

Supporting Information

## **Bis(thienyl)ethenes with $\alpha$ -methoxymethyl groups. Syntheses, spectroscopic Hammett plots, and stabilities in PMMA films**

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## Hammett and Hammett-Brown correlations

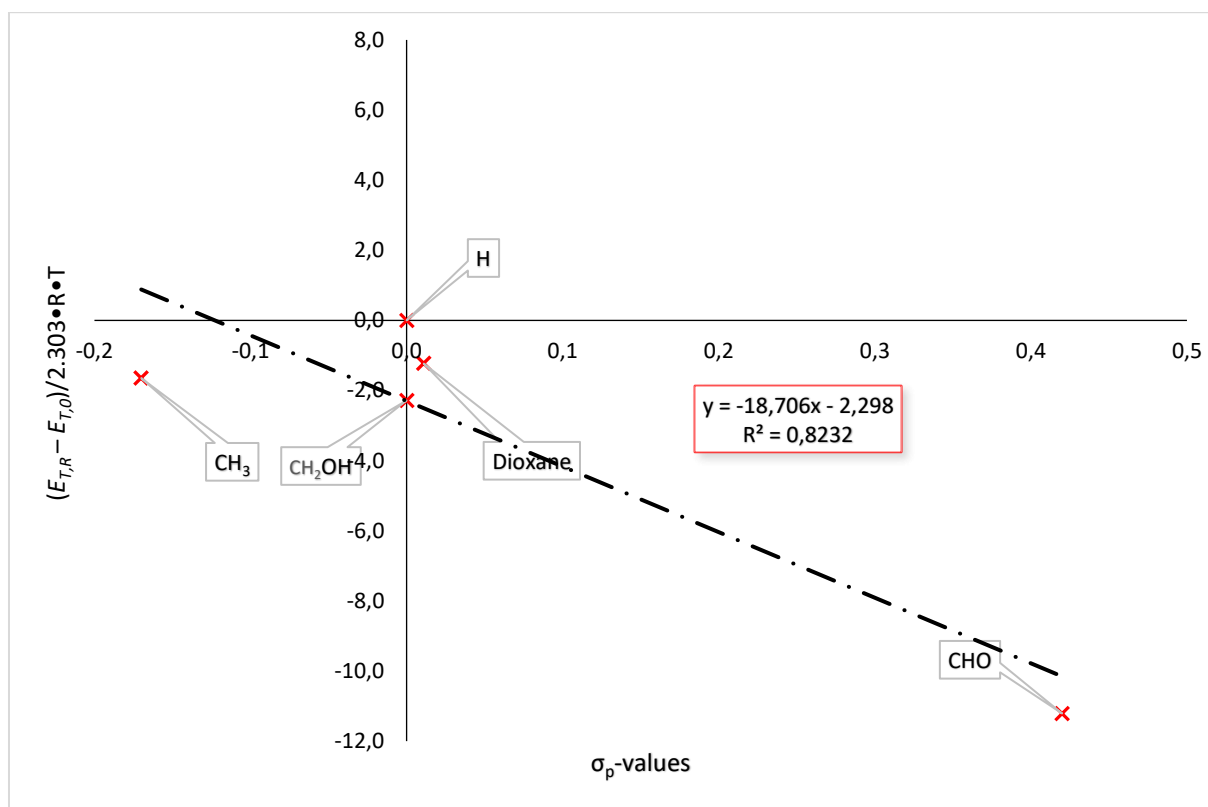


Figure S1: Hammett correlation of the BTEs (open form) applying  $\sigma_p$  values (THF).

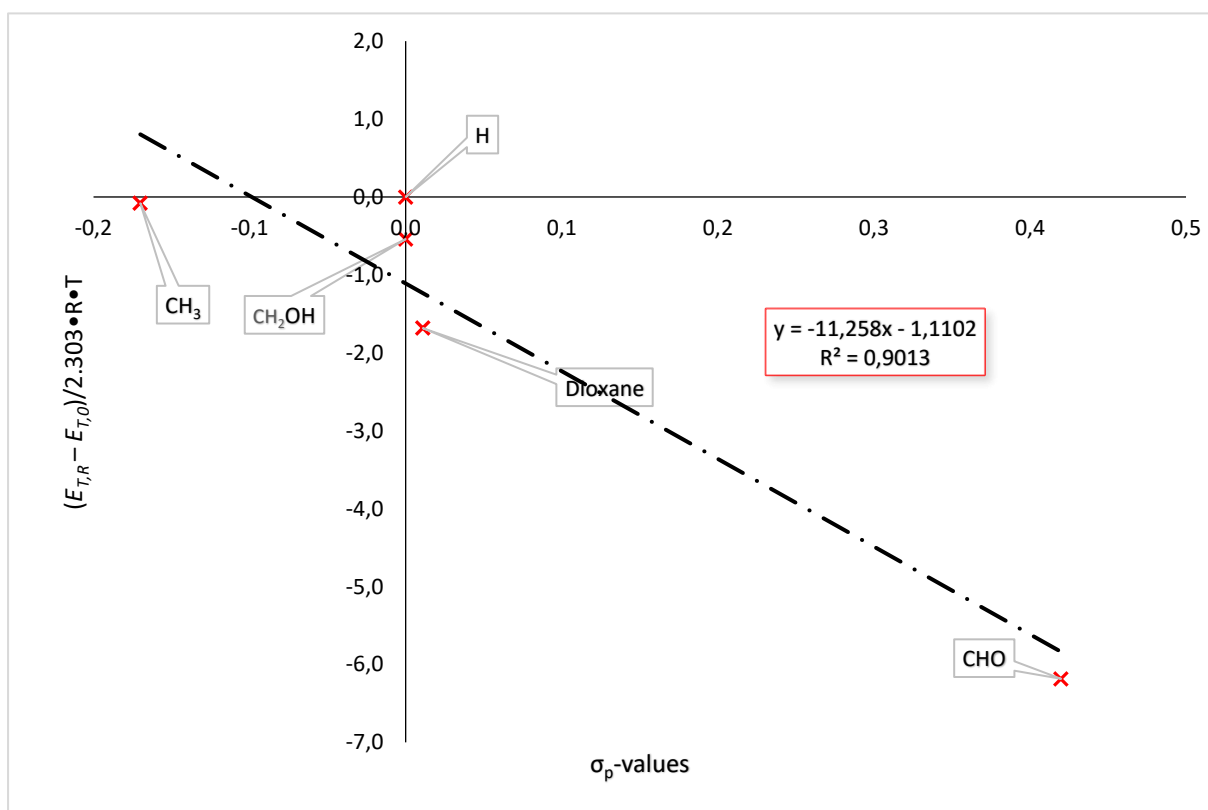


Figure S2: Hammett correlation of the BTEs (closed form) applying  $\sigma_p$  values (THF).

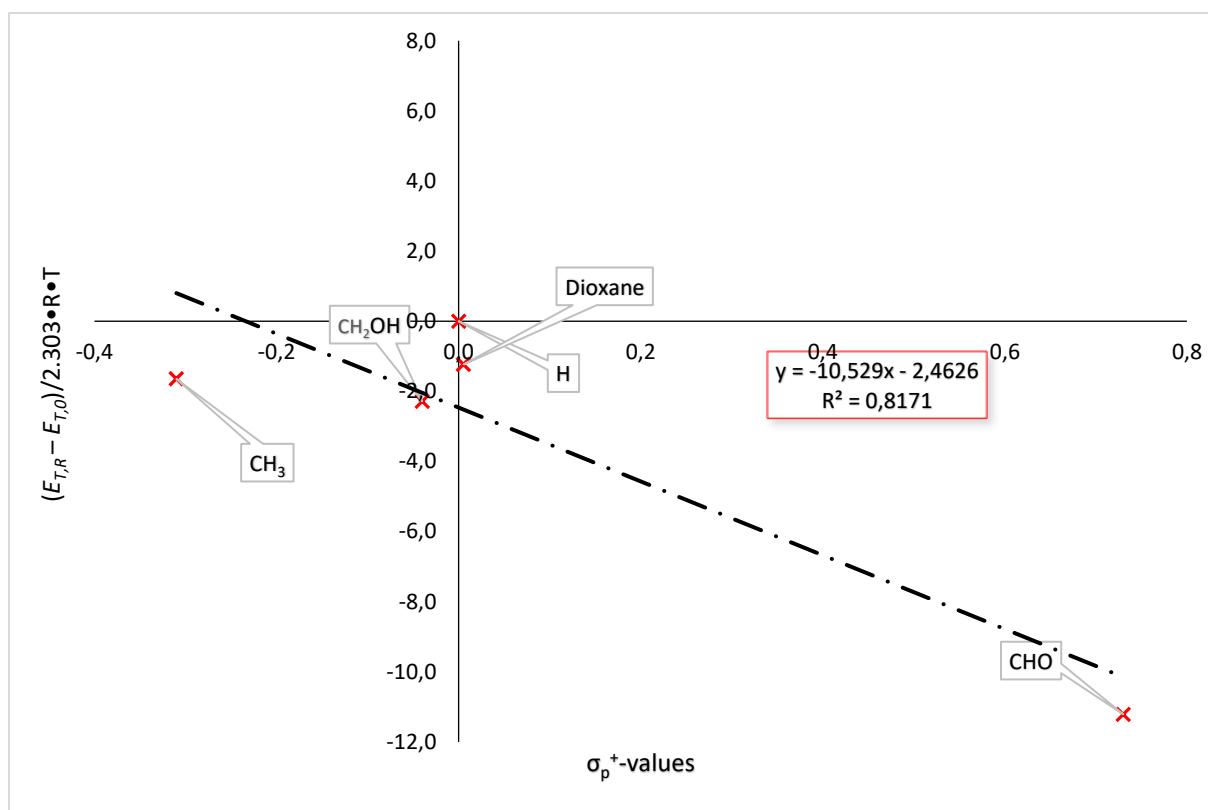


Figure S3: Hammett-Brown correlation of the BTEs (open form) applying  $\sigma_p^+$  values (THF).

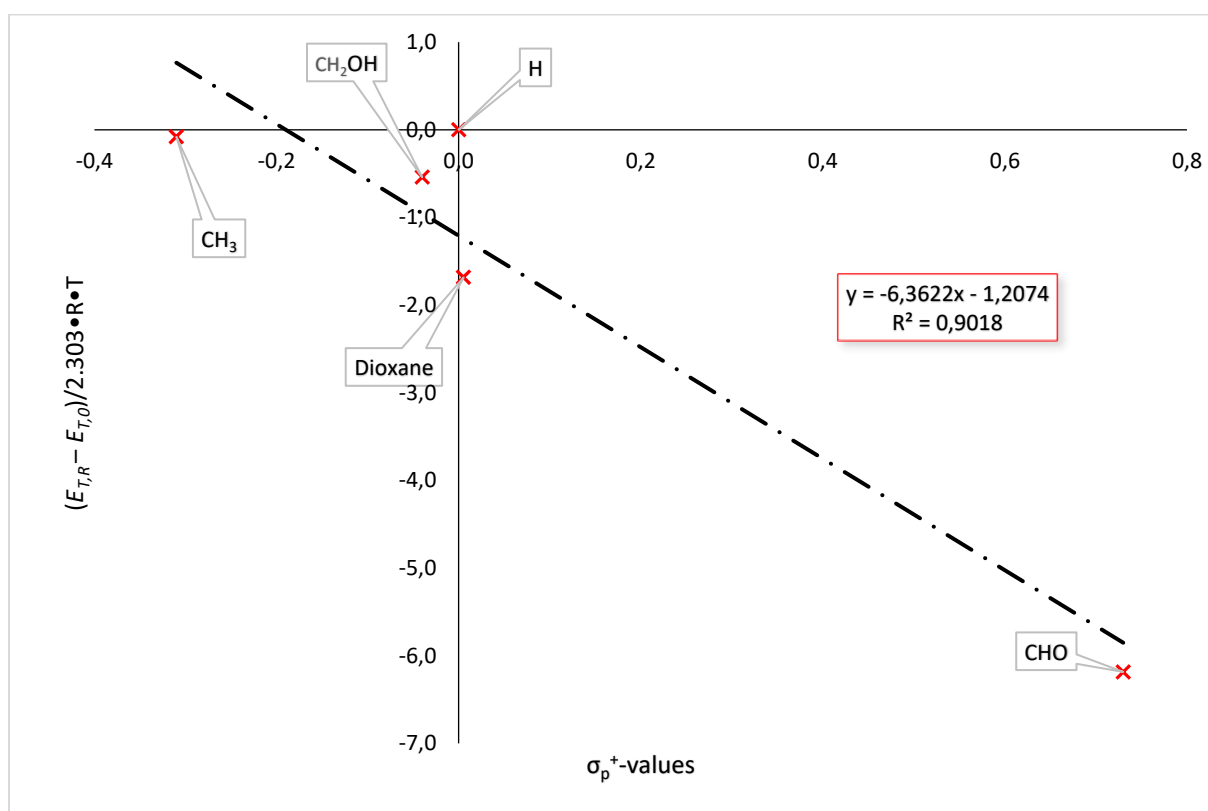


Figure S4: Hammett-Brown correlation of the BTEs (closed form) applying  $\sigma_p^+$  values (THF).

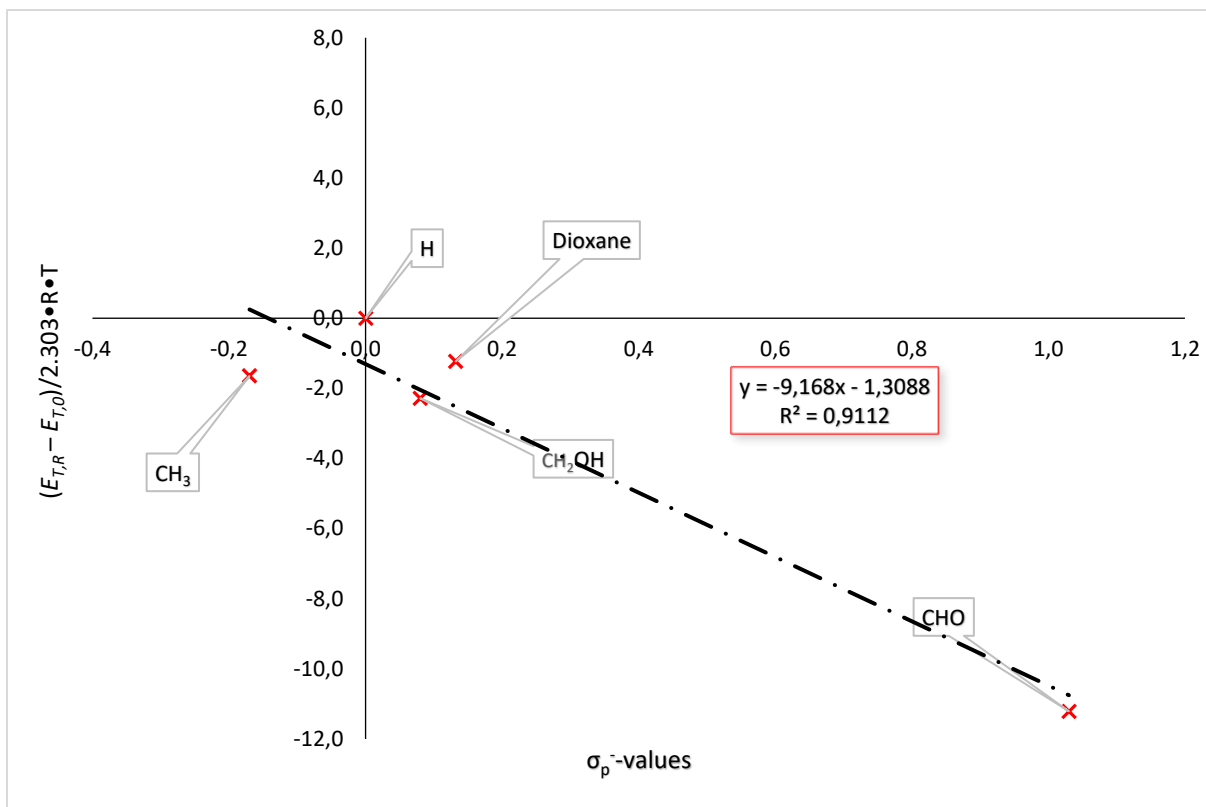


Figure S5: Hammett-Brown correlation of the BTEs (open form) applying  $\sigma_p^-$  values (THF).

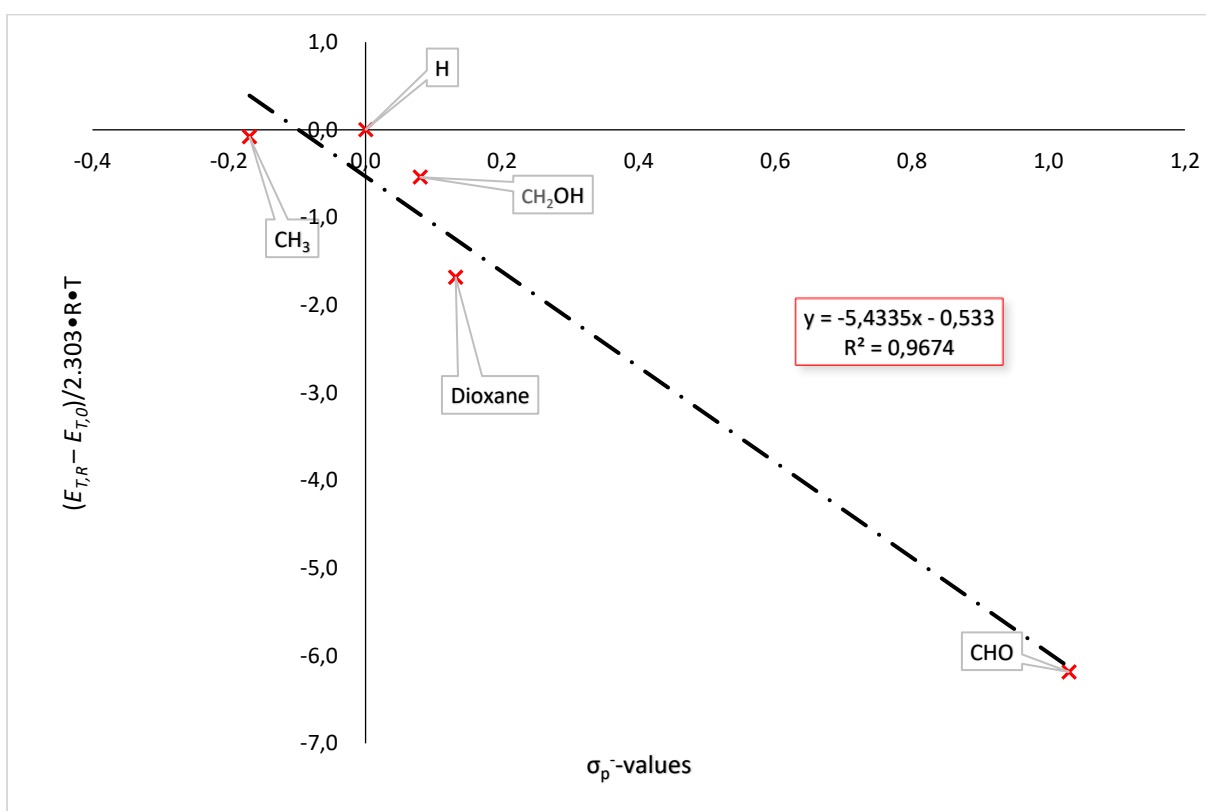


Figure S6: Hammett-Brown correlation of the BTEs (closed form) applying  $\sigma_p^-$  values (THF).

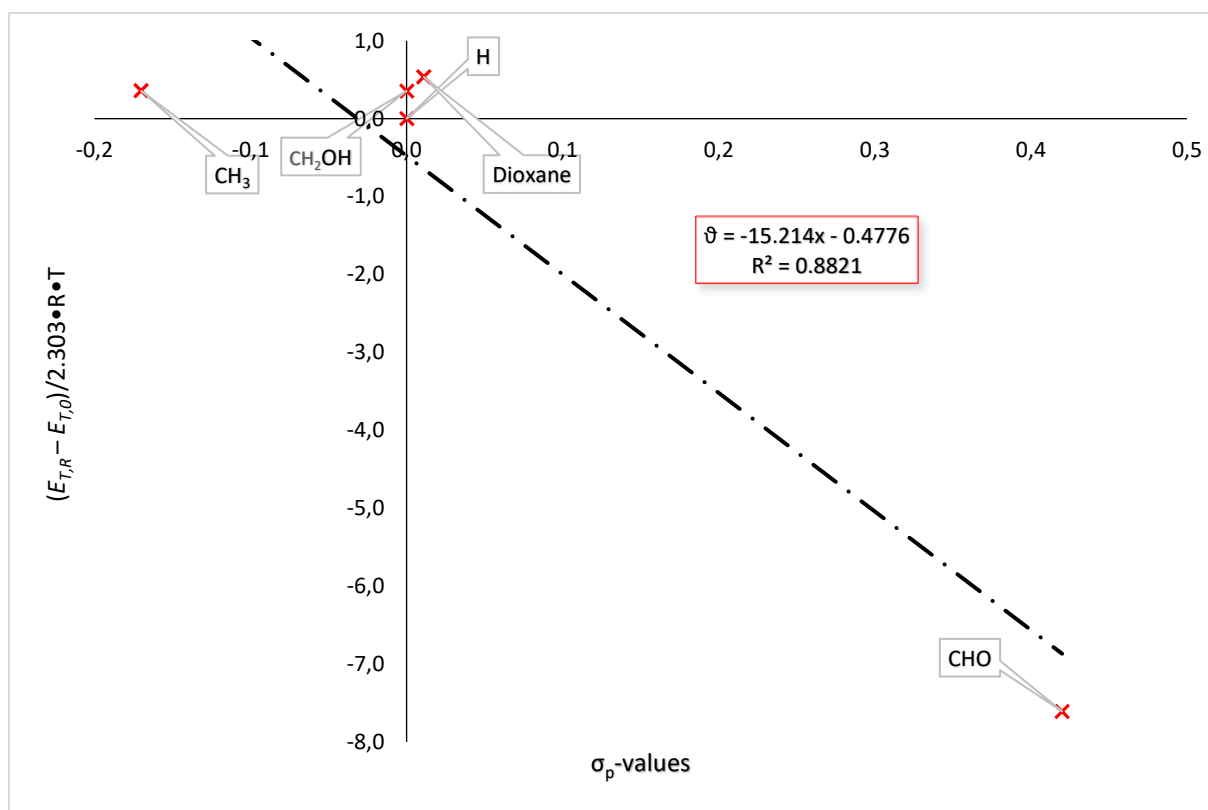


Figure S7: Hammett correlation of the BTEs (open form) applying  $\sigma_p$  values ( $\text{CHCl}_3$ ).

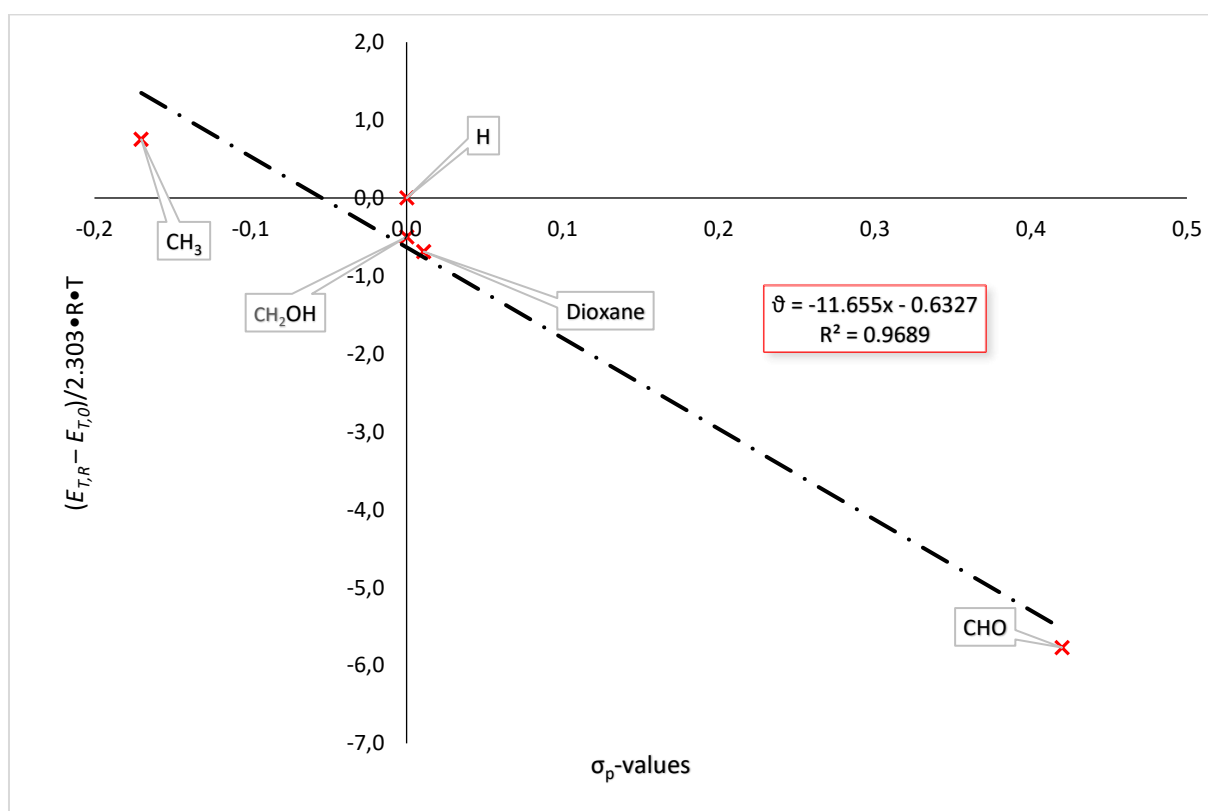


Figure S8: Hammett correlation of the BTEs (closed form) applying  $\sigma_p$  values ( $\text{CHCl}_3$ ).

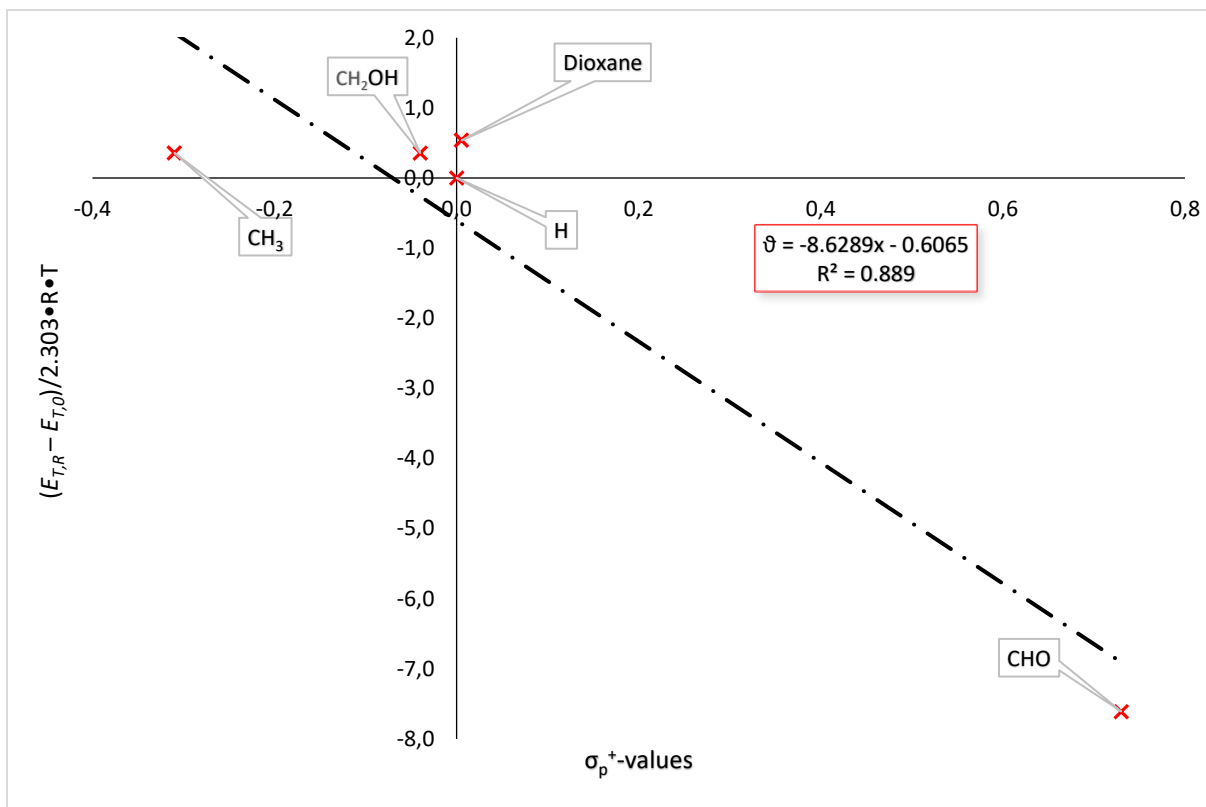


Figure S9: Hammett-Brown correlation of the BTEs (open form) applying  $\sigma_p^+$  values ( $\text{CHCl}_3$ ).

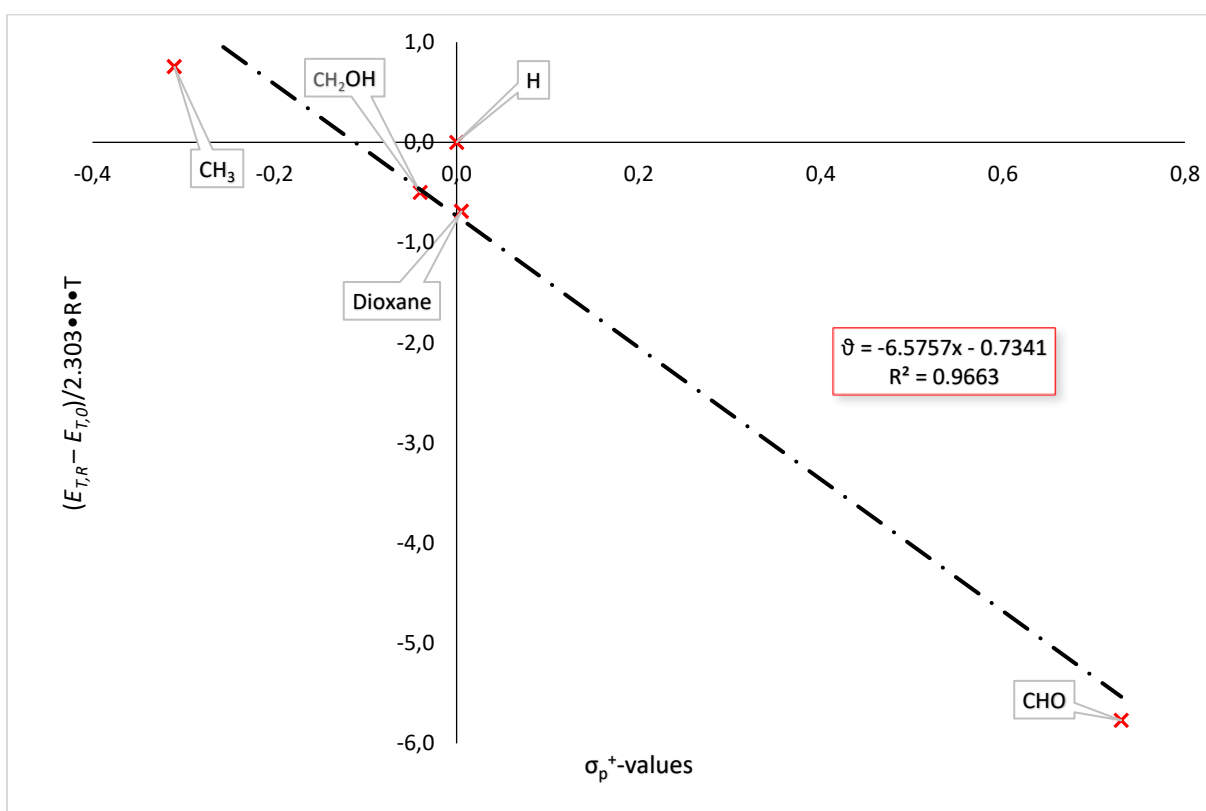


Figure S10: Hammett-Brown correlation of the BTEs (closed form) applying  $\sigma_p^+$  values ( $\text{CHCl}_3$ ).

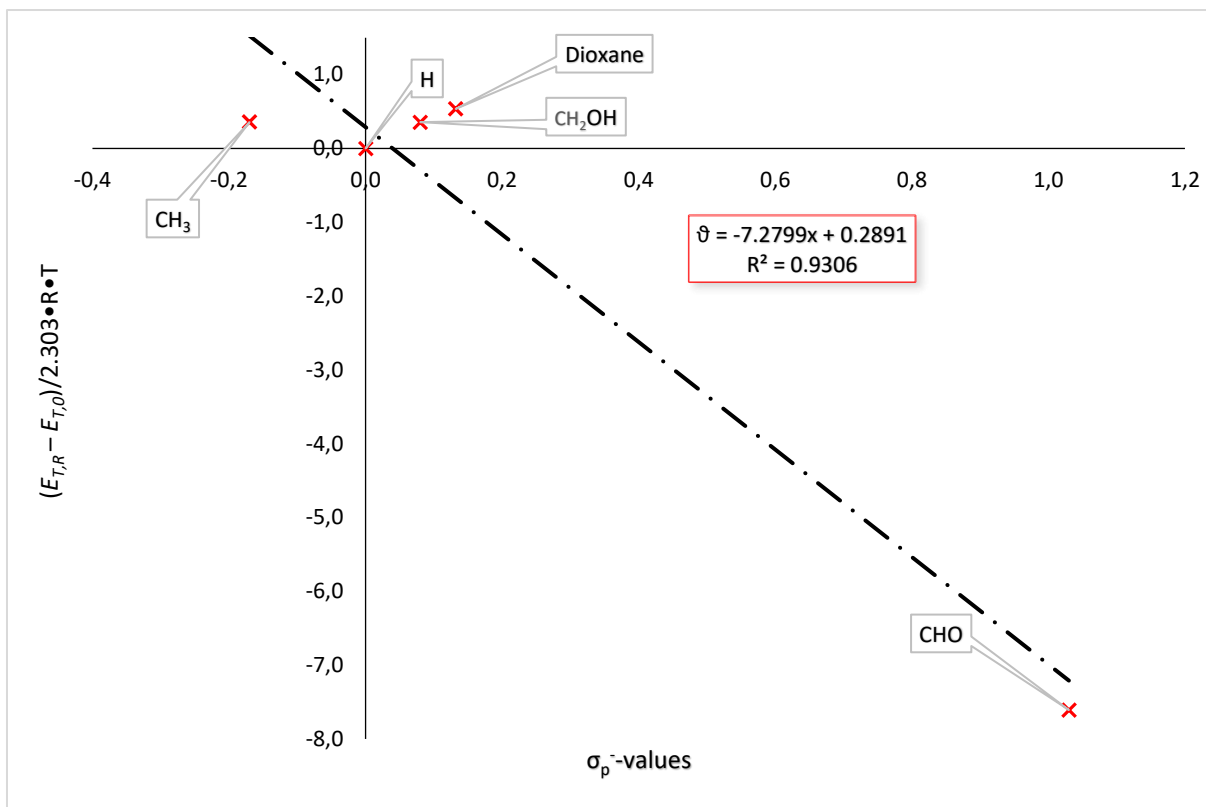


Figure S11: Hammett-Brown correlation of the BTEs (open form) applying  $\sigma_p^-$  values (CHCl<sub>3</sub>).

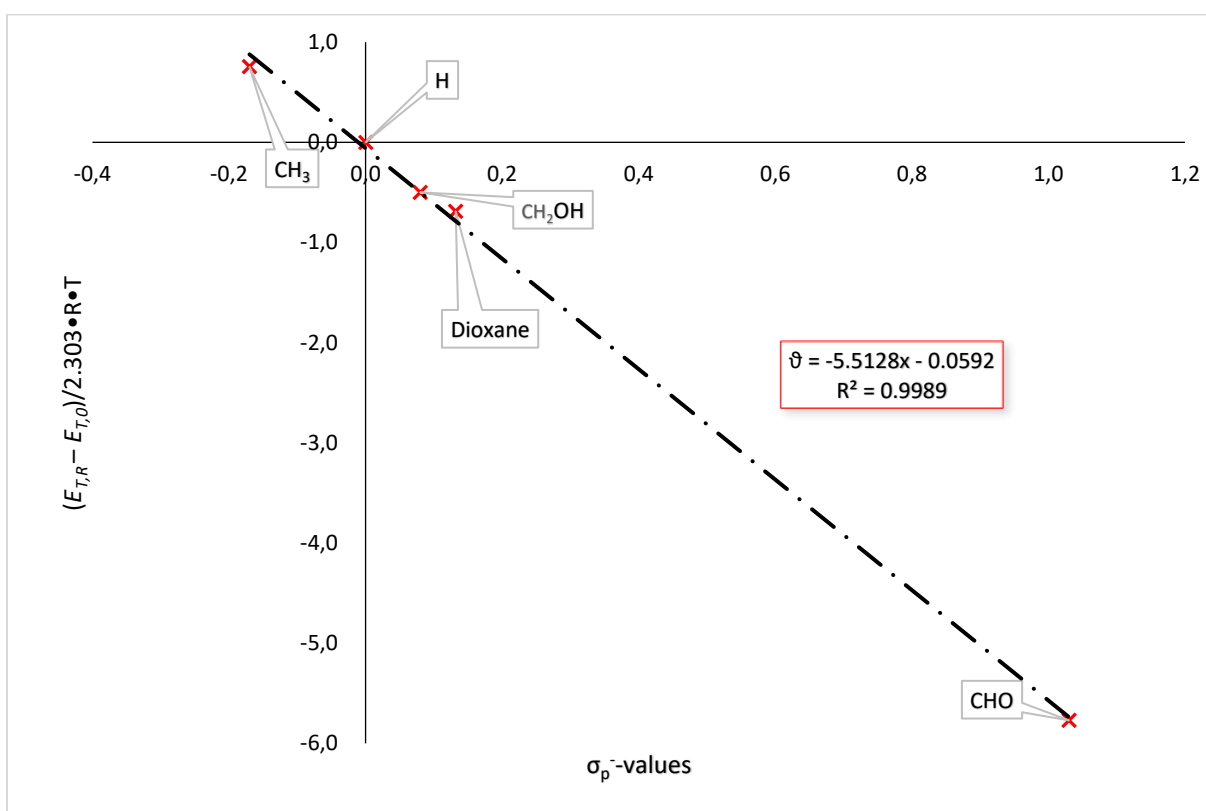


Figure S12: Hammett-Brown correlation of the BTEs (closed form) applying  $\sigma_p^-$  values (CHCl<sub>3</sub>).

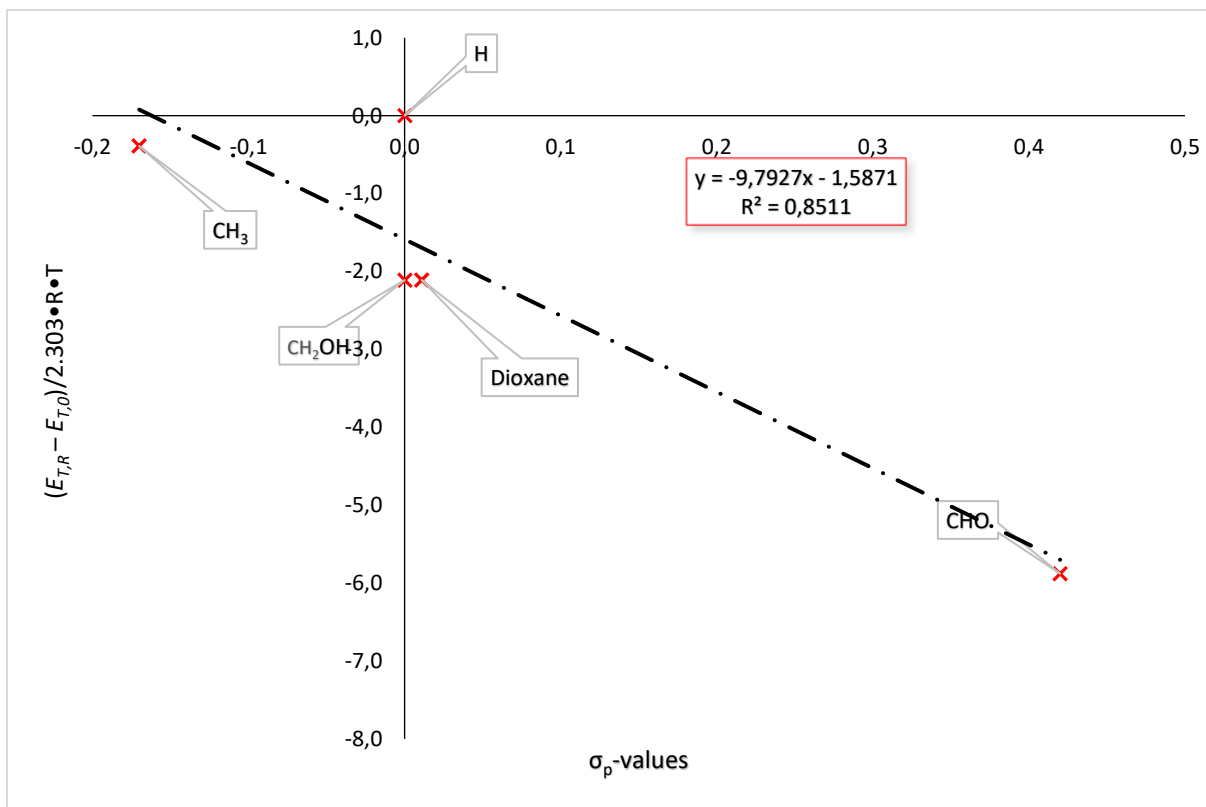


Figure S13: Hammett correlation of the BTEs (open form) applying  $\sigma_p$  values (DCM).

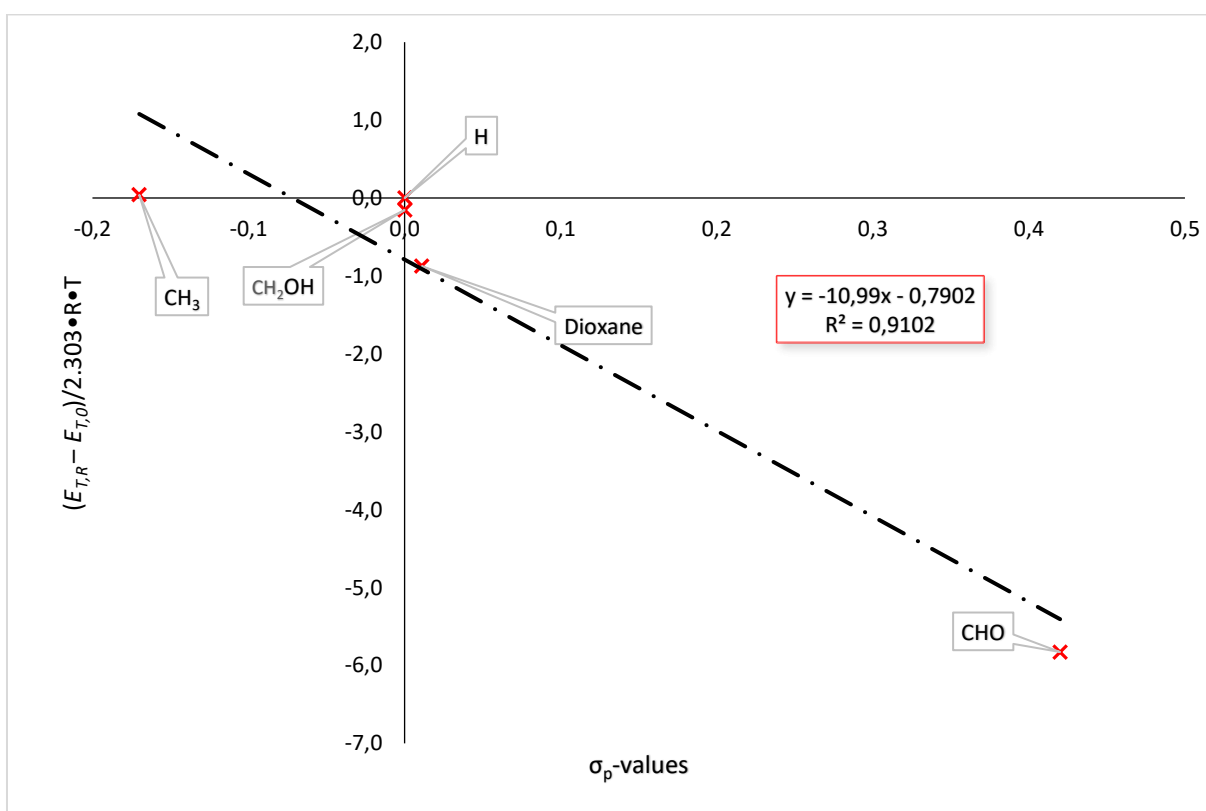


Figure S14: Hammett correlation of the BTEs (closed form) applying  $\sigma_p$  values (DCM).



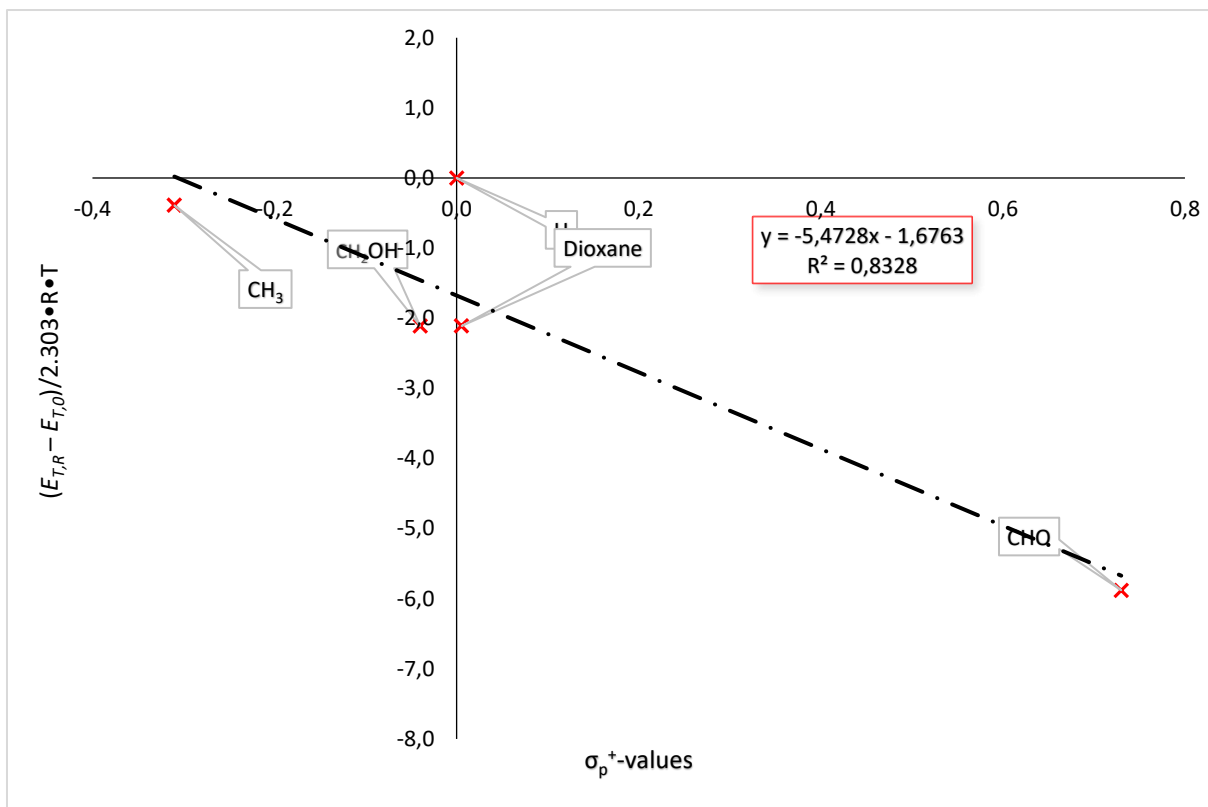


Figure S15: Hammett-Brown correlation of the BTEs (open form) applying  $\sigma_p^+$  values (DCM).

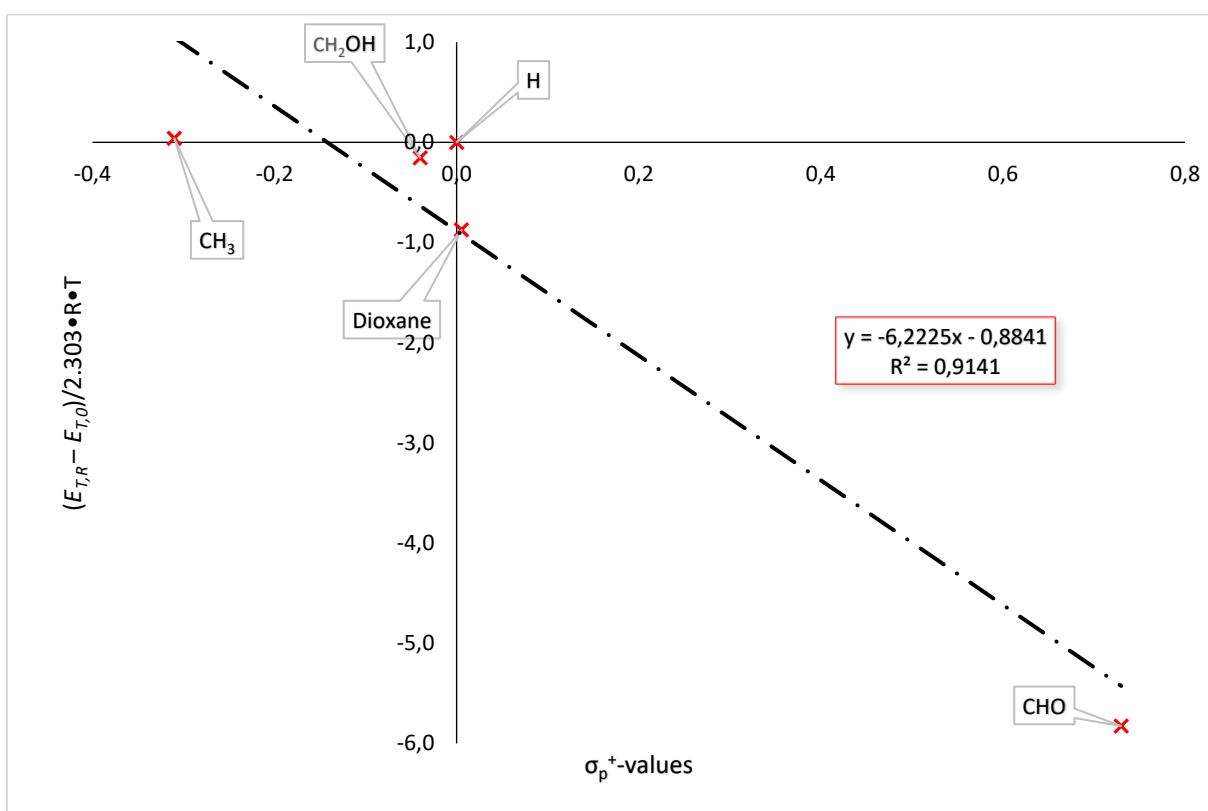


Figure S16: Hammett-Brown correlation of the BTEs (closed form) applying  $\sigma_p^+$  values (DCM).

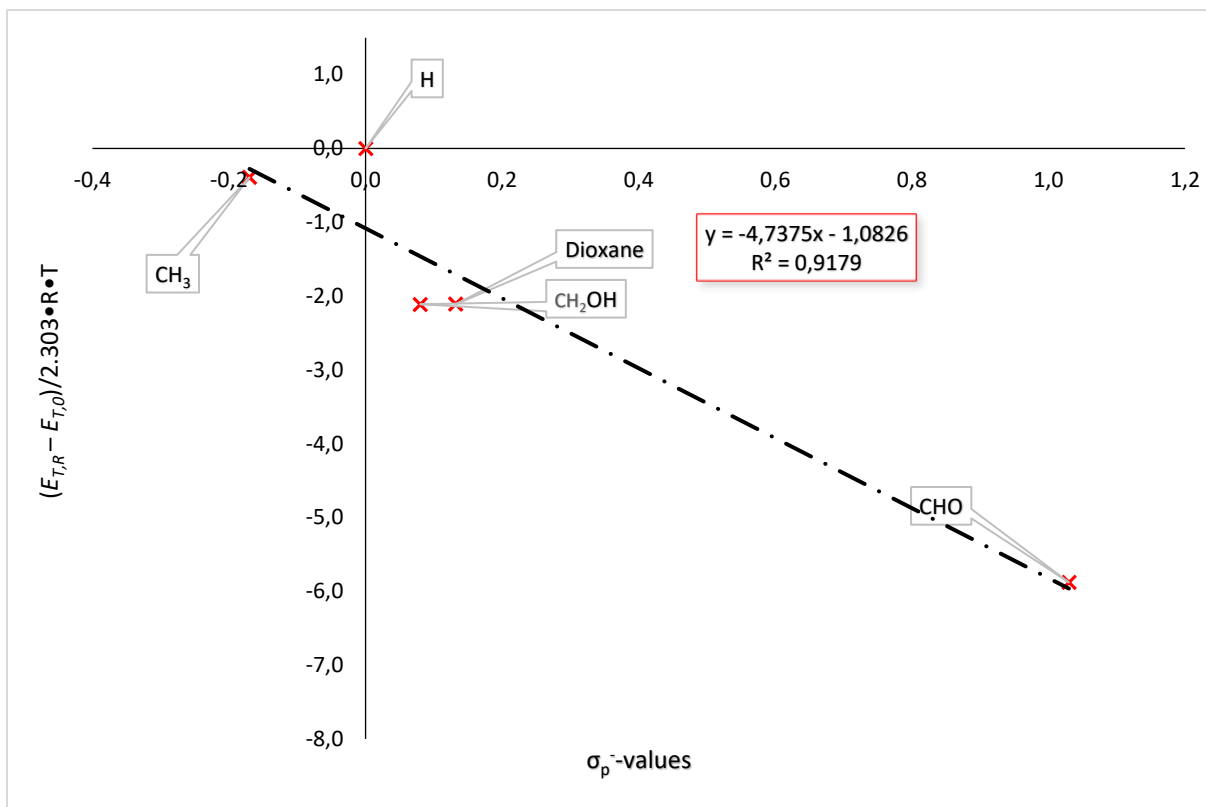


Figure S17: Hammett-Brown correlation of the BTEs (open form) applying  $\sigma_p^-$  values (DCM).

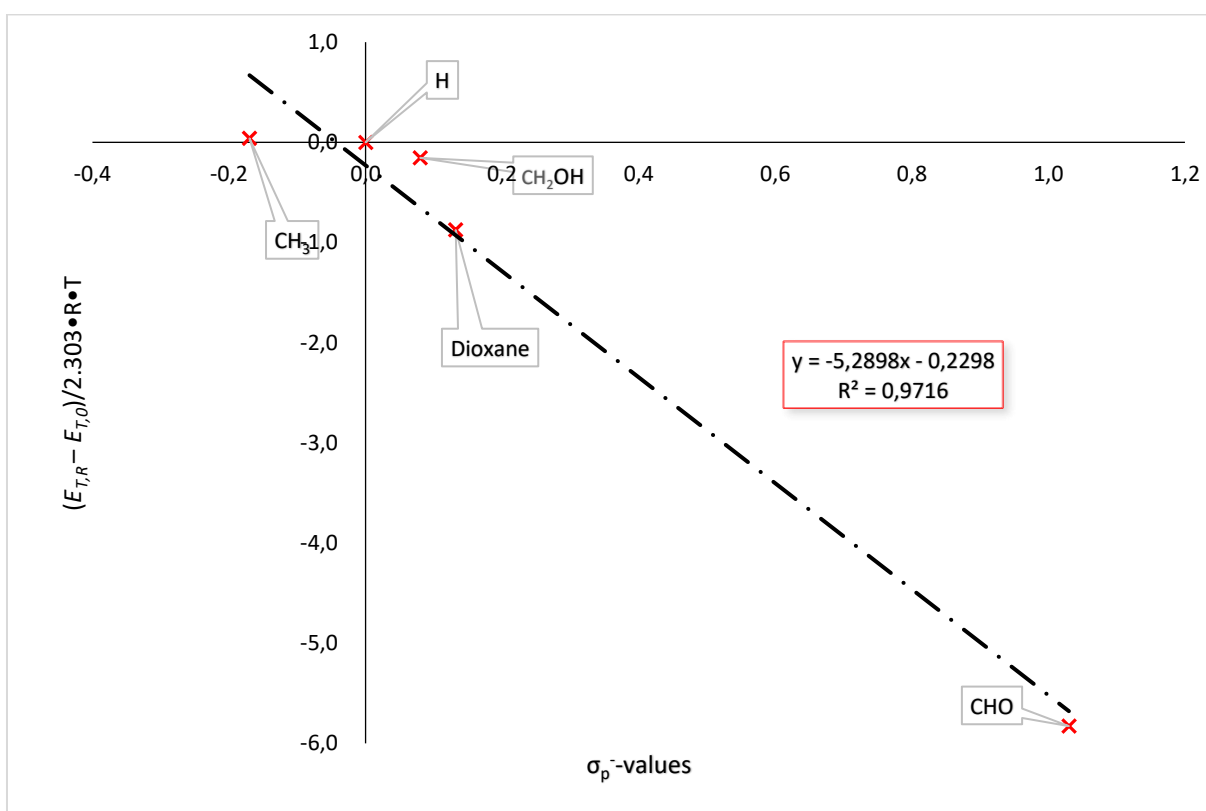


Figure S18: Hammett-Brown correlation of the BTEs (closed form) applying  $\sigma_p^-$  values (DCM).

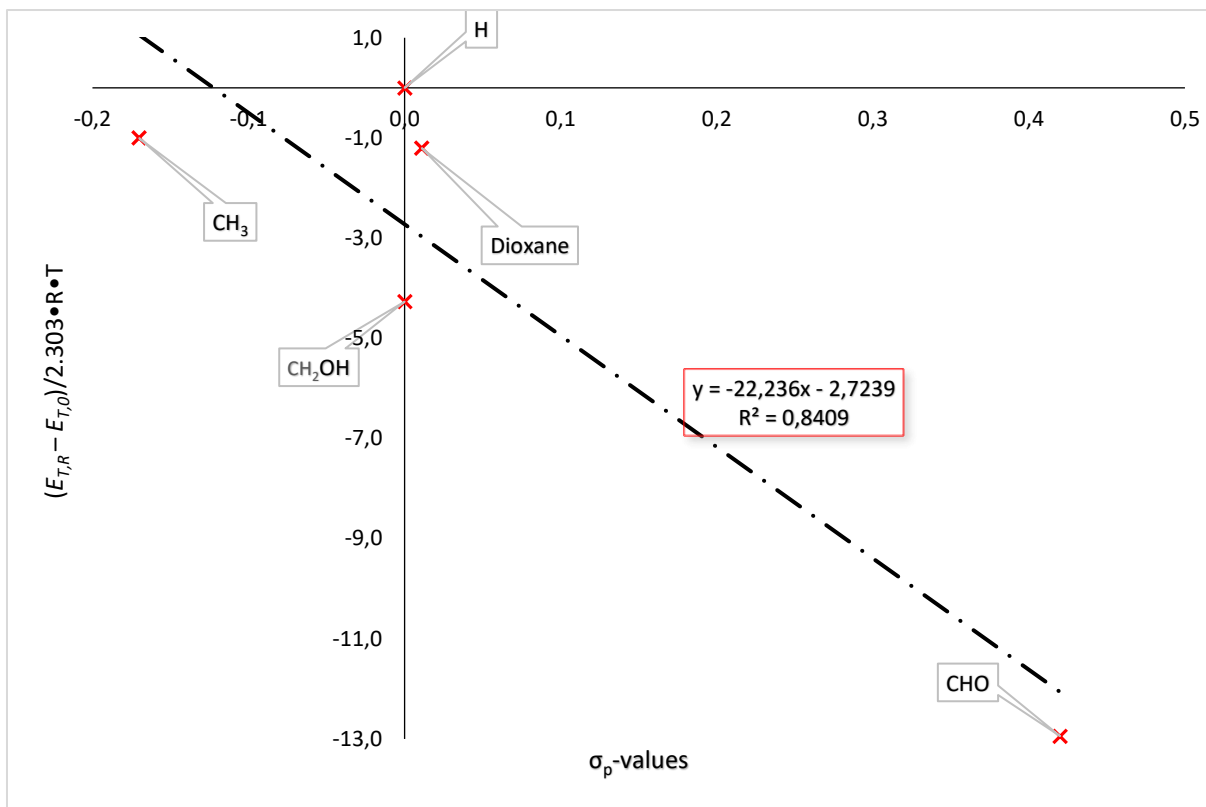


Figure S19: Hammett correlation of the BTEs (open form) applying  $\sigma_p$  values (MeOH).

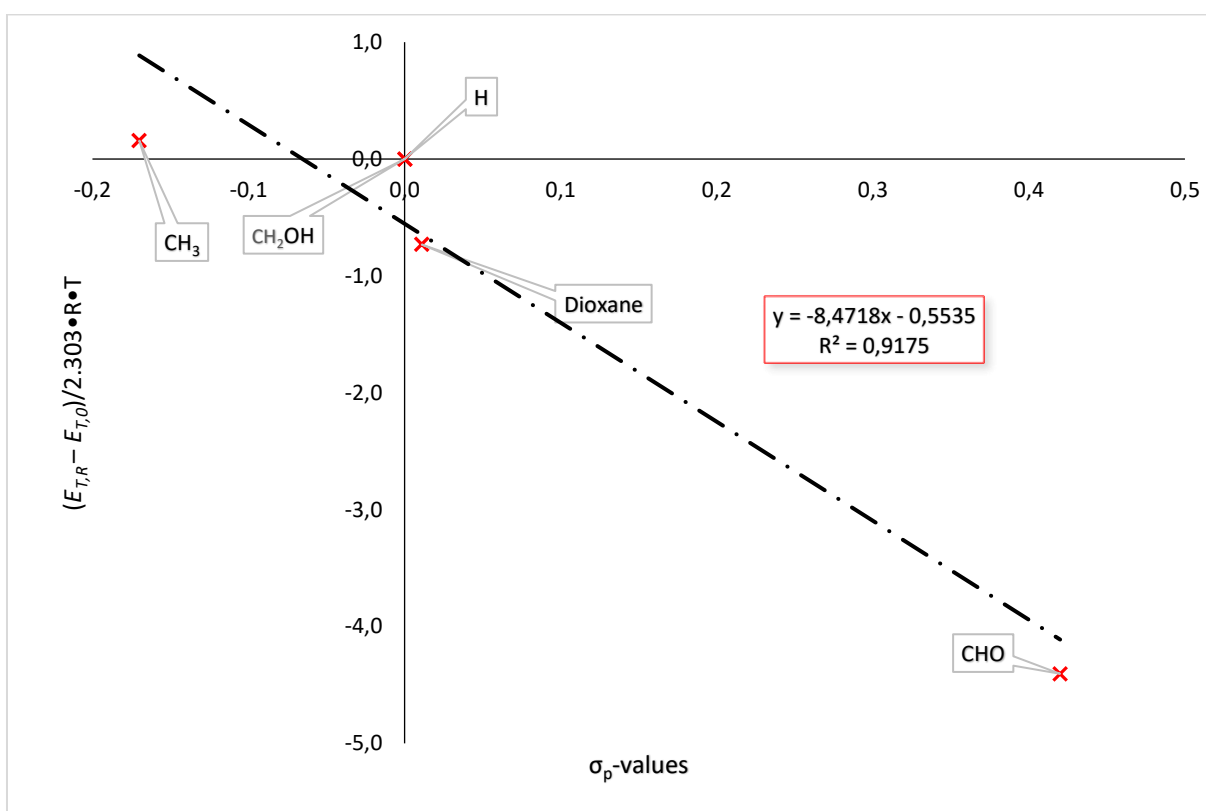


Figure S20: Hammett correlation of the BTEs (closed form) applying  $\sigma_p$  values (MeOH).

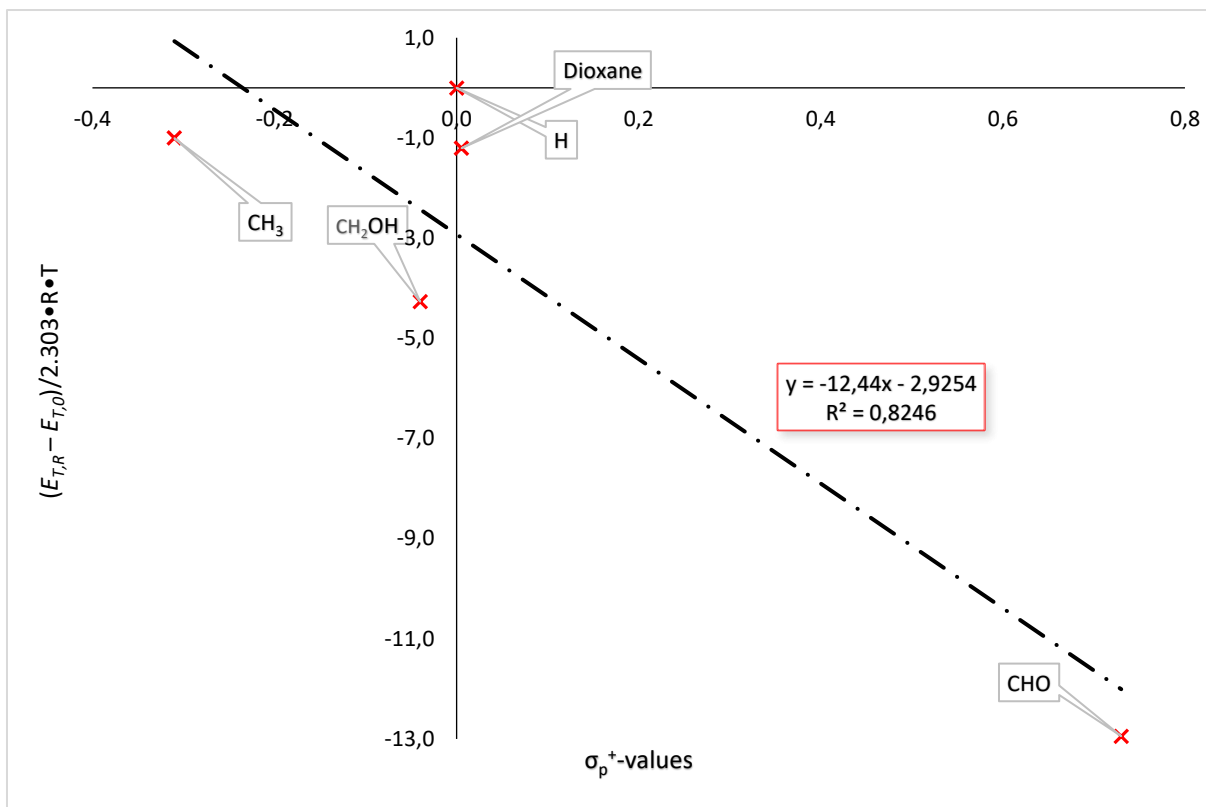


Figure S21: Hammett-Brown correlation of the BTEs (open form) applying  $\sigma_p^+$  values (MeOH).

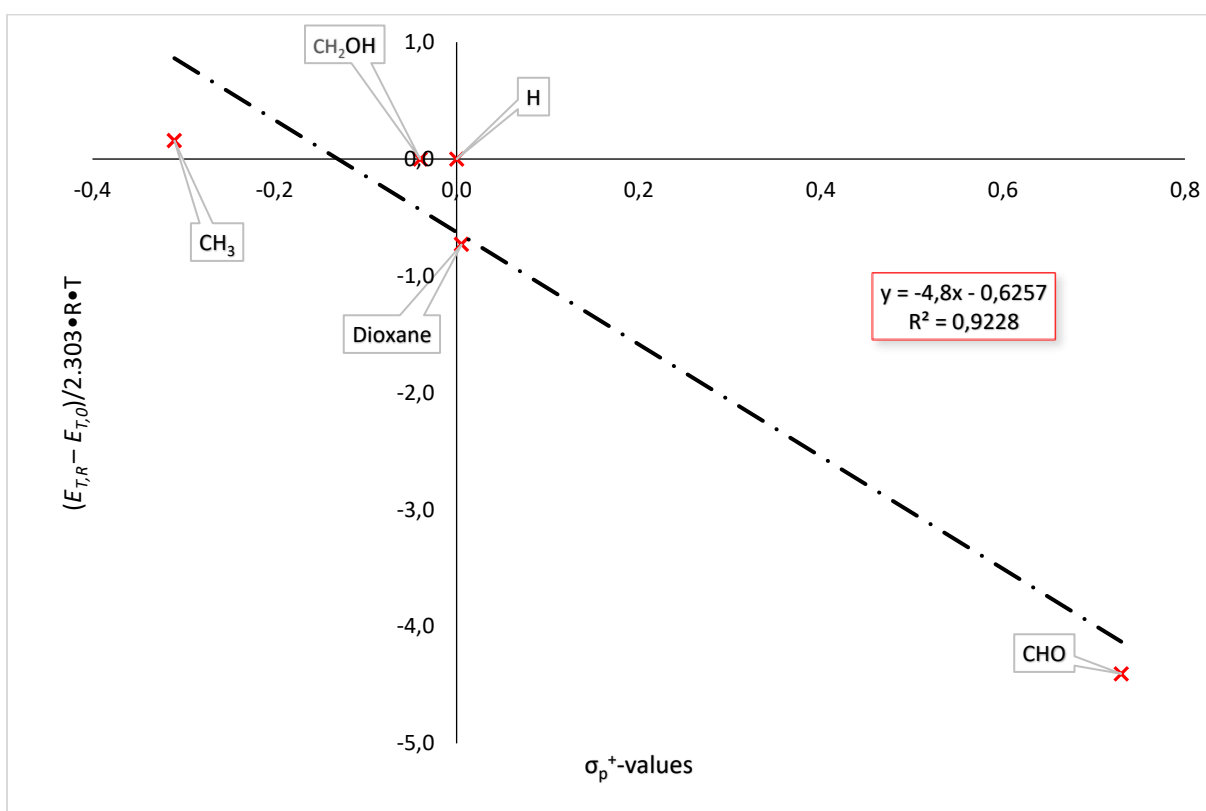


Figure S22: Hammett-Brown correlation of the BTEs (closed form) applying  $\sigma_p^+$  values (MeOH).

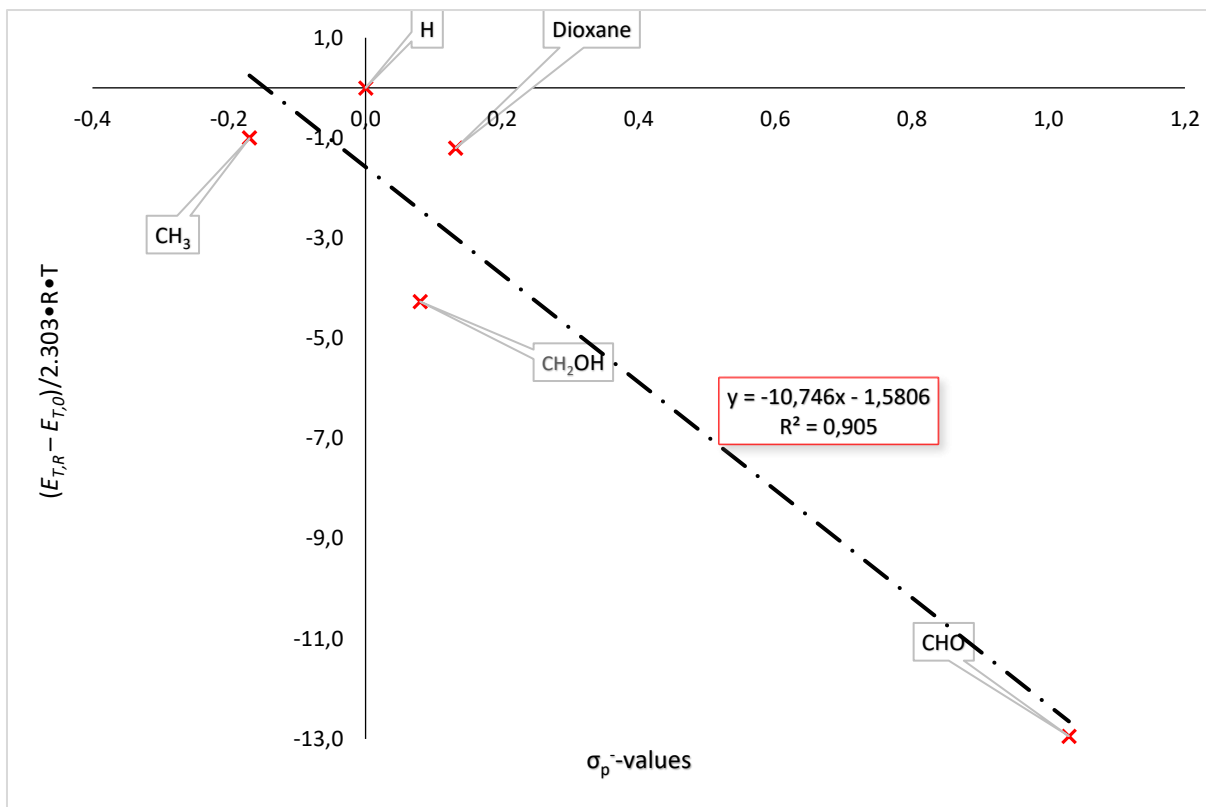


Figure S23: Hammett-Brown correlation of the BTEs (open form) applying  $\sigma_p^-$  values (MeOH).

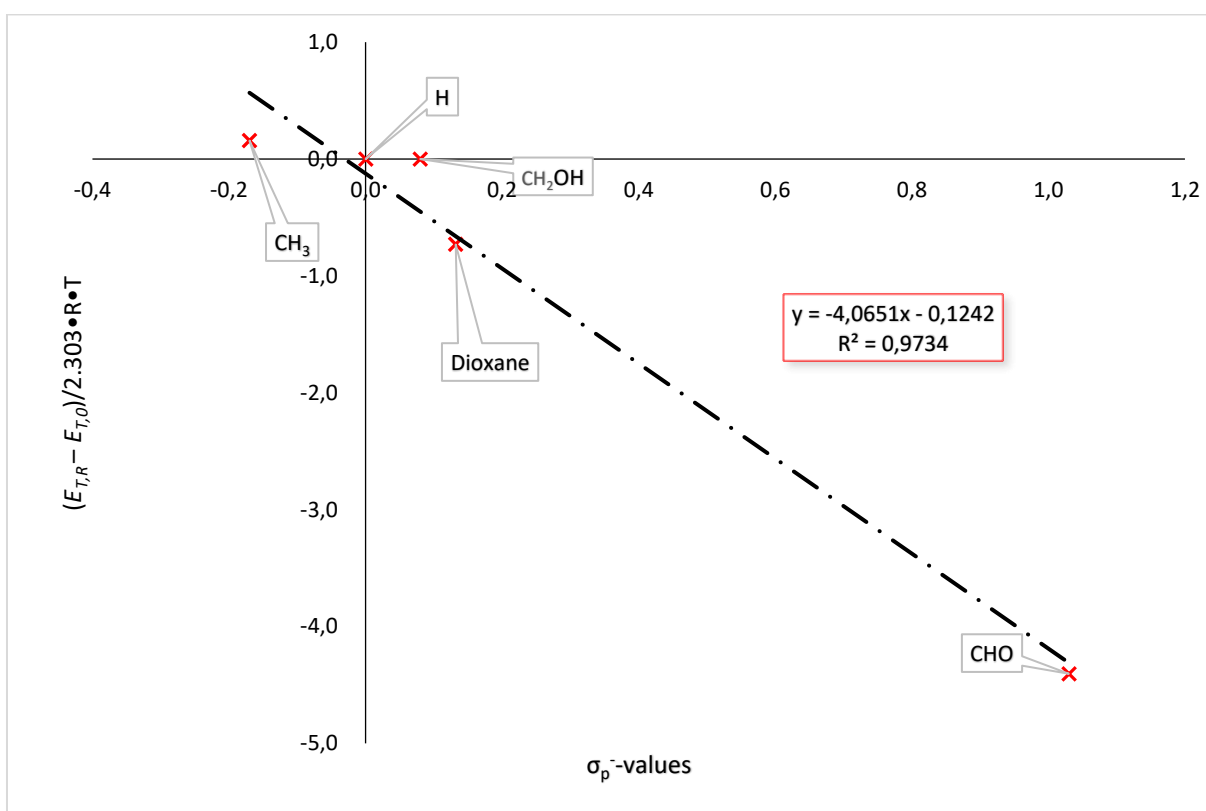


Figure S24: Hammett-Brown correlation of the BTEs (closed form) applying  $\sigma_p^-$  values (MeOH).

## $^1\text{H}$ - and $^{13}\text{C}$ NMR-spectra of 9 - 23

NMR spectroscopic measurements were performed using an Avance (400 MHz) and Avance II (600 MHz) spectrometer from Bruker. The chemical shift  $\delta$  is given in ppm. Deuterated solvents ( $\text{CDCl}_3$ ,  $\text{DMSO-d}_6$ ,  $\text{THF-d}_8$ , Deutero GmbH) were used. TopSpin 4.0.1 from Bruker was used as software to process the data and create the spectra. The samples were dried under vacuum for several days, but sometimes it was not possible to remove all solvents, so there are traces of the used solvents left, e.g. ethyl acetate or THF. The fluorinated C-Atoms of the cyclopentene unit are not always detectable, so the peaks are missing in the according spectra. Some substances proved to be unstable. Decomposition compounds are then visible in the spectra.

### REFERENCE

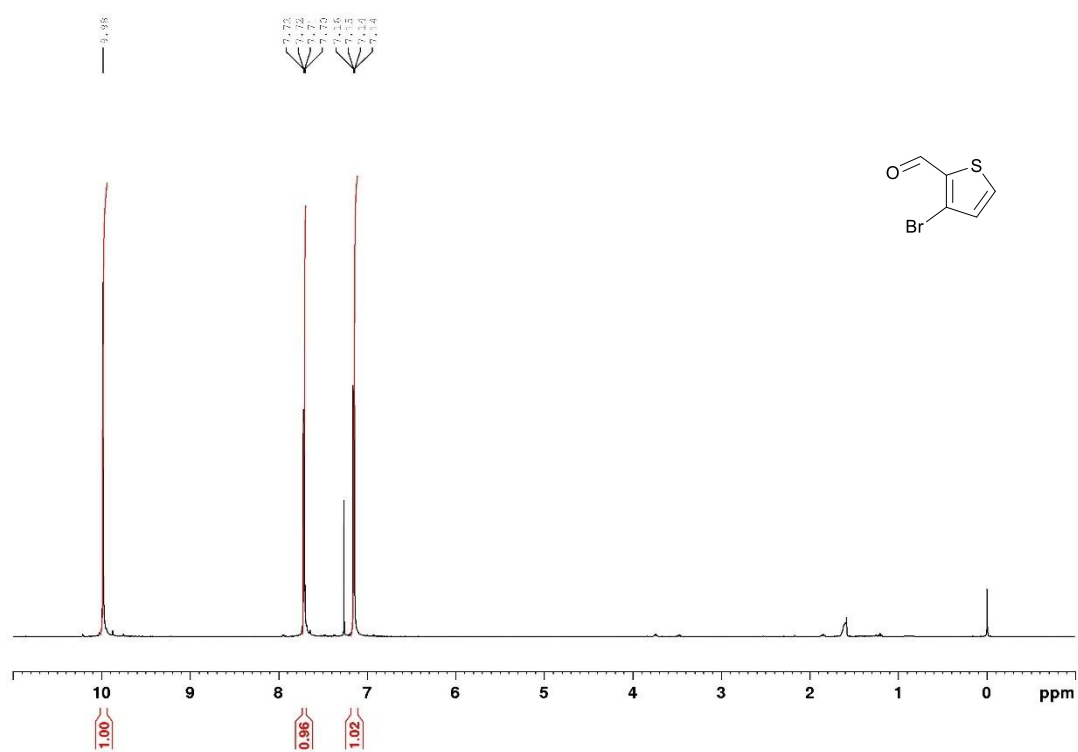


Figure S25:  $^1\text{H}$  NMR spectrum of 11a.

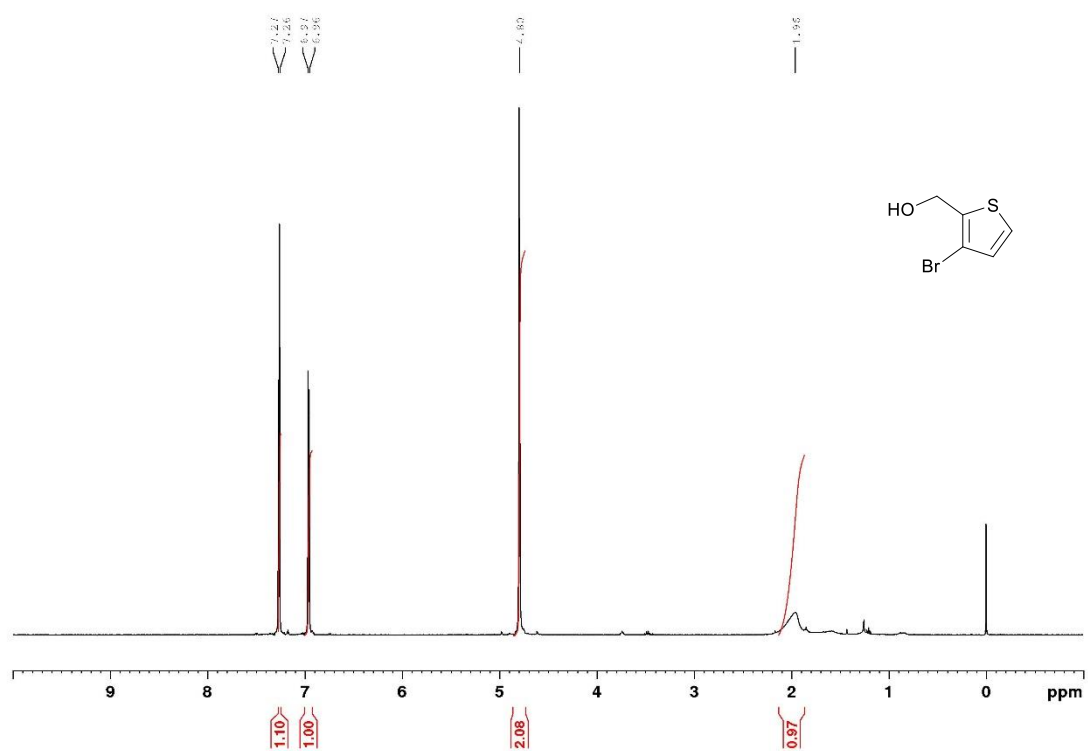


Figure S26: <sup>1</sup>H NMR spectrum of 12a.

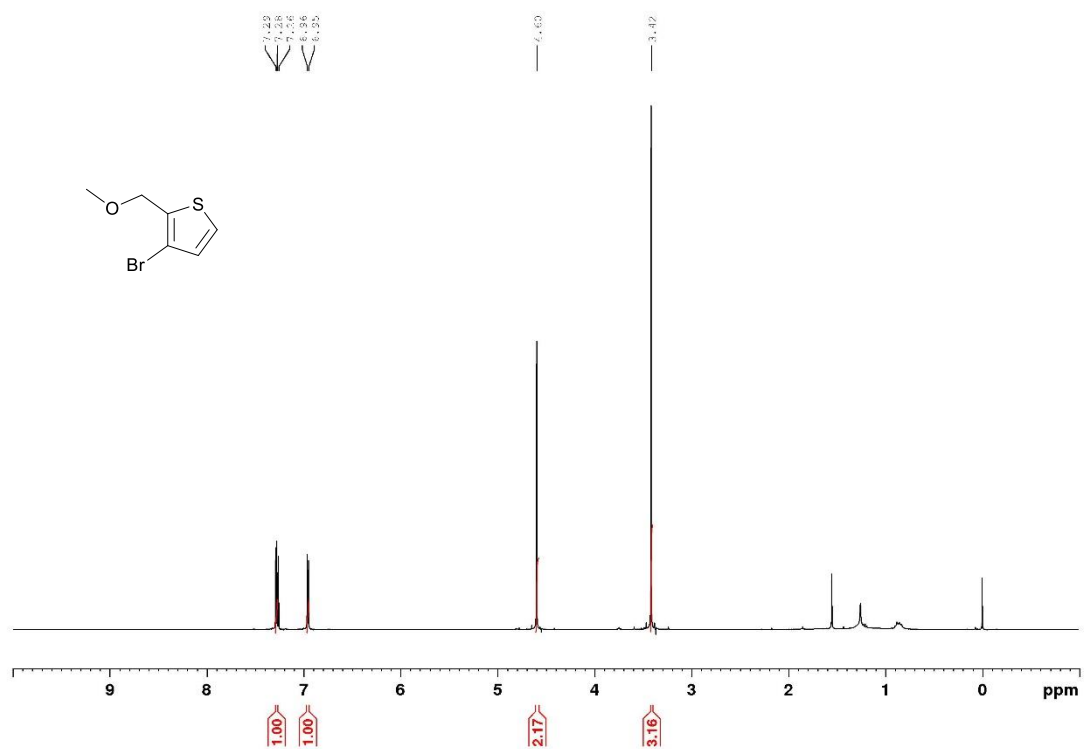


Figure S27: <sup>1</sup>H NMR spectrum of 13a.

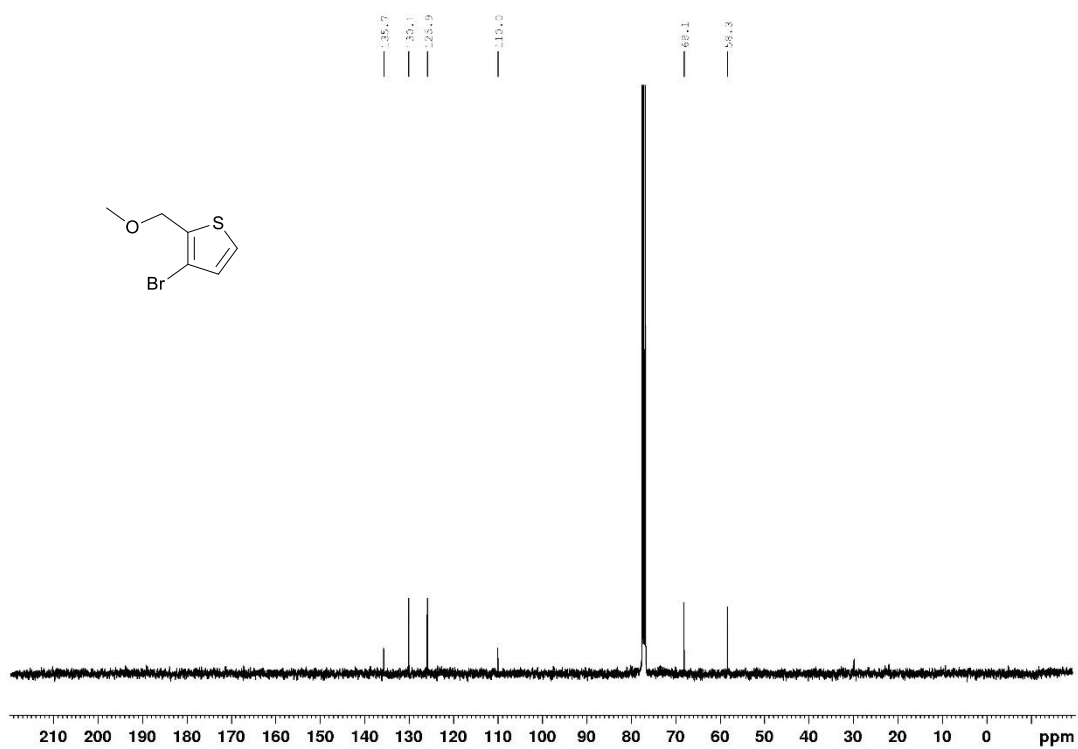


Figure S28: <sup>13</sup>C NMR spectrum of 13a.

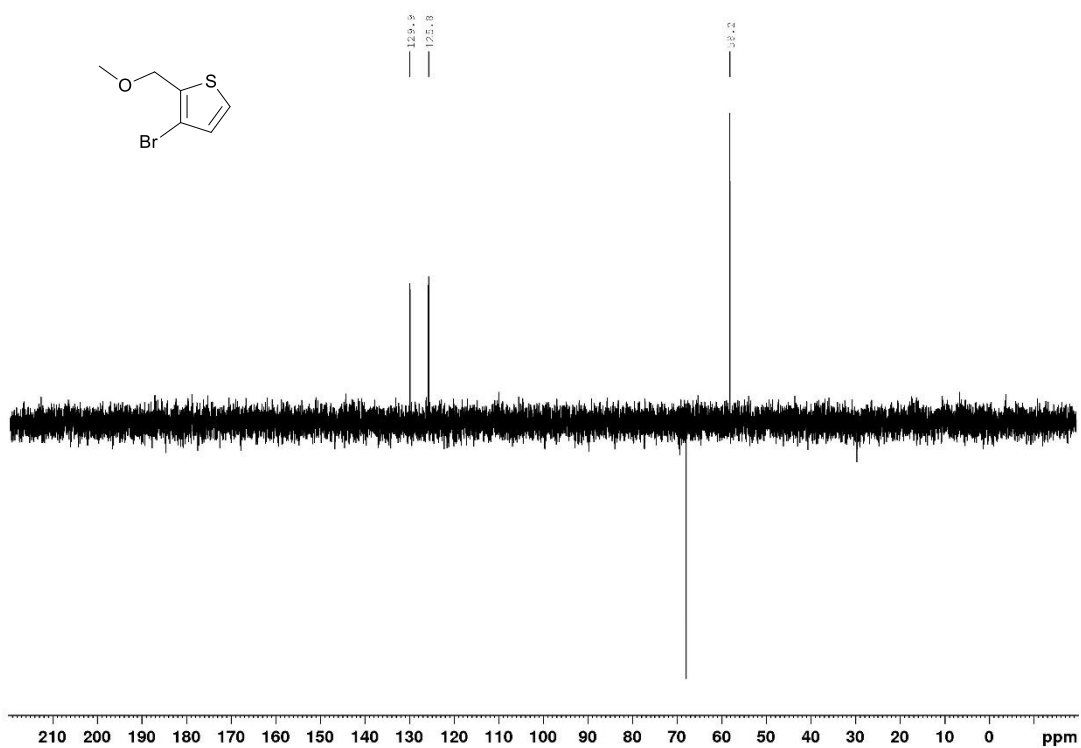


Figure S29: DEPT-NMR spectrum of 13a.



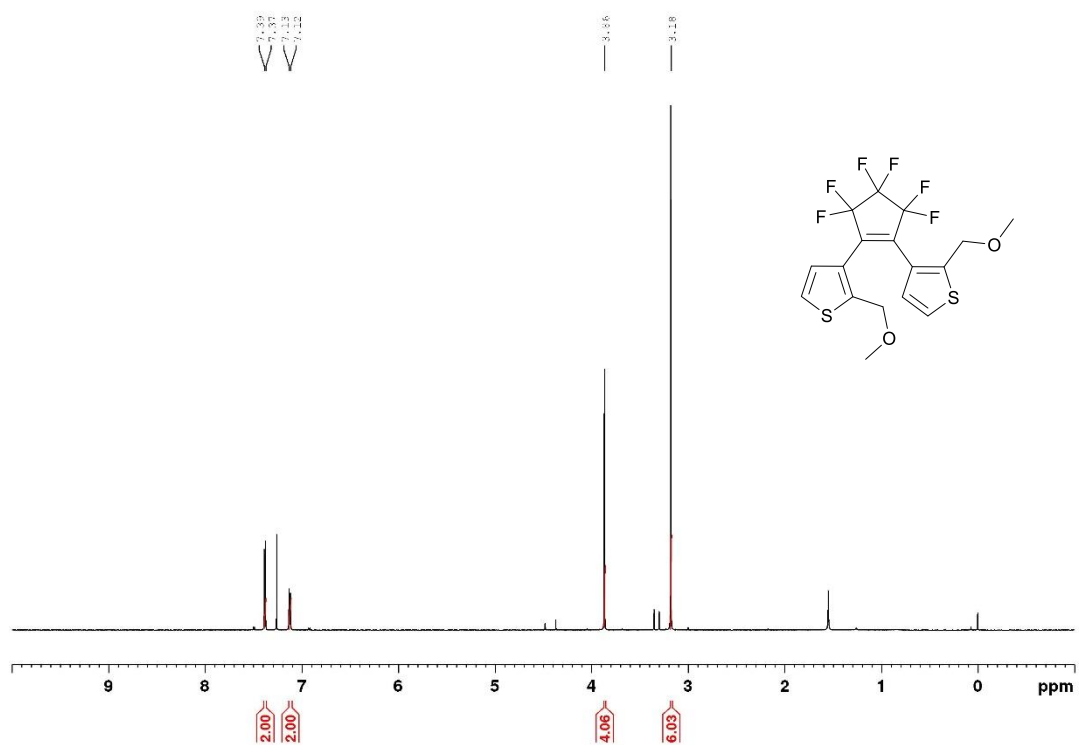


Figure S30: <sup>1</sup>H NMR spectrum of **15a**.

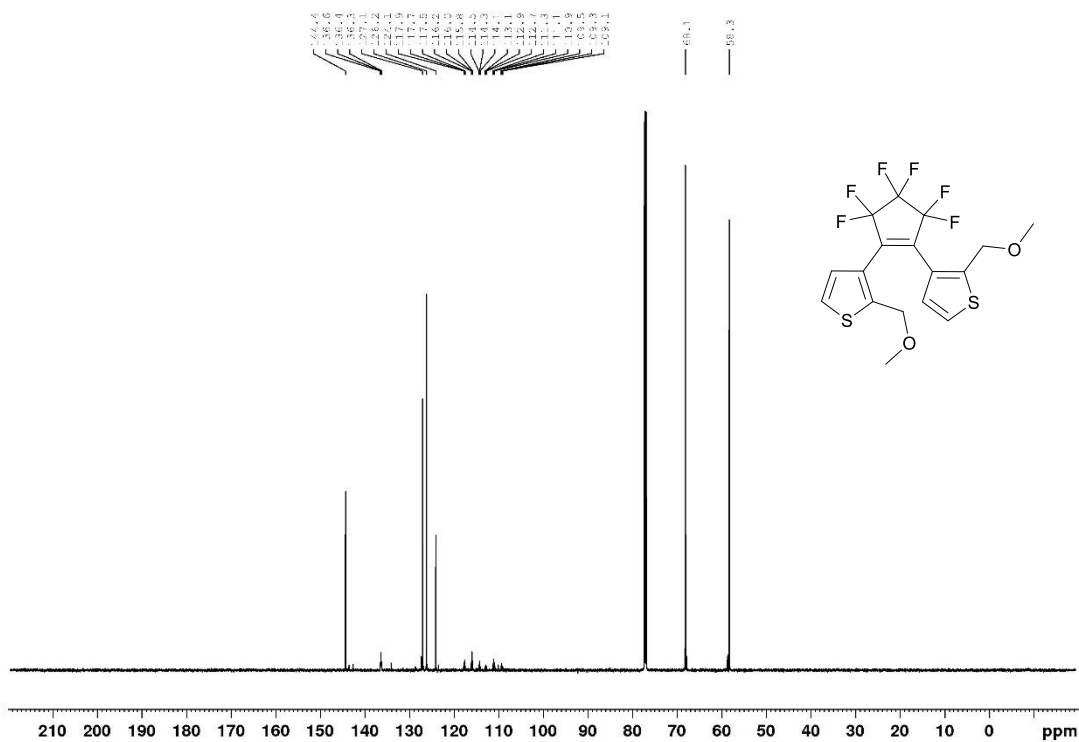


Figure S31: <sup>13</sup>C NMR spectrum of **15a**.

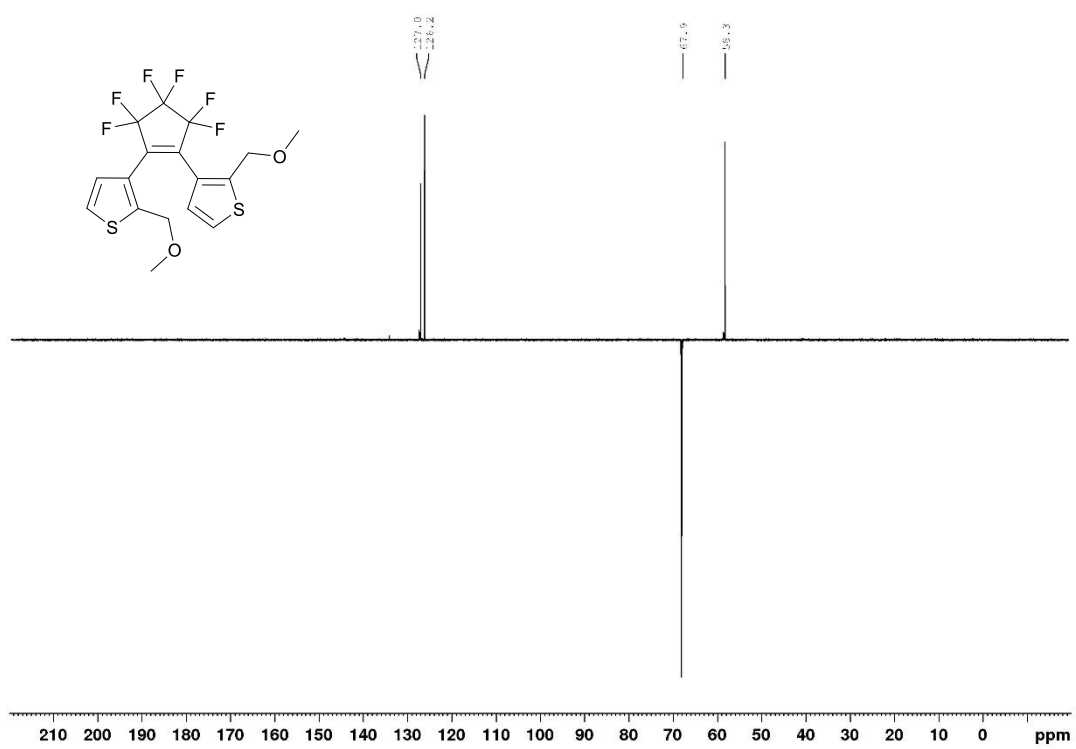


Figure S32: DEPT-NMR spectrum of **15a**.

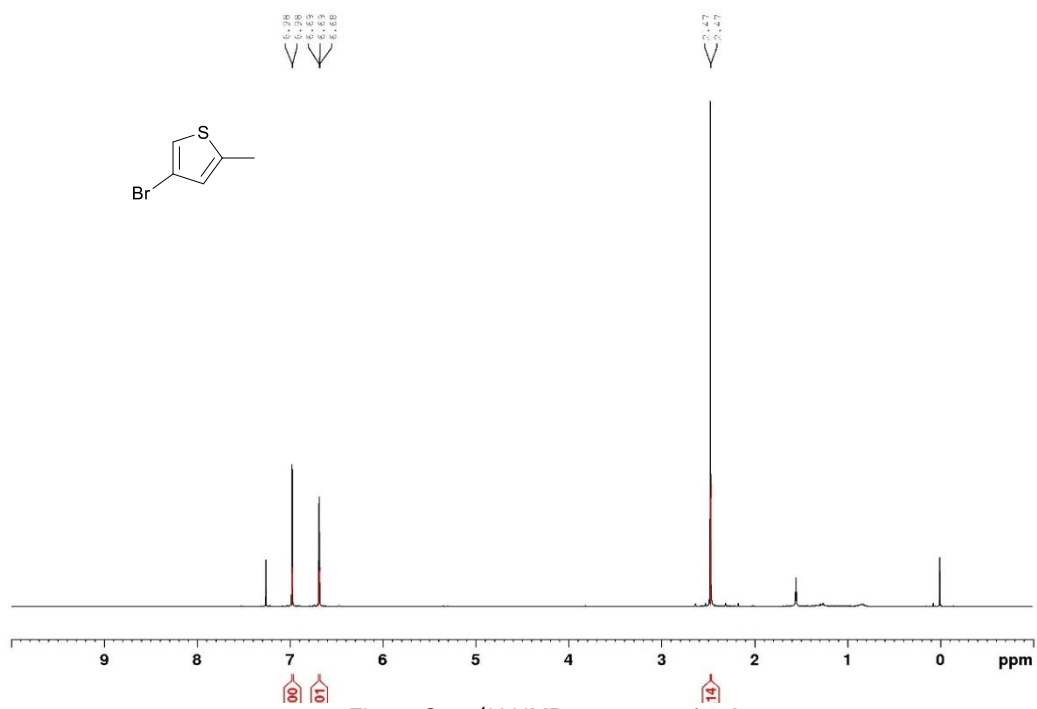


Figure S33: <sup>1</sup>H NMR spectrum of 10b.

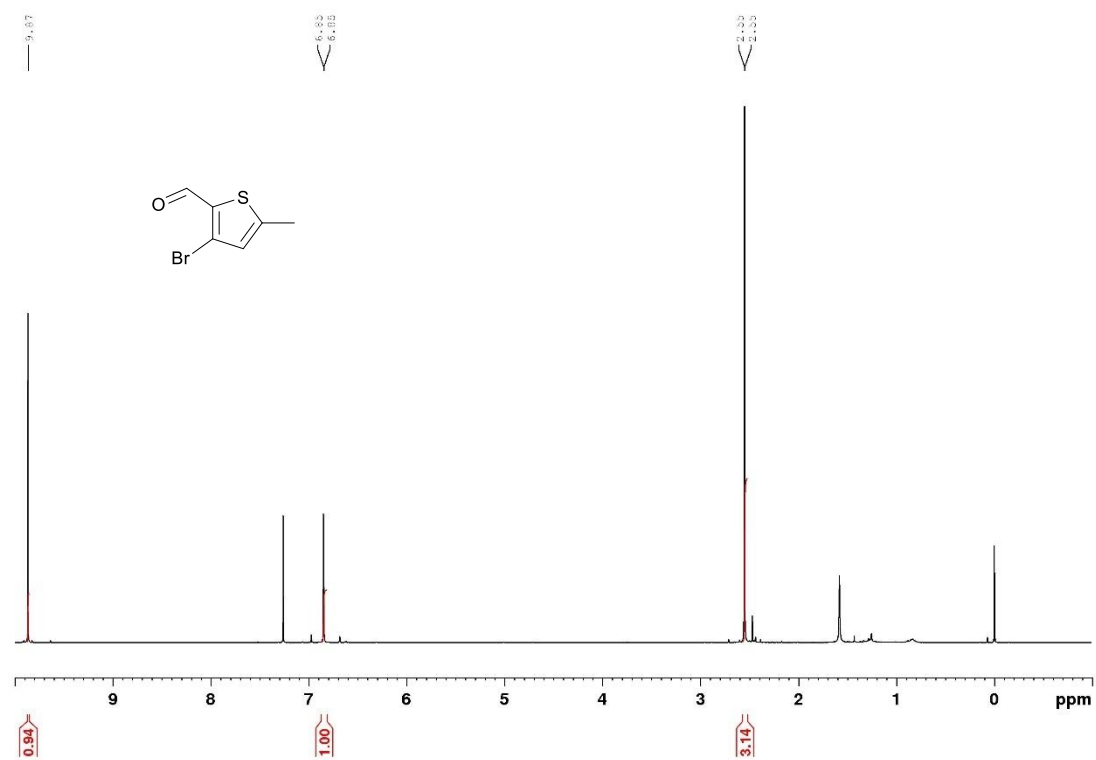


Figure S34: <sup>1</sup>H NMR spectrum of 11b.

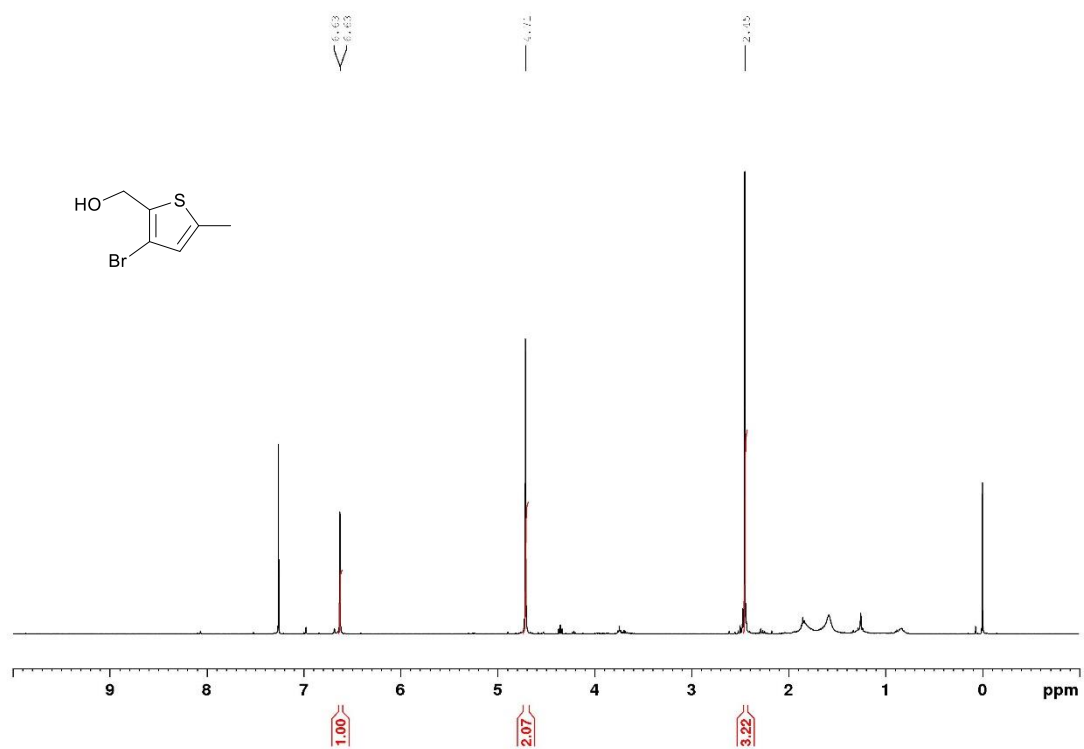


Figure S35: <sup>1</sup>H NMR-spectrum of **12b**.

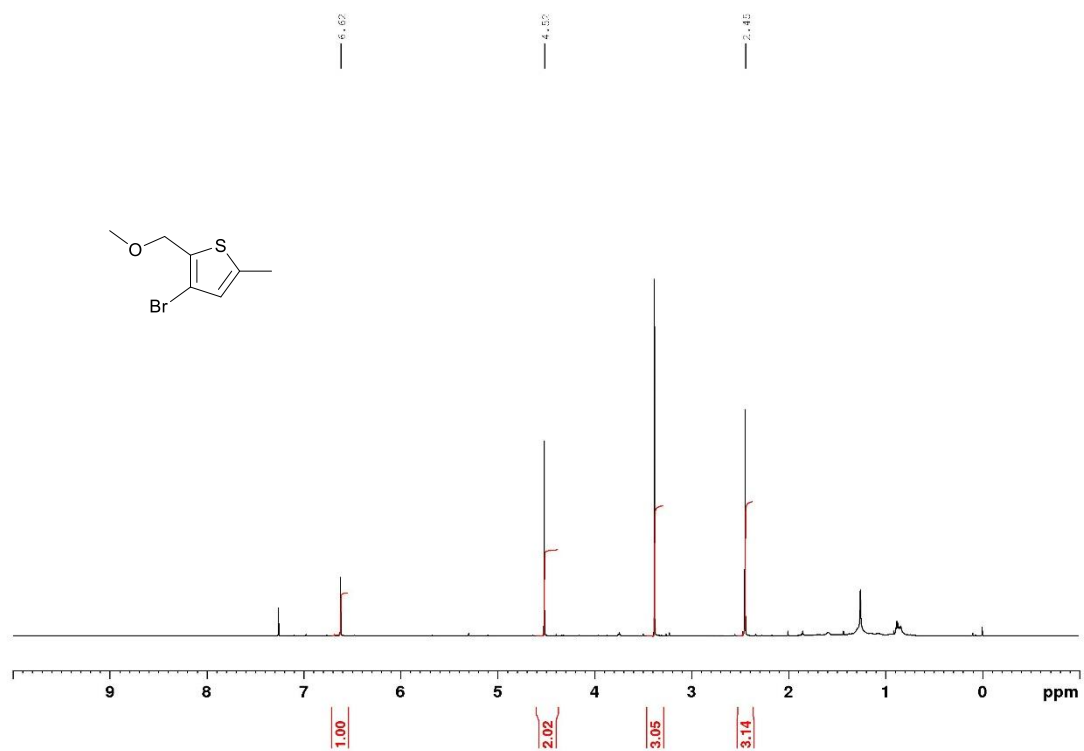


Figure S36: <sup>1</sup>H NMR-spectrum of **13b**.

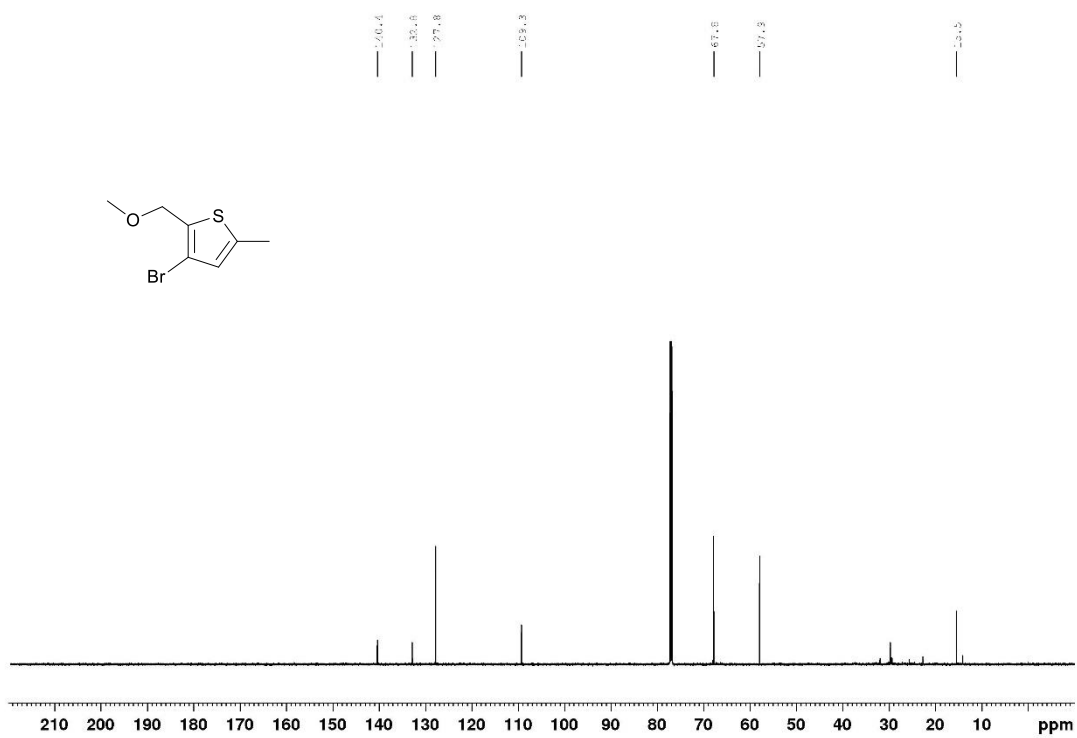


Figure S37:  $^{13}\text{C}$  NMR spectrum of **13b**.

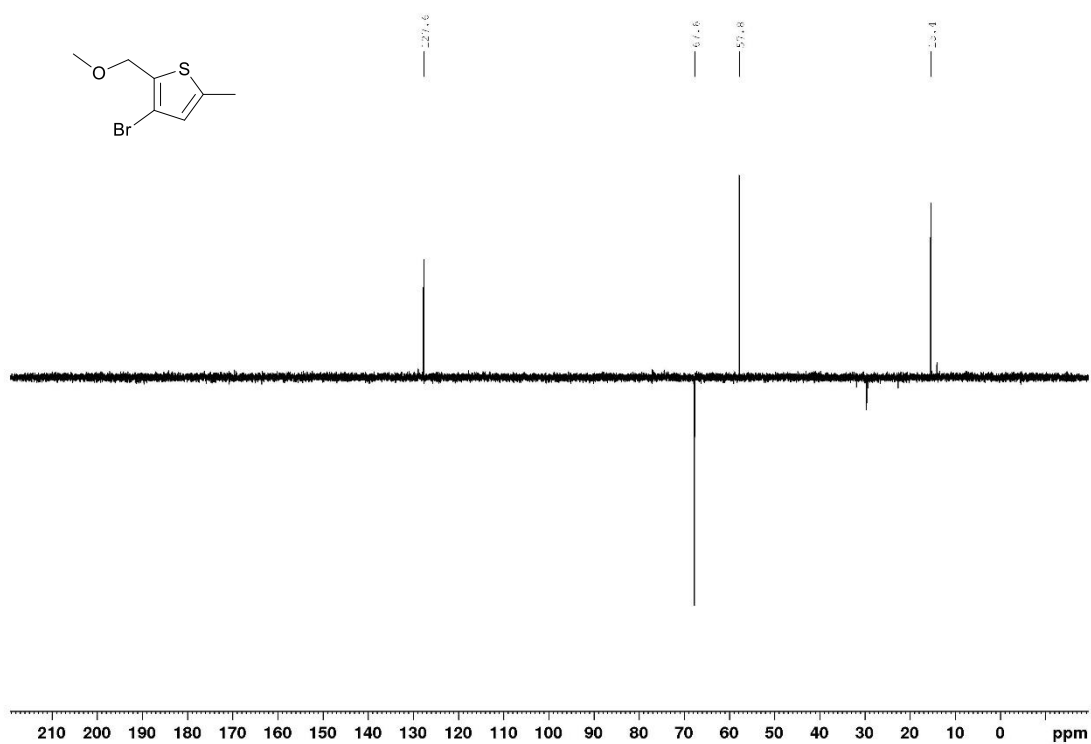


Figure S38: DEPT of **13b**.

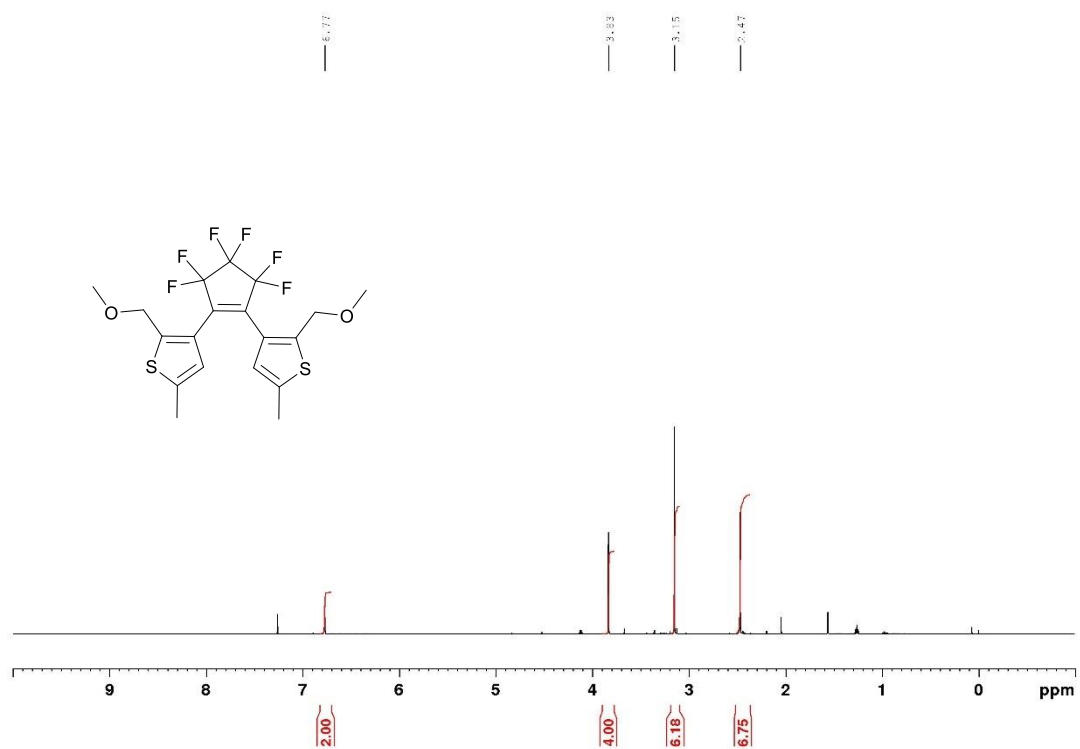


Figure S39: <sup>1</sup>H NMR-spectrum of **15b**.

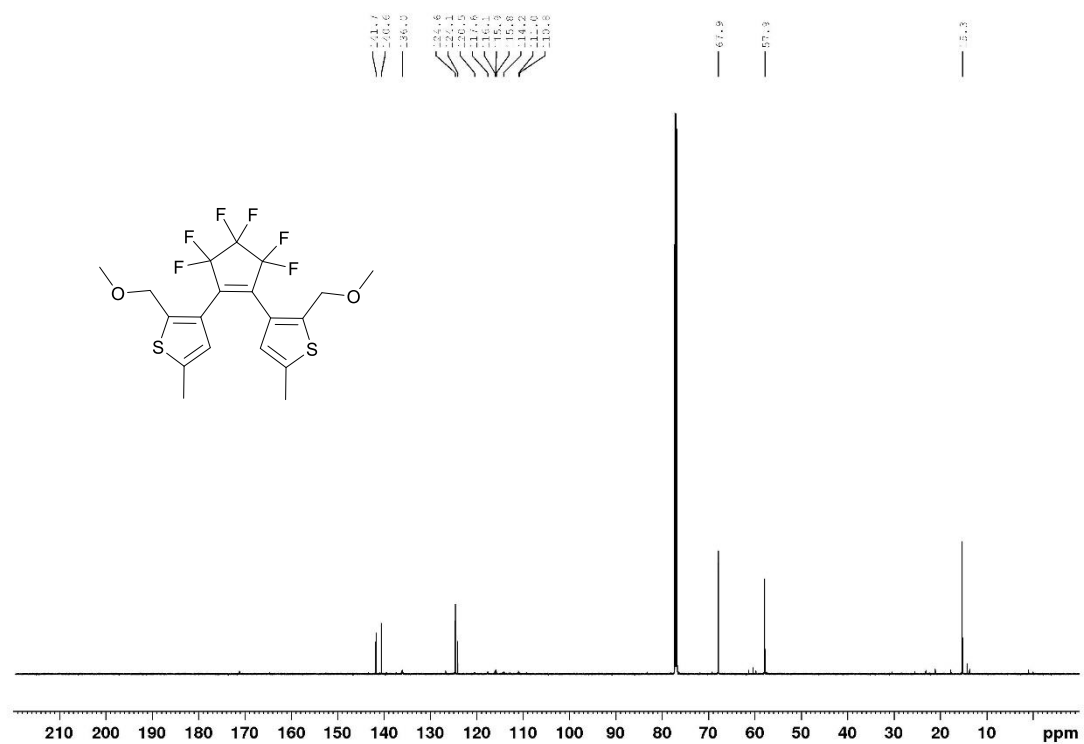


Figure S40: <sup>13</sup>C NMR-spectrum of **15b**.

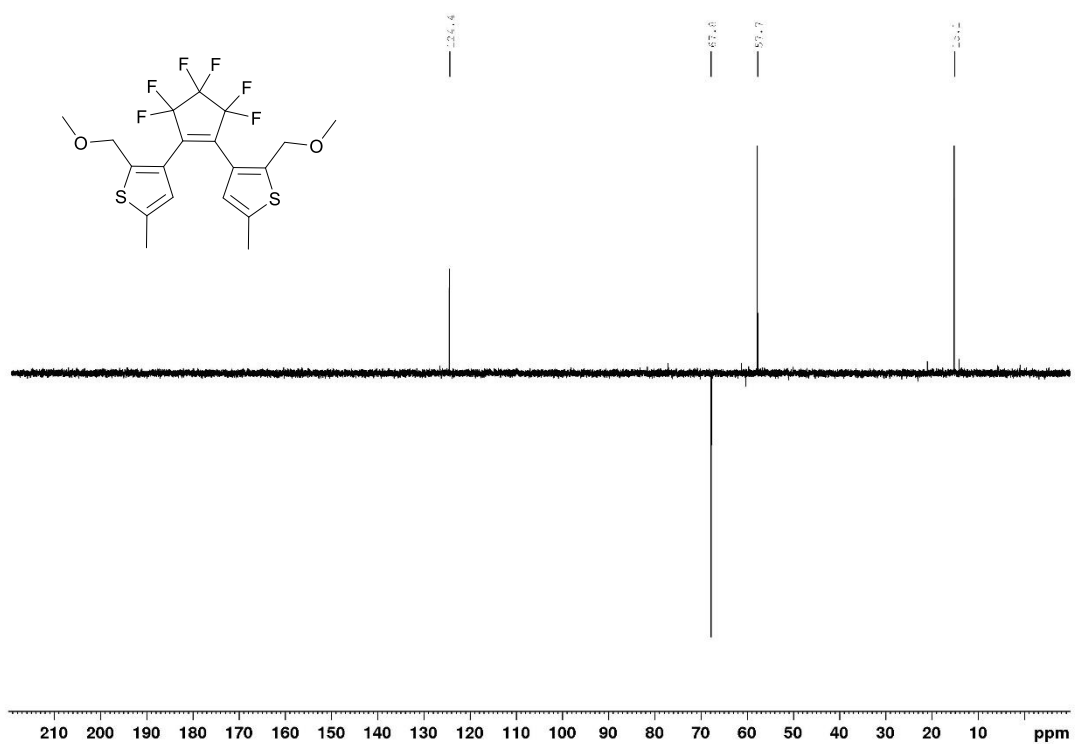


Figure S41: DEPT of **15b**.







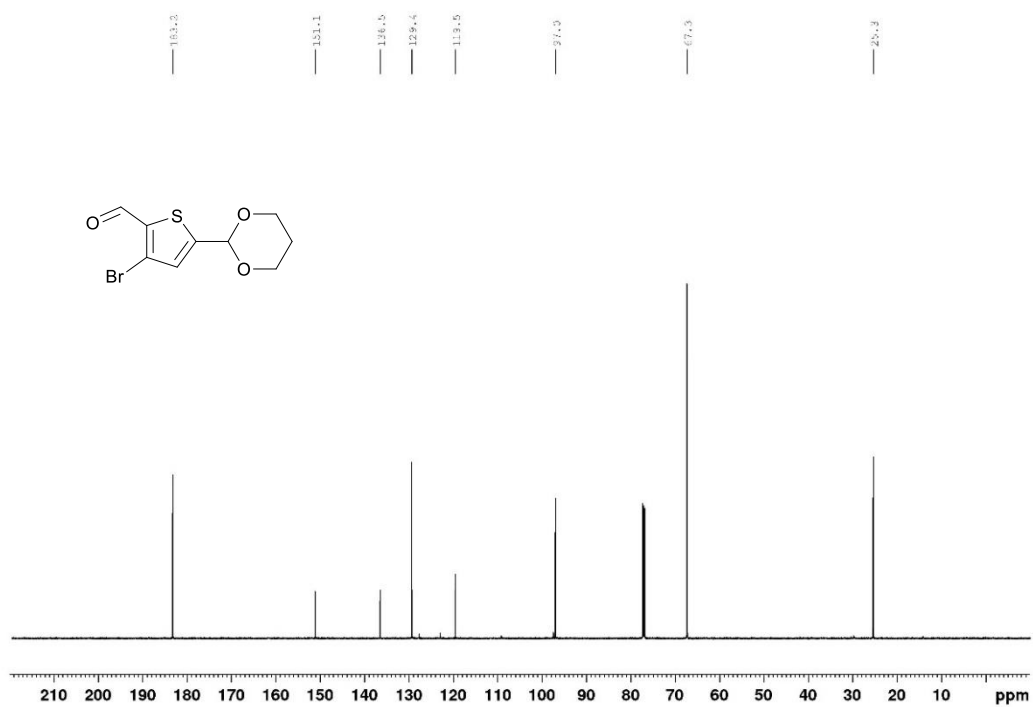


Figure S46:  $^{13}\text{C}$  NMR spectrum of **11c**.



Figure S47: DEPT-NMR spectrum of **11c**.



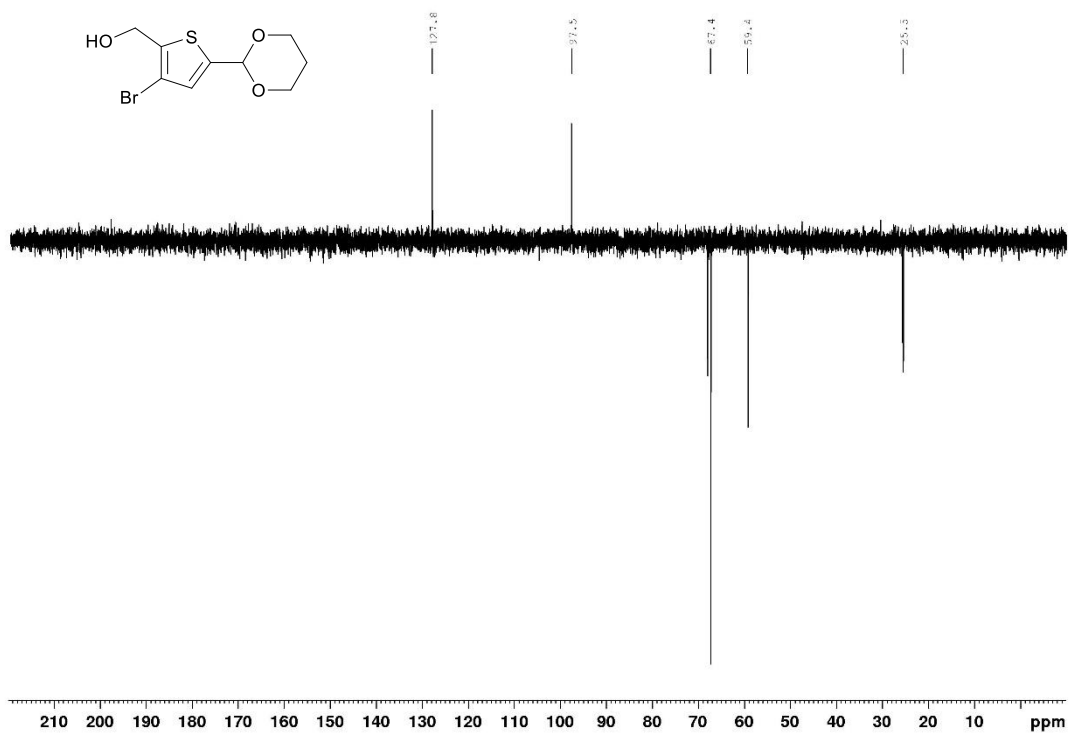


Figure S50: DEPT-NMR spectrum of **12c**.

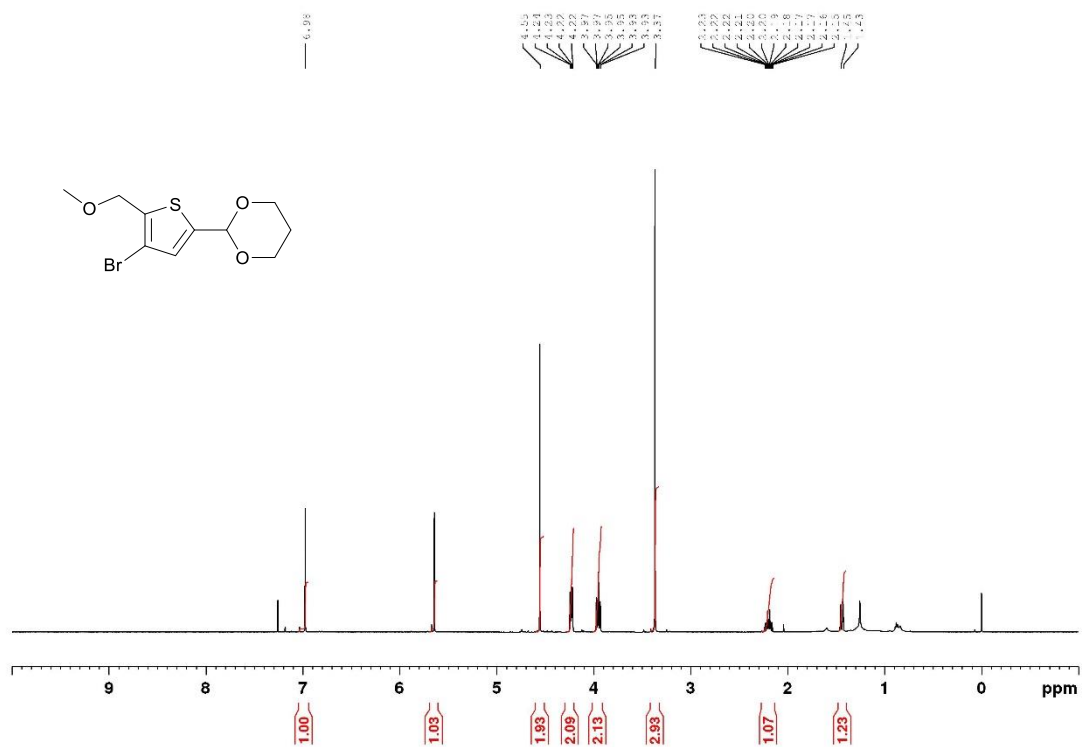


Figure S51: <sup>1</sup>H NMR spectrum of **13c**.

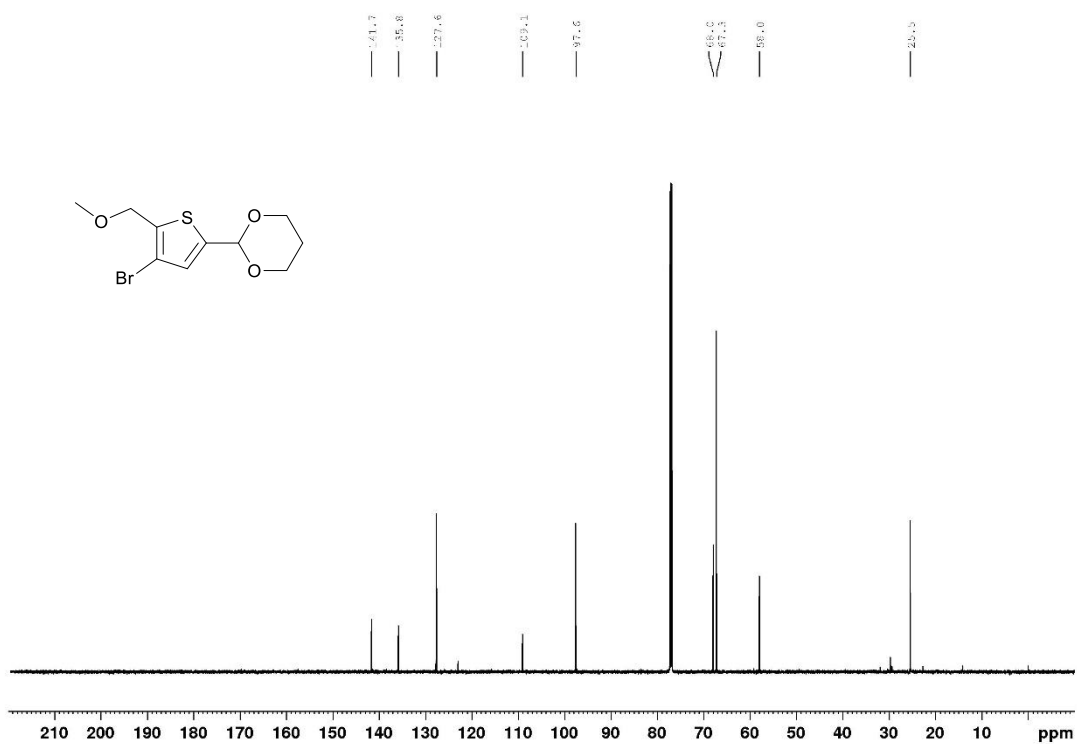


Figure S52:  $^{13}\text{C}$  NMR spectrum of **13c**.

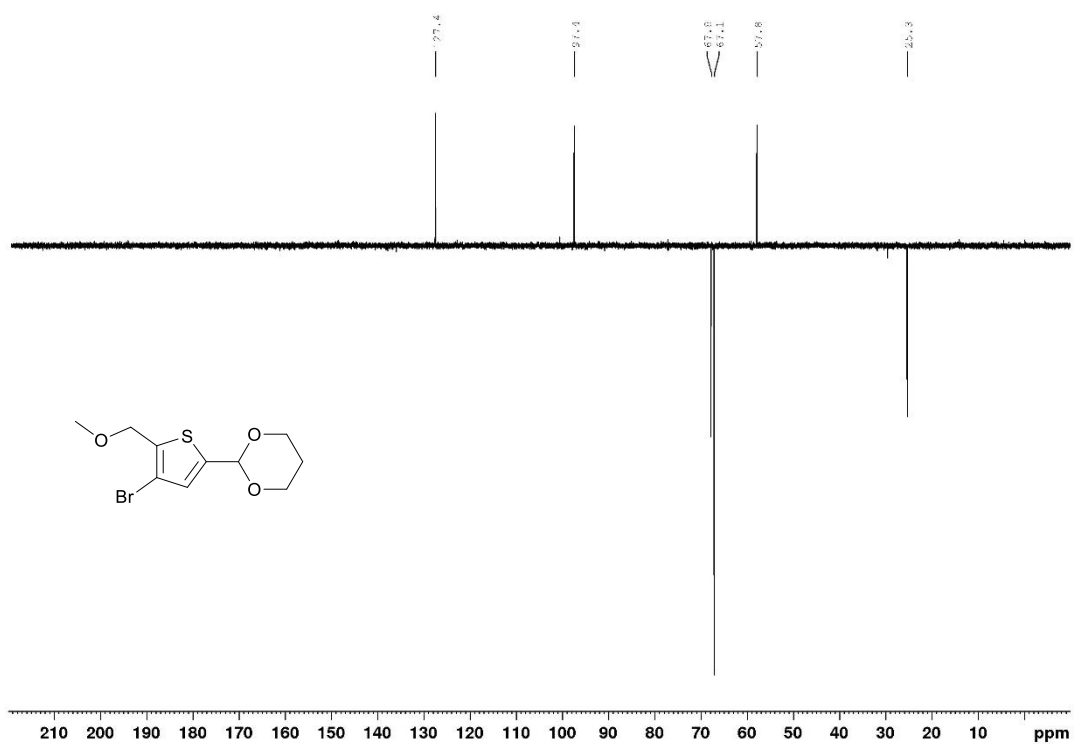


Figure S53: DEPT-NMR spectrum of **13c**.

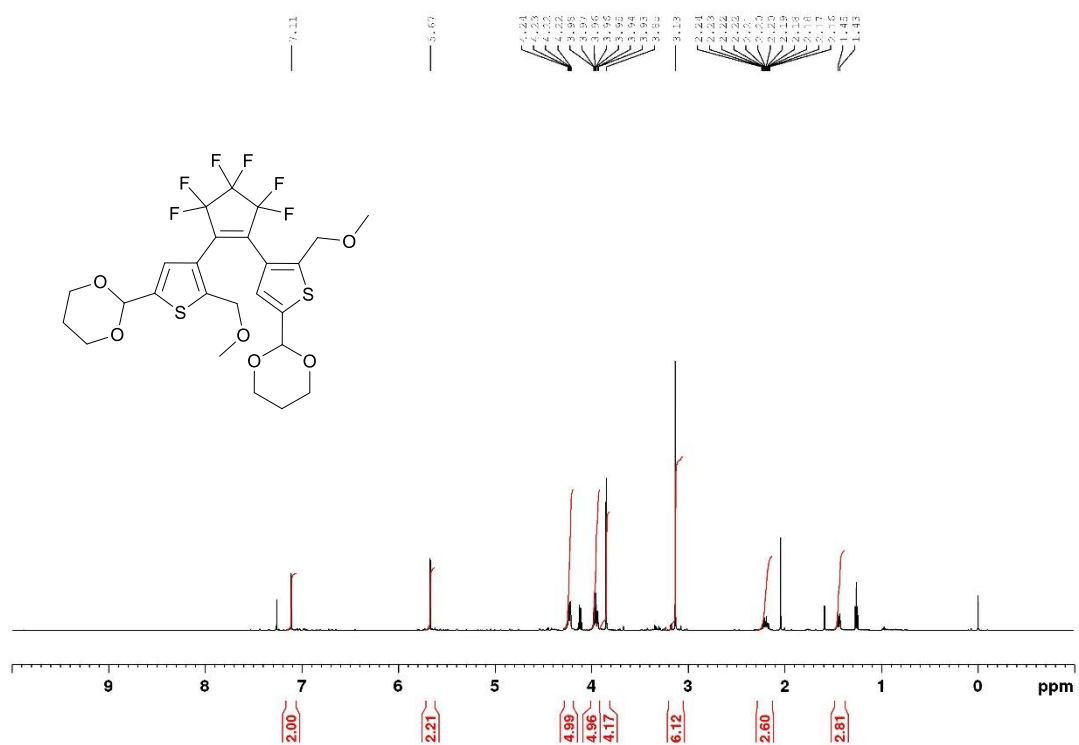


Figure S54:  $^1\text{H}$ NMR spectrum of **15c**.

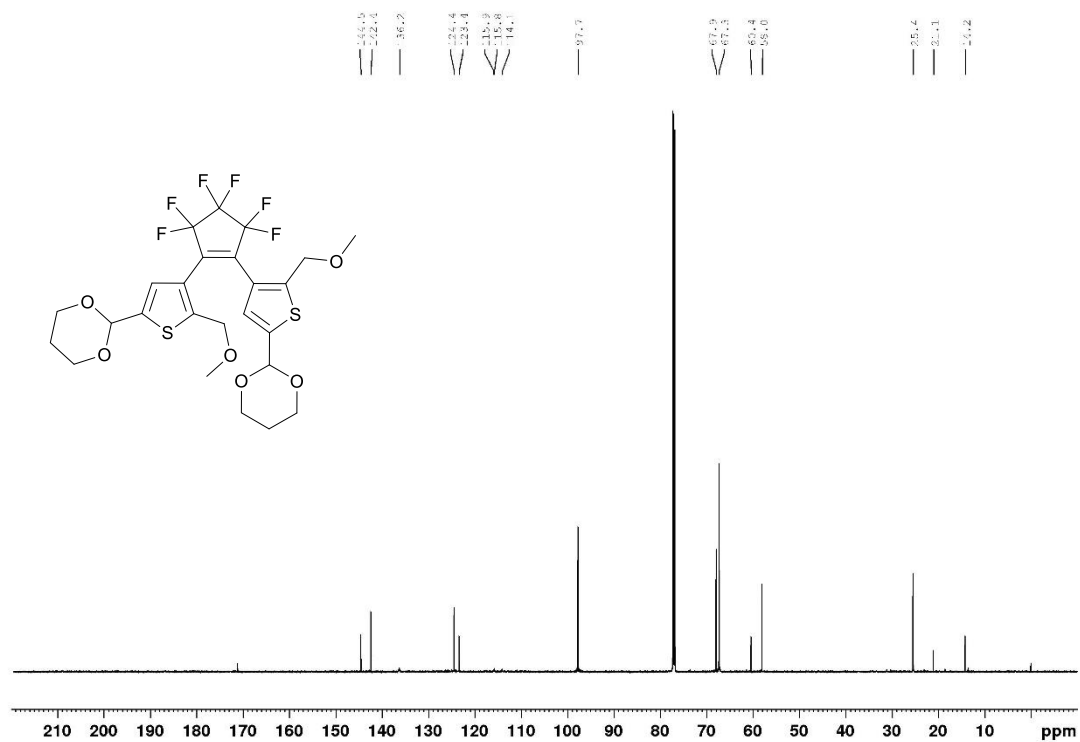


Figure S55:  $^{13}\text{C}$  NMR spectrum of **15c**.

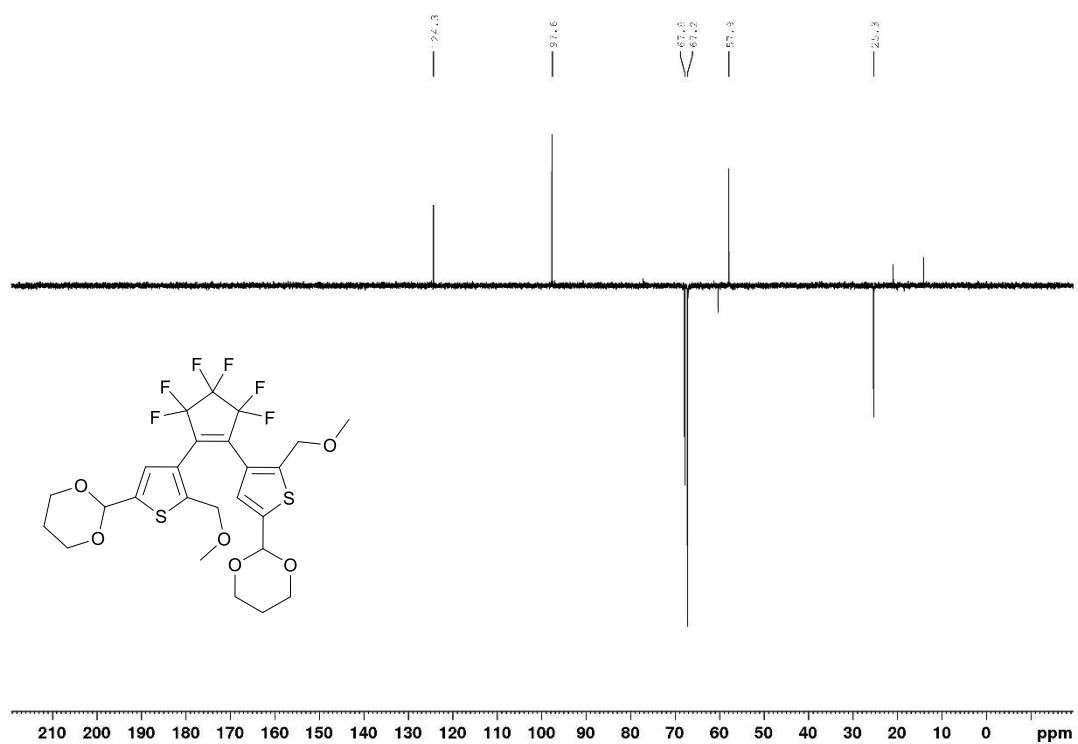


Figure S56: DEPT-NMR spectrum of **15c**.

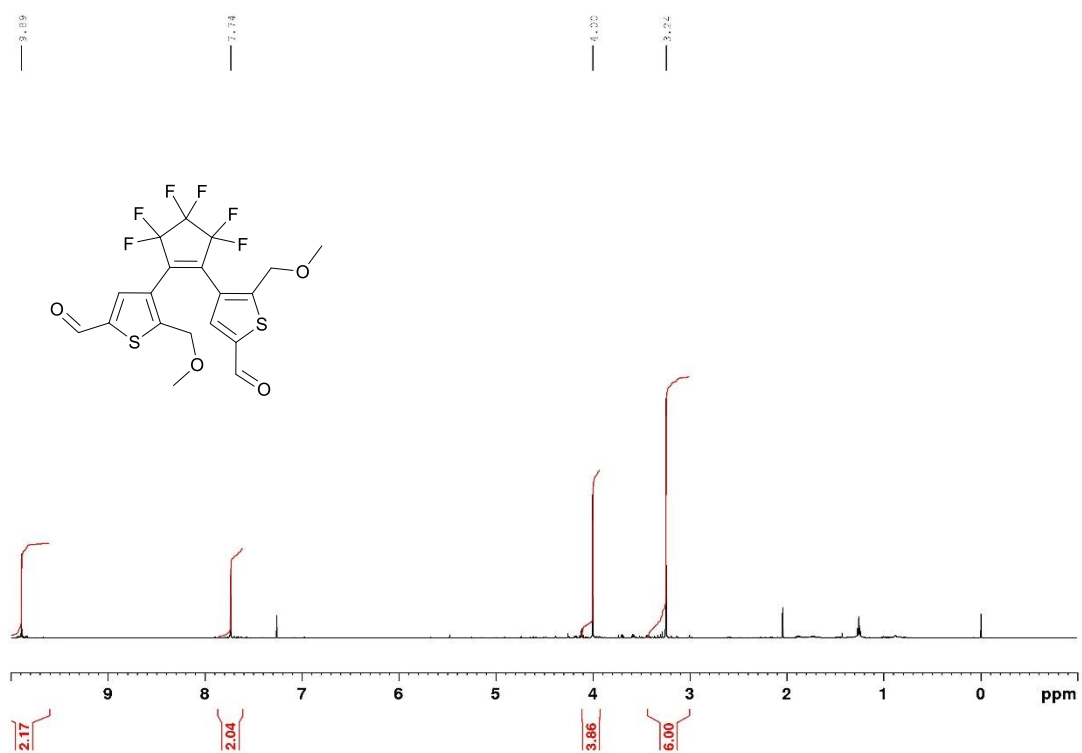


Figure S57:  $^1\text{H}$  NMR spectrum of **16**.





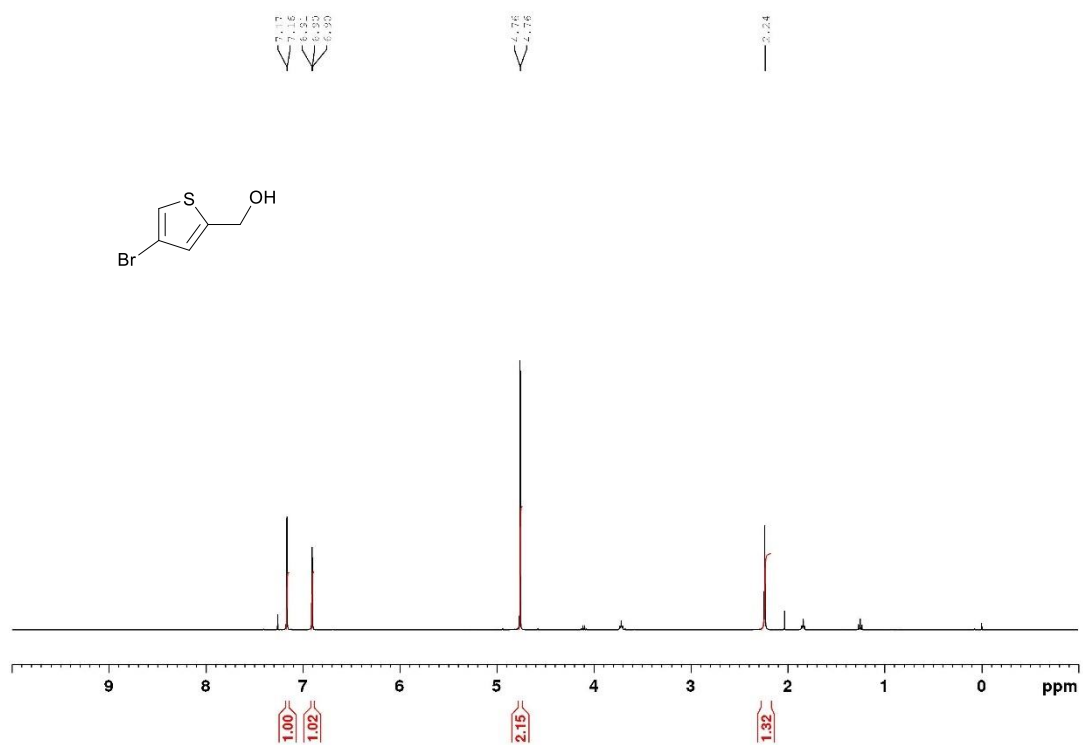


Figure S60: <sup>1</sup>H NMR spectrum of **17**.

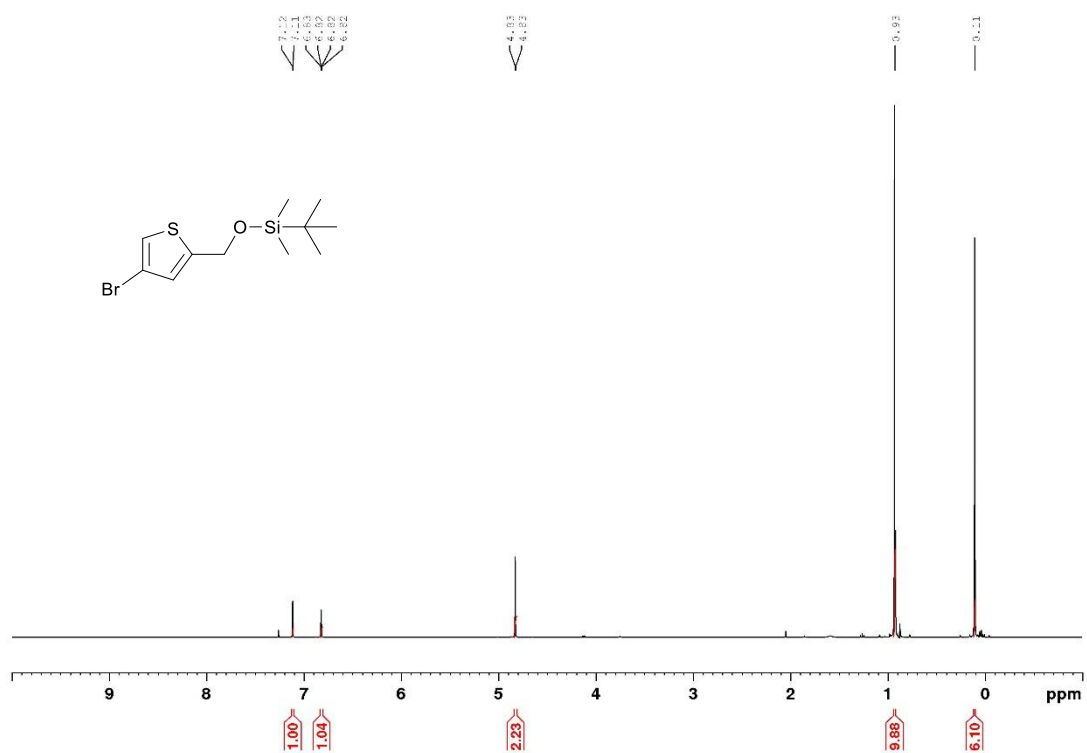


Figure S61: <sup>1</sup>H NMR spectrum of **18**.

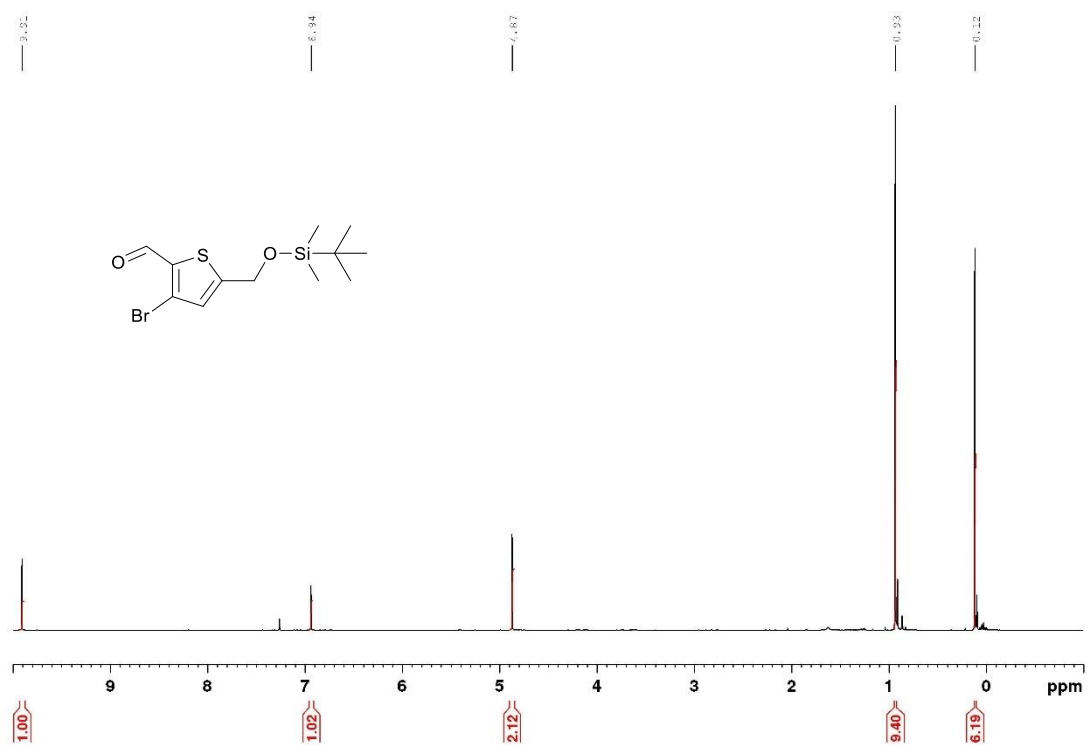


Figure S62: <sup>1</sup>H NMR spectrum of **19**.

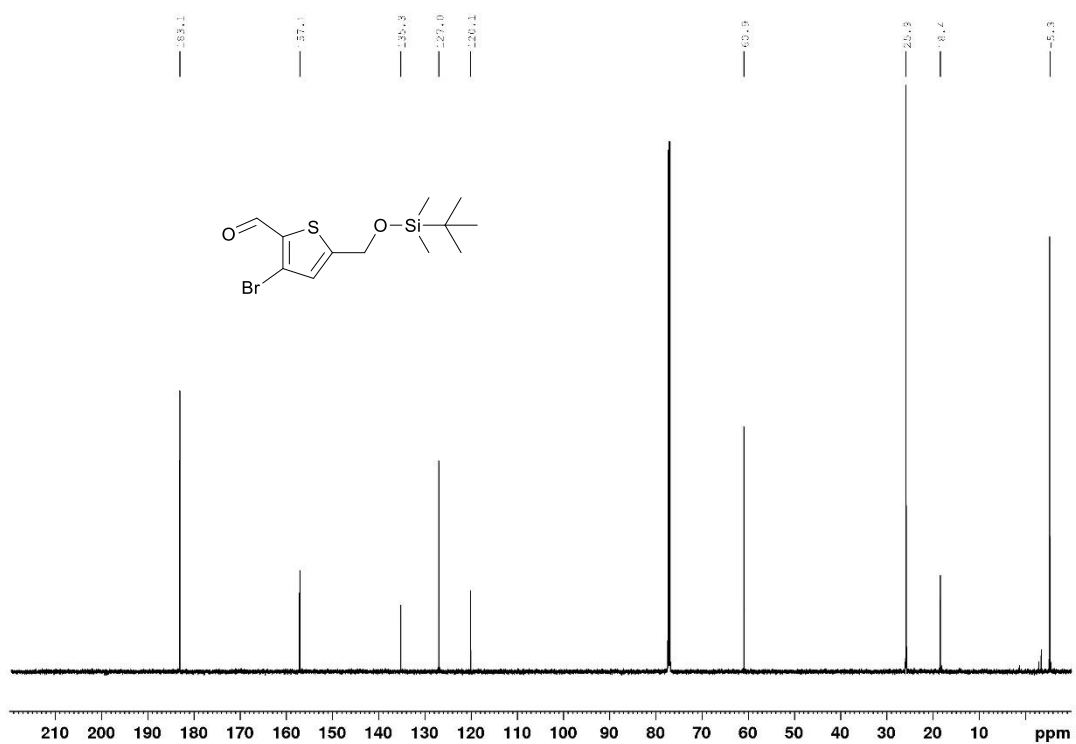


Figure S63: <sup>13</sup>C NMR spectrum of **19**.

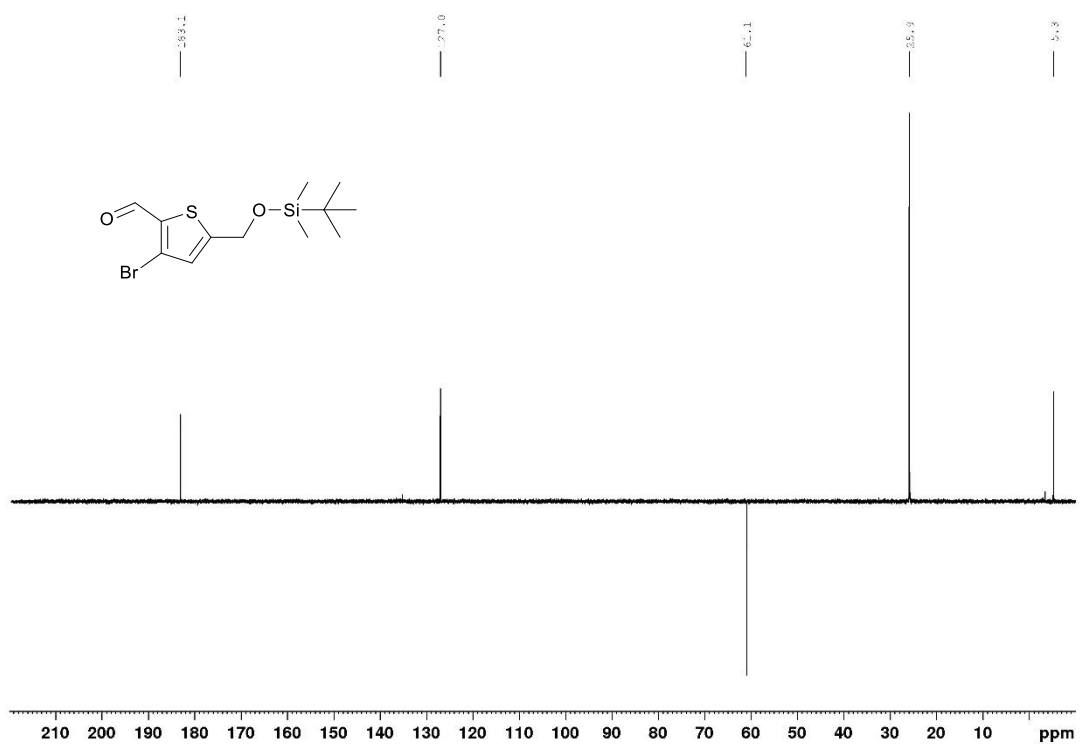


Figure S64: DEPT-NMR spectrum of **19**.

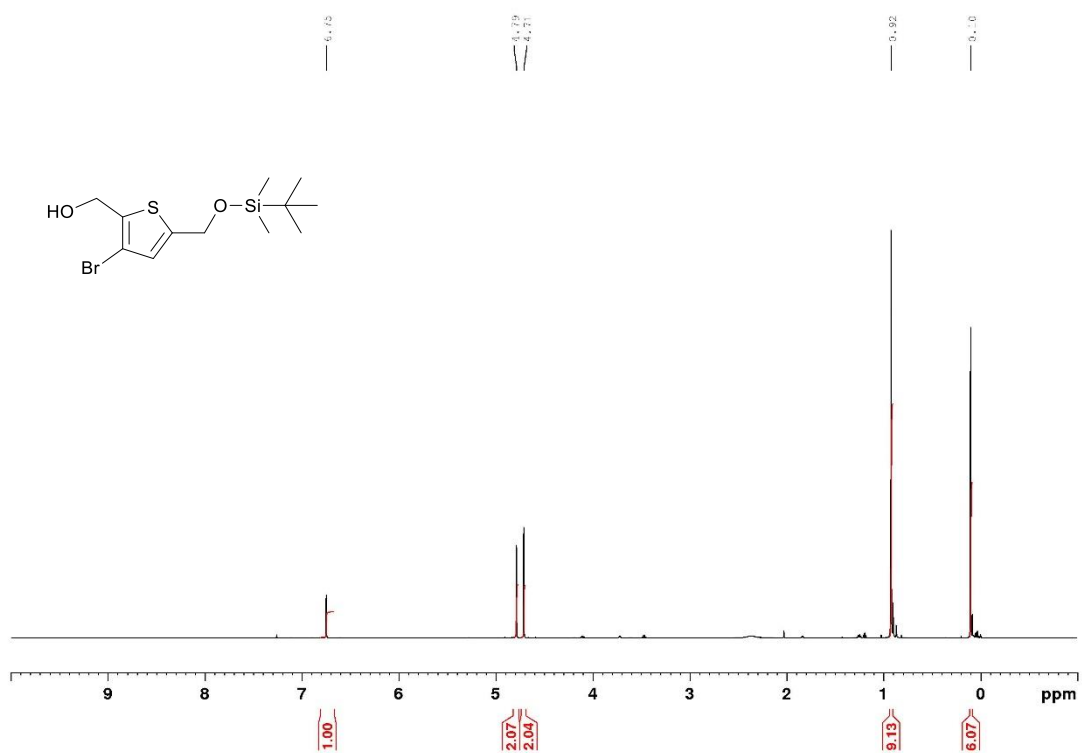


Figure S65:  $^1\text{H}$  NMR spectrum of **20**.

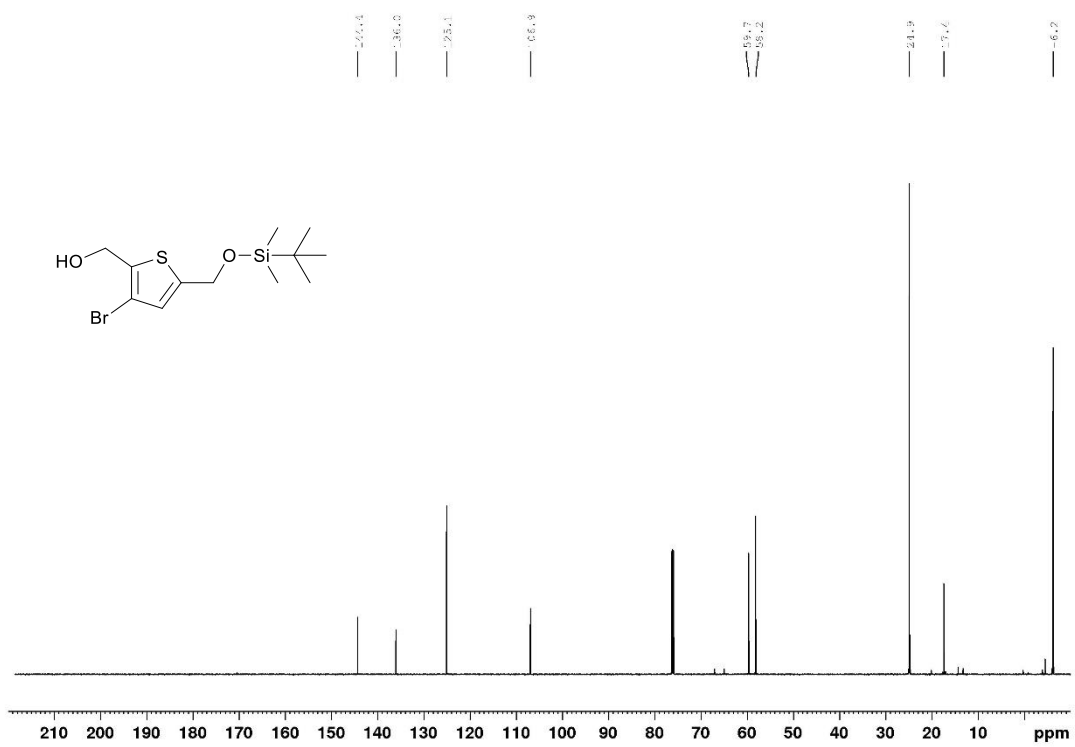


Figure S66:  $^{13}\text{C}$  NMR spectrum of **20**.

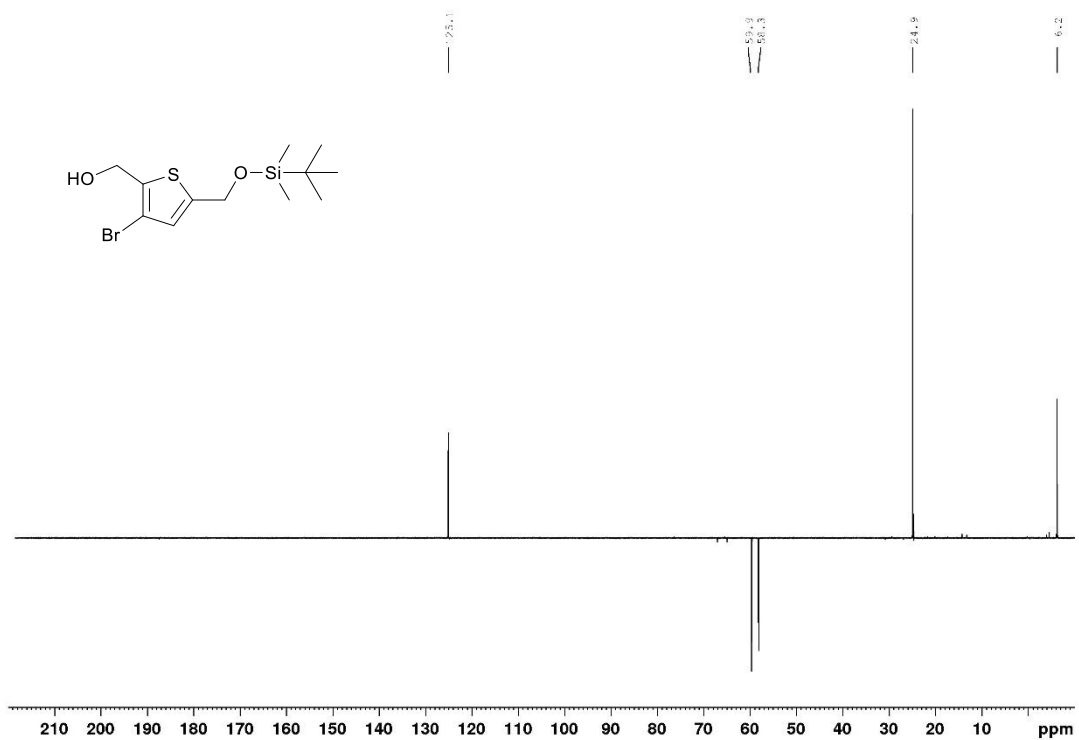


Figure S67: DEPT-NMR spectrum of **20**.

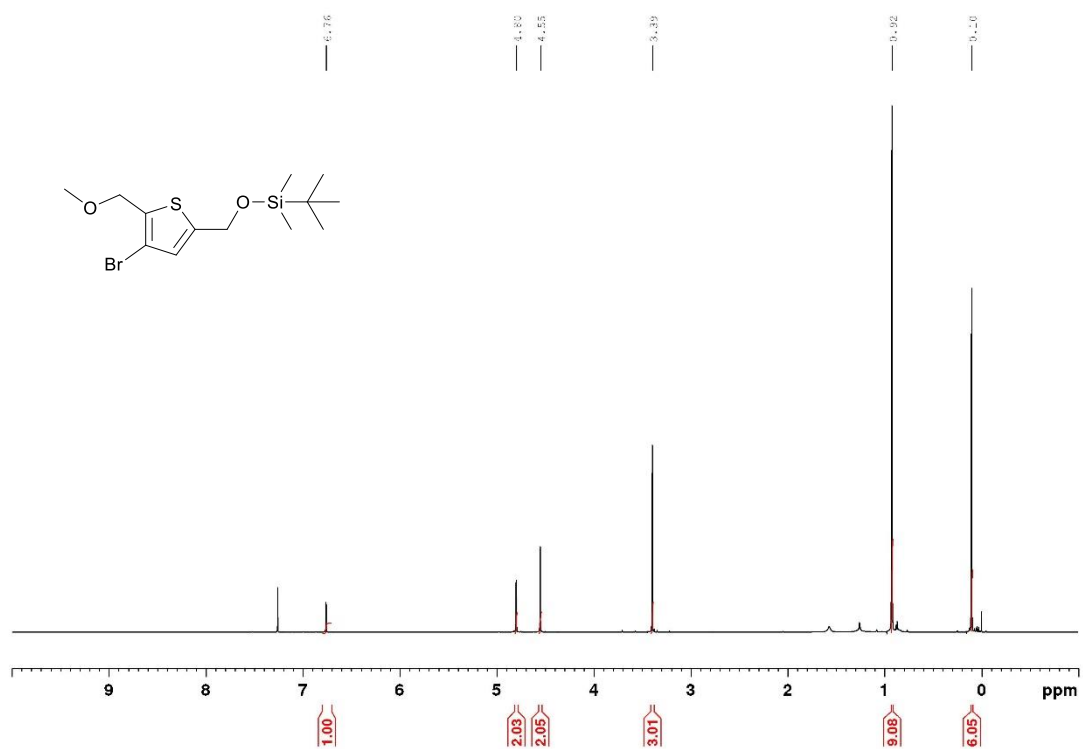


Figure S68: <sup>1</sup>H NMR spectrum of **21**.

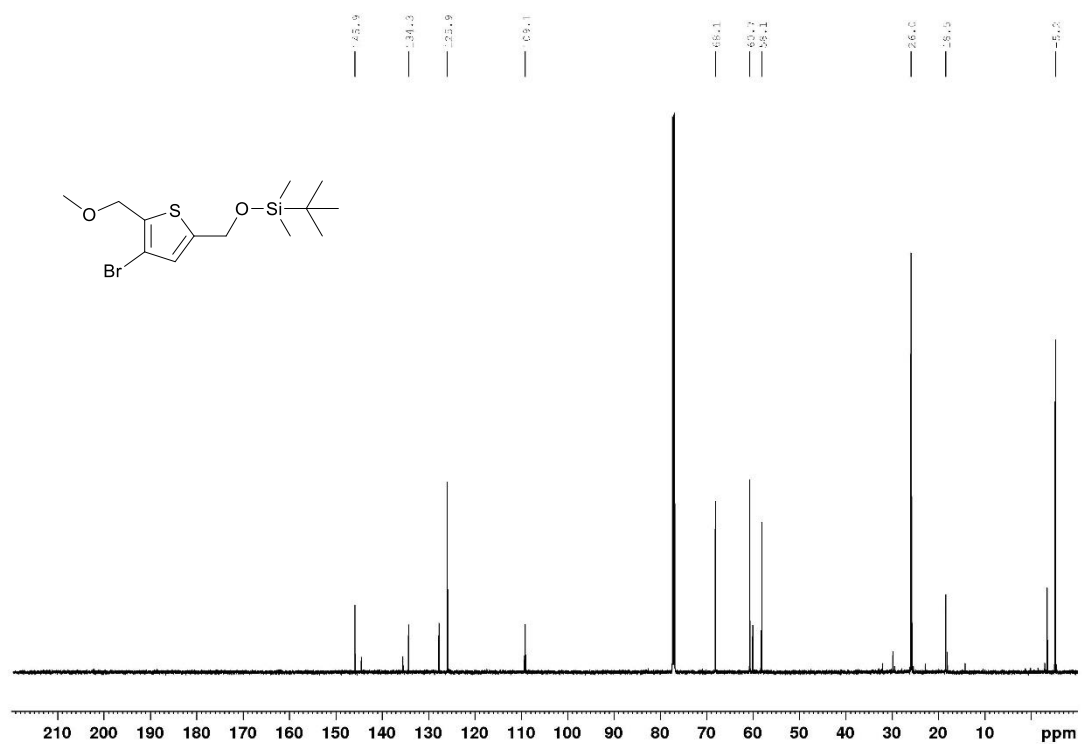


Figure S69: <sup>13</sup>C NMR spectrum of **21**.

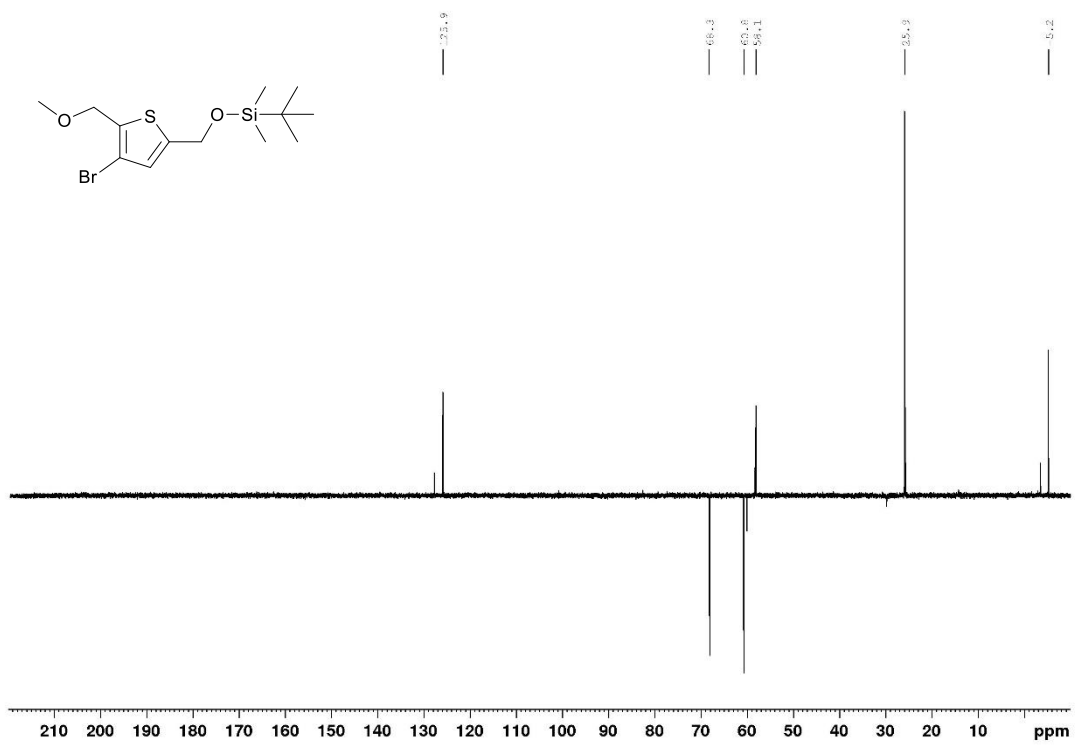


Figure S70: DEPT-NMR spectrum of **21**.

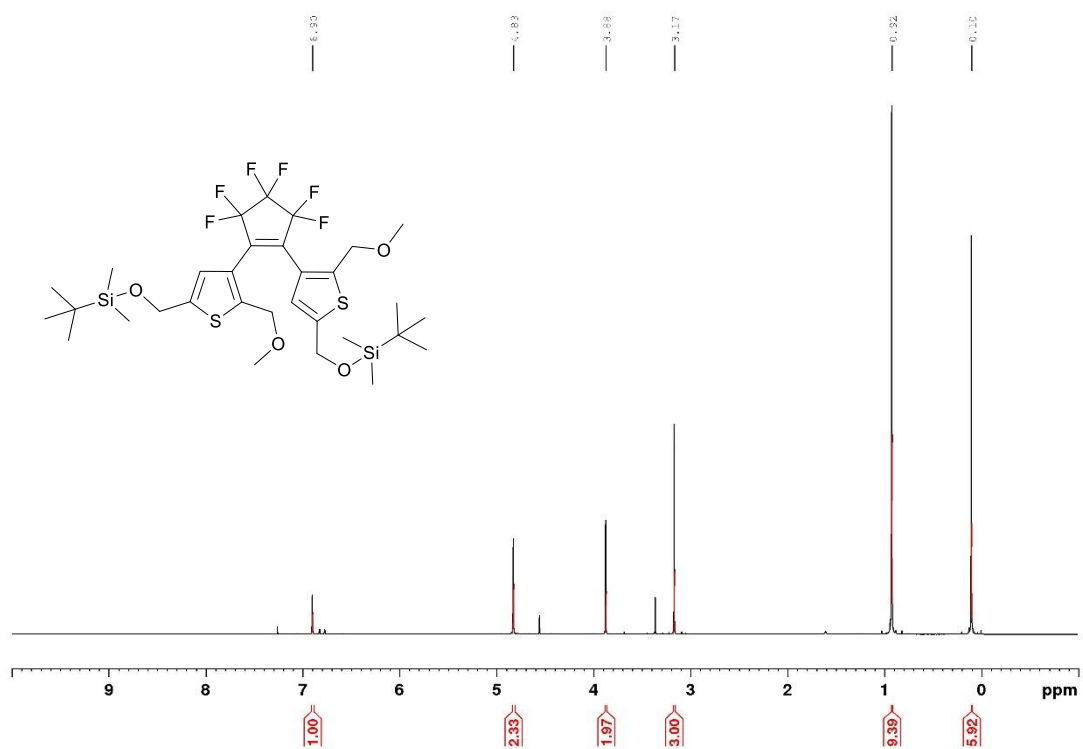


Figure S71:  $^1\text{H}$  NMR spectrum of **22**.



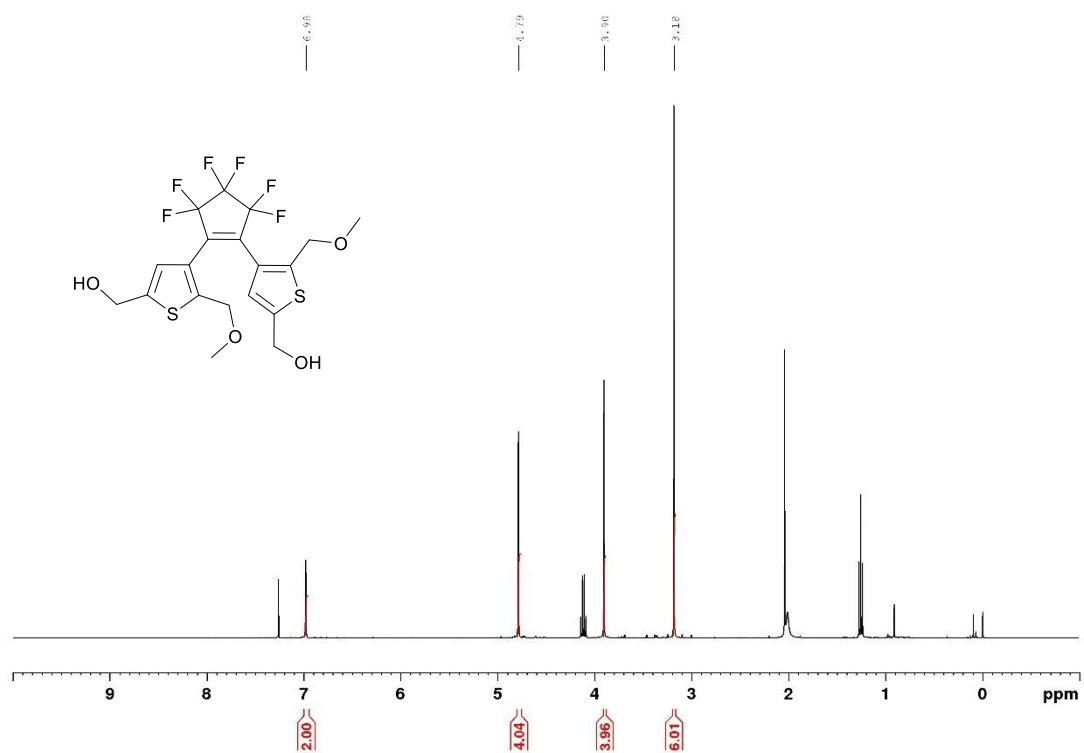


Figure S74: <sup>1</sup>H NMR spectrum of **23**.

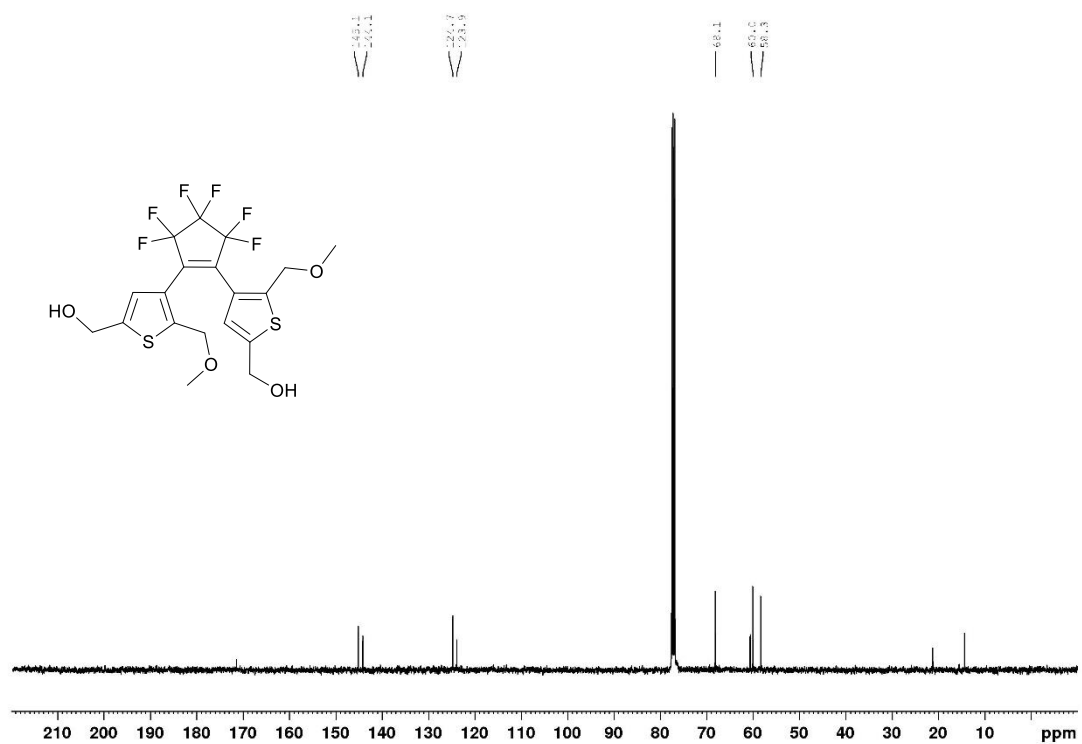


Figure S75: <sup>13</sup>C NMR-spectrum of **23**.



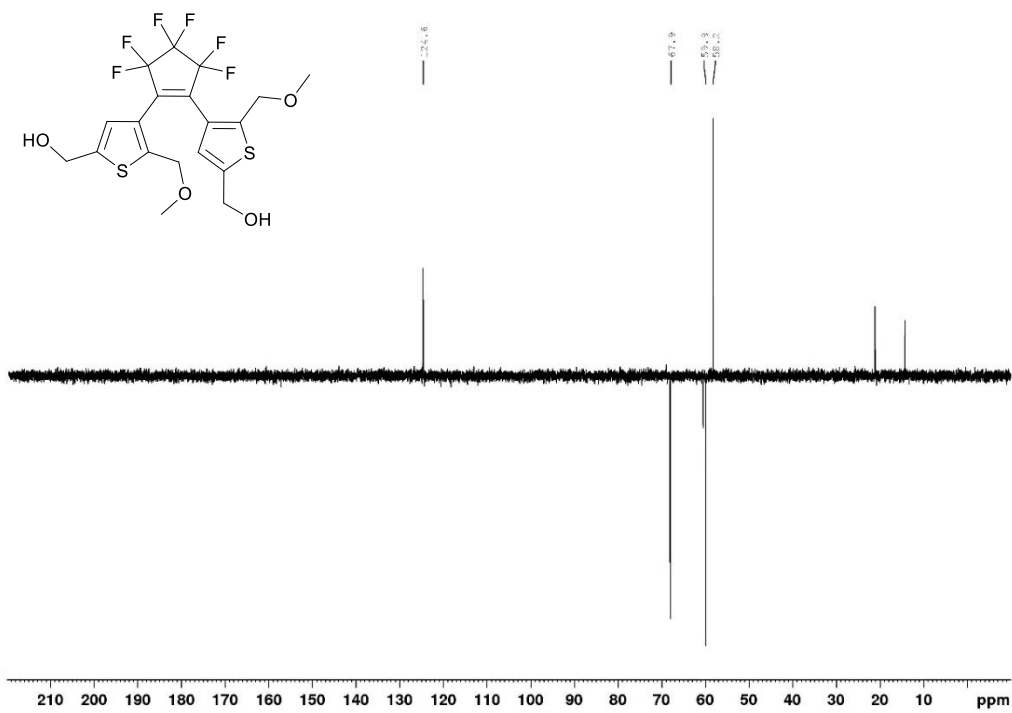


Figure S76: DEPT-NMR spectrum of **23**.

## UV spectra

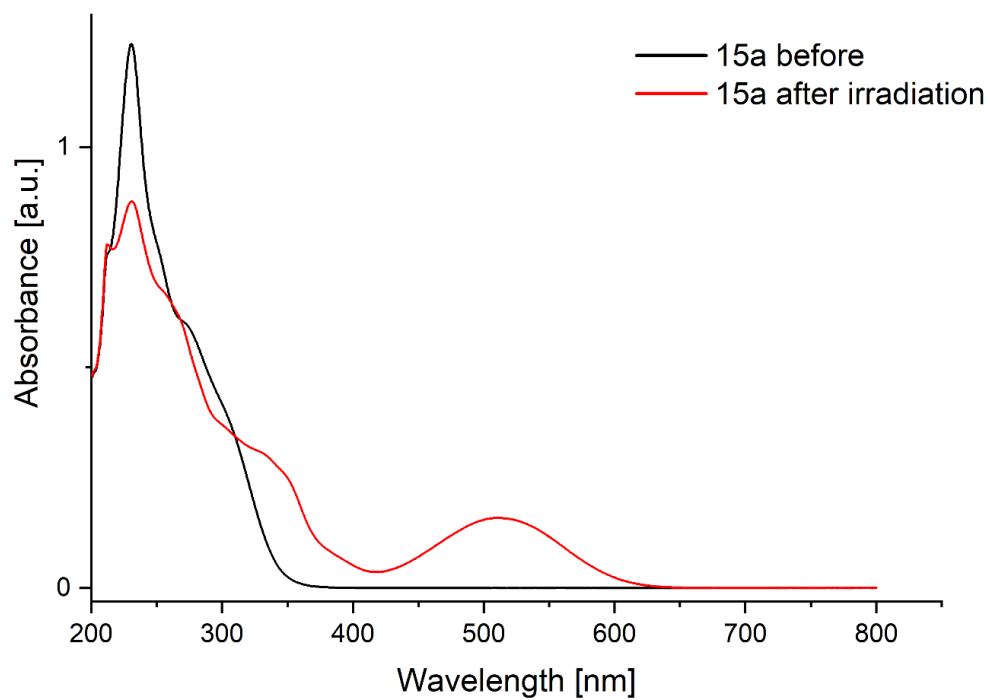


Figure S77: UV/Vis-spectrum of 15a before and after irradiation in THF.

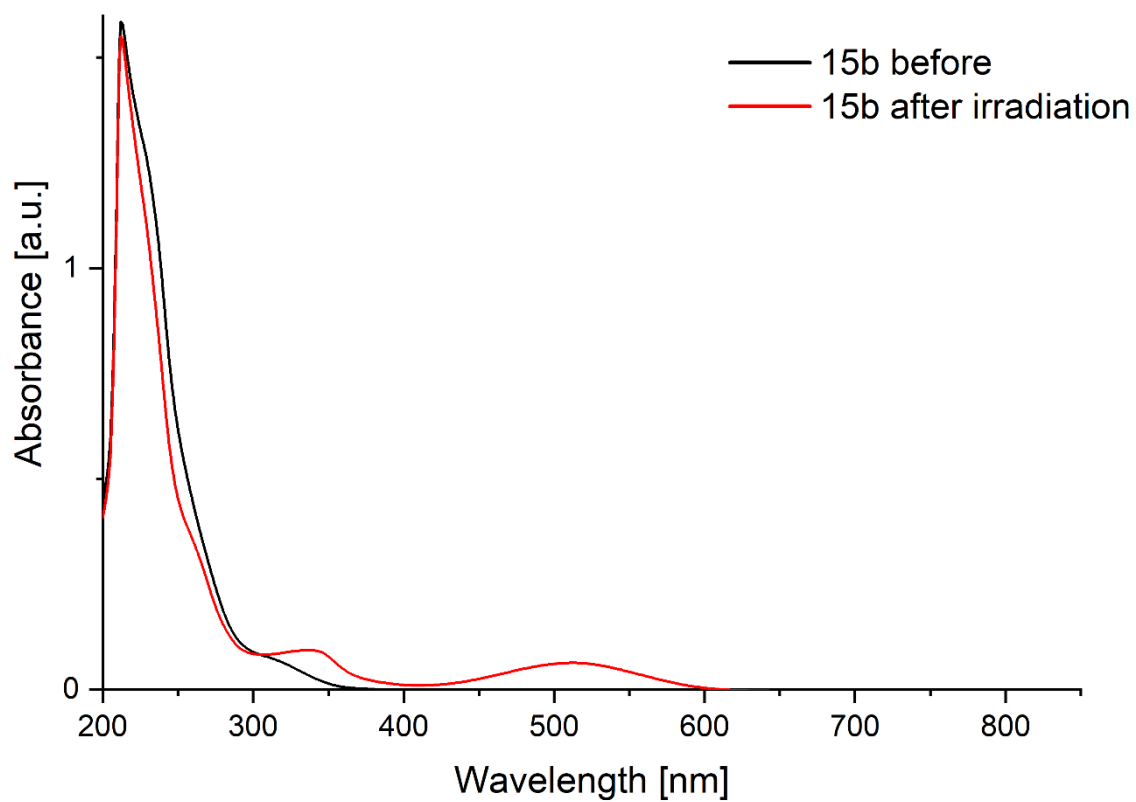


Figure S78: UV/Vis-spectrum of 15b before and after irradiation in THF.

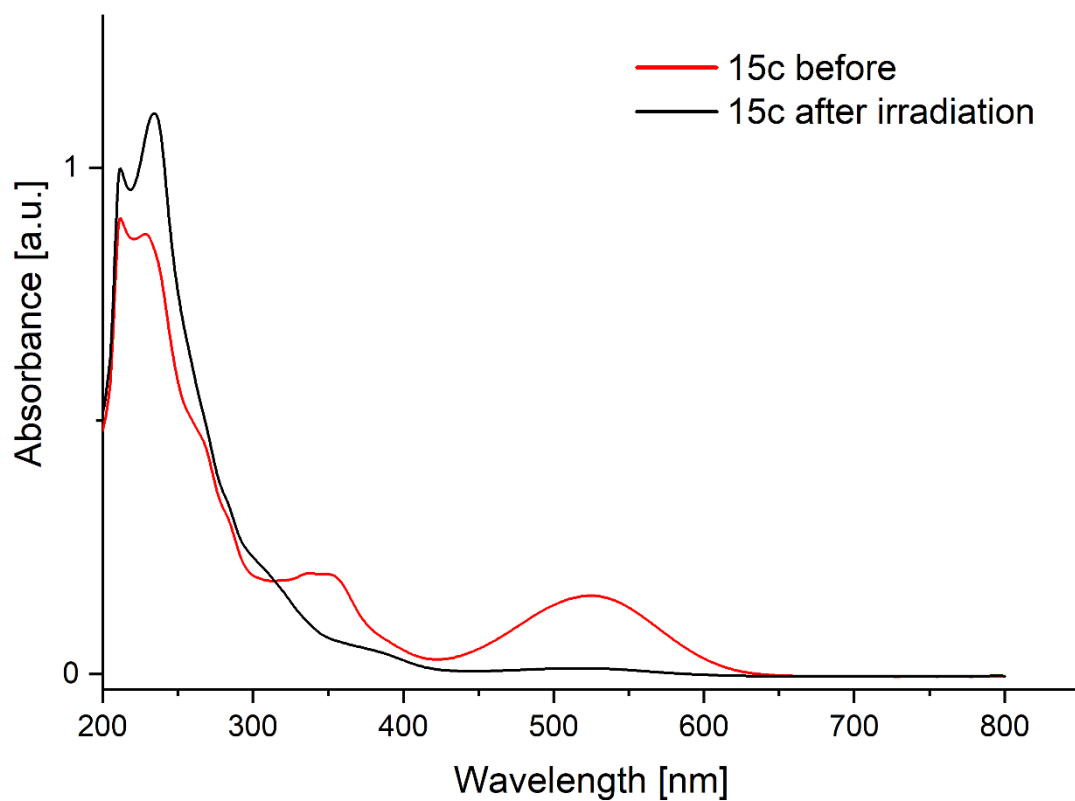


Figure S79: UV/Vis-spectrum of 15c before and after irradiation in THF.

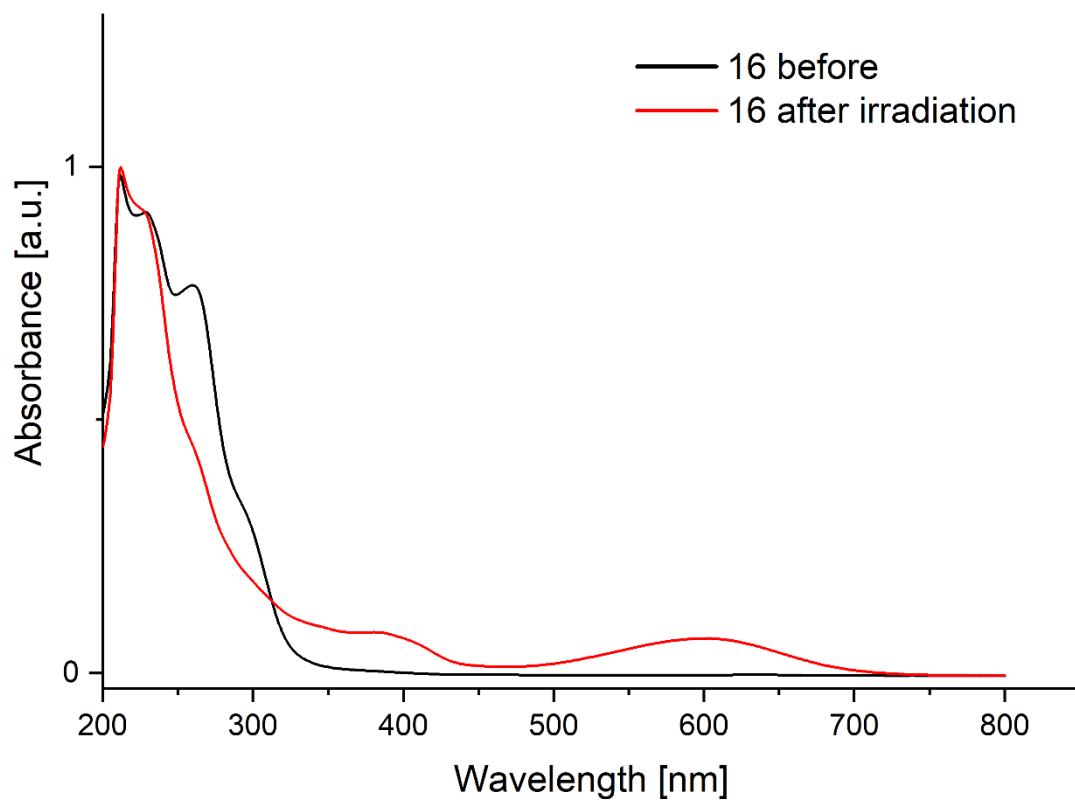


Figure S80: UV/Vis-spectrum of 16 before and after irradiation in THF.

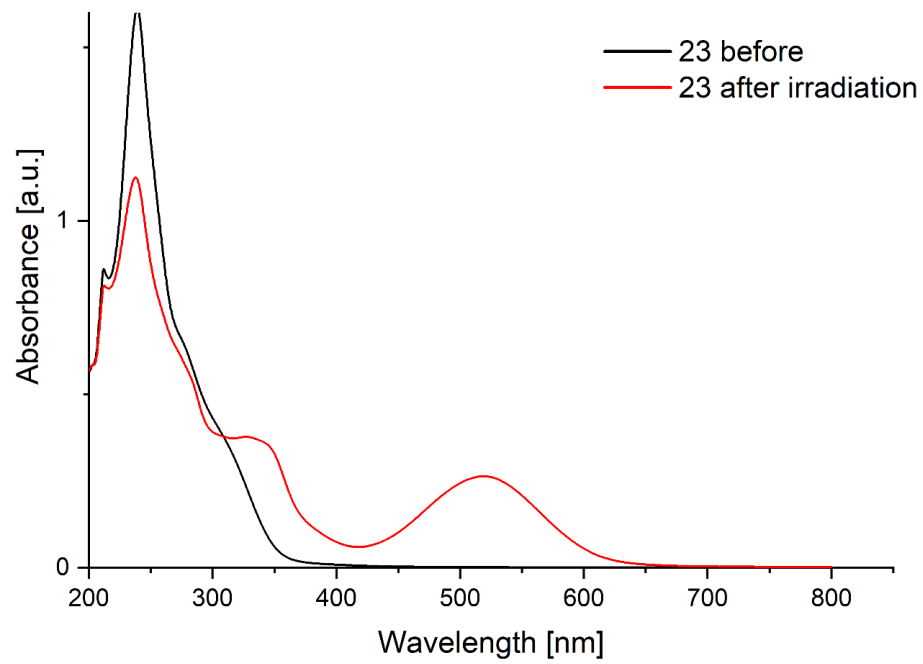


Figure S81: UV/Vis-spectrum of 23 before and after irradiation in THF.

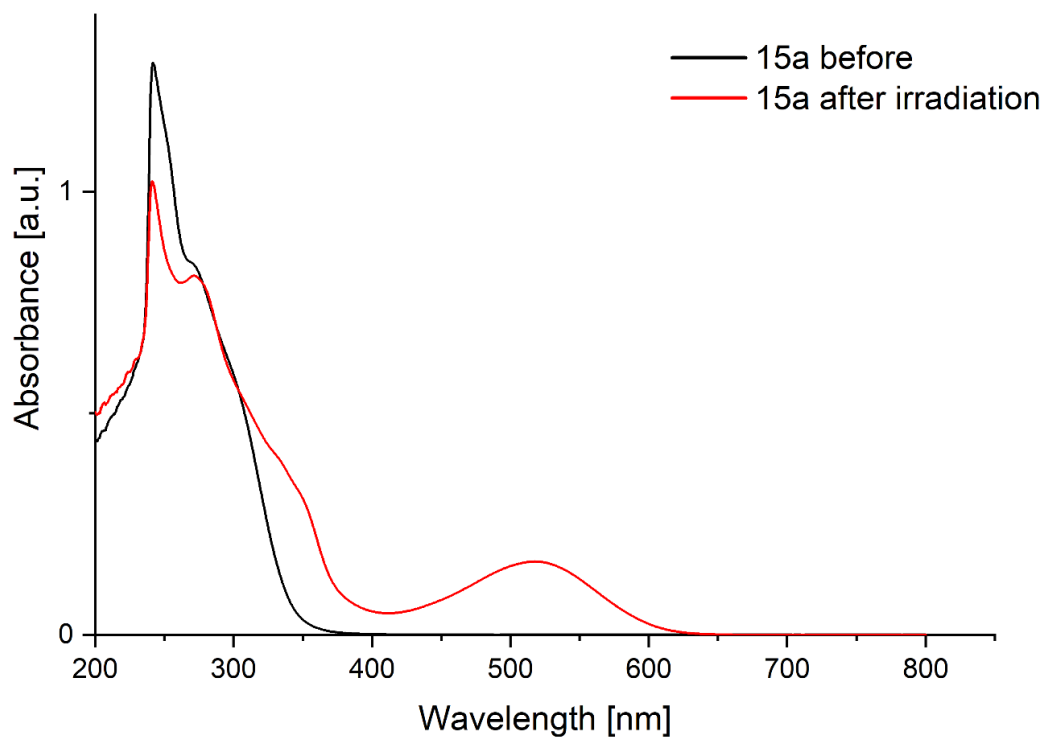


Figure S82: UV/Vis-spectrum of 15a before and after irradiation in chloroform

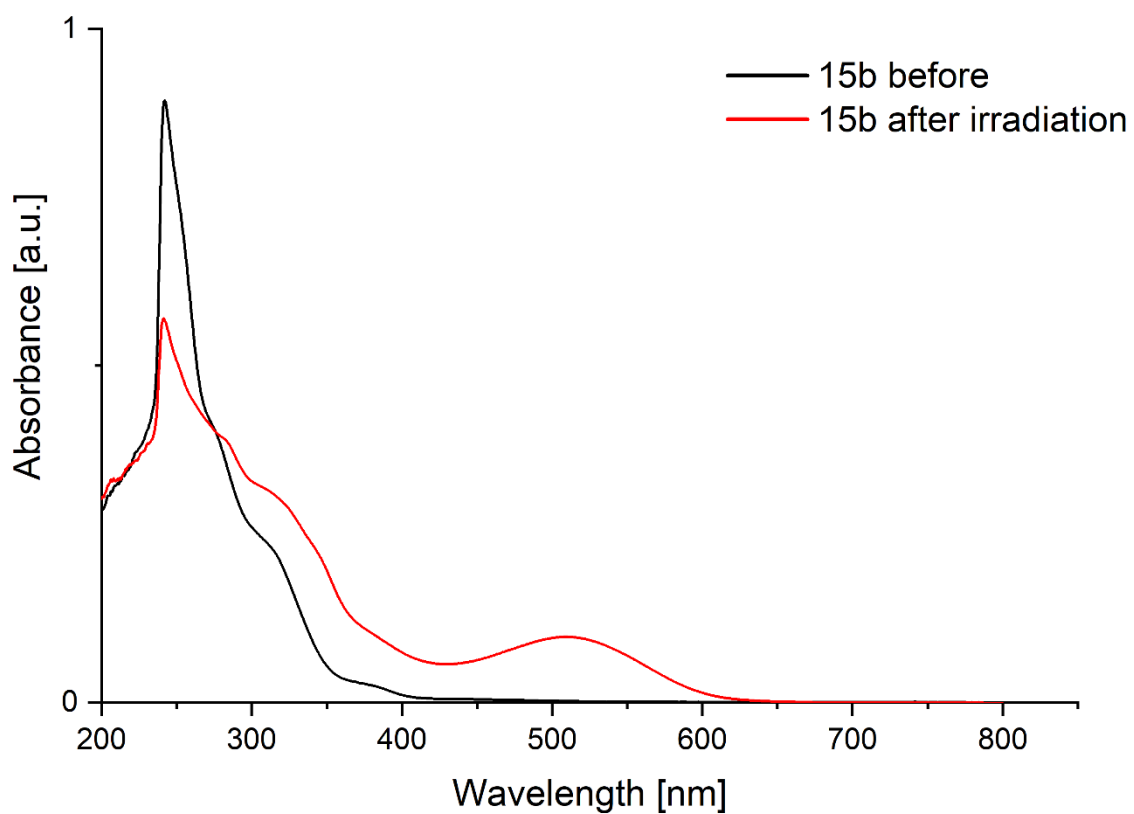


Figure S83: UV/Vis-spectrum of 15b before and after irradiation in chloroform.

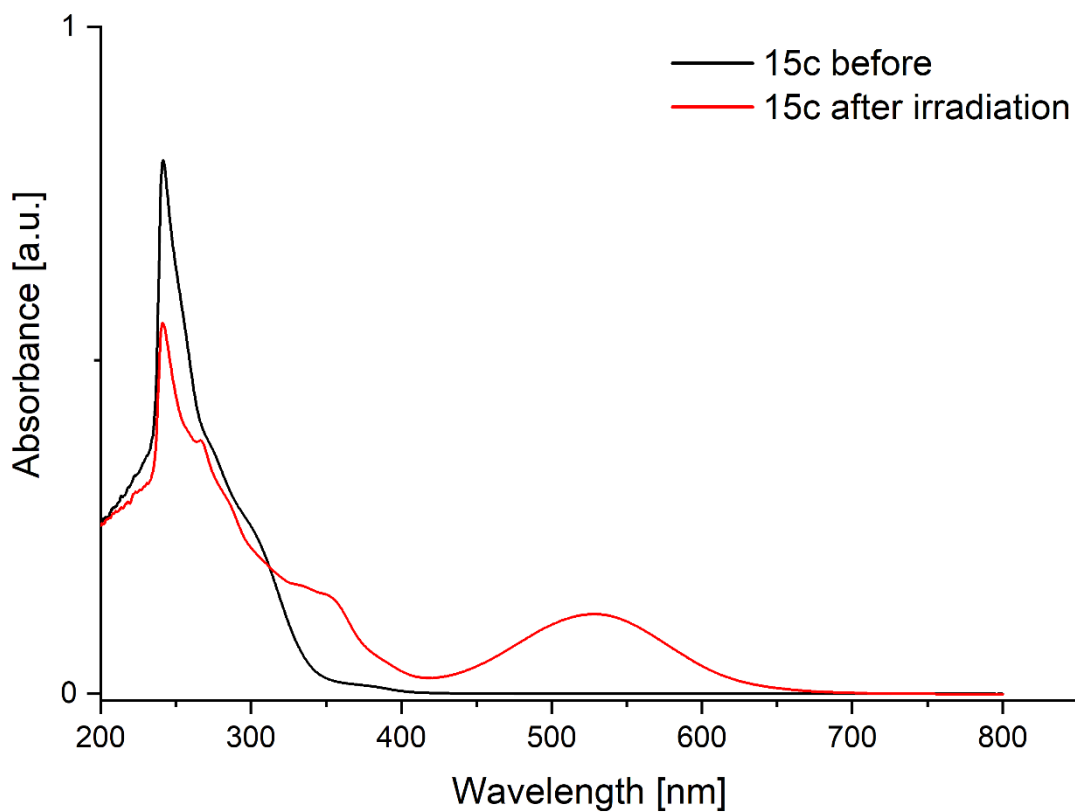


Figure S84: UV/Vis-spectrum of 15c before and after irradiation in chloroform.

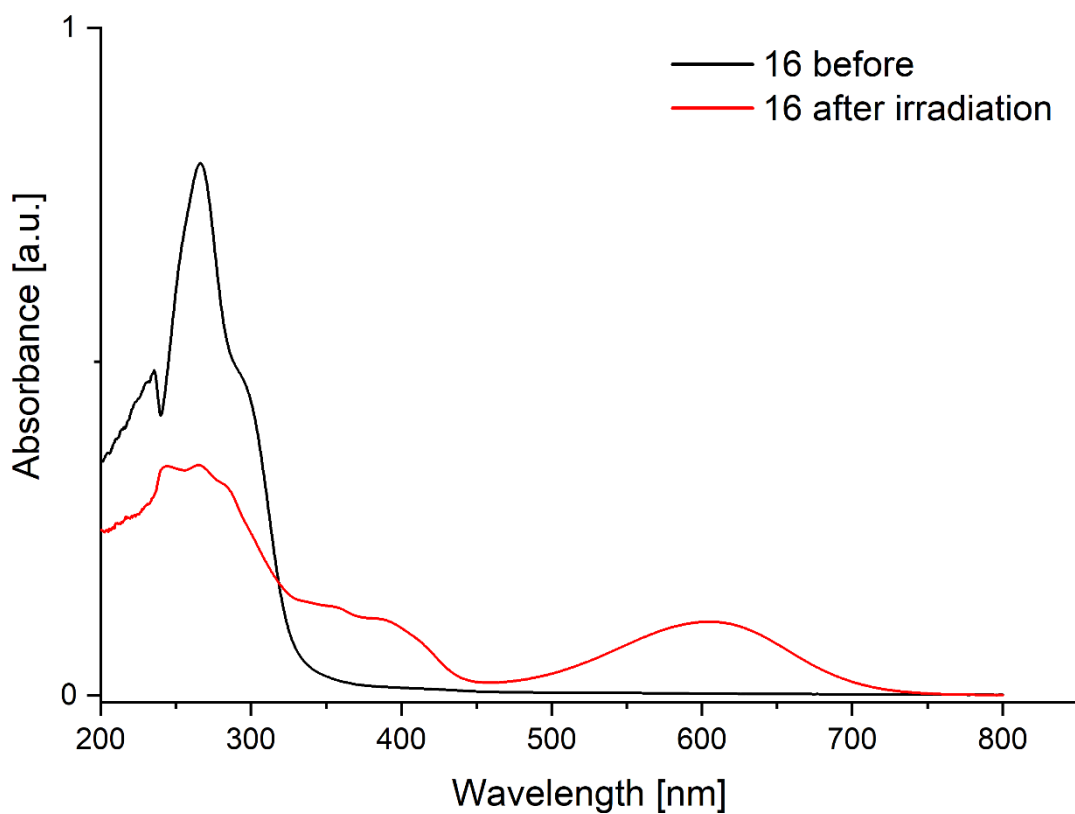


Figure S85: UV/Vis-spectrum of 16 before and after irradiation in chloroform.

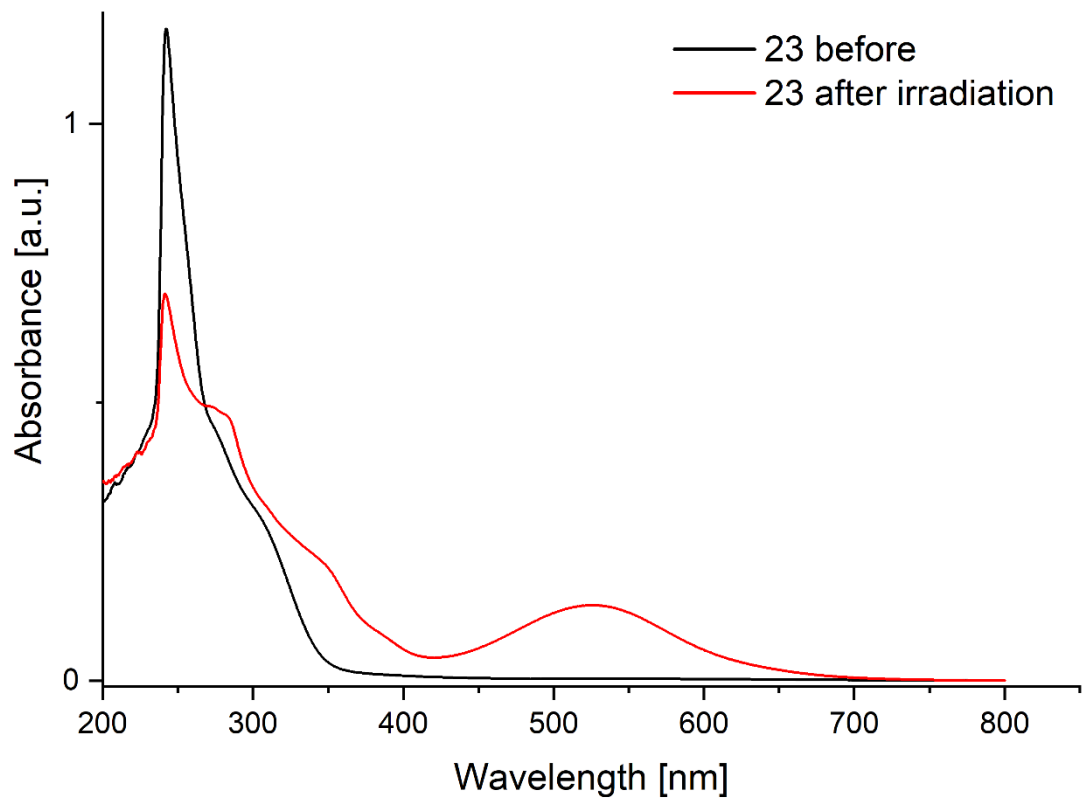


Figure S86: UV/Vis-spectrum of 23 before and after irradiation in chloroform.

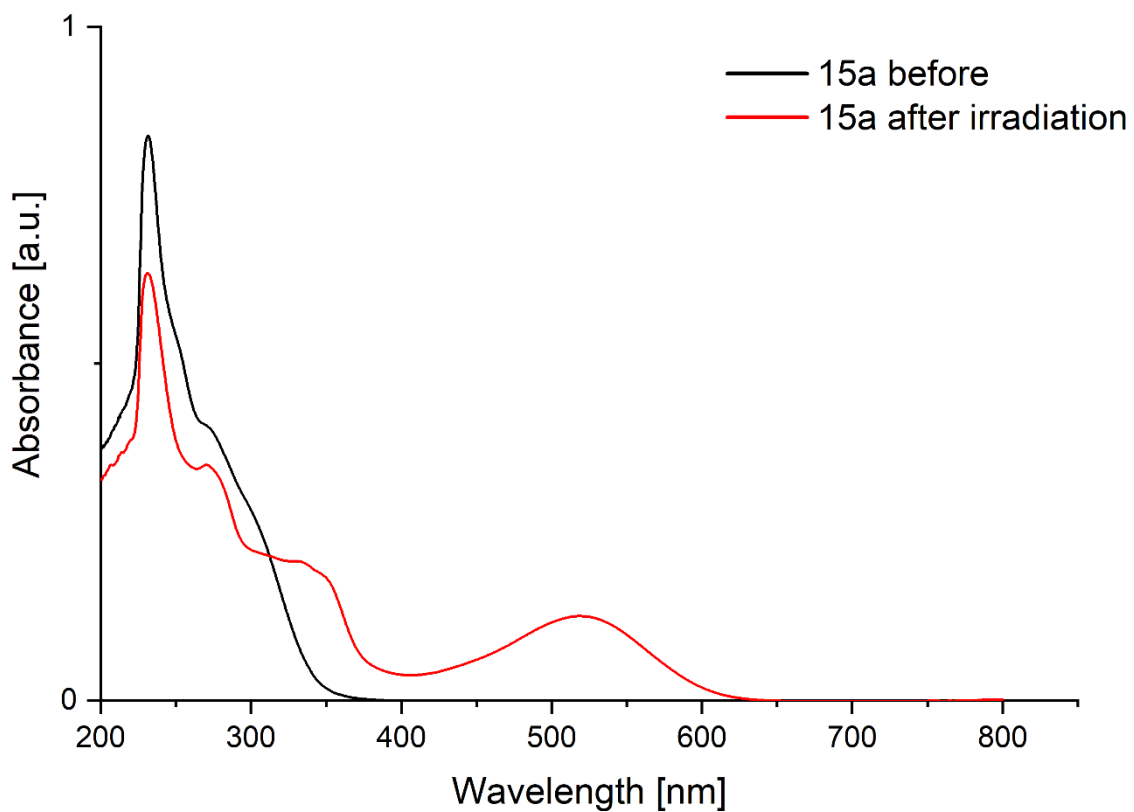


Figure S87: UV/Vis-spectrum of 15a before and after irradiation in dichloromethane.

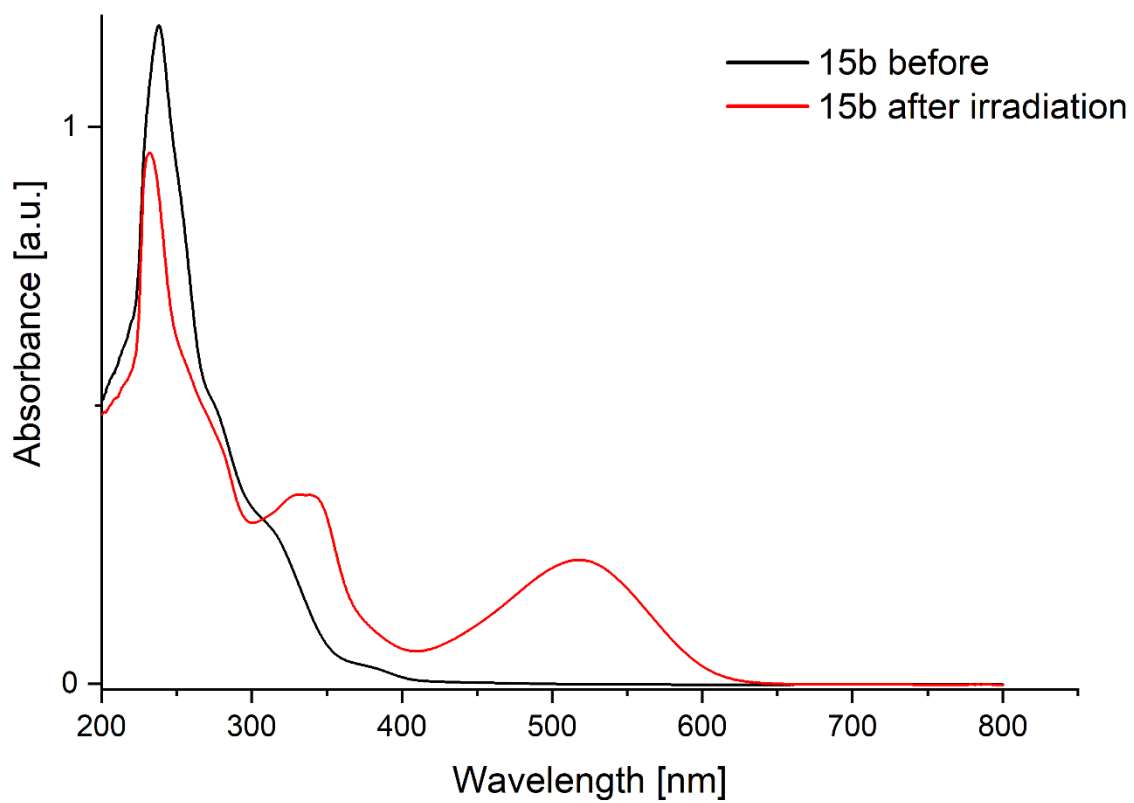


Figure S88: UV/Vis-spectrum of 15b before and after irradiation in dichloromethane.



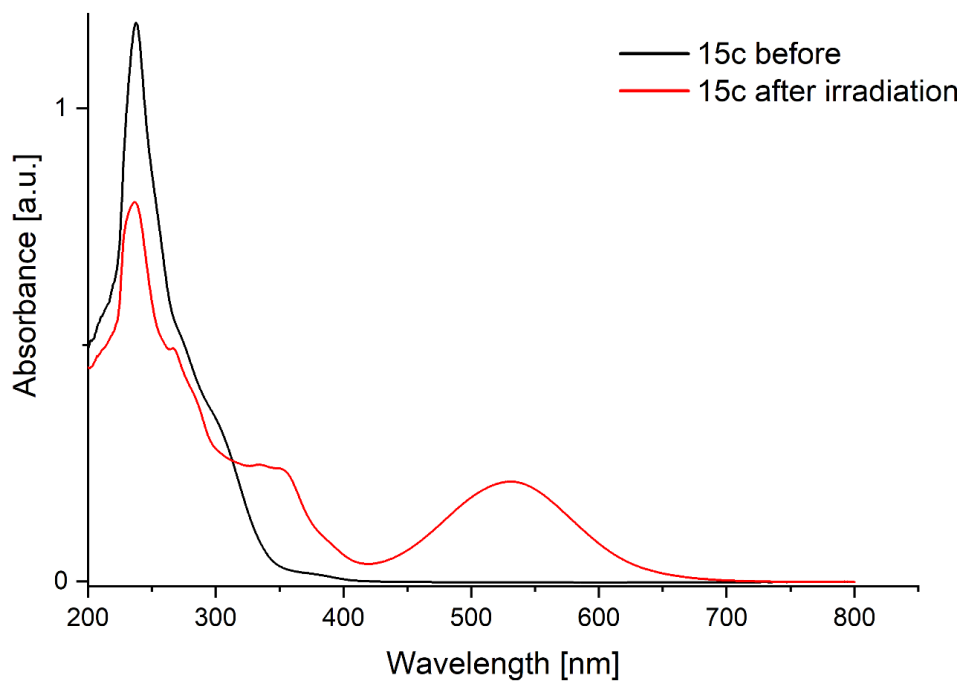


Figure S89: UV/Vis-spectrum of 15c before and after irradiation in dichloromethane.

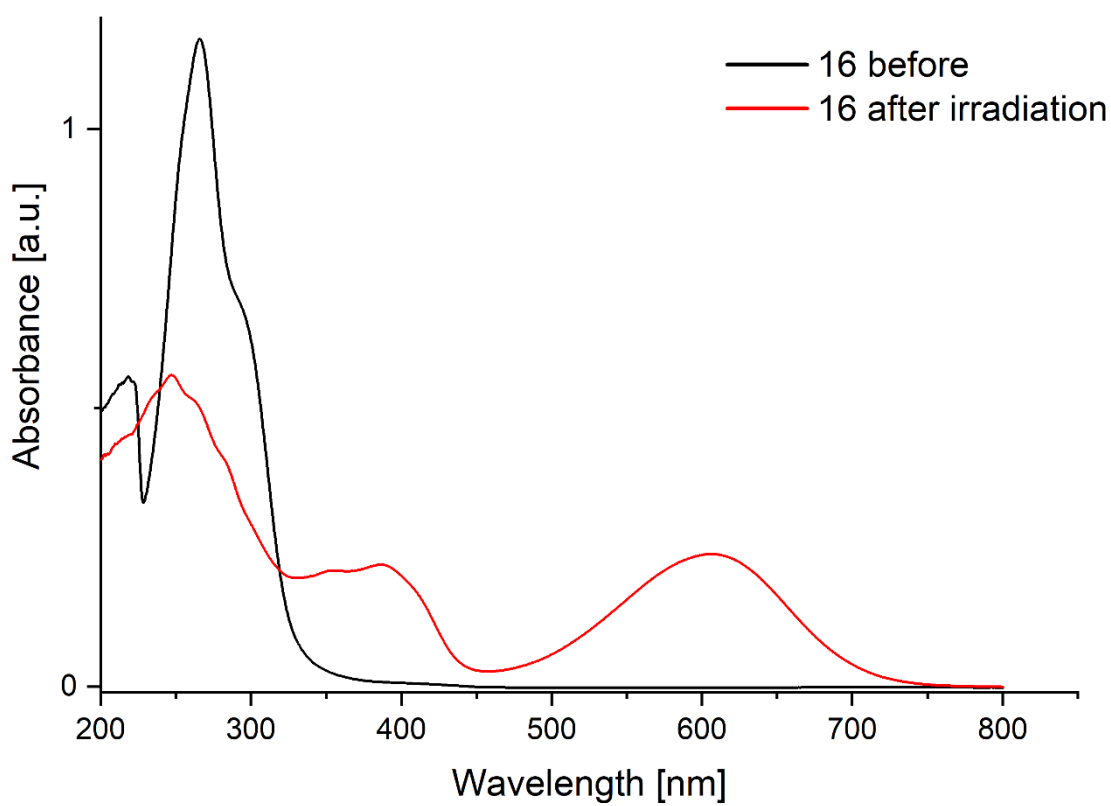


Figure S90: UV/Vis-spectrum of 16 before and after irradiation in dichloromethane.

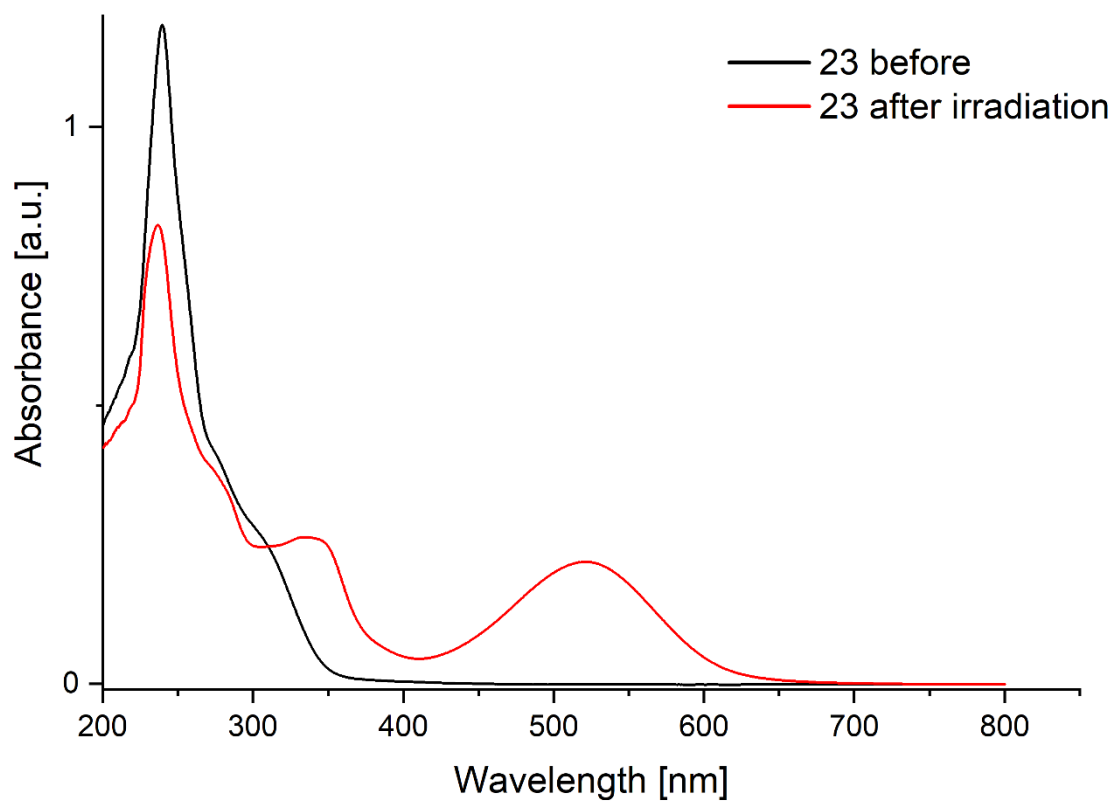


Figure S91: UV/Vis-spectrum of 23 before and after irradiation in dichloromethane.

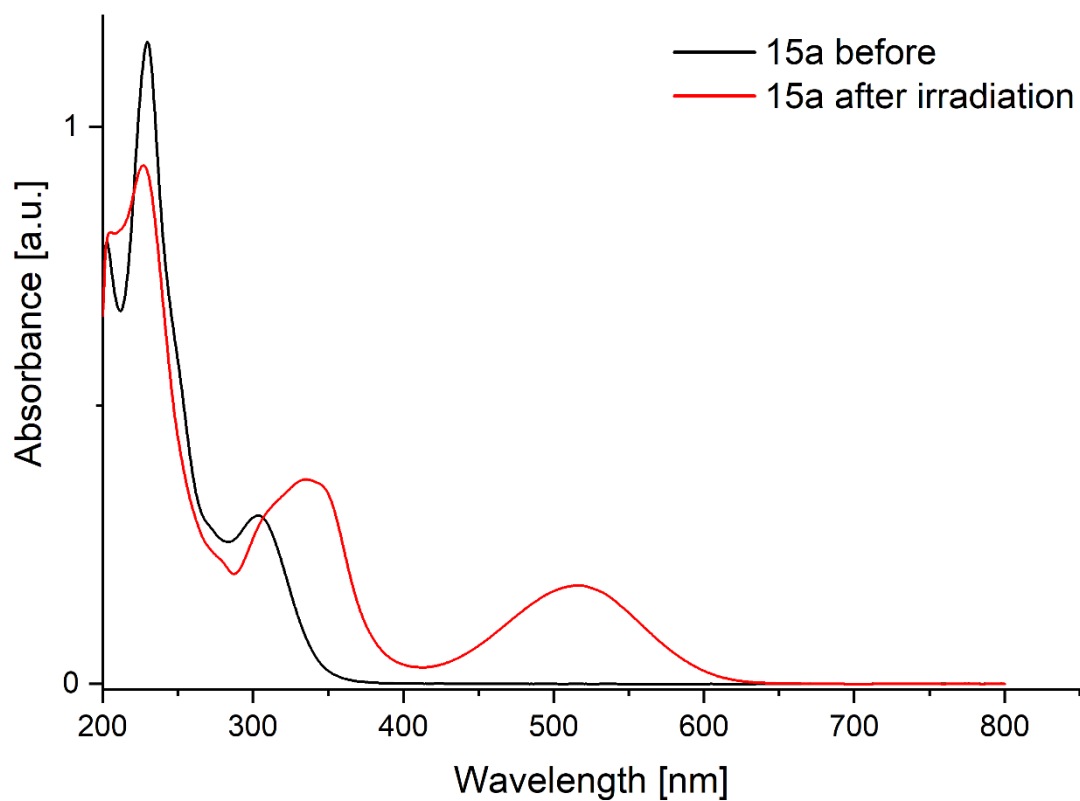


Figure S92: UV/Vis-spectrum of 15a before and after irradiation in methanol.

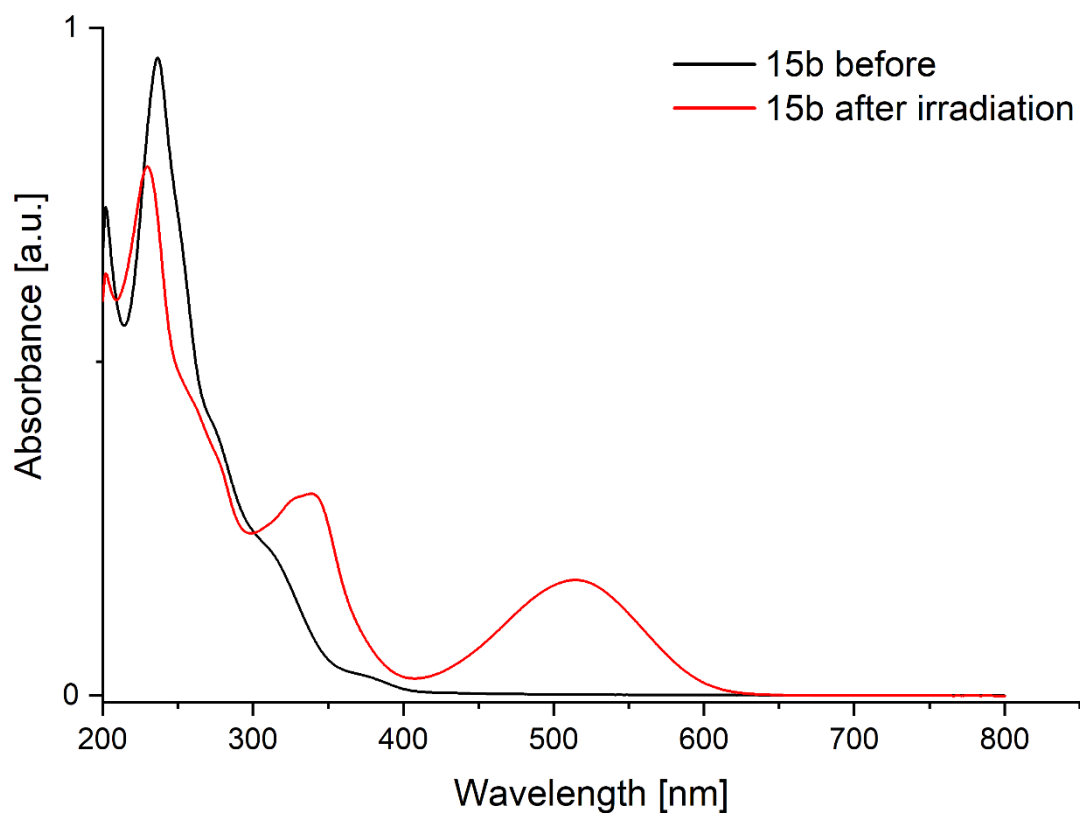


Figure S93: UV/Vis-spectrum of 15b before and after irradiation in methanol.

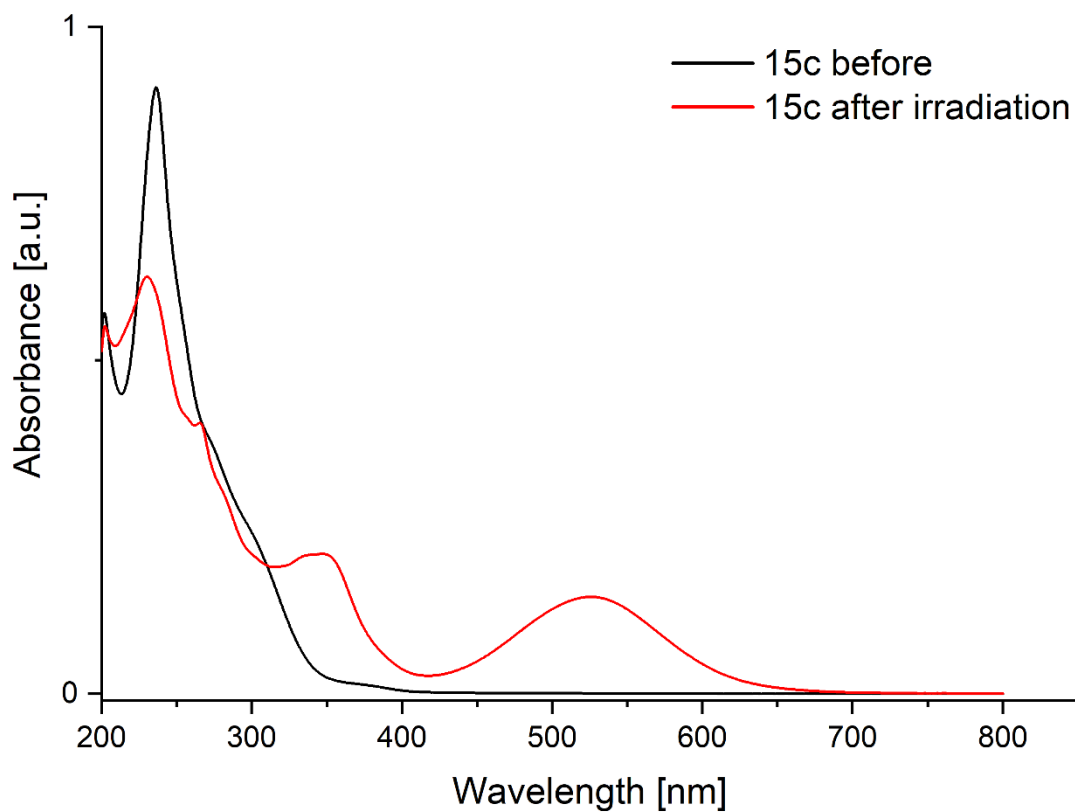


Figure S94: UV/Vis-spectrum of 15c before and after irradiation in methanol.

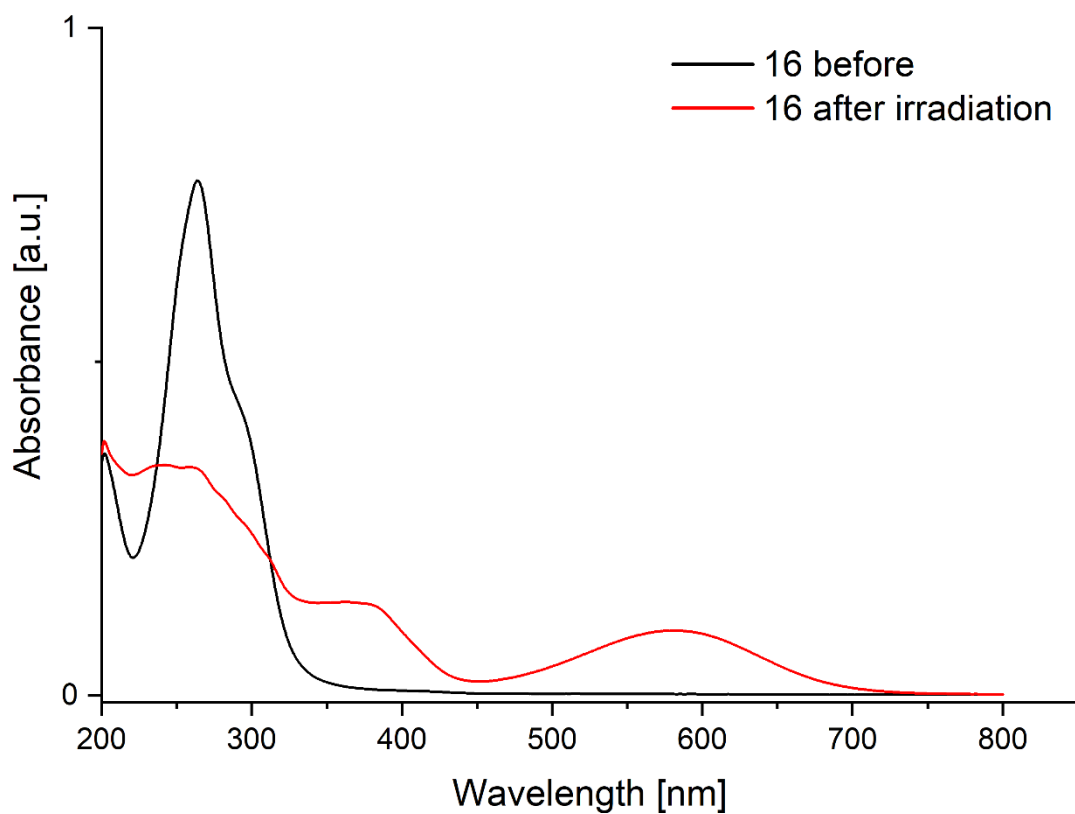


Figure S95: UV/Vis-spectrum of 16 before and after irradiation in methanol.

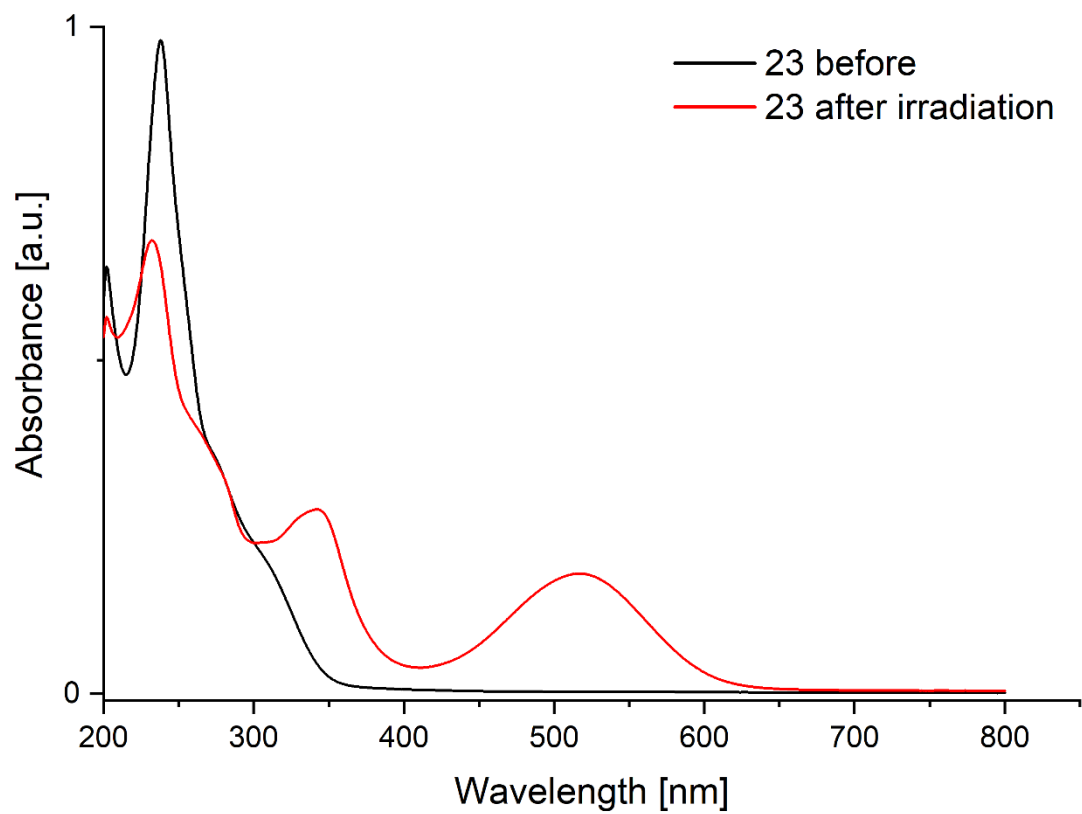


Figure S96: UV/Vis-spectrum of 23 before and after irradiation in methanol.

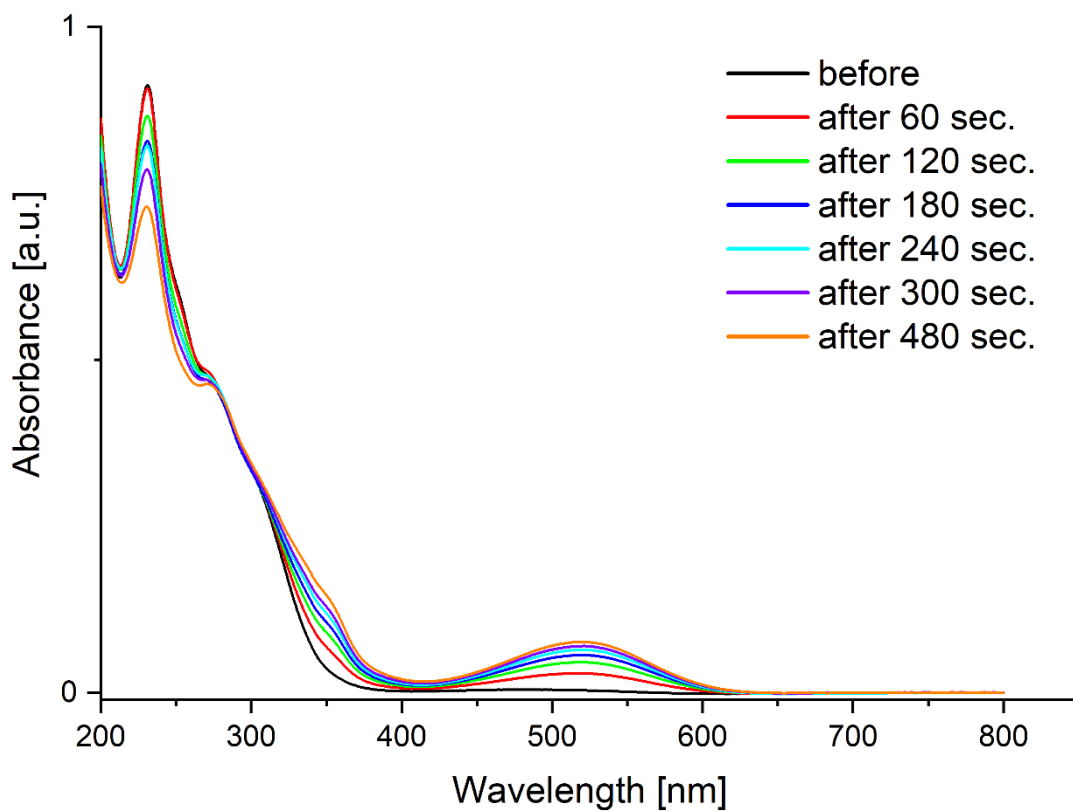


Figure S97 UV/Vis-spectrum / kinetics of **15a** on quartz sample (produced at 2500 rpm).

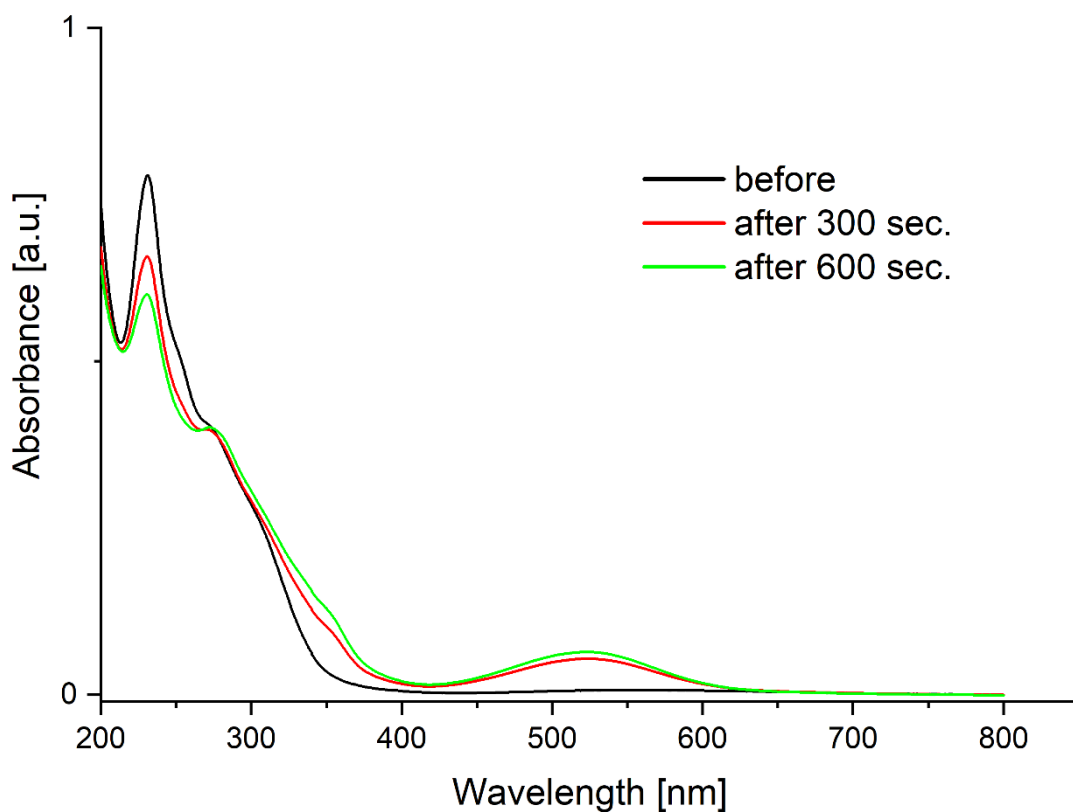


Figure S98: UV/Vis-spectrum / kinetics of BTE **15a** on quartz sample (produced at 3000 rpm).

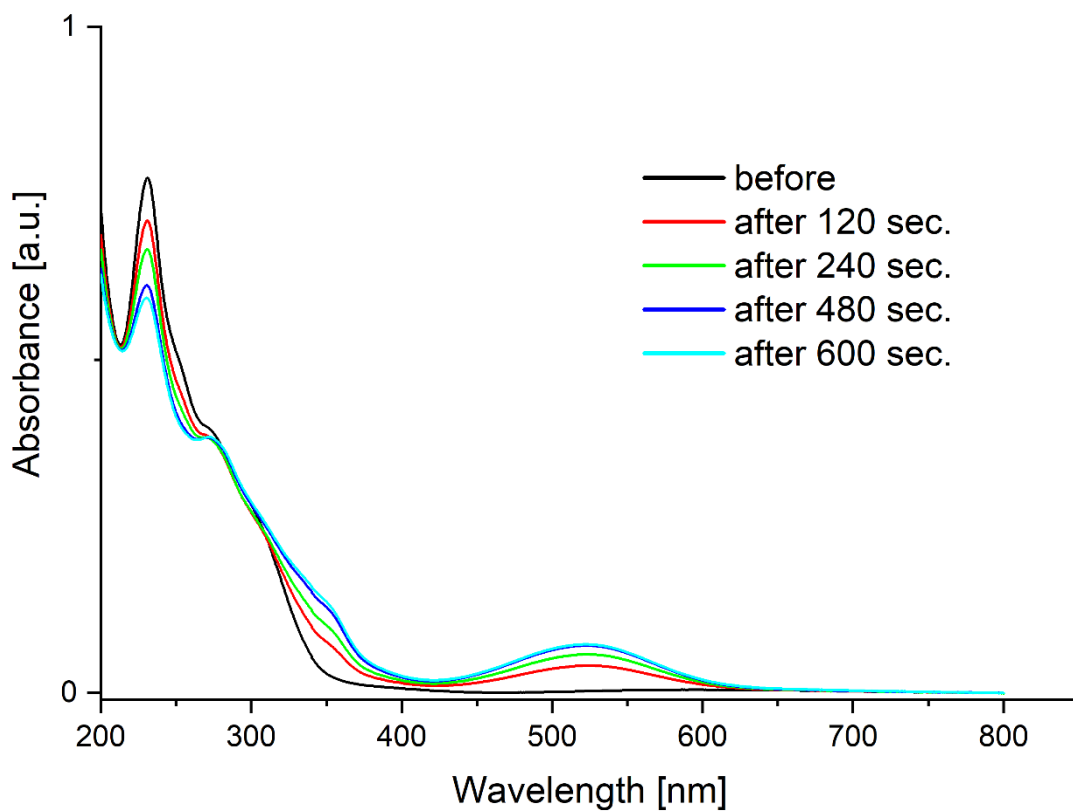


Figure S99: UV/Vis-spectrum / kinetics of BTE **15a** on quartz sample (produced at 3500 rpm).

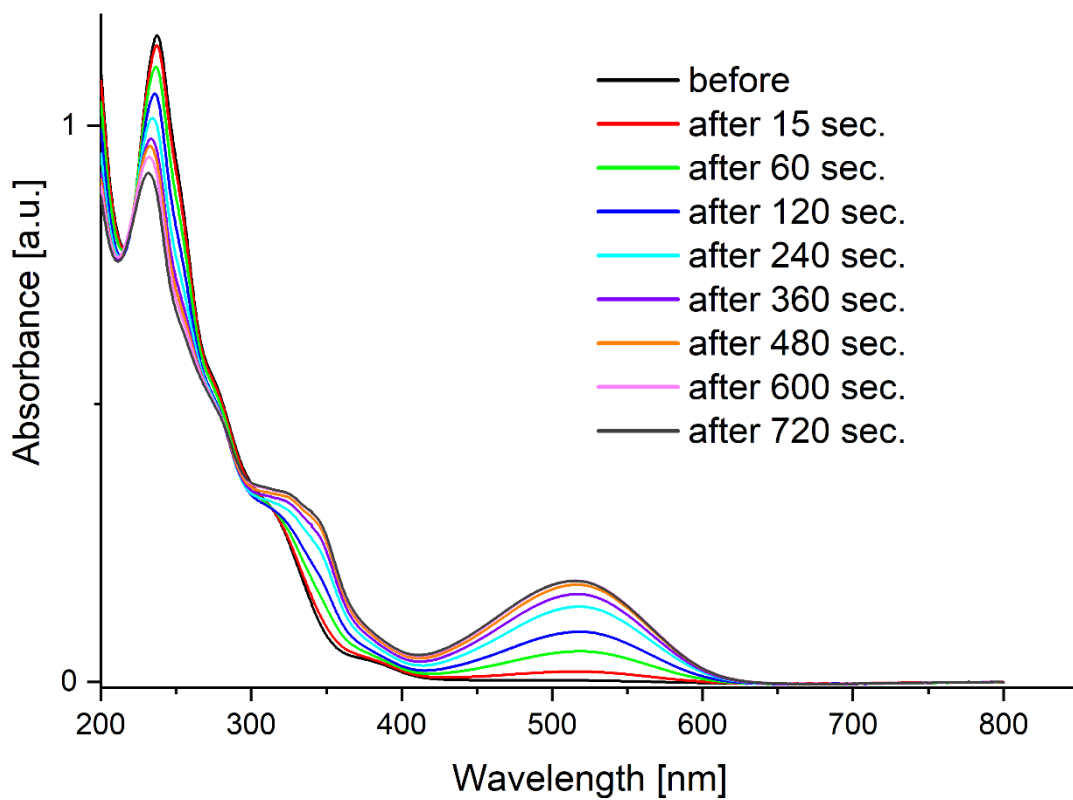


Figure S100: UV/Vis-spectrum / kinetics of BTE **15b** on quartz sample (produced at 2500 rpm).

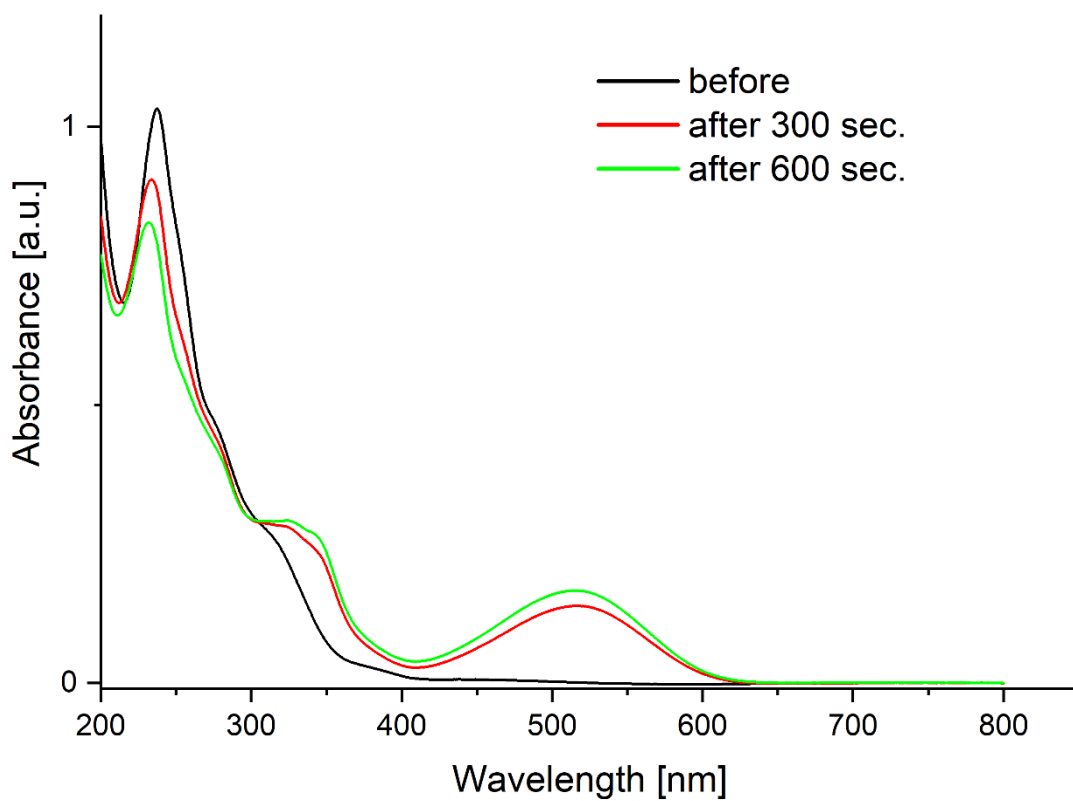


Figure S101: UV/Vis-spectrum / kinetics of BTE **15b** on quartz sample (produced at 3000 rpm).

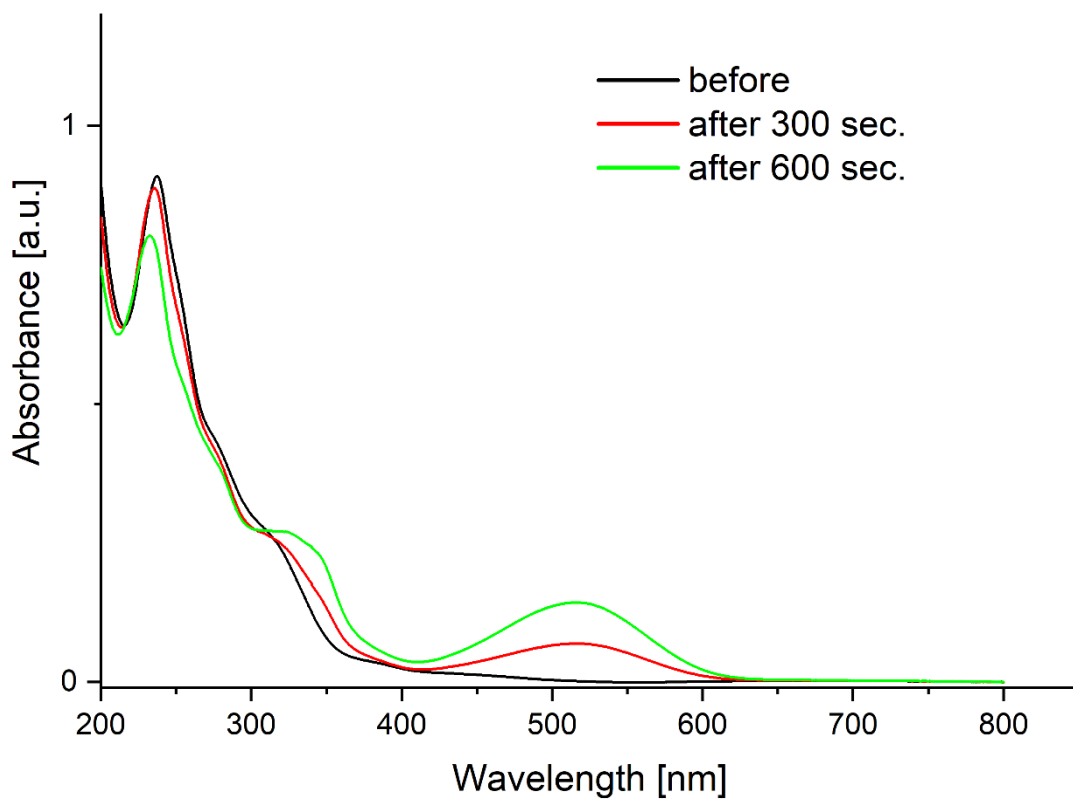


Figure S102: UV/Vis-spectrum / kinetics of BTE **15b** on quartz sample (produced at 3500 rpm).



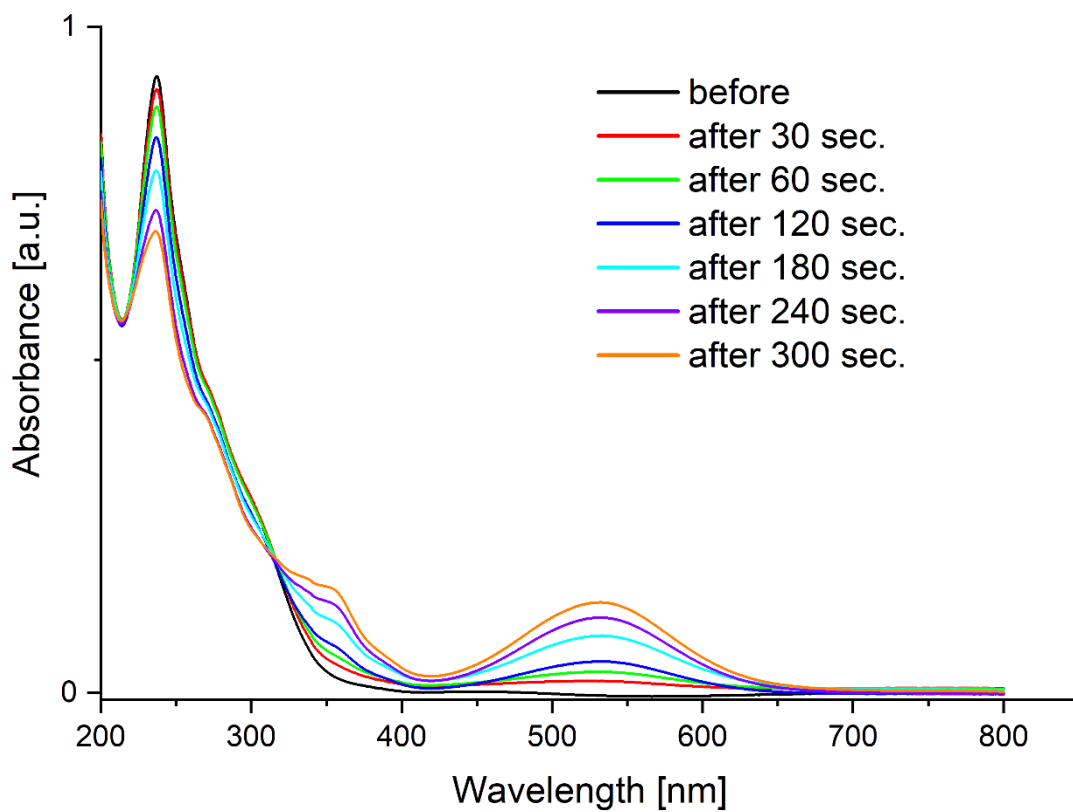


Figure S103: UV/Vis-spectrum / kinetics of BTE **15c** on quartz sample (produced at 2500 rpm).

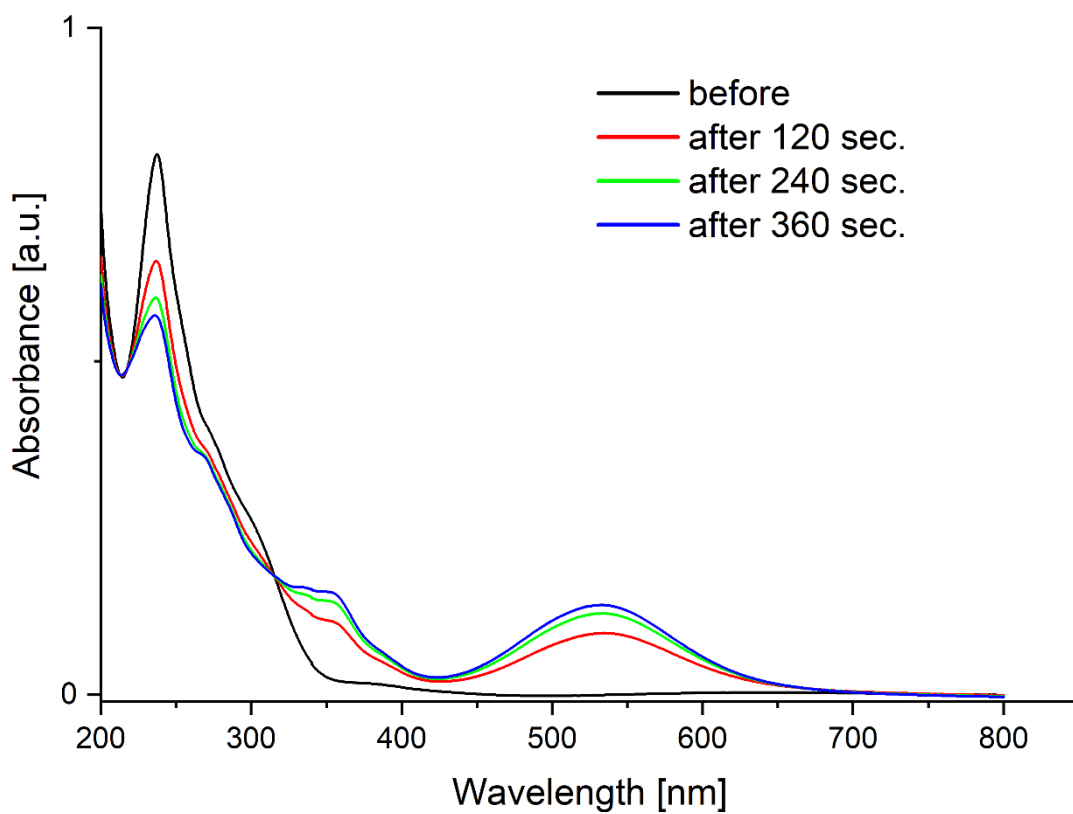


Figure S104: UV/Vis-spectrum / kinetics of BTE **15c** on quartz sample (produced at 3000 rpm).

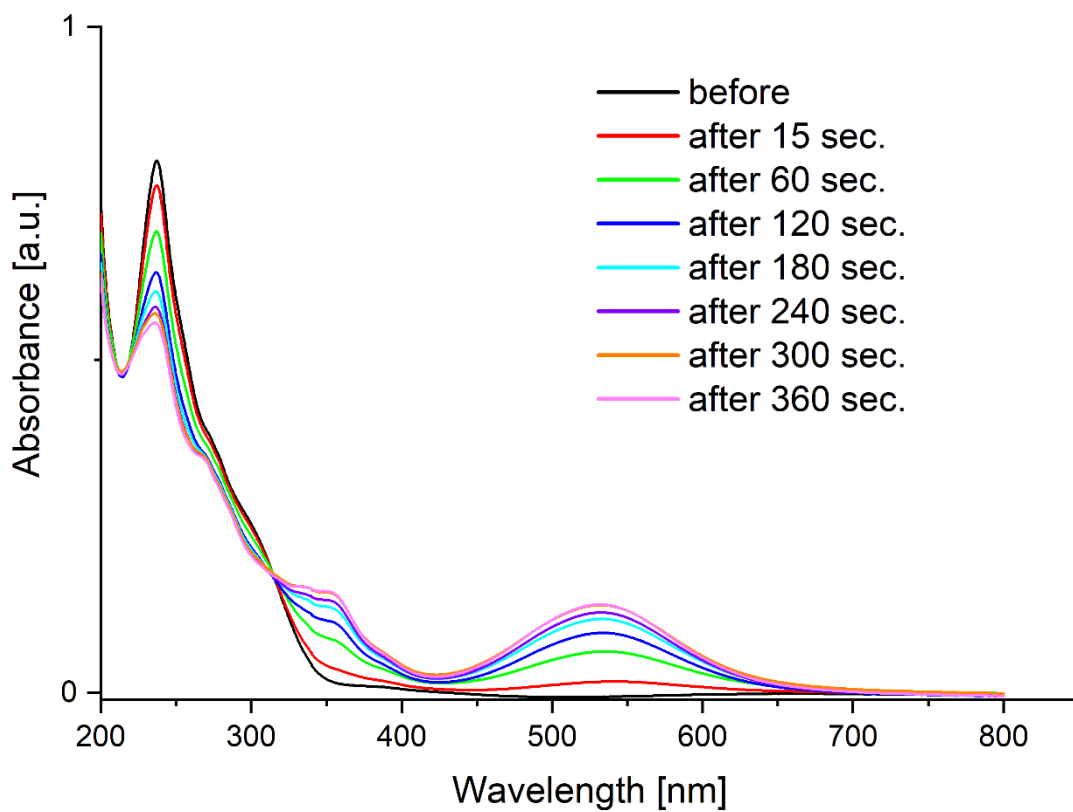


Figure S105: UV/Vis-spectrum / kinetics of BTE **15c** on quartz sample (produced at 3500 rpm).

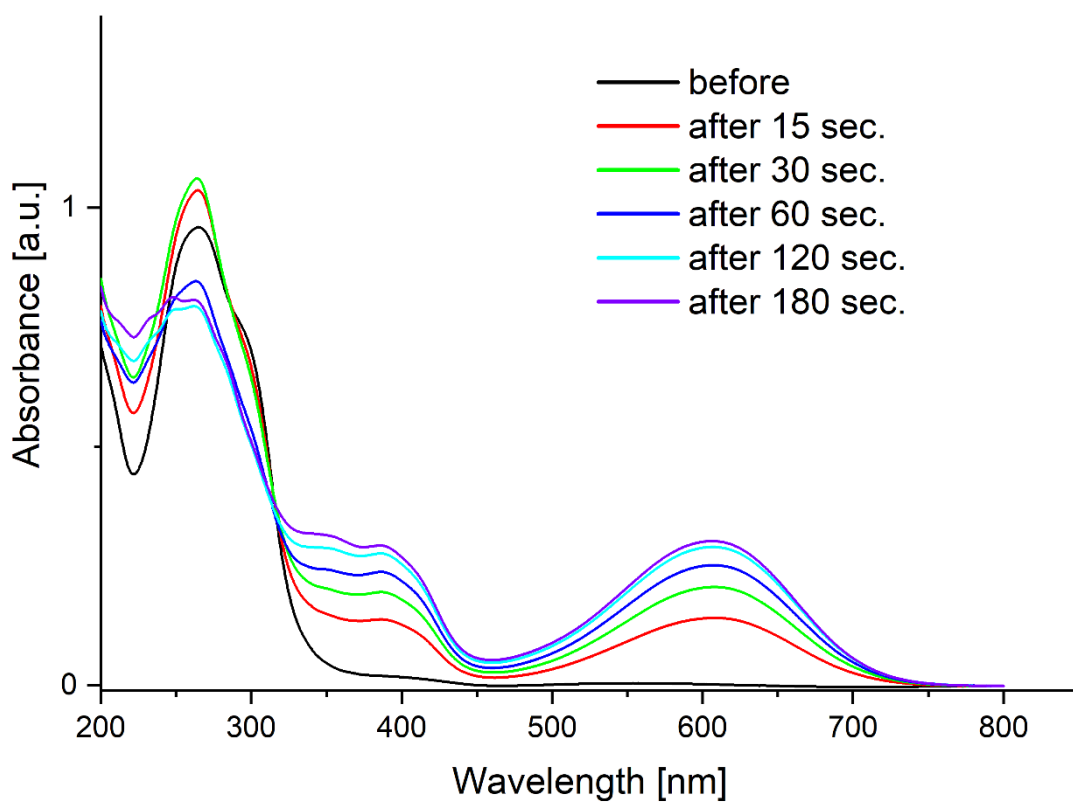


Figure S106: UV/Vis-spectrum / kinetics of BTE **16** on quartz sample (produced at 3500 rpm).

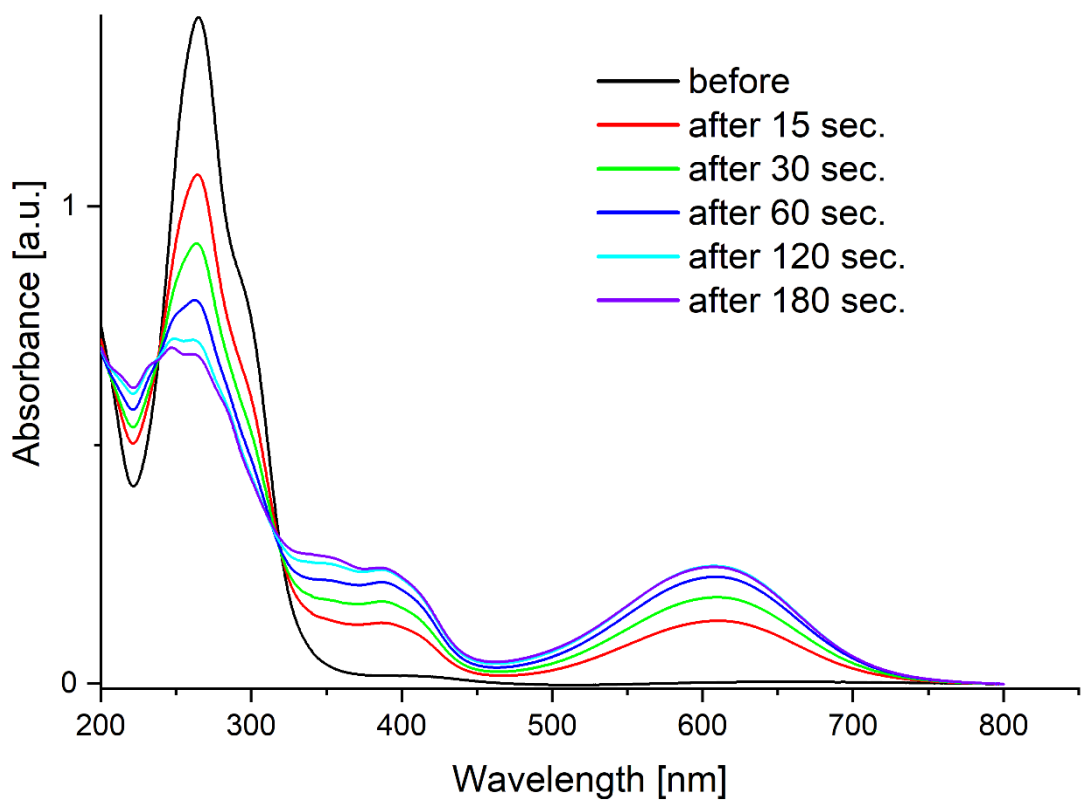


Figure S107: UV/Vis-spectrum / kinetics of BTE **16** on quartz sample (produced at 2500 rpm).

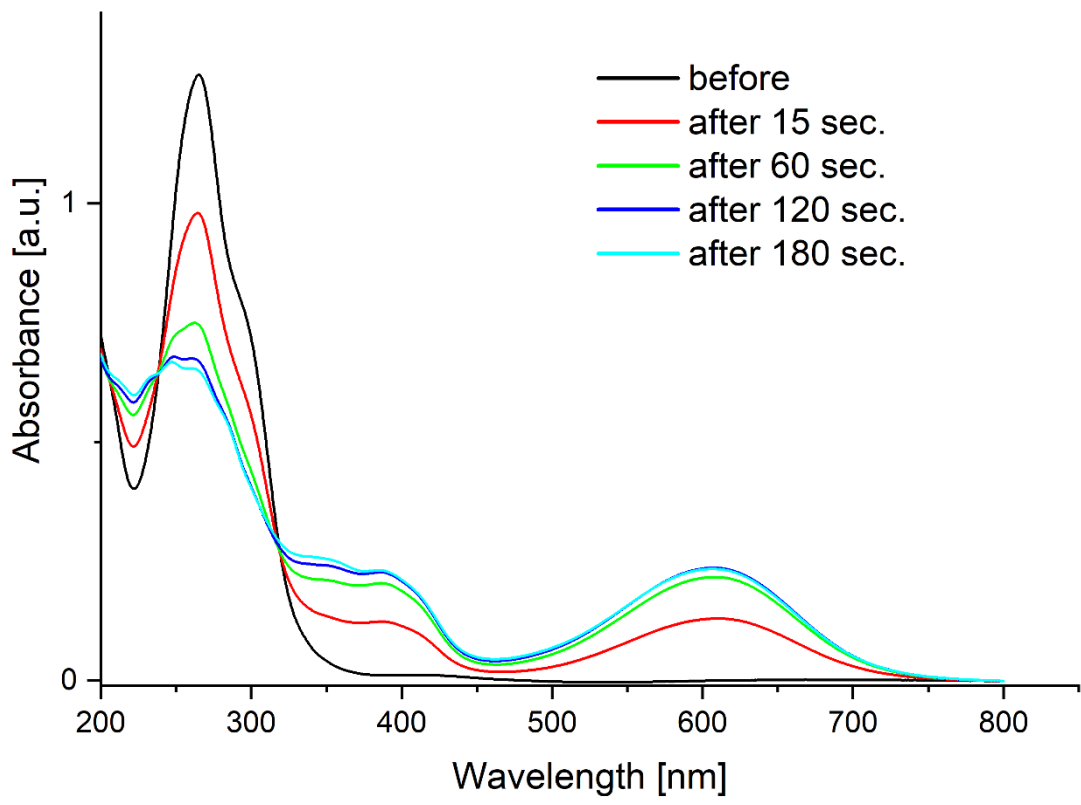


Figure S108: UV/Vis-spectrum / kinetics of BTE **16** on quartz sample (produced at 3000 rpm).

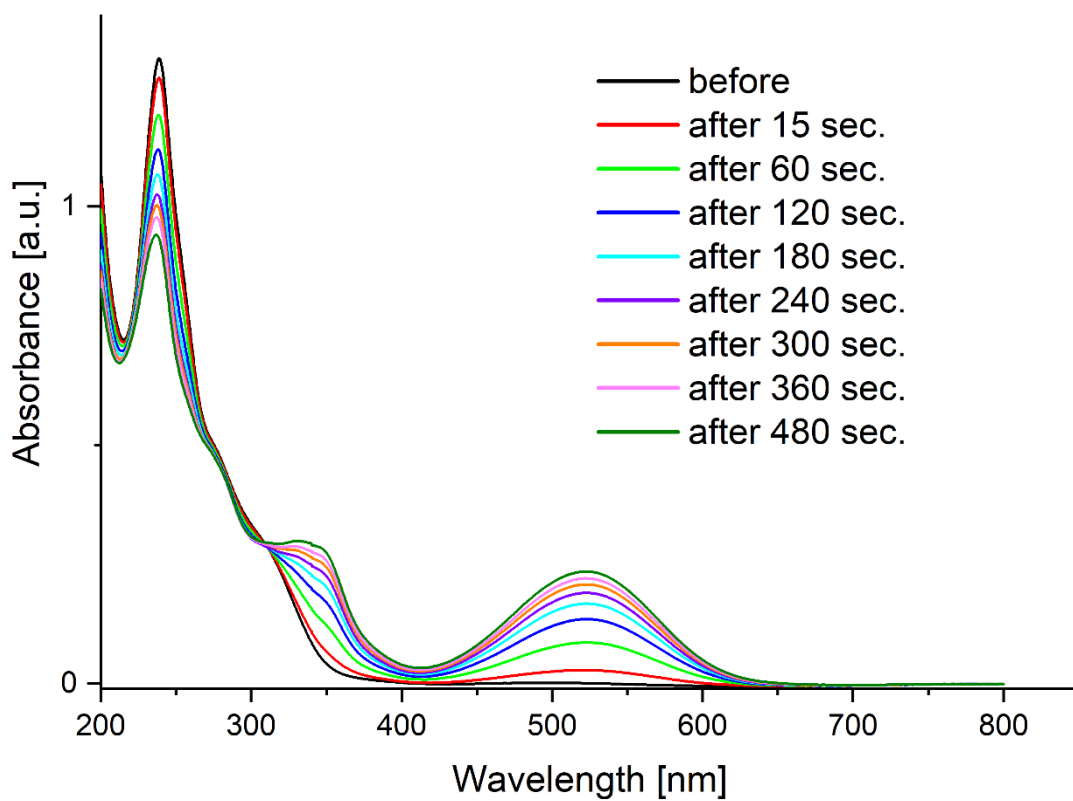


Figure S109: UV/Vis-spectrum / kinetics of BTE **23** on quartz sample (produced at 2500 rpm).

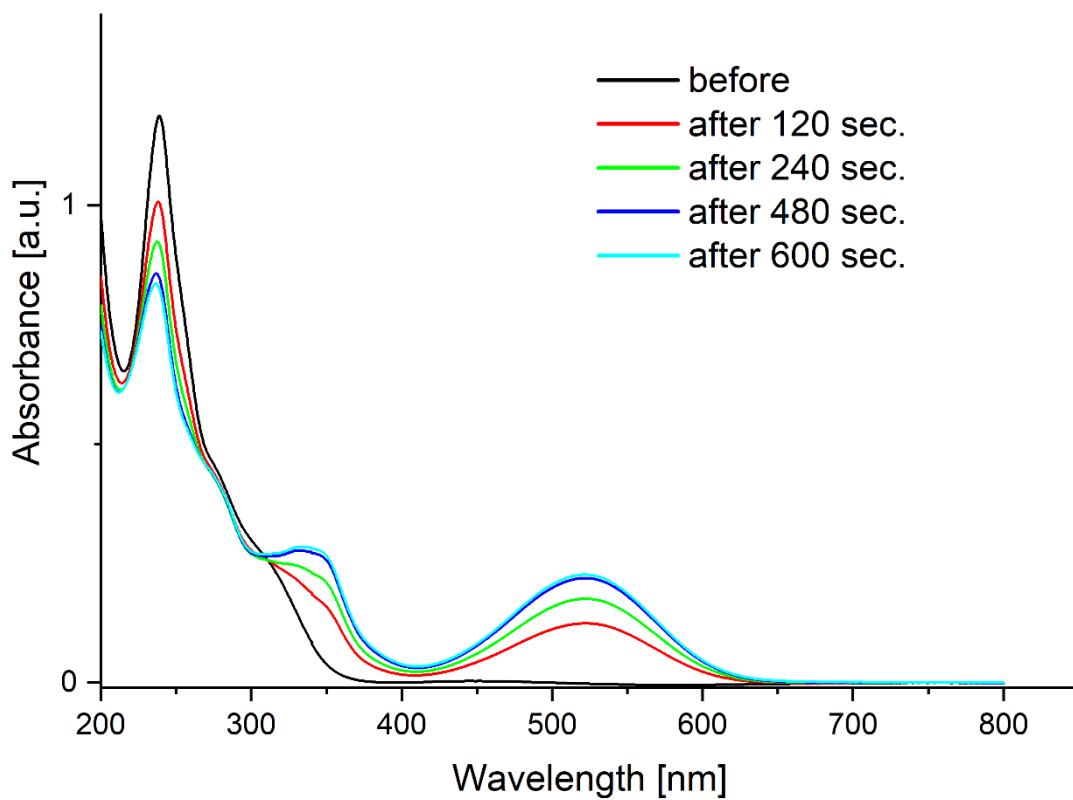


Figure S110: UV/Vis-spectrum / kinetics of BTE **23** on quartz sample (produced at 3000 rpm).

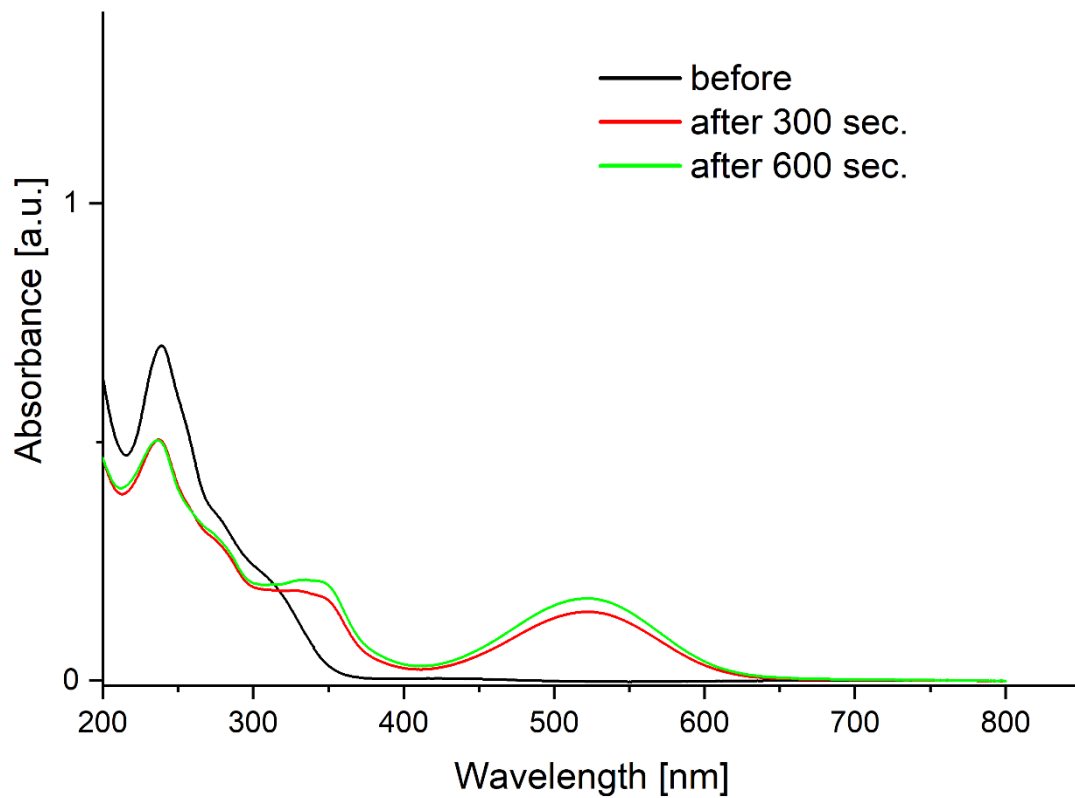


Figure S111: UV/Vis-spectrum / kinetics of BTE 23 on quartz sample (produced at 3500 rpm).

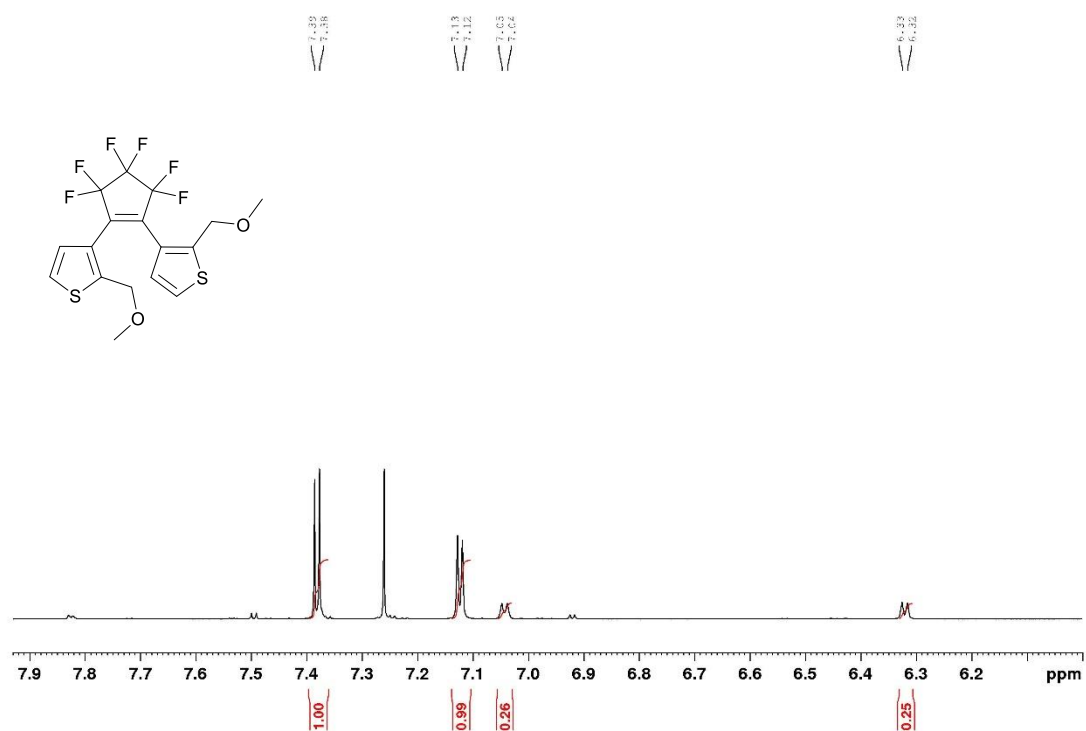


Figure S112: <sup>1</sup>H-NMR spectrum of **15a** (close-up after irradiating for 2h).

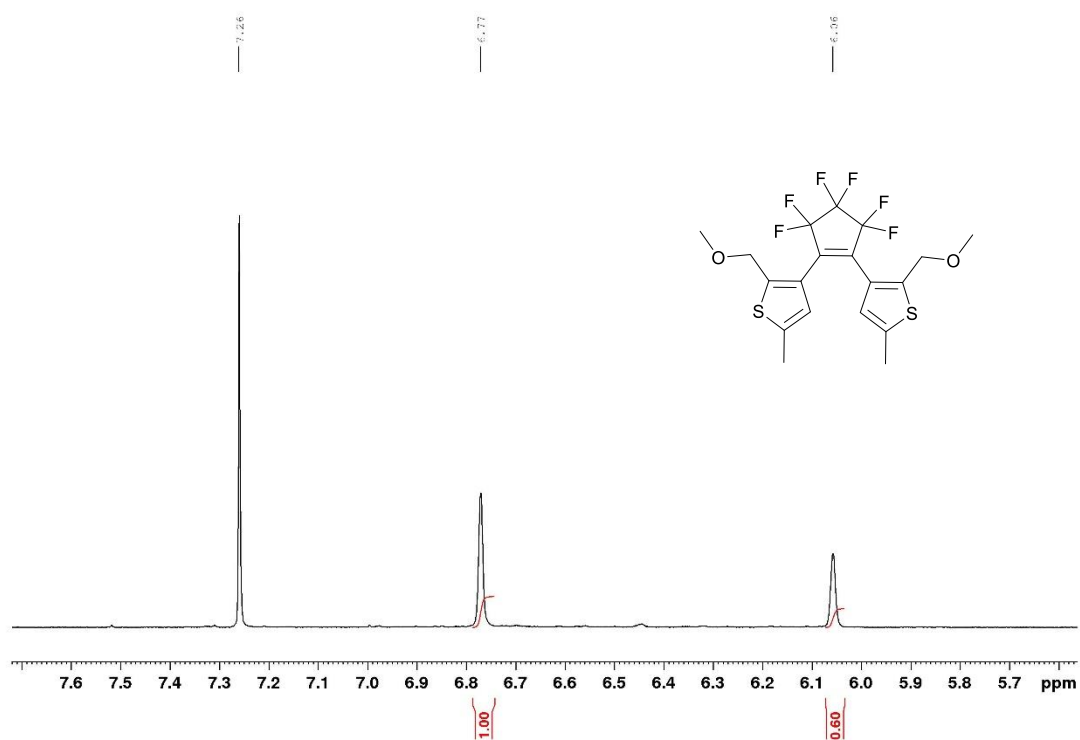


Figure S113: <sup>1</sup>H-NMR spectrum of **15b** (close-up after irradiating for 2h).

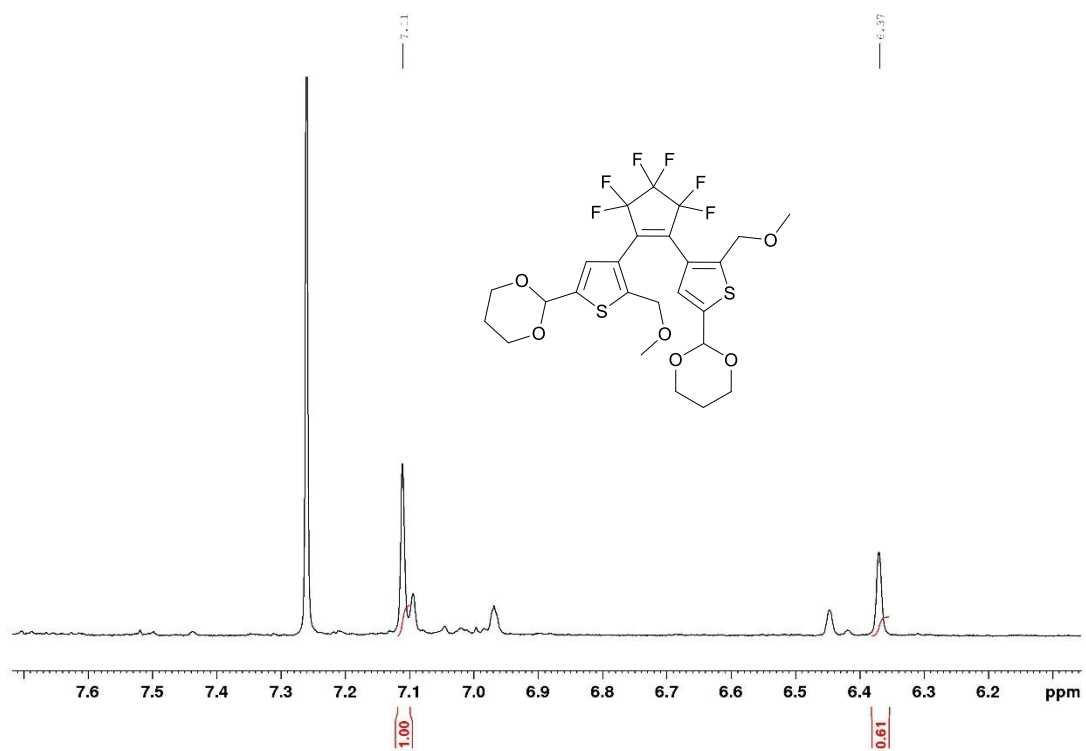


Figure S114: <sup>1</sup>H-NMR spectrum of **15c** (close-up after irradiating for 2h).

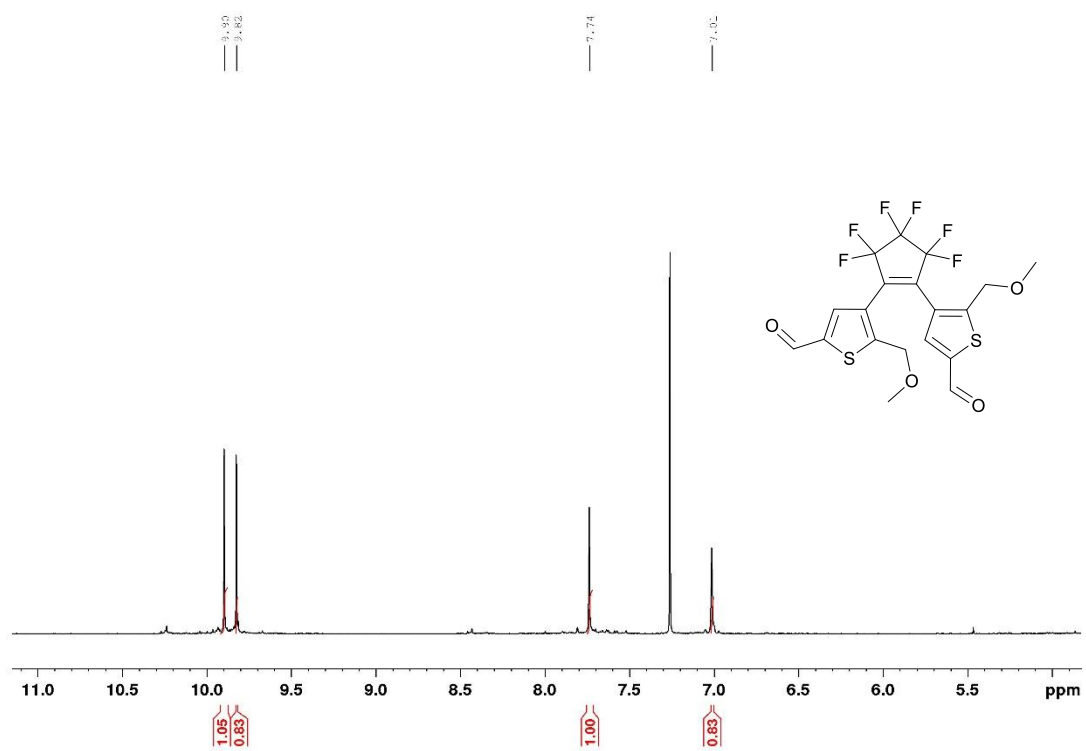


Figure S115: <sup>1</sup>H-NMR spectrum of **16** (close-up after irradiating for 2h).

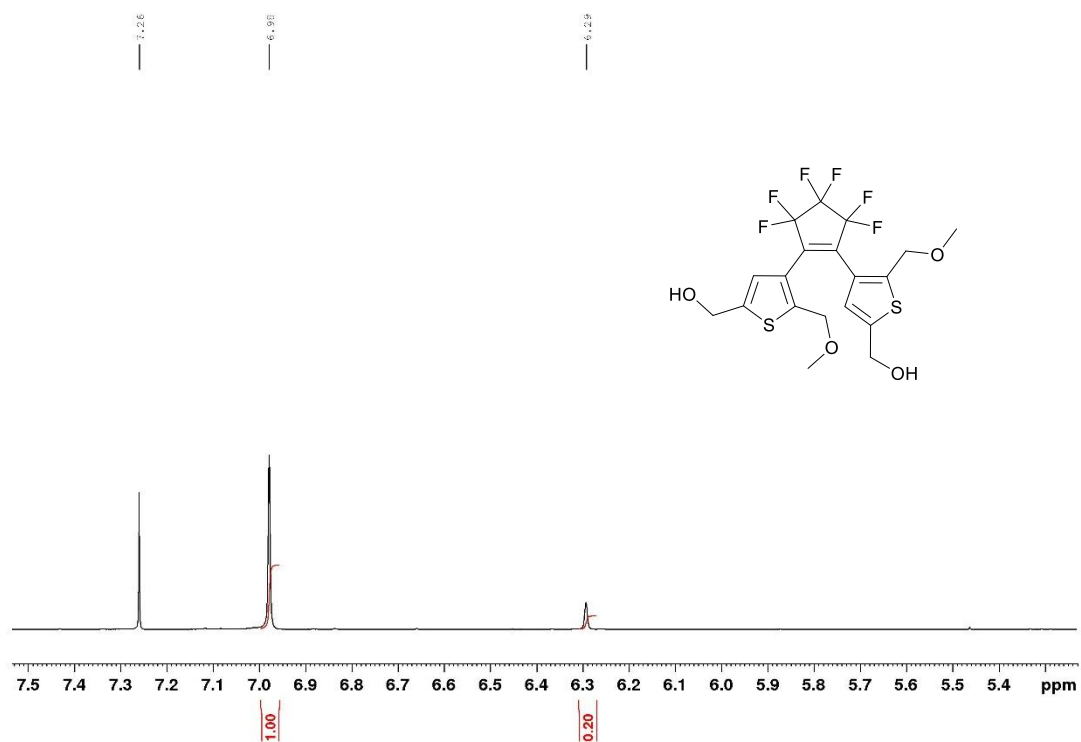


Figure S116: <sup>1</sup>H-NMR spectrum of **23** (close-up after irradiating for 2h).