Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

1. Characterization of the CAU-1 type compounds

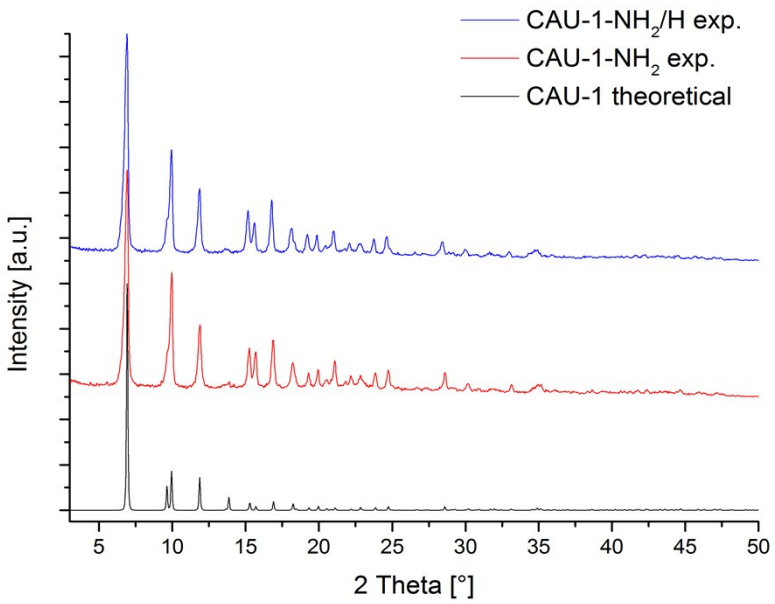

Fig. S1: PXRD patterns of the two CAU-1 samples one containing exclusively aminoterephthalate ions (CAU-1-NH_2) and the other containing terephthalate and aminoterephthalate ions in a molar ratio 3 to 1 (CAU-1-NH_2/H).

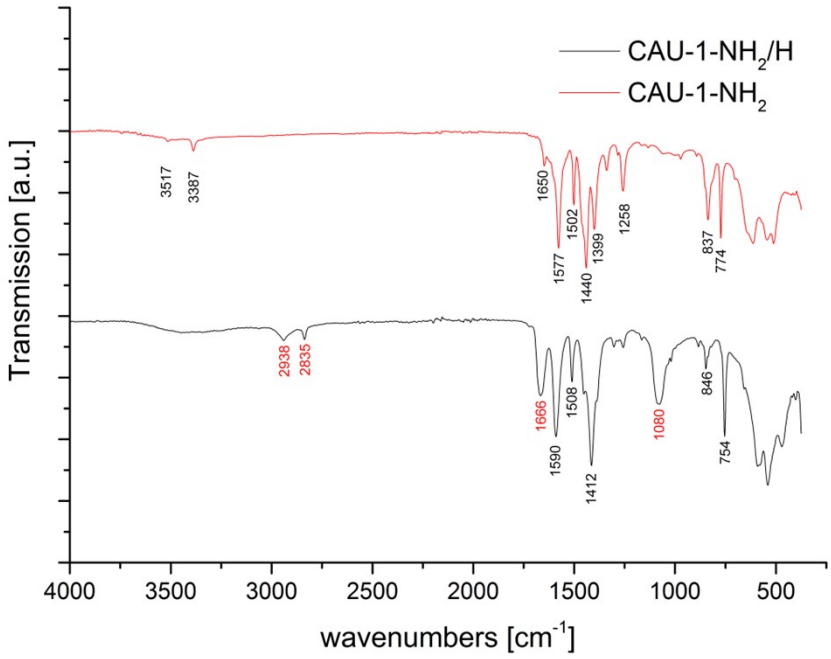

Fig. S2: IR-spectra of the two CAU-1 samples one containing exclusively aminoterephthalate ions (CAU-1-NH_2) and the other containing terephthalate and aminoterephthalate ions in a molar ratio 3 to 1 (CAU-1-NH_2/H). Bands corresponding to residual DMF present in the sample are represented in red.

Table S1: Vibrations and corresponding band positions for the IR-spectra of CAU-1-NH_2 and CAU-1-NH_2/H.

Vibration	Position for CAU-1-NH_2 [cm^{-1}]	Position for CAU-1-NH_2/H [cm^{-1}]	Comment
$\nu_{as}(NH_2)$	3517	n.v.	
$\nu_{s}(NH_2)$	3387	n.v.	
$\nu(C=C)_{ring}$	1650	overlapped by DMF	
$\nu_{as}(COO)$	1577	1590	
$\nu(C=C)_{ring}$	1502	1508	
$\nu_{s}(COO)$	1440	1412	
$\nu(C=C)_{ring}$	1399	n.v.	
$\nu(C-NH_2)$	1258	n.v.	
γ(C-H)	837	846	1,2,4- Substitution (CAU-1-NH_2) and
(C-H)	774	754	1,4-Substitution (CAU-1-NH_2/H)
ν(C-H)	-------	2938	DMF
$\nu(N-CH_3)$	-------	2835	DMF
ν(C=O)	-------	1666	DMF
$\gamma(N-CH_3)$	-------	1080	DMF

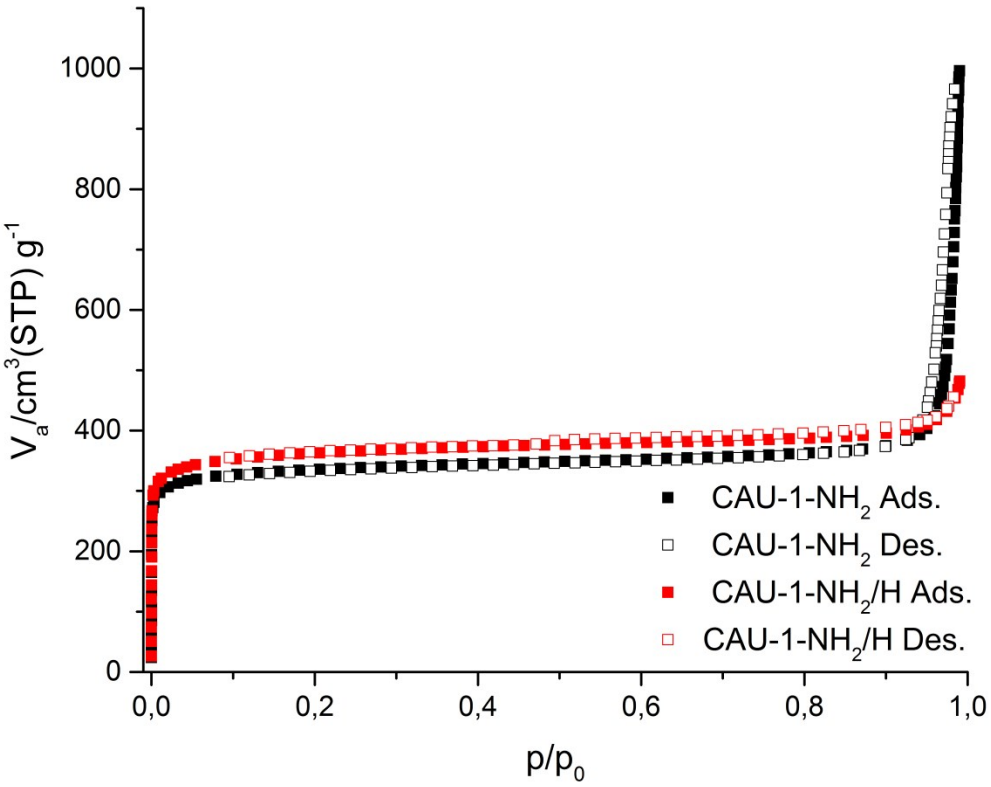

Fig. S3: The N_2-sorption isotherms (77 K) of the two CAU-1 samples one containing exclusively aminoterephthalate ions (CAU-1-NH_2) and the other containing terephthalate and aminoterephthalate ions in a molar ratio 3 to 1 (CAU-1-NH_2/H).

Table S2: Specific BET surface areas and micropore volumes for the samples CAU-1-NH_2 and CAU-1-NH_2/H compared to the values reported in literature[16].

Compound	spec. BET surface area [m²/g]	micropore volume [cm³/g]
Literature[16]	1530	0.64
CAU-1-NH_2	1316	0.54
CAU-1-NH_2/H	1416	0.58

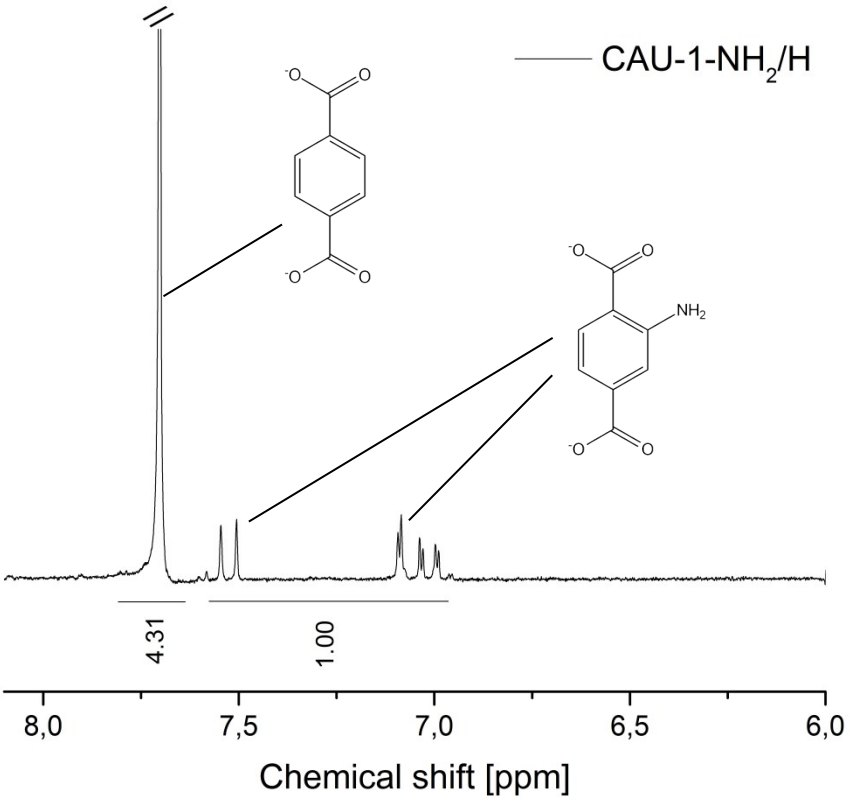

Fig. S4: ^{1}H-NMR spectrum of CAU-1-NH_2/H in NaOD/D_2O (5%) to determine the ratio of terephthalate to aminoterephthalate ions.

Characterization of the CAU-10 type compounds

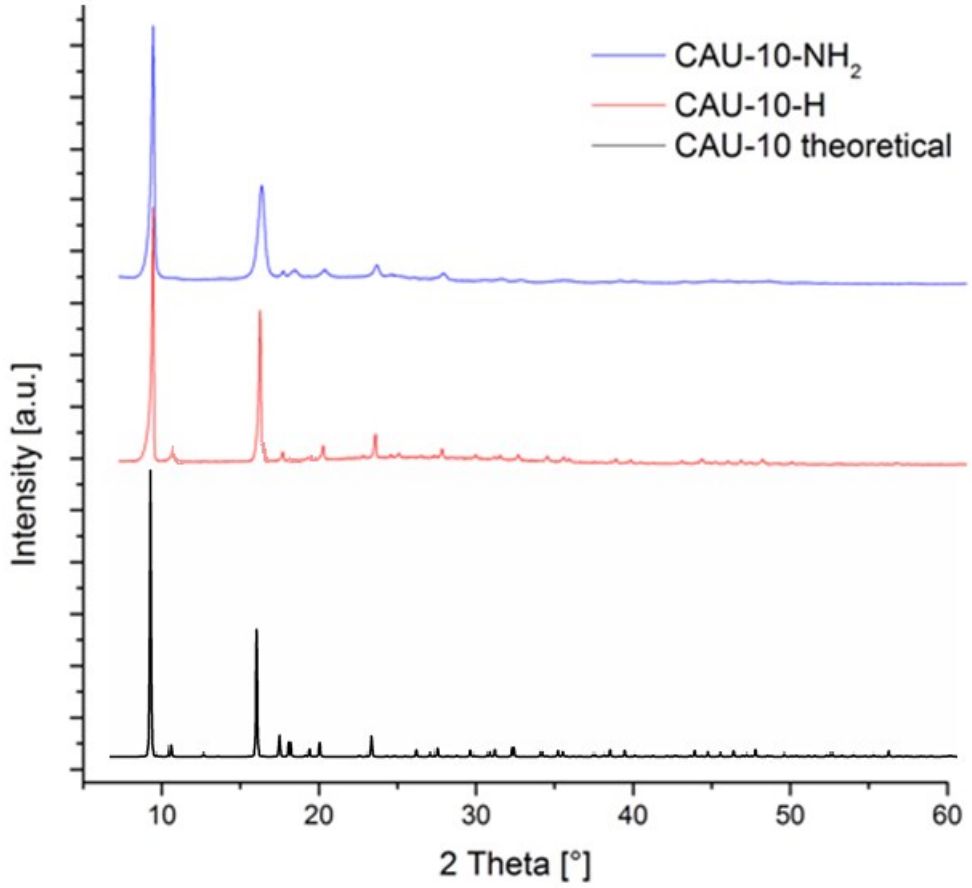

Fig. S5: PXRD patterns of the two CAU-10 samples containing either isophthalate (CAU-10-H) or aminoisoterephthalate (CAU-10-NH_2) ions.

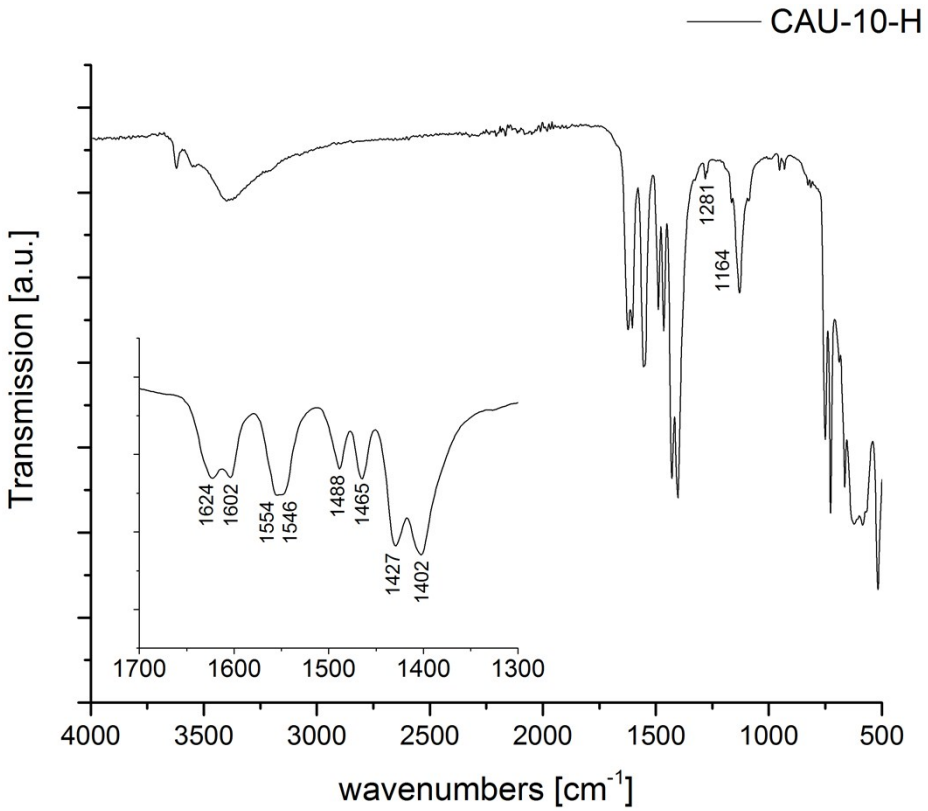

Fig. S6: IR-spectrum of CAU-10-H containing only isoterephthalate ions.

Table S3: Vibrations and corresponding band positions for the IR-spectrum of CAU-10-H.

Vibration	Band position for CAU-10-H [cm^{-1}]
ν (COO)	1624
ν (C=C)	1602
ν_{as} (COO)	1554
ν_{as} (COO)	1546
ν (C=C) $_{ring}$	1488
ν (C=C) $_{ring}$	1465
ν (C=C) $_{ring}$	1427
ν_{s} (COO)	1402
δ (C-H)	1281
δ (C-H)	1164

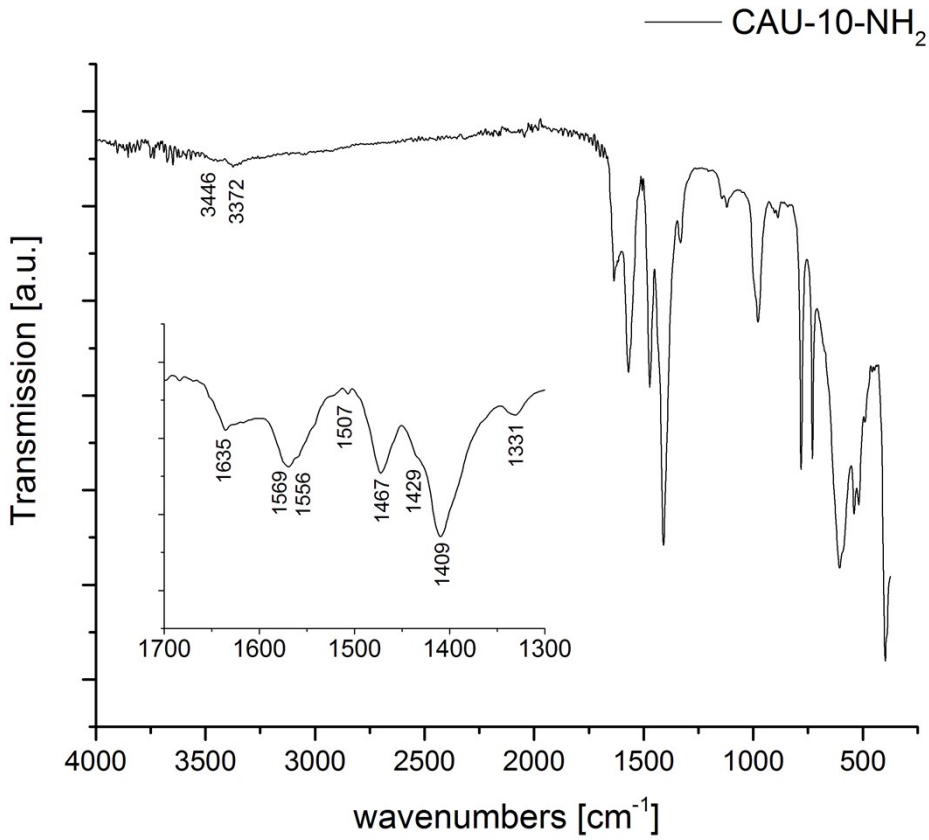

Fig. S7: IR-spectrum of CAU-10-NH_2 containing exclusively aminoisoterephthalate ions.

Table S4: Vibrations and corresponding band positions for the IR-spectrum of CAU-10-H.

Vibration	Position for CAU-10-NH_2 [cm^{-1}]
ν_{as} (NH_2)	3372
ν_s (NH_2)	3446
ν (CO_2)	1635
ν_{as} (CO_2)	1569
ν_{as} (CO_2)	1556
δ(NH)	1507
ν (CC)	1467
ν (CC)	1429
ν_s (CO_2)	1409
ν (CN)	1331

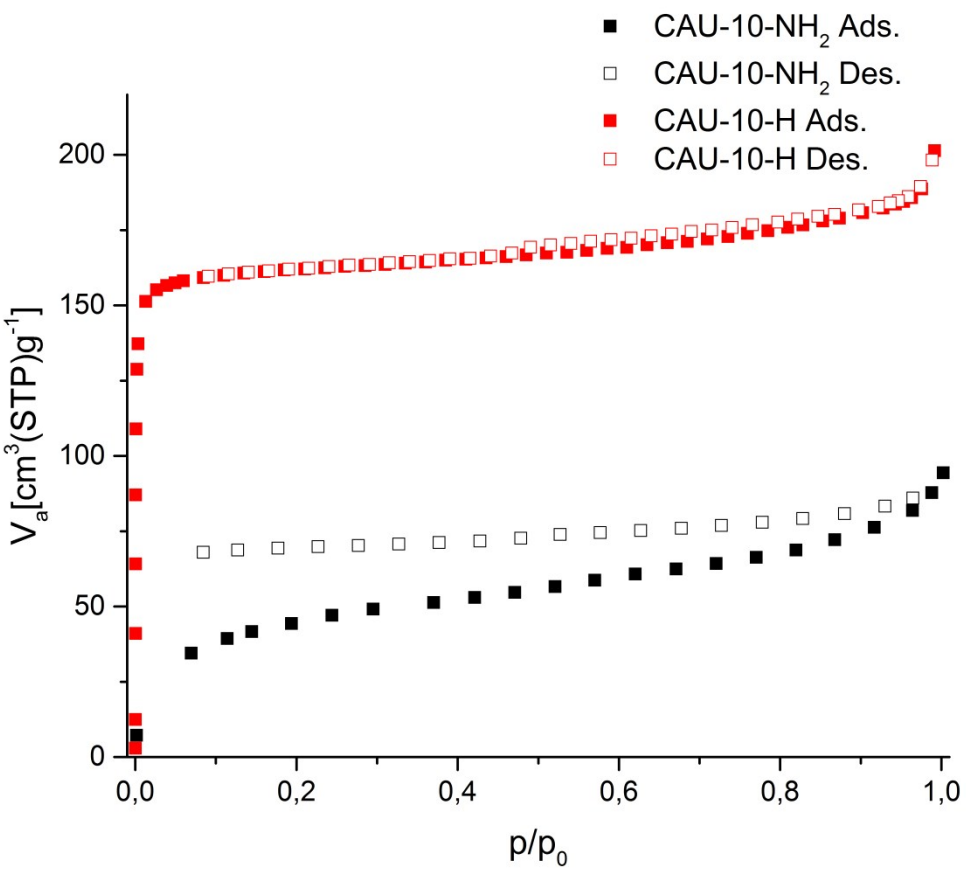

Fig. S8: The results of the N_2 sorption measurements at 77 K of the two CAU-10 samples containing either isophthalate (CAU-10-H) or aminoisoterephthalate (CAU-10-NH_2) ions.

Table S5: Specific BET surface areas and micropore volumes for the samples CAU-10-H and CAU-10-NH_2 compared to the values reported in literature[26a]. The BET evaluation in the case of CAU-10-NH_2 is problematic due to kinetic hindrance.

Compound	spec. BET surface area [m²/g]	micropore volume [cm³/g]
Literature CAU-10-H[26b]	640	0.25
CAU-10-H	656	0.25
CAU-10-NH_2	[159]	0.08

2. Catalytic studies

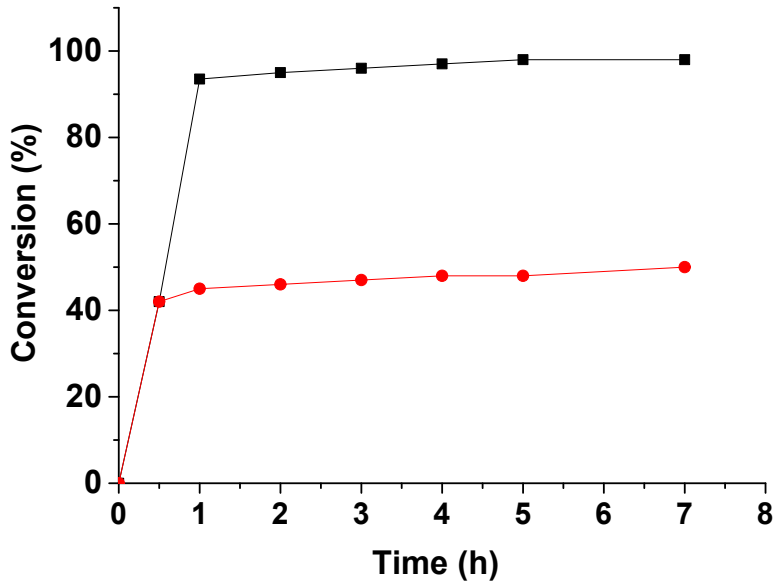

Fig. S9: Result of the hot filtration experiment on CAU-1-NH_2. Time conversion plots for the reaction between benzaldehyde and malononitrile in the presence of CAU-1-NH_2 (black square) and conversion plot after removal of the catalyst after 30 minutes (red dots).

3. Characterisation of the CAU-1 type materials after the catalytic investigation

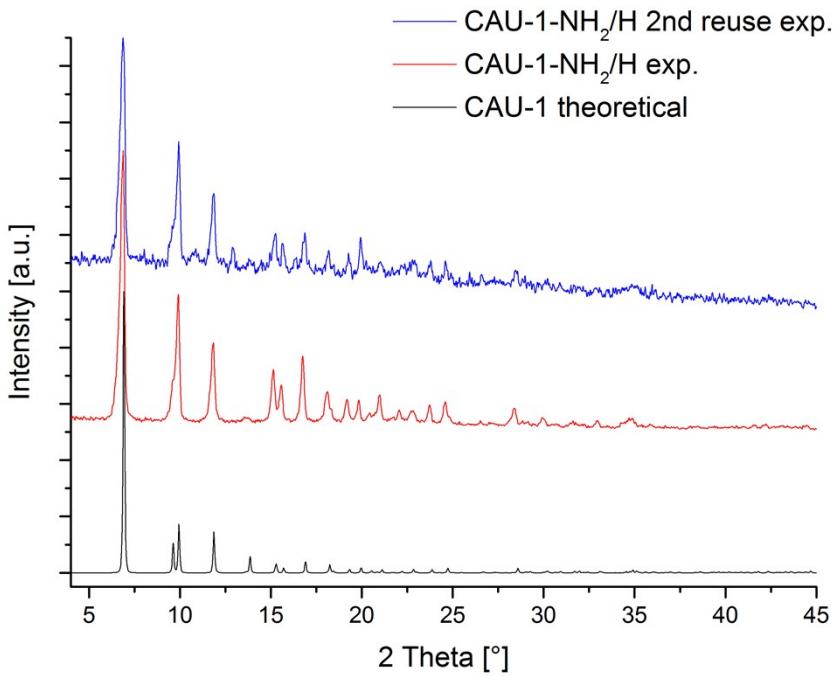

Fig. S10: PXRD patterns of fresh and recovered CAU-1-NH_2/H catalysts.

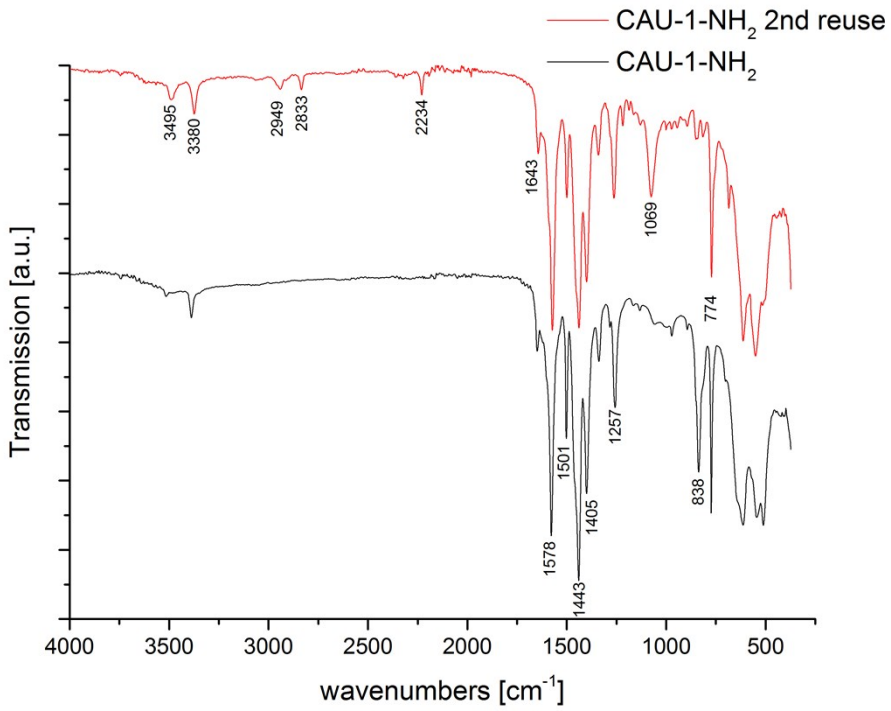

Fig. S11: IR spectra of fresh and recovered CAU-1-NH_2 catalysts. The additionally observed bands in the IR spectrum of the recovered catalyst are due to presence of solvent molecules (ethanol) and the product benzylidenmalonitrile: 1069 cm^{-1} (C-O stretching in ethanol), 2234 cm^{-1} (CN stretching in product), 2833 cm^{-1} (CH stretching in product), 2949 cm^{-1} (CH stretching from ethanol).

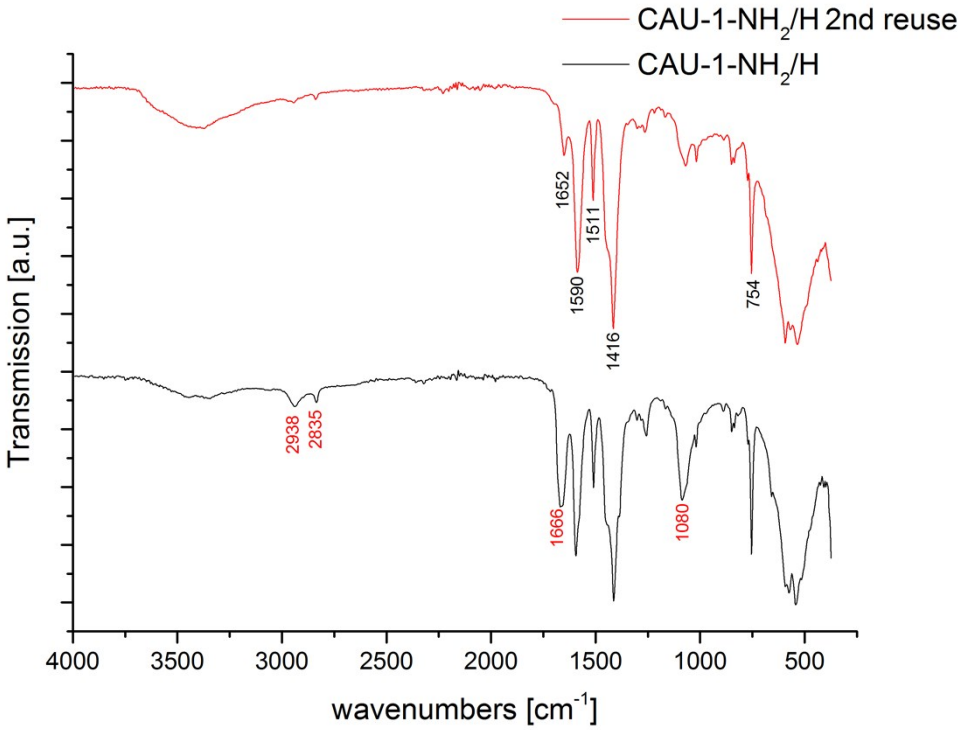

Fig. S12: IR spectra of fresh and recovered CAU-1-NH_2/H catalysts.