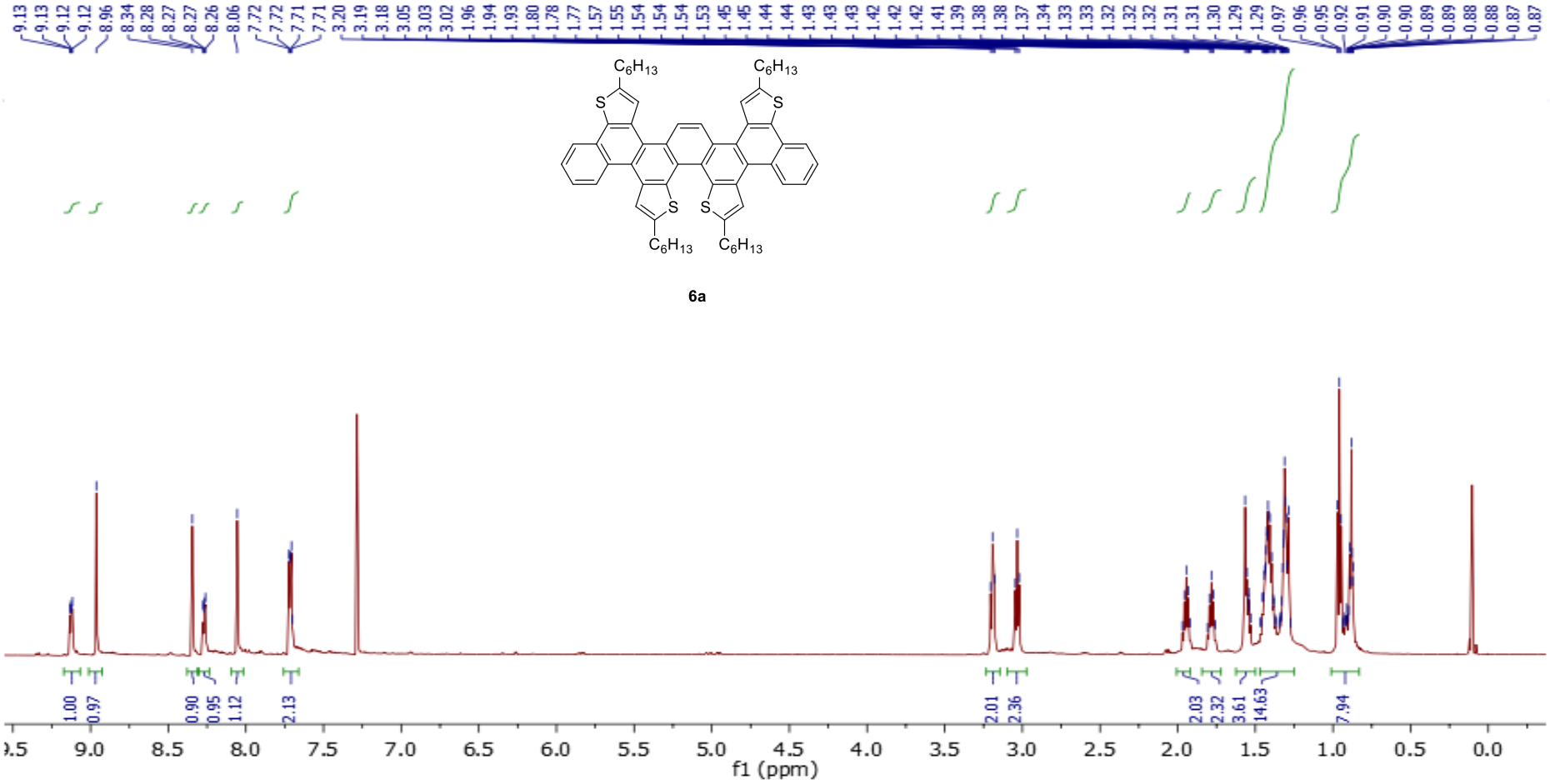
(101 MHz, $CDCl_3$)



5b

^{1}H NMR

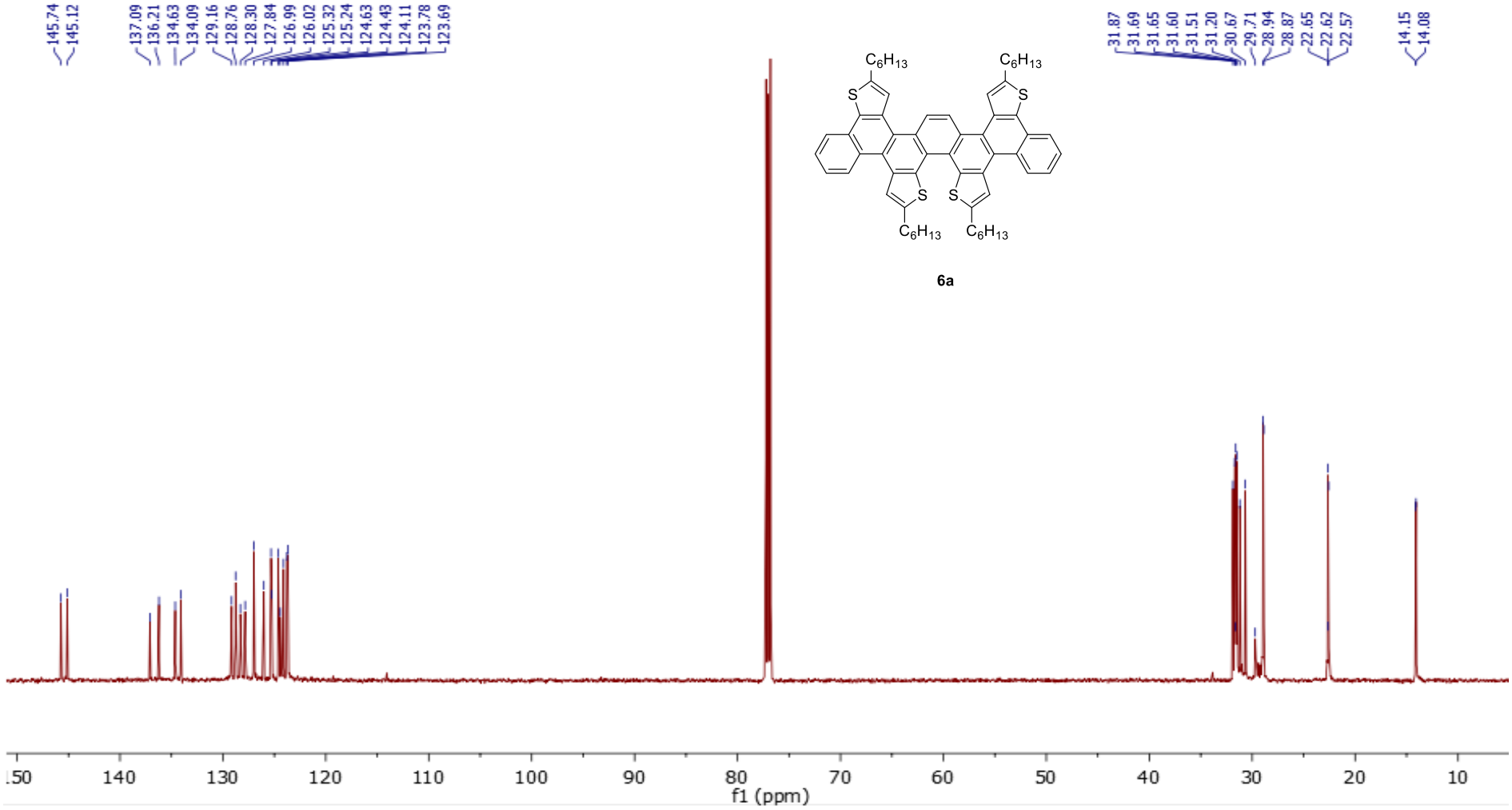
(400 MHz, $CDCl_3$)



6a

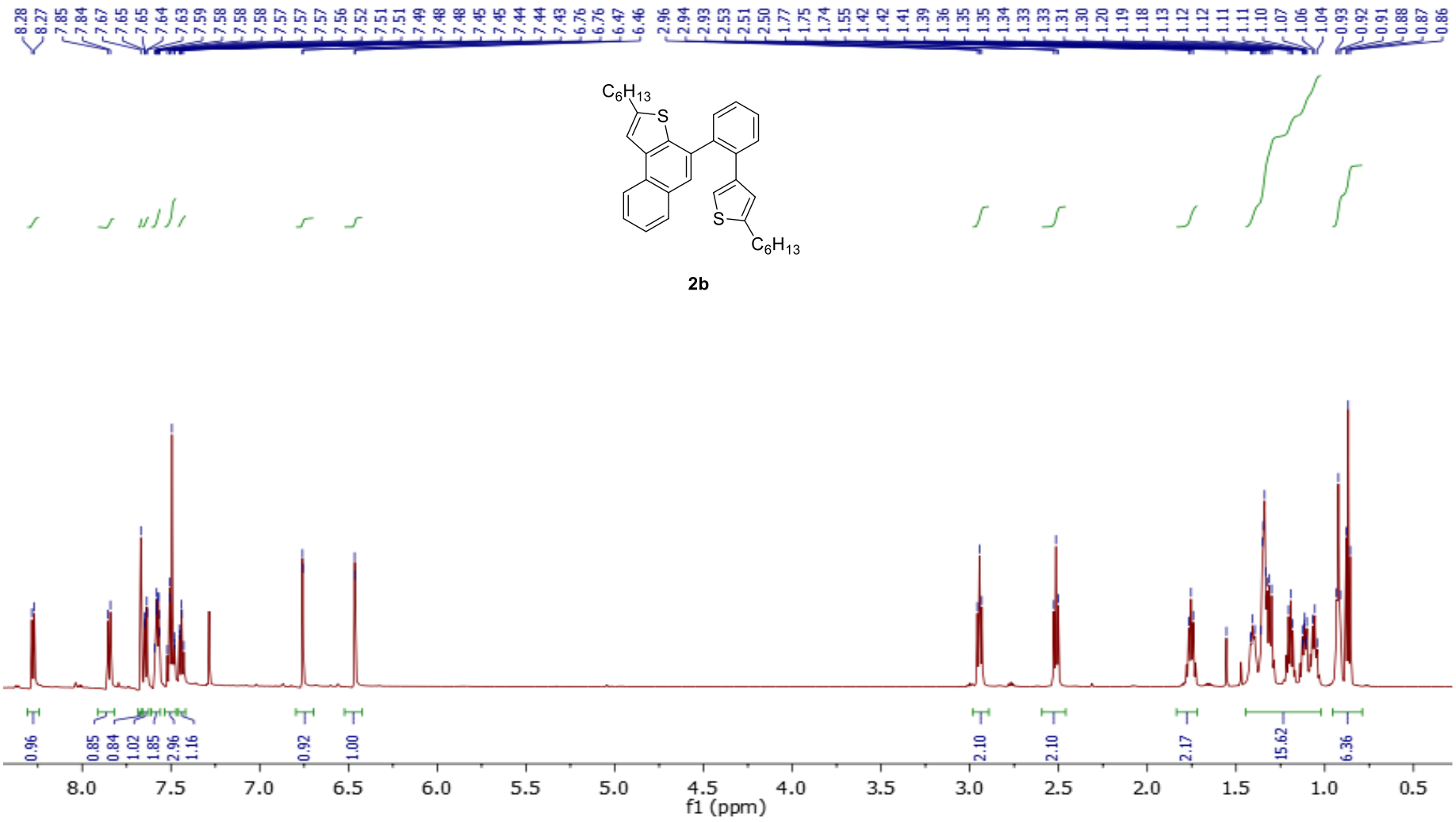
^{13}C NMR

(101 MHz, $CDCl_3$)



^{1}H NMR

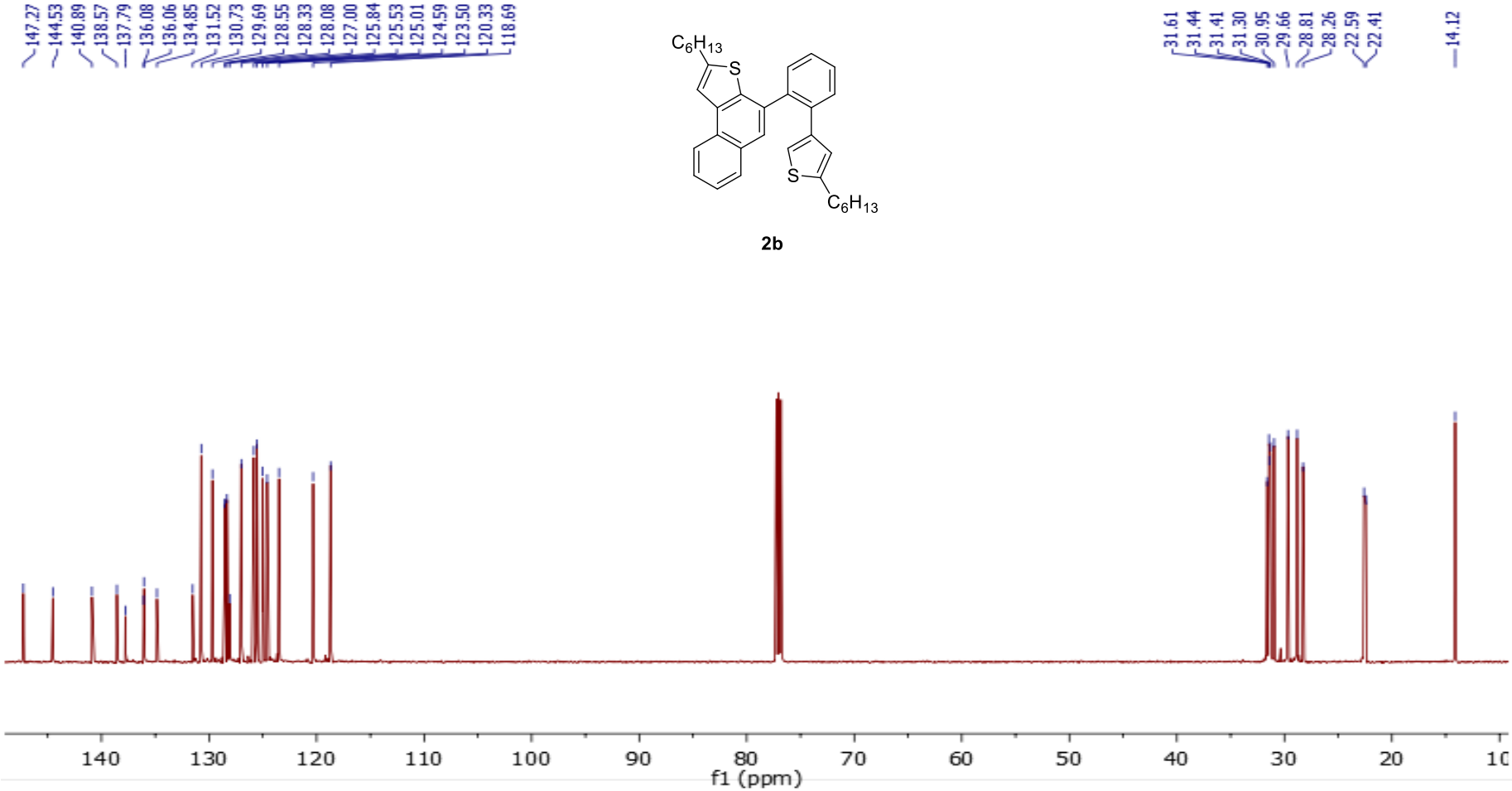
(400 MHz, $CDCl_3$)



2b

^{13}C NMR

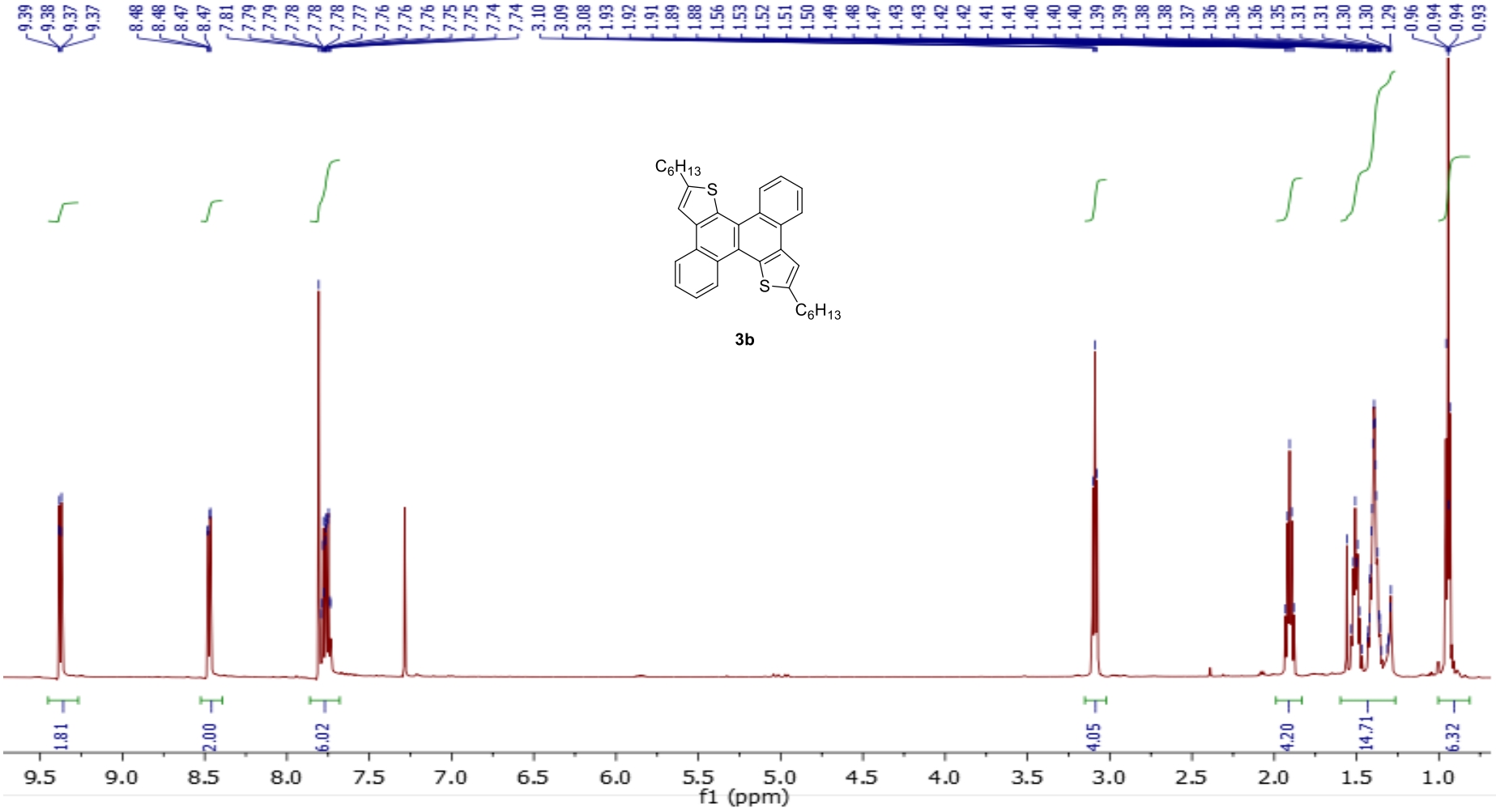
(101 MHz, $CDCl_3$)



2b

^{1}H NMR

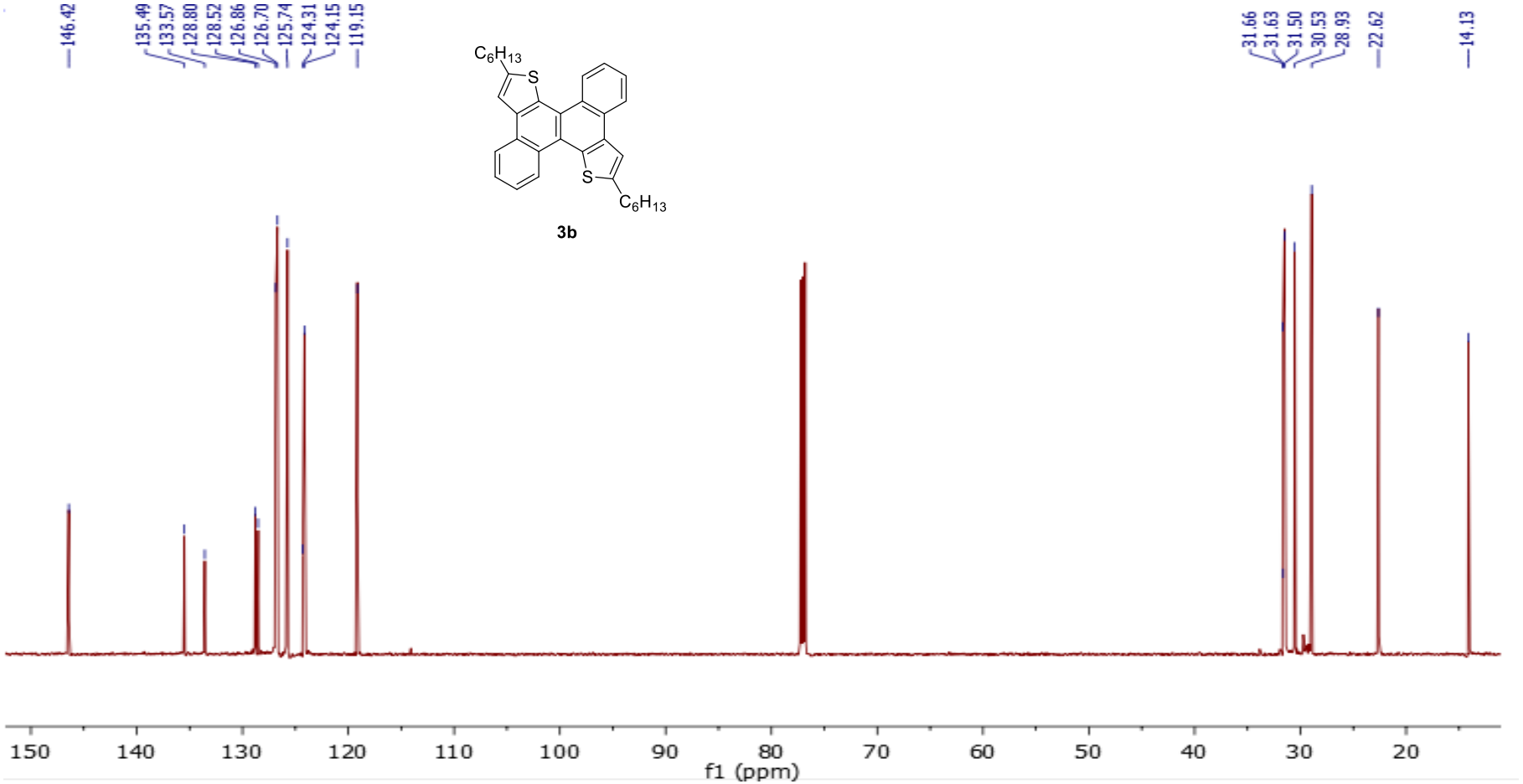
(400 MHz, $CDCl_3$)



3b

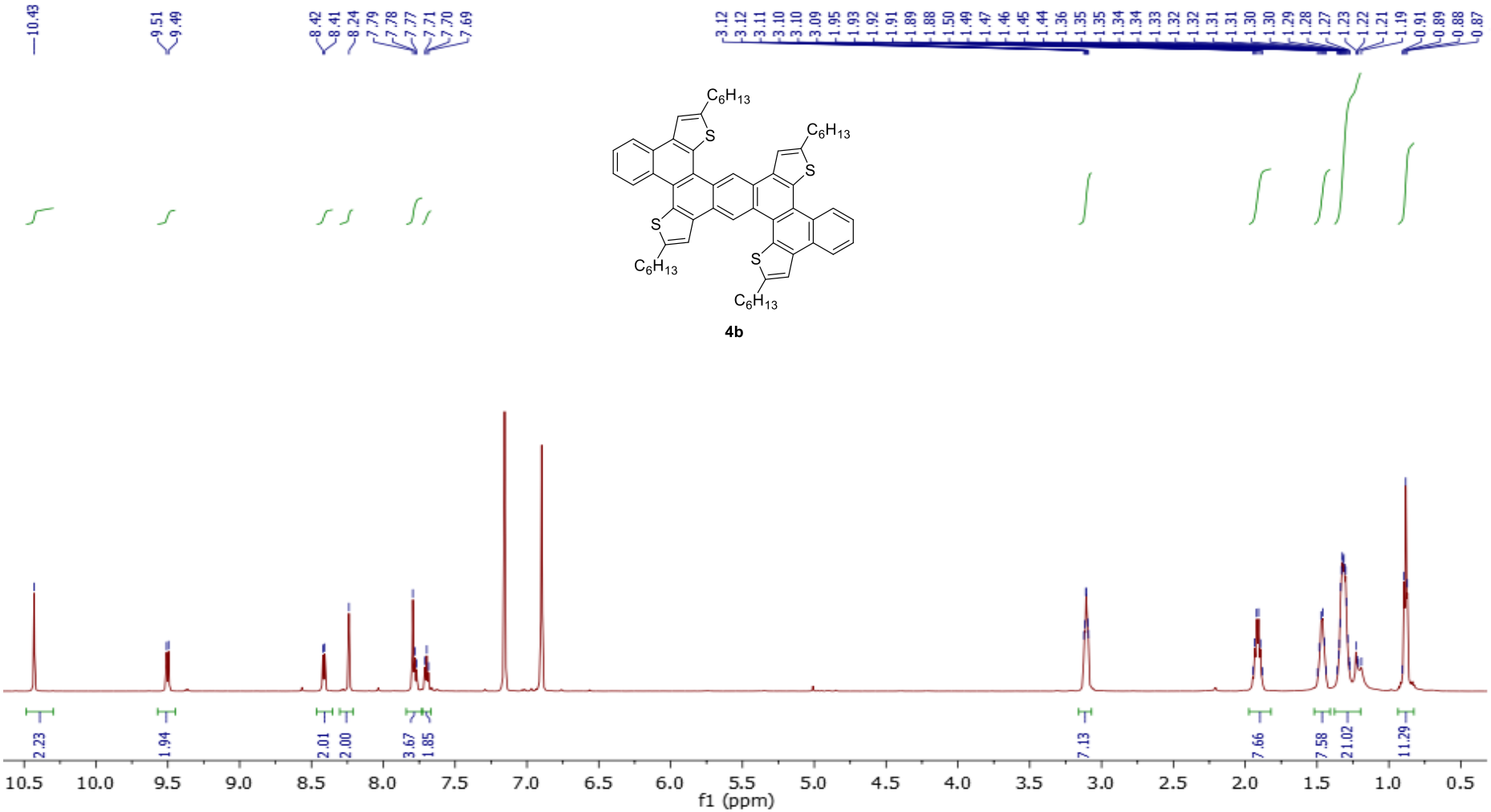
^{13}C NMR

(101 MHz, $CDCl_3$)



^{1}H NMR

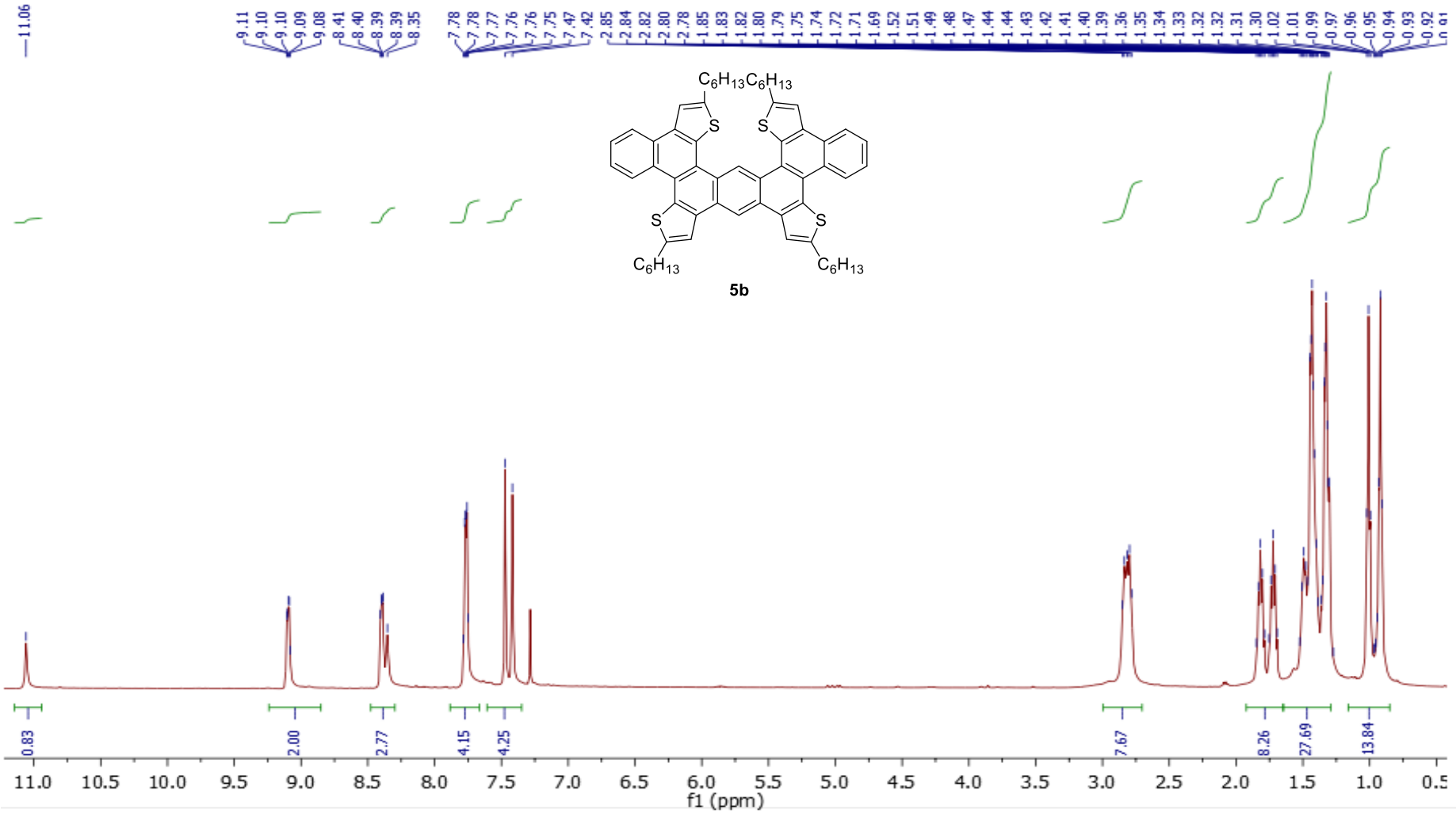
(400 MHz, dichlorobenzene)



4b

^{1}H NMR

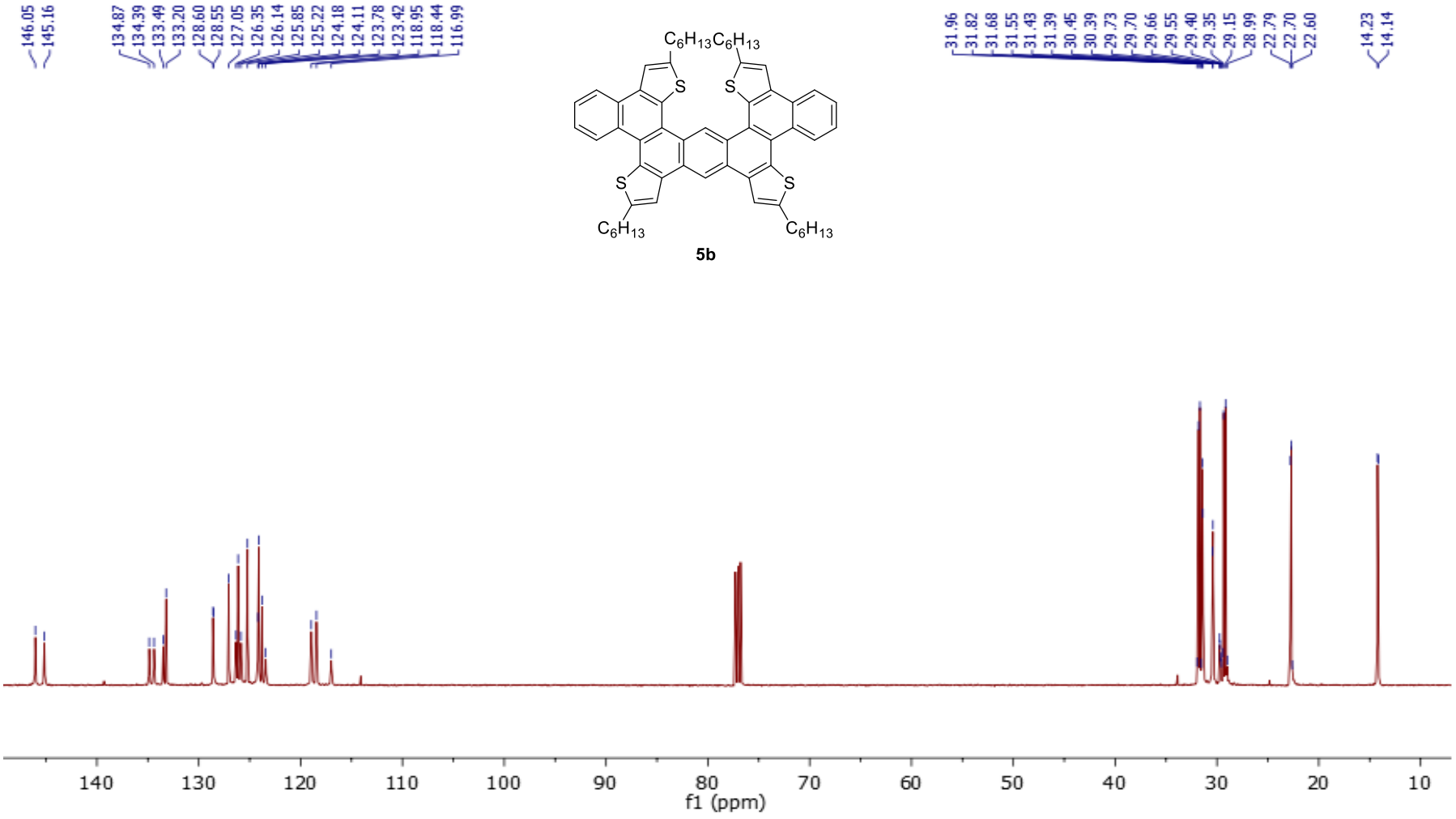
(400 MHz, $CDCl_3$)



5b

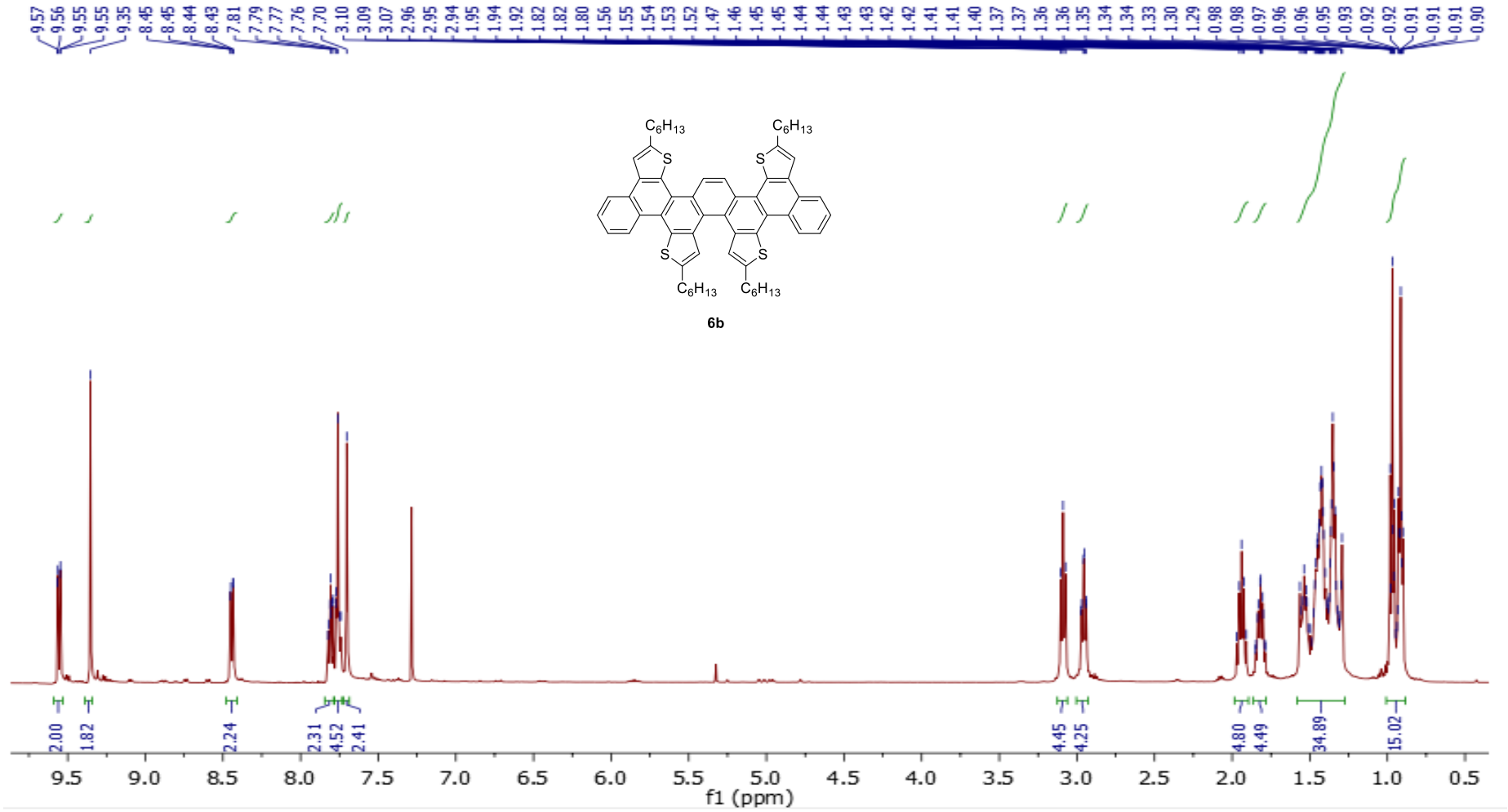
^{13}C NMR

(101 MHz, $CDCl_3$)



5b

^{1}H NMR
(400 HZ, $CDCl_3$)



^{13}C NMR

(101 MHz, $CDCl_3$)