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Supplementary Information

Chalcogen-substituted PCBM derivatives as ternary component in PM6:Y6 solar cells.

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Synthetic procedures and compound characterization

1. Reagents, Solvents, and Other Materials

Chemicals and reagents for synthesis were purchased from commercial suppliers and used as received. Air-sensitive reactions were carried out under argon atmosphere. Anhydrous solvents were dried using a SPS purification system. Chromatography was performed using silica gel (40-60µ, Acros Organics). Analytical thin layer chromatography (TLC) was performed using aluminum coated Macherey Nagel™ Standard SIL G Silica Layers on Alugram™ Aluminum Sheets UV254.

2. Characterization

Nuclear magnetic resonance spectroscopy (NMR). All the NMR spectra were recorded on a Bruker Advance 300 (^{1}H: 300 MHz; 13C: 75 MHz) spectrometer at 298 K and referenced to deuterated solvent (e.g., $CHCl_3$-*d* corrected to 7.26 and 77.16 ppm; DCM-d_2 to 5.32 and 54.00 ppm; DMSO-d_6 to 2.50 and 39.52 ppm for 1H and ^{13}C NMR spectra, respectively). Chemical shifts (δ) are reported in ppm. Multiplicities are denoted as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), br s (broad singlet), br m (broad multiplet). The coupling constants *J* are given in Hz.

Fourier-transform infrared spectroscopy (FT-IR). The FT-IR spectra were recorded on pure samples using a Bruker ALPHA ATR-IR spectrometer.

MALDI-TOF measurements. High-Resolution Matrix-Assisted Laser Desorption Ionization, coupled to a Time-Of-Flight (TOF) experiments (MALDI-TOF) were performed on a Bruker Ultraflex III. All data were acquired at a maximum accelerating potential of 20 kV in the linear negative ion mode. DCTB was used as a matrix and AgTFA was added as the cationic ionization agent.

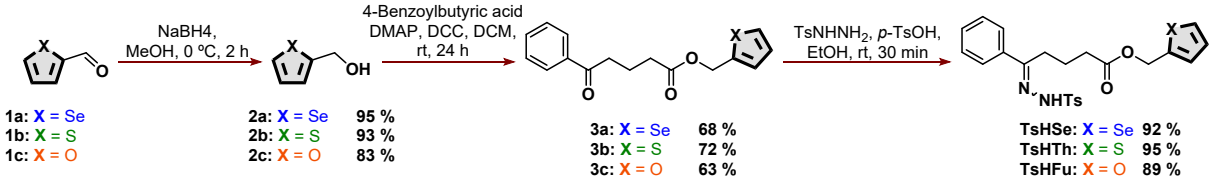
Differential Scanning Calorimetry (DSC). DSC measurements were done in a Mettler Toledo 822e differential scanning calorimeter under nitrogen atmosphere following a ramp from 30 to 300 ºC at a heating rate of 10ºC/min.

3. Electrochemical Measurements.

Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a three-electrode electrochemical cell, consisting of a glassy carbon disk working electrode (Ø = 3 mm, CH Instruments, CHI104), a platinum wire counter electrode (Ø = 0.5 mm, CH Instruments, CHI115), and a silver wire pseudoreference electrode (Ø = 0.5 mm, CH Instruments, CHI112). All experiments were run at a scan rate of 100 mV/s in degassed *o*-DCB:AcN (4:1) electrolyte containing 1 mM active species and 0.1 M Bu4NPF6 with added 0.5 mM ferrocene as an internal voltage reference (Fc/Fc+ = 0.00 V).

4. Synthesis of tosylhydrazones TsHX

The synthesis of **TsHX** is represented in Scheme S1. The details and the spectroscopy data are described below. Selenophene-2-carboxaldehyde **1a** was prepared according to a literature procedure based on the Vilsmeier-Haack reaction[1] and thiophene-2-carboxaldehyde **1b** and furan-2-carboxaldehyde **1c** were bought from Sigma Aldrich



Scheme S1. Synthetic route for **4a-c** derivatives

Selenophene-2-carbaldehyde (1a): ^{1}H NMR (300 MHz, $CHCl_3$-*d*) δ [ppm] = 9.81 (d, *J* = 1.1 Hz, 1H), 8.49 (dt, *J* = 5.4, 1.1 Hz, 1H), 8.01 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.47 (dd, *J* = 5.4, 3.9 Hz, 1H). The NMR data corresponded to those reported in the literature.[1]

General procedure for the synthesis of alcohols 2a-c: $NaBH_4$ (85.1 mg, 2.25 mmol) was added slowly portion wise for 20 min at 0 ºC to each aldehyde **1a-c** (4.50 mmol) dissolved in methanol (15 mL). The reactions were

stirred for 1 h at 0 °C, then allowed to reach room temperature and stirred for 1 h more. Thereafter, HCl 2M was added until neutral pH and the mixtures were washed with $NaHCO_3$ saturated solution, brine, and water. The organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to give colorless liquids.

Selenophen-2-ylmethanol (2a): (692.4 mg, 4.28 mmol, yield 95 %). ^{1}H NMR (300 MHz, $CHCl_3$-*d*) δ [ppm] = 7.96 (dd, *J* = 5.5, 1.1 Hz, 1H), 7.19 (dd, *J* = 5.5, 3.7 Hz, 1H), 7.15 – 7.12 (m, 1H), 4.81 (d, *J* = 1.1 Hz, 2H), 2.61 (s, 1H). ^{13}C NMR (75 MHz, $CHCl_3$-*d*) δ [ppm] = 151.6, 130.8, 129.2, 127.0, 62.1.

Thiophen-2-ylmethanol (2b): (477.8 mg, 4.19 mmol, yield 93 %). ^{1}H NMR (300 MHz, $CHCl_3$-*d*) δ [ppm] = 7.30 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.02 – 6.98 (m, 2H), 4.80 (s, 2H), 2.55 (s, 1H). The NMR data corresponded to those reported in the literature.[2]

Furan-2-ylmethanol (2c): (366.4 mg, 3.74 mmol, yield 83 %). ^{1}H NMR (300 MHz, $CHCl_3$-*d*) δ [ppm] = 7.42 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.39 – 6.34 (m, 1H), 6.34 – 6.29 (m, 1H), 4.63 (s, 2H), 1.92 (s, 1H). The NMR data corresponded to those reported in the literature.[2]

General procedure for the synthesis of ketoesters 3a-c: 4-benzoylbutyric acid (576.6 mg, 3.00 mmol), DMAP (549.8 mg, 4.50 mmol) and the corresponding alcohol **2a-c** (3.30 mmol) were dissolved in degassed dry DCM (3 mL). The mixtures were cooled and DCC (1238.0 mg, 6.00 mmol) dissolved in dry DCM (3 mL) was added dropwise. The reactions were stirred overnight at room temperature. Precipitates were filtered off and the filtrates were concentrated under reduced pressure. The residues were purified by column chromatography, eluting with DCM to afford **3a-b** as pale-yellow oils.

Selenophen-2-ylmethyl 5-oxo-5-phenylpentanoate (3a): (684.0 mg, 2.04 mmol, yield 68 %).^{1}H NMR (300 MHz, $CHCl_3$-*d*) δ [ppm] = 8.03 (dd, *J* = 5.6, 1.2 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.62 – 7.55 (m, 1H), 7.53 – 7.42 (m, 2H), 7.30 – 7.25 (m, 1H), 7.22 (dd, *J* = 5.6, 3.7 Hz, 1H), 5.35 (s, 2H), 3.06 (t, *J* = 7.1 Hz, 2H), 2.51 (t, *J* = 7.1 Hz, 2H), 2.12 (p, *J* = 7.1 Hz, 2H). ^{13}C NMR (75 MHz, $CHCl_3$-*d*) δ [ppm] = 199.4, 173.1, 144.6, 136.9, 133.2, 132.7, 130.3, 129.0, 128.7, 128.1, 62.9, 37.4, 33.4, 19.4.

Thiophen-2-ylmethyl 5-oxo-5-phenylpentanoate (3b): (622.9 mg, 2.16 mmol, yield 72 %). ^{1}H NMR (300 MHz, $CHCl_3$-*d*) δ [ppm] = 7.94 – 7.90 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 7.30 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.97 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.28 (s, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 2.08 (p, *J* = 7.2 Hz, 2H). The NMR data corresponded to those reported in the literature.[3]

Furan-2-ylmethyl 5-oxo-5-phenylpentanoate (3c): (514.6 mg, 1.89 mmol, yield 63 %). ^{1}H NMR (300 MHz, $CHCl_3$-*d*) δ [ppm] = 7.94 – 7.90 (m, 2H), 7.57 – 7.50 (m, 1H), 7.47 – 7.40 (m, 2H), 7.40 – 7.37 (m, 1H), 6.40 – 6.36 (m, 1H), 6.35 – 6.31 (m, 1H), 5.06 (s, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.06 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CHCl_3$-*d*) δ [ppm] = 199.4, 172.9, 149.5, 143.3, 136.9, 133.1, 128.6, 128.1, 110.7, 110.6, 58.0, 37.4, 35.0, 33.2.

General procedure for the synthesis of tosylhydrazones TsHX:
p-Toluenesulfonyl hydrazide (223.5 mg, 1.20 mmol) was added to a mixture of ketoester **3a-c** (1.00 mmol) with p-toluenesulfonic acid (12% in acetic acid, 28.7 mg, 0.02 mmol) in EtOH (2 mL). After 30 minutes stirring at room temperature, the solvent was removed under reduced pressure and the residues were crystallized from methanol to yield **TsHX** as white solids.

Selenophen-2-ylmethyl 5-phenyl-5-(2-tosylhydrazineylidene)pentanoate (TsHSe): (463.2 mg, 0.92 mmol, yield 92 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ [ppm] = 10.70 (s, 1H), 8.18 (dd, *J* = 5.5, 1.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.54 (m, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.21 (dd, *J* = 5.5, 3.7 Hz, 1H), 5.30 (s, 2H), 2.73 – 2.60 (m, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.67 – 1.51 (m, 2H). ^{13}C NMR (300 MHz, DMSO-d_6) δ [ppm] = 172.4, 154.8, 144.6, 143.4, 136.2, 133.6, 130.5, 129.5, 129.4, 128.8, 128.5, 127.4, 126.0, 62.4, 33.0, 25.8, 21.1, 21.0.

Thiophen-2-ylmethyl 5-phenyl-5-(2-tosylhydrazineylidene)pentanoate (TsHTh): (433.8 mg, 0.95 mmol, yield 95 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ [ppm] = 10.70 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.55 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.20 – 7.15 (m, 1H), 7.02 (dd, *J* = 5.1, 3.5 Hz, 1H),

5.27 (s, 2H), 2.71 – 2.62 (m, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 2.36 (s, 3H), 1.66 – 1.53 (m, 2H). The NMR data corresponded to those reported in the literature.[3]

Furan-2-ylmethyl 5-phenyl-5-(2-tosylhydrazineylidene)pentanoate (TsHFu): (392.1 mg, 0.89 mmol, yield 89 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ [ppm] = 10.69 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.62 (m, 1H), 7.62 – 7.57 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.31 (m, 3H), 6.54 – 6.51 (m, 1H), 6.47 – 6.45 (m, 1H), 5.06 (s, 2H), 2.71 – 2.62 (m, 2H), 2.45 – 2.37 (m, 2H), 2.36 (s, 3H), 1.62 – 1.53 (m, 2H). ^{13}C NMR (300 MHz, DMSO-d_6) δ [ppm] = 172.1, 156.6, 154.9, 149.3, 143.7, 143.4, 136.2, 129.5, 129.4, 128.5, 127.4, 126.0, 110.8, 110.7, 57.5, 33.3, 32.8, 25.7, 21.0.

5. Synthesis of PCBX derivatives:

Using the tosylhydrazones **TsHX**, **PCBX** derivatives were synthetized as it is illustrated in Scheme 1.

Under argon atmosphere, tosylhydrazone **TsHX** (0.30 mmol) was dissolved in degassed dry pyridine (5 mL), MeONa (24.3 mg, 0.45 mmol) was added and the mixture was stirred at room temperature. After 15 min, a solution of C_{60} (324.0 mg, 0.45 mmol) dissolved in degassed dry *o*-DCB (30 mL) was added and stirred at 80 ºC for 24 h and then at 180 ºC for 24 h more to complete the conversion of the [5,6]-open isomers to the [6,6]-closed isomers. The mixture resulting was purified by chromatography on silica gel, eluting with CS_2 to remove the unreacted C_{60} and toluene to collect the final products **PCBX** as a dark brown solids.

[6,6]-phenyl C_{61}-butyric acid 2-methylselenophene ester (PCBSe): (131.0 mg, 0.13 mmol, yield 42 %). ^{1}H NMR (300 MHz, CS_2:$CHCl_3$-*d* 9:1) δ [ppm] = 8.01 – 7.96 (m, 1H), 7.96 – 7.87 (m, 2H), 7.56 – 7.43 (m, 3H), 7.25 – 7.15 (m, 2H), 5.29 (s, 2H), 2.95 – 2.88 (m, 2H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.26 – 2.18 (m, 2H). ^{13}C NMR (75 MHz, CS_2:$CHCl_3$-*d* 9:1) δ [ppm] = 168.6, 146.0, 145.1, 143.3, 142.6, 142.5, 142.4, 142.2, 142.1, 141.9, 141.6, 141.2, 140.6, 140.51, 140.47, 140.4, 139.7, 139.6, 139.5, 138.5, 138.3, 135.7, 135.2, 134.1, 130.4, 129.5, 128.1, 128.0, 127.6, 126.4, 126.3, 126.1, 125.8, 125.3, 125.1, 122.9, 60.1, 49.4, 31.3, 31.2, 20.1. FT-IR (ATR) *v* [cm^{-1}] = 1732 (C=O), 1153 (C-O), 523 (C_{60}, C-C). HR-MS (MALDI-TOF) = *m*/*z* calculated for $[C_{76}H_{16}O_2Se+Ag]^+$: 1146.94; found: 1146.955.

[6,6]-phenyl C_{61}-butyric acid 2-methylthiophene ester (PCBTh): (137.0 mg, 0.14 mmol, yield 46 %). ^{1}H NMR (300 MHz, CS_2:DCM-d_2 9:1) δ [ppm] = 7.96 – 7.92 (m, 2H), 7.58 – 7.49 (m, 3H), 7.31 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.98 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.25 (s, 2H), 2.97 – 2.88 (m, 3H), 2.54 (t, *J* = 7.3 Hz, 3H), 2.26 – 2.15 (m, 3H). ^{13}C NMR (75 MHz, CS_2:$CHCl_3$-*d* 9:1) δ [ppm] = 171.8, 149.2, 149.0, 148.7, 148.6, 148.5, 147.6, 147.3, 147.0, 145.9, 145.7, 145.5, 145.10, 145.07, 145.0, 144.8, 144.7, 144.6, 144.4, 144.0, 143.8, 143.7, 143.0, 142.91, 142.86, 142.13, 142.05, 142.00, 140.9, 132.0, 128.4, 128.2, 128.1, 126.82, 126.77, 79.6, 60.3, 51.7, 33.9, 33.6, 22.4. FT-IR (ATR) *v* [cm^{-1}] = 1731 (C=O), 1150 (C-O), 523 (C_{60}, C-C). HR-MS (MALDI-TOF) = *m*/*z* calculated for $[C_{76}H_{16}O_2S+Ag]^+$: 1098.99; found: 1098.930.

[6,6]-phenyl C_{61}-butyric acid 2-methylfuran ester (PCBFu): (111.4 mg, 0.11 mmol, yield 38 %). ^{1}H NMR (300 MHz, CS_2:DCM-d_2 9:1) δ [ppm] = 10.69 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.71 – 7.62 (m, 1H), 7.62 – 7.57 (m, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.31 (m, 3H), 6.54 – 6.51 (m, 1H), 6.47 – 6.45 (m, 1H), 5.06 (s, 2H), 2.71 – 2.62 (m, 2H), 2.43 – 2.34 (m, 5H), 1.62 – 1.53 (m, 2H). ^{13}C NMR (75 MHz, CS_2:$CHCl_3$-*d* 9:1) δ [ppm] = 171.3, 148.37, 147.43, 145.6, 145.1, 145.0, 144.9, 144.8, 144.6, 144.5, 144.3, 143.9, 143.6, 142.9, 142.81, 142.76, 142.7, 142.0, 141.95, 141.88, 140.9, 140.65, 140.60, 137.9, 137.5, 136.4, 131.9, 128.3, 128.2, 128.1, 110.6, 110.5, 79.5, 57.7, 51.6, 33.6, 33.5, 22.3. FT-IR (ATR) *v* [cm^{-1}] = 1731 (C=O), 1151 (C-O), 523 (C_{60}, C-C). HR-MS (MALDI-TOF) = *m*/*z* calculated for $[C_{76}H_{16}O_3+Ag]^+$: 1083.02; found: 1083.073.

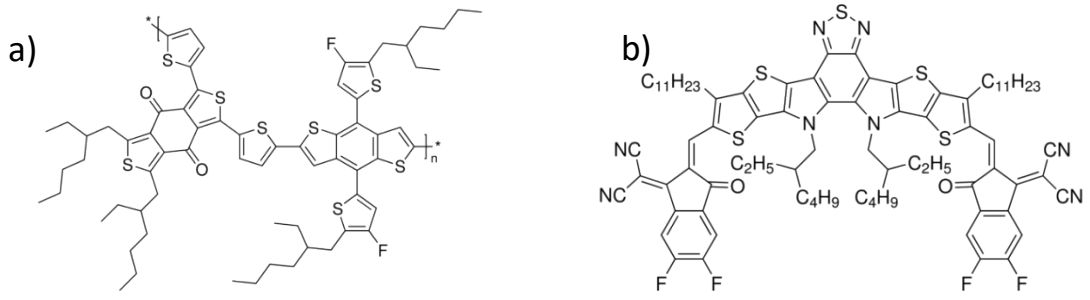


Fig. S1 Chemical structure of (a) PM6 and (b) Y6

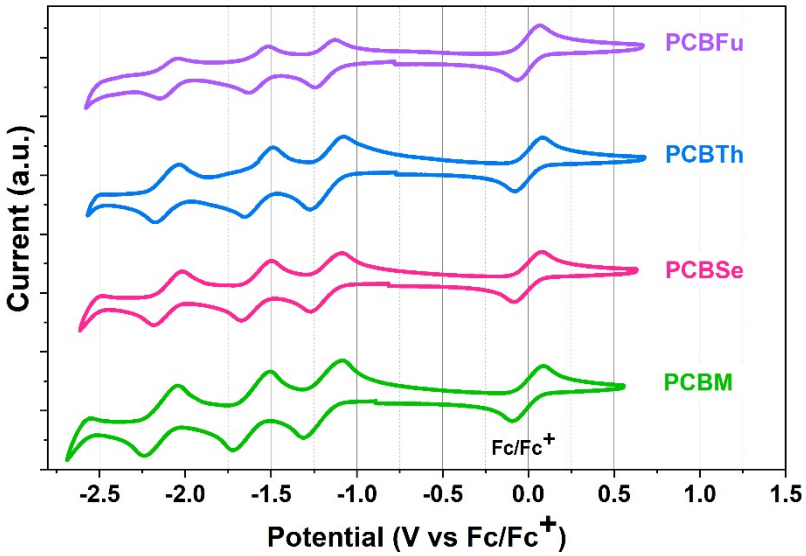


Fig. S2 Cyclic voltammetry measurements for PCBM-derivatives.

NMR Spectra

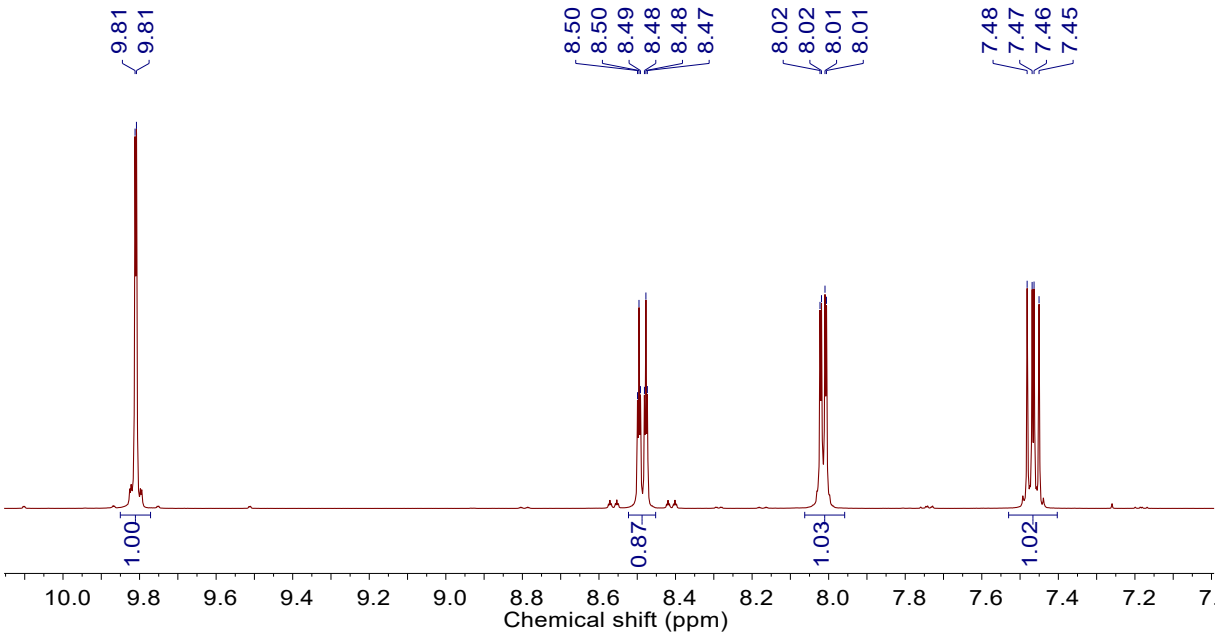


Fig. S3 ^{1}H NMR spectrum of **1a** in $CHCl_3$-*d* at 300 Hz

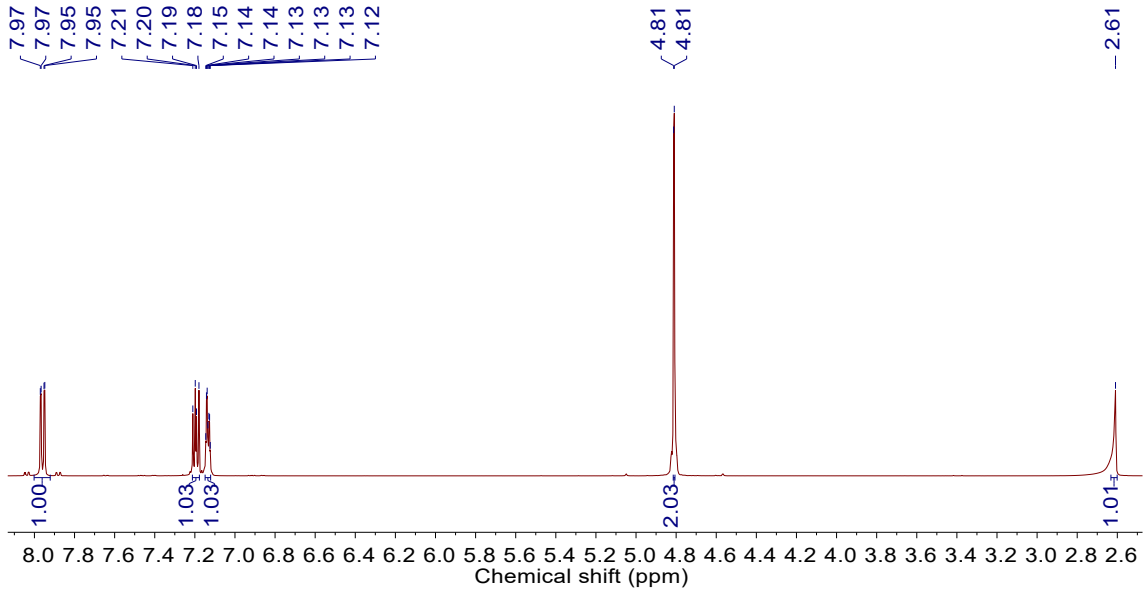


Fig. S4. ^{1}H NMR spectrum of **2a** in $CHCl_3$-*d* at 300 Hz

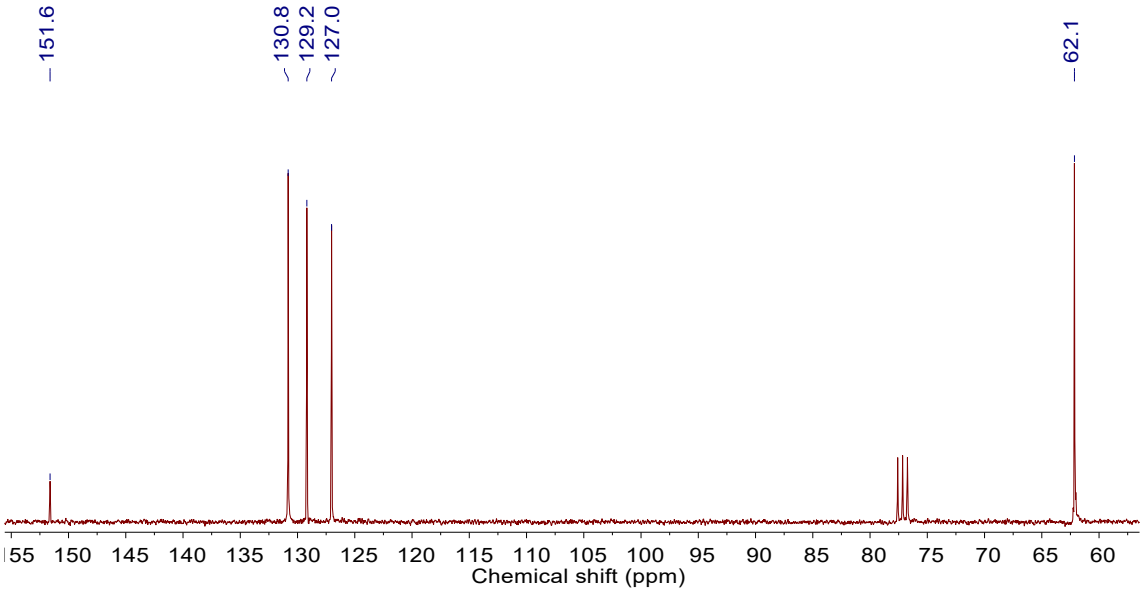


Fig. **S5** ^{13}C NMR spectrum of **2a** in $CHCl_3$-*d* at 75 Hz

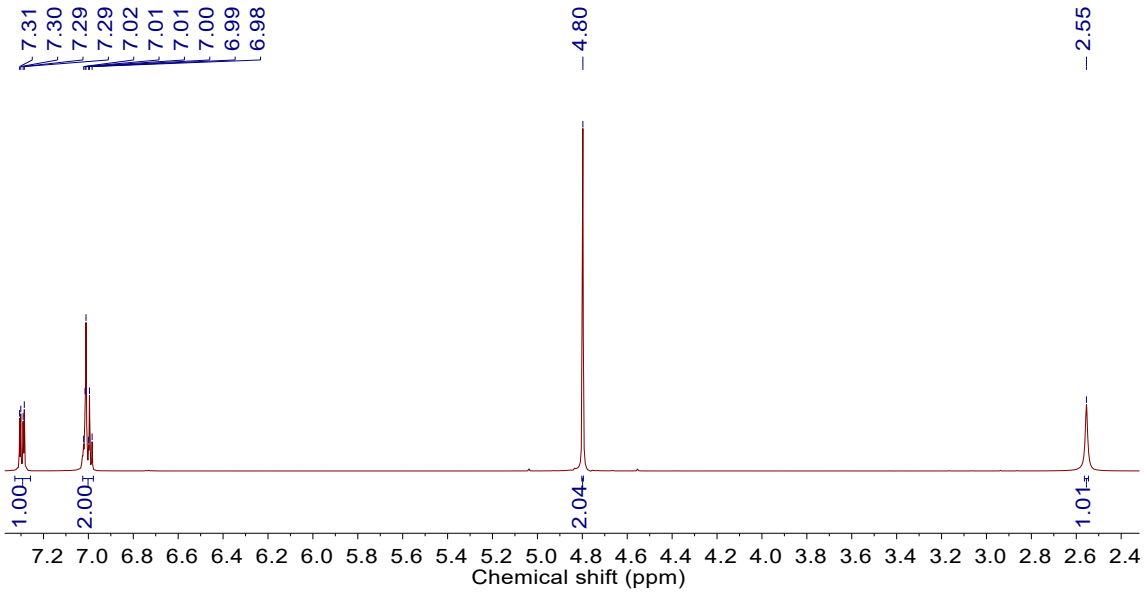


Fig. S6 ^{1}H NMR spectrum of **2b** in $CHCl_3$-*d* at 300 Hz

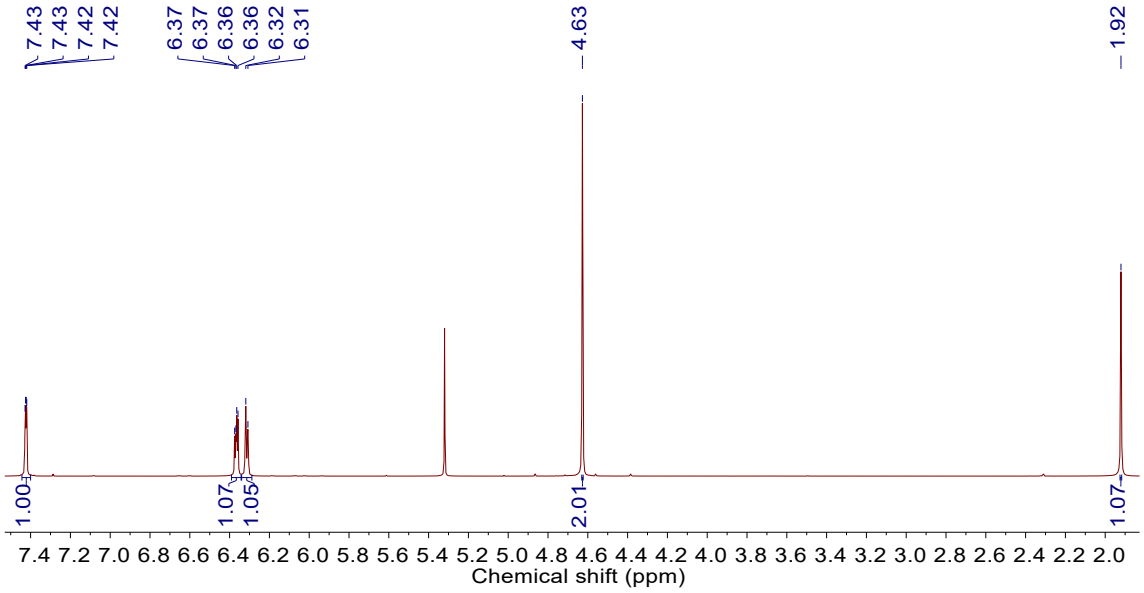


Fig. S7 ^{1}H NMR spectrum of **2c** in DCM-d_2 at 300 Hz

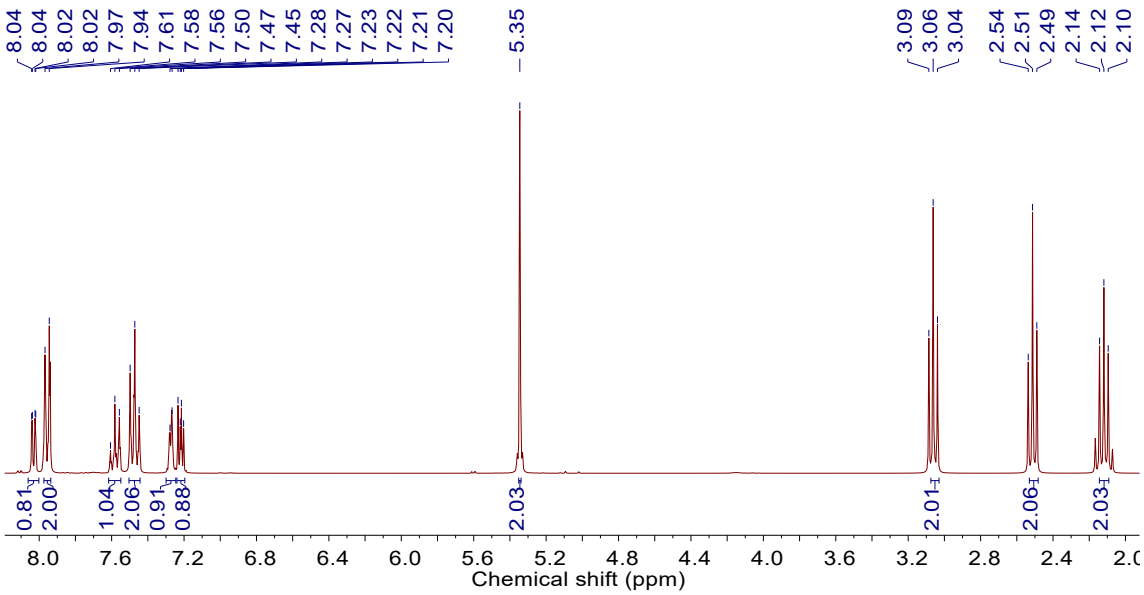


Fig. S8 ^{1}H NMR spectrum of **3a** in $CHCl_3$-*d* at 300 Hz

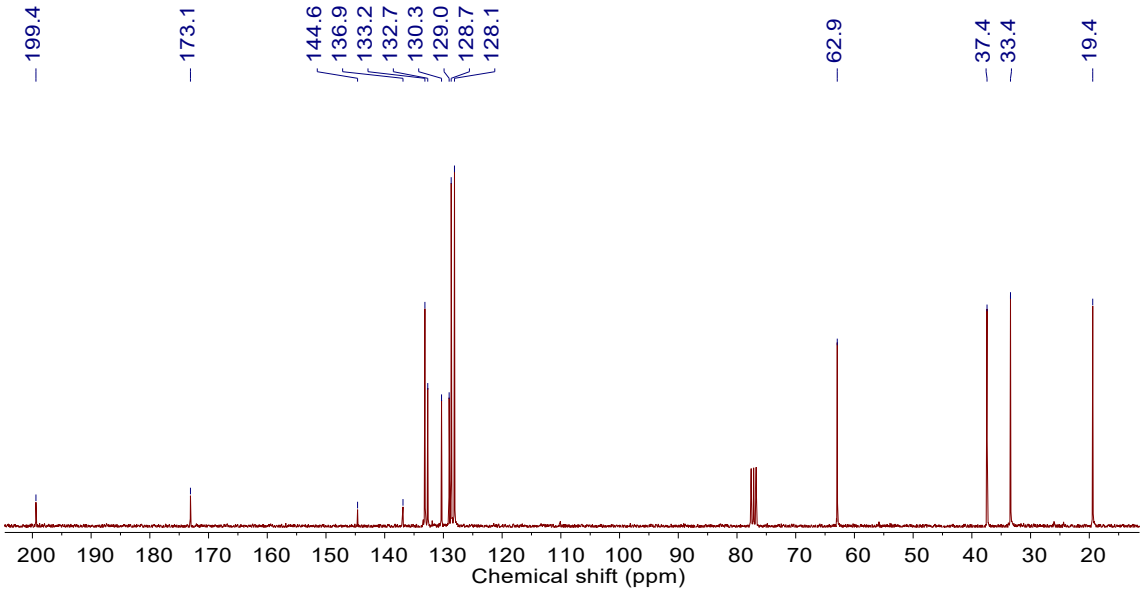


Fig. S9 ^{13}C NMR spectrum of **3a** in $CHCl_3$-*d* at 75 Hz

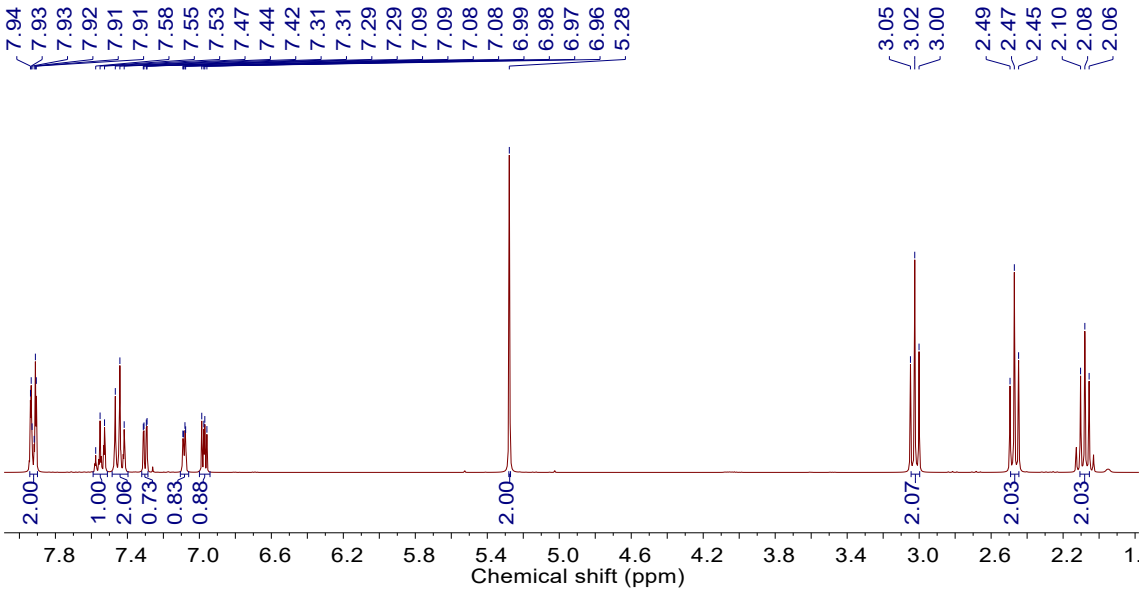


Fig. S10 1H NMR spectrum of **3b** in $CHCl_3$-*d* at 300 Hz

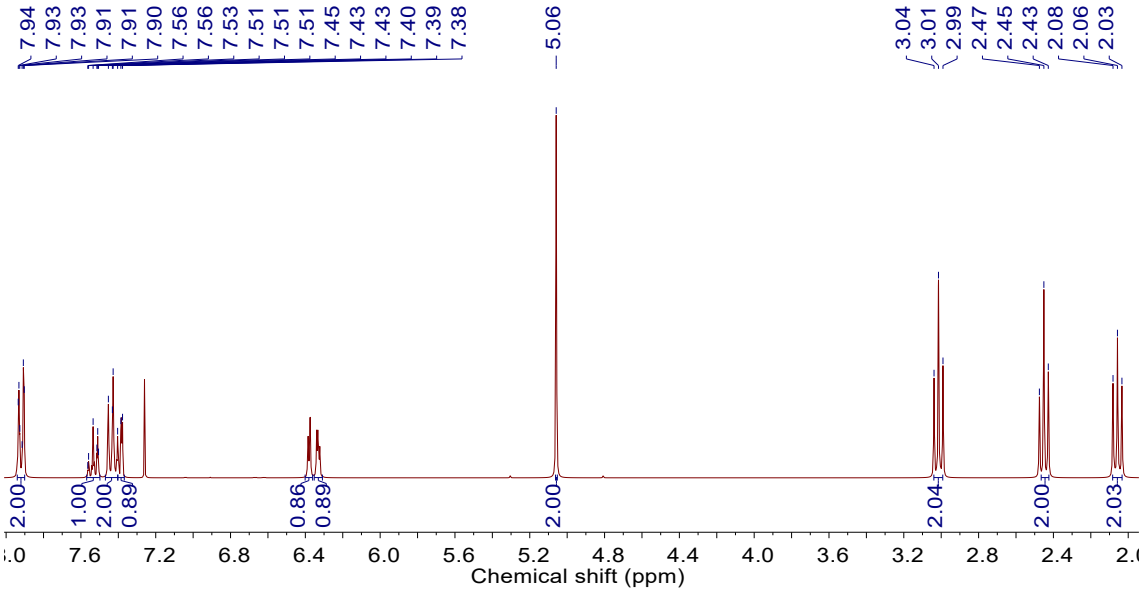


Fig. S11 ^{1}H NMR spectrum of **3c** in $CHCl_3$-*d* at 300 Hz

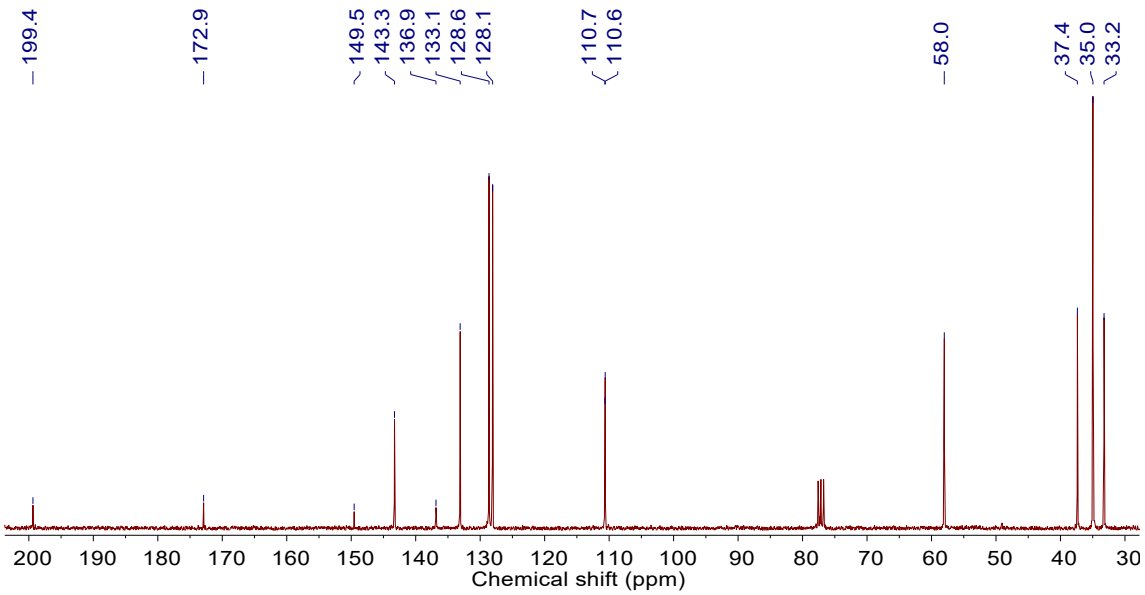


Fig. S12 ^{13}C NMR spectrum of **3c** in $CHCl_3$-*d* at 300 Hz

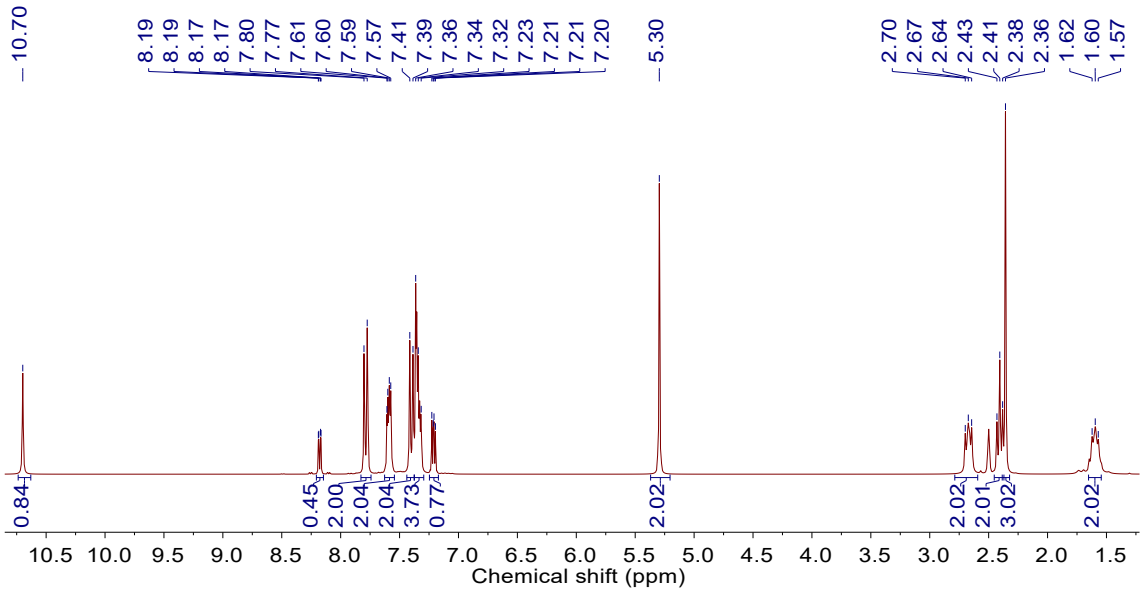


Fig. S13 ^{1}H NMR spectrum of **TsHSe** in DMSO-d_6 at 300 Hz

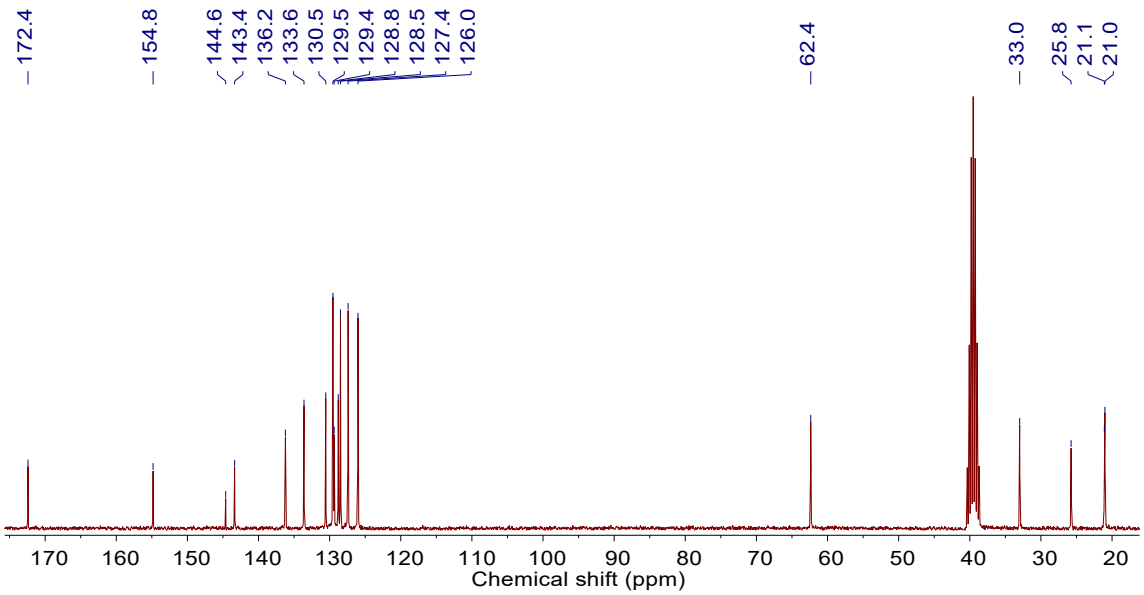


Fig. S14 ^{13}C NMR spectrum of **TsHSe** in DMSO-d_6 at 75 Hz

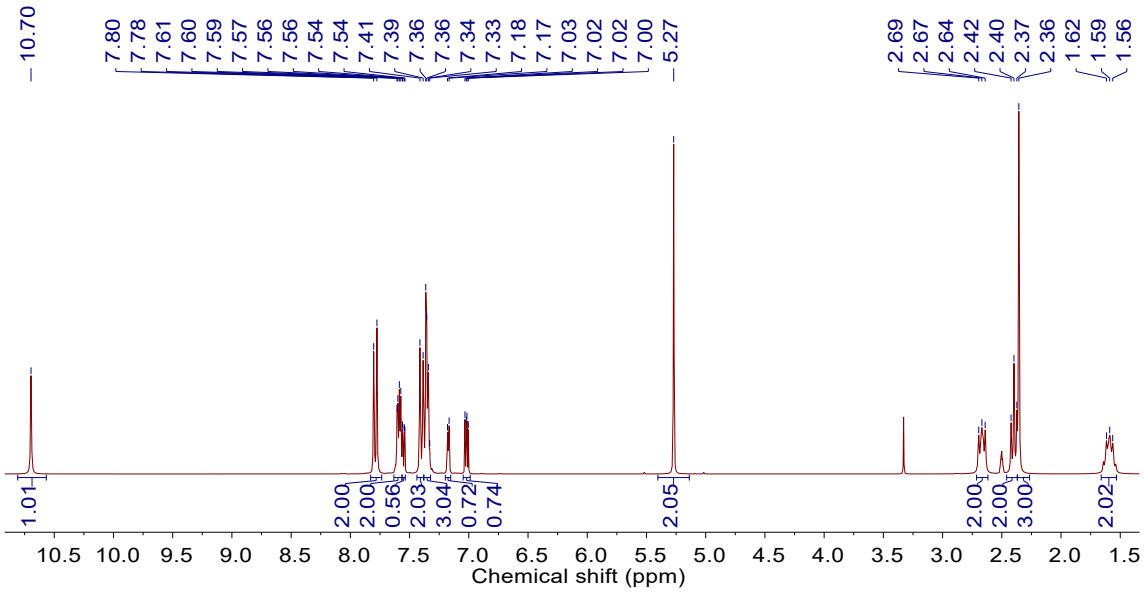


Fig. S15 1H NMR spectrum of **TsHTh** in DMSO-d_6 at 300 Hz

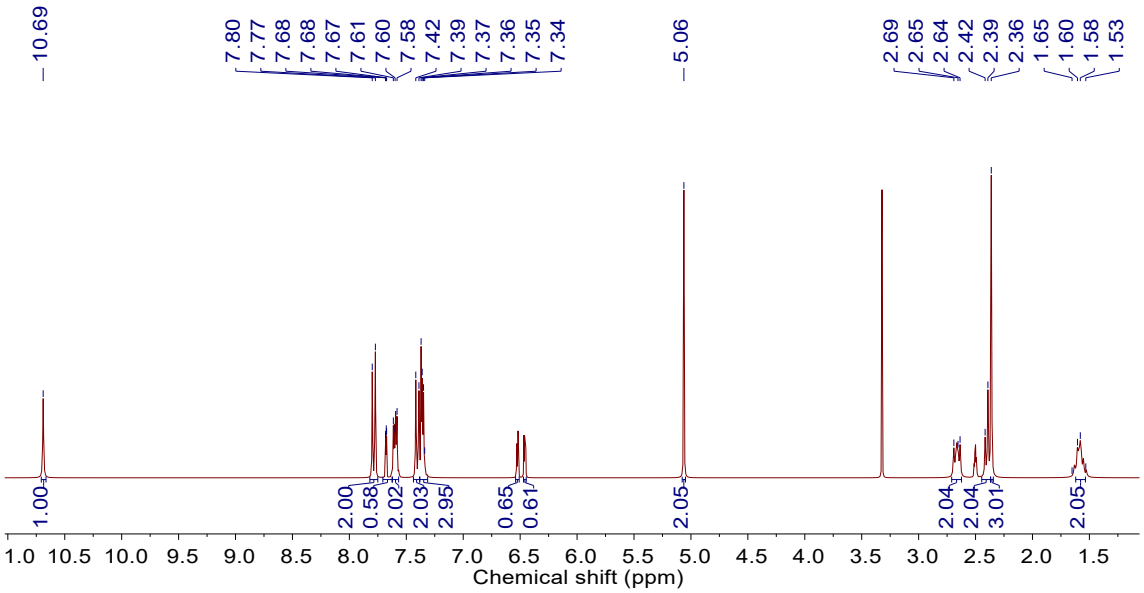


Fig.S16 [1]H NMR spectrum of **TsHFu** in DMSO-d_6 at 300 Hz

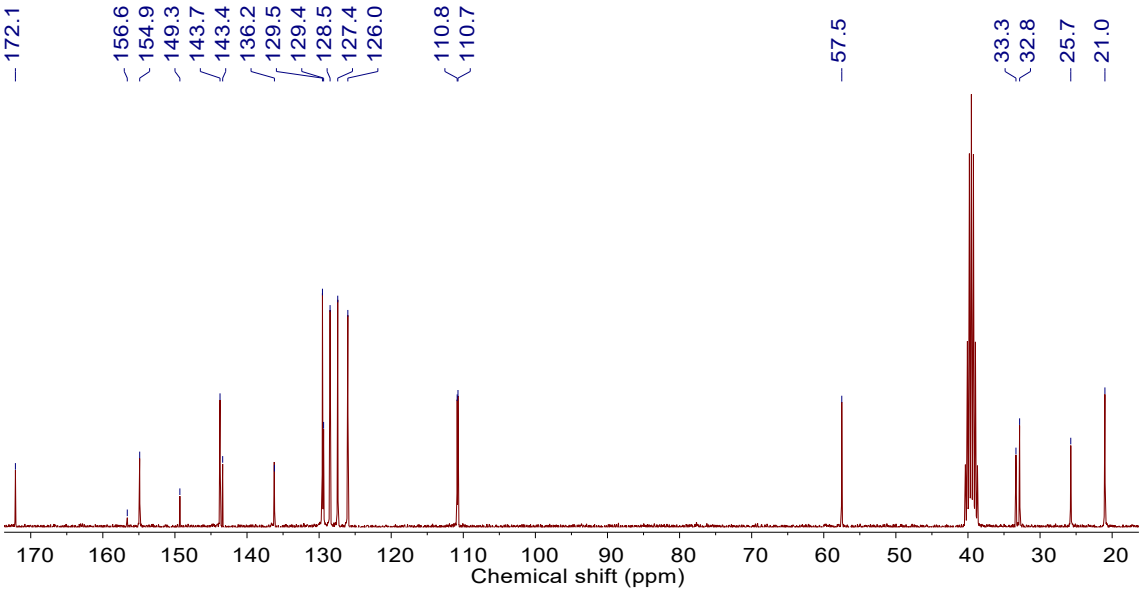


Fig. S17 ^{13}C NMR spectrum of **TsHFu** in DMSO-d_6 at 300 Hz

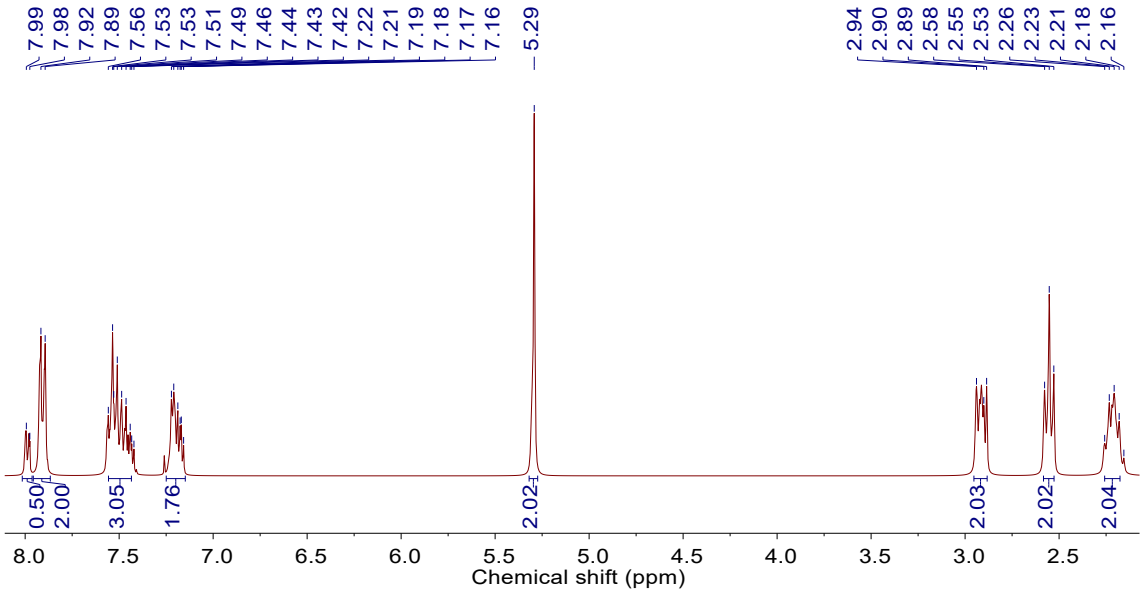


Fig. S18 ^{1}H NMR spectrum of **PCBSe** in CS_2:$CHCl_3$-*d* (9:1) at 300 Hz

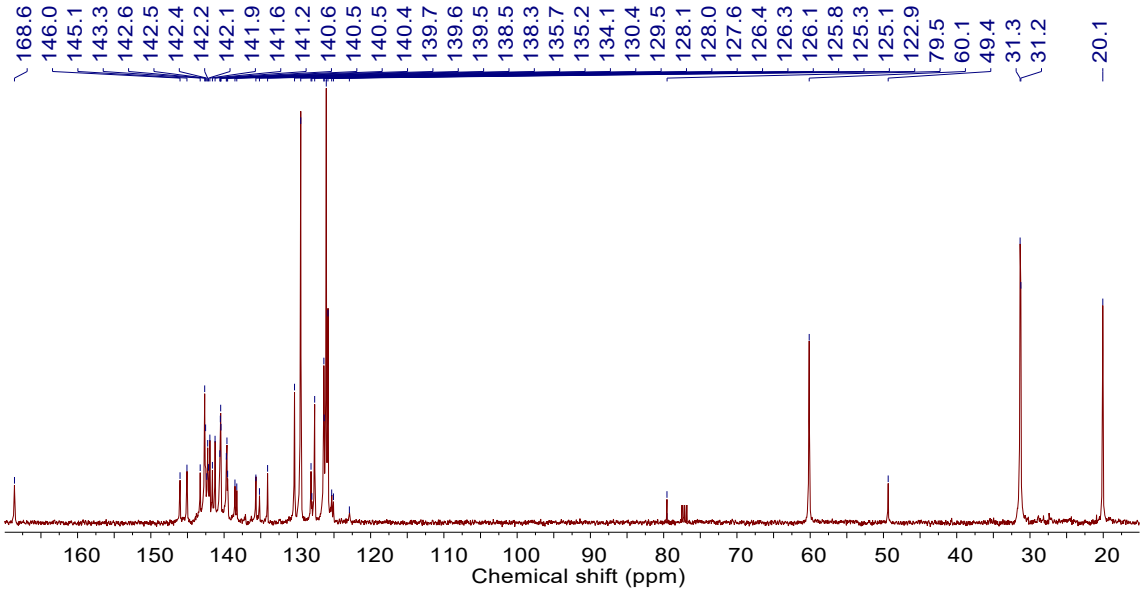


Fig. S19 ^{13}C NMR spectrum of **PCBSe** in CS_2:$CHCl_3$-*d* (9:1) at 75 Hz

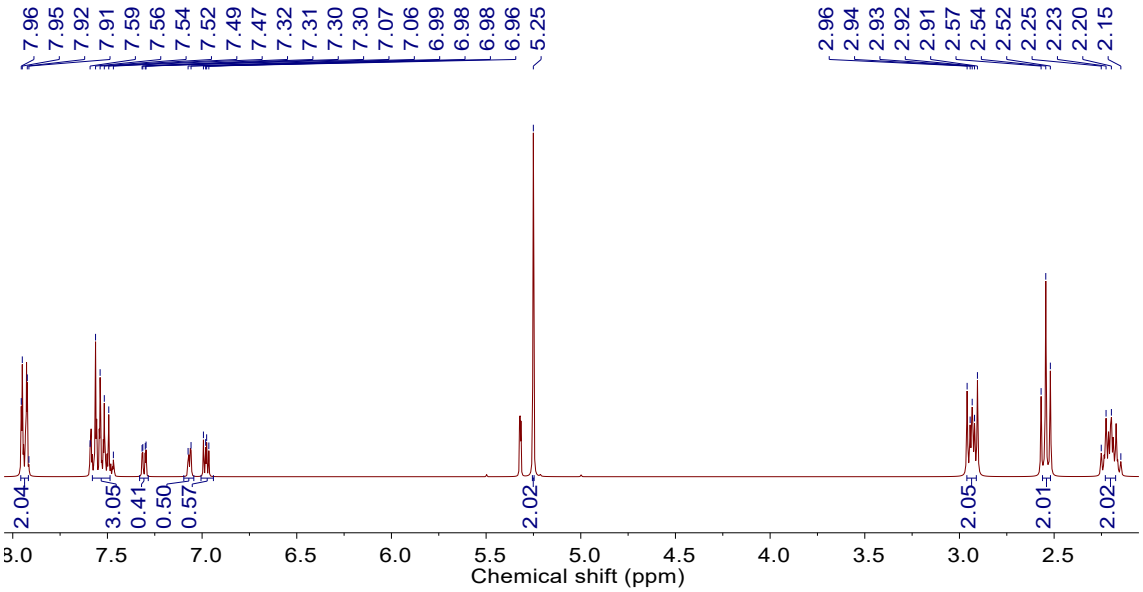


Fig. S20 ^{1}H NMR spectrum of **PCBTh** in CS_2:DCM-d_2 (9:1) at 300 Hz

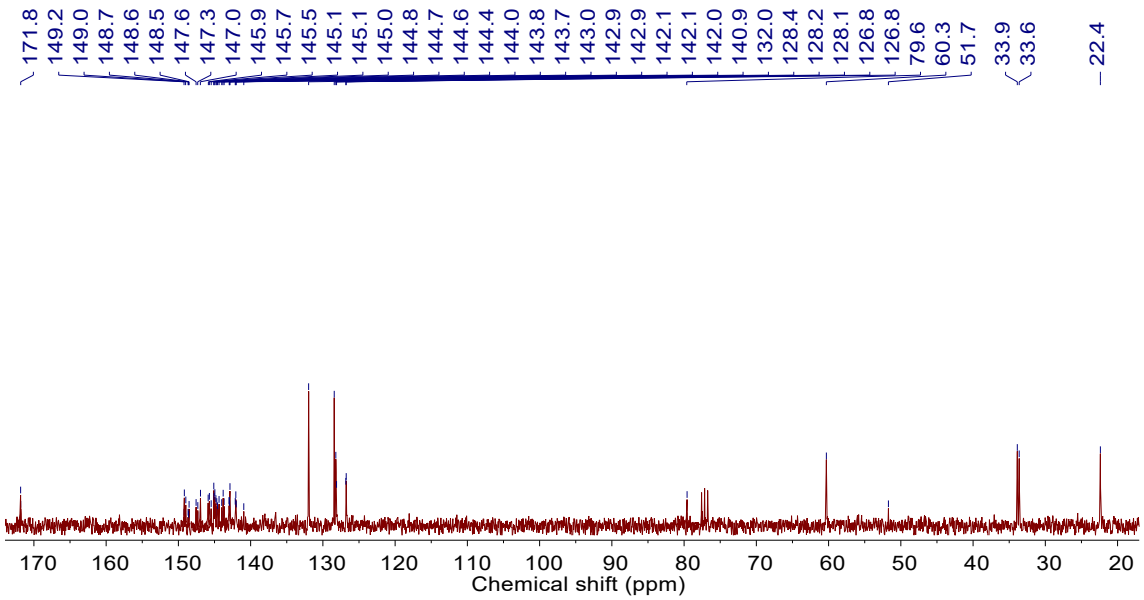


Fig. S21 ^{13}C NMR spectrum of **PCBTh** in CS_2:$CHCl_3$-*d* (9:1) at 75 Hz

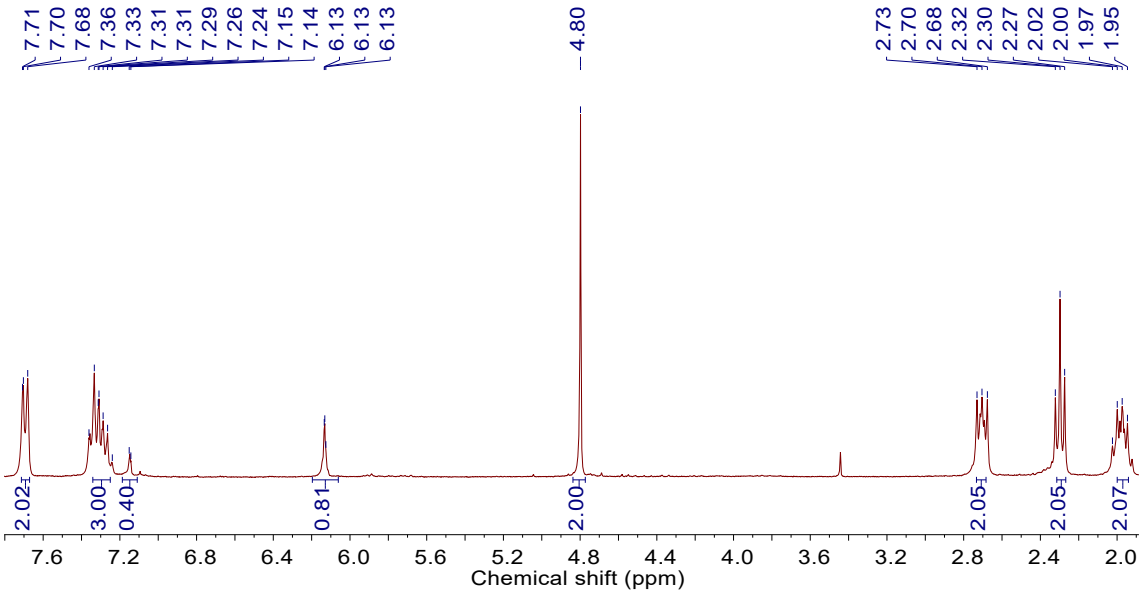


Fig. S22 ^{1}H NMR spectrum of **PCBFu** in CS_2:$CHCl_3$-*d* (9:1) at 300 Hz

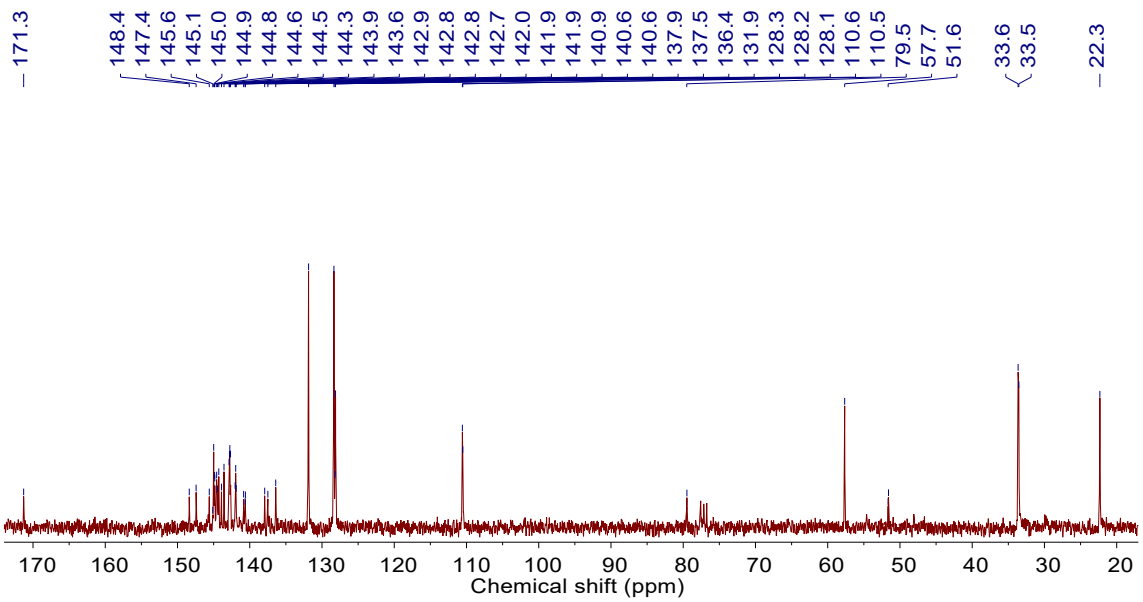


Fig. S23 ^{13}C NMR spectrum of **PCBFu** in CS_2:$CHCl_3$-*d* (9:1) at 75 Hz

FT-IR spectra

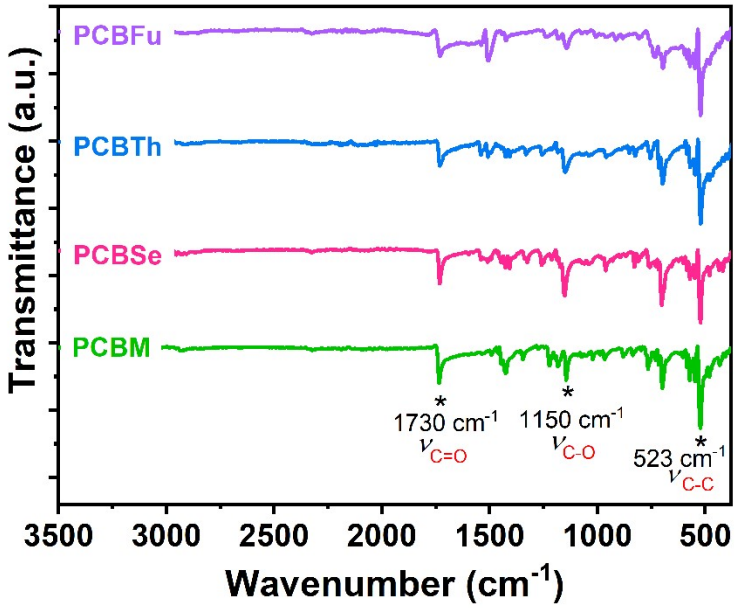


Fig. S24 FT-IR spectra of **PCBM**, **PCBSe**, **PCBTh** and **PCBFu**.

MALDI-TOF mass spectra

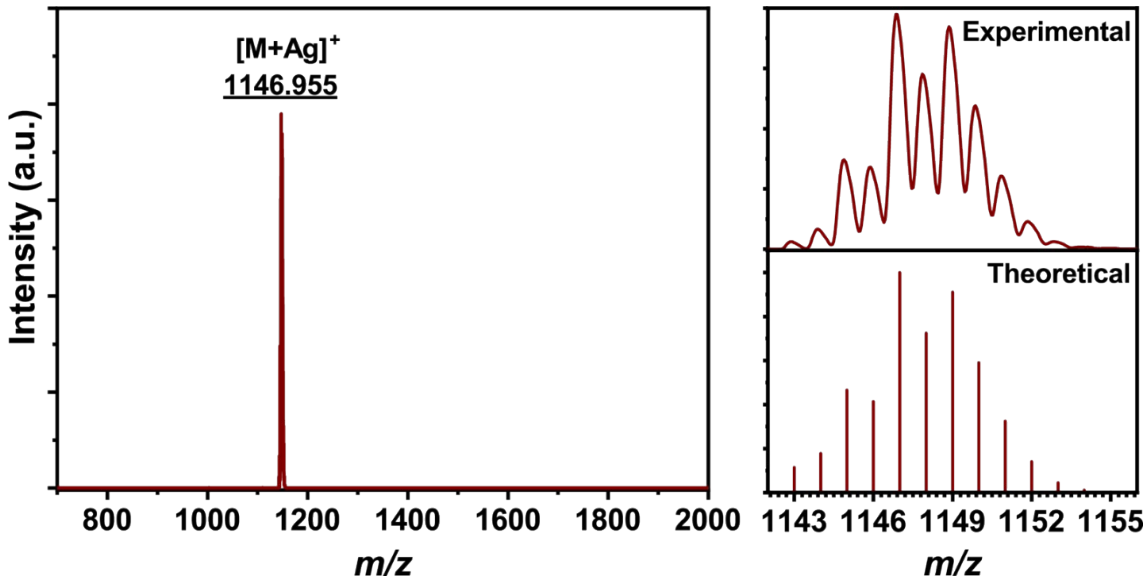


Fig. S25 MALDI-TOF mass spectrum of **PCBSe**

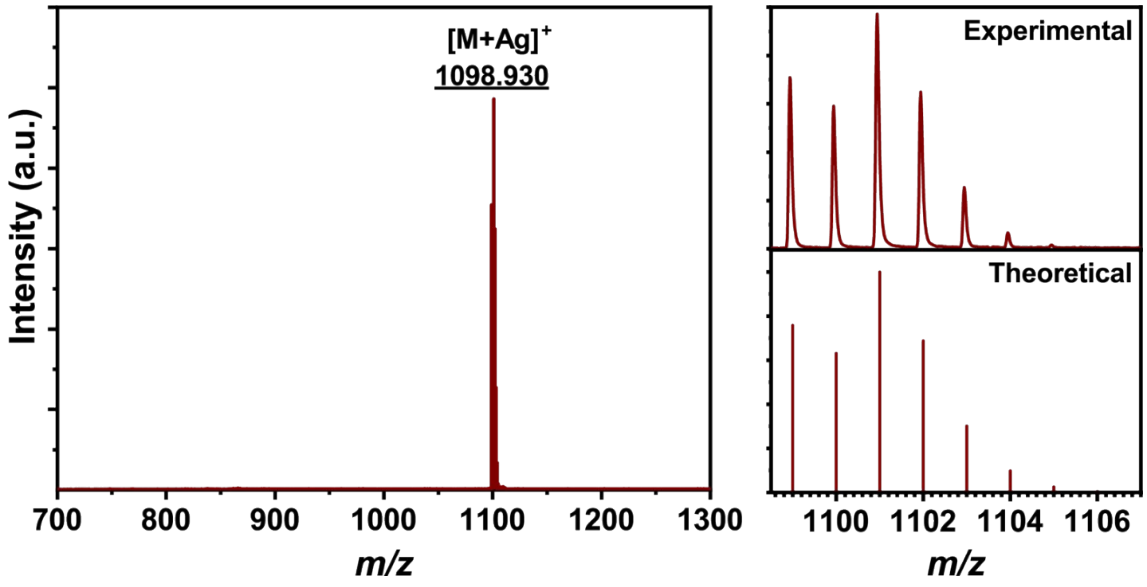


Fig. S26 MALDI-TOF mass spectrum of **PCBTh**

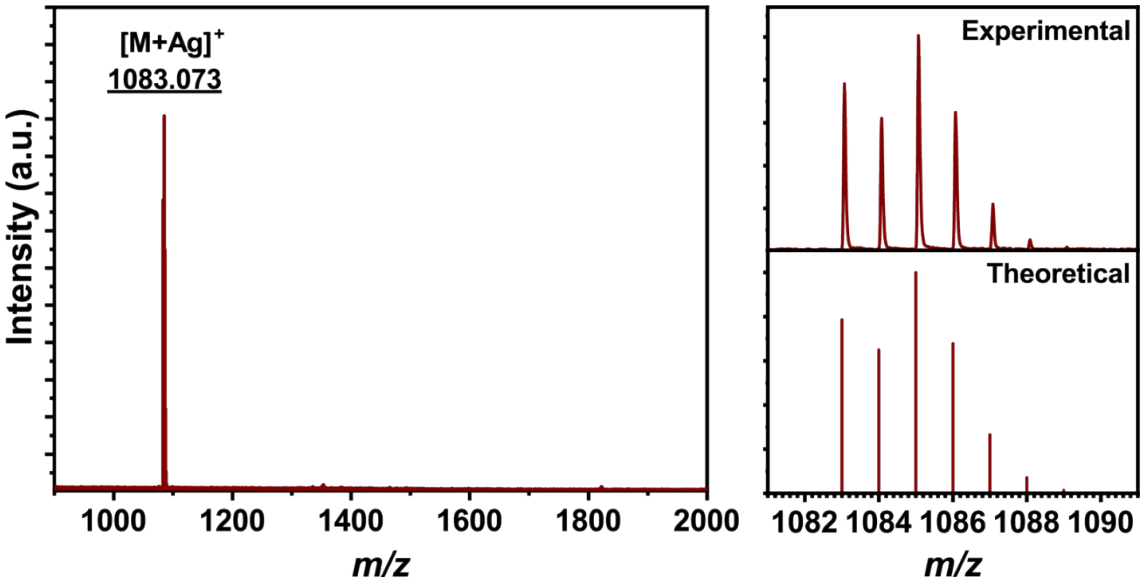


Fig. S27 MALDI-TOF mass spectrum of **PCBFu.**

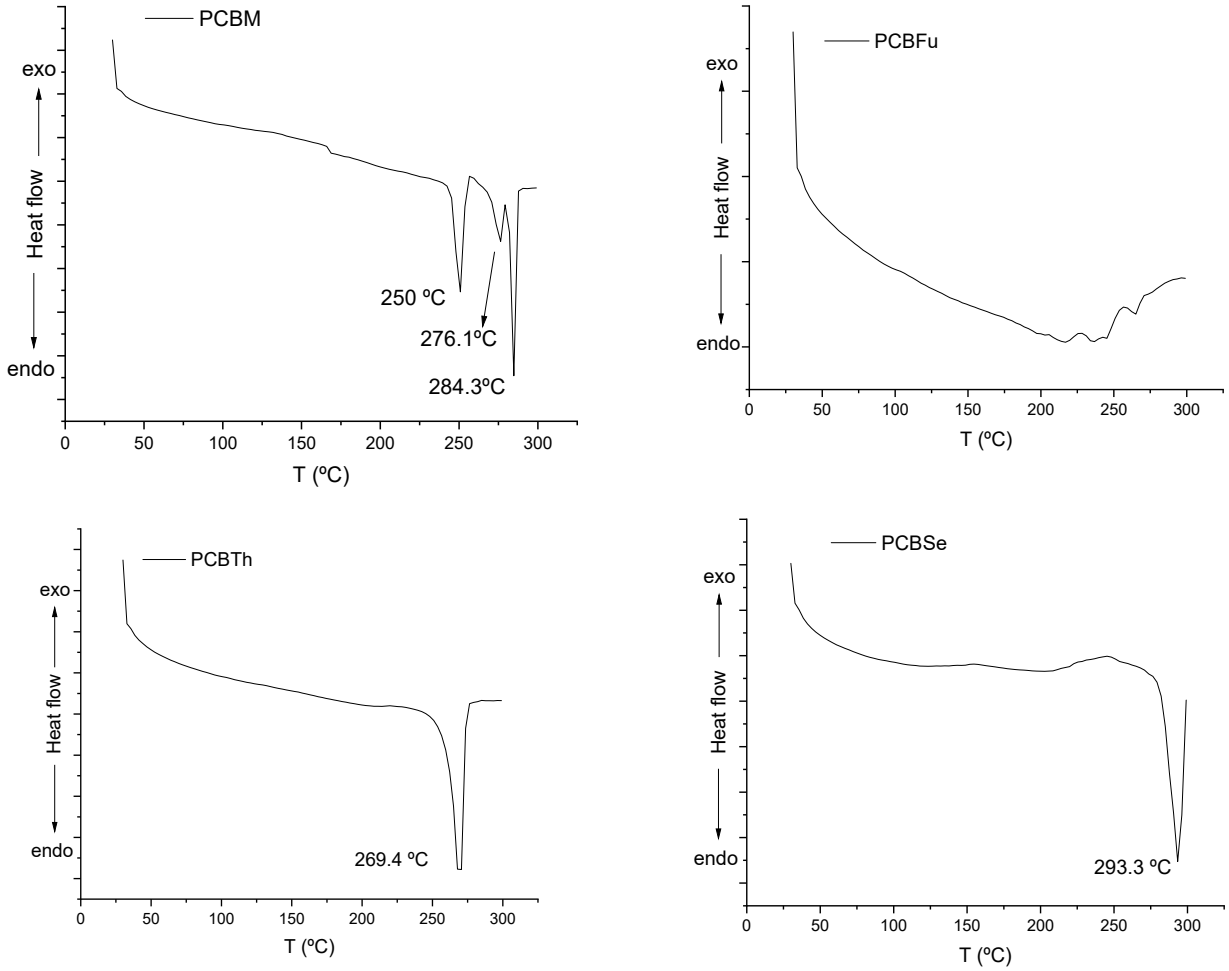


Fig. S28 DSC thermograms of the PCBM, PCBFu, PCBTh and PCBSe molecules.

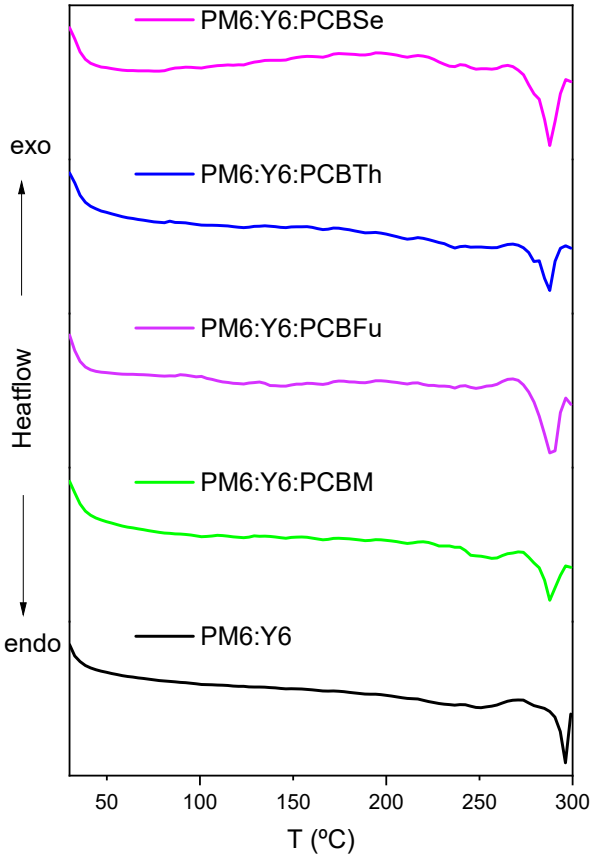


Fig. S29 DSC thermograms of the blend films.

Table S1. Temperature of the transition and enthalpy associated for each of the blend films.

Sample	Temperature of the transition (ºC)	Enthalpy (mJ)
PM6:Y6	250.7	9.7
	296.3	29.7
PM6:Y6:PCBM	286.8	15.3
PCBM:Y6:PCBFu	289.2	33.9
PM6:Y6:PCBTh	280.5	1.1
	287	10.9
PM6:Y6:PCBSe	287.8	30.9

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