Supplementary Material

Sesquiterpene lactones with the 12,8- guaianolide skeleton from Algerian *Centaurea omphalotricha*

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A portion (3.3 g) of the $CHCl_3$ extract of *C. omphalotricha* was first fractionated by SiO_2-gel column chromatography by eluting with a gradient of CH_2Cl_2 in petroleum ether (PE), and subsequently with a gradient of acetone in CH_2Cl_2 to obtain 43 fractions (C1-C43). Nine selected fractions (C13, C16, C19, C-24, C27, C29, C30, C34, C37) were taken into consideration after TLC chromatography analysis and preliminary ^{1}H-NMR inspection. Fraction C13 (13.0 mg) was loaded onto a semipreparative TLC and developed with $CHCl_3$/Acetone, 8:2 to yield a UV band at R*f* 0.5 corresponding to vanillin [1,2]. A portion (50 mg) of fraction C16 (86 mg) was loaded onto a $AgNO_3$ silicagel column using as eluent petroleum ether and increasing amount of Et_2O. Subfractions eluted with petroleum ether/Et_2O 6:4 and 1:1 contained 2 mg of pure α-costic acid. A small part (20 mg) of fraction C19 (65.5 mg) was purified by semipreparative TLC with petroleum ether/Et_2O 1:1 to yield methyl-4-hydroxy benzoate (2.0 mg) [3,4]. A portion of C24 (32.3 mg) was also purified by semipreparative TLC in *n*-hexane/AcOEt 1:1 to give two UV compounds, tomentosin (2.0 mg) at R*f* 0.6 and 1β,5β-epoxyxanthatin at R*f* 0.5. Fraction C27 (94.8 mg) was purified by silicagel column using as eluent system petroleum ether with increasing amount of Et2O to give 12 subfractions. Subfraction C27-7 (27.7 mg) eluted with petroleum ether/Et_2O 4:6 contained scopoletin (5.0 mg) [5,6] that was further purified by recrystallization in MeOH. Fraction C29 (200 mg) was loaded onto a silicagel column packed in PE and eluted initially with an increasing gradient of Et_2O in PE (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10), then with $CHCl_3$, and finally with MeOH affording 13 subfractions C29-1 – C29-13. (for the new compounds see main text). Subfraction C29-6 (12.0 mg) was loaded onto a semipreparative TLC in petroleum ether/Et_2O 1:1 showing a UV band at Rf 0.45 that was identified as 3,5,11(13)-trien-eudesma-12-oic acid. Subfraction C29-10 (10.2 mg) was purified by semipreparative TLC ($CHCl_3$/MeOH, 9.5:0.5) to give 2.7 mg of 11β,13-dehydromelitensin. A portion (10.0 mg) of fraction C30 (54.4 mg) was purified by semipreparative TLC ($CHCl_3$/Et_2O, 1:1) to obtain 1.0 mg of cirsimaritin [7,8]. Half portion (130 mg) of fraction C34 (260.0 mg) was purified by silicagel column in a gradient of Et2O in petroleum ether to give 11 subfraction C34-1-C34-11. Subfraction C34-7 (20.0 mg) was further purified on a 10% $AgNO_3$ silicagel pipette Pasteur using a gradient of petroleum ether in $CHCl_3$ to yield 5.3 mg of viscic acid. A portion (150.0 mg) of fraction C37 (203.0 mg) was fractionated by silicagel column using first a gradient of Et_2O in petroleum ether, then CHCl3 and MeOH to give 15 subfractions. Subfraction C37-7 (28.7 mg) was recrystallized in MeOH to get 5.0 mg of ilicic acid.

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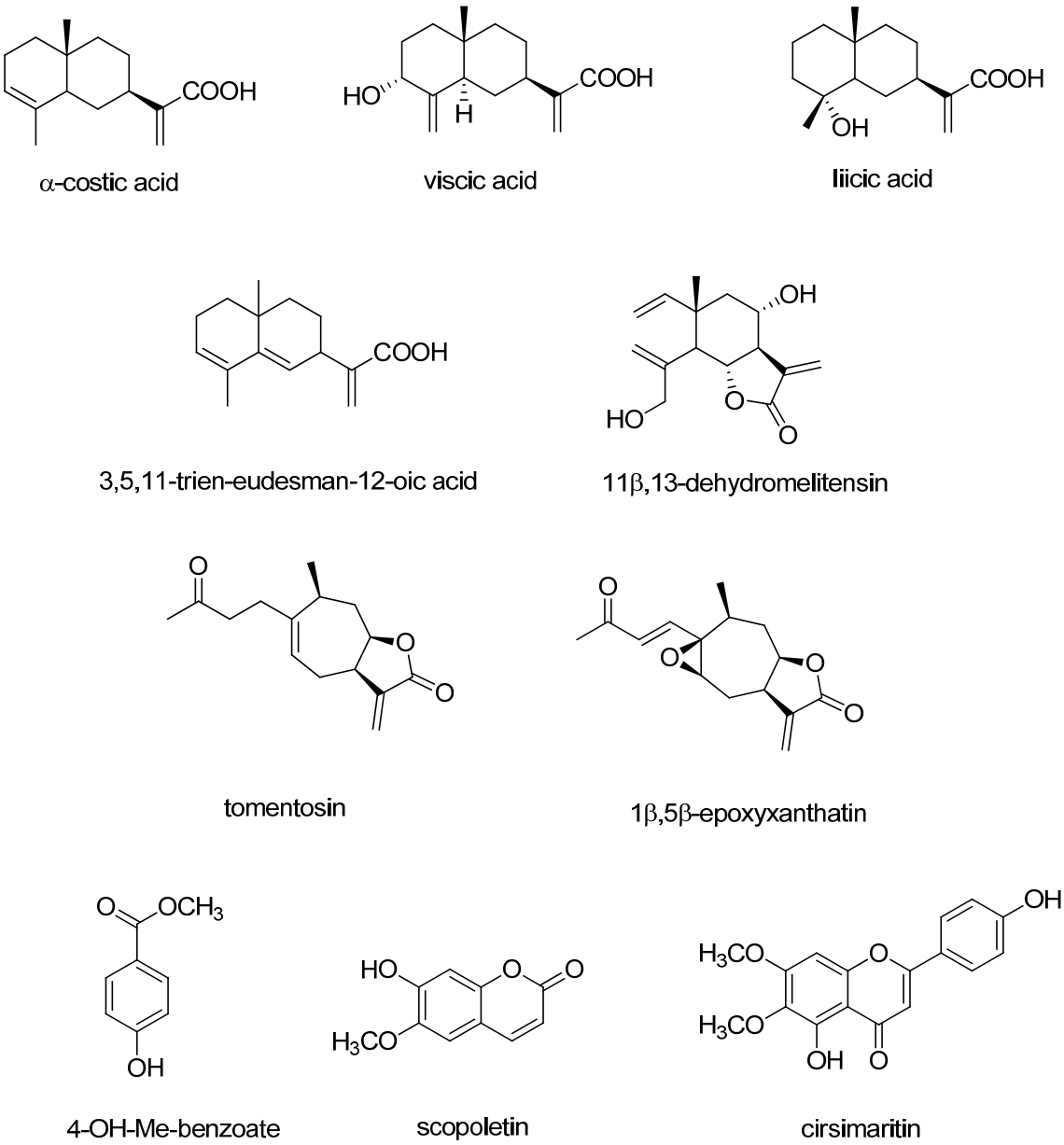
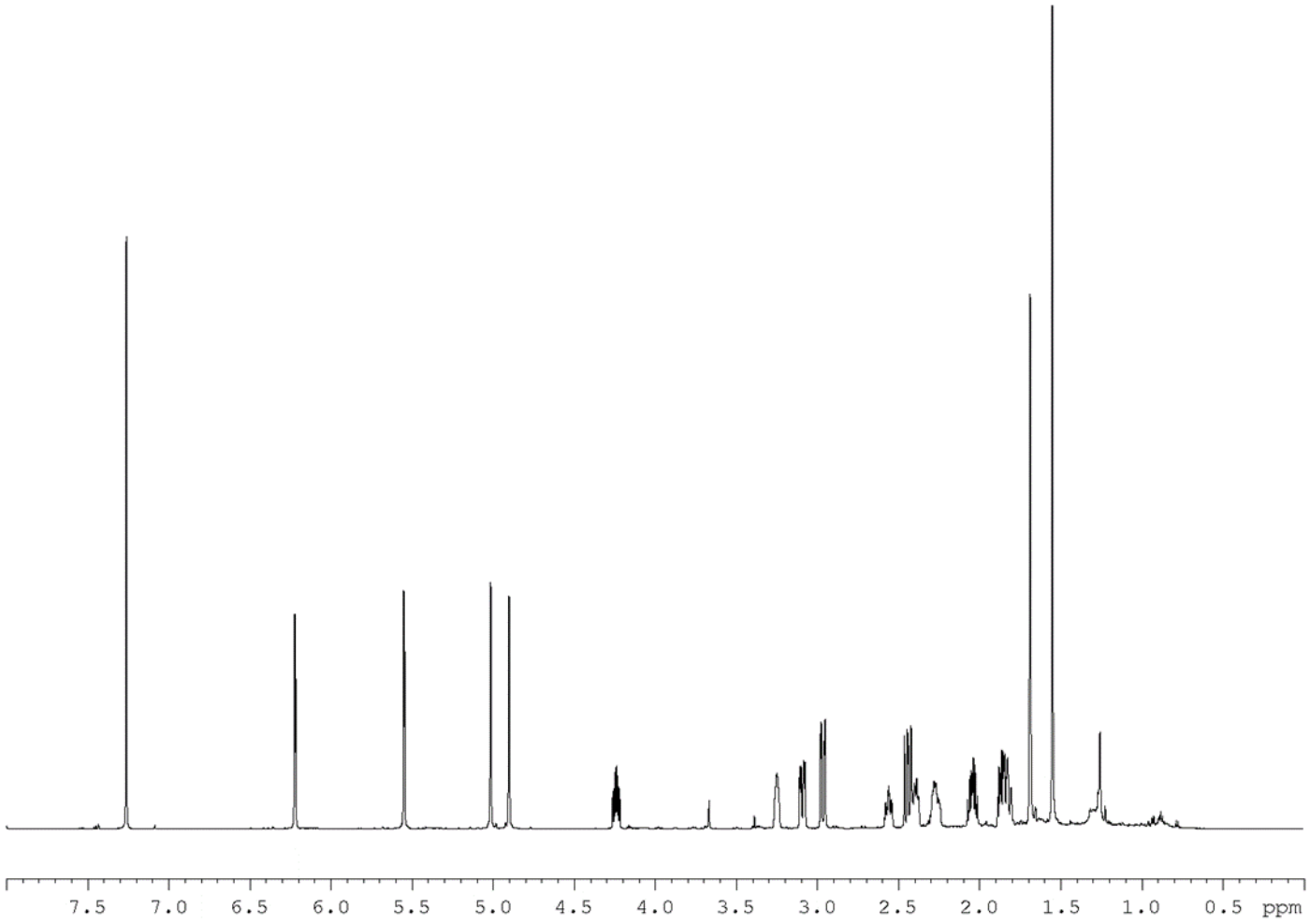
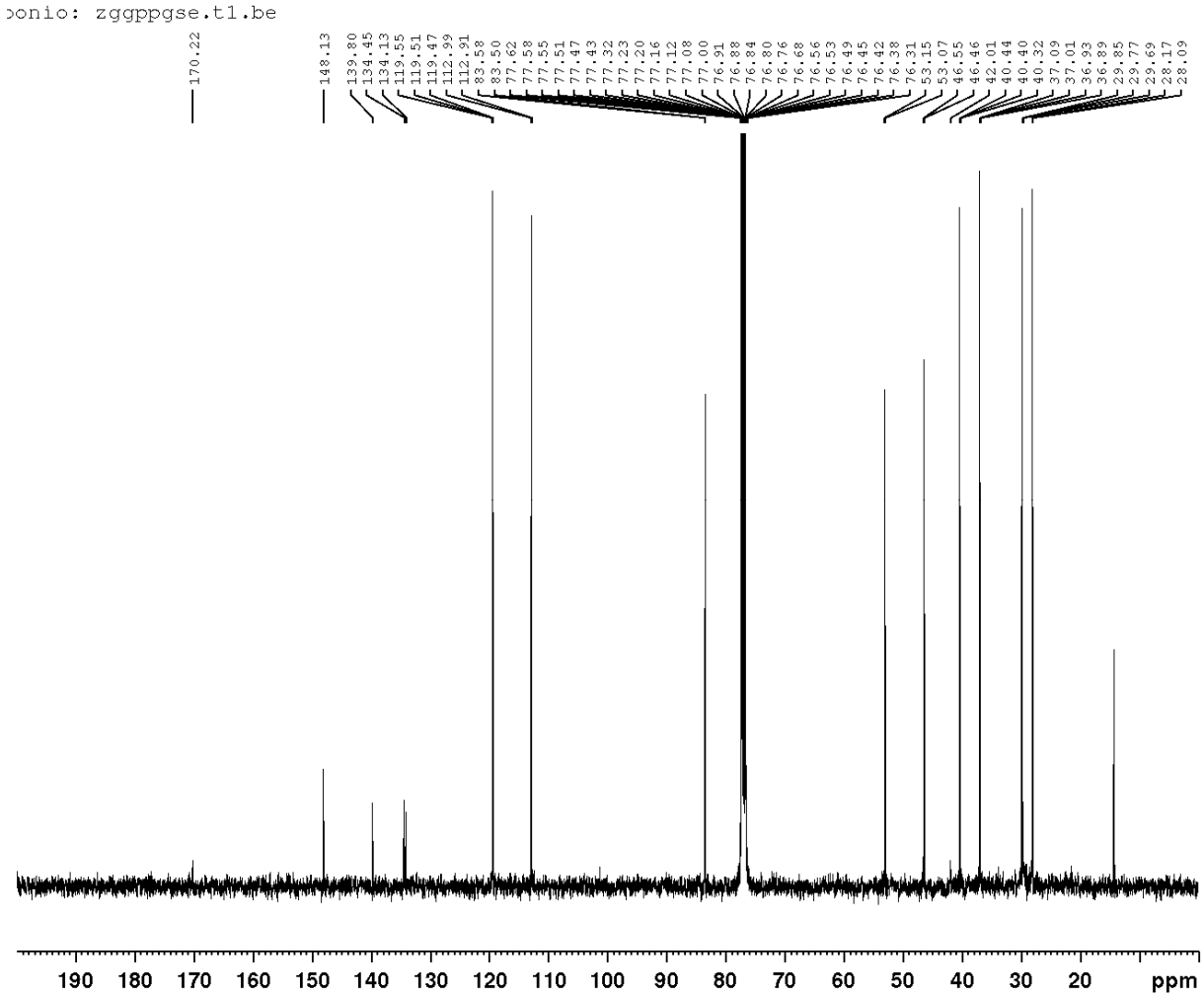


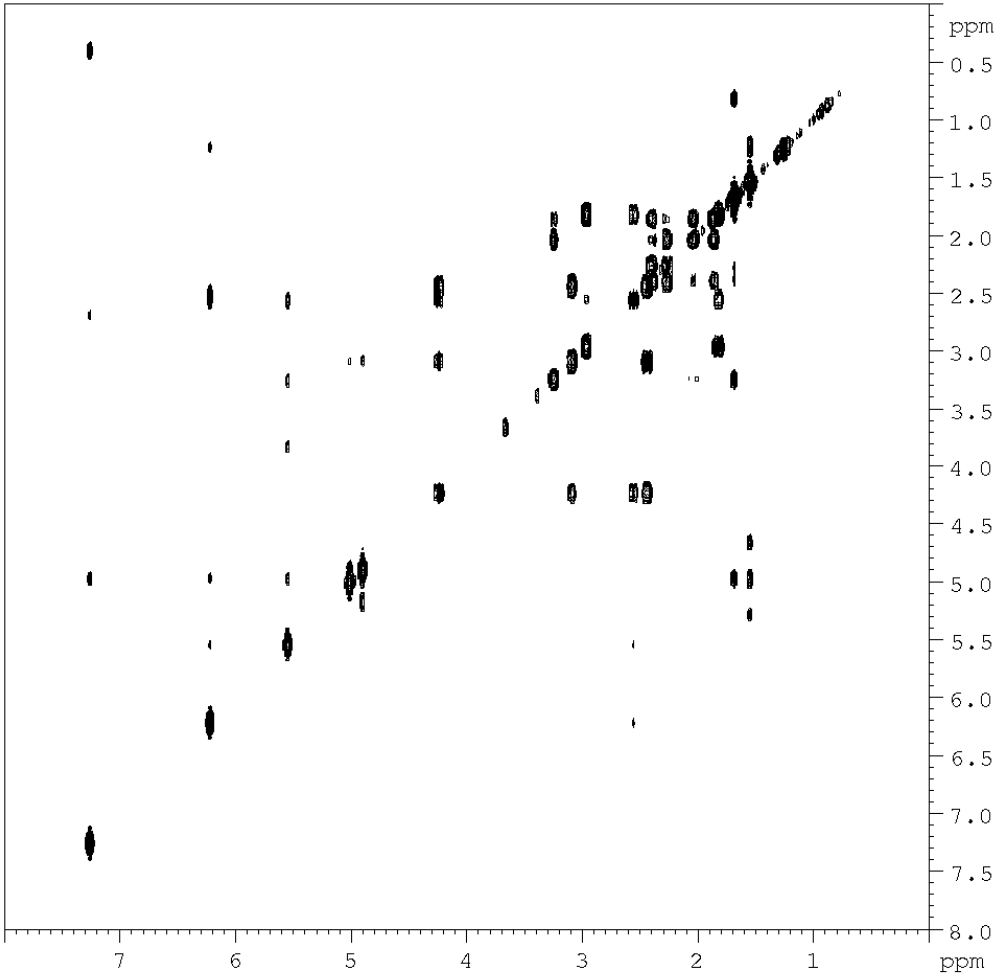
S2. Chemical structures of known compounds isolated from *C.omphalotricha*



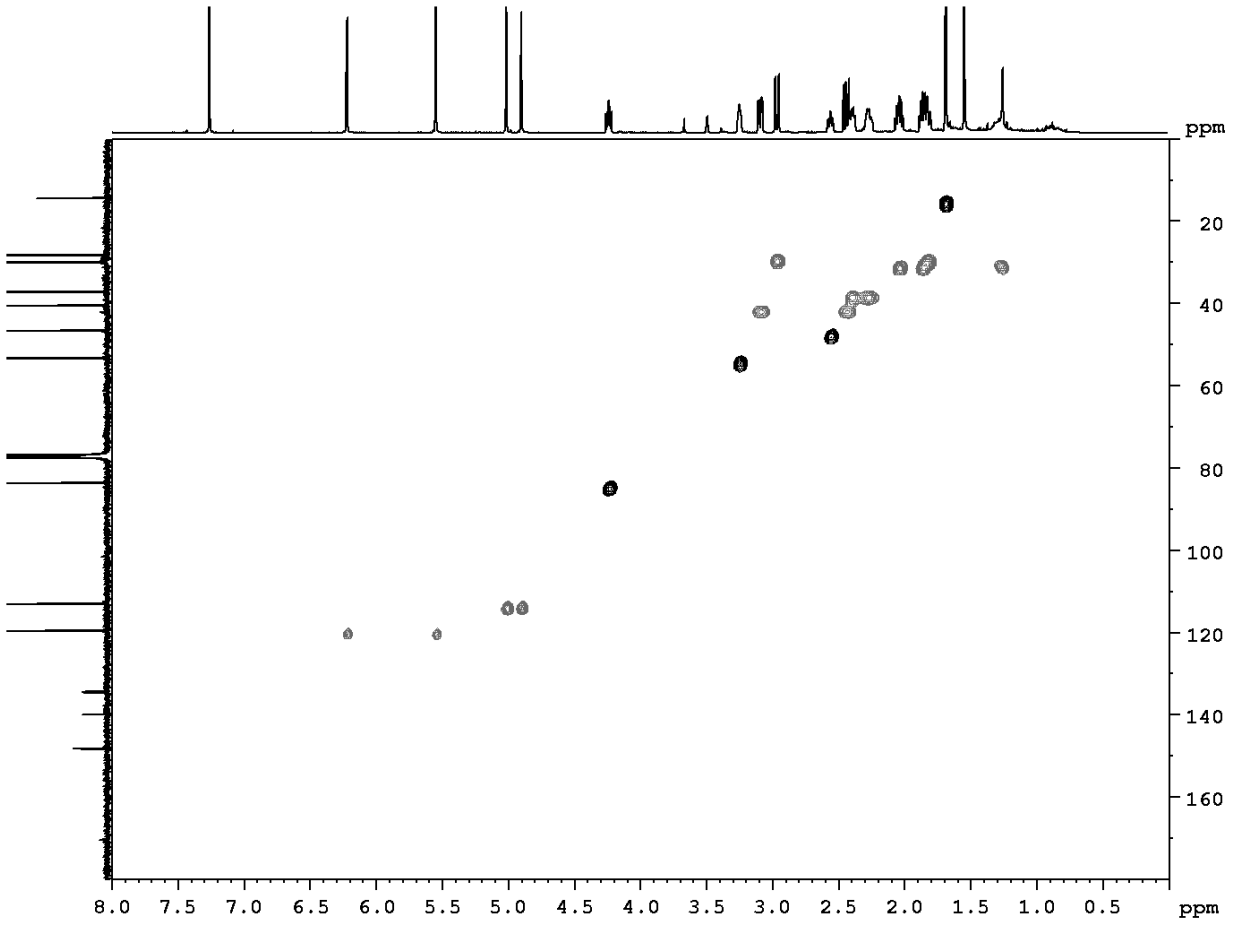
S3. ^{1}H NMR spectrum of centaurolide A (**1**) (600 MHz, $CDCl_3$)



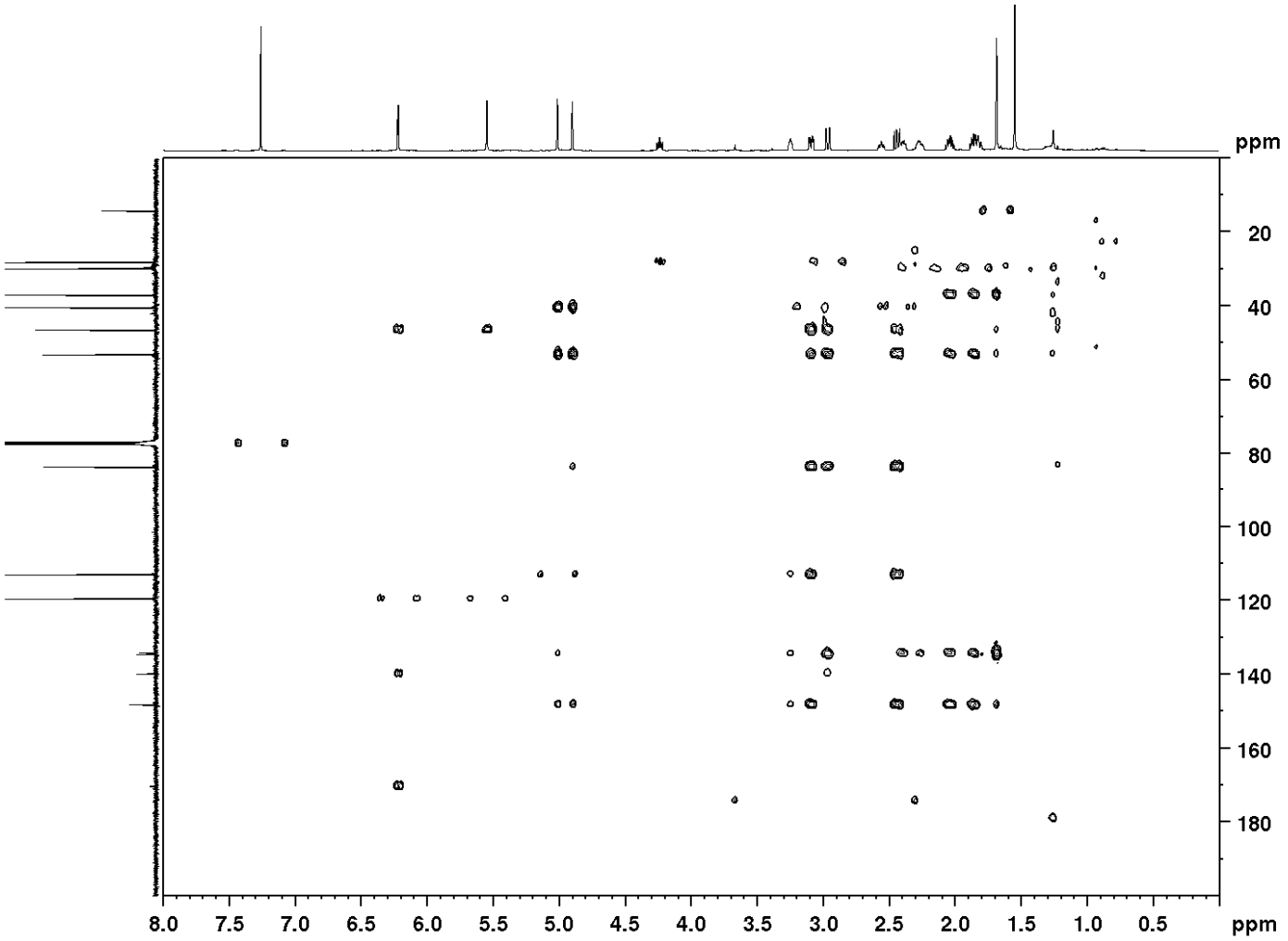
S4. ^{13}C NMR spectrum of centaurolide A (**1**) (100 MHz, $CDCl_3$)



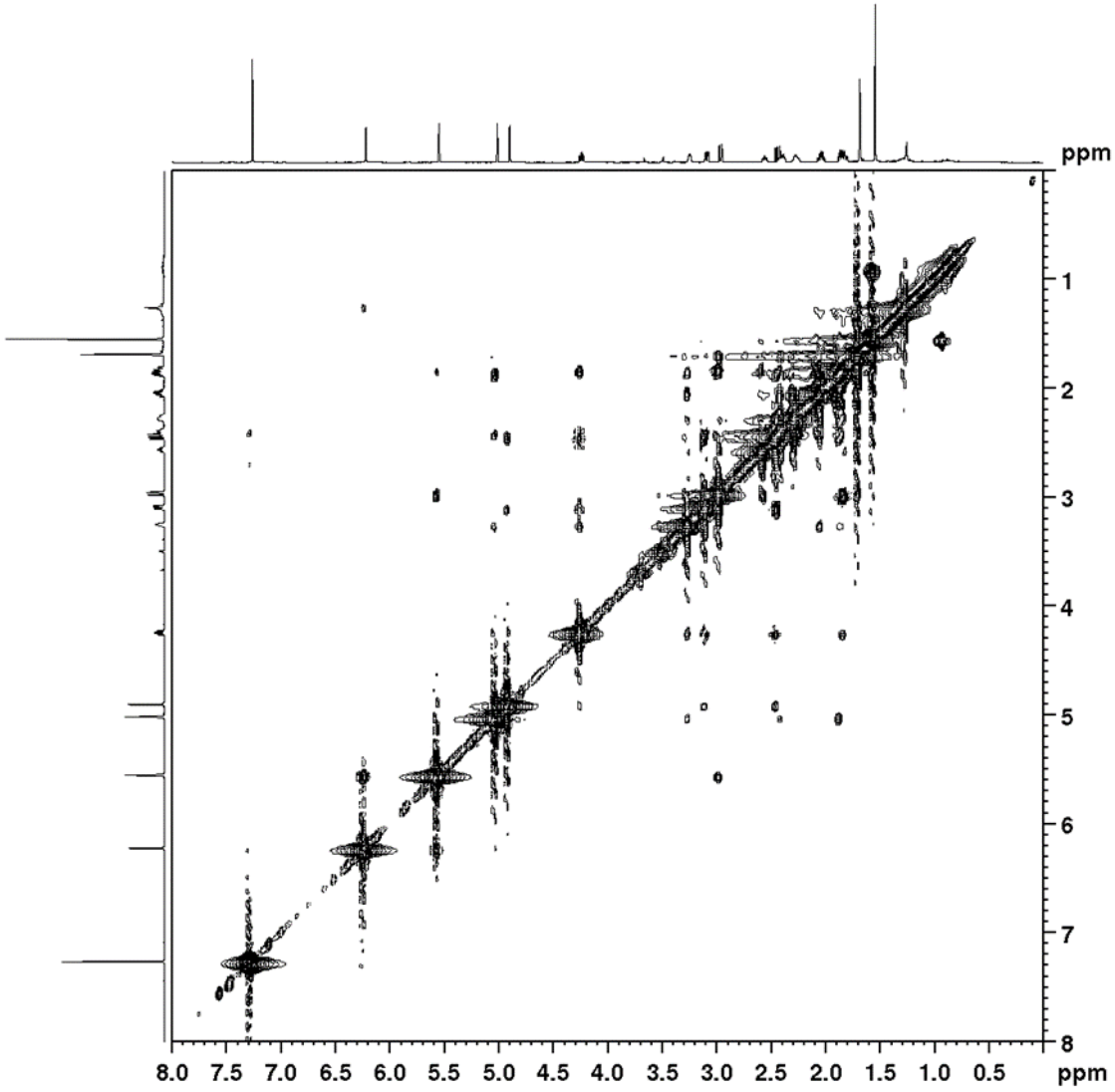
S5. COSY spectrum of centaurolide A (**1**) (600 MHz, $CDCl_3$)



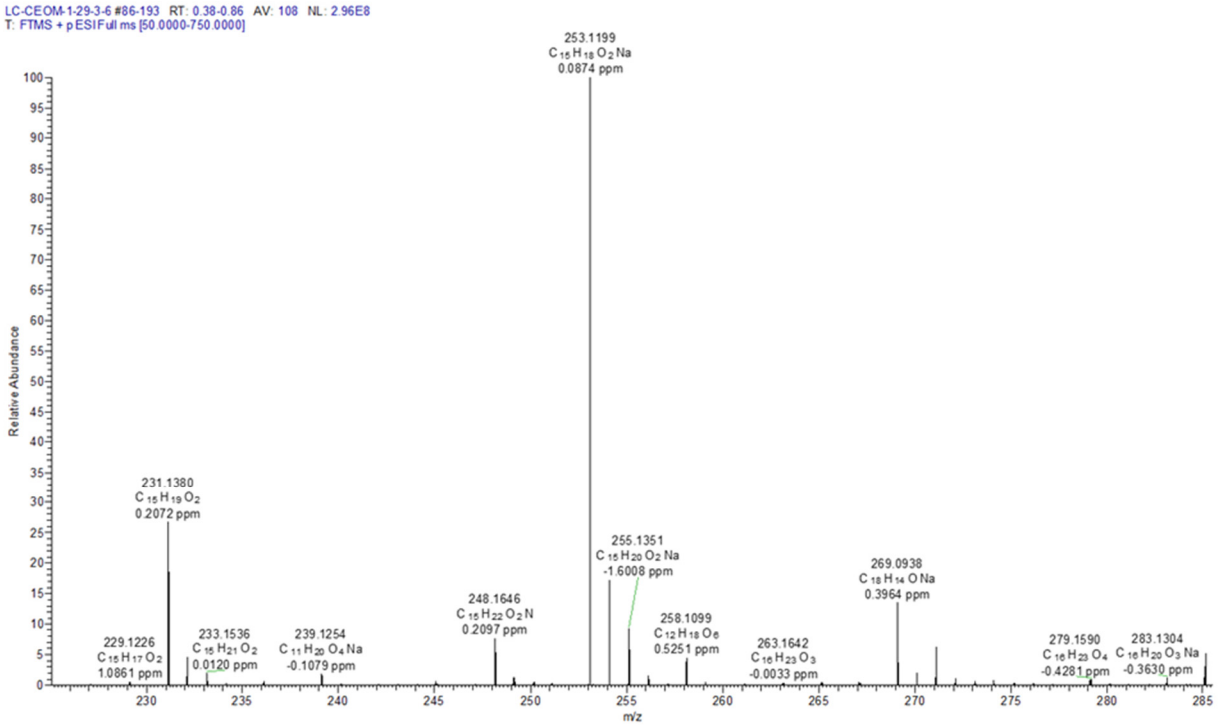
S6. ed-HSQC spectrum of centaurolide A (**1**) (600 MHz, $CDCl_3$)



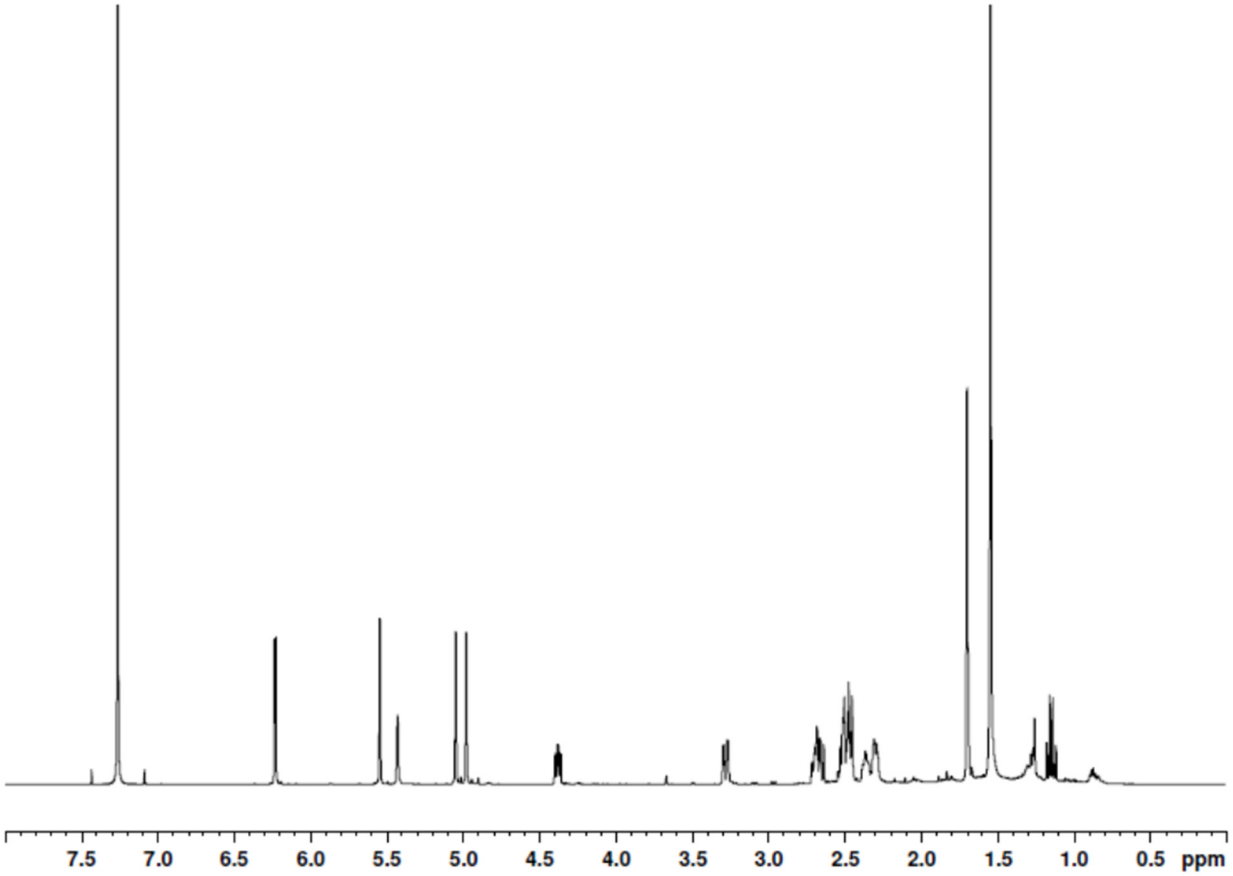
S7. HMBC spectrum of centaurolide A (**1**) (600 MHz, $CDCl_3$)



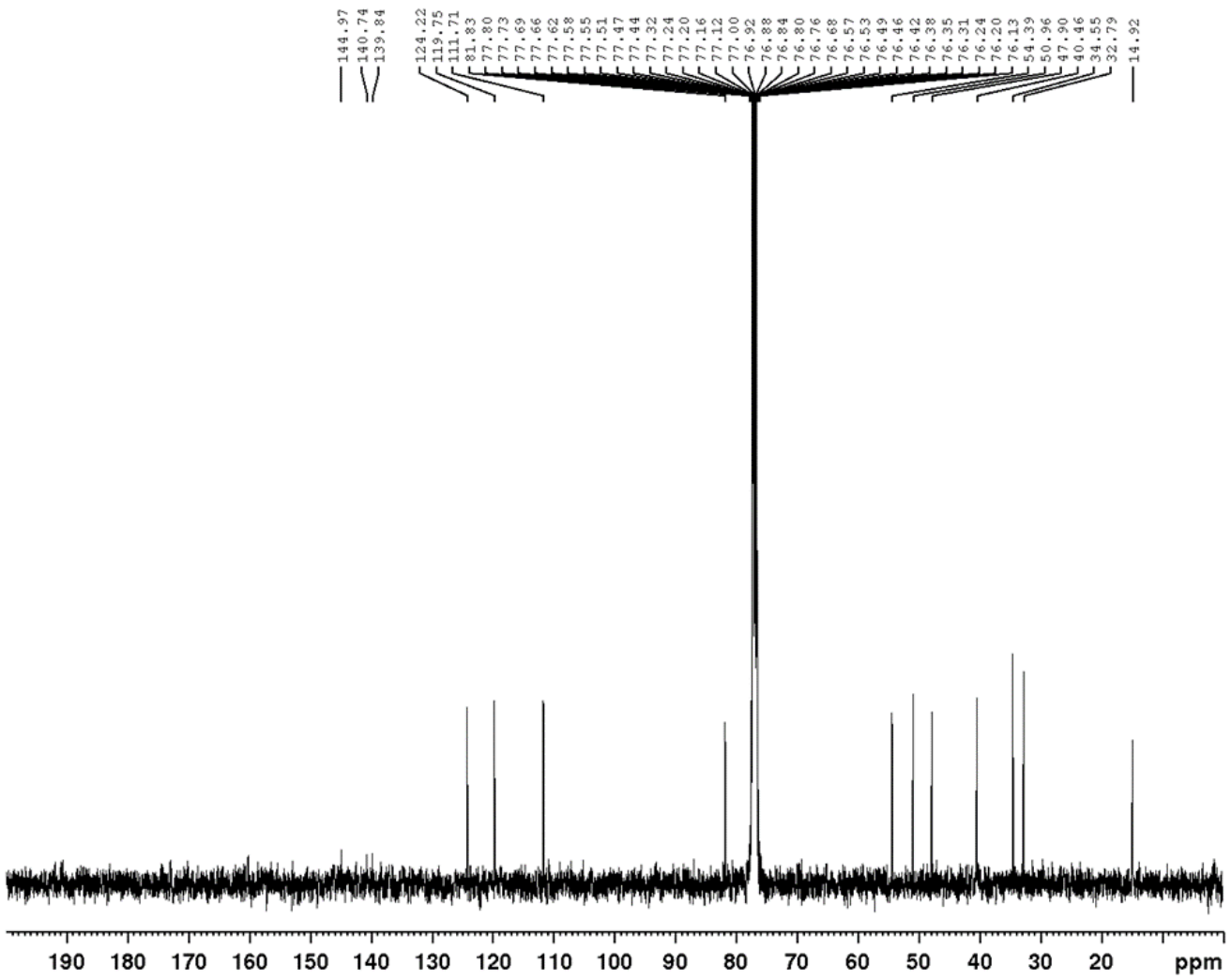
S8. NOESY spectrum of centaurolide A (**1**) (600 MHz, CDCl3.



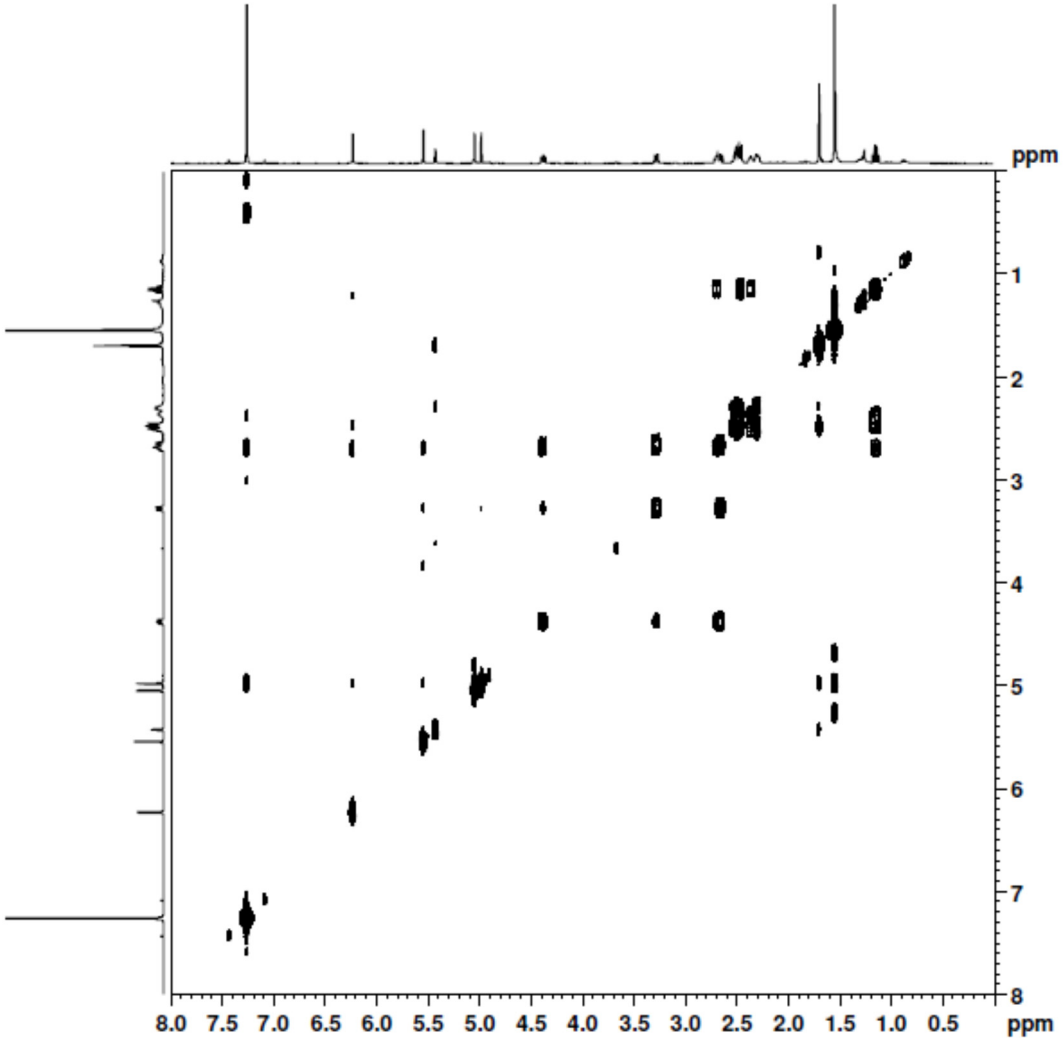
S9. HR ESIMS spectrum of centaurolide A (**1**)



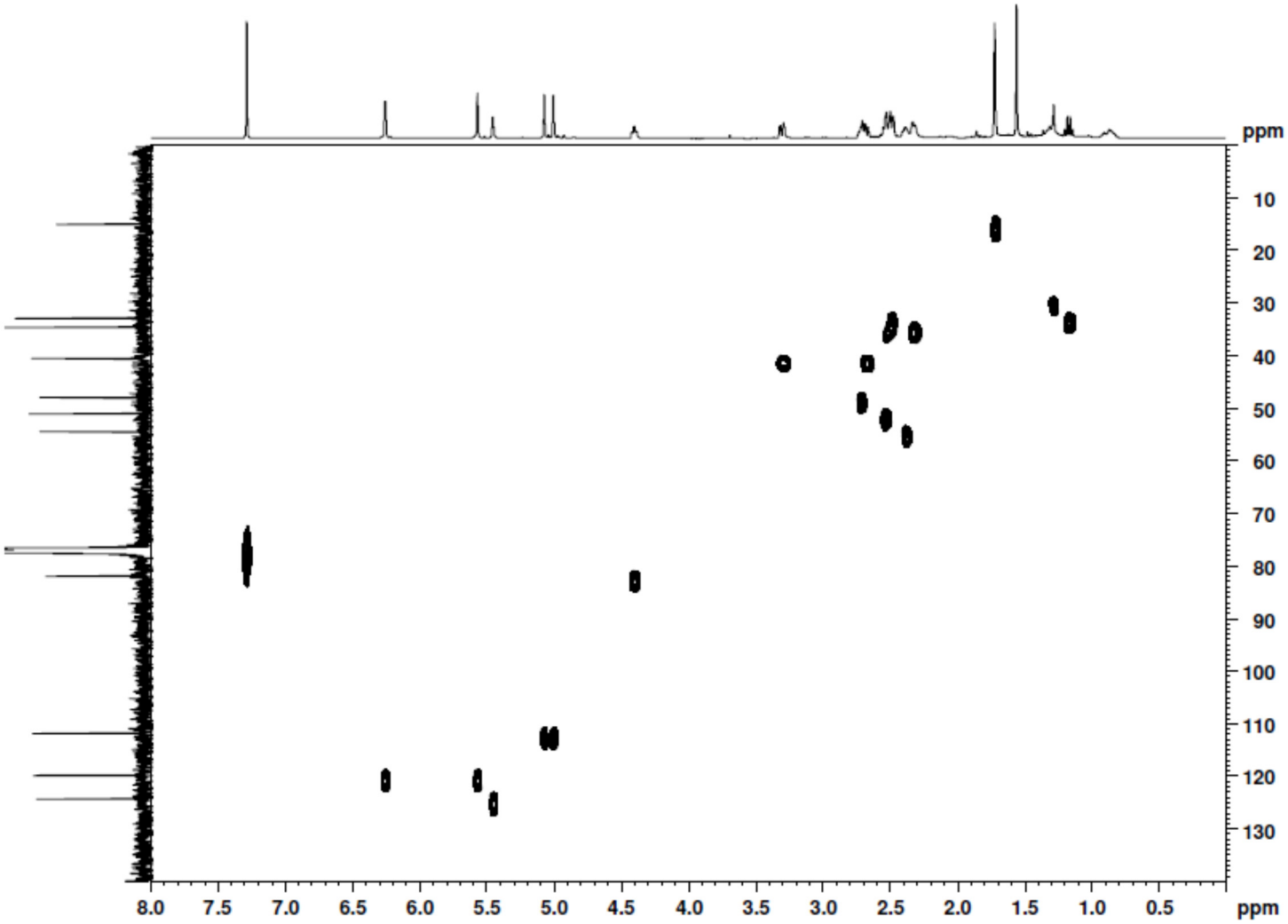
S10. ^{1}H NMR spectrum of centaurolide B (**2**) (600 MHz, $CDCl_3$)



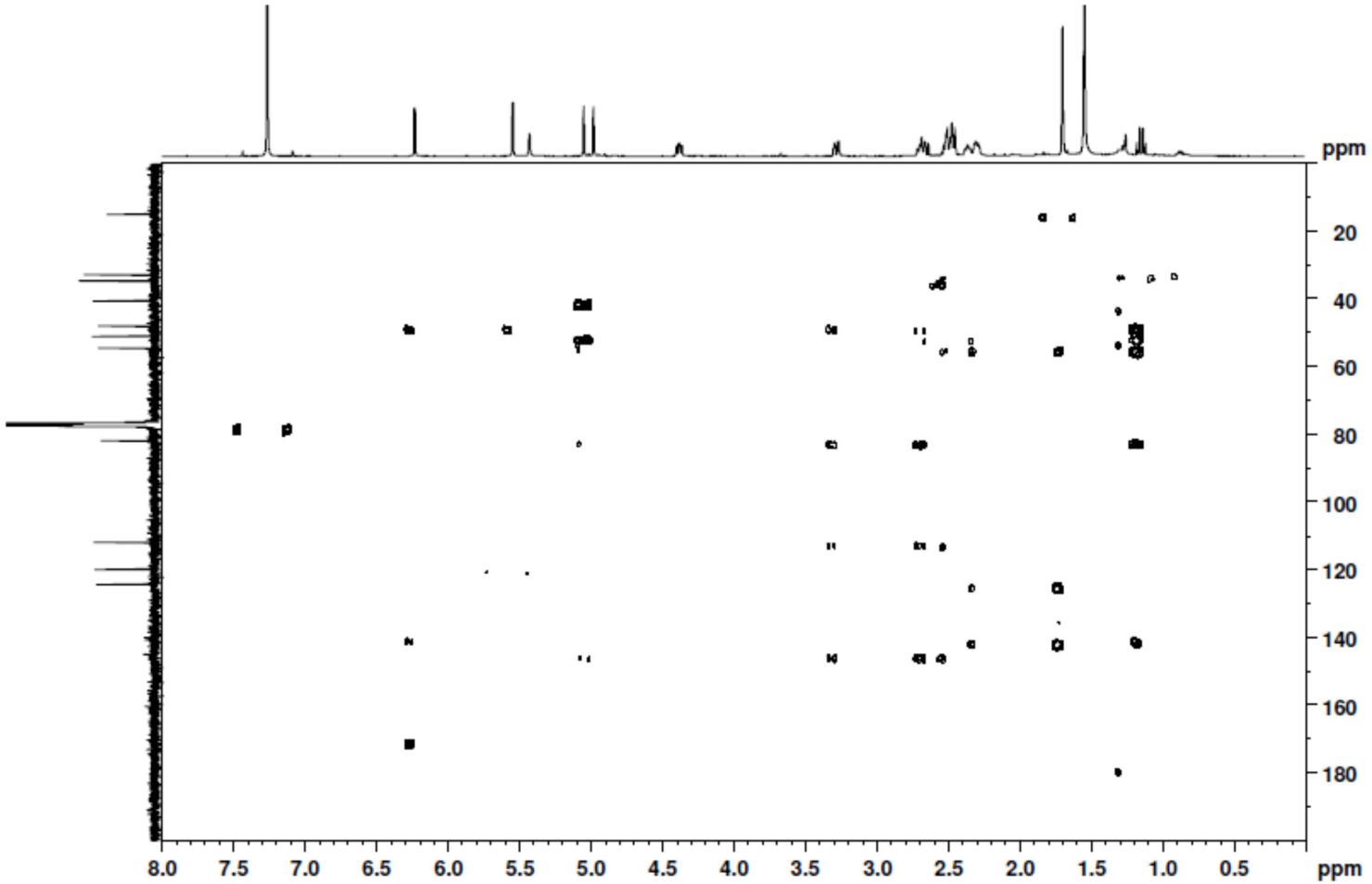
S11. ^{13}C NMR spectrum of centaurolide B (**2**) (100 MHz, $CDCl_3$)



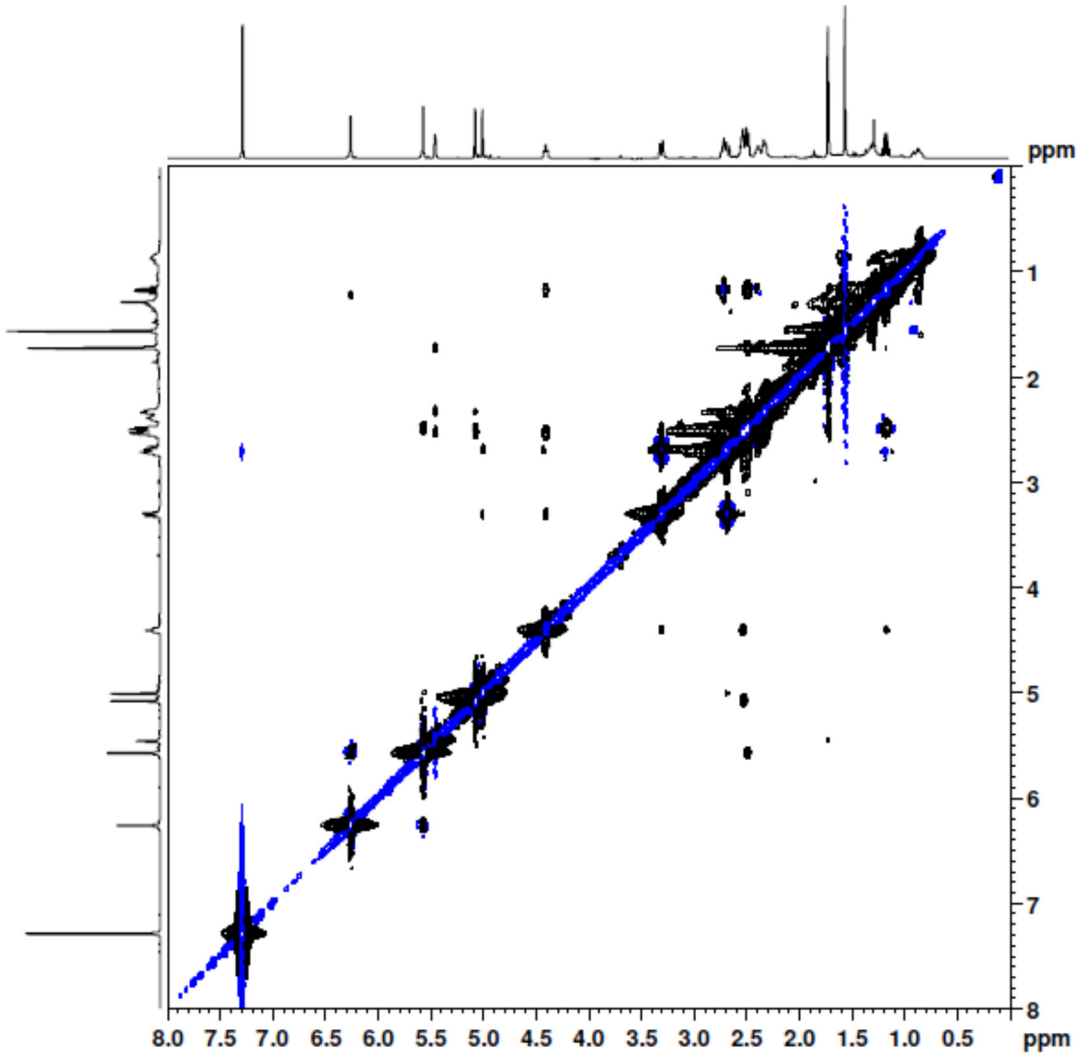
S12. COSY spectrum of centaurolide B (**2**) (400 MHz, CDCl3)



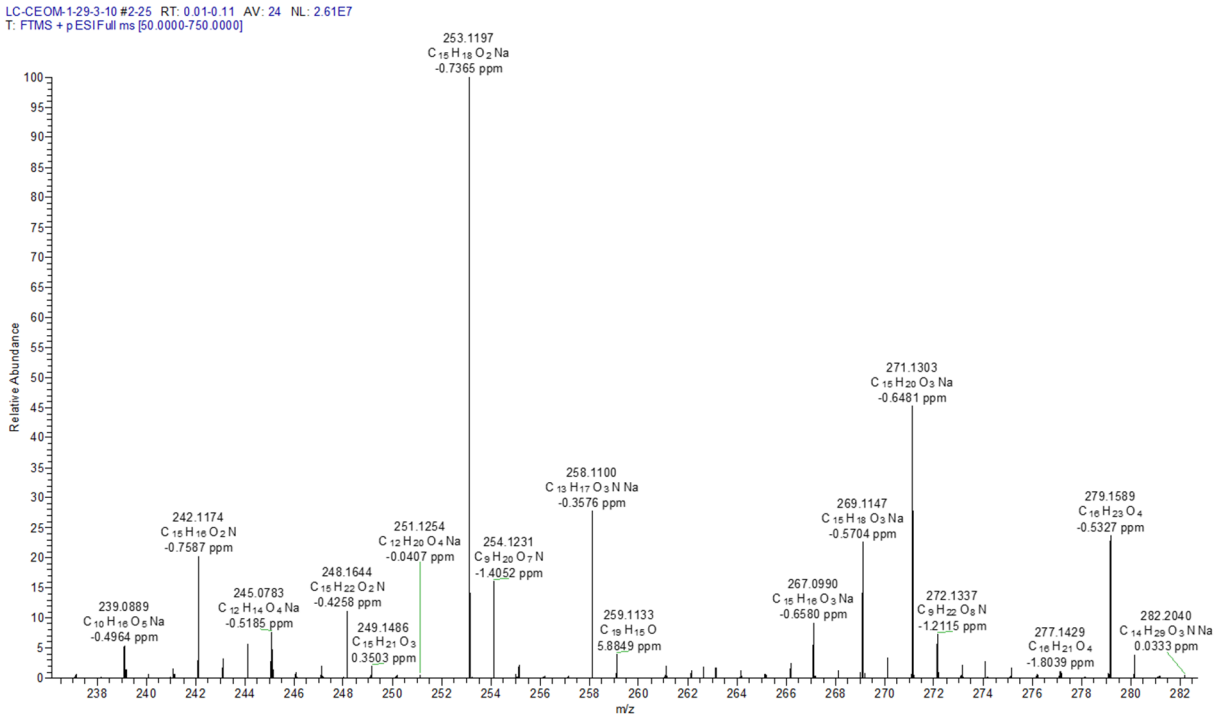
S13. HSQC spectrum of centaurolide B (**2**) (400 MHz, $CDCl_3$)



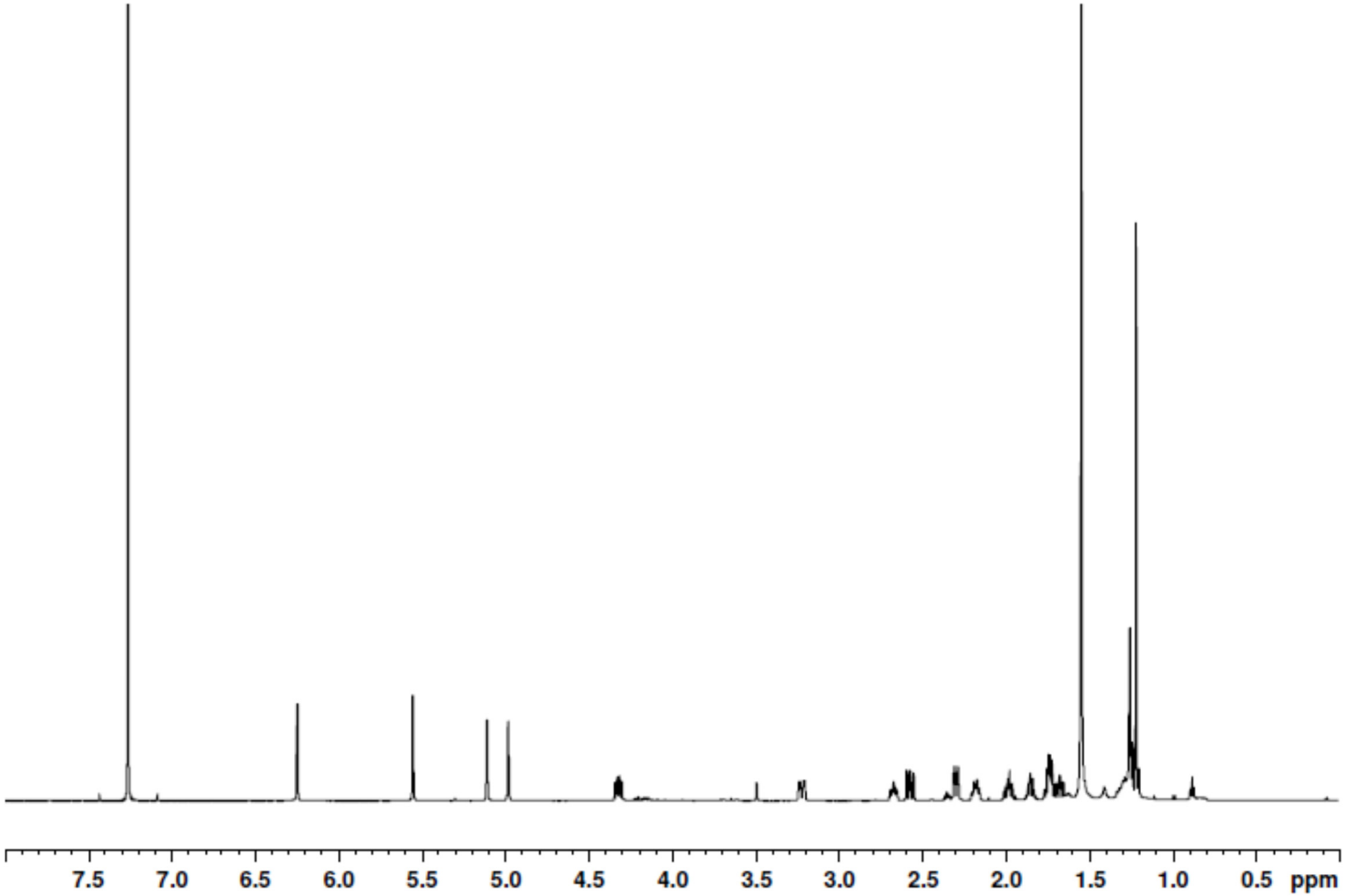
S14. HMBC spectrum of centaurolide B (**2**) (600 MHz, $CDCl_3$)



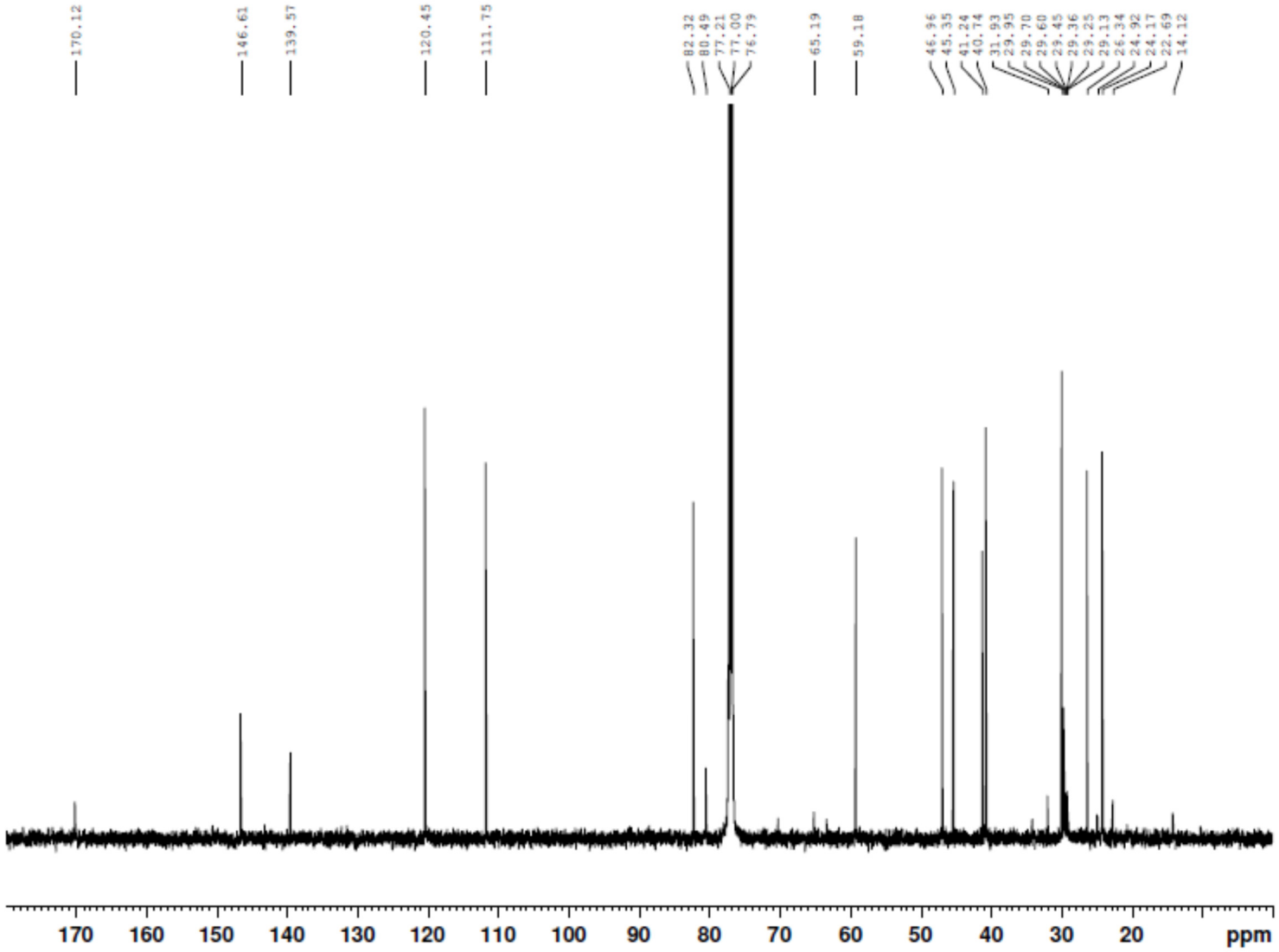
S15. NOESY spectrum of centaurolide B (**2**) (600 MHz, $CDCl_3$)



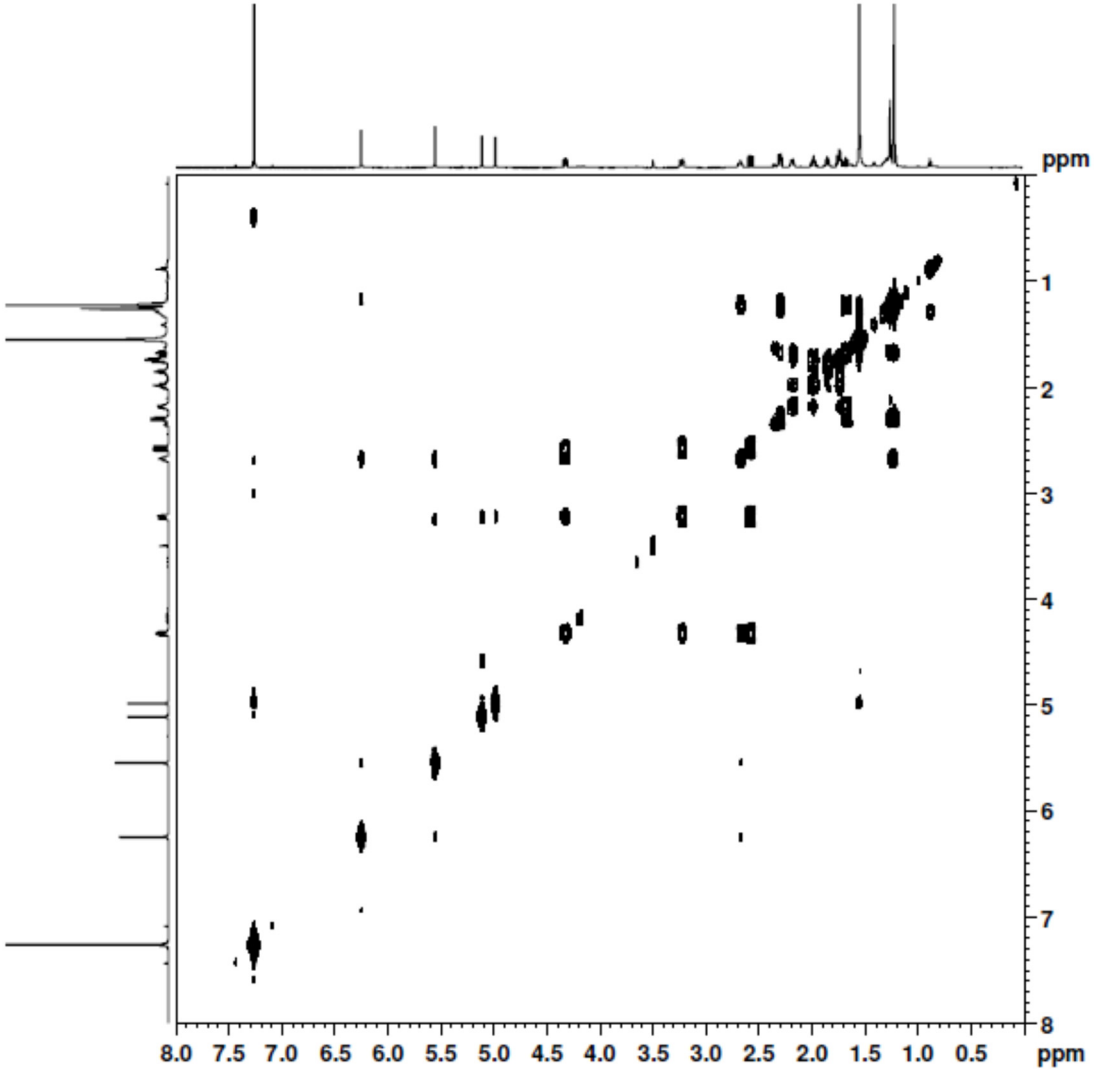
S16. HR ESIMS spectrum of centaurolide B (**2**)



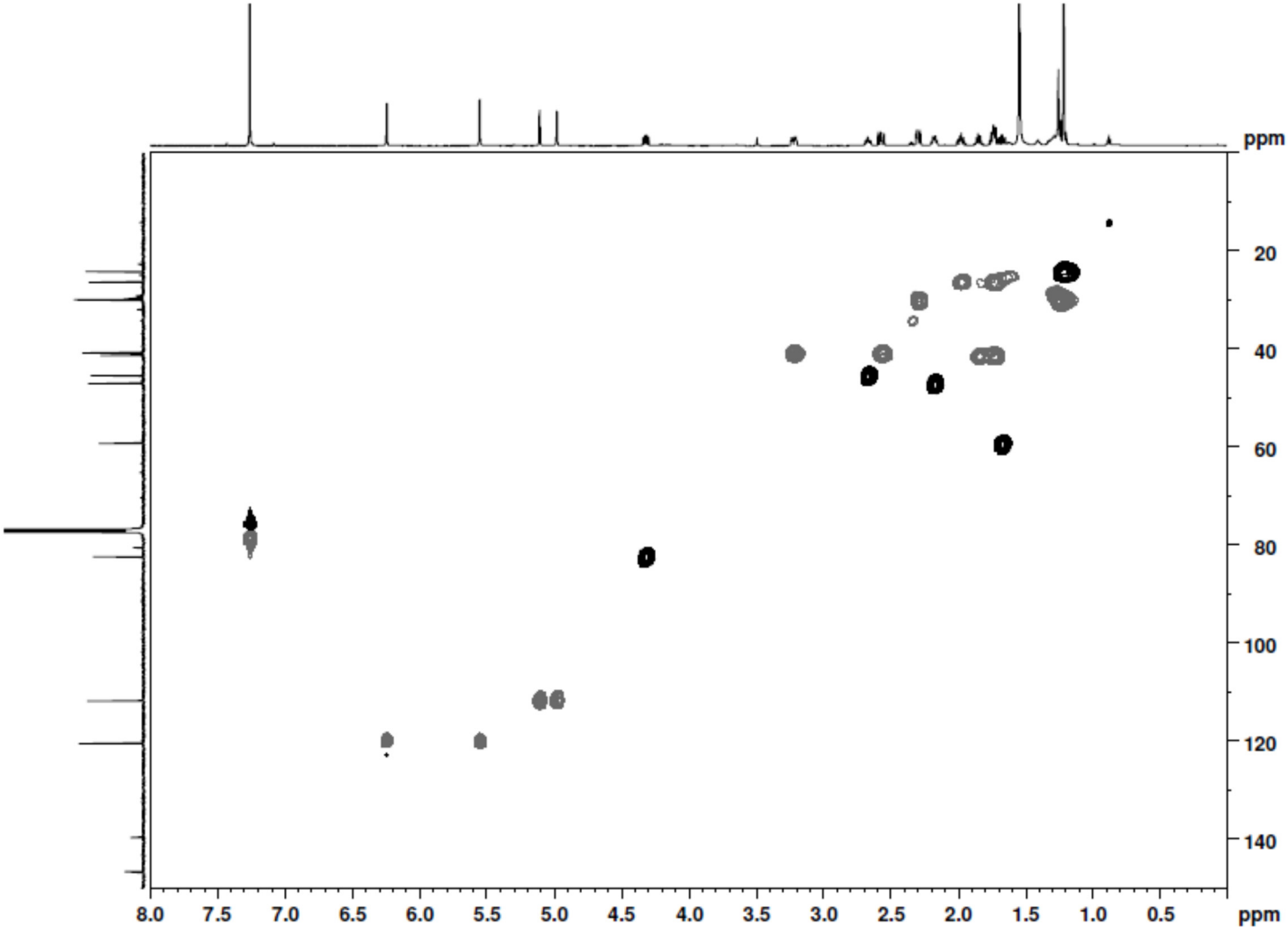
S17. ^{1}H NMR spectrum of inuviscolide (**3**) (600 MHz, $CDCl_3$)



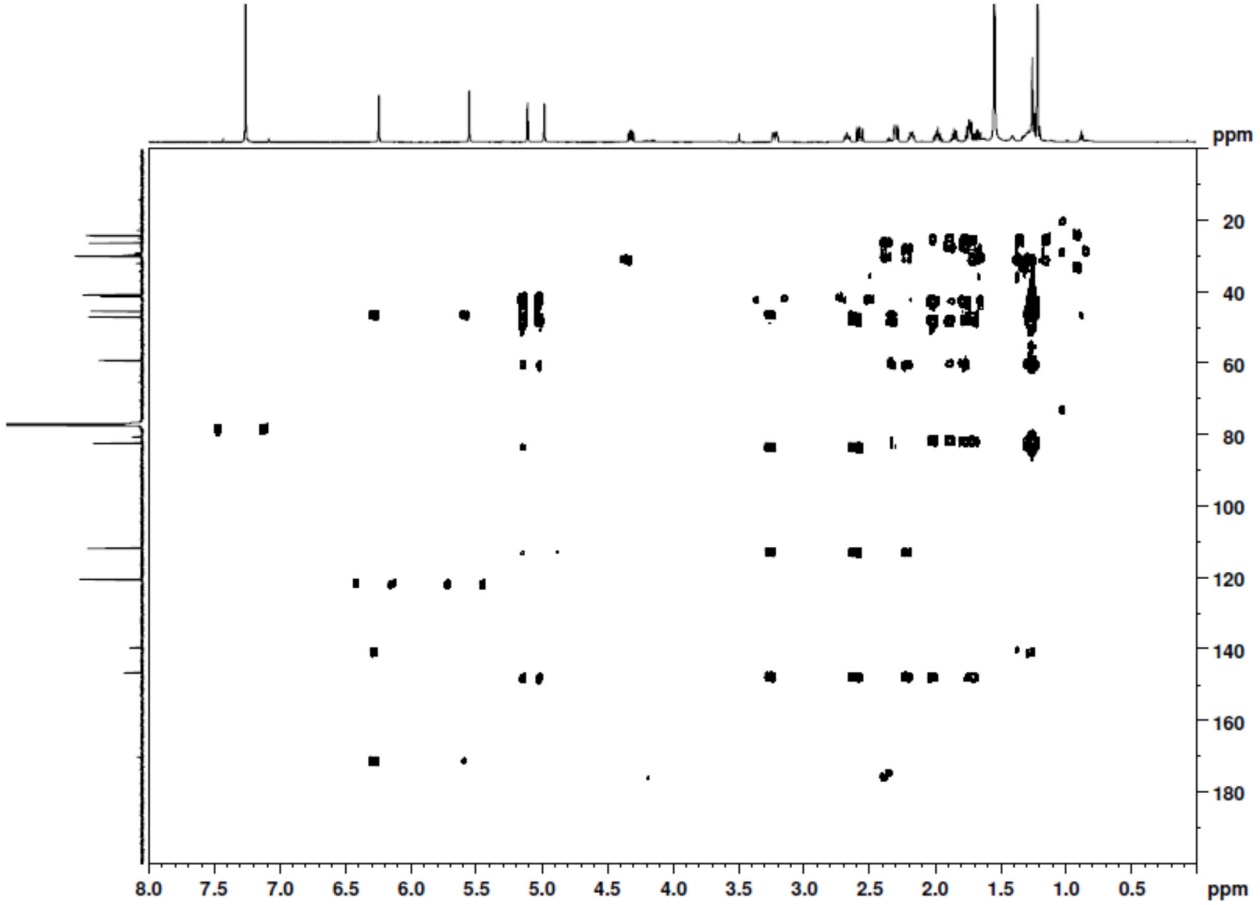
S18. ^{13}C NMR spectrum of inuviscolide (**3**) (150 MHz, $CDCl_3$)



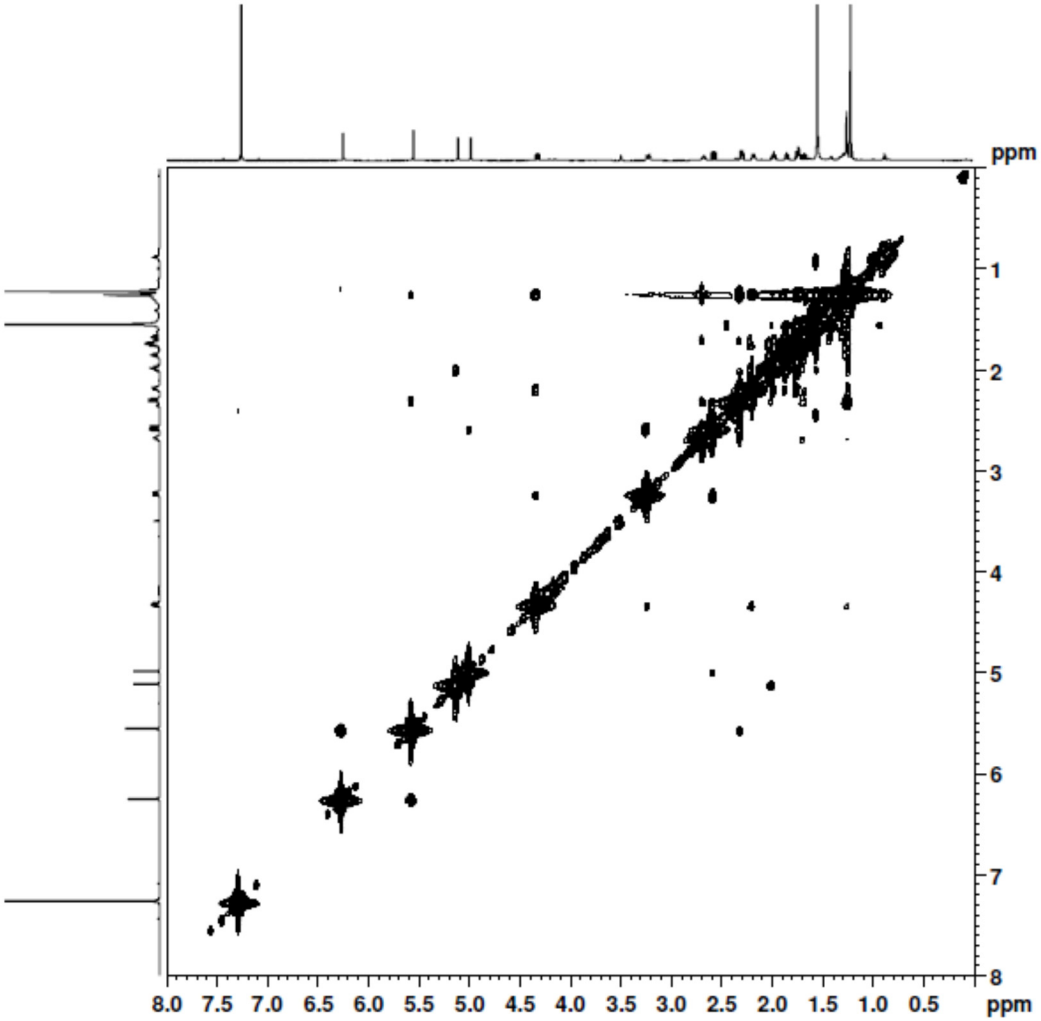
S19. COSY spectrum of inuviscolide (**3**) (600 MHz, $CDCl_3$)



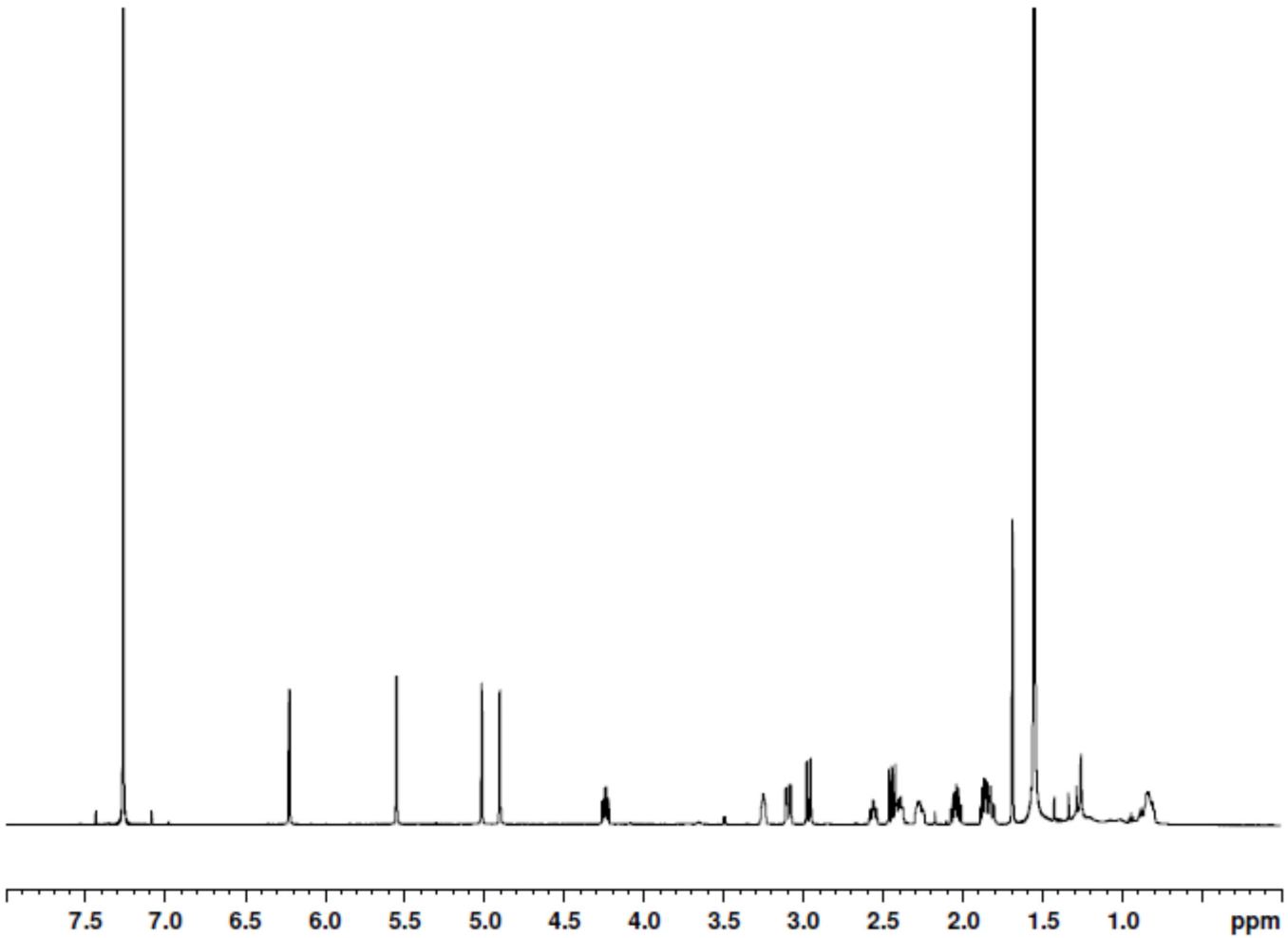
S20. ed-HSQC spectrum of inuviscolide (**3**) (600 MHz, CDCl3)



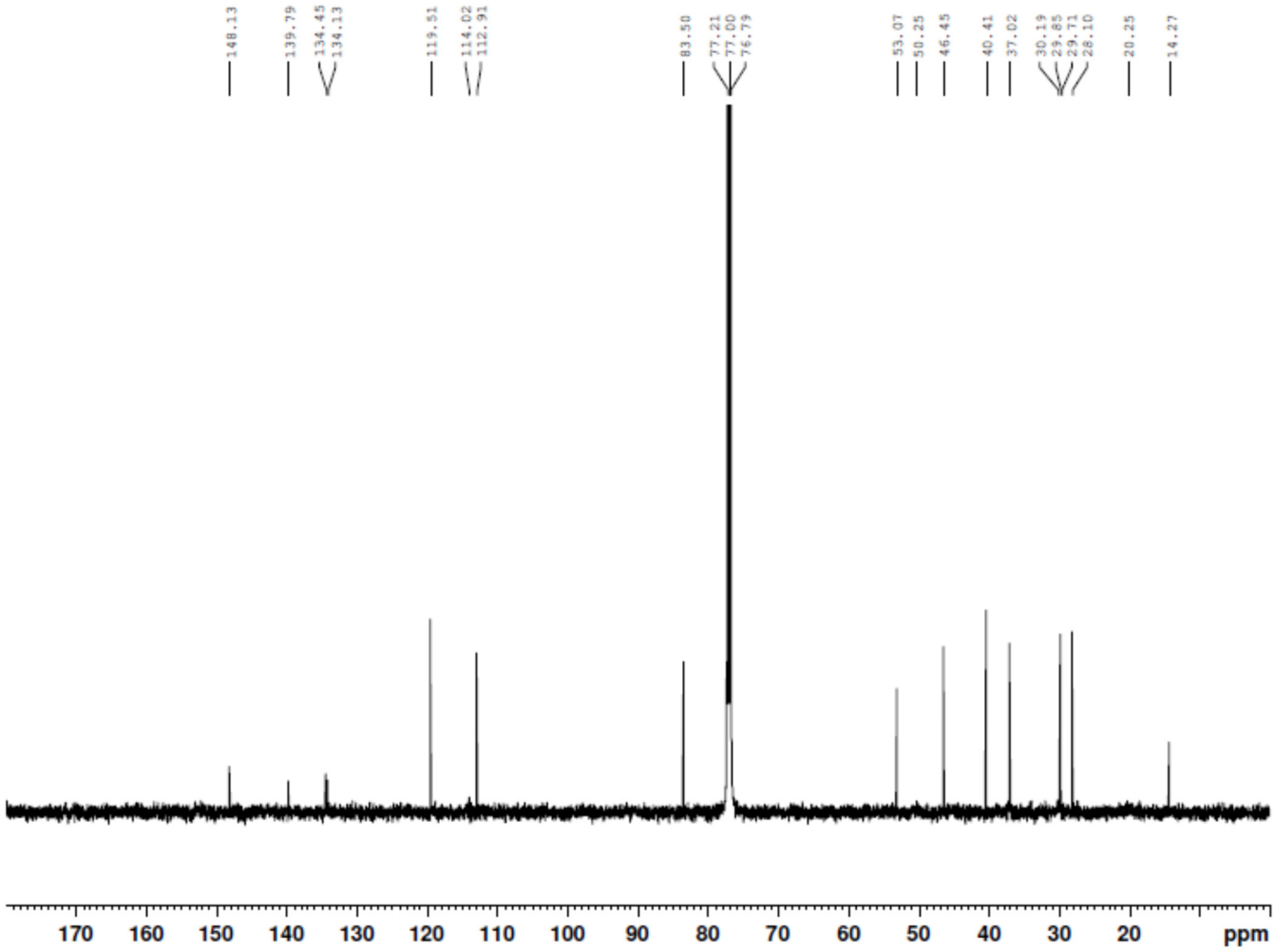
S21. HMBC spectrum of inuviscolide (**3**) (600 MHz, CDCl3)



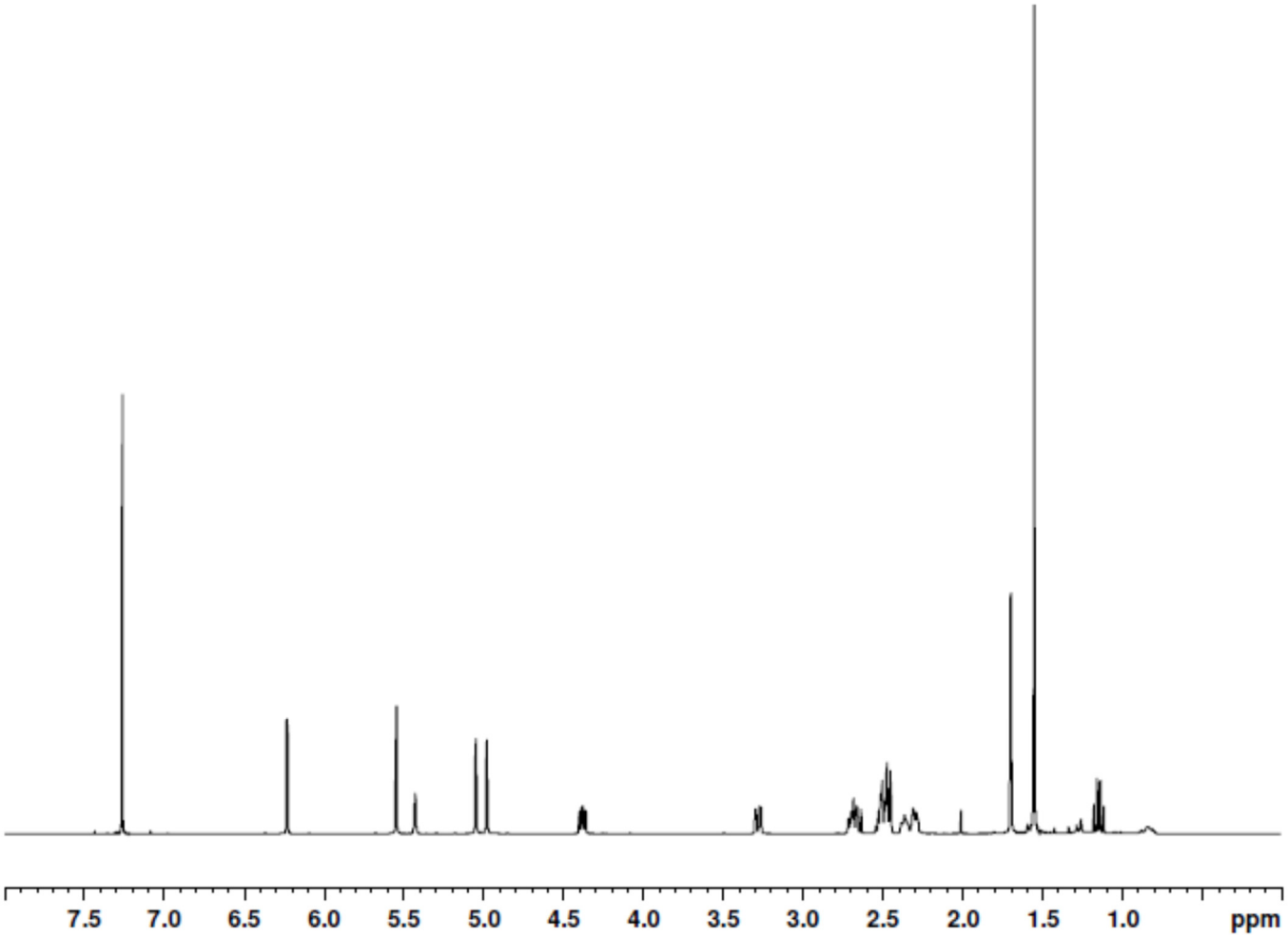
S22. NOESY spectrum of inuviscolide (**3**) (600 MHz, $CDCl_3$)



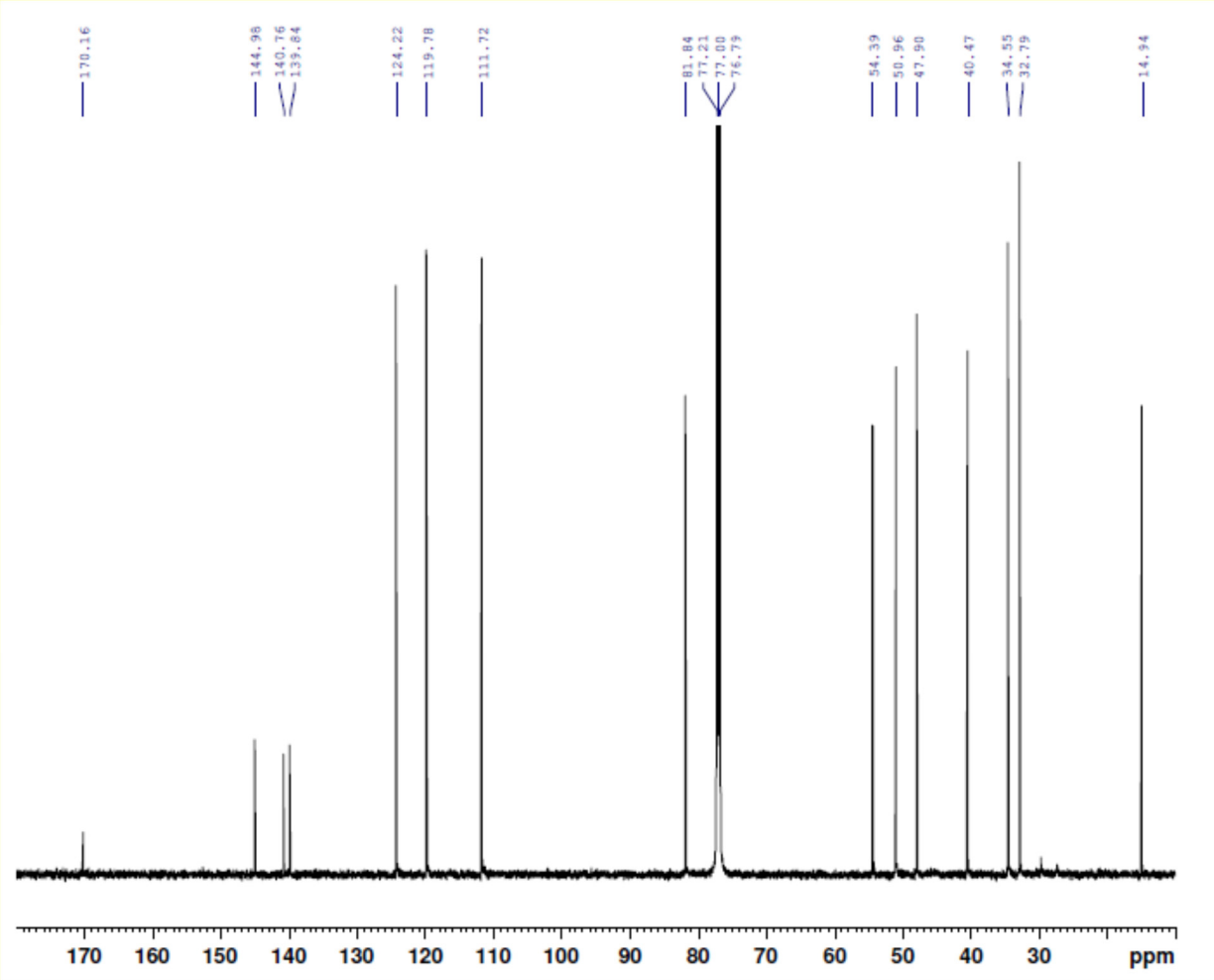
S23. ^{1}H NMR spectrum of dehydration derivative of inuviscolide (600 MHz, $CDCl_3$)



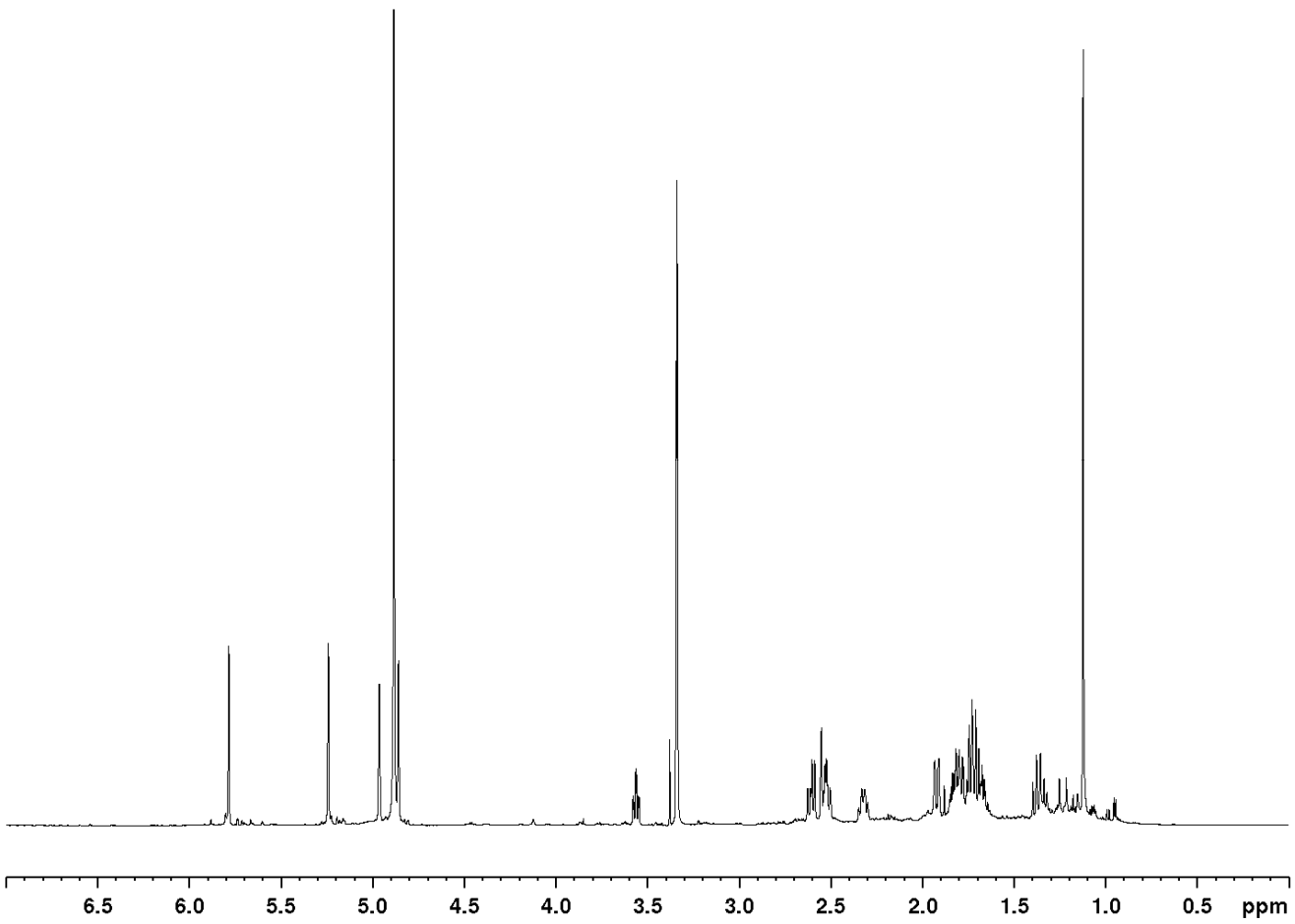
S24. ^{13}C NMR spectrum of dehydration derivative of inuviscolide (600 MHz, $CDCl_3$)



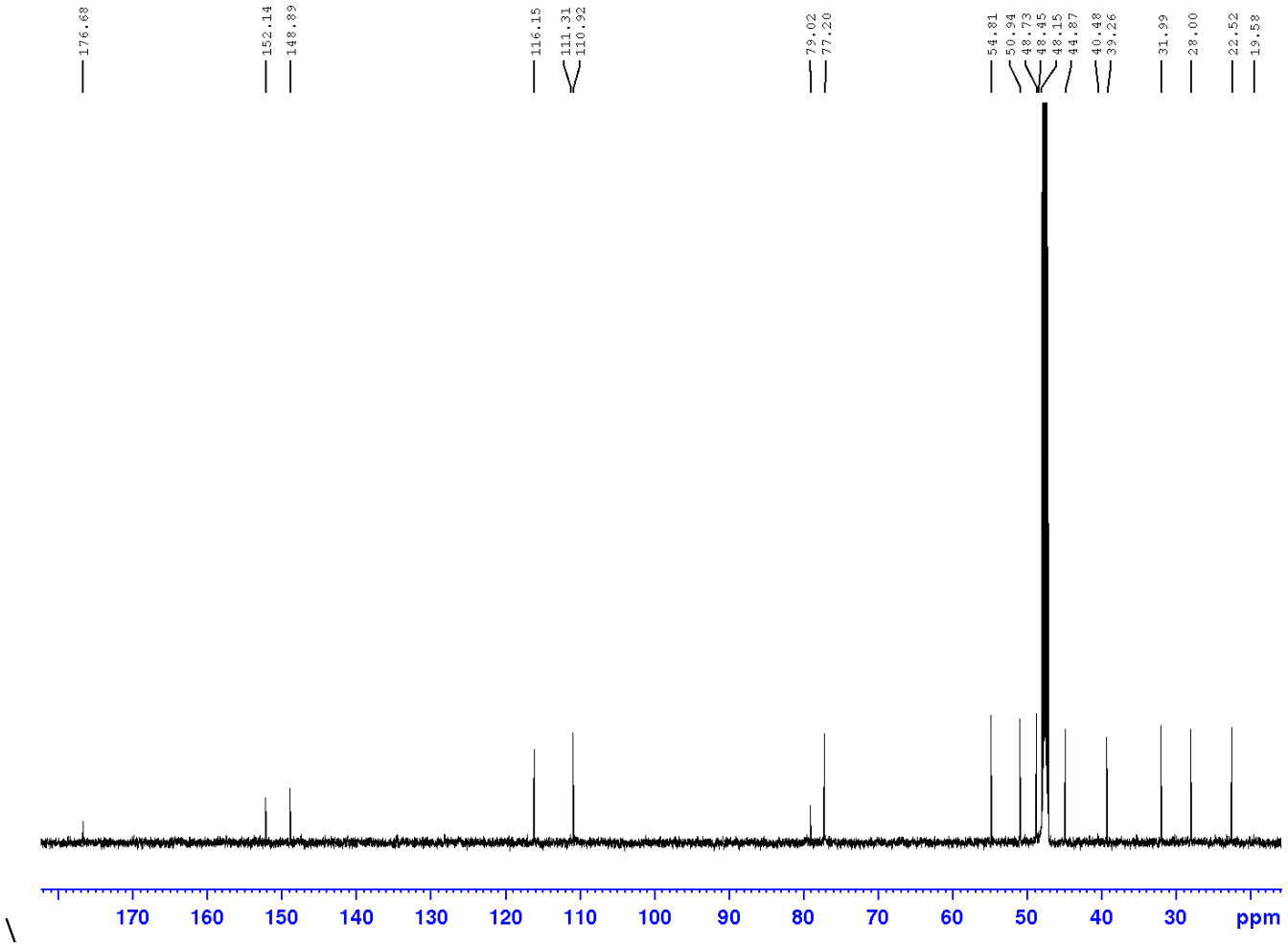
S25. ^{1}H NMR spectrum of dehydration derivative of inuviscolide (600 MHz, $CDCl_3$)



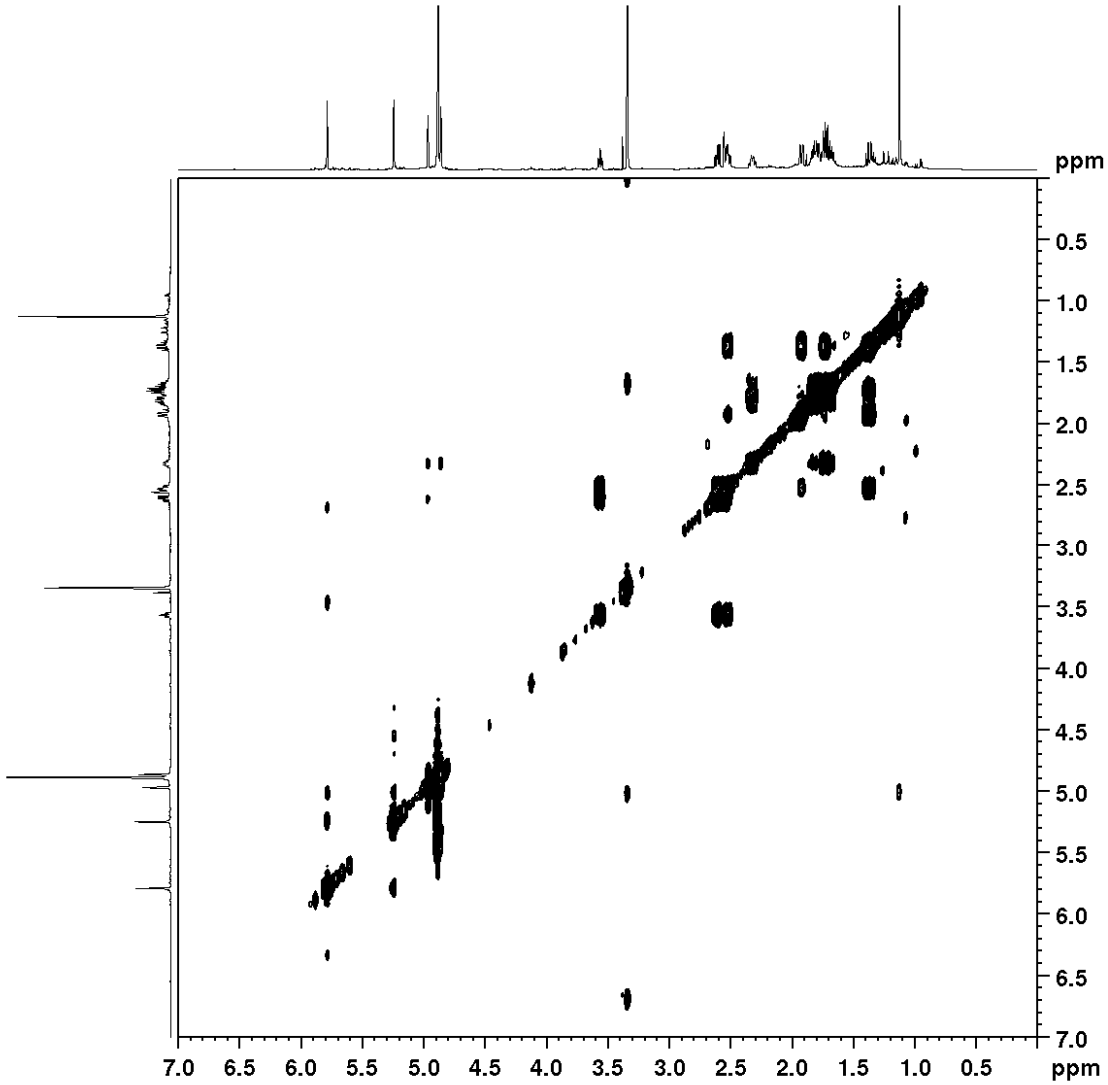
S26. ^{13}C NMR spectrum of dehydration derivative of inuviscolide (600 MHz, $CDCl_3$)



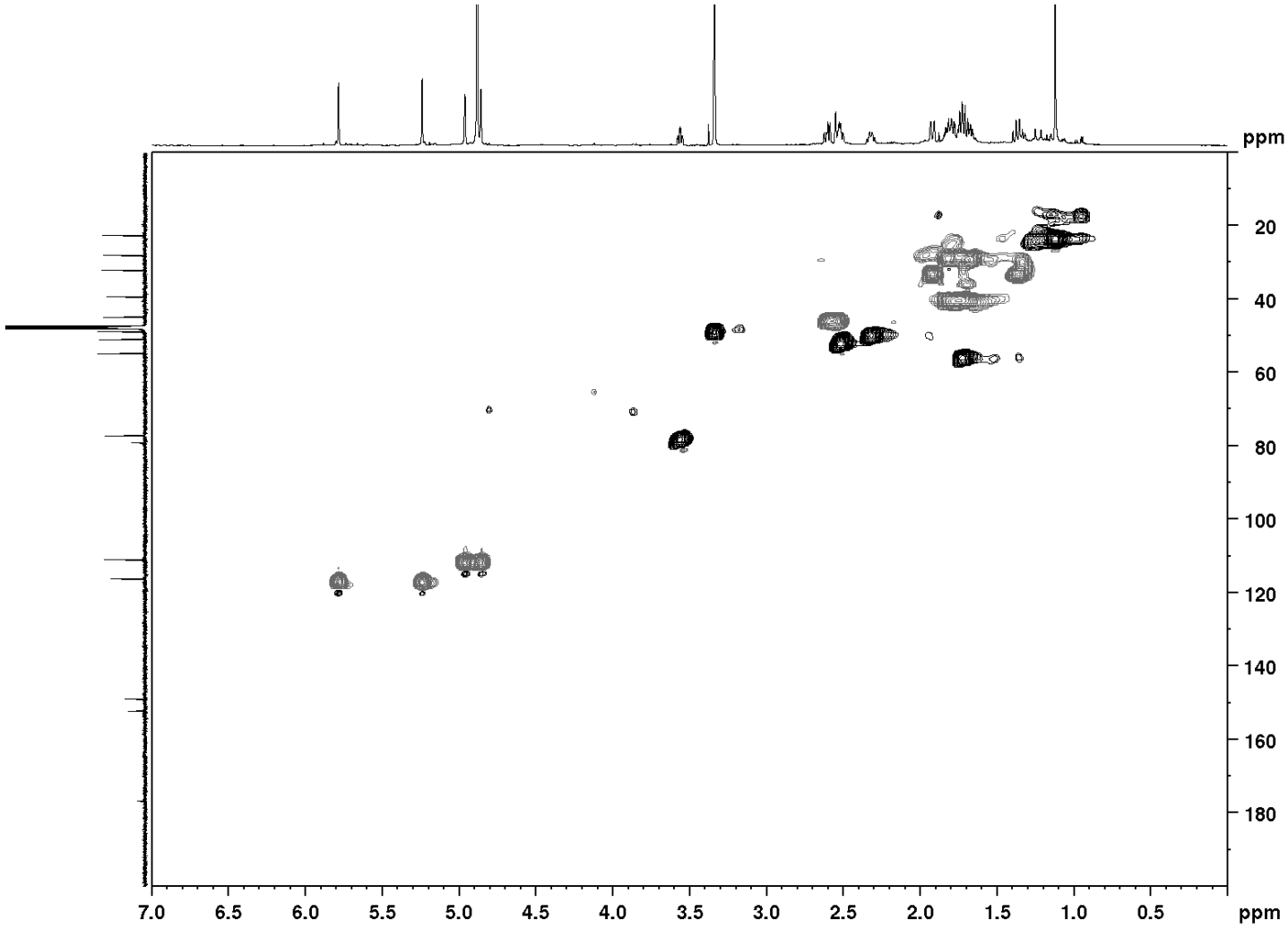
S27. ^{1}H NMR spectrum of alcohol (**4**) (600 MHz, $CDCl_3$)



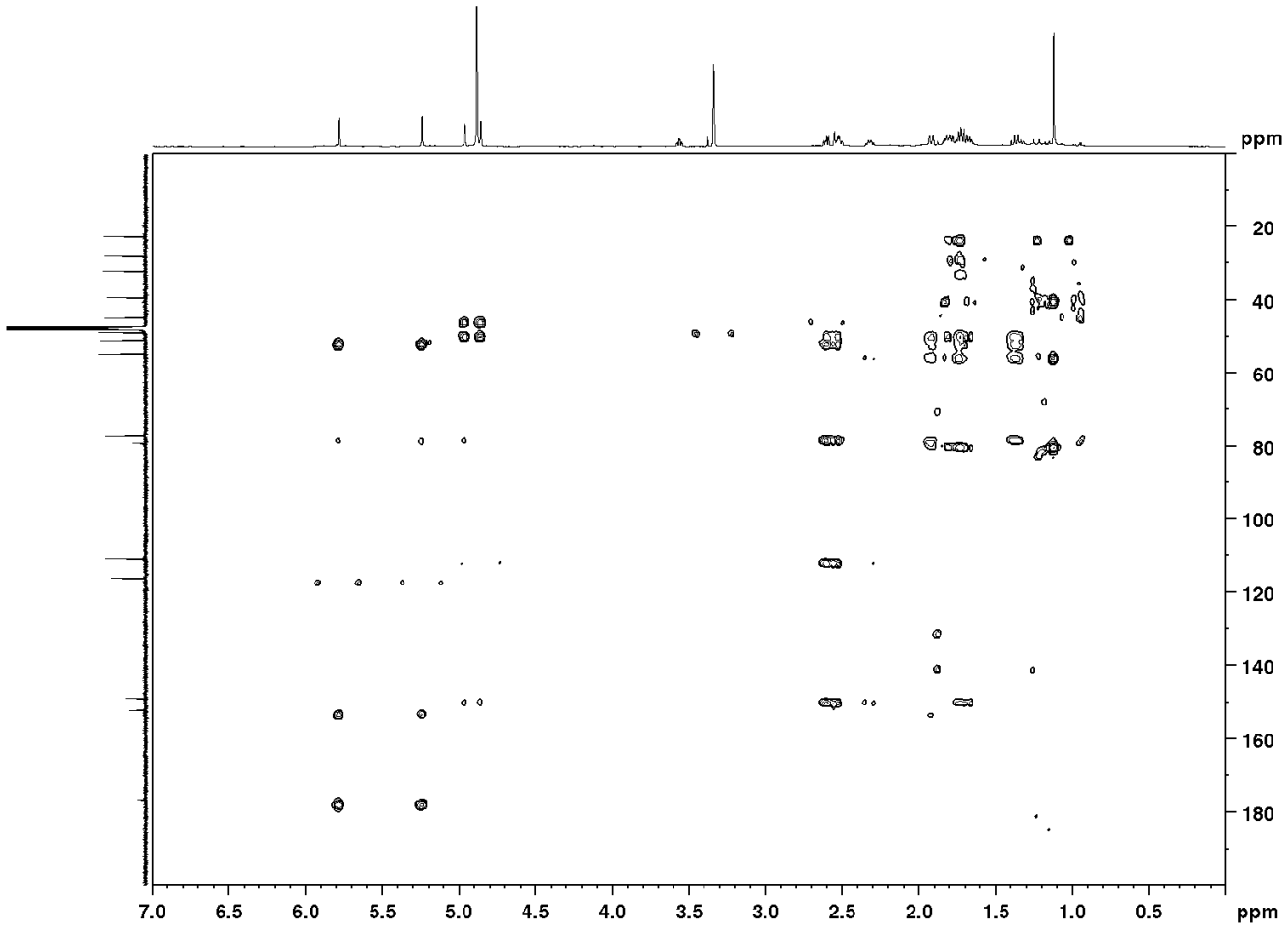
S28. ^{13}C NMR spectrum of alcohol (**4**) (150 MHz, $CDCl_3$)



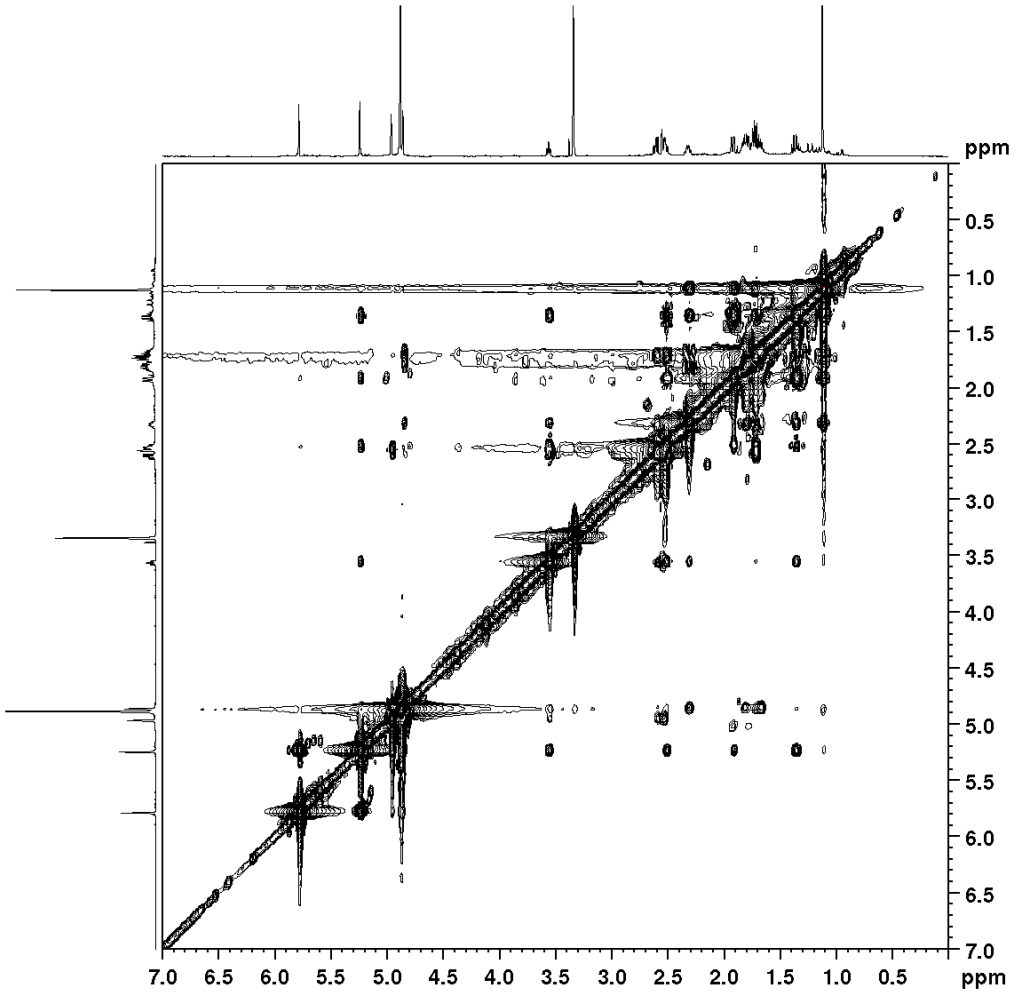
S29. COSY spectrum of alcohol (**4**) (600 MHz, $CDCl_3$)



S30. ed-HSQC spectrum of alcohol (**4**) (600 MHz, $CDCl_3$)



S31. HMBC spectrum of alcohol (**4**) (600 MHz, CDCl3)



S32. NOESY spectrum of alcohol (**4**) (600 MHz, $CDCl_3$)