

Supplemental Table 1. Summary of NMR data for tembetarine.

C number	δ (^{13}C) (ppm)	δ (^1H) ppm	INT	m	J (Hz)	gCOSY	HSQC ($\text{H}\rightarrow\text{C}$) (ppm)	HSQC (m) / RING ID	HMBC ($\text{H}\rightarrow\text{C}$) (ppm)
1	74.04	4.55	1.00	dd	9.2, 4.0	H9 α , H9 β	74.04	CH/CH ₃	C9 (vw)
3 α	55.79	3.54	1.00	m	-	H3 β , H4	55.79	CH ₂	C11 (w)
3 β	55.79	3.82	1.00	m	-	H3 α , H4	55.79	CH ₂	C4 (vw), NMe(β) (w)
4	24.16	3.17	2.00	m	-	H3 α , H3 β	24.16	CH ₂	C3 (w), C5 (w), C10 (w), C11 (w)
5	112.10	6.81	1.00	s	-	-	112.10	CH/CH ₃	C4 (s), C7 (s), C8 (m), C10 (s)
6	149.60	-	-	-	-	-	-	-	C11 (s)
6-OMe	56.14	3.85	3.00	s	-	-	56.14	CH/CH ₃	C6 (vs)
7-OH	146.17	-	-	-	-	-	-	-	-
8	115.93	5.96	1.00	s	-	-	115.93	CH/CH ₃	C1 (s), C6 (s), C7 (s)
9 α	38.51	2.91	1.00	dd	13.6, 9.2	H1, H9 β	38.51	CH ₂	C1 (m), C2' (w), C6' (w), C10 (w)
9 β	38.51	3.54	1.00	m	-	H1, H9 α	38.51	CH ₂	C1 (w), C2' (w), C6' (w), C10 (w)
10	123.67	-	-	-	-	-	-	-	-
11	120.16	-	-	-	-	-	-	-	-
1'	129.02	-	-	-	-	-	-	-	-
2'	117.51	6.53	1.00	d	2.20	H6'	117.51	CH/CH ₃	C3' (m), C4' (s), C6' (s), C9 (m)
3'-OH	147.71	-	-	-	-	-	-	-	-
4'	148.24	-	-	-	-	-	-	-	-
4'-OMe	56.14	3.83	3.00	s	-	-	56.14	CH/CH ₃	C4' (vs), C6' (vw)
5'	112.55	6.83	1.00	d	8.20	H6'	112.55	CH/CH ₃	C1' (s), C3' (s), C4' (m)
6'	122.00	6.46	1.00	dd	8.2, 2.2	H5', H2'	122.00	CH/CH ₃	C2' (s), C4' (m), C9 (w)
NMe(α)	51.32	3.11	1.00	s	-	HNMe(β)	51.32	CH/CH ₃	C1 (vs), C3 (s), NMe(β) (vs)
NMe(β)	52.50	3.36	1.00	s	-	HNMe(α)	52.50	CH/CH ₃	C1 (vs), C3 (s), NMe(α) (vs)