Electronic Supplementary Information (ESI)

Synthesis and characterization of two isomeric dithienopyrrole series and the corresponding electropolymers

Sebastian Förtsch and Peter Bäuerle*
Institute of Organic Chemistry II and Advanced Materials,
University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany
E-mail: peter.baeuerle@uni-ulm.de

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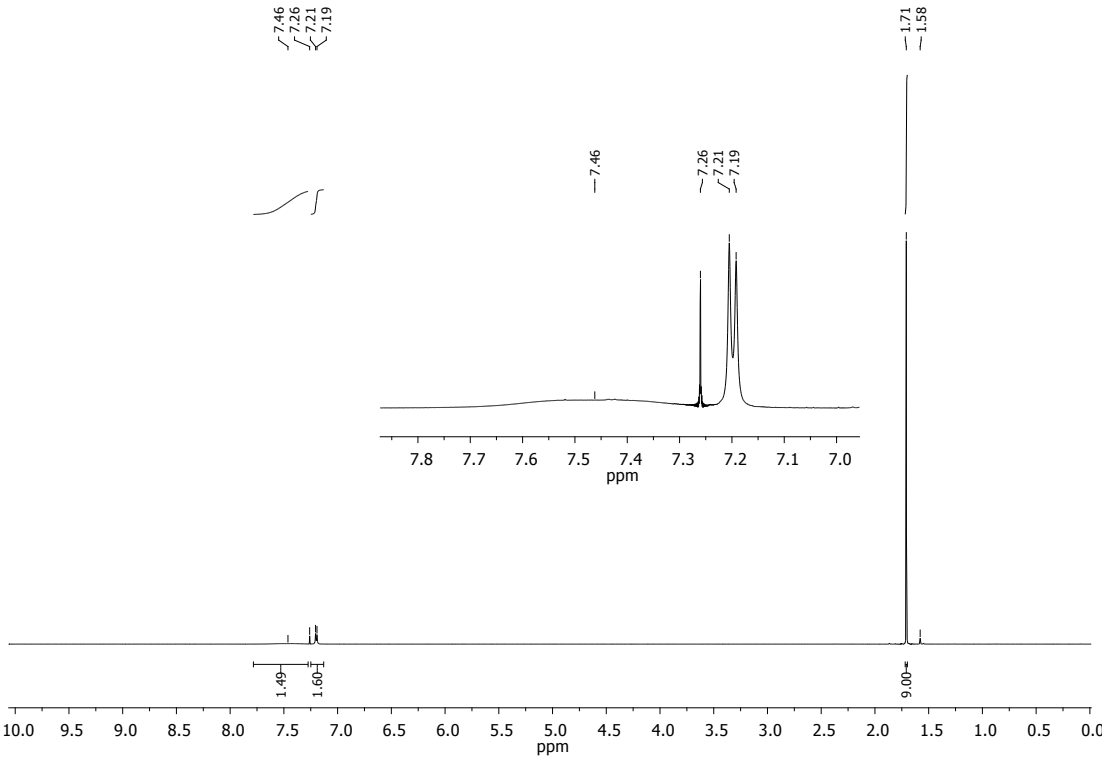

Figure 1: ^{1}H NMR spectrum of the Boc-substituted DTP **8** recorded in $CDCl_3$.

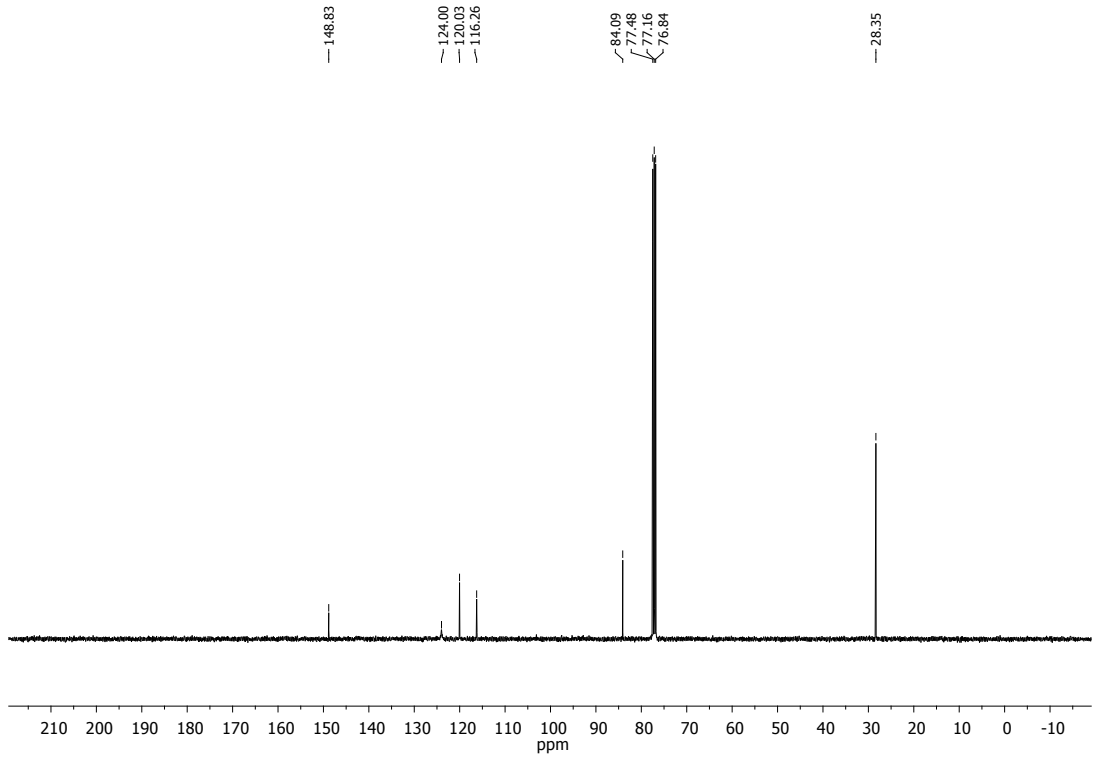

Figure 2: ^{13}C NMR spectrum of the Boc-substituted DTP **8** recorded in $CDCl_3$.

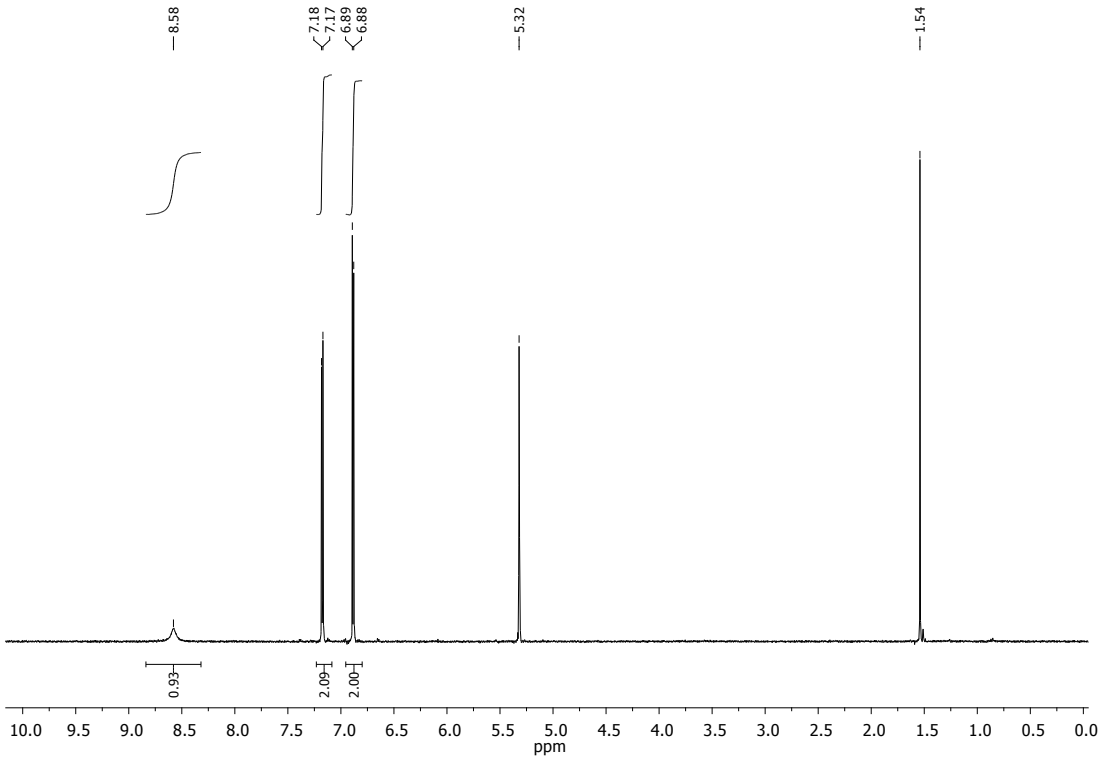

Figure 3: ^{1}H NMR spectrum of the unsubstituted iso-DTP **2** recorded in CD_2Cl_2.

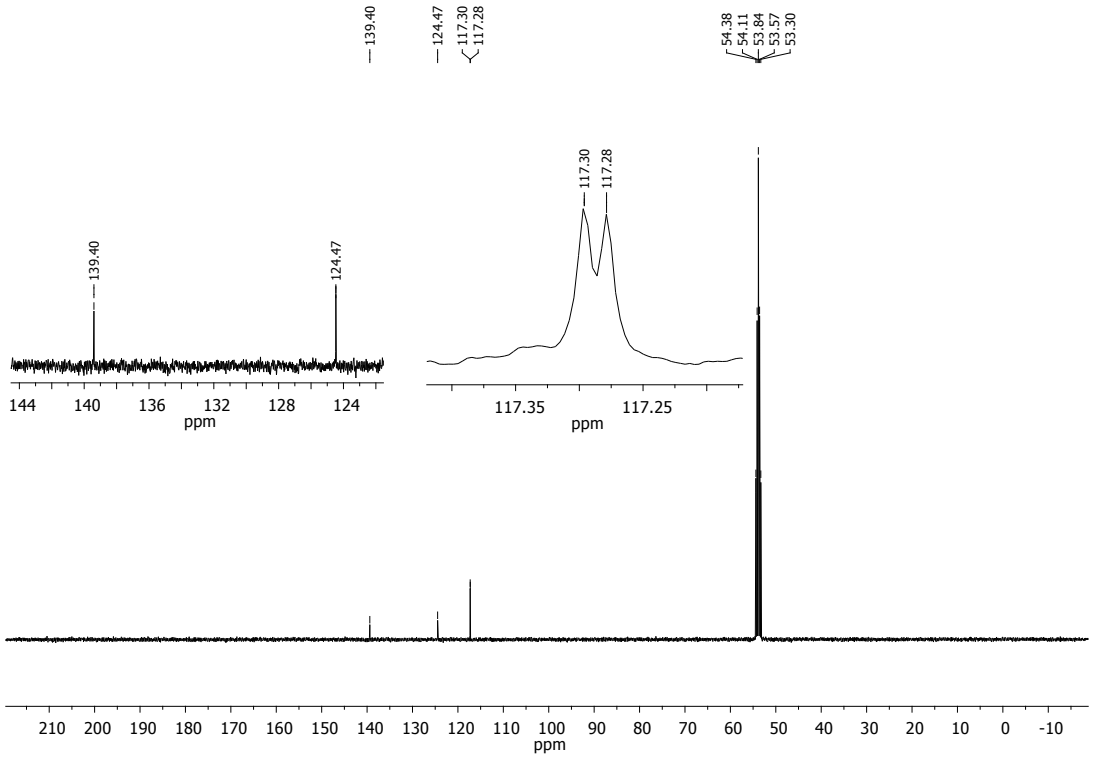

Figure 4: ^{13}C NMR spectrum of the unsubstituted iso-DTP **2** recorded in CD_2Cl_2.

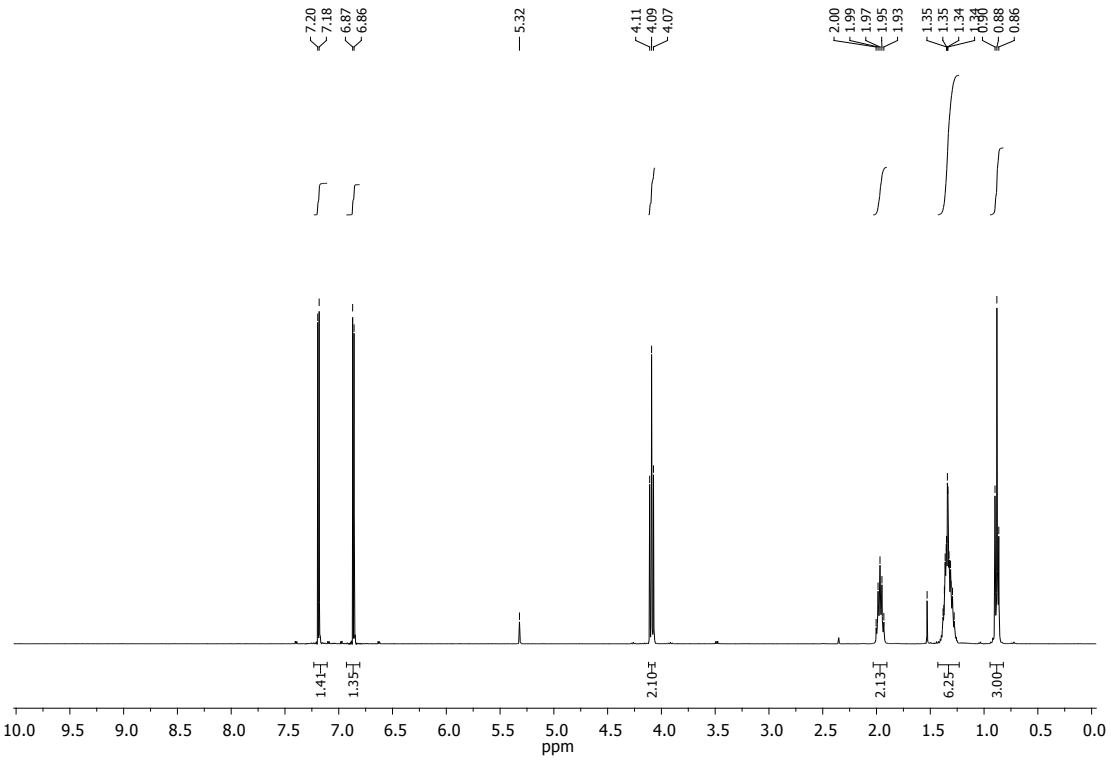

Figure 5: ^{1}H NMR spectrum of the hexyl-substituted iso-DTP **11** recorded in CD_2Cl_2.

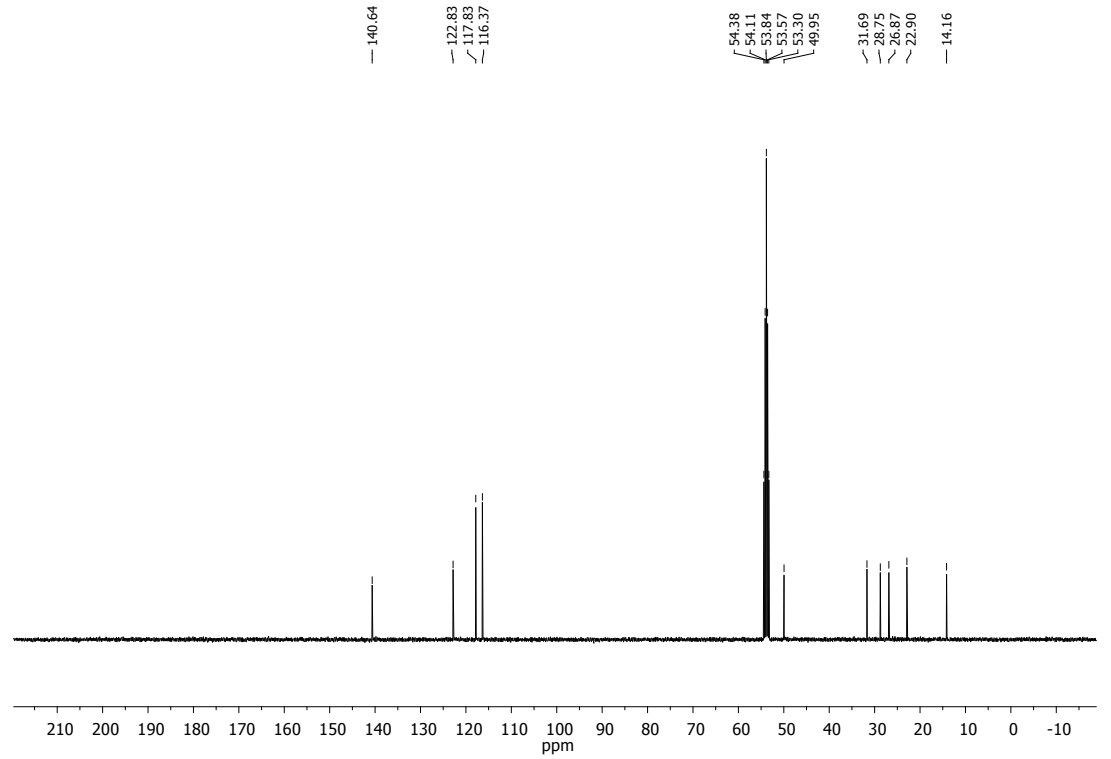

Figure 6: ^{13}C NMR spectrum of the hexyl-substituted iso-DTP **11** recorded in CD_2Cl_2.

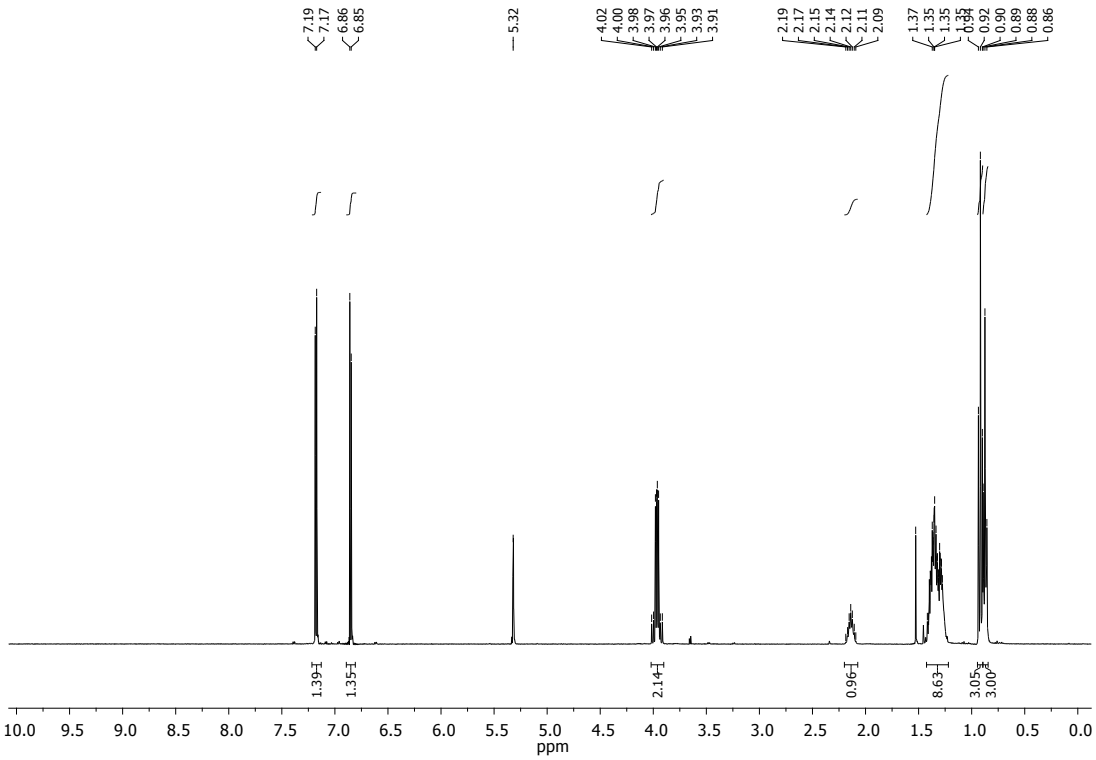

Figure 7: ^{1}H NMR spectrum of the 2-ethylhexyl-substituted iso-DTP **12** recorded in CD_2Cl_2.

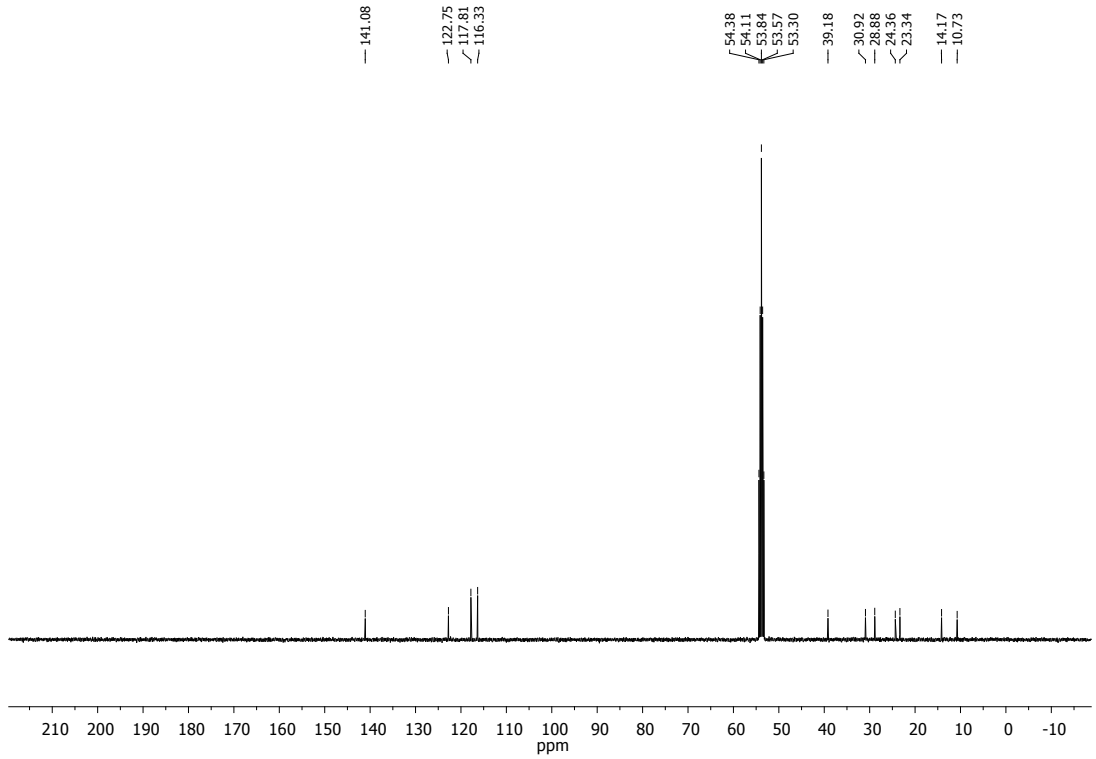

Figure 8: ^{13}C NMR spectrum of the 2-ethylhexyl-substituted iso-DTP **12** recorded in CD_2Cl_2.

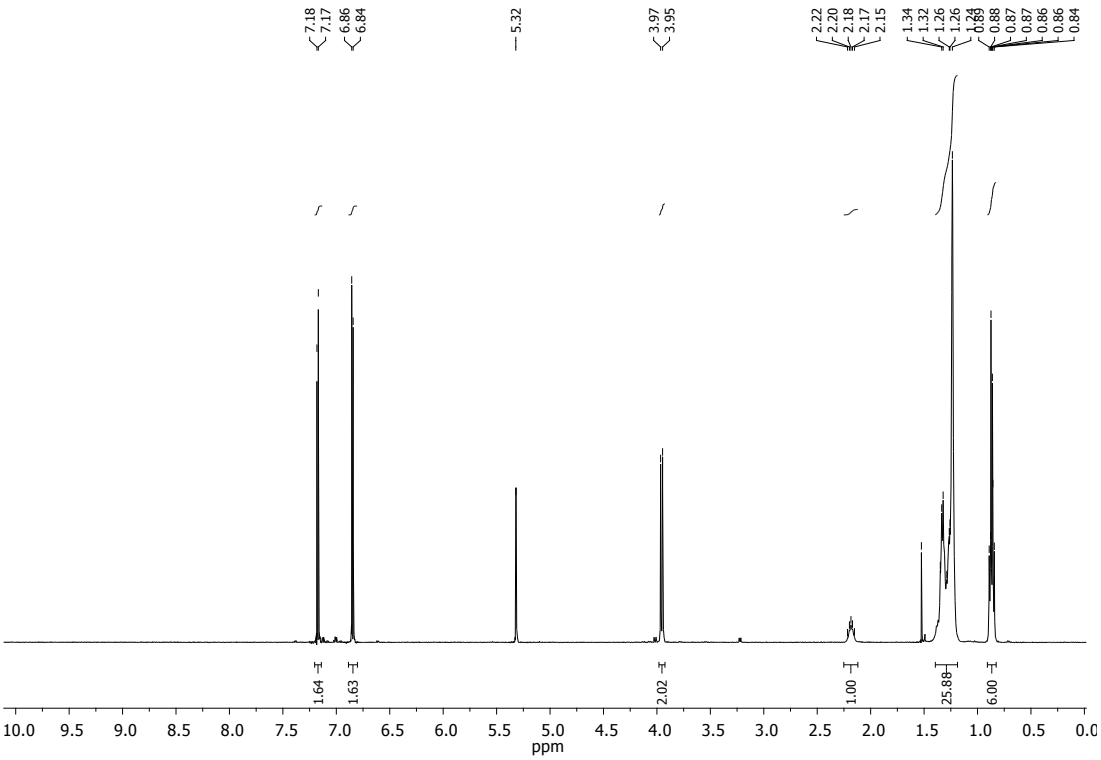

Figure 9: ^{1}H NMR spectrum of the 2-hexyldecyl-substituted iso-DTP **13** recorded in CD_2Cl_2.

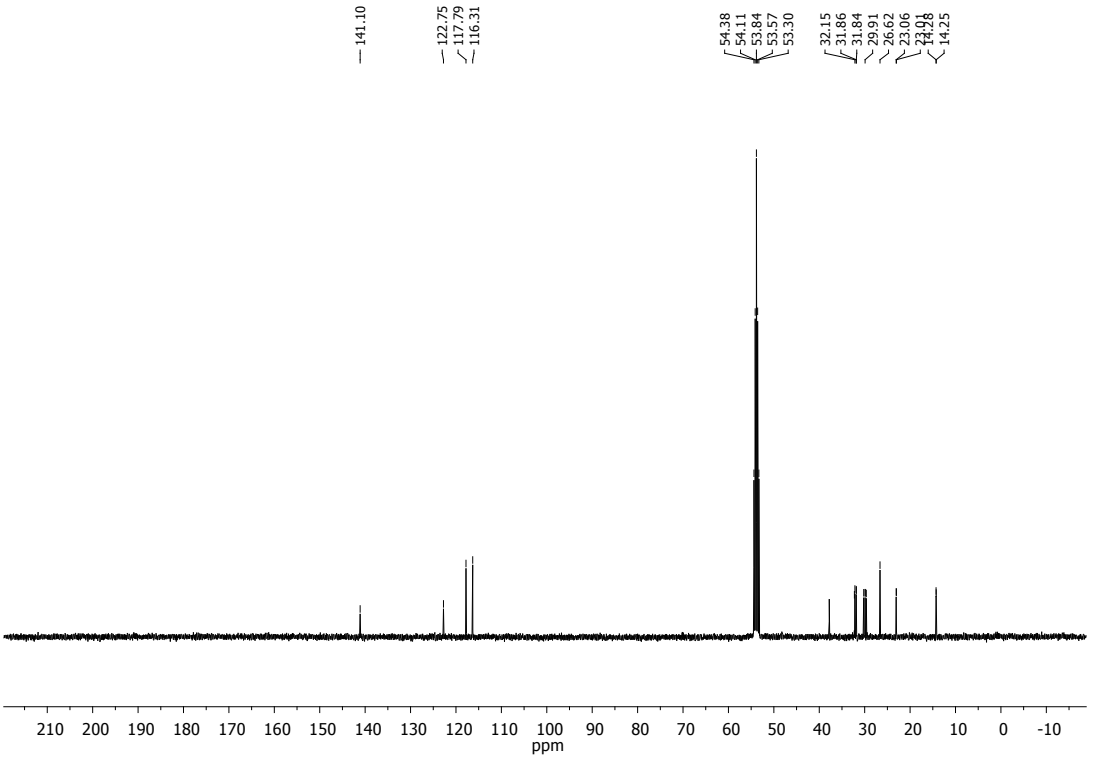

Figure 10: ^{13}C NMR spectrum of the 2-hexyldecyl-substituted iso-DTP **13** recorded in CD_2Cl_2.

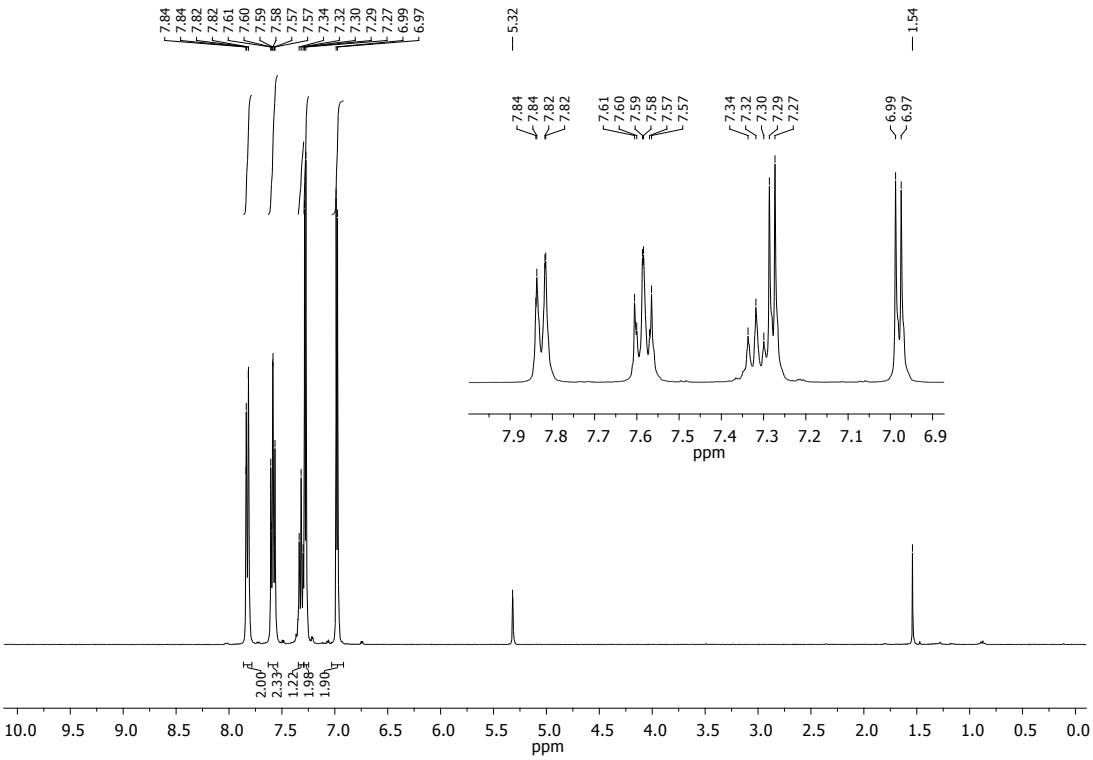

Figure 11: ^{1}H NMR spectrum of the phenyl-substituted iso-DTP **14** recorded in CD_2Cl_2.

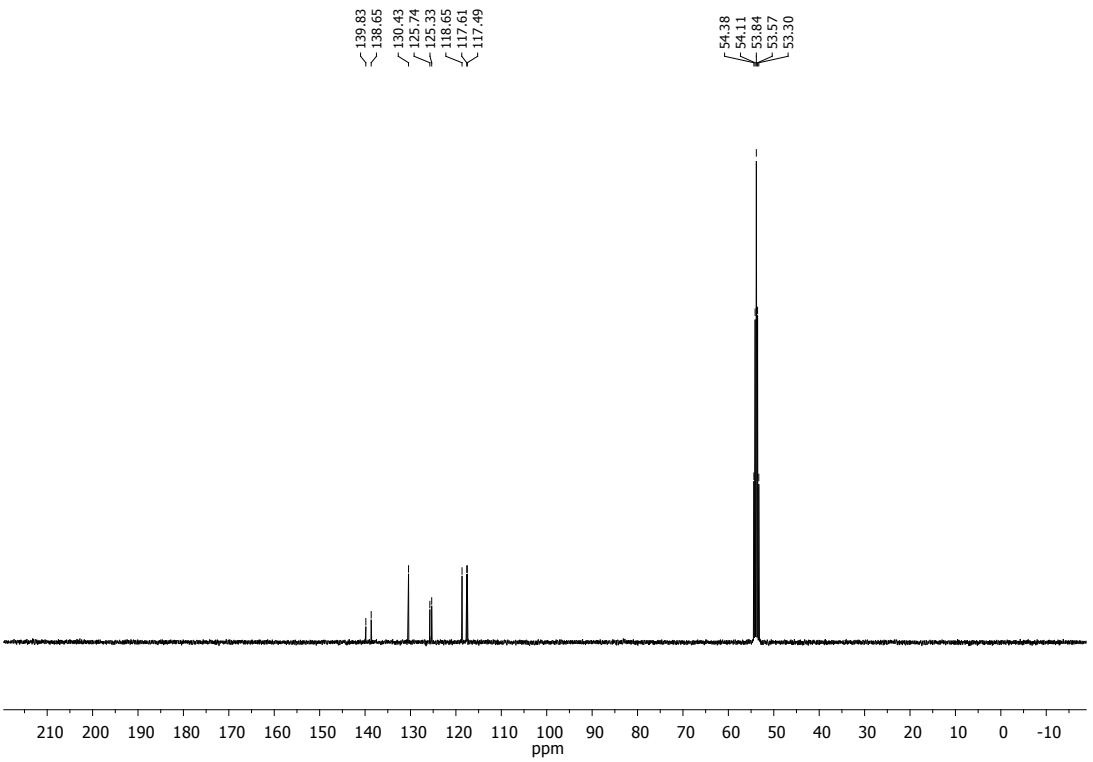

Figure 12: ^{13}C NMR spectrum of the phenyl-substituted iso-DTP **14** recorded in CD_2Cl_2.

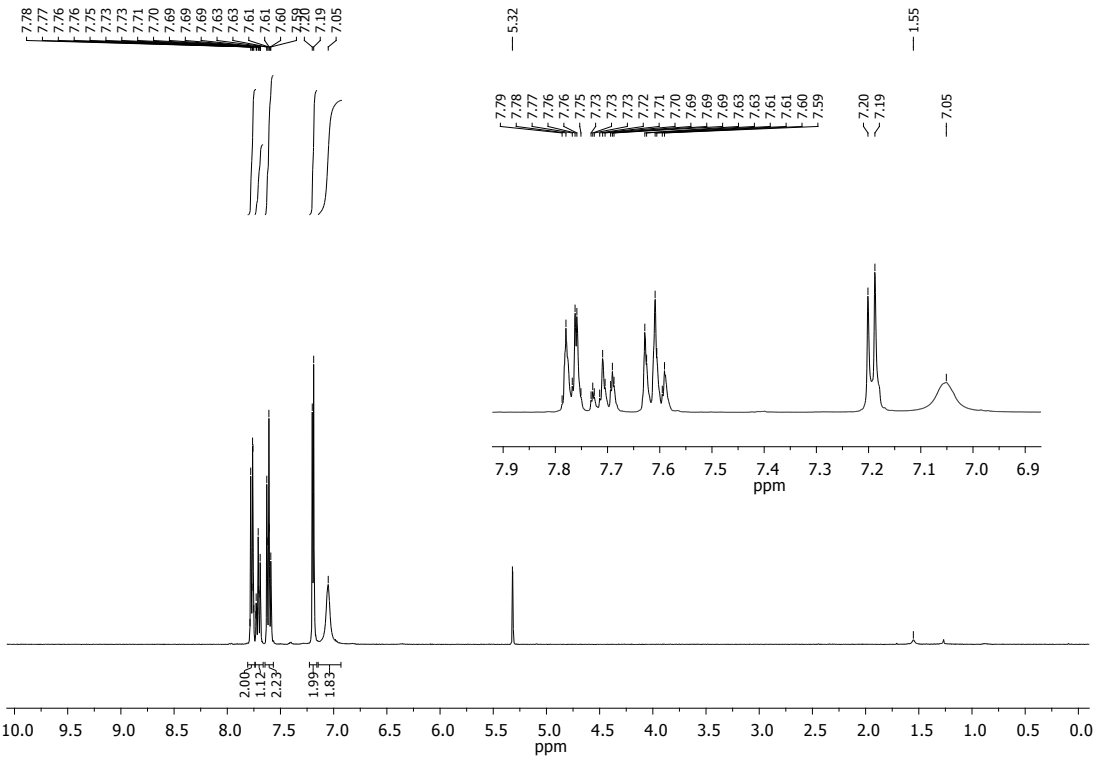

Figure 13: ^{1}H NMR spectrum of the benzoyl-substituted iso-DTP **15** recorded in CD_2Cl_2.

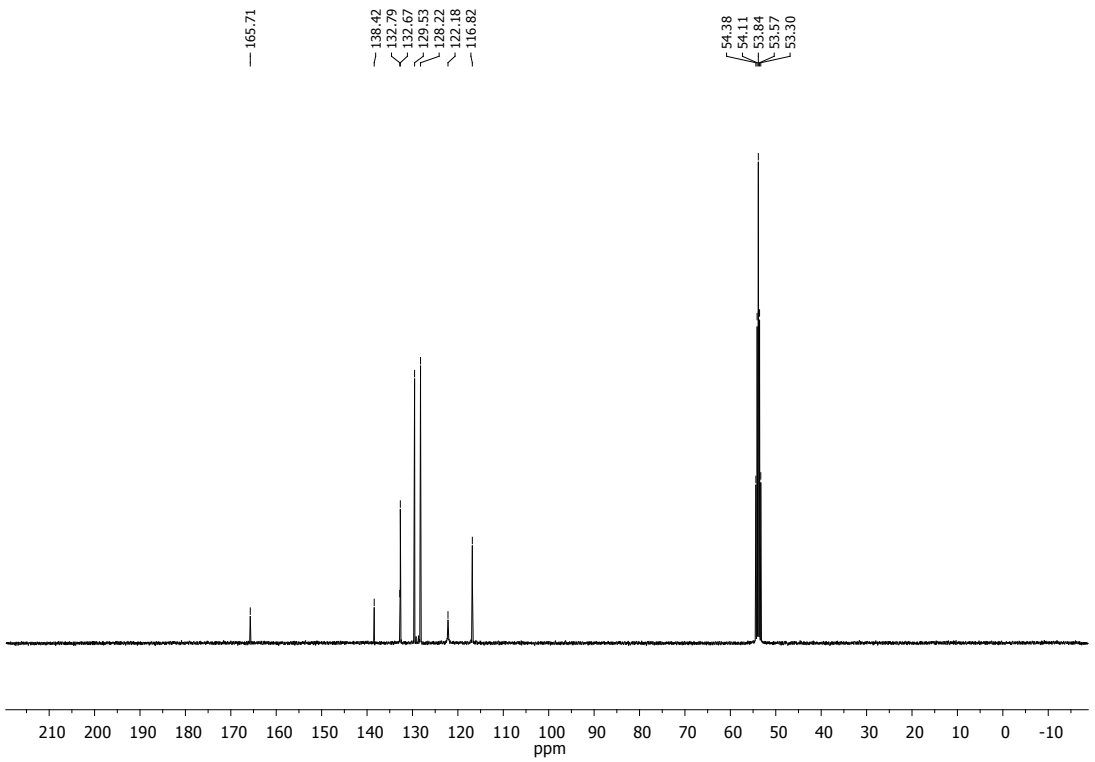

Figure 14: ^{13}C NMR spectrum of the benzoyl-substituted iso-DTP **15** recorded in CD_2Cl_2.

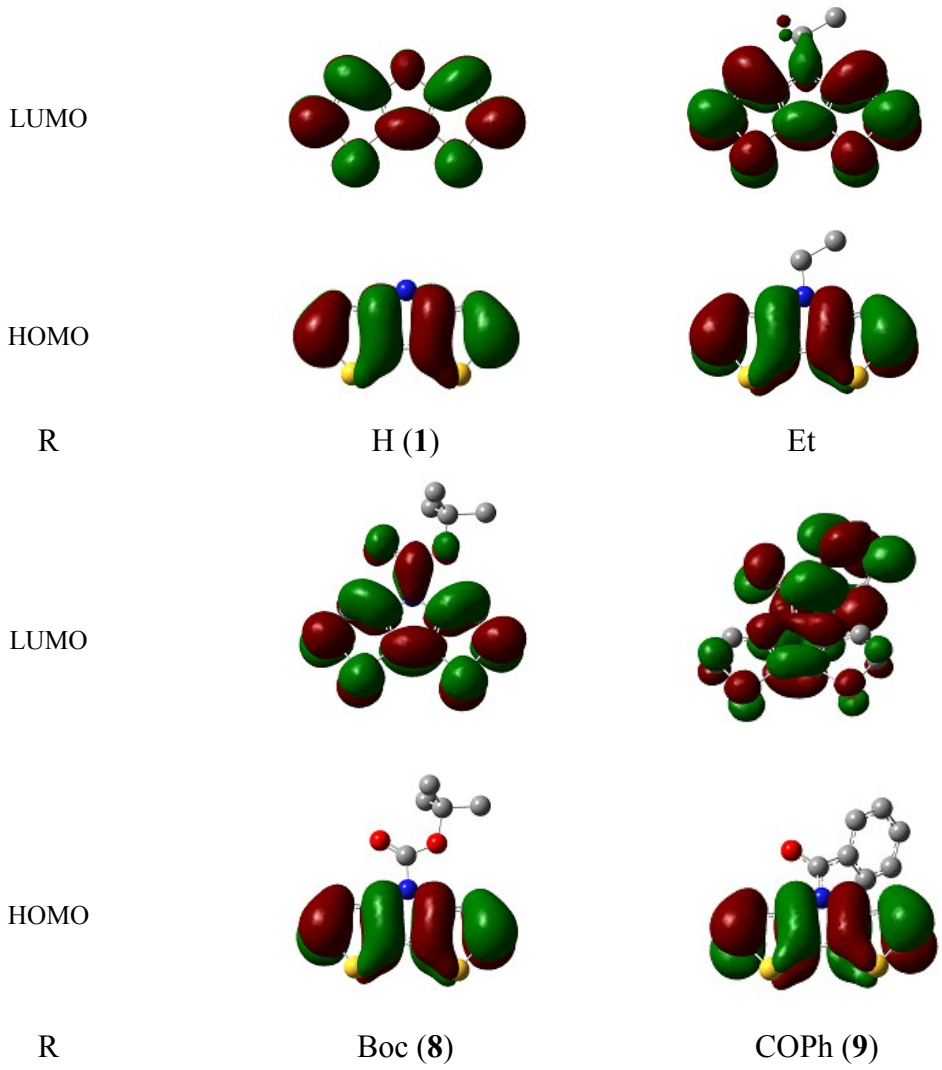

Figure 15: Molecular orbital surfaces of DTPs with different residues R at the nitrogen.

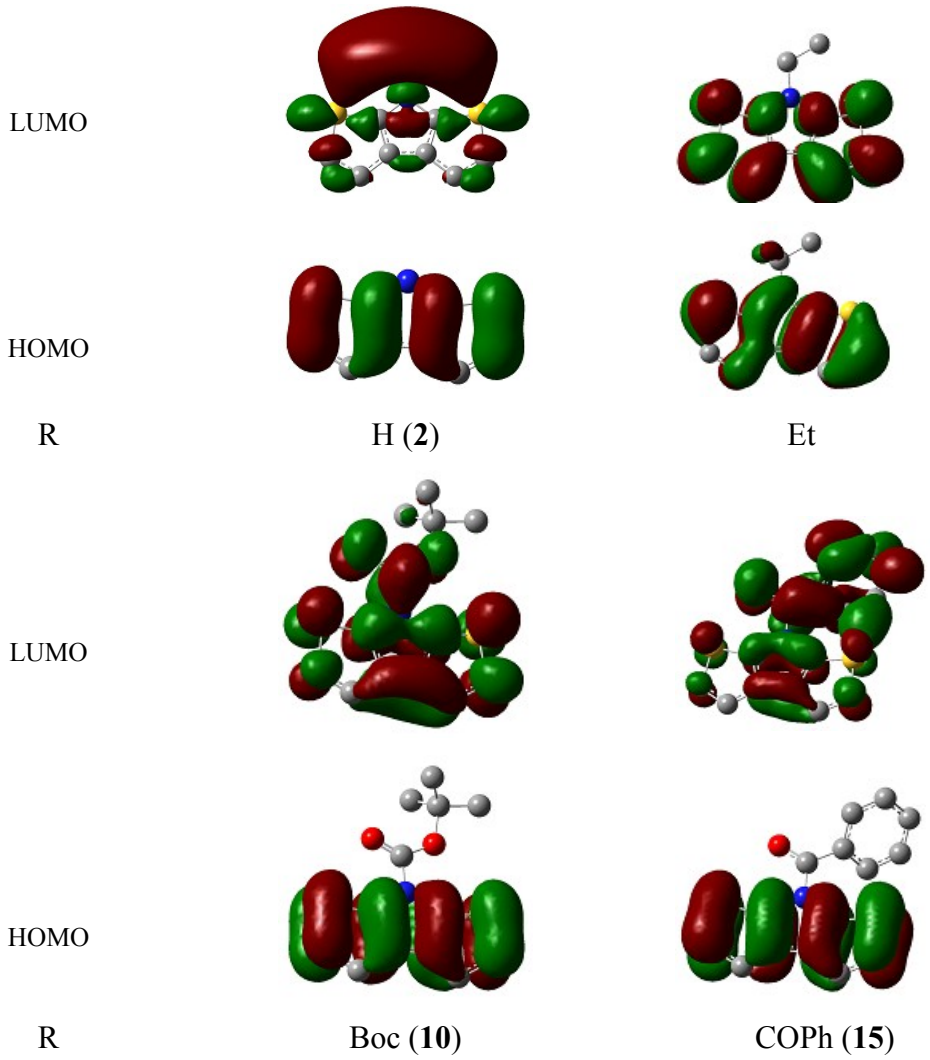

Figure 16: Molecular orbital surfaces of iso-DTPs with different residues R at the nitrogen.

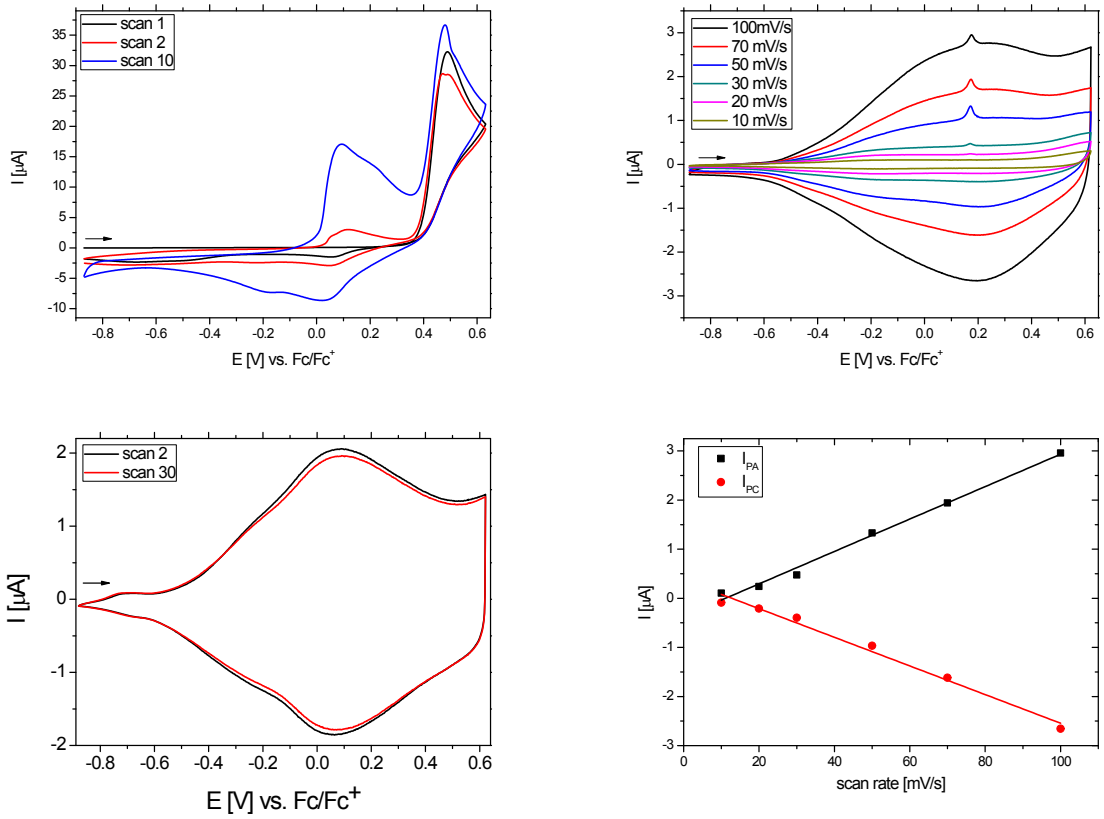

Figure 17: Electropolymerization of the DTP monomer **1** with a H residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

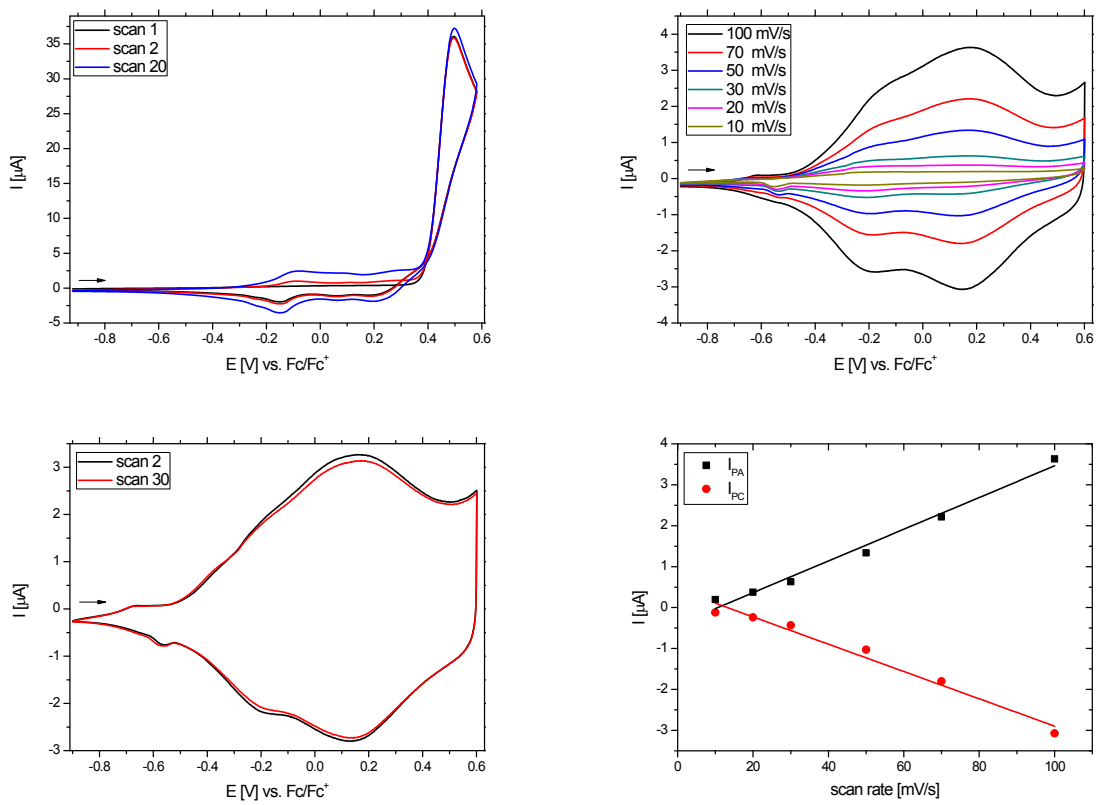

Figure 18: Electropolymerization of the DTP monomer **5** with a 2-ethylhexyl residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

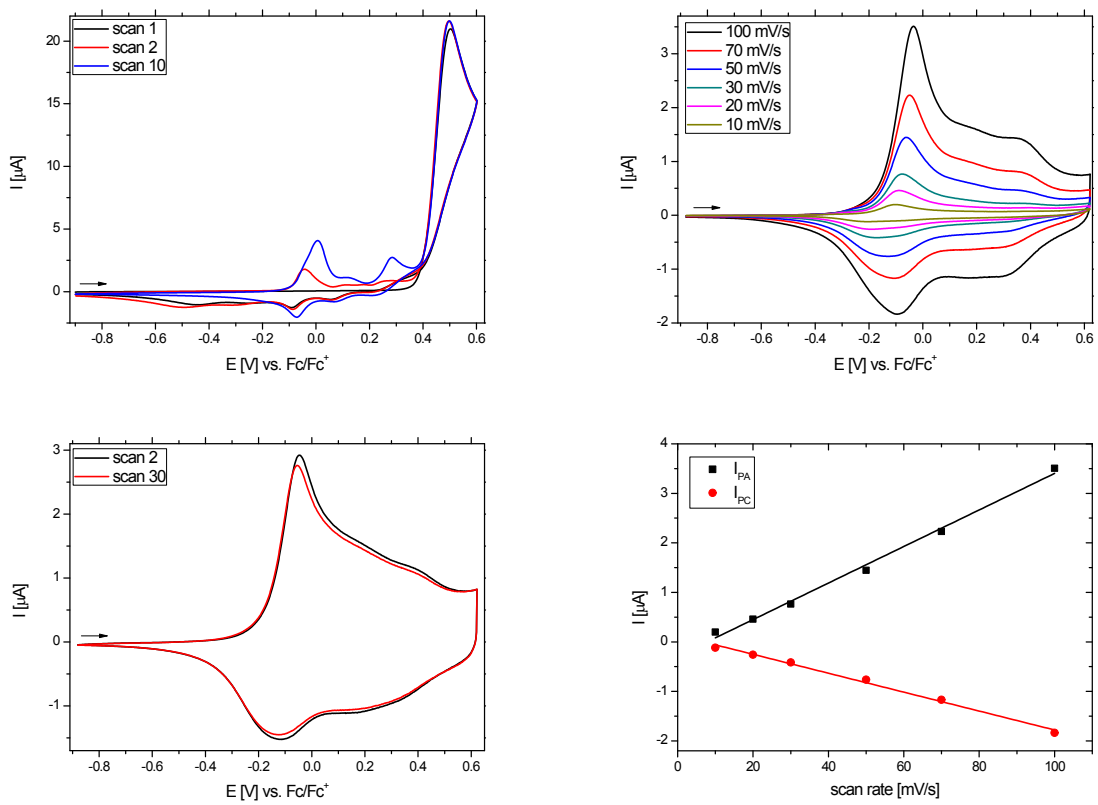

Figure 19: Electropolymerization of the DTP monomer **6** with a 2-hexyldecyl residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

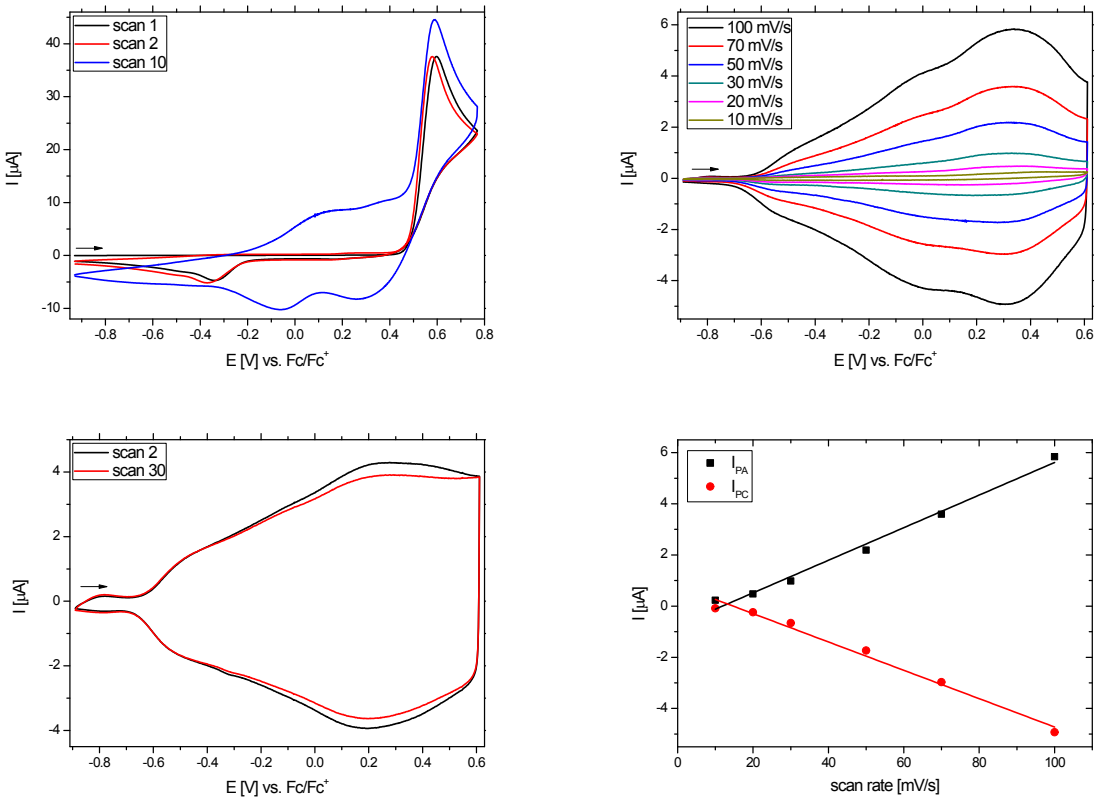

Figure 20: Electropolymerization of the DTP monomer **7** with a phenyl residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

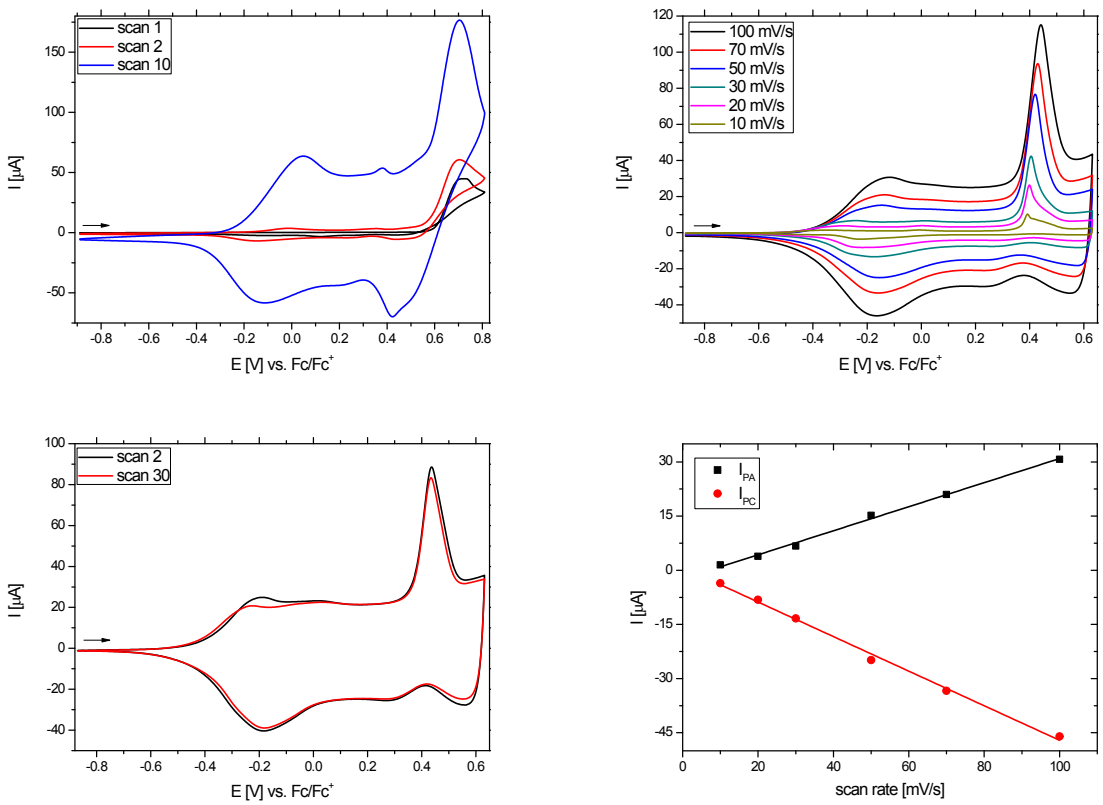

Figure 21: Electropolymerization of the DTP monomer **8** with a Boc residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

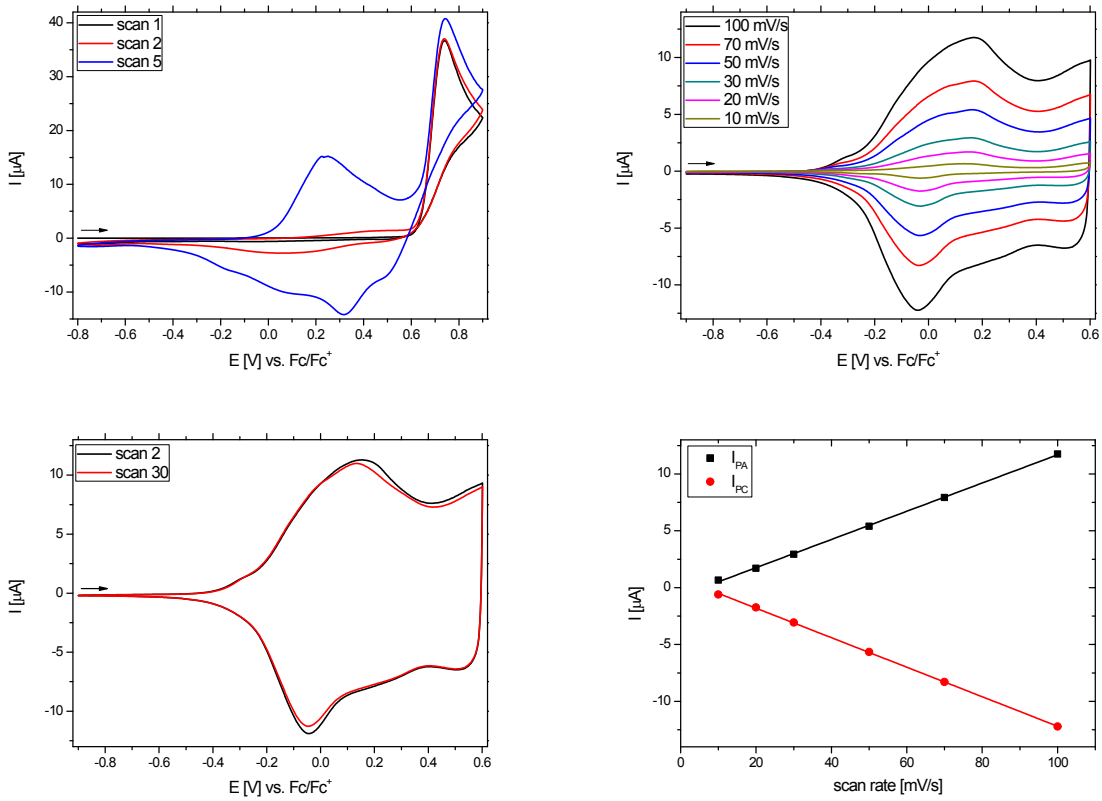

Figure 22: Electropolymerization of the DTP monomer **9** with a benzoyl residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

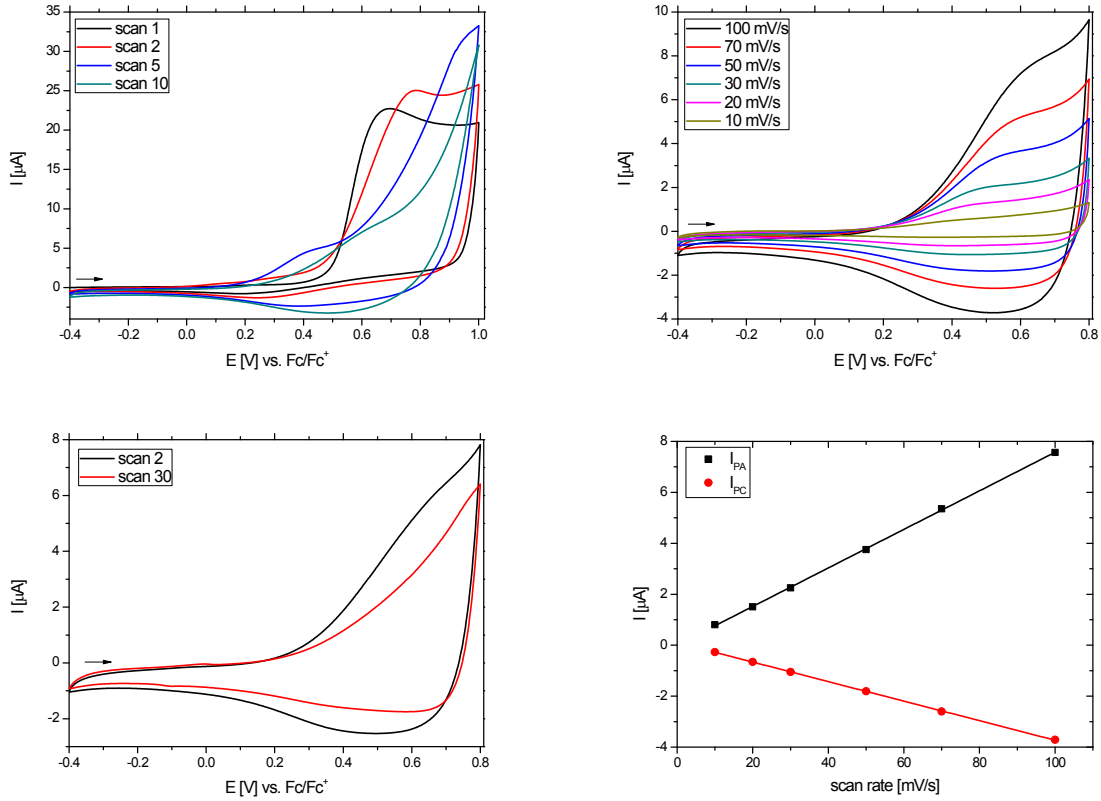

Figure 23: Electropolymerization of the iso-DTP monomer **2** with a H residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} at 0.63 V and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

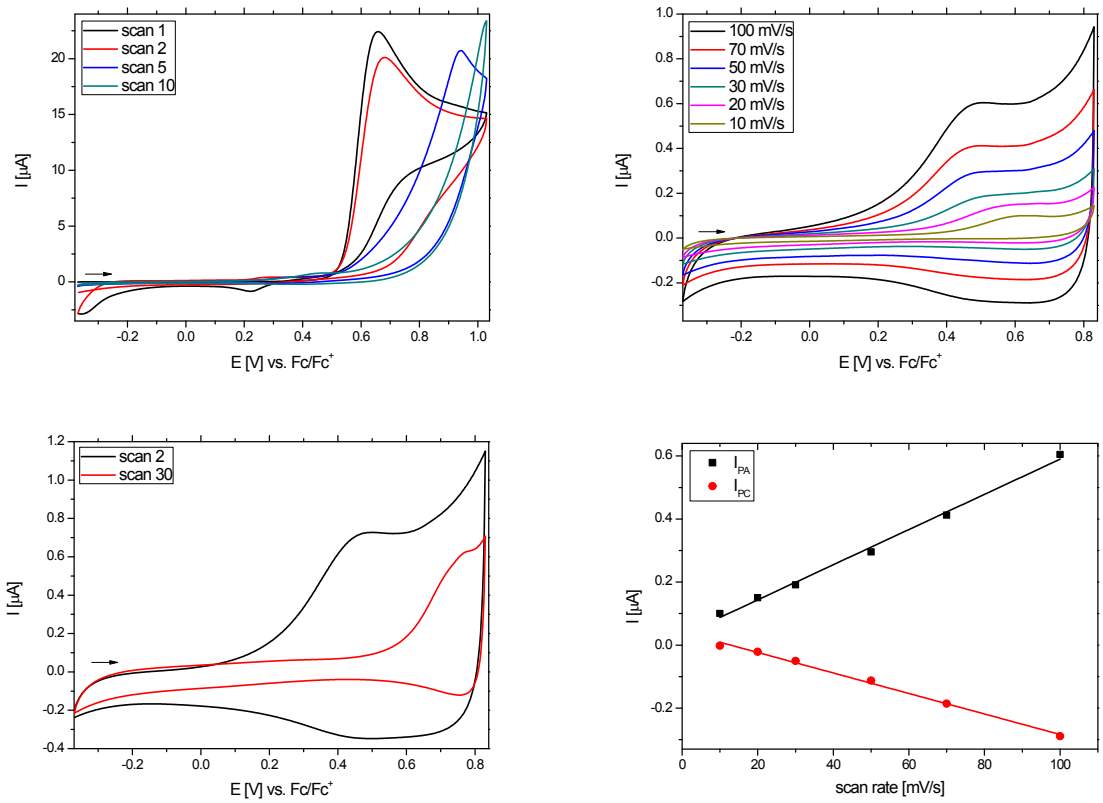

Figure 24: Electropolymerization of the iso-DTP monomer **12** with a 2-ethylhexyl residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

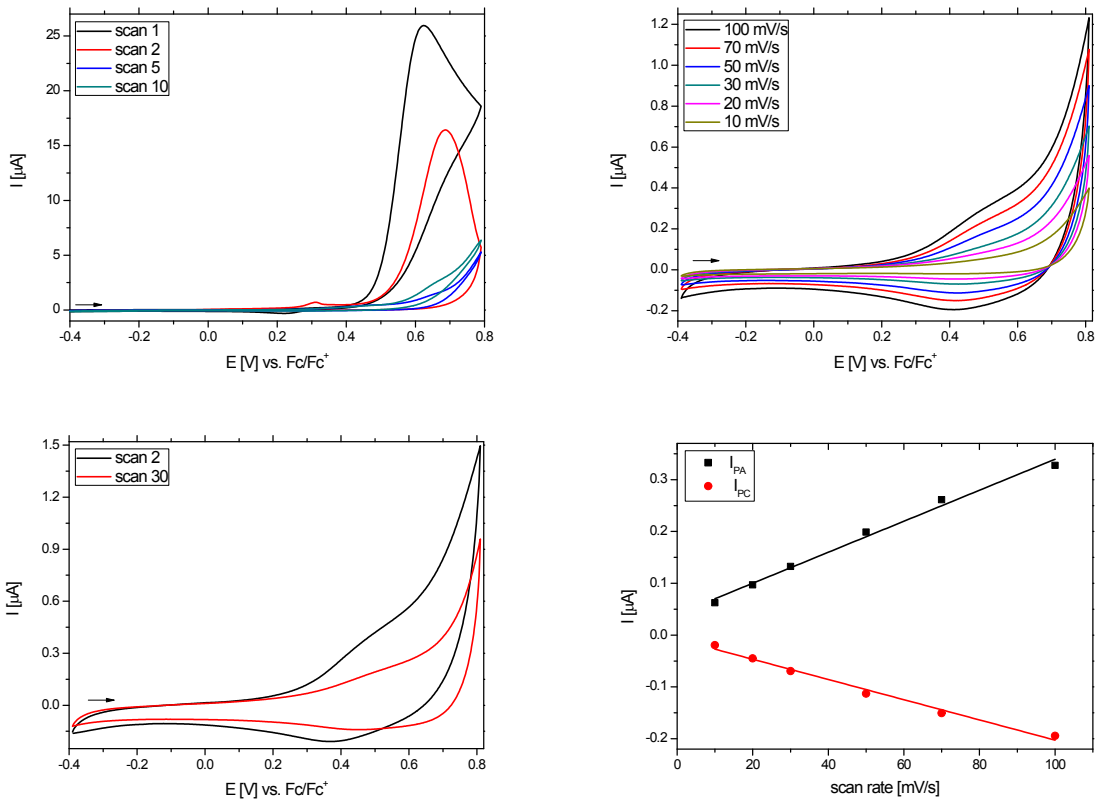

Figure 25: Electropolymerization of the iso-DTP monomer **13** with a 2-hexyldecyl residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} at 0.53 V and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

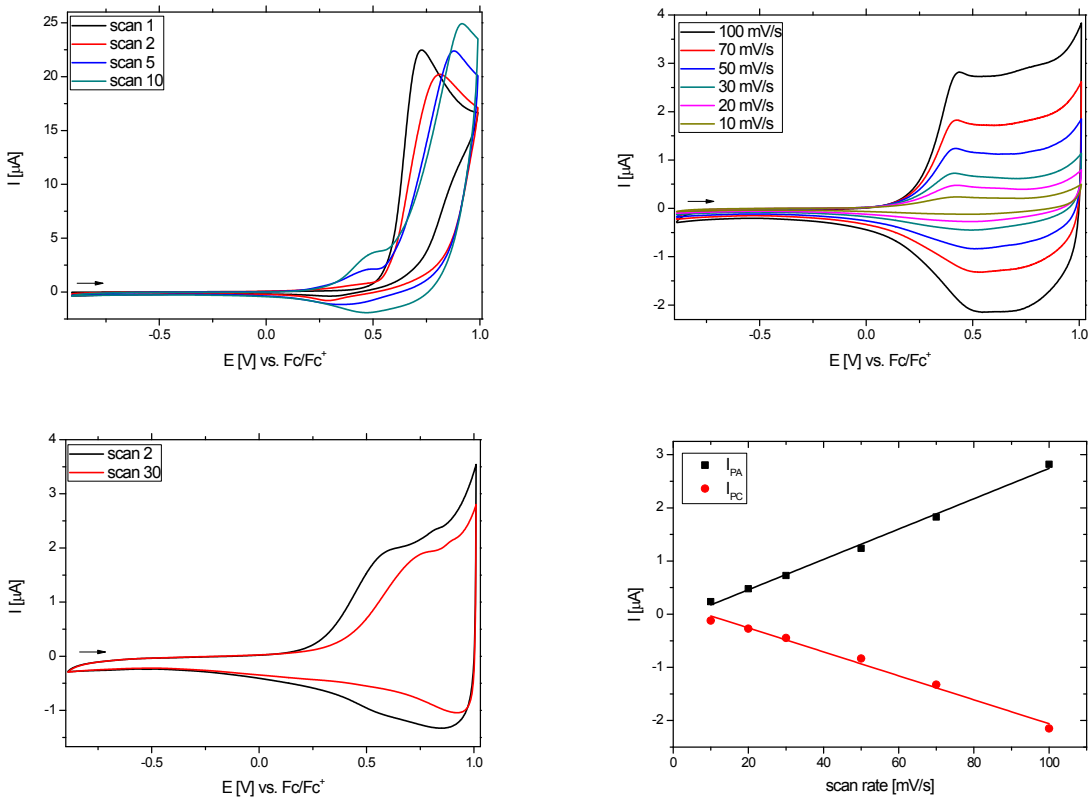

Figure 26: Electropolymerization of the iso-DTP monomer **14** with a phenyl residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

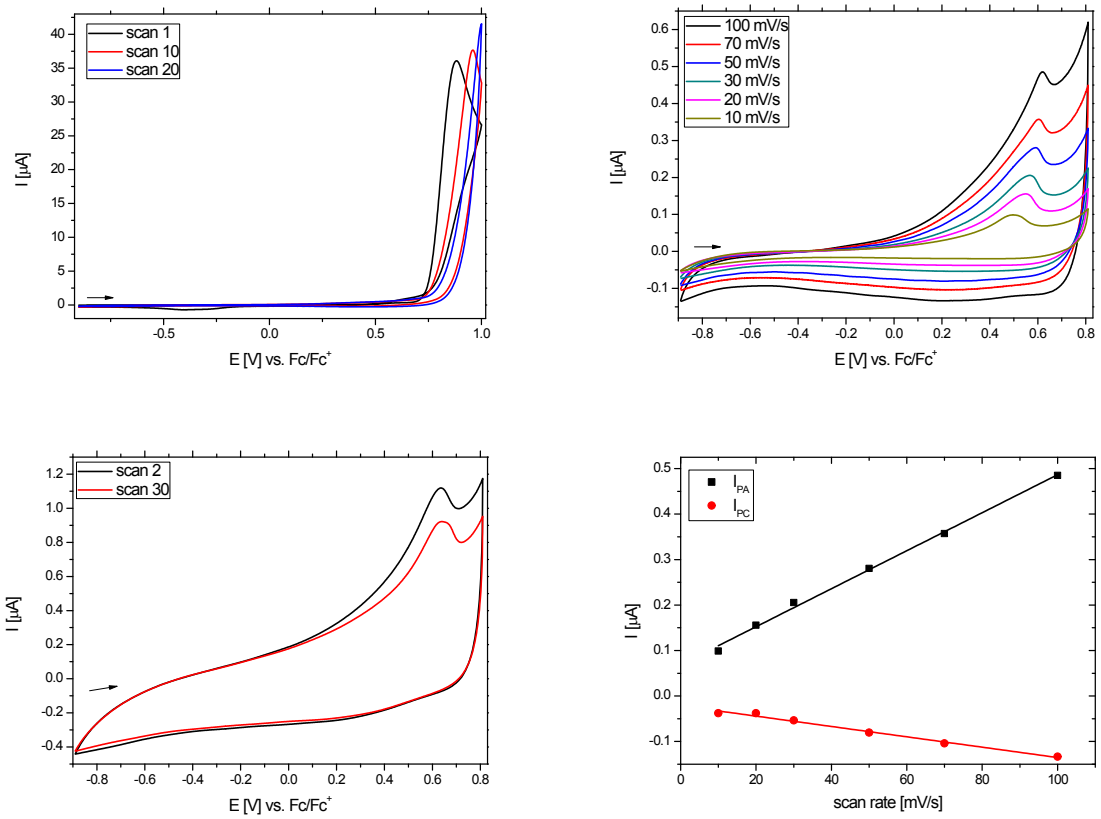

Figure 27: Electropolymerization of the iso-DTP monomer **10** with a Boc residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

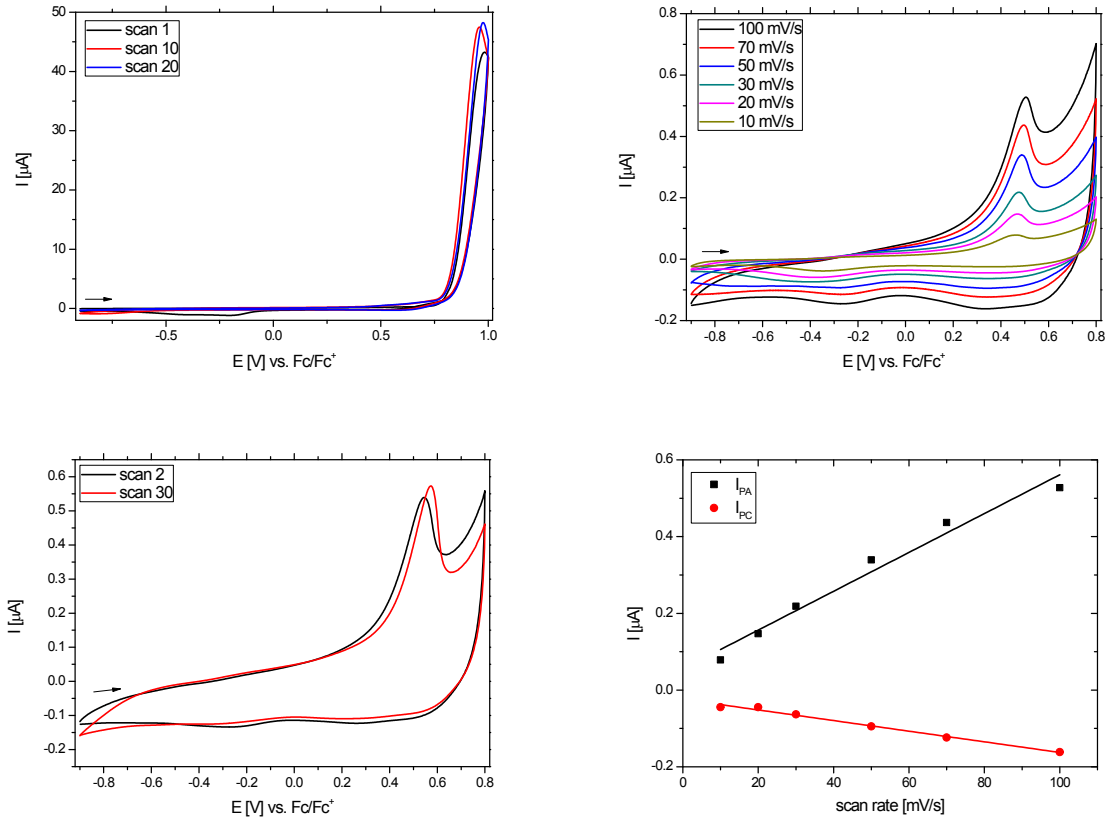

Figure 28: Electropolymerization of the iso-DTP monomer **15** with a benzoyl residue at the nitrogen (top left) and the characterization of the obtained film using different scan rates (top right) and carrying out 30 scans at a rate of 100 mV/s (bottom left). Dependency of the anodic peak currents I_{PA} and the cathodic peak currents I_{PC} from the applied scan rate (bottom right).

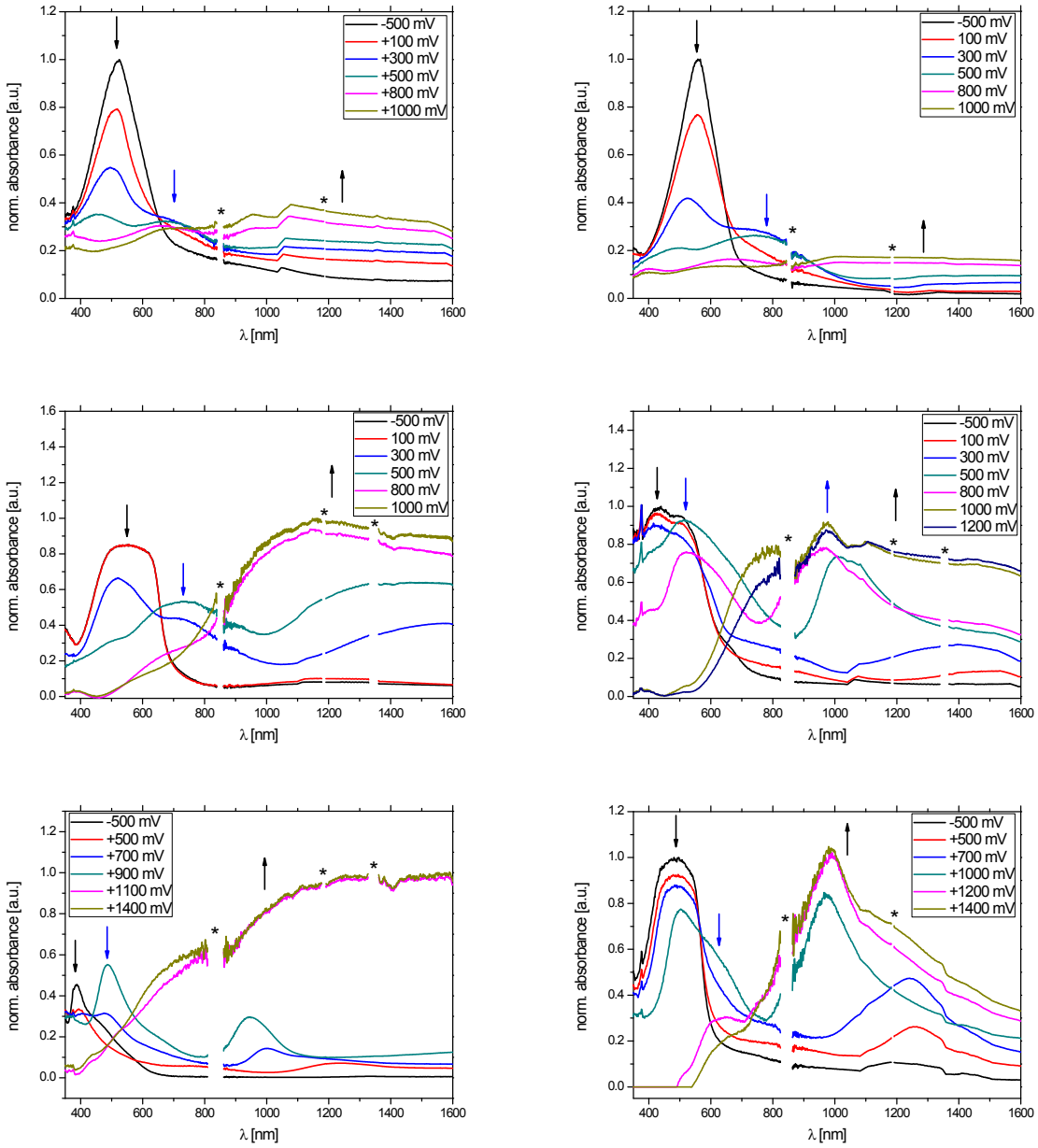

Figure 29: UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of the p(DTP)s bearing H (**P1**, top left), 2-ethylhexyl (**P5**, top right), 2-hexyldecyl (**P6**, middle left), phenyl (**P7**, middle right), Boc (**P8**, bottom left), or benzoyl (**P9**, bottom right) residues at the nitrogen, respectively. Applied voltages are stated vs. Ag/AgCl. Black arrows show the changes starting at low potentials, blue arrows indicate the further changes at high potentials. Artefacts are marked with * in the spectra.

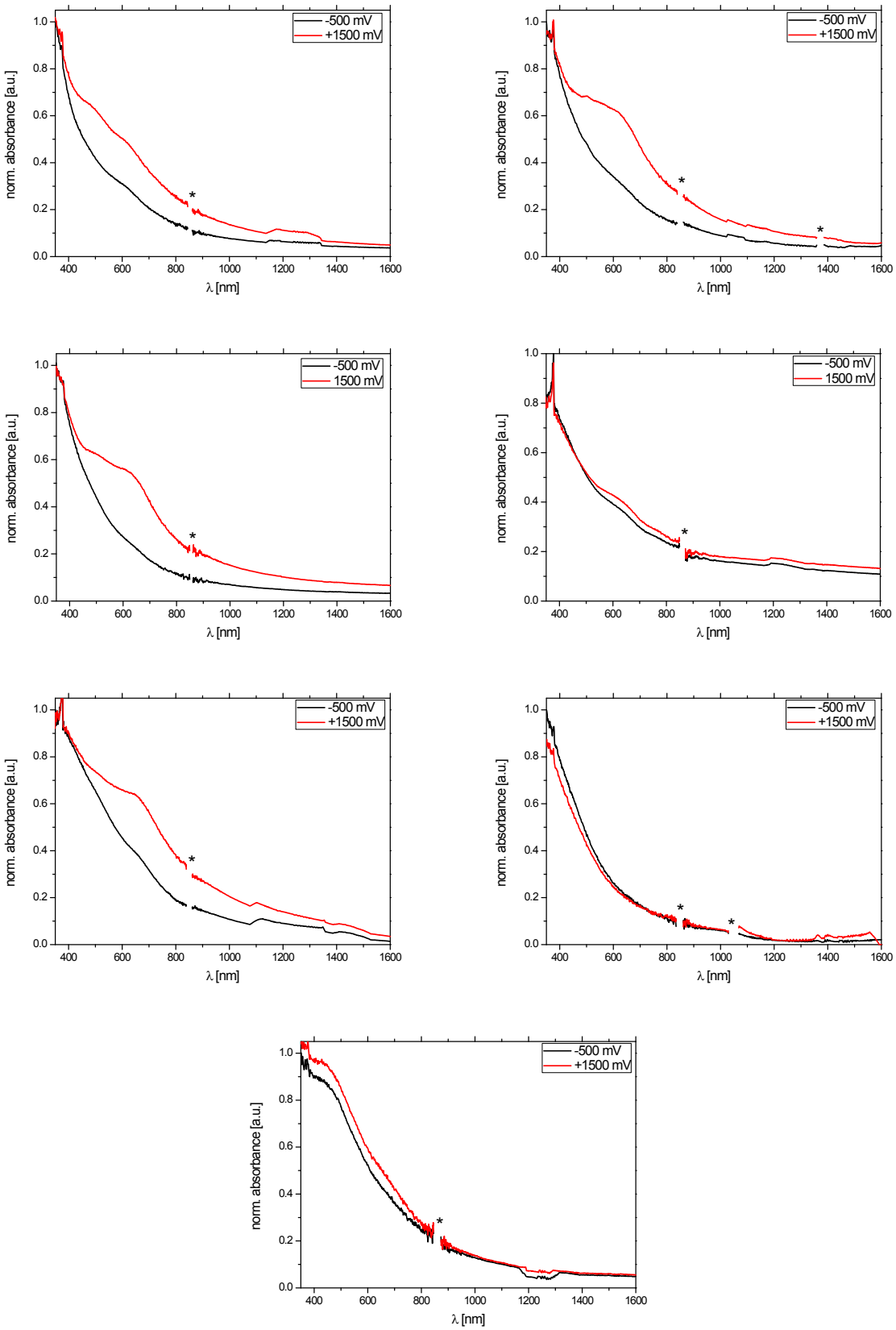

Figure 30: UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of the p(iso-DTP)s bearing H (**P2**, top left), hexyl (**P11**, top right), 2-ethylhexyl (**P12**, middle left), 2-hexyldecyl (**P13**, middle right), phenyl (**P14**, bottom left), Boc (**P10**, botttom right), or benzoyl (**P15**, bottom) residues at the nitrogen, respectively. Applied voltages are stated vs. Ag/AgCl. Artefacts are marked with * in the spectra.