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# A heteropolyacid-based ionic liquid immobilized onto magnetic fibrous nano-silica as robust and recyclable heterogeneous catalysts for the synthesis of tetrahydrodipyrazolopyridines in water

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**Table S1** Comparison of the catalytic efficiency of $Fe_3O_4/SiO_2/KCC\text{-}1/SO_4H$ MNPs with various catalysts.

| Entry | Catalyst | Solvent | Amount catalyst (mol%) | T (°C) | Time (h) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | $ZnCl_2$ | EtOH | 10 | Reflux | 5 | 88 [51] |
| 2 | $FeCl_3$ | EtOH | 10 | Reflux | 5 | 85 [51] |
| 3 | $MgCl_2$ | EtOH | 10 | Reflux | 5 | 84 [51] |
| 4 | $Yb(OTf)_3$ | EtOH | 5 | Reflux | 3 | 90 [51] |
| 5 | $Cu(ClO_4)_2\_6H_2O$ | EtOH | 5 | Reflux | 3 | 90 [51] |
| 6 | Vitamin B1 | EtOH | 5 | Reflux | 4 | 88 [51] |
| 7 | TsOH | EtOH | 10 | Reflux | 4 | 88 [51] |
| 8 | $NH_2SO_3H$ | EtOH | 10 | Reflux | 4 | 86 [51] |
| 9 | - | EtOH | - | Reflux | 5 | 79 [52] |
| 10 | - | $H_2O$/EtOH | - | Reflux | 6 | 40 [52] |
| 11 | - | [Hmim]TFA | - | Reflux | 12 | 60 [52] |
| 12 | p-TSA | $H_2O$ | -[b] | Reflux | 6 | 36 [52] |
| 13 | $K_2CO_3$ | $H_2O$ | -[b] | Reflux | 9 | 68 [52] |
| 14 | Piperidine | $H_2O$ | -[b] | Reflux | 9 | 43 [52] |
| 15 | $Fe_3O_4$/KCC-1/IL/HPW | $H_2O$ | 0.4 | r.t. | 0.5 | 96 [52] |

[a] Reaction conditions: benzaldehyde (1 mmol), phenylacetylene (1 mmol), 1H-benzo[d]imidazol-2-amine (1 mmol) in different amounts of catalyst, temperature, and time.
[b] The amount of catalyst is not mentioned in the article.