

Supplementary material

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

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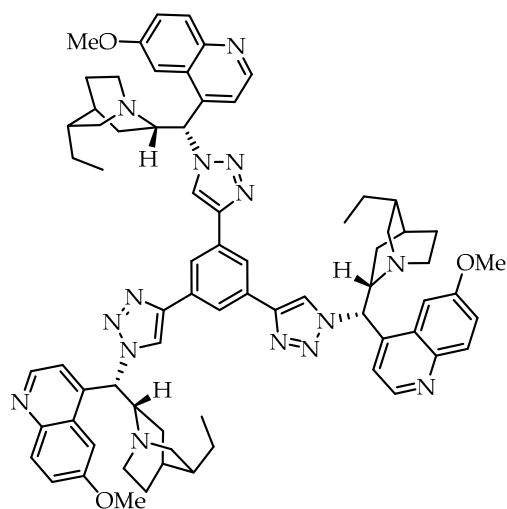
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Keywords: cinchona, organocatalysis, C₃-symmetry, size-enlargement, nanofiltration, asymmetric reaction

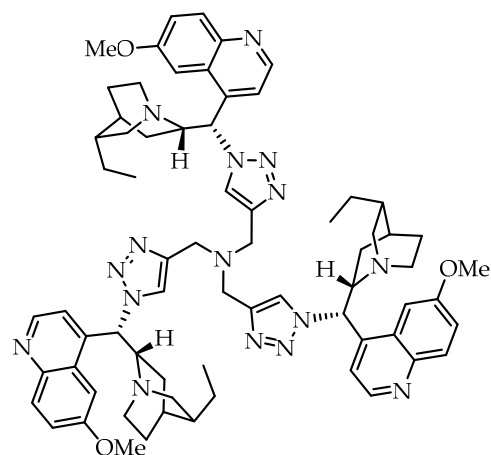
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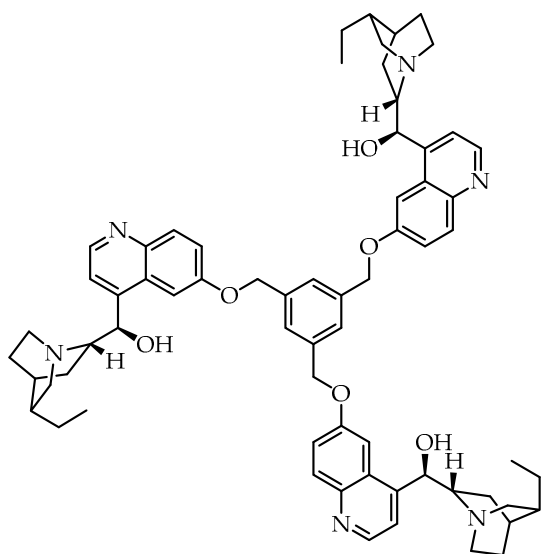
1. Structures of the prepared C₃-symmetric hub-cinchonas



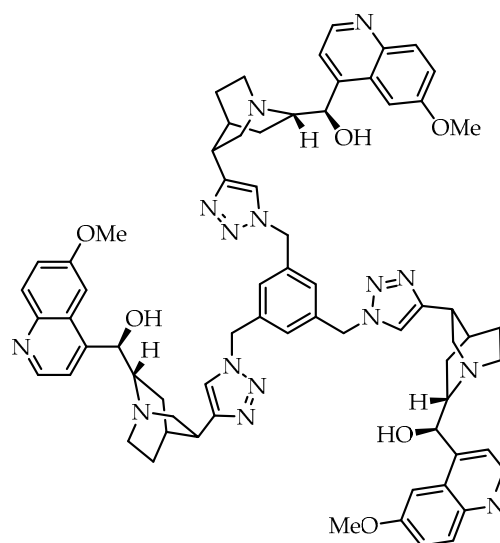
Hub¹-cinchona



Hub²-cinchona



Hub³-cinchona



Hub⁴-cinchona

Figure S1. Structures of the prepared hub-cinchonas.

2. NMR spectra of **Hub¹⁻⁴-cinchonas**

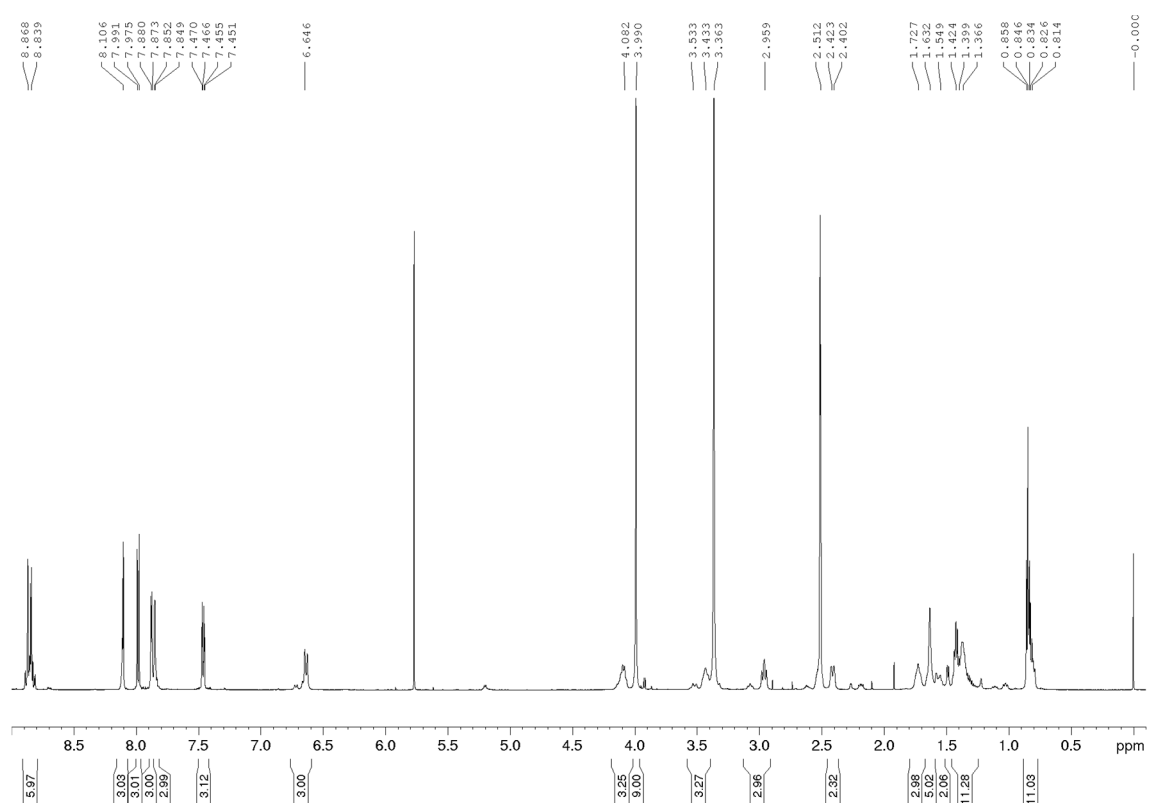


Figure S2. ¹H NMR spectrum of **Hub¹-cinchona** (DMSO-*d*₆).

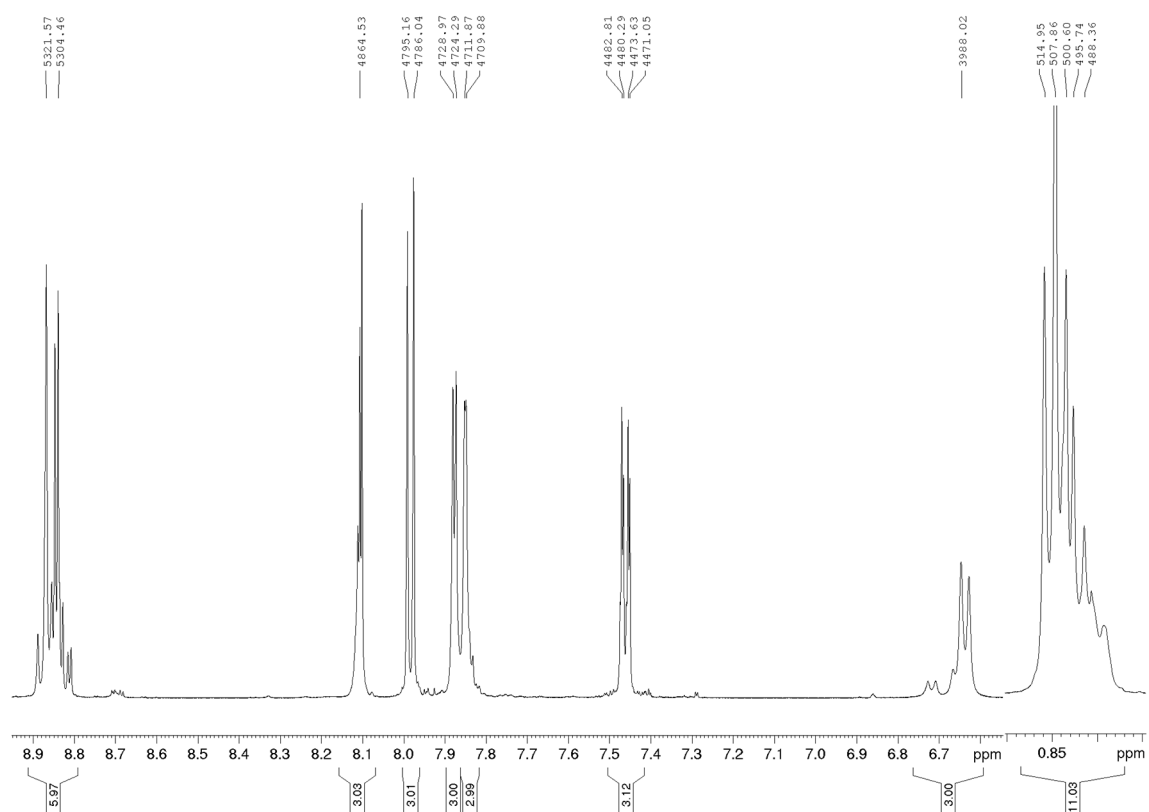


Figure S3. Selected ¹H NMR spectral regions of **Hub¹-cinchona** (DMSO-*d*₆).

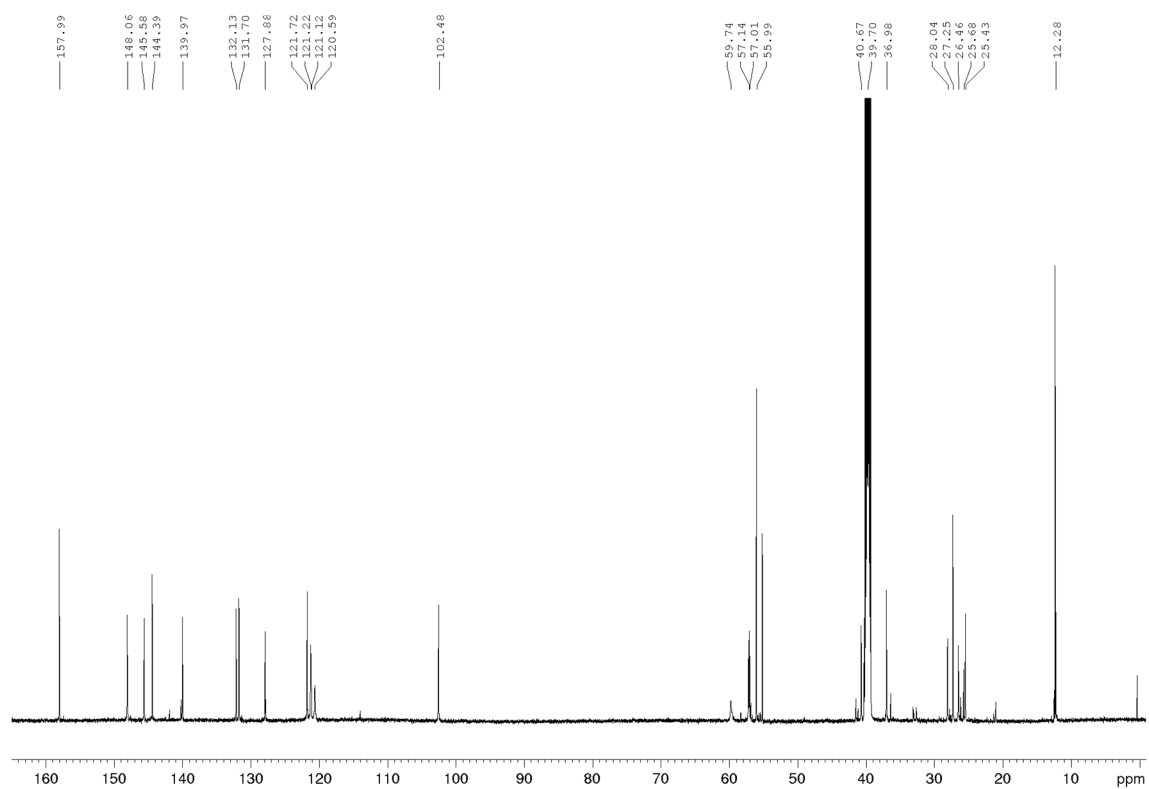


Figure S4. ^{13}C NMR spectrum of **Hub¹-cinchona** (DMSO- d_6).

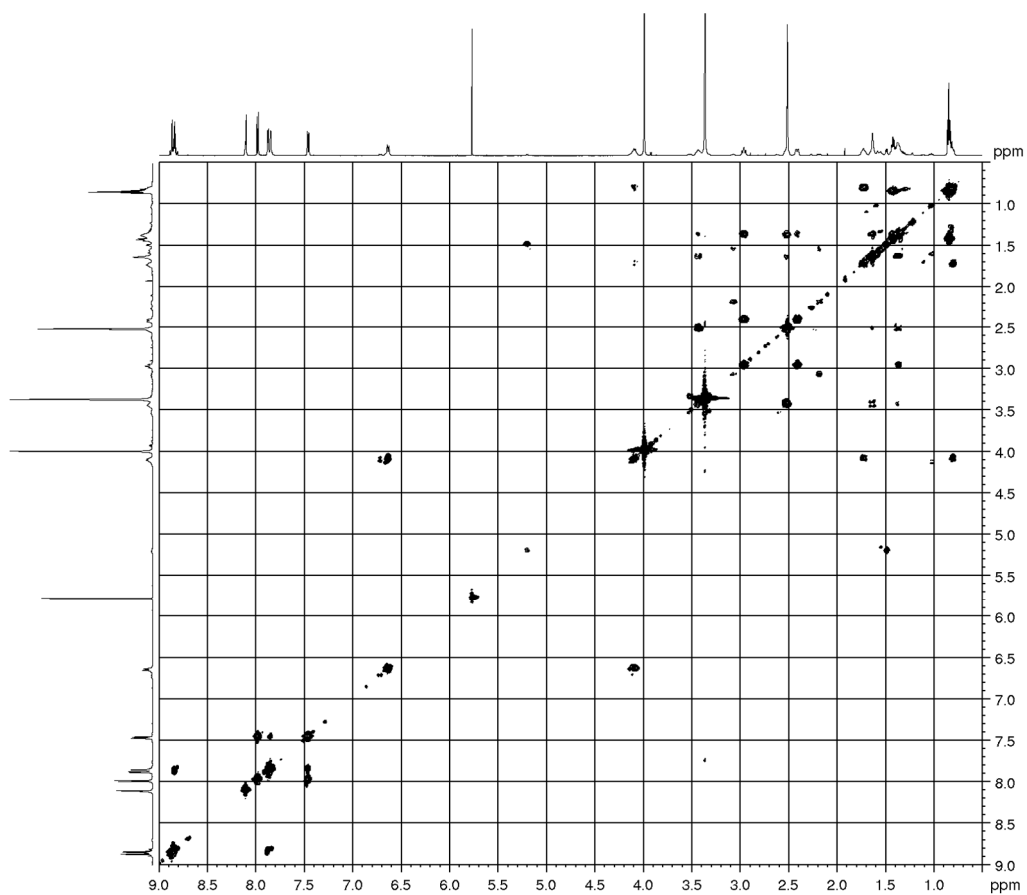


Figure S5. COSY spectrum of **Hub¹-cinchona** (DMSO- d_6).

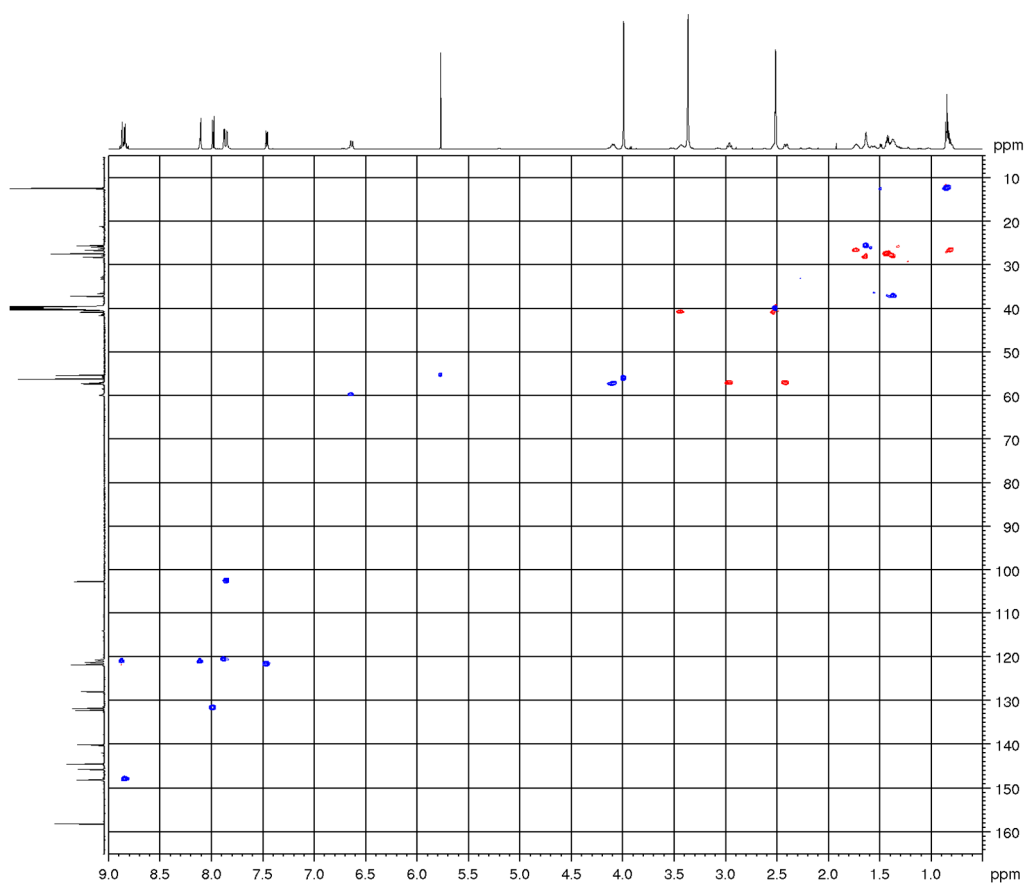


Figure S6. HSQC spectrum of **Hub¹-cinchona** (DMSO- d_6).

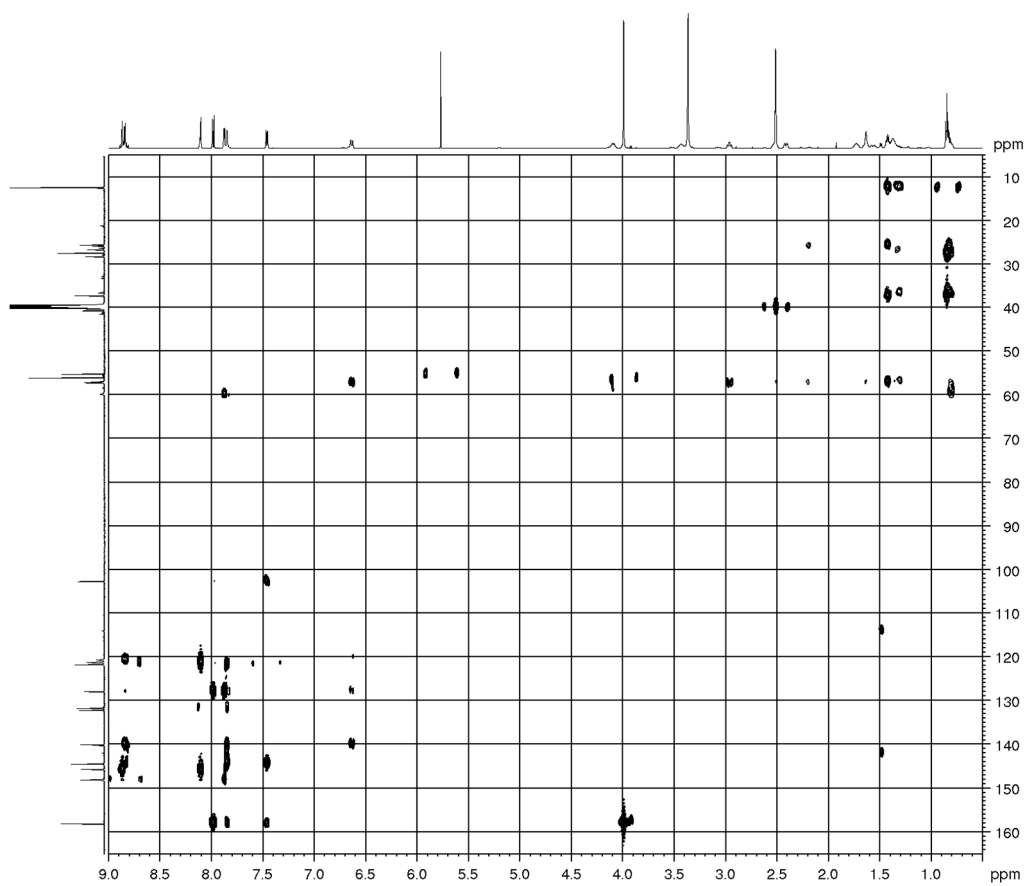


Figure S7. HMBC spectrum of **Hub¹-cinchona** (DMSO- d_6).

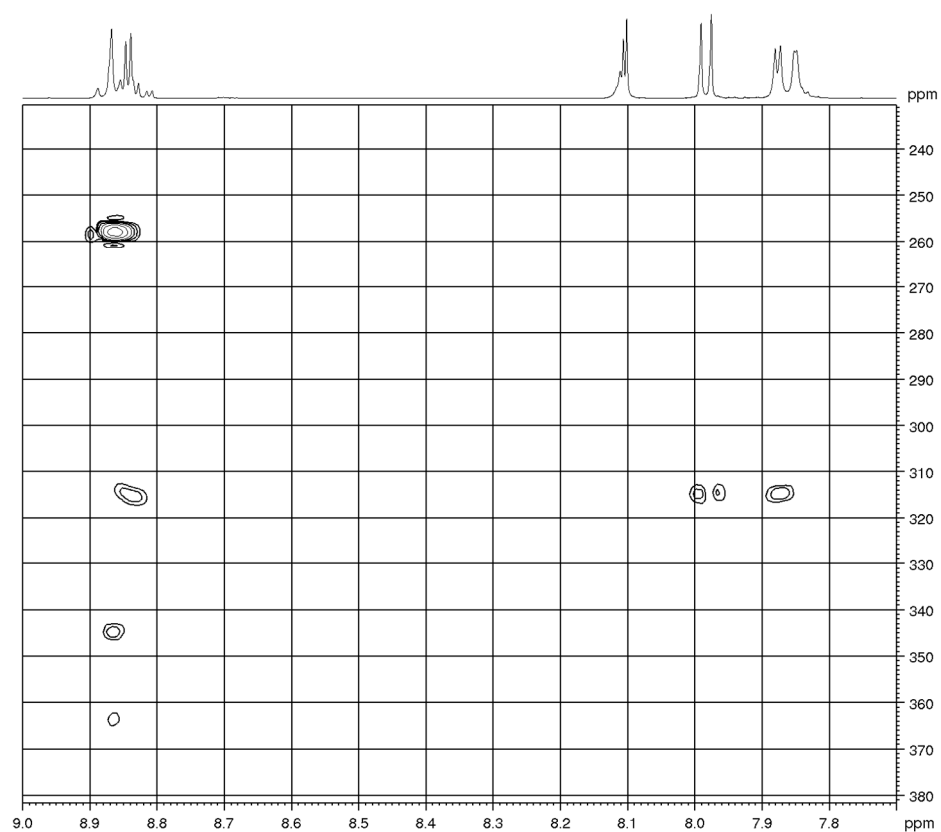


Figure S8. ^{15}N - ^1H HMBC spectrum of **Hub¹-cinchona** (DMSO-d_6).

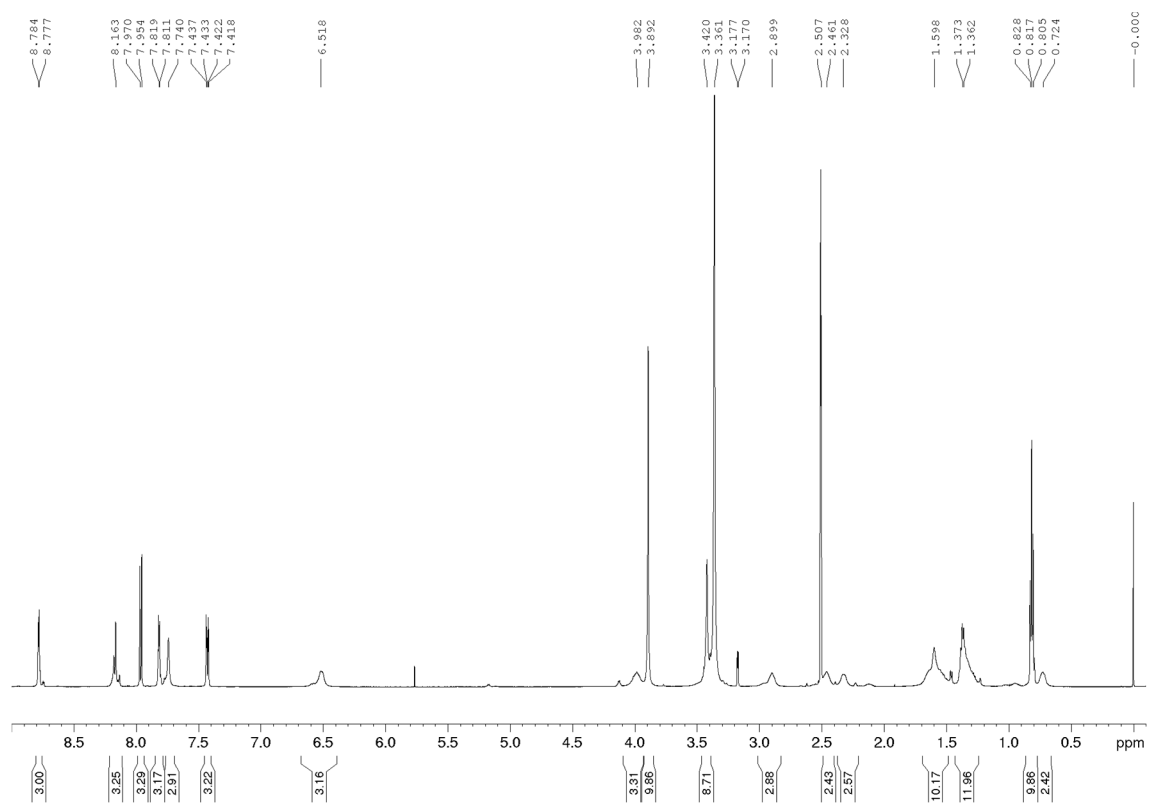


Figure S9. ¹H NMR spectrum of Hub²-cinchona (DMSO-d₆).

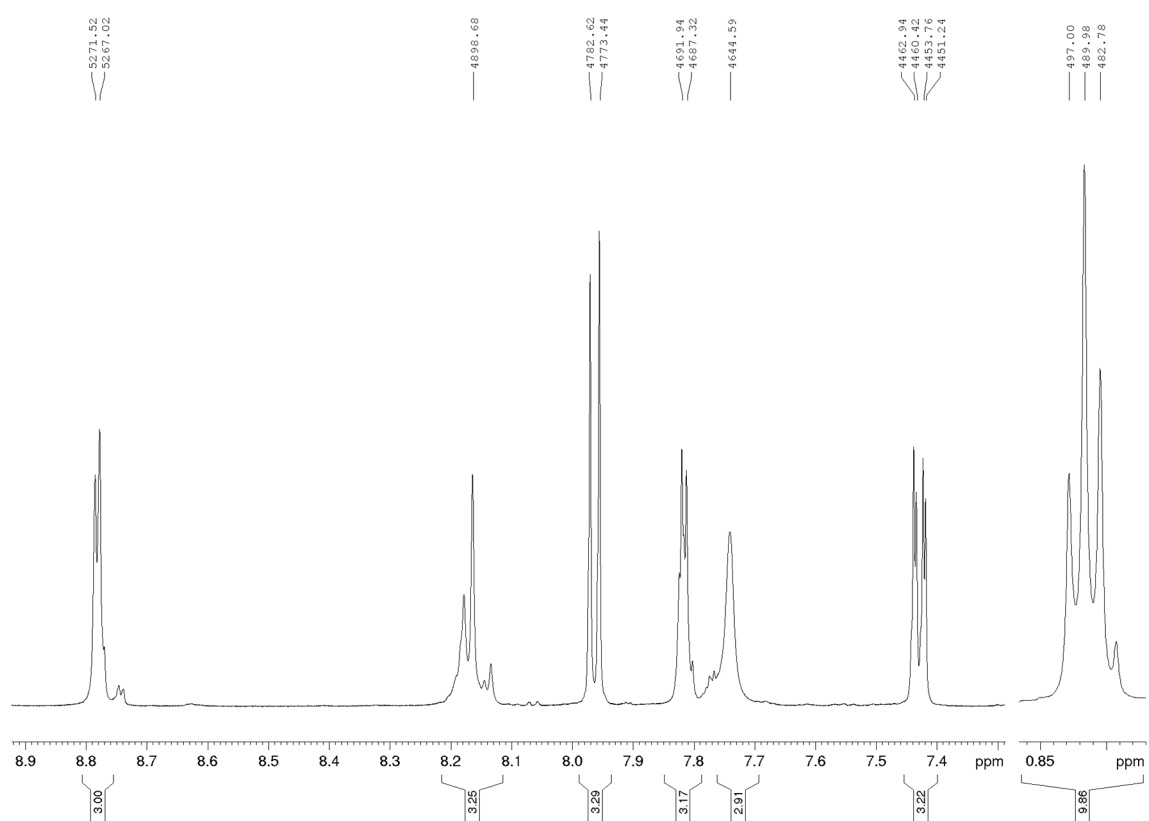


Figure S10. Selected ¹H NMR spectral regions of Hub²-cinchona (DMSO-d₆).

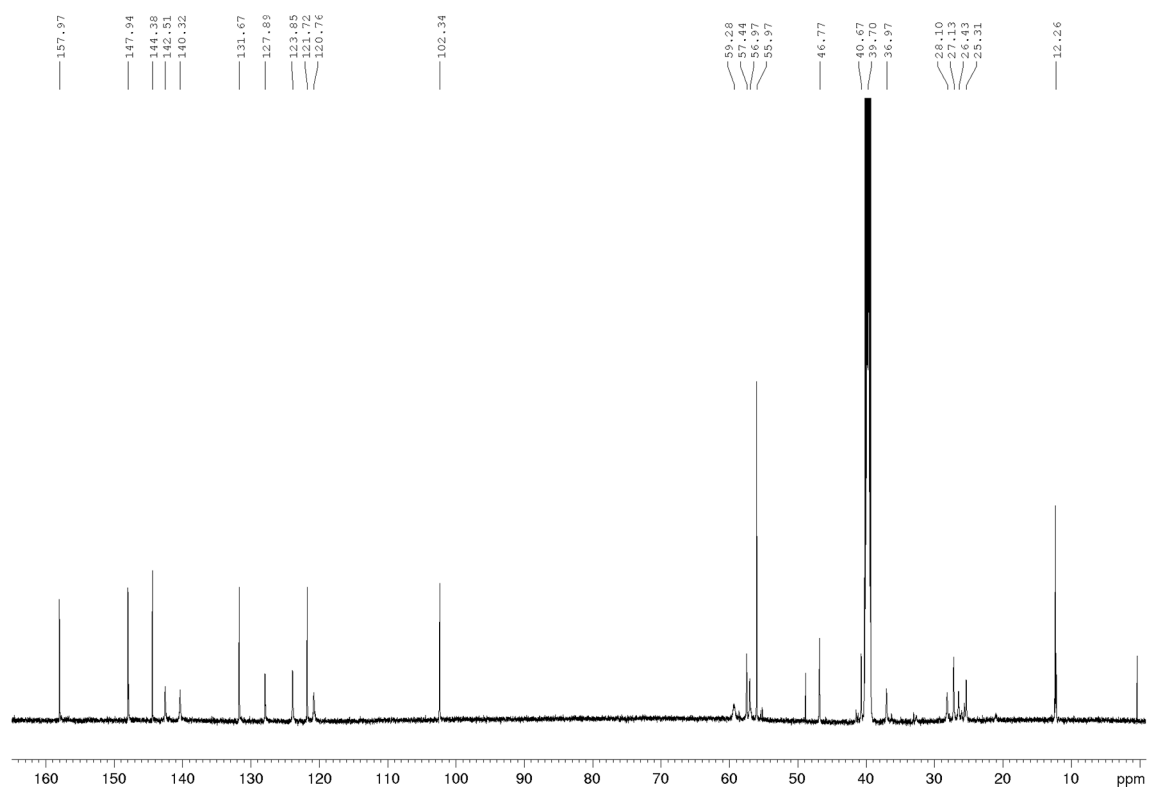


Figure S11. ^{13}C NMR spectrum of **Hub²-cinchona** (DMSO- d_6).

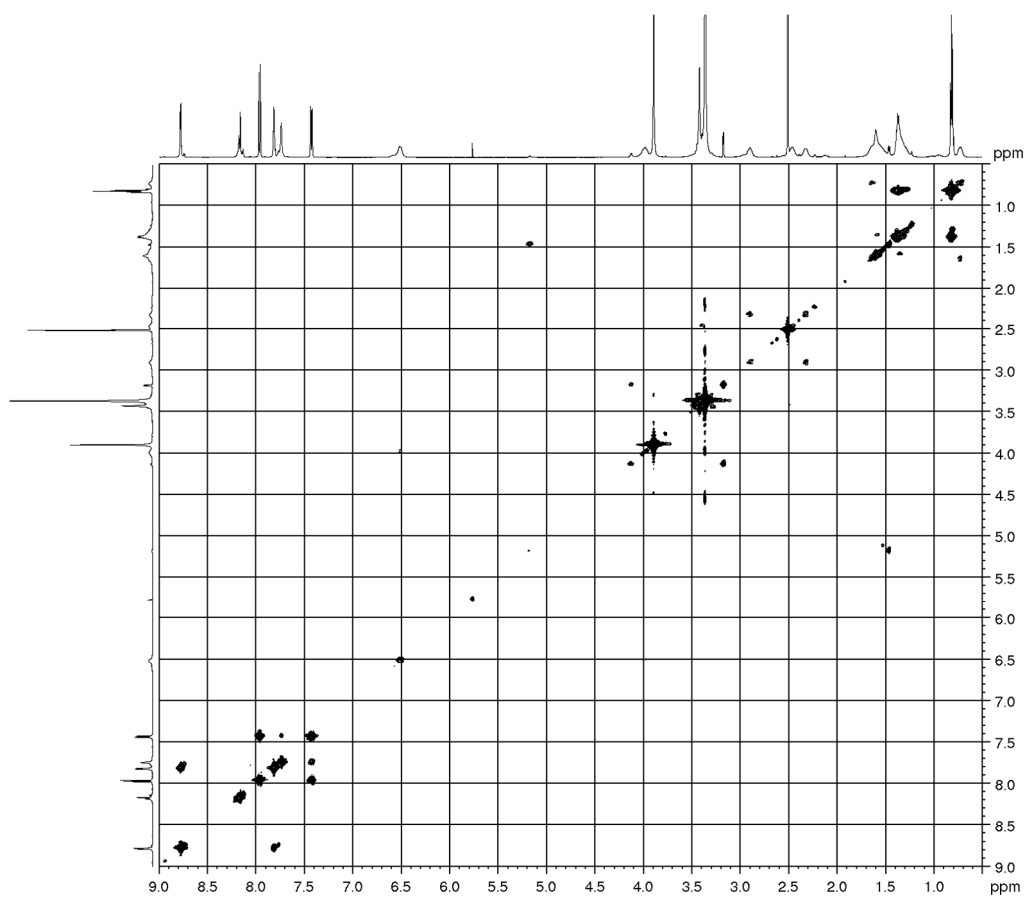


Figure S12. COSY spectrum of **Hub²-cinchona** (DMSO- d_6).

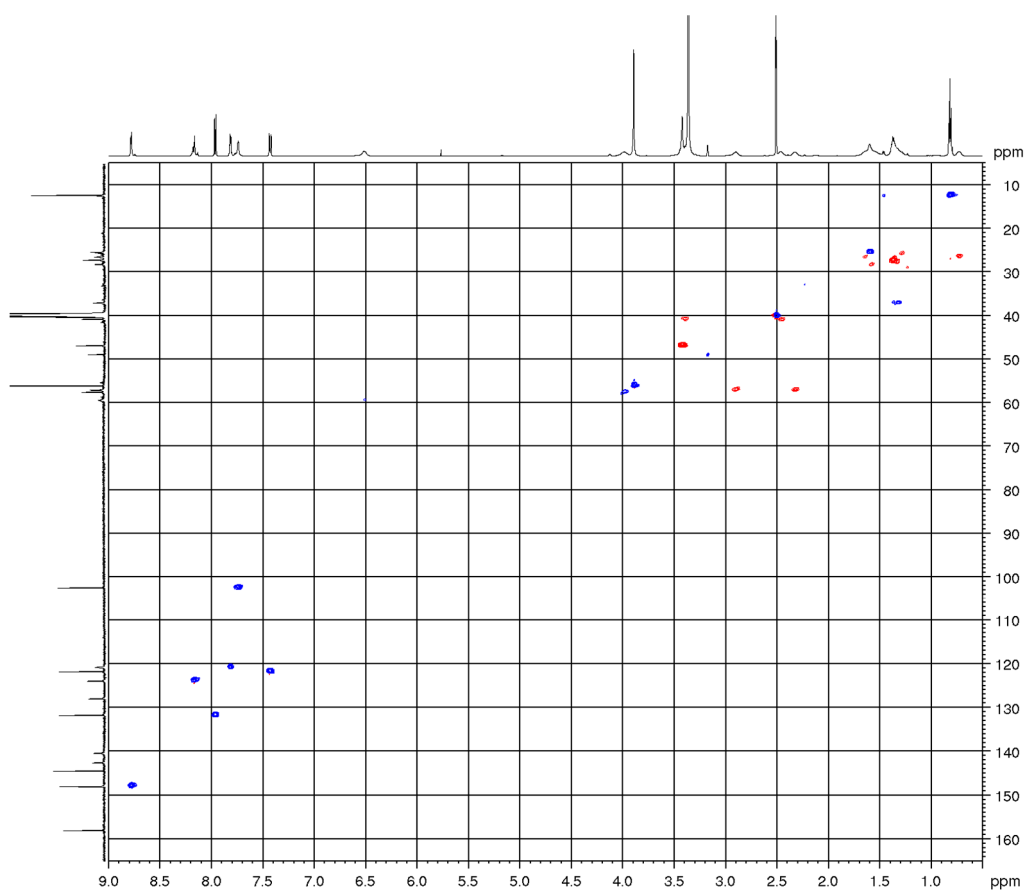


Figure S13. HSQC spectrum of **Hub²-cinchona** (DMSO- d_6).

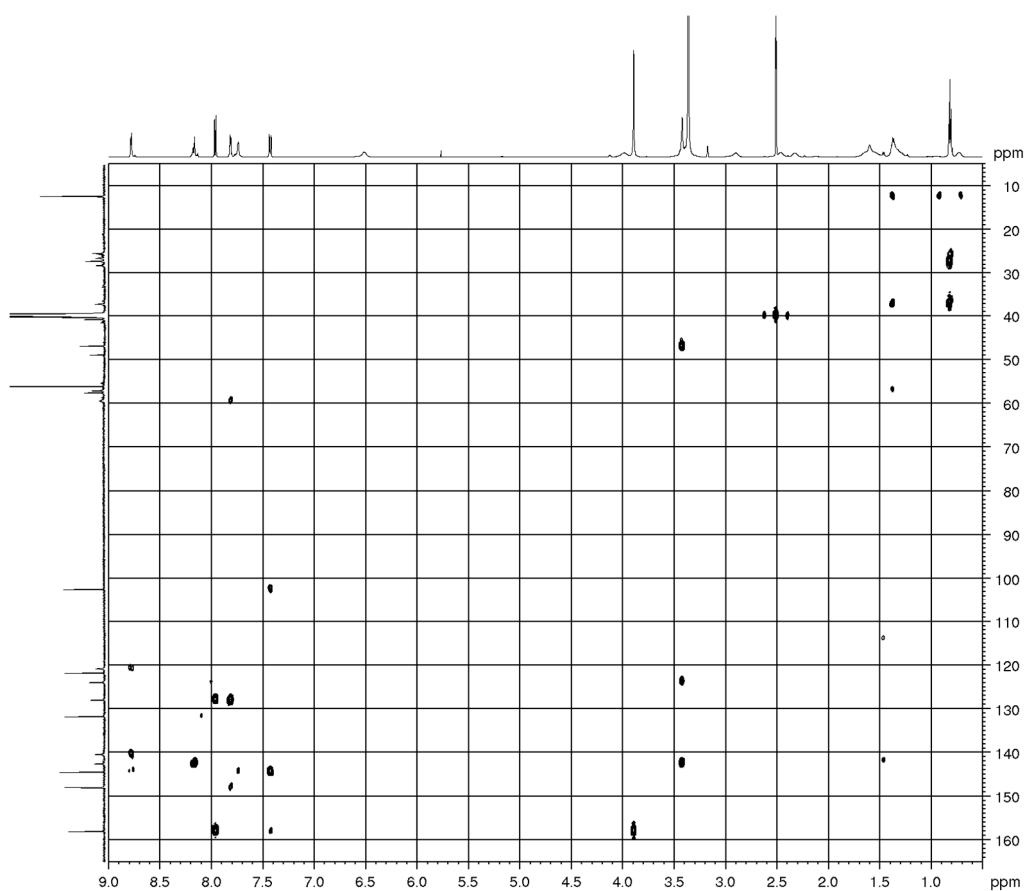


Figure S14. HMBC spectrum of **Hub²-cinchona** (DMSO- d_6).

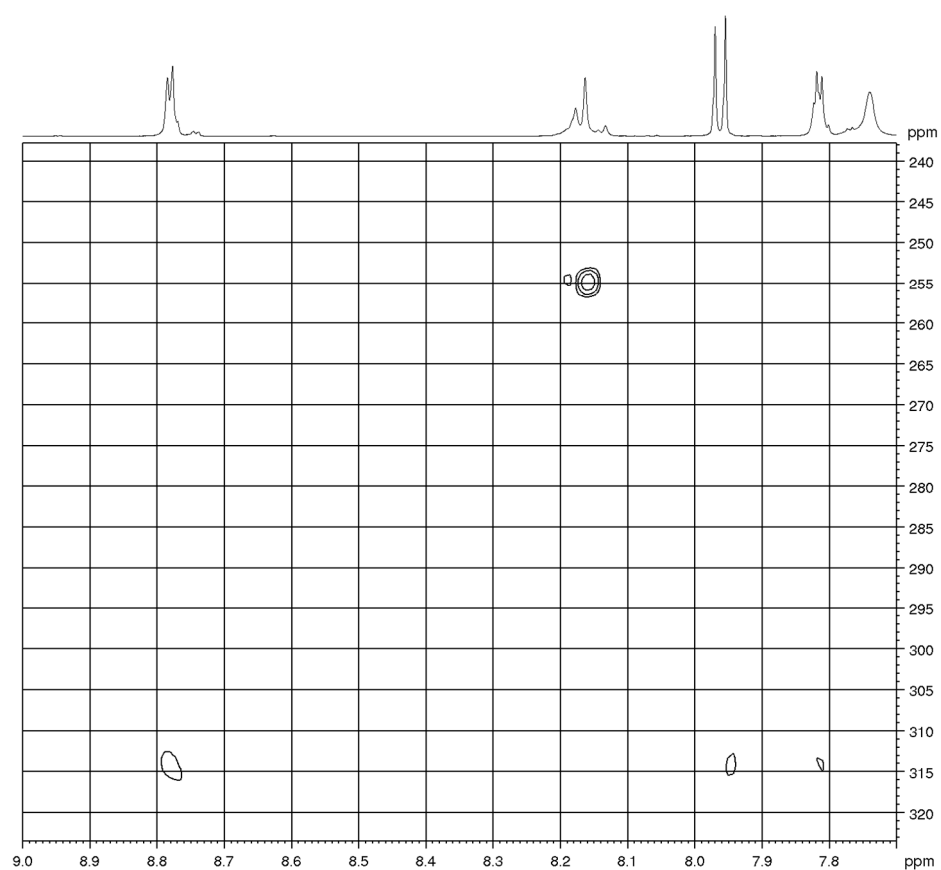


Figure S15. ^{15}N - ^1H HMBC spectrum of **Hub²-cinchona** (DMSO- d_6).

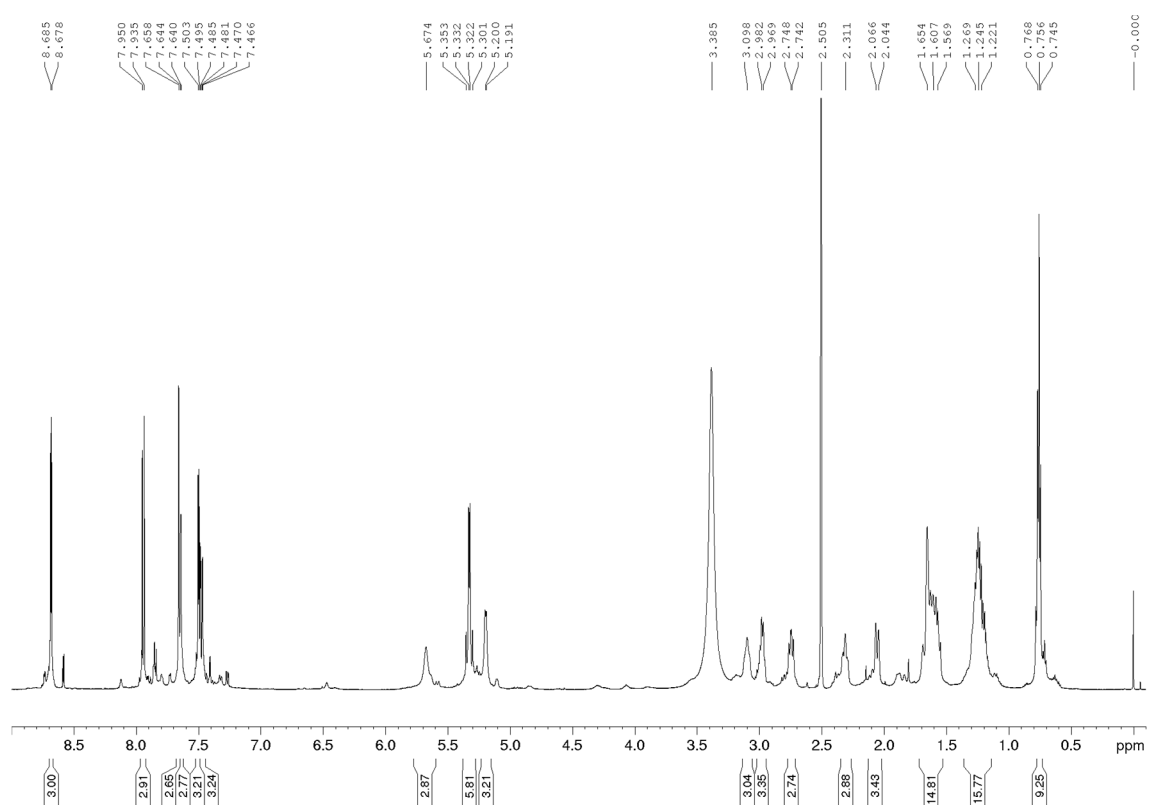


Figure S16. ^1H NMR spectrum of **Hub³-cinchona** (DMSO-d_6).

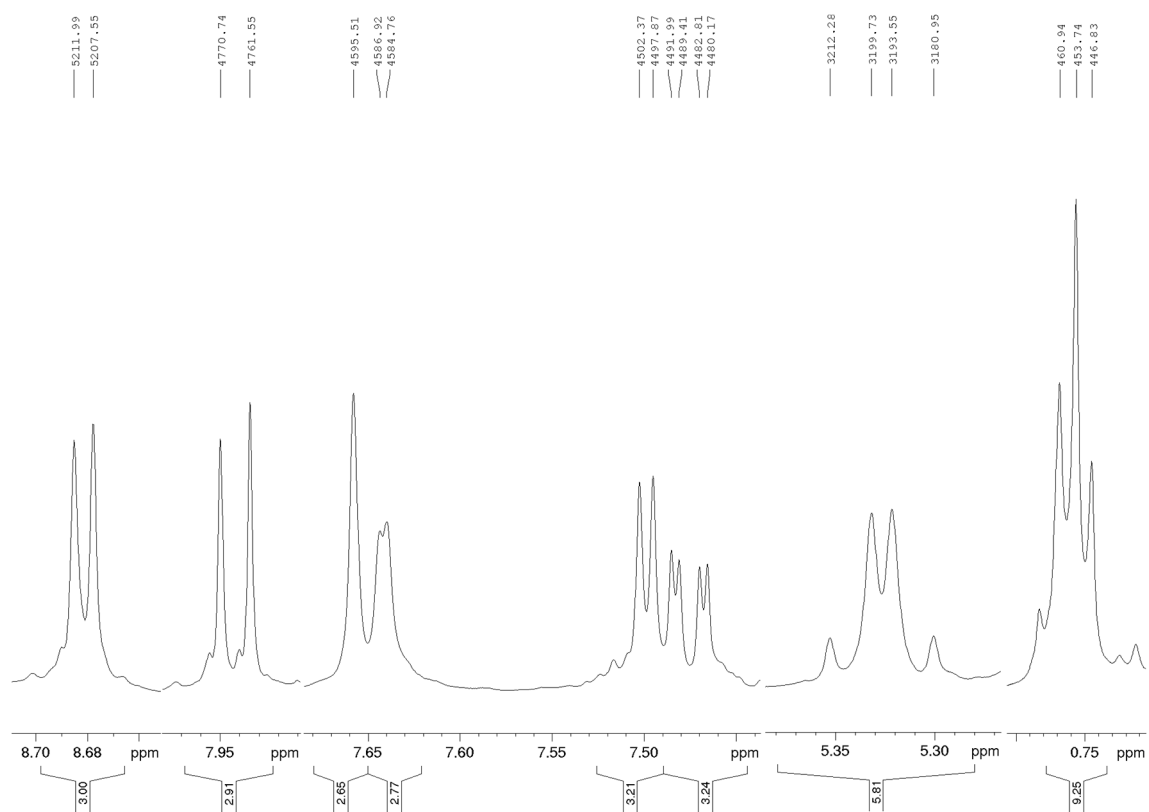


Figure S17. Selected ^1H NMR spectral regions of **Hub³-cinchona** (DMSO-d_6).

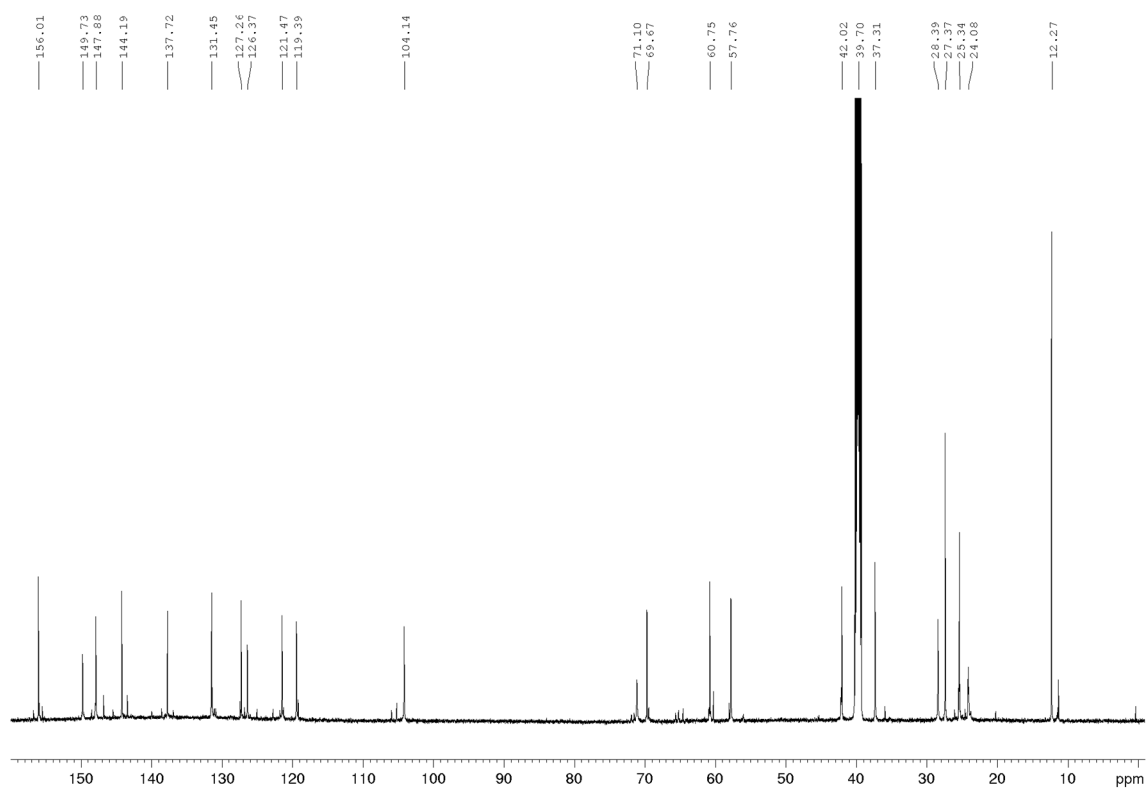


Figure S18. ^{13}C NMR spectrum of **Hub³-cinchona** (DMSO- d_6).

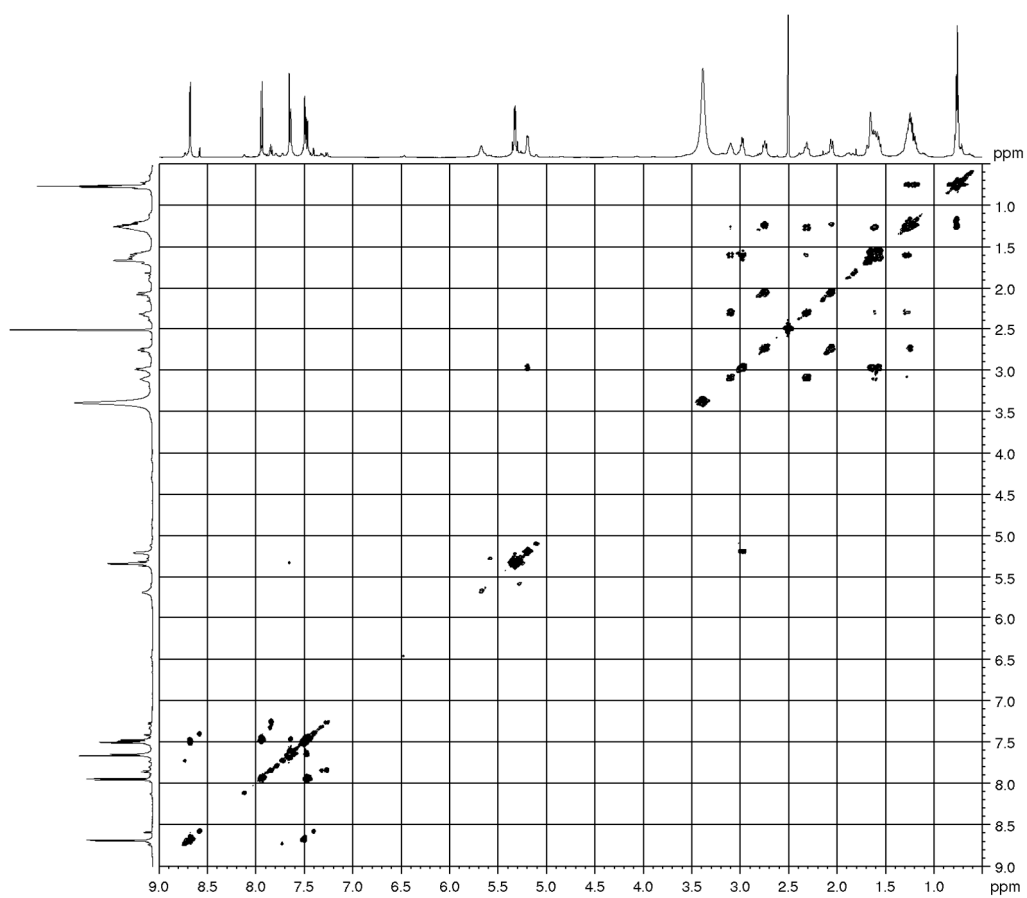


Figure S19. COSY spectrum of **Hub³-cinchona** (DMSO- d_6).

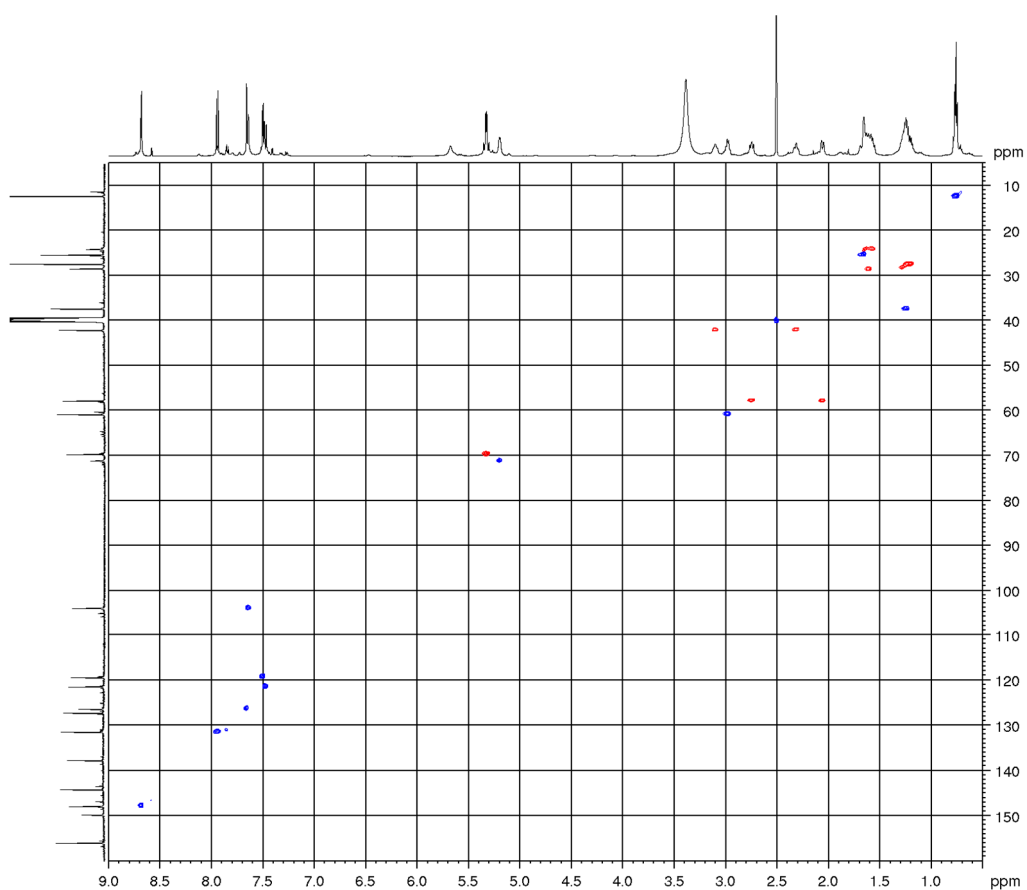


Figure S20. HSQC spectrum of **Hub³-cinchona** (DMSO-d₆).

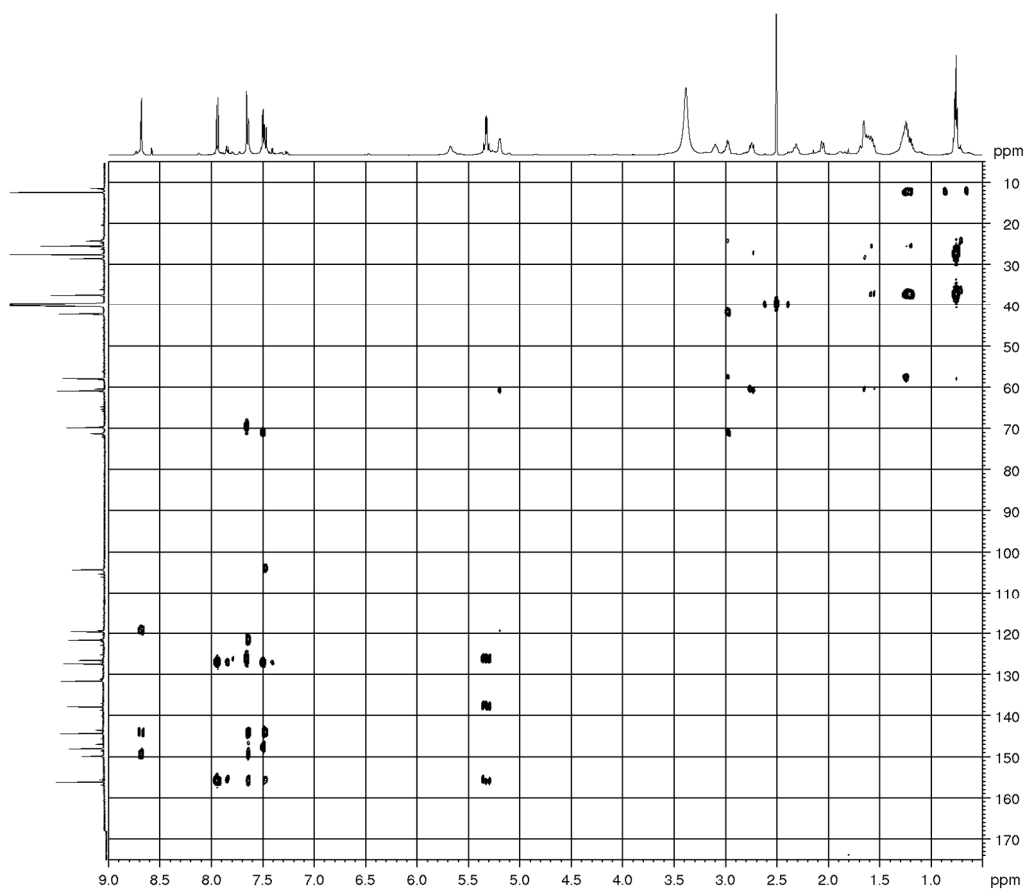


Figure S21. HMBC spectrum of **Hub³-cinchona** (DMSO-d₆).

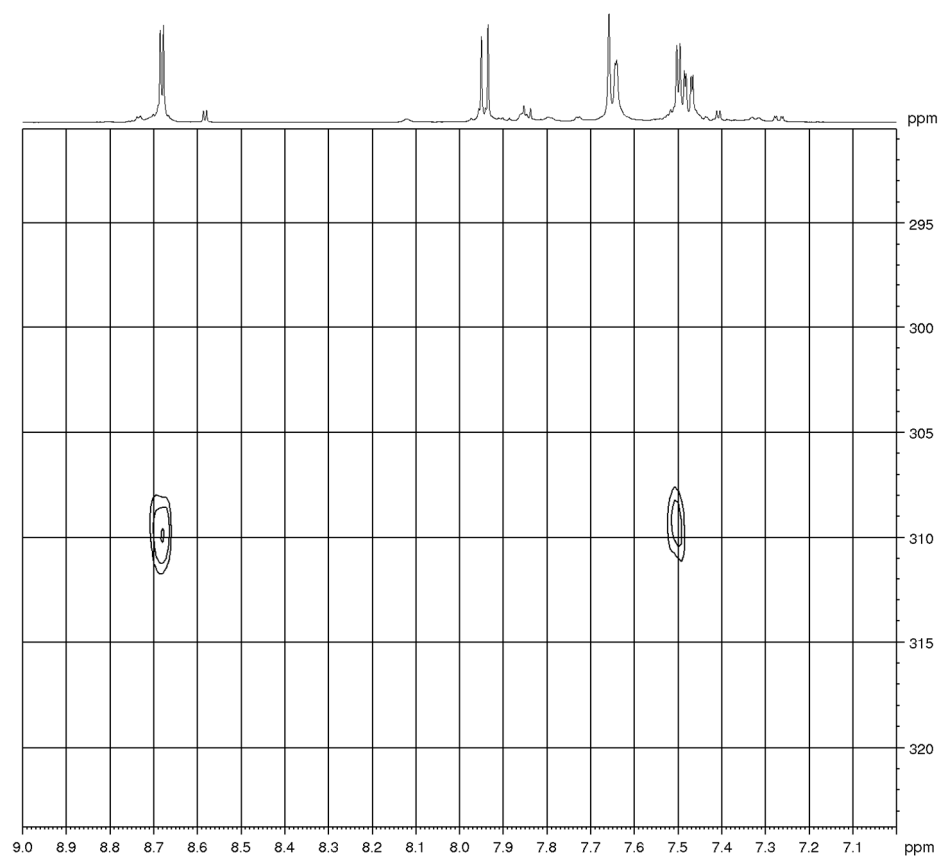


Figure S22. ^{15}N - ^1H HMBC spectrum of **Hub³-cinchona** (DMSO- d_6).

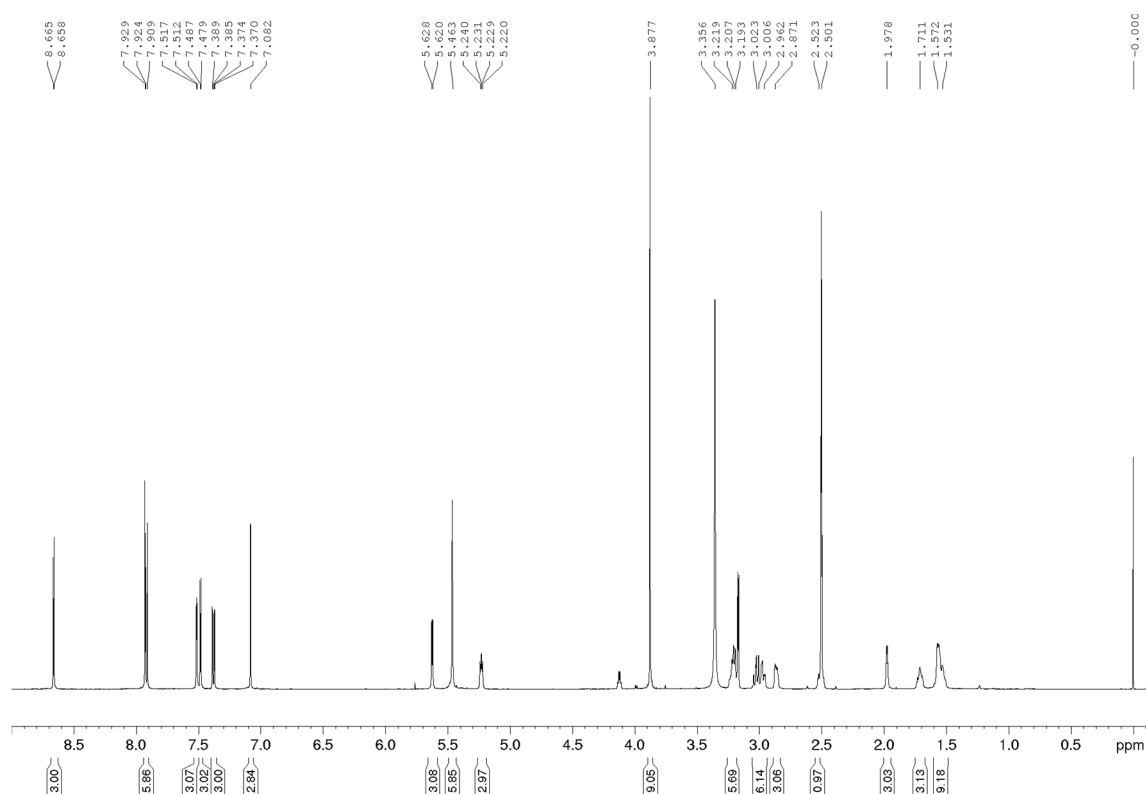


Figure S23. ^1H NMR spectrum of **Hub⁴-cinchona** (DMSO- d_6).

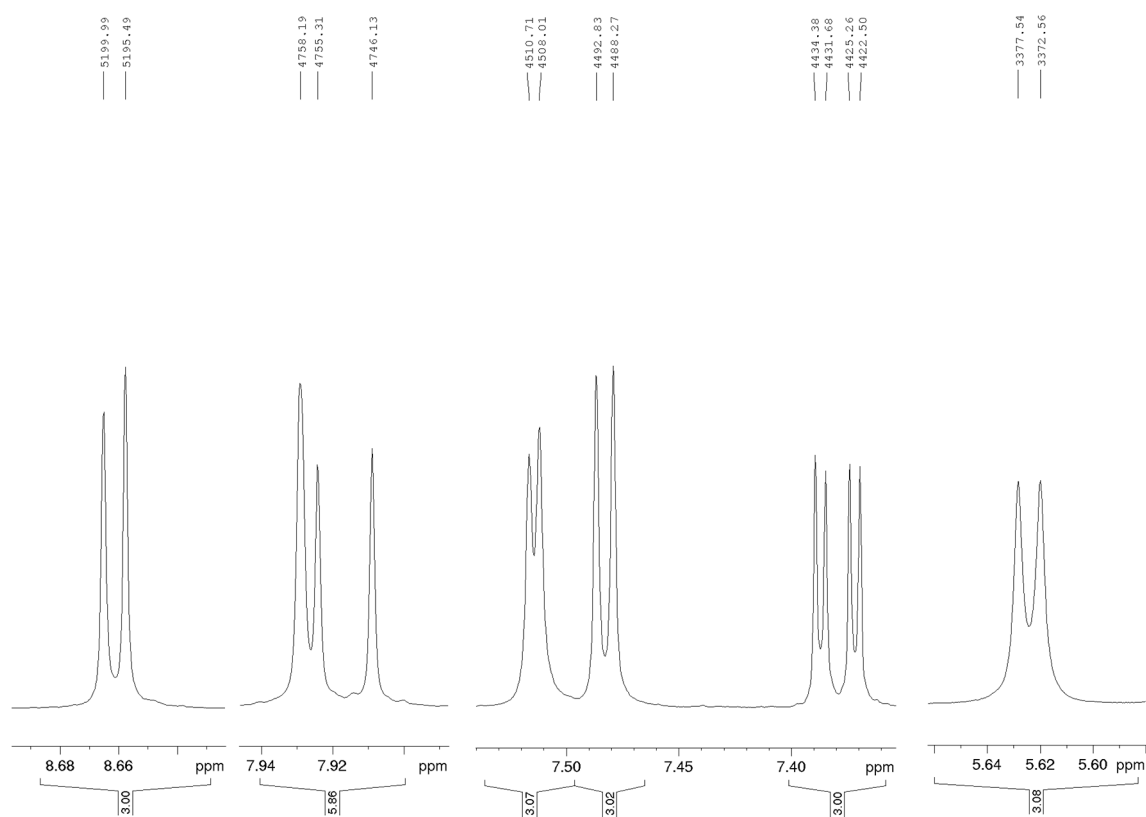


Figure S24. Selected ^1H NMR spectral regions of **Hub⁴-cinchona** (DMSO- d_6).

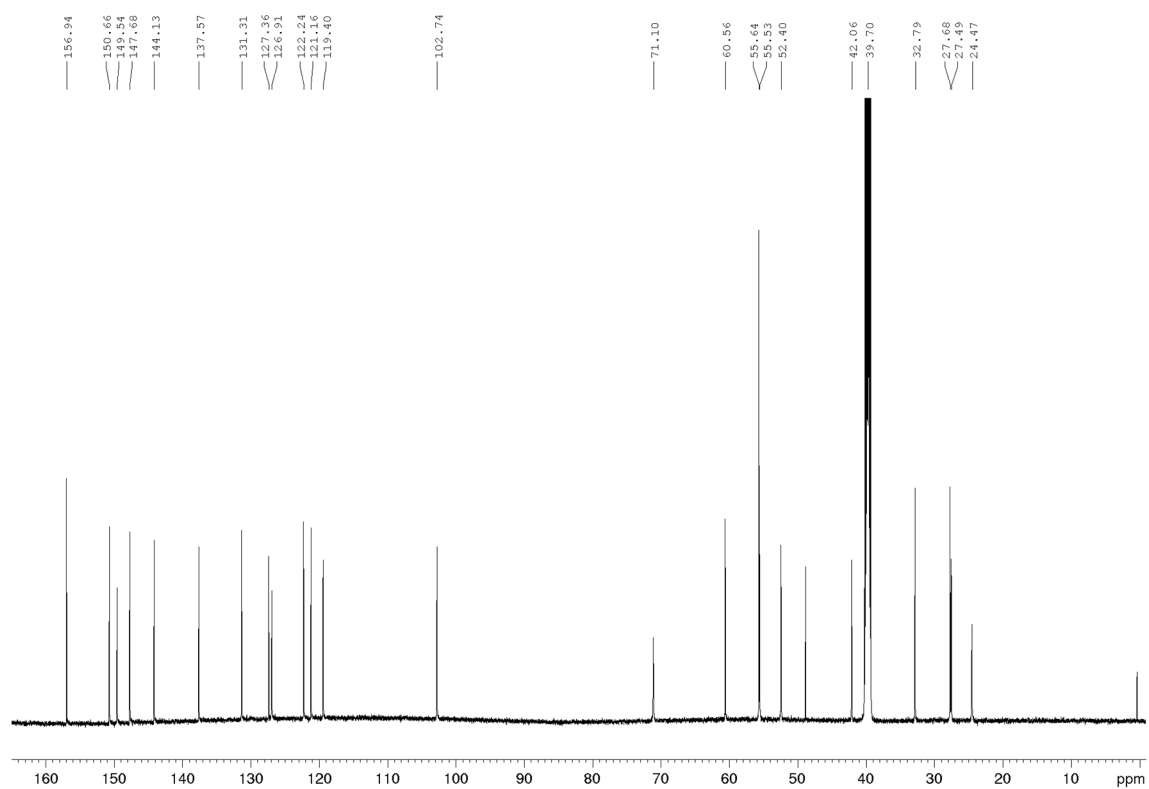


Figure S25. ^{13}C NMR spectrum of **Hub⁴-cinchona** (DMSO- d_6).

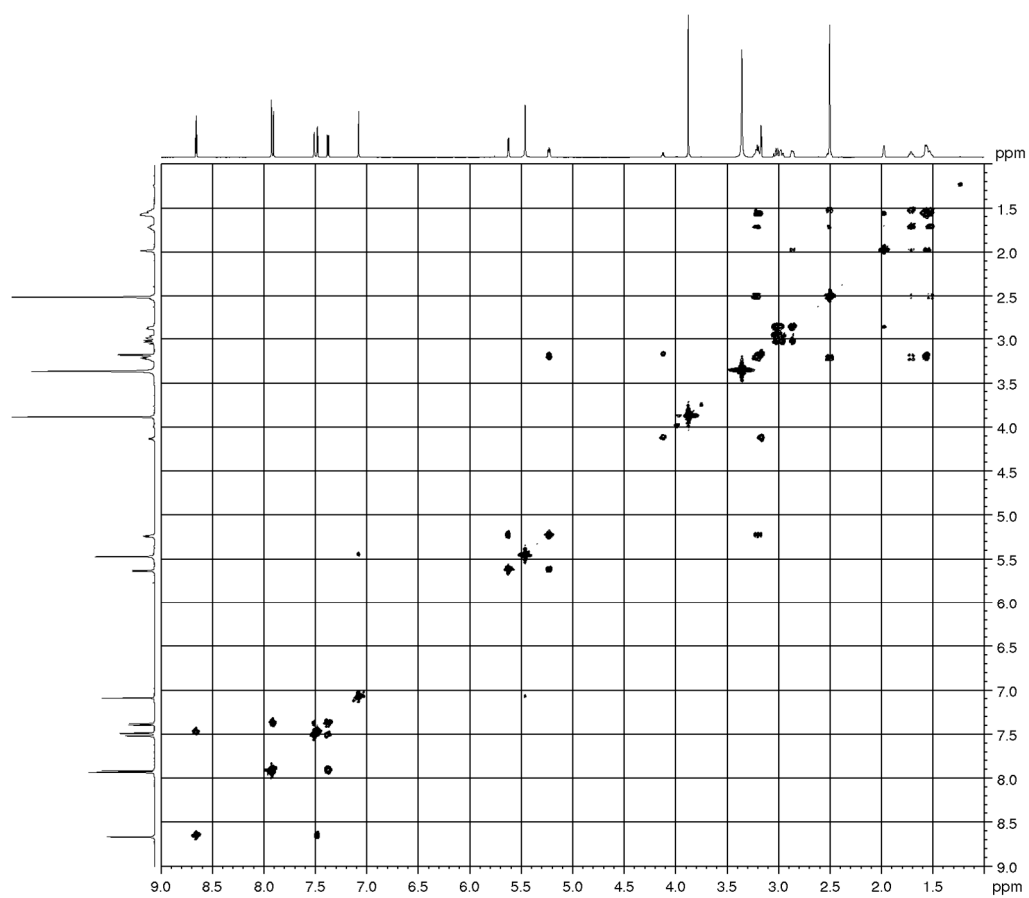


Figure S26. COSY spectrum of **Hub⁴-cinchona** (DMSO- d_6).

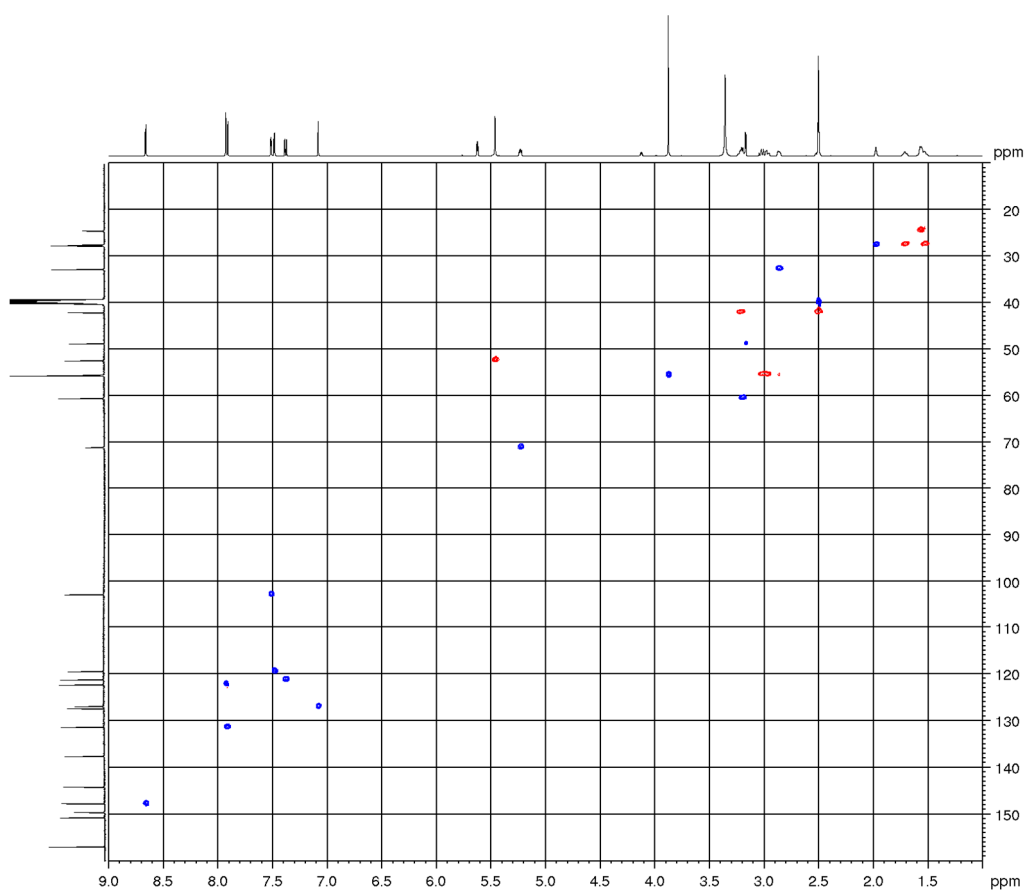


Figure S27. HSQC spectrum of Hub⁴-cinchona (DMSO-d₆).

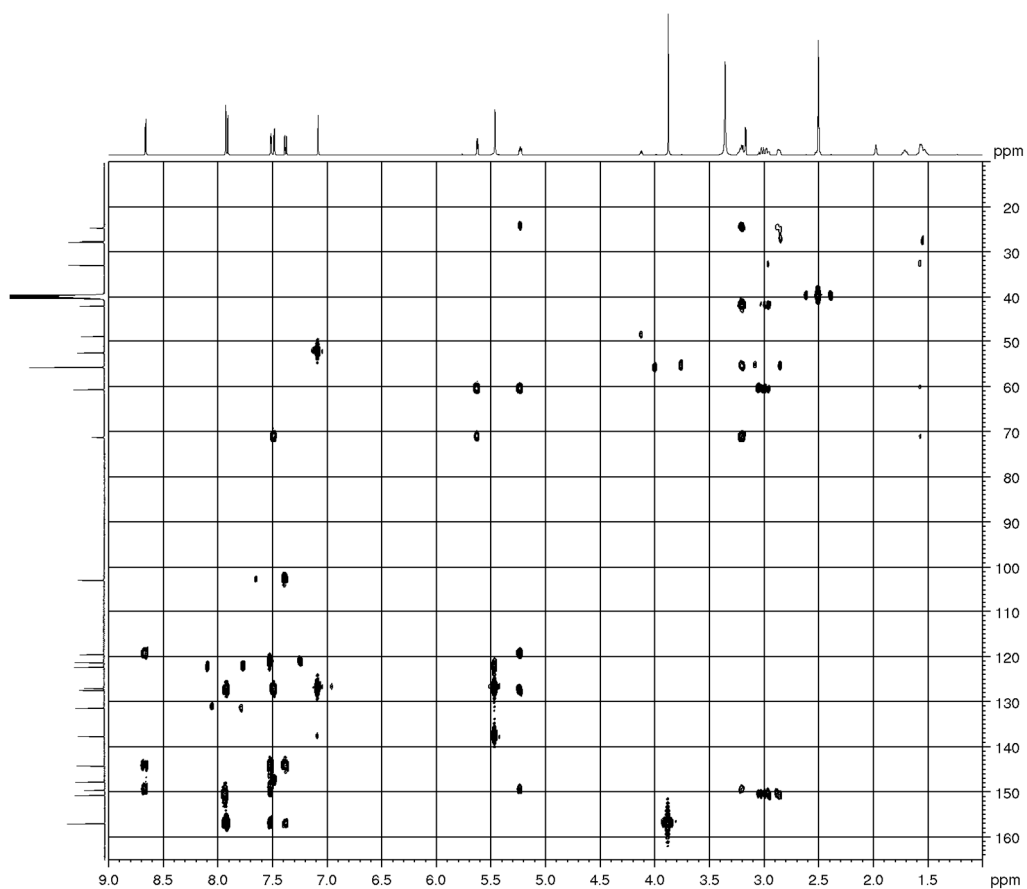


Figure S28. HMBC spectrum of Hub⁴-cinchona (DMSO-d₆).

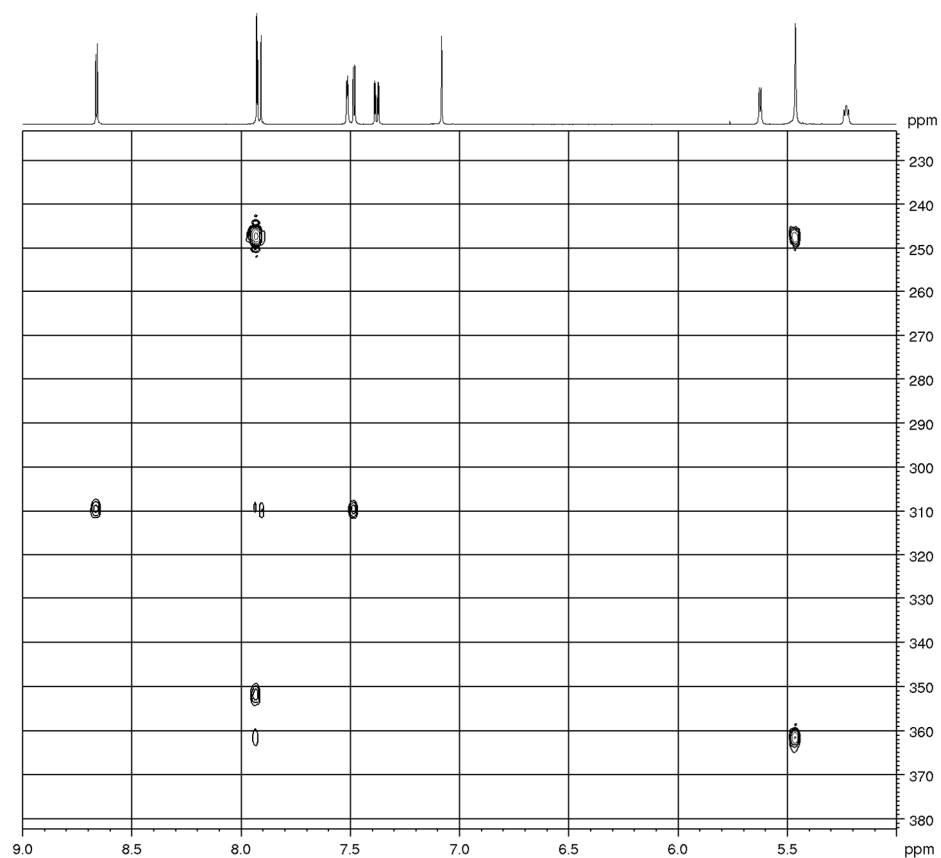


Figure S29. ^{15}N - ^1H HMBC spectrum of **Hub⁴-cinchona** (DMSO- d_6).

3. MS spectra of Hub¹⁻⁴-cinchonas

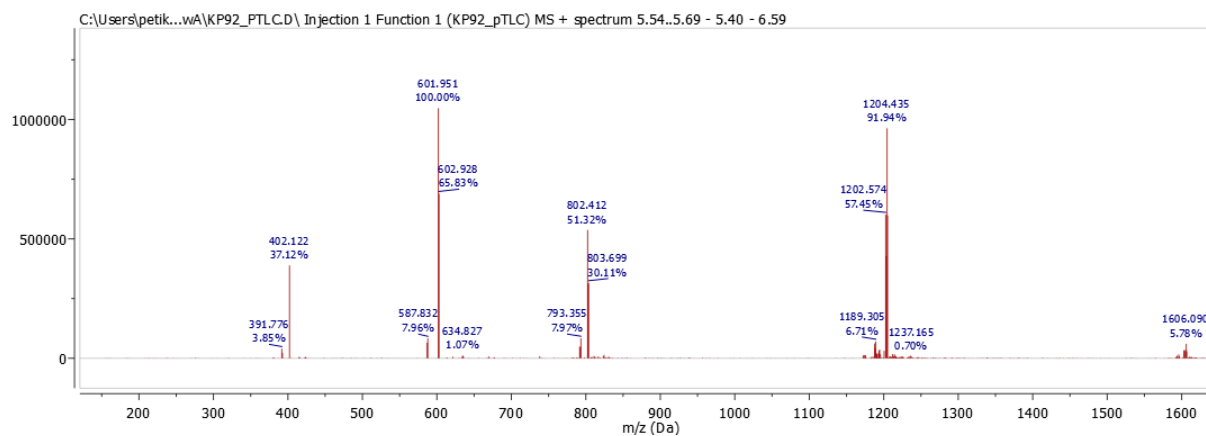


Figure S30. HPLC-MS spectrum of Hub¹-cinchona.

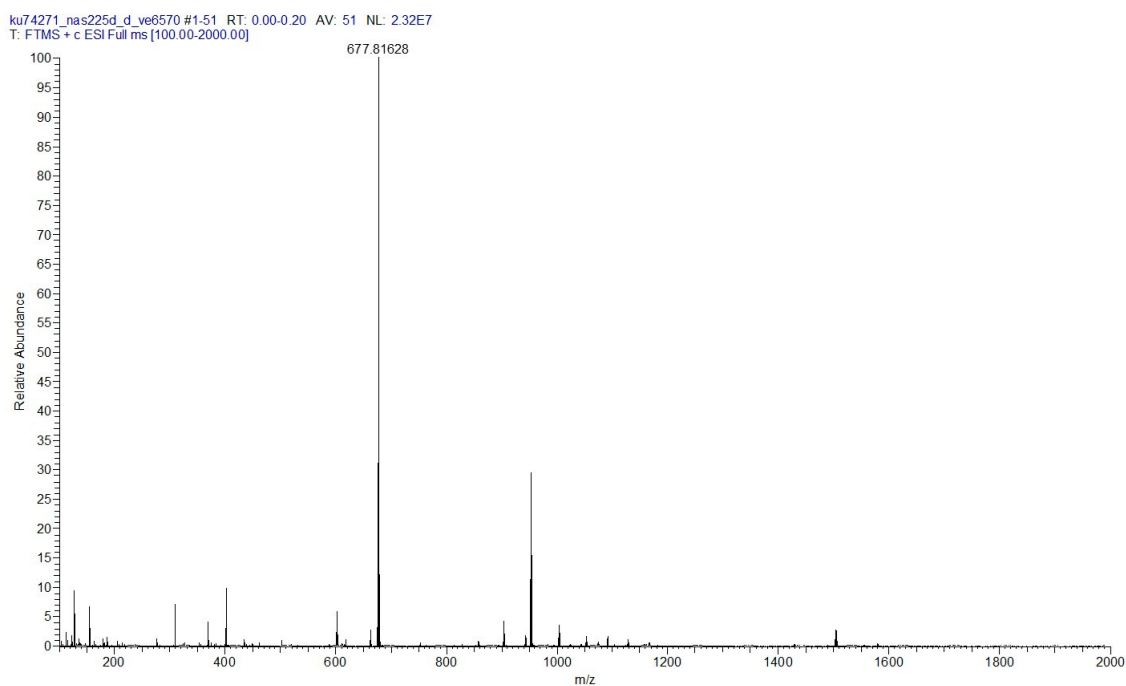


Figure S31. HRMS spectrum of Hub¹-cinchona triflate salt.

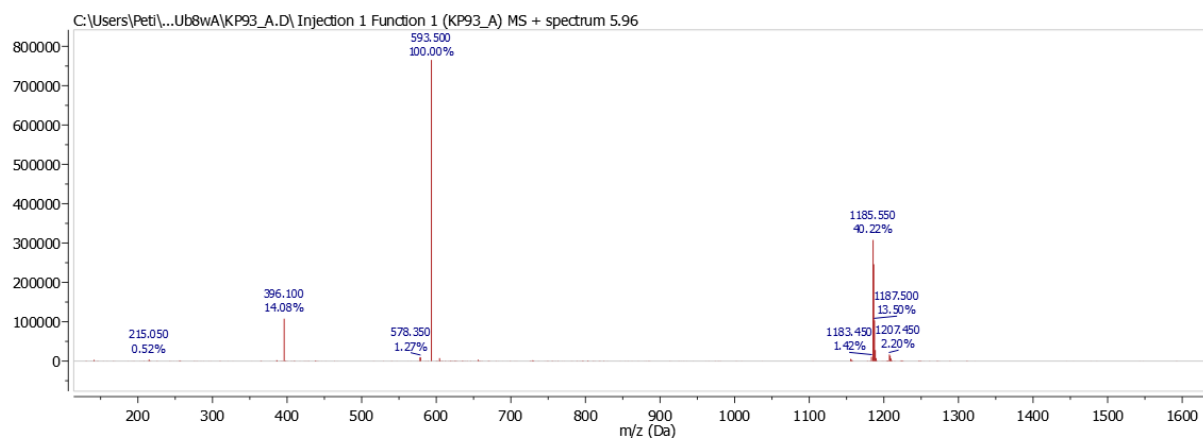


Figure S32. HPLC-MS spectrum of **Hub²-cinchona**.

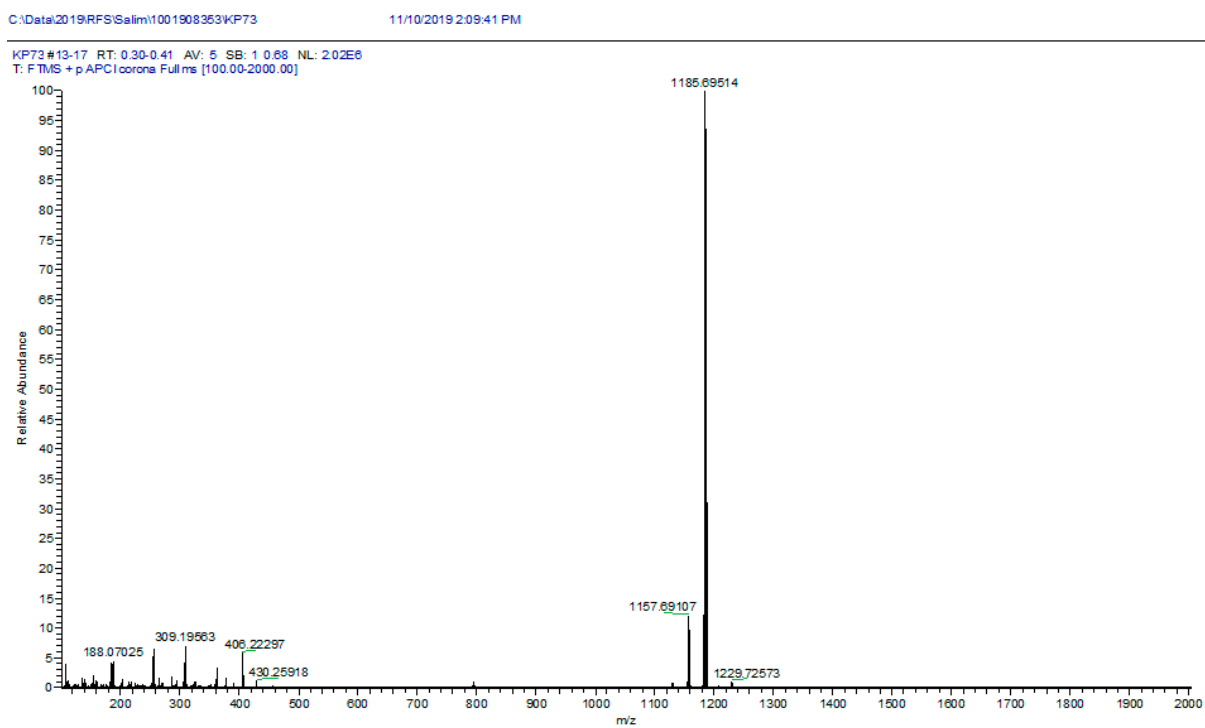


Figure S33. Full scan HRMS spectrum of **Hub²-cinchona**.

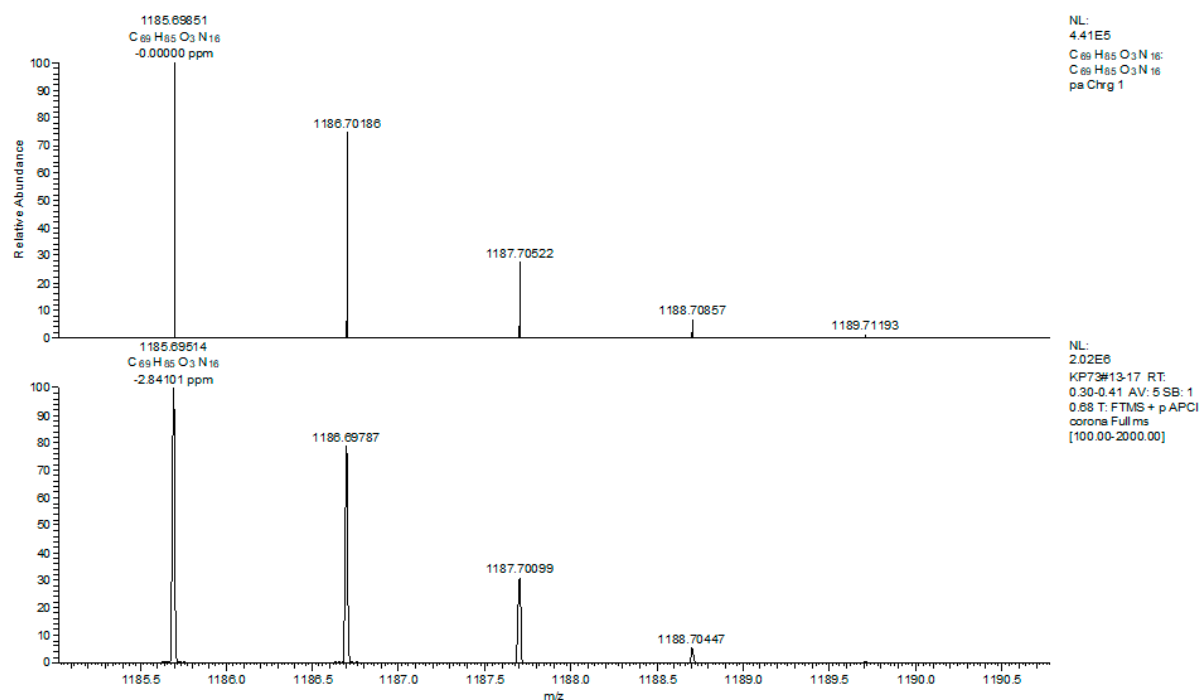


Figure S34. HRMS spectrum of Hub²-cinchona.

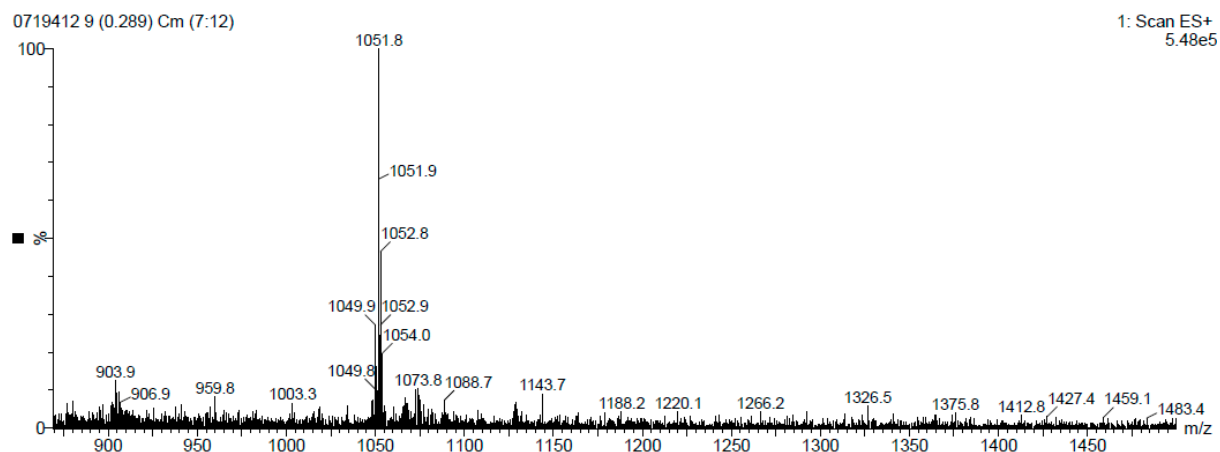


Figure S35. HPLC-MS spectrum of Hub³-cinchona.

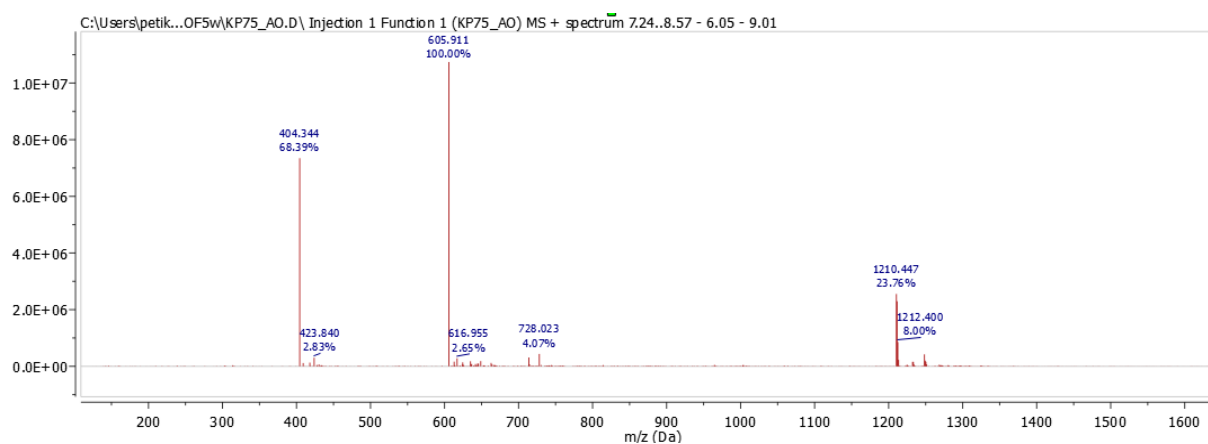


Figure S36. HPLC-MS spectrum of **Hub⁴-cinchona**.

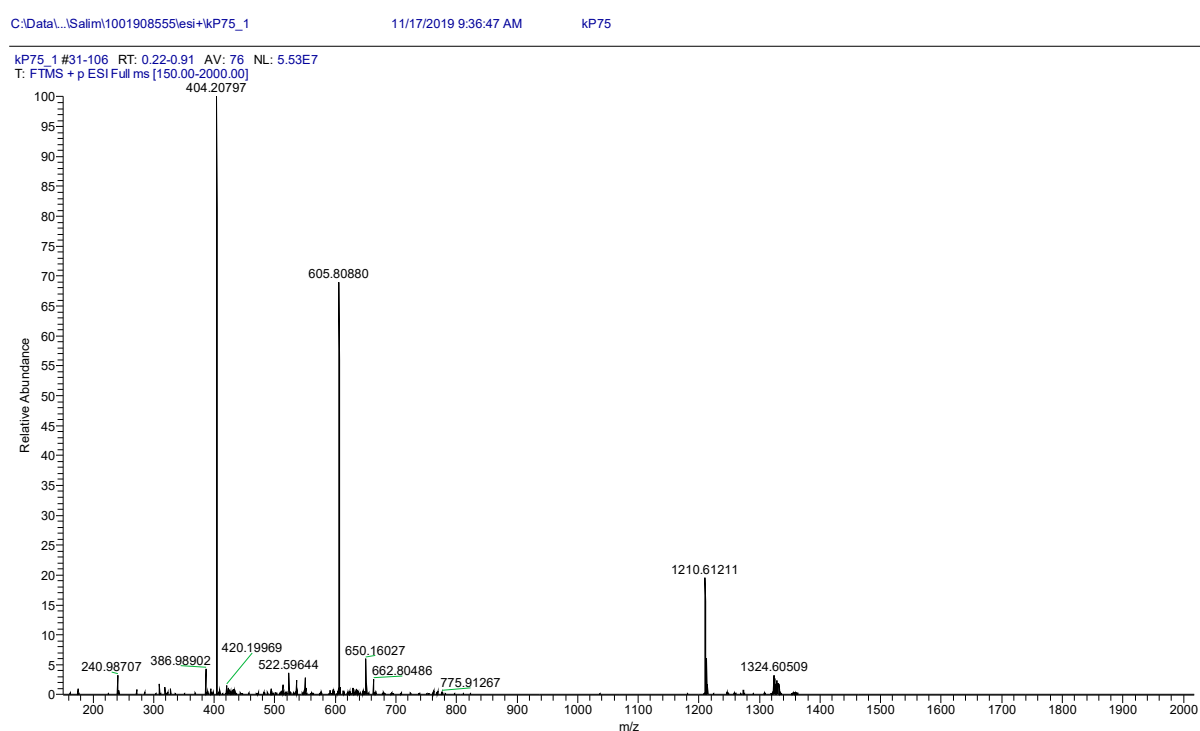


Figure S37. Full scan HRMS spectrum of **Hub⁴-cinchona**.

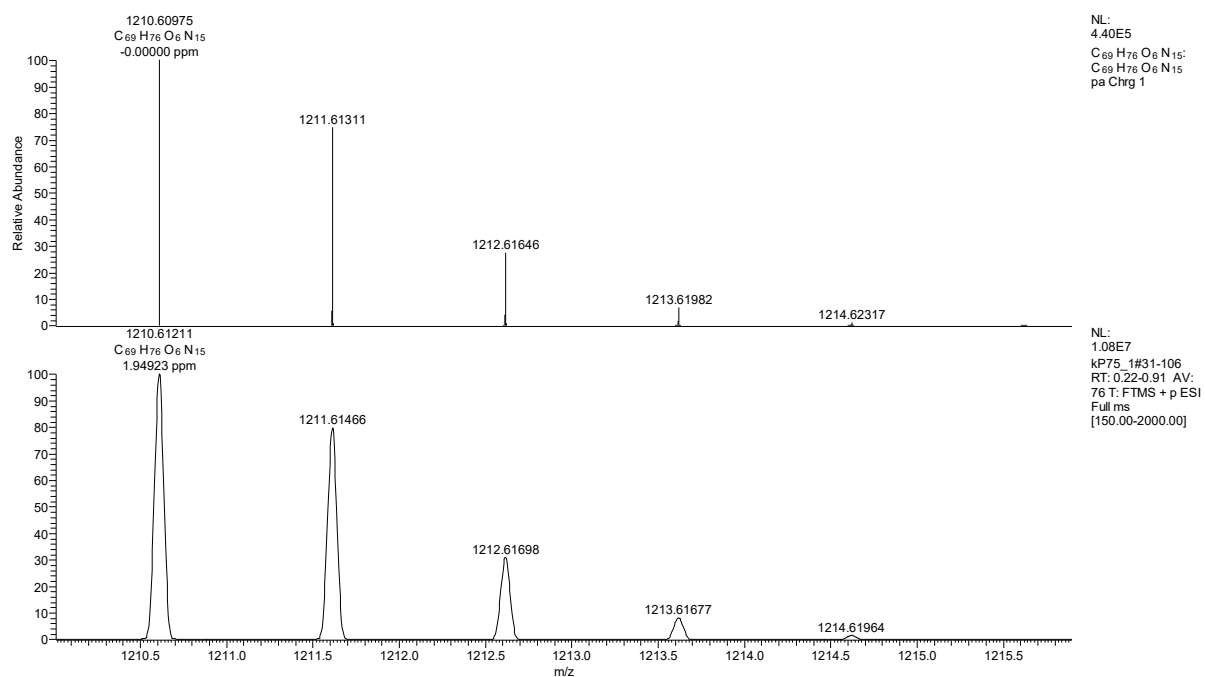


Figure S38. HRMS spectrum of **Hub⁴-cinchona**.

4. HPLC chromatograms

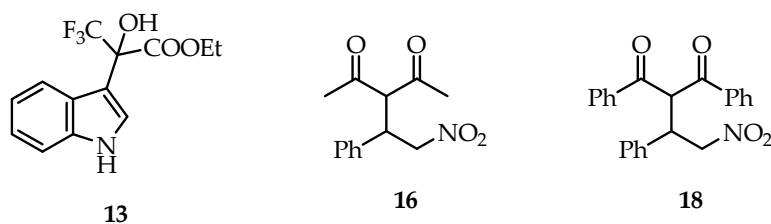


Figure S39. Products of the organocatalytic Michael and Friedel–Crafts-reactions.

Analyst: System

Sample ID: Racem ref Cell 1 70 30 NH₄OAc 08 ml/min 222 b

Injection Volume: 15

Vial: C;1

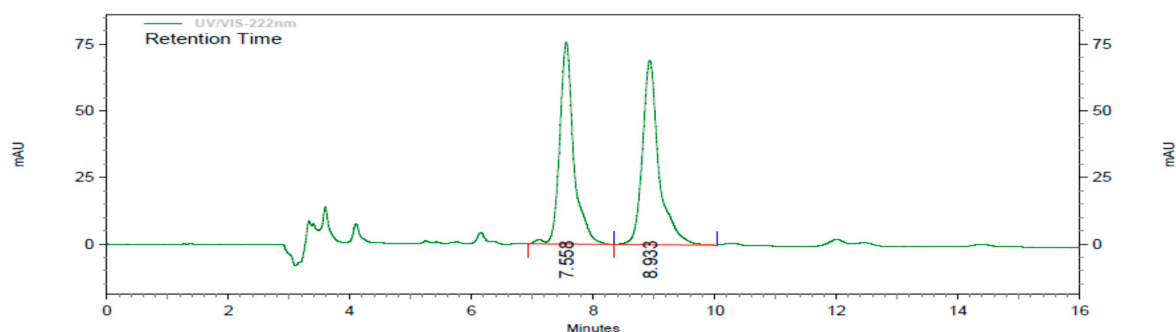


Figure S40. Chiral HPLC chromatogram of racemic **18** (Phenomenex Lux Cellulose-1 column (5 μ m, 250 $\times$ 4.6 mm), eluent water (0.1 % NH₄OAc)/MeCN = 30/70, isocratic mode; 0.8 mL $\cdot$ min⁻¹, temperature 20 $^{\circ}$ C, UV detector 222 nm. Retention time for (*S*)-**18**: 7.6 min, for (*R*)-**18**: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

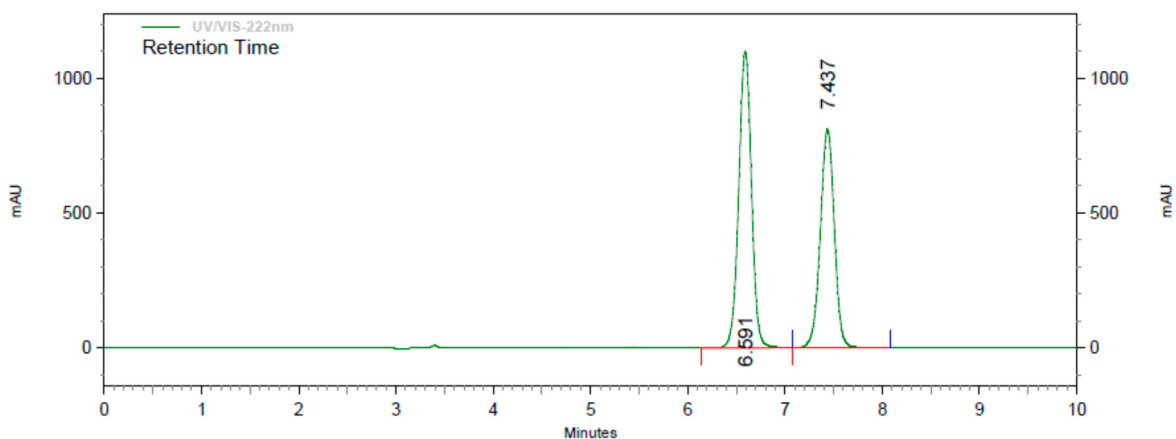


Figure S41. Chiral HPLC chromatogram of non-racemic **13** (Phenomenex Lux Cellulose-1 (5 μ m, 250 $\times$ 4.6 mm) column, eluent water (0.1% NH₄OAc)/MeCN = 40/60, 0.8 mL min⁻¹, UV detector 222 nm. Retention time for (*R*)-**13** and (*S*)-**13** are 6.5 min and 7.2 min, respectively).

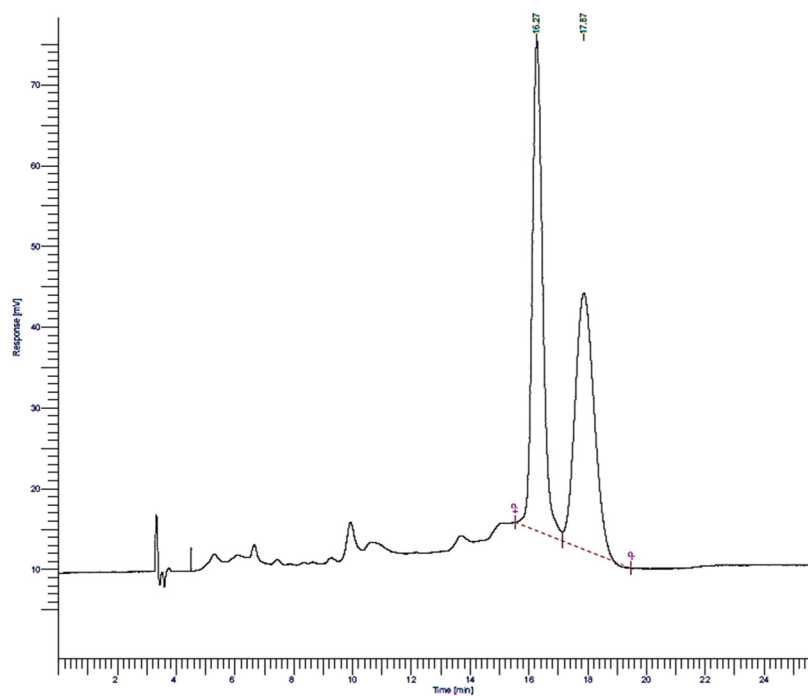


Figure S42. Chiral HPLC chromatogram of racemic **16** (Phenomenex Lux Cellulose-1 column (5 μ m, 250 $\times$ 4.6 mm), eluent hexane/ethanol = 85/15, isocratic mode; 0.8 mL min⁻¹; temperature 20 °C, UV detector 254 nm. Retention time for (*S*)-**16**: 16.1 min, for (*R*)-**16**: 17.6 min).