Supplementary material

Synthesis of C₃-symmetric cinchona-based organocatalysts and their application in asymmetric Michael and Friedel–Crafts reactions

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1. Structures of the prepared C₃-symmetric hub-cinchonas

![Structures of the prepared hub-cinchonas](image)

**Figure S1.** Structures of the prepared hub-cinchonas.
2. NMR spectra of Hub\textsuperscript{1-4}-cinchonas

![Figure S2. \textsuperscript{1}H NMR spectrum of Hub\textsuperscript{1}-cinchona (DMSO-d\textsubscript{6}).](image)

![Figure S3. Selected \textsuperscript{1}H NMR spectral regions of Hub\textsuperscript{1}-cinchona (DMSO-d\textsubscript{6}).](image)
Figure S4. $^{13}$C NMR spectrum of Hub$^1$-cinchona (DMSO-d$_6$).

Figure S5. COSY spectrum of Hub$^1$-cinchona (DMSO-d$_6$).
Figure S6. HSQC spectrum of Hub1-cinchona (DMSO-d<sub>6</sub>).

Figure S7. HMBC spectrum of Hub1-cinchona (DMSO-d<sub>6</sub>).
Figure S8. $^{15}$N – $^1$H HMBC spectrum of Hub$^1$-cinchona (DMSO-d$_6$).
Figure S9. $^1$H NMR spectrum of Hub$^2$-cinchona (DMSO-d$_6$).

Figure S10. Selected $^1$H NMR spectral regions of Hub$^2$-cinchona (DMSO-d$_6$).
Figure S11. $^{13}$C NMR spectrum of Hub$^2$-cinchona (DMSO-d$_6$).

Figure S12. COSY spectrum of Hub$^2$-cinchona (DMSO-d$_6$).
Figure S13. HSQC spectrum of Hub²-cinchona (DMSO-d₆).

Figure S14. HMBC spectrum of Hub²-cinchona (DMSO-d₆).
Figure S15. $^{15}$N – $^1$H HMBC spectrum of Hub$^2$-cinchona (DMSO-d$_6$).
Figure S16. $^1$H NMR spectrum of $\text{Hub}^3$-cinchona (DMSO-d$_6$).

Figure S17. Selected $^1$H NMR spectral regions of $\text{Hub}^3$-cinchona (DMSO-d$_6$).
Figure S18. $^{13}$C NMR spectrum of Hub$^3$-cinchona (DMSO-d$_6$).

Figure S19. COSY spectrum of Hub$^3$-cinchona (DMSO-d$_6$).
Figure S20. HSQC spectrum of Hub₁-cinchona (DMSO-d₆).

Figure S21. HMBC spectrum of Hub₁-cinchona (DMSO-d₆).
Figure S22. $^{15}$N – $^1$H HMBC spectrum of Hub$^3$-cinchona (DMSO-$d_6$).
Figure S23. $^1$H NMR spectrum of Hub^4-cinchona (DMSO-d$_6$).

Figure S24. Selected $^1$H NMR spectral regions of Hub^4-cinchona (DMSO-d$_6$).
Figure S25. $^{13}$C NMR spectrum of Hub$^4$-cinchona (DMSO-d$_6$).

Figure S26. COSY spectrum of Hub$^4$-cinchona (DMSO-d$_6$).
Figure S27. HSQC spectrum of Hub4-cinchona (DMSO-d$_6$).

Figure S28. HMBC spectrum of Hub4-cinchona (DMSO-d$_6$).
Figure S29. $^{15}$N – $^1$H HMBC spectrum of Hub$^4$-cinchona (DMSO-d$_6$).
3. MS spectra of \textbf{Hub\textsuperscript{1-4}-cinchonas}

\textbf{Figure S30.} HPLC-MS spectrum of \textbf{Hub\textsuperscript{1}-cinchona}.

\textbf{Figure S31.} HRMS spectrum of \textbf{Hub\textsuperscript{1}-cinchona} triflate salt.
Figure S32. HPLC-MS spectrum of Hub^2-cinchona.

Figure S33. Full scan HRMS spectrum of Hub^2-cinchona.
Figure S34. HRMS spectrum of Hub²-cinchona.

Figure S35. HPLC-MS spectrum of Hub³-cinchona.
Figure S36. HPLC-MS spectrum of Hub⁴-cinchona.

Figure S37. Full scan HRMS spectrum of Hub⁴-cinchona.
Figure S38. HRMS spectrum of Hub4-cinchona.
4. HPLC chromatograms

**Figure S39.** Products of the organocatalytic Michael and Friedel–Crafts-reactions.

**Figure S40.** Chiral HPLC chromatogram of racemic 18 (Phenomenex Lux Cellulose-1 column (5 μm, 250 × 4.6 mm), eluent water (0.1 % NH₄OAc)/MeCN = 30/70, isocratic mode; 0.8 mL min⁻¹, temperature 20 °C, UV detector 222 nm. Retention time for (S)-18: 7.6 min, for (R)-18: 8.9 min)

**Figure S41.** Chiral HPLC chromatogram of non-racemic 13 (Phenomenex Lux Cellulose-1 (5 μm, 250 x 4.6 mm) column, eluent water (0.1% NH₄OAc)/MeCN = 40/60, 0.8 mL min⁻¹, UV detector 222 nm. Retention time for (R)-13 and (S)-13 are 6.5 min and 7.2 min, respectively).
Figure S42. Chiral HPLC chromatogram of racemic 16 (Phenomenex Lux Cellulose-1 column (5 μm, 250 × 4.6 mm), eluent hexane/ethanol = 85/15, isocratic mode; 0.8 mL min⁻¹; temperature 20 °C, UV detector 254 nm. Retention time for (S)-16: 16.1 min, for (R)-16: 17.6 min).