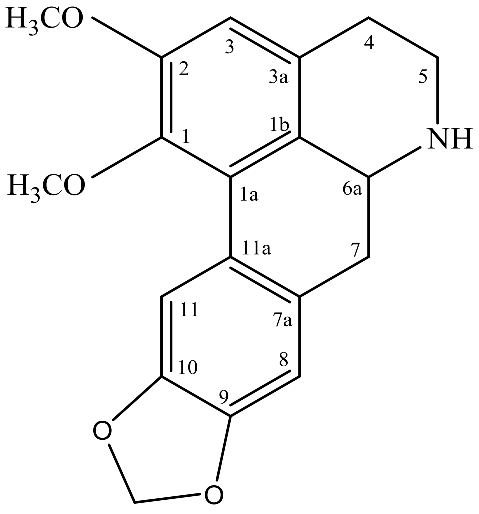
3.2.4 Alkaloid CD4: Nornantenine 66



66

Alkaloid **CD 4** was isolated as a brownish amorphous solid. The UV spectrum indicated the absorption bands at 218, 282, and 308 nm. The IR spectrum showed absorptions at 929 and 1040 cm^{-1} indicated the existing of methylenedioxy group in the structure. The ESIMS (positive mode) spectrum gave a pseudomolecular ion peak, $[M+H]^+$ at m/z 326.14 corresponding to molecular formula of $C_{19}H_{19}NO_4$, which can deduce eleven degrees of unsaturation.

The ^1H NMR spectrum (Figure 3.21) showed three aromatic proton signals appeared as singlet at δ 7.95 (*s*, H-11), 6.72 (*s*, H-8), and 6.60 (*s*, H-3). Two distinct methoxyl peaks at δ 3.87 and 3.66 were assignable to attached to C-2 and C-1 respectively. Hence, H-8 and H-11 resonated as two singlets at δ 6.72 and 7.95 respectively thus, implying that the OCH_2O group is at C-9,10. H-11 is more deshielded due to the anisotropic effect caused by ring A. The aliphatic protons appeared as multiplets at the region of δ 2.57-3.79. Those chemical shifts in ^1H NMR were apparent for 1,2,9,10-tetrahydroaporphine type[60].

The ^{13}C NMR spectrum (Figure 3.22) gave a total of nineteen carbons. The methoxyl carbons were observed at δ 55.98 and 60.32 along with nine quaternary carbons which further supported the structure of alkaloid **CD4**. DEPT experiment showed that there are two methyls, four methylenes, four methines and nine quaternary carbons present in the molecule. The ^{1}H NMR and ^{13}C NMR data are shown in Table 3.4. The OCH_2O peak was displayed at δ 100.96 and it was supported by HMQC data (Figure 3.23) which showed the correlations between methylene proton at δ 5.96 and methylene carbon at δ 100.96.

The COSY spectrum indicated correlation between H-4/H-5 and H-6a/H-7. The HMBC spectrum verified the relative position of the substituents of the aromatic ring and further supported the connectivities and the assignments of all the carbons of the aporphine moiety. This spectrum (Figure 3.24) revealed clearly the cross-peaks between H5/C6a, H-7/C-6a, H-4/C-6a, H-4/C-1b, H-7/C-1b, H5/C-3a and H-3/C-4. The full assignments of all the carbons and protons are depicted in Table 3.4.

Thorough analysis of the COSY, HMQC, HMBC and NOESY spectra allowed the complete assignments of all protons and carbons of nornantenine[92-94] **66**.

Table 3.4: ^{1}H NMR (in $CDCl_3$, 400MHz) and ^{13}C NMR (in $CDCl_3$, 100MHz) of **66**.

Position	δ_H, ppm (J in Hz)	δ_C (ppm)	COSY	HMQC	HMBC (H→C)
1		144.94			
1a		126.76			
1b		128.02			
2		152.37			
3	6.60 (*s*)	111.23		H-3	4, 1b, 1, 2
3a		128.81			
4	3.01 (*d*, 8.68)	29.08	H-4/H-5	H-4α	6a, 1b
	2.70 (*m*)				
			H-4α/H-4β	H-4β	
5	3.37 (*d*, 6.88)	43.11	H-5α/H-5β	H-5α	3a, 6a
	3.01 (*d*, 8.68)			H-5β	
6a	3.80 (*dd*, 5.04, 13.28)	53.72	H-6a/H-7	H-6a	
7	2.70 (*m*)	37.47		H-7	1b, 6a
7a		130.55			
8	6.72 (*s*)	108.28		H-8	7, 10, 11a
9		146.68			
10		146.68			
11	7.95 (*s*)	109.05		H-11	9, 7a, 11a
11a		125.66			
1-OMe	3.66 (*s*)	60.32			1
2-OMe	3.87 (*s*)	55.98			2
9, 10-OCH_2O	5.96 (*d*, 3.64)	100.96			9

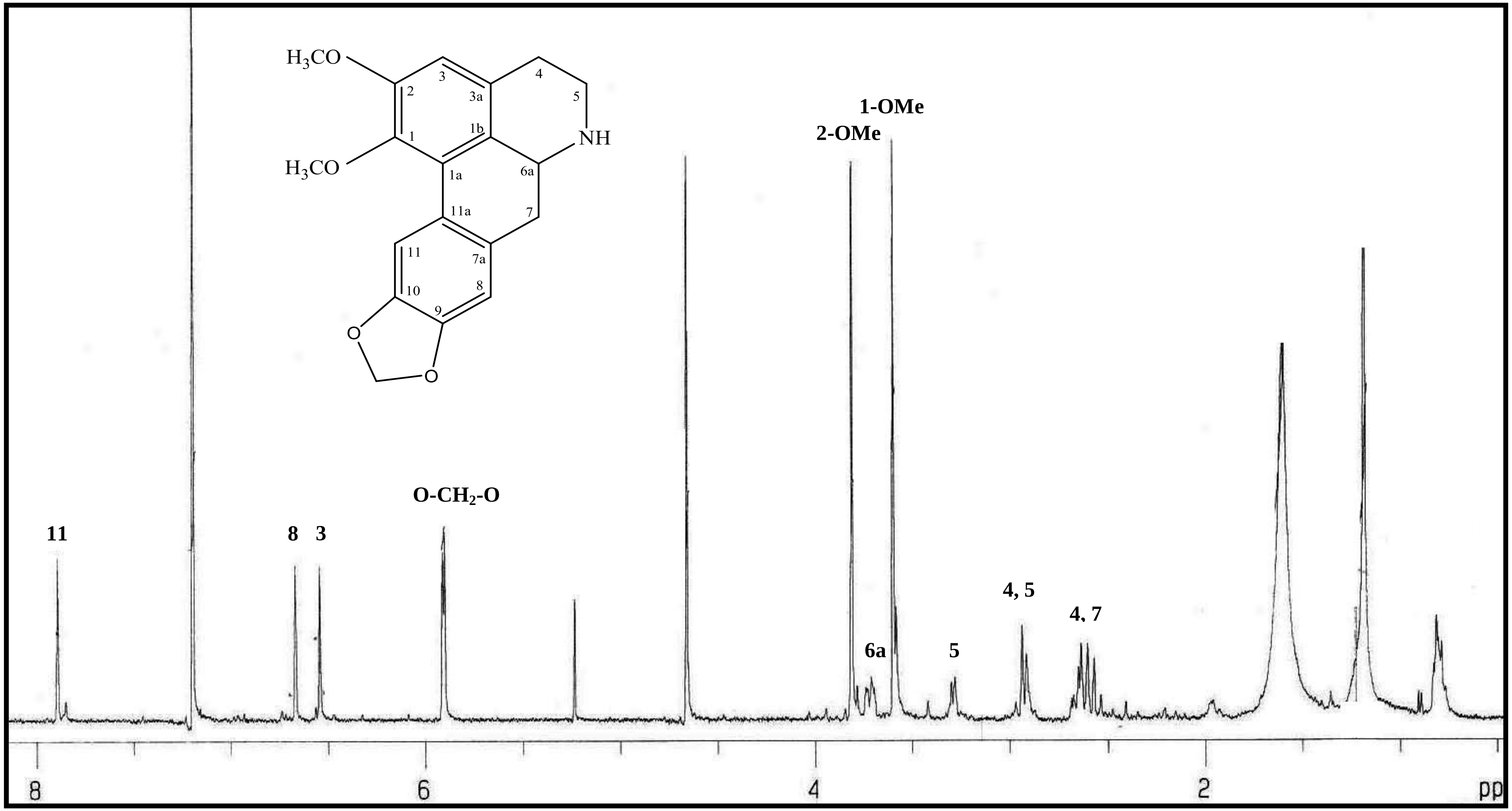


Figure 3.21: ^{1}H NMR Spectrum of Nornantenine **66**

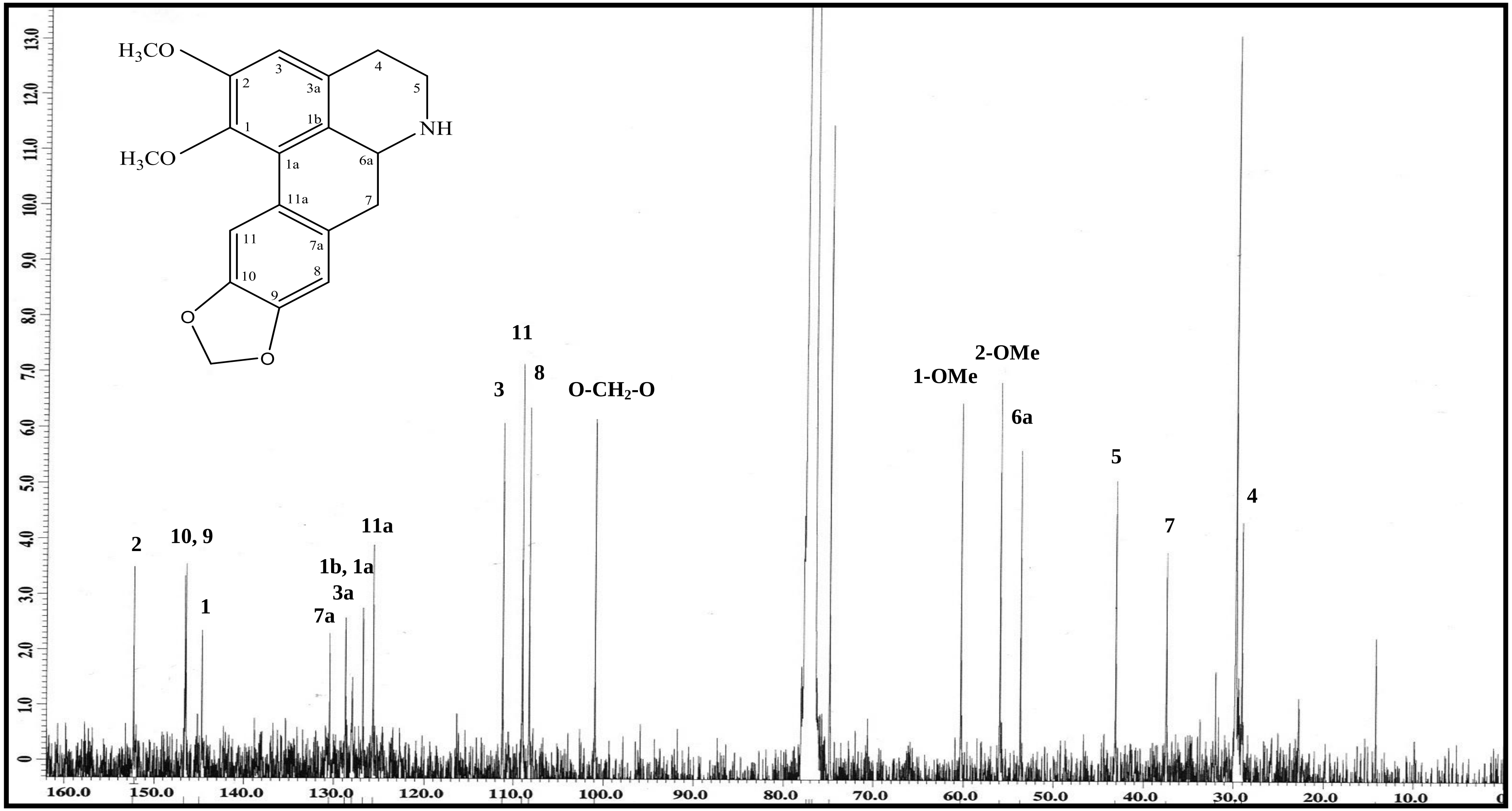


Figure 3.22: ^{13}C NMR Spectrum of Nornantenine **66**

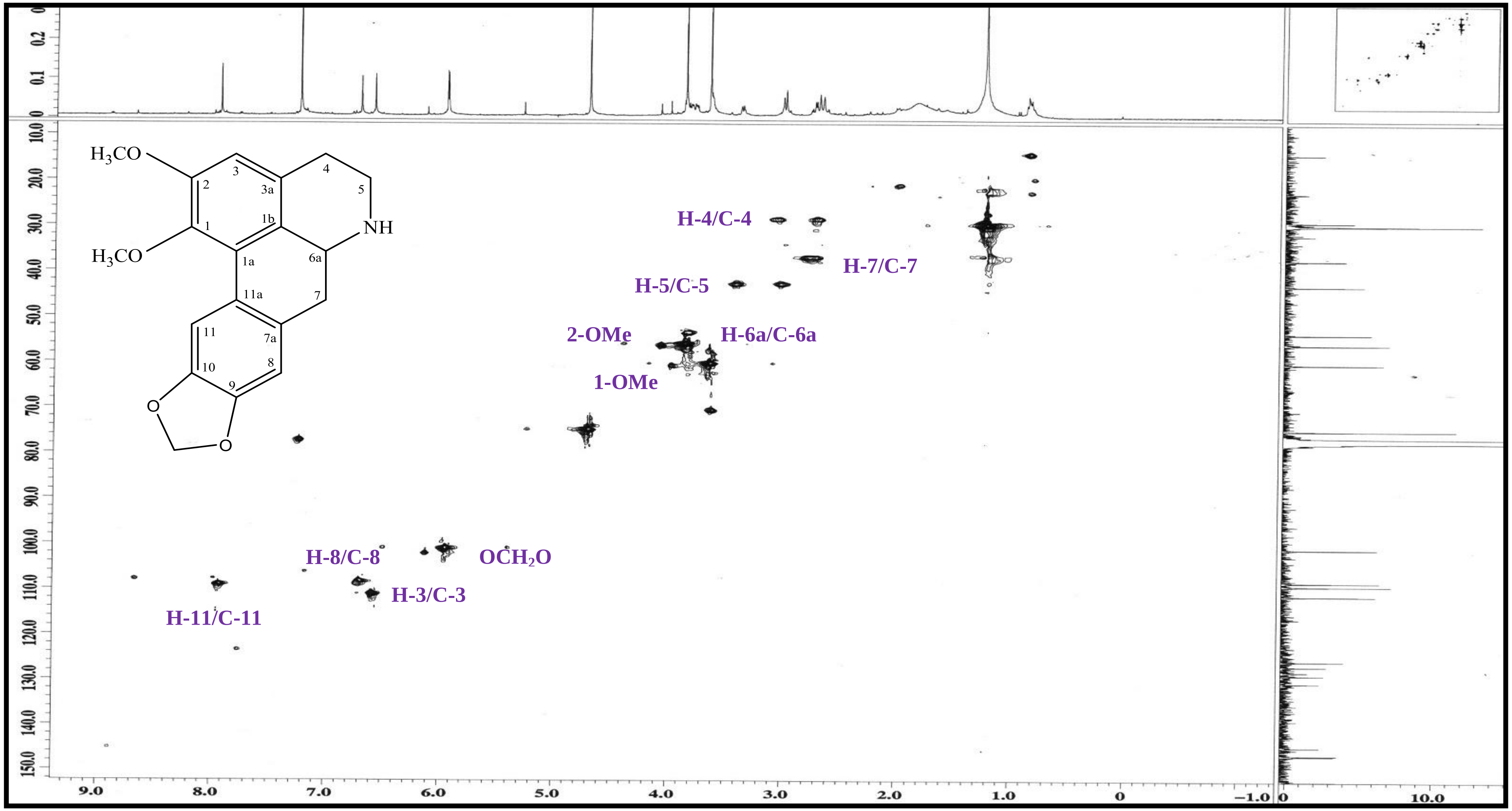


Figure 3.23: HMQC Spectrum of Nornantenine **66**

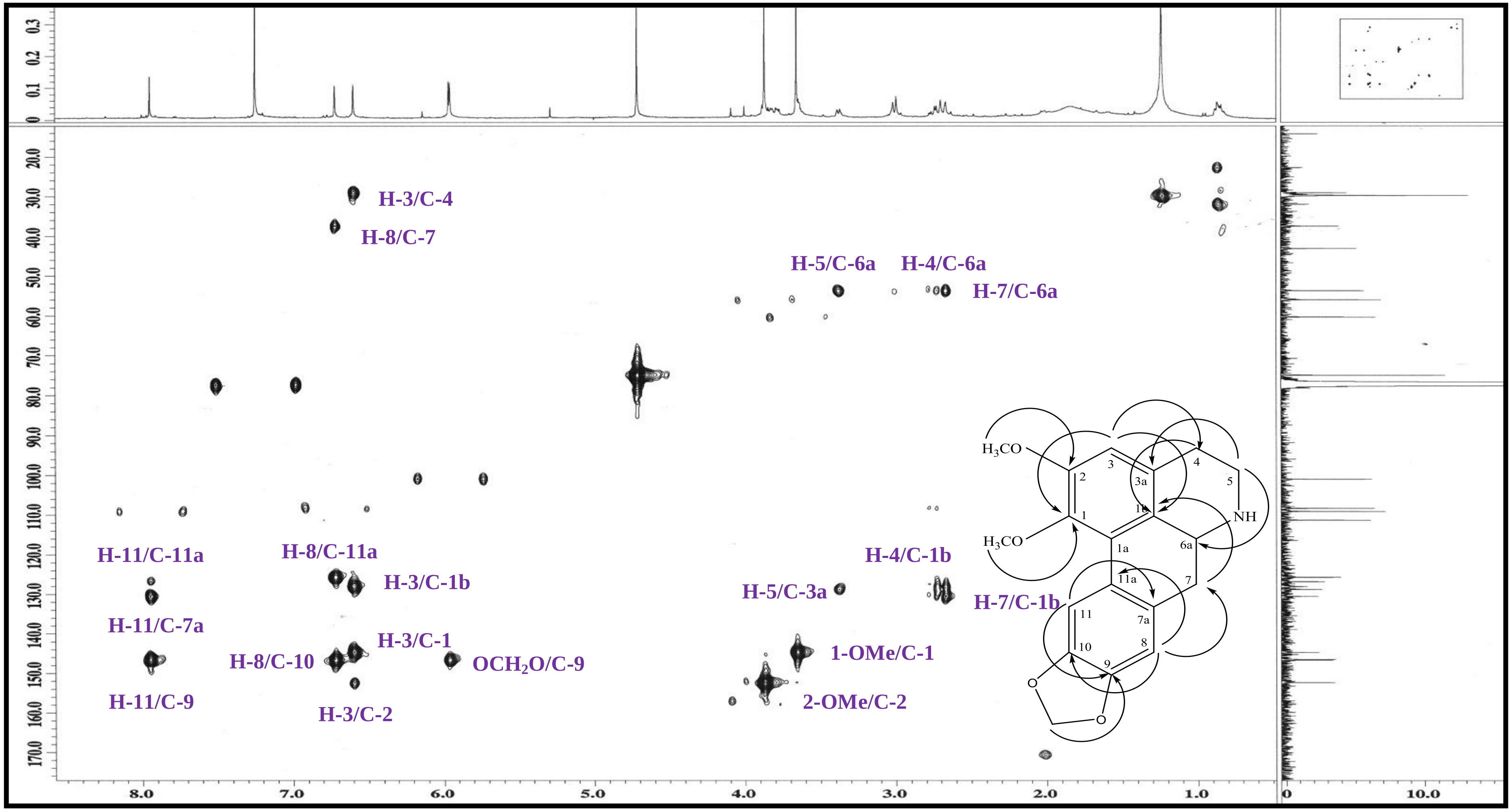


Figure 3.24: HMBC Spectrum of Nornantenine **66**

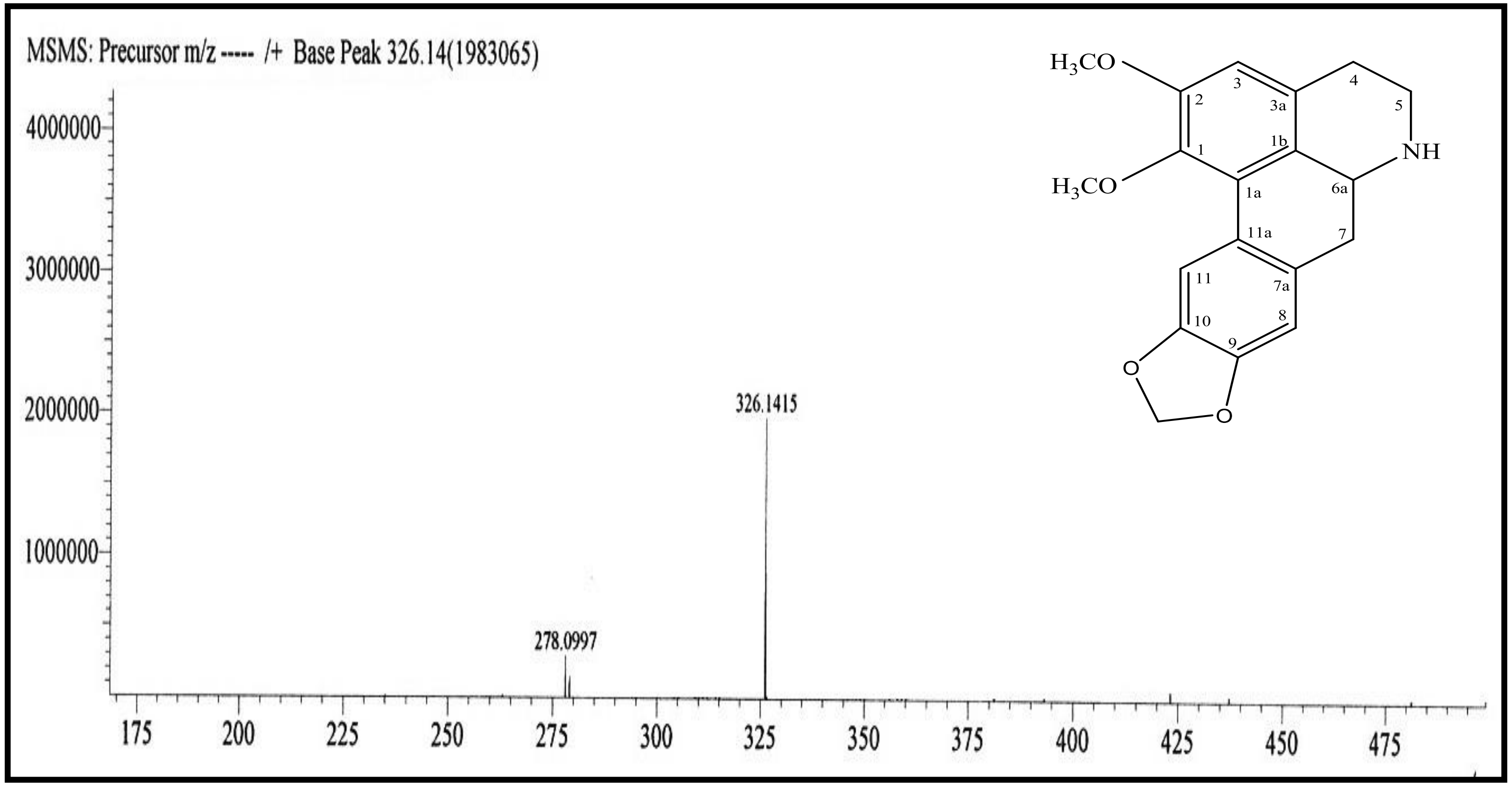


Figure 3.25: LCMS Spectrum of Nornantenine **66**