Supporting information:

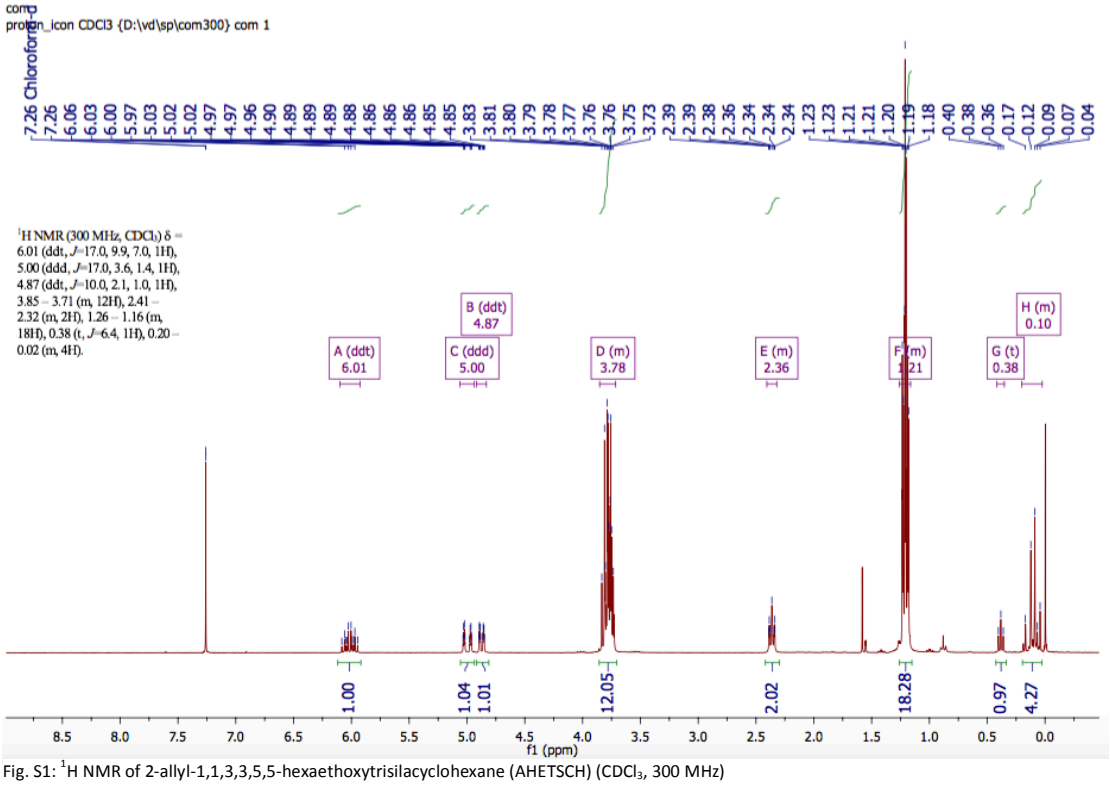

Fig. S1: ^{1}H NMR of 2-allyl-1,1,3,3,5,5-hexaethoxytrisilacyclohexane (AHETSCH) ($CDCl_3$, 300 MHz)

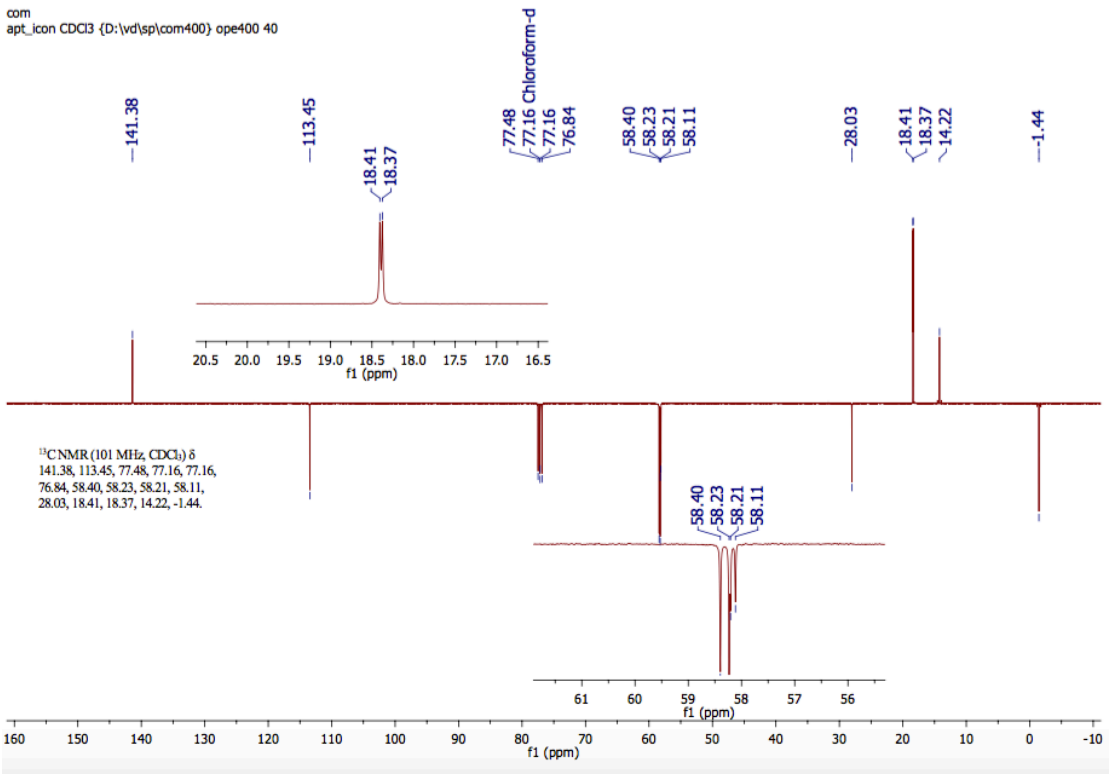

Fig. S2: ^{13}C NMR of 2-allyl-1,1,3,3,5,5-hexaethoxytrisilacyclohexane (AHETSCH) ($CDCl_3$, 400MHz)

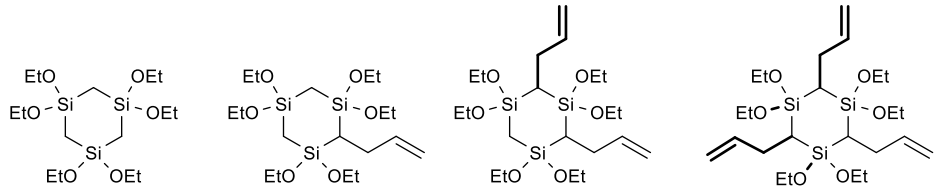

Fig. S3: Mixture of HETSCH and AHETSCH precursors used in the synthesis of mixAR

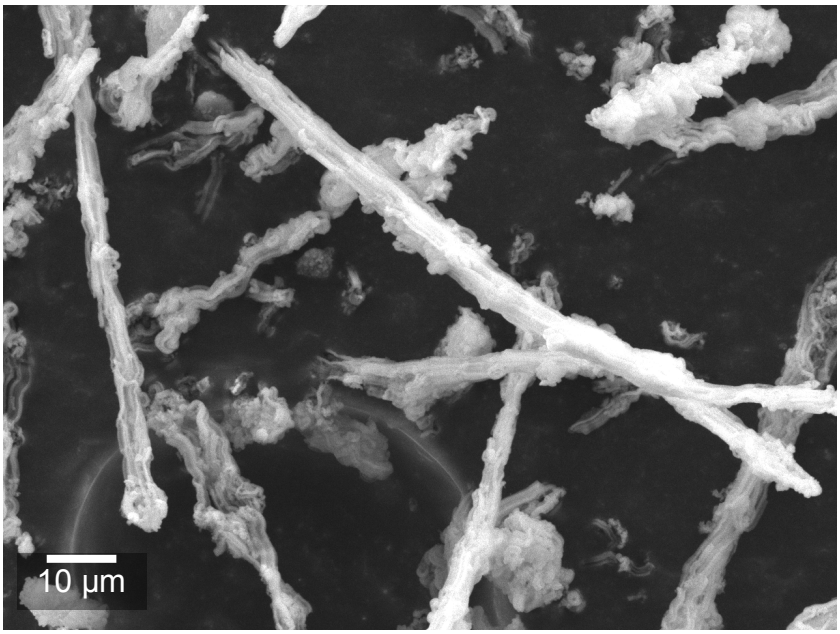

Fig. S4: SEM image of mAR particles

Table S1: N_2 sorption data of a new batch mAR (REF) and the same material treated at 25°C for 3h with a (pH13-3h), 24h 0.1M NaOH solution (pH13-24h) and treated for 24 with a 1M HCl solution (pH0-24h).

	S_{BET} (m^2/g)	PS_{BJH} (nm)
REF	529	5.0
pH13 – 3h	539	5.0
pH13 – 24h	461	4.7
pH0 – 24h	540	5.0

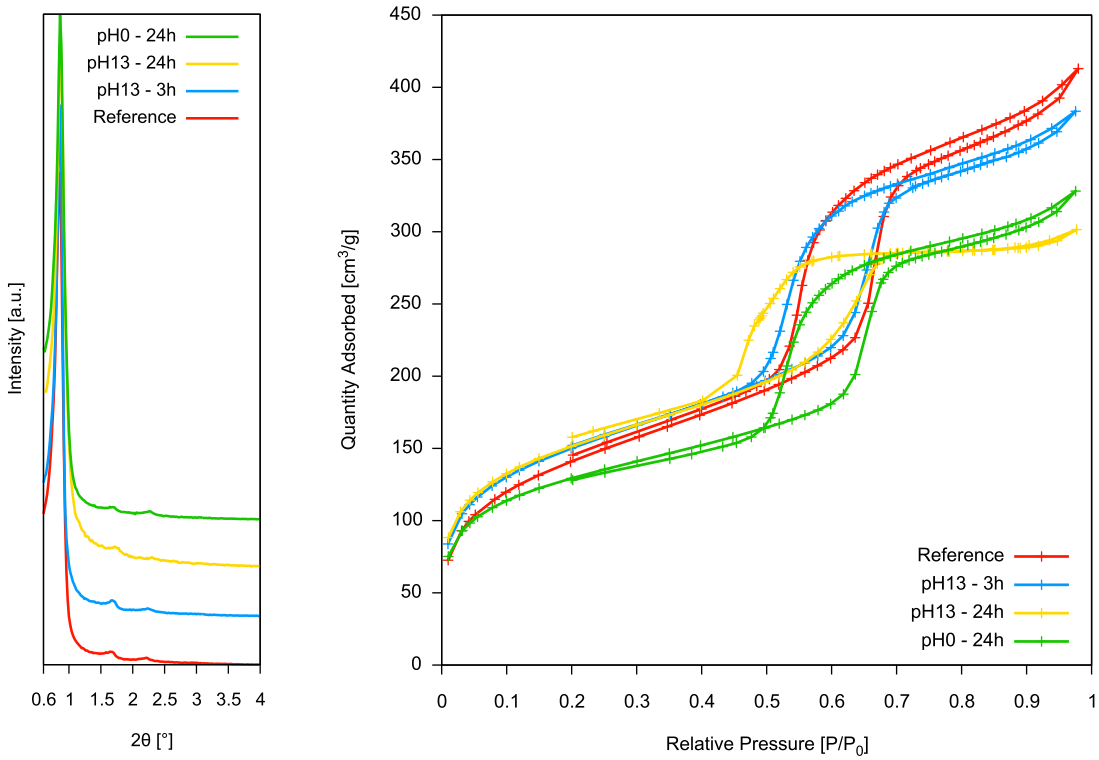

Fig. S5: XRD diffractograms and N_2 sorption isotherms of hydrolytically stressed mAR (Reference)

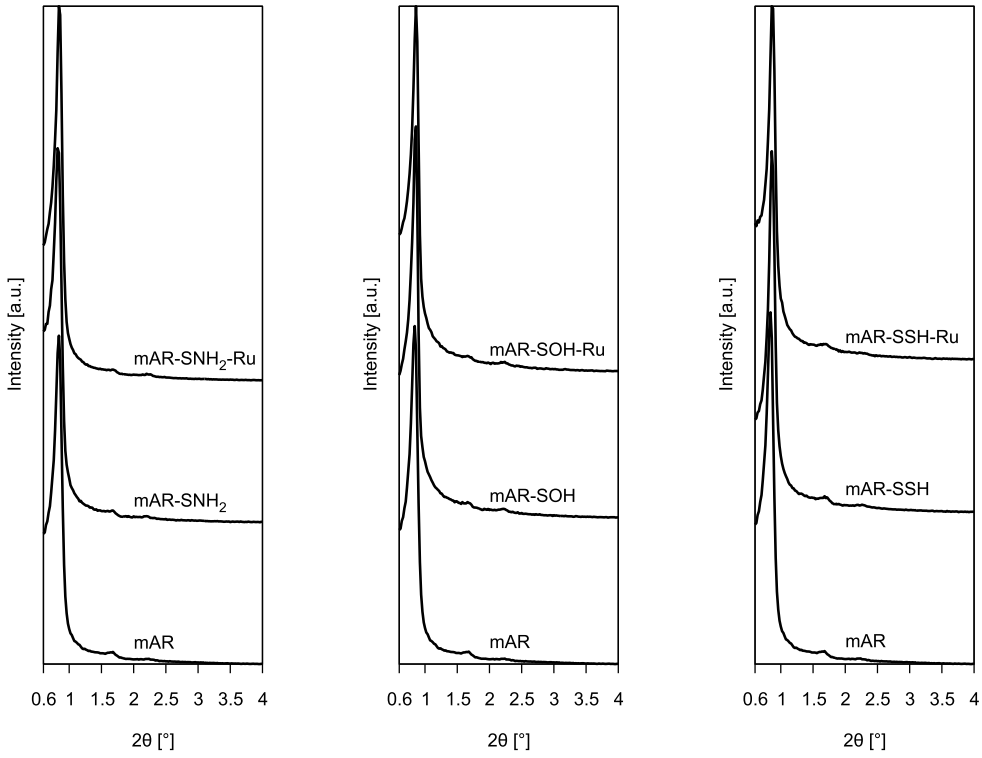

Fig. S6: XRD diffractograms after thiol-ene 'click' post-modification and anchoring of $[Ru(acac)_2(CH_3CN)_2]PF_6$.

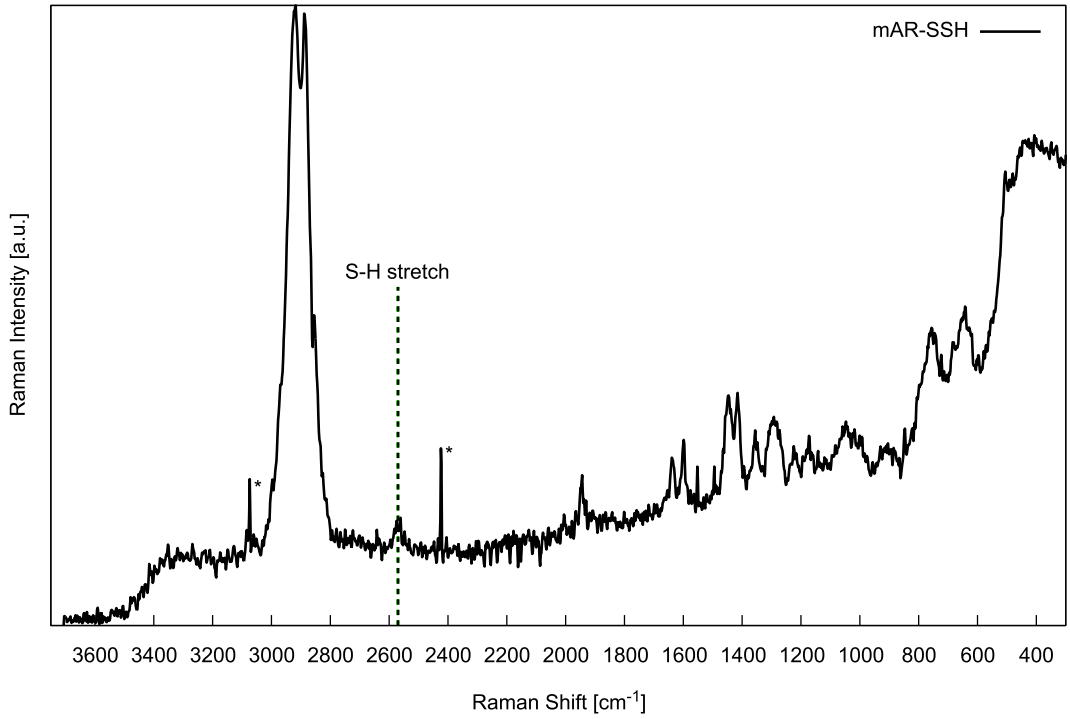

Fig. S7: Raman spectrum of mAR-SSH (Laser power 0.45W, 4200 scans). S-H stretch Raman signal of free thiol groups is observed at 2570 cm^{-1}. Sharp peaks (*) arise from the glass vial in which the spectrum was recorded.

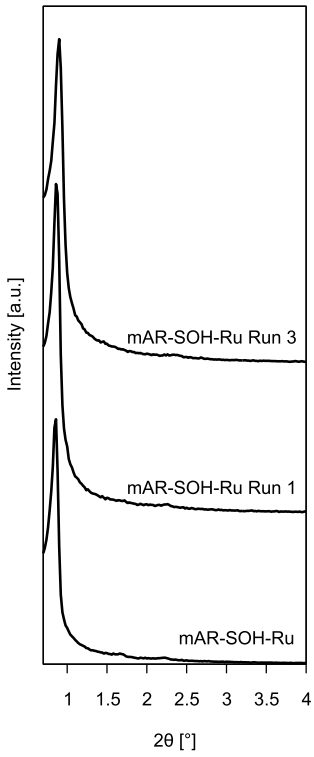

Fig. S8: XRD diffractograms of mAR-SOH-Ru as fresh catalyst (bottom), after 1 run (middle) and after 3 runs (top)

Computational details:

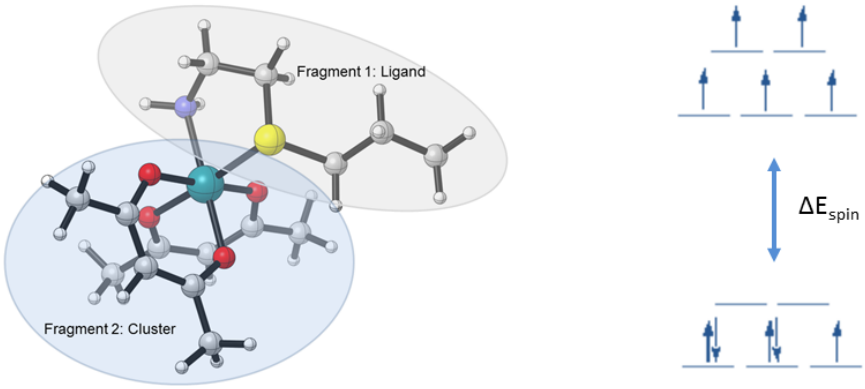

Fig. 9: Model for computational calculations. Two separate fragments are considered: the ligand (fragment 1) and the ruthenium cluster (fragment 2). Fragment 1 has a zero charge and a singlet spin state, except when the protonated ligand is considered (charge +1). Fragment 2 comprises the ruthenium centre and two acac ligands. The ruthenium is in a 3+ state and hence has a d5 configuration. The two possible spin states (doublet and sextuplet) have been examined and both DFT-functionals indicate that the expected doublet state is the most stable. Since the two acac groups are negatively charged, the charge of this cluster is +1. The total fragment has a charge of +1 and a doublet spin state.

The complexation free energies provided in the main article are calculated using the following equation:

$$\Delta G_{\text{complex}} = (G_{\text{total}} - [G_{\text{fragment1}} + G_{\text{fragment2}}] + CP) \quad (1)$$

with G_{total} the free energy of the total system and $G_{fragment}$ the energies of the respective fragments. CP is the counterpoise correction energy for the BSSE error. Next to this value, we calculated the free energy cost to remove 2 actonitrile groups (the original complex, cfr. Fig.6 in the main article) and added this to the free energy of complexation. Table 2 represents the results for the different ligand topologies:

Table 2: All energy differences are expressed in kcal/mol and include dispersion corrections. ΔE_{el} represents the purely electronic energy with zero-point energy correction (same as eq.1, without CP correction and free energy contribution). ΔG is the Gibbs free energy calculated from the frequency analysis (via eq.1, without CP correction). CP is the Counterpoise correction term.

	B3LYP		OPBE		
Ligand	ΔE_{el}	ΔG	ΔE_{el}	ΔG	CP
S—NH_2	-93	-79	-92	-75	2.2
S—SH	-83	-70	-86	-71	1.4
S—OH	-74	-59	-70	-55	2.1
CH_3CN	-32	-21	-34	-24	1.0

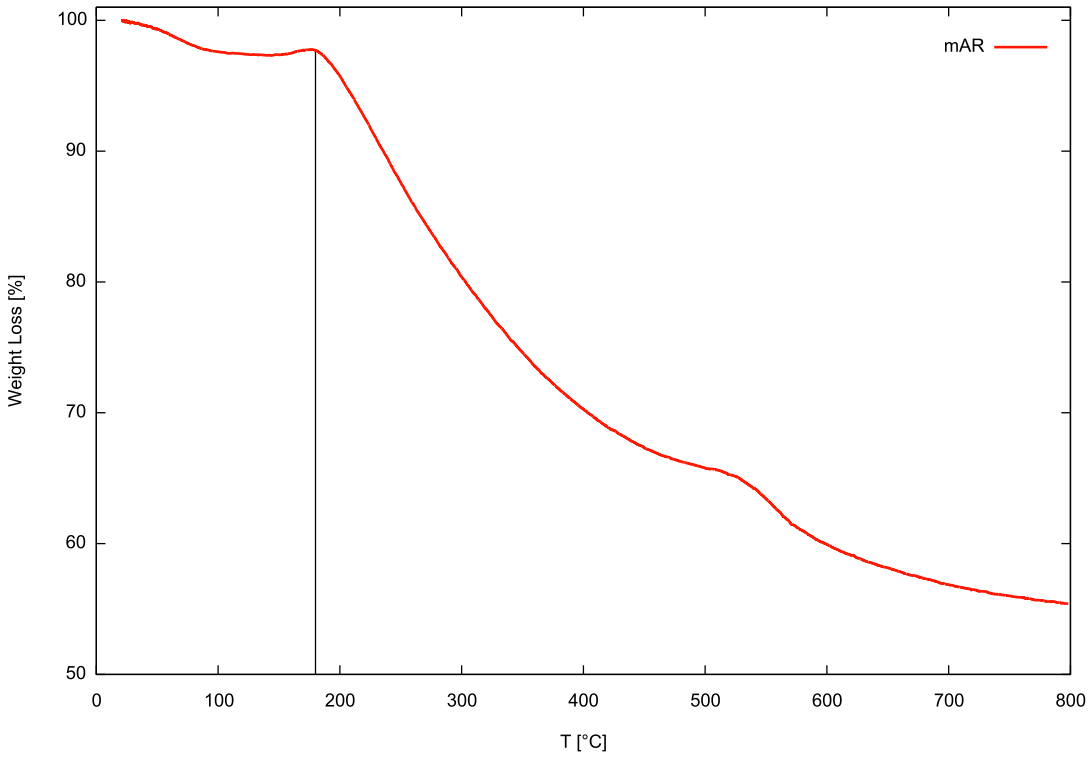

Fig. S9: Thermogravitational analysis of the mAR-PMO (air, heating rate 10°C/min). An initial 3% mass loss around 60°C is ascribed to adsorbed H_2O. At 180°C a small weight increase is witnessed, as a result of the oxidation of the allyl functional group. Thereafter, decomposition of the organic groups results in a major weight loss (approximately 42%).

Synthesis of aminopropyl grafted silica (SBA-15) and anchoring of $[Ru(acac)_2(CH_3CN)_2]PF_6$

4g of P123 is dissolved in 120ml of a 2M HCl solution and 30 ml H_2O at 45°C. 9.1 ml TEOS is added at once and the solution is stirred heavily for 5h at 45°C. Then, stirring is stopped and temperature is raised to 90°C and the solution is left to stand for 18h. Hereafter, the white solid is filtered off and washed with 3x10 ml H_2O. Finally the SBA-15 powder is calcined for 6h at 550°C with a heating rate of 2°C/min. (S_{BET} = 670 m^2/g)
0.5 g of SBA-15 is suspended in 10 ml of dry toluene and 1.427 ml of aminopropyl-(triethoxy)silane (APTES) is added. The mixture is then reacted for 24 h at reflux temperature. The product is filtered off and washed with 3x10 ml CH_2Cl_2 and dried under vacuum at 120°C.
$[Ru(acac)_2(CH_3CN)_2]PF_6$ is anchored in the same conditions as for the PMOs (experimental section).