

SUPPLEMENTARY INFORMATION

Figure S1: IR spectrum of voacamine A.

Figure S2: Mass spectrum of voacamine A.

Figure S3: ^1H NMR (500 MHz, CDCl_3) spectrum of voacamine A.

Figure S4: ^{13}C NMR (125 MHz, CDCl_3) spectrum of voacamine A.

Figure S5: ^1H - ^1H COSY spectrum of voacamine A.

Figure S6: ^1H - ^1H NOESY spectrum of voacamine A.

Figure S7: ^1H - ^1H HSQC spectrum of voacamine A.

Figure S8: ^1H - ^1H HSQC and ^1H - ^{13}C HMBC spectra of voacamine A.

Figure S9: ^1H - ^{15}N -HSQC and ^1H - ^{15}N -HMBC spectra of voacamine A.

Figure S10: ^1H NMR (500 MHz, CDCl_3) spectrum of voacangine.

Figure S11: ^{13}C NMR (125 MHz, CDCl_3) spectrum of voacangine.

Figure S12: ^1H NMR (500 MHz, CDCl_3) spectrum of voacristine.

Figure S13: ^{13}C NMR (125 MHz, CDCl_3) spectrum of voacristine.

Figure S14: ^1H NMR (500 MHz, CDCl_3) spectrum of coronaridine.

Figure S15: ^{13}C NMR (125 MHz, CDCl_3) spectrum of coronaridine.

Figure S16: ^1H NMR (500 MHz, CDCl_3) spectrum of tabernanthine.

Figure S17: ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of tabernanthine.

Figure S18: ^1H NMR (500 MHz, MeOD) spectrum of iboxygaine.

Figure S19: ^{13}C NMR (125 MHz, CDCl_3) spectrum of iboxygaine.

Figure S20: ^1H NMR (500 MHz, DMSO-d_6) spectrum of voacamine.

Figure S21: ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of voacamine.

Figure S22: ^1H NMR (500 MHz, CDCl_3) spectrum of voacorine.

Figure S23: ^{13}C NMR (125 MHz, CDCl_3) spectrum of voacorine.

Figure S24: ^1H NMR (500 MHz, CDCl_3) spectrum of conoduramine.

Figure S25: ^{13}C NMR (125 MHz, CDCl_3) spectrum of conoduramine.

Figure S26: Percentage sequence identity and similarity values to our target.

Figure S27: Ramachandran plot (ϕ/ψ) distribution of the backbone conformation.

Figure S28: Chemical structure of auranofin.

Figure S29: Docking poses of (A) compound **1a**, (B) compound **5**, (C) compound **6**, (D) compound **7a**.

Figure S30: Docking poses of (A) compound **7**, (B) compound **8**, (C) compound **9**, (D) compound **9b**.

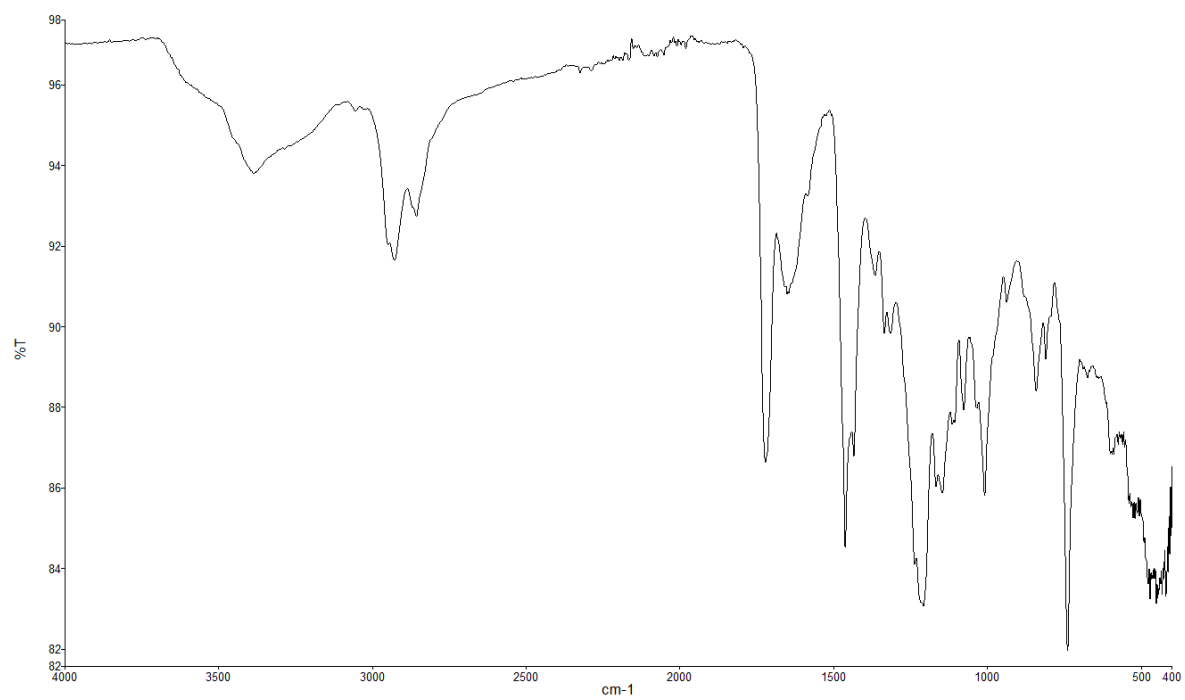


Figure S1: IR spectrum of voacamine A.

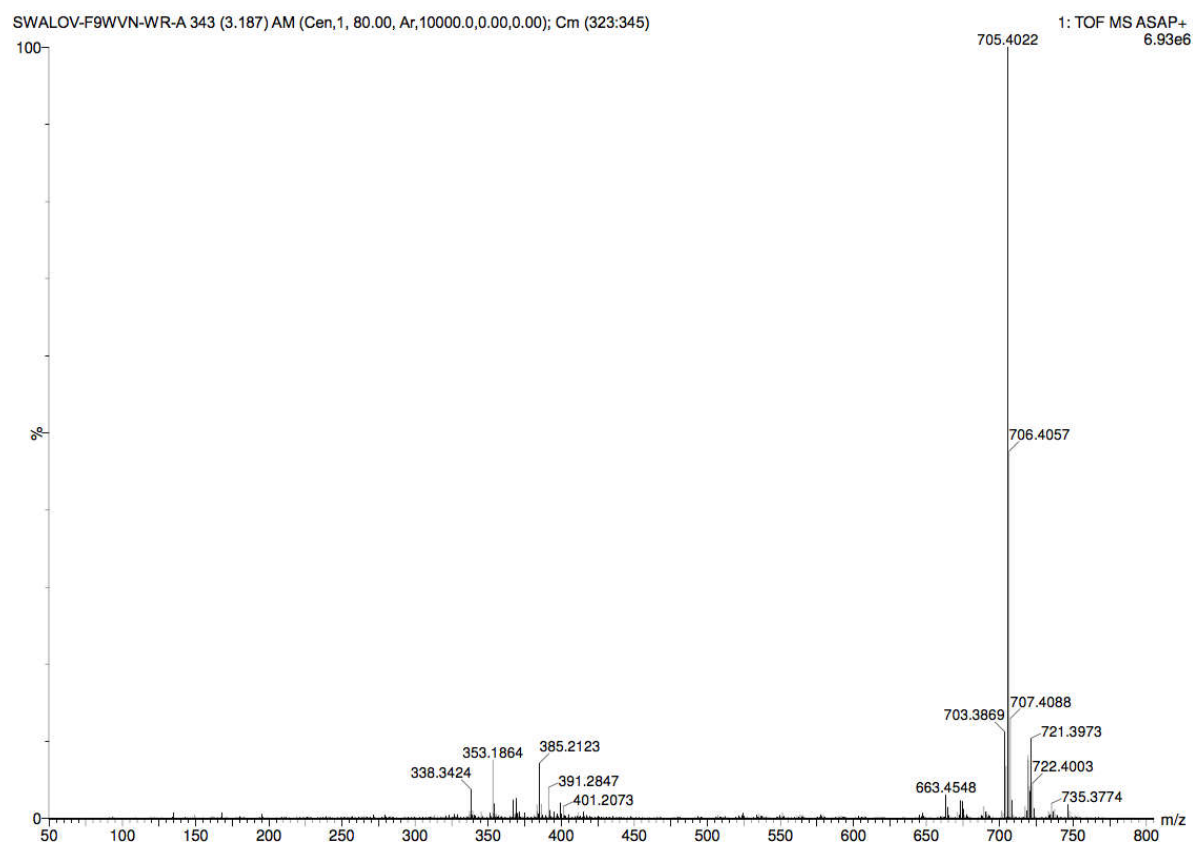


Figure S2: Positive-ion mass spectrum of voacamine A.

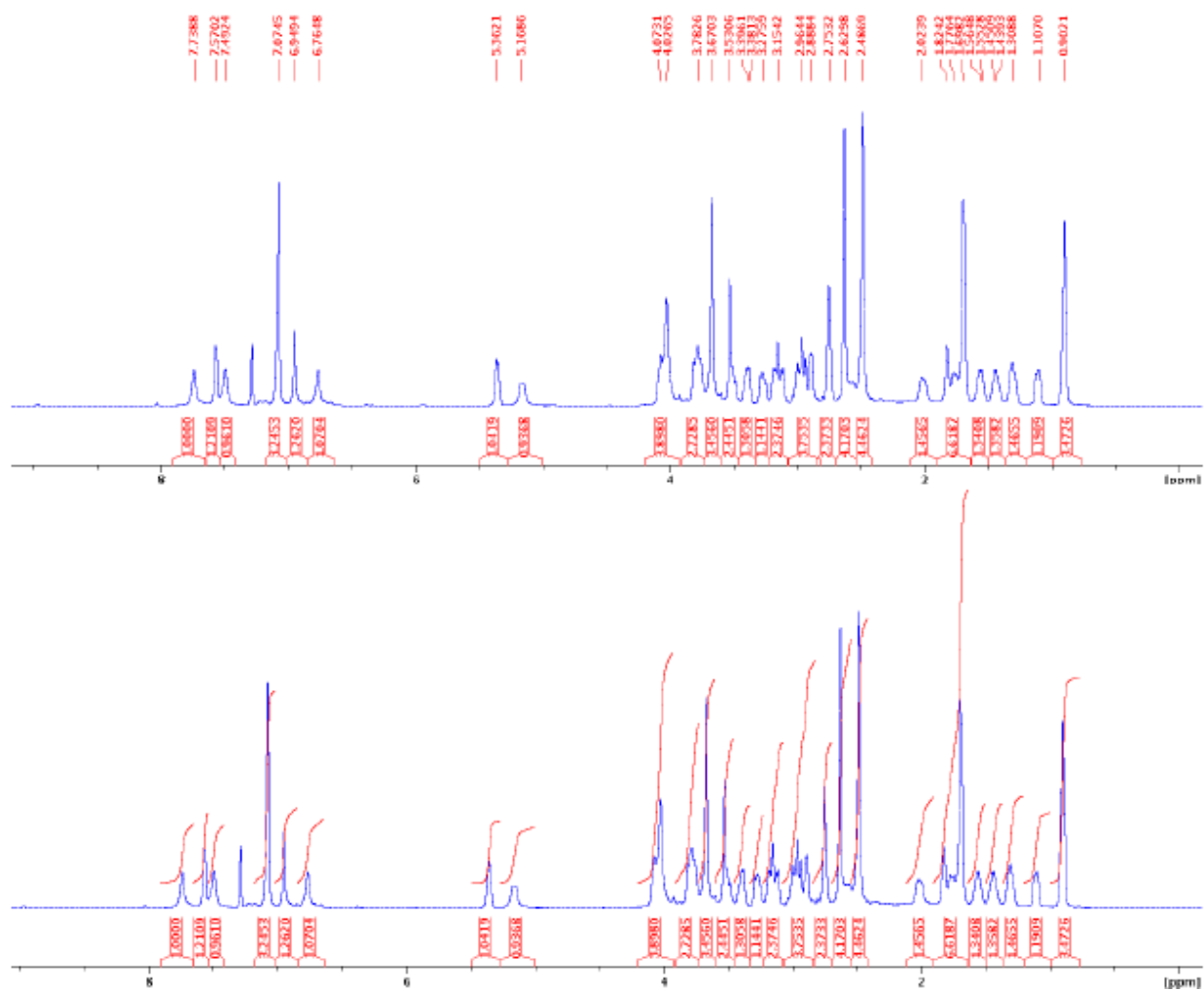


Figure S3: ^1H NMR (500 MHz, CDCl_3) spectrum of voacamine A.

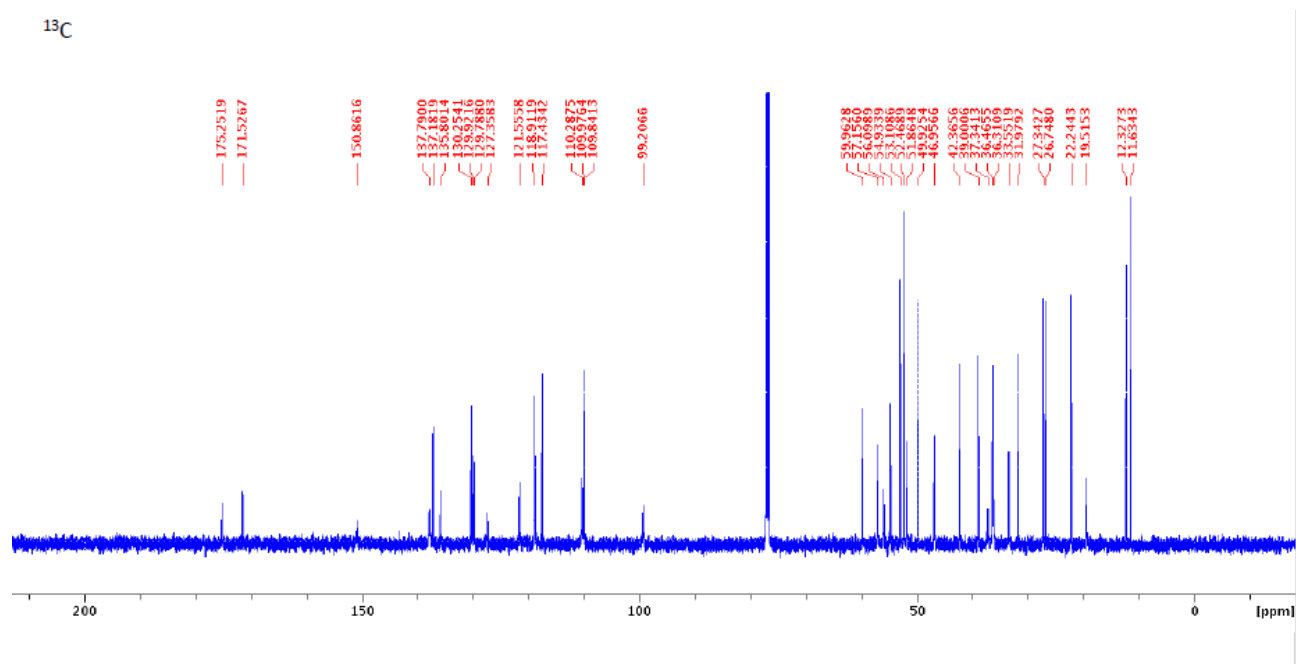


Figure S4: ¹³C NMR (125 MHz, CDCl₃) spectrum of voacamine A.

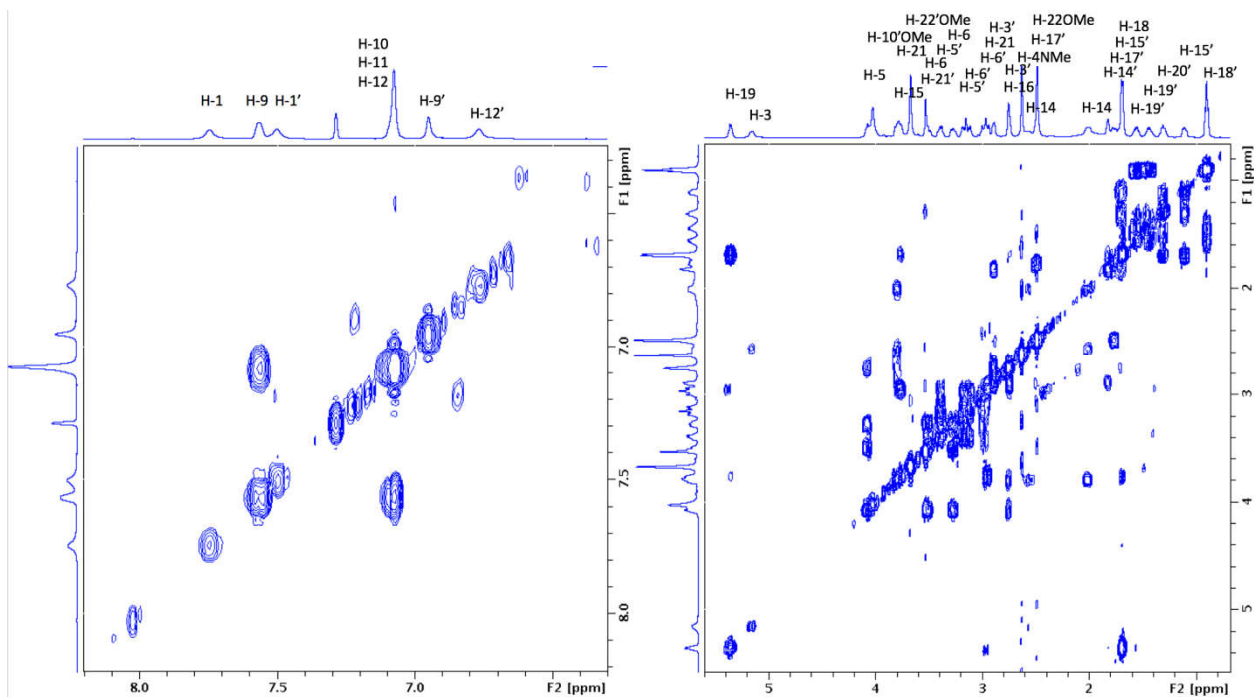


Figure S5: ^1H - ^1H COSY spectrum of voacamine A. Atom labels on the 1D spectrum are positioned so the centre of the H corresponds to the resonant frequency.

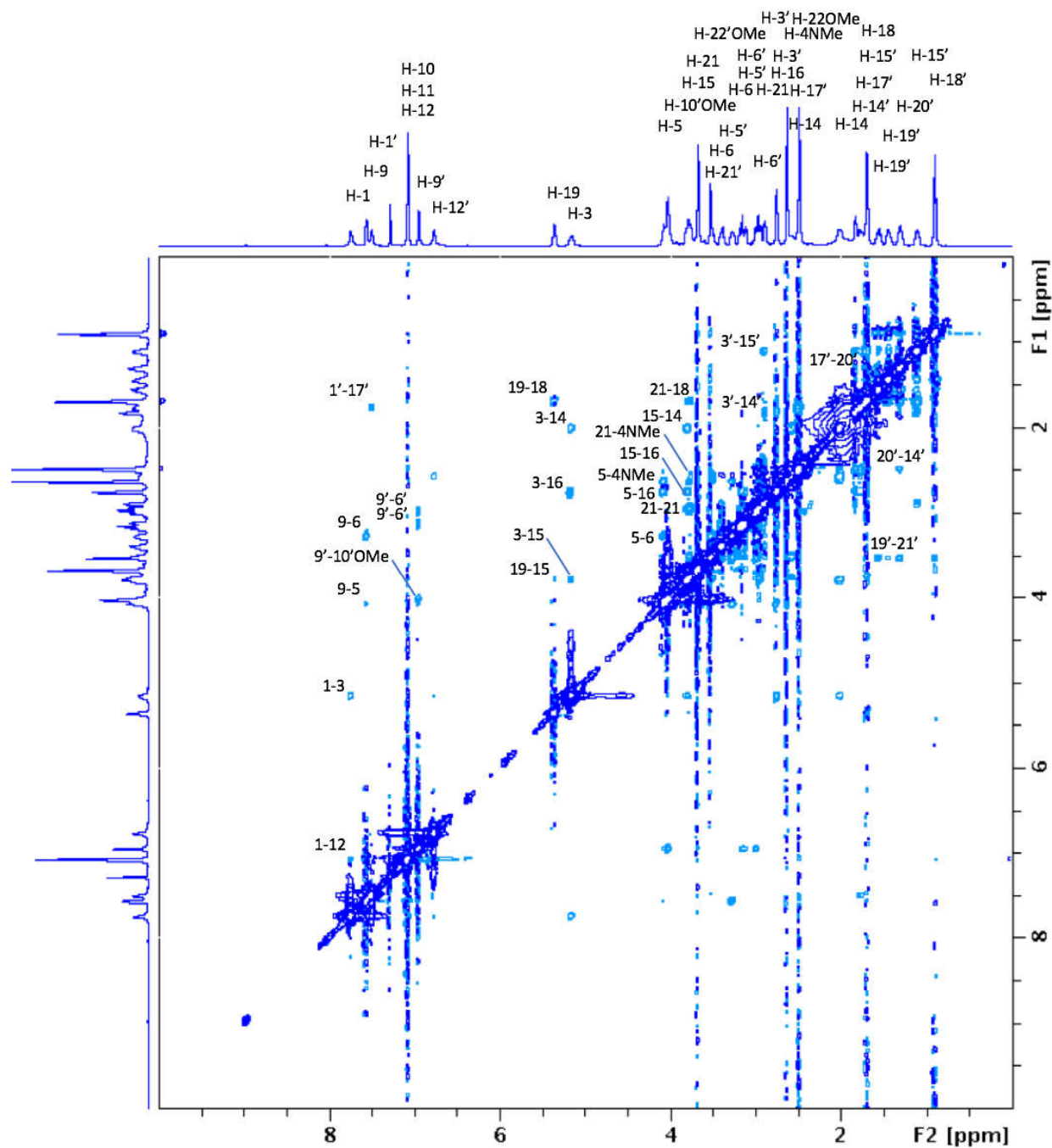


Figure S6: ^1H - ^1H NOESY spectrum of voacamine A. Atom labels on the 1D spectrum are positioned so the centre of the H corresponds to the resonant frequency.

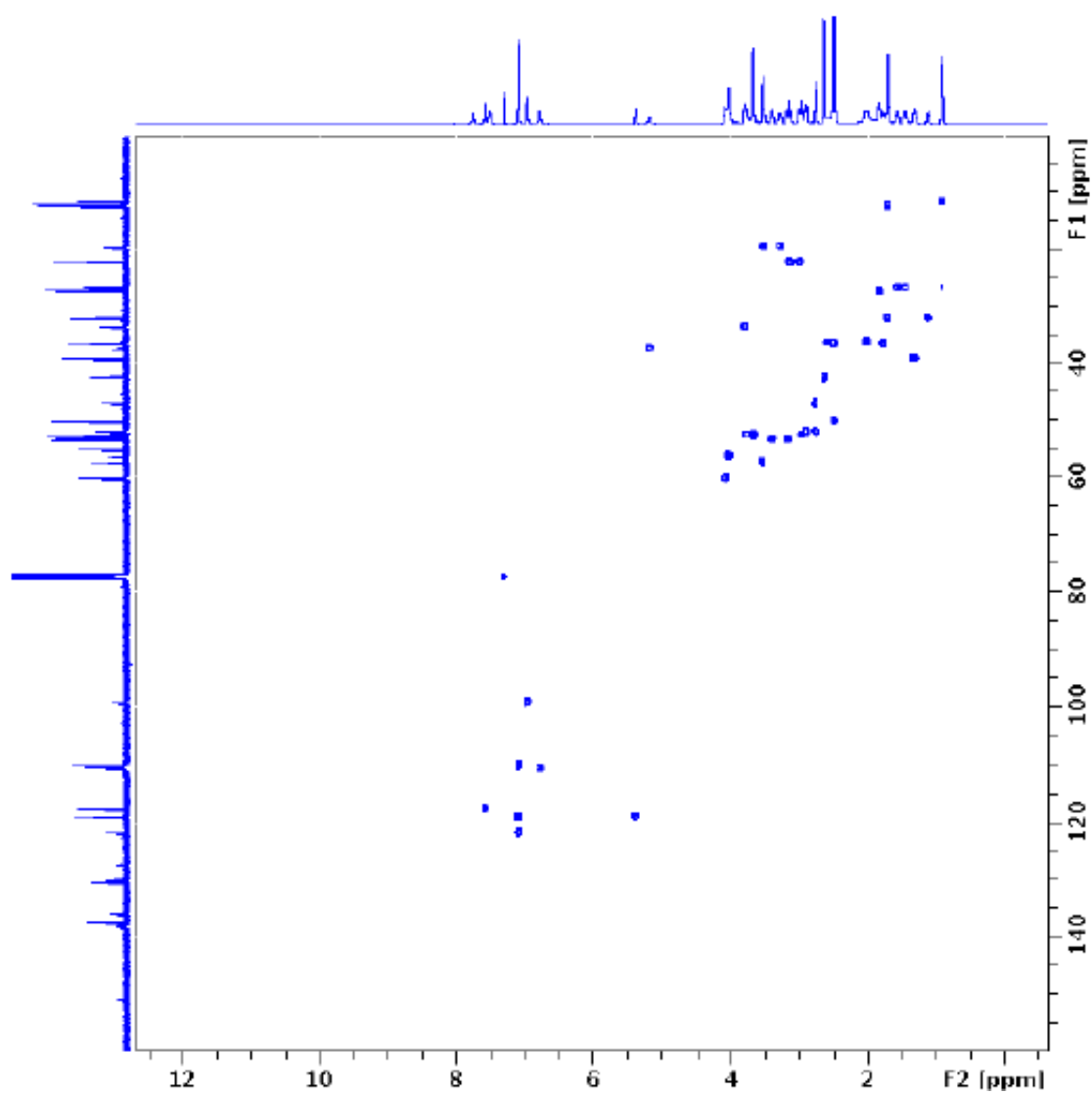


Figure S7: ^1H - ^{13}C HSQC spectrum of voacamine A.

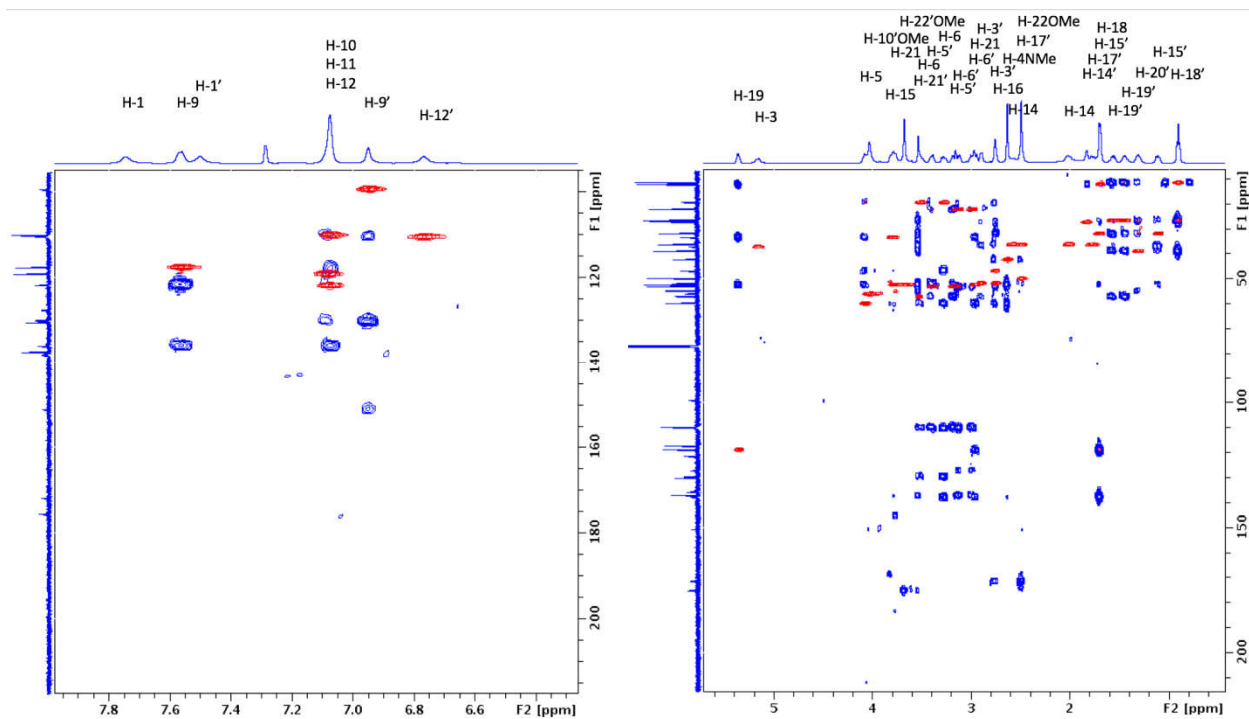


Figure S8: ^1H - ^{13}C CHSQC and ^1H - ^{13}C HMBC spectra of voacamine A. Atom labels on the 1D ^1H spectrum are positioned so the centre of the H corresponds to the resonant frequency.

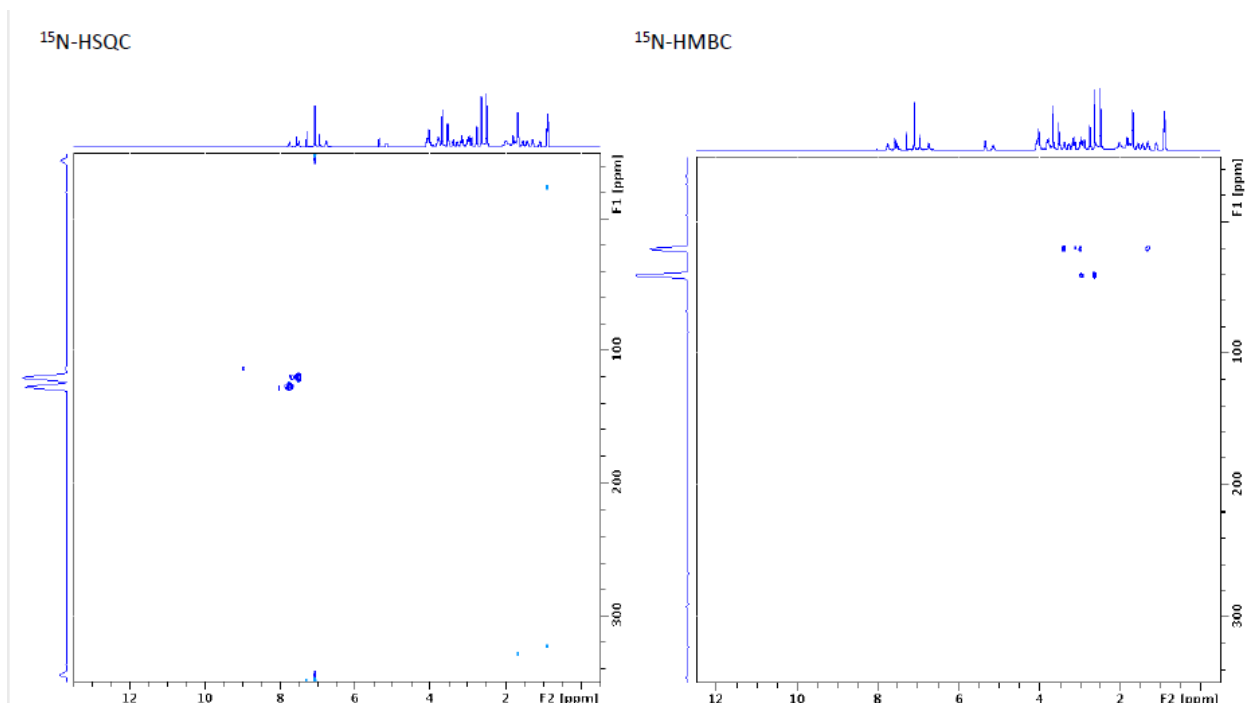


Figure S9: ^1H - ^{15}N -HSQC and ^1H - ^{15}N -HMBC spectra of voacamine A.

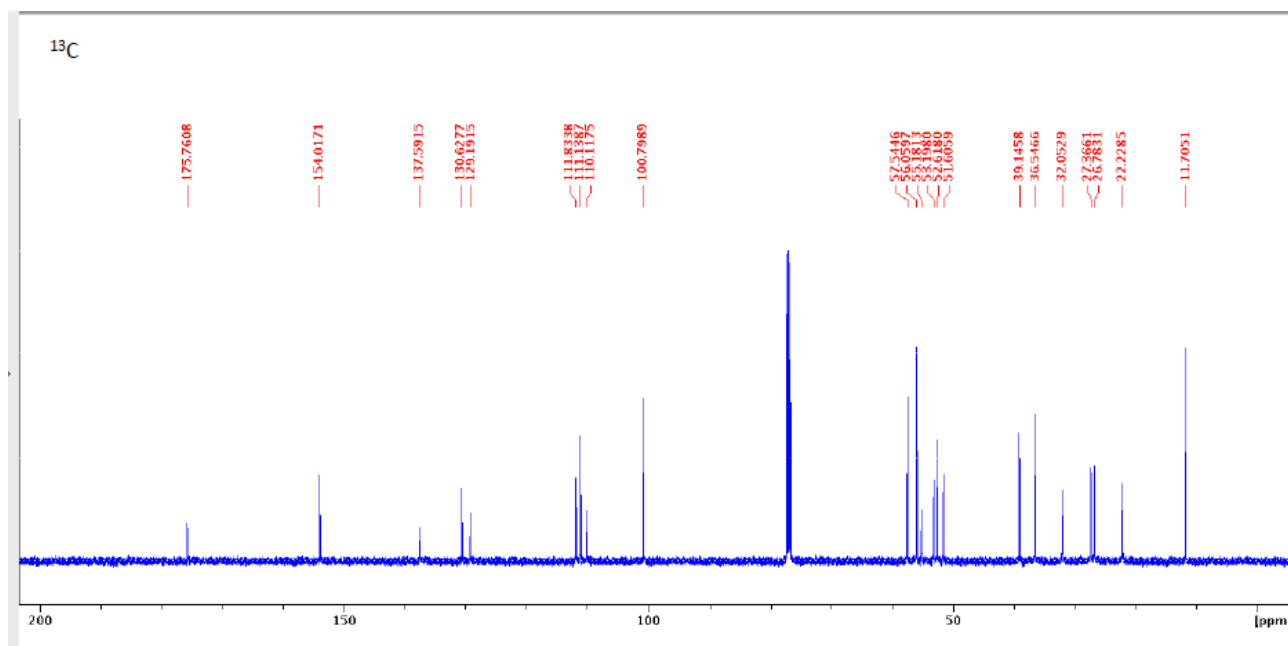


Figure S11: ¹³C NMR (125 MHz, CDCl₃) spectrum of voacangine.

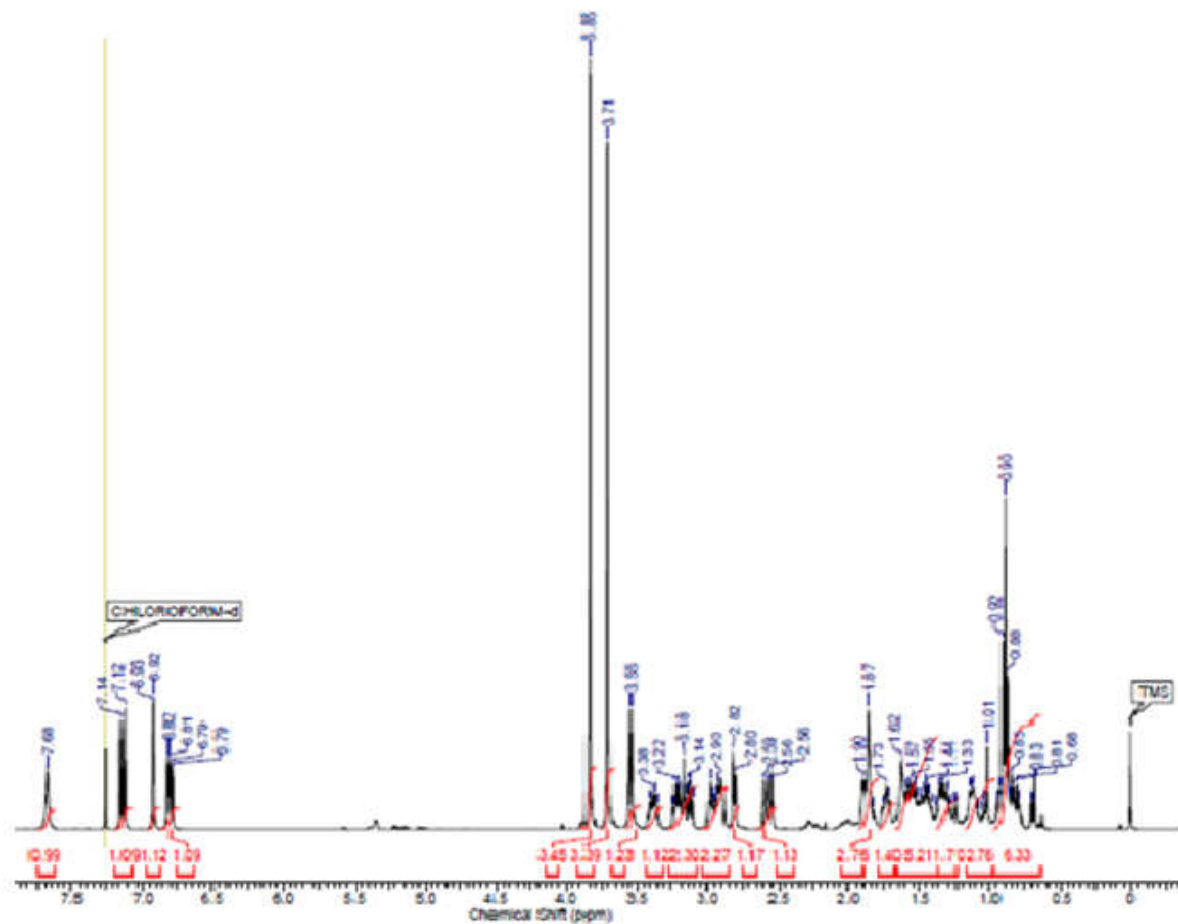


Figure S12: ^1H NMR (500 MHz, CDCl_3) spectrum of voacristine.

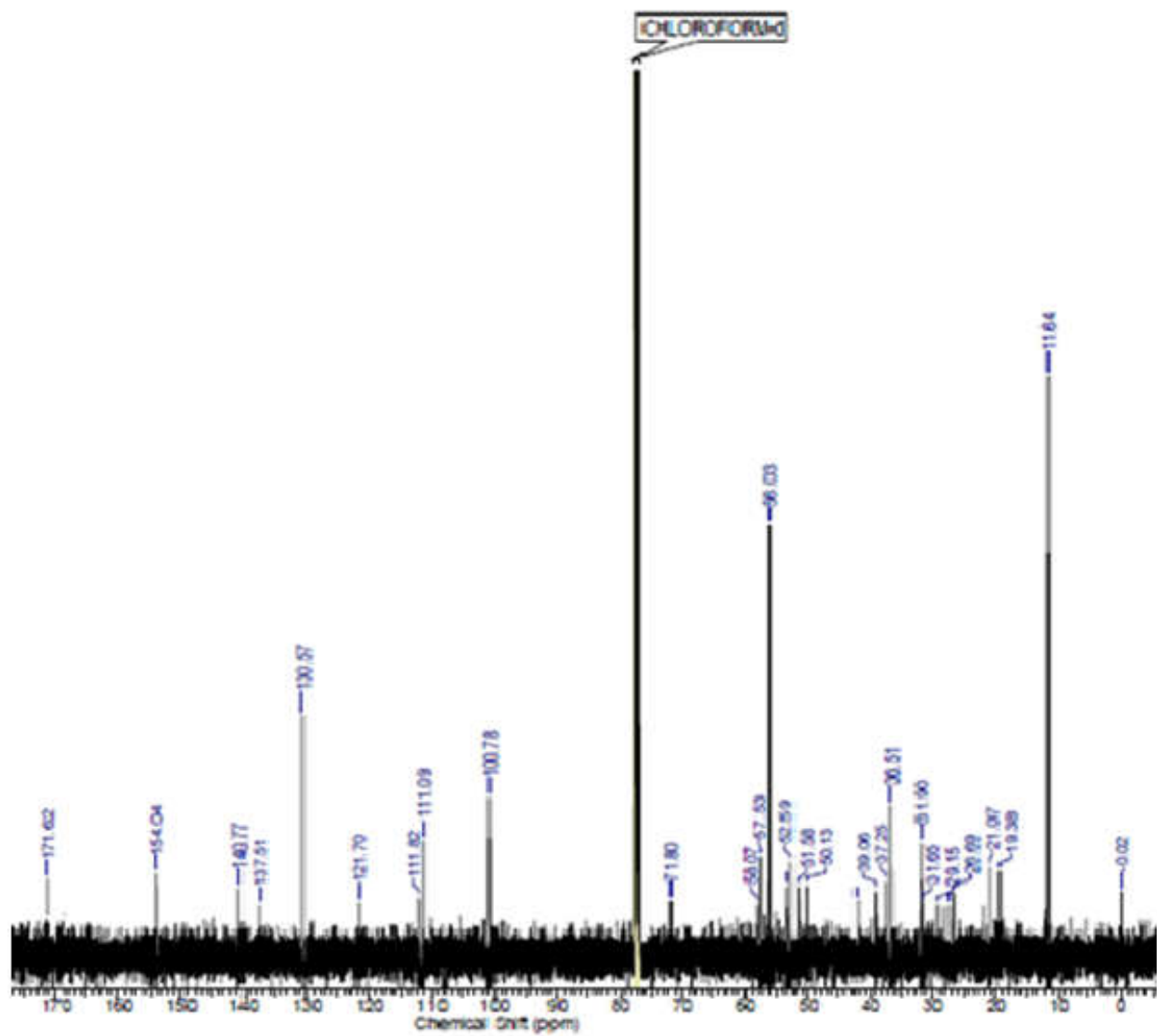


Figure S13: ¹³C NMR (125 MHz, CDCl₃) spectrum of voacristine.

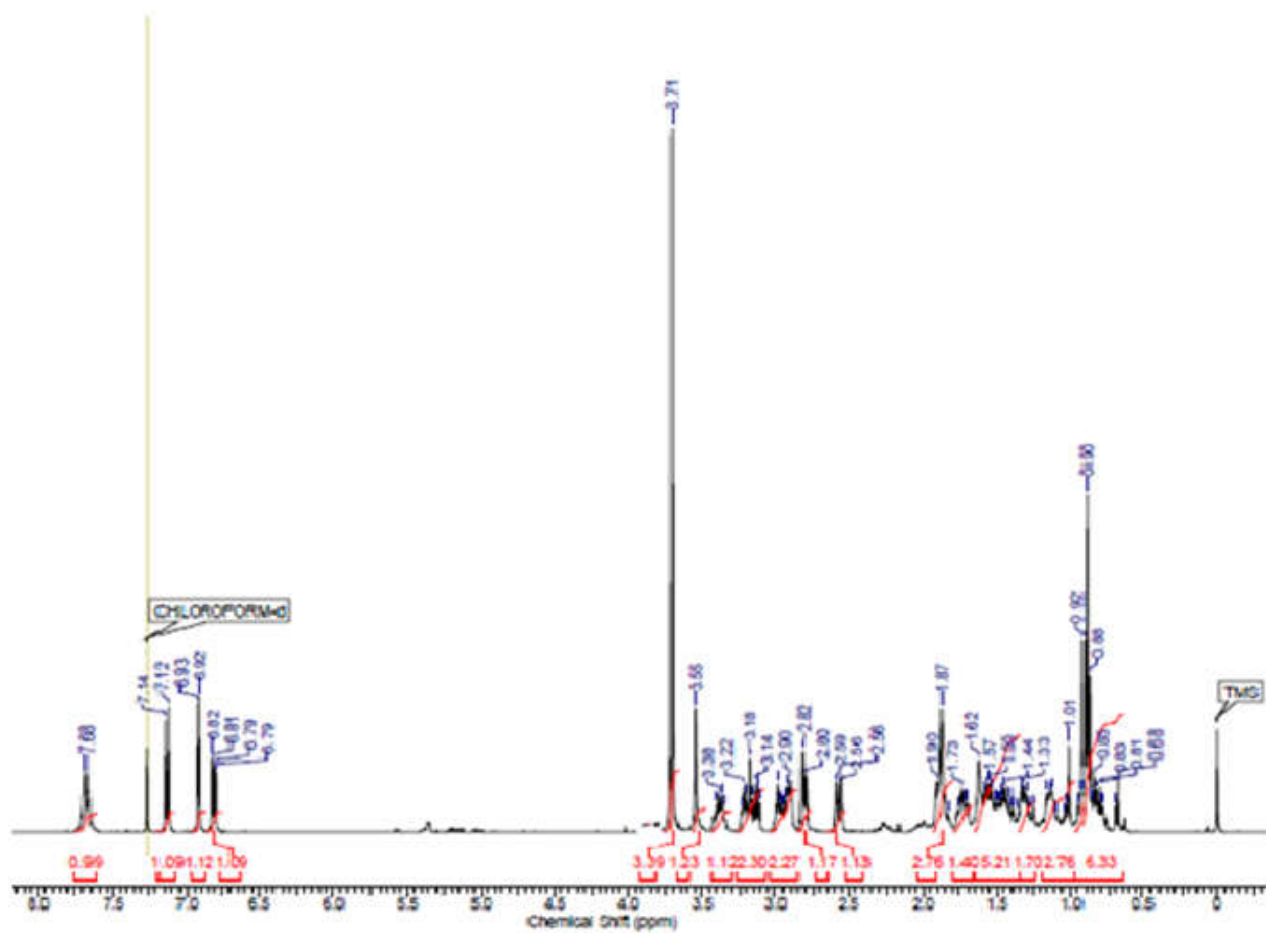


Figure S14: ¹H NMR (500 MHz, CDCl₃) spectrum of coronaridine.

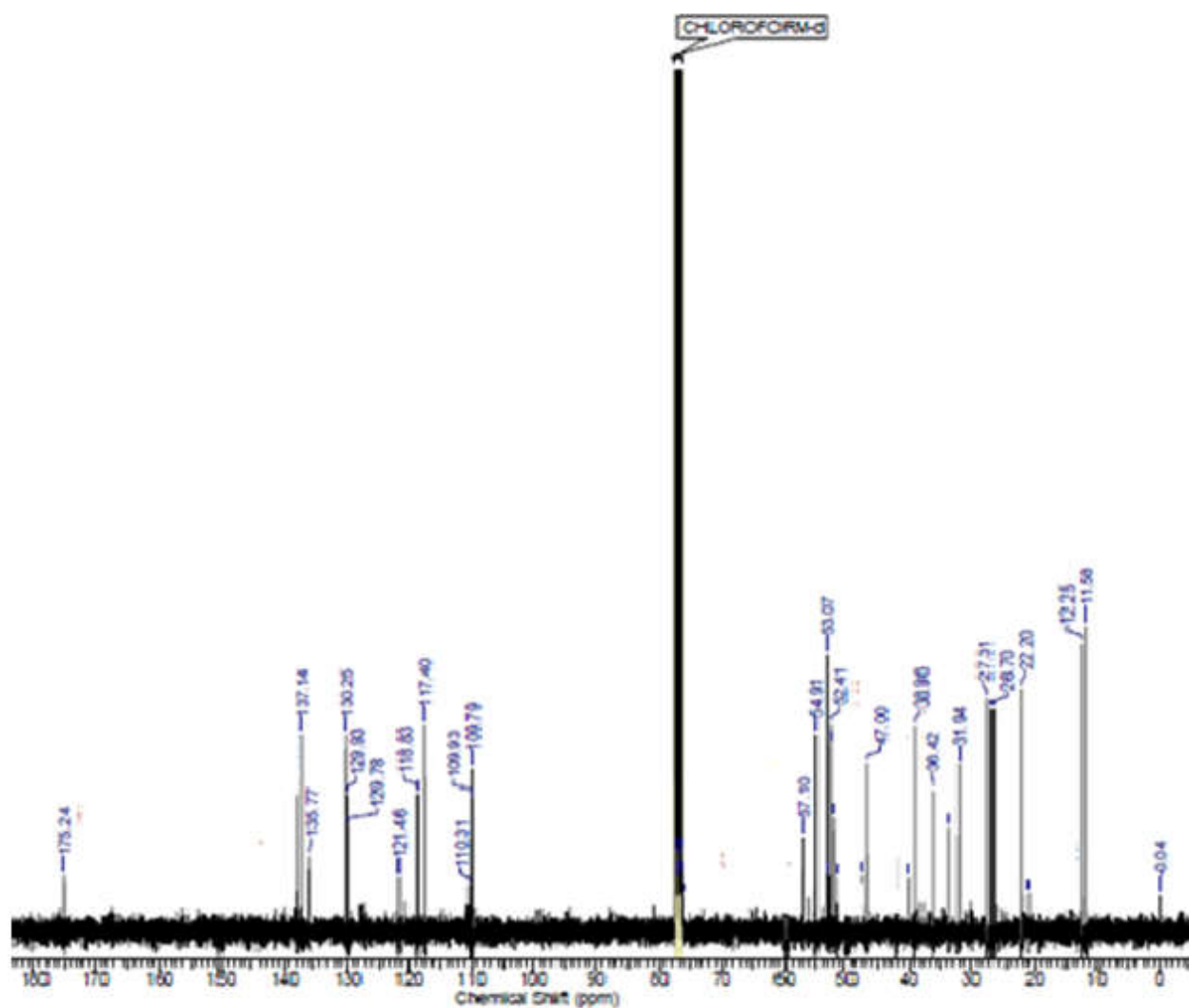


Figure S15: ¹³C NMR (125 MHz, CDCl₃) spectrum of coronaridine.

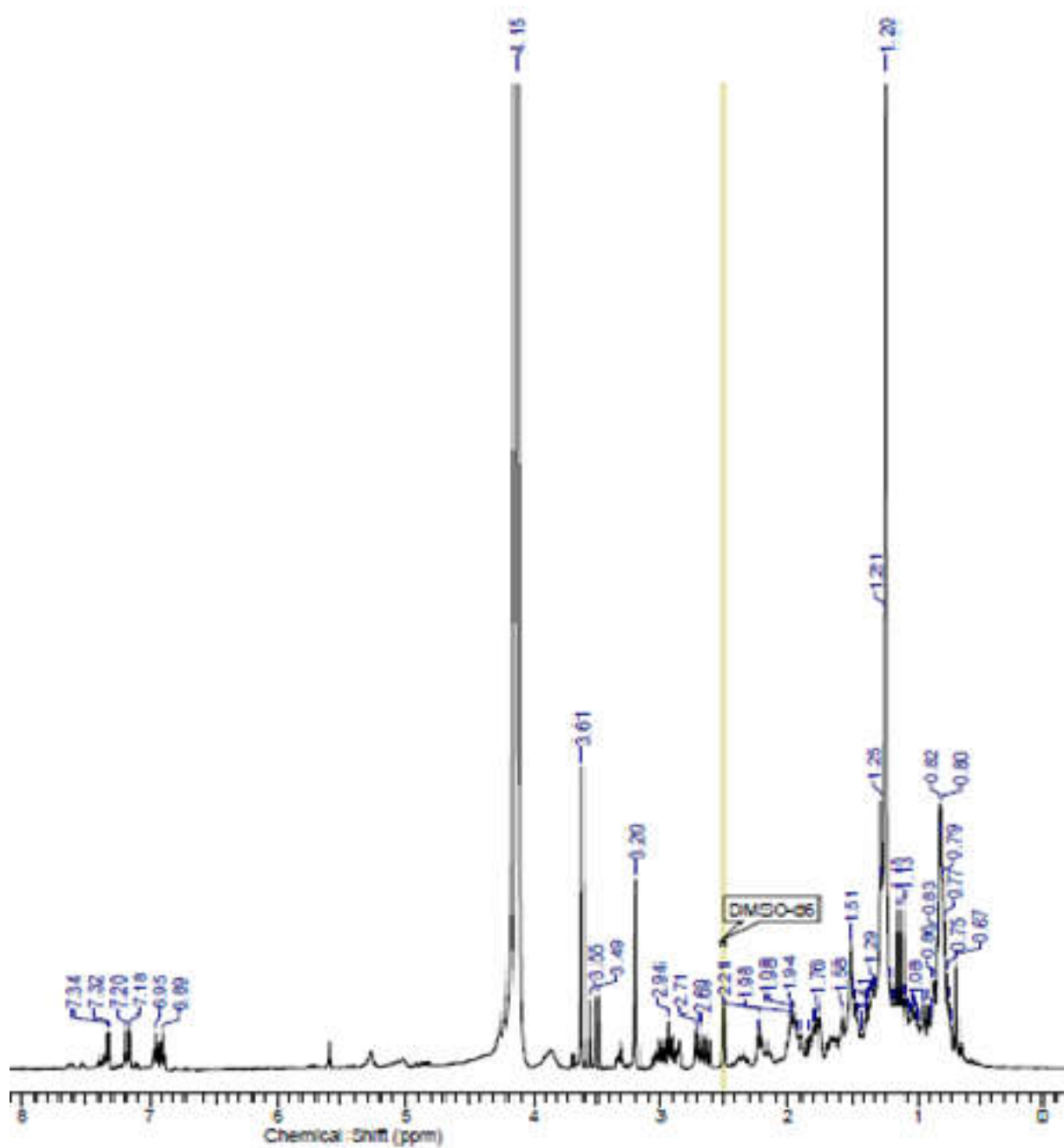


Figure S16: ^1H NMR (500 MHz, DMSO-d_6) spectrum of tabernanthine.

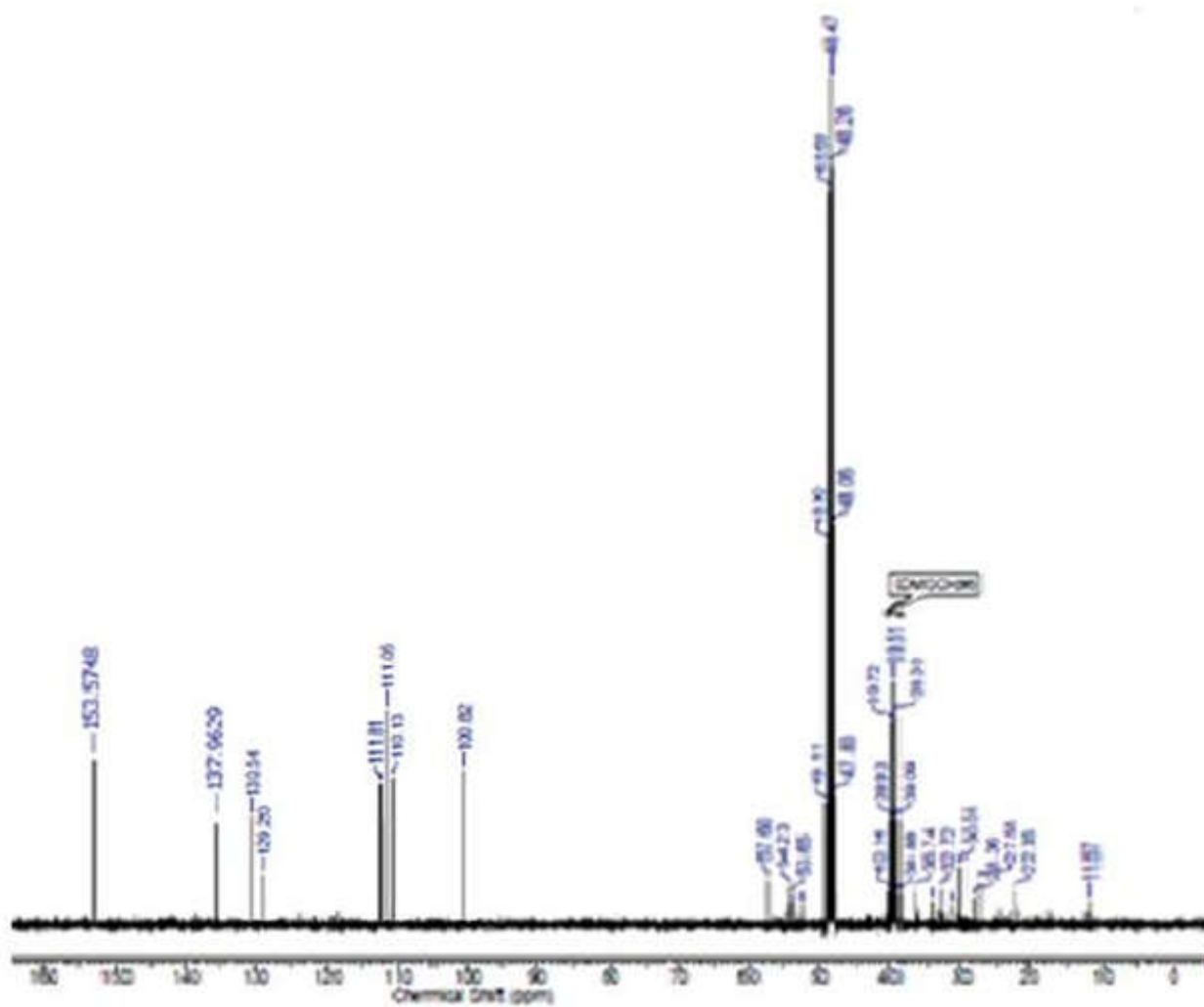


Figure S17: ¹³C NMR (125 MHz, MeOD) spectrum of tabernanthine.

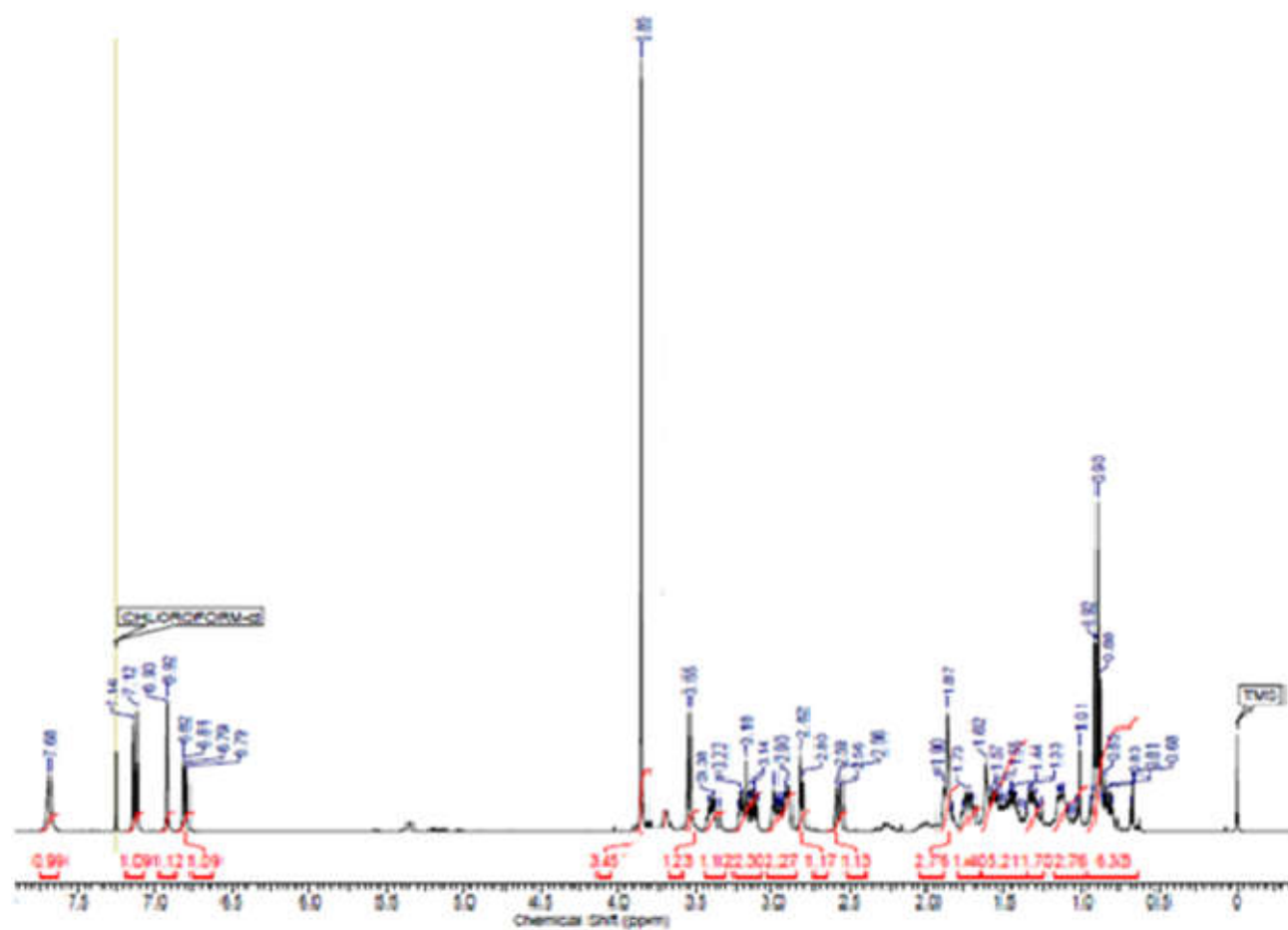


Figure S18: ^1H NMR (500 MHz, CDCl_3) spectrum of iboxygaine.

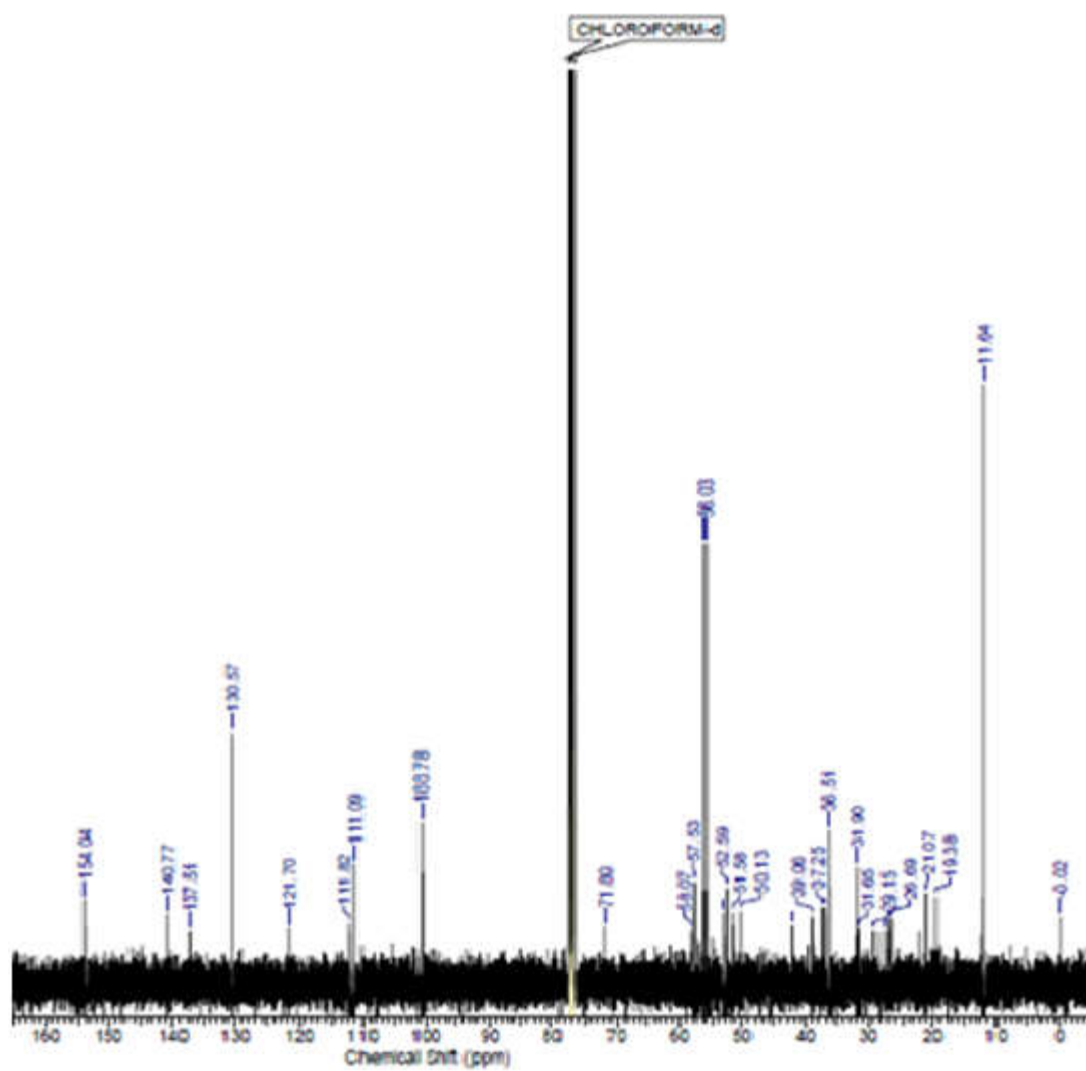


Figure S19: ^{13}C NMR (125 MHz, CDCl_3) spectrum of iboxygaine.

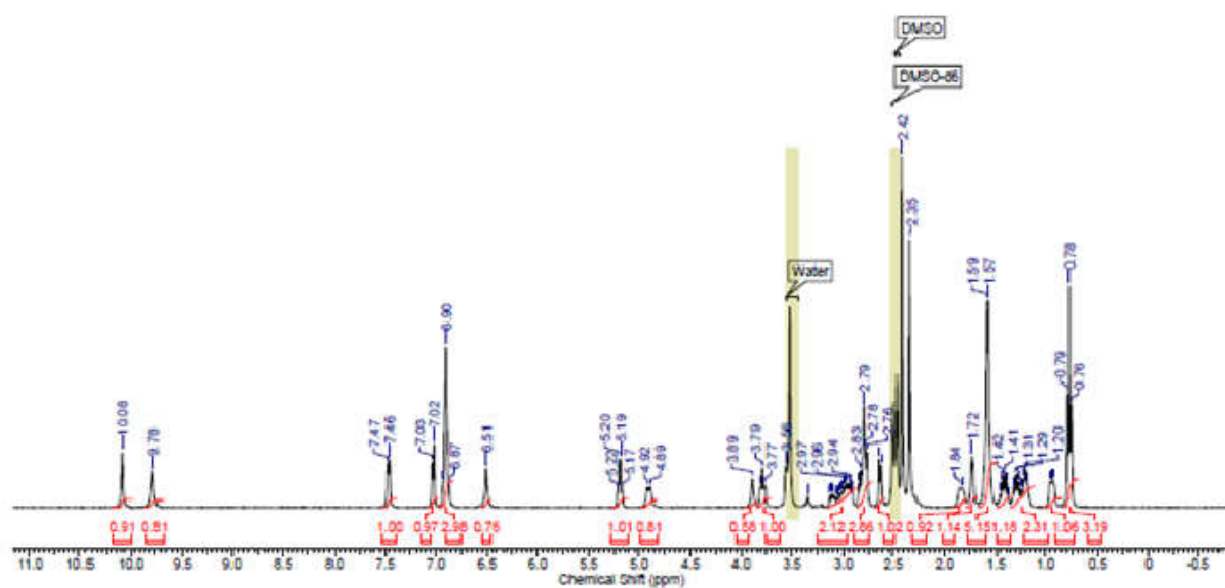


Figure S20: ^1H NMR (500 MHz, DMSO-d_6) spectrum of voacamine.

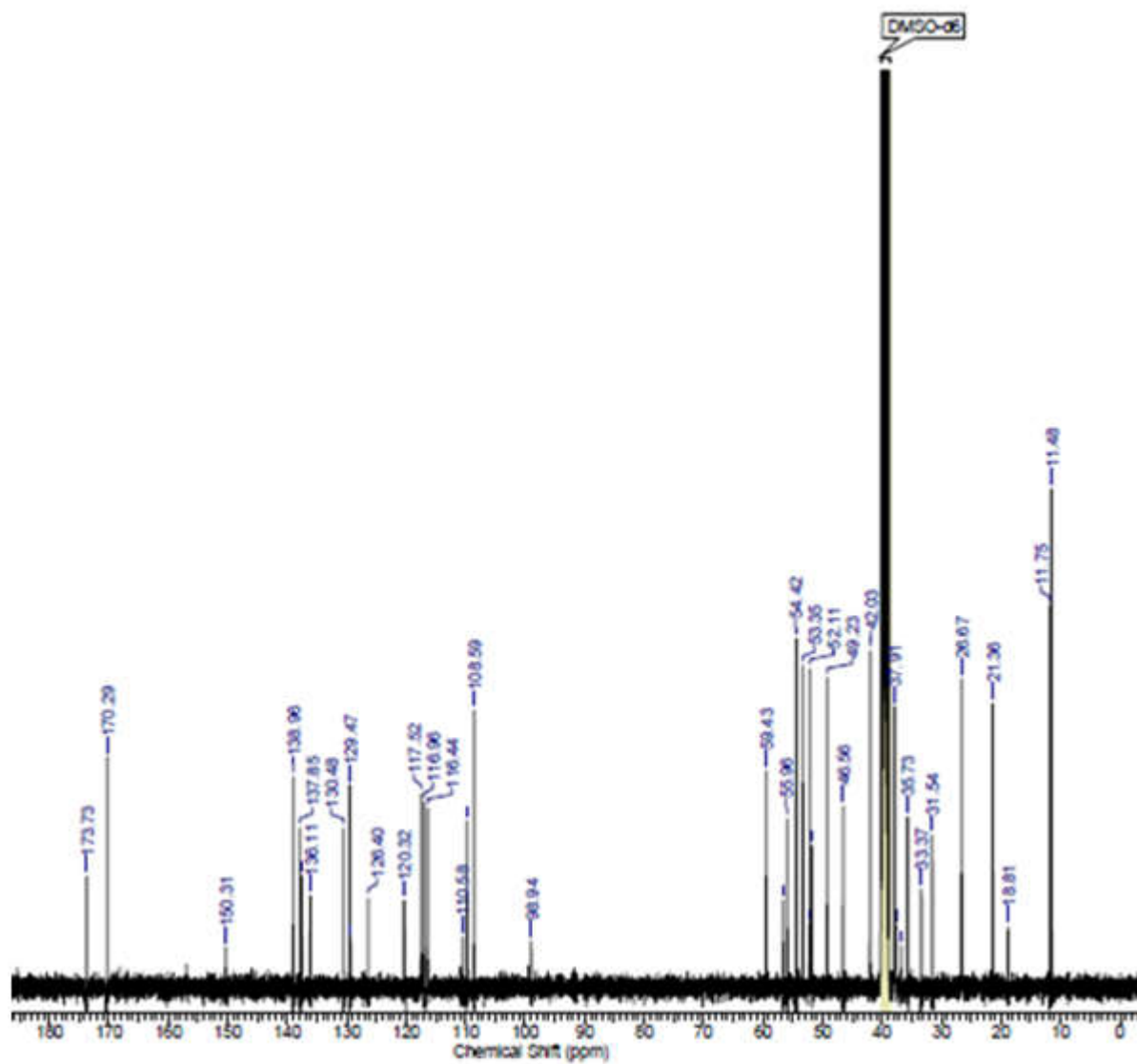


Figure S21: ¹³C NMR (125 MHz, DMSO-d₆) spectrum of voacamine.

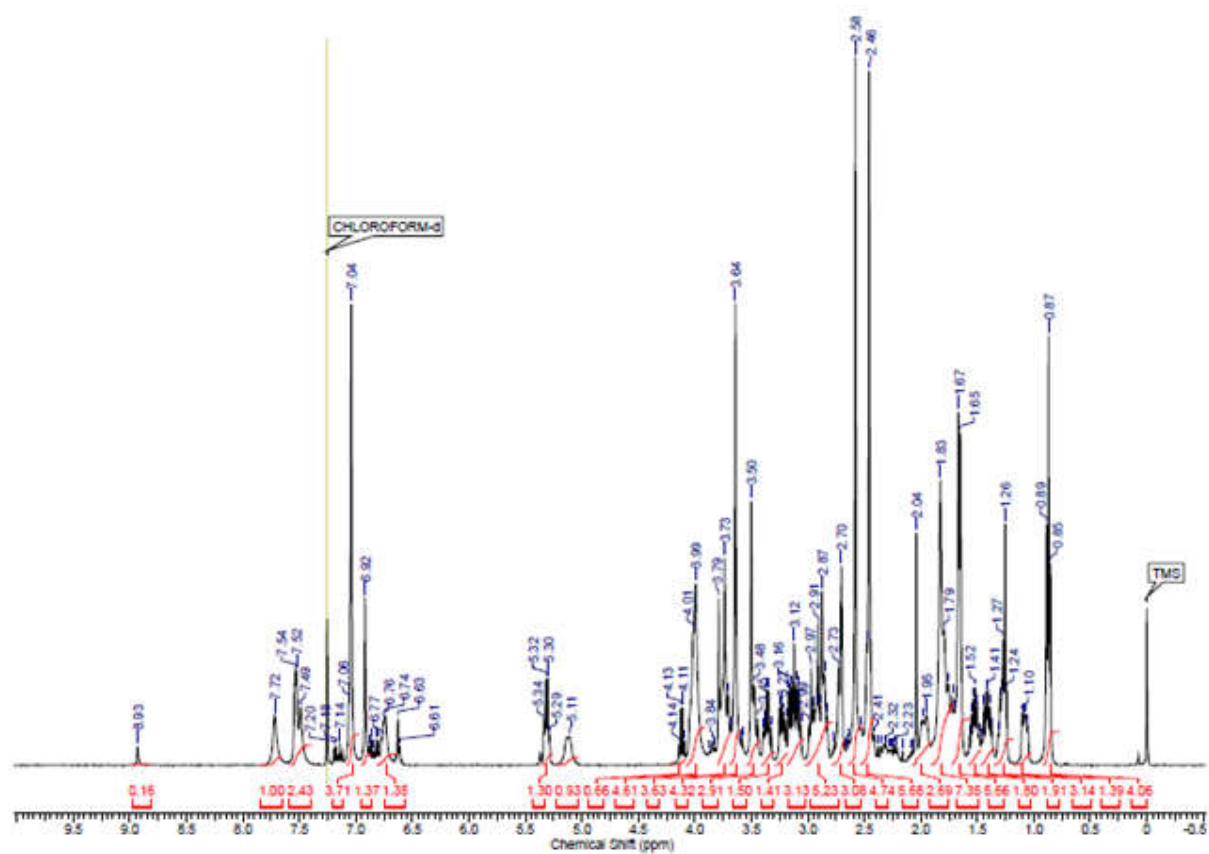


Figure S22: ^1H NMR (500 MHz, CDCl_3) spectrum of voacordine.

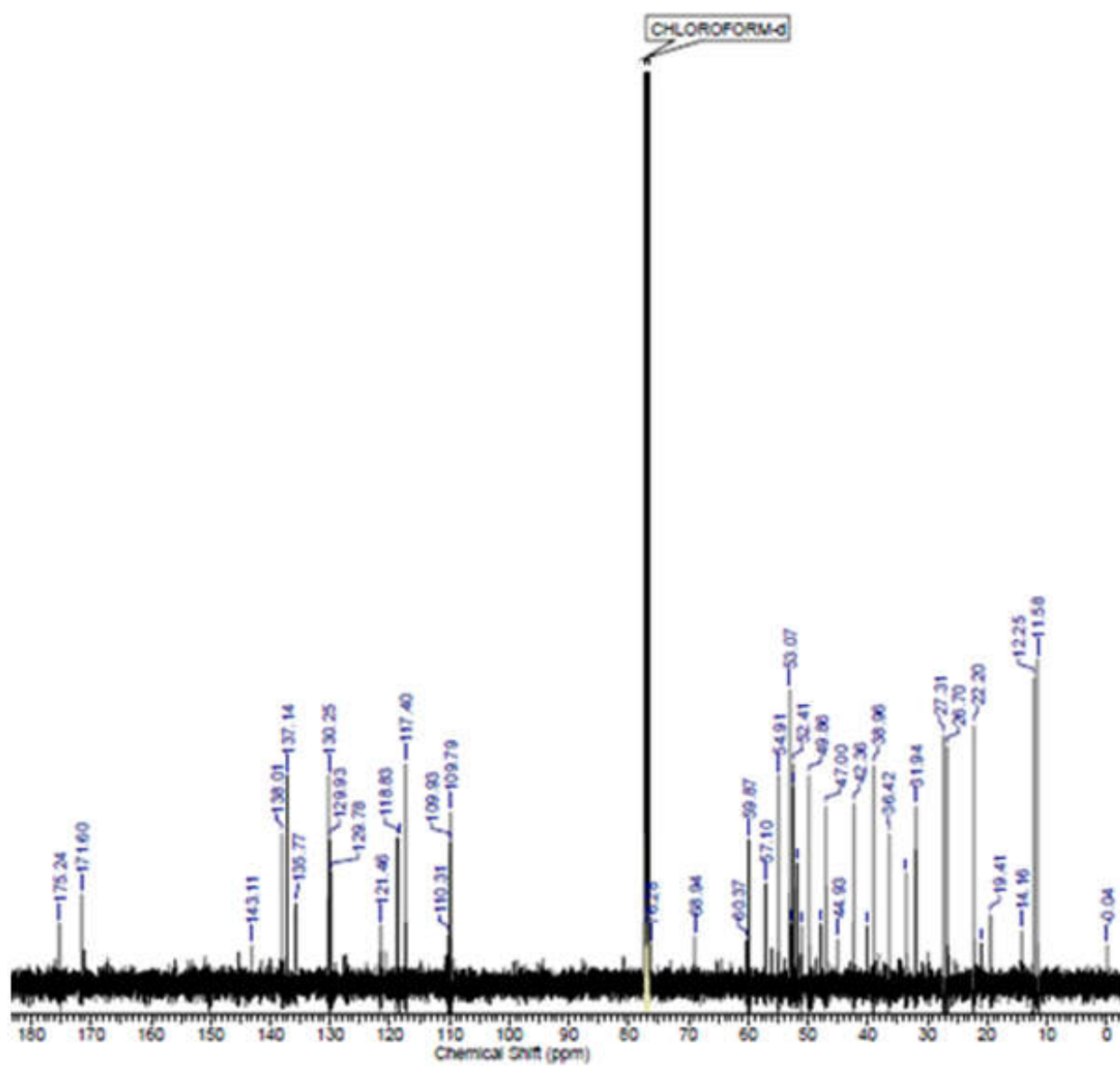


Figure S23: ^{13}C NMR (125 MHz, CDCl_3) spectrum of voacordine.

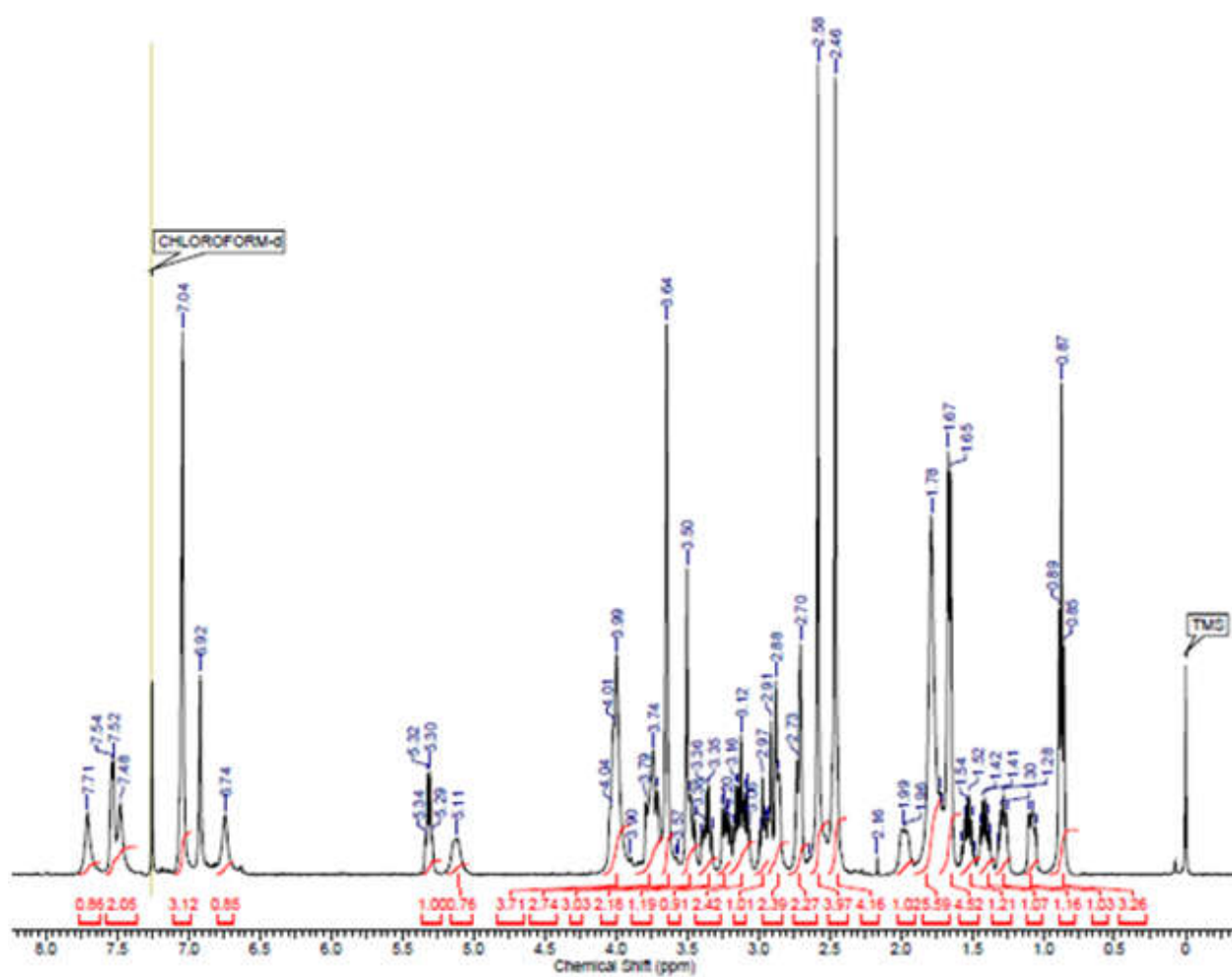


Figure S24: ^1H NMR (500 MHz, CDCl_3) spectrum of conoduramine.

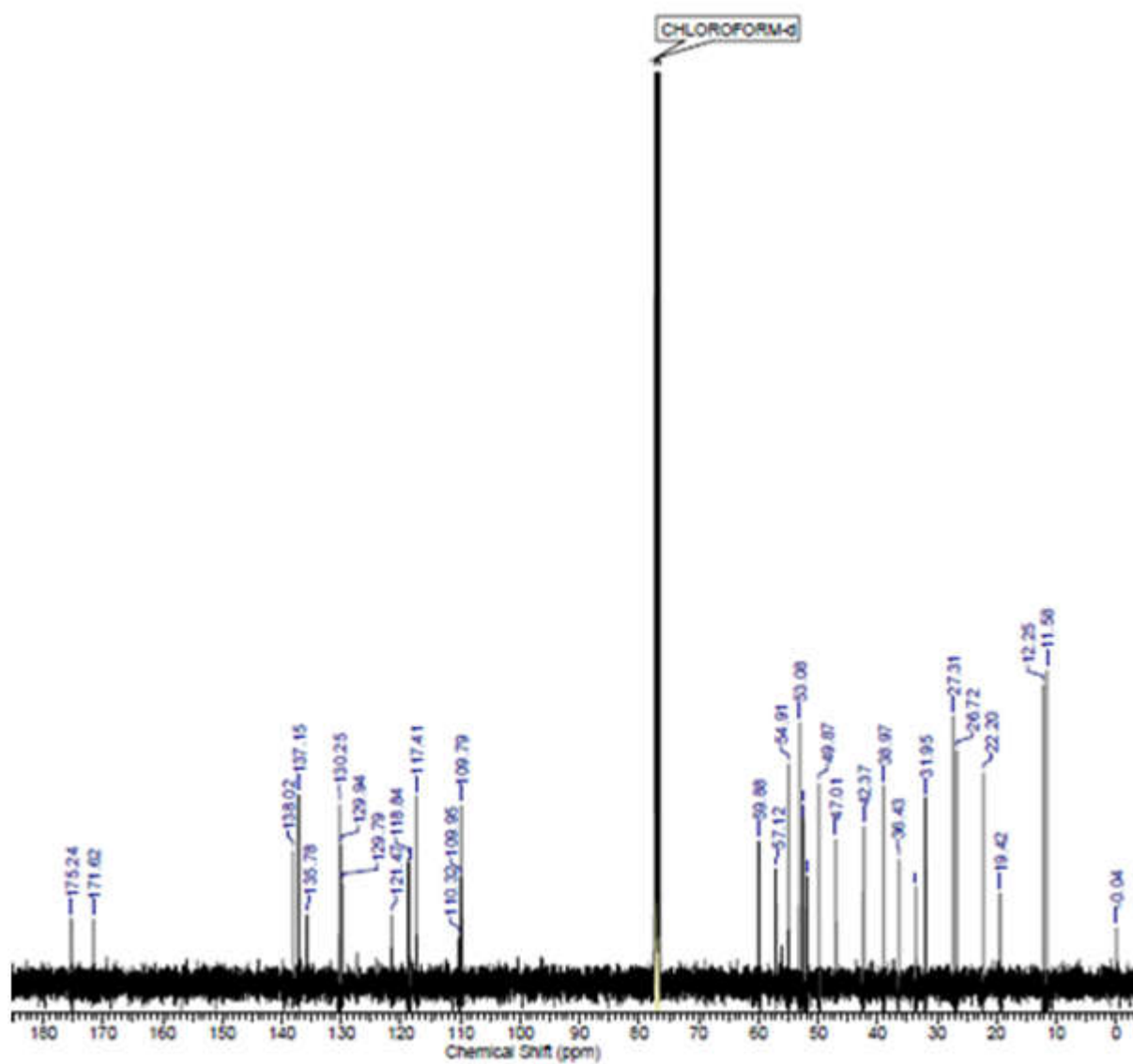
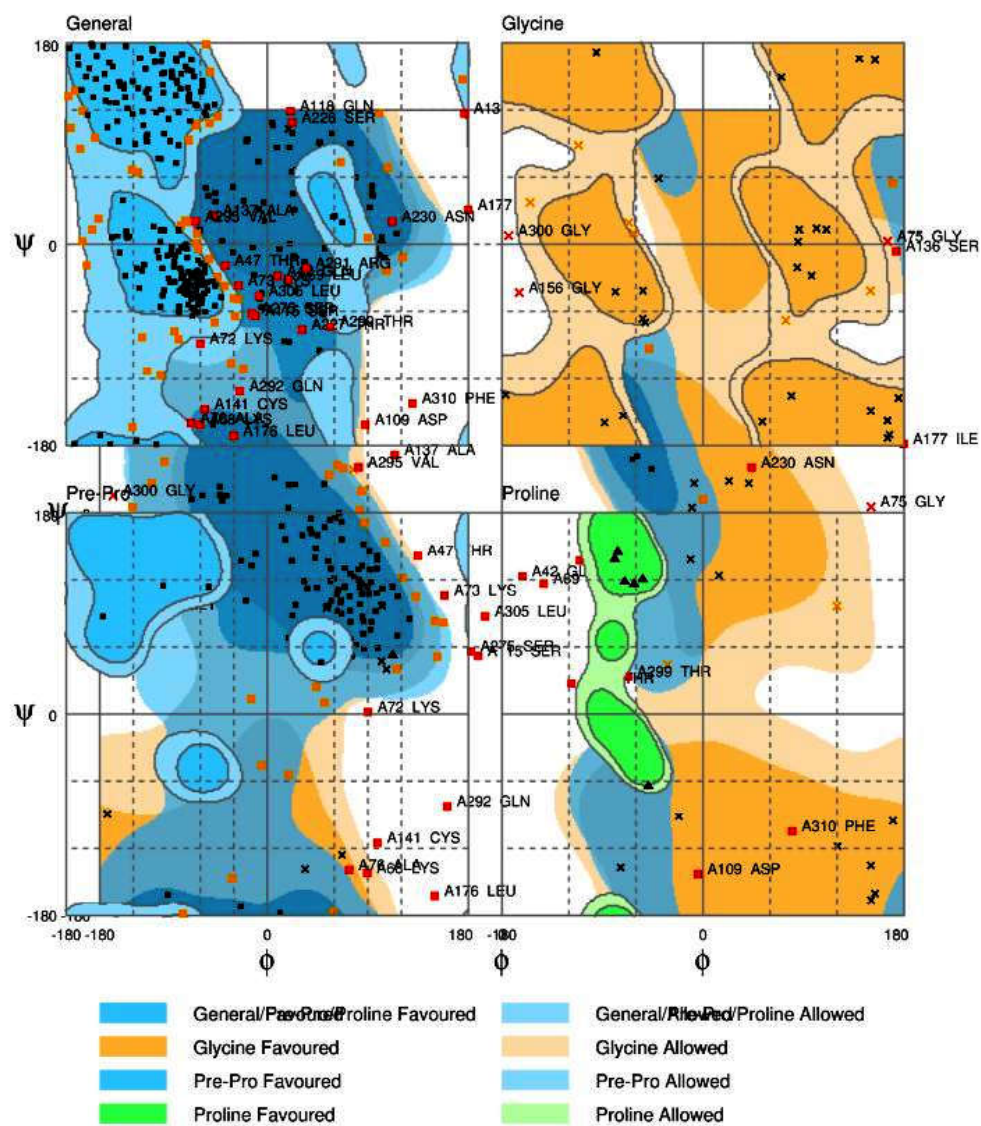


Figure S25: ¹³C NMR (125 MHz, CDCl₃) spectrum of conoduramine.

A	1	4	7	10	13	16
1:4JNQ.A		56.7	54.8	42.7	42.7	51.9
4:6BWT.B	56.9		64.5	45.2	45.2	54.4
7:5U63.A	55.3	64.9		44.9	44.9	50.0
10:4CBQ.A	42.1	44.5	43.9		100.0	41.2
13:4CCR.A	42.1	44.5	43.9	100.0		41.2
16:tr I7IAK1 ...	51.9	54.2	49.5	41.7	41.7	

B	1	4	7	10	13	16
1:4JNQ.A		74.6	71.7	60.5	60.5	68.6
4:6BWT.B	74.8		82.9	65.6	65.6	70.1
7:5U63.A	72.3	83.4		63.4	63.4	70.4
10:4CBQ.A	59.7	64.6	62.0		100.0	61.3
13:4CCR.A	59.7	64.6	62.0	100.0		61.3
16:tr I7IAK1 ...	68.6	69.9	69.8	62.1	62.1	

Figure S26:Percentage sequence identity and similarity values to our target.



Number of residues in favoured region (~98.0% expected) : 238 (75.8%)
 Number of residues in allowed region (~2.0% expected) : 48 (15.3%)
 Number of residues in outlier region : 28 (8.9%)

RAMPAGE by Paul de Bakker and Simon Lovell available at <http://www-cryst.bioc.cam.ac.uk/rampage/>
 Please cite: S.C. Lovell, I.W. Davis, W.B. Arendall III, P.I.W. de Bakker, J.M. Word, M.G. Pisant, J.S. Richardson & D.C. Richardson (2002)
 Structure validation by C α geometry: ϕ/ψ and C β deviation. *Proteins: Structure, Function & Genetics* 50: 437-450

Figure S27: Ramachandran plot (ϕ/ψ) distribution of the backbone conformation.

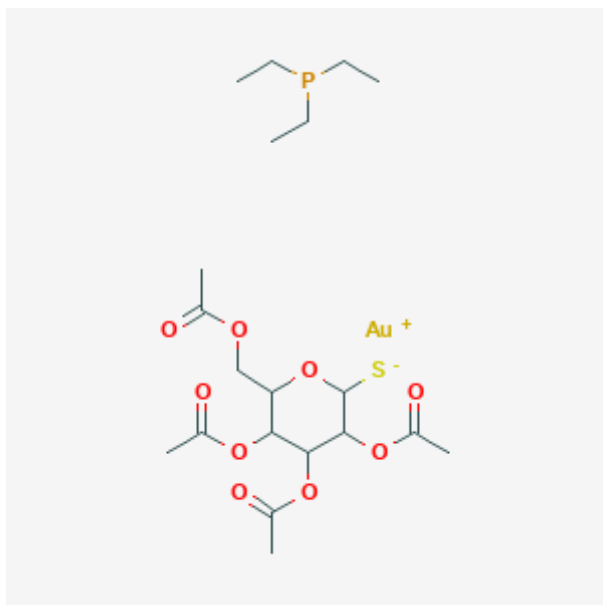
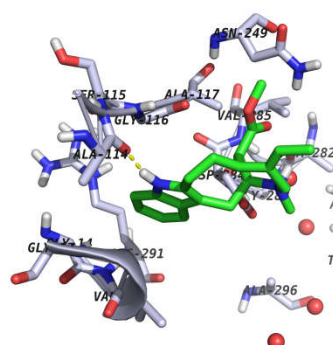
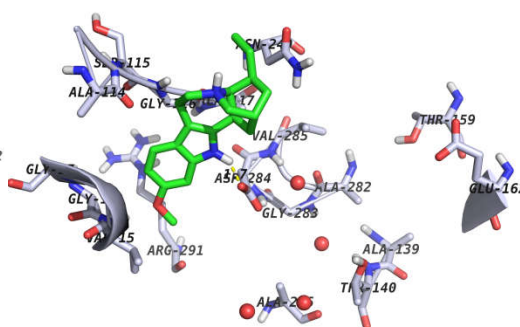


Figure S28: Chemical structure of auranofin.

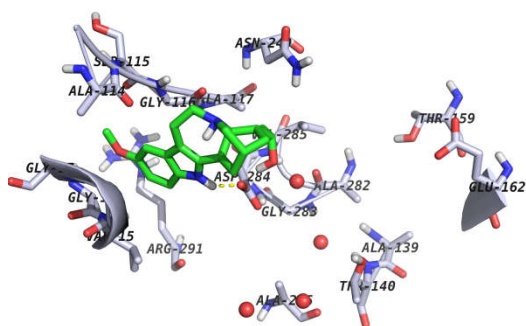
A



B



C



D

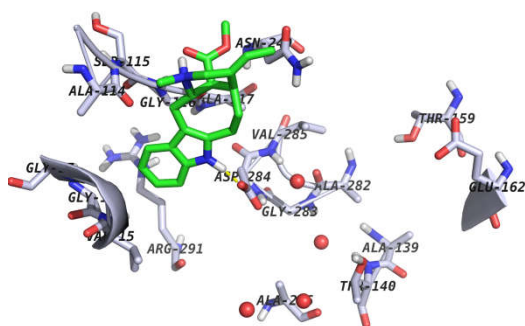
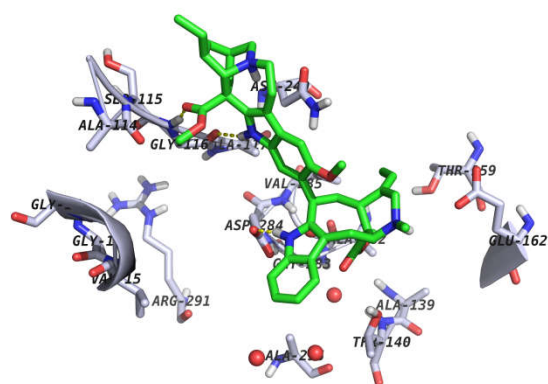
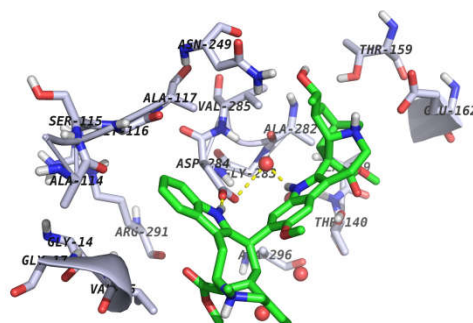


Figure S29: Docking poses of (A) compound 1a, (B) compound 5, (C) compound 6, (D) compound 7a.

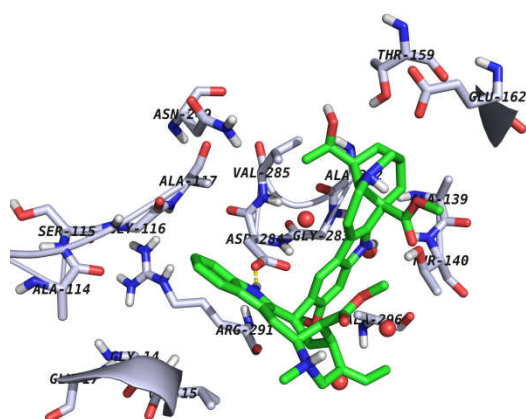
A



B



C



D

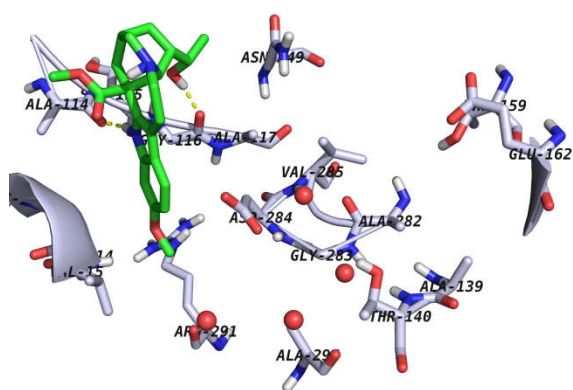


Figure S30: Docking poses of (A) compound 7, (B) compound 8, (C) compound 9, (D) compound 9b.