Electronic Supplementary Information

Friedelane triterpenoids: transformations toward A-ring modifications including 2-*homo*derivatives

Jayanta Das,[†] Antara Sarkar[†] and Pranab Ghosh*

Natural Products and Polymer Chemistry Laboratory, Department of Chemistry, North Bengal University, Darjeeling-734013, India

[†]These authors contributed equally to this paper.

*Corresponding author. Fax: +91353 2699 001; Tel: +91 353 2776 381; email: pizy12@yahoo.com

Contents

ES1. A very brief account on the synthetic utilization of enol acetates:

The transformative reactions of enol-acetates include aldol reactions, either directly from enol acetates,[1] or its lithium salts[2] or potassium salts,[3] the catalytic α-alkylation,[3b,4] catalytic Michael reaction,[3b,5]Mannich type reaction,[6]catalytic asymmetric hydrogenation[7], halogenation,[8] synthesis of chiral acetates,[9]regioselective hydroxymethylation,[10]acyl transfer reactions,[11] methylation of enol acetates[12]catalytic preparation of aldehydes and ketones from alcohols,[13] 1,4-diketones from cyclic β-oxo esters,[14]δ-lactones in presence of Ce^{+3} catalyst,[15]β-ketosulfones *via* sulfonised enol acetates[16]etc. Enantioselective Rh-catalyzed hydrogenation of enol acetates were useful towards the preparation of chiral esters and chiral alcohols.[17]Chiral enol acetates were found to be effective to furnish β-substituted aldehydes and ketones.[18] During the preparation of the chiral acetates regio- and enantioselective allylic alkylation of unsaturated aldehydes were also carried

out.[18a] Using enol acetates, substituted aldehydes were also prepared by direct coupling reaction with silyl ethers in presence of catalysts.[19] Applying photoinduced electron transfer process α-arylated ketones were prepared from enol acetates and aryl diazonium salts.[20]Besides, enol acetate-based syntheses of some natural products are also reported whereas in some cases it has been found that the enol acetates are biologically more potent than the corresponding carbonyl compounds.[21]

ES2.Copies of ^{1}H and ^{13}C NMR spectra of the isolated products:

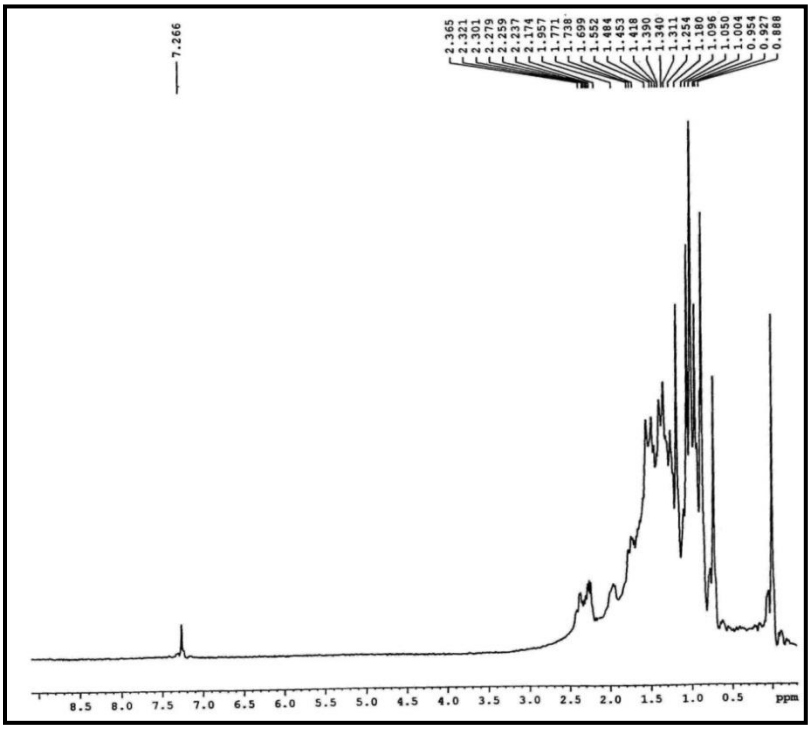

Figure S1.[1]H NMR spectrum of friedelin (**2**).

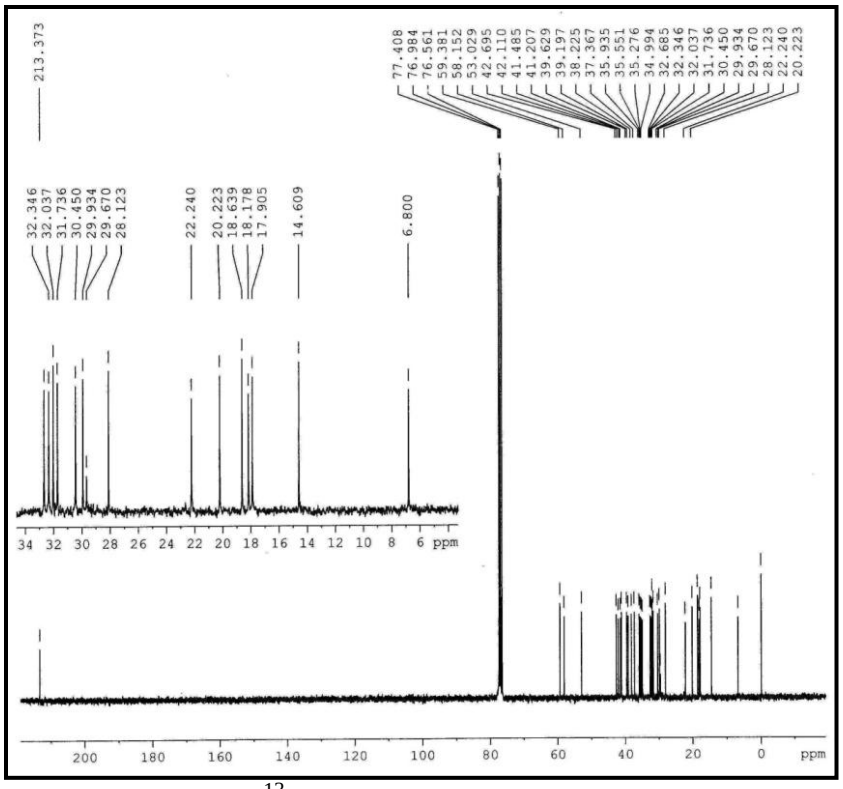

Figure S2. ^{13}C NMR spectrum of friedelin (**2**).

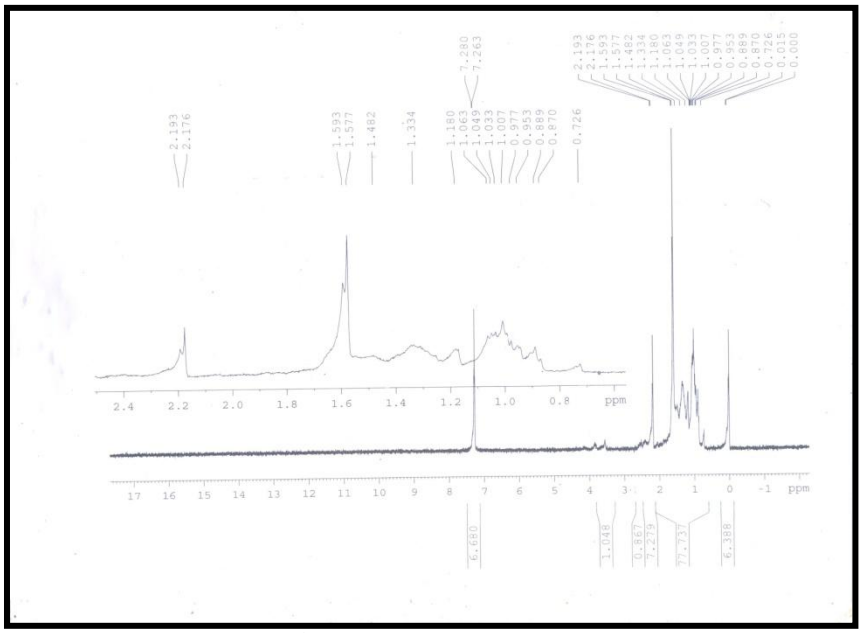

Figure S3. ^{1}H NMR spectrum of cerin (**3**).

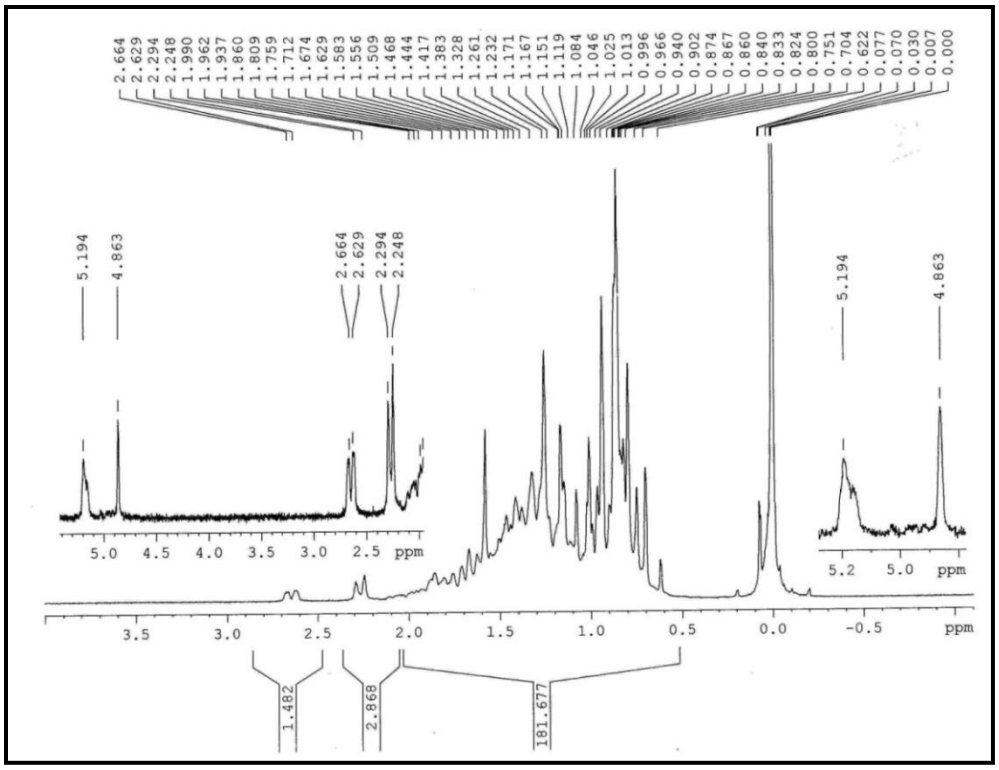

Figure S4. ^{1}H NMR spectrum (with little impurity) of friedel-2-ene (**4**).

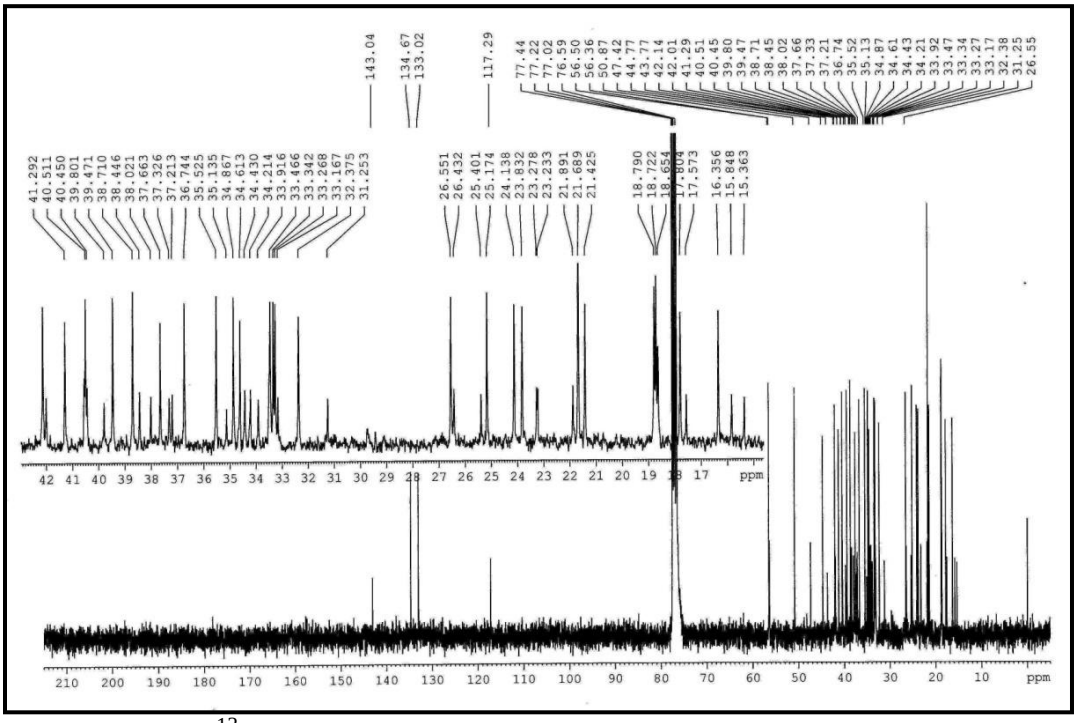

Figure S5. ^{13}C NMR spectrum (with little impurity) of friedel-2-ene (**4**).

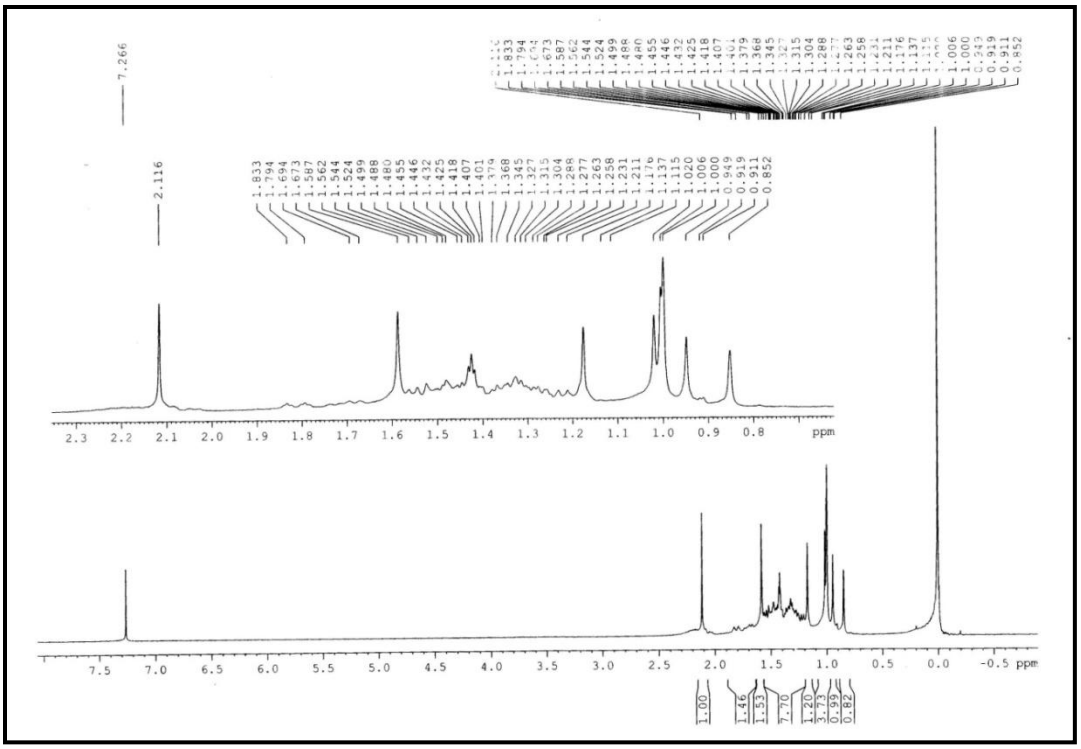

Figure S6. ^{1}H NMR spectrum of friedel-3-enol acetate (**5**).

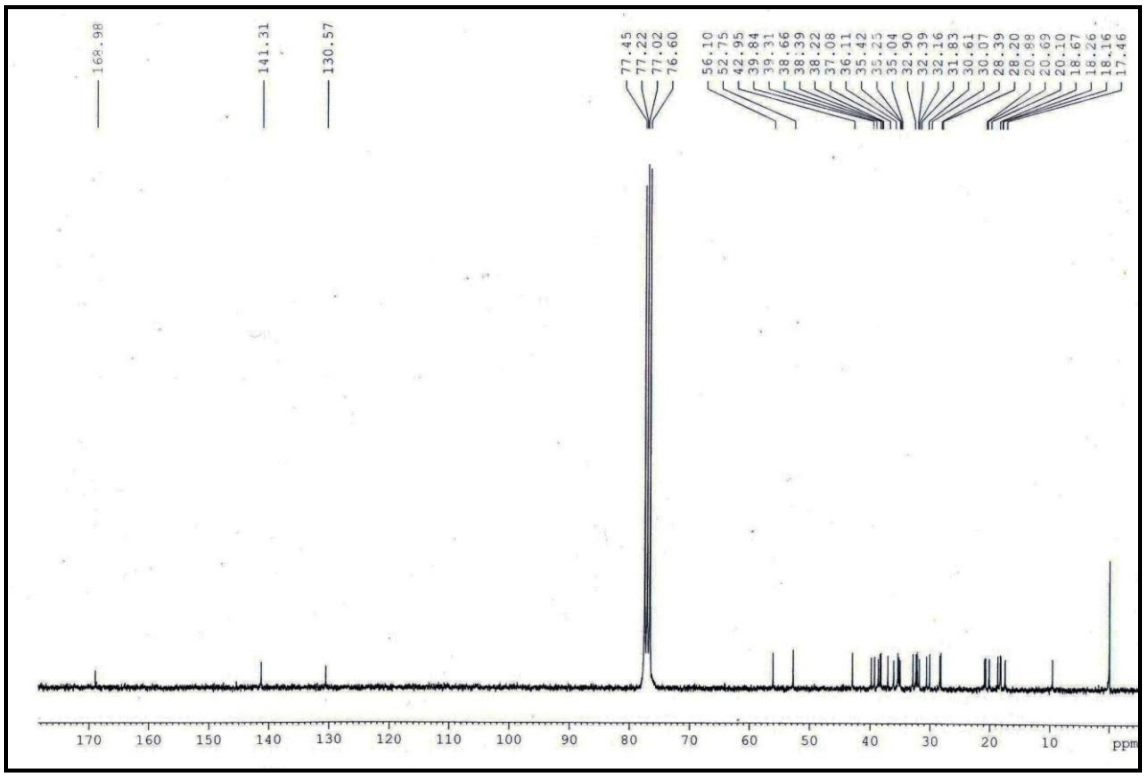

Figure S7. ^{13}C NMR spectrum of friedel-3-enol acetate (**5**).

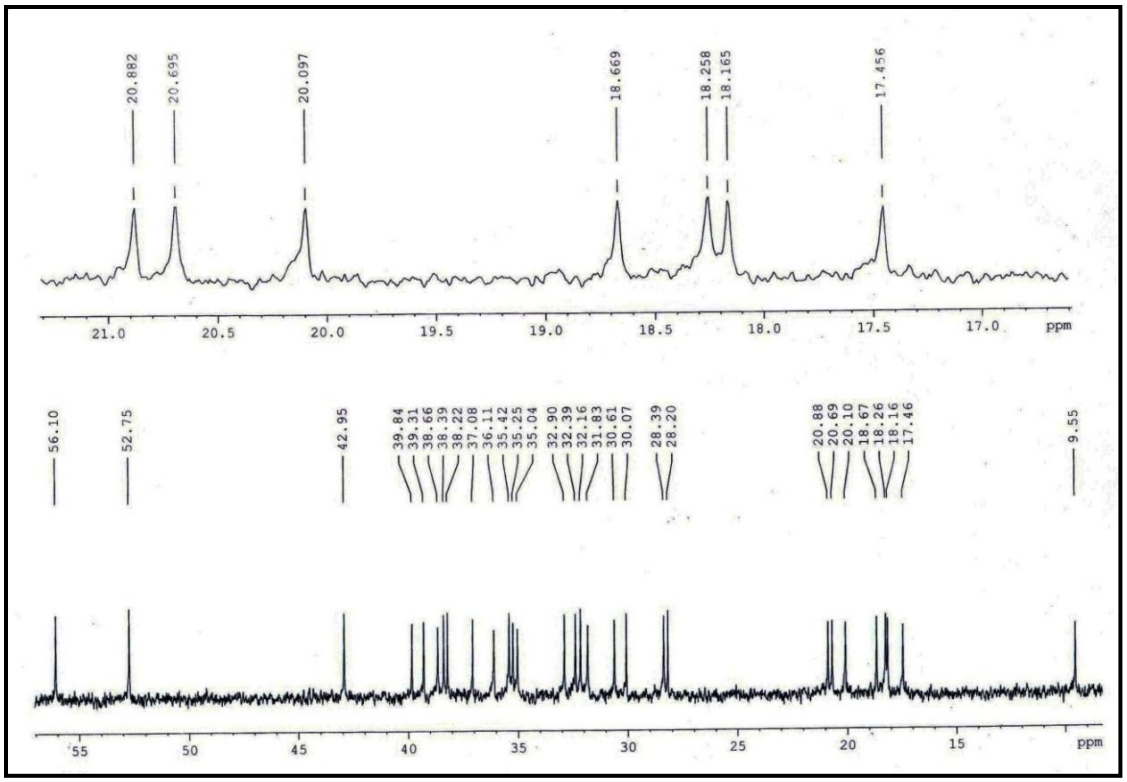

Figure S8. ^{13}C NMR spectrum (partially expanded) of friedel-3-enol acetate (**5**).

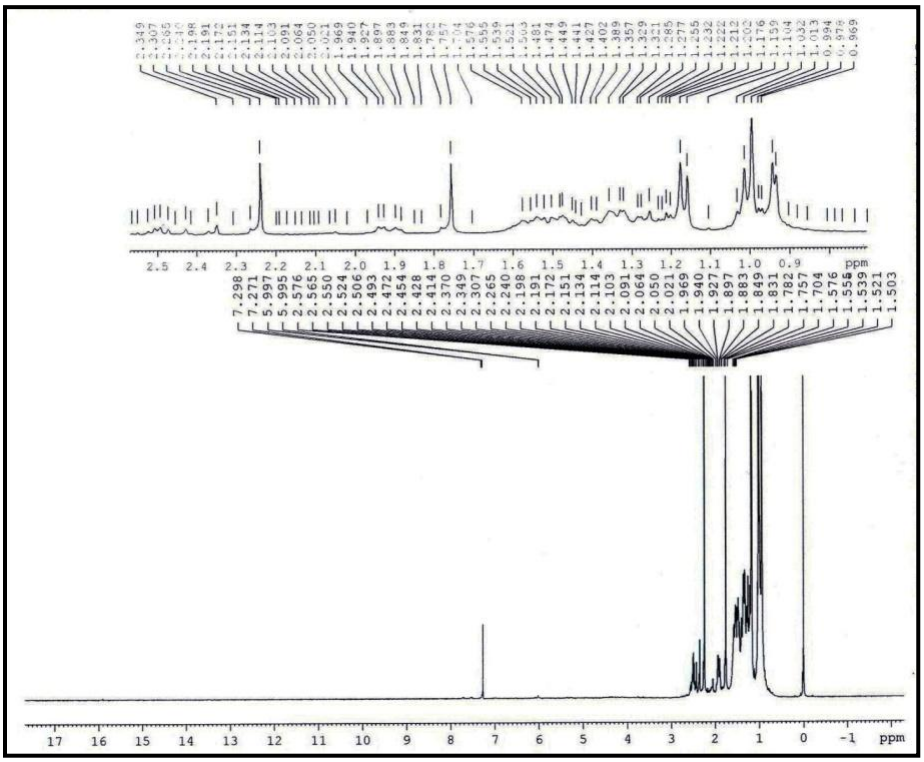

Figure S9. ^{1}H NMR spectrum of friedel-2-oxo-3-enol acetate (**6**).

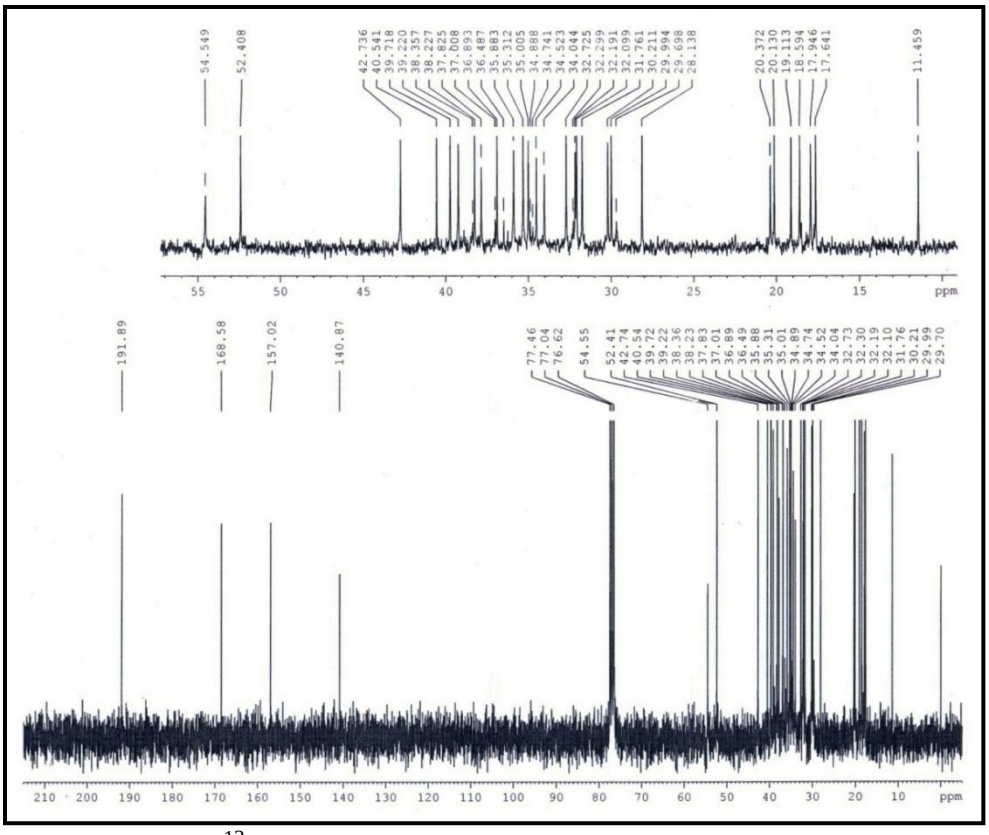

Figure S10. ^{13}C NMR spectrum of friedel-2-oxo-3-enol acetate (**6**).

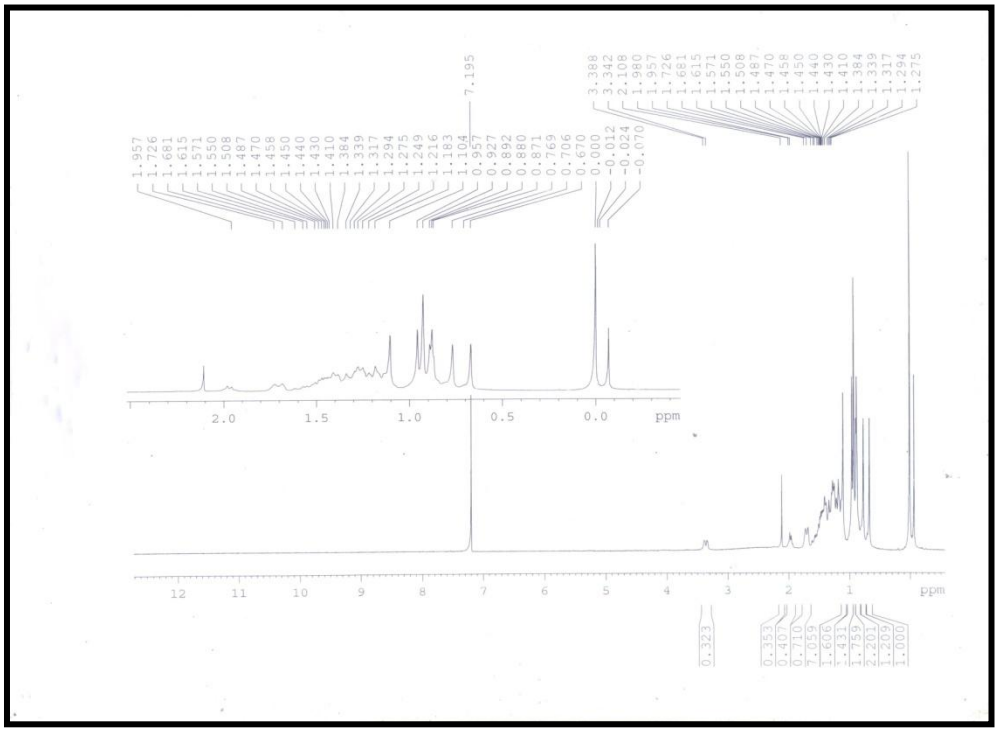

Figure S11.^{1}H NMR spectrum of friedelane-3-hydroxyimino (**7**).

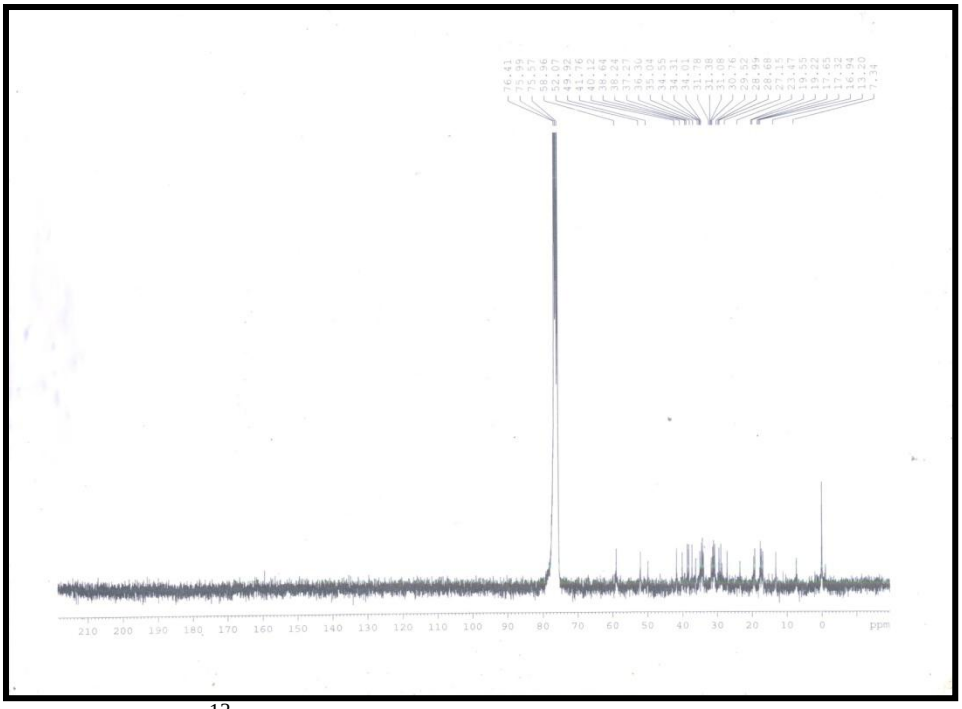

Figure S12. ^{13}C NMR spectrum of friedelane-3-hydroxyimino (**7**).

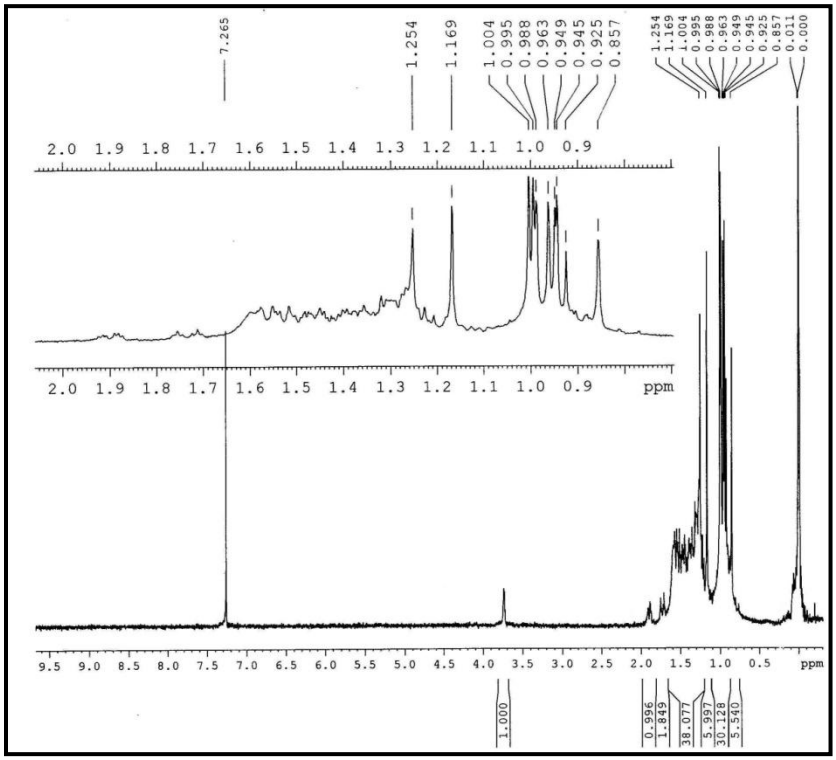

Figure S13. ^{1}H NMR spectrum of friedelan-3β-ol (**8**).

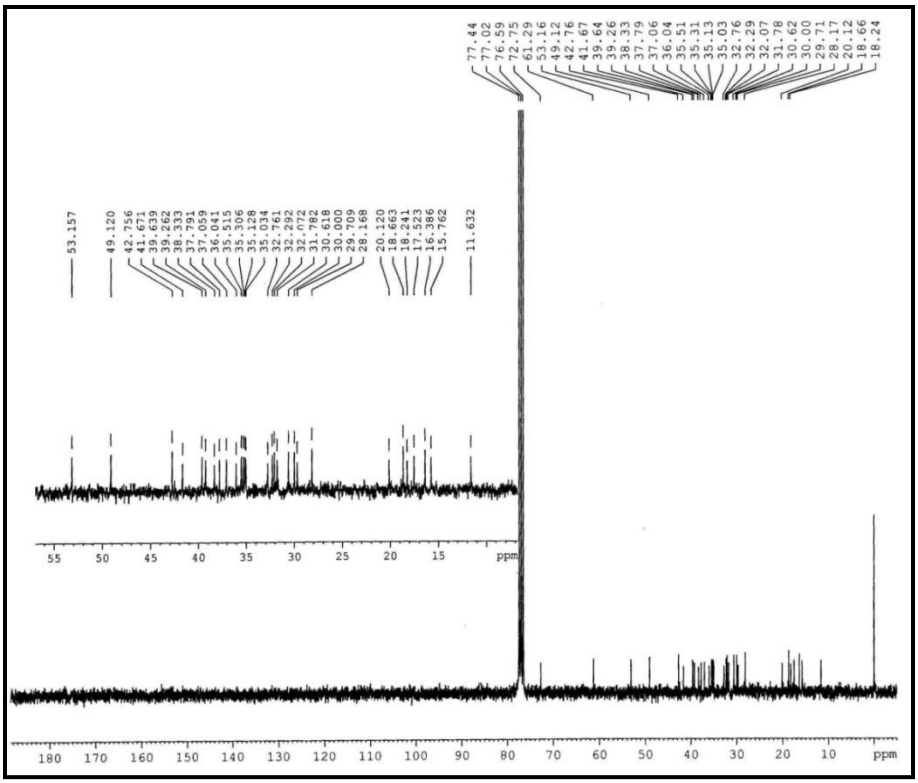

Figure S14. ^{13}C NMR spectrum of friedelan-3β-ol (**8**).

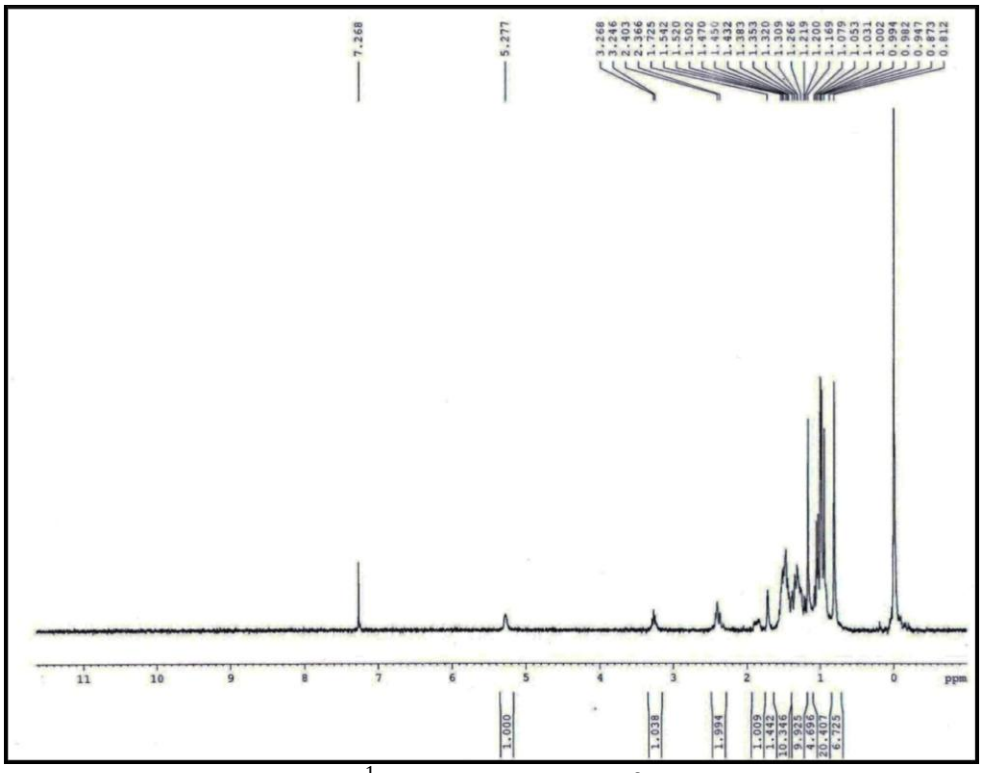

Figure S15. ^{1}H NMR spectrum of lactam **9**.

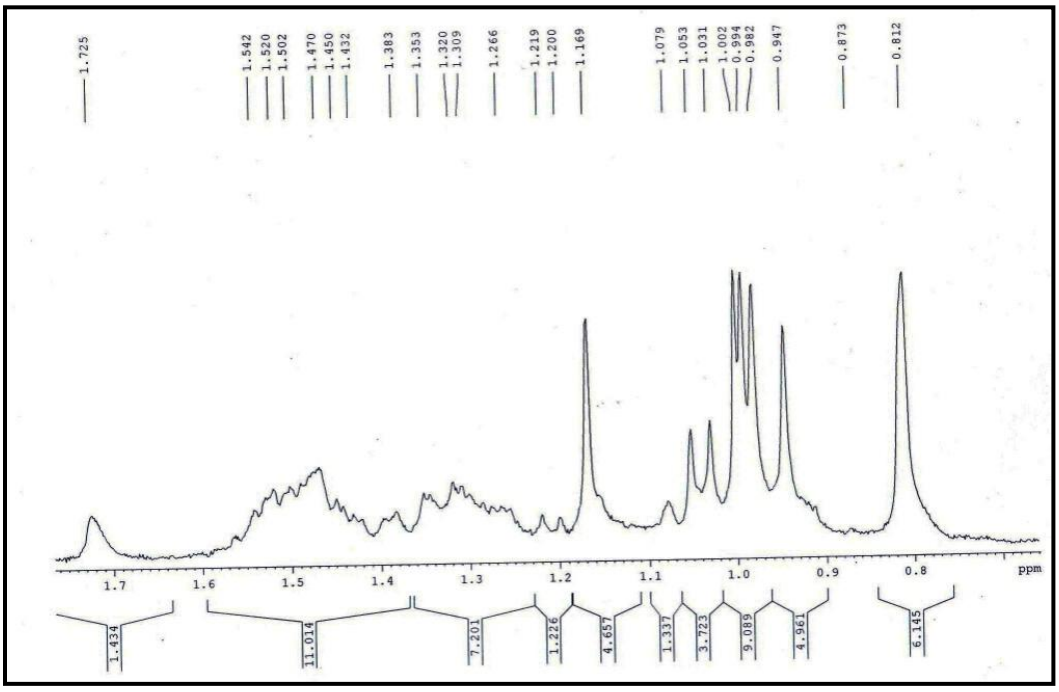

Figure S16. ^{1}H NMR spectrum (partially expanded 1) of lactam **9**.

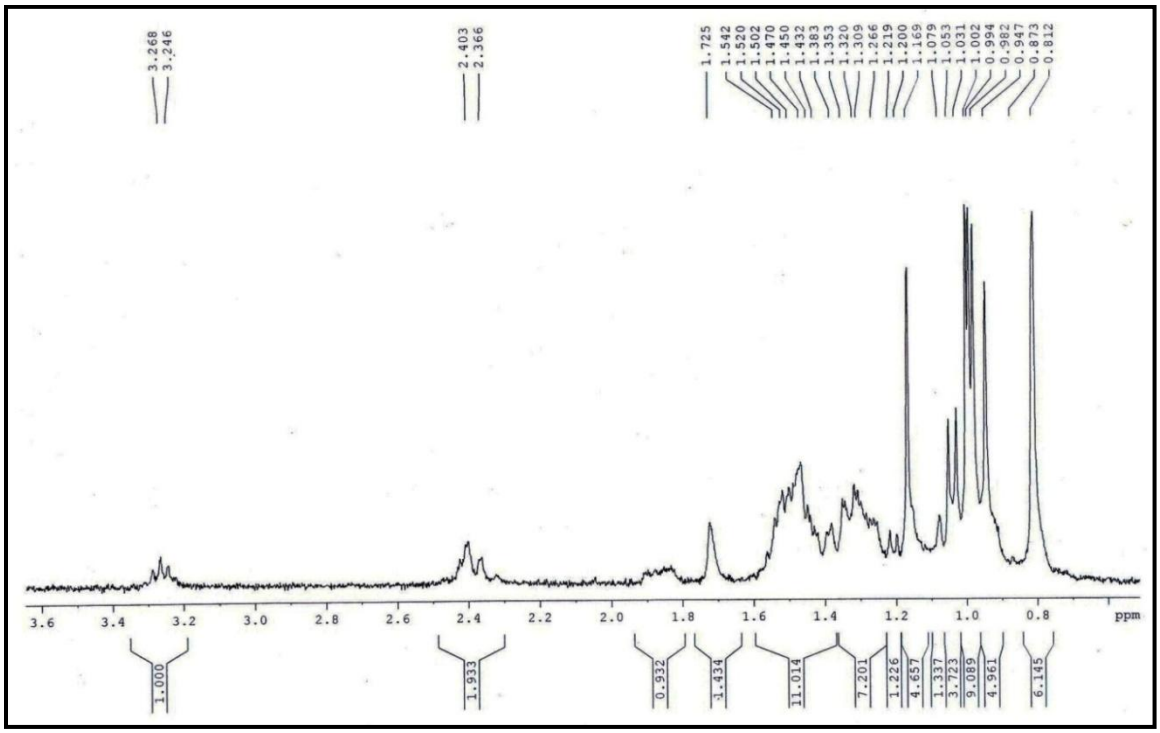

Figure S17. ^{1}H NMR spectrum (partially expanded 2) of lactam **9**.

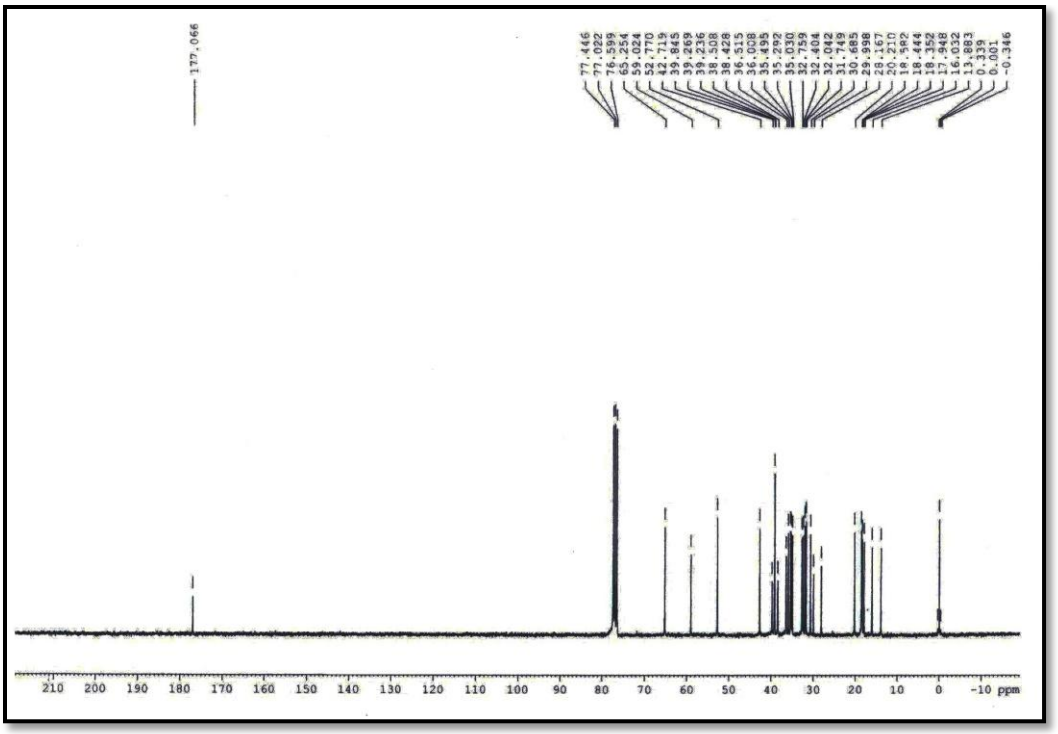

Figure S18. ^{13}C NMR spectrum of lactam **9**.

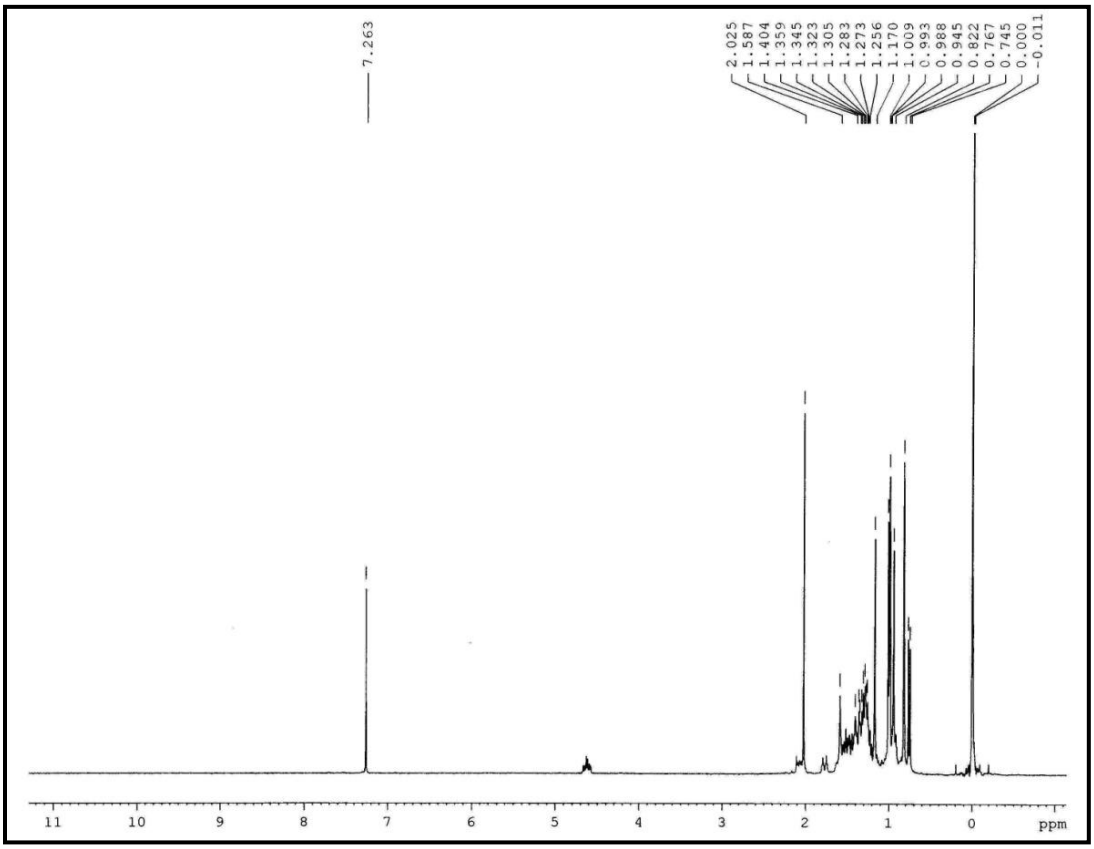

Figure S19. ^{1}H NMR spectrum of friedelane-3β-acetate (**10**).

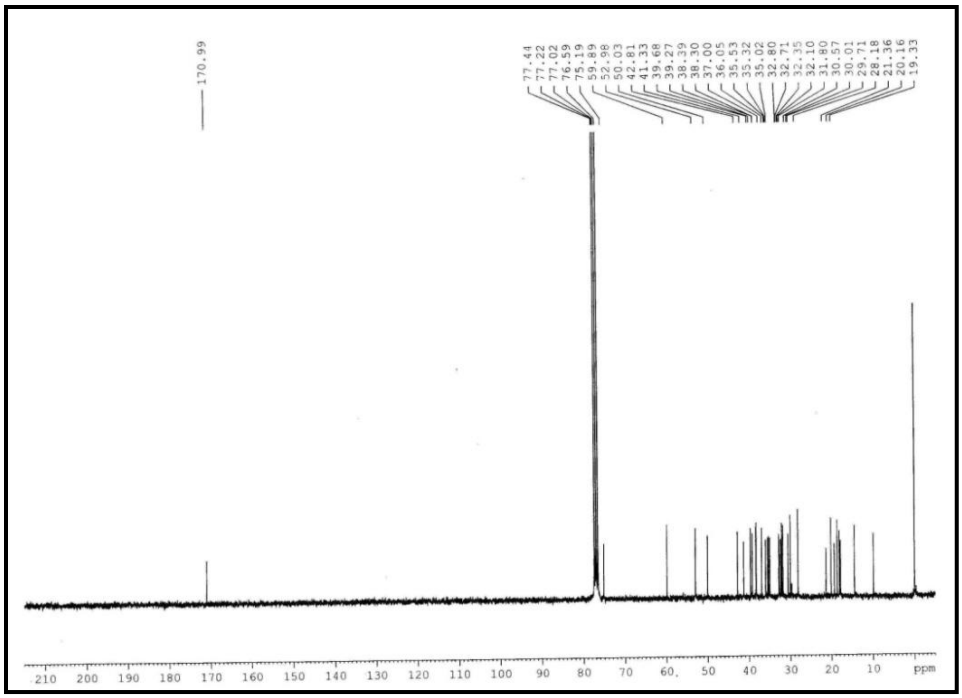

Figure S20. ^{13}C NMR spectrum of friedelane-3β-acetate (**10**).

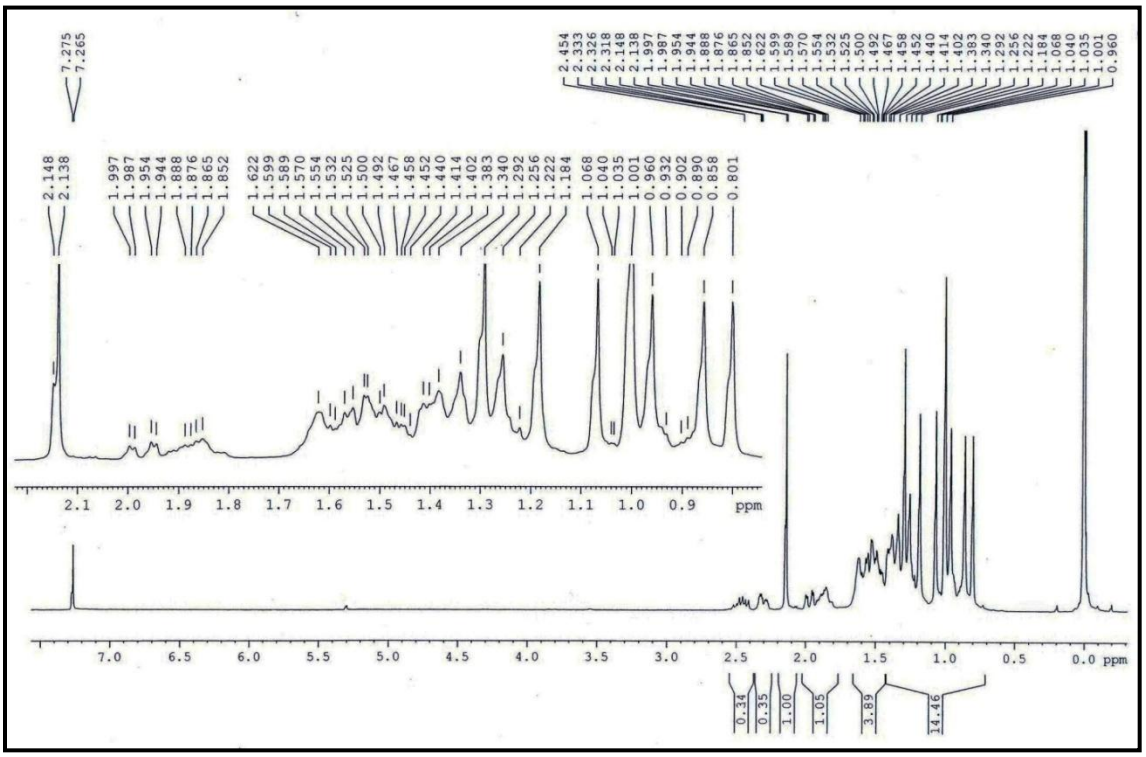

Figure S21. ^{1}H NMR spectrum of friedel-3-oxo-4α-acetate (**11**).

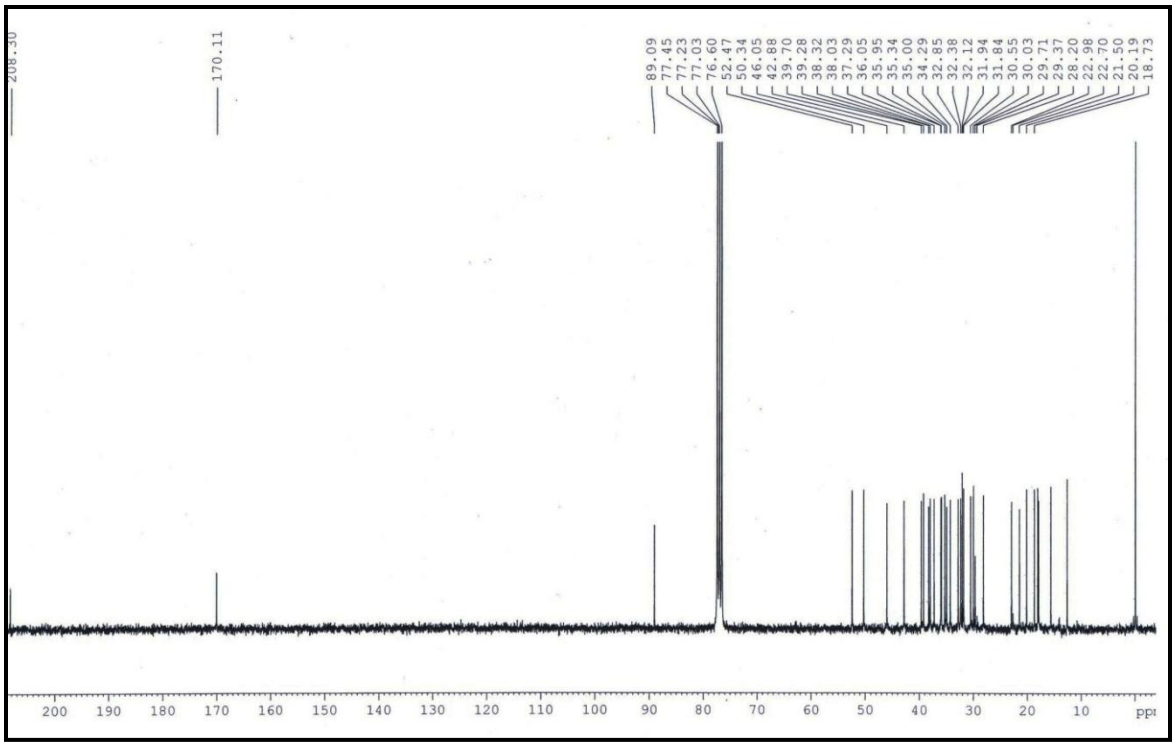

Figure S22. ^{13}C NMR spectrum of friedel-3-oxo-4α-acetate (**11**).

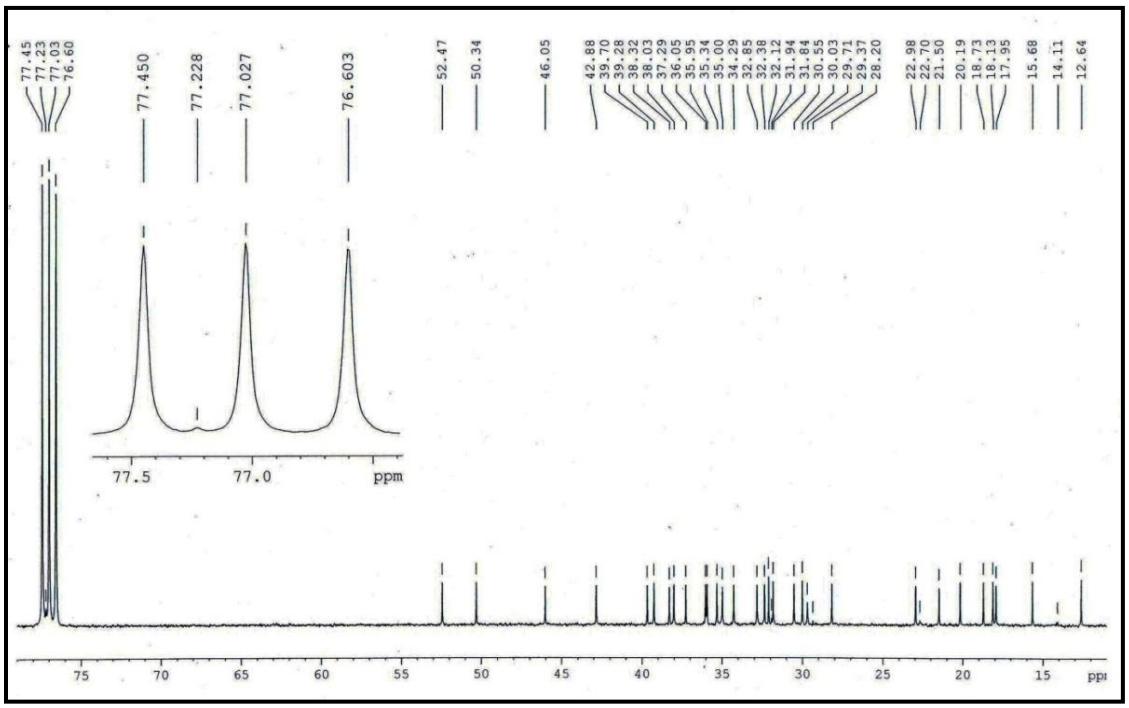

Figure S23. ^{13}C NMR spectrum (partially expanded) of friedel-3-oxo-4α-acetate (**11**)

.

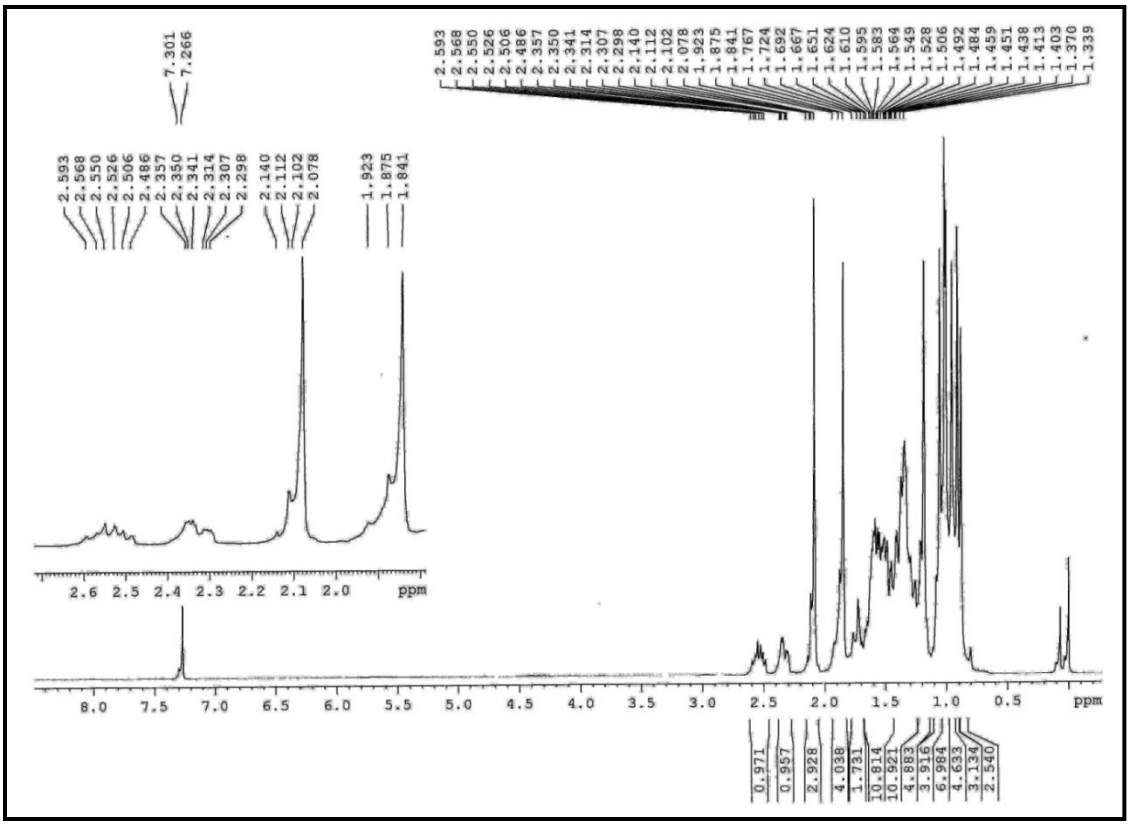

Figure S24.[1]H NMR spectrum of friedel-3-oxo-4β-acetate (**12**).

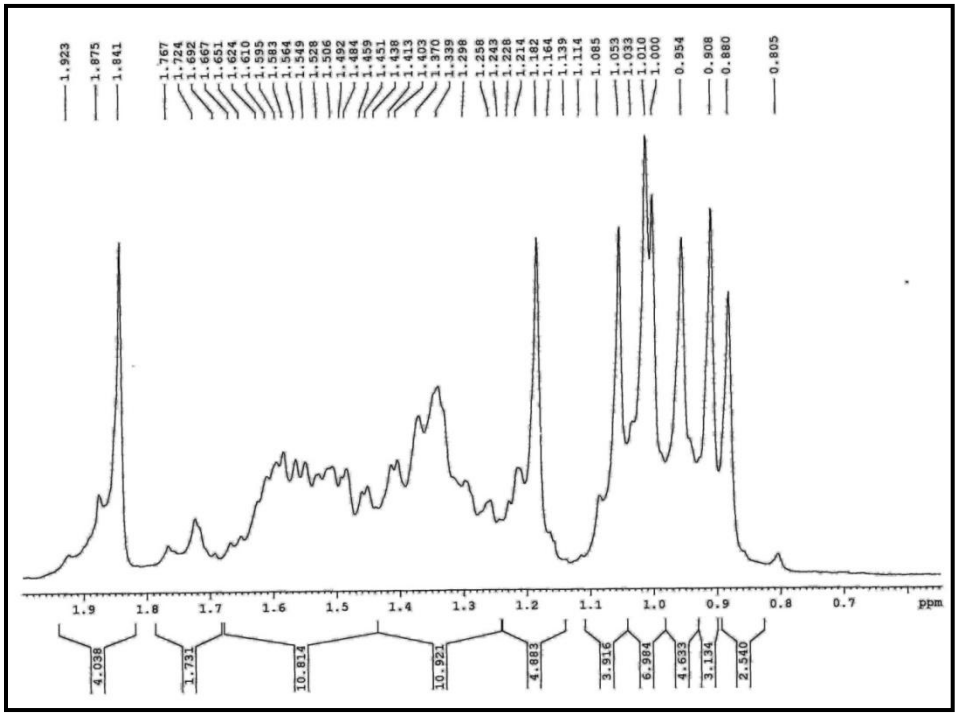

Figure S25. [1]H NMR spectrum (partially expanded) of friedel-3-oxo-4β-acetate (**12**).

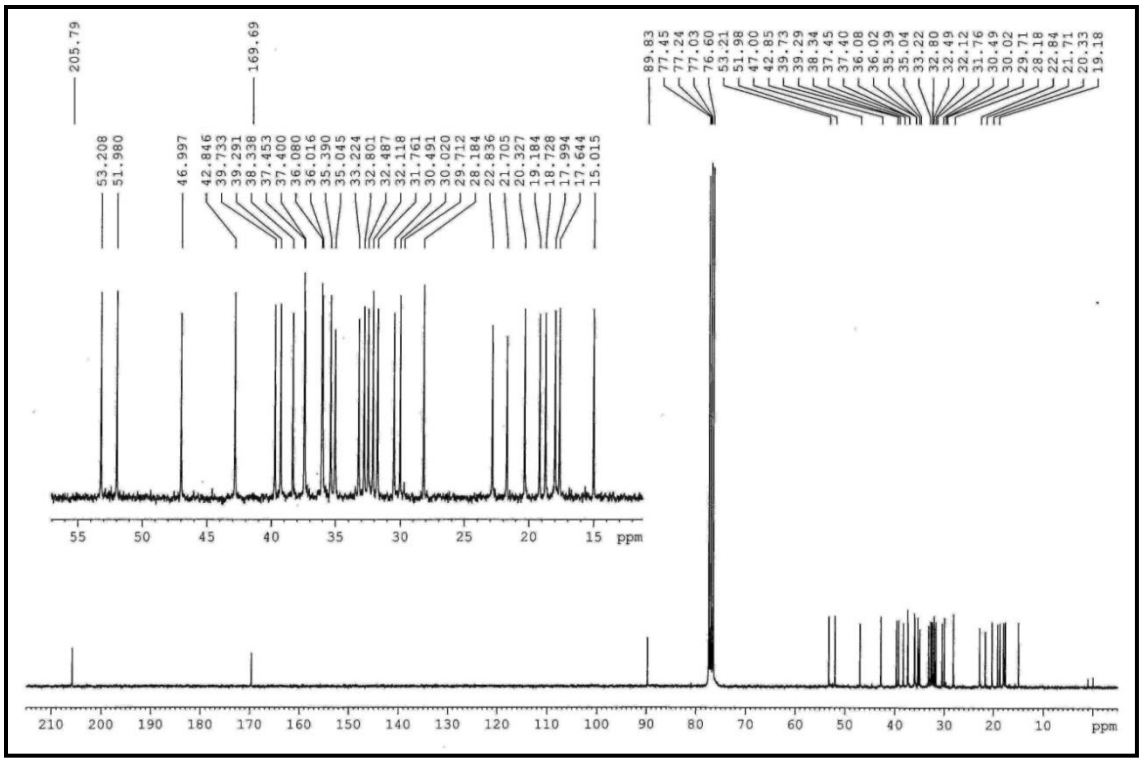

Figure S26. ^{13}C NMR spectrum of friedel-3-oxo-4β-acetate (**12**).

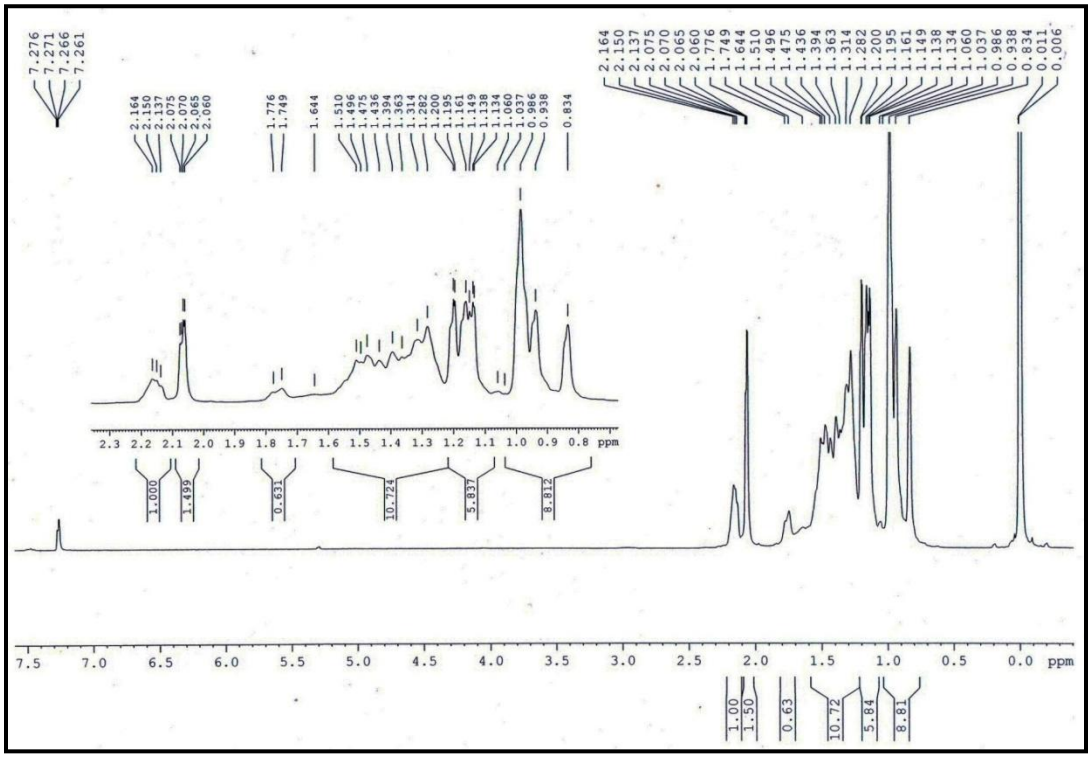

Figure S27.^{1}H NMR spectrum of friedel-3β-ol-4α-acetate (**13**).

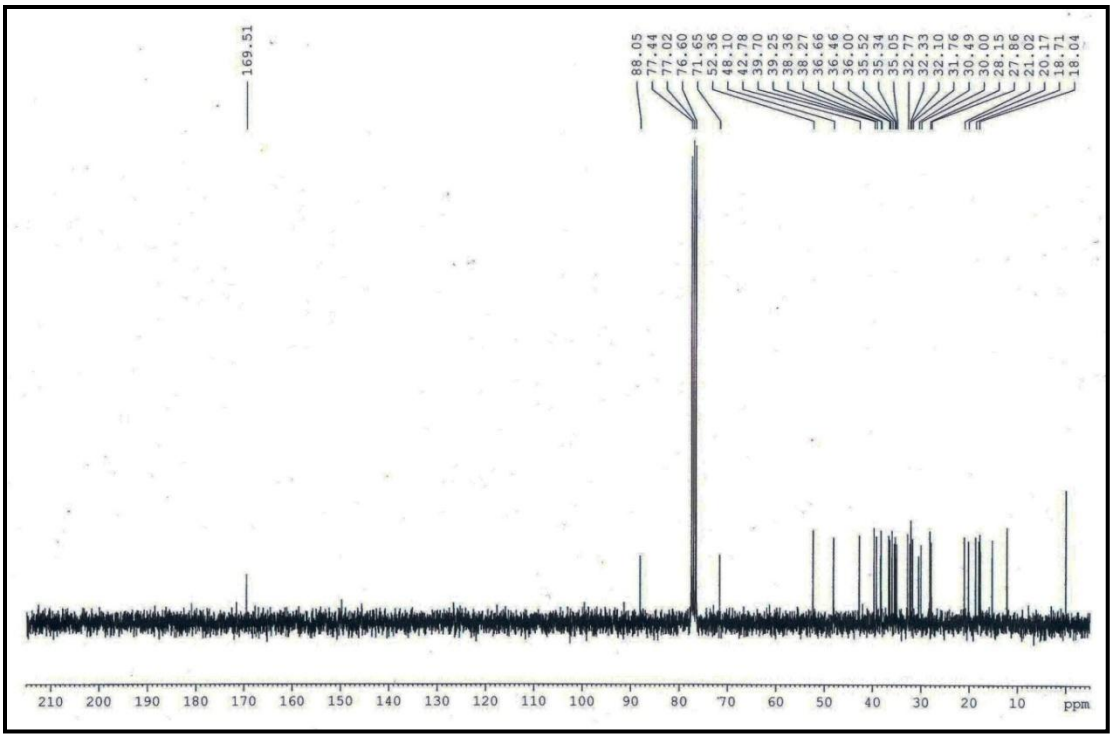

Figure S28. ^{13}C NMR spectrum of friedel-3β-ol-4α-acetate (**13**).

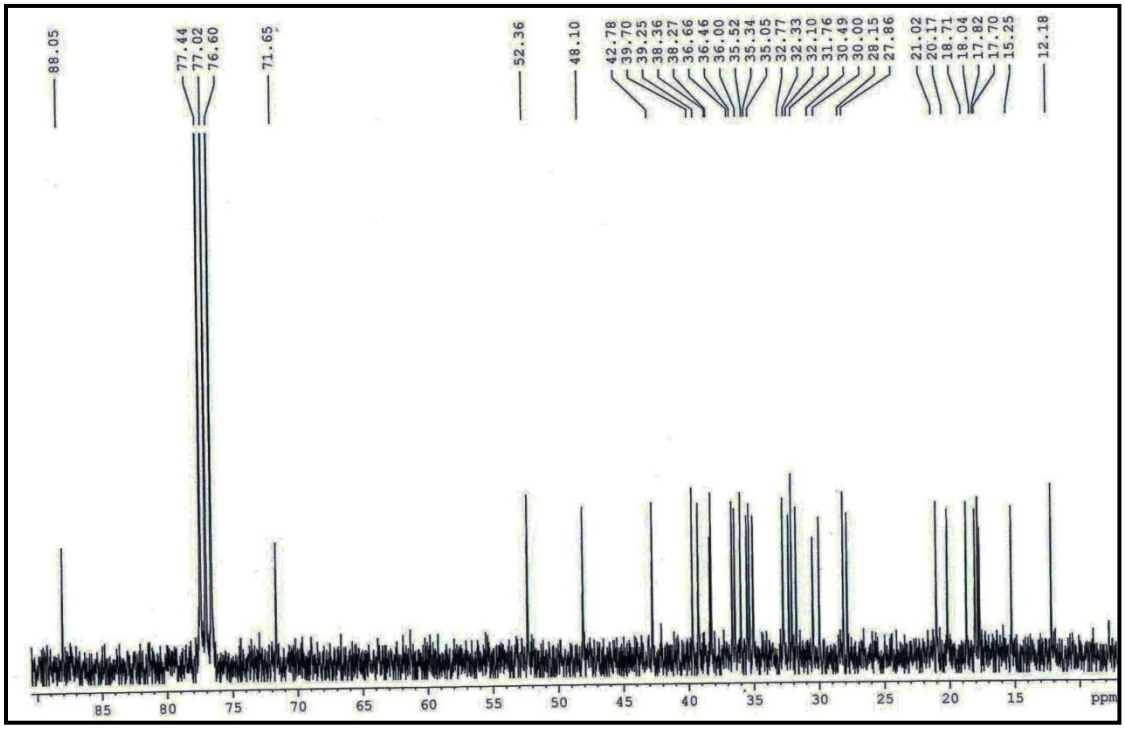

Figure S29. ^{13}C NMR spectrum (partially expanded) of friedel-3β-ol-4α-acetate (**13**).

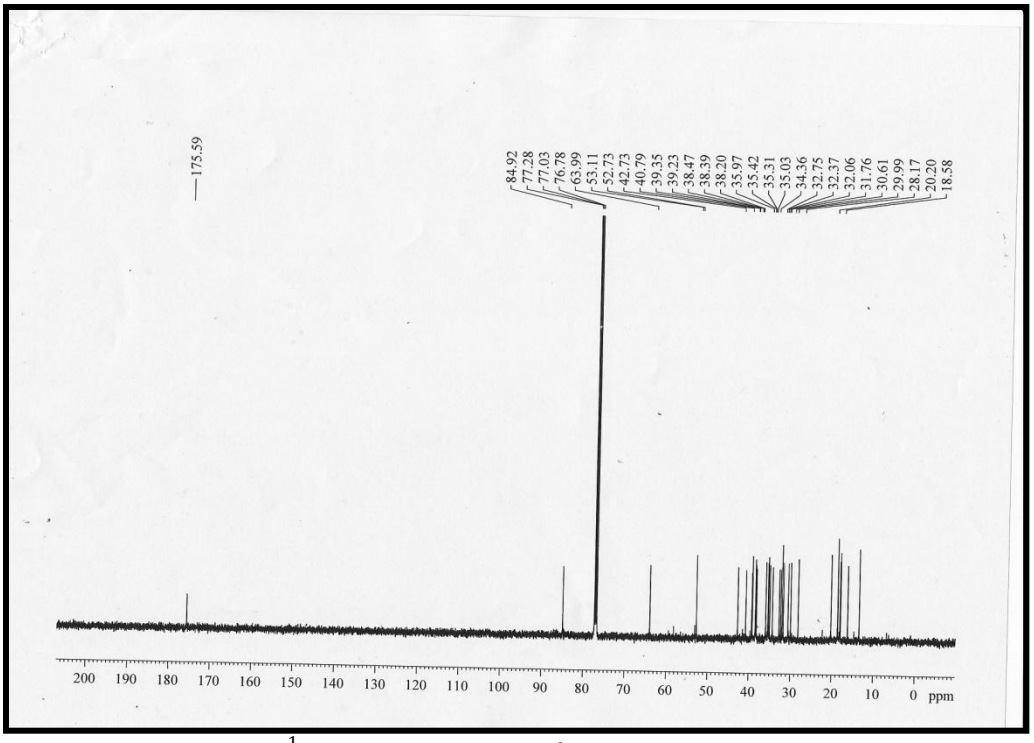

Figure S30. ^{1}H NMR spectrum of Friedelin-2,3-lacton (**14**).

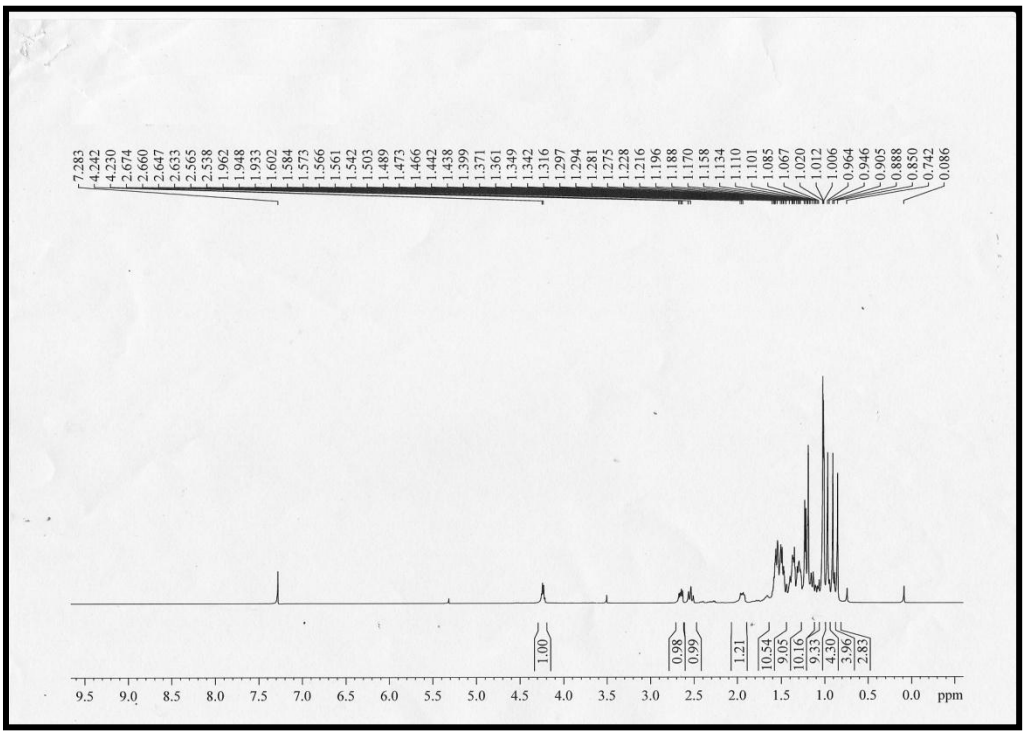

Figure S31. ^{13}C NMR spectrum of Friedelin-2,3-lacton (**14**).

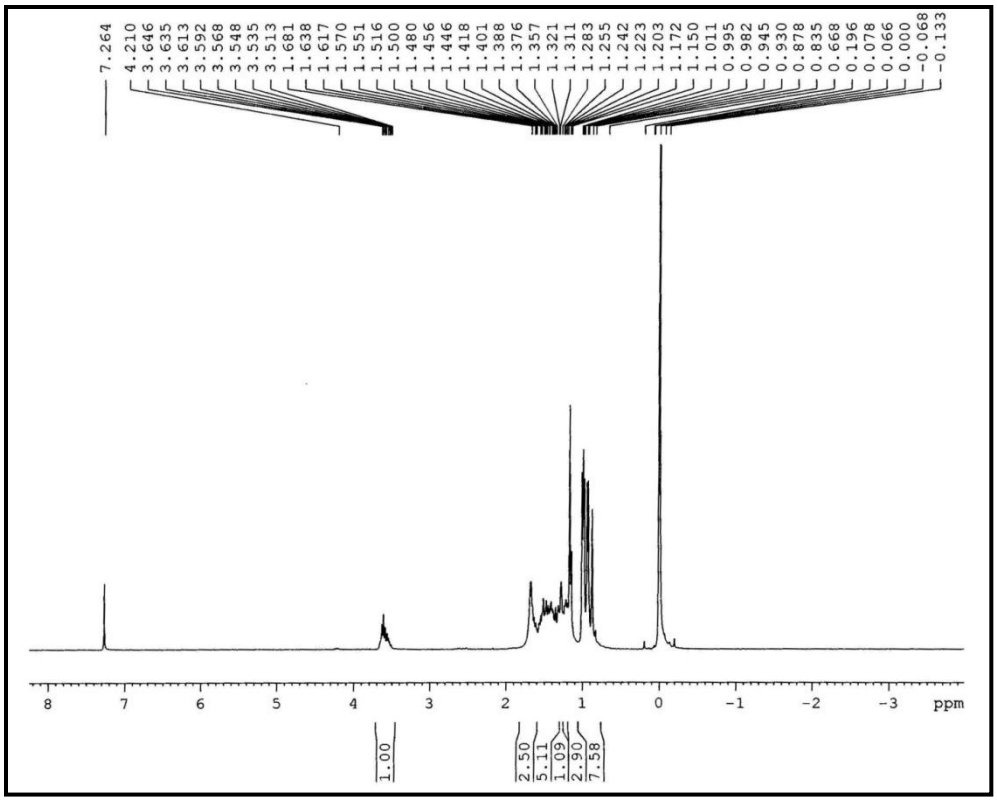

Figure S32.[1]H NMR spectrum of 3,4-*seco*friedelane-3,4-diol (**15**).

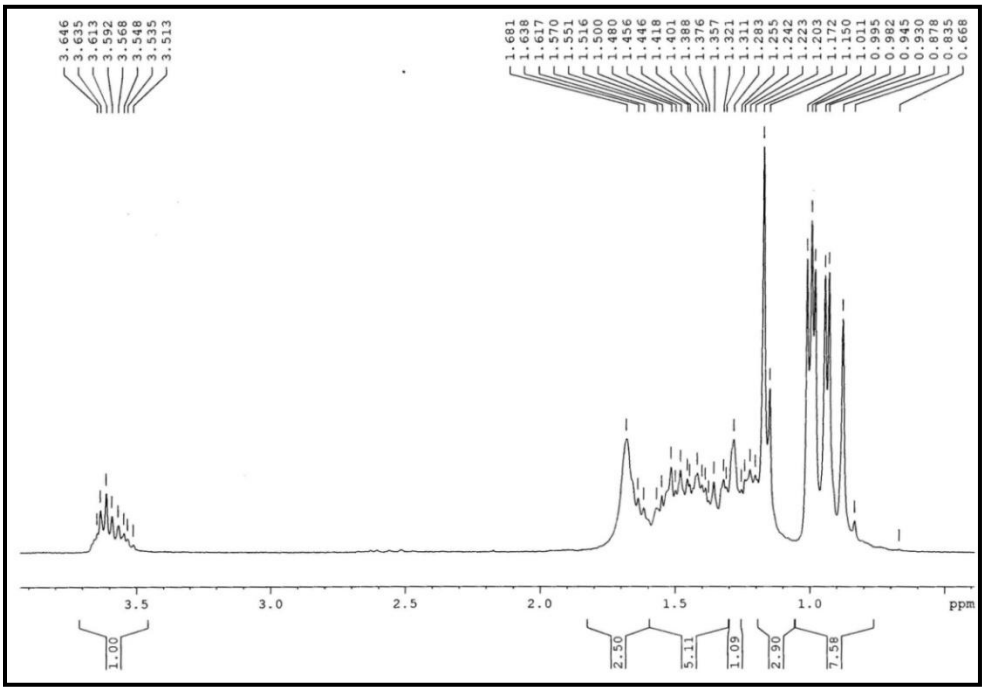

Figure S33.[1]H NMR spectrum (partially expanded) of 3,4-*seco*friedelane-3,4-diol (**15**).

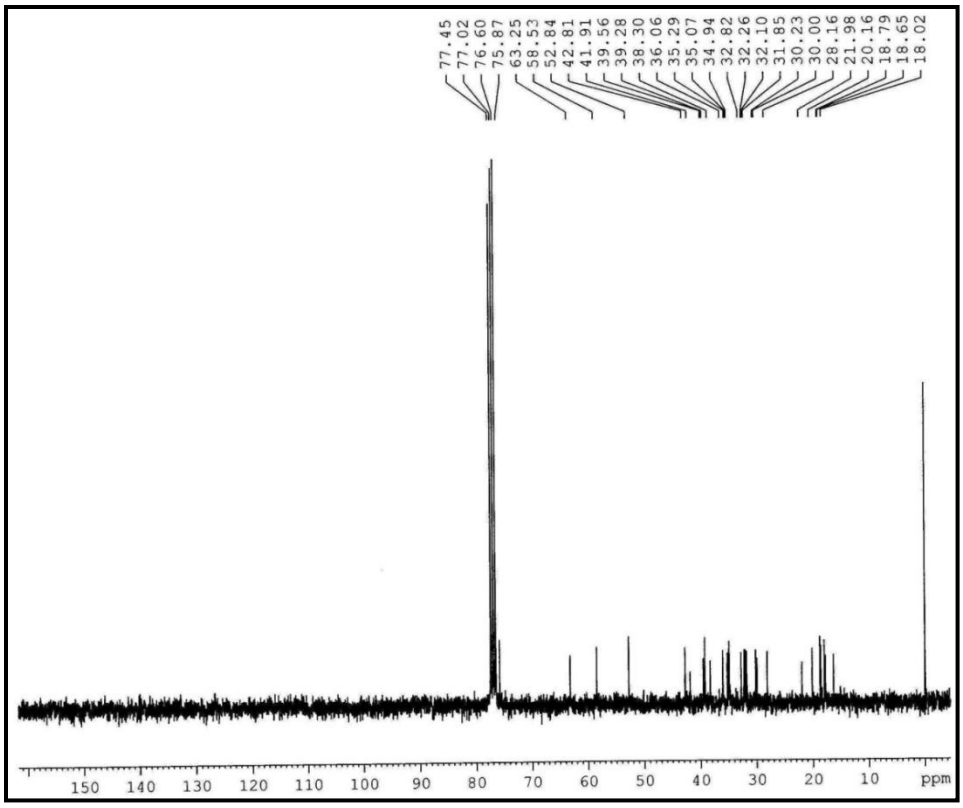

Figure S34. ^{13}C NMR spectrum of 3,4-*seco*friedelane-3,4-diol (**15**).

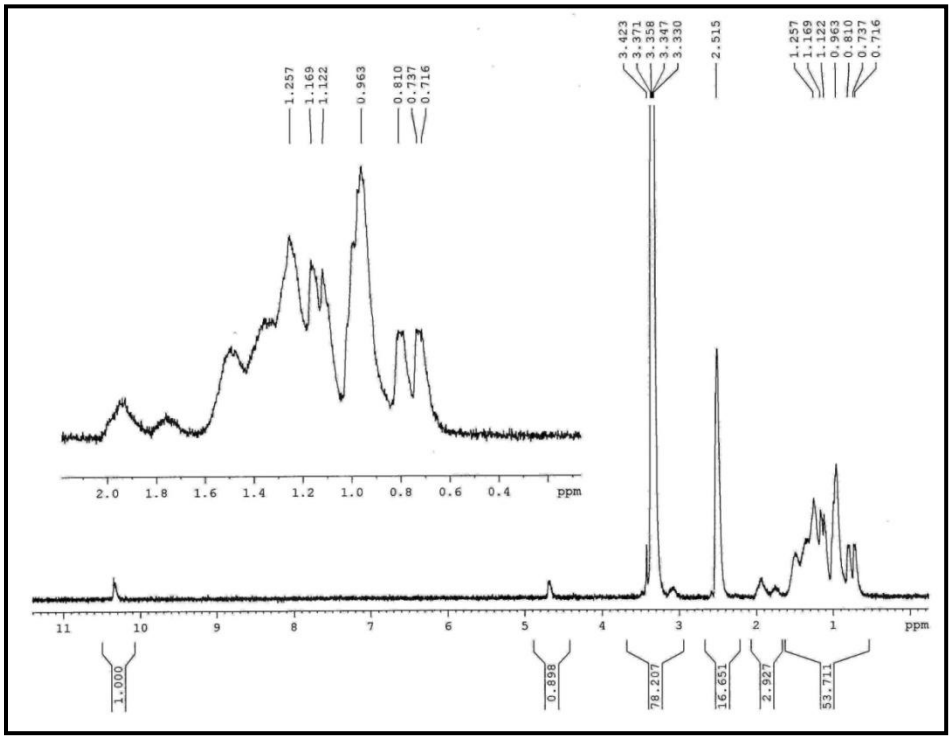

Figure S35. ^{1}H NMR spectrum of friedelane-3-oximino-4α–ol (**16**).

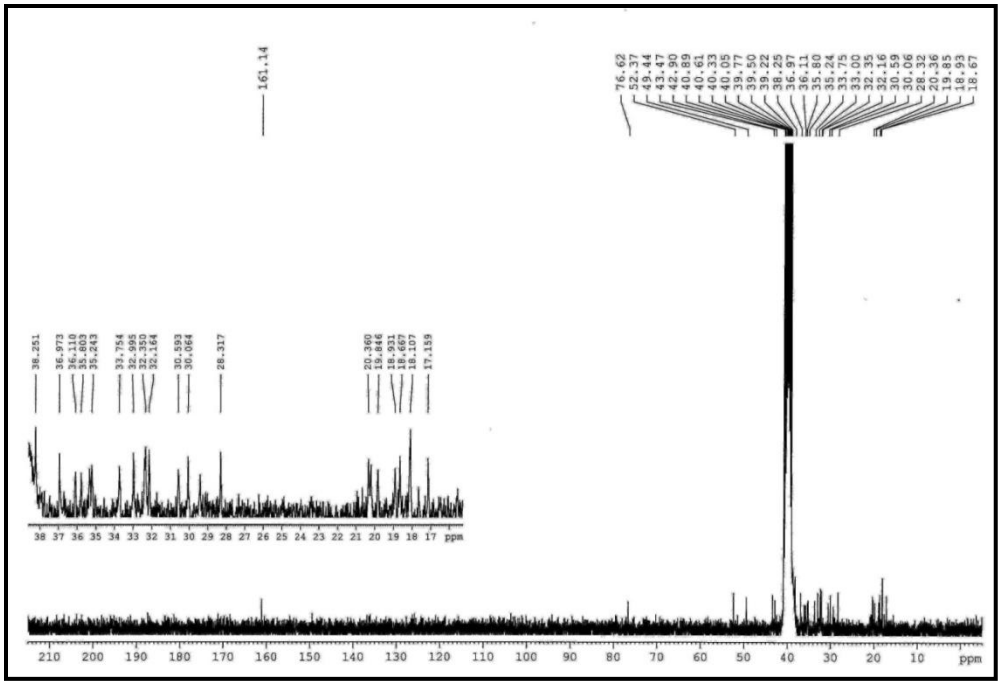

Figure S36. ^{13}C NMR spectrum of friedelane-3-oximino-4α–ol (**16**).

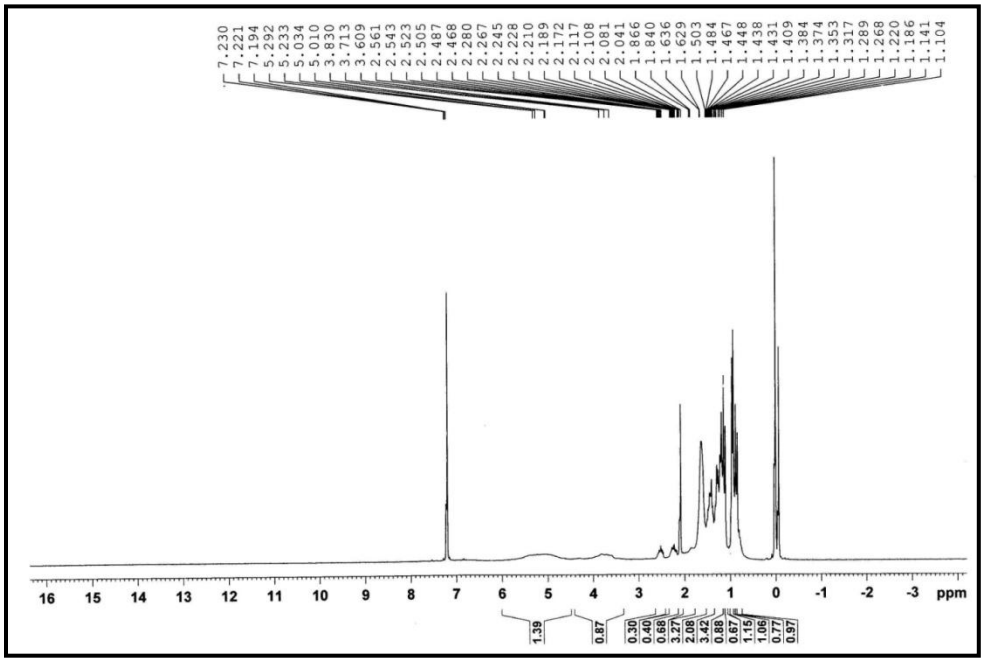

Figure S37. ^{1}H NMR spectrum of friedelan-3β-amine-4α-ol (**17**).

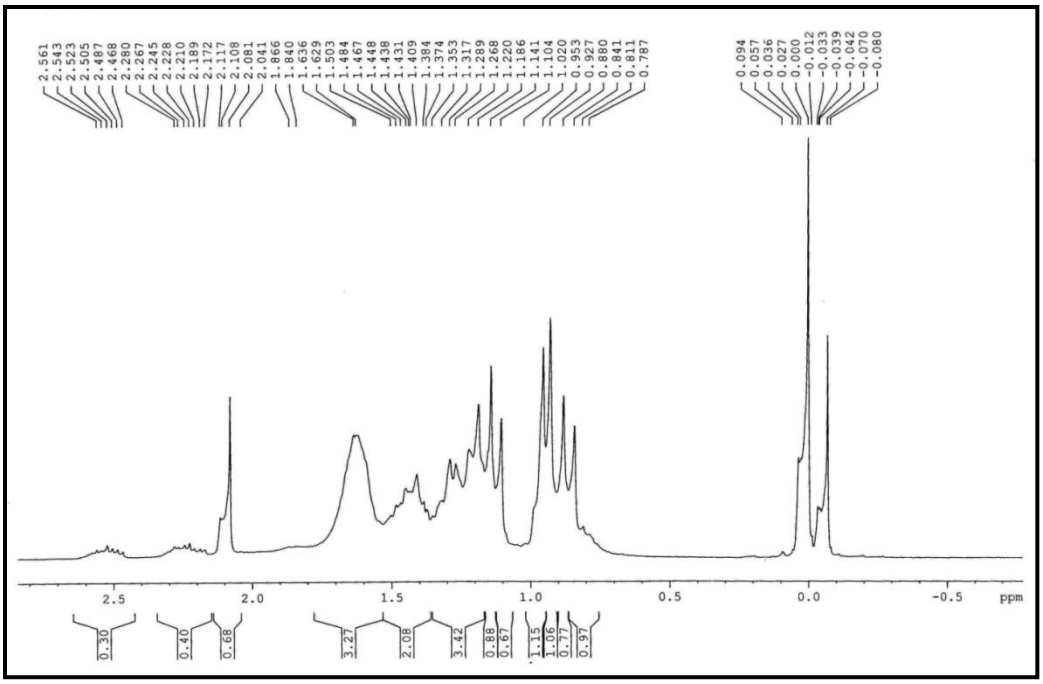

Figure S38. ^{1}H NMR spectrum (partially expanded) of friedelan-3β-amine-4α-ol (**17**).

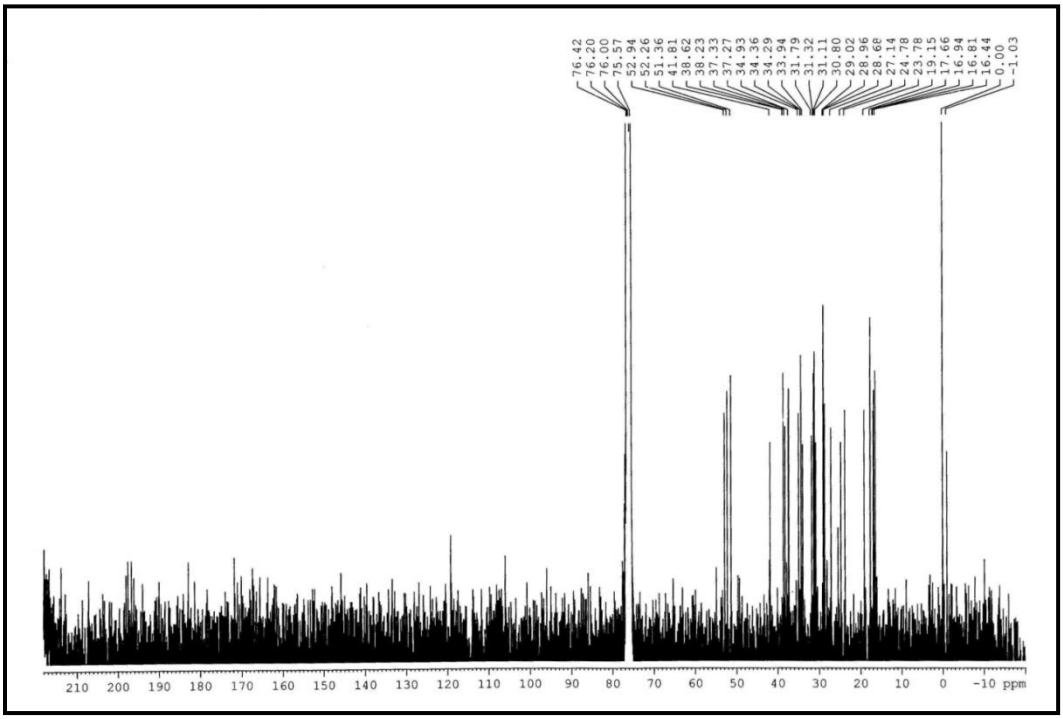

Figure S39. ^{13}C NMR spectrum of friedelan-3β-amine-4α-ol (**17**).

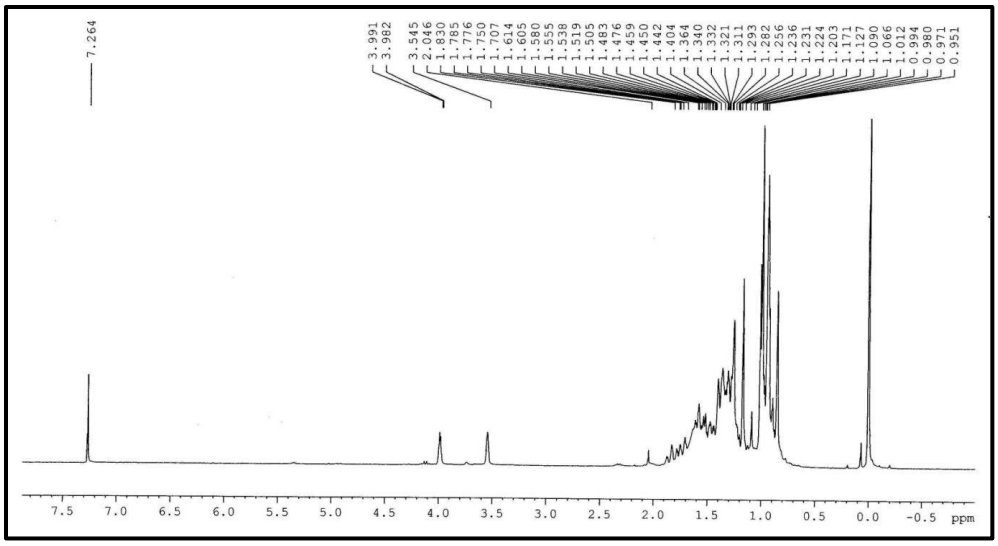

Figure S40. ^{1}H NMR spectrum of friedelane-2α,3β-diol (**18**).

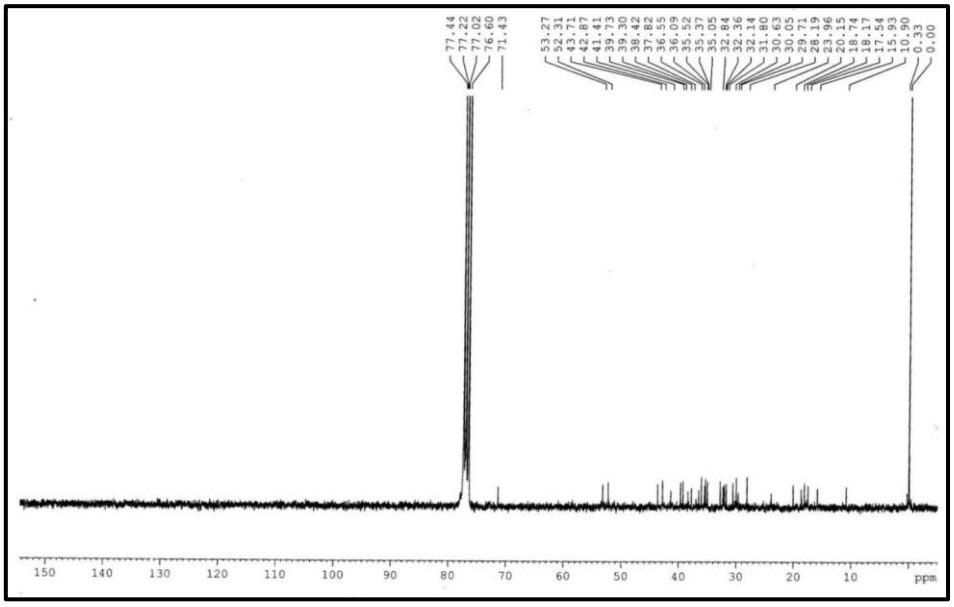

Figure S41. ^{13}C NMR spectrum of friedelane-2α,3β-diol (**18**).

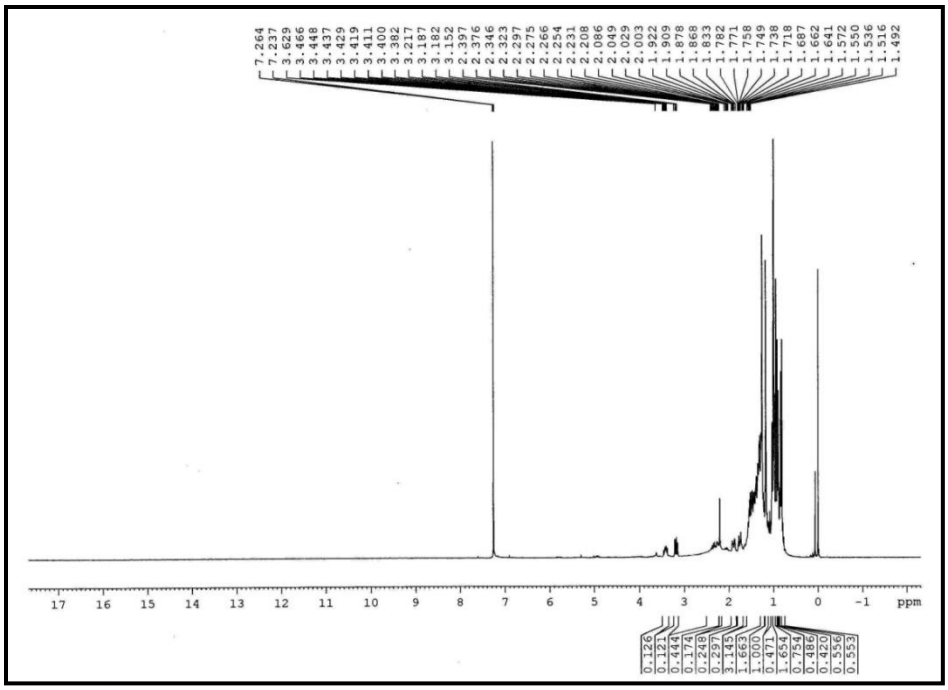

Figure S42. ^{1}H NMR spectrum of 3-*epi*pachysandiol A (**19**).

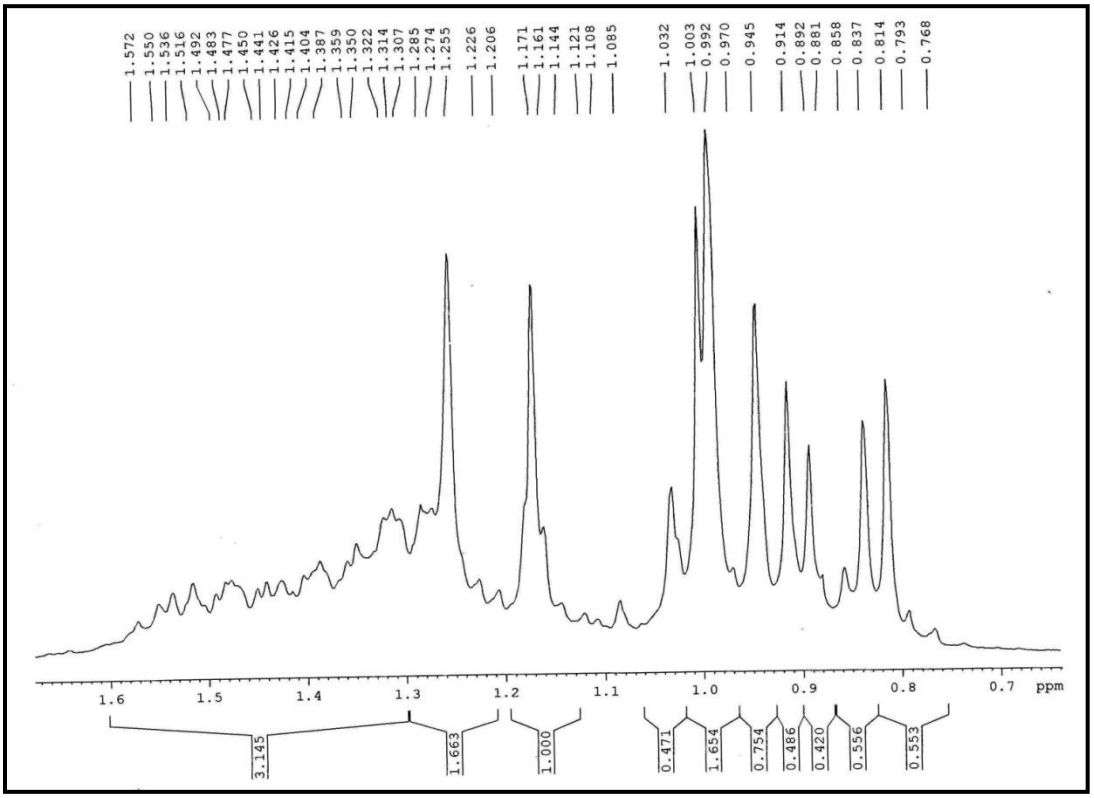

Figure S43. ^{1}H NMR spectrum (partially expanded) 3-*epi*pachysandiol A (**19**).

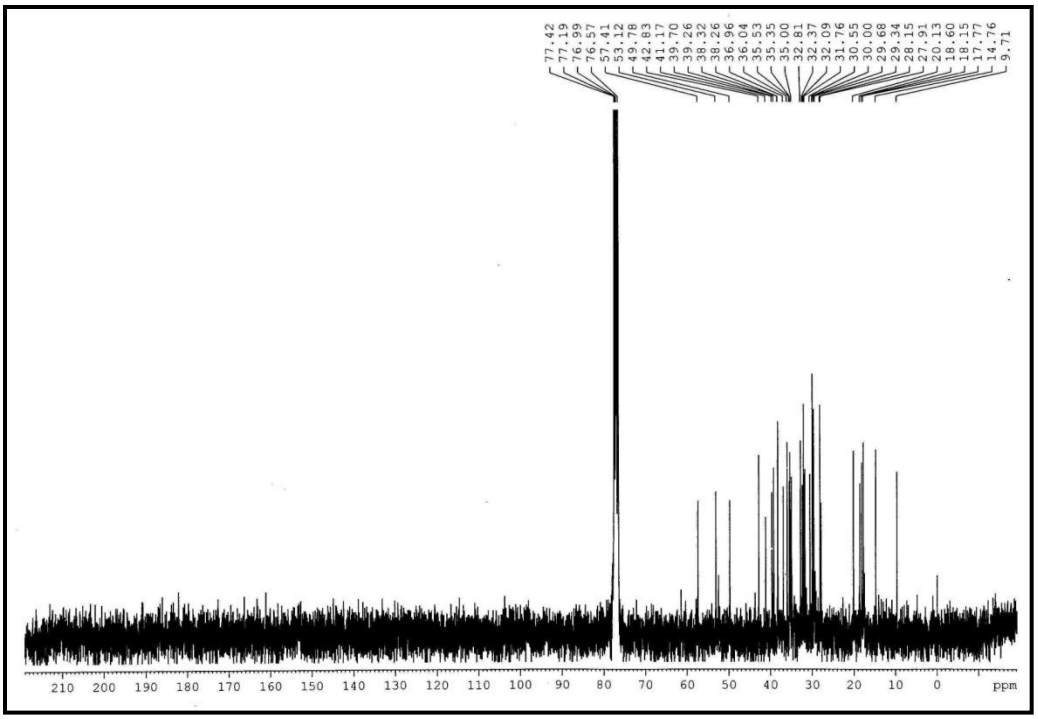

Figure S44. ^{13}C NMR spectrum of 3-*epi*pachysandiol A (**19**).

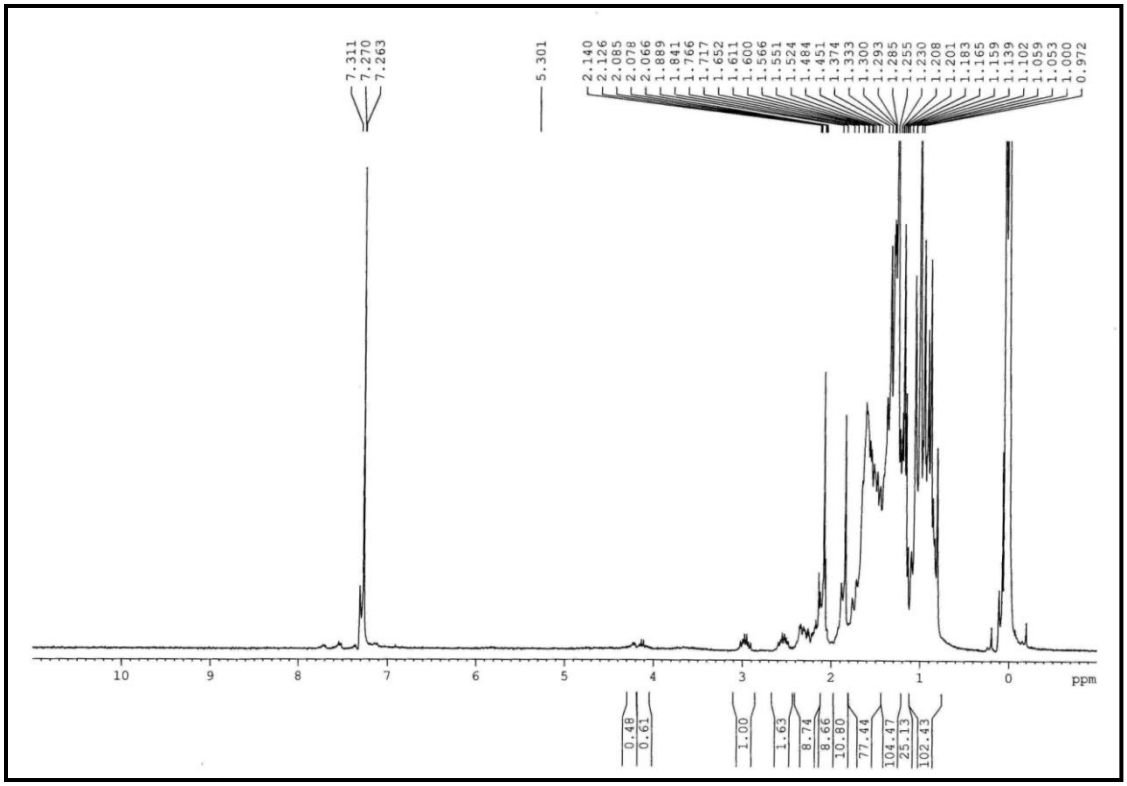

Figure S45. ^{1}H NMR spectrum of friedelane-3β,4α-diacetate (**20**).

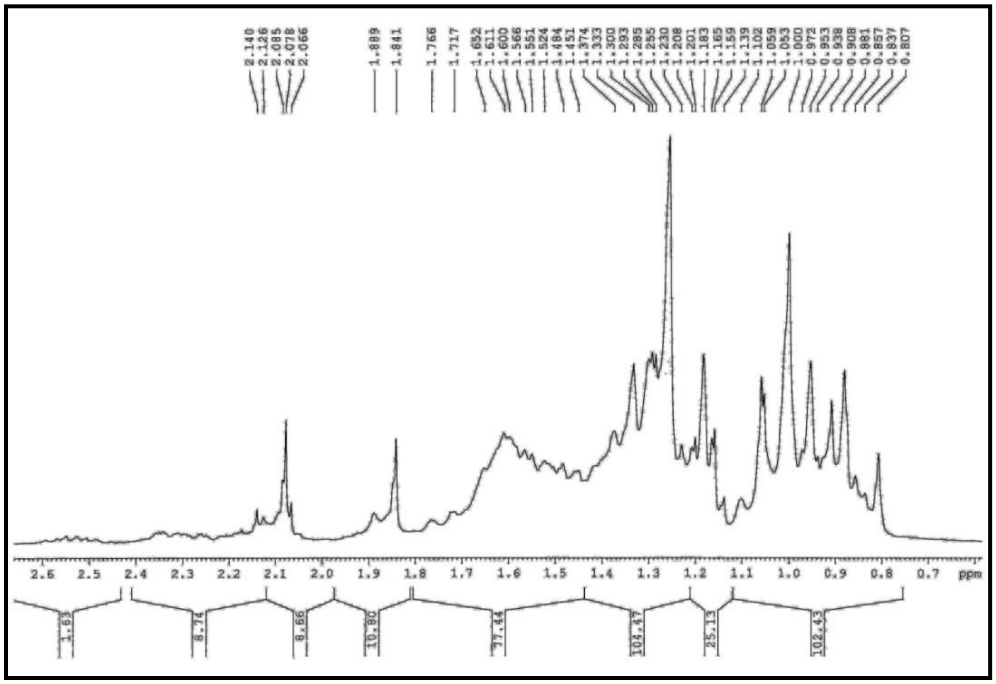

Figure S46. [1]HNMR spectrum (partially expanded) of friedelane-3β,4α-diacetate (**20**).

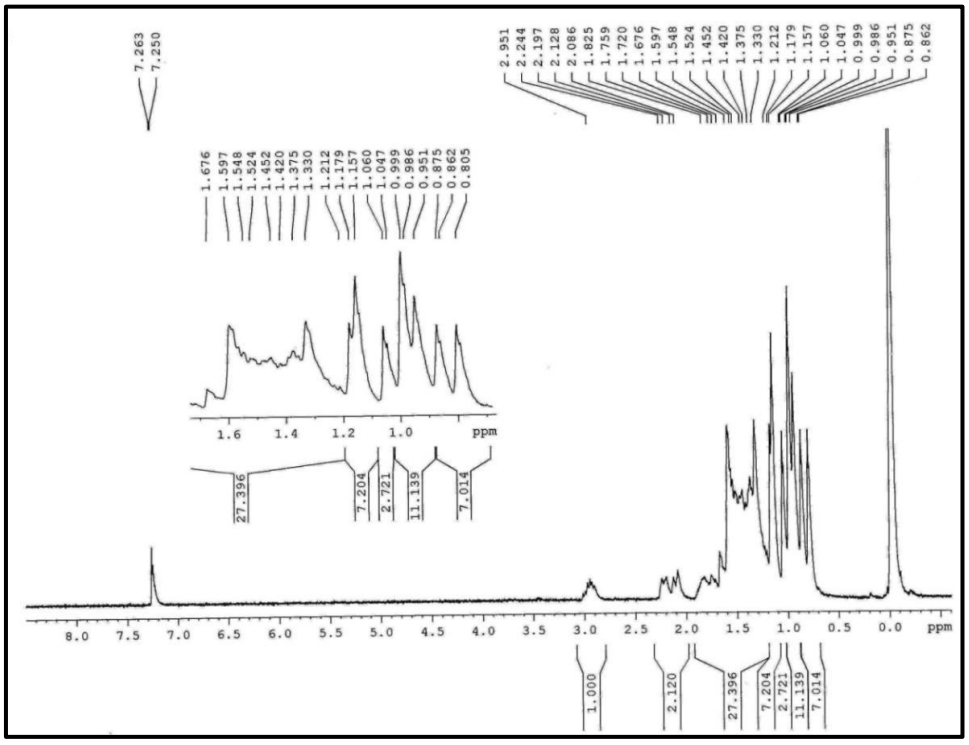

Figure S47. [1]H NMR spectrum of friedelan-3-oxo-4α-ol (**21**).

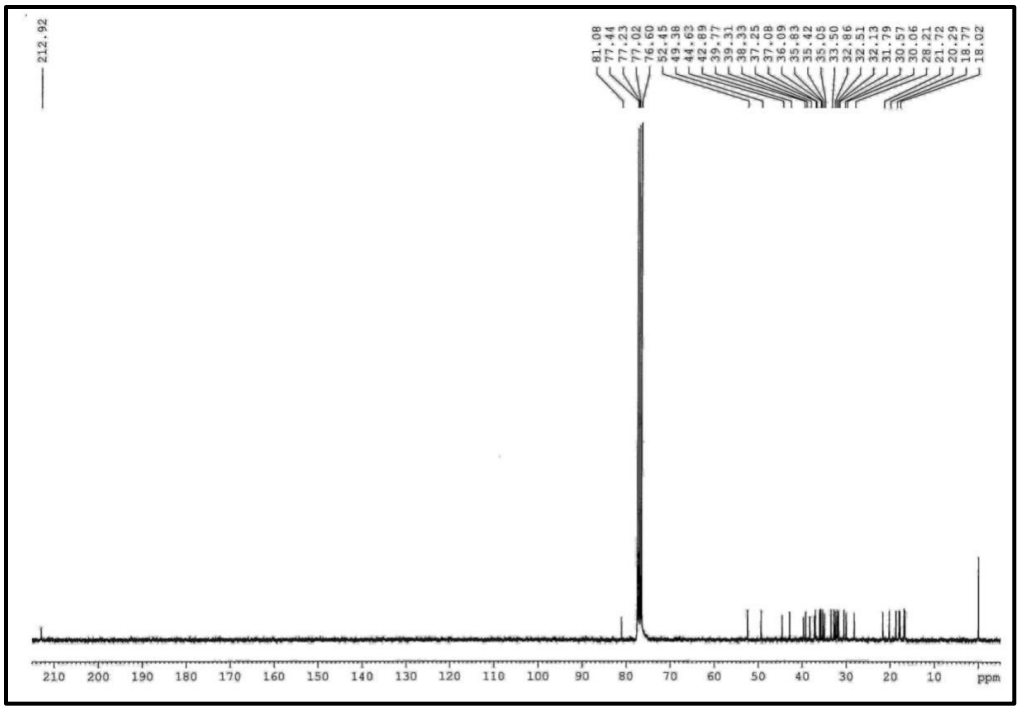

Figure S48. ^{13}C NMR spectrum of friedelan-3-oxo-4α-ol (**21**).

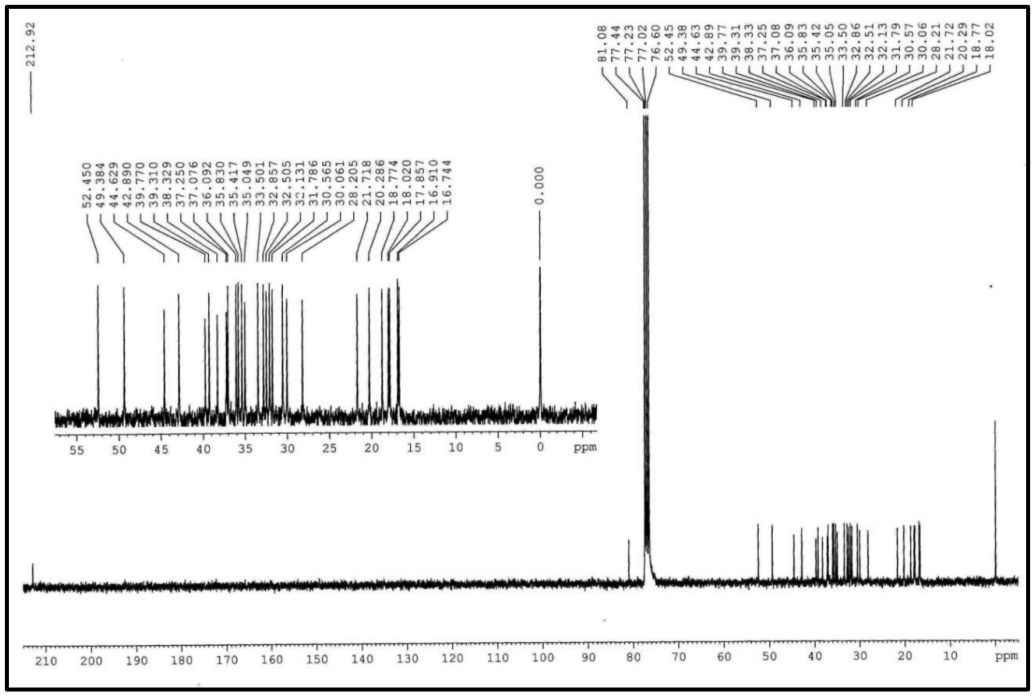

Figure S49. ^{13}C NMR spectrum (partially expanded) of friedelan-3-oxo-4α-ol (**21**).

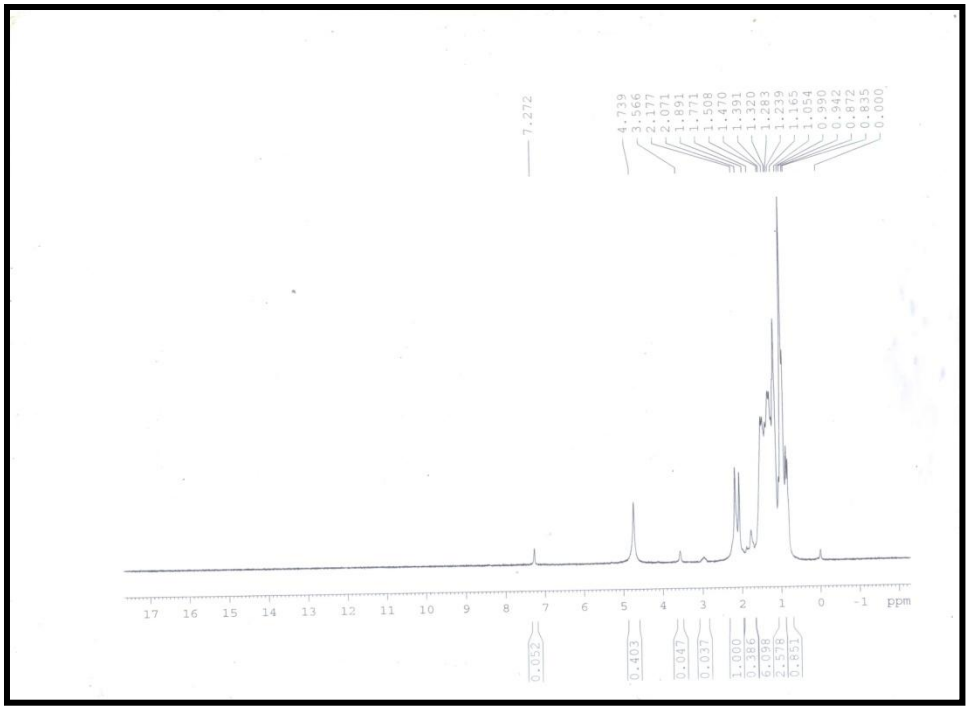

Figure S50. ^{1}H NMR spectrum of friedelane-3β,4α-diol (**22**).

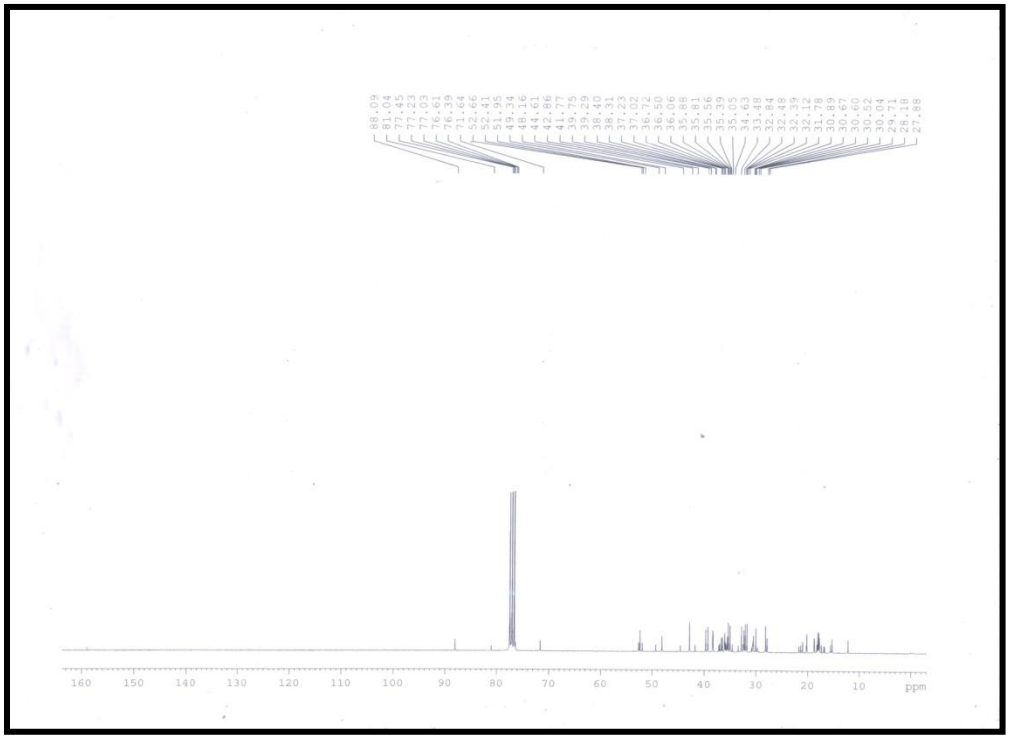

Figure S51. ^{13}C NMR spectrum of friedelane-3β,4α-diol (**22**).

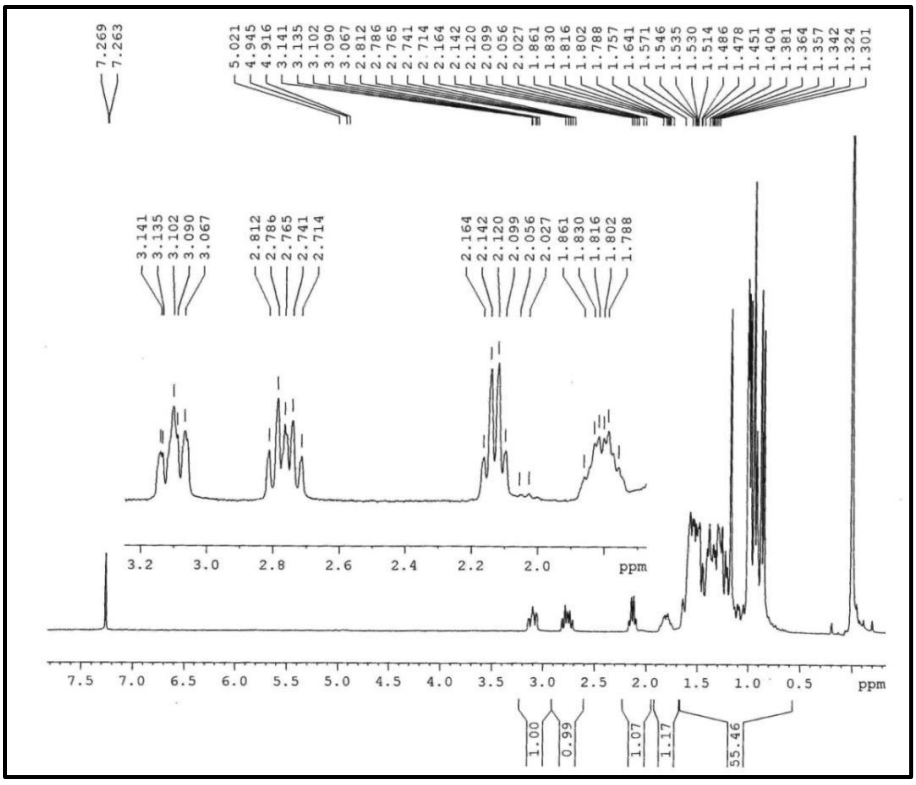

Figure S52. ^{1}H NMR spectrum of cyclic amine **23**.

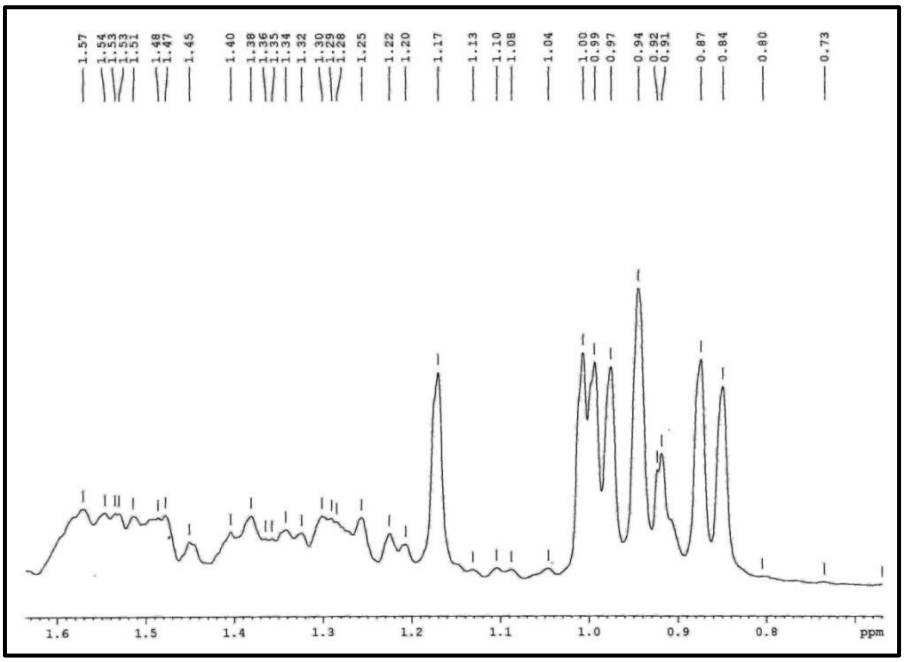

Figure S53. ^{1}H NMR spectrum (partially expanded) of cyclic amine **23.**

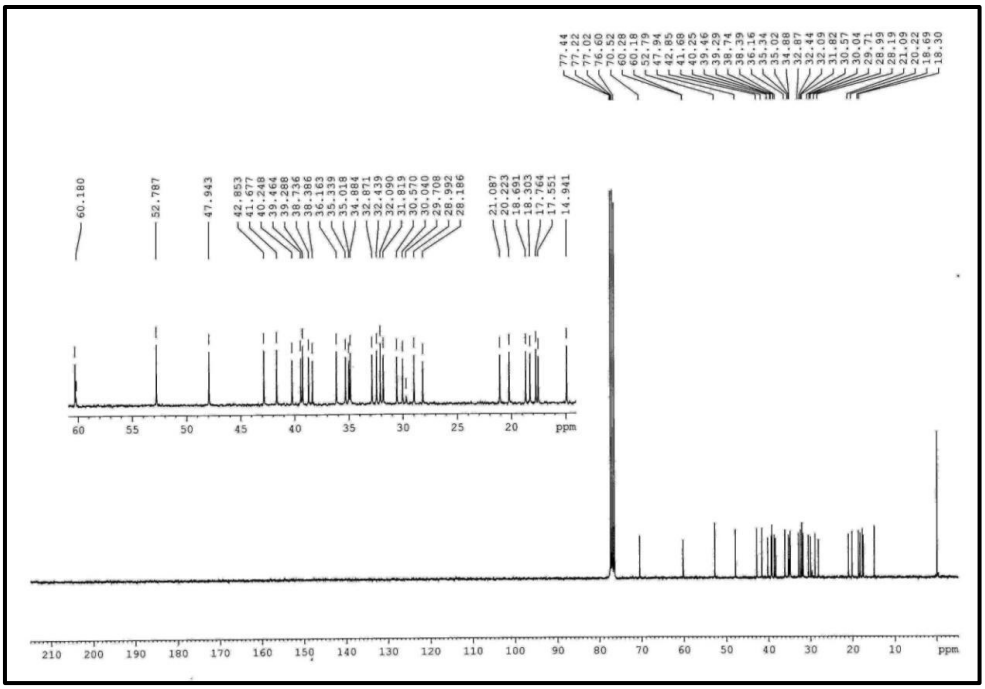

Figure S54. ^{13}C NMR spectrum of cyclic amine **23**.

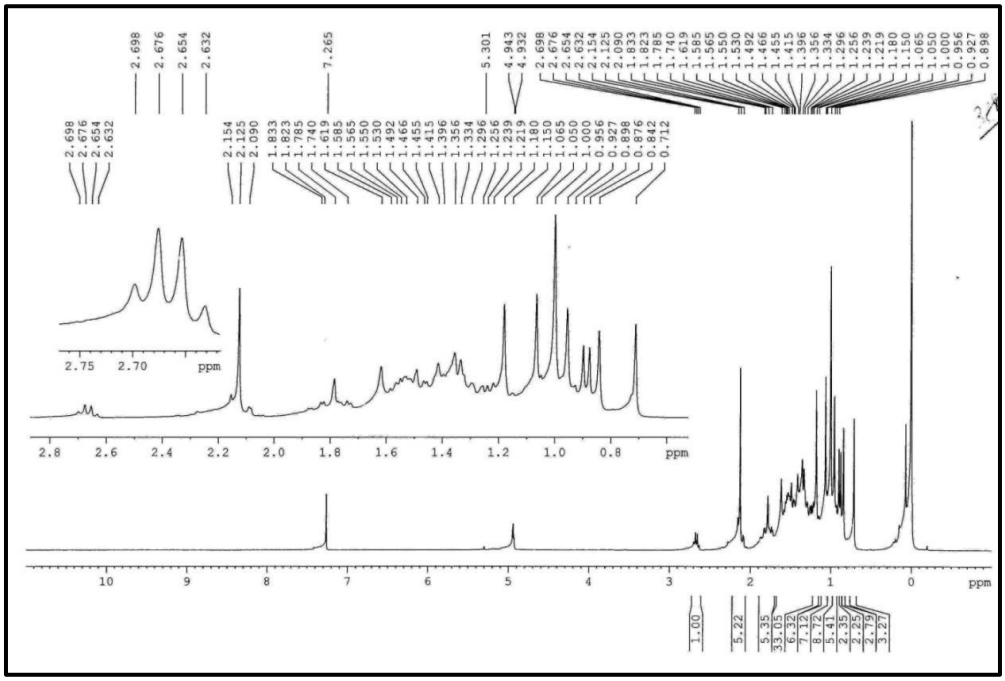

Figure S55. ^{1}H NMR spectrum of friedelan-3-oxo-2α−acetate (**24**).

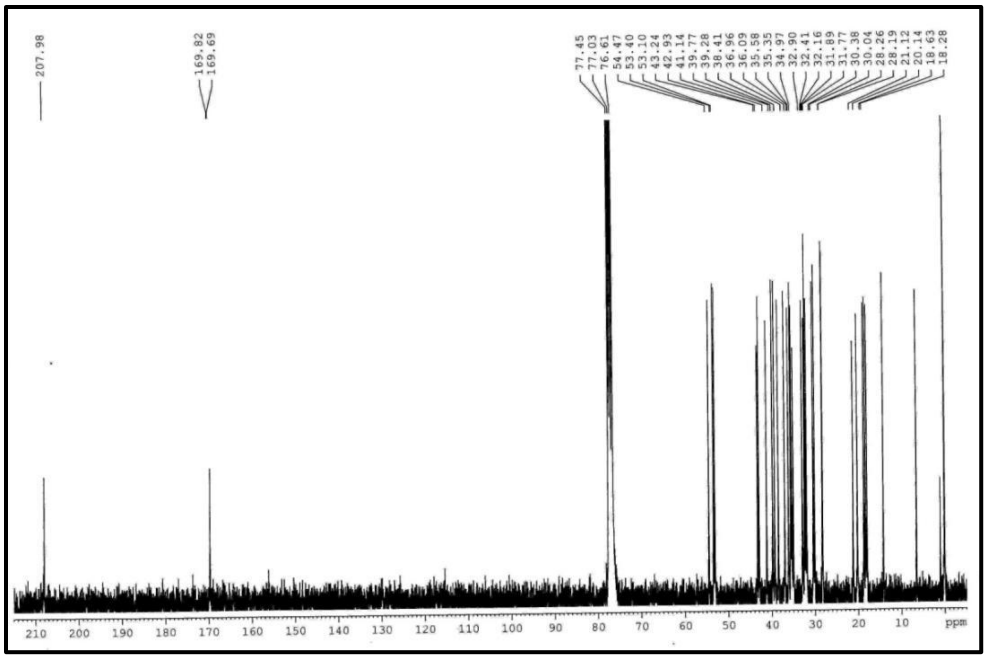

Figure S56. ^{13}C NMR spectrum of friedelan-3-oxo-2α–acetate (**24**).

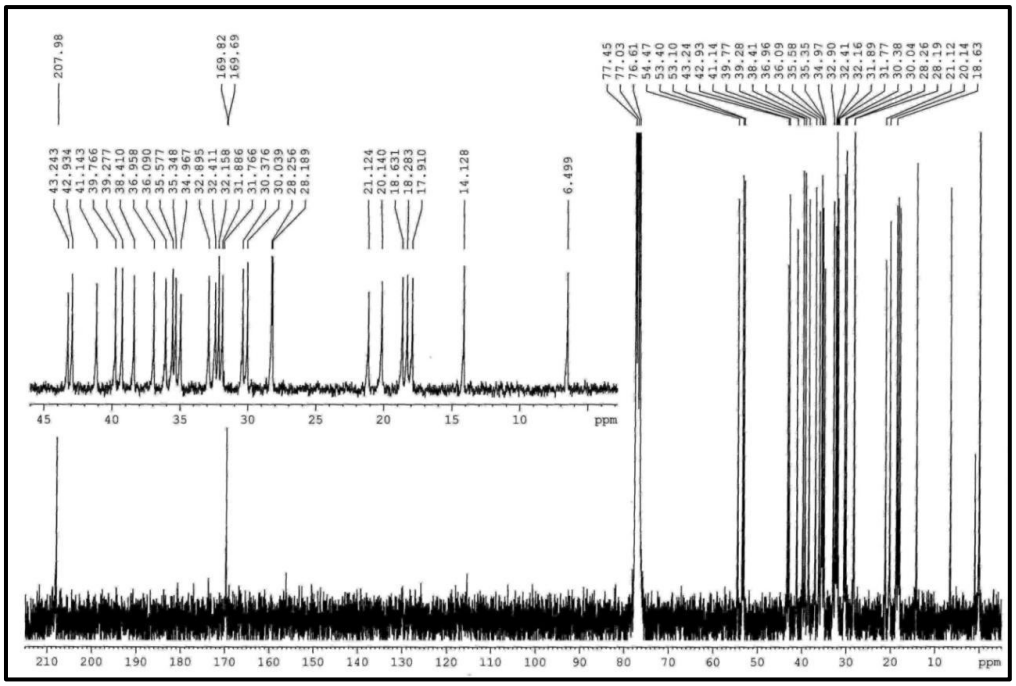

Figure S57. ^{13}C NMR spectrum (partially expanded) of friedelan-3-oxo-2α–acetate (**24**).

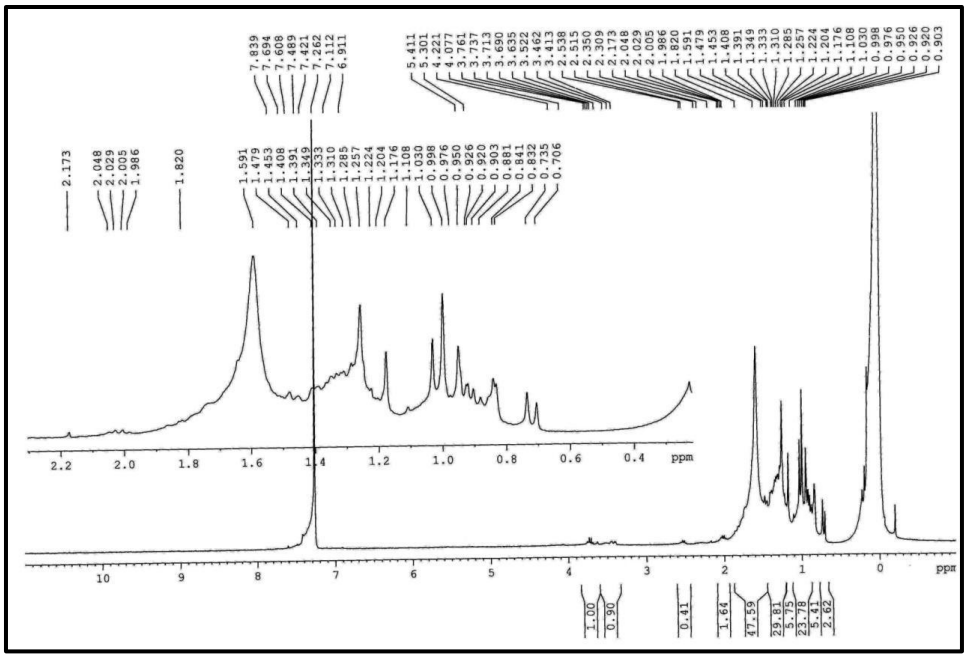

Figure S58. ^{1}H NMR spectrum of friedelan-3-oximino-2α–ol (**25**).

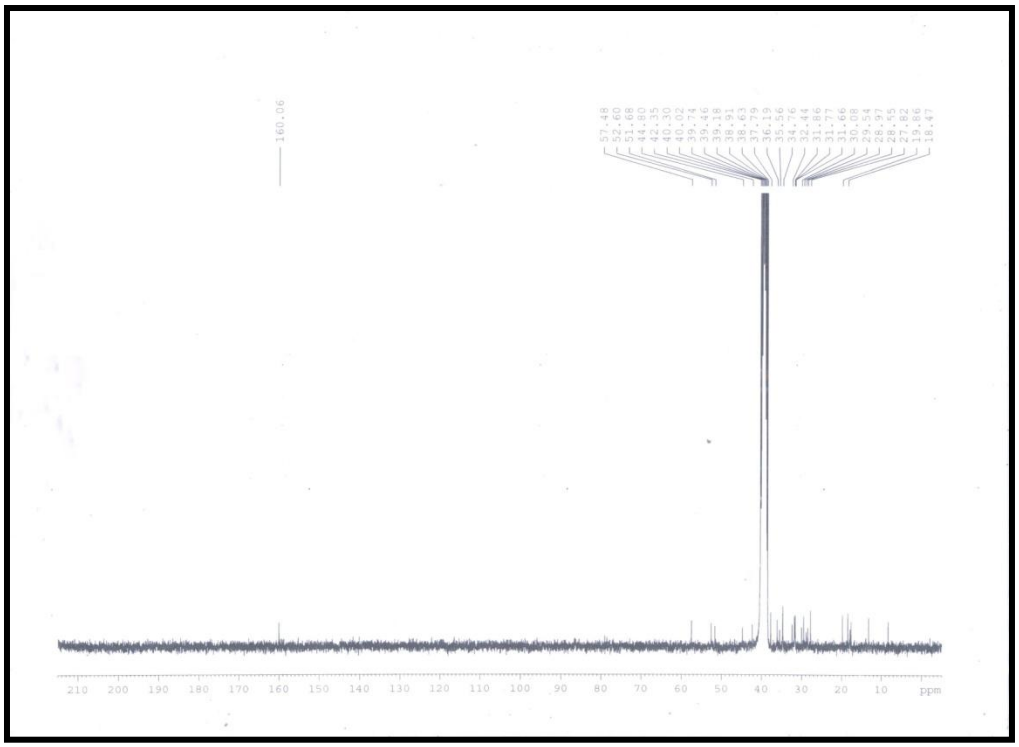

Figure S59. ^{13}C NMR spectrum of friedelan-3-oximino-2α–ol (**25**).

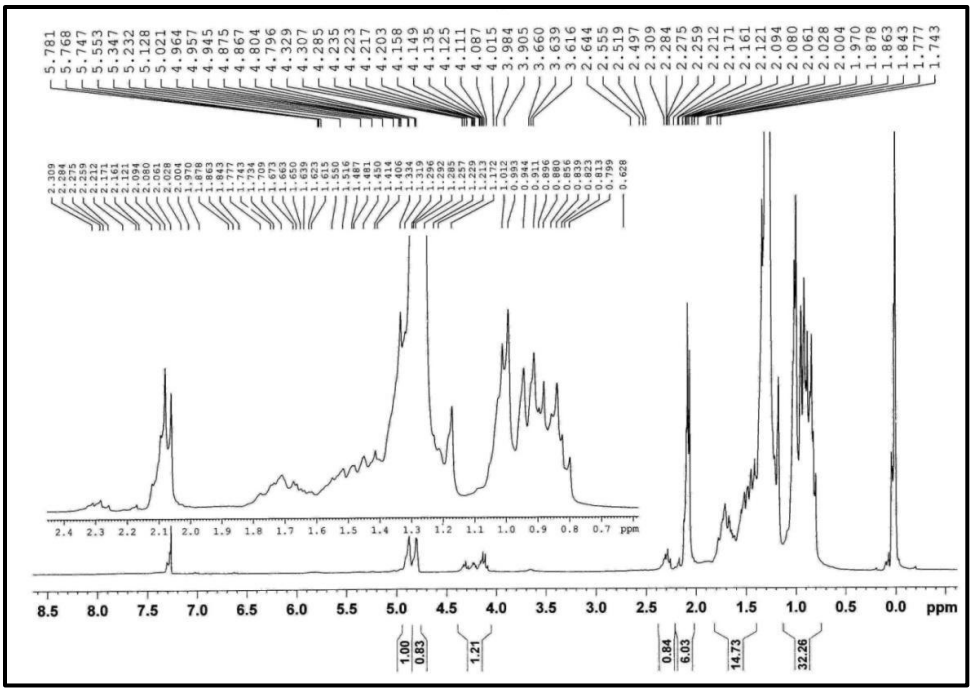

Figure S60. ^{1}H NMR spectrum of friedelane-2α,3β-diacetate (**26**).

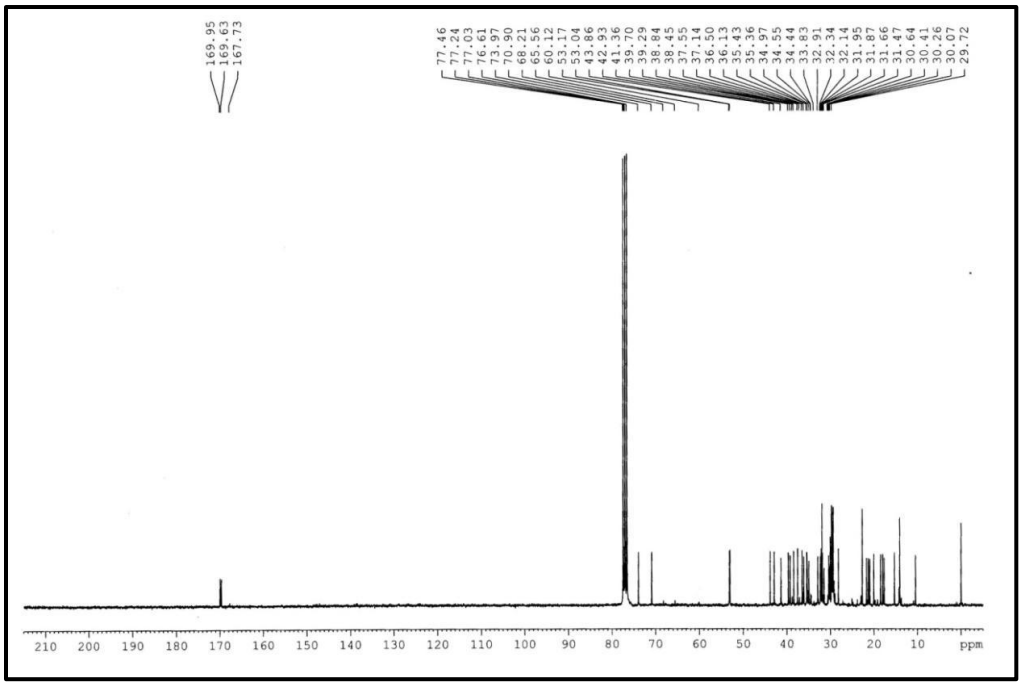

Figure S61. ^{13}C NMR spectrum of friedelane-2α,3β-diacetate (**26**).

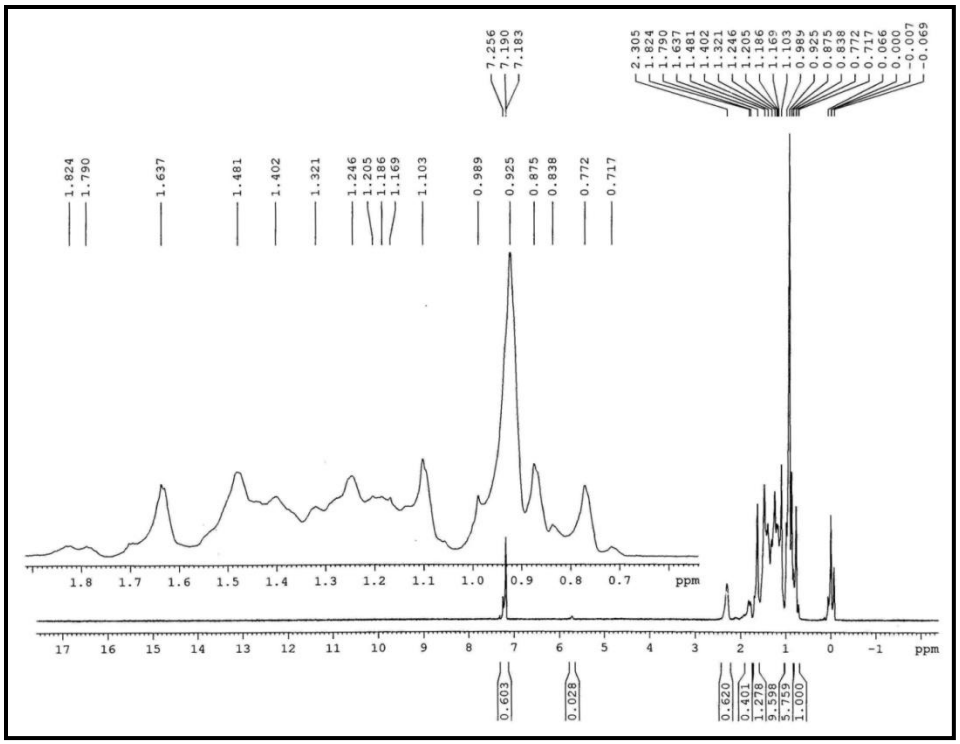

Figure S62. ^{1}H NMR spectrum of 3-chlorofriedel-3-ene (**27**).

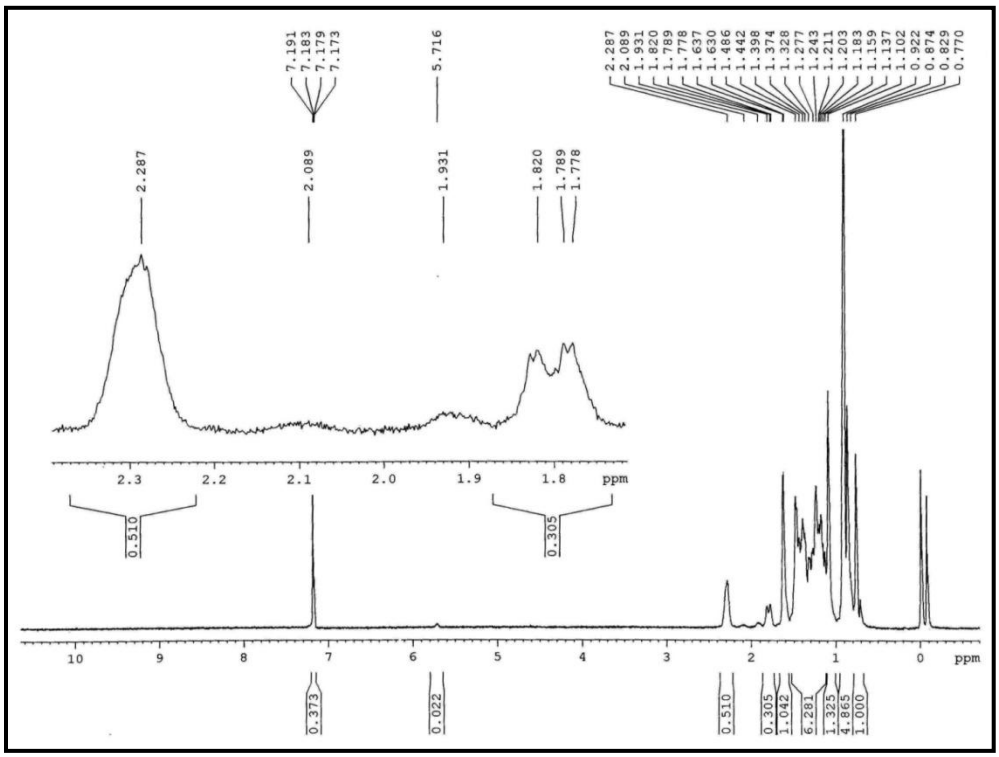

Figure S63. ^{1}H NMR spectrum (partially expanded) of 3-chlorofriedel-3-ene (**27**).

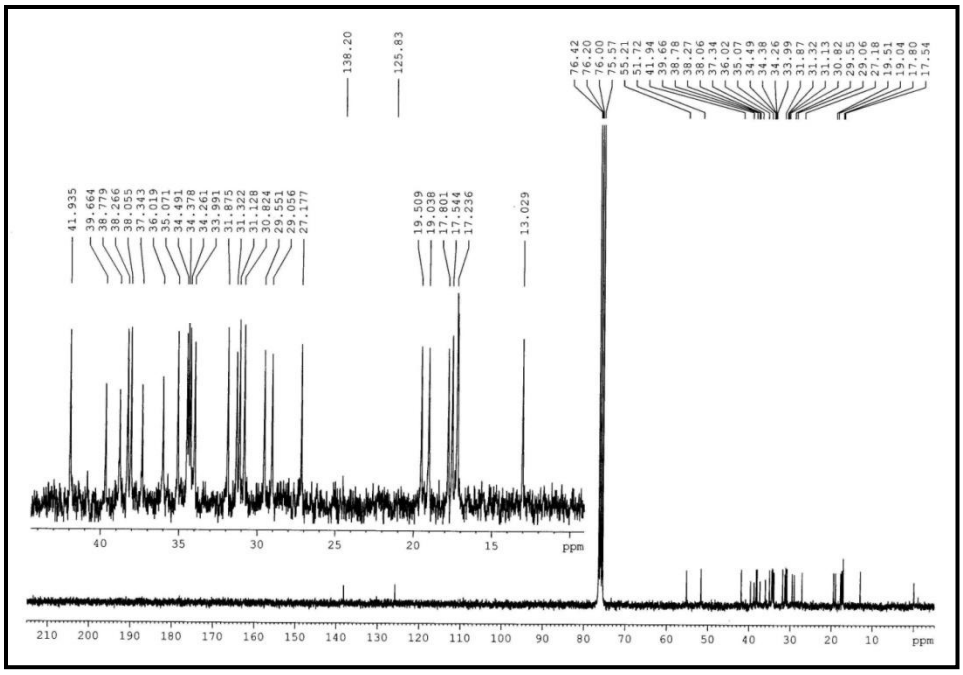

Figure S64. ^{13}C NMR spectrum of 3-chlorofriedel-3-ene (**27**).

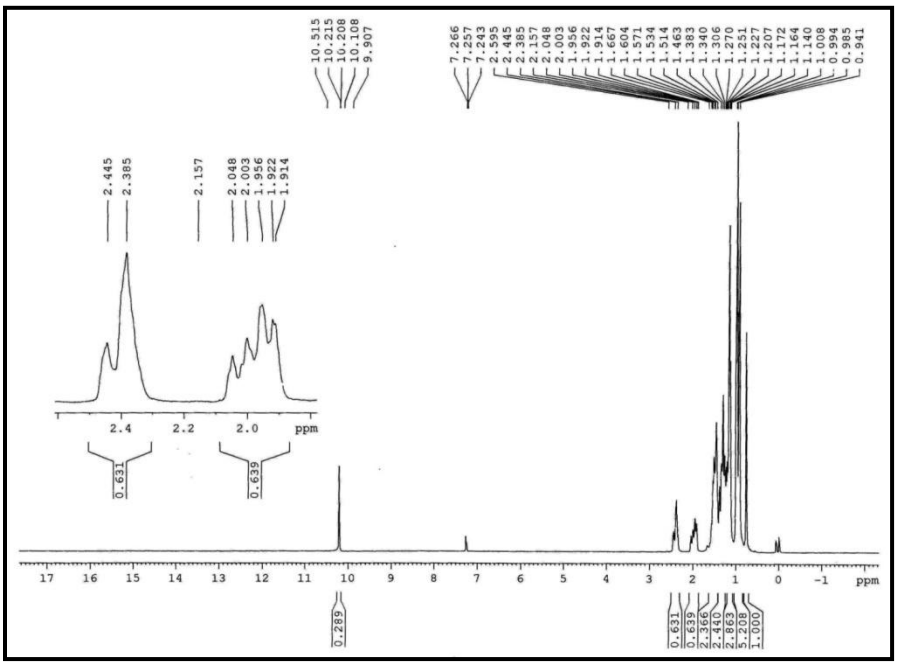

Figure S65. ^{1}H NMR spectrum of 3-chlorofriedel-2-ene-2-carbaldehyde (**28**).

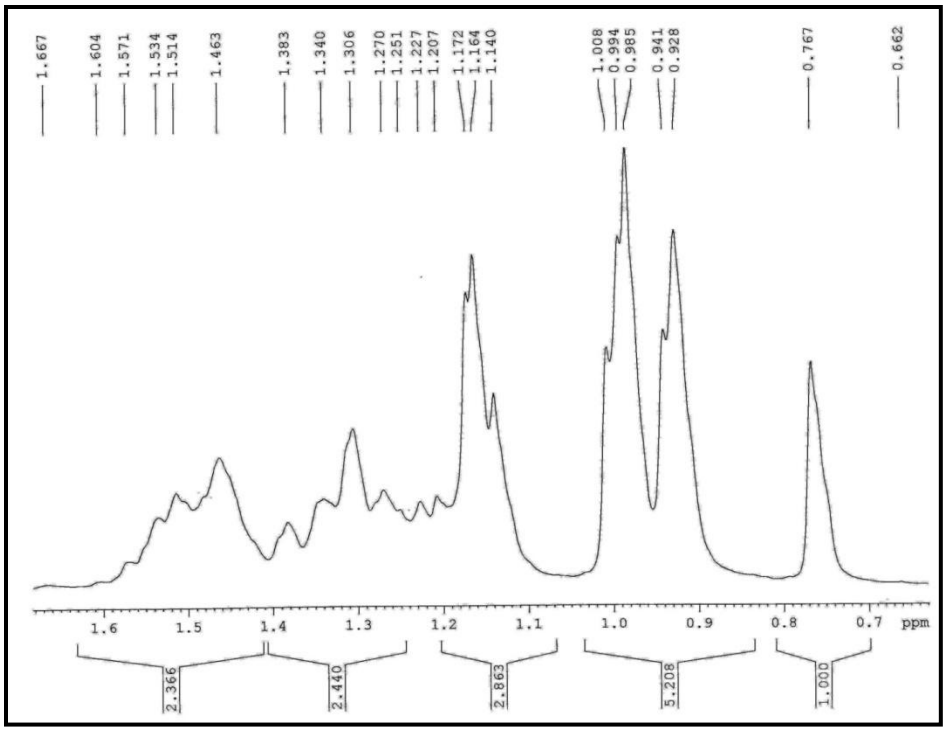

Figure S66. ^{1}H NMR spectrum (partially expanded) of 3-chlorofriedel-2-ene-2-carbaldehyde (**28**).

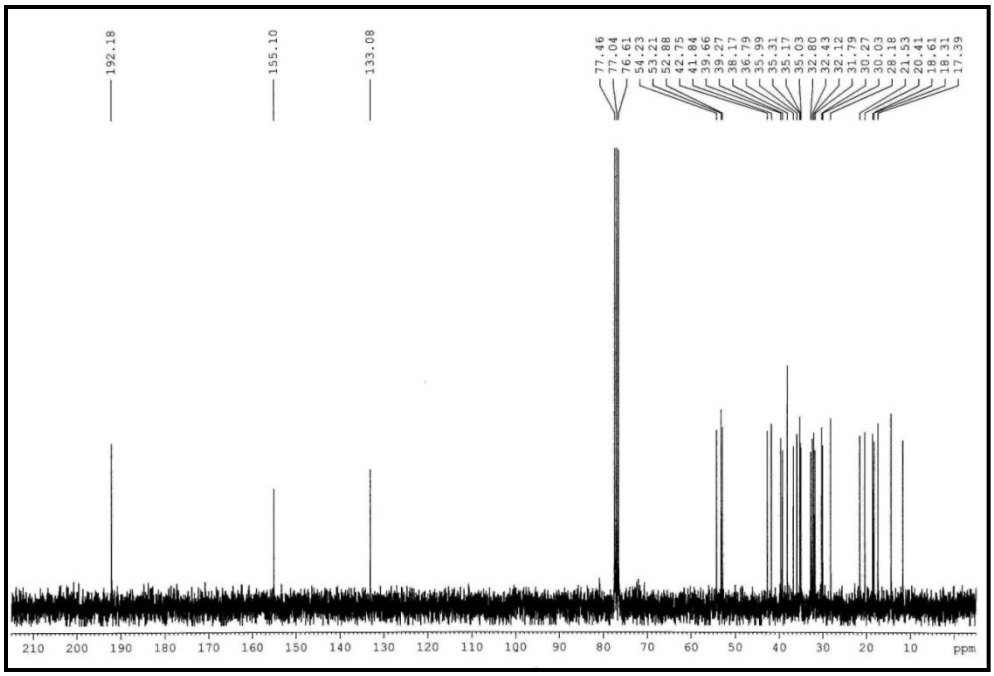

Figure S67. ^{13}C NMR spectrum of 3-chlorofriedel-2-ene-2-carbaldehyde (**28**).

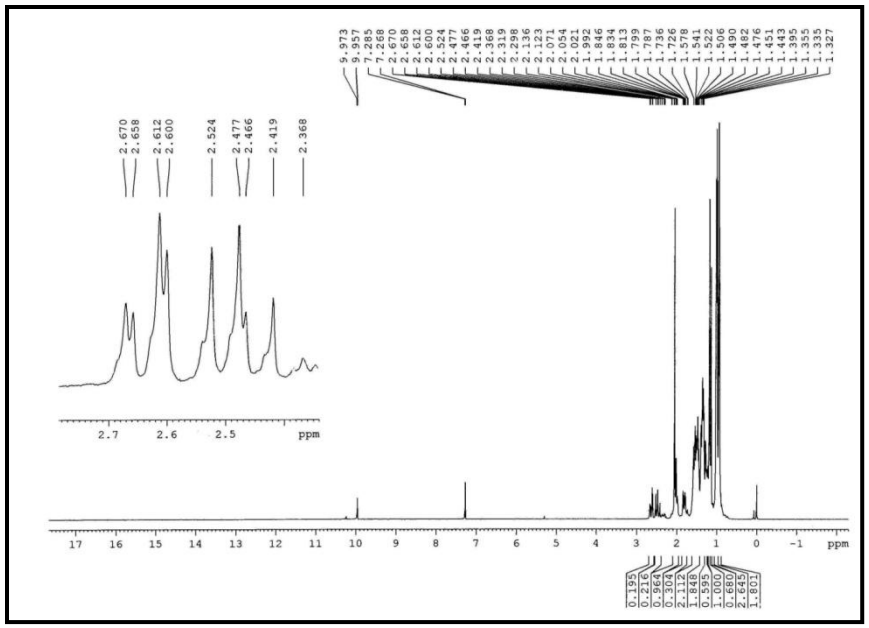

Figure S68. ^{1}H NMR spectrum of friedel-2-en-3-ol-2-carbaldehyde (**29**).

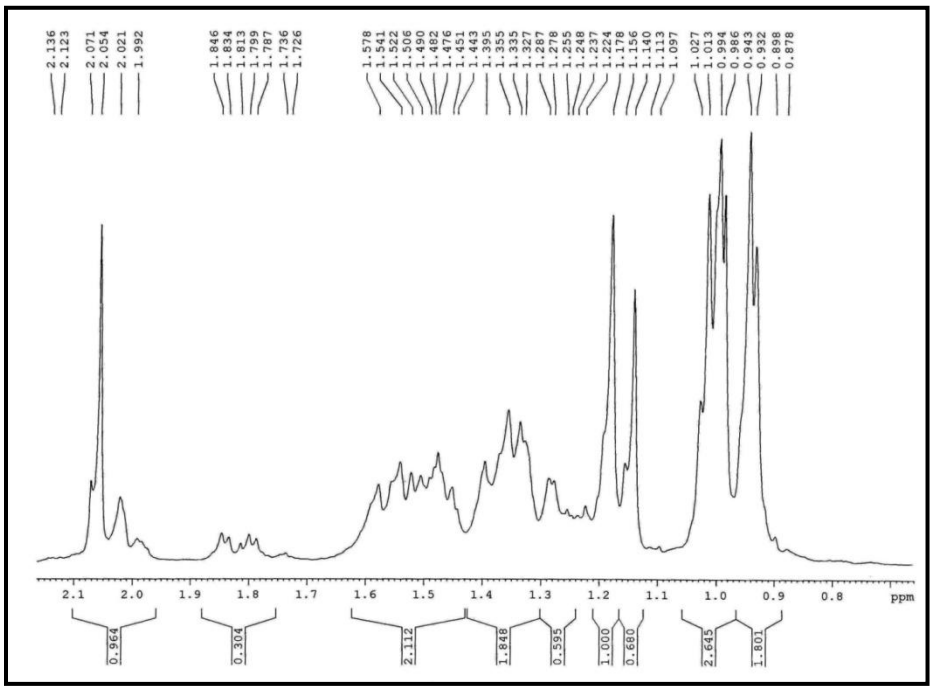

Figure S69. ^{1}H NMR spectrum (partially expanded) of friedel-2-en-3-ol-2-carbaldehyde (**29**).

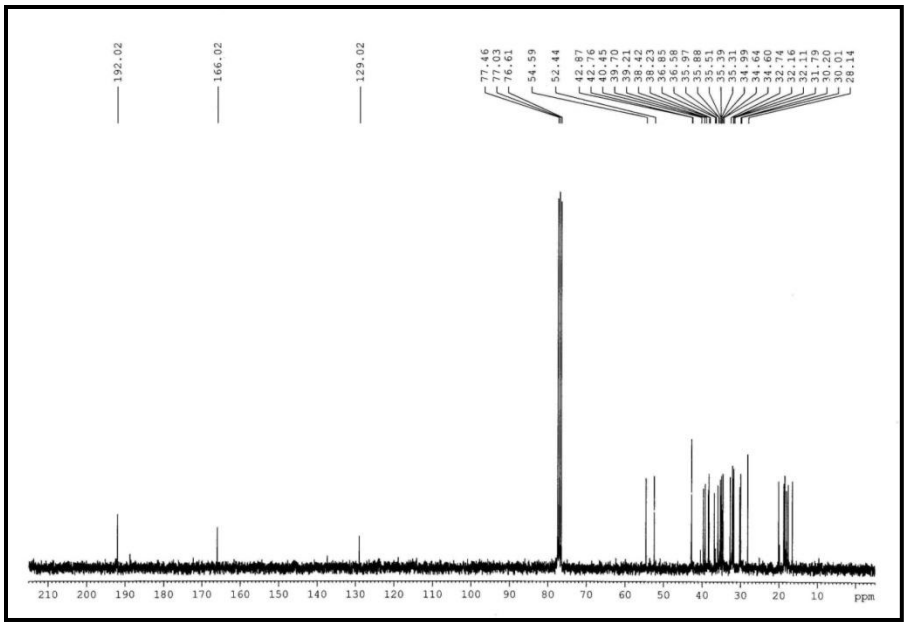

Figure S70. ^{13}C NMR spectrum of friedel-2-en-3-ol-2-carbaldehyde (**29**).

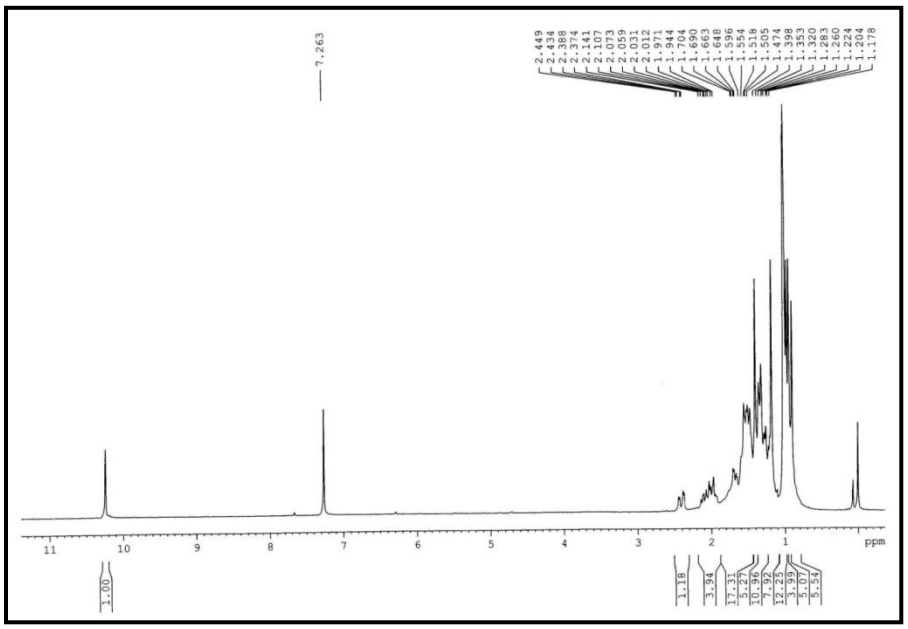

Figure S71. ^{1}H NMR spectrum of 3-chlorofriedel-2-en-4α-ol-2-carbaldehyde (**30**).

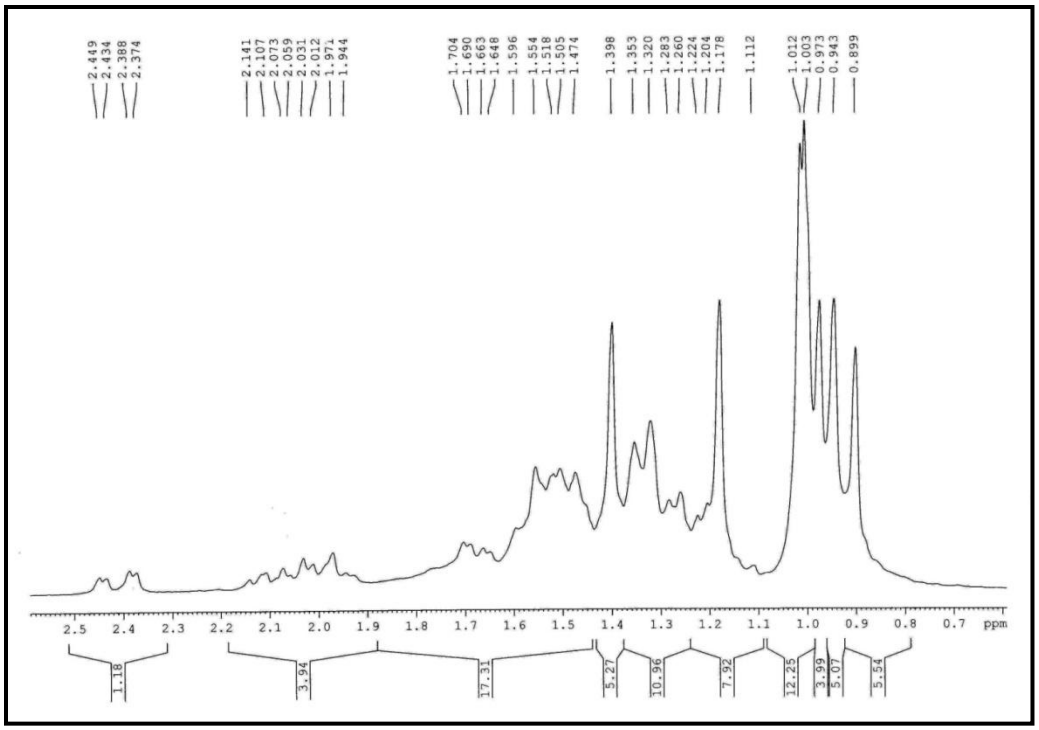

Figure S71. [1]H NMR spectrum (partially expanded) of 3-chlorofriedel-2-en-4α-ol-2-carbaldehyde (**30**).

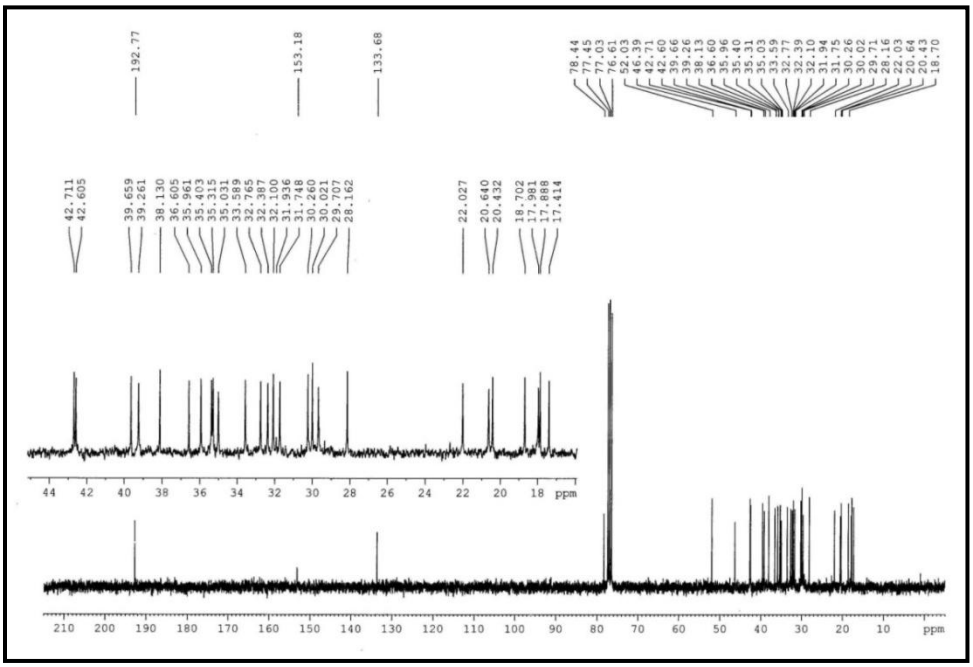

Figure S72. [13]C NMR spectrum of 3-chlorofriedel-2-en-4α-ol-2-carbaldehyde (**30**).

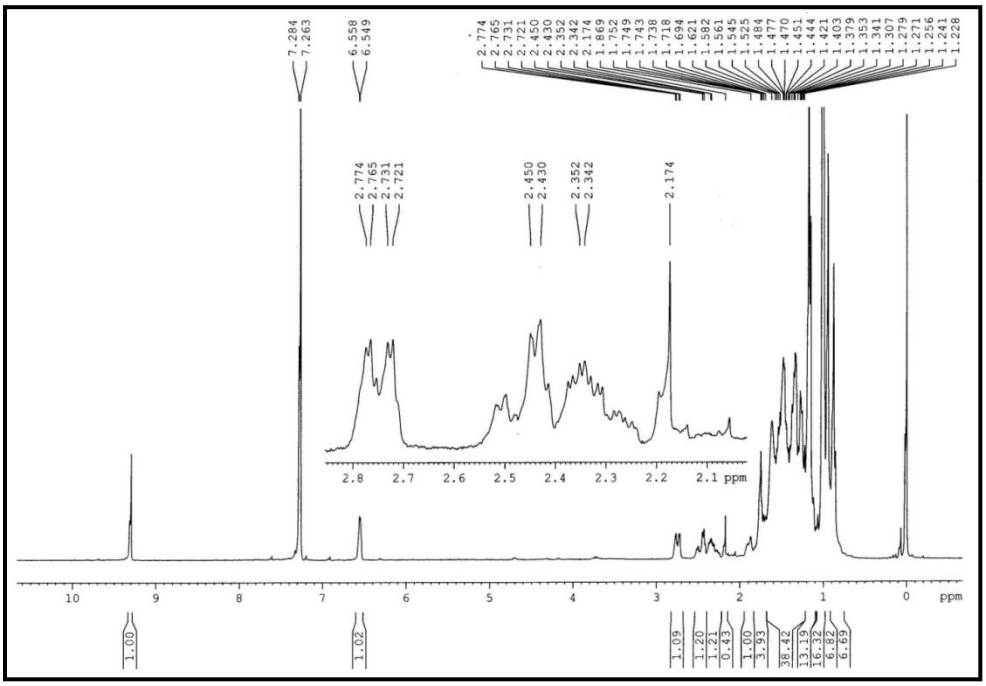

Figure S73. ^{1}H NMR spectrum of friedel-3-en-23-al (**31**).

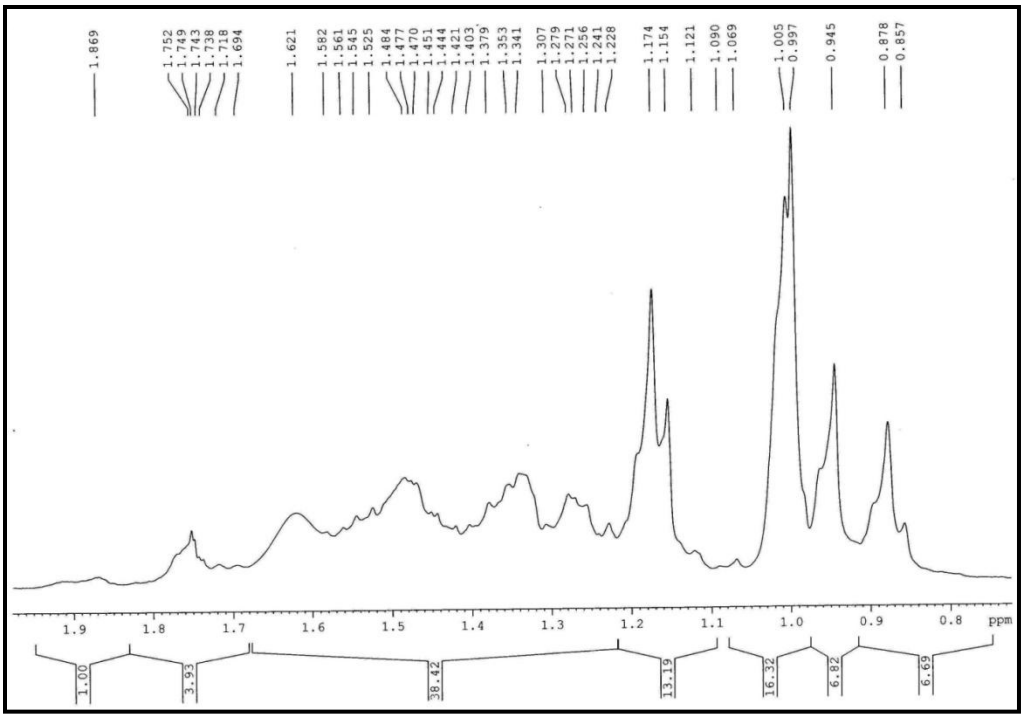

Figure S74. ^{1}H NMR spectrum (partially expanded) of friedel-3-en-23-al (**31**).

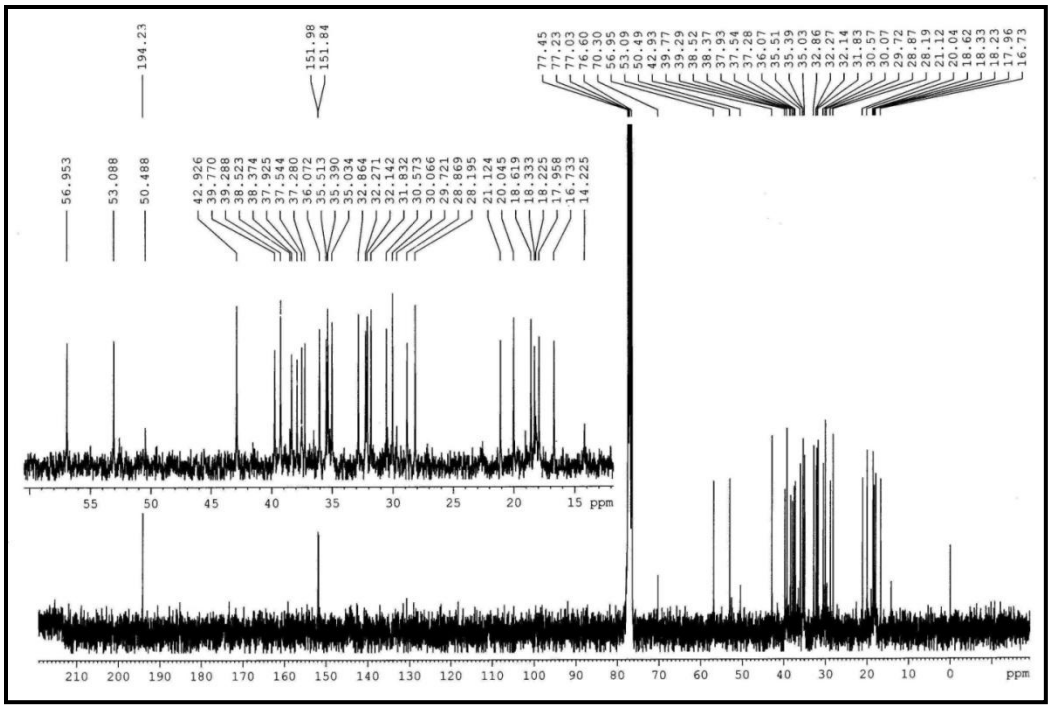

Figure S75. ^{13}C NMR spectrum of friedel-3-en-23-al (**31**).

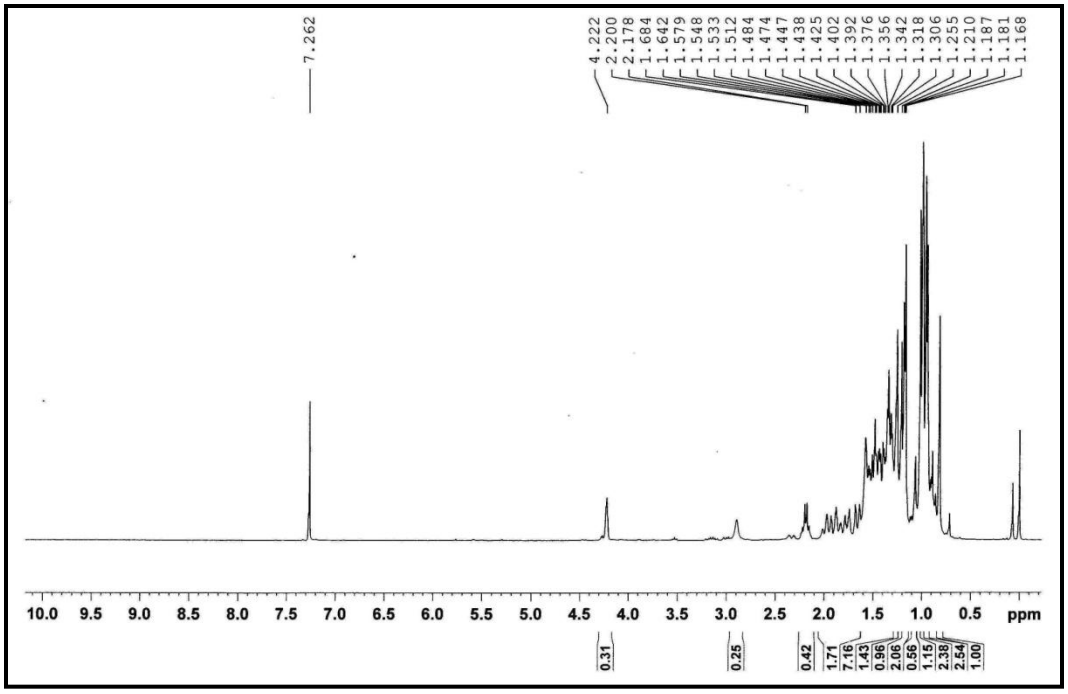

Figure S76. ^{1}H NMR spectrum of friedelan-3α,4α-epoxide (**32**).

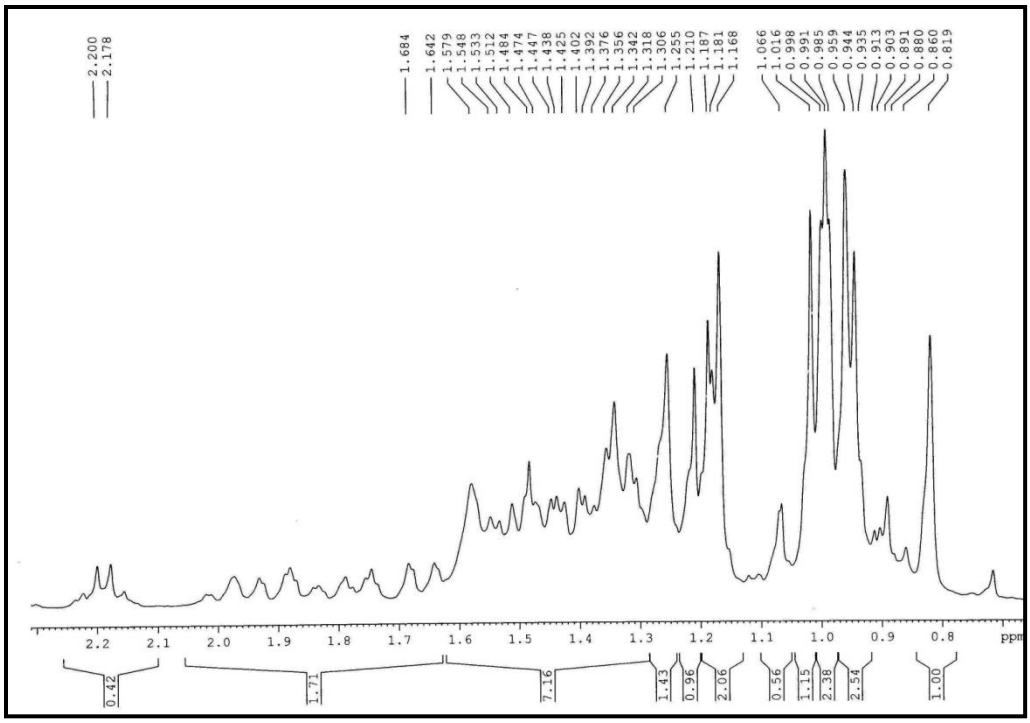

Figure S77. Expanded ^{1}H NMR spectrum of friedelan-3α,4α-epoxide (**32**).

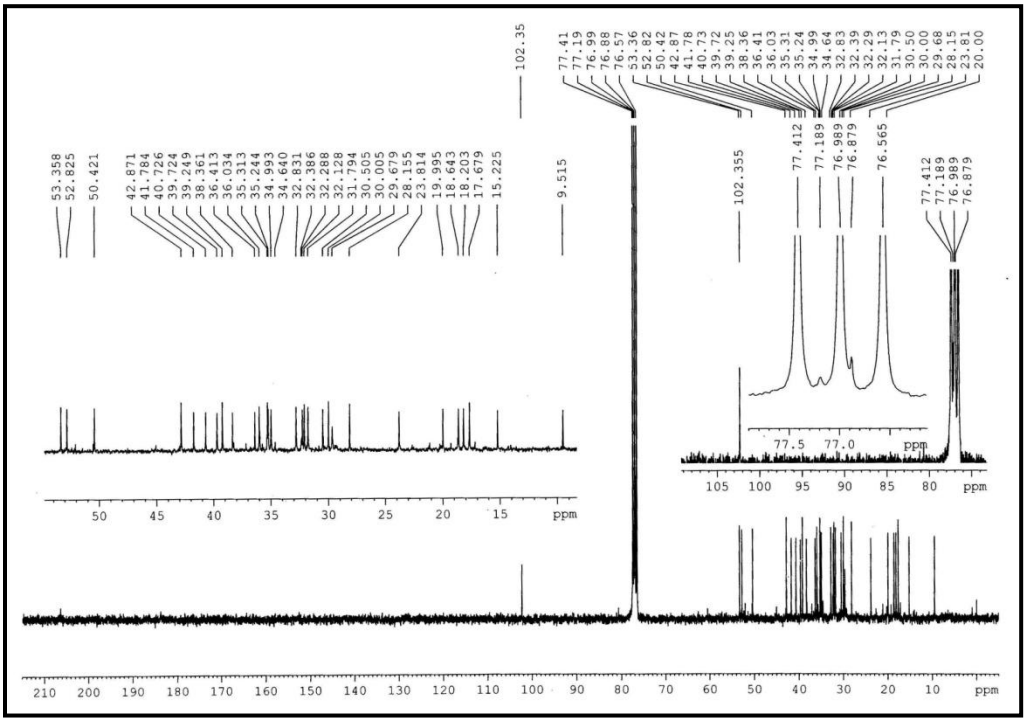

Figure **S78.** ^{13}C NMR spectrum of friedelan-3α,4α-epoxide (**32**).

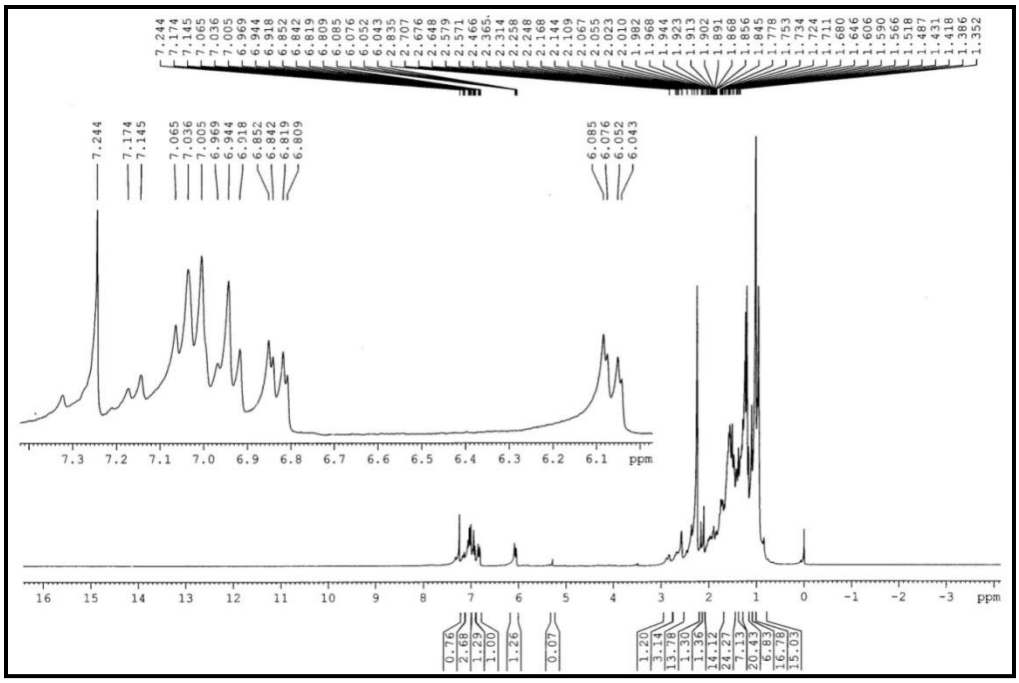

Figure S79. [1]H NMR spectrum of 24-*nor*friedel-1, 3, 5 (10), 6-tetraene (**33**).

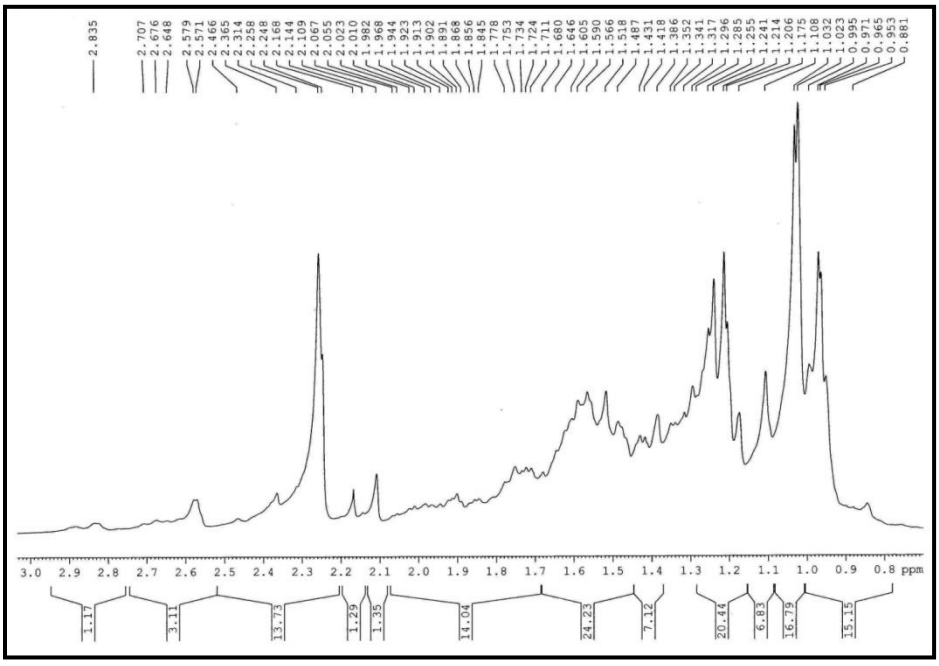

Figure S80. [1]H NMR spectrum (partially expanded) of 24-*nor*friedel-1,3,5(10),6-tetraene (**33**).

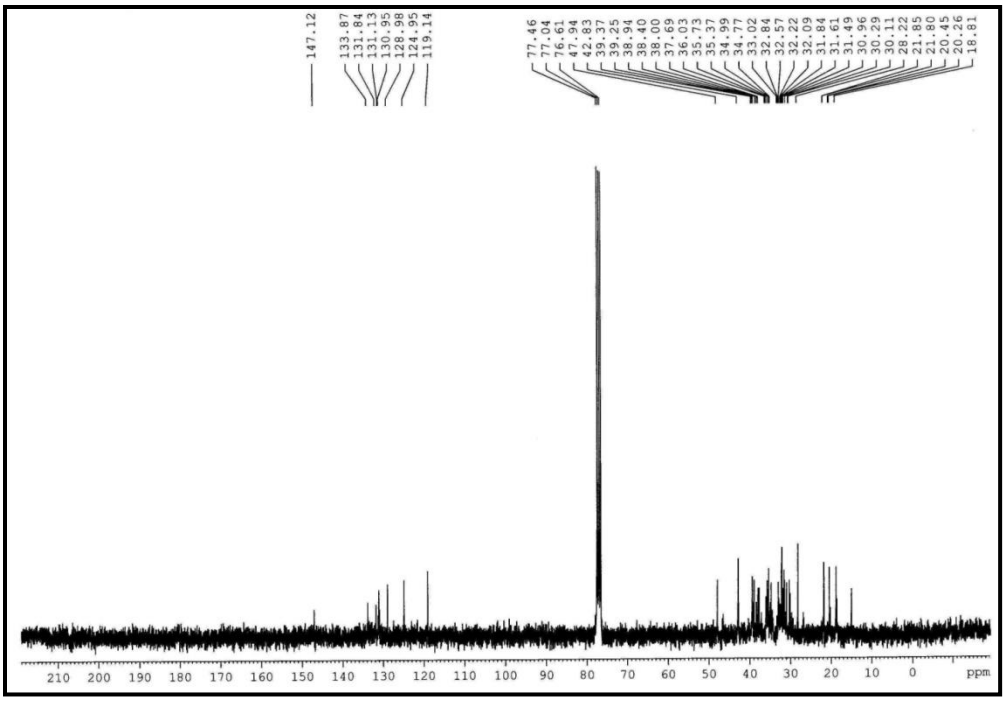

Figure S81. ^{13}C NMR spectrum (partially expanded) of 24-*nor*friedel-1,3,5(10),6-tetraene (**33**).

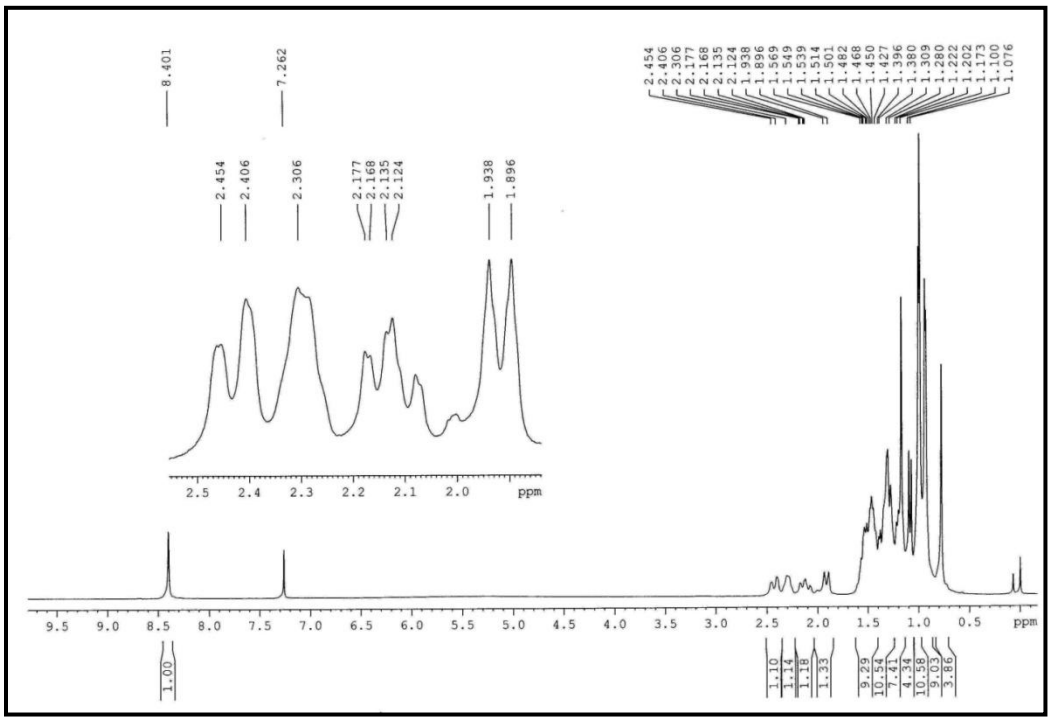

Figure S82. ^{1}H NMR spectrum of 3-chlorofriedel-2-ene-2-carboxaldoxime (**34**).

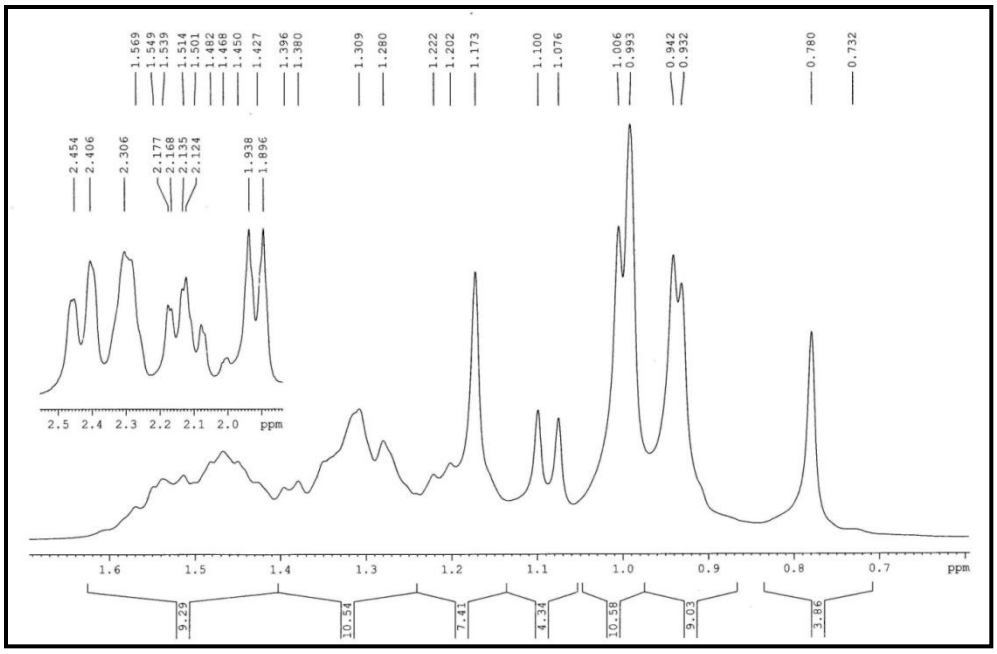

Figure S83. ^{1}H NMR spectrum (partially expanded) of 3-chlorofriedel-2-ene-2-carboxaldoxime (**34**).

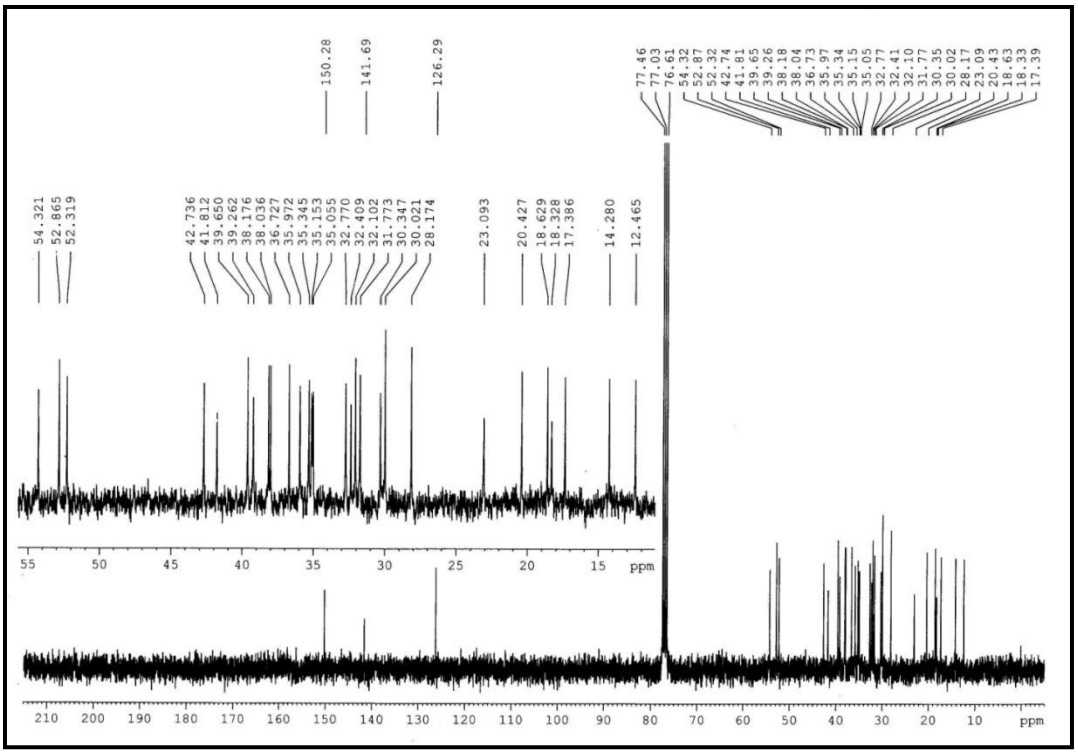

Figure S84. ^{13}C NMR spectrum of 3-chlorofriedel-2-ene-2-carboxaldoxime (**34**).

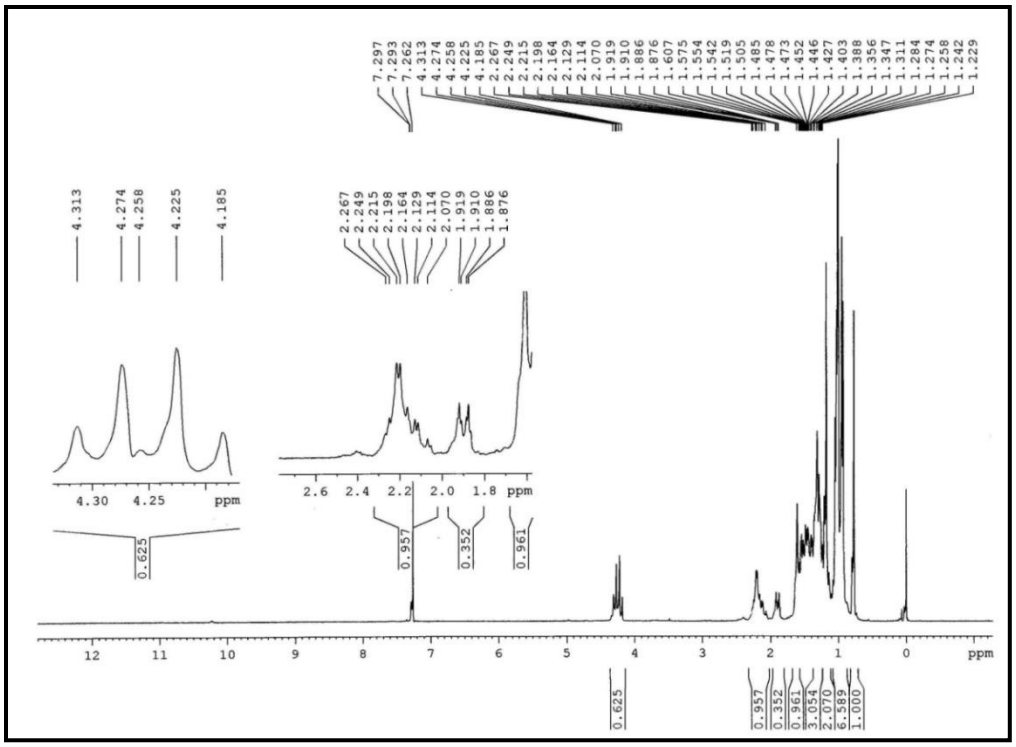

Figure S85. ^{1}H NMR spectrum of 3-chlorofriedel-2-ene-2-methanol (**35**).

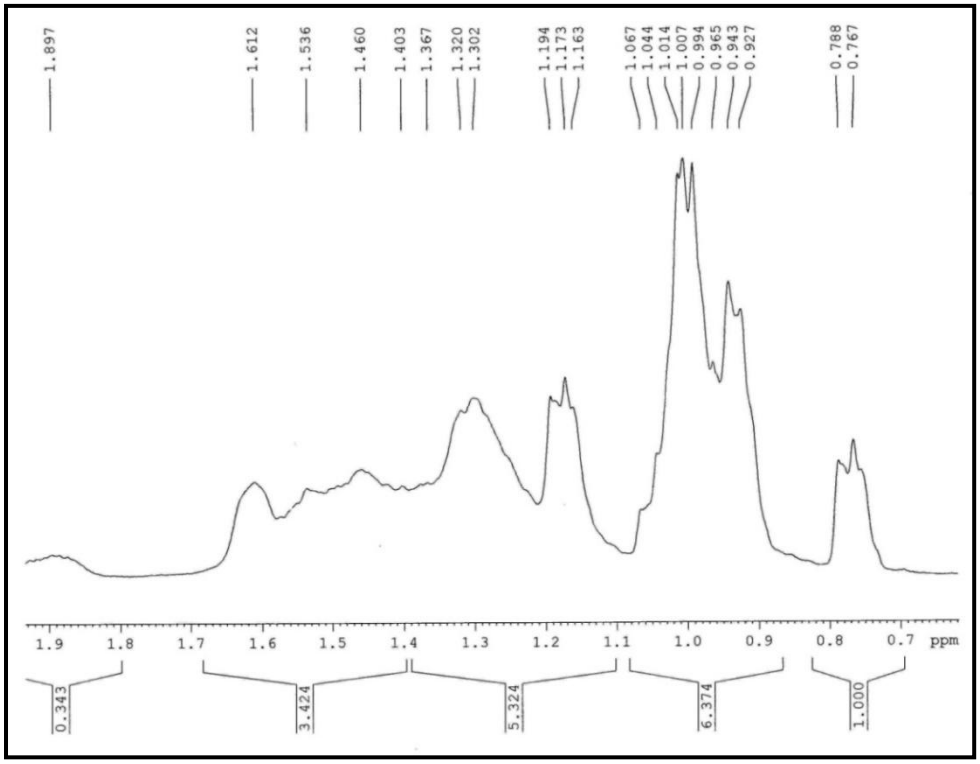

Figure S86. ^{1}H NMR spectrum (partially expanded) of 3-chlorofriedel-2-ene-2-methanol (**35**).

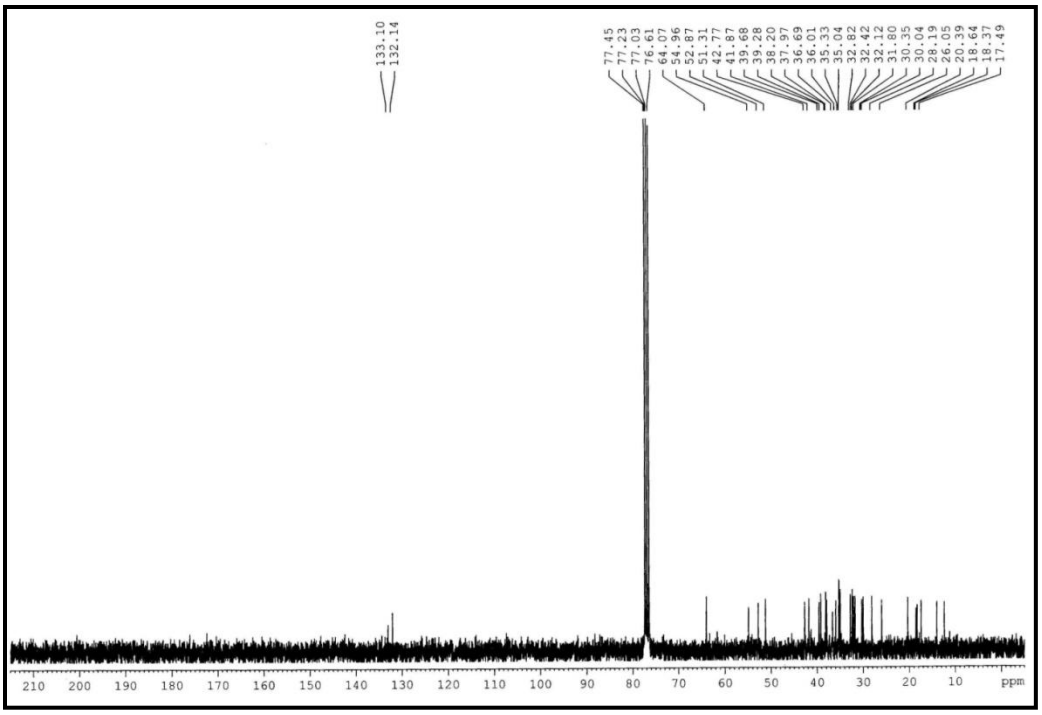

Figure S87. ^{13}C NMR spectrum of 3-chlorofriedel-2-ene-2-methanol (**35**).

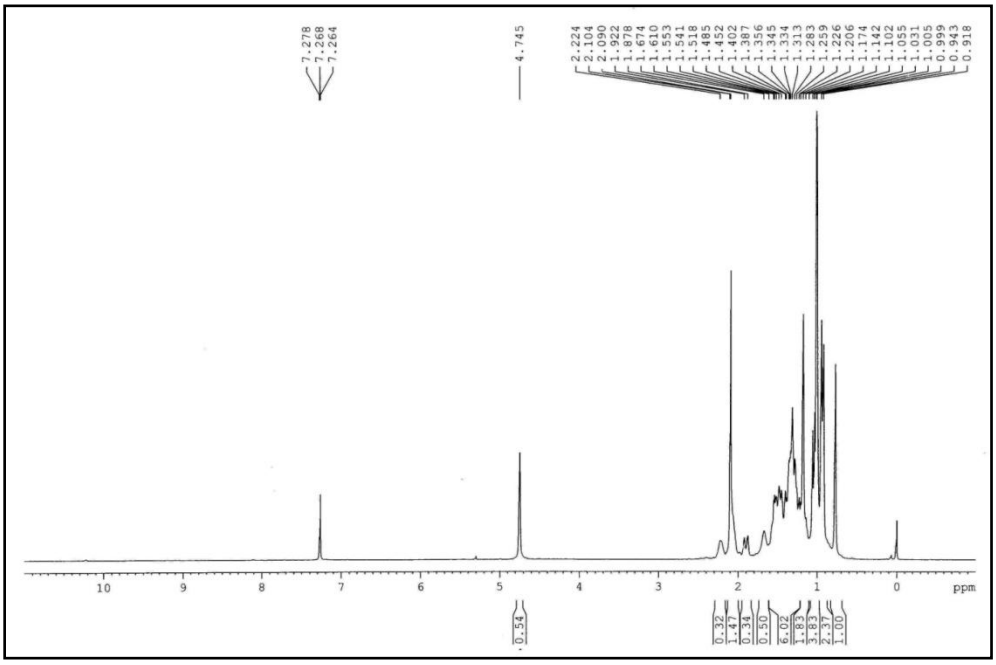

Figure S88. ^{1}H NMR spectrum of 3-chlorofriedel-2-ene-2-methanol acetate (**36**).

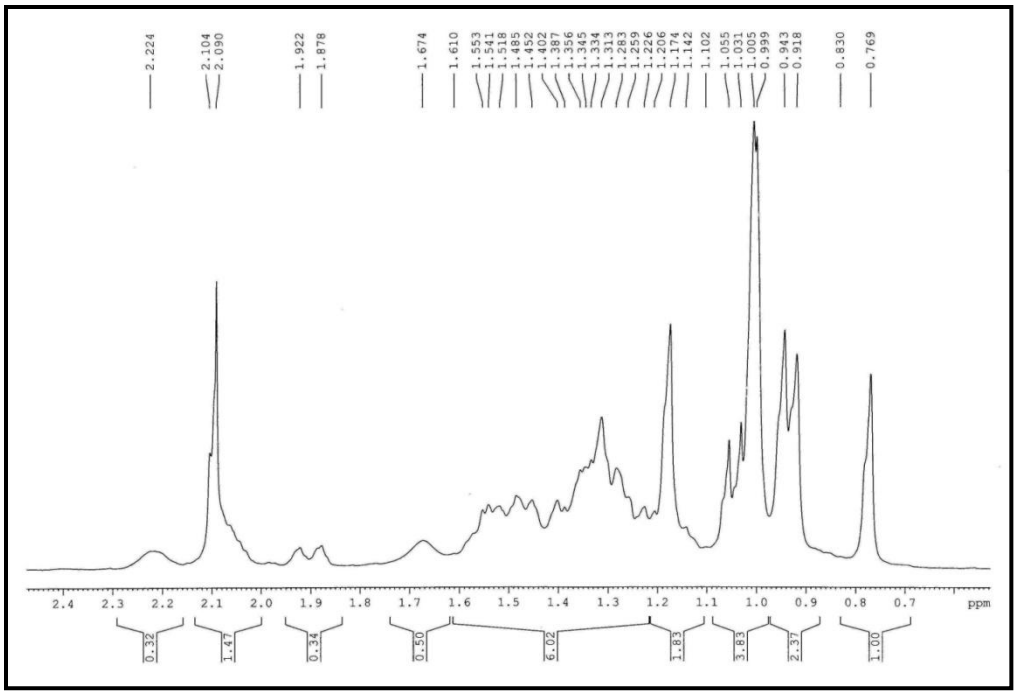

Figure S89. ^{1}H NMR spectrum (with partial expansion) of 3-chlorofriedel-2-ene-2-methanol acetate (**36**).

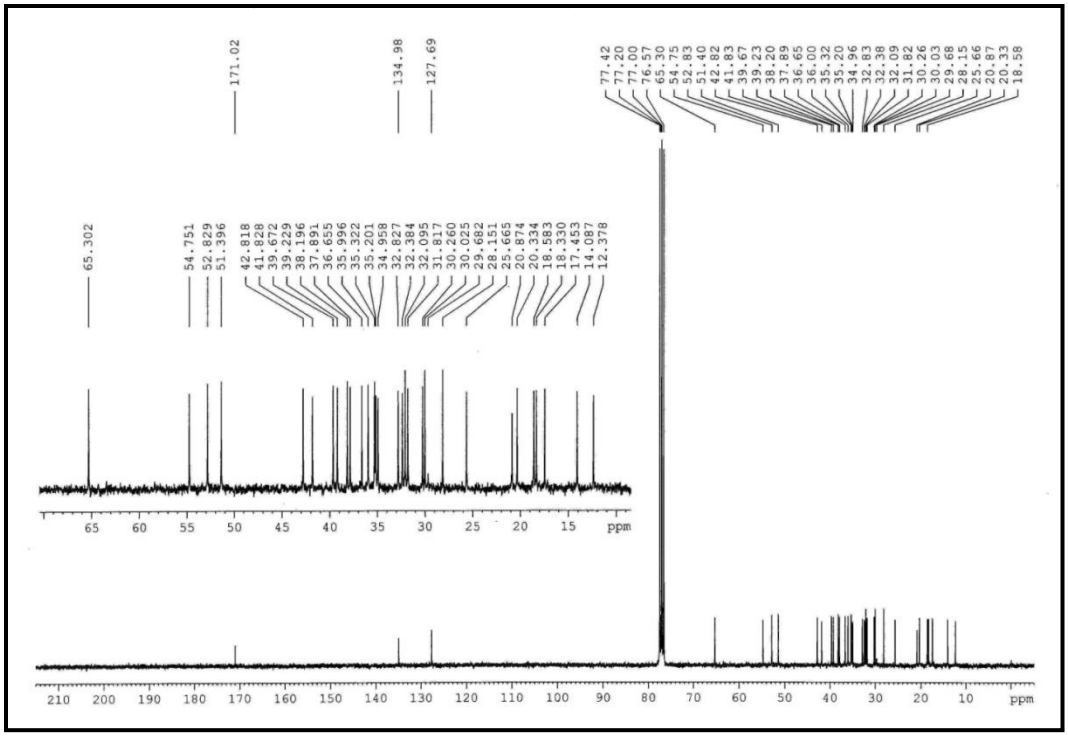

Figure S90. ^{13}C NMR spectrum of 3-chlorofriedel-2-ene-2-methanol acetate (**36**).

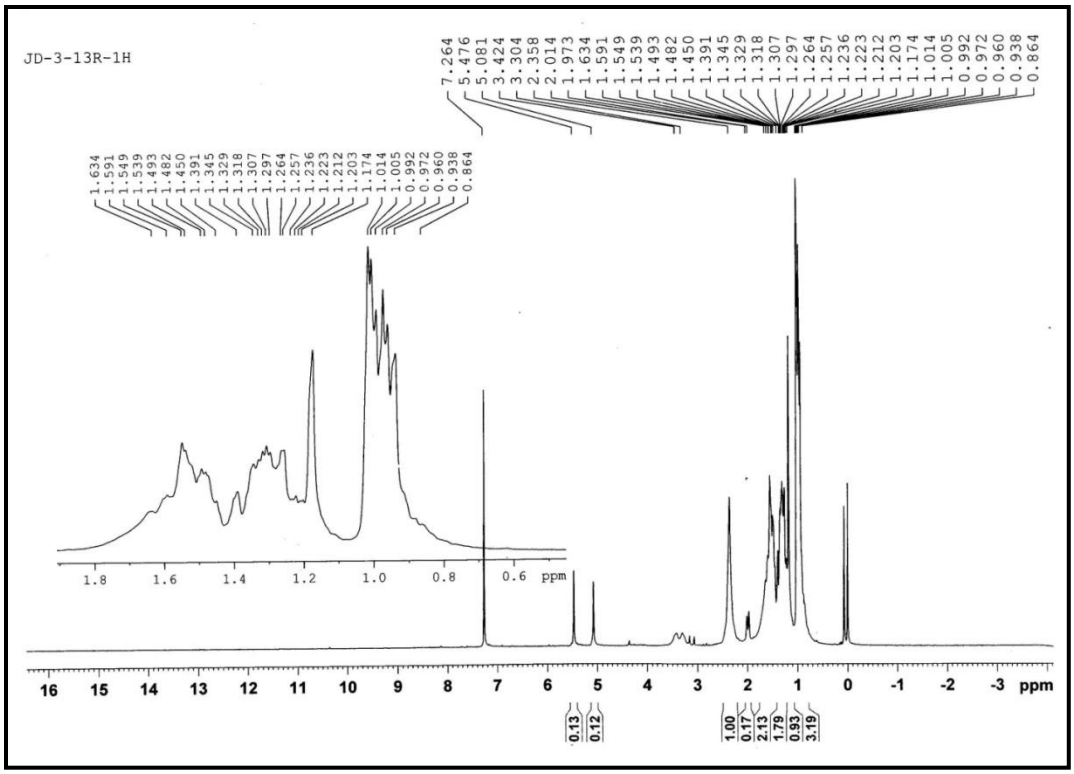

Figure S91. [1]H NMR spectrum of 3-chlorofriedel-2-ene-2-carboxamide (**37**).

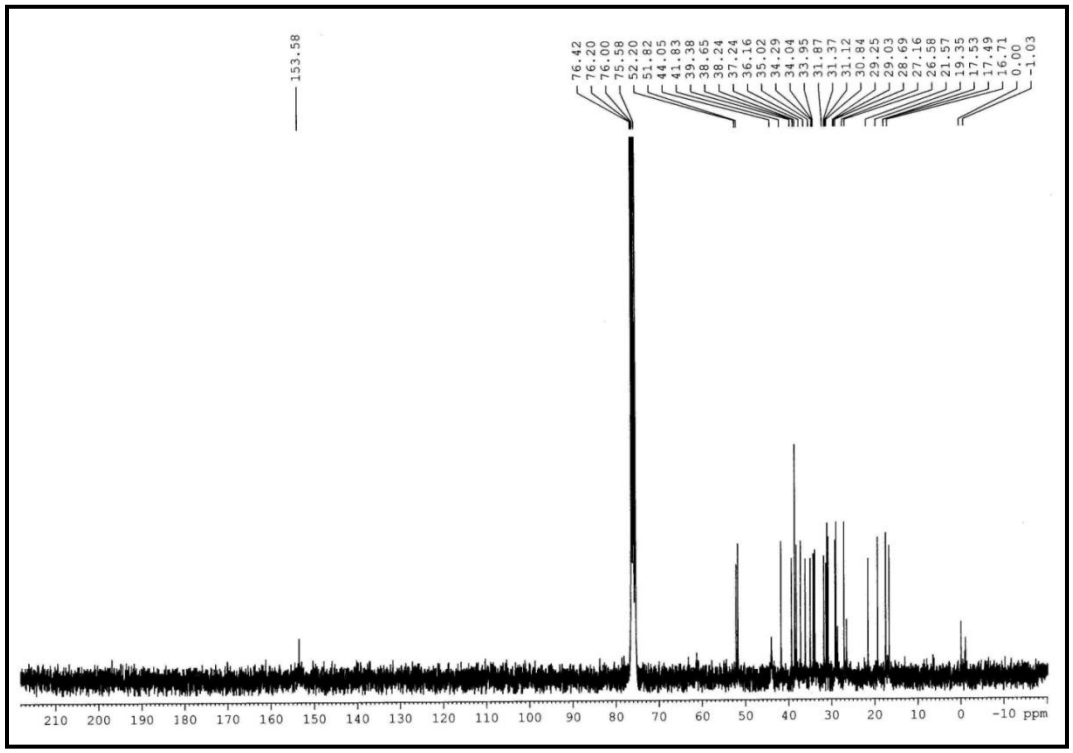

Figure S92. [13]C NMR spectrum of 3-chlorofriedel-2-ene-2-carboxamide (**37**).

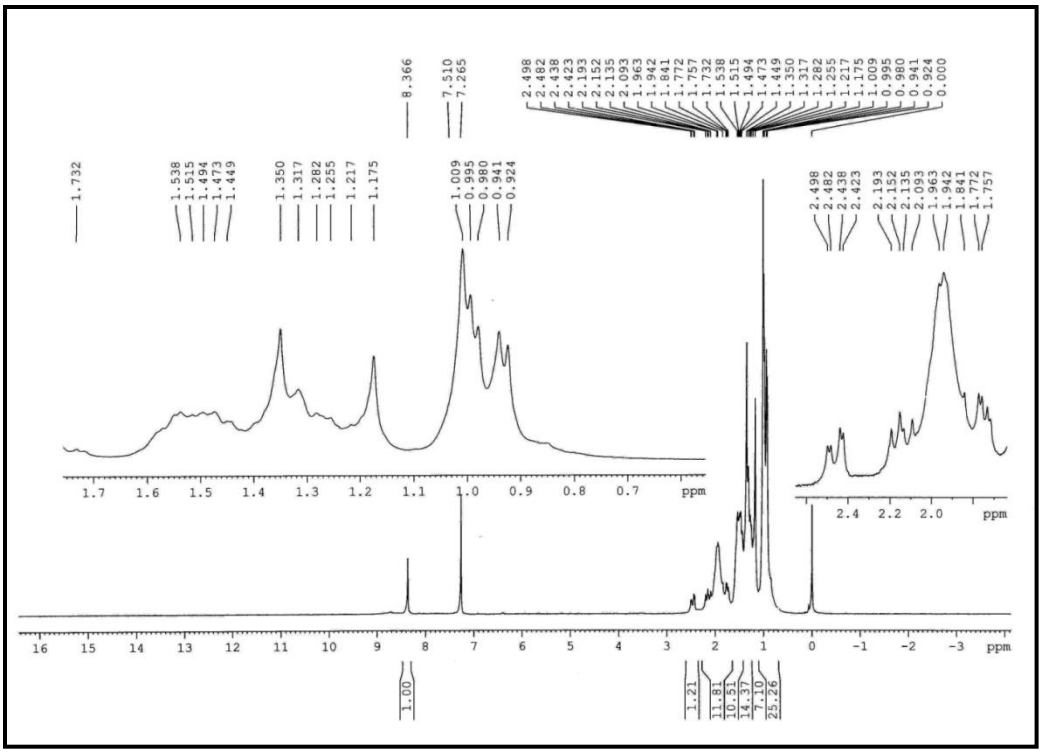

Figure S93. ^{1}H NMR spectrum of 3-chloro-4α-hydroxy-2-ene-2-carboxaldoxime (**37**).

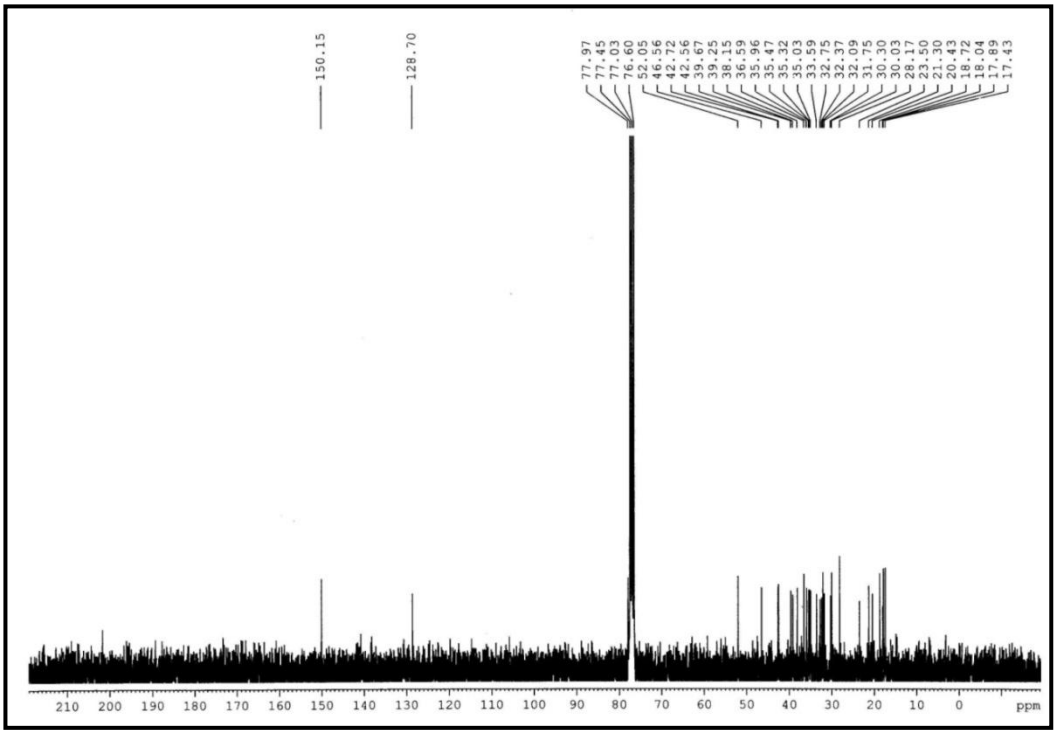

Figure S94. ^{13}C NMR spectrum of 3-chloro-4α-hydroxy-2-ene-2-carboxaldoxime (**37**).

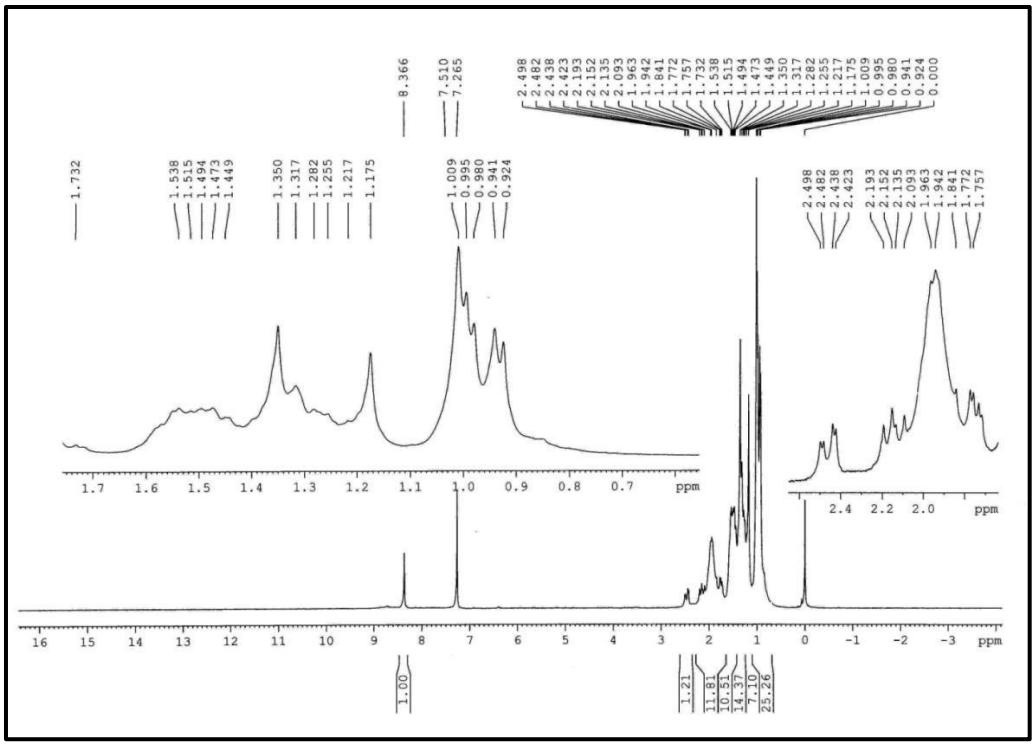

Figure S95. ^{1}H NMR spectrum of 3-chloro-4α-hydroxy-2-ene-2-carboxaldoxime (**38**).

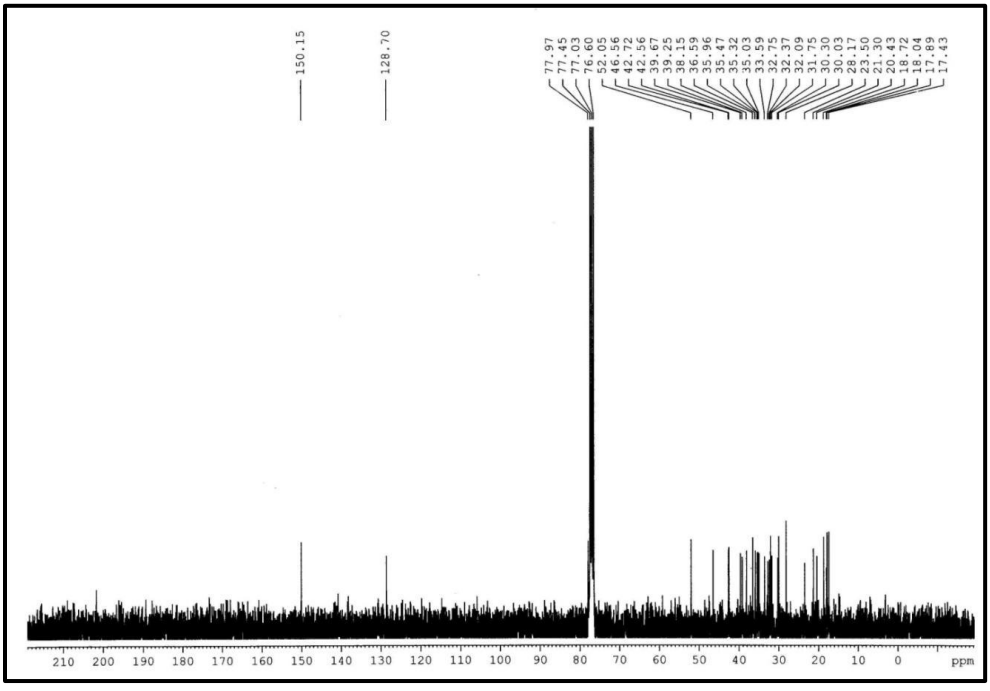

Figure S96. ^{13}C NMR spectrum of 3-chloro-4α–hydroxy-2-ene-2-carboxaldoxime (**38**).

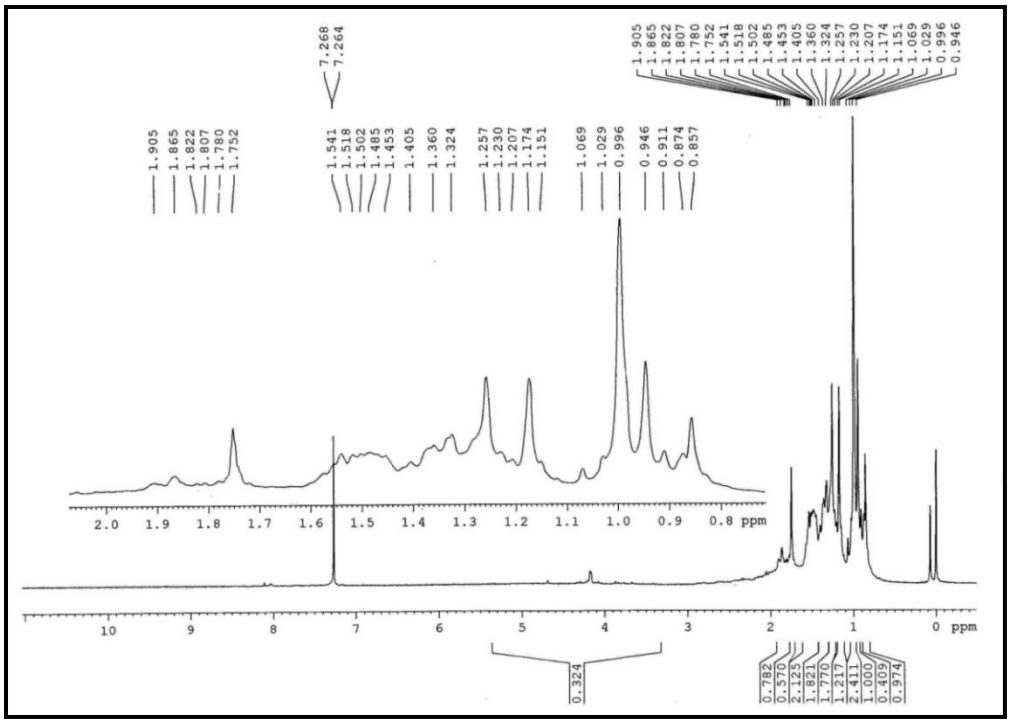

Figure S97. ^{1}H NMR spectrum of 3-chlorofriedel-2-en-4α-ol-2-methanol (**39**).

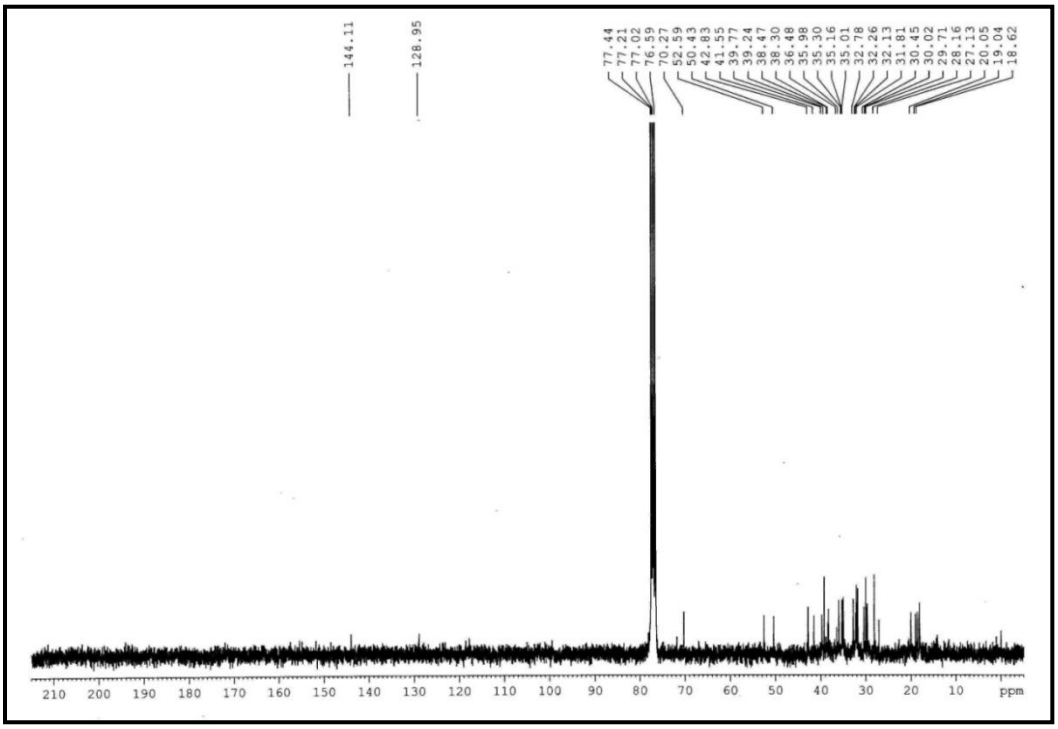

Figure S98. ^{13}C NMR spectrum of 3-chlorofriedel-2-en-4α-ol-2-methanol (**39**).

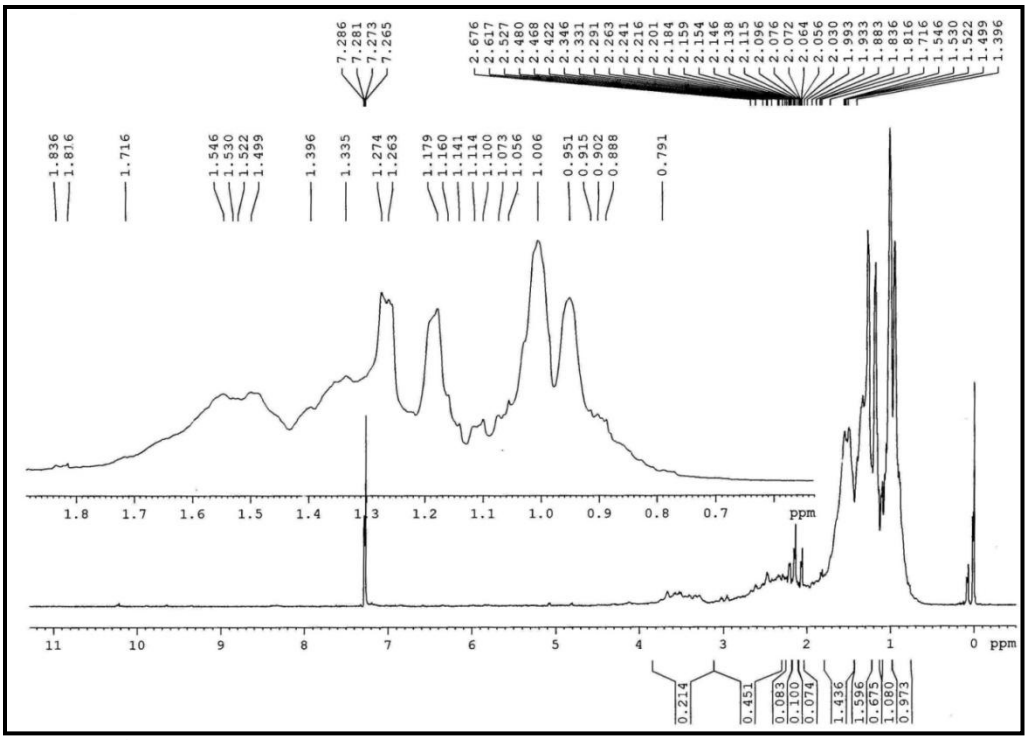

Figure S99. [1]H NMR spectrum of 2-formyl-3-(1*H*-piperidin-1-yl)-friedel-2-ene (**40**).

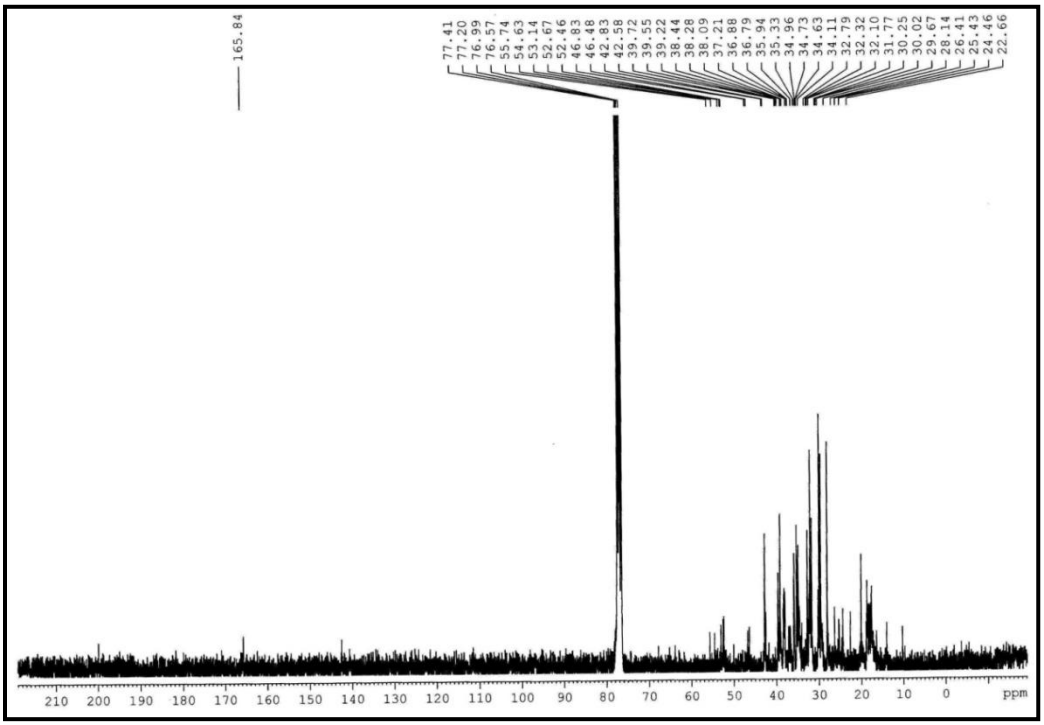

Figure S100. [13]C NMR spectrum of 2-formyl-3-(1*H*-piperidin-1-yl)-friedel-2-ene (**40**).

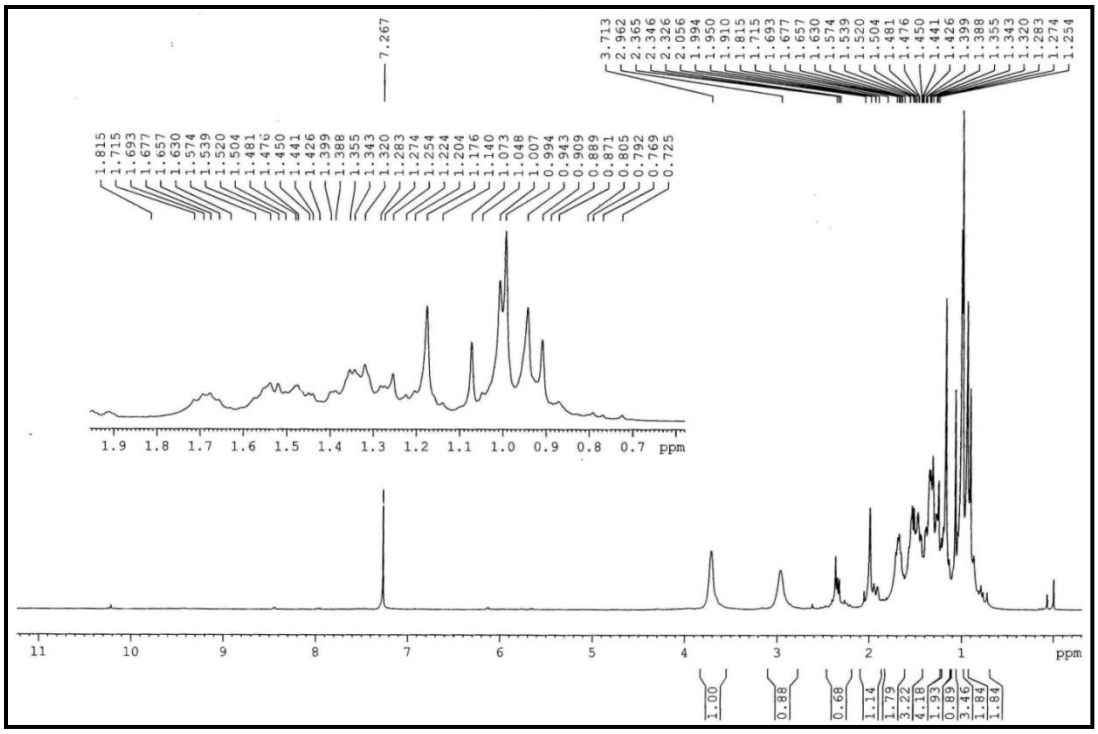

Figure S101. [1]H NMR spectrum of 2-formyl-3-(1*H*-morpholin-4-yl)-friedel-2-ene (**41**).

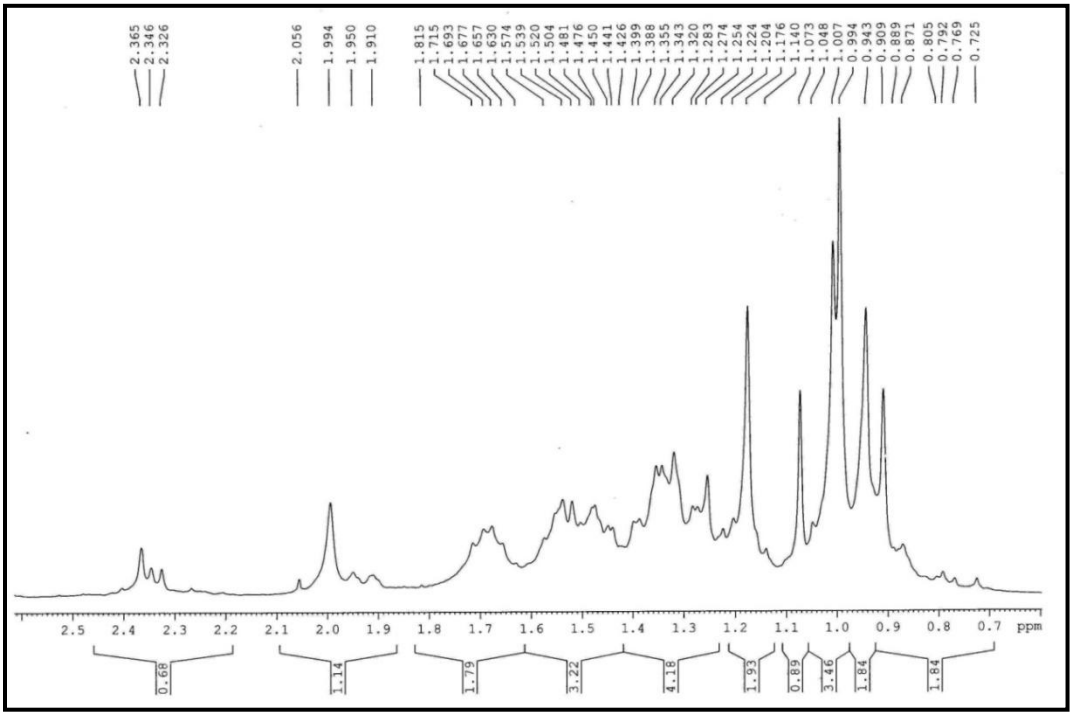

Figure S102.[1]H NMR spectrum (partially expanded) of 2-formyl-3-(1*H*-morpholin-4-yl)-friedel-2-ene (**41**).

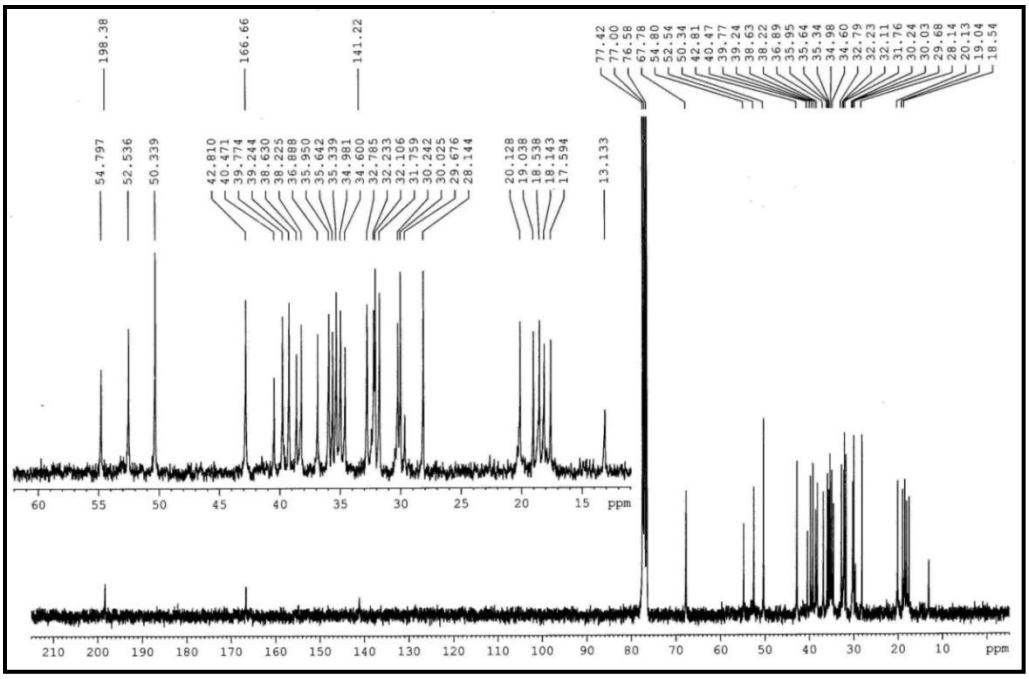

Figure S103. ^{13}C NMR spectrum of 2-formyl-3-(1*H*-morpholin-4-yl)-friedel-2-ene (**41**).

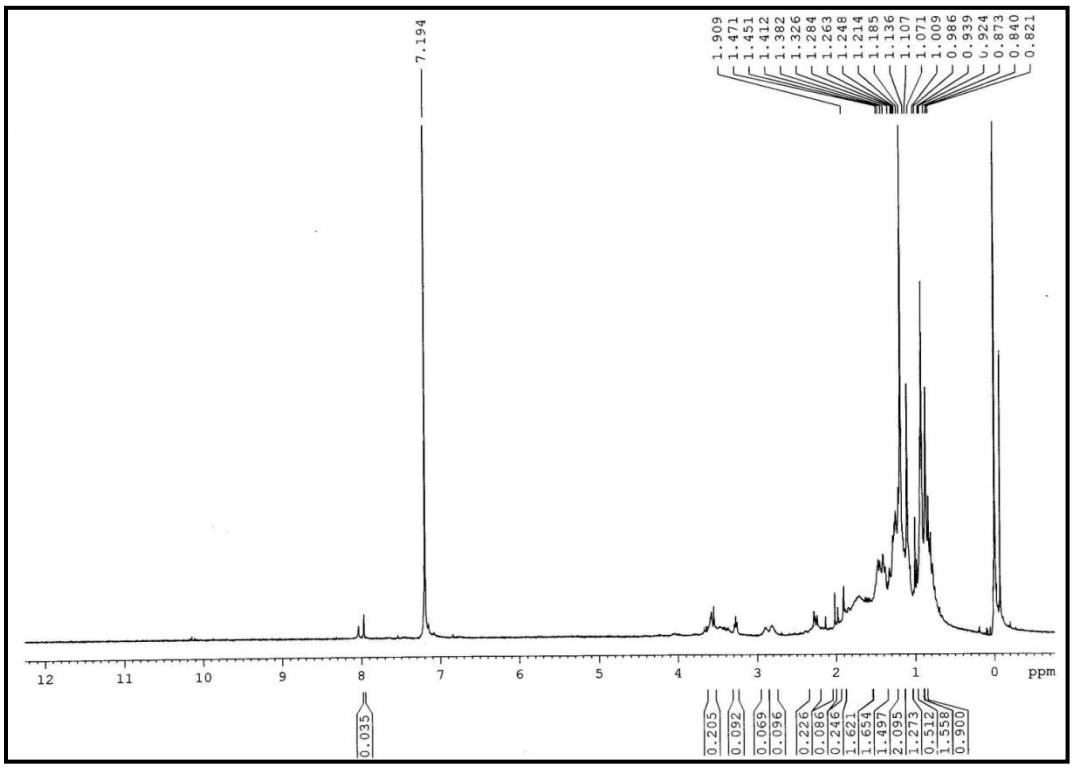

Figure S104. ^{1}H NMR spectrum of 2-formyl-3-(1*H*-piperazin-1-yl)-friedel-2-ene (**42**).

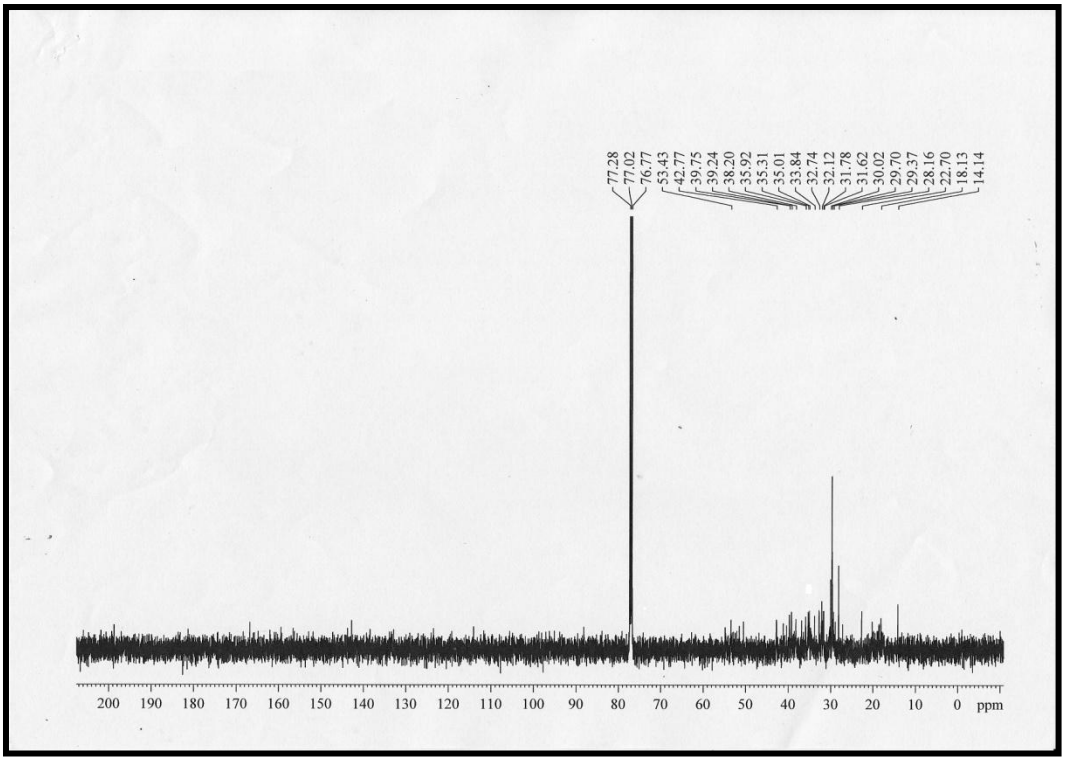

Figure S105. ^{13}C NMR spectrum of 2-formyl-3-(1*H*-piperazin-1-yl)-friedel-2-ene (**42**).

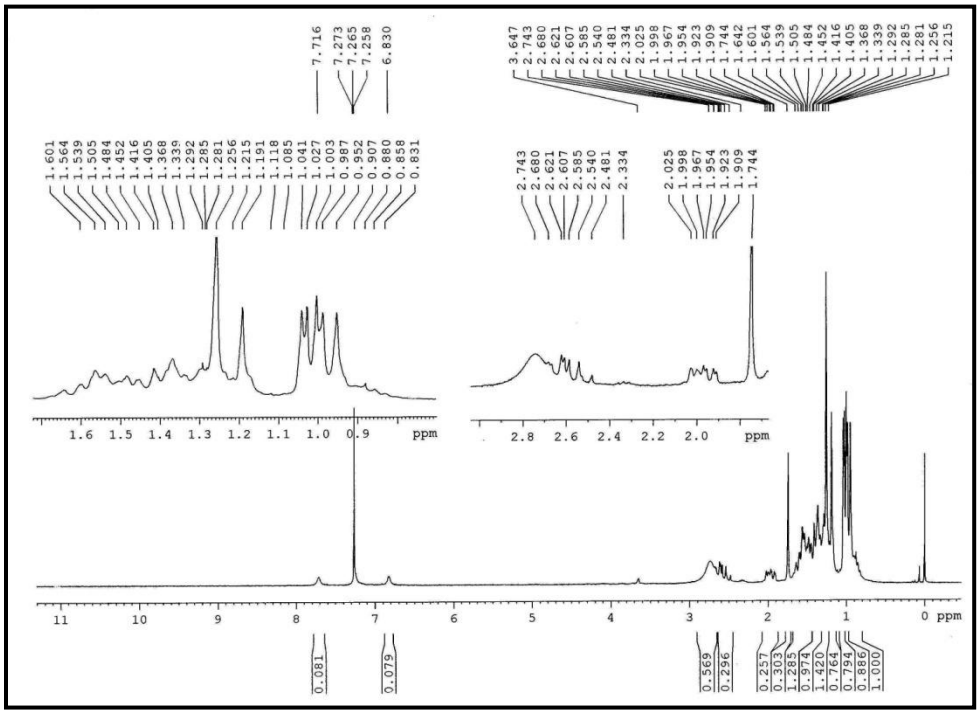

Figure S106. ^{1}H NMR spectrum of 2-formyl-3-(1*H*-imidazol-1-yl)-friedel-2-ene (**43**).

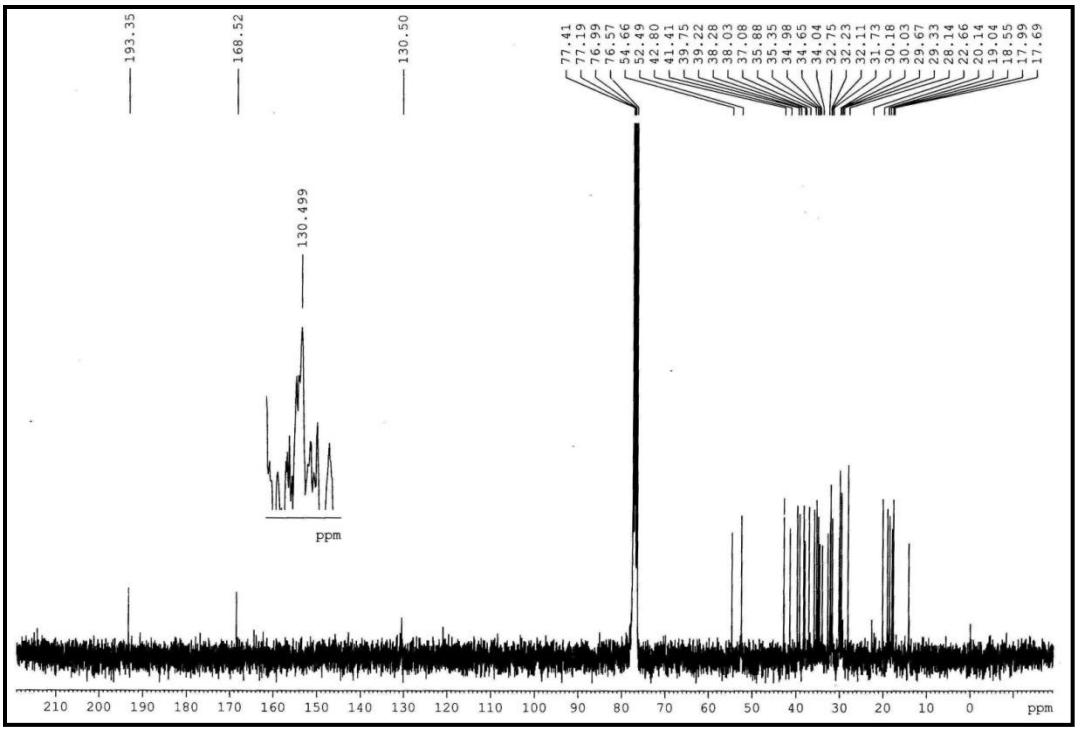

Figure S107. ^{13}C NMR spectrum of 2-formyl-3-(1*H*-imidazol-1-yl)-friedel-2-ene (**43**).

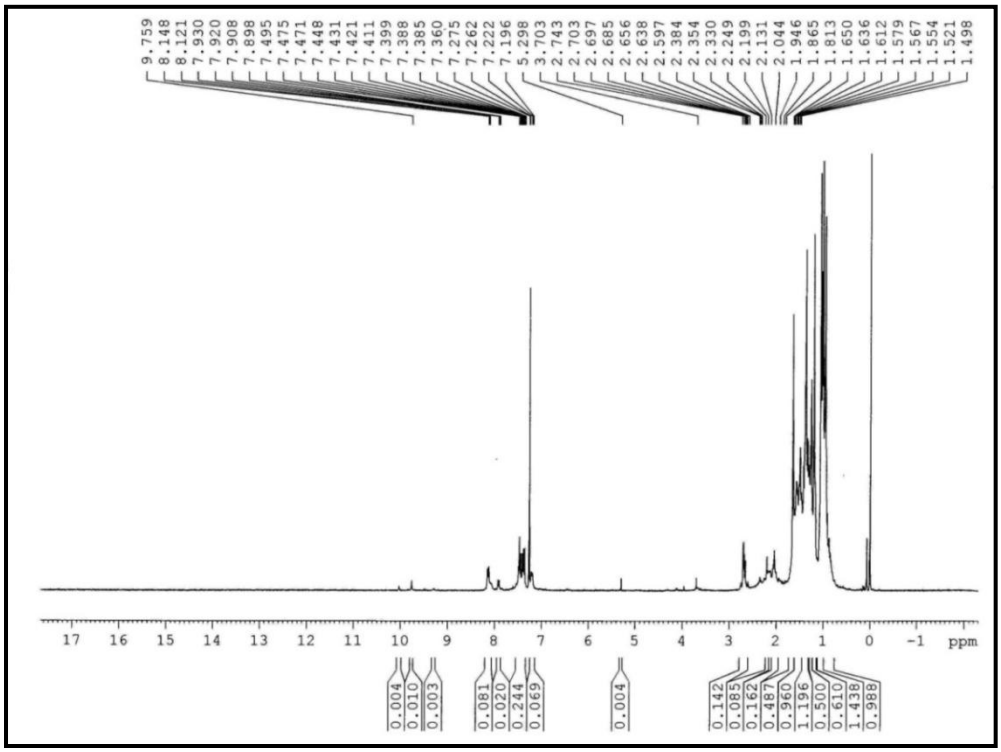

Figure S108. ^{1}H NMR spectrum of 2-formyl-3-(1*H*-benzimidazol-1-yl)-friedel-2-ene (**44**).

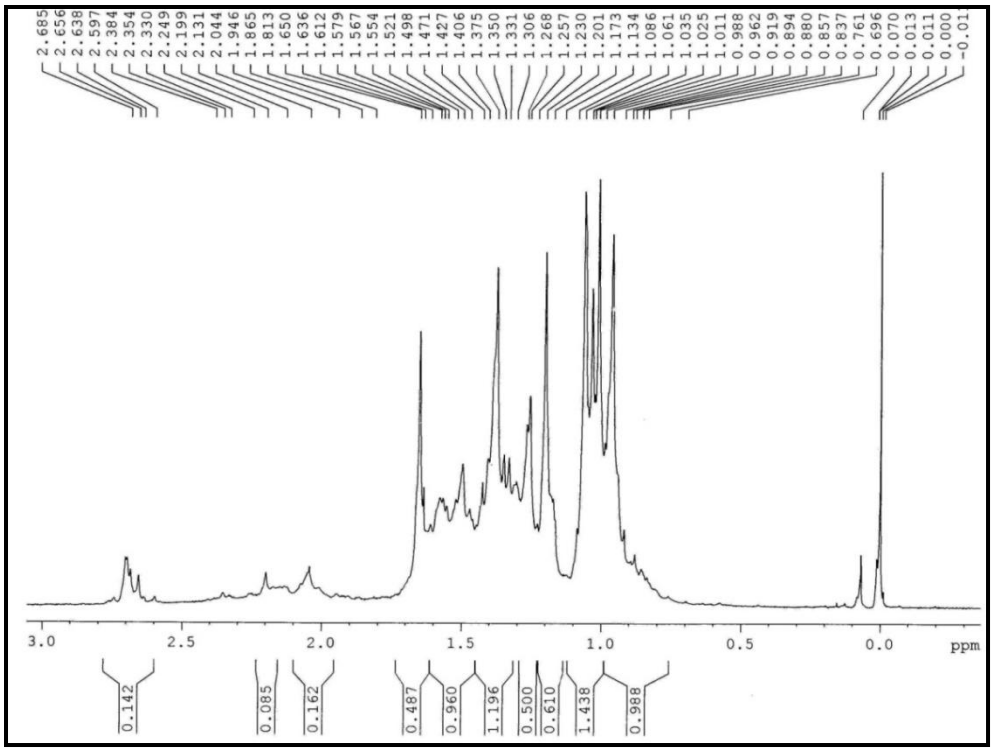

Figure S109. ^{1}H NMR spectrum (with partial expansion) of 2-formyl-3-(1*H*-benzimidazol-1-yl)-friedel-2-ene (**44**).

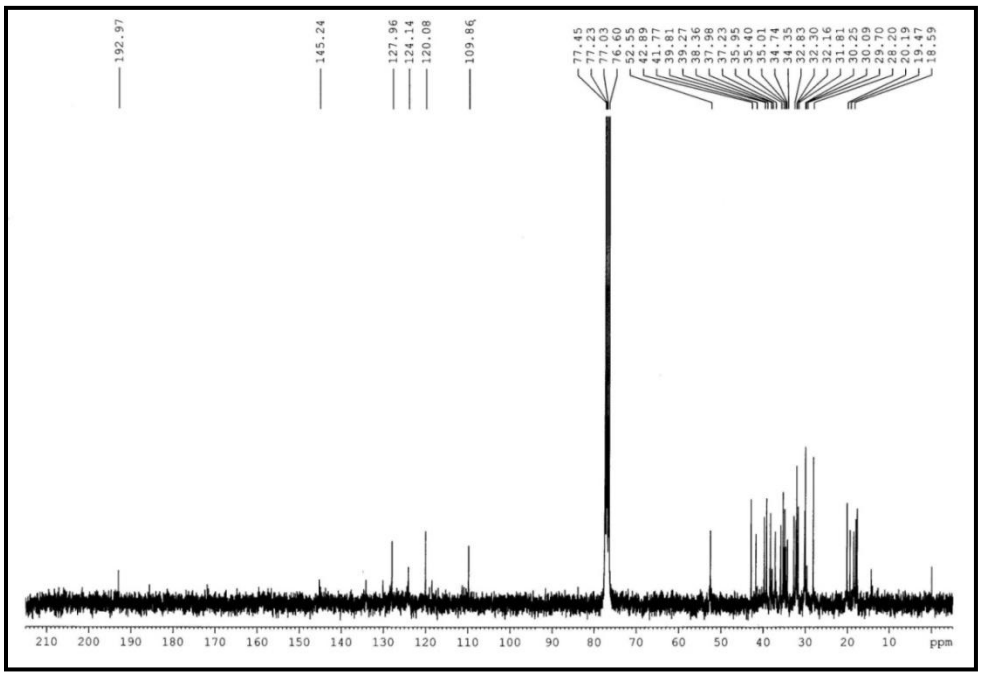

Figure S110. ^{13}C NMR spectrum of 2-formyl-3-(1*H*-benzimidazol-1-yl)-friedel-2-ene (**44**).

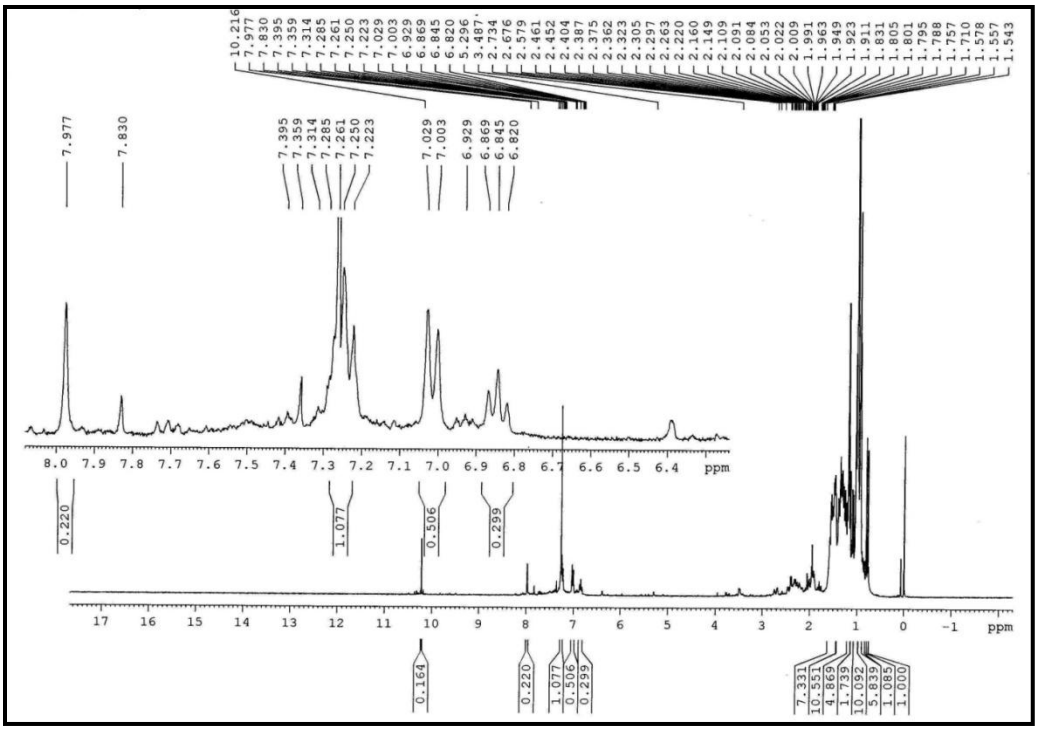

Figure S111. [1]H NMR spectrum of 2-formyl-3-(1*H*-1, 2, 3-benzotriazol-1-yl)-friedel-2-ene (**45**).

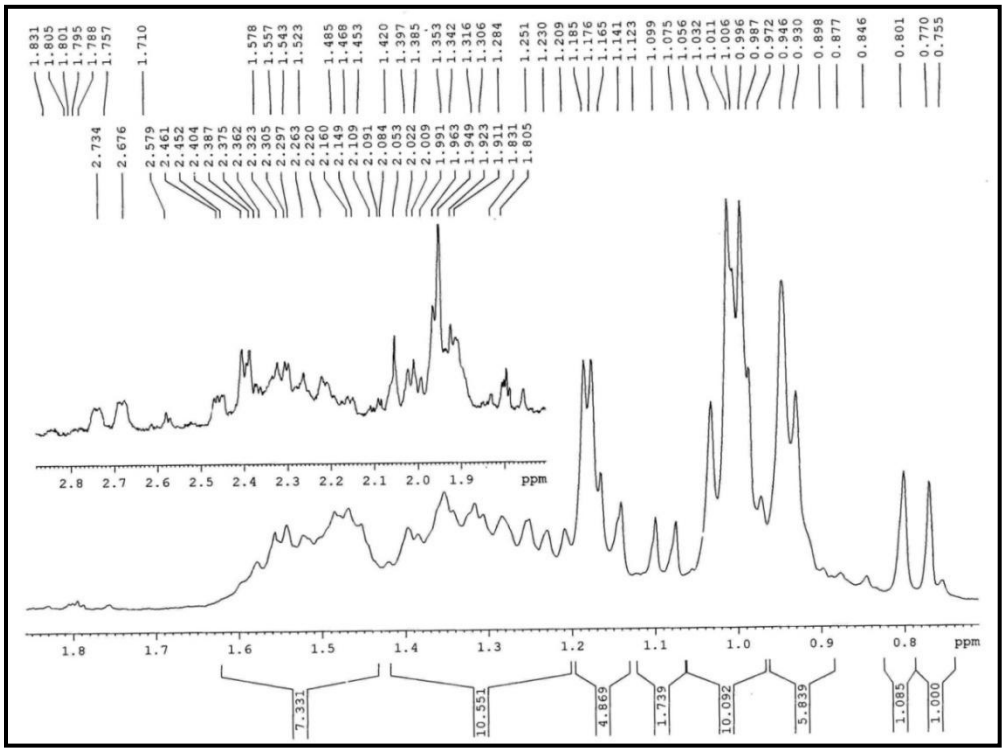

Figure S112. [1]H NMR spectrum (partially expanded) of 2-formyl-3-(1*H*-1, 2, 3-benzotriazol-1-yl)-friedel-2-ene (**45**).

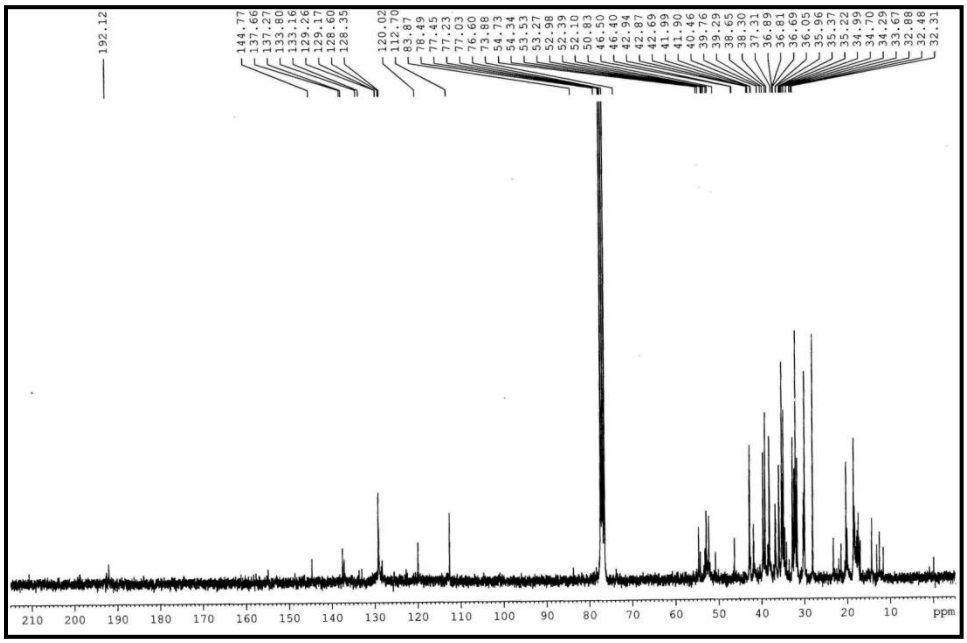

Figure S113. ^{13}C NMR spectrum of 2-formyl-3-(1*H*-1, 2, 3-benzotriazol-1-yl)-friedel-2-ene (**45**).

ES3. References:

1. (a)Y. Masuyama, Y. Kobayashi, Y. Kurusu, *J. Chem. Soc. Chem. Commun*. **1994**, 1123; (b) M. Yanagisawa, T. Shimamura, D. Iida, J-I. Matsuo, T. Mukaiyama, *Chem. Pharm. Bull.* **2000**, *48*, 1838-1840.
2. C. Paloma, M. Oiarbide, A. González, J. M. García, F. Berrée, A. Linden, *Tetrahedron Lett.***1996**, *37*, 6931-6934.
3. a) J. J. Song, J. Xu, Z. Tan, J. T. Reeves, N. Grinberg, H. Lee, K. Kuzmich, X. Feng, N. K. Yee, C. H. Senanayake, *Org. Process Res. Dev.***2007**, *11*, 534-538; b) D. Cahard, P. Duhamel, *Eur. J. Org. Chem.***2001**, 1023-1031.
4. Y. Nishimoto, Y. Onishi, M. Yasuda, A. Baba, *Angew. Chem. Int. Ed*. **2009**, *48*, 9131-9134.

5. Y. Onishi, Y. Yoneda, Y. Nishimoto, M. Yasuda, A. Baba, *Org. Lett*. **2012**, *14*, 5788-5791.
6. C. Palomo, M. Oiarbide, A. Landa, M. C. Gonza´lez-Rego, J. M. Garcı´a, A. Gonza´ lez, J. M. Odriozola, M. Martı´n-Pastor, A. Linden,*J. Am.Chem. Soc*, **2002**, *124*, 8637-8643.
7. (a) W. Tang, D. Liu, X. Zhang, *Org. Lett.* **2003**, *5*, 205-207; (b) S. Wu, W. Wang, W. Tang, M. Lin, X. Zhang, *Org. Lett.* **2002**, *4*, 4495-4497.
8. M. P. Hartshorn, E. R. H. Jones, *J. Chem. Soc.***1962**, 1312-1323; (b) M. P. Hartshorn, *J. Chem. Soc.***1962**, 3168-3172.
9. (a) H. M. Jung, J. H. Koh, M-J. Kim, J. Park, *Org. Lett.***2000**, *2*, 409-411; (b) H. M. Jung, J. H. Koh, M-J. Kim, J. Park, *Org. Lett.***2000**, *2*, 2487-2490; c) M. Feñanãs-Mastral, B. L. Feringa, *J. Am.Chem. Soc*. **2010**, *132*, 13152-13153.
10. J. R. Hwu, S-C. Tsay, L. C. Lin, L. L. Chueh, *J. Am. Chem. Soc.* **2001**, *123*, 5104-5105.
11. M-H. Lin, T. V. Rajanbabu, *Org. Lett.* **2000**, *2*, 997-1000.
12. E. H. Jones, D. A. Wilson, **1965**, *J. Chem. Soc*. 2933-2944.
13. R. Umeda, Y. Takahashi, Y. Nishiyama, *Tetrahedron Lett.***2014**, *50*, 6113-6116.
14. I. Geibel, J. Christoffers, *Eur. J. Org. Chem.***2016**, 918-920.
15. I. Geibel, A. Dierks, M. Schmidtmann, J. Christoffers, *J. Org. Chem*. **2016**, *81*, 7790-7798.
16. a) V. K. Yadav, V. P. Srivastava, L. Dhar, S. Yadav, *Synlett***2016**, *27*, 427–431; b) V. K. Yadav, V. P. Srivastava, L. Dhar, S. Yadav, *Tetrahedron Lett*. 2016, *57*, 2236–2238.
17. L. Panella, B. L. Feringa, J. G. de Vries, A. J. Minnaard, *Org. Lett*. **2005**, *7*, 4177-4180.
18. a) M. Feñanãs-Mastral, B. L. Feringa, *J. Am. Chem. Soc.* **2010**, *132*, 13152-13153; b) Y. Tang, Y. Fan, Y. Zhang, X. Li, X. Xu, *Synlett***2016**, *27*, 1860–1863.
19. Y. Onishi, Y. Nishimoto, M.Yasuda, A. Baba, *Org. Lett.***2011**, *13*, 2762-2765.
20. T. Hering, D. P. Hari, B. König, *J. Org. Chem*. **2012**, *77*, 10347-10352.
21. J. P. Burkhart, J. R. Koehl, S. Mehdi, S. L. Durham, M. J. Janusz, E. W. Huber, M. R. Angelastro, S. Sunder, W. A. Metz, P. W. Shum, T-M. Chen, P. Bey, C. R. Cregge, N. P. Peet, *J. Med. Chem*. **1995**, *38*, 223-233.