Electronic Supplementary Information (ESI)

Aromatic Polymers made by Reductive Polydehalogenation of Oligocyclic Monomers as Conjugated Polymers of Intrinsic Microporosity (C-PIMs)

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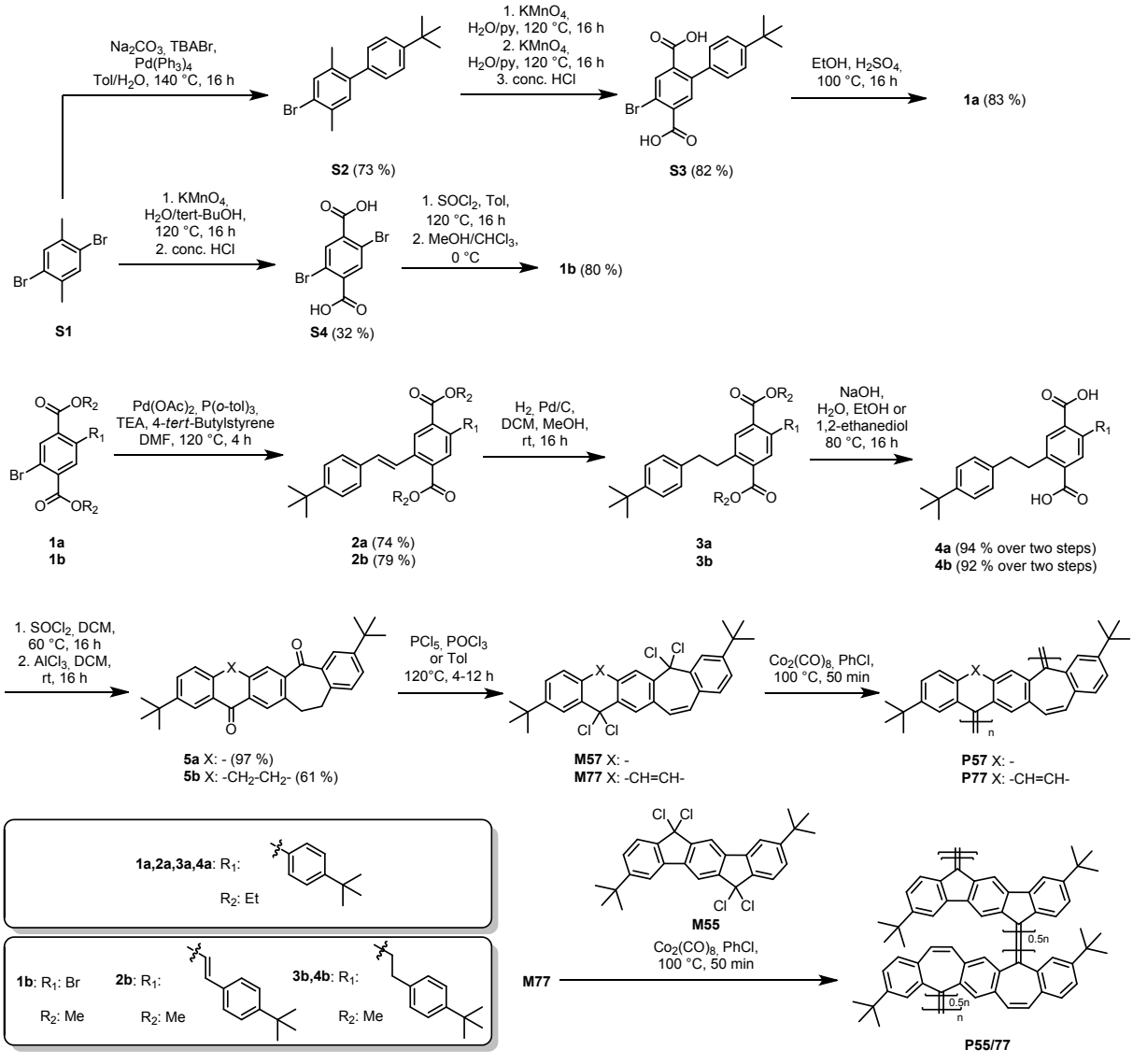
1. Materials and Methods

Experimental details

Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification, unless otherwise stated. The solvents used were of commercial p.a. quality. The reactions were carried out under argon with standard and Schlenk techniques. **Solution NMR measurements.** Solution ^{1}H and $^{13}C\{^{1}H\}$ NMR data of the monomers were recorded on a Bruker ARX 400 or Brucker AVANCE III 600 spectrometer using the solvent proton or carbon signals as internal standard at 300 K unless otherwise stated. Coupling constants are given in Hz and the multiplicity of signals is described as bs (broad singlet), s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), q (quartet) and m (multiplet). **Mass spectrometry analysis.** Mass spectrometry analysis was performed on a time-of-flight mass spectrometer (Bruker Daltonics MicrOTOF) equipped with a homemade multipurpose ion source (MPIS). For FD mass analysis of **DK57** a AccuTOF-GCX, JEOL (Germany) GmbH, Freising Mass spectrometer was used. **Nitrogen sorption measurements.** Nitrogen sorption isotherms for **P55** film and all CO_2 isotherms were measured using Micromeritics ASAP 2020 volumetric adsorption analyzer, Nitrogen and Hydrogen isotherms for other samples were measured using Micromeritics ASAP 2420 volumetric adsorption analyzer. Surface areas were calculated in the relative pressure (P/P_0) range from 0.05 to 0.16 of the adsorption branch. All samples were degassed offline at >100°C for 16 hours under dynamic vacuum. **scCO2 drying**. Supercritical carbon dioxide drying was carried out as described in the literature.[1] **UV/Vis spectroscopy.** UV/Vis absorption spectra were recorded in chloroform solutions or as spin-coated films (**P77**) on a quartz substrate with a JASCO V-670 spectrometer. **Photoluminescence spectroscopy**. Fluorescence measurements were carried out on Fluoromax-4 equipped with a Quanta-Phi integration sphere (Horiba) (used for photoluminescence quantum yield (PLQY) measurements in solution) at room temperature. **Gel permeation chromatography (GPC).** GPC measurements were carried out on a PSS/Agilent SECurity GPC System equipped with polystyrene gel columns using chloroform as eluent using polystyrene (PS) as an internal standard. **Thermogravimetric analysis (TGA).** Thermogravimetric analysis was performed on an EXSTAR6000 by heating samples at 10°C min^{-1} under nitrogen in open platinum pans from room temperature to 800 °C. **Secondary electron microscopy (SEM)** SEM images were recorded on a Tescan S8000G. Sample was dropped onto conducting carbon film and sputter coated with chromium (> 1nm). Images were recorded at 1 keV with a current of 30 pA. **Powder X-ray diffraction**. PXRD measurements were performed on a PANalytical Empyrean MPD, with a copper X-ray source producing Cu-*K*α (λ = 1.5418 Å) radiation in high throughput

transmission mode with focusing mirror and PIXCEL 1D detector. **Chemicals and solvents** All chemicals and solvents were purchased from abcr, TCI, Fisher Chemicals, Acros Organics, Strem, Roth, Sigma Aldrich, Grüssing GmbH and Oxchem and were used without purification. Dry DMF, dry toluene and dry chlorobenzene were purchased dried over molecular sieve (AcroSeal®) from Acros Organics. Dichloromethane was dried by filtering it through activated aluminum oxide into a dry flask with molecular sieve under an argon atmosphere. Poly(indenofluorene) (**P55** or **PIF**) and poly(diindenonaphthalene) (**PDIN**) were prepared as described in the literature.[2,3]

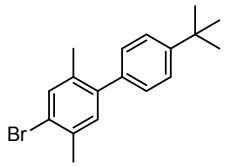
2. Materials Synthesis and Purification



Scheme S1: Syntheses scheme for monomers **M57** and **M77** and polymers **P57**, **P77** and **P55/77**.

Synthetic procedures

4-Bromo-4'-(*tert*-butyl)-2,5-dimethyl-1,1'-biphenyl (S2)

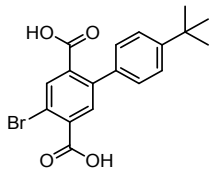


S2

S2 was prepared following a procedure described in the literature.[4] Under an argon atmosphere, 10.0 g (56 mmol) (4-*tert*-butylphenyl) boronic acid, 11.9 g (112 mmol) sodium carbonate, 1.8 g (5.6 mmol) TBABr, 25.6 g (97 mmol) **S1** and 0.65 g (0.56 mmol) tetrakis(triphenylphosphine) palladium(0) were added into a 1L three necked round bottom flask. The solids were dissolved in 300 mL of toluene and 150 mL of water under light exclusion and heated to reflux for 16 h. After cooling, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The organic layers were washed with brine and dried over $MgSO_4$. After drying *in vacuo*, the colourless liquid was purified by column chromatography with silica gel using *n*-hexane as eluent. After drying, the product **S2** was obtained in 73 % yield (13.1 g) as a colourless liquid that solidifies overnight.

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] 7.43 (m, 3H), 7.22 (dt, *J* = 8.2, 4.0 Hz, 2H), 7.10 (s, 1H), 2.38 (s, 3H), 2.23 (s, 3H), 1.37 (s, 9H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ [ppm] 150.1, 141.2, 138.1, 135.0, 134.9, 133.8, 132.3, 128.8, 125.2, 123.4, 34.7, 31.5, 22.4, 19.9. **MS-flow injection (APCI)**: m/z [M^+] = 316.0821 (calc. m/z [M^+] = 316.0821)

4-Bromo-4'-(*tert*-butyl)-[1,1'-biphenyl]-2,5-dicarboxylic acid (S3)

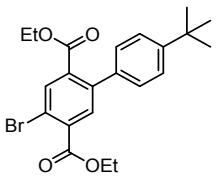


S3

S3 was prepared following a procedure described in the literature with modifications.[4] In a 1 L three necked round bottom flask, 13.4 g (42.2 mmol) **S2** was suspended in 180 mL of pyridine and heated to reflux, followed by dropwise addition of 180 mL of a hot saturated solution (46.7 g, 296 mmol in water) potassium permanganate. After complete addition, the mixture was heated to reflux overnight. After filtering the warm solution, the brown precipitate was washed with hot water and ethyl acetate. The filtrate was poured into dilute potassium hydroxide solution and the aqueous phase was extracted with ethyl acetate five times. The aqueous layer contains the product and was put aside. The organic layers were dried *in vacuo* and the residue was subjected to this same reaction sequence repeatedly one more time. The combined aqueous layers were acidified by dropwise addition of concentrated hydrochloric acid, followed by addition of sodium chloride to the aqueous layer and extraction with ethyl acetate for six times. The organic layer was washed with brine, dried over magnesium sulfate and the solvent was removed *in vacuo* to give **S3** as white powder in 82 % yield (13.8 g).

^{1}H NMR (600 MHz, DMSO) δ [ppm] 13.61 (bs, 1H), 13.35 (bs, 1H), 7.97 (s, 1H), 7.70 (s, 1H), 7.47 (dt, *J* = 8.4, 4,1 Hz 2H), 7.32 (dt, *J* = 8.4, 4,1 Hz, 2H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ [ppm] 167.8, 166.6, 150.3, 139.7, 135.9, 135.8, 135.5 133.7, 132.3, 127.9, 125.2, 118.4, 34.3, 31.1. **MS-flow injection (APCI)**: m/z [M^++H^+] = 377.0388 (calc. m/z [M^++H^+] = 377.0383)

4-Bromo-4'-(*tert*-butyl)-[1,1'-biphenyl]-2,5-diethylester (1a)



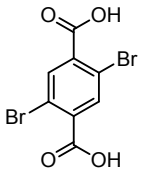
1a

4-Bromo-4'-(*tert*-butyl)-[1,1'-biphenyl]-2,5-diethyl ester was prepared following a procedure described in the literature with modifications.[4] In a 250 mL round bottom flask, 7.0 g (19 mmol) **S3** were suspended in 56 mL of ethanol, followed by careful addition of 9.1 mL concentrated sulfuric acid. The reaction mixture was heated to reflux for 16 h. After cooling,

the mixture was poured into water and extracted with ethyl acetate three times. The organic layers were dried over magnesium sulfate and the solvents were removed *in vacuo*. After column chromatography over silica gel using ethyl acetate:*n*-hexane 5:95 as eluent, **1a** was obtained as a white waxy solid in 83 % yield (6.7 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 8.06 (d, *J* = 3.1 Hz, 1H), 7.77 (s, 1H), 7.42 (dt, *J* = 8.5, 4,2 Hz, 2H), 7.24 (dt, *J* = 8.5, 4.2 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.35 (s, 9H), 0.98 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ [ppm] 167.0, 165.7, 151.1, 141.4, 136.6, 135.2, 134.9, 134.7, 133.2, 128.1, 125.3, 119.9, 62.1, 61.6, 34.7, 31.5, 14.3, 13.6. **MS-flow injection (APCI)**: m/z [M^++H^+] = 433.1016 (calc. m/z [M^++H^+] = 433.1009)

2,5-Dibromoterephthalic acid (S4)

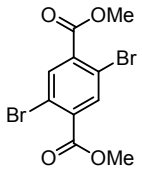


S4

S4 was prepared following a procedure described in the literature.[5] In a 2 L-three necked round bottom flask, 1,4-dibromo-2,5-dimethylbenzene (26.2 g, 99 mmol) was suspended in 100 mL of *tert*-butanol, followed by addition of 1 L of water. The mixture was heated to 100°C, followed by careful and portion wise addition of potassium permanganate (76.0 g, 481 mmol). The mixture was heated at 100°C for 16 h, afterwards 10 mL of ethanol was carefully added. The mixture was filtered, and the filtrate was acidified with concentrated, aqueous HCl solution. The precipitate was washed with dichloromethane and dried *in vacuo*. The product was obtained as a white solid (10.3 g, 32 %)

^{1}H NMR (400 MHz, d_6-DMSO) δ [ppm] 13.89 (bs, 2H), 8.01 (s, 2H). **^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO)** δ [ppm] 165.5, 137.0, 134.9, 118.8.

Dimethyl 2,5-dibromoterephthalate (1b)

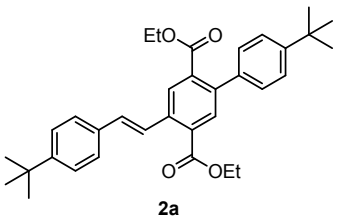


1b

In a dry 250 mL two necked round bottom flask, 13.7 g (42 mmol) **S4** was suspended in 150 mL of dry toluene under argon atmosphere. After addition of 2 drops DMF, 9.2 mL (127 mmol) thionyl chloride were added dropwise. The mixture was heated to reflux for 4 h. After cooling to room temperature, the volatile compounds were removed by vacuum distillation at 90°C. The remaining yellow solid was dissolved in 10 mL of dry chloroform, followed by the addition of 50 mL of methanol. The solvents were removed *in vacuo* and the residue was two times recrystallized from ethanol to yield **1b** as beige crystals (11.9 g, 80 %).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] 8.04 (s, 2H), 3.95 (s, 6H). **^{13}C{^{1}H} NMR (101 MHz, $C_2D_2Cl_4$)** δ [ppm] 164.4, 136.4, 135.2, 120.1, 53.0.

(*E*)-4'-(*tert*-Butyl)-4-(4-(*tert*-butyl)styryl)-[1,1'-biphenyl]-2,5-diethylester (2a)



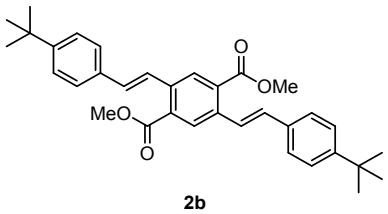
2a

2a was prepared following a procedure described in the literature.[4] In a dry three necked round bottom flask, 6.0 g (14 mmol) **1a**, 0.16 g (0.69 mmol) palladium(II)acetate and 0.21 g (0.69 mmol) tri(*o*-tolyl)phosphine were dissolved in 110 mL of dry DMF under an argon atmosphere. After the subsequent addition of 7.6 mL (42 mmol) of 4-*tert*-butylstyrene and 7.7 mL (55 mmol) of triethylamine the mixture was stirred for 20 minutes. Then, the mixture was heated to 110°C for 4 h. After cooling, the mixture was poured into 100 mL of water and extracted with ethyl acetate for six times. The organic phases were combined and washed three times with 6M aqueous hydrochloric acid, water and brine. After drying with magnesium

sulfate, the solvents were removed *in vacuo* to give a yellow liquid. After final purification by silica column chromatography using DCM:*n*-hexane 2:8 as eluent and recrystallisation from DCM:ethanol **2a** was obtained as a pale yellow solid (5.3 g, 74 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 8.13 (s, 1H), 7.99-7.93 (m, 2H), 7.53 (dt, *J* = 8.3, 4.0 Hz, 2H), 7.46-7.40 (m, 4H), 7.30 (dt, *J* = 8.5, 4.2 Hz, 2H), 7.14 (d, *J* = 16.3 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.38 (s, 9H), 1.36 (s, 9H), 0.97 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ [ppm] 168.7, 167.0, 151.5, 150.7, 140.4, 137.9, 137.5, 134.7, 134.6, 132.8, 132.3, 130.9, 128.2, 128.1, 126.9, 125.8, 125.3, 125.2, 61.5, 61.4, 34.8, 34.7, 31.5, 31.4, 14.5, 13.6. **MS-flow injection (APCI)**: m/z [M^++H^+] = 513.3003 (calc. m/z [M^++H^+] = 513.2999)

Dimethyl 2,5-bis((*E*)-4-(*tert*-butyl)styryl)terephthalate (2b)

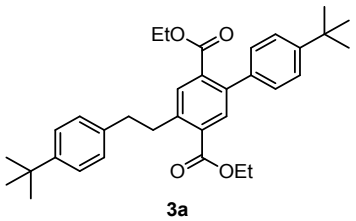


2b

2b was prepared following essentially the same procedure as described for **2a**, starting from 10.0 g (28 mmol) **1b**, 0.64 g (2.8 mmol) palladium(II)acetate, 0.87 g (2.8 mmol) tri(*o*-tolyl)phosphine, 100 mL of DMF, 31.2 mL (170 mmol) of 4-*tert*-butylstyrene and 48 mL (340 mmol) of trimethylamine. The product was purified by silica column chromatography using ethyl acetate:*n*-hexane 9:1 as eluent and recrystallization from ethyl acetate and DCM. The product was obtained as a yellow solid (11.5 g, 79 %).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] 8.24 (d, *J* = 6.9 Hz, 1H), 7.86 (d, *J* = 16.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 16.2 Hz, 1H), 4.00 (s, 3H), 1.36 (s, 9H). **^{13}C{^{1}H} NMR (101 MHz, $C_2D_2Cl_4$)** δ [ppm] 167.2, 151.5, 137.1, 134.0, 131.9, 131.3, 128.9, 126.6, 125.7, 125.0, 52.6, 34.5, 31.2. **MS-flow injection (APLI)**: m/z [M^+] = 510.2155 (calc. m/z [M^+] = 510.2770)

4'-(*tert*-Butyl)-4-(4-(*tert*-butyl)phenethyl)-[1,1'-biphenyl]-2,5-diethylester (3a)

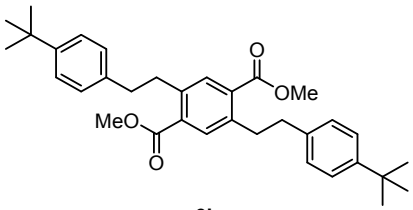


3a

In a 250 mL Büchi miniclave pressure reactor **2a** (5.2 g, 10 mmol) was dissolved in 50 mL of DCM. After subsequent addition of 0.43 g (0.43 mmol) palladium on carbon (10 %) and 88 mL of methanol, the reaction vessel was closed and evacuated and filled with hydrogen (1.5 bar) (**Caution:** mixtures of palladium on carbon and alcohols can self-ignite). The hydrogen pressure was adjusted to 1.5 bar several times until the manometer did not show a loss of pressure (usually after 16 h). The reaction mixture was filtered over celite and the solvents were removed *in vacuo* to give **3a** as white waxy solid (5.2 g, >99 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] 7.91 (s, 1H), 7.67 (s, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.33-3.28 (m, *J* = 16.7 Hz, 2H), 2.96-2.91 (m, *J* = 16.7 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 4H), 1.37 (s, 9H), 1.33 (s, 9H), 0.96 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ [ppm] 168.6, 167.1, 150.6, 149.0, 142.4, 139.9, 138.9, 137.7, 134.4, 132.8, 132.3, 132.2, 128.3, 128.3, 125.4, 125.2, 61.3, 61.2, 37.6, 36.3, 34.7, 34.5, 31.6, 31.5, 14.5, 13.6. **MS-flow injection (APCI)**: m/z [M^++H^+] = 515.3159 (calc. m/z [M^++H^+] = 515.3156)

Dimethyl 2,5-bis(4-(*tert*-butyl)phenethyl)terephthalate (3b)

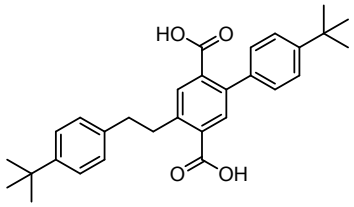


3b

3b was prepared following essentially the same procedure as described for **3a**, using 2.96 g of **3b** (5.75 mmol) 0.19 g (0.18 mmol) palladium on carbon (10 %), 70 mL of DCM, and 100 mL of propan-2-ol. The product was obtained as white solid (3.0 g, >99 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] 7.75 (s, 2H), 7.34 (dt, *J* = 8.3, 4.1 Hz, 4H), 7.19 (dt, *J* = 8.3, 4.1 Hz, 4H), 3.92 (s, 6H), 3.25-3.21 (m, 4H), 2.90-2.85 (m, 4H), 1.33 (s, 18H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ [ppm] 167.5, 148.9, 141.2, 138.8, 133.3, 132.6, 128.3, 125.4, 52.3, 37.7, 36.3, 34.5, 31.6. **MS-flow injection (APCI)**: m/z [M^++H^+] = 515.3055 (calc. m/z [M^++H^+] = 515.3156)

4'-(*tert*-Butyl)-4-(4-(*tert*-butyl)phenethyl)-[1,1'-biphenyl]-2,5-dicarboxylic acid (4a)

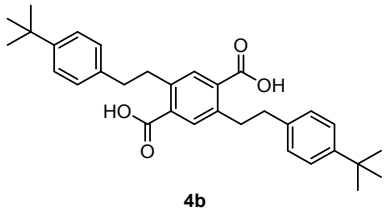


4a

In a 250 mL round bottom flask, 5.2 g (10 mmol) **3a** and 11.2 g (85 w%, 170 mmol) potassium hydroxide in 13 mL of water were suspended in 65 mL of ethanol. The reaction mixture was heated to reflux for 16 h. After cooling, the solution was acidified with 6M aqueous hydrochloric acid. The mixture was extracted with ethyl acetate five times. After drying with magnesium sulfate, the organic phase was dried and the solvents were removed *in vacuo*. The product was obtained as a white powder 4.4 g (94 %).

^{1}H NMR (600 MHz, d_6-DMSO) δ [ppm] 13.04 (bs, 2H), 7.77 (s, 1H), 7.64 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.33-7.28 (m, 4H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.24-3.17 (m, 2H), 2.85-2.79 (m, 2H), 1.31 (s, 9H), 1.27 (s, 9H). **^{13}C{^{1}H} NMR (151 MHz, d_6-DMSO)** δ [ppm] 169.2, 168.0, 149.7, 148.2, 141.4, 138.6, 137.9, 136.8, 135.1, 132.3, 132.0, 131.1, 127.9, 125.1, 125.0, 36.8, 35.5, 34.2, 34.0, 31.2, 31.1. **MS-flow injection (APCI)**: m/z [M^++H^+] = 459.2539 (calc. m/z [M^++H^+] = 459.2530)

2,5-Bis(4-(*tert*-butyl)phenethyl)terephthalic acid (4b)

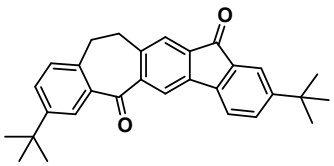


4b

4b was prepared following essentially the same procedure as described for **4a**, using 4.1 g (8.0 mmol) **3b**, 5.4 g (136 mmol) sodium hydroxide, 20 mL of water and 150 mL of ethylene glycol. The mixture was heated to 160°C for 16 h. The product was obtained as white powder (3.6 g, 92 %).

^{1}H NMR (600 MHz, d_6-DMSO) δ [ppm] 13.17 (s, 2H), 7.73 (s, 2H), 7.30 (d, *J* = 8.2 Hz, 4H), 7.17 (d, *J* = 8.2 Hz, 4H), 3.18-3.10 (m, 4H), 2.81-2.74 (m, 4H), 1.26 (s, *J* = 12.4 Hz, 18H). **^{13}C{^{1}H} NMR (151 MHz, d_6-DMSO)** δ [ppm] 168.3, 148.1, 140.0, 138.5, 133.1, 132.4, 127.9, 124.9, 36.9, 35.5, 34.0, 31.2. **MALDI-TOF**: m/z [M^++Na^+] = 509.2655 (calc. m/z [M^++H^+] = 509.2668)

2,8-Di-*tert*-butyl-11,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]fluorene-6,14-dione (5a)



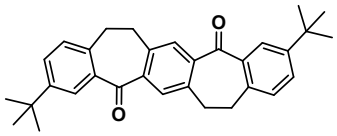
5a

5a was prepared based on a literature procedure with minor modifications[4]: In a dry three necked round bottom flask, 2.0 g (4.4 mmol) **4a** was suspended in 50 mL of dry DCM under an argon atmosphere. After addition of two drops of DMF, 5.3 mL (27 mmol) thionyl chloride were added dropwise. The reaction mixture was heated to reflux for 16 h. During this time, the white solid dissolved and the solution turned yellow. The volatile compounds were removed by vacuum distillation. The yellow solid was dissolved in 250 mL of dry DCM under argon atmosphere, 1.3 g (9.4 mmol) aluminium chloride was added at 0 C and the reaction turned orange immediately. The reaction was allowed to warm up to room temperature and

after 16 h the reaction mixture was poured into 100 mL of 10 % aqueous hydrochloric acid. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate three times. The organic phase was dried over magnesium sulfate and the solvents were removed *in vacuo*. The product was purified by silica gel column chromatography with *n*-hexane:ethyl acetate (gradient 95:5 → 90:10) as eluent to give **5a** as a yellow solid (1.8 g, 97 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] 8.06 (d, *J* = 2.2 Hz, 1H), 7.98 (s, 1H), 7.72 (dd, *J* = 1.8, 0.5 Hz, 1H), 7.57 – 7.46 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 1H), 3.24 – 3.16 (m, 4H), 1.36 (s, 9H), 1.35 (s, 9H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ [ppm] 196.3, 194.0, 153.1, 150.0, 144.8, 142.6, 142.5, 141.7, 139.4, 137.4, 137.3, 134.6, 132.3, 130.4, 129.9, 127.6, 125.1, 121.9, 121.7, 120.5, 35.2, 34.8, 34.7, 34.5, 31.4, 31.3. **MS-flow injection (APCI)**: m/z [M^++H^+] = 423.2359 (calc. m/z [M^++H^+] = 423.2319)

3,11-Di-*tert*-butyl-7,8,15,16-tetrahydrodibenzo[*d*,*d*']benzo[1,2-*a*;4,5-*a*']dicyclodi[7]-annulene-5,13-dione (5b)

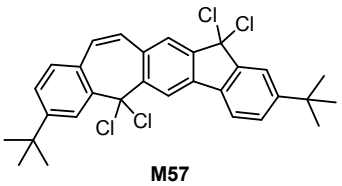


5b

5b was prepared following essentially the same procedure described for **5a**, by using 3.8 g (7.9 mmol) **5b**, 6.9 mL (95 mmol) thionyl chloride in 180 mL of DCM in the chlorination reaction of the diacid. The cyclization was carried out using 6.5 g (49 mmol) aluminium chloride and 200 mL of DCM for 3 h. After silica gel column chromatography with *n*-hexane:ethyl acetate (gradient 95:5 → 90:10), the product was obtained as a pale yellow solid (2.2 g, 61 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] 8.05 (d, *J* = 2.2 Hz, 2H), 7.84 (s, 2H), 7.49 (dd, *J* = 8.0, 2.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.24-3.18 (m, 8H), 1.35 (s, 18H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ [ppm] 195.8, 149.8, 141.9, 139.9, 139.6, 137.7, 131.4, 130.2, 129.7, 127.5, 34.8, 34.7, 34.4, 31.4. **MS-flow injection (APCI)**: m/z [M^++H^+] = 451.2639 (calc. m/z [M^++H^+] = 451.2632).

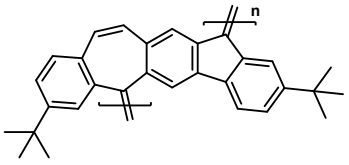
2,8-Di-*tert*-butyl-6,6,14,14-tetrachloro-6,11,12,14-tetrahydrobenzo[4,5] cyclohepta[1,2-b]fluorene (M57)



M57

M57 was prepared based on a literature procedure[6,7]: In a dry 50 mL two necked round bottom flask, 1.4 g (3.3 mmol) **5a** and 3.6 g (18 mmol) phosphorous pentachloride were dissolved in 10 mL of toluene under an argon atmosphere. The reaction mixture was heated to 120°C for 12 h followed by vacuum distillation/sublimation of the volatile compounds. The residue was dried for 45 minutes at 90°C *in vacuo*. The product was obtained as a yellow, waxy solid and was used directly without further purification.

Polymer P57

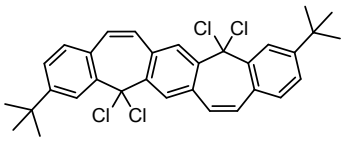


P57

P57 was prepared following a literature procedure[2]: In a dry 50 mL Schlenk-tube, 0.80 g (1.5 mmol) **M57** and 1.8 g (5.2 mmol) dicobalt octacarbonyl were dissolved in 15 mL of dry chlorobenzene under an argon atmosphere and heated to 100°C in a preheated oil bath for 50 minutes (**Caution:** reaction evolves large amounts of CO gas, Co_2CO_8 should be handled carefully because of possible self-ignition). After addition of 6.1 mL of 1,2-dibromoethane, the reaction mixture was heated for further 10 minutes. The mixture was cooled down and added dropwise into a mixture of 600 mL of cold methanol and 100 mL of 2M aqueous HCl solution. The precipitate was collected by filtration and washed with methanol. The red solid was extracted with methanol, acetone and ethyl acetate using a Soxhlet extractor. After re-precipitation into cold methanol the product was filtered as a red solid (acetone-fraction: 0.30 g, 51 %; ethyl acetate fraction: 0.19 g, 33 %).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] 9.08-6.07 (m, 10 H), 1.79-0.40 (m, 21 H). The signals in the carbon NMR appear as distinctly broadened sets of indistinguishable signals, therefore the signal areas are stated below: **^{13}C{^{1}H} NMR (101 MHz, $C_2D_2Cl_4$)** δ [ppm] 154.4-147.0, 143.2-135.3, 134.0-115.6, 35.4-33.6, 31.3. **GPC** ($CHCl_3$): M_n: 10,400 g/mol; M_w: 14,400 g/mol, M_w/M_n: 1.39. **S_{BET}**: 444 m²/g. **UV/Vis** ($CHCl_3$), λ_{max}: 321, 485 nm.

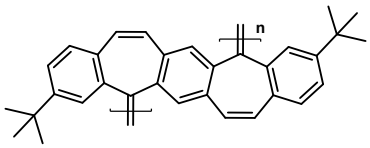
3,11-Di-*tert*-butyl-5,5‘,13,13‘-tetrachlor-dibenzo[*d*,*d*’]benzo[1,2-*a*:4,5-*a*’]di[7]annulene (M77)



M77

M77 was prepared based on a literature procedure[6,7]: In a dry 50 mL two necked round bottom flask, 1.2 g (2.7 mmol) **5a** and 2.5 g (11.9 mmol) phosphorous pentachloride were dissolved in 10 mL of phosphorous oxychloride under an argon atmosphere. The reaction mixture was heated to 120°C for 4 h (progress of the reaction is monitored by NMR) followed by vacuum distillation/sublimation of the volatile compounds. The residue was dried for 45 minutes at 90 C *in vacuo*. The product was obtained as a yellow waxy solid and was used without further purification.

Polymer P77



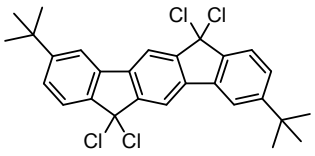
P77

P77 was prepared following essentially the same procedure described for **P57**, using 1.4 g (2.5 mmol) **M77**, 2.9 g (8.5 mmol) dicobalt octacarbonyl, 20 mL of chlorobenzene and 10 mL of 1,2-dibromoethane. The product was obtained as yellow solid (acetone-fraction: 0.84 g, 81 %; ethyl acetate fraction: 0.16 g, 16 %).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] 7.64-6.06 (m, *J* = 53.7 Hz, 1H), 1.66-0.19 (m, 2H). The signals in the carbon NMR appear as distinctly broadened sets of indistinguishable signals, therefore the signal areas are stated below: **^{13}C{^{1}H} NMR (151 MHz, $C_2D_2Cl_4$)** δ [ppm] 152.8-145.8, 143.5-133.5, 133.5-119.6, 35.3-32.8, 32.8-29.2. **GPC**($CHCl_3$), M_n: 9,500 g/mol; M_w:

20,200 g/mol, M_w/M_n:1.39. **S_{BET}**: 101 m²/g. **UV/Vis** ($CHCl_3$), λ_{max}: 331 nm, PLQY ($CHCl_3$): 2.54 %.

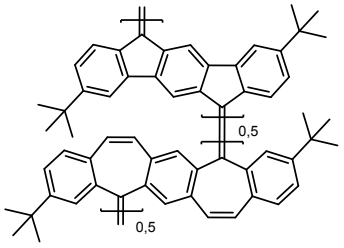
3,9-Di-*tert*-butyl-6,6,12,12-tetrachloro-6,12-dihydroindeno[1,2-*b*]fluorene (M55)



M55

M55 was prepared based on a literature procedure[8]: 1.4 g (3.31 mmol) 3,9-di-*tert*-butyl-6,12-dioxo-6,12-dihydroindeno[l,2-b]fluorene and 3.6 g (17.49 mmol) phosphorous pentachloride were dissolved in 10 mL of dry toluene under an argon atmosphere. The mixture was heated to reflux for 12 h, followed by vacuum distillation/sublimation of volatile compounds at 90°C. The yellow solid was used directly without further purification.

Polymer P55/77

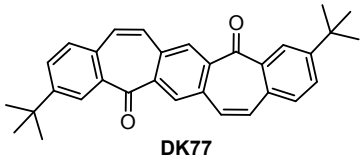


P55/77

P55/77 was prepared following essentially the same procedure as described for **P57**, using 0.50 g (1.0 mmol) **M55** and 0.56 g (1.0 mmol) **M77**, 18 mL of chlorobenzene and 8.1 mL of 1,2-dibromoethane. The product was obtained as deep blue solid (acetone-fraction: 0.32 g, 21 %; ethyl acetate fraction: 0.20 g, 13 %).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] 9.32-6.17 (m, 1H), 1.89-0.70 (m, 2H). The signals in the carbon NMR appear as distinctly broadened sets of indistinguishable signals, therefore the signal areas are stated below: **^{13}C{^{1}H} NMR (151 MHz, $C_2D_2Cl_4$)** δ [ppm] 155.3-151.9, 143.1-138.4, 137.4-134.4, 132.5-120.7, 118.7-113.2, 36.6-32.5, 32.5-28.7. **GPC** ($CHCl_3$): M_n: 5,500 g/mol; M_w: 7,400 g/mol, M_w/M_n: 1.35. **S_{BET}**: 609 m²/g. **UV/Vis** ($CHCl_3$), λ_{max}: 705, 511(sh), 309 nm.

3,11-Di-*tert*-butyl-dibenzo[*d*,*d*']benzo[1,2-*a*:4,5-*a*']di[7]annulene-5,13-dione (DK77)

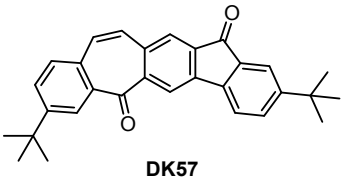


DK77

DK77 was prepared using modified a literature procedure.[4] Under an argon atmosphere in a dry 500 mL two necked round bottom flask 1.8 g (4.0 mmol) **5b**, 1.6 g (8.8 mmol) *N*-bromosuccinimide and 0.014 g (0.040 mmol) dibenzoylperoxide were dissolved in 200 mL of tetrachloromethane and refluxed for 5 h. After cooling, the reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was redissolved in 70 mL of DMF and cooled to 0 C. After addition of 1.3 mL (10.0 mmol) 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN) the color of the reaction mixture turned from yellow to brown. After heating to 80°C for 4 h, the color of the mixture turned to black. After addition of 500 mL of a 10% aqueous HCl solution, the mixture was extracted with DCM three times. After silica gel column chromatography with *n*-hexane:ethyl acetate (8:2) as eluent and recrystallization from toluene, the product was obtained as yellow crystals (0.86 g, 49 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 8.37 (s, 2H), 8.27 (d, *J* = 2.1 Hz, 2H), 7.69 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 12.0 Hz, 2H), 7.05 (d, *J* = 12.1 Hz, 2H), 1.40 (s, 18H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** 192.5, 152.6, 140.3, 137.9, 134.7, 133.5, 132.8, 132.4, 131.4, 130.4, 130.1, 126.9, 35.1, 31.2. **MS-flow injection (APLI)**: m/z [M^++H^+] = 447.2321 (calc. m/z [M^++H^+] = 447.2319)

2,8-Di-*tert*-butyl-benzo[4,5]cyclohepta[1,2-b]fluorene-5,11-dione (DK57)



DK57

DK57 was prepared using essentially the same procedure described for **DK77**, by using 0.20 g (0.47 mmol) **5a**, 0.22 g (1.2 mmol) N-bromosuccinimide and 2 mg (5 μmol) dibenzoylperoxide in 23 mL of tetrachloromethane. After filtering the suspension and removal of tetrachloromethane, the residue was dissolved in 8 mL of DMF, and 0.1 mL (0.7 mmol)

DBN was added. After work-up the residue was purified by silica gel column chromatography with *n*-hexane:ethyl acetate (95:5) as eluent and recrystallization from toluene. The product was obtained as yellow crystals (0.13 g, 66 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] 8.29 (s, 1H), 8.22 (d, *J* = 2.1 Hz, 1H), 7.79 (s, 1H), 7.77 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.71 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.60 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 12.0 Hz, 1H), 7.03 (d, *J* = 12.0 Hz, 1H), 1.41 (s, 9H), 1.36 (s, 9H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ [ppm] 193.5, 193.2, 153.7, 153.0, 143.1, 143.1, 141.6, 138.1, 137.1, 136.1, 135.1, 132.8, 132.7, 132.2, 131.2, 130.5, 130.2, 126.8, 126.8, 122.0, 121.7, 121.1, 35.3, 35.3, 31.3, 31.3. **FD(MS)**: m/z = 420.2493 (calc. m/z =420.2089).

3. NMR data for new compounds

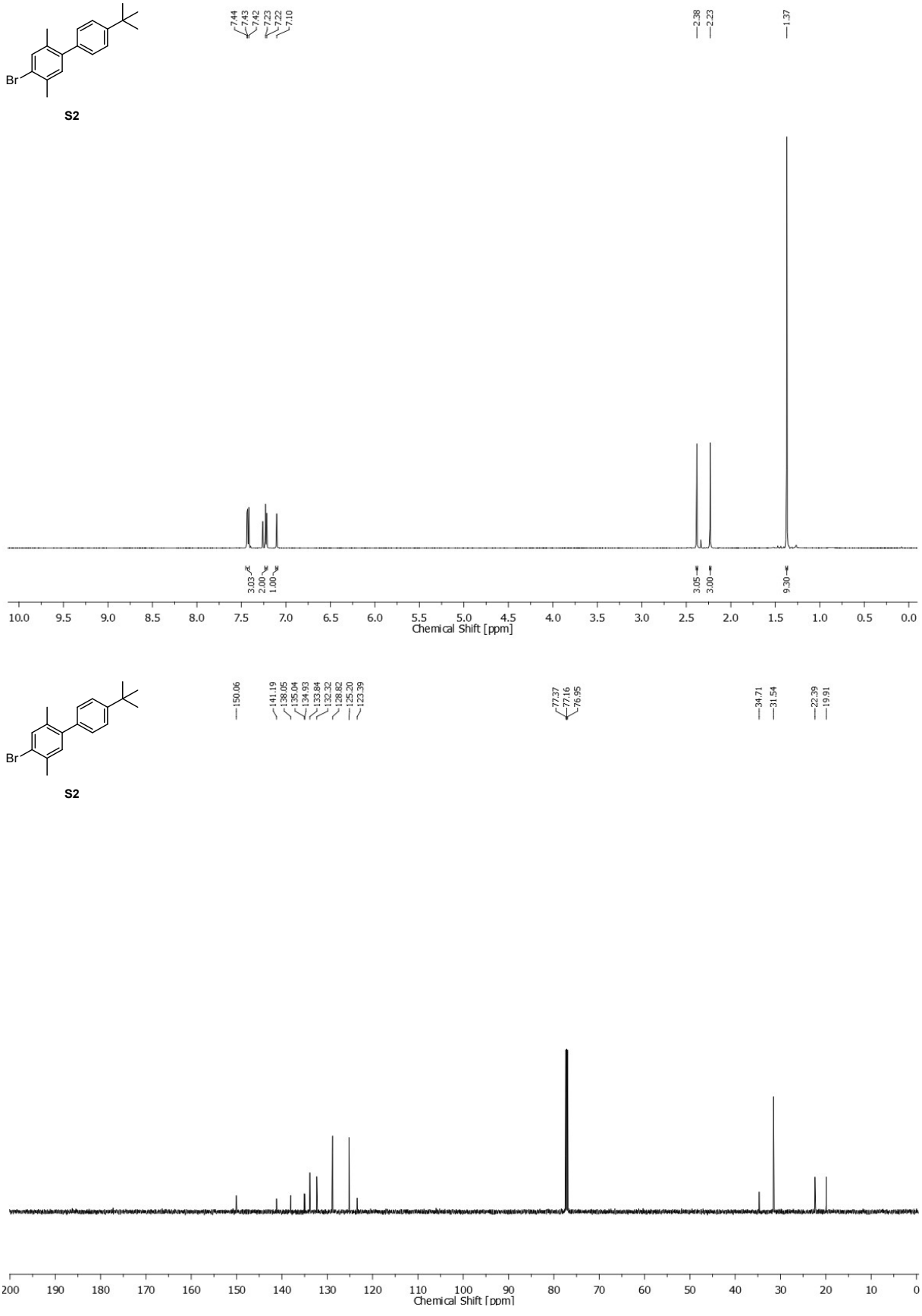


Figure S1: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **S2** recorded in $CDCl_3$.

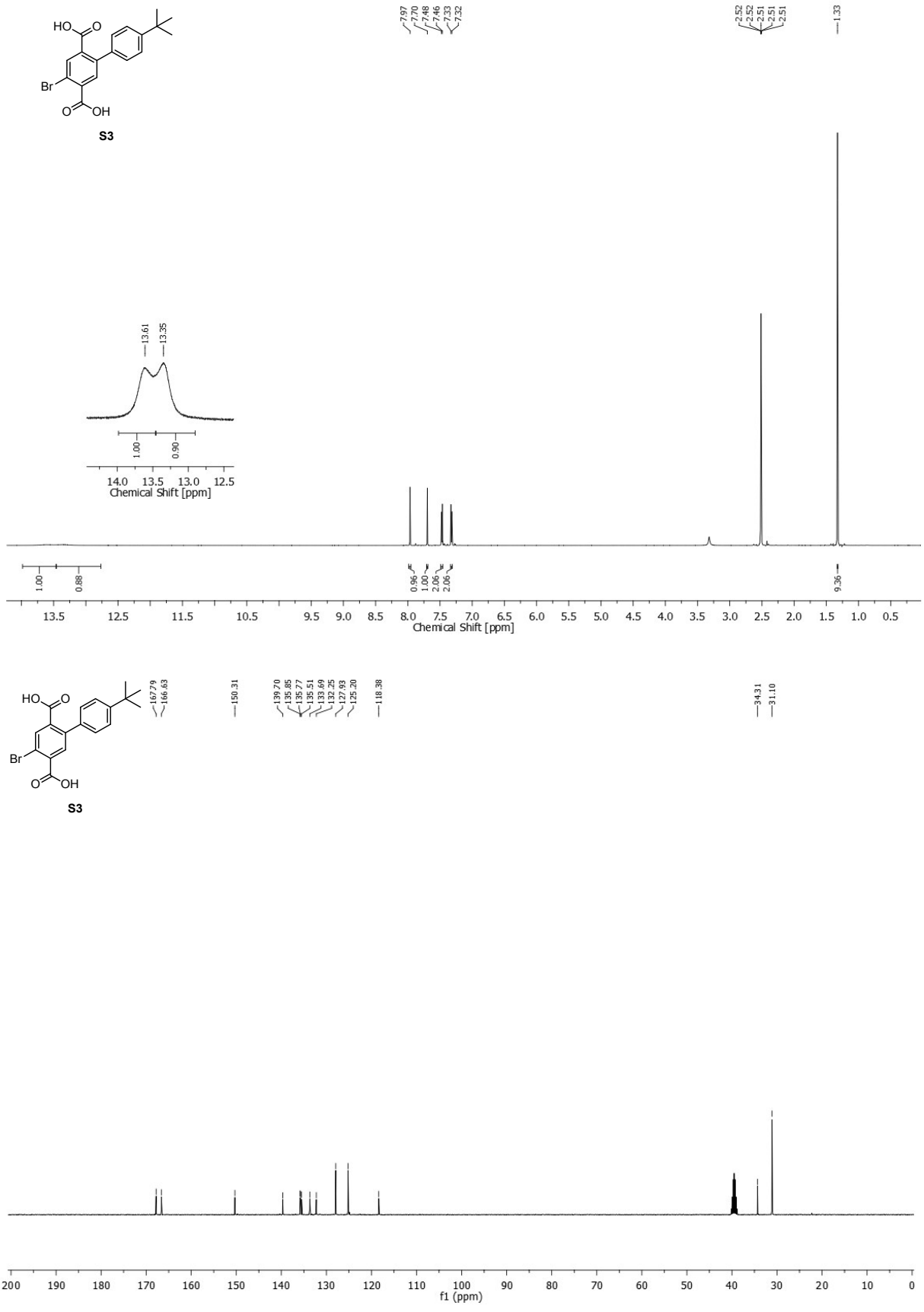


Figure S2: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) (bottom) of **S3** recorded in DMSO-d_6.

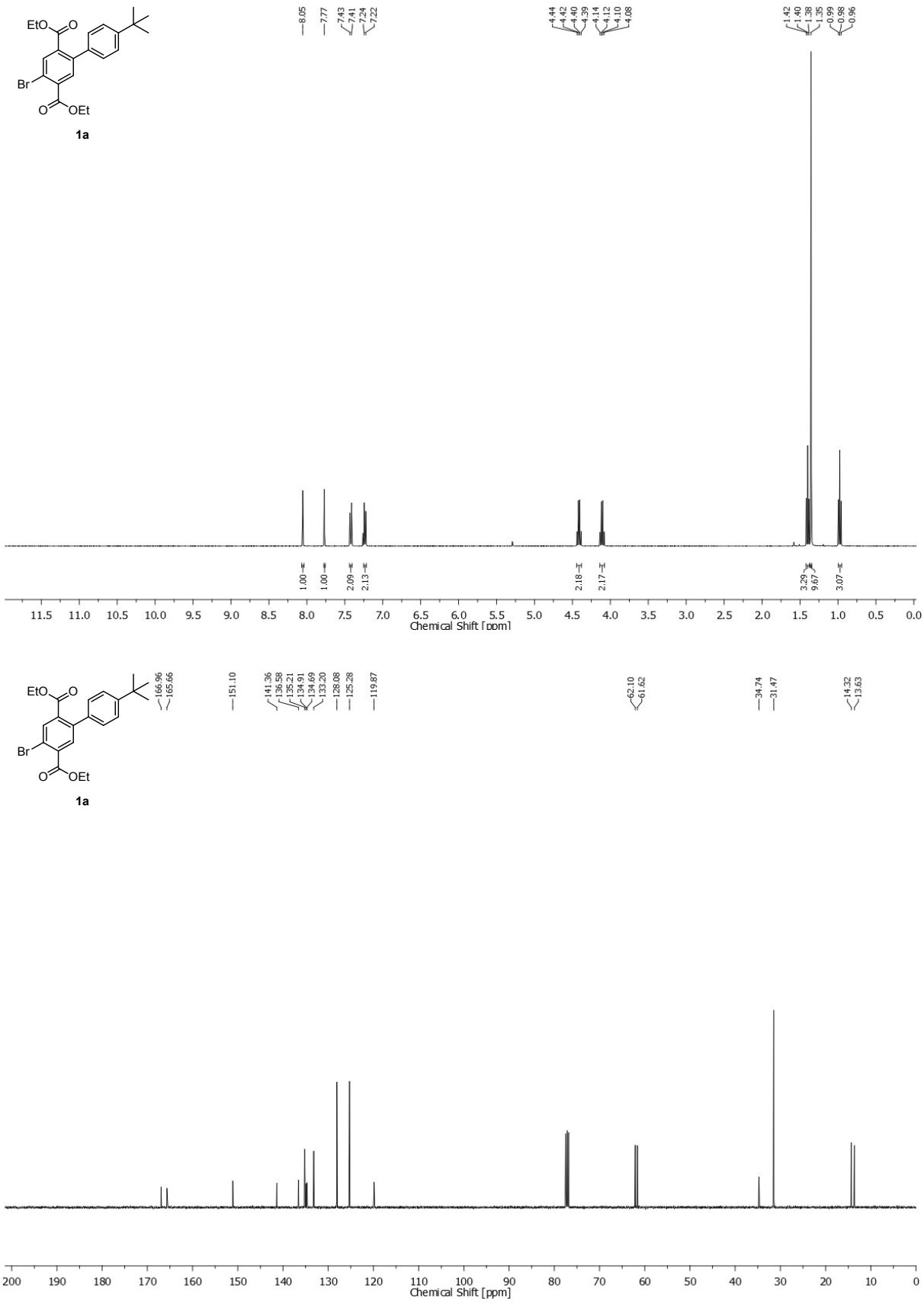


Figure S3: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **1a** recorded in $CDCl_3$.

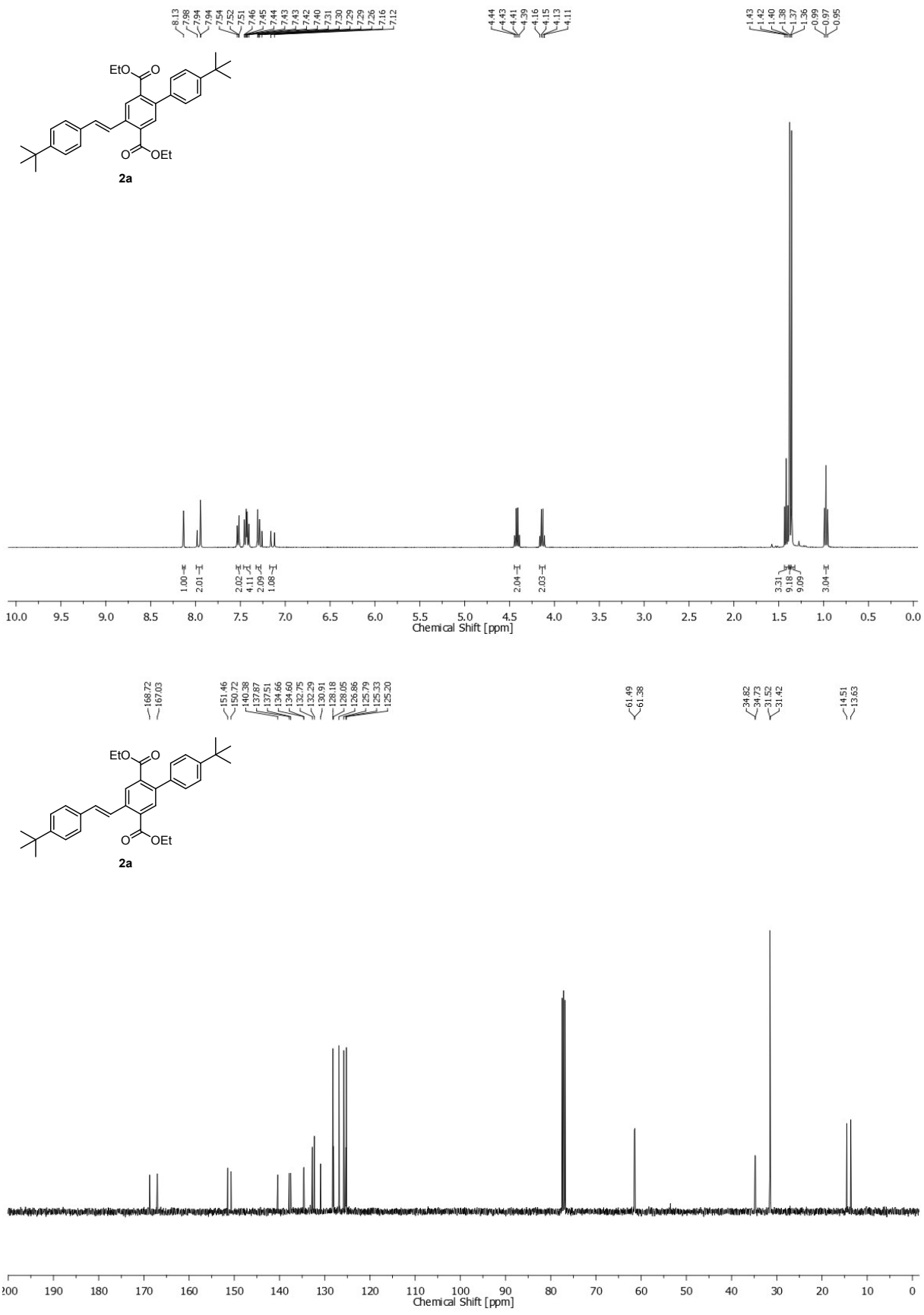


Figure S4: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **2a** recorded in $CDCl_3$.

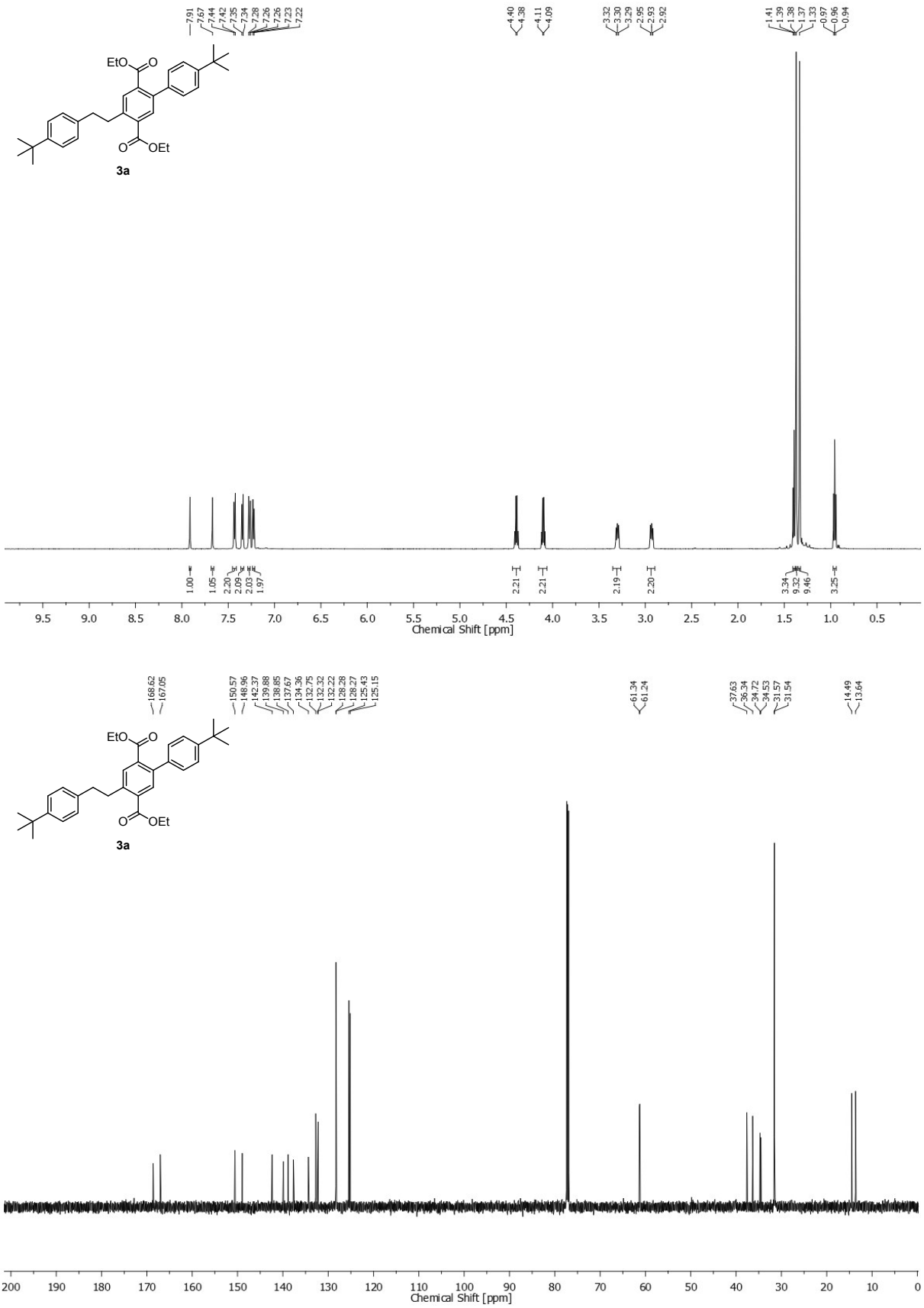


Figure S5: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **3a** recorded in $CDCl_3$.

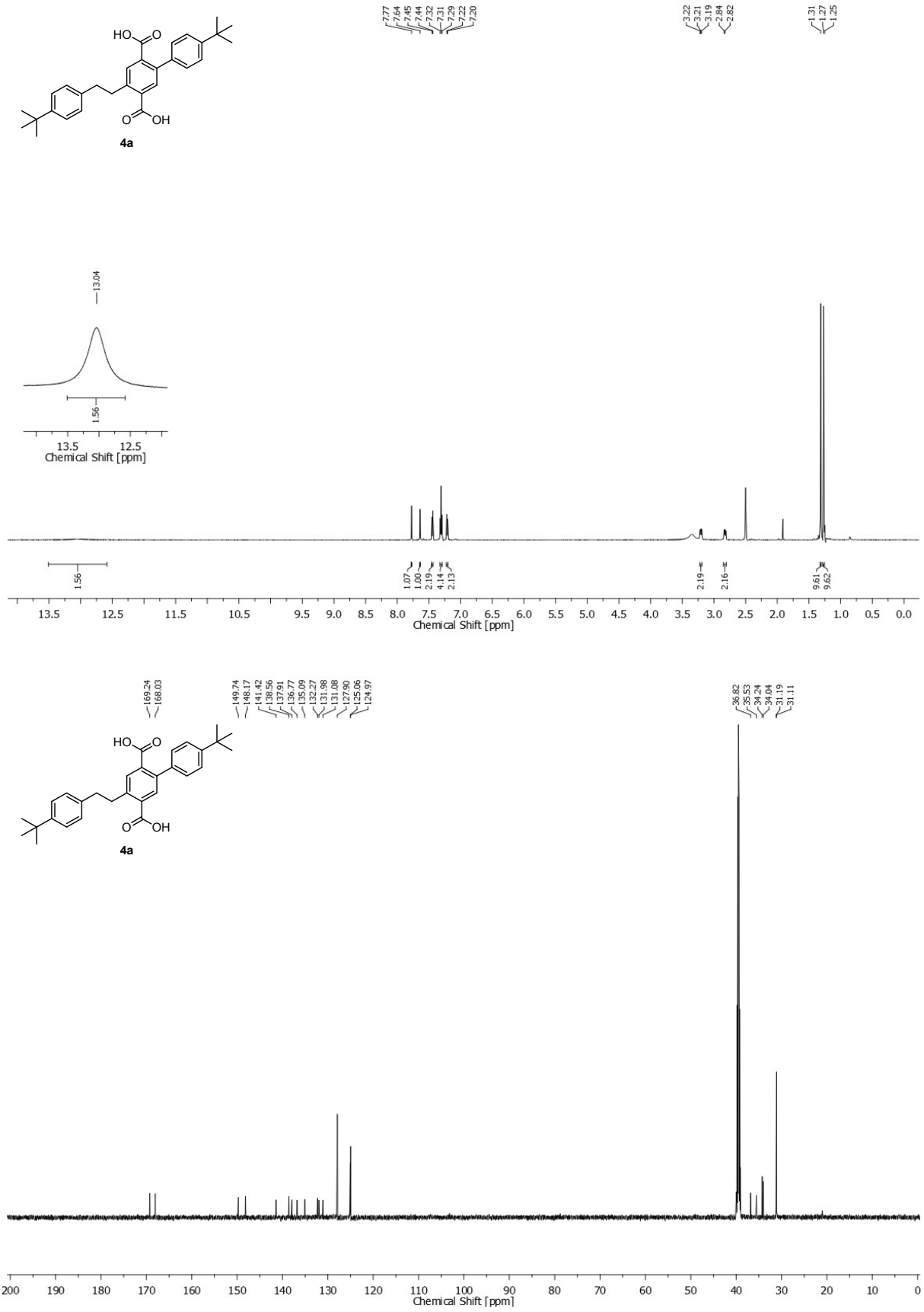


Figure S6: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **4a** recorded in DMSO-d_6.

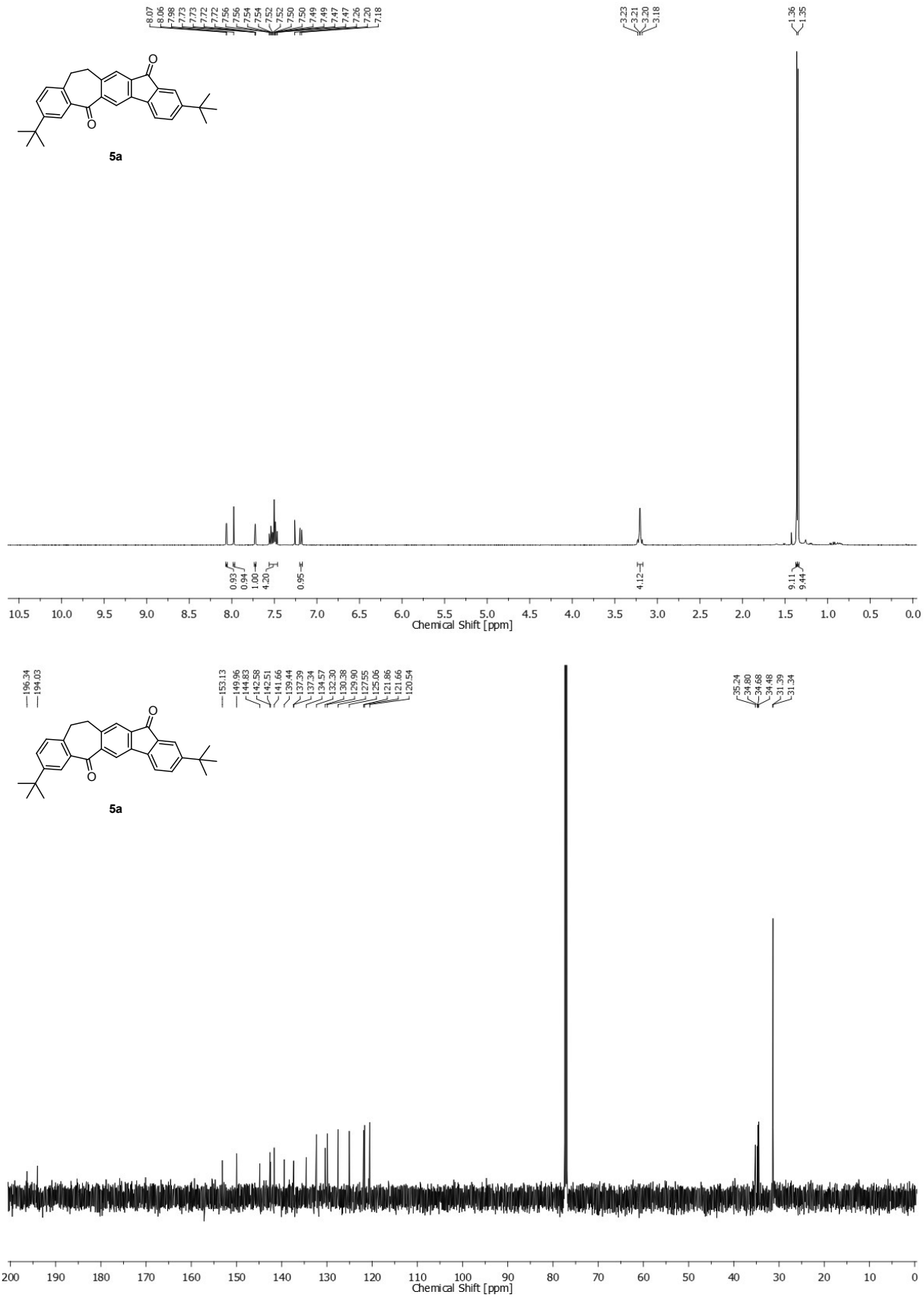


Figure S7: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **5a** recorded in $CDCl_3$.

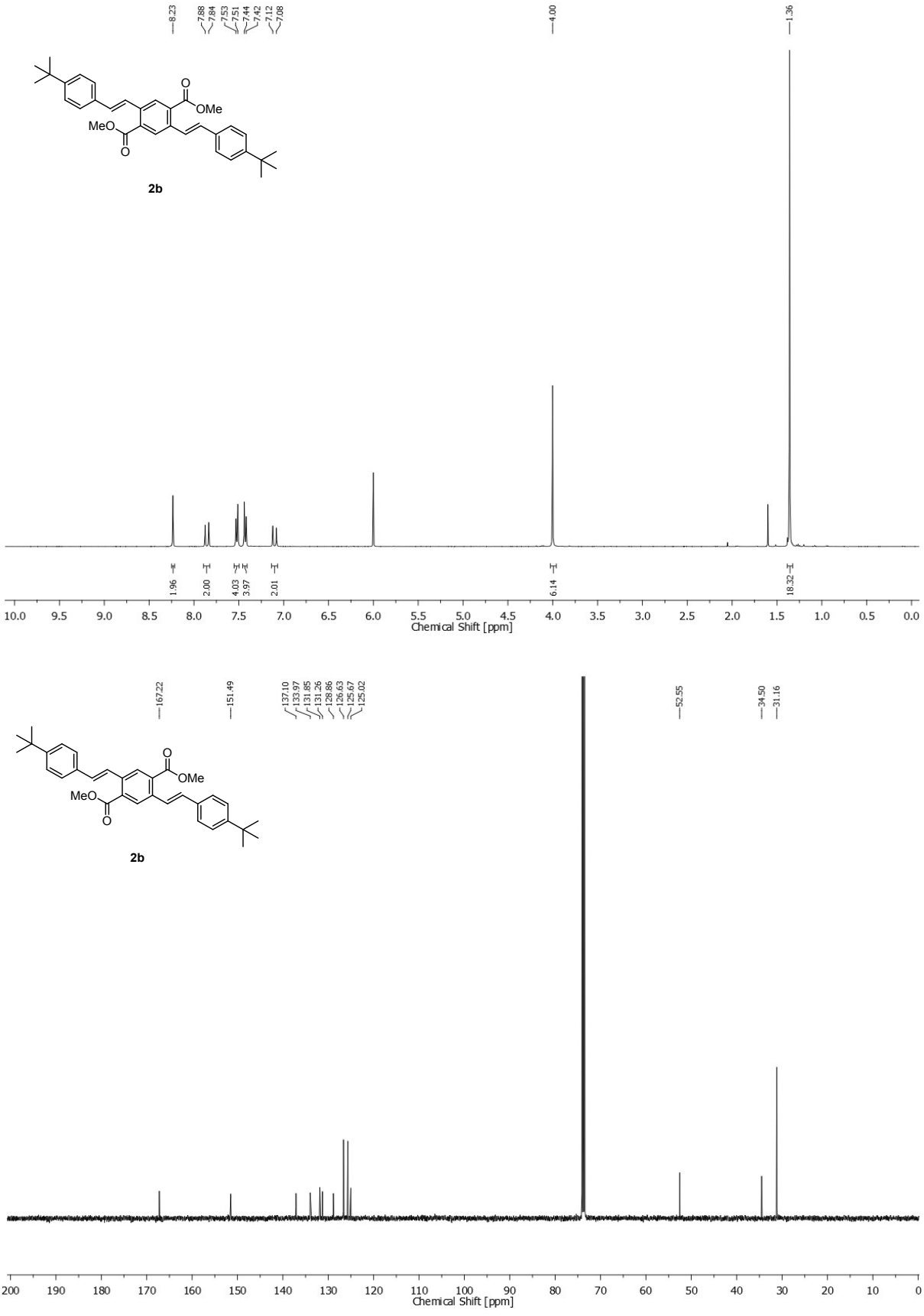


Figure S8: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **2b** recorded in $C_2D_2Cl_4$.

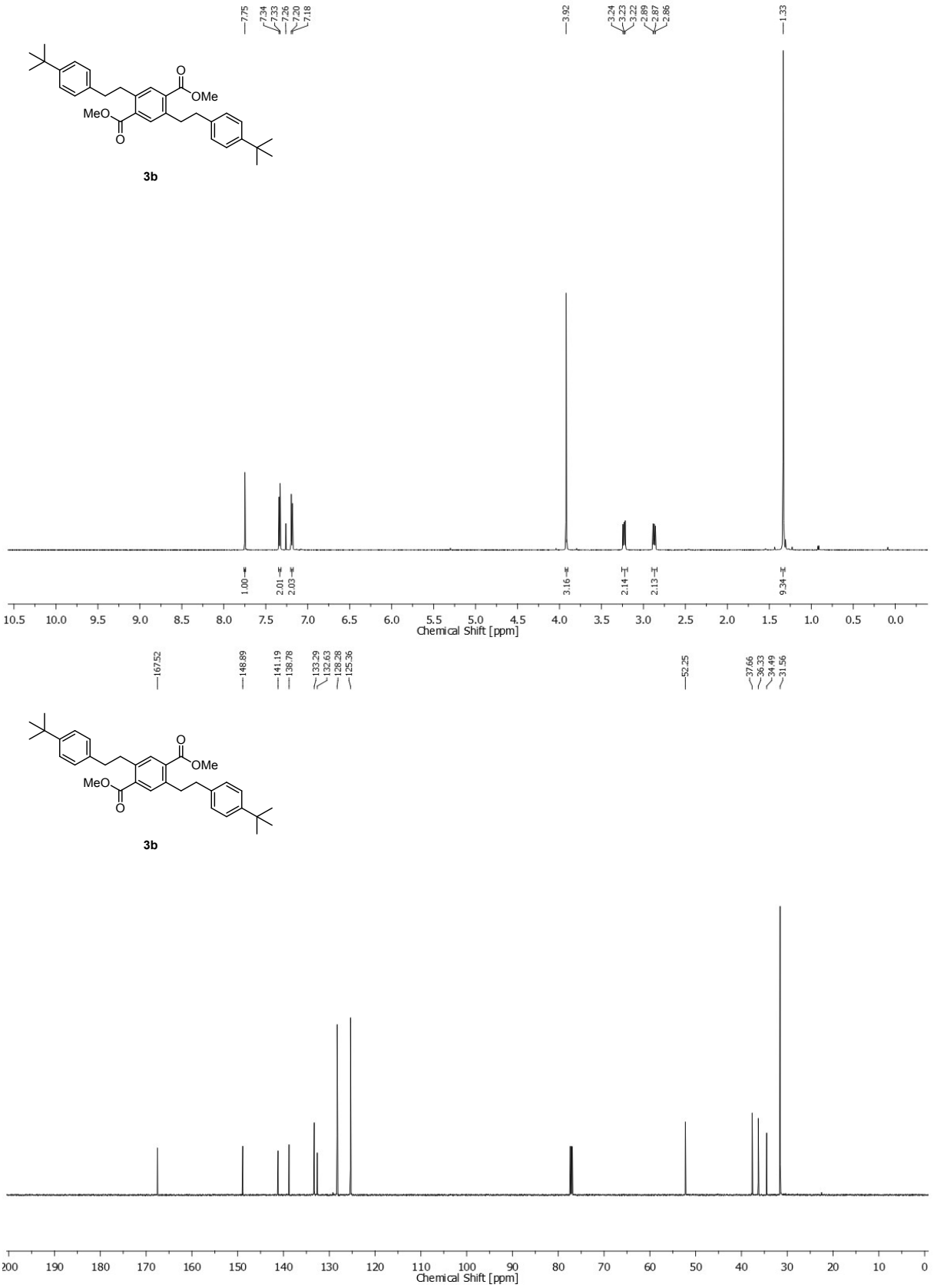


Figure S9: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **3b** recorded in $CDCl_3$.

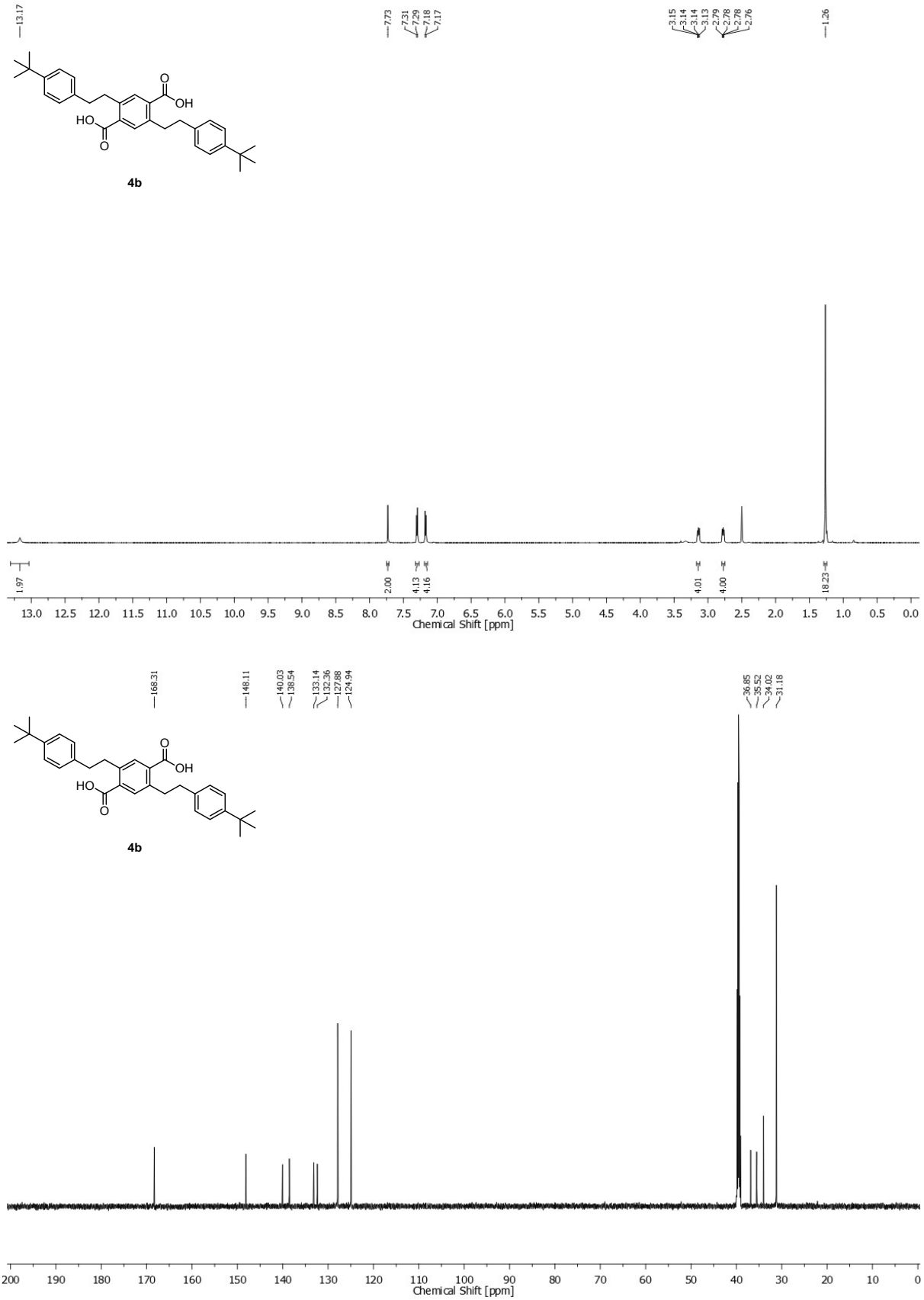


Figure S10: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **4b** recorded in DMSO-d_6.

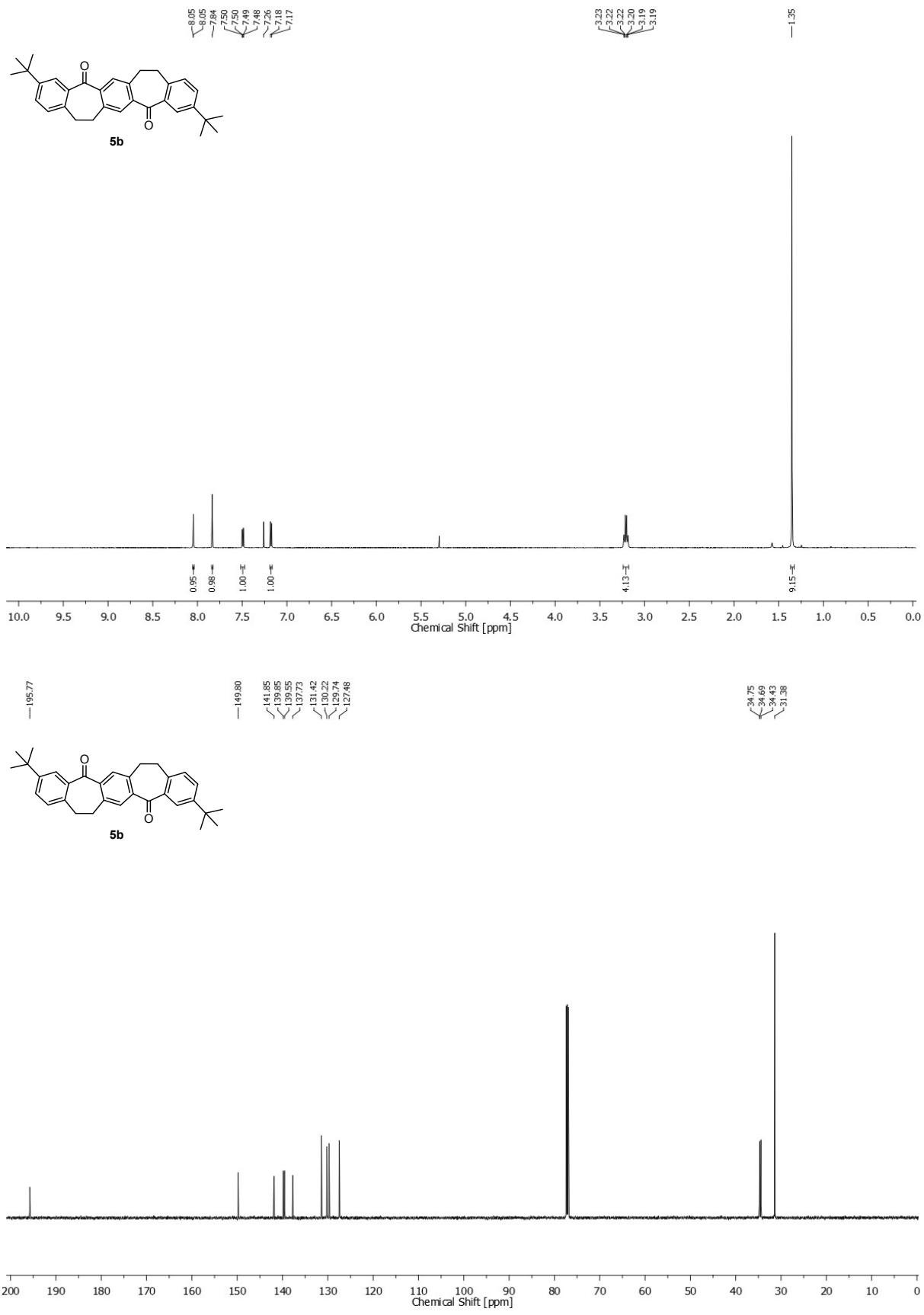


Figure S11: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **5b** recorded in $CDCl_3$.

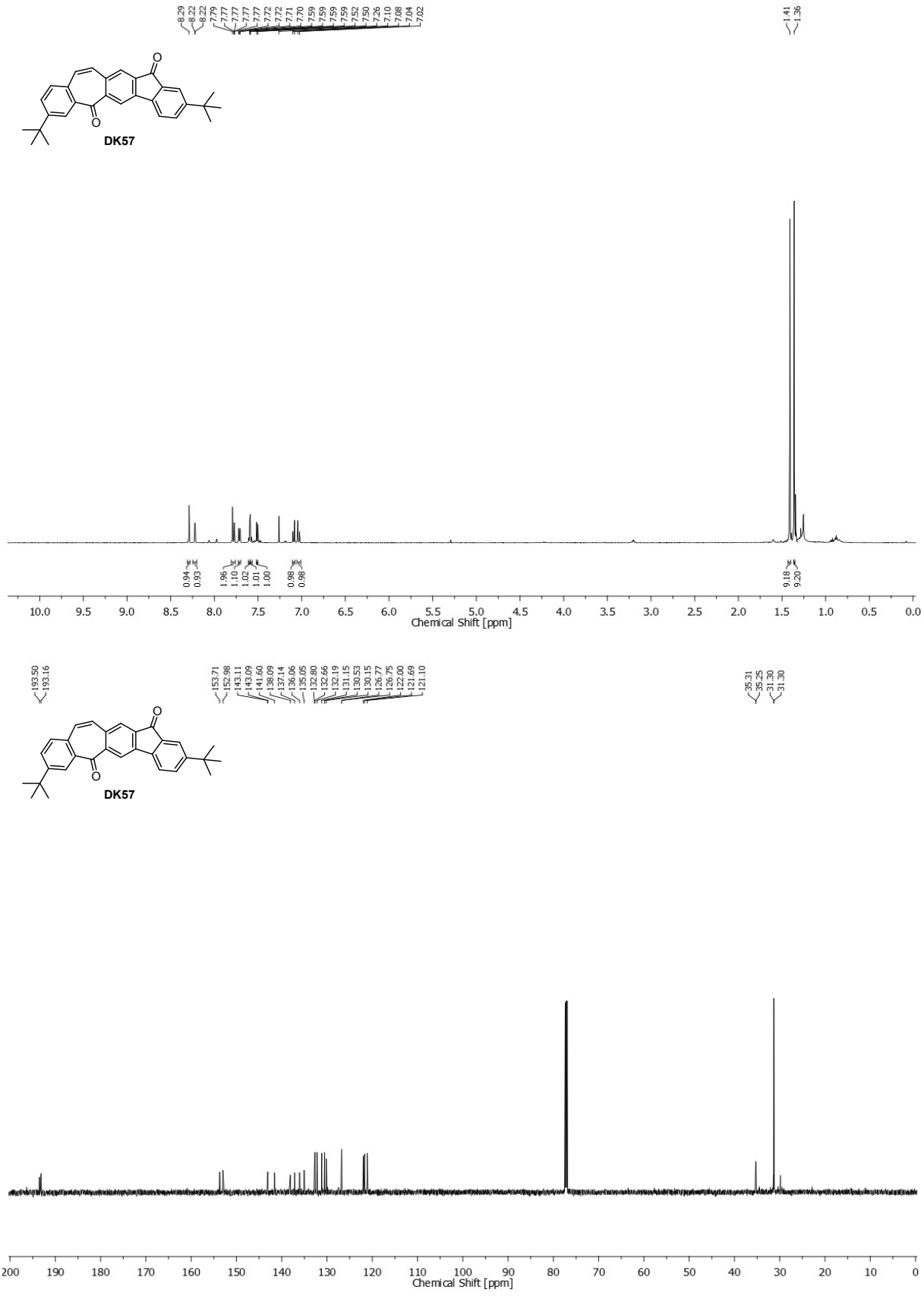


Figure S12: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **DK57** recorded in $CDCl_3$.

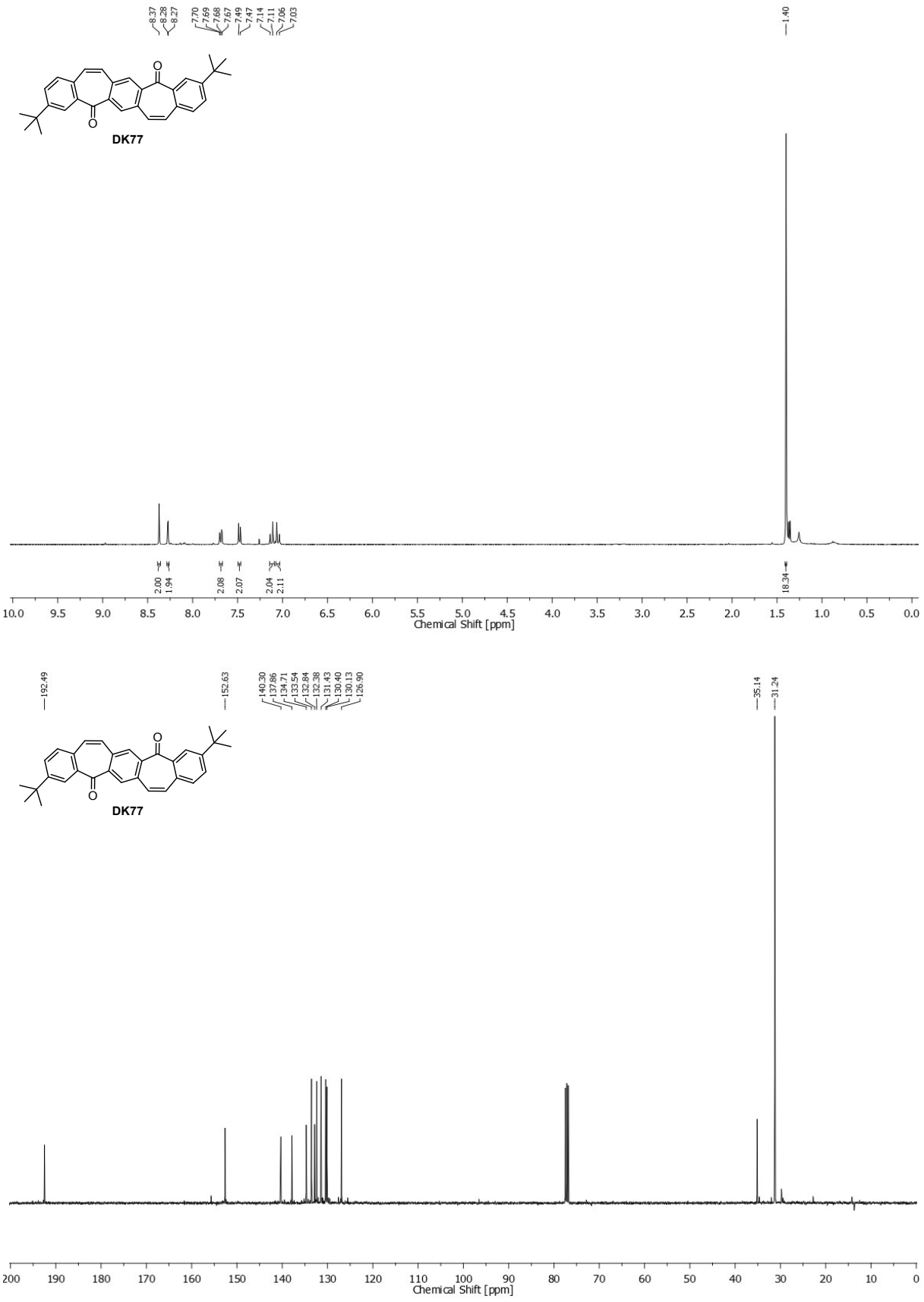


Figure S13: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **DK77** recorded in $CDCl_3$.

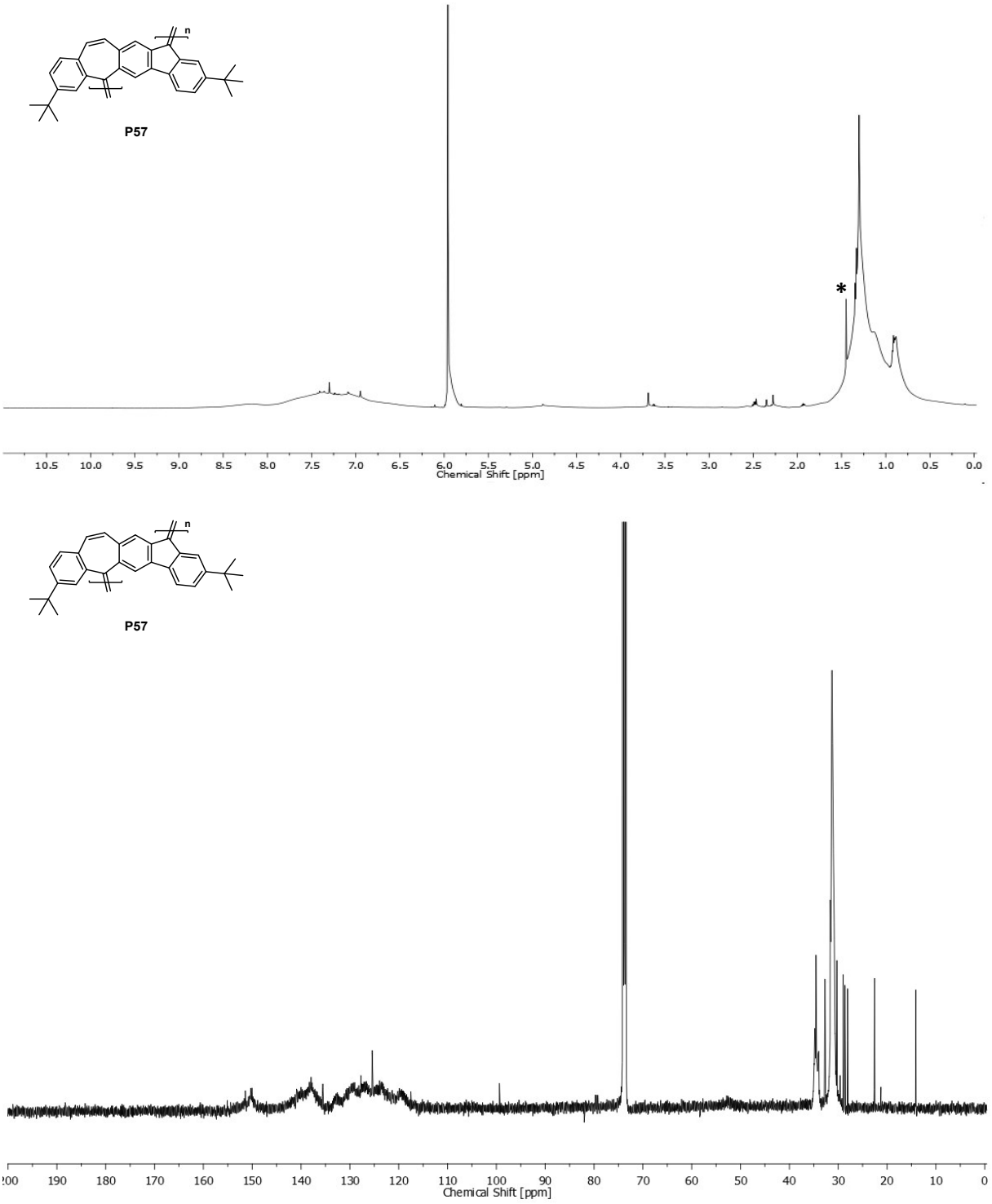


Figure S14: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **P57** recorded in $C_2D_2Cl_4$. *(*Signal from H_2O, in general, it is hard to remove all solvent traces from the solid polymer samples by drying due to their high intrinsic microporosity.)*

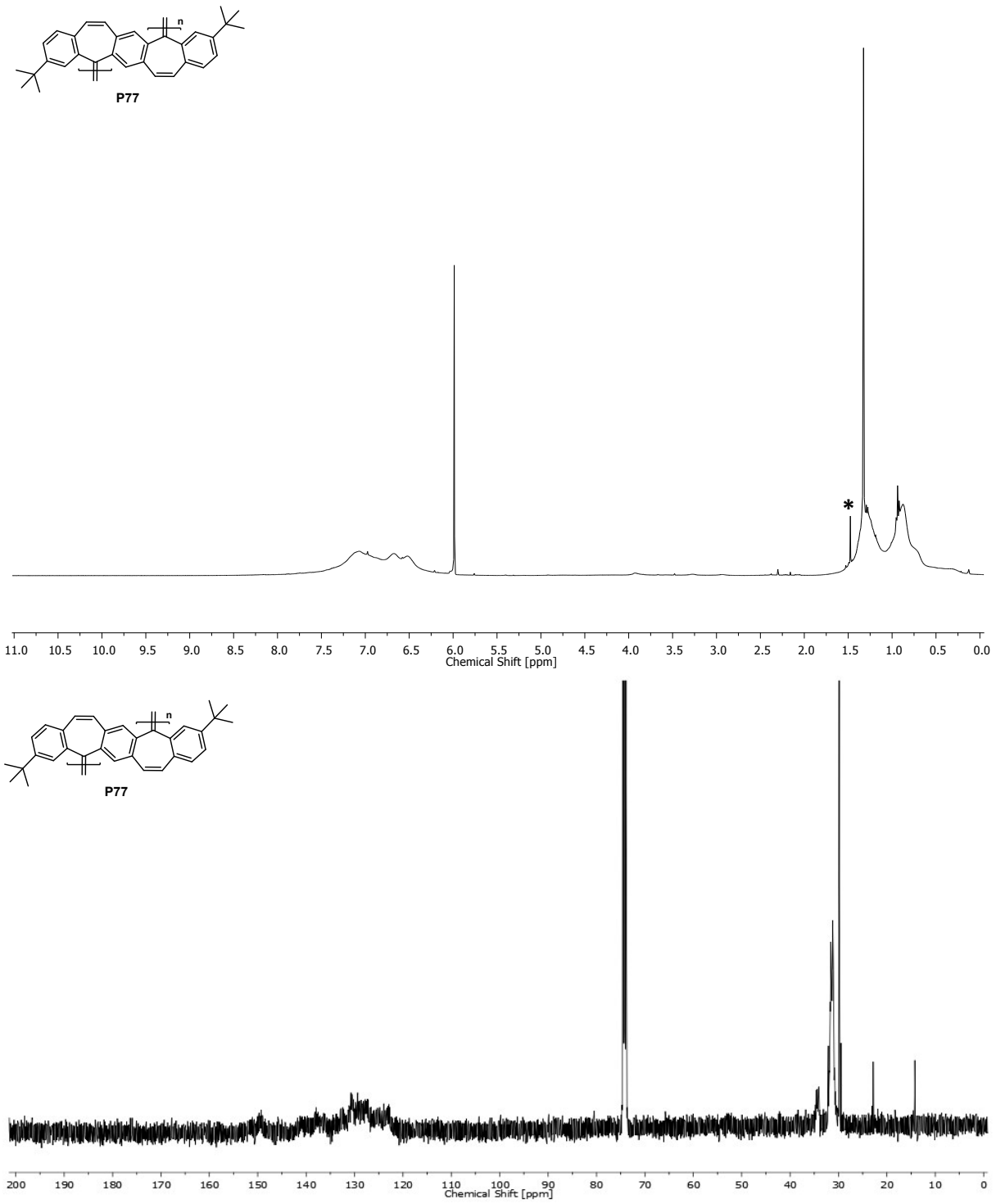


Figure S15: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **P77** recorded in $C_2D_2Cl_4$. *(*Signal from H_2O, in general, it is hard to remove all solvent traces from the solid polymer samples by drying due to their high intrinsic microporosity.)*

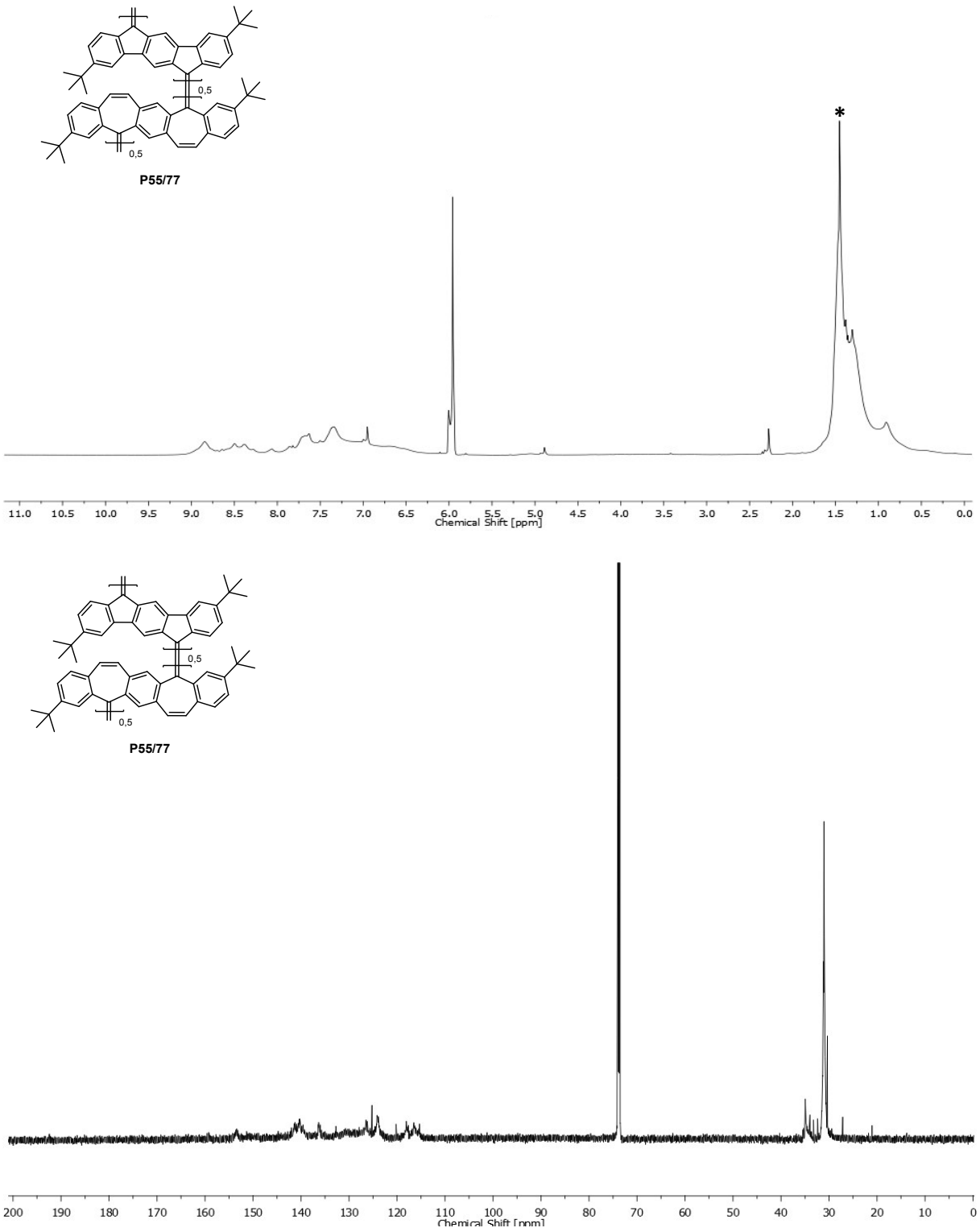


Figure S16: ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **P55/77** recorded in $C_2D_2Cl_4$ at 353 K. *(*Signal from H_2O, in general, it is hard to remove all solvent traces from the solid polymer samples by drying due to their high intrinsic microporosity.)*

4. Gas sorption data, TGA, PXRD, SEM, Optical data for P77 film

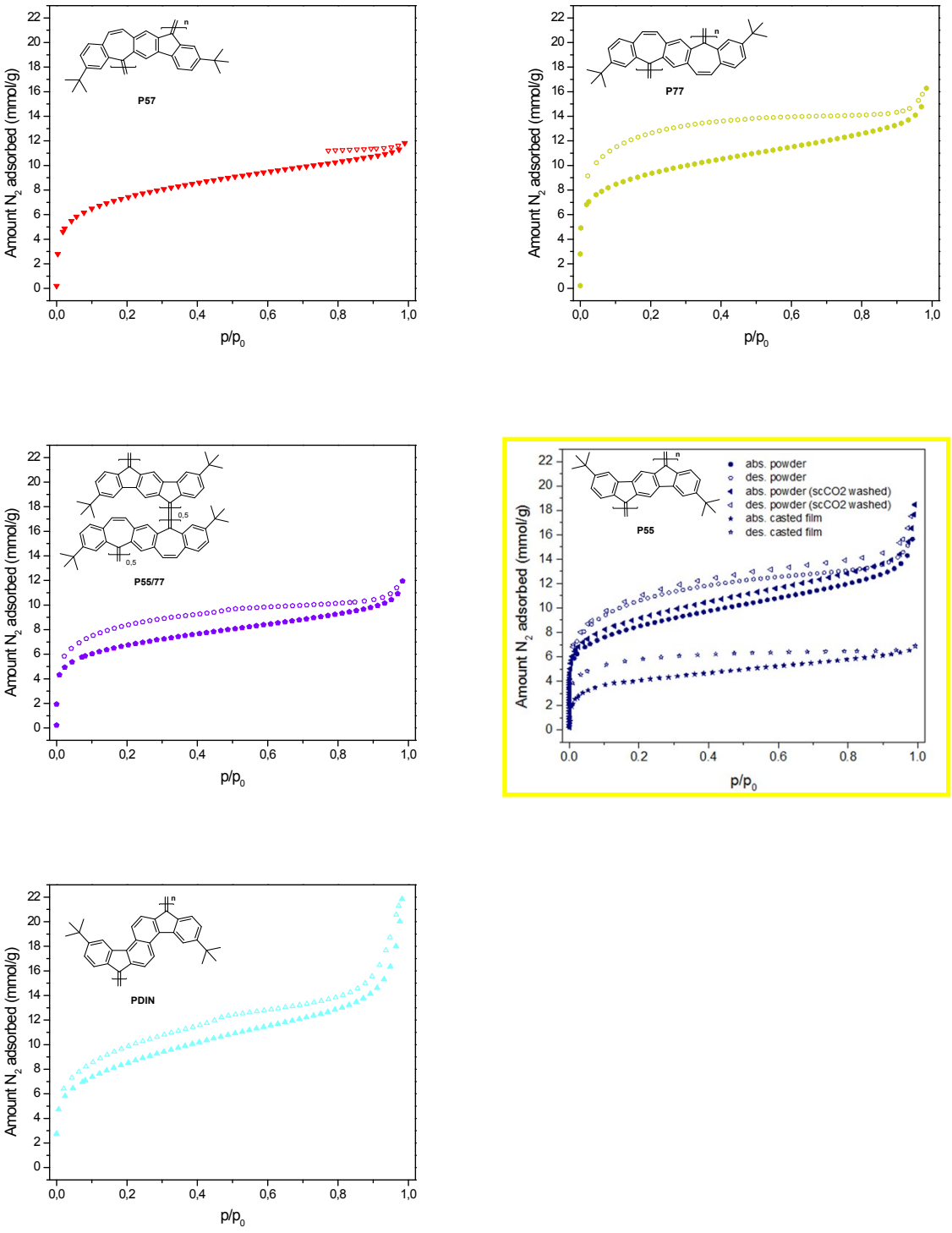


Figure S17: Nitrogen gas sorption gas adsorption (filled symbols) and desorption (open symbols) isotherms for polymers **P57**, **P77**, **P55/77**, **P55** (as powder and casted film) and **PDIN**. Please note that for the film a longer equilibration time of 45 seconds instead of 30 seconds was used for each data point.

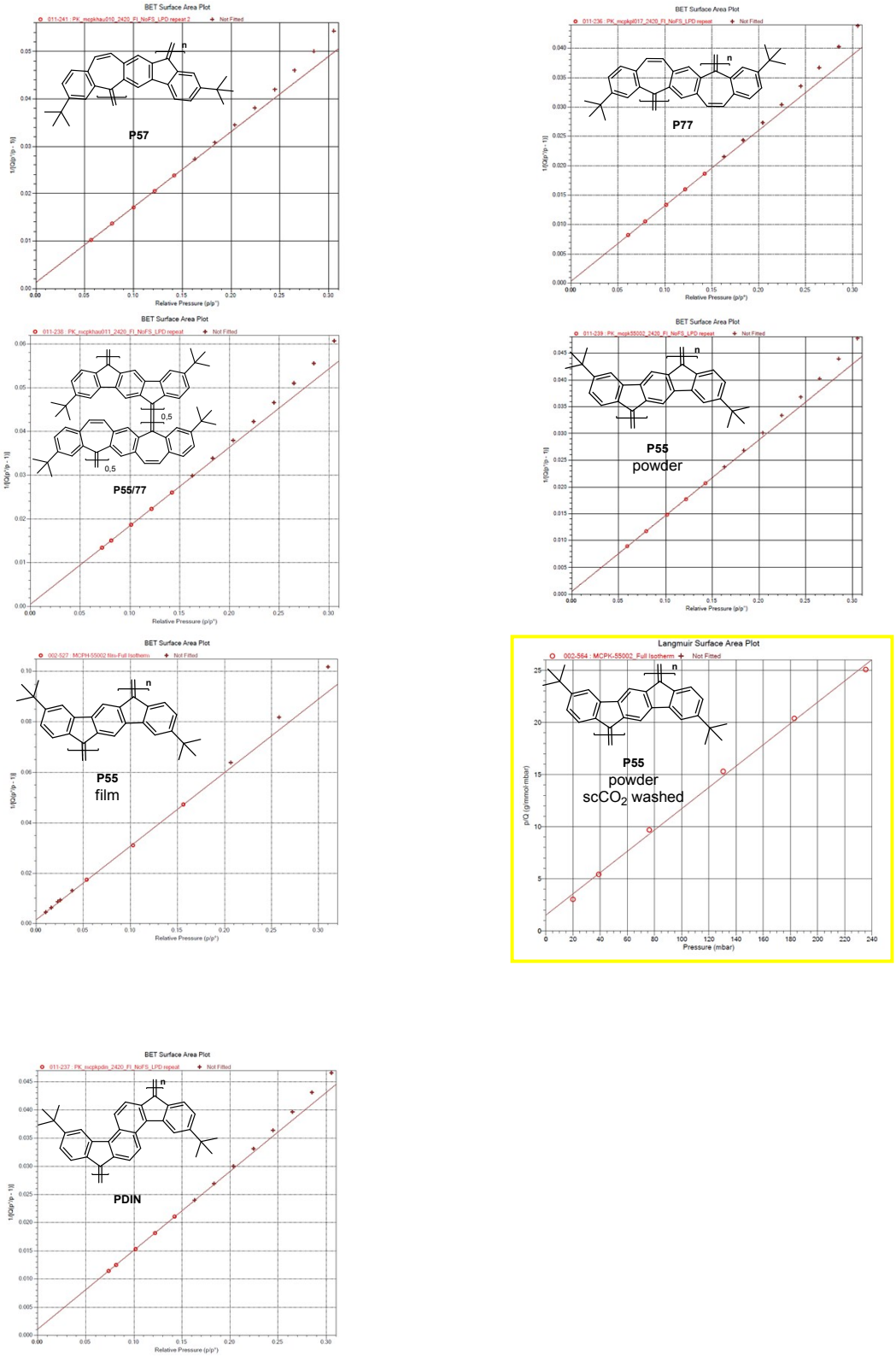


Figure S18: BET surface area fit for polymers **P57**, **P77**, **P55/77**, **P55** (powder, powder ($scCO_2$ washed) and film) and **PDIN**.

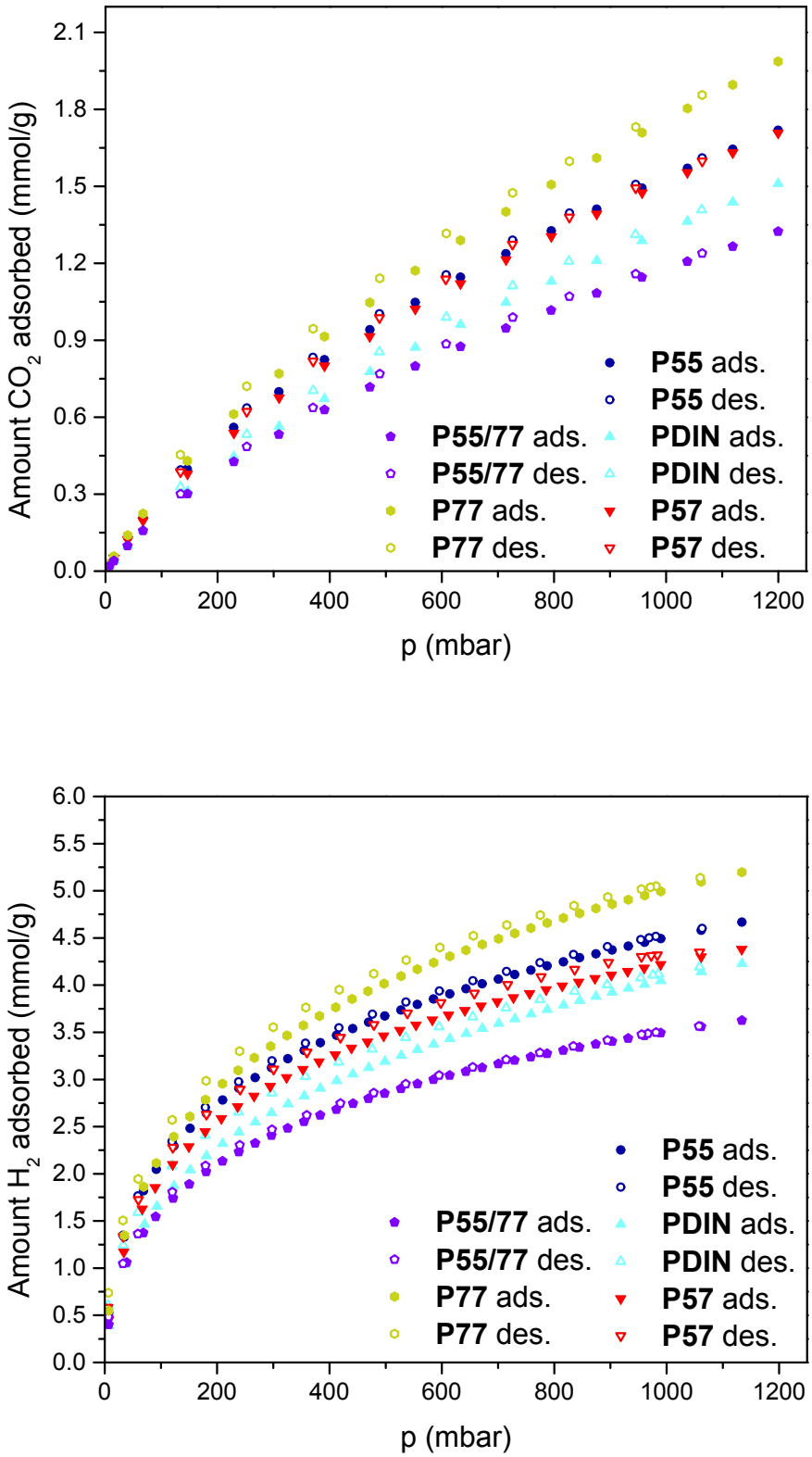


Figure S19: Carbon dioxide (273 K) and hydrogen (77 K) gas adsorption (filled symbols) and desorption (open symbols) isotherms of polymers **P57**, **P77**, **P55/77**, **P55** and **PDIN**.

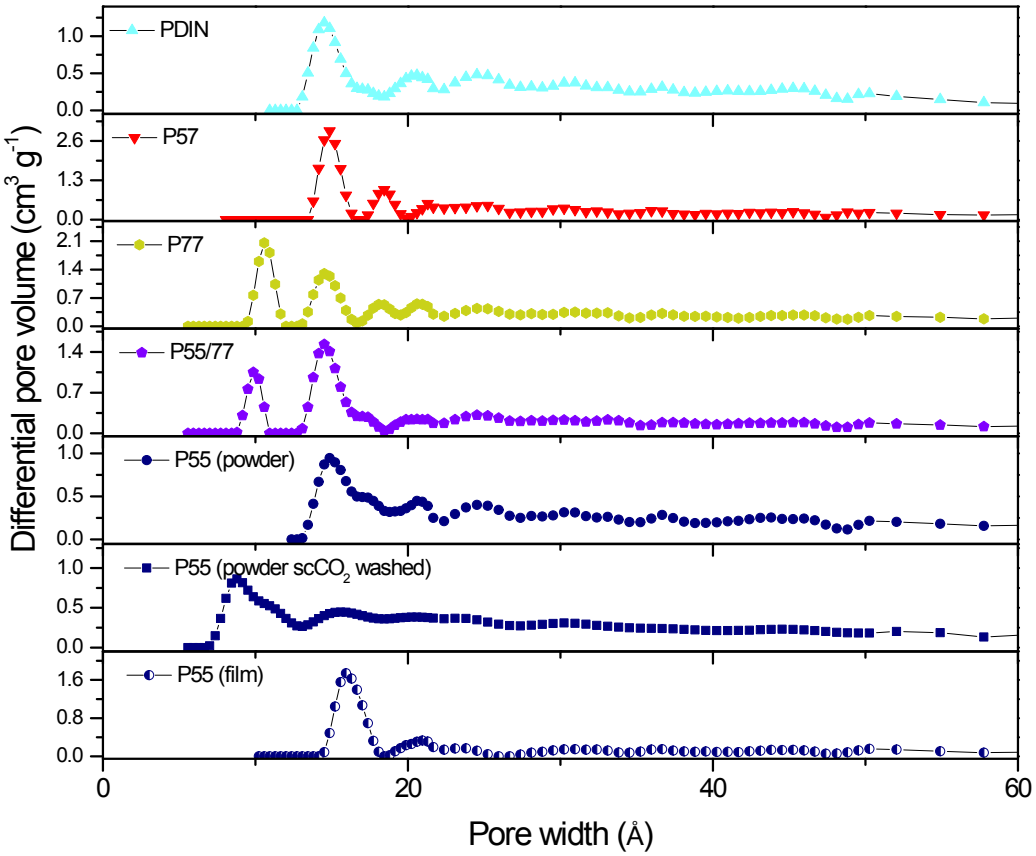


Figure S20: Pore size distributions for polymers **P57**, **P77**, **P55/77**, **P55** and **PDIN**. The values were calculated by applying a hybrid density functional theory model to the nitrogen sorption isotherms at 77 K.

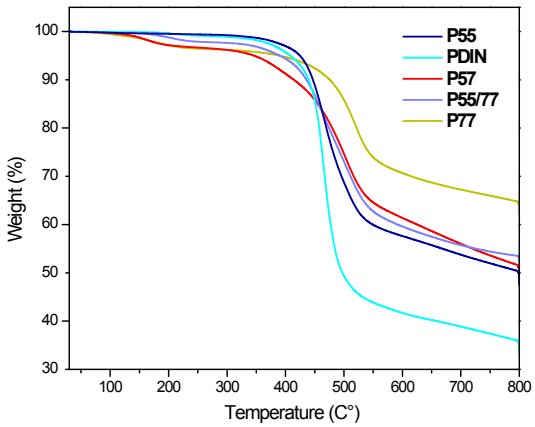


Figure S21: Thermorgavimetric data for polymers **P57**, **P77**, **P55/77**, **P55** and **PDIN**.

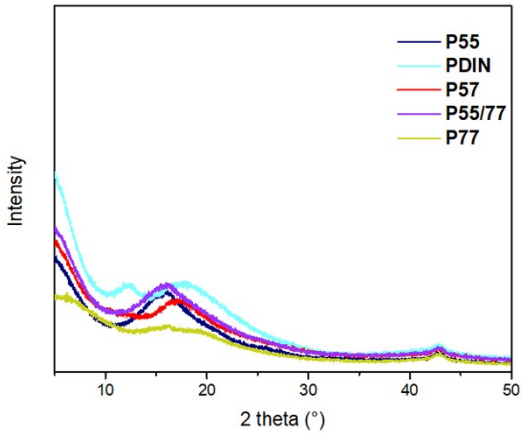


Figure S22: PXRD patterns for polymers **P57**, **P77**, **P55/77**, **P55** and **PDIN**.

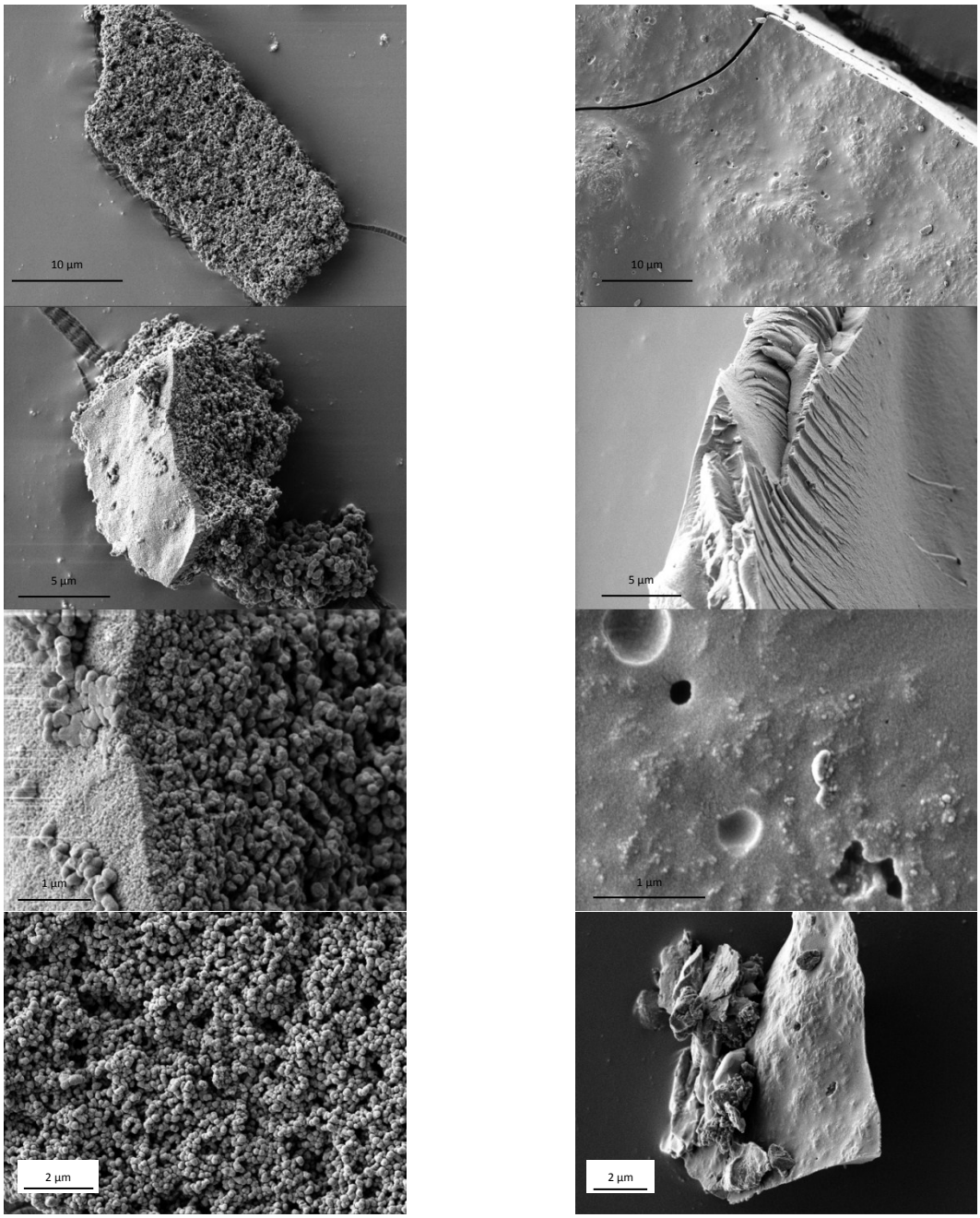


Figure S23: SEM images of the polymer powder of **P55** (left) and a casted film of **P55** (right), shown at comparable magnification for each pair of images.

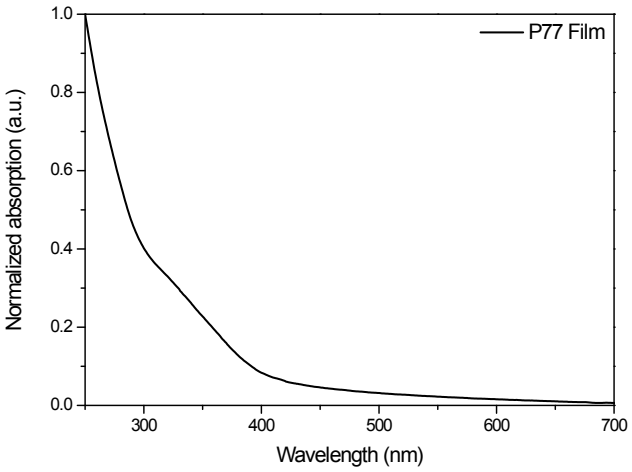


Figure S24: Normalized absorption spectrum of a **P77** (film) on a quartz plate.

5. Comparative Table for linear PIMs

Table S1: Comparison of S_{BET} surface areas obtained from N_2 sorption isotherms at 77 K for different linear/soluble PIMs.

	Materials	S_{BET} m²/g	Porosity to N_2 in casted films	Reference
Not π-conjugated	**PIM 1**	760	yes	Ref[9]
	PIM 2	600	-	Ref[9]
	PIM 3	560	-	Ref[9]
	PIM 4	450	-	Ref[9]
	PIM 5	540	-	Ref[10]
	PIM 6	550	-	Ref[9]
	PIM 7	750	-	Ref[9]
	DAE-PIM	395	-	Ref[11]
	P(Fc-DEB)	238	insoluble	Ref[12]
	CANAL LP	200 - 600	-	Ref[13]
π-conjugated	**c-PIMs A-R**	293 - 728	yes for polymer D	Ref[14]
	P16-18	"modest"	insoluble	Ref[15]
	P33 & P35	114 & 192	insoluble	Ref[16]
	P(TMSP)	550	yes	Ref[17]
	p-PTMSDPA	635	yes	Ref[18]
	PDPA	341	yes	Ref[18]
	SCMP1	505	no	Ref[19]
	P64	127	insoluble	Ref[20]
This work	**P55**	687	yes	This work
	P77	757	-	This work
	PDIN	691	-	This work
	P57	609	-	This work
	P55/77	543	-	This work

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