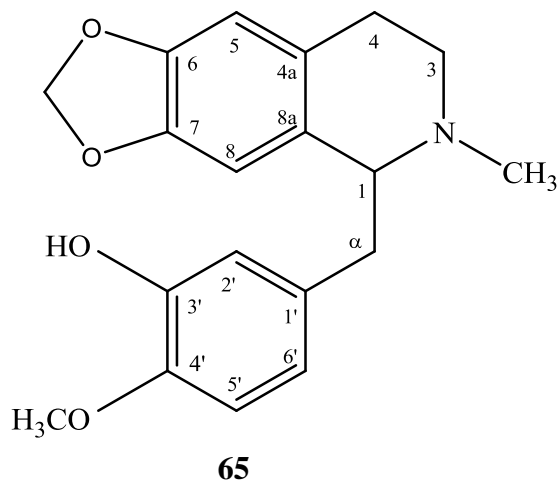


3.2.3 Alkaloid CD3: *N*-Demethylphyllodyptine 65



Alkaloid **CD3** was isolated as a dark brown amorphous. The UV spectrum showed absorption band at 286 nm which was a characteristic of a benzylisoquinoline alkaloid⁵⁸. The IR spectrum gave a broad band at 3419.45 cm^{-1} due to the presence of hydroxyl group in the structure. The ESIMS (positive mode) spectrum showed the pseudomolecular ion, $[\text{M}+\text{H}]^+$ peak at m/z 328.15 corresponding to a molecular formula of $\text{C}_{19}\text{H}_{21}\text{NO}_4$.

The ^1H NMR spectrum (Figure 3.13) exhibited two singlets of aromatic protons, H-5 and H-8 at δ 6.51 and 6.22 respectively. A doublet of doublets signal appeared at δ 6.56 belongs to H-6' with the coupling constants of 1.92 and 8.30 Hz due to this signal is *ortho* to H-5' and *meta* to H-2'. A singlet peak appeared at δ 3.84 could be assigned to methoxyl group at C-4'. The signals due to two methylenedioxy protons resonating as a doublet appeared at δ 5.85 and 5.87 ($J_1 = 1.36$) respectively. These two signals corresponded to C-6 and C-7 in the HMBC spectrum (Figure 3.17). The chemical shift values of the aliphatic proton appeared as a multiplet between δ 3.17-2.50 and *N*-methyl proton revealed at δ 2.45.

The ^{13}C NMR spectrum (Figure 3.14) exhibited nineteen carbons resonances which closely resembled those reported for *N*-demethylphyllocryptine **65**¹². In addition, the signals comprising of two methyls, four methylenes, six methines and seven quaternary carbons in this molecule. The signal at δ 100.61 was related to the methylenedioxy OCH_2O . The COSY spectrum (Figure 3.15) revealed the correlations between H-5'/H-6', H-3/H-4 and H-1/H- α . The HMBC experiment (Figure 3.17) further confirmed the structure of alkaloid **CD3**. In this spectrum, cross-peaks between H-1/C-3, H-1/C-8, H-3/C-4, H-4/C-3, H-5/C-4 and H-8/C-1 were seen. Other cross-peak correlations are shown in Figure 3.17.

Comparison of the empirical data with the literature values of the known compound^{10, 12, 18}, confirmed that alkaloid **CD3** is *N*-demethylphyllocryptine **65**.

Table 3.3: ^1H NMR (in CDCl_3 , 400 MHz) and ^{13}C NMR (in CDCl_3 , 400 MHz) of **65**.

Position	δ_{H} , ppm (J in Hz)	δ_{C} (ppm)	COSY	HMQC	HMBC (H \rightarrow C)
1	3.66 (<i>t</i> , 6.12)	65.11	H-1/H- α	H-1	α , 3, 8, 4a, 8a, 1'
3	2.73-2.75 (<i>m</i>) 3.11-3.17 (<i>m</i>)	46.37	H-3/H-4	H-3	1, 4, 4a
4	2.82 (<i>dd</i> , 5.92, 16.00) 2.56 (<i>m</i>)	25.41		H-4	3, 4a, 8a, 5
4a		126.95			
5	6.51 (<i>s</i>)	108.43		H-5	4, 8a, 7
6	-	145.43			
7	-	145.43			
8	6.22 (<i>s</i>)	107.94		H-8	1, 4a, 6
8a	-	130.50			
α	3.01 (<i>dd</i> , 5.88, 13.92)	41.07		H- α	1, 2', 6', 8a, 1'
1'	2.73 (<i>d</i> , 6.88)	133.03			
2'	6.74 (<i>d</i> , 1.96)	115.65		H-2'	α , 6', 4'
3'	-	145.43			
4'	-	145.09			
5'	6.72 (<i>d</i> , 8.08)	110.51	H-5'/H-6'	H-5'	1', 3'
6'	6.56 (<i>dd</i> , 1.92, 8.28)	120.98		H-6'	α , 2', 4'
6,7-	5.83 (<i>d</i> , 1.44)	100.61			6, 7
OCH ₂ O					
4'-OMe	3.84 (<i>s</i>)	55.99			4'
N-Me	2.45 (<i>s</i>)	42.38			3, 1

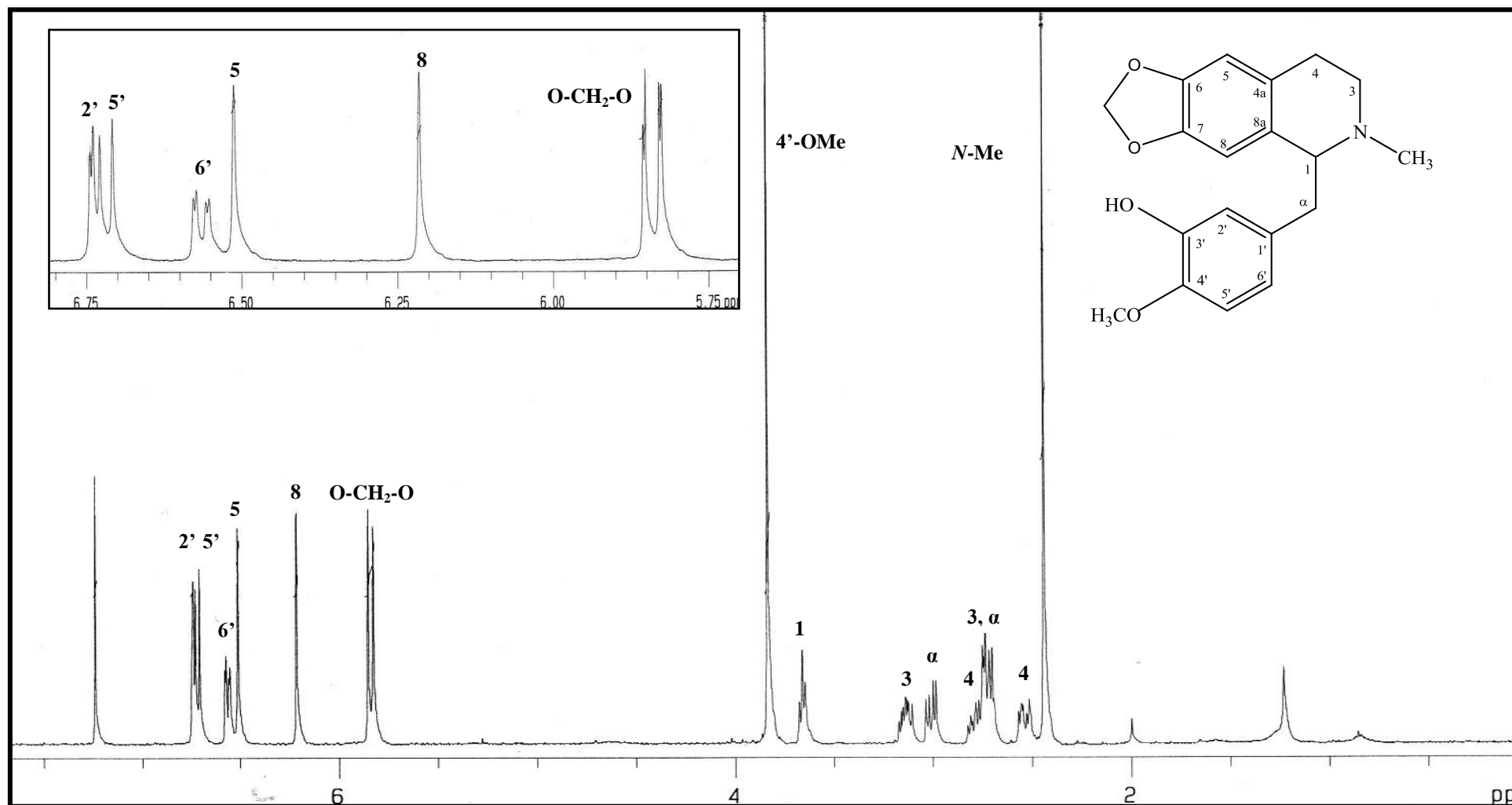


Figure 3.13: ^1H NMR Spectrum of *N*-Demethylphylllocryptine **65**

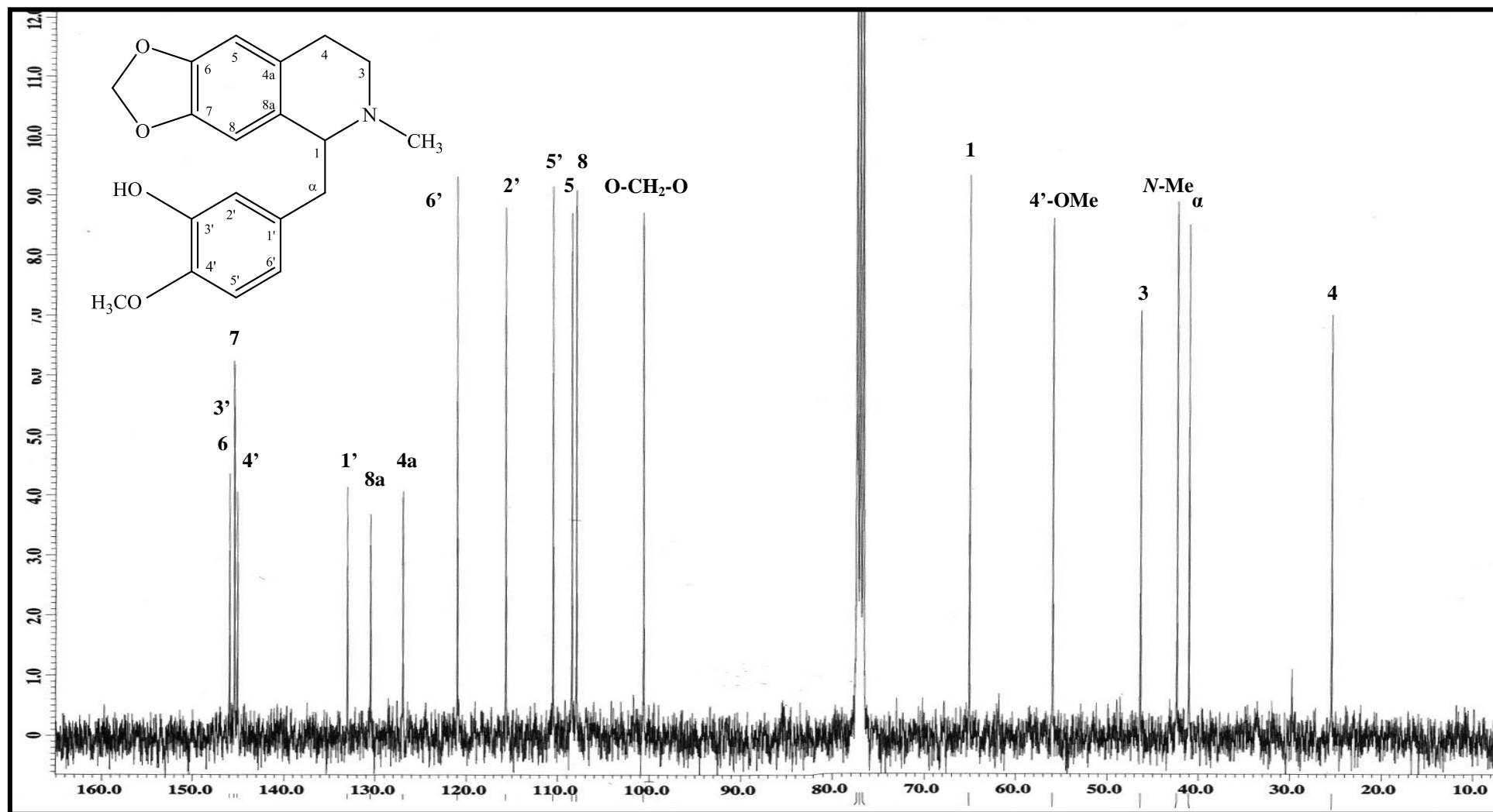


Figure 3.14: ^{13}C NMR Spectrum of *N*-Demethylphyllodyptine 65

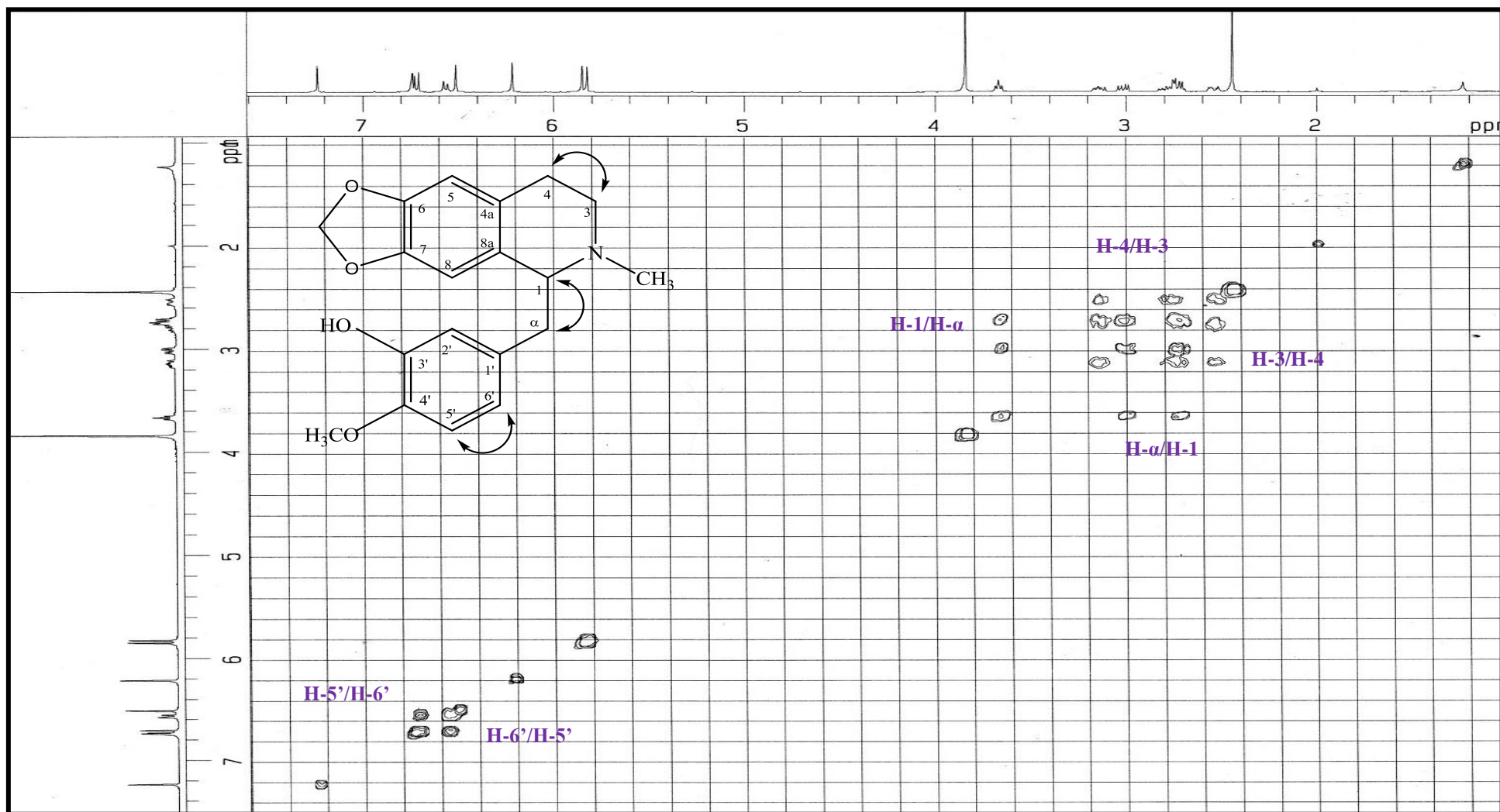


Figure 3.15: COSY Spectrum of *N*-Demethylphyllocryptine **65**

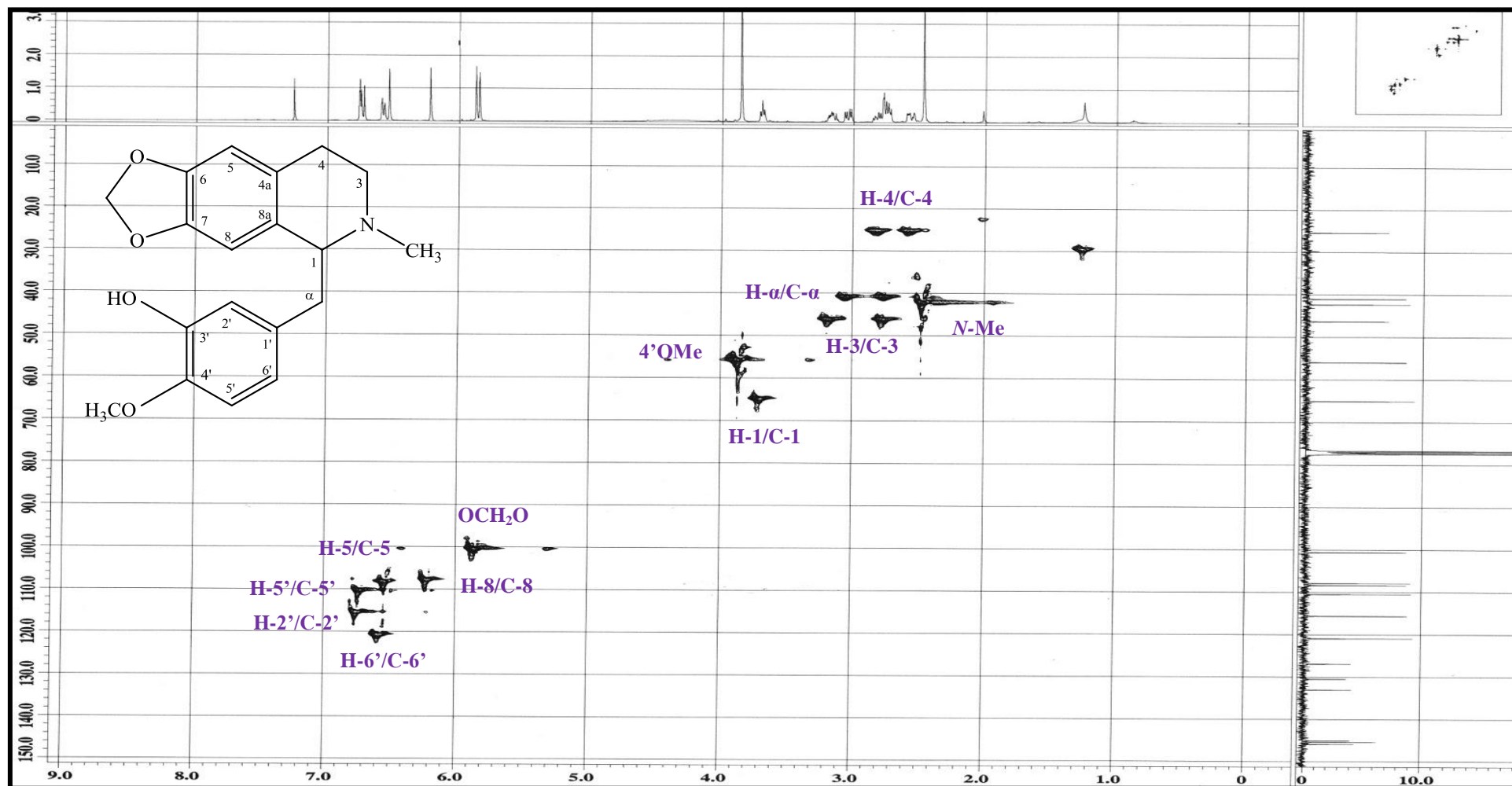


Figure 3.16: HMBC Spectrum of *N*-Demethylphyllodyptine 65

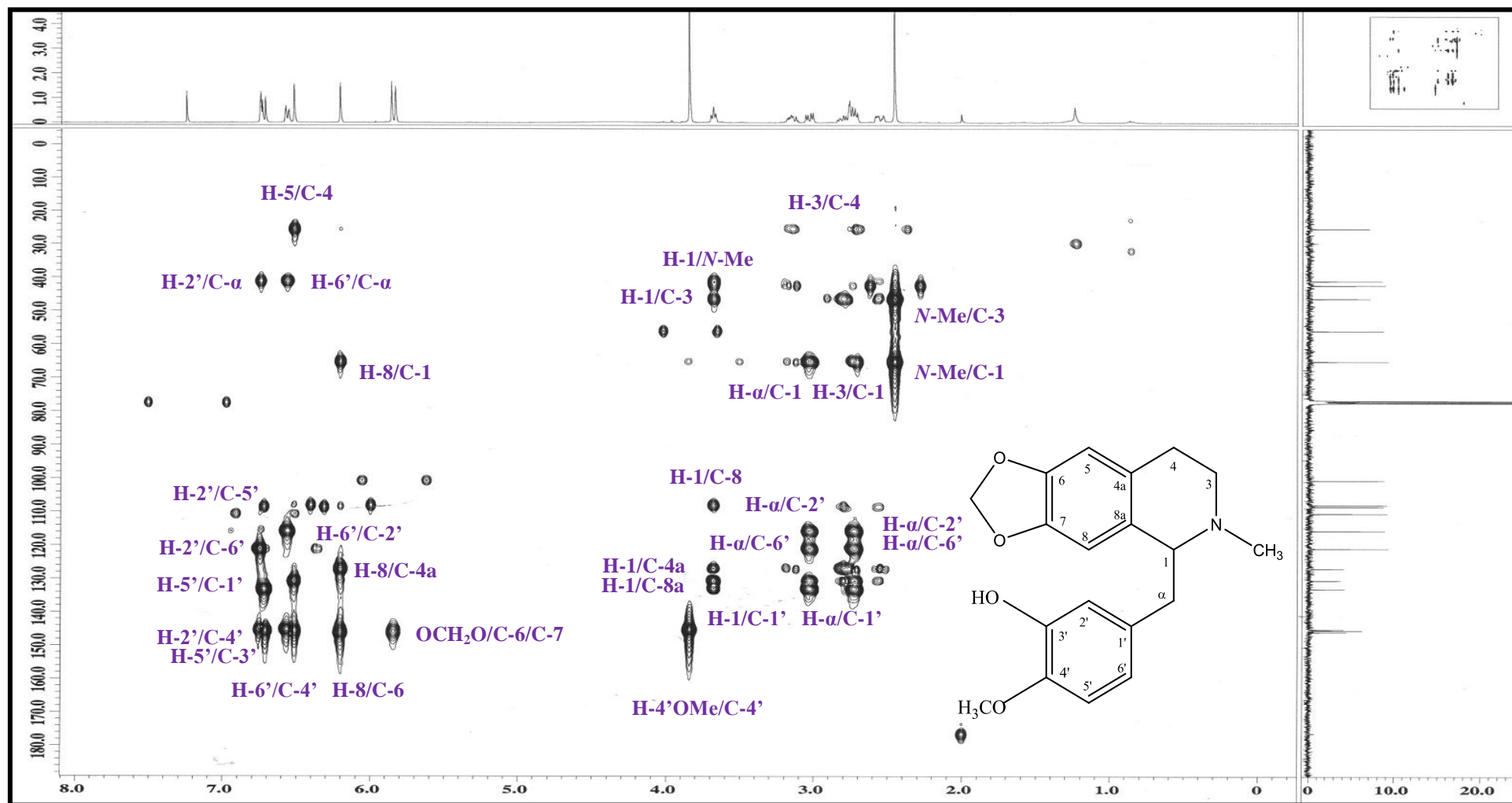


Figure 3.17: HMBC Spectrum of *N*-Demethylphylloriptine **65**

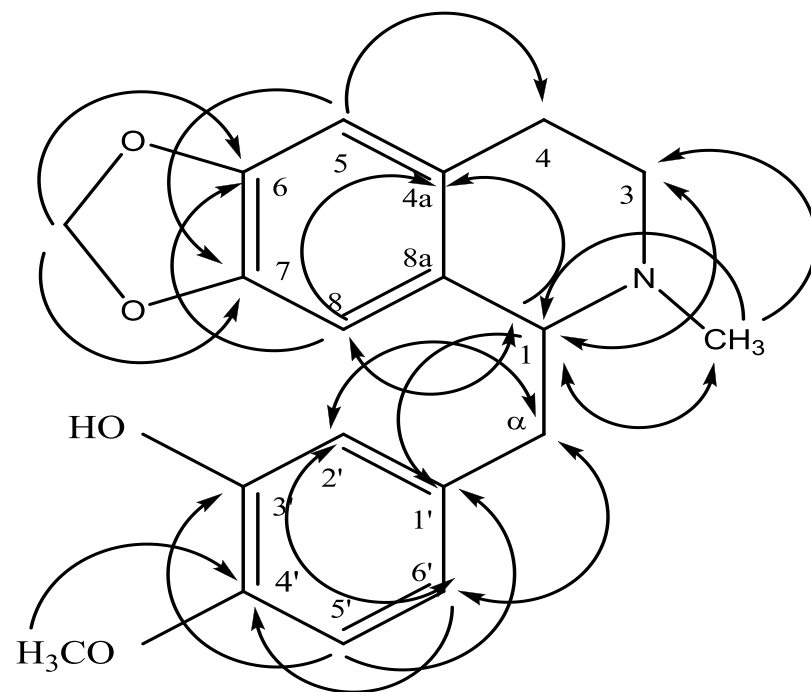


Figure 3.18: The ¹H – ¹³C HMBC Long Range Correlation of Alkaloid *N*-demethylphylloryptine **65**.

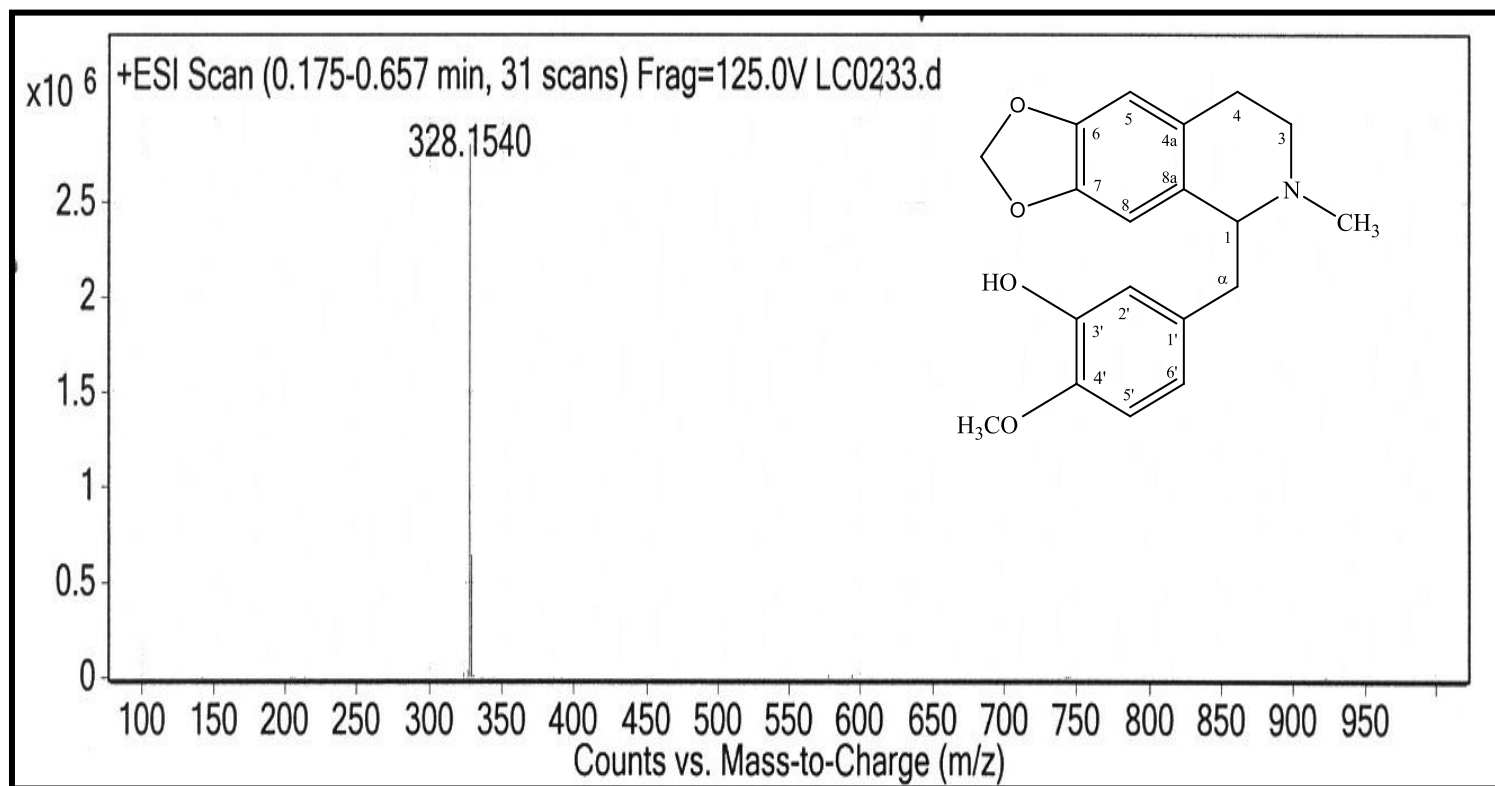


Figure 3.19: LCMS Spectrum of *N*-Demethylphyllocryptine **65**

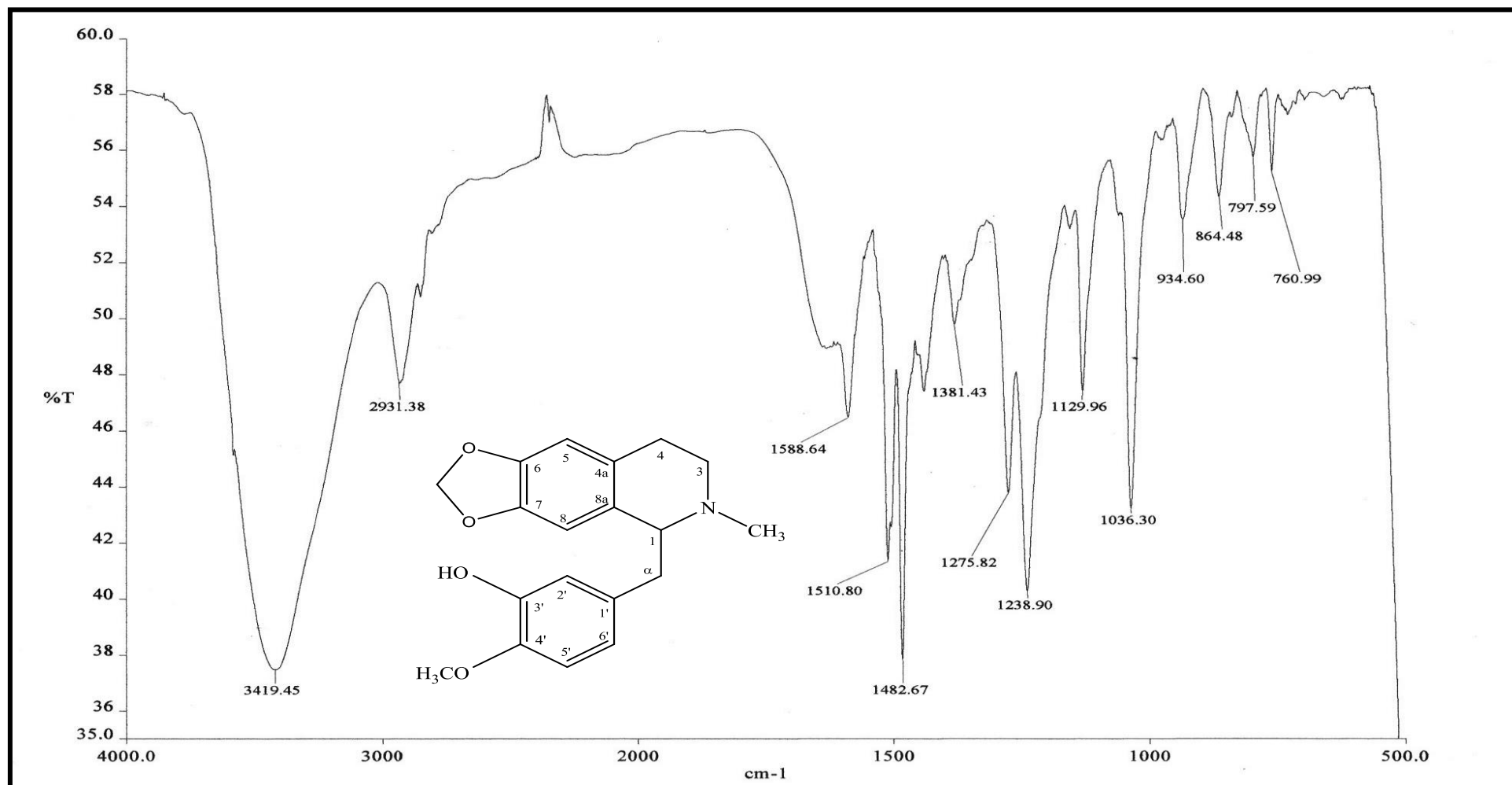


Figure 3.20: IR Spectrum of *N*-Demethylphyllocryptine **65**