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Facile synthesis of unsymmetrical and π-extended furan-diketopyrrolopyrrole derivatives through C-H direct (hetero)arylation using a heterogeneous catalyst system

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SUPPORTING INFORMATION

General Methods

Preparations were carried out on a bench top or under a nitrogen atmosphere using Schlenk line techniques and/or a glove box unless otherwise stated. Purification by flash column chromatography was performed using a Biotage® Isolera flash system.

Materials: The heterogeneous catalyst SiliaCat® DPP-Pd was provided by SiliCycle. For details on the catalyst system please see: ***RSC Adv.***, 2015, **5**, 26097-26106. The homogeneous catalyst $Pd(OAc)_2$ was purchased from Strem Chemicals Inc. N,N'-dimethylformamide (DMF), 2-cyanofuran and pivalic acid (PivOH) were purchased from TCI America and used without further purification. 2-ethylhexylbromide, 4,4'-dibromobiphenyl, 4-bromotriphenylamine, 9,10-dibromoanthracene and tris(4-bromophenyl)amine were purchased from Sigma-Aldrich and were used without further purification. Anhydrous potassium carbonate (K_2CO_3) was purchased from ACP Chemicals, and after initial usage, was stored in a Gallenkamph Hotbox oven at 100°C. All solvents were purchased from the Dalhousie solvent exchange program and used without further purification, unless otherwise noted.

NMR Characterization: ^{1}H NMR spectroscopy was used to evaluate conversion to product. ^{1}H NMR spectra were recorded on Bruker Avance 300 MHz or 500 MHz spectrometer at 300 K. Chemical shifts are referenced to tetramethylsilane, and all experiments performed in $CDCl_3$. Starting materials **1a**, **1b**, and 5-bromo-N-(2-ethylpropyl)-phthalimide were synthesized according to their respective literature procedures.[1,2,3]

UV-Visible Spectroscopy (UV-vis): UV-vis spectra were recorded using an Agilent Cary 60 spectrophotometer at room temperature. All solution UV-vis experiments were run in $CHCl_3$ in Teflon® capped 10 mm quartz cuvettes under. Films were prepared by spin-coating solutions from $CHCl_3$ onto glass substrates cut from corning micro slides at 1000 rpm for 30 seconds. The thin films on glass were annealed at 100 °C for 5 min by direct mounting on a hotplate.

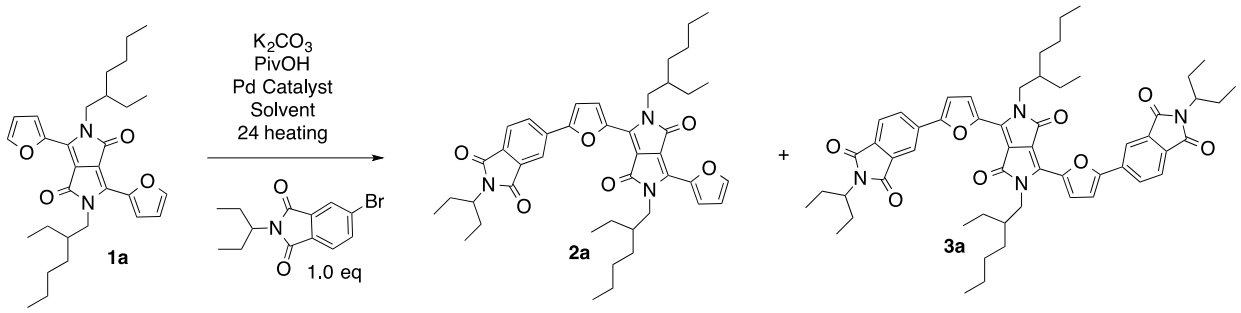
Fluorescence Spectroscopy: The emission profiles were recorded on a Cary Eclipse spectrophotometer. Solution spectra were recorded in $CHCl_3$.

Cyclic Voltammetry (CV): All experiments were carried out using a BASi cell stand instrument and BASi Epsilon EC software. Measurements were performed in a three-electrode, one compartment configuration equipped with Ag/AgCl electrode, Pt wire and glassy carbon electrode (dia. 3 mm), as the pseudo reference, counter electrode and working electrode respectively, as well as a nitrogen bubbler. Glassy carbon electrodes were polished with alumina. The CV experiments were performed in anhydrous dichloromethane solution with ~0.1 M tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. All solutions were scanned at 100 mV/s, both with and without a ferrocence standard. Solutions were purged with nitrogen for several minutes to agitate the solution and remove oxygen prior to running the voltage scan. Under these conditions, the ferrocence standard was calibrated to be ~0.48 V. Solution CV measurements were carried out with a small molecule concentration of ~1mg/mL in dichloromethane. The ionization energy (IE) and electron affinity (EA) values were obtained by correlating the onsets of oxidation and reduction (Eox, Erd) to the normal hydrogen electrode (NHE), assuming ionization energy (IE) of Fc/Fc^+ to be 4.8 eV.

Mass Spectrometry: Mass spectrometry measurements were performed courtesy of Xiao Feng in the Dalhousie University Analytical Laboratory. A Bruker-Daltronics Micro TOF Mass Spectrometer was used and run in APCI mode.

Synthetic methods

Direct Arylation reaction (DHA) reaction with furan-DPP (1a)



On the bench top, 3,6-(bis-furan-2-yl)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dione (**1a**, 500 mg, 1.02 mmol), 5-bromo-N-(2-ethylpropyl)-phthalimide (301 mg, 1.02 mmol), potassium carbonate, (K_2CO_3, 352 mg, 2.55 mmol), SiliaCat® DPP-Pd (204 mg, 0.051 mmol Pd) and pivalic acid (PivOH, 21 mg, 0.204 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. N,N'- dimethylformamide (DMF, ~10 mL) was then added as the solvent. The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2, and heated in an oil bath at the appropriate temperature (55 ˚C, optimized temperature) for 24 hours. Analogous reactions carried out in air (i.e. without the N_2 purge) gave similar results. The reaction vial was cooled to room temperature and the vial contents were diluted with dichloromethane (CH_2Cl_2, ~200 mL) and passed through a short SiO_2 plug to remove catalyst and inorganic reagents/by-products. The solvent was removed using a rotary evaporator and the product was loaded on SiO_2 for purification using column chromatography. A pentane to CH_2Cl_2 solvent gradient was used to purify the reaction mixture and 3 fractions were obtained: ***1st fraction***, orange, ~40 % CH_2Cl_2, ~60 % Pentane (unsubstituted DPP starting material **1a**); ***2nd fraction***, ~95 % CH_2Cl_2, ~5 % pentane (mono-arylated DPP **2a**); ***3rd fraction***, ~95 % CH_2Cl_2, ~5 % ethyl acetate. (bis-arylated DPP **3a**). The solvent was removed from each fraction using a rotary evaporator and the products were slurried in water:methanol (9:1) and filtered using a Buchner funnel to isolate the products **2a** and **3a**.

Changes to Reaction Conditions:

70 °C reaction:

The reported reaction was repeated using the same reaction conditions described above except the temperature was changed to 70 °C.

Yield 1st fraction: 114 mg **23** % (unsubstituted **1a** stating material).
Yield 2nd fraction: 297 mg **41** % (mono-arylated **2a**).
Yield 3rd fraction: 210 mg **21** % (bis-arylated **3a**).

85 °C reaction:

The reported reaction was repeated using the same reaction conditions described above except the temperature was changed to 85 °C.

Yield 1st fraction: 106 mg **21** % (unsubstituted **1a** stating material).
Yield 2nd fraction: 273 mg **38** % (mono-arylated **2a**).
Yield 3rd fraction: 258 mg **26** % (bis-arylated **3a**).

Toluene, 85 °C reaction:

The reported reaction was repeated using the same reaction conditions described above except the solvent was changed to toluene and the reaction temperature was changed to 85 °C.

Yield 1st fraction: 323 mg **64** % (unsubstituted **1a** stating material).
Yield 2nd fraction: 131 mg **18** % (mono-arylated **2a**).
Yield 3rd fraction: 21 mg **2** % (bis-arylated **3a**).

$Pd(OAc)_2$ reaction:

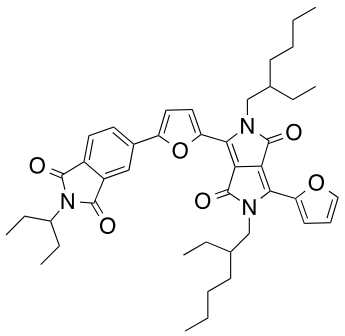
The reported reaction was repeated using the same reaction conditions described above except the catalyst was changed to $Pd(OAc)_2$.

Yield **1**st fraction: 46 mg **9** % (unsubstituted **1a** stating material).
Yield **2**nd fraction: 181 mg **25** % (mono-arylated **2a**).
Yield **3**rd fraction: 320 mg **34** % (bis-arylated **3a**).

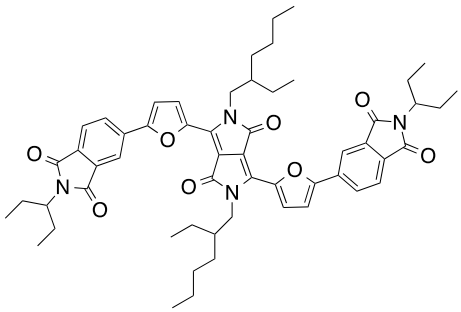
55 °C Scaled Up Reaction in Air

The reported reaction was repeated using 1.0g of **1a**. A 50 mL round-bottom flask fitted with a reflux condenser was used instead of a sealed Teflon® container. The reaction was heated at 55 °C in an oil bath for 24 hours with the reaction vessel open to the atmosphere to demonstrate the insensitive nature of the heterogeneous catalyst towards atmospheric oxygen and water.

Yield **1**st fraction: 480 mg **48** % (unsubstituted **1a** stating material).
Yield **2**nd fraction: 472 mg **33** % (mono-arylated **2a**).
Yield **3**rd fraction: 144 mg **8** % (bis-Arylated **3a**).

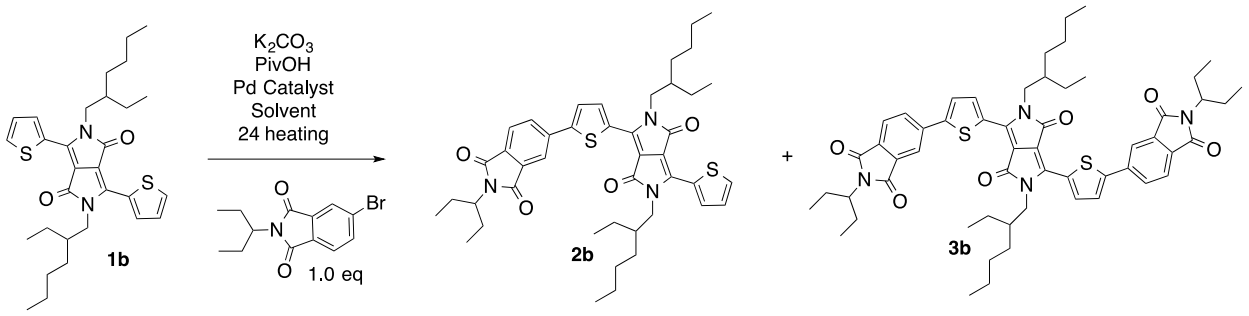


2a: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.42, (dd, J= 6.0, 3.8 Hz, 2H), 8.16 (s, 1H), 8.09 (d, J= 9.0 Hz, 1H), 7.91 (d, J= 7.8 Hz, 1H), 7.66 (s, 1H), 7.17 (d, J= 3.8 Hz, 1H), 6.74 (dd, J= 3.5, 1.3 Hz, 1H), 4.21 (d, J= 7.8 Hz, 2H), 4.10-4.05 (m, 3H), 2.18-2.13 (m, 2H), 1.92-1.79 (m, 4H), 1.42-1.24 (m, 16H), 0.95-0.81 (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 168.45, 168.29, 161.20, 154.55, 145.68, 145.46, 144.77, 134.89, 134.73, 133.25, 132.77, 130.93, 129.12, 124.06, 122.14, 121.11, 118.92, 113.85, 112.06, 108.26, 106.87, 56.09, 46.85, 46.48, 40.15, 39.75, 30.78, 30.58, 28.88, 28.78, 25.49, 24.11, 23.82, 23.31, 23.24, 14.25, 14.17, 11.36, 10.95, 10.79; MS *m/z*, calcd for $C_{43}H_{53}N_3O_6$ $(M+H)^+$: 708.4; found: 708.4; Melting point 146-148 ˚C

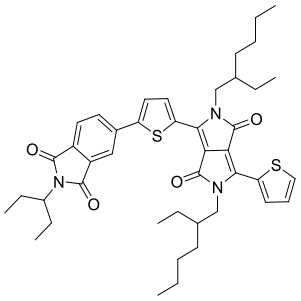


3a: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.50 (d, J= 3.8 Hz, 2H), 8.17 (s, 2H), 8.10 (d, J= 7.8 Hz, 2H), 7.91 (d, J= 7.8 Hz, 2H), 7.19 (d, J= 3.8 Hz, 2H), 4.21 (d, J= 7.7 Hz, 4H), 4.11-4.01 (m, 2H), 2.18-2.02 (m, 4H), 1.95-1.83 (m, 6H), 1.46-1.25 (m, 16H), 0.95-0.84 (m, 24H); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 168.38, 168.23, 161.19, 154.94, 145.54, 134.75, 133.30, 133.27, 131.08, 129.20, 124.08, 122.79, 118.97, 112.17, 108.39, 50.10, 46.94, 39.75, 30.57, 28.76, 25.48, 23.83, 23.30, 14.16, 11.35, 10.77; MS *m/z*, calcd for $C_{56}H_{66}N_4O_8$ $(M+H)^+$: 923.5; found: 923.5; Elemental analysis: Calcd. C 72.82, H 7.21, N 6.07, Found C 72.46, H 6.93, N 6.02; Melting point 265-266 ˚C

DHA reaction with thiophene-DPP (1b)

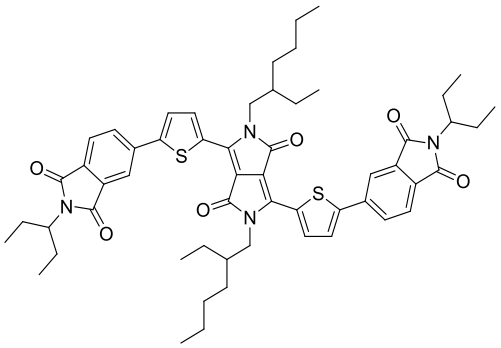


On the bench top, 3,6-(bis-furan-2-yl)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dione (**1b**, 100 mg, 0.191 mmol), 5-bromo-N-(2-ethylpropyl)-phthalimide (56.4 mg, 0.191 mmol), potassium carbonate, (K_2CO_3 66 mg, 0.48 mmol), SiliaCat® DPP-Pd (38 mg, 0.0096 mmol Pd) and pivalic acid (PivOH, 4 mg, 0.038 mmol) were added to a 2-5 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~4 mL) was then added as a solvent. The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2 and heated in an oil bath at 55 °C for 24 hours. The reaction vial was cooled to room temperature and the vial contents were diluted with dichloromethane (CH_2Cl_2, ~200 mL) and passed through a short SiO_2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The solvent was removed using a rotary evaporator and the product was loaded on SiO_2 for purification using column chromatography. A pentane to CH_2Cl_2 solvent gradient was used to purify the reaction mixture and 3 fractions were obtained: ***1st fraction***, orange, ~40 % CH_2Cl_2, ~60 % Pentane (unsubstituted DPP stating material **1b**); ***2nd fraction***, ~95 % CH_2Cl_2, 5 % Pentane (mono-arylated DPP **2b**); ***3rd fraction***, ~95 % CH_2Cl_2, ~5 % ethyl acetate. (bis-Arylated DPP **3b**). The solvent was removed from each fraction using a rotary evaporator and the products were slurried in water:methanol (9:1) and filtered using a Buchner funnel to isolate the product mono-adduct (**2b**) in 42% yield and bis-adduct (**3b**) in 22% yield.



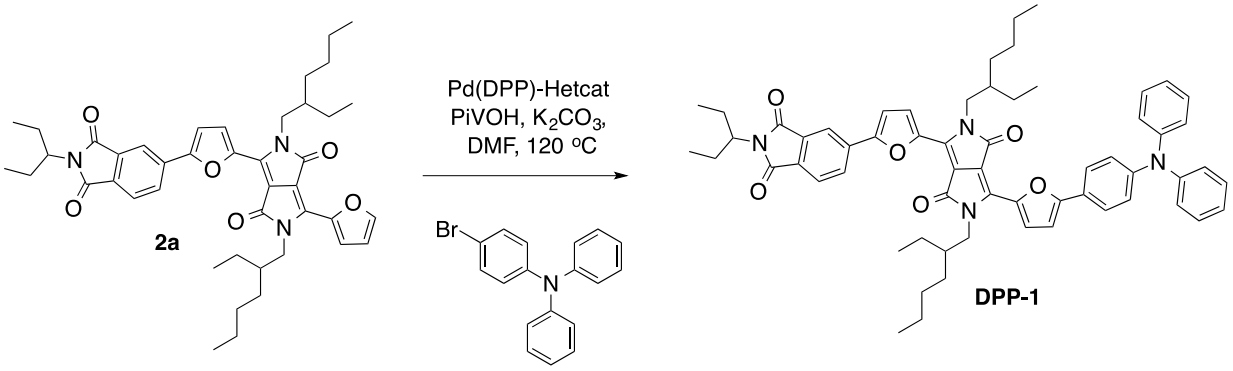
2b: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 8.95 (dd, J= 3.9, 1.1 Hz, 1H), 8.92 (d, J= 4.1 Hz, 1H), 8.10 (m, 1H), 7.98 (t, J= 1.6 Hz, 1H), 7.86 (d, J= 7.2 Hz, 1H), 7.66 (dd, J= 5.0, 1.1 Hz, 1H), 7.62 (d, J= 4.1 Hz, 1H), 7.29 (t, J= 3.9, Hz, 1H), 4.20-4.01 (m, 5H), 1.85-1.71 (m, 4H), 1.31-1.27 (m, 16H), 0.98-0.84 (m, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 168.26, 161.73, 161.57, 146.36, 141.08, 139.13, 138.90, 136.30, 135.75, 133.09, 130.99, 130.91, 130.84, 129.72, 128.53, 126.39, 123.94, 120.18, 108.99, 108.03, 55.88, 45.98, 39.28, 30.31,30.22, 28.54, 25.28, 23.69, 23.56,

23.05, 14.03, 14.00, 11.16, 10.55, 10.48; MS *m/z*, calcd for $C_{43}H_{53}N_3O_4S_2$ $(M+H)^+$: 970.4; found: 970.4



3b: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 8.98 (d, J= 4.1 Hz, 2H), 8.11 (m, 2H), 8.00 (~~dd~~ t, J= 1.5 Hz, 2H), 7.88 (d, J= 7.8 Hz, 2H), 7.64 (d, J= 4.2 Hz, 2H), 4.21-4.10 (m, 6H), 2.11 (m, 4H), 1.85-1.71 (m, 6H), 1.44-1.27 (m, 16H), 0.96-0.86 (m, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 168.24, 161.61, 146.88, 139.82, 138.81, 136.77, 133.12, 130.91, 130.76, 126.49, 123.98,120.25, 109.09, 55.91, 46.11, 39.29, 30.32, 28.55, 25.28, 23.71, 23.06, 14.04, 11.16, 10.56; MS(EI) *m/z*, calcd for $C_{56}H_{66}N_4O_6S_2$ $(M+H)^+$: 955.4; found: 955.5

Synthesis of DPP-1

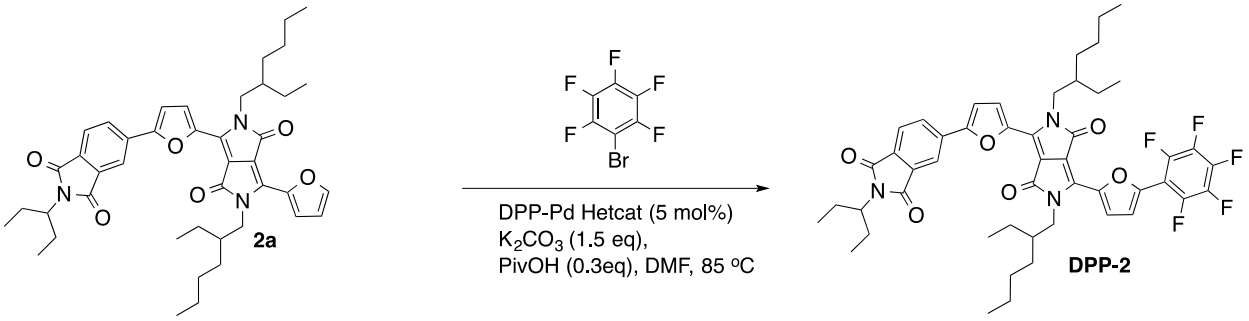


On the bench top 3-(furan-2-yl)-6-(5-(furan-2-yl)- N-(2-ethylpropyl)-phthalimide)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dione (**2a**, 100 mg, 0.14 mmol), 4-bromotriphenylamine (50 mg, 0.15 mmol), potassium carbonate, (K_2CO_3 48 mg, 0.35 mmol), SiliaCat® DPP-Pd (28 mg, 0.007 mmol Pd) and pivalic acid (PivOH, 4 mg, 0.03 mmol) were added to a 2-5 mL glass tube equipped with a stir bar. N,N'- dimethylformamide (DMF, ~3 mL) was then added as a solvent. The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2 and heated in an oil bath at 120 °C for 24 hours. Temperatures under 120 °C were found to be insufficient to promote product formation. The reaction vial was then cooled to room temperature and the vial contents were diluted with dichloromethane (CH_2Cl_2, ~100 mL) and passed through a short SiO_2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The solvent was removed using a rotary evaporator and the product was loaded on SiO_2 for purification using column chromatography. A pentane to CH_2Cl_2 solvent gradient was used to purify the reaction mixture.

The solvent was removed from the product fraction using a rotary evaporator and the obtained dark blue solid was recrystallized from CH_2Cl_2/methanol layering with approximately 5 mL of solvent (CH_2Cl_2) used to dissolve ~100 mg of compound before layering the counter solvent (methanol). After a 24 hour recrystallization period the solids were collected by filtration using a Buchner funnel and washed with methanol to yield the product as a dark blue solid. Yield: 70 mg (52 %)

DPP-1: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 8.55 (d, J= 3.8 Hz, 1H), 8.38 (d, J= 3.8 Hz, 1H), 8.14 (s, 1H), 8.08 (d, J= 9.2 Hz, 1H), 7.89 (d, J= 7.8 Hz, 1H), 7.62 (d, J= 8.8 Hz, 2H), 7.48-7.28 (m, 4H), 7.20- 7.08 (m, 6H), 7.10 (d, J= 7.4 Hz, 3H), 6.86 (d, J= 3.9 Hz, 1H), 4.30-4.20 (m, 4H), 4.07 (m, 1H), 2.15-1.77 (m, 6H), 1.46-1.21 (m, 16H), 0.98-0.90 (m, 12H), 0.88-0.80 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 168.49, 168.33, 161.67, 161.04, 158.10, 154.26, 149.08, 147.20, 145.93, 143.57, 135.00, 134.49, 133.26, 131.56, 130.79, 129.70, 129.01, 125.98, 125.43, 124.89, 124.51, 124.13, 124.07, 122.65, 122.52, 121.54, 118.85, 112.11, 108.70, 108.45, 106.60, 56.08, 46.91, 39.79, 39.61, 30.62, 28.88, 28.82, 25.51, 23.87; MS *m/z*, calcd for $C_{61}H_{66}N_4O_6$ $(M+H)^+$: 951.5 found: 951.6; Elemental analysis: Calcd. C 77.02, H 6.99, N 5.89, Found C 76.13, H 6.72, N 5.88; Melting point 213-215 ˚C

Synthesis of DPP-2

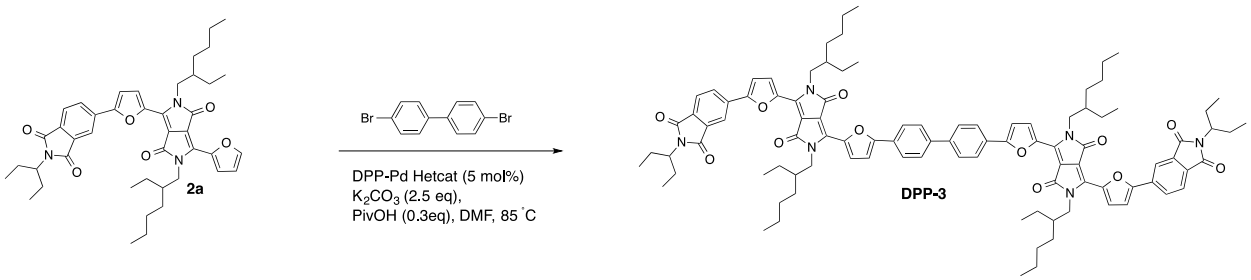


On the bench top, compound **2a** (200 mg, 0.28 mmol), bromo-pentafluorobenzene (100 mg, 0.42 mmol), potassium carbonate (97 mg, 0.7 mmol), pivalic acid (8.6 mg, 0.08 mmol) and SiliaCat® DPP-Pd (56 mg, 0.014 mmol), were added to a 10-20 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~5 mL) was then added as a solvent. The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2 and heated in an oil bath 85 ˚C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH_2Cl_2 and was filtered through a short SiO_2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH_2Cl_2 gradient with the product eluting using a CH_2Cl_2:methanol (99:1) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark brown powder. Yield: 167 mg (67%).

DPP-2: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.56 (d, J= 3.4 Hz, 1H), 8.48 (d, J= 3.5 Hz, 1H), 8.17 (s, 1H), 8.10 (d, J= 7.9 Hz, 1H), 7.95 (d, J= 7.9 Hz, 1H), 7.19 (d, J= 3.5 Hz, 1H), 7.09 (s, 1H), 4.23 (d, J= 7.7 Hz, 2H), 4.20 (d, J= 7.7 Hz, 2H), 4.15-4.10 (m, 1H), 2.18-2.10 (m, 2H), 1.94-1.82

(m, 4H), 1.44-1.26 (m, 16H), 0.92-0.83 (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.49, 168.33, 161.44, 161.38, 154.84, 145.60, 144.70, 134.83, 134.19, 133.29, 133.03, 131.03, 129.22, 124.12, 122.62, 122.51, 119.00, 115.76, 112.18, 108.50, 107.82, 56.16, 47.00, 46.57, 39.77, 30.59, 30.39, 28.77, 25.50, 23.85, 23.70, 23.32, 23.29, 14.17, 14.10, 11.37, 10.82, 10.80; 19F NMR (CDCl3, 282 MHz) δ -142.3 (d, J= 14.6 Hz, 4F), -161.74 (d, J= 14.1 Hz, 1F) MS *m/z*, calcd for $C_{42}H_{52}F_5N_3O_6$ $(M+H)^+$: 872.4 found: 872.4; Melting point 219-220 ˚C

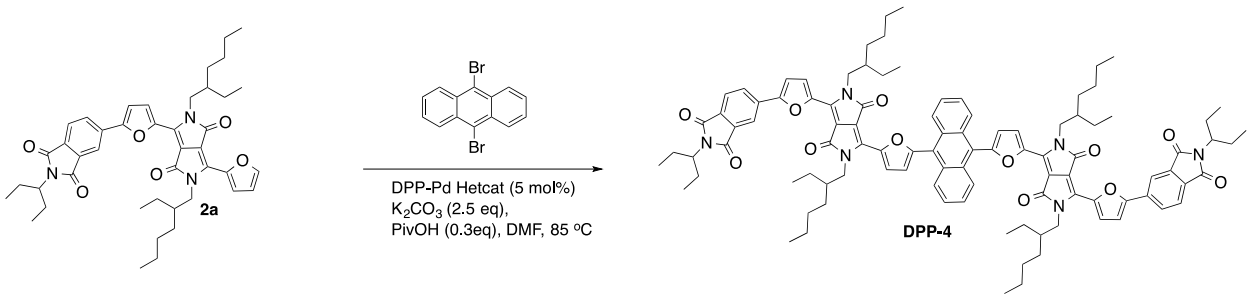
Synthesis of DPP-3



On the bench top, compound **2a** (226 mg, 0.32 mmol), 4,4-dibromobiphenyl (40 mg, 0.12 mmol), potassium carbonate (111 mg, 0.79 mmol), pivalic acid (10 mg, 0.09 mmol) and SiliaCat® DPP-Pd (63 mg, 0.015 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~5 mL) was then added as a solvent. The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2 and heated an oil bath at 85 ˚C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH_2Cl_2 and was filtered through a short SiO_2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH_2Cl_2 gradient with the product eluting using a CH_2Cl_2:Et_3N (98:2) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark purple powder. Yield: 167 mg (83%).

DPP-3: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.57 (d, J= 3.8 Hz, 2H), 8.45 (d, J= 3.8 Hz, 2H), 8.16 (s, 2H), 8.09 (d, J= 7.7 Hz, 2H), 7.90 (d, J= 7.8 Hz, 2H), 7.87 (d, J= 8.3 Hz, 4H), 7.75 (d, J= 8.3 Hz, 4H), 7.18 (d, J= 3.8 Hz, 2H), 7.06 (d, J= 3.8 Hz, 2H), 4.22 (t, J= 8.2 Hz, 8H), 4.15-4.05 (m, 2H), 2.12-1.83 (m, 12H), 1.43-1.29 (m, 32H), 0.96-0.84 (m, 36H); MS *m/z*, calcd for $C_{98}H_{112}N_6O_{12}$ $(M+H)^+$: 1566.8 found: 1566.7; Elemental analysis: Calcd. C 75.16, H 7.21, N 5.37 Found C 74.31, H 6.84, N 5.26; Melting point 324-325 ˚C. Note: The ^{13}C NMR signal of **DPP-3** in aromatic region in $CDCl_3$ was below the detection limit.

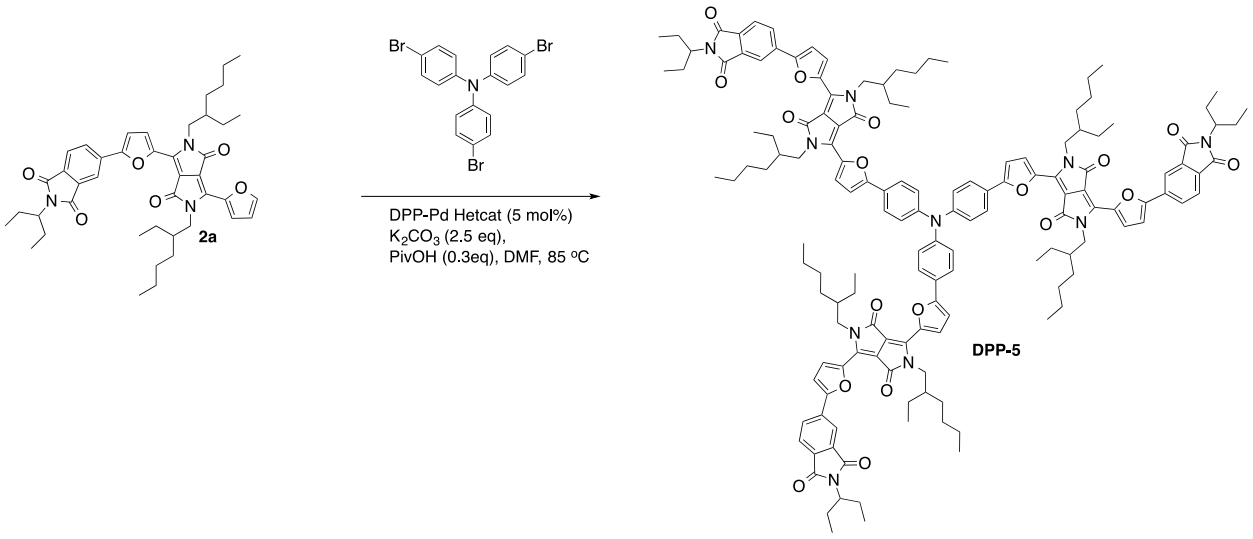
Synthesis of DPP-4



On the bench top, compound **2a** (200 mg, 0.28 mmol), 9,10-dibromoanthracene (45 mg, 0.13 mmol), potassium carbonate (97 mg, 0.7 mmol), pivalic acid (8 mg, 0.08 mmol) and SiliaCat® DPP-Pd (56 mg, 0.014 mmol)were added to a 10-20 mL glass vial equipped with a stir bar The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2 and heated in an oil bath at 85 ˚C for 24 hours. N,N'- dimethylformamide (DMF, ~10 mL) was then added as a solvent. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH_2Cl_2 and was filtered through a short SiO_2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH_2Cl_2 gradient with the product eluting using a CH_2Cl_2:Et_3N (98:2) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark blue powder. Yield: 190 mg (89%).

DPP-4: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.85 (d, J= 8.8 Hz, 2H), 8.46 (d, J= 3.5 Hz, 2H), 8.17 (s, 2H), 8.11 (d, J= 7.6 Hz, 2H), 8.01-7.95 (m, 4H), 7.91 (d, J= 7.8 Hz, 2H), 7.60-7.50 (m, 4H), 7.18 (d, J= 3.5 Hz, 2H), 7.09 (d, J= 3.3 Hz, 2H), 4.27 (d, J= 6.9 Hz, 4H), 4.12-4.08 (m, 2H), 4.01-3.94 (m, 4H), 2.10-1.79 (m, 12H), 1.47-1.14 (m, 24H), 1.04-0.76 (m, 32H), 0.50-0.58 (m, 6H), 0.40-0.45 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 168.46, 168.31, 161.54, 161.35, 154.67, 154.07, 145.74, 145.46, 134.91, 134.44, 133.30, 132.79, 131.39, 131.01, 129.16, 127.07, 126.37, 124.11, 122.61, 122.31, 118.96, 117.03, 112.15, 108.47, 107.22, 56.12, 46.98, 46.64, 40.02, 39.85, 30.65, 28.85, 28.56, 25.52, 23.87, 23.76, 23.38, 23.04, 14.24, 13.91, 11.38, 10.86; MS *m/z*, calcd for $C_{100}H_{112}N_6O_{12}$ $(M+H)^+$: 1590.8; found: 1590.8; Elemental analysis: Calcd. C 74.72, H 7.17, N 5.93 Found C 72.95, H 6.89, N 5.65; Melting point 174-176 ˚C.

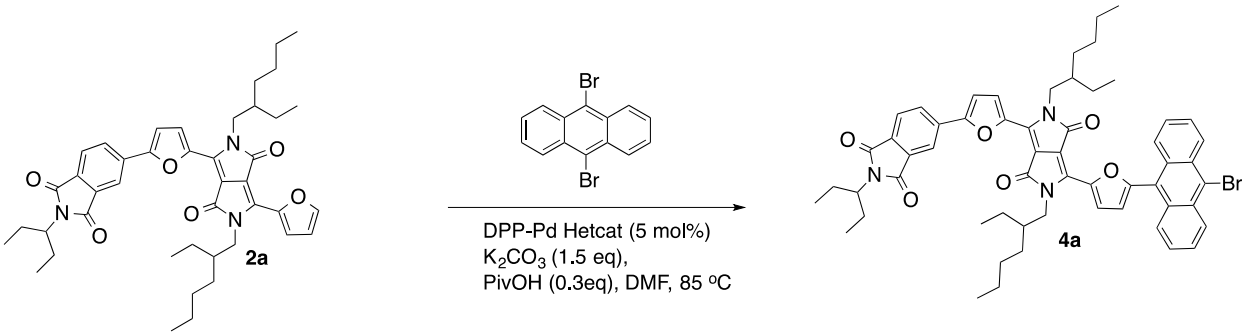
Synthesis of DPP-5



On the bench top, compound **2a** (257 mg, 0.36 mmol), tris(4-bromophenyl)amine (50 mg, 0.1 mmol), potassium carbonate (126 mg, 0.90 mmol), pivalic acid (10 mg, 0.09 mmol) and SiliaCat® DPP-Pd (72 mg, 0.018 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~10 mL) was then added as a solvent. The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2 and heated in an oil bath at 85 ˚C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH_2Cl_2 and was filtered through a short SiO_2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane toCH_2Cl_2 gradient with the product eluting using a CH_2Cl_2:Et_3N (98:2) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark blue powder. Yield: 170 mg (69%).

DPP-5: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.54 (d, J= 3.7 Hz, 3H), 8.43 (d, J= 3.8 Hz, 3H), 8.16 (s, 3H), 8.10 (d, J= 8.7 Hz, 3H), 7.91 (d, J= 7.8 Hz, 3H), 7.75 (d, J= 8.7 Hz, 6H), 7.27 (d, J= 8.6 Hz, 6H), 7.18 (d, J= 3.8 Hz, 3H) 6.96 (d, J= 3.8 Hz, 3H), 4.31-4.21 (m, 12H), 4.15-4.10 (m, 3H), 2.18-2.12 (m, 6H), 1.94-1.83 (m, 12H), 1.44-1.26 (m, 48H), 0.99-0.94 (m, 36H), 0.89-0.84 (m, 18H): ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 168.45, 168.31, 161.53, 161.23, 161.12, 157.19, 154.48, 147.38, 145.81, 144.05, 134.92, 134.17, 133.27, 132.10, 130.89, 129.07, 126.23, 124.94, 124.84, 124.07, 123.93, 121.91, 118.89, 112.12, 109.23, 108.58, 107.10, 56.09, 46.91, 39.78, 39.62, 30.61, 28.88, 28.81, 25.50, 23.87, 23.37, 23.34, 14.27, 14.19, 11.37, 10.84, 10.78; MS *m/z*, calcd for $C_{147}H_{168}N_{10}O_{18}$ $(M+H)^+$: 2363.3 found: 2363.0; Elemental analysis: Calcd. C 75.54, H 7.10, N 5.29 Found C 75.41, H 6.86, N 5.24; Melting point 255-256 ˚C.

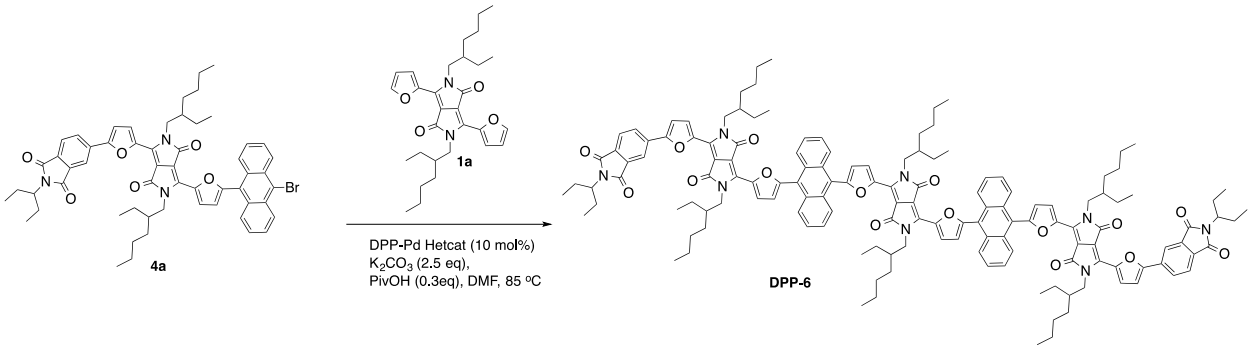
Synthesis of 4a



On the bench top, compound **2a** (270 mg, 0.38 mmol), 9,10-dibromoanthracene (384 mg, 1.1 mmol), potassium carbonate (78 mg, 0.57 mmol), pivalic acid (11 mg, 0.1 mmol) and SiliaCat® DPP-Pd (76 mg, 0.019 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~10 mL) was then added as a solvent. The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2 and heated in an oil bath at 85 ˚C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH_2Cl_2 and was filtered through a short SiO_2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH_2Cl_2 gradient. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark blue powder. Yield: 220 mg (61%).

4a: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.82 (d, J= 3.6 Hz, 1H), 8.66 (d, J= 8.8 Hz, 2H), 8.44 (d, J= 3.8 Hz, 1H), 8.16 (s, 1H), 8.11 (d, J= 7.9 Hz, 1H), 7.94-7.85 (m, 3H), 7.69-7.60 (m, 2H), 7.58-7.51 (m, 2H), 7.16 (d, J= 3.7 Hz, 1H), 7.05 (d, J= 3.6 Hz, 1H), 4.26 (d, J= 7.7 Hz, 2H), 4.15-4.08 (m, 1H), 3.98-3.92 (m, 2H), 2.12-1.78 (m, 6H), 1.46-1.27 (m, 12H), 0.96-0.69 (m, 16H), 0.55 (t, J= 7.3 Hz, 3H), 0.42 (t, J= 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 168.46, 168.31, 161.53, 161.32, 154.61, 154.08, 145.74, 145.34, 134.91, 134.49, 133.29, 132.99, 132.70, 132.37, 130.97, 130.48, 129.14, 128.51, 127.52, 127.24, 126.59, 126.35, 124.70, 124.10, 122.58, 122.23, 122.15, 118.94, 116.93, 112.13, 108.47, 107.11, 56.11, 46.95, 46.65, 39.99, 39.83, 30.63, 28.84, 28.52, 25.51, 23.84, 23.72, 23.37, 23.00, 14.23, 13.79, 11.38; MS *m/z*, calcd for $C_{57}H_{60}BrN_3O_6$ $(M+H)^+$: 962.4; found: 962.4

Synthesis of DPP-6



On the bench top, compound **1a** (30 mg, 0.06 mmol), **4a** (128 mg, 0.13 mmol), potassium carbonate (21 mg, 0.15 mmol pivalic acid (2 mg, 0.02 mmol) and SiliaCat® DPP-Pd (24 mg, 0.013 mmol) were added to a 2-5 mL glass vial equipped with a stir bar. N,N'- dimethylformamide (DMF, ~3 mL) was then added as a solvent. The reaction vial was crimped with a Teflon ® cap, briefly purged with N_2 and heated in an oil bath at 85 ˚C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH_2Cl_2 and was filtered through a short SiO_2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography with using a pentane to CH_2Cl_2 gradient with the product eluting using a CH_2Cl_2:Et_3N (98:2) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark blue powder. Yield: 113 mg (82%).

DPP-6: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.86 (d, J= 3.7 Hz, 2H), 8.81 (d, J= 3.57 Hz, 2H), 8.46 (d, J= 3.8 Hz, 2H), 8.17 (s, 2H), 8.11 (d, J= 8.5 Hz, 2H), 8.05-7.95 (m, 8H), 7.91 (d, J= 7.8 Hz, 2H), 7.58-7.50 (m, 8H), 7.18 (d, J= 3.7 Hz, 2H), 7.10-7.04 (m, 4H), 4.28 (d, J= 7.3 Hz, 4H), 4.18-4.05 (m, 2H), 4.03-3.94 (m, 8H), 2.15-1.79 (m, 14H), 1.45-1.04 (m, 28H), 0.97-0.82 (m, 44H), 0.64-0.46 (m, 24H); MS *m/z*, calcd for $C_{144}H_{158}N_8O_{16}$ $(M+H)^+$: 2257.2 found: 2257.2; Elemental analysis: Calcd. C 76.64, H 7.06, N 4.97 Found C 76.03, H 6.78, N 4.97; Melting point 186-188 ˚C. Note: The ^{13}C NMR signal of **DPP-6** in aromatic region in $CDCl_3$ was below the detection limit.

PL Spectra

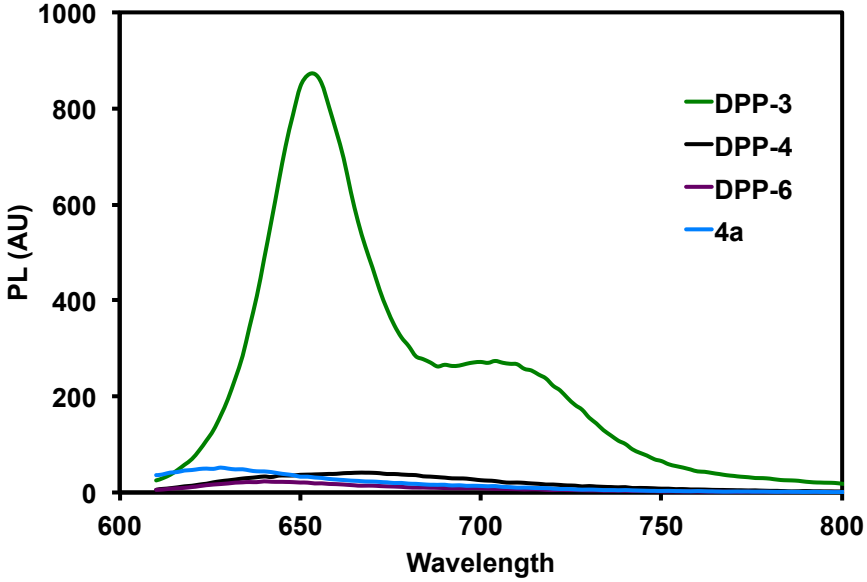


Figure S1. Photoluminescence spectra of **DPP-3**, **DPP-4**, **DPP-6** and **4a** in ($6x10^{-6}$ M $CHCl_3$), excited at 600 nm.

CV Data

Table S1. Electrochemical properties of **3a** and **DPP-1** to **DPP-6.**

Entry	E_{ox}	E_{red}
3a	$0.44_{(onset)}$, 0.57, 0.90	$-1.22_{(onset)}$, -1.38, -1.69, -1.98
DPP-1	$0.18_{(onset)}$, 0.33, 0.58	$-1.32_{(onset)}$, -1.47, -1.73
DPP-2	$0.34_{(onset)}$, 0.51, 0.81	$-1.27_{(onset)}$, -1.55, -1.79
DPP-3	$0.32_{(onset)}$, 0.51, 0.84	$-1.31_{(onset)}$, -1.42, -1.71
DPP-4	$0.36_{(onset)}$, 0.54, 0.87	$-1.24_{(onset)}$, -1.34, -1.87
DPP-5	$0.19_{(onset)}$, 0.32, 0.46, 0.64, 0.81	$-1.37_{(onset)}$, -1.51, -1.79
DPP-6	$0.40_{(onset)}$, 0.63, 1.00	$-1.20_{(onset)}$, -1.31, -1.42, -1.68

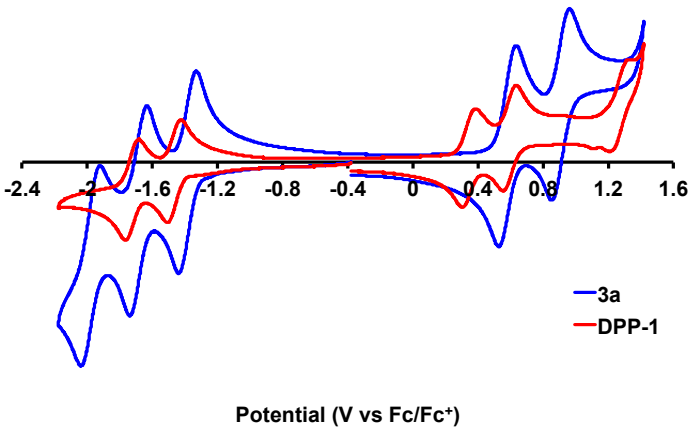


Figure S2 Cyclic voltammetry plots of compound **3a** and **DPP-1** in 0.1 M $TBAPF_6/CH_2Cl_2$ at scan rate 100 mV/s.

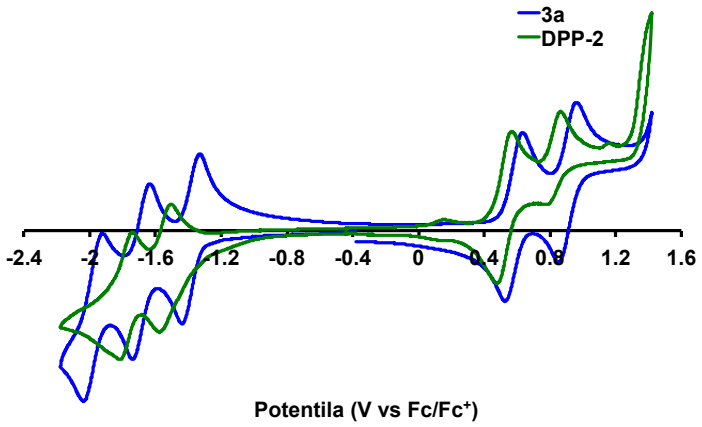


Figure S3 Cyclic voltammetry plots of compound **3a** and **DPP-2** in 0.1 M $TBAPF_6/CH_2Cl_2$ at scan rate 100 mV/s.

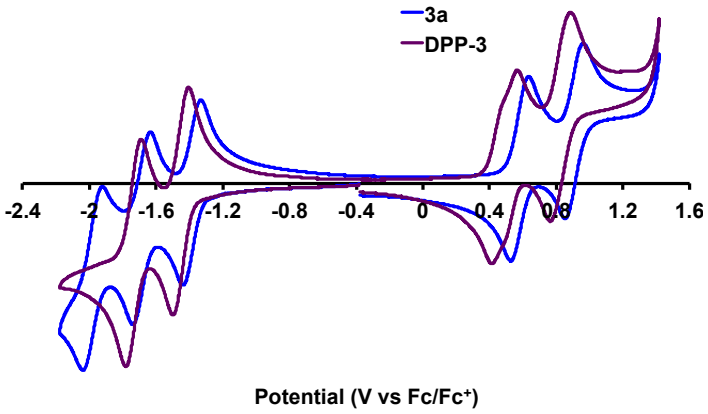


Figure S4 Cyclic voltammetry plots of compound **3a** and **DPP-3** in 0.1 M $TBAPF_6/CH_2Cl_2$ at scan rate 100 mV/s.

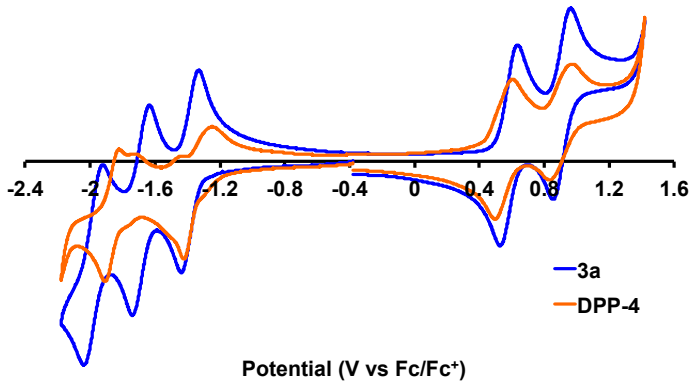


Figure S5 Cyclic voltammetry plots of compound **3a** and **DPP-4** in 0.1 M $TBAPF_6/CH_2Cl_2$ at scan rate 100 mV/s.

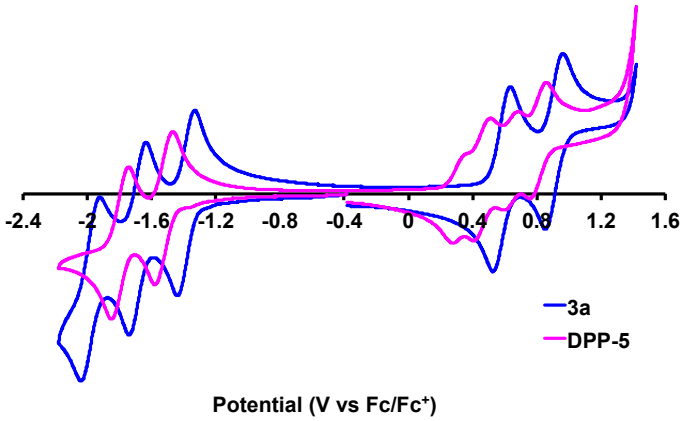


Figure S6 Cyclic voltammetry plots of compound **3a** and **DPP-5** in 0.1 M $TBAPF_6/CH_2Cl_2$ at scan rate 100 mV/s.

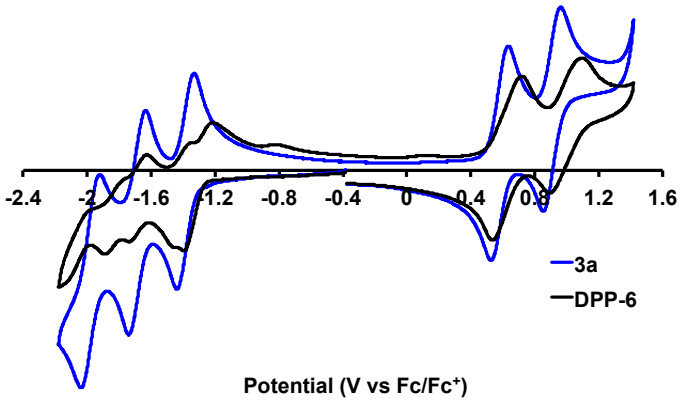


Figure S7 Cyclic voltammetry plots of compound **3a** and **DPP-6** in 0.1 M $TBAPF_6/CH_2Cl_2$ at scan rate 100 mV/s.

UV-Vis Data

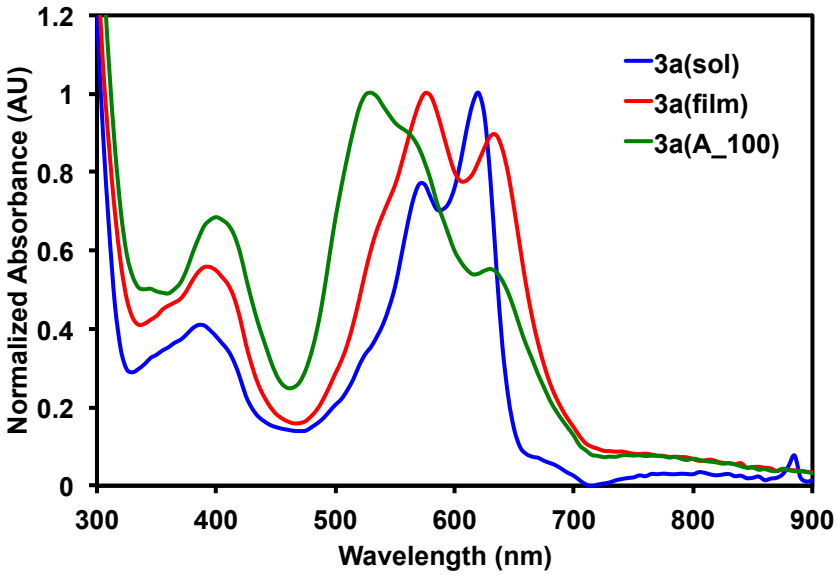


Figure S8. UV-Visible spectra of compounds **3a** in $CHCl_3$ solution, thin films were cast at from 1 % wt/volume $CHCl_3$ solutions onto glass substrates and films annealed at 100 ºC for 5 min.

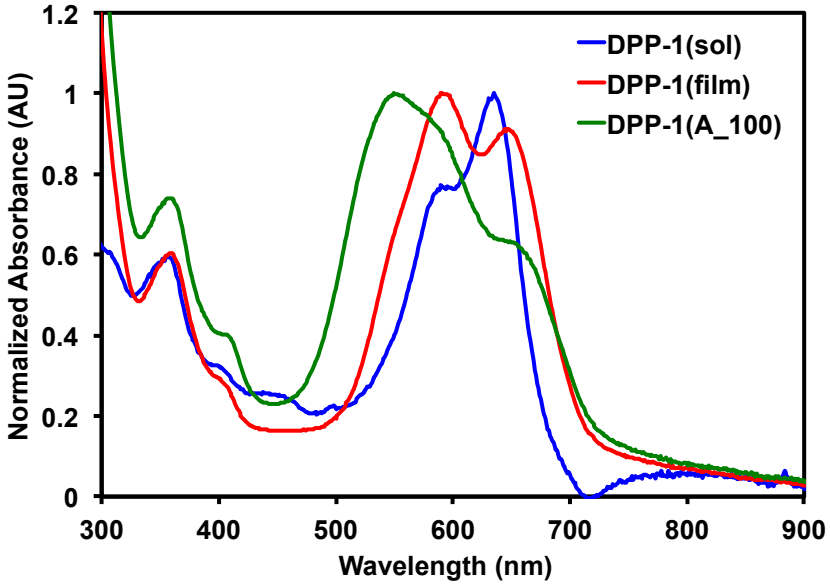


Figure S9. UV-Visible spectra of **DPP-1** in $CHCl_3$ solution, thin films were cast at from 1 % wt/volume $CHCl_3$ solutions onto glass substrates and films annealed at 100 ºC for 5 min.

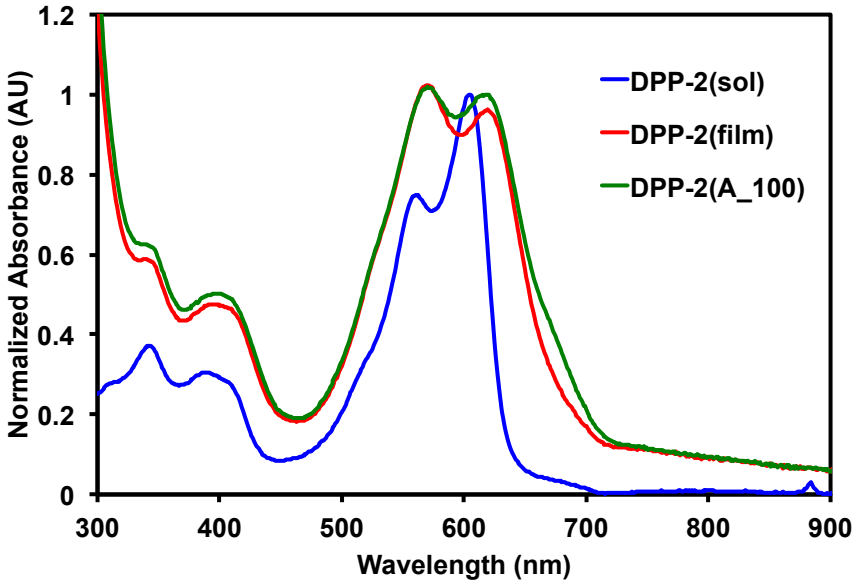


Figure S10 UV-Visible spectra of **DPP-2** in $CHCl_3$ solution, thin films were cast at from 1 % wt/volume $CHCl_3$ solutions onto glass substrates and films annealed at 100 ºC for 5 min.

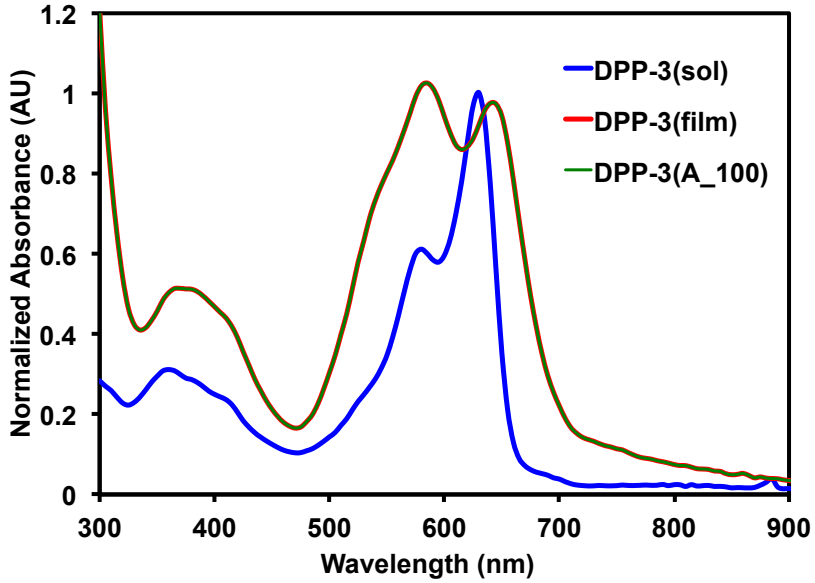


Figure S11. UV-Visible spectra of **DPP-3** in $CHCl_3$ solution, thin films were cast at from 1 % wt/volume $CHCl_3$ solutions onto glass substrates and films annealed at 100 ºC for 5 min. The as-cast and thermally annealed films give nearly identical absorption spectra.

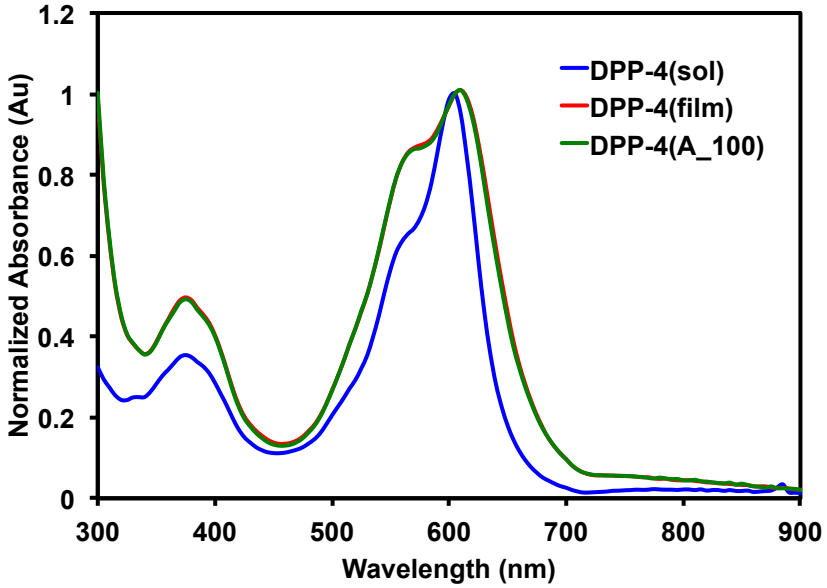


Figure S12. UV-Visible spectra of **DPP-4** in $CHCl_3$ solution, thin films were cast at from 1 % wt/volume $CHCl_3$ solutions onto glass substrates and films annealed at 100 ºC for 5 min.

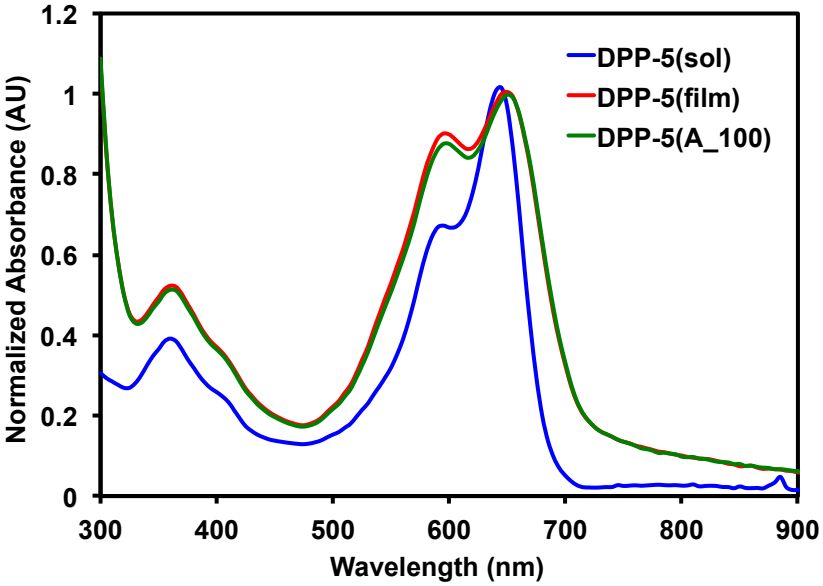


Figure S13. UV-Visible spectra of **DPP-5** in $CHCl_3$ solution, thin films were cast at from 1 % wt/volume $CHCl_3$ solutions onto glass substrates and films annealed at 100 ºC for 5 min.

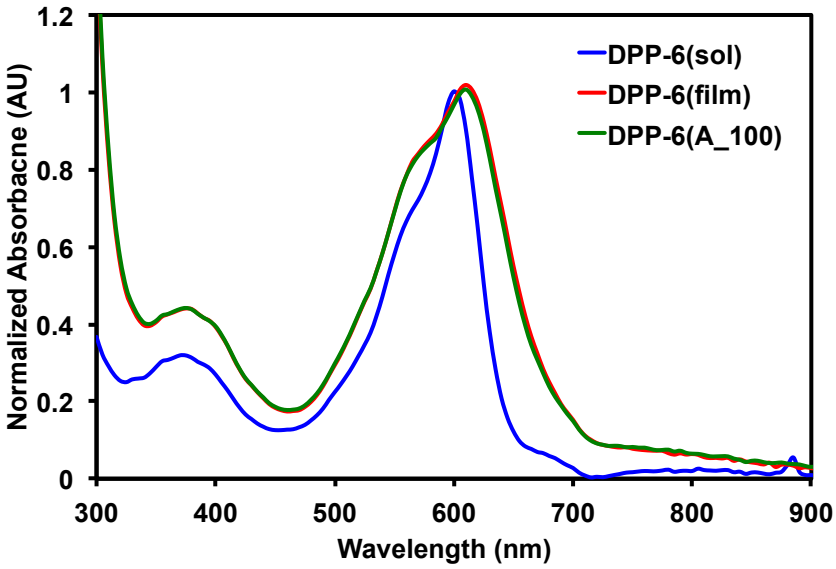


Figure S14. UV-Visible spectra of **DPP-6** in $CHCl_3$ solution, thin films were cast at from 1 % wt/volume $CHCl_3$ solutions onto glass substrates and films annealed at 100 ºC for 5 min.

NMR Spectra

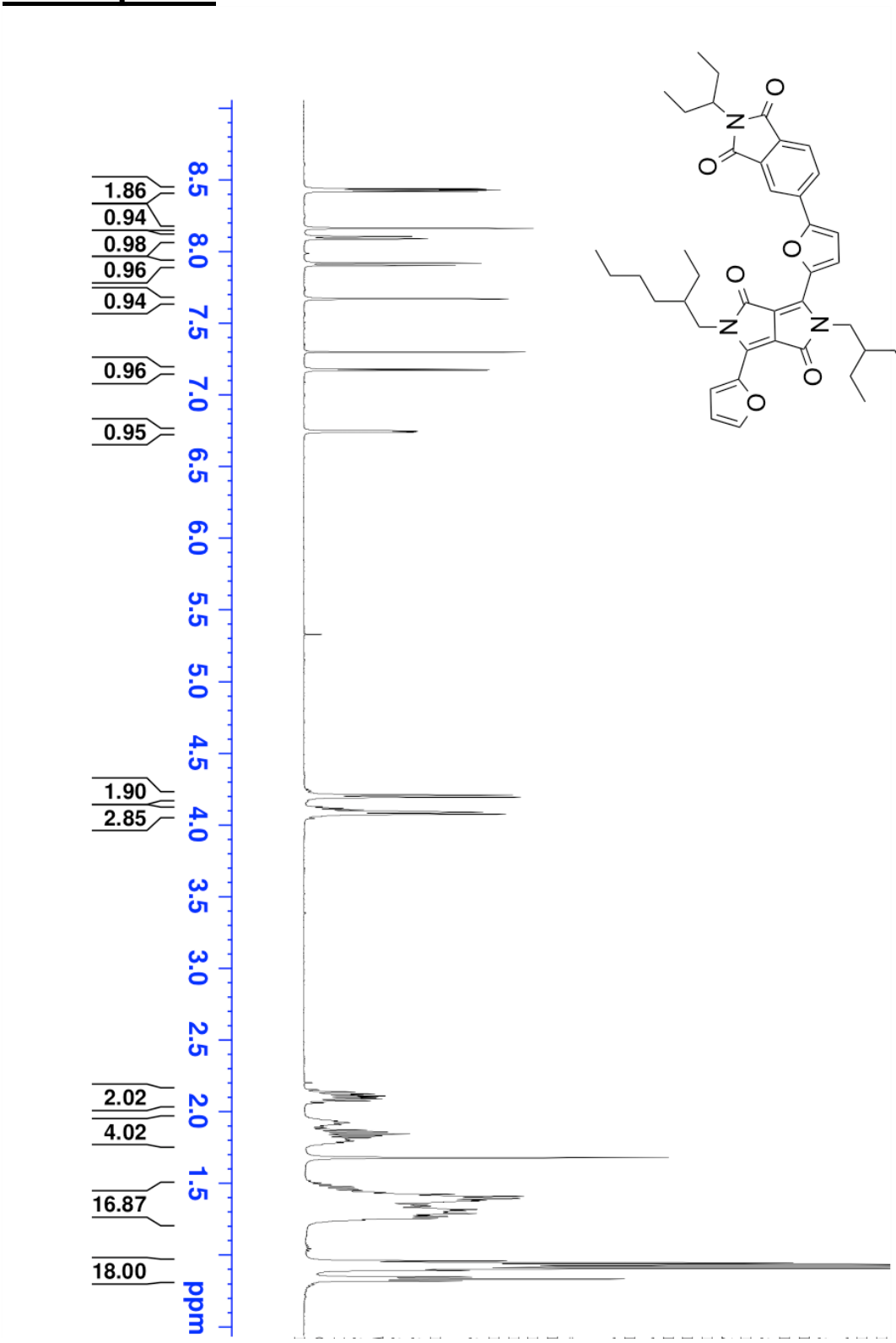


Figure S15. ^{1}H NMR spectra of compound **2a** in $CDCl_3$

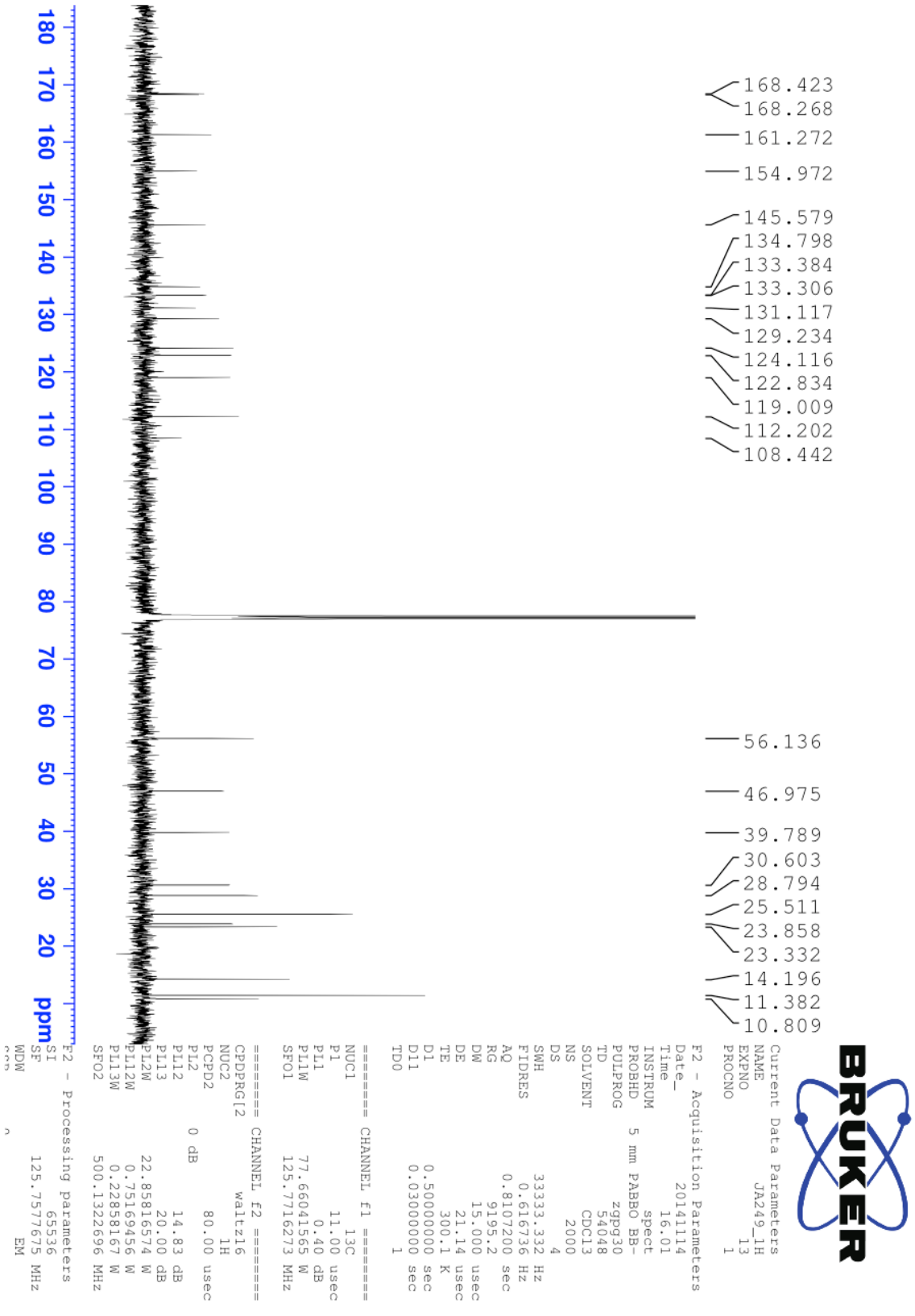


Figure S16. ^{13}C NMR spectra of compound **2a** in $CDCl_3$

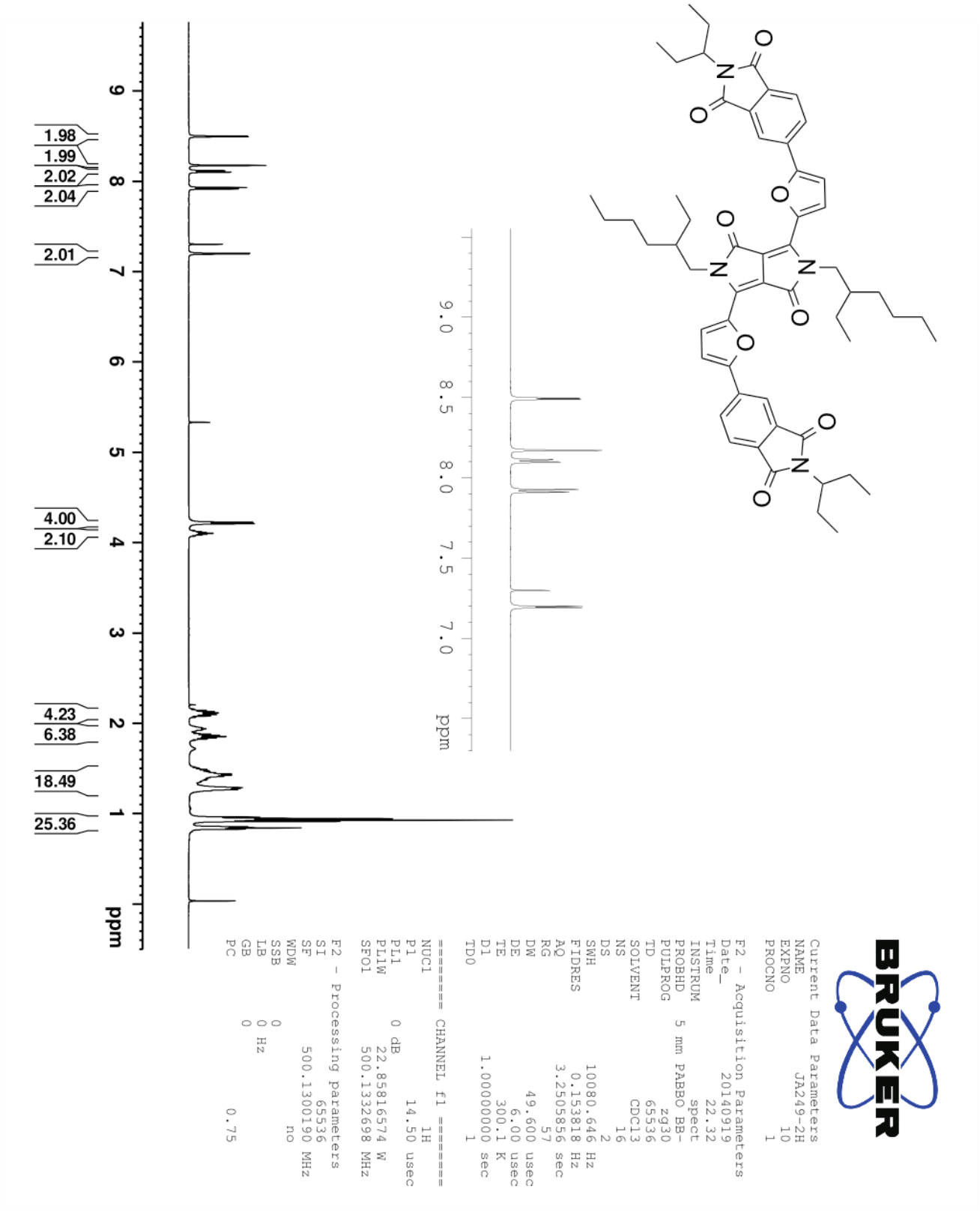


Figure S17. ^{1}H NMR spectra of compound **3a** in $CDCl_3$

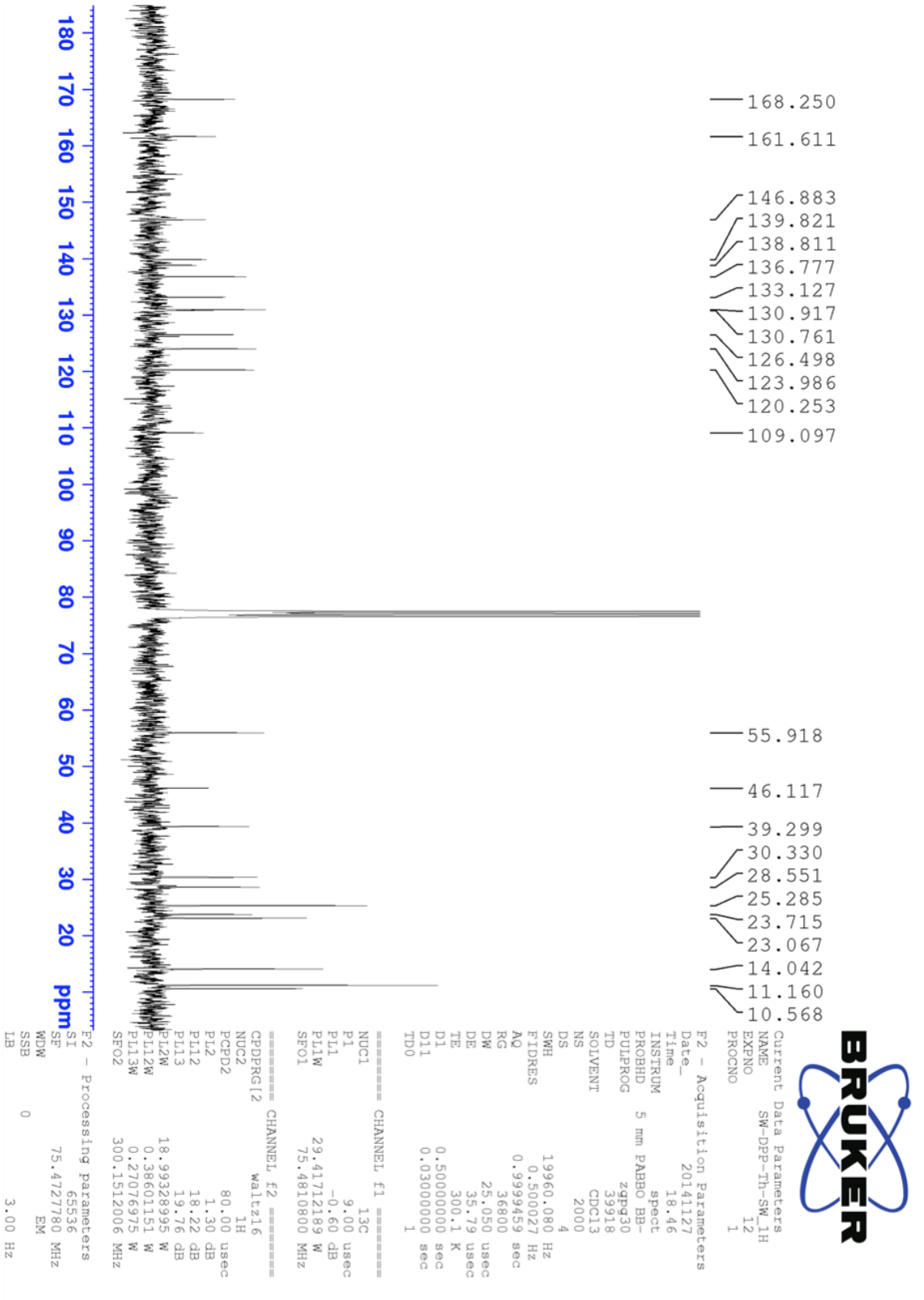


Figure S18. ^{13}C NMR spectra of compound **3a** in $CDCl_3$

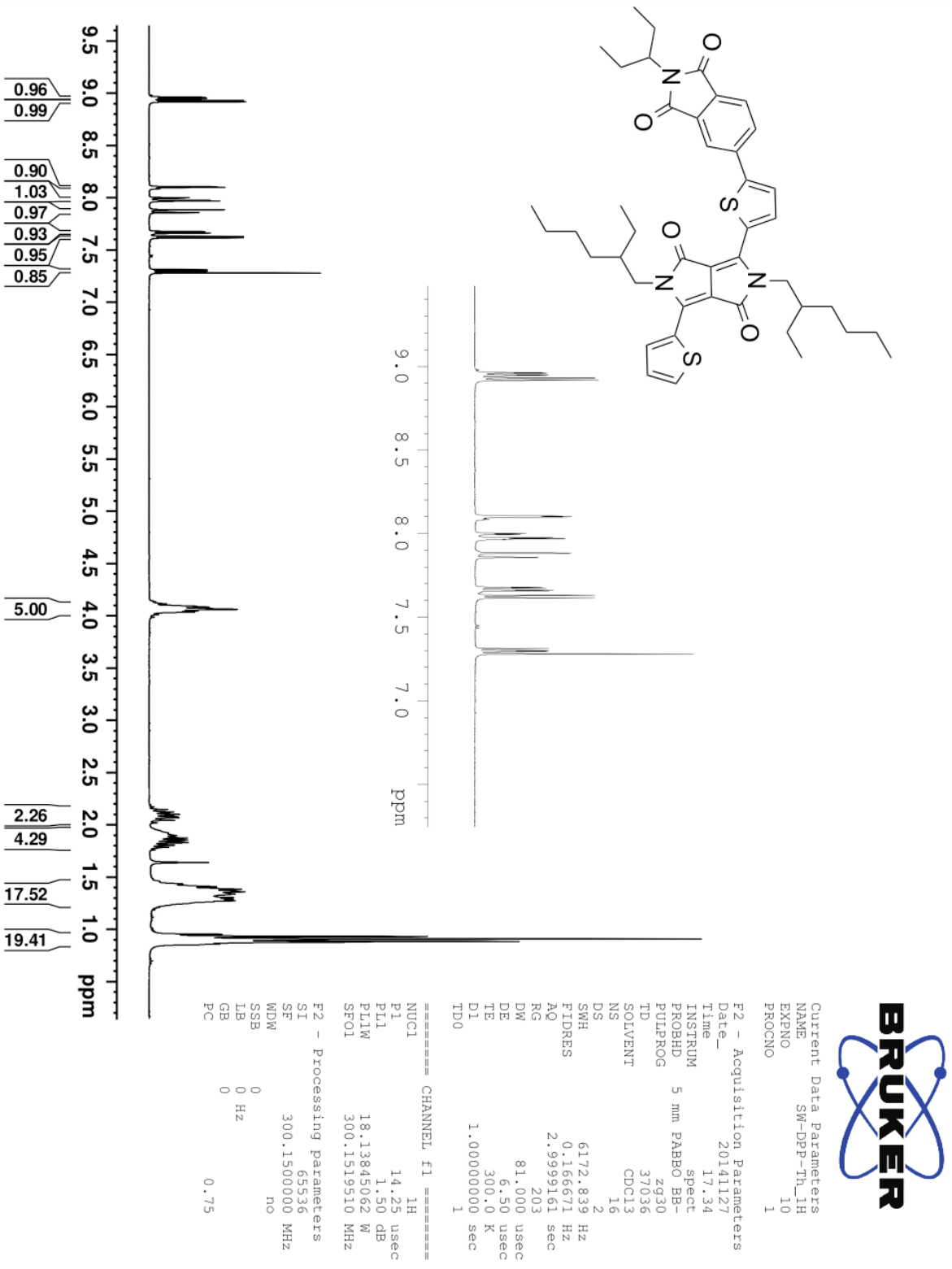


Figure S19. ^{1}H NMR spectra of compound **2b** in $CDCl_3$

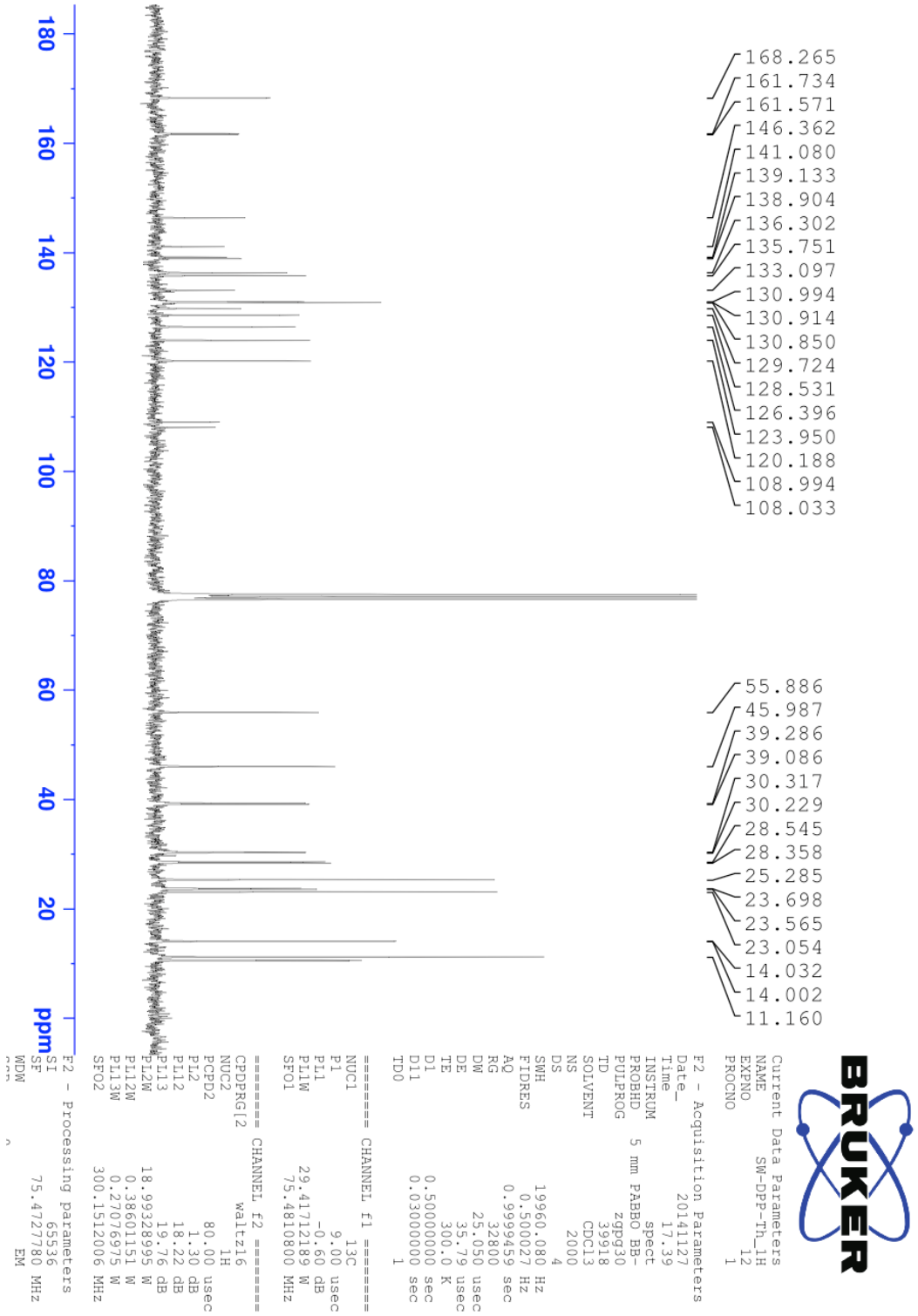


Figure S20. ^{13}C NMR spectra of compound **2b** in $CDCl_3$

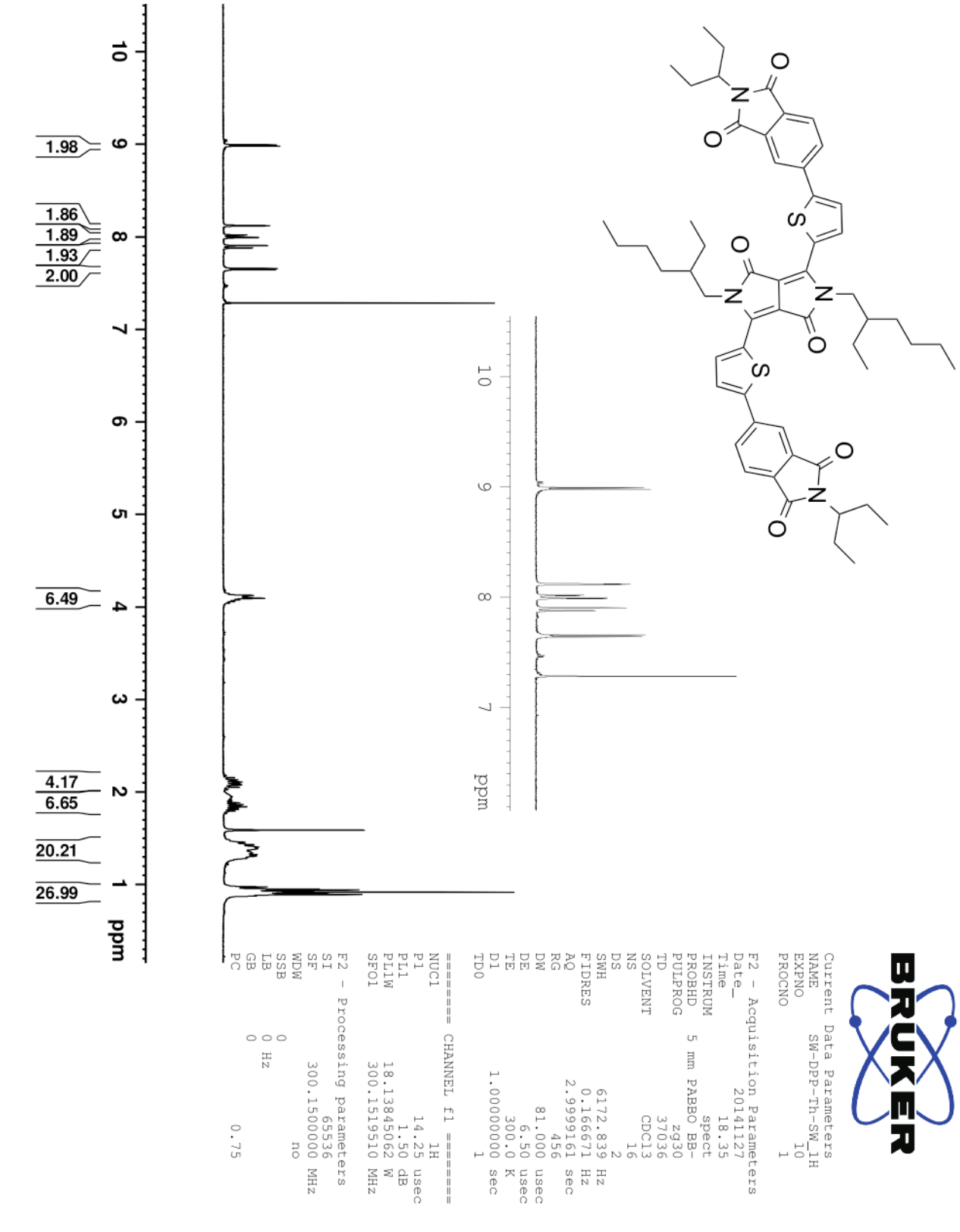


Figure S21. ^{1}H NMR spectra of compound **3b** in $CDCl_3$

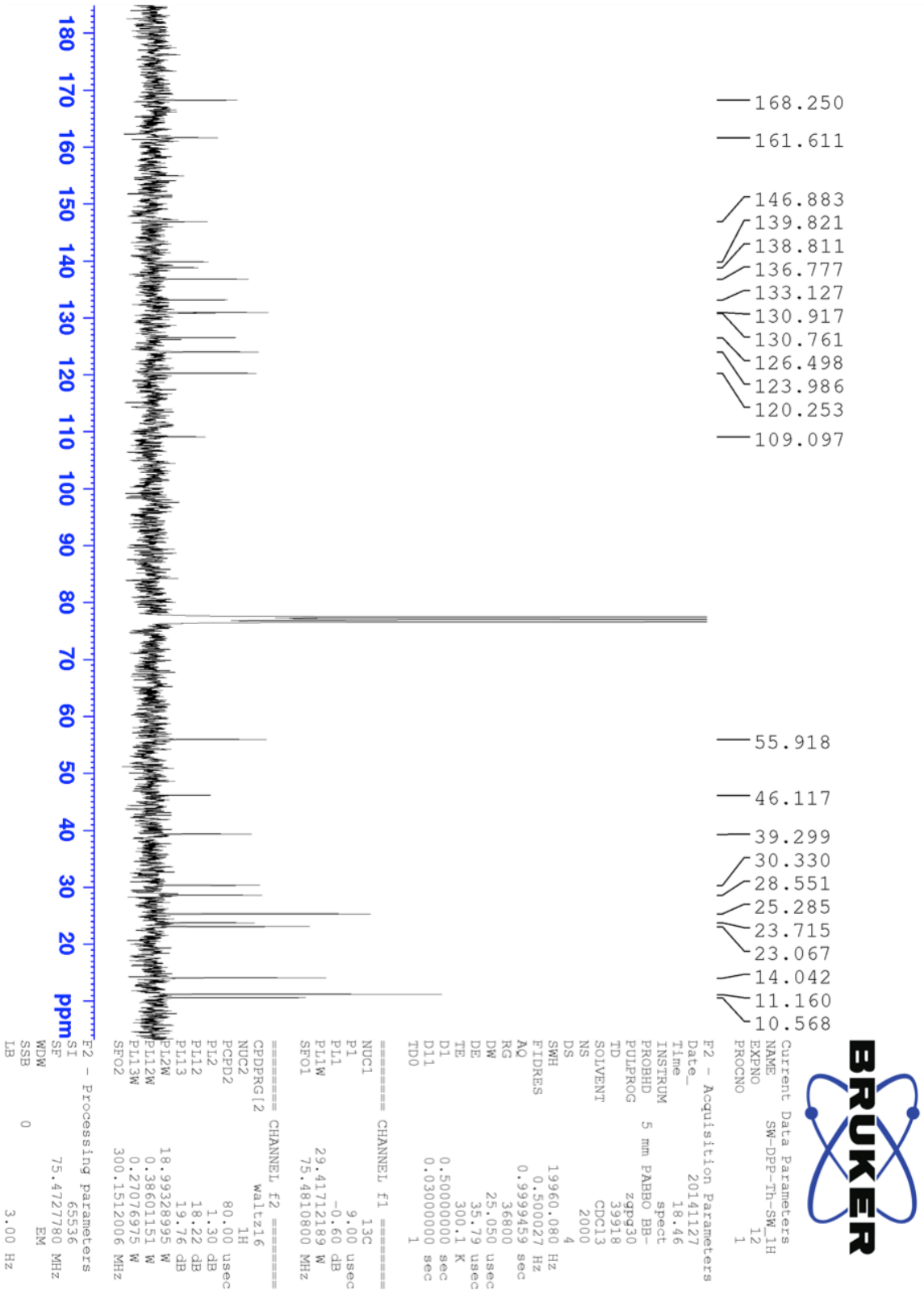


Figure S22. ^{13}C NMR Spectra of compound **3b** in $CDCl_3$

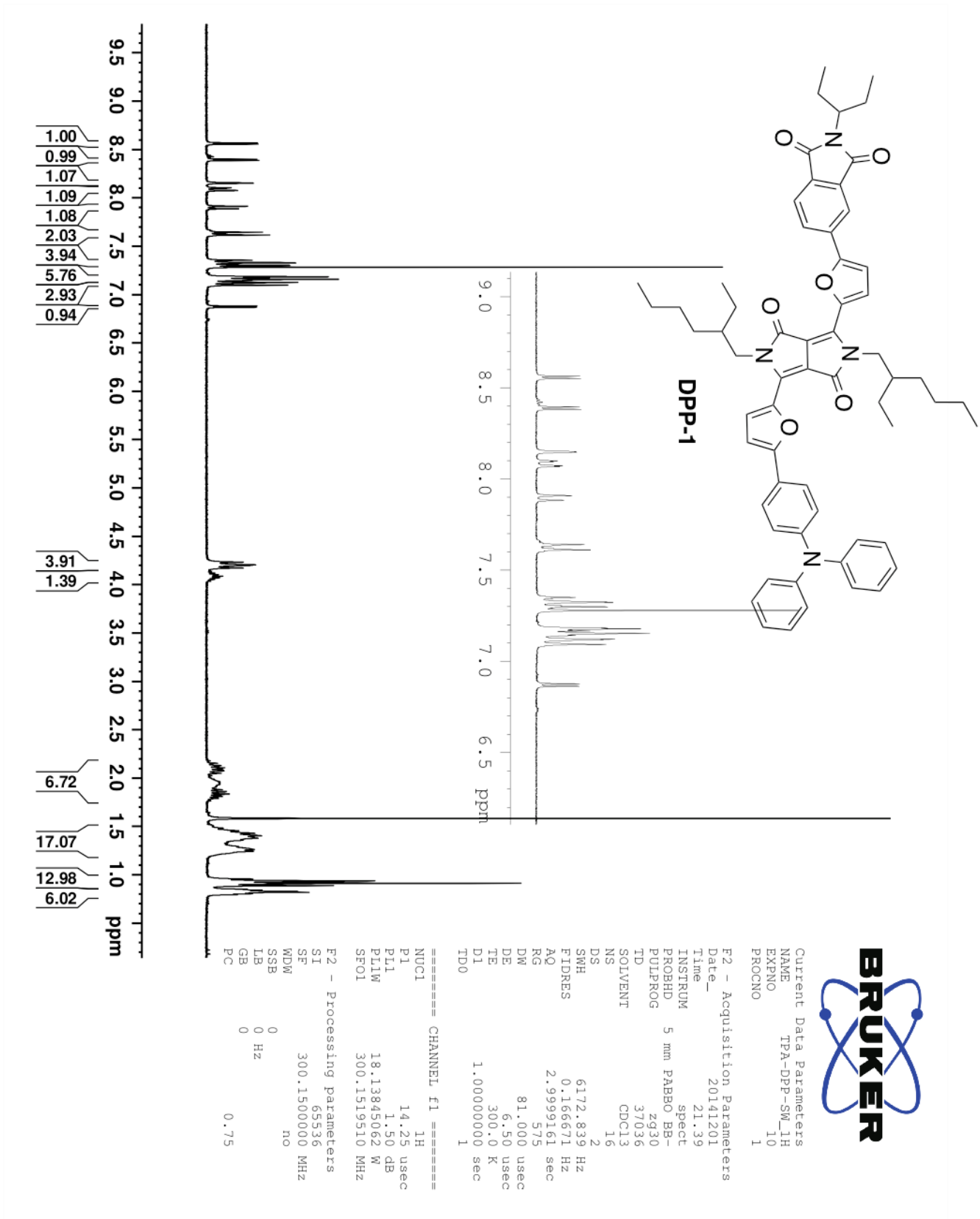


Figure S23. ^{1}H NMR of **DPP-1** in $CDCl_3$

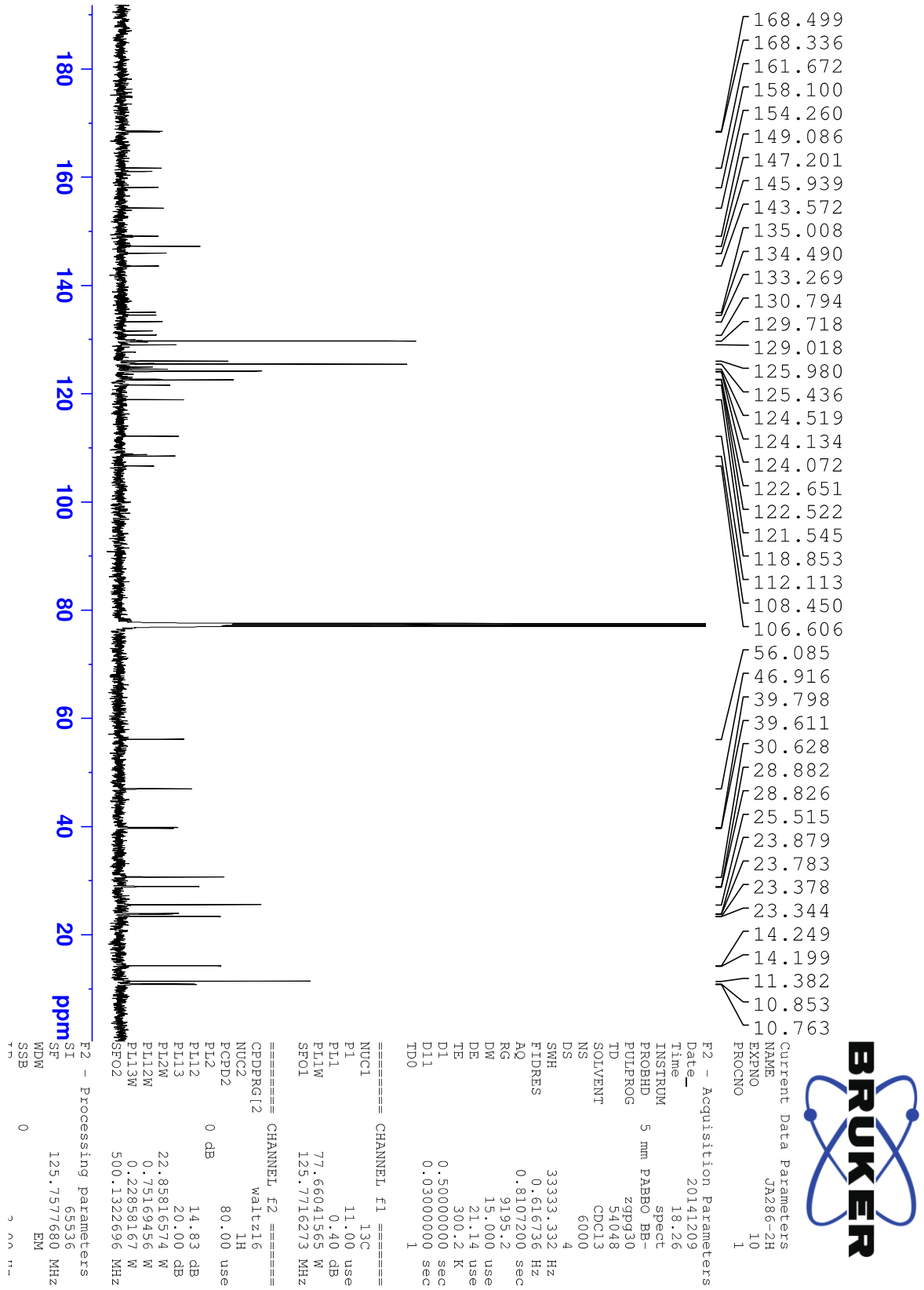


Figure S24. ^{13}C NMR of **DPP-1** in $CDCl_3$

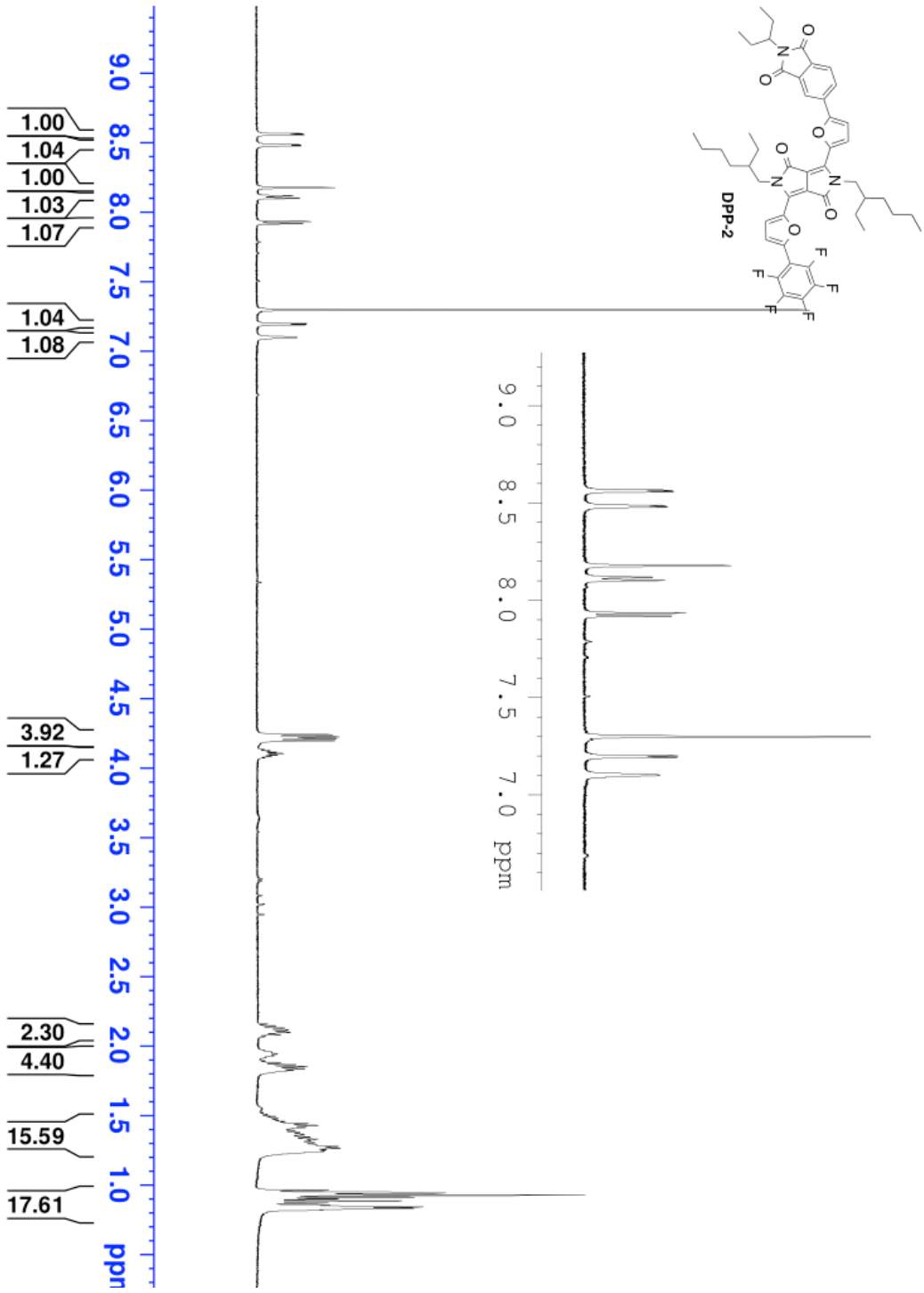


Figure S25. ^{1}H NMR of **DPP-2** in $CDCl_3$

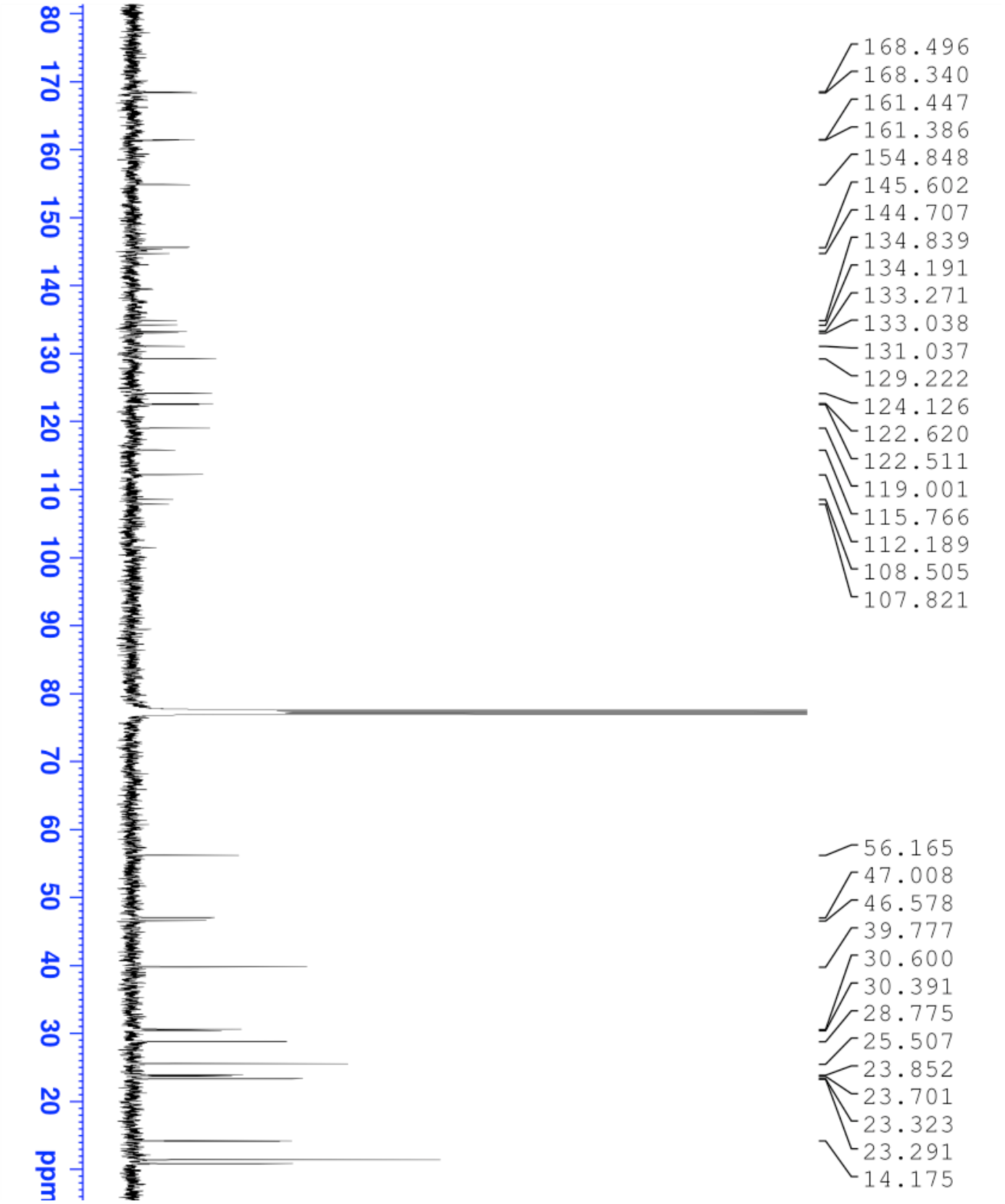


Figure S26. ^{13}C NMR of **DPP-2** in $CDCl_3$

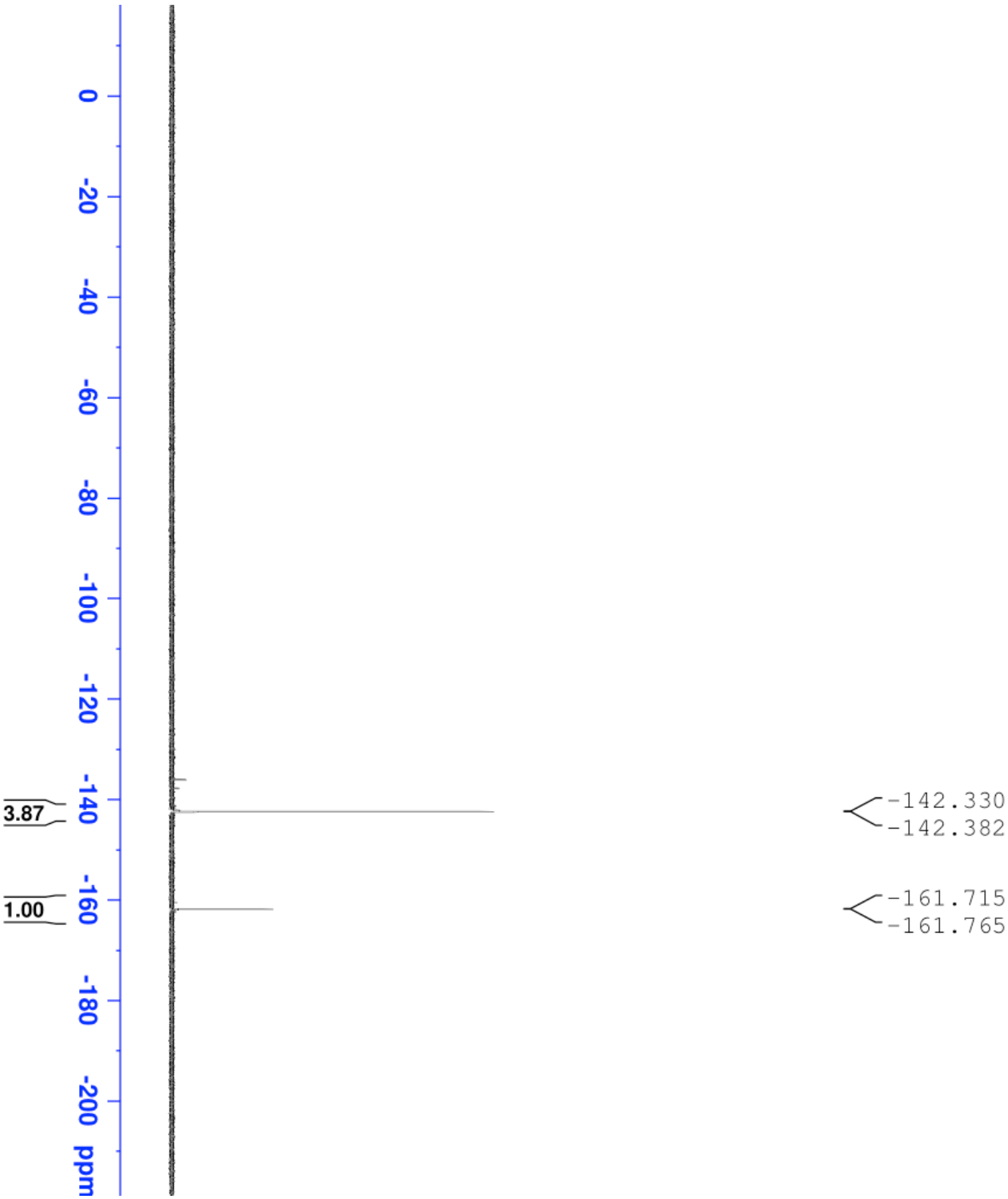


Figure S27. ^{19}F NMR of **DPP-2** in $CDCl_3$

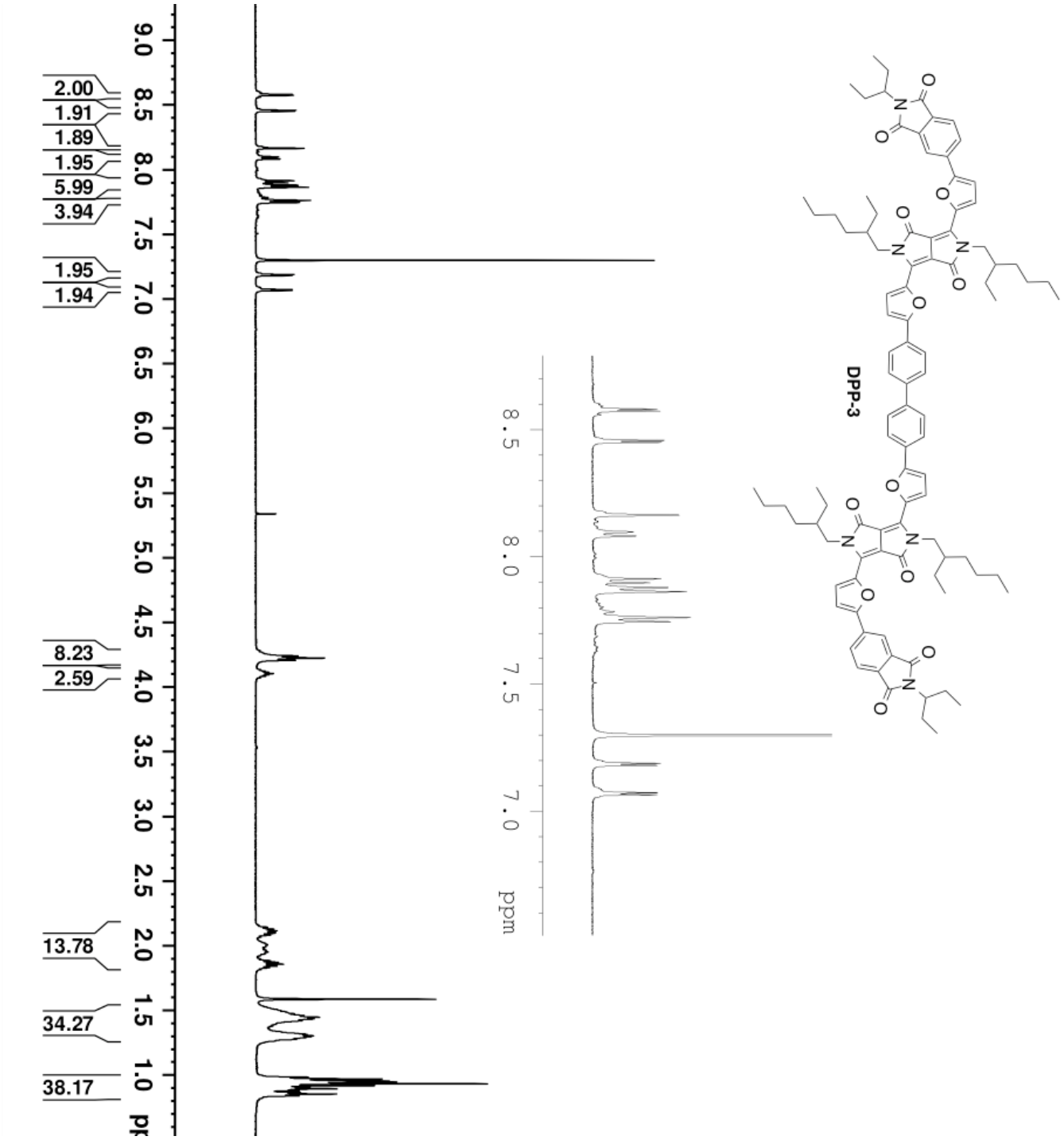


Figure S28. ^{1}H NMR spectra of **DPP-3** in $CDCl_3$

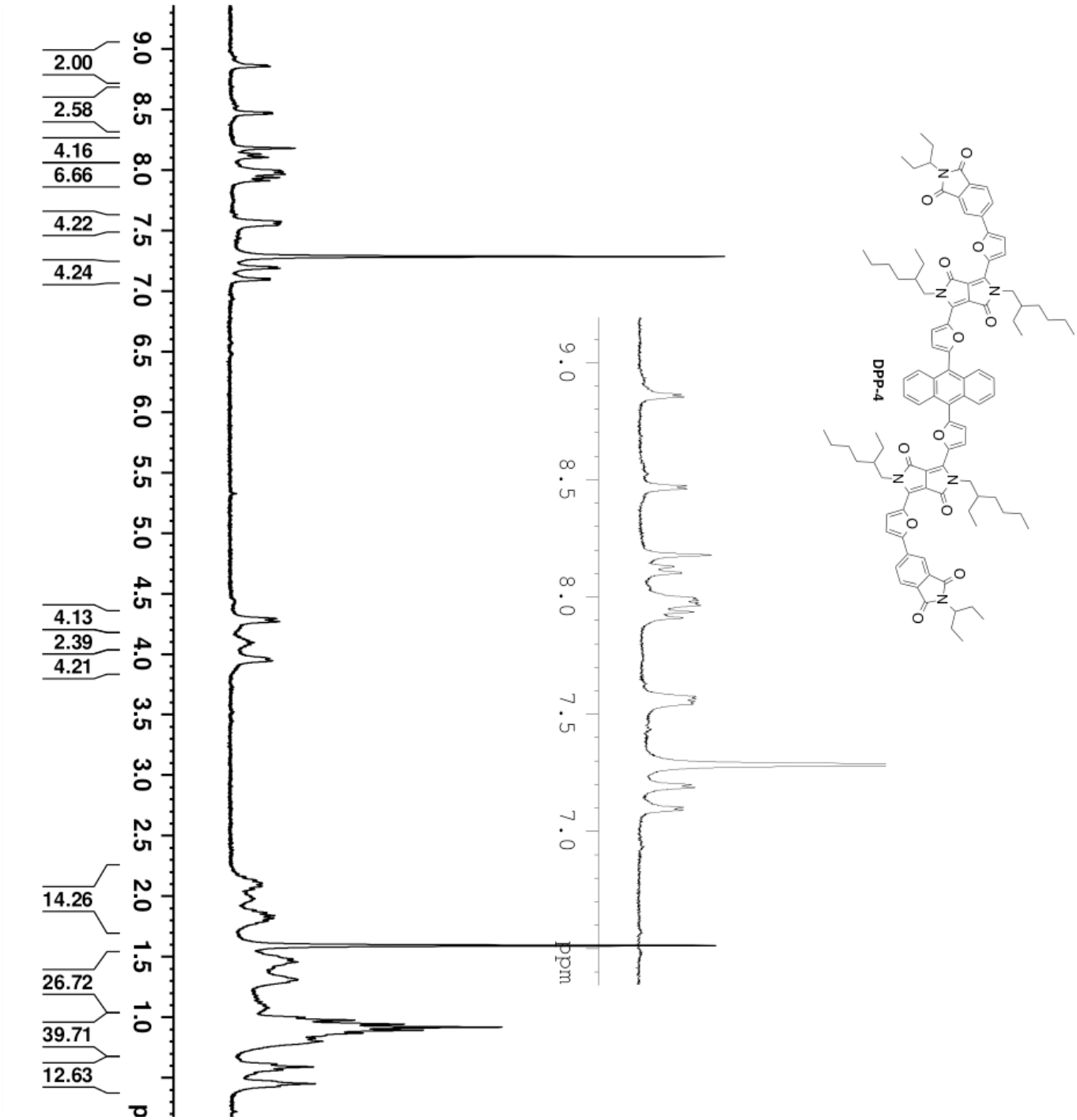


Figure S29. ^{1}H NMR spectra of **DPP-4** in $CDCl_3$

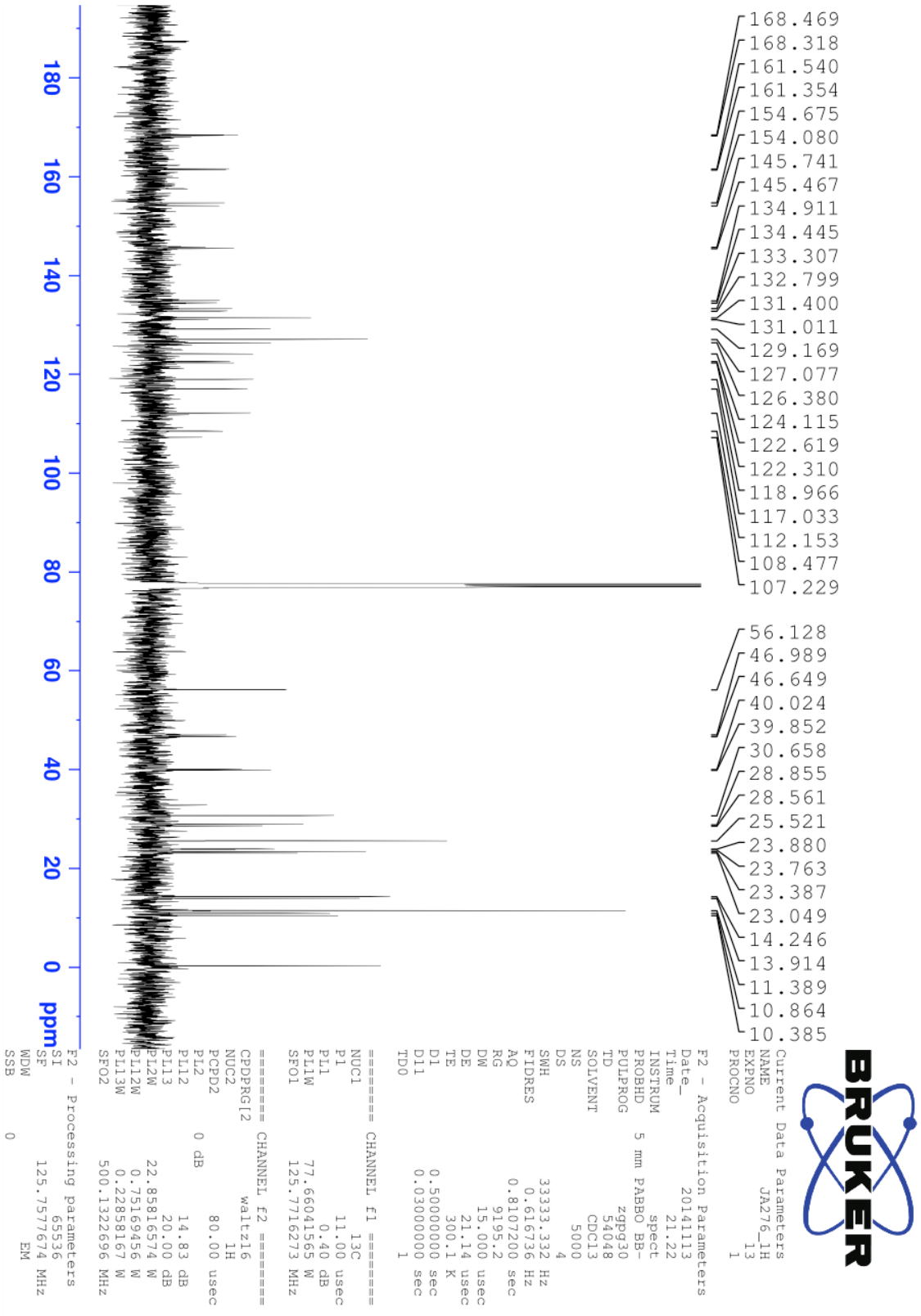


Figure S30. ^{13}C NMR spectra of **DPP-4** in $CDCl_3$

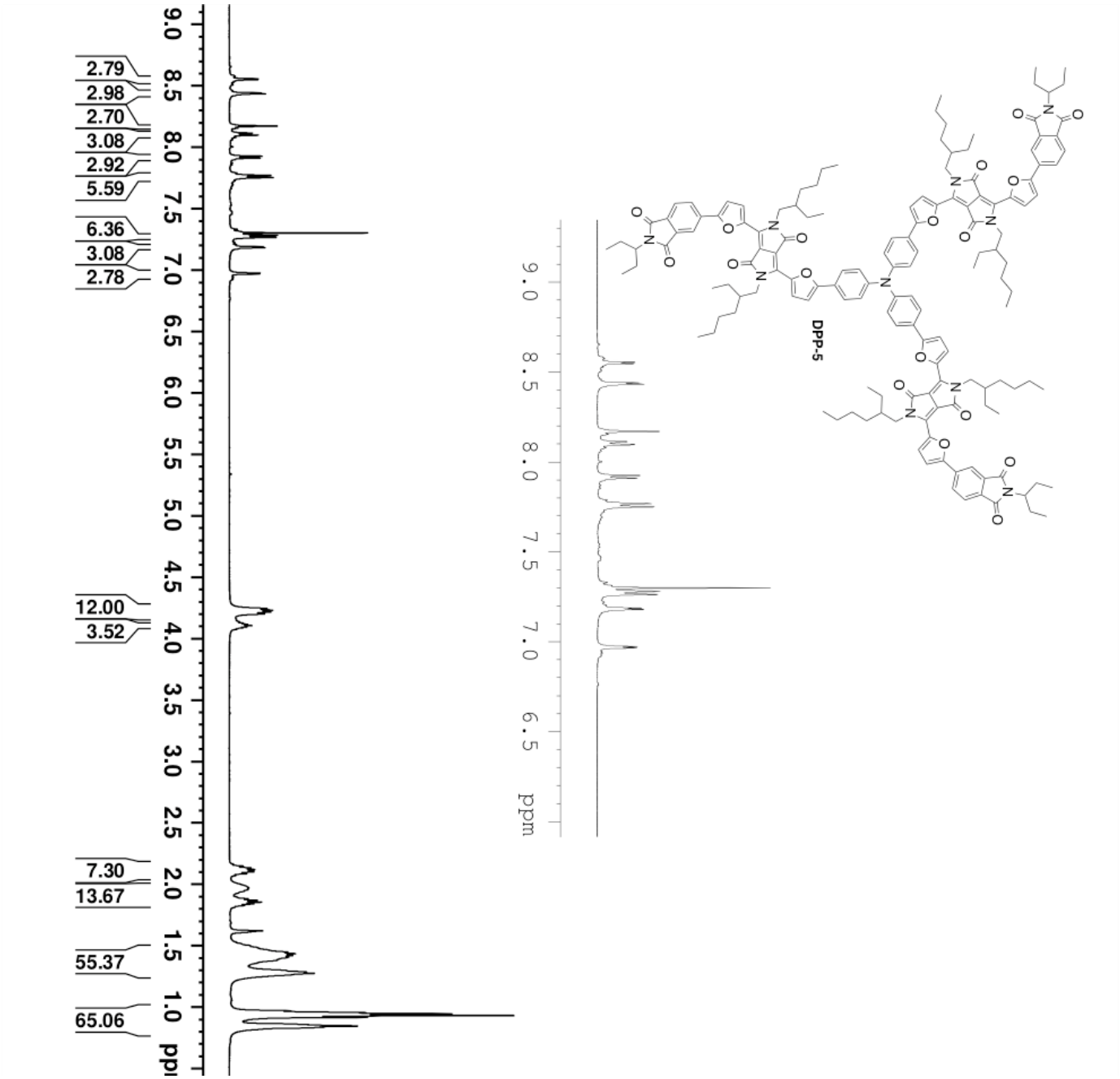


Figure S31. ^{1}H NMR spectra of **DPP-5** in $CDCl_3$

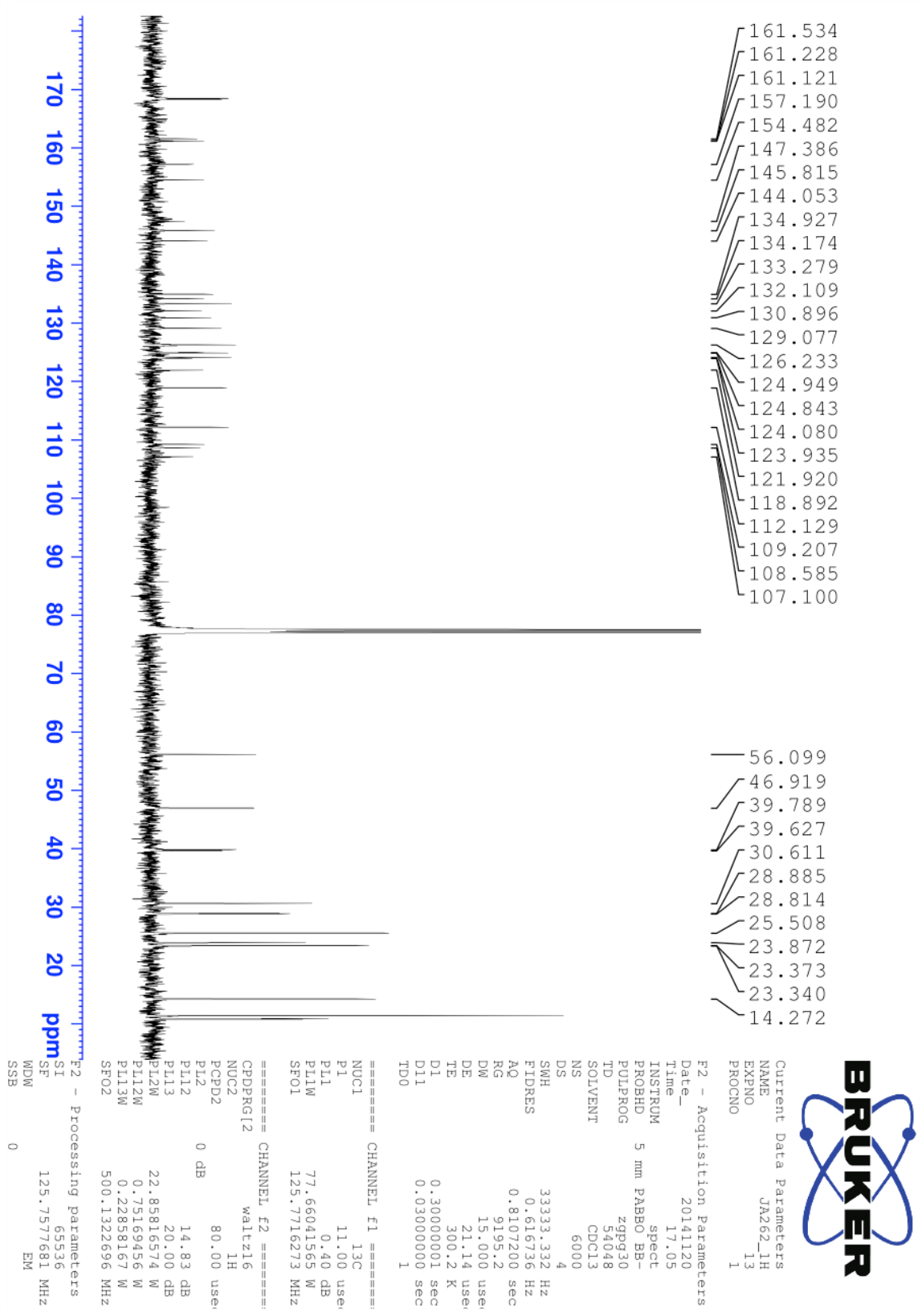


Figure S32. ^{13}C NMR spectra of **DPP-5** in $CDCl_3$

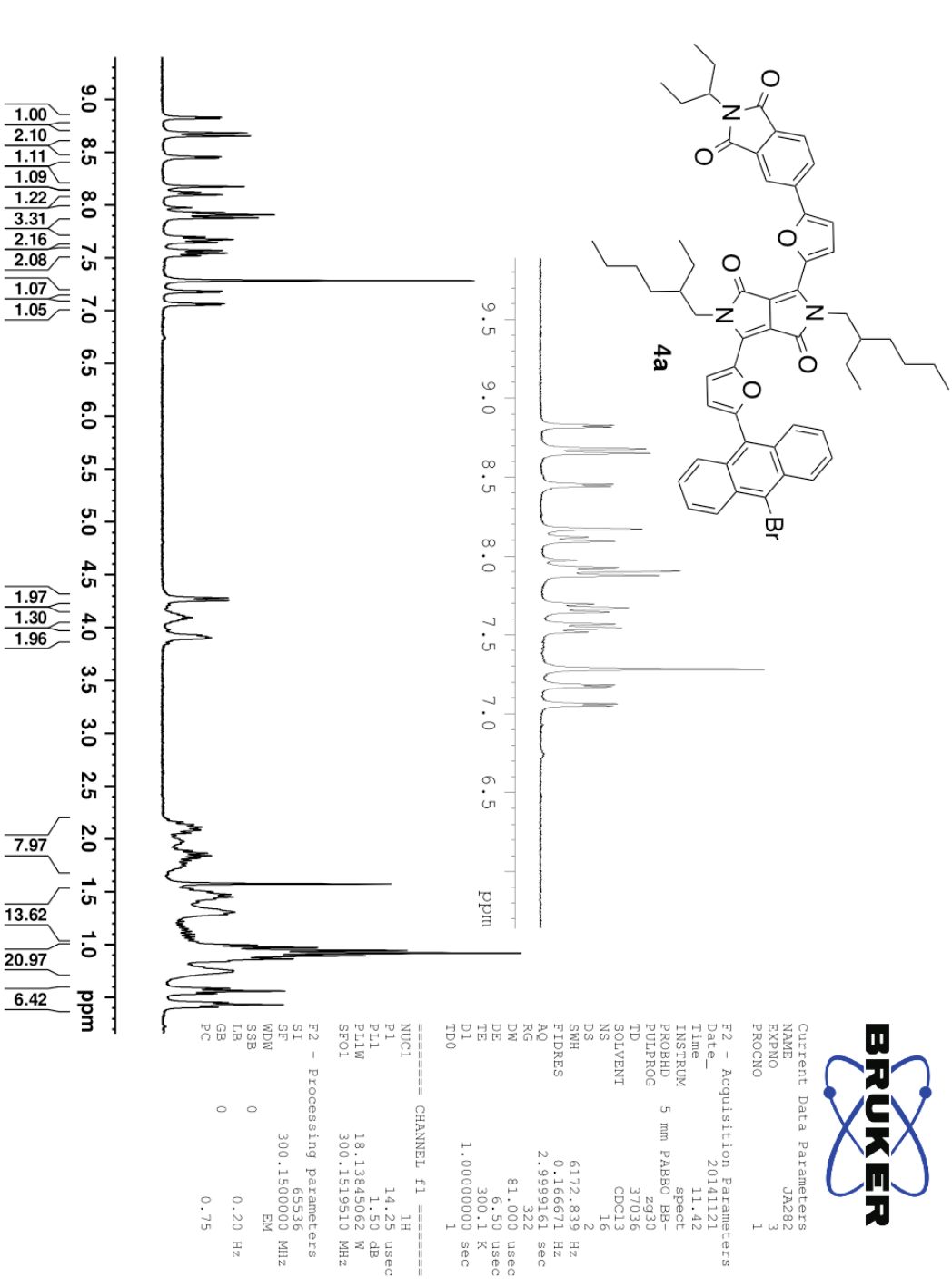


Figure S33. ^{1}H NMR spectra of compound **4a** in $CDCl_3$

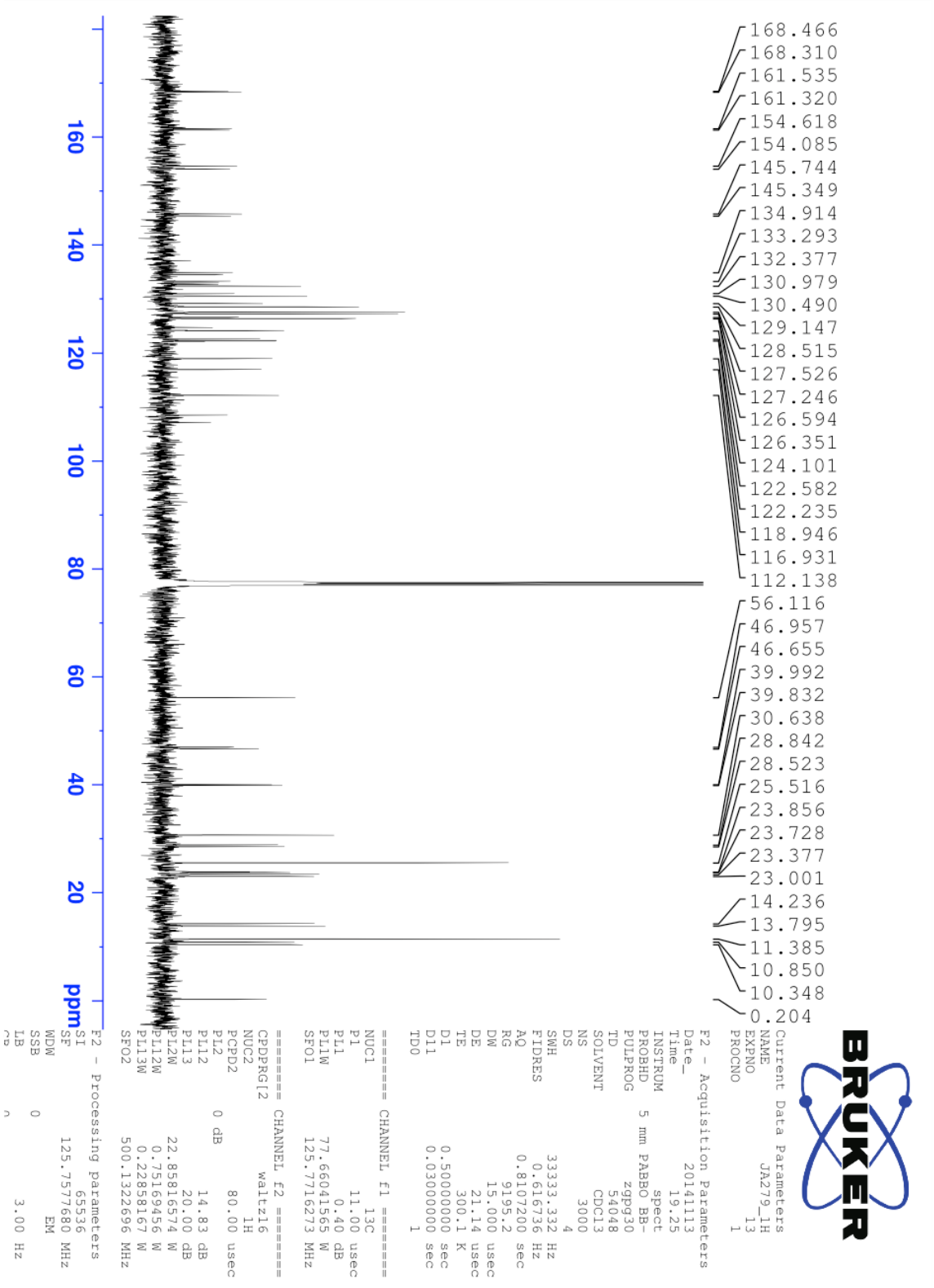


Figure S34. ^{13}C NMR spectra of compound **4a** in $CDCl_3$

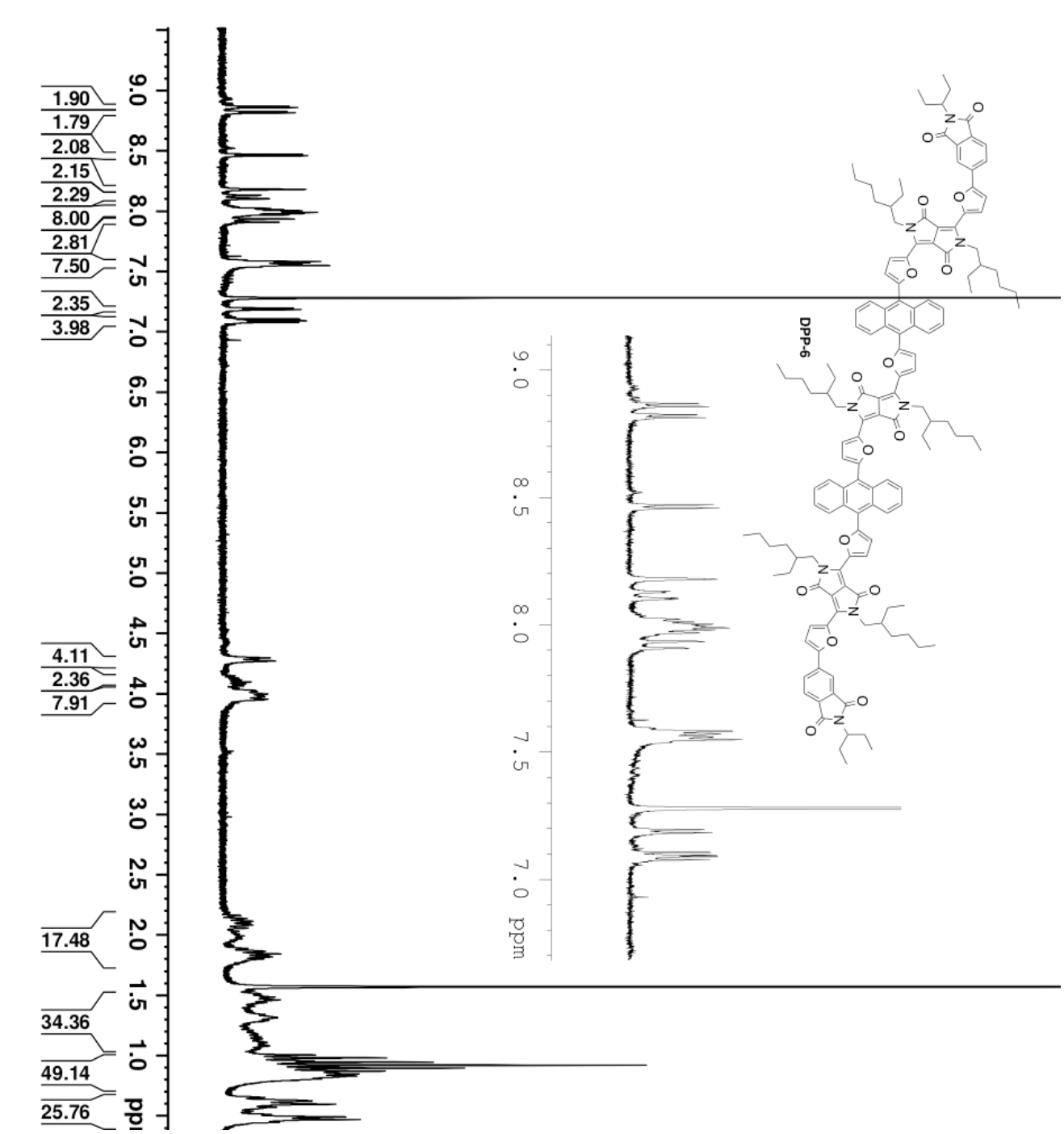


Figure S35. ^{1}H NMR spectra of **DPP-6** in $CDCl_3$

REFERENCES

[1] B. M. Kobilka, B. J. Hale, M. D. Ewan, A. V. Dubrovskiy, T. L. Nelson, V. Duzhkoc, M. Jeffries-EL, *Polym. Chem.* **2013**, *4*, 5329-5336

[2] A. D. Hensbee, J. –P. Sun, L. R. Rutledge, I. G. Hill, G. C. Welch, *J. Mater. Chem. A*, **2014**, *2*, 4198-4207

[3] S. M. McAfee, J. M. Topple, A. –J. Payne, J. –P. Sun, I. G. Hill, G. C. Welch, *ChemPhysChem*, **2015**, *16*, 1190-1202.