## **Supplementary Information for**

## New alkaloids from Daphniphyllum himalense

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Figure S39. HSQC spectrum for alkaloid 5 in CD<sub>3</sub>OD.

Figure S40. HMBC spectrum for alkaloid 5 in CD<sub>3</sub>OD.

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Figure S42. IR spectrum for alkaloid 5.

Figure S43. (+)-ESIMS spectrum for alkaloid 5.

Figure S44. (+)-HRESIMS spectrum for alkaloid 5.

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Figure S51. IR spectrum for alkaloid 6.
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**Figure S54.** <sup>1</sup>H NMR spectrum for alkaloid **7** in CD<sub>3</sub>OD. **Figure S55.** <sup>13</sup>C NMR spectrum for alkaloid **7** in CD<sub>3</sub>OD. **Figure S56.**  $^{1}\text{H}^{-1}\text{H}$  COSY spectrum for alkaloid **7** in CD<sub>3</sub>OD.

Figure S57 HSQC spectrum for alkaloid 7 in CD<sub>3</sub>OD.

Figure S58. HMBC spectrum for alkaloid 7 in CD<sub>3</sub>OD.

Figure S59. NOESY spectrum for alkaloid 7 in CD<sub>3</sub>OD.

Figure S60. IR spectrum for alkaloid 7.

Figure S61. (+)-ESIMS spectrum for alkaloid 7.

Figure S62. (+)-HRESIMS spectrum for alkaloid 7.

**Figure S63.** <sup>1</sup>H NMR spectrum for alkaloid **8** in CDCl<sub>3</sub>.

Figure S64. <sup>13</sup>C NMR spectrum for alkaloid 8 in CDCl<sub>3</sub>.

Figure S65. <sup>1</sup>H–<sup>1</sup>H COSY spectrum for alkaloid 8 in CDCl<sub>3</sub>.

Figure S66 HSQC spectrum for alkaloid 8 in CDCl<sub>3</sub>.

Figure S67. HMBC spectrum for alkaloid 8 in CDCl<sub>3</sub>.

Figure S68. NOESY spectrum for alkaloid 8 in CDCl<sub>3</sub>.

Figure S69. IR spectrum for alkaloid 8.

Figure S70. (+)-ESIMS spectrum for alkaloid 8.

Figure S71. (+)-HRESIMS spectrum for alkaloid 8.

Figure S72. <sup>1</sup>H NMR spectrum for alkaloid 9 in CDCl<sub>3</sub>.

Figure S73. <sup>13</sup>C NMR spectrum for alkaloid 9 in CDCl<sub>3</sub>.

Figure S74. HSQC spectrum for alkaloid 9 in CDCl<sub>3</sub>.

Figure S75. HMBC spectrum for alkaloid 9 in CDCl<sub>3</sub>.

Figure S76. NOESY spectrum for alkaloid 9 in CDCl<sub>3</sub>.

Figure S77. IR spectrum for alkaloid 9.

Figure S78. (+)-ESIMS spectrum for alkaloid 9.

Figure S79. (+)-HRESIMS spectrum for alkaloid 9.



Figure I. Key 2D NMR correlations for alkaloid 2.



Figure II. Key 2D NMR correlations for alkaloid 3.



Figure III. Key 2D NMR correlations for alkaloid 7.



Figure IV. Key 2D NMR correlations for alkaloid 8.

		2		3
No.	$\delta_{ m C}$	$\delta_{\rm H}$ , mult ( <i>J</i> in Hz)	$\delta_{ m C}$	$\delta_{\rm H}$ , mult ( <i>J</i> in Hz)
1	215.1		214.0	
2	45.4	2.32, brd (4.3)	45.1	2.40, brd (3.7)
3	20.7	2.19, brdd (15.3, 4.3)	20.5	2.22, brdd (15.3, 4.3)
		2.12, ddd 1(5.3, 5.0, 1.7)		2.16, ddd (15.3, 4.9, 1.4)
4	65.7	3.33, brd (5.0)	65.8	3.38, brd (4.9)
5	50.6		50.6	
6	52.8	2.33, m	52.6	2.36, m
7	54.7	2.98, dd (13.0, 9.6)	54.6	2.97, dd (13.0, 9.8)
		2.84, dd (9.6, 6.1)		2.89, dd (9.8, 6.5)
8	65.9		65.5	
9	181.9		178.5	
10	140.6		146.3	
11	18.9	2.42, ddd (16.0, 4.8, 2.8)	19.35	2.48, m
		2.02, brdd 16.0, (13.3)		2.06, m
12	25.2	1.92, m	24.5	1.94, m
		1.71, m		1.75, m
13	47.3	3.50, brd (18.5)	45.6	3.63, d (18.1)
		2.85, brd (18.5)		3.05, d (18.1)
14	126.8	5.88 (m)	127.0	
15	145.2		154.1	
16	ND	ND	ND	ND
17	208.3		206.1	
18	33.6	2.75, m	33.5	2.76, m
19	50.4	2.88, dd (14.5, 7.3)	50.3	2.92, dd (14.3, 7.5)
		2.56, dd (14.5, 10.5)		2.60, dd (14.3, 10.5)
20	19.4	1.03, d ( 6.8)	19.26	1.04, d (6.8)
21	23.2	1.22, s	23.2	1.25, s
22			166.2	
OMe			52.5	3.77 (s)
ND Sign	als not dete	ected due to deuteration.		

Table S1. NMR data for alkaloids 2 and 3 in CD<sub>3</sub>OD.

Compds no.	Concentration (µg/mL)	Inhibition (%)	Standard error (%)
1	20	48.81	3.20
2	20	39.63	3.55
3	20	26.60	11.14
4	20	26.01	12.47
5	20	1.38	19.53
6	20	0.47	11.44
7	20	27.61	5.61
8	20	27.86	3.98
9	20	37.78	6.39
calyciphylline Q	20	27.31	4.07
daphniyunnine A	20	39.96	6.31
daphniyunnine B	20	0.75	7.36
daphniyunnine C	20	25.33	7.75
daphniyunnine D	20	41.18	4.46
daphniyunnine E	20	2.78	4.37
daphlongamine E	20	13.97	5.08
daphlongamine F	20	25.13	6.66
daphnilongeranin A	20	30.49	2.79
daphnilongeranin B	20	20.90	11.45
daphnipaxianine A	20	31.72	8.04
daphnipaxinin	20	5.52	9.51
dehydroxymacropodumine A	20	25.08	1.91
deoxycalyciphylline B	20	21.27	8.93
deoxyisocalyciphylline B	20	27.23	2.23
longistylumphylline A	20	32.34	7.26
Oleanolic acid was used as posit	ive control with an IC50 value	of $1.12 \pm 0.08 \ \mu g/m$	nL.

 Table S2. PTP1B inhibitory assay results.

Compds no.	Concentration (µg/mL)	Inhibition (%)	Standard error (%)
1	20	6.98	0.26
2	20	14.58	2.96
3	20	27.08	11.54
4	20	28.78	5.45
5	20	31.50	12.56
6	20	21.13	5.52
7	20	17.18	3.73
8	20	16.54	0.80
9	20	28.11	3.45
calyciphylline Q	20	17.07	10.07
daphniyunnine A	20	27.69	10.73
daphniyunnine B	20	14.71	8.48
daphniyunnine C	20	34.10	0.10
daphniyunnine D	20	16.98	0.12
daphniyunnine E	20	17.35	3.62
daphlongamine E	20	21.85	0.84
daphlongamine F	20	17.72	6.92
daphnilongeranin A	20	14.21	0.54
daphnilongeranin B	20	18.54	1.09
daphnipaxianine A	20	18.76	4.19
daphnipaxinin	20	14.89	1.39
dehydroxymacropodumine A	20	18.00	4.54
deoxycalyciphylline B	20	25.07	0.54
deoxyisocalyciphylline B	20	20.31	5.61
longistylumphylline A	20	30.08	3.87
Staurosporine was used as positi	ve control with an IC50 valu	e of $31.1 \pm 1.6$ nM.	

Table S3. Aurora kinase A inhibitory assay results.

Compds no.	Concentration (µg/mL)	Inhibition (%)	Standard error (%)			
1	20	-7.32	0.77			
2	20	1.86	1.29			
3	20	0.72	2.83			
4	20	10.51	1.77			
5	20	11.93	4.16			
6	20	-2.12	2.12			
7	20	4.92	0.04			
8	20	-6.02	7.22			
9	20	3.86	8.31			
calyciphylline Q	20	3.48	6.42			
daphniyunnine A	20	11.82	6.26			
daphniyunnine B	20	4.88	2.74			
daphniyunnine C	20	3.09	0.53			
daphniyunnine D	20	1.89	3.02			
daphniyunnine E	20	-0.50	2.05			
daphlongamine E	20	2.44	2.74			
daphlongamine F	20	0.11	1.34			
daphnilongeranin A	20	-3.95	1.92			
daphnilongeranin B	20	8.55	5.02			
daphnipaxianine A	20	-1.07	3.45			
daphnipaxinin	20	6.63	1.44			
dehydroxymacropodumine A	20	8.13	6.87			
deoxycalyciphylline B	20	2.27	1.67			
deoxyisocalyciphylline B	20	-12.23	6.21			
longistylumphylline A	20	5.45	2.96			
SAHA (Suberoylanilide hydroxamic acid) was used as positive control with an IC <sub>50</sub> value of $105 \pm 25$ nM.						

 Table S4. HDAC6 inhibitory assay results.

Compds no.	Concentration (µg/mL)	Inhibition (%)	Standard error (%)
1	20	8.28	4.36
2	20	11.99	4.08
3	20	21.21	4.43
4	20	18.91	2.61
5	20	28.93	2.43
6	20	21.77	2.88
7	20	16.53	3.91
8	20	17.38	3.18
9	20	27.60	5.71
calyciphylline Q	20	18.41	2.46
daphniyunnine A	20	19.01	3.73
daphniyunnine B	20	8.77	5.59
daphniyunnine C	20	17.26	0.47
daphniyunnine D	20	13.75	2.18
daphniyunnine E	20	10.64	1.61
daphlongamine E	20	20.67	1.12
daphlongamine F	20	15.20	1.21
daphnilongeranin A	20	11.33	1.33
daphnilongeranin B	20	20.49	5.15
daphnipaxianine A	20	31.45	3.68
daphnipaxinin	20	16.19	4.59
dehydroxymacropodumine A	20	11.57	0.21
deoxycalyciphylline B	20	17.71	5.95
deoxyisocalyciphylline B	20	18.42	3.90
longistylumphylline A	20	17.64	3.17
Staurosporine was used as posit	tive control with an inhibition	n of 89.52±0.72% at 1	μM.

**Table S5**. IKK- $\beta$  inhibitory assay results.

 Table S6. Crystal data and structure refinement for alkaloid 10.

Identification code	cu_dm16061_0m				
Empirical formula	C24 H35 N O5				
Formula weight	417.53				
Temperature	293.15 К				
Wavelength	1.54178 Å				
Crystal system	Monoclinic				
Space group	P 1 21 1				
Unit cell dimensions	$a = 10.7411(2) \text{ Å}$ $\alpha = 90^{\circ}.$				
	b = 9.0530(2)  Å	β=93.4430(10)°.			
	c = 11.5845(2)  Å	$\gamma = 90^{\circ}$ .			
Volume	1124.43(4) Å <sup>3</sup>				
Z	2				
Density (calculated)	1.233 Mg/m <sup>3</sup>				
Absorption coefficient	0.689 mm <sup>-1</sup>				
F(000)	452				
Crystal size	0.28 x 0.25 x 0.2 mm <sup>3</sup>				
Theta range for data collection	3.822 to 69.726°.				
Index ranges	-13<=h<=12, -10<=k<=10, -13	<=l<=13			
Reflections collected 8067					
Independent reflections $3732 [R(int) = 0.0311]$					
Completeness to theta = $67.679^{\circ}$	99.3 %				
Absorption correction	Semi-empirical from equivalent	its			
Max. and min. transmission	0.7532 and 0.5620				
Refinement method	Full-matrix least-squares on F <sup>2</sup>				
Data / restraints / parameters	3732 / 1 / 281				
Goodness-of-fit on F <sup>2</sup>	1.074				
Final R indices [I>2sigma(I)]	R1 = 0.0502, $wR2 = 0.1568$				
R indices (all data)	R1 = 0.0511, $wR2 = 0.1582$				
Absolute structure parameter	0.19(11)				
Extinction coefficient	0.022(3)				
Largest diff. peak and hole	0.228 and -0.332 e.Å <sup>-3</sup>				



Figure S1. <sup>1</sup>H NMR spectrum for alkaloid 1 in CDCl<sub>3</sub>.



Figure S2. <sup>13</sup>C NMR spectrum for alkaloid 1 in CDCl<sub>3</sub>.



**Figure S3.** <sup>1</sup>H–<sup>1</sup>H COSY spectrum for alkaloid **1** in CDCl<sub>3</sub>.

Figure S4. HSQC spectrum for alkaloid 1 in CDCl<sub>3</sub>.





Figure S5. HMBC spectrum for alkaloid 1 in CDCl<sub>3</sub>.

Figure S6. NOESY spectrum for alkaloid 1 in CDCl<sub>3</sub>.



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Figure S7. IR spectrum for alkaloid 1.



**Display Report** 

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Elemental Composition Report				
Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3				
Monoisotopic Mass, Even Electron Ions 307 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-4 O: 0-20				

DH-64	H-64 LCT PXE KE324								29-Aug-2014		
DH-64_0829 45 (1.005) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (45:56)					10:46:5 1: TOF MS ES+						
100						368.2230			2.696	+003	
0	358.3	737 360.2117	361.2700	365.1892	366.2055	369.	2268 370.2316 371.2380	373.8275	375.3922	m/z	
Minimu Maximu	um: um:		5.0	10.0	-1.5 50.0	500.0	570.0 572.0	374.0	376.0		
Mass		Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
368.22	30	368.2226	0.4	1.1	9.5	80.9	0.0	C23 H30	N 03		







**Figure S11.** <sup>13</sup>C NMR spectrum for alkaloid **2** in  $C_5D_5N$ .



**Figure S12.**  ${}^{1}H-{}^{1}H$  COSY spectrum for alkaloid **2** in C<sub>5</sub>D<sub>5</sub>N.



Figure S13. HSQC spectrum for alkaloid 2 in  $C_5D_5N$ .



Figure S14. HMBC spectrum for alkaloid 2 in  $C_5D_5N$ .



%透过率 100 94-84--06 92--96 78-86--88 -86 -08 82-4000 76. 3438.74 3000 2955.57 2921.83 2867.35 2000 \_波数(cm-1) 1698.30 1636.05 15001440.95 1383.83 1301.09 1224.38 1060.64  $1\,000$ 1033. 79 937.08





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## Figure S18. (+)-HRESIMS spectrum for alkaloid 2.

Elemental Composition Report Page 1									
Single Mas Tolerance = Element pres Number of is	Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3								
Monoisotopic 156 formula(e Elements Use C: 5-80 H: DH-57-1	Monoisotopic Mass, Even Electron Ions 156 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-2 O: 0-20 DH-57-1 LCT PXE KE324 04-Jun-2014								
DH-57-1_0604	25 (0.549) AM2 (Ar,10	0000.0,0.00,1	.00); ABS	S; Cm (13:29)				1: TOF MS ES+	
100 %					324.1965			2.200.004	
					325.2	003			
305.15	310.1576.311	1.1974 314.1	920	320.8913 322.1	813 34	328.3533	333.0860	338.1759 m/z	
305.0	310.0	315.0		320.0	325.0	330.0	335.0		
Minimum: Maximum:		5.0	5.0	-1.5 50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
324.1965	324.1964	0.1	0.3	9.5	155.3	0.0	C21 H26	N 02	



**Figure S19.** <sup>1</sup>H NMR spectrum for alkaloid **3** in C<sub>5</sub>D<sub>5</sub>N.



Figure S20. <sup>13</sup>C NMR spectrum for alkaloid 3 in  $C_5D_5N$ .



**Figure S21.**  $^{1}H^{-1}H$  COSY spectrum for alkaloid **3** in C<sub>5</sub>D<sub>5</sub>N.



Figure S22. HSQC spectrum for alkaloid 3 in  $C_5D_5N$ .



Figure S23. HMBC spectrum for alkaloid 3 in  $C_5D_5N$ .



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%透过率 100 98. 66--89 70-72-74-76-80-82 84--98 -88 -06 92-94--96 78 4000 3444.49 3000 2956.94 2925.65 2000 波数 (cm-1) 1701.11 1664. 58 1637. 41 15001437.91 1384.28 1353.61 1262.40 1122.56 10001062.30

## Figure S25 IR spectrum for alkaloid 3.
**Display Report** Analysis Info Analysis Name 004-0701.D Acquisition Date 02/18/14 10:20:11 Method Copy of DSOPMS2P.M Operator Administrator Sample Name yjm-DH-23 Instrument esquire3000plus Comment Re Acquisition Parameter Ion Source Type Mass Range Mode Capillary Exit Accumulation Time Alternating Ion Polarity Scan End Trap Drive Auto MS/MS Ion Polarity Scan Begin Positive 100 m/z 40.0 Volt ESI Std/Normal off 1750 m/z 85.2 158.5 Volt 15000 錠 Skim 1 3 Spectra Averages on Intens. x10<sup>7</sup> 004-0701.D: TIC +All MS 1.0 0.5 xto 004-0701.D: TIC +All MSn 2.0 1.5 1.0 0.5 0.0 004-0701.D: UV Chromatogram, 201 nm mAU 400-200-0 6 10 0 2 4 8 12 14 Time [min] ntens. x10<sup>6</sup> +MS, 3.7min (#223) 382.3 1.5 1.0 0.5 310.2 799.3 ×109 +MS, 4.1min (#241) 1.0-382.3 0.8-0.6 0.4 0.2 310.4 0.0 200 400 600 800 1000 1200 1400 1600 m/z

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## **Elemental Composition Report**

Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 208 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-2 O: 0-20 DH-23 LCT PXE KE324

DH-23	LCT PXE KE324							08-May-201			
DH-23_050	8 82 (1.784) AM2 (Ar,10	0000.0,0.00,1	.00); ABS; Cm	(69:87)				14:28:23 1: TOF MS ES+			
100		382.2014									
						384.2159					
0	358.1997 362.2339	368	3.1823 372.2	163 374.1217	380.1844	385.2196	96 390.620	4 396.2139			
355.0	360.0	365.0	370.0	375.0	380.0	385.0	390.0	395.0 m/z			
Minimum: Maximum:		5.0	10.0	-1.5 50.0							
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula				
382.2014	382.2018	-0.4	-1.0	10.5	160.0	0.0	C23 H28	N 04			

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Figure S28. <sup>1</sup>H NMR spectrum for alkaloid 4 in CDCl<sub>3</sub>.



Figure S29. <sup>13</sup>C NMR spectrum for alkaloid 4 in CDCl<sub>3</sub>.



Figure S30. HSQC spectrum for alkaloid 4 in CDCl<sub>3</sub>.



Figure S31. HMBC spectrum for alkaloid 4 in CDCl<sub>3</sub>.

fl (ppm)



Current Data Parameters NAME D4C86b EXPNO 19 F2 - Processing para SI 1 SF 400.1300 F1 - Acquisition parameters TD 320 NSTRUM - Acquisition Processing parameters 1024 0 Hz 00 States-TPPI 400.1299746 M States-TPPI 2 CHANNEL Hz Innu 400.13 States-TPP1 400. 25 C 0 400.1328 PADUI 2014071 00015620 1328009 MHz 5 Para 0.65 1.00 meters 46 MHz usec HZ Sec Sec Sec Sec Sec ters MHZ Hz Hz

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%透过率 100 76-84--06 92-94--96 -98 -88 -86 78--08 82 4000 3437.80 3000 2958.42 2924.58 2854.32 2000 \_波数 (cm-1) 1727.57 1703.40 1632.53 15001458.38 1399.55 1175.17 1000

Figure S33. IR spectrum for alkaloid 4.



# **Display Report**

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Elemental Composition Report								Page 1	
Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3									
Monoisotopic Mass, Even Electron Ions 326 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-4 O: 0-20 DH-61 LCT PXE KE324 29-Aug-2014									
DH-61_0829 18 (0.371) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (10:24) 1: TOF MS ES4									10:41:41 1: TOF MS ES+
100 %				384.2	385 2582				2.168+004
373.	373.2620373.8714 377.9463_378.7379 382.2381				386.2607	389.2	962 390.	394.4095	
•	374.0 376.0	378.0	380.0 38	2.0 384.0	386.0	388.0	390.0	392.0	394.0
Minimum: Maximum:		5.0	10.0	-1.5 50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm)	Formula	
384.2544	384.2539	0.5	1.3	8.5	151.5	0.0		С24 НЗ	4 N O3



Figure S36. <sup>1</sup>H NMR spectrum for alkaloid 5 in CD<sub>3</sub>OD.



Figure S37. <sup>13</sup>C NMR spectrum for alkaloid 5 in CD<sub>3</sub>OD.



**Figure S38.**  $^{1}H^{-1}H$  COSY spectrum for alkaloid **5** in CD<sub>3</sub>OD.







Figure S40. HMBC spectrum for alkaloid 5 in CD<sub>3</sub>OD.

Figure S41. NOESY spectrum for alkaloid 5 in CD<sub>3</sub>OD.



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Figure S42. IR spectrum for alkaloid 5.



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# Figure S44. (+)-HRESIMS spectrum for alkaloid 5.

**Elemental Composition Report** 

Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3											
Monoisotopic Mass, Even Electron Ions 159 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-2 O: 0-20 DH-47-1 LCT PXE KE324 DH-47-1 0604 29 (0.637) AM2 (4r 10000 0.000 1.00); ABS: Cm (17:20)									04-Jun-2014 15:05:47		
400 326 2114									6.65e+003		
%					327.214	12					
0	310.1886 314.	0096_315.1075	319.7443	324.1957	328	.2162	333.1806	334.212	25	:	340.1898
	310.0	315.0	320.0	325	.0	330.0		335.0			340.0
Minimum: Maximum:		5.0	10.0	-1.5 50.0							
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm)	Formu	ıla		
326.2114	326.2120	-0.6	-1.8	8.5	94.0	0.0		C21	H28	N	02

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**Figure S45.** <sup>1</sup>H NMR spectrum for alkaloid **6** in CD<sub>3</sub>OD.



Figure S46. <sup>13</sup>C NMR spectrum for alkaloid 6 in CD<sub>3</sub>OD.



**Figure S47.**  $^{1}H^{-1}H$  COSY spectrum for alkaloid **6** in CD<sub>3</sub>OD.



Figure S48 HSQC spectrum for alkaloid 6 in CD<sub>3</sub>OD.



Figure S49. HMBC spectrum for alkaloid 6 in CD<sub>3</sub>OD.





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%透过率 1100 98 98 97 97 94 91 91 88 88 88 85 84-83-82-81-81-81-81-79-79-79-77-4000 3440.37 3000 2925.60 2870.61 2000 \_波数 (cm-1) 1699.81 1629.78 15001454.76 1383.72 1269.44 1192.96 1151.30 1100.67 1075.17 1000

Figure S51. IR spectrum for alkaloid 6.



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Figure S53. (+)-HRESIMS spectrum for alkaloid 6.

## **Elemental Composition Report**

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Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: OffNumber of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron lons 159 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-2 O: 0-20 04-Jun-2014 15:34:52 1: TOF MS ES+ LCT PXE KE324 DH-50 DH-50\_0604 29 (0.636) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (25:41) 2.43e+004 326.2115 100 % 327.2148 342.2059 343.2103 348.1958 356.1796 291.3956 296.7961 301.1692 310.1770 313.6604 324.1963 328.2182 340.2210 0 345.0 11 300.0 305.0 310.0 335.0 340.0 350.0 355.0 295.0 315.0 320.0 325.0 330.0 -1.5 50.0 Minimum: 5.0 5.0 Maximum: i-FIT (Norm) Formula mDa PPM DBE i-FIT Mass Calc. Mass 326.2115 326.2120 -0.5 -1.5 8.5 156.9 0.0 C21 H28 N O2



Figure S54. <sup>1</sup>H NMR spectrum for alkaloid 7 in CD<sub>3</sub>OD.



Figure S55. <sup>13</sup>C NMR spectrum for alkaloid 7 in CD<sub>3</sub>OD.



**Figure S56.**  $^{1}H^{-1}H$  COSY spectrum for alkaloid **7** in CD<sub>3</sub>OD.



Figure S57 HSQC spectrum for alkaloid 7 in CD<sub>3</sub>OD.



Figure S58. HMBC spectrum for alkaloid 7 in CD<sub>3</sub>OD.





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Figure S60. IR spectrum for alkaloid 7.



# Figure S61. (+)-ESIMS spectrum for alkaloid 7.



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## Figure S62. (+)-HRESIMS spectrum for alkaloid 7.

**Elemental Composition Report** 

Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3									
Monoisotopic Mass, Even Electron Ions 173 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-2 O: 0-20 DH-56 LCT PXE KE324 04-Jun-2014 (5:17:07									
DH-56_0604 33 (0.724) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (29:44) 1: TOF MS ES+									
100			34	2.2061				1.3	1e+004
324,197	3	333.6854 33	3 1810	343.2087	21 348.1721	355 8904		204 4070	
0	325.0 330.	0 335.0	340.203	345.0	350.0	355.0	360.0	365.0	m/z
Minimum: Maximum:		5.0	10.0	-1.5 50.0					
Mass	Calc. Mass	mDa	PPM	DBE i	-FIT	i-FIT (Norm)	Formula		
342.2061	342.2069	-0.8	-2.3	8.5 1	23.0	0.0	C21 H2	8 N 03	

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Figure S63. <sup>1</sup>H NMR spectrum for alkaloid 8 in CDCl<sub>3</sub>.



Figure S64. <sup>13</sup>C NMR spectrum for alkaloid 8 in CDCl<sub>3</sub>.



**Figure S65.** <sup>1</sup>H–<sup>1</sup>H COSY spectrum for alkaloid **8** in CDCl<sub>3</sub>.



Figure S66 HSQC spectrum for alkaloid 8 in CDCl<sub>3</sub>.



Figure S67. HMBC spectrum for alkaloid 8 in CDCl<sub>3</sub>.



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%透过率 100 94-84--98 -86 70-72-74-76-78--08 82-88. -06 92--96 4000 3440.28 3000 2929.17 2000 \_波数 (cm-1) 1626.55 1591.61 15001483.27\ 1457.63 1396.74 1371.40 1322.20 1208.53 1178.68 1139.77 1000938.02

Figure S69. IR spectrum for alkaloid 8.



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Elemental Composition Report								
Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3								
Monoisotopic Mass, Even Electron Ions 156 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-2 O: 0-20 DH-26 LCT PXE KE324 04-Jun-2014								
DH-26_0604 34 (0.726) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (33:48) 1: TOF MS ES+								
100		324.	1955		2.93e+004			
			325.1998					
283.1566	297.1800	310.2121 322.1749	328.2268	340.1914 358.2250 365.223	232 372.1761 387.2142,			
280 285	290 295 300	305 310 315 320 3	325 330 335	340 345 350 355 360 365	370 375 380 385			
Minimum: Maximum:		5.0 10.0	-1.5 50.0					
Mass	Calc. Mass	mDa PPM	DBE	i-FIT i-FIT (Norm)	Formula			
324.1955	324.1964	-0.9 -2.8	9.5	196.4 0.0	C21 H26 N O2			



Figure S72. <sup>1</sup>H NMR spectrum for alkaloid 9 in CDCl<sub>3</sub>.



Figure S73. <sup>13</sup>C NMR spectrum for alkaloid 9 in CDCl<sub>3</sub>.







Figure S75. HMBC spectrum for alkaloid 9 in CDCl<sub>3</sub>.



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%透过率 78-4000 3440.00 3000 2960.53 2924.76 2000 \_波数 (cm-1) 1736.56 1699.43 1675.20 1628.83 15001440.71 1384.47 1237.08 1083.00 1041.28 1000

Figure S77. IR spectrum for alkaloid 9.



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Elemental Composition Report								Р	age 1	
Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3										
Monoisotopic Mass, Even Electron Ions 207 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 5-80 H: 2-120 N: 0-2 O: 0-20 DH-43 LCT PXE KE324 04-Jun-2014										
DH-43_0604 29 (0.636) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (24:39) 1: TOF MS ES+										
100	100 386.2325								46+004	
]										
%-										
-					387	.2361				
366.2010367.2257 <sup>370.2095</sup> 374.2133 376.1822378.8456 384.2180 388.2365 392.1881 396.2099 400.2097										
365.0	370.0	375.0	380.0		385.0	390.0	395.	0	400.0	m/z
Minimum: Maximum:		5.0	5.0	-1.5 50.0						
Mass (	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm)	Formula		
386.2325	386.2331	-0.6	-1.6	8.5	108.5	0.0		C23 H32	N 04	