Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of bent-shaped π-extended thienoacenes from 2,5-distannylated 3,4-dialkynethiophene

Abhijeet R. Agrawal, Neha Rani Kumar, Aditya Choudhury and Sanjio S. Zade*

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur 741246, India.

[*] email: sanjiozade@iiserkol.ac.in

Table of Contents

General Instrumentation:

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Jeol JNM-ECS 400 spectrometer (400 MHz ^{1}H, 100 MHz^{13}C) and Bruker Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometer with tetramethylsilane as the internal reference; chemical shifts (δ) are given in parts per million (ppm). Spectra were processed using Mest ReNova v5 and referenced to residual protonated solvent signals ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.16 ppm). Suitable crystals were collected on a Agilent SuperNova, Dual, Cu/Mo at zero, Eos diffractometer. The structure was solved using Olex2[1] and refined with the ShelXL[2] refinement package using Least Squares minimization. UV−visible absorption spectra were recorded on an Agilent Cary60 UV−vis spectrophotometer.

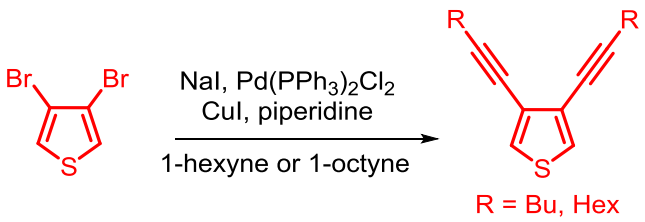
Materials:

All reagents were obtained from commercial sources (Sigma Aldrich, Spectrochem, Merck and Alfa Aesar) and used as received without further purification, unless otherwise specified. Toluene, Tetrahydrofuran (THF) and diethyether (Et_2O) were dried over sodium/benzophenone before use. Methanol and ethanol were dried using magnesium turning and iodine. Dry reactions were conducted in oven-dried glassware using a standard schlenk line under an inert atmosphere of dry nitrogen.

Caution: Trimethyltin chloride is a toxic and highly flammable compound. It is essential to perform the reaction using protective gloves/protective clothing/eye protection/face protection etc and dispose of the used syringe in the proper prescribed way for hazardous substances. (For more details, standard Material Safety Data Sheets can be referred).

Experimental Section

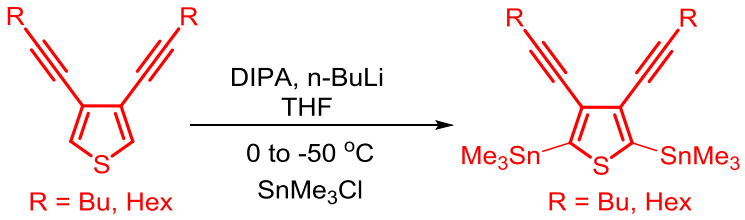
Synthesis of 3,4-di(hex-1-yn-1-yl)thiophene or 3,4-di(oct-1-yn-1-yl)thiophene



Scheme S1: Synthesis of 3,4-dialkyne substituted thiophene

To a solution of 3,4-dibromothiophene (2.0 g, 5.0 mmol), NaI (1.7 g, 11mmol), $Pd(PPh_3)Cl_2$ (0.18 g, 0.25 mmol) and CuI (0.14 g, 0.75 mmol) in distilled piperidine (50 mL) was added 1-hexyne/1-octyne (40 mmol) at room temperature. The mixture was refluxed for 24 h, and after cooling to room temperature, to the mixture was added aqueous saturated NH_4Cl, and extracted with EtOAc (3*15 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane) to afford the title compound as brown liquid.

Synthesis of (3,4-di(hex-1-yn-1-yl)thiophene-2,5-diyl)bis(trimethylstannane)

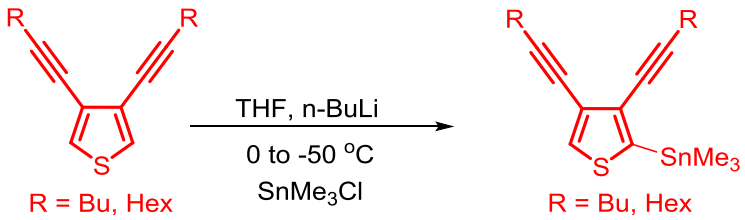


Scheme S2: Di-stannylation of 3,4-dialkyne thiophene compound

A 50 ml two-necked oven dried round bottomed flask is charged with 6 ml THF under an inert atmosphere of nitrogen. This is followed by the addition of 10.24 mmol of diisopropylamine at room temperature. The solution is then cooled to 0 ^oC. After this 6.14 ml (10.24 mmol, 1.6 M in hexane) n-butyl lithium is added dropwise in the solution and stirred for 10 minutes while the temperature of the reaction bath still kept at 0 ^oC. After 10 minutes, the temperature of the reaction mixture was reduced to -50 ^oC. Once the temperature reaches -50 ^oC, 500 mg (2.04 mmol) of dialkyne compound (pre-dissolved in 5 ml THF and purged with nitrogen for three consecutive times in a single neck round bottomed flask fitted with a rubber septum) is added dropwise into the reaction mixture and the mixture is further stirred for 1.5 hours (the temperature at this stage is also maintained at -50 ^oC). This is followed by the addition of 8 ml (8.19 mmol) of trimethyl tin chloride (1M solution in THF) to the reaction mixture all at once and then the chiller is put off and the reaction mixture is allowed to come to room temperature keeping the stirring on. Once the reaction mixture reaches room temperature, the reaction is quenched by the addition of a small amount of water, and the contents are transferred to a single neck round bottomed flask. The THF layer is evaporated and the compound is

extracted using diethyl ether. The diethyl ether layer is washed three times with a saturated solution of potassium fluoride and finally with brine. The organic layer is dried using Na_2SO_4 and the solvent evaporated under rotary evaporation to give the desired distannyl compound in quantitative yield.

Synthesis of 3,4-di(hex-1-yn-1-yl)thiophen-2-yl)trimethylstannane



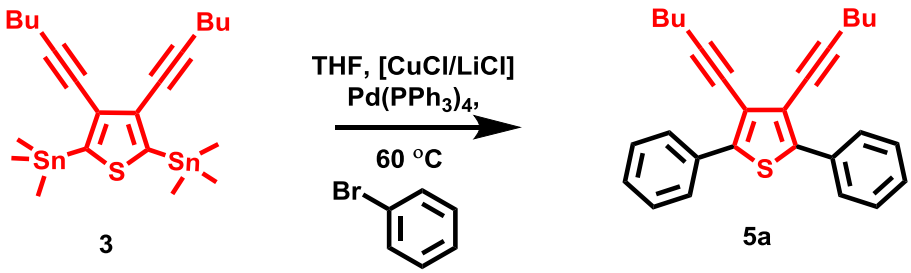
Scheme S3: Monostannylation of 3,4-dialkyne thiophene compound

A 50 ml two-necked oven dried round bottomed flask is charged with 1 equivalents of the dialkyne compound followed by the addition of 6 ml THF under an inert atmosphere of nitrogen. The reaction mixture is then cooled to -50 ^{o}C. 3 equivalents of n-butyl lithium is added to the reaction mixture at the same temperature and the mixture is further stirred for one and half hours (or 1.5 h). This is followed by the addition of 2 equivalents of trimethyl tin chloride to the reaction mixture all at once and then the chiller is put off and the reaction mixture is allowed to come to room temperature keeping the stirring on. Once the reaction mixture reaches room temperature, the reaction is quenched by the addition of a small amount of water, and the contents are transferred to a single neck round bottomed flask. The THF layer is evaporated and the compound is extracted using diethyl ether. The diethyl ether layer is washed three times with a saturated solution of potassium fluoride and finally with brine. The organic layer is dried using Na_2SO_4 and the solvent evaporated under rotary evaporation to give the desired monostannyl compound in quantitative yield.

Note: *The amount of n-butyl lithium has a significant role in this reaction. If 1.1-2.1 equivalents n-butyl lithium is used, then the product obtained is a mixture of monostannyl and starting material. Using an excess of n-butyl lithium, i.e. 3 equivalents, always gives monostannyl compound in quantitative yield. Even if the amount of n-butyl lithium is increased, it does not*

lead to any changes in the product formed (i.e. formation of distannyl compound is not observed).

Table S1: Optimization of reaction condition for Stille coupling reaction using bromobenzene as the model substrate



Catalyst	**Solvent**	**Temperature (^{0} C)**	**Yield (%)**
$Pd(PPh_3)_4$	Toluene	110	8-10
	THF	80	9
	DMF	45	2
$Pd(PPh_3)_2Cl_2$	Toluene	110	<10
	THF	80	5
$Pd(PPh_3)_4$, CuI	Toluene	110	8-10
$Pd(dba)_2$	Toluene	110	13
$PdCl_2$, $PtBu_3$, CsF,	DMF	45	20
$Pd(PPh_3)_4$, CuCl, LiCl	DMSO	70	54
	THF	**70**	**68**

Synthesis of aromatic halides used for Stille coupling reaction

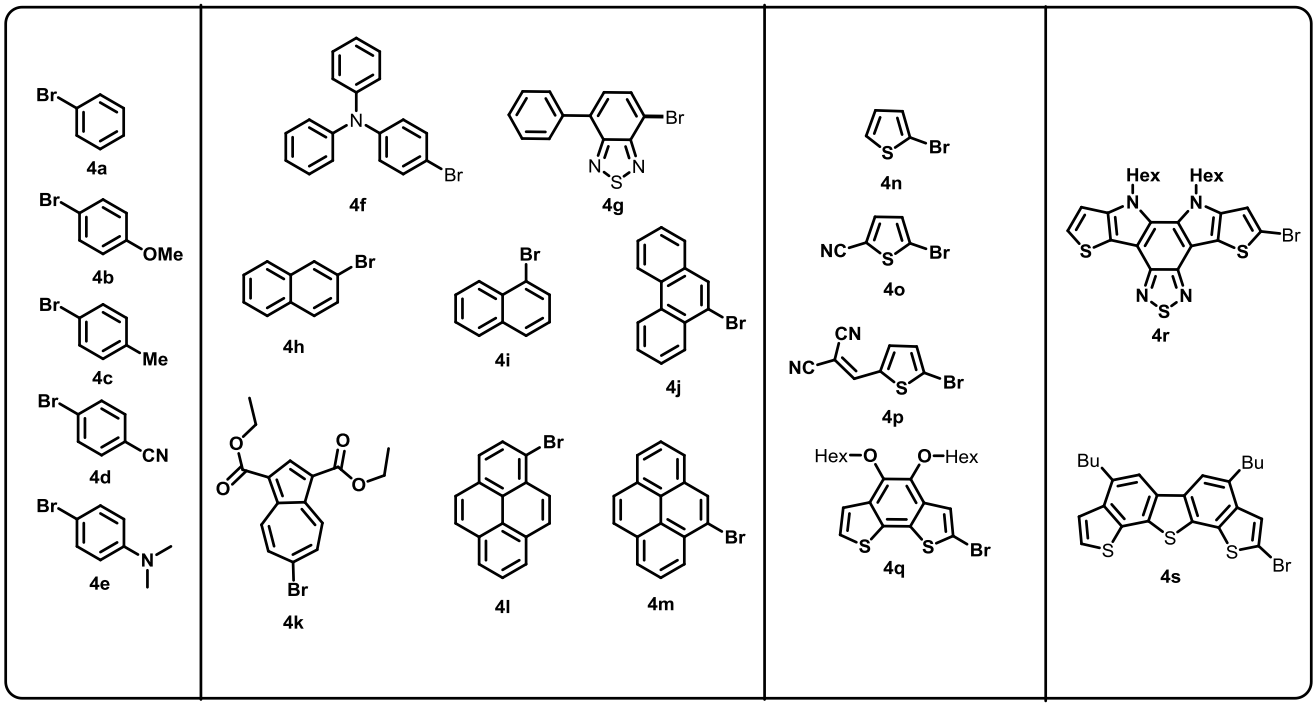
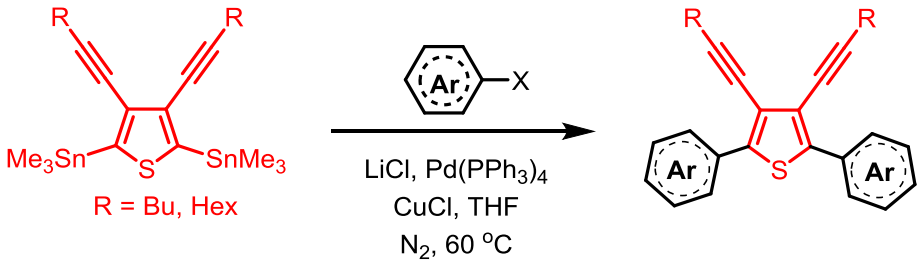


Figure S1: Aromatic halides used in Stille coupling reaction

Compounds **4a**, **4b**, **4c**, **4d**, **4e**, **4f**, **4h**, **4i**, **4j**, **4n** and **4o** were obtained from commercial sources. All other monomers were synthesized by using the approach reported elsewhere. **4g** was synthesized by using the approach described by Zhang and co-workers.[3] **4k** was synthesized by using the approach described by Gunji and group.[4] **4l** was synthesized by using the approach given by Lindgren and group.[5] **4m** was synthesized by using the approach described by Marder and group.[6] **4p**was synthesized by using the approach given by Riede and group.[7] **4q**was synthesized by using the approach given by Koeckelberghs and group.[8] **4r** was synthesized by using the approach described by Huang and group.[9] **4s** was obtained by the bromination of the syn-thienopentacene **6n** by using 1 equivalents of NBS in $CHCl_3$ and few drops of acetic acid at 0^{0} C.

General procedure for Stille coupling of aromatic halides with distannyl of thiophene[10]



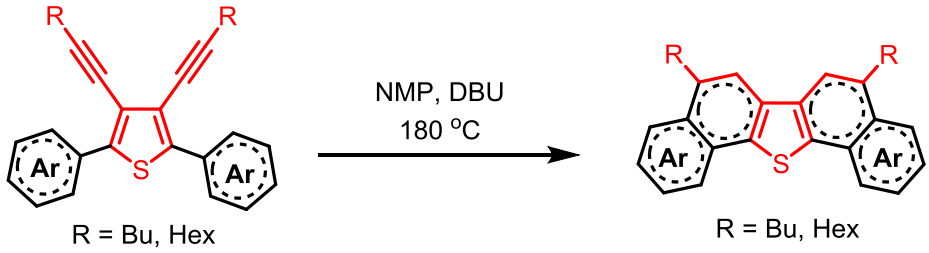
Scheme S4: Stille coupling of distannyl thiophene compounds with aromatic halides

An oven dried Schlenck tube (cooled in a dessicator) was charged with LiCl under inert atmosphere. Upon cooling, $Pd(PPh_3)_4$ and CuCl were added, and the mixture was degassed under high vacuum with N_2 purge. THF was introduced with concomitant stirring, followed by the addition of aromatic halide and the stannyl compound. The resulting mixture was further degassed three times using nitrogen balloon. The reaction mixture was stirred at room temperature for 1 h, then heated to 60 °C for the necessary period of time until the TLC indicated complete consumption of the aryl halide. The reaction mixture was then cooled, diluted with Et_2O and washed with a mixture of brine and 5% aqueous NH_4OH. The aqueous layer was further extracted with Et_2O and the combined organic layers were washed with water, then brine, dried over Na_2SO_4, and concentrated to a residue that was purified by silica gel column chromatography.

Note: *For coupling of distannyl compound with the aromatic halide the equivalents of reagents are as follows:*

Distannyl compound: 1 equivalents, CuCl: 5 equivalents, LiCl: 6 equivalents, $Pd(PPh_3)_4$: 10 mol%, Aromatic mono-halide: 3 equivalents (equivalents calculated with respect to the stannyl compound)

General procedure for NMP and DBU mediated alkyne annulations[11]



Scheme S5: DBU and NMP mediated alkyne annulation

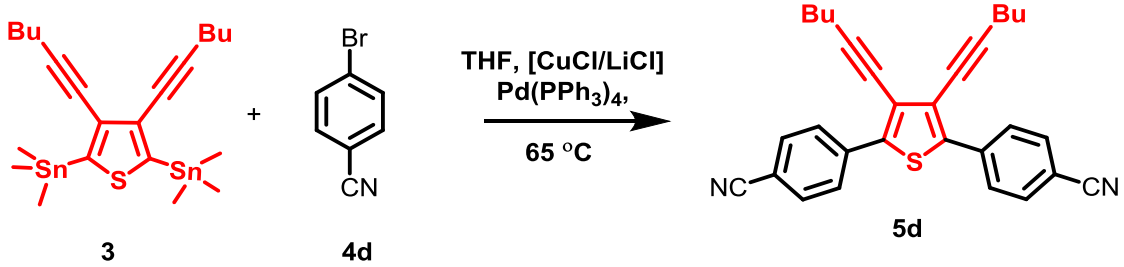
To a solution of alkyne compound (0.5 mmol, 1 equivalents) in NMP (7 mL) was added DBU (0.55 mmol, 1.1 equivalents) at room temperature. The mixture was stirred at 180 °C for 24 h. After cooling to room temperature, to the mixture was added an aqueous saturated solution of NH_4Cl, and extracted with EtOAc. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was further purified by silica gel column chromatography to afford the annulated compound.

Gram scale synthesis as a representative example for the broad application of the devised strategy

a) Gram scale synthesis of stannyl compound

A gram scale synthesis of (3,4-di(hex-1-yn-1-yl)thiophene-2,5-diyl)bis(trimethylstannane) **3** was carried out by using 2g (8.1 mmol) of the starting material using the procedure reported exactly as above. The distannyl derivative in this case was isolated in 97% yield (4.5g, 7.8 mmol) and the compound was of significant purity to use in next step.

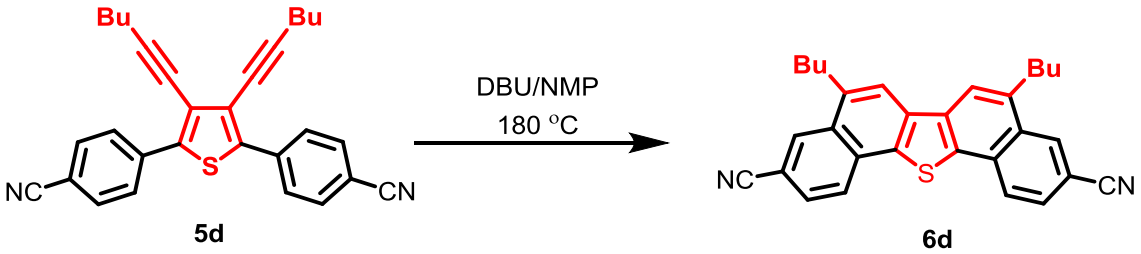
b) Gram scale synthesis of Stille coupling product



Scheme S6: Gram scale synthesis of **5d**

The gram scale synthesis of Stille coupling reaction was established by using distannyl derivative **3** (1.6 mmol) and mono-bromo compound **4d** (5 mmol) as the coupling partners using the general procedure as mentioned above. The Stille coupled product **5d** was isolated in 77 % yield (1.22 mmol).

c) Gram scale synthesis of DBU and NMP mediated alkyne annulation

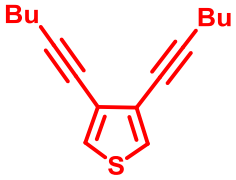


Scheme S7: Gram scale synthesis of **6d**

The gram scale synthesis DBU and NMP mediated alkyne annulation was established by using compound **5d** (1g, 2 mmol) as the starting material using the general procedure as mentioned above. The alkyne anniulated product **6d** was isolated in 87 % yield (1.7 mmol).

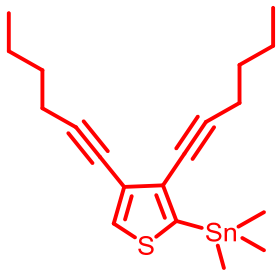
Purification procedure and characterization

*Characterization details of compound**1***



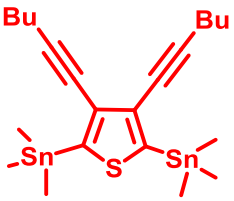
Purification: Brown liquid, Starting material used: 4 g (16.56 mmol) of 3,4-dibromo thiophene, Product obtained: 3.15 g (13.90 mmol), Percentage yield: 78%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (s, 2H), 2.43 (t, J = 8.0 Hz, 4H), 1.47 – 1.60 (m, 8H), 0.95 (t, J = 5.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 126.9, 125.8, 92.4, 74.7, 30.9, 22.1, 19.3, 13.8, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{20}SNa$: 267.1183; Found: 267.1181.

*Characterization details of compound **2***



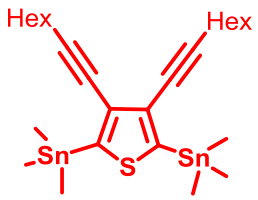
Purification: No purification required. Product obtained after work up is of significant purity, brown liquid, Starting material used: 0.5 g (2.04 mmol) of **1**, Product obtained: 0.79 g (1.94 mmol), Percentage yield: 95%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 2.43 (t, J = 8.0 Hz, 4 H), 1.48-1.58 (m, 8H), 0.95 (t, J = 8.0 Hz, 6H), 0.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 133.2, 132.1, 126.9, 92.6, 91.6, 76.8, 74.9, 30.9, 22.0, 19.4, 19.3, 13.84, 13.8, -8.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{28}SSnNa$: 431.0826; Found: 431.0822.

*Characterization details of compound **3***



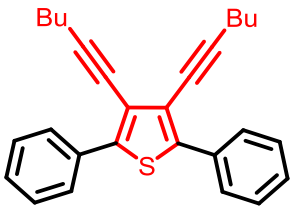
Purification: No purification required. Product obtained after work up is of significant purity, reddish sticky liquid, Starting material used: 0.5 g (2.04 mmol) of **1**, Product obtained: 1.12 g (1.96 mmol), Percentage yield: 96%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (t, J = 10.0 Hz, 4H), 1.44-1.58 (m, 8H), 0.95 (t, J = 5.0 Hz, 6H), 0.40 (s, 18H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 134.4, 92.0, 31.1, 22.1, 19.4, 13.8, -8.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{36}SSn_2Na$: 595.0479; Found: 595.0465.

*Characterization details of compound **3a***



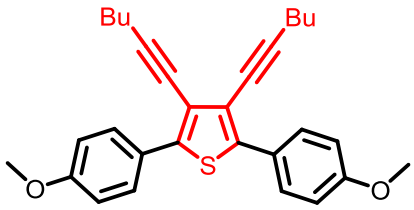
Purification: No purification required. Product obtained after work up is of significant purity, viscous yellow, Starting material used: 0.5 g (1.52 mmol) of 3,4-di(oct-1-yn-1-yl)thiophene, Product obtained: 0.93 g (1.43 mmol), Percentage yield: 94%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (t, J = 8.0 Hz, 4H), 1.58-1.63 (m, 4H), 1.44-1.48 (m, 4H), 1.31-1.33 (m, 8H), 0.91 (t, J = 8.0 Hz, 6H), 0.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 134.3, 92.1, 76.8, 31.7, 29.1, 28.9, 22.8, 19.8, 14.3, -8.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{44}SSn_2Na$: 651.1100; Found: 651.1094.

*Characterization details of compound **5a***



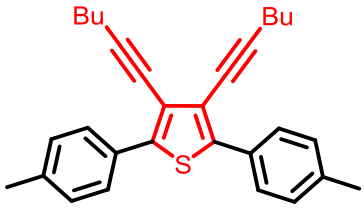
Purification: Column chromatography using silica gel (60-120 mesh),10% DCM/Hexane, light green solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.12 g (0.29 mmol), Percentage yield: 68%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 5.5, 3.5 Hz, 4H), 7.42 (t, J = 8.0 Hz, 4H), 7.35 (d, J = 8.0 Hz, 2H), 2.54 – 2.47 (m, 4H), 1.68 – 1.59 (m, 4H), 1.57 – 1.51 (m, 4H), 0.97 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 133.9, 128.8, 128.4, 127.9, 122.7, 95.4, 76.2, 31.1, 22.3, 19.8, 14.1, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{28}SNa$: 419.1804; Found: 419.1800.

*Characterization details of compound **5b***



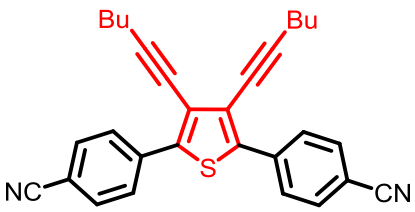
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, light green solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.11 g (0.24 mmol), Product yield: 56%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 4H), 6.93 (d, J = 8.0 Hz, 4H), 3.49 (s, 6H), 2.48 (t, J = 6.8 Hz, 4H), 1.57-1.62 (m, 4H), 1.48-1.54 (m, 4H), 0.96 (t, J = 8.0 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 141.7, 129.1, 126.8, 121.5, 114.2, 94.9, 76.4, 55.7, 30.1, 22.3, 19.8, 14.1, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}O_2SNa$: 479.2015; Found: 479.2011.

*Characterization details of compound **5c***



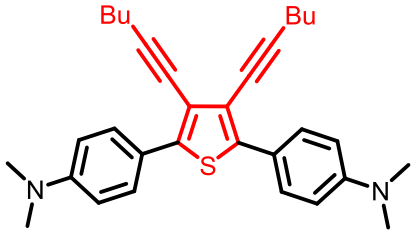
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, light green solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.11 g (0.25 mmol), Product yield: 60%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.81 (m, 4H), 7.22 (d, J = 8.0 Hz, 4H), 2.49 (t, J = 8.0 Hz, 4H), 2.40 (s, 6H), 1.49-1.64 (m, 8H), 0.97 (t, J = 8.0 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 138.0, 130.9, 129.3, 127.5, 121.9, 94.9, 76.1, 30.9, 22.1, 21.5, 19.6, 13.9, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}SNa$: 447.2117; Found: 447.2110.

*Characterization details of compound **5d***



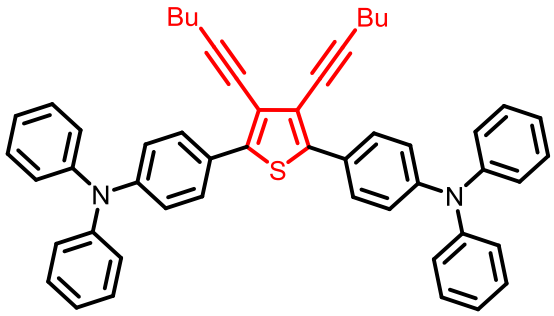
Purification: Column chromatography using silica gel (60-120 mesh), 20% DCM/Hexane, light green solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.16 g (0.35 mmol), Product yield: 80%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 4H), 7.70 (d, J = 8.5 Hz, 4H), 2.51 (t, J = 6.9 Hz, 4H), 1.67-1.59 (m, 4H), 1.52-1.47 (m, 4H), 0.97 (t, J = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 137.6, 132.5, 127.9, 125.0, 118.8, 111.7, 97.7, 75.2, 30.7, 22.2, 19.6, 13.8, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{26}N_2SNa$: 469.1709; Found: 469.1702.

*Characterization details of compound **5e***



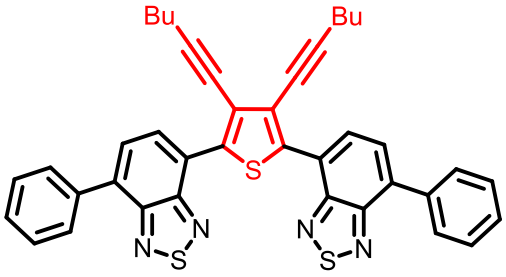
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, red solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.11 g (0.23 mmol), Product yield: 52%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 9.0 Hz, 4H), 6.74 (d, J = 9.0 Hz, 4H), 3.00 (s, 12H), 2.51 (t, J = 6.9 Hz, 4H), 1.66-1.61 (m, 4H), 1.58-1.53 (m, 4H), 0.98 (t, J = 8.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 141.6, 128.6, 128.4, 122.3, 119.9, 112.1, 94.1, 76.7, 40.5, 31.0, 22.2, 19.7, 13.9, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{38}N_2SNa$: 505.2648; Found: 505.2642.

*Characterization details of compound **5f***



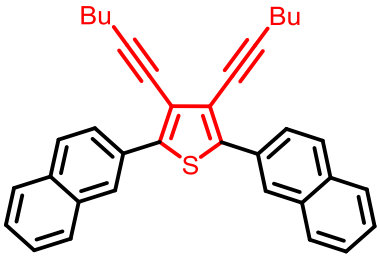
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, red solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.19 g (0.25 mmol), Product yield: 58%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.79 (m, 4H), 7.25-7.29 (m, 8H), 7.14 (d, J = 7.6 Hz, 8H), 7.03-7.07 (m, 8H), 2.48 (t, J = 6.8 Hz, 2H), 1.43-1.611(m, 8H), 0.92 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 141.5, 129.6, 128.4, 127.8, 125.1, 123.6, 123.1, 95.5, 76.5, 31.1, 22.3, 19.8, 14.1, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{52}H_{46}N_2SNa$: 753.3274; Found: 753.3272.

*Characterization details of compound **5g***



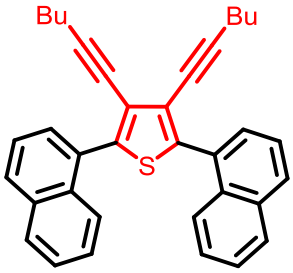
Purification: Column chromatography using silica gel (60-120 mesh), 20% DCM/Hexane, red solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.21 g (0.31 mmol), Product yield: 72%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (t, J = 4.6 Hz, 2H), 7.98-8.00 (m, 4H), 7.80 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.6 Hz, 4H), 7.43-7.47 (m, 2H), 2.55 (t, J = 8.0 Hz, 4H), 1.52-1.66 (m, 8H), 0.98 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 153.7, 139.9, 137.6, 134.1, 129.6, 128.9, 128.8, 128.6, 128.4, 128.2, 125.8, 124.6, 97.3, 76.5, 31.1, 22.4, 19.9, 14.0, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{32}N_4S_3Na$: 687.1681; Found: 687.1677.

Characterization details of compound ***5h***



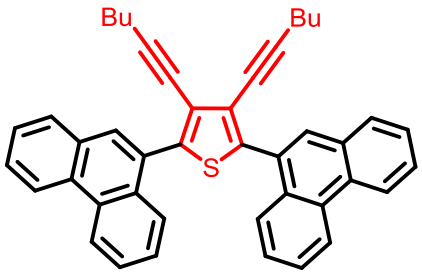
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, yellowish green solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.14 g (0.28 mmol), Product yield: 66%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 1.1 Hz, 2H), 8.06 (dd, J = 8.5, 1.7 Hz, 2H), 7.83-7.87 (m, 6H), 7.48-7.50 (m, 4H), 2.54 (t, J = 6.8 Hz, 4H), 1.61-1.68 (m, 4H), 1.52-1.57 (m, 4H), 0.97 (t, J = 7.3 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 133.7, 133.3, 131.4, 128.6, 128.4, 128.0, 126.7, 126.0, 123.2, 95.8, 76.4, 31.2, 22.4, 19.9, 14.1, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{32}SNa$: 519.2117; Found: 519.2110.

Characterization details of compound ***5i***



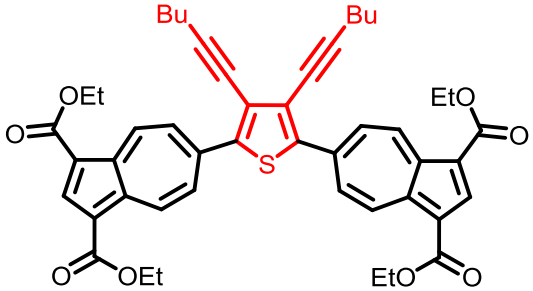
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, yellowish green solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.17 g (0.34 mmol), Product yield: 80%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.18 (m, 2H), 7.91 (dd, J = 7.2, 2.5 Hz, 4H), 7.63-7.68 (m, 2H), 7.51-7.54 (m, 6H), 2.19 (t, J = 6.8 Hz, 4H), 1.21-1.28 (m, 4H), 1.05-1.12 (m, 4H), 0.71 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 134.0, 132.1, 131.4, 129.3, 128.5, 127.1, 126.5, 126.3, 125.4, 124.8, 95.3, 75.6, 30.7, 21.8, 19.5, 13.9, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{33}SNa$: 519.2117; Found: 519.2114.

*Characterization details of compound **5j***



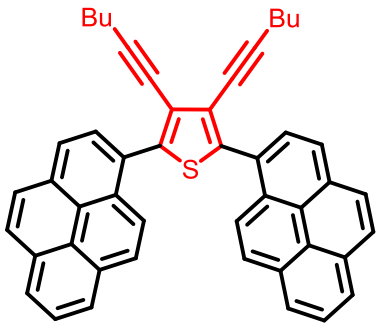
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, yellowish green solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.21 g (0.35 mmol), Product yield: 80%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, J = 15.3, 8.2 Hz, 4H), 8.25 (dd, J = 7.9, 1.0 Hz, 2H), 8.00 (s, 2H), 7.95 (d, J = 7.7 Hz, 2H), 7.63-7.70 (m, 8H), 2.18 (t, J = 6.9 Hz, 4H), 1.16-1.22 (m, 4H), 1.03-1.12 (m, 4H), 0.64 (t, J = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 131.5, 130.9, 130.5, 130.2, 129.3, 127.9, 127.5, 127.2, 127.0, 126.9, 125.2, 123.0, 122.9, 95.7, 75.6, 30.7, 21.8, 19.5, 14.5, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{36}SNa$: 619.2430; Found: 619.2424.

*Characterization details of compound **5k***



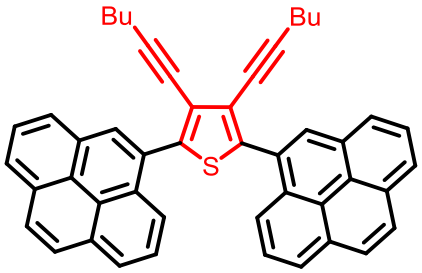
Purification: Column chromatography using silica gel (60-120 mesh), 40% DCM/Hexane, dark brown solid, Starting material used: 0.0.25 g (0.44 mmol) of **3**, Product obtained: 0.26 g (0.33 mmol), Product yield: 76%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, J = 11.2 Hz, 4H), 8.82 (s, 2H), 8.30 (dd, J = 10.1, 1.1 Hz, 4H), 4.46 (q, J = 7.2 Hz, 8H), 2.52 (t, J = 7.0 Hz, 4H), 1.56-1.62 (m, 4H), 1.46-1.52 (m, 16H), 0.95 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 144.1, 143.5, 138.3, 130.8, 119.4, 117.3, 77.0, 60.5, 30.9, 30.1, 22.4, 19.8, 14.9, 13.9, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{48}O_8SNa$: 807.2962; Found: 807.2959.

*Characterization details of compound **5l***



Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, orange, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.23 g (0.36 mmol), Product yield: 83%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 9.2 Hz, 2H), 8.23 (m, 8H), 8.15 (m, 6H), 8.05 (t, J = 7.6 Hz, 2H), 2.16 (t, J = 6.9 Hz, 4H), 1.15-1.22 (m, 4H), 0.94-1.03 (m, 4H), 0.47 (t, J = 7.3 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 131.9, 131.7, 131.4, 129.9, 129.3, 128.6, 128.3, 127.9, 127.7, 126.4, 125.6, 125.3, 125.0, 124.7, 95.4, 75.8, 30.7, 21.8, 19.5, 13.6, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{36}SNa$: 667.2430; Found: 667.2424.

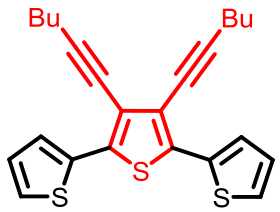
*Characterization details of compound **5m***



Purification: Column chromatography using silica gel (60-120 mesh), 20% DCM/Hexane, orange solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.225 g (0.35 mmol), Product yield: 80%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 7.8 Hz, 2H), 8.37 (s, 2H), 8.25 (t, J = 7.0 Hz, 6H), 8.10-8.16 (m, 4H), 8.04-8.08 (m, 4H), 2.14 (t, J = 6.9 Hz, 4H), 1.00-1.15 (m, 4H), 0.95-0.98 (m, 4H), 0.49 (t, J = 7.3 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 131.6, 131.5, 130.9, 130.9, 130.8, 130.2, 128.1, 127.4, 126.5, 126.2, 125.9, 125.8, 125.4, 125.1,

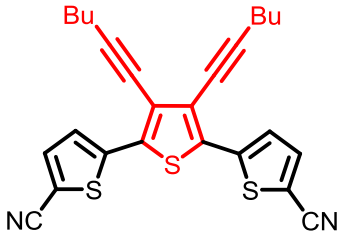
95.9, 75.7, 30.7, 21.8, 19.5, 13.6, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{36}SNa$: 667.2330; Found: 667.2327.

*Characterization details of compound **5n***



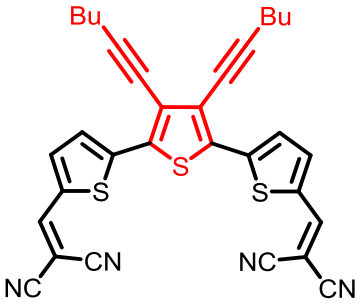
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, light green solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.093 g (0.23 mmol), Product yield: 52%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 3.9 Hz, 2H), 7.29 (d, J = 5.8 Hz, 2H), 7.04-7.06 (m, 2H), 2.56 (t, J = 7.1 Hz, 4H), 1.65-1.69 (m, 4H), 1.57-1.59 (m, 4H), 0.98 (t, J = 4 Hz, 6H).

*Characterization details of compound **5o***



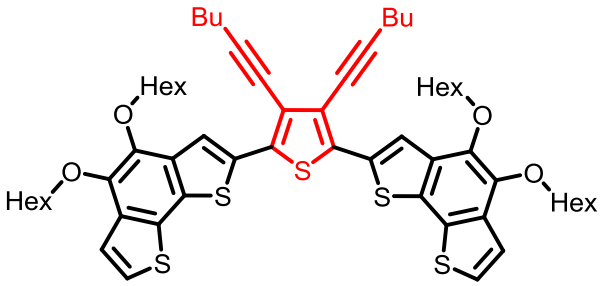
Purification: Column chromatography using silica gel (60-120 mesh), 30% DCM/Hexane, orange, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.14 g (0.29 mmol), Product yield: 68%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 3.9 Hz, 2H), 7.36 (d, J = 3.9 Hz, 2H), 2.61 (t, J = 7.0 Hz, 4H), 1.52-1.70 (m, 8H), 1.00 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 137.1, 134.4, 125.2, 124.3, 114.4, 108.9, 102.5, 75.0, 30.4, 22.2, 19.9, 13.8, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}N_2S_3Na$: 481.0837; Found: 481.0831.

*Characterization details of compound **5p***



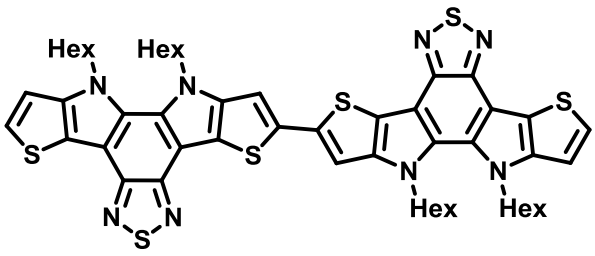
Purification: Column chromatography using silica gel (60-120 mesh), 40% DCM/Hexane, brown solid, Starting material used: 0.25 g (0.44 mmol) of **3**, Product obtained: 0.18 g (0.31 mmol), Product yield: 70%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.65 (d, J = 4.2 Hz, 2H), 7.51 (d, J = 4.2 Hz, 2H), 2.68 (t, J = 7.1 Hz, 4H), 1.51-1.70 (m, 8H), 0.98 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.2, 138.7, 135.5, 134.9, 126.5, 126.1, 114.3, 113.5, 105.3, 75.1, 30.5, 22.2, 19.8, 13.8, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{24}N_4S_3Na$: 583.1055; Found: 583.1051.

*Characterization details of compound **5q***



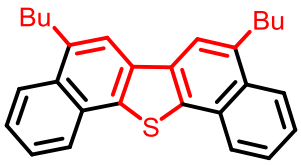
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, yellow viscous liquid, Starting material used: 0.1 g (0.18 mmol) of **3**, Product obtained: 0.1 g (0.09 mmol), Product yield: 54%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.50 (d, J = 5.4 Hz, 2H), 7.36 (d, J = 5.4 Hz, 2H), 4.17-4.23 (m, 8H), 2.66 (t, J = 7.0 Hz, 4H), 1.77-1.86 (m, 16H), 1.61-1.66 (m, 4H), 1.35-1.42 (m, 20H), 1.03 (t, J = 7.3 Hz, 6H), 0.91-96 (m, 12H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 143.6, 136.1, 135.3, 134.4, 134.1, 129.2, 129.0, 124.9, 123.1, 122.5, 120.2, 99.9, 75.9, 74.8, 74.7, 32.1, 32.1, 30.8, 30.8, 30.7, 26.2, 23.1, 23.0, 22.5, 20.2, 14.5, 14.4, 14.1, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{60}H_{68}O_8S_5Na$: 1099.3415; Found: 1099.3411.

*Characterization details of compound **5r***



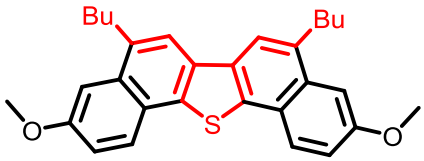
Purification: Column chromatography using silica gel (60-120 mesh), 20% DCM/Hexane, red solid, Starting material used: 0.2 g (0.33 mmol) of **4r**, Product obtained: 0.15 g (0.14 mmol), Product yield: 42%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 4.0 Hz, 2H), 7.19 (s, 2H), 7.16 (d, J = 5.0 Hz, 2H), 4.39-4.47 (m, 8H), 1.76-1.85 (m, 8H), 1.12-1.19 (m, 24H), 0.76-0.80 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 147.4, 145.9, 143.4, 132.1, 131.4, 127.3, 121.5, 115.3, 113.6, 112.0, 111.3, 110.9, 50.7, 31.6, 30.4, 26.6, 22.7, 14.2, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{52}H_{50}N_8O_4S_6Na$: 1065.2177; Found: 1065.2170.

*Characterization details of compound **6a***



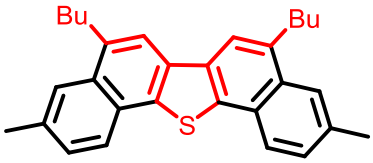
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, off-white solid, Starting material used: 0.1 g (0.25 mmol) of **5a**, Product obtained: 0.07 g (0.18 mmol), Product yield: 71%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.27 (m, 2H), 8.17-8.19 (m, 2H), 8.07 (s, 2H), 7.57-7.63 (m, 4H), 3.21-3.25 (m, 4H), 1.83-1.88 (m, 4H), 1.51-1.56 (m, 4H), 1.04 (t, J = 8.0 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 136.9, 135.6, 133.9, 131.3, 129.9, 126.7, 126.2, 125.6, 125.5, 119.9, 33.7, 30.1, 23.4, 14.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{28}SNa$: 419.1804; Found: 419.1801.

*Characterization details of compound **6b***



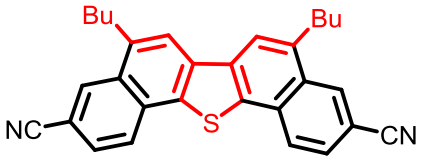
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, white solid, Starting material used: 0.1 g (0.21 mmol) of **5c**, Product obtained: 0.065 g (0.14 mmol), Product yield: 65%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 8.01 (s, 2H), 7.47 (d, J = 4.0 Hz, 2H), 7.29 (dd, J = 8.0, 2.5 Hz, 2H), 4.00 (s, 6H), 3.16-3.20 (m, 4H), 1.83-1.91 (m, 4H), 1.53-1.57 (m, 4H), 1.05 (t, J = 8.0 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 135.7, 135.1, 132.4, 126.8, 124.9, 120.2, 117.9, 115.0, 105.5, 55.8, 33.8, 33.1, 23.3, 14.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}O_2SNa$: 479.2015; Found: 479.2010.

*Characterization details of compound **6c***



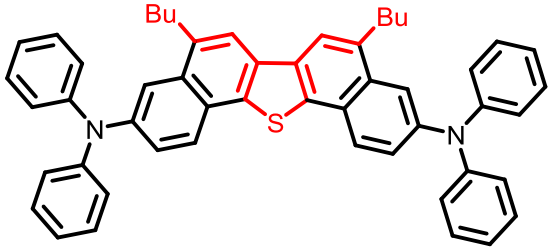
Purification: Column chromatography using silica gel (60-120 mesh), 10% DCM/Hexane, white solid, Starting material used: 0.1 g (0.24 mmol) of **5b**, Product obtained: 0.07 g (0.16 mmol), Product yield: 68%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 2H), 7.95 (s, 2H), 7.86 (s, 2H), 7.38-7.40 (m, 2H), 3.12-3.16 (m, 4H), 2.55 (s, 6H), 1.80 (t, J = 8.0 Hz, 4H), 1.47-1.51 (m, 4H), 0.98 (t, J = 8.0 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 135.8, 135.3, 133.3, 131.4, 128.6, 127.9, 125.3, 124.8, 119.9, 33.6, 33.5, 23.4, 22.5, 14.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}SN$: 447.2117; Found: 447.2111

Characterization details of compound ***6d***



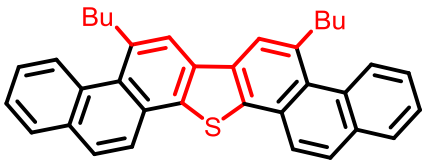
Purification: Column chromatography using silica gel (60-120 mesh), 20% DCM/Hexane, yellow solid, Starting material used: 0.15 g (0.34 mmol) of **5d**, Product obtained: 0.12 g (0.27 mmol), Product yield: 81%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 2H), 8.23 (d, J = 8.0 Hz, 2H), 8.08 (s, 2H), 7.76 (dd, J = 8.5, 1.5 Hz, 2H), 3.17-3.21 (m, 4H), 1.79-1.85 (m, 4H), 1.52-1.57 (m, 4H), 1.05 (t, J = 8.0 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 135.6, 132.6, 131.6, 130.8, 130.2, 127.7, 126.5, 121.3, 119.7, 109.9, 33.6, 30.1, 23.3, 14.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{26}N_2SNa$: 469.1709; Found: 469.1701.

Characterization details of compound ***6f***



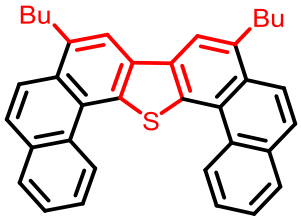
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, brownsolid, Starting material used: 0.15 g (0.2 mmol) of **5f**, Product obtained: 0.11 g (0.15 mmol), Product yield: 75%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 2H), 7.93 (s, 2H), 7.69 (d, J = 4.0 Hz, 2H), 7.37-7.40 (m, 2H), 7.30-7.32 (m, 8H), 7.20-7.26 (m, 8H), 7.07 (dd, J = 9.3, 5.3 Hz, 6H), 2.92-2.96 (m, 4H), 1.30-1.62 (m, 8H), 0.96 (d, J = 8.0 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 145.9, 136.1, 135.1, 132.9, 132.2, 129.7, 126.2, 125.8, 124.8, 124.4, 123.4, 120.1, 118.8, 33.8, 32.3, 23.1, 14.5, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{52}H_{46}N_2SNa$: 753.3274; Found: 753.3269.

*Characterization details of compound **6h***



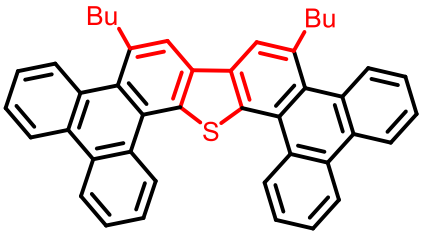
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, off white solid, Starting material used: 0.130 g (0.26 mmol) of **5h**, Product obtained: 0.09 g (0.19 mmol), Product yield: 72%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.0 Hz, 2H), 8.28 (s, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.98 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.62-7.67 (m, 4H), 3.61-3.65 (m, 4H), 2.01-2.07 (m, 4H), 1.61-1.70 (m, 4H), 1.10 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 138.1, 133.8, 131.9, 129.5, 129.1, 128.5, 127.7, 126.4, 126.2, 124.8, 123.6, 121.6, 38.9, 33.8, 23.5, 14.5, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{32}SNa$: 519.2117; Found: 519.2111.

*Characterization details of compound **6i***



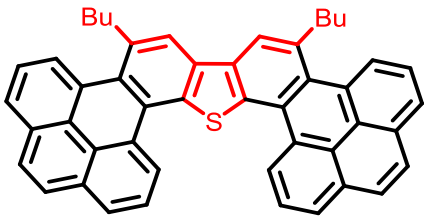
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, white solid,Starting material used: 0.150 g (0.30 mmol) of **5i**, Product obtained: 0.098 g (0.2 mmol), Product yield: 65%, ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.65 (d, *J* = 8.0 Hz, 2H), 8.42 (s, 2H), 8.22 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.96-8.00 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 3.33-3.37 (m, 4H), 1.89-1.92 (m, 4H), 1.57-1.61 (m, 4H), 1.06 (t, *J* = 8.0 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) *δ* 137.4, 134.3, 132.9, 130.8, 129.1, 128.5, 127.3, 127.0, 126.8, 126.7, 123.9, 120.9, 34.7, 34.0, 23.4, 14.5, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{32}SNa$: 519.2117; Found: 519.2111.

Characterization details of compound ***6j***



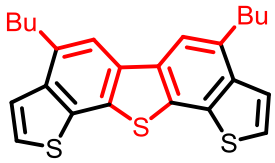
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, white solid, Starting material used: 0.2 g (0.34 mmol) of **5j**, Product obtained: 0.14 g (0.23 mmol), Product yield: 70%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, J = 8.0 Hz, 2H), 8.70 (d, J = 8.0 Hz, 2H), 8.63 (d, J = 8.0 Hz, 2H), 8.44 (s, 2H), 8.41 (d, J = 8.0 Hz, 2H), 7.81-7.84 (m, 2H), 7.73 (t, J = 7.4 Hz, 2H), 7.64 (dd, J = 10.9, 4.0 Hz, 2H), 7.56 (m, 2H), 3.52-3.56 (m, 4H), 1.93-1.99 (m, 4H), 1.43-1.46 (m, 4H), 1.00 (t, J = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 134.3, 133.3, 131.7, 130.9, 130.5, 129.3, 128.1, 127.8, 127.6, 127.1, 126.9, 125.9, 123.8, 123.6, 122.6, 37.1, 34.9, 23.4, 14.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{36}SNa$: 619.2430; Found: 619.2421.

Characterization details of compound ***6m***



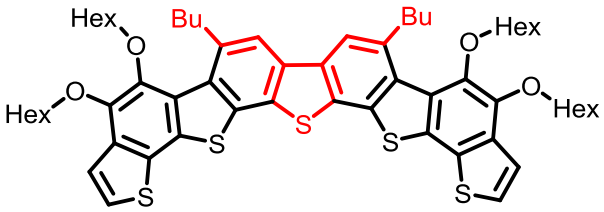
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, white solid, Starting material used: 0.05 g (0.08 mmol) of **5m**, Product obtained: 0.032 g (0.048 mmol), Product yield: 65%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (dd, J = 7.1, 1.7 Hz, 2H), 8.79 (d, J = 8.0 Hz, 2H), 8.62 (s, 2H), 8.27 (dd, J = 11.9, 4.7 Hz, 4H), 8.21 (d, J = 8.0 Hz, 2H), 8.12 (s, 4H), 8.00 (t, J = 8.0 Hz, 2H), 3.71 (t, J = 8.0 Hz, 4H), 2.06-2.13 (m, 4H), 1.54-1.57 (m, 4H), 1.05 (t, J = 8.0 Hz, 6H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 134.5, 134.2, 132.1, 131.7, 131.4, 130.1, 130.1, 128.8, 127.8, 127.6, 126.7, 126.6, 126.3, 125.1, 125.1, 124.9, 124.7, 123.2, 37.7, 30.1, 23.4, 14.5, 14.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{36}SNa$: 667.2430; Found: 667.2425.

Characterization details of compound ***6n***[13]



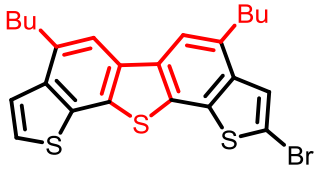
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, light green solid, Starting material used: 0.1 g (0.24 mmol) of **5n**, Product obtained: 0.075 g (0.183 mmol), Product yield: 75%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 4.0 Hz, 2H), 3.12 (t, J = 8.0 Hz, 4H), 1.79-1.83 (m, 4H), 1.47-1.50 (m, 4H), 1.01 (t, J = 8.0 Hz, 6H)

Characterization details of compound ***6q***



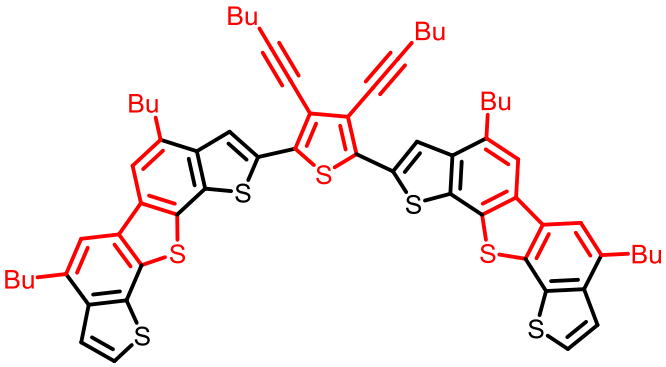
Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, light yellow, Starting material used: 0.05 g (0.05 mmol) of **5q**, Product obtained: 0.04 g (0.03 mmol), Product yield: 70%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.56 (d, J = 5.0 Hz, 2H), 7.46 (d, J = 5.0 Hz, 2H), 4.35 (t, J = 5.0 Hz, 4H), 3.95 (d, J = 8.0 Hz, 4H), 3.66-3.69 (m, 4H), 1.88-1.92 (m, 8H), 1.79-1.83 (m, 8H), 1.35-1.40 (m, 12H), 1.26-1.29 (m, 12H), 0.91 (m, 18H).^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 145.9, 139.3, 135.6, 134.8, 134.1, 133.7, 131.0, 129.9, 129.8, 128.4, 126.4, 122.3, 121.5, 75.4, 75.1, 38.6, 33.9, 32.1, 32.0, 30.8, 30.2, 30.1, 26.3, 26.0, 23.1, 22.9, 14.5, 14.4, 14.3, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{60}H_{68}O_8S_5Na$: 1099.3415; Found: 1099.3411.

*Characterization details of compound **4s***



Purification: Column chromatography using silica gel (60-120 mesh), Hexane, off white solid,Starting material used: 0.3 g (0.73 mmol) of **6n**, Product obtained: 0.29 g (0.58 mmol), Product yield: 80%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.79 (s, 2H), 7.52 (d, J = 5.0 Hz, 2H), 7.45-7.47 (m, 4H), 3.06 (t, J = 5.0 Hz, 4H), 2.96 (t, J = 5.0 Hz, 4H), 1.75-1.80 (m, 8H), 1.46-1.49 (m, 8H), 1.01 (t, J = 8.0 Hz, 12H).^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 137.9, 135.4, 134.9, 134.3, 133.9, 133.7, 133.1, 129.8, 128.8, 126.0, 124.9, 123.2, 118.3, 117.7, 113.5, 34.2, 34.1, 33.5, 33.4, 22.9, 22.9, 14.2, 14.2, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{23}BrS_3Na$: 509.0037; Found: 509.0031.

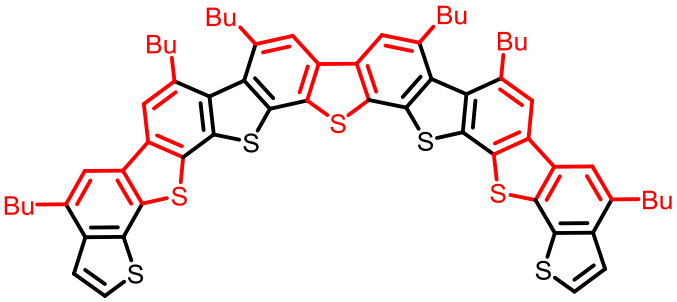
*Characterization details of compound **5s***



Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, red solid,Starting material used: 0.05 g (0.09 mmol) of **3**, Product obtained: 0.07 g (0.07 mmol), Product yield: 76%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.81 (d, J = 4.0 Hz, 4H), 7.48 (d, J = 4.0 Hz, 2H), 7.45 (d, J = 4.0 Hz, 2H), 3.03-3.10 (m, 8H), 2.72 (t, J = 8.0 Hz, 4H), 1.69-1.88 (m, 8H), 1.48-1.58 (m, 4H), 1.26-1.31 (m, 4H), 0.96-1.10 (m, 8H), 0.84-0.90 (m, 18H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.9, 135.9, 135.3, 135.1, 134.5, 134.1, 133.9, 133.6, 130.3, 129.4, 124.9, 123.4, 122.9, 120.8, 118.2, 117.8, 114.4, 100.1, 76.2, 34.4, 33.7, 33.5, 32.3, 30.9,

30.1, 23.2, 22.7, 20.3, 14.4, 14.3, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{64}H_{64}S_7Na$: 1079.2951; Found: 1079.2947.

Characterization details of compound **6s**



Purification: Column chromatography using silica gel (60-120 mesh), 5% DCM/Hexane, white solid,Starting material used: 0.05 g (0.09 mmol) of **5s**, Product obtained: 0.04 g (0.03 mmol), Product yield: 69%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 2H), 8.16 (s, 2H), 7.98 (s, 2H), 7.59 (d, J = 4.0 Hz, 2H), 7.54 (d, J = 4.0 Hz, 2H), 3.33-3.38 (m, 8H), 3.15 (t, J = 8.0 Hz, 4H), 1.85 (t, J = 8.0 Hz, 4H), 1.71-1.76 (m, 8H), 1.26-1.34 (m, 4H), 1.03 (t, J = 8.0 Hz, 8H), 0.86-0.93 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 142.7, 139.0, 137.5, 135.8, 135.5, 134.9, 134.3, 133.8, 133.6, 133.3, 131.1, 125.6, 123.9, 123.5, 120.4, 34.6, 34.5, 33.7, 32.3, 30.1, 30.1, 29.7, 23.2, 23.2, 14.5, 14.4, 14.4, HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{64}H_{64}S_7Na$: 1079.2951; Found: 1079.2945.

Table S2: Crystallographic data and structure refinement parameters

Compound	**6j**
Formula	$C_{44}H_{36}S$
Crystal system	Monoclinic
space group	P 1 21/n 1
Hall group	-P 2yn
a [Å]	12.8904(2)
b [Å]	7.48810(10)
c [Å]	31.9207(4)
α [deg]	90
β [deg]	101.5840(10)

γ [deg]	90
V [Å3]	3018.37(7)
Z	4
λ [Å]	1.54184
ρcalcd	1.313
F[000]	1264
μ [mm−1]	1.186
θ [deg]	2.77-66.0970
index ranges	−15≤ h ≤15 −6≤ k ≤8 −37≤ l ≤37
T [K]	99.99(10)
R1	0.0338
wR2	0.0875
parameters	408
CCDC No.	2053380

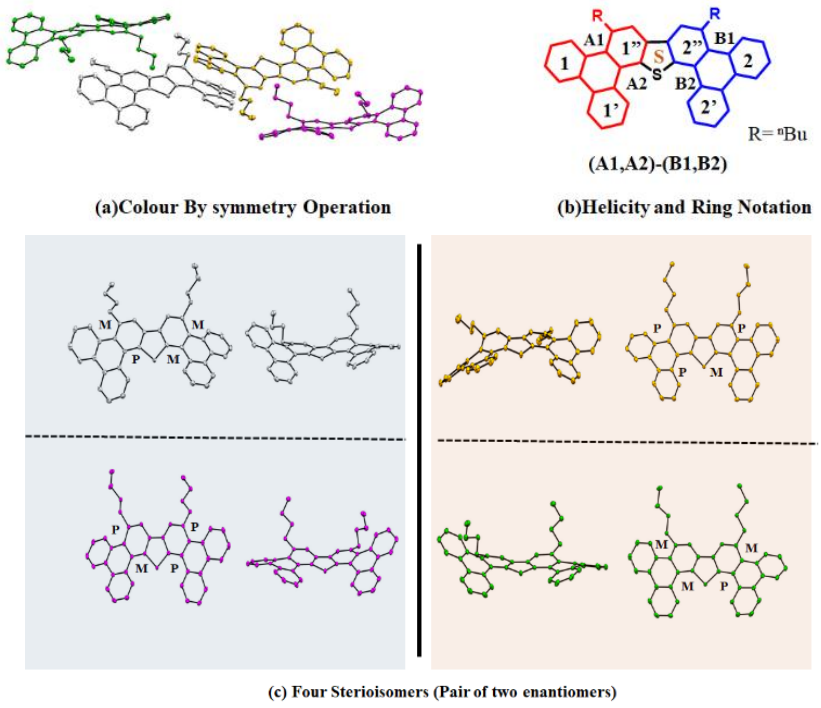


Figure S2: Crystallographic insights into the single crystal of **6j**

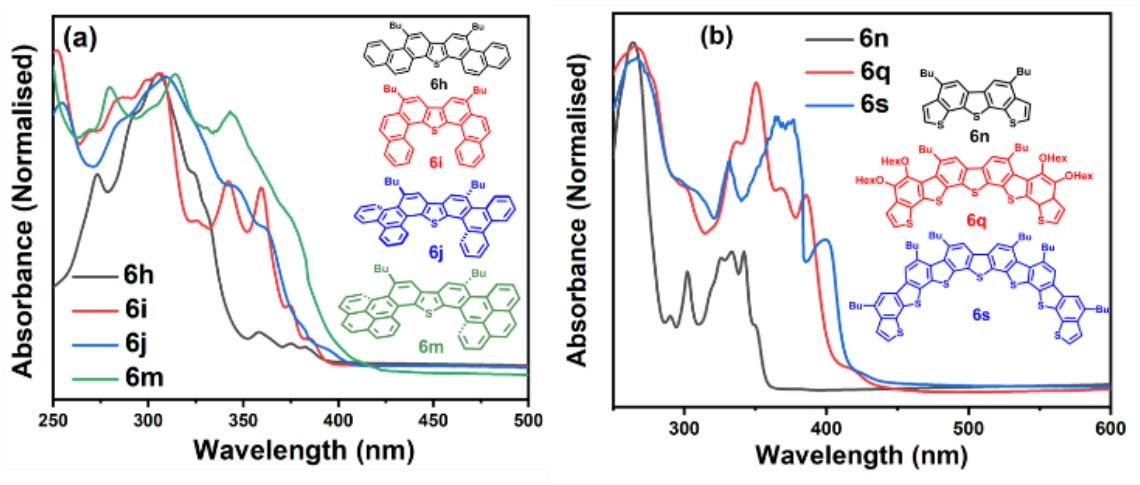


Figure S3: UV-Visible spectra of (a) **6h**, **6i**, **6j** and **6m** (b) **6n**, **6q** and **6s**

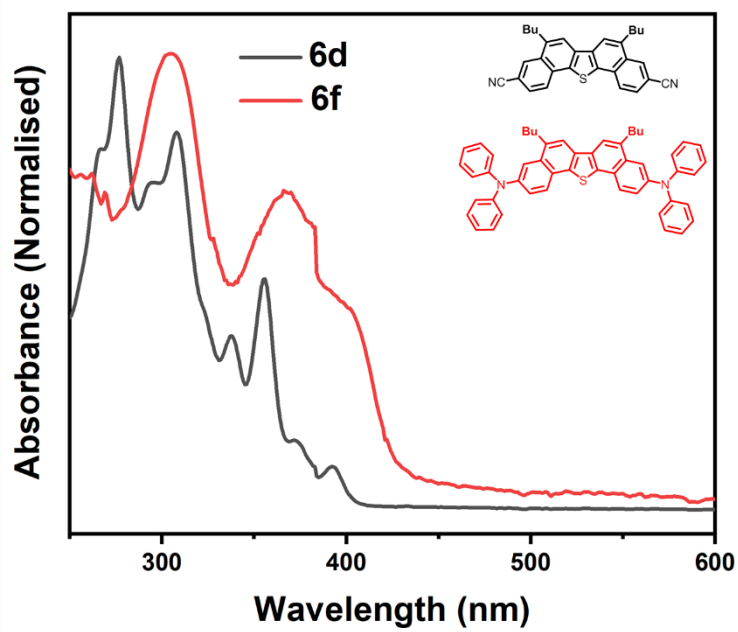


Figure S4: UV-Visible spectra of **6d** and **6f**

Computational details

All the calculations were performed using Gaussian 16 suite of programs.[12] The geometries of the molecules in their neutral, cationic and anionic states were fully optimized at B3LYP/6-31g(d). The single point energies of the optimized structures were also calculated at B3LYP/6-31g(d) level. The reorganization energies (hole and electron) were calculated by using adiabatic potential energy surfaces method. The transfer integrals for the different hopping pathways in the crystal structure were done at PW91PW91/6-31g level by fragment molecular orbital approach[13,14] and using the AOMix program.[15] The PW91PW91 functional has been successfully employed for the calculations of transfer integrals.[16] The dimers for the calculations were extracted from the crystal structure of the molecule from Mercury software.[17]

The charge mobility is one of the most crucial parameters, which measures the performance of organic electronic devices. The anisotropic charge mobilities of the organic crystals were predicted based on the combination of first-principles quantum mechanics calculations[18] and Marcus-Hush theory.[19, 20]

The drift mobility, μ can be computed according to the Einstein relation, and is expressed as

$$\mu = \frac{e}{k_b T} D \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$D = \frac{1}{2n} \sum_i d_i^2 . k_i . P_i \quad \ldots\ldots\ldots\ldots\ldots (2)$$

where, D is diffusion coefficient, e is the electronic charge, k_b is the Boltzmann constant, T is the temperature (298), d_i is the centroid to centroid distance between the i^{th} molecule and its neighbor, k_i is the hopping rate, n is the spatial dimensionality and $P_i = \frac{k_i}{\sum k_i}$ is the probability of the charge transfer to the i^{th} pathway.

The charge hopping rate for each hopping event can be expressed by Marcus-Hush equation:

$$k = \frac{4\pi^2}{h} . \frac{1}{\sqrt{4\pi\lambda k_b T}} . V_{eff}^2 . e^{-\frac{\lambda}{4k_b T}} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where h is Planck constant, λ is the internal reorganization energy, V_{eff} is the effective charge transfer integral between the molecules in the dimers given by:

$$V_{eff}^{e/h} = \frac{J_{RP} - {}^{1}/_{2}\, S_{RP}(H_{RR}/L_{RR} + H_{PP}/L_{PP})}{1 - S_{RP}^{2}} \ldots\ldots\ldots\ldots\ldots (4)$$

where, J_{RP} is the respective charge transfer integral values for hole or electrons, S_{RP} is the spatial overlap, H_{RR}/L_{RR} and H_{PP}/L_{PP} are the site energies of the fragments present in a particular dimer for hole/electron.

The reorganization energies of the compounds were calculated according to the following equation:

$$\lambda_h = [E^0M^+ - E^0M^0] + [E^+M^0 - E^+M^+] \ldots\ldots\ldots\ldots\ldots (5)$$

$$\lambda_e = [E^0M^- - E^0M^0] + [E^-M^0 - E^-M^-] \ldots\ldots\ldots\ldots\ldots (6)$$

where,E^0M^0 ,E^+M^+ and $E^-M^-$are the ground state energies of the neutral, cationic and anionic species respectively; E^0M^+ is the energy of the neutral state at the cationic geometry,E^0M^- is the energy of the neutral state at the anionic geometry,E^+M^0 is the energy of cationic state at the neutral geometry and $E^-M^0$is the energy of anionic state at the neutral geometry

For organic crystals, the value of anisotropic charge mobility are calculated along certain direction, which depends on the orientation of the crystals. For this, we analyze the mobility of the organic crystals along each directions in terms of angles (γ_i) between the charge- hopping pathways and the plane of interest ($k_i d_i \cos\gamma_i$). Φ is the angle of orientation of the transport channel relative to the reference axis (such as crystallographic axes *a*, *b* or *c*), and $\{\theta_i\}$ is the hopping angles between the dimers present in the semiconductor crystals and the reference axes. Since, in a perfect crystal, the orientation of the surrounding molecules are identical; hence, taking a particular portion into consideration, the anisotropic mobility for the whole crystal can be expressed by the following equation:

$$\mu_\Phi = \frac{e}{2k_bT}\sum_i d_i^2 . k_i . P_i . cos^2\gamma_i \, . cos^2(\theta_i - \Phi) \quad \ldots\ldots\ldots\ldots\ldots (7)$$

where, $(\theta_i - \Phi)$ is the orientation angles of the dimer present in the crystals. Since, we are assuming that by considering a particular plane of interest, it would also be applicable for the whole crystal because the surrounding molecules are identical; hence the angle(γ_i) between the charge hopping pathways and interest crystal plane is taken as zero.

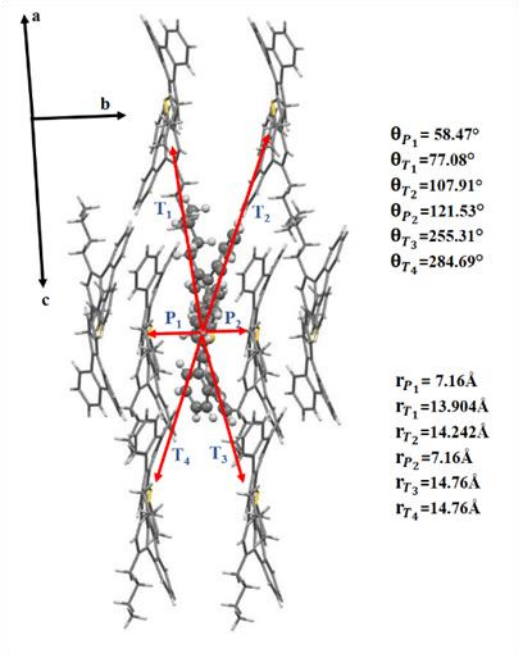


Figure S5: Charge transport pathways of compound **6j**.

Table S3: Calculated spatial overlap (S), site energy (t), effective transfer integral (V_{eff}) and the maximum simulated anisotropic hole and electron mobility of compound.

Dimers	H_{RR}/L_{RR} (eV)	H_{PP}/L_{PP} (eV)	S^{h}_{RP}/S^{e}_{RP}	V^{h}_{eff}/V^{e}_{eff}(meV)	$\mu^{h}_{\Phi}/\mu^{e}_{\Phi}$ ($cm^2\ V^{-1}\ s^{-1}$)
P_1	-4.716/ -1.826	-4.935/ -2.041	-0.0033/ 0.0008	28.7/ -4.1	
T_1	-4.815/ -1.931	-4.815/ -1.931	-0.0002/ 0.0	1/ -0.2	
T_2	-4.82/ -1.934	-4.82/ -1.934	0.0/ -0.0001	0.1/ 0.8	0.1061/0.0049
P_2	-4.935/ -2.04	-4.716/ -1.826	-0.0033/ 0.0008	28.7 /-4.1	
T_3	-4.71/ -1.82	-4.83/ -1.939	0.0/ 0.0003	0.4/ -2.1	
T_4	-4.83/ -1.938	-4.71/ -1.82	0.0/ 0.0003	0.4/ -2.1	

In the crystal structure of **6j**, two types of dimers are observed: Parallel (P) or face to face and Transverse(T) or edge to edge dimers. The value of the hopping distances between the dimers and the angles with respect to the reference axes of the crystal are depicted in the **Figure S5**. The intermolecular distances corresponding to the hopping pathways $\mathbf{P_1}$, $\mathbf{T_1}$, $\mathbf{T_2}$, $\mathbf{P_2}$, $\mathbf{T_3}$, and $\mathbf{T_4}$ are denoted as $\mathbf{r}_{P_1}$, $\mathbf{r}_{T_1}$, $\mathbf{r}_{T_2}$, $\mathbf{r}_{P_2}$, $\mathbf{r}_{T_3}$ and $\mathbf{r}_{T_4}$ and the corresponding angles are $\boldsymbol{\theta}_{P_1}$, $\boldsymbol{\theta}_{T_1}$, $\boldsymbol{\theta}_{T_2}$, $\boldsymbol{\theta}_{P_2}$, $\boldsymbol{\theta}_{T_3}$ and $\boldsymbol{\theta}_{T_4}$

The computed values of the site energies (*H*, *L*), spatial overlap (*S*) and the effective charge transfer integral (V_{eff}) of the hopping pathways are summarized in the **Table S3**. The largest value for the effective electronic coupling for hole (V_{eff}^{h}) as well as for the electron (V_{eff}^{e}) was found to be 28.7 meV for a hole and -4.1 meV for an electron along the P_1 and P_2 pathways. This is because of the smaller intermolecular distance (7.16Å) and maximum overlap in the P_1 and P_2 paths. Among the transverse paths, the T_1 dimer has a larger V_{eff}^{h} value of 1 meV whereas, the T_3 and T_4 transverse path has the larger V_{eff}^{e}. This difference in effective electronic coupling along different transverse pathways arises because of different spatial overlaps of hole and electron along with the path T_1 ,T_3 and T_4. The T_1 has path more hole spatial overlap, whereas the T_3 and T_4 paths have more electron spatial overlap. The reorganization energy of the compound was calculated as shown in **Table S4**. The hole reorganization energy was found to be 0.295 eV and the electron reorganization energy was found to be 0.231 eV

Table S4: Energies of different states of molecule and reorganization energy

Species[B3LYP/6-31G(d)]	Energy (in hartree)	λ_h(eV)	λ_e(eV)
E^0M^0	-2096.644961	0.295	0.231
E^-M^0	-2096.660504		
E^+M^0	-2096.405265		
E^0M^+	-2096.640559		
E^+M^+	-2096.411682		
E^0M^-	-2096.640689		
E^-M^-	-2096.664693		

Considering the effective intermolecular electronic coupling and the reorganization energies, the anisotropic charge carrier mobilities were calculated using the angular anisotropic mobility equation in Matlab software. The maximum hole (μ_{Φ}^{h}) and electron (μ_{Φ}^{e}) mobility values were found to be 0.1061 cm^2 V^{-1} s^{-1} and 0.0049 cm^2 V^{-1} s^{-1} respectively at an angle Φ=90°/270° for both hole and electron (**Figure S6**). Similarly, the minimum hole (μ_{Φ}^{h}) and electron (μ_{Φ}^{e}) mobility values were found to be 0.00399 cm^2 V^{-1} s^{-1} and 0.0015 cm^2 V^{-1} s^{-1}respectively at an angle Φ=0°/180° for both hole and electron. Even though the values of reorganization energy of hole (0.295eV) is greater than that of electron (0.231eV), it is found that the anisotropic hole mobility is far greater than anisotropic electron mobility. This is because the hole has larger values of the effective electronic coupling (28.7meV) when compared to that of electron (-4.1meV) along with P_1 and P_2 pathways.

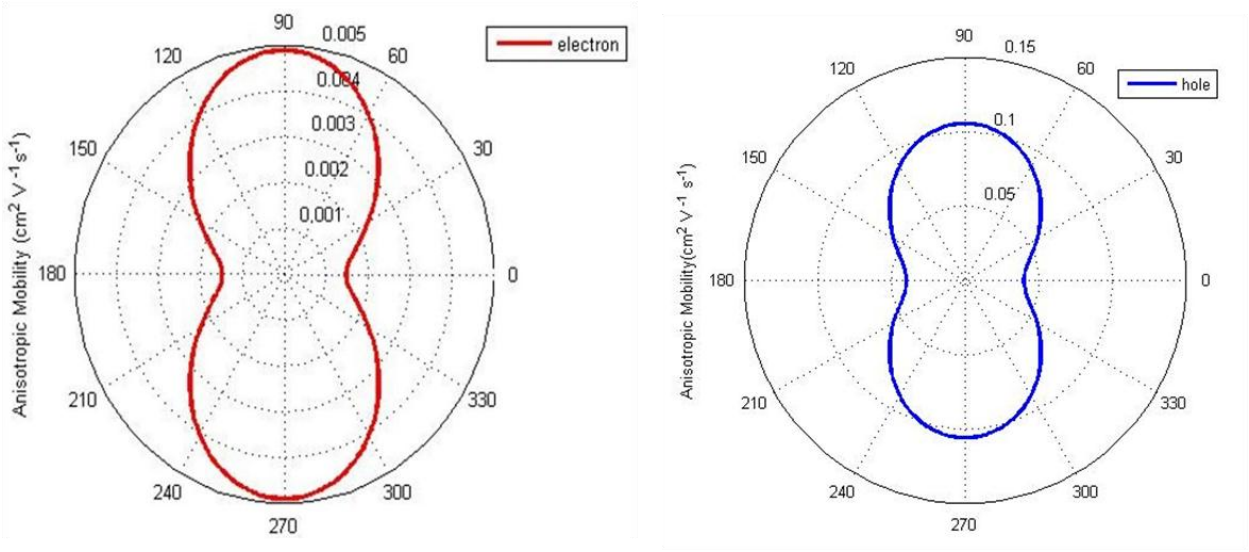


Figure S6: Anisotropic hole and electron mobility (cm^2 V^{-1} s^{-1}) of compound **6j**

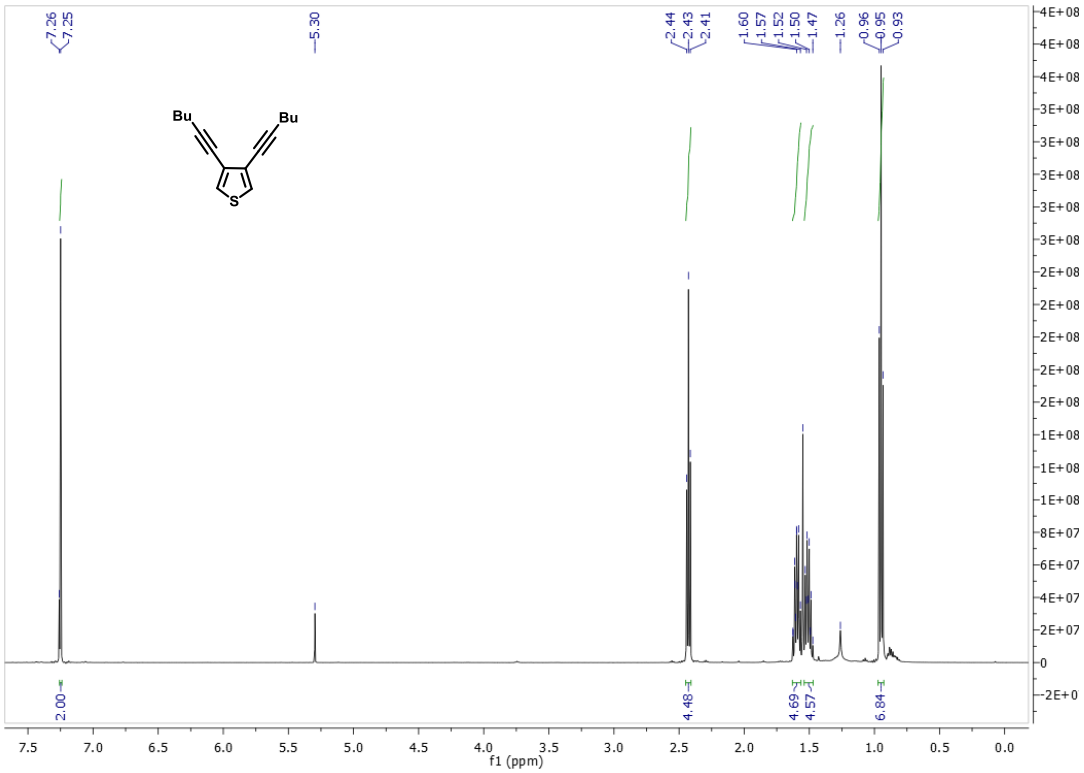


Figure S7: ^{1}H NMR spectrum of **1** ($CDCl_3$, 500 MHz)

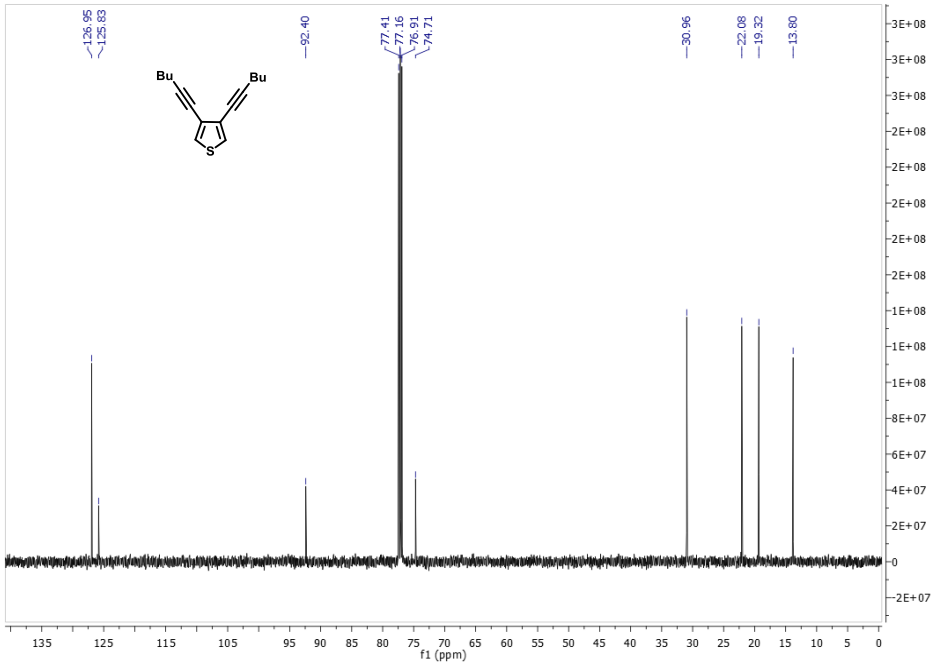


Figure S8: ^{13}C NMRspectrum of **1** (126 MHz, $CDCl_3$)

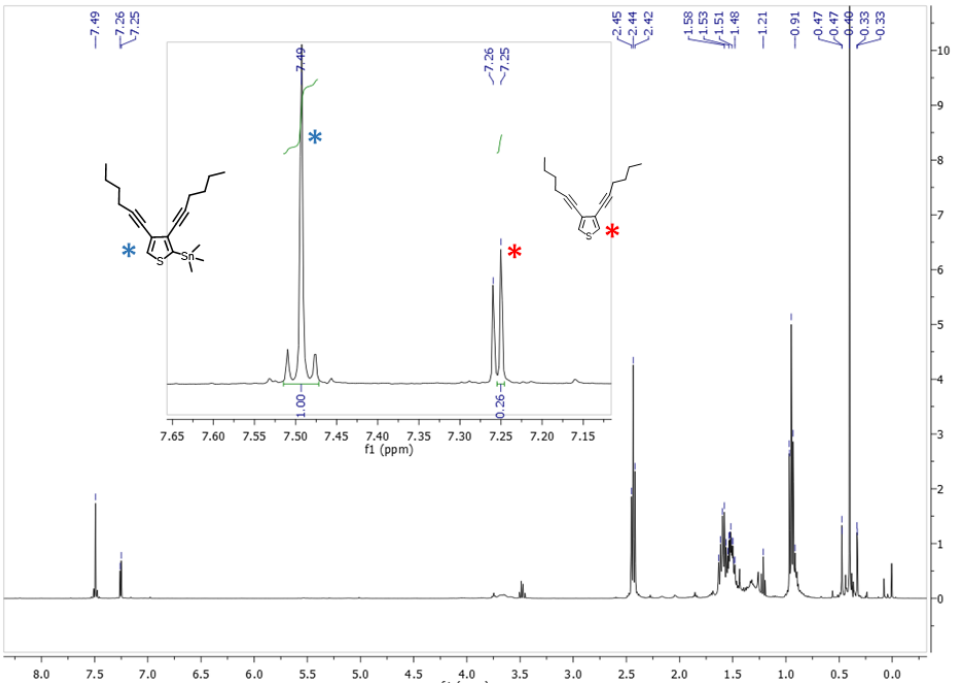


Figure S9: ^{1}H NMRspectrum of a mixture of **2** and **1** formed on using 2.1 equivalents n-BuLi (400 MHz, $CDCl_3$)

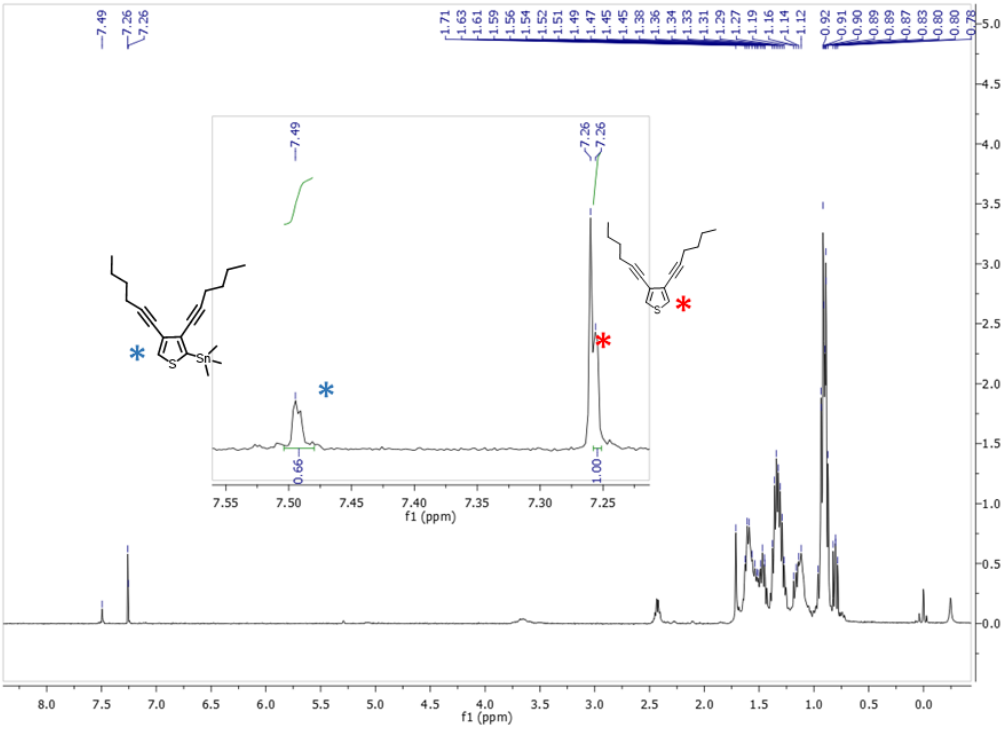


Figure S10: ^{1}H NMRspectrum of a mixture of **2** and **1** formed on carrying the reaction at elevated temperature (400 MHz, $CDCl_3$)

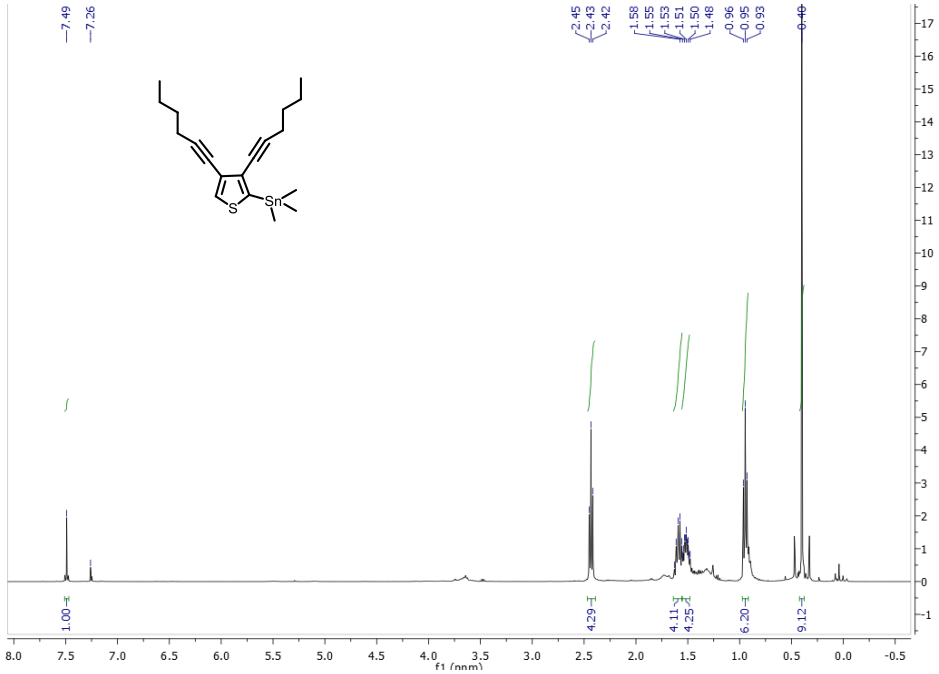


Figure S11: ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$)

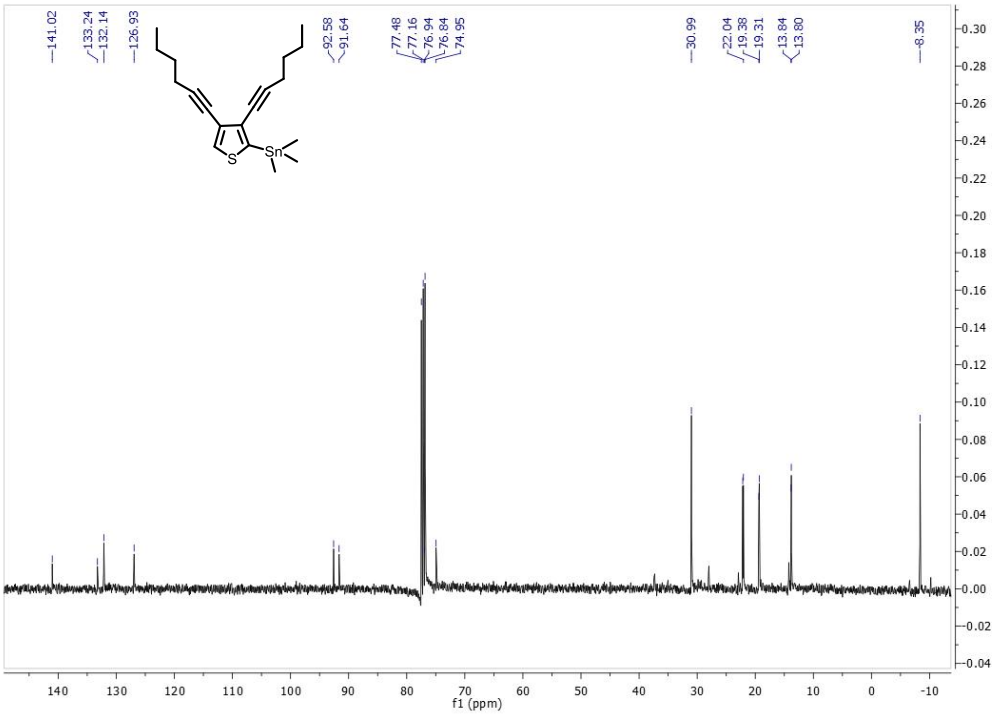


Figure S12: ^{13}C NMR spectrum of **2** (101 MHz, $CDCl_3$)

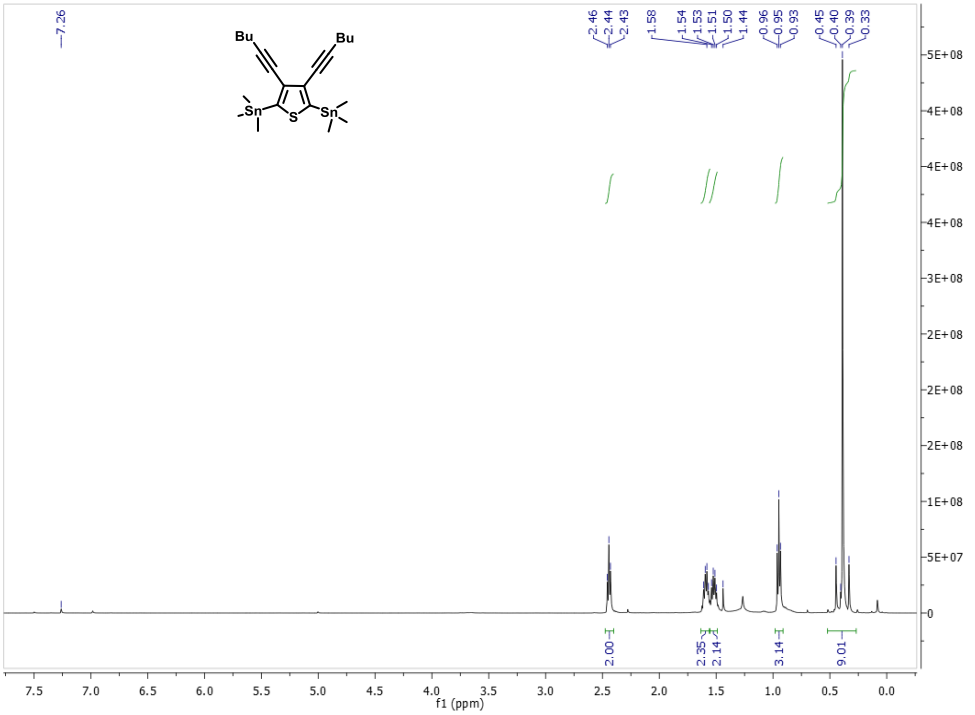


Figure S13: ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$)

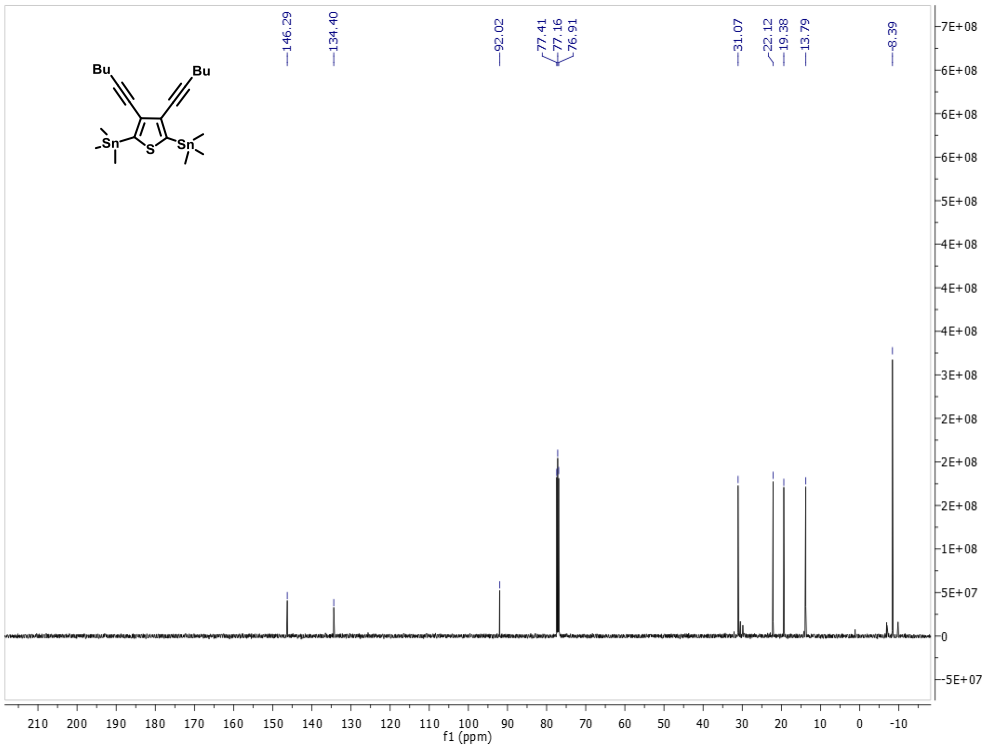


Figure S14: ^{13}C NMR spectrum of **3** (126 MHz, $CDCl_3$)

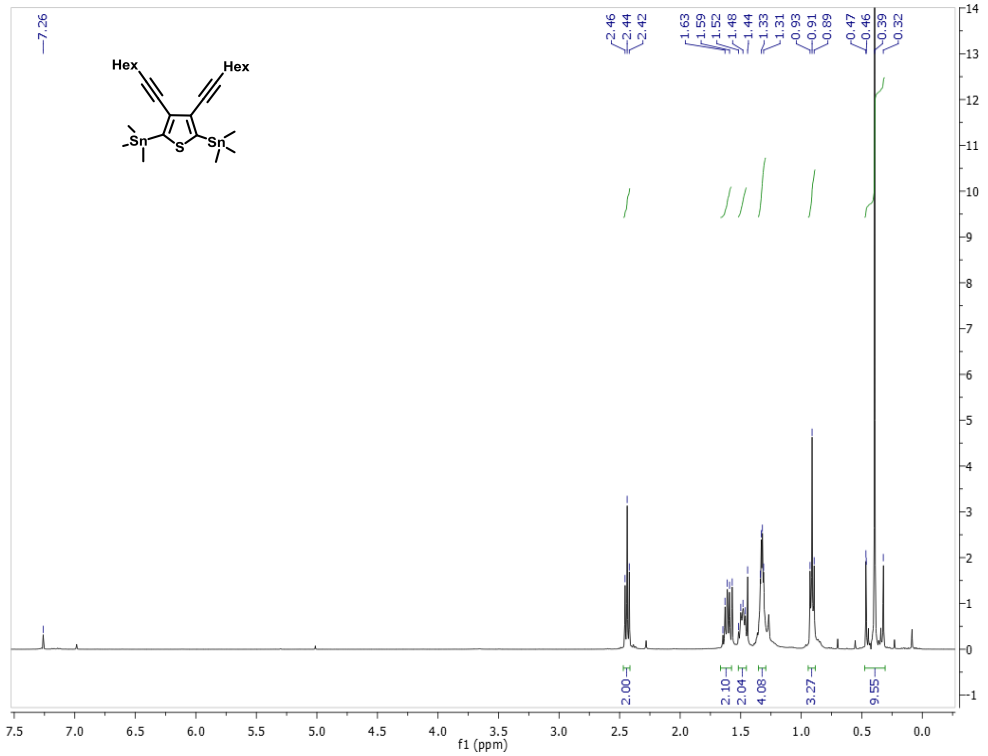


Figure S15: ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)

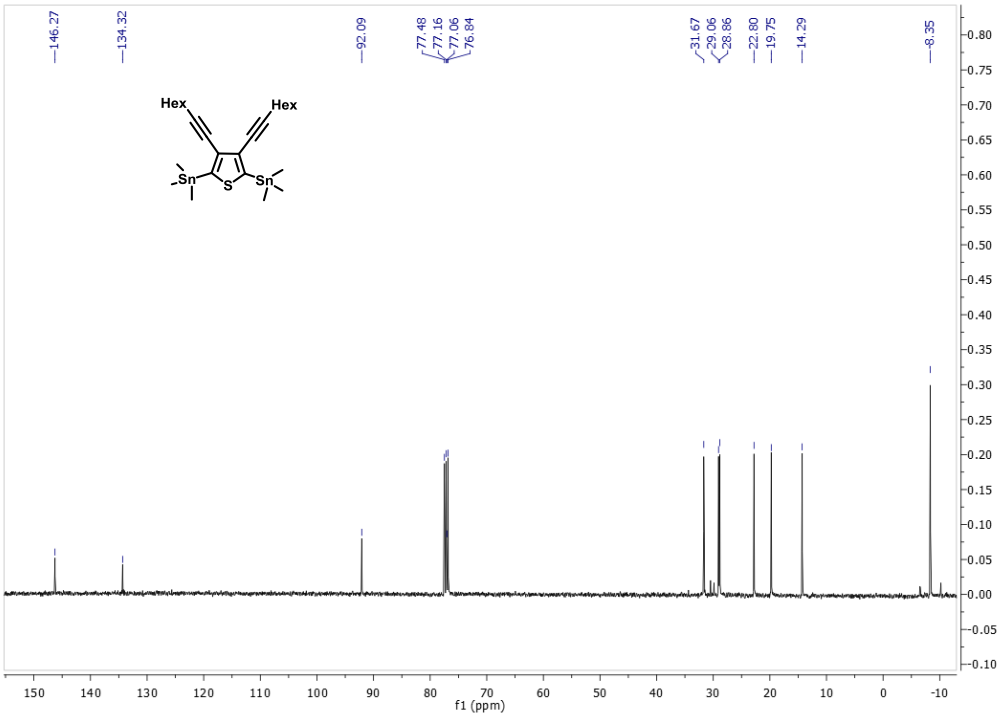


Figure S16: ^{13}C NMR spectrum of **3a** (101 MHz, $CDCl_3$)

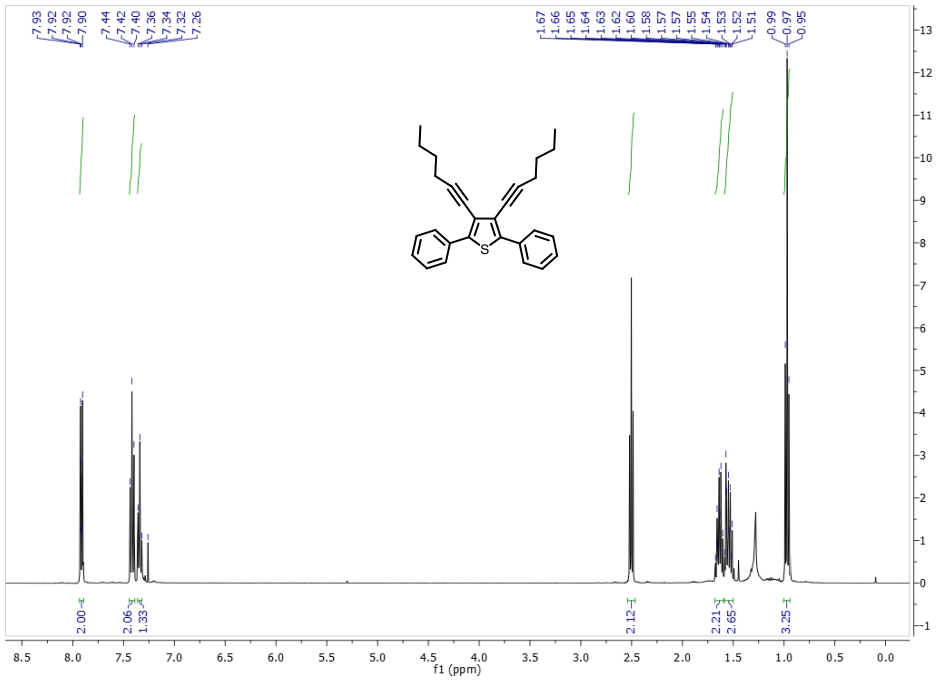


Figure S17: ^{1}H NMR spectrum of **5a**(400 MHz, $CDCl_3$)

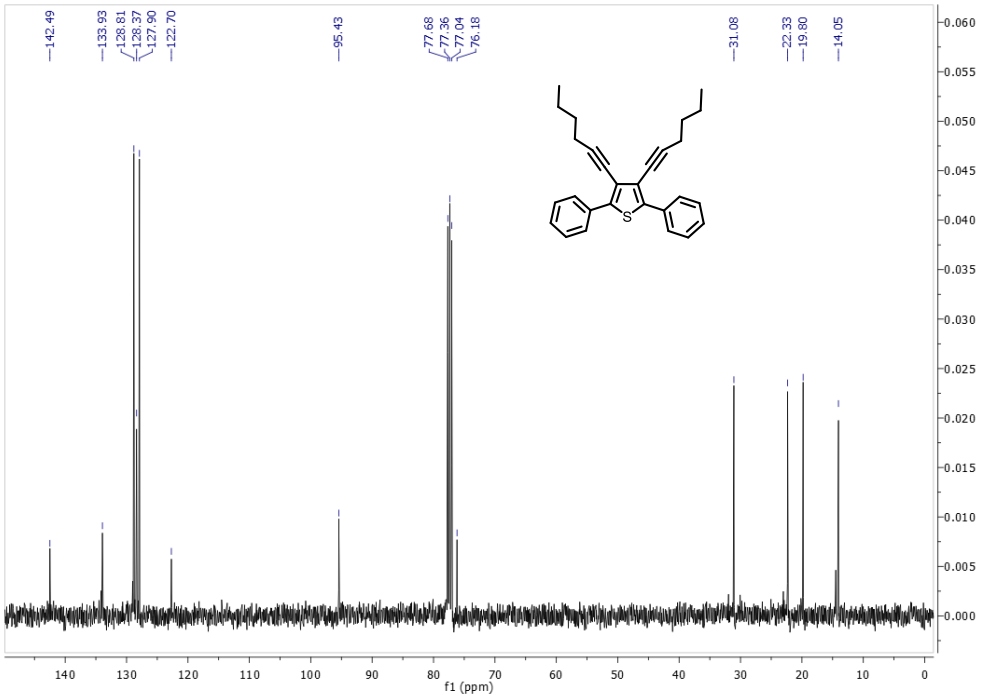


Figure S18: ^{13}C NMR spectrum of **5a** (101 MHz, $CDCl_3$)

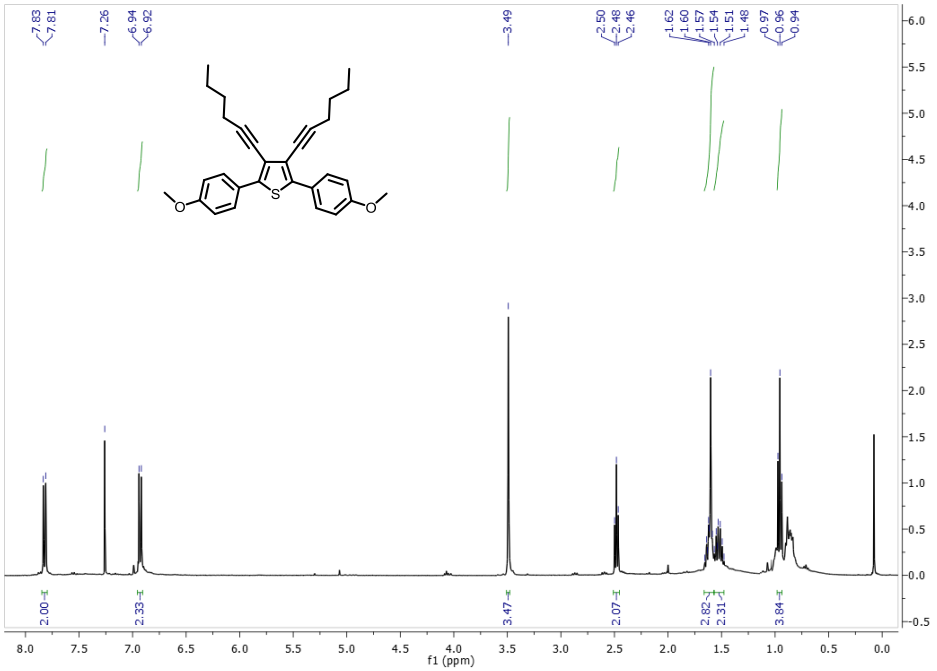


Figure S19: ^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)

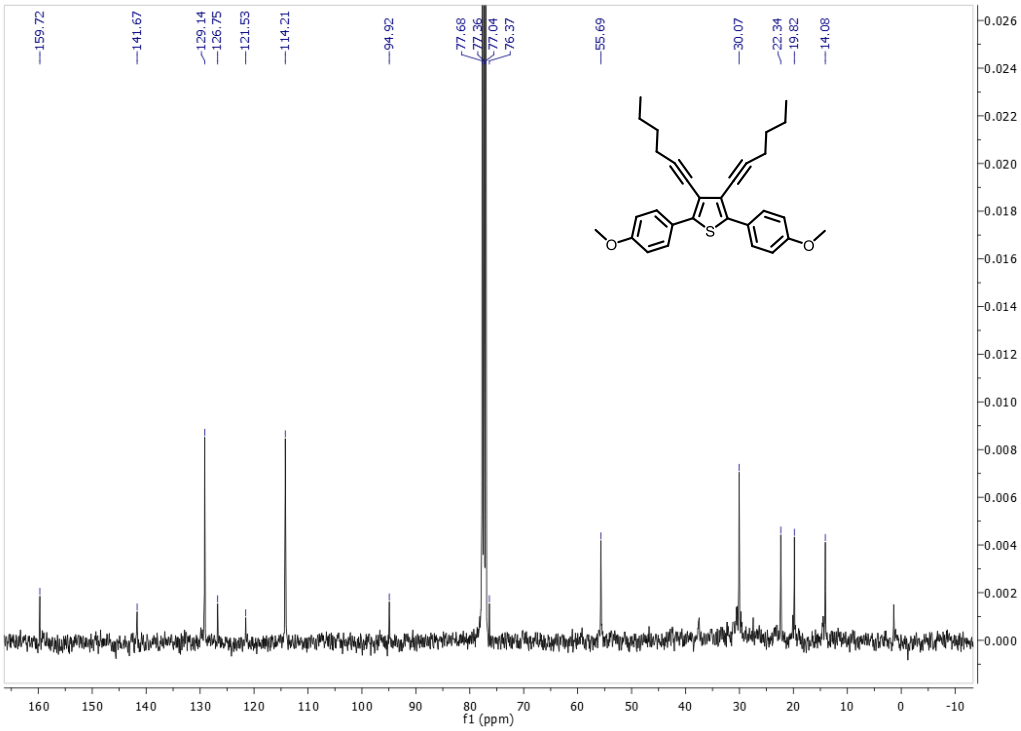


Figure S20: ^{13}C NMR spectrum of **5b** (101 MHz, $CDCl_3$)

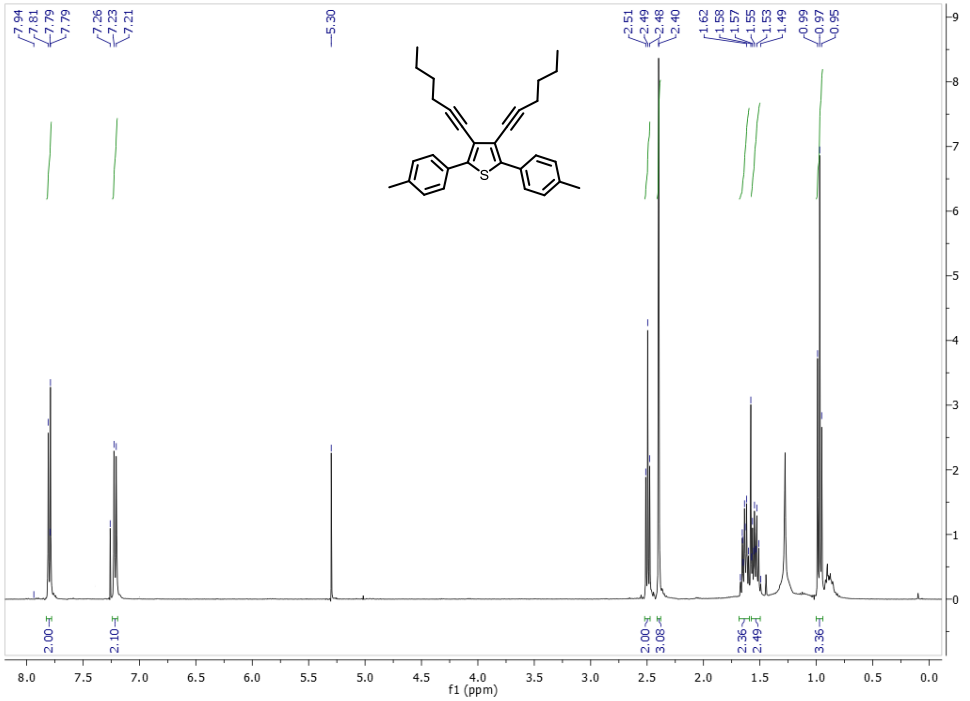


Figure S21: ^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$)

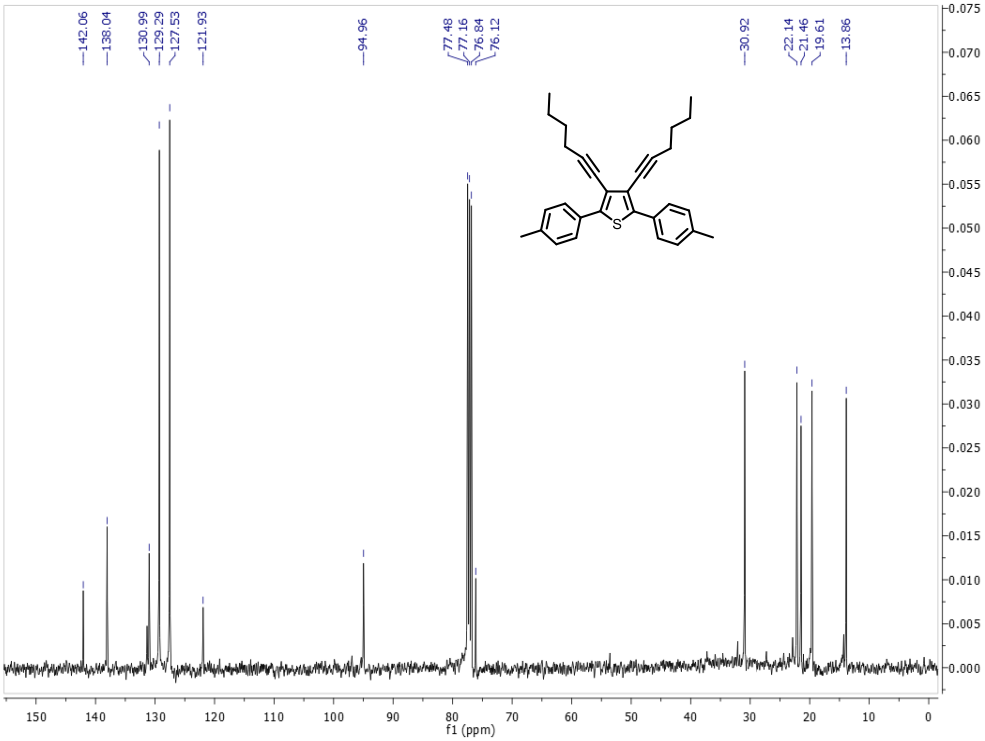


Figure S22: ^{13}C NMR spectrum of **5c** (101 MHz, $CDCl_3$)

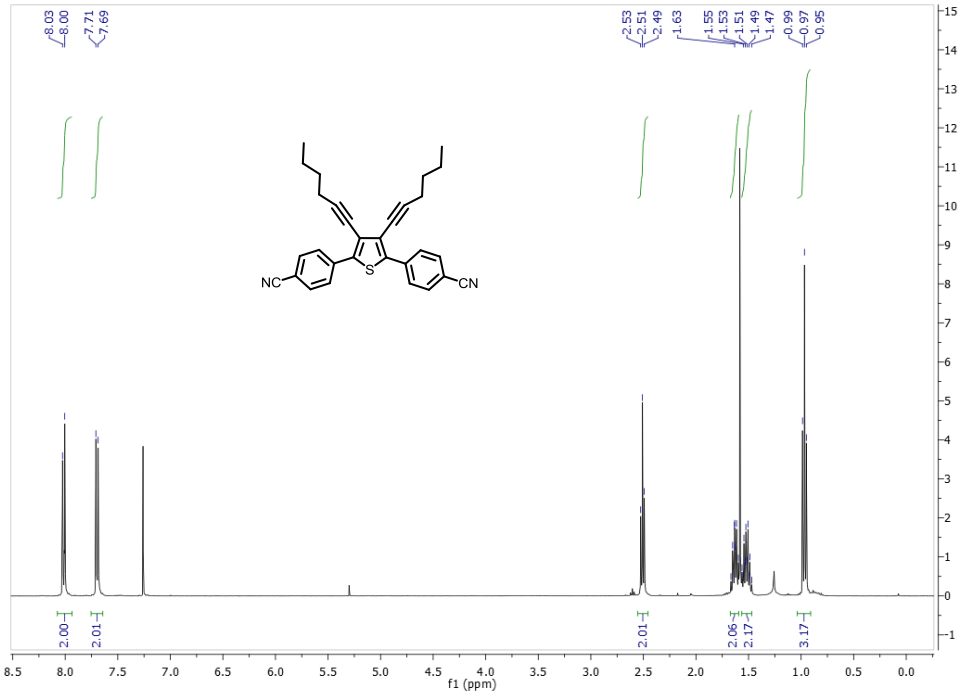


Figure S23: ^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$)

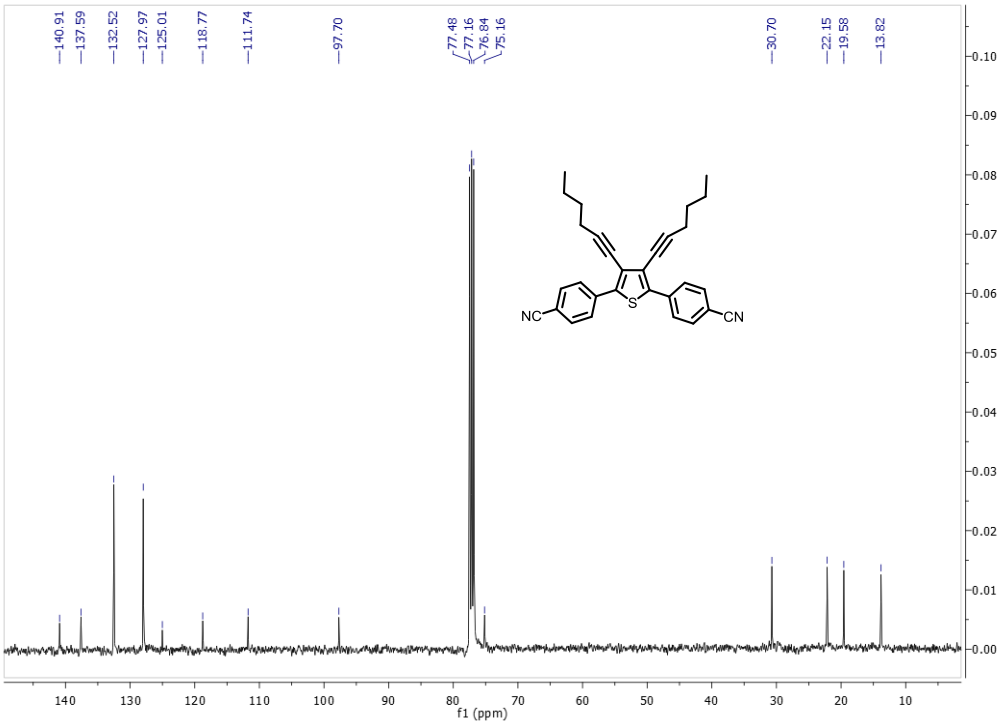


Figure S24: ^{13}C NMR spectrum of **5d** (101 MHz, $CDCl_3$)

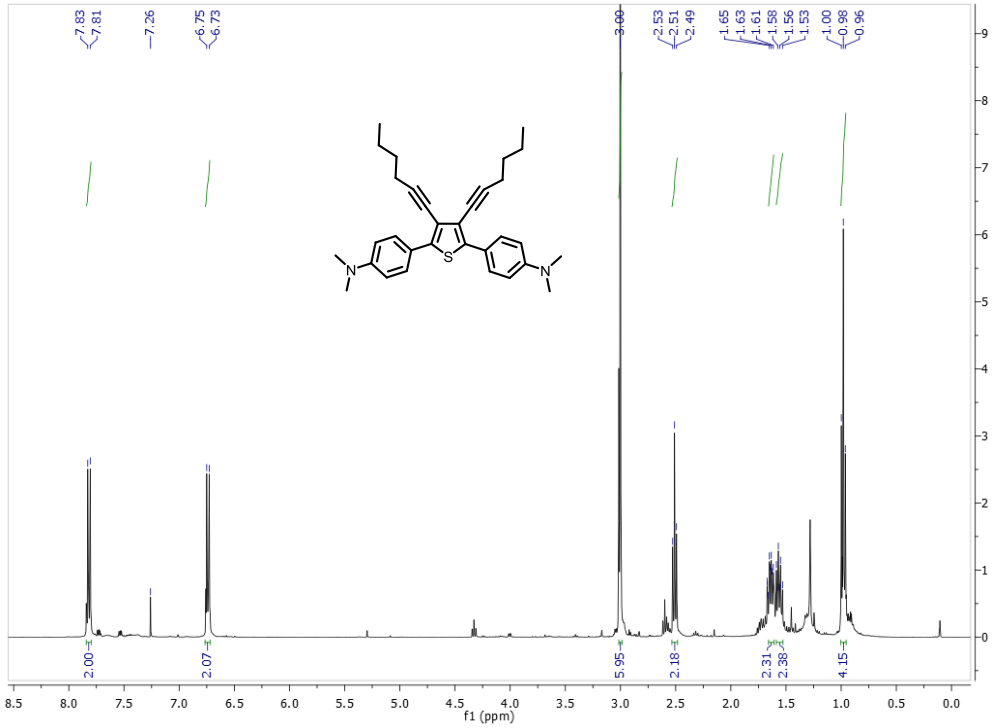


Figure S25: ^{1}H NMR spectrum of **5e** (400 MHz, $CDCl_3$)

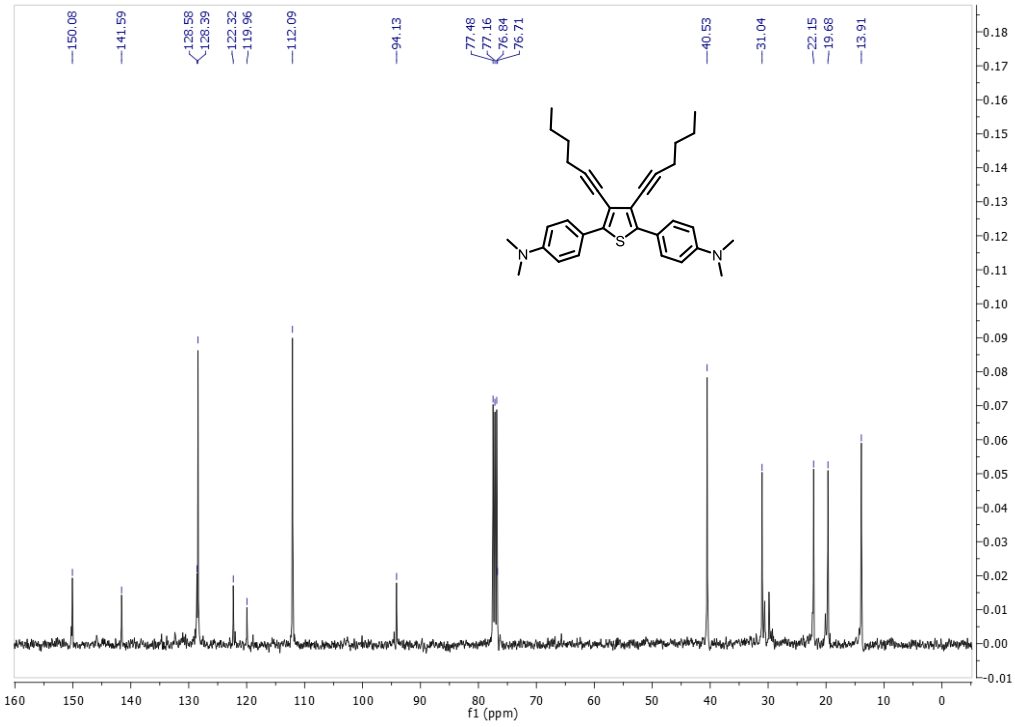


Figure S26: ^{13}C NMR spectrum of **5e** (101 MHz, $CDCl_3$)

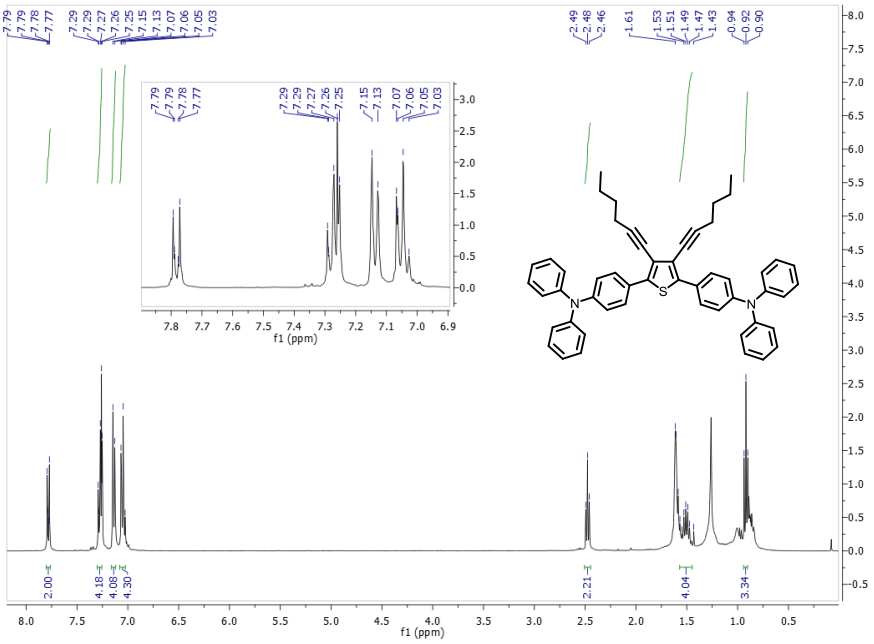


Figure S27: ^{1}H NMR spectrum of **5f** (400 MHz, $CDCl_3$)

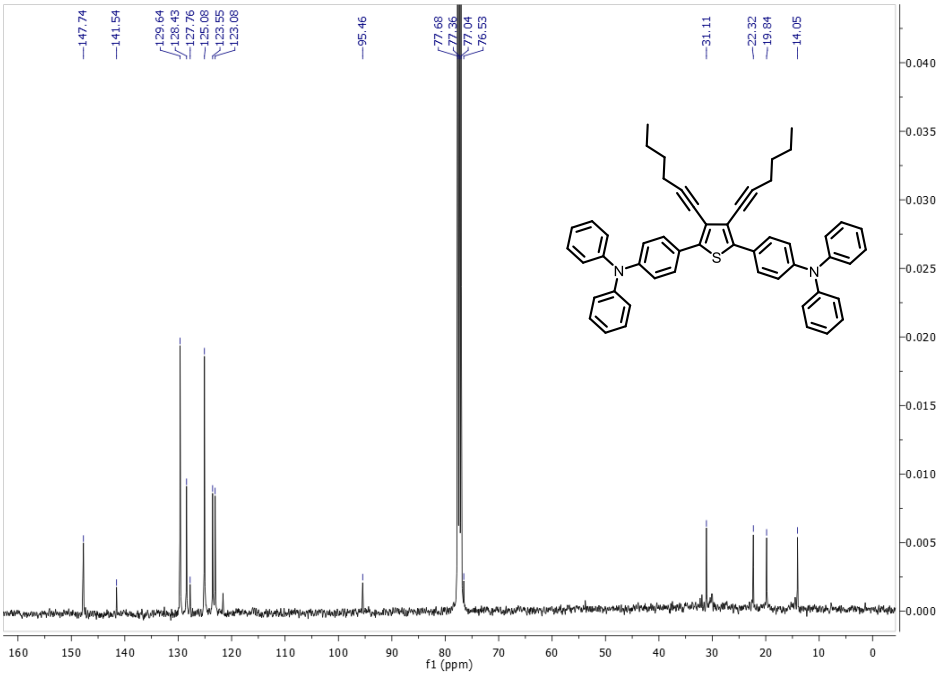


Figure S28: ^{13}C NMR spectrum of **5f** (101 MHz, $CDCl_3$)

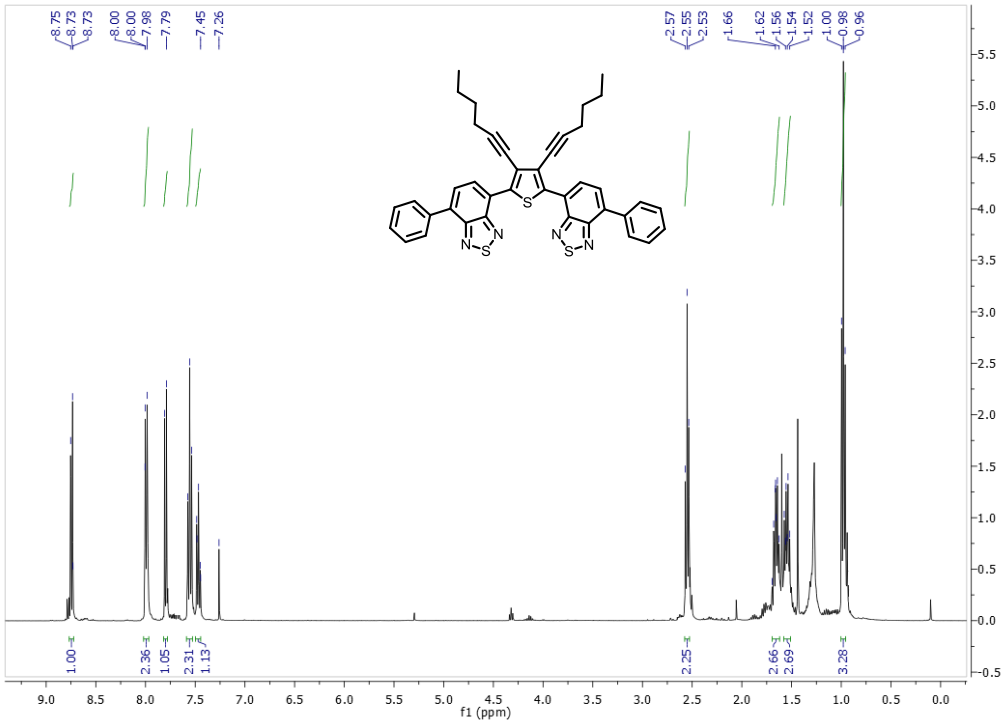


Figure S29: ^{1}H NMR spectrum of **5g** (400 MHz, $CDCl_3$)

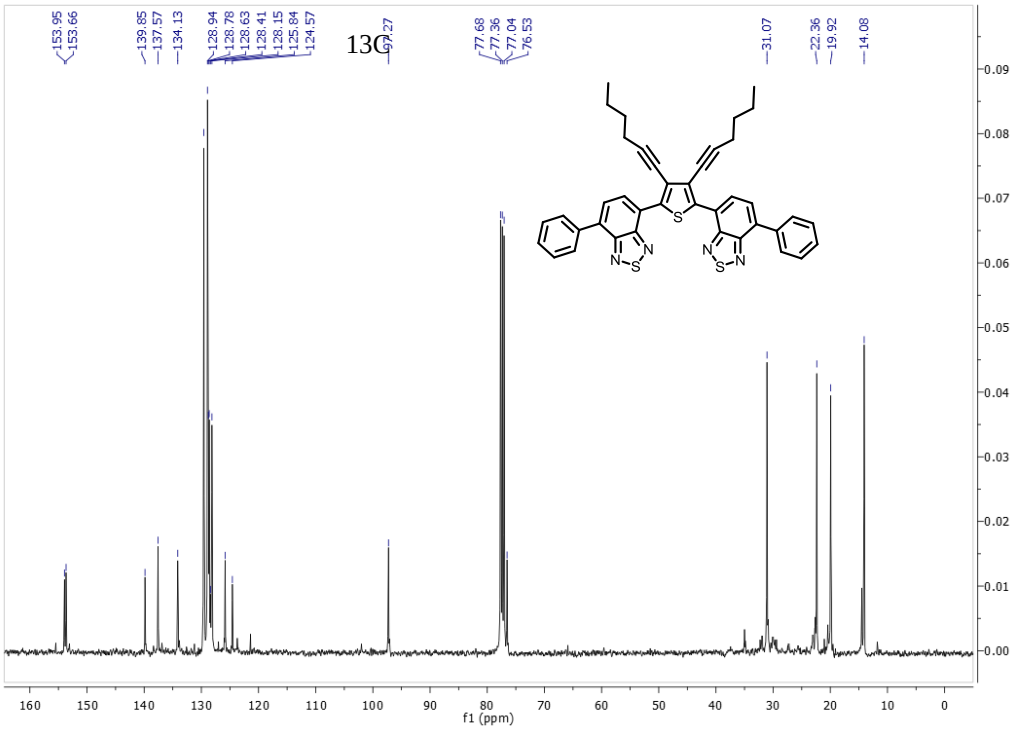


Figure S30: ^{13}C NMR spectrum of **5g** (101 MHz, $CDCl_3$)

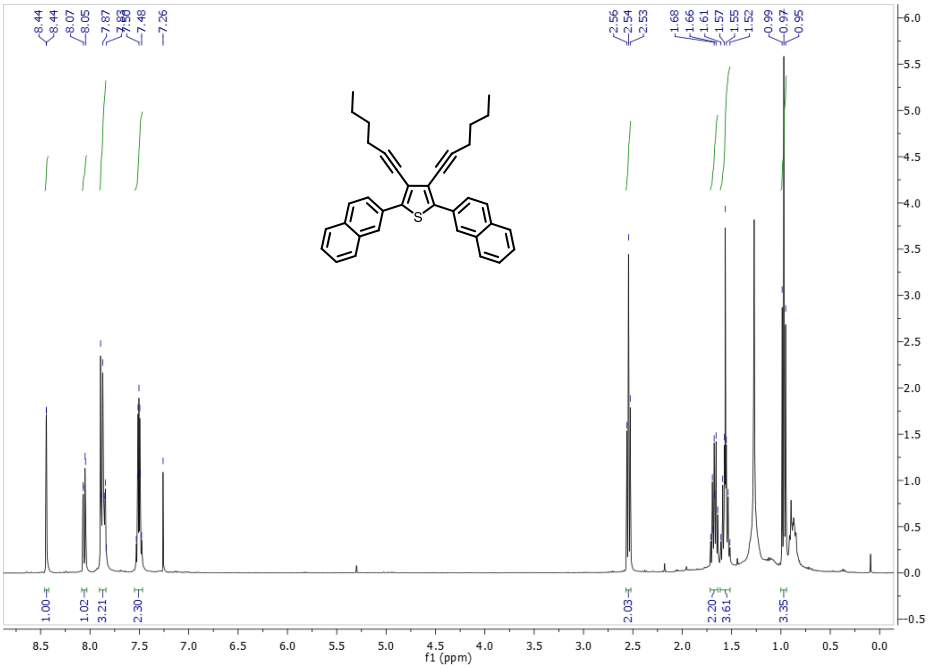


Figure S31: ^{1}H NMR spectrum of **5h** (400 MHz, $CDCl_3$)

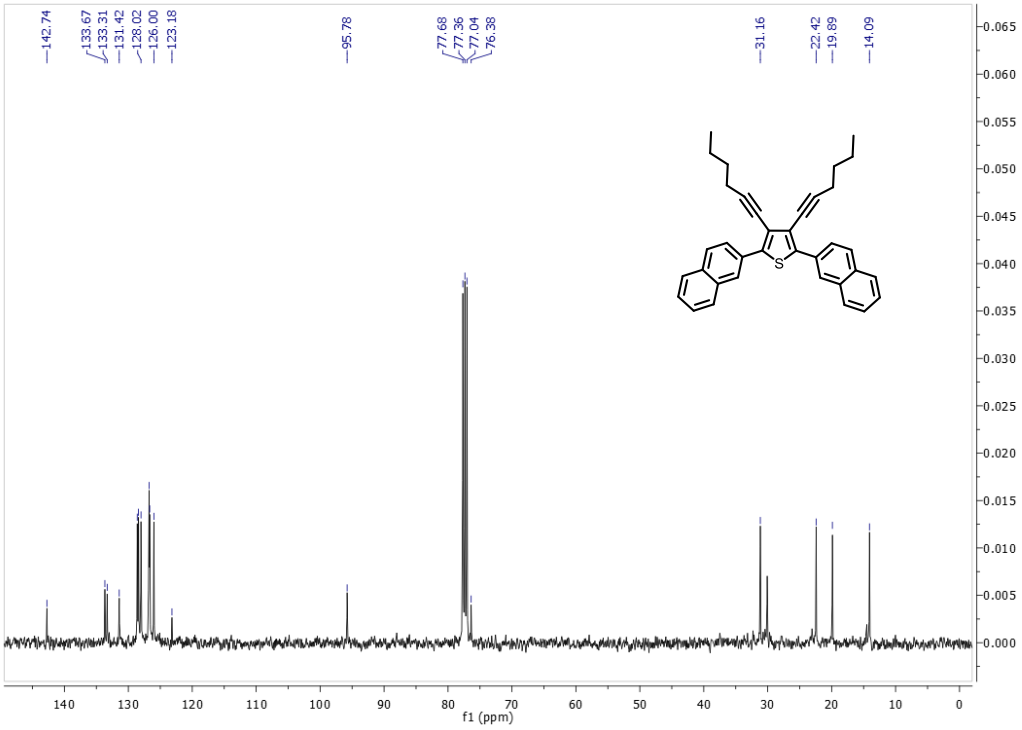


Figure S32: ^{13}C NMR spectrum of **5h** (101 MHz, $CDCl_3$)

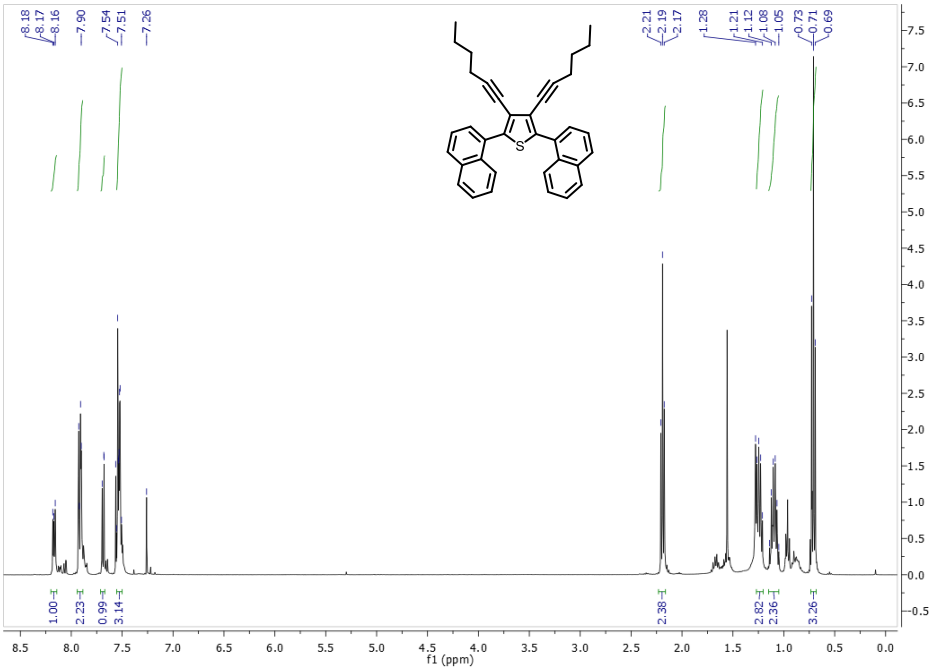


Figure S33: ^{1}H NMR spectrum of **5i** (400 MHz, $CDCl_3$)

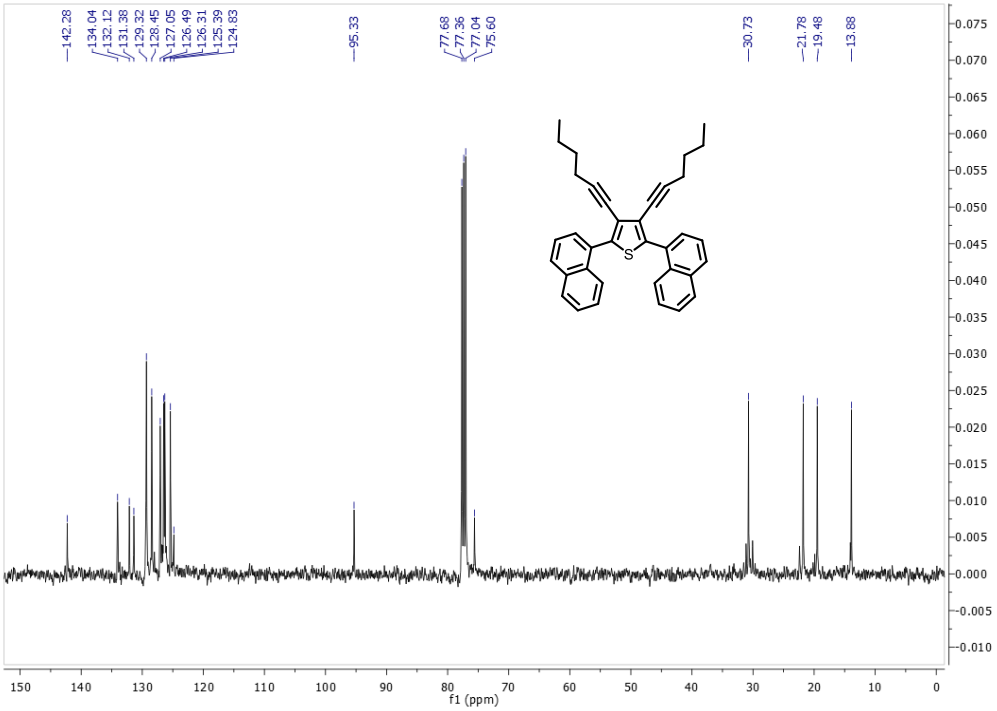


Figure S34: ^{13}C NMR spectrum of **5i** (101 MHz, $CDCl_3$)

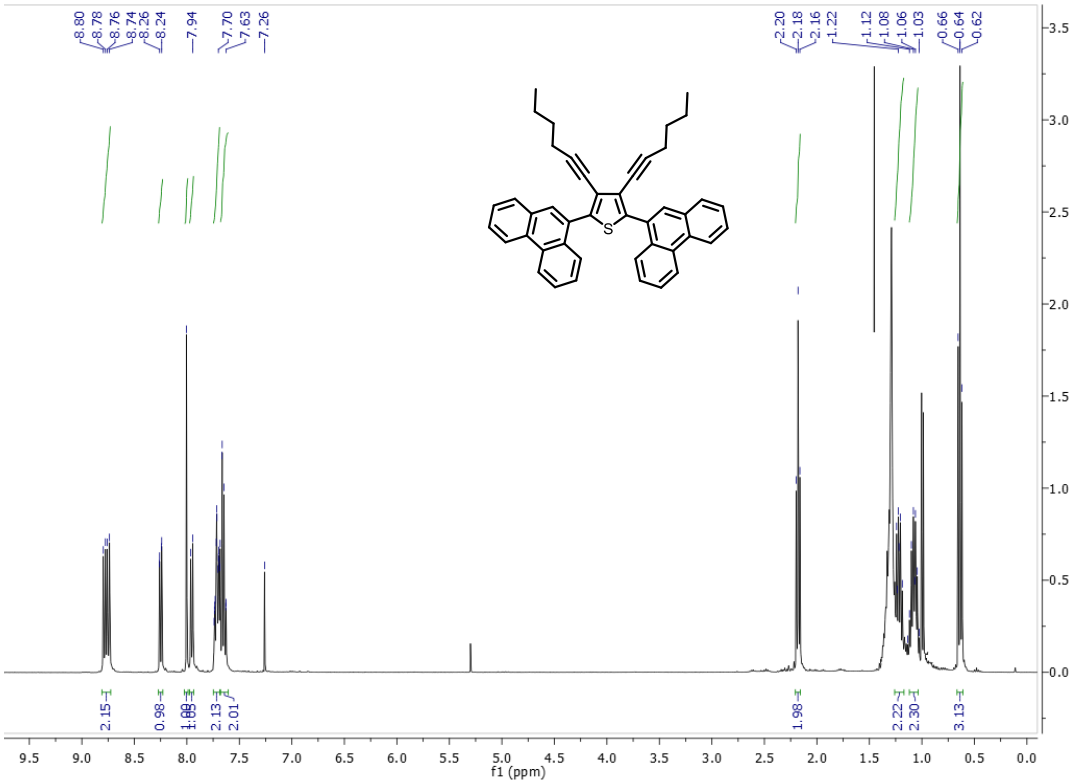


Figure S35: ^{1}H NMR spectrum of **5j** (400 MHz, $CDCl_3$)

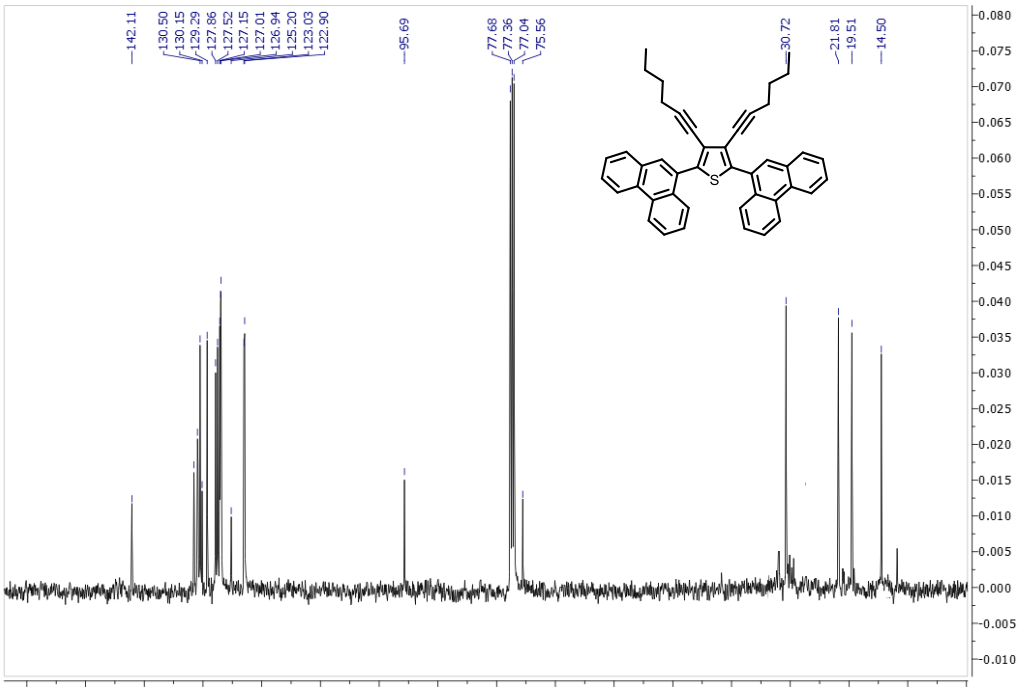


Figure S36: ^{13}C NMR spectrum of **5j** (101 MHz, $CDCl_3$)

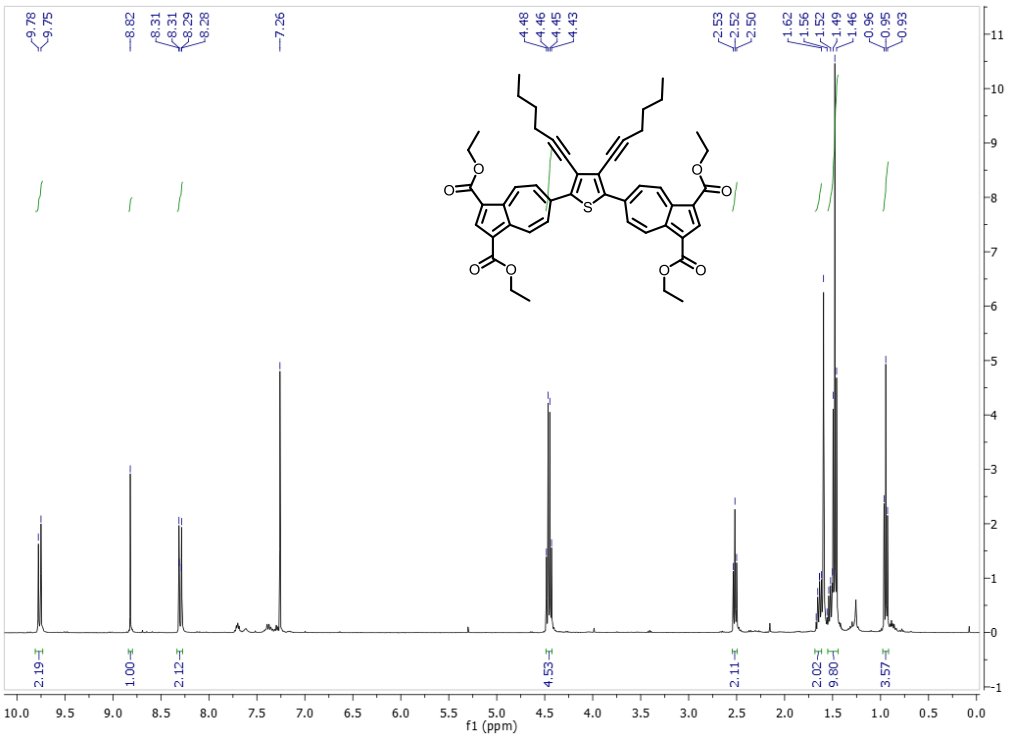


Figure S37: ^{1}H NMR spectrum of **5k** (400 MHz, $CDCl_3$)

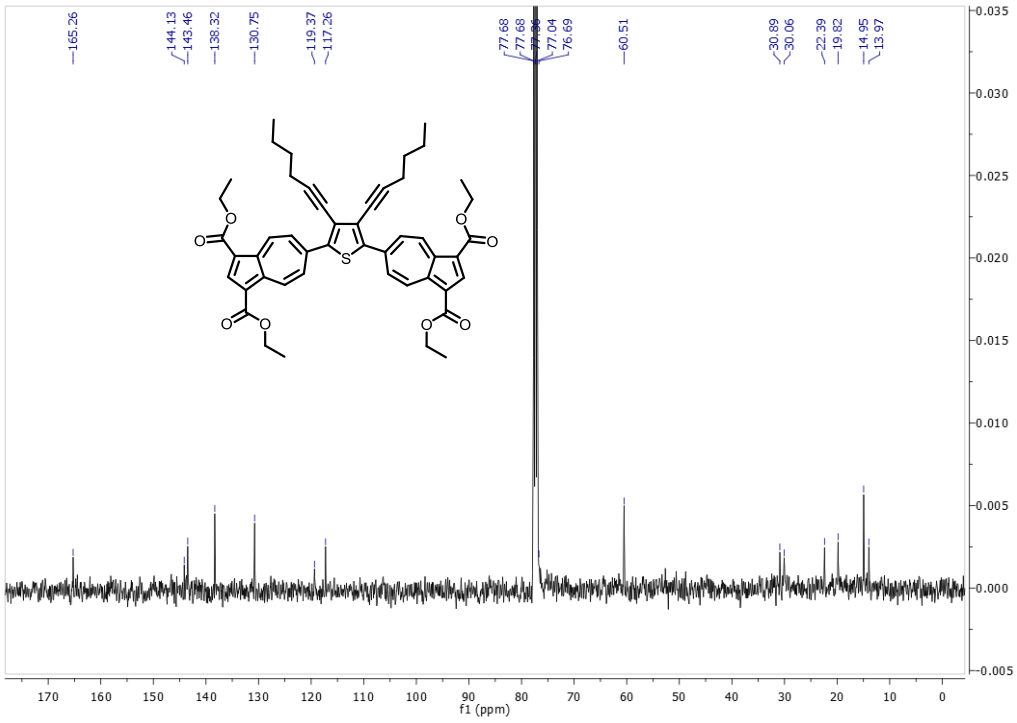


Figure S38: ^{13}C NMR spectrum of **5k**(101 MHz, $CDCl_3$)

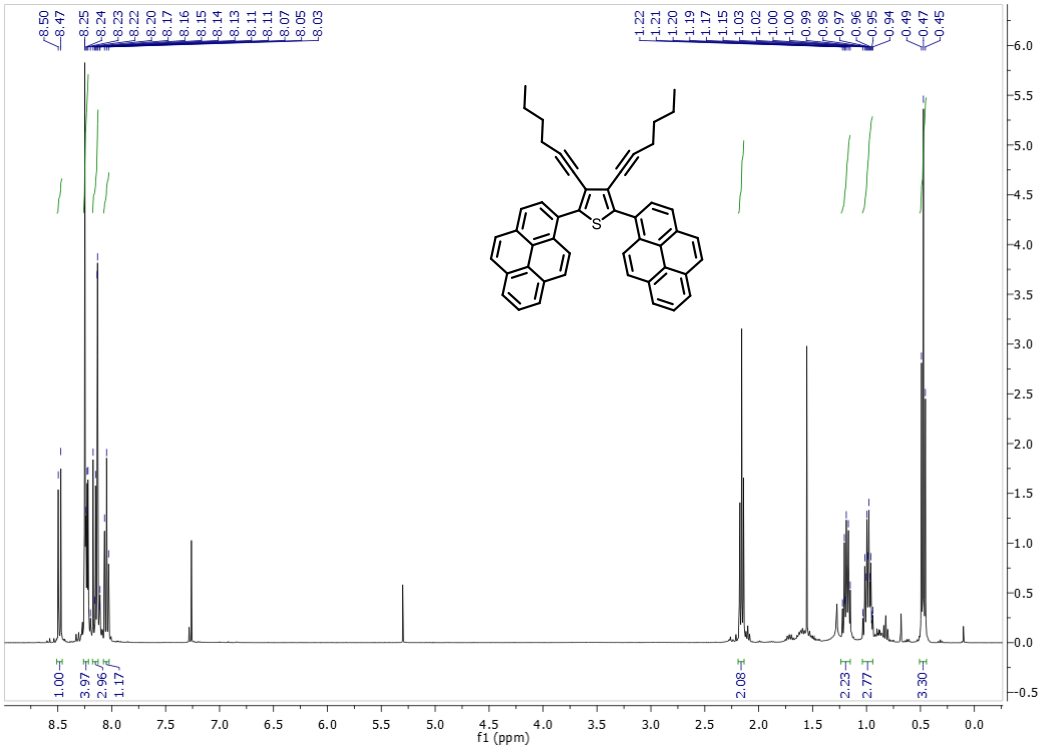


Figure S39: ^{1}H NMR spectrum of **5l** (400 MHz, $CDCl_3$)

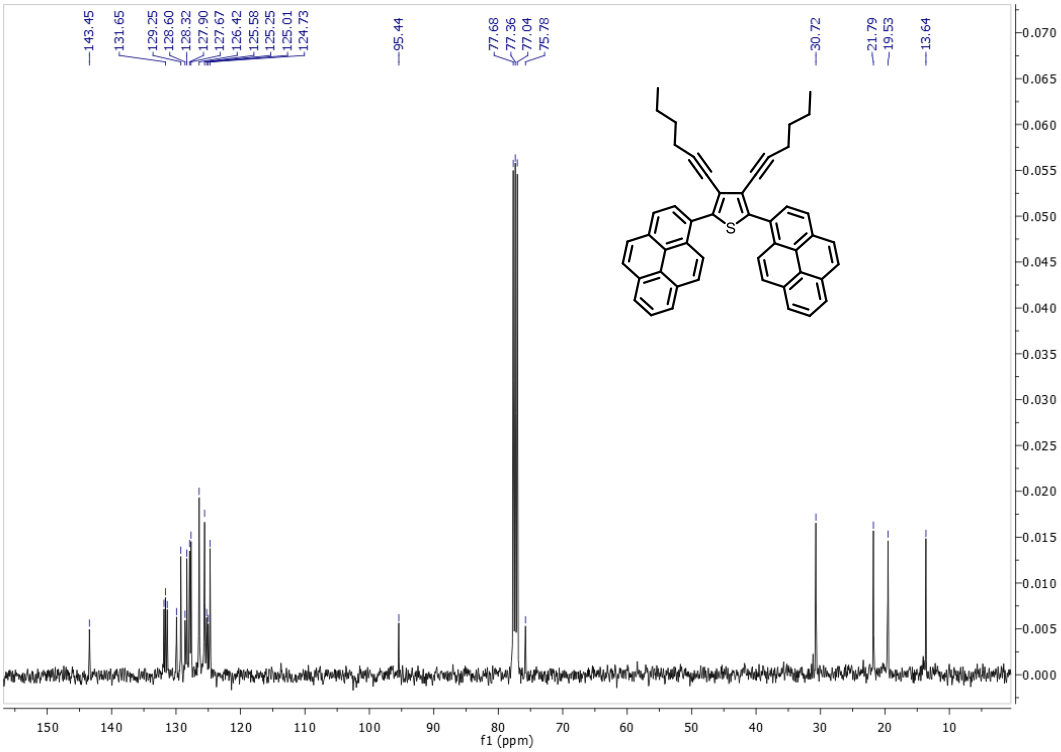


Figure S40: ^{13}C NMR spectrum of **5l** (101 MHz, $CDCl_3$)

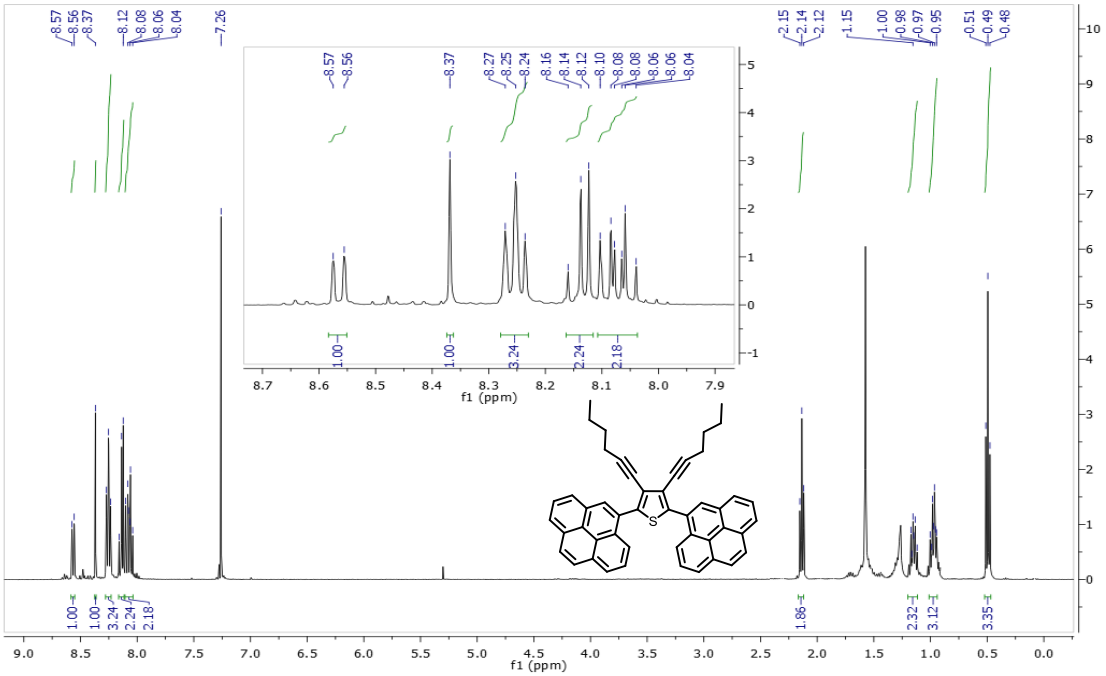


Figure S41: ^{1}H NMR spectrum of **5m** (400 MHz, $CDCl_3$)

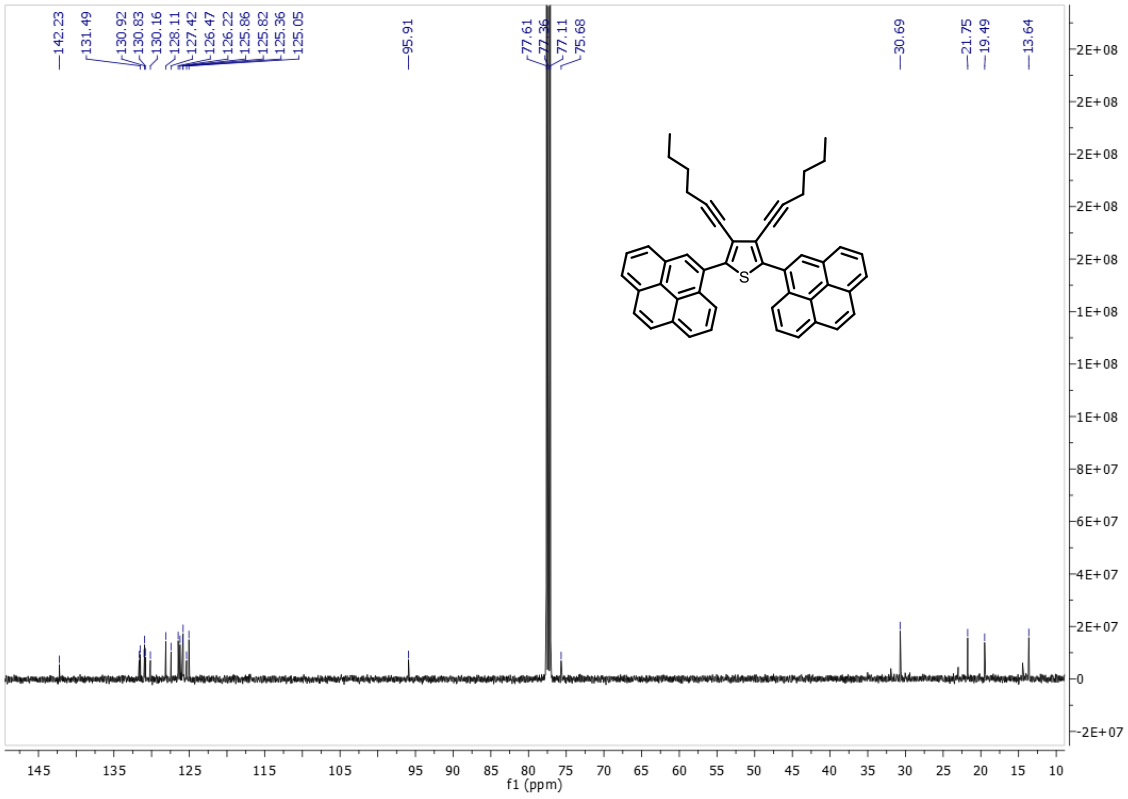


Figure S42: ^{13}C NMR spectrum of **5m** (126 MHz, $CDCl_3$)

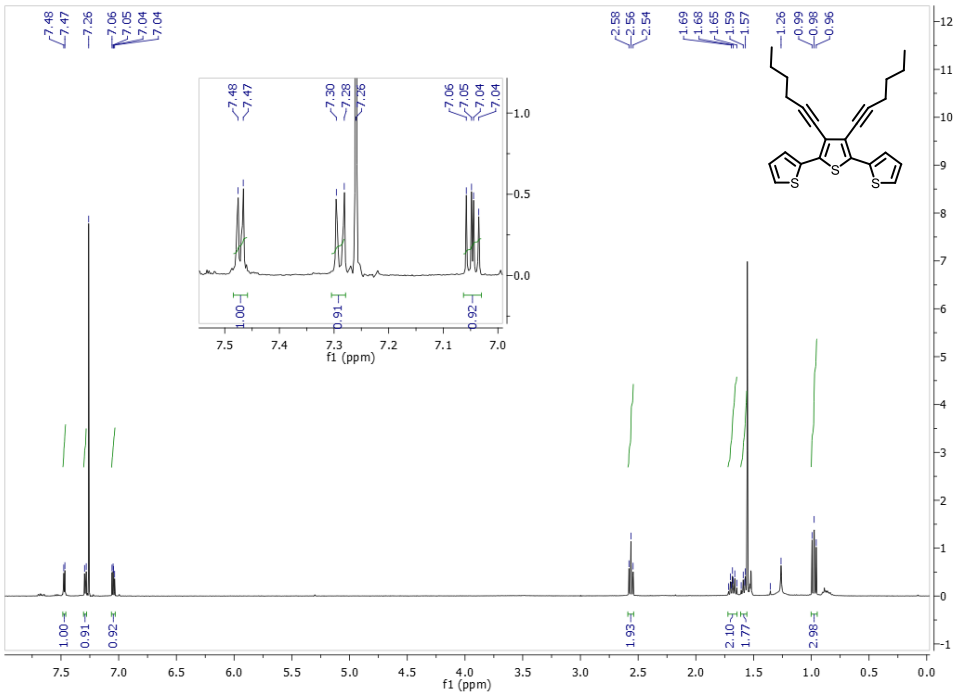


Figure S43: ^{1}H NMR spectrum of **5n** (400 MHz, $CDCl_3$)

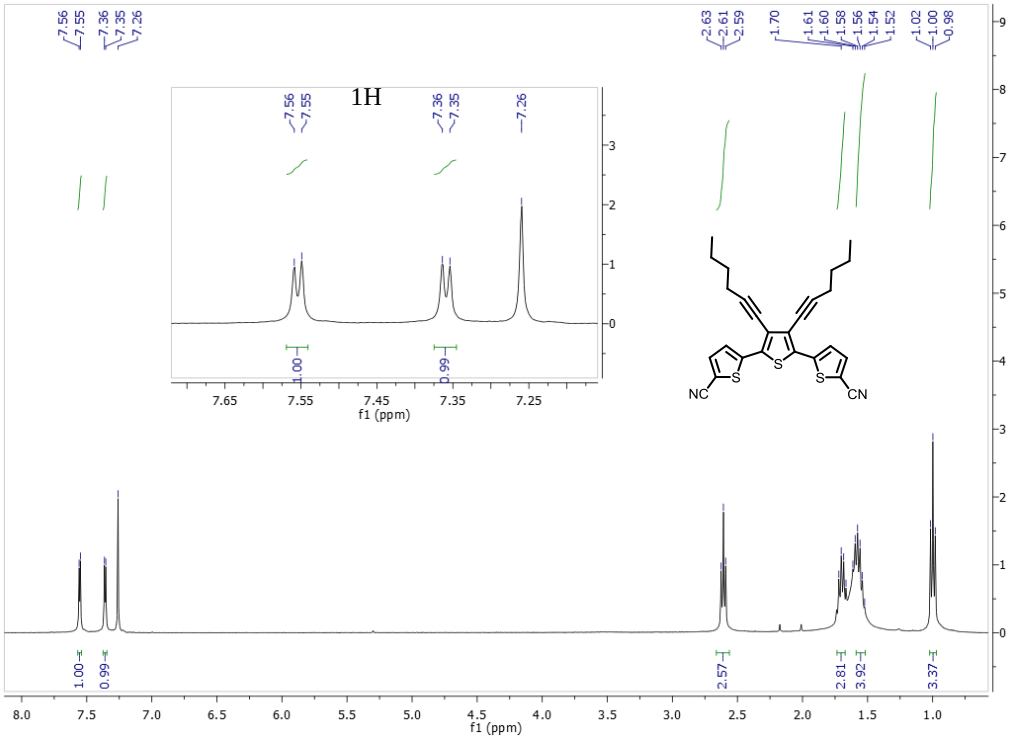


Figure S44: ^{1}H NMR spectrum of **5o** (400 MHz, $CDCl_3$)

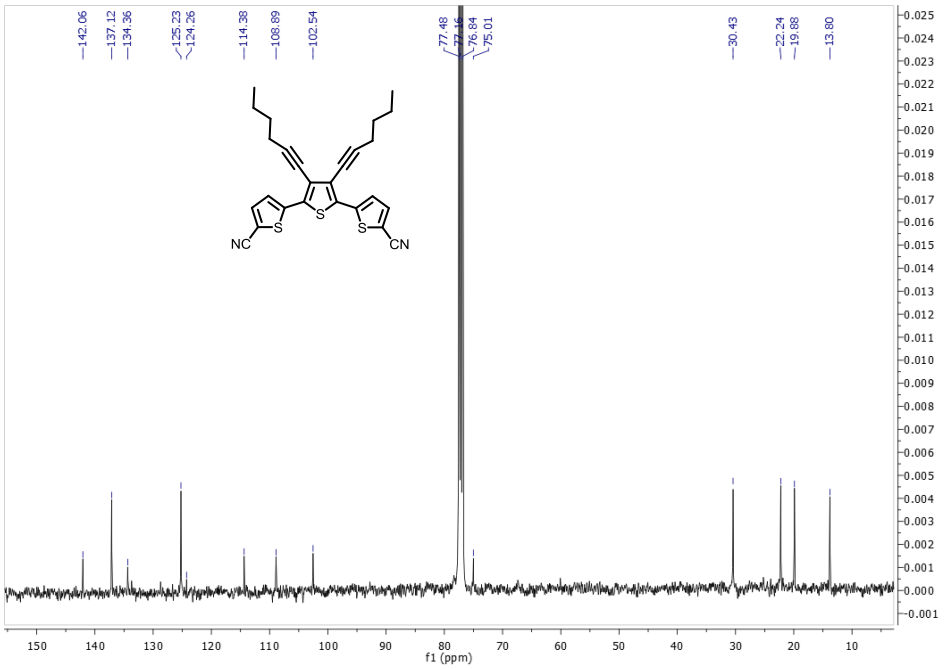


Figure S45: ^{13}C NMR spectrum of **5o** (400 MHz, $CDCl_3$)

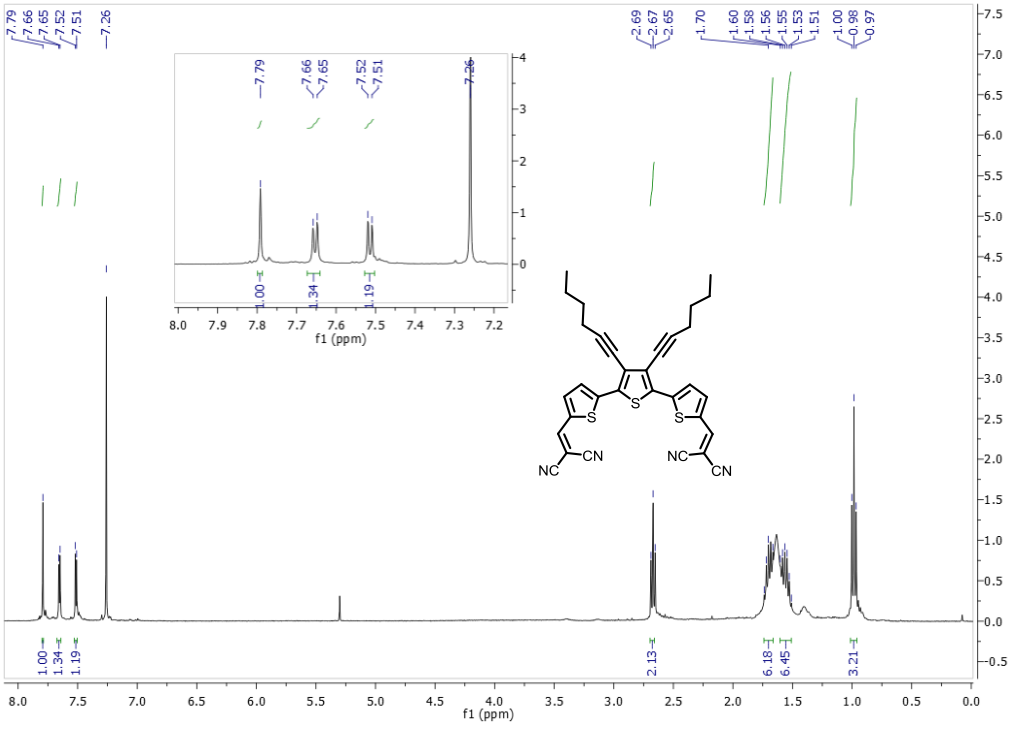


Figure S46: ^{1}H NMR spectrum of **5p** (400 MHz, $CDCl_3$)

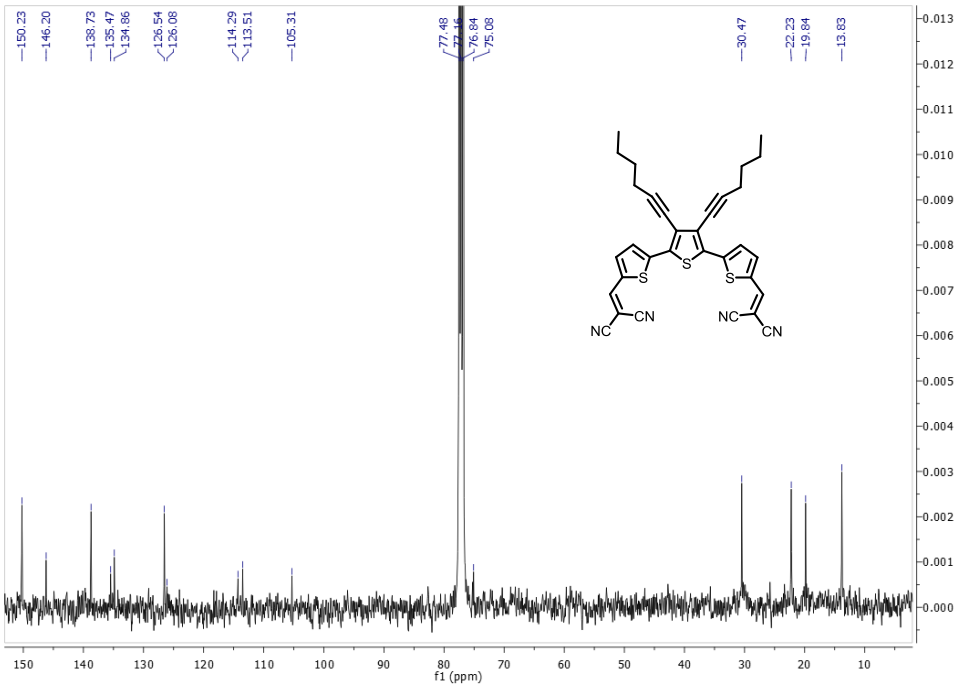


Figure S47: ^{13}C NMR spectrum of **5p** (101 MHz, $CDCl_3$)

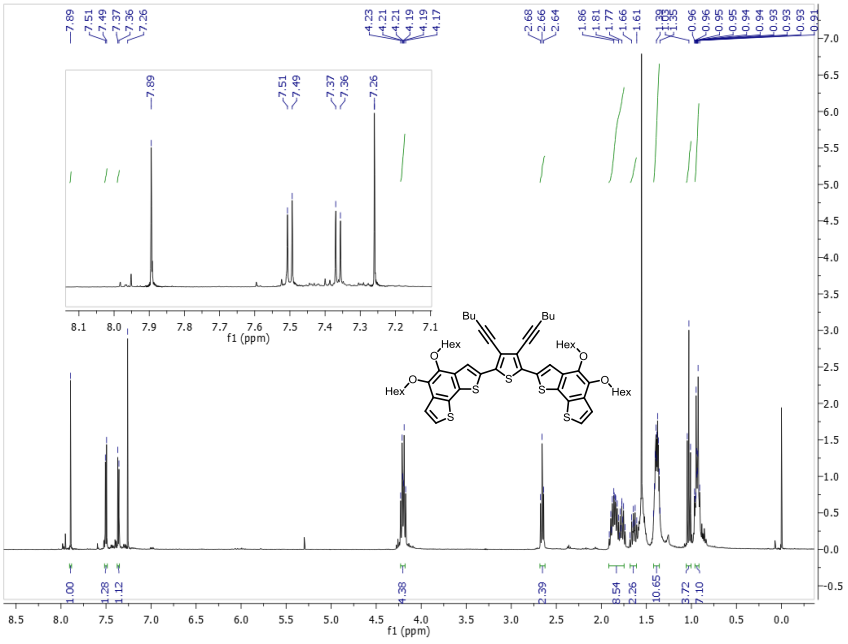


Figure S48: ^{1}H NMR spectrum of **5q** (400 MHz, $CDCl_3$)

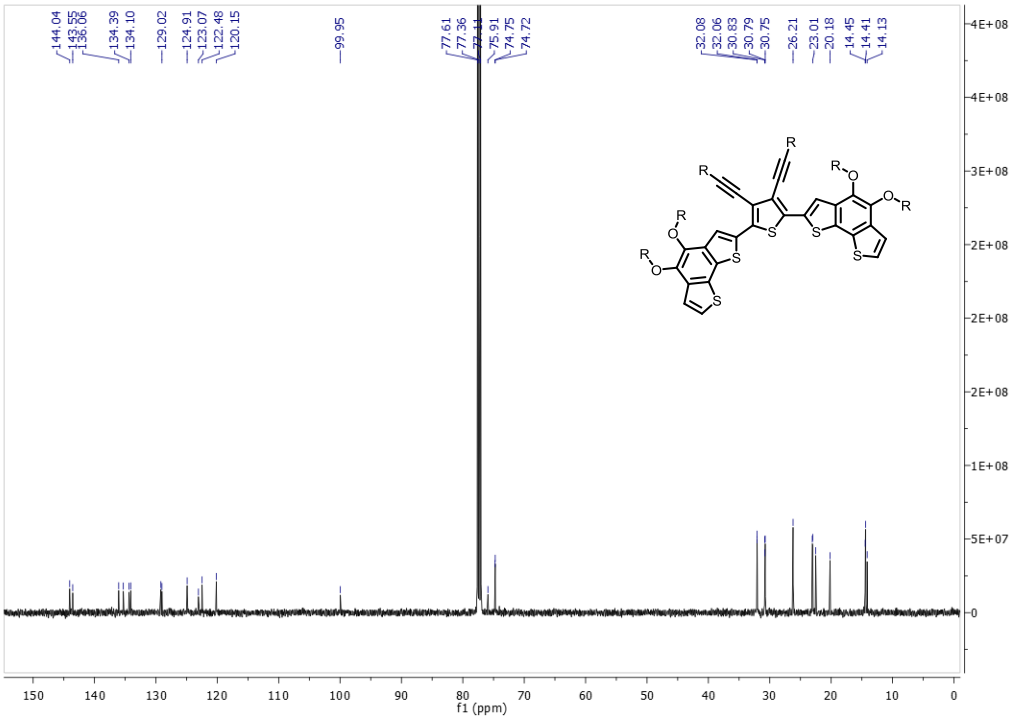


Figure S49: ^{13}C NMR spectrum of **5q** (126 MHz, $CDCl_3$)

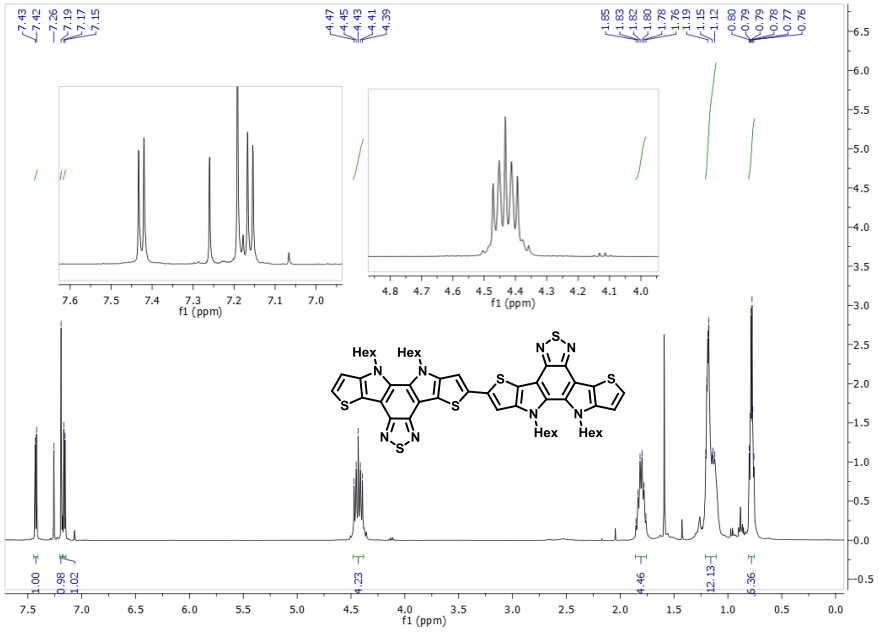


Figure S50: ^{1}H NMR spectrum of **5r** (400 MHz, $CDCl_3$)

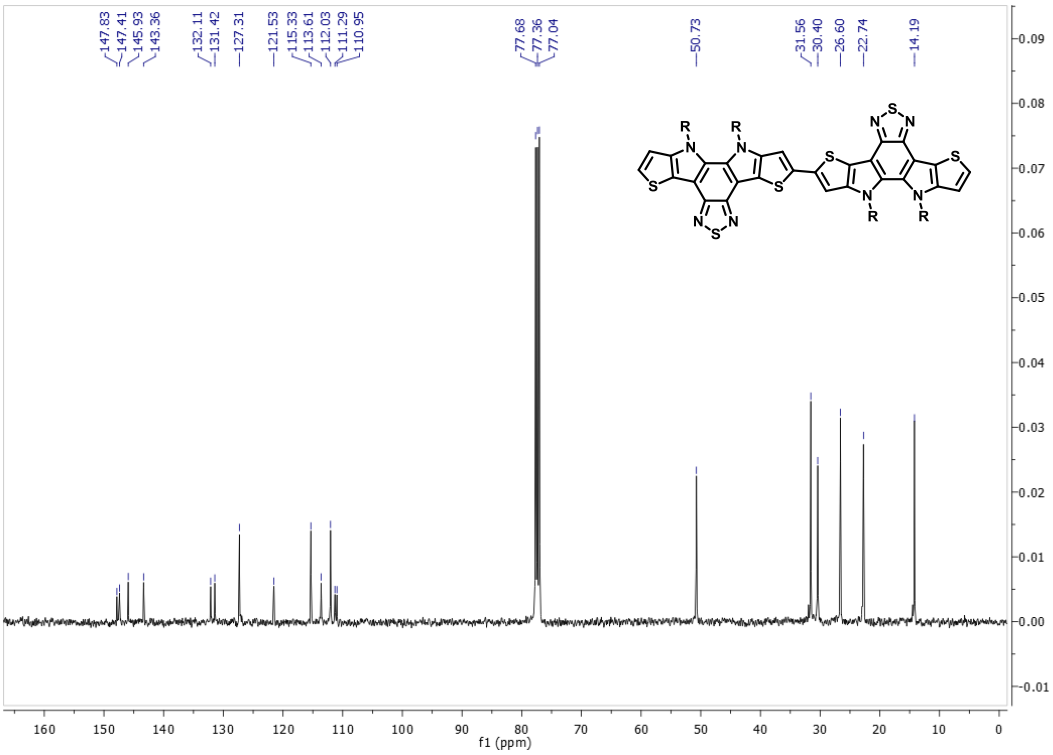


Figure S51: ^{13}C NMR ^{13}C NMR spectrum of **5r** (101 MHz, $CDCl_3$)

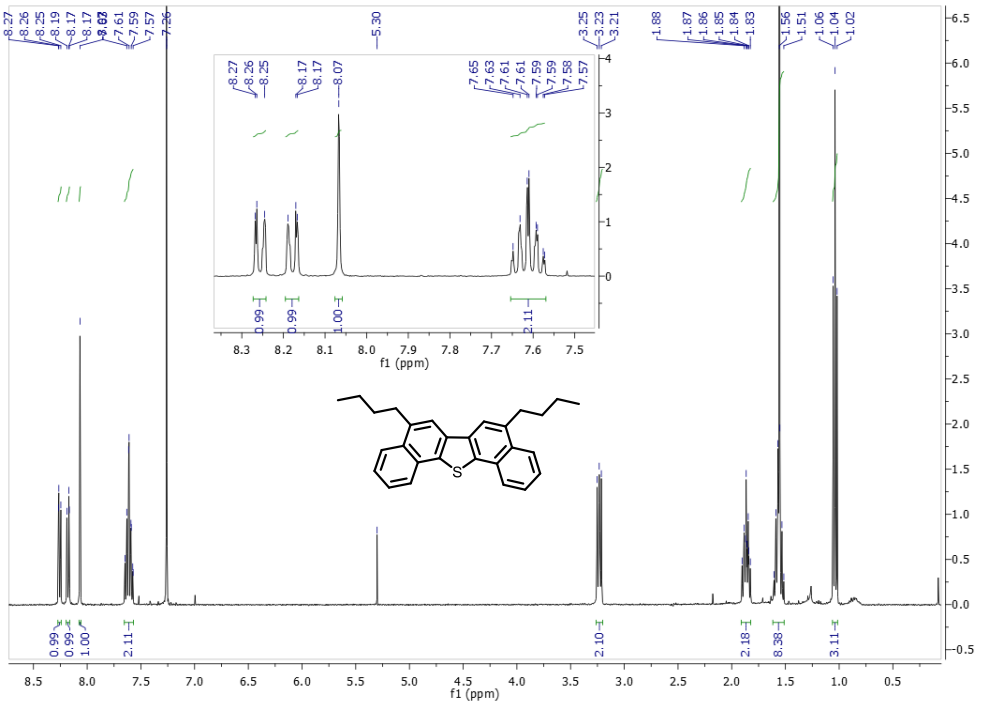


Figure S52: ^{1}H NMR spectrum of **6a** (400 MHz, $CDCl_3$)

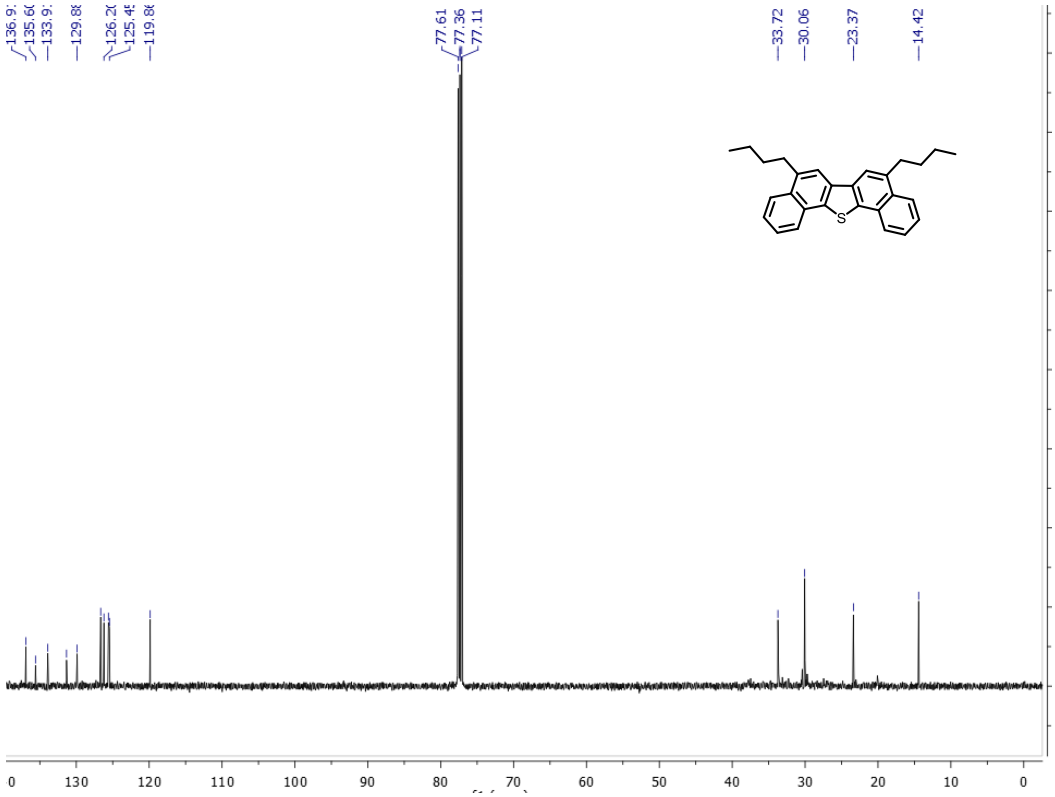


Figure S53: ^{13}C NMR spectrum of **6a** (126 MHz, $CDCl_3$)

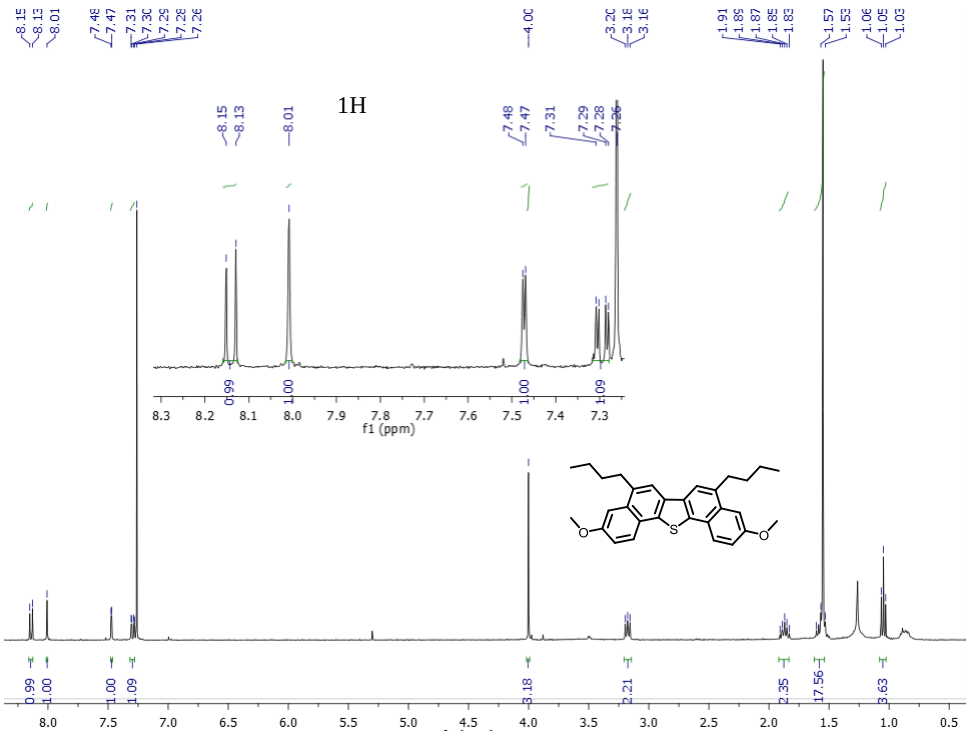


Figure S54: ^{1}H NMR spectrum of **6b** (400 MHz, $CDCl_3$)

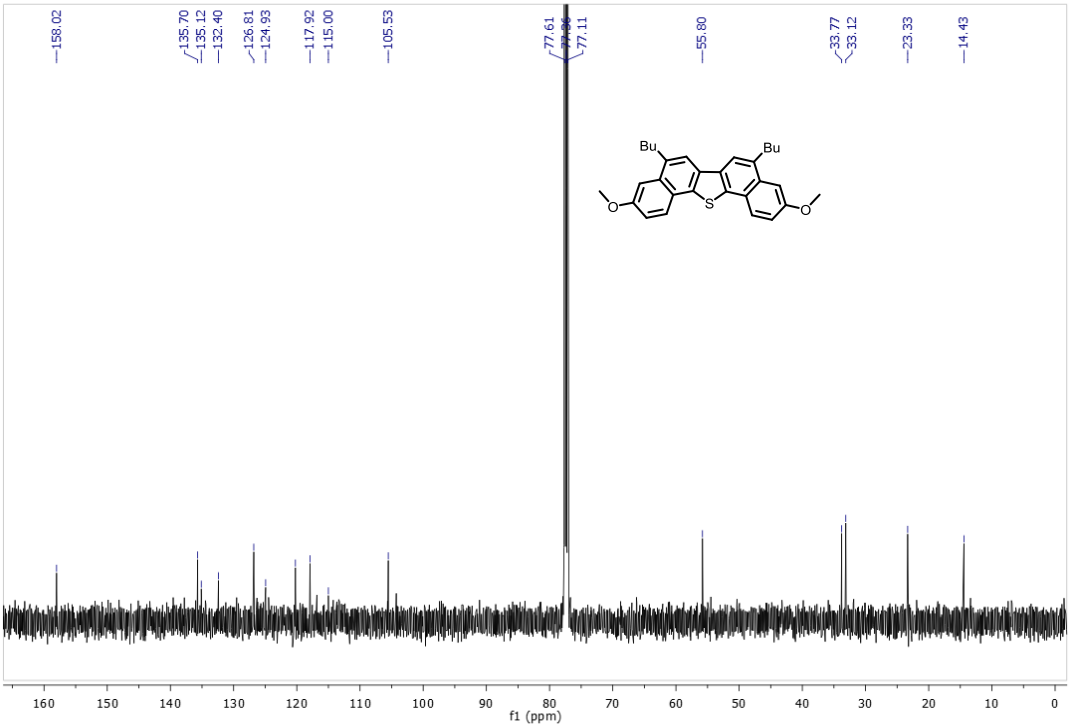


Figure S55: ^{13C} NMR spectrum of **6b** (126 MHz, $CDCl_3$)

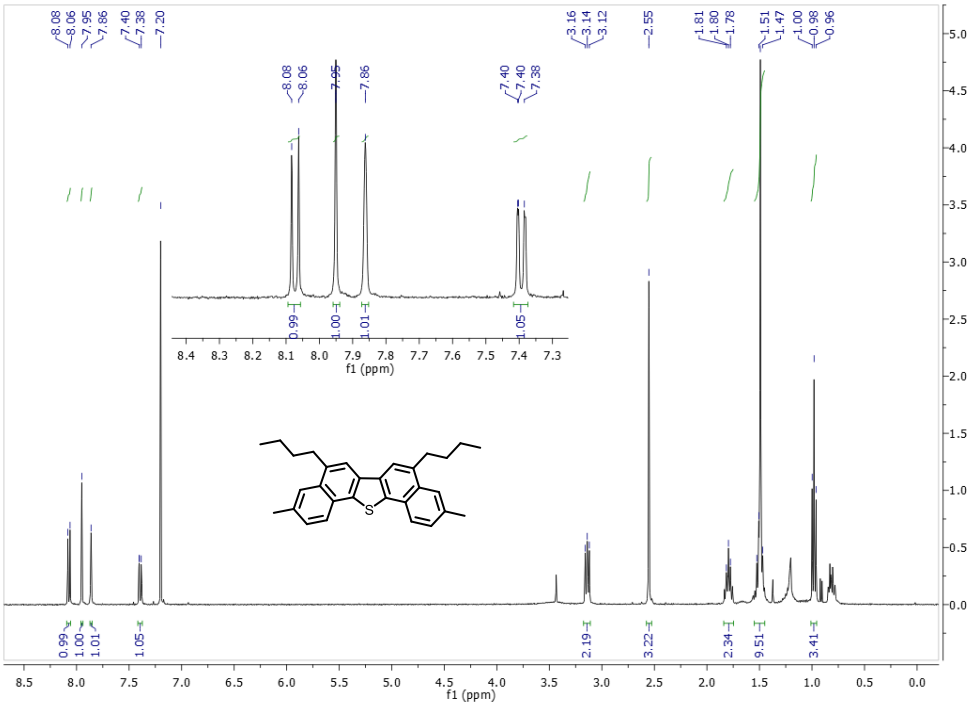


Figure S56: ^{1}H NMR spectrum of **6c** (400 MHz, $CDCl_3$)

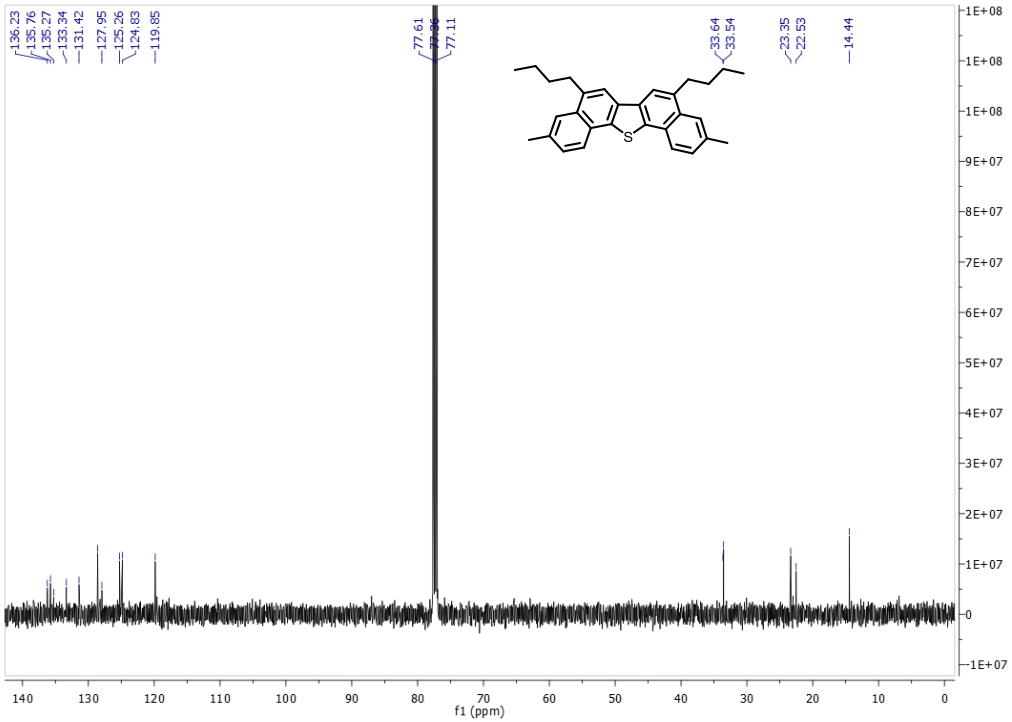


Figure S57: ^{13}C NMR spectrum of **6c** (126 MHz, $CDCl_3$)

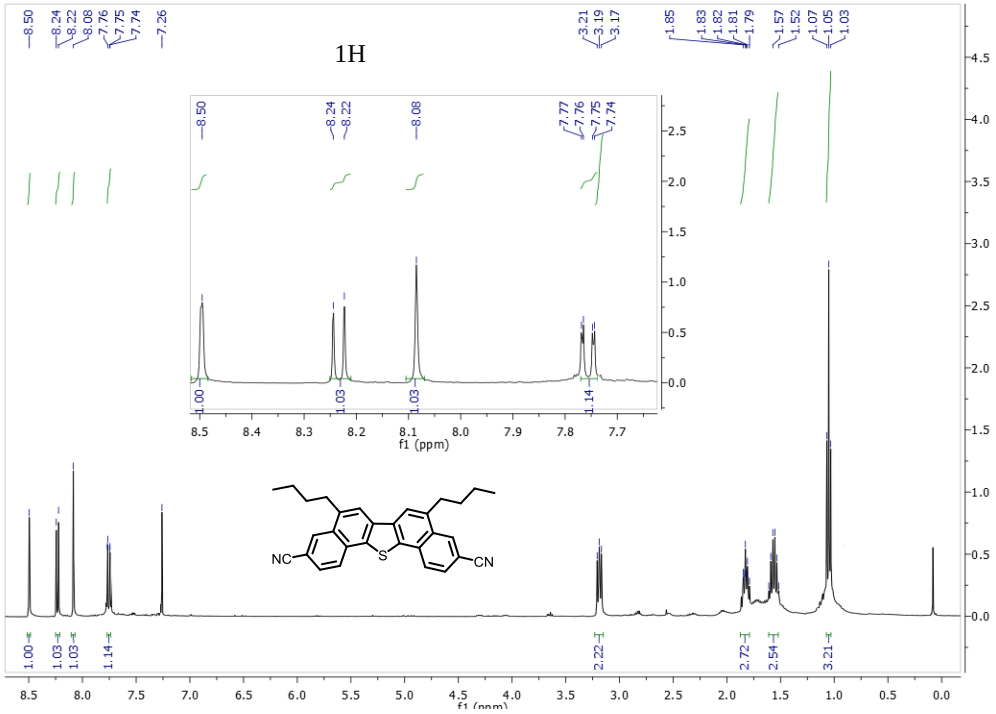


Figure S58: ^{1}H NMR spectrum of **6d** (400 MHz, $CDCl_3$)

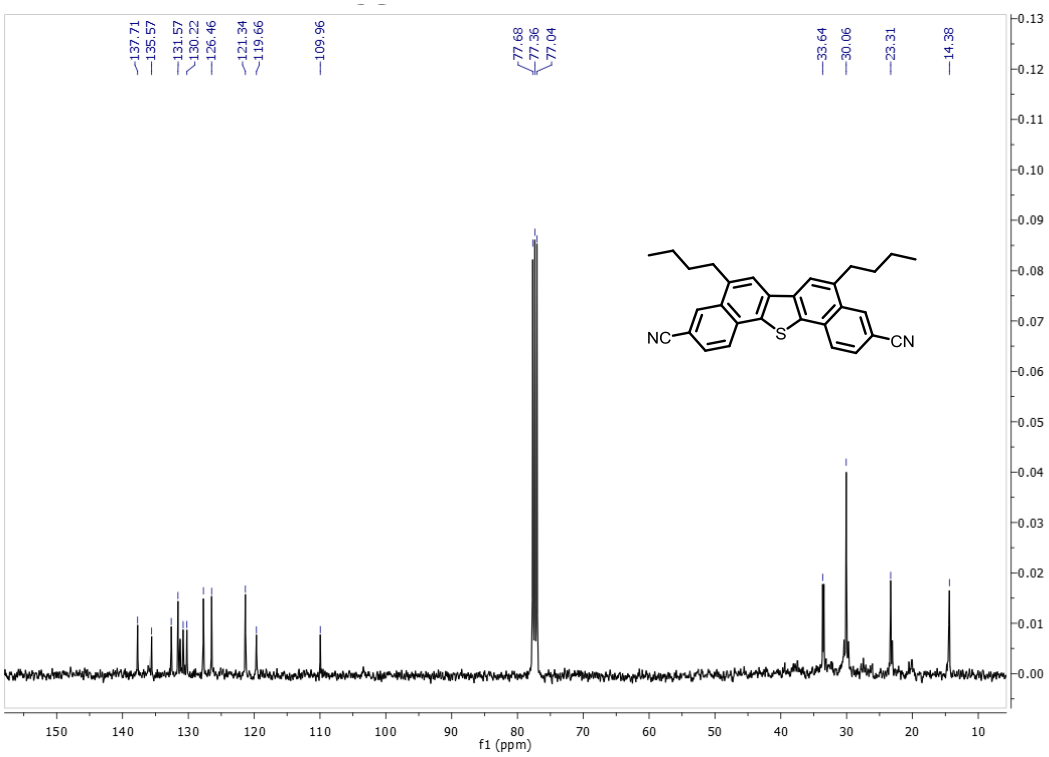


Figure S59: ^{13}C NMR spectrum of **6d** (101 MHz, $CDCl_3$)

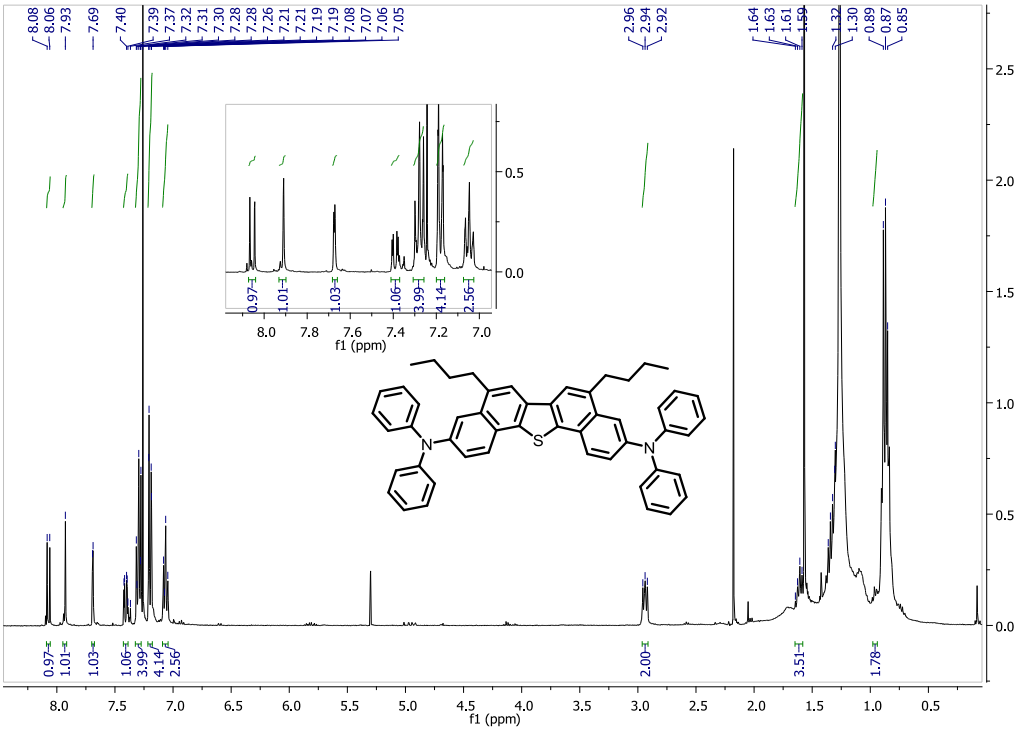


Figure S60: ^{1}H NMR spectrum of **6f** (400 MHz, $CDCl_3$)

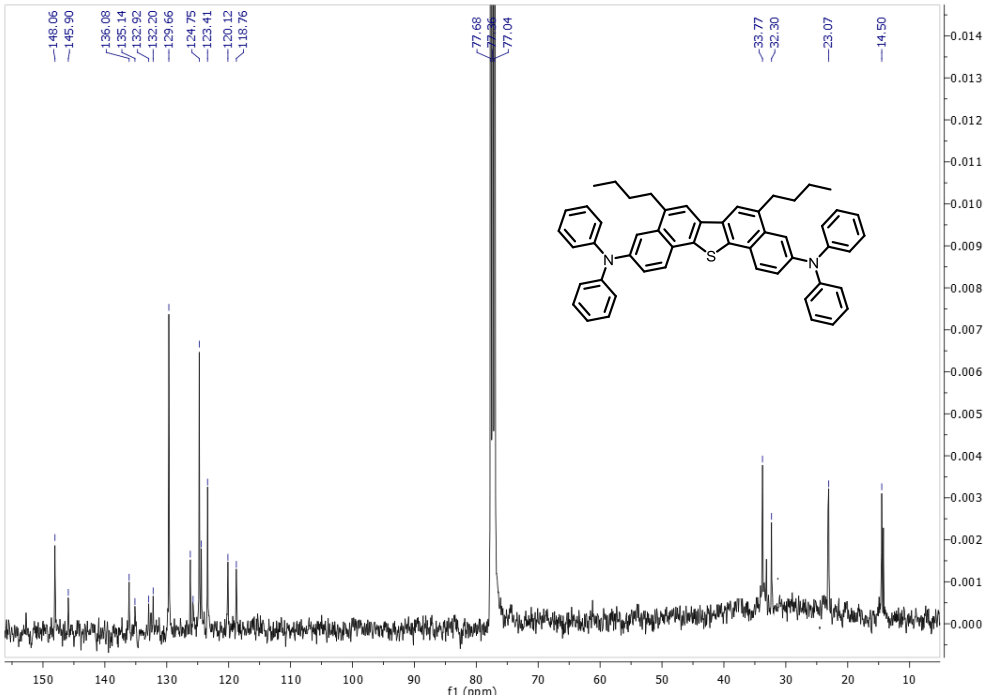


Figure S61: ^{13}C NMR spectrum of **6f** (101 MHz, $CDCl_3$)

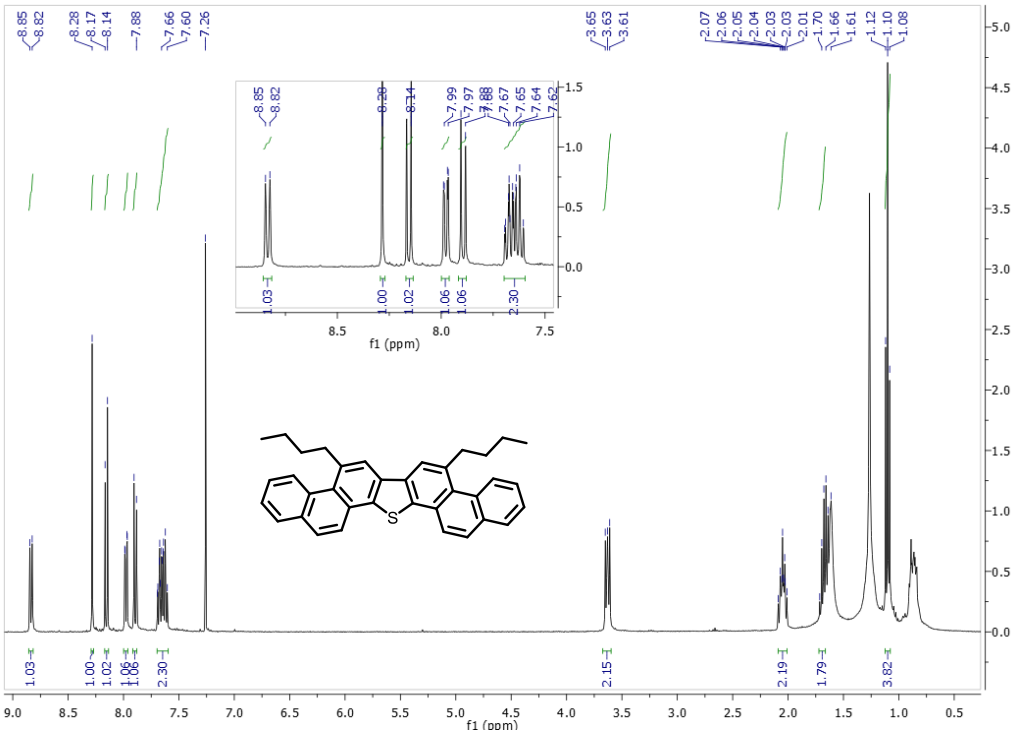


Figure S62: ^{1}H NMR spectrum of **6h** (400 MHz, $CDCl_3$)

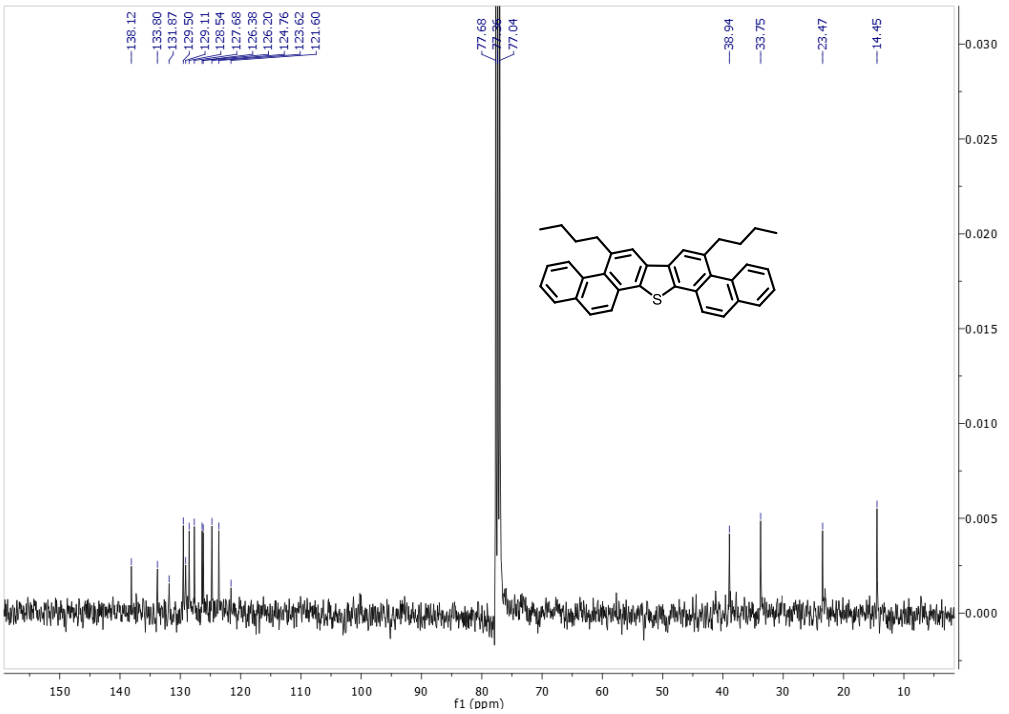


Figure S63: ^{13}C NMR spectrum of **6h** (101 MHz, $CDCl_3$)

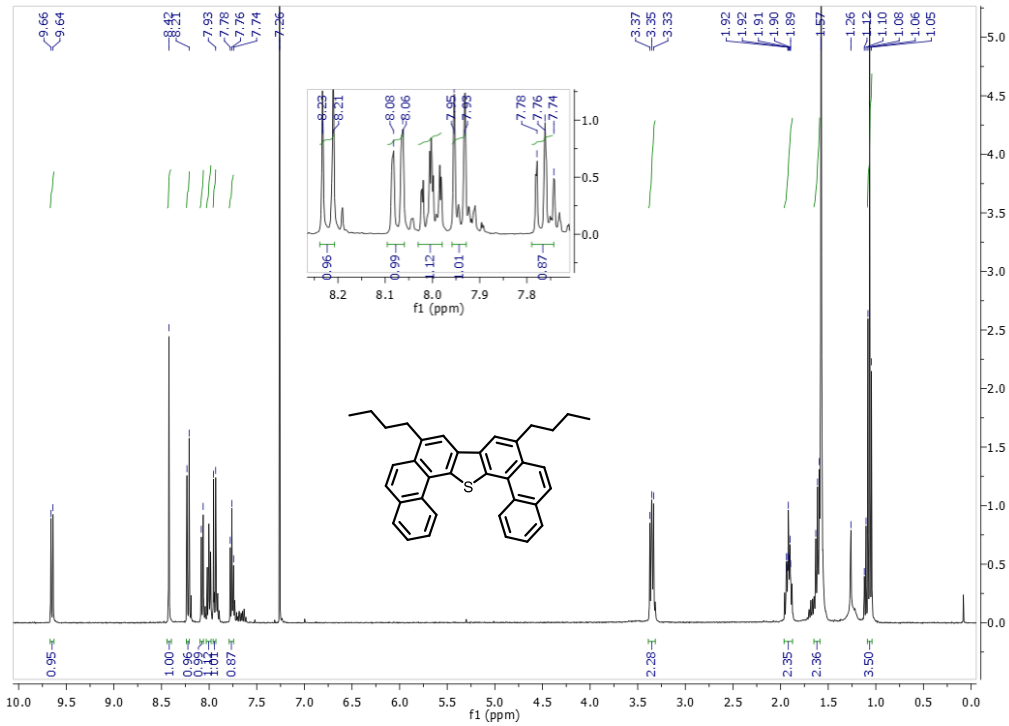


Figure S64: ^{1}H NMR spectrum of **6i** (400 MHz, $CDCl_3$)

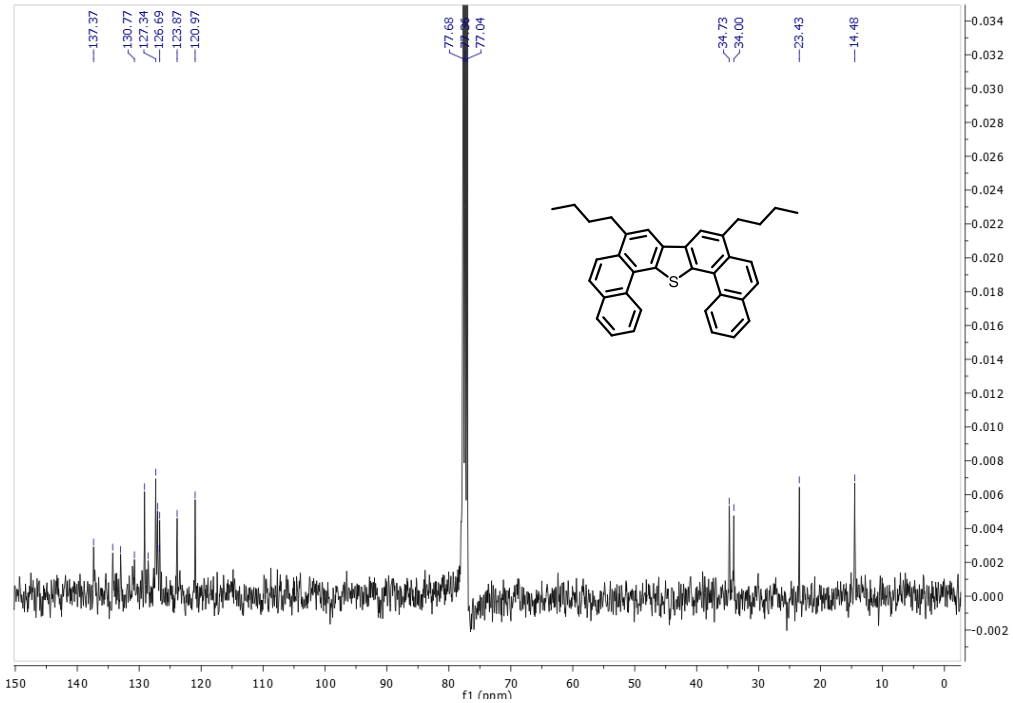


Figure S65: ^{13}C NMR spectrum of **6i** (101 MHz, $CDCl_3$)

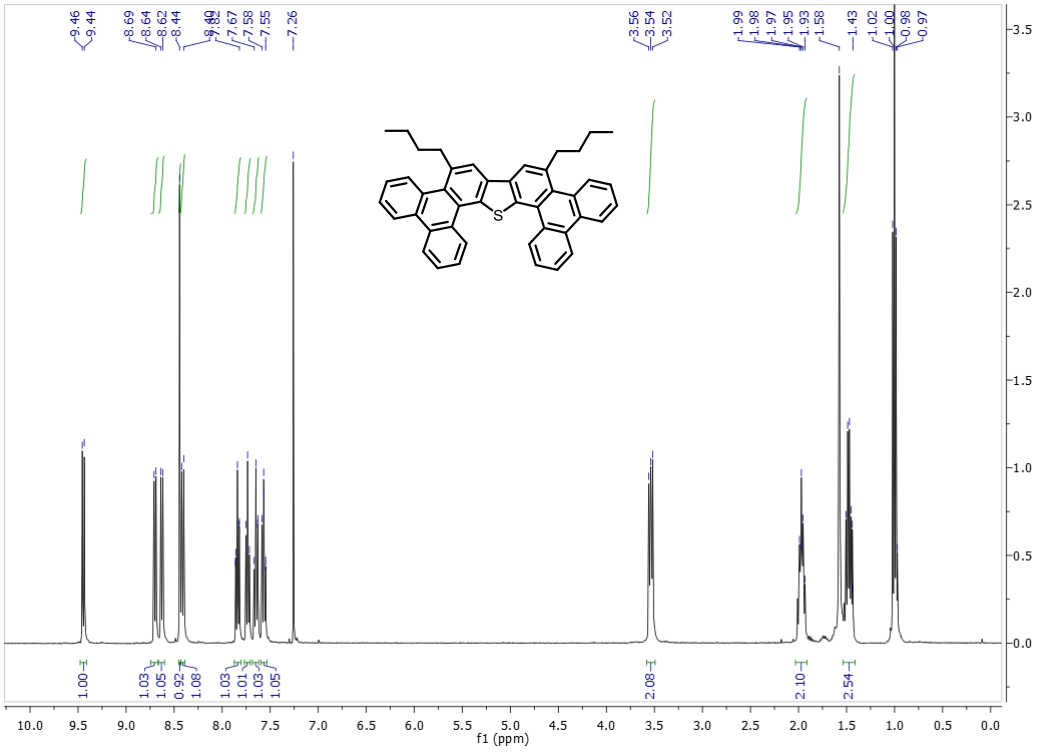


Figure S66: ^{1}H NMR spectrum of **6j** (400 MHz, $CDCl_3$)

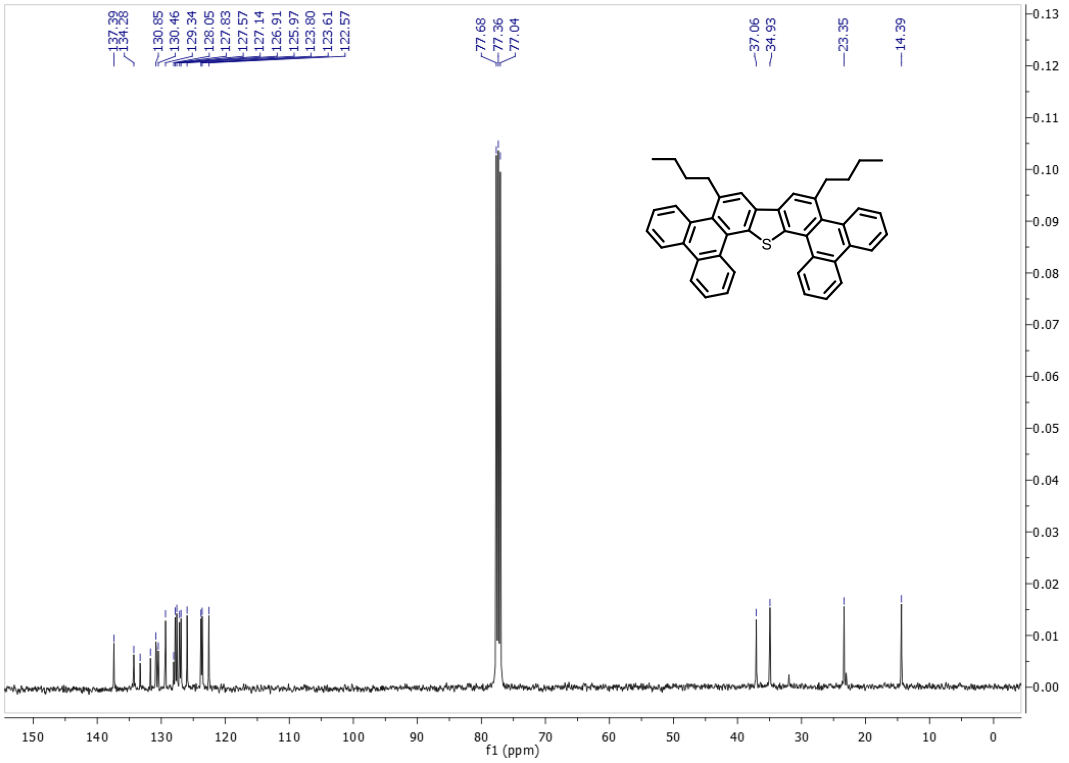


Figure S67: ^{13}C NMR spectrum of **6j** (101 MHz, $CDCl_3$)

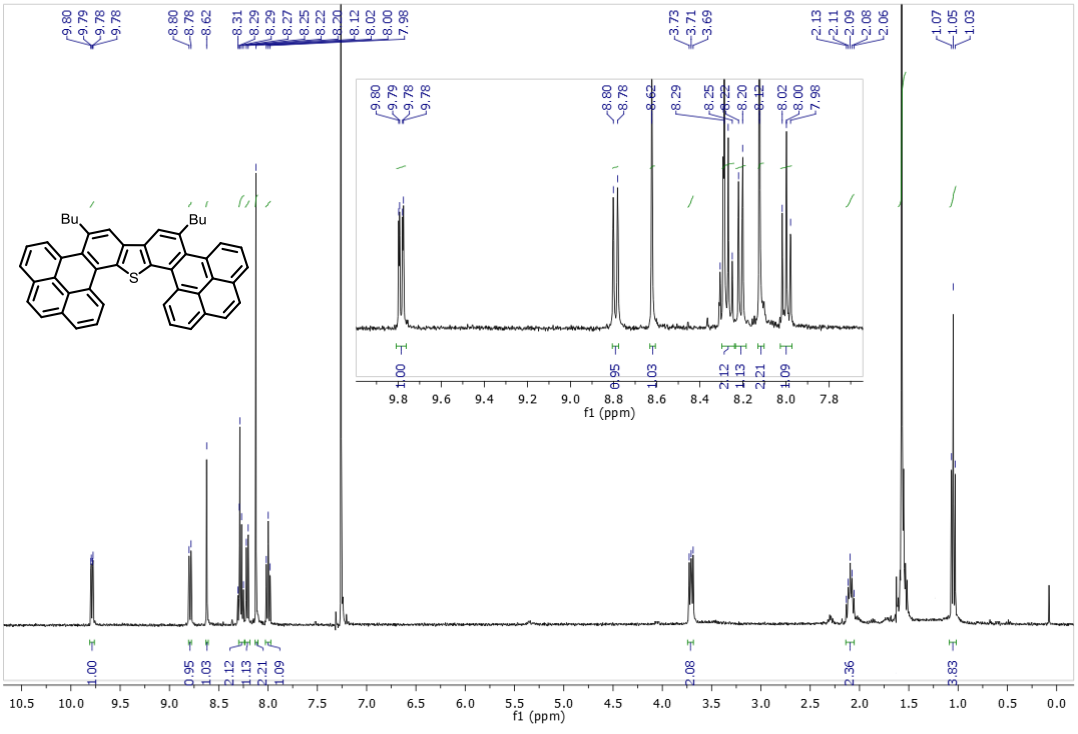


Figure S68: ^{13}C NMR spectrum of **6m** (400 MHz, $CDCl_3$)

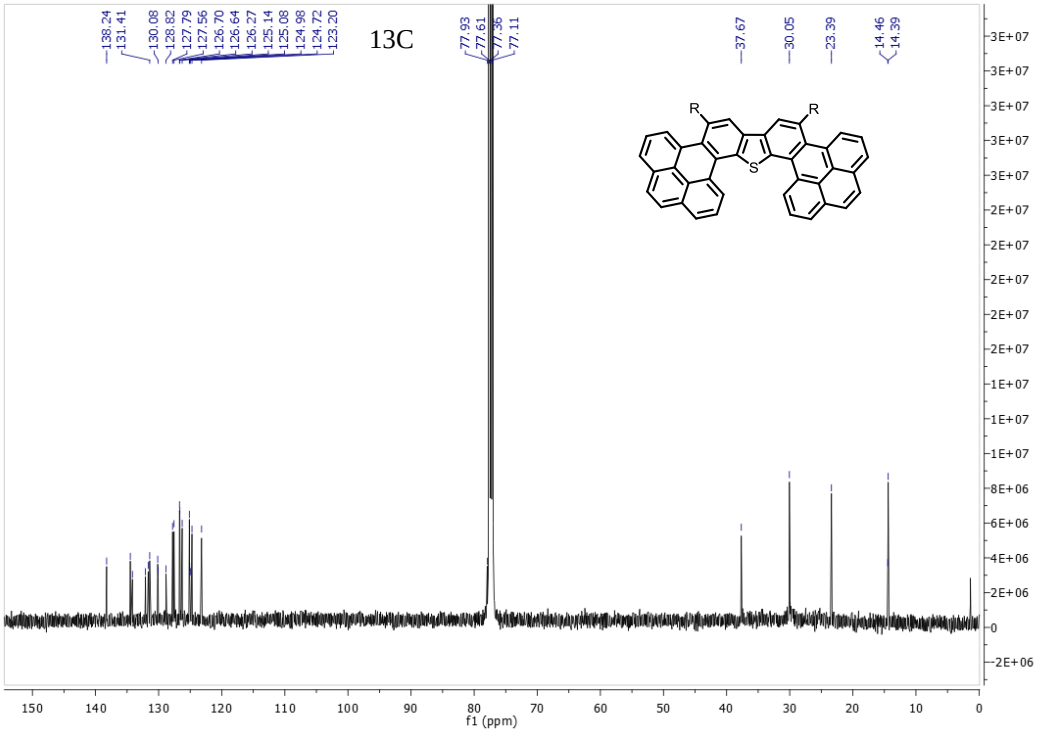


Figure S69: ^{13}C NMR spectrum of **6m** (126 MHz, $CDCl_3$)

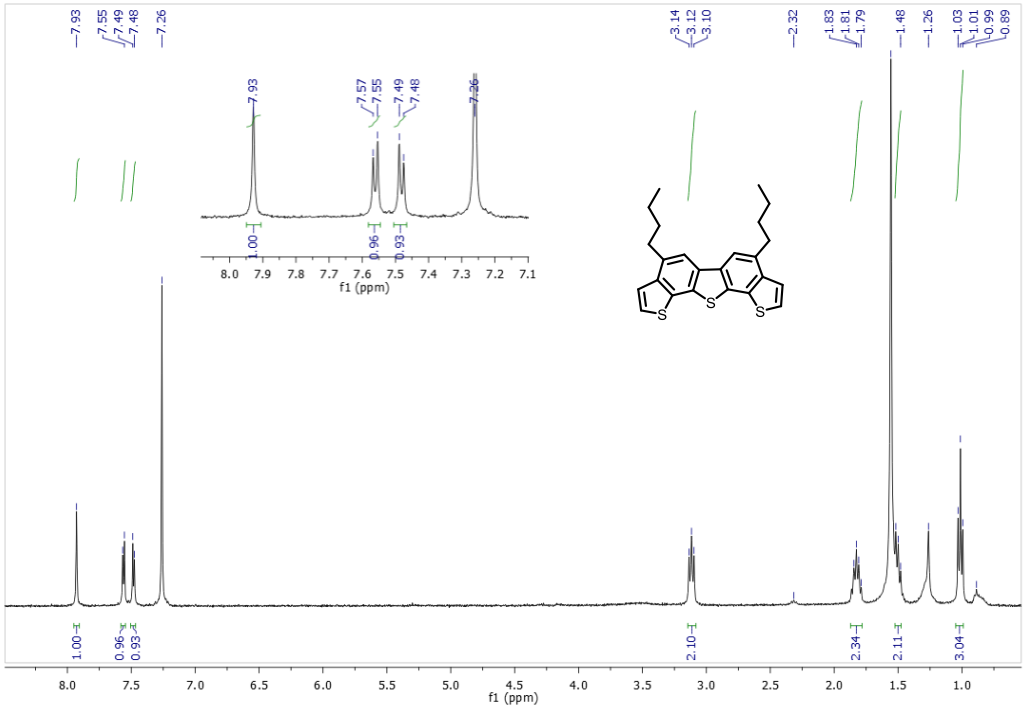


Figure S70: ^{1}H NMR spectrum of **6n** (400 MHz, $CDCl_3$)

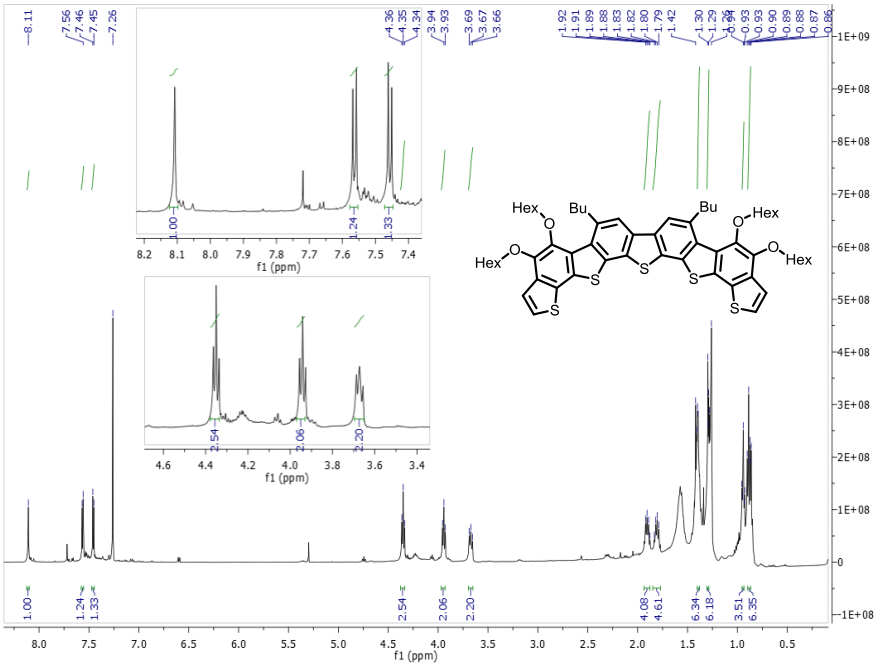


Figure S71: ^{1}H NMR spectrum of **6q** (500 MHz, $CDCl_3$)

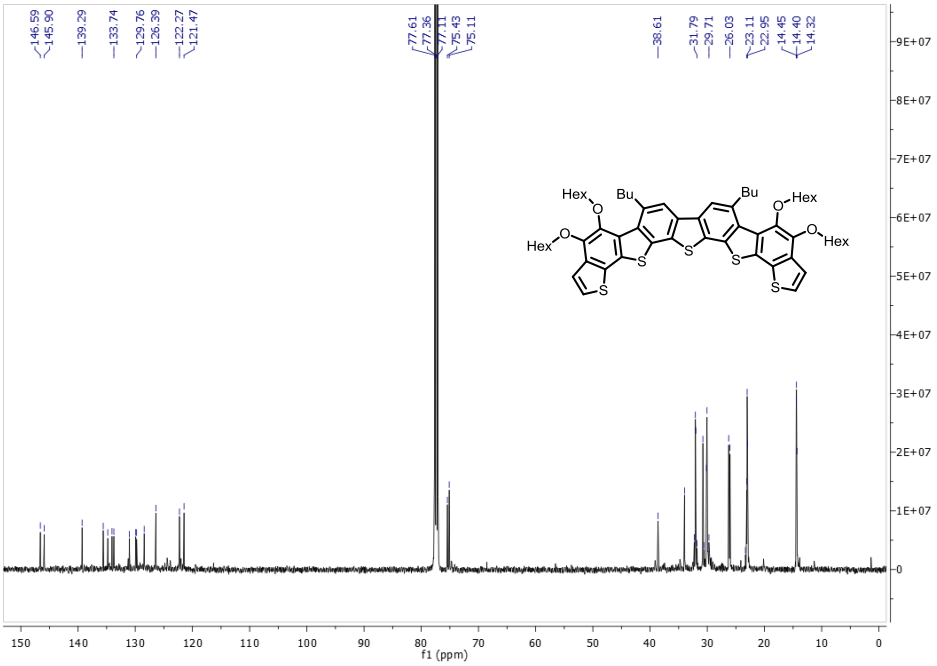


Figure S72: ^{13}C NMR spectrum of **6q** (126 MHz, $CDCl_3$)

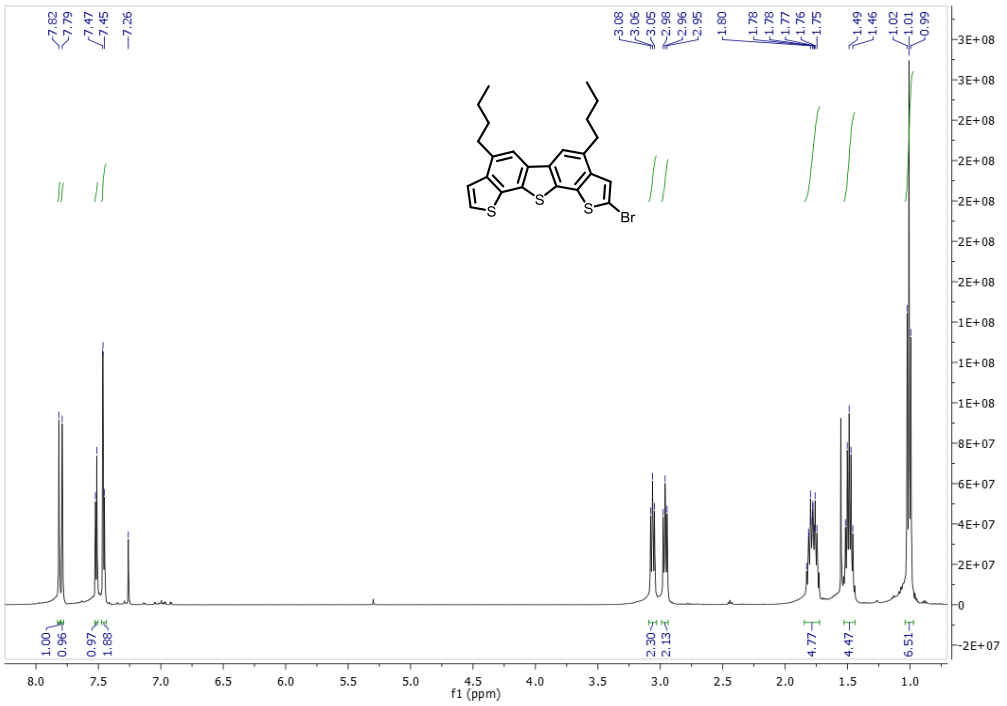
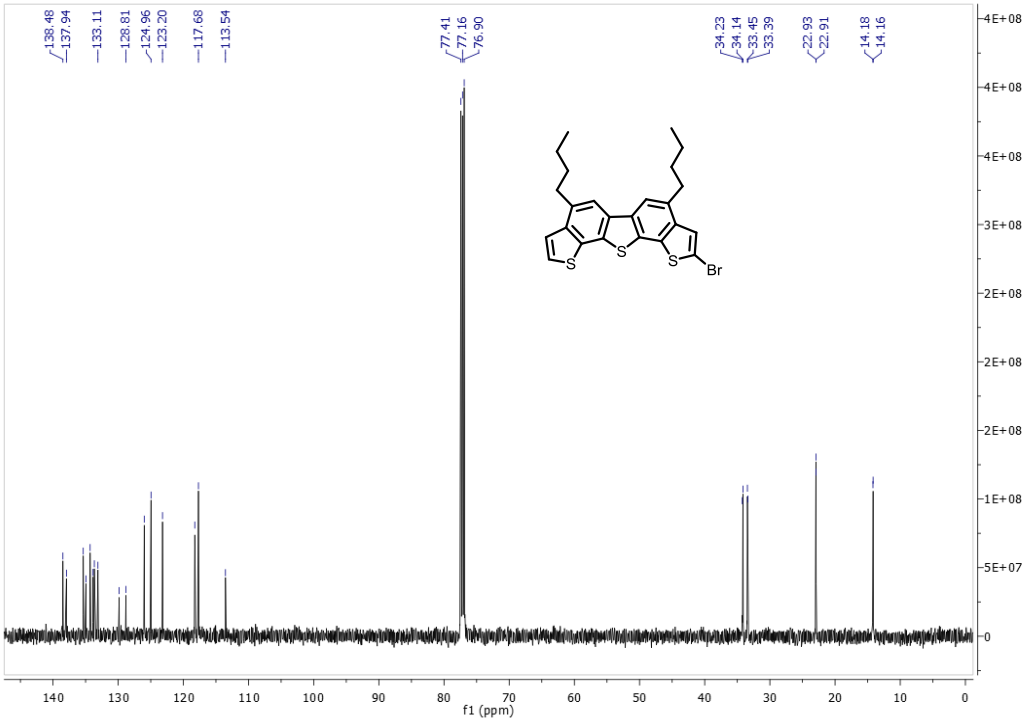


Figure S73: ^{1}H NMR spectrum of **4s** (500 MHz, $CDCl_3$)



FigureS74: ^{13}C NMR spectrum of **4s** (126 MHz, $CDCl_3$)

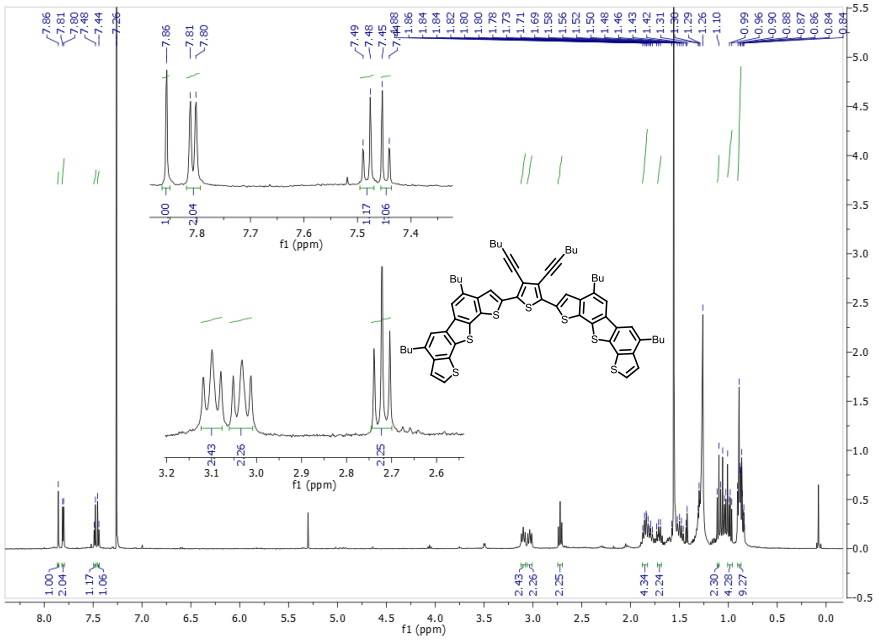


Figure S75: ^{1}H NMR spectrum of **5s** (400 MHz, $CDCl_3$)

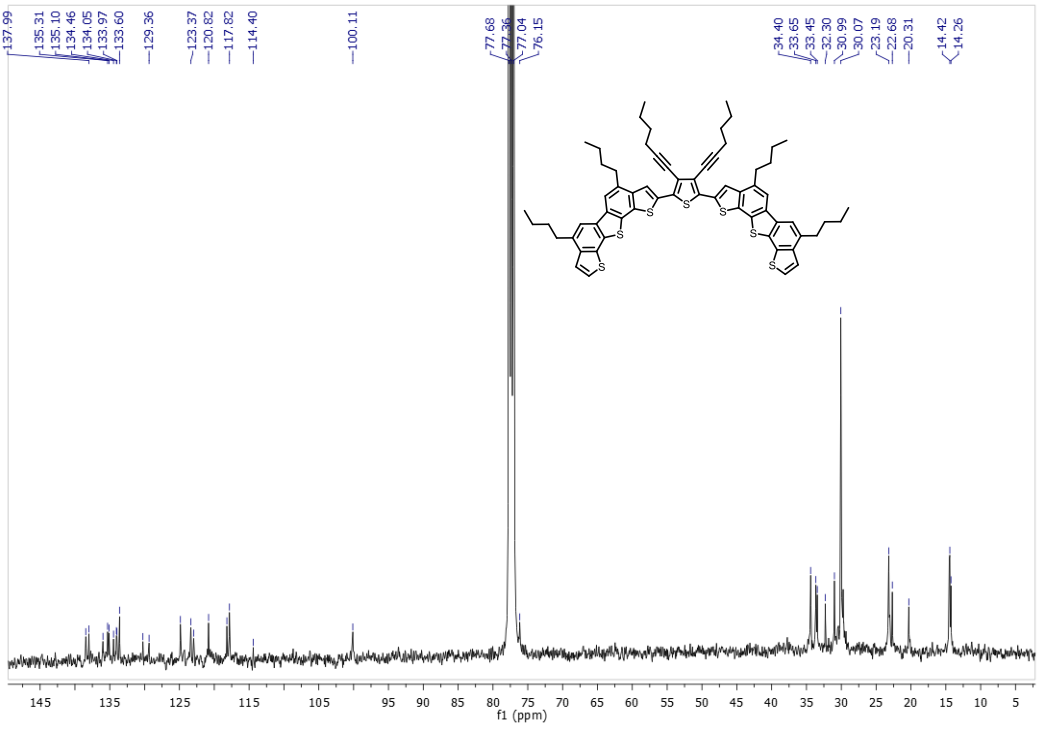


Figure S76: ^{13}C NMR spectrum of **5s** (101 MHz, $CDCl_3$)

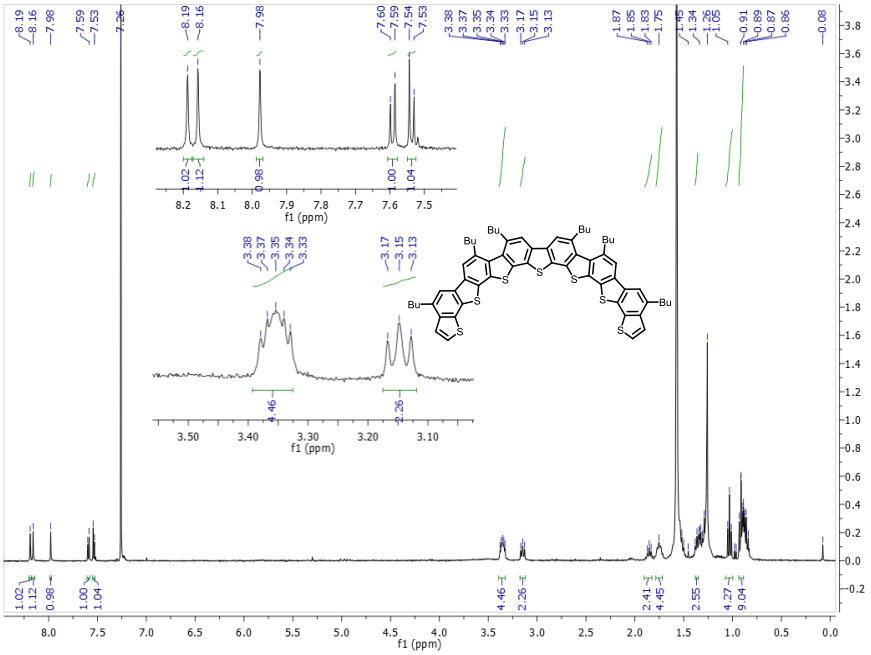
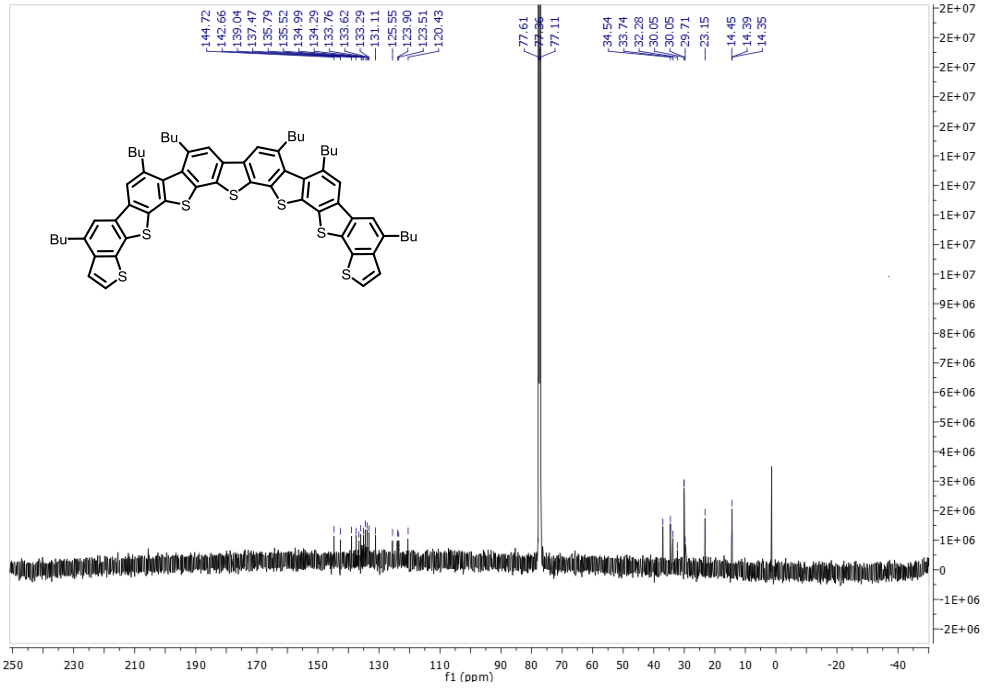


Figure S77: ^{1}H NMR spectrum of **6s** (400 MHz, $CDCl_3$)



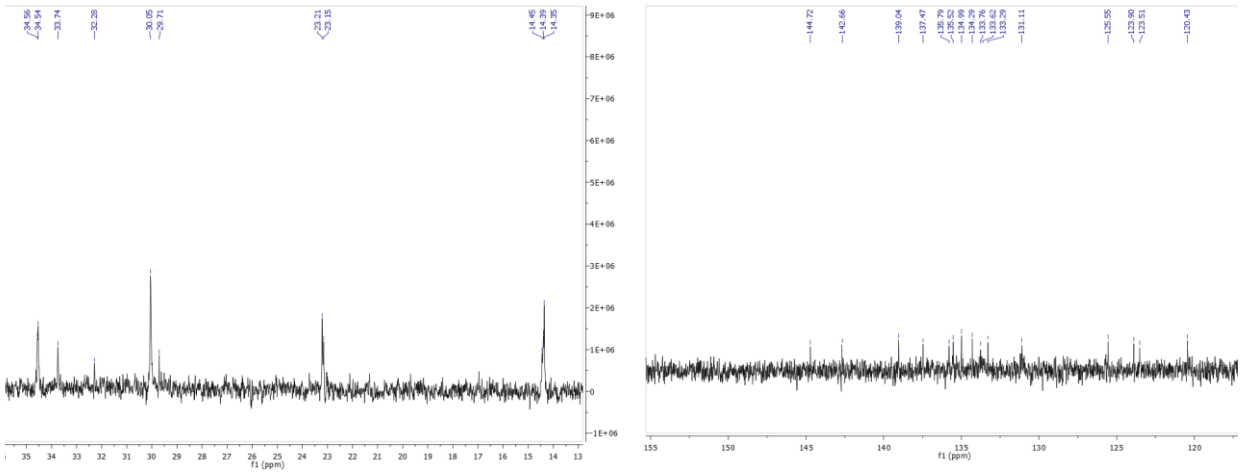


Figure S78: ^{13}C NMR spectrum of **6s**(126 MHz, $CDCl_3$)

References:

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.

[2] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.

[3] C. T. J. Ferguson, N. Huber, K. Landfester, K. A. I. Zhang, *Angew. Chem. Int. Ed*. 2019, **58**, 31, 10567-10571.

[4] K. Ohtsu, R. Hayami, T. Sagawa,; S. Tsukada, K. Yamamoto, T. Gunji, *Tetrahedron*, 2019, **75**, 130658.

[5] J. Zhang, J. Wang, A. Sandberg, X. Wu, S. Nystrom, H. III Levine, P. Konradsson, P. Hammarstrom, B. Durbeej, M. Lindgren, *ChemPhysChem* 2018, **19**, 3001-3009.

[6] Q. Lu, G. K. Kole, A. Friedrich, K. M. Buschbaum, Z. Liu, X. Yu, T. B. Marder, *J. Org. Chem*. 2020, **85**, 4256-4266.

[7] H. Ziehlke, R. Fitzner, C. Koerner, R. Gresser, E. Reinold, P. Bauerle, K. Leo, M. K. Riede, *J. Phys. Chem. A*, 2011, **115**, 8437–8446.

[8] A. Bedi, J. D. Winter, P. Gerbaux, G. Koeckelberghs, *J. Polym. Sci., Part A-1: Polym. Chem*. 2016, **54**, 1706-1712.

[9] T-Y.Quan, Q. Li, Z. Wang, H. Ma, J. Dong, Z-S.Huang, *Dyes Pigm*. 2020, **173**, 107999.

[10] X. Han, B. M. Stoltz, E. J.Corey, *J. Am. Chem. Soc.* 1999, **121**, 7600-7605.

[11] K. Mitsudo, H. Sato, A. Yamasaki, N. Kamimoto, J. Goto, H. Mandai, S. Suga, *Org. Lett.* 2015, **17**, 4858−4861.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, 2016.

[13] K. Senthilkumar, F. Grozema, F. Bickelhaupt, L. Siebbeles, *J. Chem. Phys*. 2003, **119**, 9809−9817.

[14] H. Li, J. L. Bredas, C. J. Lennartz, C. *J. Chem. Phys*. 2007, **126**, 164704

[15] S. I. Gorelsky, S. Ghosh, E. I. Solomon, *J. Am. Chem. Soc*. 2006, **128**, 278– 290.

[16] J. Huang, M. Kertesz, *Chem. Phys. Lett*. 2004, **390**, 110–115.

[17] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, P. A. Wood, *J. Appl. Cryst.* 2020, **53**, 226-235.

[18] W.Q. Deng, L. Sun, J.D. Huang, S. Chai, S.H. Wen, K. L. Han, *Nat. Protoc*. 2015, **10**, 632–642.

[19] R. A. Marcus, *I. J. Chem. Phys*. 1956, **24**, 966–978.

[20] N. S. Hush, *J. Chem. Phys*. 1958, **28**, 962–972.