Supplementary information

Solid-state red-emissive (cyano)vinylene heteroaromatics *via* Pd-catalysed C-H homocoupling

*Atul B. Nipate and M. Rajeswara Rao**

Department of Chemistry, IIT Dharwad, Dharwad-580011, Karnataka, India

Table of Contents:

List of Figures

List of Tables

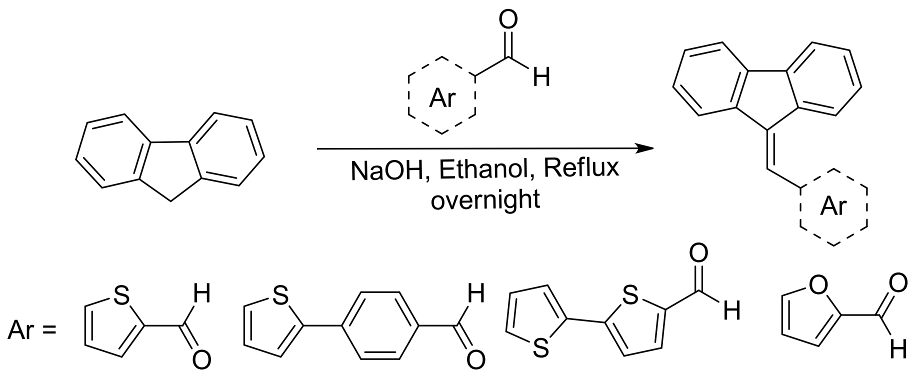
1.1 General information

Reagents and solvents employed are commercially purchased from sigma, SRL, spectrochem, TCI and used as it is. ^{1}H and ^{13}C (Nuclear magnetic resonance) solution state NMR studies are performed in Jeol:400 MHz NMR spectrometer. Agilent Cary 5000 UV-Vis-NIR spectrophotometer with diffuse reflectance and solution state accessory is employed to study the optical properties of the organic compounds synthesized. Perkin Elmer FL 6500 used to study the fluorescence properties. DFT calculations of the molecular structures (in the gas phase) and the molecular orbital energies were carried out at the B3LYP/6-31G(d) level as implemented in Gaussian 16. The figures were generated with GaussView 6.0.

1.2 Experimental Section

1.2.1 General procedure for the Knoevenagel condensation on fluorene using different aldehydes[1]

The procedure for the synthesis of these compounds have been modified compared to the literature. A mixture of fluorene (500 mg, 3 mmol, 1eq) and NaOH (265 mg, 6.6 mmol, 2.2 eq) were dissolved in 5 ml ethanol and introduced aldehyde (3 mmol, 1eq) and heated to reflux for 12 hrs. The reaction mixture was then cooled to room temperature and the brownish yellow solid was collected and purified using silica gel column chromatography (petroleum ether) to isolate the pure product. Schematic of the reaction is represented as scheme 1.



1 (70%) **2** (74%) **3** (75%) **4** (70%)

Scheme 1: Synthesis route for the synthesis of Knoevenagel condensation products of fluorenes with various aldehydes

1.2.2 Spectral Data of knoevenagel Compounds

Compound 1 yield 70%, Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13-8.11 (d, *J* = 7.8 Hz, 1H), 7.76-7.70 (m, 3H), 7.62 (s, 1H), 7.48- 7.44 (m, 2H), 7.39 – 7.30 (m, 3H), 7.23 – 7.13 (m, 2H); **^{13}C NMR (101 MHz $CDCl_3$)** δ 141.41,139.70, 139.27, 139.11, 136.67, 136.33, 129.51, 128.94, 128.43, 127.78, 127.54, 127.18, 127.03, 124.56, 120.37, 119.97, 119.80, 77.57, 77.25,76.93.

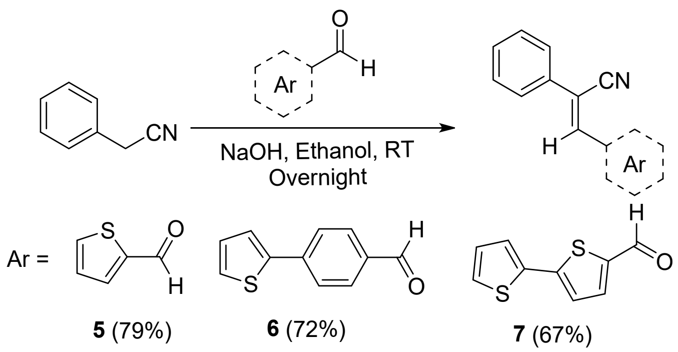
Compound 2 yield 74%, Yellow solid, **HRMS:** m/z calcd for $C_{24}H_{16}SH$ ([M+1]): 337.1051; found m/z: 337.1054; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80-7.79 (d, *J* = 7.4 Hz 1H), 7.74 – 7.79 (m, 4H), 7.67 (s,1H), 7.64-7.62 (d, *J* = 8.1 Hz 2H), 7.42-7.31 (m, 5H), 7.14-7.07 (m 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.04, 141.39, 139.59, 139.23, 136.64, 136.54, 136.02, 130.12, 128.71, 128.31, 127.10, 126.83, 125.90, 125.26, 124.53, 123.49, 120.35, 80, 119.87, 119.70. 77.44, 77.12, 76.80.

Compound 3 yield 75%, Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31- 8.29 (d, *J* = 7.8 Hz 1H), 7.75-7.70 (m, 3H), 7.56 (s,1H), 7.38 – 7.27 (m 6H), 7.22-7.21 (d, *J* = 3.7 Hz), 7.07-7.05 (dd, *J* = 5.1, 3.7 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.33, 139.73, 139.53, 138.93, 138.11,137.11, 136.14, 130.94, 128.85, 128.31, 128.12, 127.10, 127.01, 125.09, 124.55, 124.25, 120.23, 119.95, 119.74,118.75.77.43,77.11,76.80

Compound 4 yield 70% Brown solid**, ^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (d, *J* = 7.4 Hz, 1H), 7.75 - 7.69 (m, 4H), 7.41 – 7.25 (m, 5H), 6.77 – 6.76 (m, 1H), 6.59 (dd, *J* = 3.4, 1.8 Hz, 1H).

1.2.3 General Procedure for the synthesis of Benzyl cyanide substituted aldehyde.

A mixture of aryl acetonitrile (500mg 4.27 mmol) and NaOH (376 mg 9.40 mmol) were dissolved in 5 ml ethanol and introduced aldehyde (4.27 mmol) and stirred at room temperature for 12 hrs. The yellow solid thus formed was collected and purified using silica gel column chromatography [CH_2Cl_2 (5%): petroleum ether (95%)] to isolate the pure product. Schematic of the reaction is represented as scheme 2.



Scheme 2: Synthesis route for the synthesis of Knoevenagel condensation products of aryl acetonitriles with various aldehydes

1.2.4 Spectral Data of knoevenagel Compounds

Compound 5 yield 79 % light yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.67 – 7.63 (m, 4H), 7.56 – 7.54 (m, 1H), 7.45 – 7.42 (m, 2H), 7.15 (dd, *J* = 5.1, 3.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.03, 134.34, 133. 94, 132.65, 130.18, 129.21, 129.08, 127.97, 125.77, 118.30, 77.55, 77.23, 76.92.

Compound 6 yield 72% Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.71 – 7.67 (m, 4H), 7.51 (s,1H), 7.46 – 7.39 (m, 4H), 7.35 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.34 (dd, *J* = 5.1, 3.6 Hz).

Compound 7 yield 67% Brown solid, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 – 7.62 (m, 2H), 7.59 (d, 1H), 7.50 – 7.49 (m,1H), 7.44 – 7.41 (m, 2H), 7.37 – 7.29 (m, 3H), 7.19 (d, *J* = 3.9 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H).

1.2.5 General procedure for homocoupling reaction

A mixture of fluorene /aryl acetonitrile substituted thiophene (1.92 mmol), $Pd(OAc)_2$ (5mol %) KOAc (9.6 mmol, 5 eq.), pivalic Acid (0.29 mmol, 0.15eq) and DMAc (3 ml) were added to a pressure tube and purged with nitrogen gas. After the purging the mixture was heated at 140˚C for 36 hrs. The reaction mixture was brought to room temperature and extracted with ethyl acetate and concentrated in vaccum. The crude mixture was then subjected to silica gel column chromatography using petroleum ether and CH_2Cl_2 to isolate the pure product.

1.2.6 Spectral Data of Homocoupled Compounds

V1: yield 76% Red solid, **HRMS:** m/z calcd for $C_{36}H_{22}S_2$ ([M^+]): 518.1163; found m/z: 518.1165**;** **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.32 (d, *J* = 7.8 Hz, 2H), 7.76 – 7.71 (m, 6H), 7.57 (s, 2H), 7.43 – 7.23 (m, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.41, 139.71, 139.03, 138.99, 138.84, 136.50, 136.11, 131.11, 128.94, 128.41, 127.13, 127.03, 124.62, 124.57, 120.26, 119.97, 119.75, 118.75, 77.39, 77.07,76.76.

V1-iso: yield 7% Red solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (m, 2H), 7.77 – 7.68 (m, 6H), 7.59 (s 1H), 7.54 (s,1H), 7.42 – 7.25 (m, 10H), 7.17 – 7.11 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.72, 141.26 ,139.84, 138.87, 138.08, 136.22, 135.70, 131.26, 131.24, 131.15, 129,81, 128.80, 128.72, 128.27, 128.18, 128.04, 127.08, 127.05, 126.98, 126.96, 125.90, 125.81, 125.78, 124.56, 123.68, 123.17, 120.23, 120.18, 119.92, 119.89, 119,70, 119.27, 119,11, 77.42, 77.10, 76.78.

V2: yield 71% yellow solid**, HRMS:** m/z calcd for $C_{48}H_{30}S_2$ ([M^+]): 670.1789; found m/z: 670.1724; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.73 – 7.63 (m, 18H), 7.40-7.30 (m, 8H), 7.12 (t, *J* = 7.5 Hz, 2H). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.83 – 7.77 (m, 10H), 7.65 (m, 6H), 7.55 (d, *J* = 3.8 Hz 2H), 7.39 – 7.31 (m, 8H), 7.12 (t, *J* = 7.5 Hz 2H). **^{13}C NMR (101 MHz, $CDCl_3$))**δ 141.42, 139.55, 139.24, 136.71, 136.49, 130.23 ,129.87, 128.78, 128.38, 127.13, 126.83, 126.39, 125.68, 124.51, 123.81, 120.37, 119.89, 119.89, 77.42, 77.10, 76.78

V3: yield 71 % Red solid**, HRMS:** m/z calcd for $C_{44}H_{26}S_4$ ([M^++H]): 683.0990; found m/z: 683.0999**;** **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 7.8 Hz, 2H), 7.75-7.70 (m, 6.19H), 7.55 (s, 2H), 7.40 – 7.31 (m, 11.23H), 7.22 (d, *J* = 3.8 Hz, 2H), 7.18 (d, *J* = 3.8 Hz, 2H), 7.14

(d, J = 3.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.37, 139.97, 139.71, 138.95, 138.47, 136.07 ,131.10, 128.88, 128.33, 127.03, 124.54, 120. 23, 119.93, 119.72, 118.53, 77.39, 77.08, 76.76

V4: yield 65 % Red solid**, HRMS**: m/z calcd for $C_{36}H_{22}O_2$ ([M^+]): 486.1620; found m/z: 486.1624**; ^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.75 (d, J = 7.8 Hz, 2H), 7.72-7.67 (m, 8H), 7.46 - 7.23 (m, 8H), 7.0 (d, J = 4 Hz, 2H), 6.8 (d, J = 3.6 Hz, 2H). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.69 (d, J = 7.8 Hz, 2H), 7.98 – 7.93 (m, 2H), 7.92 – 7.83 (m, 4H), 7.69 (s, 2H), 7.38 – 7.31 (m, 6H), 7.25 (m, 6H), ^{13}C NMR data was not obtained due to the poor solubility of the compound.

C1: yield 78% Red solid, **HRMS:** m/z calcd for $C_{26}H_{16}N_2S_2H$ ([M+H]): 421.0828; found m/z: 421.0830**; ^{1} H NMR (400 MHz, DMSO-d_6)** δ 8.27 (s, 2H), 7.72-7.70 (m, 6H), 7.62 (m, 2H), 7.47 (m,4H), 7.41 (m, 2H); ^{13}C NMR data was not obtained due to the poor solubility of the compound.

C2: yield 69% yellow solid, **HRMS**: m/z calcd for $C_{38}H_{24}N_2S_2H$ ([M+H]): 573.1454; found m/z: 573.1459; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89-7.85 (m, 4H), 7.7-7.6 (m, 8H), 7.48-7.28 (m, 12H**). ^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.92 (m, 6H), 7.8-7.7 (m, 6H), 7.48 (m 12H) **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.30, 135.26, 134.53, 130.61, 130.10, 130.23, 129.19, 126.06, 125.41, 125.13, 124.58, 118.18, 111.29, 77.40, 77.09, 76.77.

C3: yield 66% Red solid, **HRMS**: m/z calcd for $C_{34}H_{20}N_2S_4$([M^+]): 584.0509; found m/z: 584.0518; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.6 (m, 9H), 7.4 (m, 9H) 7.1 (m 2H). **^{1} H NMR (400 MHz, DMSO-d_6)** 8.2 (s 2H), 7.72 (m 7.37H), 7.5-7.4 (m, 7.49H), 7.4 (m 4.14H); ^{13}C NMR data was not obtained due to the poor solubility of the compound.

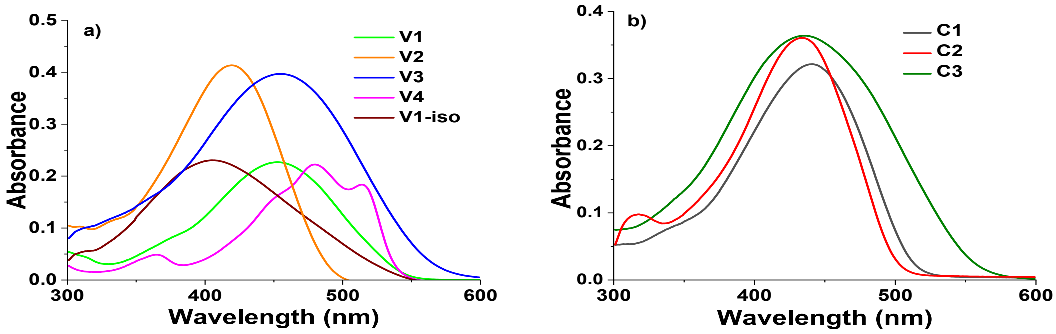


Figure S1: The solution state UV-visible absorption spectra of vinylene- and cyanovinylene-oligothiophenes ($1x10^{-5}M$, $CHCl_3$).

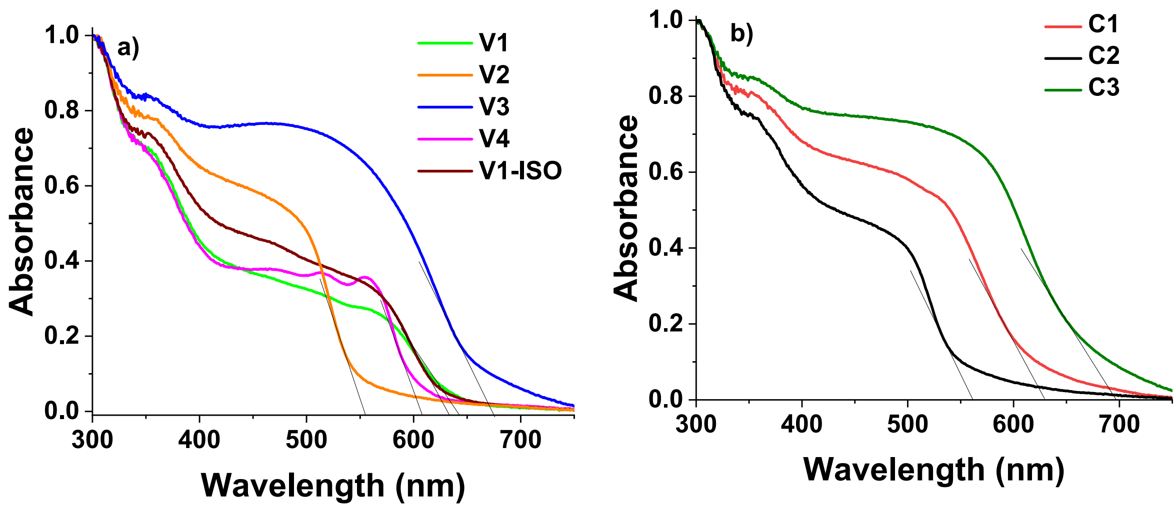


Figure S2: The solid state UV-visible absorption spectra of vinylene- and cyanovinylene-oligothiophenes

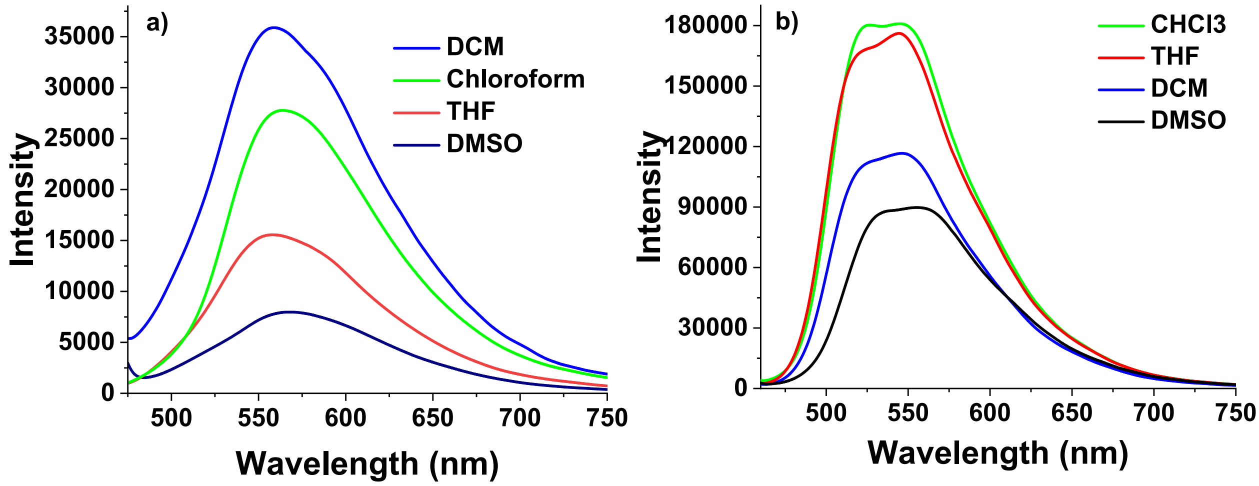


Figure S3: Solution state emission spectra of **V1** and **C1** in different solvent.

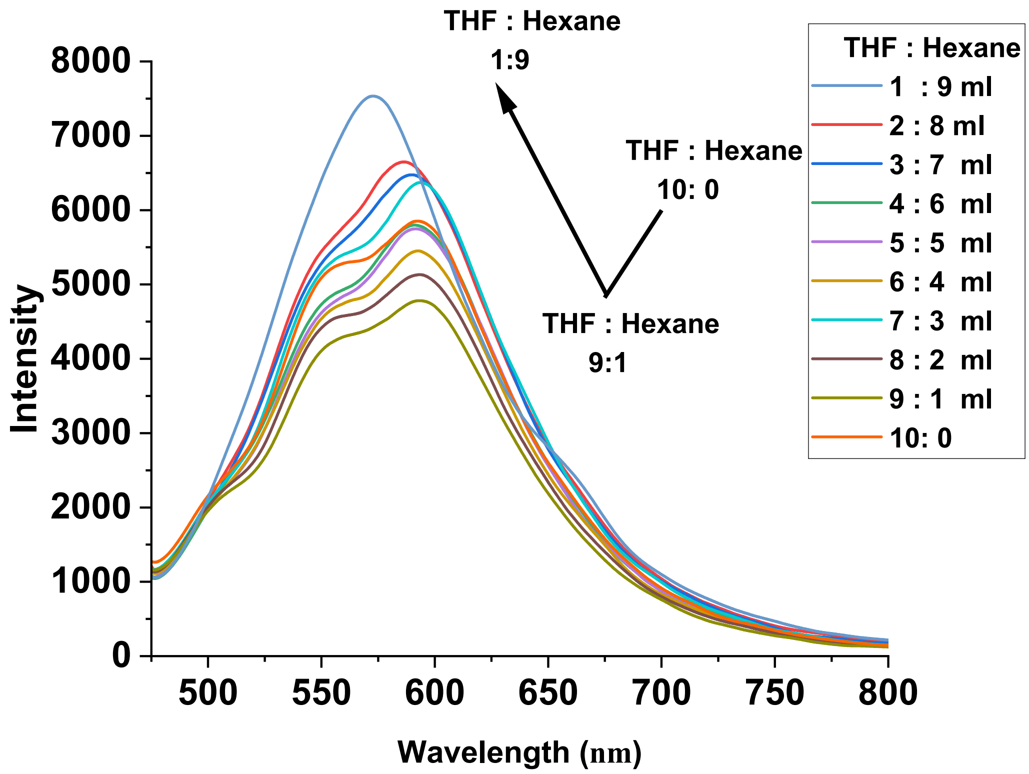


Figure S4: Aggregation Induced Emission experiment of compound **V1**

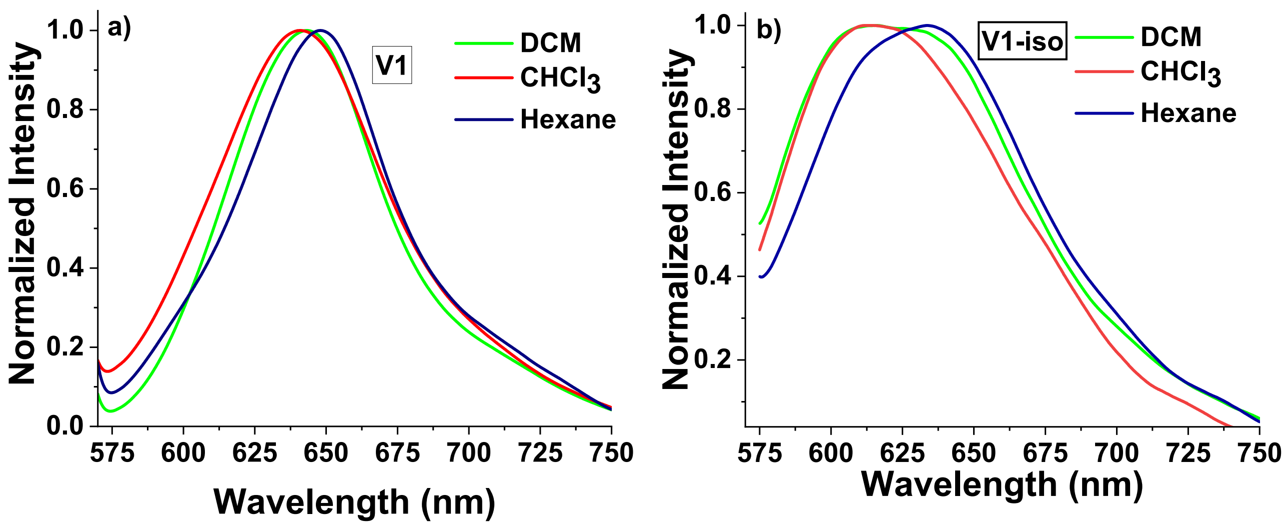


Figure S5: Solid state emission spectra of different solvents recrystallized (a) **V1** and (b) **V1-iso**

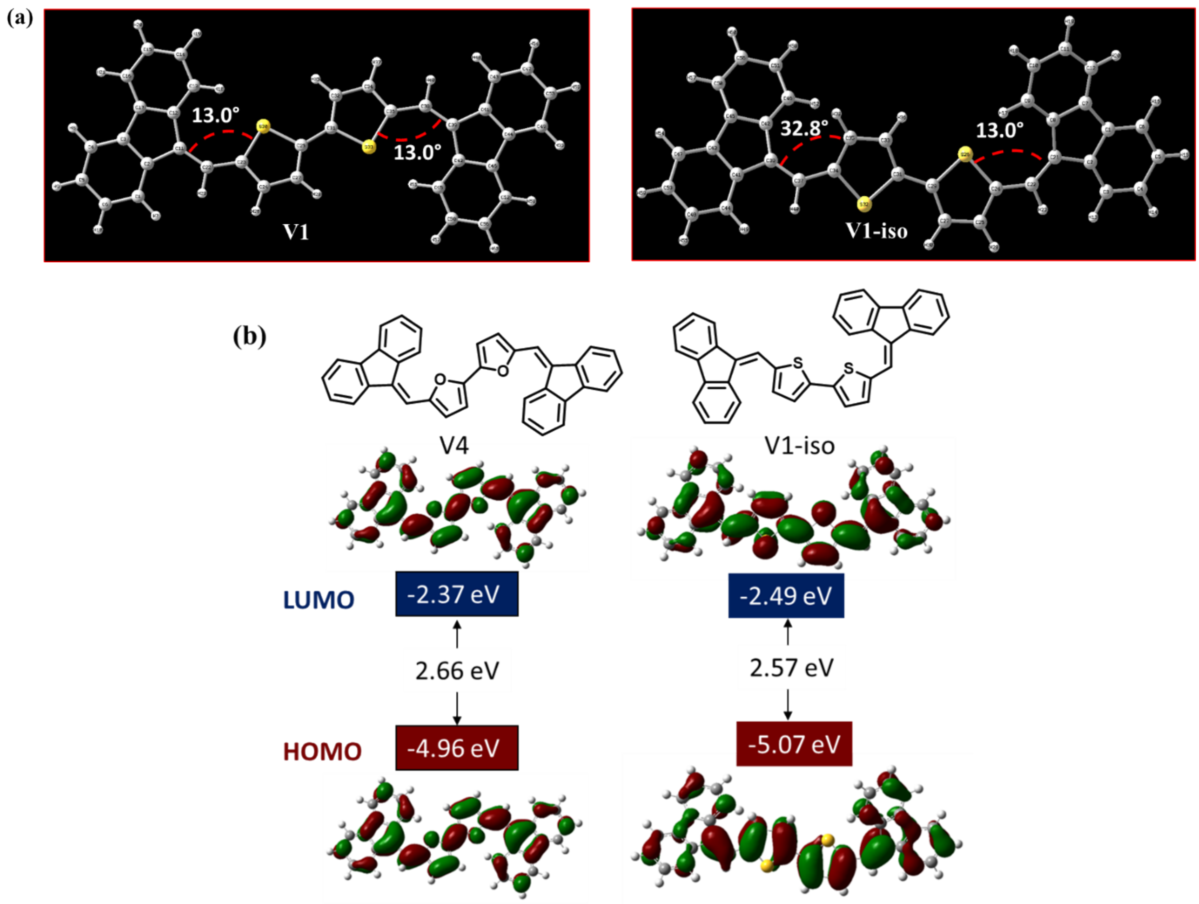
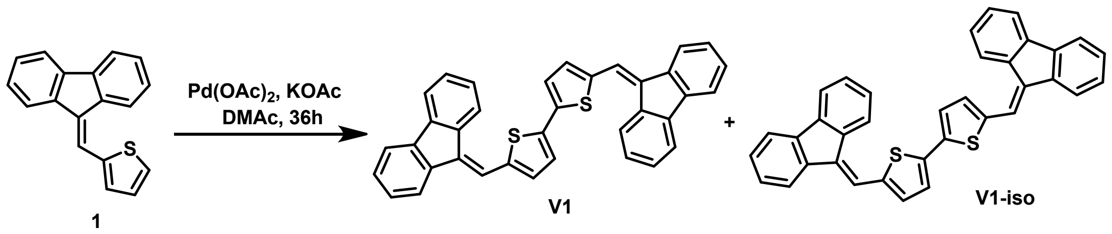


Figure S6: a) DFT optimized structures of **V1** and **V1-iso**; b) DFT calculated frontier orbitals and the energy levels of Vinyl Furan (**V4**) and Vinyl Thiophene isomer (**V1-iso**)

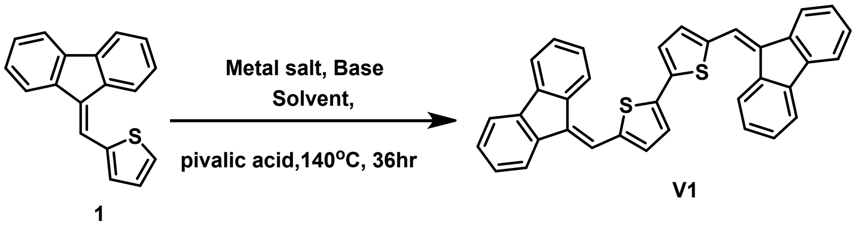
Table S1: Optimization of reaction condition of thiophene homocoupling*



Entry	Catalyst	Ligand	Acid	Base	Additive	Solvent	Yields		Temp.
							V1	**V1-iso**	
1	$Pd(OAc)_2$	PPh_3	Pivalic Acid	KOAc	-	DMAc	12%	NP	120°C
2	$Pd(OAc)_2$	-	-	KOAc	-	DMAc	40%	NP	120°C
3	$Pd(OAc)_2$	-	-	-	AgOAc	DMAc	30%	10%	120°C
4	$Pd(OAc)_2$	-	Pivalic acid	KOAc	-	DMAc	65%	traces	120°C
5	$Pd(OAc)_2$	-	TFA	KOAc	-	DMAc	5%	NP	140°C
6	$Pd(OAc)_2$		Pivalic acid	KOAc	-	DMAc	76%	7%	140°C
7	$Pd(OAc)_2$	-	Pivalic Acid	KOAc	-	DMF	20%	NP	140°C

*Reaction conditions: substrate (1.92 mmol, 1eq), catalyst (5 mol%), ligand (0.38 mmol, 0.2eq), Acid (0.29 mmol, 0.15eq), Base (9.6 mmol, 5eq), Additive (3.84 mmol, 2eq) and DMAc-3ml.

Table S2: Optimization of Reaction conditions*



Entry	Catalyst	Base	solvent	Yields
1	$Pd(OAc)_2$	KOAc	HFIP	5%
2	$PdCl_2(PPh_3)_2$	KOAc	DMAc	5%
3	$PdCl_2$	KOAc	DMAc	67%
4	$Pd_2(dba)_3$	KOAc	DMAc	10%
5	$Pd(OAc)_2$	Na_2CO_3	DMAc	69%
6	$Pd(OAc)_2$	K_2CO_3	DMAc	70%
7	$Ni(dppf)Cl_2$	KOAc	DMAc	~5%
8	$Ni(pcy_3)Cl_2$	KOAc	DMAc	~5%
9	$Pd(OAc)_2$	KOAc	Toluene	~5%
10	$Pd(OAc)_2$	KOAc	dioxane	~4%
11	$Pd(OAc)_2$	KOAc	DMSO	52%

*Reactions conditions: substrate (1.92 mmol, 1eq), catalyst (5 mol%), Base (9.6 mmol, 5eq), Additive and Solvent-3ml.

Table S3: The optical and the DFT data of the compounds

comp	Abs		Emission		QY (Ø)		DFT		Calculated Band Gap
	Solution* [Extinction coefficient (10^7), $ε_o$($M^{-1}cm^{-1}$)]	Solid	Solution CHCl$_3$ (10^{-5}M)	Solid	Solution	Solid	HOMO	LUMO	
V1	453 (4.5)	557	559	643	0.3%	10%	-5.05	-2.56	2.49
V1-ISo	407 (4.1)	560	577	650	0.8%	9%	-2.49	-5.08	2.57
V2	419 (4.2)	485	522	566	70%	~1%	-5.09	-2.21	2.87
V3	455 (4.6)	533	602	655	2%	4%	-4.91	-2.56	2.34
V4	482 (4.8), 515 (5.1)	515, 554	540,568	620	3%	6%	-4.97	-2.39	2.58
C1	440 (4.4)	531	544	625	2%	~1%	-5.39	-2.82	2.56
C2	433 (4.3)	488	513	596	5%	~1%	-5.26	-2.63	2.62
C3	436 (4.4)	558	577	647	4%	~1%	-5.11	-2.76	2.35

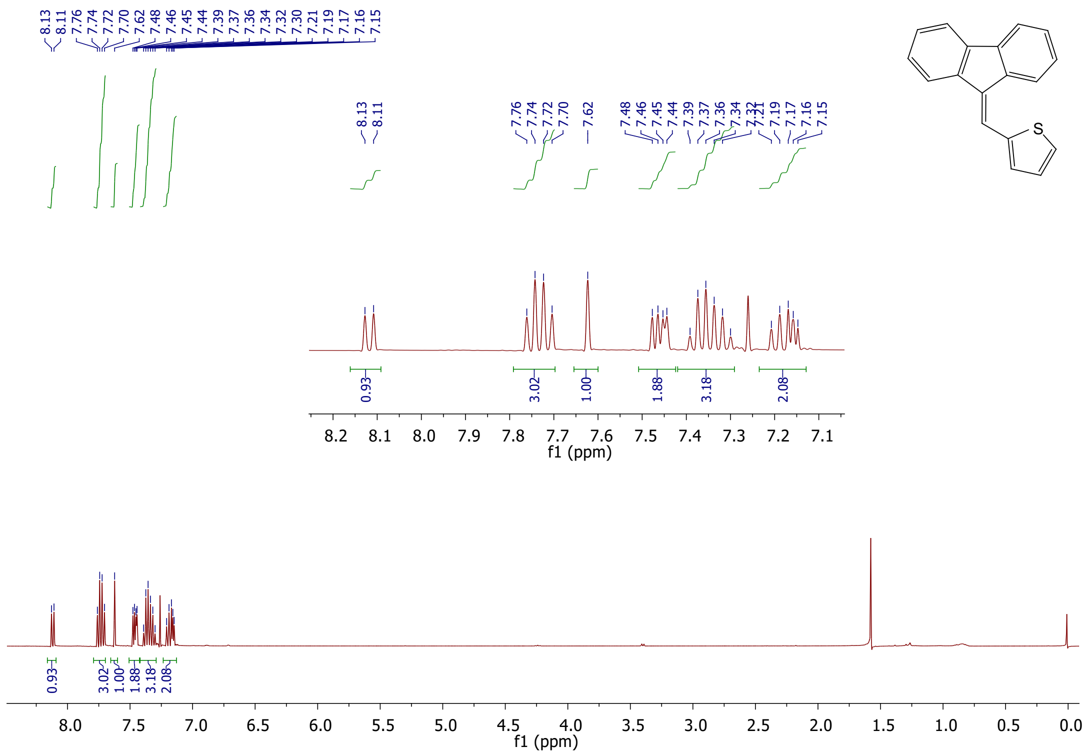


Figure S7: ^{1}H NMR of Compound **1**

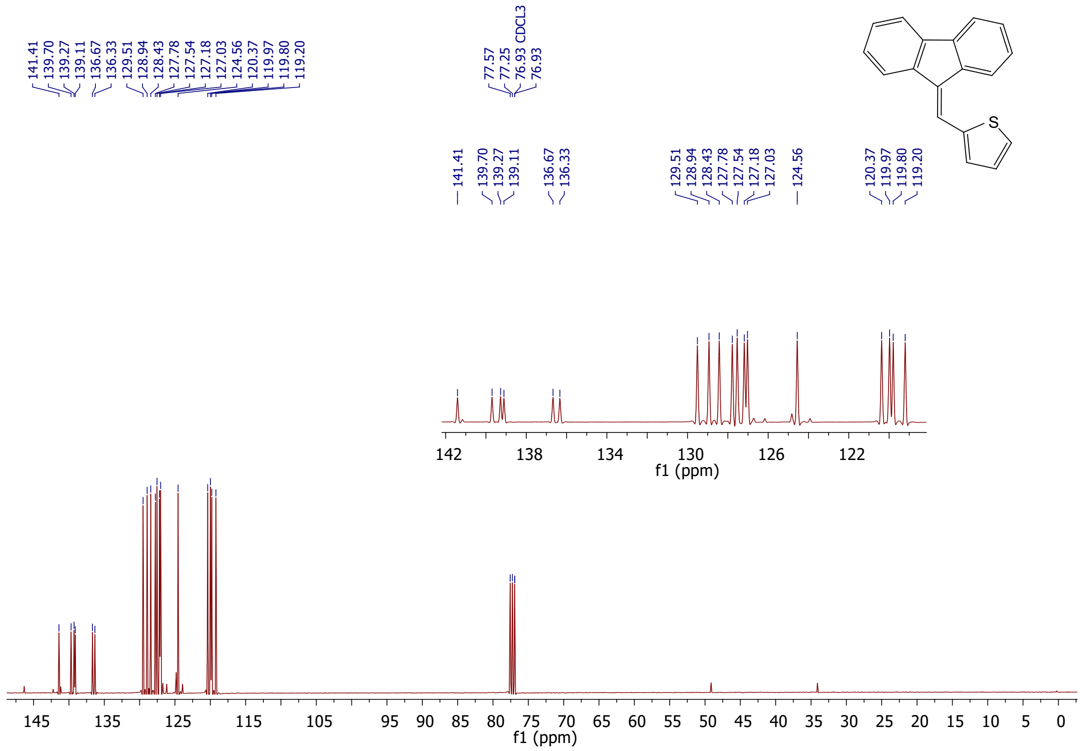
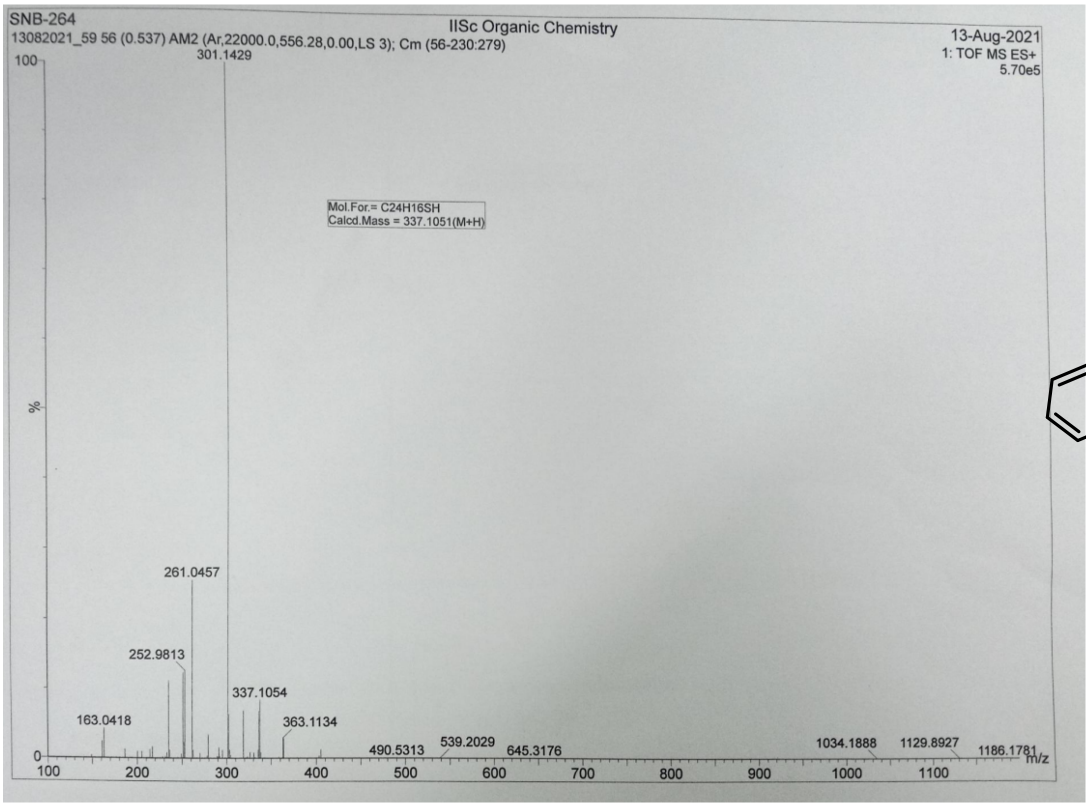


Figure S8: ^{13}C NMR of Compound **1**



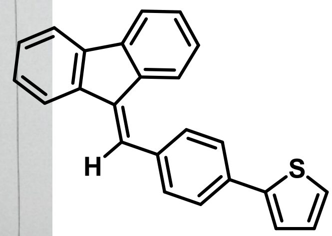


Figure S9: HRMS of Compound **2**

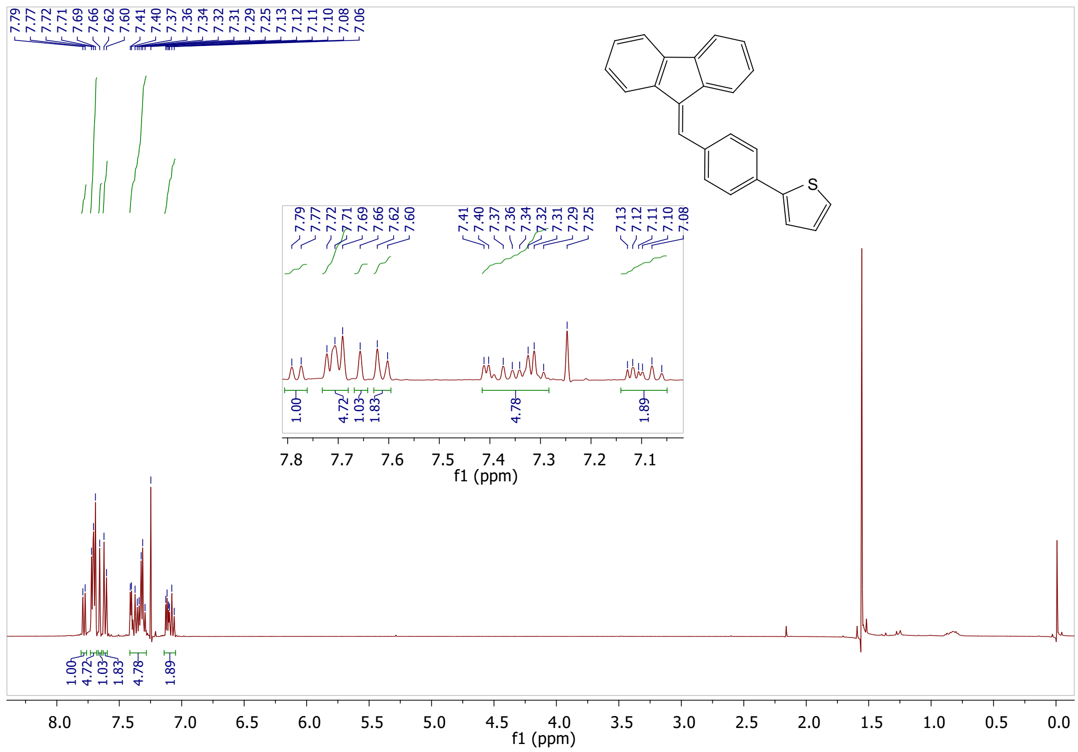


Figure S 10:[1]H NMR of Compound **2**

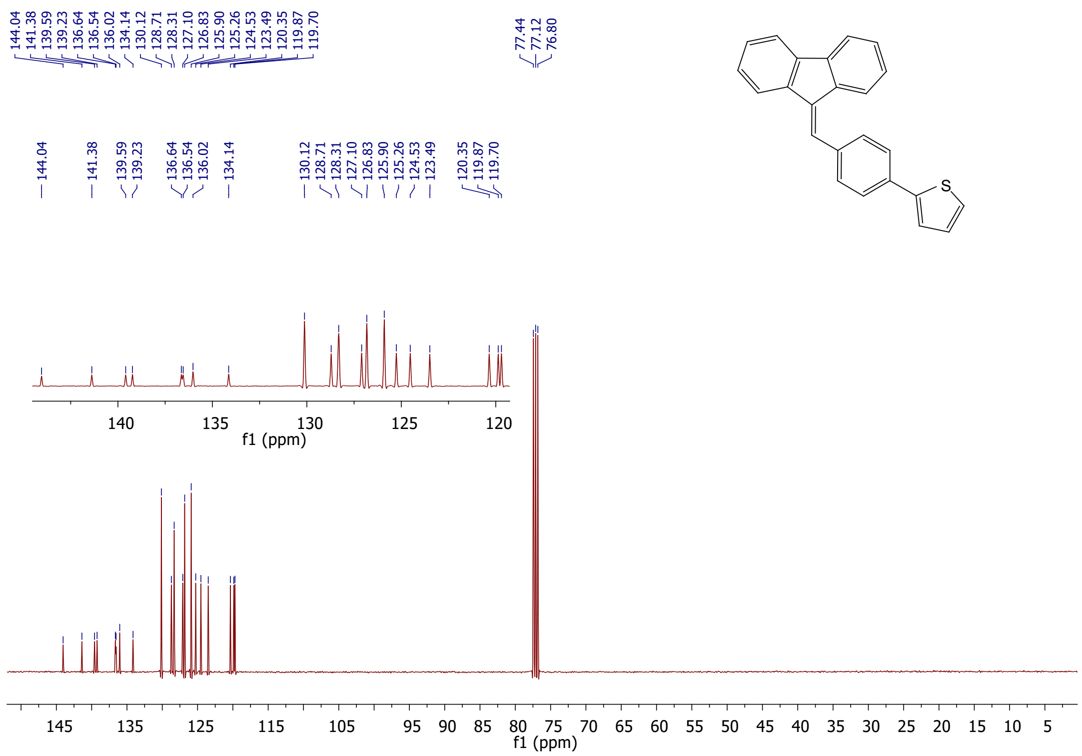


Figure S11: ^{13}C NMR of Compound **2**

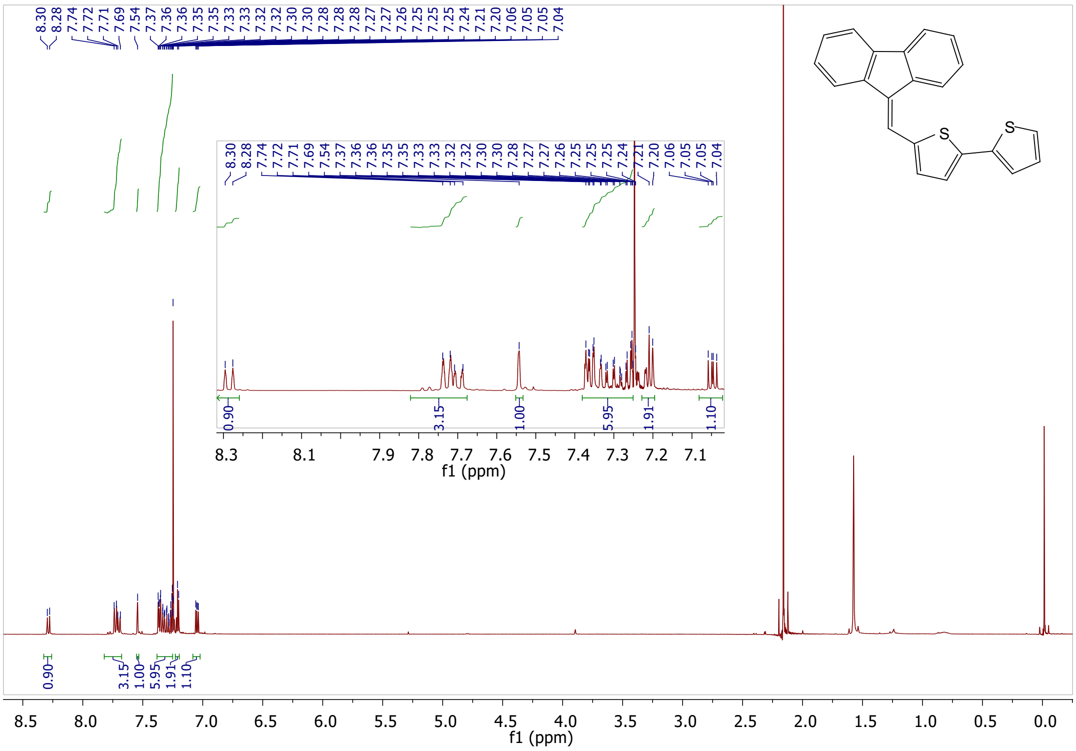


Figure S12: ^{1}H NMR of Compound **3**

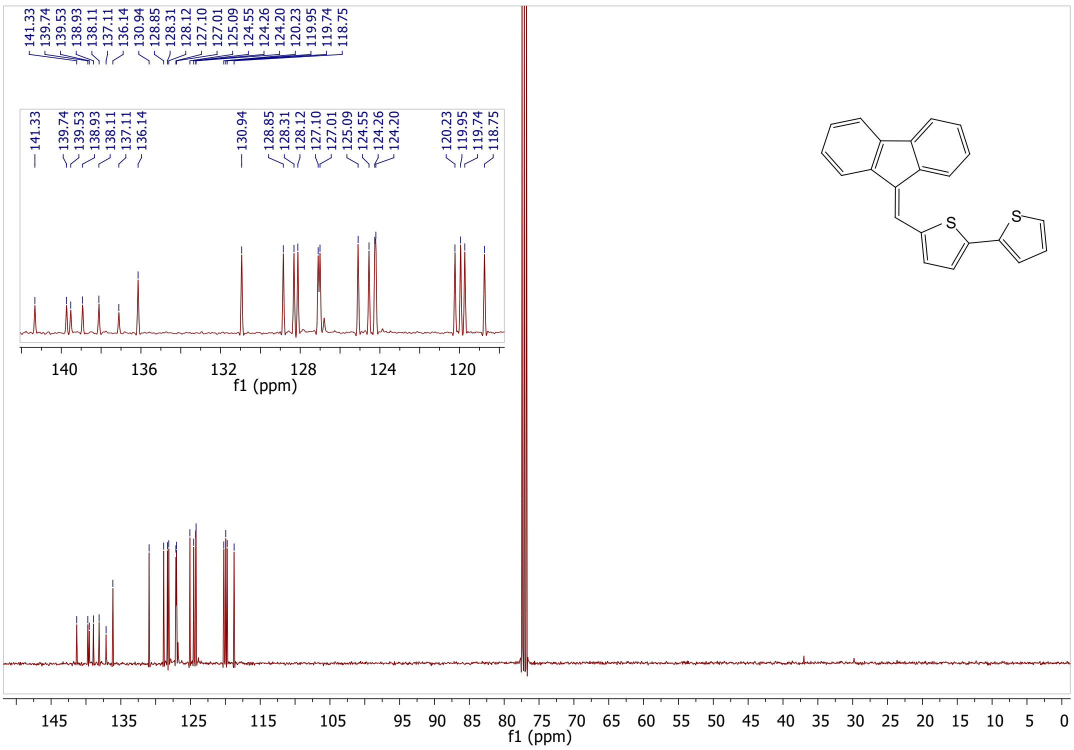


Figure S13: ^{13}C NMR of Compound **3**

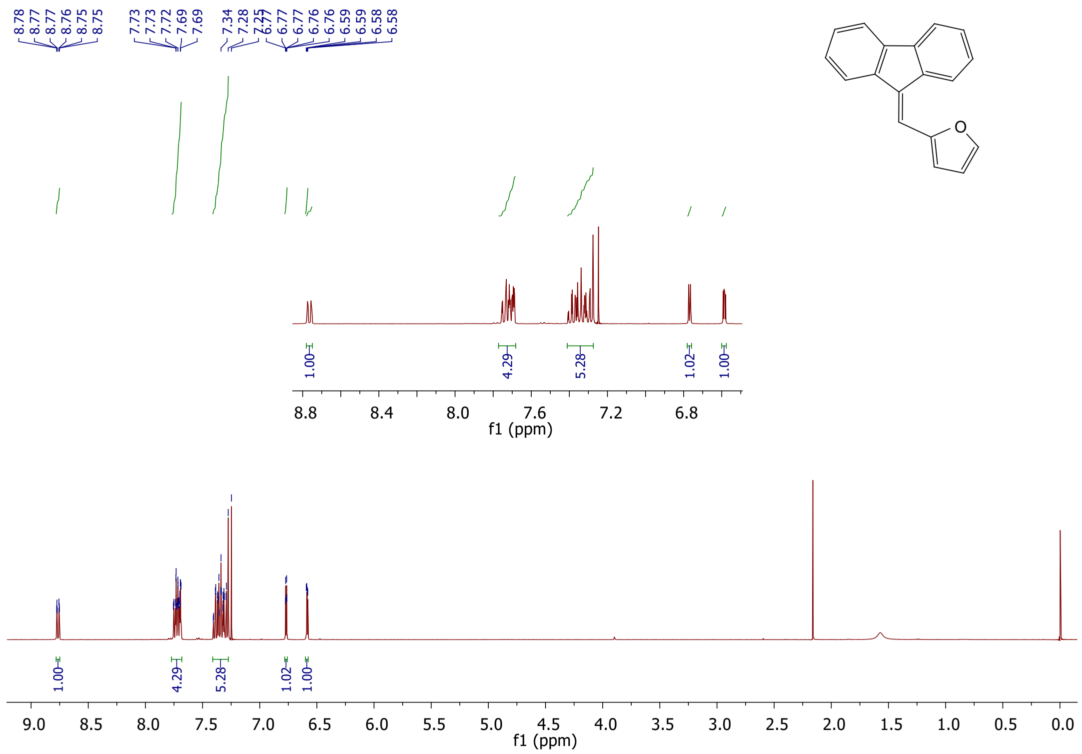


Figure S14: ^{1}H NMR of Compound **4**

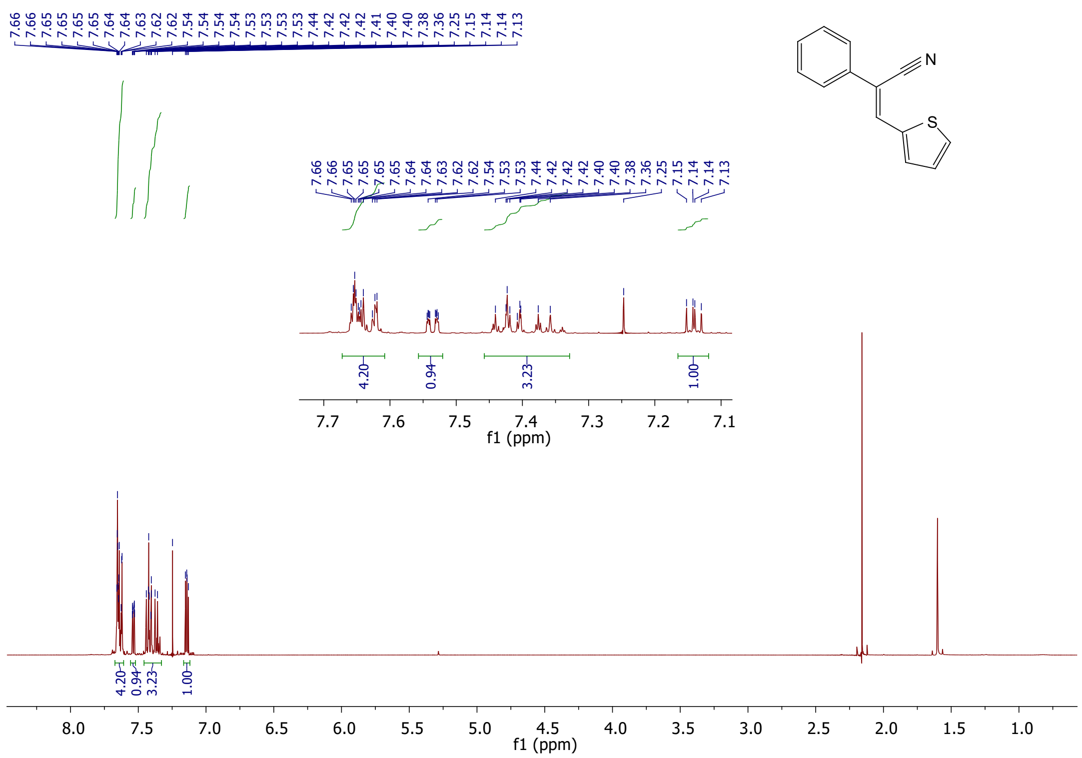


Figure S15: ^{1}H NMR of Compound **5**

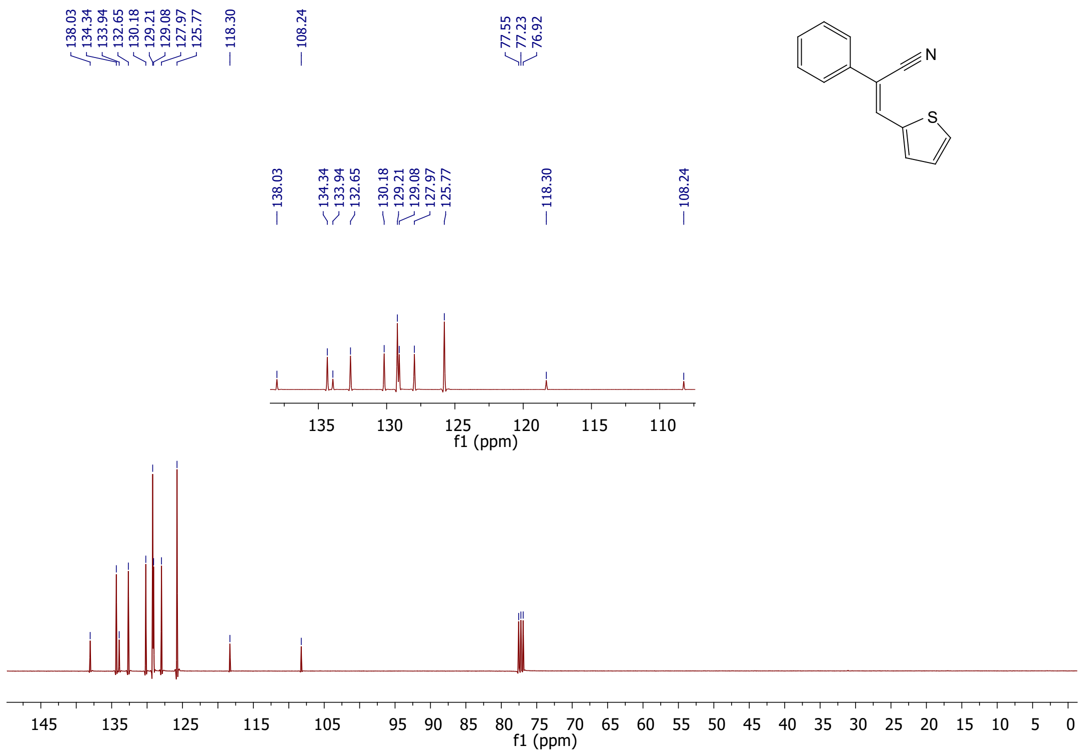
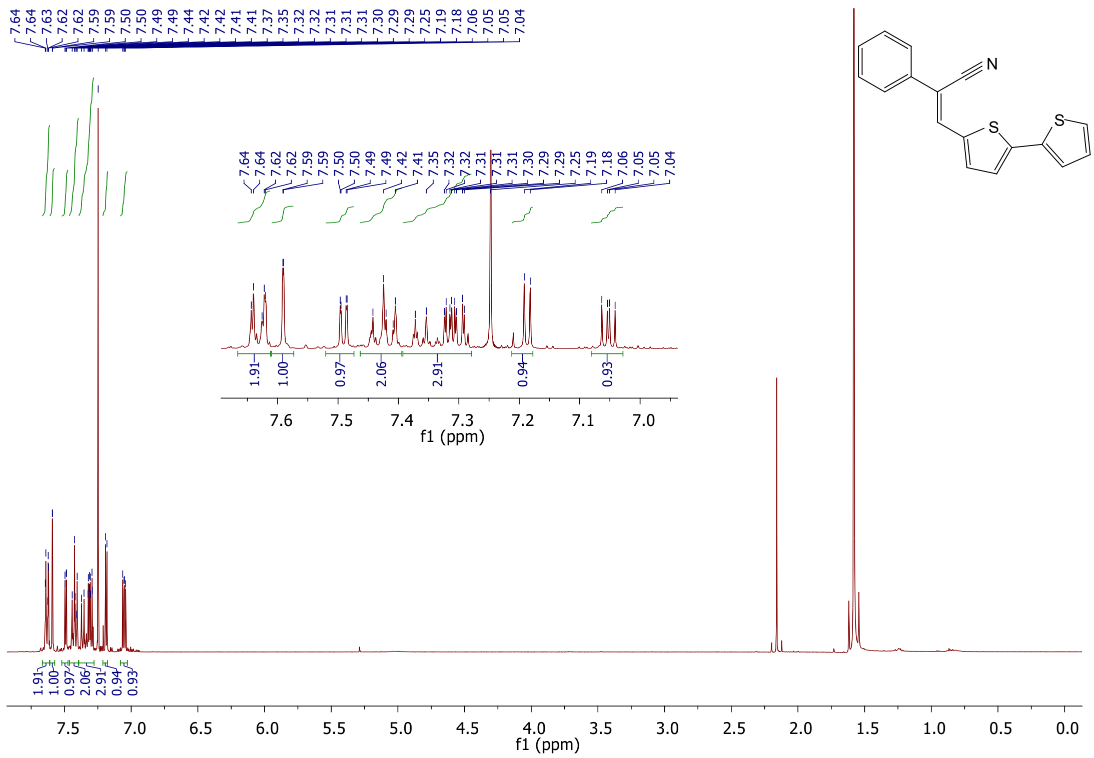


Figure S16: ^{13}C NMR of Compound **5**



Figur

e S17: ^{1}H NMR of Compound **6**

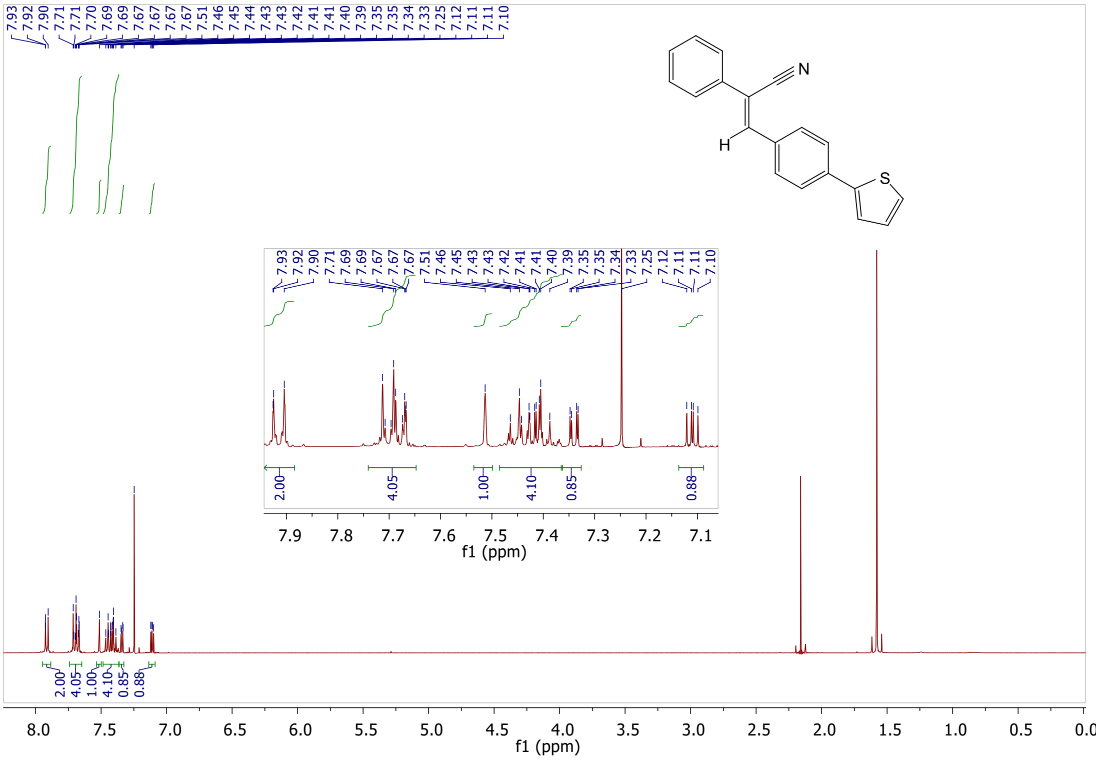


Figure S18: ^{1}H NMR of Compound **7**

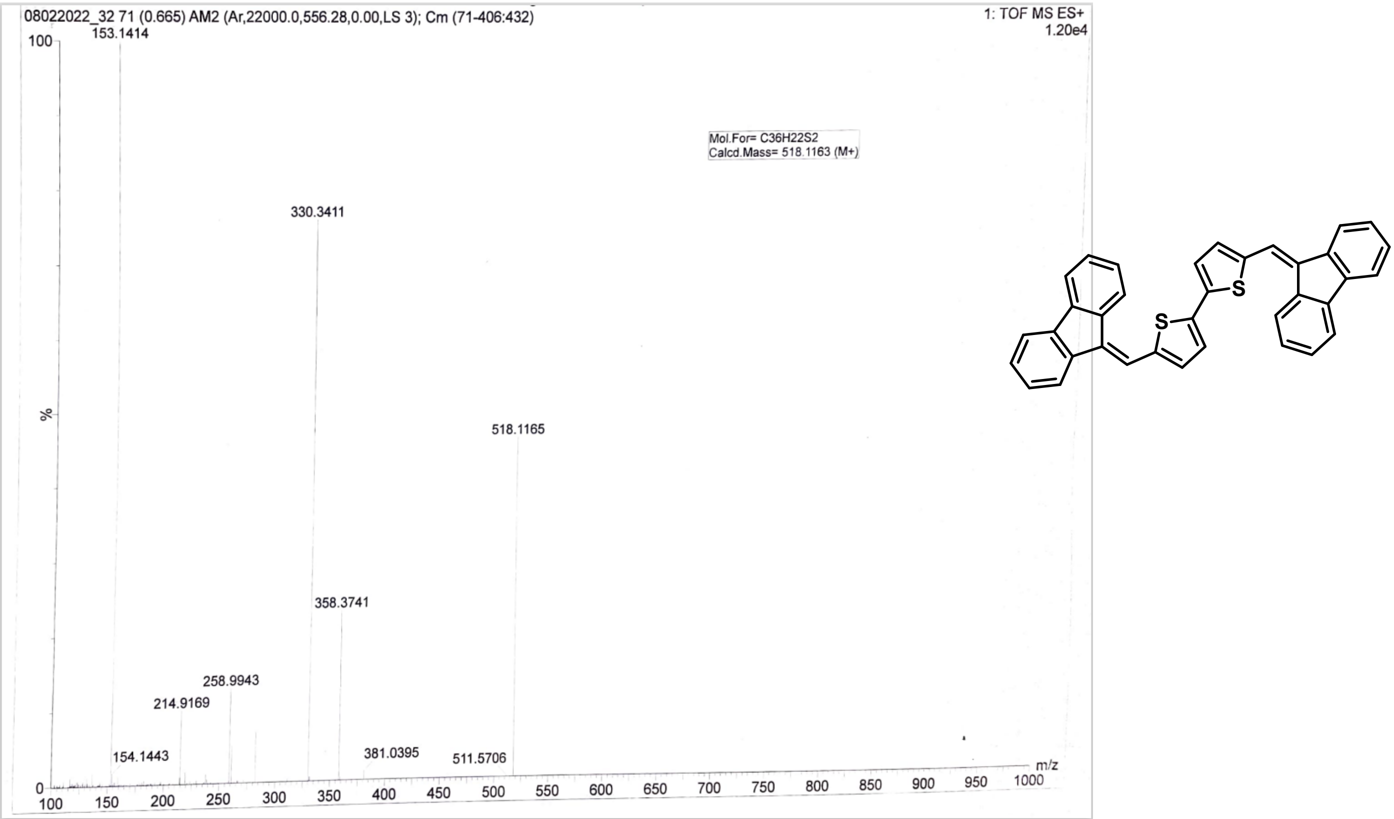


Figure S19: HRMS of Compound **V1**

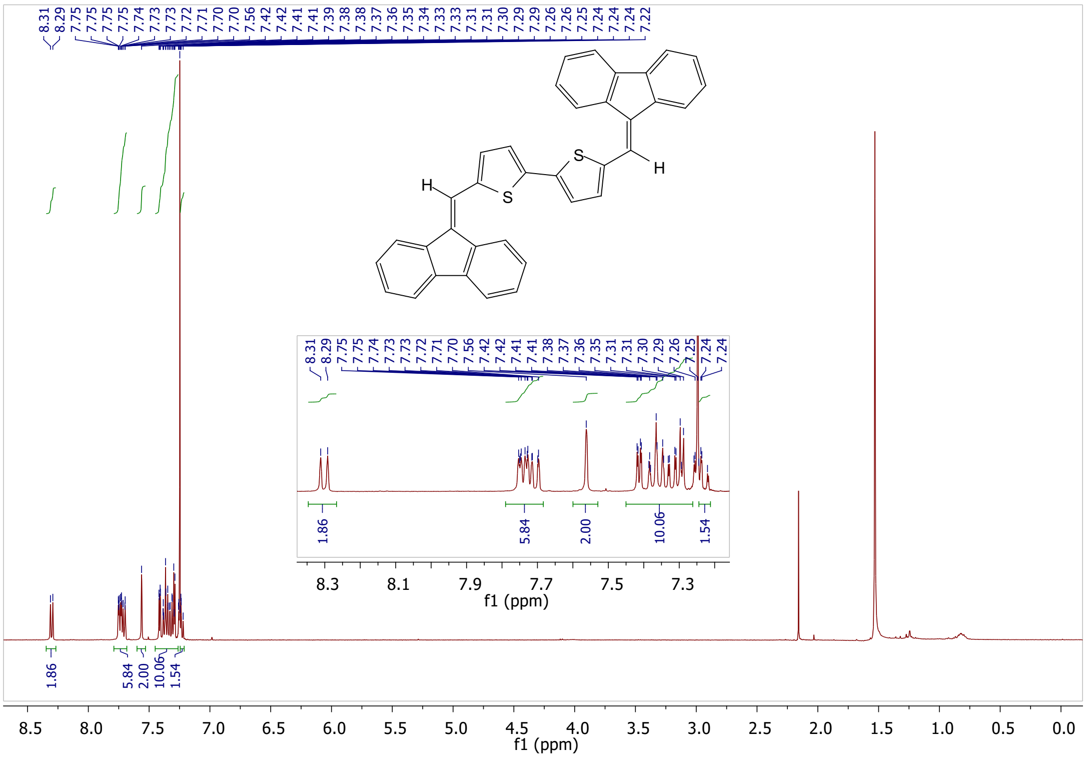


Figure S20: ^{1}H NMR of Compound **V1**

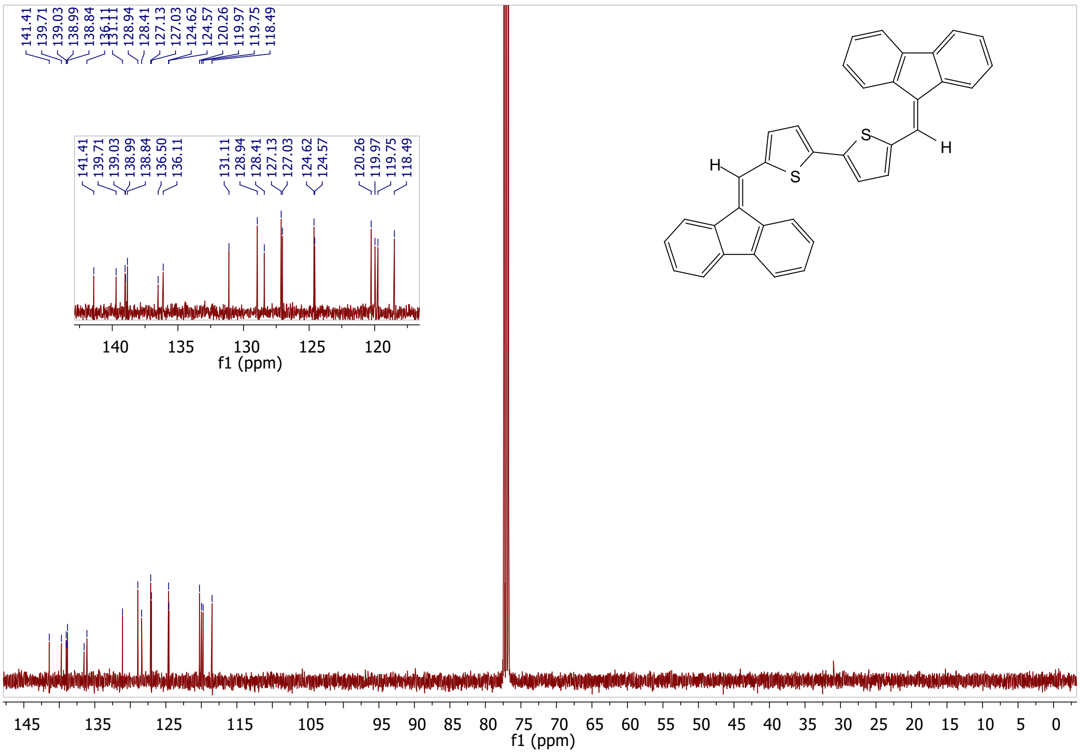


Figure S21: ^{13}C NMR of Compound **V1**

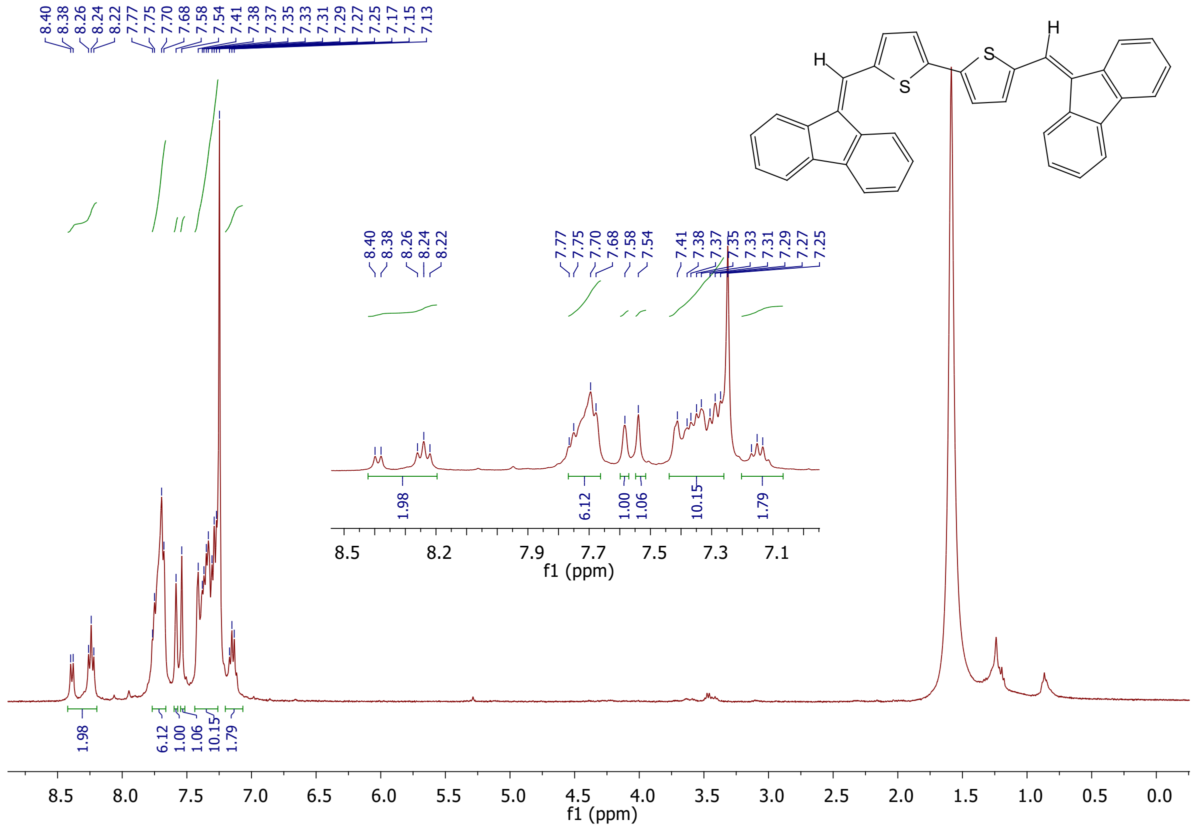


Figure S22: ¹H NMR of Compound **V1-iso**

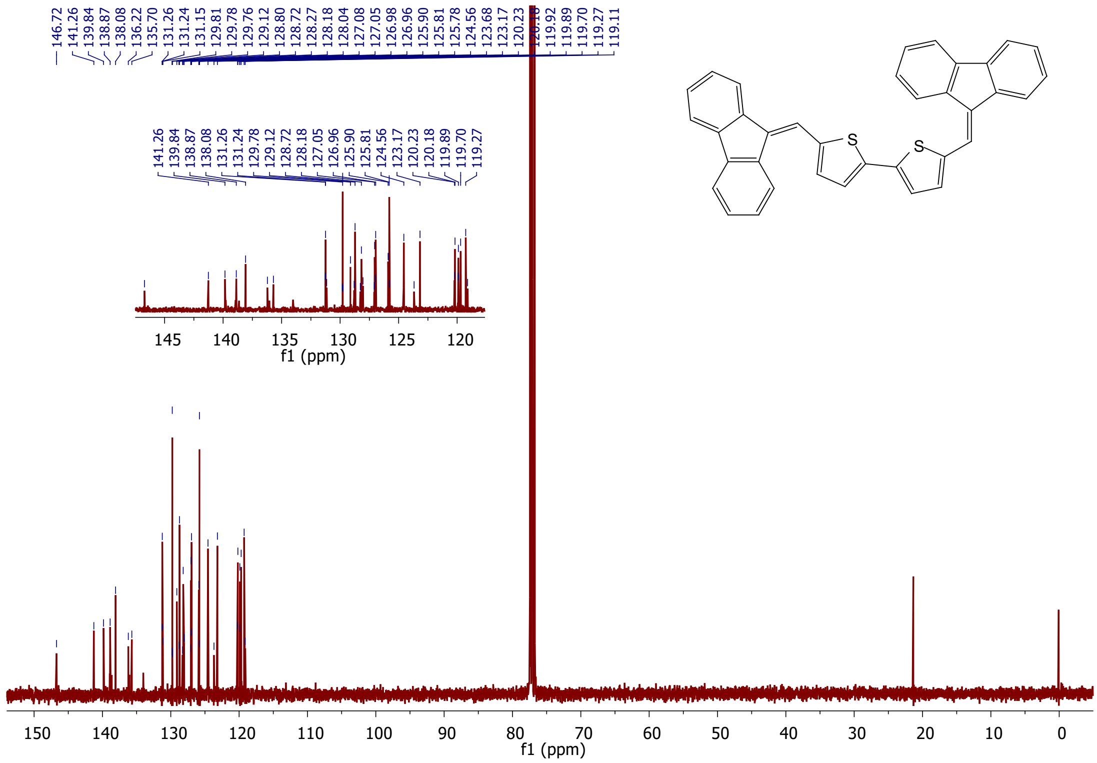


Figure S23: ¹³C NMR of Compound **V1-iso**

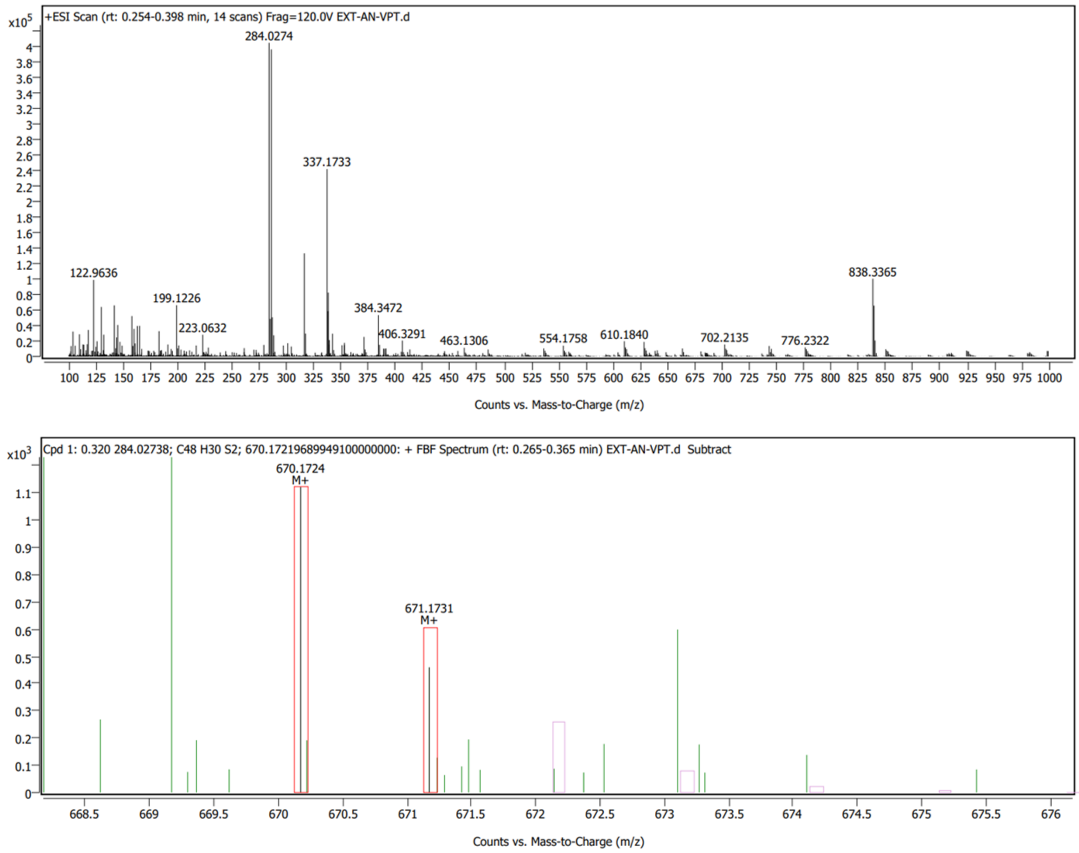


Figure S24: HRMS of Compound **V2**

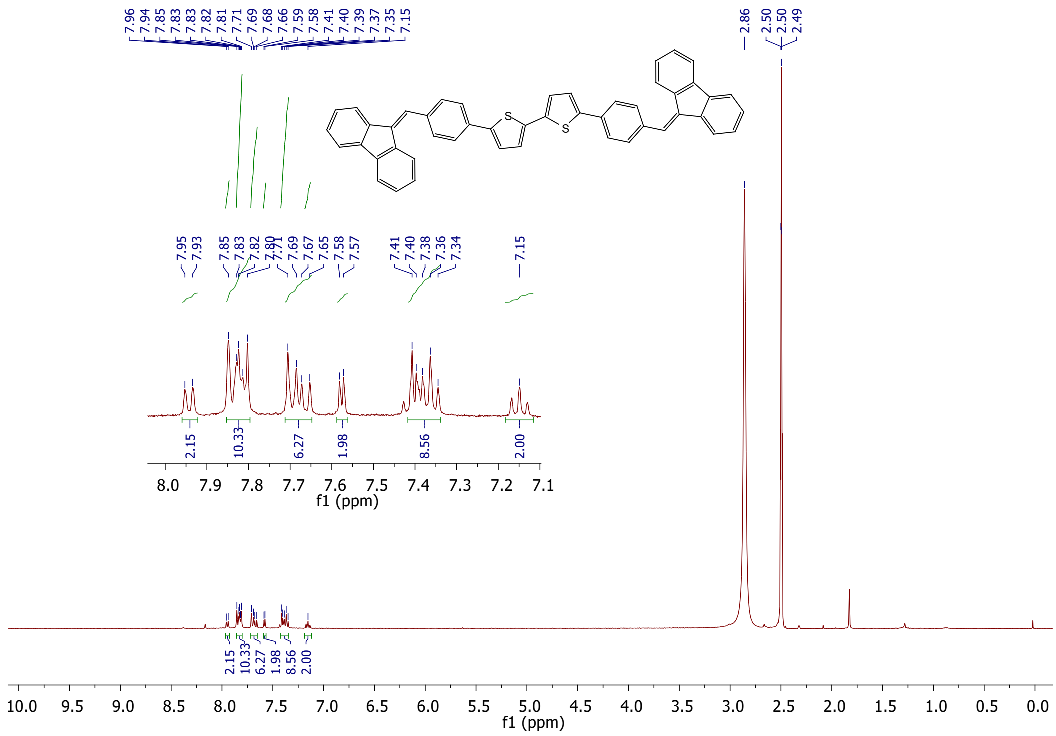


Figure S25: ^{1}H NMR of Compound **V2**

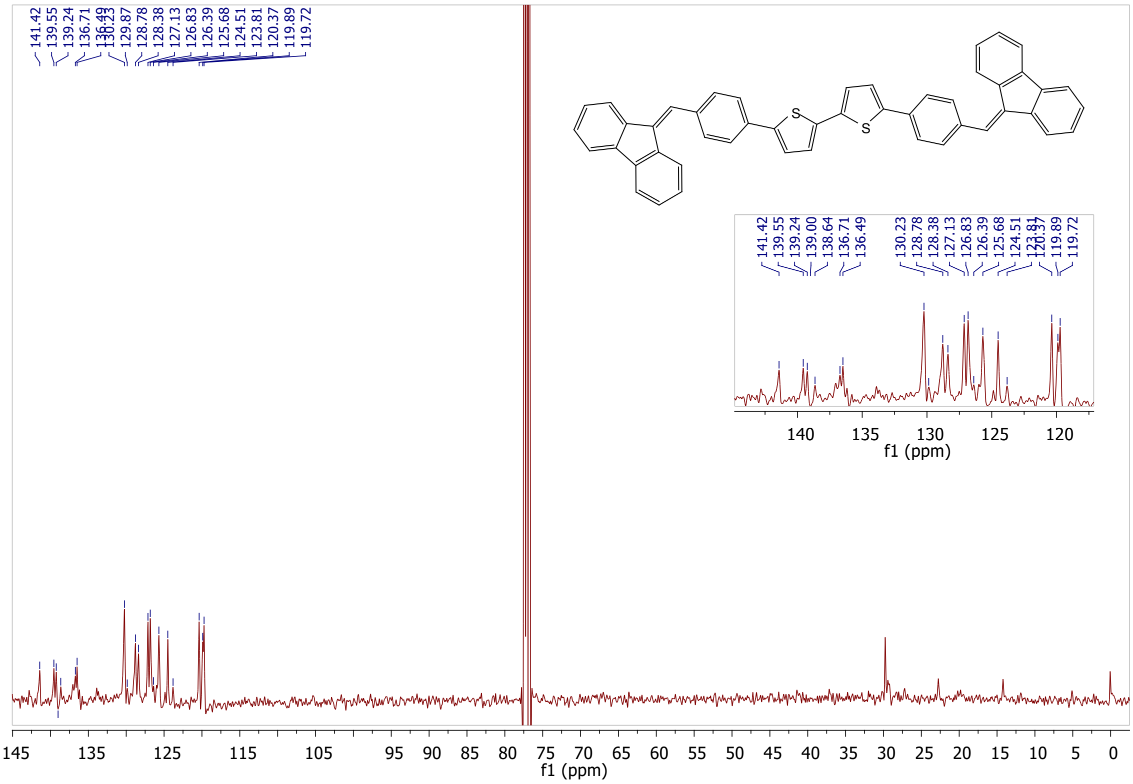


Figure S26: ^{13}C NMR of Compound **V2**

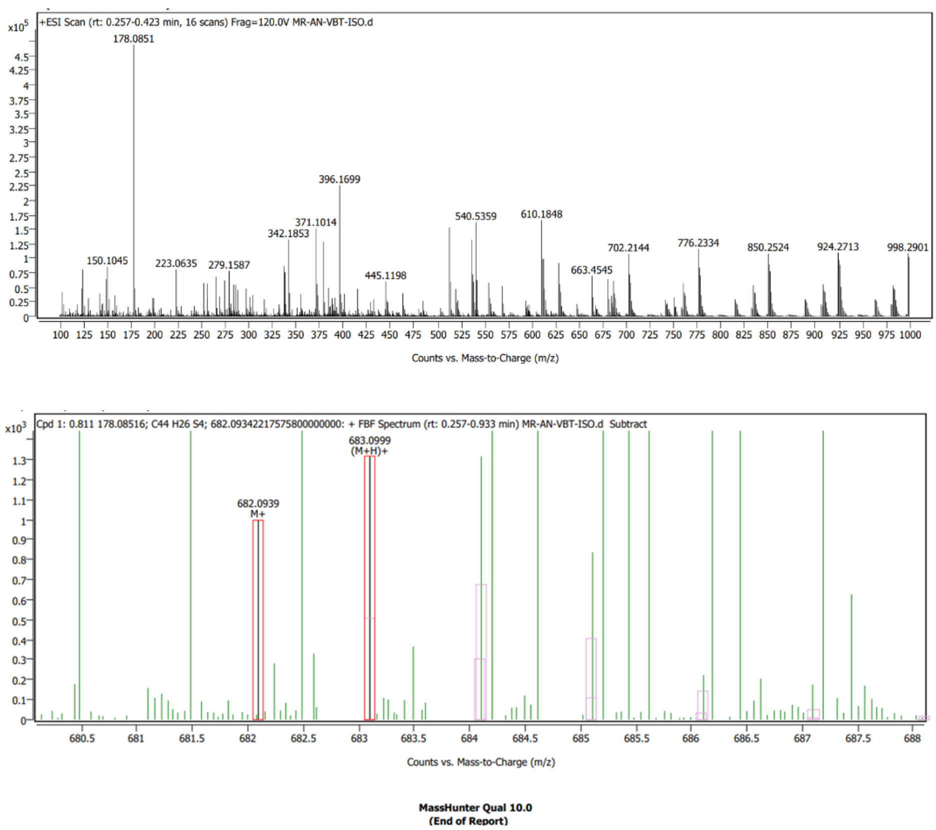


Figure S27: HRMS of Compound **V3**

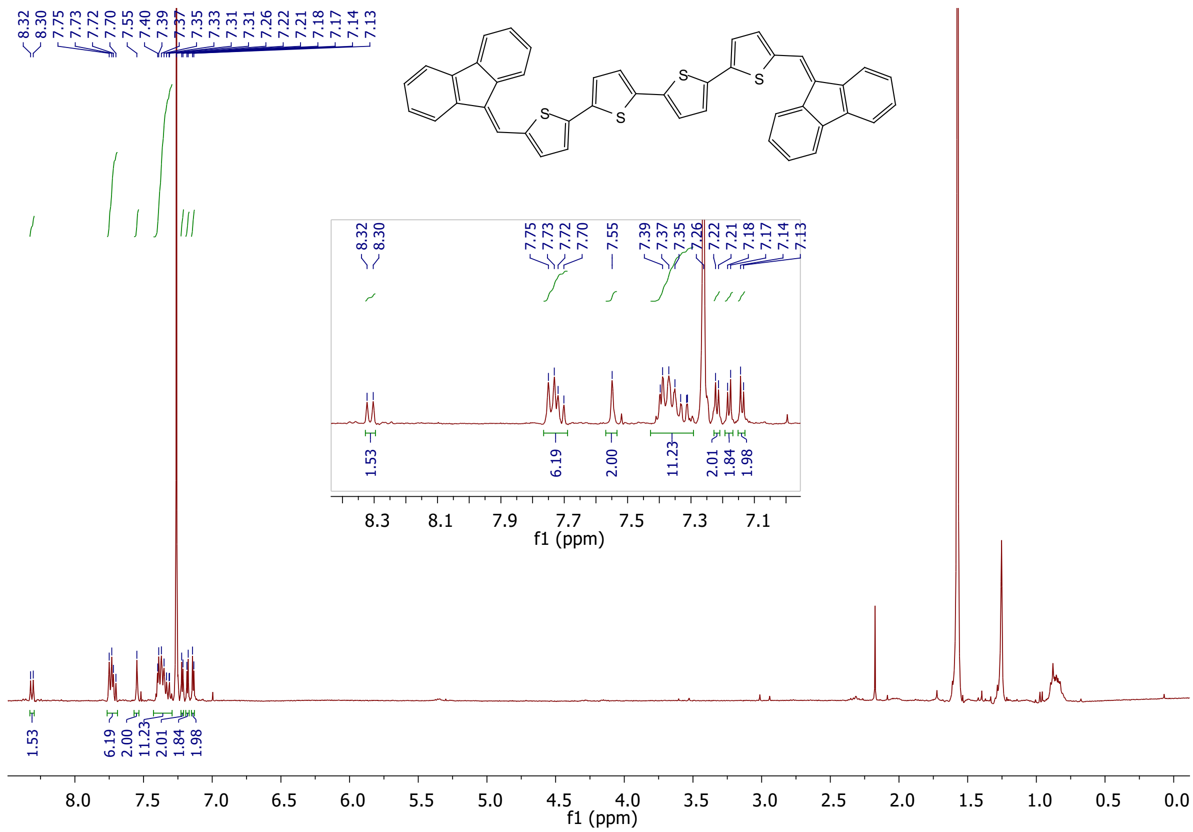


Figure S28: ^{1}H NMR of Compound **V3**

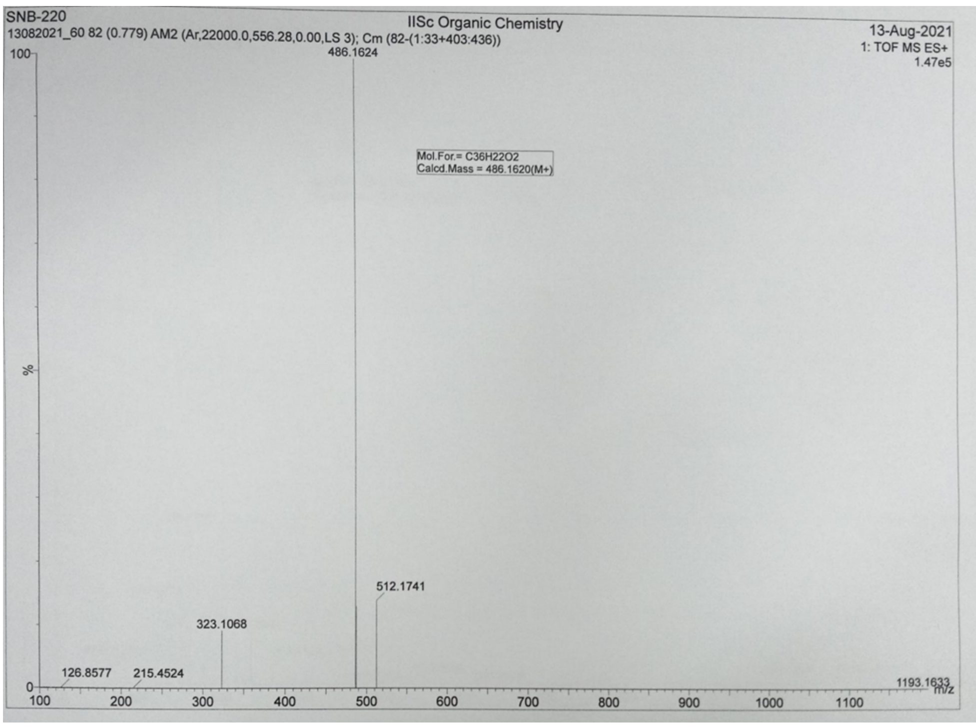


Figure S29: HRMS of Compound **V4**

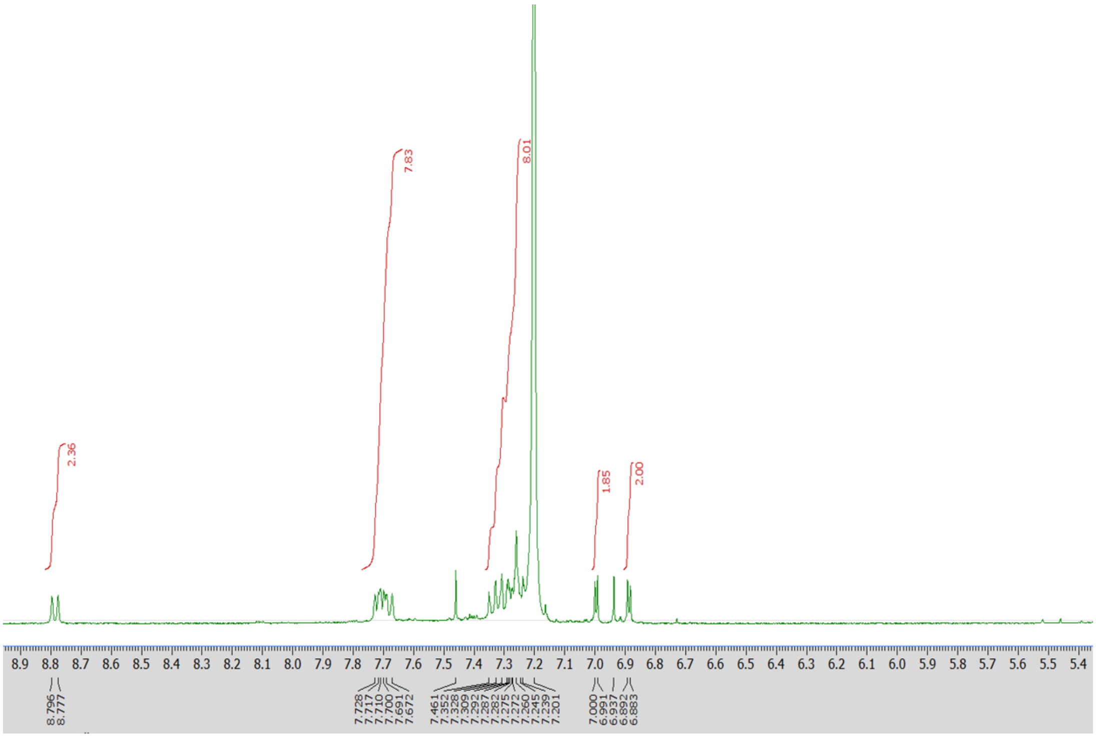


Figure S30: ^{1}H NMR of Compound **V4**

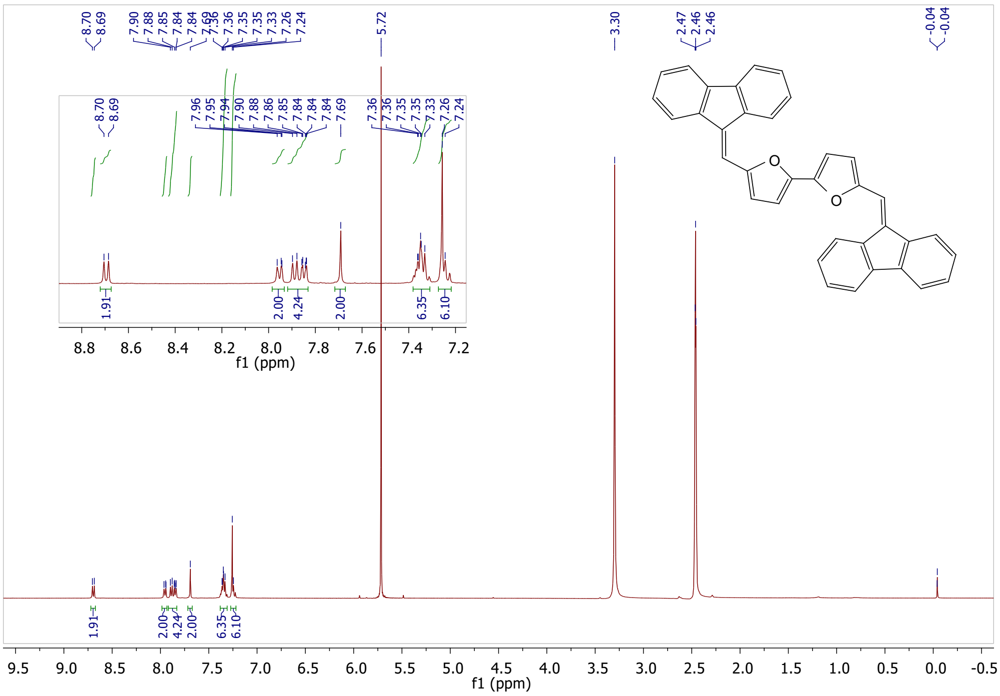


Figure S31: ^{1}H NMR of Compound **V4**

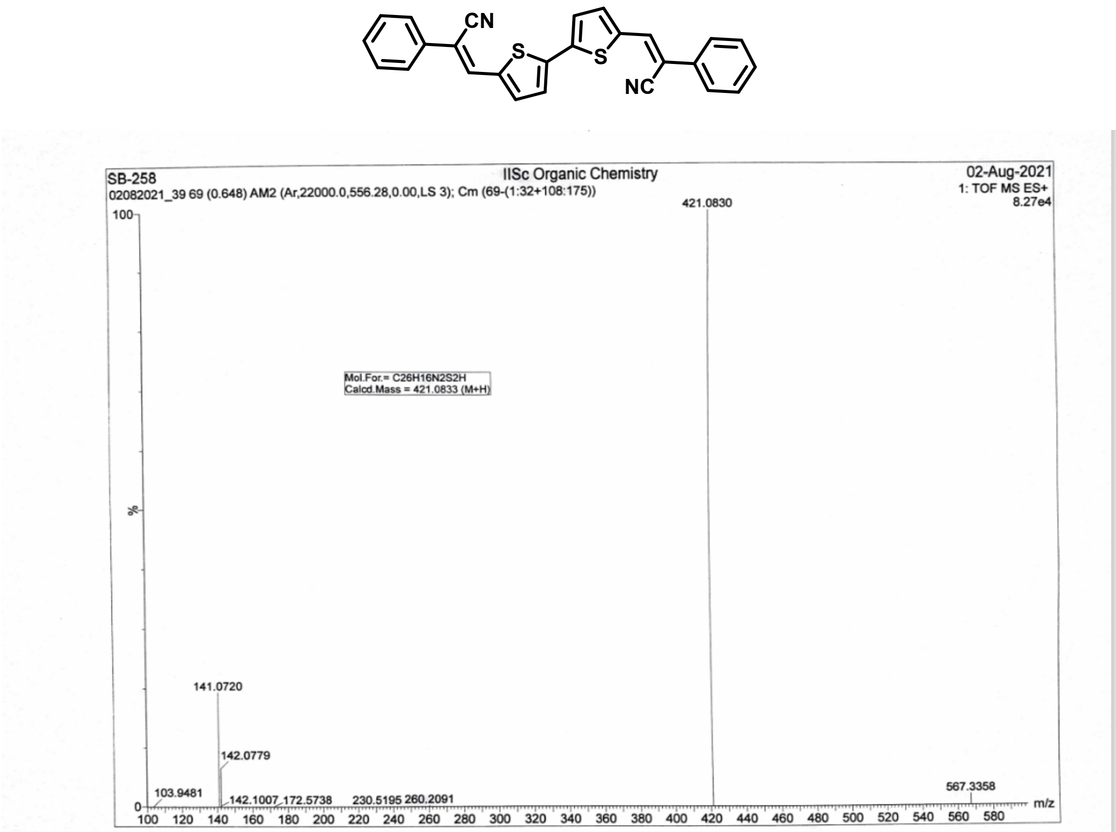


Figure S32: HRMS of Compound **C1**

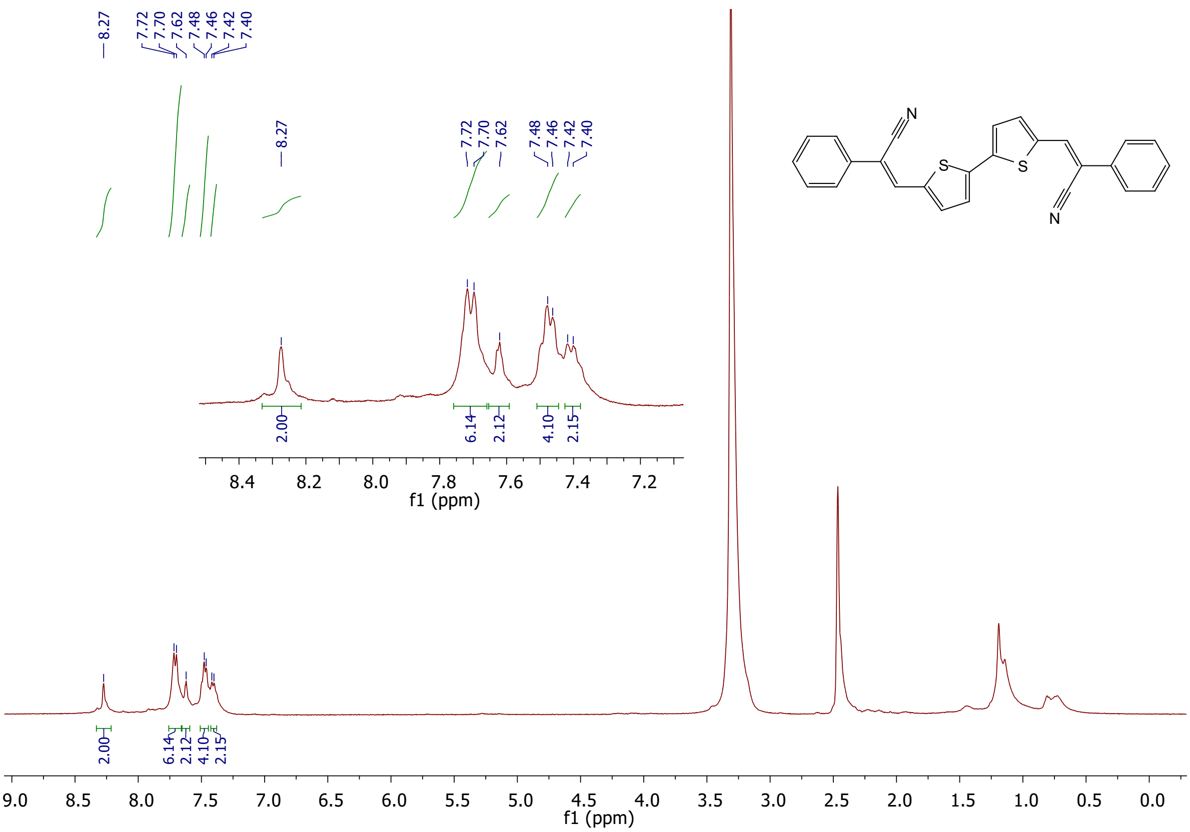
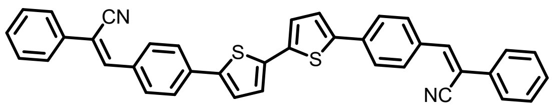


Figure S33: [1]H NMR of Compound **C1**



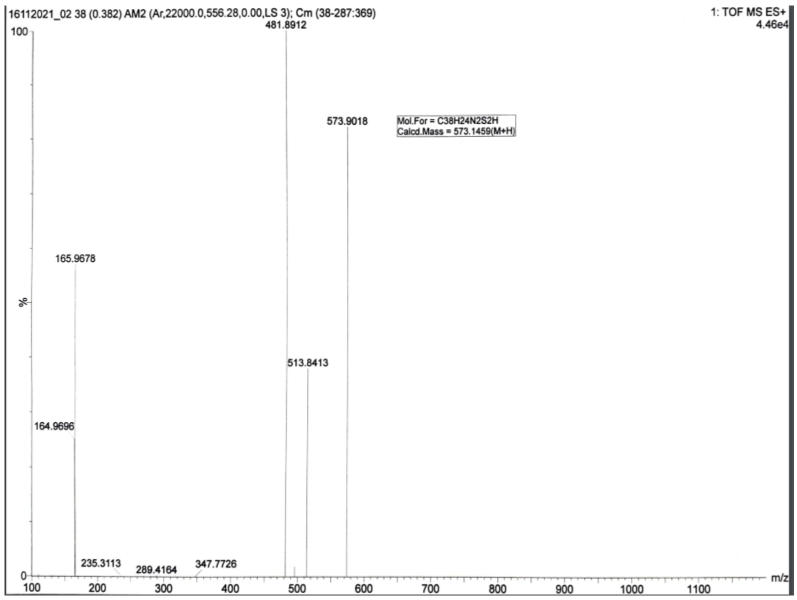


Figure S34: HRMS of Compound **C2**

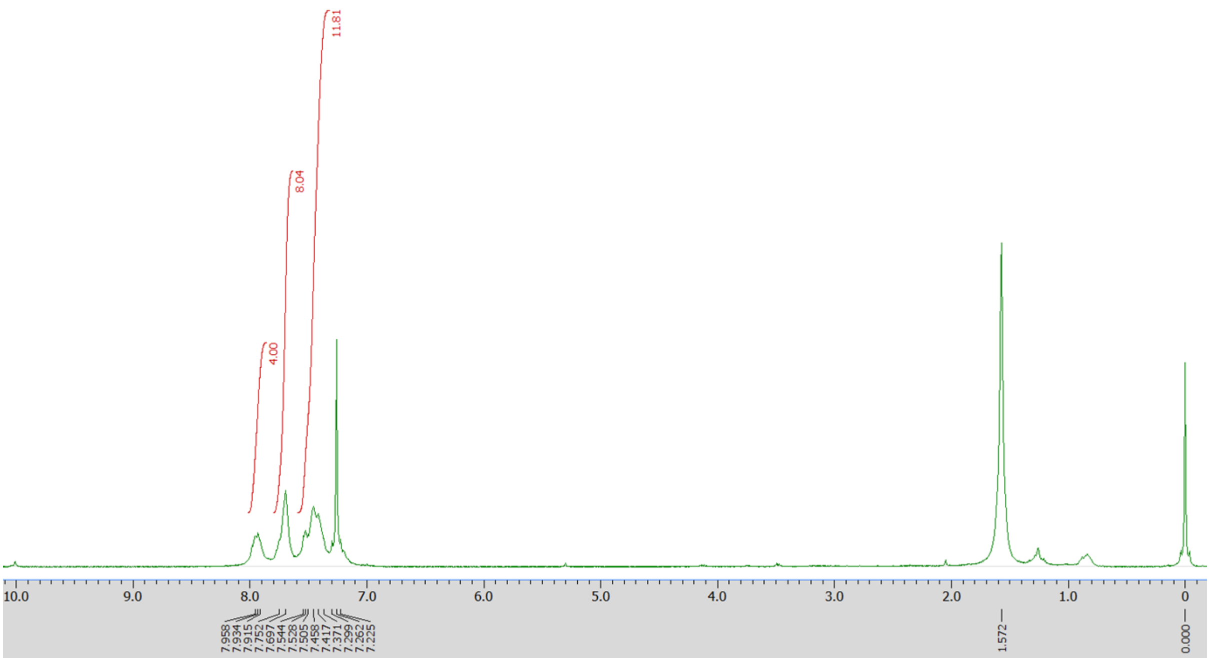


Figure S35: [1]H NMR of Compound **C3** recorded in $CDCl_3$.

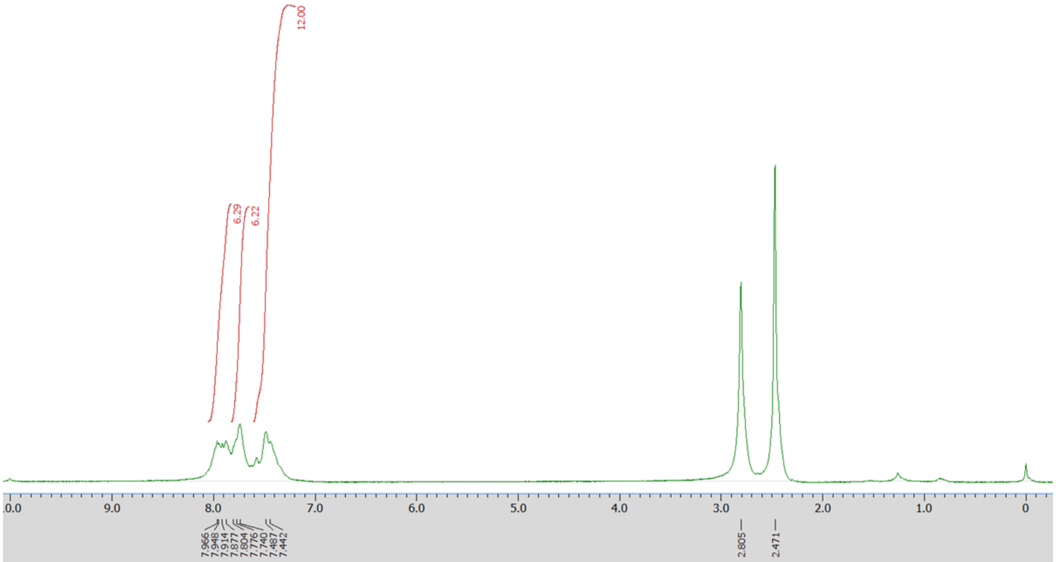


Figure S36: [1]H NMR of Compound **C2** recorded in DMSO.

Department of Chemistry I.I.T. (B)

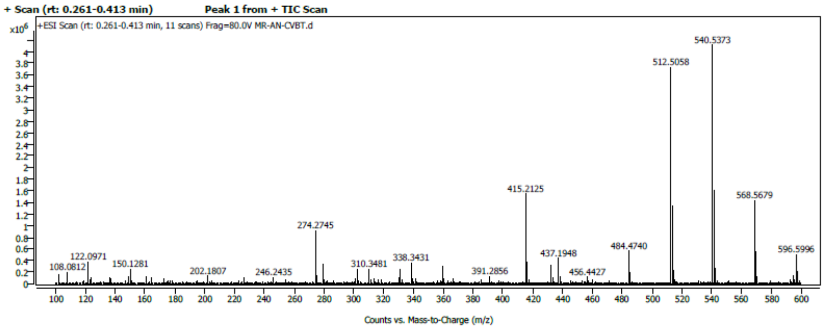
Agilent Trusted Answers

Sample Information

Name	MR-AN-CVBT	**Data File Path**	D:\MassHunter\Data\NOV-22\MR-AN-CVBT.d
Sample ID		**Acq. Time (Local)**	22-11-2022 7.52.25 PM (UTC+05:30)
Instrument	LCMS QTOF	**Method Path (Acq)**	D:\MassHunter\Methods\6545XT checkout\Methods\TRAINING\MS SCAN_AB_POS_100-600_4000-500-80.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.09.00 (B9044.0)
Inj. Vol. (ul)	2	**IRM Status**	Success
Position	P1-B5	**Method Path (DA)**	D:\MassHunter\Report Templates\REPORT METHOD\HRMS.m
Plate Pos.		**Target Source Path**	
Operator	iitb	**Result Summary**	1 qualified (1 targets)

Sample Spectra

+ Scan (rt: 0.261-0.413 min) **Peak 1 from + TIC Scan**

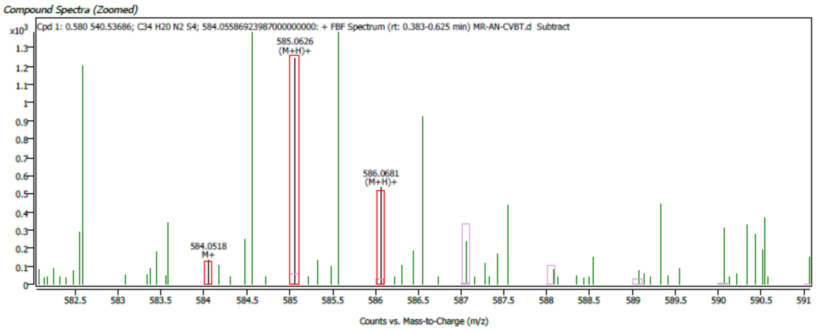


Compound Details

Cpd. 1: C34 H20 N2 S4

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C34 H20 N2 S4	584.0518	584.051828453078	4.93766706983934	8.454172064314	44.17

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Figure S37: HRMS of Compound **C3**

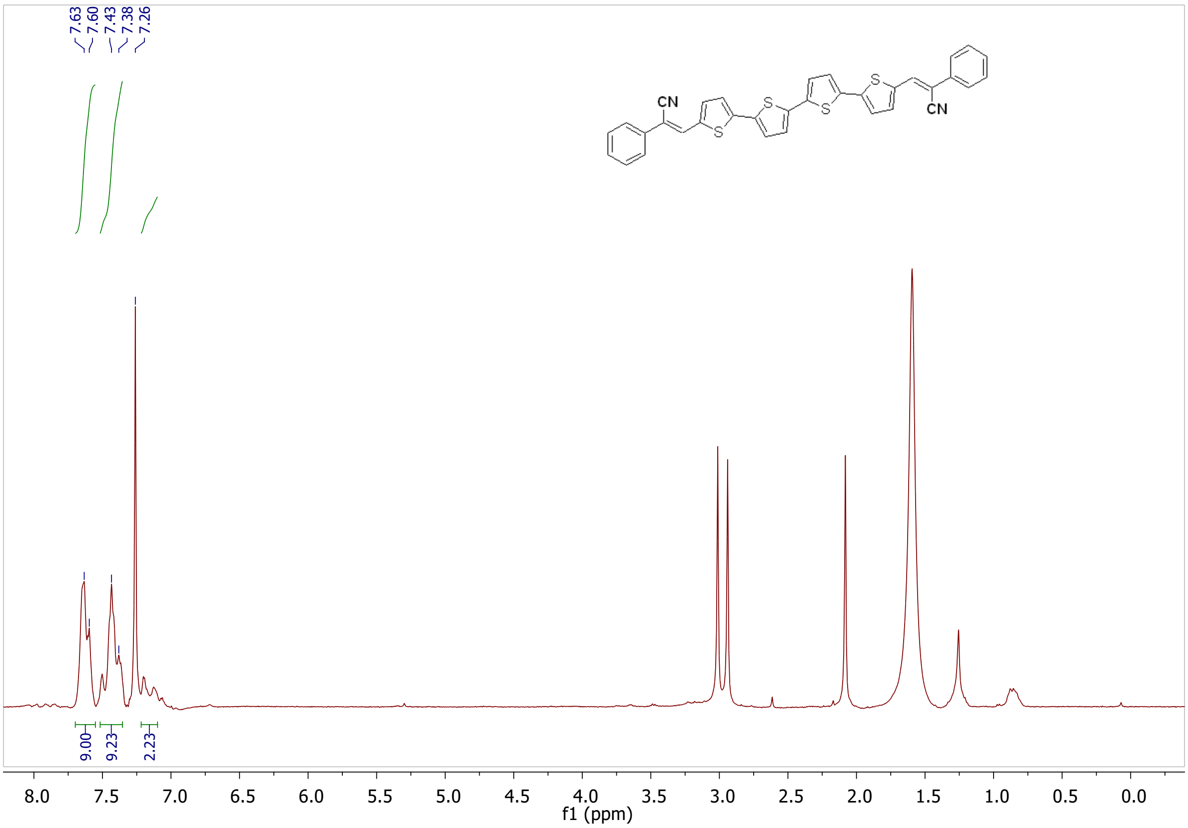


Figure S38: ¹H NMR of Compound **C3** recorded in $CDCl_3$.

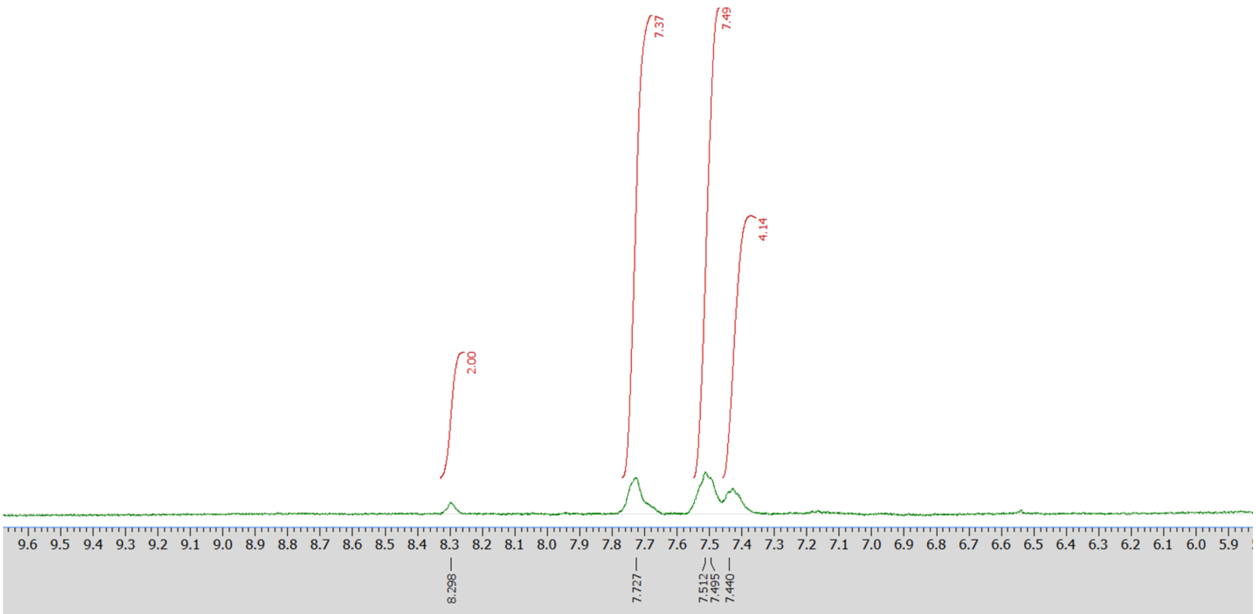


Figure S39: ¹H NMR of Compound **C3** recorded in DMSO.