

Supporting Information

Neobraclactones A–C, three unprecedented chaise longue-shaped xanthonones from *Garcinia bracteata*

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Contents

Computational methods of ECD of compound 1	3
Figure S1. B3LYP/6-31+G** optimized lowest energy 3D conformer of 1	3
Figure S2–S15. The HRMS, UV, IR, ¹ H NMR, expanded ¹ H NMR, ¹³ C NMR, HSQC, HMBC, NOESY, ECD spectra of neobraclactone A (1).....	4–10
Figure S16. The Rh ₂ (OCOCF ₃) ₄ induced ECD spectrum of neobraclactone A (1) in CDCl ₃	11
Figure S17. The bulkiness rule for secondary alcohols applied.....	11
Figure S18–S29. The HRMS, UV, IR, ¹ H NMR, expanded ¹ H NMR, ¹³ C NMR, HSQC, HMBC and NOESY spectra of neobraclactone B (2).....	12–17
Figure S30. The comparison of ¹ H NMR spectra of compounds 1 and 2	18
Figure S31. The comparison of ¹³ C NMR spectra of compounds 1 and 2	18
Figure S32–S40. The HRMS, UV, ¹ H NMR, expanded ¹ H NMR, ¹³ C NMR, HSQC, HMBC, NOESY spectra of neobraclactone C (3).....	19–23

Computational methods of ECD of compound **1**

The CONFLEX^[1, 2] searches based on molecular mechanics with MMFF94S force fields were performed for (6*R*, 7*R*, 8*R*, 17*R*, 22*S*)-**1** and its enantiomer (6*S*, 7*S*, 8*S*, 17*S*, 22*R*)-**1**, which gave 8 stable conformers. Selected conformers of (6*R*, 7*R*, 8*R*, 17*R*, 22*S*)-**1** and (6*S*, 7*S*, 8*S*, 17*S*, 22*R*)-**1** with the lowest energy were further optimized by the density functional theory method at the B3LYP/6-31+G** level in Gaussian 03 program package,^[3] which was further checked by frequency calculation and resulted in no imaginary frequencies. The ECD of the conformer of **1** was then calculated by the TDDFT method at the B3LYP/6-31+G** level, and at the B3LYP/6-311++G**//B3LYP/6-31+G** levels with the PCM model in methanol solution. The calculated ECD curve was generated using SpecDis 1.51^[4] with $\sigma = 0.16$ eV, and UV shift -5 nm.

References

- [1] Goto, H.; Osawa, E.; *J. Am. Chem. Soc.* 1989, **111**, 8950–8951.
- [2] Goto, H.; Osawa, E.; *J. Chem. Soc., Perkin Trans.* 1993, 2, 187–198.
- [3]. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2005.
- [4]. Bruhn, T.; Hemberger, Y.; Schaumlöffel, A.; Bringmann, G. *Spec Dis*, version 1.51, University of Würzburg, Germany, 2010.

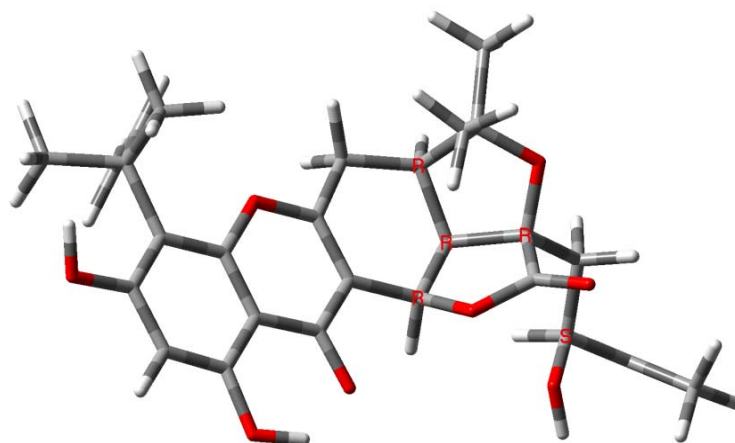


Figure S1. B3LYP/6-31+G** optimized lowest energy 3D conformer of **1**

Mass Spectrum Molecular Formula Report

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Comment			

Acquisition Parameter					
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Scan End	3000 m/z	Set Collision Cell RF	450.0 Vpp	Set Divert Valve	Source

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Formula, max.					
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Estimate Carbon	yes				

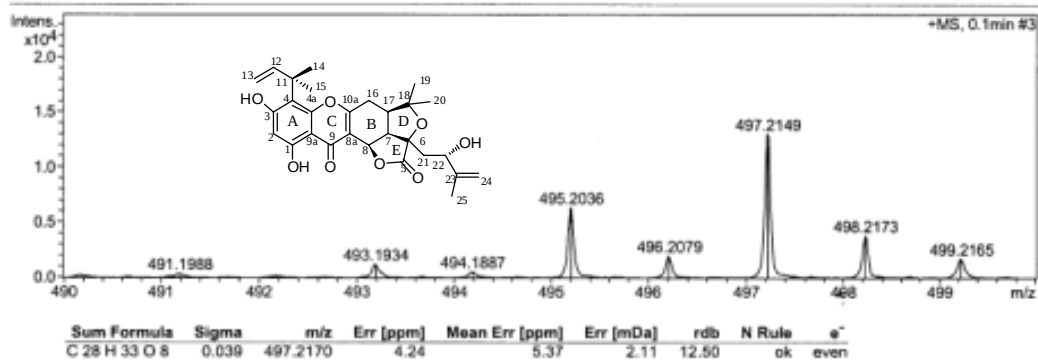


Figure S2. The HR-ESIMS spectrum of neobraclactone A (**1**)

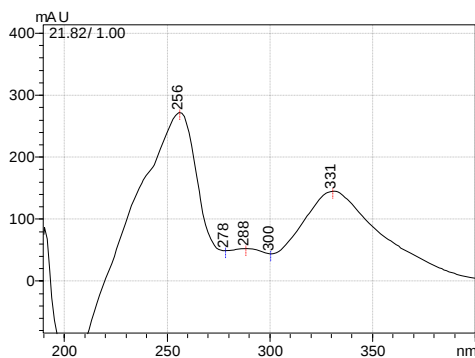


Figure S3. The UV spectrum of neobraclactone A (**1**) in CH₃OH

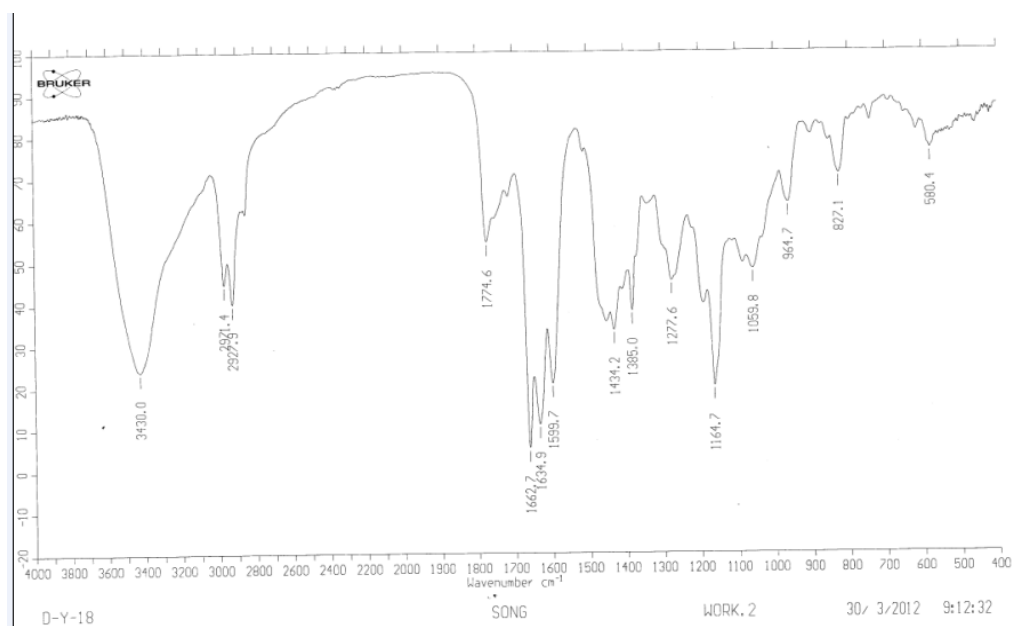


Figure S4. The IR spectrum of neobraclactone A (**1**)

AV-600-1H
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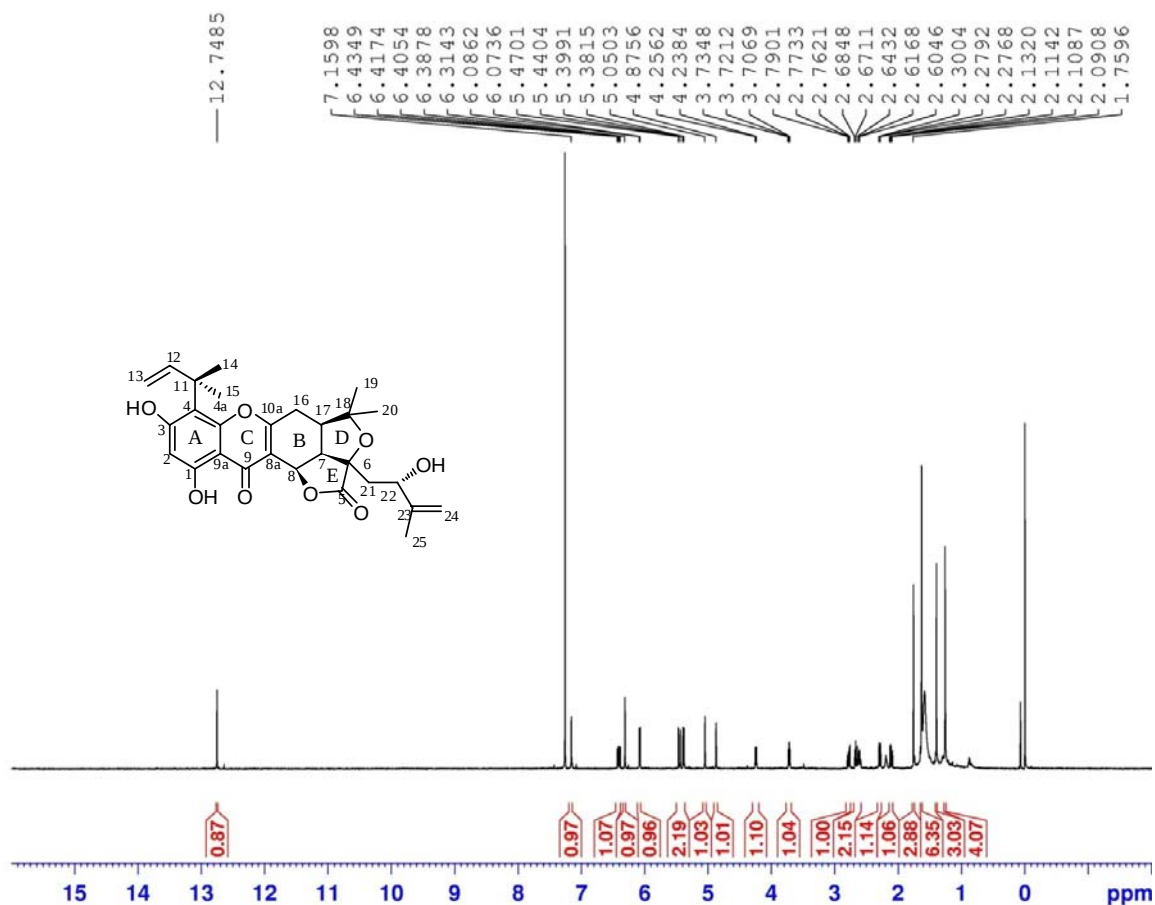


Figure S5. The ¹H NMR spectrum of neobraclactone A (**1**) in CDCl₃

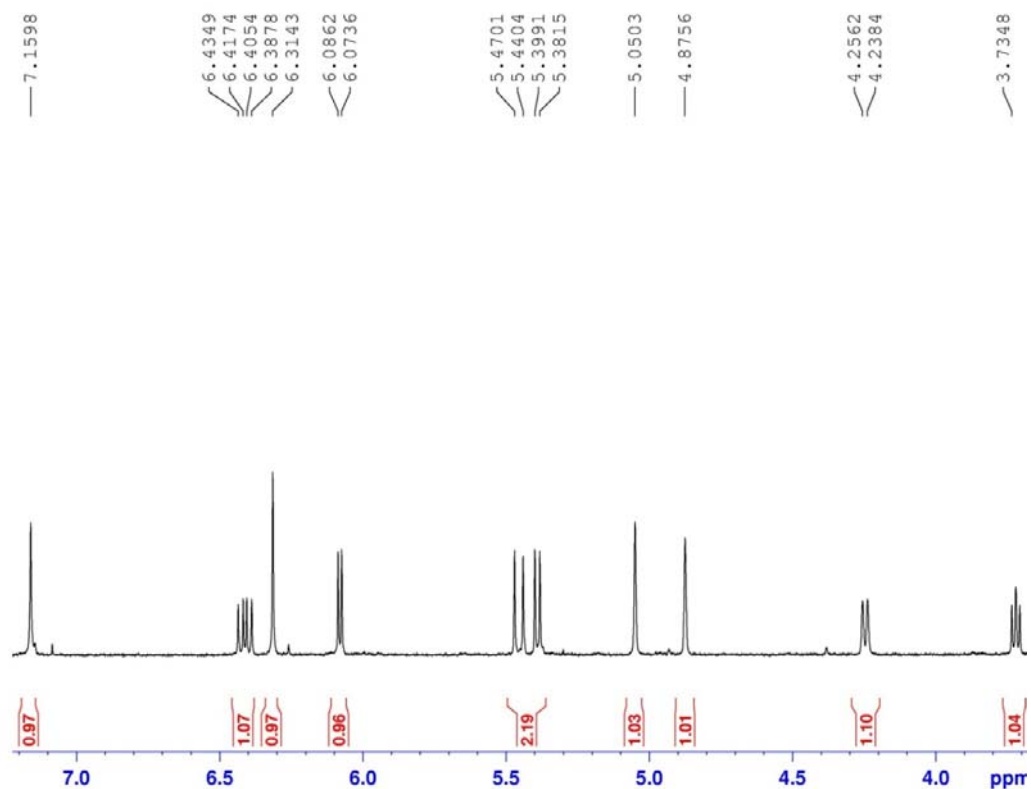


Figure S6. The expanded ^1H NMR spectrum of neobraclactone A (**1**) in CDCl_3

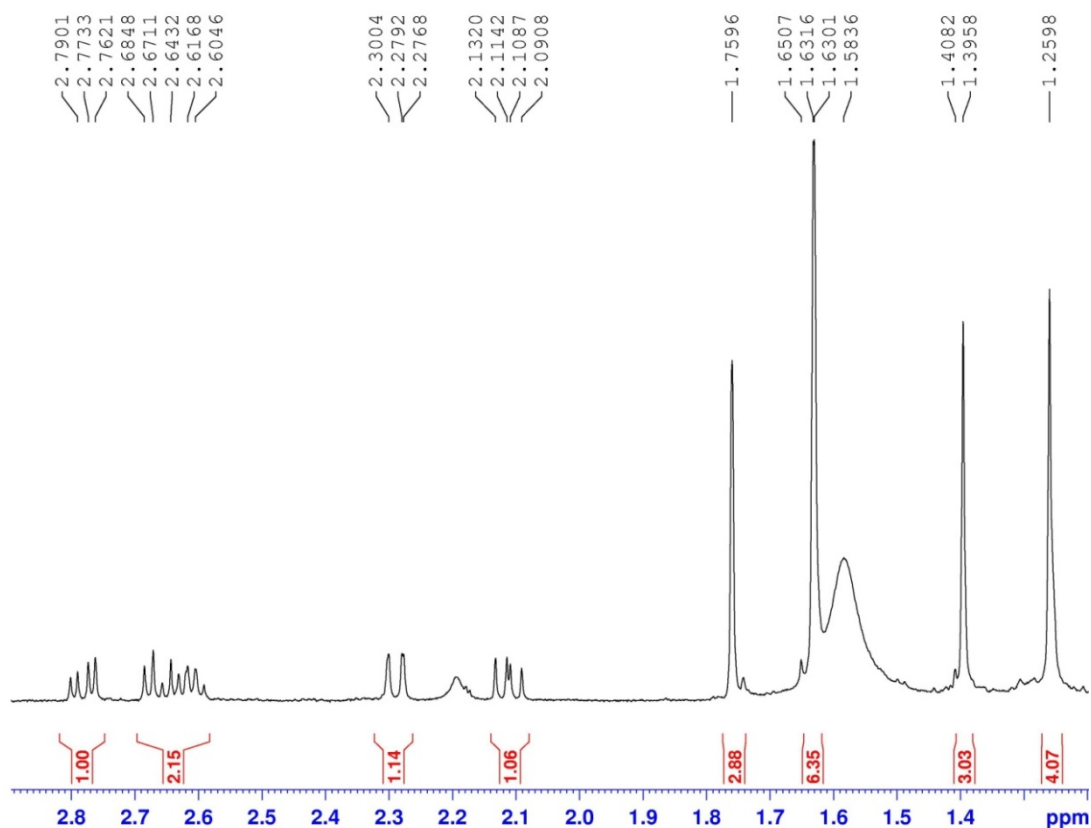


Figure S7. The expanded ^1H NMR spectrum of neobraclactone A (**1**) in CDCl_3

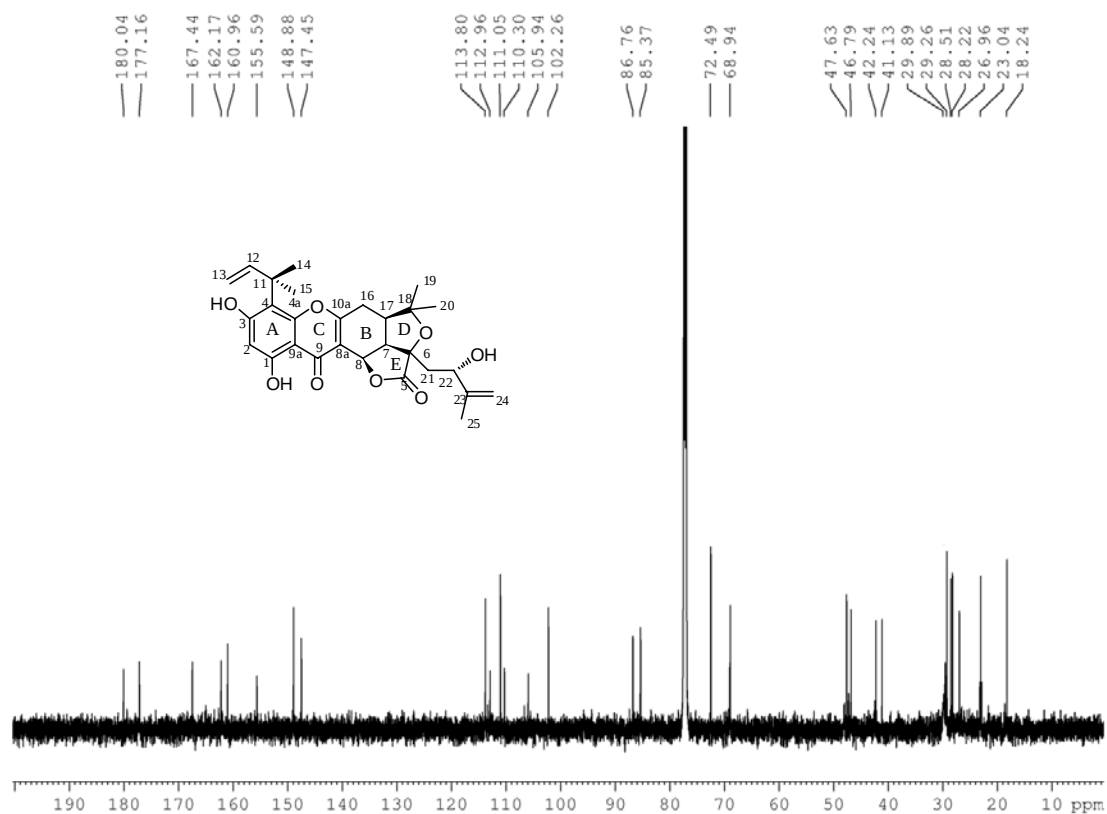


Figure S8. The ^{13}C NMR spectrum of neobraclactone A (**1**) in CDCl_3

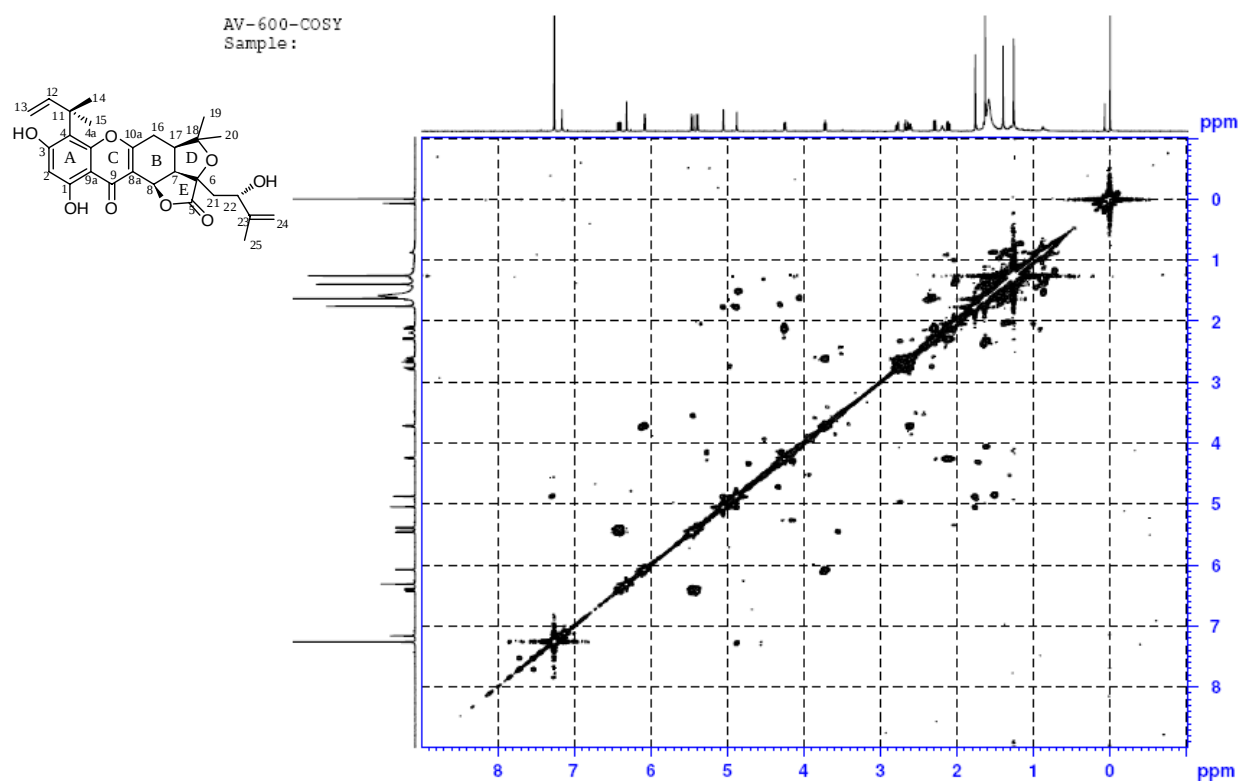


Figure S9. The ^1H - ^1H COSY spectrum of neobraclactone A (**1**) in CDCl_3

HSQC DBTH-Y-32 in CDCl₃
2012-03-21

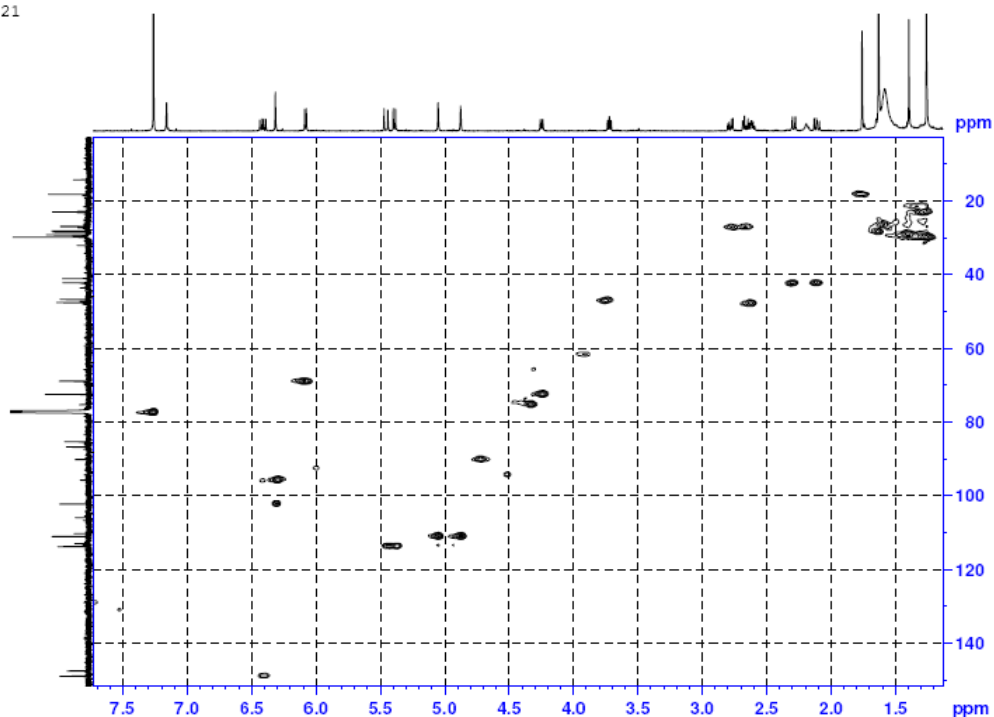


Figure S10. The HSQC spectrum of neobraclactone A (**1**) in CDCl₃

HMBC DBTH-Y-32 in CDCl₃
2012-03-21

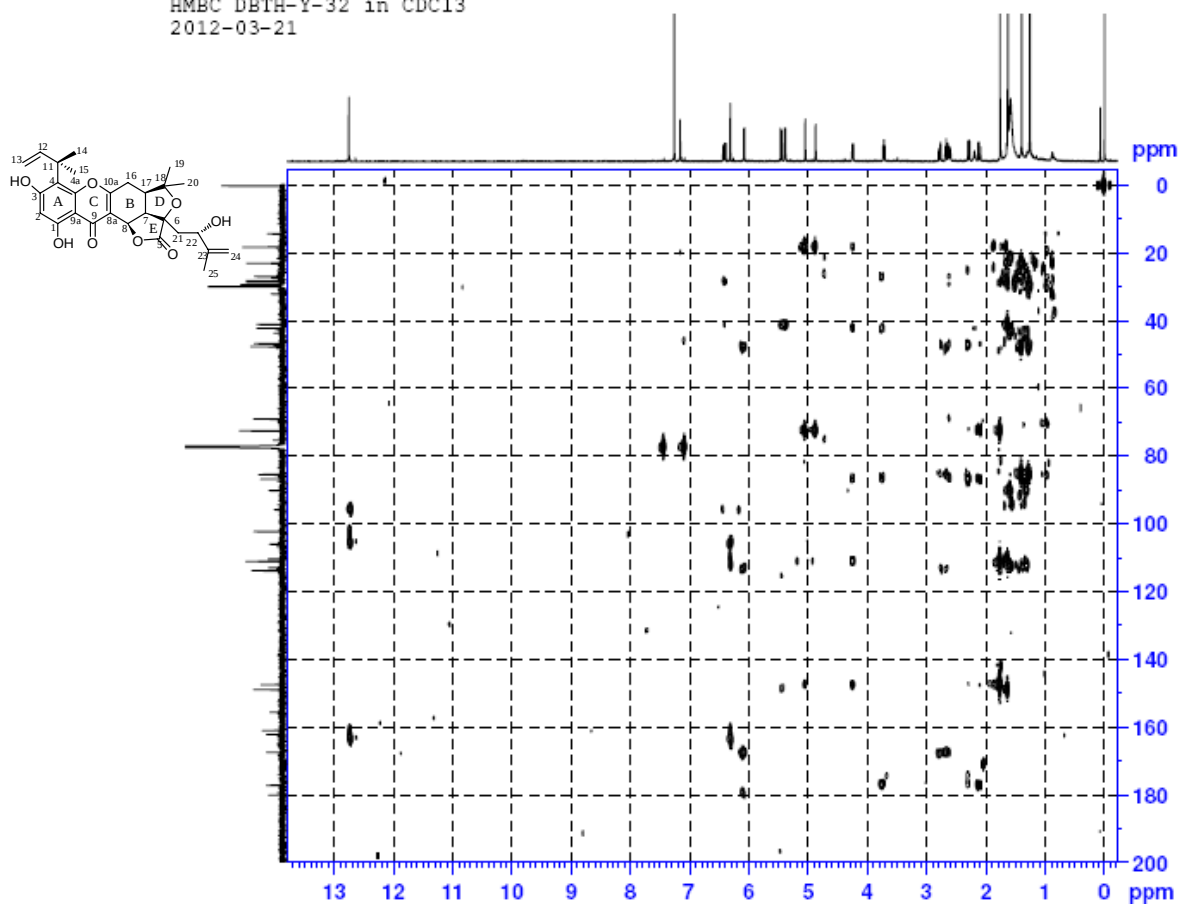


Figure S11. The HMBC spectrum of neobraclactone A (**1**) in CDCl₃

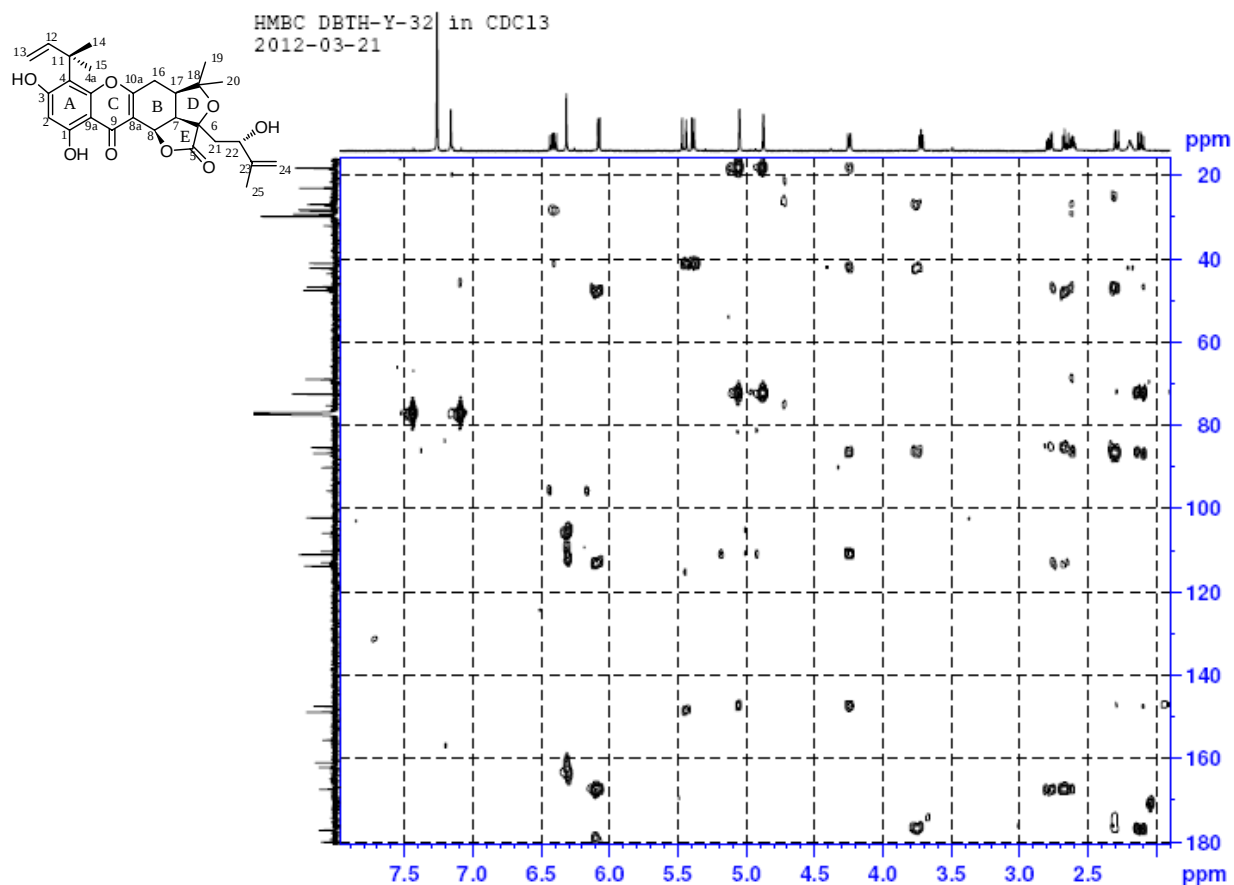


Figure S12. The expanded HMBC spectrum of neobraclactone A (**1**) in CDCl₃

AV-600-NOESY
Sample:

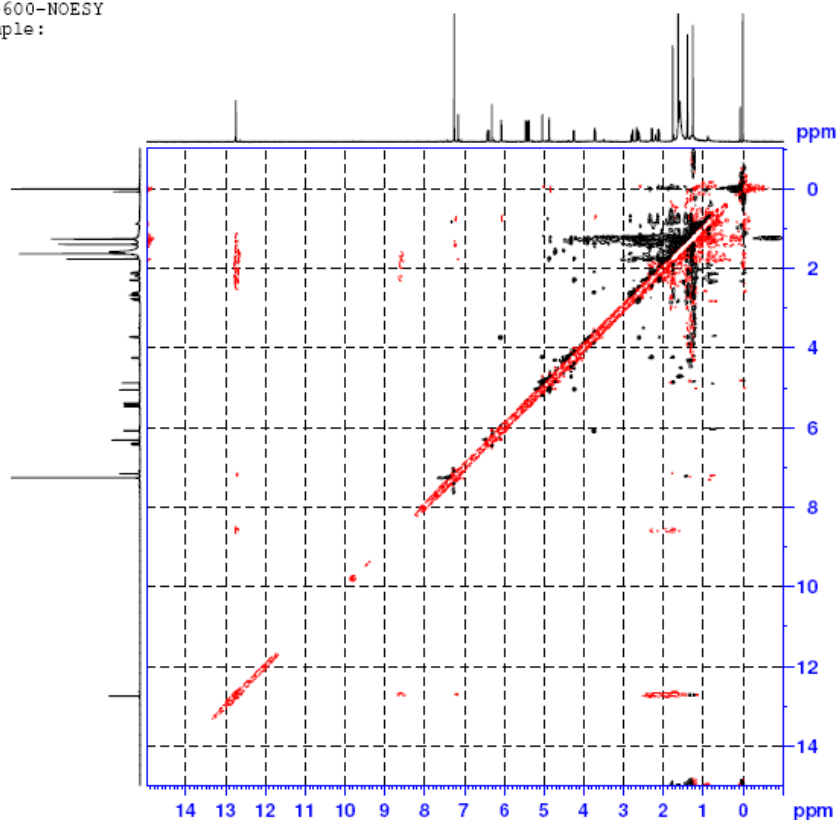


Figure S13. The NOESY spectrum of neobraclactone A (**1**) in CDCl₃

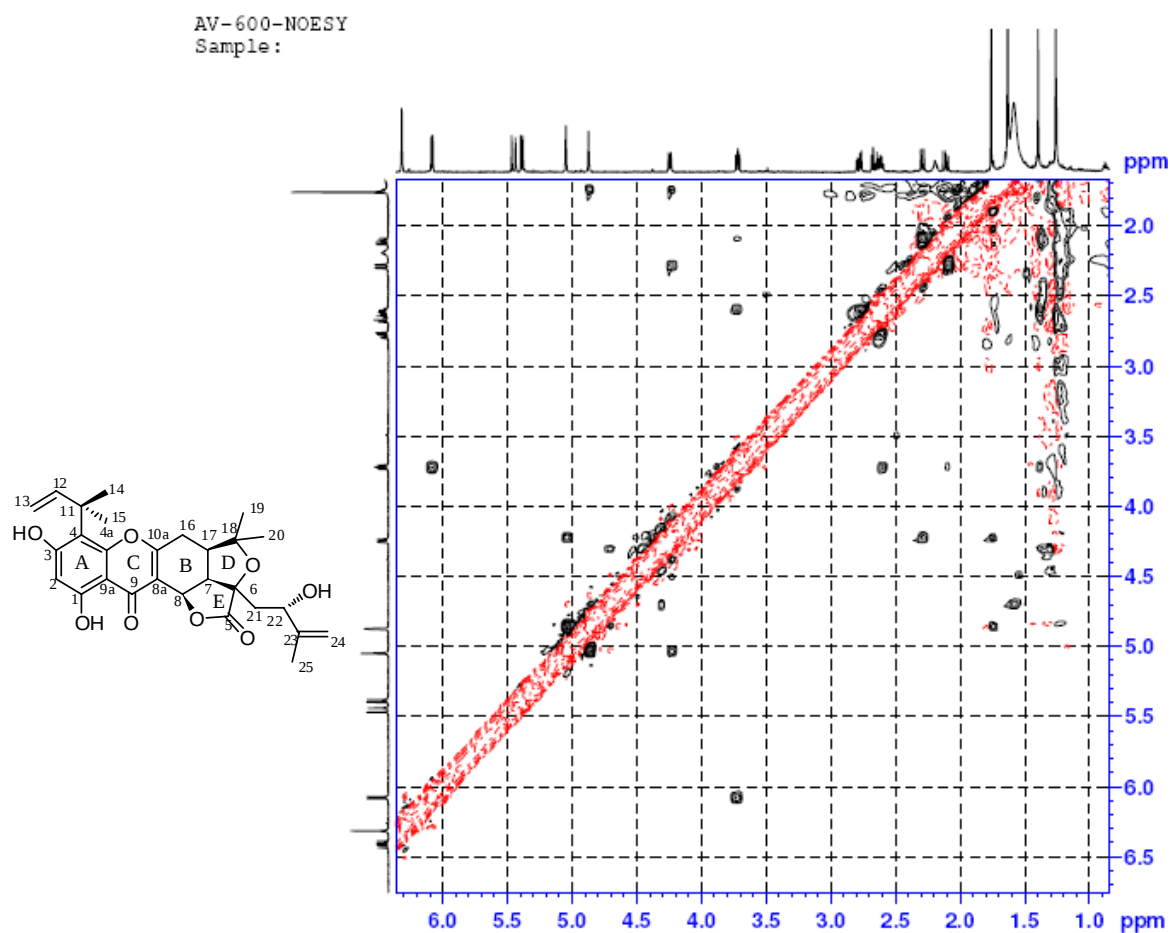


Figure S14. The expanded NOESY spectrum of neobraclactone A (**1**) in CDCl_3

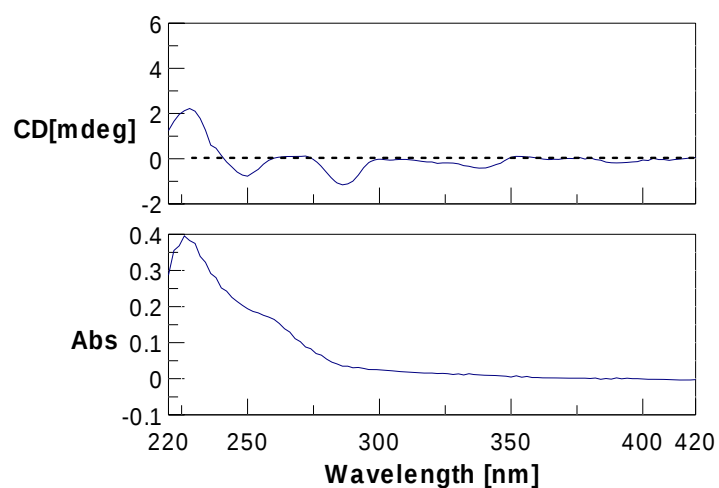


Figure S15. ECD spectrum of neobraclactone A (**1**)

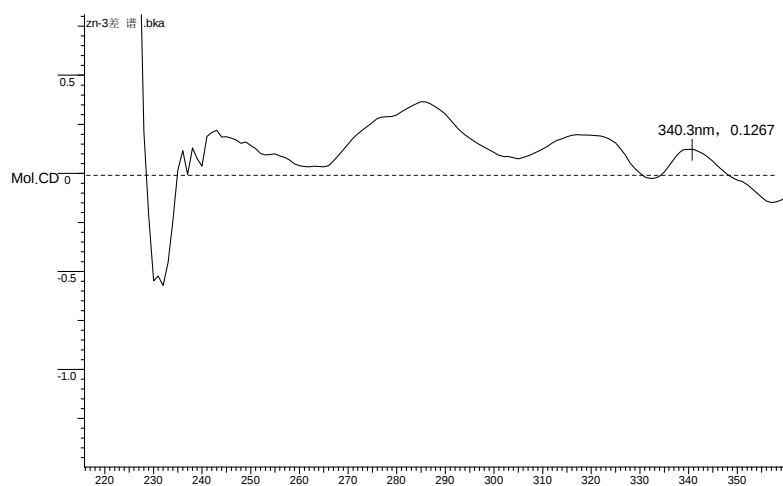


Figure S16. The $\text{Rh}_2(\text{OCOCF}_3)_4$ induced ECD spectrum of neobraclactone A (**1**)

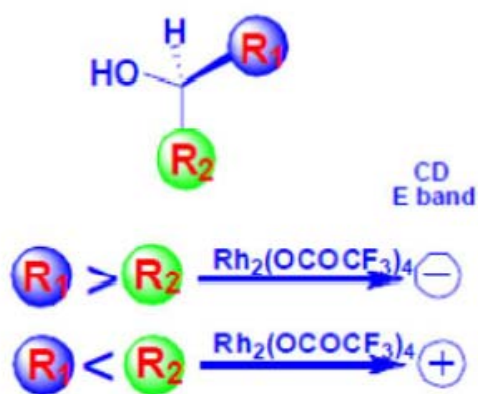


Figure S17. The bulkiest rule for secondary alcohols applied

Mass Spectrum Molecular Formula Report

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Comment			

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Scan End	3000 m/z	Set Collision Cell RF	450.0 Vpp	Set Divert Valve	Source

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Formula, max.			
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Estimate Carbon	yes	Maximum	3

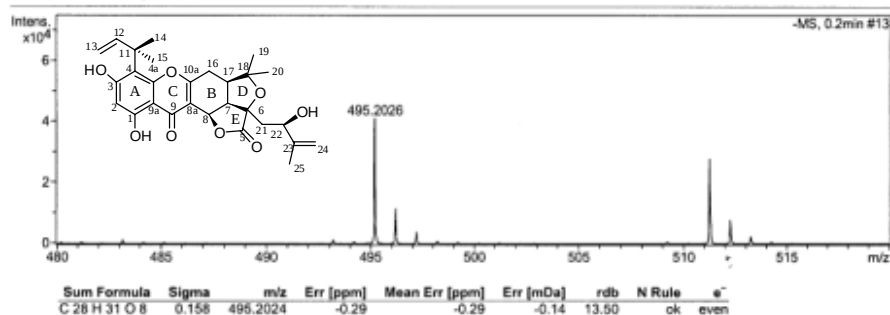


Figure S18. The HR-ESIMS spectrum of neobraclactone B (2)

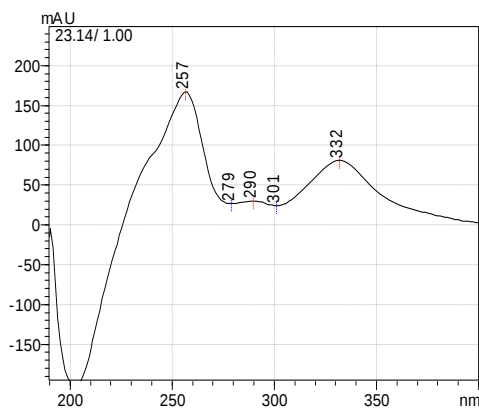


Figure S19. The UV spectrum of neobraclactone B (2)

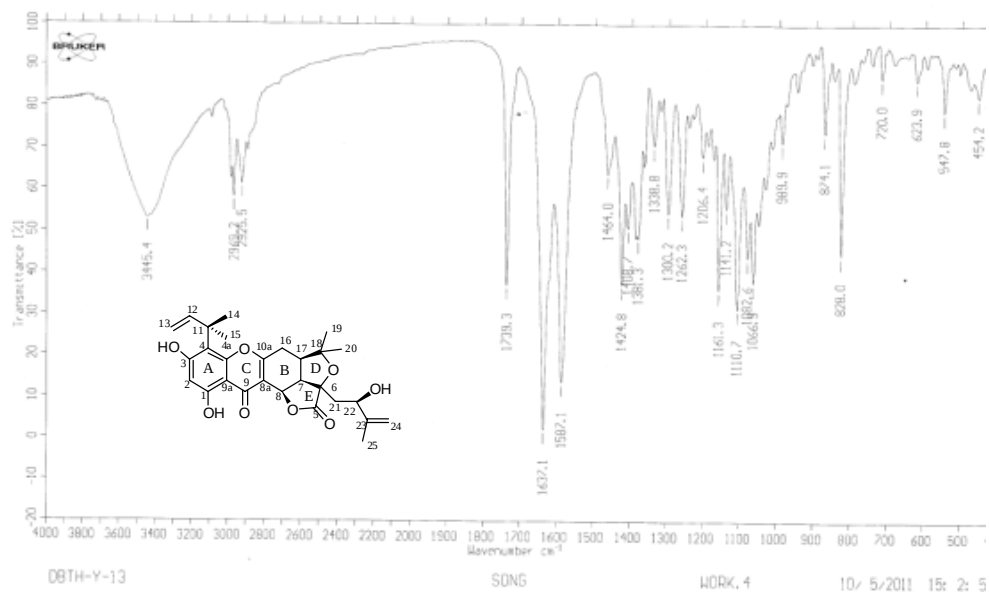


Figure S20. The IR spectrum of neobraclactone B (**2**)

¹H NMR DBTH-Y-19 in CDCl₃
2012-03-16

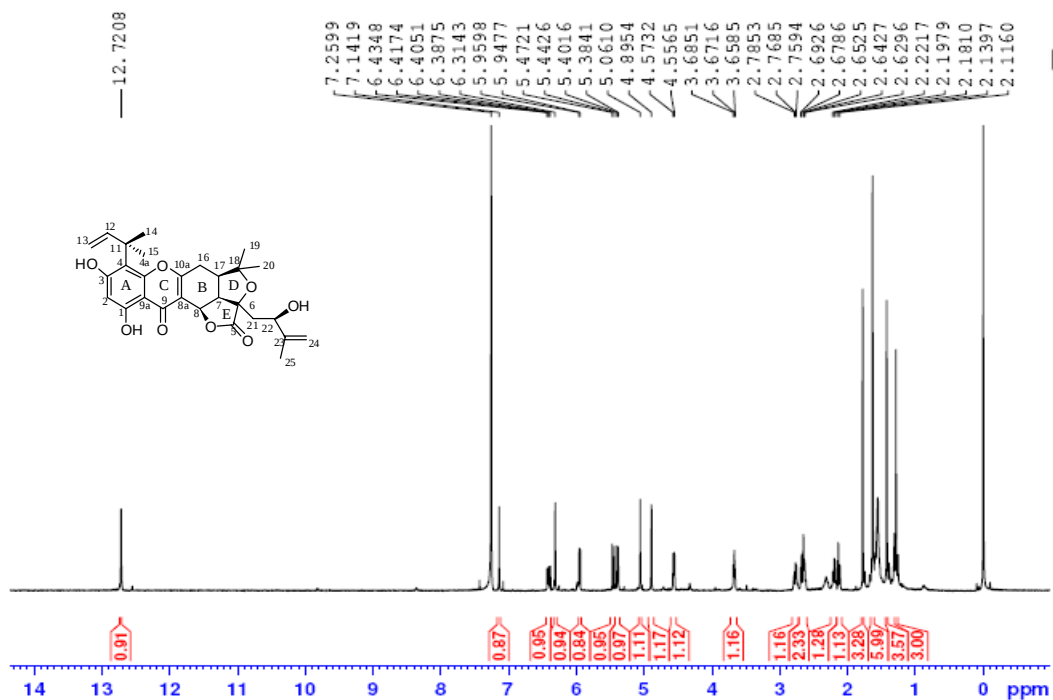


Figure S21. The ¹H NMR spectrum of neobraclactone B (**2**) in CDCl₃

MR DBTH-Y-19 in
2012-03-16

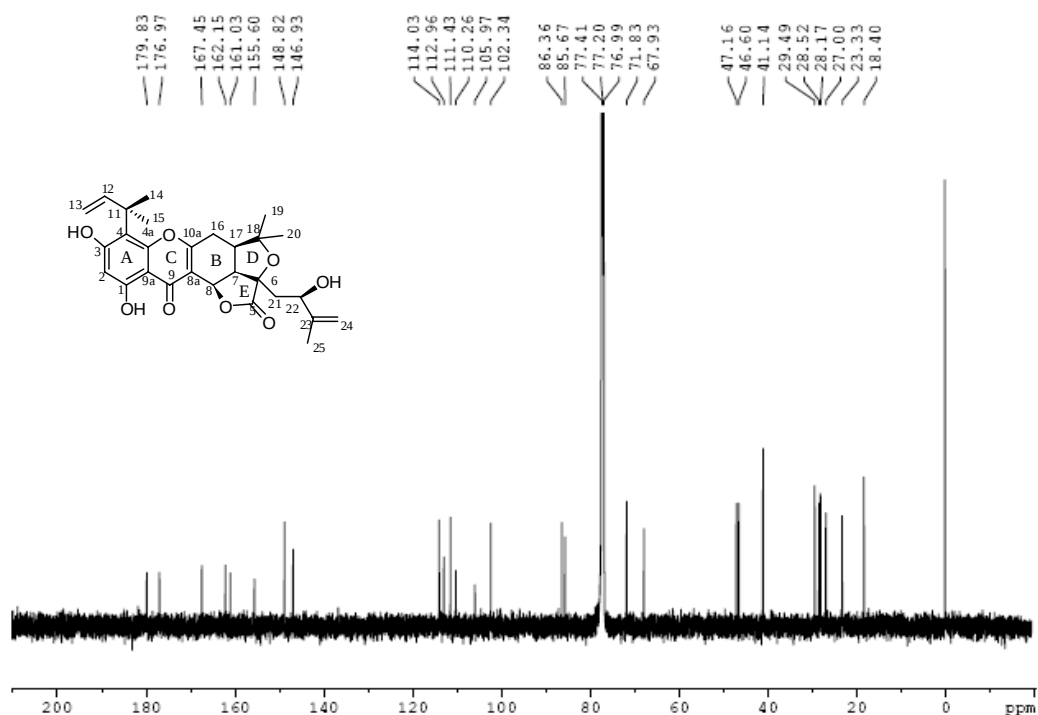


Figure S22. The ^{13}C NMR spectrum of neobraclactone B (2) in CDCl_3

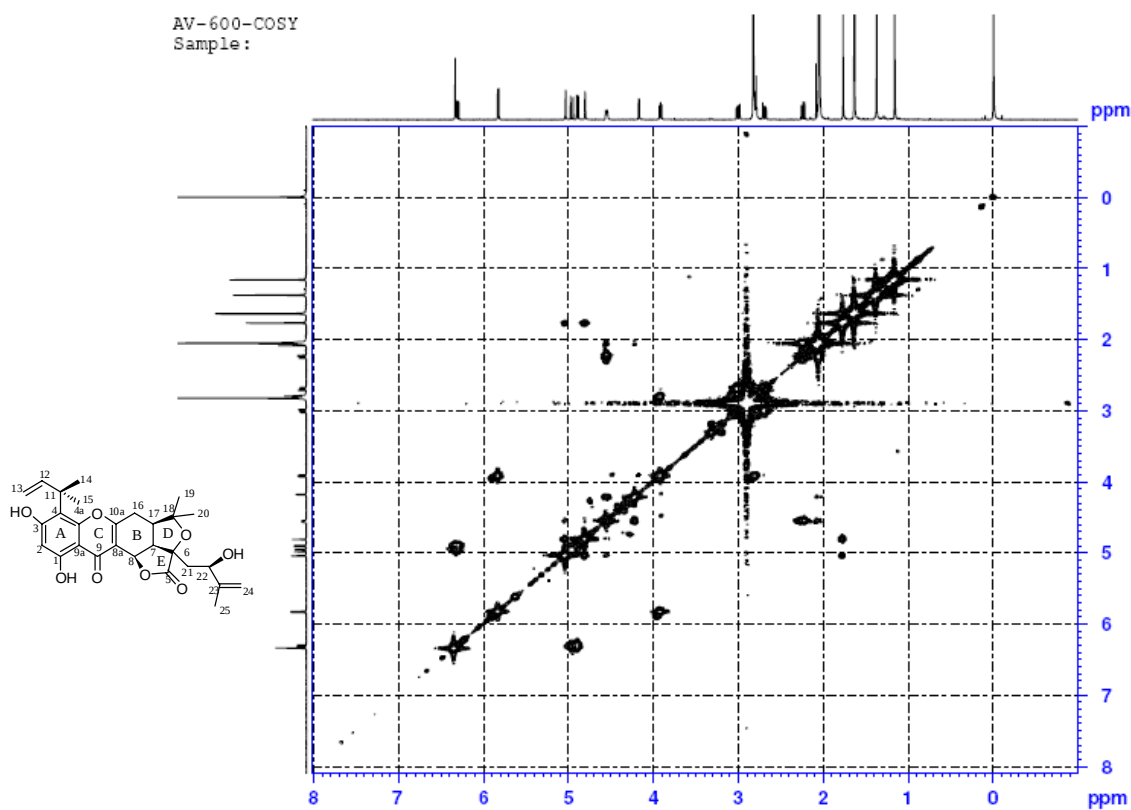


Figure S23. The ^1H - ^1H COSY spectrum of neobraclactone B (2) in CDCl_3

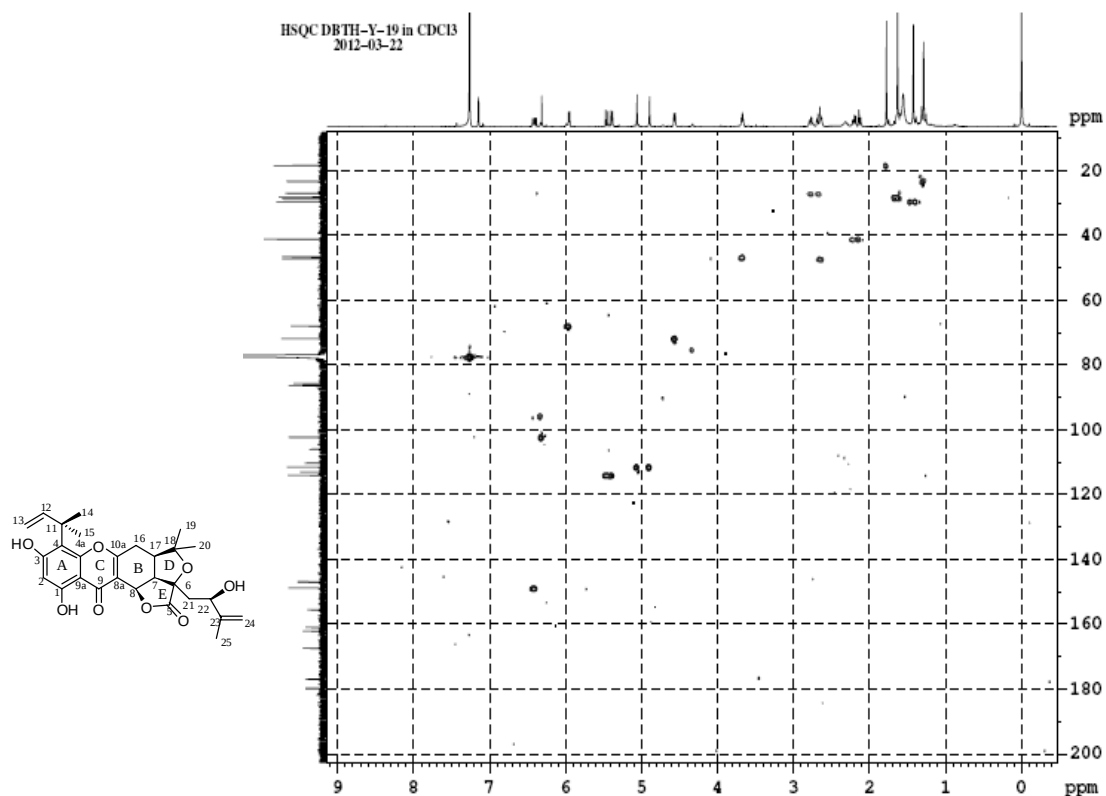


Figure S24. The HSQC spectrum of neobraclactone B (**2**) in CDCl₃

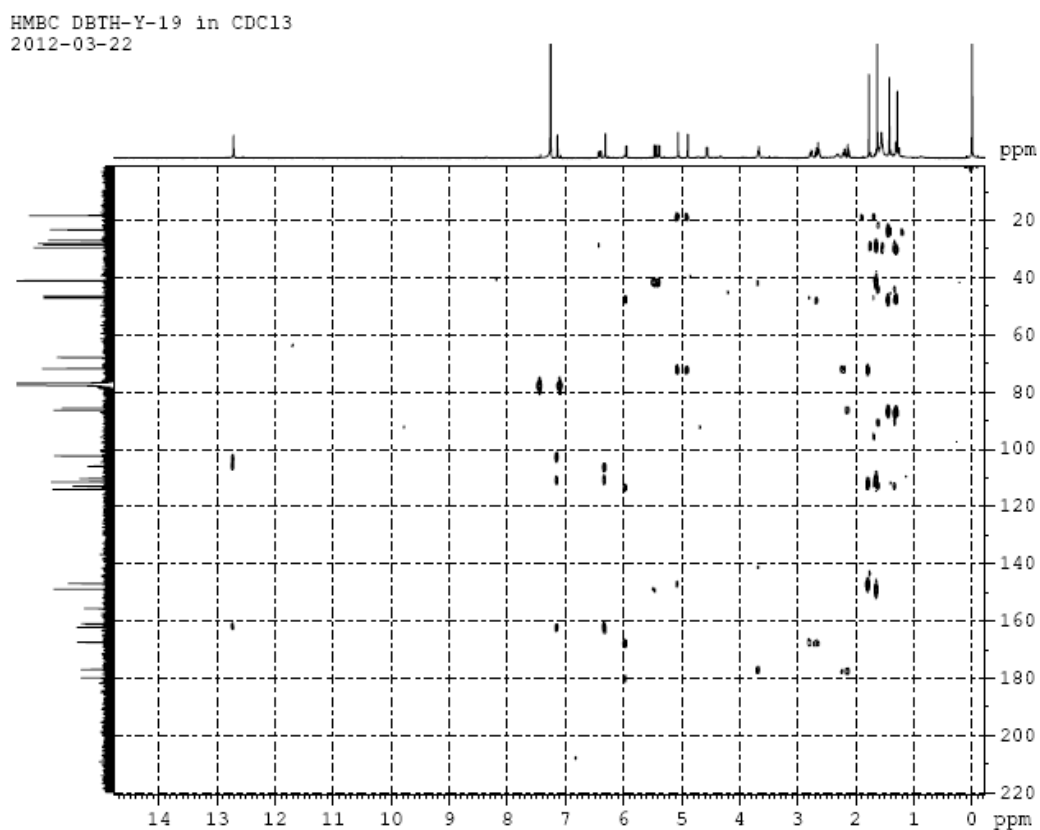


Figure S25. The HMBC spectrum of neobraclactone B (**2**) in CDCl₃

HMBC DBTH-Y-19 in CDCl₃
2012-03-22

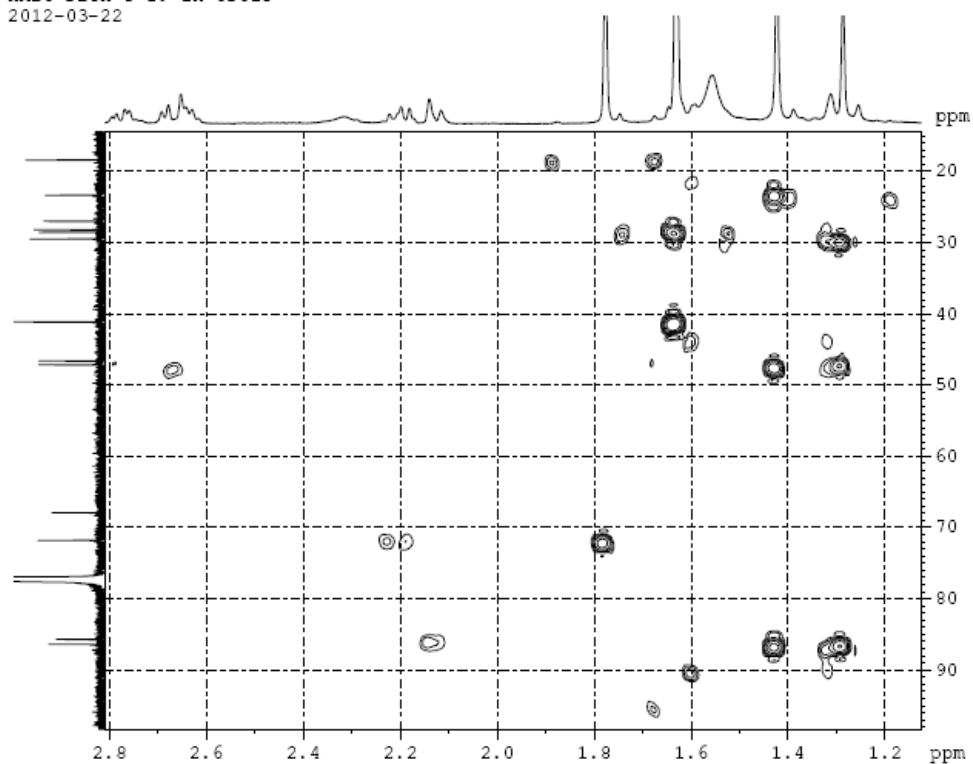


Figure S26. The expanded HMBC spectrum of neobraclactone B (**2**) in CDCl₃

HMBC DBTH-Y-19 in CDCl₃
2012-03-22

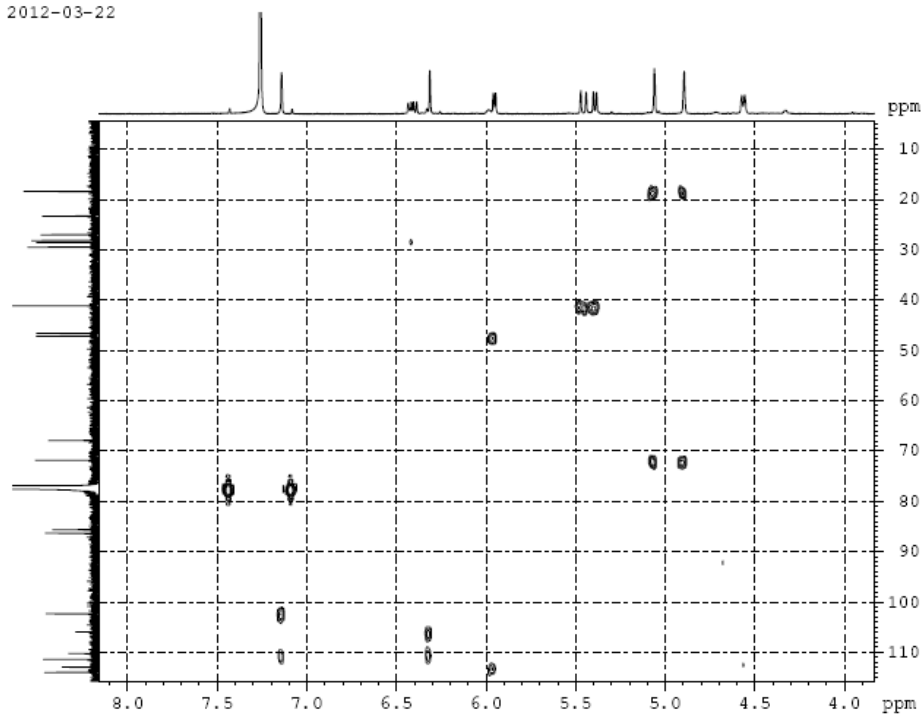


Figure S27. The expanded HMBC spectrum of neobraclactone B (**2**) in CDCl₃

AV-600-NOESY
Sample:

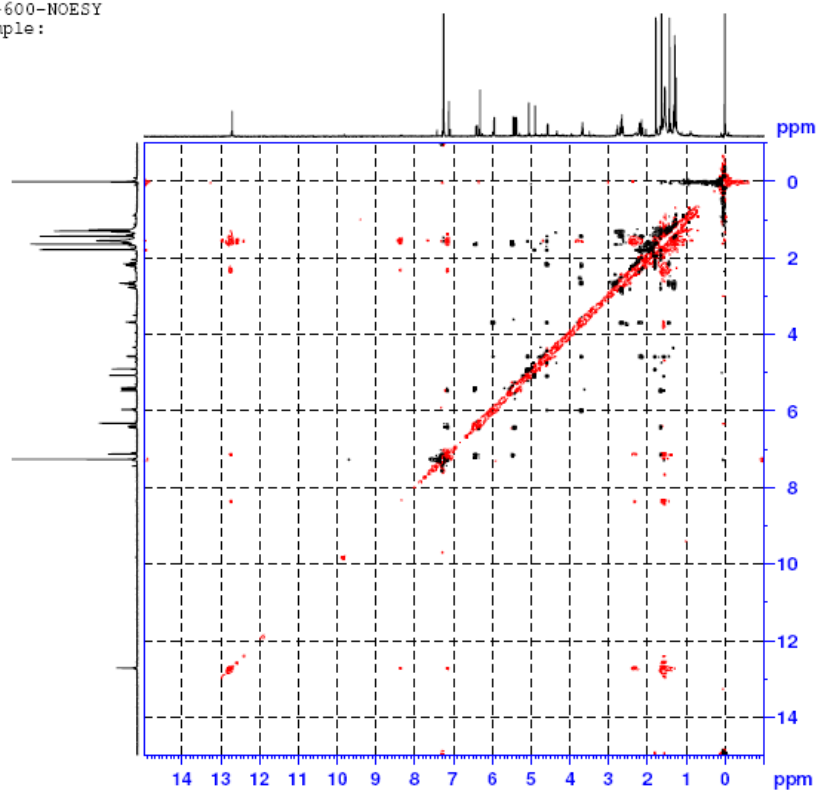


Figure S28. The NOESY spectrum of neobraclactone B (**2**) in CDCl₃

AV-600-NOESY
Sample:

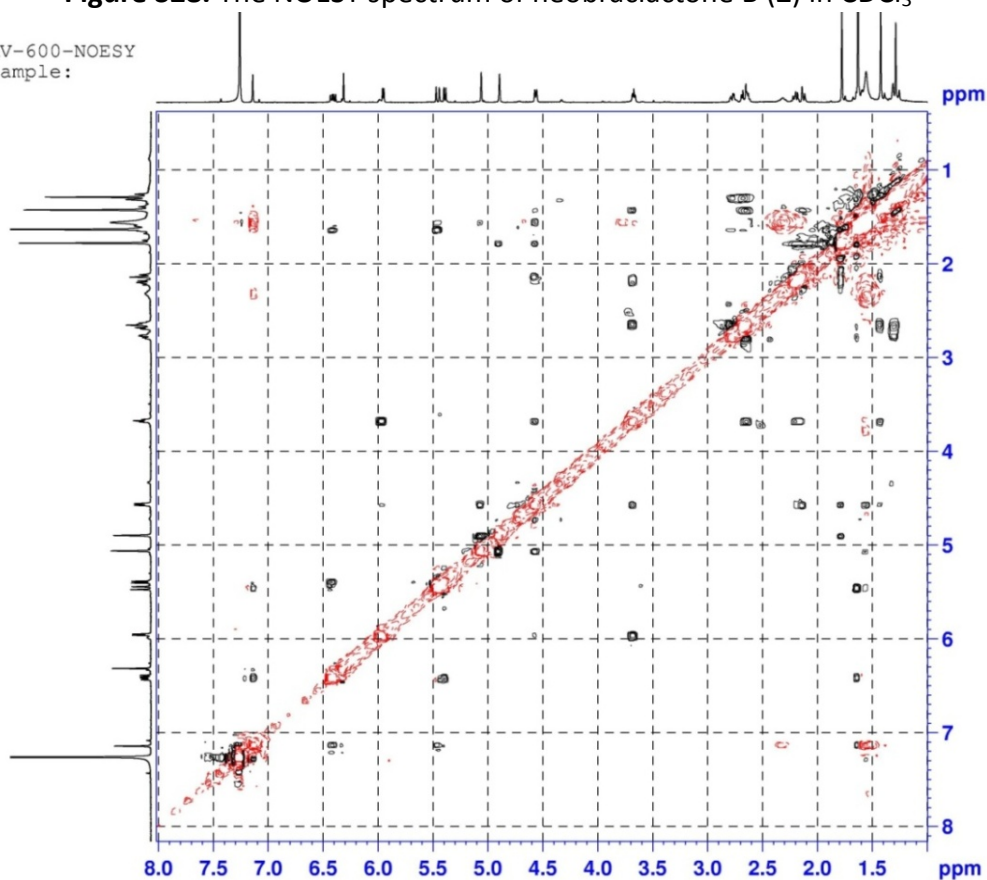


Figure S29. The expanded NOESY spectrum of neobraclactone B (**2**) in CDCl₃

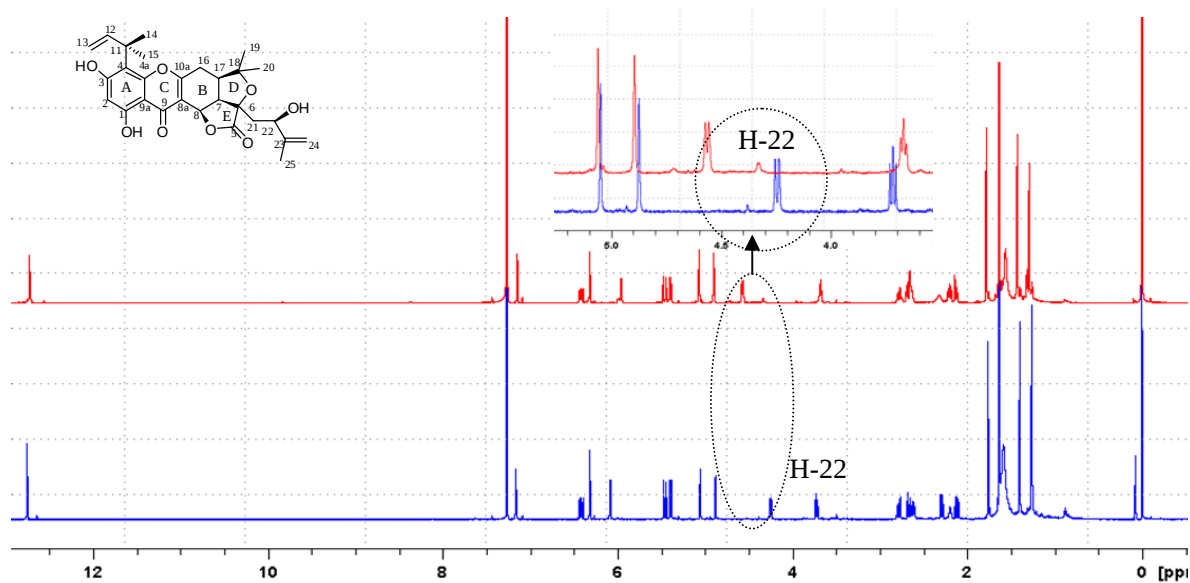


Figure S30. The comparison of the ^1H NMR spectra of compounds **1** (blue) and **2** (red) in CDCl_3

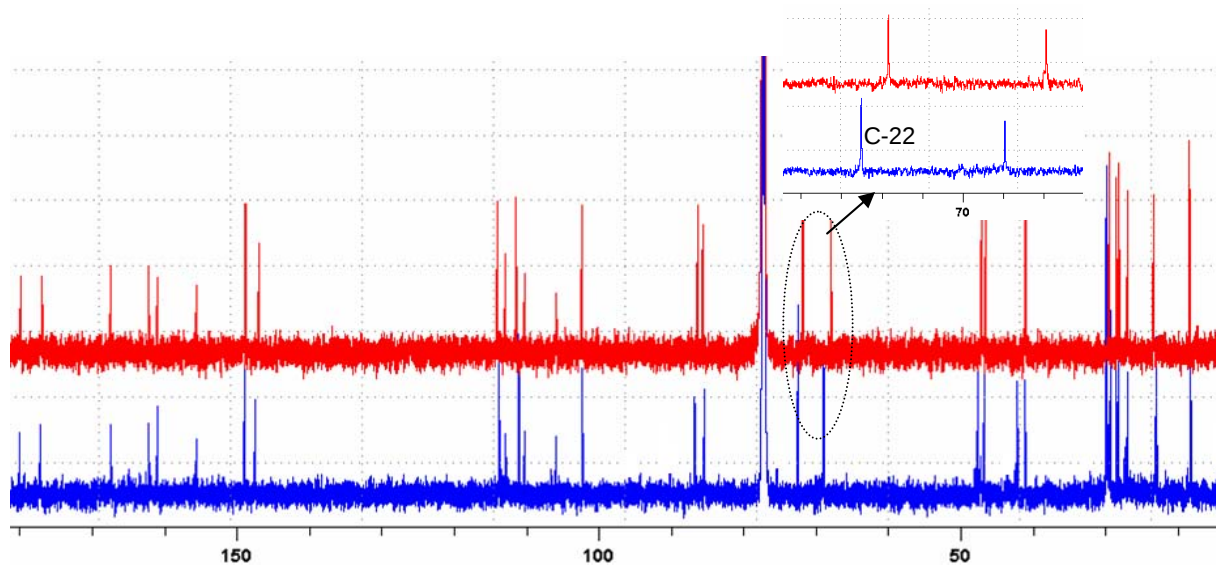


Figure S31. The comparison of the ^{13}C NMR spectra of compounds **1** (blue) and **2** (red) in CDCl_3

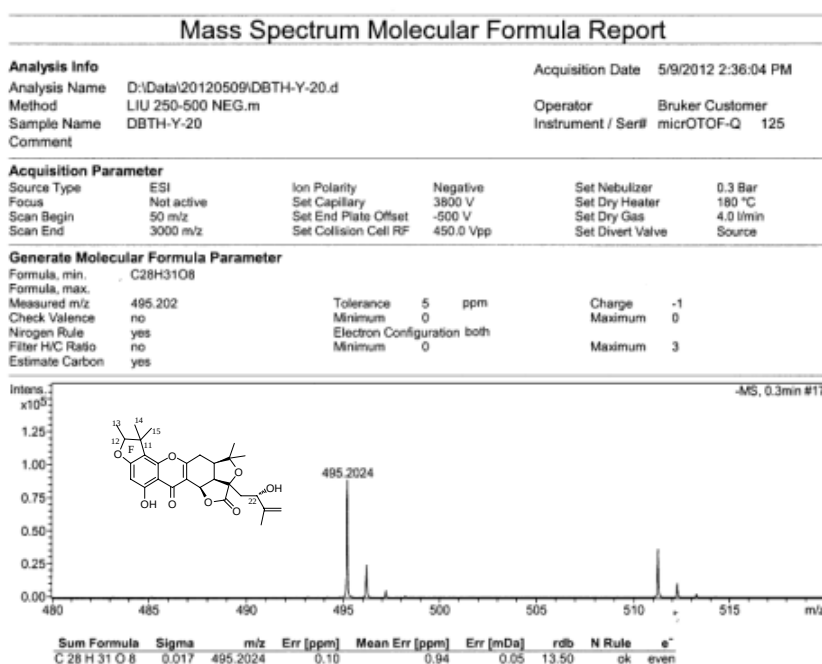


Figure S32. The HR-ESIMS spectrum of neobraclactone C (**3**) in CDCl₃

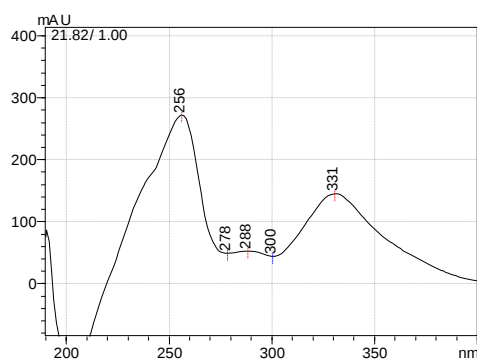


Figure S33. The UV spectrum of neobraclactone C (**3**) in CDCl₃

COSY DBTH-Y-20 in CDCl₃
2012-04-01

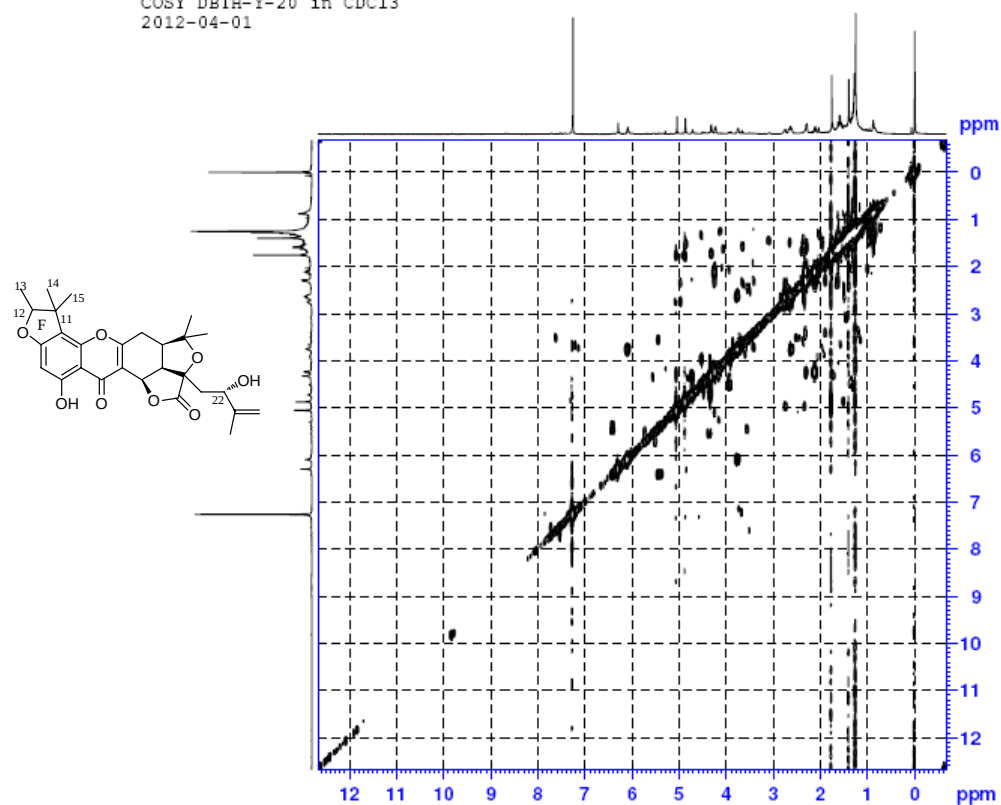


Figure S36. The ^1H - ^1H COSY spectrum of neobraclactone C (**3**) in CDCl_3

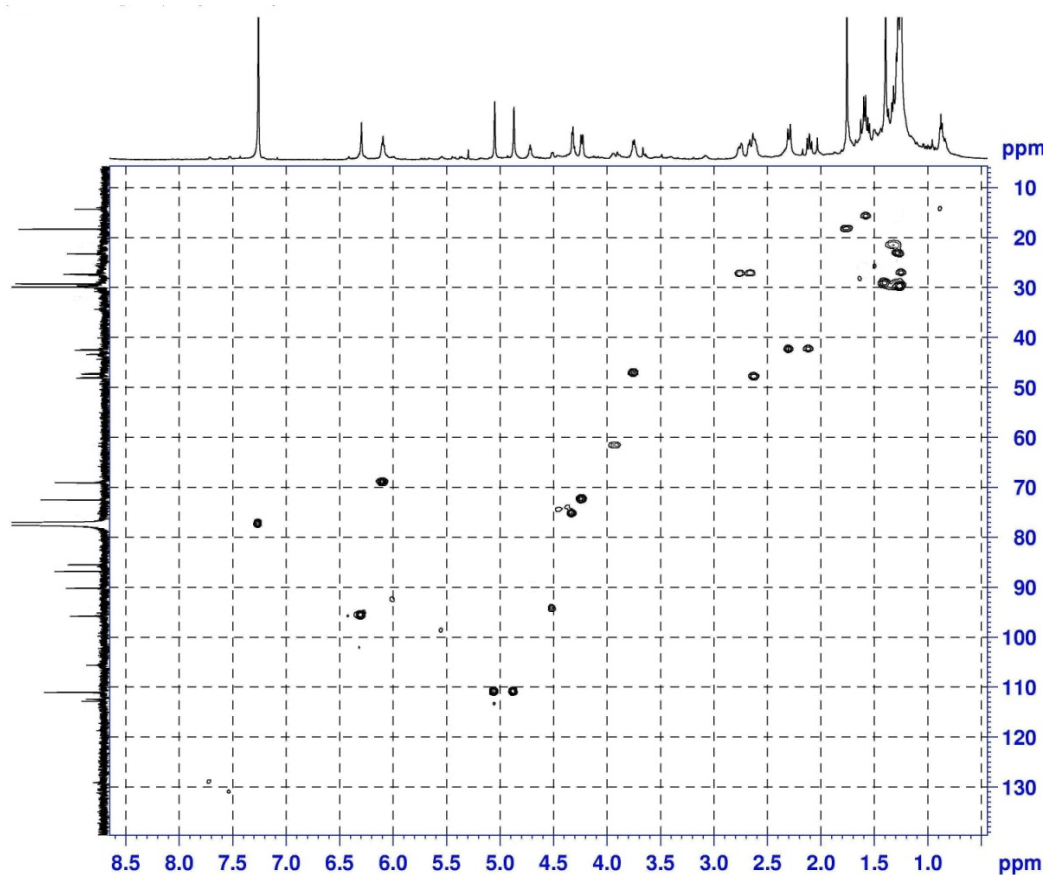


Figure S37. The HSQC spectrum of neobraclactone C (**3**) in CDCl_3

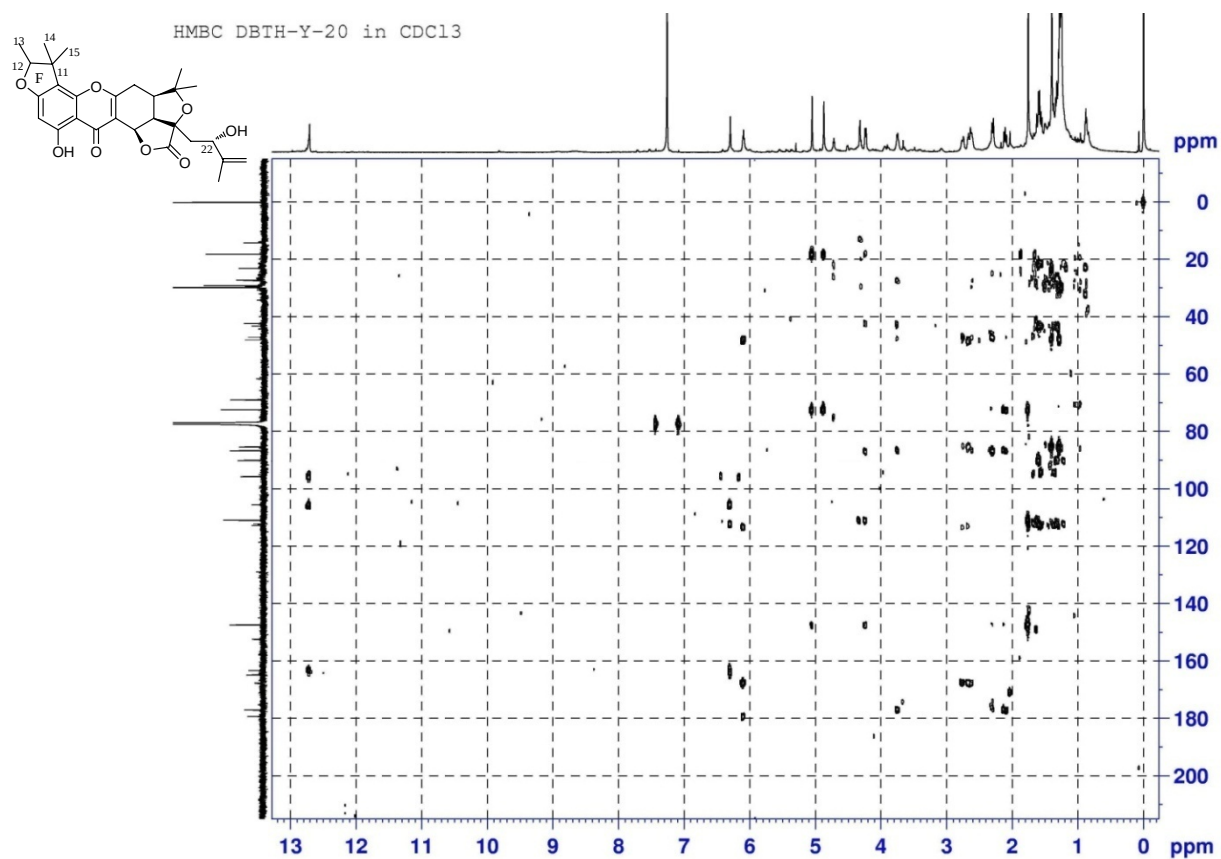


Figure S38. The HMBC spectrum of neobraclactone C (3) in CDCl₃

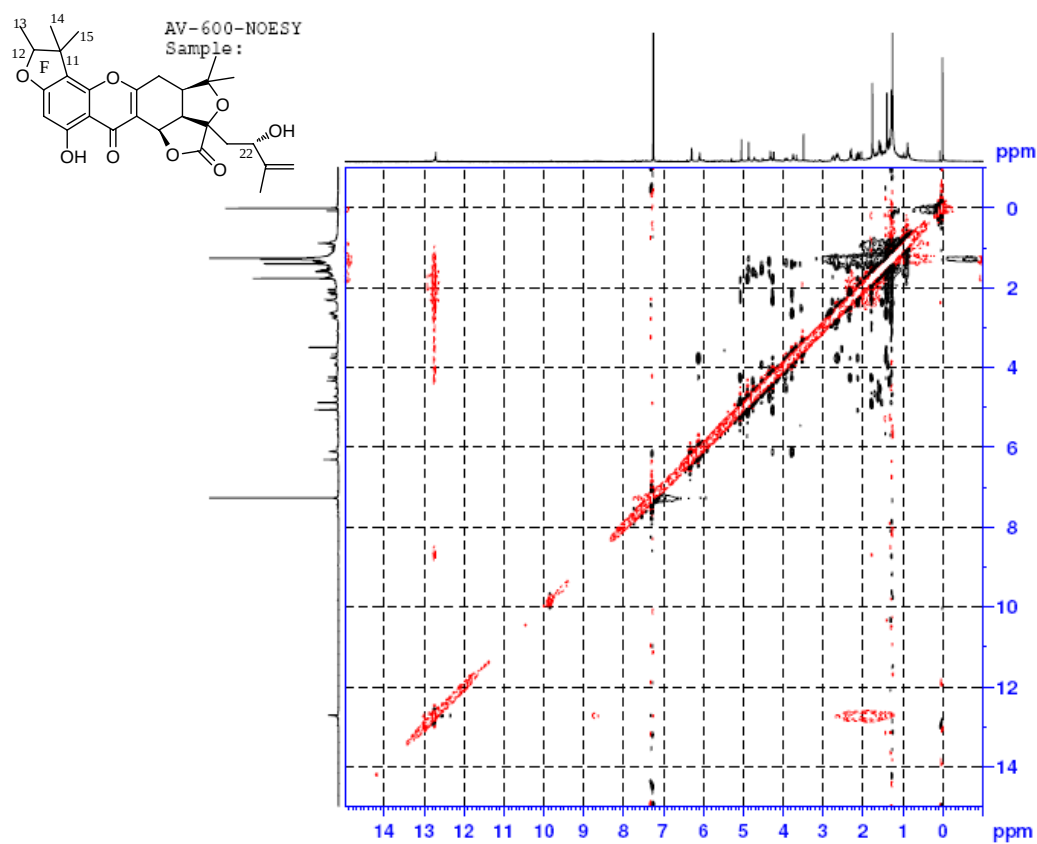


Figure S39. The NOESY spectrum of neobraclactone C (3) in CDCl₃

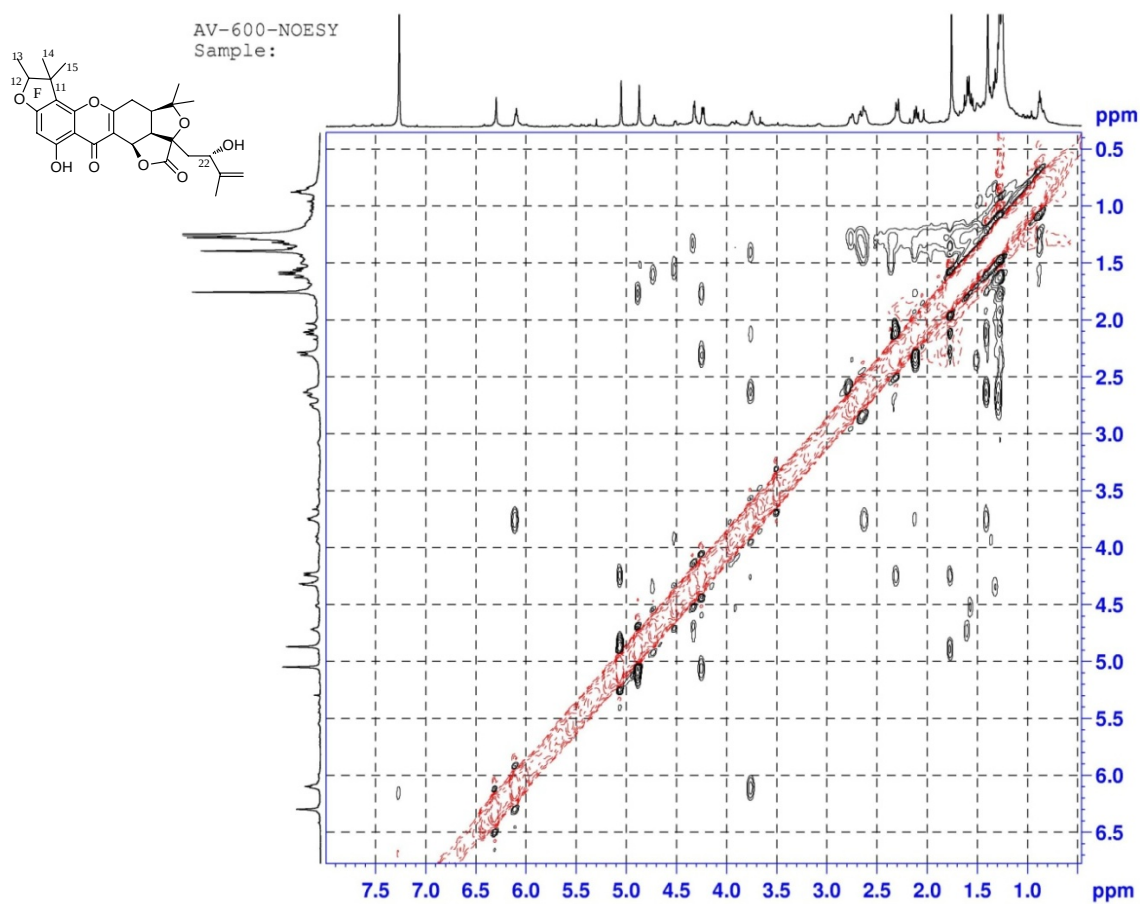


Figure S40. The expanded NOESY spectrum of neobraclactone C (**3**) in CDCl_3