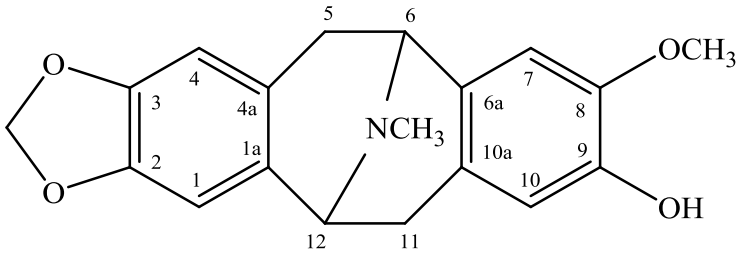
3.2.2 Alkaloid CD2: Isocaryachine 64



64

Alkaloid **CD2** was obtained as a brown amorphous. The UV spectrum exhibited maxima at 280 and 219 nm. The IR spectrum showed absorption at 3435.96 cm^{-1} indicating the presence of a hydroxyl group in the structure. The presence of a methylenedioxy group was proven by its characteristic absorption at 1229.50 and 925.16 cm^{-1} which indicated asymmetric O-C-O stretching. The ESIMS (positive mode) spectrum exhibited a pseudomolecular ion peak, $[M+H]^+$ at m/z 326.10 suggesting a molecular formula of $C_{19}H_{19}NO_4$.

The ^{1}H NMR spectrum (Figure 3.8) showed four aromatic protons resonated at δ 6.35 (*s*, 1H, H-10), δ 6.42 (*s*, 1H, H-4), δ 6.51 (*d*, *J* = 4.16, H-1) and 6.51 (*d*, *J* = 4.16 H-7). Six aliphatic protons appeared at the region of δ 3.87-2.49. The spliting pattern of aliphatic protons resembled with that of pavine alkaloids[90]. Furthermore, one *N*- methyl appeared as a singlet at δ 2.44. One distinct methoxyl signal was observed at δ 3.78 which most probably belonged to C-8. In addition, a pair of doublets at δ 5.74 and 5.79 (*d*, *J* = 1.2) were assigned to methylenedioxyl group.

The ^{13}C NMR spectrum (Figure 3.9) was in agreement with the molecular formula deduced from the mass spectrum, accounting for all nineteen carbons. Two of which were resonated upfield at δ 32.94 and 34.18 which belonged to C-11 and C-5

methylenes respectively. In the DEPT spectra (Figure 3.10), the presence of one *N*-methyl signal, one methoxyl group, one methylenedioxyl group, two methylenes, six methines, and eight quaternary carbons were observed. The ^{1}H NMR, ^{13}C NMR and COSY data for alkaloid **CD2** are tabulated in Table 3.2.

In addition, the assignments of all the aliphatic protons were determined by using the COSY spectrum at 400 MHz. The following correlations were observed: H-5α/H-5β, H-6/H-5α, H-11α/H-11β and H-12/H-11α. Based on the above findings and other spectroscopic data[16, 91], alkaloid **CD2** was identified as isocaryachine **64**.

Table 3.2: ^{1}H NMR (in $CDCl_3$, 400 MHz) and ^{13}C NMR (in $CDCl_3$, 400 MHz) of **64**.

Position	δ_H, ppm (J in Hz)	δ_C (ppm)	COSY
1	6.51 (*d*, 4.16)	109.05	
1a	-	130.90	
2	-	145.71	
3	-	146.03	
4	6.42 (*s*)	108.38	
4a	-	124.34	
5	3.24-3.34 (*m*)	34.18	H-5α/ H-5β
	2.49 (*d*, 16.08)		
6	3.87 (*d*, 8.32)	56.50	H-6/H-5α
6a	-	128.97	
7	6.51 (*d*, 4.16)	106.81	
8	-	144.17	
9	-	145.05	
10	6.35 (*s*)	114.24	
10a	-	124.72	
11	3.24-3.34 (*m*)	32.94	H-11α/H-11β
	2.49 (*d*, 16.08)		
12	3.87 (*d*, 8.32)	56.13	H-12/H-11α
8-OMe	3.78 (*s*)	55.71	
6, 12-*N*Me	2.44 (*s*)	40.59	
2, 3,-OCH_2O	5.74 (*d*, 1.2)	100.31	

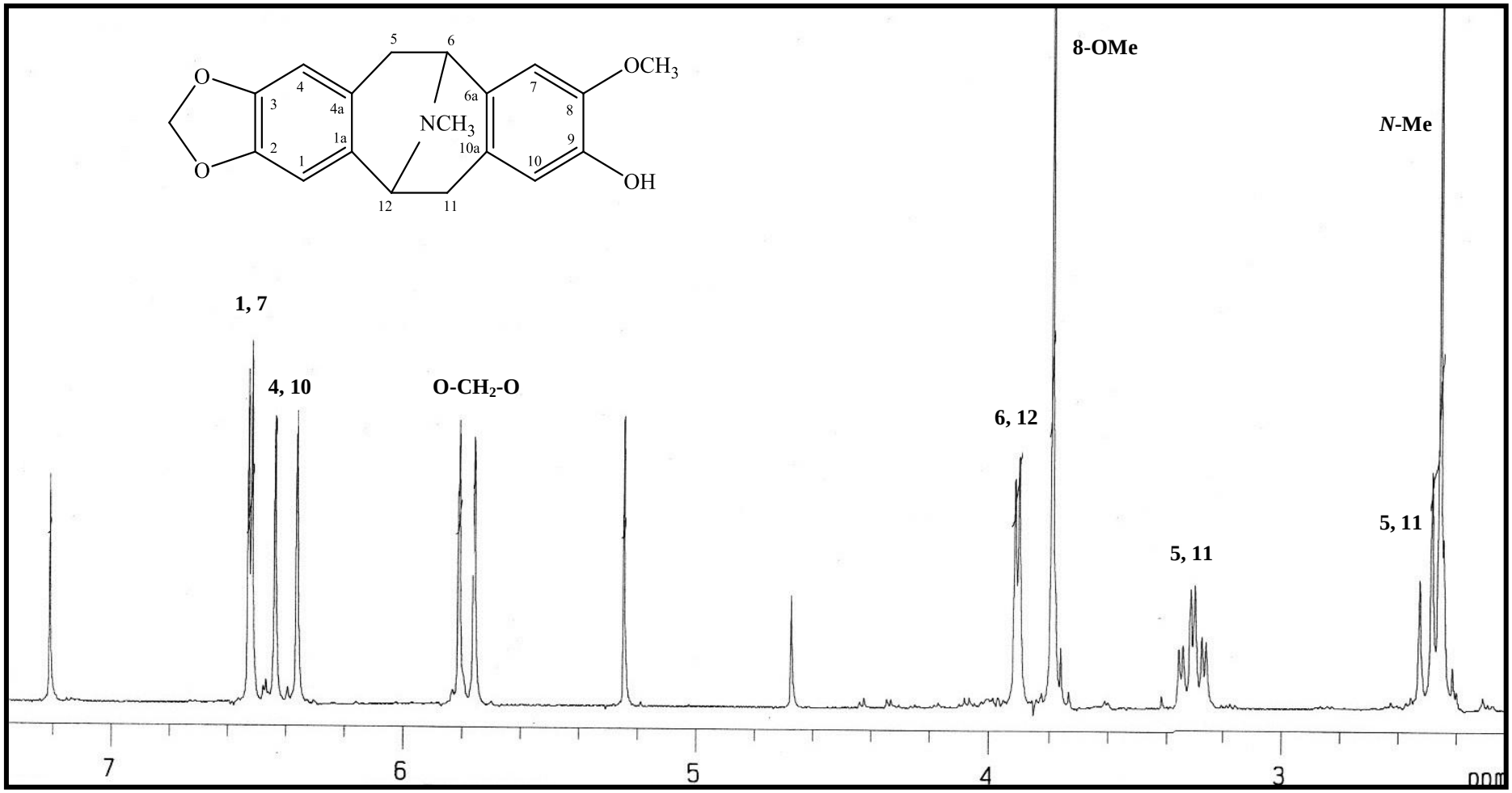


Figure 3.8: ^{1}H NMR Spectrum of Isocaryachine **64**

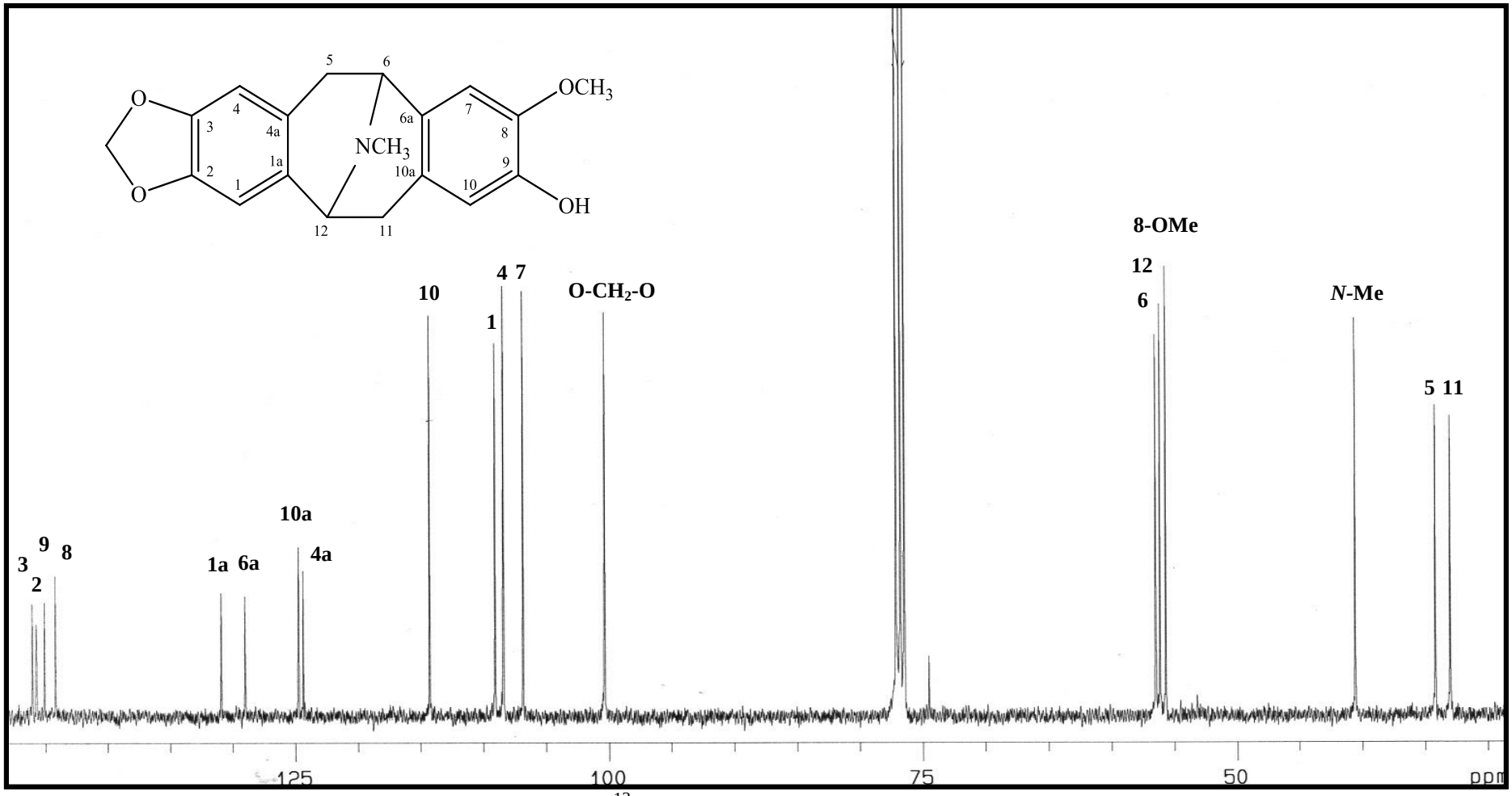


Figure 3.9: ^{13}C NMR Spectrum of Isocaryachine **64**

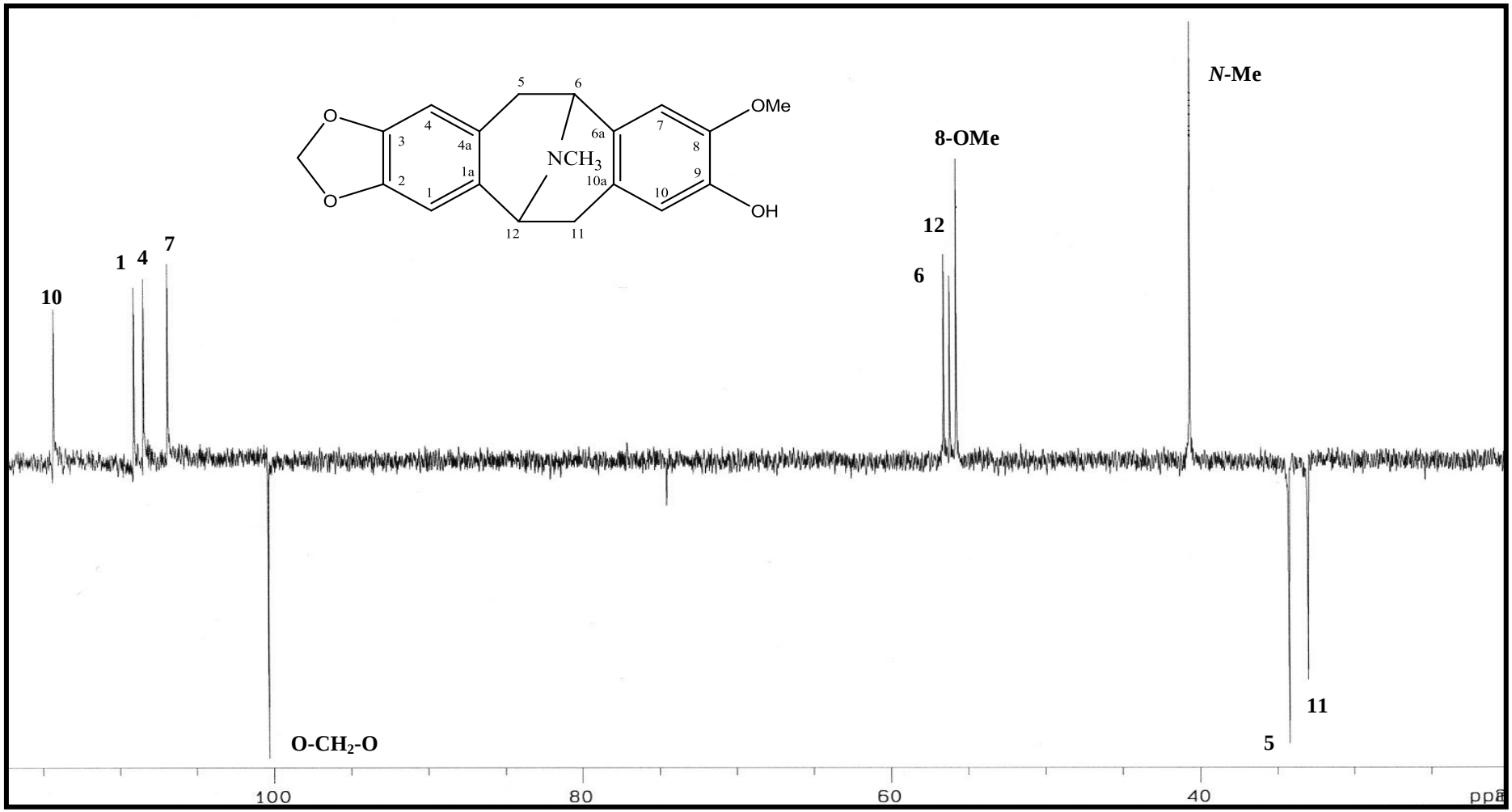


Figure 3.10: DEPT Spectrum of Isocaryachine **64**

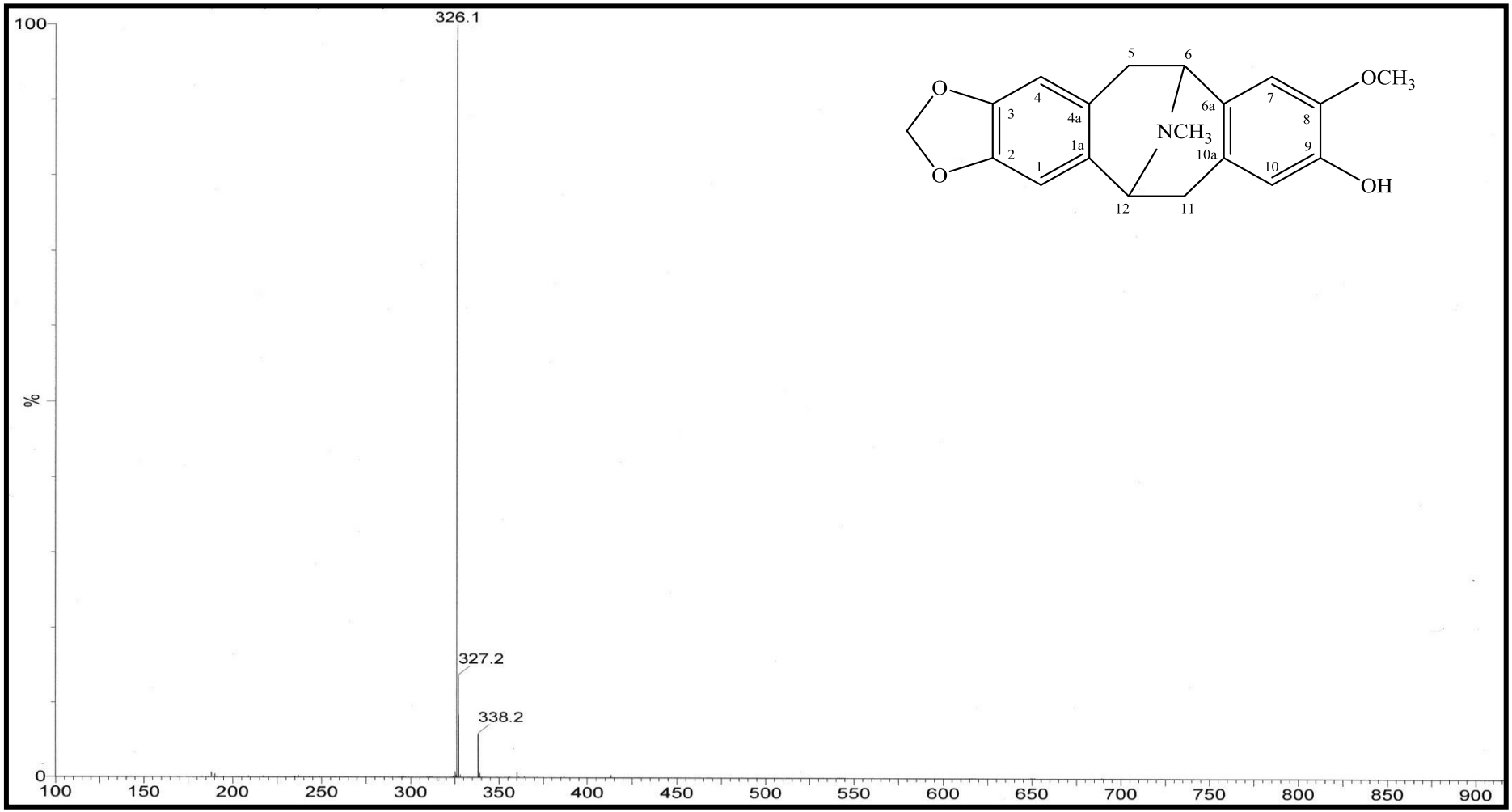


Figure 3.11: LCMS Spectrum of Isocaryachine **64**

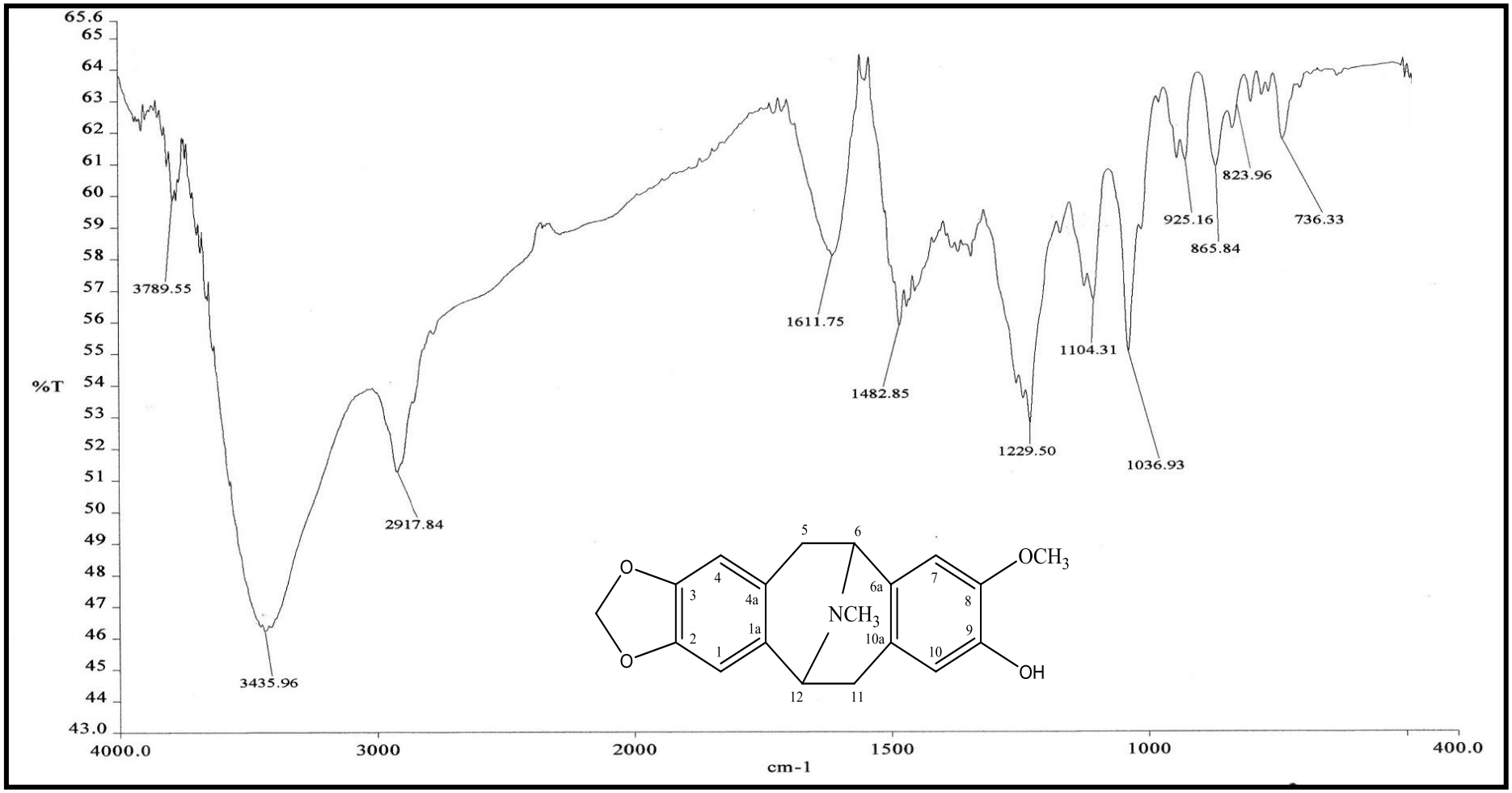


Figure 3.12: IR Spectrum of Isocaryachine **64**