Supporting Information For:

Molecular Library Synthesis Using Complex Substrates: Expanding the Framework of Triterpenoids

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General experimental details

All reactions were run in an atmosphere of dry argon unless otherwise stated. THF was distilled from benzophenone ketyl solution with sodium prior to use. Quick syringe transfers were done with disposable syringes and needles.

Column chromatography was performed with silica gel (particle size 32-63 μm). Analytical and semi-preparative HPLC separations were performed using acetonitrile and water (for HPLC, 99.9%). Analytical thin-layer chromatography (TLC) was carried out using glass-coated silica gel 0.25 mm plates with fluorescent indicator. All reactions that were monitored by TLC were visualized with a 254 nm UV-lamp or using phosphomolybdic acid (PMA) and 1,4-dinitrophenylhydrazine (DNP) stain solutions prepared by well-known protocols.

Chemical shifts of all ^{1}H and ^{13}C NMR spectra reported in δ units, part per million (ppm) with reference to the residual solvent peak ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.16 ppm, center of triplet, for ^{13}C NMR). DEPT, COSY, NOESY, HMQC, HMBC spectra were recorded using standard 2-D NMR pulse sequences.

Complete reference 46

Reference 46. Gaussian 09, Revision A.02,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,
G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian,
A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,
Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers,
K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand,
K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,
M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,
V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,
P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Figure S1. Mechanistic considerations for the formation of **10** and **11**.

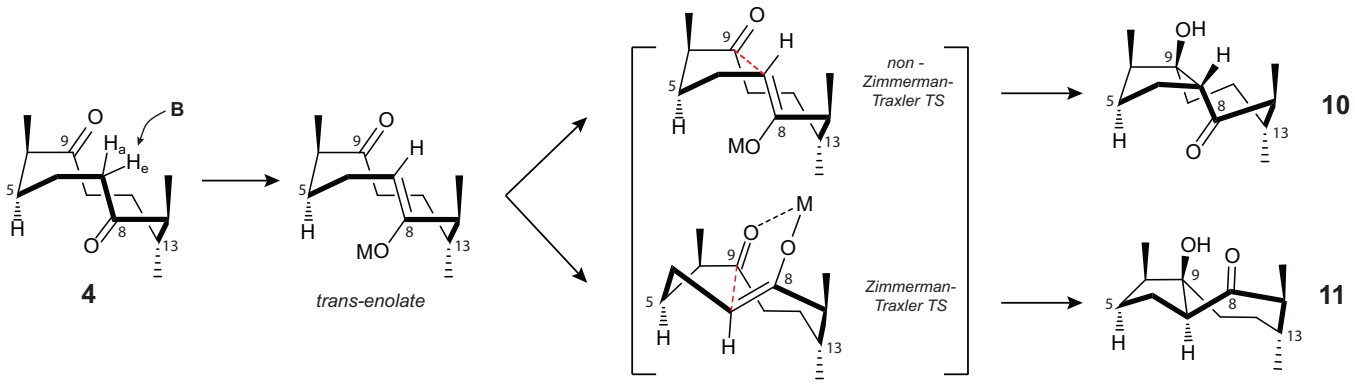
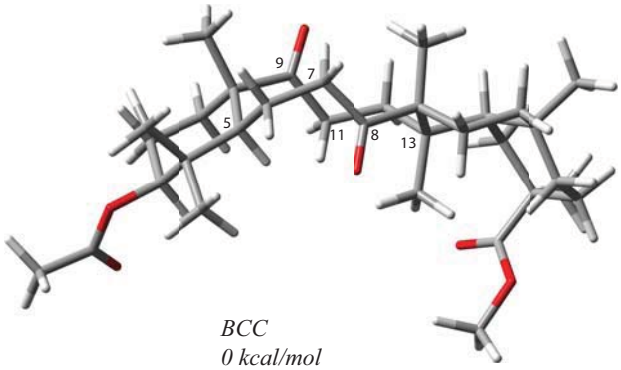


Figure S2. Conformational analyses of polyketones **4**, **6**, **16**.

Conformational analyses were carried out using Gaussian (R) 09 using B3LYP/6-311G(d,p).
Ground state conformations and electronic energies are shown.
BCC = 'boat (with bow at C-5 and stern between C-8 and C-11) -chair-chair'
CCB = 'chair-chair- boat (with bow between C-8 and C-11and stern at C-13)'

4



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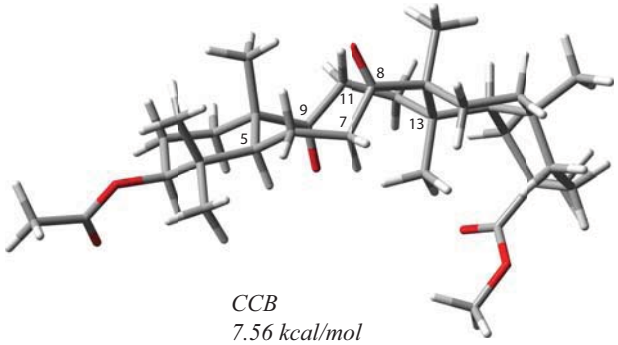

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7.56 kcal/mol

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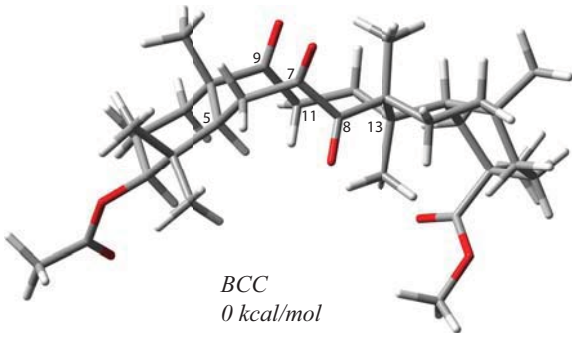

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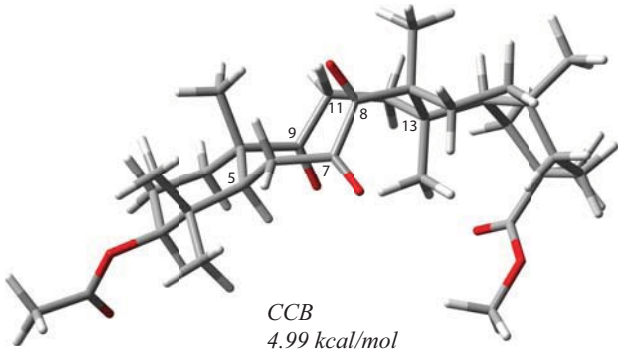

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4.99 kcal/mol

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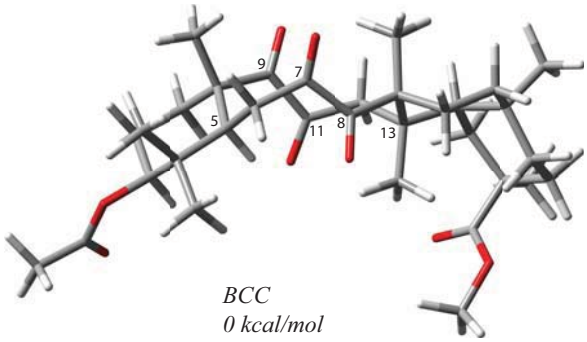

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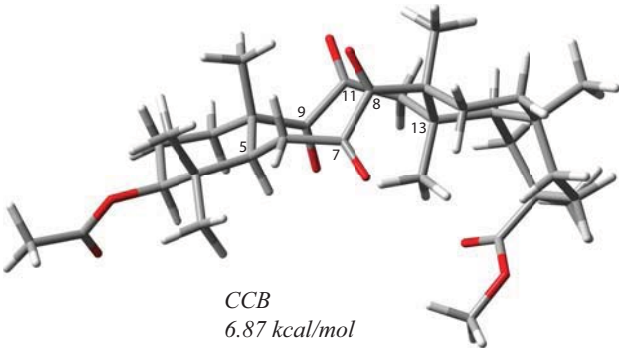
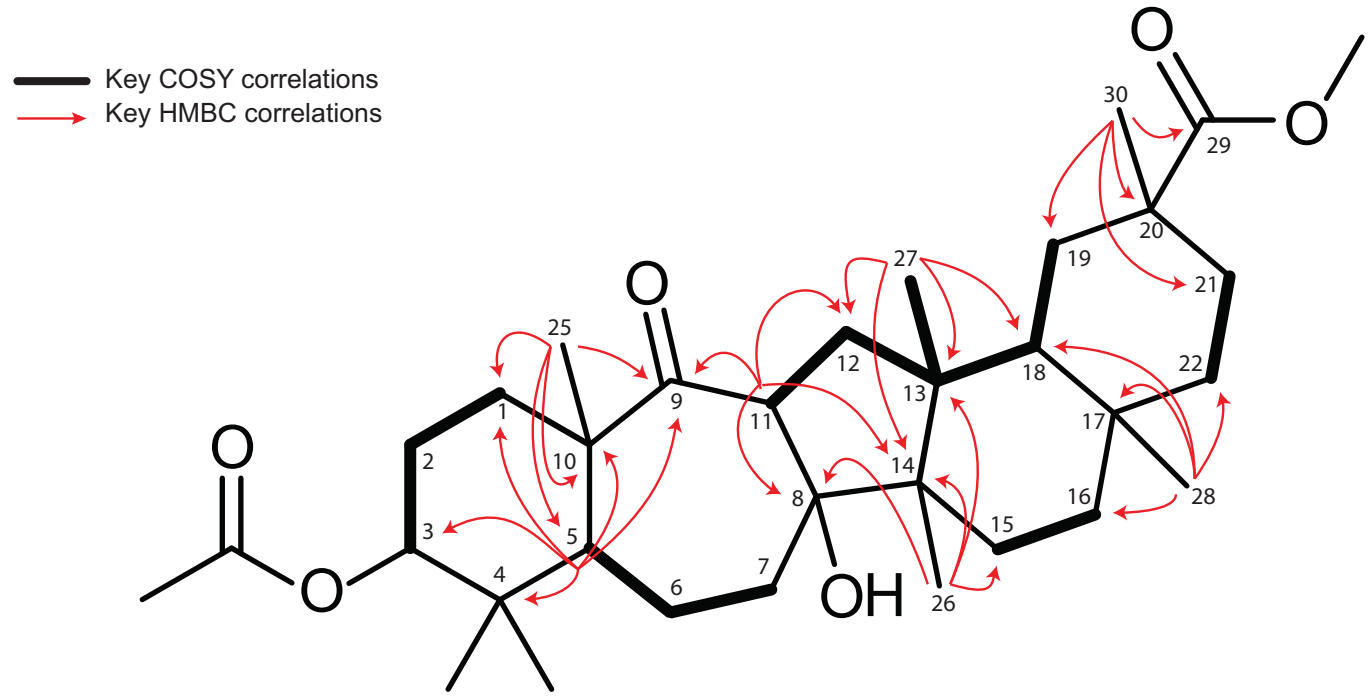
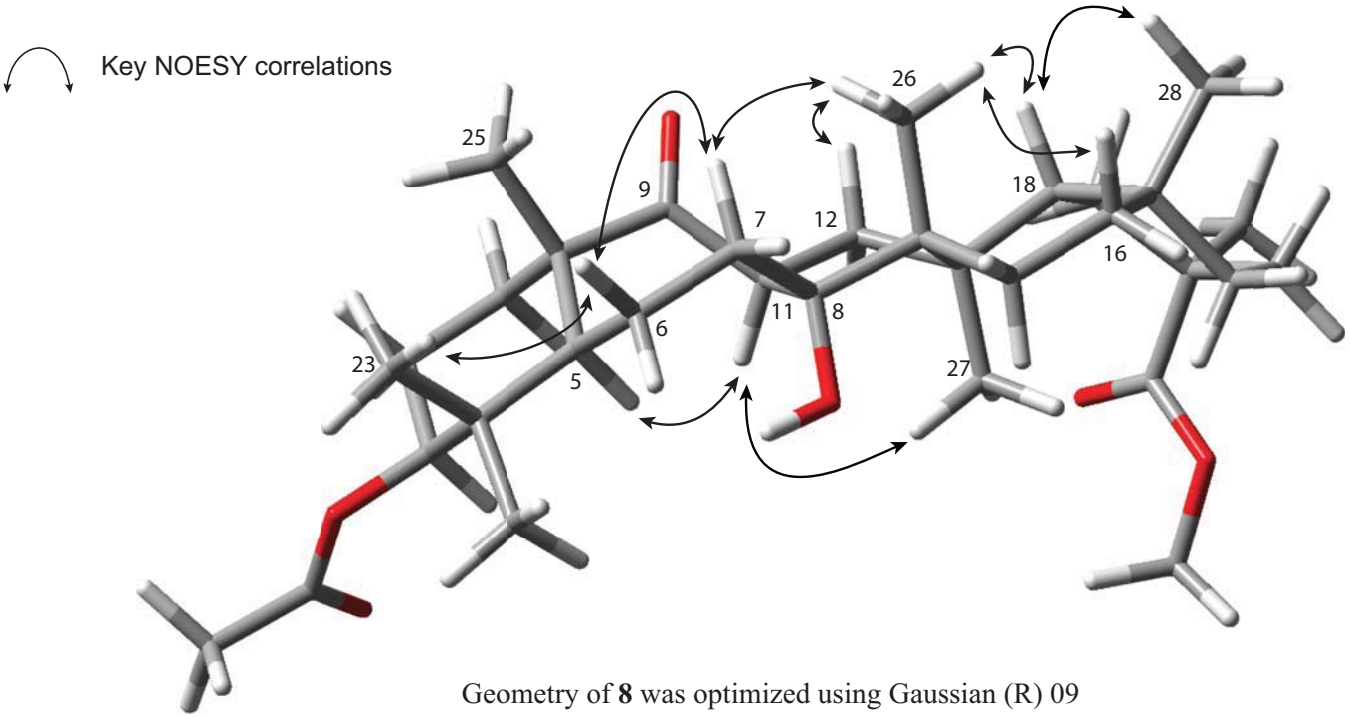


CCB
6.87 kcal/mol

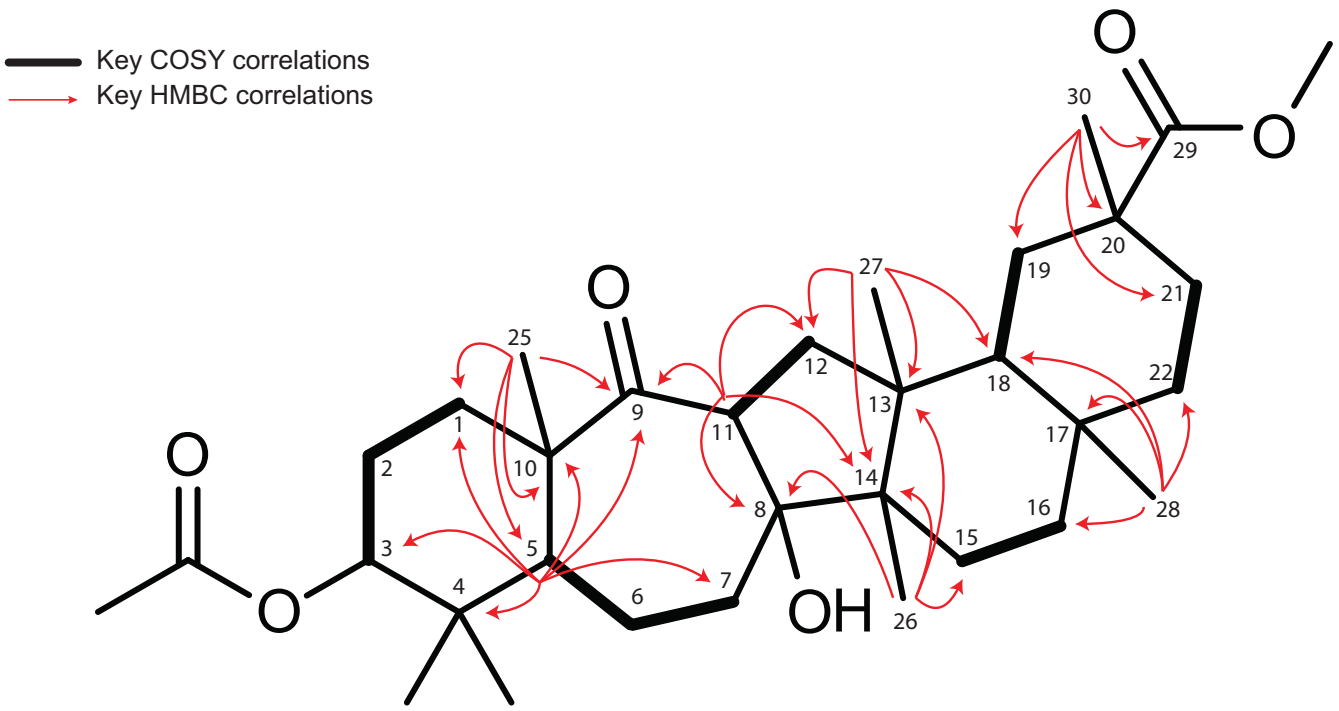
Figure S3. Key COSY, HMBC and NOESY correlations of **8** .

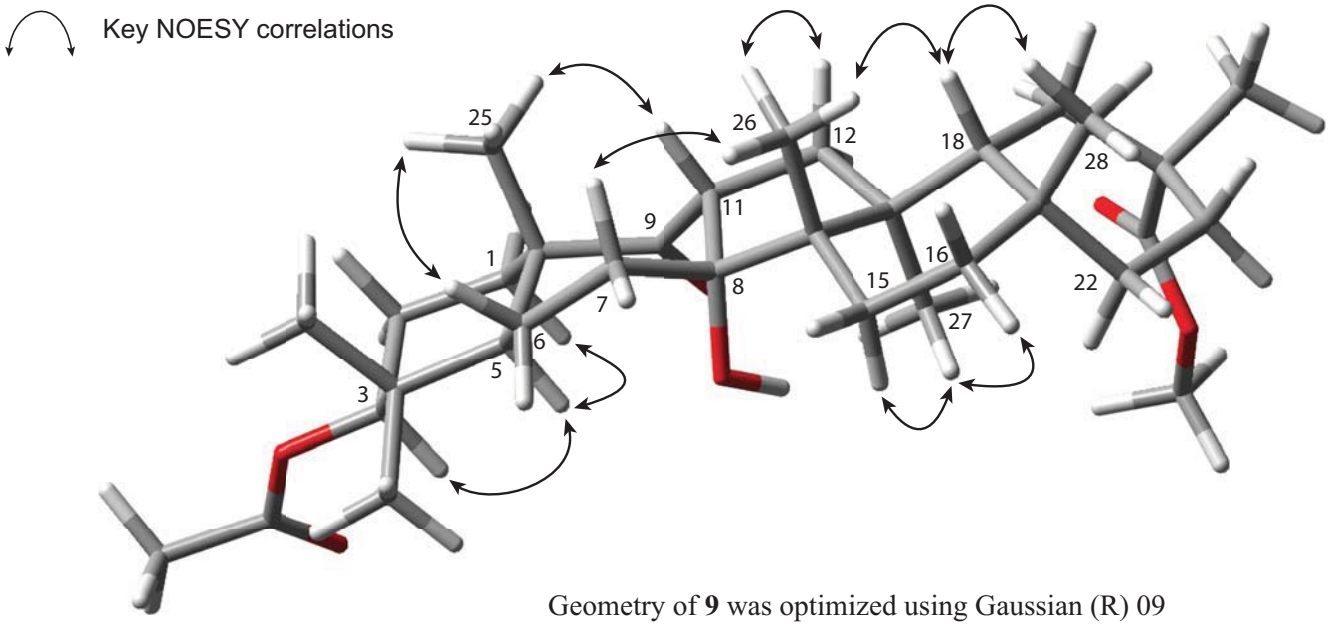




Geometry of **8** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

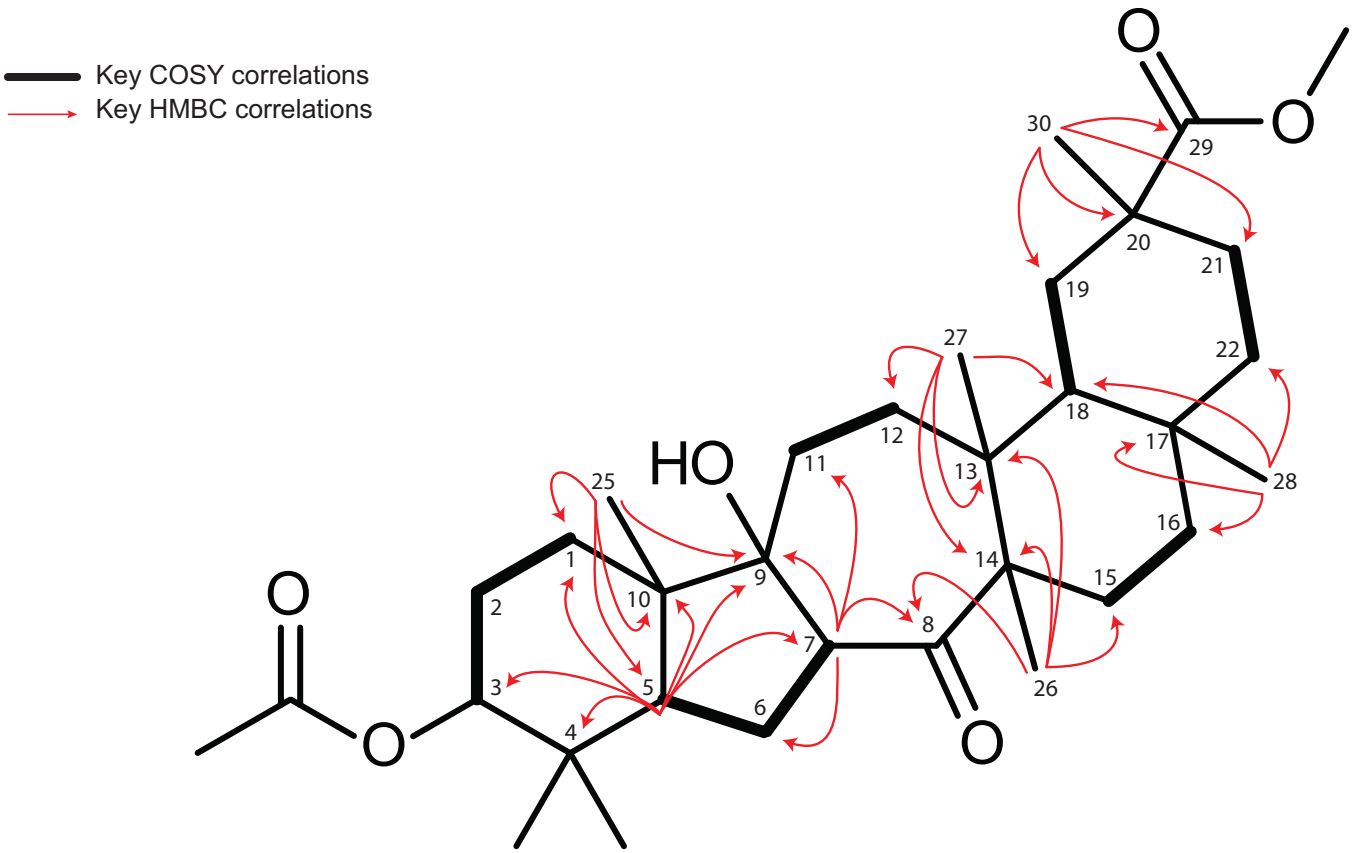
Figure S4. Key COSY, HMBC and NOESY correlations of **9** .

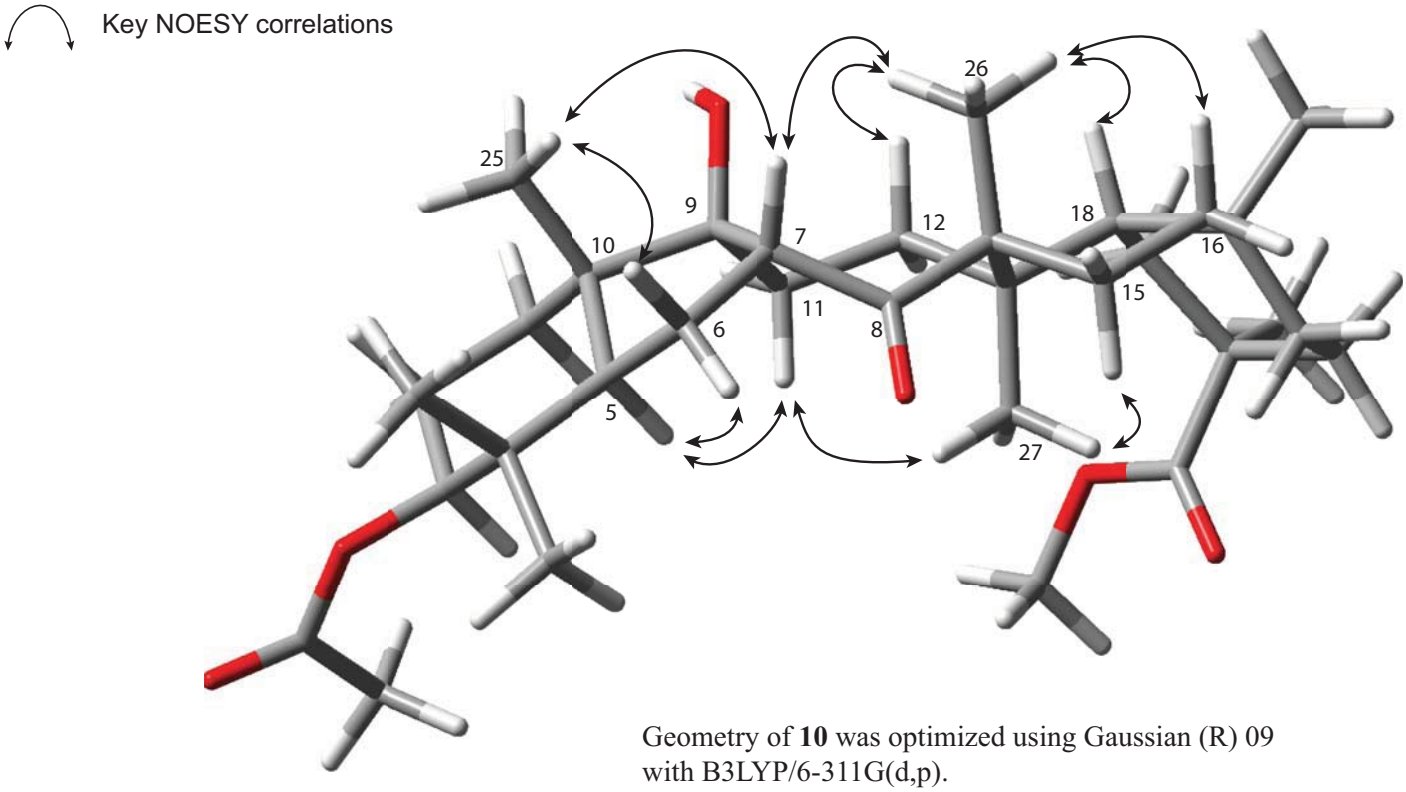




Geometry of **9** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

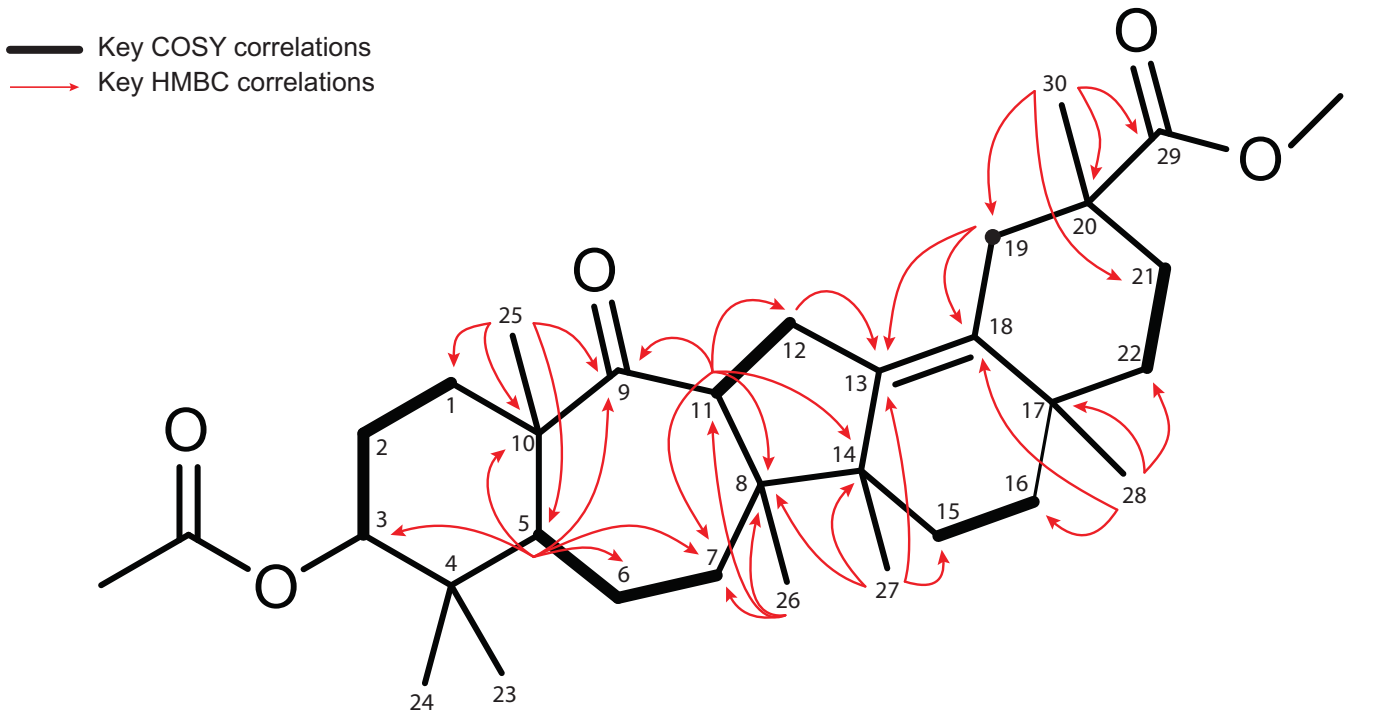
Figure S5. Key COSY, HMBC and NOESY correlations of **10** .

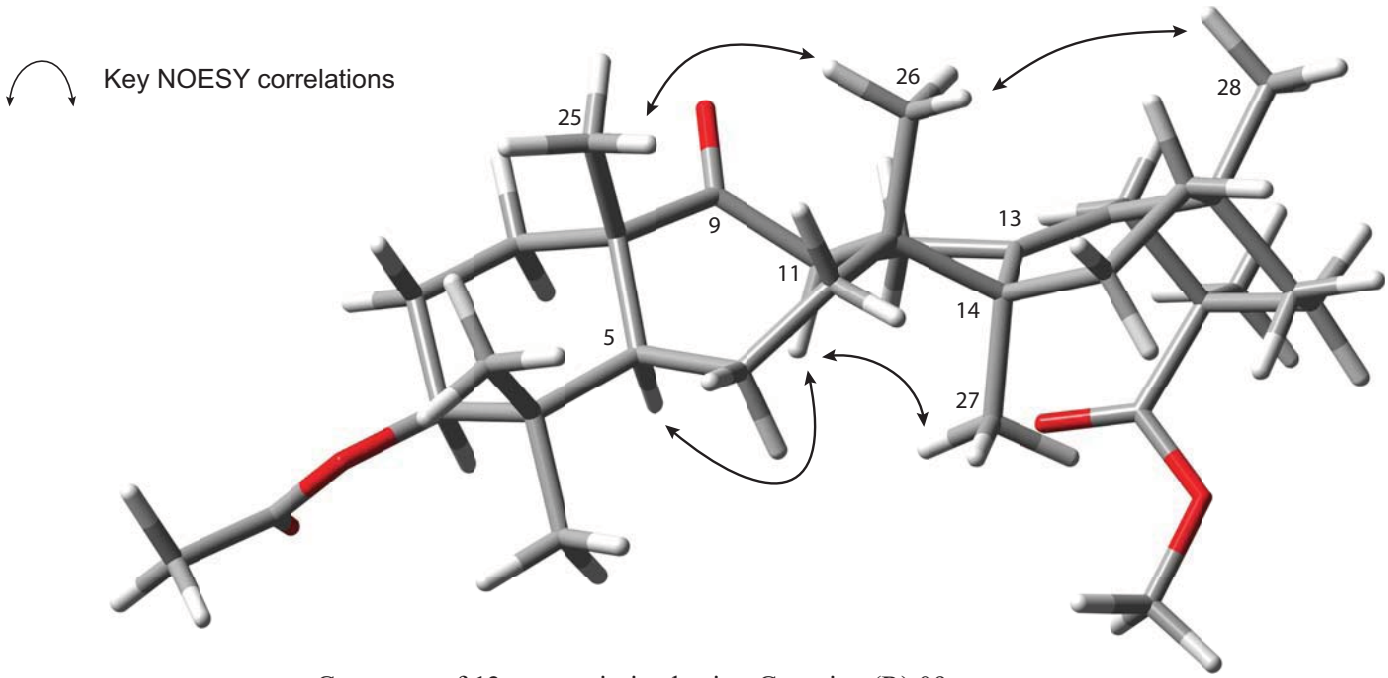




Geometry of **10** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

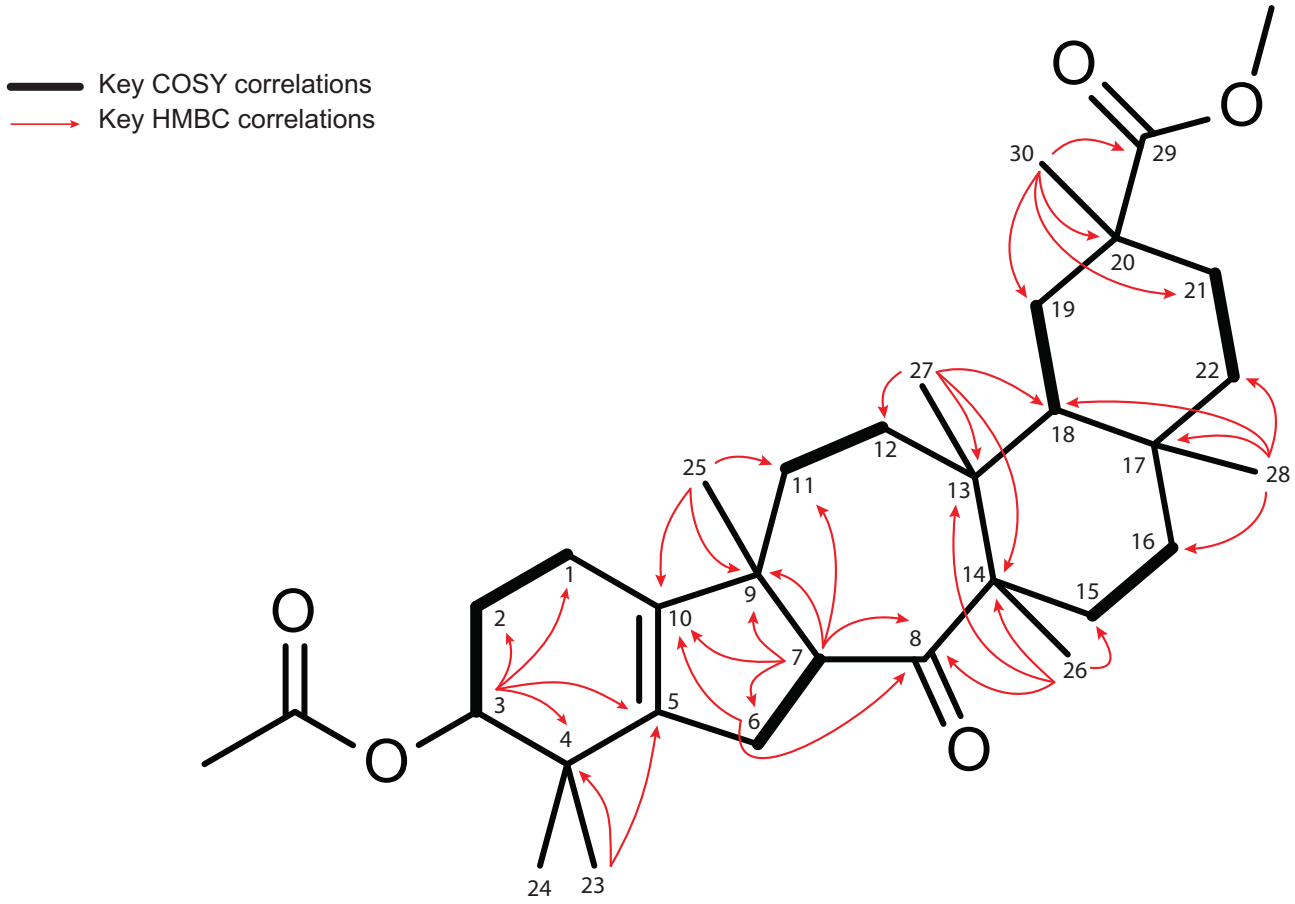
Figure S6. Key COSY, HMBC and NOESY correlations of **12** .

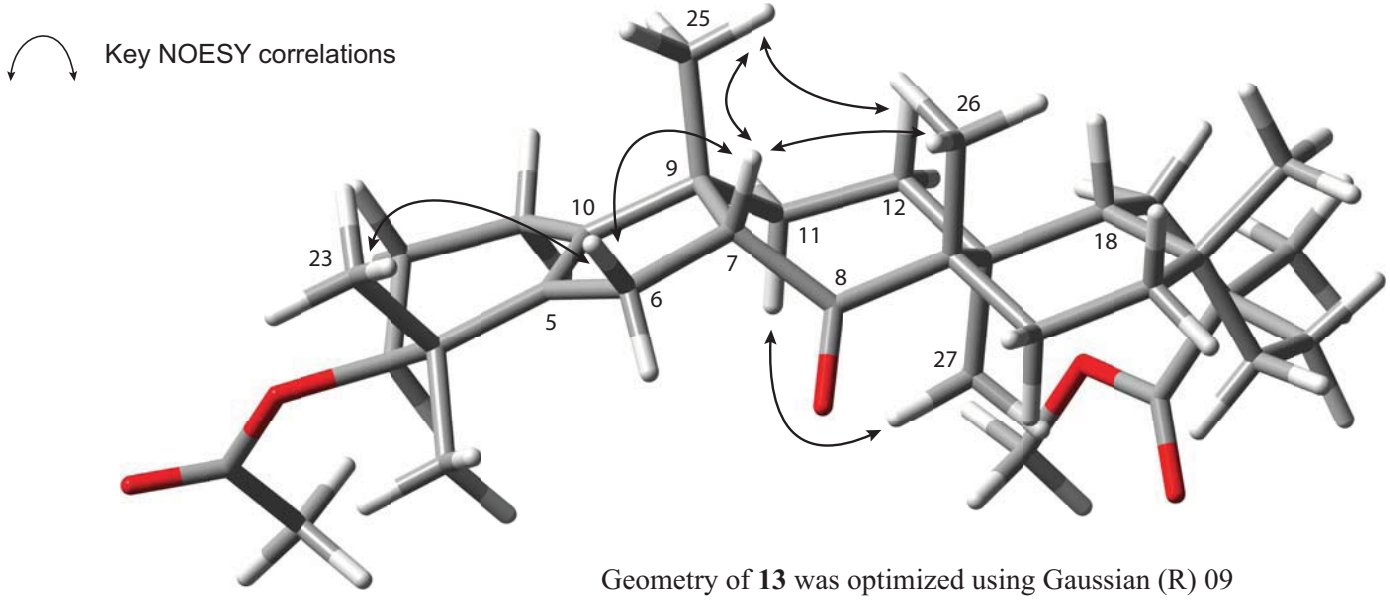




Geometry of **12** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

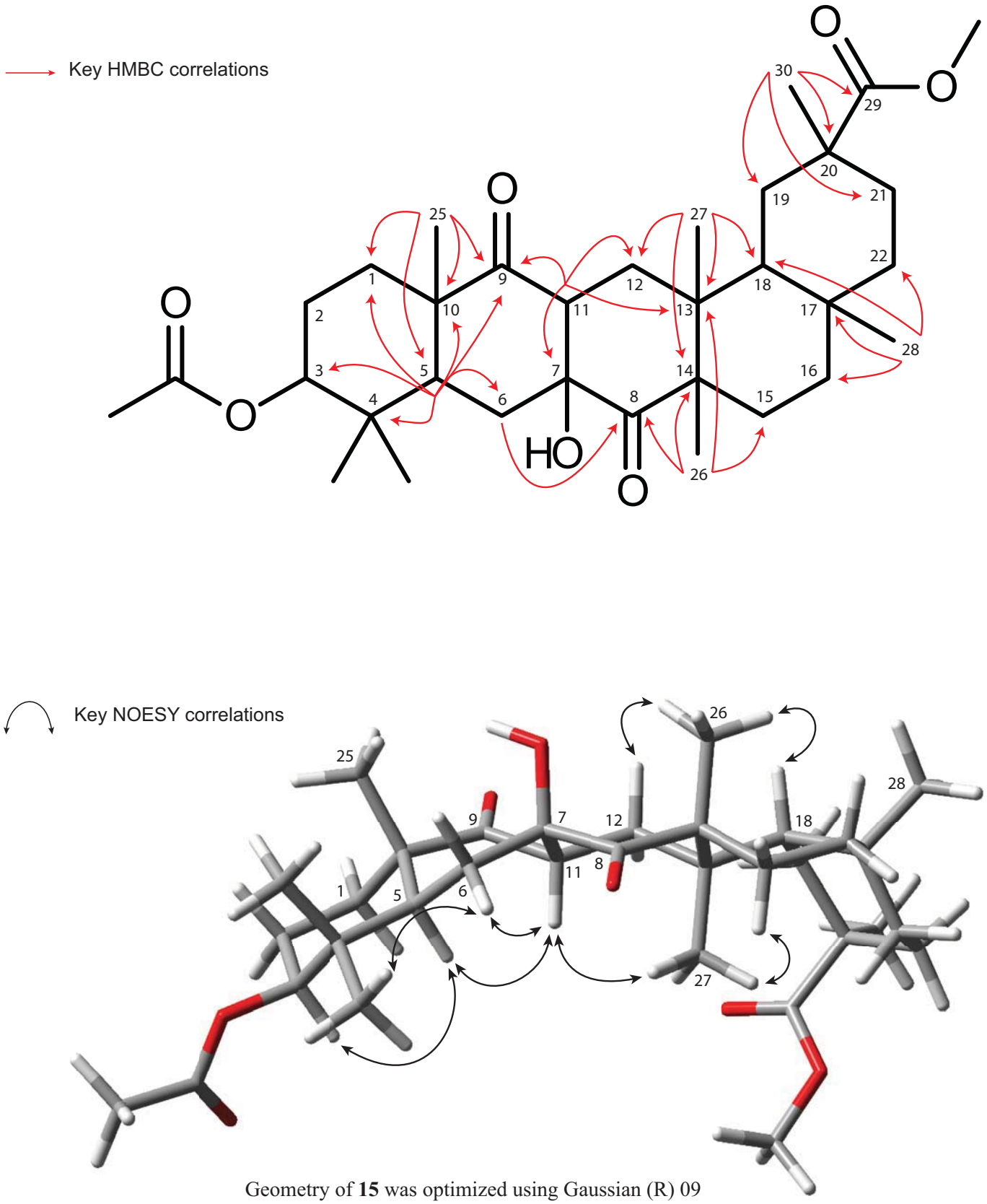
Figure S7. Key COSY, HMBC and NOESY correlations of **13** .





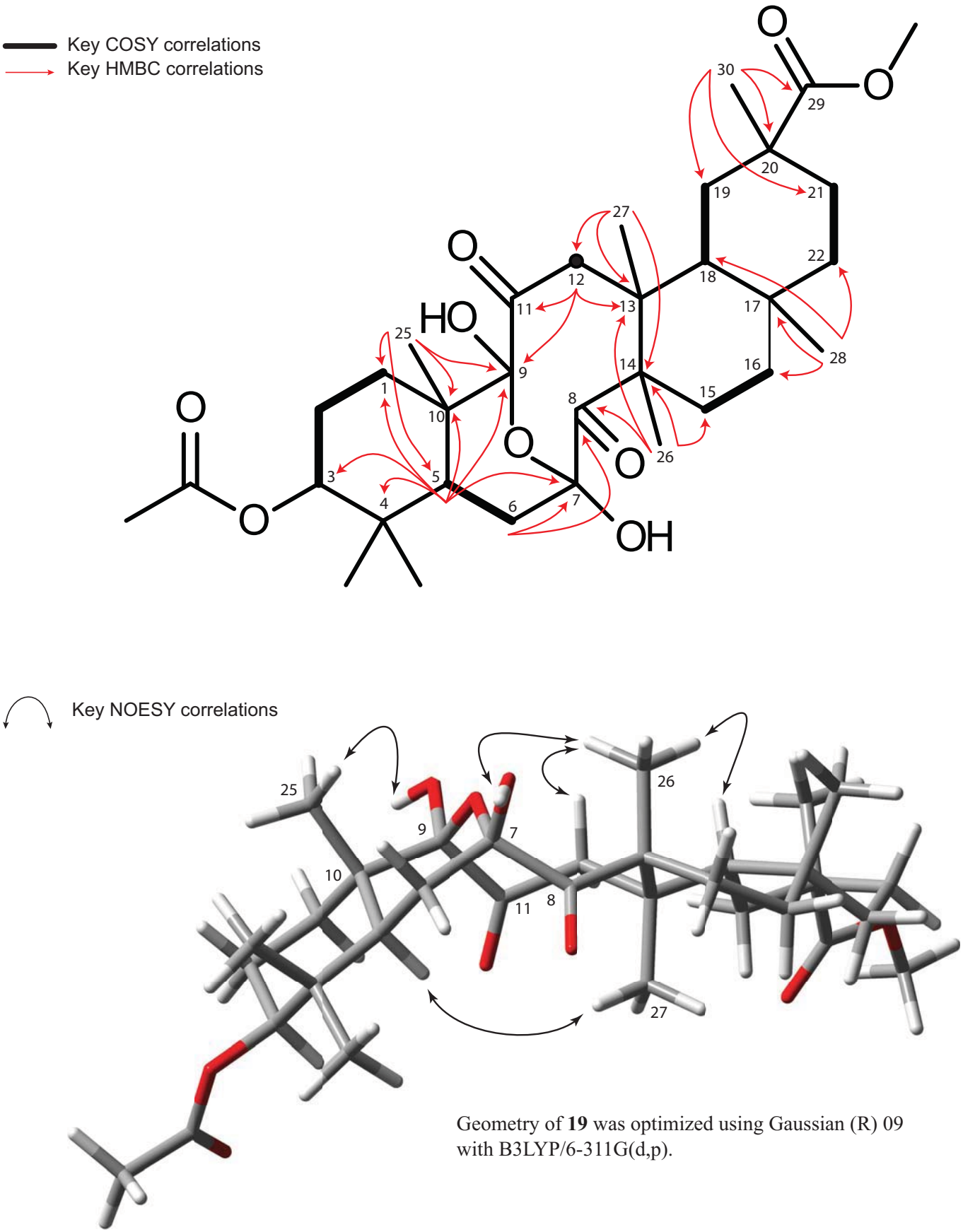
Geometry of **13** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

Figure S8. Key HMBC and NOESY correlations of **15** .



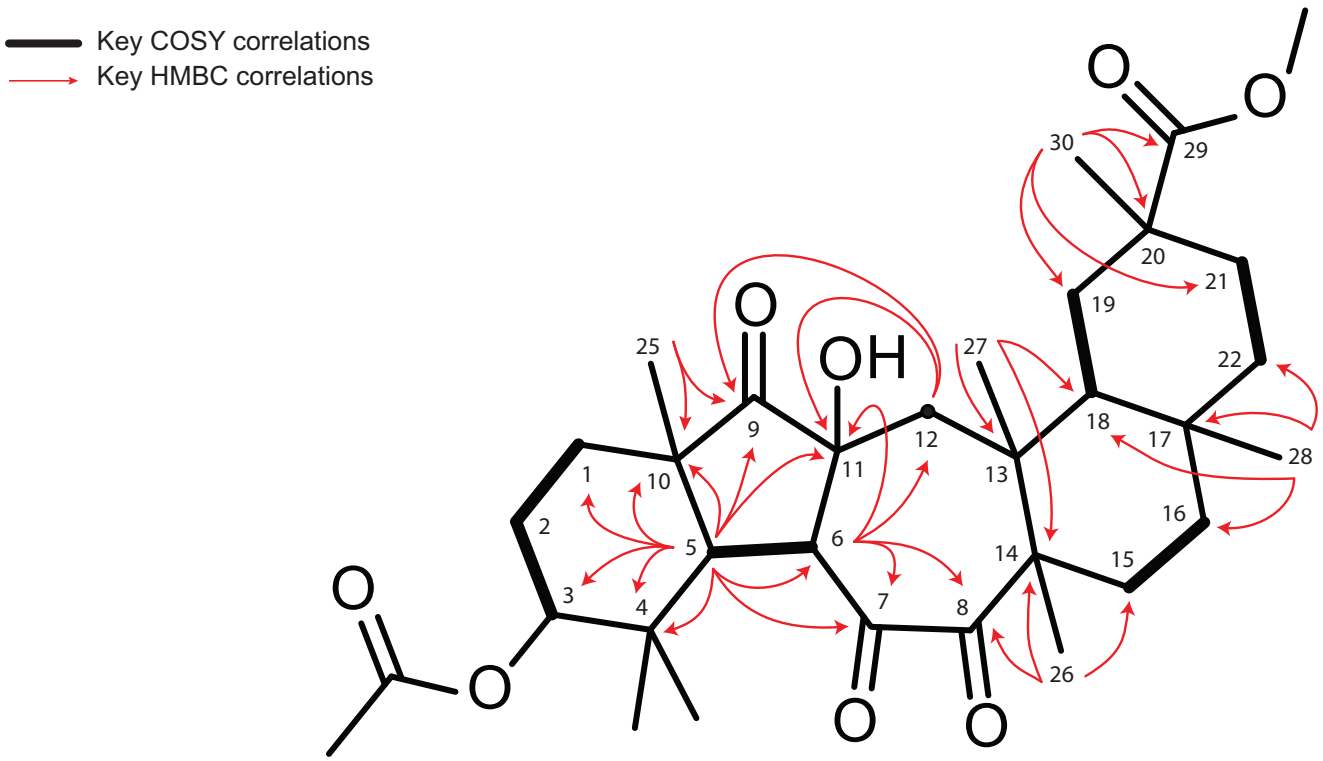
Geometry of **15** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

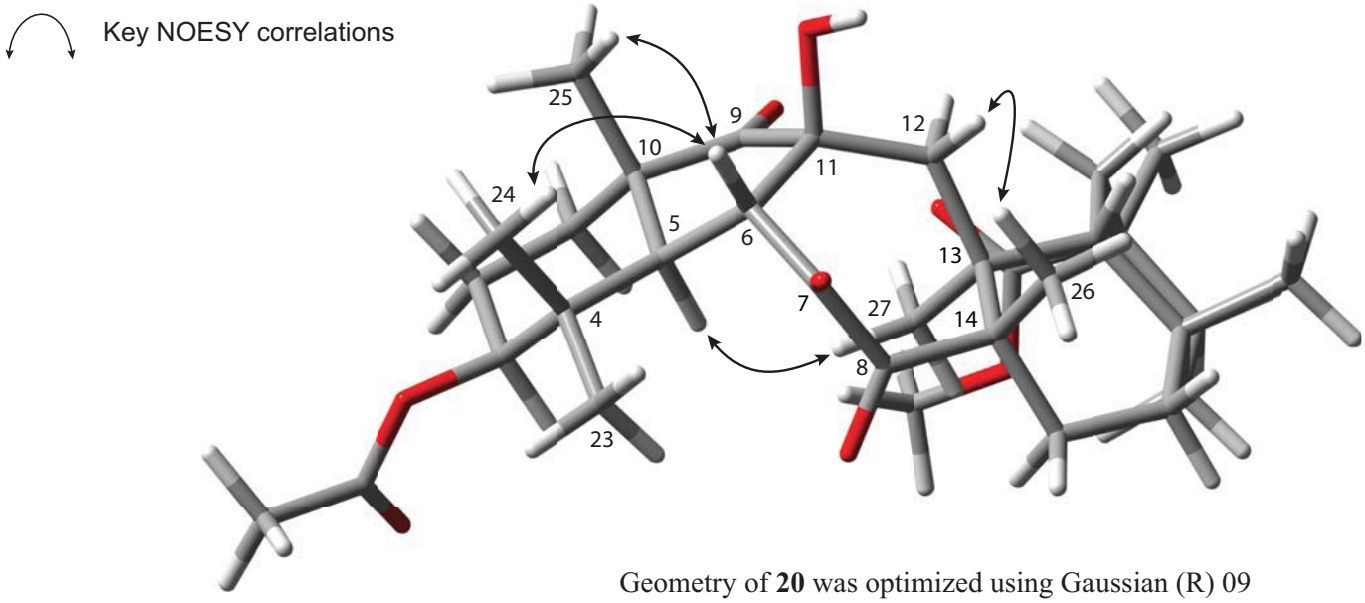
Figure S9. Key COSY, HMBC and NOESY correlations of **19** .



Geometry of **19** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

Figure S10. Key COSY, HMBC and NOESY correlations of **20** .





Geometry of **20** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

Figure S11. Key HMBC correlations of **6** .

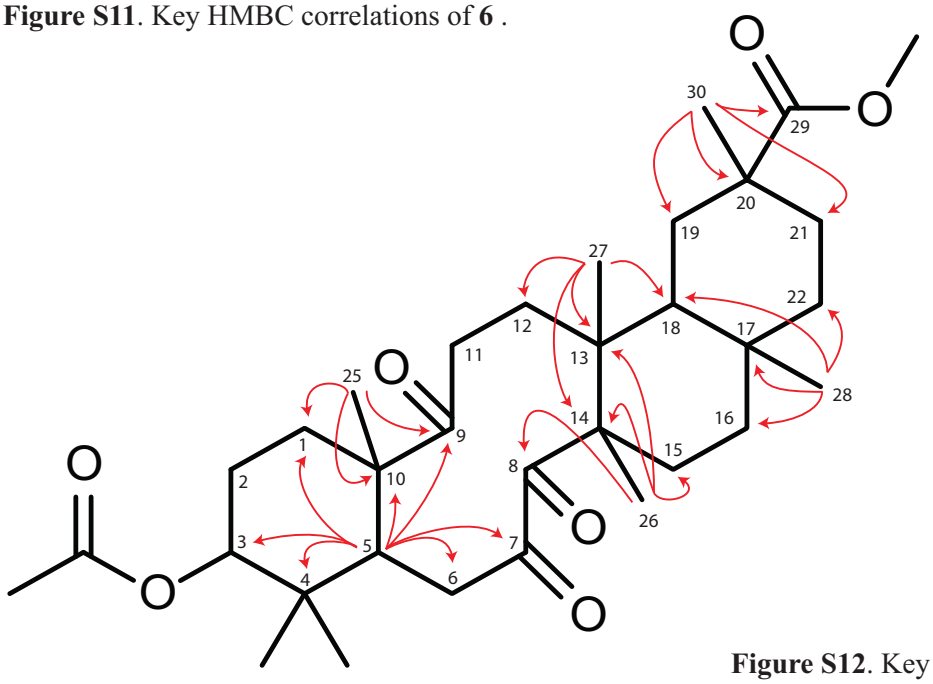


Figure S12. Key HMBC correlations of **14** .

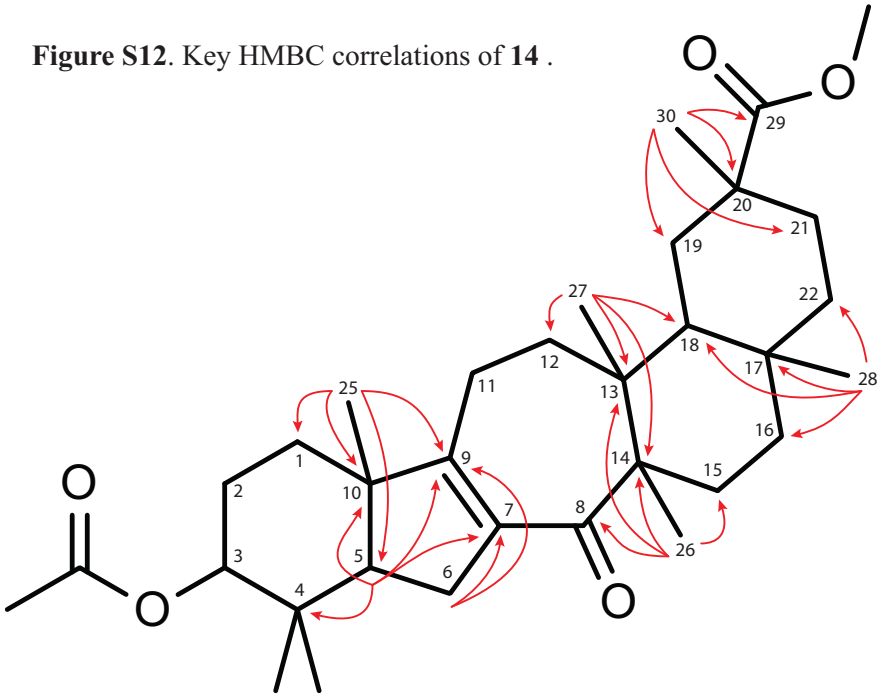


Figure S13. Key COSY and HMBC correlations of **17** .

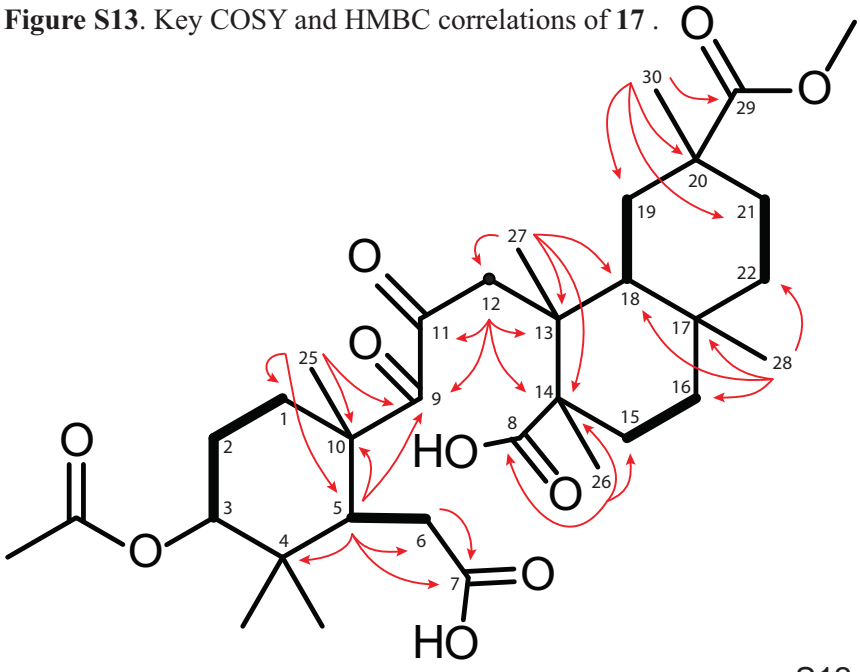
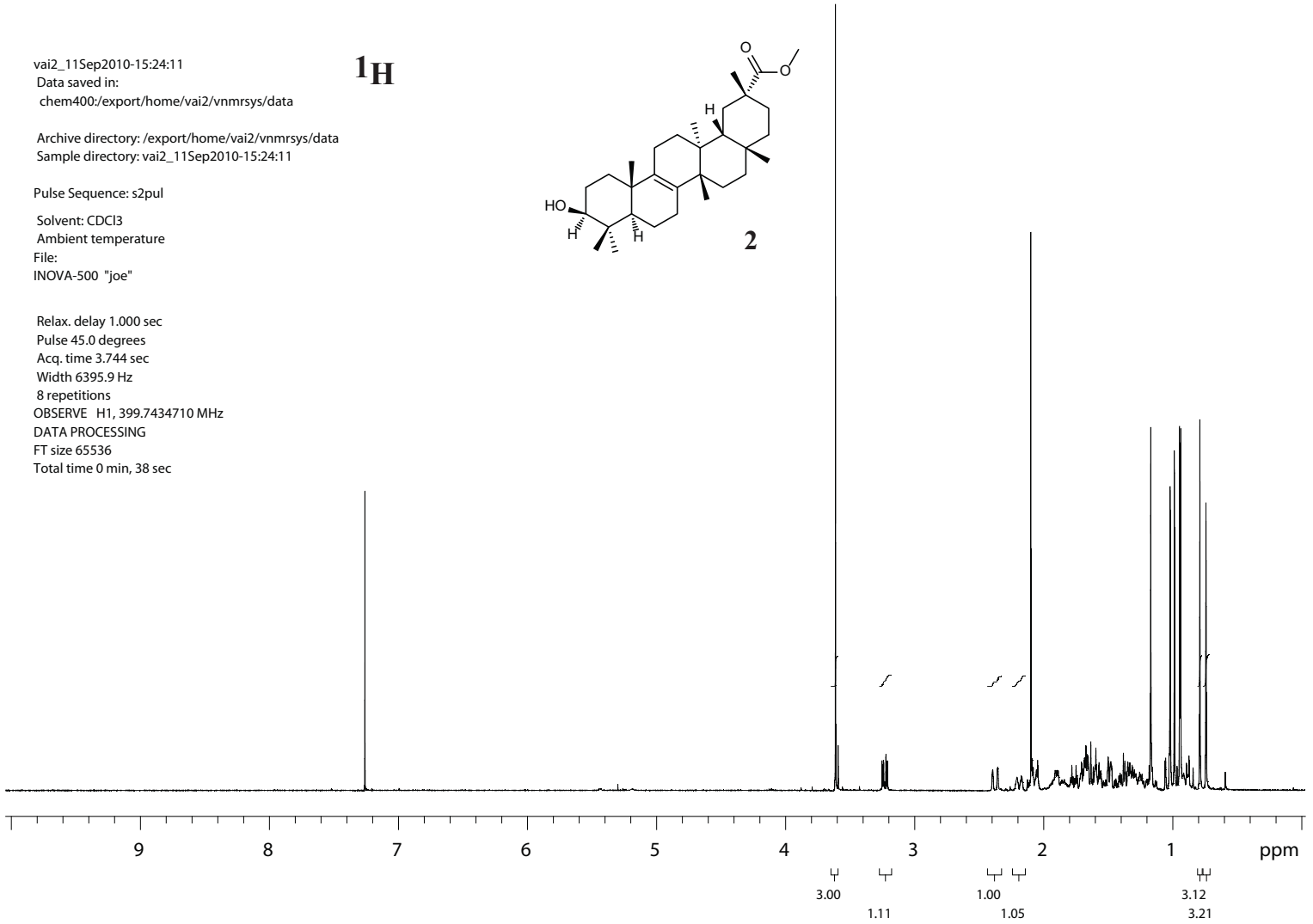


Figure S14. ^{1}H and ^{13}C spectra of **2**.



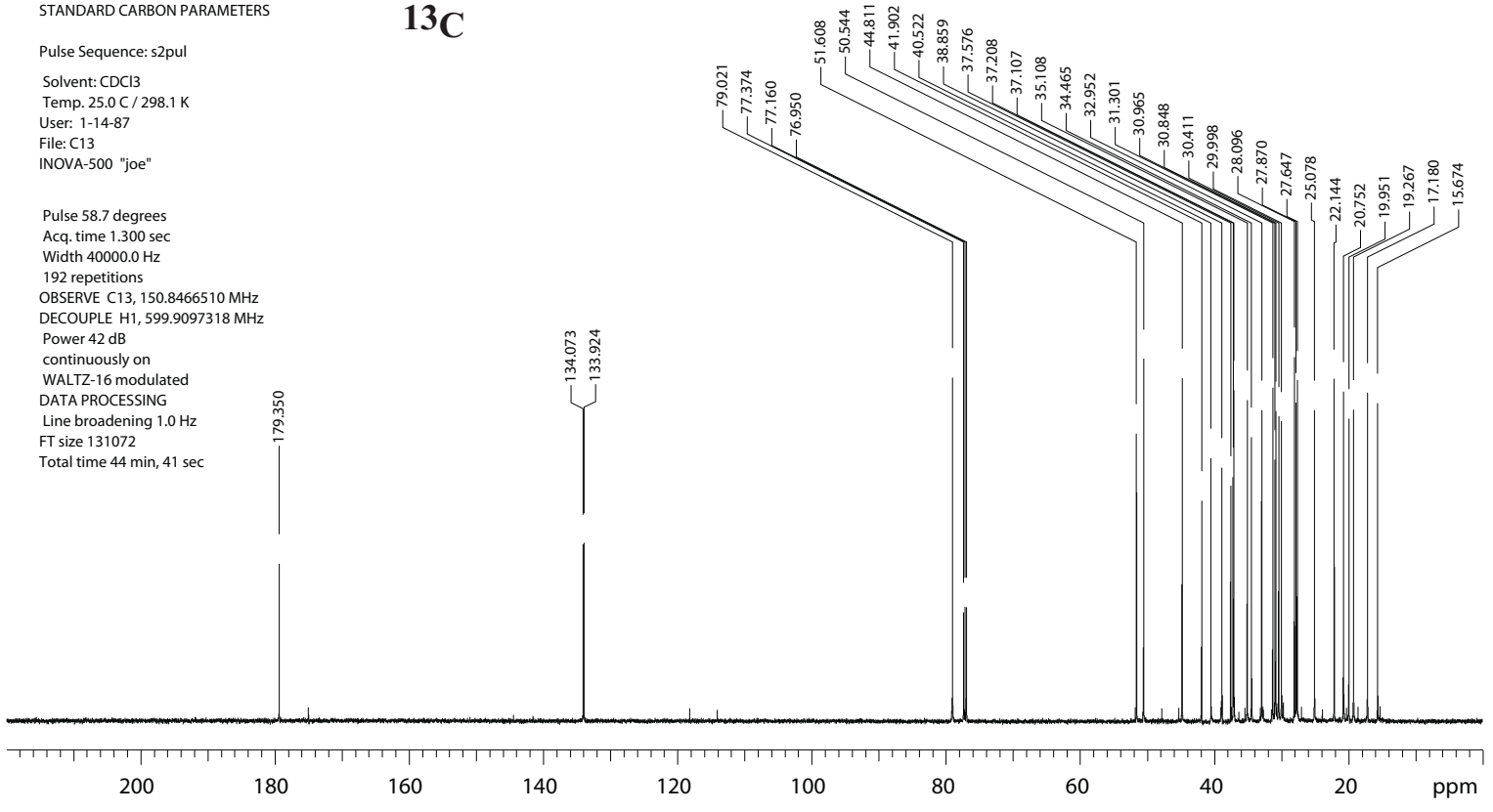
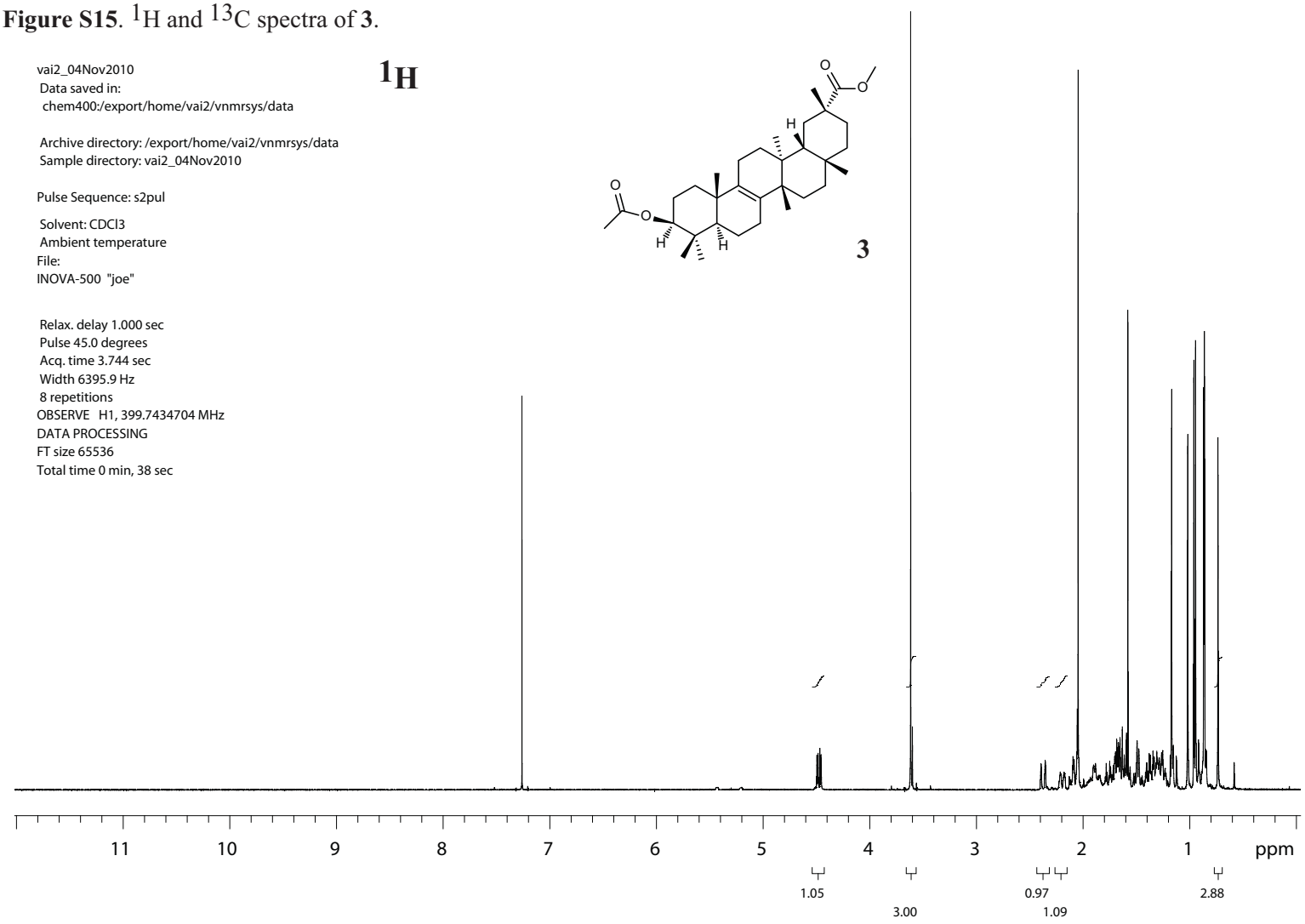


Figure S15. ^{1}H and ^{13}C spectra of **3**.



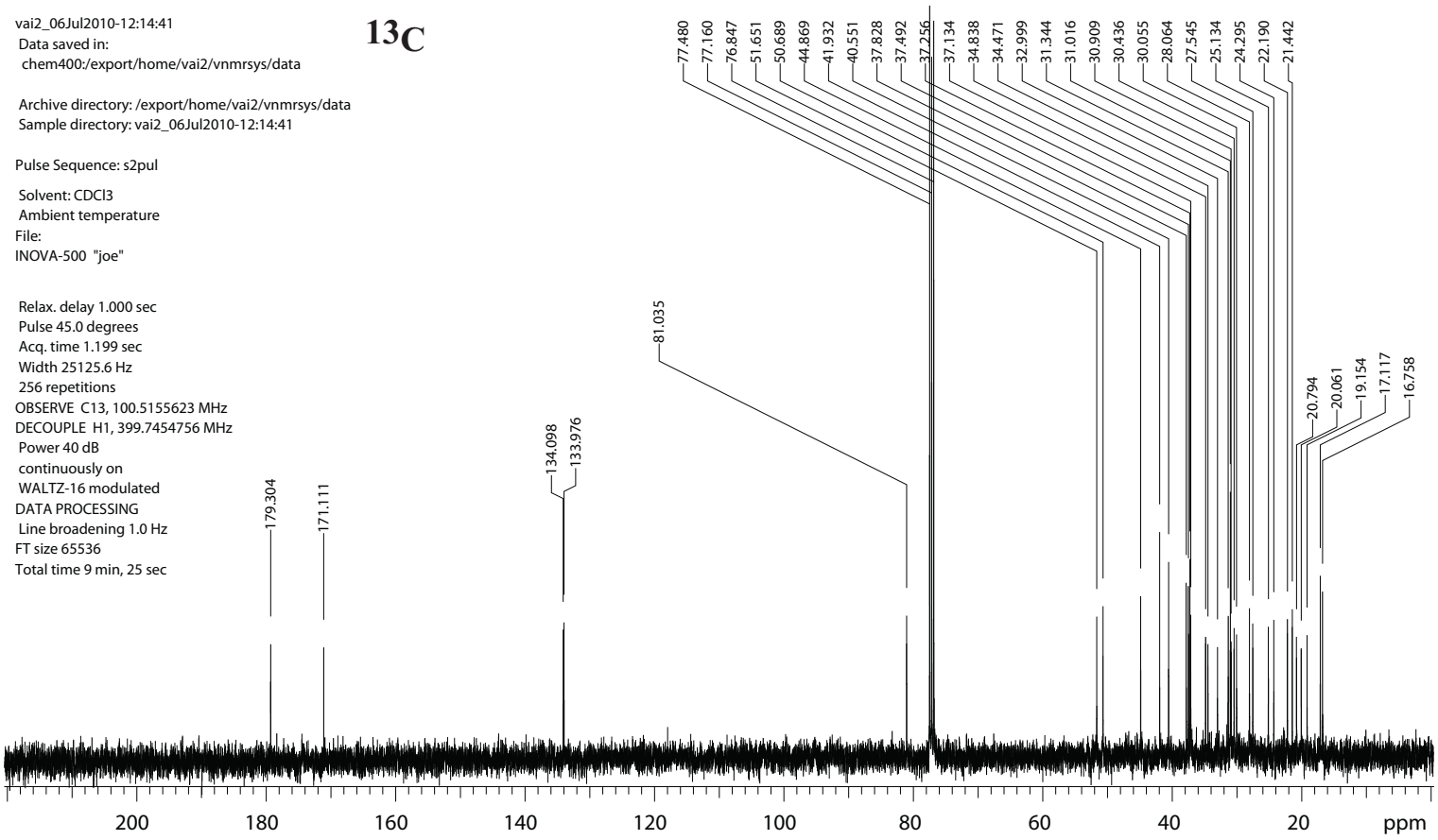
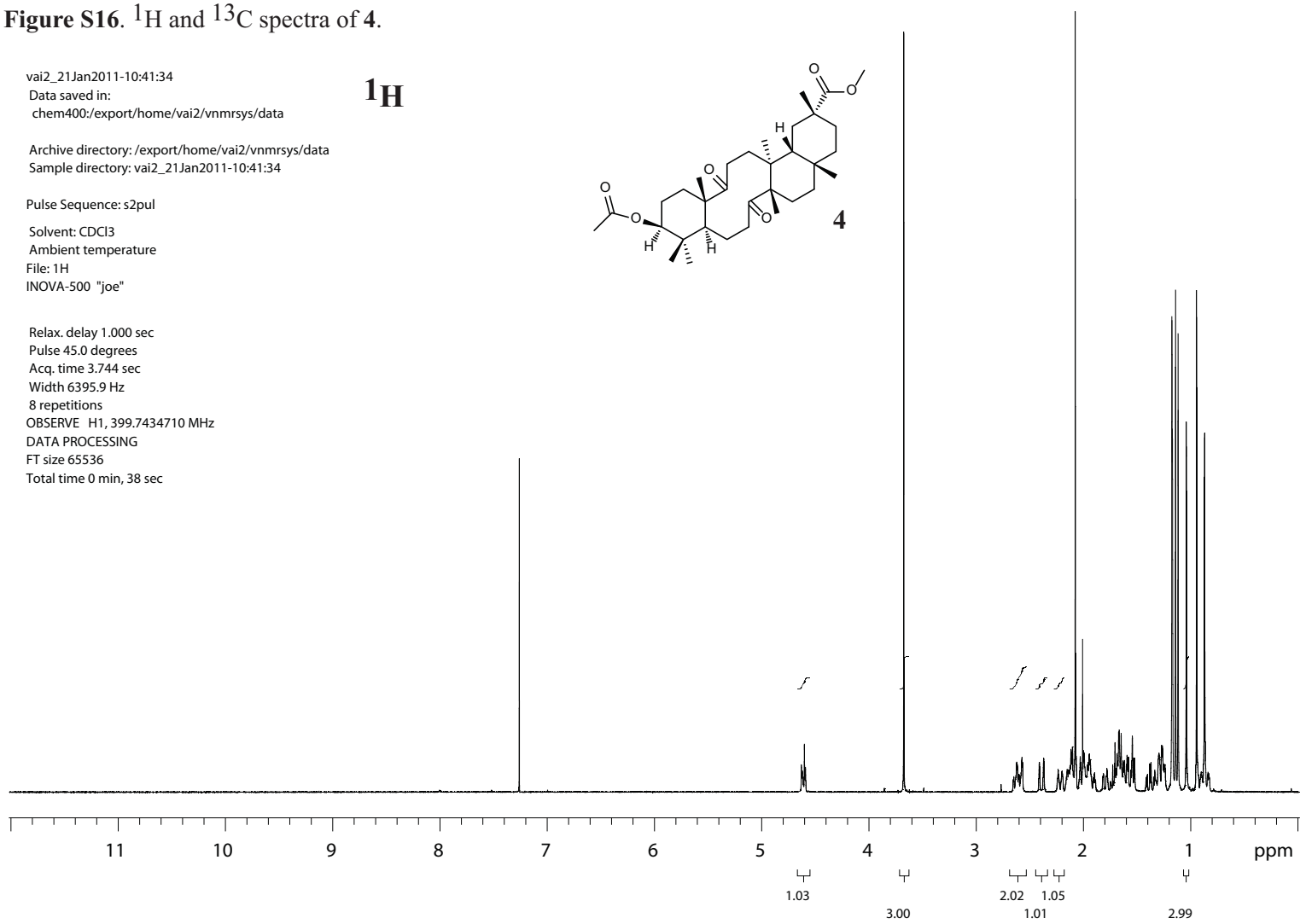


Figure S16. ^{1}H and ^{13}C spectra of **4**.



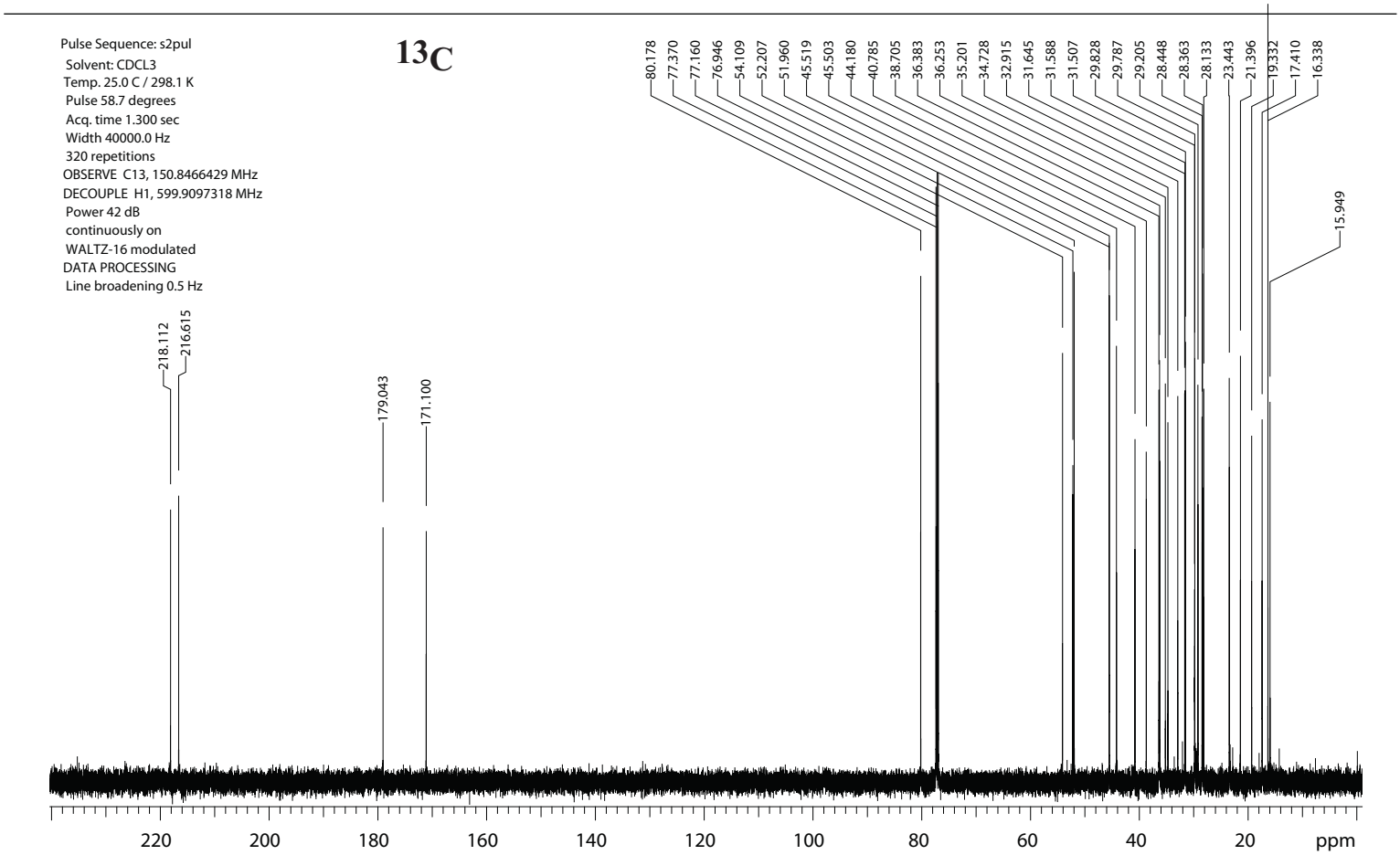
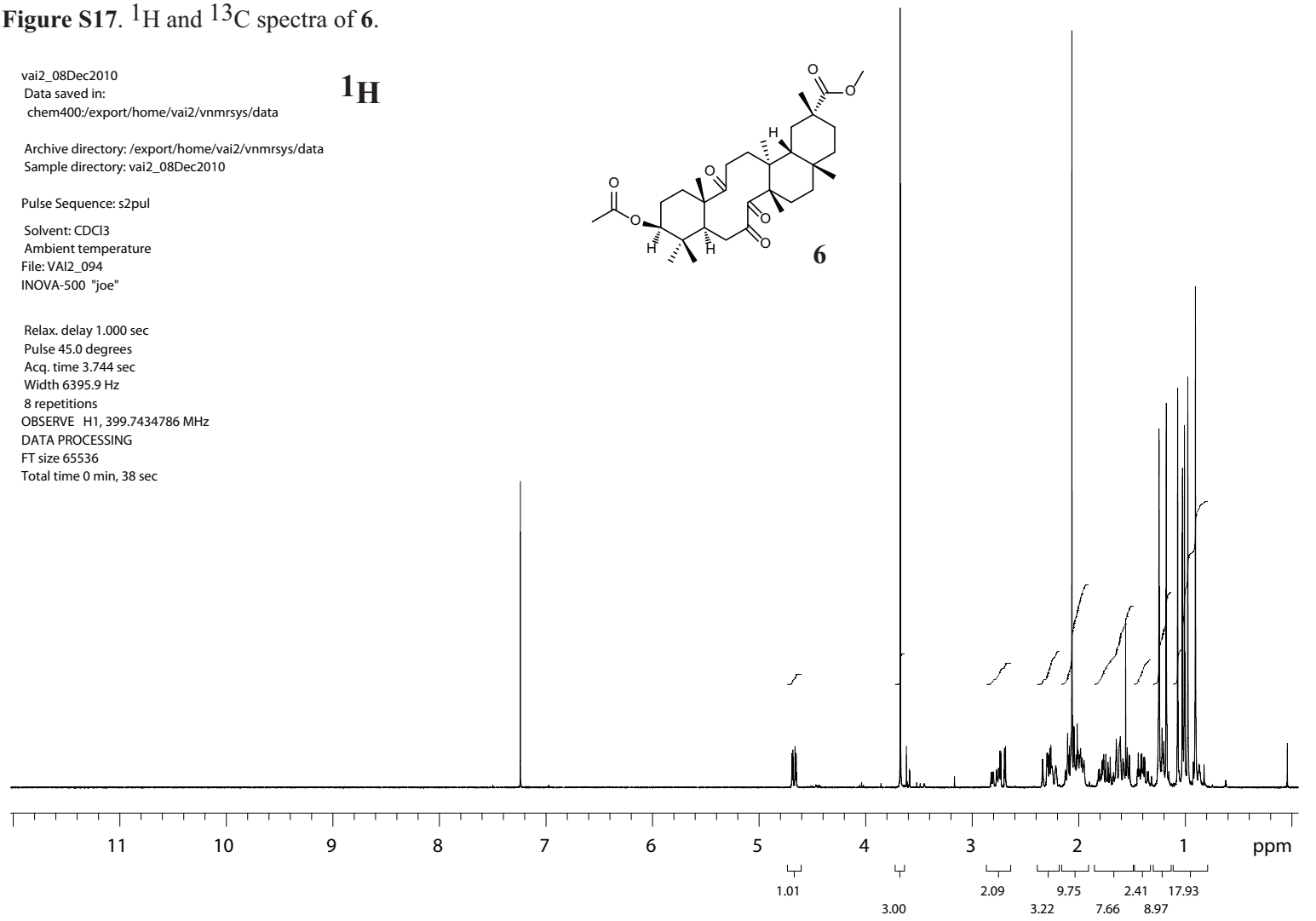


Figure S17. ^{1}H and ^{13}C spectra of **6**.



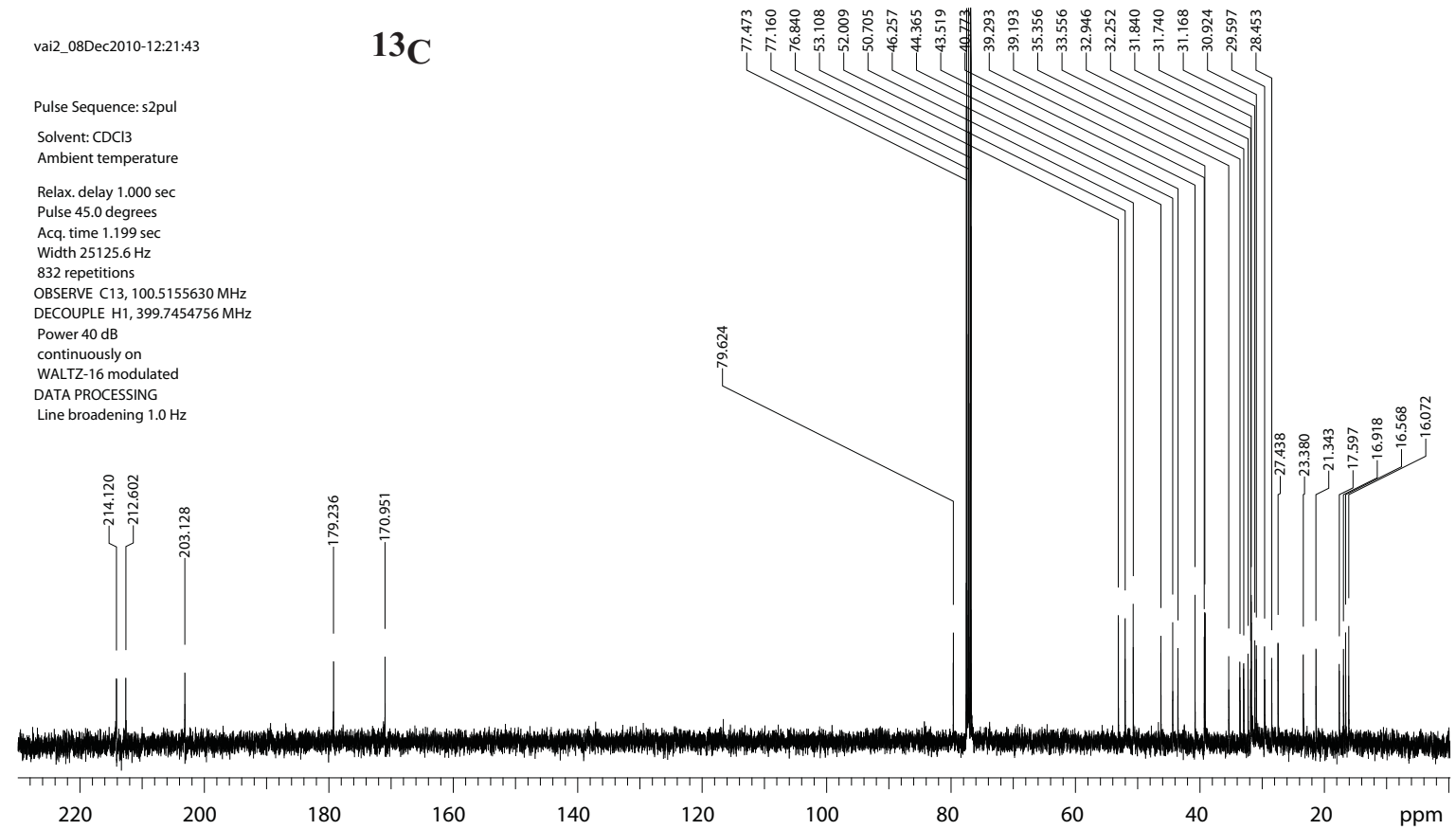
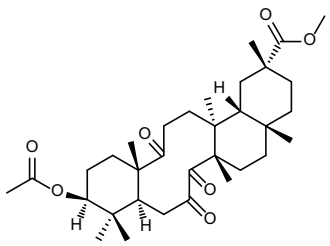


Figure S18. HMQC and HMBC spectra of **6**.



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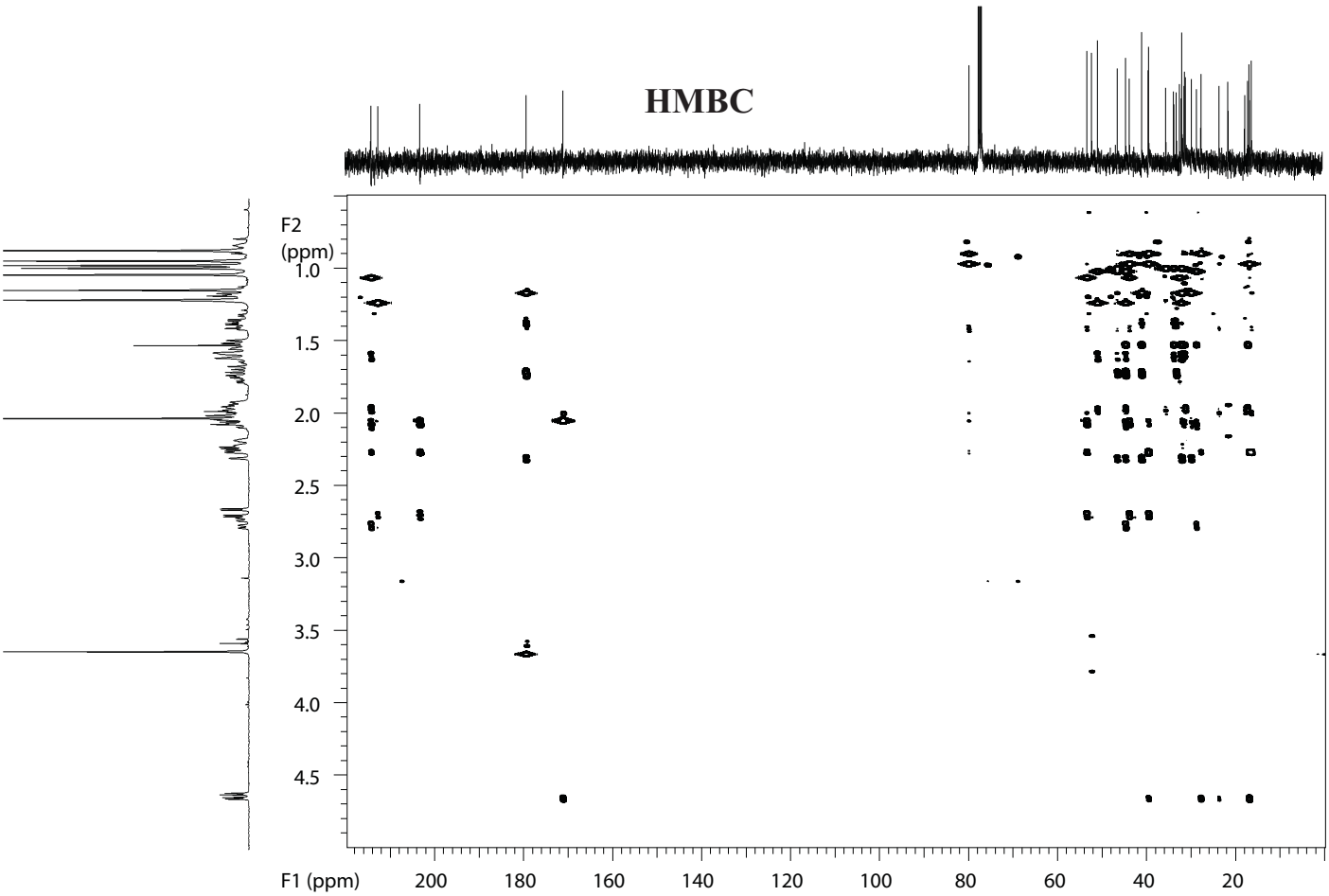


Figure S19. ^{1}H and ^{13}C spectra of **7**.

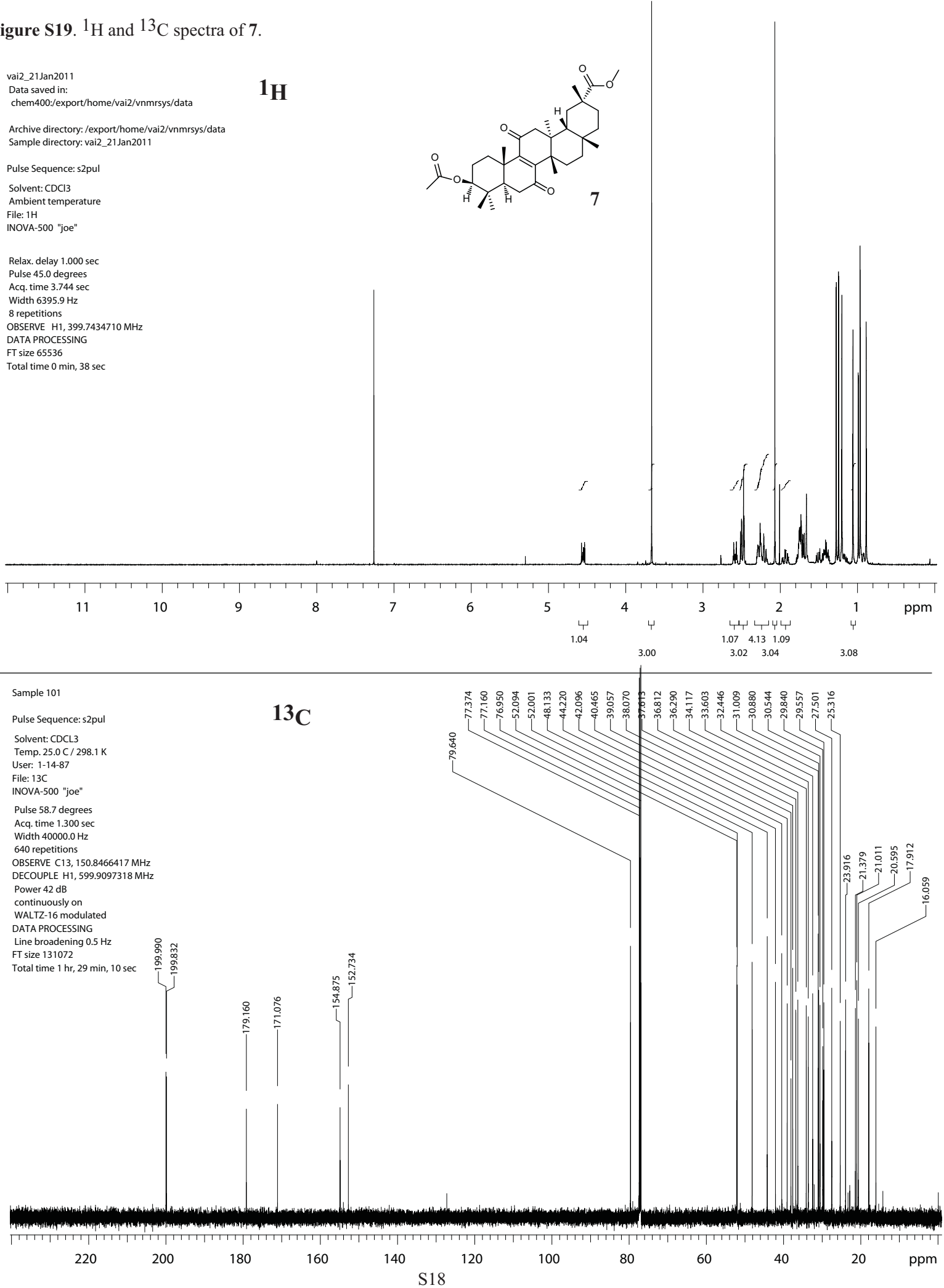
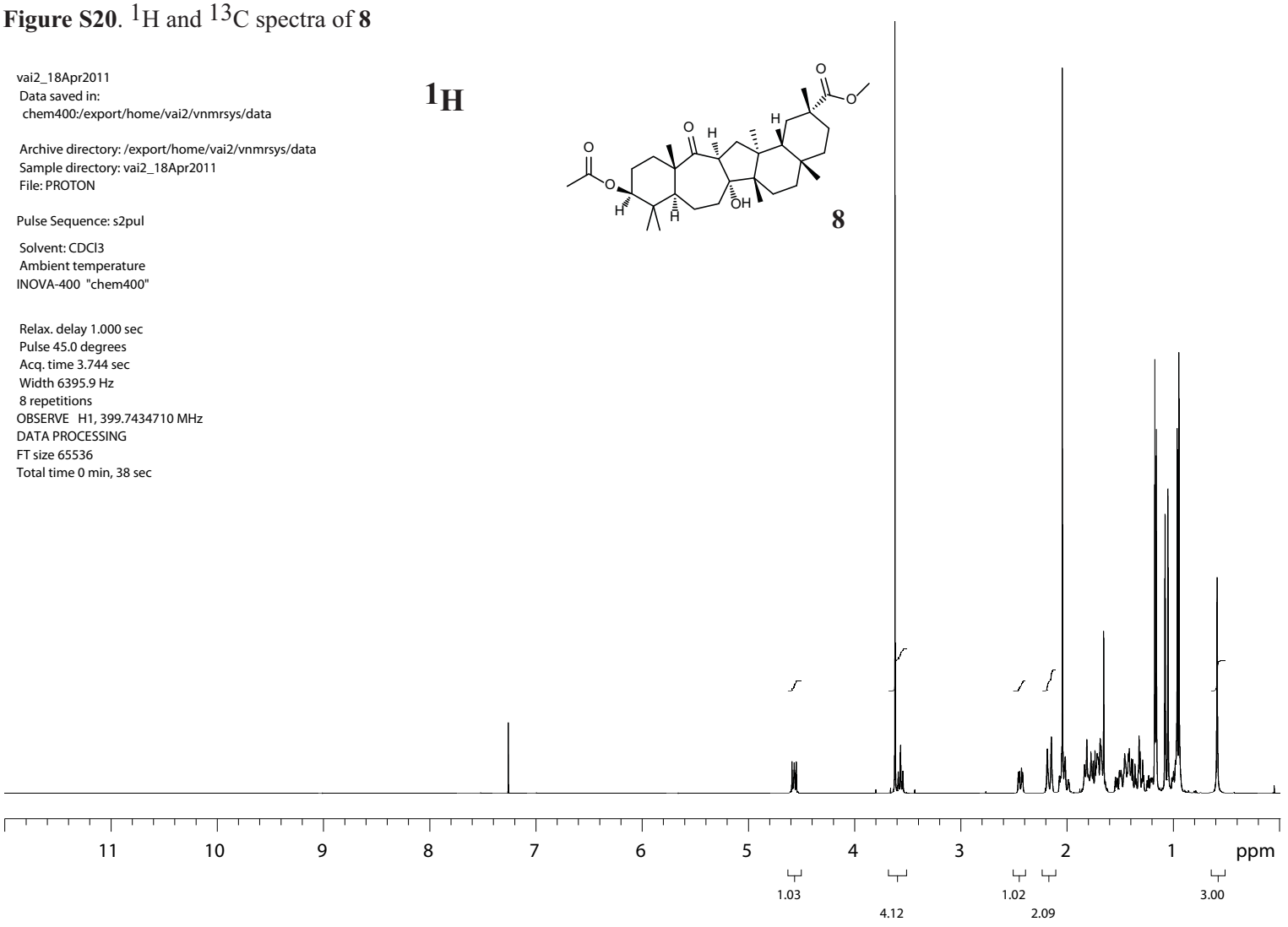


Figure S20. ^{1}H and ^{13}C spectra of **8**



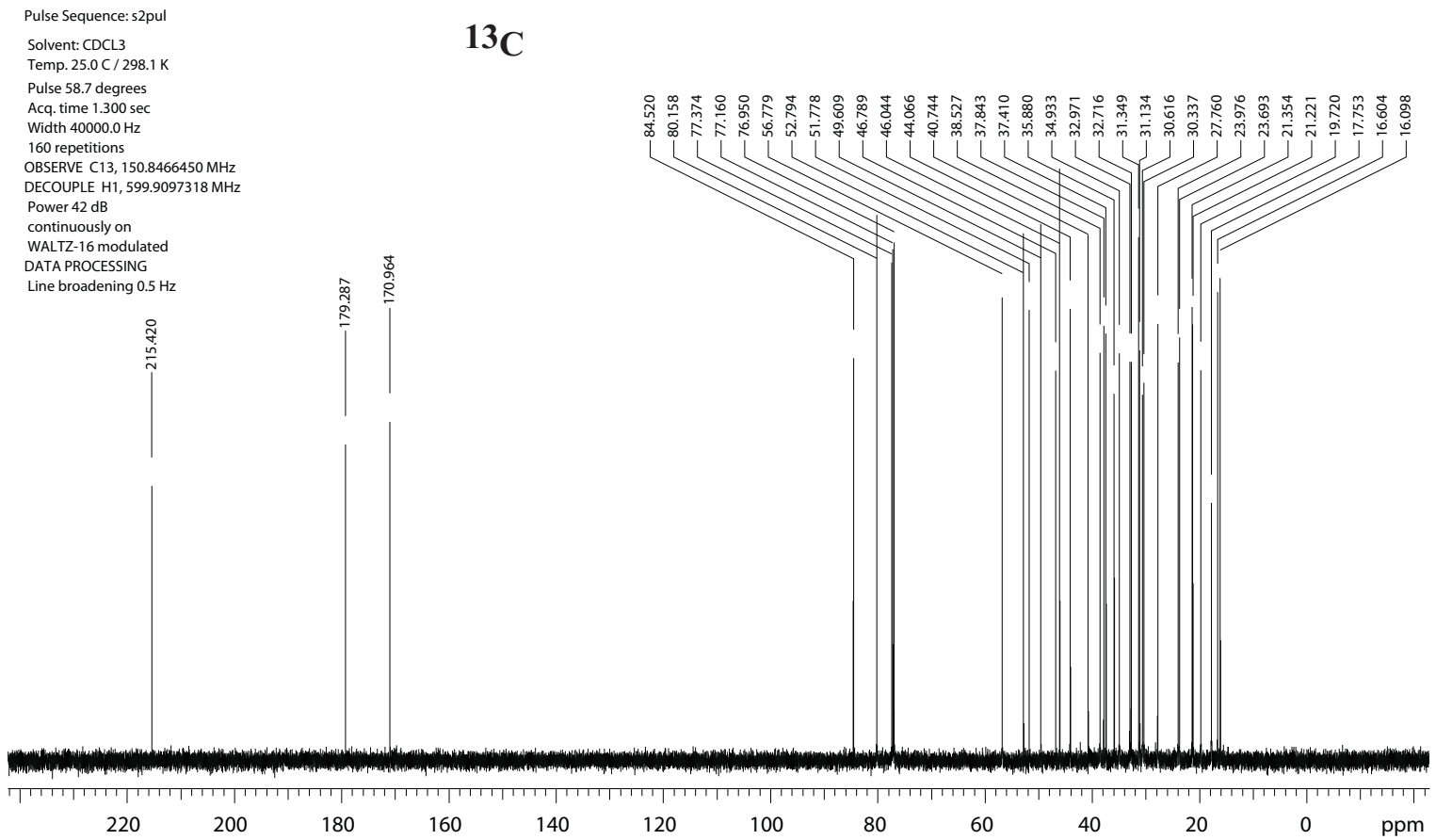
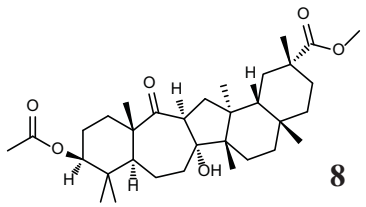


Figure S21. HMQC and HMBC spectra of **8**.



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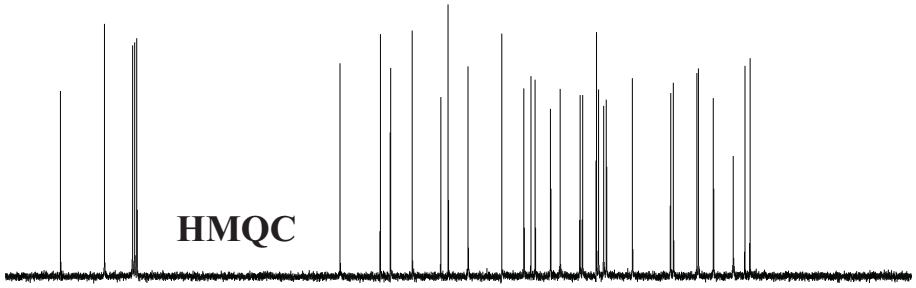
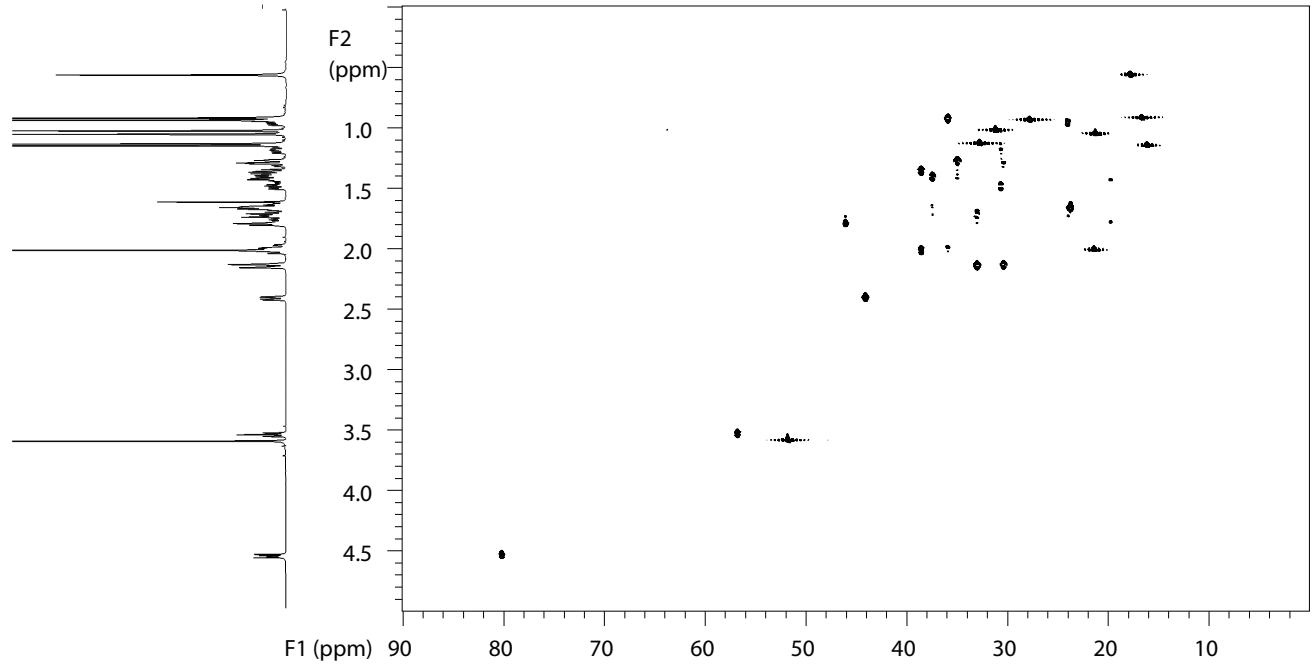
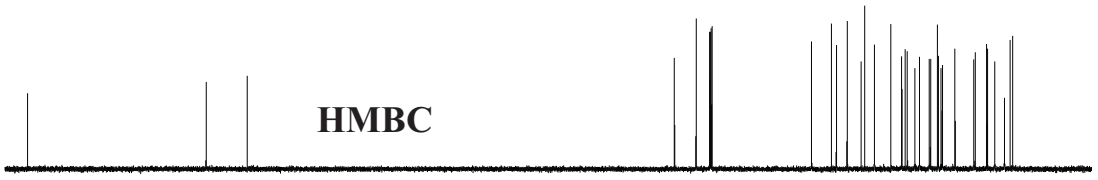






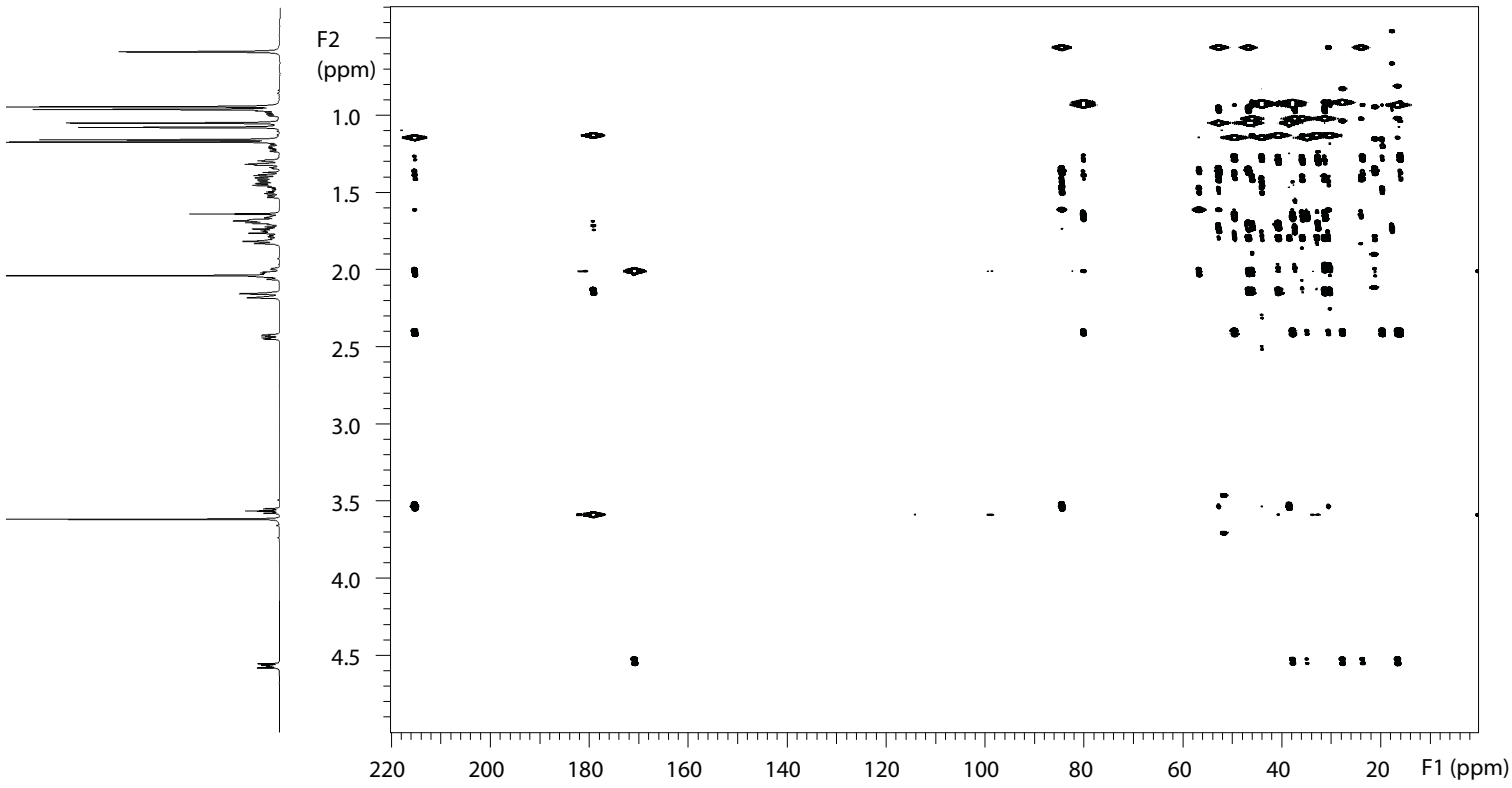
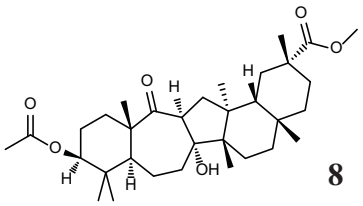


Figure S22. COSY and NOESY spectra of **8**.



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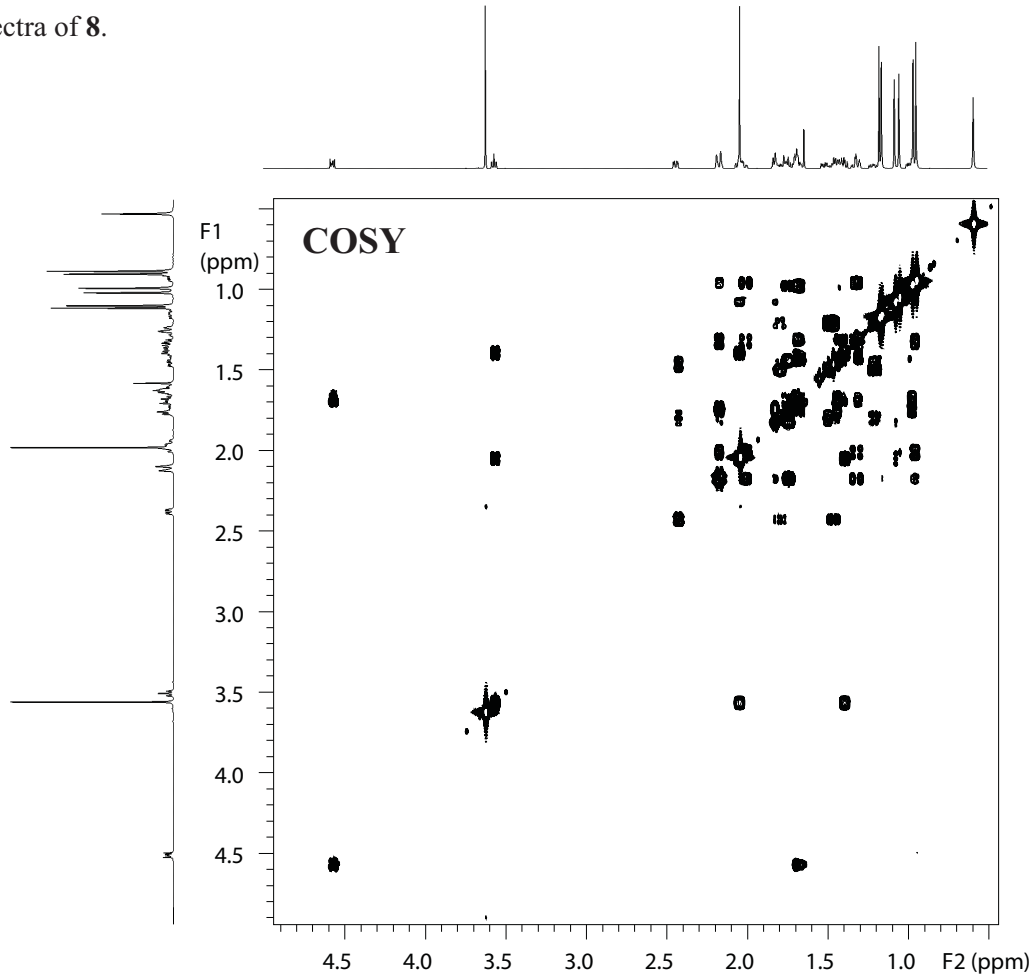


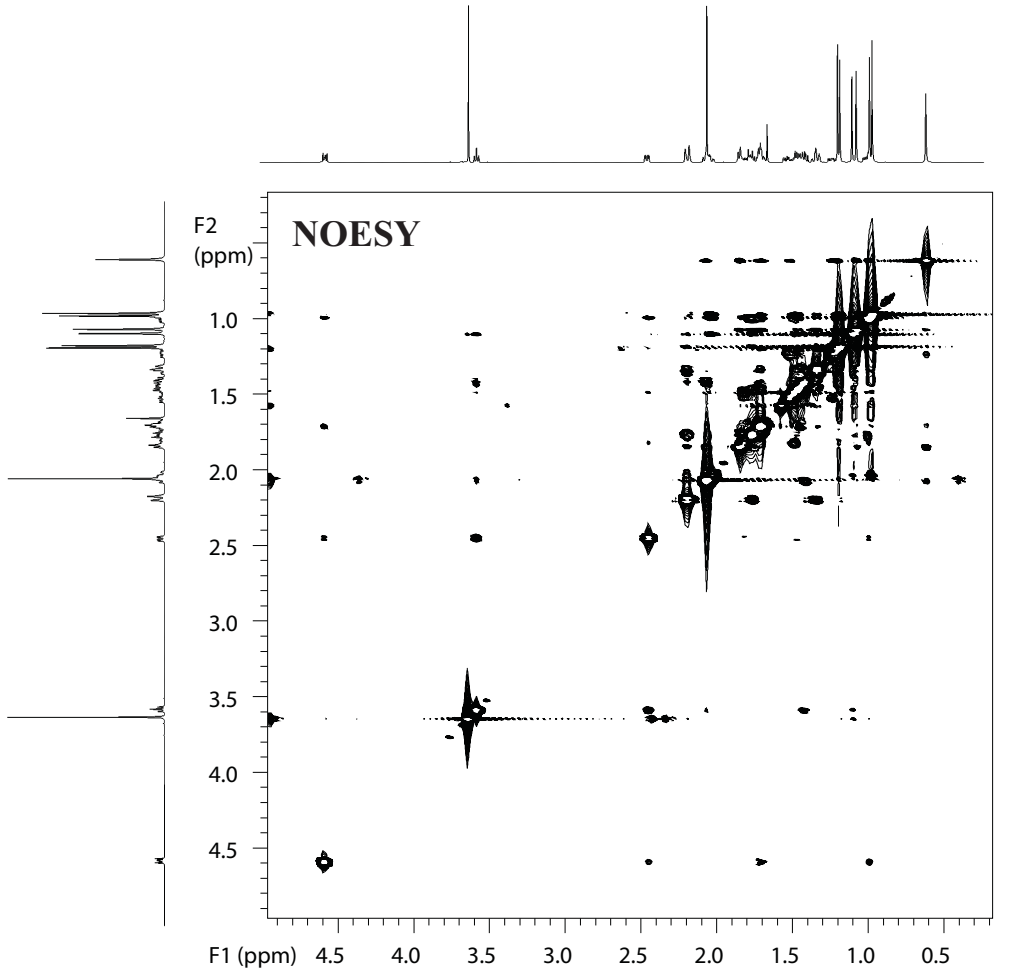
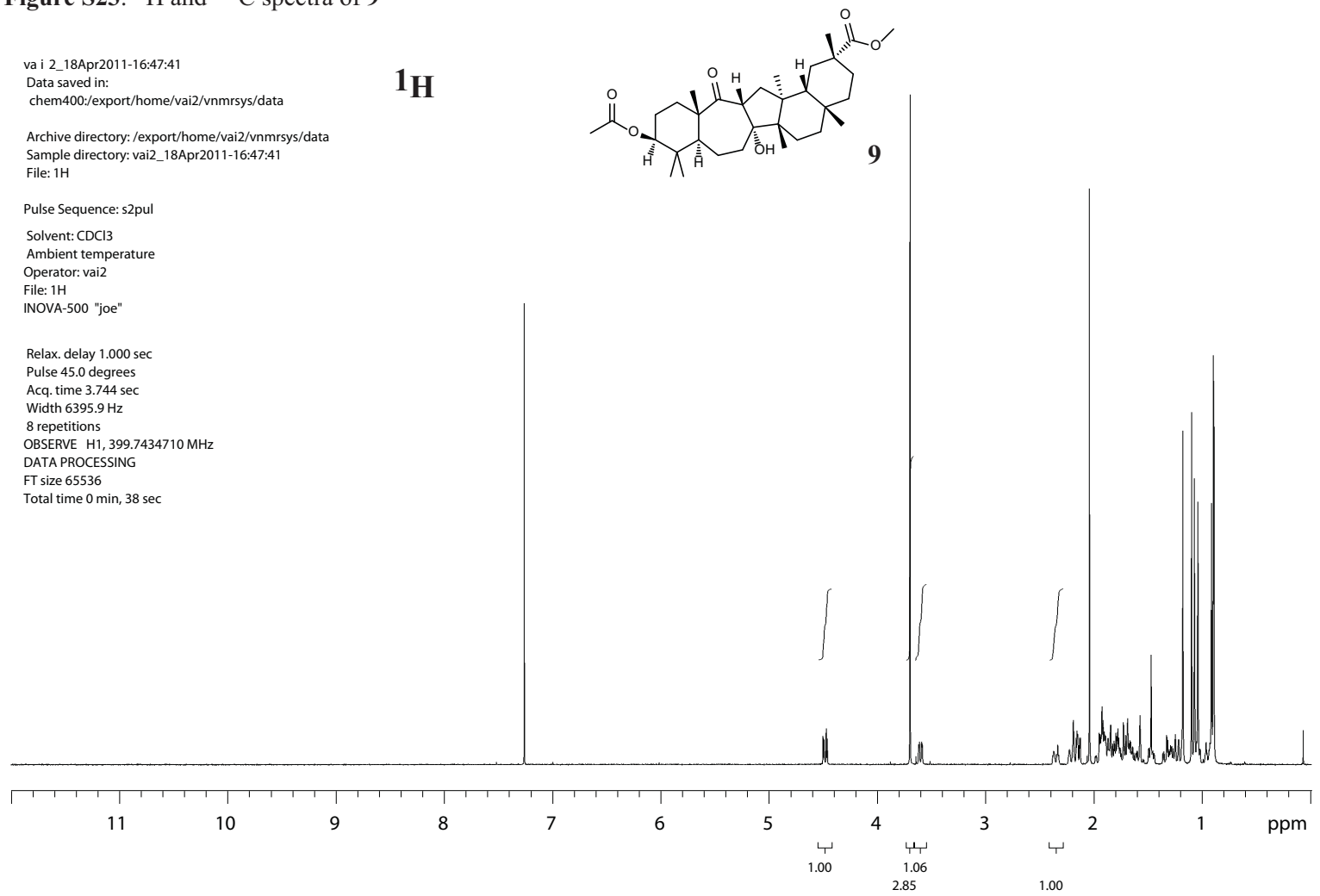


Figure S23. ^{1}H and ^{13}C spectra of **9**



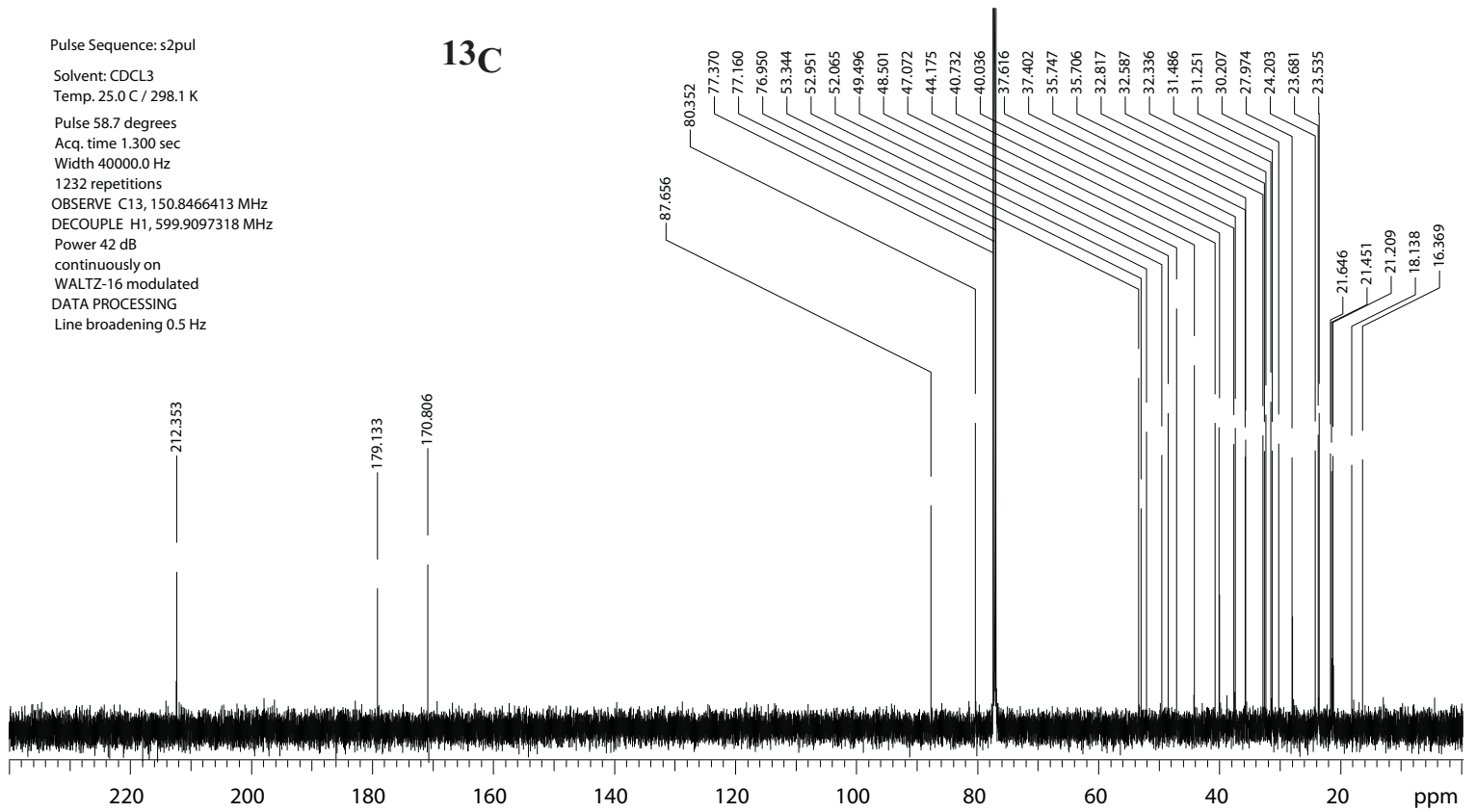
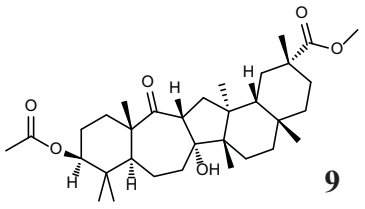


Figure S24. HMQC and HMBC spectra of **9**.



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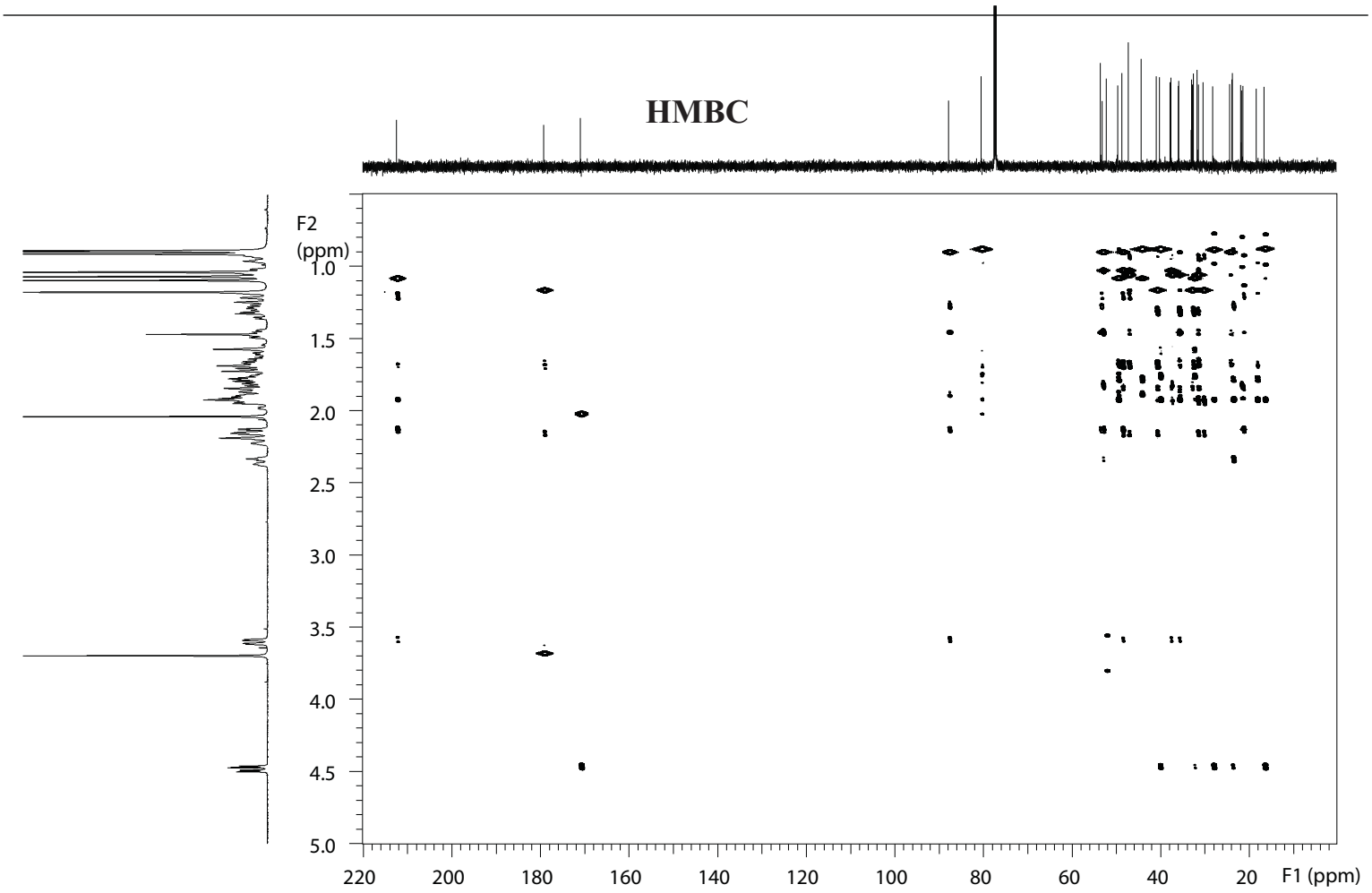
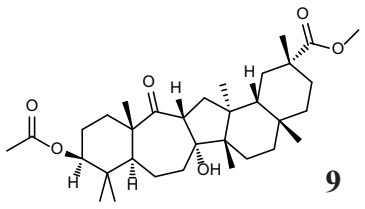


Figure S25. COSY and NOESY spectra of **9**.



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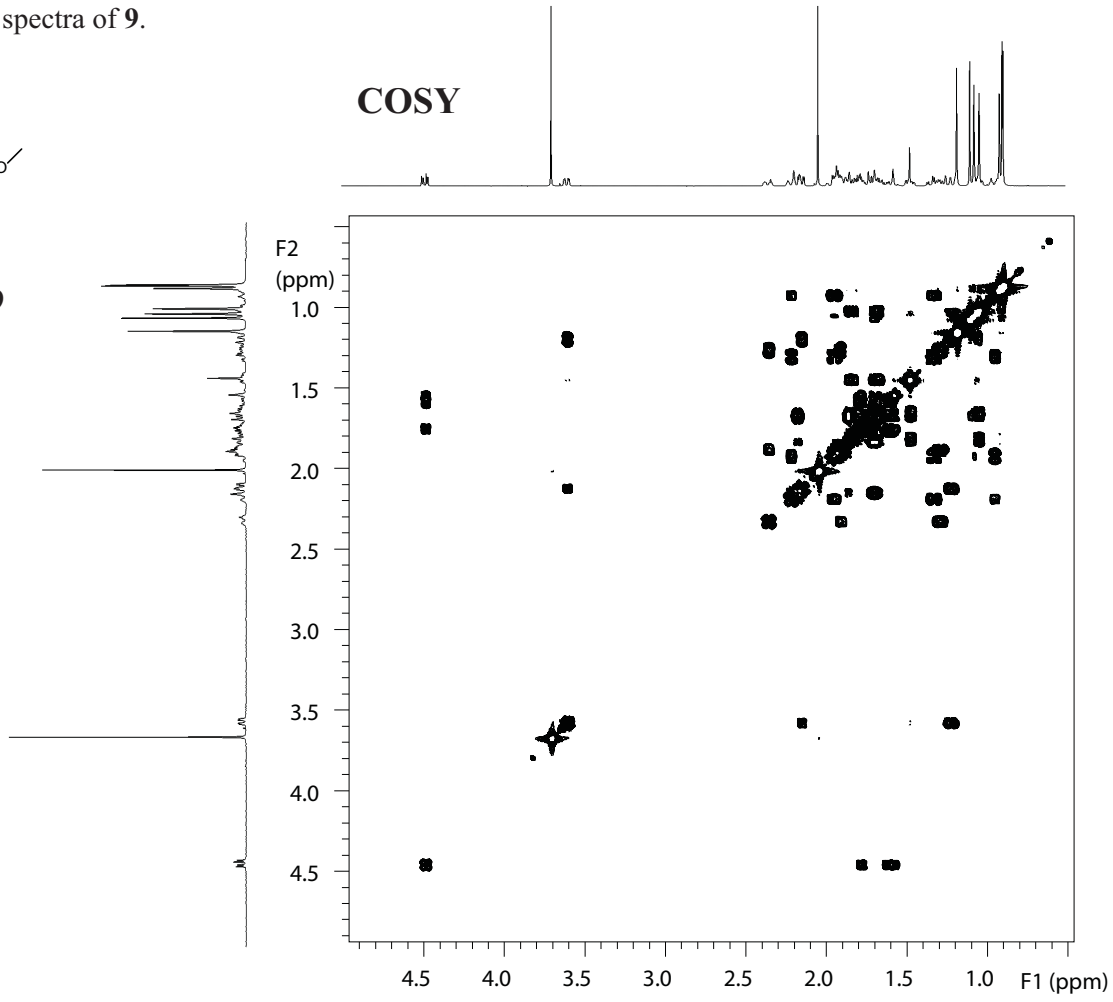


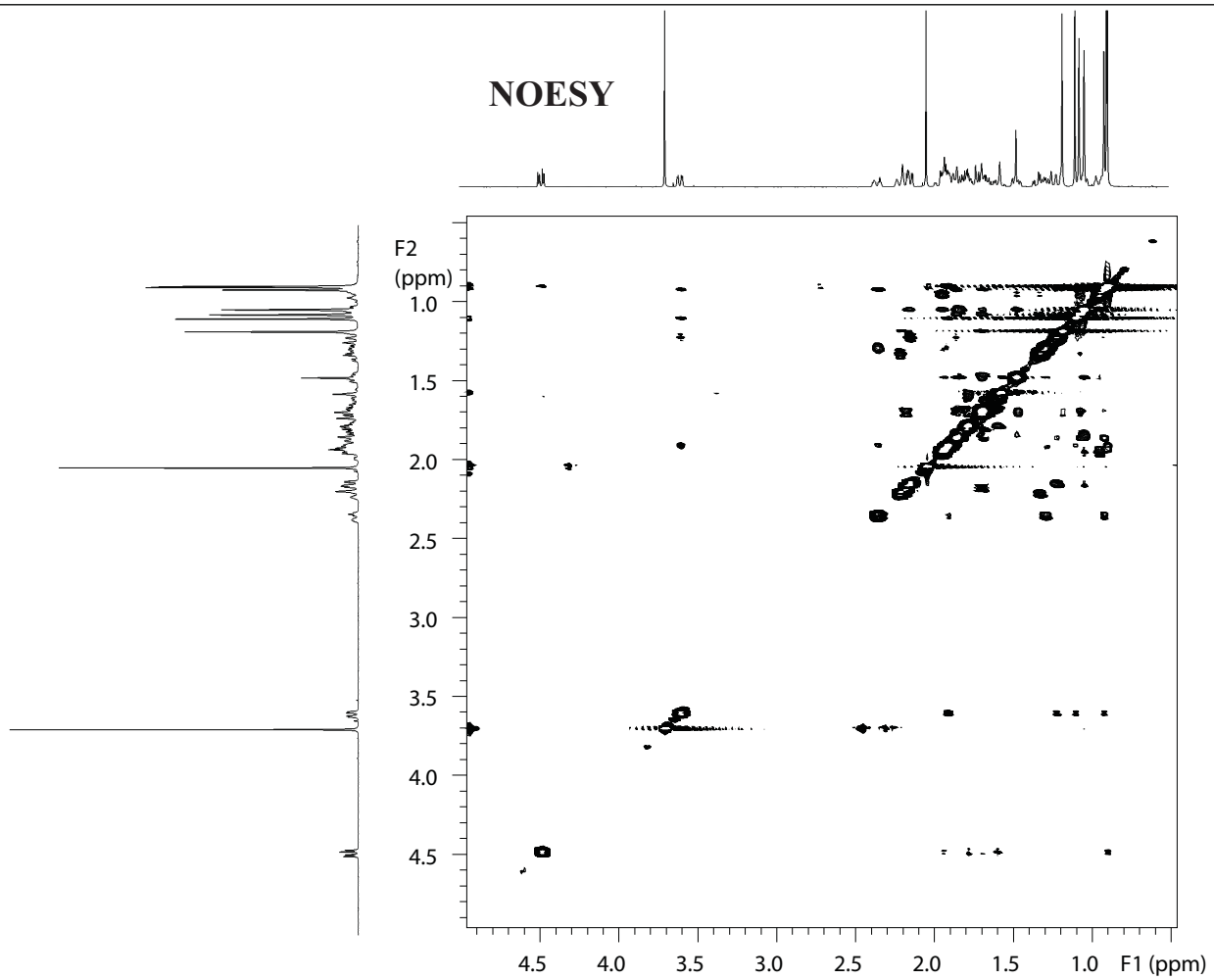
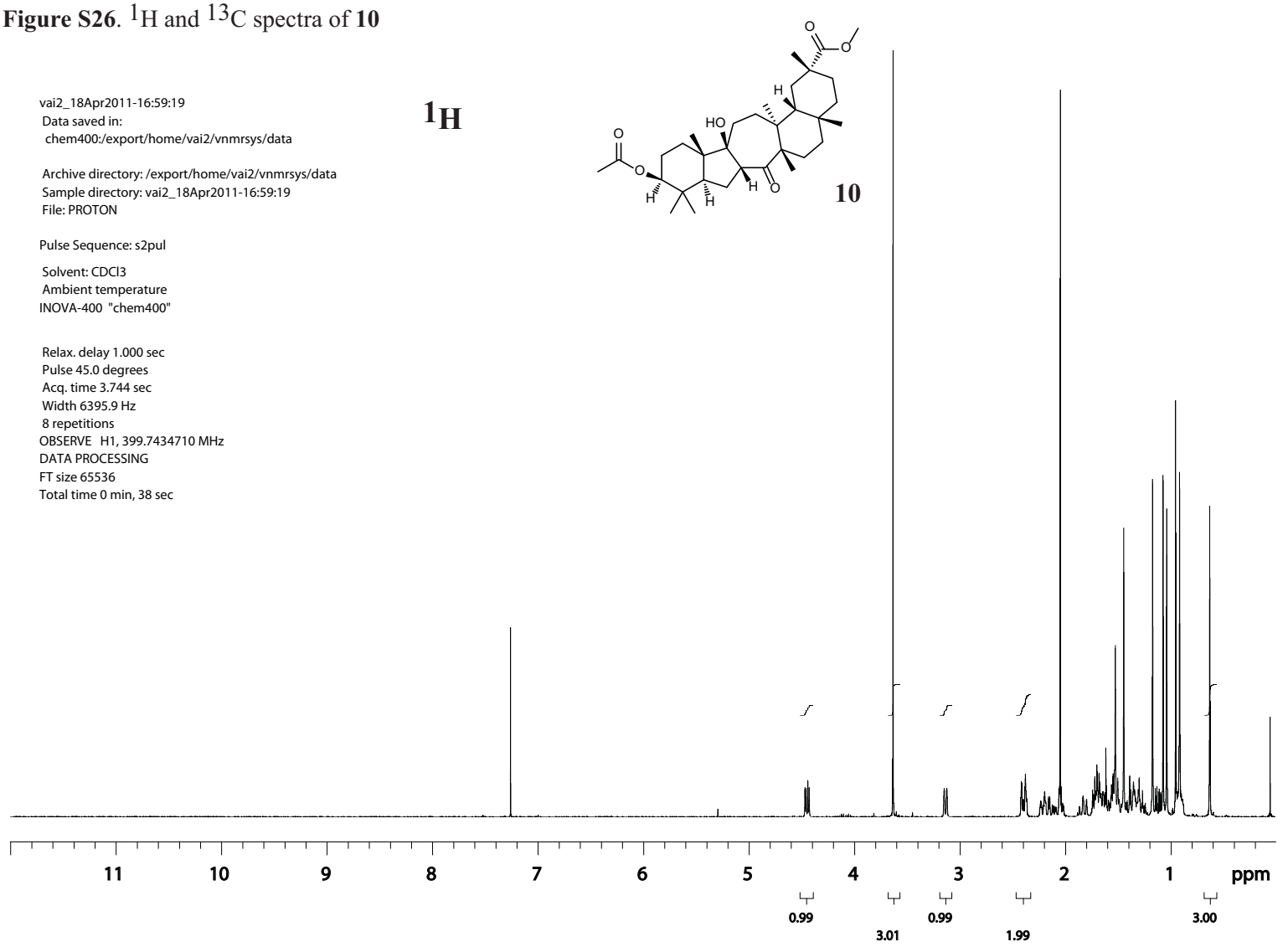


Figure S26. ^{1}H and ^{13}C spectra of **10**



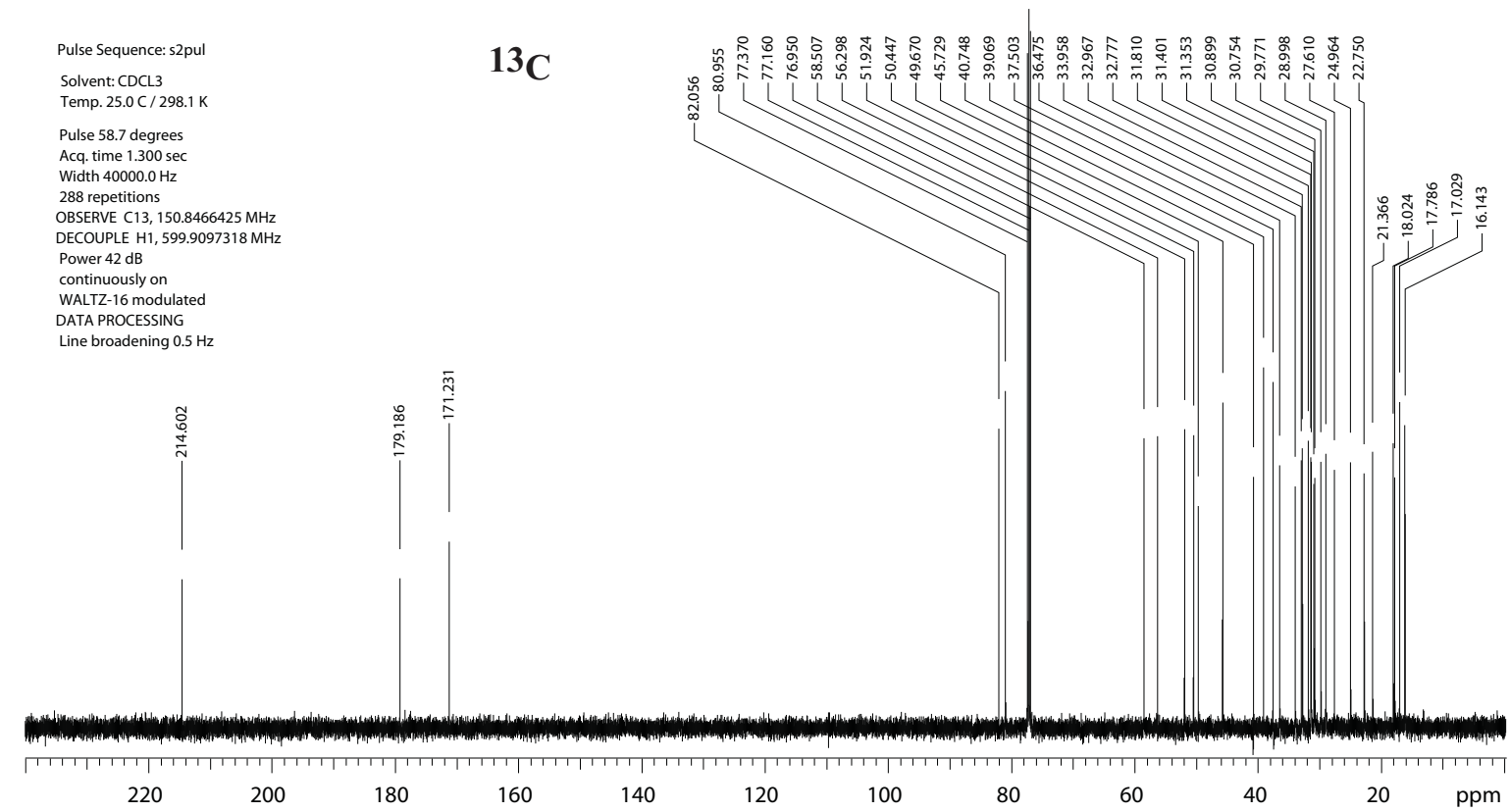
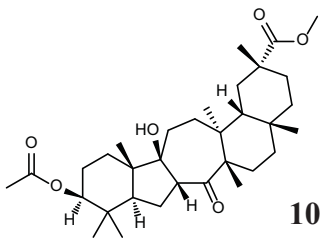


Figure S27. HMQC and HMBC spectra of **10**.



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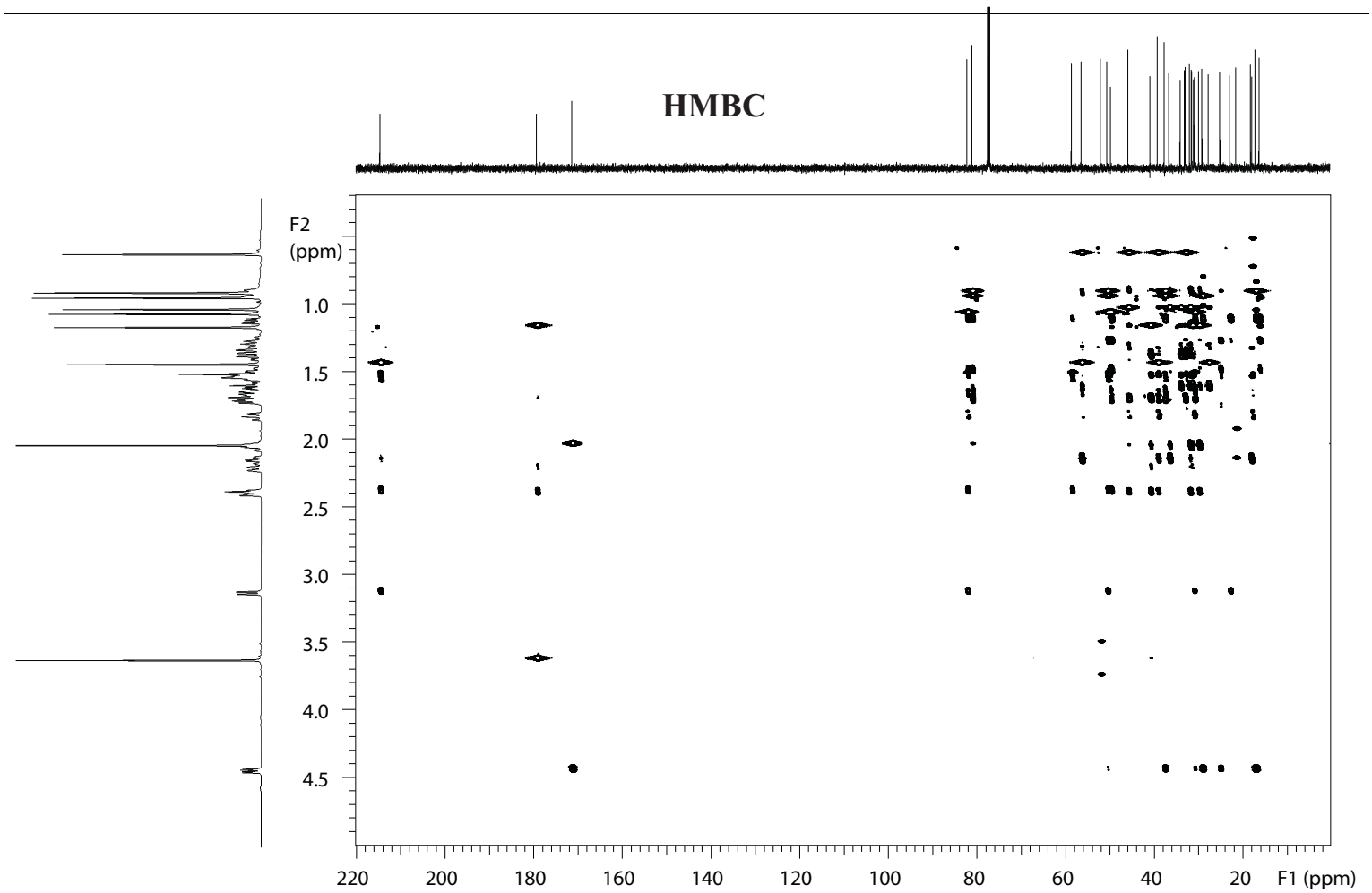
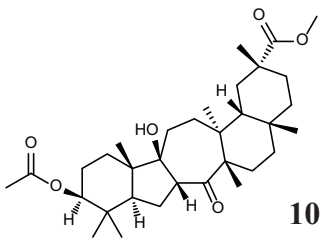


Figure S28. COSY and NOESY spectra of **10**.



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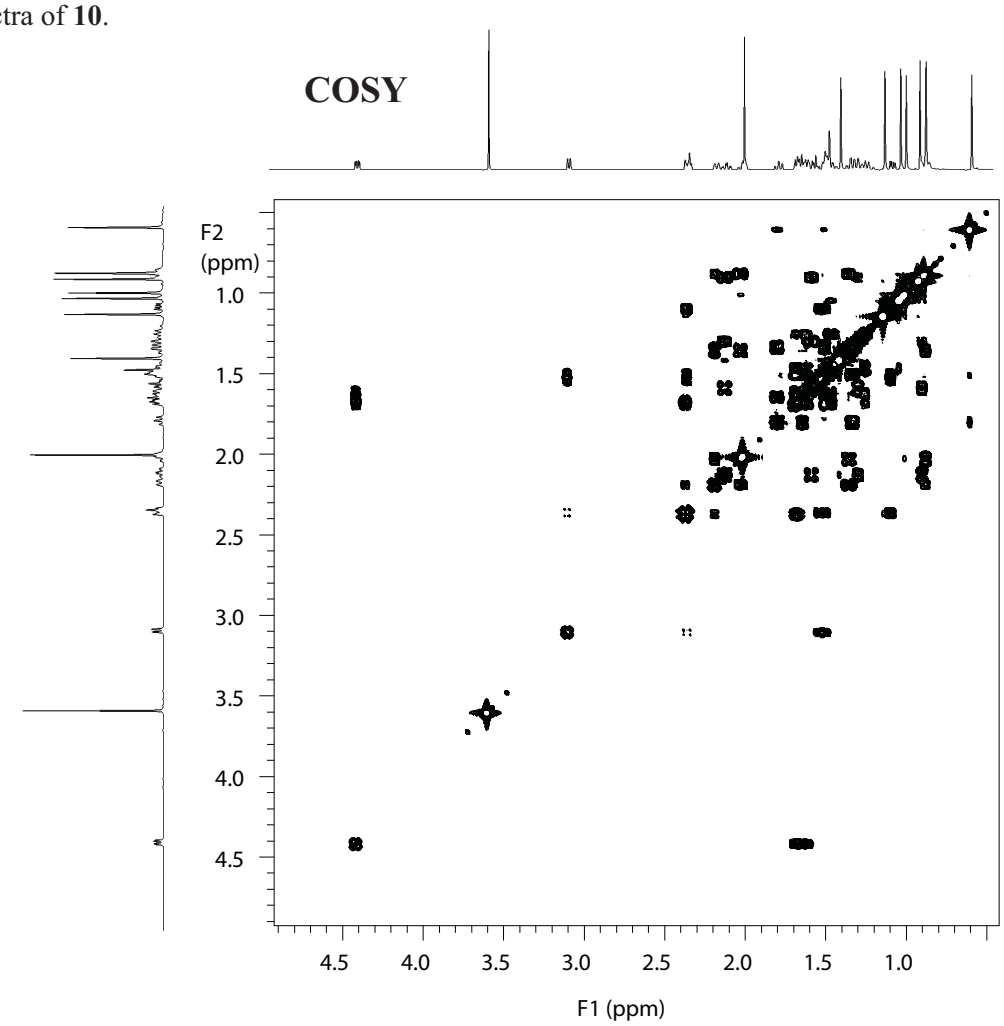


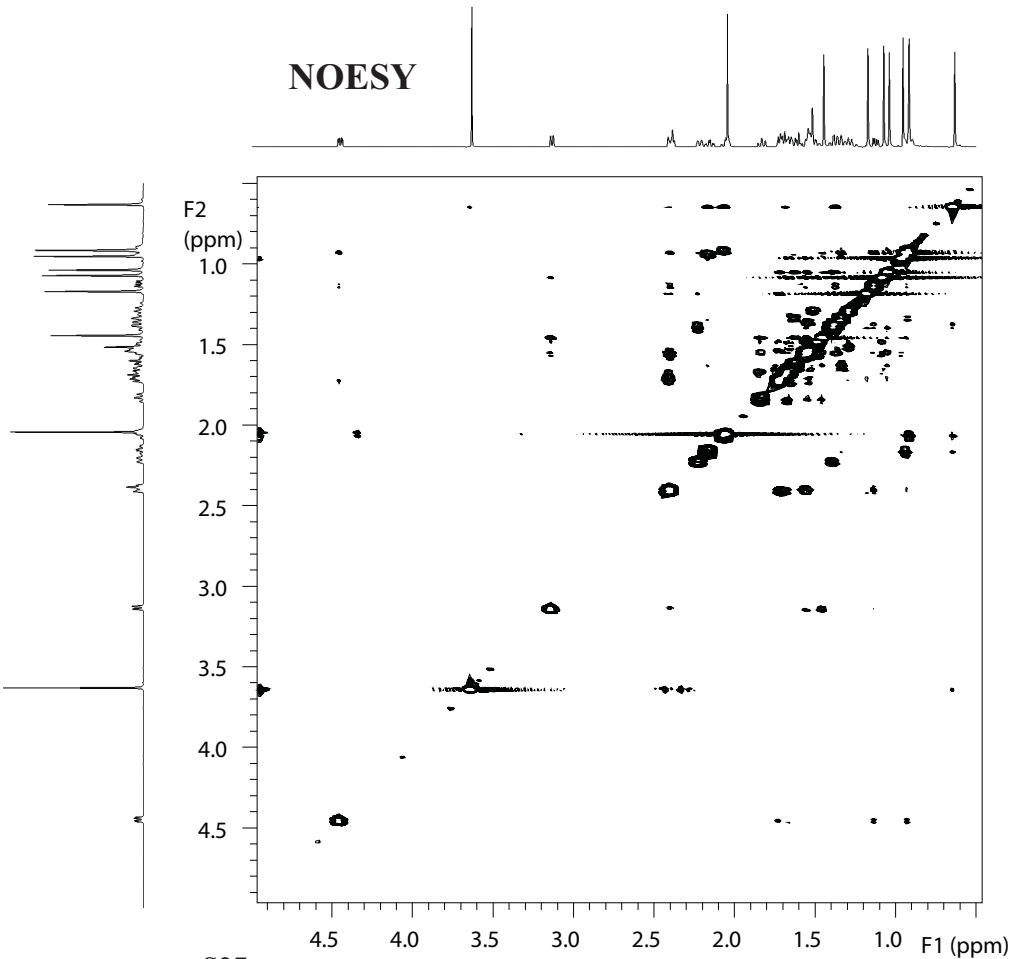
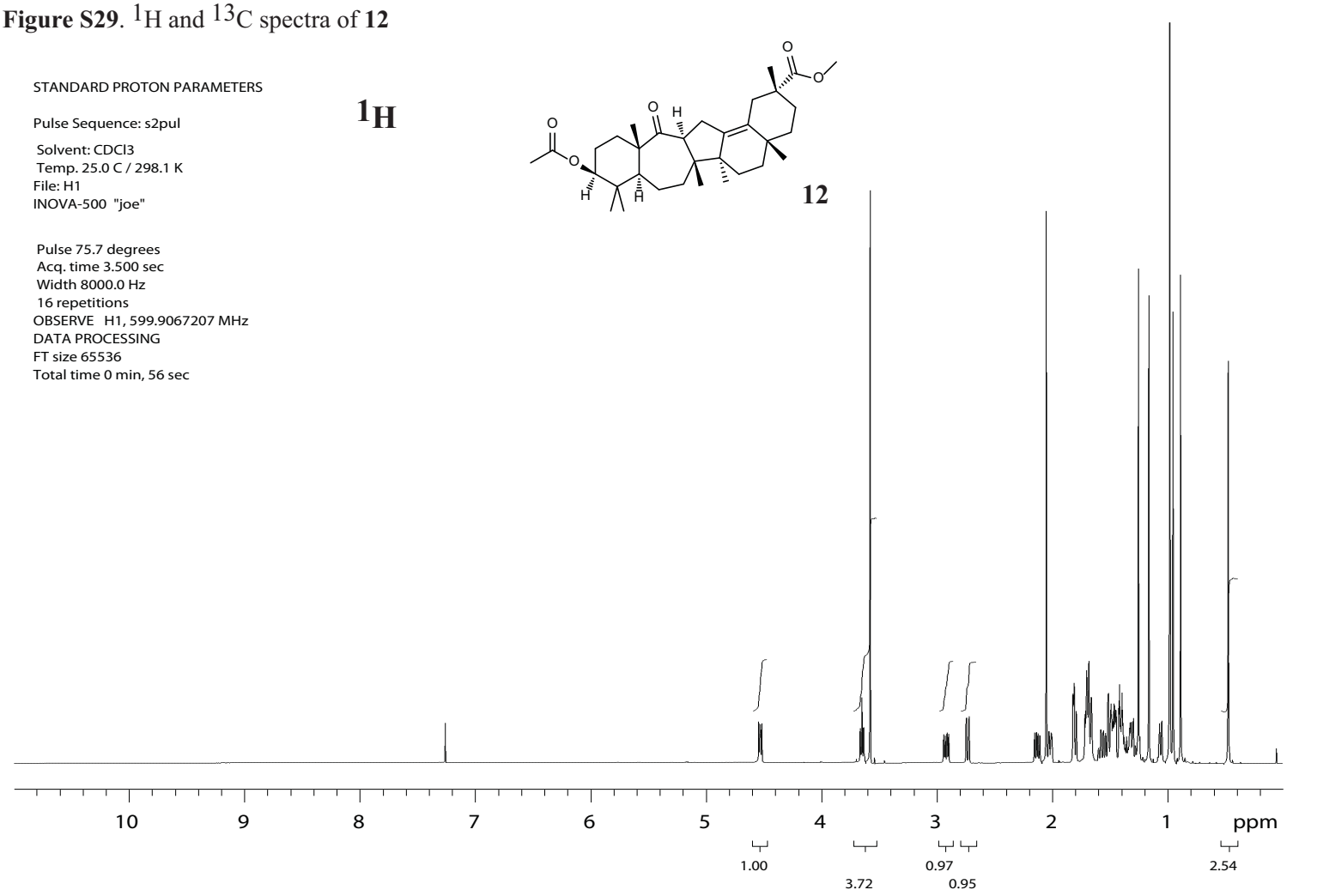


Figure S29. ^{1}H and ^{13}C spectra of **12**



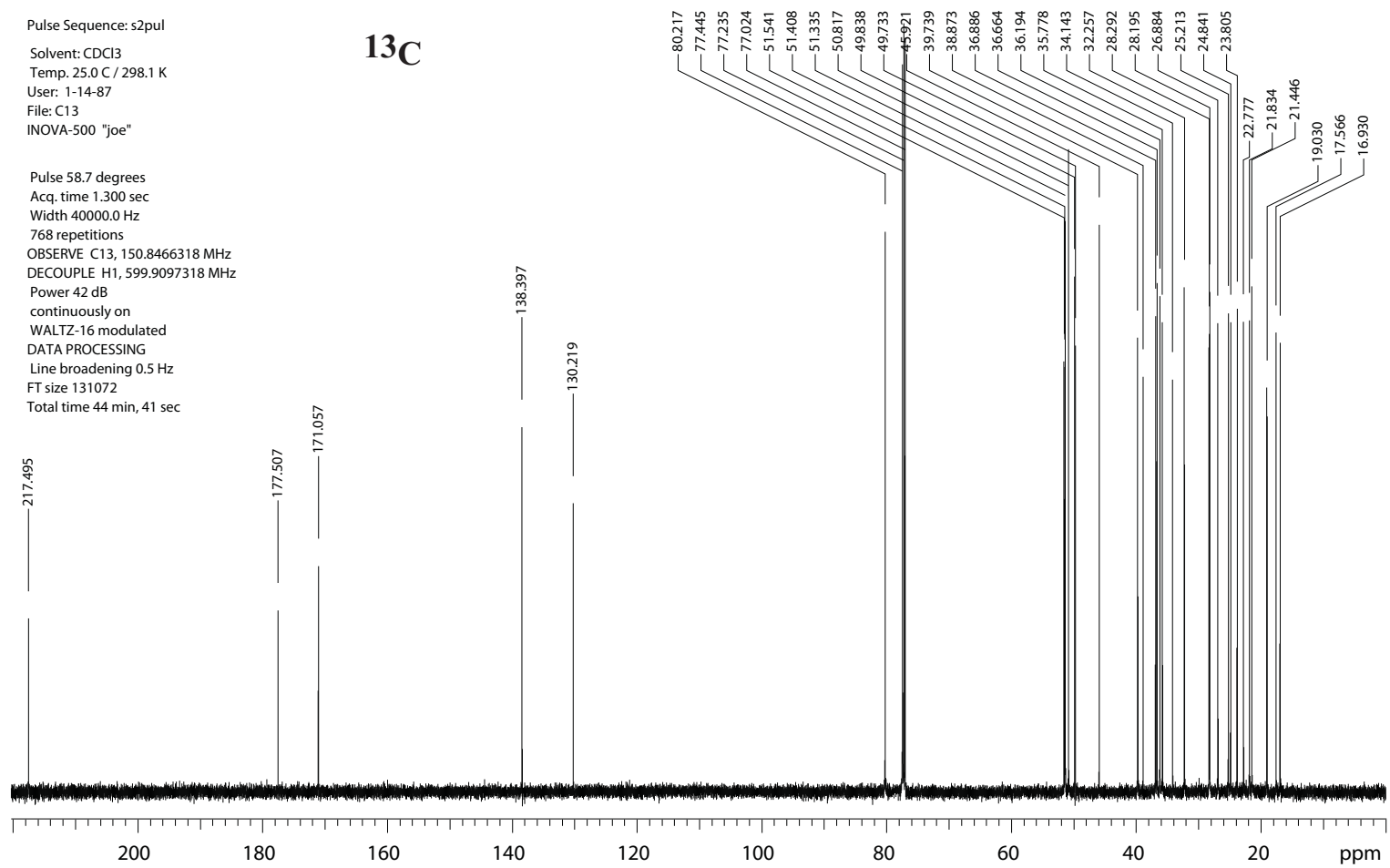
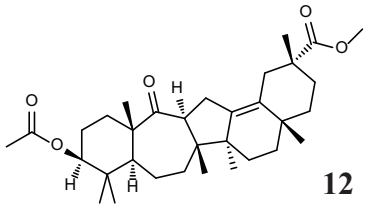


Figure S30. HMQC and HMBC spectra of **12**.



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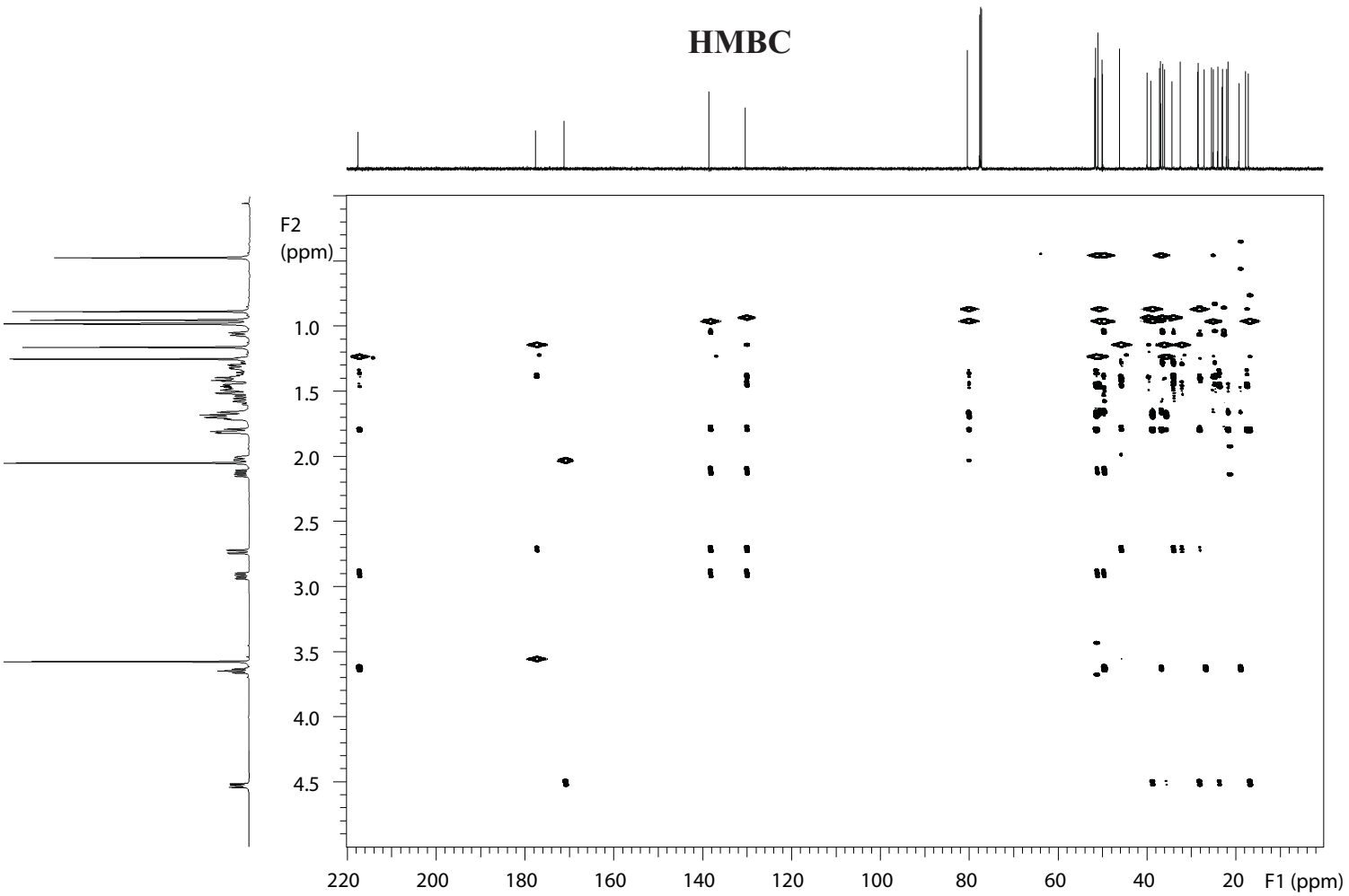
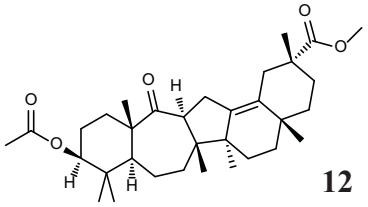
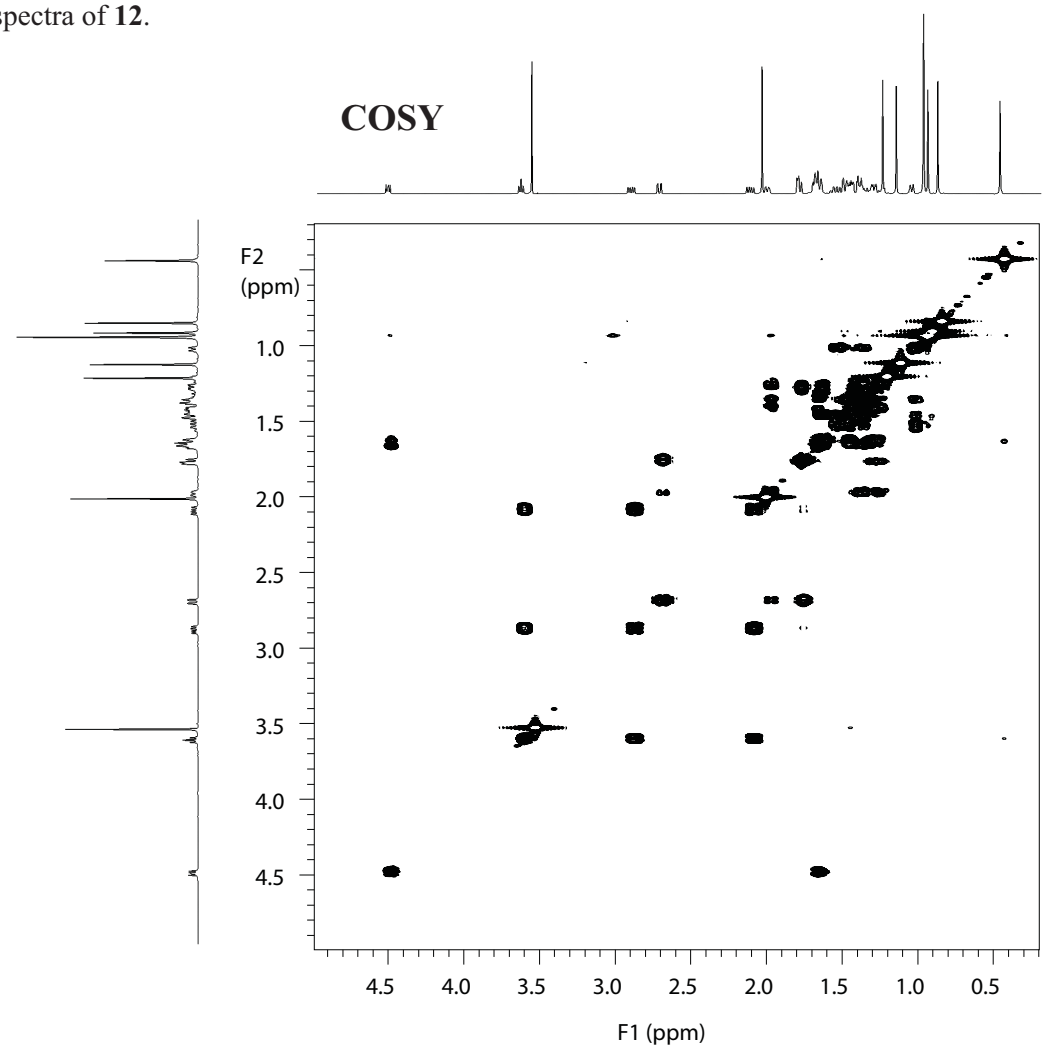


Figure S31. COSY and NOESY spectra of **12**.



12



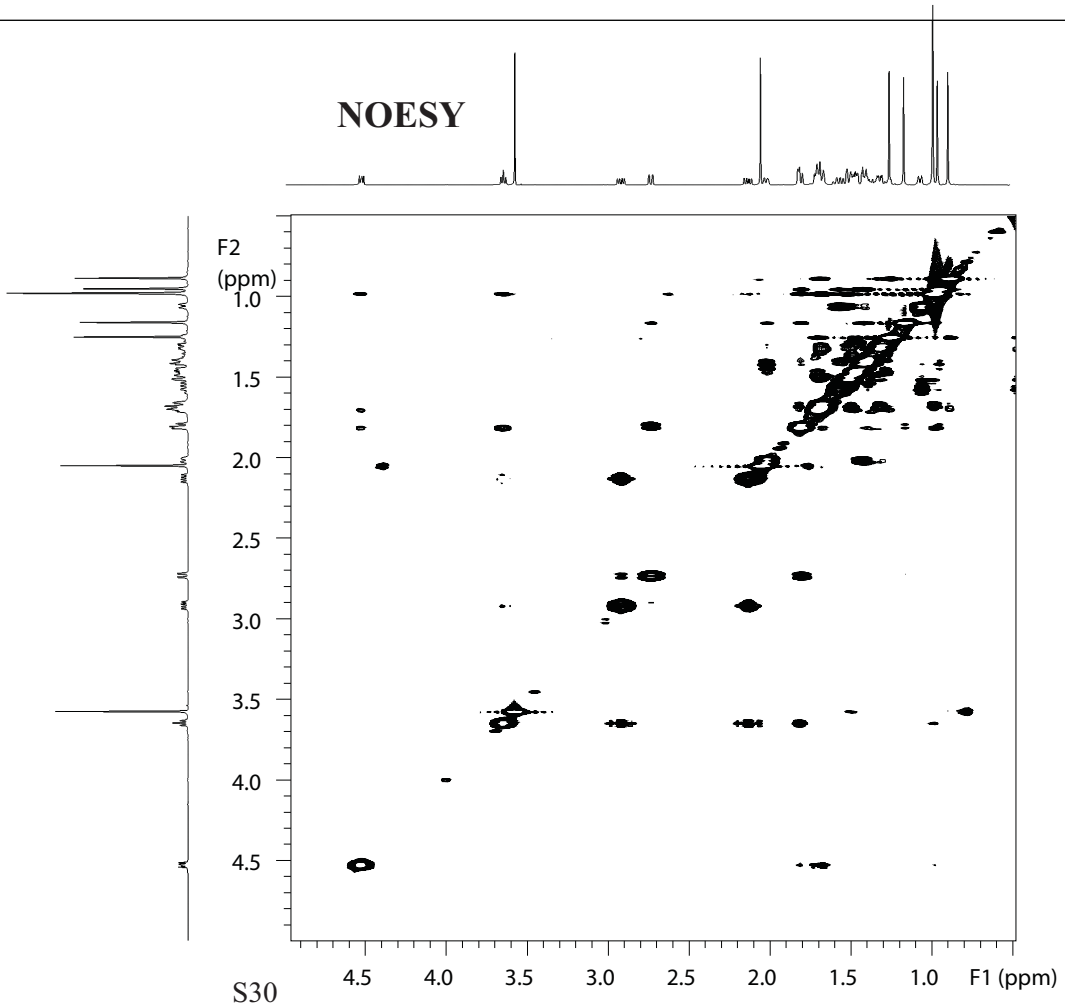
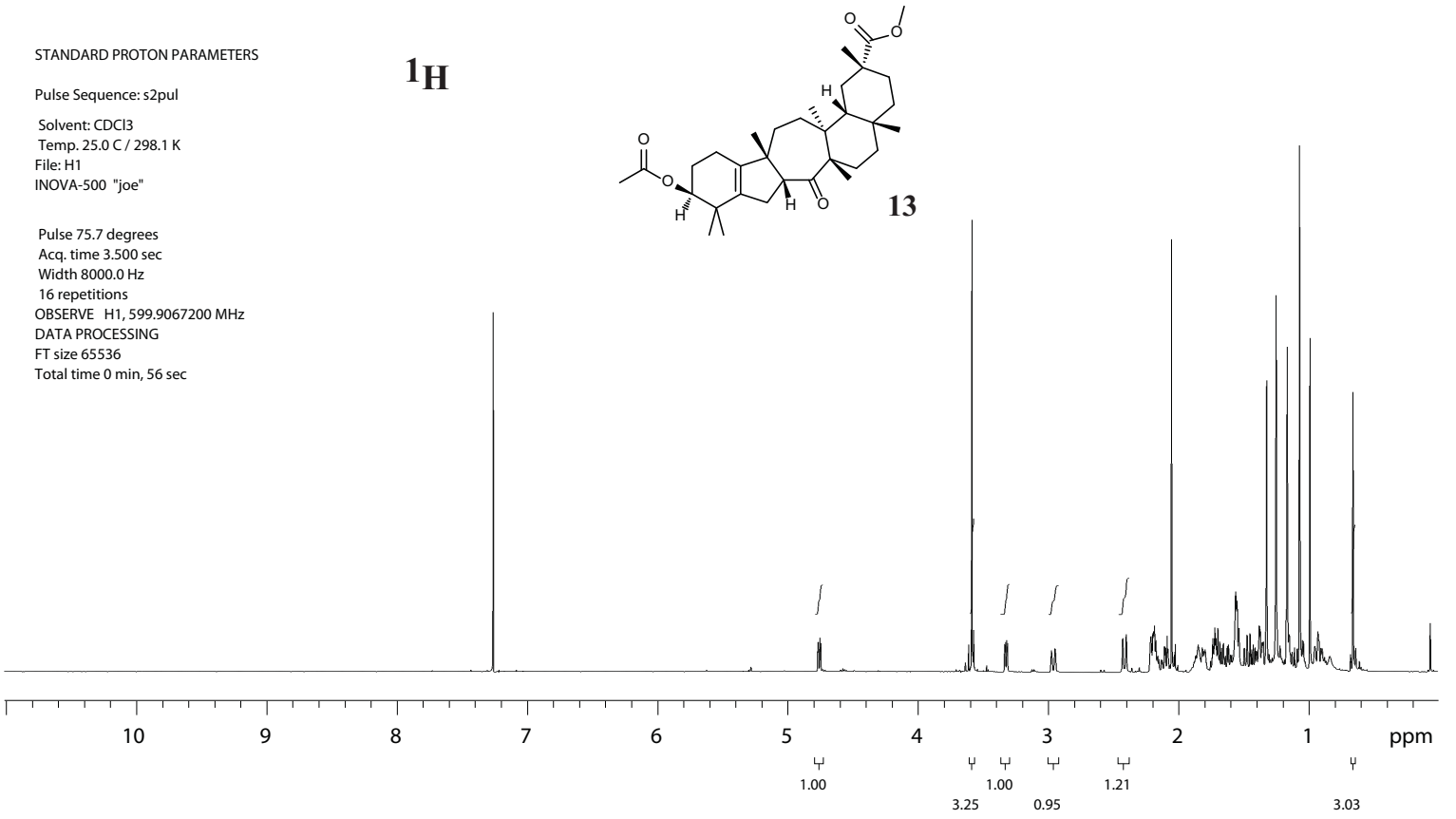


Figure S32. ^{1}H and ^{13}C spectra of **13**



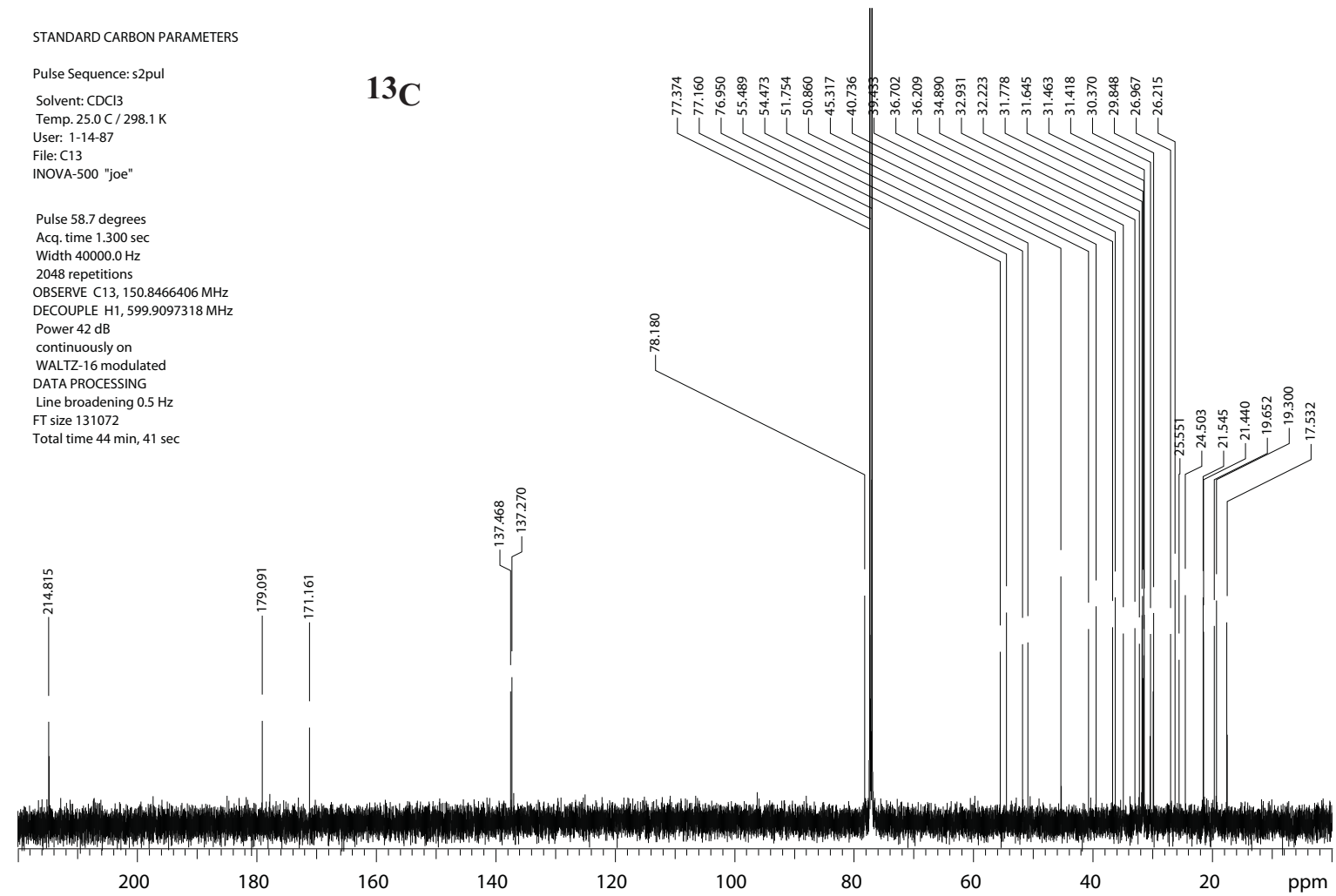
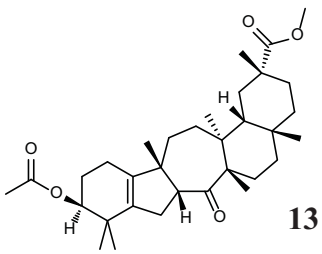


Figure S33. HMQC and HMBC spectra of **13**.



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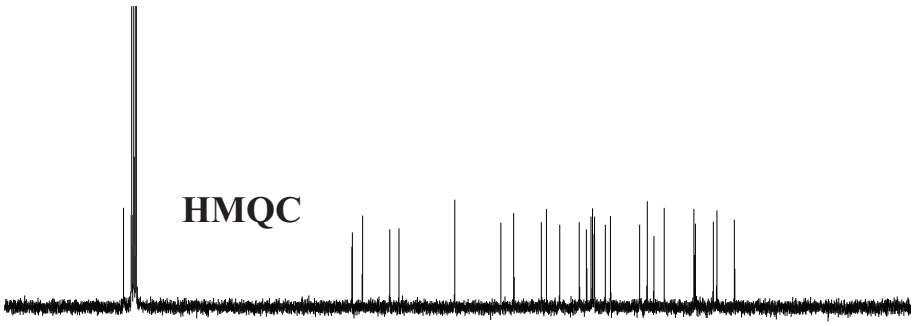
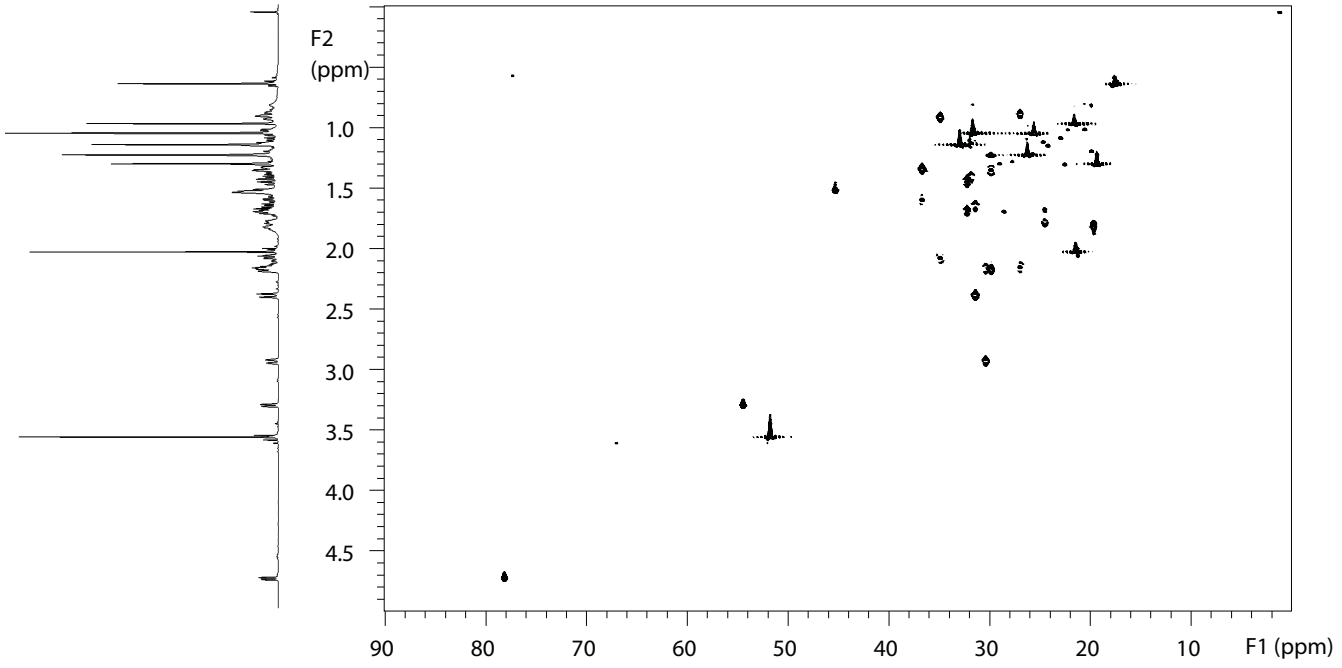
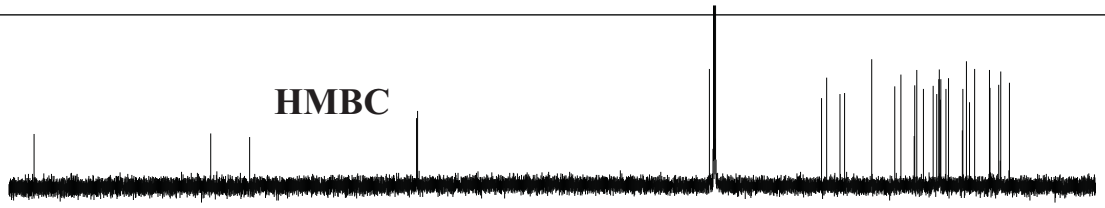






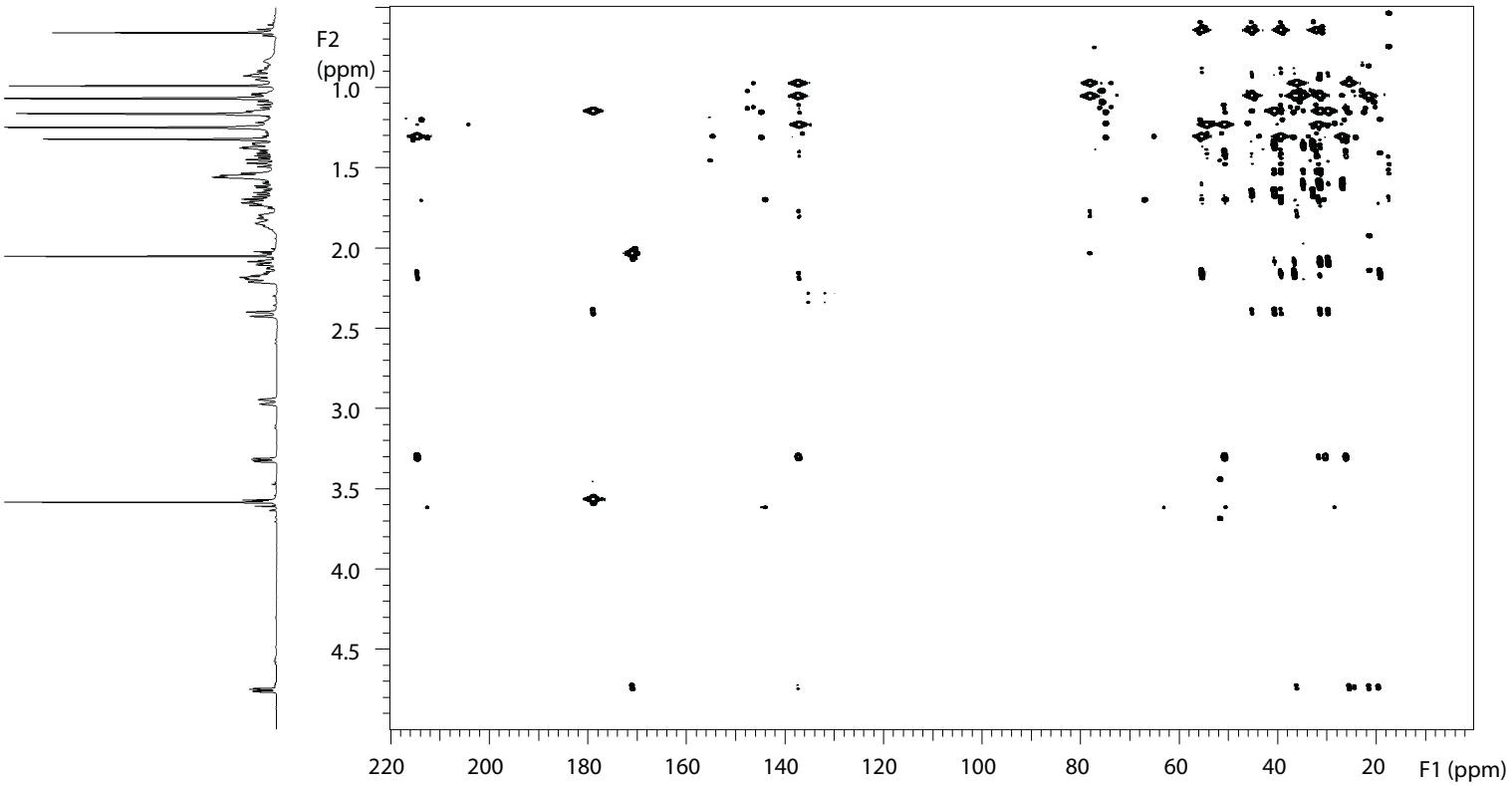
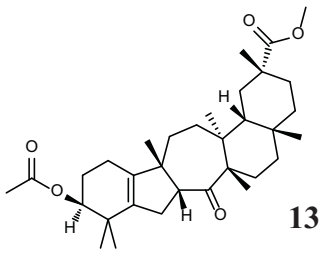


Figure S34. COSY and NOESY spectra of **13**.



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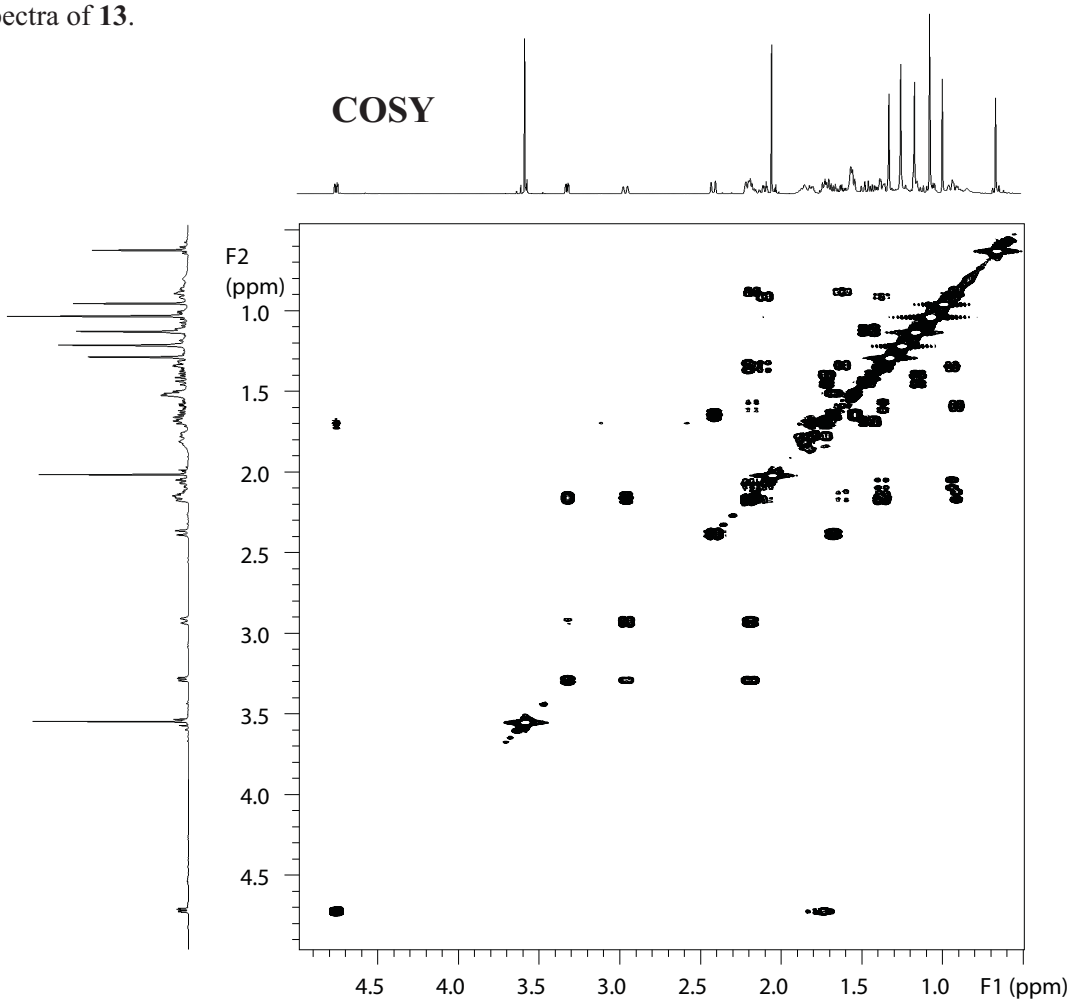


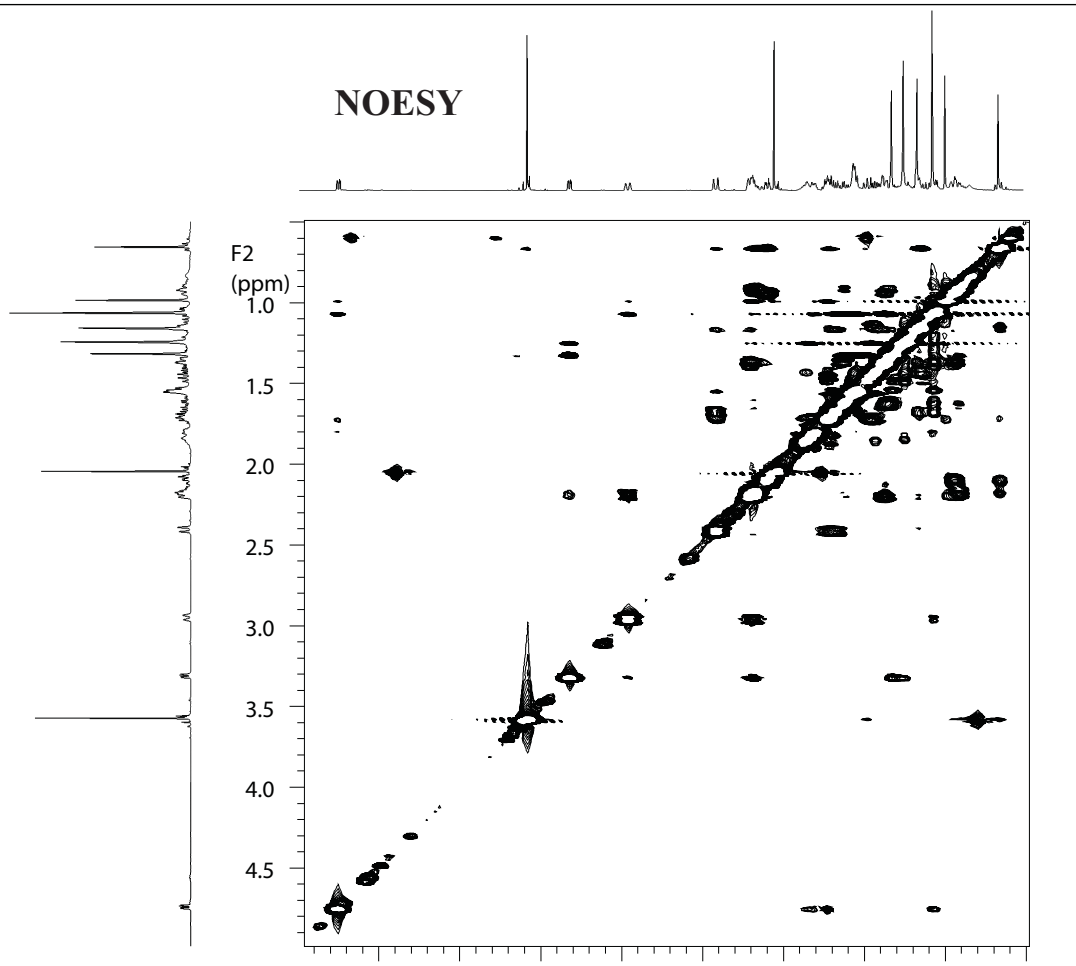
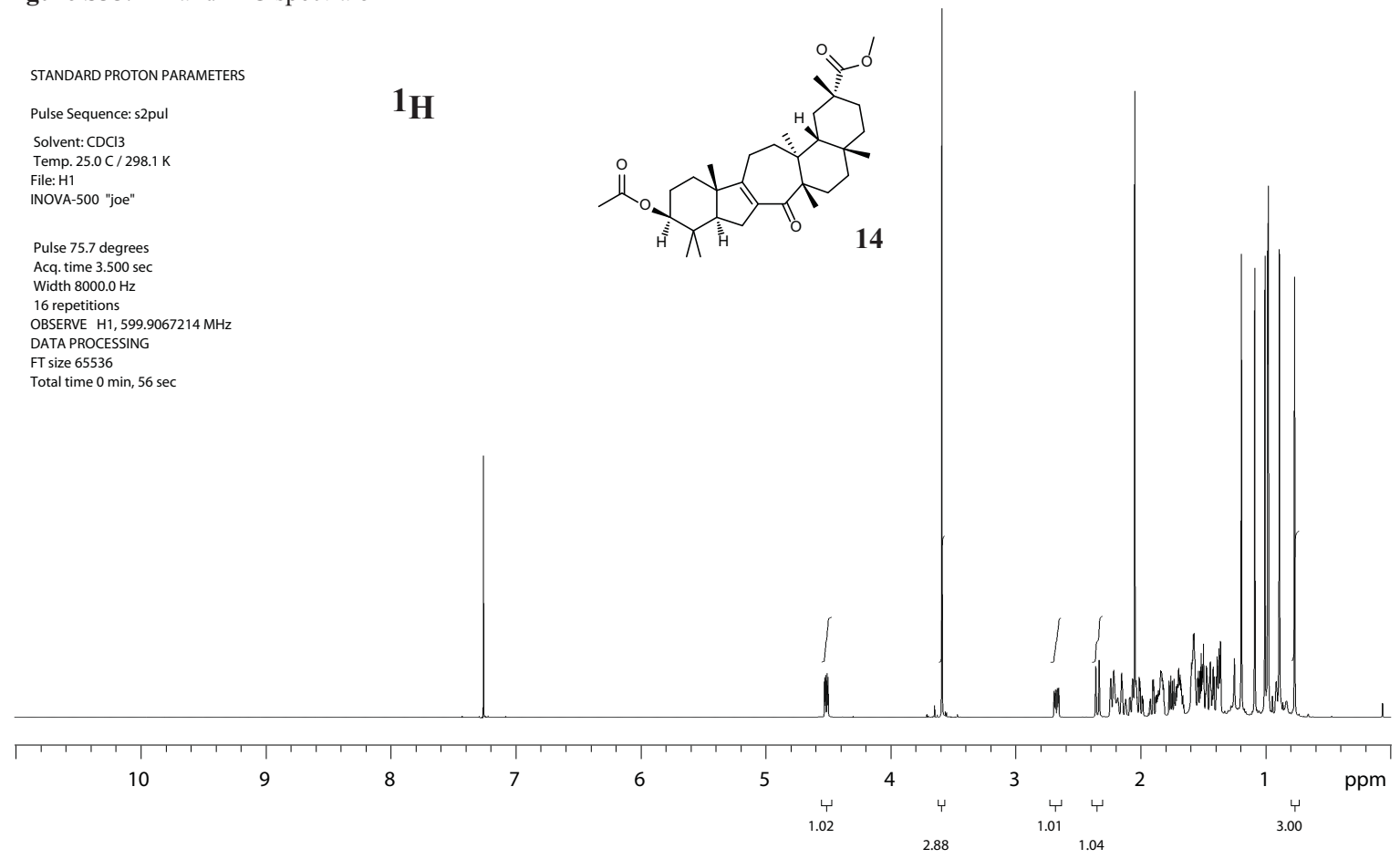


Figure S35. ^{1}H and ^{13}C spectra of **14**



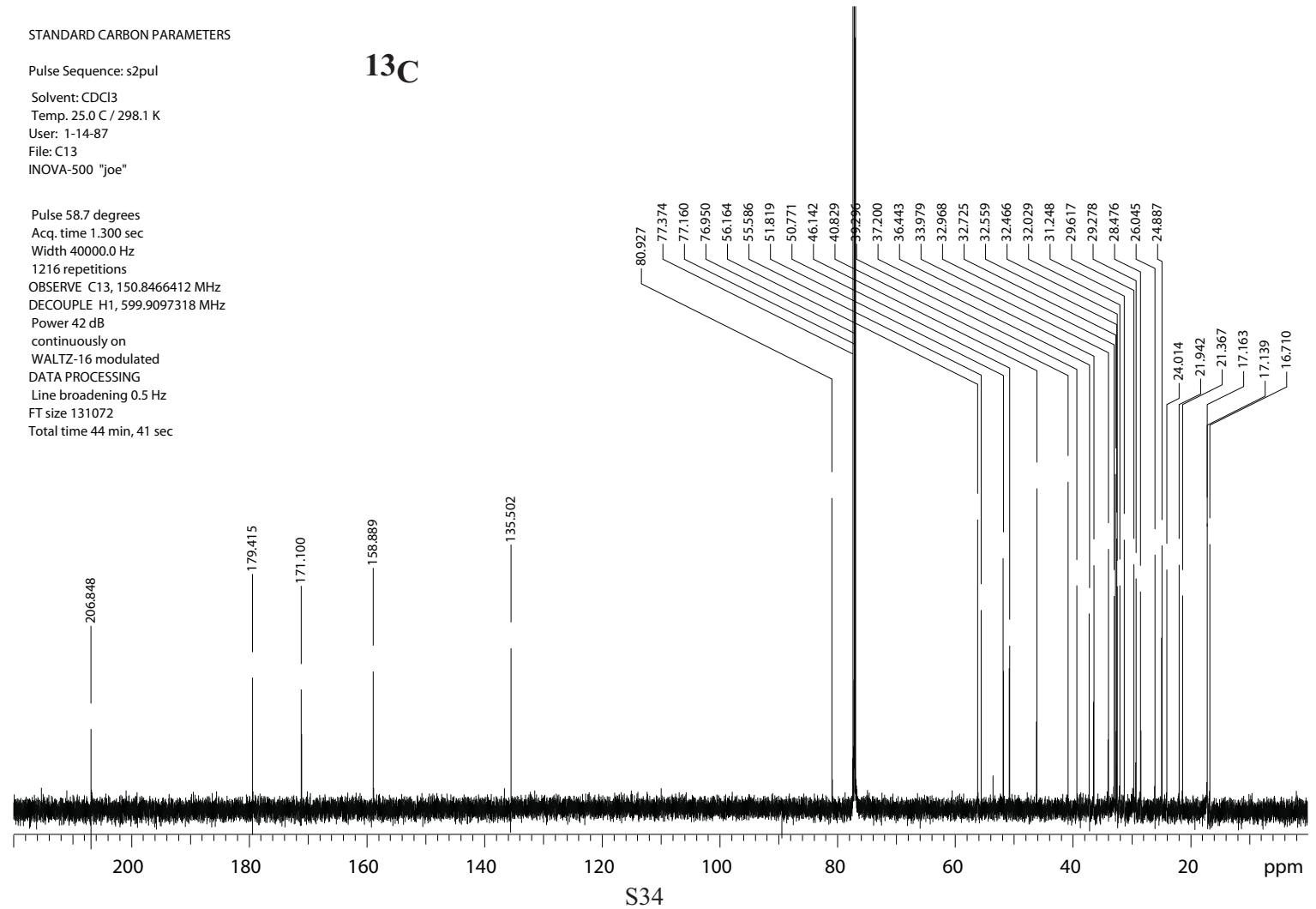
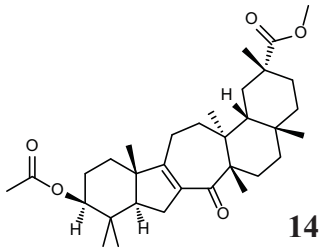


Figure S36. HMQC and HMBC spectra of **14**.



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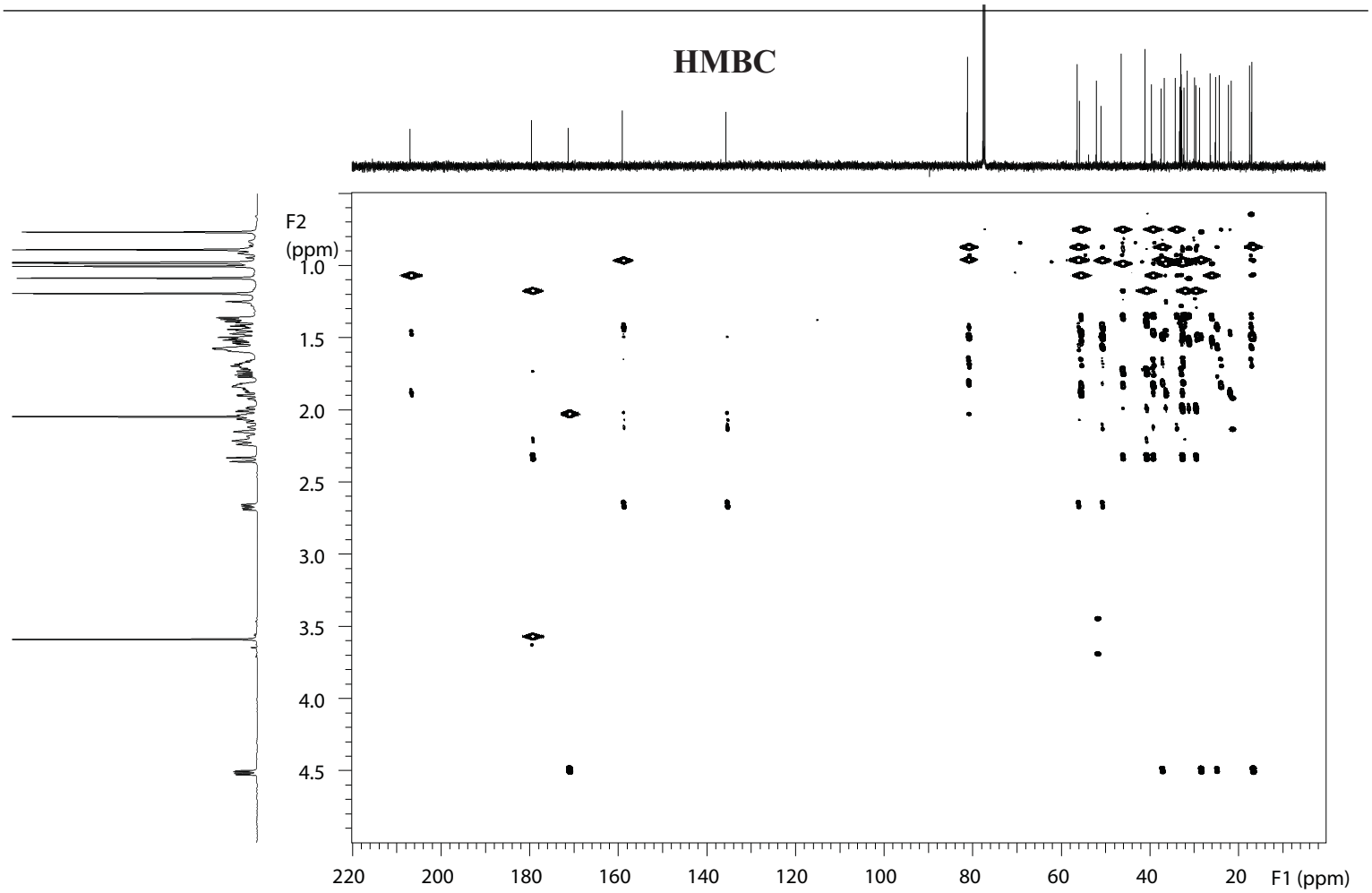
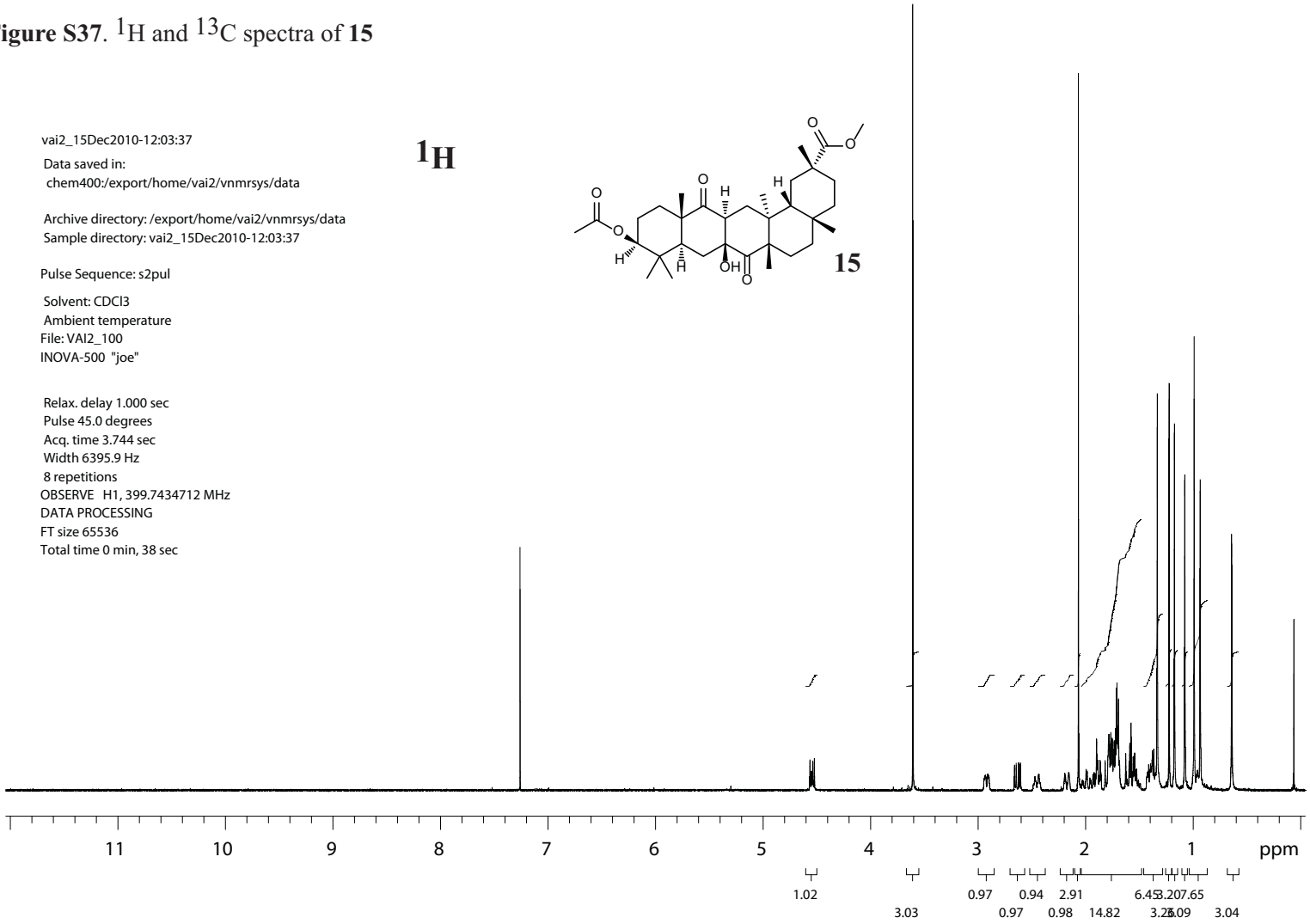


Figure S37. ^{1}H and ^{13}C spectra of **15**



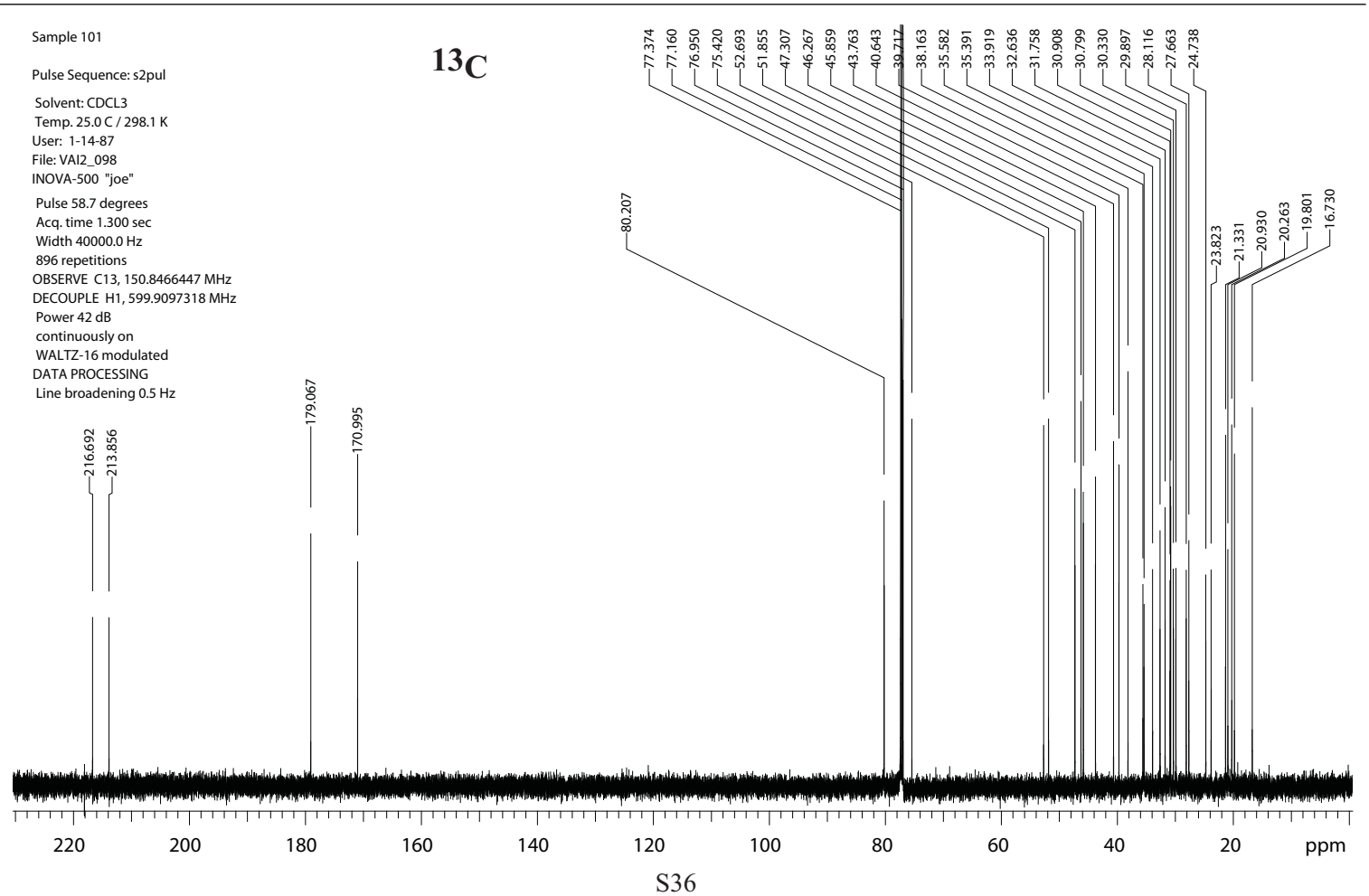
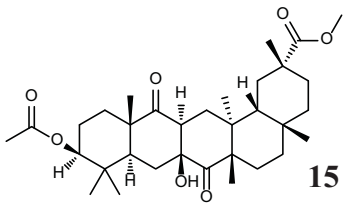


Figure S38. HMQC and HMBC spectra of **15**.



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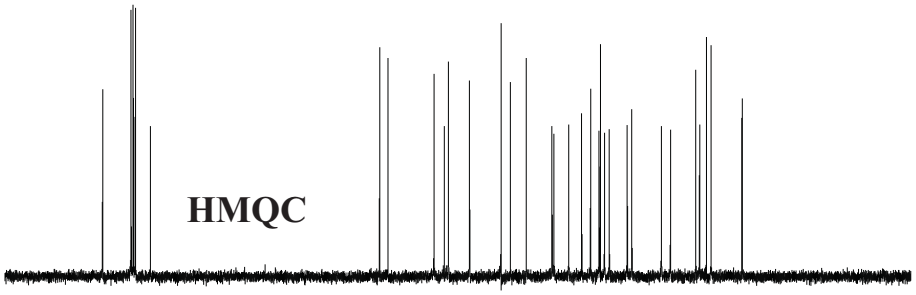
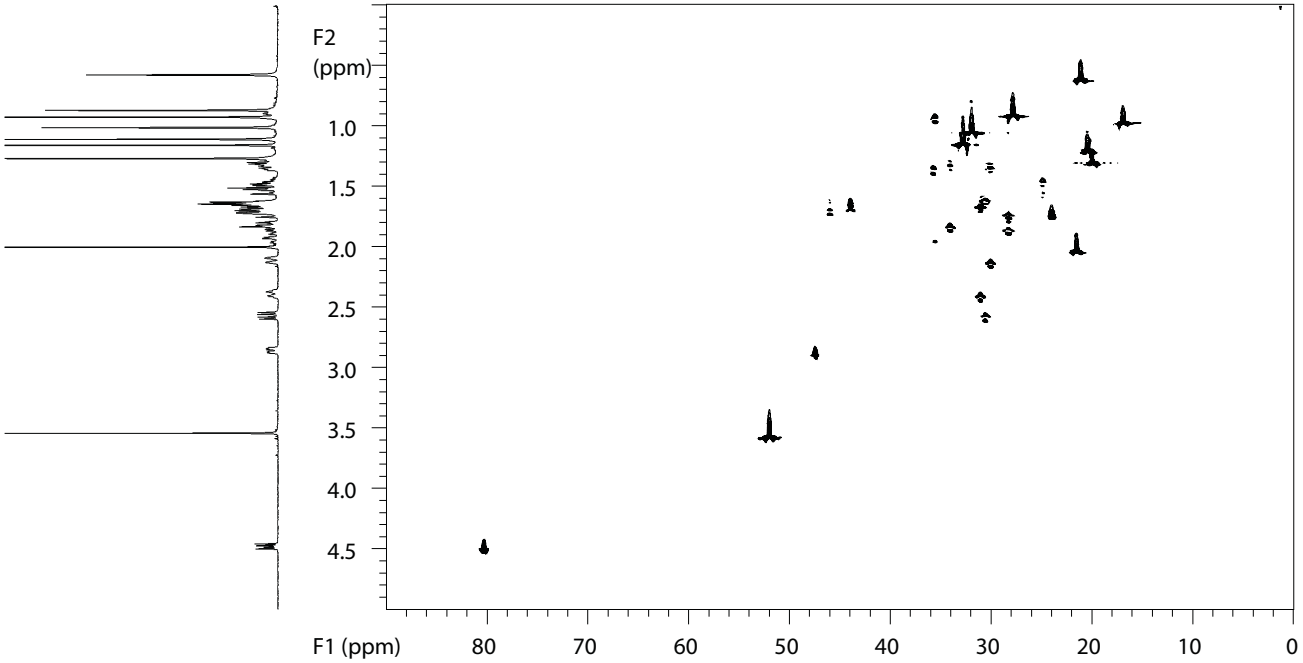




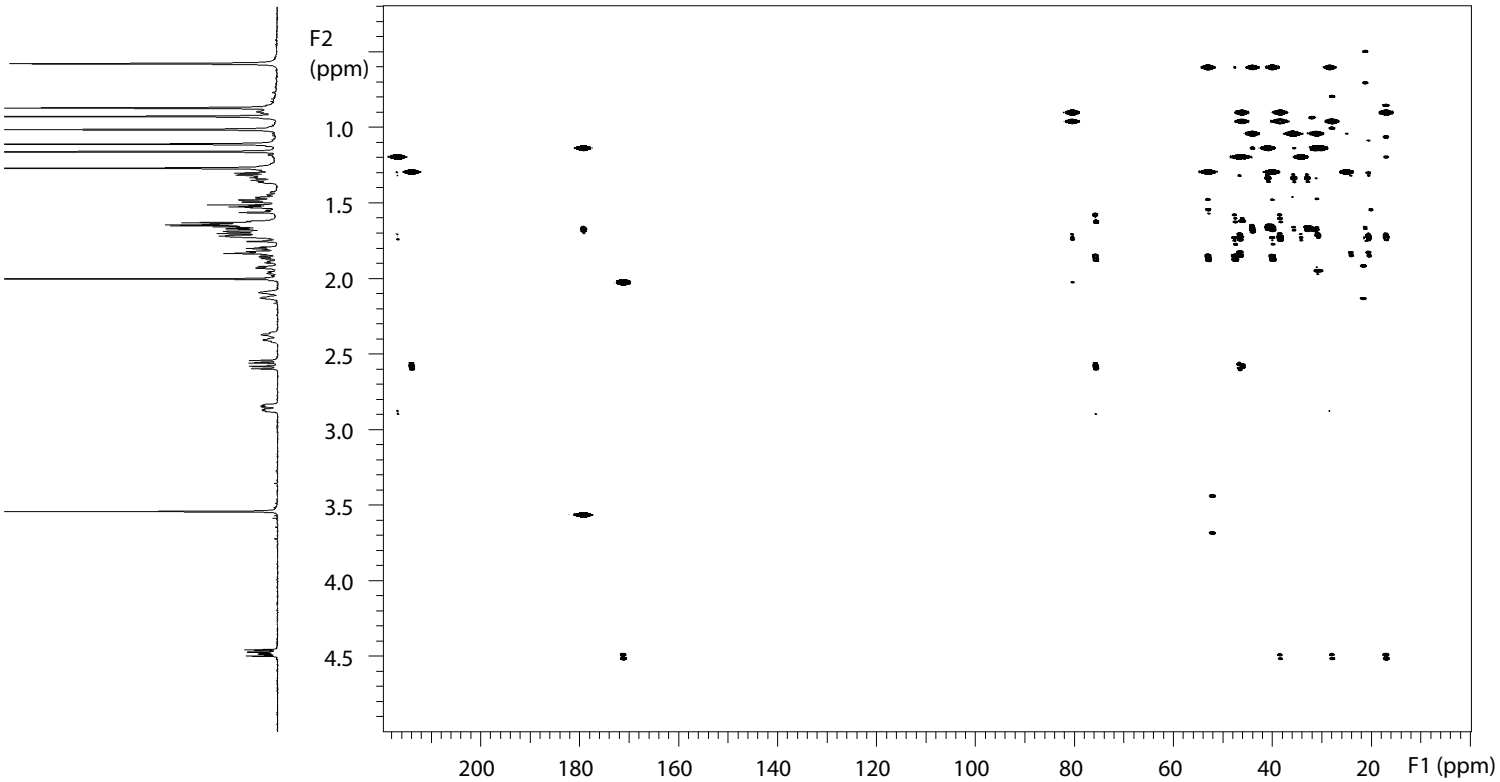
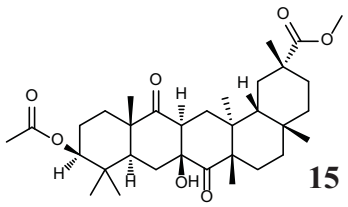


Figure S39. COSY and NOESY spectra of **15**.



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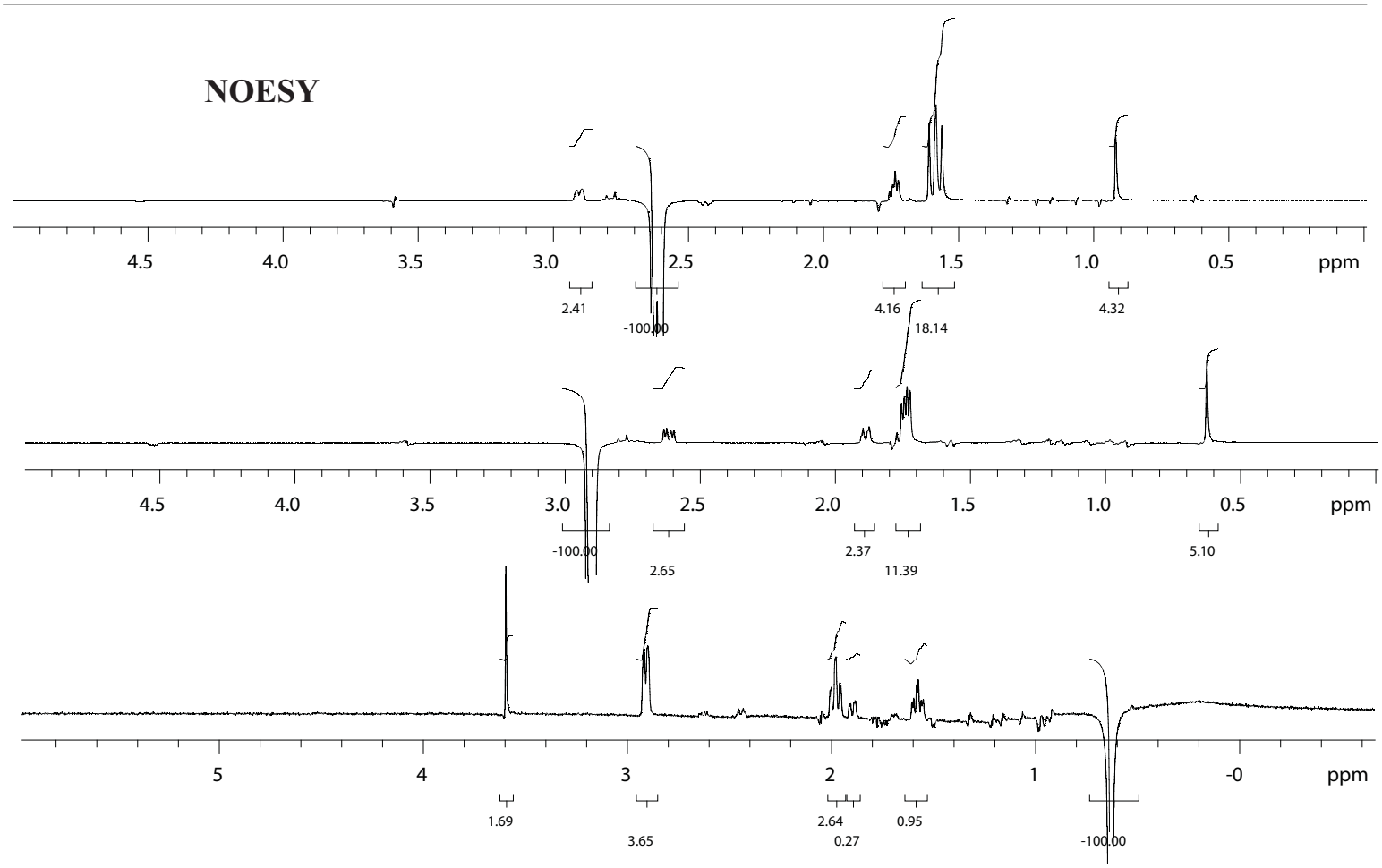
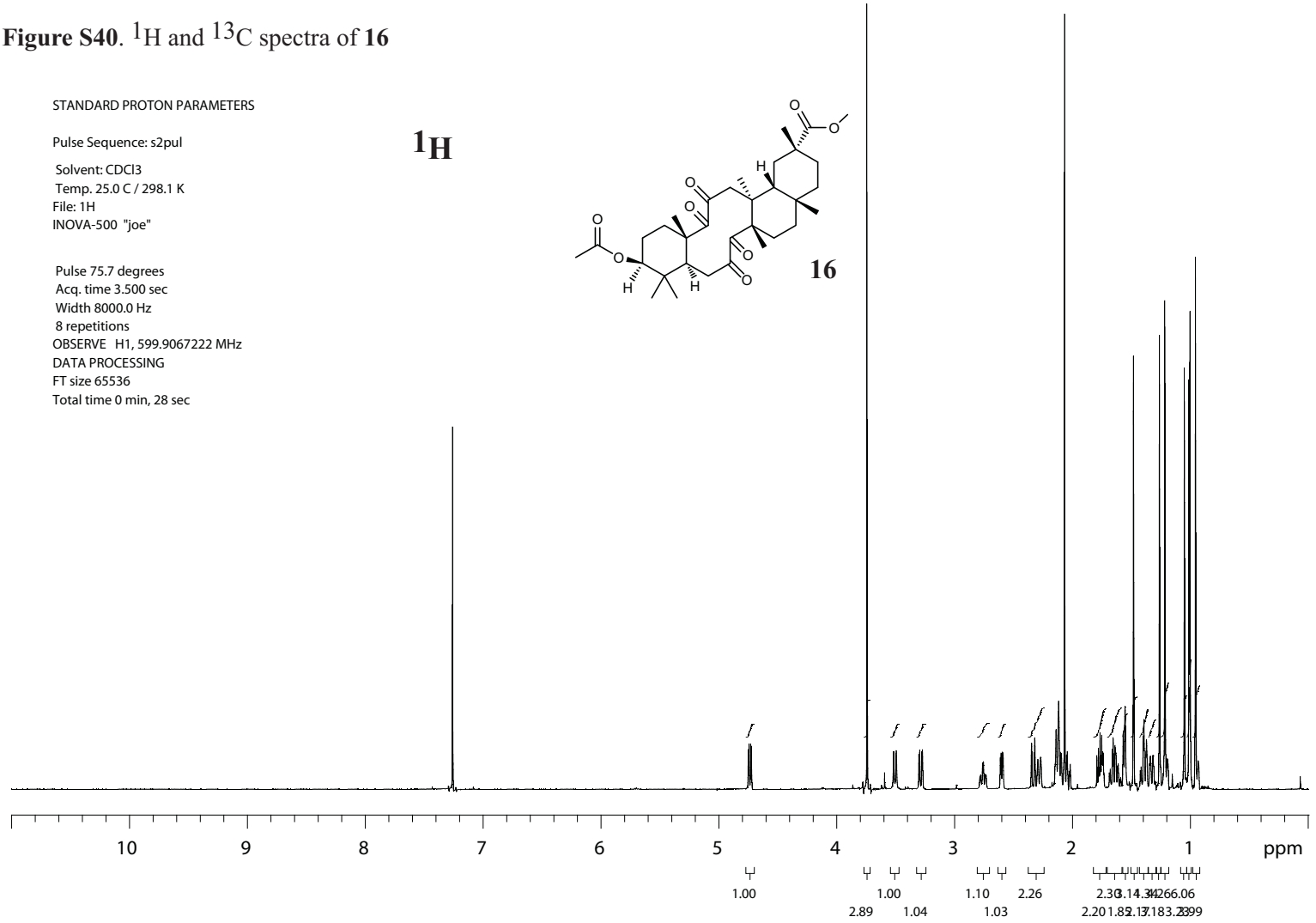


Figure S40. ^{1}H and ^{13}C spectra of **16**



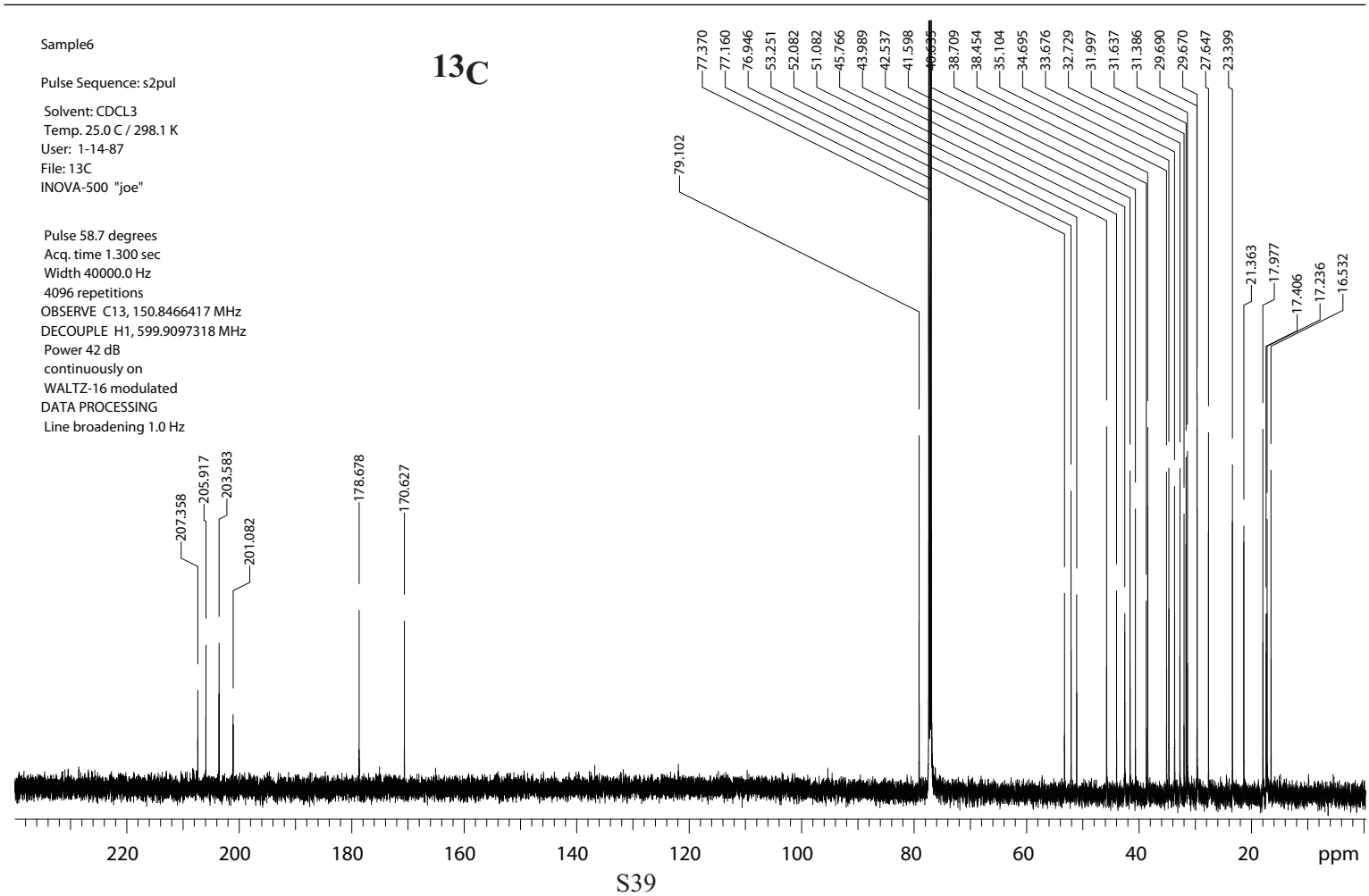
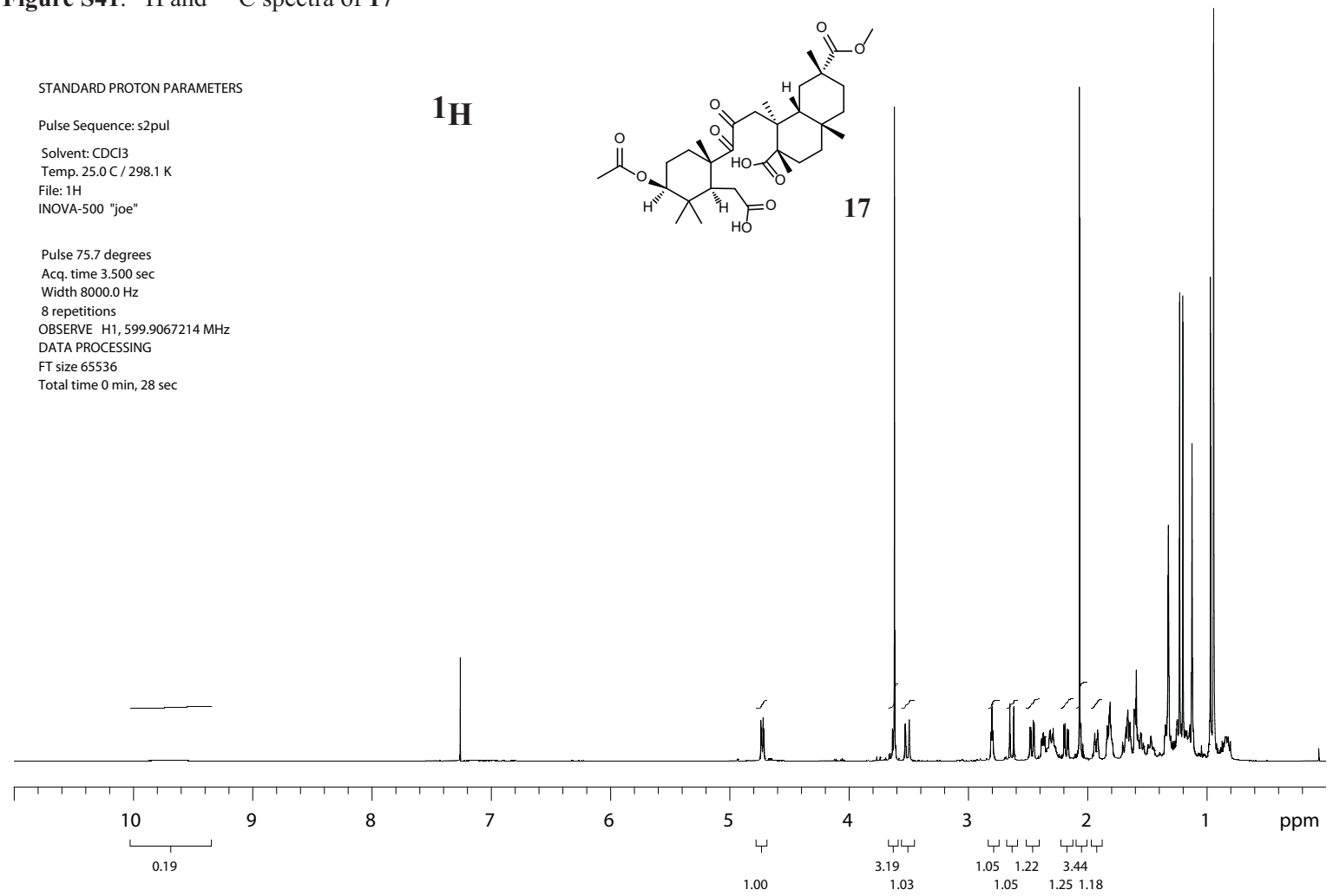


Figure S41. ^{1}H and ^{13}C spectra of **17**



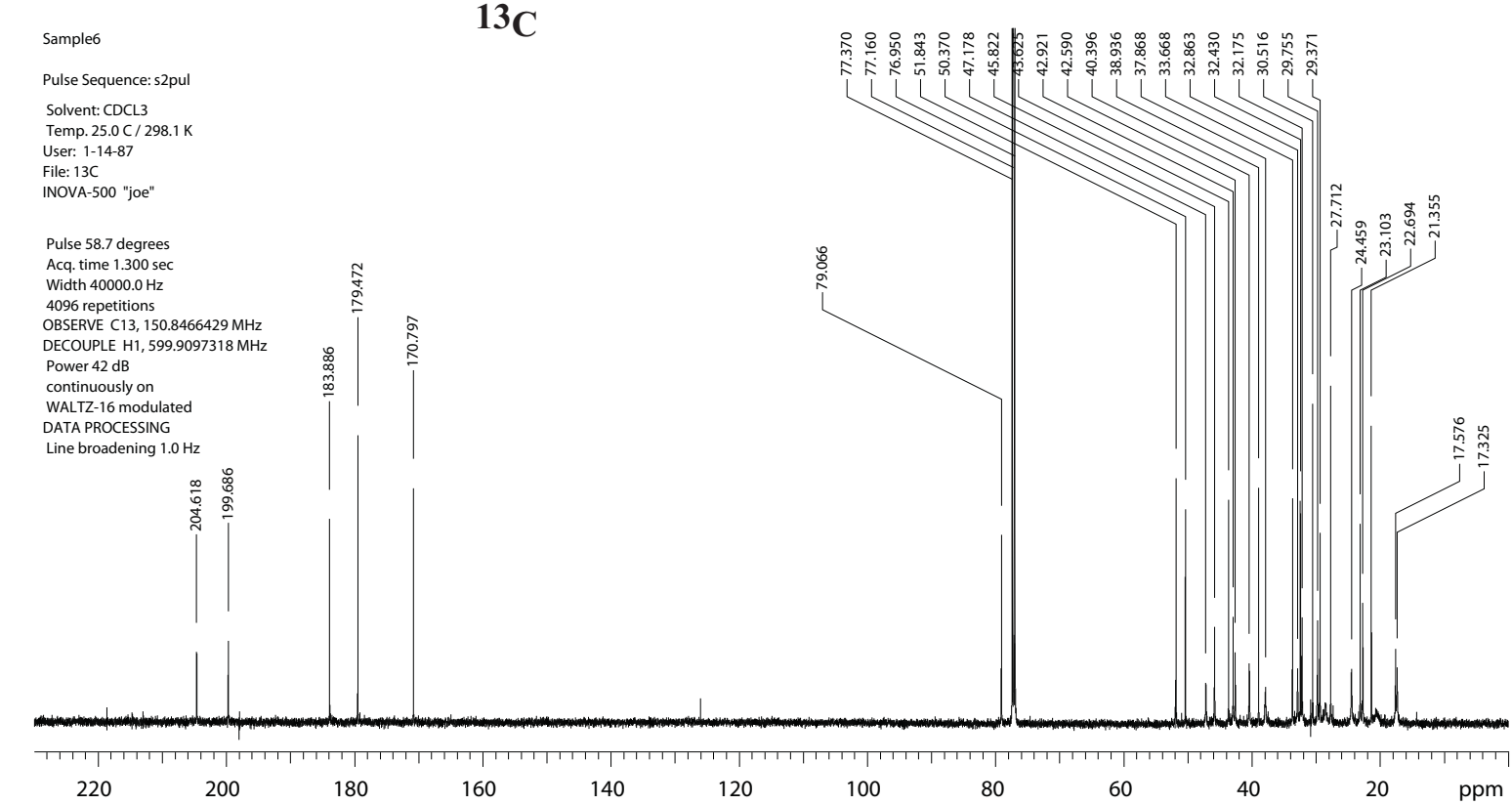
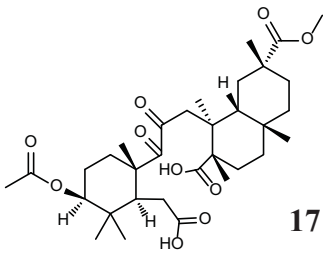


Figure S42. HMQC and HMBC spectra of **17**.



17

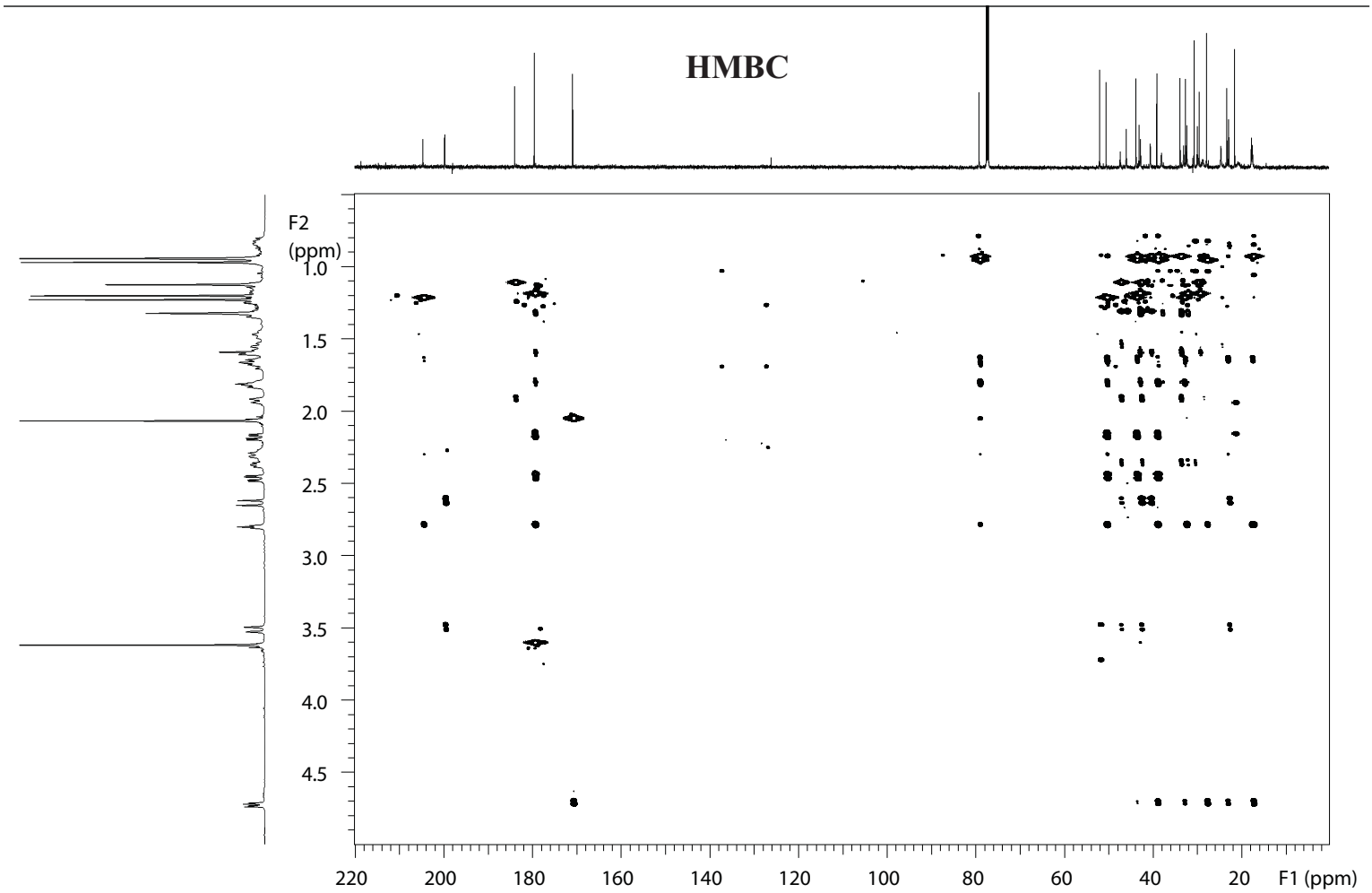
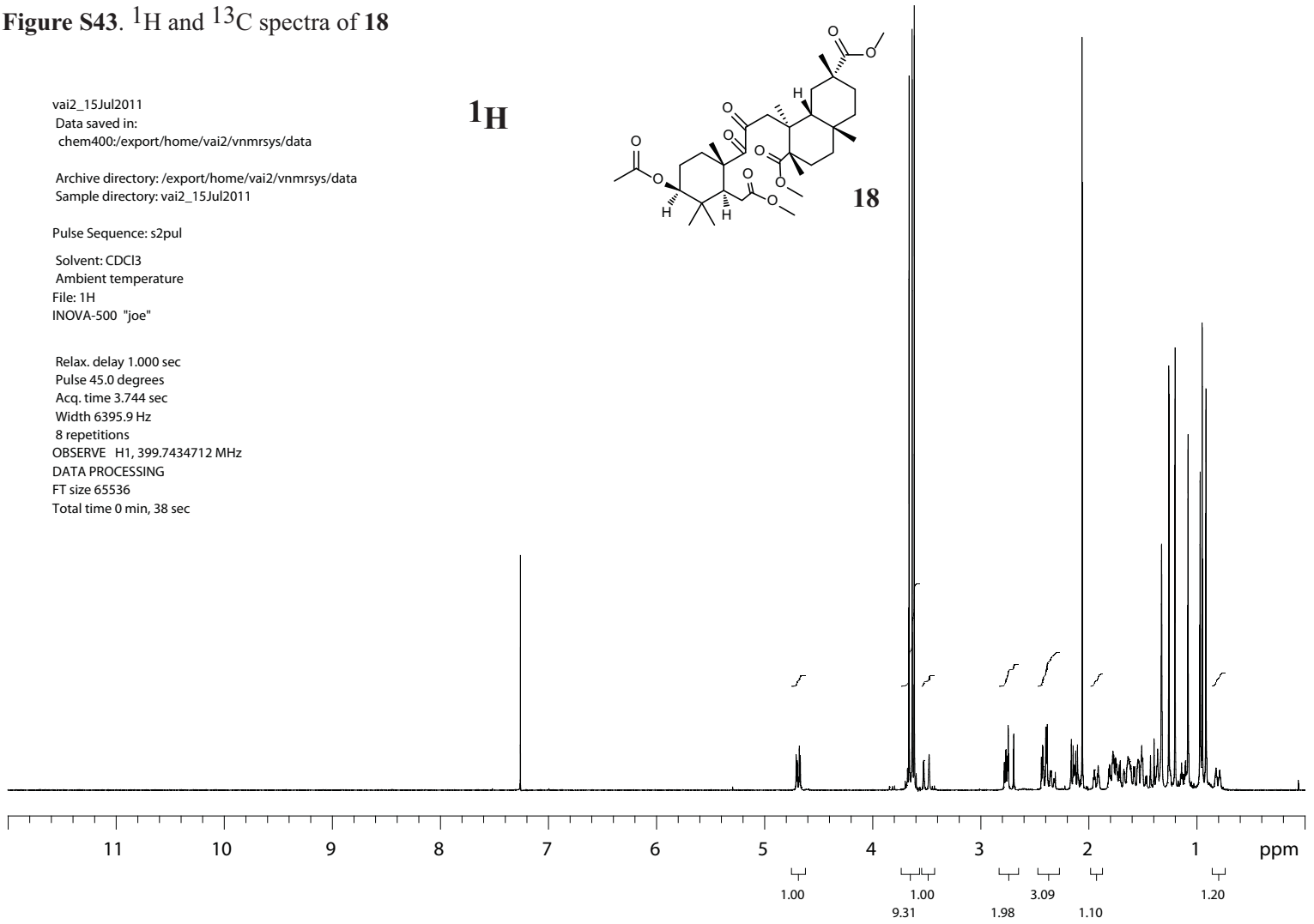


Figure S43. ^{1}H and ^{13}C spectra of **18**



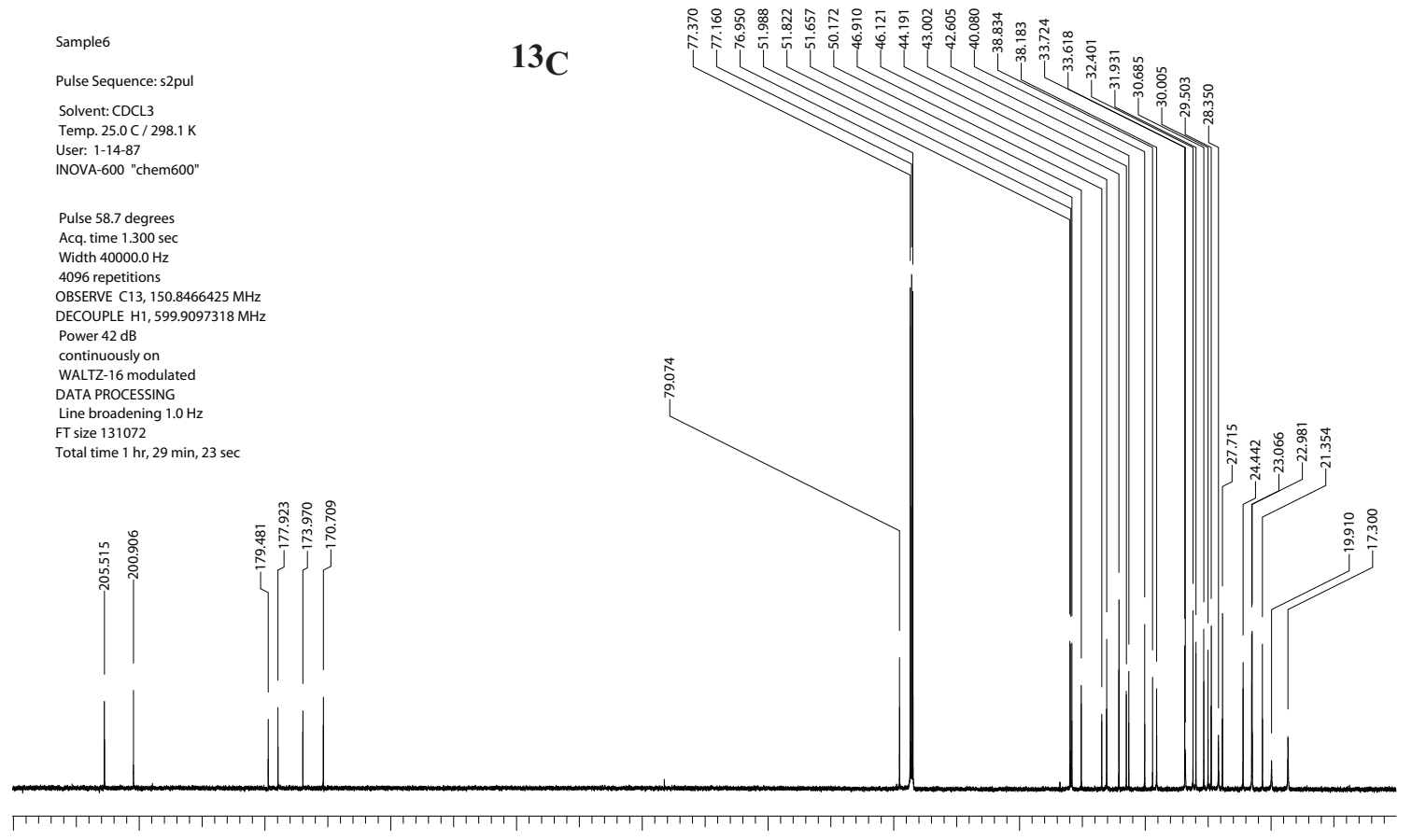
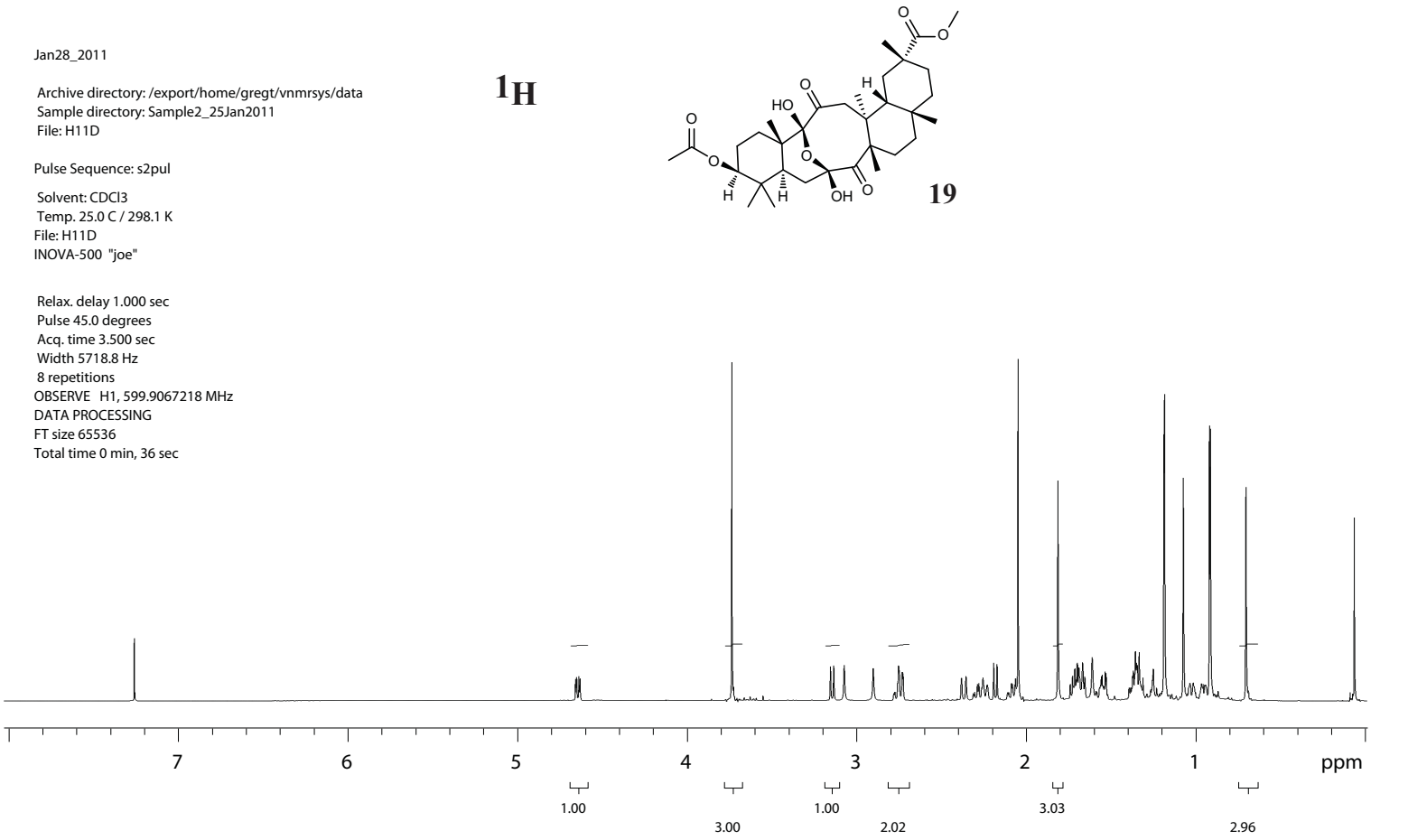


Figure S44. ^{1}H and ^{13}C spectra of **19**



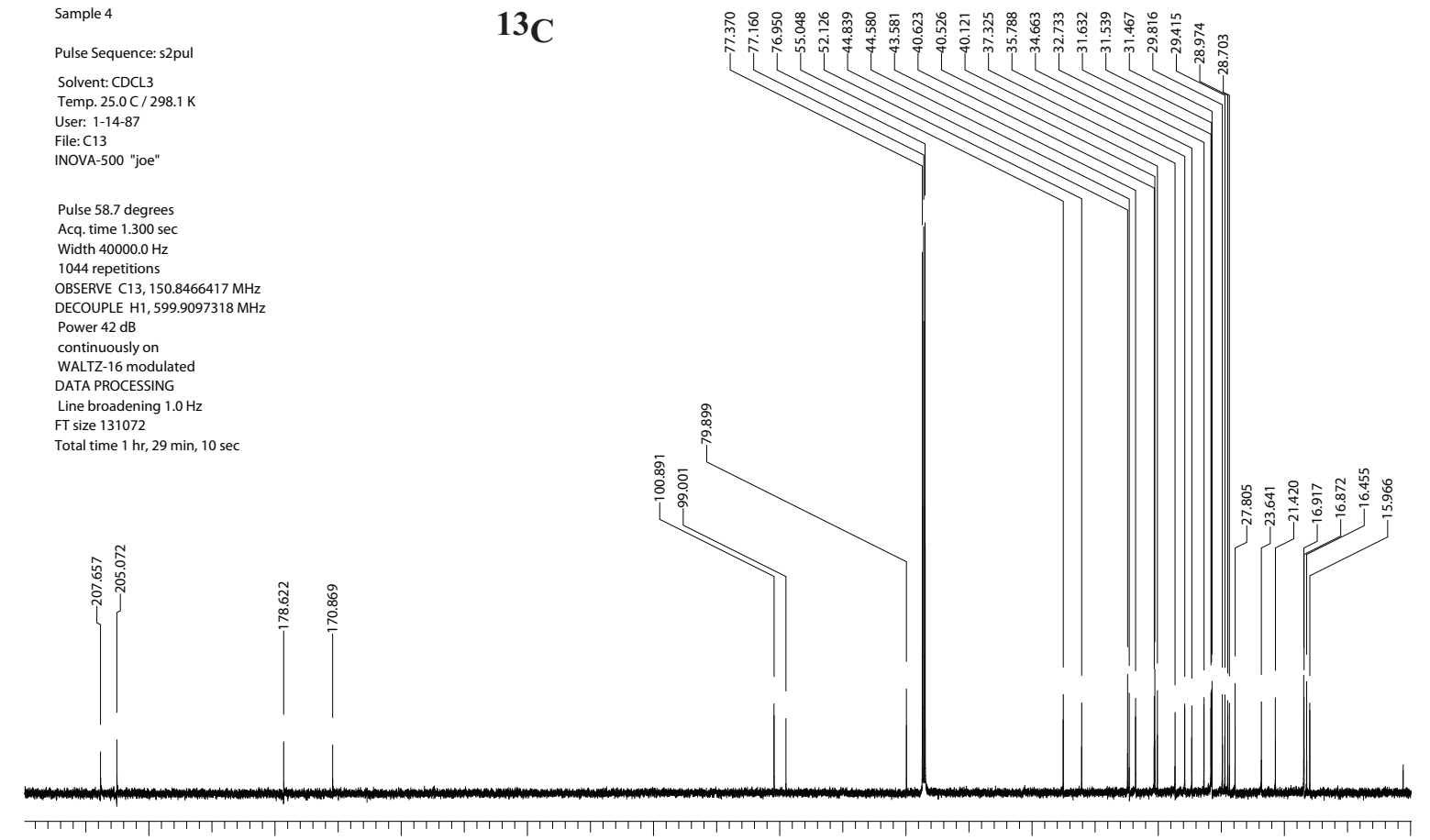
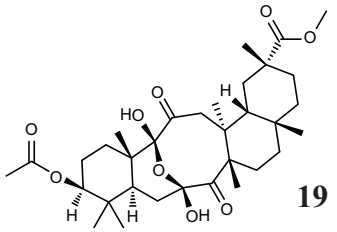
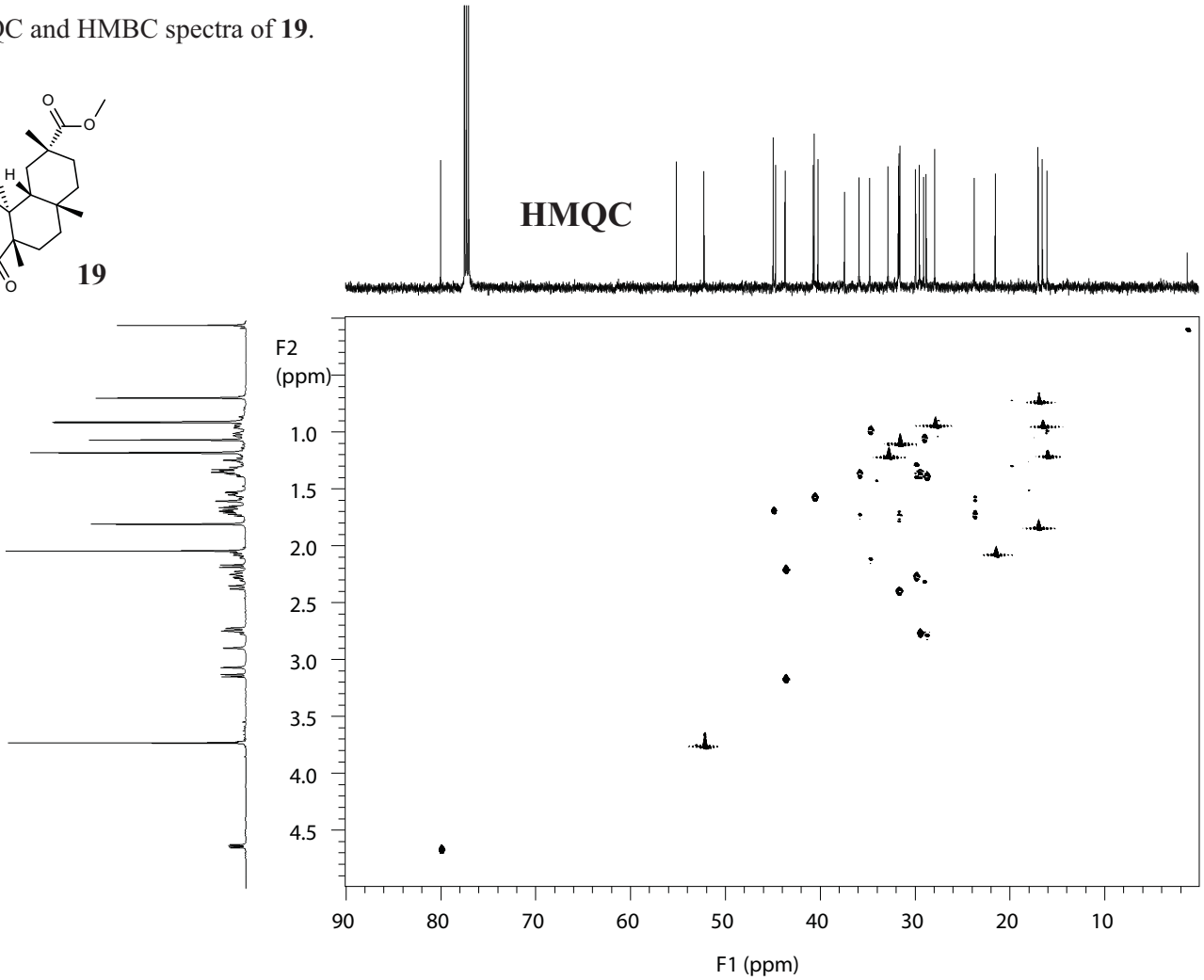


Figure S45. HMQC and HMBC spectra of **19**.



19



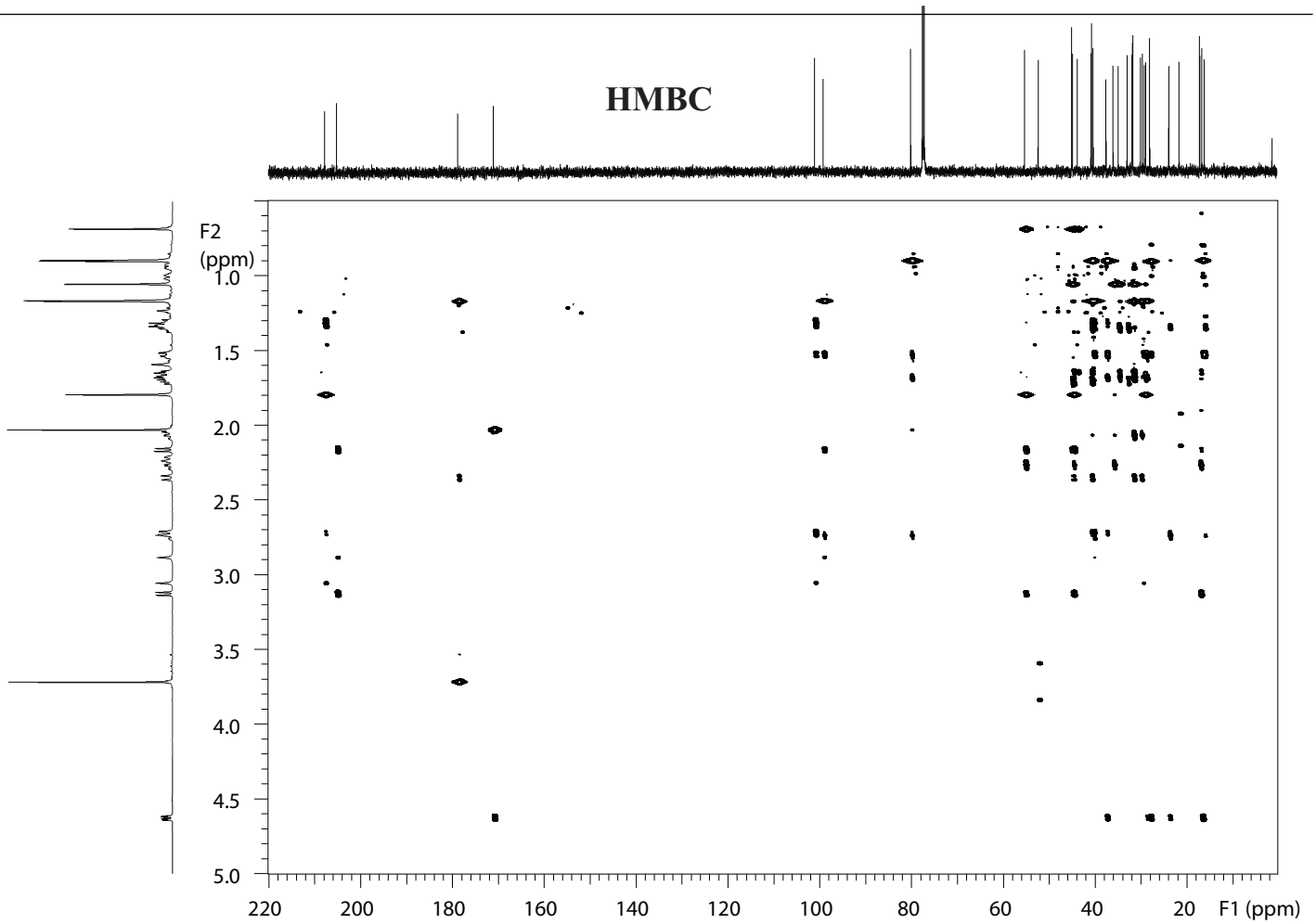
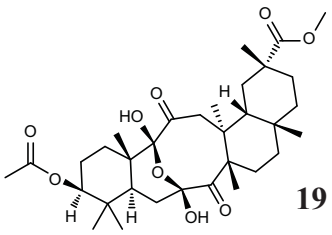
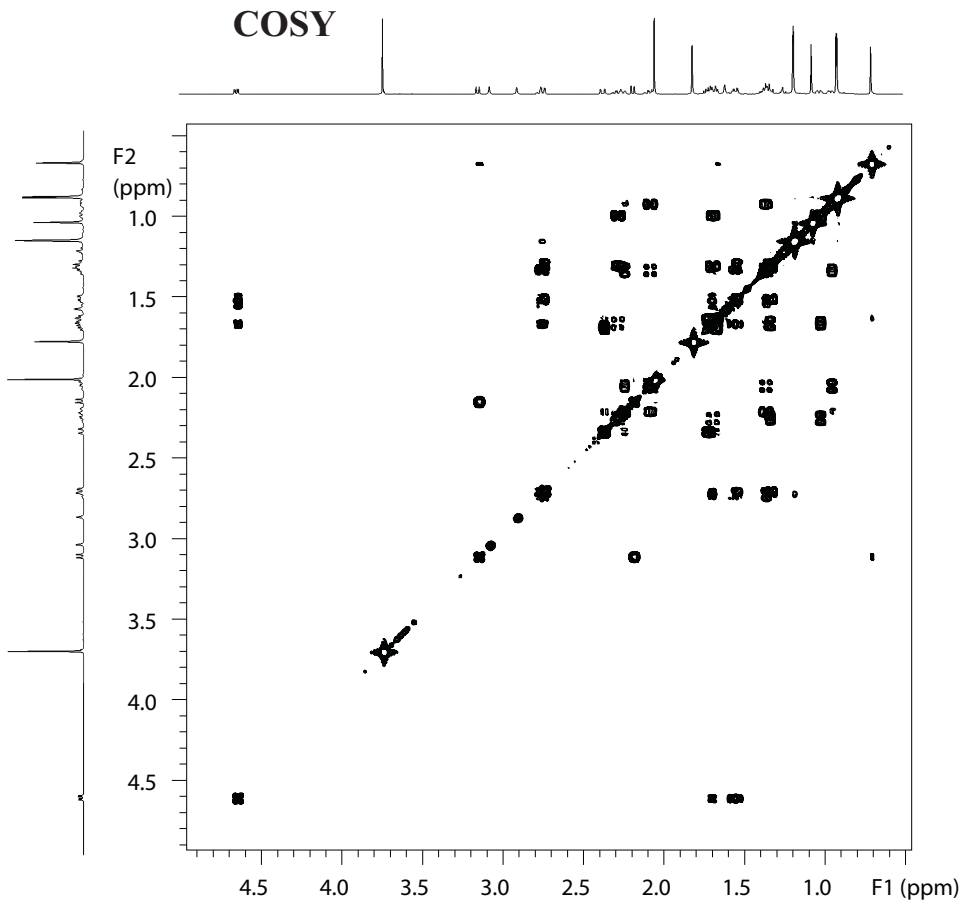


Figure S46. COSY and NOESY spectra of **19**.



19



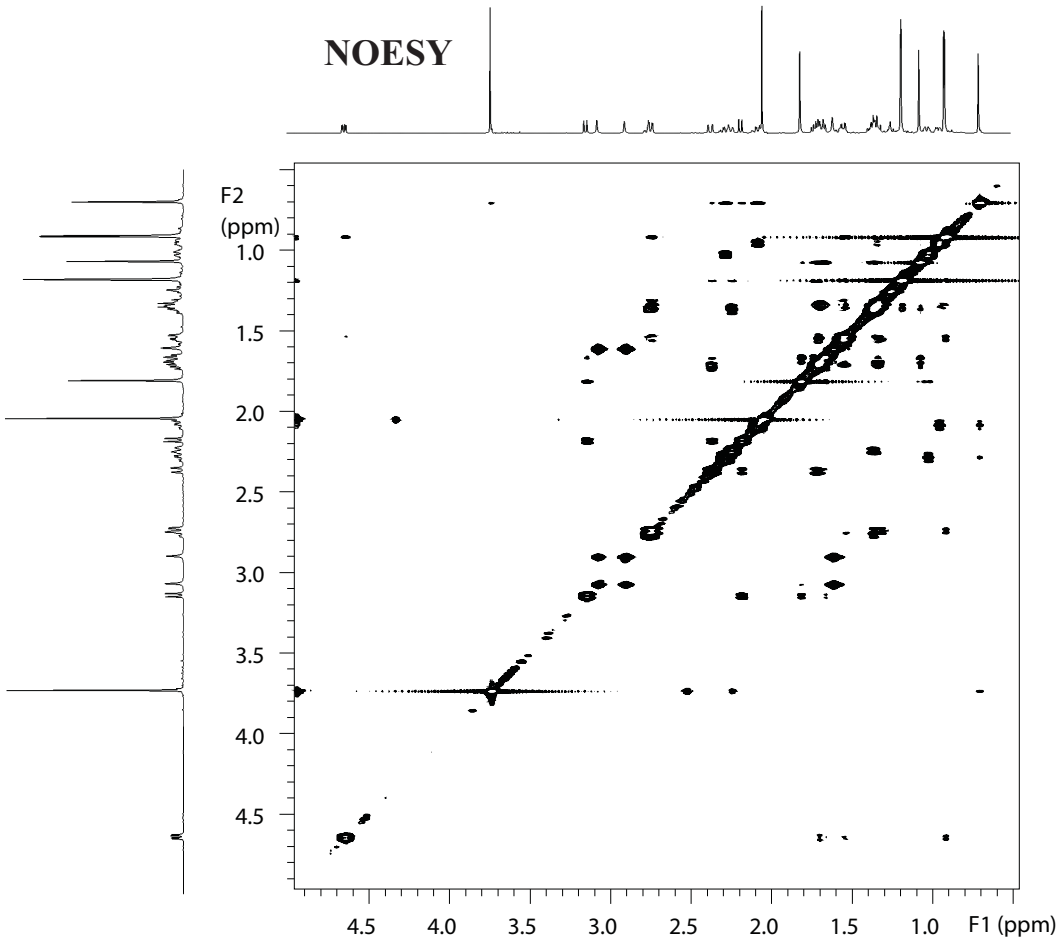
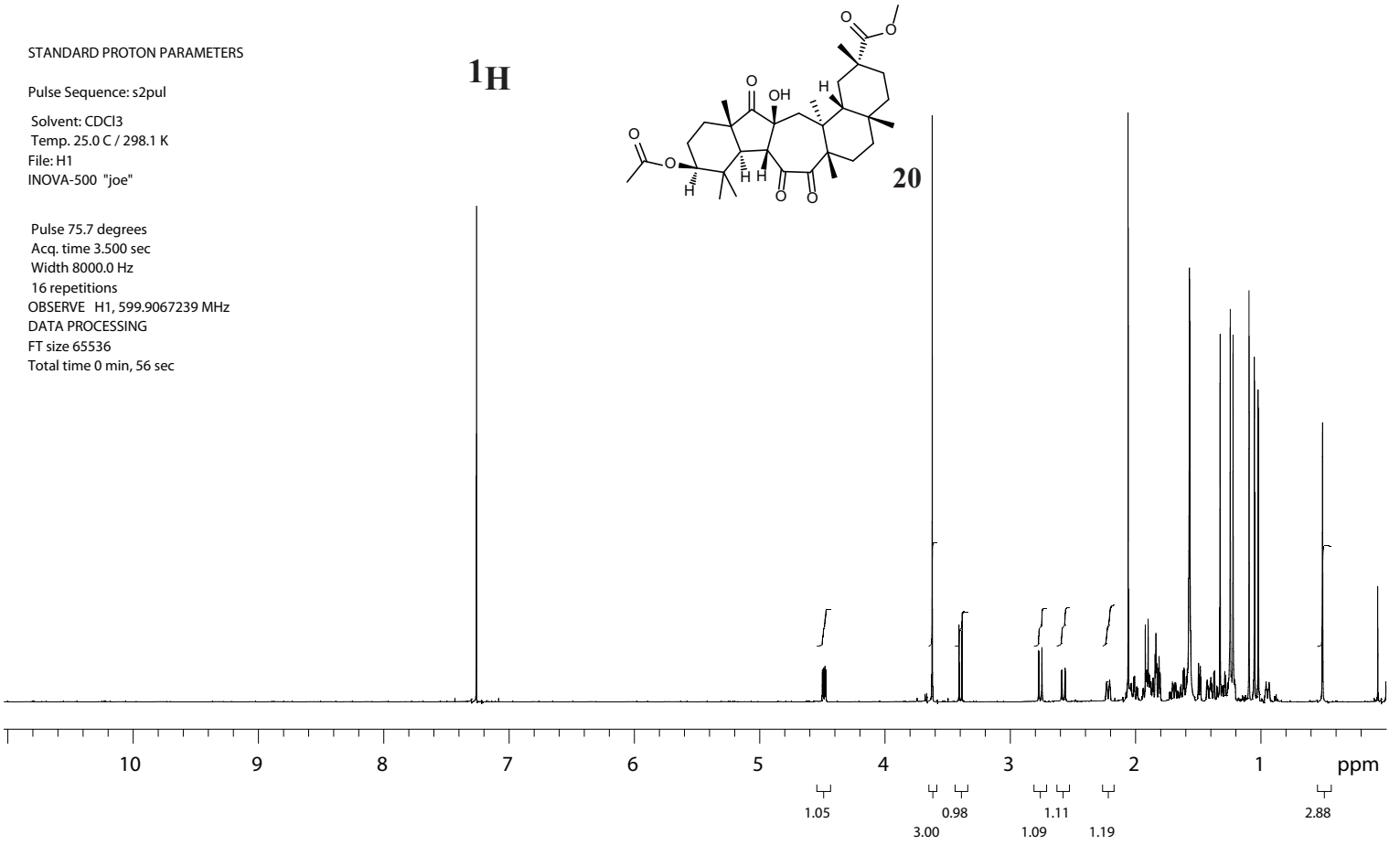


Figure S47. ^{1}H and ^{13}C spectra of **20**



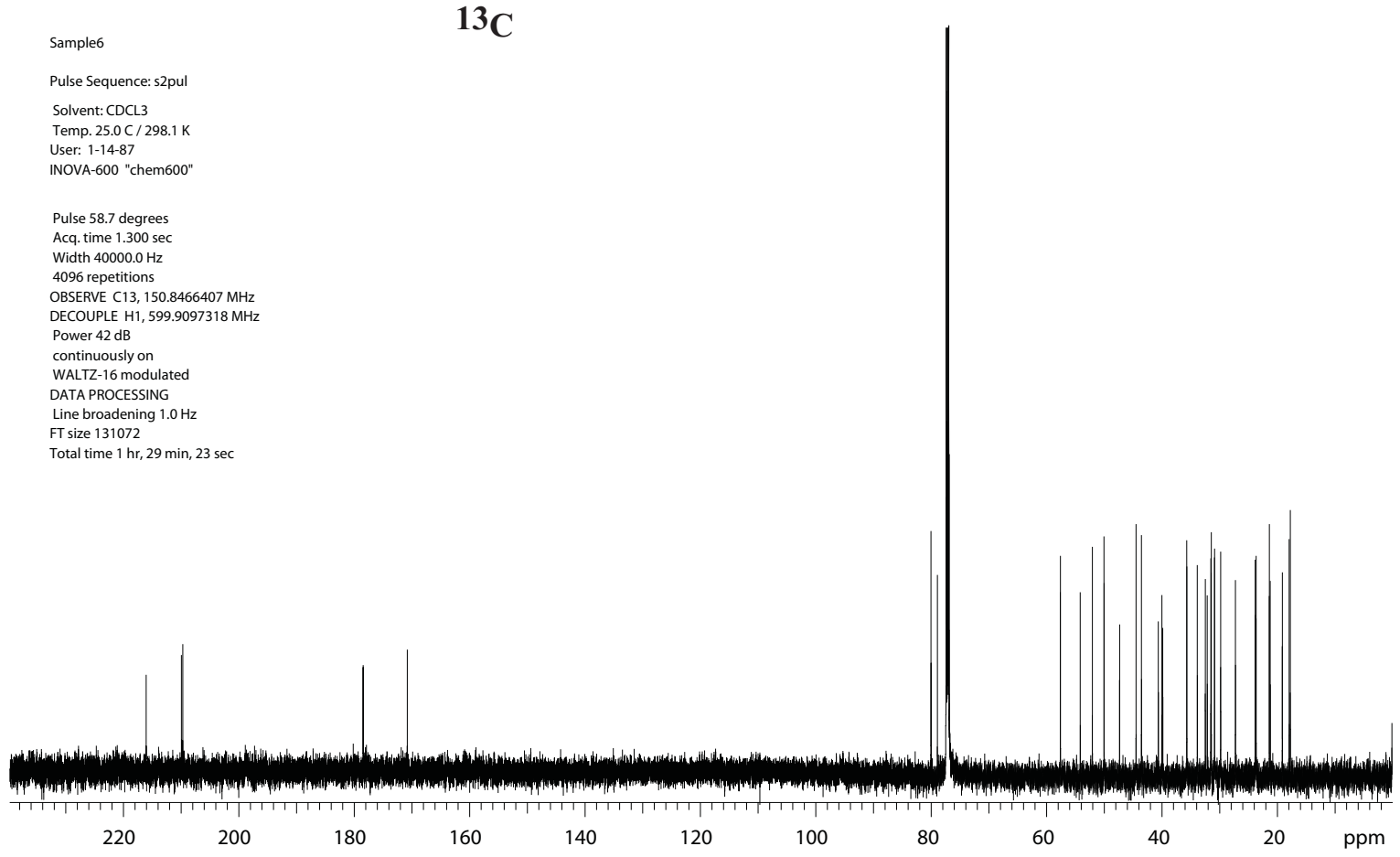
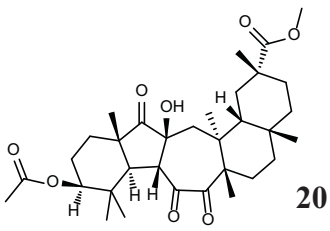


Figure S48. HMQC and HMBC spectra of **20**.



20

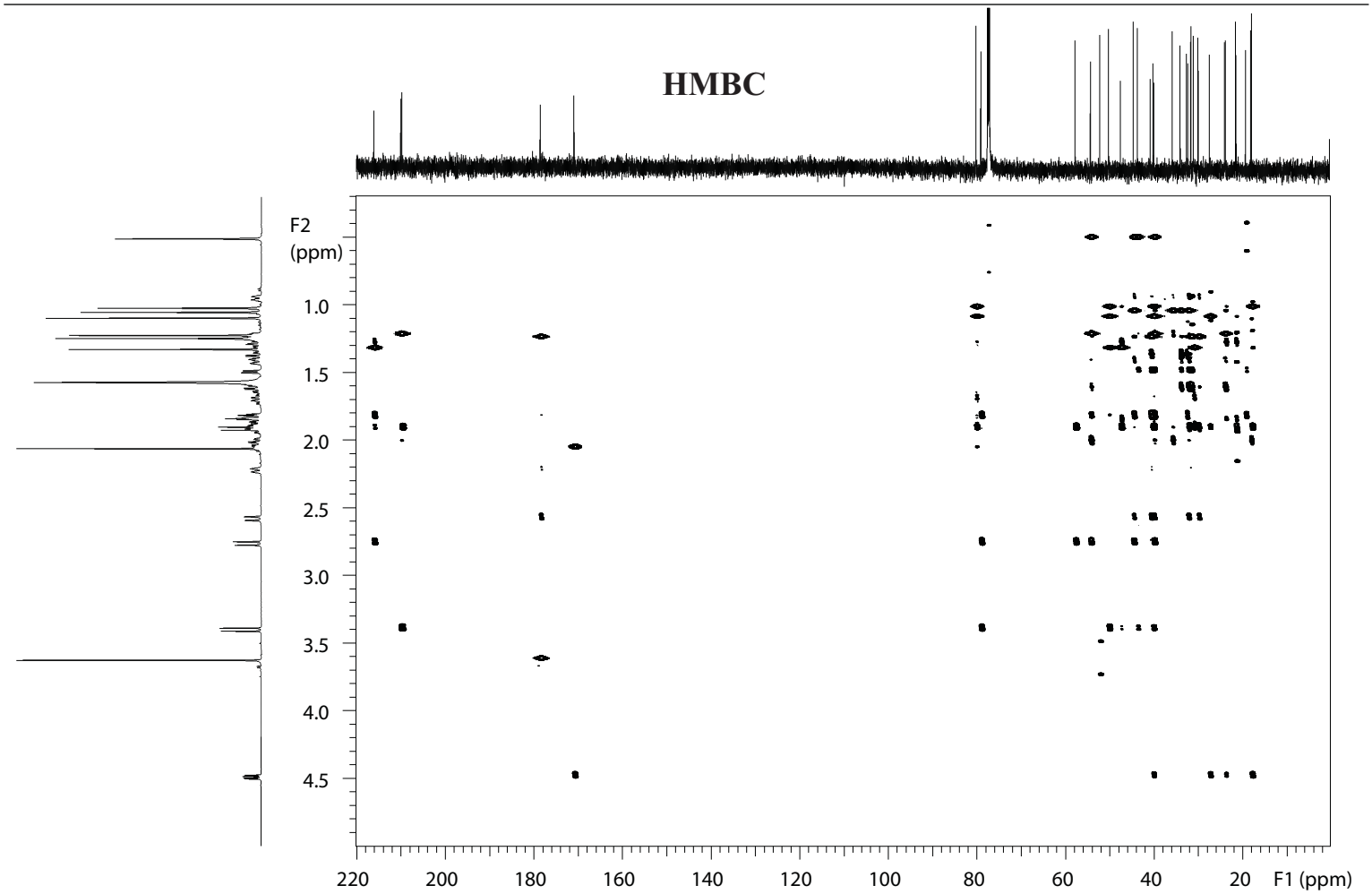
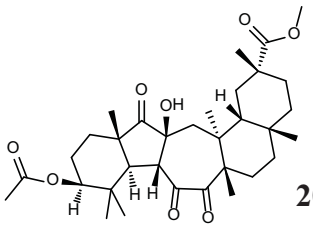


Figure S49. COSY and NOESY spectra of **20**.



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