Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

High-field and fast-spinning ^{1}H MAS NMR spectroscopy for the characterization of two-dimensional covalent organic frameworks

Nikolaj Lopatik,[a] Ankita De,[b] Silvia Paasch,[a] Andreas Schneemann,[b] and Eike Brunner[a]*

[a] Chair for Bioanalytical Chemistry, Faculty of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden, Germany

[b] Chair for Inorganic Chemistry I, Faculty of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden, Germany

1. Sample characterization

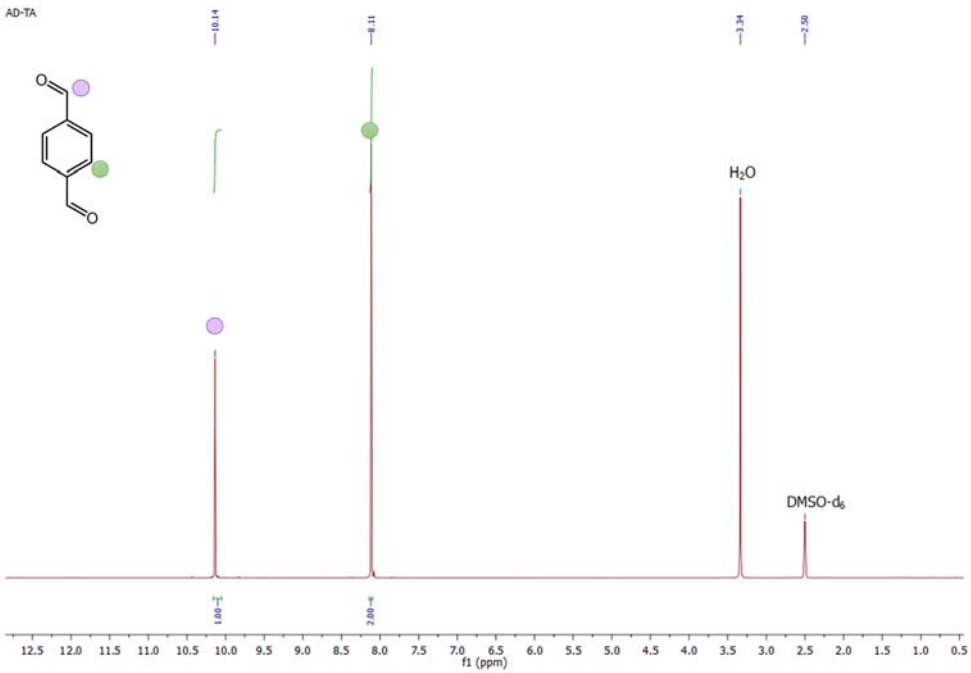

Figure S1: ^{1}H NMR spectra of terephthalaldehyde.

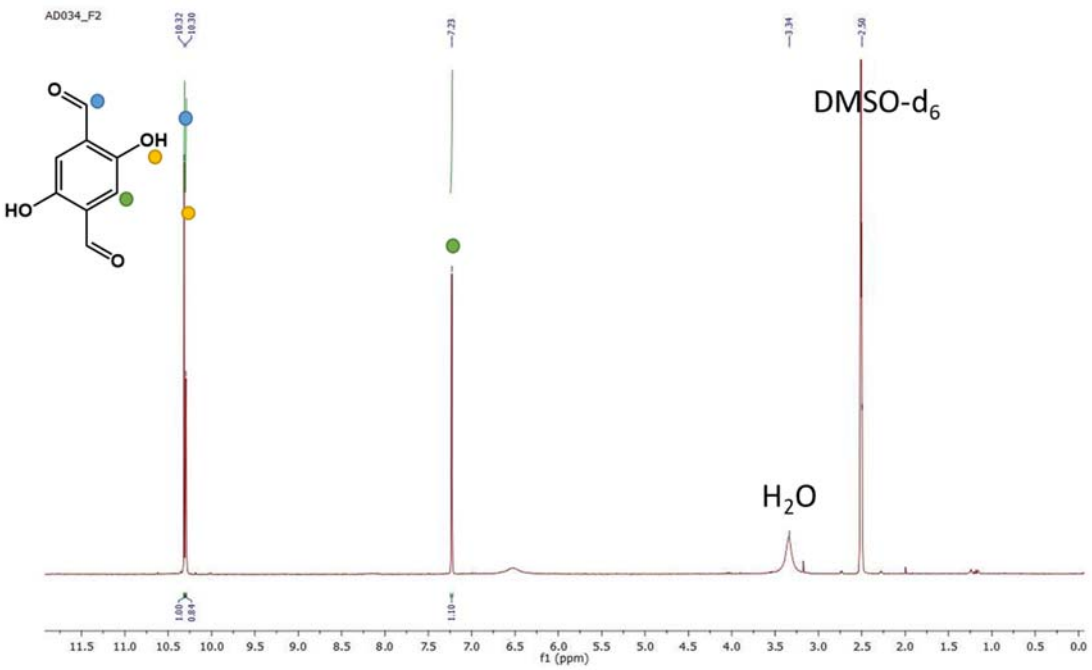

Figure S2: [1]H NMR of 2,5-dihydroxyterephthalaldehyde.

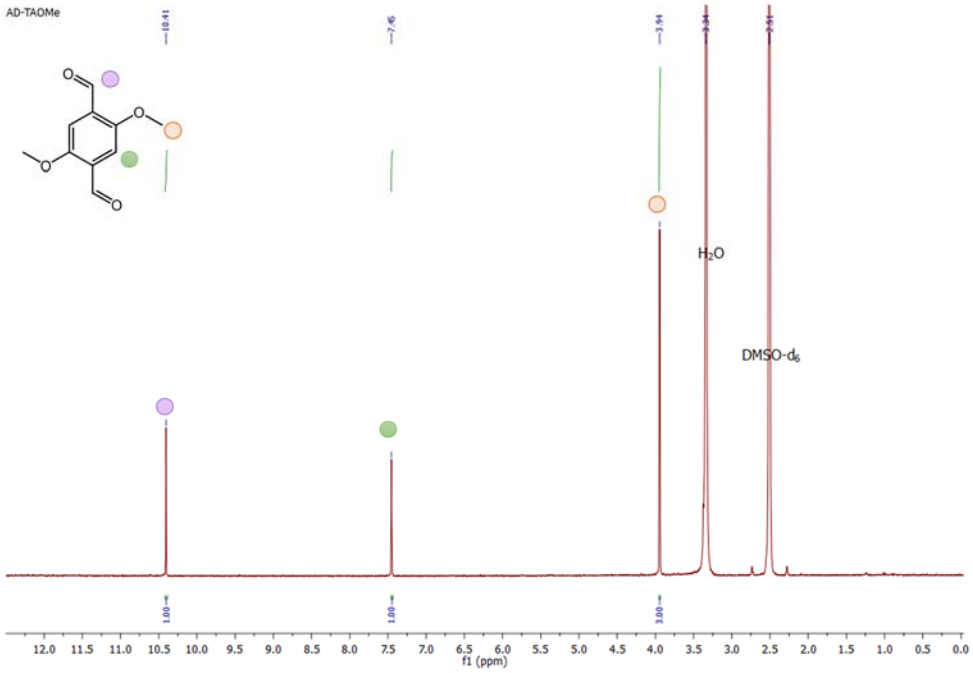

Figure S3: [1]H NMR spectra of 2,5-dimethoxyterphthalaldehyde.

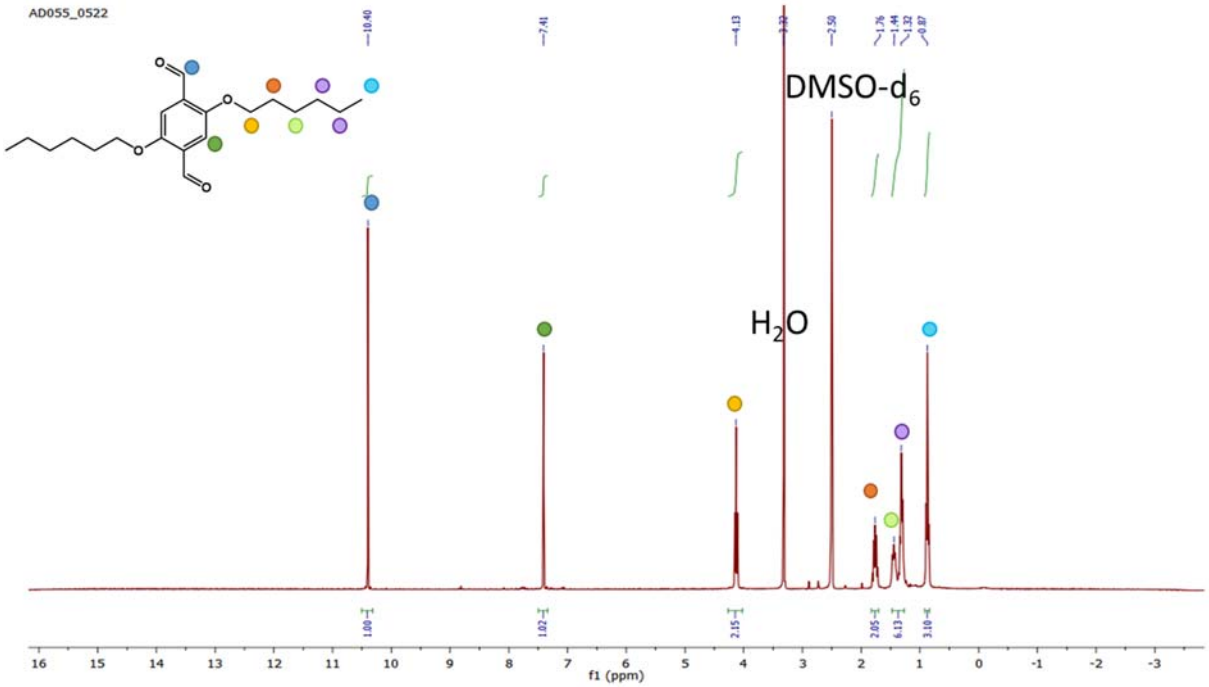

Figure S4: ^{1}H NMR spectra of 2,5-dihexoxyterphthalaldehyde.

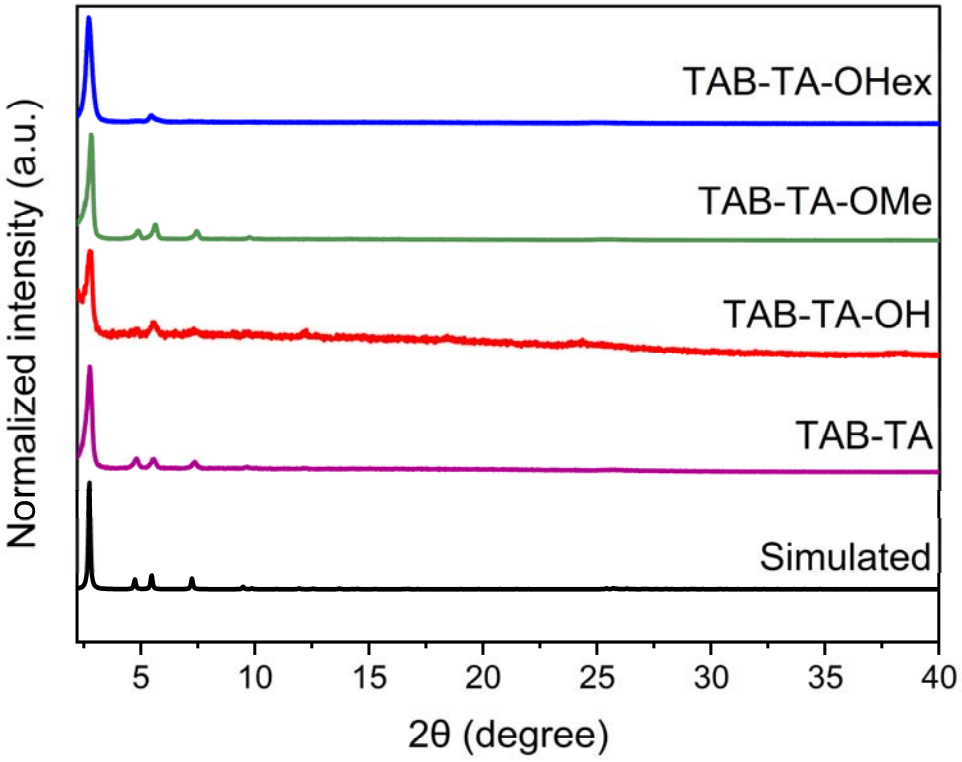

Figure S5: Powder X-ray diffractograms of the investigated samples including a simulated pattern.

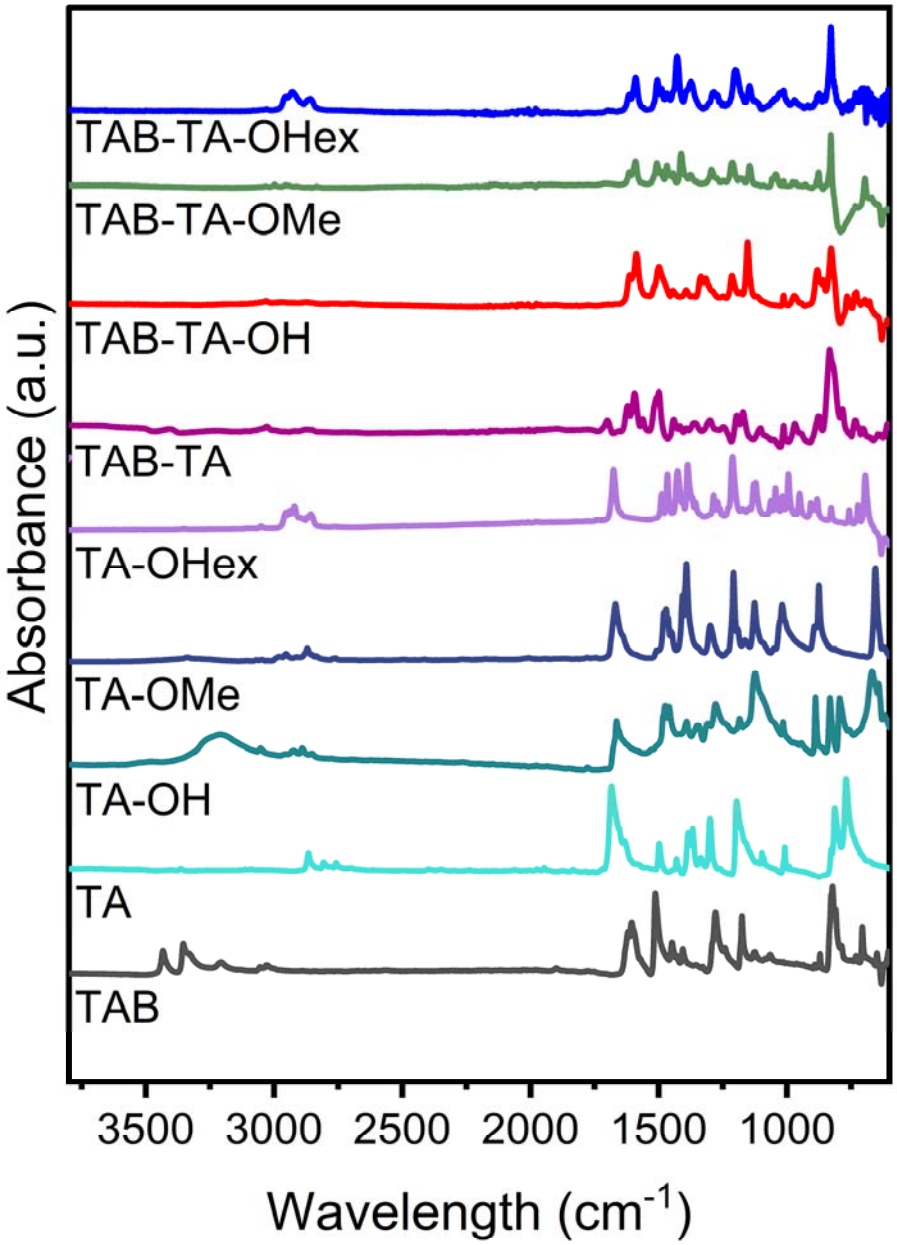

Figure S6: Infrared spectra of the studied samples and of intermediate products.

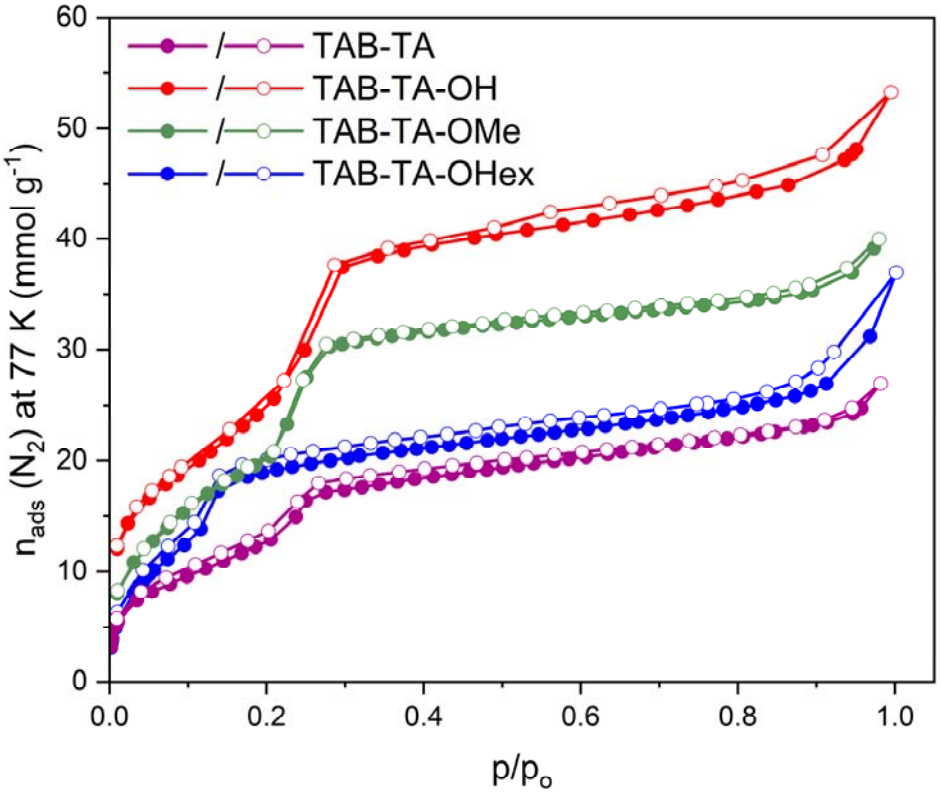

Figure S7: Nitrogen adsorption isotherms measured at 77 K.

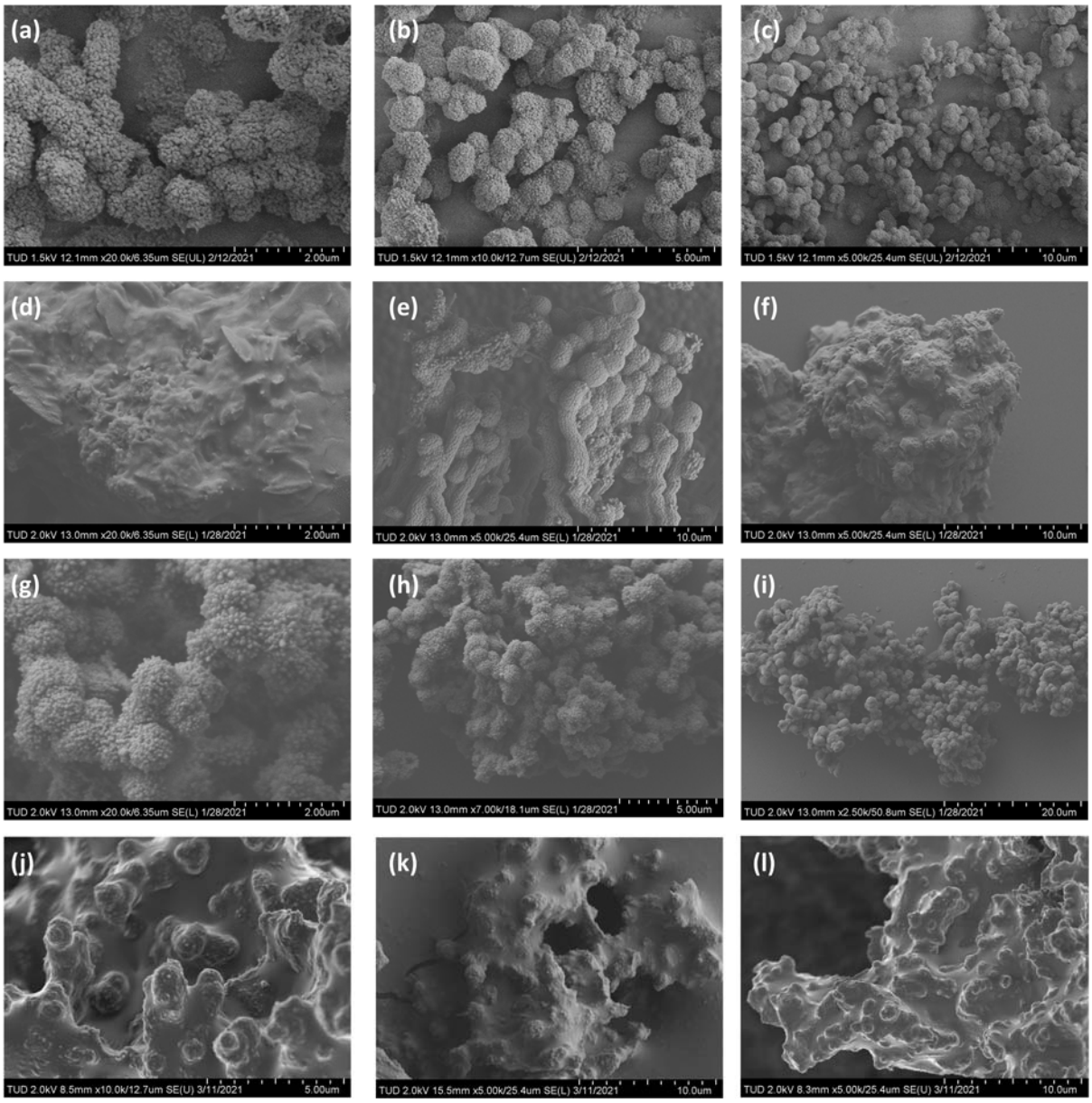

Figure S8: SEM images of the studied samples. a, b, c: TAB-TA, d, e, f: TAB-TA-OH, g, h, i: TAB-TA-OMe, j, k, l: TAB-TA-OHex.

2. Solid-state NMR experiments

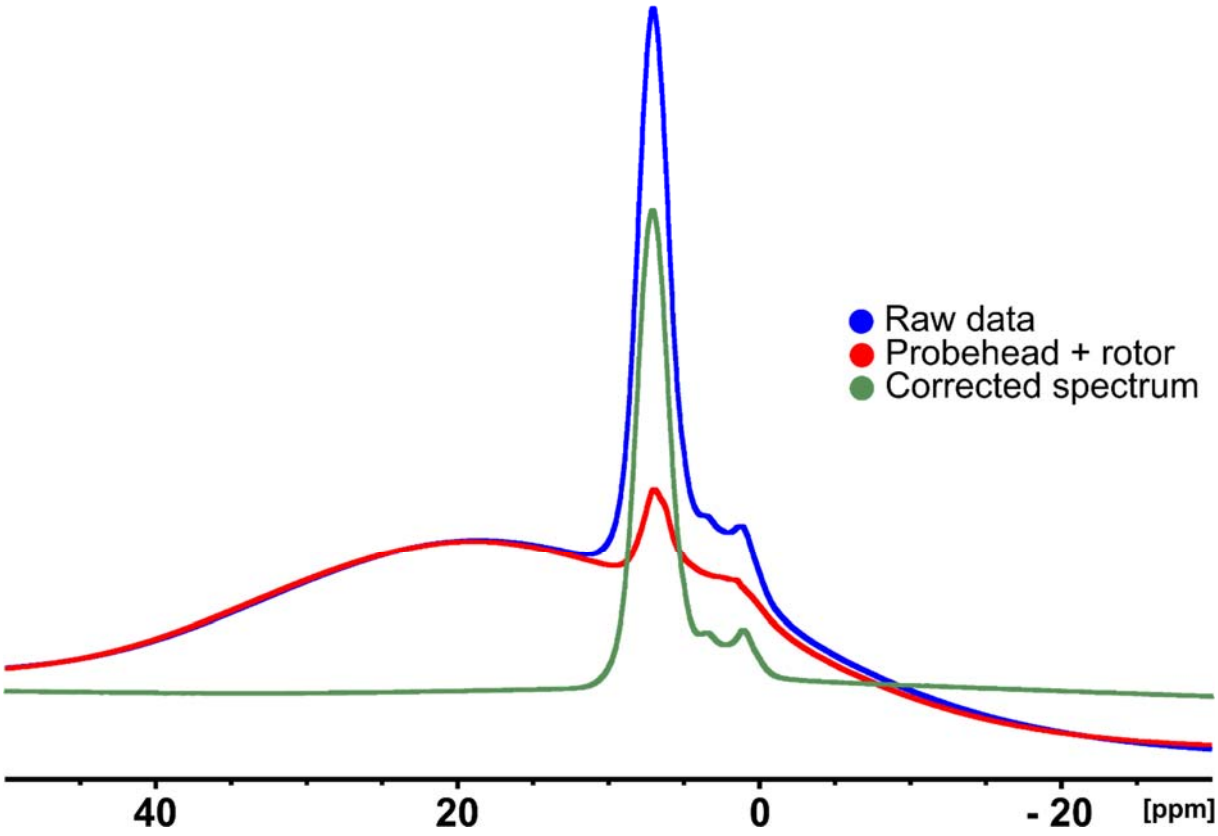

Figure S9: Demonstration of the subtraction of the ^{1}H MAS NMR signals due to probehead and rotor for TAB-TA measured 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate. Blue: Measured raw data for the sample filled into the rotor. Red: Spectrum measured for the empty, cleaned rotor spinning at 50 kHz. Green: Difference, i.e., background corrected spectrum of the sample.

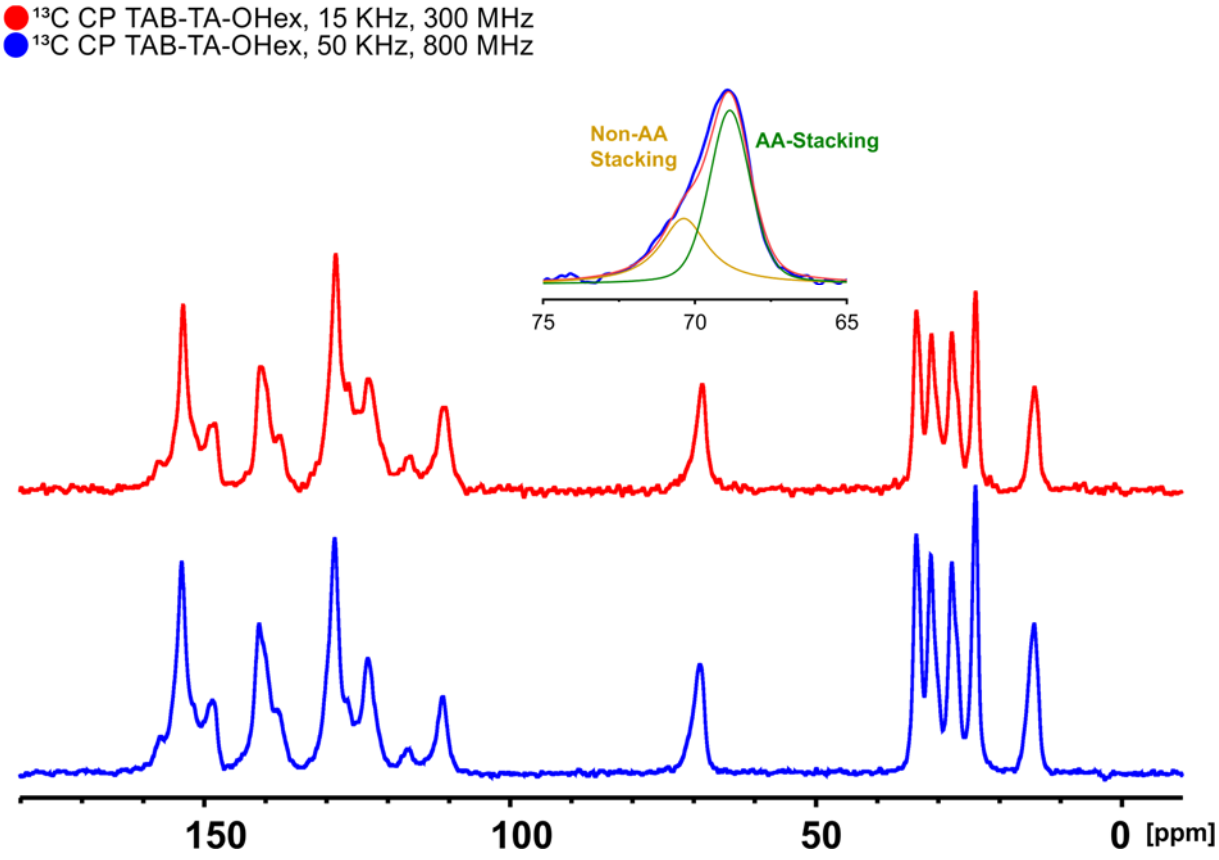

Figure S10: Proton-decoupled ^{13}C CP MAS NMR spectra of TAB-TA-OHex measured at field strengths corresponding to 300 and 800 MHz ^{1}H resonance frequency (CP contact time: 4 ms and 2 ms, respectively). Note that the measurements are carried out at different sample spinning rates (15 kHz and 50 kHz for 300 and 800 MHz ^{1}H resonance frequency, respectively).

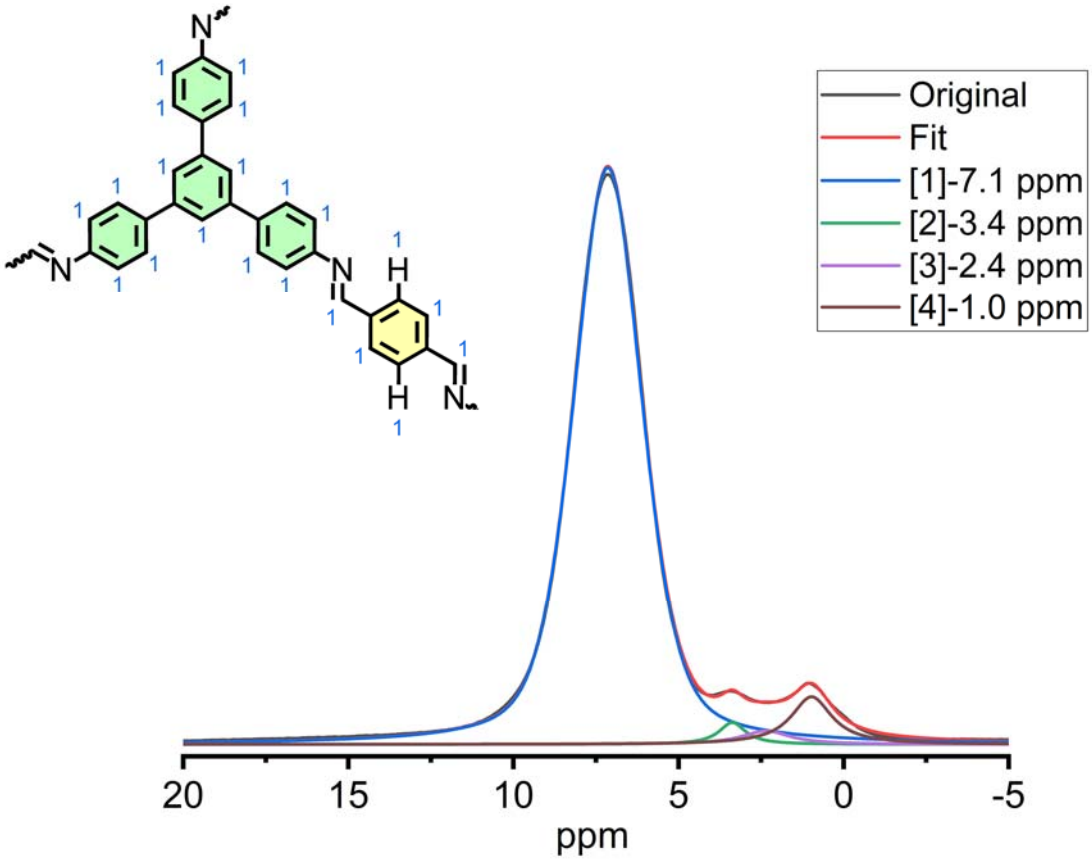

Figure S11: ^{1}H MAS NMR spectrum of TAB-TA measured 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate. The decomposition of the spectrum into the different lines is also provided. Signal assignments are indicated by numbers in the sketch showing the structure of TAB-TA.

Table S1: Predicted as well as measured chemical shifts and relative signal intensities for the lines determined by the decomposition of the ^{1}H MAS NMR spectrum of TAB-TA measured at 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate (cf. Figure S11).

^{1}H Signal	Predicted shift/ ppm	Measured shift/ ppm	Relative intensity/ %
1	7.0	7.1	91
2	-	3.4	2
3	-	2.4	2
4	-	1.0	5

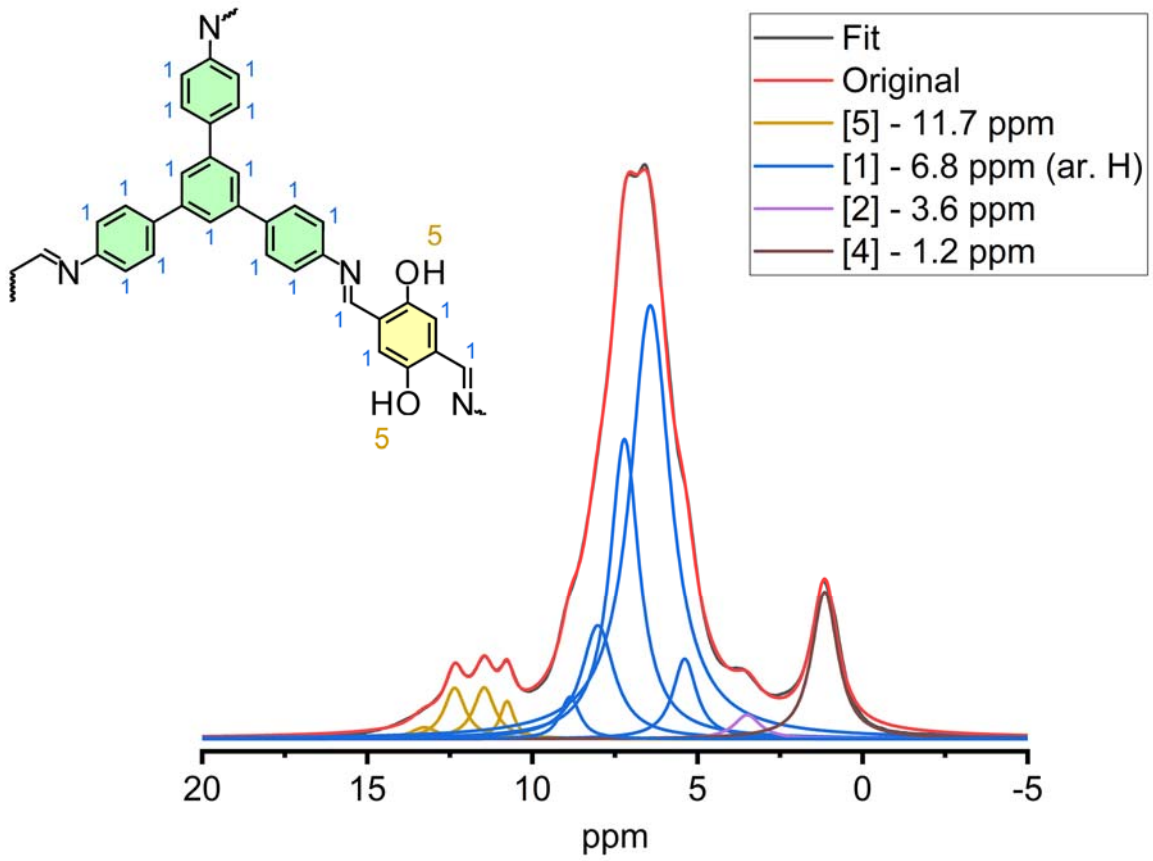

Figure S12: ^{1}H MAS NMR spectrum of TAB-TA-OH measured 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate. The decomposition of the spectrum into the different lines is also provided. Signal assignments are indicated by numbers in the sketch showing the structure of TAB-TA-OH.

Table S2: Predicted as well as measured chemical shifts and relative signal intensities for the lines determined by the decomposition of the ^{1}H MAS NMR spectrum of TAB-TA-OH measured at 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate (cf. Figure S12). * Weighted average position of the different signals in the decomposition shown in Figure S12.

^{1}H Signal	Predicted shift/ ppm	Measured shift/ ppm	Relative intensity/ %
1	7.0	6.8*	78
2	-	3.6	4
4	-	1.2	11
5	11.9	11.7* (10.8, 11.5, 12.4)	7

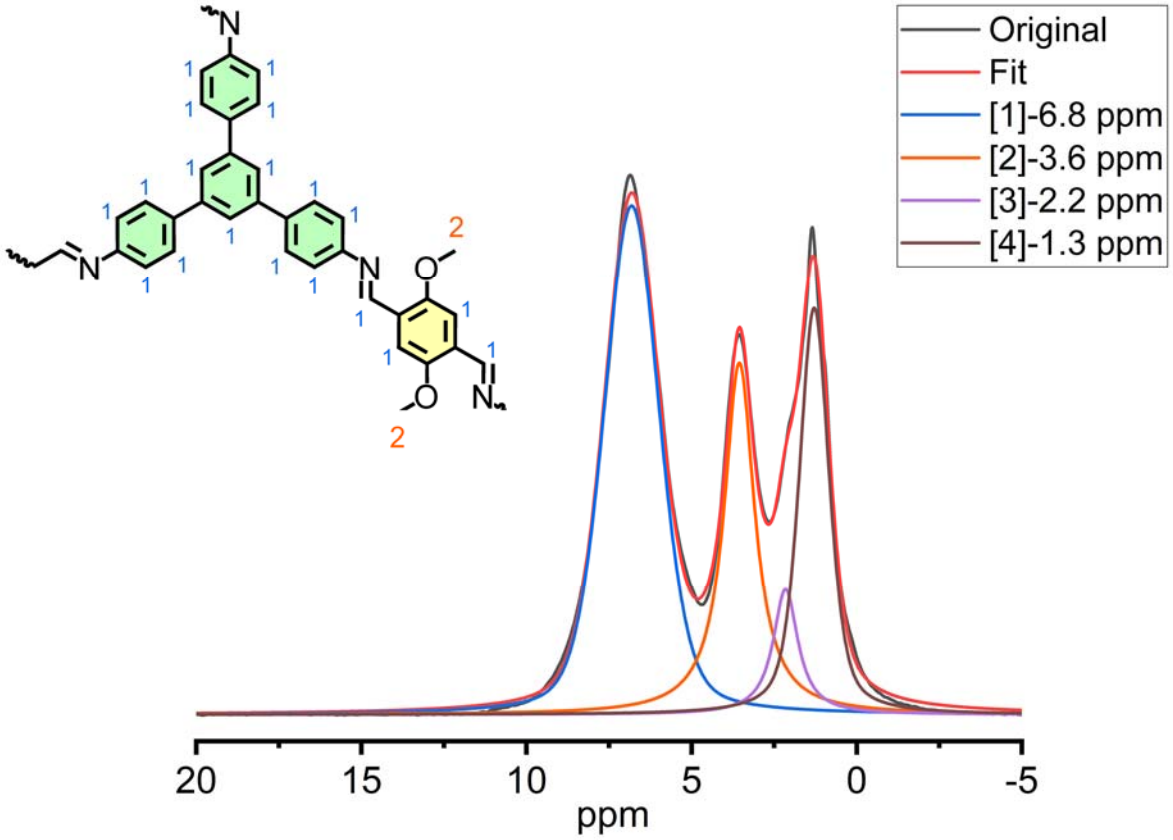

Figure S13: ^{1}H MAS NMR spectrum of TAB-TA-OMe measured 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate. The decomposition of the spectrum into the different lines is also provided. Signal assignments are indicated by numbers in the sketch showing the structure of TAB-TA-OMe.

Table S3: Predicted as well as measured chemical shifts and relative signal intensities for the lines determined by the decomposition of the ^{1}H MAS NMR spectrum of TAB-TA-OMe measured at 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate (cf. Figure S13).

^{1}H Signal	Predicted shift/ ppm	Measured shift/ ppm	Relative intensity/ %
1	7.0	6.8	47
2	3.8	3.6	24
3	-	2.2	7
4	-	1.3	22

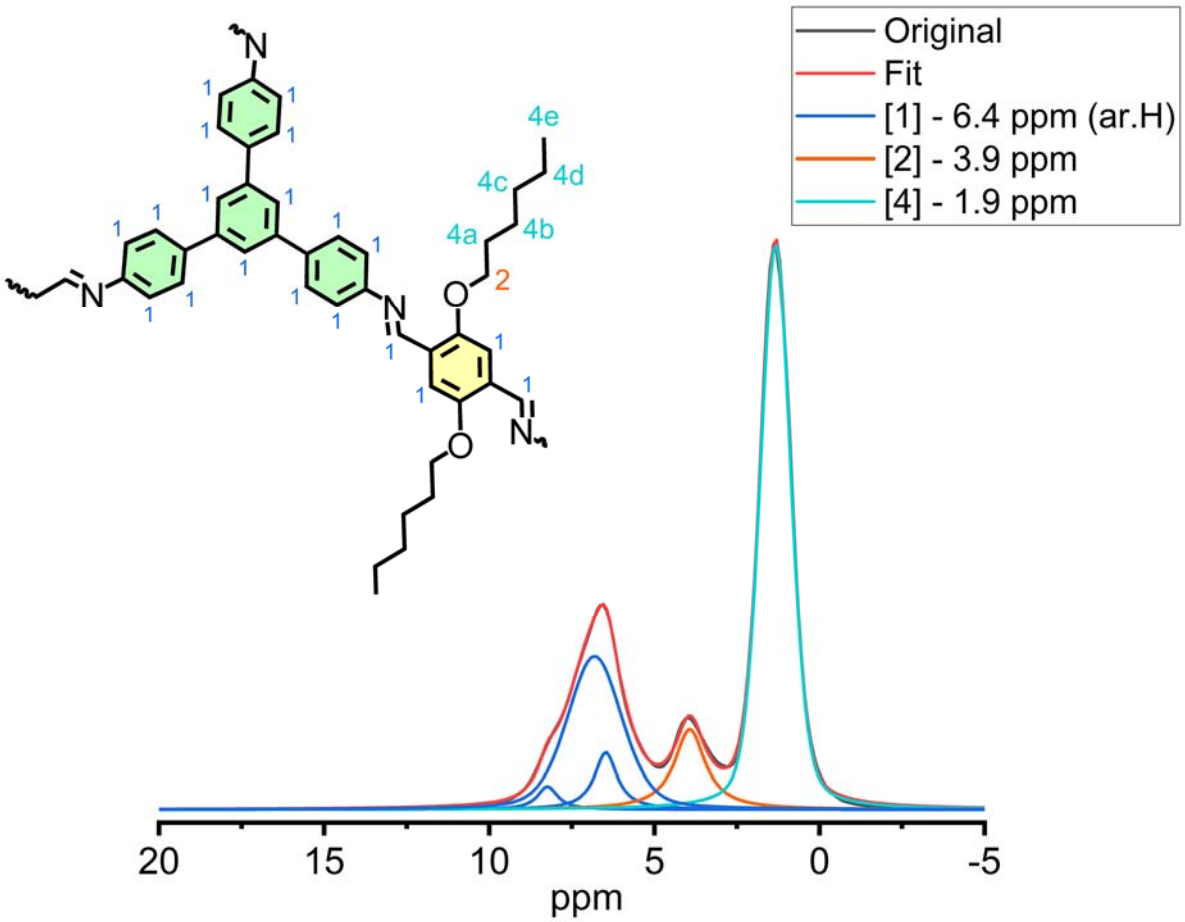

Figure S14: ^{1}H MAS NMR spectrum of TAB-TA-OHex measured 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate. The decomposition of the spectrum into the different lines is also provided. Signal assignments are indicated by numbers in the sketch showing the structure of TAB-TA-OHex.

Table S4: Predicted as well as measured chemical shifts and relative signal intensities for the lines determined by the decomposition of the ^{1}H MAS NMR spectrum of TAB-TA-OHex measured 800 MHz ^{1}H resonance frequency and 50 kHz sample spinning rate (cf. Figure S14). * Weighted average position of the different signals in the decomposition shown in Figure S14.

^{1}H Signal	Predicted shift/ ppm	Measured shift/ ppm	Relative intensity/ %
1	7.0	6.4*	34
2	4.0	3.9	10.5
4	1.6	1.9	55.5

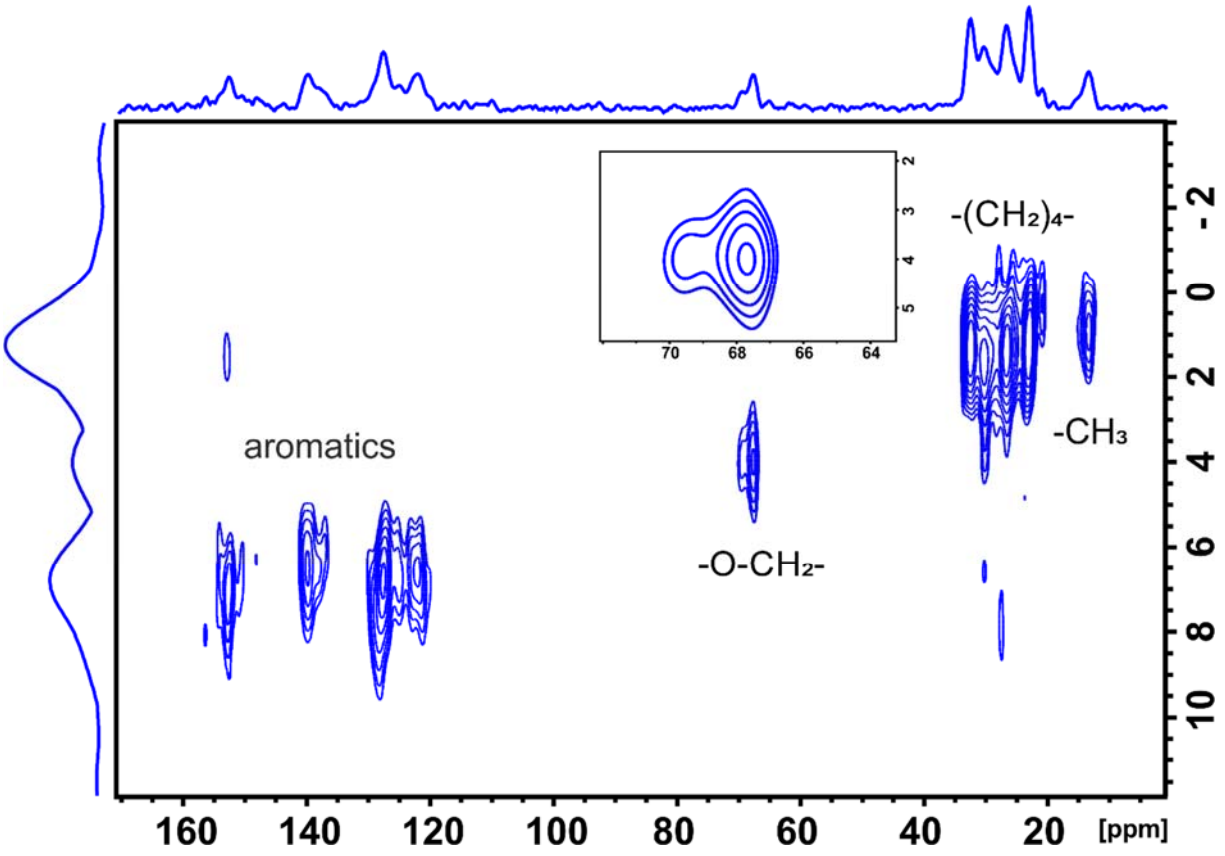

Figure S15: ^{1}H-^{13}C HETCOR spectrum of TAB-TA-OHex measured at a field strength corresponding to 800 MHz ^{1}H resonance frequency (CP contact time: 4 ms). Note the presence of two signal components for the ^{13}C signal of -O-CH_2- groups demonstrated in the insert.

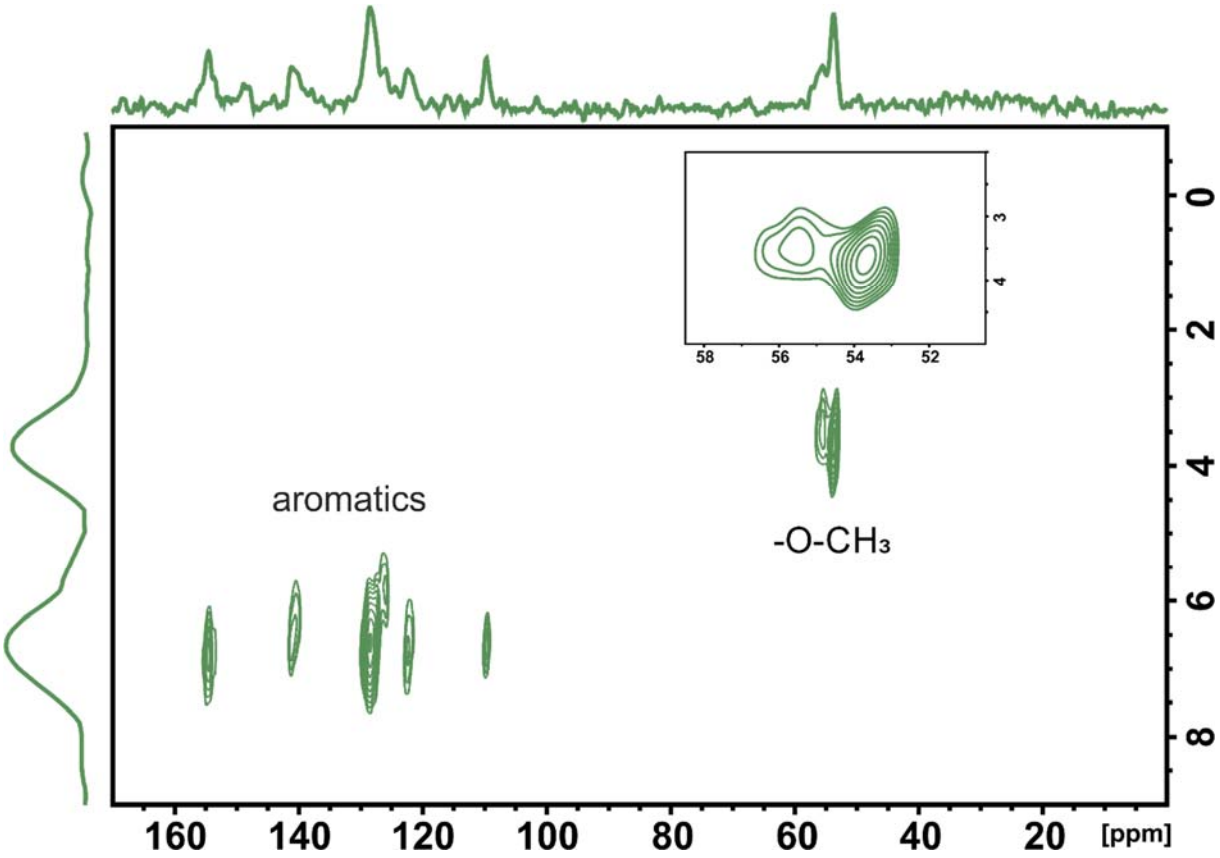

Figure S16: ^{1}H-^{13}C HETCOR spectrum of TAB-TA-OMe measured at a field strength corresponding to 800 MHz ^{1}H resonance frequency (CP contact time: 4 ms). Note the presence of two signal components for the ^{13}C signal of -O-CH_3 groups demonstrated in the insert.