

## Supplementary Information

**Table S1.** NMR data of smenamide A (**1**) ( $\text{CD}_3\text{OD}$ ).

**Figure S1.** Positive ion mode high-resolution ESI mass spectrum of smenamide A (**1**).

**Figure S2.** Positive ion mode high-resolution ESI MS/MS spectrum of smenamide A (**1**).

**Figure S3.**  $^1\text{H}$ -NMR spectrum of smenamide A (**1**) (700 MHz,  $\text{CD}_3\text{OD}$ ).

**Figure S4.** ROESY spectrum of smenamide A (**1**) (700 MHz,  $\text{CD}_3\text{OD}$ ).

**Figure S5.** HMBC spectrum of smenamide A (**1**) (700 MHz,  $\text{CD}_3\text{OD}$ ).

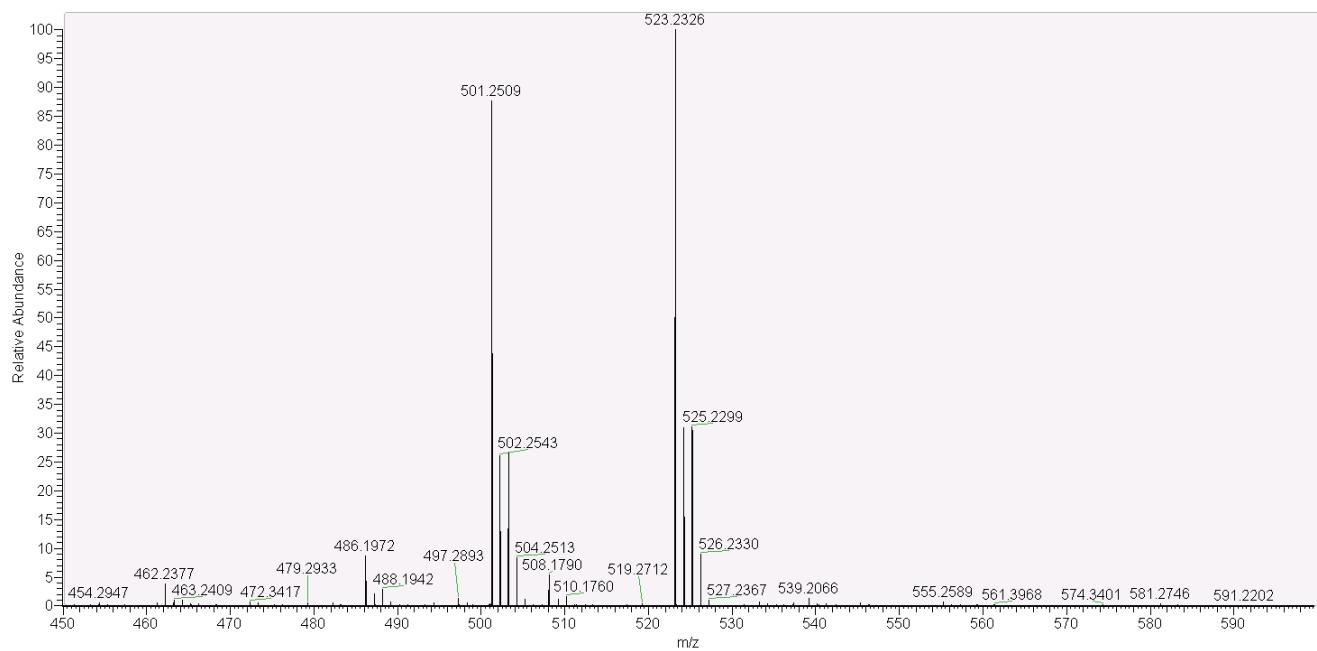
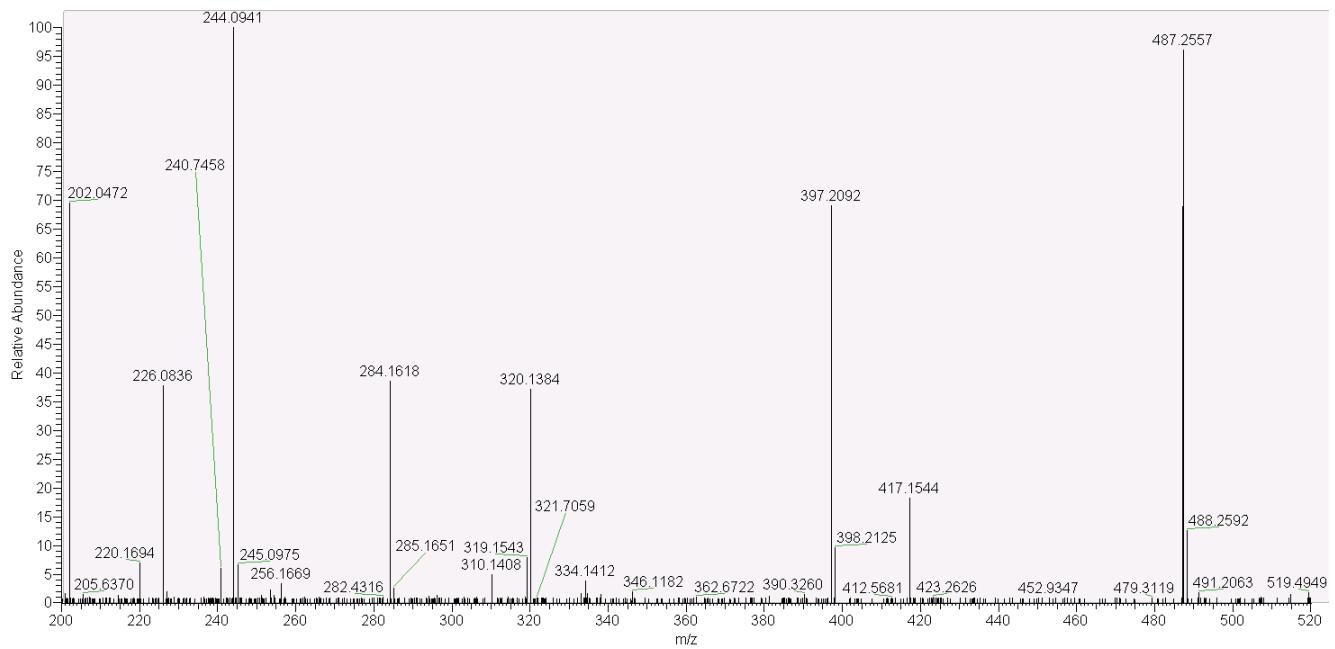
**Figure S6.** Positive ion mode high-resolution ESI mass spectrum of smenamide B (**2**).

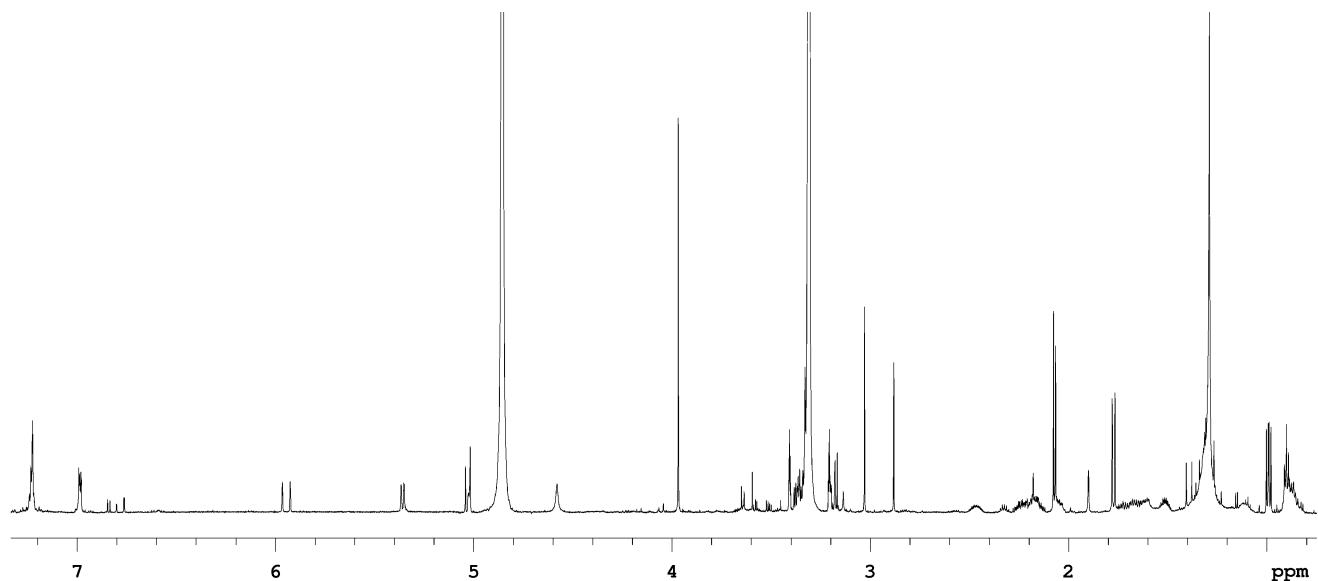
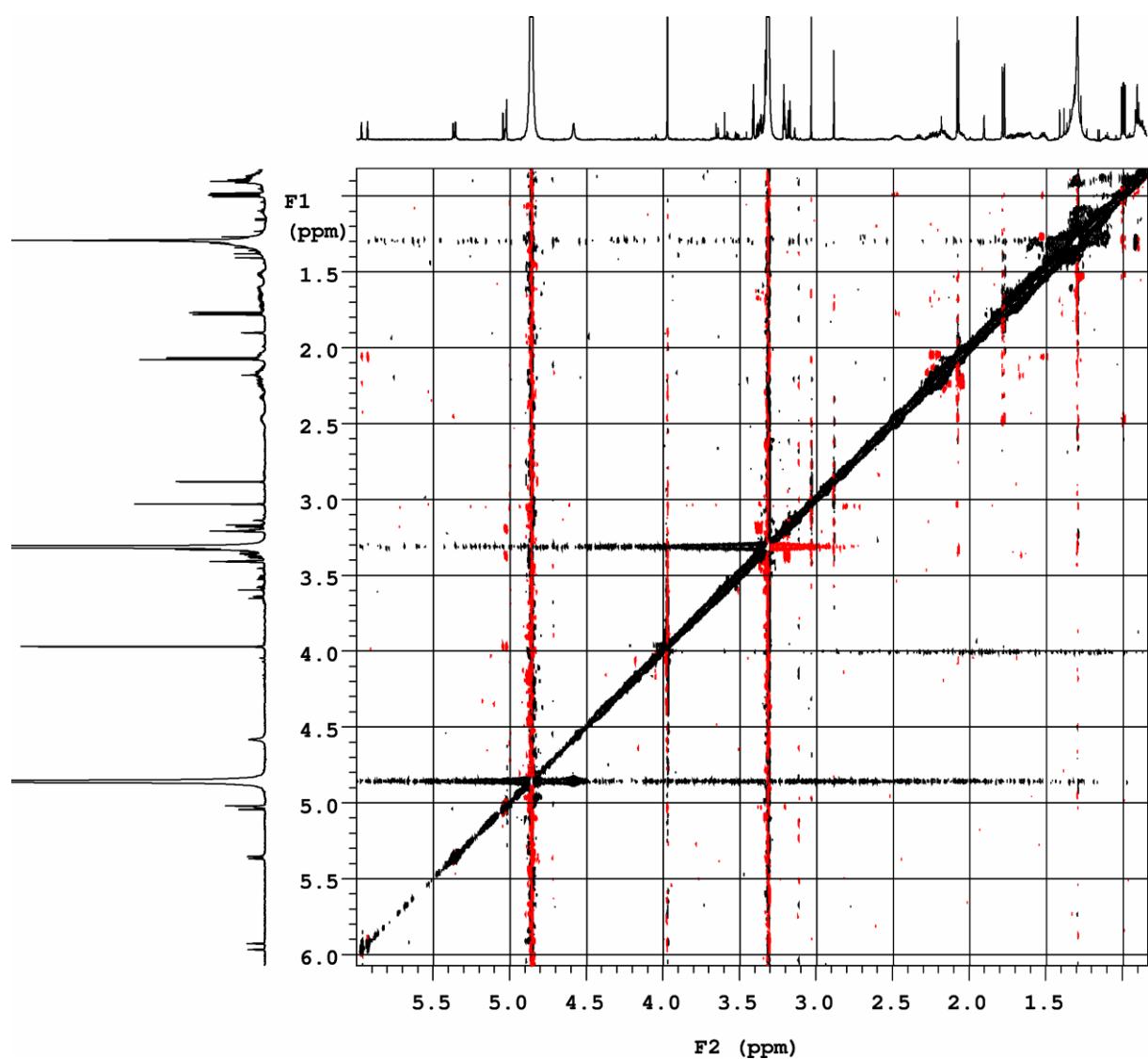
**Figure S7.** Positive ion mode high-resolution ESI MS/MS spectrum of smenamide B (**2**).

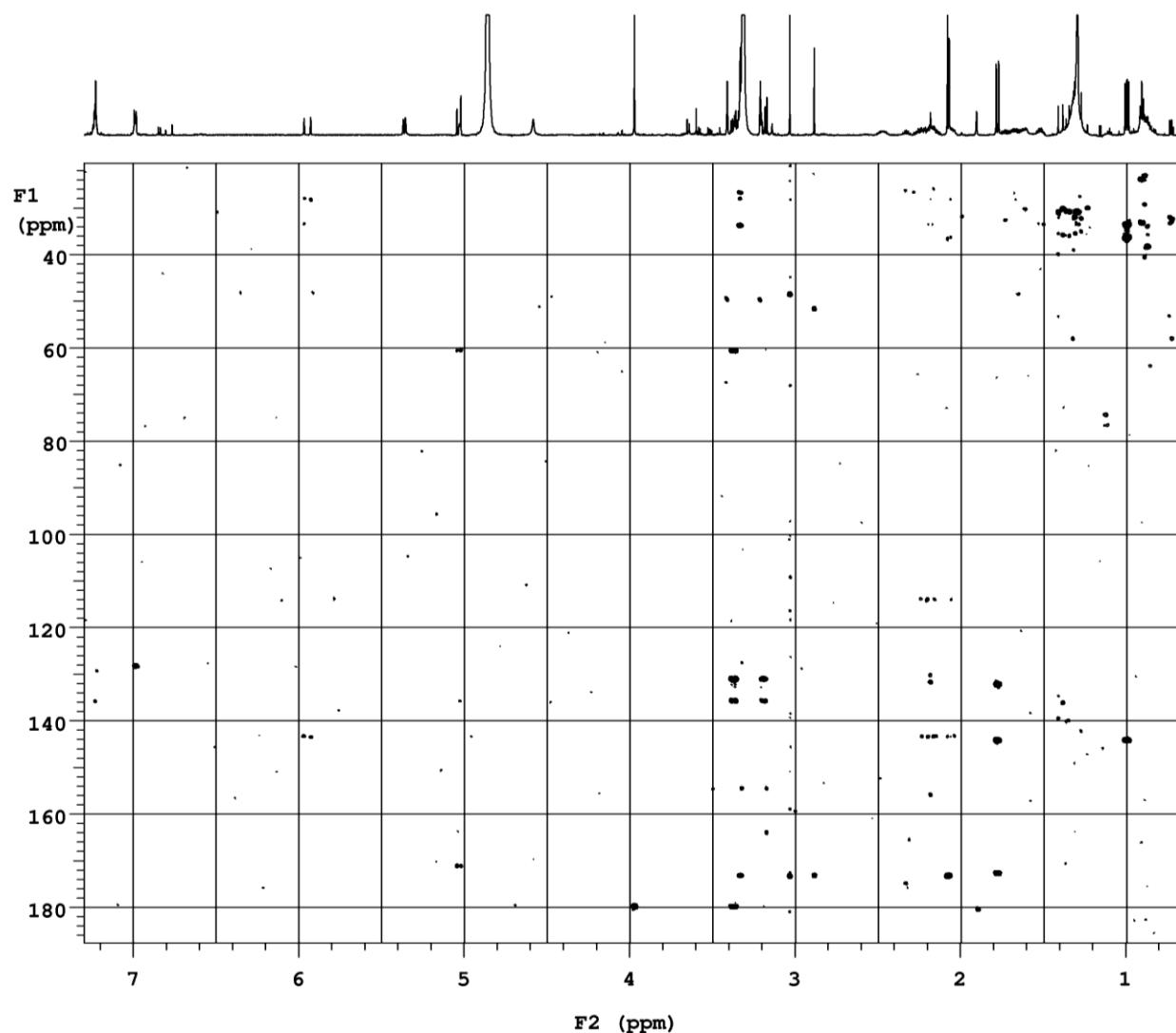
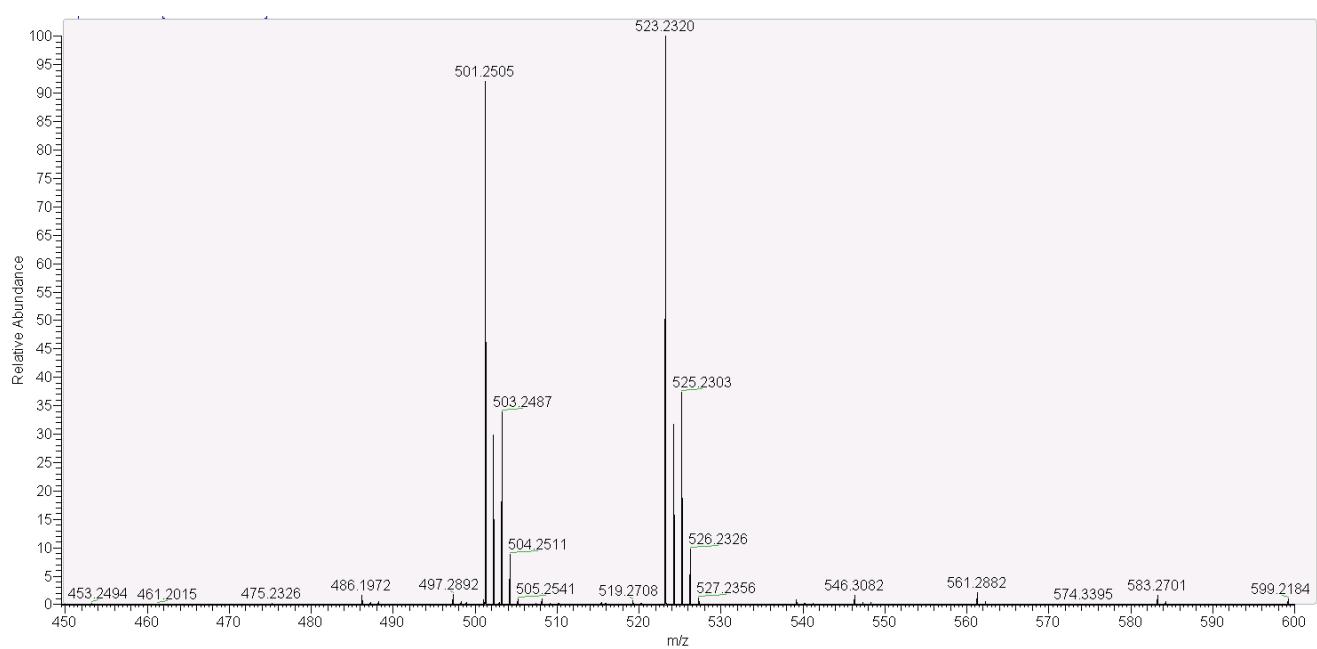
**Figure S8.**  $^1\text{H}$ -NMR spectrum of smenamide B (**2**) (700 MHz,  $\text{CD}_3\text{OD}$ ).

**Table S1.** NMR data of smenamide B (**2**) (700 MHz, CD<sub>3</sub>OD).

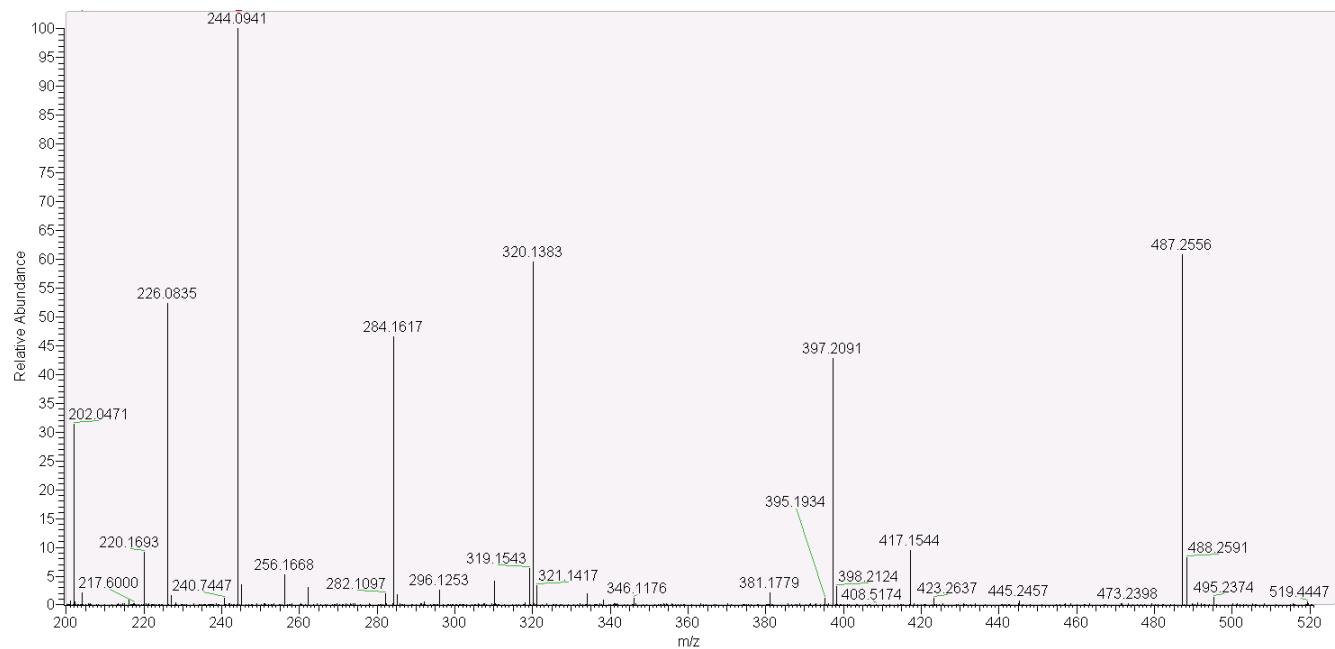
Position	Z-Conformer		E-Conformer		COSY	HMBC
	$\delta_{\text{H}}$ [Mult., J (Hz)]	$\delta_{\text{C}}$ [Mult.]	$\delta_{\text{H}}$ [Mult., J (Hz)]	$\delta_{\text{C}}$ [Mult.]		
1	—	135.5 (C)	—	135.5 (C)		
2/6	7.00 (m)	131.0 (CH)	7.00 (m)	131.0 (CH)	3/5, 7b	4, 6/2, 7
3/5	7.22 (ovl)	129.4 (CH)	7.22 (ovl)	129.4 (CH)	2/6	1
4	7.21 (ovl)	128.3 (CH)	7.21 (ovl)	128.3 (CH)	2/6	
7	a b	3.54 (m) 3.20 (ovl)	35.3 (CH <sub>2</sub> ) 3.20 (ovl)	3.54 (m) 60.7 (CH)	7b, 8 2/6, 7a, 8	1, 2/6, 8, 9 1, 2/6, 8
8		4.95 (m)	60.7 (CH)	4.95 (m)	7a, 7b	
9		—	180.7 (C)	—	180.7 (C)	
10		5.05 (br. s)	95.6 (CH)	5.02 (br. s)	95.6 (CH)	8, 11
11		—	171.0 (C)	—	171.0 (C)	
12		—	171.5 (C)	—	171.5 (C)	
13		—	134.2 (C)	—	134.2 (C)	
14		1.788 (d, 1.5)	20.2 (CH <sub>3</sub> )	1.784 (d, 1.5)	20.2 (CH <sub>3</sub> )	15 12, 13, 15
15		5.13 (br. d, 10.1)	137.2 (CH)	5.13 (br. d, 10.1)	137.2 (CH)	14, 16 12, 14
16		2.10	35.4 (CH)	2.13	35.4 (CH)	15, 17, 18a, 18b
17		0.95 (d, 7.1)	21.2 (CH <sub>3</sub> )	0.96 (d, 7.1)	21.2 (CH <sub>3</sub> )	16 15, 18, 19
18	a b	1.37 (ovl) 1.31 (ovl)	36.1 (CH <sub>2</sub> ) 3.32 (ovl)	1.39 (ovl) 2.10 (ovl)	35.9 (CH <sub>2</sub> ) 16, 18b, 19a, 19b 16, 18a, 19a	
19	a b	2.08 (ovl) 1.92 (ovl)	33.3 (CH <sub>2</sub> ) —	2.10 (ovl) 1.93 (ovl)	33.3 (CH <sub>2</sub> ) 18a, 18b, 19b, 21 18a, 19a	20, 21
20		—	143.2 (C)	—	143.2 (C)	
21		5.81 (br. s)	113.9 (CH)	5.86 (br. s)	113.9 (CH)	19a
22		2.13 (ovl)	28.2 (CH <sub>2</sub> )	2.18 (ovl)	28.0 (CH <sub>2</sub> )	23 20, 21
23		1.61 (m)	25.9 (CH <sub>2</sub> )	1.70 (m)	26.6 (CH <sub>2</sub> )	22, 24 22, 24
24		3.34 (ovl)	48.4 (CH <sub>2</sub> )	3.34 (ovl)	51.4 (CH <sub>2</sub> )	23 22, 23, 25, 27
25		—	173.4 (C)	—	173.2 (C)	
26		2.07 (s)	21.3 (CH <sub>3</sub> )	2.08 (s)	21.1 (CH <sub>3</sub> )	27 25
27		3.02 (s)	36.5 (CH <sub>3</sub> )	2.90 (s)	33.6 (CH <sub>3</sub> )	26 24, 25
OMe		3.95 (s)	59.7 (CH <sub>3</sub> )	3.94 (s)	59.7 (CH <sub>3</sub> )	9

**Figure S1.** Positive ion mode high-resolution ESI MS spectrum of smenamide A (**1**).**Figure S2.** Positive ion mode high-resolution ESI MS/MS spectrum of smenamide A (**1**), parent ion at  $m/z$  523.23.

**Figure S3.**  $^1\text{H}$  NMR spectrum of smenamide A (**1**) ( $\text{CD}_3\text{OD}$ , 700 MHz).**Figure S4.** ROESY spectrum of smenamide A (**1**) ( $\text{CD}_3\text{OD}$ , 700 MHz).

**Figure S5.** HMBC spectrum of smenamide A (**1**) ( $\text{CD}_3\text{OD}$ , 700 MHz).**Figure S6.** Positive ion mode high-resolution ESI MS spectrum of smenamide B (**2**).

**Figure S7.** Positive-ion high-resolution ESI MS/MS spectrum of smenamide B (**2**), parent ion at  $m/z$  523.23.



**Figure S8.**  $^1\text{H}$  NMR spectrum of smenamide B (**2**) ( $\text{CD}_3\text{OD}$ , 700 MHz).

