

Supplementary Material

A-Ring-Modified Triterpenoids and Their Spermidine–Aldimines with Strong Antibacterial Activity

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¹H NMR and ¹³C NMR data of compounds:

3-Deoxy-3a-homo-3a-aza -lup-20(29)-en-28-ol (1) ¹ H and ¹³ C NMR spectra (CDCl ₃)	3
3-Deoxy-3a-homo-3a-aza-19β,28-epoxy-18α-oleanane (2) ¹ H and ¹³ C NMR spectra (CDCl ₃)	4
3-Deoxy-3a-homo-3a-aza -lup-20(29)-en-28-methylenamine (5) ¹ H and ¹³ C NMR spectra (CDCl ₃)	5
3-Amino-3,4-seco-28-hydroxy-urs-12(13)-en (6) ¹ H and ¹³ C NMR spectra (CDCl ₃)	6
3-Oxo-lup-20(29)-en-28-N-(4-aminobutyl)-N-propylamin-28-imine (7) ¹ H and ¹³ C NMR spectra (CDCl ₃)	7
3-Deoxy-3a-homo-3a-aza-lup-20(29)-en-28-N-(4-aminobutyl)-N-propylamin-28-imine (8) ¹ H and ¹³ C NMR spectra (CDCl ₃)	8
3-Amino-3,4-seco-urs-12(13)-en-28-N-(3-aminopropyl)-N-(butane-1,4-diamine)-N-propylamin-28-imine (9) ¹ H and ¹³ C NMR spectra (CDCl ₃)	9
3-Oxo-urs-12(13)-en-28-N-(2-((2-aminoethyl)amino)ethyl)-2-ethylamide (10) ¹ H and ¹³ C NMR spectra (CDCl ₃)	10
3-Oxo-olean-12(13)-en-28-N-(2-((2-aminoethyl)amino)ethyl)-2-ethylamide (11) ¹ H and ¹³ C NMR spectra (CDCl ₃)	11
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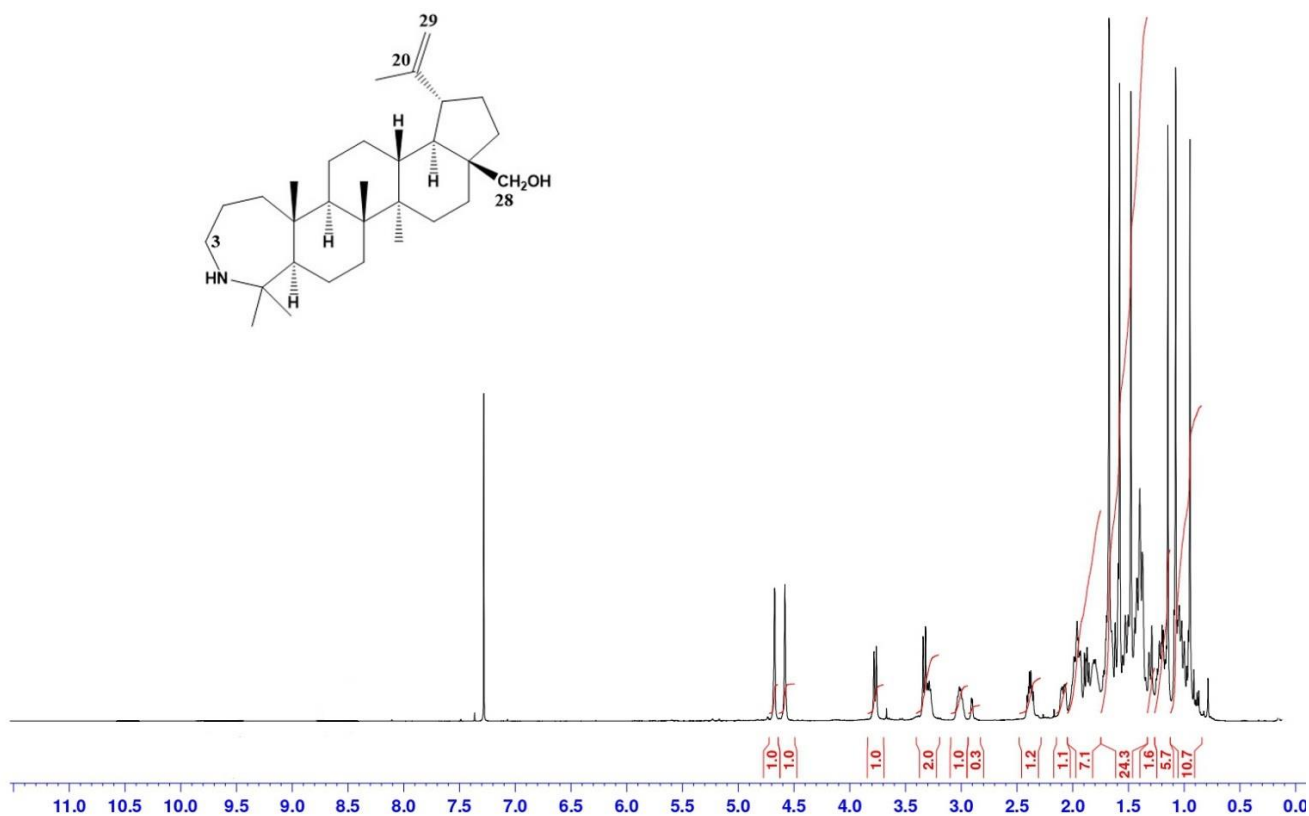


Figure S1. ^1H NMR spectrum of compound **1**

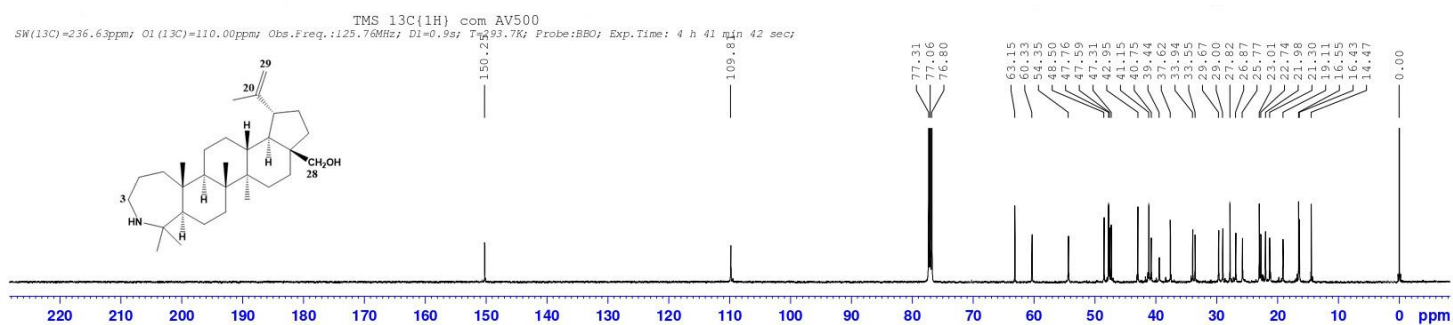


Figure S2. ^{13}C NMR spectrum of compound **1**

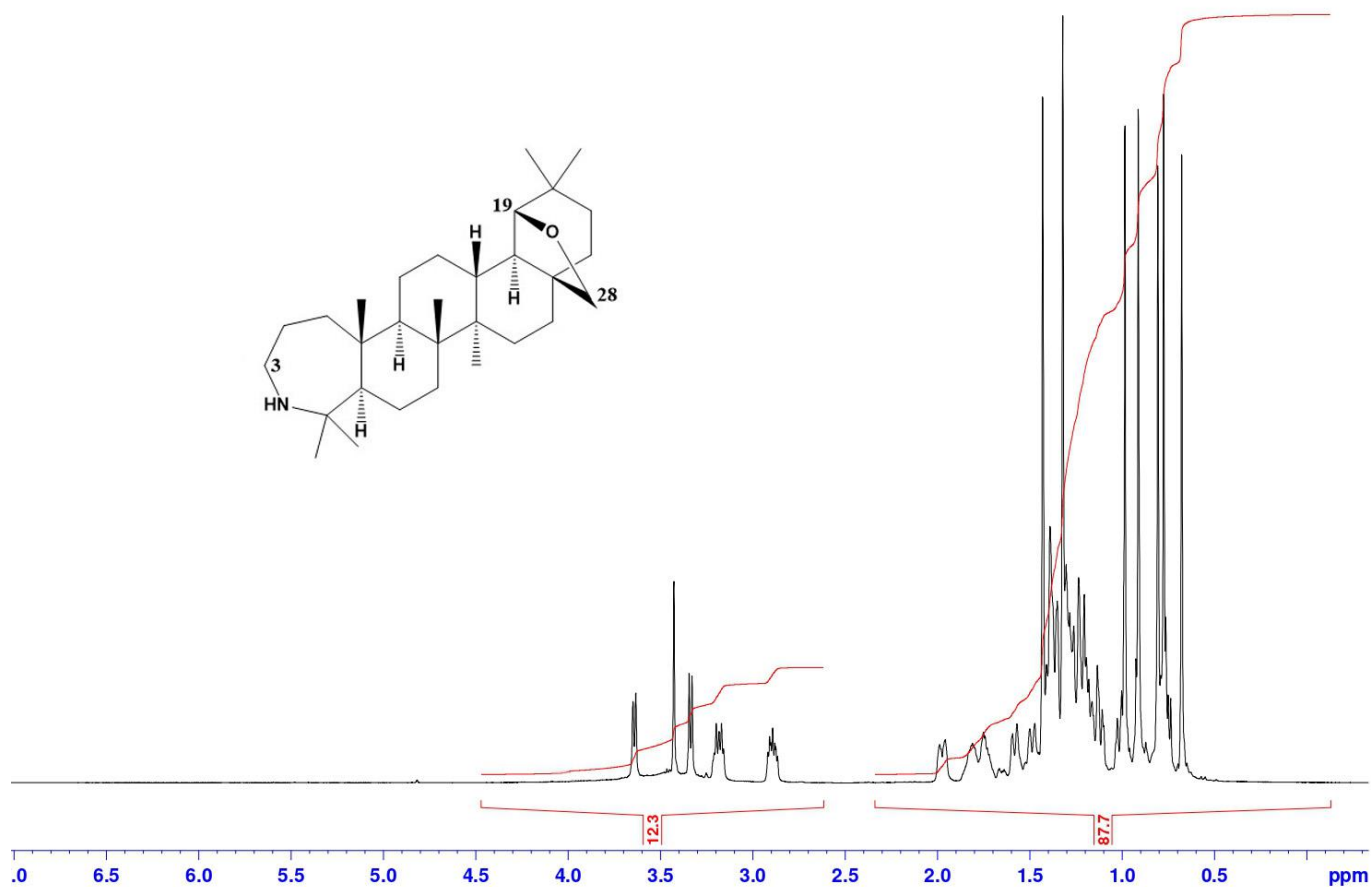


Figure S3. ^1H NMR spectrum of compound 2

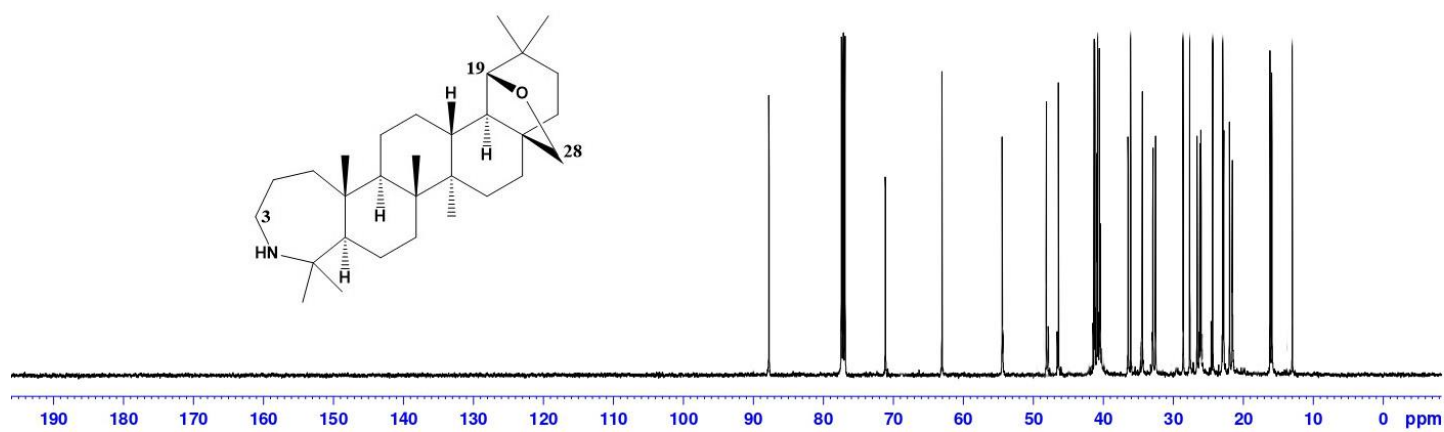


Figure S4. ^{13}C NMR spectrum of compound 2

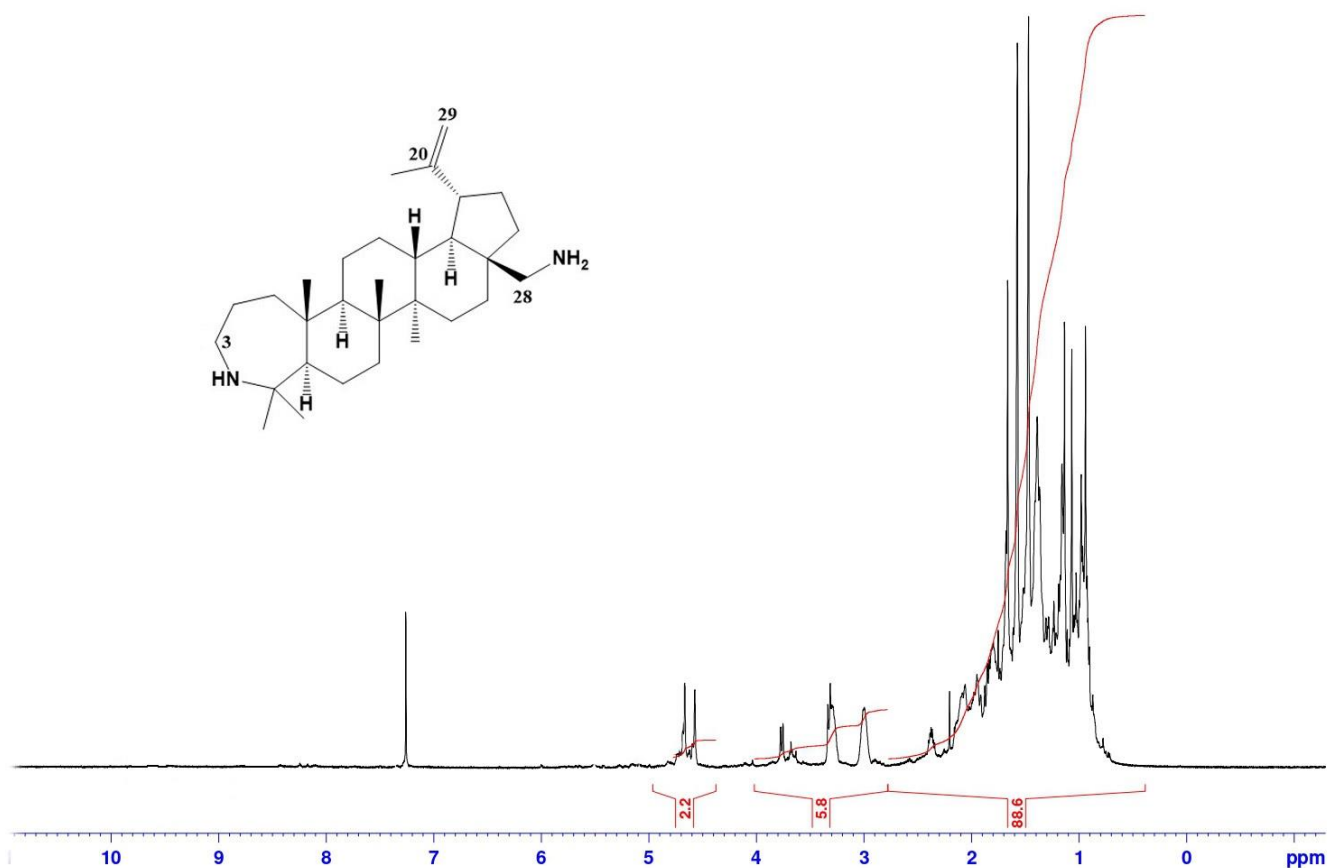


Figure S5. ^1H NMR spectrum of compound 5

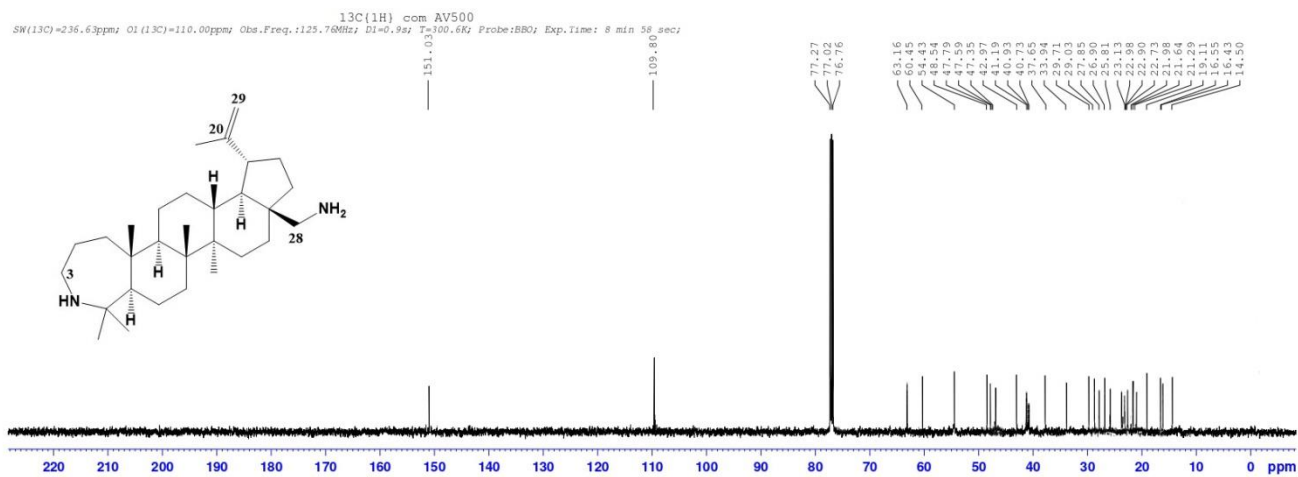


Figure S6. ^{13}C NMR spectrum of compound 5

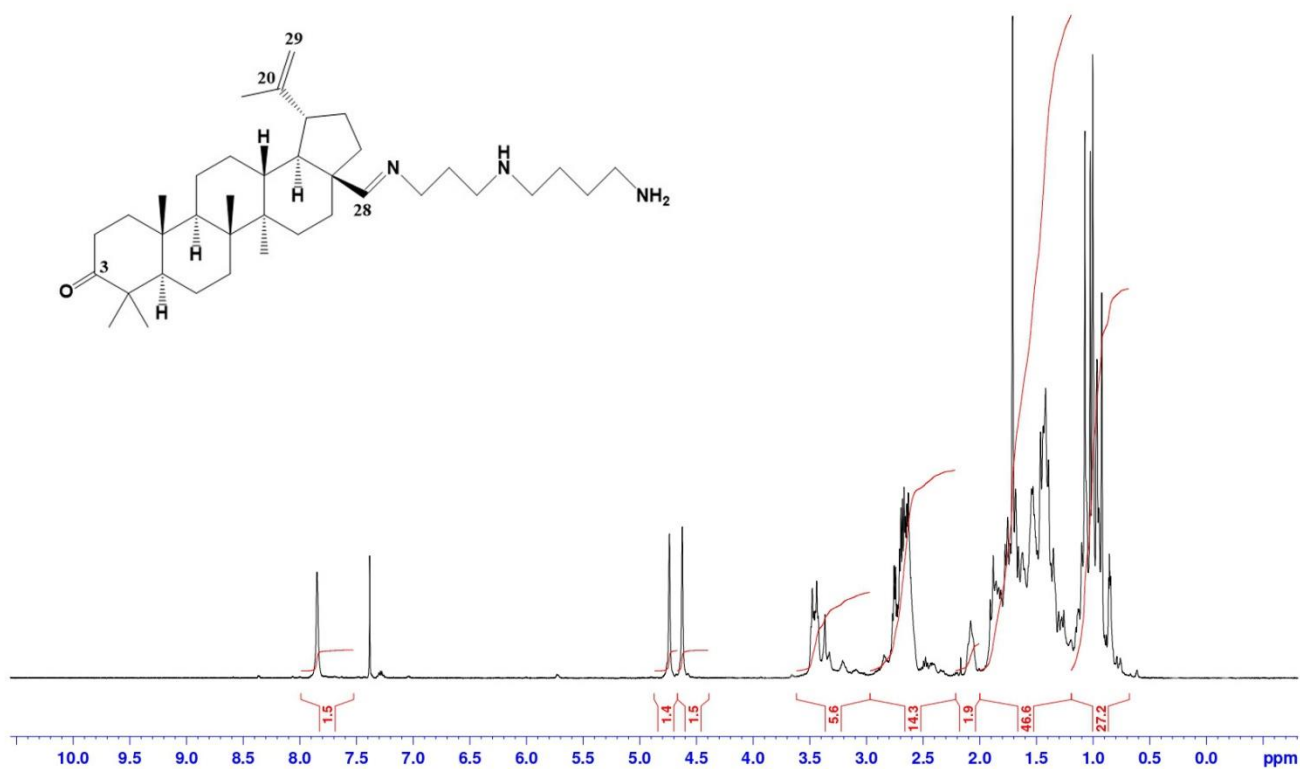


Figure S9. ^1H NMR spectrum of compound 7

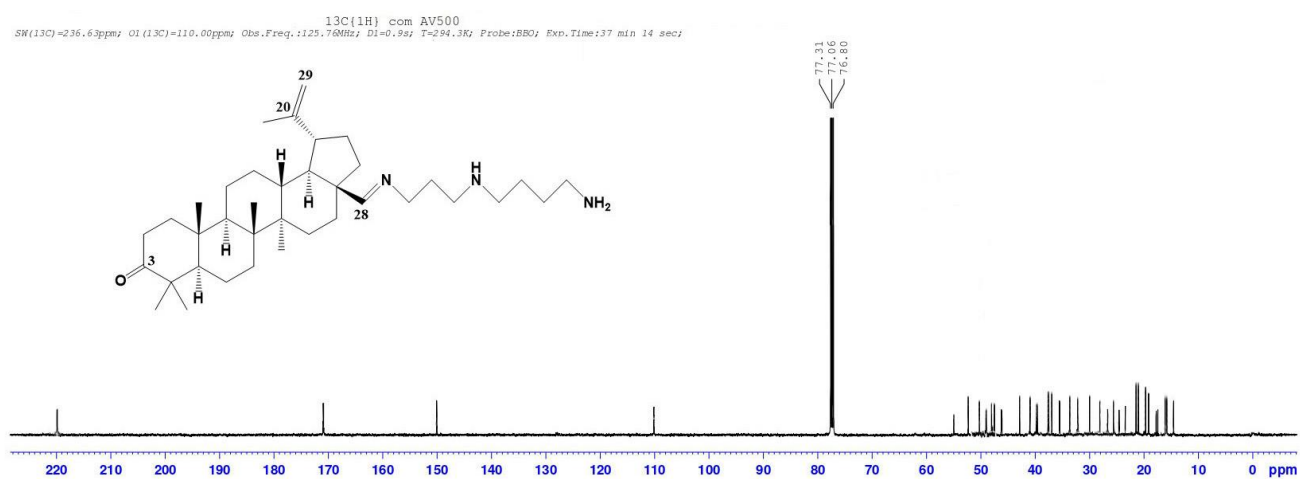


Figure S10. ^{13}C NMR spectrum of compound 7

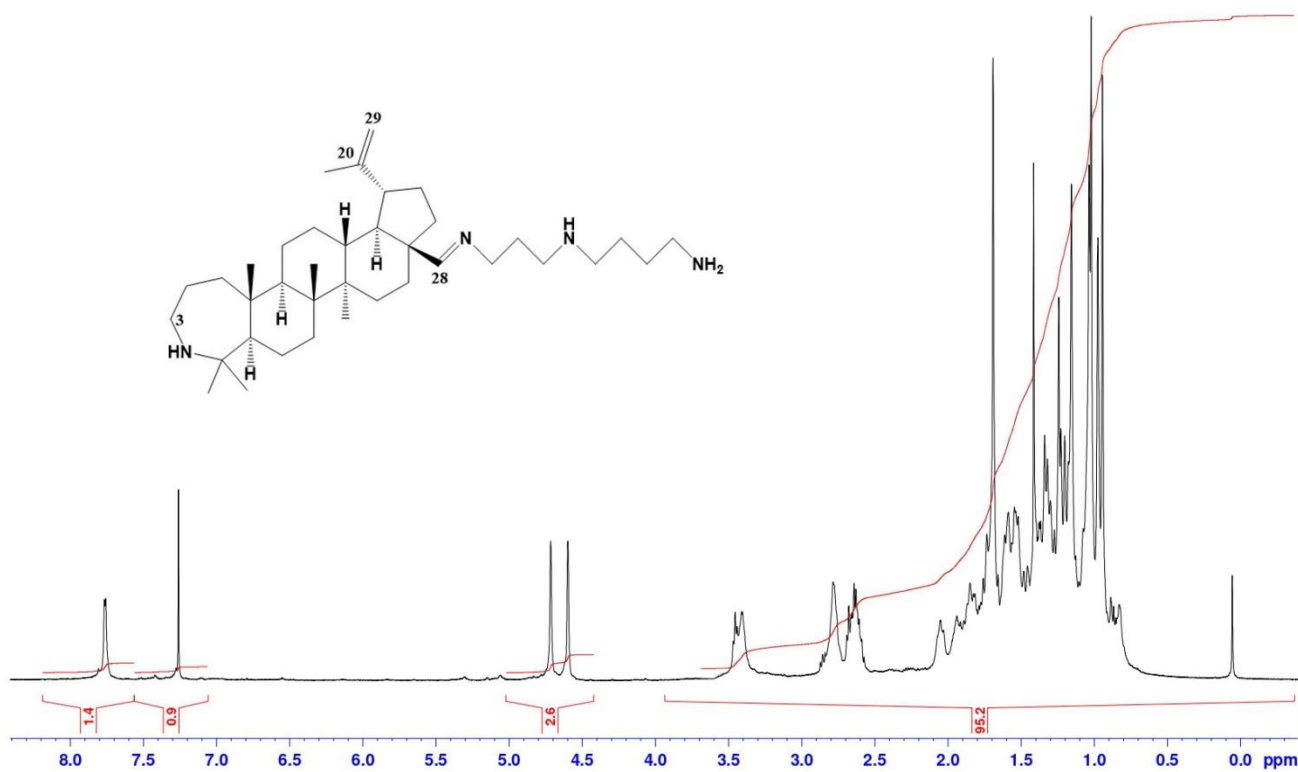


Figure S11. ^1H NMR spectrum of compound **8**

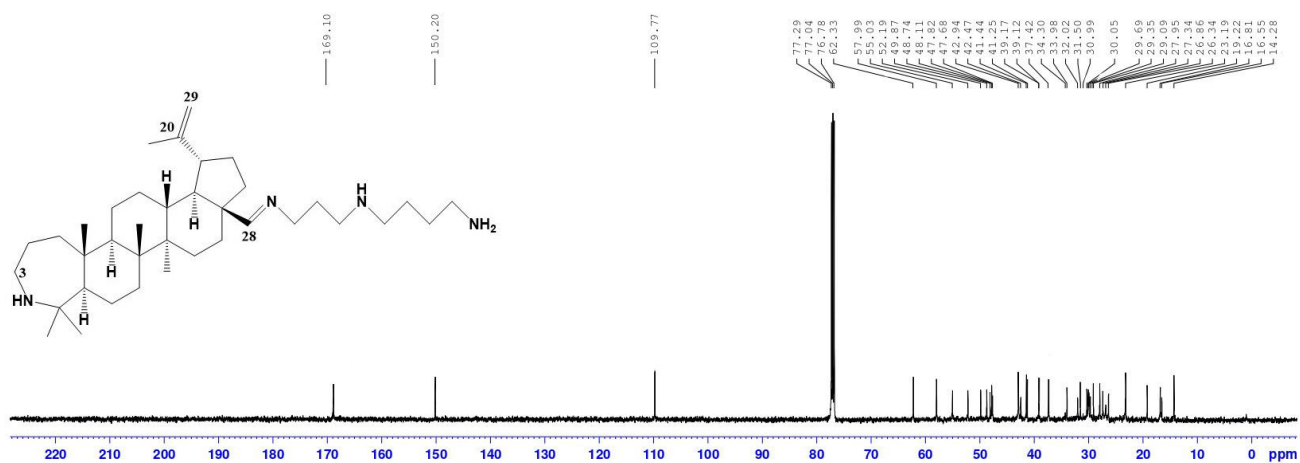


Figure S12. ^{13}C NMR spectrum of compound **8**

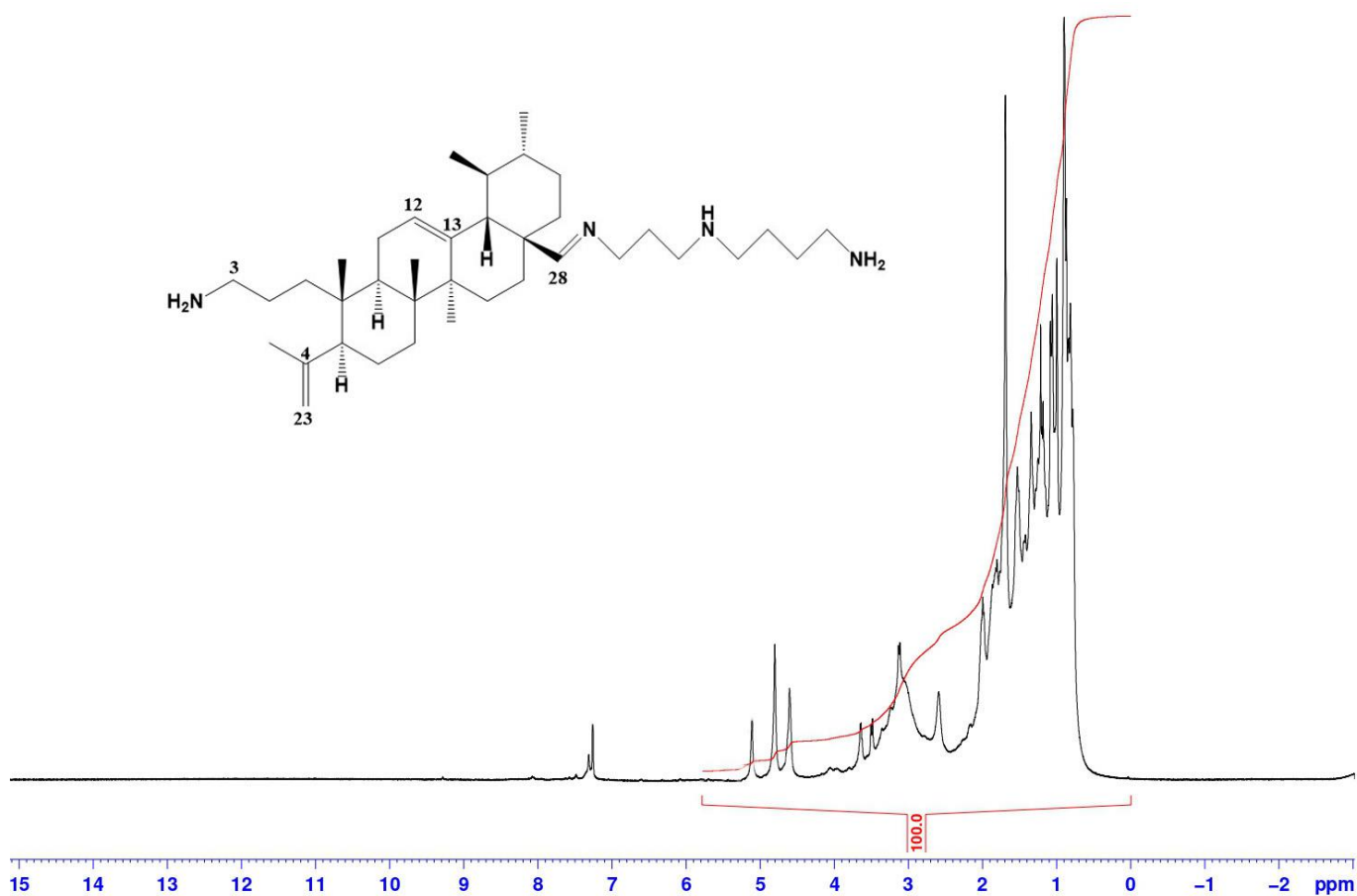


Figure S13. ^1H NMR spectrum of compound **9**

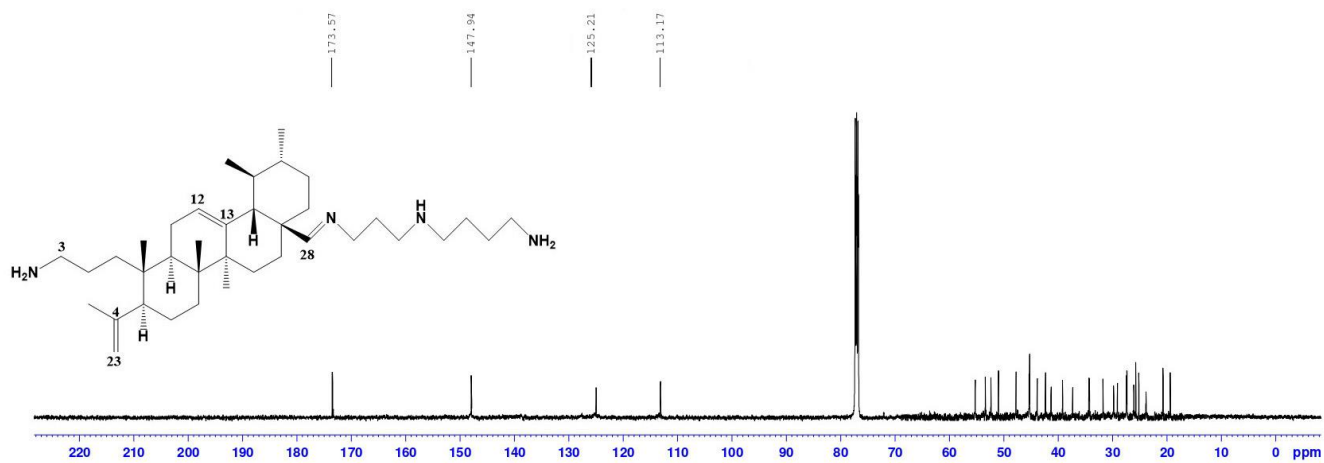


Figure S14. ^{13}C NMR spectrum of compound **9**

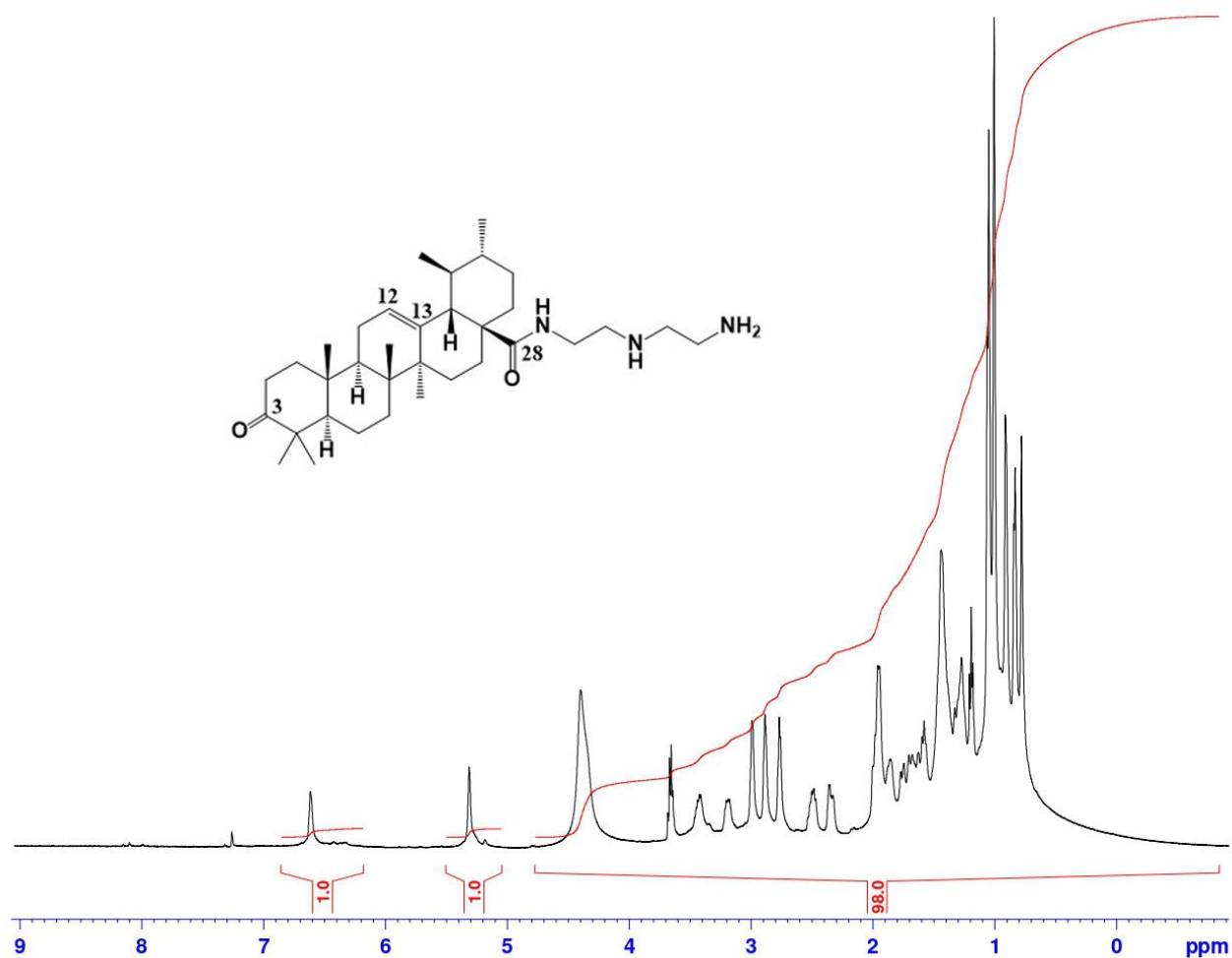


Figure S15. ¹H NMR spectrum of compound 10

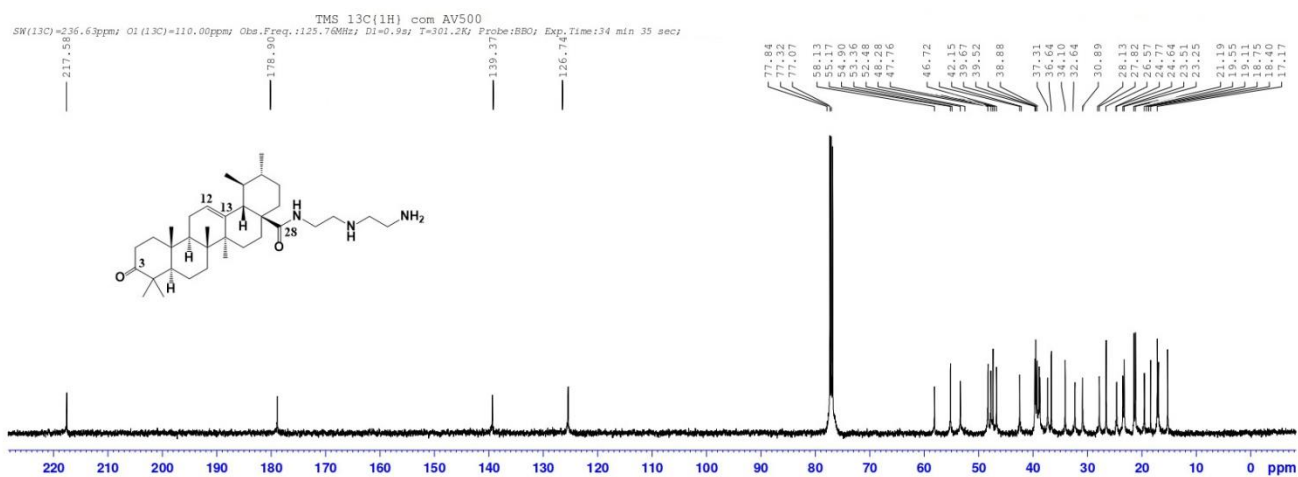


Figure S16. ¹³C NMR spectrum of compound 10

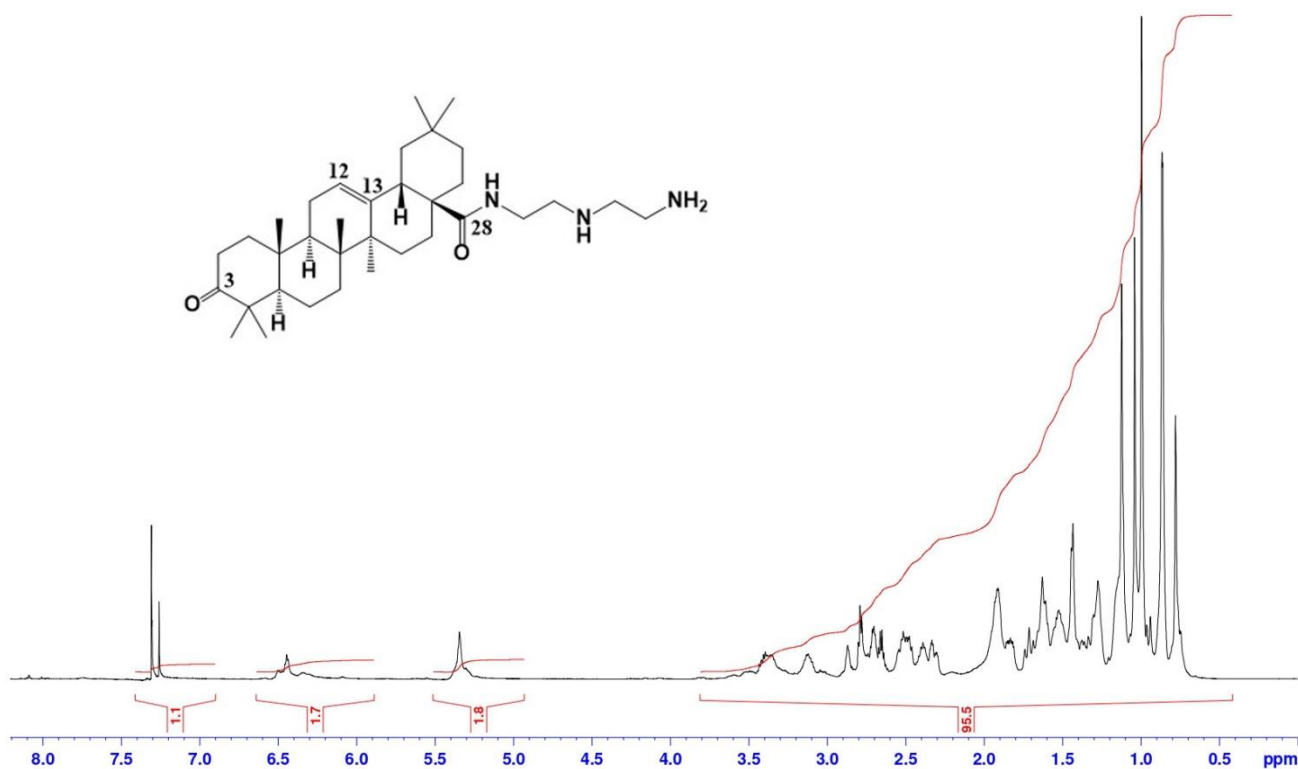


Figure S17. ¹H NMR spectrum of compound

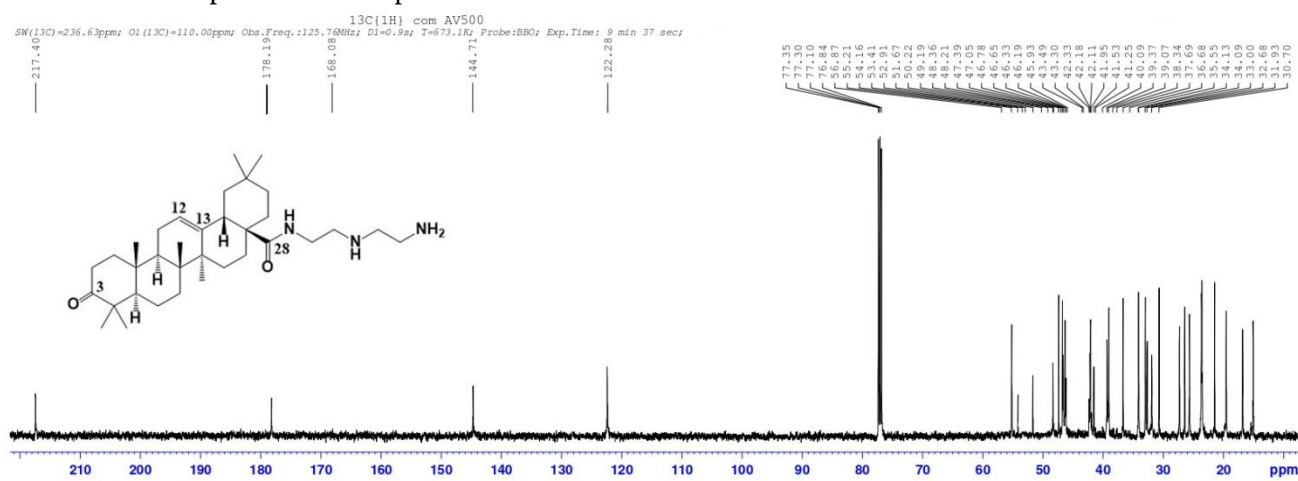
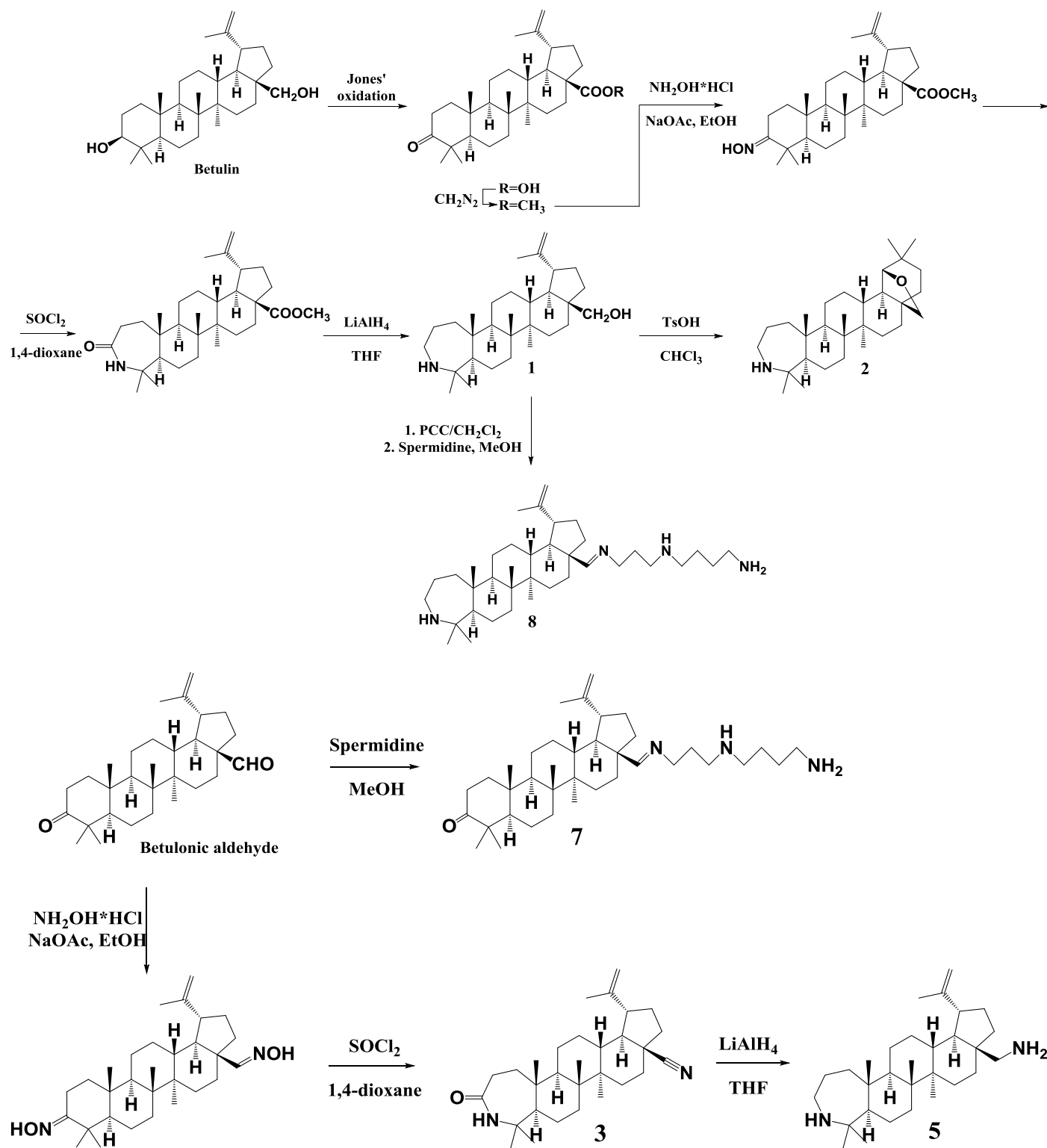
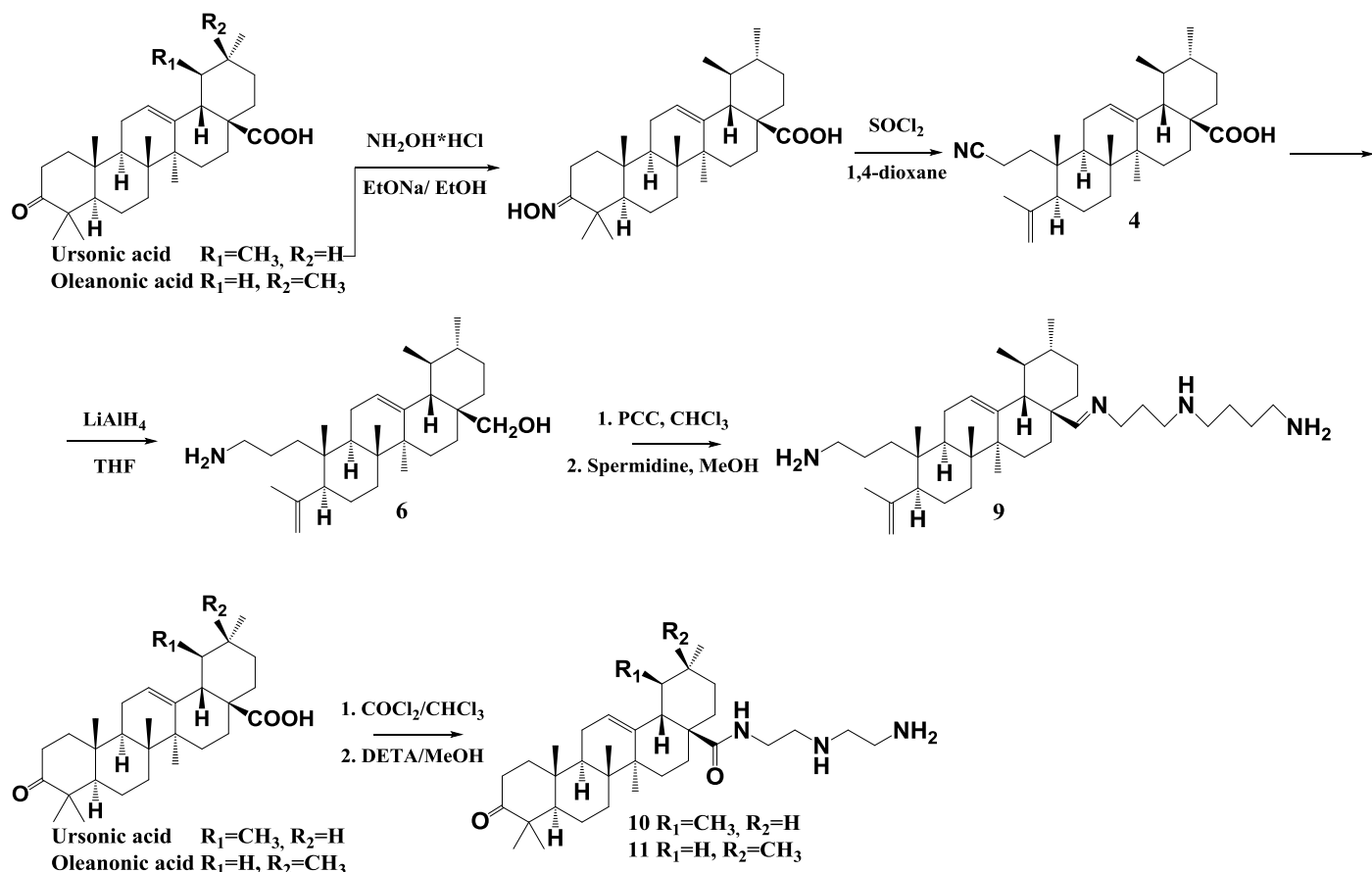


Figure S18. ¹³C NMR spectrum of compound 11



*The route to compound **1** is described in [1]; the route to compound **3** is described in [2]

Scheme S1. Full synthetic route from betulin to compounds **1**, **2** and **8*** and from betulonic aldehyde to compounds **3**, **5** and **7***



*The route from ursonic acid to compound 4 is described in [3]

Scheme S2. Full synthetic route from ursonic and oleanonic acids to compounds 4, 6 and 9–11*

References

1. Medvedeva, N.I.; Kazakova, O.B.; Lopatina, T.V.; Smirnova, I.E.; Giniyatullina, G.V.; Baikova, I.P.; Kataev, V.E. Synthesis and antimycobacterial activity of triterpenic A-ring azepanes. *Eur. J. Med. Chem.* **2018**, *143*, 464–472, doi:10.1016/j.ejmech.2017.11.035.
2. Khusnutdinova, E.F.; Petrova, A.V.; Nguyen, Thi Thu Ha; Le, Thi Tu Anh; Nguyen, Thanh Tra; Ba, Thi Cham; Babkov, D.A.; Kazakova, O.B. Structural modifications of 2,3-indolobetulinic acid: Design and synthesis of highly potent α -glucosidase inhibitors. *Bioorg. Chem.* **2019**, *88*, article 102957, doi:10.1016/j.bioorg.2019.102957.
3. Dalla-Vechia, L.; Dassonville-Klimpt, A.; Grellier, P.; Sonnet, P.; Gosmann G.; Gnoatto, S.C.B. The Beckmann rearrangement applied to ursolic acid with antimalarial activity in medicinal chemistry studies. *Lett. Org. Chem.* **2012**, *9*, 92–95, doi:10.1002/chin.201228213.