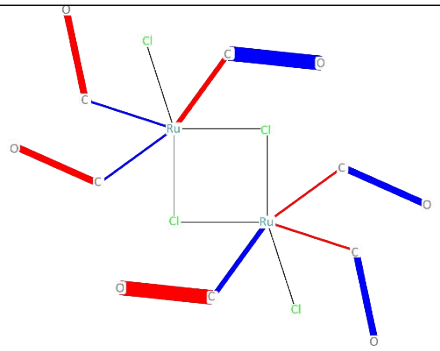
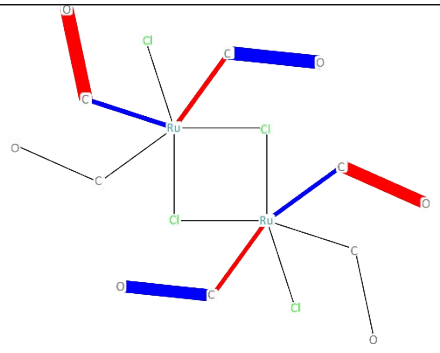
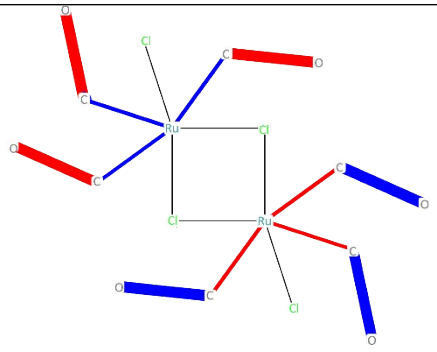
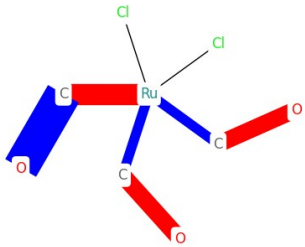
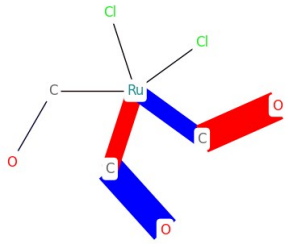
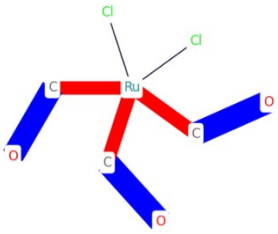
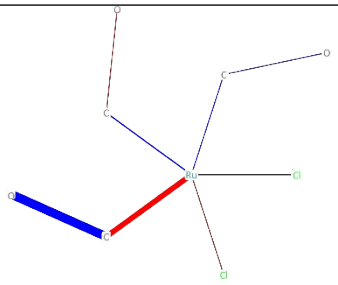
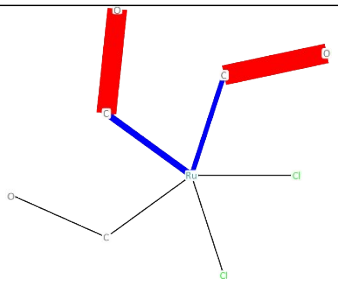
Supporting Information

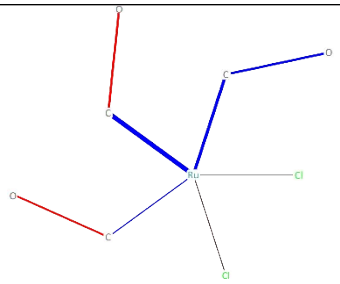
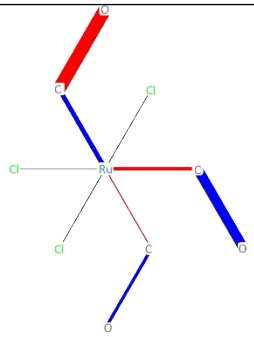
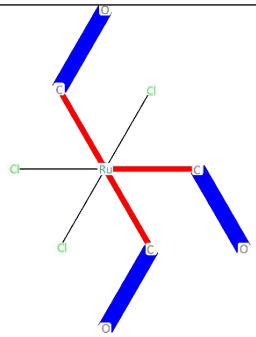
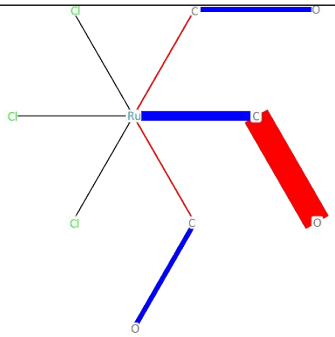
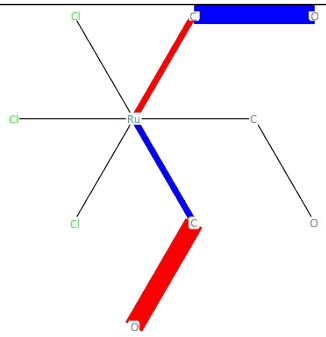
This supporting information contains more details on the vibrations calculated by DFT, the experimental setup used for the continuous flow experiments and additional IR data on the heating behavior of the SILP system.

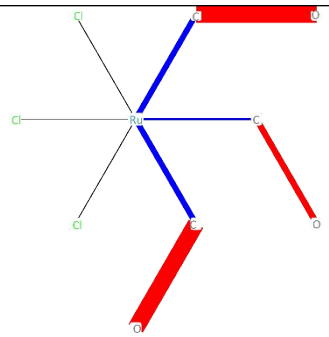
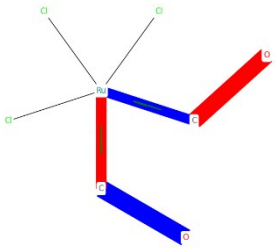
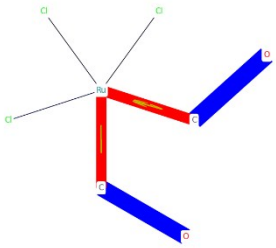
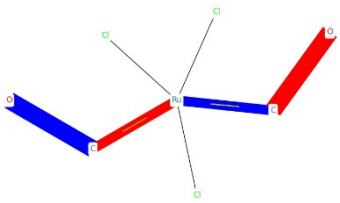
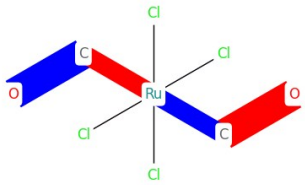
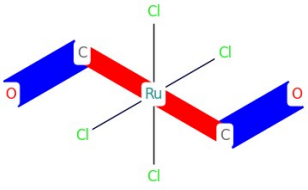
1) $[Ru(CO)_xCl_y]_n$ vibrations calculated with DFT

Table 1 summarizes all C-O stretching features assigned in the manuscript. The intensity of the most intense peak is set to 100%, only vibrations in the carbonyl regions are shown, all others are of small intensity (< 5%, except for carbonyls) anyway. Table 1 includes a 2D visualization for every vibrational mode. The visual representation was performed with QVibePlot.[1] Stretching, angle and torsion deformations are mapped onto the two-dimensional image of the molecule using different colors (red/blue, green/yellow). Increased line widths, radii and curve length indicate higher intensity of the respective stretching, angle and torsion motion, respectively.

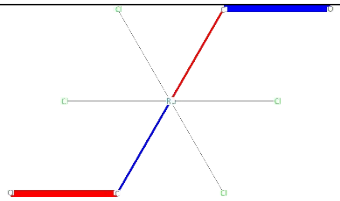
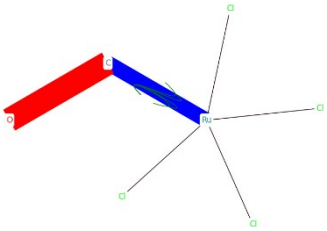
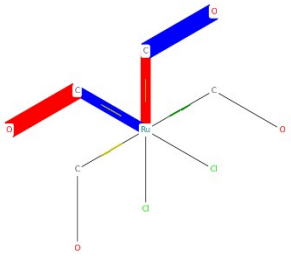
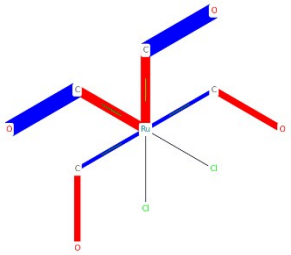
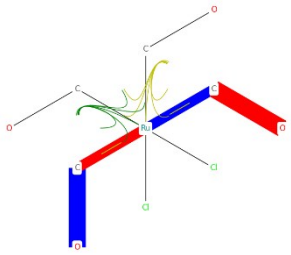
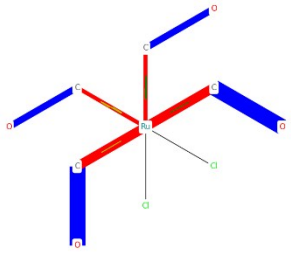
Frequency [cm^{-1}]	2D-Visualization	Relative intensity [%]
$[Ru(CO)_3Cl_2]_2$ – trans		
2040		92
2041		100

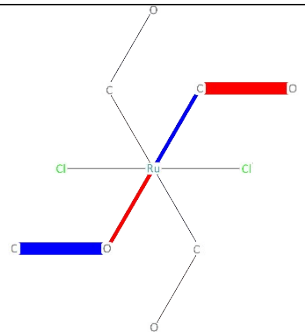
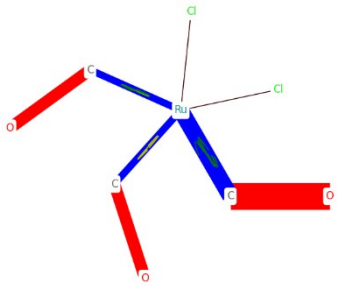
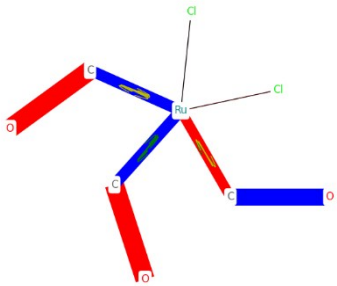
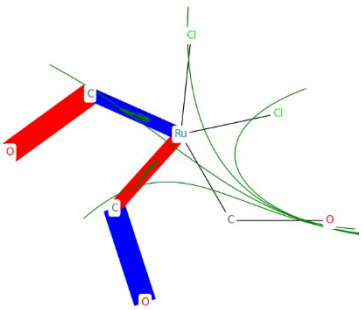
2108		88
$[Ru(CO)_3Cl_2]$ – square pyramid – cis		
2025		100
2033		90
2102		51
$[Ru(CO)_3Cl_2]$ – square pyramid – trans		
2015		57
2054		100

2130		2
$[Ru(CO)_3Cl_3]^-$ – facial		
1983		100
2063		68
$[Ru(CO)_3Cl_3]^-$ – meridial		
1972		56
2003		100

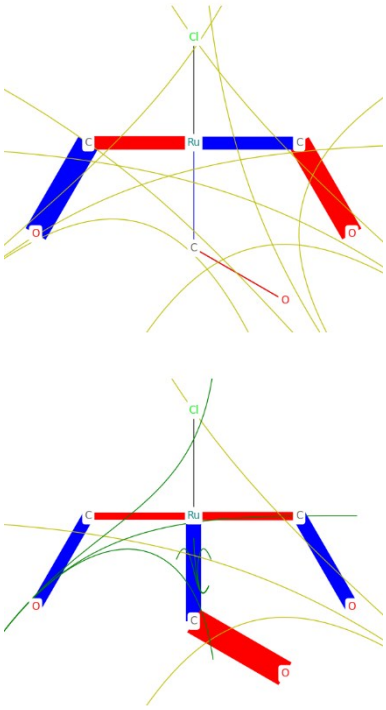
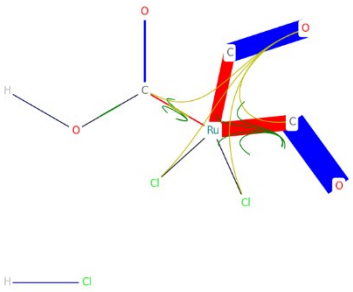
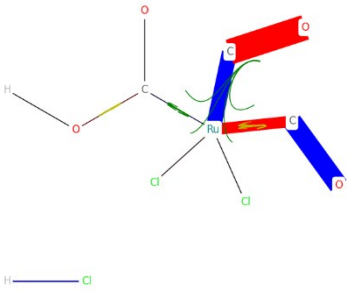
2091		2
$[Ru(CO)_2Cl_3]^-$ – square pyramid – cis		
1939		100
2010		63
$[Ru(CO)_2Cl_3]^-$ – square pyramid – trans		
1943		100
$[Ru(CO)_2Cl_4]^{2-}$ – cis		
1893		100
1969		80

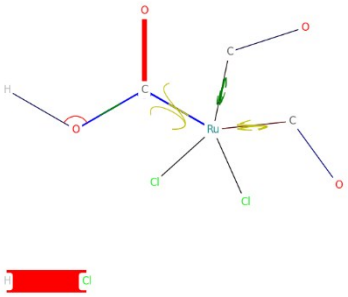
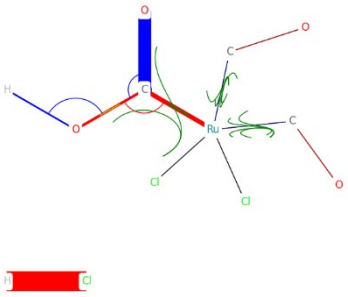
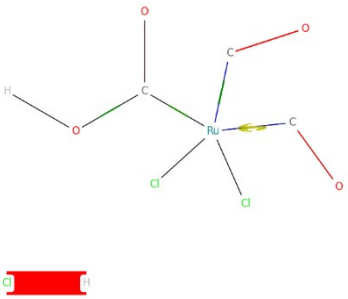
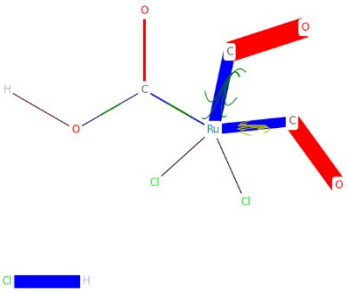
1

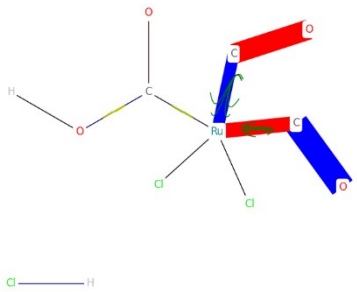
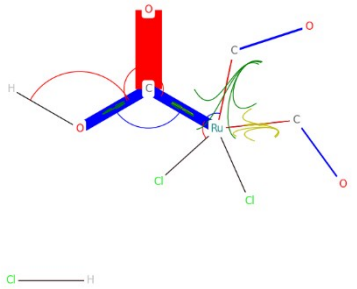
$[Ru(CO)_2Cl_4]^{2-}$ – trans		
1894		100
$[Ru(CO)Cl_4]^{2-}$ – square pyramid		
1862		100
$[Ru(CO)_4Cl_2]$ – cis		
2035		77
2066		59
2086		100
2149		4

$[Ru(CO)_4Cl_2]$ – trans		
2060		100
$[Ru^0(CO)_3Cl_2]^{2-}$ – trig.-bipyr. cis		
1910		45
1803		52
1787		100

1

$[Ru^0(CO)_3Cl_2]^{2-}$ – trig.-bipyr. trans		
1777		100
$[Ru^{II}(CO)_2(CO\text{-}OH)HCl_3]$*		
2025		52
1953		73

1704		100
1678		29
$[Ru^{II}(CO)_2(CO\text{-}OH)Cl_2] + HCl^*$		
2117		100
2013		26

1944		40
1728		21

1 *HCl is plotted separately from the molecule in the 2D visualization

2

Experimental setup of the continuous test rig for TOF

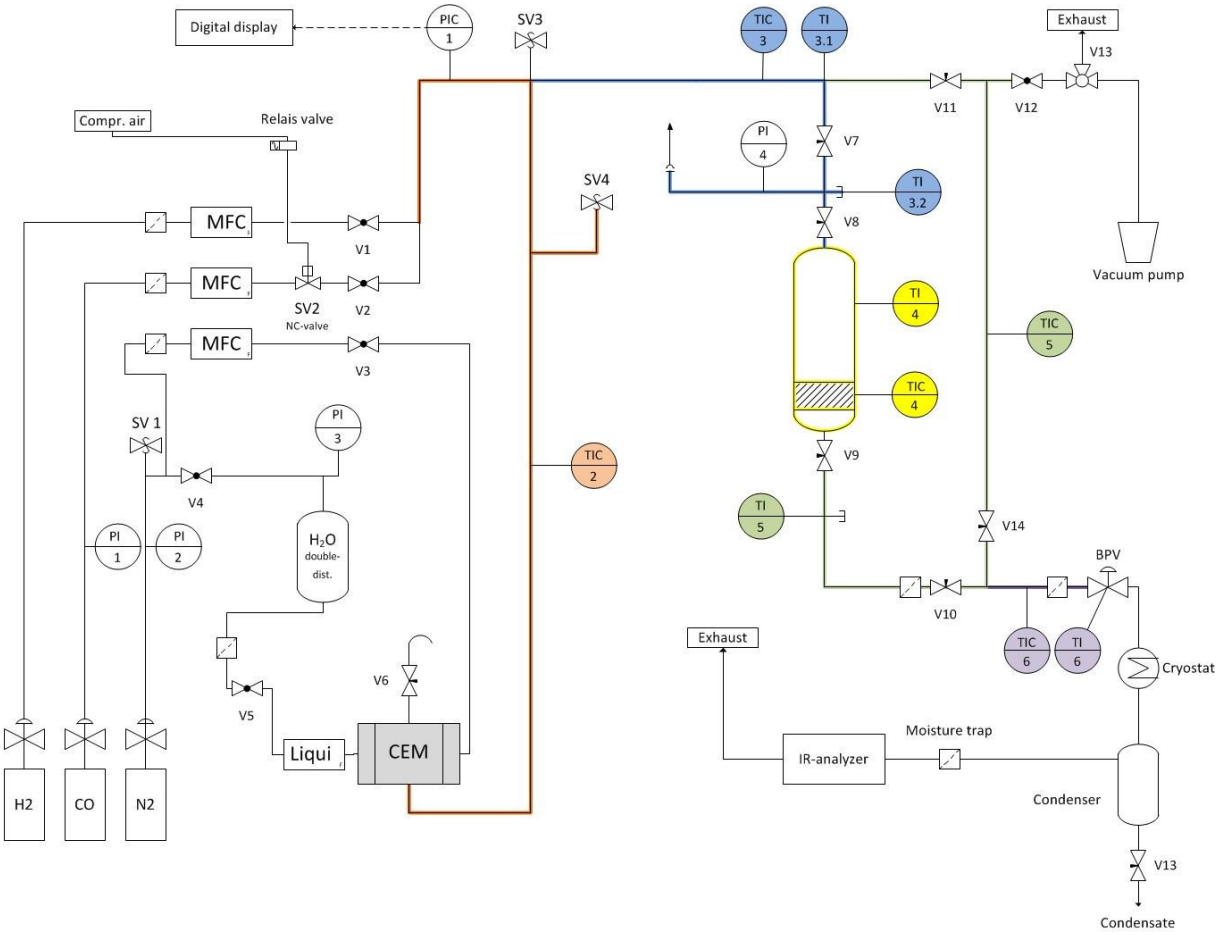


Figure S1: Flow sheet of the continuous test rig for the TOF measurements

After the desired amount of SILP catalyst is placed in the tubular reactor (yellow part) on a frit, covered with a small amount of glass wool to keep the fixed bed in place, a pressure test is taking place. Subsequently, the test rig is heated to the requested temperature levels and the streams of CO, N_2 and H_2O are adjusted (p_{N2}:p_{CO}:p_{H2O} = 7:1:2; p_{tot} = 1 bar) in the bypass mode by closing valves 7 and 10 and opening valves 11 and 14. When the IR-Analyzer (X-STREAM Enhanced XEGP, Emerson) shows stable values, the data logger is started to take reference values (one data point per 30 seconds) before switching into reactor mode (valves 11 and 14 closed, valves 7 and 10 open). The temperature of the tubular reactor is varied at constant volume flows between 120 °C and 140 °C in 5 °C-steps. Every setpoint is kept for at least 3 hours after reaching steady state.

Heating of $[C_4C_1C_1Im]Cl/Al_2O_3$

As reference for the temperature-dependent behavior of the investigated samples, we performed a heating ramp with the corresponding supported IL, i.e. the same system but without any catalytically

active Ru species. The background spectrum was taken at room temperature on the same sample, thus the plotted and offset spectra are difference spectra.

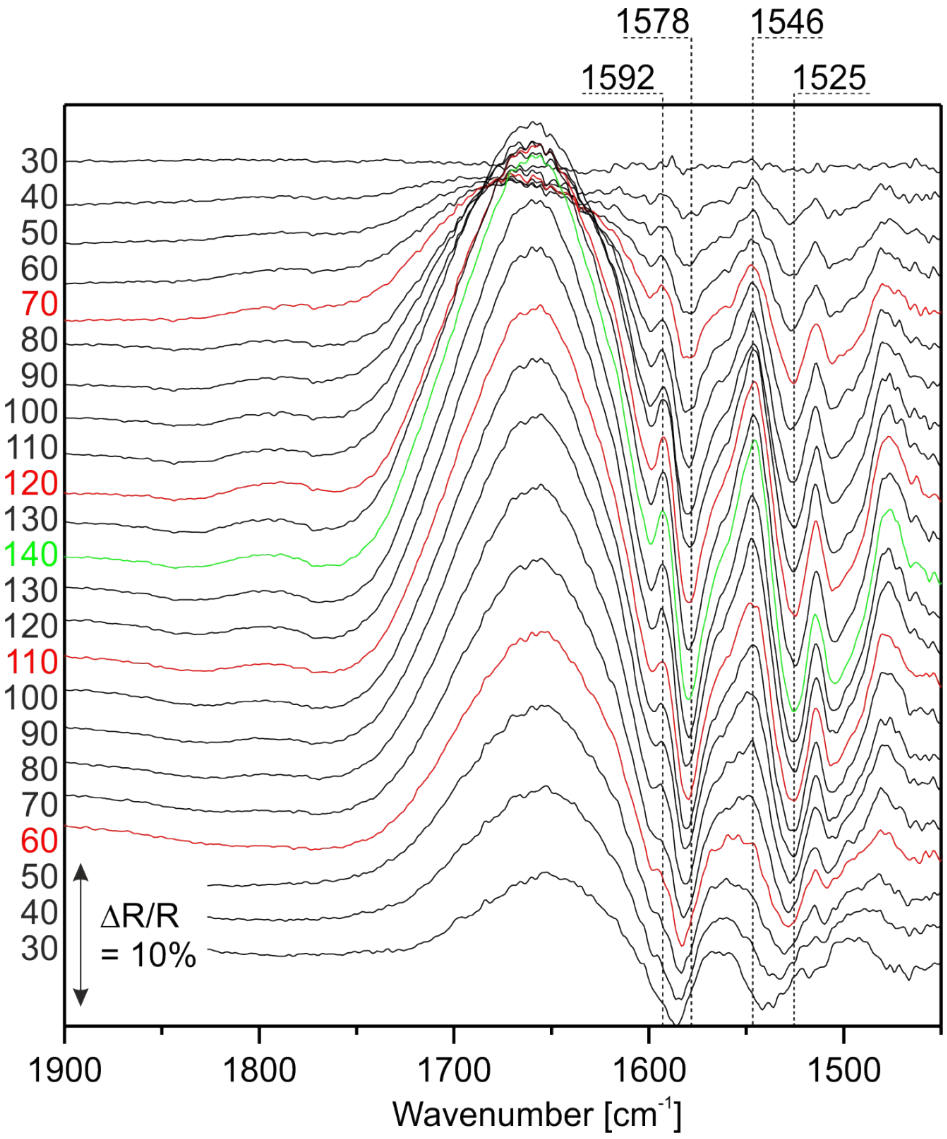


Figure S2: Offset difference spectra obtained during heating/cooling cycle on $[C_4C_1C_1Im]Cl/Al_2O_3$

Figure S2 shows, that upon heating the IL peaks at 1588 and 1540 cm^{-1} get more intense and red-shifted. This can be seen in the difference spectra via s-shaped peaks. Furthermore, apart from a water-loss signal at 1650 cm^{-1} heating the IL does not lead to any spectral features above 1600 cm^{-1}.

Different aging methods of the $[C_4C_1C_1Im]Cl/[Ru(CO)_2Cl_3]_2$ DCM solutions

We examined the interaction between the IL and Ru-dimer in DCM solution and deposited on an IR-transparent support under vacuum (1 mbar, air).

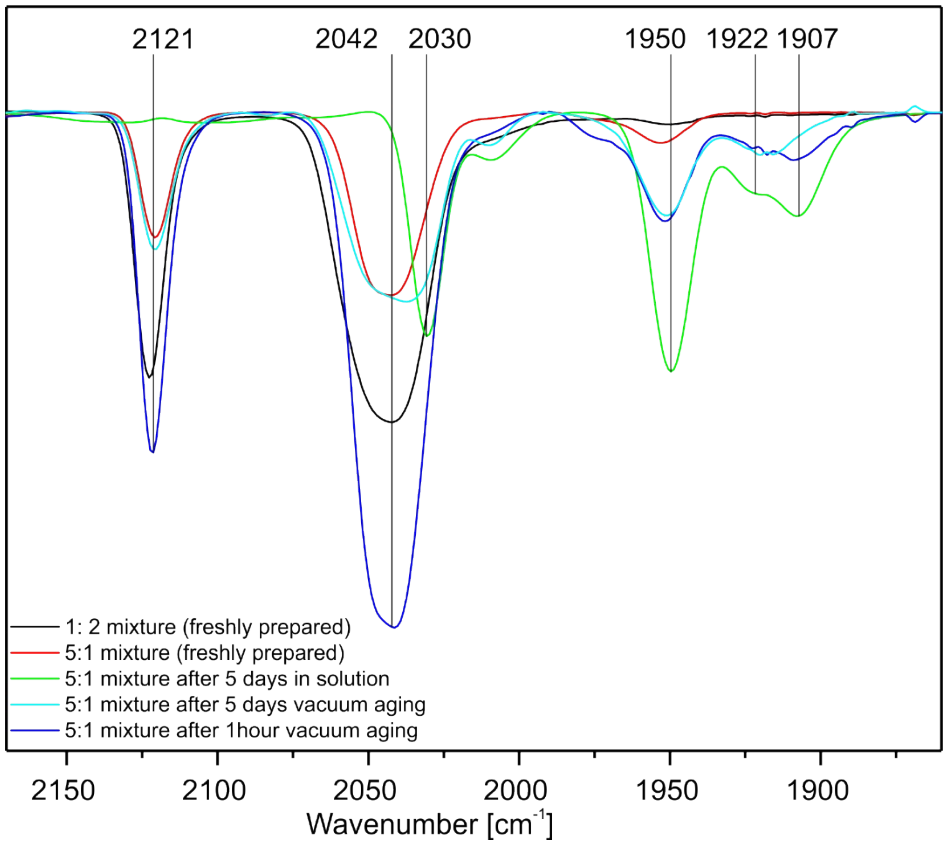


Figure S3: Normalized TIR spectra of differently treated IL/Ru-dimer deposits

Figure S3 shows the resulting transmission spectra. The recorded spectra show that the transformation of the dimer to the various complexes mentioned in the manuscript is independent from the aging procedure.

1. M. Laurin, *J. Chem. Educ.*, 2013, **90**, 944-946.