Supporting Information for:

A Versatile and Efficient Synthesis of Bithiophene-Based Dicarboxaldehydes

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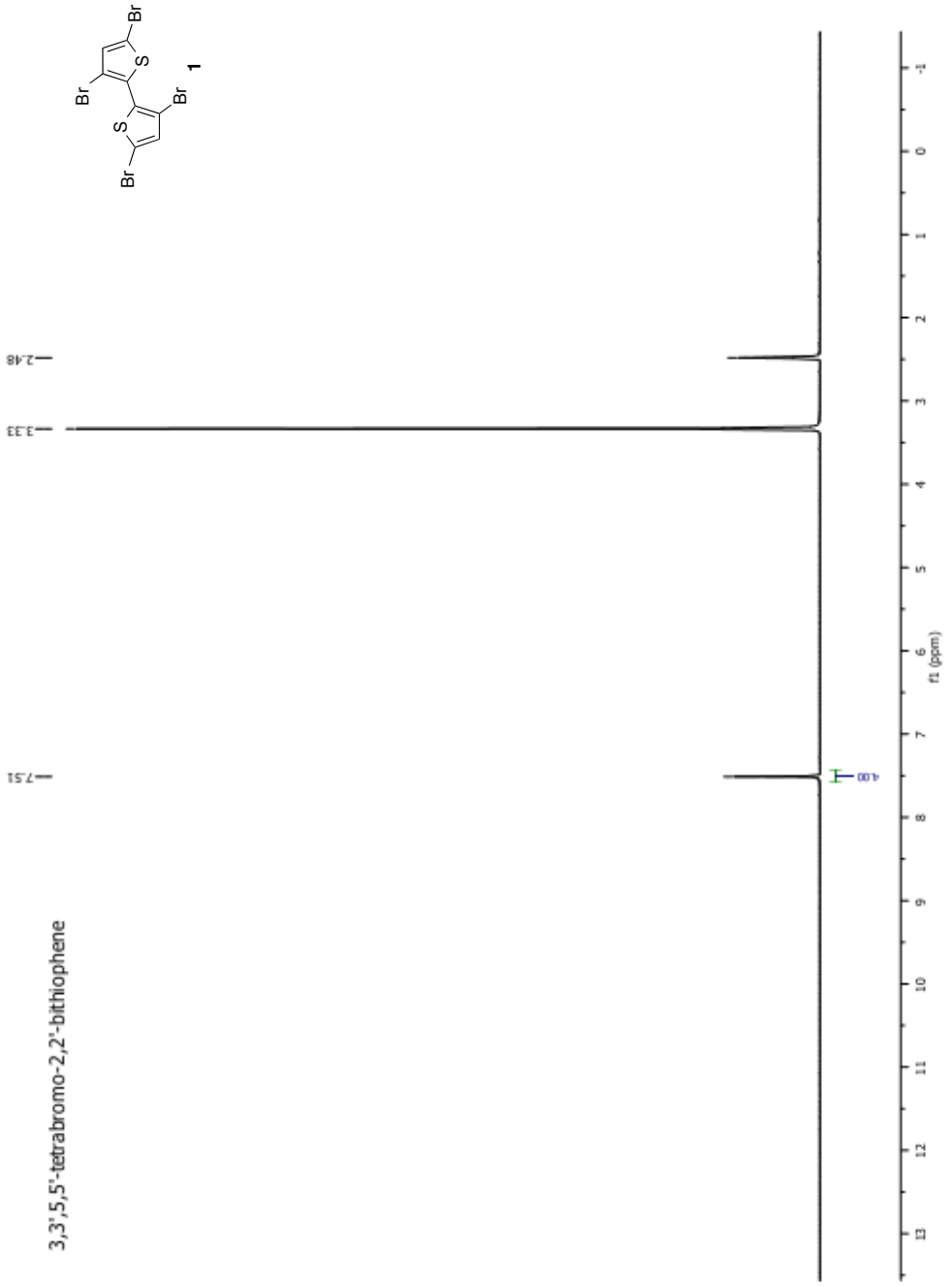


Figure S1: ^{1}H NMR spectra of compound 1

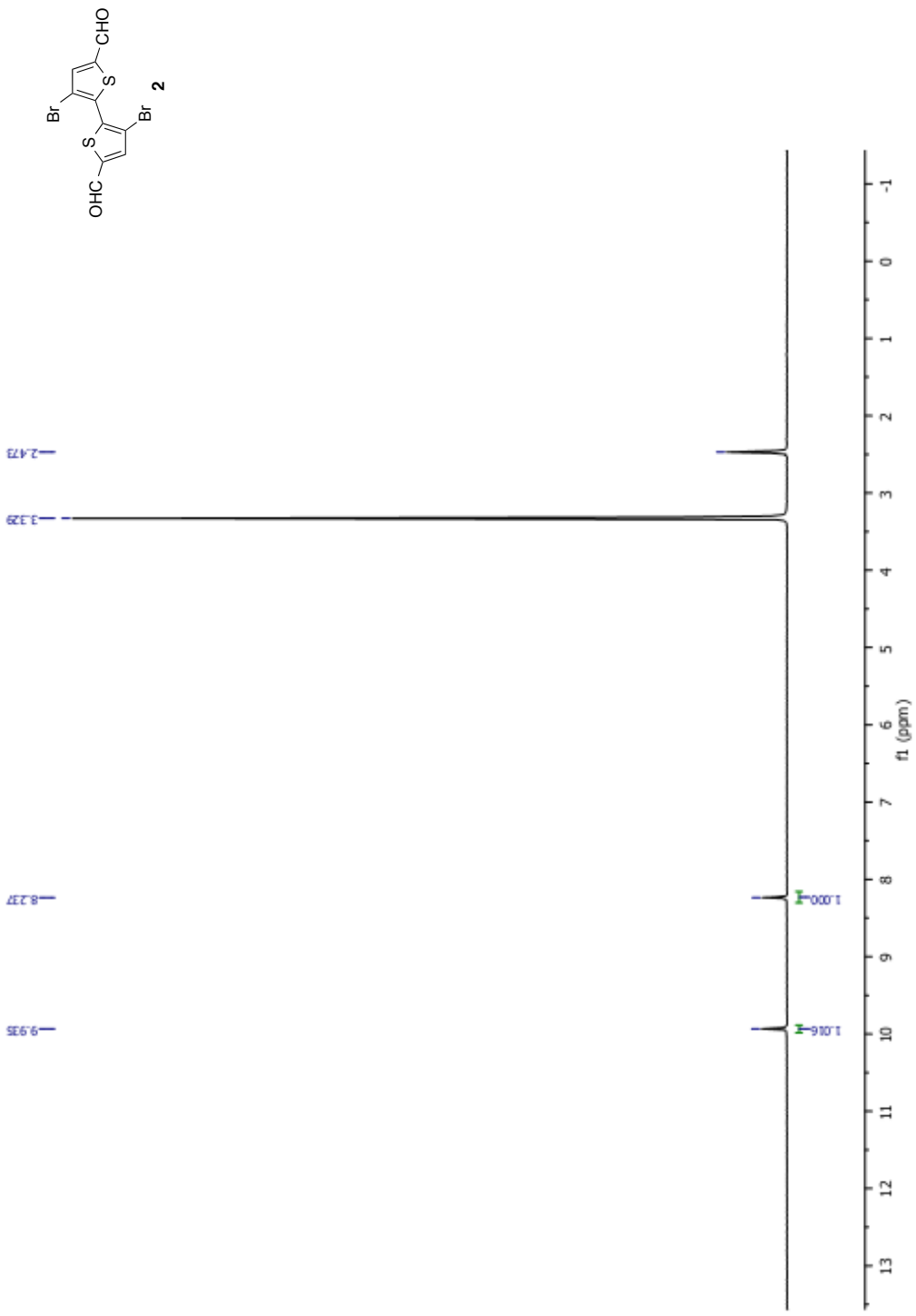


Figure S2: ^{1}H NMR spectra of compound 2

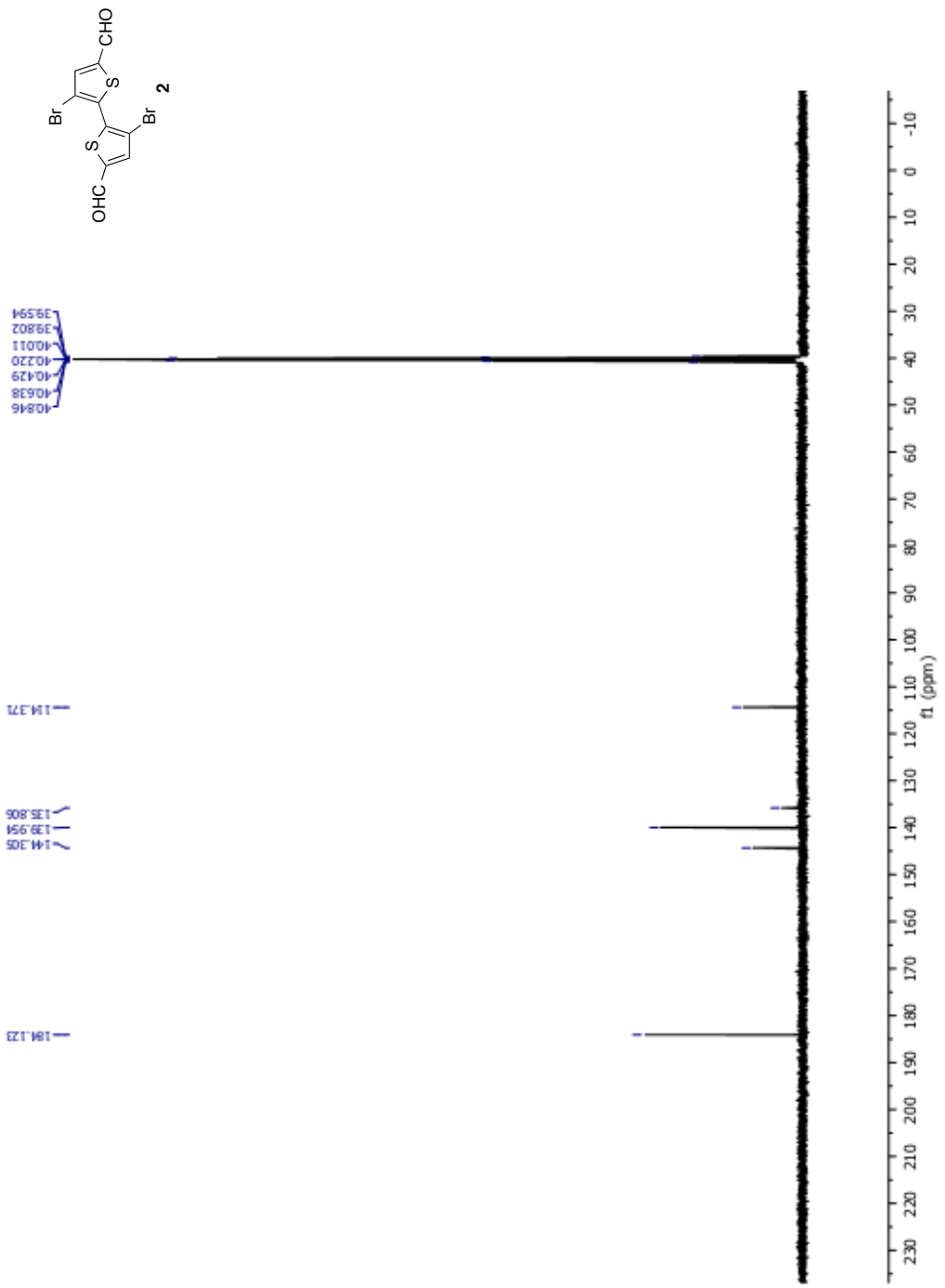


Figure S3: ^{13}C NMR spectra of compound 2

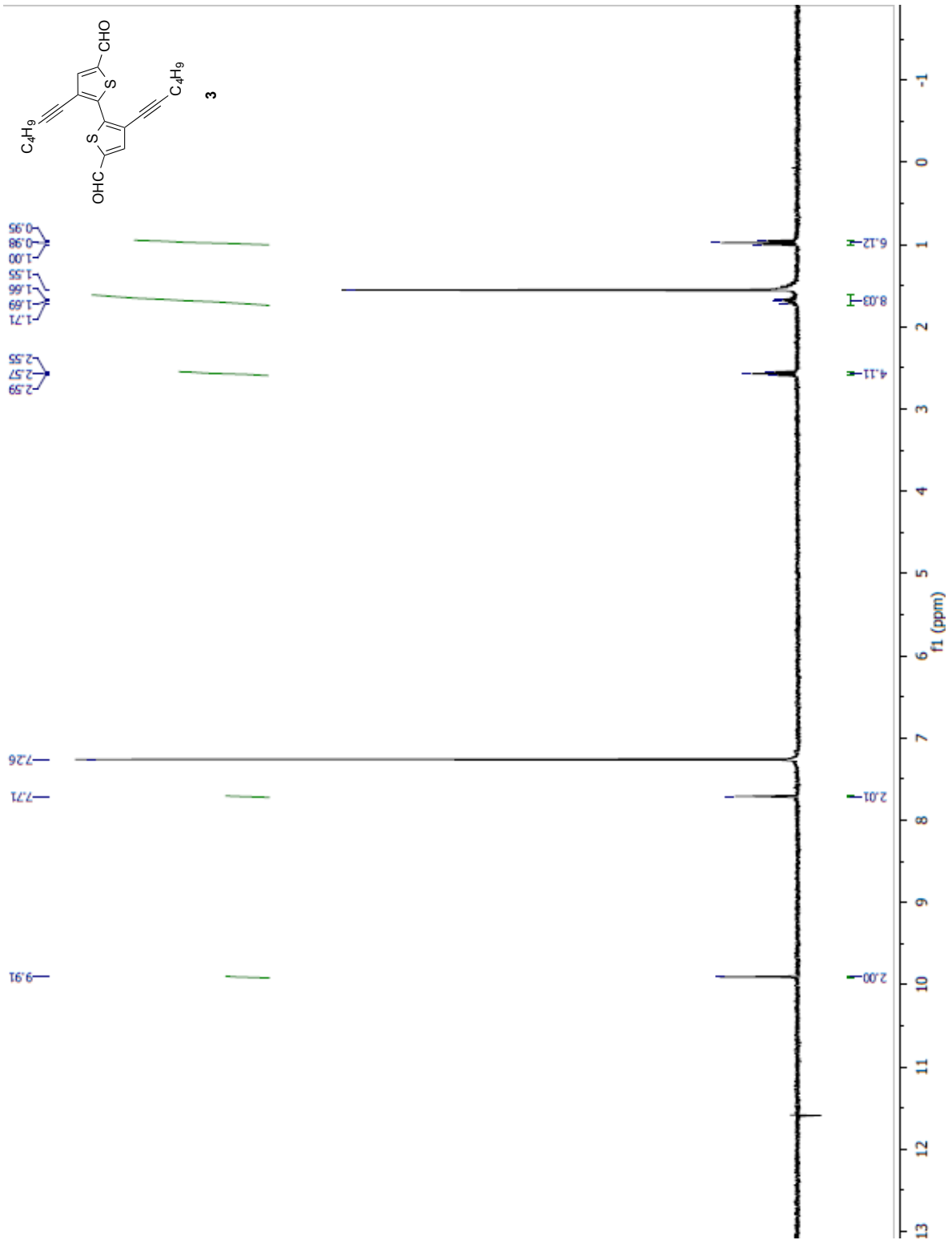


Figure S4: ^{1}H NMR spectra of compound 3

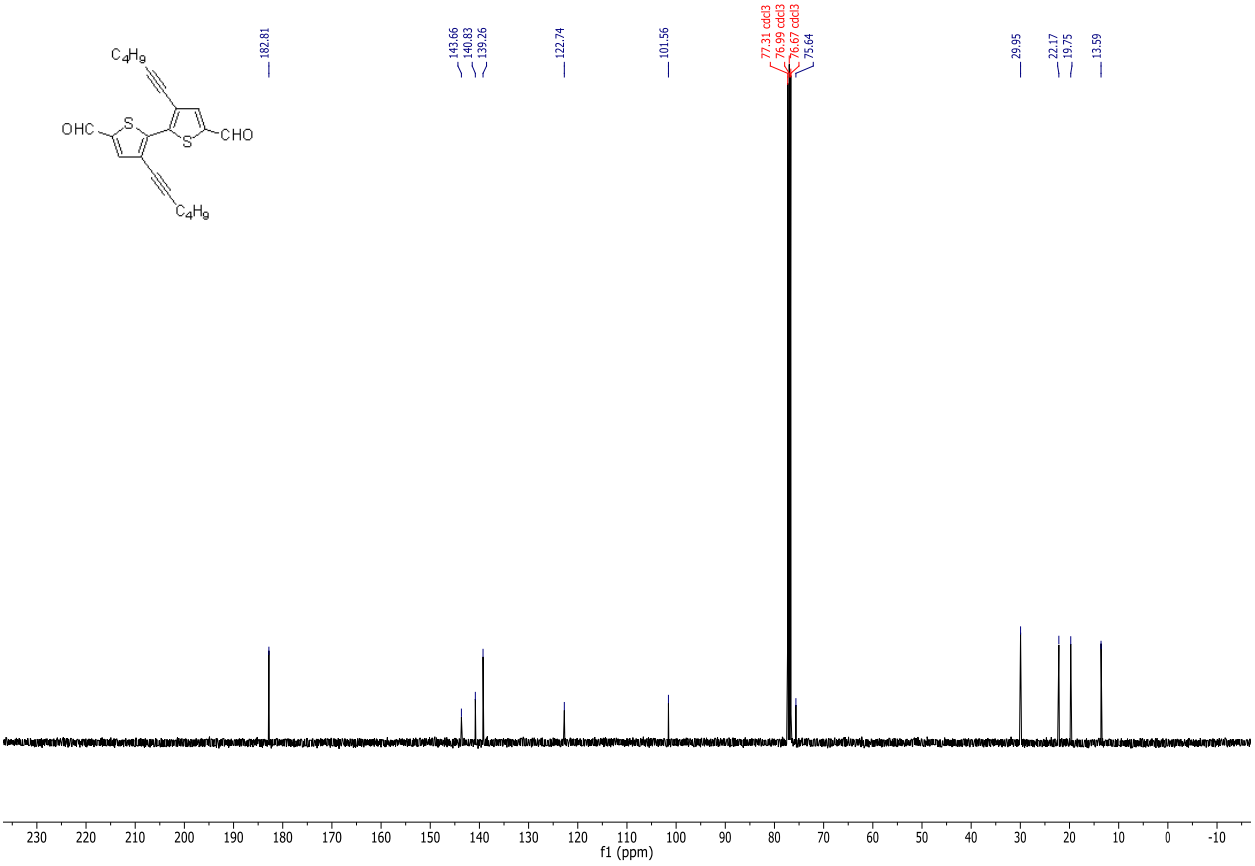


Figure S5: ^{13}C NMR spectra of compound 3

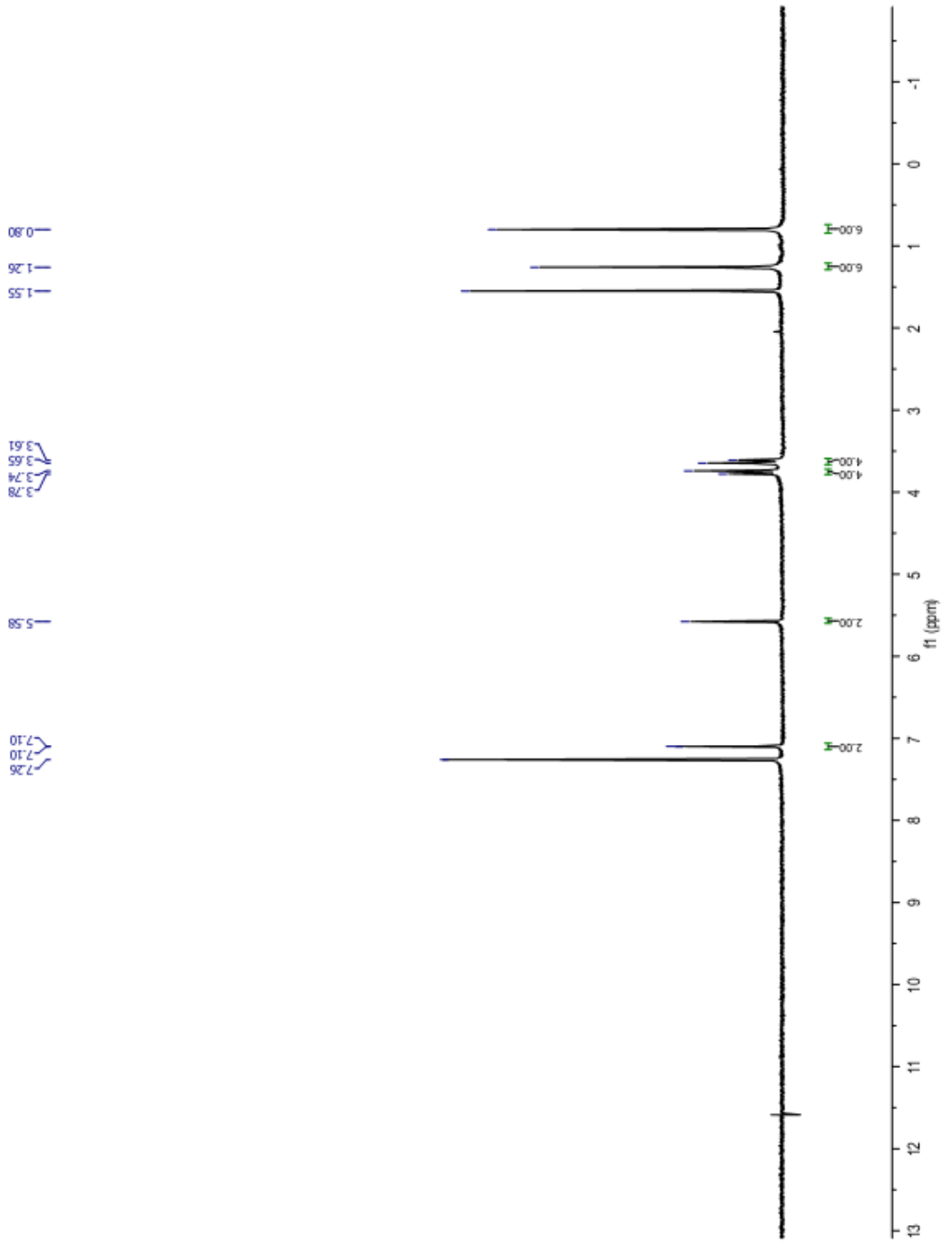


Figure S6: ^{1}H NMR spectra of compound 4

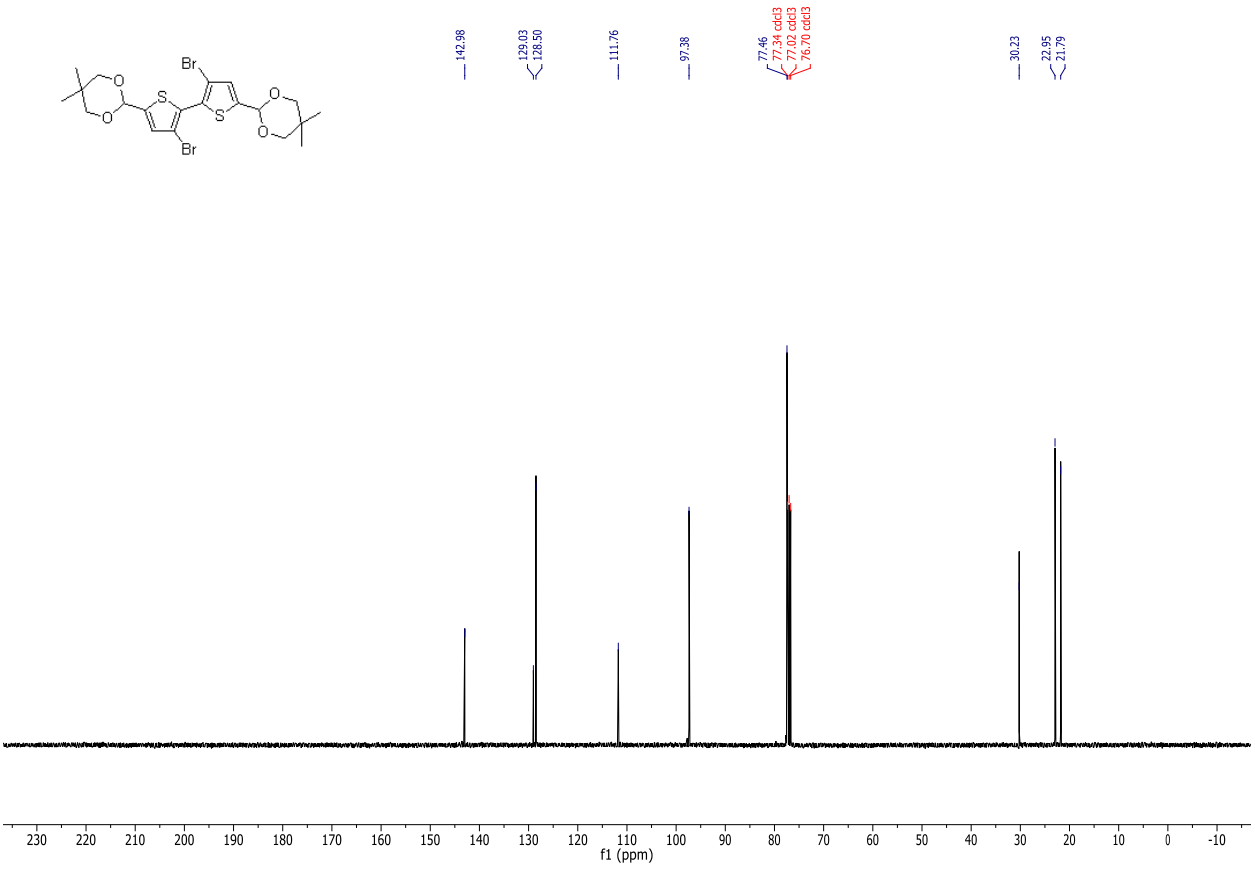


Figure S7: ^{13}C NMR spectra of compound 4

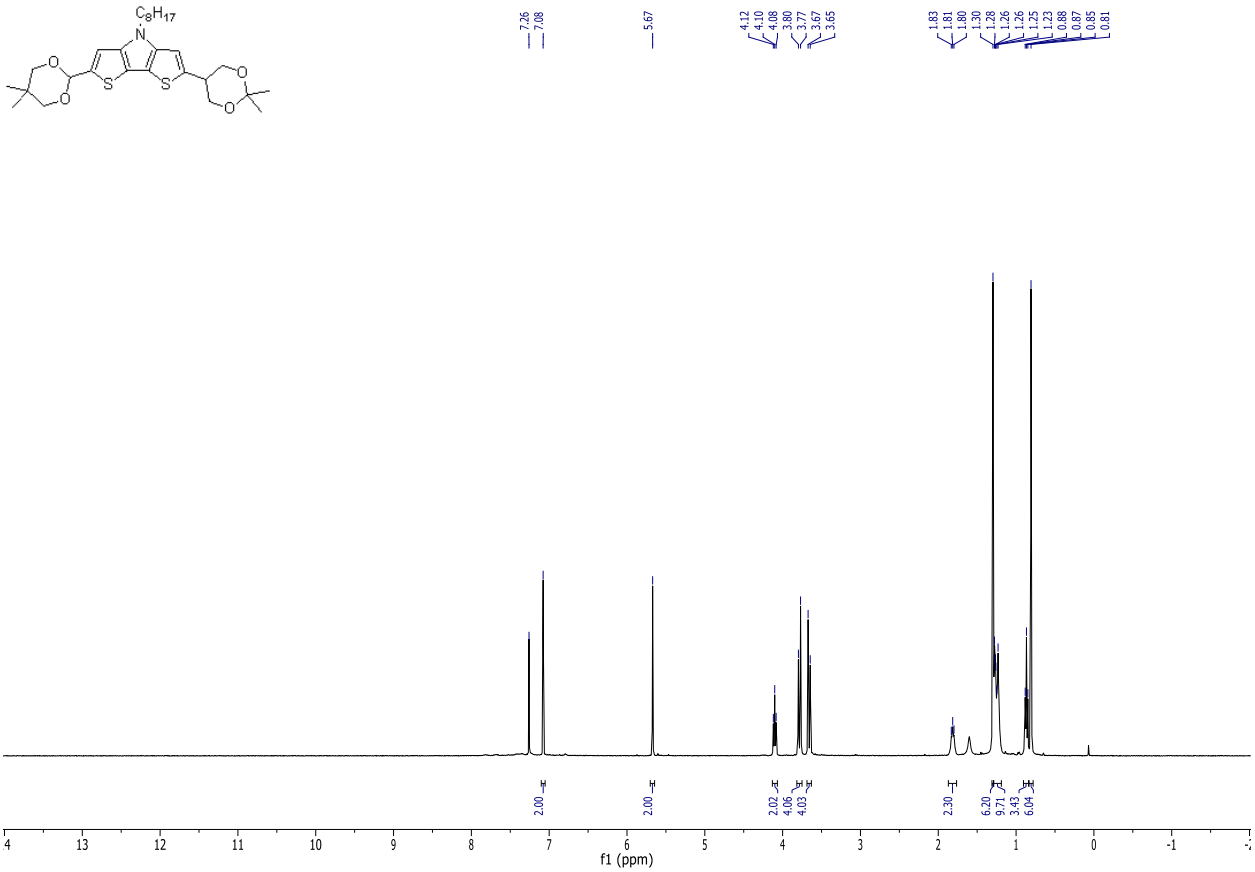


Figure S8: ^{1}H NMR spectra of compound 5a

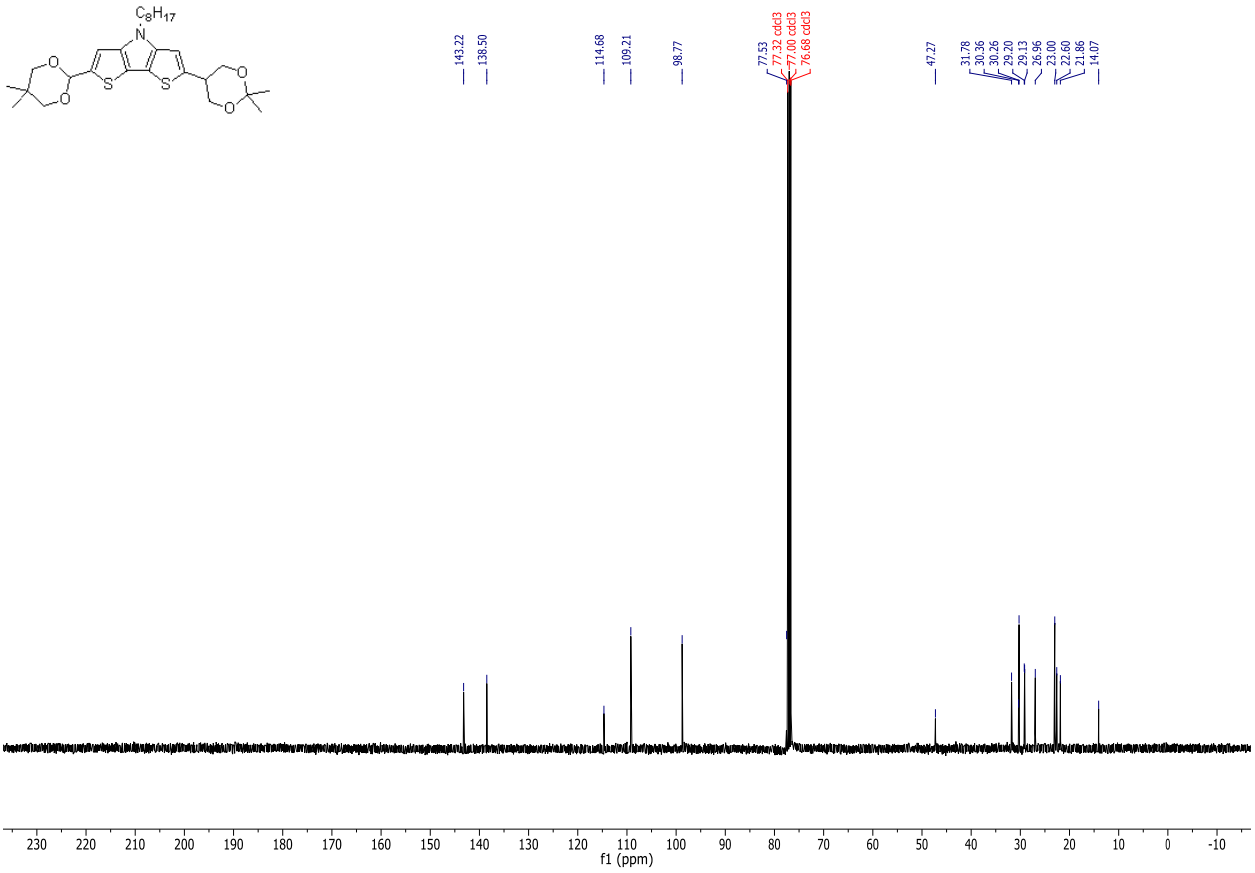


Figure S9: ^{13}C NMR spectra of compound 5a

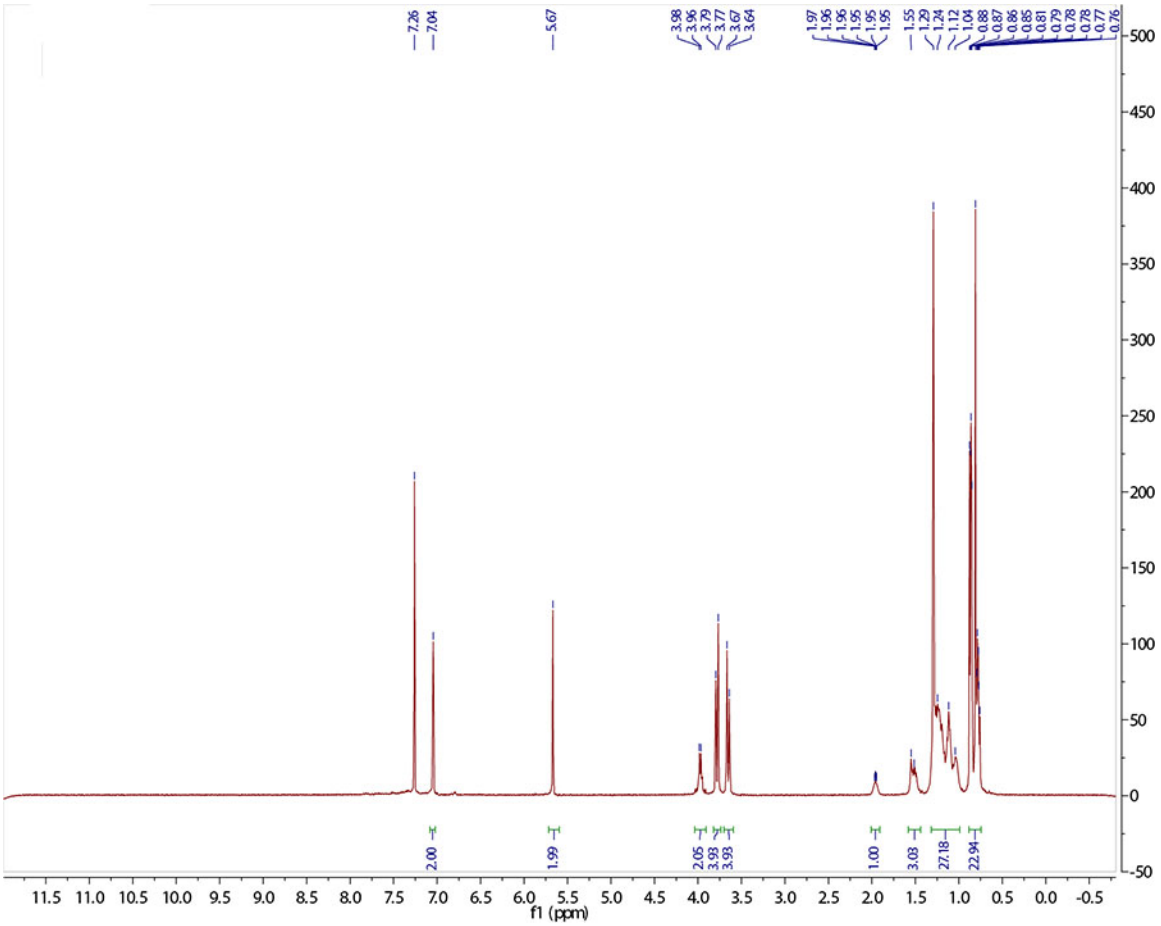


Figure S10: ^{1}H NMR spectra of compound 5b

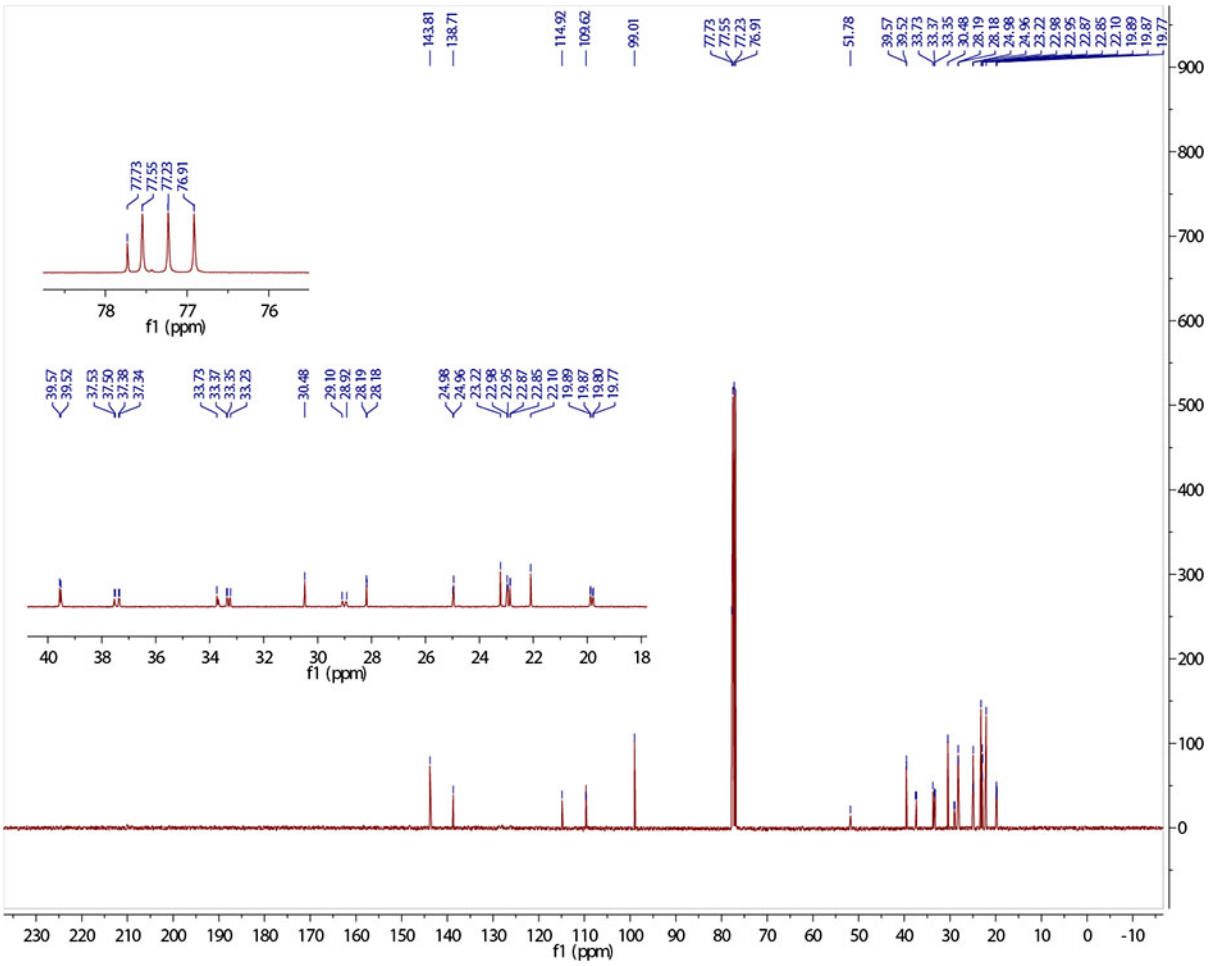


Figure S11: ^{13}C NMR spectra of compound 5b

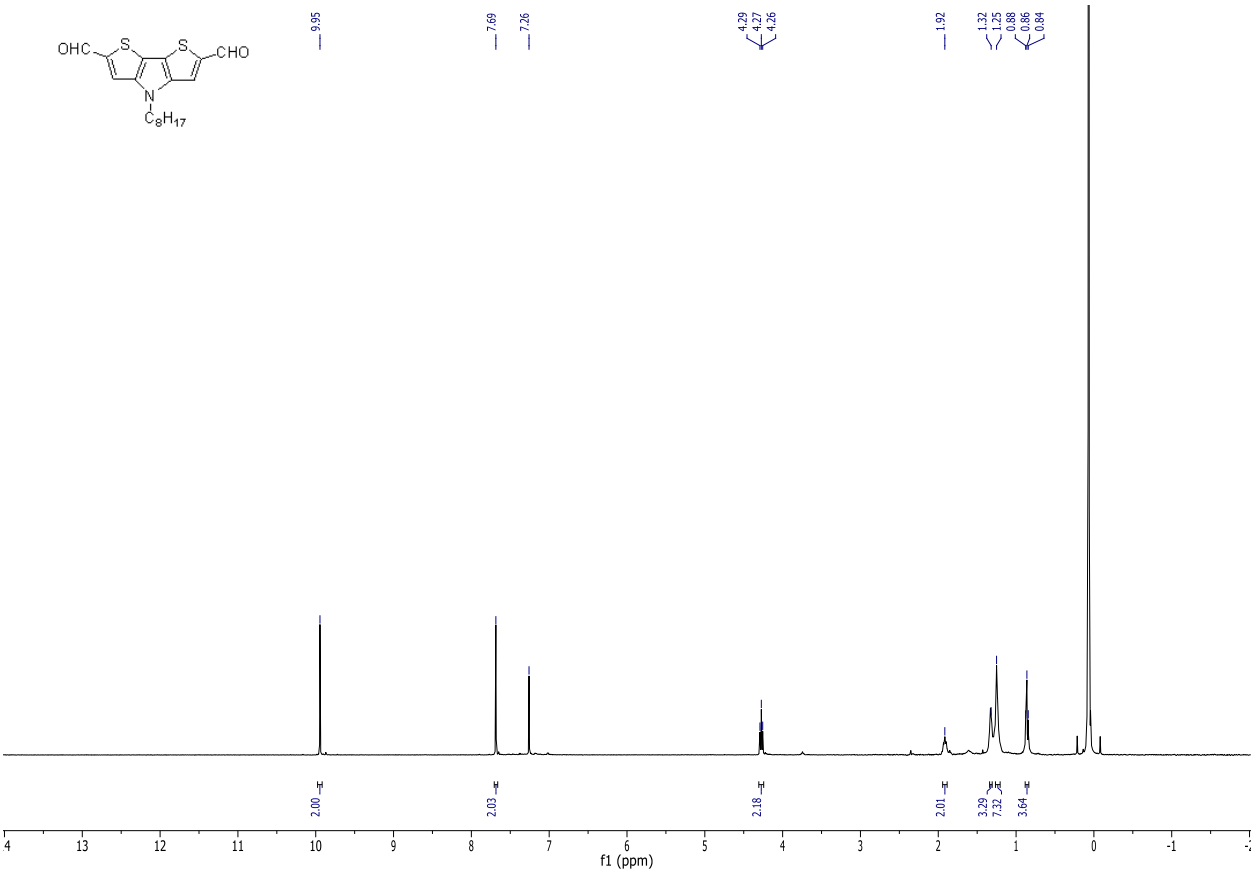


Figure S12: ^{1}H NMR spectra of compound 6a

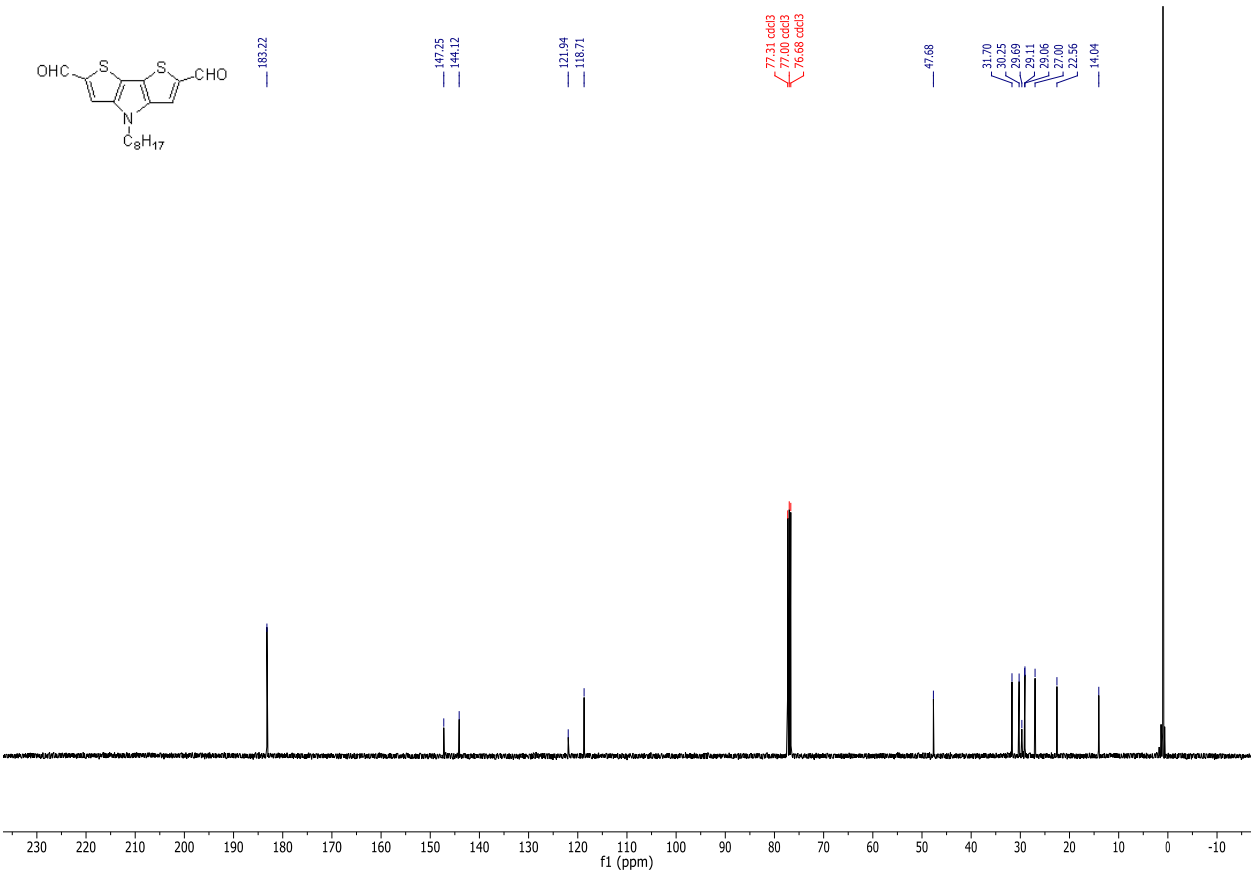


Figure S13: ^{1}C NMR spectra of compound 6a

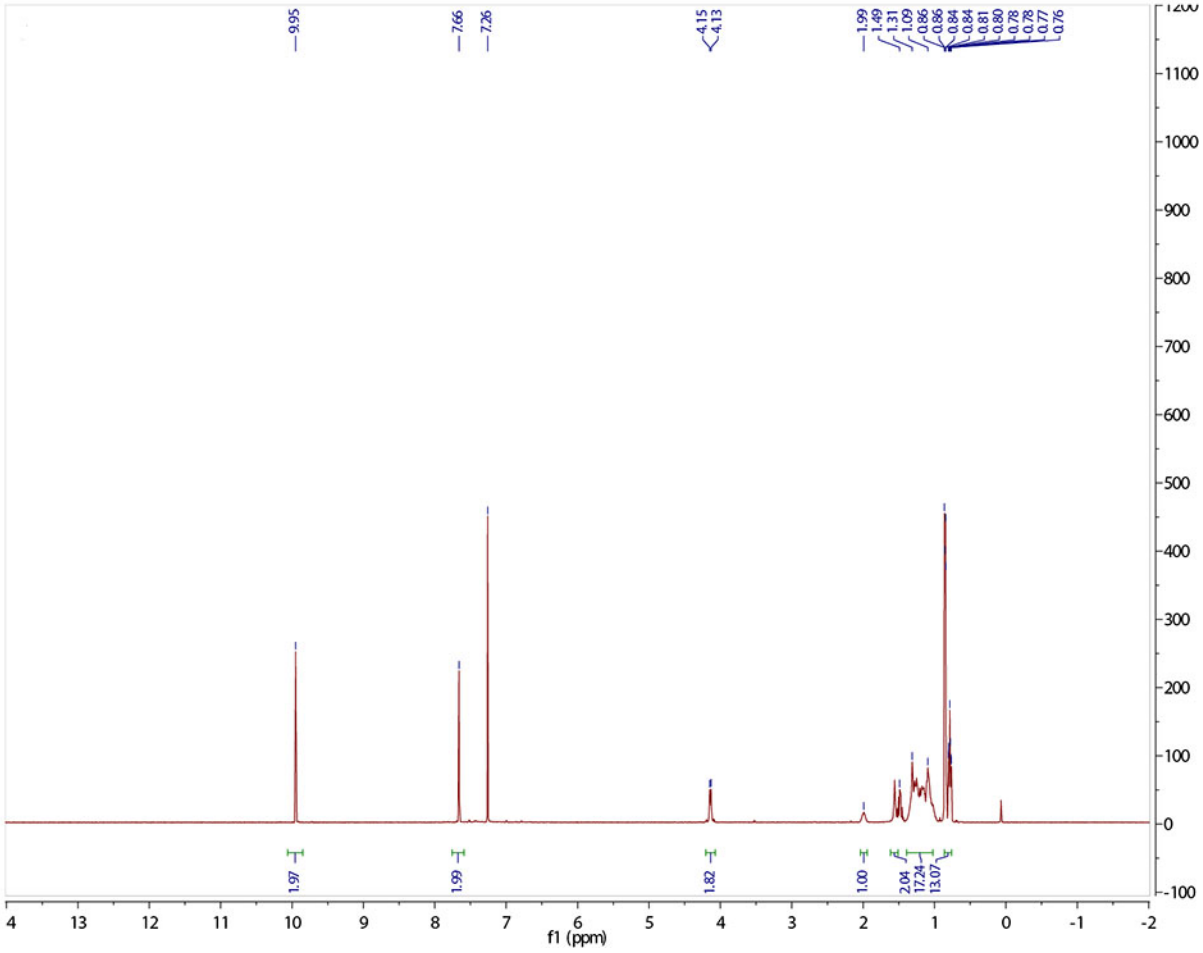


Figure S14: ^{1}H NMR spectra of compound 6b

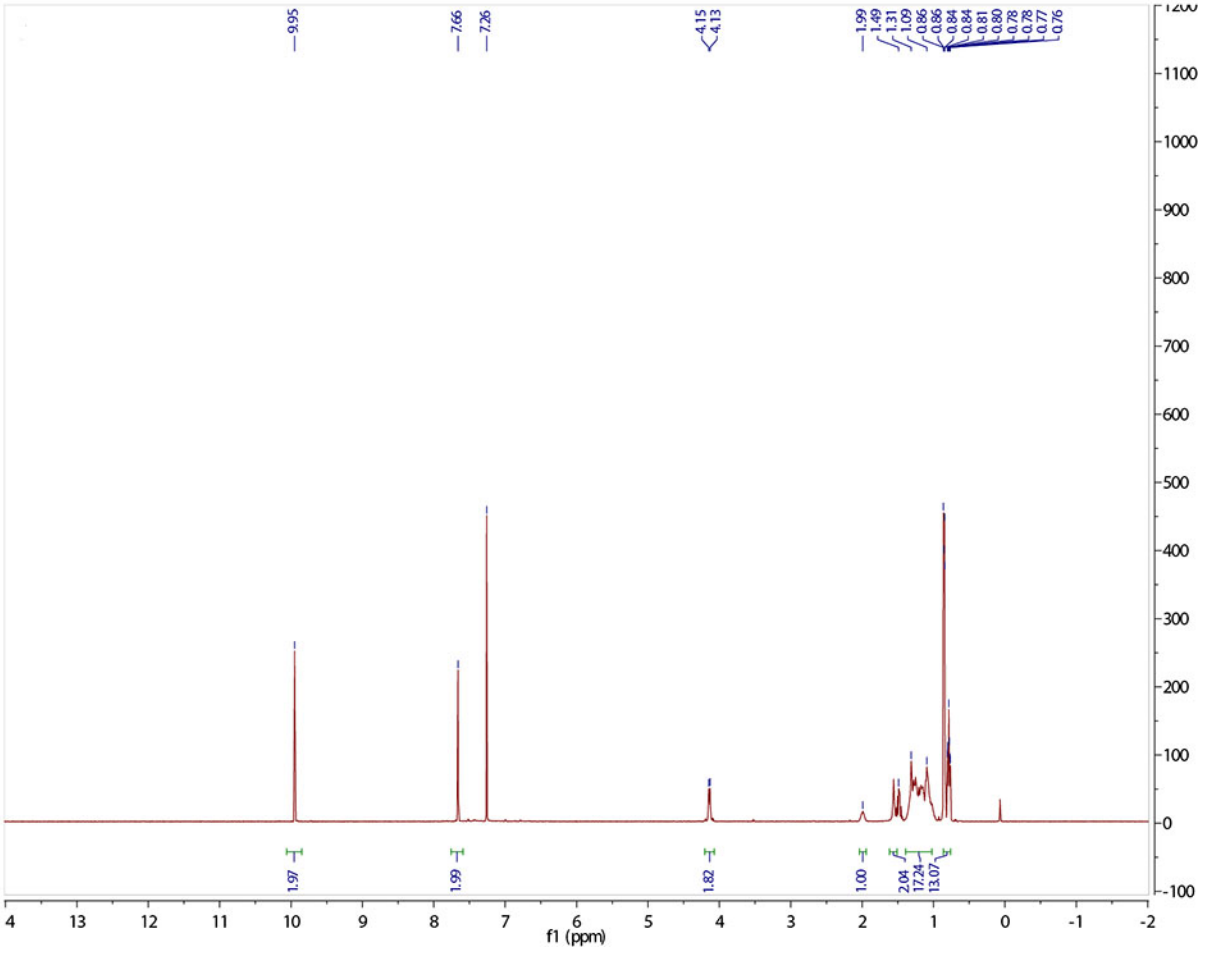


Figure S15: ^{1}H NMR spectra of compound 6b

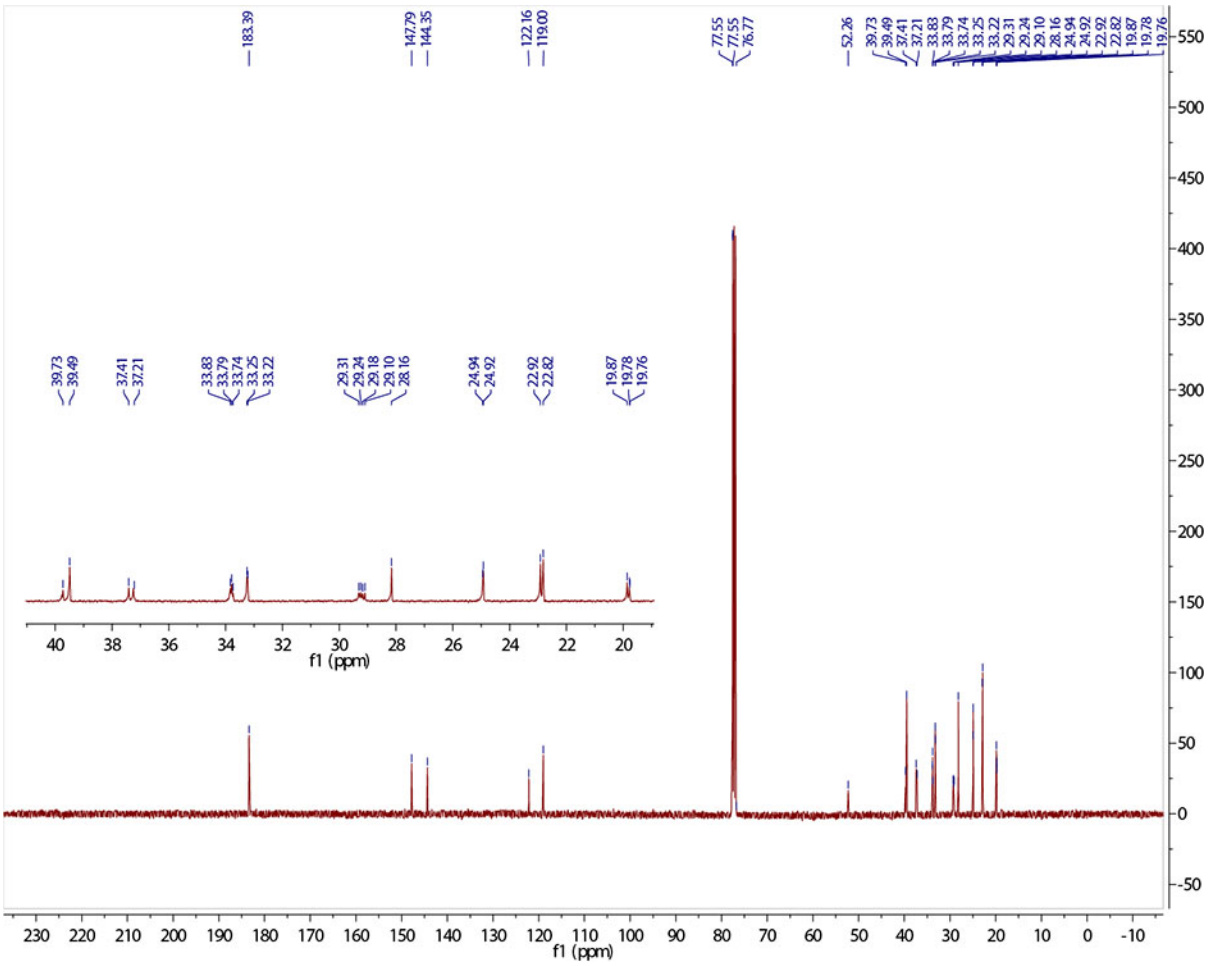
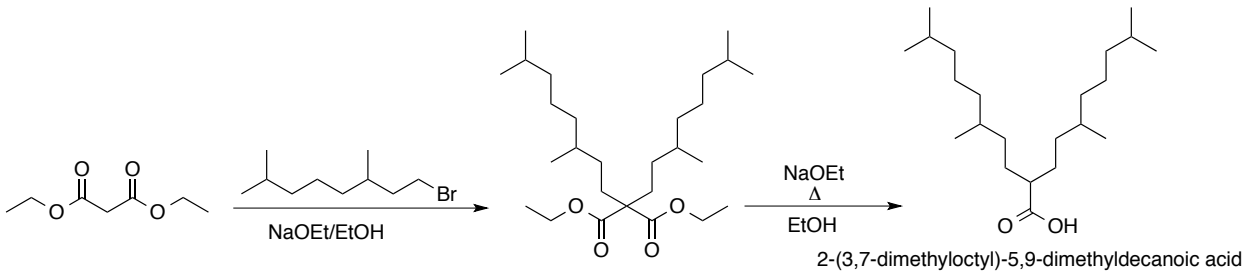


Figure S16: ^{1}C NMR spectra of compound 6b

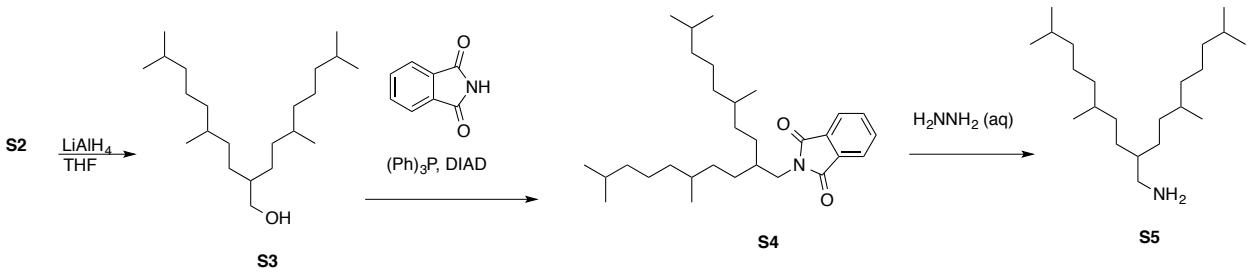


2-(3,7-dimethyloctyl)-5,9-dimethyldecanoic acid

S2

diethyl 2,2-bis(3,7-dimethyloctyl)malonate (S1) A concentrated solution of sodium ethoxide (35mL) was slowly added to a mixture of diethyl malonate (31.21 mmol) and 1-bromo-3,7-dimethyl bromide (78.04 mmol) with continuous stirring and the temperature was maintained between 5 – 10°C. After the addition of NaOEt, the cold-water bath was removed and the mixture was allowed to stir overnight at rt. Excess solvent was removed and the residue was added to water and then extracted with diethyl ether. The organic phase was washed with brine and water and dried over $MgSO_4$ and then evaporated to give a yellow liquid. The crude material was distilled under high vacuum to yield pure product (7.9g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80-0.83 (br, 18H), 0.89 – 1.30 (br, 22H), 1.31 (m, 2H), 1.48 (m, 2H), 1.82 (m, 4H), 4.14 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.214, 11.531, 19.246, 19.265, 20.068, 20.429, 21.528, 26.568, 26.649, 27.623, 29.284, 30.738, 75.033, 95.868, 125.083, 138.437, 138.930, 146.937.

2-(3,7-dimethyloctyl)-5,9-dimethyldecanoic acid (S2) In a round bottom flask **S1** (7.9 g, 17.93 mmol) was dissolved in ethanol (110 mL). Then a 50% wt./wt. solution of KOH(aq) 88 g was added and the reaction heated to 80 ^{0}C overnight. The reaction was then cooled to room temperature and acidified to a pH~2.5 using concentrated HCl. The reaction mixed was then extracted with hexanes and the organic layer washed with water, then brine. Lastly, the hexanes layer was dried over sodium sulfate and the solvent removed in vacuo to yield the product as an oil (5.96g, 99%). This was used without further purification. NMR (400 MHz, $CDCl_3$) δ 0.86 (m, 18H), 1.00 - 1.26 (m, 21H), 1.95 (m, 4H), 11.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$: δ 18.06, 19.60, 22.77, 22.87, 24.83, 28.11, 31.89, 33.03, 33.41, 36.98, 39.41.



2-(3,7-dimethyloctyl)-5,9-dimethyldecan-1-ol (S3). $LiAlH_4$ (95%, 672 mg, 16.81 mmol) was suspended in 16 mL of anhydrous THF in a three-neck round bottom flask fitted with an addition funnel and a condenser. Then a solution of **S2** (5.96g, 16.81 mmol) in THF (16 mL) was added drop wise at 0^0C. After the addition, the reaction was heated to reflux for 3 hours and then cooled back to 0^0C.The reaction was diluted with 25 mL of diethyl ether and then the excess $LiAlH_4$ quenched by adding 1 mL of water followed by 1 mL of 15% NaOH (aq). The reaction was the washed with water and the organic layer dried over $MgSO_4$. The solvent was removed in vacuo to afford the product (5.00g, 91%). This was used without further purification. NMR (400 MHz, $CDCl_3$) δ 0.85 (m, 17H), 1.07 - 1.29 (m, 24H), 1.53 (m, 2H), 3.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$: δ 19.93, 19.98, 22.86, 22.96, 25.03, 28.21, 28.30, 28.48, 28.51, 33.37, 33.41, 34.30, 34.35, 34.39, 37.43, 37.45, 37.50, 39.57, 41.35.

2-(2-(3,7-dimethyloctyl)-5,9-dimethyldecyl)isoindoline-1,3-dione (S4). A three-neck round bottom flask fitted with an addition funnel and a condenser was charged with triphenyl phosphine (5.16g, 19.69 mmol), **S3** (6.34g, 19.69 mmol) and phthalimide (4.19g, 19.69 mmol). Then 20 mL of anhydrous ether was added and the reaction cooled to 0 ^{0}C and purged with Ar. Then a solution of DIAD (2.90g, 19.69 mmol) was added and the reaction allowed to warm up to room temperature. After stirred overnight the reaction was filtered and washed with water. The solvent was removed in vacuo and the crude solid purified by column chromatography (1:1 hexanes/ethyl ether) to afford the product (4.76g, 53%). NMR (400 MHz, $CDCl_3$) δ 0.84 (m, 19H), 1.07 - 1.29 (m, 25H), 1.51 (m, 3H), 1.96 (m, 1H), 3.66 (d, J = 4.0 Hz, 2H), 7.69 (d, J = 2.0 Hz, 2H), 7.84 (d, 2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$: δ 19.83, 19.84, 19.90, 19.91, 21.78, 22.80, 22.90, 24.88, 22.90, 24.93, 28.13, 28.83, 28.89, 29.01, 33.20, 33.23, 33.49, 33.51, 33.59, 37.25, 37.28, 37.42, 37.45, 37.52, 39.48, 39.50, 42.52, 123.30, 132.28, 133.98, 168.83.

2-(3,7-dimethyloctyl)-5,9-dimethyldecan-1-amine (S5). A three-neck round bottom flask fitted with an addition funnel and a condenser was charged with **S4** (2.13g, 4.67 mmol) and 10 mL of absolute ethanol. Then a solution of hydrazine hydrate (55%, 821 mg, 14.02 mmol) in 2 mL of ethanol is added and the reaction is heated at reflux for 48 hours. After that time 15 mL of 6M HCl and 5 mL of ethanol was added and the reaction refluxed for another hour. The reaction was filtered, washed with water and then concentrated in vacuo. The crude solid was taken up into 25 mL of NaOH and extracted with ether (2 x 150 mL). The organic layer was dried over $MgSO_4$ and concentrated to afford the product in near quantitative yield (1.50g, 99%). The product can be distilled. NMR (400 MHz, $CDCl_3$) δ 0.86 (m, 18H), 1.06 - 1.28 (m, 25H), 2.51 (m, 2H), 2.56 2m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$: δ 19.95, 19.99, 22.84, 22.93, 25.01, 28.19, 28.86, 29.04, 29.92, 33.36, 33.40, 34.17, 34.20, 34.24, 34.27, 37.44, 37.47, 37.49, 39.56, 41.73, 45.33, 45.50, 45.67.

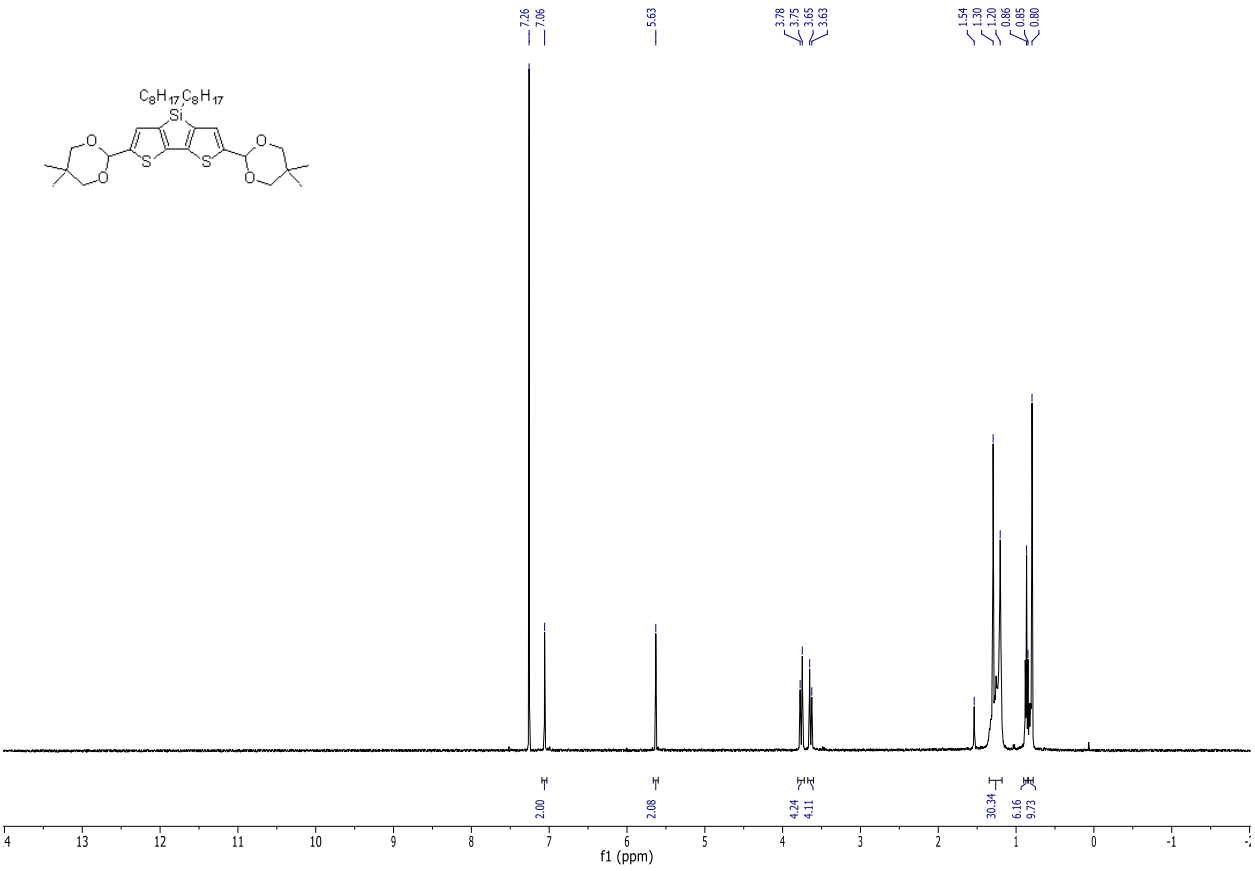


Figure S17: ^{1}H NMR spectra of compound 7

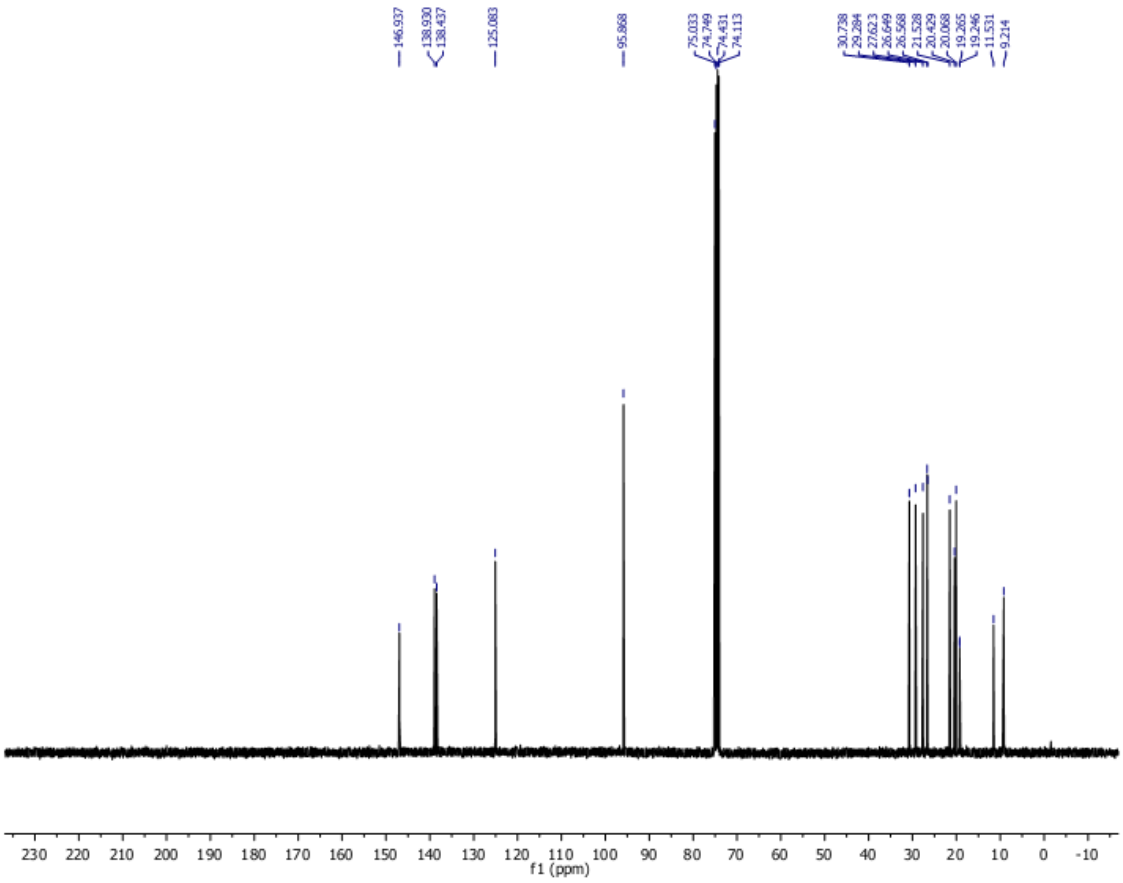


Figure S18: ^{13}C NMR spectra of compound 7

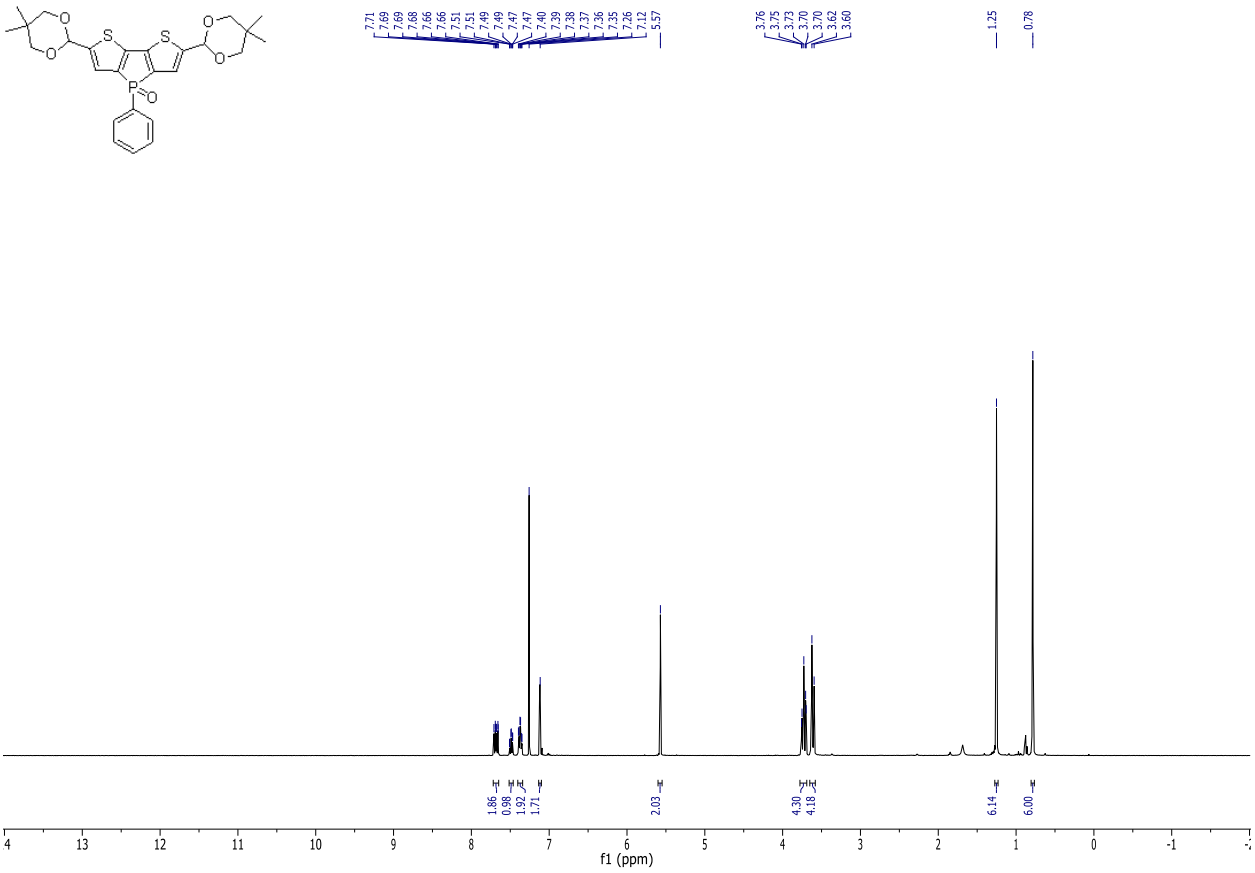


Figure S19: ^{1}H spectra of compound 8

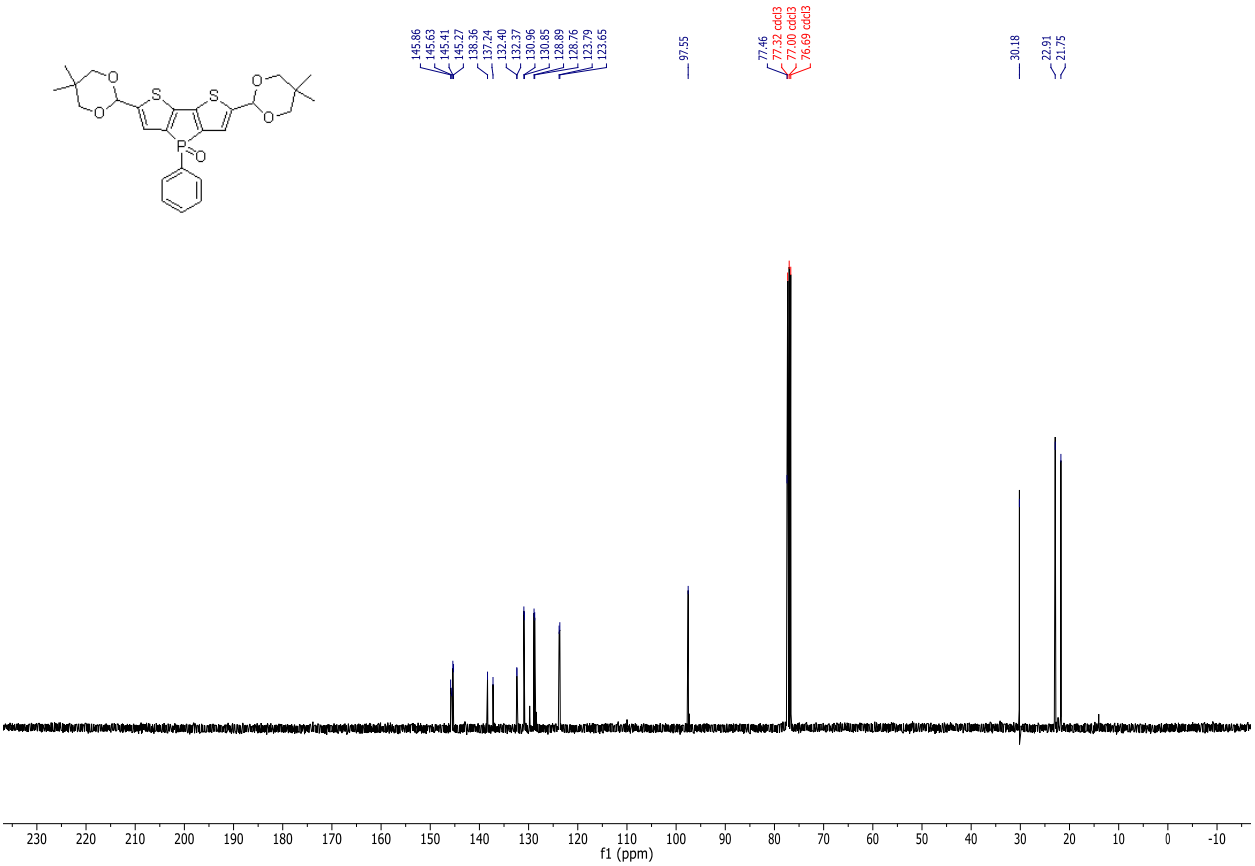


Figure S20: ^{13}C NMR spectra of compound 8

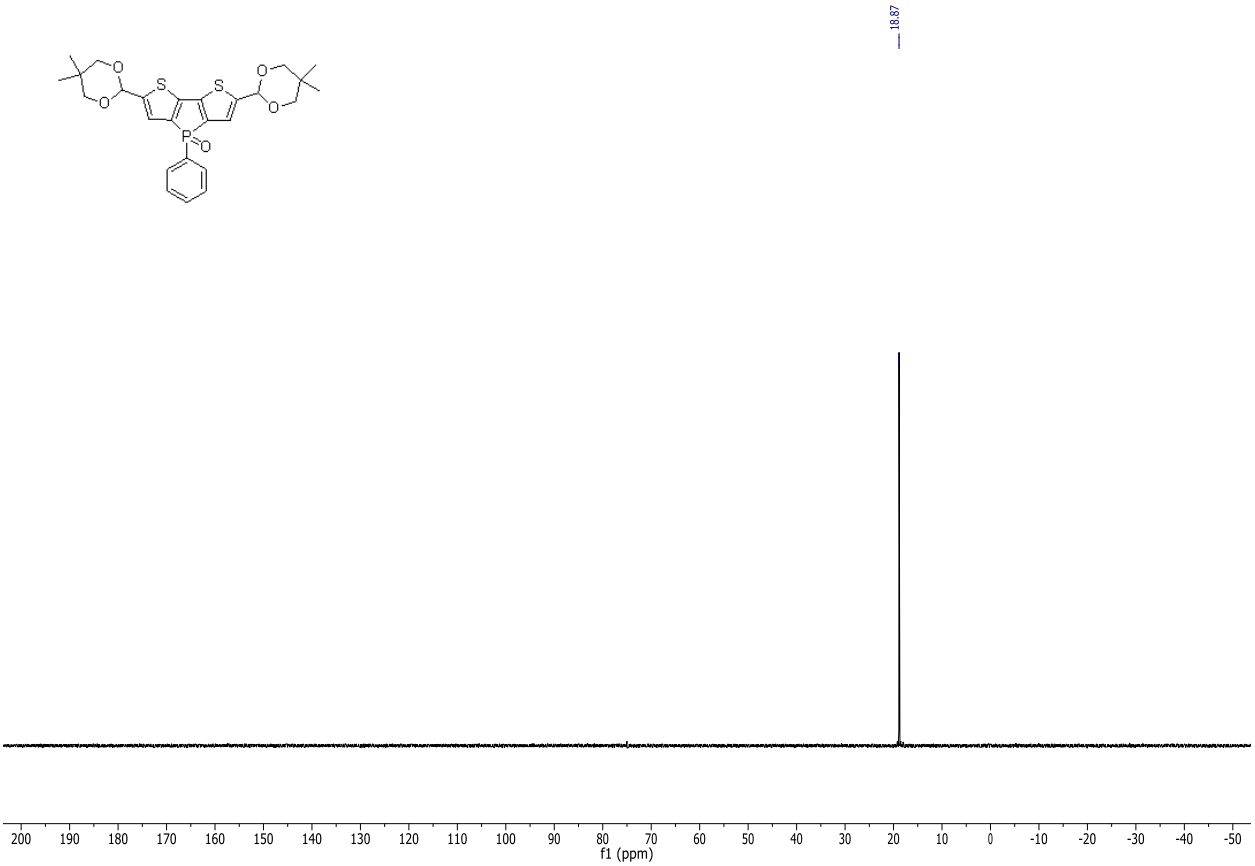


Figure S21: ^{31}P NMR spectra of compound 8

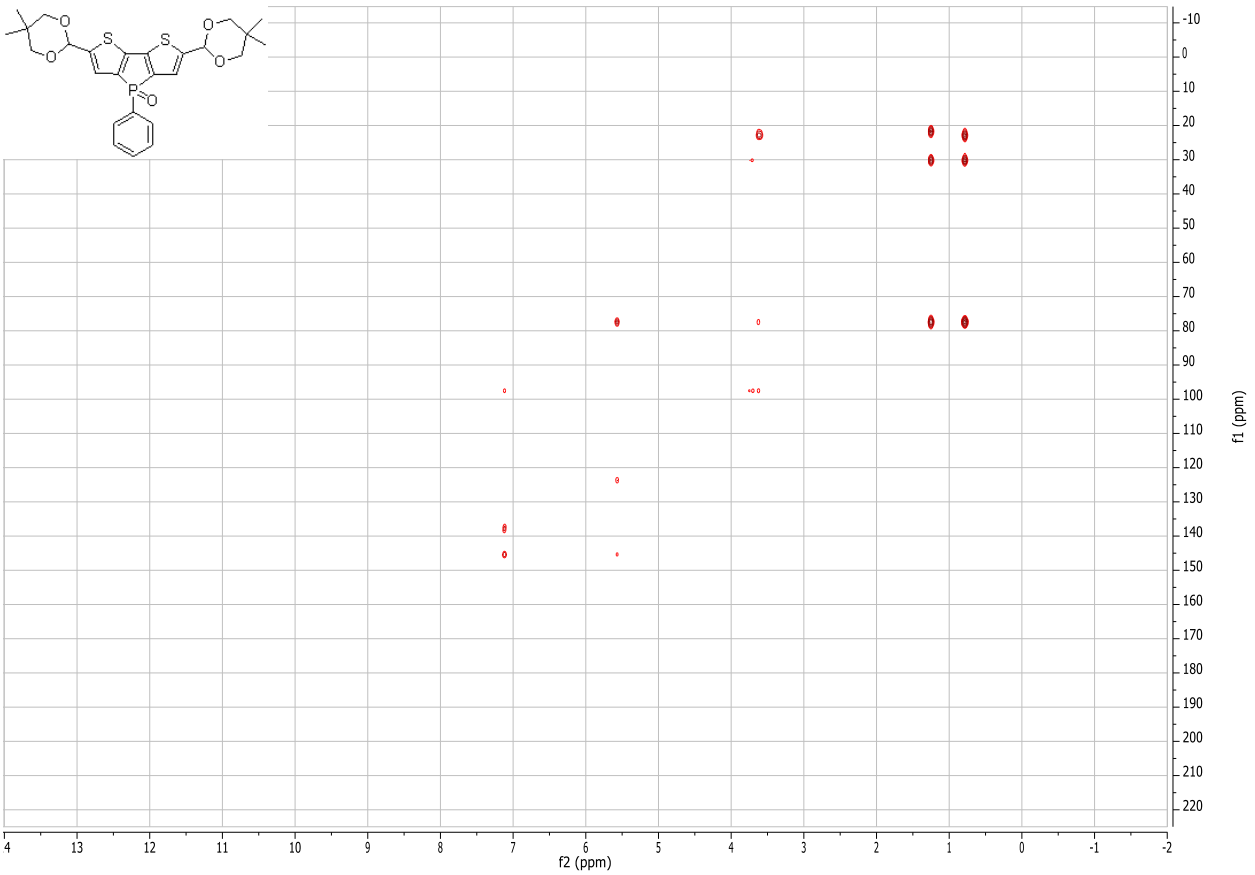


Figure S22: CIGARAD spectra of compound 8

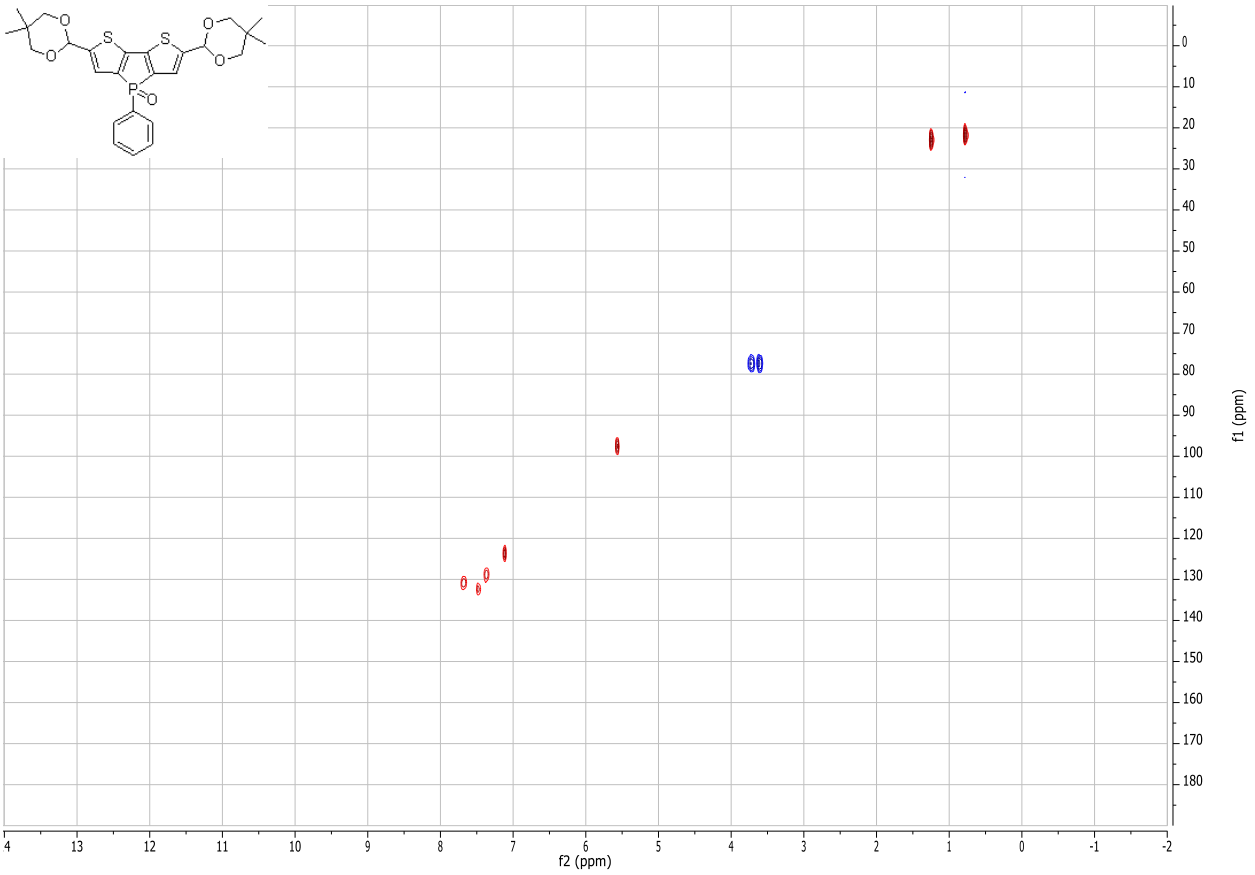


Figure S23: HSQC spectra of compound 8

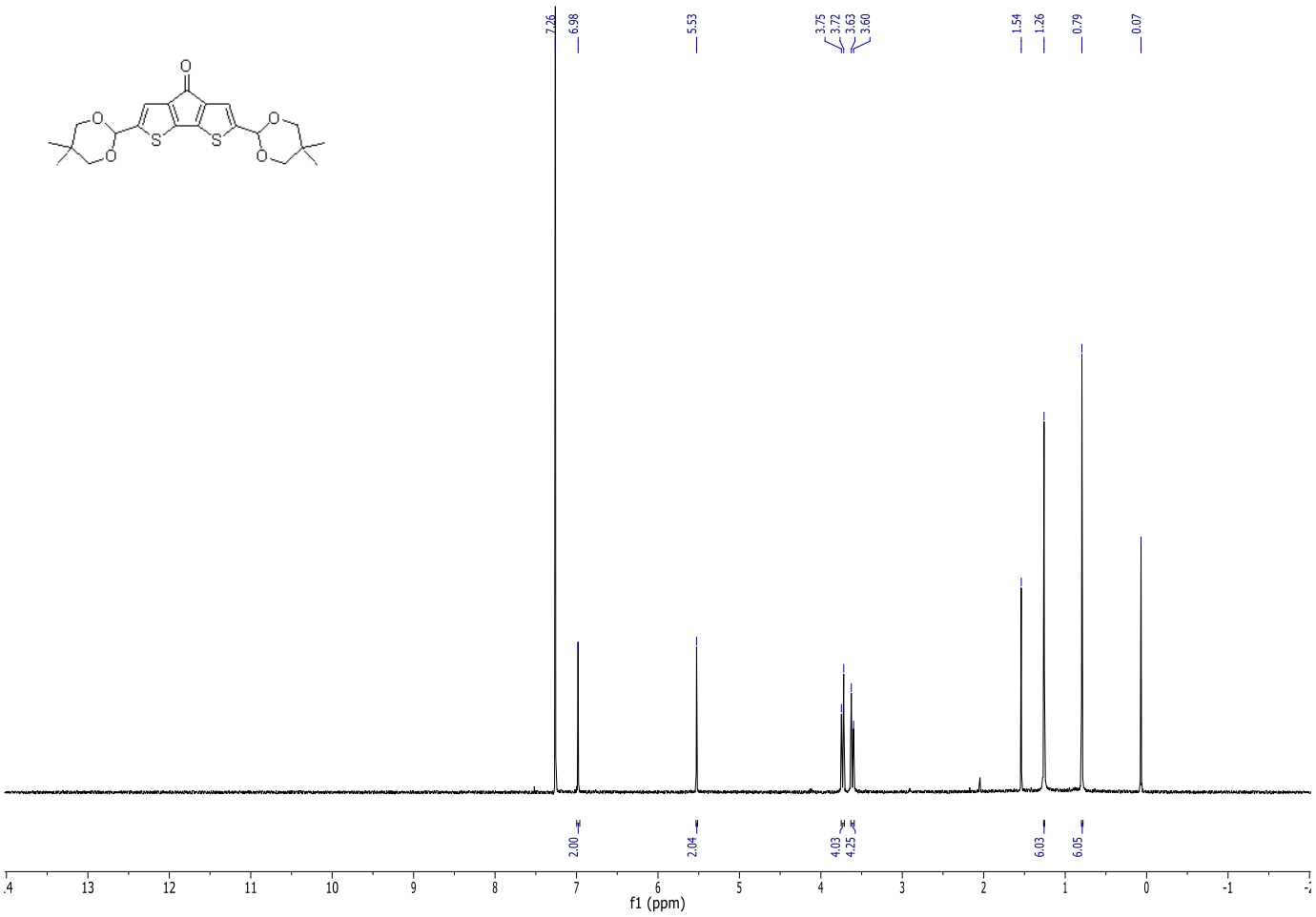


Figure S24: ^{1}H NMR spectra of compound 9

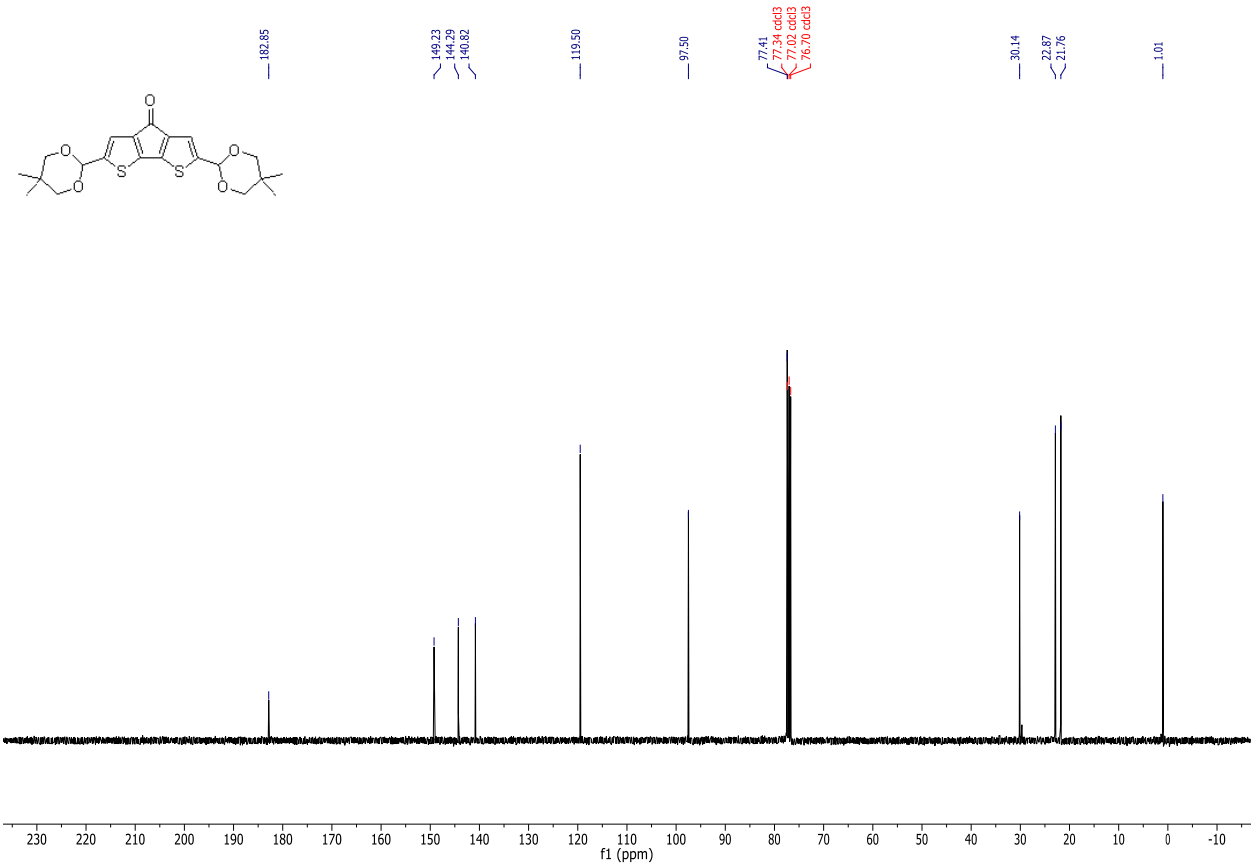


Figure S25: ^{13}C NMR spectra of compound 9

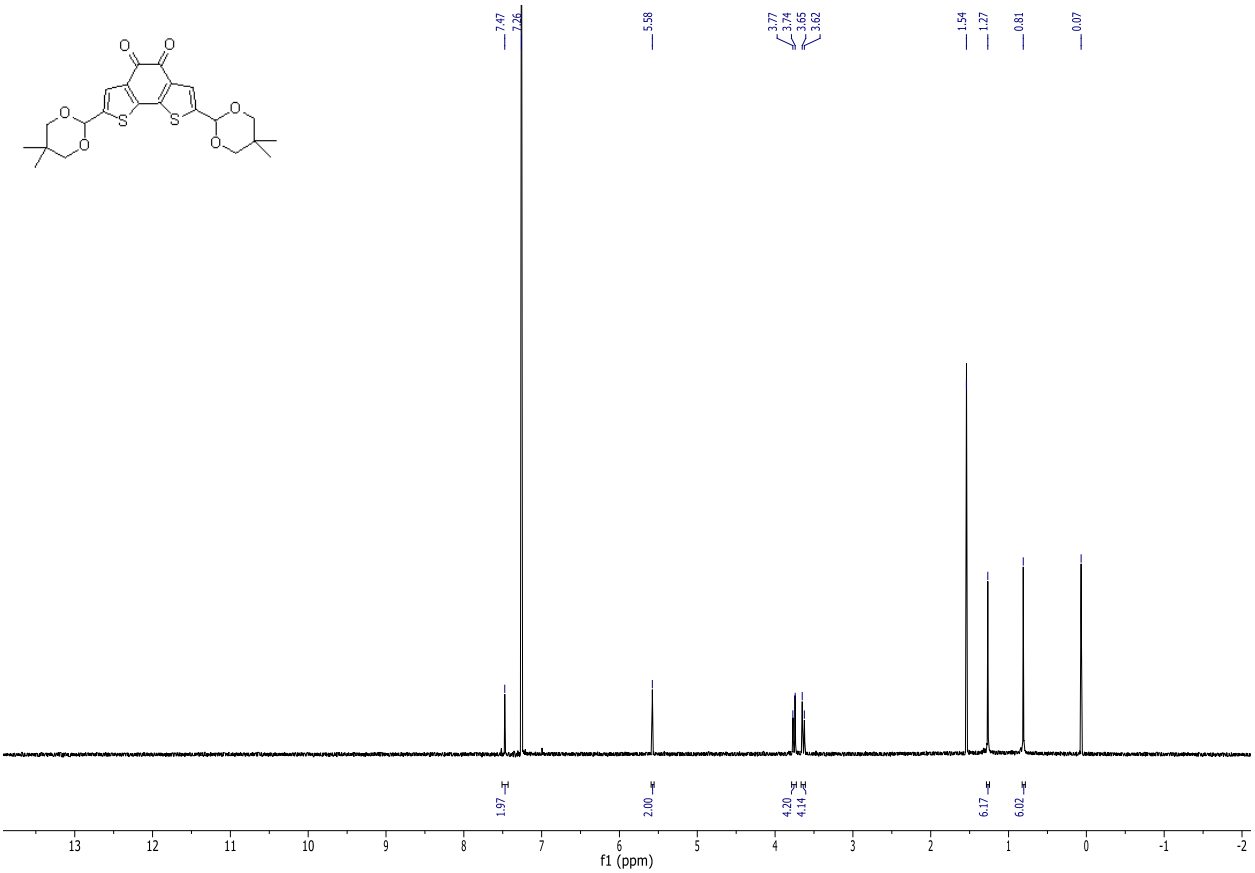


Figure S26: ^{1}H NMR spectra of compound 10

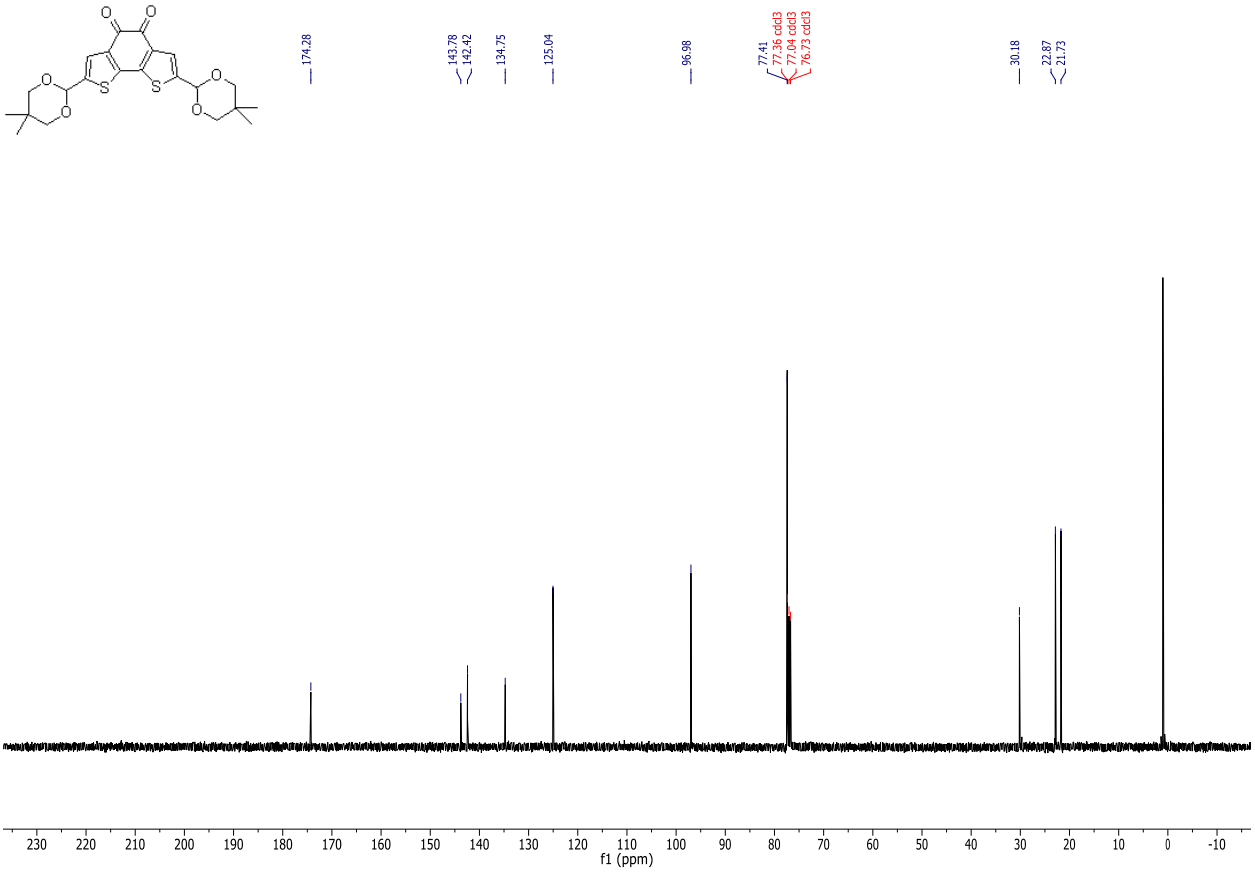


Figure S27: ^{13}C NMR spectra of compound 10

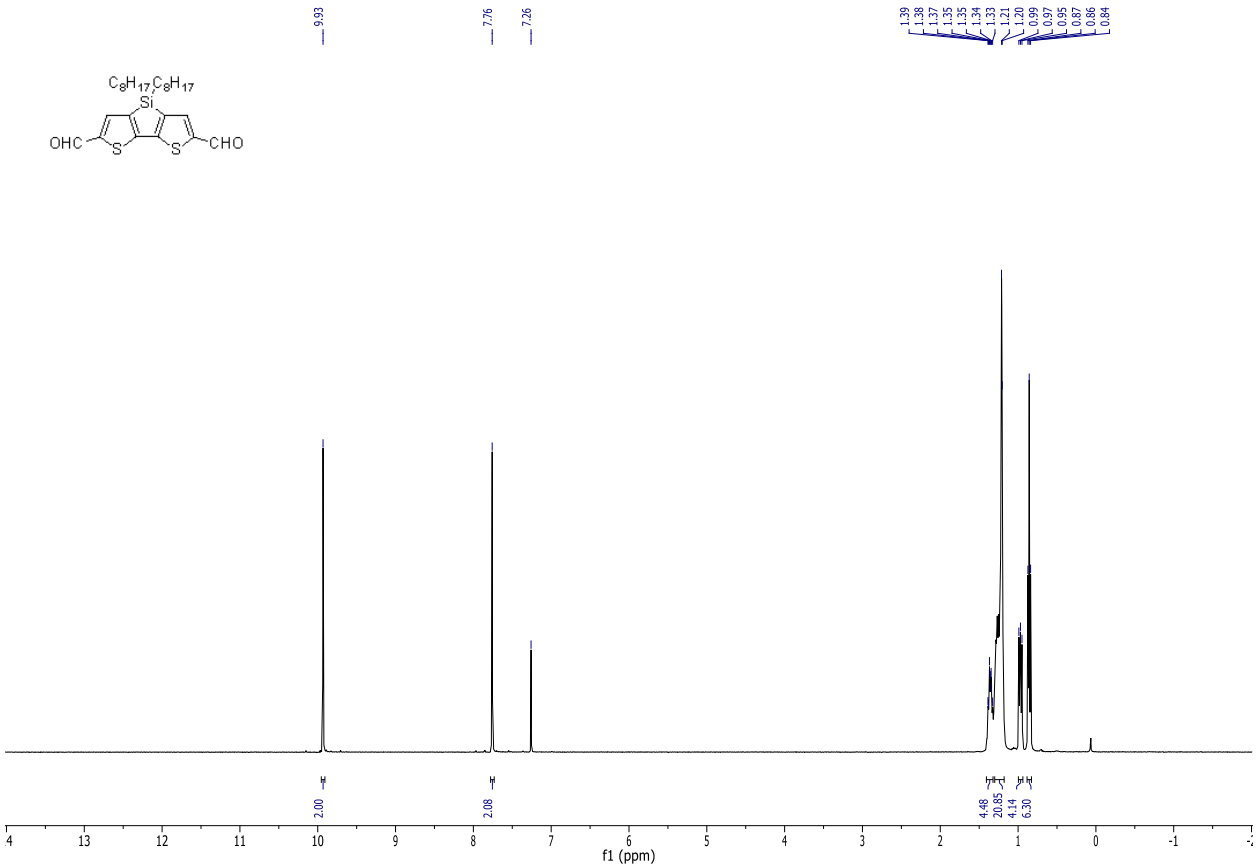


Figure S28: ^{1}H NMR spectra of compound 11

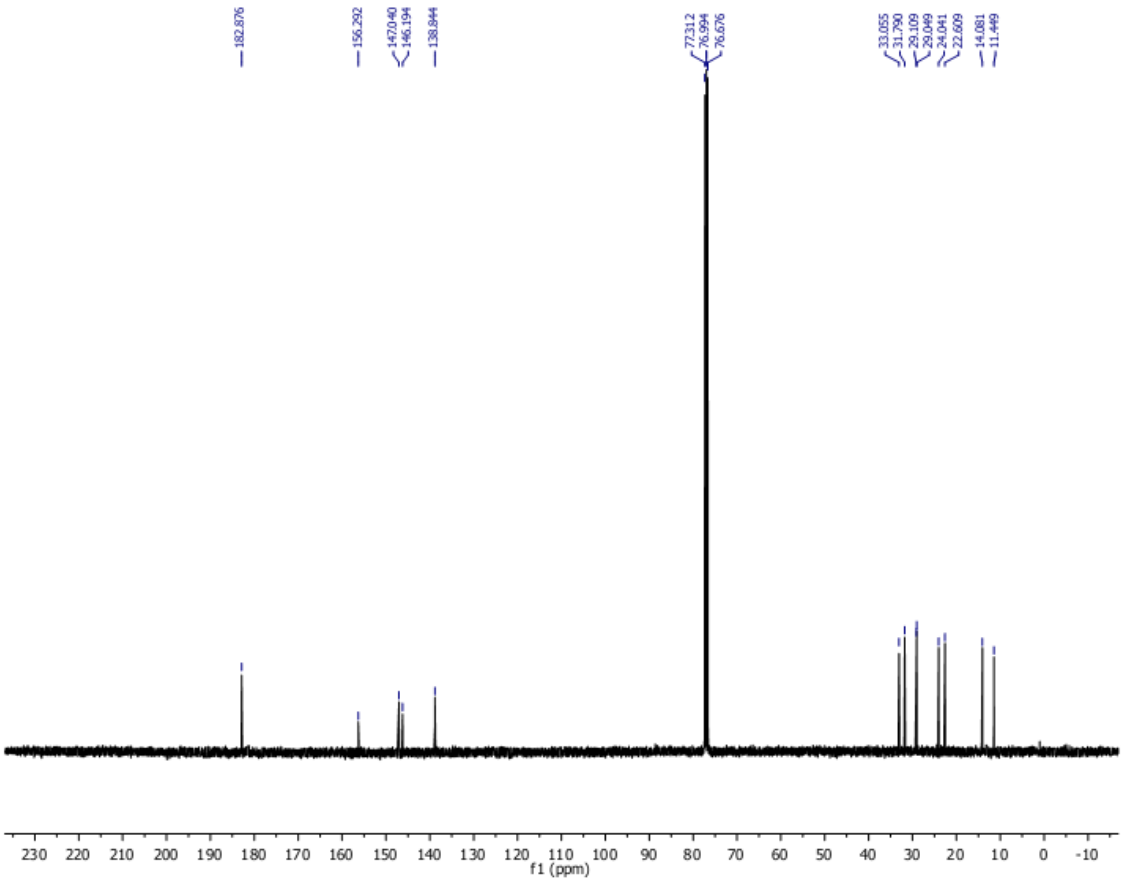


Figure S29: ^{13}C NMR spectra of compound 11

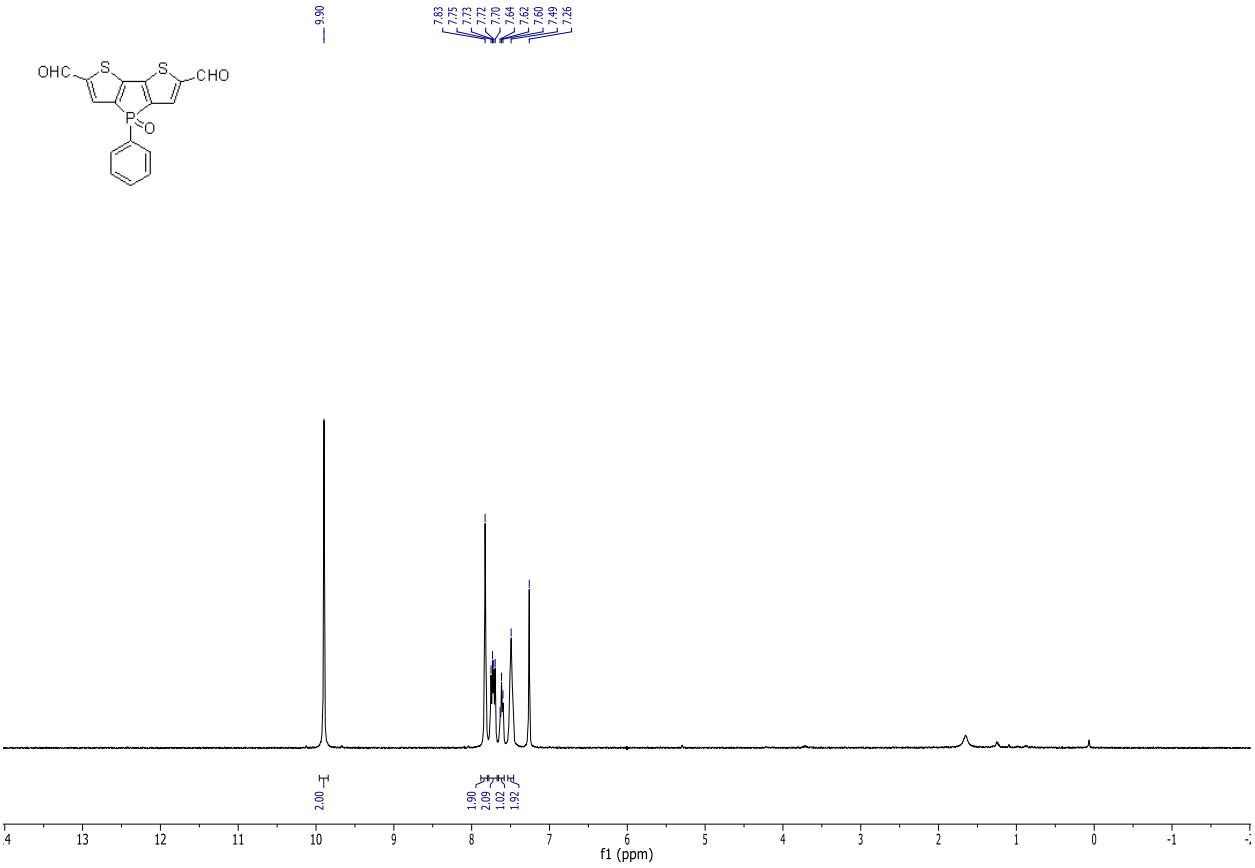


Figure S30: ^{1}H spectra of compound 12

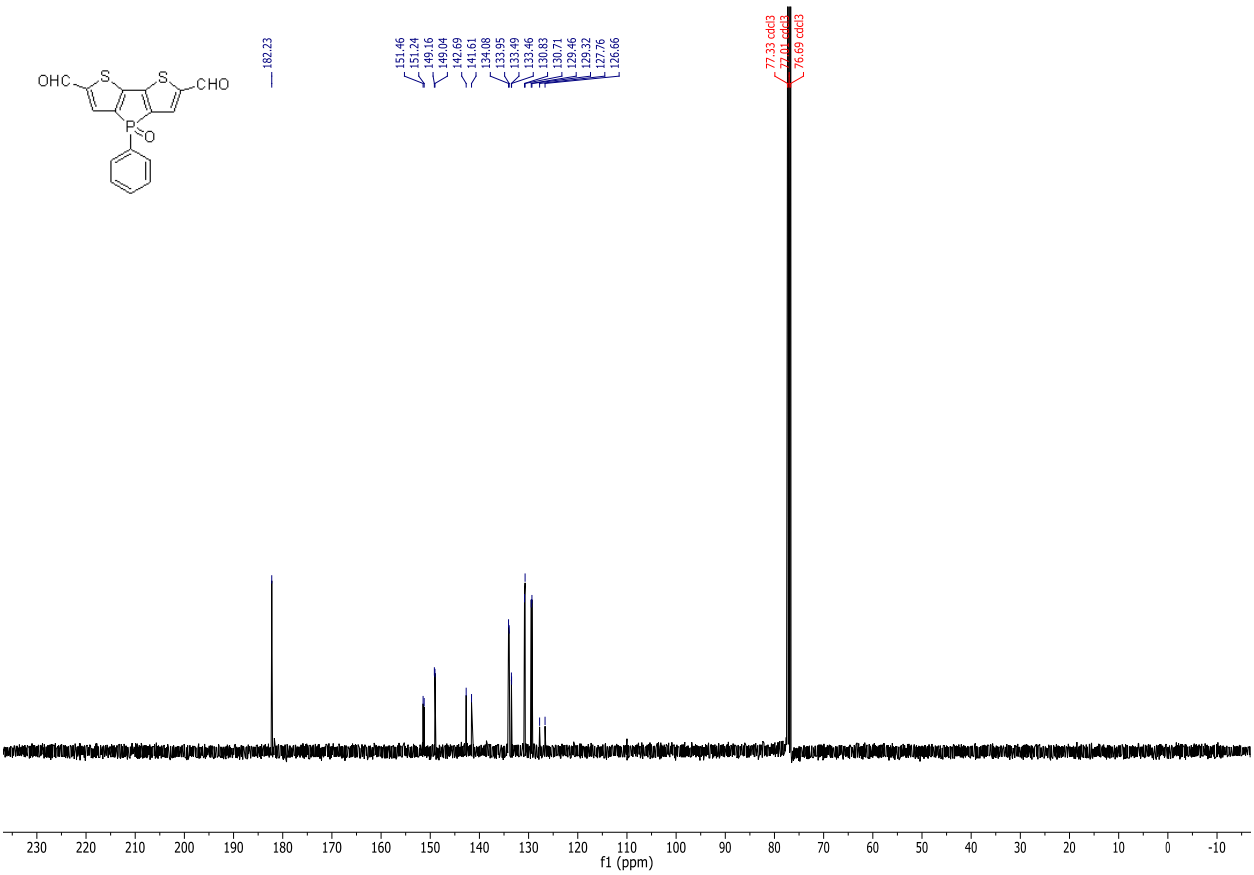


Figure S27: ^{13}C spectra of compound 12

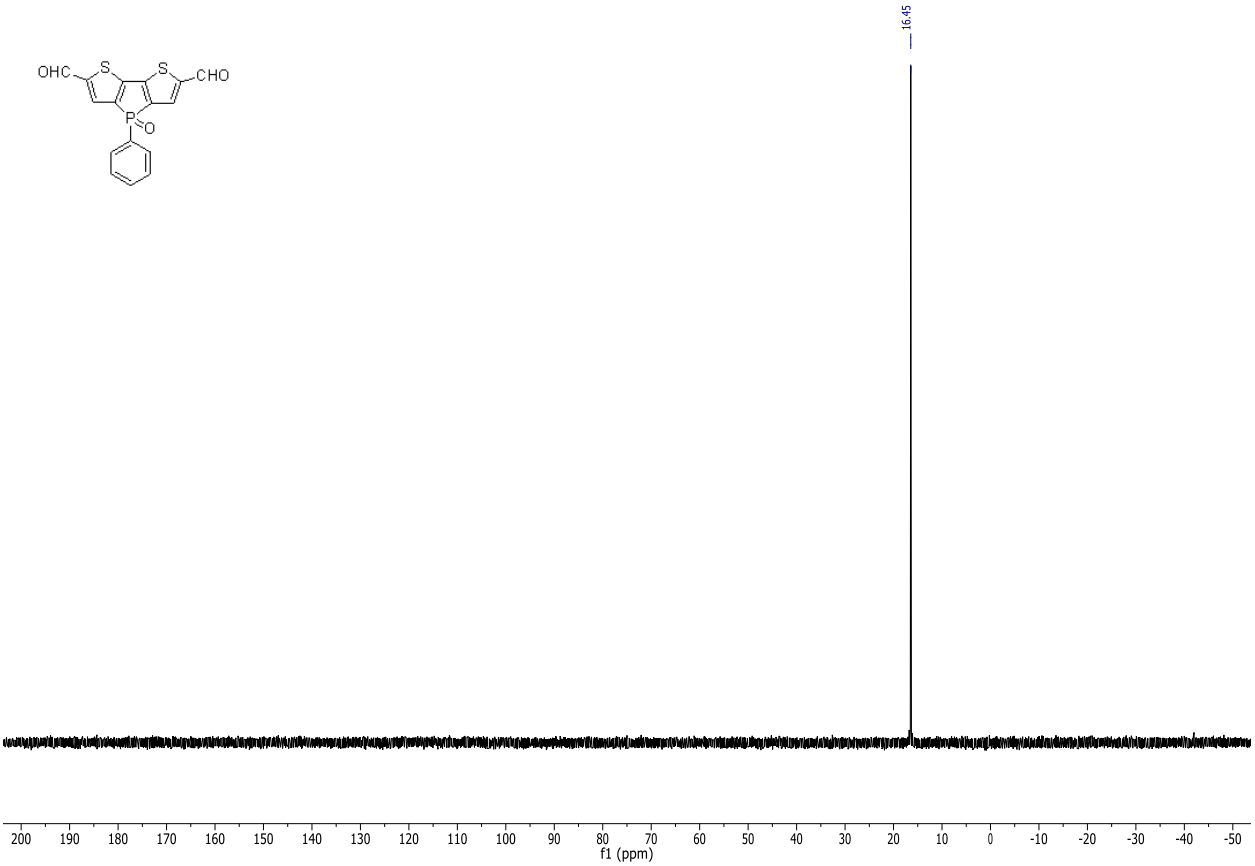


Figure S28: ^{31}P spectra of compound 12

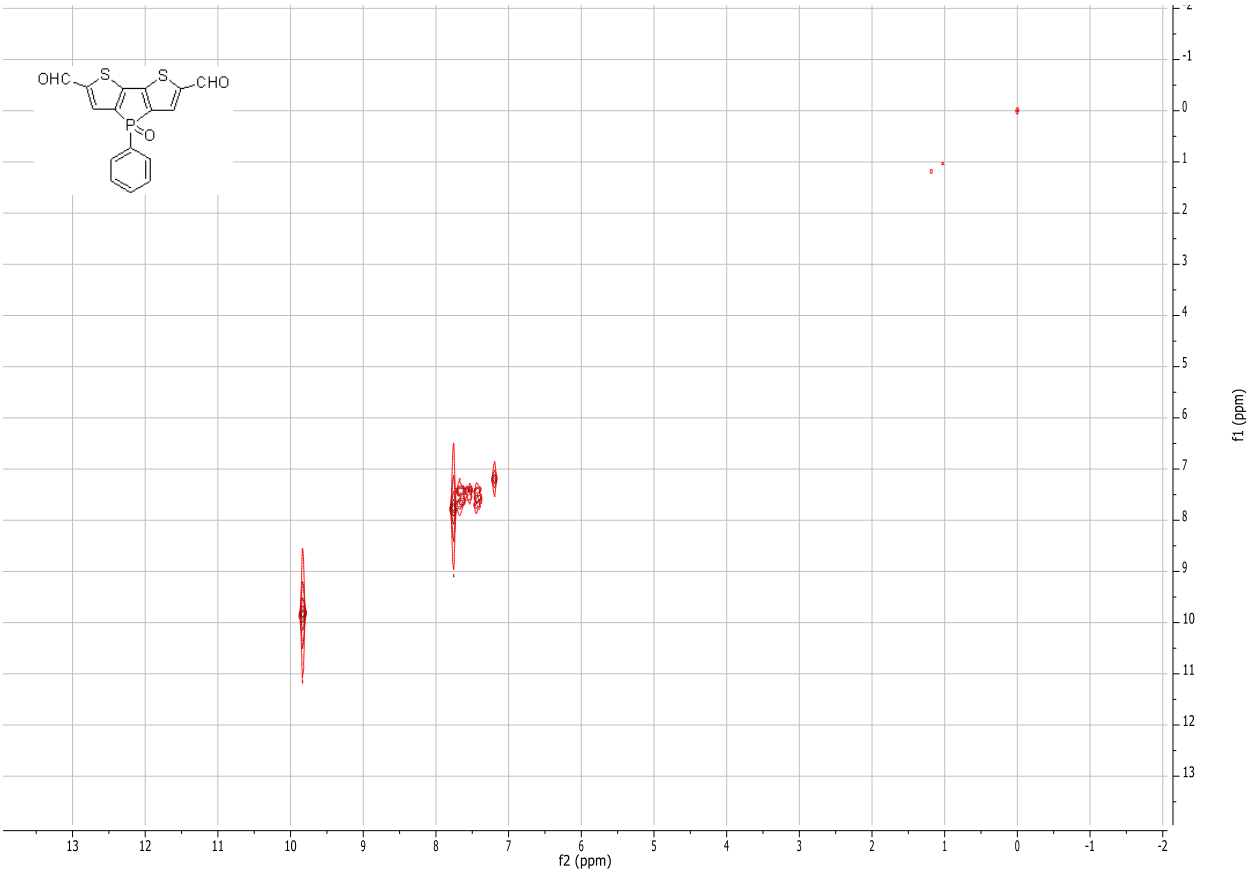


Figure S29: COSY spectra of compound 12

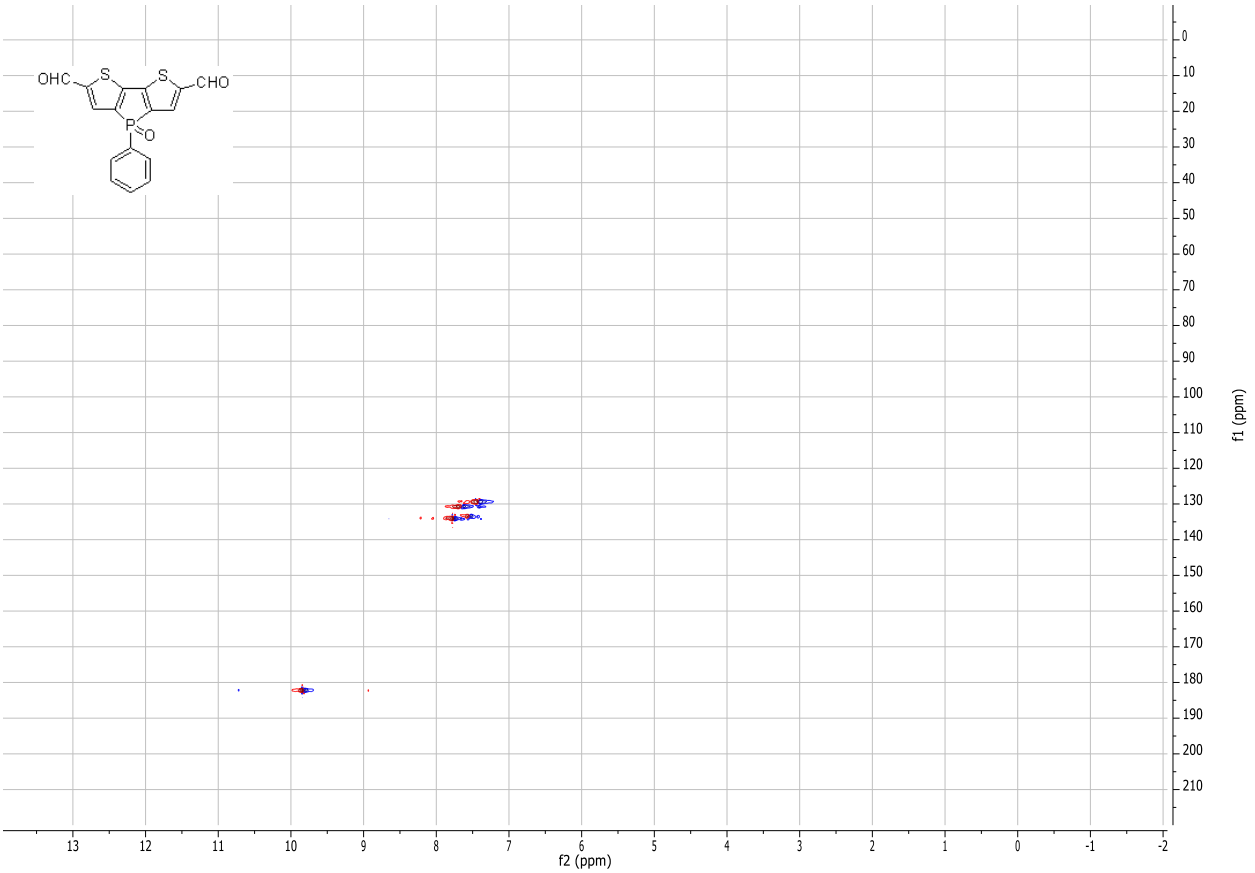


Figure S29: HSQC spectra of compound 11

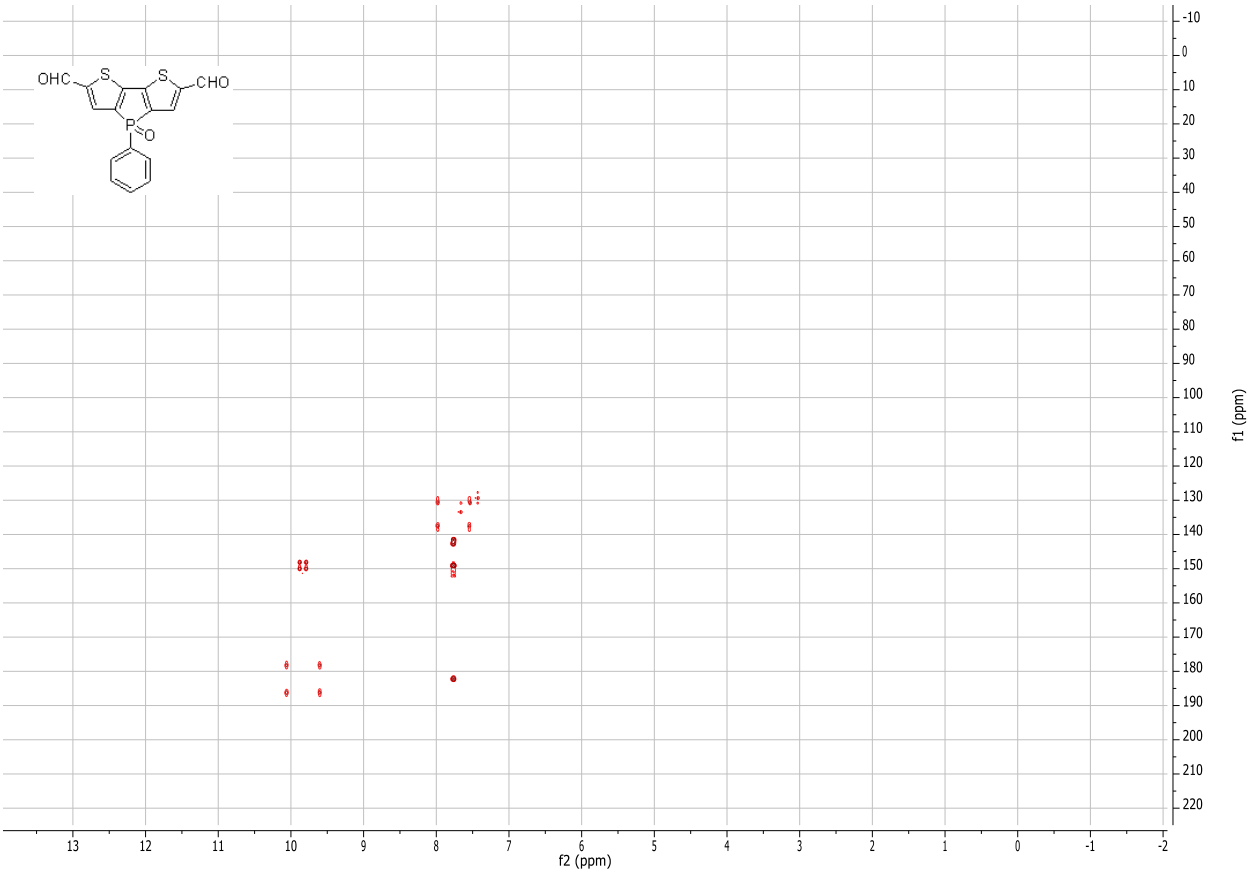


Figure S30: CIGARAD spectra of compound 11

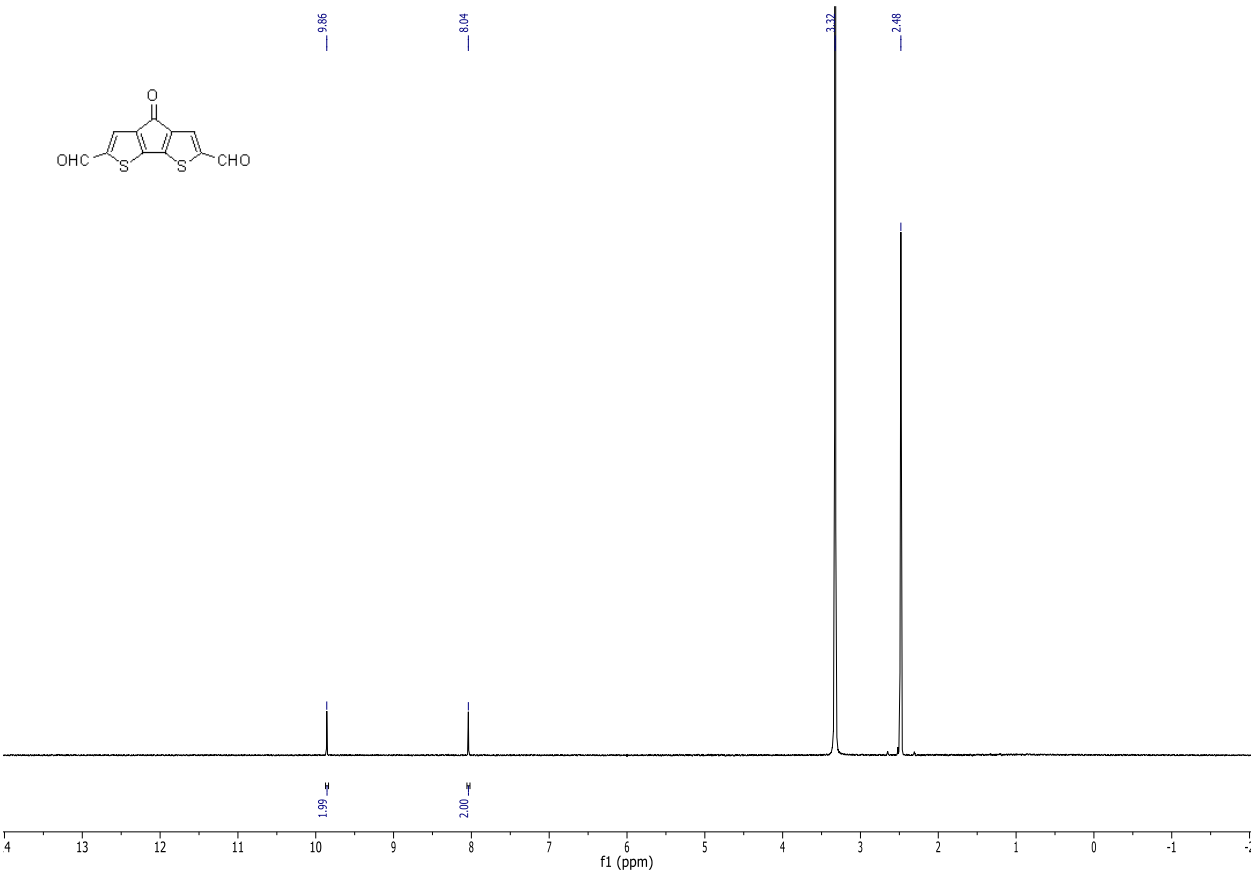


Figure S31: ^{1}H NMR spectra of compound 12

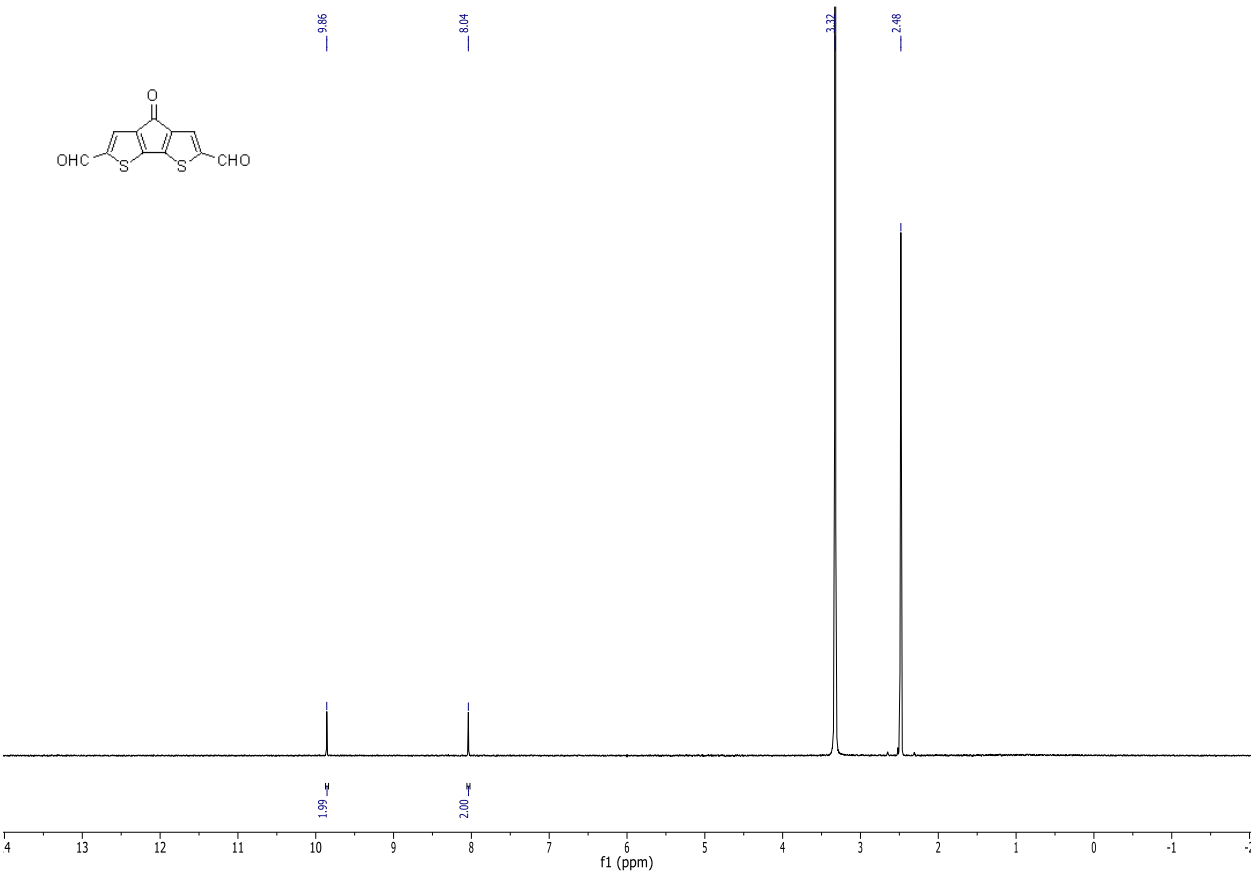


Figure S32: ^{13}C NMR spectra of compound 12

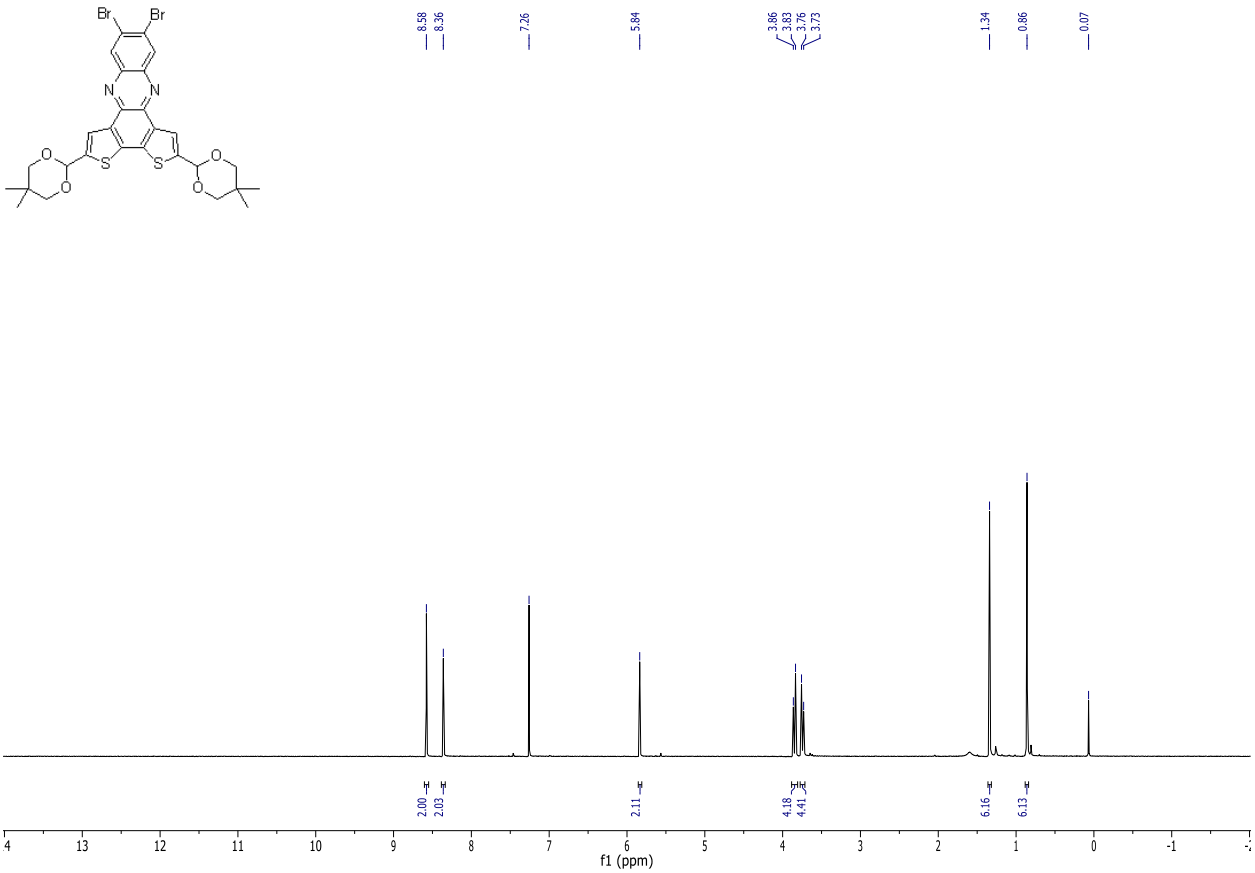


Figure S33: ^{1}H NMR spectra of compound 13

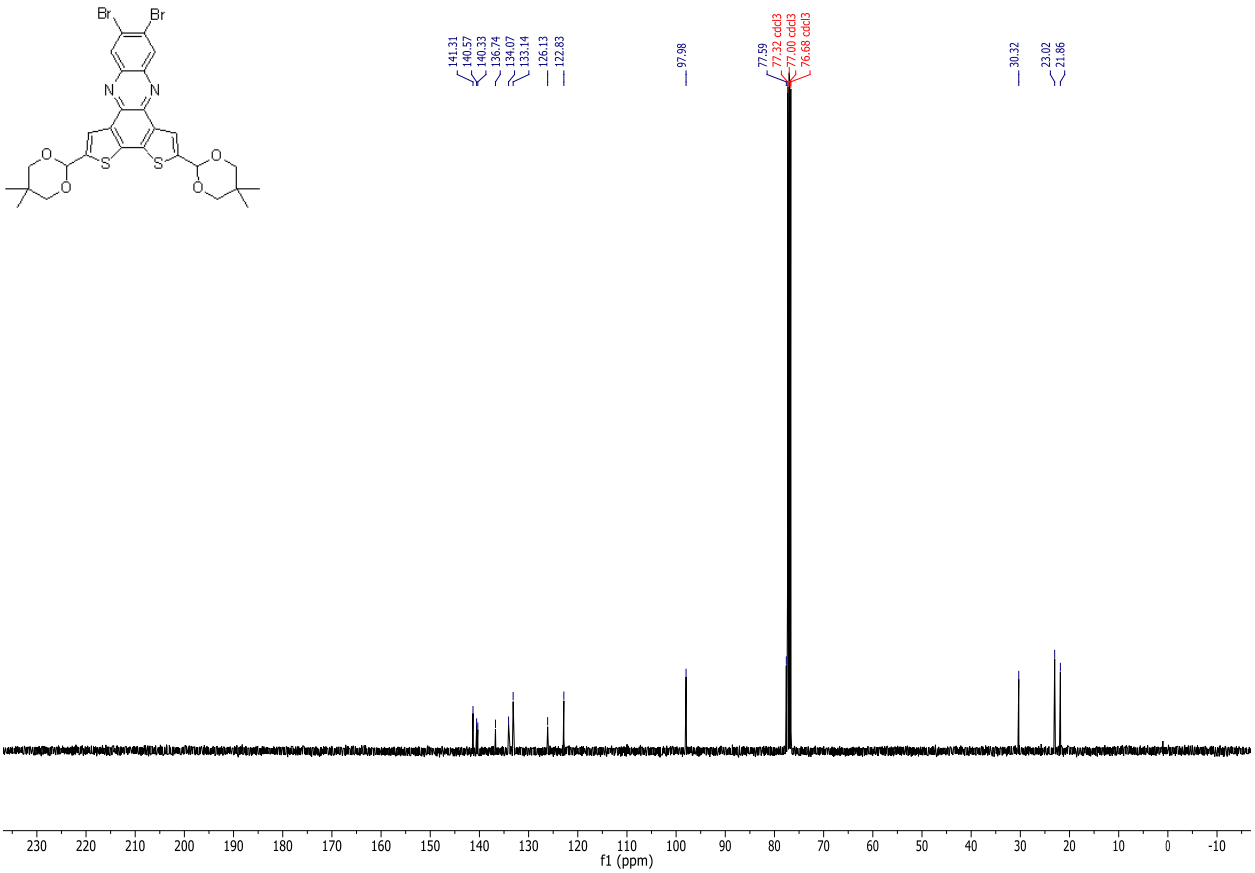


Figure S34: ^{13}C NMR spectra of compound 13

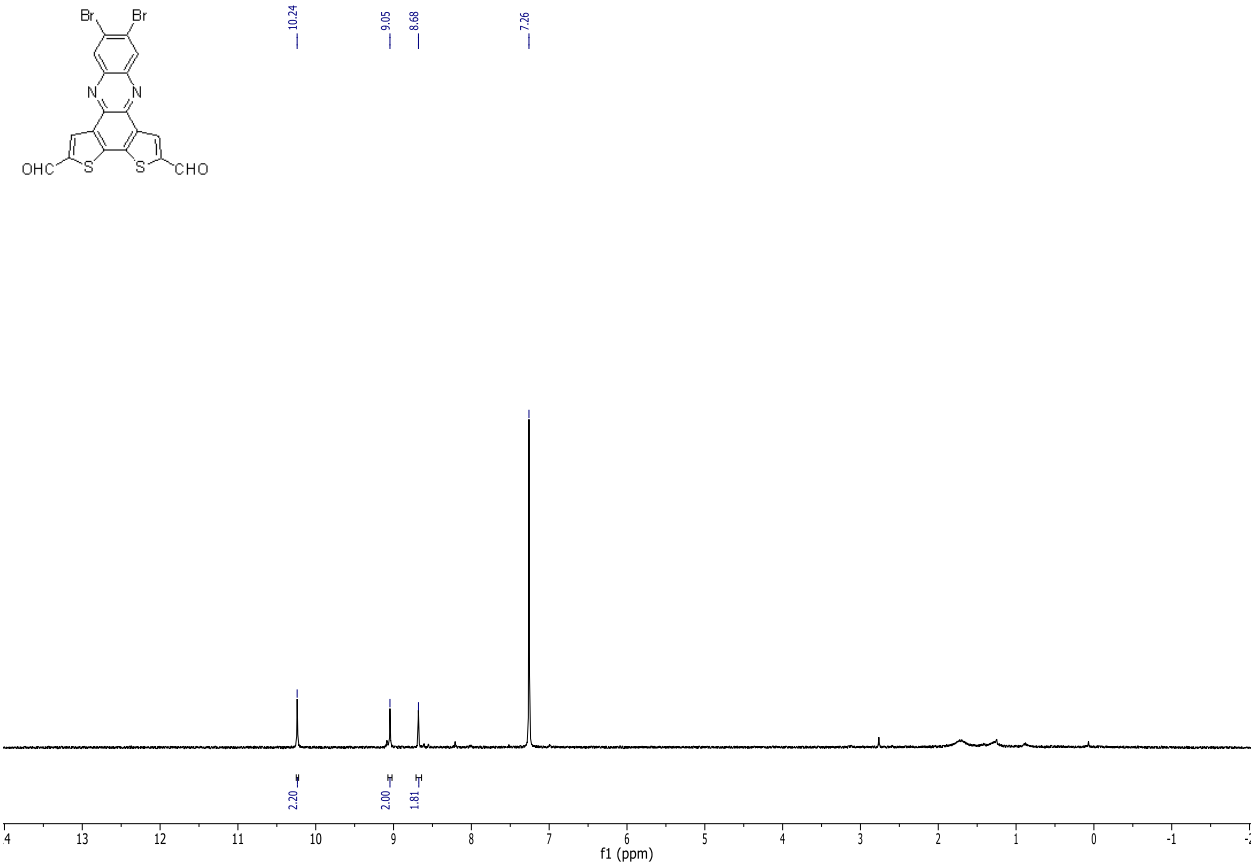


Figure S35: ^{1}H NMR spectra of compound 14