Electronic Supplementary Information (ESI)

Novel carbocyclic scaffolds with a 6,5+5,5 ring system, named nor-allodammarane, from the enzymatic reactions of 27-nor-(oxido)squalenes with hopene synthase

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Contents

1. Enzymatic reaction of racemic mixture of (3*R*, *S*)-27-nor-2,3-oxidosqualenes (27-norOXSQ, 18 and 19) with the native SHC.

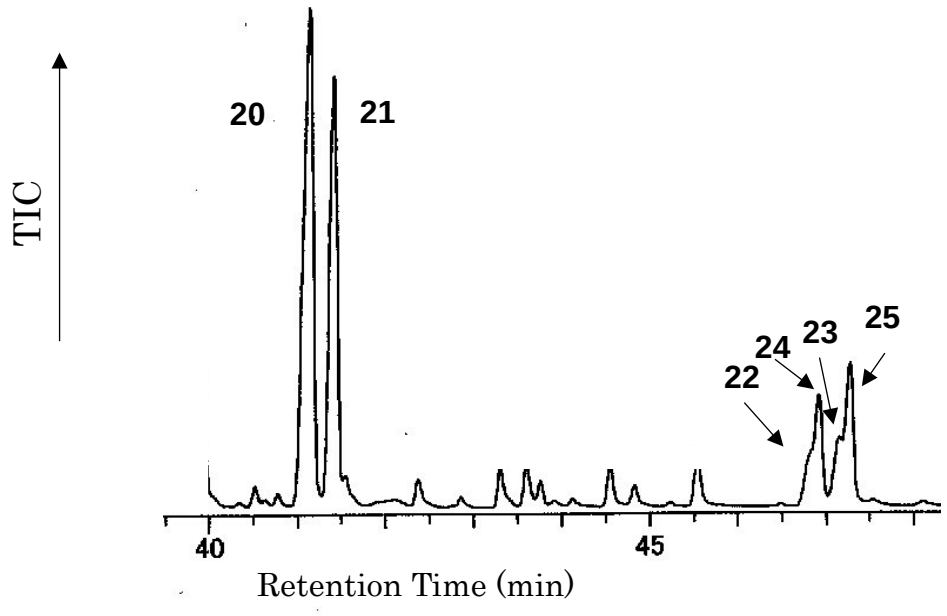
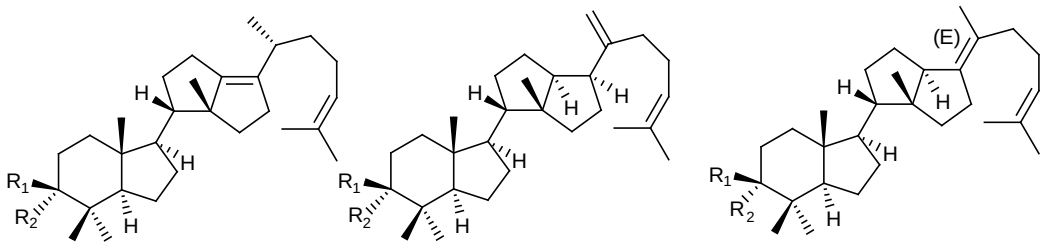


Fig. S1.1. GCMS profile (TIC) of Products 20─25 from 18 and 19

GC-TOFF MS conditions: Inject temp : 280°C; Column temp: 150-280°C (3°C /min); Flow : 1.0 mL/min

Product structures are shown below.

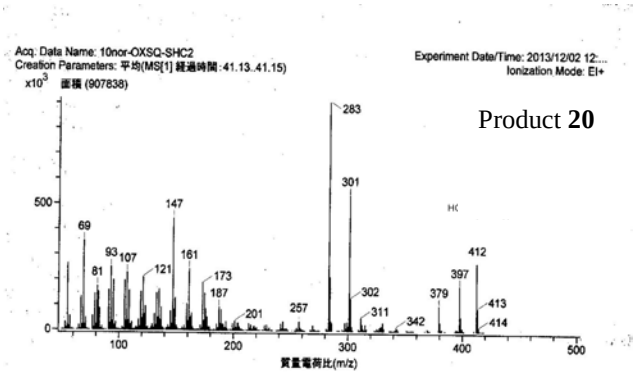


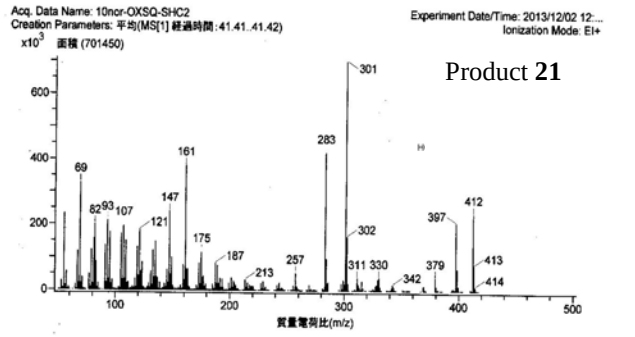
20: R_1=H, R_2=OH (38.2%)
21: R_1=OH, R_2=H (33.1%)

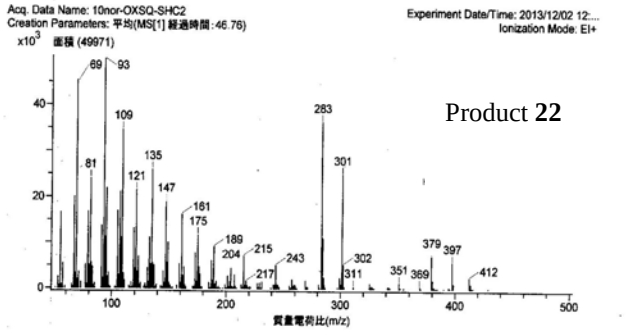
22: R_1=H, R_2=OH (4.1%)
23: R_1=OH, R_2=H (5.2%)

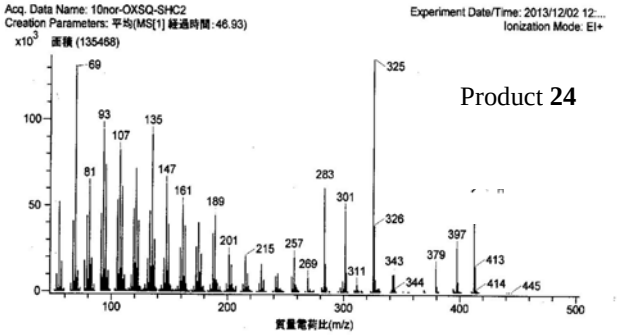
24: R_1=H, R_2=OH (8.6%)
25: R_1=OH, R_2=H (10.8%)

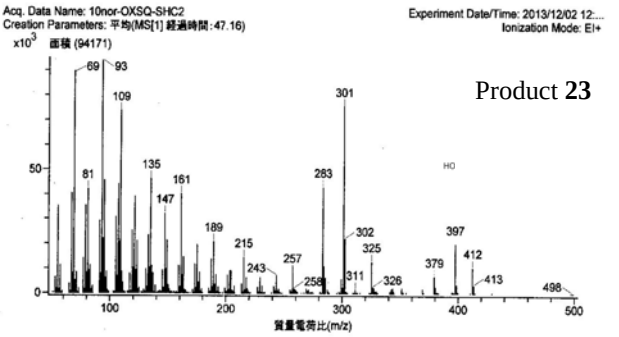
Compound names are as follows: **20**,3α-hydroxy-(8*R*,10*S*,14*R*,20*R*)-30-nor-allodammara-13(17),24-diene; **21**, 3β-hydroxy-(8*R*,10*S*,14*R*,20*R*)-30-nor-allodammara-13(17),24-diene; **22**, 3α-hydroxy-(8*R*,10*S*,13*S*,14*S*,17*S*)-30-nor-allodammara-20(21),24-diene; **23**, 3β-hydroxy-(8*R*,10*S*, 13*S*,14*S*, 17*S*)-30-nor-allodammara-20(21),24-diene; **24**, 3α-hydroxy-(8*R*,10*S*,13*R*, 14*R*)-30-nor-allodammara-(*E*)-17(20),24-diene; and **25**, 3β-hydroxy-(8*R*,10*S*,13*R*,14*R*)-30-nor-allodammara-(*E*)-17(20),24-diene.











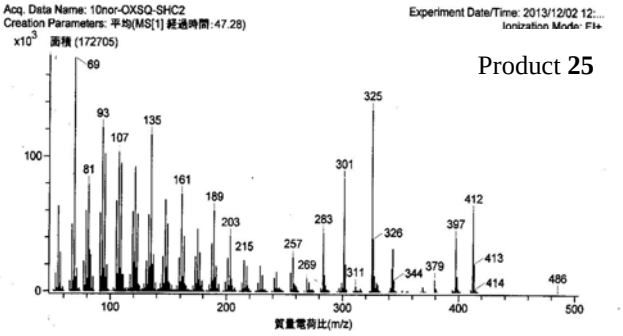


Fig. S1.2. EI-MS spectra of products **20-25**

2. Enzymatic reaction of 13a(b) with SHC.

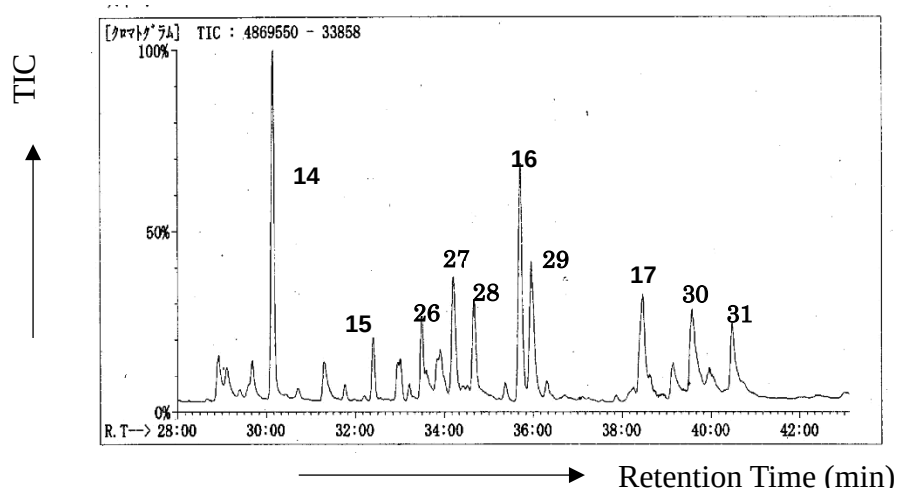
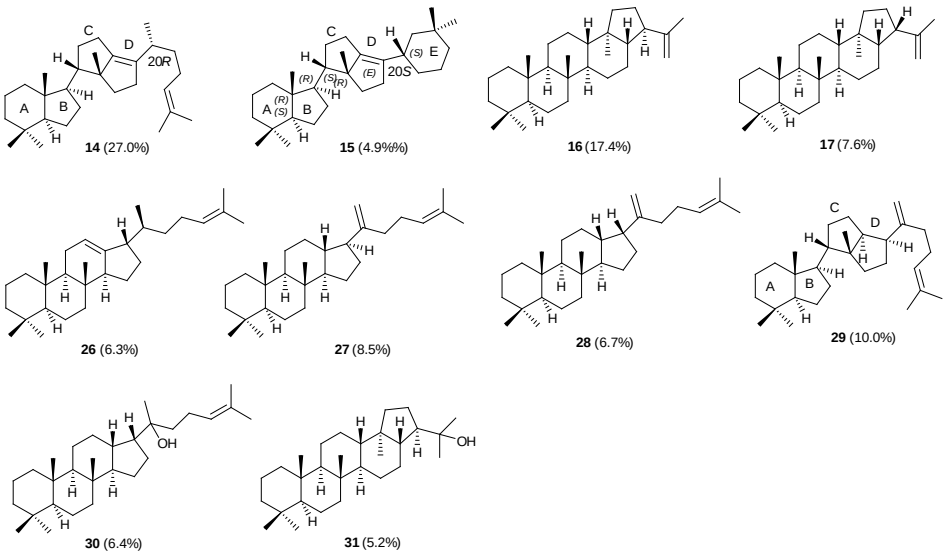


Fig. S2. GC-MS trace (TIC) of the hexane-extract of the incubation mixture of **13a(13b).**
GC-Q-MS conditions: Inject temp : 280°C; Column temp: 150-280°C (3°C /min); Flow : 1.0 mL/min.

Structures of products **14**, **15**, **16** and **17** were reported in our previous paper (T. Hoshino and S. Ohashi, *Org. Let.*, **2002**, *4*, 2553-2556). However, the stereochemistry at C-20 of **14** and **15** has remained ambiguous. In addition to **14** and **15**, many enzymatic products **26**–**31** were newly found from the incubation mixture of **13a** and **13b** with the native SHC. Notably, product **29**, which is a key intermediate for predicting the configurations at C-20 of **14** and **15**, was detected in a substantial amount. Product structures are shown below.



Compound names are as follows: **14**, (8*R*,10*S*,14*R*,20*R*)-30-nor-allodammara-13(17),24-diene; **15**, (8*R*,10*S*,14*R*,20*S*)-30-nor-allogammacer-13(17)-ene; **16**, 27-nor-isohopene (21-*epi*-hop-22(29)-ene; **17**, 27-nor-hopene; **26**, (20*S*)-30-nor-isodammara-12(13),24-diene (30-nor-17-*epi*-dammara-12(13),24-diene); **27**, 30-nor-dammara-20(21),24-diene; **28**, 30-nor-isodammara-20(21),24-diene (30-nor-17-*epi*-dammara-20(21),24-diene); **29**, (8*R*,10*S*, 13*S*, 14*S*, 17*S*)-30-nor-allodammara-20(21),24-diene; **30**, 30-nor-20-hydroxy-isodammar-24-ene (17-*epi*-20-hydroxy-dammarene); and **31**, 27-nor-isohopanol (21-*epi*-27-norhopanol).

3. NMR spectra of product 21 in $CDCl_3$.

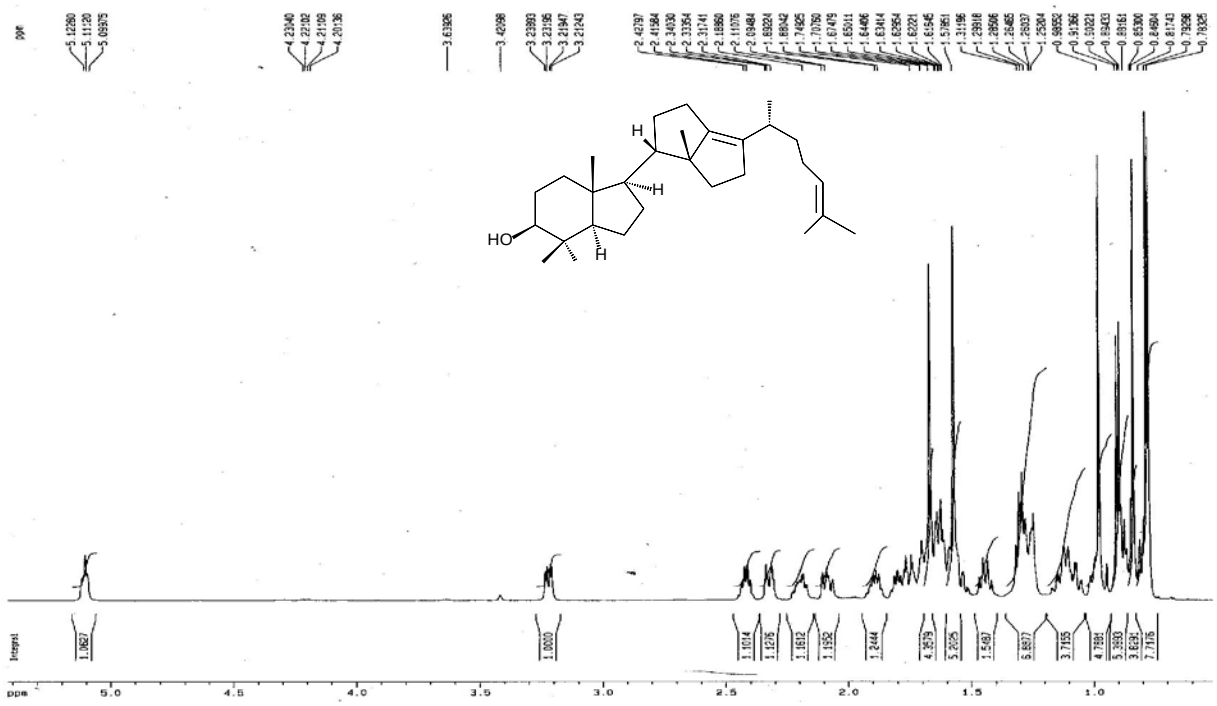


Fig. S3.1. ^{1}H-NMR spectrum of product **21** in $CDCl_3$ (600 MHz).

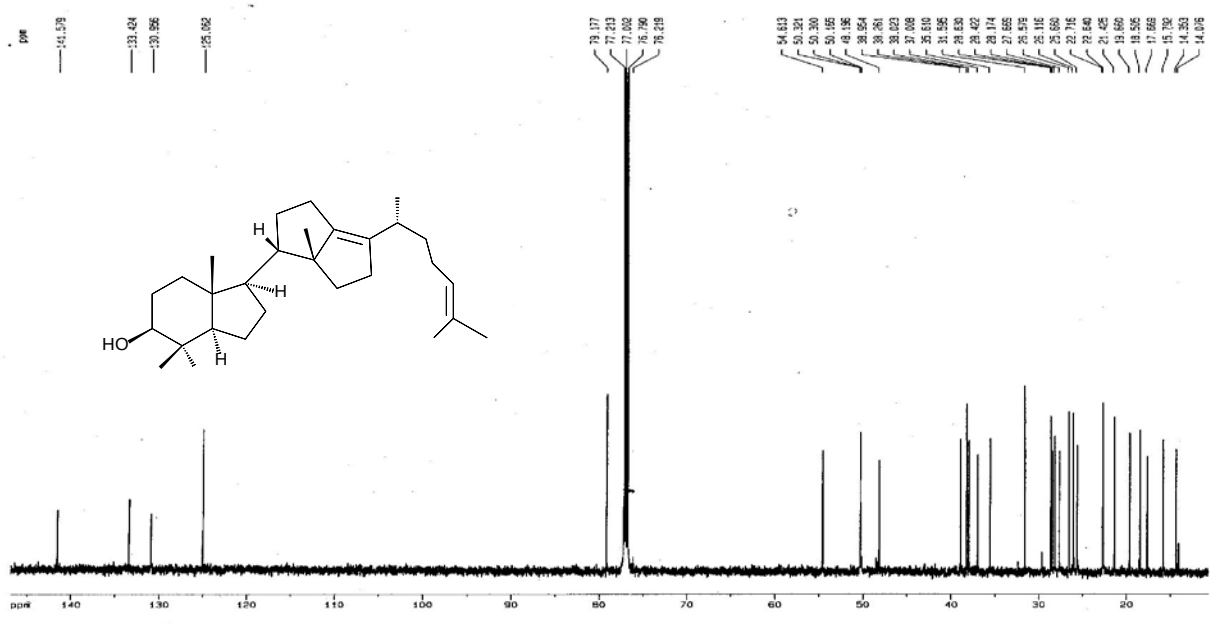


Fig. S3.2. ^{13}C NMR spectrum of product **21** in $CDCl_3$ (600 MHz) (150 MHz).

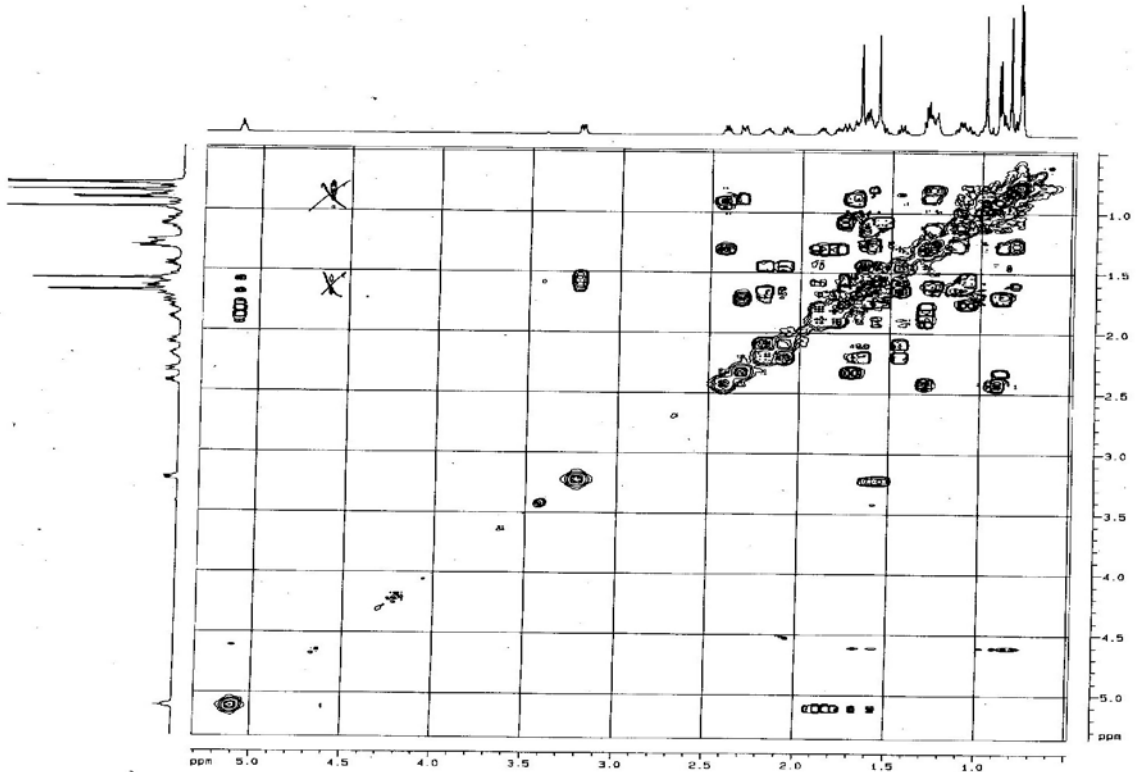


Fig. S3.3. ^{1}H-^{1}H COSY spectrum of product **21** in $CDCl_3$.

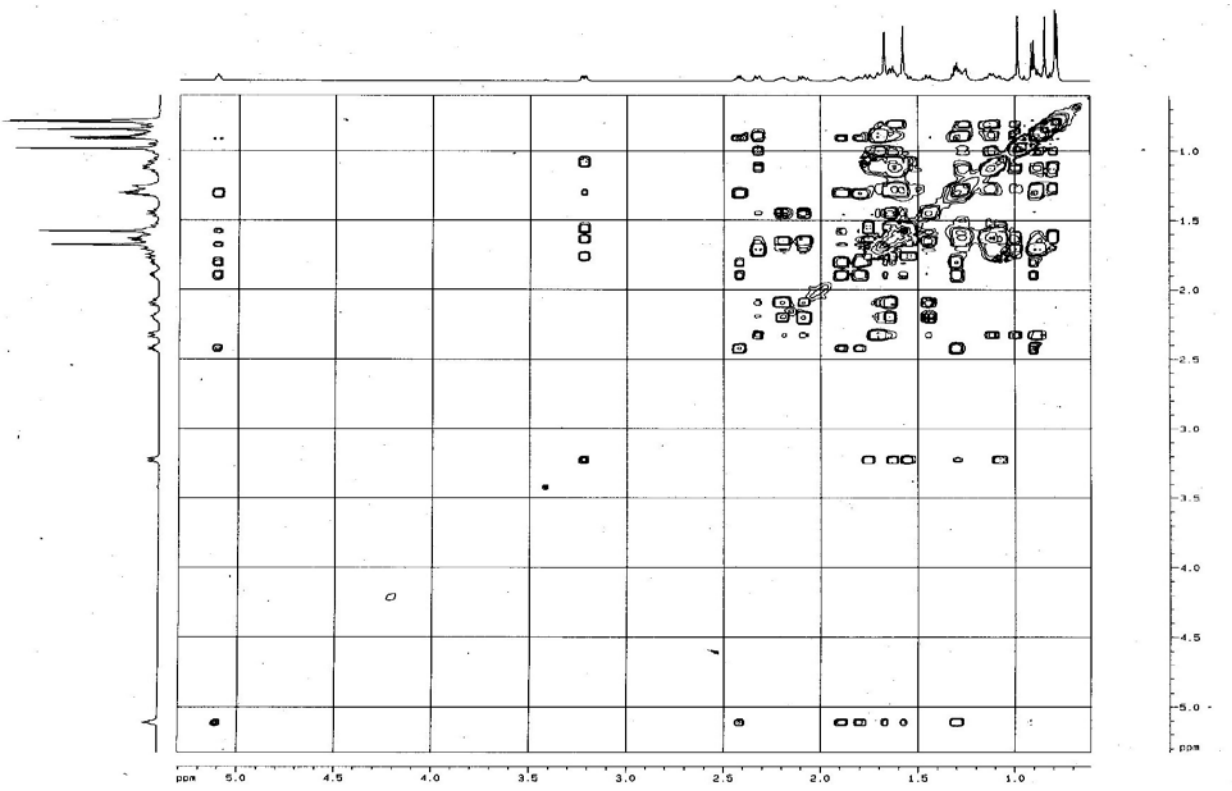


Fig. S3.4. TOCSY spectrum of product **21** in $CDCl_3$.

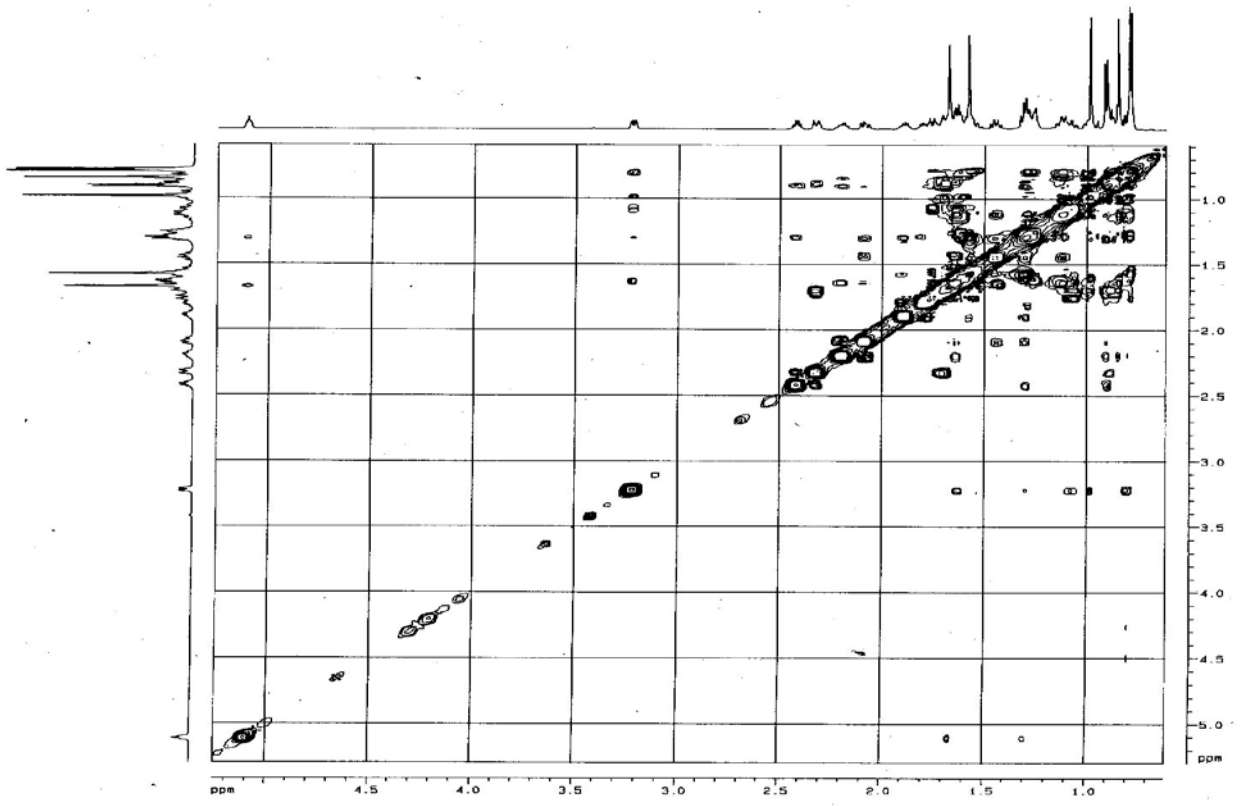


Fig. S3.5. NOESY spectrum of product **21** in $CDCl_3$.

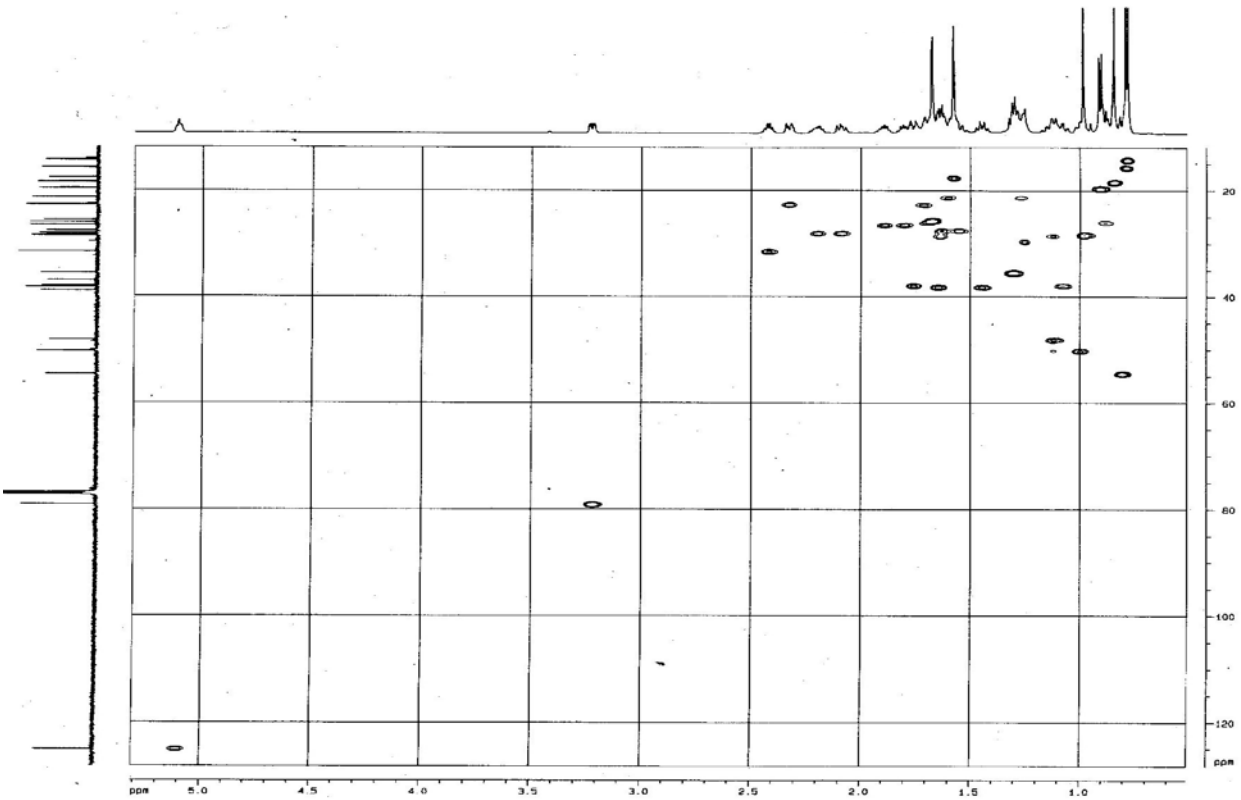


Fig. S3.6. HSQC spectrum of product **21** in $CDCl_3$.

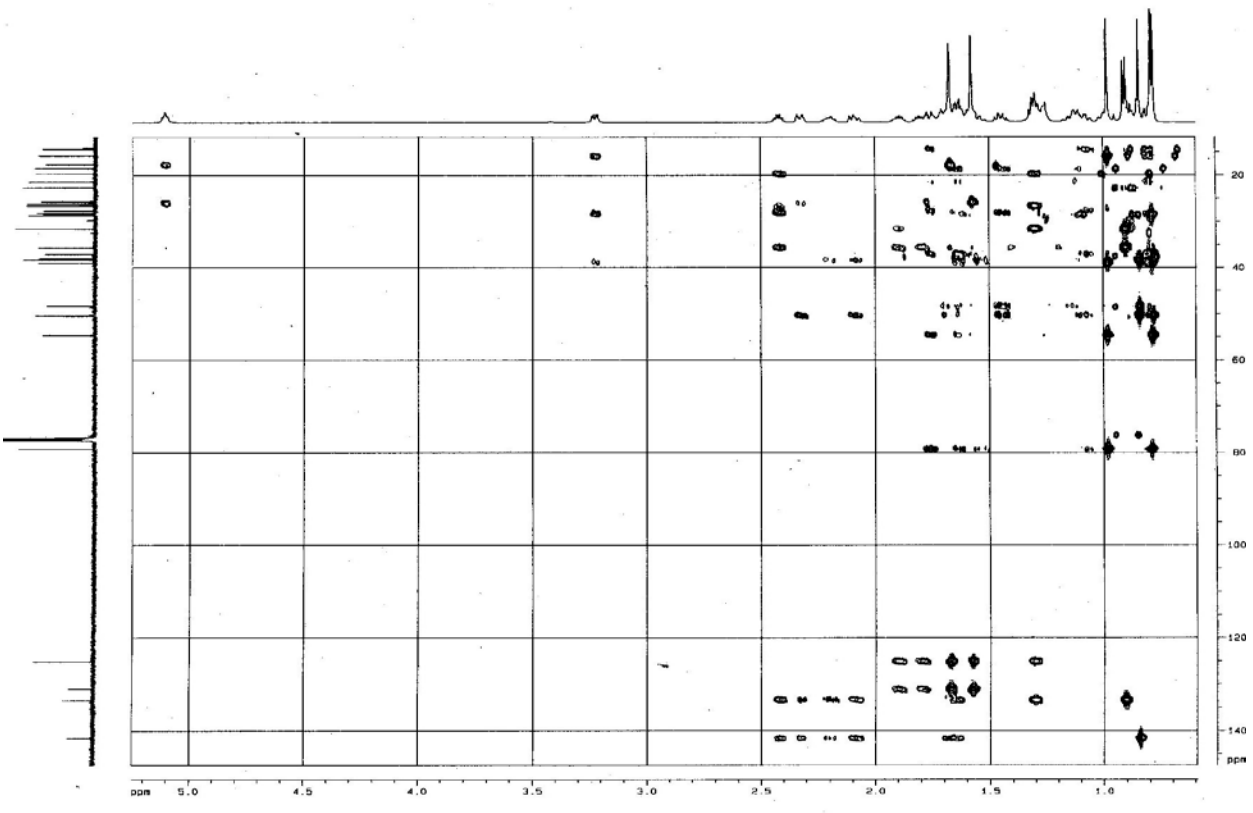
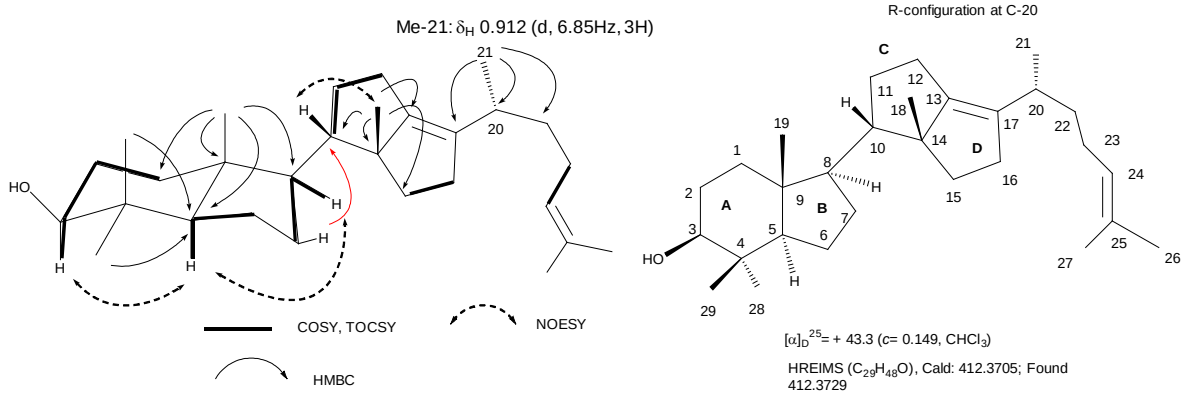


Fig. S3.7. HMBC spectrum of product **21** in $CDCl_3$.

Product **21** from (3*S*)-27-norOXSQ **21**



600 MHz, in $CDCl_3$; the residula solvent peak: δ_H 7.26; δ_C 77.0 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	1.07(m,1H);1.77(m,1H)	**38.02(t)**	9	——	**37.01(s)**	17	——	**133.4(s)**	25	——	**130.9(s)**
2	1.55(m);1.62(m)	**27.67(t)**	10	1.12(m, 1H)	**48.20(d)**	18	0.846(s, 3H)	**18.50(q)**	26	1.675(s,3H)	**22.72(q)**
3	3.23 (dd, J=11.7 Hz;4.2 Hz, 1H)	**79.18(d)**	11	0.90(m, 1H); 1.70(m,1H)	**26.11(t)**	19	0.783(s,3H)	**14.35(q)**	27	1.578 (s, 3H)	**17.67(q)**
4	——	**38.95(s)**	12	1.70(m,1H); 2.32(m,1H)	**22.71(t)**	20	2.42(m, 1H)	**31.59(d)**	28	0.985(s,3H)	**28.42(q)**
5	0.81(m, 1H)	**54.61(d)**	13	——	**141.6(s)**	21	0.912(d, 6.85Hz, 3H)	**19.66(q)**	29	0.793(s,3H)	**15.79(q)**
6	1.26(m,1H); 1.60(m, 1H)	**21.42(t)**	14	——	**50.32 (s)**	22	1.31(m, 2H)	**35.61(t)**			
7	1.12(m, 1H); 1.63(m, 1H)	**28.63(t)**	15	1.45(m,1H); 1.63(m, 1H)	**38.26(t)**	23	1.80(m,1H); 1.89(m,1H)	**26.58(t)**			
8	1.00 (m, 1H)	**50.30(d)**	16	2.08(m,1H); 2.19(m,1H)	**28.17(t)**	24	5.11(br s, 1H)	**125.1(d)**			

Fig. S3.8. Assignments of NMR data of product **21** in $CDCl_3$, HR-EIMS and optical rotation.

4. NMR spectra of product 21 in C_6D_6.

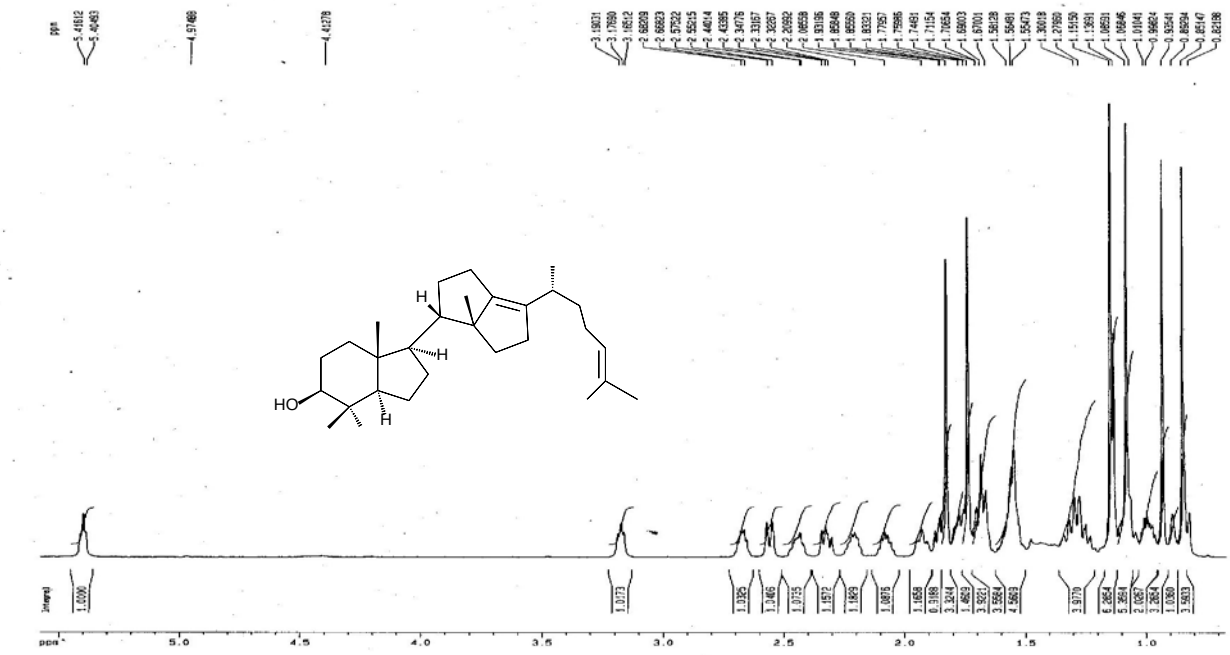


Fig. S4.1. ^{1}H NMR spectra of product **21** in C_6D_6 (600 MHz).

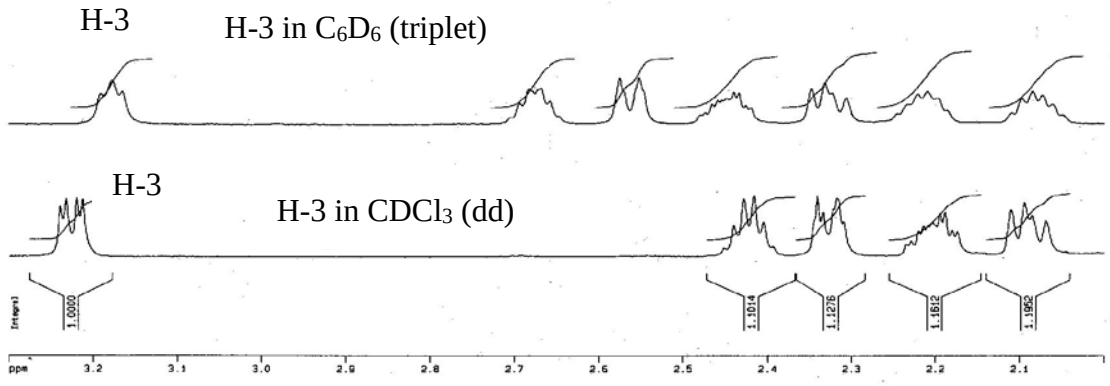


Fig. S4.2. Comparison of ^{1}H NMR spectra of product **21** between $CDCl_3$ and C_6D_6 solutions (600 MHz).

The coupling constants of H-3 were compared between the solutions of C_6D_6 and $CDCl_3$. δ_H in C_6D_6: 3.18 (br t, J=8.0 Hz); δ_H in $CDCl_3$: 3.23 ((dd, J=11.7 Hz and 4.2 Hz). The coupling constants (splitting pattern) in $CDCl_3$ solution clearly demonstrated that the OH group is β-oriented, although the splitting pattern (triplet) in C_6D_6 suggests that the OH group is α-oriented. This contradictory argument was resolved by the definitive NOE between H-3 and H-5 in the C_6D_6 solution. Consequently, the OH at C-3 of product **1** was credibly determined to be β-oriented. The ^{1}H-NMR spectra of products **23** and **25** in C_6D_6 solution also showed triplet splitting pattern, but dd splitting in the $CDCl_3$ solution.

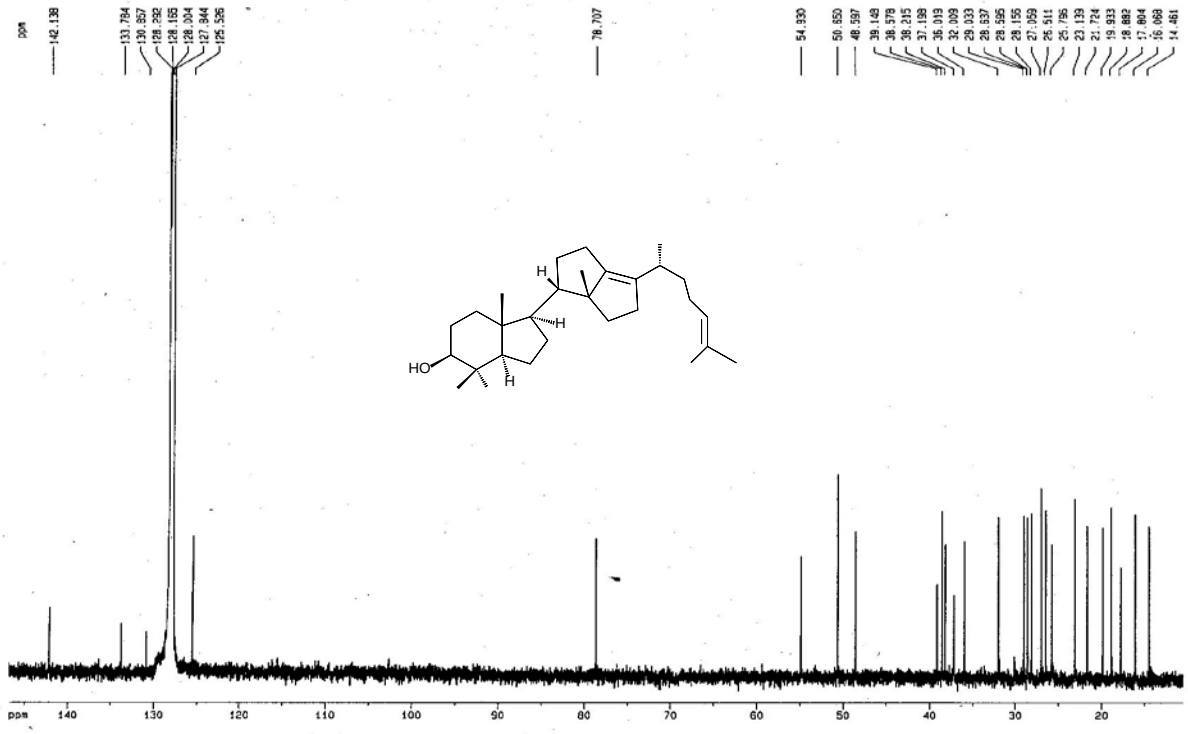


Fig. S4.3. ^{13}C NMR spectrum of product **21** in C_6D_6 (150 MHz).

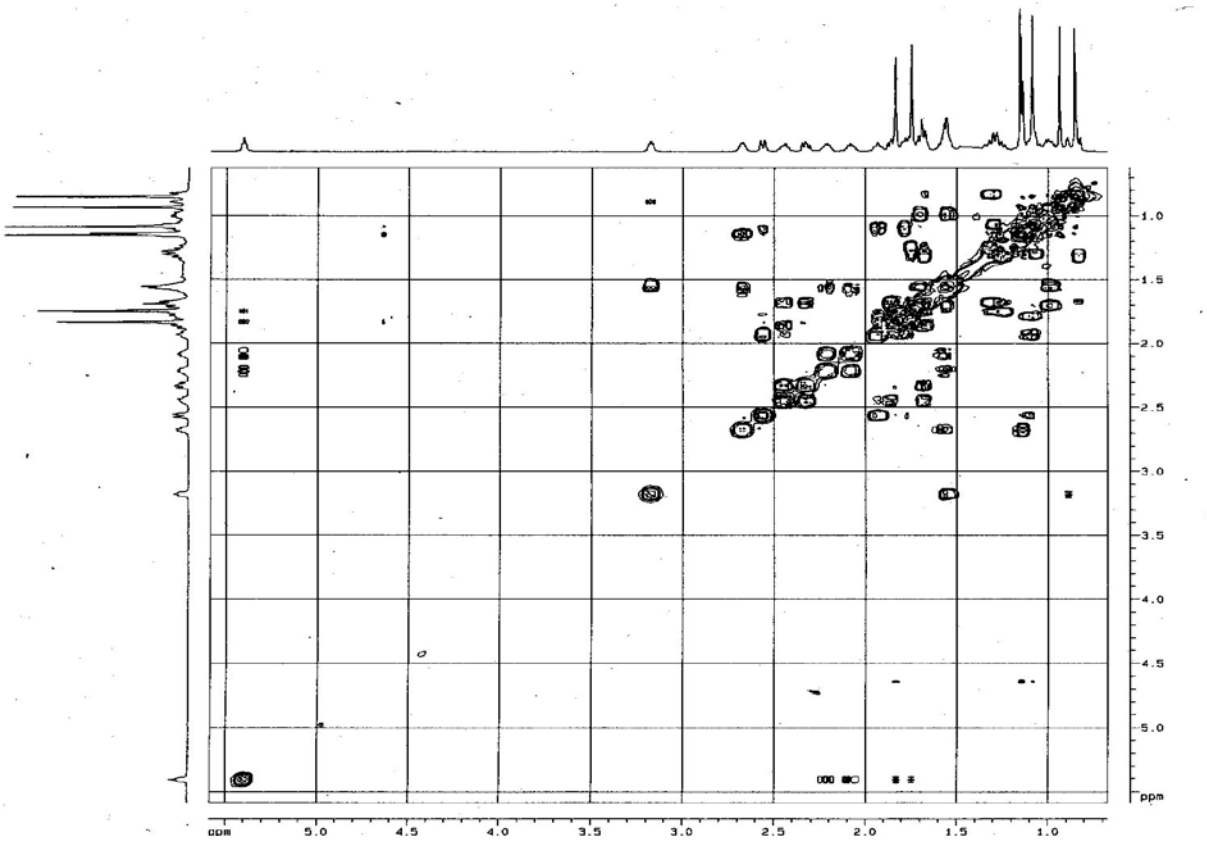


Fig. S4.4. ^{1}H-^{1}H COSY spectrum of product **21** in C_6D_6.

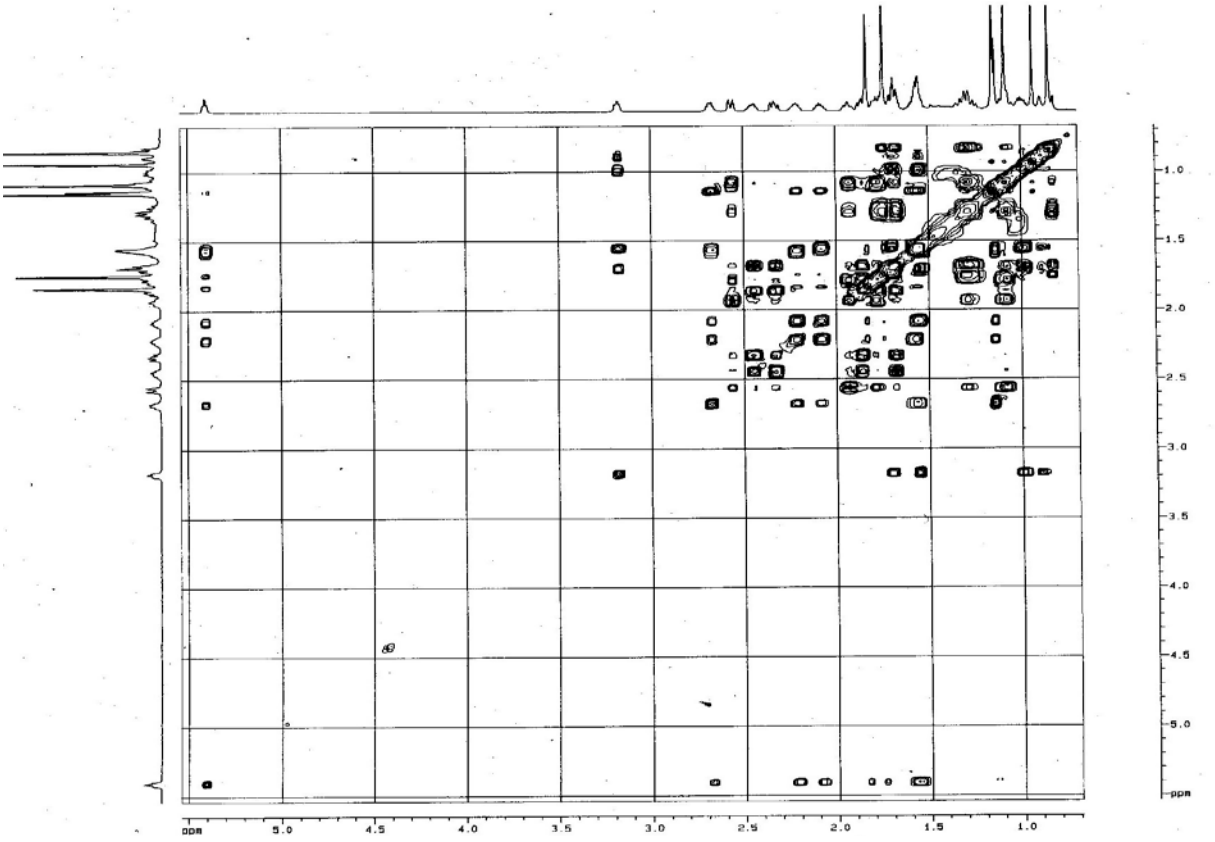


Fig. S4.5. TOCSY spectrum of product **21** in C_6D_6.

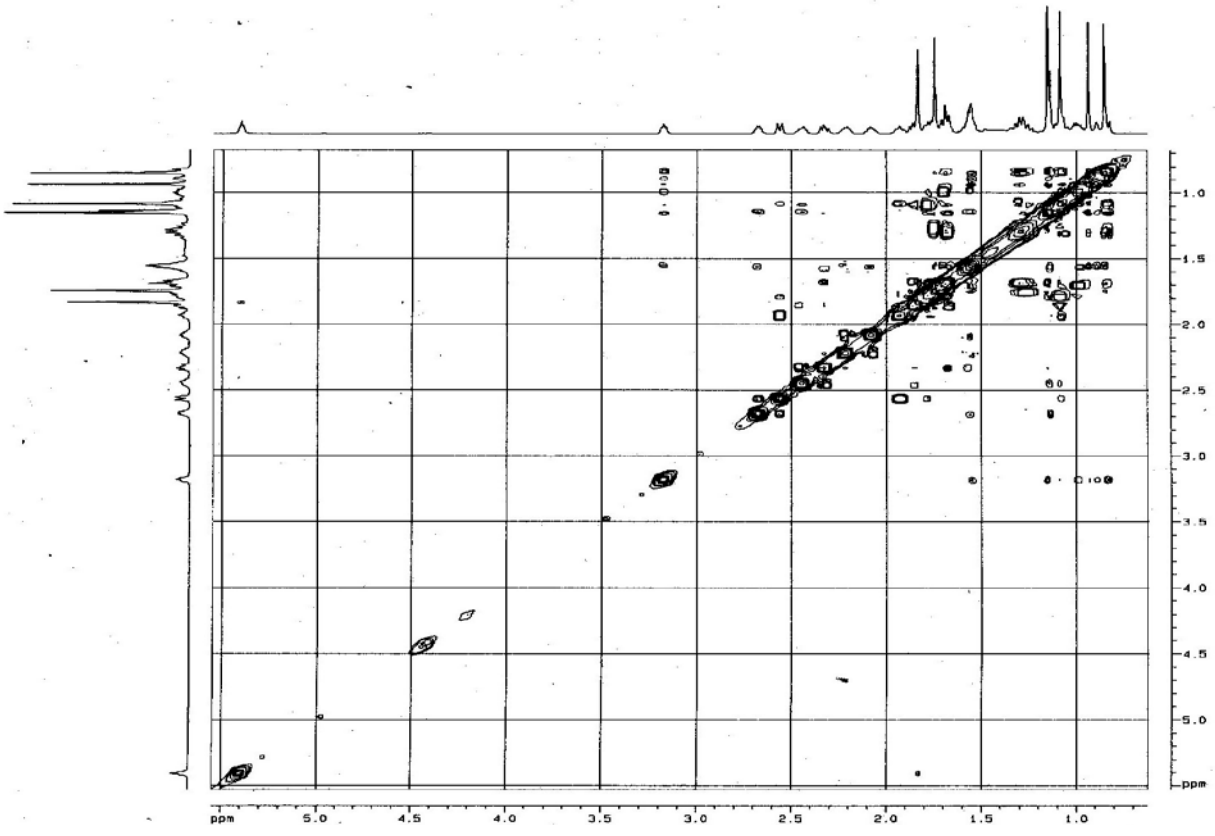


Fig. S4.6. NOESY spectrum of product **21** in C_6D_6.

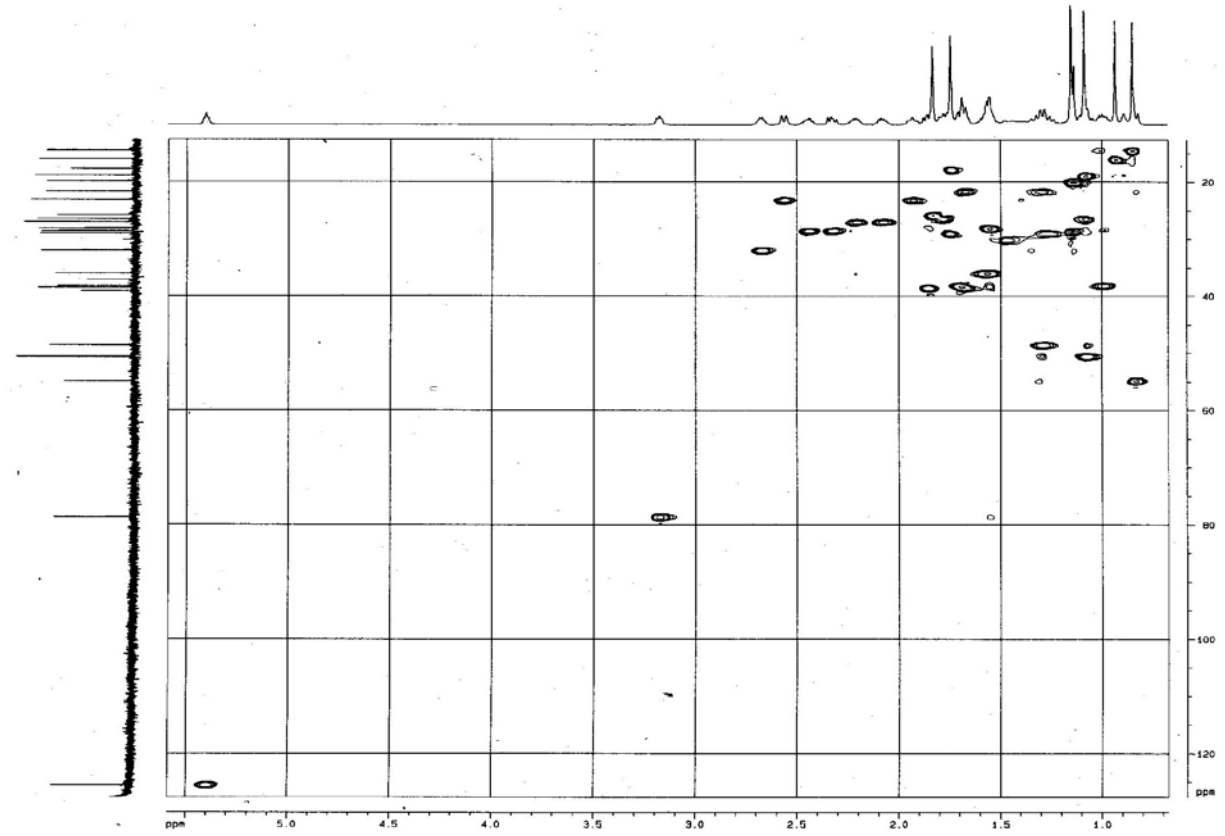


Fig. S4.7. HSQC spectrum of product **21** in C_6D_6.

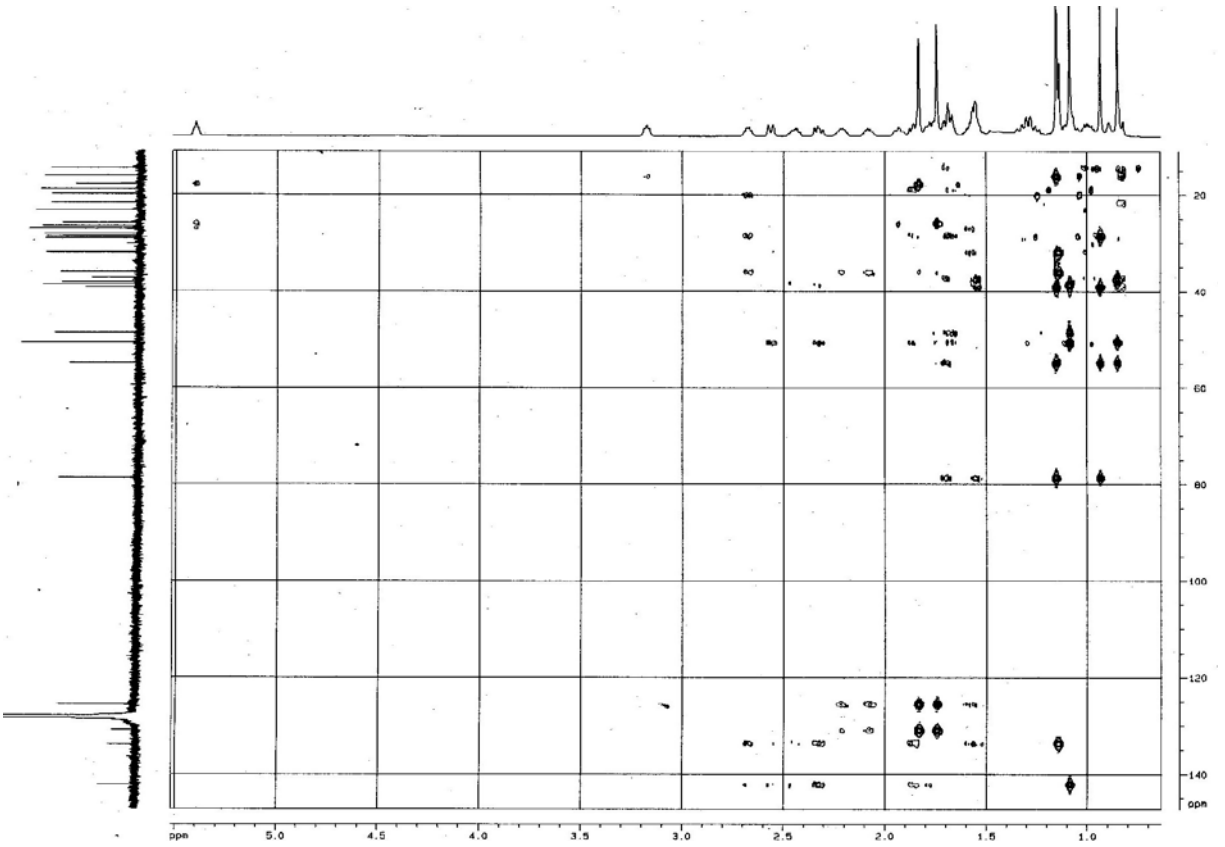
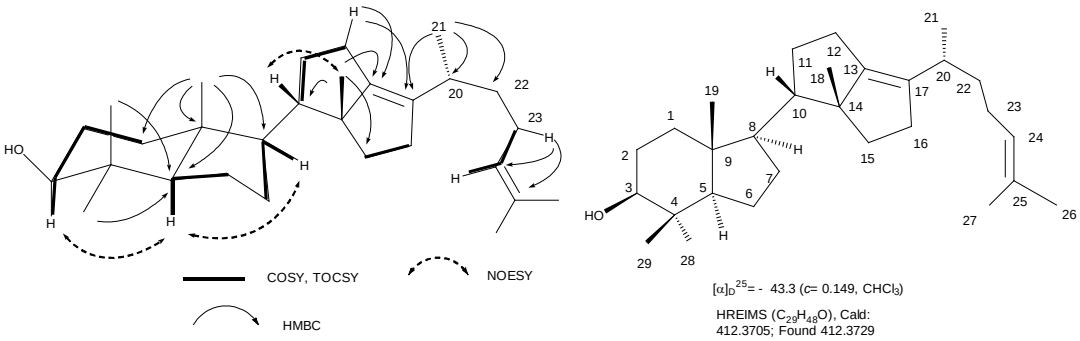


Fig. S4.8. HMBC spectrum of product **21** in C_6D_6.

Product **21** in C_6D_6

Me-21: δ_H 1.14 (d, J=8.7 Hz, 3H)

R-configuration at C-20



$[\alpha]_D^{25}$= - 43.3 (*c*= 0.149, $CHCl_3$)

HREIMS ($C_{29}H_{48}O$), Cald: 412.3705; Found 412.3729

600 MHz, in C_6D_6; the residula solvent peak: δ_H 7.26; δ_C 77.0 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	1.00(m,1H) ;1.68(m,1H)	**38.21(t)**	9	——	**37.20(s)**	17	——	**133.8(s)**	25	——	**130.9(s)**
2	1.54(m, 2H)	**28.16(t)**	10	1.29(m, 1H)	**48.60(d)**	18	1.068(s, 3H)	**18.88(q)**	26	1.833(s, 3H)	**25.80(q)**
3	3.18 (bt, J=6.7 Hz, 1H)	**78.71(d)**	11	1.26(m, 1H); 1.74(m,1H)	**29.03(t)**	19	0.851(s, 3H)	**14.46(q)**	27	1.745 (s, 3H)	**17.80(q)**
4	——	**39.15(s)**	12	1.93(m,1H); 2.56(bd, J=13.2Hz,1H)	**23.14(t)**	20	2.67(m, 1H)	**32.01(d)**	28	1.151(s,3H)	**28.64(q)**
5	0.81(m, 1H)	**54.93(d)**	13	——	**142.1(s)**	21	1.14 (d, J=7.2 Hz, 3H)	**19.93(q)**	29	0.935(s,3H)	**16.07(q)**
6	1.31(m,1H); 1.67(m, 1H)	**21.73(t)**	14	——	**50.65 (s)**	22	1.55(m, 2H)	**36.02(t)**			
7	1.09(m, 1H); 1.78(m, 1H)	**26.51(t)**	15	1.57(m,1H); 1.85(m, 1H)	**38.58(t)**	23	2.08(m,1H); 2.20(m,1H)	**27.06(t)**			
8	1.07 (m, 1H)	**50.65(d)**	16	2.32(m,1H); 2.44(m,1H)	**28.59(t)**	24	5.40(bt, J=6.7 Hz,1H)	**125.5(d)**			

Fig. S4.9. Assignments of NMR data of product **21** in C_6D_6, HR-EIMS and optical rotation.

5. NMR spectra of product 23 in C_6D_6.

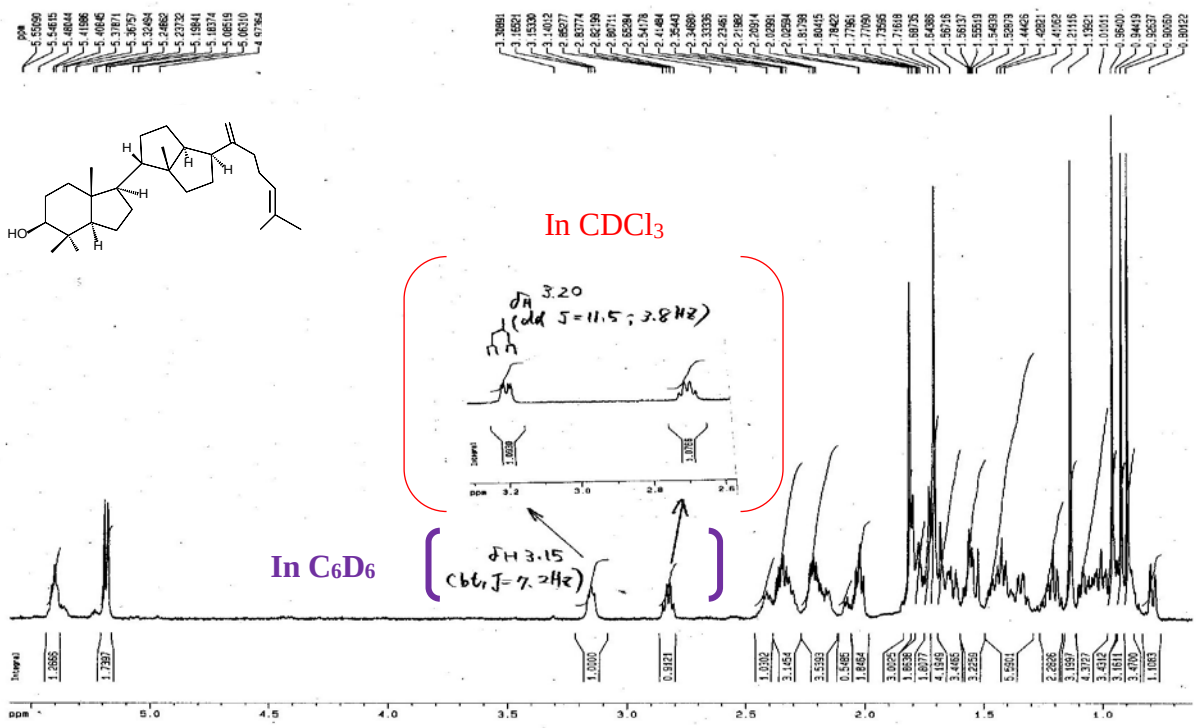


Fig. S5.1. ^{1}H NMR spectrum of product **23.**

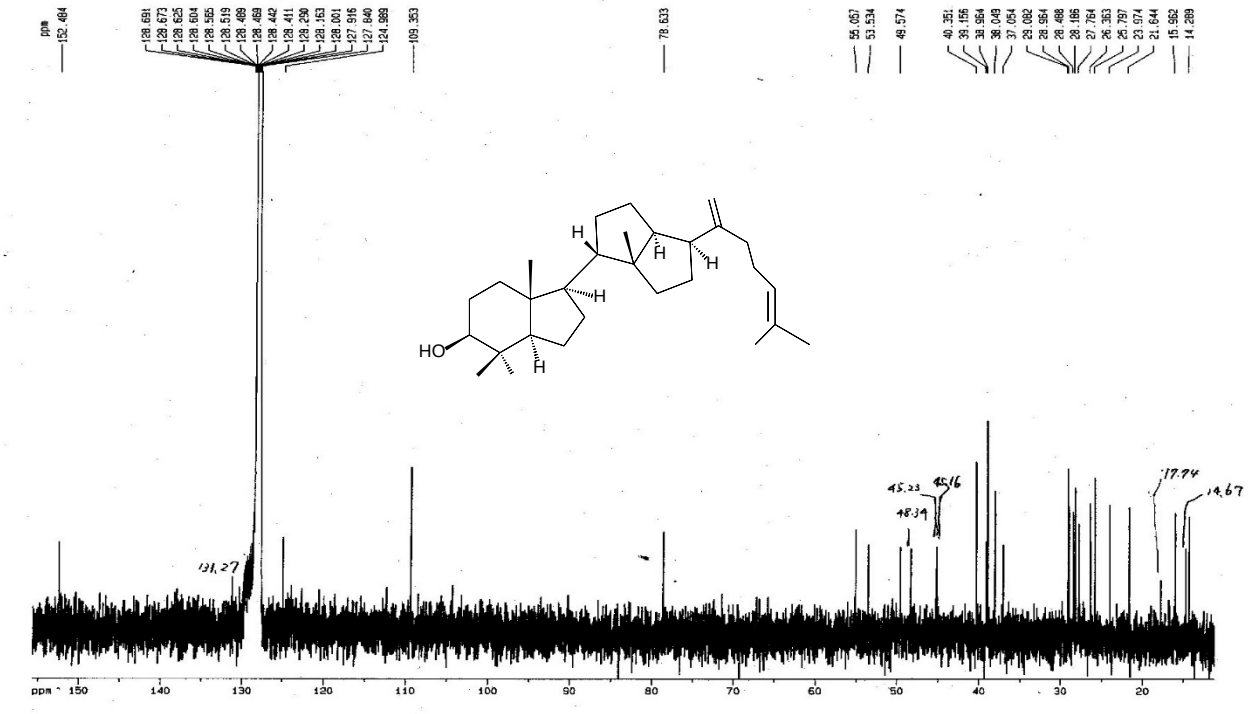


Fig. S5.2. ^{13}C NMR spectrum of product **23**.

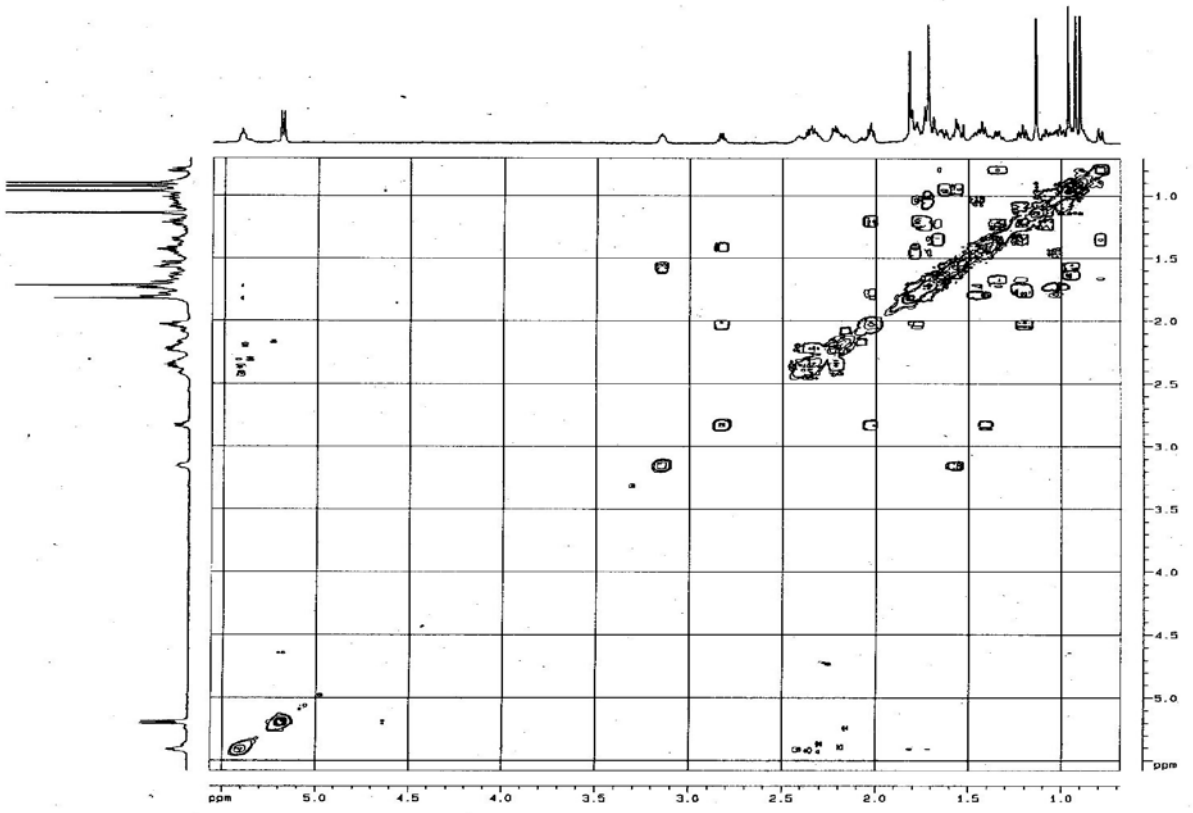


Fig. S5.3. COSY spectrum of product **23**.

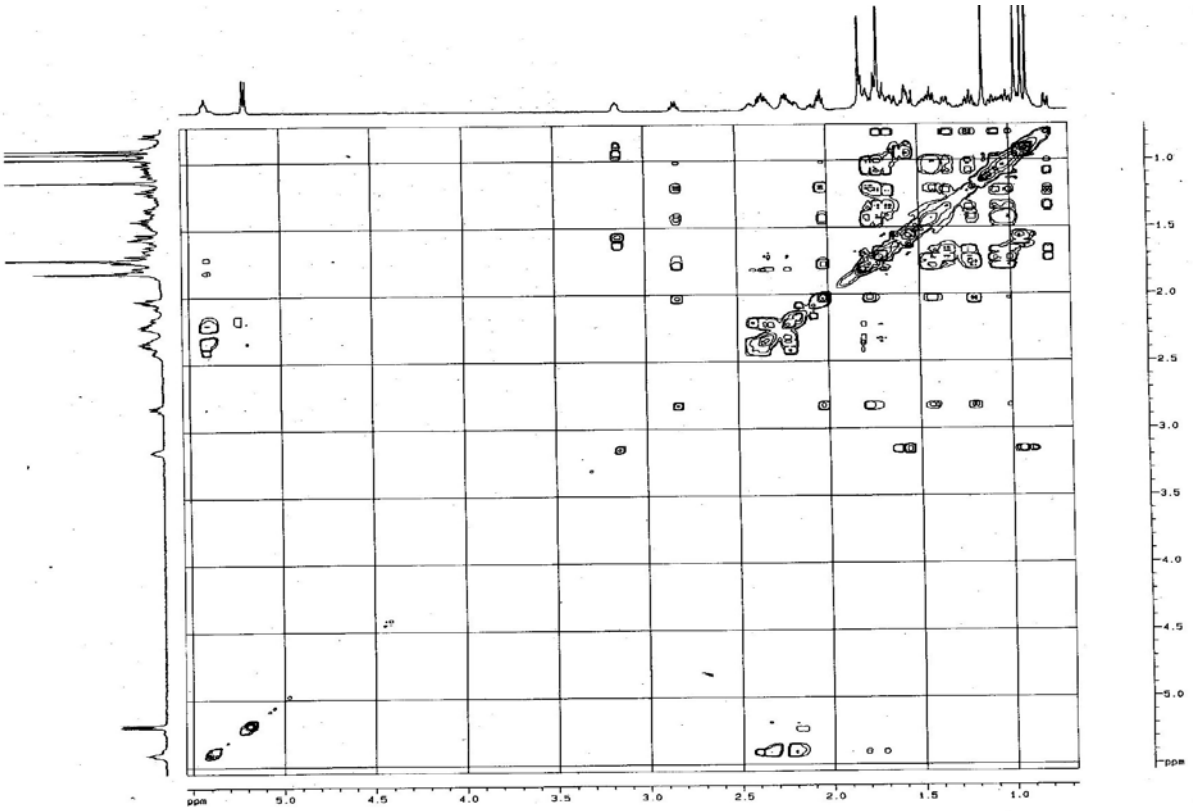


Fig. S5.4. TOCSY spectrum of product **23**

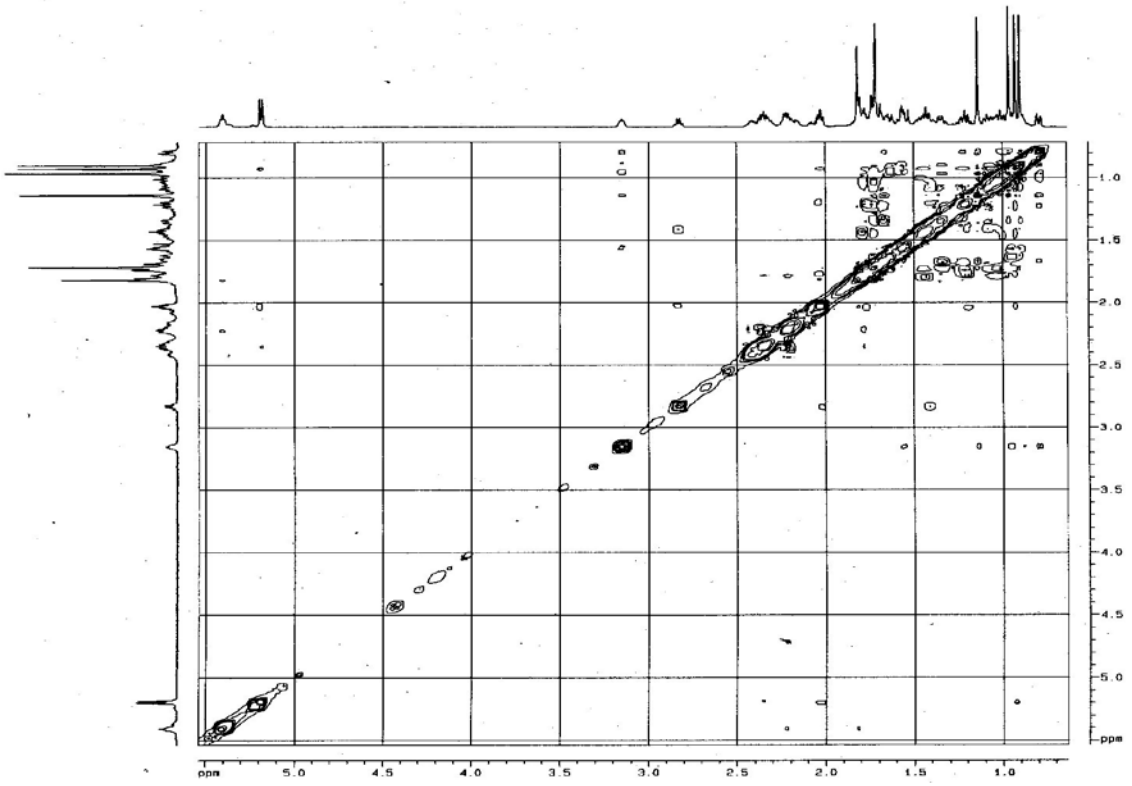


Fig. S5.5. NOESY spectrum of product **23.**

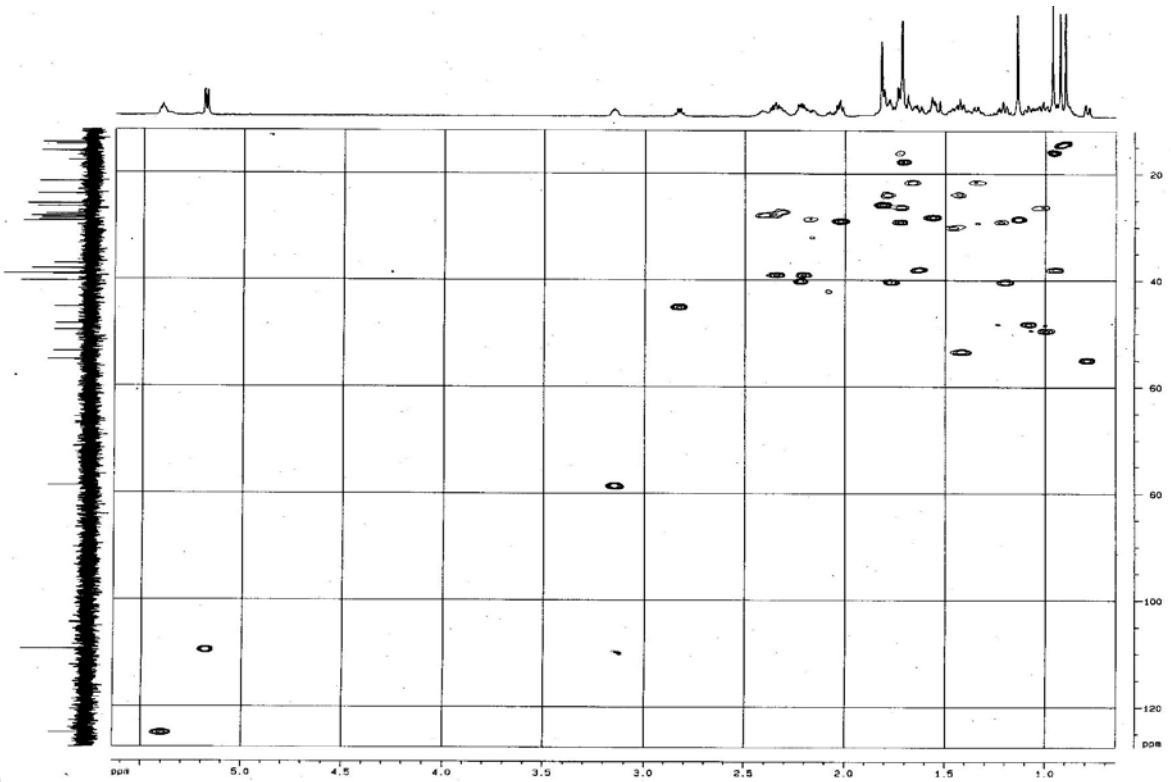


Fig. S5.6. HSQC spectrum of product **23.**

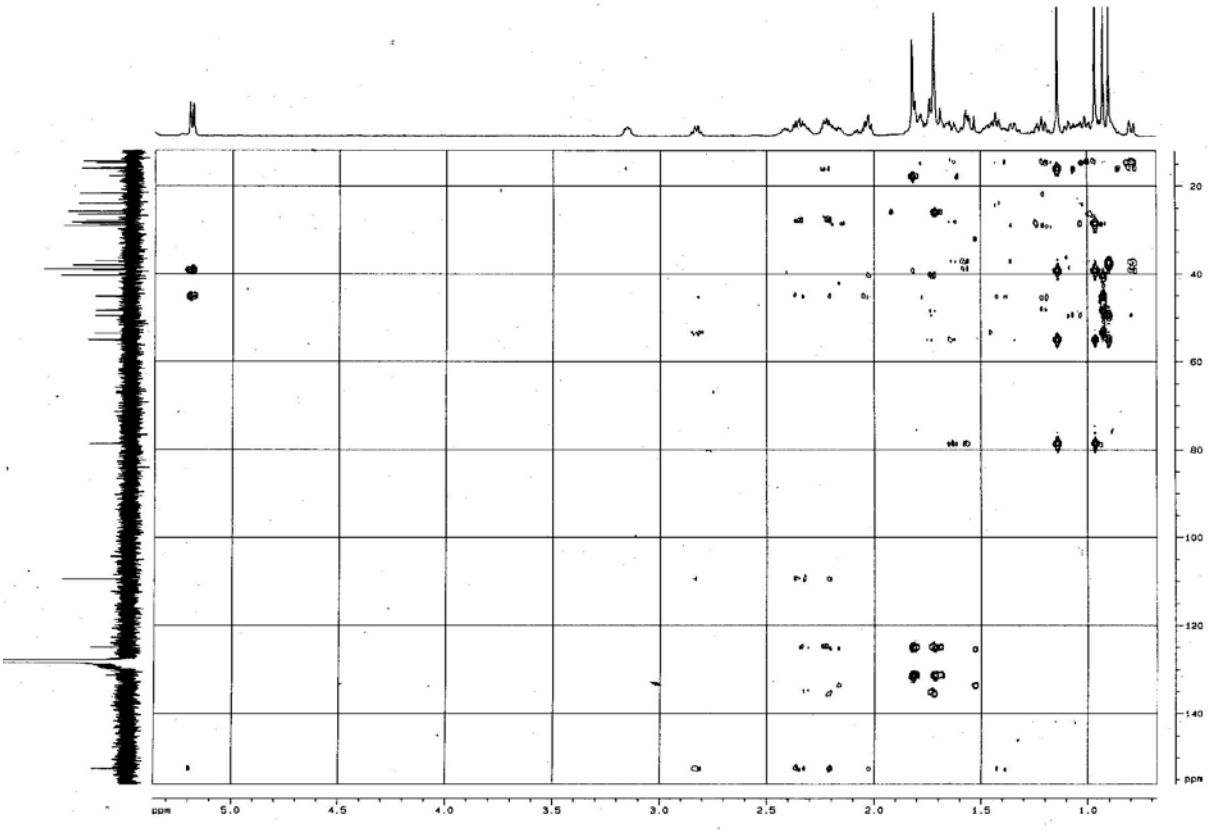
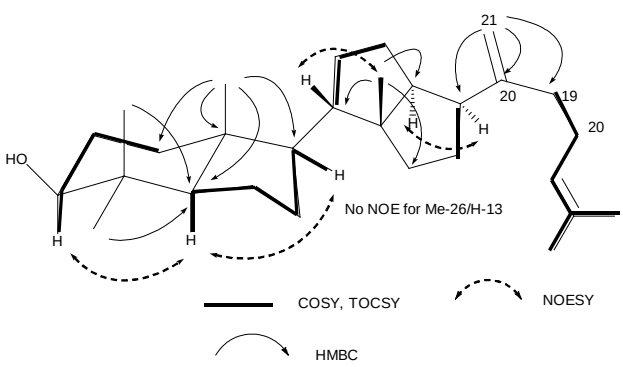
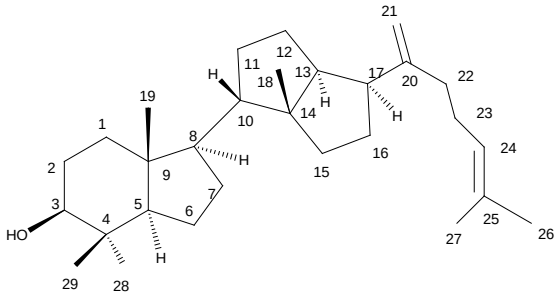


Fig. S5.7. HMBC spectrum of product **23.**

Product **23**





$[\alpha]_D^{25}$= - 61 (*c*= 0.03, $CHCl_3$)

HREIMS ($C_{29}H_{48}O$), Cald: 412.3705;
Found 412.3720

600 MHz, in C_6D_6; the residual solvent peak: δ_H 7.28; δ_C 128.0 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	0.94(m,1H);1.62(m,1H)	**38.05(t)**	9	——	**37.05(s)**	17	2.83(dt, J=9.0 Hz, 1H)	**45.16(d)**	25	——	**131.3(s)**
2	1.56 (m, 2H)	**28.19(t)**	10	1.08(m, 1H)	**48.34(d)**	18	0.926(s, 3H)	**14.67(q)**	26	1.818(s, 3H)	**25.80(q)**
3	3.15 (br t, J=7.2 Hz, 1H)	**78.63(d)**	11	1.02(m, 1H); 1.72(m,1H)	**26.36(t)**	19	0.901(s, 3H)	**14.29(q)**	27	1.716 (s, 3H)	**17.74(q)**
4	——	**39.16(s)**	12	1.43(m,1H); 1.78(m,1H)	**23.97(t)**	20	——	**152.5(s)**	28	1.14(s,3H)	**28.49(q)**
5	0.794(dd, J=11.8; 2.1 Hz, 1H)	**55.06(d)**	13	1.42 (m, 1H)	**53.53(d)**	21	5.18 (s, 1H,) 5.20(s, 1H)	**109.3(t)**	29	0.964(s,3H)	**15.97(q)**
6	1.34(m,1H); 1.67(m, 1H)	**21.64(t)**	14	——	**45.23 (s)**	22	2.21(m); 2..33(m)	**38.96(t)**			
7	1.22(m, 1H); 1.73(m, 1H)	**29.08(t)**	15	1.20(m,1H); 1.77(m, 1H)	**40.35(t)**	23	2.36(m,1H); 2.41(m,1H)	**27.76(t)**			
8	1.00 (m, 1H)	**49.57(d)**	16	2.03(m,2H)	**28.96(t)**	24	5.41(t, *J*=6.8 Hz, 1H)	**125.0(d)**			

Fig. S5.8. Assignments of NMR data of product **23** in C_6D_6, HR-EIMS and optical rotation.

Remark; In the C_6D_6 solution, the H-3 showed br triplet splitting pattern, but in the $CDCl_3$ solution, H-3 showed the dd splitting pattern (δ_H 3.20, dd, *J*=11.5 and 3.8 Hz, see Fig. S6.1), thus strongly indicating that the OH at C-3 is positioned in a β-orientation. A definitive NOE for H-3/H-5 further supported β-OH orientation at C-3 in the NOESY spectrum (C_6D_6 solution). (See Fig. S6.5).

6. NMR spectra of product 25 in C_6D_6.

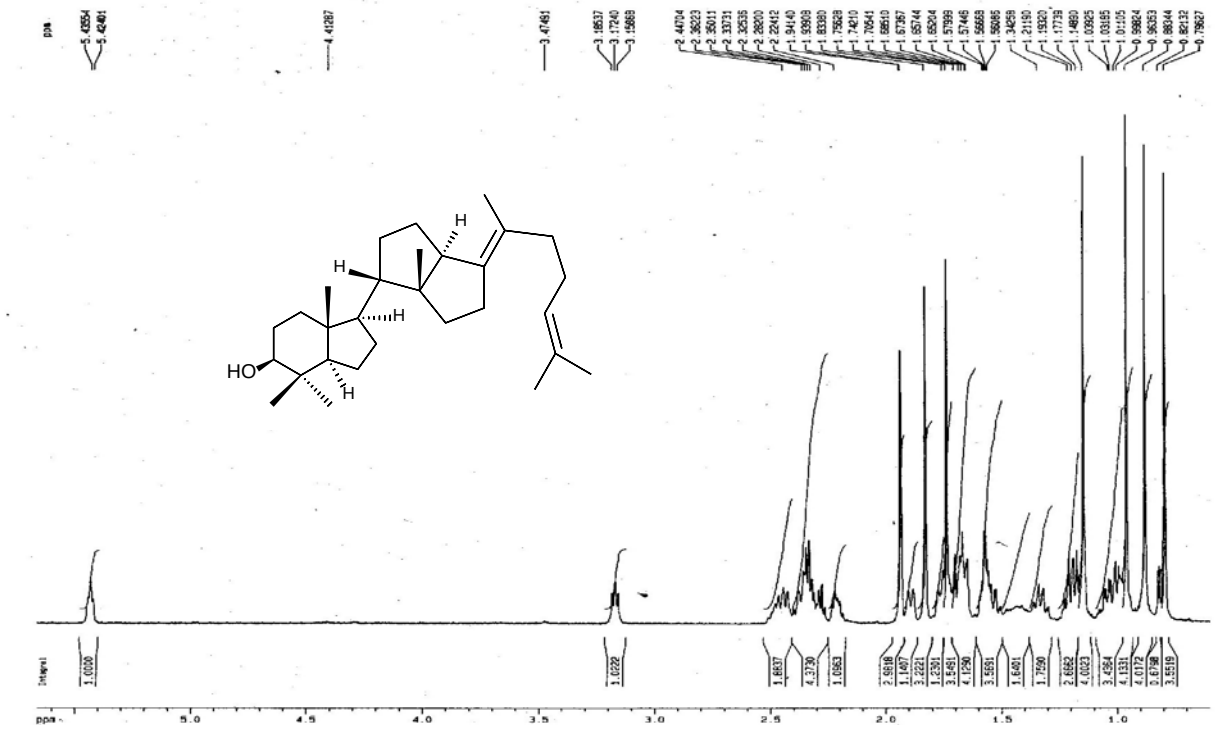


Fig. S6.1. ^{1}H NMR spectrum of product **25**

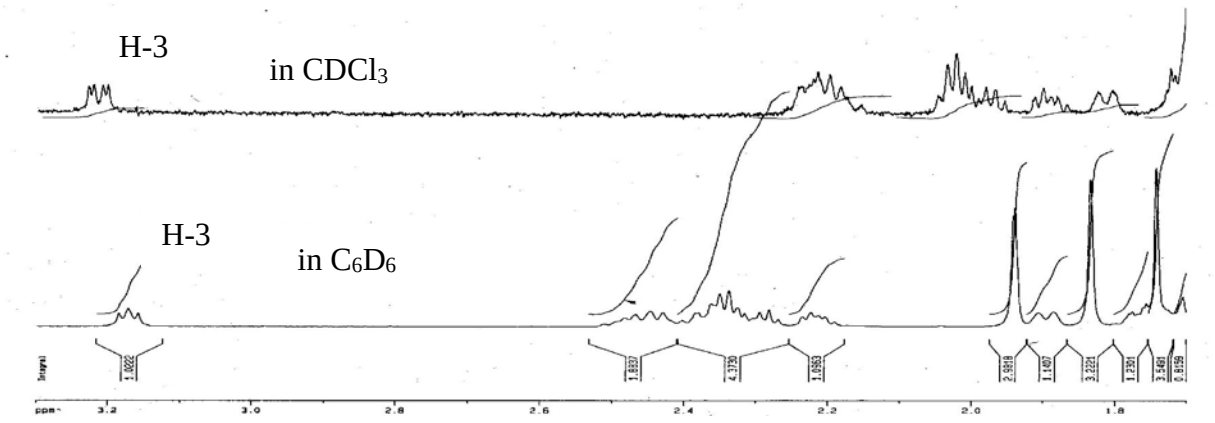


Fig. S6.2. Comparison of ^{1}H NMR spectra of product **25** between $CDCl_3$ and C_6D_6 solutions (600 MHz).

The coupling constants of H-3 were compared between the solutions of C_6D_6 and $CDCl_3$. δ_H in C_6D_6: 3.17 (br t, J=8.0 Hz); δ_H in $CDCl_3$: 3.21 (dd, J=11.7 Hz and 4.3 Hz). The coupling constants (splitting pattern) in $CDCl_3$ solution clearly demonstrated that the OH group is β-oriented, although the splitting pattern (triplet) in C_6D_6 suggests that the OH group is α-oriented. This contradictory argument was resolved by the definitive NOE between H-3 and H-5 in the C_6D_6 solution. Consequently, the OH at C-3 of product **25** was credibly determined to be β-oriented. The ^{1}H-NMR spectra of products **21** and **23** in C_6D_6 solution also triplet splitting pattern, but dd splitting in $CDCl_3$.

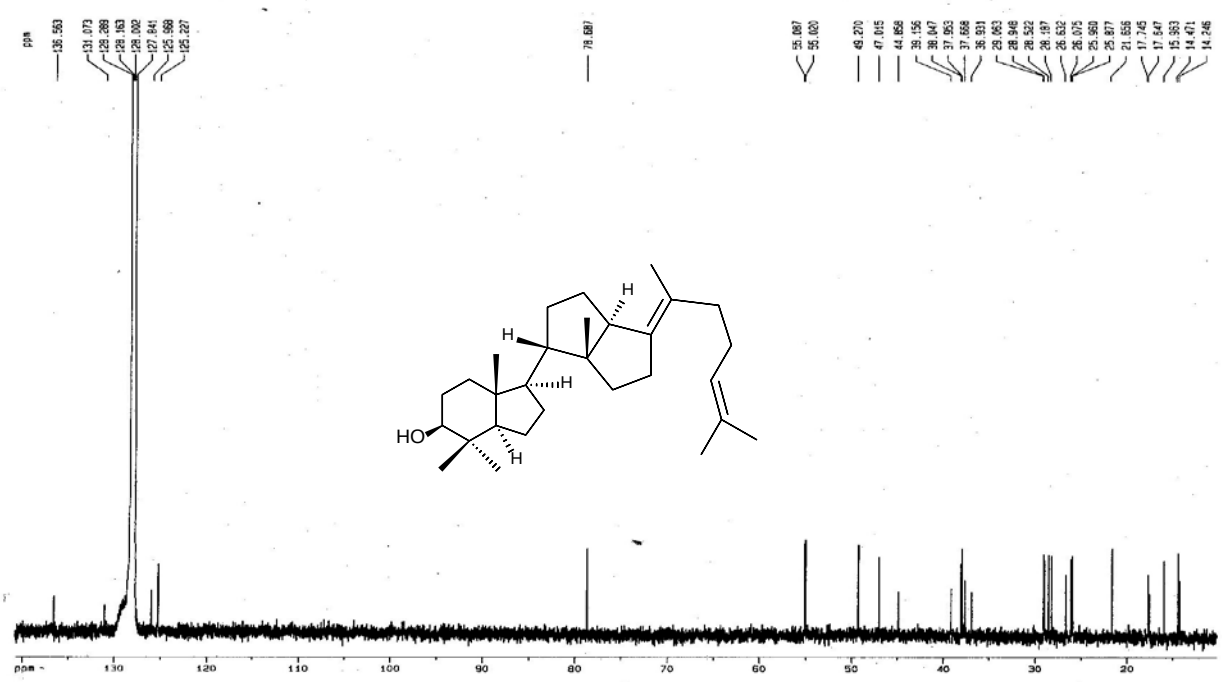


Fig. S6.3. ^{13}C NMR spectrum of product **25**

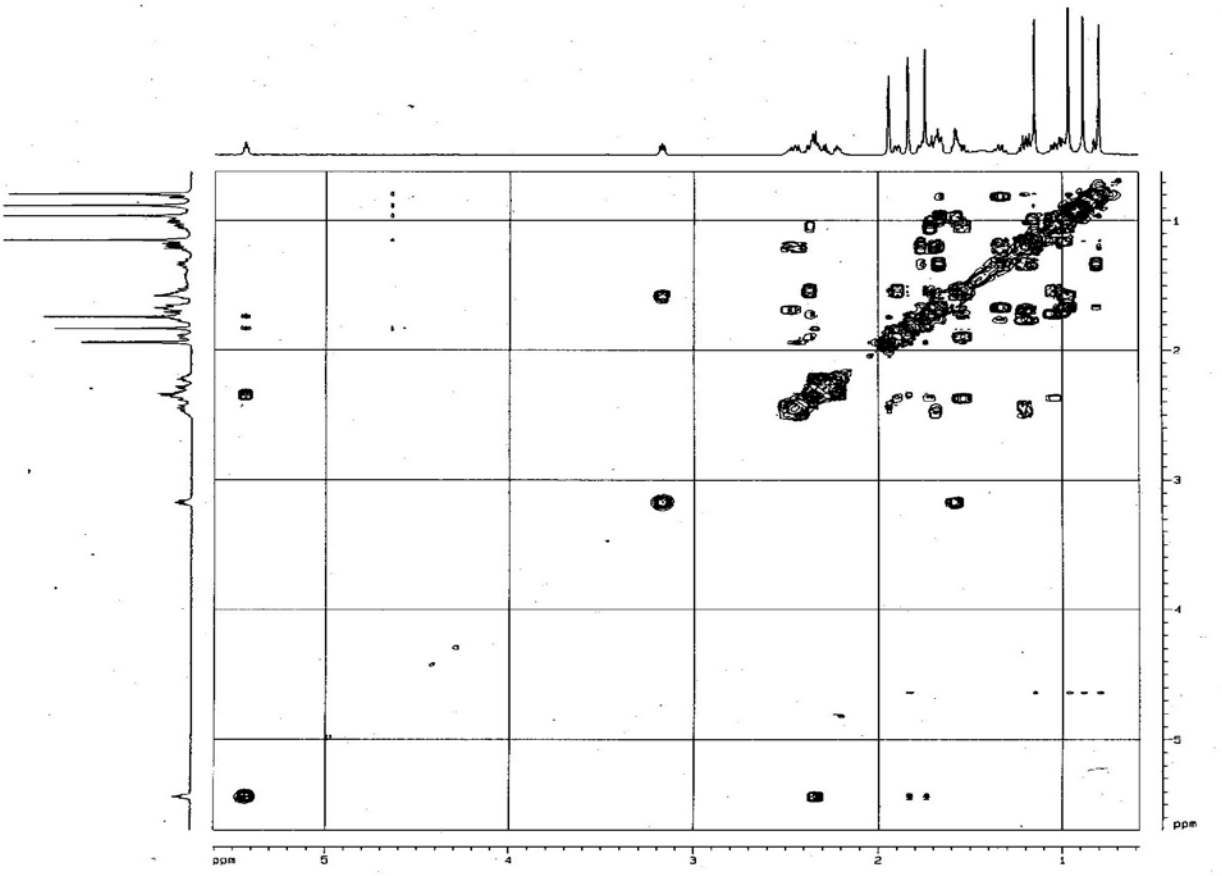


Fig. S6.4. COSY spectrum of product **25**

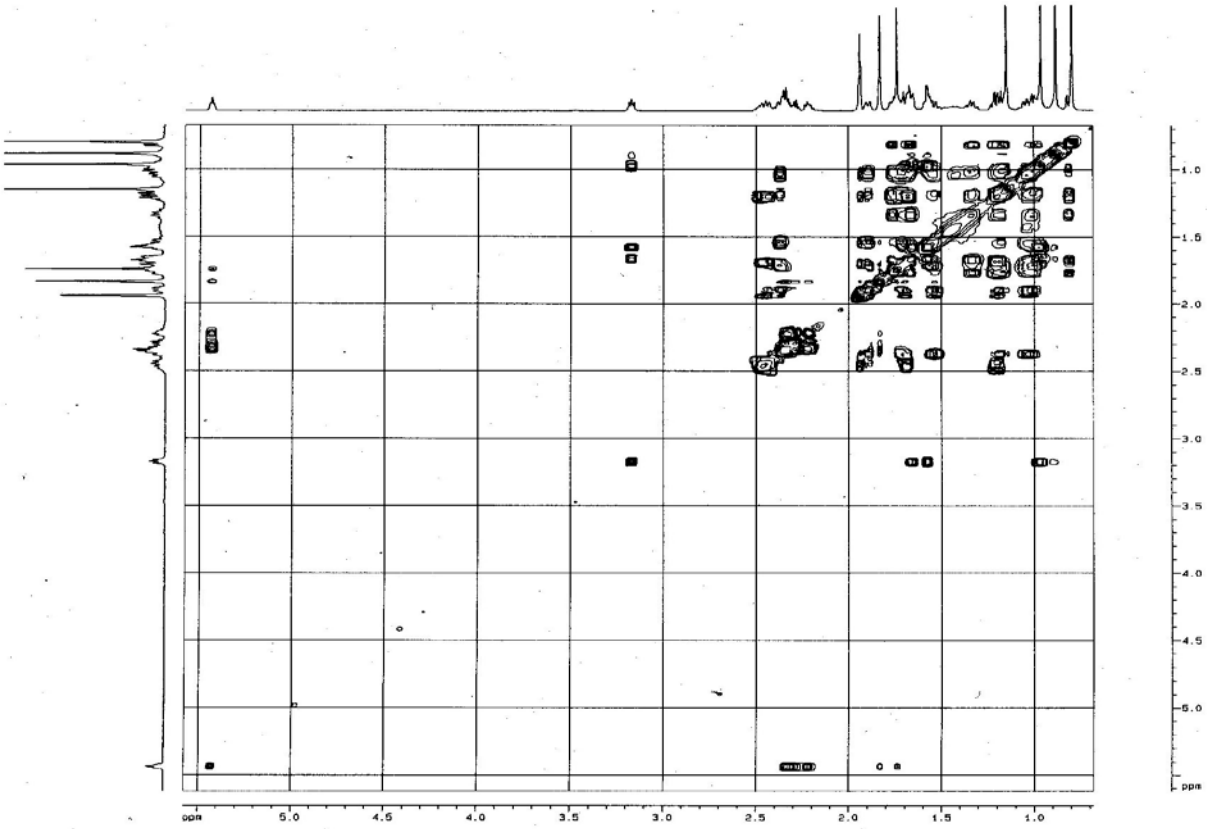


Fig. S6.5. TOCSY spectrum of product **25**

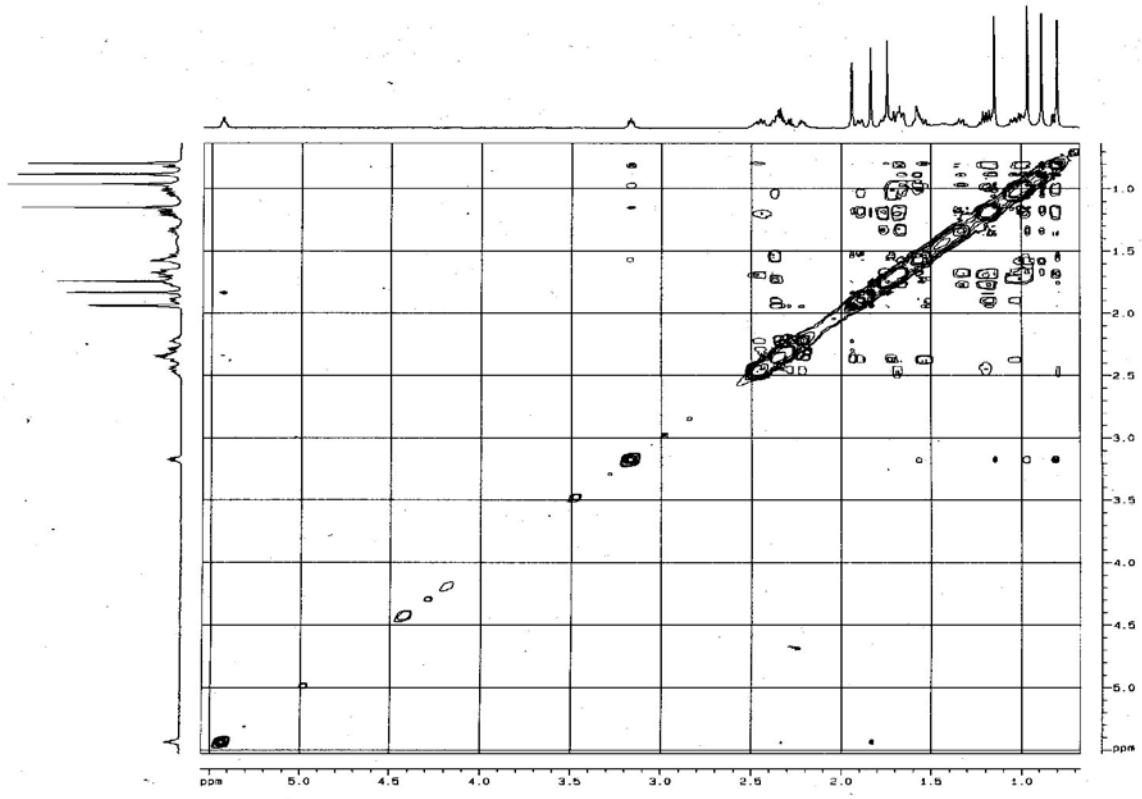


Fig. S6.6. NOESY spectrum of product **25**

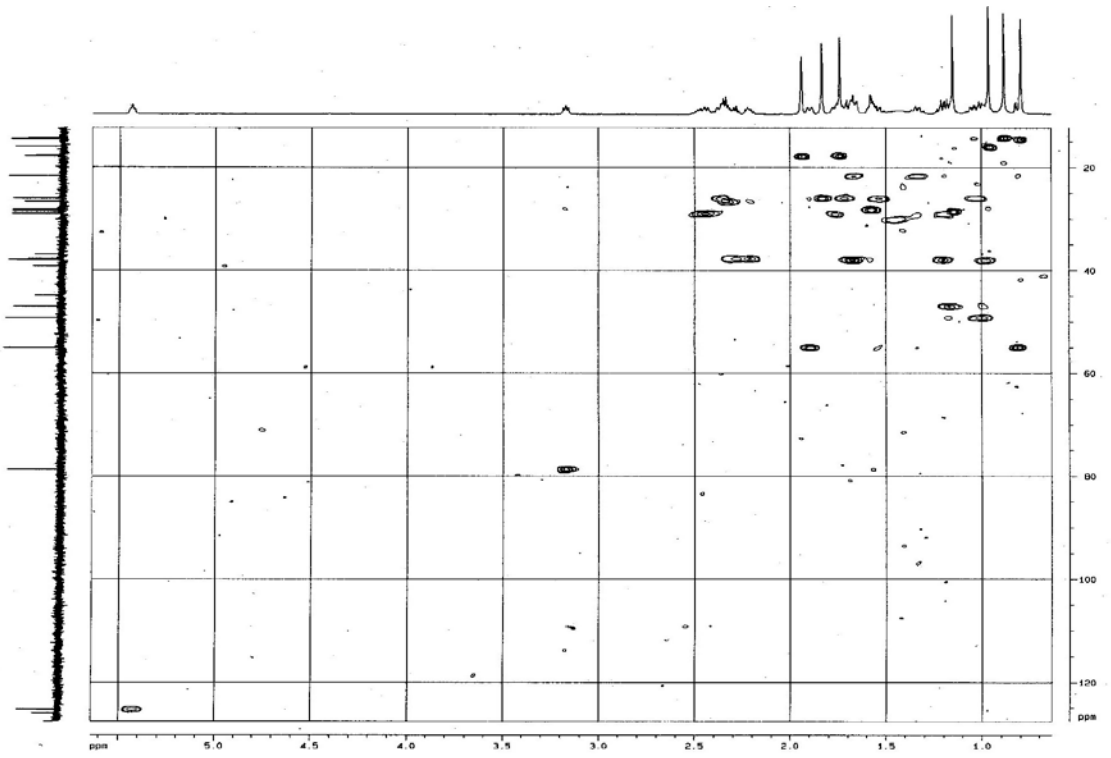


Fig. S6.7. HSQC spectrum of product **25**

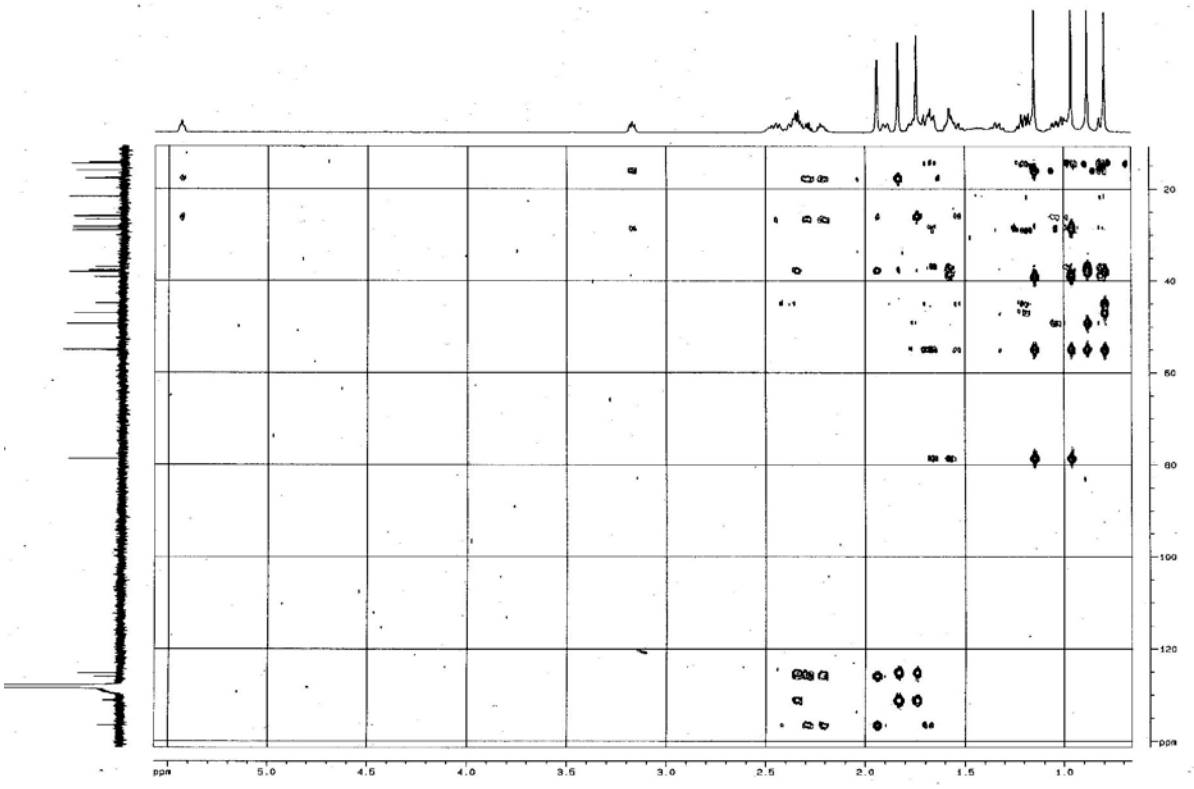
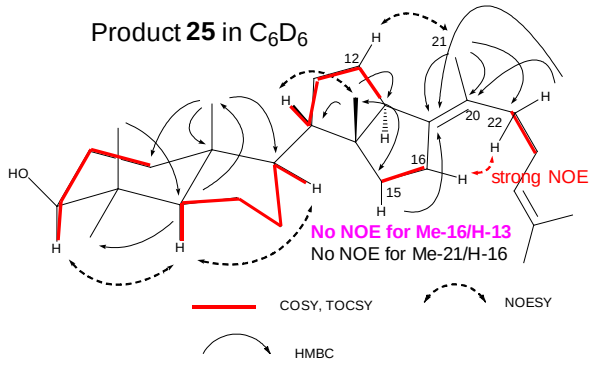
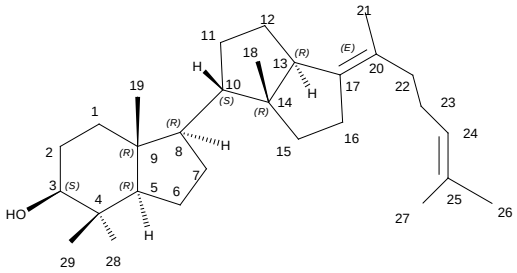


Fig. S6.8. HMBC spectrum of product **25**

Fig. S6.9. Assignments of NMR data of product **25** in C_6D_6, HR-EIMS and optical rotation.





Remark: H-3, δ_H 3.21, but dd, J=11.7 Hz and 4.3 Hz in $CDCl_3$

$[\alpha]_D^{25}$= - 23.7 (*c*= 0.03, $CHCl_3$)

HREIMS ($C_{29}H_{48}O$), Cald: 412.3705; Found: 412.3710

600 MHz, in C_6D_6; the residual solvent peak: δ_H 7.28; δ_C 128.0 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	0.97(m,1H);1.68(m,1H)	**37.95(t)**	9	——	**36.93(s)**	17	——	**136.6(s)**	25	——	**131.0(s)**
2	1.57(m, 2H)	**28.19(t)**	10	1.16 (m, 1H)	**42.01(d)**	18	0.796(s, 3H)	**14.47(q)**	26	1.834 (s, 3H)	**25.96(q)**
3	3.17 (bt, J=8.0 Hz, 1H)	**78.69(d)**	11	1.02(m, 1H); 1.72(m,1H)	**25.88(t)**	19	0.883(s,3H)	**14.24(q)**	27	1.742(s,3H)	**17.65(q)**
4	——	**39.16(s)**	12	1.55(m,1H); 2.35(m,1H)	**26.07(t)**	20	——	**125.9(s)**	28	1.489(s,3H)	**28.52(q)**
5	0.82(m, 1H)	**55.09(d)**[a]	13	1.90 (bd, J=13.0 Hz, 1H)	**55.02(d)**[a]	21	1.940 (bs, 3H)	**17.74(q)**	29	0.963(s,3H)	**15.93(q)**
6	1.33(m,1H); 1.67(m, 1H)	**21.65(t)**	14	——	**44.85 (s)**	22	2.21(m, 1H);2.30(m, 1H)	**37.68(t)**			
7	1.20(m, 1H); 1.77(m, 1H)	**29.06(t)**	15	1.20(m,1H); 1.68(m, 1H)	**38.05(t)**	23	2.35 (m, 2H)	**26.93(t)**			
8	1.00(m, 1H)	**49.27(d)**	16	2.45(m, 2H)	**28.95(t)**	24	5.43(bd, J=6.7 Hz, 1H)	**125.2(d)**			

a) The assignment of C-5 and C-13 may be exchangeable.

Remark. The H-3 showed br triplet splitting patter (Figs. S14.2) in the C_6D_6 solution. However, in the $CDCl_3$ solution, H-3 showed the dd splitting pattern (δ_H 3.21, d, *J*=11.7 Hz and 4.3 Hz), thus strongly indicating that the OH at C-3 is β-oriented. The finding of a clear NOE in the C_6D_6 solution (Fig. S14.6) further supported the β-orientation of 3-OH.

7. EIMS and NMR data of product 26

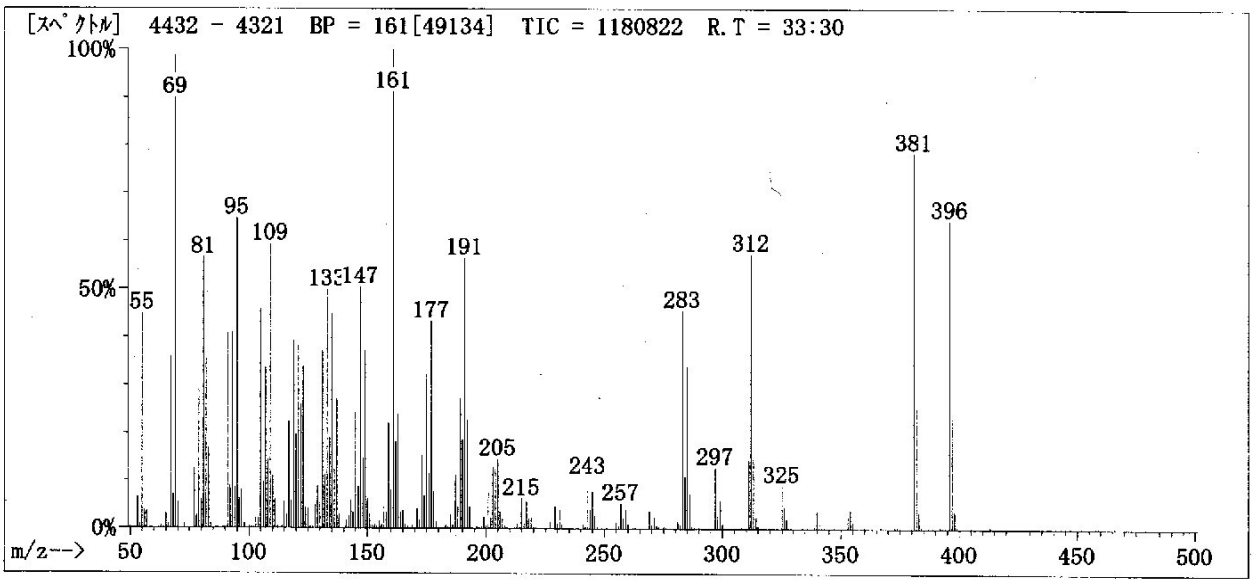


Fig. S7.1. EIMS of product **26**.

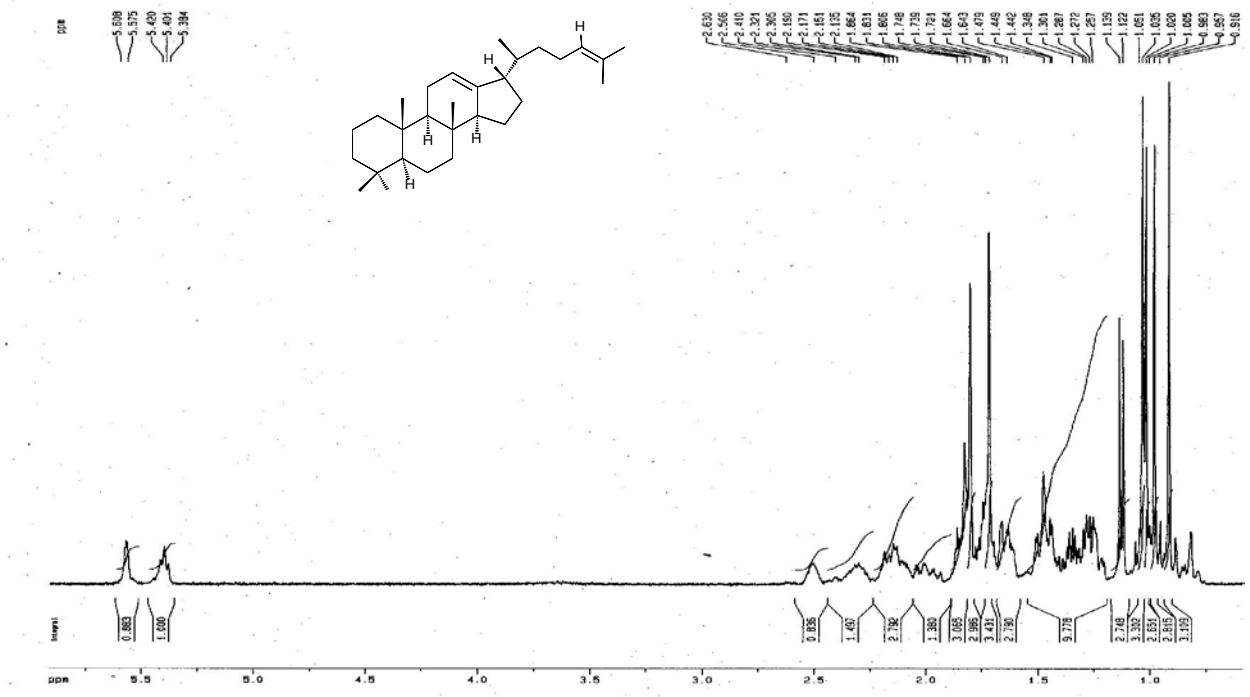


Fig. S7.2.1. ^{1}H NMR spectrum of product **26** (400 MHz, C_6D_6).

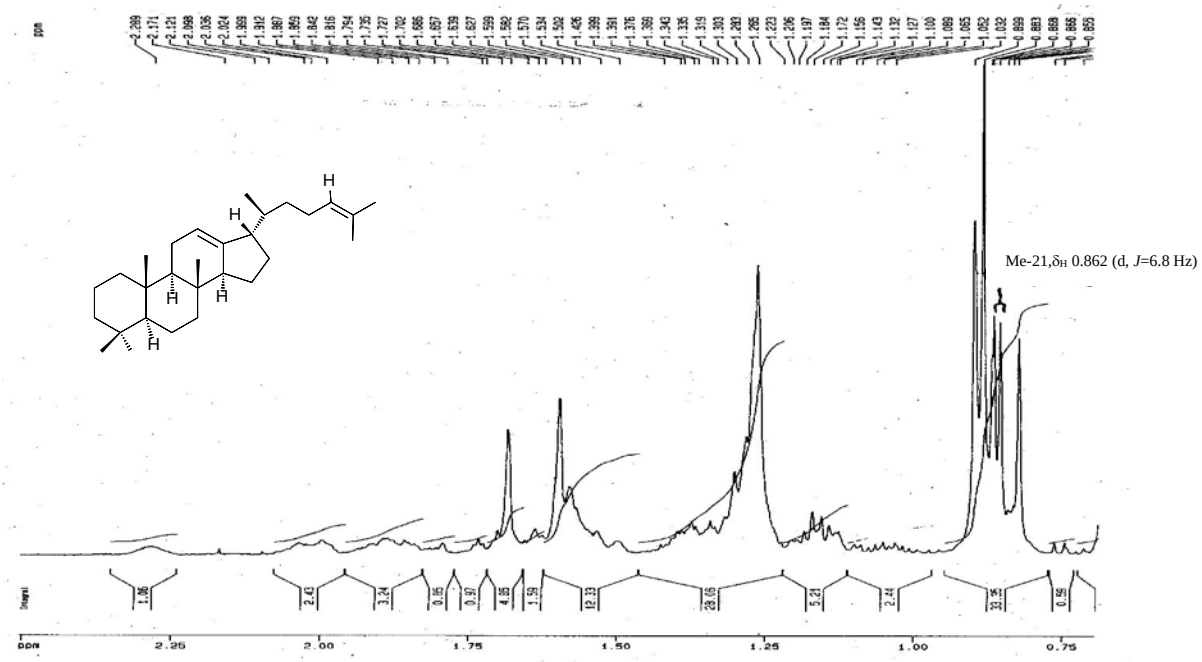


Fig. S7.2.2. ^{1}H NMR spectrum (expanded region) of product **26** (400 MHz, $CDCl_3$)

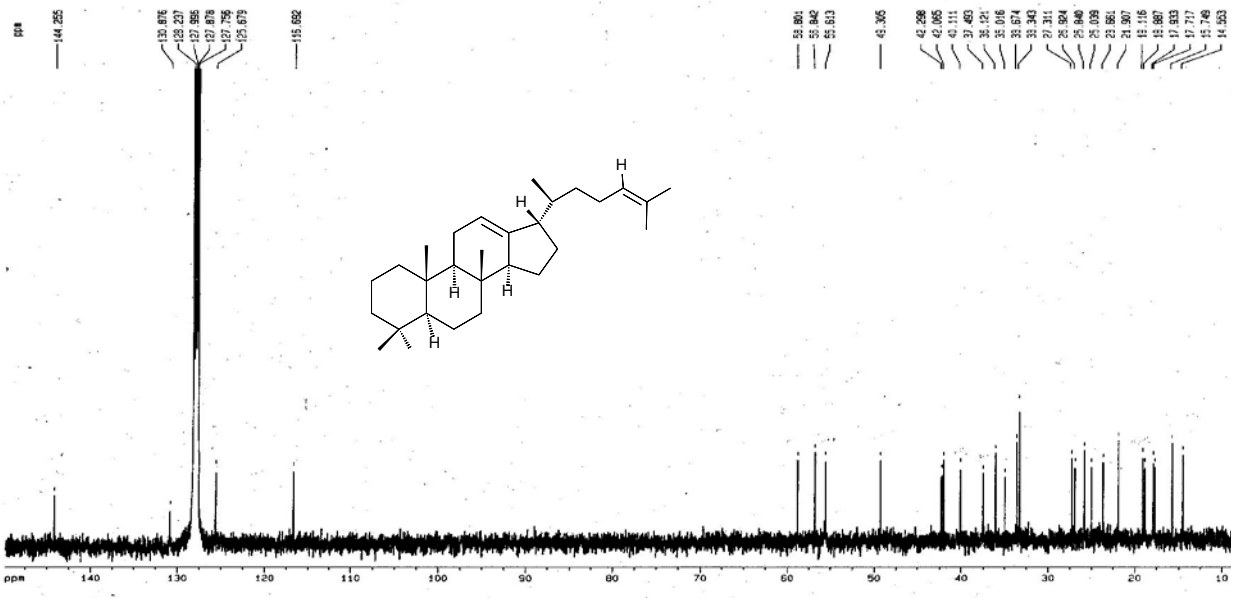


Fig. S7.3. ^{13}C NMR of product **26** (100 MHz, C_6D_6).

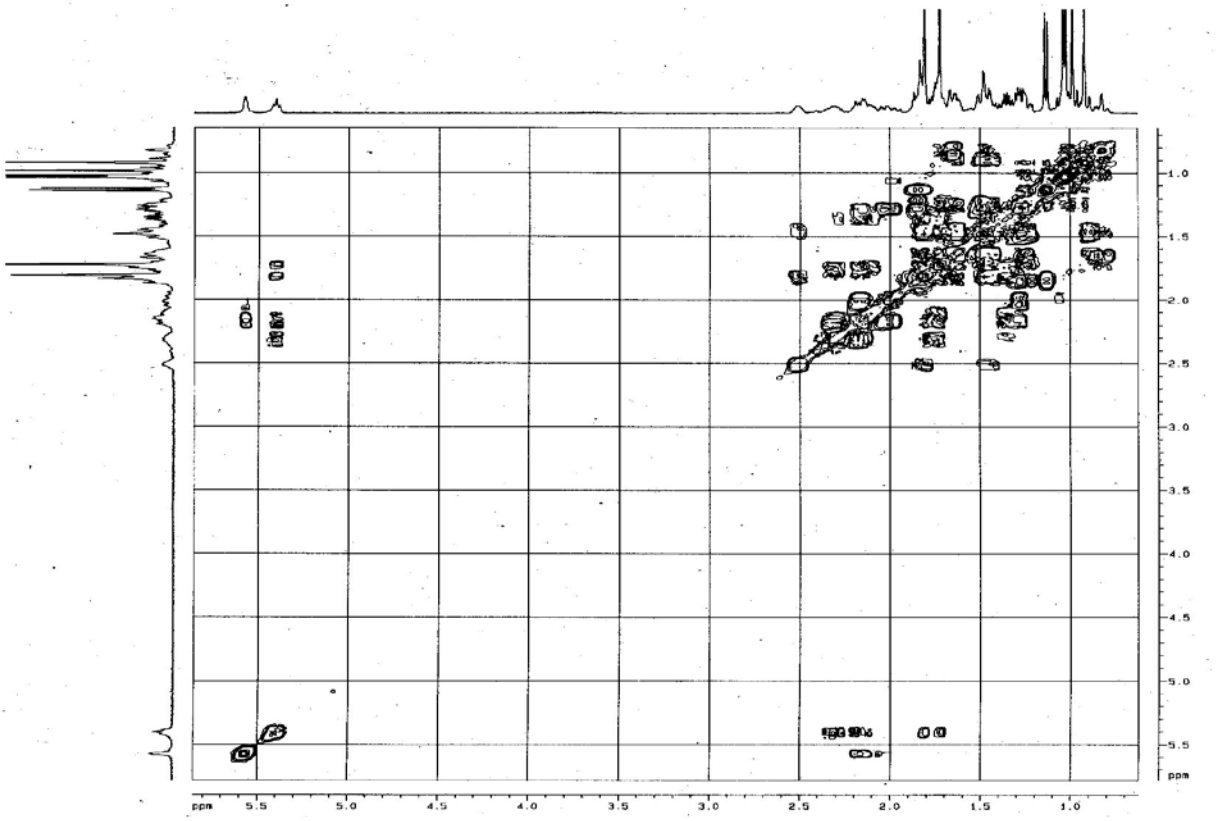


Fig. S7.4. ^{1}H-^{1}H COSY of product **26** (400 MHz, C_6D_6).

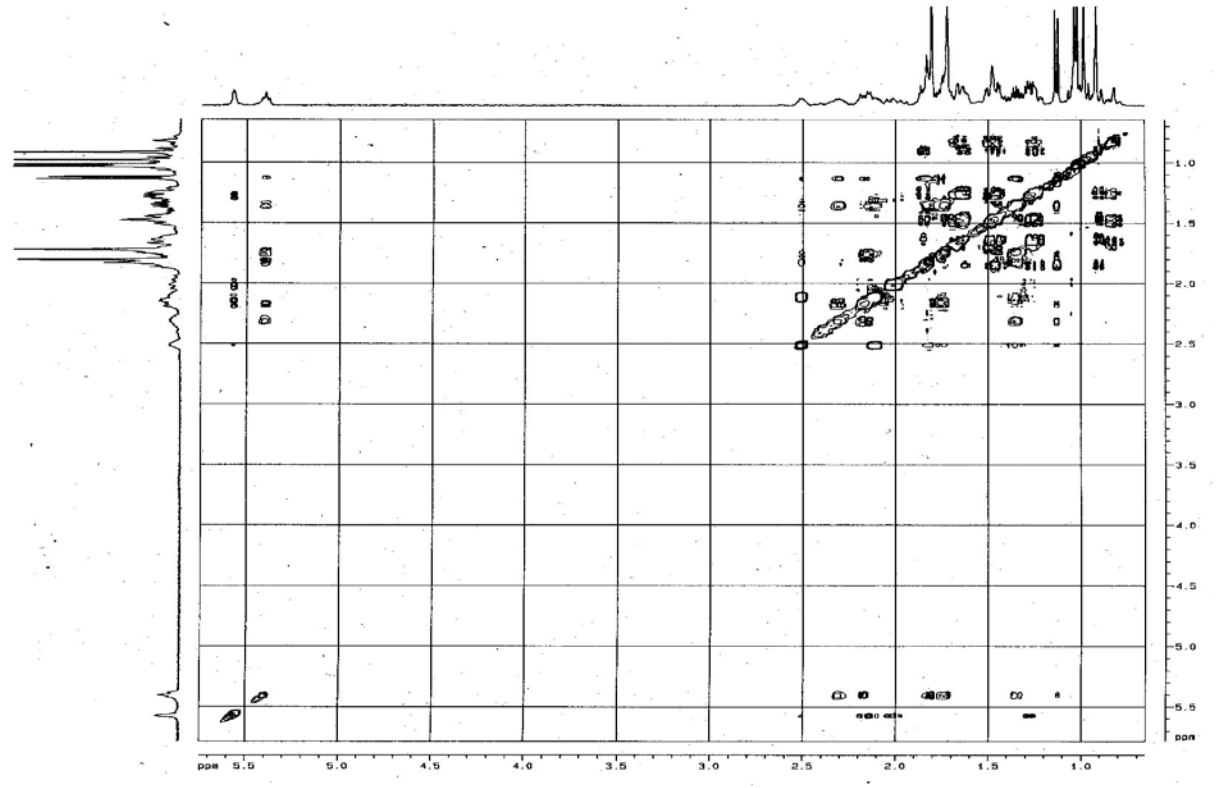


Fig. S7.5. TOCSY of Product **26** (400 MHz, C_6D_6).

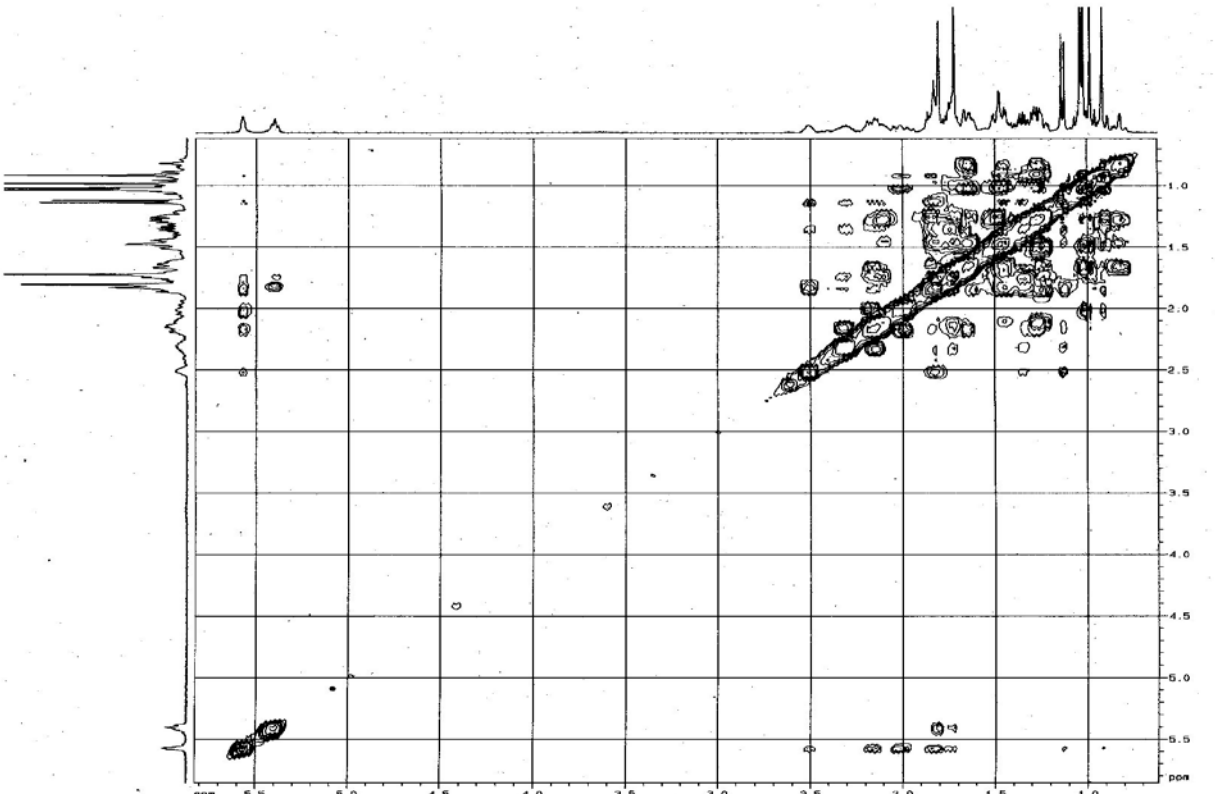


Fig. S7.6. NOESY of Product **26** (400 MHz, C_6D_6).

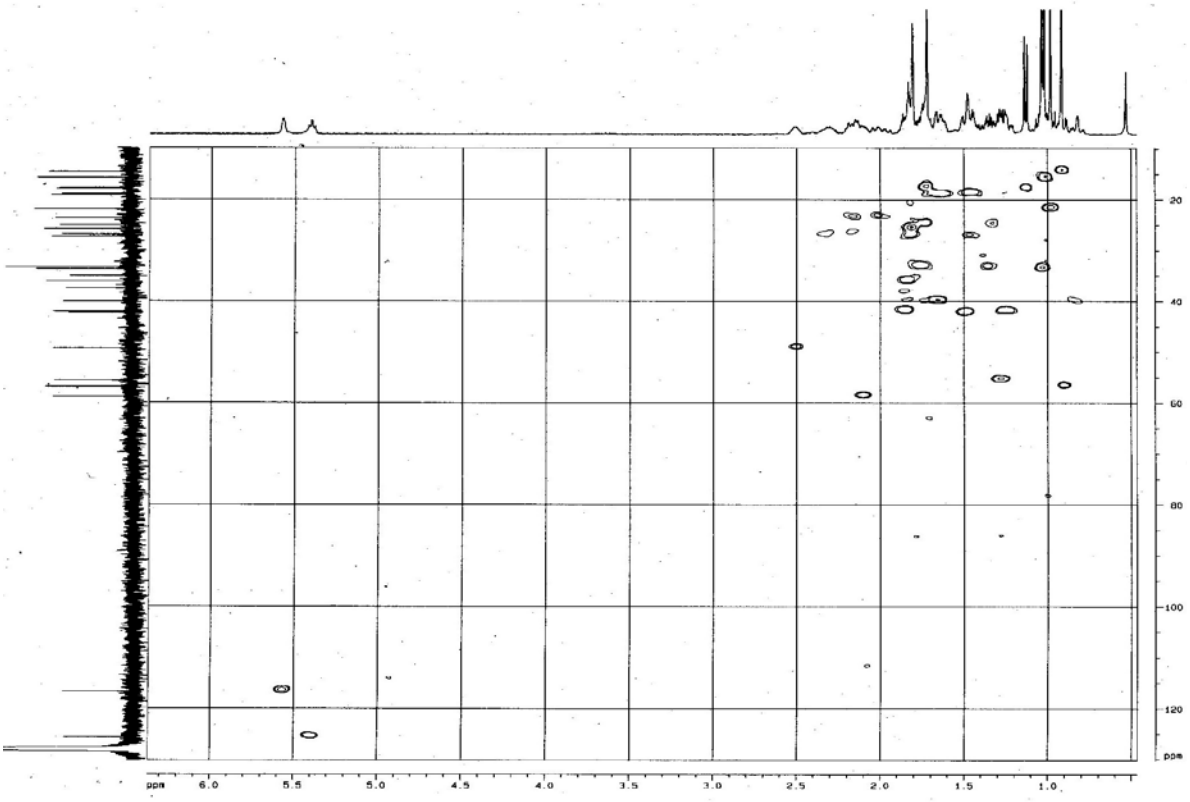


Fig. S7.7. HSQC of Product **26** (400 MHz, C_6D_6).

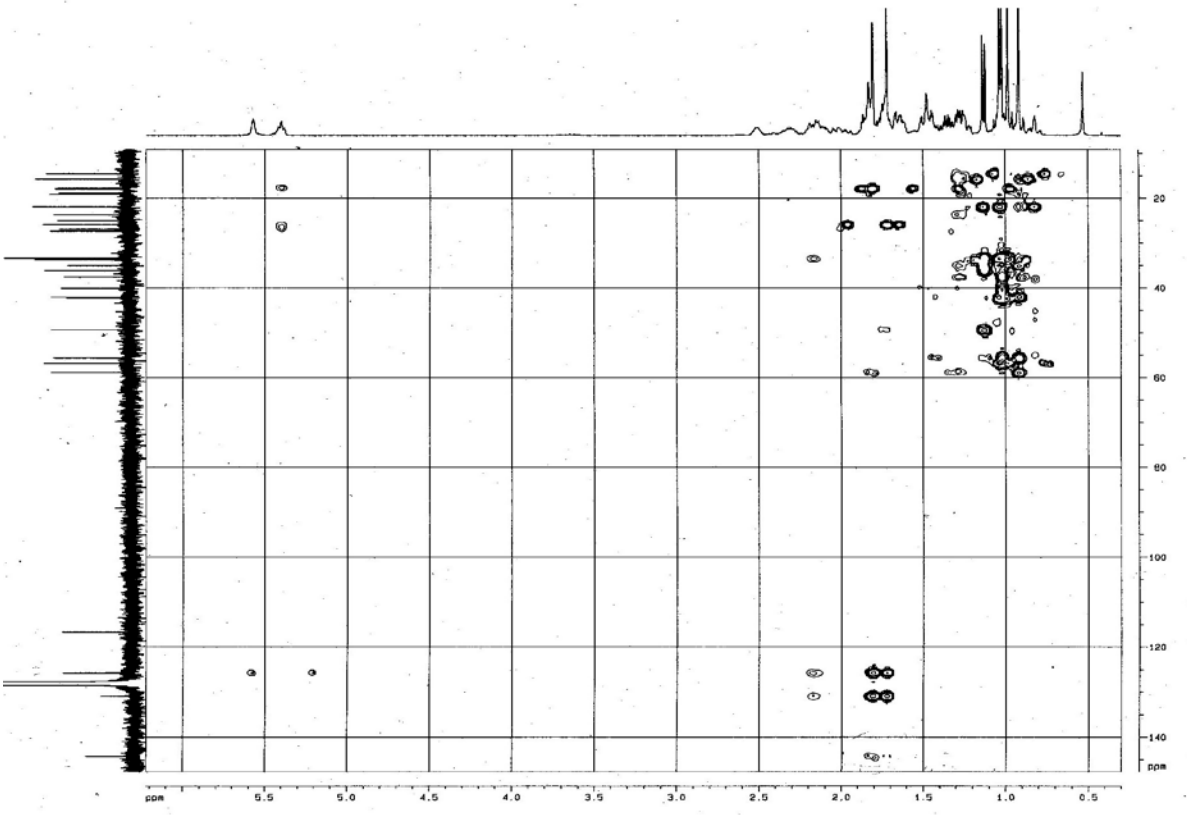
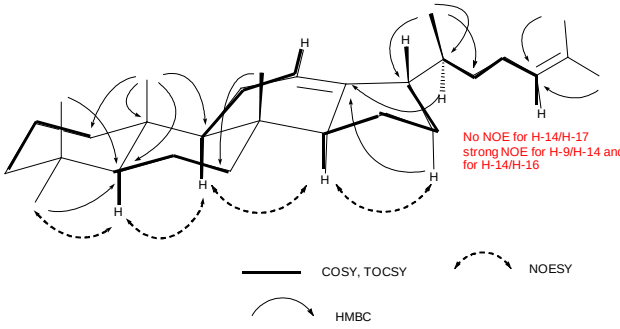
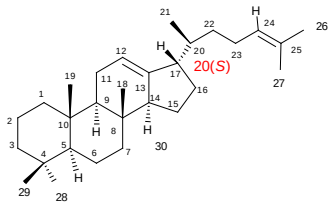


Fig. S7.8. HMBC of Product **26** (400 MHz, C_6D_6).

Product **26** from 28-norSQ (**13b**)





(20*S*)-30-nor-dammara-12(13),24-diene

$[\alpha]_D^{25}$= + 14.2 (c= 0.058, $CHCl_3$)

HREIMS ($C_{29}H_{48}$), Cald 396.3756; Found 396.3764

400 MHz, in C_6D_6; the residual solvent peak: δ_H 7.28; δ_C 128.0 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	0.83(m,1H) ;1.65(m,1H)	**40.11(t)**	9	1.28 (m, 1H)	**55.61(d)**	17	2.51 (m, 1H)	**49.30(d)**	24	5.40(t, J=7.2 Hz, 1H)	**125.7(d)**
2	1.45(m,1H); 1.64(m, 1H)	**18.89(t)**[a]	10	——	**37.49(s)**	18	0.916(s, 3H)	**14.55(q)**	25	——	**130.9(s)**
3	1.47(m, 2H)	**42.30(t)**	11	2.02(m, 1H); 2.17(m,1H)	**23.66(t)**	19	1.020(s, 3H)	**15.75(q)**	26	1.806(s, 3H)	**25.84(q)**
4	——	**33.34(s)**	12	5.58 (bs,1H)	**116.7(d)**	20	1.84 (m, 1H)	**36.12(d)**	27	1.721 (s, 3H)	**17.72(q)**
5	0.91 (m, 1H)	**56.84(d)**	13	——	**142.2(s)**	21	1.130(d, J=6.8Hz, 3H)	**17.93(q)**	28	1.035(s,3H)	**33.67(q)**
6	1.45(m,1H); 1.64(m, 1H)	**19.12(t)**[a]	14	2.10 (m, 1H)	**58.80 (d)**	22	1.37(m, 1H); 1.77(m, 1H)	**33.34(t)**	29	0.983(s,3H)	**21.91(q)**
7	1.23(m, 1H); 1.84(m, 1H)	**42.06(t)**	15	1.34(m,1H); 1.73(m, 1H)	**25.04(t)**	23	2.17(m,1H); 2.34(m,1H)	**26.92(t)**			
8	——	**35.01(s)**	16	1.47(m,1H);1.82(m, 1H)	**27.31(t)**						

Me-27: δ_H=0.862 (d, *J*=6.8 Hz) in $CDCl_3$, which is indicative of 18-*S* stereochemistry.

Fig. S7.9. Assignments of NMR data of product **26** in C_6D_6, HR-EIMS and optical rotation.

8. EIMS and NMR data of product 27.

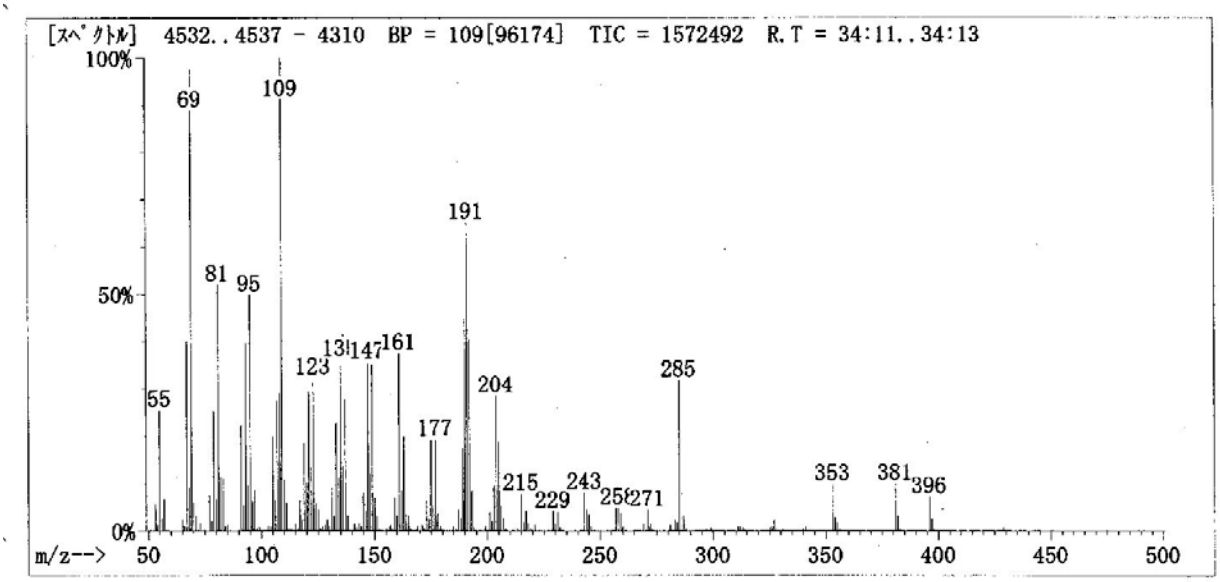


Fig. S8.1. EIMS of product **27**.

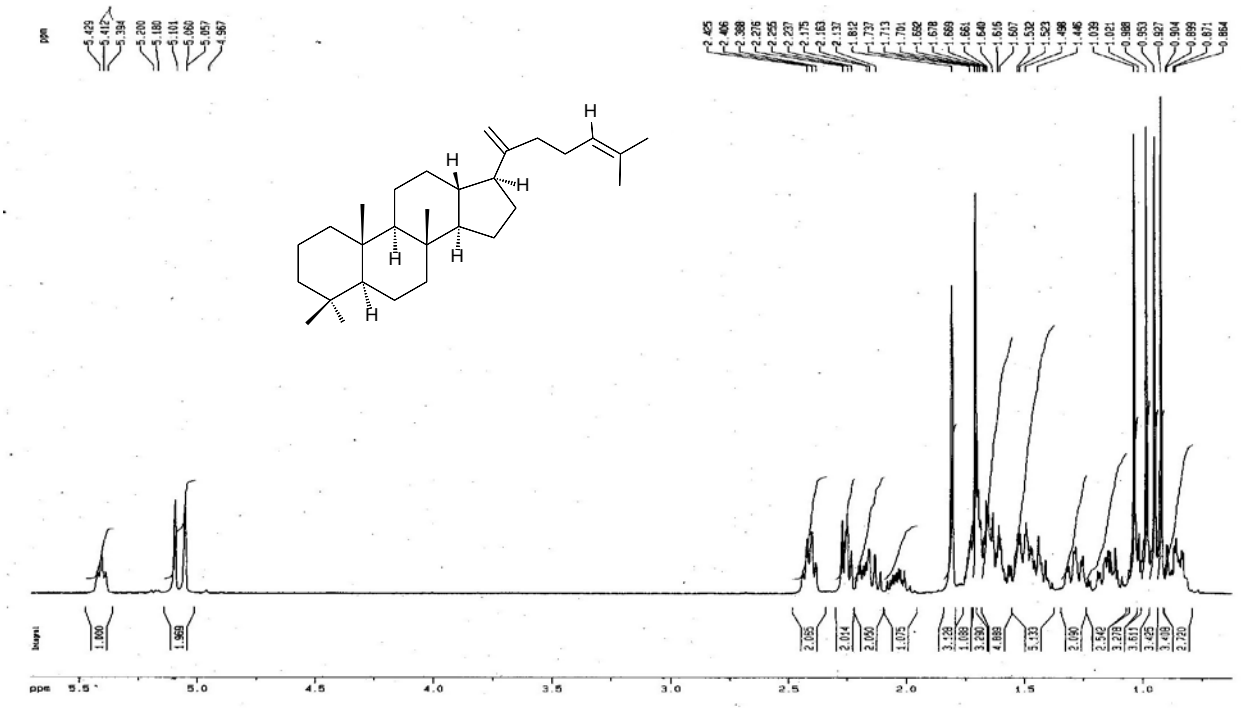


Fig. S8.2. ^{1}H NMR of Product **27** (400 MHz, C_6D_6).

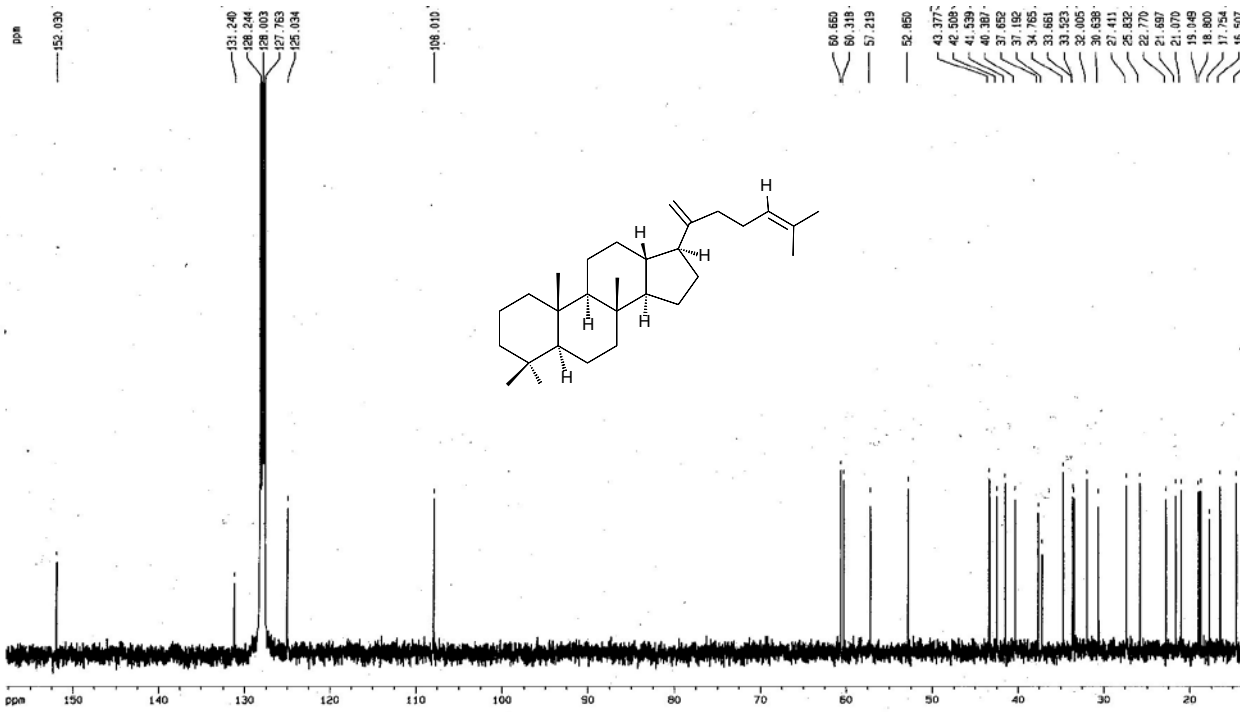


Fig. S8.3. ^{13}C NMR of Product **27** (100 MHz, C_6D_6).

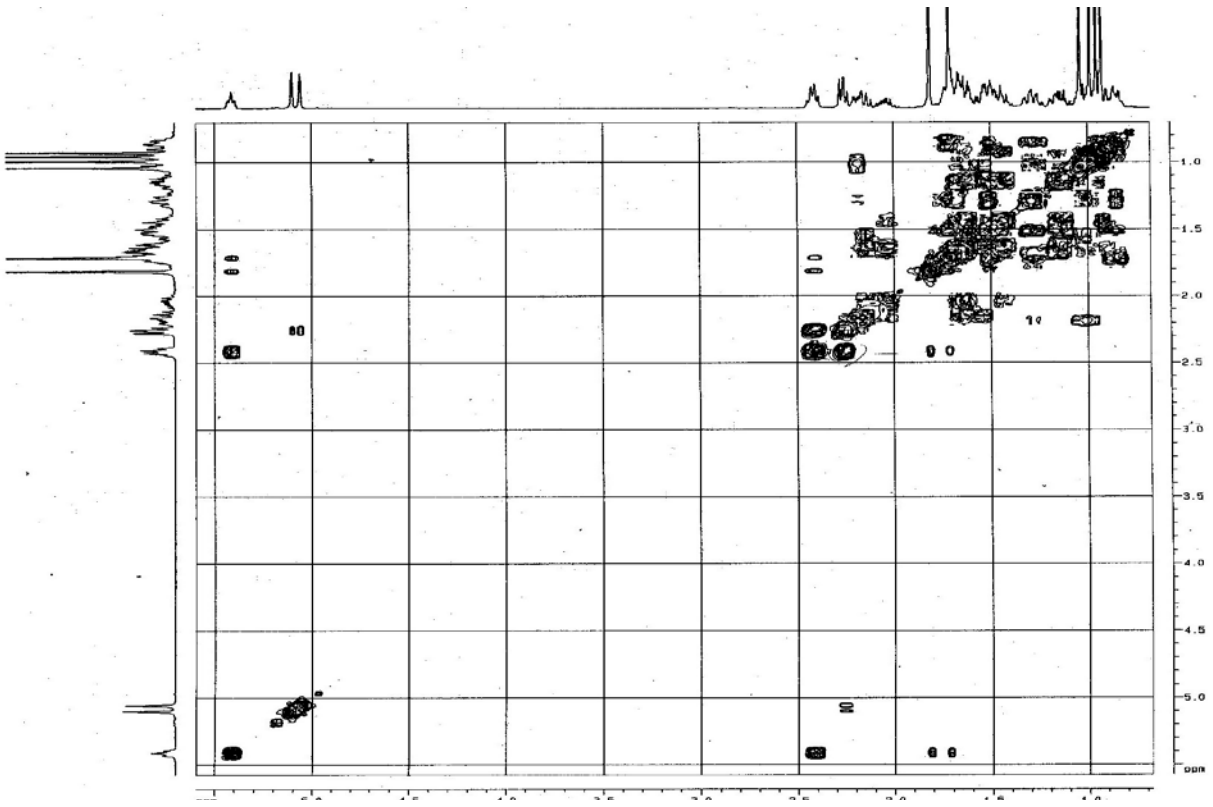


Fig. S8.4. ^{1}H-^{1}H COSY of product **27** (400 MHz, C_6D_6).

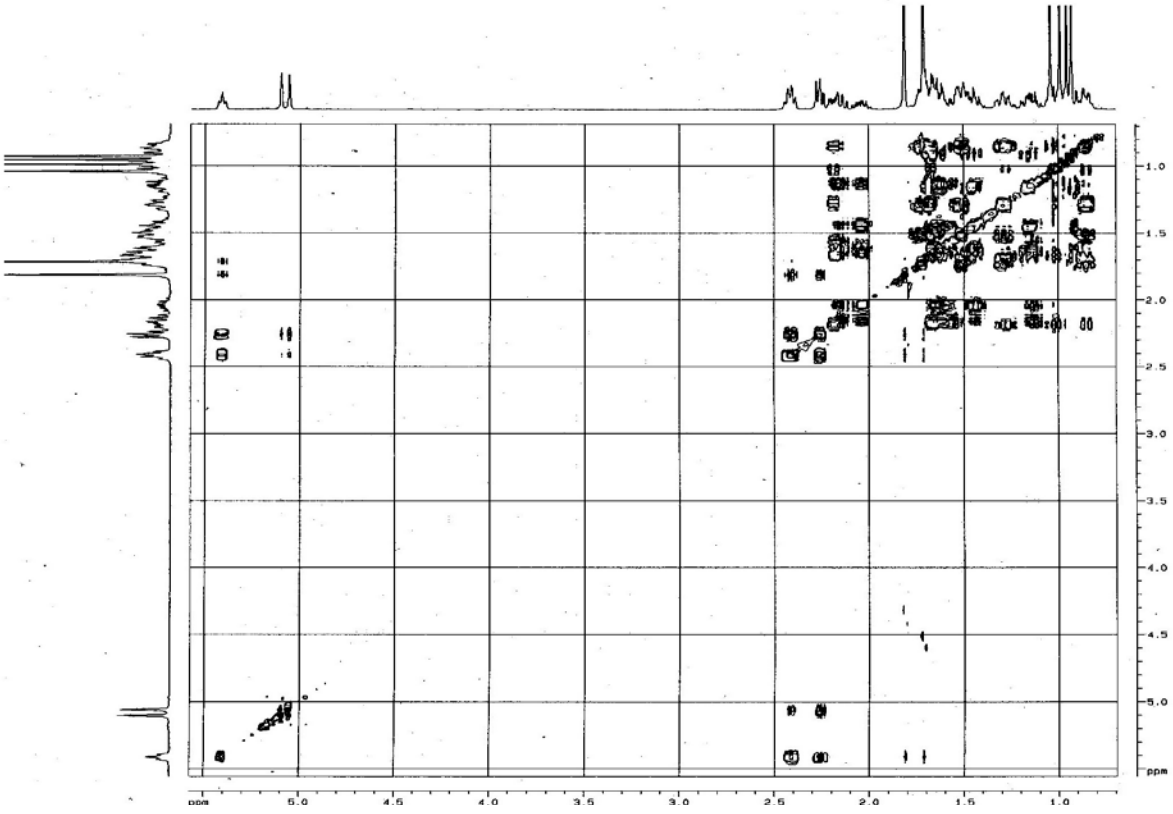


Fig. S8.5. TOCSY of **27** (400 MHz, C_6D_6).

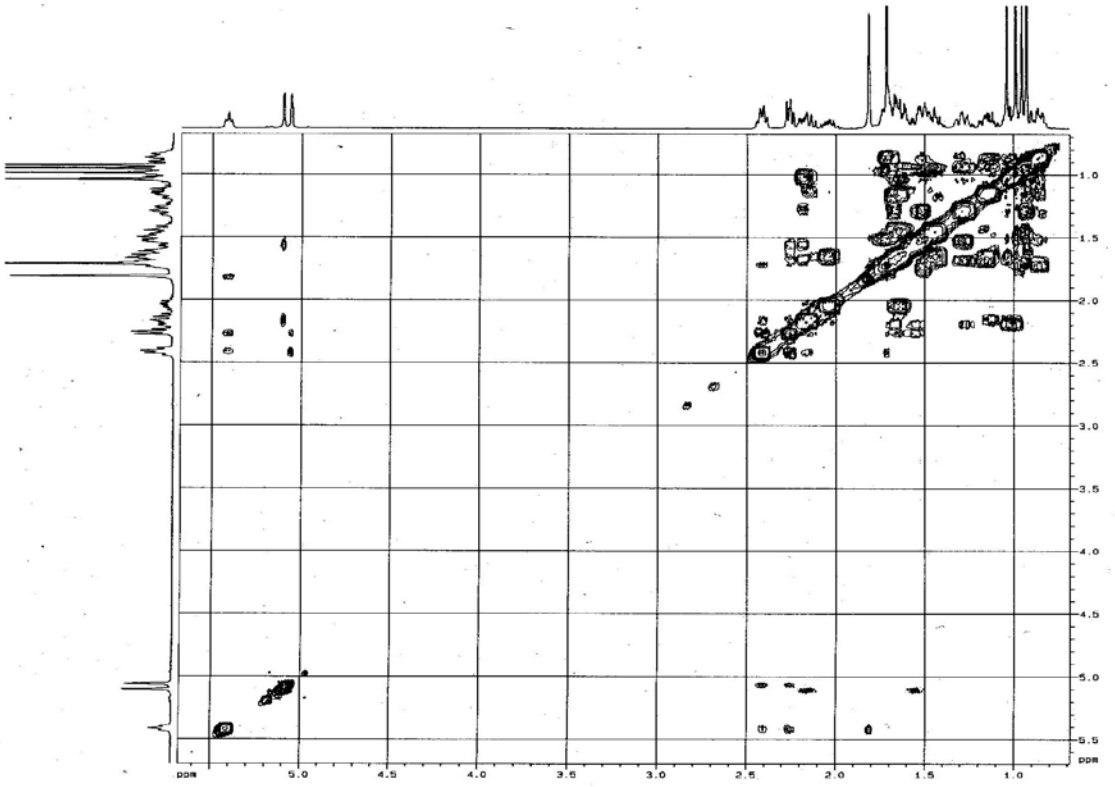


Fig. S8.6. NOESY of **27** (400 MHz, C_6D_6).

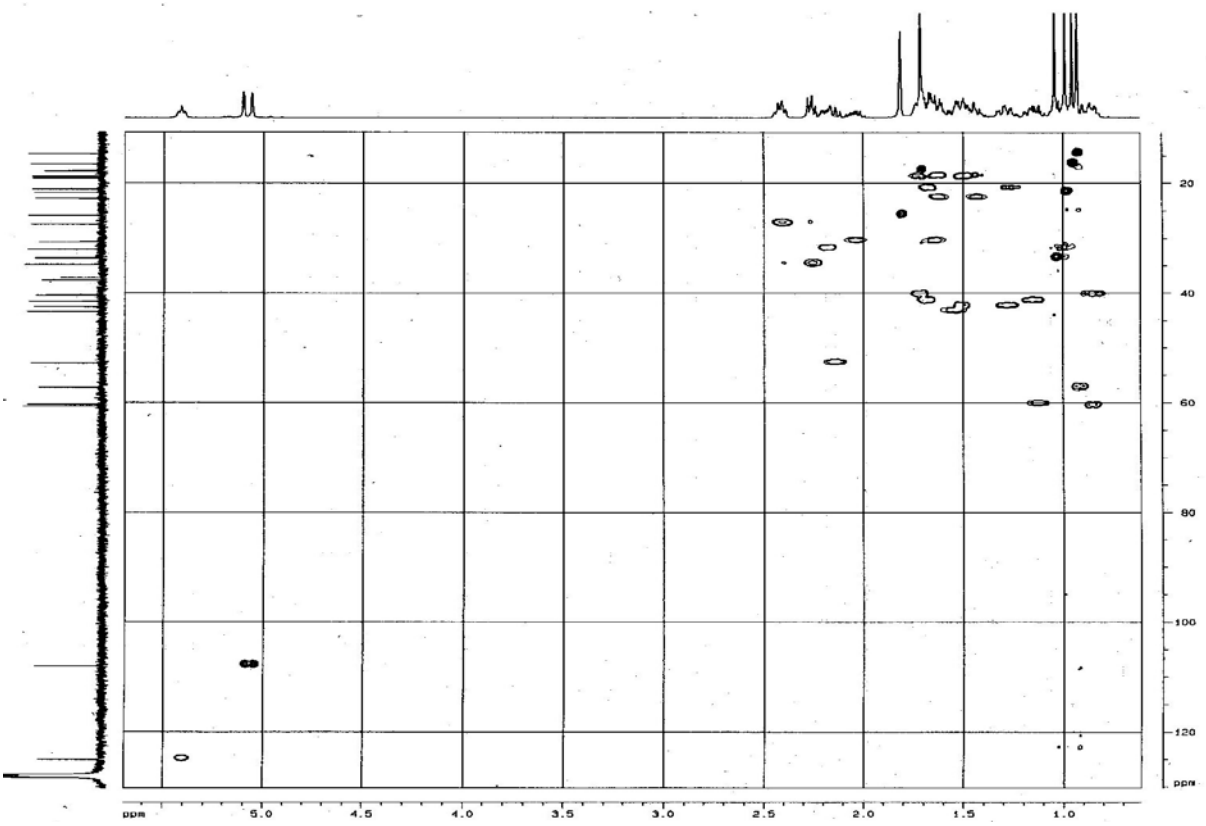


Fig. S8.7. HSQC of **27** (400 MHz, C_6D_6).

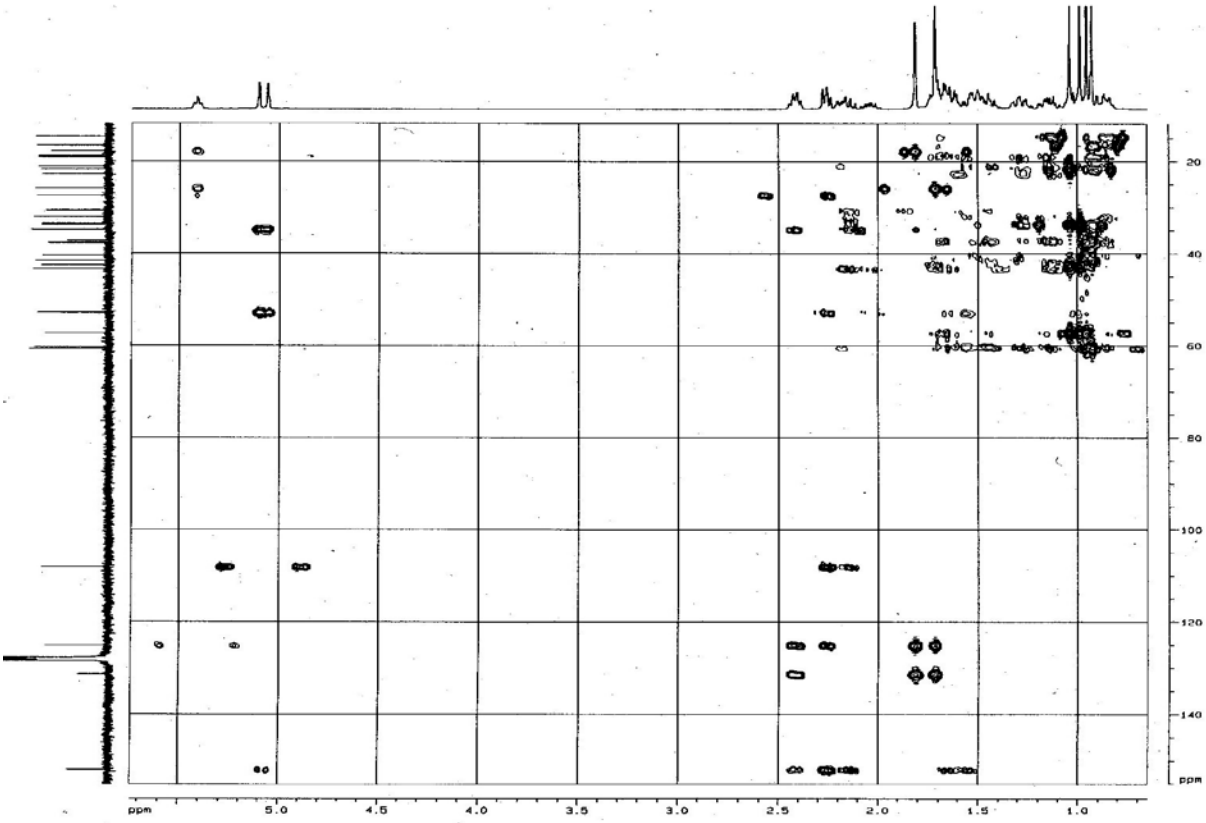
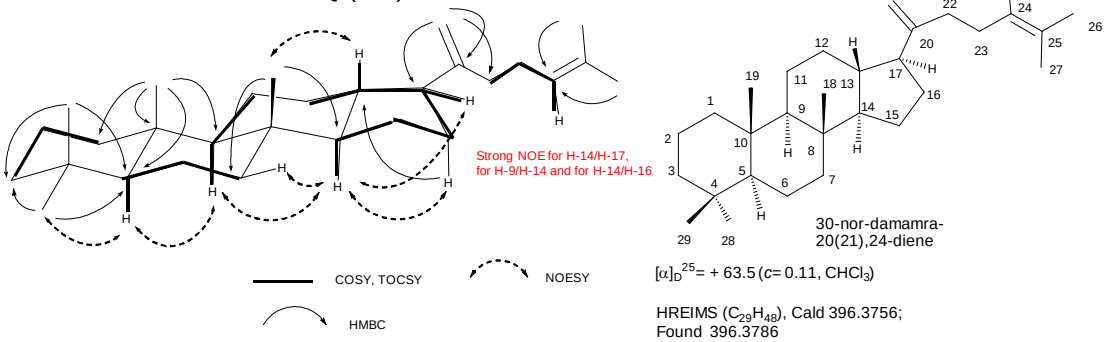


Fig. S8.8. HMBC of **27** (400 MHz, C_6D_6).

Product **27**from 28-norSQ (**13b**)



$[\alpha]_D^{25}$= + 63.5 (c= 0.11, $CHCl_3$)

HREIMS ($C_{29}H_{48}$), Cald 396.3756;
Found 396.3786

400 MHz, in C_6D_6; the residual solvent peak: δ_H 7.28; δ_C 128.0 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	0.86(m,1H);1.72(m,1H)	**40.39(t)**	9	0.86 (m, 1H)	**60.66(d)**	17	2.14 (m, 1H)	**52.85(d)**	24	5.41(t, *J*=6.8 Hz, 1H)	**125.0(d)**
2	1.46(m,1H); 1.73(m, 1H)	**19.05(t)**	10	——	**37.65(s)**	18	0.927(s, 3H)	**14.61(q)**	25	——	**131.2(s)**
3	1.27(m, 1H);1.51 (m,1H)	**42.51(t)**	11	1.26(m, 1H); 1.67(m,1H)	**21.07(t)**	19	0.953(s,3H)	**16.50(q)**	26	1.812(s,3H)	**25.83(q)**
4	——	**33.52(s)**	12	0.99(m,1H); 2.18(m, 1H)	**32.00(t)**	20	——	**152.0(s)**	27	1.713 (s, 3H)	**17.75(q)**
5	0.91 (m, 1H)	**57.22(d)**	13	1.56 (m, 1H)	**43.38(d)**	21	5.06(bs, 1H); 5.10(brs, 1H)	**108.0(t)**	28	1.039(s,3H)	**33.66(q)**
6	1.50(m,1H); 1.64(m, 1H)	**18.80(t)**	14	1.13 (m, 1H)	**60.32 (d)**	22	2.25(m, 2H)	**34.76(t)**	29	0.983(s,3H)	**21.70(q)**
7	1.13(m, 1H); 1.68(m, 1H)	**41.54(t)**	15	1.43(m,1H); 1.63(m, 1H)	**22.77(t)**	23	2.41(m,2H)	**27.41(t)**			
8	——	**37.19(s)**	16	1.65(m,1H);2.05(m,1H)	**30.64(t)**						

Fig. S8.9. Assignments of NMR data of product **27** in C_6D_6, HR-EIMS and optical rotation.

9. EIMS and NMR data of product 28.

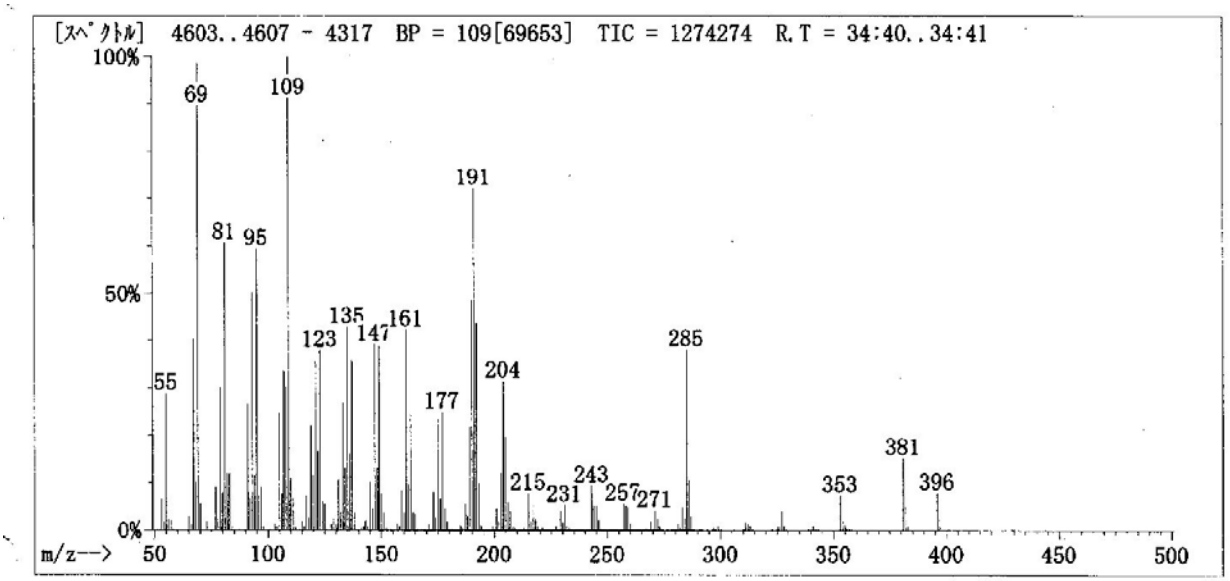


Fig. S9.1. EIMS of product **28**.

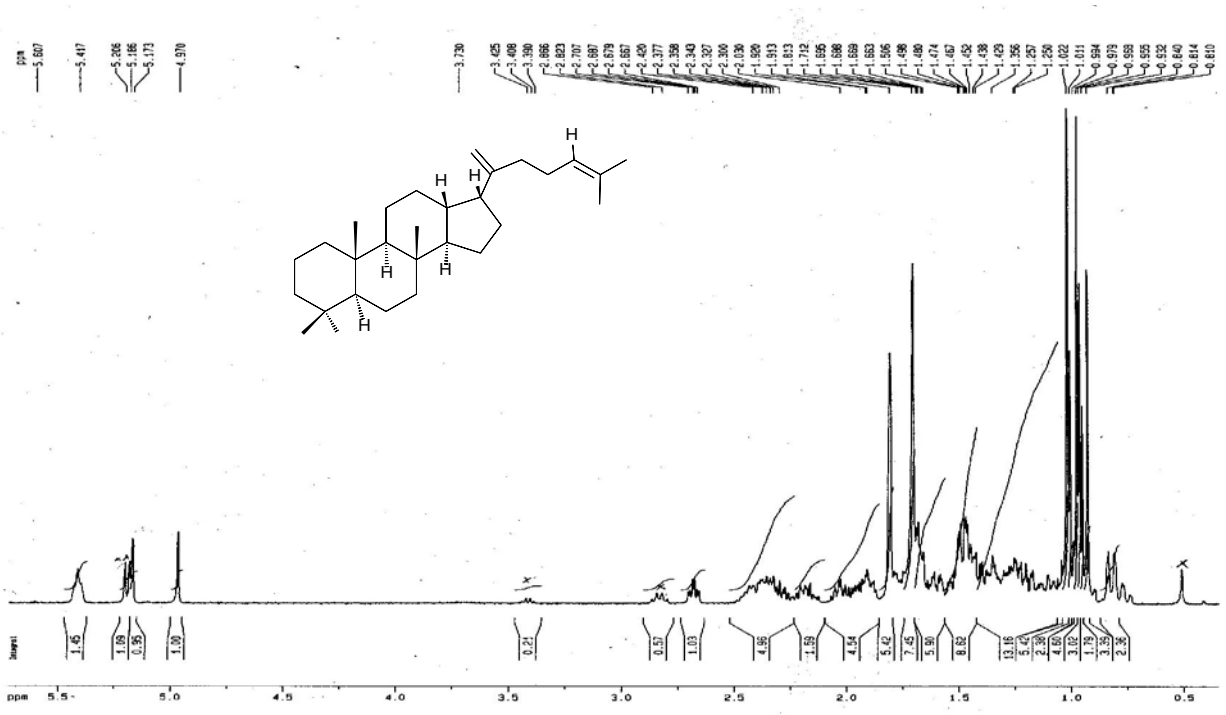


Fig. S9.2. ^{1}H NMR of Product **28** (400 MHz, C_6D_6).

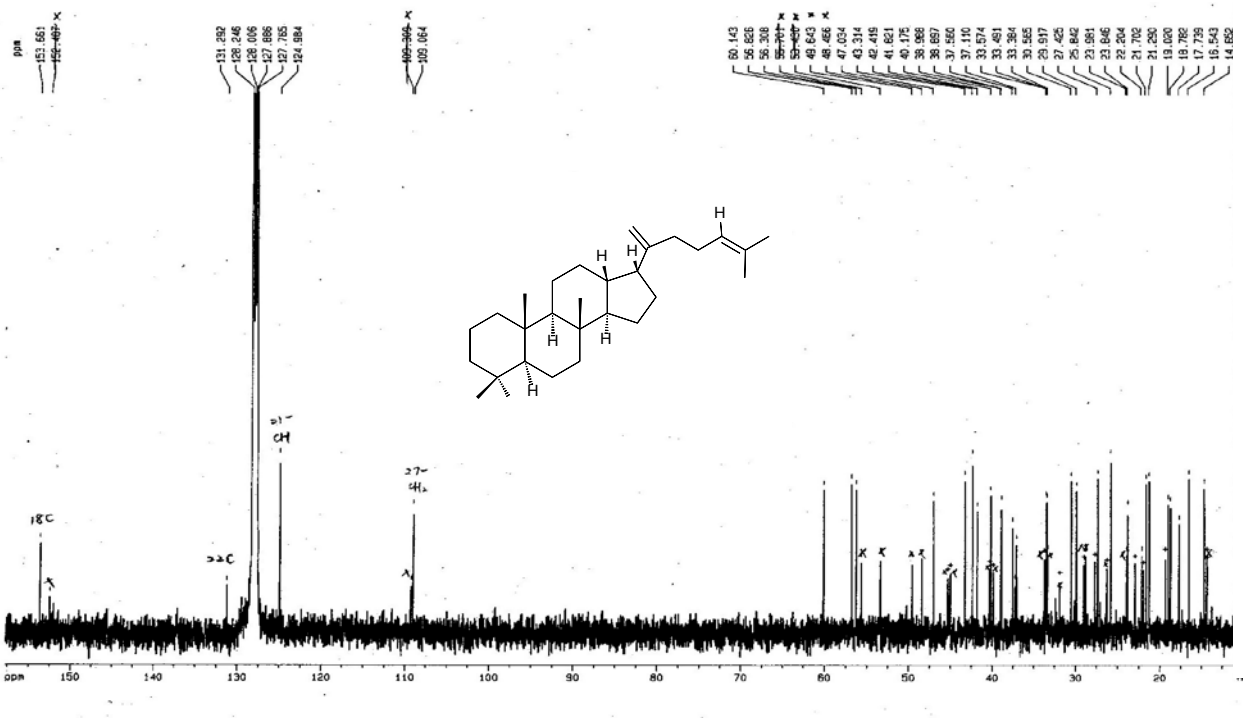


Fig. S9.3. ^{13}C NMR of Product **28** (100 MHz, C_6D_6).

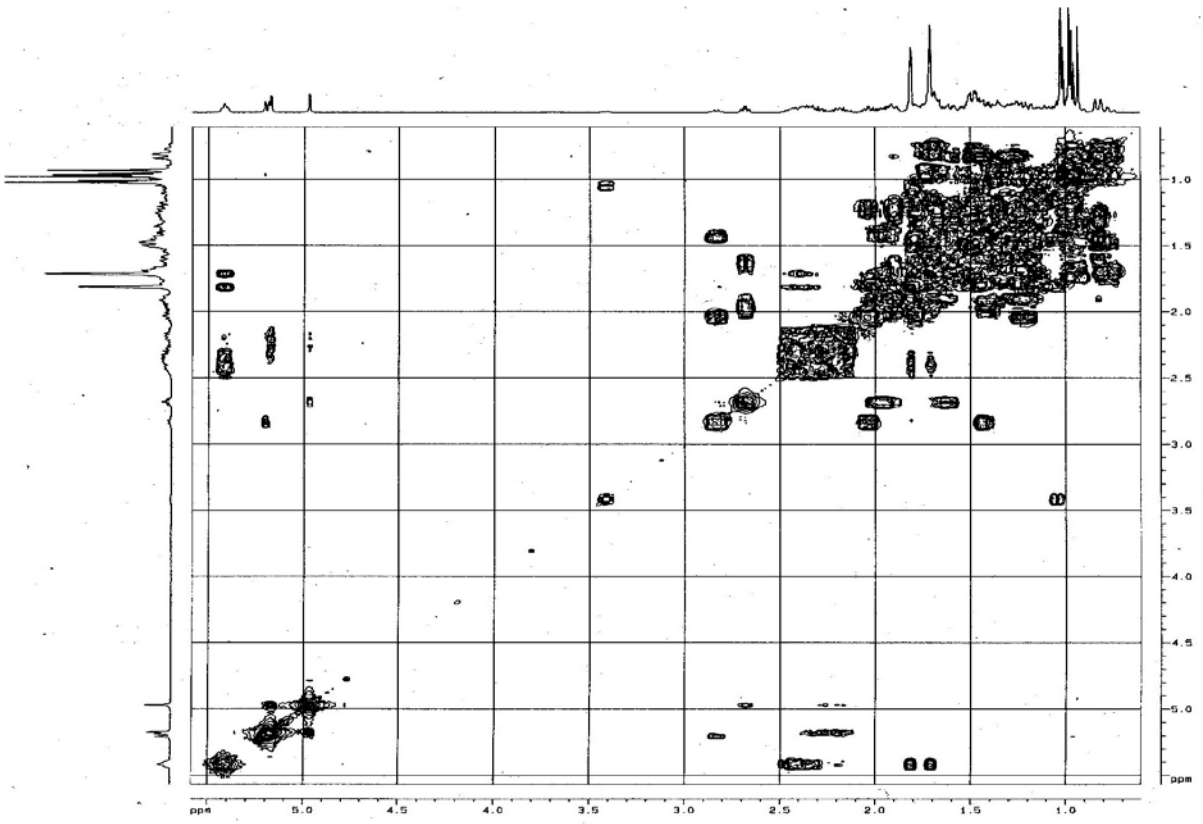


Fig. S9.4. ^{1}H-^{1}H COSY of product **28** (400 MHz, C_6D_6).

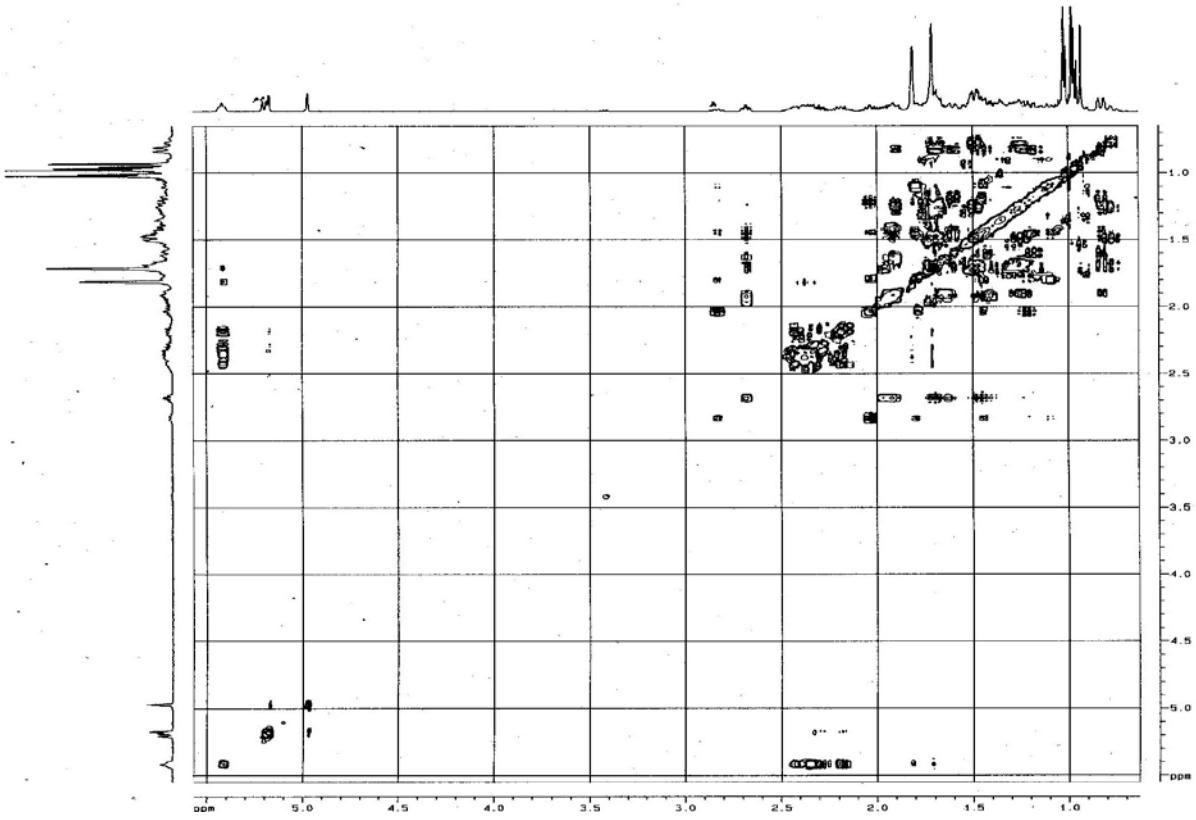


Fig. S9.5. TOCSY of **28** (400 MHz, C_6D_6).

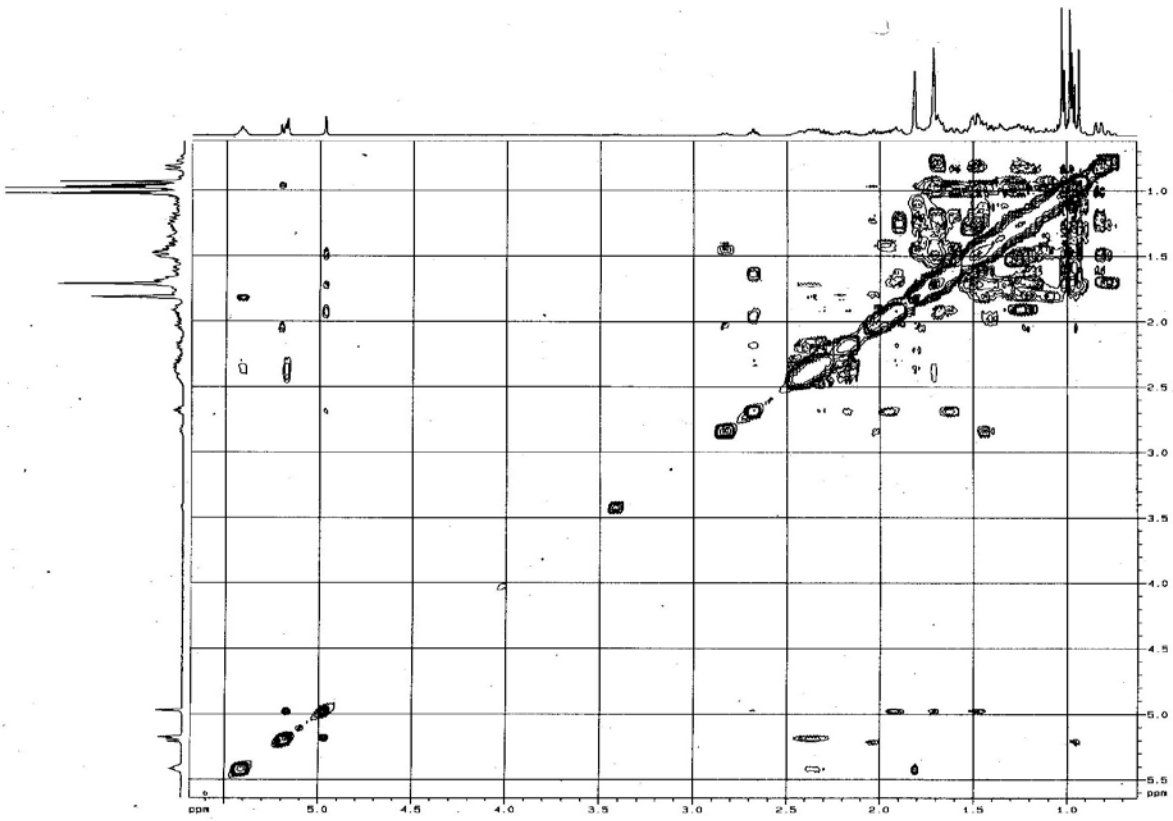


Fig. S9.6. NOESY of **28** (400 MHz, C_6D_6).

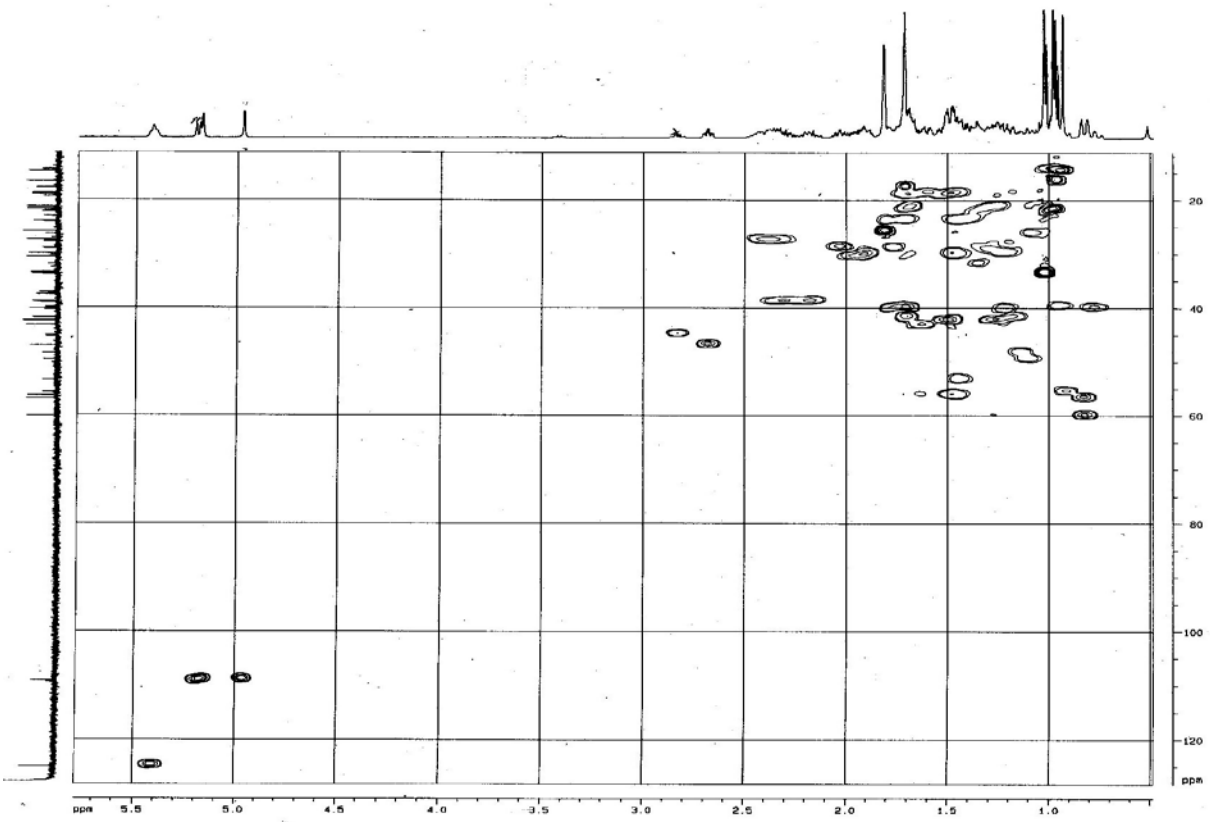


Fig. S9.7. HSQC of **28** (400 MHz, C_6D_6).

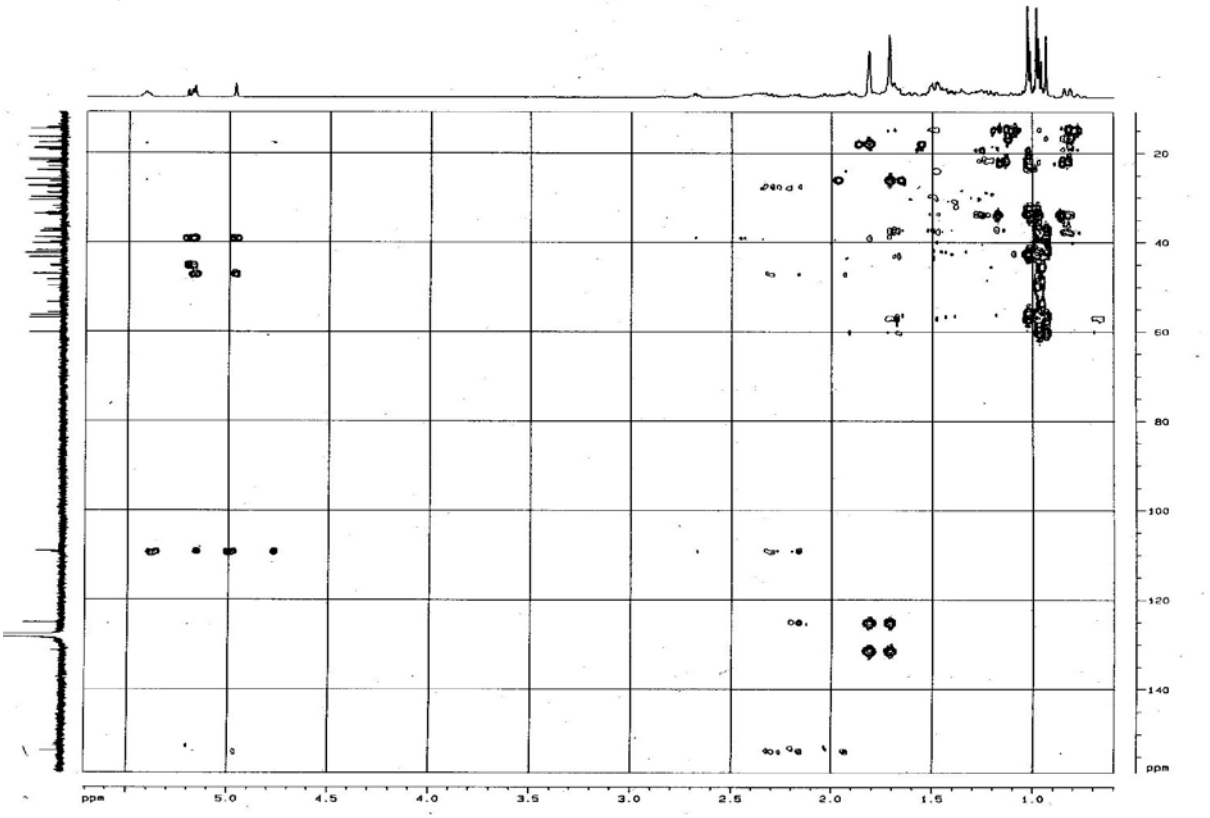
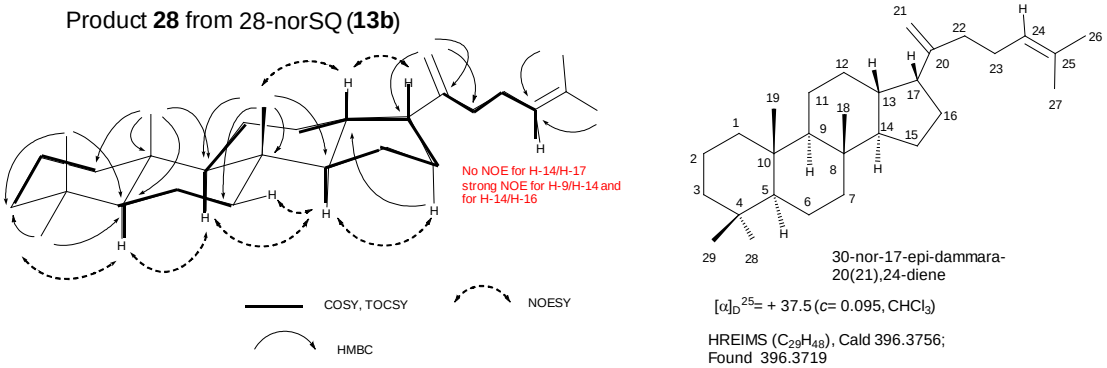


Fig. S9.8. HMBC of **28** (400 MHz, C_6D_6).



400 MHz, in C_6D_6; the residual solvent peak: δ_H 7.28; δ_C 128.0 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	0.78(m,1H);1.70(m,1H)	**40.18(t)**	9	0.82 (m, 1H)	**60.14(d)**	17	2.68 (dt, *J*=3.2, 8.0Hz, 1H)	**47.03(d)**	24	5.42(t, *J*=6.8 Hz, 1H)	**125.0(d)**
2	1.47(m,1H); 1.69(m, 1H)	**19.02(t)**	10	——	**37.56(s)**	18	0.932(s,3H)	**14.65(q)**	25	——	**131.3(s)**
3	1.27(m, 1H);1.49 (m,1H)	**42.42(t)**	11	1.26(m, 1H); 1.67(m,1H)	**21.29(t)**	19	0.968(s,3H)	**16.54(q)**	26	1.813(s,3H)	**25.84(q)**
4	——	**33.49(s)**	12	1.22(m,1H); 1.91(m, 1H)	**29.92(t)**	20	——	**153.7(s)**	27	1.712 (s, 3H)	**17.74(q)**
5	0.93 (m, 1H)	**56.83(d)**	13	1.62 (m, 1H)	**43.31(d)**	21	4.97(bs, 1H); 5.17(brs, 1H)	**109.0(t)**	28	1.022(s,3H)	**33.57(q)**
6	1.43(m,1H); 1.57(m, 1H)	**18.78(t)**	14	1.47 (m, 1H)	**56.31 (d)**	22	2.17(m, 1H);2.32(m, 1H)	**38.90(t)**	29	0.979(s,3H)	**21.70(q)**
7	1.16(m, 1H); 1.69(m, 1H)	**41.82(t)**	15	1.43(m,1H); 1.76(m, 1H)	**23.84(t)**	23	2.38(m,2H)	**27.42(t)**			
8	——	**37.11(s)**	16	1.68(m,1H);1.98(m, 1H)	**30.56(t)**						

Fig. S9.9. Assignments of NMR data of product **28** in C_6D_6, HR-EIMS and optical rotation.

10. EIMS and NMR data of product 29.

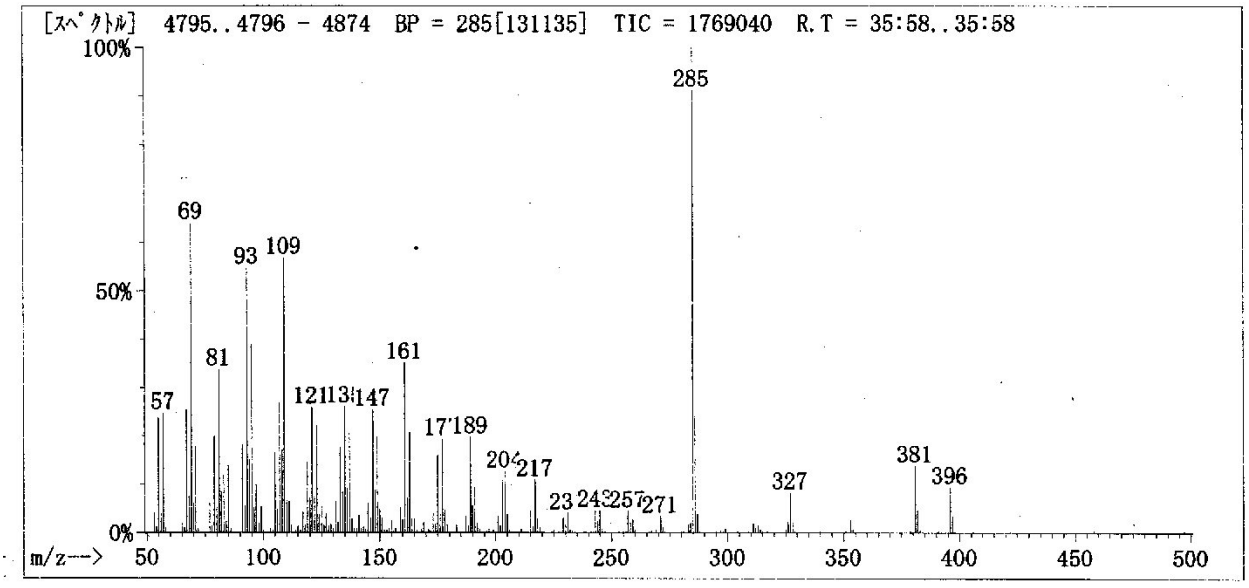


Fig. S10.1. EIMS of product **29**.

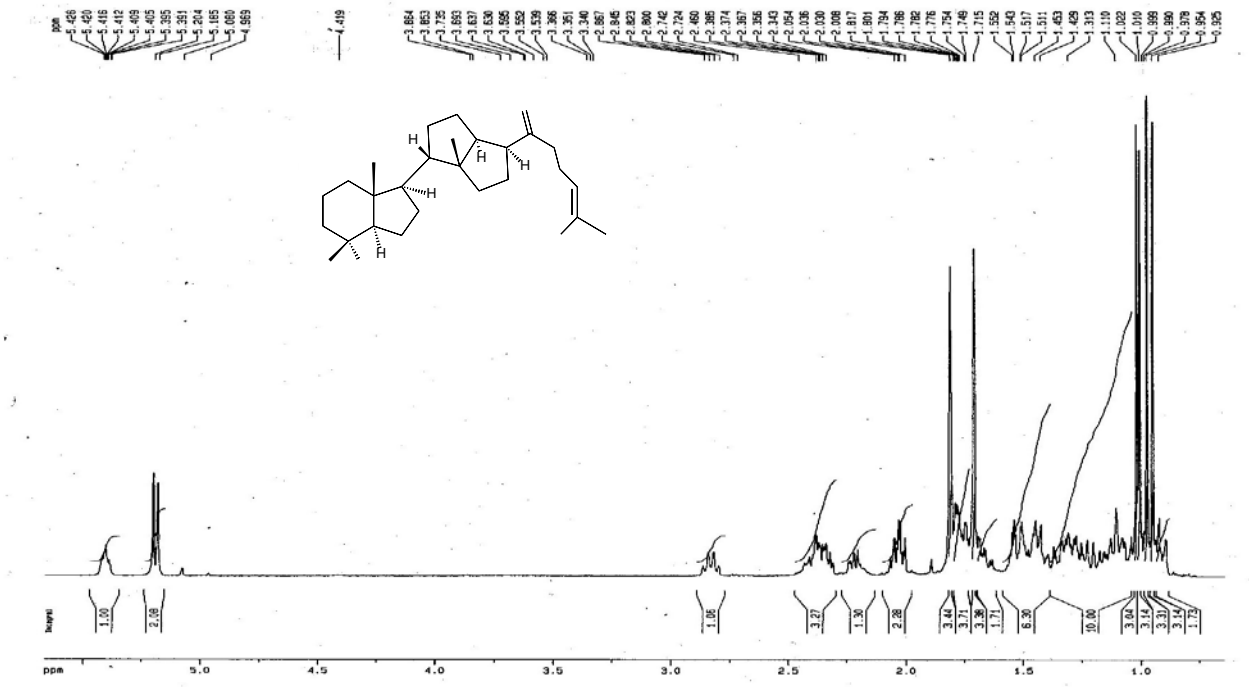


Fig. S10.2. ^{1}H NMR of Product **29** (400 MHz, C_6D_6).

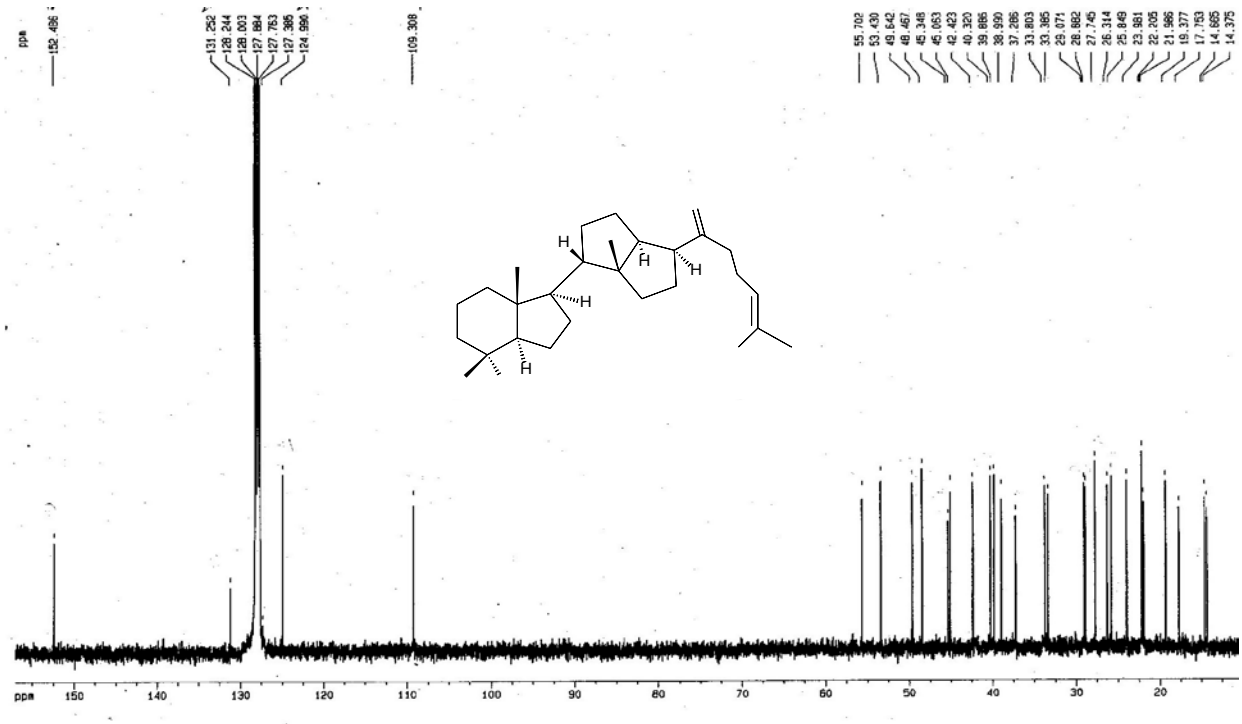


Fig. S10.3. ^{13}C NMR of Product **29** (100 MHz, C_6D_6).

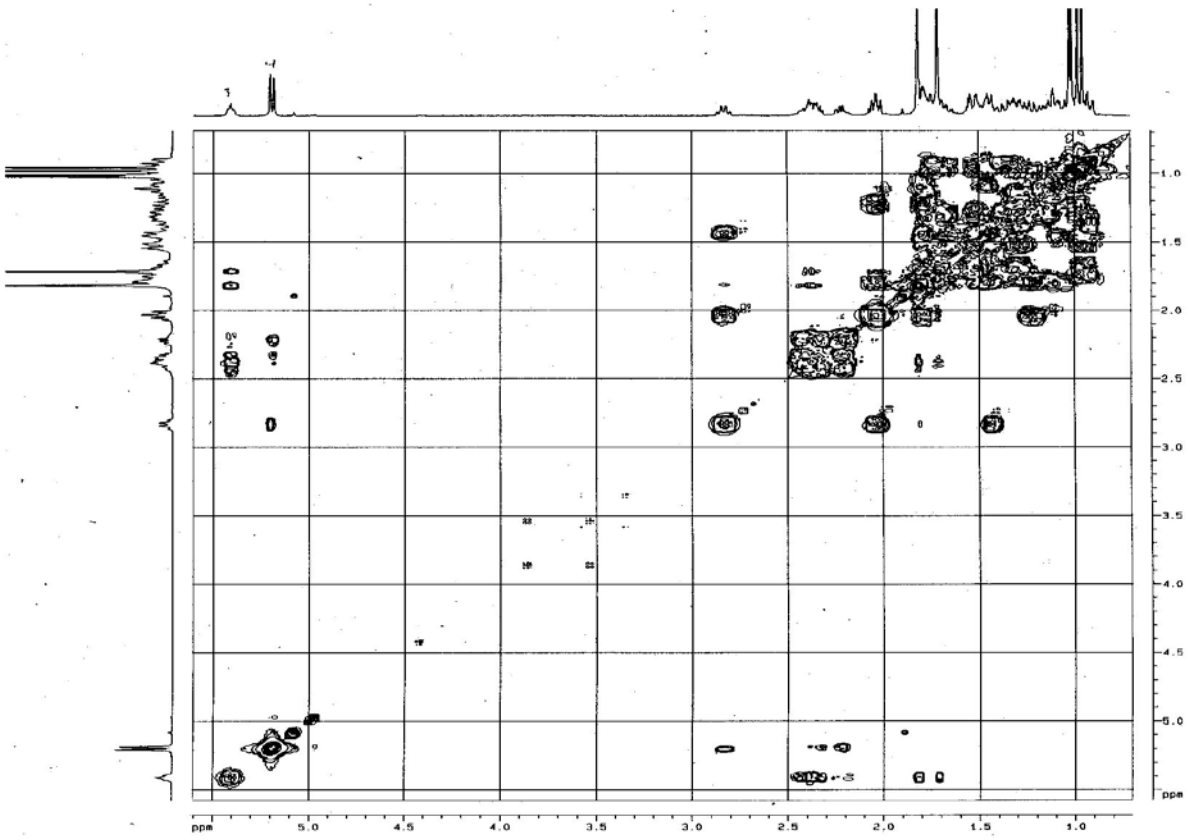


Fig. S10.4. ^{1}H-^{1}H COSY of product **29** (400 MHz, C_6D_6).

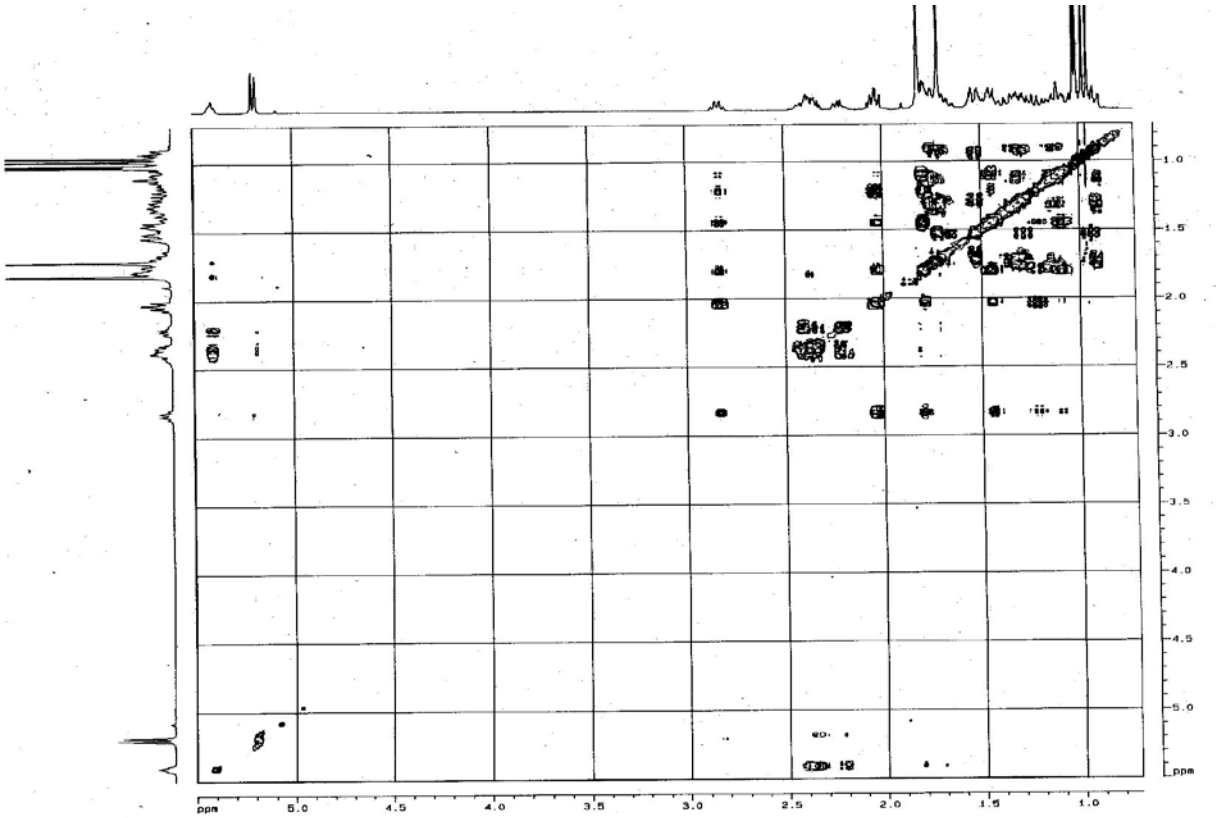


Fig. S10.5. TOCSY of **29** (400 MHz, C_6D_6).

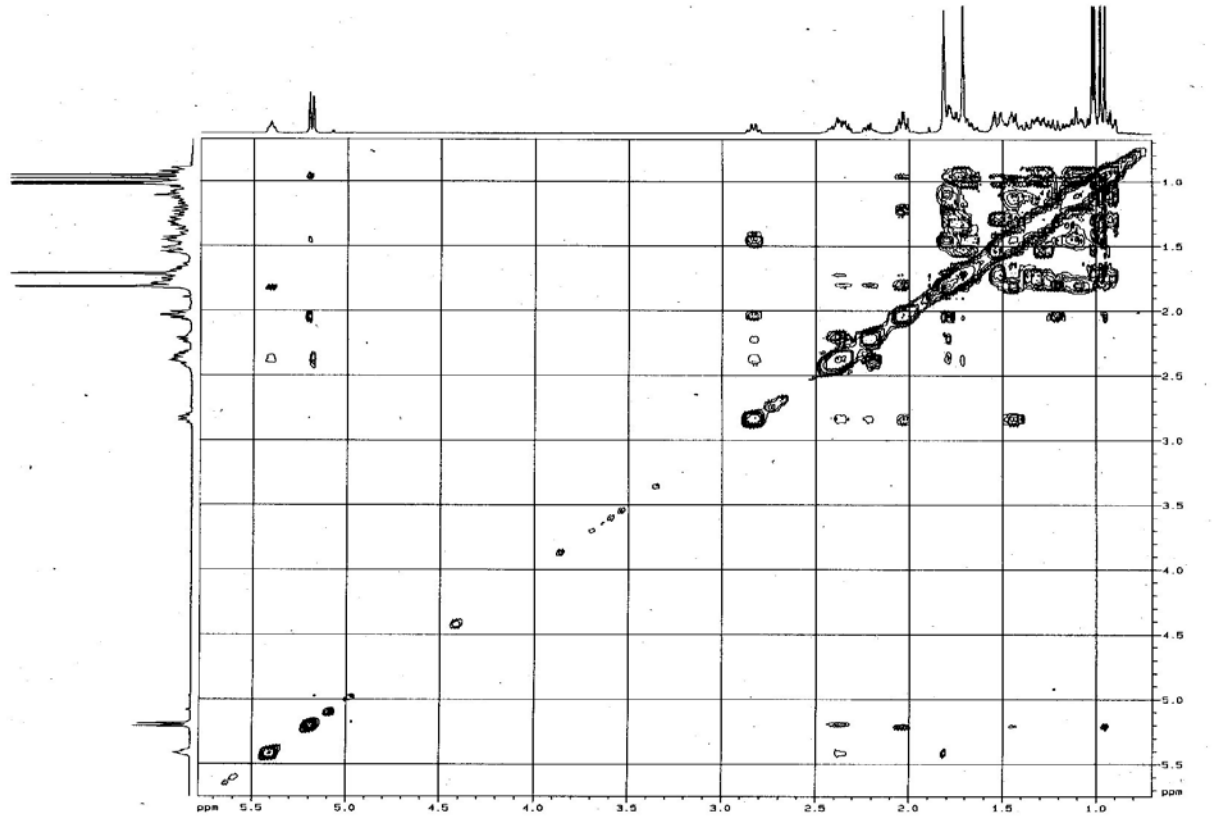


Fig. S10.6. NOESY of **29** (400 MHz, C_6D_6).

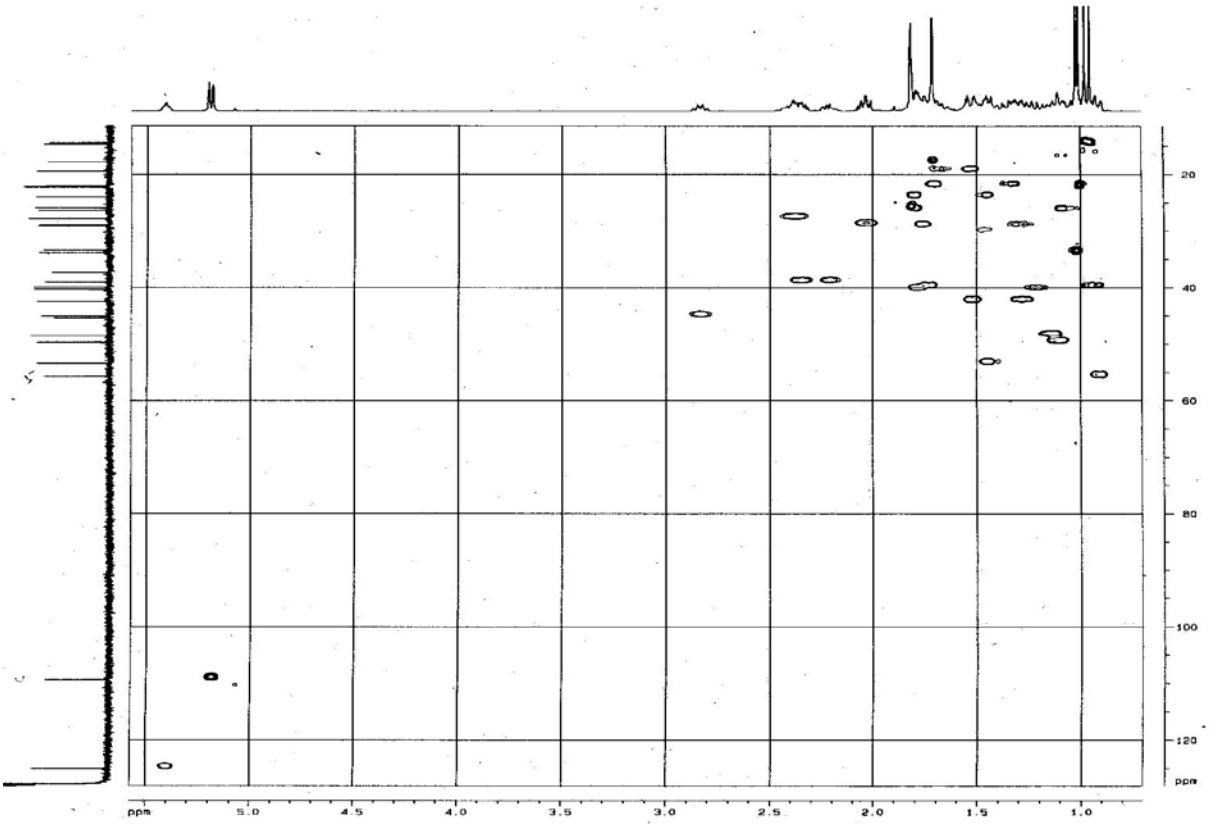


Fig. S10.7. HSQC of **29** (400 MHz, C_6D_6).

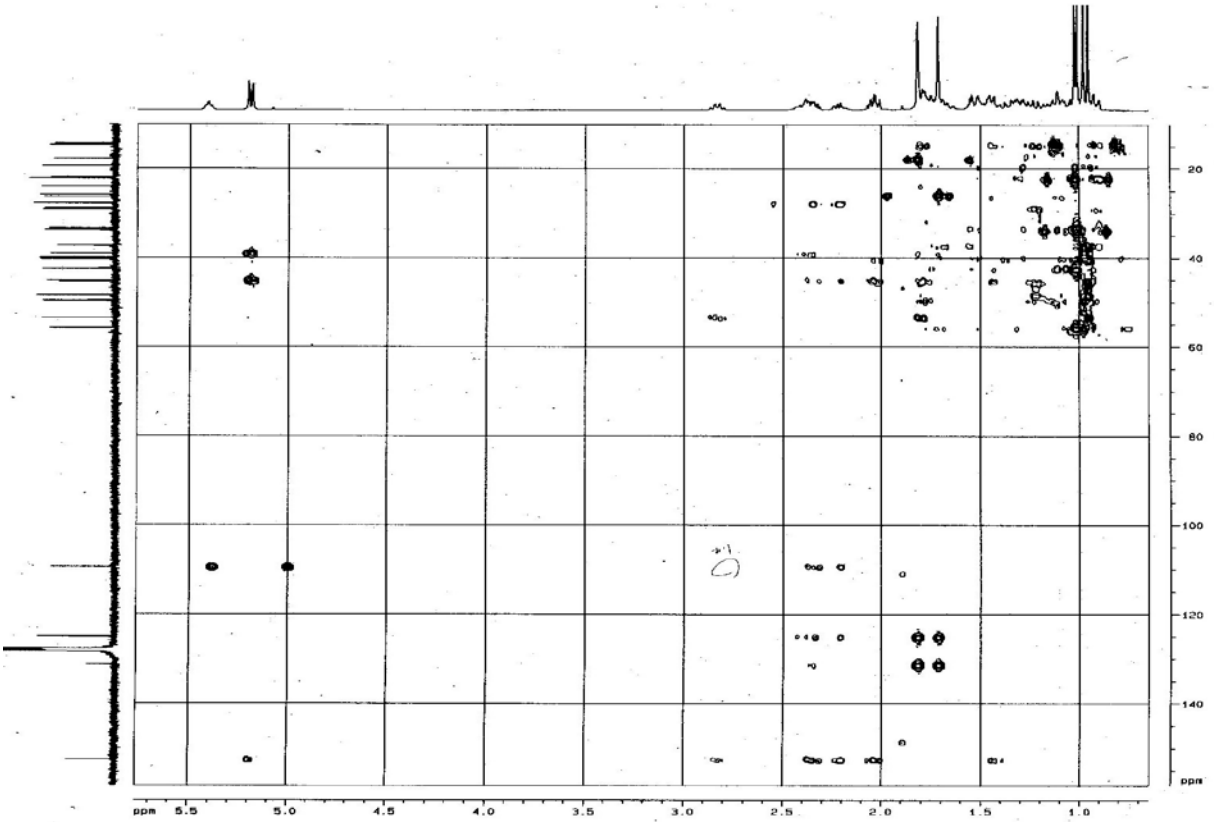
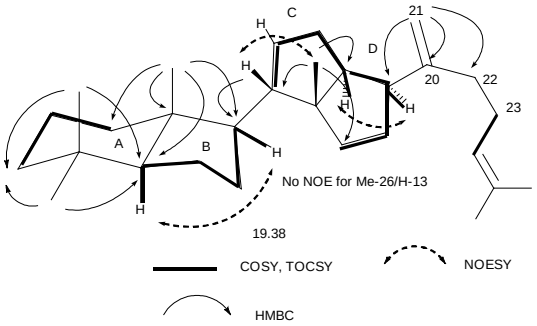
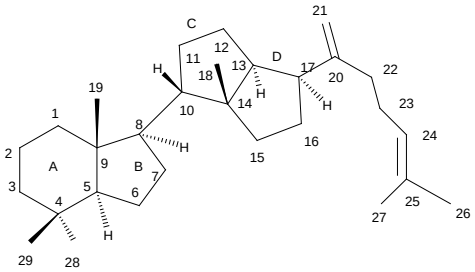


Fig. S10.8. HMBC of **29** (400 MHz, C_6D_6).

Product **29** from 27-norSQ **13a**





$[\alpha]_D^{25}$= - 5.6 (*c* = 0.149, $CHCl_3$)

HREIMS ($C_{29}H_{48}O$), Cald: 396.3756;
Found 396.3713

400 MHz, in C_6D_6; the residual solvent peak: δ_H 7.28; δ_C 128.0 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	0.94(m,1H) ;1.71(m,1H)	**39.89(t)**	9	——	**37.28(s)**	17	2.83(dt, J=9.0 Hz, 1H)	**45.06(d)**	25	——	**131.3(s)**
2	1.54 (m, 1H);1.67(m, 1H)	**19.38(t)**	10	1.14(m, 1H)	**48.47(d)**	18	0.954(s,3H)	**14.66(q)**	26	1.817(s,3H)	**25.85(q)**
3	1.27 (m, 1H); 1.52(m,1H)	**42.42(t)**	11	1.07(m, 1H); 1.78(m,1H)	**26.31(t)**	19	0.978(s,3H)	**14.37(q)**	27	1.715 (s, 3H)	**17.75(q)**
4	——	**33.38(s)**	12	1.45(m,1H); 1.80(m,1H)	**23.98(t)**	20	——	**152.5(s)**	28	1.022(s,3H)	**33.80(q)**
5	0.91(m, 1H)	**55.70(d)**	13	1.45 (m, 1H)	**53.43(d)**	21	5.18 (1H, s); 5.20(s, 1H)	**109.3(t)**	29	1.010(s,3H)	**22.20(q)**
6	1.34(m,1H); 1.71(m, 1H)	**21.98(t)**	14	——	**45.35 (s)**	22	2.21(m); 2..34(m)	**38.99(t)**			
7	1.30(m, 1H); 1.75(m, 1H)	**29.07(t)**	15	1.22(m,1H); 1.77(m, 1H)	**40.32(t)**	23	2.36(m,2H)	**27.74(t)**			
8	1.10 (m, 1H)	**49.64(d)**	16	2.03(m,2H)	**28.88(t)**	24	5.41(t, J=6.8 Hz, 1H)	**125.0(d)**			

Fig. S10.9. Assignments of NMR data of product **29** in C_6D_6, HR-EIMS and optical rotation.

11. EIMS and NMR data of product 30.

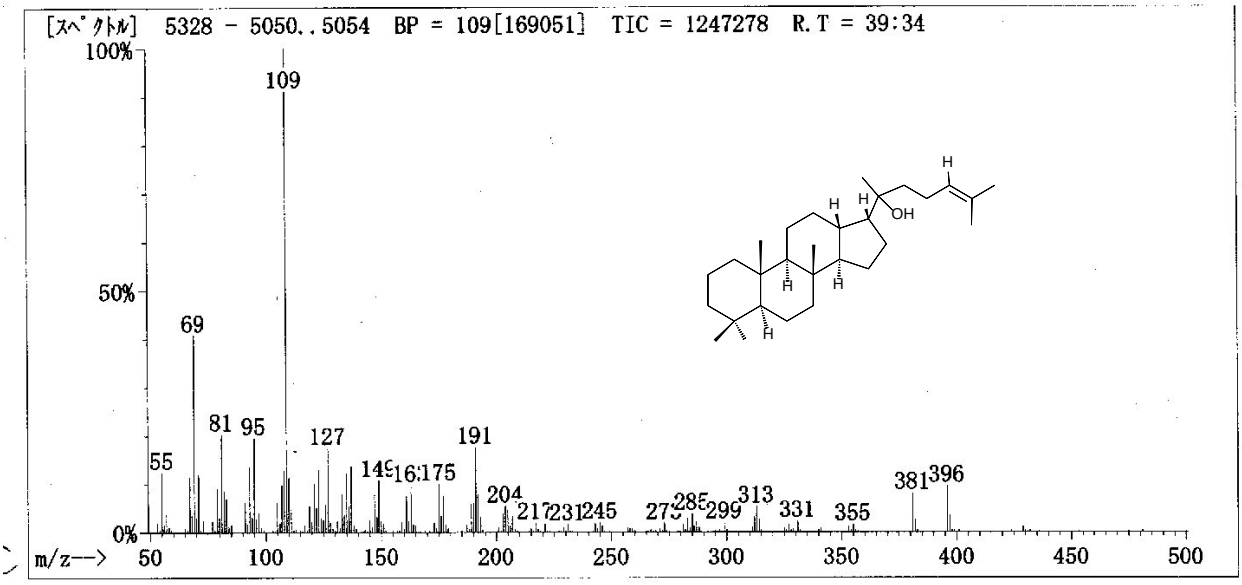


Fig. S11.1. EIMS of product **30**.

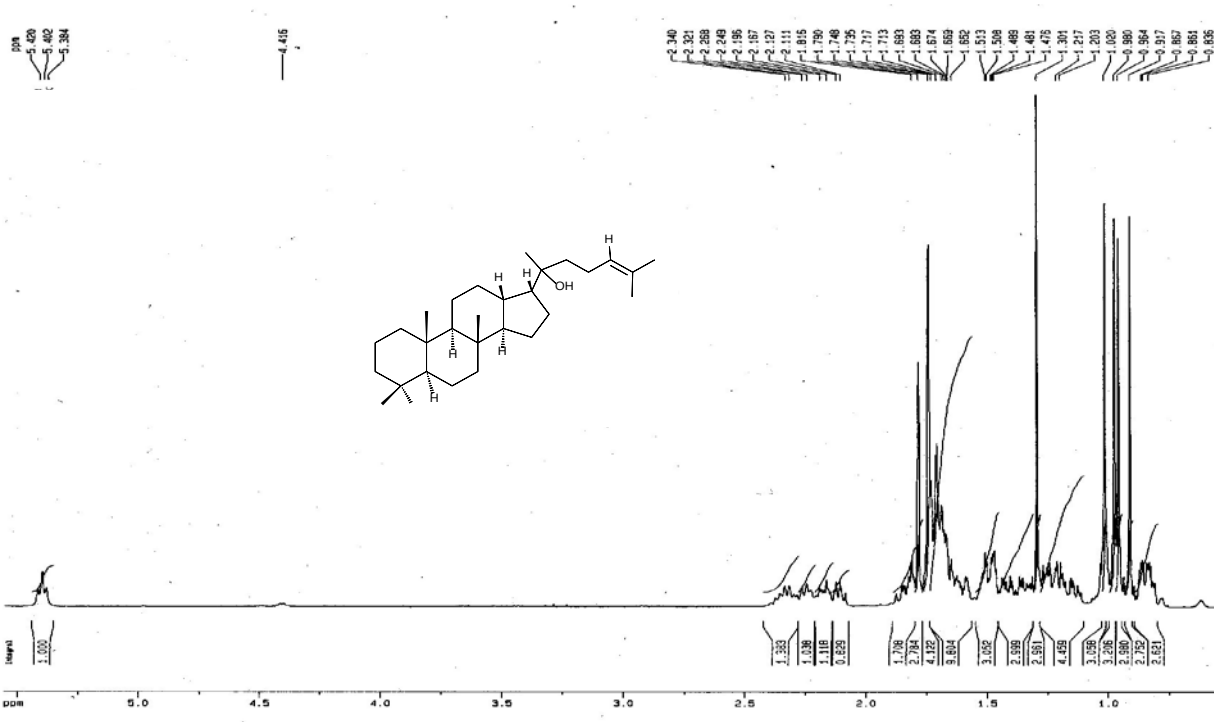


Fig. S11.2. ^{1}H NMR of Product **30** (400 MHz, C_6D_6).

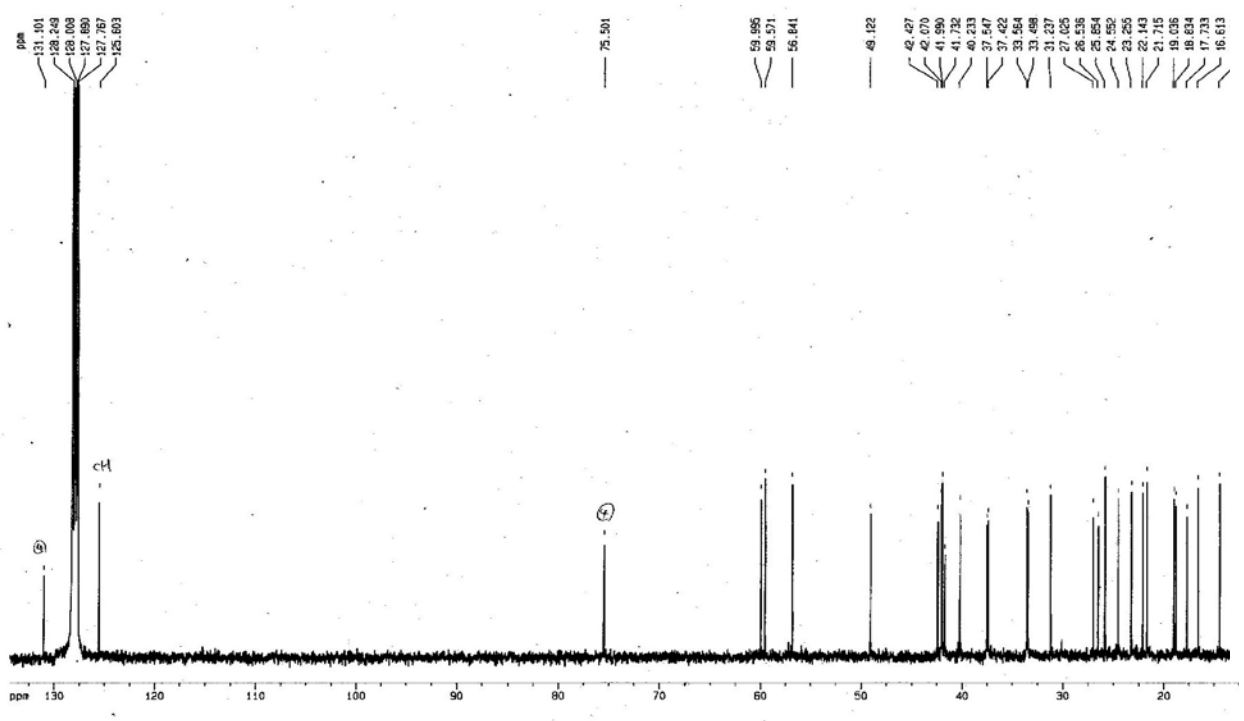


Fig. S11.3. ^{13}C NMR of Product **30** (100 MHz, C_6D_6).

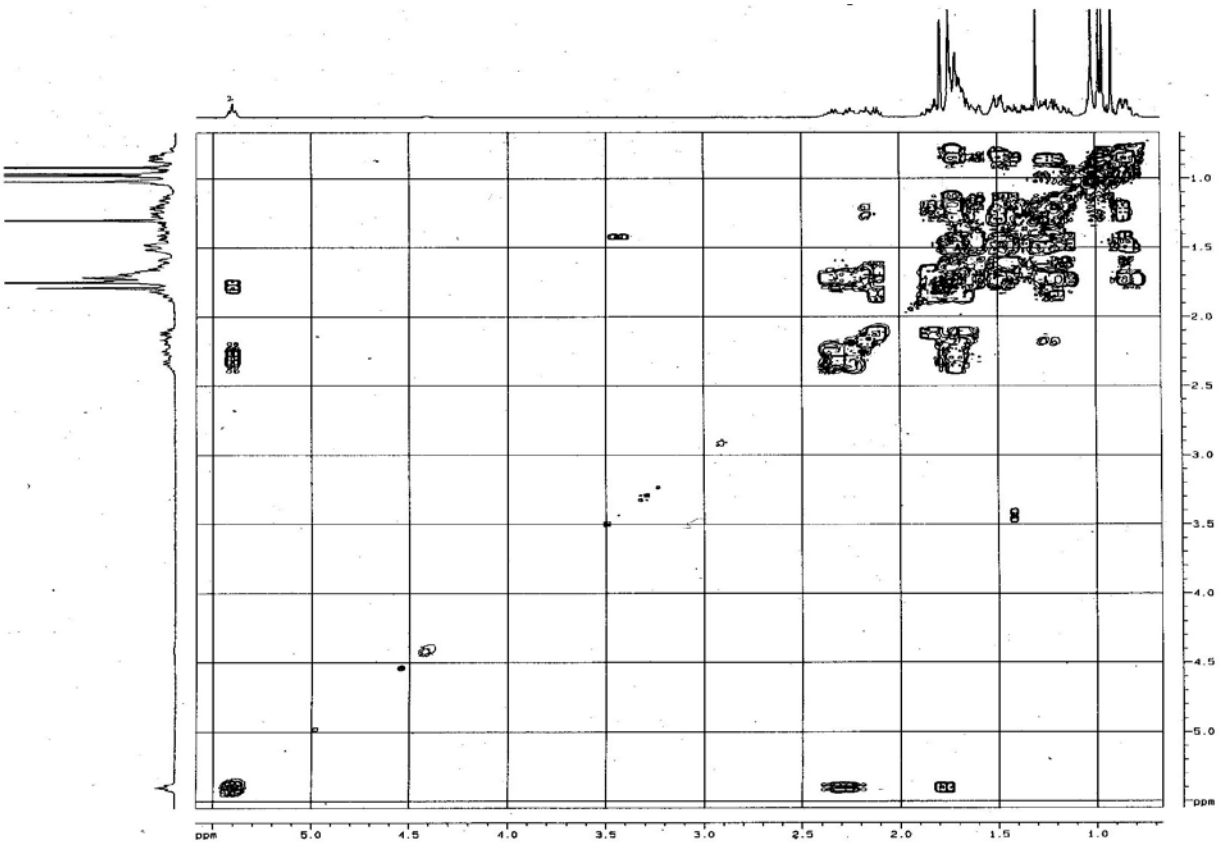


Fig. S11.4. ^{1}H-^{1}H COSY of product **30** (400 MHz, C_6D_6).

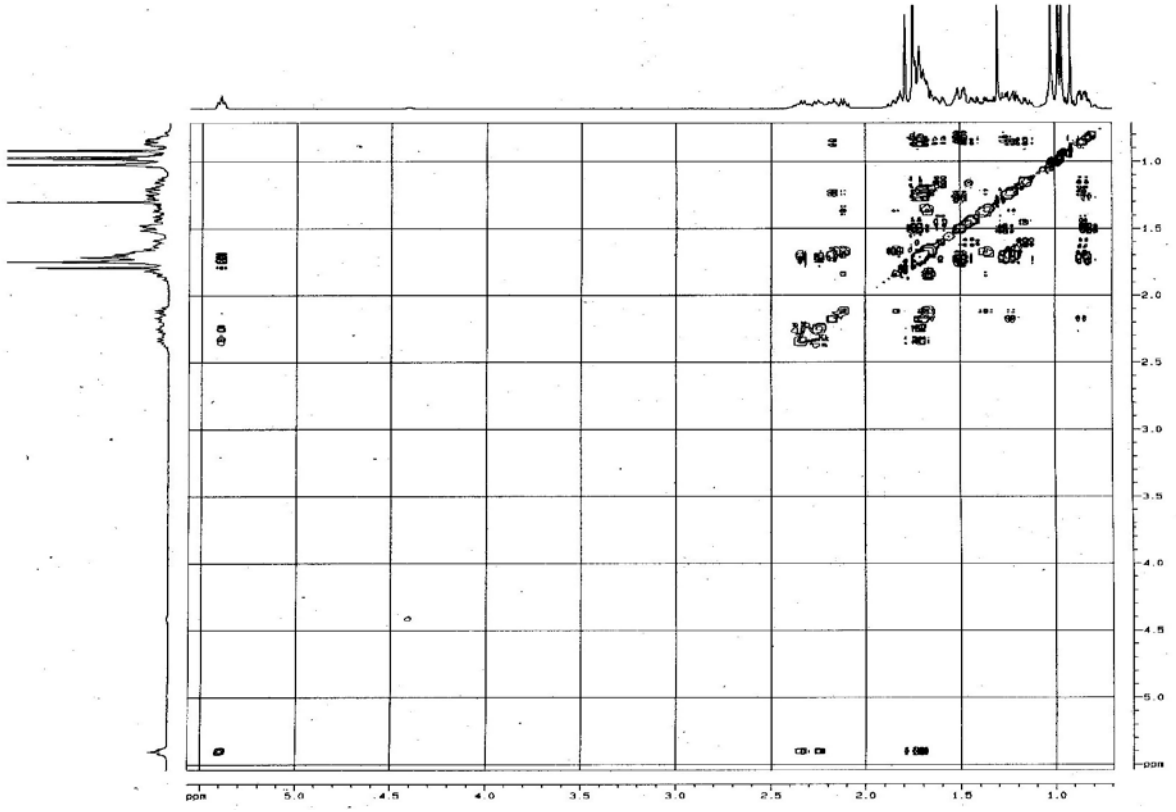


Fig. S11.5. TOCSY of **30** (400 MHz, C_6D_6).

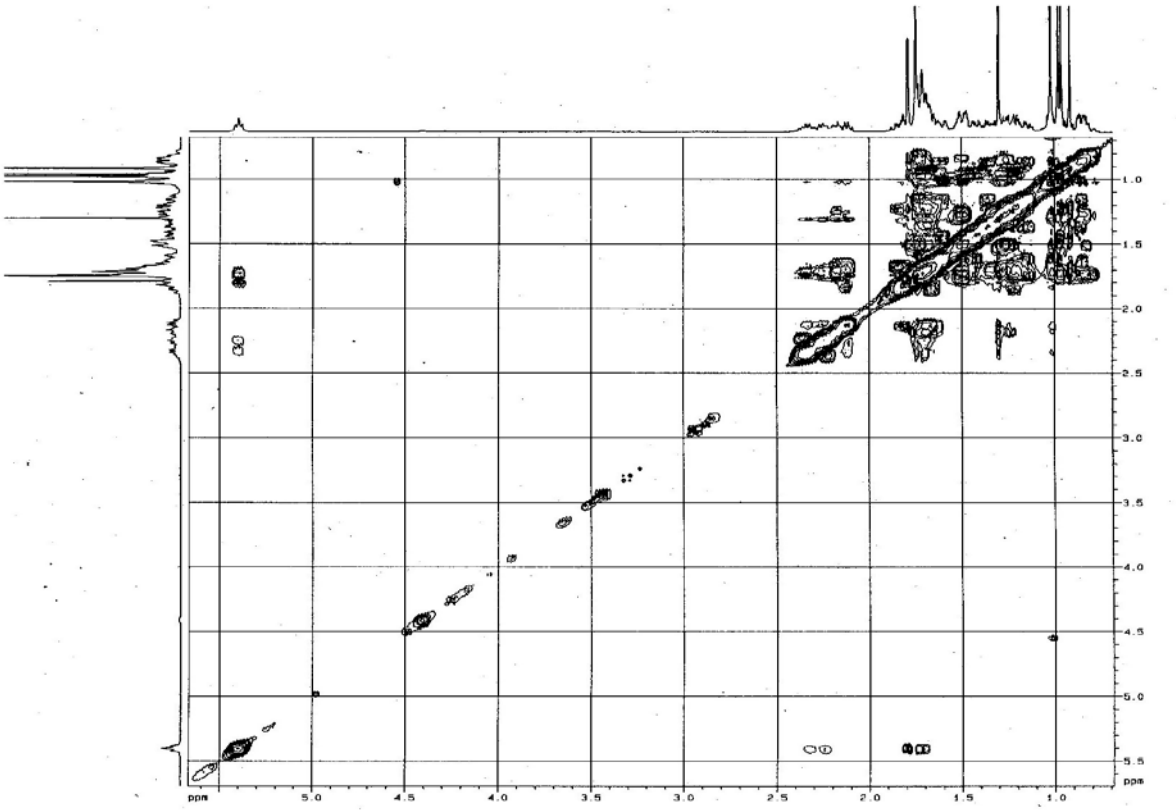


Fig. S11.6. NOESY of **30** (400 MHz, C_6D_6).

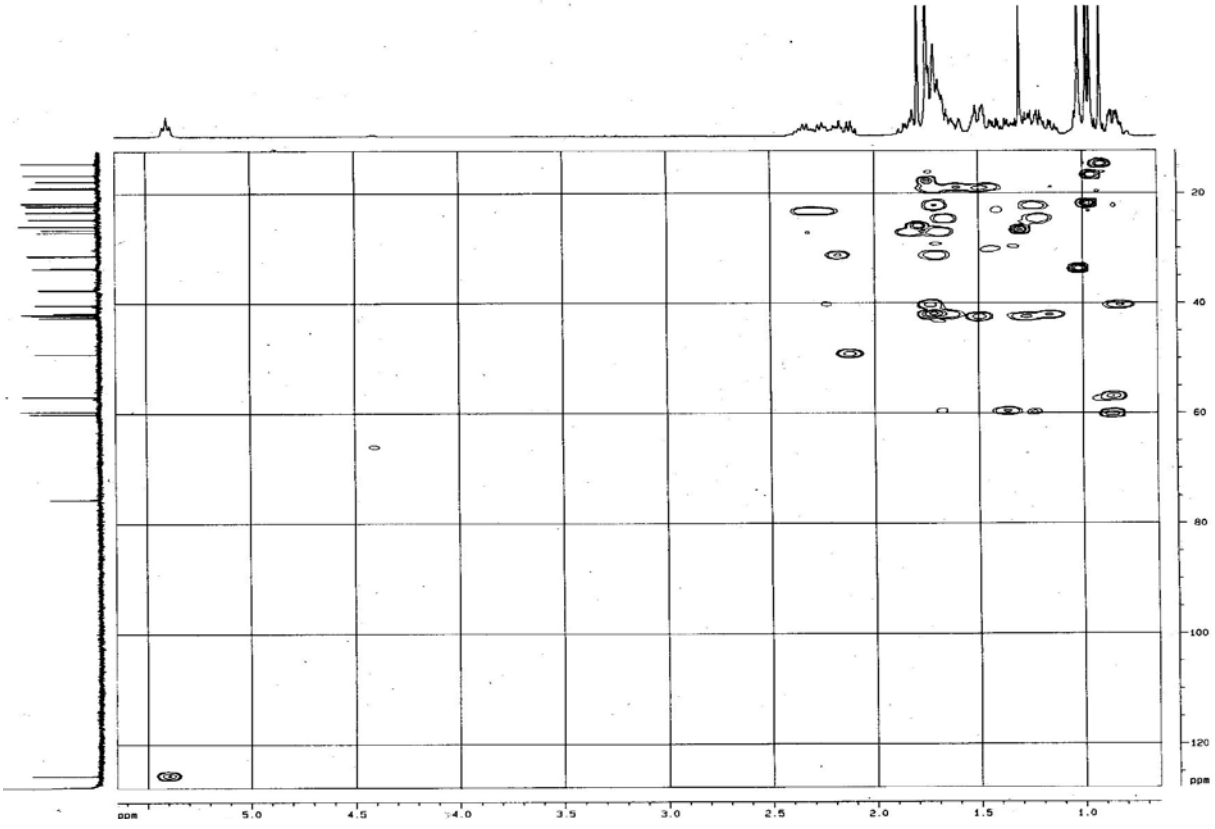


Fig. S11.7. HSQC of **30** (400 MHz, C_6D_6).

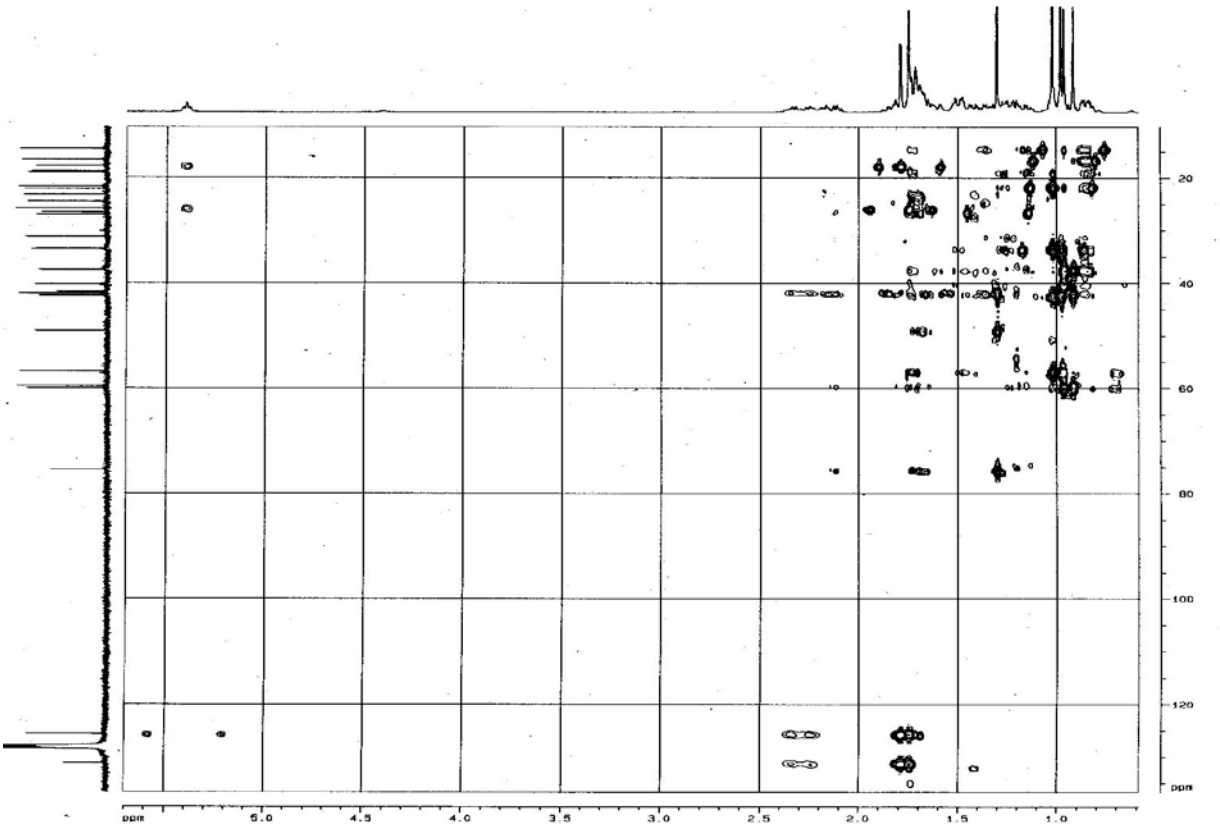
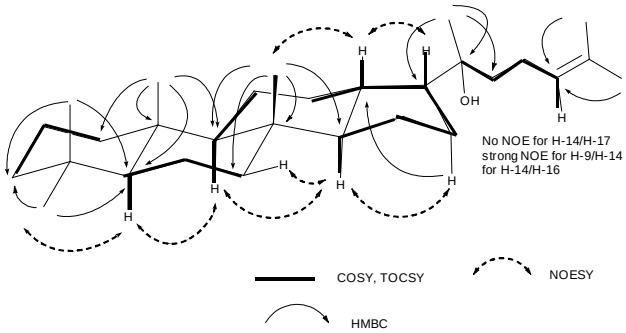
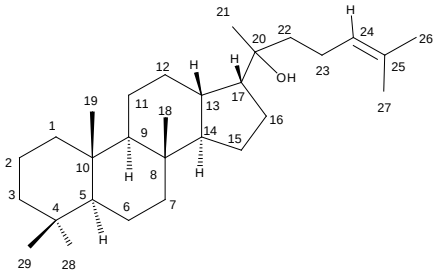


Fig. S11.8. HMBC of **30** (400 MHz, C_6D_6).

Product **30** from 28-norSQ (**13b**)





$[\alpha]_D^{25}$= + 11.4 (*c*= 0.3235, $CHCl_3$)

HREIMS (M^+- H_2O: $C_{29}H_{48}$), Cald 396.3756; Found 396.3769

400 MHz, in C_6D_6; the residual solvent peak: δ_H 7.28; δ_C 128.0 ppm

NO.	^1H	^{13}C	NO.	^1H	^{13}C	NO.	^1H	^{13}C	NO.	^1H	^{13}C
1	0.82(m,1H) ;1.72(m,1H)	**40.23(t)**	9	0.86 (m, 1H)	**60.00(d)**	17	2.12 (m, 1H)	**49.12(d)**	25	——	**131.1(s)**
2	1.47(m,1H); 1.73(m, 1H)	**19.03(t)**	10	——	**37.55(s)**	18	0.917(s,3H)	**14.49(q)**	26	1.790(s, 3H)	**25.85(q)**
3	1.27(m, 1H);1.49 (m,1H)	**42.43(t)**	11	1.23(m, 1H); 1.70(m,1H)	**22.14(t)**	19	0.964(s, 3H)	**16.61(q)**	27	1.748 (s, 3H)	**17.73(q)**
4	——	**33.50(s)**	12	1.70(m,1H); 2.18(m, 1H)	**31.24(t)**	20	——	**75.50(s)**	28	1.020(s,3H)	**33.56(q)**
5	0.86 (m, 1H)	**56.84(d)**	13	1.63(m, 1H)	**41.99(d)**	21	1.301 (s, 3H)	**26.54(t)**	29	0.980(s,3H)	**21.72(q)**
6	1.43(m,1H); 1.60(m, 1H)	**18.83(t)**	14	1.36 (m, 1H)	**59.57 (d)**	22	1.72 (m, 2H)	**41.73(t)**			
7	1.16(m, 1H); 1.69(m, 1H)	**42.07(t)**	15	1.21(m,1H); 1.65(m, 1H)	**24.55(t)**	23	2.23(m,2H);2.34(m, 1H)	**23.25(t)**			
8	——	**37.42(s)**	16	1.67(m,1H);1.83(m, 1H)	**27.02(t)**	24	5.40(t, *J*=7.2 Hz, 1H)	**125.6(d)**			

Fig. S11.9. Assignments of the NMR data of product **30** in C_6D_6, HR-EIMS and optical rotation.

12. EIMS and NMR data of product 31.

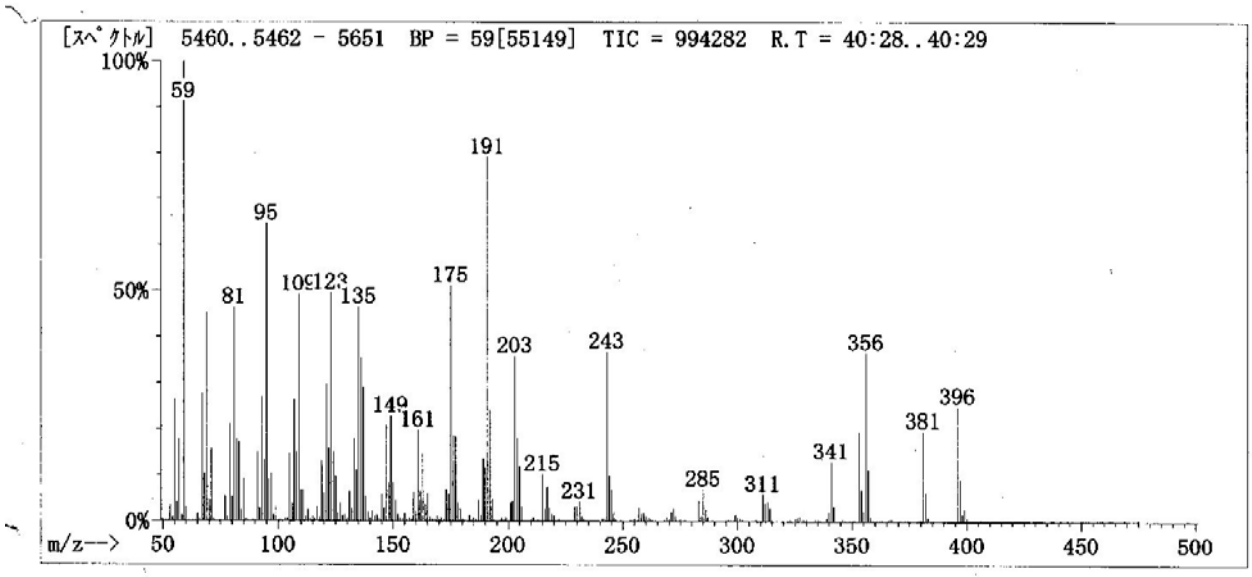


Fig. S12.1. EIMS of product **31**.

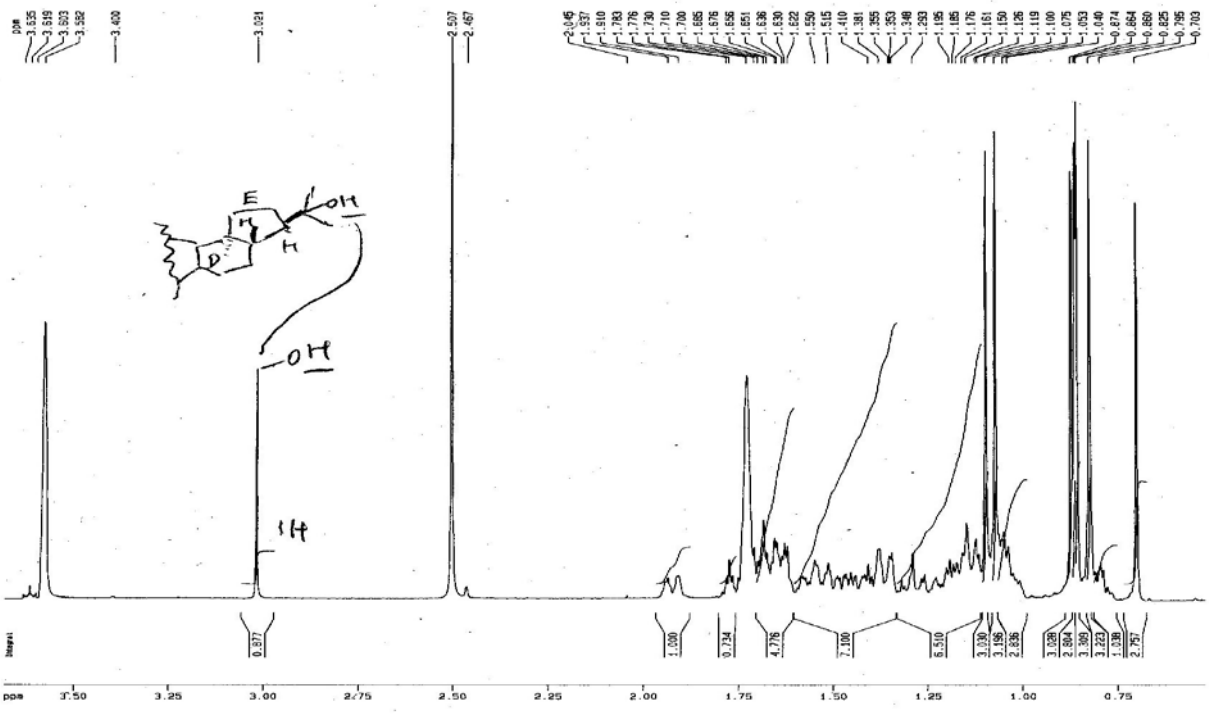


Fig. S12.2. ^{1}H NMR (whole spectrum) of Product **31** (400 MHz, THF d_8).

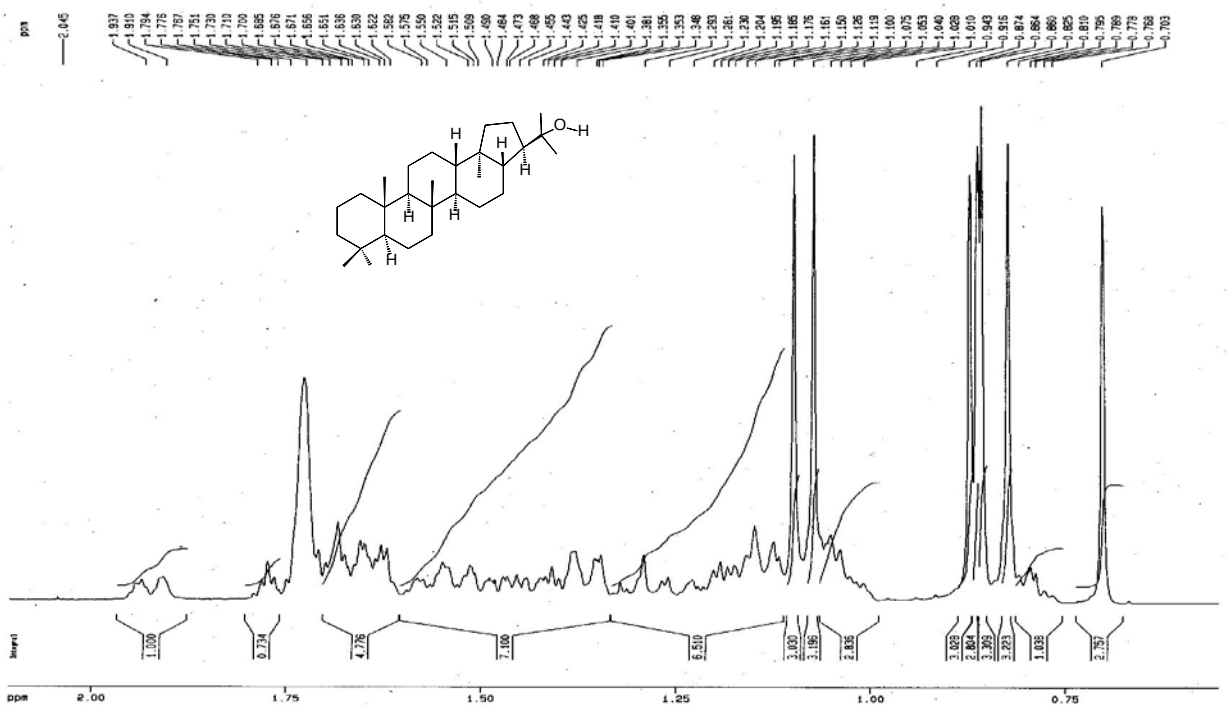


Fig. S12.3. ^{1}H NMR (expanded region) of Product **31** (400 MHz, THF d_8).

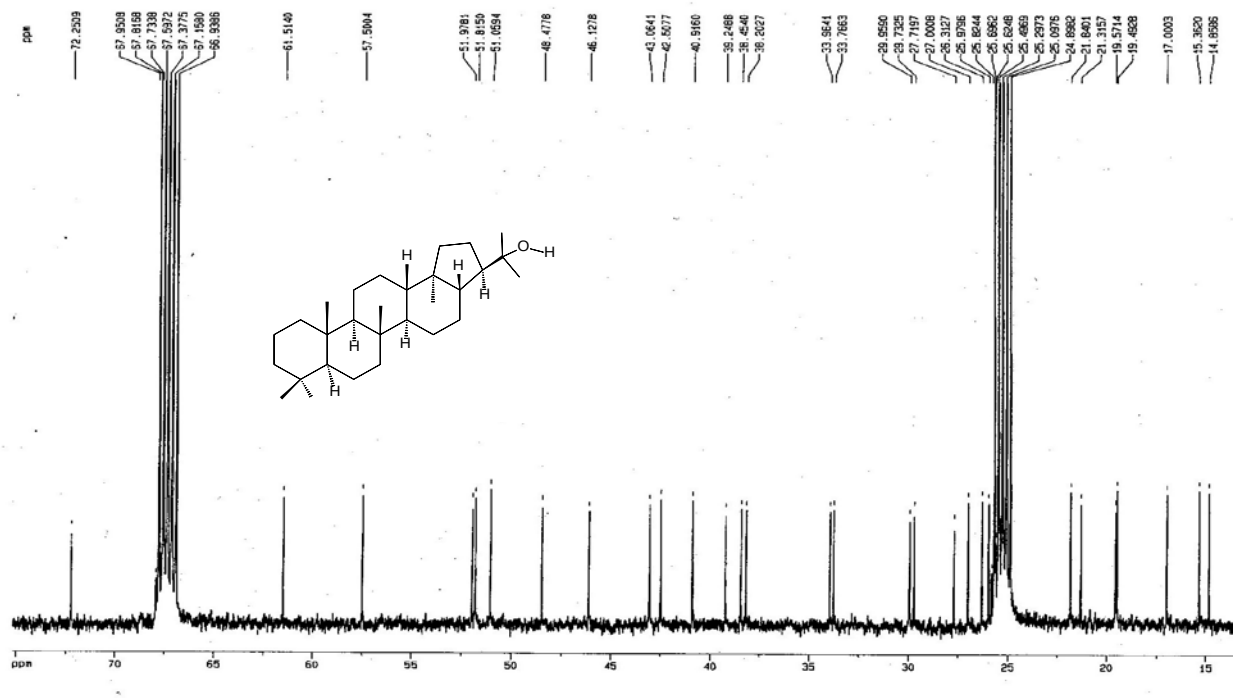


Fig. S12.4. ^{13}C NMR of Product **31** (400 MHz, THF d8).

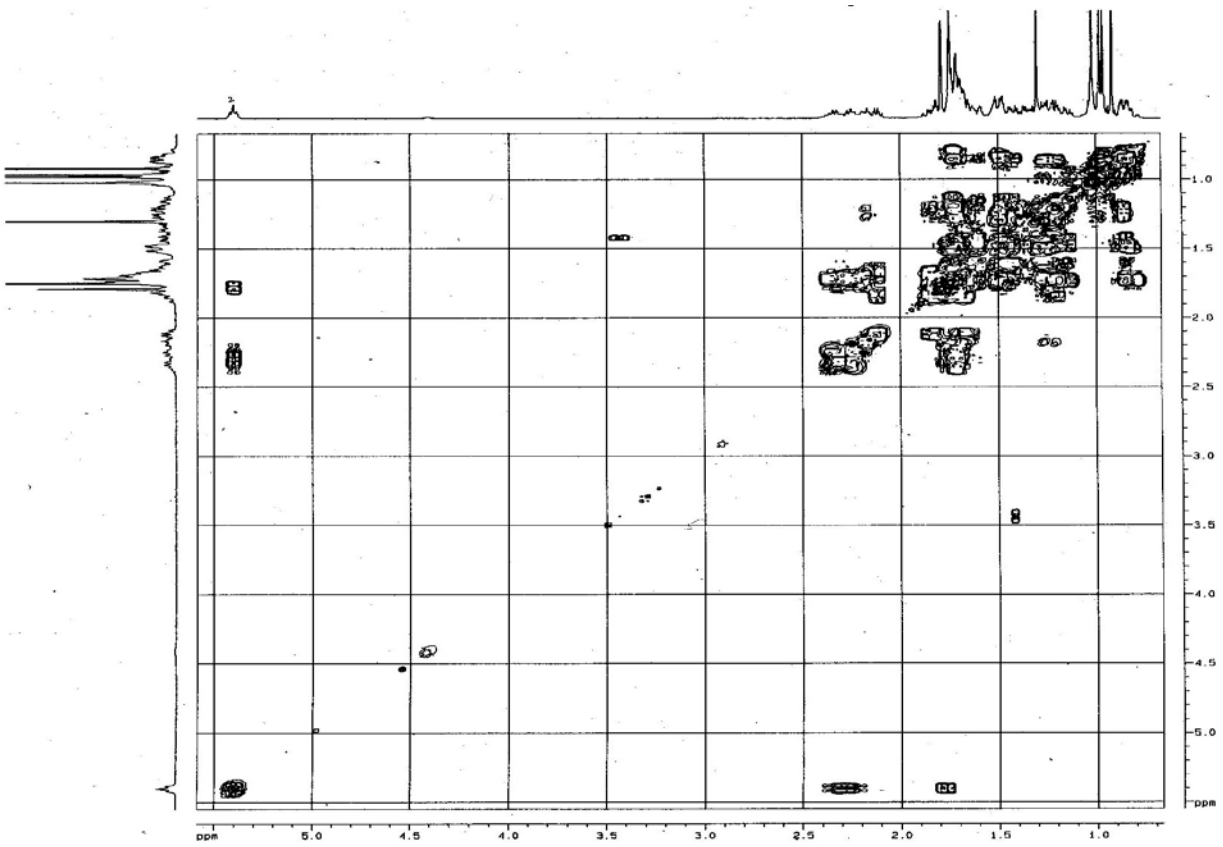


Fig. S12.5. ^{1}H-^{1}H COSY of product **31** (400 MHz, THF d_8).

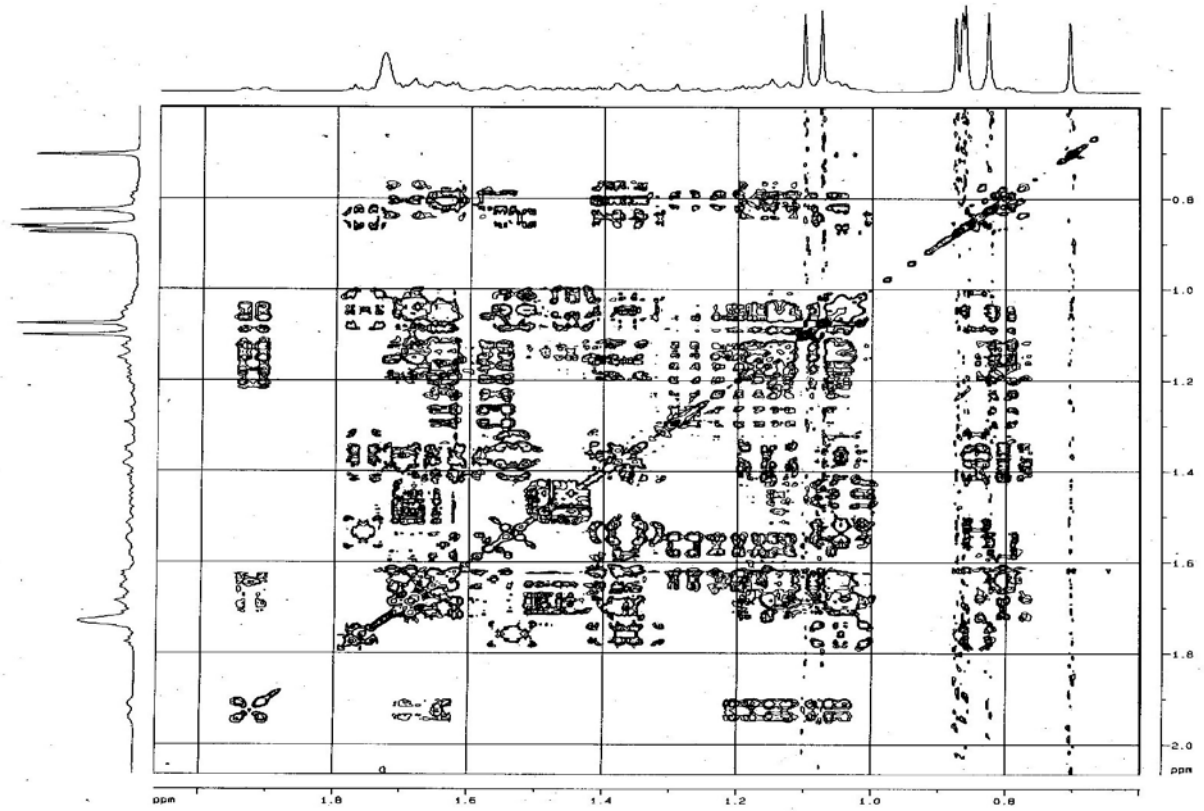


Fig. S12.6. TOCSY of **31** (400 MHz, THF d_8).

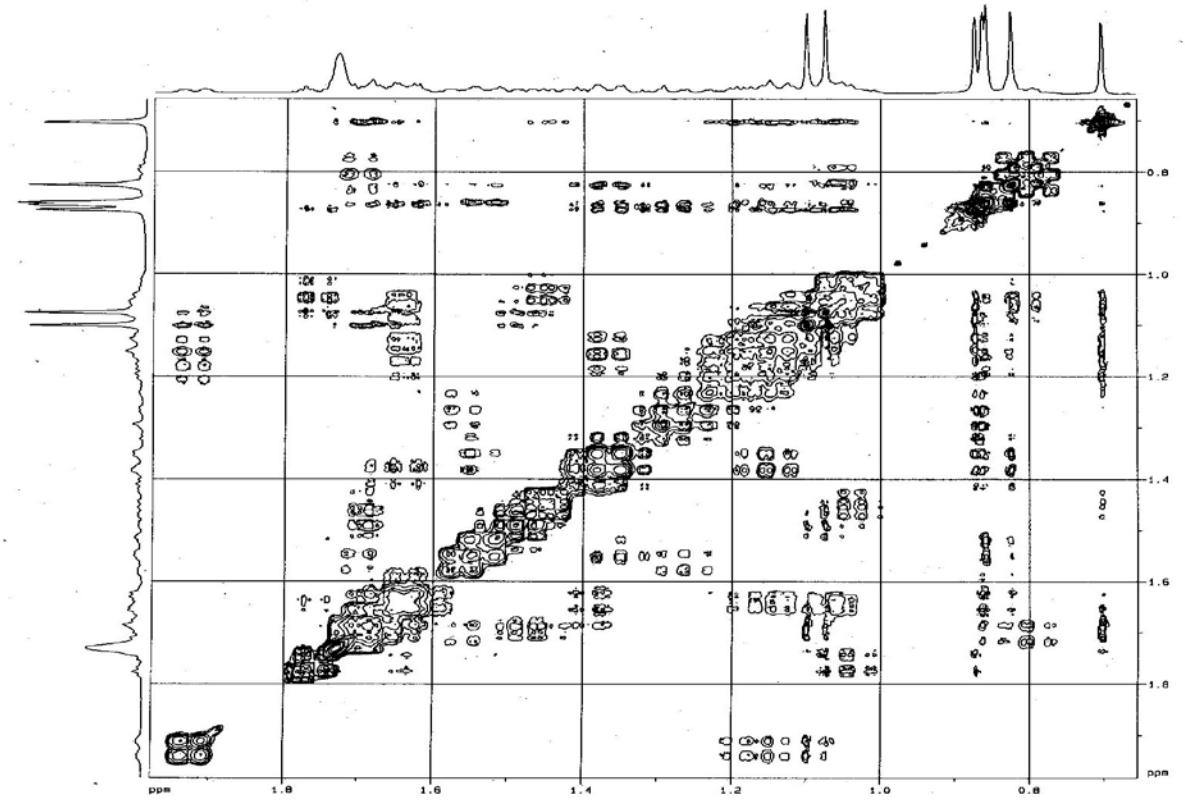


Fig. S12.7. NOESY of **31** (400 MHz, THF d_8).

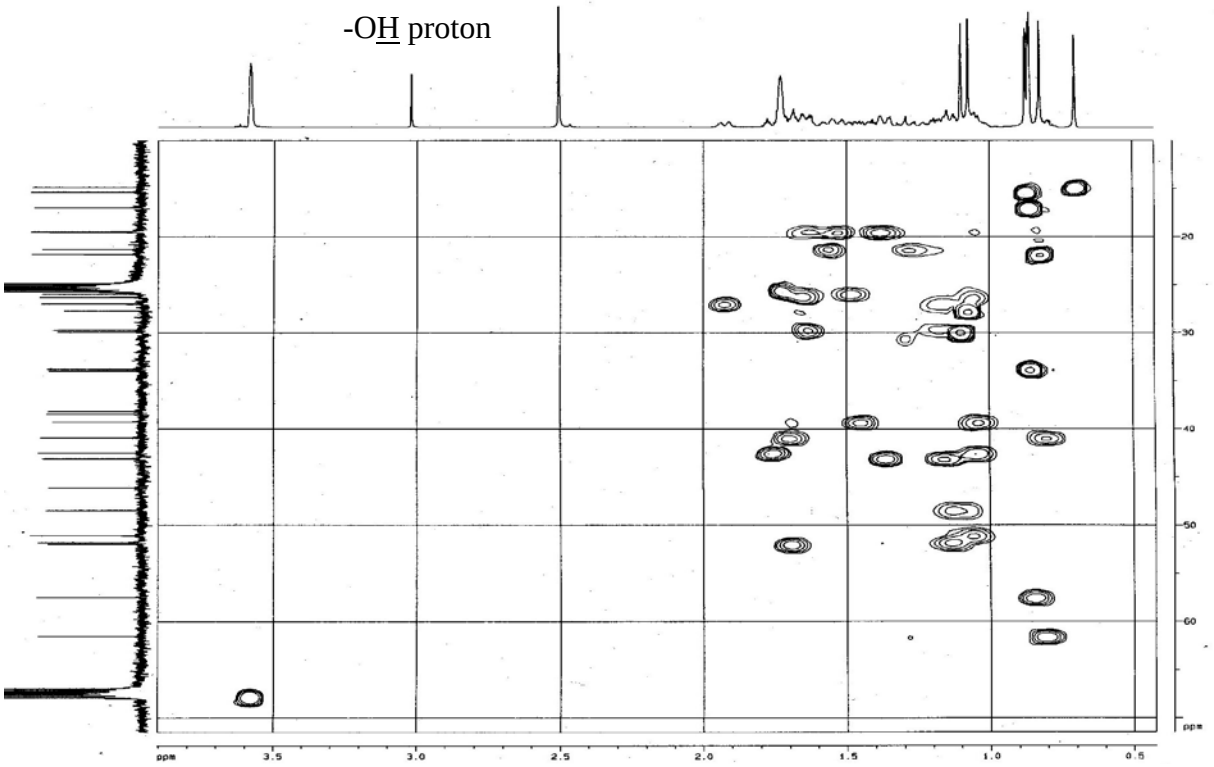


Fig. S13.8. HSQC (whole spectrum) of **31** (400 MHz, THF d_8).

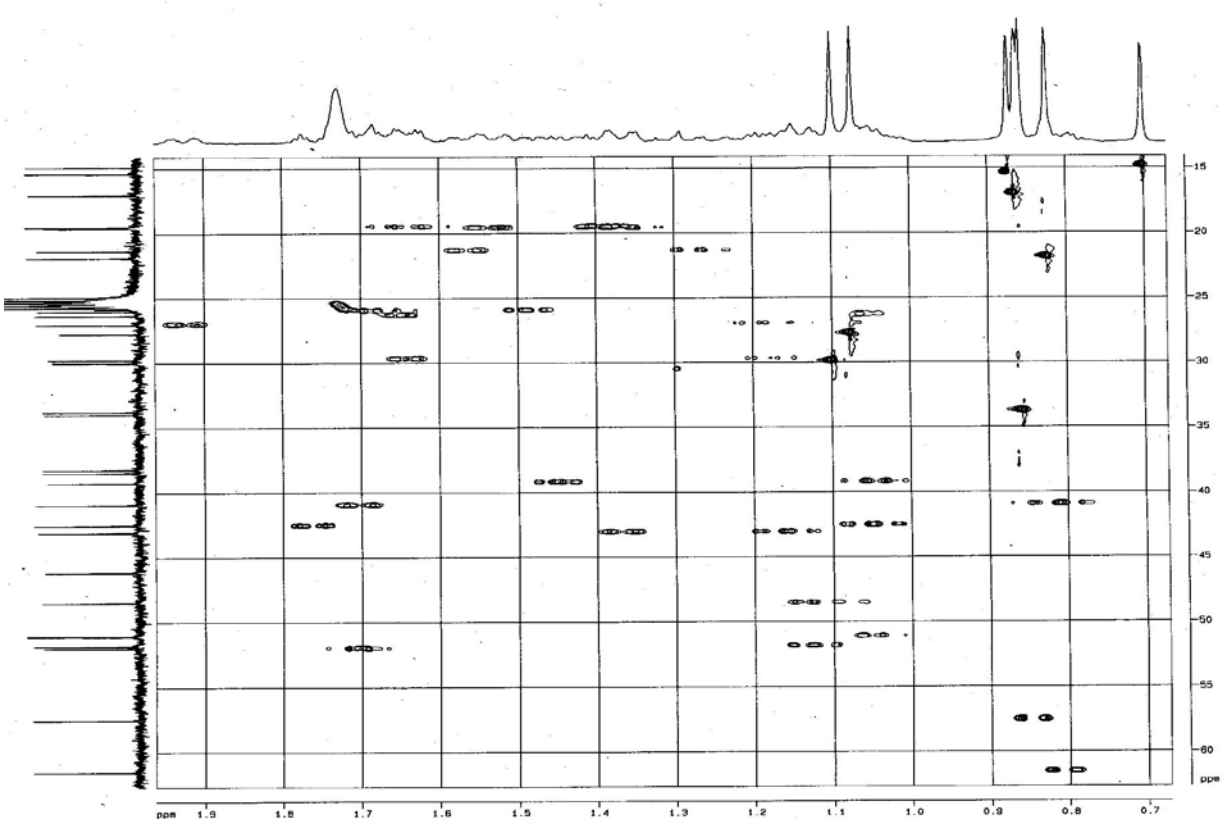


Fig. S12.9. HSQC (Expanded region) of **31** (400 MHz, THF d_8).

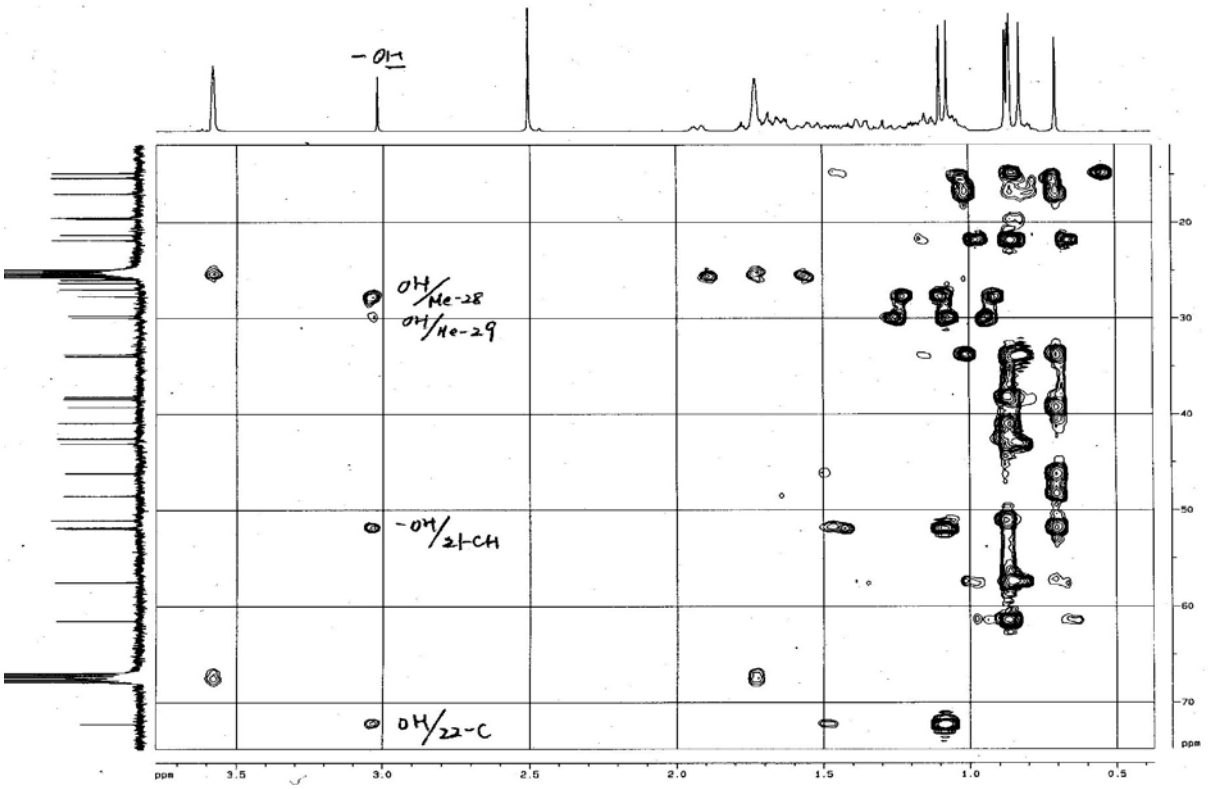


Fig. S12.10. HMBC (whole spectrum) of **31** (400 MHz, THF d_8).

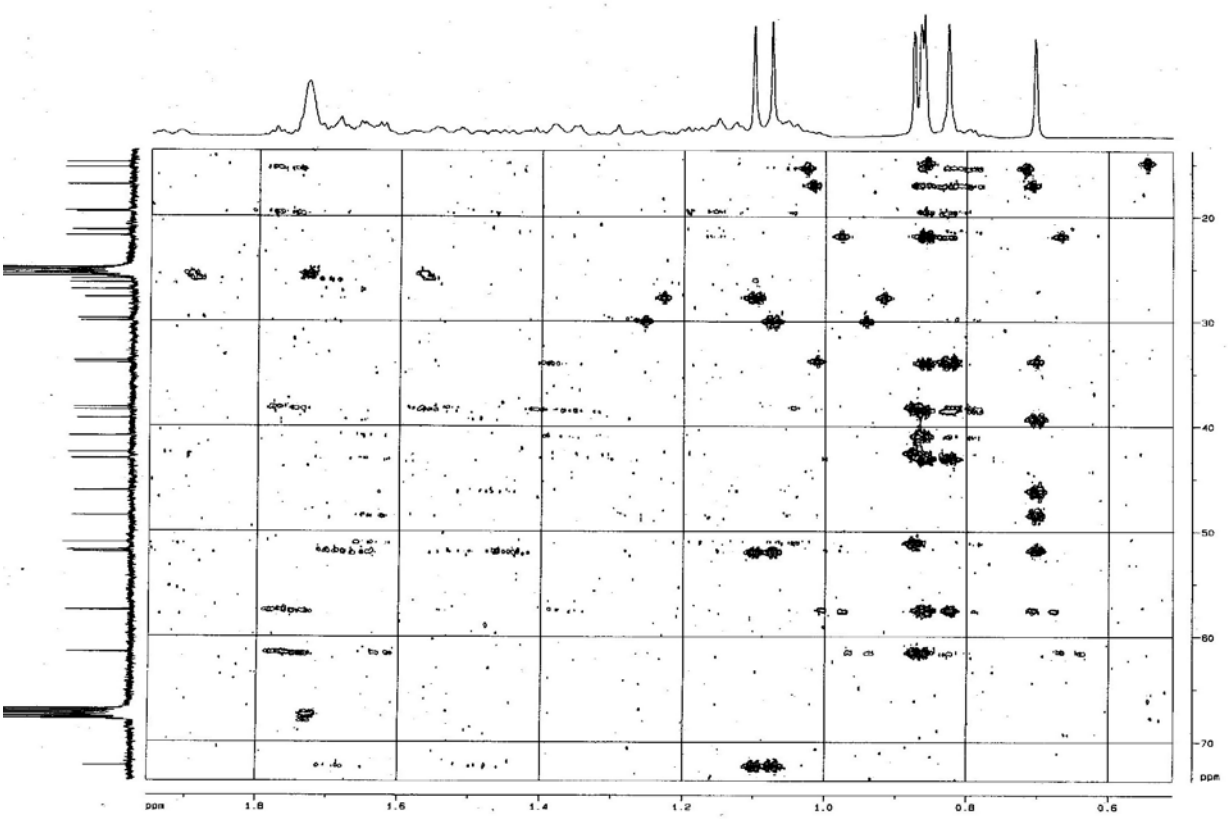
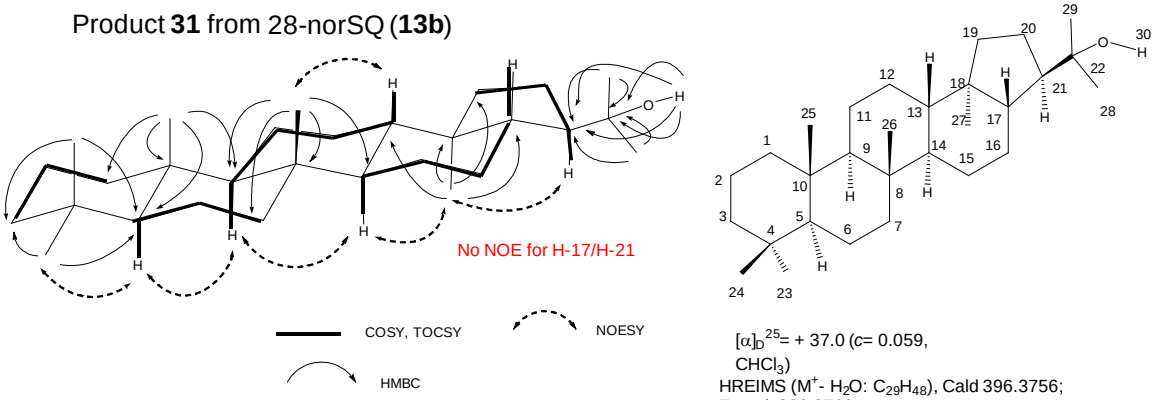


Fig. S12.11. HMBC (expanded region) of **31** (400 MHz, THF d_8).



$[\alpha]_D^{25}$= + 37.0 (*c*= 0.059, $CHCl_3$)

HREIMS (M^+- H_2O: $C_{29}H_{48}$), Cald 396.3756; Found 396.3768

400 MHz, in THF-d_8; the residual solvent peak: δ_H 1.73; δ_C 25.3 ppm

NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C	NO.	^{1}H	^{13}C
1	0.82(m,1H) ;1.70(m,1H)	**46.28(t)**	9	0.80 (m, 1H)	**61.51(d)**	17	1.12 (m, 1H)	**51.81(d)**	25	0.864(s, 3H)	**17.00(q)**
2	1.53(m,1H); 1.65(m, 1H)	**19.49(t)**	10	——	**38.45(s)**	18	——	**46.13(s)**	26	0.874(s,3H)	**15.36(q)**
3	1.16(m, 1H);1.37 (m,1H)	**43.06(t)**	11	1.26(m, 1H); 1.56(m,1H)	**21.32(t)**	19	1.05 (m, 1H);1.45(m, 1H)	**39.25(t)**	27	0.703 (s, 3H)	**14.86(q)**
4	——	**33.96(s)**	12	1.17(m,1H); 1.64(m, 1H)	**29.73(t)**	20	1.48(m,1H);1.68(m, 1H)	**25.98(t)**	28	1.100(s, 3H)[a]	**29.96(q)**[a]
5	0.85 (m, 1H)	**57.50(d)**	13	1.01(m, 1H)	**48.48(d)**	21	1.70(m, 1H)	**51.98(d)**	29	1.075 (s, 3H) [a]	**27.72(q)**[a]
6	1.37(m,1H); 1.53(m, 1H)	**16.97(t)**	14	1.09(m, 1H)	**51.06 (d)**	22	——	**72.25(s)**	30	3.02 (s, 1H)	——
7	1.05(m, 1H); 1.76(m, 1H)	**42.51(t)**	15	1.19(m,1H); 1.65(m, 1H)	**26.31(t)**	23	0.860(s,3H)	**33.77(q)**			
8	——	**38.20(s)**	16	1.18(m,1H);1.92(m, 1H)	**27.00(t)**	24	0.825(s,3H)	**21.84(q)**			

a: exchangeable

Fig. S12.12. Assignments of the NMR data of product **41** in THF d_8, HR-EIMS and optical rotation.