Supporting Information

Two metal-organic frameworks with a tetratopic linker: Solvent dependent polymorphism and post-synthetic bromination

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Experimental Details

(1) Synthesis of the linker

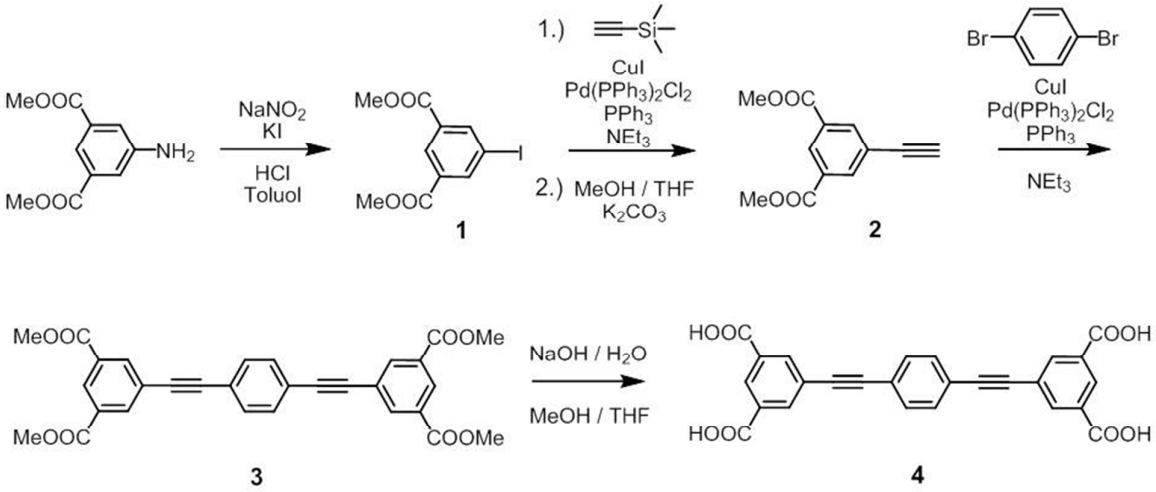


Figure S1: Synthesis scheme of the linker 5,5'-(1,4-Phenylenedi-2,1-ethinyl)bis(1,3-benzene-dicarboxylic acid).

Chemicals. 1,4-dibromobenzene (Fluka, ≥ 97%), trimethylsilylacetylene (ABCR, 98%), dichlorobis(triphenylphosphine)palladium (ABCR, 99%), copper iodide (Sigma-Aldrich, ≥ 99.5%), triphenylphosphine (Sigma-Aldrich, ≥ 95.0%), dimethyl 5-aminoisophthalate (Sigma-Aldrich), sodium nitrite (Merck, extra pure) and potassium iodide (Applichem, 99.0%) were used without further purification. Triethylamine (Grüssing, 99%) was used after drying; Methanol (Honeywell, for HPLC), tetrahydrofuran (THF) (Grüssing, 99.5%), bromine (Merck, *for synthesis*) *N*,*N*-dimethylformamide (DMF) (Sigma-Aldrich, ≥ 99.8%), dioxane (Honeywell, *pure*) and ethanol (Merck, *absolute*) were used as obtained.

Methods. NMR spectra were acquired using a Bruker Fourier 300 NMR spectrometer. Infrared spectra were recorded with a Bruker Vertex 70 FT-IR spectrometer. PXRD patterns

were obtained at room temperature using a STOE STADI P transmission powder diffractometer with Cu Kα radiation (40 kV, 30 mA, counting time 20 s, step size: 0.01° (2θ)).

Synthesis of the linker 5,5'-(1,4-Phenylenedi-2,1-ethinyl)-bis(1,3-benzenedicarboxylic acid). *Dimethyl 5-iodoisophthalate (**3**).* 26.0 g (124 mmol) of dimethyl 5-aminoisophthalate were suspended in 100 mL aq. hydrochloric acid (6 M) and cooled to -10 °C before a solution of 8.63 g (125 mmol) sodium nitrate in 50 mL water was added over a period of 1 hour. Afterward, 200 mL of toluol as well as a solution of 42.0 g (253 mmol) potassium iodide in 50 mL water were added. The reaction mixture was stirred for 18 hours at room temperature and then heated under reflux for one hour. After cooling and phase separation the organic phase was extracted with aq. $Na_2S_2O_3$ solution and HCl (1 M) and dried over sodium sulfate. After evaporating the solvent in vacuum the raw product was obtained, which was purified by recrystallization from methanol to give 24.3 g (75.9 mmol, yield: 61%) of a pale yellow powder.

^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm]: 8.63 (t, 1H), 8.55 (d, 2H), 3.95 (s, 6H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ [ppm]: 164.89, 142.56, 132.26, 129.96, 93.56, 52.78; IR [cm^{-1}]: 3023, 3023, 1709, 1568, 1432, 1291, 1235, 1099, 990, 964, 746, 714.

*Dimethyl 5-ethinylisophthalate (**2**)*. Under nitrogen atmosphere 10.0 g (31.2 mmol) of (1), 1.19 g (6.25 mmol) CuI, 1.64 g (6.25 mmol) triphenylphosphine and 1.10 g (1.56 mmol) dichlorobis(triphenylphosphine) palladium were dissolved in 200 mL of dried triethylamine. After heating to 90 °C 6.0 mL (37.5 mmol) of trimethylsilylacetylene were added dropwise and the reaction mixture was stirred at 90 °C for 15 h. After separating the insoluble residue the organic solvent was evaporated in vacuum. The raw product was purified by column chromatography with dichloromethane to give a light yellow powder. Afterward, this product was dissolved in 150 mL MeOH/THF (1:1) and 5.0 g (21.7 mmol) potassium carbonate was added. The reaction mixture was stirred for 2 hours at room temperature. Then, the organic

phase was removed and the water phase was extracted with DCM. After drying the DCM over sodium sulfate, the solvent was evaporated in vacuum to give 5.12 g (23.5 mmol, yield: 75%) of a light yellow powder.

^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm]: 8.62 (t, 1H), 8.30 (d, 2H), 3.94 (s, 6H), 3.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ [ppm]: 165.54, 137.15, 131.06, 130.77, 123.29, 81.65, 79.31, 52.69; IR [cm^{-1}]: 3270, 3067, 2957, 2104, 1593, 1488, 1381, 781.

5,5´-(1,4-Phenylenedi-2,1-ethinyl)bis(dimethyl 1,3-benzenedicarboxylic acid) (**3**). Under nitrogen atmosphere 2.16 g (9.16 mmol) 1,4-dibromobenzene, 0.35 g (1.83 mmol) CuI, 0.48 g (1.83 mmol) triphenylphosphine and 0.32 g (0.46 mmol) dichlorobis(triphenylphosphine) palladium were dissolved in 60 mL of dried triethylamine. After heating to 90 °C 5.00 g (22.9 mmol) of (2) dissolved in 40 mL THF were added dropwise and the reaction mixture was stirred at 90 °C for 15 h. Then, the precipitate was separated from the solvent, washed with THF and dissolved in dichloromethane. The solution was extracted twice with water and aq. sodium chloride. After drying the DCM over sodium sulfate, the solvent was evaporated in vacuum to give 2.79 g (5.46 mmol, yield: 60%) of a light brown powder.

^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm]: 8.64 (t, 2H) 8.38 (d, 4H) 7.55 (s, 4H) 3.97 (s, 12H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ [ppm]: 165.8, 136.7, 132.0, 131.3, 130.5, 124.3, 123.1, 91.0, 89.7, 52.8; IR [cm^{-1}]: 3080, 2953, 2216, 1726, 1593, 1435, 1428, 1242, 997.

5,5'-(1,4-Phenylenedi-2,1-ethinyl)bis(1,3-benzenedicarboxylic acid) (**4**). 2.55 g (5.0 mmol) of (3) was dissolved in 50 mL of MeOH/THF (1:1). After addition of 100 mL of aq. KOH (3M) the reaction mixture was heated under reflux for 4 hours. Afterward, the solvent was evaporated in vacuum and the aq. solution was acidified with HCl (6M) to give a precipitate, which was filtrated and dried under vacuum. 1.71 g (3.76 mmol, yield: 75%) of a light orange product was obtained.

^{1}H NMR (DMSO-d6, 300 MHz): δ [ppm]: 8.4 (t, 2H), 8.3 (d, 4H), 7.7 (s, 4H); ^{13}C NMR (DMSO-d6, 300 MHz): δ [ppm]: 165.8, 135.6, 132.1, 132.0, 129.9, 123.1, 122.3, 90.4, 89.6; IR [cm^{-1}]: 2847, 2518, 2362, 1692, 1438, 1277, 907, 757, 693.

(2) Thermal analysis of UHM-8 and UHM-9

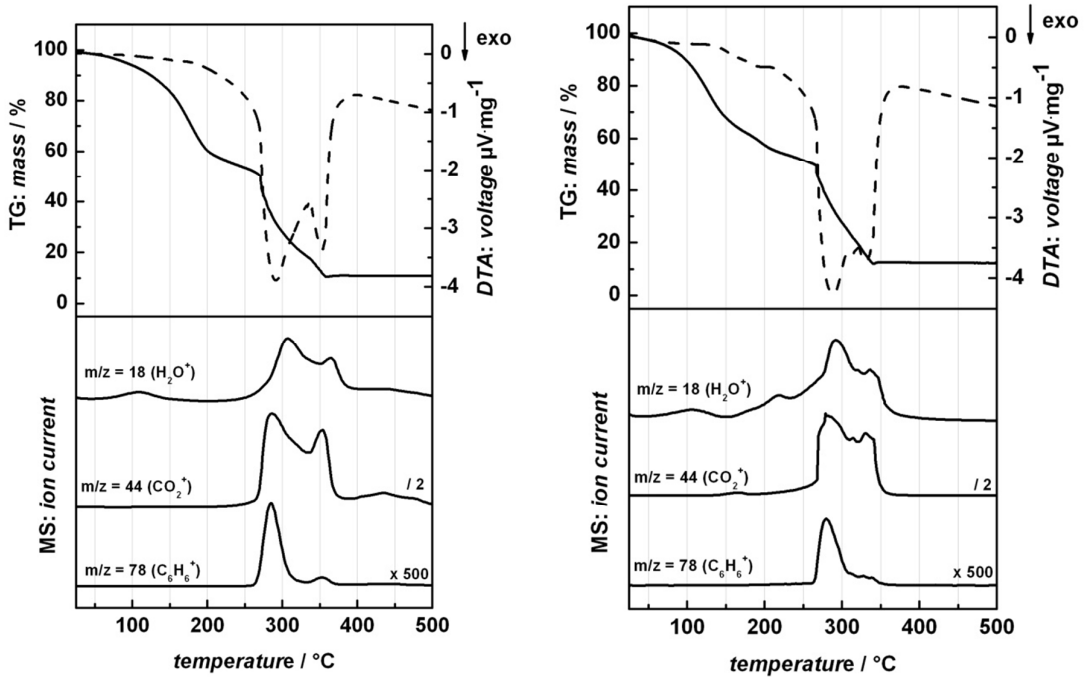


Figure S2: Thermogravimetric analysis of UHM-8 (left) and UHM-9 (right).

(3) PXRDs of the five different phases

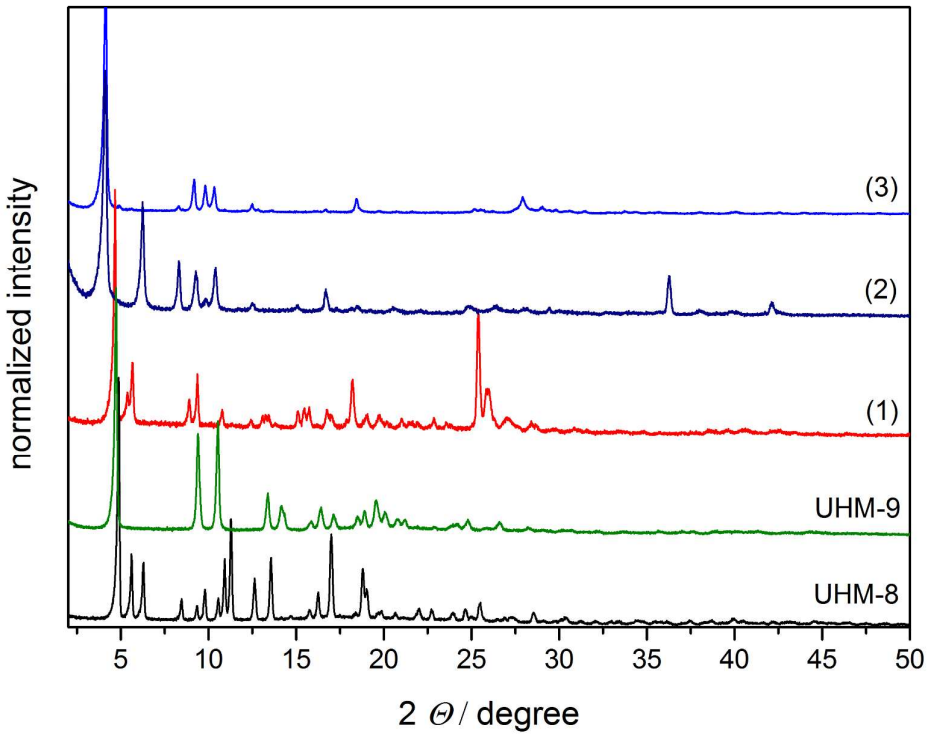
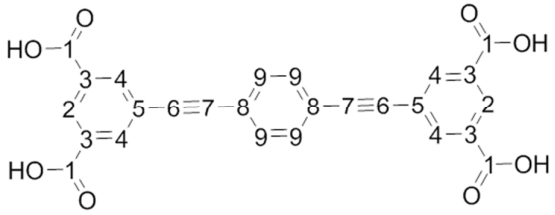


Figure S3: PXRDs of the two polymorphs UHM-8 and UHM-9 (black and green) in comparison with the PXRDs of three further phases (red, light blue and dark blue) that have been synthesized with slightly different synthesis parameters.

(4) Isolation and characterization of the linker after bromination of the MOF

UHM-8-Br was dissolved with the help of diluted hydrochloric acid and the linker was recrystallized and dried. The isolated brominated linker was characterized using ^{1}H- and ^{13}C-NMR spectroscopy whereby the complete bromination of the triple bond is confirmed. The signals at 89.6 and 90.4 ppm in the spectrum of the original linker (Figure S5), characteristic for the carbon atoms in triple bonds, disappeared. Instead, new signals at 118.9 and 116.4 ppm appear, indicating the presence of C=C double bonds with bromine substituents (Figure S7). All signals could be assigned explicitly to a completely brominated linker. Hence, the existence of a linker mixture of brominated/half brominated and unbrominated linker can be excluded. The bromination of the aromatic ring could also be excluded because no change in the proton NMR after the bromination process was observed (Figure S4 and S6).

^{1}H-, ^{13}C- NMR data of the unbrominated linker



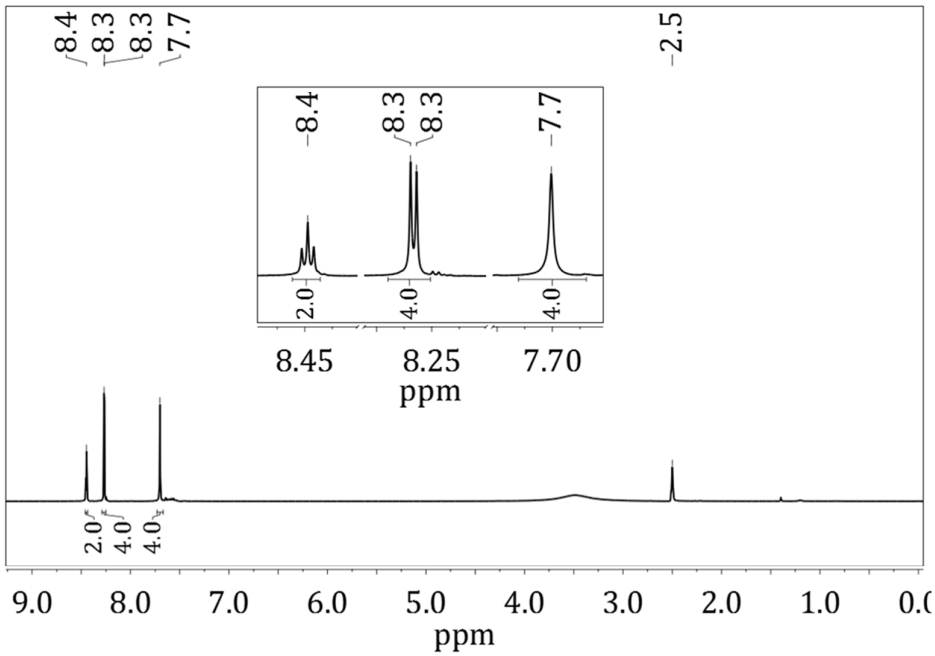


Figure S4: [1]H-NMR (DMSO-d6, 300 MHz) of the unbrominated linker: δ[ppm]: 8.4 (t, 2H, H2), 8.3 (d, 4H, H4), 7.7 (s, 4H, H9), other signals: δ [ppm]: 2.5 (DMSO).

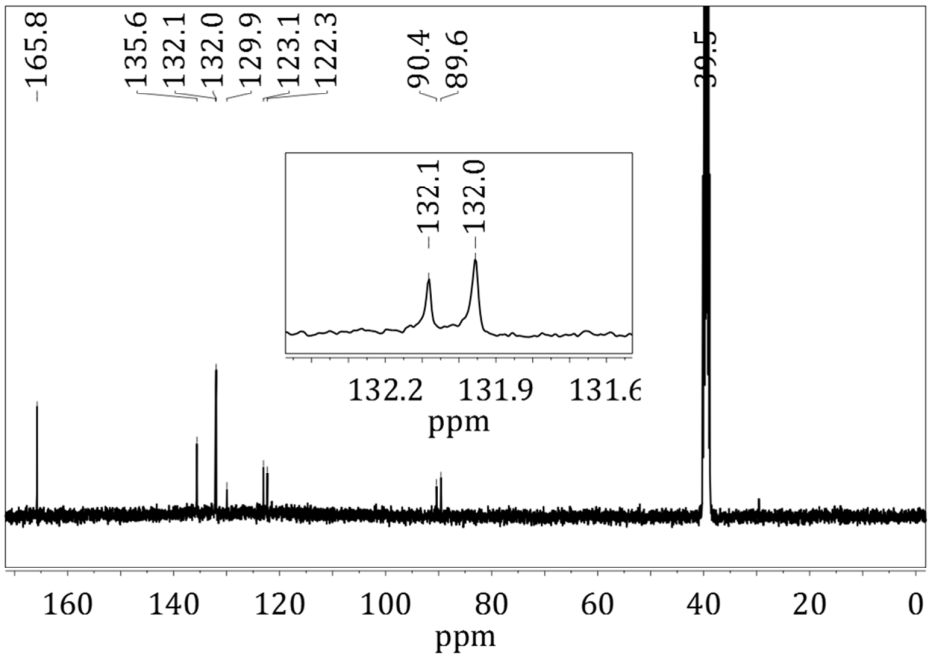
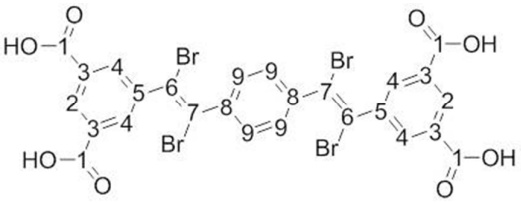


Figure S5: [13]C-NMR (DMSO-d6, 300 MHz) of the brominated linker after recrystallization: δ[ppm]: 165.8 (C1), 135.6 (C4), 132.1 (C3), 132.0 (C9), 129.9 (C2), 123.1 (C5), 122.3 (C7), 90.4 (C7), 89.6 (C6), other signals: δ [ppm]: 39.5 (DMSO).

^{1}H-, ^{13}C- NMR data of the brominated linker



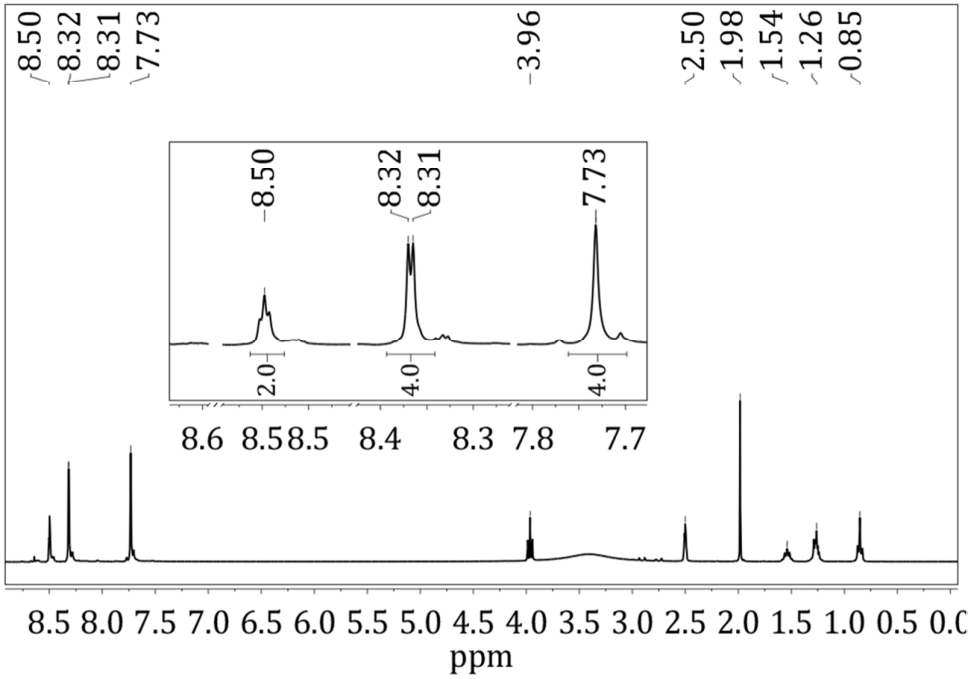


Figure S6: ^{1}H-NMR (DMSO-d6, 300 MHz) of the brominated linker after recrystallization: δ[ppm]: 8.5 (t, 2H, H2), 8.3 (d, 4H, H4), 7.7 (s, 4H, H9), other signals: δ [ppm]: 2.5 (DMSO), 4.0, 2.0, 1.5, 1.3, 0.9 (pentyl acetate).

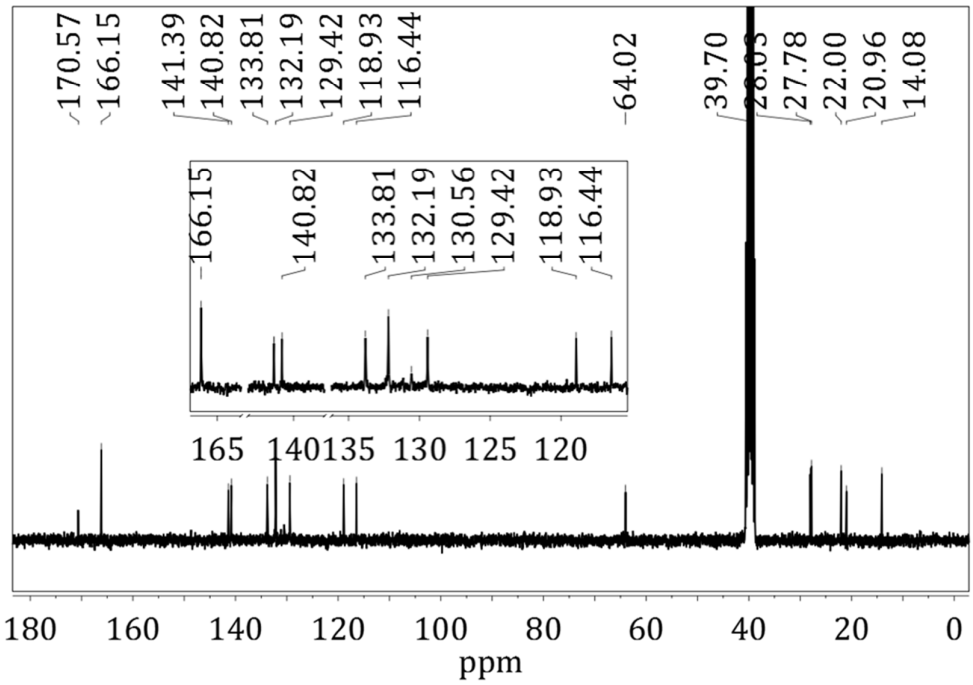


Figure S7: ^{13}C-NMR (DMSO-d6, 300 MHz) of the brominated linker after recrystallization: δ[ppm]: 166.2 (C1), 141.4 (C5), 140.8 (C8), 133.8 (C4), 132.2 (C3), 130.6 (C2), 129.4 (C9), 118.9 (C7), 116.4 (C6), other signals: δ [ppm]: 39.7 (DMSO), 170.6, 64.0, 28.0, 27.8, 22.0, 21.0, 14.1 (pentyl acetate).