Supporting Information**Rearrangement of 5-Trimethylsilylthebaine on Treatment with L-Selectride: An Efficient Synthesis of (+)-Bractazonine**

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Proton NMR of 5

7
6
5
4
3
2
1
0

X-Ray data for (+)-Neodihydrothebaine (**6**)

Figure S1. (+)-Neodihydrothebaine (solvent molecules omitted for clarity, relative stereochemistry shown). Thermal ellipsoids shown at 20% probability level.

Table S1. Crystal data and structure refinement for (+)-Neodihydrothebaine.

Empirical formula	$C_{22}H_{31}NO_5$	
Formula weight	389.48	
Temperature	298(2) °K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P 2_1$	
Unit cell dimensions	$a = 7.7239(8)$ Å	$\alpha = 90^\circ$
	$b = 11.9850(13)$ Å	$\beta = 97.740(4)^\circ$
	$c = 11.3934(13)$ Å	$\gamma = 90^\circ$
	$1045.1(2)$ Å ³	
Volume	2	
Z	2	
Density (calculated)	1.238 Mg/m ³	
Absorption coefficient	0.706 mm ⁻¹	
F(000)	416	
Crystal size	0.40 x 0.36 x 0.34 mm ³	
Theta range for data collection	3.92 to 67.05°	
Index ranges	-8 ≤ h ≤ 9, -13 ≤ k ≤ 14, -13 ≤ l ≤ 13	
Reflections collected	4592	
Independent reflections	2844 [R(int) = 0.0360]	
Completeness to theta = 67.05°	93.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.788 and 0.723	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2844 / 4 / 262	
Goodness-of-fit on F ²	1.272	
Final R indices [I > 2σ(I)]	R1 = 0.0771, wR2 = 0.2108	
R indices (all data)	R1 = 0.0819, wR2 = 0.2191	
Largest diff. peak and hole	0.909 and -0.629 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-Neodihydrothebaine. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	6184(6)	16(4)	7594(4)	48(1)
O(1)	4451(4)	246(3)	7546(3)	60(1)
C(2)	6805(6)	-657(4)	6732(4)	52(1)
O(2)	5543(4)	-1077(3)	5895(3)	65(1)
C(2A)	6061(8)	-1482(6)	4832(5)	73(2)
C(3)	8570(6)	-890(4)	6808(5)	55(1)
C(4)	9741(5)	-423(4)	7726(4)	50(1)
C(4A)	9145(5)	246(4)	8572(4)	45(1)
C(5)	10438(5)	787(4)	9531(4)	48(1)
C(6)	11698(5)	1598(4)	9056(4)	47(1)
N(7)	10890(5)	2505(3)	8275(3)	46(1)
C(7)	12335(6)	3165(5)	7861(5)	60(1)
C(8)	9681(6)	3256(4)	8825(4)	51(1)
C(9)	7742(6)	2945(4)	8594(4)	50(1)
C(9A)	6970(5)	2307(4)	9535(4)	45(1)
C(10)	6411(5)	2858(4)	10508(4)	47(1)
C(11)	5578(5)	2317(4)	11346(4)	50(1)
C(12)	5248(5)	1176(4)	11228(4)	49(1)
O(12)	4396(5)	550(4)	11953(3)	67(1)
C(12A)	3508(8)	1091(6)	12834(5)	77(2)
C(13)	5829(5)	619(4)	10265(4)	46(1)
C(14)	6667(5)	1144(4)	9448(3)	44(1)
C(15)	7334(5)	468(3)	8517(4)	43(1)
O(1S)	12293(4)	334(3)	5553(3)	59(1)
C(1S)	8177(9)	2162(6)	4274(5)	77(2)
C(2S)	8937(6)	2408(4)	5486(4)	63(1)
O(2S)	9688(5)	1765(3)	6169(3)	60(1)
C(3S)	8821(5)	3556(3)	5852(3)	41(1)

Table S3. Bond lengths [Å] and angles [°] for (+)-Neodihydrothebaine.

C(1)-O(1)	1.361(5)	C(1)-C(15)	1.391(6)
C(1)-C(2)	1.405(6)	O(1)-H(1A)	0.8200
C(2)-O(2)	1.365(6)	C(2)-C(3)	1.382(6)
O(2)-C(2A)	1.412(6)	C(2A)-H(2AA)	0.9600
C(2A)-H(2AB)	0.9600	C(2A)-H(2AC)	0.9600
C(3)-C(4)	1.404(7)	C(3)-H(3A)	0.9300
C(4)-C(4A)	1.378(6)	C(4)-H(4A)	0.9300
C(4A)-C(15)	1.417(6)	C(4A)-C(5)	1.523(6)
C(5)-C(6)	1.526(6)	C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700	C(6)-N(7)	1.488(6)
C(6)-H(6A)	0.9700	C(6)-H(6B)	0.9700
N(7)-C(8)	1.494(6)	N(7)-C(7)	1.496(6)
C(7)-H(7A)	0.9600	C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600	C(8)-C(9)	1.531(6)
C(8)-H(8A)	0.9700	C(8)-H(8B)	0.9700
C(9)-C(9A)	1.504(6)	C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700	C(9A)-C(10)	1.408(6)
C(9A)-C(14)	1.414(6)	C(10)-C(11)	1.382(7)
C(10)-H(10A)	0.9300	C(11)-C(12)	1.394(7)
C(11)-H(11A)	0.9300	C(12)-O(12)	1.351(6)
C(12)-C(13)	1.408(6)	O(12)-C(12A)	1.444(6)
C(12A)-H(12A)	0.9600	C(12A)-H(12B)	0.9600
C(12A)-H(12C)	0.9600	C(13)-C(14)	1.359(6)
C(13)-H(13A)	0.9300	C(14)-C(15)	1.482(6)
O(1S)-H(1S)	0.959(6)	O(1S)-H(2S)	0.960(6)
C(1S)-C(2S)	1.455(7)	C(1S)-H(1SA)	0.9600
C(1S)-H(1SB)	0.9600	C(1S)-H(1SC)	0.9600
C(2S)-O(2S)	1.189(6)	C(2S)-C(3S)	1.444(5)
C(3S)-H(3SA)	0.9600	C(3S)-H(3SB)	0.9600
C(3S)-H(3SC)	0.9600		

Symmetry transformations used to generate equivalent atoms:

Table S3 (cont.). Bond lengths [Å] and angles [°] for (+)-Neodihydrothebaine.

O(1)-C(1)-C(15)	118.4(4)	O(1)-C(1)-C(2)	121.0(4)
C(15)-C(1)-C(2)	120.6(4)	C(1)-O(1)-H(1A)	109.5
O(2)-C(2)-C(3)	125.1(4)	O(2)-C(2)-C(1)	114.9(4)
C(3)-C(2)-C(1)	119.9(4)	C(2)-O(2)-C(2A)	117.9(4)
O(2)-C(2A)-H(2AA)	109.5	O(2)-C(2A)-H(2AB)	109.5
H(2AA)-C(2A)-H(2AB)	109.5	O(2)-C(2A)-H(2AC)	109.5
H(2AA)-C(2A)-H(2AC)	109.5	H(2AB)-C(2A)-H(2AC)	109.5
C(2)-C(3)-C(4)	119.8(4)	C(2)-C(3)-H(3A)	120.1
C(4)-C(3)-H(3A)	120.1	C(4A)-C(4)-C(3)	120.7(4)
C(4A)-C(4)-H(4A)	119.7	C(3)-C(4)-H(4A)	119.7
C(4)-C(4A)-C(15)	119.9(4)	C(4)-C(4A)-C(5)	120.0(4)
C(15)-C(4A)-C(5)	120.0(4)	C(4A)-C(5)-C(6)	113.9(3)
C(4A)-C(5)-H(5A)	108.8	C(6)-C(5)-H(5A)	108.8
C(4A)-C(5)-H(5B)	108.8	C(6)-C(5)-H(5B)	108.8
H(5A)-C(5)-H(5B)	107.7	N(7)-C(6)-C(5)	116.2(3)
N(7)-C(6)-H(6A)	108.2	C(5)-C(6)-H(6A)	108.2
N(7)-C(6)-H(6B)	108.2	C(5)-C(6)-H(6B)	108.2
H(6A)-C(6)-H(6B)	107.4	C(6)-N(7)-C(8)	115.2(3)
C(6)-N(7)-C(7)	107.7(3)	C(8)-N(7)-C(7)	110.4(4)
N(7)-C(7)-H(7A)	109.5	N(7)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	N(7)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
N(7)-C(8)-C(9)	115.7(4)	N(7)-C(8)-H(8A)	108.4
C(9)-C(8)-H(8A)	108.4	N(7)-C(8)-H(8B)	108.4
C(9)-C(8)-H(8B)	108.4	H(8A)-C(8)-H(8B)	107.4
C(9A)-C(9)-C(8)	118.3(4)	C(9A)-C(9)-H(9A)	107.7
C(8)-C(9)-H(9A)	107.7	C(9A)-C(9)-H(9B)	107.7
C(8)-C(9)-H(9B)	107.7	H(9A)-C(9)-H(9B)	107.1
C(10)-C(9A)-C(9)	116.9(4)	C(10)-C(9A)-C(9)	121.1(4)
C(14)-C(9A)-C(9)	121.9(4)	C(11)-C(10)-C(9A)	123.0(4)
C(11)-C(10)-H(10A)	118.5	C(9A)-C(10)-H(10A)	118.5
C(10)-C(11)-C(12)	119.3(4)	C(10)-C(11)-H(11A)	120.3
C(12)-C(11)-H(11A)	120.3	O(12)-C(12)-C(11)	125.7(4)
O(12)-C(12)-C(13)	116.5(4)	C(11)-C(12)-C(13)	117.8(4)
C(12)-O(12)-C(12A)	119.5(5)	O(12)-C(12A)-H(12A)	109.5
O(12)-C(12A)-H(12B)	109.5	H(12A)-C(12A)-H(12B)	109.5
O(12)-C(12A)-H(12C)	109.5	H(12A)-C(12A)-H(12C)	109.5
H(12B)-C(12A)-H(12C)	109.5	C(14)-C(13)-C(12)	123.1(4)
C(14)-C(13)-H(13A)	118.5	C(12)-C(13)-H(13A)	118.5
C(13)-C(14)-C(9A)	119.9(4)	C(13)-C(14)-C(15)	118.7(4)
C(9A)-C(14)-C(15)	121.3(4)	C(1)-C(15)-C(4A)	119.1(4)
C(1)-C(15)-C(14)	120.4(3)	C(4A)-C(15)-C(14)	120.5(4)
H(1S)-O(1S)-H(2S)	114(5)	C(2S)-C(1S)-H(1SA)	109.5
C(2S)-C(1S)-H(1SB)	109.5	H(1SA)-C(1S)-H(1SB)	109.5
C(2S)-C(1S)-H(1SC)	109.5	H(1SA)-C(1S)-H(1SC)	109.5
H(1SB)-C(1S)-H(1SC)	109.5	O(2S)-C(2S)-C(3S)	118.1(4)
O(2S)-C(2S)-C(1S)	126.1(5)	C(3S)-C(2S)-C(1S)	115.7(5)
C(2S)-C(3S)-H(3SA)	109.5	C(2S)-C(3S)-H(3SB)	109.5
H(3SA)-C(3S)-H(3SB)	109.5	C(2S)-C(3S)-H(3SC)	109.5

H(3SA)-C(3S)-H(3SC) 109.5

H(3SB)-C(3S)-H(3SC) 109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-Neodihydrothebaine. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	48(2)	57(2)	42(2)	-5(2)	13(2)	0(2)
O(1)	45(1)	87(2)	49(2)	-19(2)	10(1)	6(2)
C(2)	53(2)	59(3)	47(2)	-10(2)	16(2)	-4(2)
O(2)	54(2)	85(3)	55(2)	-26(2)	13(2)	-4(2)
C(2A)	70(3)	98(4)	53(3)	-21(3)	18(2)	-4(3)
C(3)	54(2)	55(3)	61(3)	-8(2)	25(2)	1(2)
C(4)	43(2)	54(2)	55(2)	0(2)	14(2)	6(2)
C(4A)	45(2)	44(2)	46(2)	4(2)	10(2)	2(2)
C(5)	47(2)	54(2)	43(2)	5(2)	8(2)	7(2)
C(6)	40(2)	57(2)	44(2)	1(2)	3(2)	-1(2)
N(7)	46(2)	52(2)	40(2)	-1(1)	6(1)	-1(1)
C(7)	55(2)	72(3)	56(3)	7(2)	15(2)	-8(2)
C(8)	59(2)	50(2)	46(2)	0(2)	14(2)	-3(2)
C(9)	54(2)	52(2)	45(2)	5(2)	8(2)	6(2)
C(9A)	39(2)	54(2)	41(2)	0(2)	3(2)	2(2)
C(10)	49(2)	51(2)	40(2)	-8(2)	3(2)	2(2)
C(11)	48(2)	64(3)	39(2)	-10(2)	8(2)	2(2)
C(12)	45(2)	62(3)	40(2)	-4(2)	9(2)	1(2)
O(12)	79(2)	75(2)	51(2)	-5(2)	30(2)	-9(2)
C(12A)	78(3)	101(4)	59(3)	-13(3)	32(3)	-12(3)
C(13)	46(2)	48(2)	44(2)	-2(2)	6(2)	0(2)
C(14)	38(2)	53(2)	40(2)	-2(2)	5(2)	6(2)
C(15)	43(2)	45(2)	41(2)	4(2)	9(2)	2(2)
O(1S)	55(2)	72(2)	51(2)	-13(2)	7(1)	0(2)
C(1S)	84(4)	84(4)	55(3)	4(3)	-11(3)	-12(3)
C(2S)	49(2)	97(4)	43(2)	17(2)	9(2)	1(2)
O(2S)	72(2)	61(2)	44(2)	-2(1)	-2(2)	4(2)
C(3S)	51(2)	38(2)	34(2)	9(1)	3(2)	2(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-Neodihydrothebaine.

	x	y	z	U(eq)
H(1A)	3940	65	6896	90
H(2AA)	5055	-1749	4323	109
H(2AB)	6880	-2081	5007	109
H(2AC)	6600	-891	4443	109
H(3A)	8980	-1354	6253	66
H(4A)	10930	-565	7765	60
H(5A)	11109	205	9976	57
H(5B)	9791	1183	10074	57
H(6A)	12416	1938	9726	57
H(6B)	12469	1174	8619	57
H(7A)	13097	2673	7507	91
H(7B)	12985	3541	8523	91
H(7C)	11851	3706	7287	91
H(8A)	9815	4008	8534	61
H(8B)	10039	3266	9674	61
H(9A)	7079	3630	8445	60
H(9B)	7558	2509	7871	60
H(10A)	6612	3620	10592	56
H(11A)	5240	2710	11981	60
H(12A)	2956	538	13268	116
H(12B)	2639	1591	12452	116
H(12C)	4338	1503	13369	116
H(13A)	5629	-144	10185	55
H(1S)	11300(30)	790(30)	5640(60)	89
H(2S)	12020(80)	-340(30)	5120(40)	89
H(1SA)	7706	2834	3899	115
H(1SB)	7261	1622	4280	115
H(1SC)	9063	1869	3845	115
H(3SA)	7650	3713	5998	62
H(3SB)	9121	4039	5238	62
H(3SC)	9615	3679	6564	62

Proton NMR of 6

X-Ray data for (+)-Bractazonine (7)

Figure S2. (+)-Bractazonine, relative stereochemistry shown. Thermal ellipsoids shown at 20% probability level.

Table S6. Crystal data and structure refinement for (+)-Bractazonine.

Empirical formula	C ₁₉ H ₂₃ N O ₃	
Formula weight	313.38	
Temperature	298(2) °K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 5.68020(10) Å	α = 90°
	b = 10.4703(2) Å	β = 90°
	c = 28.1144(5) Å	γ = 90°
Volume	1672.06(5) Å ³	
Z	4	
Density (calculated)	1.245 Mg/m ³	
Absorption coefficient	0.672 mm ⁻¹	
F(000)	672	
Crystal size	0.41 x 0.11 x 0.07 mm ³	
Theta range for data collection	3.14 to 67.07°	
Index ranges	-6 ≤ h ≤ 6, -10 ≤ k ≤ 12, -32 ≤ l ≤ 30	
Reflections collected	8667	
Independent reflections	2903 [R(int) = 0.0283]	
Completeness to theta = 67.07°	97.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.954 and 0.846	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2903 / 0 / 213	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R1 = 0.0627, wR2 = 0.1769	
R indices (all data)	R1 = 0.0653, wR2 = 0.1814	
Extinction coefficient	0.029(3)	
Largest diff. peak and hole	0.838 and -0.344 e.Å ⁻³	

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-Bractazonine. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	3451(5)	-727(2)	1240(1)	56(1)
O(1)	3308(4)	-1410(2)	1652(1)	69(1)
C(2)	2112(5)	-1064(3)	846(1)	63(1)
O(2)	612(4)	-2080(2)	918(1)	80(1)
C(2A)	-1109(8)	-2309(4)	566(2)	99(1)
C(3)	2341(7)	-390(3)	432(1)	73(1)
C(4)	3914(6)	633(3)	413(1)	74(1)
C(4A)	5225(6)	992(3)	800(1)	65(1)
C(5)	6918(7)	2110(3)	765(1)	83(1)
C(6)	5756(9)	3402(4)	676(2)	108(1)
N(7)	3846(6)	3697(3)	988(1)	86(1)
C(7)	2843(13)	4883(5)	784(2)	131(2)
C(8)	4048(8)	3811(3)	1488(1)	90(1)
C(9A)	5462(4)	1782(2)	1930(1)	54(1)
C(9)	3418(6)	2611(3)	1779(1)	67(1)
C(10)	6678(5)	2101(3)	2341(1)	57(1)
C(11)	8514(5)	1361(3)	2507(1)	59(1)
O(11)	9576(4)	1782(2)	2921(1)	76(1)
C(11A)	11574(6)	1102(4)	3084(1)	82(1)
C(12)	9196(5)	286(3)	2263(1)	68(1)
C(13)	8003(6)	-27(3)	1850(1)	69(1)
C(14)	6159(5)	698(2)	1676(1)	55(1)
C(15)	4940(5)	319(2)	1229(1)	56(1)

Table S8. Bond lengths [Å] and angles [°] for (+)-Bractazonine.

C(1)-O(1)	1.364(3)	C(1)-C(15)	1.385(4)
C(1)-C(2)	1.390(4)	O(1)-H(1A)	0.8200
C(2)-C(3)	1.366(4)	C(2)-O(2)	1.377(4)
O(2)-C(2A)	1.411(4)	C(2A)-H(2AA)	0.9600
C(2A)-H(2AB)	0.9600	C(2A)-H(2AC)	0.9600
C(3)-C(4)	1.396(5)	C(3)-H(3A)	0.9300
C(4)-C(4A)	1.371(4)	C(4)-H(4A)	0.9300
C(4A)-C(15)	1.406(4)	C(4A)-C(5)	1.518(5)
C(5)-C(6)	1.526(6)	C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700	C(6)-N(7)	1.429(5)
C(6)-H(6A)	0.9700	C(6)-H(6B)	0.9700
N(7)-C(8)	1.415(5)	N(7)-C(7)	1.482(6)
C(7)-H(7A)	0.9600	C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600	C(8)-C(9)	1.541(5)
C(8)-H(8A)	0.9700	C(8)-H(8B)	0.9700
C(9A)-C(10)	1.388(3)	C(9A)-C(14)	1.397(3)
C(9A)-C(9)	1.511(4)	C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700	C(10)-C(11)	1.380(4)
C(10)-H(10A)	0.9300	C(11)-C(12)	1.375(4)
C(11)-O(11)	1.381(3)	O(11)-C(11A)	1.416(4)
C(11A)-H(11A)	0.9600	C(11A)-H(11B)	0.9600
C(11A)-H(11C)	0.9600	C(12)-C(13)	1.382(4)
C(12)-H(12A)	0.9300	C(13)-C(14)	1.383(4)
C(13)-H(13A)	0.9300	C(14)-C(15)	1.490(3)

Symmetry transformations used to generate equivalent atoms:

Table S8 (cont.). Bond lengths [Å] and angles [°] for (+)-Bractazonine.

O(1)-C(1)-C(15)	118.0(2)	O(1)-C(1)-C(2)	120.8(3)
C(15)-C(1)-C(2)	121.2(2)	C(1)-O(1)-H(1A)	109.5
C(3)-C(2)-O(2)	125.7(3)	C(3)-C(2)-C(1)	119.6(3)
O(2)-C(2)-C(1)	114.6(2)	C(2)-O(2)-C(2A)	117.1(3)
O(2)-C(2A)-H(2AA)	109.5	O(2)-C(2A)-H(2AB)	109.5
H(2AA)-C(2A)-H(2AB)	109.5	O(2)-C(2A)-H(2AC)	109.5
H(2AA)-C(2A)-H(2AC)	109.5	H(2AB)-C(2A)-H(2AC)	109.5
C(2)-C(3)-C(4)	119.5(3)	C(2)-C(3)-H(3A)	120.3
C(4)-C(3)-H(3A)	120.3	C(4A)-C(4)-C(3)	121.8(3)
C(4A)-C(4)-H(4A)	119.1	C(3)-C(4)-H(4A)	119.1
C(4)-C(4A)-C(15)	118.8(3)	C(4)-C(4A)-C(5)	120.2(3)
C(15)-C(4A)-C(5)	121.0(3)	C(4A)-C(5)-C(6)	114.9(3)
C(4A)-C(5)-H(5A)	108.5	C(6)-C(5)-H(5A)	108.5
C(4A)-C(5)-H(5B)	108.6	C(6)-C(5)-H(5B)	108.6
H(5A)-C(5)-H(5B)	107.5	N(7)-C(6)-C(5)	114.8(3)
N(7)-C(6)-H(6A)	108.6	C(5)-C(6)-H(6A)	108.6
N(7)-C(6)-H(6B)	108.6	C(5)-C(6)-H(6B)	108.6
H(6A)-C(6)-H(6B)	107.5	C(8)-N(7)-C(6)	124.5(4)
C(8)-N(7)-C(7)	110.2(3)	C(6)-N(7)-C(7)	103.6(4)
N(7)-C(7)-H(7A)	109.5	N(7)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	N(7)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
N(7)-C(8)-C(9)	116.1(3)	N(7)-C(8)-H(8A)	108.3
C(9)-C(8)-H(8A)	108.3	N(7)-C(8)-H(8B)	108.3
C(9)-C(8)-H(8B)	108.3	H(8A)-C(8)-H(8B)	107.4
C(10)-C(9A)-C(14)	118.7(2)	C(10)-C(9A)-C(9)	118.6(2)
C(14)-C(9A)-C(9)	122.8(2)	C(9A)-C(9)-C(8)	116.0(3)
C(9A)-C(9)-H(9A)	108.3	C(8)-C(9)-H(9A)	108.3
C(9A)-C(9)-H(9B)	108.3	C(8)-C(9)-H(9B)	108.3
H(9A)-C(9)-H(9B)	107.4	C(11)-C(10)-C(9A)	121.5(2)
C(11)-C(10)-H(10A)	119.2	C(9A)-C(10)-H(10A)	119.2
C(12)-C(11)-O(11)	124.0(2)	C(12)-C(11)-C(10)	120.2(2)
O(11)-C(11)-C(10)	115.8(2)	C(11)-O(11)-C(11A)	117.5(2)
O(11)-C(11A)-H(11A)	109.5	O(11)-C(11A)-H(11B)	109.5
H(11A)-C(11A)-H(11B)	109.5	O(11)-C(11A)-H(11C)	109.5
H(11A)-C(11A)-H(11C)	109.5	H(11B)-C(11A)-H(11C)	109.5
C(11)-C(12)-C(13)	118.4(3)	C(11)-C(12)-H(12A)	120.8
C(13)-C(12)-H(12A)	120.8	C(14)-C(13)-C(12)	122.5(3)
C(14)-C(13)-H(13A)	118.7	C(12)-C(13)-H(13A)	118.7
C(13)-C(14)-C(9A)	118.7(2)	C(13)-C(14)-C(15)	120.3(2)
C(9A)-C(14)-C(15)	121.0(2)	C(1)-C(15)-C(4A)	119.1(2)
C(1)-C(15)-C(14)	118.4(2)	C(4A)-C(15)-C(14)	122.5(2)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-Bractazonine. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	63(1)	56(1)	48(1)	-2(1)	-4(1)	6(1)
O(1)	78(1)	71(1)	56(1)	13(1)	-14(1)	-13(1)
C(2)	73(2)	59(1)	58(1)	-10(1)	-10(1)	6(1)
O(2)	93(2)	67(1)	79(1)	-4(1)	-28(1)	-13(1)
C(2A)	102(3)	104(2)	91(2)	-13(2)	-35(2)	-17(2)
C(3)	95(2)	76(2)	47(1)	-8(1)	-13(1)	11(2)
C(4)	97(2)	75(2)	48(1)	4(1)	1(1)	8(2)
C(4A)	76(2)	64(2)	54(1)	5(1)	4(1)	5(1)
C(5)	82(2)	88(2)	80(2)	17(2)	7(2)	-8(2)
C(6)	117(3)	91(2)	115(3)	8(2)	15(3)	-18(2)
N(7)	99(2)	84(2)	75(2)	-1(1)	13(2)	-20(2)
C(7)	156(5)	125(4)	112(3)	50(3)	-26(3)	-21(4)
C(8)	126(3)	65(2)	79(2)	-4(1)	-25(2)	19(2)
C(9A)	56(1)	56(1)	49(1)	1(1)	1(1)	2(1)
C(9)	67(2)	74(2)	60(1)	-3(1)	-6(1)	17(1)
C(10)	63(1)	60(1)	49(1)	-6(1)	-2(1)	5(1)
C(11)	59(1)	63(1)	55(1)	-3(1)	-5(1)	-1(1)
O(11)	77(1)	86(1)	65(1)	-14(1)	-23(1)	17(1)
C(11A)	72(2)	106(2)	68(2)	0(2)	-17(2)	11(2)
C(12)	67(2)	69(2)	67(2)	-8(1)	-11(1)	12(1)
C(13)	69(2)	66(2)	72(2)	-12(1)	-8(1)	10(1)
C(14)	59(1)	57(1)	49(1)	-1(1)	1(1)	-1(1)
C(15)	62(1)	55(1)	50(1)	-5(1)	0(1)	4(1)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-Bractazonine.

	x	y	z	U(eq)
H(1A)	2346	-1987	1620	103
H(2AA)	-2032	-3040	655	148
H(2AB)	-351	-2468	267	148
H(2AC)	-2114	-1576	538	148
H(3A)	1457	-610	166	87
H(4A)	4077	1084	130	88
H(5A)	8021	1942	509	100
H(5B)	7813	2159	1058	100
H(6A)	6942	4064	707	129
H(6B)	5183	3422	351	129
H(7A)	2735	4800	444	196
H(7B)	3842	5592	861	196
H(7C)	1301	5024	913	196
H(8A)	3038	4505	1591	108
H(8B)	5656	4050	1563	108
H(9A)	2579	2880	2062	80
H(9B)	2346	2094	1592	80
H(10A)	6245	2829	2509	69
H(11A)	12229	1529	3355	123
H(11B)	12730	1063	2835	123
H(11C)	11116	251	3171	123
H(12A)	10428	-219	2373	81
H(13A)	8459	-753	1683	83

Proton NMR of 7

7

6

5

4

3

2

1

0

Proton NMR of 8

Figure S3. Model of Thebaine (**1**) and 5-Trimethylsilylthebaine (**5**) showing relative orientations of the phenyl and alkyl groups.

Above a representation of thebaine and 5-trimethylsilylthebaine showing planes defined by the diene system and the bonds involved in the migration. The reference diene plane (R) is defined by the carbon atom in green and the two carbon atoms in red, the two red carbon atoms and the carbon in dark blue define the plane of the methylene bond (M) while the two carbons in light blue and the connected carbon atom in red define the plane of the bond to the phenyl group (P).

Thebaine and 5-Trimethylsilylthebaine were built using SYBYL6.4 (Tripos Associates; St. Louis) and the atoms were assigned Gasteiger -Hückel charges. The molecules were then energy minimized to a convergence gradient of 0.05 kcal/molÅ. The minimized structures were then optimized to default tolerances using Gaussian 98 (Gaussian Inc; Pittsburgh) at the HF/6-31g* level of theory.

The ability of either the phenyl group or methylene group migration was assessed by measuring the angles between the planes formed by the two groups and the diene system. The atoms used to define the planes have been color coded in Figure 3.

Table S11: The angles between the planes containing the diene bonds (R), the methylene bond (M) and the phenyl bond (P).

Compound	Angle	
	Plane M to R	Plane P to R
Thebaine (1)	46.9°	70.0°
5-TMS-thebaine (5)	41.9°	72.0°