Electronic Supplementary Information for

Pd(II) NCSe-Pincer Complexes for Regioselective Cross-Dehydrogenative Coupling of Arylthiophenes with Hetero(arenes)

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General Information:

Standard Schlenk line techniques were used for synthesizing new ligands **L1**-**L2** and complexes **C1**-**C2**. The AR grade solvents like acetone (for washing glassware and plasticware), acetonitrile, DCM, MeOH, EtOH, DMF, $CHCl_3$, Ethyl acetate, DMSO, Toluene, and acetic acid were used as purchased. Chemicals such as $Pd(CH_3CN)_2Cl_2$, KBr for FTIR, $Cu(OAc)_2.H_2O$, $NaBH_4$, 1-adamantyl amine, and $CDCl_3$ (for NMR spectroscopy) were purchased from Sigma-Aldrich. In contrast, PhSeSePh, thiophene derivatives, phenylboronic acid derivatives, and heteroarenes derivatives were purchased from TCI chemicals. 3-hydroxybenzaldehyde, K_2CO_3, Et_3N, $(CH_3)_3CNH_2$, Ag_2O, $AgNO_3$, Ag_2CO_3, and AgOAc were purchased from Spectrochem Chemicals. All other reagents for catalysis reaction were purchased from local commercial sources and used as they are. ^1H NMR and $^{13}C\{^1H\}$NMR were recorded in a standard capped NMR tube at room temperature using Bruker 500 MHz spectrometers in $CDCl_3$ solvent. The ^1H internal residual and $^{13}C\{^1H\}$ peaks were at 7.260 (s) ppm and 77.00 (t) ppm. The abbreviations denoted in NMR spectrums are s, d, dd, t, and m: singlet, doublet, double doublet, triplet, and multiplet. In NMR data interpretation, *J* stands for coupling constant, expressed in Hertz. In contrast, chemical shift δ is expressed in terms of parts per million concerning TMS as an internal reference. As needed, the silica gel used for column chromatography was 60-120 and 240-400 mesh size. The Ocean Optics UV-spectrometer was used for the UV-visible experiments at room temperature using a transparent cuvette with a length of 1 cm. The Perkin-Elmer FTIR instrument was used to perform the IR experiments using KBr pallets for paste formation, mortal-pastel, and diset. The melting point of solid compounds was determined by the Buchi melting point apparatus using a one-sided sealed melting point capillary. The HRMS data were obtained by using Agilent Technologies 6545 Q-TOF LC/MS instrument. The single-crystal X-ray diffraction studies used a BRUKER Quest X-ray (fixed-Chi geometry) diffractometer. The reaction status was monitored by TLC using 0.25 mm silica gel 60-F254 and a UV chamber having 254 nm and 395 nm lamps. The $PhSeCH_2Cl$ was prepared using earlier reported literature procedure.[s1]

X-Ray Crystallography:

The single crystals of palladium pincer complexes **C1** and **C2** suitable for X-ray diffraction were grown by the slow evaporation of DCM: CH_3CN solution at room temperature. Fine crystals of **C1** and **C2** were obtained as brown blocks and colorless blocks, respectively. A Leica MZ 7_5 microscope was used to identify the suitable crystals with well-defined faces with dimensions (max, intermediate, and min) 0.082 x 0.034 x 0.023 and 0.107 x 0.062 x 0.041 mm^3 for complexes **C1** and **C2,** respectively. The crystal mounted on a nylon loop was placed in a cold nitrogen stream (Oxford) maintained at 110 K. The X-ray diffraction studies (crystal screening, unit cell determination, and data collection) were done by a BRUKER Venture X-ray (kappa geometry) diffractometer for complexes **C1** and **C2**. The goniometer was controlled using the **APEX3** software suite.[s2] The sample was optically centered with a video camera, so no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a Cu-Iμs X-ray tube (K_α = 1.5418Å with a potential of 50 kV and a current of 1.0 mA). The data collected from crystallography were tabulated in **Tables s1-s4**. The cell parameters obtained from 45 data frames were taken at widths of 1° scan and refined with reflections 40574 and 53876, which were used for **C1** and **C2**, respectively, to determine the unit cell. The unit cell was verified by examining several data frames *h k l* overlays. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (28 and 38 sets for **C1** and **C2**, respectively) was initiated using omega and phi scans. Integrated intensity information for each reflection was obtained by reducing the data frames with the APEX3.[s2] The integration method employed a three-dimensional profiling algorithm, and all data were corrected for Lorentz and polarization factors and crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[s3] was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests of the data suggested the space group *P-1* and $P2_1/c$ of **C1** and **C2**, respectively. A solution was obtained readily (Z=4, Z'=2, and Z=4 for C**1** and **C2**, respectively) using XT/XS in APEX3.[s2, s4] Hydrogen atoms were placed in idealized positions and were set riding on the

respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The absence of additional symmetry or voids was confirmed using PLATON (ADDSYM).[s5] The structure was refined (weighted almost minor squares refinementF^2) to convergence.[s4,s6] Olex2 was employed for the final data presentation, and structure plots[s6] Appropriate restraints and constraints were added to keep the bond distances and thermal ellipsoids meaningful. In **C1** and **C2**, the final refinements were set with the same restraint (chemical meaningfulness), which was refined to 6695 / 0 / 421 and 4150 / 0 / 262 for **C1** and **C2**, respectively. The complex **C1** crystallized with two independent molecules in the unit cell (Figure s1). In complex **C1**, the unit cell has four molecules (Z= 4) in which one set of molecules is non-equivalent to the other (Z'=2) (Figures s2), whereas, in complex **C2**, the unit cell has four molecules, which are equivalent (Figures s3).

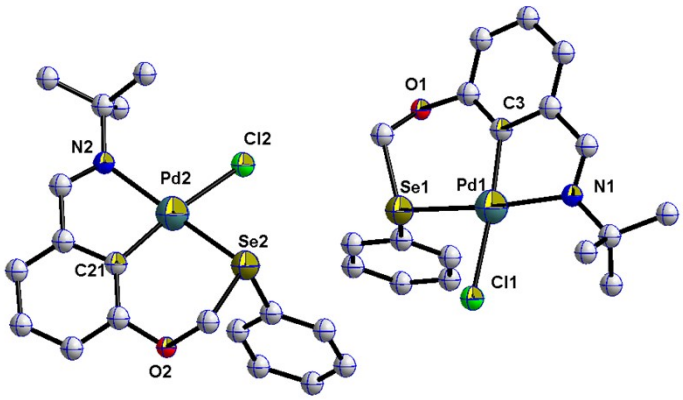

Figure s1: Molecular structure of **C1** showing two independent molecules in the unit cell.

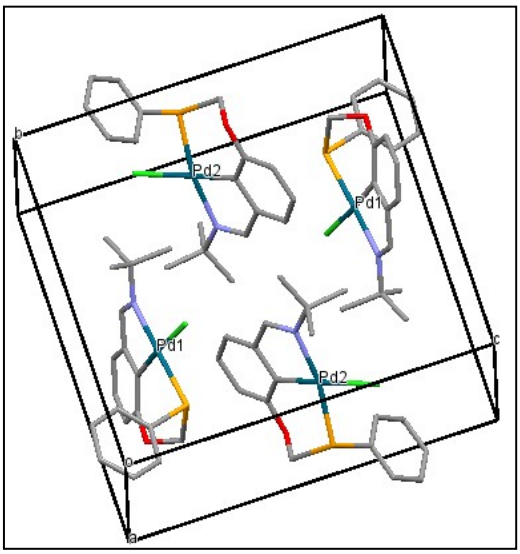

Figure s2: The Unit cell diagram of **C1**.

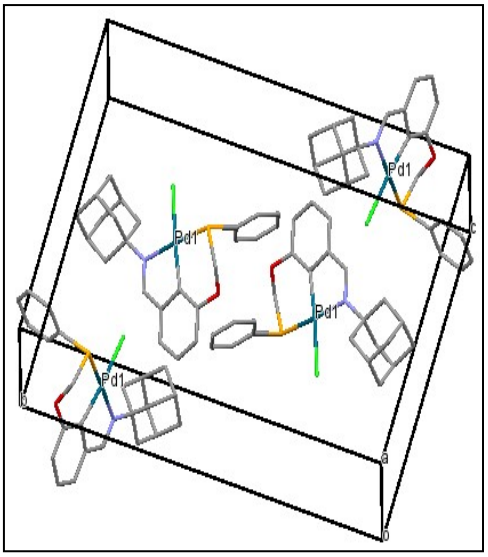

Figure s3: The Unit cell diagram of **C2**.

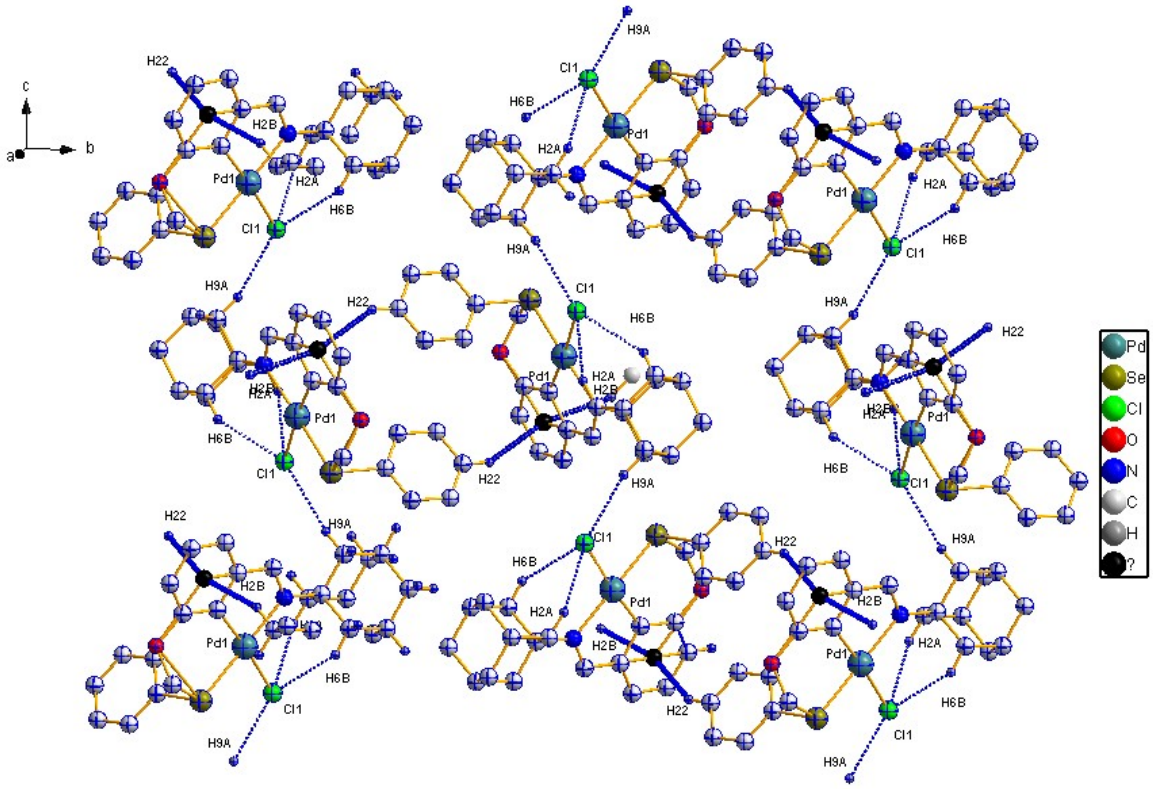

Figure s4: Packing diagram showing non-covalent Interaction in complex **C2**.

Table s1: Summary of key crystallographic data:

	C1	**C2**
identification code	hjss202	hjss116
empirical formula	C18 H20 Cl N O Pd Se	C24 H26 Cl N O Pd Se
formula weight	487.16	565.27
temperature [K]	110.00 K	110.00 K
wavelength [Å]	1.54178 Å	1.54178 Å
crystal system	Triclinic	Monoclinic
space group	*P-1*	P 1 21/c 1
Unit cell dimensions:		
A[Å]	9.2684(3)	6.7272(5)
b [Å]	13.6019(4)	20.8455(15)
c [Å]	14.1589(5)	15.5747(11)
α[°]	86.5300(10)	90
β [°]	85.3220(10)	90
γ[°]	82.6850(10)	90
V[Å^3]	1762.29(10) Å^3	2182.2(3) Å^3
Z	4	4
ρ_{calc}[Mg/m^3]	1.836 Mg/m^3	1.721 Mg/m^3
μ[mm^{-1}]	12.268 mm^{-1}	10.007 mm^{-1}
F(000)	960	1128
crystal size [mm^3]	0.082 x 0.034 x 0.023 mm^3	0.107 x 0.062 x 0.041 mm^3
θ limit[°]	3.136 to 70.176°.	3.544 to 70.247°.
Index ranges (*h*, *k*, *l*)	-10<=h<=11, -16<=k<=16, -17<=l<=17	-8<=h<=8, -25<=k<=25, -18<=l<=17
reflections collected	40574	53876
independent reflections	6695	4150
R(int)	0.0401	0.0481
completeness to θ	99.8 %	99.9 %
absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
max. and min. transmission	0.3841 and 0.2130	0.4684 and 0.3162
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data/restraints/parameters	6695 / 0 / 421	4150 / 0 / 262
Goodness-of-fit on F^2	1.056	1.170
R indices (final) [*I*>2*σ*(*I*)]		
R1	0.0194	0.0210
wR2	0.0513	0.0512
R indices (all data)		
R1	0.0197	0.0212
wR2	0.0516	0.0513
Extinction coefficient	na	na
Largest diff. Peak and hole [eÅ^{-3}]	0.474 and -0.773 e.Å^{-3}	0.505 and -0.338 e.Å^{-3}

Table s2: Some selected bond angles of complexes **C1** and **C2**.

C1				C2	
Bond Angles	**Values (°)**	**Bond Angles**	**Values (°)**	**Bond Angles**	**Values (°)**
Se(1)-Pd(1)-Cl(1)	81.862(14)	Se(2)-Pd(2)-Cl(2)	83.781(13)	C17-Pd1-Cl1	175.26
N(1)-Pd(1)-Se(1)	173.91(5)	N(2)-Pd(2)-Se(2)	166.69(4)	Se1-Pd1-N1	173.81
N(1)-Pd(1)-Cl(1)	102.42(5)	N(2)-Pd(2)-Cl(2)	102.57(5)	C17-Pd1-Se1	93.96
C(3)-Pd(1)-Se(1)	93.90(6)	C(21)-Pd(2)-Se(2)	94.05(6)	C17-Pd1-N1	81.71
C(3)-Pd(1)-Cl(1)	175.29(6)	C(21)-Pd(2)-Cl(2)	169.95(6)	Cl1-Pd1-Se1	82.20
C(3)-Pd(1)-N(1)	81.65(8)	C(21)-Pd(2)-N(2)	81.64(7)	Cl1-Pd1-N1	102.32
C(1)-Se(1)-Pd(1)	104.00(6)	C(19)-Se(2)-Pd(2)	102.62(6)	C17-Pd1-Cl1	175.26
C(9)-Se(1)-Pd(1)	104.38(7)	C(27)-Se(2)-Pd(2)	108.74(6)		
C(8)-N(1)-Pd(1)	110.82(14)	C(20)-C(21)-Pd(2)	131.42(15)		
C(15)-N(1)-Pd(1)	128.64(13)	C(22)-C(21)-Pd(2)	112.18(14)		
C(2)-C(3)-Pd(1)	132.73(16)	C(26)-N(2)-Pd(2)	111.38(13)		
C(4)-C(3)-Pd(1)	111.50(15)	C(33)-N(2)-Pd(2)	127.94(12)		

Table s3: Some selected bond lengths of Complexes **C1** and **C2**.

C1				C2	
Bond length	**Values(Å)**	**Bond length**	**Values(Å)**	**Bond length**	**Values(Å)**
Pd(1)-Se(1)	2.3679(3)	Pd(2)-Se(2)	2.3702(2)	Pd(1)-Se(1)	2.3682(3)
Pd(1)-Cl(1)	2.4106(5)	Pd(2)-Cl(2)	2.4114(5)	Pd(1)-Cl(1)	2.4142(6)
Pd(1)-N(1)	2.1192(17)	Pd(2)-N(2)	2.1215(16)	Pd(1)-N(1)	2.1057(18)
Pd(1)-C(3)	2.005(2)	Pd(2)-C(21)	1.994(2)	Pd(1)-C(17)	2.005(2)
Se(1)-C(1)	1.964(2)	Se(2)-C(19)	1.971(2)	Se(1)-C(18)	1.967(2)
Se(1)-C(9)	1.933(2)	Se(2)-C(27)	1.924(2)	Se(1)-C(19)	1.926(2)
O(1)-C(1)	1.397(3)	O(2)-C(19)	1.403(2)	O(1)-C(16)	1.395(3)
O(1)-C(2)	1.399(3)	O(2)-C(20)	1.395(2)	O(1)-C(18)	1.395(3)
N(1)-C(8)	1.286(3)	N(2)-C(26)	1.284(3)	N(1)-C(1)	1.483(3)
N(1)-C(15)	1.494(3)	N(2)-C(33)	1.494(2)	N(1)-C(11)	1.285(3)

Table s4: Bond parameters related to non-covalent interactions in complexes **C1-C2** (bond distances in Å)

C1			C2		
SR.No.	Interaction	$D_{Atom\ 1\cdots Atom\ 2}$ (Å)	SR.No.	Interaction	$D_{Atom\ 1\cdots Atom\ 2}$ (Å)
1.	$Cl_1\cdots H_{18c}$	2.730(1)	1.	$Cl_1\cdots H_{6B}$	2.633(0)
2.	$Cl_1\cdots H_{16A}$	2.588(1)	2.	$Cl_1\cdots H_{2A}$	2.595(0)
3.	$Cl_1\cdots H_{36A}$	2.886(1)	3.	$Cl_1\cdots H_{9A}$	2.769(0)
4.	$Cl_2\cdots H_{34A}$	2.616(0)	4.	$CH_{22}\cdots \pi$	2.637(0)
5.	$Cl_2\cdots H_{35c}$	2.701(1)	5.	$CH_{2B}\cdots \pi$	2.606(0)
6.	$Cl_2\cdots H_{19A}$	2.874(1)			

7.	$Cl_2\cdots H_{1A}$	2.699(1)			
8.	$CH_{16C}\cdots \pi$	2.648(0)			

Spectroscopic Data (^{1}H NMR ^{13}C{^{1}H} NMR, FTIR and HRMS)

5'-Phenyl-[2,2'-bithiophene]-5-carbaldehyde (**3aa**): Yellow Solid, 89%; **m.p**.; 153-154 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 9.87 (s, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 3.9 Hz, 2H), 7.29 – 7.27 (m, 2H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 182.4, 147.1, 146.2, 141.6, 137.3, 135.1, 133.5, 129.1, 128.3, 127.1, 125.8, 124.2, 124.0; **HRMS (ESI)** ***m/z*** cacld for $C_{15}H_{11}OS_2$ $[M+H]^+$ 271.0251, found 271.0246.

5'-Phenyl-[2,2'-bithiophene]-5-carbonitrile (**3ab**): Yellow Solid, 84%; **m.p**.; 126.7-127.7 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.62 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 3.9 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 4.3 Hz, 2H), 7.15 (d, *J* = 3.9 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 146.0, 144.7, 138.3, 133.9, 133.3, 129.1, 128.4, 126.9, 125.8, 124.1, 123.2, 114.3, 107.2; **HRMS (ESI)** ***m/z*** cacld for $C_{15}H_{13}N_2S_2$ $[M+NH_4]^+$ 285.0520, found 285.0511.

1-(5'-Phenyl-[2,2'-bithiophen]-5-yl)ethenone (3ac): Yellow solid, 82%; **m.p**.; 115.2-118.9 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.61 (t, *J* = 6.3 Hz, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (dd, *J* = 17.6, 5.6 Hz, 2H), 7.26 (d, *J* = 3.9 Hz, 1H), 7.19 (d, *J* = 3.9 Hz, 1H), 2.56 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 190.4, 145.8, 145.5, 142.3, 135.4, 133.6, 133.4, 129.1, 128.1, 126.6, 125.8, 124.1, 123.9, 26.5; **HRMS (ESI)** ***m/z*** cacld for $C_{16}H_{14}NOS_2$ $[M+NH_4]^+$ 300.0517, found 300.0501.

5-Bromo-5'-phenyl-2,2'-bithiophene (3ad):[s7] Yellow solid, 83%; **m.p**.; 133-137 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.59 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 3.8 Hz, 1H), 7.08 (d, *J* = 3.8 Hz, 1H), 6.98 (d, *J* = 3.8 Hz, 1H), 6.94 (d, *J* = 3.8 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 143.7, 138.9, 135.5, 133.9, 130.7, 128.9, 127.8, 125.7, 124.9, 123.8, 123.7, 110.9.

5-Phenyl-2,2'-bithiophene (3ae):[s8] Yellow solid, 86%; **m.p**.; 120-124 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.64 (d, *J* = 5.7 Hz, 1H), 7.50 (d, *J* = 6.1 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.28 (dd, *J* = 18.7, 10.4 Hz, 3H), 7.06 (s, 1H), 6.97 (d, *J* = 16.0 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 143.1, 142.3, 137.0, 134.3, 128.9, 128.8, 128.3, 127.4, 126.3, 125.7, 123.6, 121.9.

5-Methyl-5'-phenyl-2,2'-bithiophene (3af):[s9] Yellow solid, 79%; **m.p**.; 94-99 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.60 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.29 (dd, *J* = 7.3, 6.2 Hz, 1H), 7.21 (d, *J* = 3.7 Hz, 1H), 7.07 (d, *J* = 3.7 Hz, 1H), 7.00 (d, *J* = 3.5 Hz, 1H), 6.73 – 6.65 (m, 1H), 2.50 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 142.5, 139.3, 137.2, 135.1, 134.2, 128.9, 127.4, 126.0, 125.6, 123.9, 123.6, 123.5, 15.4.

5-(5-Phenylthiophen-2-yl)furan-2-carbaldehyde (3ag):[s10] Red solid, 78%; **m.p**.; 114-117 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 9.62 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 3.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39–7.28 (m, 3H), 6.69 (d, *J* = 3.7 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** .8, 154.8, 151.5, 146.7, 133.5, 130.5, 129.1, 128.3, 127.2, 125.9 124.1, 107.5.

2-(5-Phenylthiophen-2-yl)pyridine (3ah):[s11] Yellow solid, 72%; **m.p**.; 100-102 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.59 (d, *J* = 3.6 Hz, 1H), 7.69 (d, *J* = 4.0 Hz, 3H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 3.1 Hz, 1H), 7.41 (t, *J* = 6.3 Hz, 2H), 7.37–7.28 (m, 2H), 7.18 (dd, *J* = 9.0, 4.4 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 152.5, 149.6, 136.6, 128.9, 127.8, 127.6, 125.8, 125.6, 125.4, 124.5, 124.0, 121.9, 118.6.

4-(5-Phenylthiophen-2-yl)benzaldehyde (3ai):[s12] White solid, 83%; **m.p**.; 167-169 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 10.00 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.50–7.39 (m, 3H), 7.34 (d, *J* = 3.9 Hz, 2H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 191.4, 145.9, 141.7, 140.0, 135.0, 133.8, 130.5, 129.1, 128.1, 126.08, 125.8, 125.7, 124.4.

2-(4-(Tert-butyl)phenyl)-5-phenylthiophene (3aj):[s13] White solid; 84%; **m.p**.; 135-137 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.67 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.49–7.40

(m, 4H), 7.34–7.27 (m, 3H), 1.39 (s, 9H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ** 150.7, 143.8, 143.1, 134.5, 131.6, 128.9, 127.4, 125.9, 125.6, 125.4, 123.9, 123.6, 34.7, 31.3.

2,5-Diphenylthiophene (3ak):[s14] White solid, 86 %; **m.p**.; 147-150 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.67 (d, *J* = 7.5 Hz, 4H), 7.42 (t, *J* = 7.5 Hz, 4H), 7.33-7.32 (m 1H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ** 143.7, 134.4, 128.9, 127.5, 125.6, 124.0.

4-([2,2'-Bithiophen]-5-yl)benzaldehyde (3bf):[s12] Yellow solid, 82%; **m.p**.; 169-171°C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 10.02 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 3.7 Hz, 1H), 7.30 – 7.29 (m, 1H), 7.27 (d, *J* = 3.5 Hz, 1H), 7.21 (d, *J* = 3.7 Hz, 1H), 7.09 – 7.05 (m, 1H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ** 191.4, 141.1, 139.7, 138.9, 136.9, 135.1, 130.5, 128.0, 125.8, 125.6, 125.1, 124.9, 124.3.

4-([2,2'-Bithiophen]-5-yl)benzonitrile (3cf):[s8] Yellow solid, 80%; **m.p**.; 140-142 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 6.95 (d, *J* = 3.4 Hz, 2H), 6.90 (d, *J* = 4.8 Hz, 2H), 6.86 (d, *J* = 2.5 Hz, 1H), 6.80 (d, *J* = 3.4 Hz, 2H), 6.70–6.66 (m, 2H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ** 140.4, 139.1, 138.3, 136.7, 132.8, 128.1, 125.9, 125.7, 125.2, 124.9, 124.4, 118.9, 110.5.

5-(4-Bromophenyl)-2,2'-bithiophene (3df):[s15] Yellow solid, 76%; **m.p**.; 279 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.67 (dd, *J* = 25.9, 6.5 Hz, 2H), 7.47 (d, *J* = 6.6 Hz, 1H), 7.39 (d, *J* = 6.9 Hz, 1H), 7.25 (dd, *J* = 32.2, 14.3 Hz, 3H), 7.08 (d, *J* = 21.5 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ** 128.9, 127.9, 127.6, 127.5, 126.9, 125.9, 124.7, 124.6, 124.4, 124.3, 123.8, 123.7.

5-(4-(Tert-butyl)phenyl)-2,2'-bithiophene (3ef):[s16] Yellow solid, 76%; **m.p**.; 97 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.56 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.22 (dd, *J* = 9.2, 4.3 Hz, 3H), 7.15 (d, *J* = 3.6 Hz, 1H), 7.07 – 7.00 (m, 1H), 1.37 (s, 9H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ** 150.8, 143.3, 137.6, 136.2, 131.3, 127.9, 125.9, 125.4, 124.6, 124.2, 123.5, 123.3, 34.7, 31.3.

5-(4-Methoxyphenyl)-2,2'-bithiophene (3ff):[s17] Yellow solid, 78%; **m.p**.; 151-156 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.57 (d, *J* = 8.7 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.26–7.19 (m, 1H), 7.15 (dd, *J* = 8.3, 3.7 Hz, 1H), 7.06 (dd, *J* = 4.9, 3.7 Hz, 1H), 7.01 (dd, *J* = 11.5, 8.7 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 3.87 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (125 MHz,**

$CDCl_3$) δ 159.3, 143.1, 137.6, 136.6, 135.7, 127.8, 126.9, 124.6, 124.1, 123.40, 122.7, 114.4, 55.4.

5-(Naphthalen-1-yl)-2,2'-bithiophene (3gf):[s8] Yellow solid, 73%; **m.p**.; 94-98 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.38 (dd, *J* = 6.0, 3.4 Hz, 1H), 8.01 (dd, *J* = 8.0, 4.1 Hz, 1H), 7.96 (dd, *J* = 5.9, 3.4 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 6.9 Hz, 1H), 7.61–7.53 (m, 3H), 7.31 (dd, *J* = 10.8, 4.0 Hz, 2H), 7.22 (d, *J* = 3.6 Hz, 1H), 7.16–7.07 (m, 1H); **^{13}C NMR (126 MHz, $CDCl_3$) δ** 140.9, 137.7, 137.4, 134.0, 132.1, 128.6, 128.5, 128.2, 128.1, 127.9, 126.6, 126.2, 125.7, 125.4, 124.5, 124.1, 123.8.

[2,2':5',2''-Terthiophene]-5-carbaldehyde (3ha):[s18] Yellow solid, 79%; **m.p**.; 138-142 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 9.86 (s, 1H), 7.68 (d, *J* = 3.8 Hz, 1H), 7.31–7.27 (m, 2H), 7.24 (d, *J* = 3.3 Hz, 2H), 7.13 (d, *J* = 3.6 Hz, 1H), 7.08 – 7.04 (m, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 182.5, 146.9, 141.6, 139.2, 137.4, 136.4, 134.5, 128.1, 126.9, 125.4, 124.7, 124.5, 124.1.

5-Bromo-2,2':5',2''-terthiophene (3hd):[s19] Yellow solid, (79%); **m.p**.; 135-140 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.24 (t, *J* = 4.6 Hz, 1H), 7.18 (d, *J* = 2.8 Hz, 1H), 7.07 (d, *J* = 3.7 Hz, 1H), 7.05 – 7.02 (m, 1H), 7.01 (d, *J* = 3.7 Hz, 1H), 6.99 – 6.97 (m, 1H), 6.91 (d, *J* = 3.5 Hz, 1H);**^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 138.6, 136.9, 136.7, 135.1, 130.7, 127.9, 124.7, 124.6, 124.3, 123.9, 123.7, 111.1.

5-(Methoxymethyl)-2,2':5',2''-terthiophene (3hl):[s20] Yellow solid, 74%; **m.p**.; 179 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.24 – 7.22 (m, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.07 (dd, *J* = 9.8, 3.7 Hz, 2H), 7.04 (dd, *J* = 6.0, 2.4 Hz, 2H), 6.91 (d, *J* = 3.5 Hz, 1H), 4.60 (s, 2H), 3.42 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 140.1, 137.6, 137.1, 136.3, 136.2, 127.9, 127.2, 124.5, 124.3, 124.3, 123.7, 123.2, 69.1, 57.8.

2,2':5',2''-Terthiophene (3hf):[s21] Yellow solid, 82%; **m.p**.; 92-95 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.23 (dd, *J* = 5.5, 1 Hz, 2H), 7.19-7.18(m, 4H), 7.09 (s, 2H), 7.04-7.02 (m, 4H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 137.2, 136.3, 127.9, 124.5, 124.3, 123.7.

5-(Benzo[*b*]thiophen-2-yl)thiophene-2-carbaldehyde (3ia):[s22] Yellow solid, 72%; **m.p**.; 182-185 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 9.89 (s, 1H), 7.82–7.77 (m, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.59 (s, 1H), 7.40–7.35 (m, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 182.5, 146.9, 144.6, 139.9, 139.8, 137.1, 135.6, 125.6, 125.5, 125.1, 124.1, 122.5, 122.3.

5-(Benzo[*b*]thiophen-2-yl)thiophene-2-carbonitrile (3ib):[s22] Yellow solid, 70%; **m.p**.; 176-179 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.82–7.77 (m, 2H), 7.56 (d, *J* = 4.0 Hz, 1H), 7.52 (s, 1H), 7.41–7.36 (m, 2H), 7.24 (d, *J* = 4.0 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 144.5, 139.8, 139.7, 138.2, 134.4, 125.7, 125.2, 124.4, 124.1, 122.4, 122.3, 114.0, 108.6.

1-(5-(Benzo[*b*]thiophen-2-yl)thiophen-2-yl)ethenone (3ic):[s22] Yellow solid, 65%; **m.p**.; 174-179 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.81–7.76 (m, 2H), 7.61 (d, *J* = 4.0 Hz, 1H), 7.54 (s, 1H), 7.39–7.32 (m, 2H), 7.27 (d, *J* = 4.0 Hz, 1H), 2.57 (s, 3H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 190.3, 145.5, 140.0, 139.7, 135.9, 133.1, 125.4, 125.3, 124.9, 124.0, 122.2, 121.9, 26.6.

5-(Benzo[*b*]thiophen-2-yl)furan-2-carbaldehyde (3ig):[s22] Yellow solid, 68%; **m.p**.; 168-172 ℃; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 9.67 (s, 1H), 7.87-7.82 (m, 2H), 7.8 (s, 1H), 7.42–7.39 (m, 2H), 7.34 (d, *J* = 4.5 Hz, 1H), 6.82 (d, *J* = 4.5 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 177.1, 154.5, 152.1, 139.9, 139.7, 131.0, 125.7, 125.1, 124.4, 123.1, 122.7, 122.4, 109.2.

5,5'-Diphenyl-2,2'-bithiophene (1a'):[s23] Yellow solid, 25%; **m.p.**; 234-240 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.64 (dd, *J* = 8.2, 0.9 Hz, 4H), 7.40 (t, *J* = 7.6 Hz, 4H), 7.34 – 7.28 (m, 5H), 7.10 (dd, *J* = 5.0, 3.6 Hz, 1H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 128.9, 128.9, 128.0, 127.48, 126.0, 125.7, 124.8, 123.1.

[2,2'-Bithiophene]-5,5'-dicarbaldehyde (2a'):[s24] Yellow solid, 17%; **m.p.**: 216-221 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 9.92 (s, 2H), 7.73 (d, *J* = 5.0 Hz, 2H), 7.43 (d, *J* =5.0 Hz, .2H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 182.6, 144.9, 143.9, 137.0, 126.5.

Spectral Images (^{1}H NMR ^{13}C{^{1}H} NMR, FTIR and HRMS)

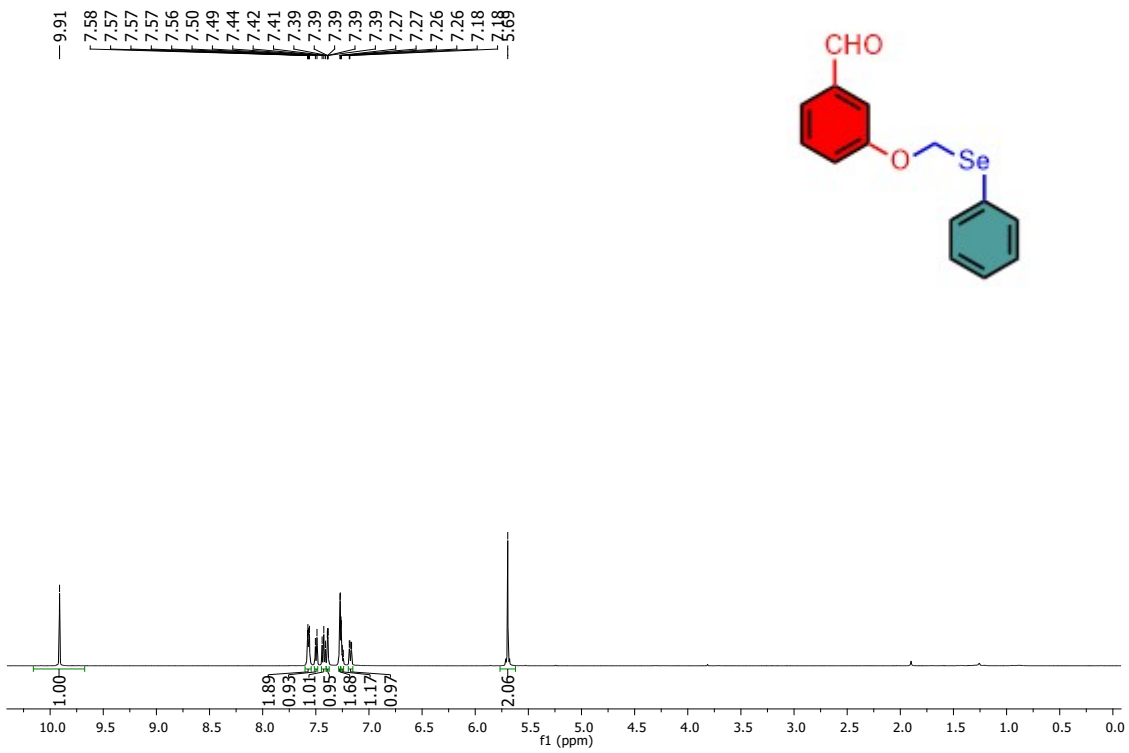

Figure s5: ^{1}H NMR spectrum of **P**.

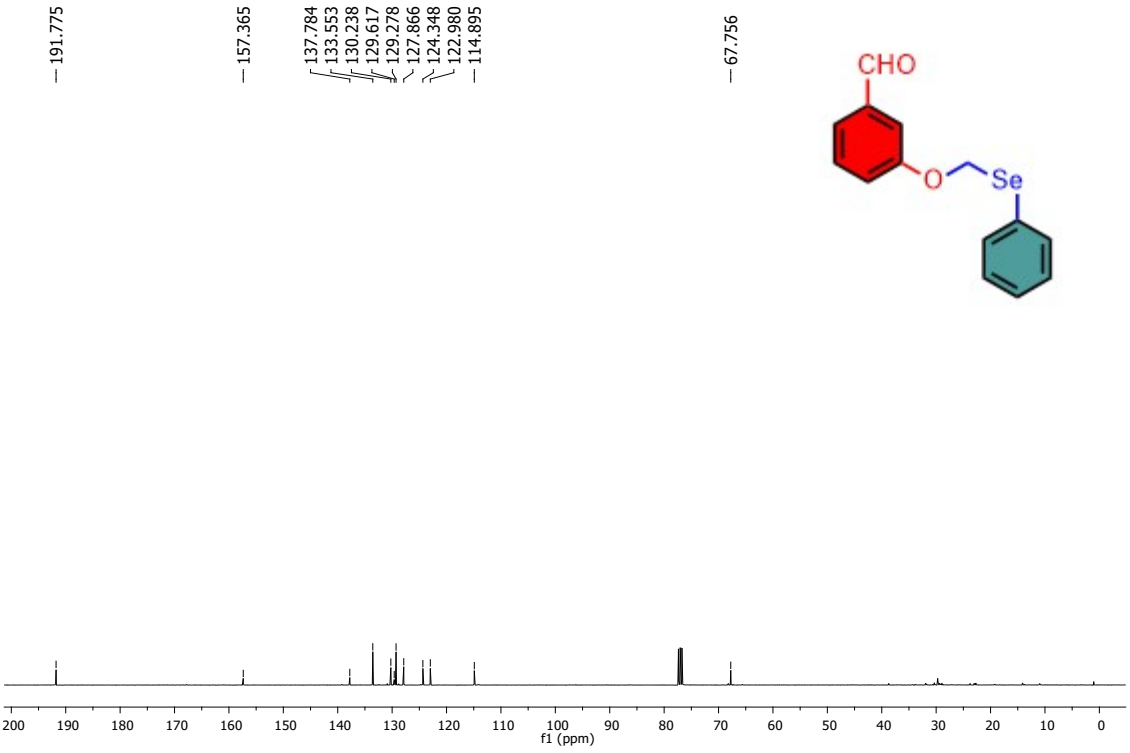

Figure s6: $^{13}C\{^{1}H\}$ NMR spectrum of **P**.

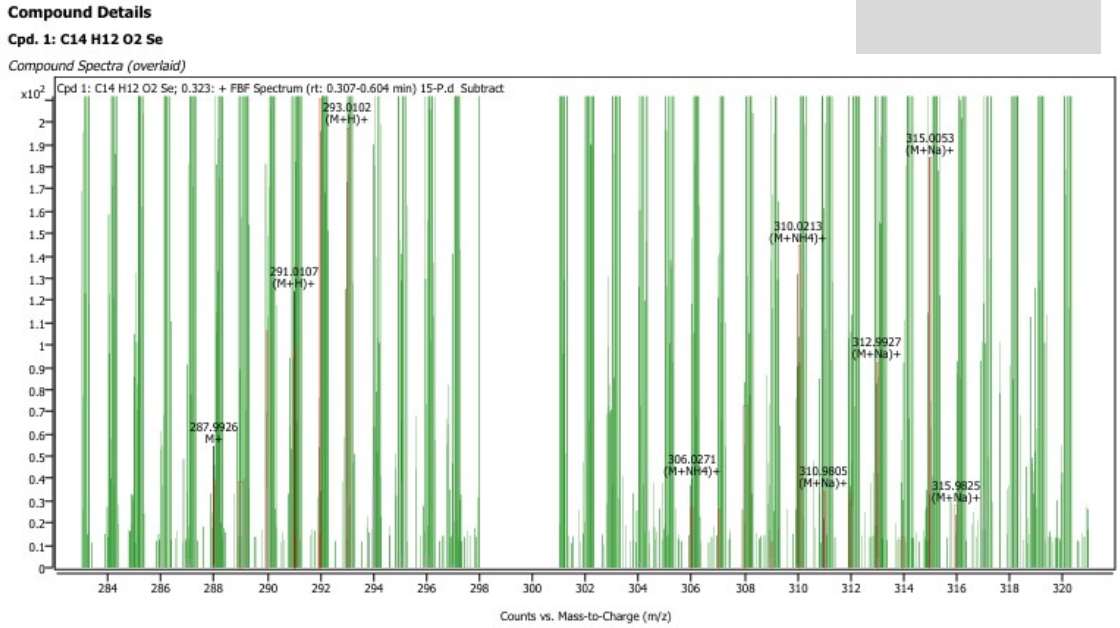

Figure s7: HRMS spectrum of **P**.

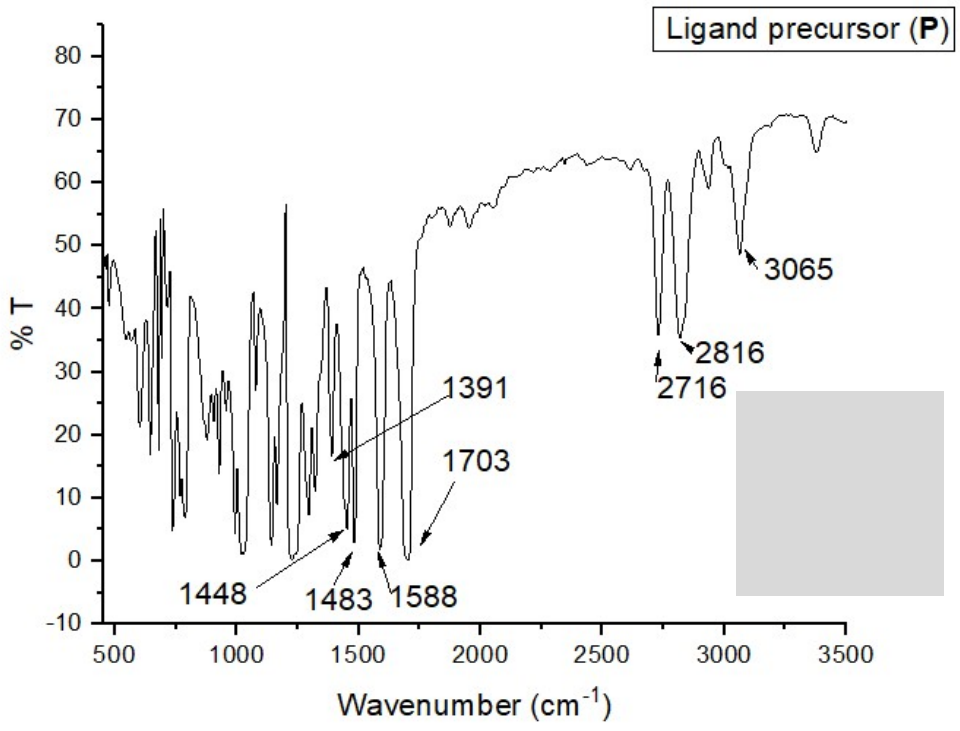

Figure s8: FTIR spectrum of **P**.

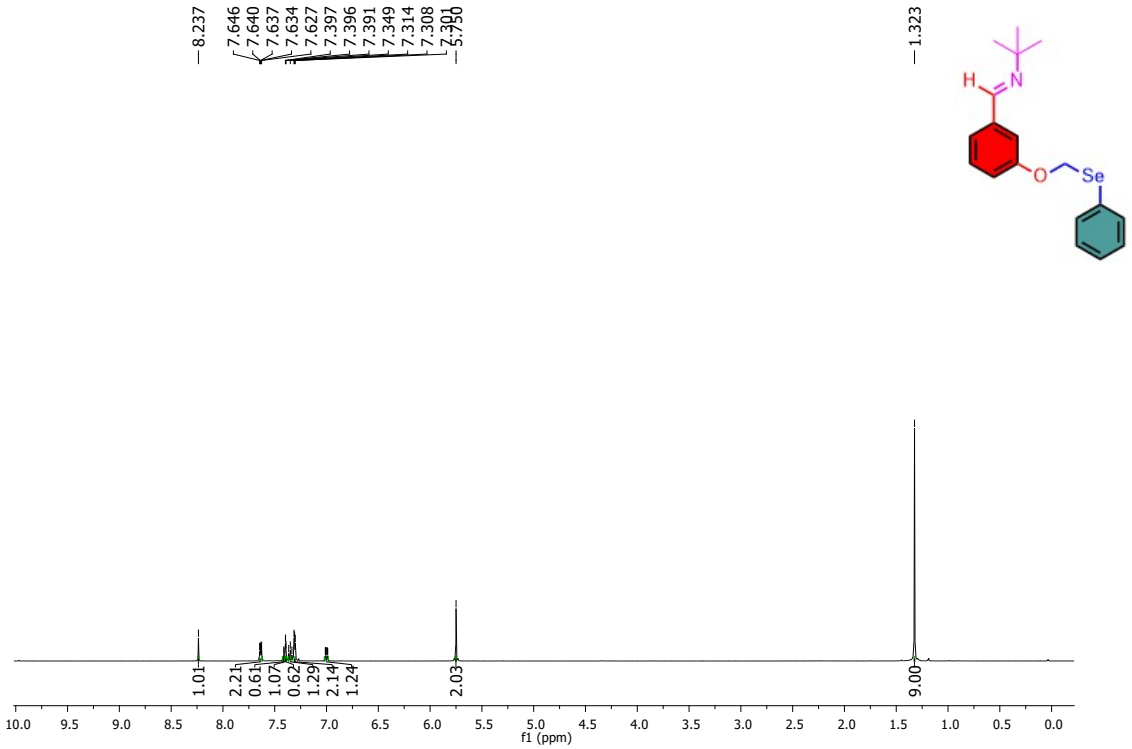

Figure s9: ^{1}H NMR spectrum of **L1**.

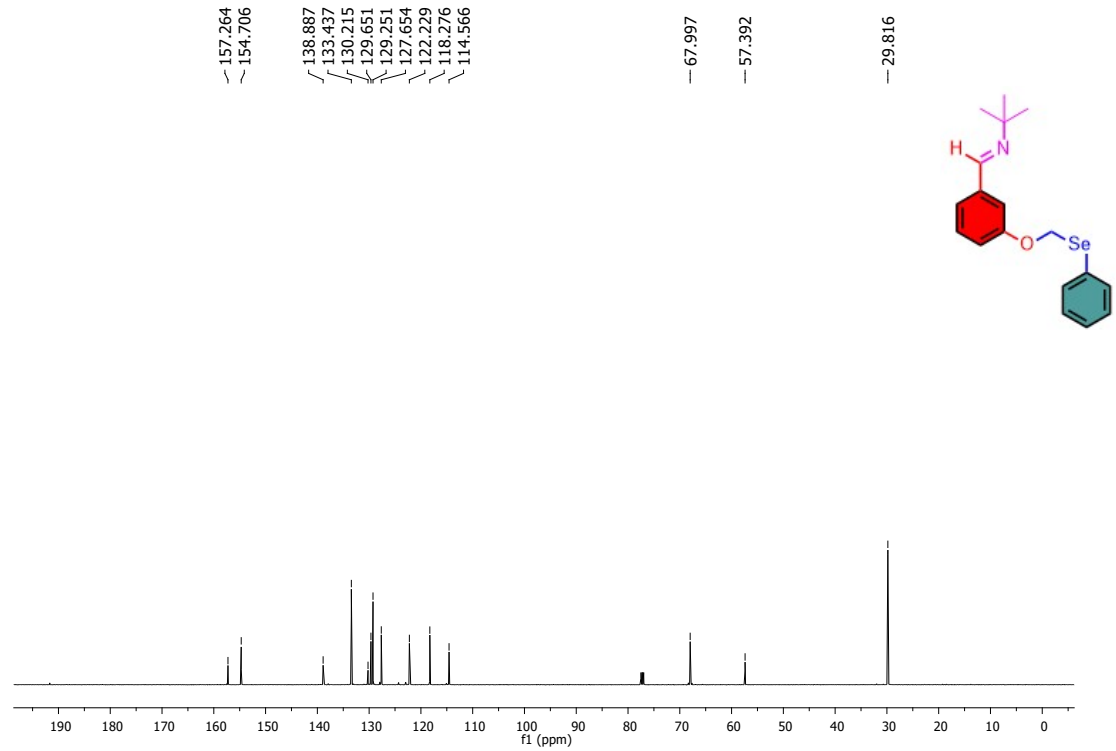

Figure s10: ^{13}C{^{1}H} NMR spectrum of ligand **L1**.

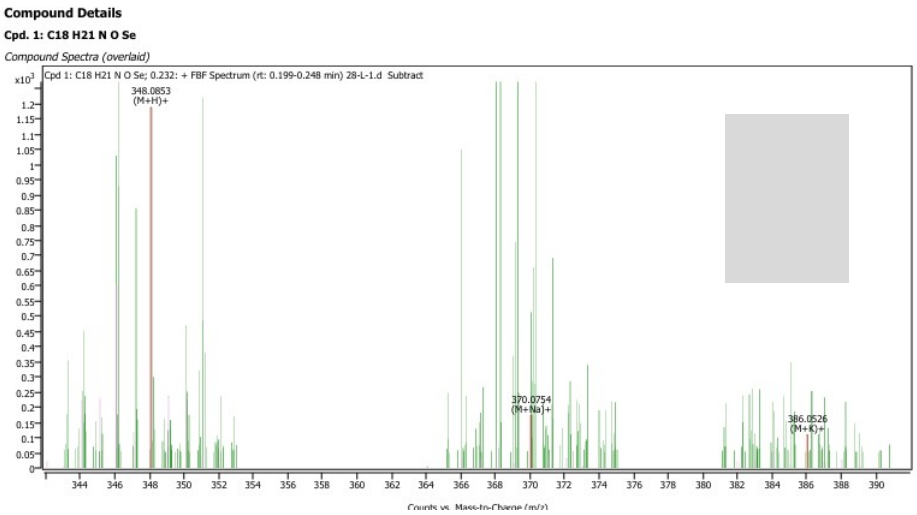

Figure s11: HRMS spectrum of **L1**.

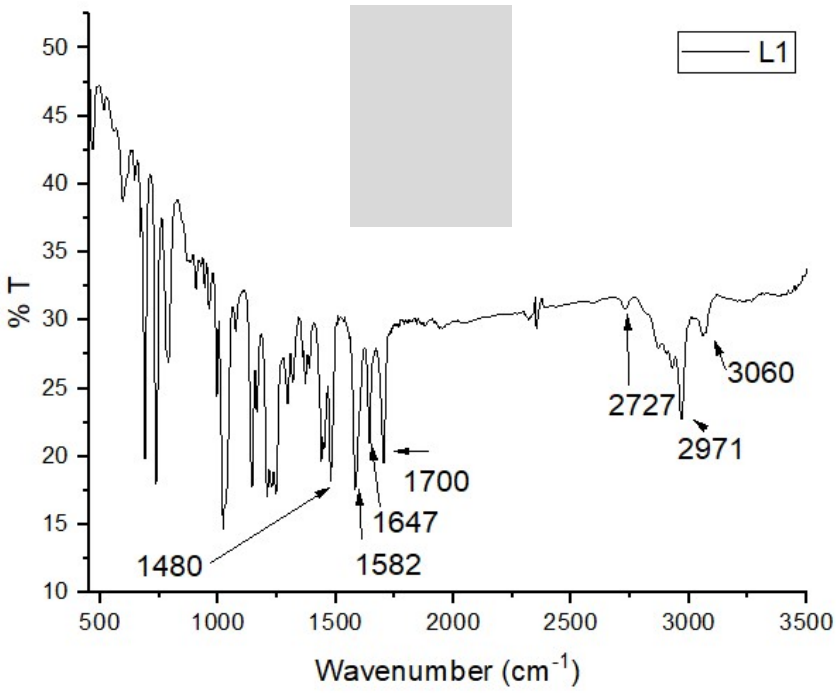

Figure s12: FTIR spectrum of **L1**.

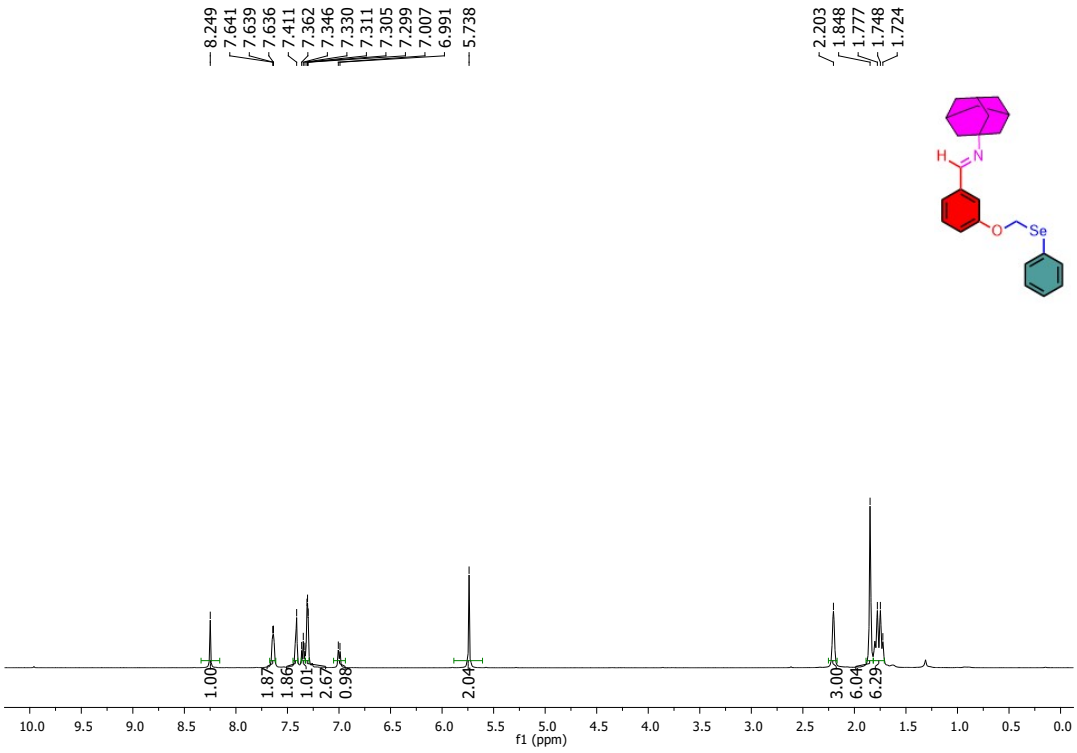

Figure s13: ^{1}H NMR spectrum of **L2**.

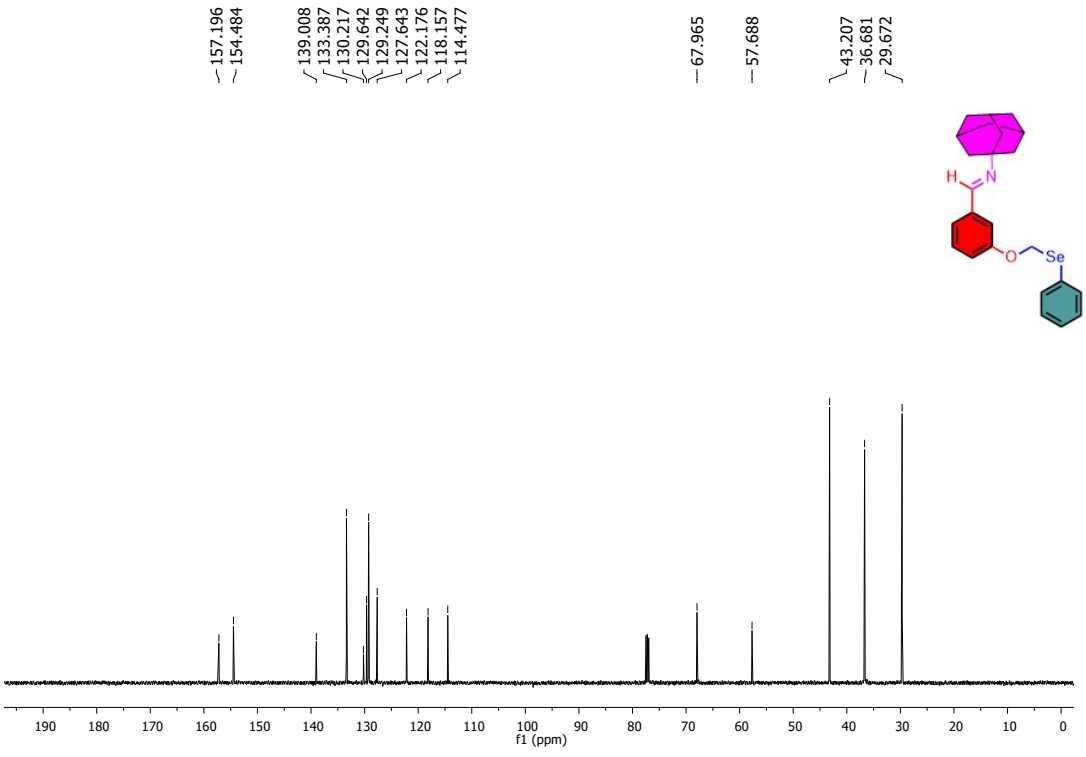

Figure s14: $^{13}C\{^{1}H\}$ NMR spectrum of **L2**.

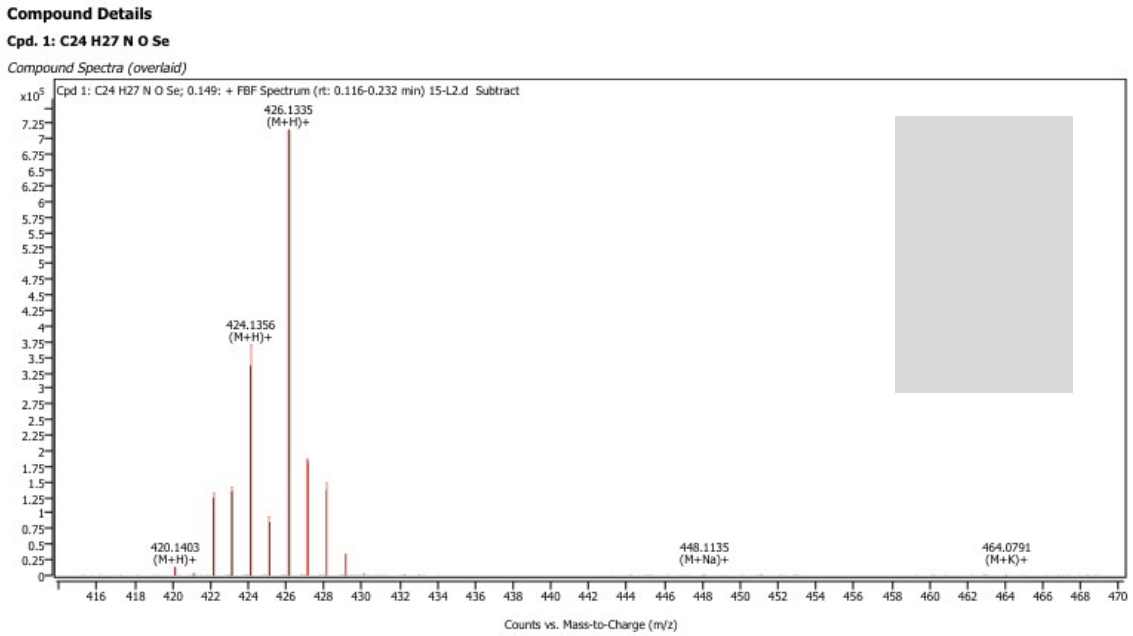

Figure s15: HRMS spectrum of **L2**.

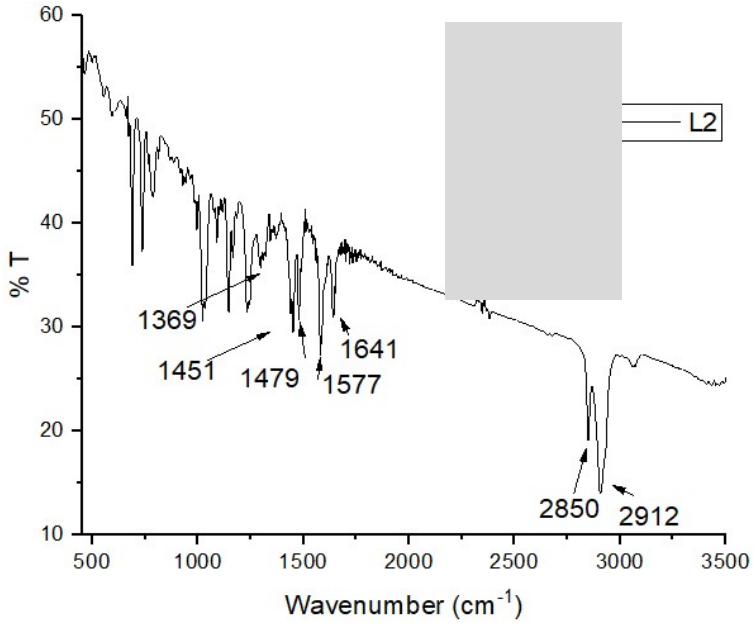

Figure s16: FTIR spectrum of **L2**.

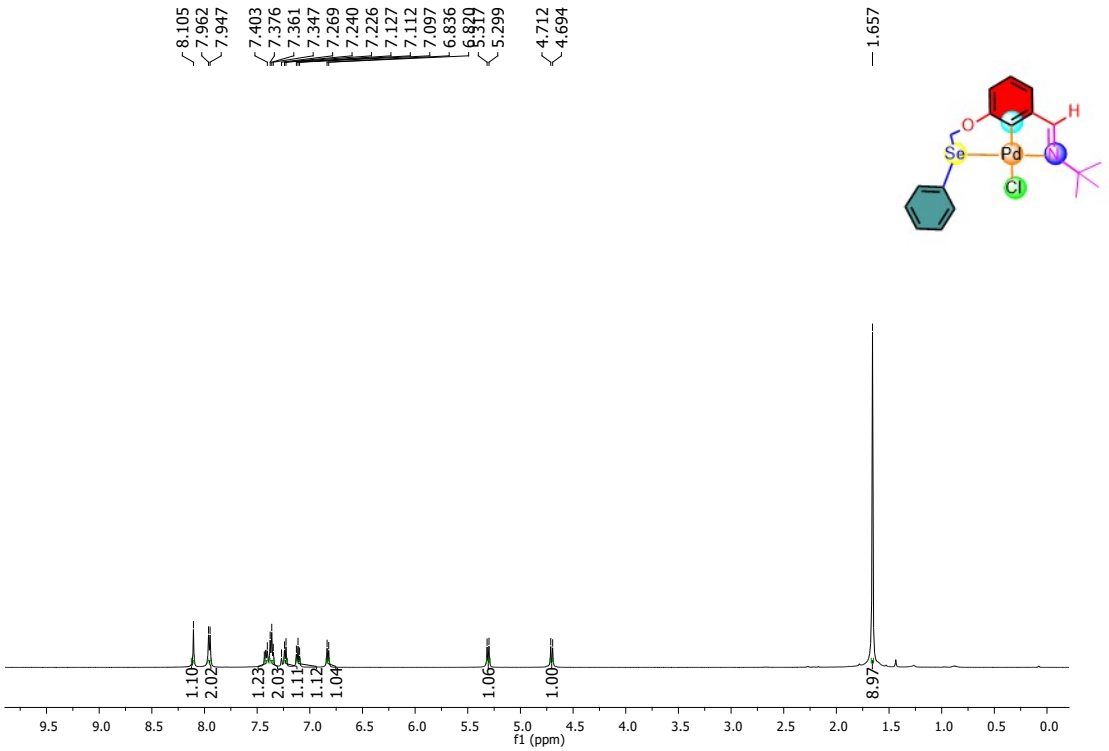

Figure s17: ^{1}H NMR spectrum of **C1**.

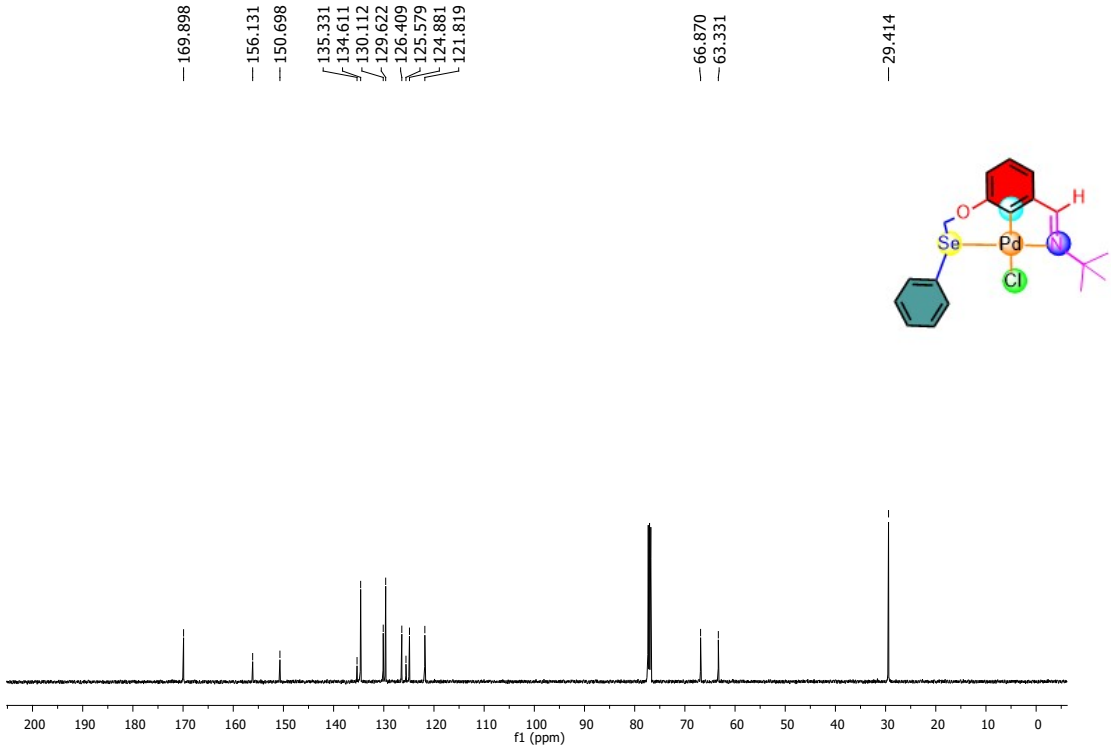

Figure s18: ^{13}C{^{1}H} NMR spectrum of **C1**.

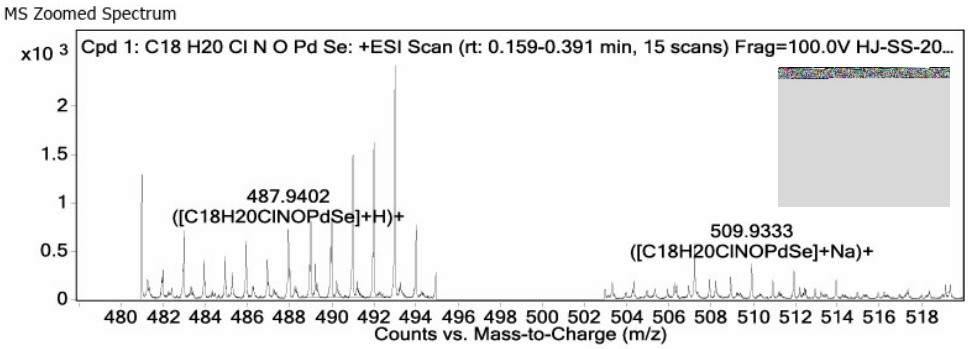

Figure s19: HRMS spectrum of **C1**.

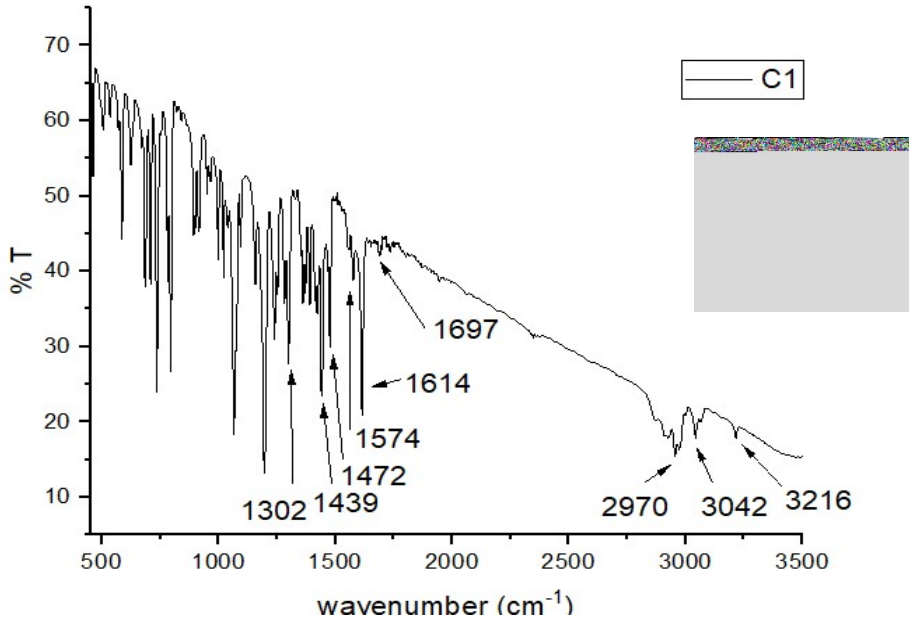

Figure s20: FTIR spectrum of **C1**.

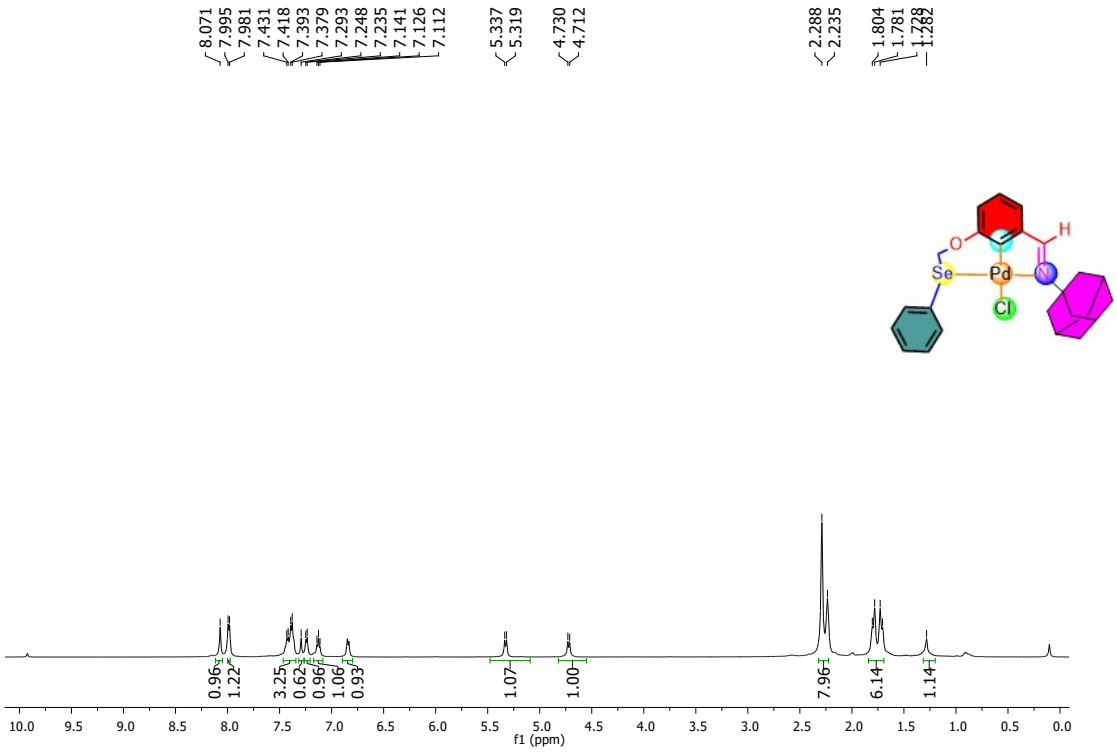

Figure s21: ^{1}H NMR spectrum of **C2**.

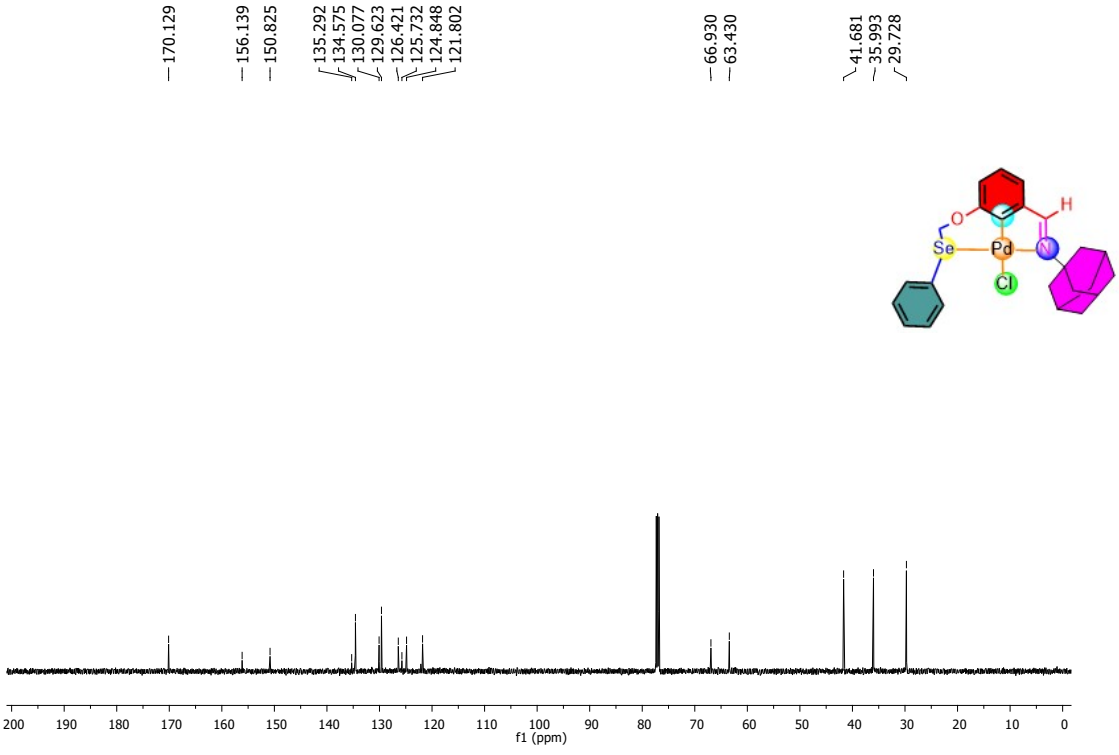

Figure s22: ^{13}C{^{1}H} NMR spectrum of **C2**.

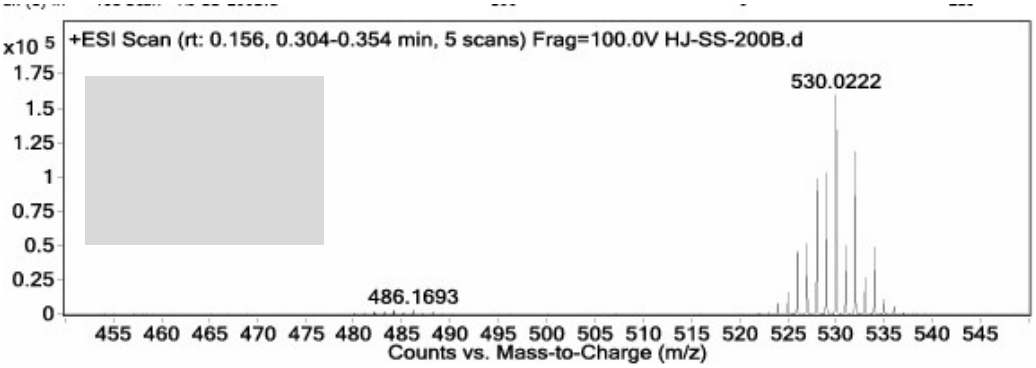

Figure s23: HRMS spectrum of **C2**.

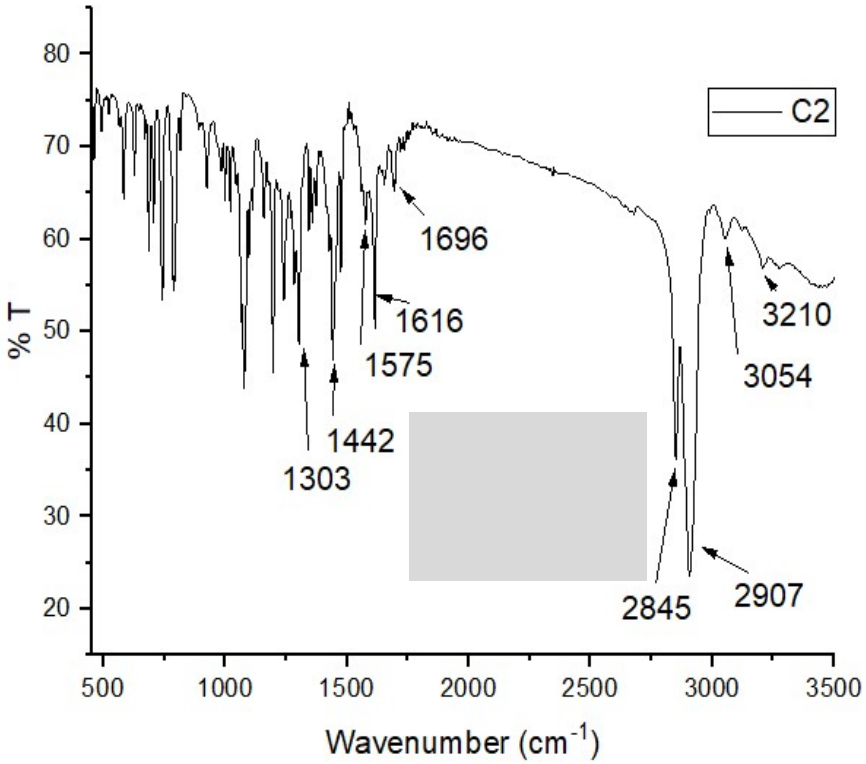

Figure s24: FTIR spectrum of **C2**.

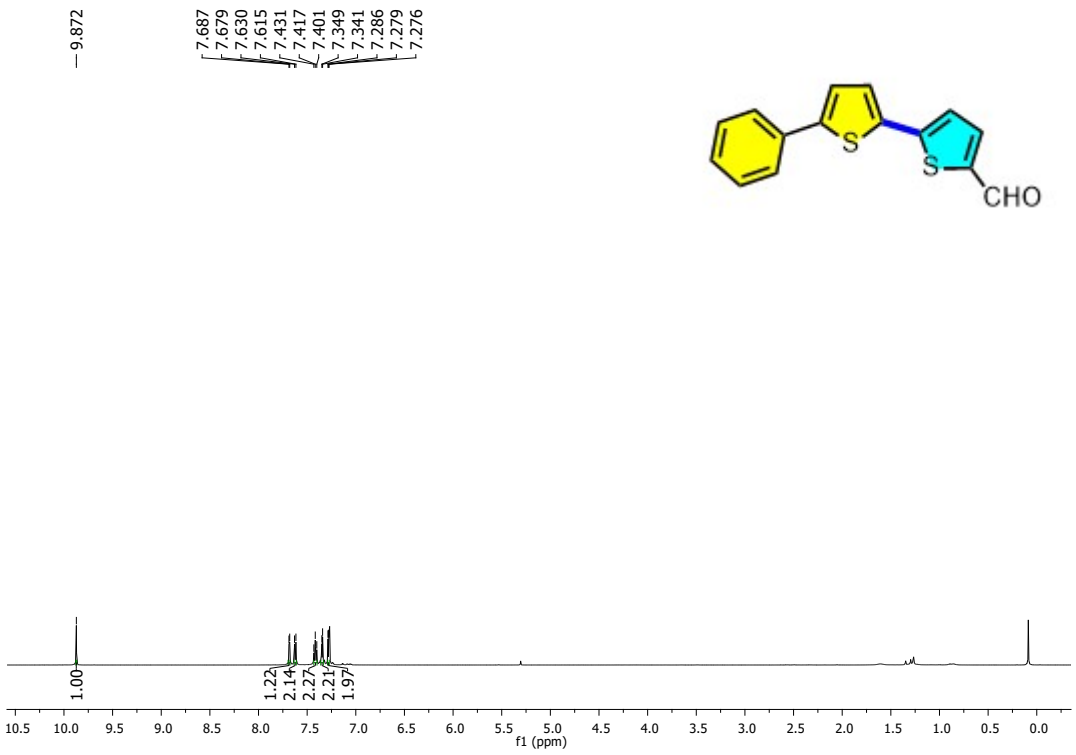

Figure s25: ^{1}H NMR spectrum of compound **3aa**.

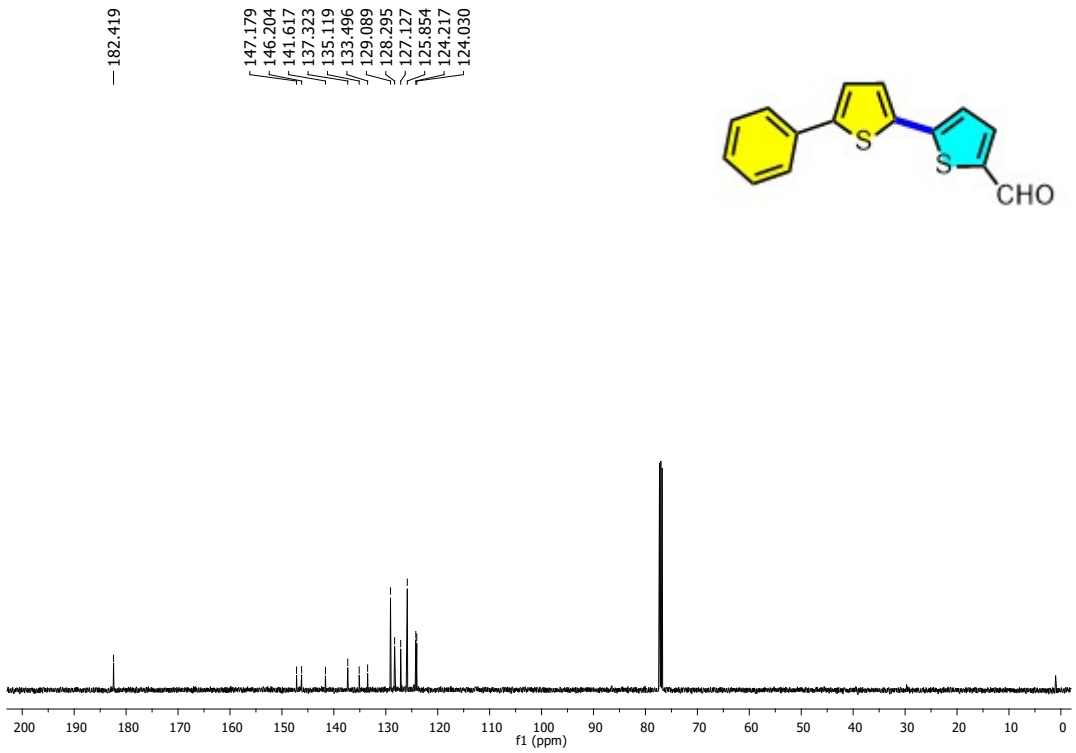

Figure s26: ^{13}C{^{1}H} NMR spectrum of compound **3aa**.

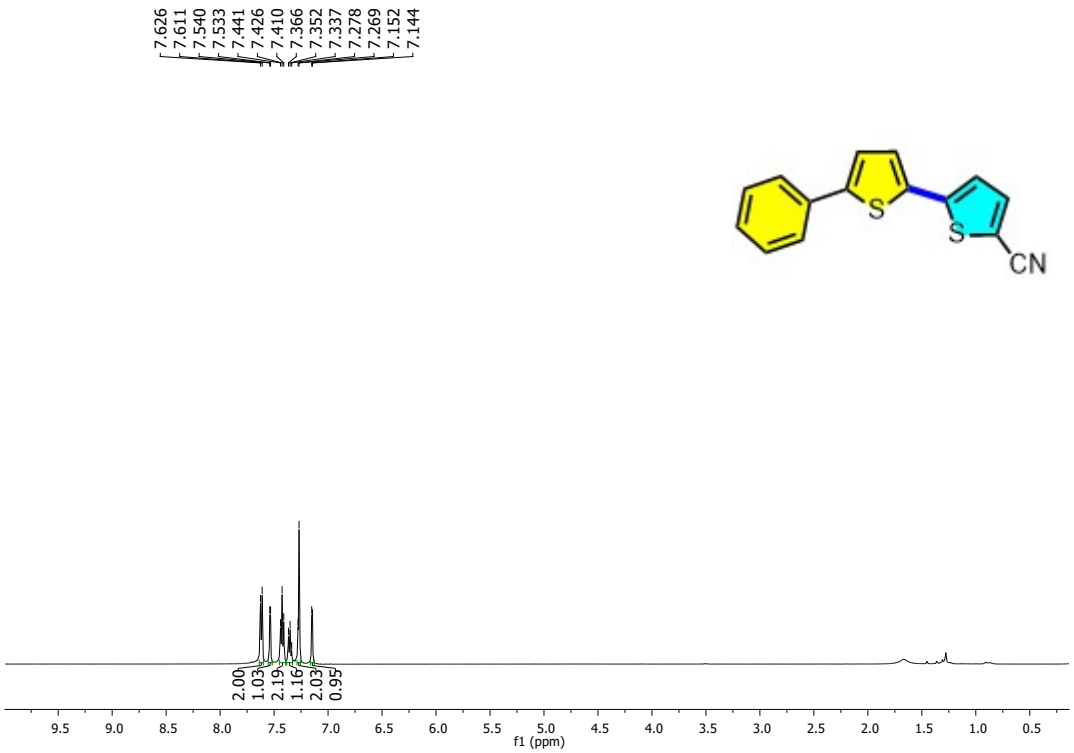

Figure s27: ^{1}H NMR spectrum of compound **3ab**.

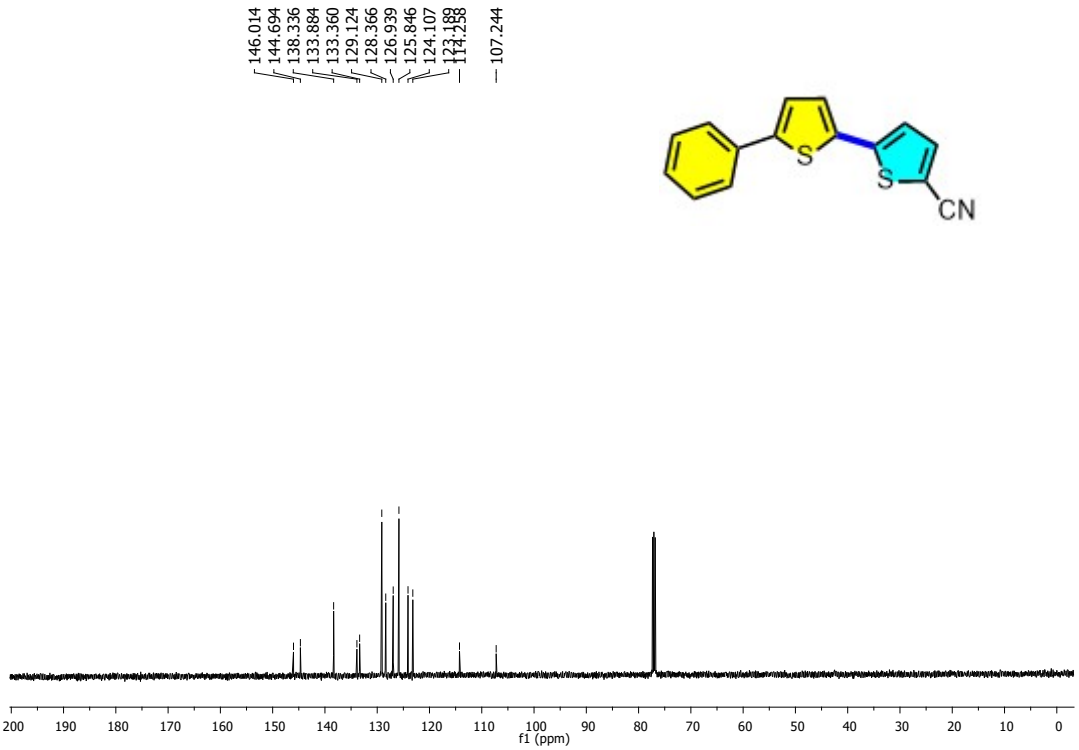

Figure s28: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ab**.

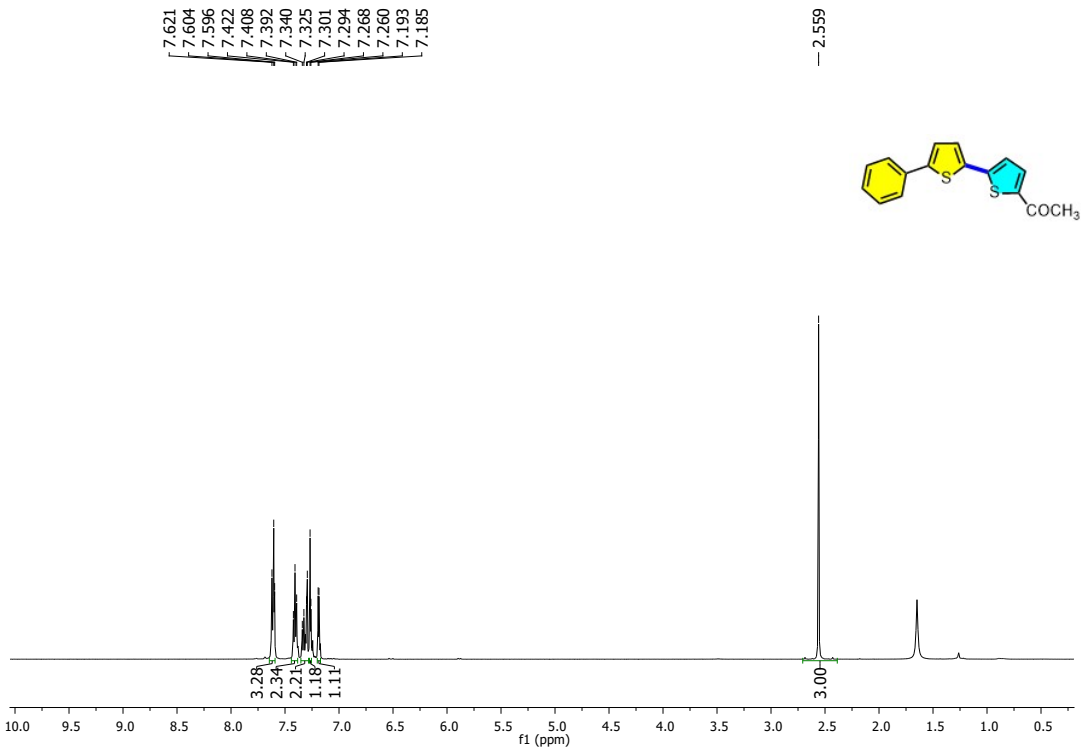

Figure s29:[1]H NMR spectrum of compound **3ac**.

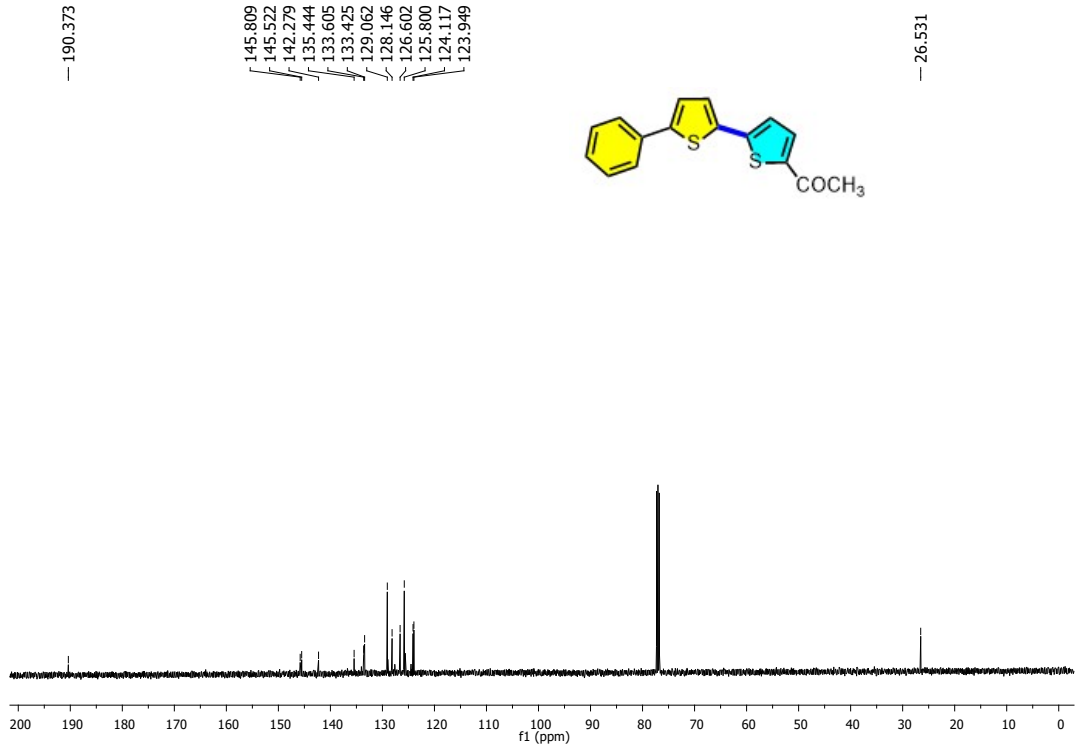

Figure s30: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ac**.

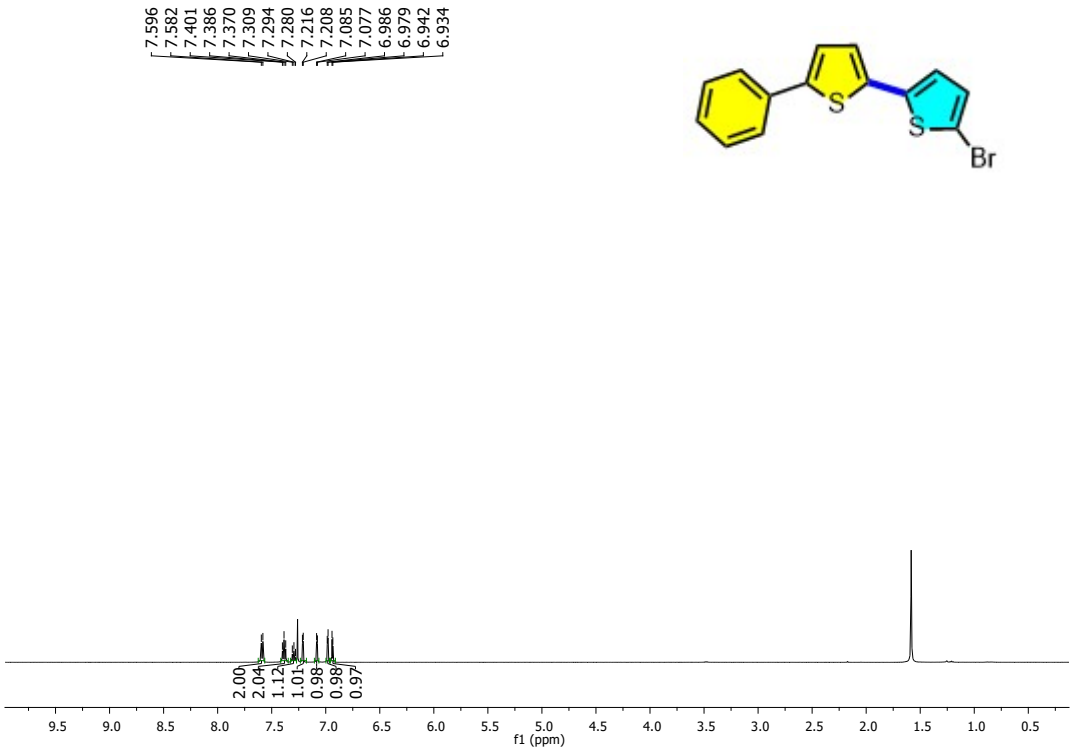

Figure s31: ^{1}H NMR spectrum of compound **3ad**.

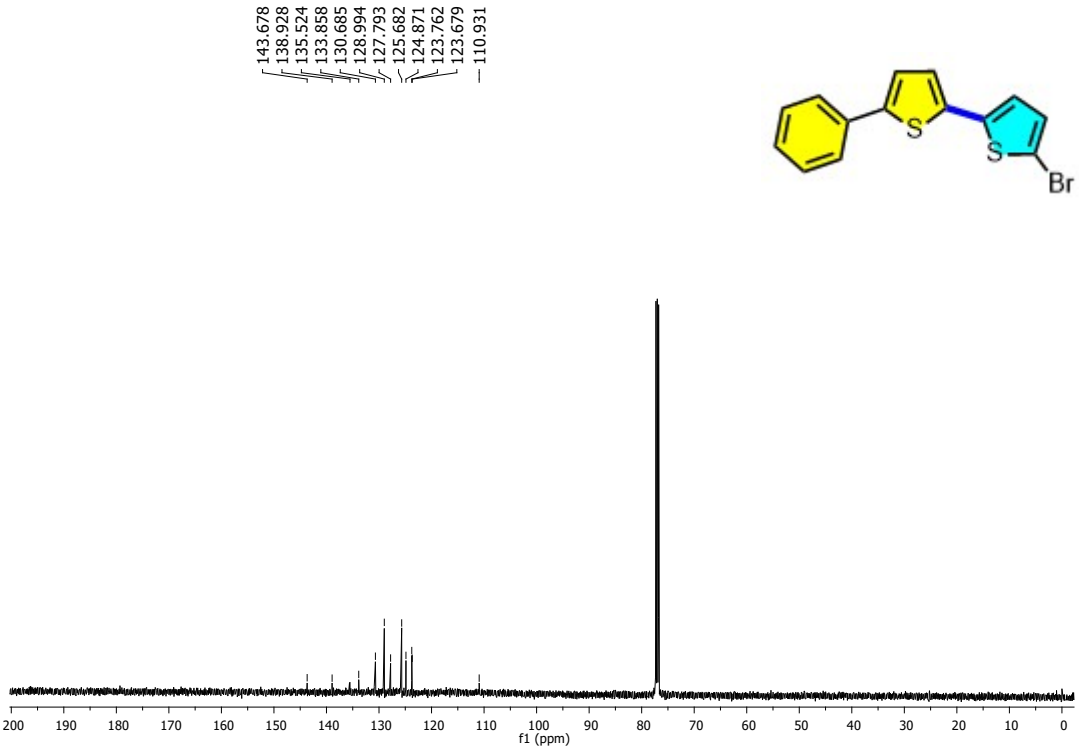

Figure s32: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ad**.

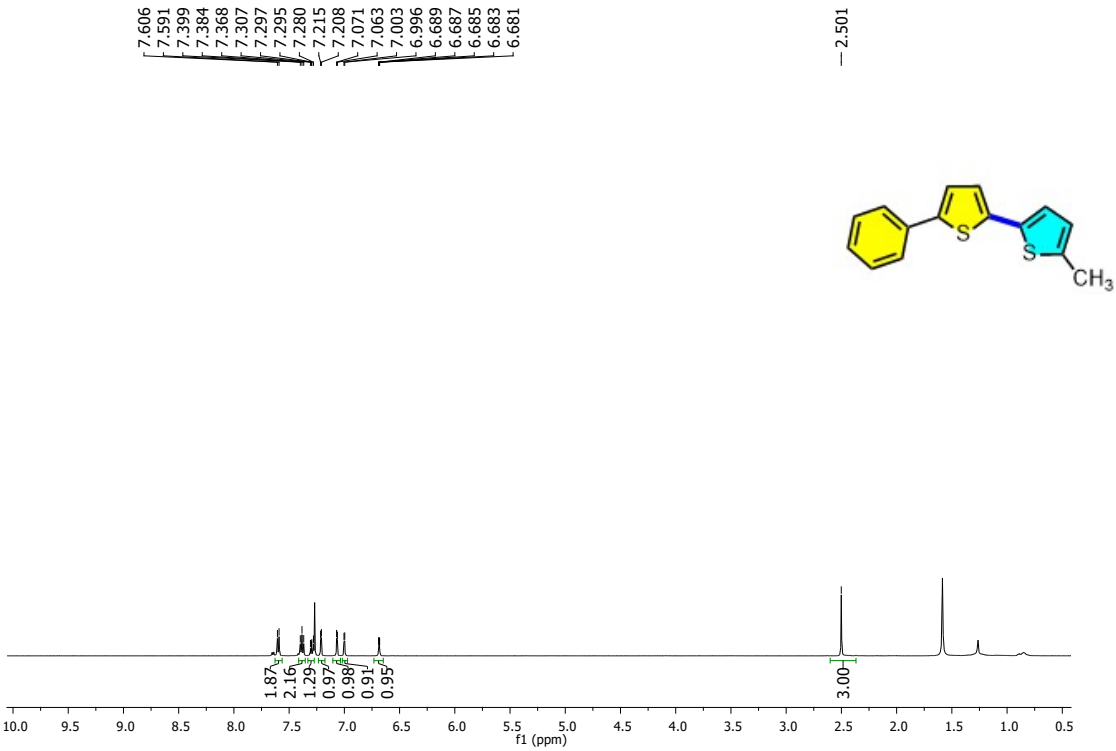

Figure s33: ^{1}H NMR spectrum of compound **3ae**.

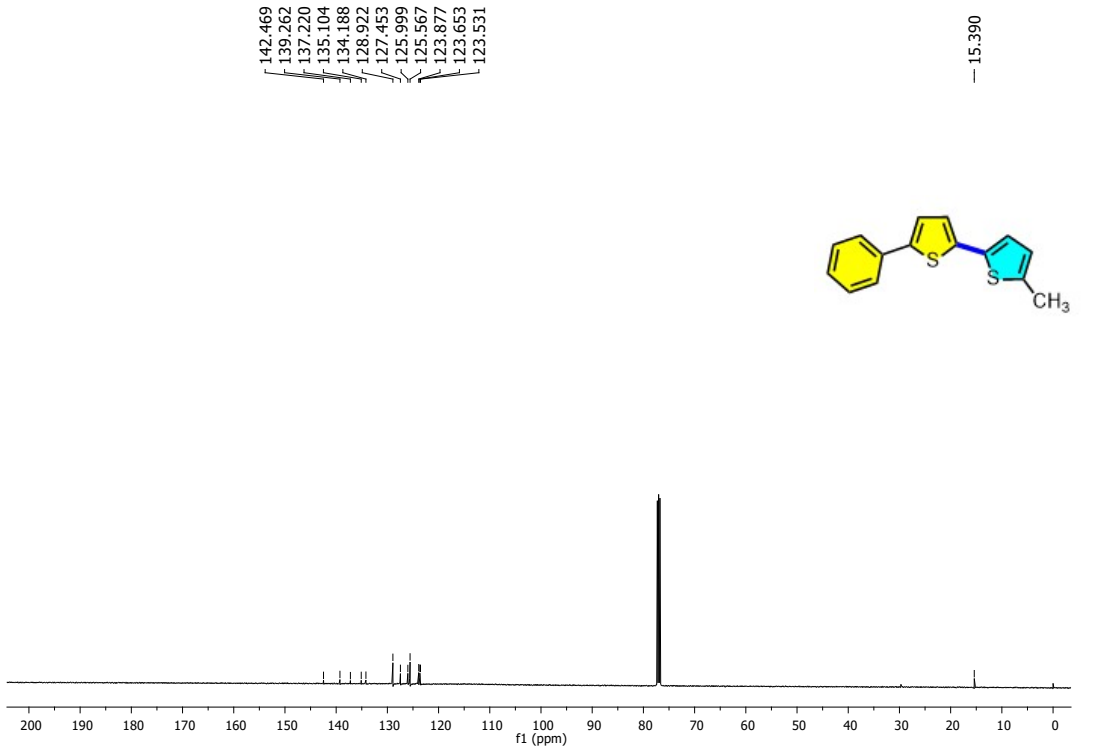

Figure s34: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ae**.

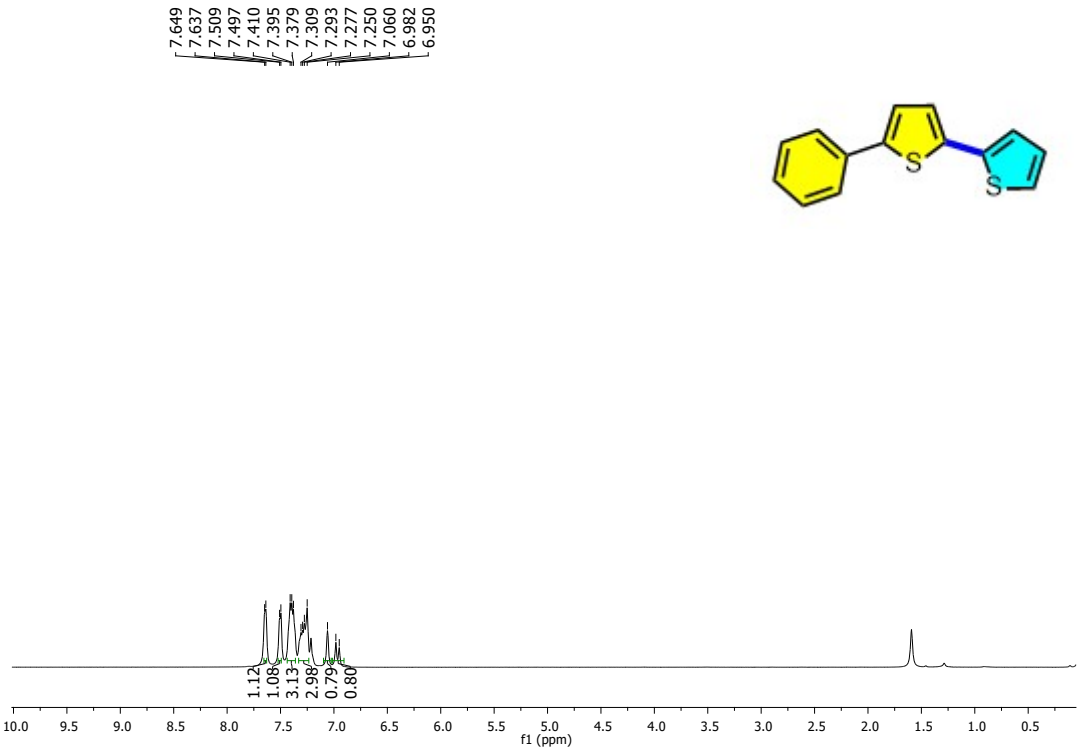

Figure s35: ^{1}H NMR spectrum of compound **3af**.

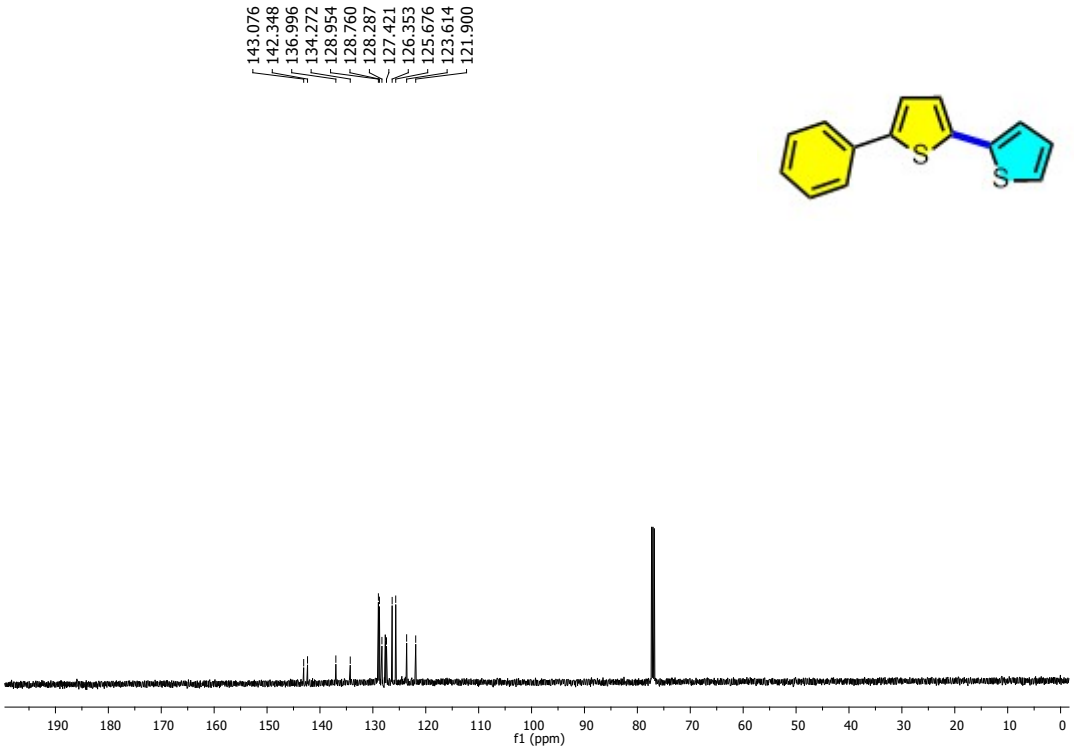

Figure s36: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3af**.

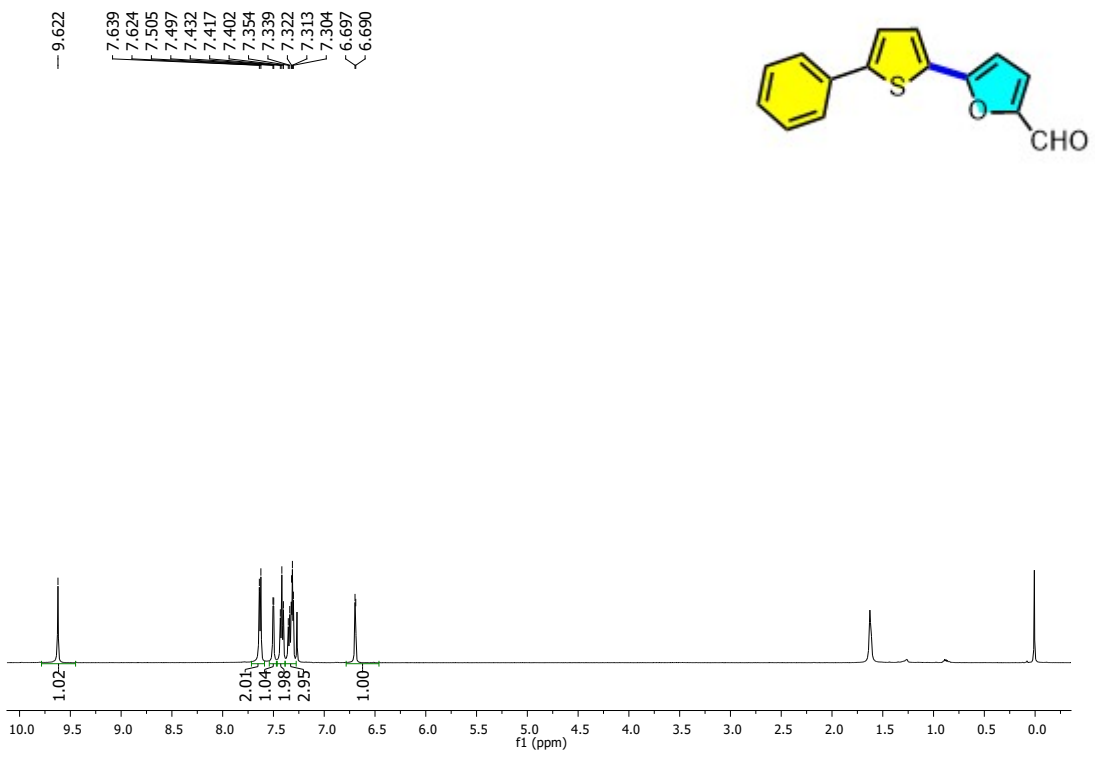

Figure s37: ^{1}H NMR spectrum of compound **3ag**.

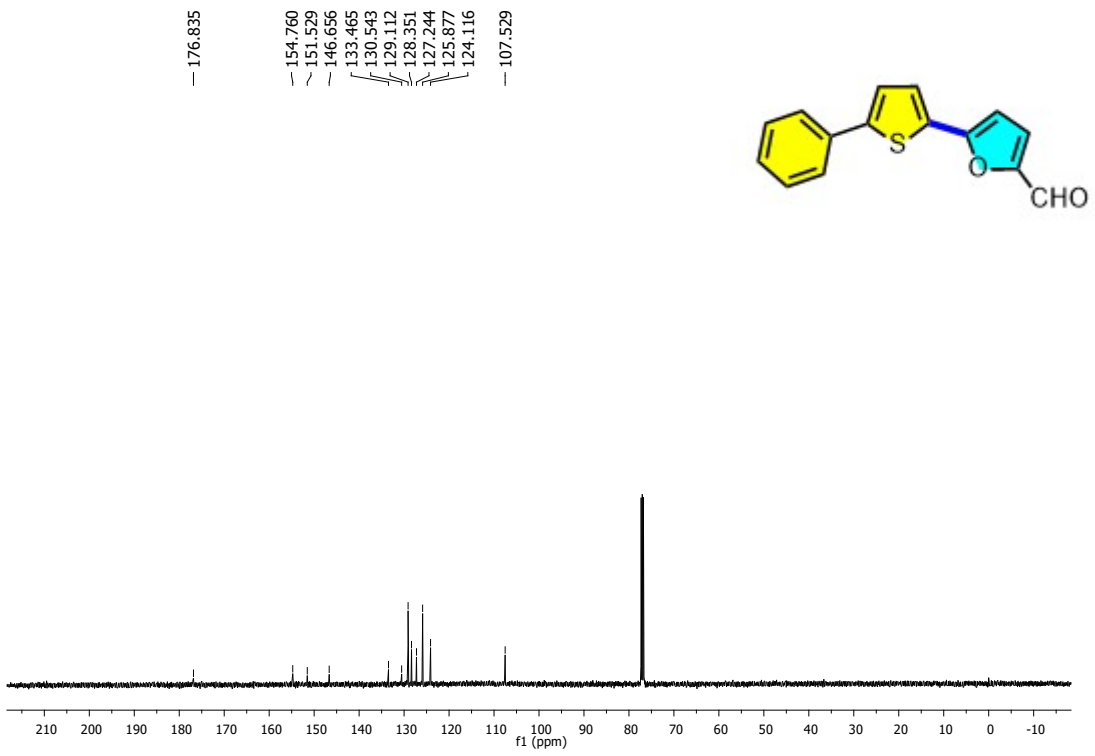

Figure s38: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ag**.

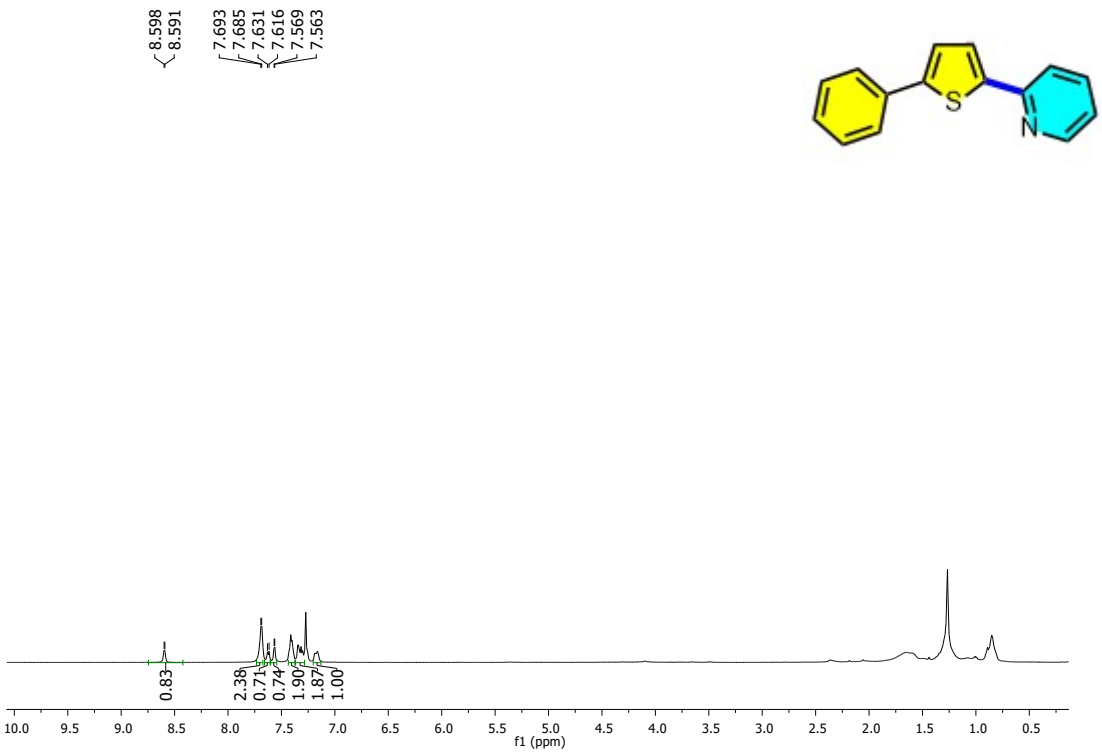

Figure s39: ^{1}H NMR spectrum of compound **3ah**.

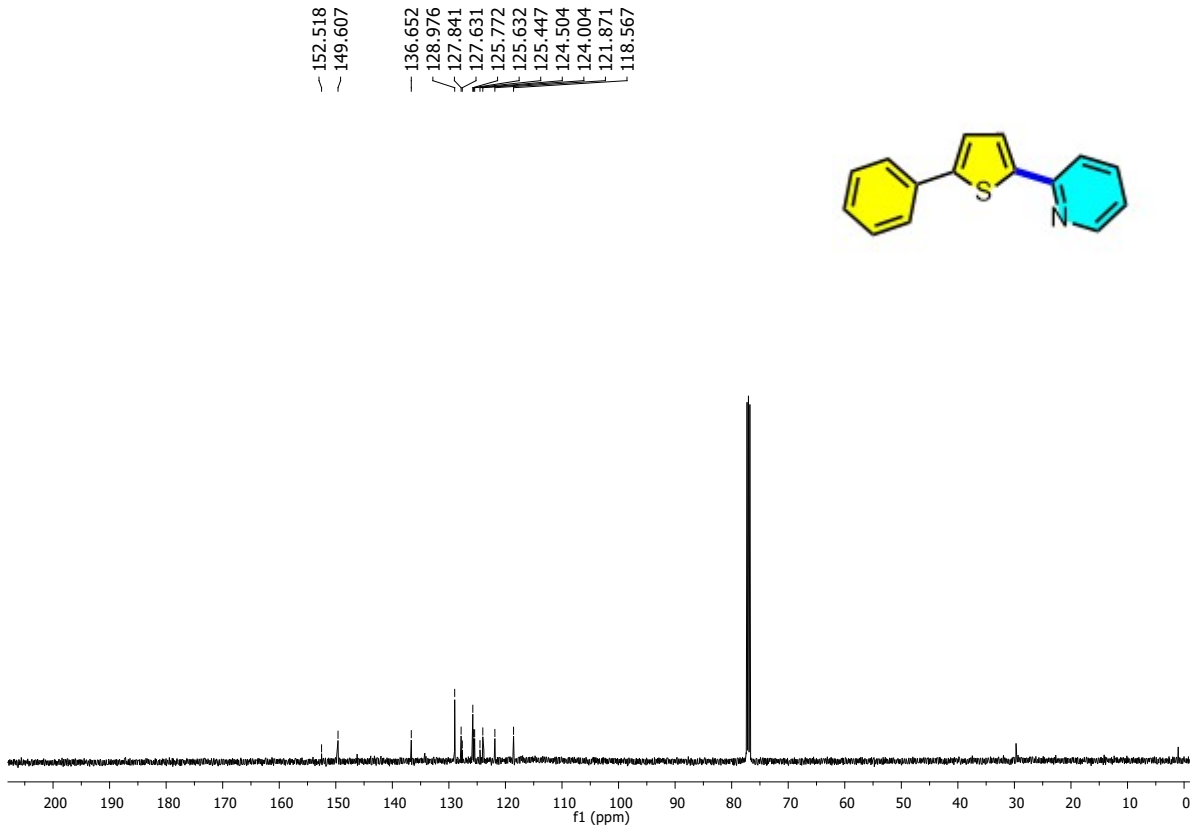

Figure s40: ^{13}C{^{1}H} NMR spectrum of compound **3ah**.

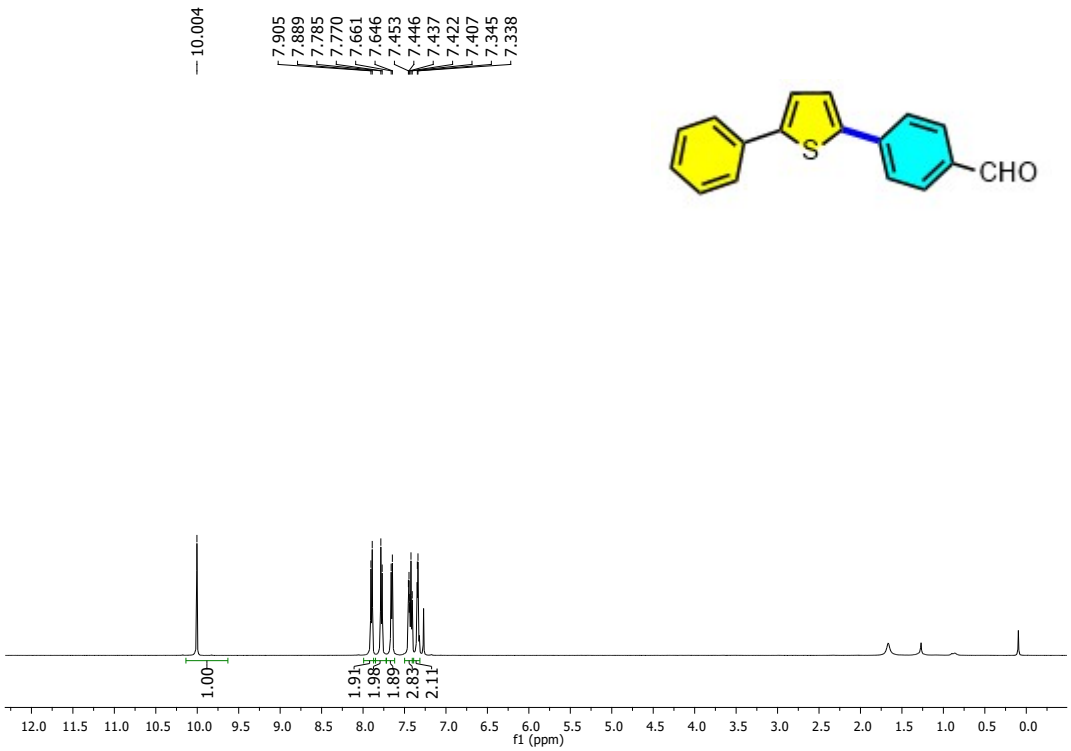

Figure s41: ^{1}H NMR spectrum of compound **3ai**.

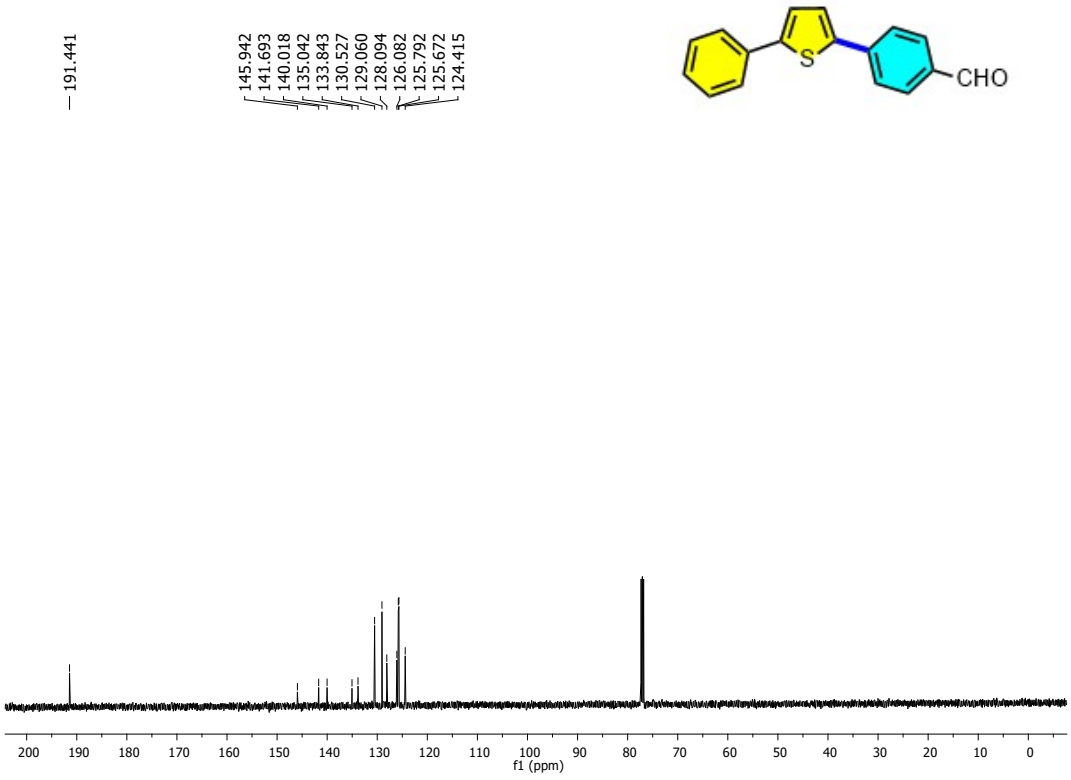

Figure s42: ^{13}C{^{1}H} NMR spectrum of compound **3ai**.

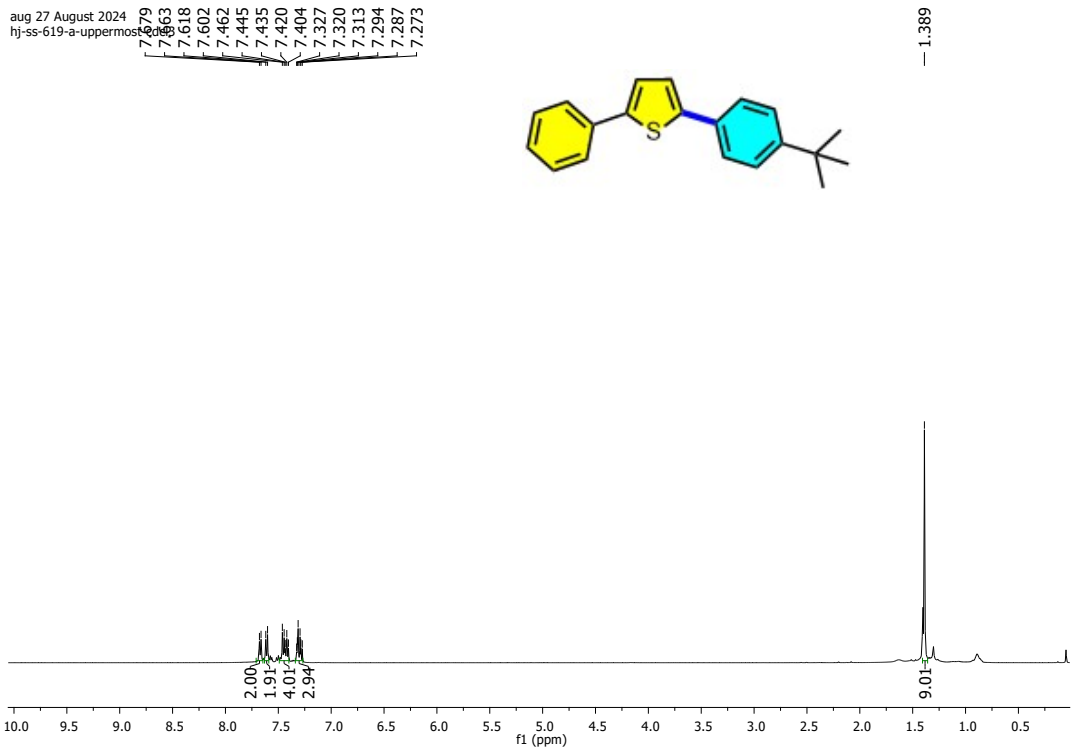

Figure s43: ^{1}H NMR spectrum of compound **3aj**.

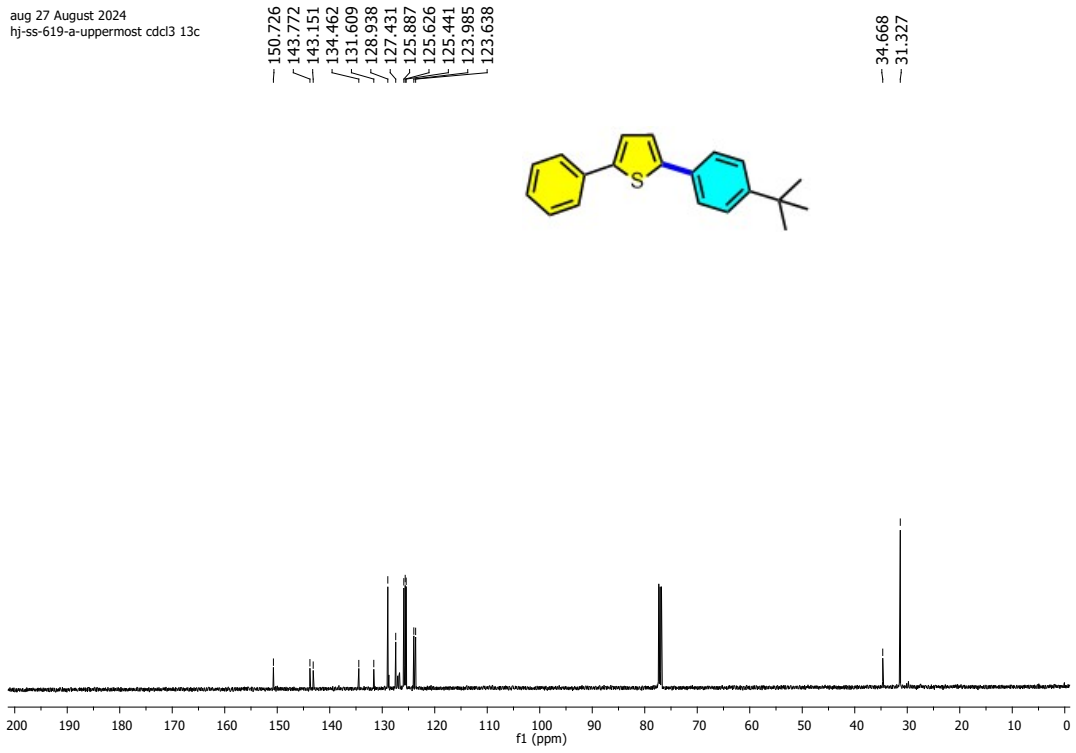

Figure s44: ^{13}C{^{1}H} NMR spectrum of compound **3aj**.

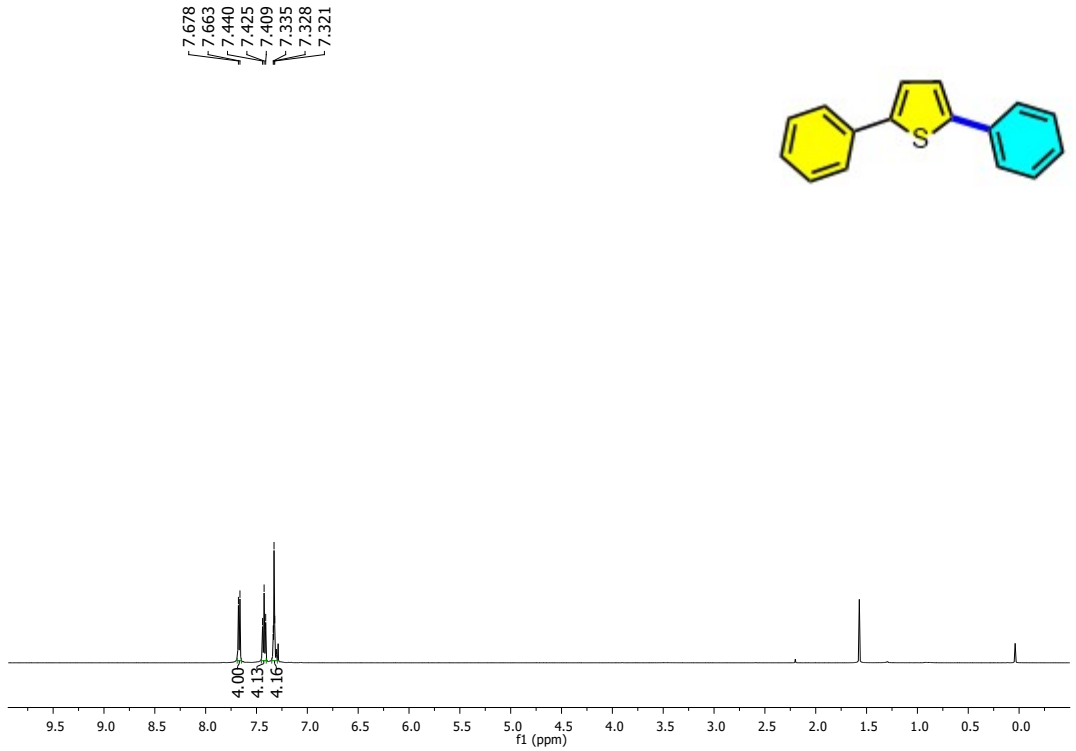

Figure s45: ^{1}H NMR spectrum of compound **3ak**.

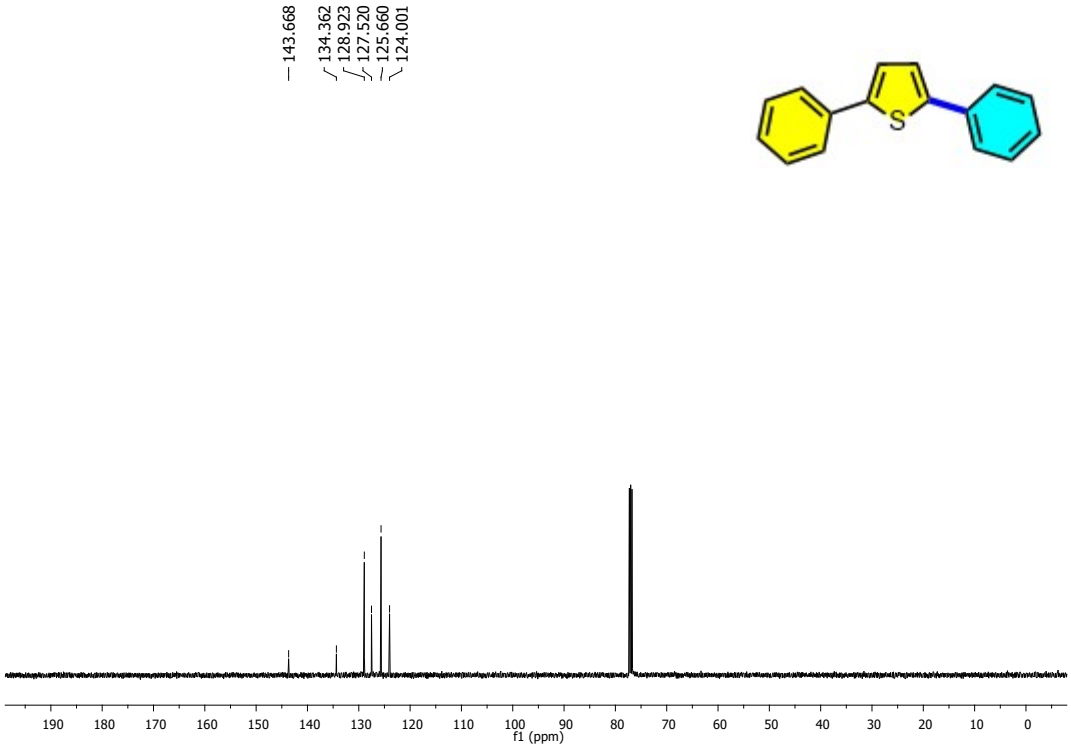

Figure s46: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ak**.

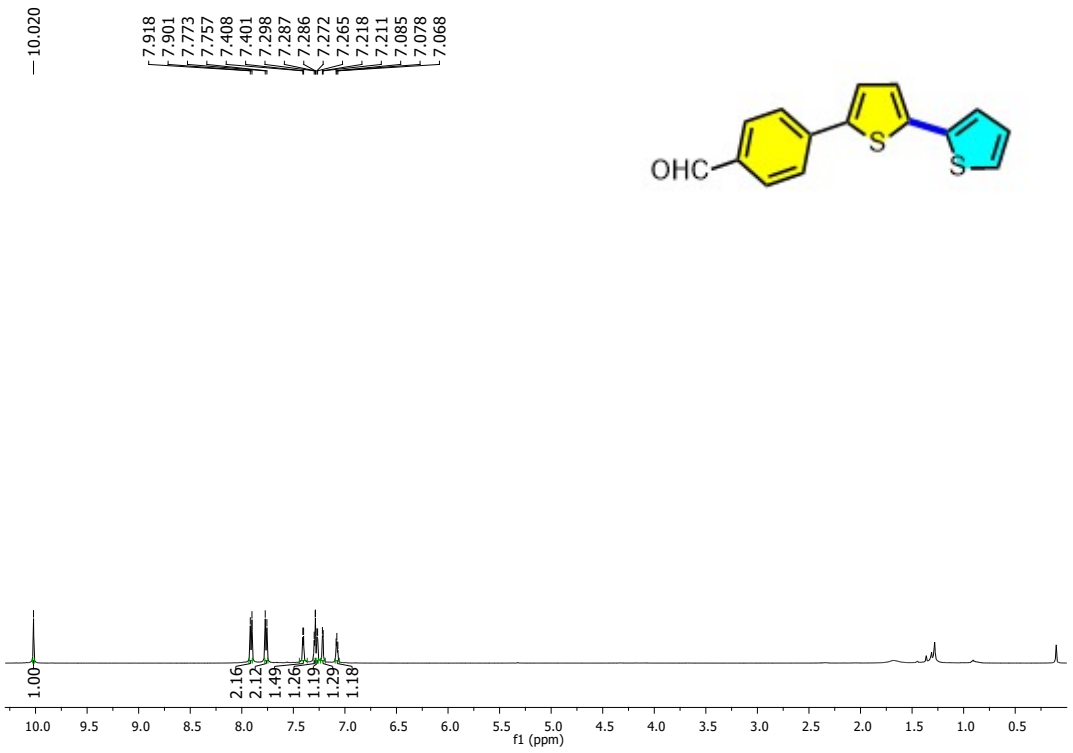

Figure s47: ^{1}H NMR spectrum of compound **3bf**.

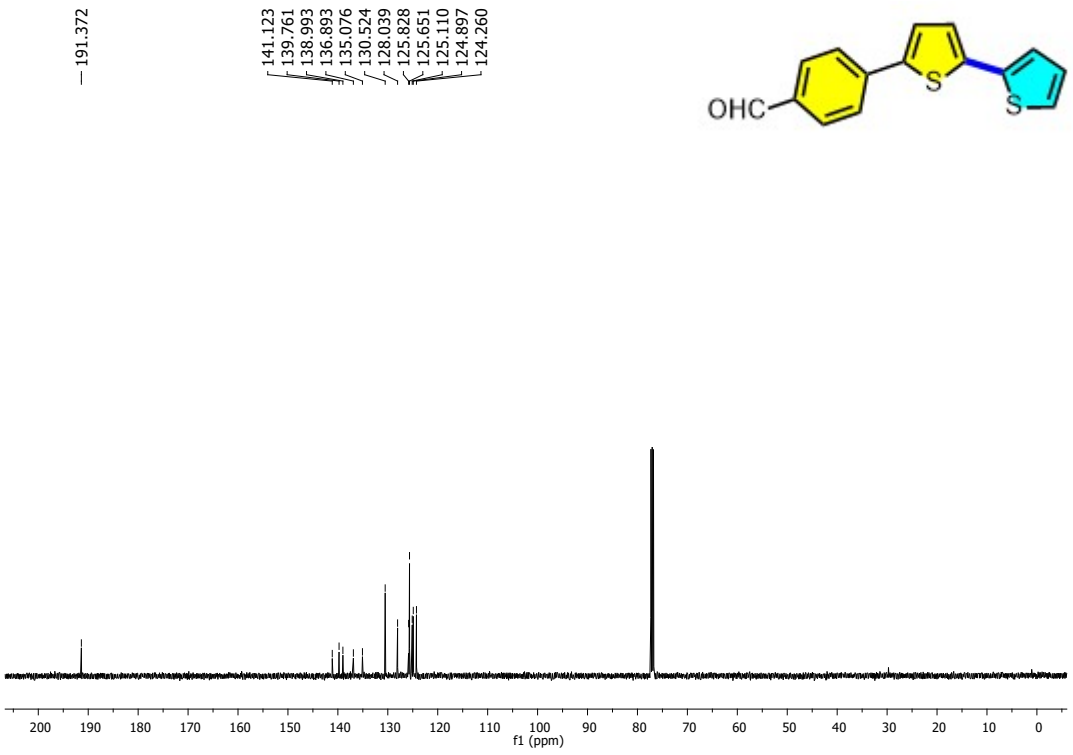

Figure s48: ^{13}C{^{1}H} NMR spectrum of compound **3bf**.

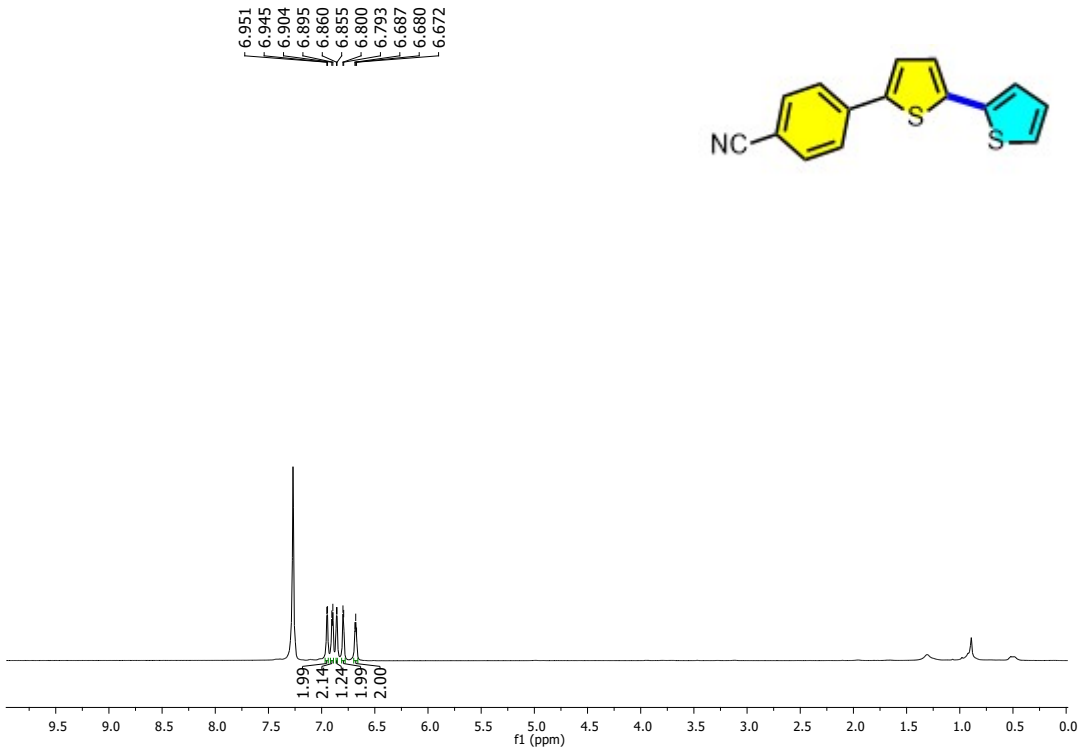

Figure s49: ^{1}H NMR spectrum of compound **3cf**.

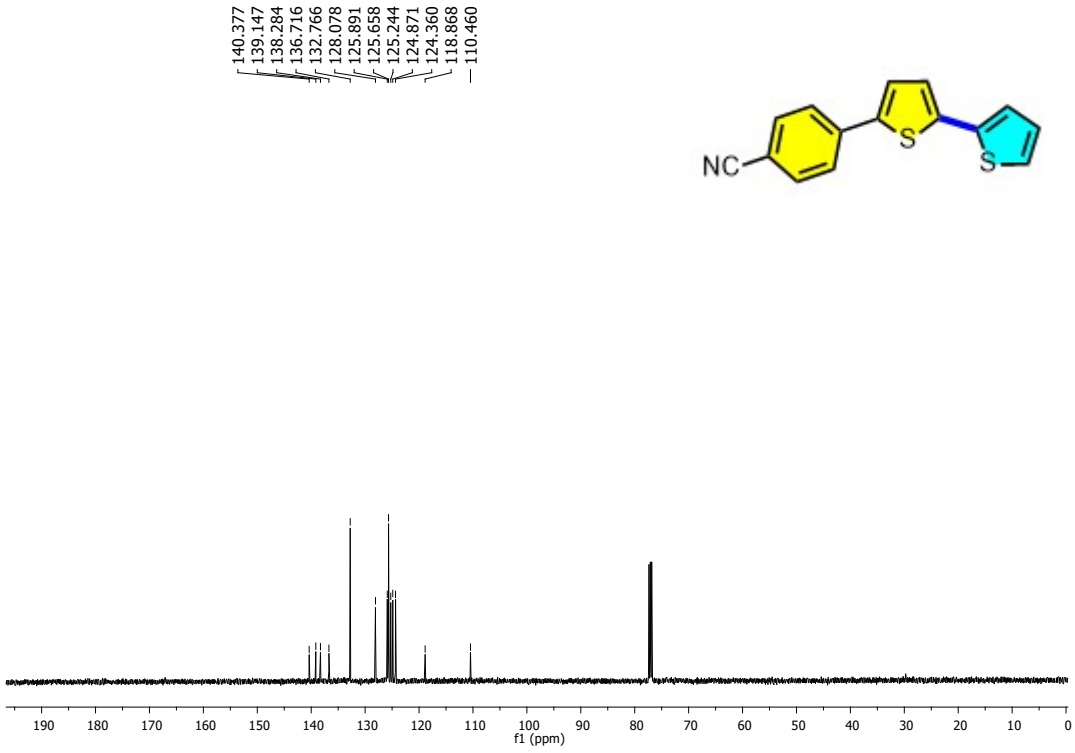

Figure s50: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3cf**.

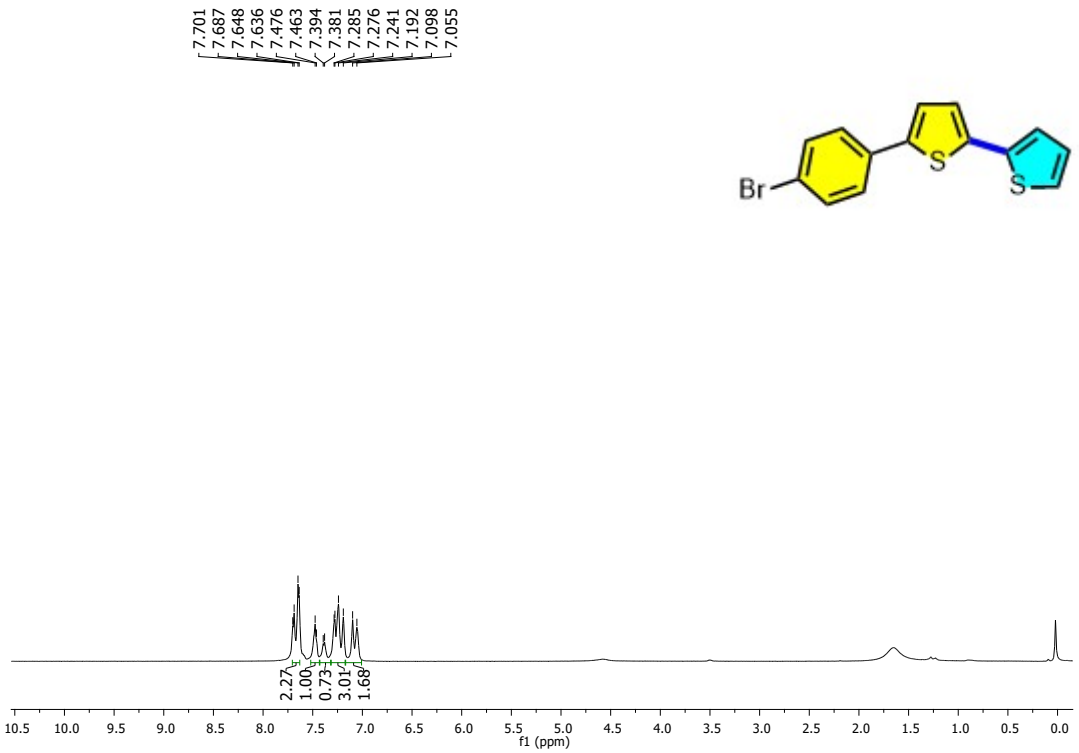

Figure s51: ^{1}H NMR spectrum of compound **3df**.

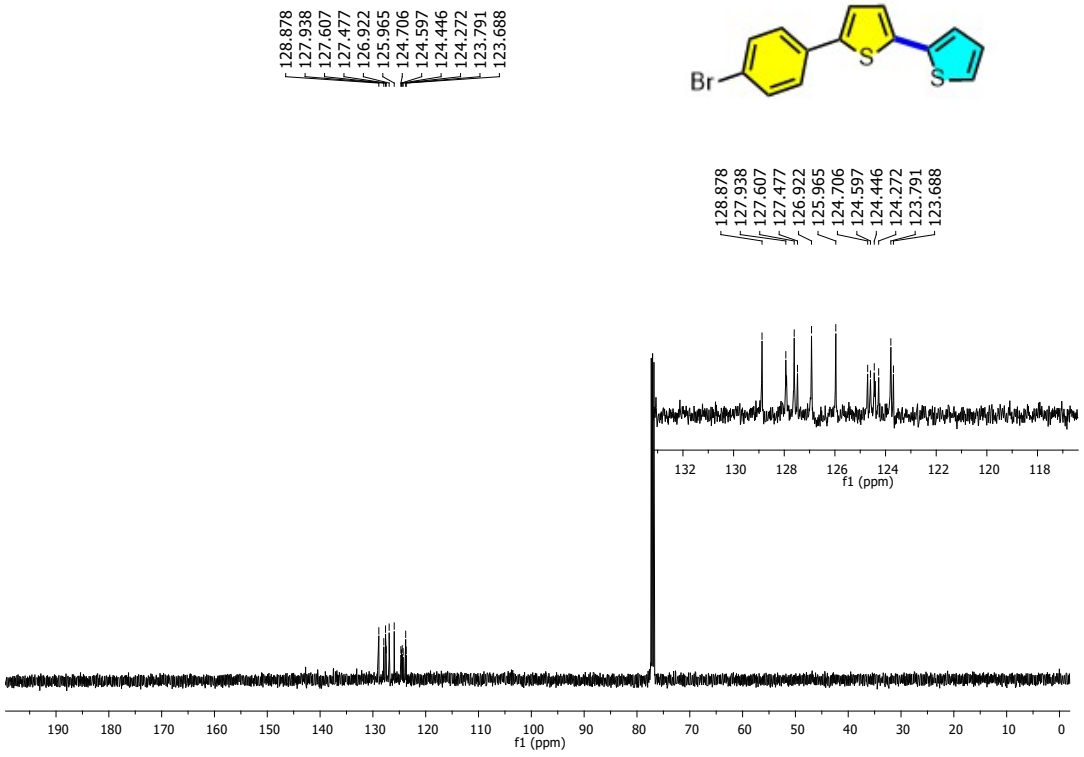

Figure s52: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3df**.

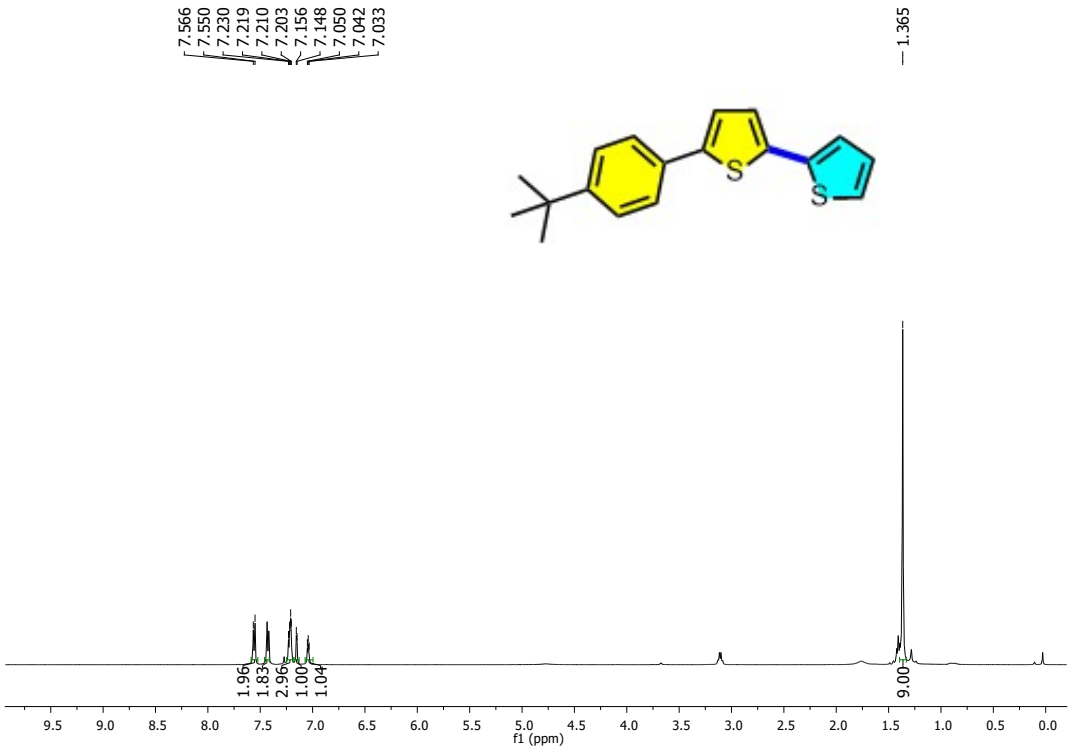

Figure s53: ^{1}H NMR spectrum of compound **3ef**.

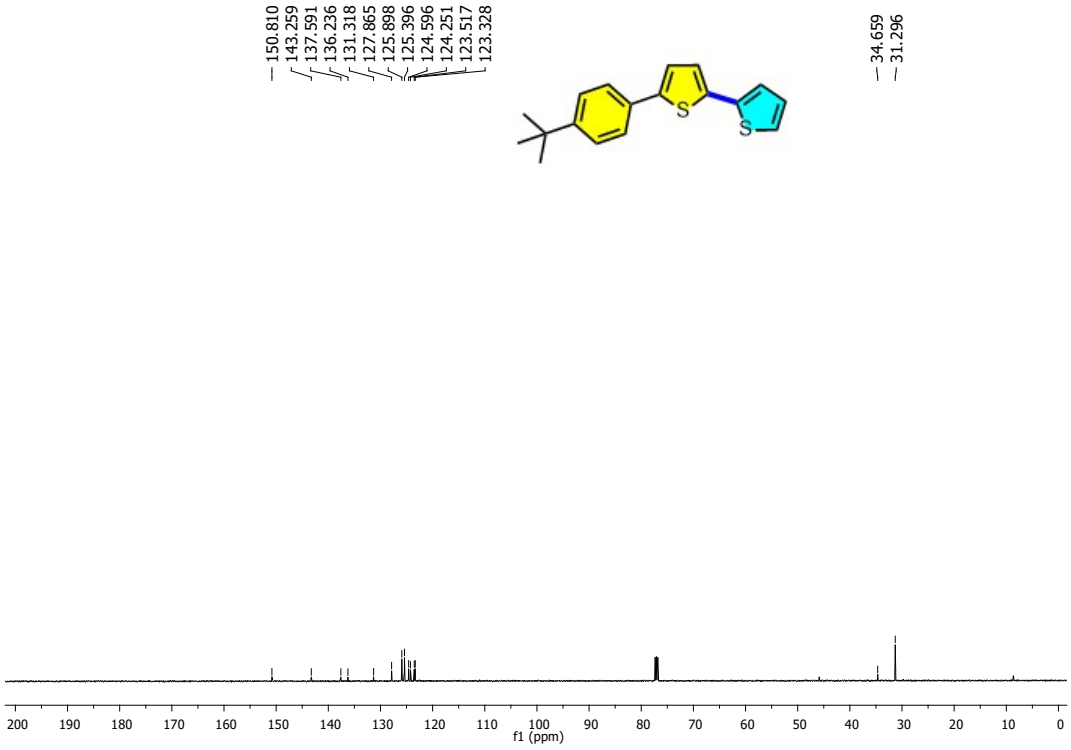

Figure s54: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ef**.

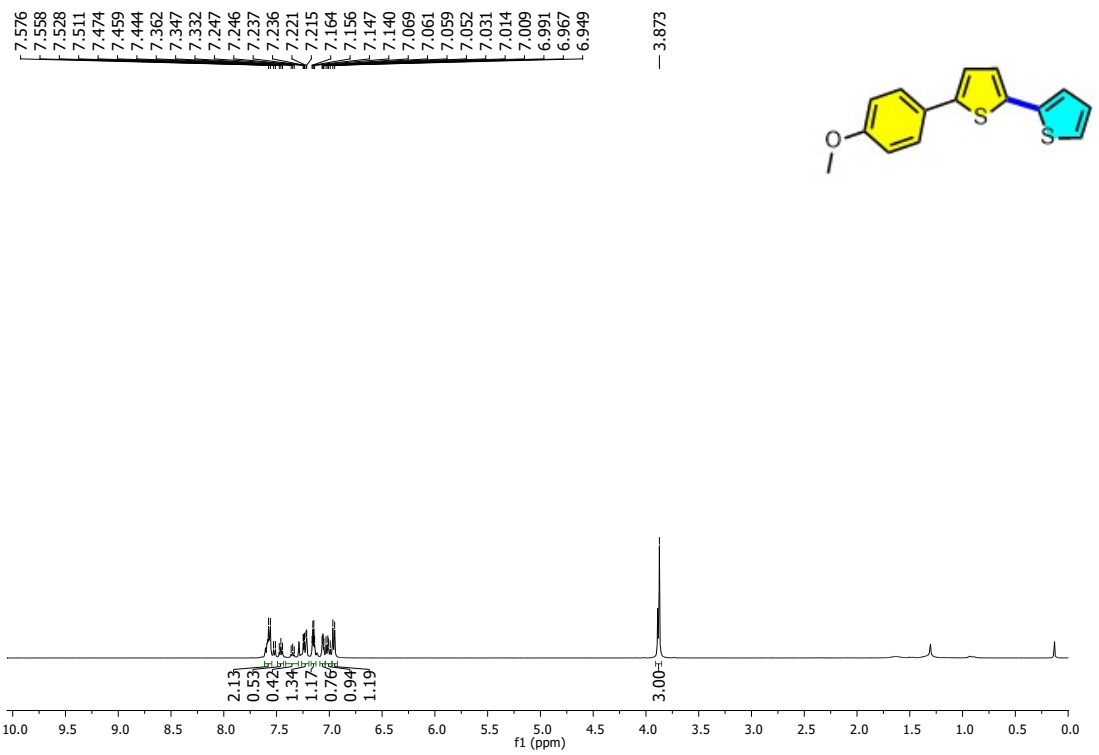

Figure s55: ^{1}H NMR spectrum of compound **3ff**.

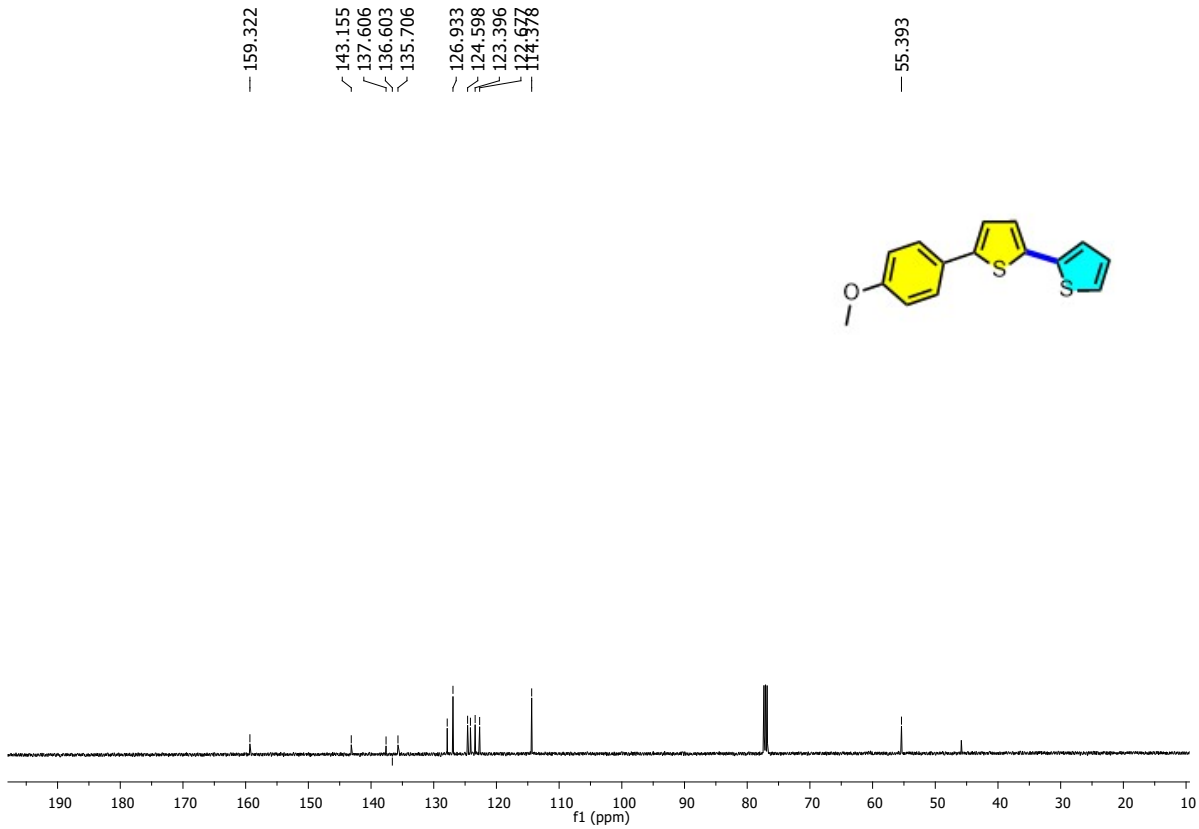

Figure s56: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ff**.

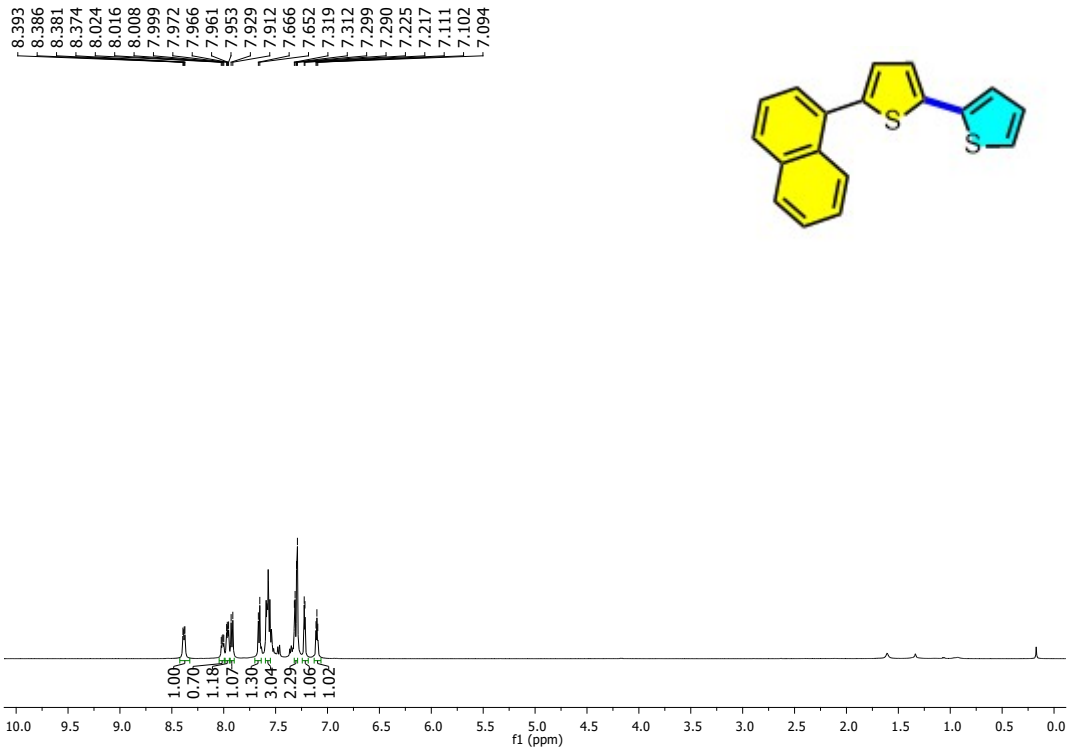

Figure s57: ^{1}H NMR spectrum of compound **3gf**.

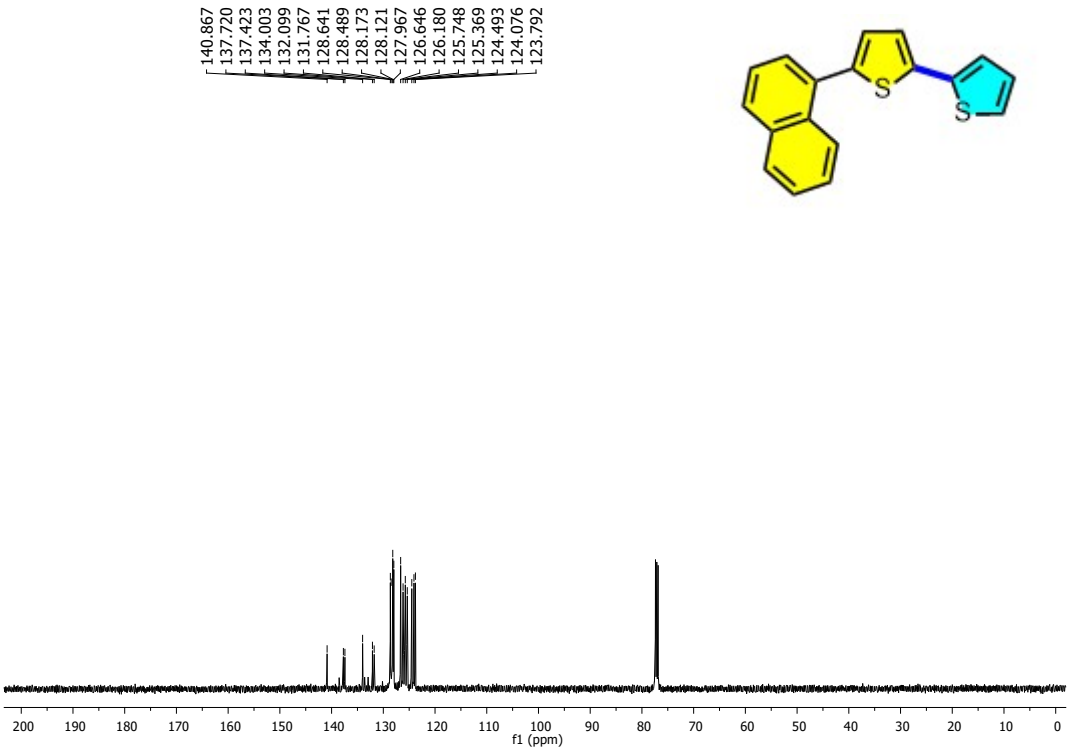

Figure s58: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3gf**.

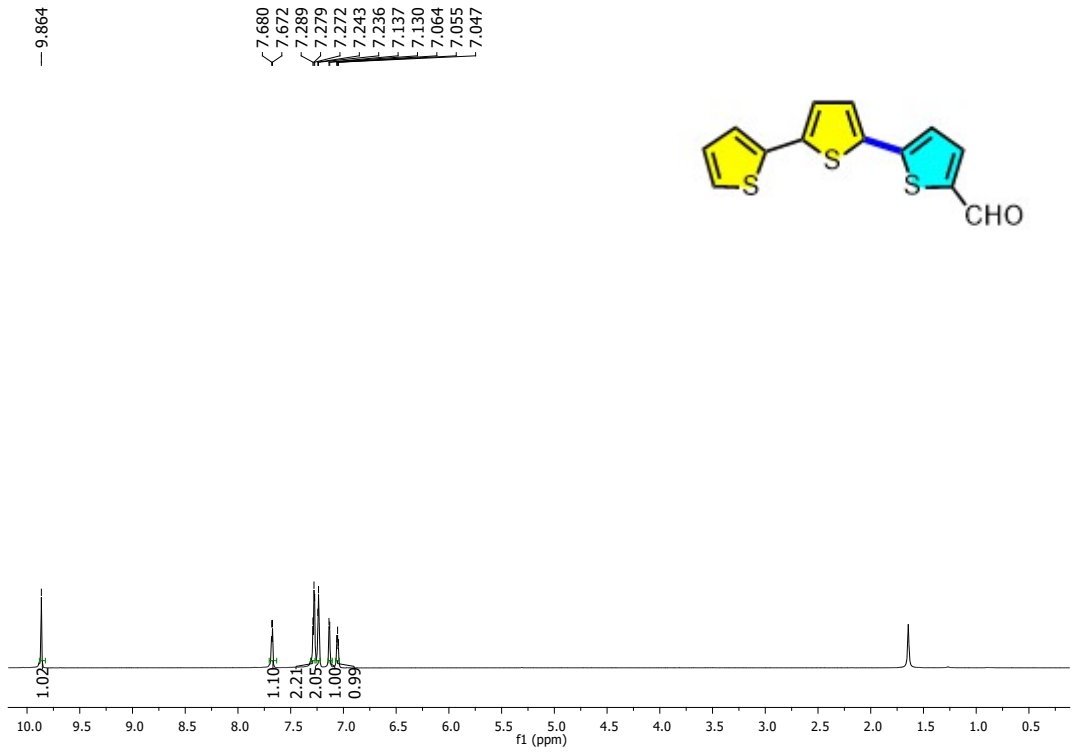

Figure s59: ^{1}H NMR spectrum of compound **3ha**.

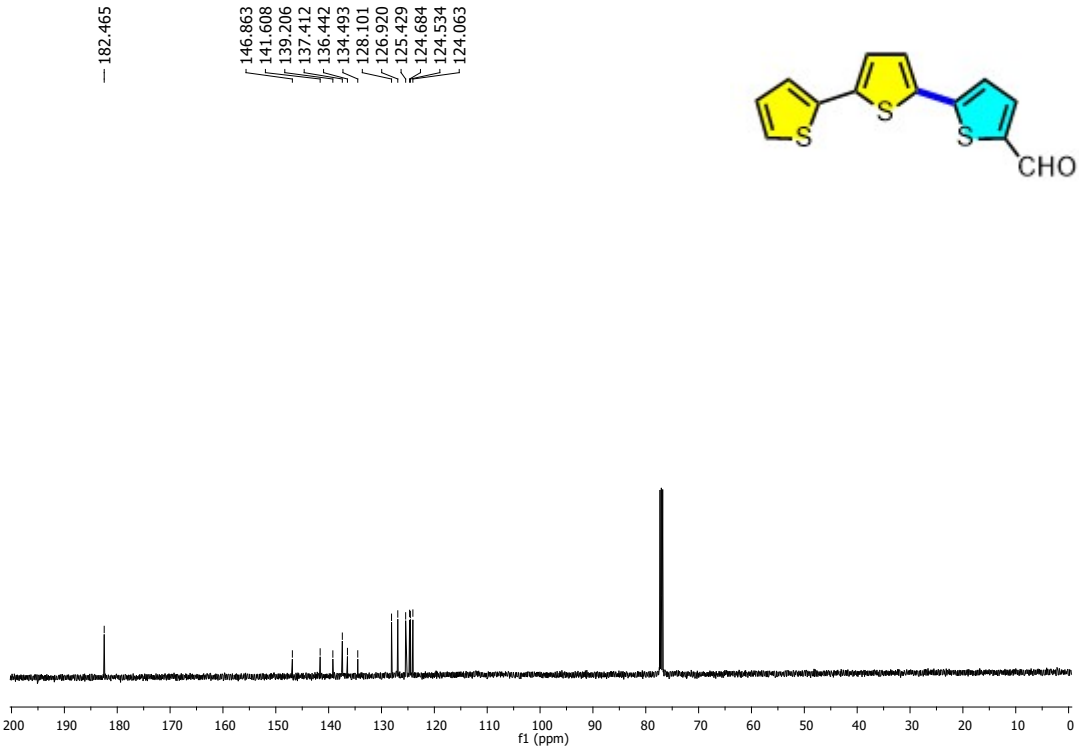

Figure s60: ^{13}C{^{1}H} NMR spectrum of compound **3ha**.

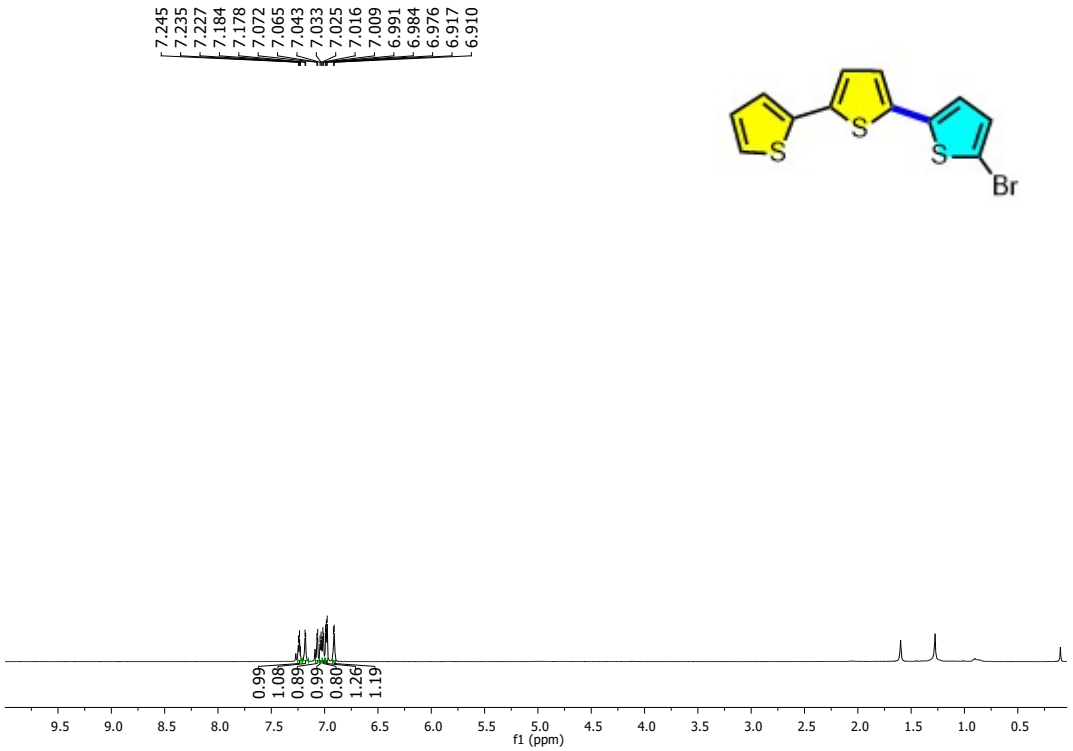

Figure s61: ^{1}H NMR spectrum of compound **3hd**.

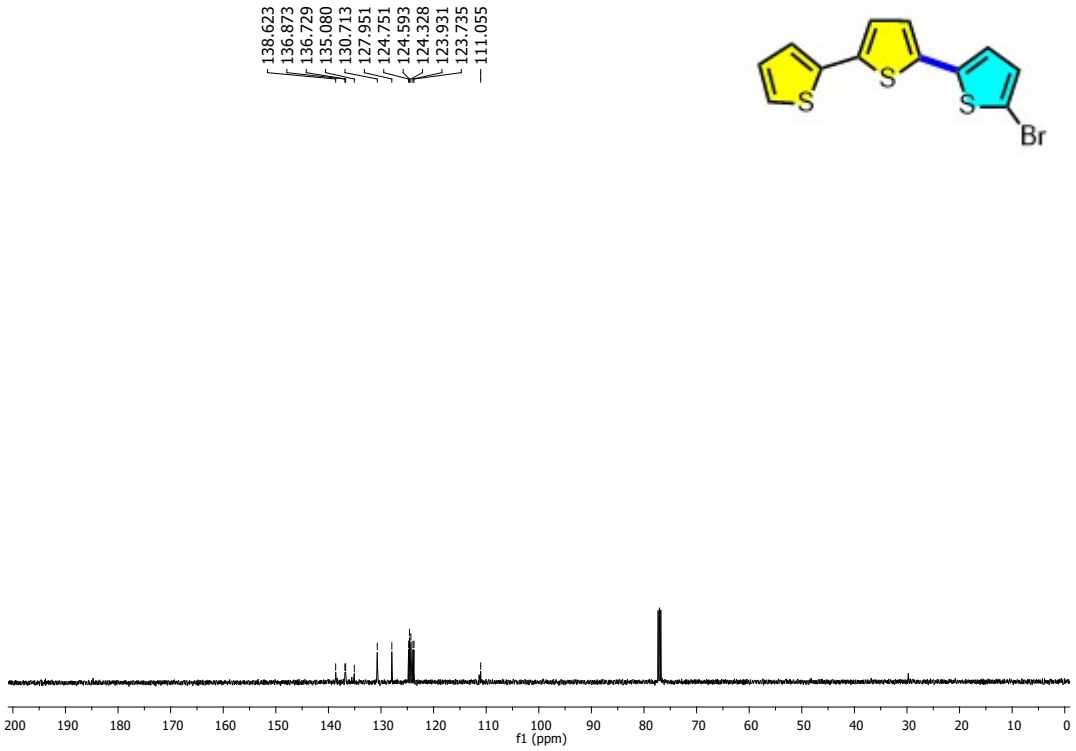

Figure s62: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3hd**.

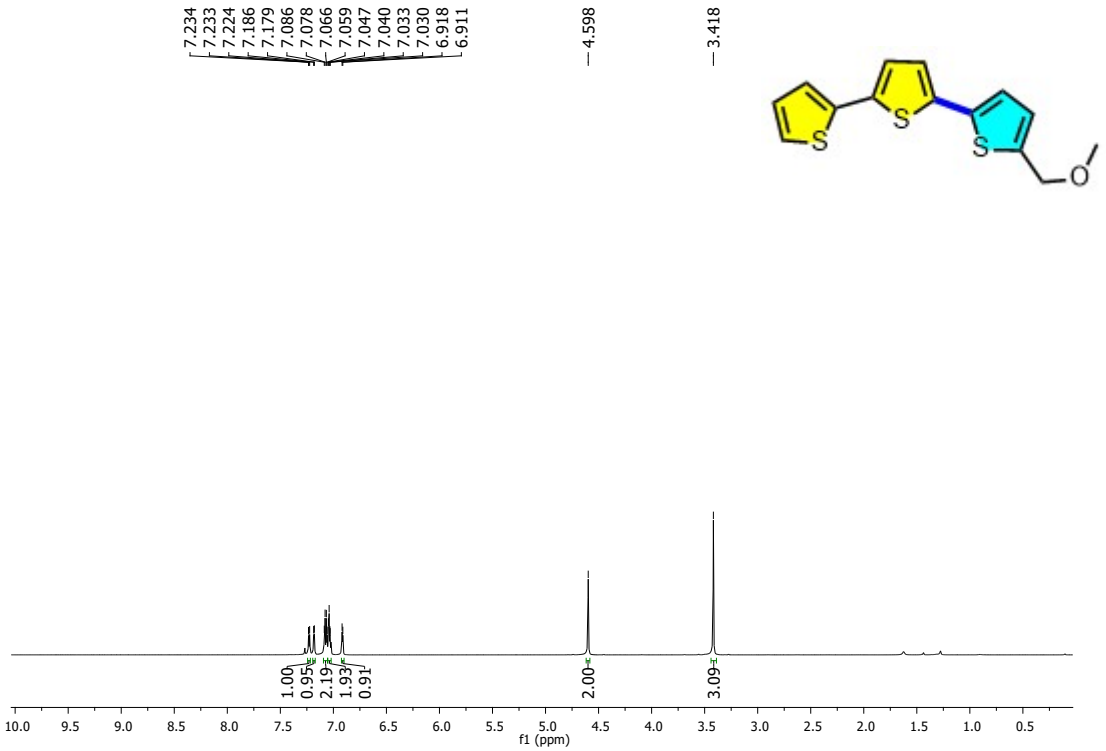

Figure s63: ^{1}H NMR spectrum of compound **3hi**.

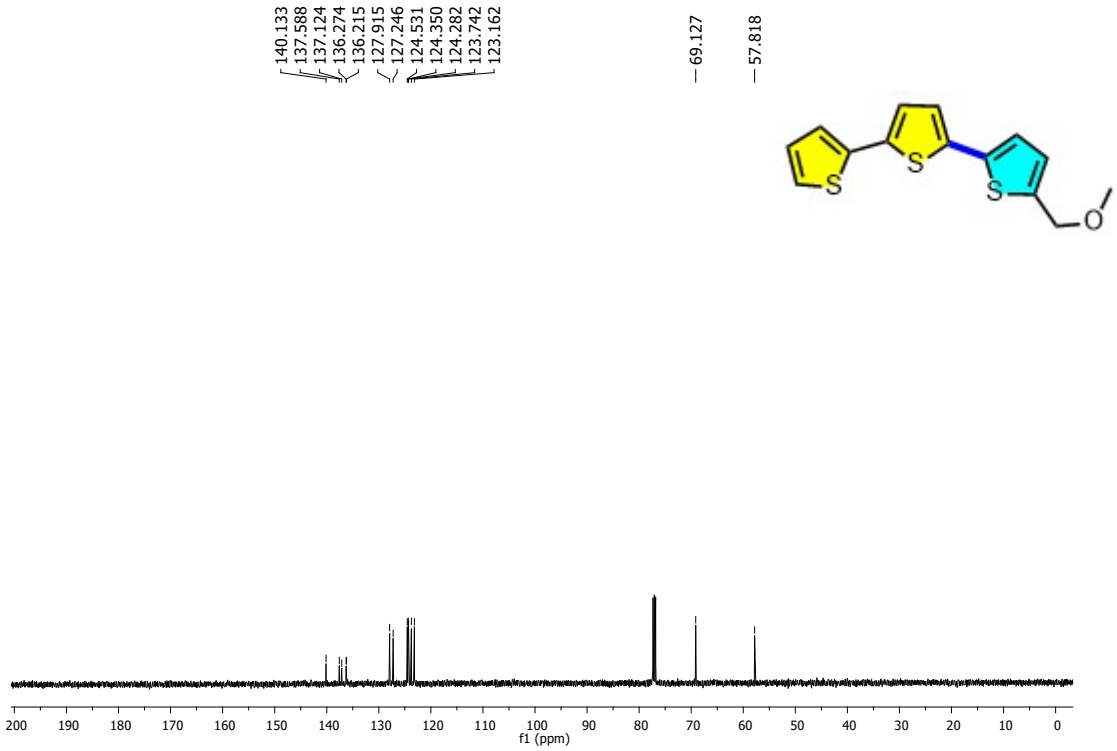

Figure s64: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3hi**.

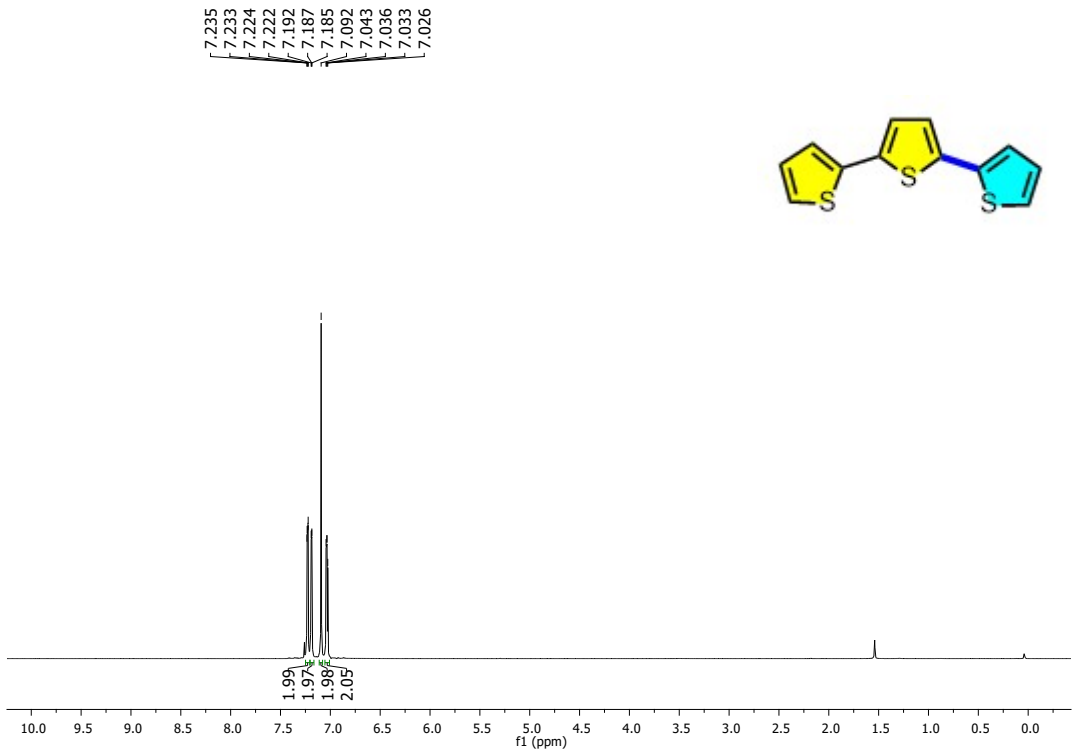

Figure s65: ^{1}H NMR spectrum of compound **3hf**.

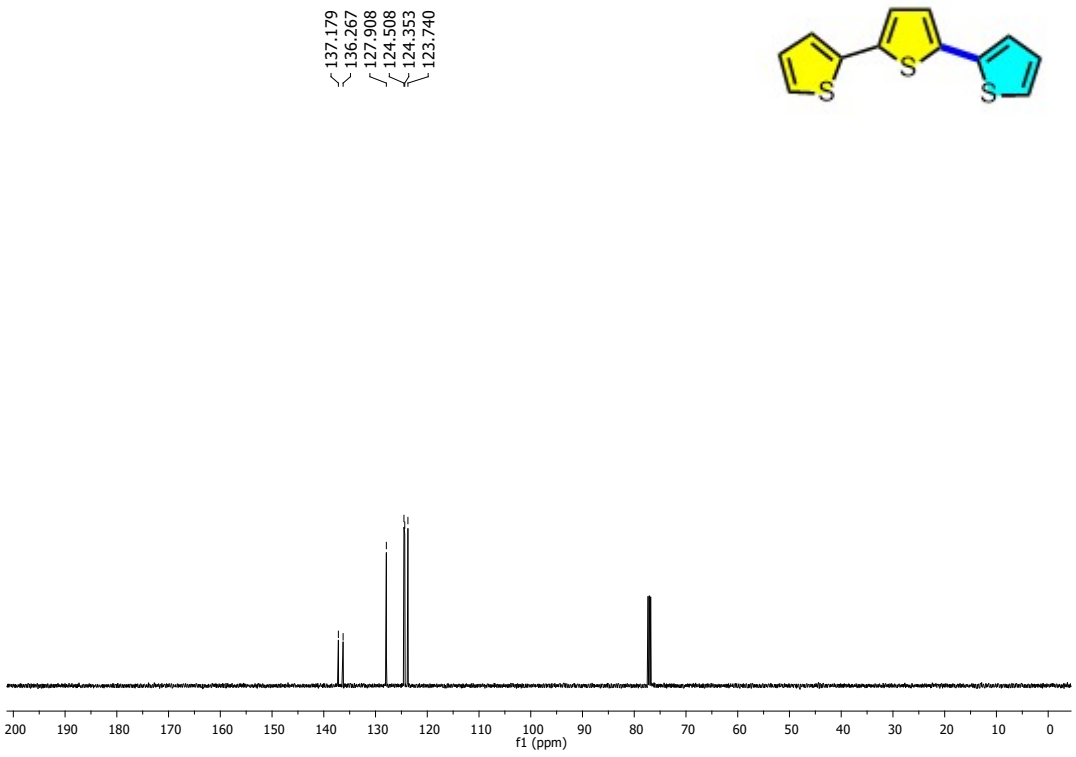

Figure s66: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3hf**.

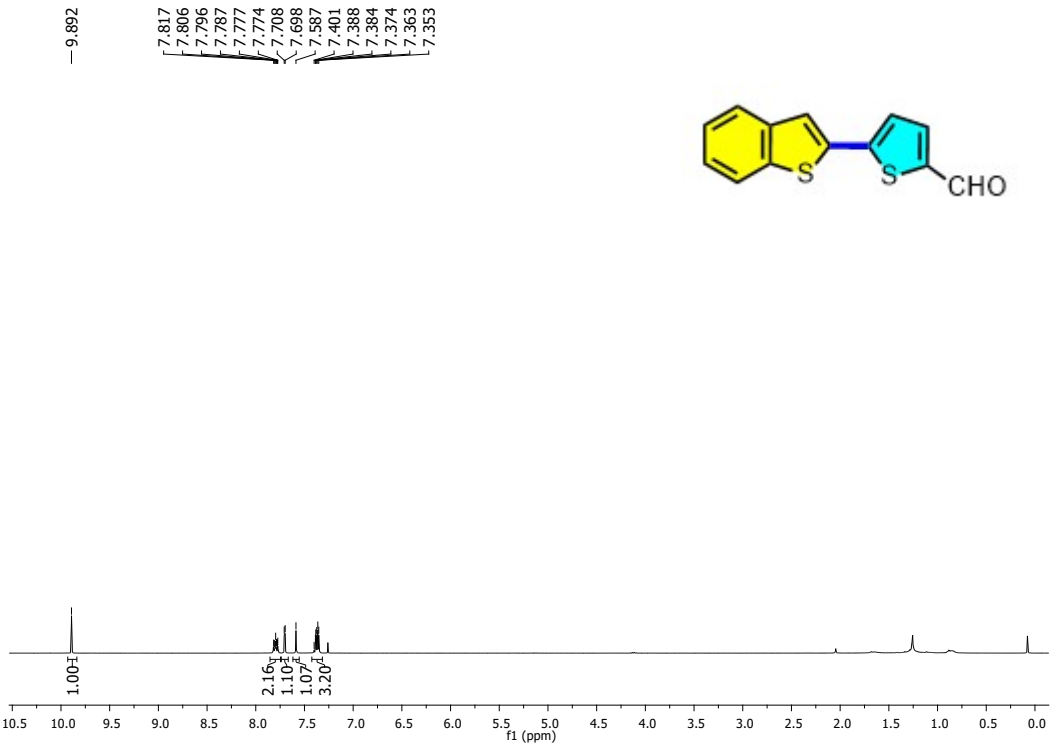

Figure s67: ^{1}H NMR spectrum of compound **3ia**.

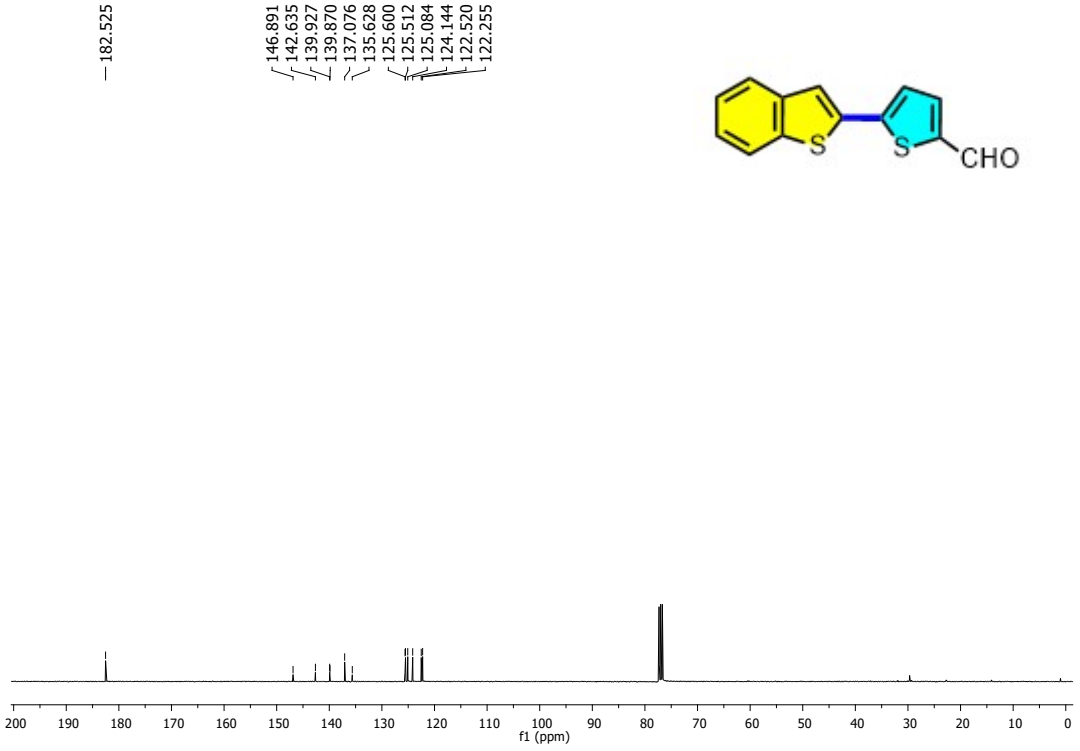

Figure s68: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ia**.

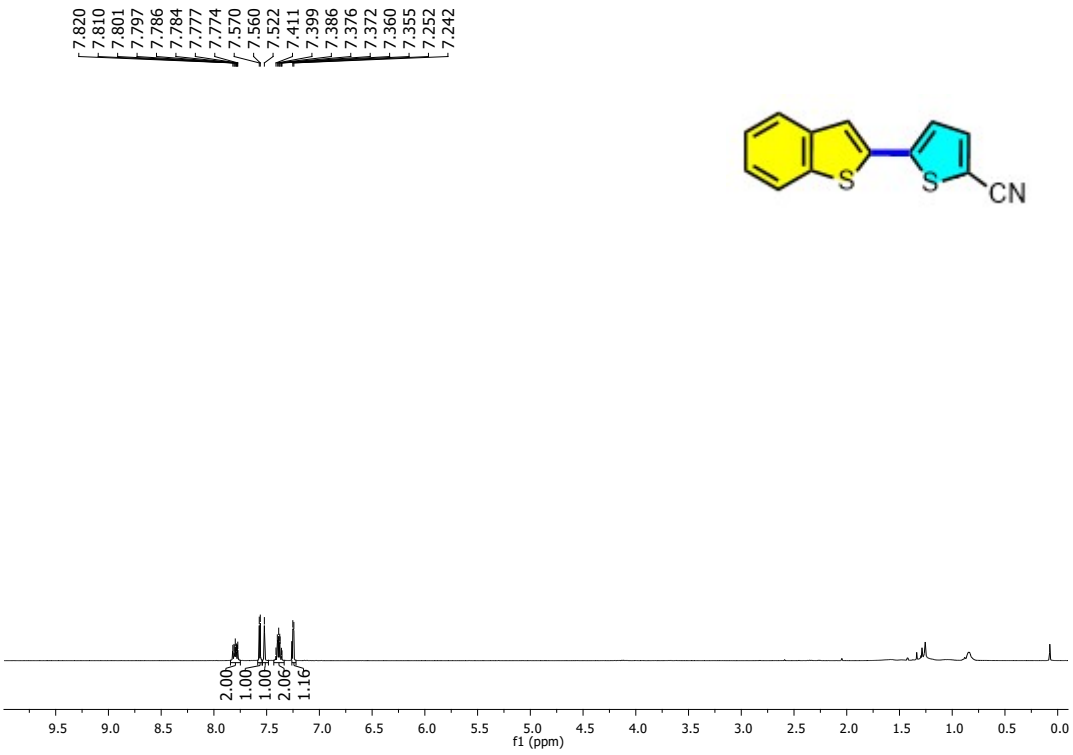

Figure s69: ^{1}H NMR spectrum of compound **3ib**.

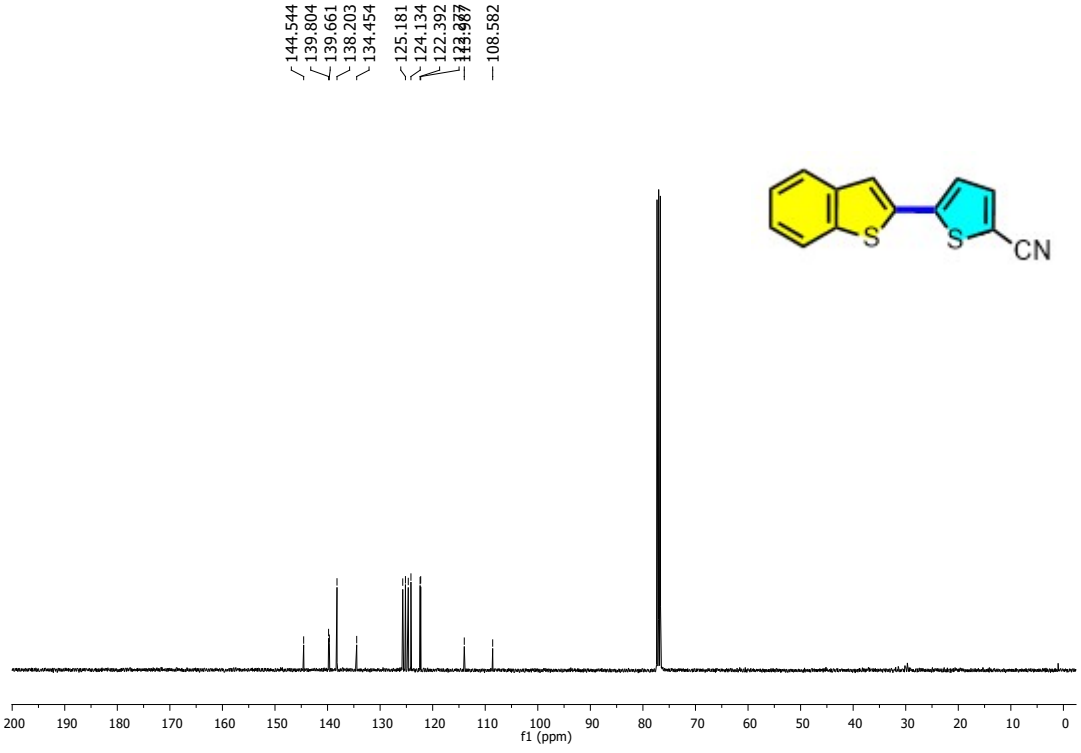

Figure s70: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ib**.

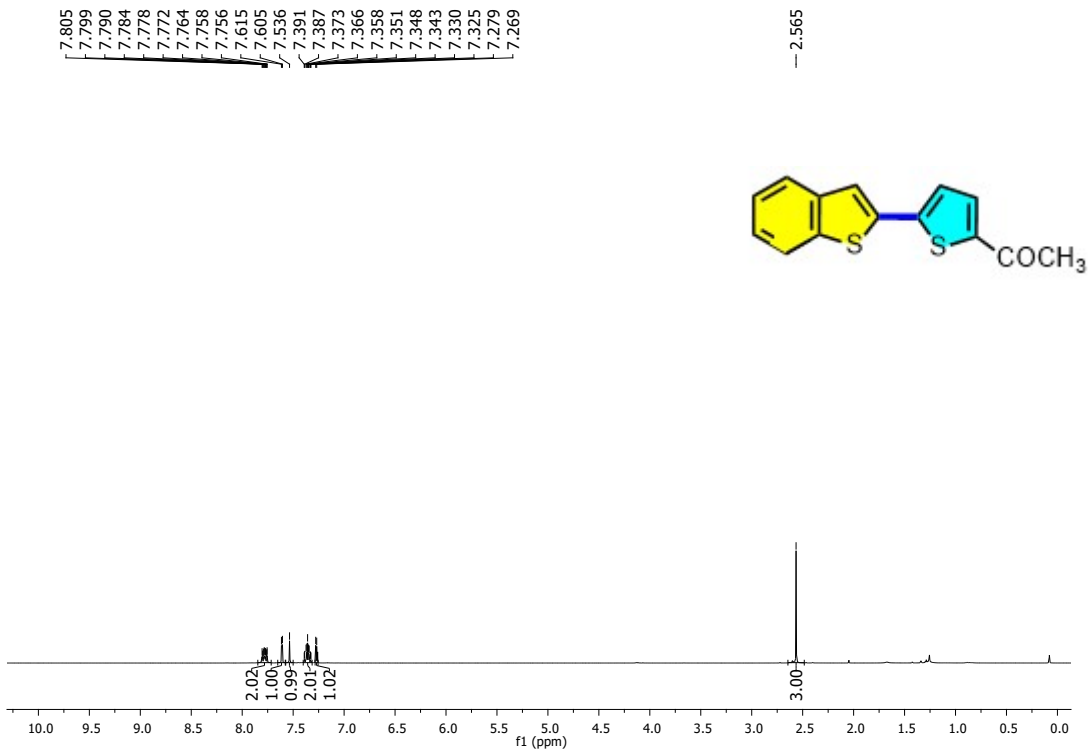

Figure s71: ^{1}H NMR spectrum of compound **3ic**.

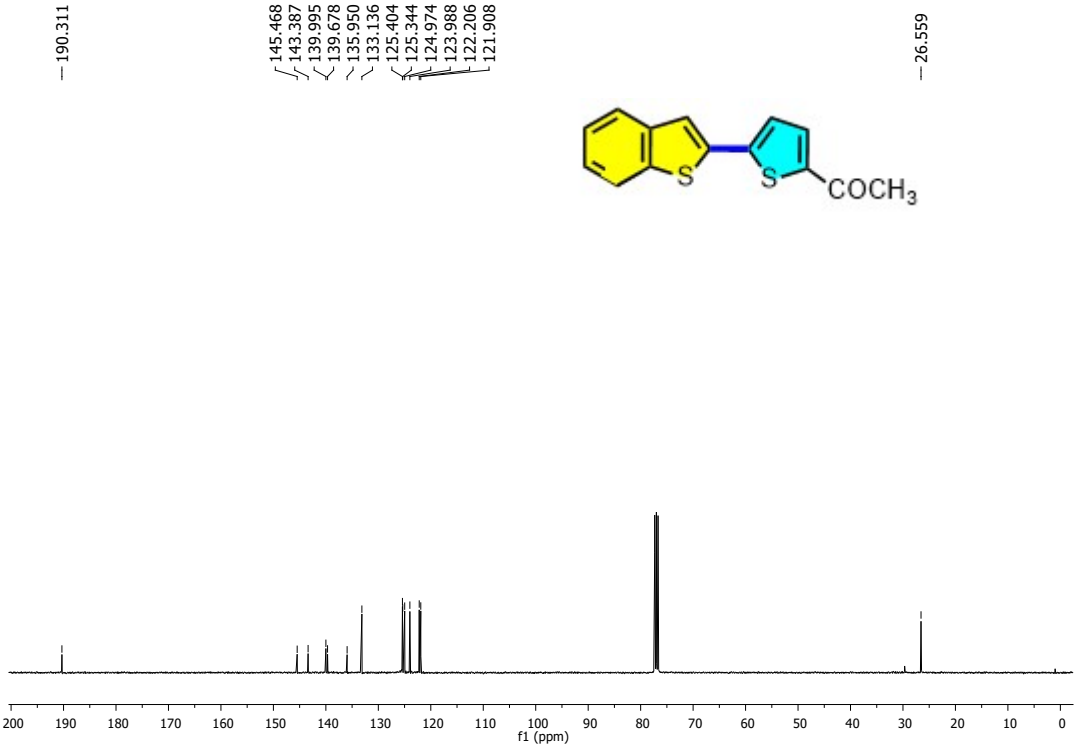

Figure s72: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ic**.

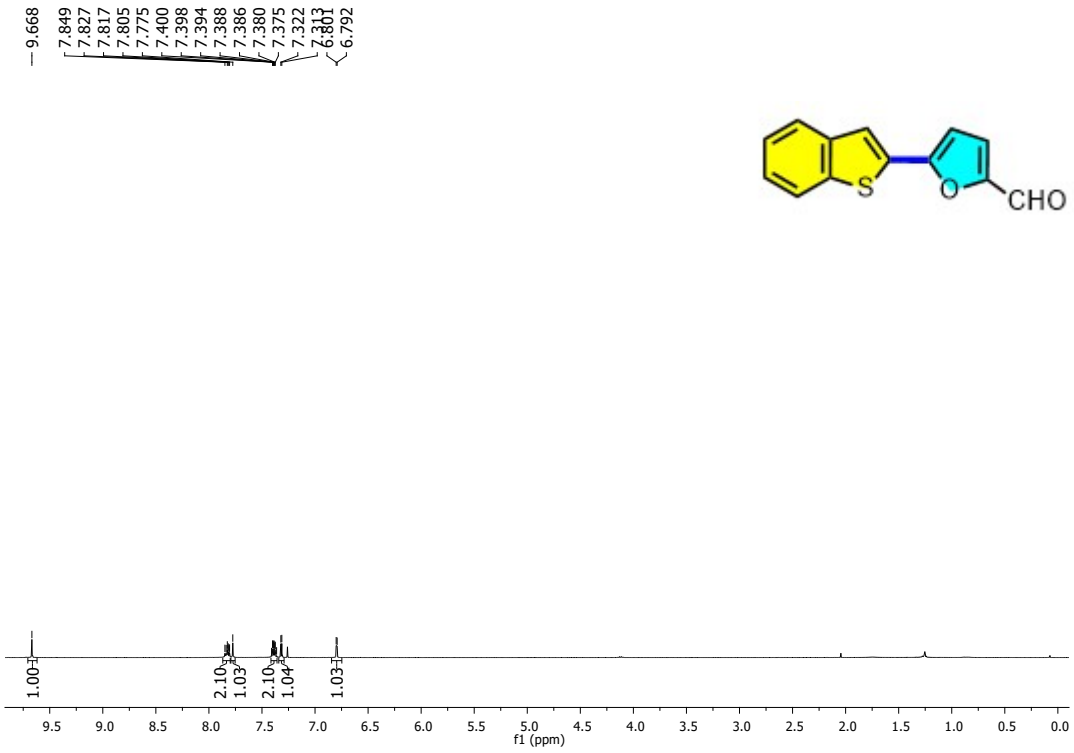

Figure s73: ^{1}H NMR spectrum of compound **3ig**.

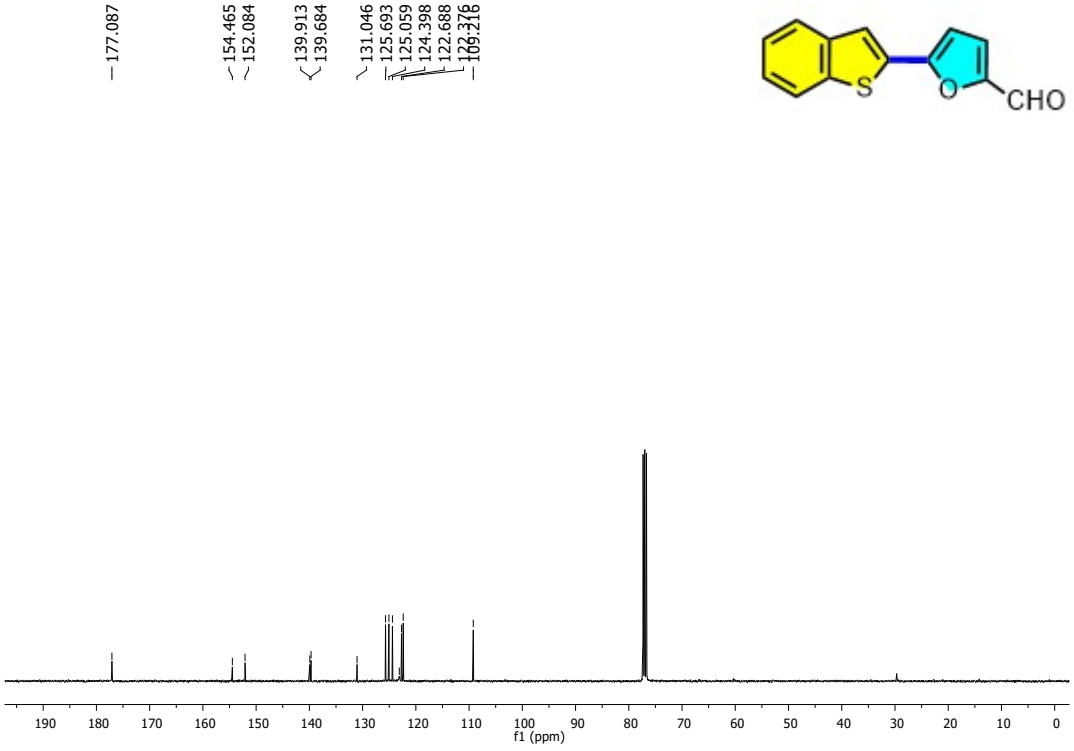

Figure s74: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3ig**.

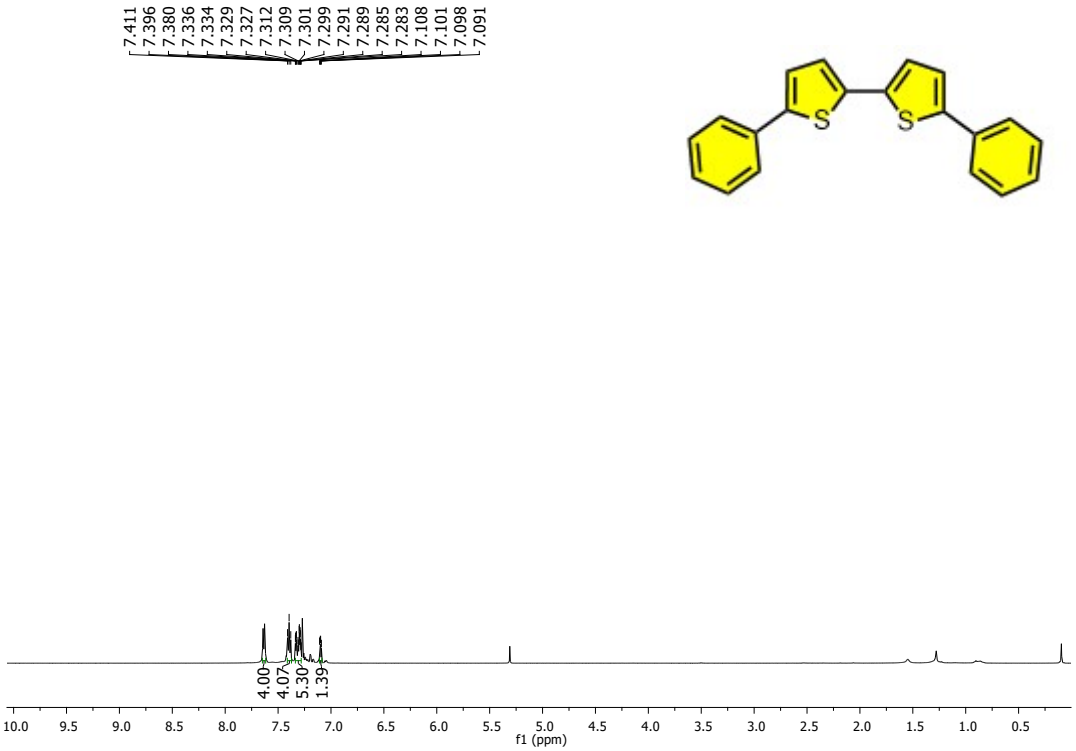

Figure s75: ^{1}H NMR spectrum of compound **1a'**.

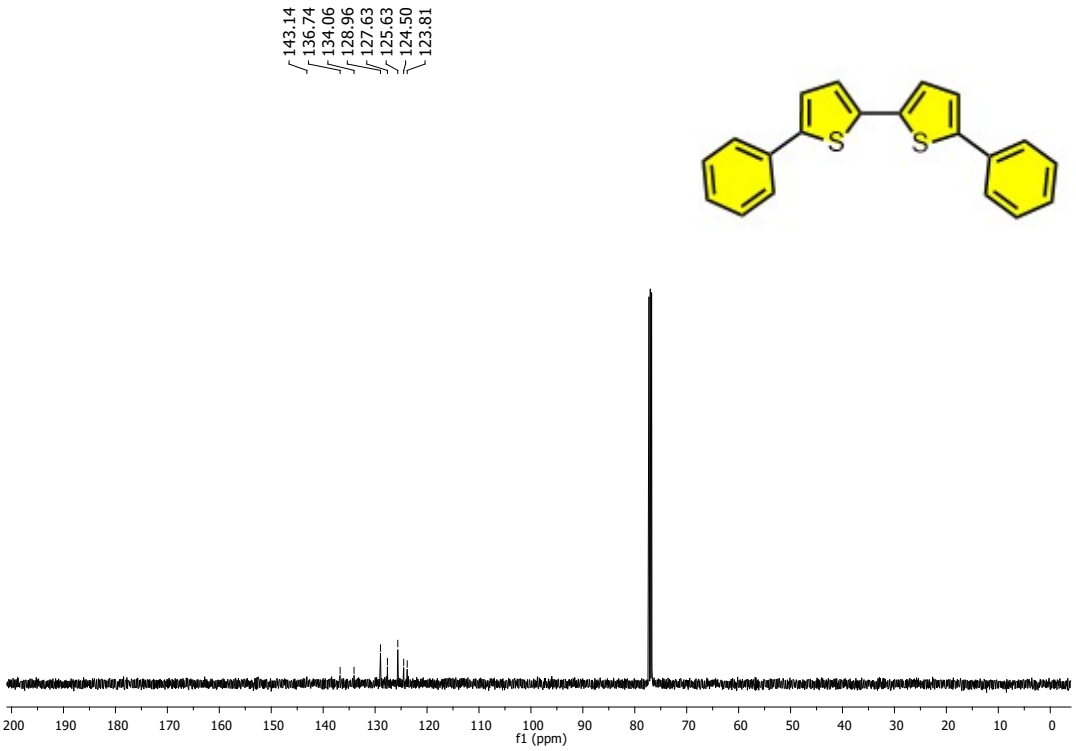

Figure s76: $^{13}C\{^{1}H\}$ NMR spectrum of compound **1a**.

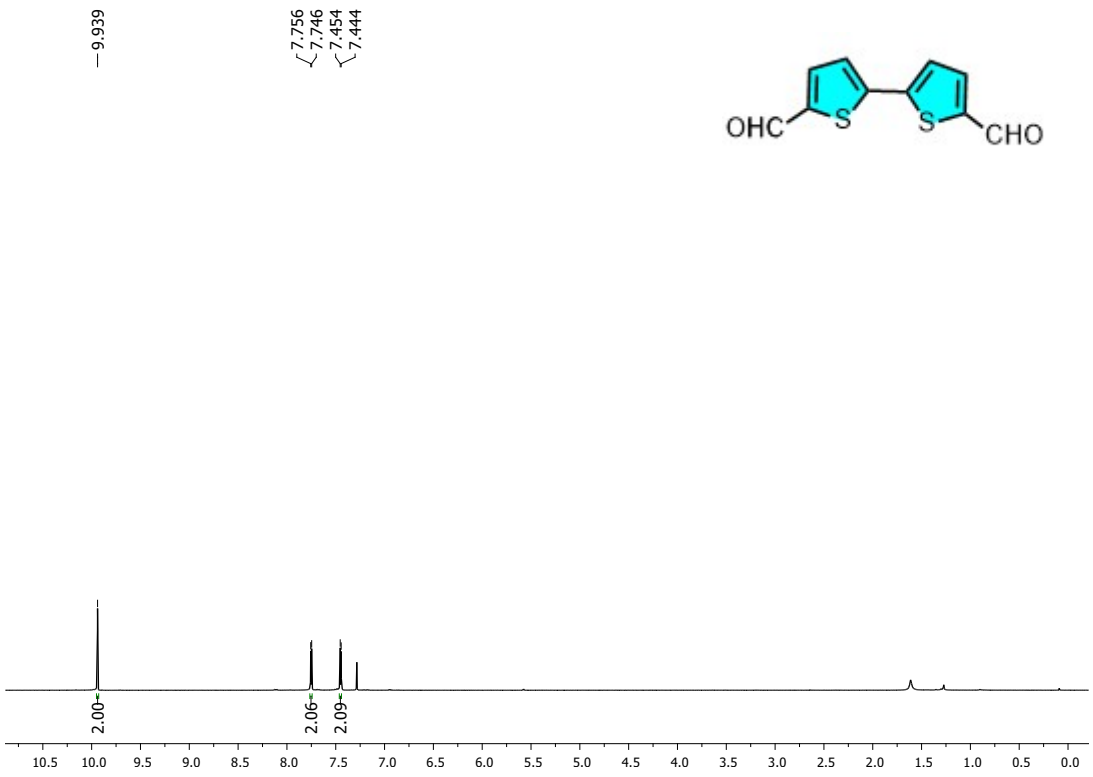

Figure s77: ^{1}H NMR spectrum of compound **2a'**.

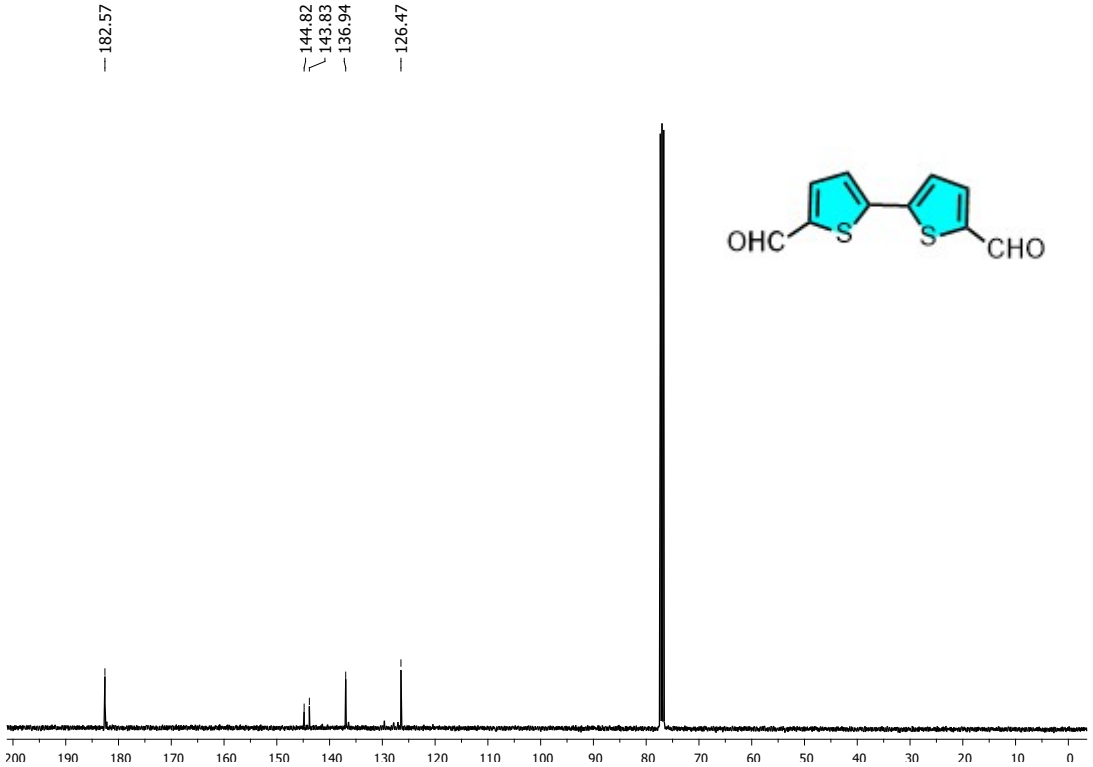

Figure s78: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2a'**.

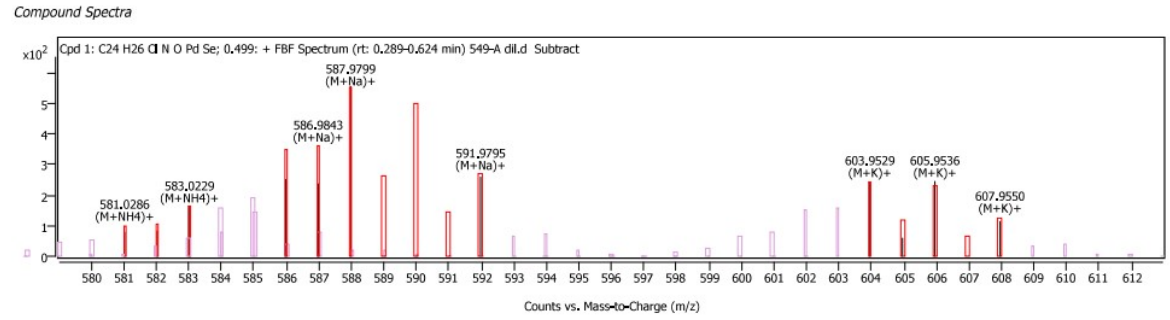

Figure s79: HRMS spectrum of Catalyst **C2 s**howing **HRMS (ESI)** ***m/z*** cacld for: $C_{24}H_{26}ClNOPdSeNa$ $[M+Na]^+$ 587.9801, found 587.9799.

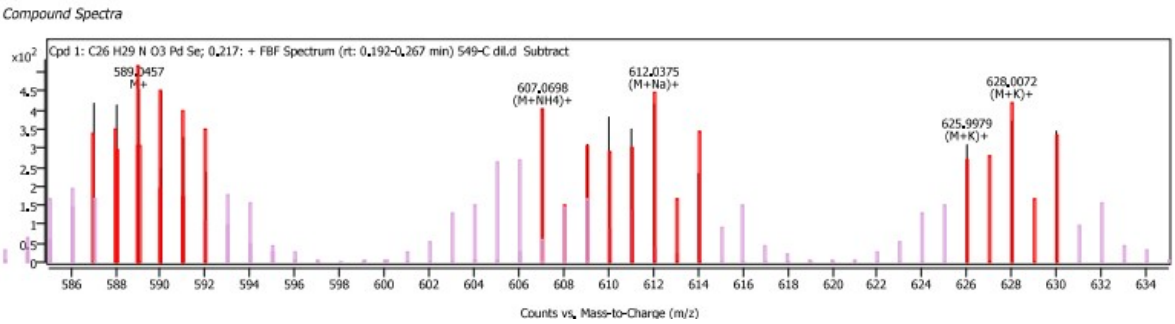

Figure s80: HRMS spectrum of intermediate **C3 s**howing **HRMS (ESI)** ***m/z*** cacld for $C_{26}H_{33}N_2O_3PdSe$ $[M+NH_4]^+$ 607.0691, found 607.0698.

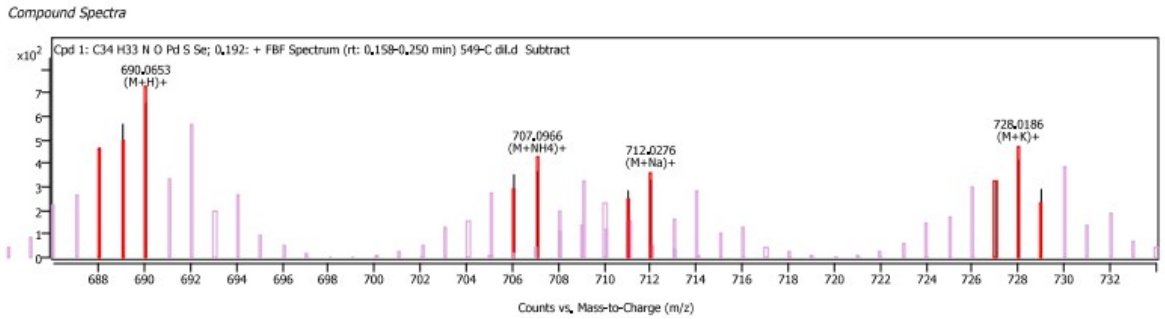

Figure s81: HRMS spectrum of intermediate **A s**howing **HRMS (ESI)** ***m/z*** cacld for $C_{34}H_{33}NOPdSSeK$ $[M+K]^+$ 728.0120, found 728.0186

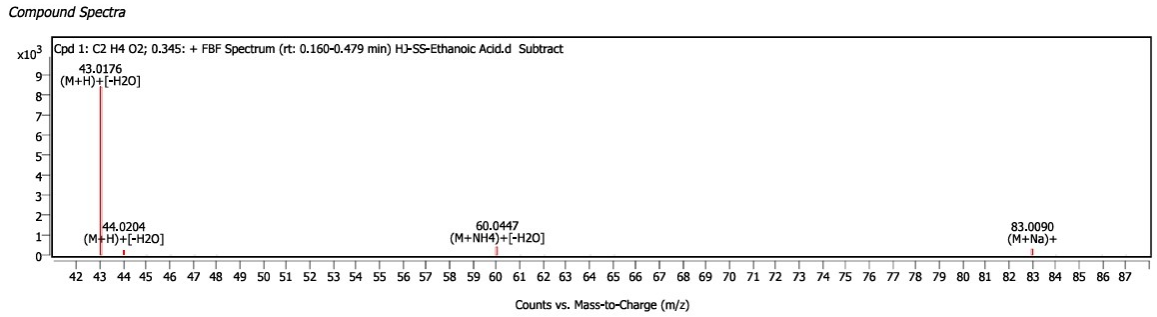

Figure s82: HRMS spectrum of intermediate acetyl ion of acetic acid $[\mathbf{CH_3CO}]^+$ **and** $[\mathbf{M+Na}]^+$ **s**howing **HRMS (ESI)** ***m/z*** cacld for $[\mathbf{CH_3CO}]^+$ $[CH_3COOH+H-H_2O]^+$ 43.0184, found 43.0176 and $C_2H_{32}OHNa$ 83.0109, found 83.0090.

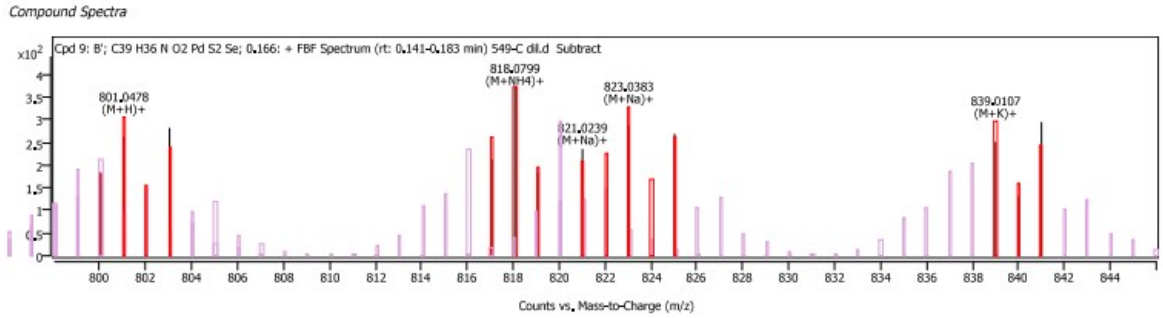

Figure s83: HRMS spectrum of intermediate **B s**howing **HRMS (ESI)** ***m/z*** cacld for $C_{39}H_{38}NO_2PdS_2Se$ $[M+H]^+$ 801.0466, found 801.0478

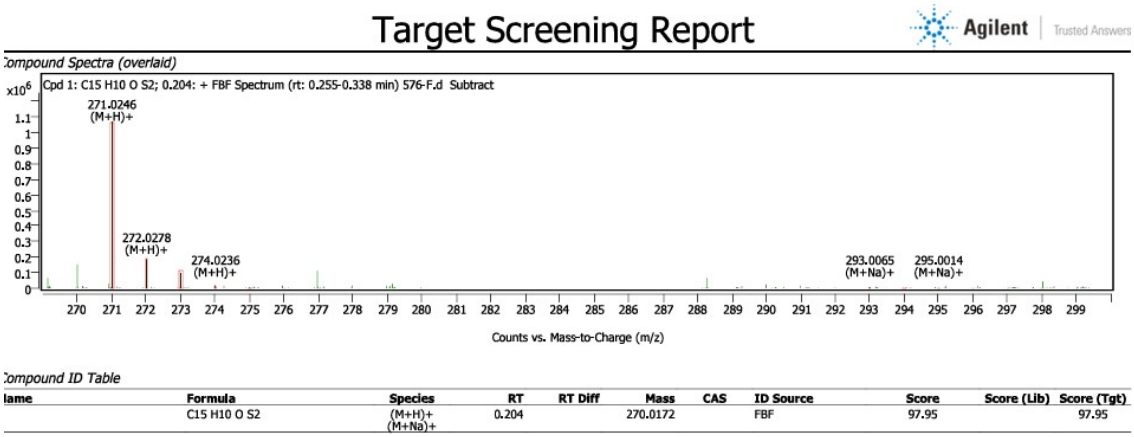

Figure s84: HRMS spectrum of compound **3aa s**howing **HRMS (ESI)** ***m/z*** cacld for $C_{15}H_{11}OS_2$ $[M+H]^+$ 271.0251, found 271.0246.

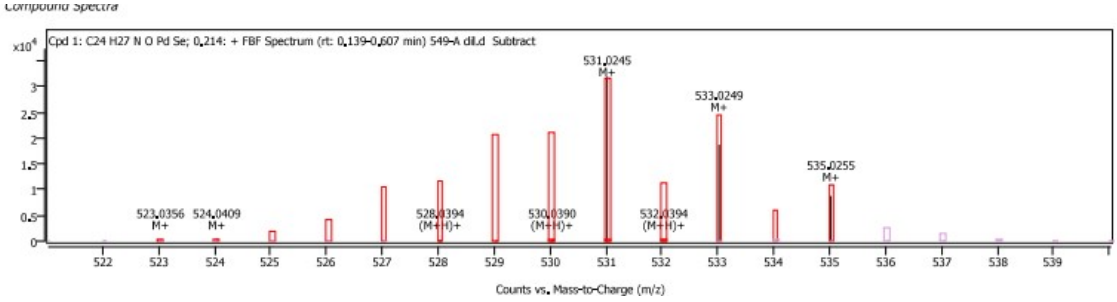

Figure s85: HRMS spectrum of intermediate **C s**howing **HRMS (ESI)** ***m/z*** cacld for $C_{24}H_{27}NOPdSe$ $[M]^+$ 532.0371, found 532.0394.

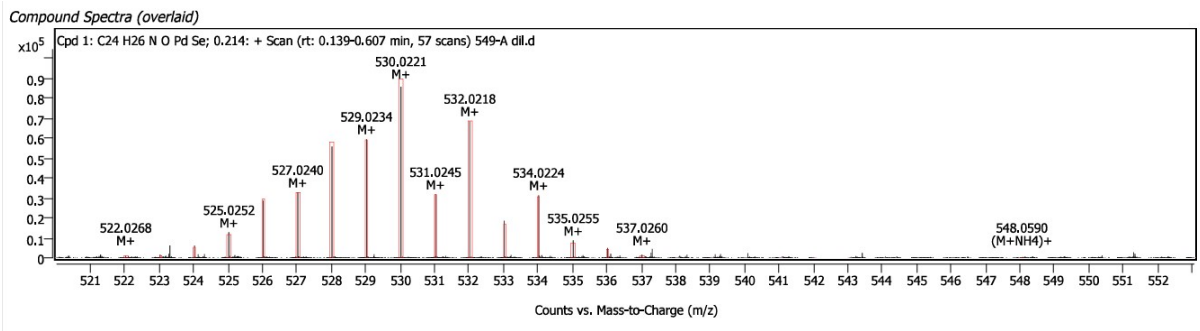

Figure s86: HRMS spectrum of intermediate [**C**]$^{+}$ **s**howing **HRMS (ESI)** ***m/z*** cacld for $C_{24}H_{26}NOPdSe$ $[M]^{+}$ 530.0214, found 530.0221.

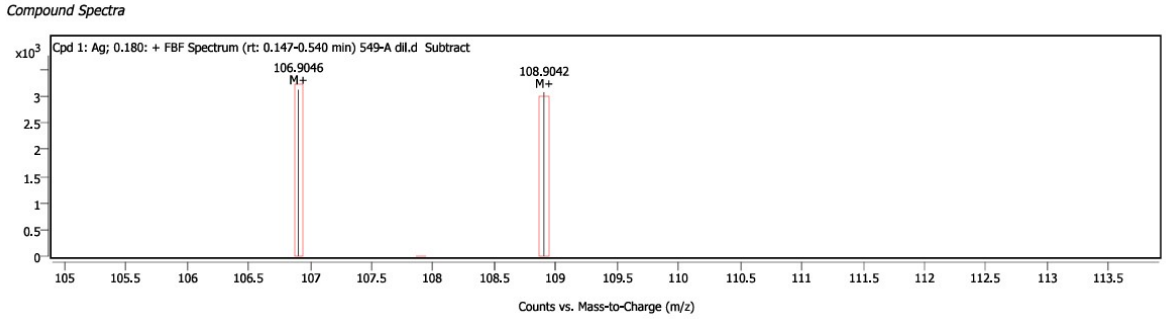

Figure s87: HRMS spectrum of intermediate **Ag**$^{+}$ **s**howing **HRMS (ESI)** ***m/z*** cacld for Ag $[M]^{+}$ 106.9051, found 106.9046.

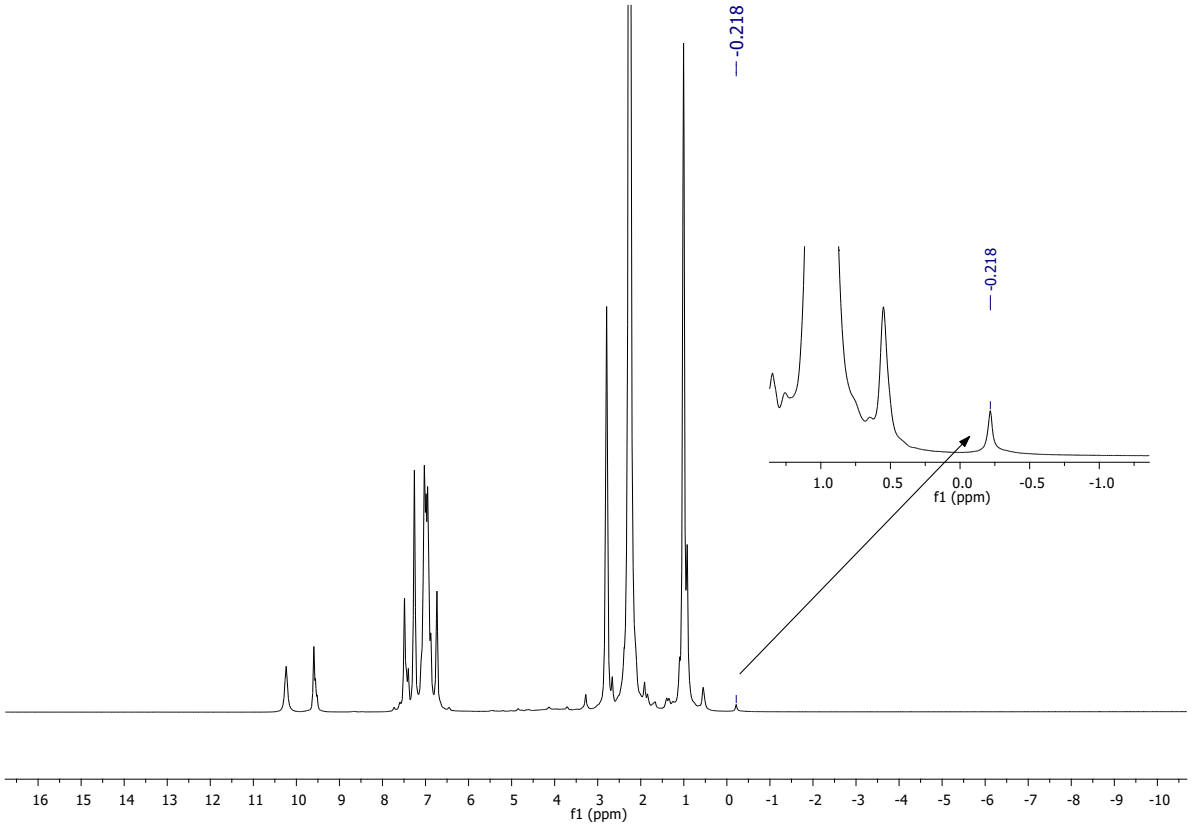

Figure s88: ^{1}H NMR spectrum of reaction mixture showing a peak corresponding to the AgH at ***δ*= -0.218 ppm**.[s25]

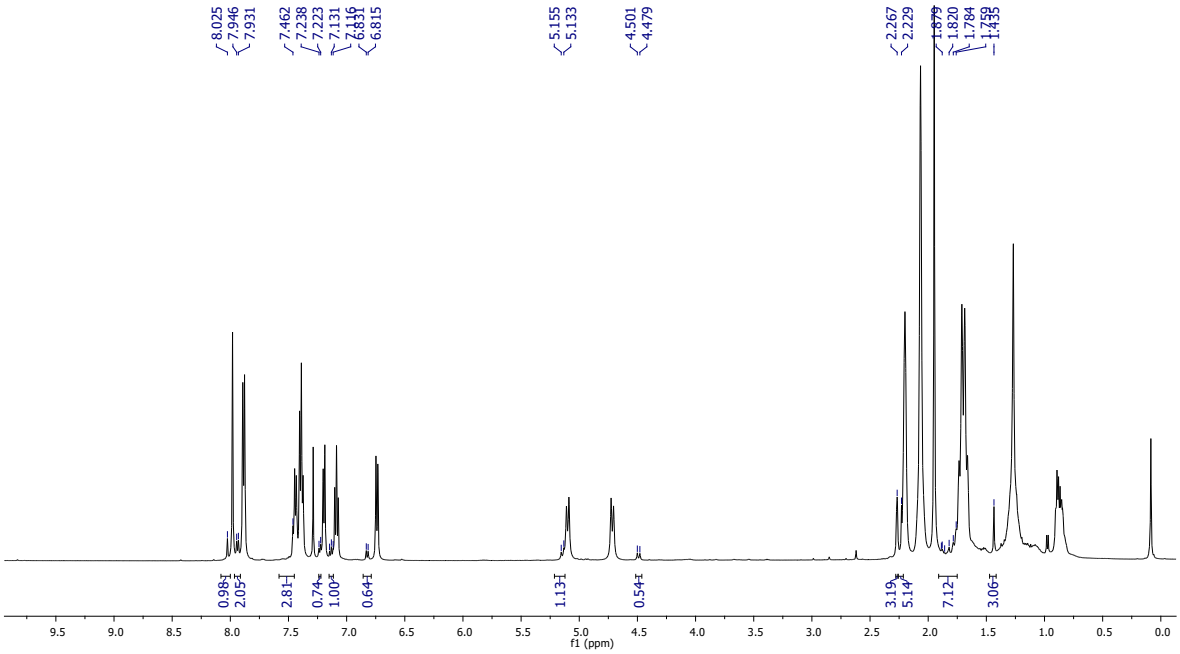

Figure s89 (a): ^{1}H NMR spectrum of crude reaction mixture between **C2** and AgOAc for synthesizing **C3** (Note: the smaller peaks denotes formation of **C3**).

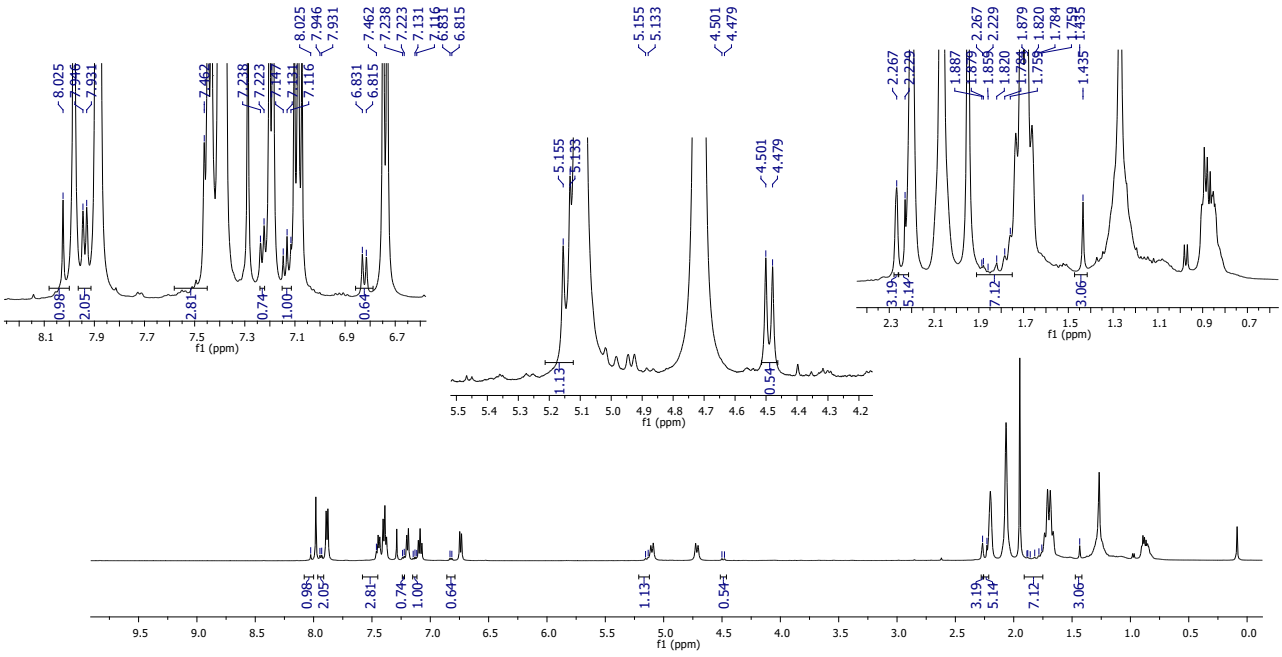

Figure s89 (b): ^{1}H NMR spectrum (zoomed version) of crude reaction mixture between **C2** and AgOAc for synthesizing **C3** (Note: the smaller peaks denotes formation of **C3**).

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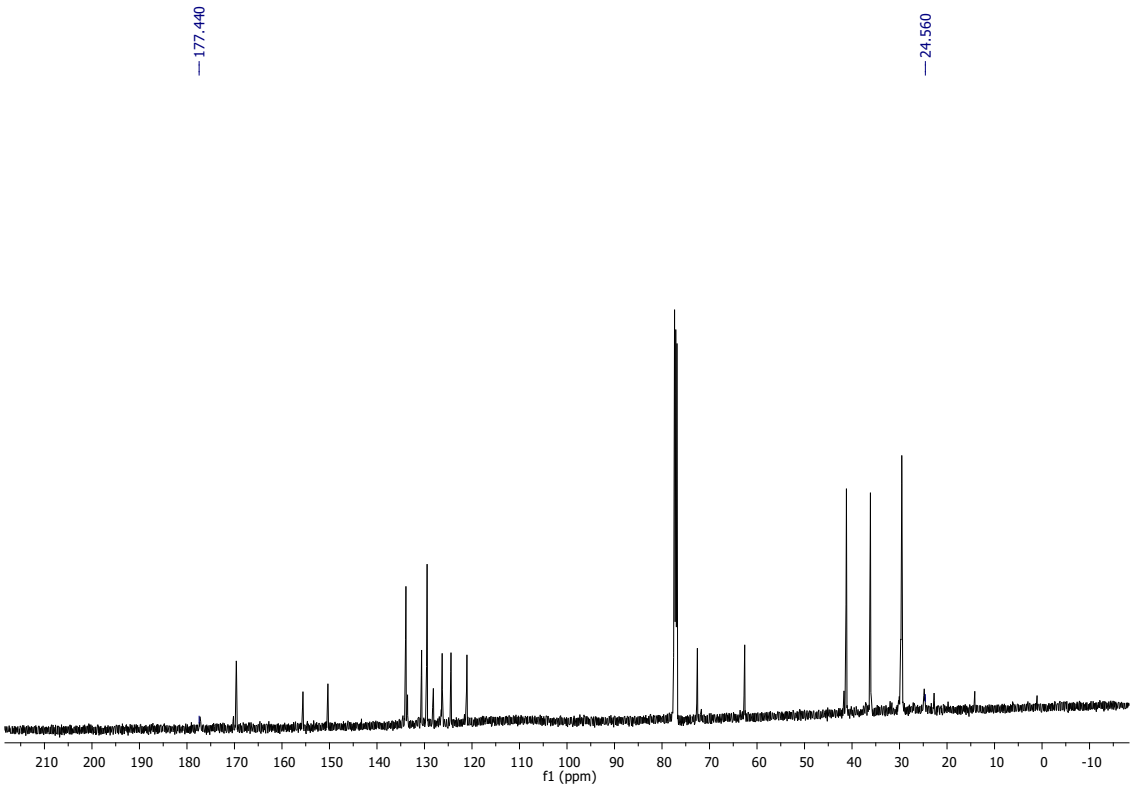

Figure s90: $^{13}C\{^{1}H\}$ spectrum of crude reaction mixture between **C2** and AgOAc for synthesizing **C3** (Note: the smaller peaks denotes formation of **C3**).

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