Supplementary Information for:

Interplay between hydrophobicity and basicity toward the catalytic activity of isoreticular organocatalyst MOFs

Sedigheh Abedi, Alireza Azhdari Tehrani, Hosein Ghasempour and Ali Morsali,*

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

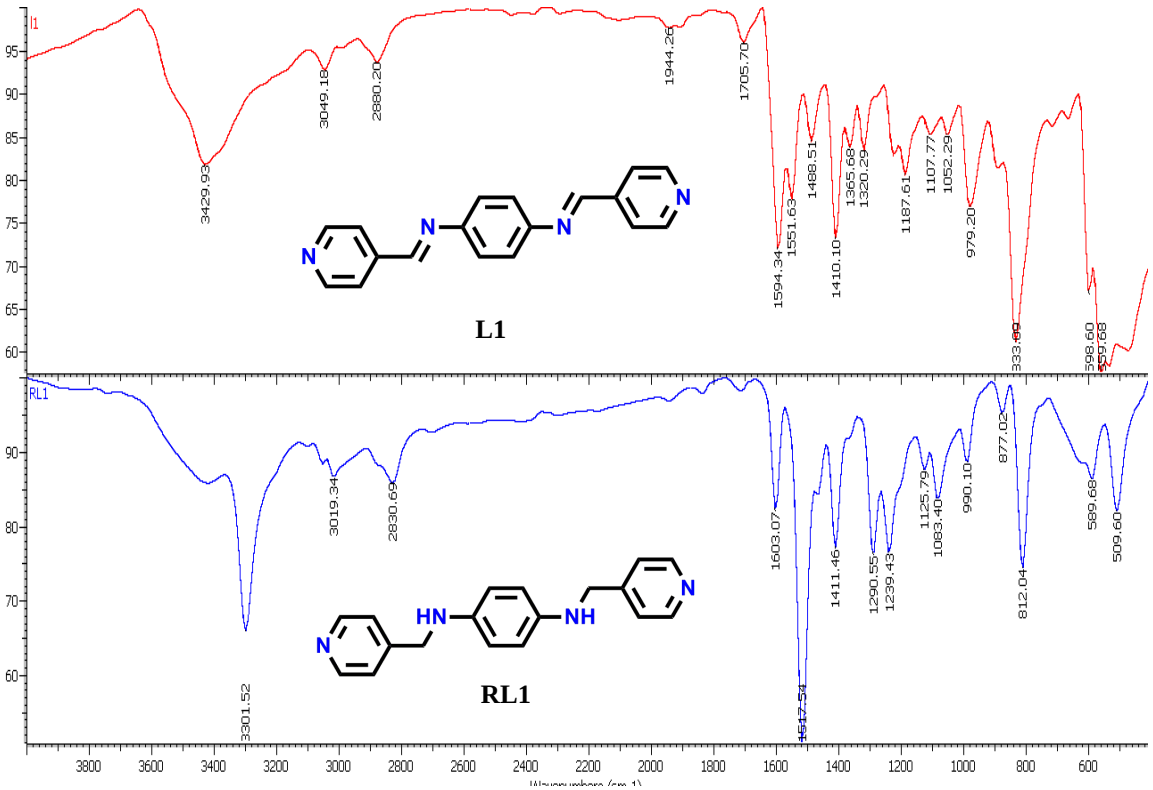


Figure S1. FT-IR spectra of the ligands, L1 and RL1.

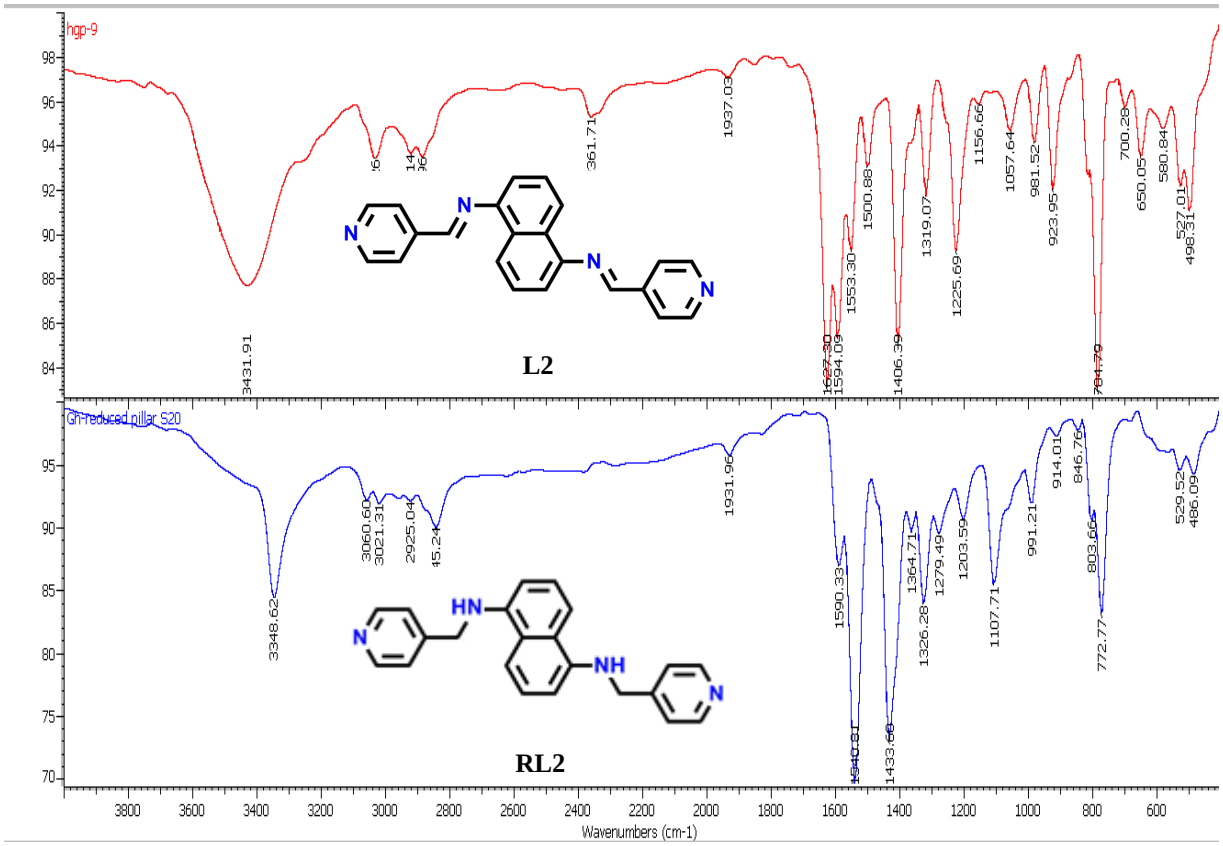


Figure **S2**. FT-IR spectra of the ligands, L2 and RL2.

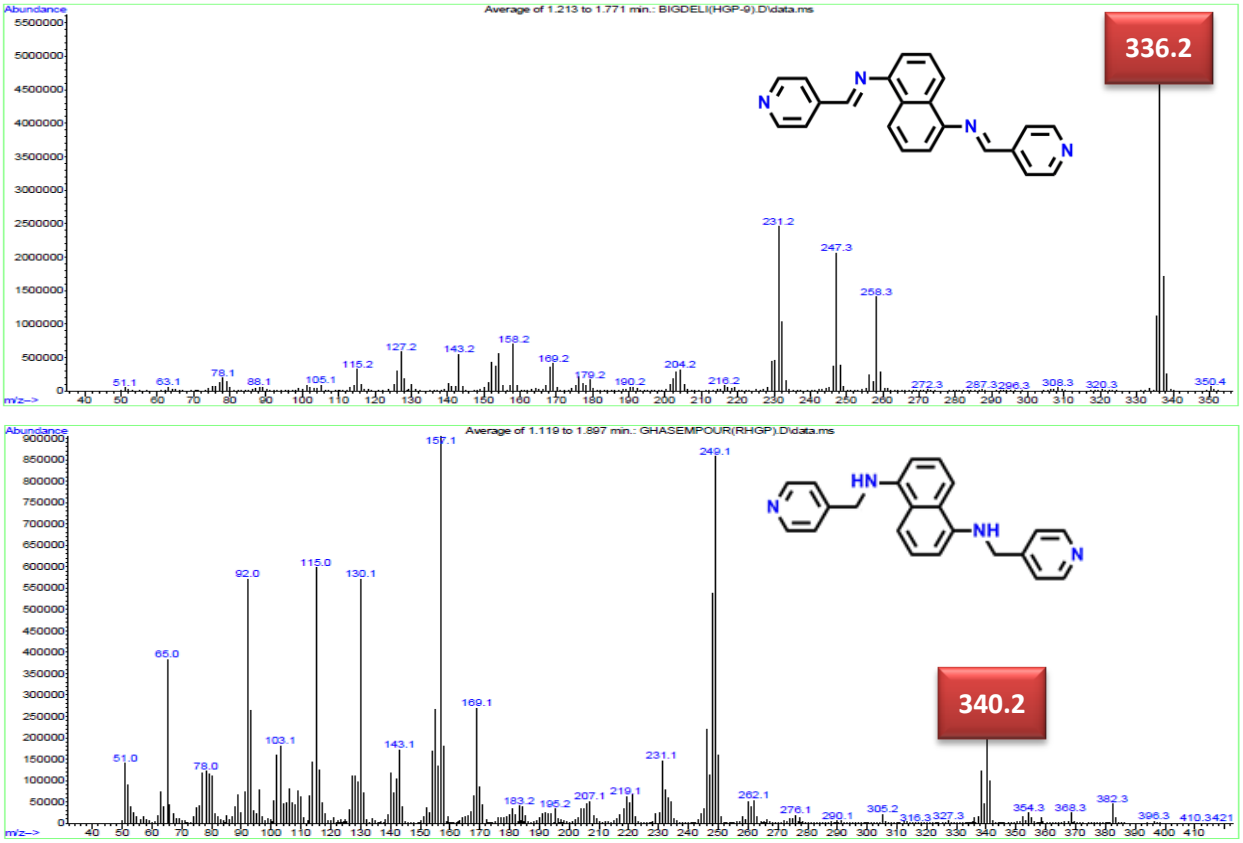


Figure **S3**. Mass spectra of the ligands, L2 and RL2.

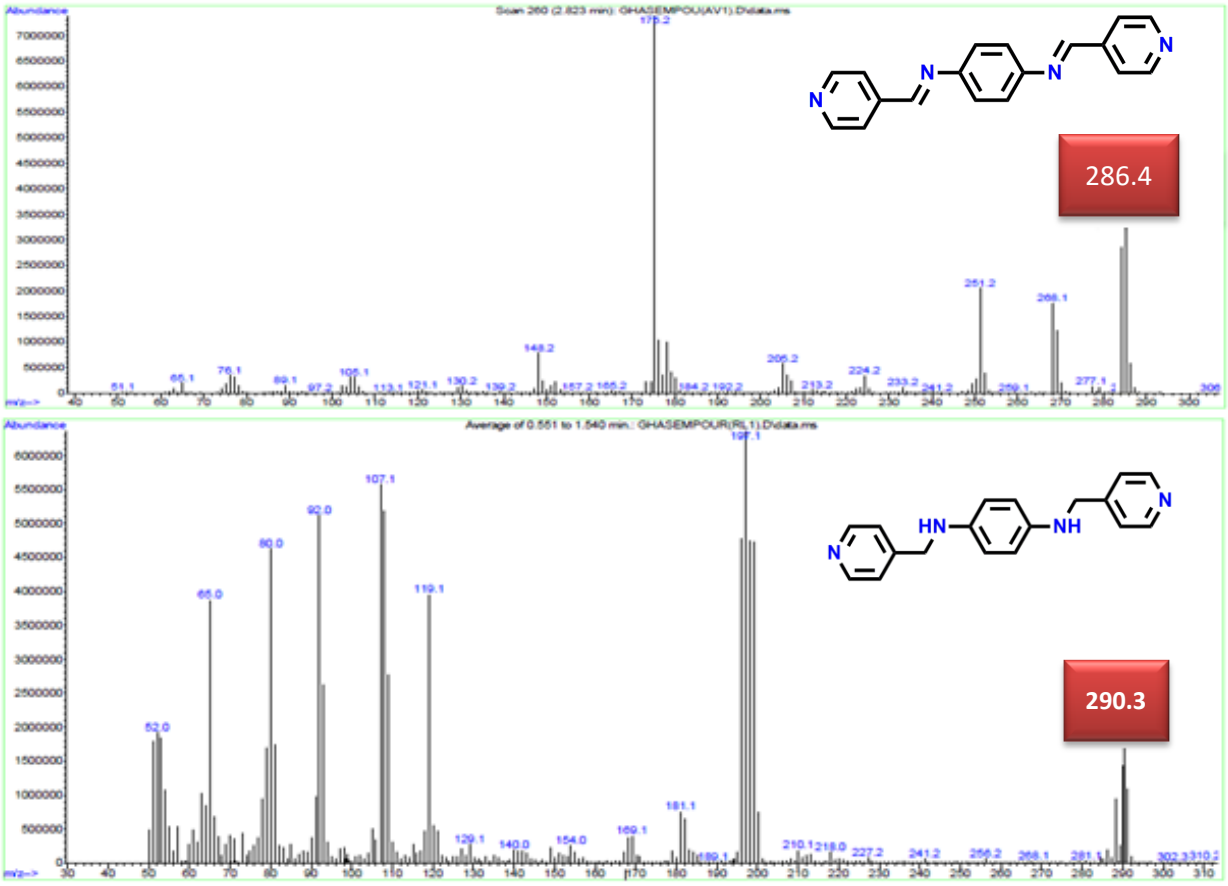


Figure S4. Mass spectra of the ligands, L1 and RL1.

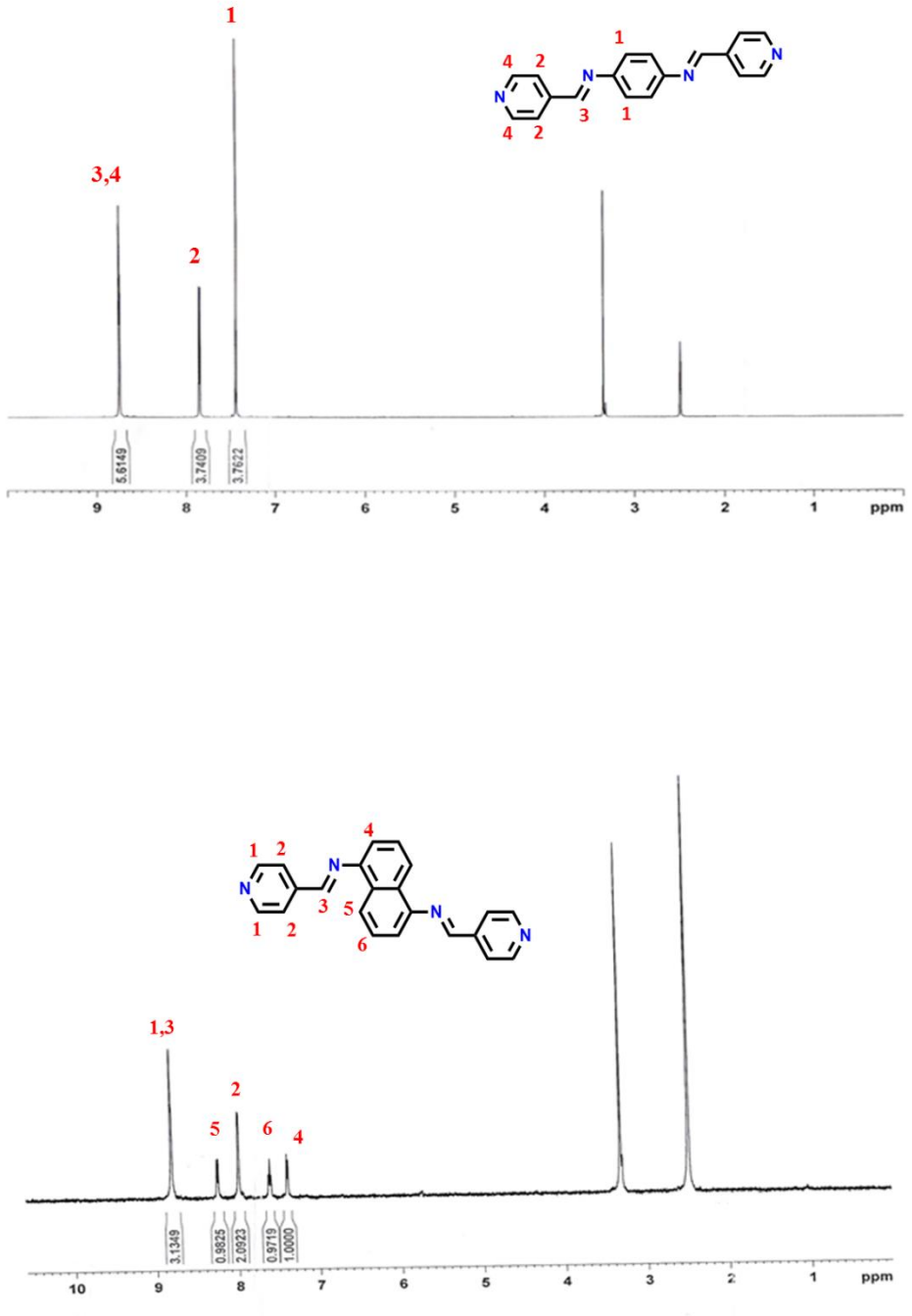


Figure S5 (a). 1H-NMR spectra of L1 and L2

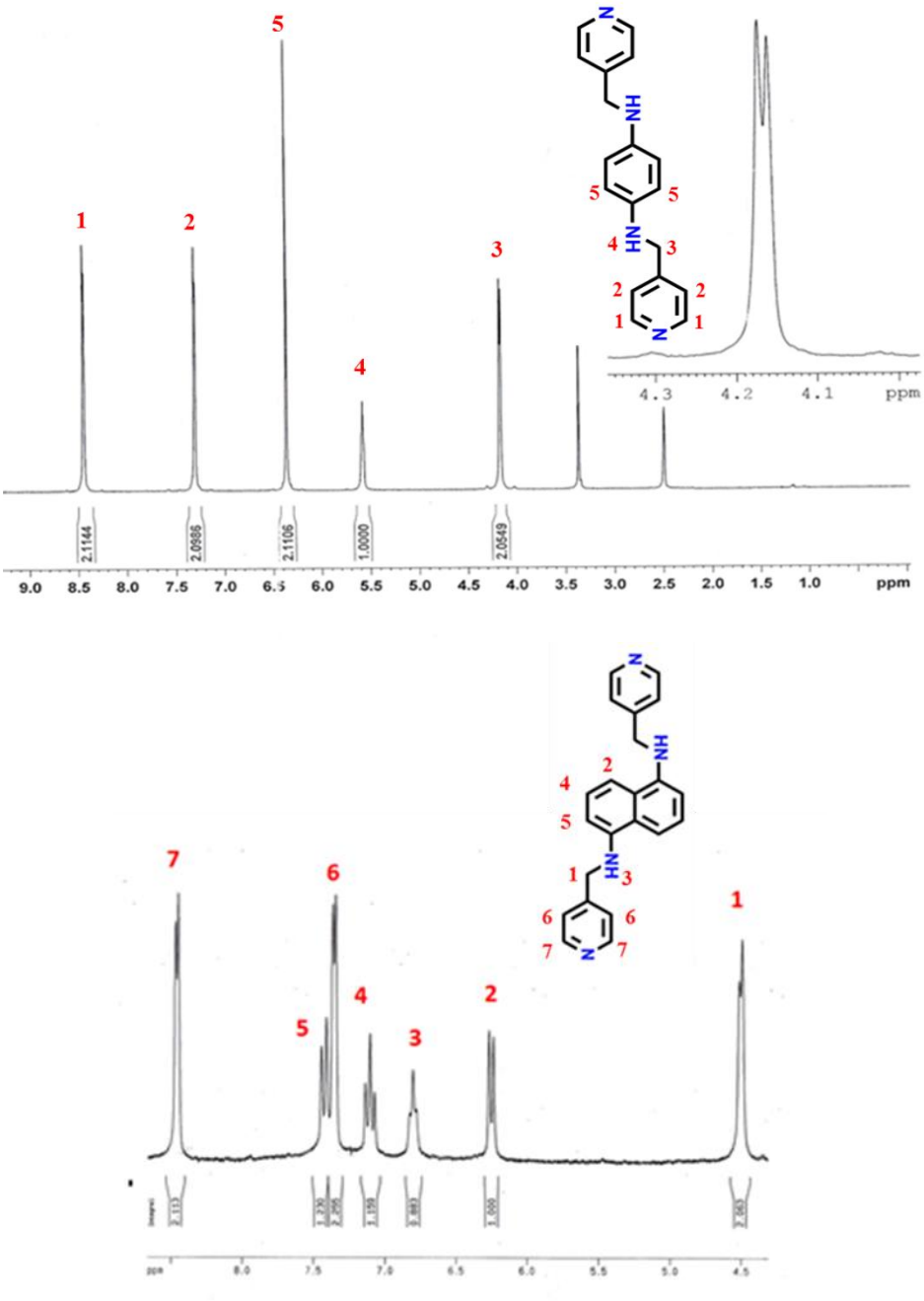


Figure S5 (b). 1H-NMR spectra of RL1 and RL2.

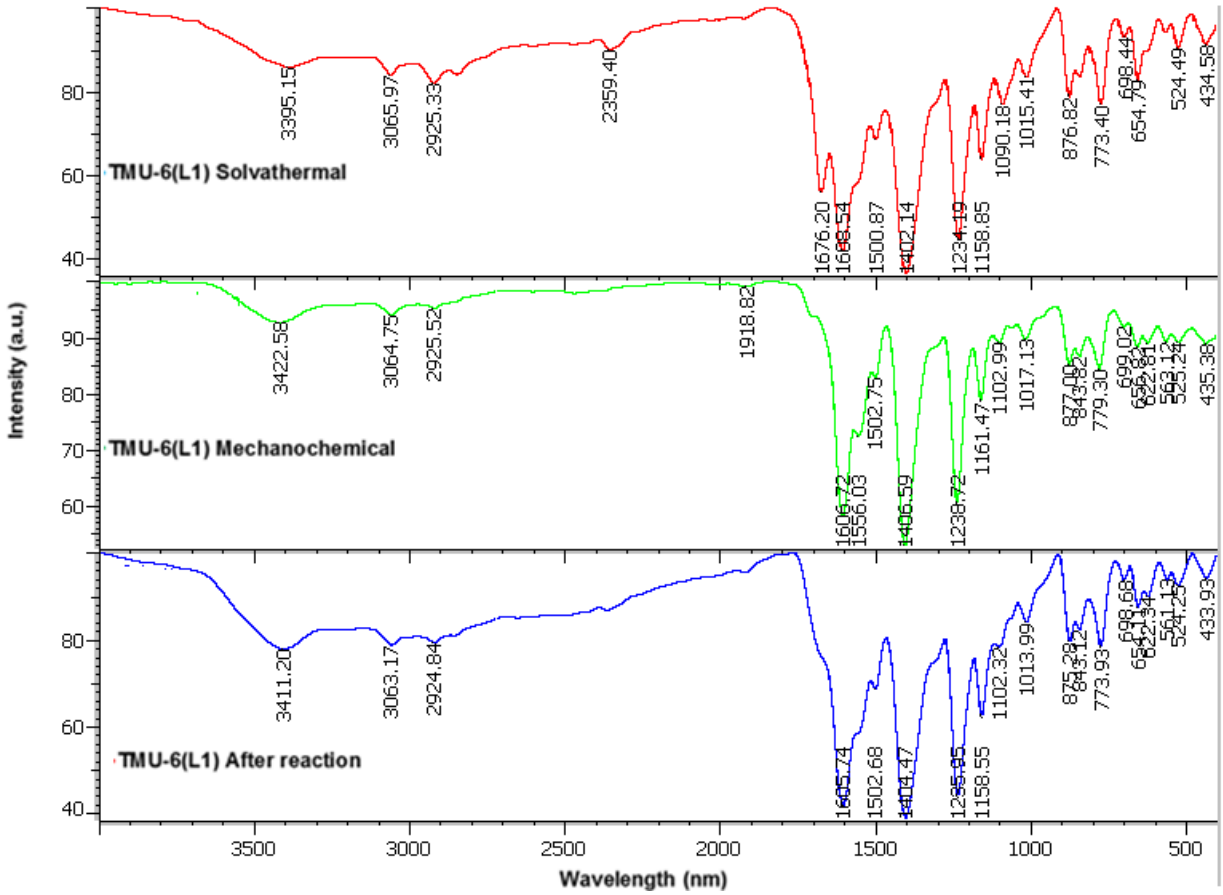


Figure S6. Comparative FT-IR spectra of TMU-6(L1) synthesized with different method and the recycled one after the condensation reaction.

The FT-IR spectrum of the MOFs shows the same characteristic bands of the dicarboxylate groups of the H_2oba ligands at ca. 1606 and 1404 cm^{-1} for the asymmetric and symmetric vibrations, respectively, which indicate coordination of carboxylate ligands to metal ions. The absence of the expected characteristic bands at 1730–1690 cm^{-1} for the protonated carboxylate groups indicates the complete deprotonation of H_2oba ligand in the reaction with Zn ions.
This point exists in FT-IR spectrum of all prepared MOFs.

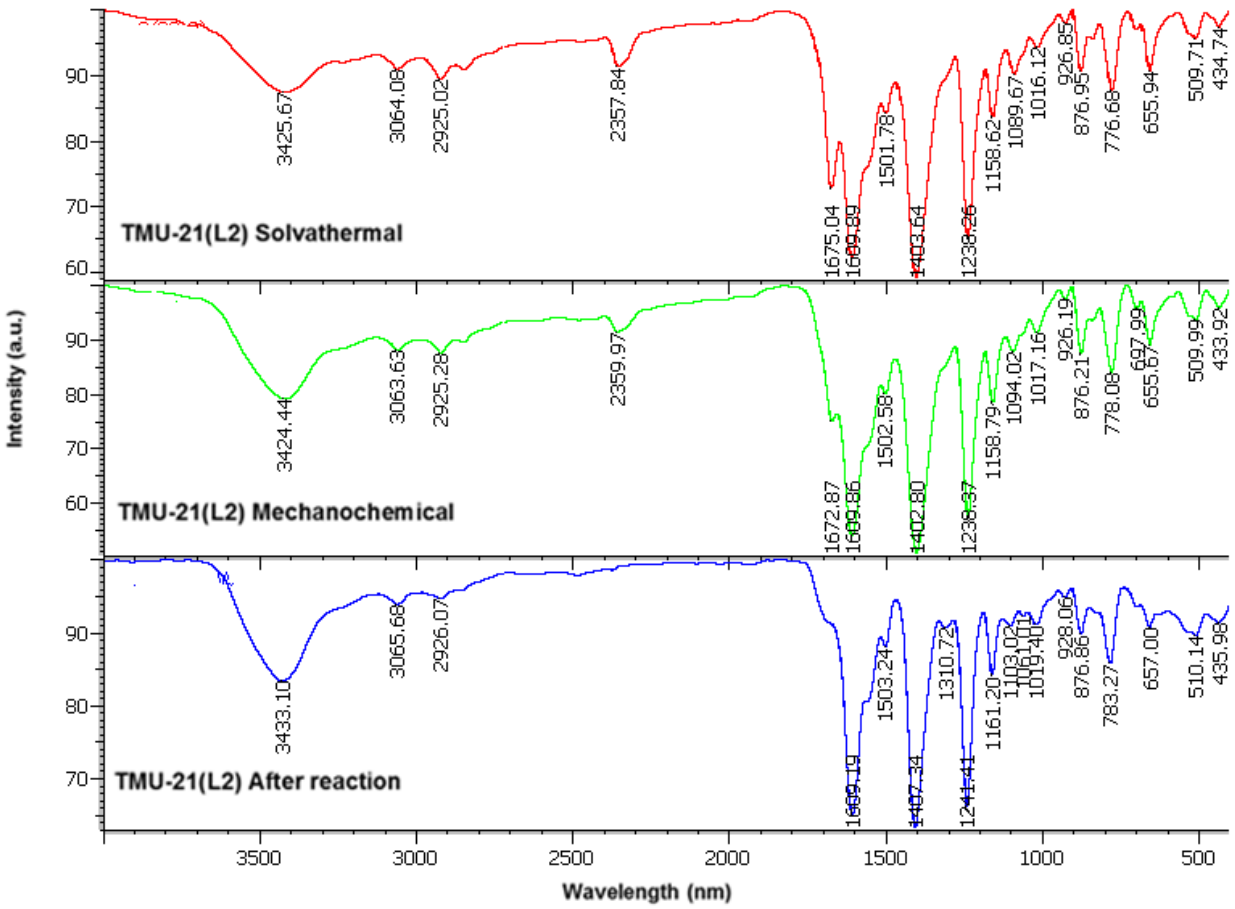


Figure S7. Comparative FT-IR spectra of TMU-21(L2) synthesized with different method and the recycled one after the condensation reaction.

The FT-IR spectrum of the MOFs shows the same characteristic bands of the dicarboxylate groups of the H_2oba ligands at ca. 1609 and 1402 cm^{-1} for the asymmetric and symmetric vibrations, respectively, which indicate coordination of carboxylate ligands to metal ions.

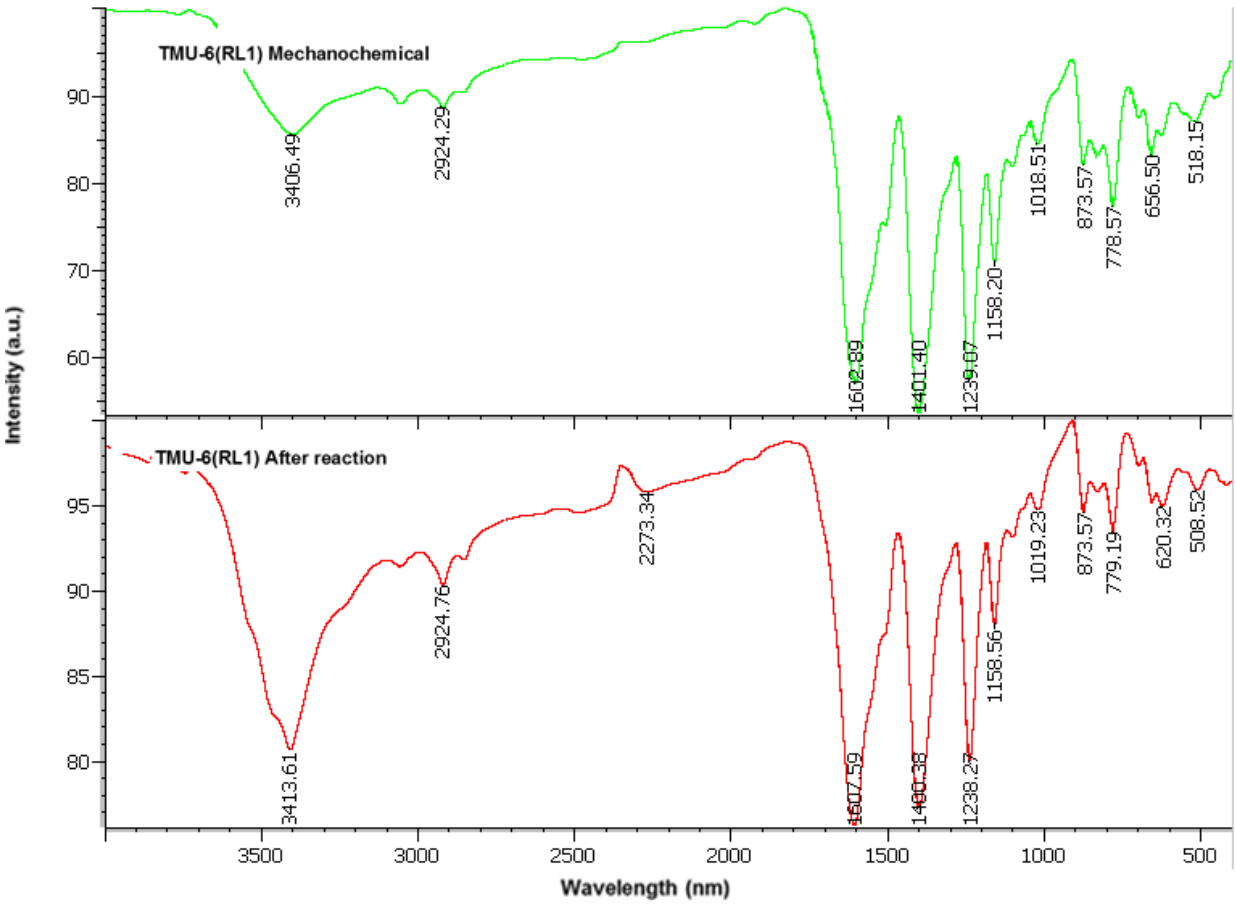


Figure S8. Comparative FT-IR spectra of TMU-6(RL1) and the recycled one after the condensation reaction.

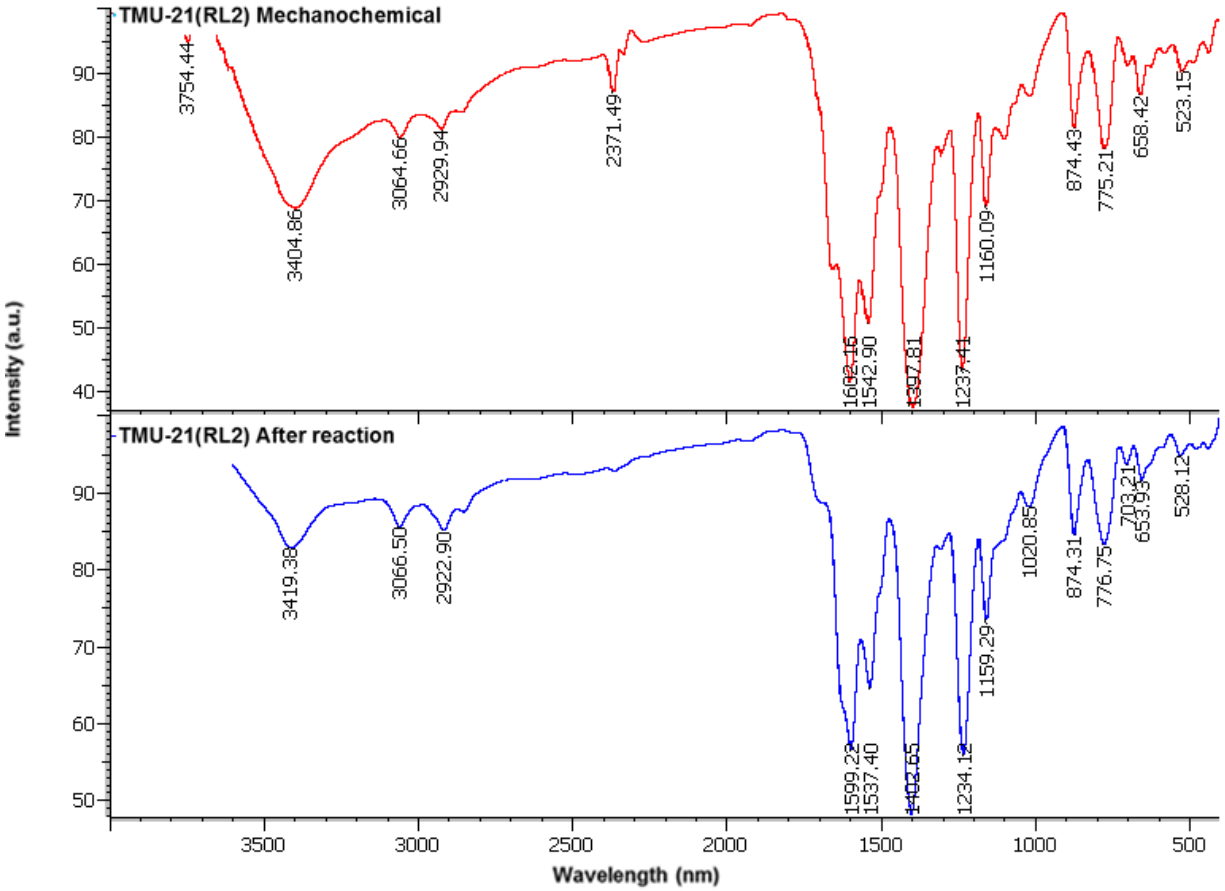


Figure S9. Comparative FT-IR spectra of TMU-21(RL2) synthesized and the recycled one after the condensation reaction.

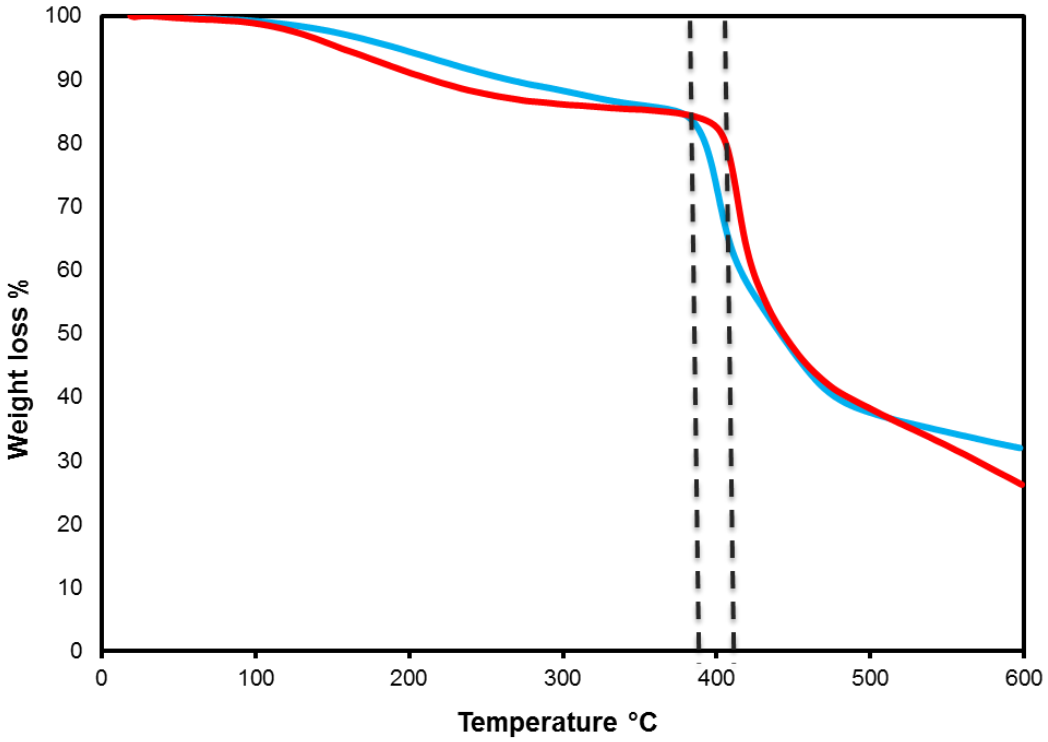


Figure S10. Thermogravimetric analysis of TMU-6(L1) (blue line) and TMU-21(L2) (red line)

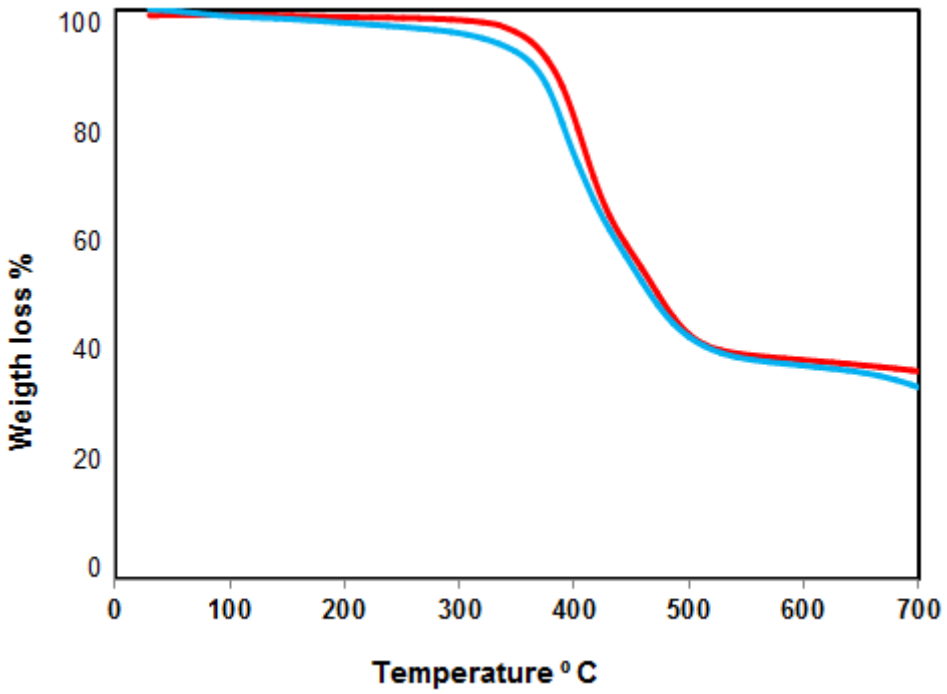


Figure S11. Thermogravimetric analysis of TMU-6(RL1) (blue line) and TMU-21(RL2) (red line)

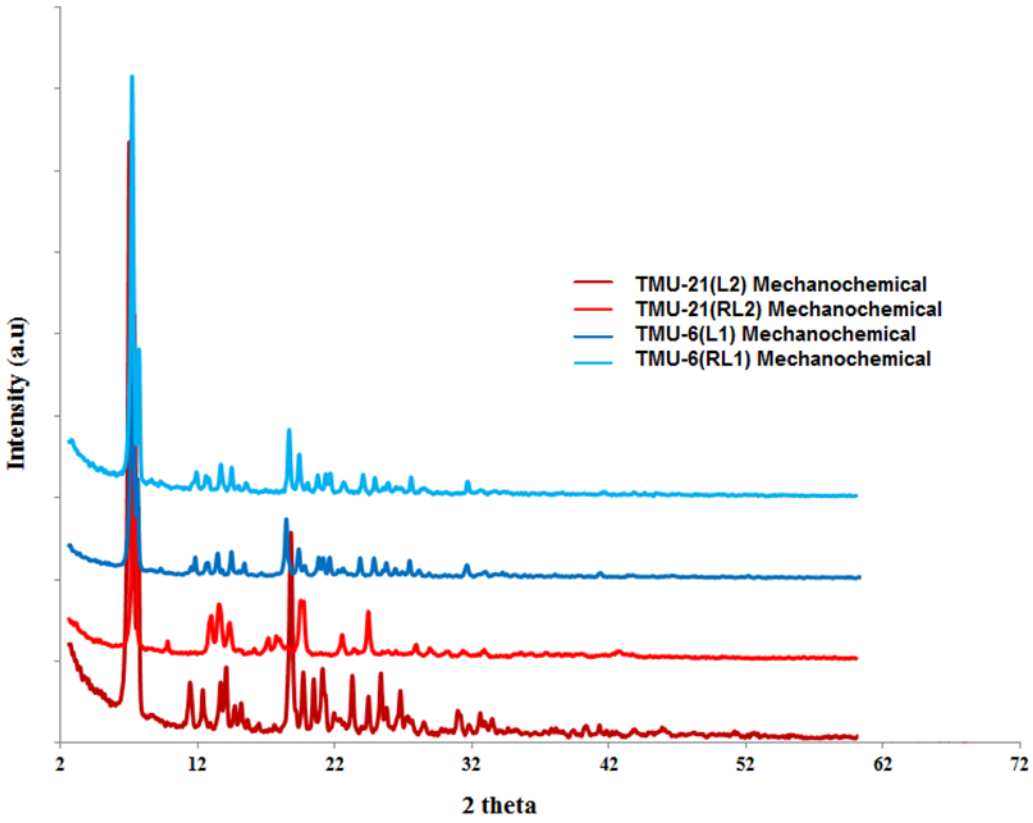


Figure S12. PXRD patterns of TMU-6(L1), TMU-6(RL1), TMU-21(L2) and TMU-21(RL2) revealed that these four MOFs are isoreticular framework.

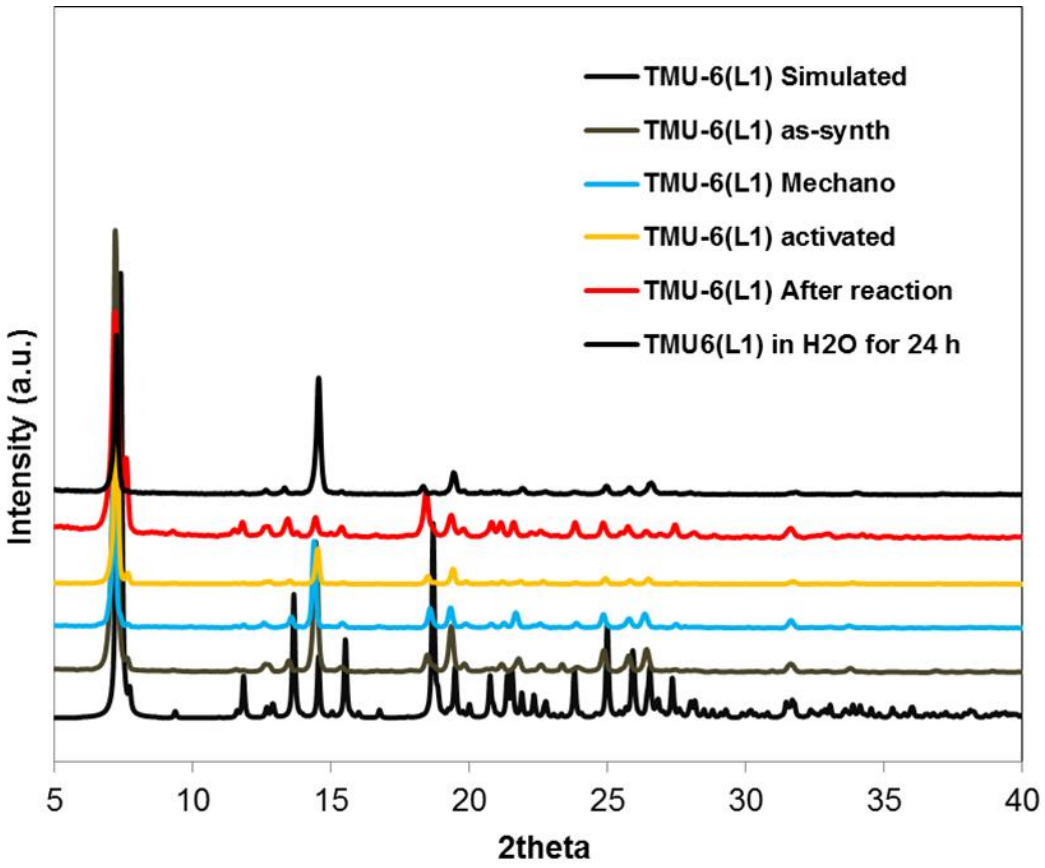


Figure S13. PXRD patterns of simulated, as-synthesized, mechano-synthesized, activated, after reaction and water stability of TMU-6(L1). The recycling PXRD of the MOFs were recorded after 7^{th} cycle of reusability test.

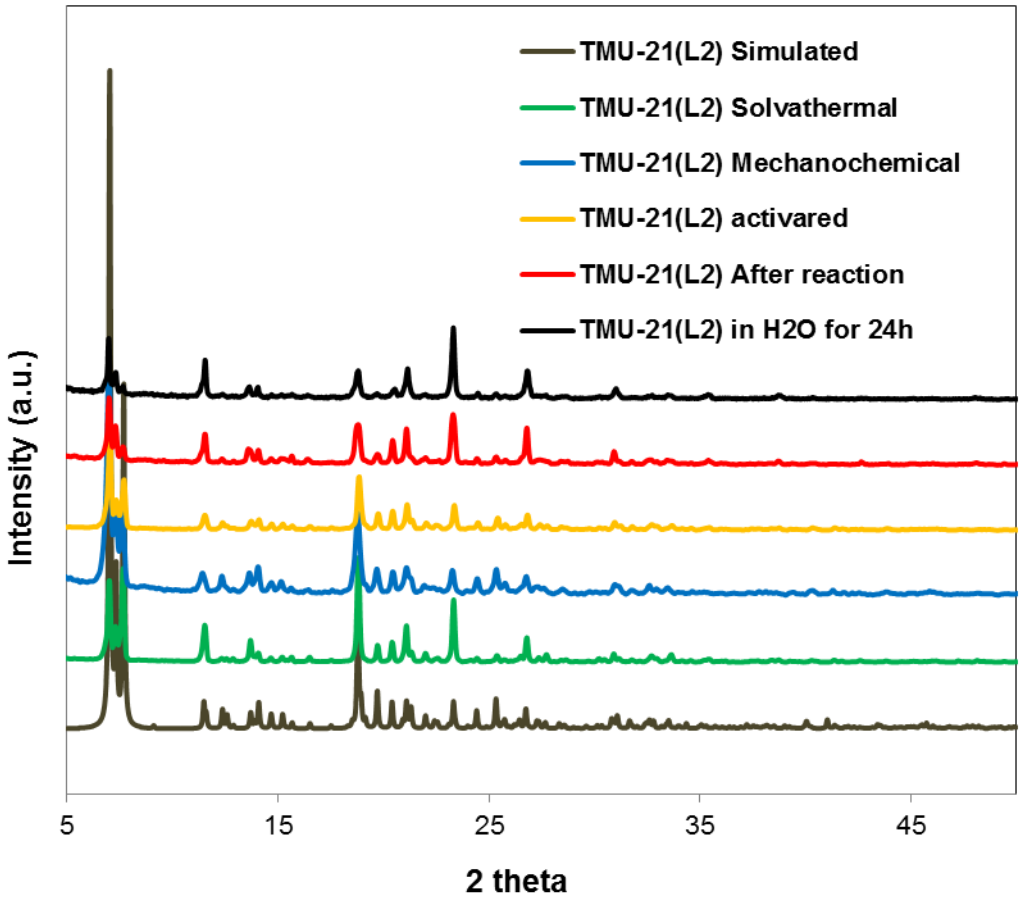


Figure S14. PXRD patterns of simulated, as-synthesized, mechano-synthesized, activated, after reaction and water stability of TMU-21(L2). The recycling PXRD of the MOFs were recorded after 7th cycle of reusability test.

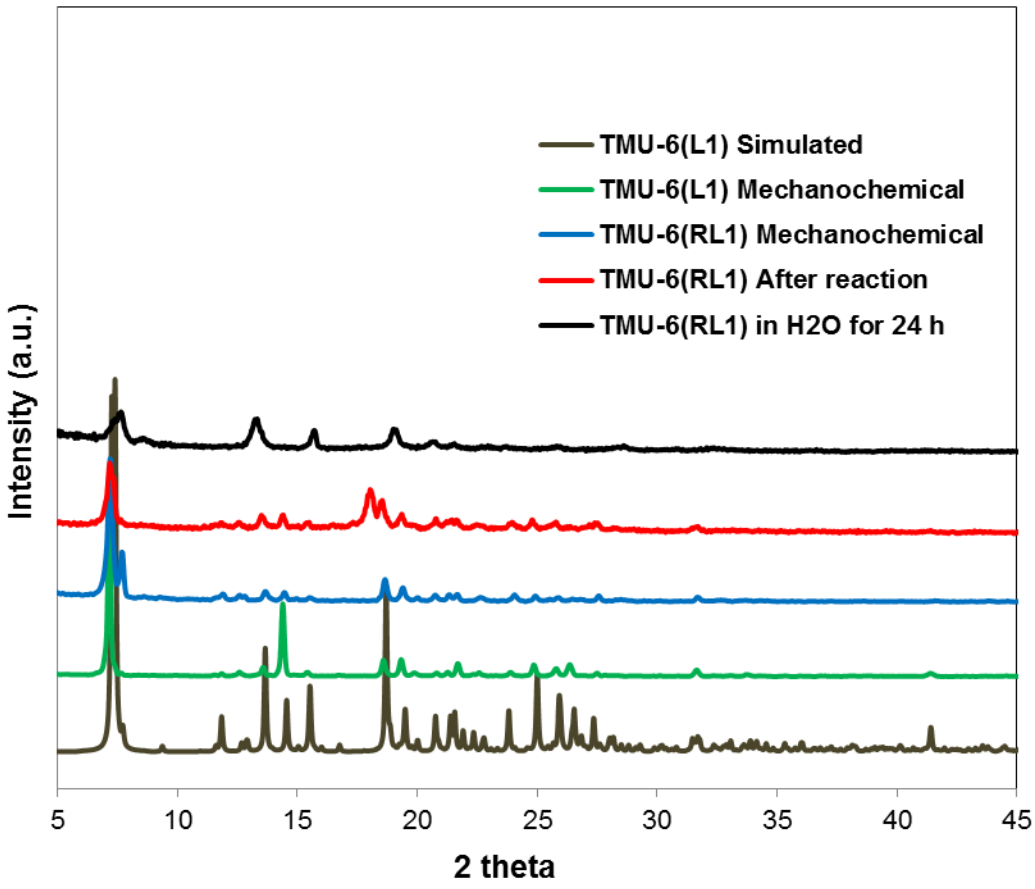


Figure S15. PXRD patterns of simulated, mechano-synthesized, after reaction and water stability of TMU-6(L1) and TMU-6(RL1). The recycling PXRD of the MOFs were recorded after 7th cycle of reusability test.

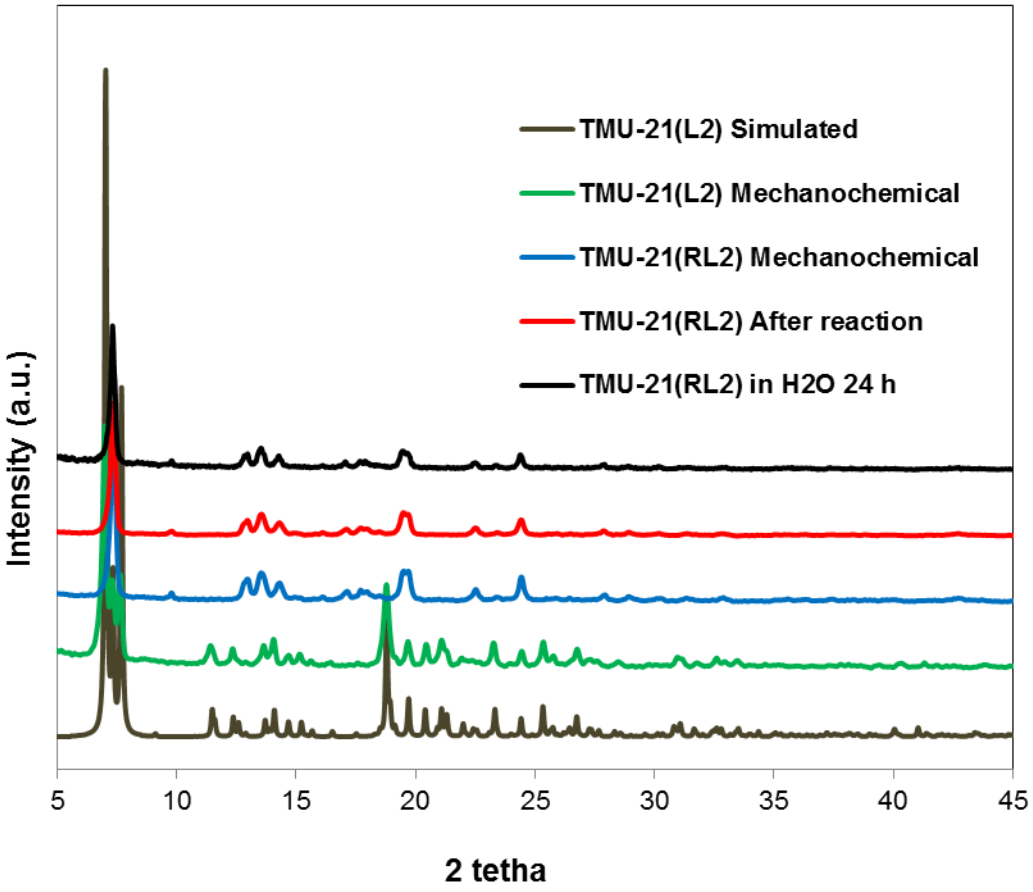
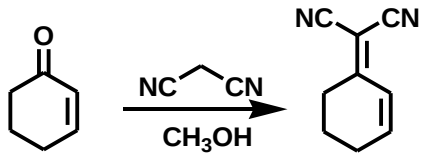


Figure S16. PXRD patterns of simulated, mechano-synthesized, after reaction and water stability of TMU-21(L2) and TMU-21(RL2). The recycling PXRD of the MOFs were recorded after 7th cycle of reusability test.



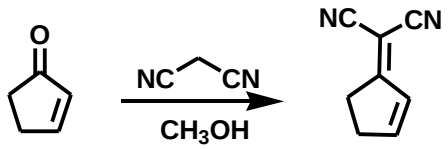
Time	**TMU-21(L2)**	**TMU-6(L1)**	**TMU-6(RL1)**	**TMU-21(RL2)**	**control**
MeOH R.T.	30	16.5	11	7.6	0.0
MeOH 60°C	60.5	45	40	36	0.0
EtOH 60°C	19.4	13	13.2	10	0.0

Table S1. Catalytic performance of TMU-6(L1), TMU-6(RL1), TMU-21(L2) and TMU-21(RL2), obtained by mechanochemical synthesis, within aldol condensation of malonitrile with 2-cyclohexen-1-one, 24h.

Identification of the product: 2-(cyclohex-2-enylidene)malononitrile

FT-IR data (KBr pellet, ν/cm-1): 436(m), 570(m), 806(w), 1024(m), 1095(m), 1260(w), 1443(w), 1637(s), 2203(s), 2925(s), 3432(m)

^{1}H NMR (500 MHz, $CDCl_3$): 1.86 (m, 2H), 2.44 (m, 2H), 2.55 (t, 2H), 6.13 (m, 1H), 6.70 (d, 1H)



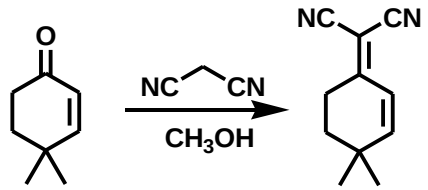
Time	**TMU-6(RL1)**	**TMU-6(L1)**	**TMU-21(L2)**	**TMU-21(RL2)**
12 h	54	47.8	40.2	25
24 h	93.7	89	76.3	60
36 h	97.3	99.2	93	80
60 h	---	---	99.5	95.4

Table S2. Time in depended catalytic performance of TMU-6(L1), TMU-6(RL1), TMU-21(L2) and TMU-21(RL2), obtained by mechanochemical synthesis within aldol condensation of malonitrile with 2-cyclopenten-1-one.

Identification of the product: 2-(cyclopent-2-enylidene)malononitrile

FT-IR data (KBr pellet, ν/cm^{-1}): 566(m), 1097(m), 1304(m), 1439(m), 1577(s), 1642(vs), 2204(vs), 2948(m), 3234(m), 3350(m)

^{1}H NMR (500 MHz, $CDCl_3$): 1.61 (m, 2H), 2.06 (t, 2H), 5.09 (m, 1H), 5.82 (d, 1H)



Time	**TMU-21(L2)**	**TMU-6(L1)**	**TMU-6(RL1)**	**TMU-21(RL2)**
12 h	53.5	42.8	38.5	27.6
24 h	72.7	53.4	48	31.3
36 h	87	72.4	69	63
60 h	91.4	80.8	77.8	70.3

Table S3. Time in depended catalytic performance of TMU-6(L1), TMU-6(RL1), TMU-21(L2) and TMU-21(RL2), obtained by mechanochemical synthesis, within aldol condensation of malonitrile with 4,4-dimethylcyclohexen-1-one.

Identification of the product: 2-(4,4-dimethylcyclohex-2-enylidene)malononitrile

FT-IR data (KBr pellet, ν/cm^{-1}): 682(m), 1022(m), 1219(m), 1456(m), 1553(m), 1605(s), 2192(s), 2959(m), 3209(m), 3347(m)

^{1}H NMR (500 MHz, $CDCl_3$): 1.14 (s, 6H), 1.71 (t, 2H), 2.83 (t, 2H), 6.45 (d, 1H), 6.62 (d, 1H)

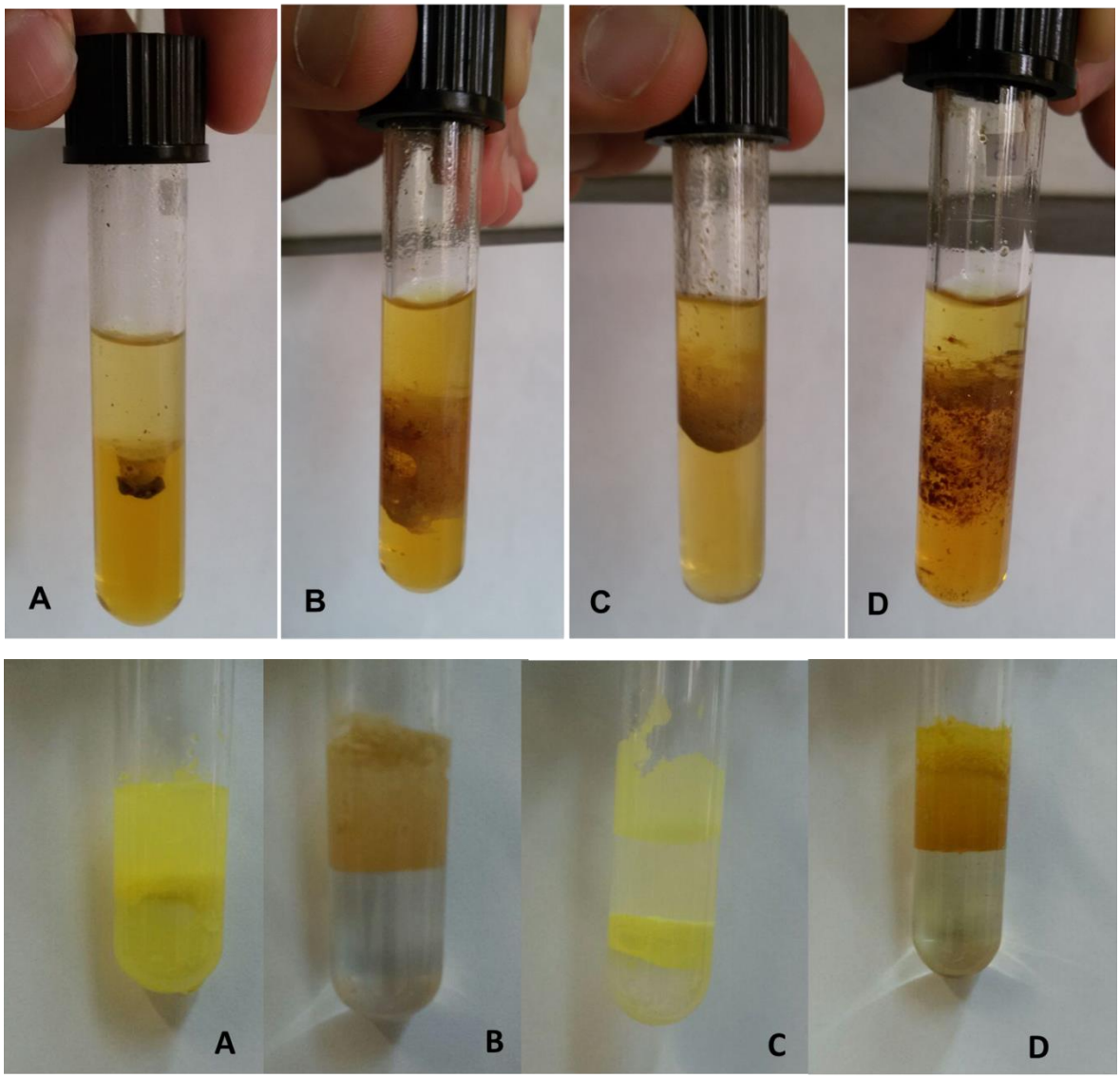


Figure S17. The images of the catalysts in H_2O solvents after addition of toluene (up), in H_2O solvents after addition of dichloromethane (down) (a) TMU-21(L2), (b) TMU-21(RL2), (c) TMU-6(L1) and (d) TMU-6(RL1).

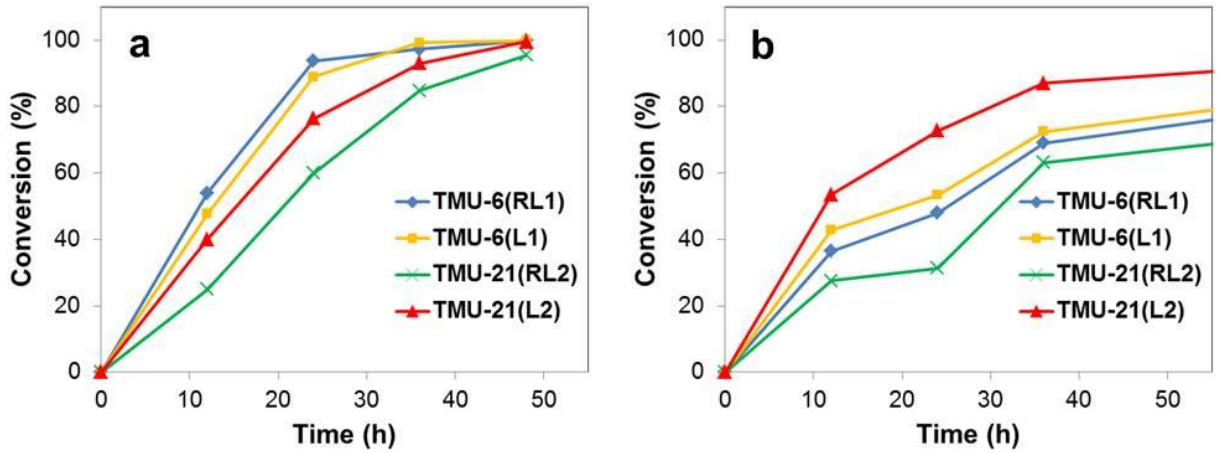


Figure S18. Yield-versus-time profile of aldol-type condensation reaction of (a) 2-cyclopenten-1-one and (b) 4,4-dimethyl-2-cyclohexen-1-one catalyzed by four MOF structures in the reaction conditions indicated in Table 1 of the manuscript.

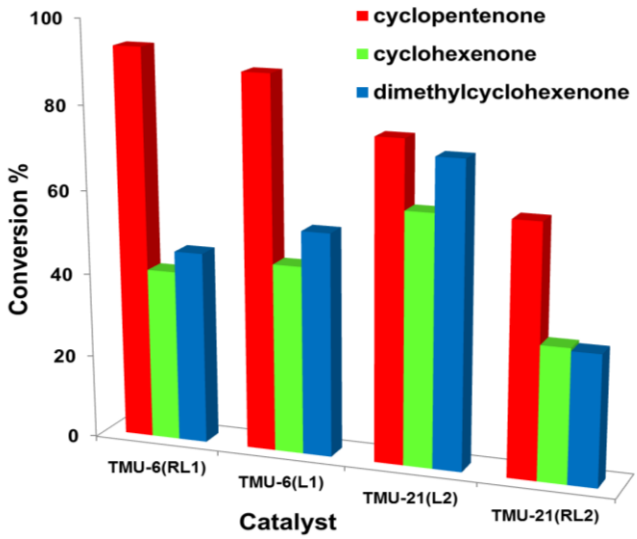


Figure S19 Comparison of the catalyst reactivity of various substrates in the presence of different basic MOFs.

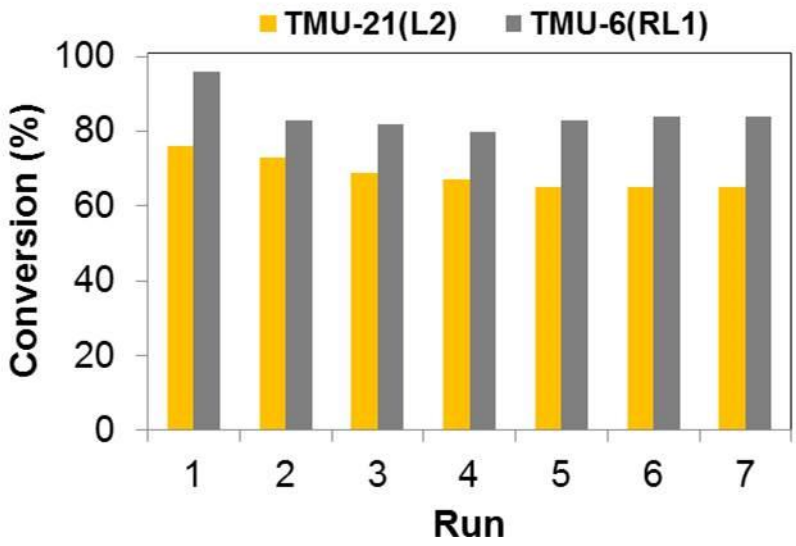


Figure S20. Reusability of TMU-6(RL1) (gray) and TMU-21(L2) (orange) in aldol-type condensation reaction of 2-cyclopenten-1-one and 4,4-dimethyl-2-cyclohexen-1-one (0.6 mmol), respectively. (Conditions: catalyst (5 mol%), malononitrile (0.9 mmol), MeOH, 60 °C, 24h)