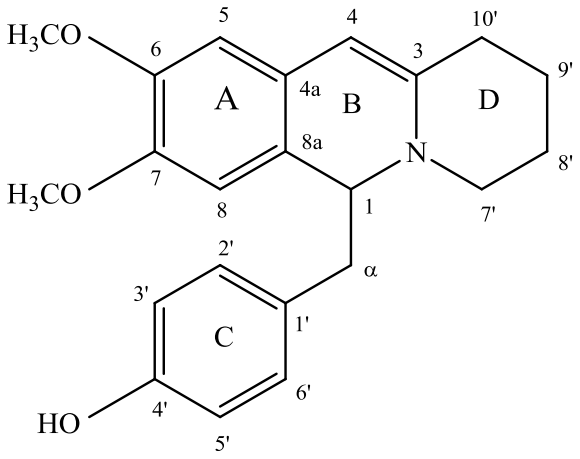
### 3.2.9 Alkaloid CD9: Cryptocaryadine 68




**68**

The new alkaloid **CD9** was afforded as a pale brownish amorphous solid. The UV spectrum showed absorption band at 302 nm, which indicated the existence of aromatic system. The IR spectrum showed absorption peak at 3448.18 $cm^{-1}$ indicated the presence of hydroxyl group in the structure. HRESIMS of alkaloid **CD9** revealed a molecular ion peak $[M+H]^+$ at m/z 352.1921 compatible with the molecular formula $C_{22}H_{25}NO_3$ (calculated for $C_{22}H_{25}NO_3$, 352.1868) from which we can deduce eleven degrees of unsaturation.

The $^1H$ NMR spectrum (Figure 3.44) showed five signals in the aromatic region. The significant signals for benzylisoquinoline type were observed at δ 6.43, δ 6.59, δ 6.58 δ 6.82 and δ 6.60 for H-5, H-4, H-8 H-2'/6', H-3'/5' respectively. H-4 appeared as a singlet at δ 6.59 thus, indicating that, C-3 is substituted. The absence of the signal around δ 7.00 suggested[108] the partial structure -HC=CH-N- for a normal oxoaporphine was absent in the structure of **CD9**. Instead, an existence of another ring was suggested by the following evidence. The ring D closure was found to attach at C-3 and *N*-2 by observing the correlations of H-10' to C-3 and H-7' to C-1 in the HMBC spectrum

(Figure 3.47). Furthermore, the HMBC spectrum also revealed cross-peaks of H-7' to C-9', C-8' and C-α, on one hand and H-2'/H-6' showed the long range correlations to the signals at C-4', C-6' and C-3' on the other hand. Thus, the structure is depicted as shown in structure **68** and the complete assignment of $^{1}H$ and $^{13}C$ data are shown in Table 3.9. The aliphatic protons of H-α, H-7', H-8', H-9' and H-10' were observed in the range of δ 3.84-1.59. The most downfield peak was H-α due to its adjacent to benzene ring. The COSY spectrum (Figure 3.49) displayed the correlations of H-9''/H-9', H-α'/H-α, H-2'/H-3' and H-5'/H-6'.

The position of 6-OMe and 7-OMe were established from NOESY spectrum (see Figure 3.50). The correlations were found between H-5 (δ 6.43)/6-OMe (δ 3.48), and H-8 (δ 6.58)/7-OMe (δ 3.75), indicating that the oxygenated C-4' was hydroxylated.

The $^{13}C$ NMR, DEPT-135 and HMQC spectra revealed the presence of twenty two carbons: seven $sp^2$ methines, one $sp^3$ methine, five $sp^3$ methylenes, two methyls and seven $sp^2$ quaternary carbons, of which three oxygenated carbons were resonating at δ 147.9, 147.2 and 155.4 assignable to C-6, C-7 and C-4' respectively.

Based on the analysis of all the spectroscopic data, the author concluded that alkaloid **CD9** is a novel compound namely cryptocaryadine **68**.

Table 3.9: $^{1}H$ NMR (in $CDCl_3$, 400MHz) and $^{13}C$ NMR (in $CDCl_3$, 100MHz) of **68**

| Position | $\delta_H$, ppm (J in Hz) | $\delta_C$ (ppm) | COSY | HMQC | HMBC |
|---|---|---|---|---|---|
| 1 | 2.40 (*d*, 10.52) | 60.70 | | H-1 | |
| 3 | - | 132.4 | | | |
| 4 | 6.59 (*s*) | 120.8 | | H-4 | 5 |
| 4a | - | 134.8 | | | |
| 5 | 6.43 (*d*, 1.36) | 112.9 | | H-5 | 4, 7, 8a |
| 6 | - | 147.9 | | | |
| 7 | - | 147.2 | | | |
| 8 | 6.58 (*d*, 1.84) | 110.5 | | H-8 | 4, 6 |
| 8a | - | 132.5 | | | |
| α | 3.84 (*d*, 16.48) | 57.8 | H-α/H-α’ | H-α | 1, 1’, 8a |
| | 3.09 (*d*, 16.48) | | | | |
| 1’ | - | 132.3 | H-2’/H-3’ | | |
| 2’ | 6.82 (*d*, 8.68) | 130.2 | | H-2’ | 3’, 4’, 6’ |
| 3’ | 6.60 (*d*, 8.68) | 115.3 | | H-3’ | 1’, 4’, 5’ |
| 4’ | - | 155.4 | | | |
| 5’ | 6.60 (*d*, 8.68) | 115.3 | H-5’/H-6’ | H-5’ | 1’, 3’, 4’ |
| 6’ | 6.82 (*d*, 8.68) | 130.2 | | H-6’ | 2’, 4’, 5’ |
| 7’ | 3.29 (*t*, 9.16) | 54.2 | | H-7’ | 8’, 10’, α |
| | 2.27 (*dd*, 8.72, 17.88) | | | | |
| 8’ | 2.08 (*m*) | 30.5 | | H-8’ | |
| | 1.59 (*m*) | | | | |
| 9’ | 1.95 (*m*) | 21.4 | H-9’-H-9’’ | | 3 |
| | 1.83 (*m*) | | | | |
| 10’ | 2.70 (*d*, 16.0) | 37.8 | | H-10’ | 1, 3 |
| | 2.48 (*m*) | | | | |
| 6-OMe | 3.48 (*s*) | 55.5 | | | 6 |
| 7-OMe | 3.75 (*s*) | 55.7 | | | 7 |

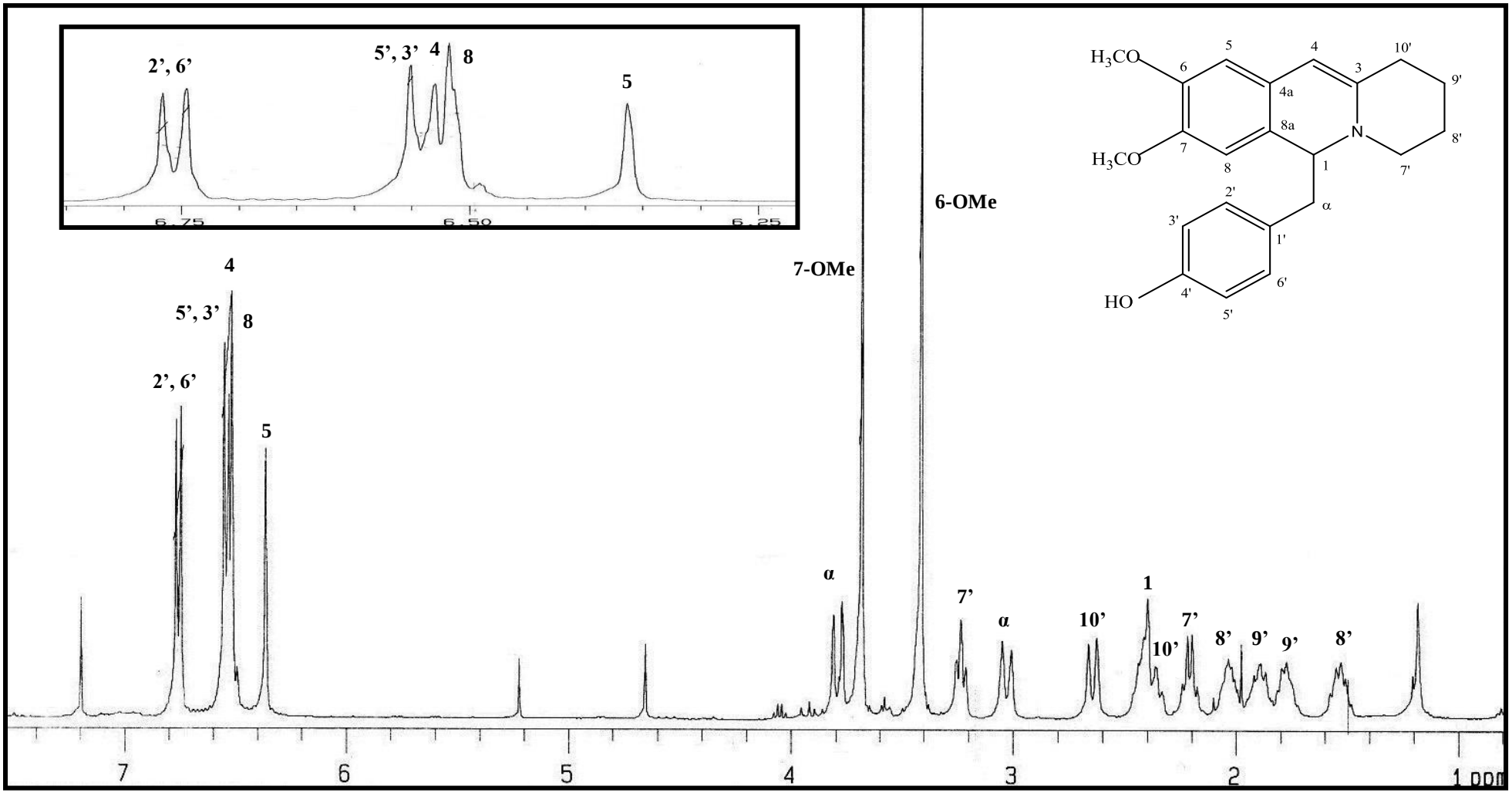



Figure 3.44: $^{1}$H NMR Spectrum of Cryptocaryadine of **68**

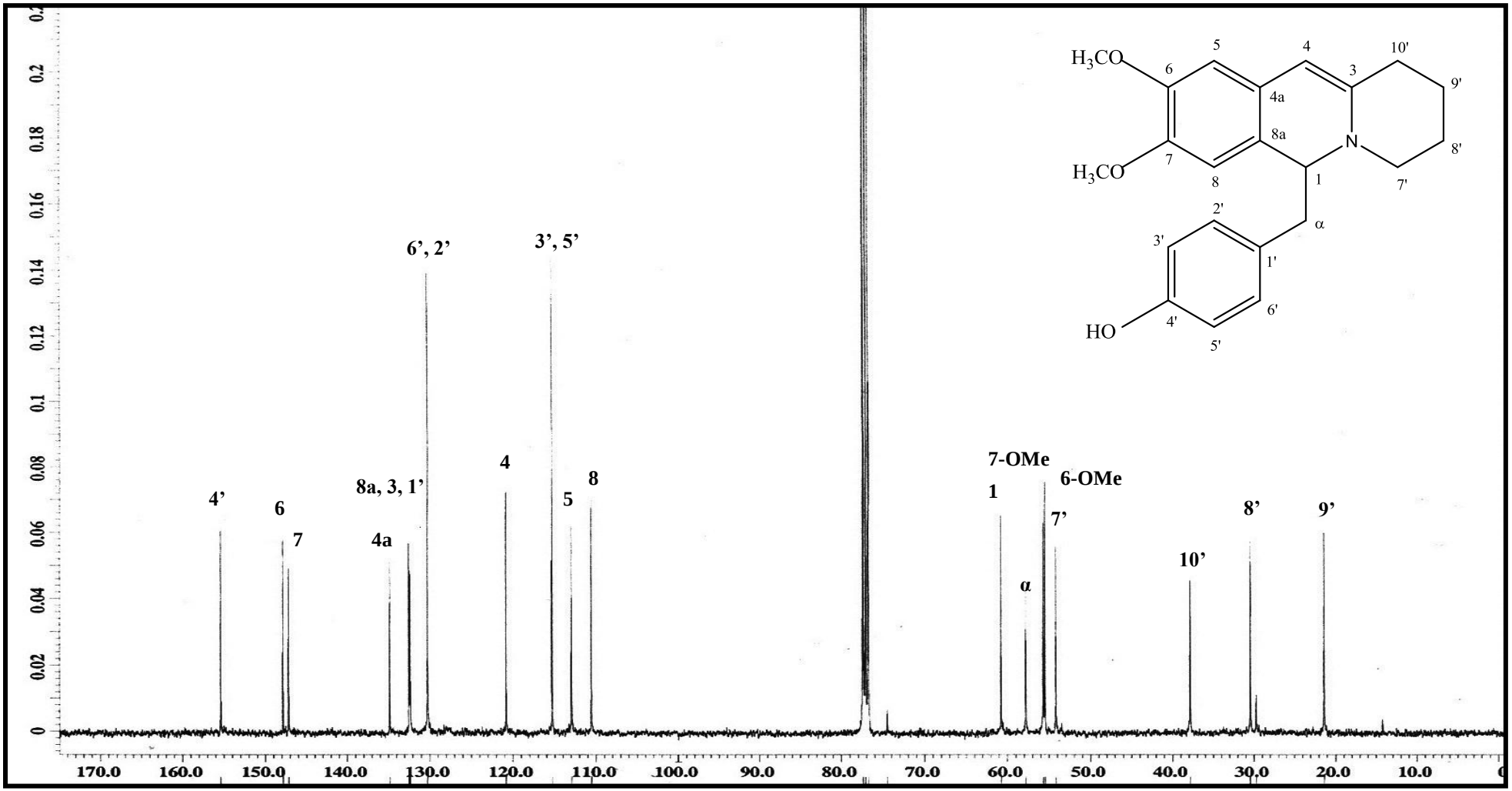



Figure 3.45: $^{13}$C NMR Spectrum of Cryptocaryadine of **68**

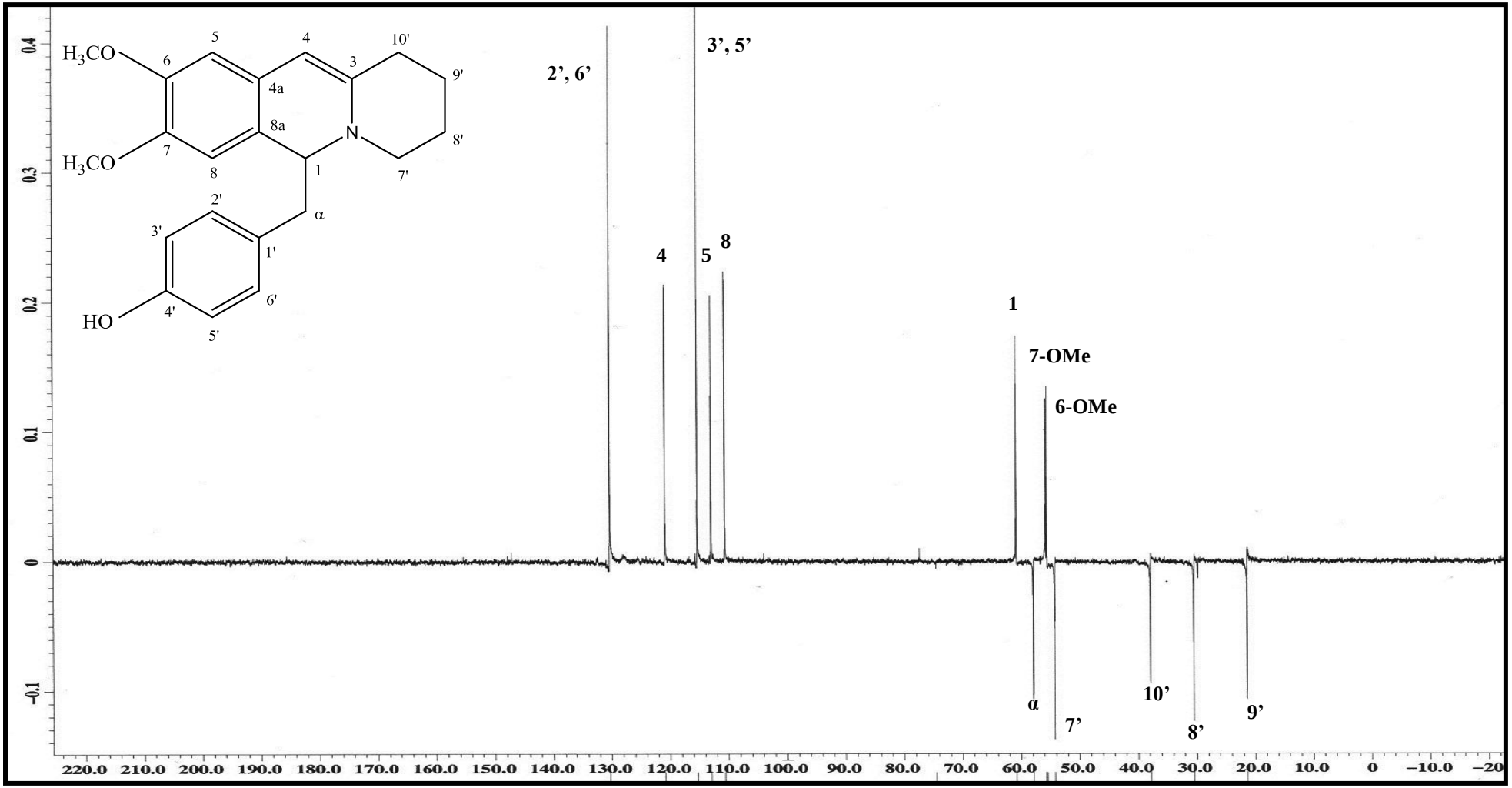



Figure 3.46: DEPT Spectrum of Cryptocaryadine of **68**

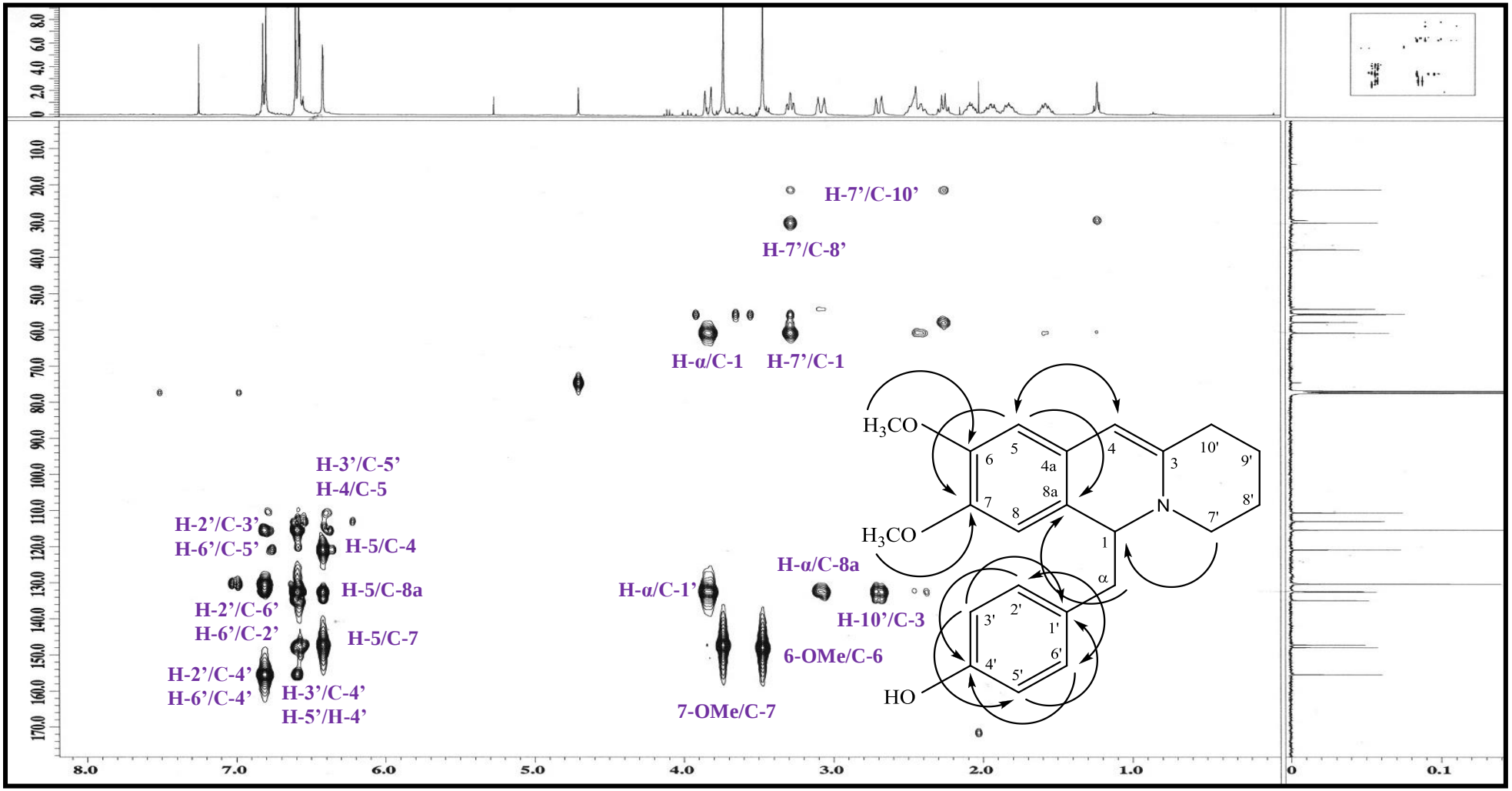



Figure 3.47: HMBC Spectrum of Cryptocaryadine of **68**

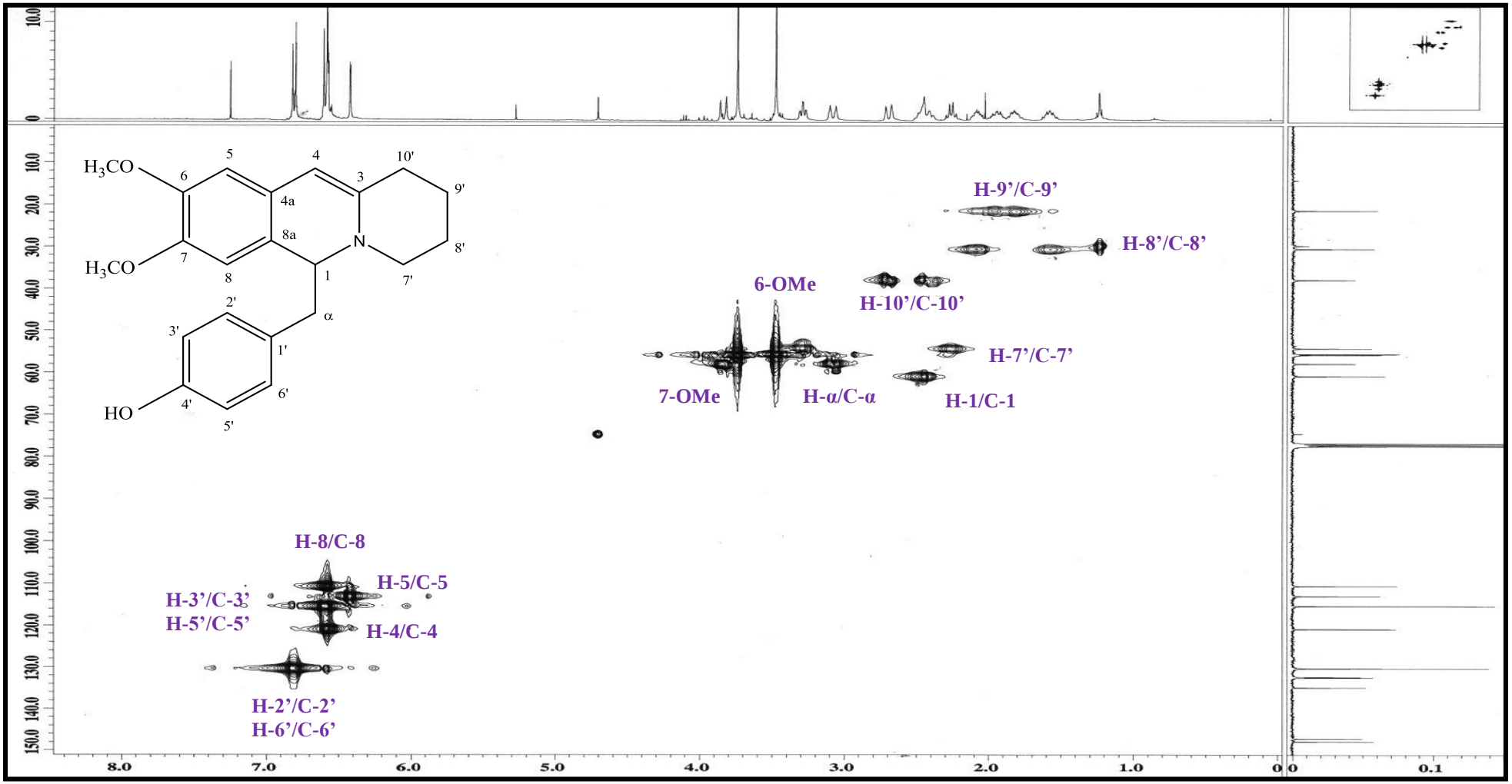



Figure 3.48: HMQC Spectrum of Cryptocaryadine **68**

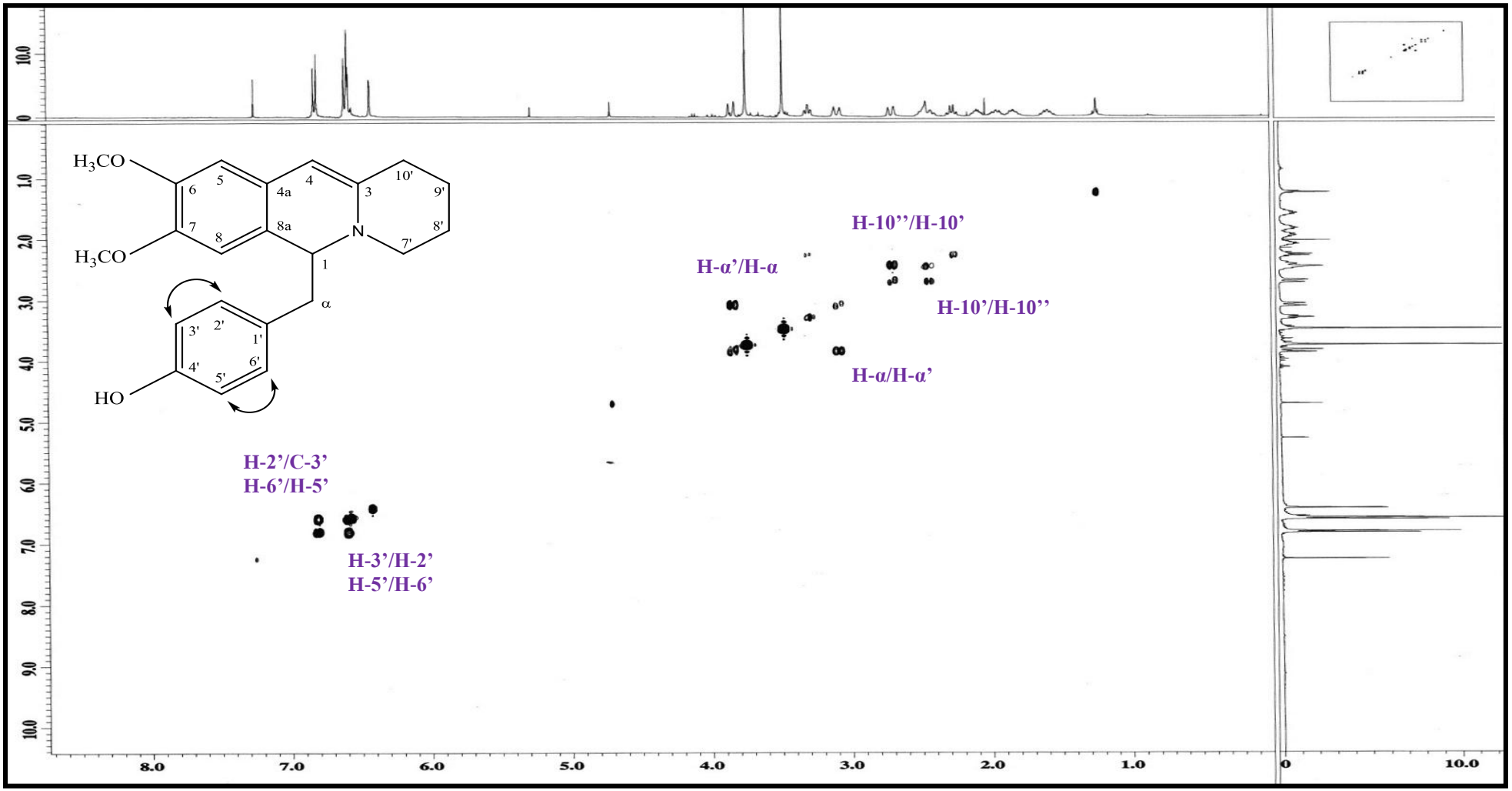



Figure 3.49: COSY Spectrum of Cryptocaryadine **68**

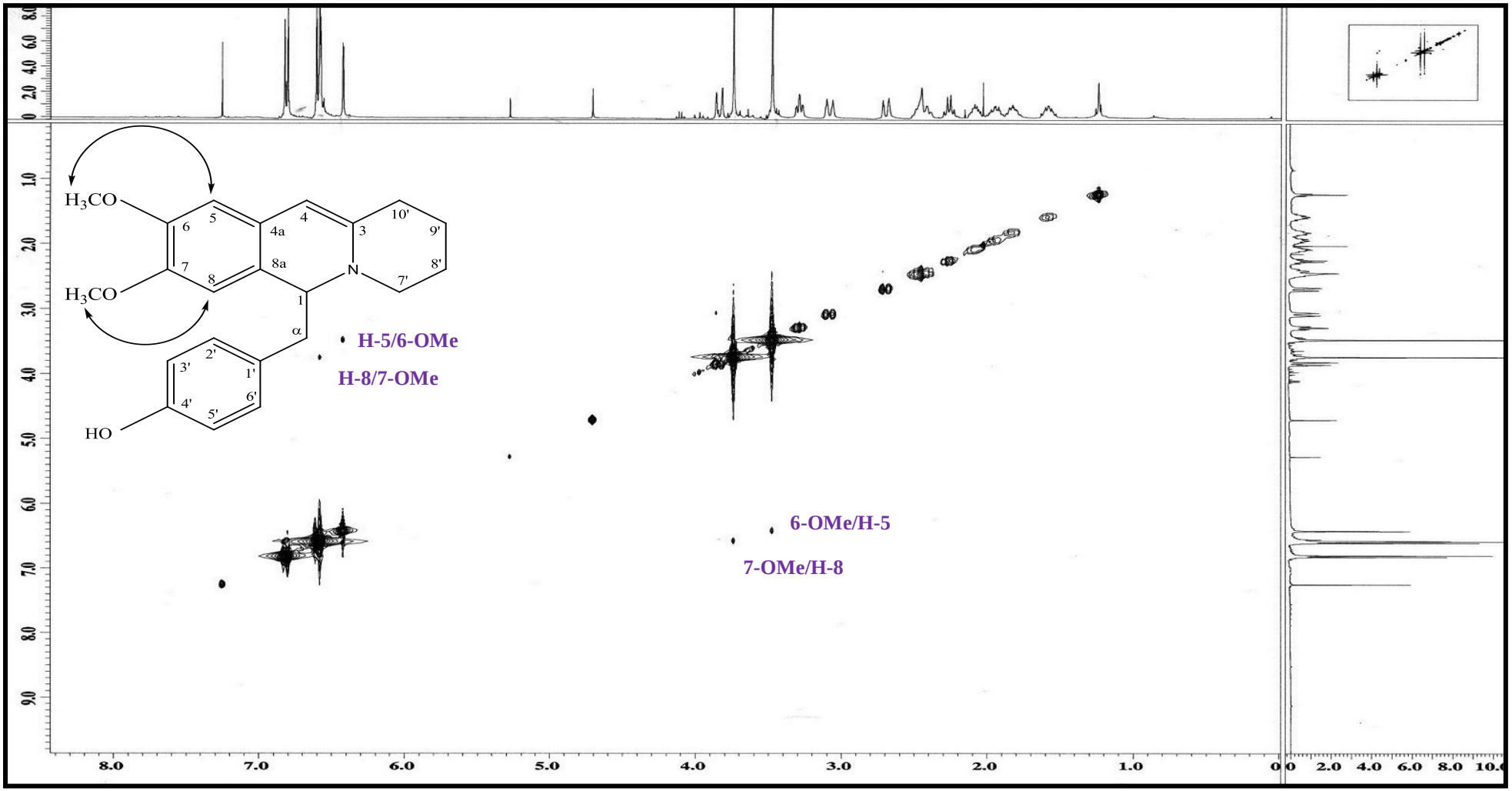



Figure 3.50: NOESY Spectrum of Cryptocaryadine **68**

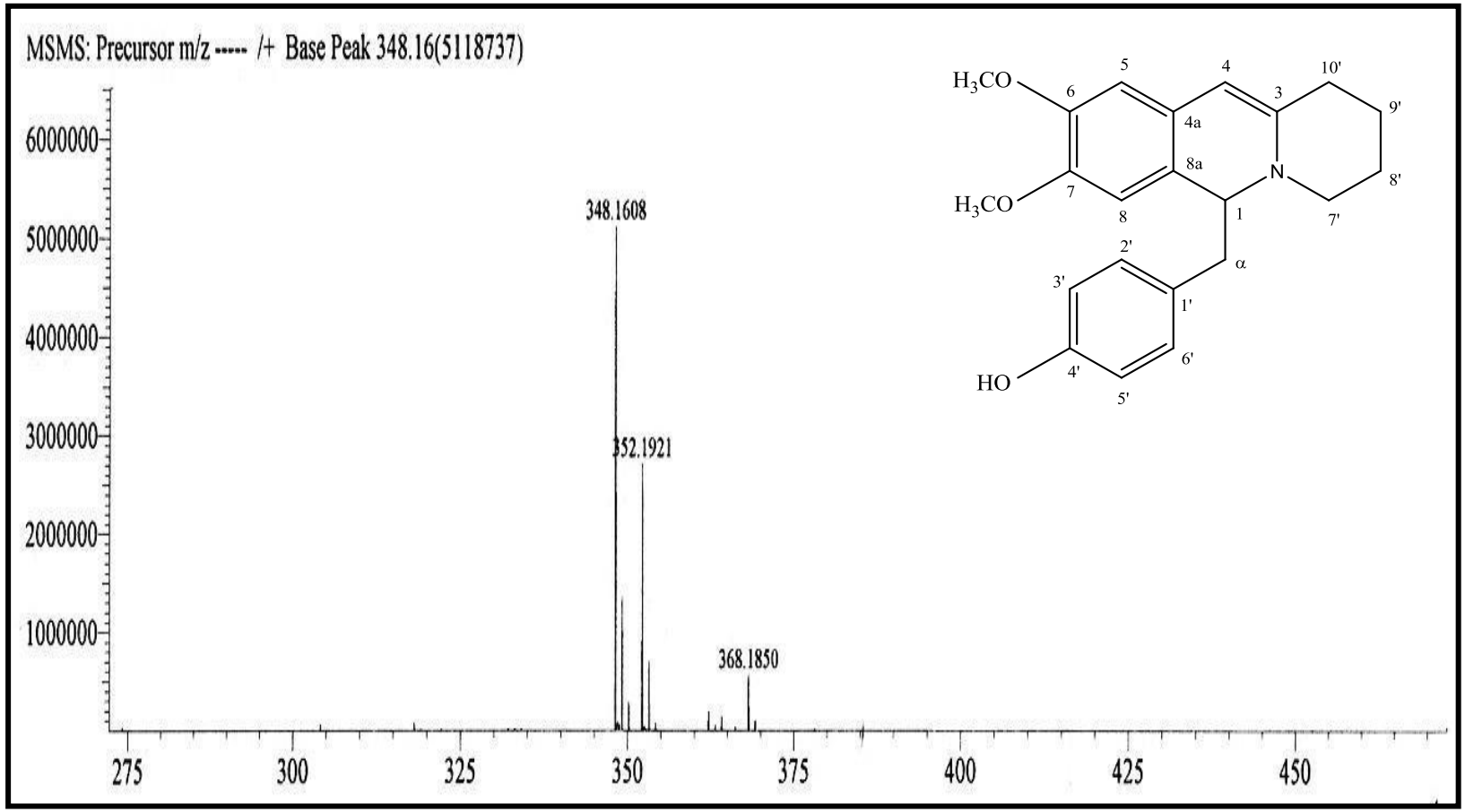



Figure 3.51: LCMS Spectrum of Cryptocaryadine **68**

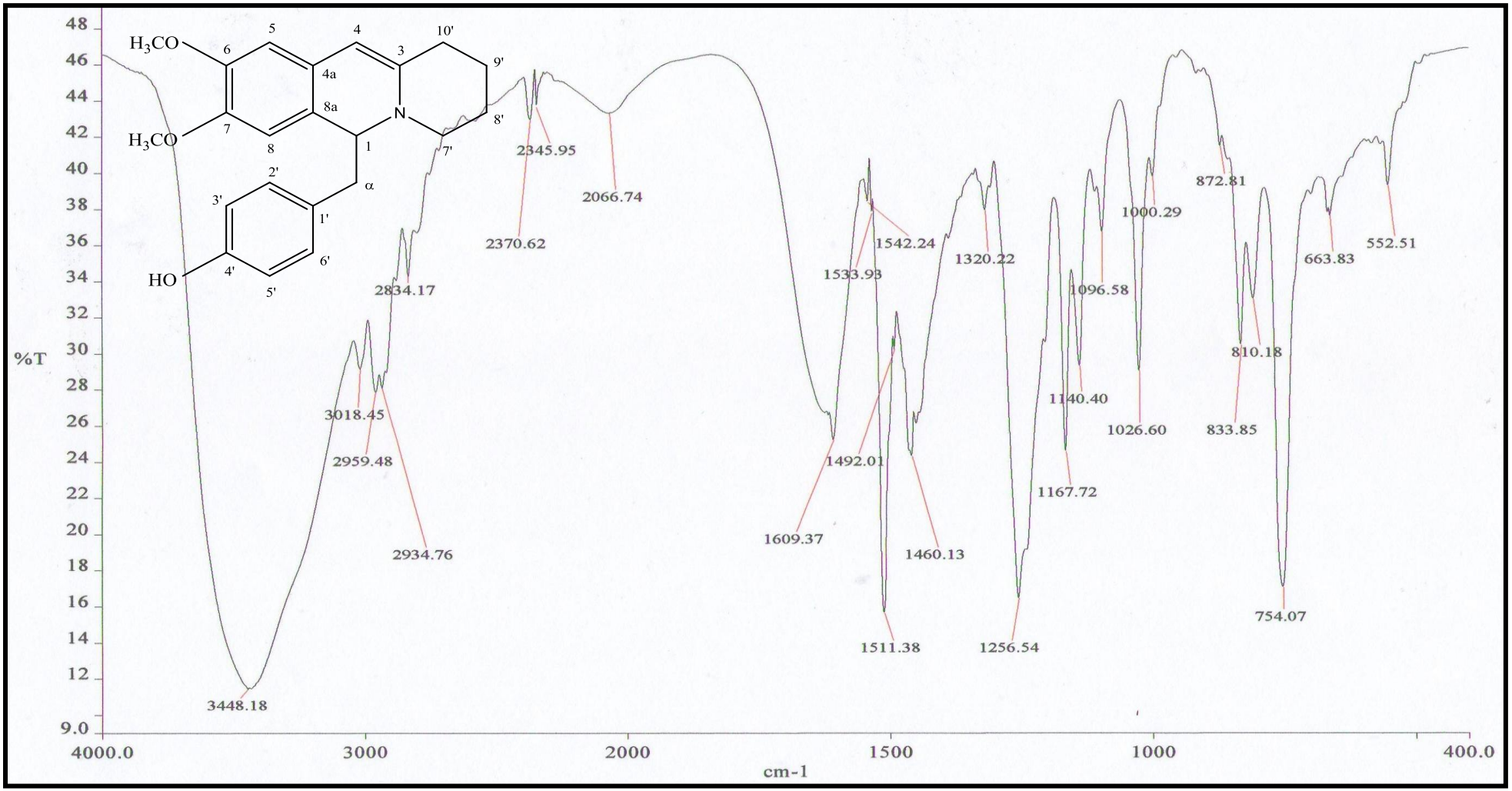



Figure 3.52: IR Spectrum of Cryptocaryadine **68**