Supporting Information

Screening Metal-Organic Frameworks for Separation of Binary Solvent Mixtures by Compact NMR Relaxometry
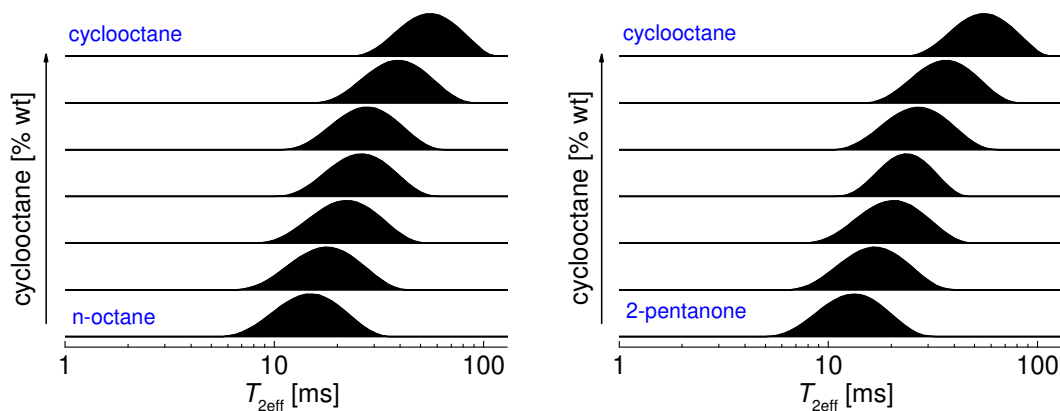
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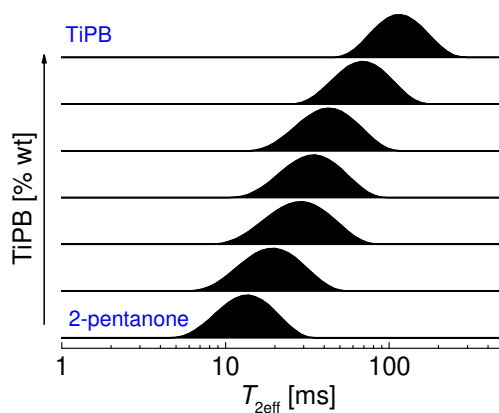
Results

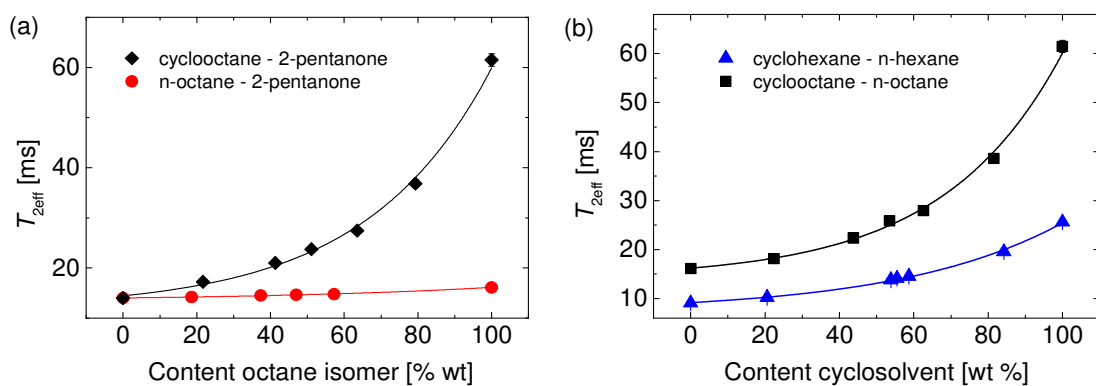**Figure S1**. Exemplarily ILT spectra of various investigated mixtures.

Figure S2. Correlation curves for different binary mixtures. The continuous lines are the fit results using a single exponential function and has for all samples a correlation factor higher than 0.99. The fit equations are: T_{2eff} (cyclooctane – 2-pentanone) = 4.04*exp(content/39.53)+10.67; T_{2eff} (n-octane – 2-pentanone) = 0.60*exp(content/68.03)+13.48; T_{2eff} (cyclohexane – n-hexane) = 1.75*exp(content/44.76)+7.18; T_{2eff} (cyclooctane – n-octane) = 1.49*exp(content/29.15)+15.15.
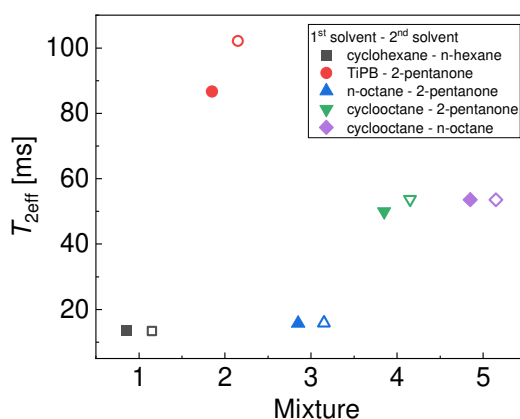
Figure S3. Changes in the effective relaxation times before (closed symbols) and after separation (open symbols) with UiO-66(Zr) for all investigated mixtures.

Table S1. Proton transverse relaxation times T_{2eff} of the pure solvents measured using the NMR-MOUSE at room temperature and using the experimental conditions described in the experimental section. Diffusion coefficients and viscosity values are also shown for better understanding the obtained values for the T_{2eff}.

Solvent	T_{2eff} [ms]	Diffusion coefficient at room temperature [10^{-9} m^2 s^{-1}]	Viscosity [mPa s]	Kinetic diameter [Å]
n-pentane	6.34	5.72[1]	0.24 (20 °C)[1]	4.3[5]
2-pentanone	14.01	-	0.50 (20 °C)[1]	
n-hexane	9.07	4.1[1]	0.3 (25 °C)[2]	4.3[5]
cyclohexane	25.61	1.48[3]	0.89 (25 °C)[3]	6[5]
n-octane	16.13	2.35[3]	0.51 (25 °C)[3]	4.3[5]
cyclooctane	61.46	0.56[3]	1.96 (25 °C)[3]	8[6]
TiPB	113.62	0.14[4]	3.53 (20 °C)[4]	8.5[7]

[1]https://en.wikipedia.org

[2]https://wiki.anton-paar.com/en/hexane

[3]Tofts, P. S.; Lloyd, D.; Clark, C. A.; Barker, G. J.; Parker G. J. M.; McConville, P.; Baldock, C.; Pope, J. M. Test liquids for quantitative MRI measurements of self-diffusion coefficient in vivo. *Magn. Reson. Med.* **2000**, 43, 368–374.

[4]Fischer, J.; Weiss, A. Transport properties of liquids. V. self-diffusion, viscosity, and mass density of ellipsoidal shaped molecules in the pure liquid phase. *Ber. Bunsenges. Phys. Chem*. **1986**, 90, 896–905.

[5]H Funke, H. H.; Argo, A. M.; Falconer, J. L.; Noble, R. D. Separations of Cyclic, Branched, and Linear Hydrocarbon Mixtures through Silicalite Membranes. *Ind. Eng. Chem. Res*. **1997**, *36*, 137-143.

[6]Chua, L. M.; Hitchcock, I.; Fletcher, R. S.; Holt, E. M.; Lowe, J.; Rigby, S. P. Understanding the Spatial Distribution of Coke Deposition within Bimodal Micro-/Mesoporous Catalysts using a Novel Sorption Method in Combination with Pulsed-gradient Spin echo NMR. *J. Catal.* **2012**, 286, 260–265.

[7]Van der Perre, S.; Van Assche, T.; Bozbiyik, B.; Lannoye, J.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. Adsorptive Characterization of the ZIF-68 Metal-Organic Framework: A Complex Structure with Amphiphilic Properties. *Langmuir* **2014**, 30, 8416–8424.
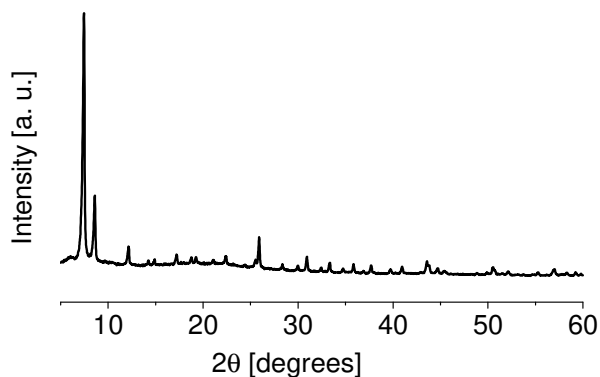
Materials and Methods

Figure S4. Experimental diffraction patterns of activated UiO-66 (Zr) showing the presence of a fully crystalline structure.
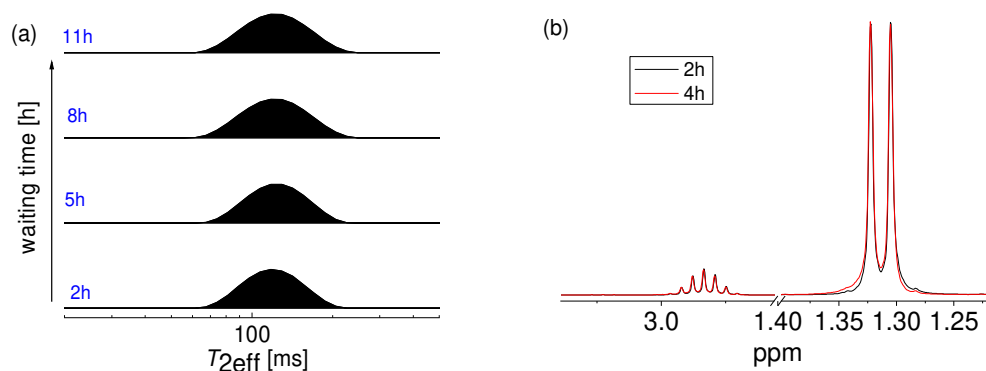

Figure S5. Typical ILT of the proton CPMG decays (a) and ^{1}H spectra (b) of the solvent mixture after different mixing times with the metal–organic framework. The solvent-MOF system equilibrates within around 2 hours as no changes between the results can be detected at longer times.

Table S2. Reproducibility of the NMR relaxation measurements with exemplification on different mixtures.

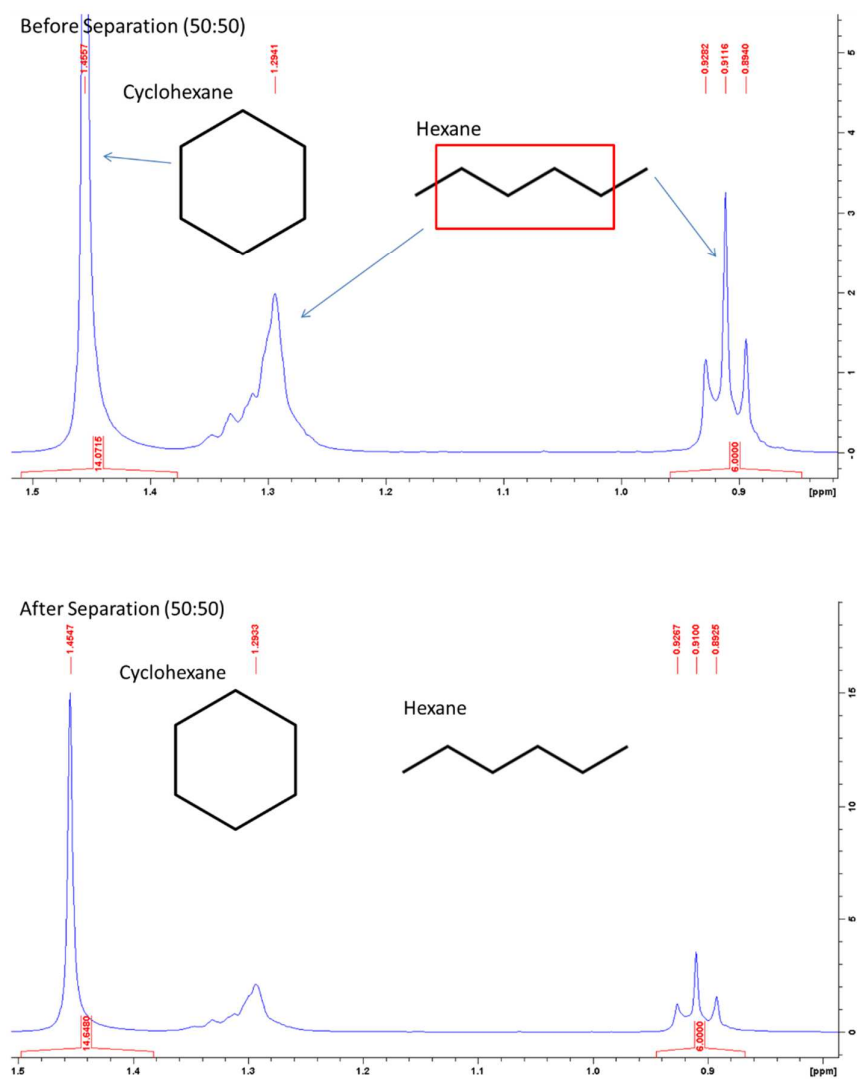| Solvent		Solvent ratio [% wt]		T_{2eff} [ms]			Averaged T_{2eff} [ms]	Standard deviation [ms]
1	2	1	2	Exp.1	Exp.2	Exp.3		
n-octane	2-pentanone	15	85	14.36	14.16	14.07	14.20	0.15
cyclooctane	n-octane	54	46	26.24	25.73	25.83	25.93	0.27
cyclooctane	2-pentanone	75	25	37.06	36.94	36.50	36.83	0.29
TiPB	2-pentanone	23	77	29.17	28.92	28.74	28.94	0.22

Figure S6. [1]H high-field spectra of the binary mixture cyclohexane – n-hexane before (top) and after the separation (bottom) by UiO-66(Zr). The two solvents were mixed in a ratio of about 50:50.
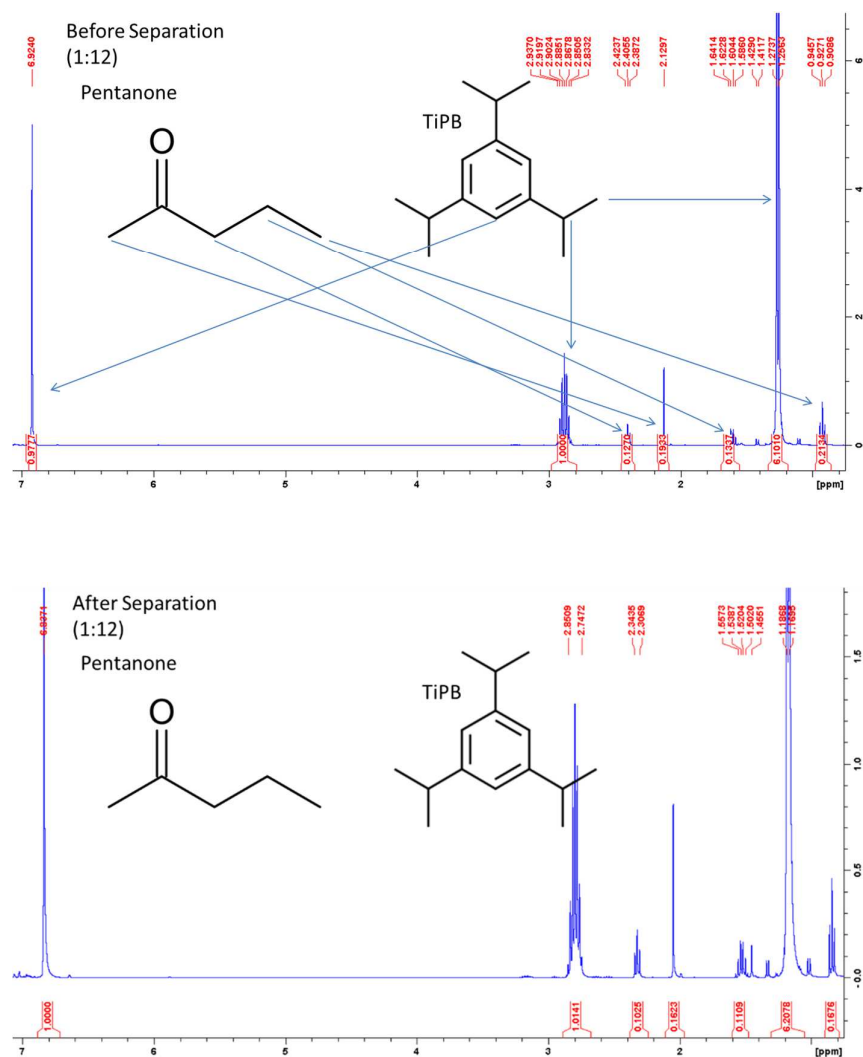
Figure S7. ¹H high-field spectra of the binary mixture TiPB – 2-pentanone before (top) and after the separation (bottom) by UiO-66(Zr). The two solvents were mixed in a ratio of about 1:12 as described in the experimental section.
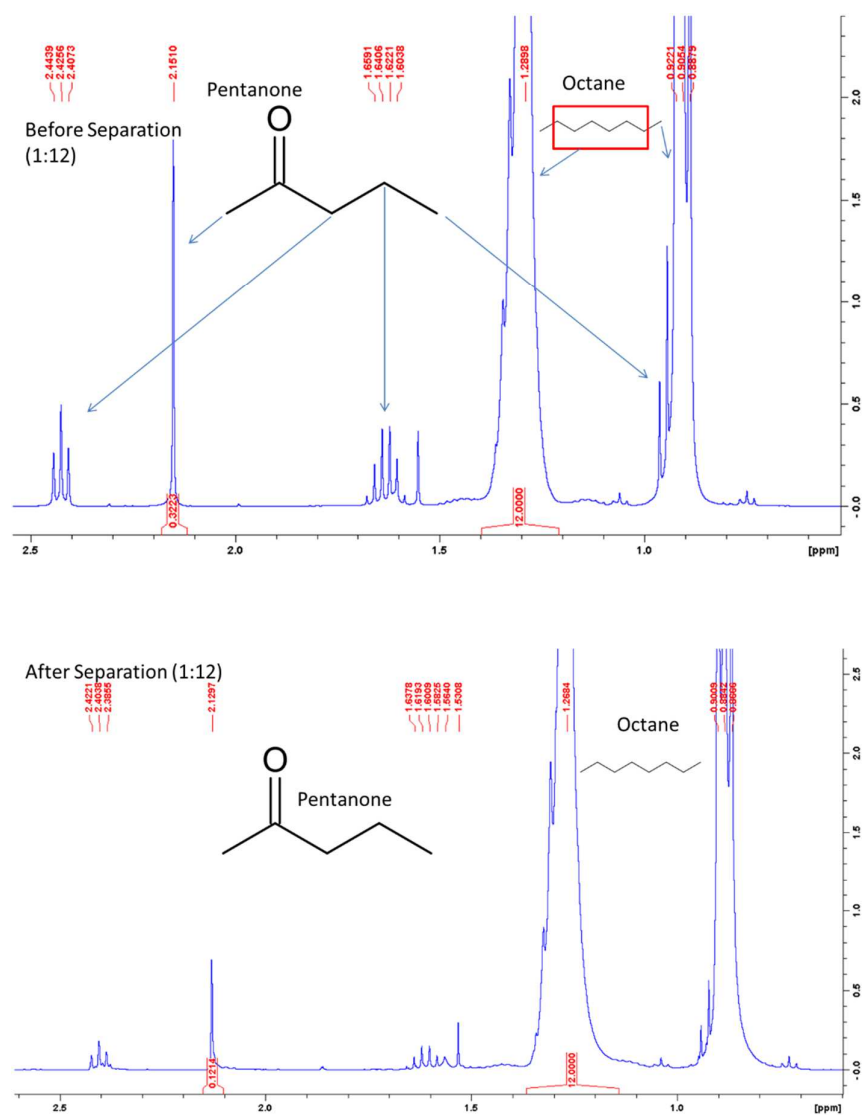
Figure S8. [1]H high-field spectra of the binary mixture n-octane – 2-pentanone before (top) and after the separation (bottom) by UiO-66(Zr). The two solvents were mixed in a ratio of about 1:12 as described in the experimental section. For better view of smaller signals, the signals of n-octane are not shown in full amplitude.
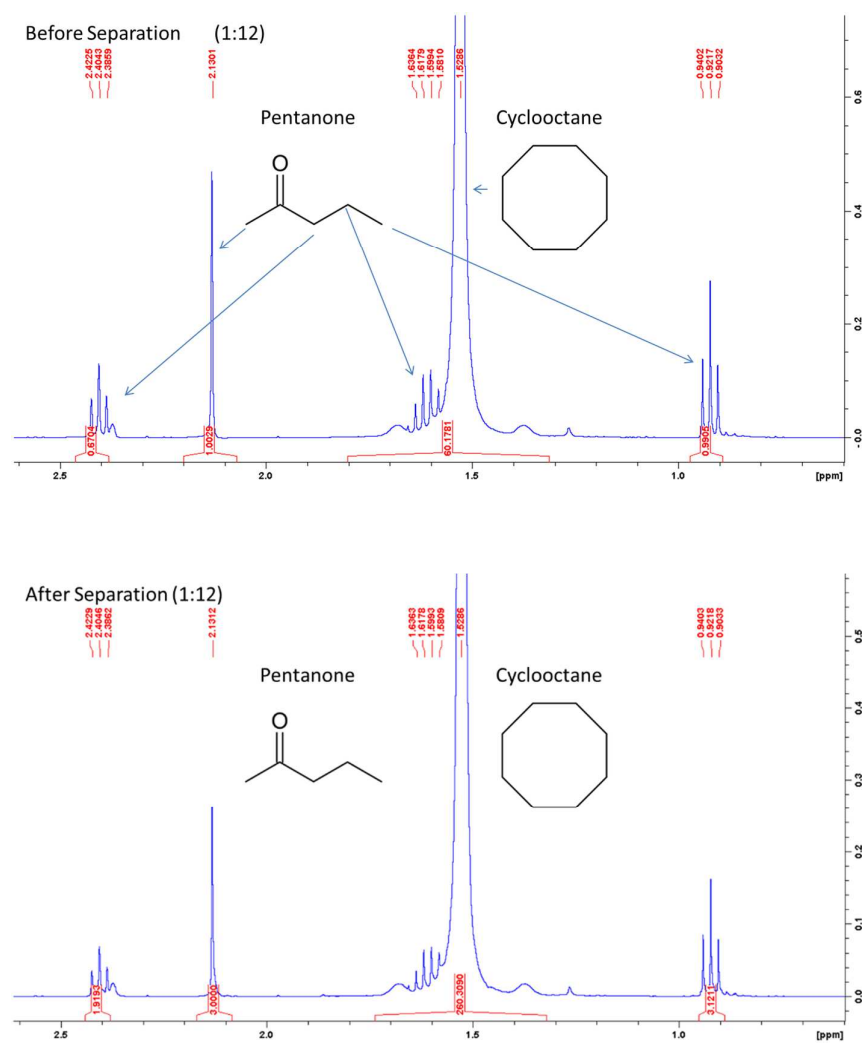
Figure S9. [1]H high-field spectra of the binary mixture cyclooctane – pentanone before (top) and after the separation (bottom) by UiO-66(Zr). The two solvents were mixed in a ratio of about 1:12 as described in the experimental section. For better view of smaller signals, the signal of cyclooctane is not shown in full amplitude.
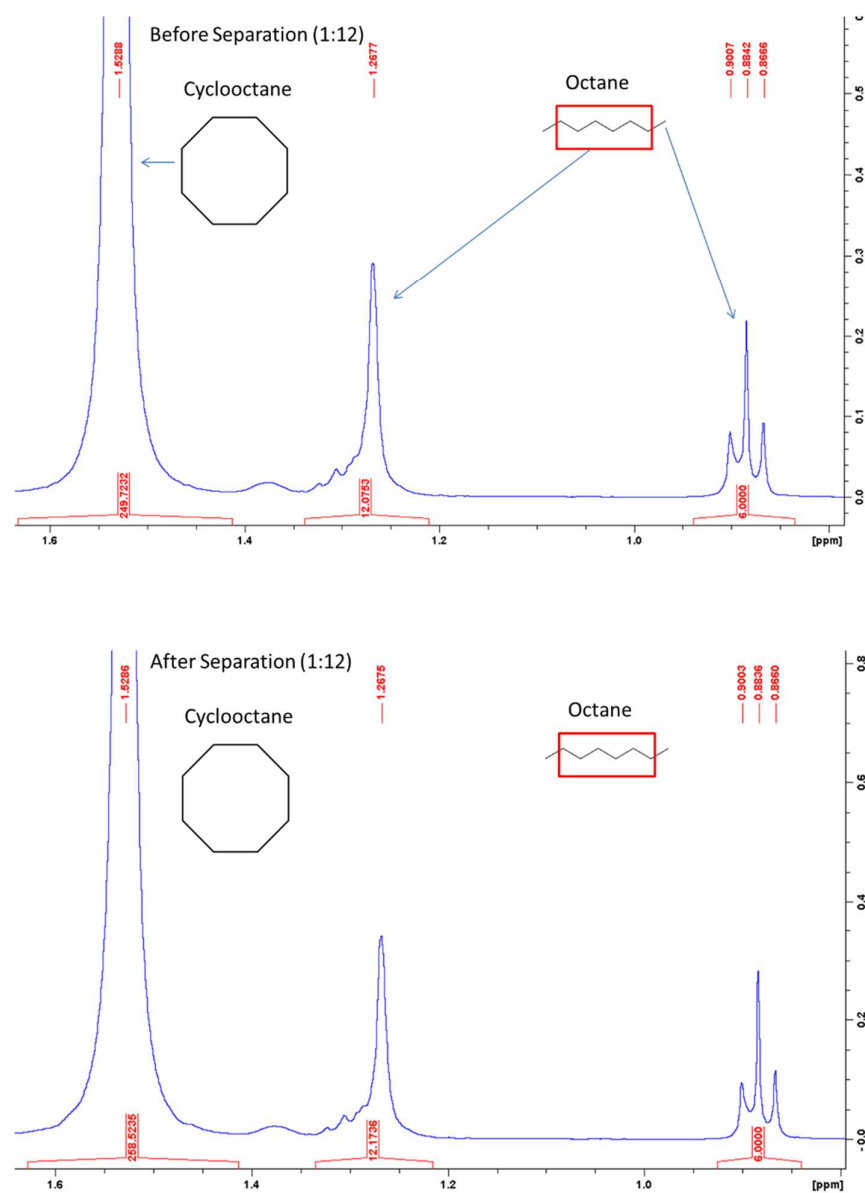
Figure S10. ¹H high-field spectra of the binary mixture cyclooctane – n-octane before (top) and after the separation (bottom) by UiO-66(Zr). The two solvents were mixed in a ratio of about 1:12 as described in the experimental section. For better view of smaller signals, the signal of cyclooctane is not shown in full amplitude.