Electronic Supplementary Information

Electrooxidative Generation of Polymer Films from Rigid Tricarbazole Monomers

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Content

1 Experimental Procedures

1.1 Materials and Instruments

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used without further purification. Air- and water-sensitive reactions were carried out under argon atmosphere in dry solvents. NMR spectra were recorded at 400 MHz (Bruker Avance) or 600 MHz (Bruker Avance III) spectrometers for ^{1}H-NMR spectra, corresponding to 101 MHz or 151 MHz for ^{13}C-NMR spectra, respectively. Unless otherwise mentioned, the NMR spectra were recorded at 300 K. Chemical shifts are given in parts per million and referred to the deuterated solvents used. The followed abbreviations are used to describe the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublet), td (triplet of doublets), dt (doublet of triplet). Coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were measured on a Bruker microTOF with APCI (atmospheric pressure chemical ionization) as ionisation method or on a JOEL AccuTOF-GCX with FD (field desorption) as ionisation method. UV/Vis spectra were recorded on a Jasco V-670 spectrometer at room temperature. Photoluminescence spectra were obtained on a Horiba FluoroMax-4 spectrometer at room temperature. IR spectroscopy was carried out on a FT-IR-4700 spectrometer equipped with an ATR unit. Flash chromatography was performed using 60 A silica gel form Fischer Scientific GmBH or using the flash chromatography system Reveleris X2 Grace equipped with FlashPure ID columns. AFM (atomic force microscopy) measurements were performed on a diInnova Bruker machine in tapping mode. Analytical scale HPLC (high performance liquid chromatography) was carried out on a system from Jasco Deutschland GmBH with UV detection (UV-2075) and an Orbit 100 C18 (250 x 4.6 mm, 5 µm) column. The purifications by preparative scale HPLC were done on a System from Jasco Deutschland GmbH with DAD detection (MD-2015) and an Orbit 100 C18 (250 x 20 mm, 5 µm) column.

1.2 Electrochemical Procedures

The cyclovoltammetric measurements were carried out in a three-electrode cell with the potentiostat VersaSTAT 4 from Princeton Applied Research. The gravimetric measurements were carried out on a EQCM (electrochemical quartz crystal microbalance) system QCM9224A from Princeton Applied Research. Ag^{0}/Ag^{+} ($AgNO_3$ c = 0.01 mol/L, TBAP c = 0.1 mol/L,

Acetonitrile, U = 0.60 V vs. SHE) was used as reference electrode. Analytical scale film generations were carried out in a 5 mL cell with Pt-disc electrode (d = 1 mm) as working electrode and a Pt-wire (d = 0.7 mm) as counter electrode. Preparative scale film generation was done in a 10 mL cell with an ITO coated glass electrode as working electrode and a Pt net as counter electrode. EQCM measurements were carried out in a 20 mL cell with a Pt coated quartz crystal (A = 0.165 cm^2) as working electrode, and a Pt wire (d = 0.7 mm) as counter electrode. The collected polymer films were removed from the ITO electrode and carefully washed. After storage in ethanol for three days, the films were washed with supercritical CO_2 in a Tousimis Sandri-795 in four cycles (0.5, 1, 2,5, 18 h for supercritical state) and dried. The gas sorption measurements were carried out on a BEL Japan surface analyser with Krypton at 77 K (p/p_0: 0.0–0.6).

1.3 Monomer Synthesis

1.3.1 aTC

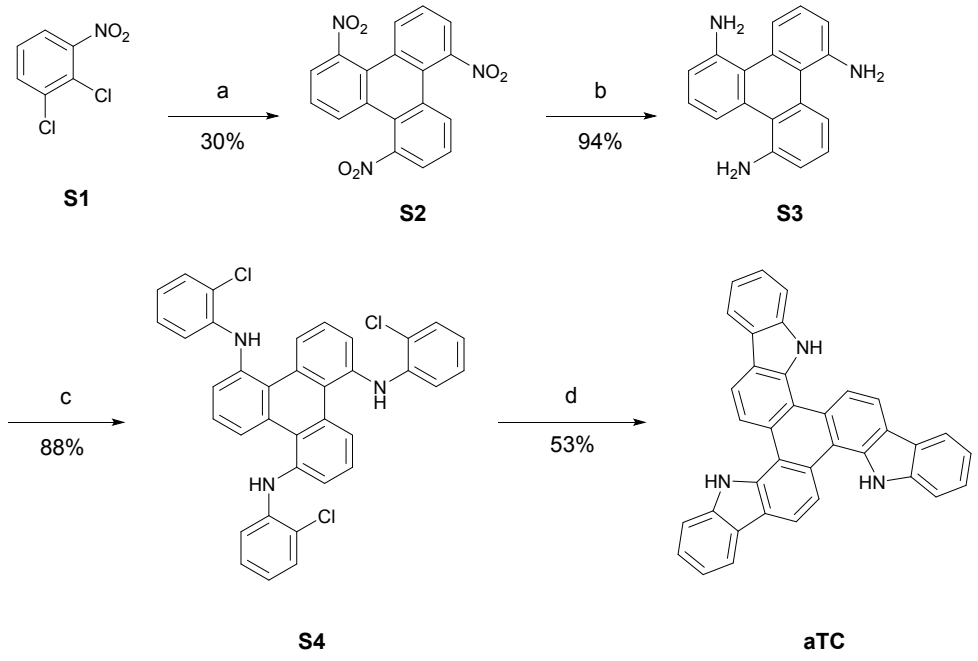
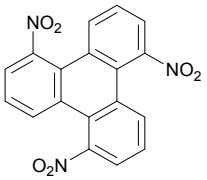


Figure S1: *Synthetic route to* ***aTC****.* ***a****) Cu, DMF, 200 °C, 12 h;* ***b****)* H_2 *(2.3 bar), Pd/C, ethyl acetate (EA)/ethanol (EtOH) 10/1;* ***c****) t-BuONa, 1-bromo-2-chlorobenzene, DavePhos catalyst, 1,4-dioxane, 125 °C, 18 h;* ***d****) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),* $Pd(OAc)_2$*,* $P(t\text{-}Bu)_3$*, o-xylene , 140 °C, 18 h (53%).*

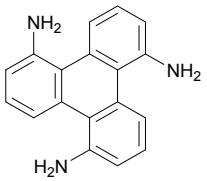
1,5,9-Trinitrotriphenylene (Method A) (S2)



S2

S2 was prepared according to an adapted literature procedure.[I] To 2,3-dichloronitrobenzene (30 g, 156 mmol) and copper powder (60.00 g, 937.50 mmol) DMF (240 mL) was added. The mixture was stirred for 18 h at 195 °C. After cooling to 120 °C, the mixture was filtered through celite and the celite washed with DMF (3 x 40 mL). The filtrate was added slowly to a 6.25% aqueous ammonia solution (1.2 L). The precipitated solid was filtered off and washed several times with the aqueous ammonia solution and finally with water. The brownish solid was recrystallized from acetone to obtain a brownish solid (24% yield, ca. 90% purity from ^{1}H NMR). The solid was used in the next step without further purification. For analytical measurements, a small amount was purified by flash chromatography with dichloromethane (DCM):hexane (Hex) (1:9 → 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.15 (dd, *J* = 8.3, 1.2 Hz, 3H), 7.93 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.70–7.65 (m, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ [ppm] = 149.6, 129.5, 128.4, 128.3, 125.4, 122.4. **HRMS (FD): m/z** $[M]^+$ found: 363.0466, calcd. for $C_{18}H_9N_3O_6$: 363.0491.

Triphenylene-1,5,9-triamine (Method B) (S3)

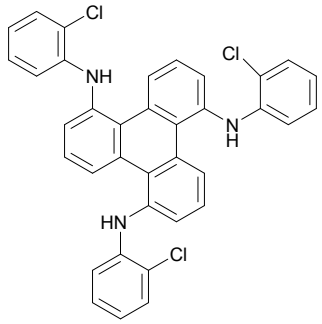


S3

S3 was prepared according to an adapted literature procedure with some modification.[I] **S2** (1 g, 2.75 mmol), ethyl acetate (100 mL) and ethanol (10 mL) were put into an autoclave (Büchi GmbH). Subsequently, palladium on activated carbon (10%) (1.17 g, 1.10 mmol) was added to the mixture. After stirring under hydrogen (2.3 bar) for 24 h, the mixture was filtrated through celite and the celite washed with DCM. The filtrate was concentrated *in vacuo* to yield the amine as a light-yellow solid (95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.21 (d, *J* = 8.0 Hz, 3H), 7.16 (t, *J* = 7.9 Hz, 3H), 6.87 (d, *J* = 7.7 Hz, 3H), 5.31 (s,

6H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ [ppm] = 145.6, 131.9, 126.0, 117.8, 114.5, 113.5. **HRMS (FD): m/z** $[M]^+$ found: 273.1330, calcd. for $C_{18}H_{15}N_3$: 273.1266.

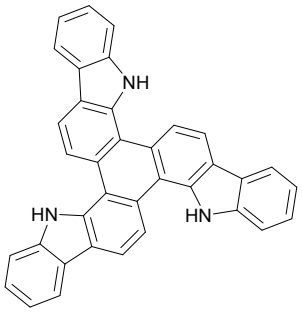
*N*1,*N*5,*N*9-Tris(2-chlorophenyl)triphenylene-1,5,9-triamine (Method C) (S4)



S4

S4 was prepared similar to an adapted procedure.[II] **S3** (700 mg, 2.59 mmol), sodium-*tert*-butoxide (812 mg, 8.45 mmol) and DavePhos-Pd-G3 (195 mg, 256 µmol) were added to an oven-dried vial (20 mL). The vial was sealed, evacuated and refilled with argon three times. 1-Bromo-2-chlorobenzene (1 mL, 9 mmol) and 1,4-dioxane were injected quickly. The resulting mixture was vigorously shaken, and the vial was placed in a preheated oil-bath (100 °C). After stirring for 16 h the dark mixture was filtrated through silica gel with dichloromethane. The solvent was removed *in vacuo* and the crude product was dried under high vacuum at 80 °C. Finally, the dark solid was purified by flash chromatography with DCM:Hex (1:19 → 2:3) as eluent to yield a colourless solid (78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 8.83 (dd, *J* = 7.5, 2.1 Hz, 3H), 7.60 (s, 3H), 7.37 (dd, *J* = 7.9, 1.5 Hz, 3H), 7.33–7.23 (m, 6H), 6.92 (ddd, *J* = 8.4, 7.3, 1.5 Hz, 3H), 6.72 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 3H), 6.42 (dd, *J* = 8.2, 1.5 Hz, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ [ppm] = 141.5, 137.7, 130.8, 129.1, 127.0, 126.1, 125.1, 124.9, 121.6, 120.5, 119.4, 115.0. **HRMS (FD): m/z** $[M]^+$ found: 603.1357, calcd. for $C_{36}H_{24}N_3Cl_3$: 603.1036.

12,19-Dihydro-5*H*-benzo[1,2-a:3,4-a':5,6-a'']tricarbazole (aTC) (Method D)



aTC

aTC was prepared according to an adapted literature procedure with some modifications.[III] $Pd(AcO)_2$ (78 mg, 349 µmol) and **S4** (800 mg, 1.16 mmol) were dissolved in *o*-xylene (20 mL). Subsequently, tri-*tert*-butylphosphine (86 µl, 349 µmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.8 mL, 5.29 mmol) were added and the mixture heated up to 140 °C. After stirring for 16 h the dark mixture was filtrated trough a pad of silica, with dichloromethane as eluent. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography with DCM:Hex (1:7) as eluent. Finally, the product was recrystallized from acetonitrile to give a dark yellow powder (53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 11.99 (s, 3H), 9.04 (d, *J* = 8.4 Hz, 3H), 8.63 (d, *J* = 8.4 Hz, 3H), 8.36 (d, *J* = 7.7 Hz, 3H), 7.86 (d, *J* = 7.9 Hz, 3H), 7.51 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 3H), 7.32 (ddd, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ [ppm] = 140.6, 135.7, 126.8, 125.4, 122.5, 122.0, 119.8, 119.8, 119.4, 117.3, 117.2, 112.1. **HRMS (FD): m/z** $[M]^+$ found: 495.1733, calcd. for $C_{36}H_{21}N_3$: 495.1736. **IR**: $\tilde{\nu}$ (cm^{-1}) = 3401, 3053, 2970, 2916, 1595, 1575. **UV/Vis** (chloroform) $\lambda_{max.}$ [nm] = *331*, (359), (389), (417). **PL** (chloroform) $\lambda_{max.}$ [nm] ($\lambda_{exc.}$ = 331) = (420), *435*, (463). **Energy-level/Bandgap**: E_{HOMO} [eV] = −5.23, E_{LUMO} [eV] = −2.14, E_g [eV] = 3.09.

1.3.2 bTC

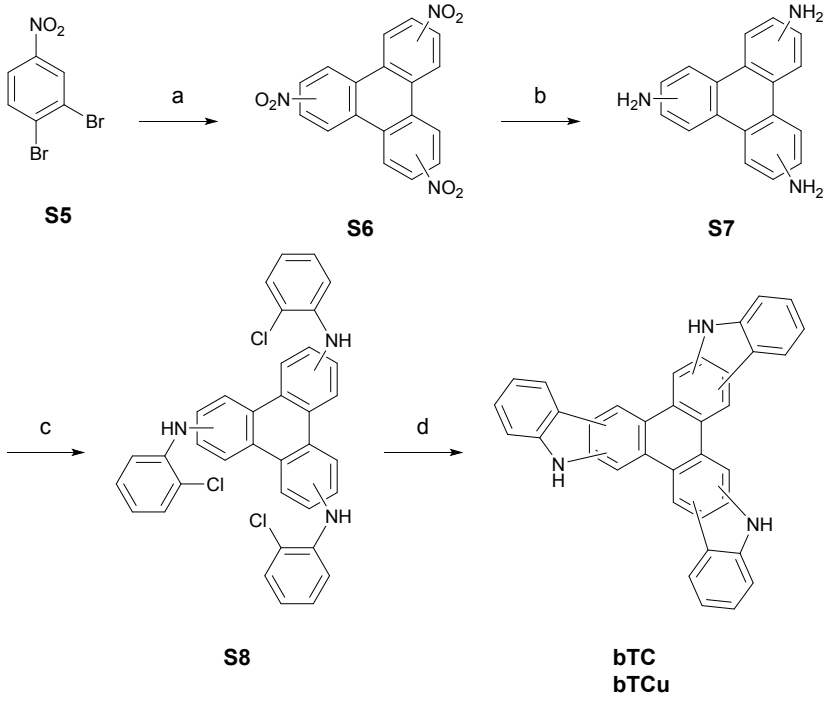
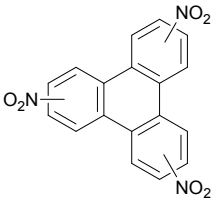


Figure S2*: Synthetic route to* ***bTC*** *and* ***bTCu****.* ***a****) Cu, DMF, 200 °C, 12 h (16%);* ***b****) H_2, Pd/C, EA:EtOH (10:1) (97%);* ***c****) t-BuONa, 1-bromo-2-chlorobenzene, DavePhos catalyst, 1,4-dioxane, 125 °C, 18 h (29%);* ***d****) DBU, $Pd(OAc)_2$, $P(t\text{-}Bu)_3$, o-xylene , 140 °C, 18 h (53%).*

The synthesis of the b-connected tricarbazole monomers was carried out with a mixture of regioisomers. The separation step was implemented after the final synthetic step by preparative HPLC. The resulting mixtures of the individual synthesis steps were characterized by mass spectrometry.

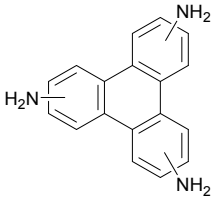
Regioisomeric mixture of trinitrotriphenylenes (S6)



S6

Following method **A**: Copper powder (48 g, 0.75 mol), 1,2-dibromo-4-nitrobenzene (35 g, 0.12 mol), dimethylformamide (125 mL), yield: 16%. **HRMS (FD): m/z** $[M]^+$ found: 363.0458, calcd. for $C_{18}H_9N_3O_6$: 363.0491.

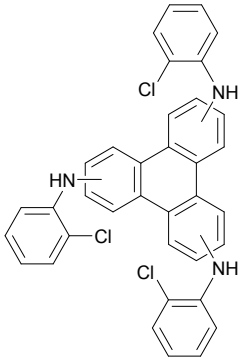
Regioisomeric mixture of triaminotriphenylenes (S7)



S7

Following method **B**: **S6** (2.31 g, 6.36 mmol), Pd/C (10%) (2.03 g, 1.91 mmol), ethyl acetate (100 mL), ethanol (10 mL). Yield: 83%. **HRMS (FD): m/z** $[M]^+$ found: 273.1357, calcd. for $C_{18}H_{15}N_3$: 273.1266.

Regioisomeric Mixture of Tris(2-chlorophenyl)triphenylene-triamines (S8)



S8

Following method **C**: **S7** (800 mg, 2.93 mmol), sodium-*tert*-butoxide (928 mg, 9.66 mmol), DavePhos-Pd-G3 (201 mg, 263 µmol), 1-bromo-2-chlorobenzene (1.1 mL, 9.37 mmol), 1,4-dioxane (9 mL). **HRMS (FD): m/z** $[M]^+$ found: 363.0458, calcd. for $C_{18}H_9N_3O_6$: 363.0491.

At this point, the regioisomeric ratio was calculated with the help of the integrals of the amino-related protons (^{1}H NMR, **Figure 3**). Ratio **S8a**:**S8b** (9:91)

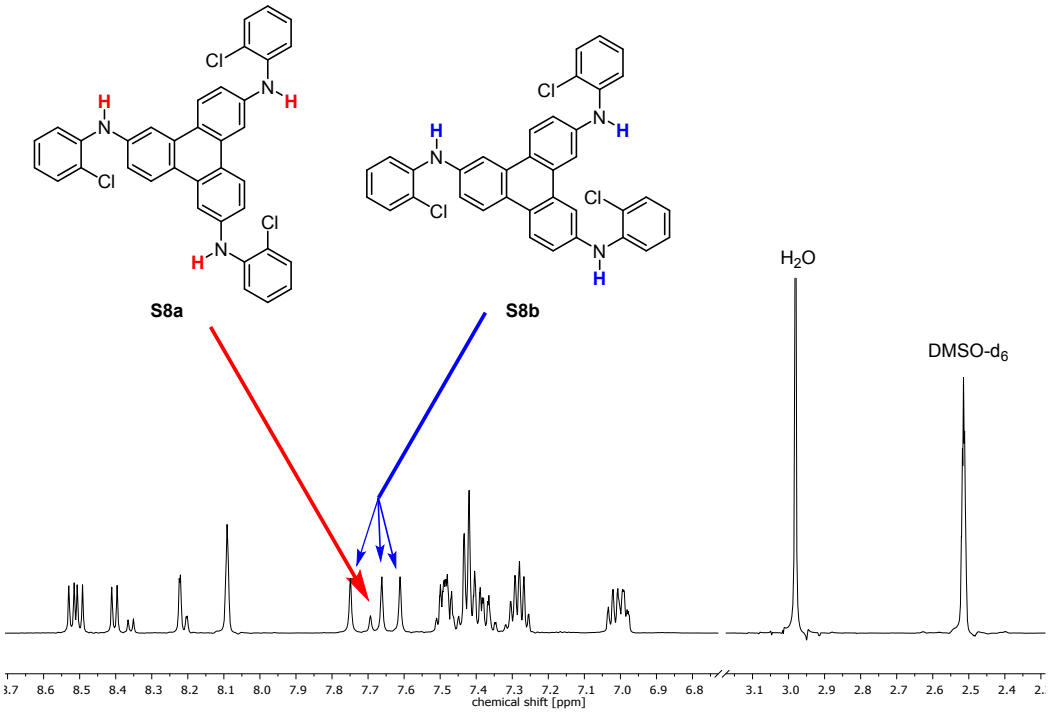
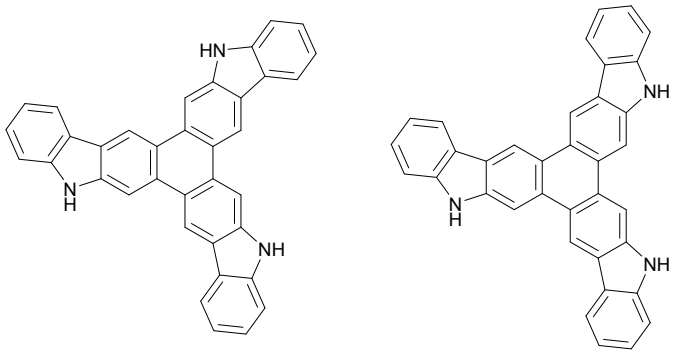


Figure S3: *^{1}H NMR spectrum of* ***S8a/b*** *in DMSO-d_6.*

Mixture of 8,15-dihydro-5*H*-benzo[1,2-b:3,4-b':6,5-b'']tricarbazole and 12,19-dihydro-5*H*-benzo[1,2-b:3,4-b':5,6-b'']tricarbazole



bTC **bTCu**

Following method **D**: $Pd(AcO)_2$ (45 mg, 0.20 mmol), **S8** (400 mg, 661 µmol), tri-*tert*-butylphosphine (41 mg, 0,20 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.4 mL, 2.64 mmol), *o*-xylene (10 mL). HPLC (1:9 H_2O/CAN, isocratic, 1mL/min).

bTC: After recrystallisation with ACN, a brownish powdery precipitate is isolated (5%). **^{1}H NMR** (600 MHz, DMSO-d_6) δ [ppm] = 11.6 (s, 3H), 9.58 (s, 3H), 8.93 (s, 3H), 8.46 (d, *J* = 7.7 Hz, 3H), 7.59 (d, *J* = 7.8 Hz, 3H), 7.48 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 3H), 7.30–7.23 (m, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ [ppm] = 141.6, 140.2, 126.2, 122.8, 122.8, 122.0, 120.8, 115.1, 103.3, 103.3.***** **HRMS (FD): m/z** $[M]^+$ found: 495.1800, calcd. for $C_{36}H_{21}N_3$: 495.1736. **IR**: ṽ (cm^{-1}) = 3296, 2954, 2923, 2854, 1765, 1718, 1632, 1608. **UV/Vis** (chloroform) $\lambda_{max.}$ [nm] = *324*, (387). **PL** (chloroform) $\lambda_{max.}$ [nm] ($\lambda_{exc.}$ = 387) = (411), *424*, (457). **Energy-level/Bandgap**: E_{HOMO} [eV] = −5.23, E_{LUMO} [eV] = −2.04, E_g [eV] = 3.19.

****** *Only the main signals are listed. The low solubility of the products does not allow for a resolution of all signals.*

bTCu: Obtained as a yellow solid (32 %). **^1H NMR** (600 MHz, DMSO-d_6) δ [ppm] = 11.40 (s, 1H), 11.34 (s, 1H), 11.31 (s, 1H), 9.78 (s, 1H), 9.76 (s, 1H), 9.61 (s, 1H), 8.92 (s. 1H), 8.76 (s, 1H), 8.74 (s. 1H), 8.52–8.44 (m, 3H), 7.62–7.57 (m, 3H), 7.53–7.45 (m, 3H), 7.34–7.26 (m, 3H). **$^{13}C\{^1H\}$ NMR** (151 MHz, DMSO-d_6) δ [ppm] = 141.6, 140.0, 139.6, 139.5, 128.9, 128.7, 127.9, 126.4, 126.3, 126.1, 123.6, 123.4, 123.0, 122.9, 122.9, 122.7, 122.7, 122.6, 121.0, 120.8, 120.6, 199.0, 118.7, 118.6, 118.5, 115.1, 115.1, 114.7, 114.6, 110.9, 103.6, 103.5, 103.4, 103.3, 103.2.***** **HRMS (FD): m/z** $[M]^+$ found: 495.1752, calcd. for $C_{36}H_{21}N_3$: 495.1736. **IR**: ṽ (cm^{-1}) = 3545, 3410, 3050, 2981, 2966, 2918, 2853, 1933, 1609. **UV/Vis** (Chloroform) $\lambda_{max.}$ [nm] = *312*, (336), (357), (407). **PL** (chloroform) $\lambda_{max.}$ [nm] ($\lambda_{exc.}$ = 360) = *427*, (442). **Energy-level/Bandgap**: E_{HOMO} [eV] = −5.22, E_{LUMO} [eV] = −2.10, E_g [eV] = 3.12.

1.3.3 Triptycene-based monomers

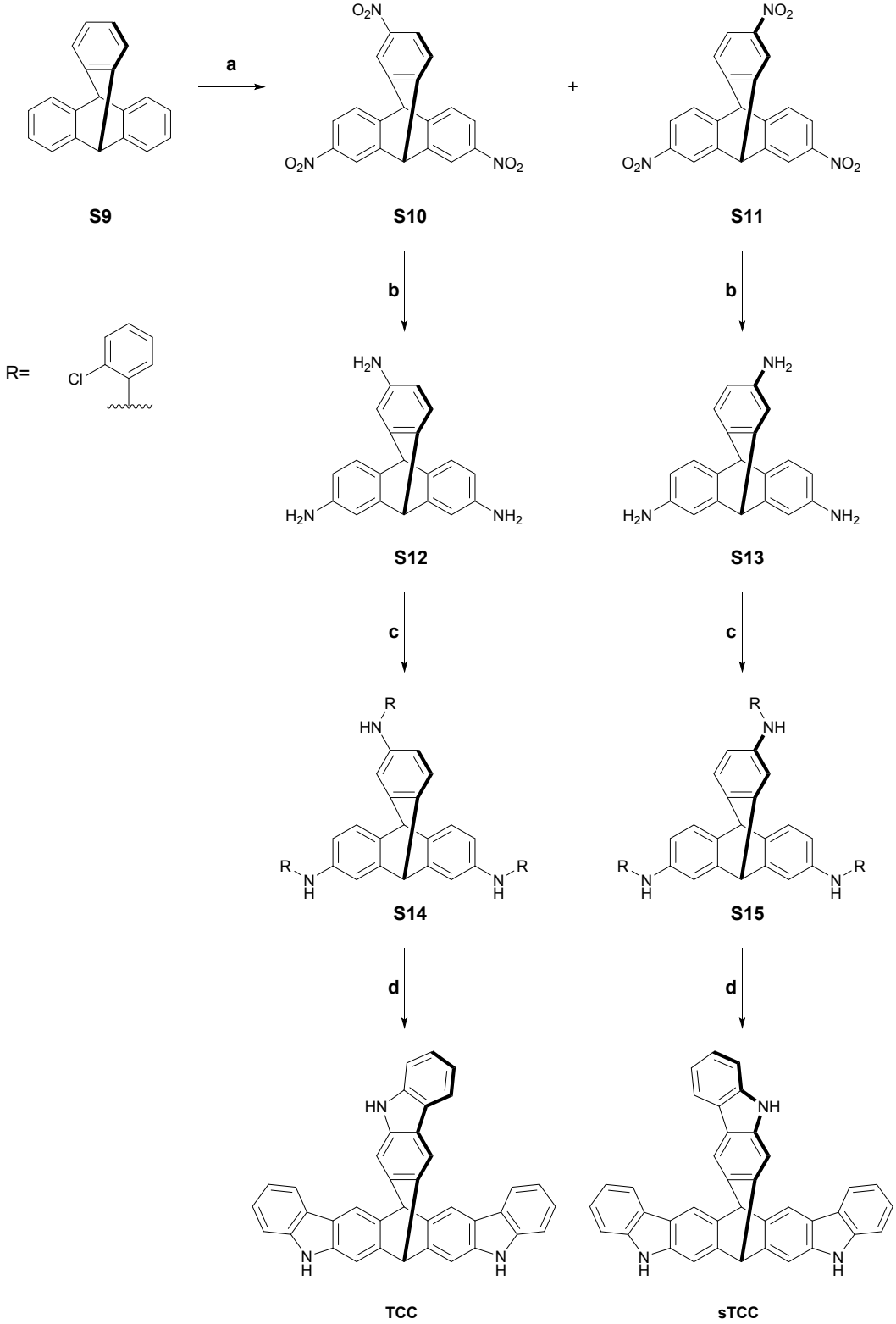
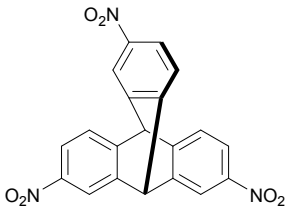
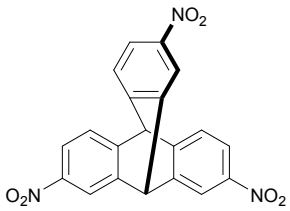


***Figure S4**: **a**) 70% HNO_3, 80 °C, 4 h (**S10** 70%, **S11** 20%); **b**) H_2, Pd/C, EA:EtOH (10:1) (**S12** 88%, **S13** 99%); **c**) t-BuONa, 1-bromo-2-chlorobenzene, DavePhos-catalyst, 1,4-dioxane, 125 °C, 18 h (**S14** 49%, **S15** 89%); **d**) PivOH, **K1** , K_2CO_3, DMAc, 110 °C, 16 h (**TCC** 48%, **sTCC** 23%).*

2,6,14-Trinitro-9,10-dihydro-9,10-[1,2]benzenoanthracene (S10) and 2,7,15-Trinitro-9,10-dihydro-9,10-[1,2]benzenoanthracene (S11)



S10



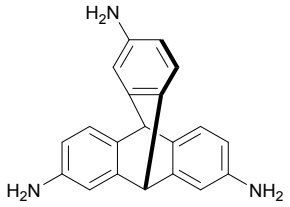
S11

The **S10**/**S11** mixture was prepared according to an adapted literature procedure.[II] Triptycene (7 g, 27.52 mmol) was added slowly to nitric acid (70%, 180 mL) at 0 °C. After 2 h, the mixture was heated up to 80 °C for 4 h. After that the brown mixture was poured into ice water (500 mL). The precipitate solid was filtered off, re-dissolved in ethyl acetate, washed with water and brine, and dried over magnesium sulphate. Next, the solvent was removed *in vacuo*. The crude product mixture was separated by flash chromatography with EA/Hex (3:17→3:7).

S10 is obtained as light-yellow solid (yield: 70%): **^{1}H NMR** (400 MHz, DMSO-d_6) δ [ppm] = 8.42 (d, *J* = 2.3 Hz, 1H), 8.40 (d, *J* = 2.3 Hz, 2H), 8.05 (dd, *J* = 2.3; 1.4 Hz, 1H), 8.03 (dd, *J* = 2.3; 1.5 Hz, 2H), 7.82 (s, 2H), 7.80 (s, 1H), 6.43 (s, 1H), 6.41 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ [ppm] = 150.5, 150.1, 145.5, 144.9, 144.5, 141.4, 125.6, 125.5, 122.1, 122.0, 119.5, 119.5, 51.4, 51.2, 39.9. **HRMS (FD): m/z** $[M]^+$ found: 389.0749, calcd. for $C_{20}H_{11}N_3O_6$: 389.0647.

S11 is obtained as colourless solid (yield: 20%): **^{1}H NMR** (400 MHz, DMSO-d_6) δ [ppm] = 8.39 (d, *J* = 2.3 Hz, 3H), 8.03 (dd, *J* = 8.2, 2.3 Hz, 3H), 7.82 (d, *J* = 8.2 Hz, 3H), 6.44 (s, 1H), 6.39 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ [ppm] = 149.7, 145.5, 145.3, 125.6, 122.1, 119.4, 51.7, 51.0. **HRMS (FD): m/z** $[M]^+$ found: 389.6253, calcd. for $C_{20}H_{11}N_3O_6$: 389.0647.

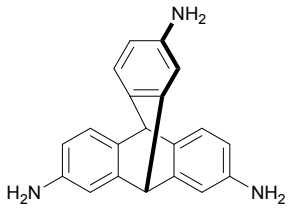
9,10-Dihydro-9,10-[1,2]benzenoanthracene-2,6,14-triamine (S12)



S12

Following method **B**: **S10** (1 g, 2.57 mmol), Pd/C (10%) (1.09 g, 1.03 mmol), ethyl acetate (80 mL), ethanol (8 mL), colourless solid (88%). **^{1}H NMR** (600 MHz, DMSO-d_6) δ [ppm] = 6.95 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 2H), 6.60 (dd, *J* = 20.6, 2.2 Hz, 3H), 6.10 (td, *J* = 8.1, 2.2 Hz, 3H), 5.06 (s, 6H), 4.91 (s, 2H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ [ppm] = 147.7, 146.9, 145.0, 144.8, 134.4, 133.5, 123.3, 122.9, 110.4, 110.0, 108.8, 108.5, 52.4, 51.3. **HRMS (FD): m/z** $[M]^+$ found: 300.1495, calcd. for $C_{20}H_{18}N_3$: 300.1495.

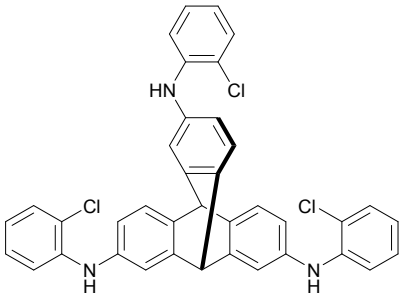
9,10-Dihydro-9,10-[1,2]benzenoanthracene-2,7,15-triamine (S13)



S13

Following method **B**: **S11** (1.10 g, 2.83 mmol), Pd/C (10 %) (1.20 g, 1.13 mmol), ethyl acetate (80 mL), ethanol (8 mL). Yellow solid (99%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ [ppm] = 6.93 (d, *J* = 7.8 Hz, 3H), 6.68 (d, *J* = 2.1 Hz, 3H), 6.16 (dd, *J* = 7.8, 2.2 Hz, 3H), 5.35–5.27 (m, 6H), 4.97 (d, *J* = 5.1 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ [ppm] = 146.1, 143.9, 135.6, 122.6, 111.0, 109.4, 53.4, 50.1. **HRMS (FD): m/z** $[M]^+$ found: 299.1489, calcd. for $C_{20}H_{17}N_3$: 299.1423.

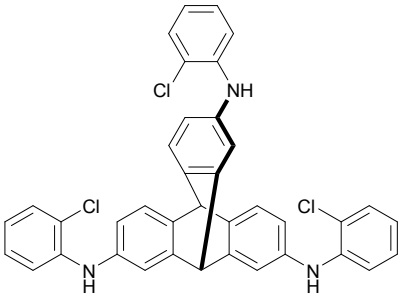
*N*2,*N*6,*N*14-Tris(2-chlorophenyl)-9,10-dihydro-9,10-[1,2]benzenoanthracene-2,6,14-triamine (S14)



S14

Following method **C**: **S12** (270 mg, 0,90 mmol), sodium-*tert*-butoxide (286 mg, 2.98 mmol), DavePhos-Pd-G3 (68.8 mg, 90 µmol), 1-bromo-2-chlorobenzene (330µL, 2.80 mmol), 1,4-dioxane (8 mL), colourless solid (49%). **^{1}H NMR** (600 MHz, DMSO-d_6) δ [ppm] = 7.48 (d, *J* = 4.4 Hz, 3H), 7.39 (dd, *J* = 8.1, 3.1 Hz, 3H), 7.26 (dd, *J* = 7.9, 2.1 Hz, 3H), 7.19–7.12 (m, 9H), 6.90–6.82 (m, 3H), 6.67 (td, *J* = 7.9, 2.2 Hz, 3H), 5.37 (d, *J* = 3.4 Hz, 2H) **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ [ppm] = 147.0, 146.6, 140.5, 140.5, 139.9, 139.8, 138.4, 137.8, 129.8, 127.7, 123.9, 123.6, 122.7, 122.6, 121.2, 121.2, 118.5, 118.4, 114.7, 114.3, 114.2, 114.0, 52.2, 51.4. **HRMS (ESI): m/z** $[M+H]^+$ found: 630.1266, calcd. for $C_{38}H_{27}Cl_3N_3$: 630.1265.

*N*2,*N*7,*N*15-Tris(2-chlorophenyl)-9,10-dihydro-9,10-[1,2]benzenoanthracene-2,7,15-triamine (S15)

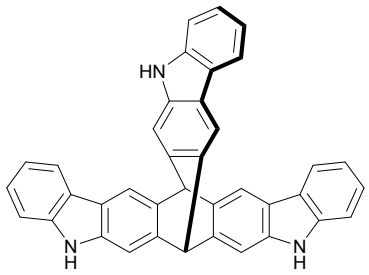


S15

Following method **C**: **S13** (840 mg, 2.81 mmol), sodium-*tert*-butoxide (890 mg, 9.26 mmol), DavePhos-Pd-G3 (214 mg, 281 µmol), 1-bromo-2-chlorobenzene (1 mL, 8.70 mmol), 1,4-dioxane (8 mL). colorless solid (17%). **^{1}H NMR** (600 MHz, DMSO-d_6) δ [ppm] = 7.48 (d, *J* = 7.0 Hz, 3H), 7.41–7.35 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 3H), 7.19–7.13 (m, 9H), 6.85 (ddd, *J* = 8.0, 5.5, 3.4 Hz, 3H), 6.68 (dd, *J* = 7.9, 2.2 Hz, 3H), 5.38 (d, *J* = 9.7 Hz, 2H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ [ppm] = 146.1, 140.6, 139.6, 138.9, 129.8, 127.7, 123.4, 122.6, 121.1, 118.4,

115.0, 114.5, 52.9, 50.6. **HRMS (FD): m/z** $[M]^+$ found: 629.1220, calcd. for $C_{38}H_{26}N_3Cl_3$: 629.1192.

5,7,13,15-Tetrahydro-7,15-[2,3]epicarbazolobenzo[1,2-b:4,5-b']dicarbazole (TCC) (Method E)

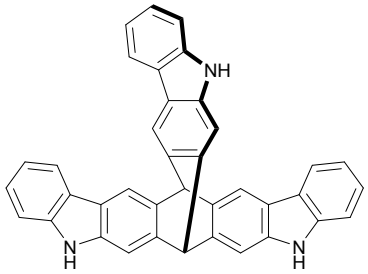


TCC

TCC was prepared according to an adapted literature procedure.[II] Potassium carbonate (552 mg, 3.99 mmol), pivalic acid (41 mg, 0.40 mmol), **S14** (280 mg, 444 µmol) and the tricyclohexylphosphine-Bruno-Precatalyst (**K1**) (87 mg, 0.13 mmol)[IV] were added into a vial (20 mL). The vial was sealed, evacuated and refilled with argon three times. Subsequently dimethylacetamide (10 mL) was injected quickly. The resulting mixture was vigorously shaken, and the vial was placed in a preheated oil bath (110 °C). After 16 h the reaction mixture was cooled down to room temperature and poured into brine. Next, the mixture was extracted with DCM (5 x). The organic layer was dried over magnesium sulphate, and the solvent was removed *in vacuo*. The crude product was dried. Diethyl ether was added to the resulting black oil, the mixture sonicated and cooled down to −24 °C for 18 h in a freezer. After short cooling to −78 °C, the white precipitate was filtered off and washed with diethyl ether (cooled to −78 °C). The grey solid was further purified by recrystallization from toluene (six times, concentration: 10 mg/1 mL). Yield: 48%. **^{1}H NMR** (600 MHz, DMSO-d_6) δ [ppm] = 11.13 (d, *J* = 2.2 Hz, 3H), 8.17 (s, 3H), 8.06–8.00 (m, 3H), 7.64–7.62 (m, 3H), 7.46–7.37 (m, 3H), 7.31–7.25 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 3H), 5.90 (s, 1H), 5.88 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ [ppm] = 146.5, 140.0, 137.3, 129.2, 125.5, 124.5, 122.5, 119.5, 118.3, 110.8, 110.8.* **HRMS (FD): m/z** $[M]^+$ found: 521.2142, calcd. for $C_{36}H_{21}N_3$: 521.1892. **IR**: $\tilde{\nu}$ (cm^{-1}) = 3407, 3052, 2928, 2863, 1716, 1567. **UV/Vis** (Chloroform)$\lambda_{max.}$ [nm] = *309*, (340). **PL** (chloroform) $\lambda_{max.}$ [nm] ($\lambda_{exc.}$ = 310) = *356*, (366), 443, 474, 512. **Energy-level/Bandgap**: E_{HOMO} [eV] = −5.24, E_{LUMO} [eV] = −1.63, E_g [eV] = 3.61.

***** Only the main signals are listed. The low solubility of the products does not allow for a resolution of all signals.*

5,7,9,15-Tetrahydro-7,15-[2,3]epicarbazolobenzo[1,2-b:5,4-b']dicarbazole (sTCC)



sTCC

Following method **E**: Potassium carbonate (483 mg, 3.49 mmol), pivalic acid (36 mg, 0.35 mmol) **S15** (245 mg, 388 µmol), tricyclohexylphosphine-Bruno-Precatalyst (**K1**)[IV] (776 mg, 0,12 mmol), DMA (5 mL). Yield: 23%. **^{1}H NMR** (600 MHz, DMSO-d_6) δ [ppm] = 11.10 (s, 3H), 8.16 (s, 3H), 8.04–8.00 (m, 3H), 7.62 (s, 3H), 7.41–7.38 (m, 3H), 7.26 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 3H), 7.08 (td, *J* = 7.5, 6.9, 1.0 Hz, 3H), 5.91 (s, 1H), 5.85 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ [ppm] = 143.5, 139.9, 137.4, 137.2, 124.4, 122.4, 119.5, 118.7, 114.4, 110.8, 106.8.***** **HRMS (FD): m/z** $[M]^+$ found: 521.1890, calcd. for $C_{38}H_{23}N_3$: 521.1892. **IR**: ṽ (cm^{-1}) = 3403, 3050, 2923, 2852, 1764, 1716, 1595. **UV/Vis** (chloroform)$\lambda_{max.}$ [nm] = *310*, 345. **PL** (Chloroform) $\lambda_{max.}$ [nm] ($\lambda_{exc.}$ = 310) = *356*, (366). **Energy-level/Bandgap**: E_{HOMO} [eV] = −5.23, E_{LUMO} [eV] = −1.63, E_g [eV] = 3.60.

** Only the main signals are listed. The low solubility of the products does not allow for a resolution of all signals.*

2 NMR Data

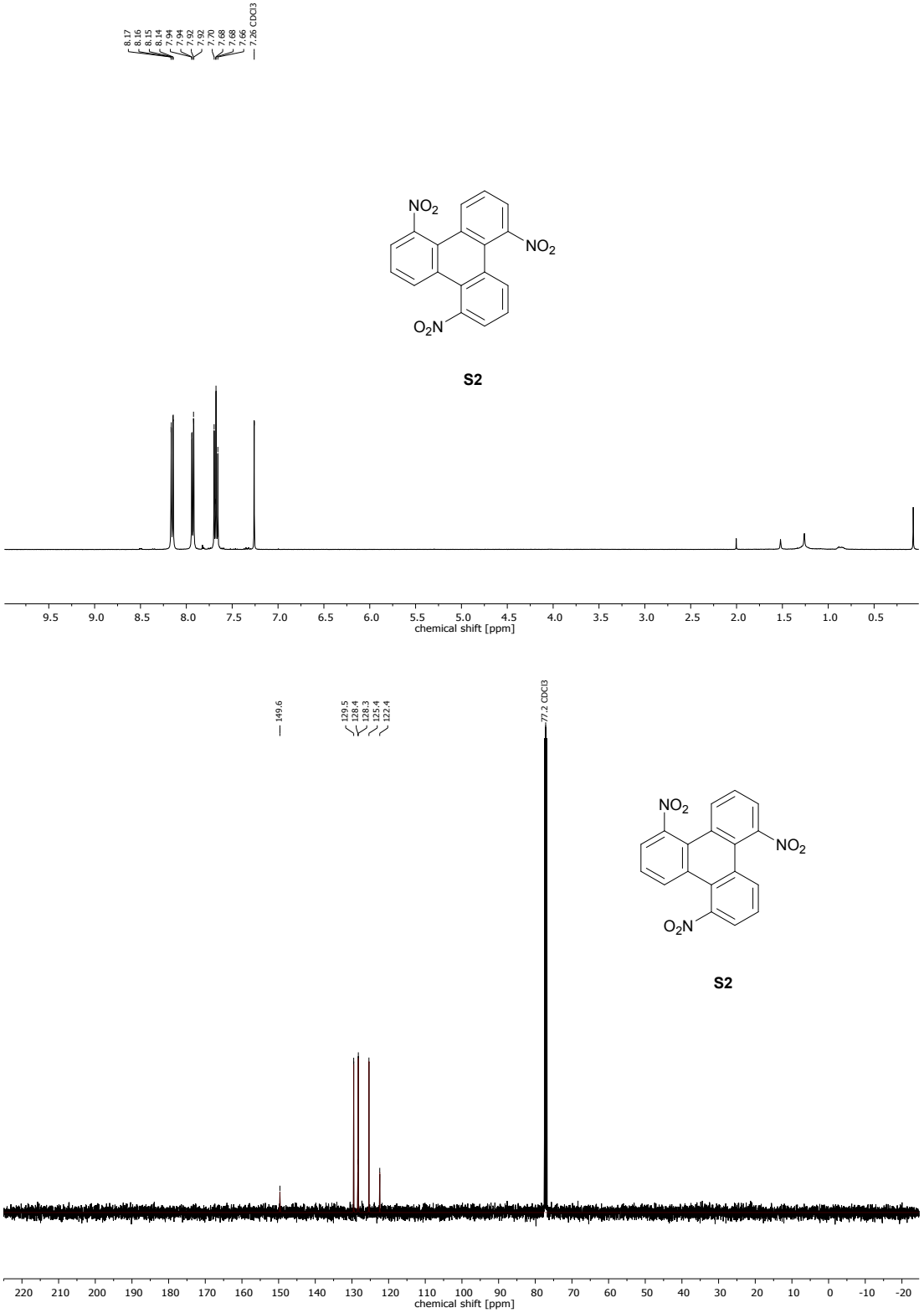


Figure S5: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of* ***S2*** *in chloroform.*

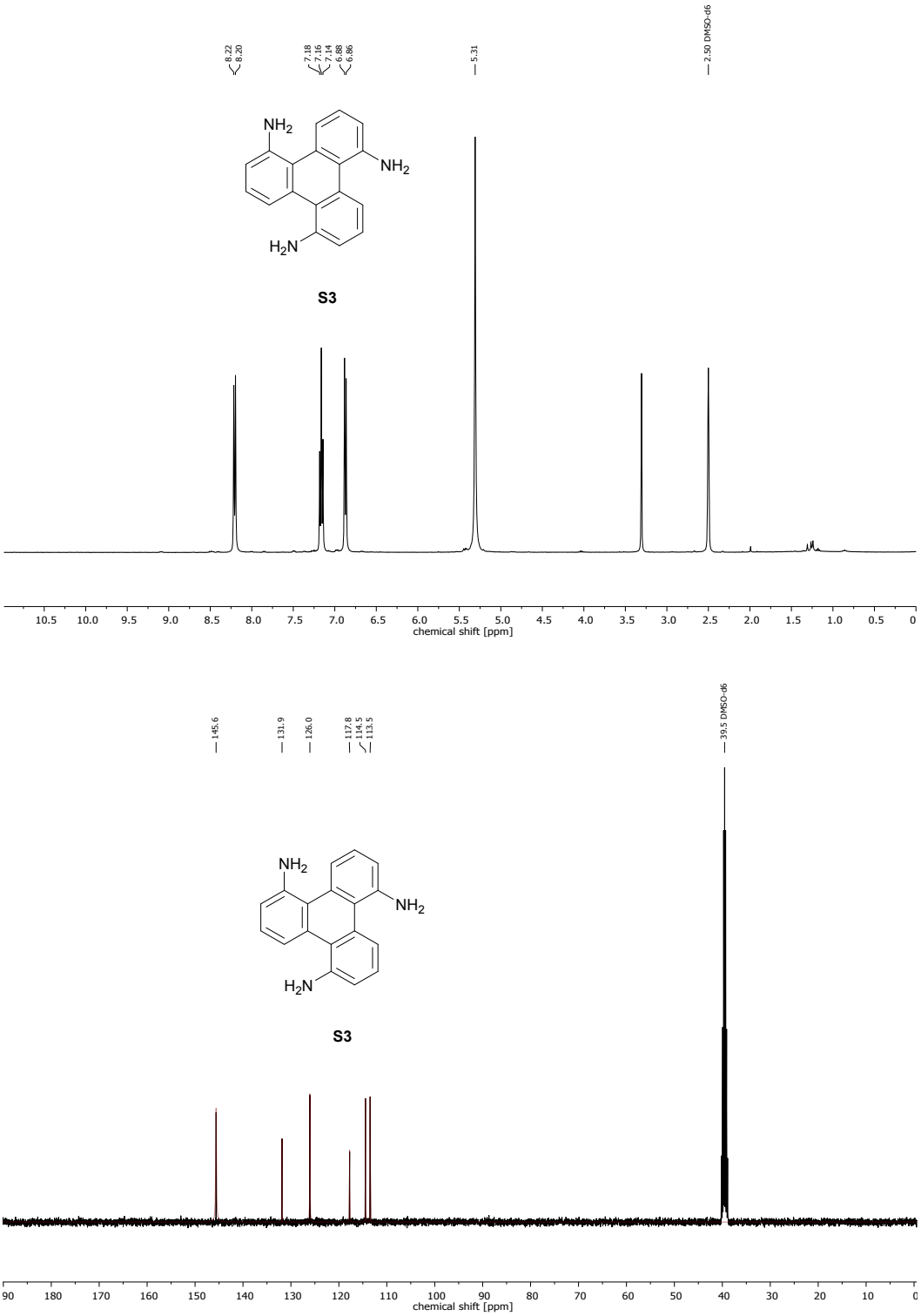


Figure S6: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of* ***S3*** *in DMSO-d_6.*

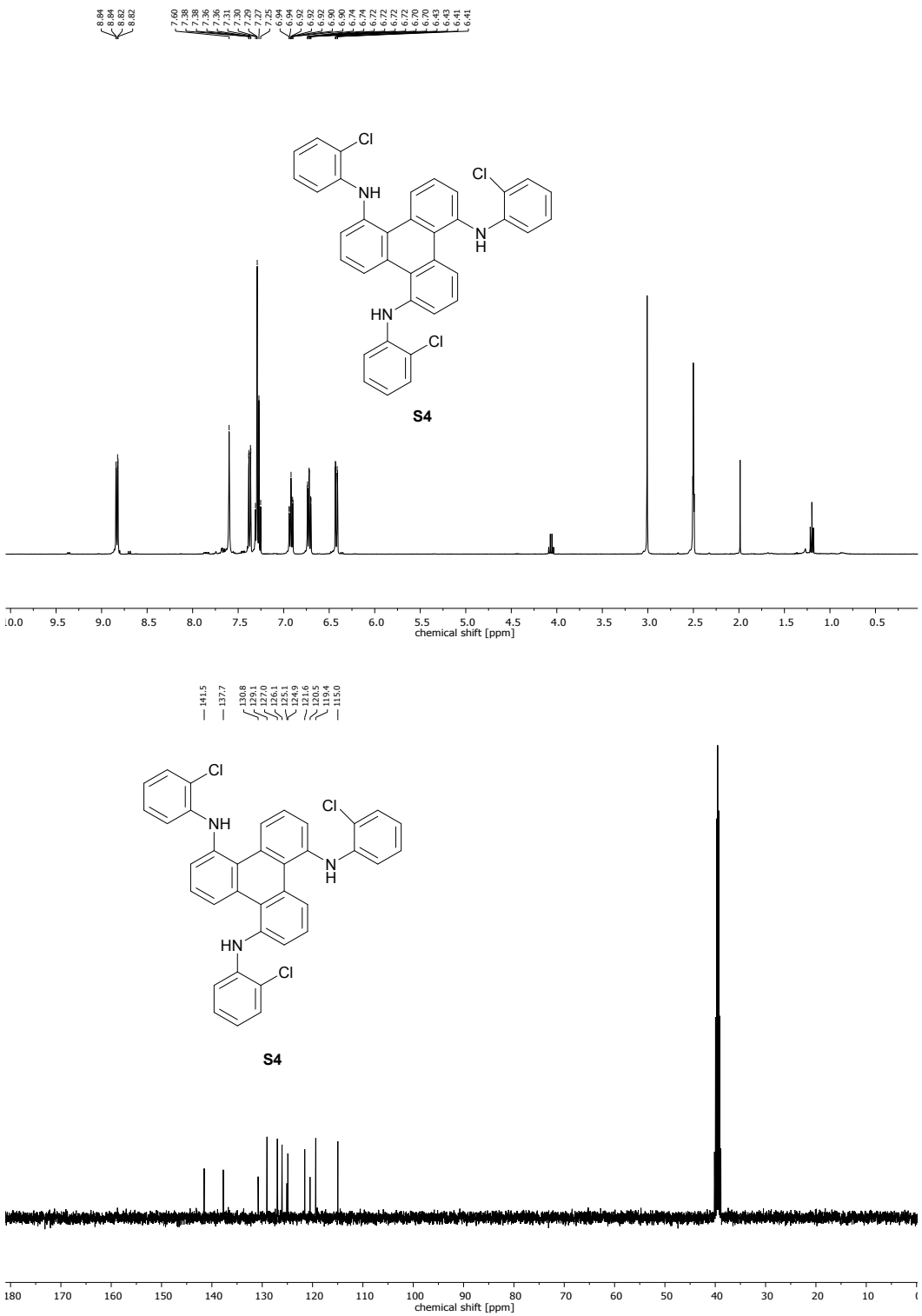
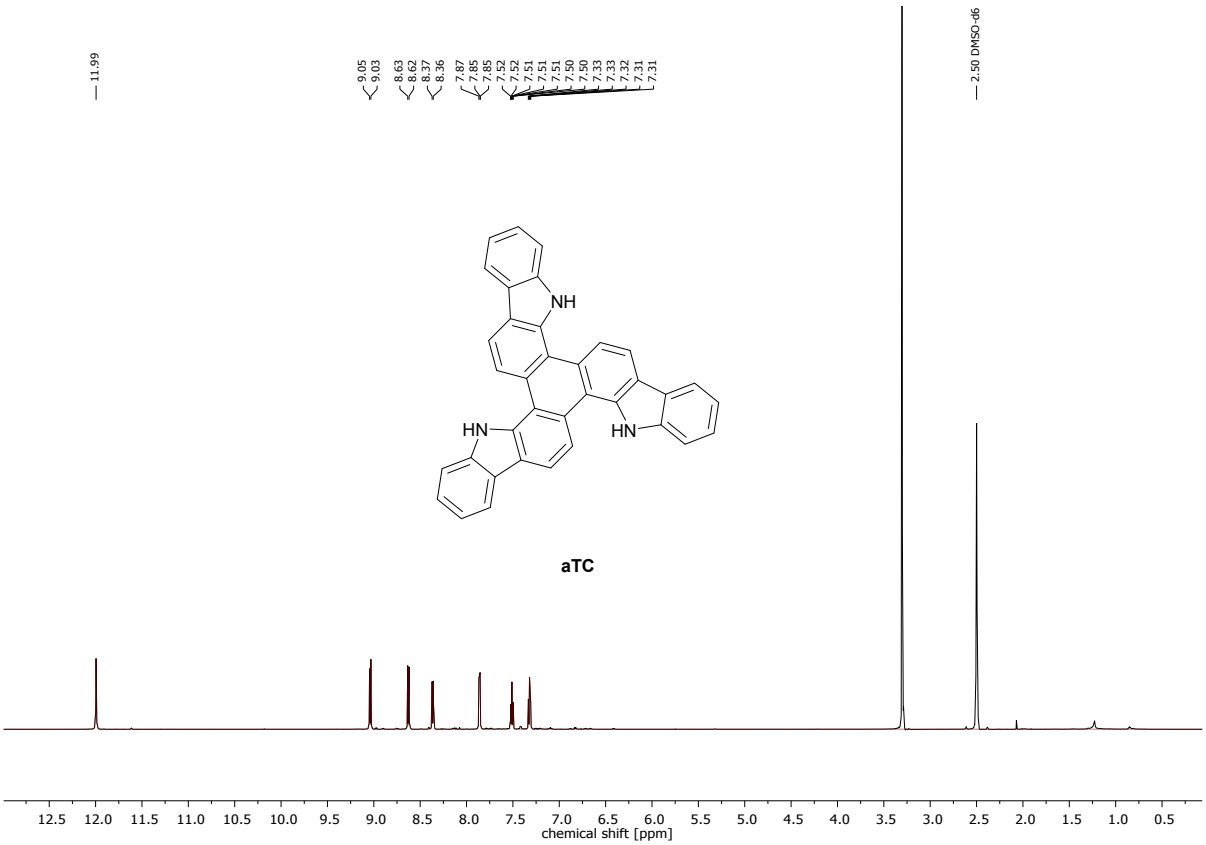


Figure S7: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of **S4** in DMSO-d_6.*



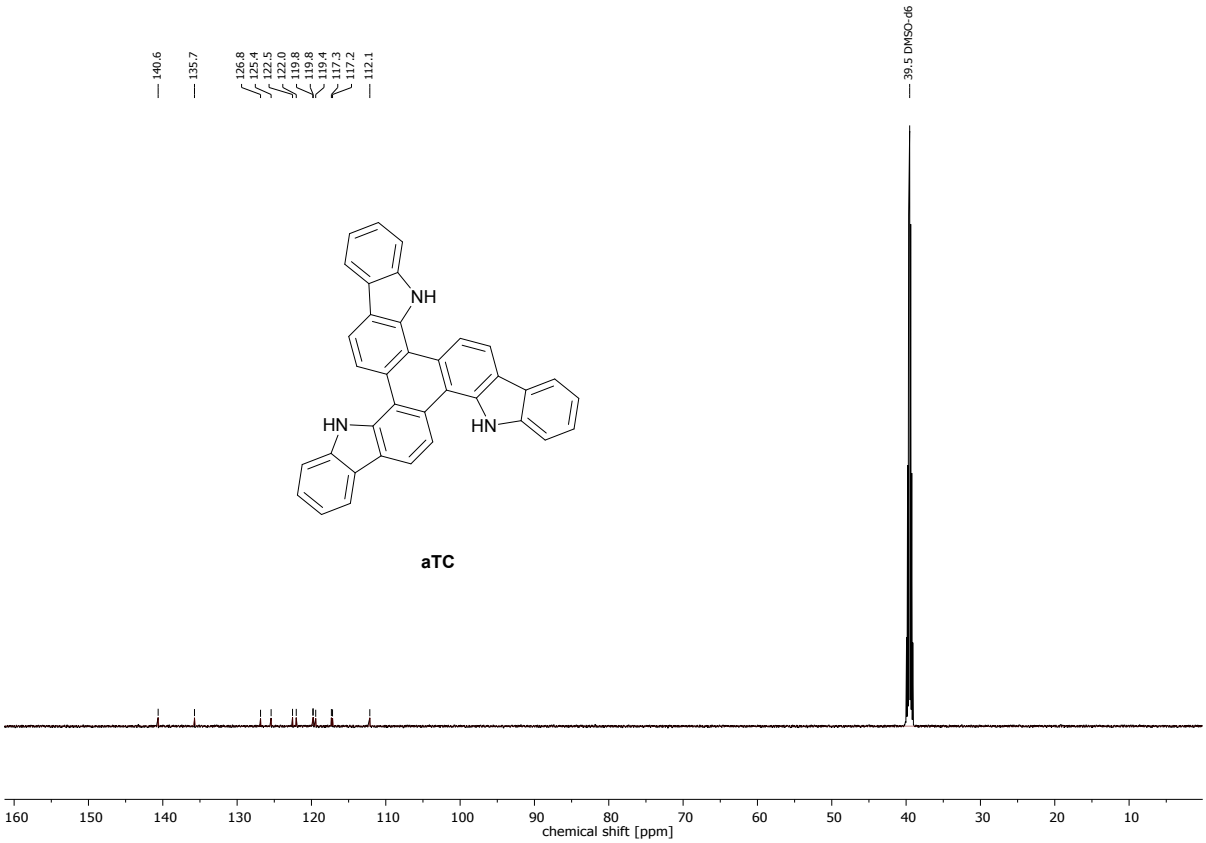


Figure S8: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of* ***aTC*** *in DMSO-d_6.*

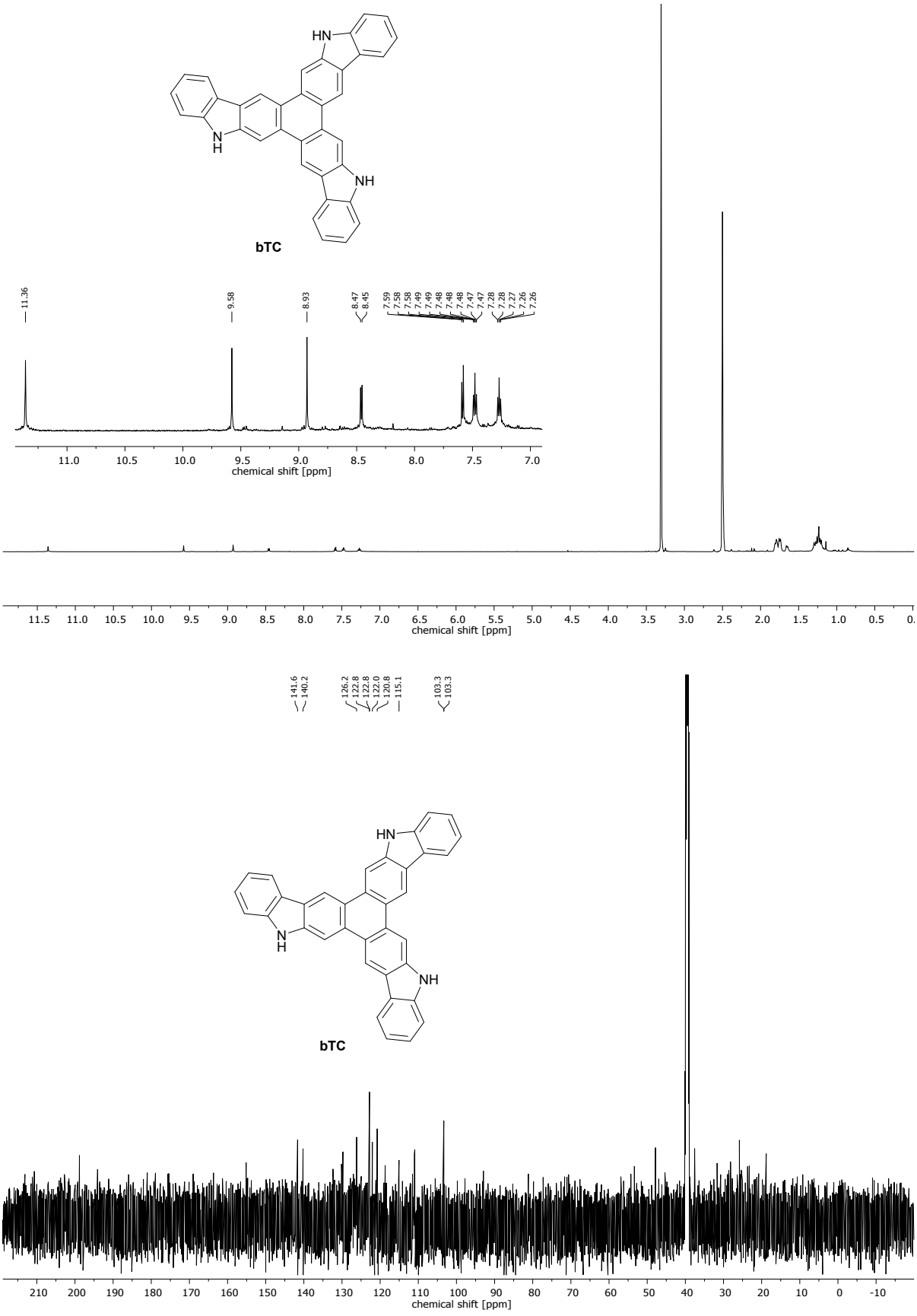


Figure S9: *^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of* ***bTC*** *in DMSO-d_6.*

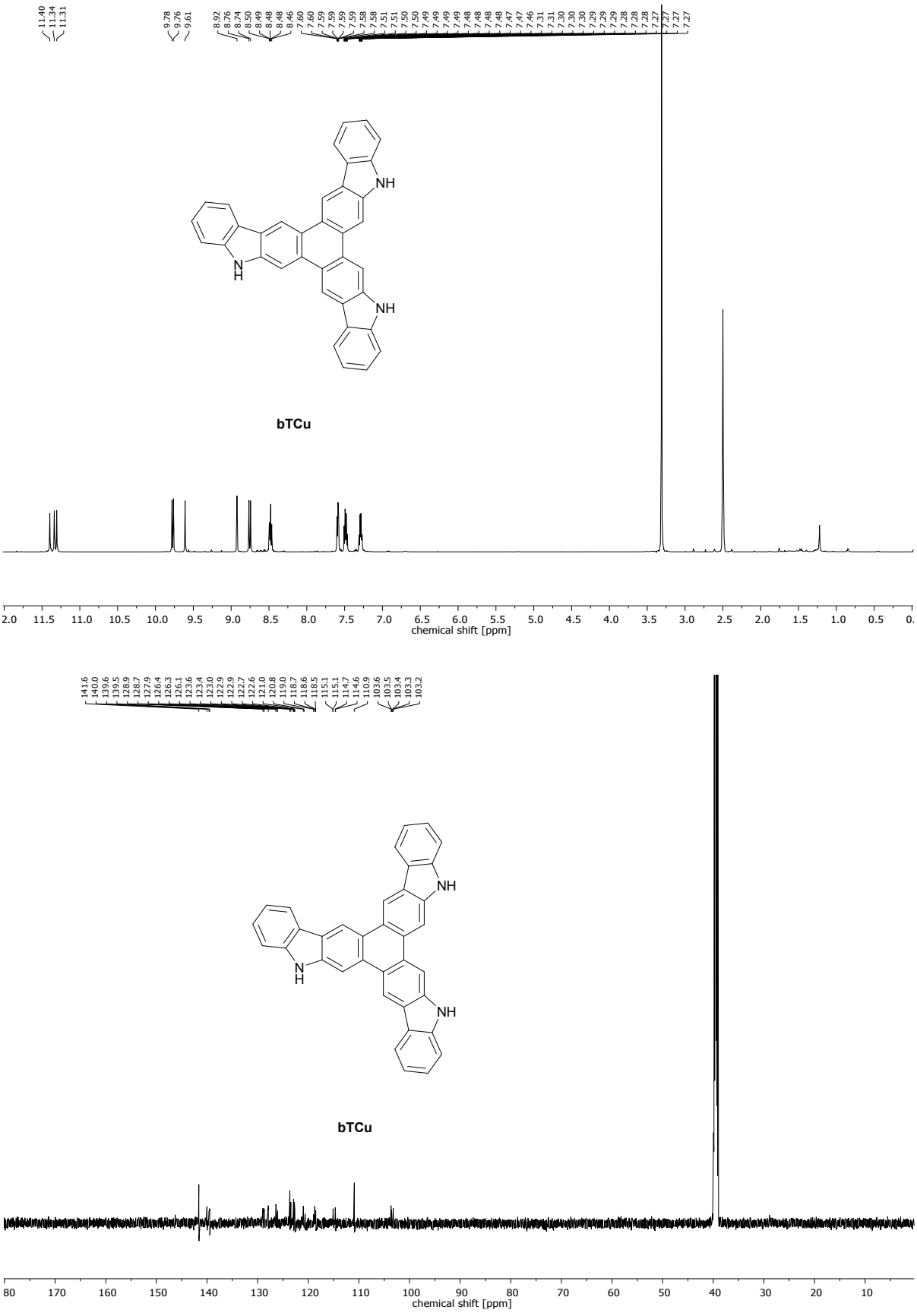


Figure S10: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of* ***bTCu*** *in DMSO-d_6.*

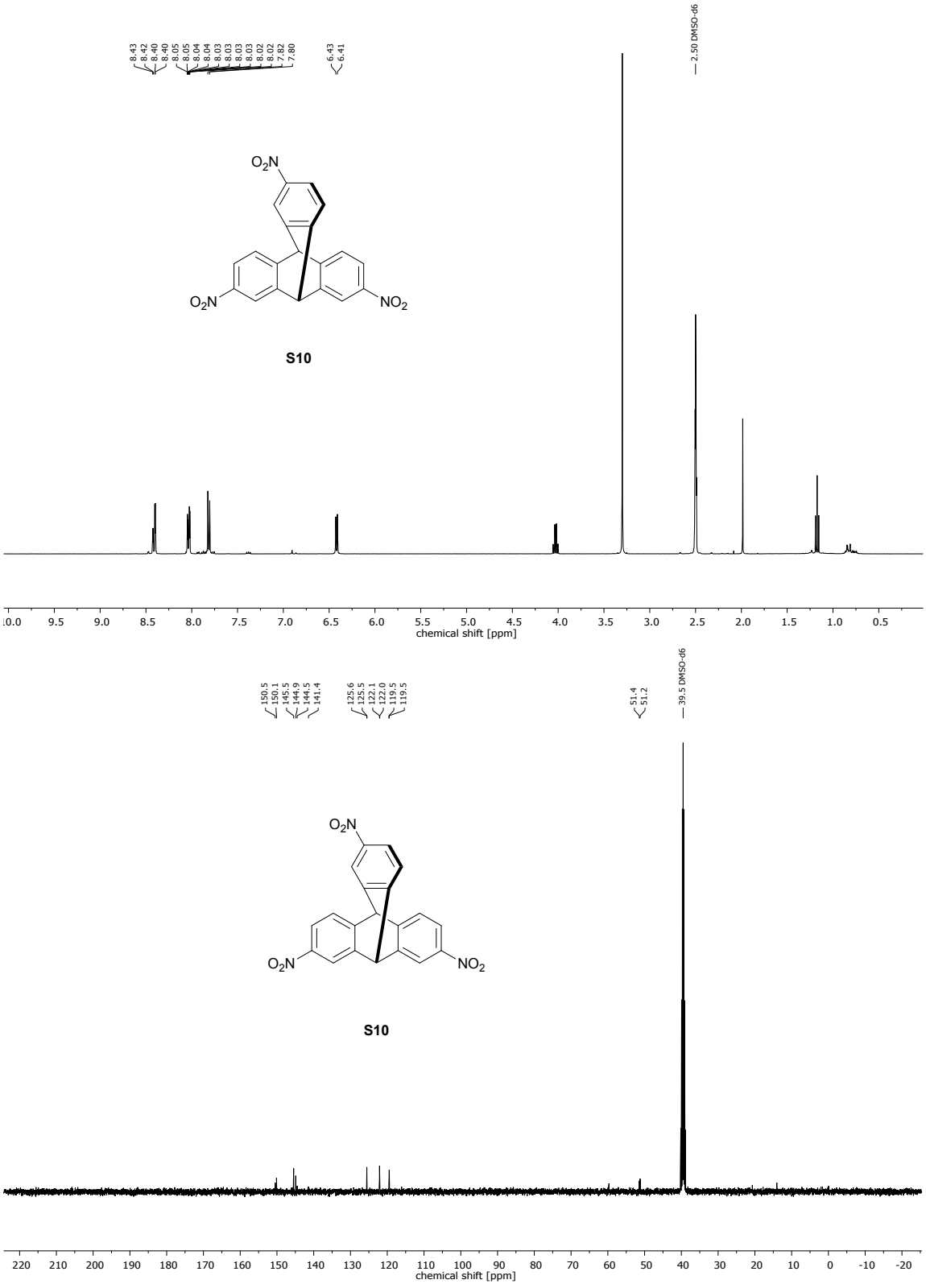


Figure S11: *^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of **S10** in DMSO-d_6.*

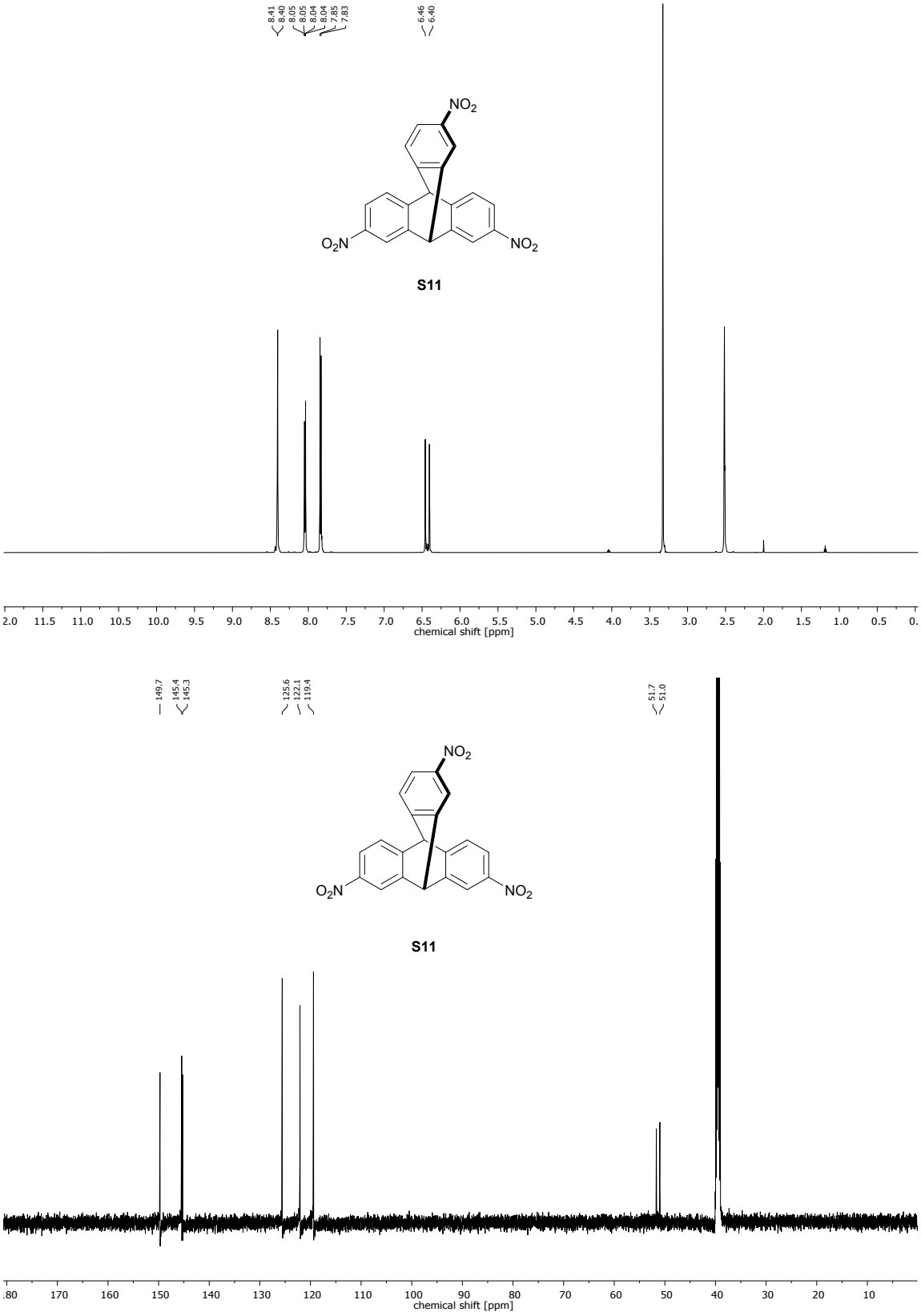


Figure S12: *^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of S**11** in DMSO-d_6.*

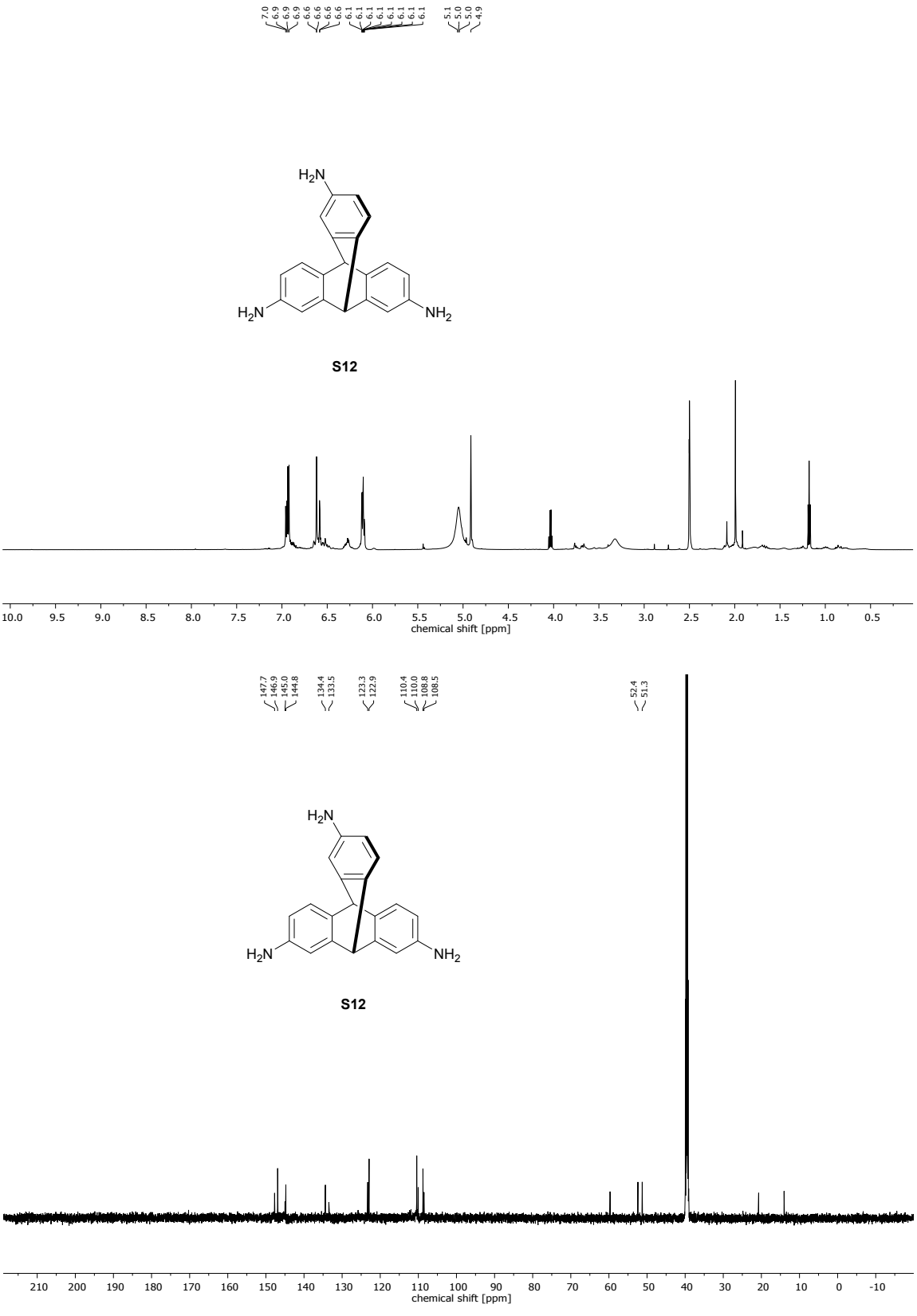


Figure S13: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of* ***S12*** *in DMSO-d_6.*

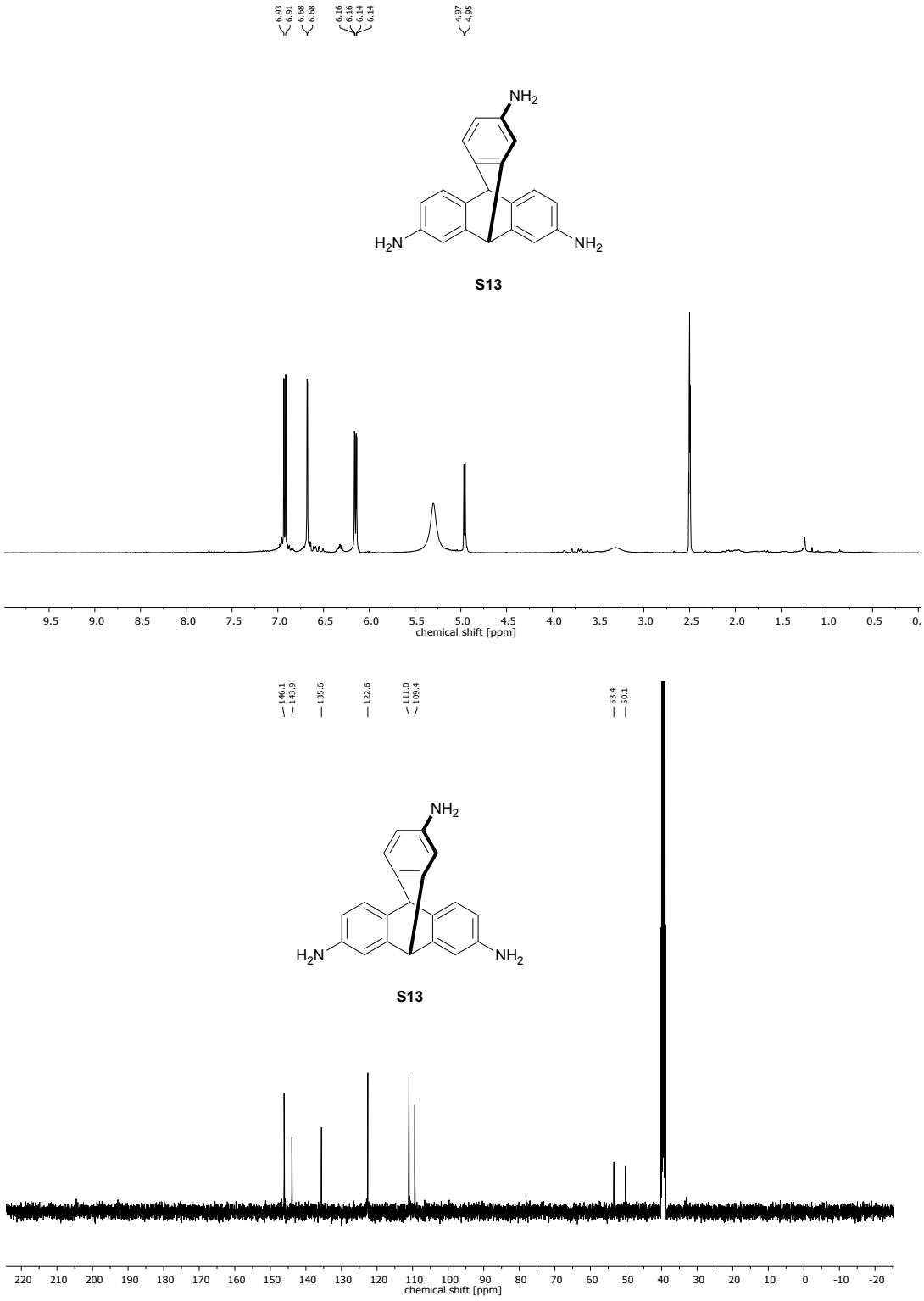


Figure S14: *^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of* ***S13*** *in DMSO-d_6.*

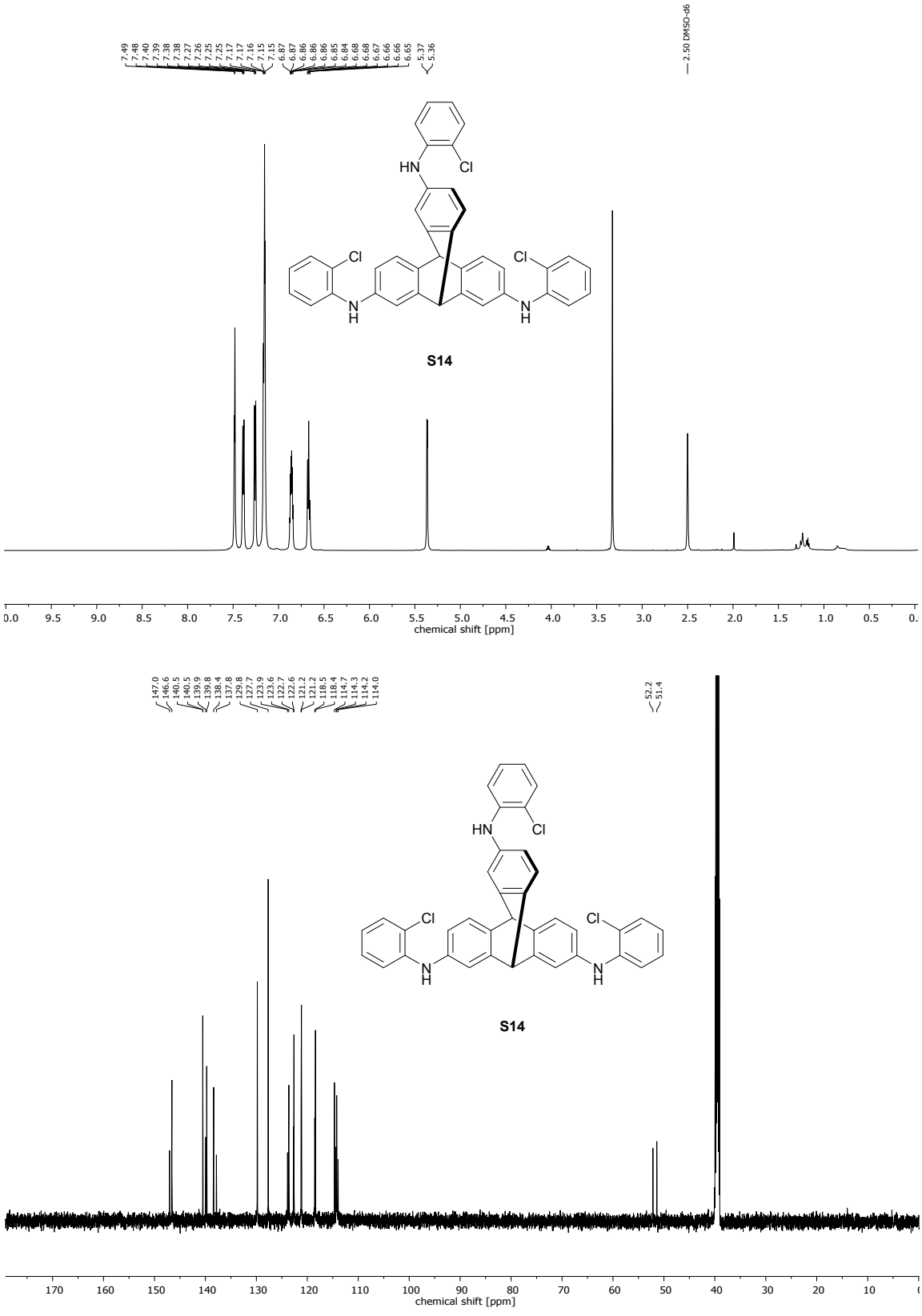


Figure S15: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of* ***S14*** *in DMSO-d_6.*

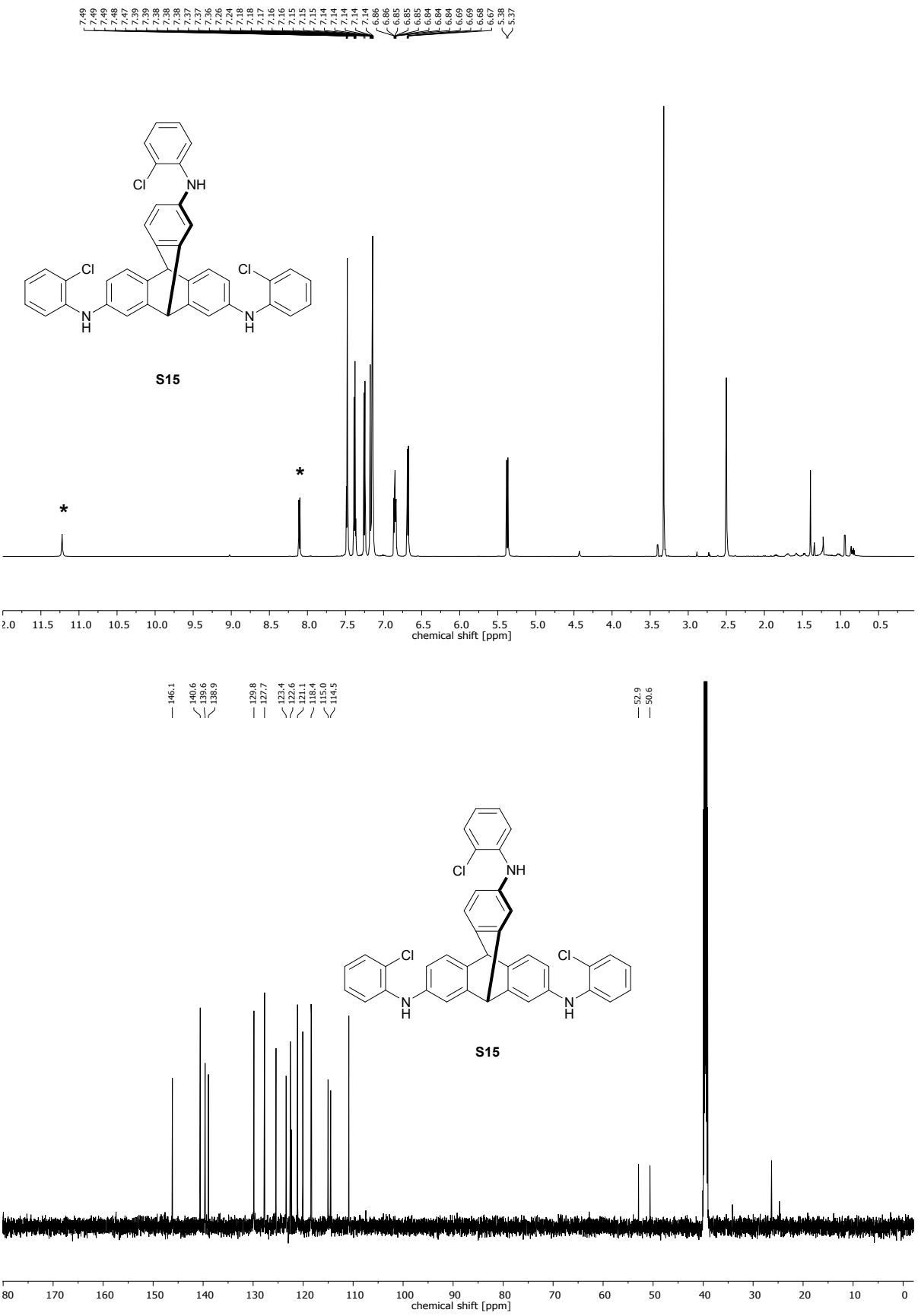


Figure S16: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of **S15** in DMSO-d_6. (*unknown impurity)*

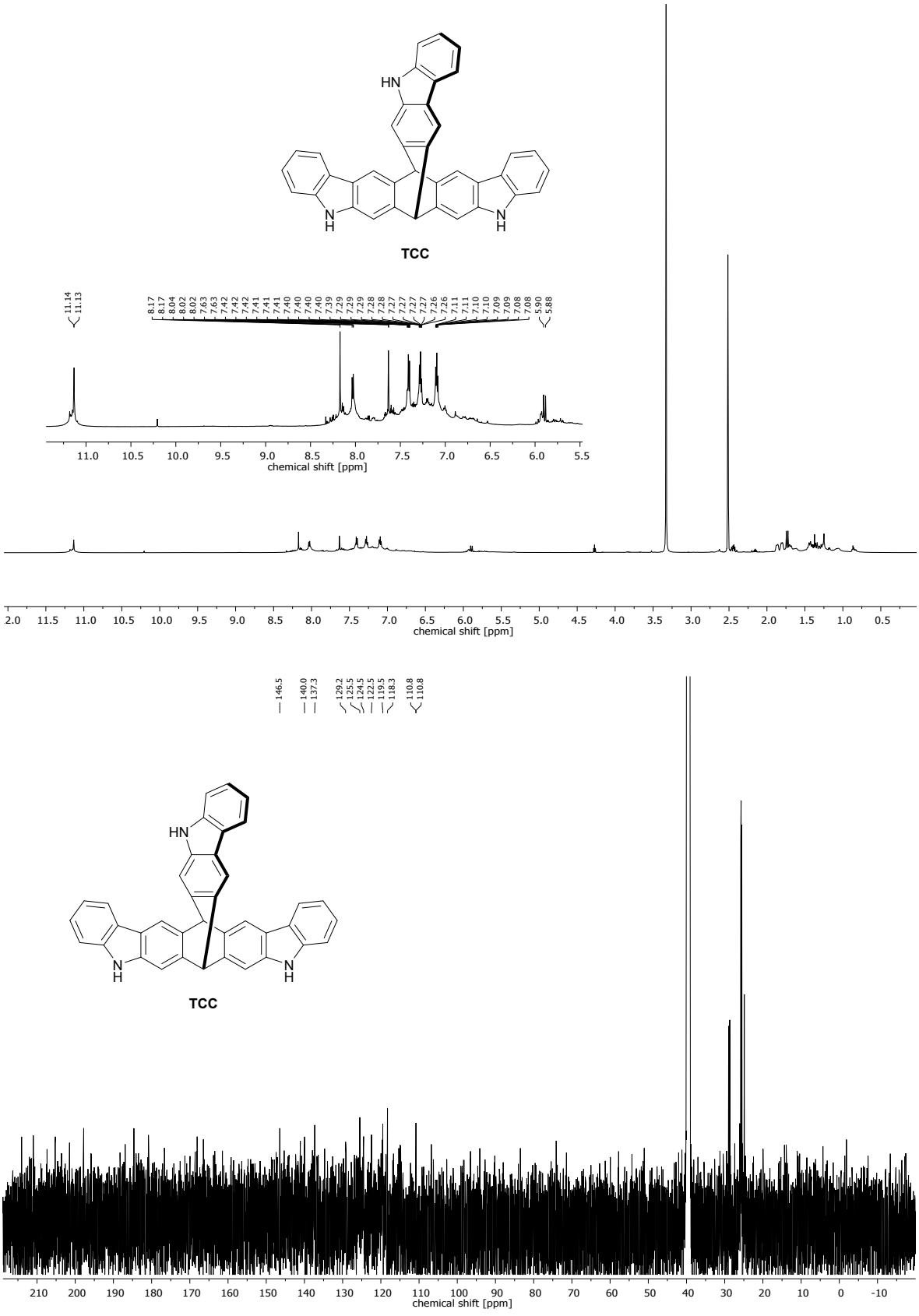


Figure S17: *^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectra (bottom) of* ***TCC*** *in DMSO-d_6.*

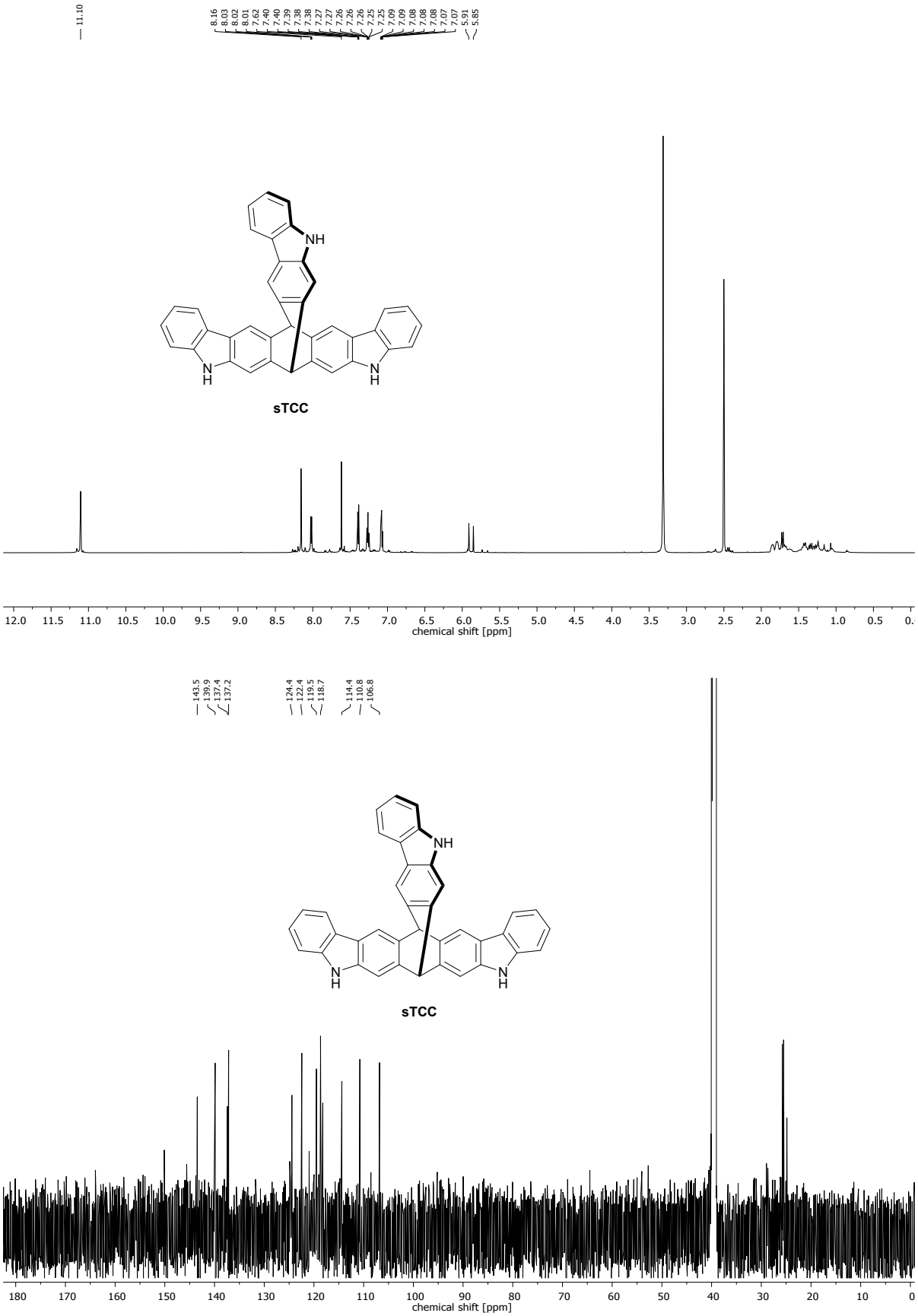


Figure S18: *^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectra (bottom) of* ***sTCC*** *in DMSO-d_6.*

3 Electropolymerization Data

3.1 aTC

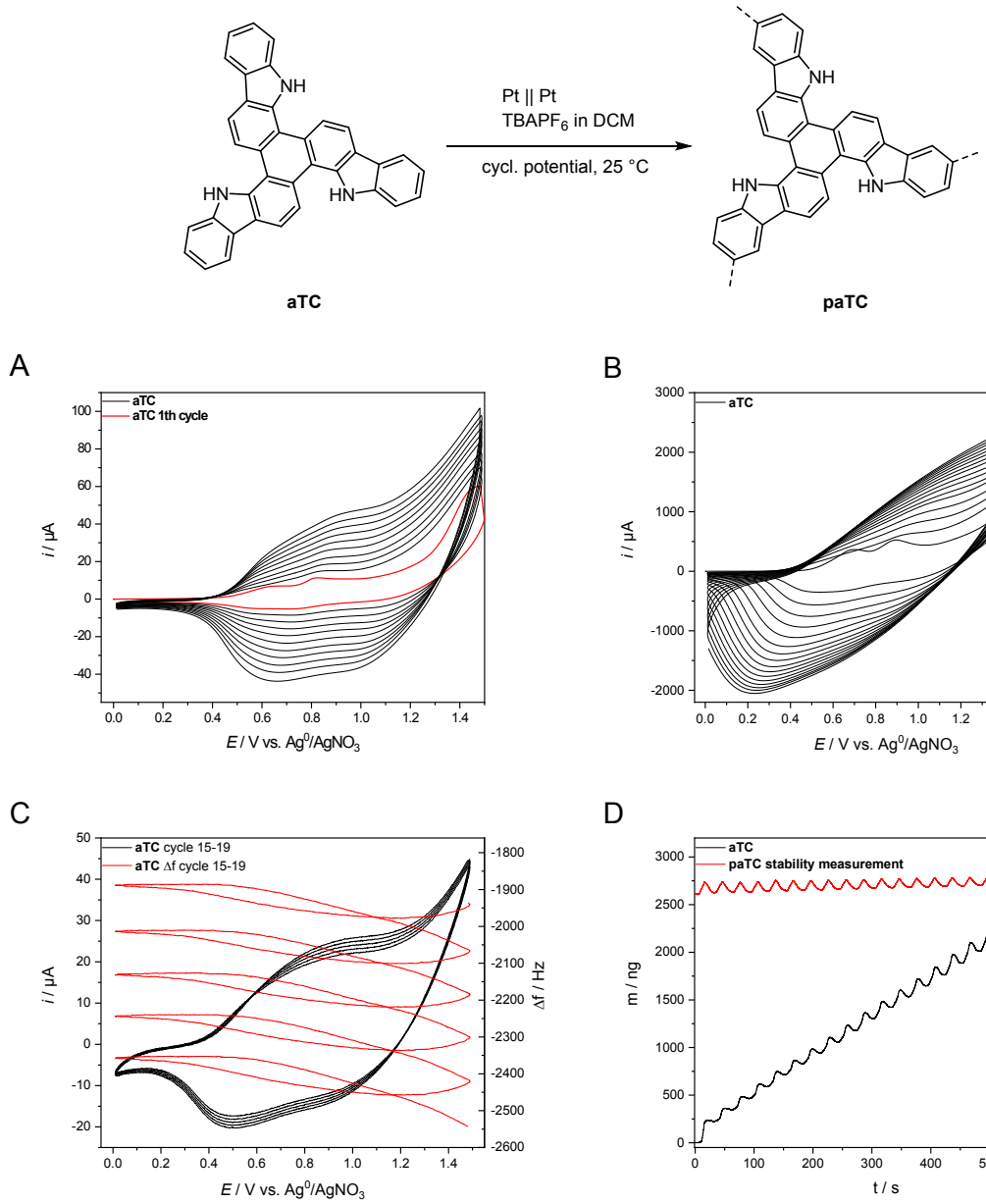
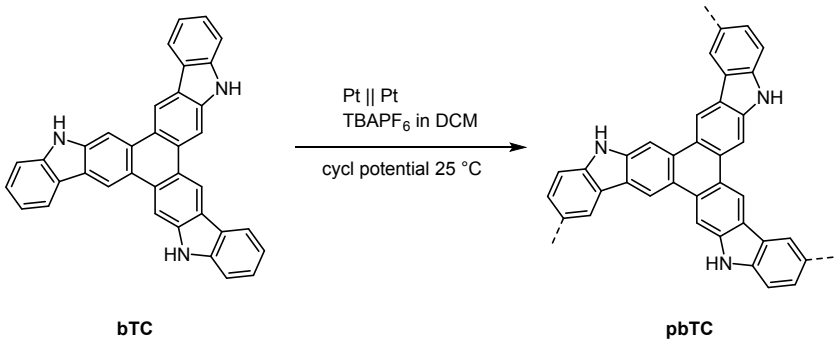


Figure S19: *Electropolymerization of* ***aTC****.* ***A****) analytical scale film generation on a Pt-disc electrode, c = 1 mM in DCM, TBAPF$_6$, 0–1.5 V, 0.1 V^{-1}.* ***B****) preparative scale film generation on an ITO-electrode, c = 1 mM in DCM, TBAPF$_6$, 0–1.7 V, 0.1 Vs^{-1}.* ***C****) EQCM, c = 1 mM in DCM, TBAPF$_6$, 0–1.5 V, 0.1 Vs^{-1}.* ***D****) EQCM 20 cycles, c = 1 mM in DCM, TBAPF$_6$, 0–1.5 V, 0.1 Vs^{-1}.*

3.2 bTC



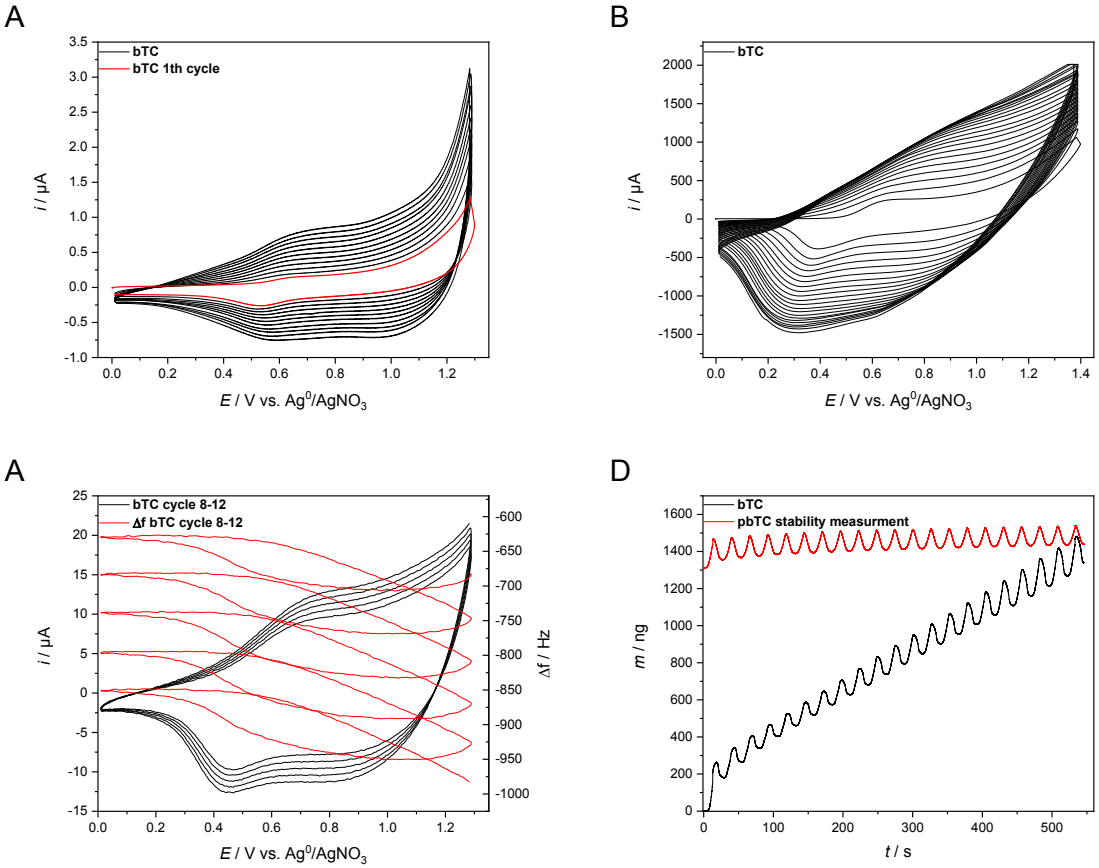
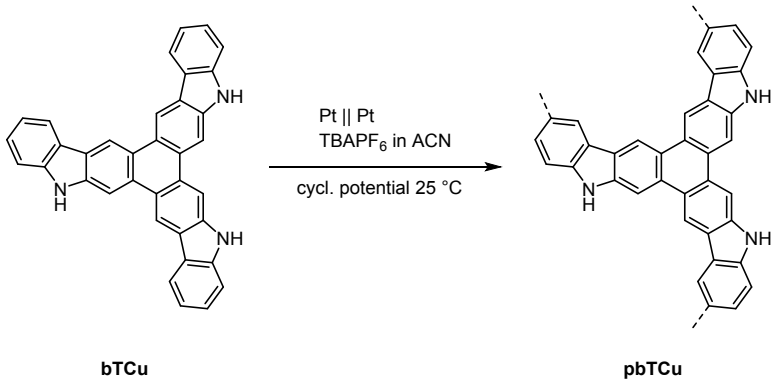


Figure S20: *Electropolymerization of* ***bTC****.* ***A****) analytical scale film generation on a Pt-disc electrode, c = 0.5 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.* ***B****) preparative scale film generation on an ITO-electrode, c = 1 mM in DCM, TBAPF$_6$, 0–1.4 V, 0.1 Vs^{-1},* ***C****) EQCM, c = 0.1 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1},* ***D****) EQCM 20 cycles, c = 0.11 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 V^{-1}.*

3.3 bTCu



bTCu **pbTCu**

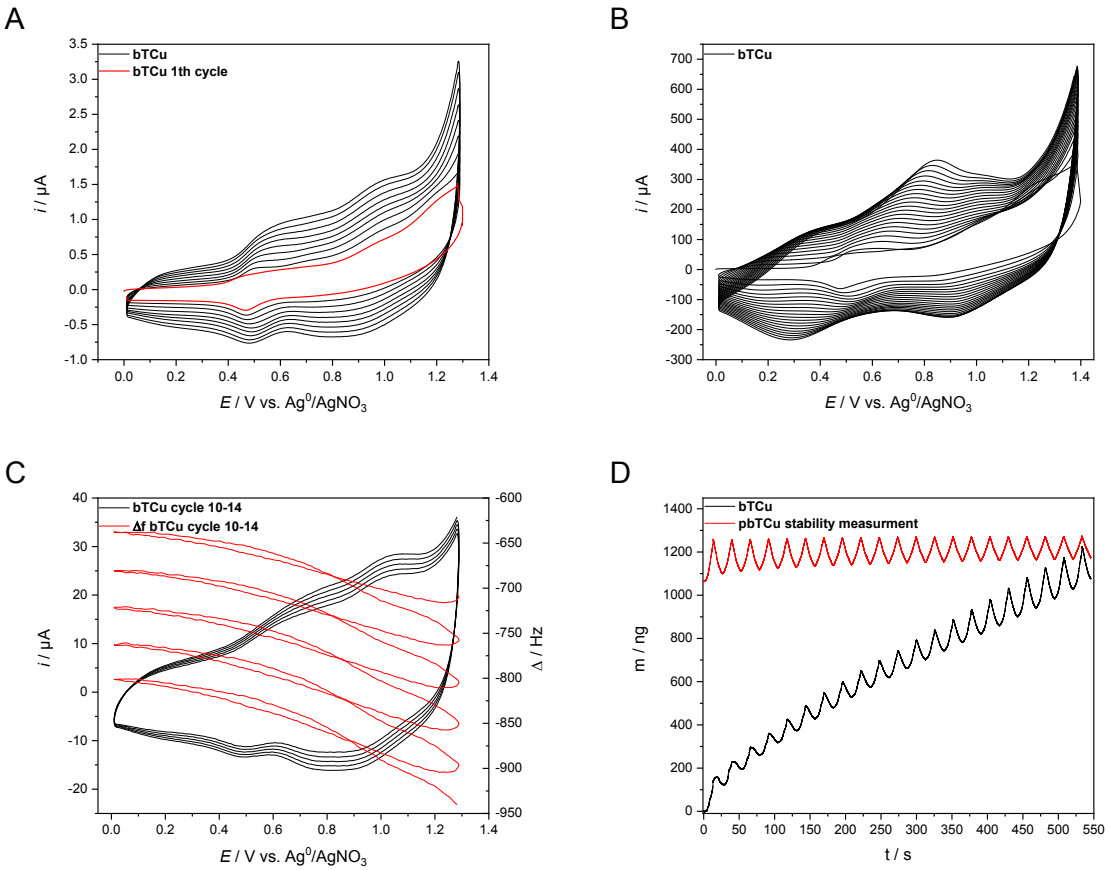
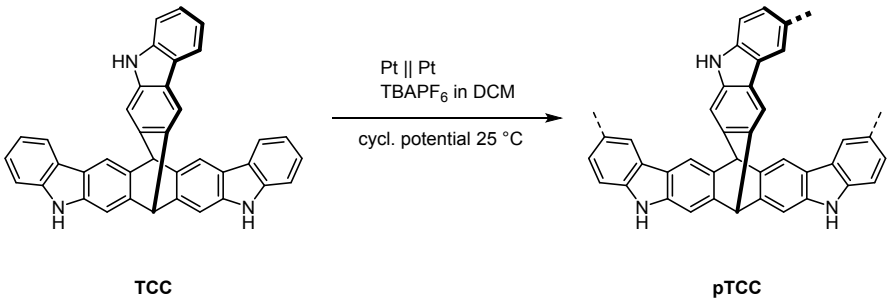


Figure S21: *Electropolymerization of* ***bTCu****.* ***A****) analytical scale film generation on a Pt-disc electrode, c = 0.1mM in ACN, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.* ***B****) preparative scale film generation on an ITO-electrode, c = 0.1 mM in ACN, TBAPF$_6$, 0–1.4 V, 0.1 Vs^{-1}* ***C****) EQCM, c = 0.1 mM in ACN, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.* ***D****) EQCM 20 cycles, c = 0.1 mM in ACN, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.*

3.4 TCC



TCC **pTCC**

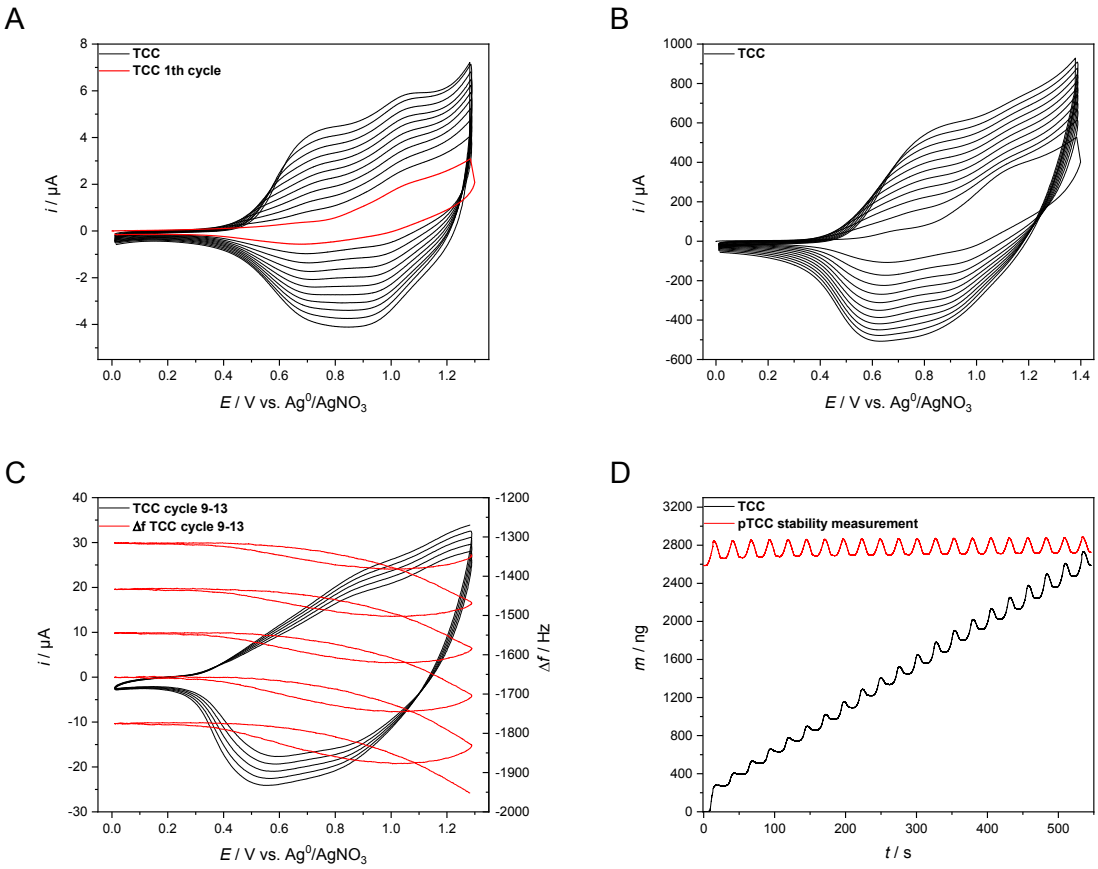


Figure S22: *Electropolymerization of* ***TCC****.* ***A****) analytical scale film generation on a Pt-disc electrode, c = 0.5 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.* ***B****) preparative scale film generation on an ITO-electrode, c = 0.5 mM in DCM, TBAPF$_6$, 0–1.4 V, 0.1 Vs^{-1},* ***C****) EQCM, c = 0.1 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.* ***D****) EQCM 20 cycles, c = 0,1 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.*

3.5 sTCC

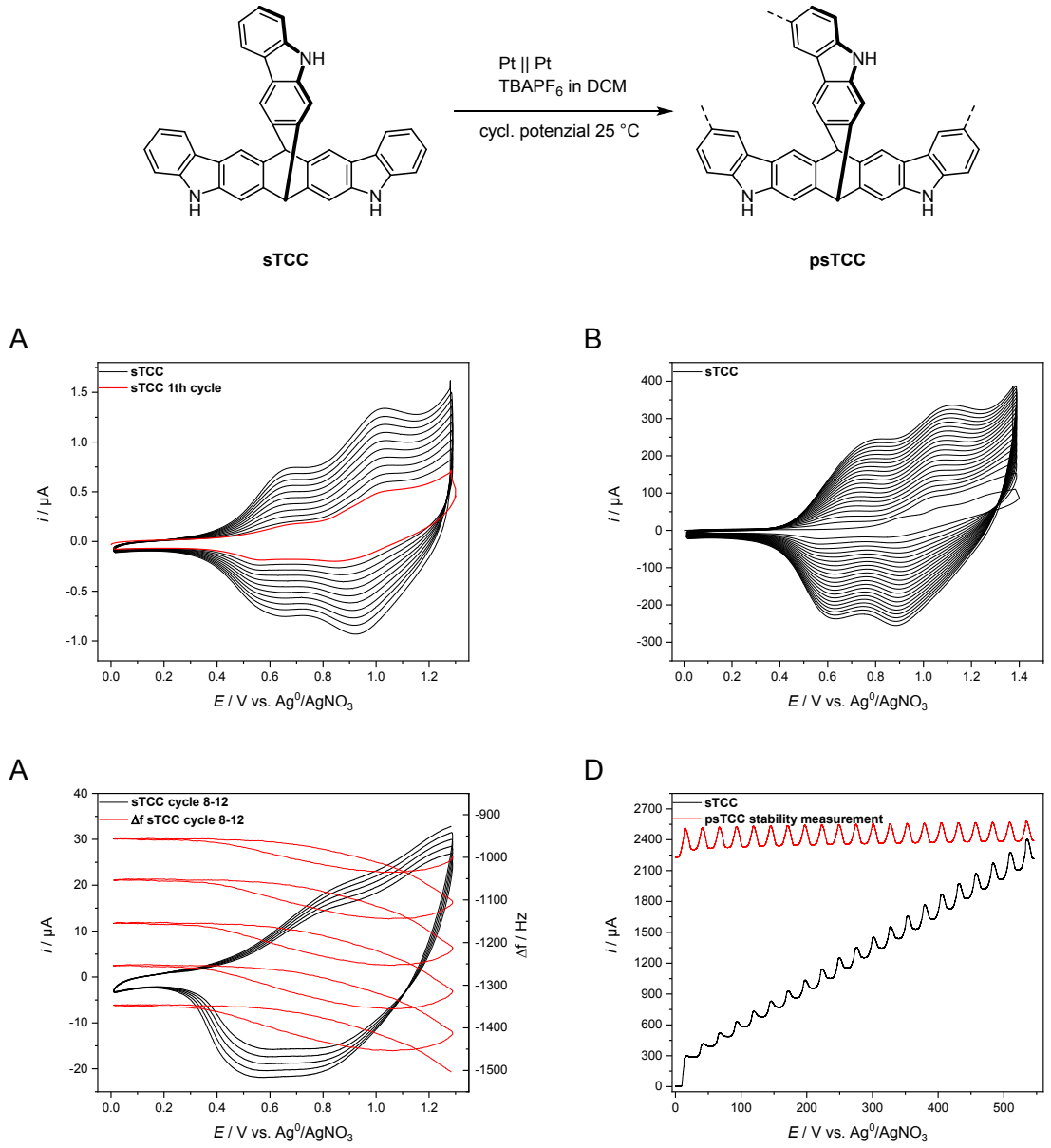


Figure S23: *Electropolymerization of* ***sTCC****.* ***A****) analytical scale film generation on a Pt-disc electrode, c = 0.1 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.* ***B****) preparative scale film generation on an ITO-electrode, c = 0.1 mM in DCM, TBAPF$_6$, 0–1.4 V, 0.1 Vs^{-1},* ***C****) EQCM, c = 0.1 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.* ***D****) EQCM 20 cycles, c = 0,1 mM in DCM, TBAPF$_6$, 0–1.3 V, 0.1 Vs^{-1}.*

3.6 Stability Measurements

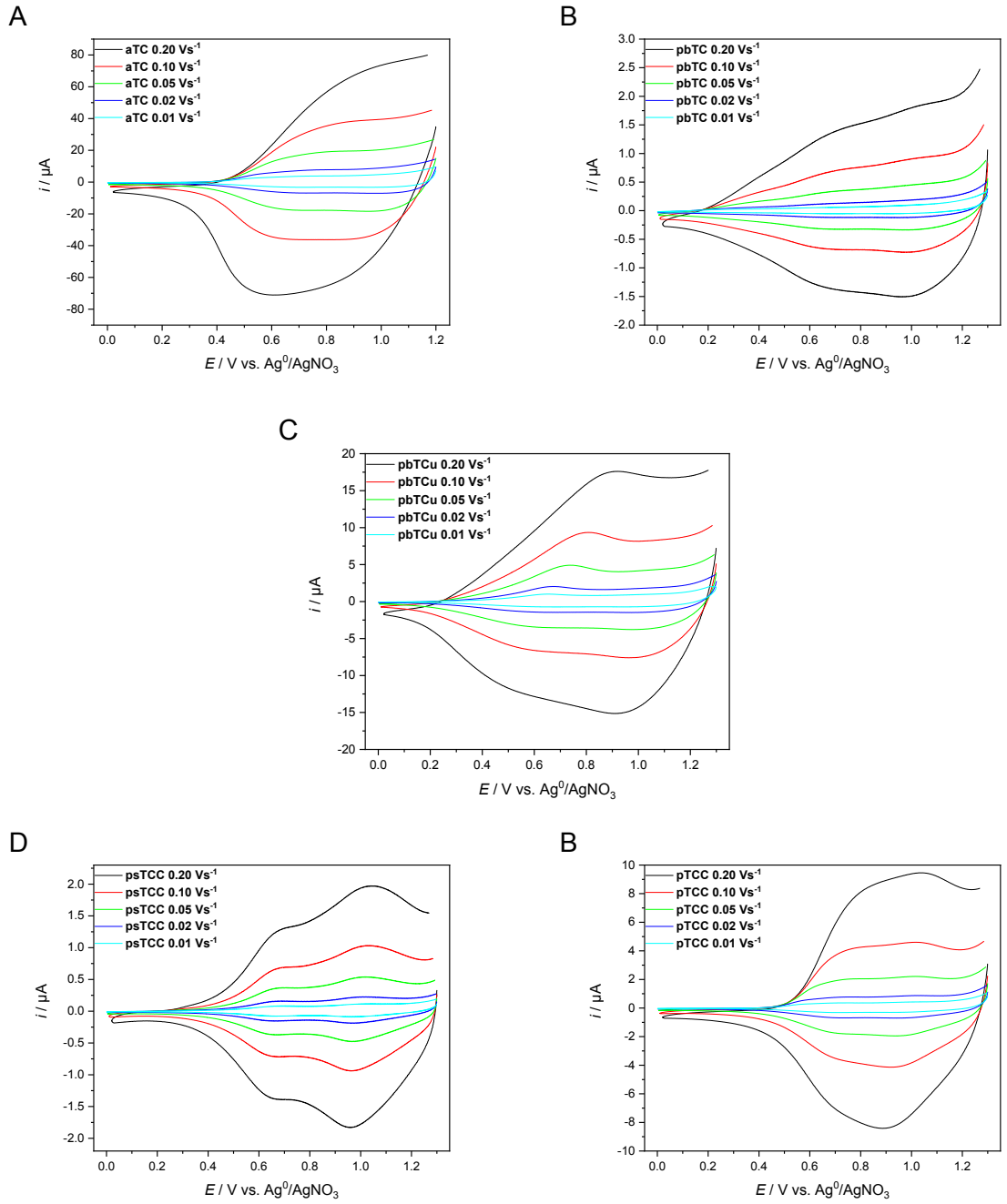


Figure S24: *Cyclic voltammograms of as-prepared polymer films on a Pt-disc electrode in monomer-free solution. A)* ***paTC****, B)* ***pbTC****, C)* ***pbTCu****, D)* ***psTCC****, E)* ***pTCC****.*

4 UV-Vis/PL Spectra

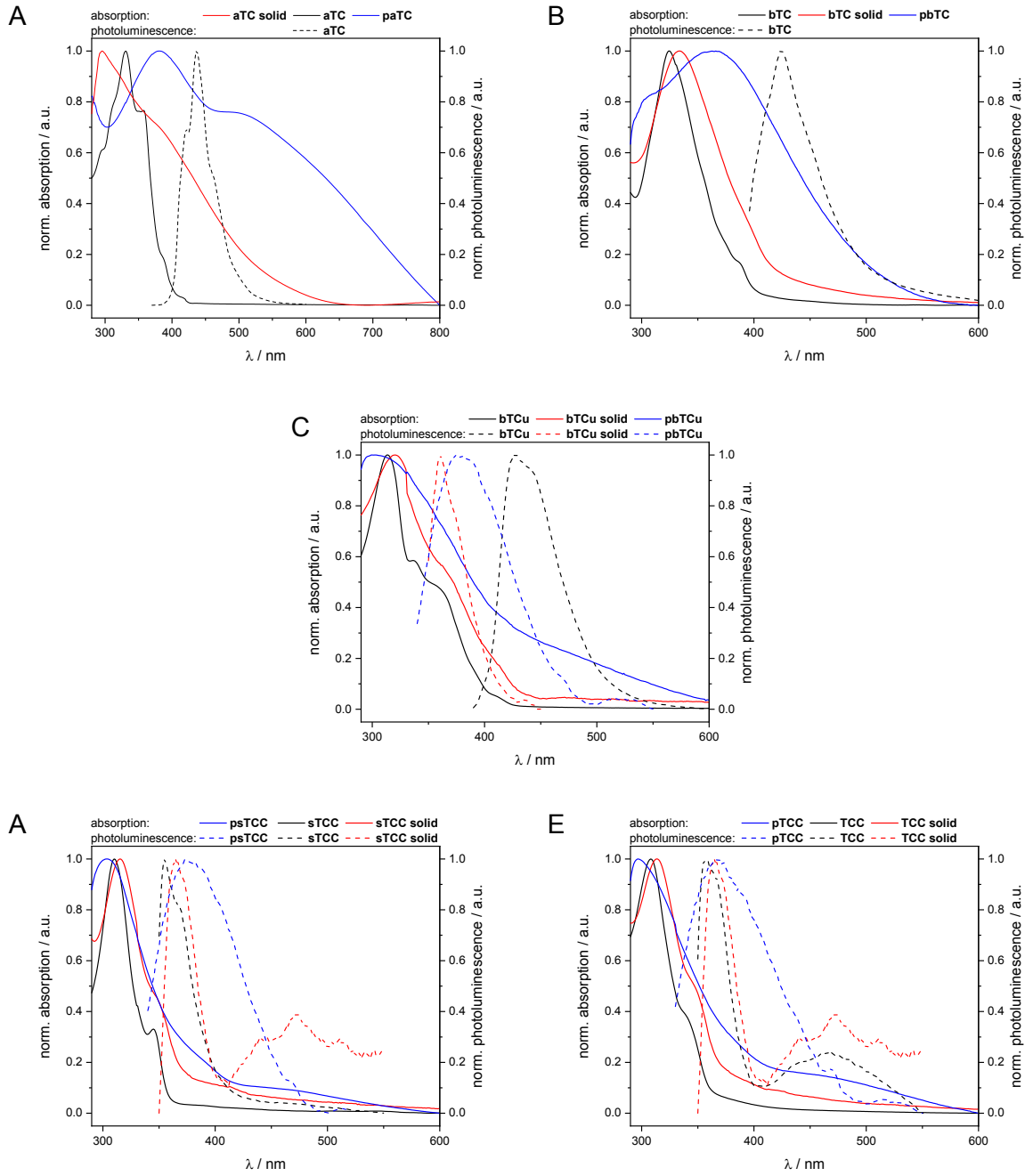


Figure S25: *UV-Vis (solid lines) and PL (dashed lines) spectra. Black lines (monomer spectra in diluted chloroform solution), red lines (solid state spectra of monomers spin coated onto quartz glass), blue lines (electrogenerated polymer films on ITO-coated glass). A)* ***paTC****, B)* ***pbTC****, C)* ***pbTCu****, D)* ***psTCC****, E)* ***pTCC****.*

5 AFM Measurements

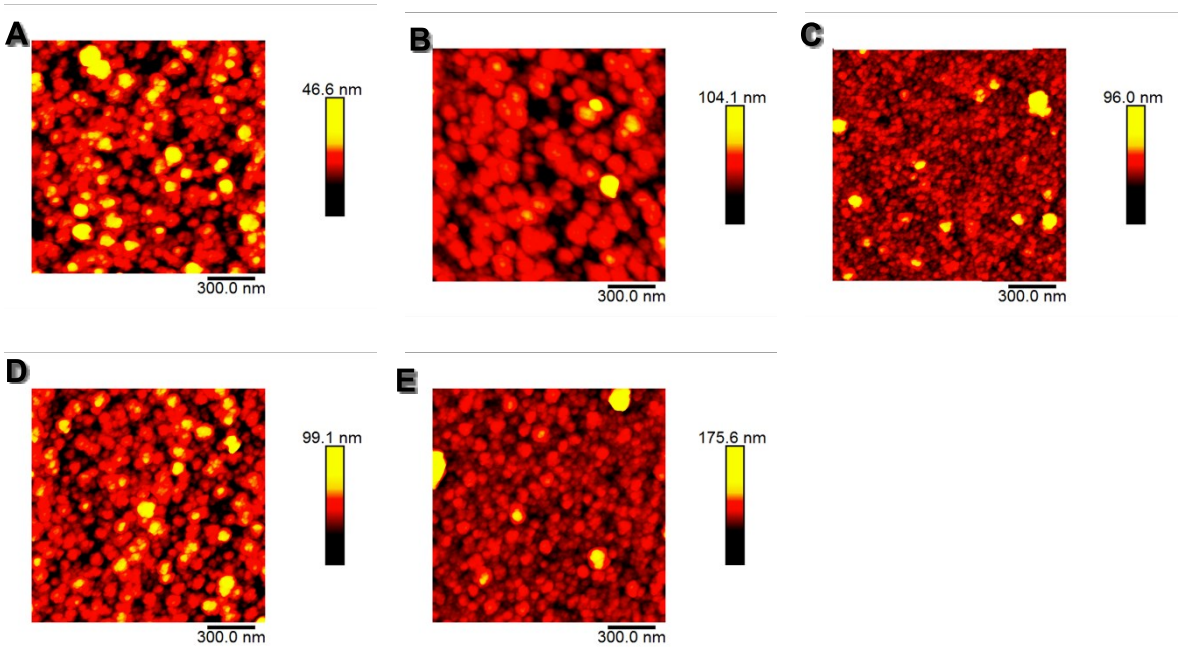


Figure S26: *AFM topology images (tapping mode) of electropolymerized films of the different polycarbazole networks. A)* ***paTC****, B)* ***pbTC****, C)* ***bTCu****, D)* ***psTCC****, E)* ***pTCC****.*

[I] Y. Li, Y.-X. Wang, X.-K. Ren, L. Chen, *Mater. Chem. Front.* **2017**, *1*, 2599.

[II] Stephen L. Buchwald, US Patent No. 2014/0124762 Al, **2013**.

[III] Hideki Hagiwara, JP Patent No. 2014169273 A, **2014**.

[IV] N. C. Bruno, M. T. Tudge, S. L. Buchwald, *Chem. Sci.* **2013**, *4*, 916.