Efficient Synthesis of Rhodanine-Based Amides via Passerini Reaction using Tetramethylguanidine-Functionalized Silica Nanoparticles as Reusable Catalyst

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Characterization of catalyst

The catalyst structure was characterized by elemental analysis (CHN), Fourier-transform infrared (FTIR) spectroscopy, termogravimetric analysis (TGA), X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM).

FTIR spectra of nano-SiO₂, SiO₂-Cl and TMG-SiO₂ NPs are shown in Figure S1. The peaks around 460, 805 and 1100 cm⁻¹ are the typical Si–O–Si band attributed to the condensed silica network present in pure and modified silica. For all samples, the absorption bands at 1630 and 3445 cm⁻¹ can be associated to the O–H vibration of silanol groups and absorbed water. The characteristic peaks at about 2850 and 2913 cm⁻¹, which are related to the C–H stretching of alkyl groups (Figures S1b, S1c); in addition, the absorption bands at 1445 cm⁻¹ and 1620 cm⁻¹ due to stretching vibrations of C–N and C=N groups displayed, indicating that tetramethylguanidine (TMG) has been loaded into the support (Figure S1c).

TG curve of TMG-SiO₂ NPs (Figure S2) revealed an initial weight loss of 3.24% below 150 °C due to the adsorbed water on the surface of catalyst. Complete loss of the organic species was observed in the temperature range of 220-600 °C, with the amount of organic moiety nearly 7.65% (0.5 mmol of TMG per 1.0 g of the catalyst).

XRD diffractogram of TMG-SiO₂ NPs shows strong broad peak at 22° (2θ), which is characteristic of amorphous nano silica (Figure S3).

From the multiple FE-SEM images, it can be determined that the average diameter of SiO₂ nanoparticles after immobilization of TMG is about 40 nm (Figure S4). Moreover, the FE-SEM image of the recycled catalyst after the 5th reaction run revealed that nanostructure of TMG-SiO₂ NPs was retained during the catalysis and the recycling experiments.

Figure S1. FTIR spectra of (a) SiO₂, (b) SiO₂-Cl and (c) TMG-SiO₂ NPs.

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**Figure S2.** Thermal gravimetric analysis of TMG-Si₂O₅ NPs.

**Figure S3.** XRD pattern of the TMG-Si₂O₅ NPs.
Figure S4. FE-SEM images of nano silica (a); TMG-SiO2 NPs before use (b) and after reuse five times (c).
Figure S5. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4a.

Figure S6. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4a.
Figure S7. Mass spectrum of 4a.

Figure S8. IR spectrum (KBr) of 4a.
Figure S9. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4b.

Figure S10. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4b.
Figure S11. Mass spectrum of 4b.

Figure S12. IR spectrum (KBr) of 4b.
Figure S13. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4c.

Figure S14. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4c.
Figure S15. Mass spectrum of 4c.

Figure S16. IR spectrum (KBr) of 4c.
Figure S17. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4d.

Figure S18. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4d.
Figure S19. Mass spectrum of 4d.

Figure S20. IR spectrum (KBr) of 4d.
Figure S21. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4e.

Figure S22. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4e.
Figure S23. Mass spectrum of 4e.

Figure S24. IR spectrum (KBr) of 4e.
Figure S25. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4f.

Figure S26. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4f.
Figure S27. Mass spectrum of 4f.

Figure S28. IR spectrum (KBr) of 4f.
Figure S29. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4g.

Figure S30. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4g.
Figure S31. Mass spectrum of 4g.

Figure S32. IR spectrum (KBr) of 4g.
Figure S33. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4h.

Figure S34. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4h.
Figure S35. Mass spectrum of 4h.

Figure S36. IR spectrum (KBr) of 4h.
Figure S37. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4i.

Figure S38. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4i.
Figure S39. Mass spectrum of 4i.

Figure S40. IR spectrum (KBr) of 4i.
Figure S41. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4j.

Figure S42. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4j.
Figure S43. Mass spectrum of 4j.

Figure S44. IR spectrum (KBr) of 4j.