Supporting information for

# Ansavaricins A–E: five new streptovaricin derivatives from *Streptomyces* sp. S012

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## List of contents

Table S1. NMR spectroscopy data (pyridine-d <sub>5</sub> ) for compound 1	4
Table S2. NMR spectroscopy data (pyridine-d5) for compound 2	5
Table S3. NMR spectroscopy data (pyridine-d <sub>5</sub> ) for compound 3	6
Table S4. NMR spectroscopy data (pyridine-d5) for compound 4	7
Table S5. NMR spectroscopy data (pyridine-d5) for compound 5	8
Table S6. NMR spectroscopy data (pyridine-d5) for compound 6	9
Table S7. NMR spectroscopy data (pyridine-d <sub>5</sub> ) for compound 7	10
Table S8. NMR spectroscopy data (pyridine-d <sub>5</sub> ) for compound 8	.11
Figure S1. Key <sup>1</sup> H- <sup>1</sup> H COSY, HMBC and ROESY correlations for 1	12
Figure S2. Key <sup>1</sup> H- <sup>1</sup> H COSY, HMBC and ROESY correlations for 2.	12
Figure S3. Key <sup>1</sup> H- <sup>1</sup> H COSY, HMBC and ROESY correlations for 3.	12
Figure S4. Key <sup>1</sup> H- <sup>1</sup> H COSY, HMBC and ROESY correlations for 4	13
Figure S5. Key <sup>1</sup> H- <sup>1</sup> H COSY, HMBC and ROESY correlations for 5	13
Figure S6. Key <sup>1</sup> H- <sup>1</sup> H COSY and HMBC correlations for 6	13
Figure S7. Key <sup>1</sup> H- <sup>1</sup> H COSY and HMBC correlations for 7	14
Figure S8. Key <sup>1</sup> H- <sup>1</sup> H COSY and HMBC correlations for 8	14
Figure S9. <sup>1</sup> H NMR (600 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 1	15
Figure S10. <sup>13</sup> C NMR (151 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 1	15
Figure S11. <sup>1</sup> H- <sup>1</sup> H COSY spectrum for compound 1	16
Figure S12. HSQC spectrum for compound 1	16
Figure S13. HMBC spectrum for compound 1	. 17
Figure S14. ROESY spectrum for compound 1	. 17
Figure S15. <sup>1</sup> H NMR (600 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 2	18
Figure S16. <sup>13</sup> C NMR (151 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 2	18
Figure S17. <sup>1</sup> H- <sup>1</sup> H COSY spectrum for compound 2	19
Figure S18. HSQC spectrum for compound 2	. 19
Figure S19. HMBC spectrum for compound 2	20
Figure S20. ROESY spectrum for compound 2	20
Figure S21. <sup>1</sup> H NMR (600 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 3	21
Figure S22. <sup>13</sup> C NMR (151 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 3	21
Figure S23. <sup>1</sup> H- <sup>1</sup> H COSY spectrum for compound 3	22
Figure S24. HSQC spectrum for compound 3	. 22
Figure S25. HMBC spectrum for compound 3	23
Figure S26. ROESY (Acetone-d6) spectrum for compound 3	23
Figure S27. <sup>1</sup> H NMR (400 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 4	. 24
Figure S28. <sup>13</sup> C NMR (101 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 4	24
Figure S29. <sup>1</sup> H- <sup>1</sup> H COSY spectrum for compound 4	25
Figure S30. HSQC spectrum for compound 4	. 25
Figure S31. HMBC spectrum for compound 4	26
Figure S32. ROESY spectrum for compound 4	. 26
Figure S33. <sup>1</sup> H NMR (600 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 5	. 27
Figure S34. <sup>13</sup> C NMR (151 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 5	27

Figure S35.	<sup>1</sup> H- <sup>1</sup> H COSY spectrum for compound 5	28
Figure S36.	HSQC spectrum for compound 5	28
Figure S37.	HMBC spectrum for compound 5	29
Figure S38.	ROESY spectrum for compound 5	29
Figure S39.	<sup>1</sup> H NMR (600 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 6	30
Figure S40.	<sup>13</sup> C NMR (151 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 6	30
Figure S41.	<sup>1</sup> H- <sup>1</sup> H COSY spectrum for compound 6	31
Figure S42.	HSQC spectrum for compound 6	31
Figure S43.	HMBC spectrum for compound 6	32
Figure S44.	ROESY spectrum for compound 6	32
Figure S45.	<sup>1</sup> H NMR (600 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 7	33
Figure S46.	<sup>13</sup> C NMR (151 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 7	33
Figure S47.	<sup>1</sup> H- <sup>1</sup> H COSY spectrum for compound 7	34
Figure S48.	HSQC spectrum for compound 7	34
Figure S49.	HMBC spectrum for compound 7	35
Figure S50.	ROESY spectrum for compound 7	35
Figure S51.	<sup>1</sup> H NMR (400 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 8	36
Figure S52.	<sup>13</sup> C NMR (101 MHz, pyridine- <i>d</i> <sub>5</sub> ) spectrum for compound 8	36
Figure S53.	<sup>1</sup> H- <sup>1</sup> H COSY spectrum for compound 8	37
Figure S54.	HSQC spectrum for compound 8	37
Figure S55.	HMBC spectrum for compound 8	38
Figure S56.	ROESY spectrum for compound 8	38
Figure S57.	High-resolution ESIMS spectrum for compound 1	39
Figure S58.	High-resolution ESIMS spectrum for compound 2	39
Figure S59.	High-resolution ESIMS spectrum for compound 3	40
Figure S60.	High-resolution ESIMS spectrum for compound 4	40
Figure S61.	High-resolution ESIMS spectrum for compound 5	41
Figure S62.	High-resolution ESIMS spectrum for compound 6	41
Figure S63.	High-resolution ESIMS spectrum for compound 7	42
Figure S64.	High-resolution ESIMS spectrum for compound 8	42
Figure S65.	The proposed streptovaricin biosynthetic logic	43

Pos.	$\delta_{\rm H}$ (mult., J Hz)	$\delta_{ m C}$	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1		185.4s		
2		140.8s		
3		138.2s		
4		185.1s		
5	7.53 (s)	108.8d		C-1/C-4, C-6, C-7, C-9
6		163.1s		
7		118.3s		
8		164.7s		
9		108.4s		
10		132.8s		
11	2.41 (s)	9.0q		C-6, C-7, C-8
12		168.4s		
13		132.2s		
14	7.93 (d, 11.7)	130.8d	H-15	C-12, C-16, C-30
15	6.70 (t, 11.3)	125.7d	H-14, H-16	C-14, C-17
16	6.20 (t, 10.6)	139.0d	H-15, H-17	C-14, C-18
17	3.25 (m)	34.9d	H-16, H-18, H-31	
18	4.80 (dd, 1.7, 10.5)	83.7d	H-17, H-19	C-16, C-19, C-20, C-31
19	2.62 (m)	36.0d	H-18, H-20, H-32	C-18
20	4.34 (t, 2.3)	74.0d	H-19, H-21	C-18, C-32, C-33
21	3.38 (t, 2.2)	51.6d	H-20, H-22	C-19, C-20, C-22, C-33
22	3.73 (d, 1.7)	85.5d	H-21, H-23	C-20, C-33
23	3.03 (m)	39.4d	H-22, H-24, H-34	C-22, C-24, C-34
24	3.65 (d, 10.6)	82.3d	H-23	C-23, C-25
25		74.4s		
26	3.81 (d, 8.4)	85.3d	H-27	C-22, C-24, C-25, C-27, C-36
27	3.28 (m)	40.8d	H-26, H-36	C-26, C-28, C-36
28		176.1s		
29	2.30 (s)	14.1q		C-2, C-3, C-1/C-4
30	2.31 (s)	13.9q		C-12, C-13, C-14
31	1.20 (d, 6.9)	19.1q	H-17	C-16, C-17, C-18
32	1.29 (d, 6.9)	13.8q	H-19	C-18, C-19, C-20
33		170.8s		
34	1.31 (d, 6.4)	14.5q	H-23	C-22, C-23, C-24
35	1.75 (s)	15.6q		C-24, C-25, C-26
36	1.57 (d, 6.8)	16.5q	H-27	C-26, C-27, C-28
37	3.74 (s)	52.1q		C-28
NH	10.11 (s)			

 Table S1. NMR spectroscopy data (pyridine-d5) for compound 1.



Pos.	$\delta_{\rm H}$ (mult., J Hz)	$\delta_{ m C}$	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1		185.4s		
2		140.7s		
3		138.3s		
4		185.1s		
5	7.52 (s)	108.8d		C-1/C-4, C-7
6		163.1s		
7		118.3s		
8		164.7s		
9		108.4s		
10		132.2s		
11	2.41 (s)	9.0q		C-6, C-7, C-8
12		168.3s		
13		133.0s		
14	7.76 (d, 11.7)	130.5d	H-15	C-12, C-30
15	6.55 (t, 11.4)	125.7d	H-14, H-16	C-14, C-17
16	5.90 (t, 10.7)	138.6d	H-15, H-17	C-14
17	3.15 (m)	34.5d	H-16, H-31	
18	3.95 (dd, 2.2, 10.7)	87.0d	H-19	C-16, C-31,
19	2.52 (m)	32.5d	H-18, H-32	C-20
20	6.92 (br s)	148.2d		C-18, C-19, C-22, C-32, C-33
21		134.2s		
22	5.0 (br s)	75.0d	H-23	C-20, C-21, C-23, C-24, C-33
23	3.15 (m)	38.4d	H-22, H-34	C-22, C-34
24	4.65 (s)	76.8d		C-22, C-23, C-26, C-34, C-35
25		77.0s		
26	7.71 (s)	147.9d		C-25, C-28, C-36
27		128.1s		
28		170.1s		
29	2.31 (s)	14.5g		C-2, C-3, C-1/C-4
30	2.26 (s)	13.8q		C-12, C-13, C-14
31	1.09 (d, 6.7)	18.4q	H-17	C-16, C-17, C-18
32	0.96 (d, 7.0)	16.6q	H-19	C-18, C-19, C-20
33		165.4s		
34	1.54 (d, 6.9)	13.6q	H-23	C-22, C-23, C-24
35	1.76 (s)	27.2q		C-24, C-25, C-26
36	2.52 (m)	14.2q		C-26, C-27, C-28
37	3.67 (s)	52.2q		C-28
NH	10.03 (s)			C-2, C-12

 Table S2. NMR spectroscopy data (pyridine-d5) for compound 2.



Pos.	$\delta_{\rm H}$ (mult., J Hz,	$\delta_{\rm H}$ (mult., J Hz,	$\delta_{ m C}$	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1	pyridine- <i>a</i> <sub>5</sub> )	acetone- $a_6$ )	153.76	(pyridine- <i>a</i> <sub>5</sub> )	(pyridine- <i>a</i> <sub>5</sub> )
2			133.78 128.4s		
3			128.43		
4			126.25 146.4s		
5			107.58		
6			193.9s		
7			86.0s		
8			200.7s		
9			110.3s		
10			127.5s		
11	1.59 (s)	1.45 (s)	27.9q		C-6, C-7, C-8
12			175.0s		
13			131.4s		
14	6.91 (d, 11.0)	6.40 (t, 11.0)	128.8d	H-15, H-30	C-12, C-16, C-30
15	6.40 (t, 10.9)	6.10 (t, 10.9)	124.1d	H-14, H-16	C-13, C-17
16	5.85 (t, 10.3)	5.38 (t, 10.6)	147.1d	H-15, H-17	C-14, C-18
17	3.37 (m)	2.78 (m)	40.7d	H-16, H-18, H-31	C-18, C-31
18	3.55 (d, 9.3)	3.15 (m)	82.5d	H-17, H-19	C-16, C-17, C-19, C-20, C-32
19	2.08 (m)	1.74 (m)	36.7d	H-18, H-20, H-32	C-20, C-32
20	4.83 (d, 10.4)	4.21 (dd, 10.4, 5.3)	72.9d	H-19, H-21	C-19, C-21, C-22, C-32, C-33
21	3.17 (s)	2.85 (s)	48.3d	H-20	C-19, C-20, C-22, C-23, C-33
22	3.85 (d, 10.5)	3.44 (d, 10.5)	80.9d	H-23	C-20, C-21, C-23, C-24, C-26, C-26, C-26, C-26, C-27, C-27
22	2(2(m))	2.09 (m)	20.74	11 22 11 24 11 25	C-26, C-33, C-35
23	2.03 (m) 3.74 (m)	2.08 (m)	39.70 82.24	н-22, н-24, н-35	$C_{-22}$
24	5.74 (III)	5.15 (III)	82.20 74.5s		C-25, C-25, C-55, C-56
23			74.58		C 22 C 24 C 25 C 27
26	3.91 (s)	4.09 (d, 6.2)	88.3d		C-22, C-24, C-25, C-27, C-28, C-36, C-37
27	4 99 (m)	436(a, 71)	34 5d	H-37	C-26 C-28 C-37
28	1.99 (III)	1.50 ( <b>q</b> , 7.1)	170.9s	11 57	0 20, 0 20, 0 37
29	2.65(s)	2.74(s)	12.7a		C-1 (w). C-2. C-3. C-4
30	2.34(s)	1.95(s)	14.4a	H-14	C-12, C-13, C-14
31	0.50 (d. 6.7)	0.26 (d. 6.7)	19.1a	H-17	C-16, C-17, C-18
32	1.15 (d, 6.8)	0.86 (d, 6.8)	17.6q	H-19	C-18, C-19, C-20
33			174.0s		
34	3.88 (s)	3.84 (s)	52.1q		C-33
35	1.34 (d, 6.5)	1.01 (d, 6.5)	14.7q	H-23	C-22, C-23, C-24
36	1.82 (s)	1.34 (s)	17.8q		C-24, C-25, C-26
37	1.65 (d, 7.0)	1.50 (d, 6.9)	12.2q	H-27	C-26, C-27, C-28
NH	9.89 (s)				
HO-20	3.73 (br s)			H-20	C-19, C-20, C-21

### Table S3. NMR spectroscopy data for compound 3.



Pos.	$\delta_{ m H}$ (mult., $J$ Hz)	$\delta_{ m C}$	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1		199.5s		
2		132.3s		
3		144.6s		
4		85.9s		
5		120.4s		
6		163.1s		
7		113.5s		
8		164.0s		
9		109.3s		
10		127.5s		
11	2.19 (s)	9.5q		C-6, C-7, C-8
12		171.8s		
13		131.1s		
14	7.47 (d, 10.9)	130.3d	H-15	C-12, C-16, C-33
15	6.50 (t, 11.0)	125.6d	H-14, H-16	C-13, C-17
16	5.91 (t, 10.4)	142.1d	H-15, H-17	C-14, C-34
17	3.10 (m)	36.9d	H-16, H-34	
18	3.73 (dd, 1.8, 7.7)	83.7d	H-19	C-16, C-19, C-34, C-35
19	2.22 (m)	37.5d	H-18, H-20, H-35	C-17, C-18, C-20, C-35
20	4.736-4.76 (m)	76.7d	H-19, H-21	C-18, C-19, C-21, C-22, C-36
21	3.44 (m)	49.4d	H-20	C-19, C-20, C-22, C-36
22	4.45 (d, 10.6)	71.7d	H-23	C-20, C-23, C-24, C-36, C-38
23	3.57 (m)	37.5d	H-22, H-24, H-38	C-22, C-38
24	4.74-4.76 (m)	79.1d	H-23	C-25, C-26, C-38, C-39
25		77.6s		
26	7.51 (br s)	151.0d		C-25, C-27, C-28, C-40
27		137.9s		
28		200.0s		
29		168.8s		
30	2.36(s)	21.2q		C-29
31	2.01(s)	11.6g		C-3, C-4, C-10
32	3.51 (s)	51.8g		C-4
33	1.97(s)	14.0q		C-12, C-13, C-14
34	1.26 (d, 6.5)	19.4g	H-17	C-16, C-17, C-18
35	1.06 (d, 6.6)	16.7q	H-19	C-18, C-20, C-23
36		174.0s		
37	3.50 (s)	51.6q		C-36
38	1.44 (d, 7.0)	11.7q	H-23	C-22, C-23, C-24
39	1.80 (s)	30.5q		C-24, C-25, C-26
40	2.80 (s)	12.7q		C-26, C-27, C-28
NH	10.61 (s)			C-12
HO-8	13.91 (s)			C-7, C-8, C-9

 Table S4. NMR spectroscopy data (pyridine-d5) for compound 4.



Pos.	$\delta_{\rm H}$ (mult., J Hz)	$\delta_{ m C}$	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1		193.5s		
2	6.00 (d, 6.9)	59.7d		C-1, C-3, C-29
3		76.8s		
4		81.4s		
5		112.7s		
6		164.7s		
7		129.6s		
8	7.86 (s)	133.4d		C-1, C-6, C-10, C-11
9		121.0s		
10		147.5s		
11	2.26 (s)	15.6q		C-6, C-7, C-8
12		172.4s		
13		132.6s		
14	7.70 (d, 10.6)	129.9d	H-15	C-12, C-16, C-30
15	6.58 (t, 11.2)	125.3d	H-14, H-16	C-13, C-17
16	5.76 (t, 10.0)	140.8d	H-15, H-17	C-14, C-31
17	2.75 (t, 7.9)	40.0d	H-16, H-31	C-15, C-16, C-19
18	3.73 (d, 5.3)	83.9d	H-19	C-16, C-19, C-31, C-32
19	2.50 (m)	43.7d	H-18, H-20, H-32	C-17, C-18, C-20, C-32
20	3.95 (d, 9.2)	80.1d	H-19	C-18, C-21, C-22, C-33
21	2.00 (m)	35.1d	H-33	C-20, C-33
22	4.70 (d, 9.3)	70.1d	H-23	C-23, C-24, C-20, C-33
23	2.17 (m)	38.3d	H-22, H-34	C-22, C-34
24	4.24 (d, 10.3)	71.2d	H-25	C-3, C-22, C-23, C-26, C-34
25	2.87 (m)	29.8d	H-24, H-35	C-24, C-26, C-27
26	2.93 (d, 9.2)	64.0d		C-4, C-10, C-25, C-28, C-35
27		88.9s		
28		202.2s		
29	1.59 (s)	17.4q		C-2, C-3, C-4
30	2.21 (s)	14.4q		C-12, C-13, C-14
31	1.19 (d, 6.8)	22.4q	H-17	C-16, C-17, C-18
32	1.07 (d, 6.7)	16.9q	H-19	C-19, C-20, C-18
33	1.30 (d, 7.0)	11.3q	H-21	C-20, C-21, C-22
34	1.17 (d, 7.0)	9.5q	H-23	C-22, C-23, C-24
35	0.85 (d, 6.6)	16.1q	H-25	C-24, C-25, C-26
36	1.65 (s)	14.3q		C-26, C-27, C-28
NH	8.69 (d, 6.5)		H-2	

 Table S5. NMR spectroscopy data (pyridine-d5) for compound 5.



Pos.	$\delta_{\rm H}$ (mult., J Hz)	$\delta_{ m C}$	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1		156.0s		
2		136.7s		
3		125.3s		
4		125.1s		
5		137.7s		
6		160.5s		
7		107.3s		
8		189.3s		
9		101.8s		
10		114.6s		
11	1.95 (s)	8.3q		C-6, C-7, C-8
12		171.9s		
13		134.0s		
14	8.03 (d, 11.5)	130.8d	H-15	C-12, C-16, C-33
15	6.56 (t, 11.2)	124.5d	H-14, H-16	C-13, C-14, C-17
16	5.79 (t, 9.6)	144.1d	H-15, H-17	C-14, C-17, C-18, C-34
17	3.70 (m)	39.9d	H-34	C-18, C-34
18	3.70 (m)	82.8d		C-16, C-17, C-19, C-20, C-34, C-35
19	2.36 (m)	35.4d	H-35	C-17, C-20, C-35
20	4.79 (dd, 11.2, 20.6)	75.8d	H-21	C-18, C-19, C-21, C-22, C-35
21	3.70 (m)	54.8d	H-20, H-22	C-22, C-36
22	4.79 (dd, 11.2, 20.6)	72.1d	H-21, H-23	C-20, C-23, C-24, C-36
23	2.73 (m)	38.9d	H-22, H-24, H-38	C-22, C-38
24	4.70 (br s)	78.0d		C-22, C-23, C-25, C-26, C-38, C-39
25		76.9s		
26	6.66 (s)	147.0d		C-25, C-27, C-28, C-40
27		131.6s		
28		170.8s		
29	2.68 (s)	14.6q		C-2, C-3, C-4
30		169.8s		
31	2.34 (s)	21.6q		C-30
32	5.28 (d, 4.6)	90.5t		C-6, C-28
22	2.15 (a)	12.70		C 12 C 12 C 14
33	2.13(8)	13.7q 18.0g	Ц 17	C = 12, C = 13, C = 14
34	1.05 (d, 5.4)	10.9q	H-17	$C_{-10}, C_{-17}, C_{-18}$
35	1.40 (d, 7.1)	22.5q	11-19	C-18, C-19, C-20
30	363(s)	51 Qa		C 36
38	0.03(8)	12 1a	Н_23	$C_{-22} C_{-23} C_{-24}$
30	1.75 (a, 0.7)	12.14 20.8a	11-23	$C_{-22}, C_{-23}, C_{-24}$
39 40	1.73(8) 2.75(s)	29.04 15.6a		C-25, C-20 C-26, C-27, C-28
-+0 OH-1	2.73 (8) 14 80 (s)	15.04		$C^{-}20, C^{-}27, C^{-}20$
NH	10.85 (s)			C-12

 Table S6. NMR spectroscopy data (pyridine-d5) for compound 6.



Pos.	$\delta_{\rm H}$ (mult., J Hz)	$\delta_{ m C}$	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1		186.1s		
2		141.4s		
3		136.0s		
4		185.5s		
5		131.2s		
6		162.8s		
7		119.1s		
8		162.8s		
9		107.8s		
10		125.9s		
11	2.24 (s)	9.6q		C-6, C-7, C-8
12		171.Îs		
13		133.4s		
14	7.86 (d, 11.2)	132.9d	H-15	C-12, C-16, C-30
15	6.46 (t, 11.1)	124.0d	H-14, H-16	C-13, C-17
16	5.76 (t, 10.1)	145.2d	H-15, H-17	C-14, C-18, C-31
17	3.48 (m)	40.2d	H-31	C-18, C-31
18	3.61 (m)	82.4d		C-16, C-32
19	2.28 (m)	35.5d		
20	4.83 (m)	75.6d	H-21	C-18, C-19, C-22, C-32, C-33
21	3.61 (m)	55.0d	H-20, H-22	C-19, C-20, C-33
22	4.83 (m)	72.0d	H-21	C-21, C-23, C-35
23	2.76 (m)	39.2d	H-24, H-35	C-22, C-25, C-35
24	4.83 (m)	77.7d	H-23	C-25, C-26, C-36
25		76.2s		
26	746(s)	145 7d		C-25 C-28 C-37
20		129.0		0 20, 0 20, 0 07
21		100.5		
20	2.35 (c)	199.38		C 2 C 3 C 4
29	2.33(8)	14.74 12.22a		C = 12 C = 12
30	2.10(3)	13.33y	Н 17	C = 12, C = 13
31	1.42 (d. 7.0)	10.4q	11-1/	$C_{10}, C_{11}, C_{10}$
32	1.43 (d, 7.0)	22.3q 174.2a		C-18, C-19, C-20
33	3 42 (s)	174.28 51.5a		C 22
34	3.42(8)	12.4g	Ц 22	$C^{-33}$
33 36	1.20 (0, 0.7)	12.44 20.6a	п-23	$C_{22}, C_{23}, C_{24}$
27	1.03(8) 2.71(c)	29.04 12.25a		$C_{-24}, C_{-23}, C_{-20}$
J/ NU	2.71(8)	15.559		$C^{-20}, C^{-21}, C^{-20}$
INFI	10.97 (8)			C-3

 Table S7. NMR spectroscopy data (pyridine-d5) for compound 7.



Pos.	$\delta_{\rm H}$ (mult., J Hz)	$\delta_{ m C}$	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1		186.4s		
2		139.1s		
3		137.1s		
4		181.6s		
5		126.5s		
6		160.4s		
7		133.3s		
8	8.06 (s)	130.3d		C-1, C-4, C-6, C-11
9		125.3s		
10		136.0s		
11	2.43 (s)	17.7q		C-6, C-7, C-8
12		167.8s		
13		129.1s		
14	8.03 (d, 11.5)	136.0d	H-15	C-12, C-13, C-16, C-30
15	6.59 (t, 11.4)	124.7d	H-14, H-16	C-13, C-14, C-17
16	5.99 (t, 9.6)	144.9d	H-15, H-17	C-14, C-31
17	3.28 (m)	37.9d	H-31	C-16
18	3.72 (d, 7.5)	84.1d	H-19	C-16, C-19, C-31, C-32
19	2.62 (m)	41.2d	H-18, H-20, H-32	C-18, C-20, C-32
20	3.96 (d, 8.4)	82.5d		C-18, C-22, C-33
21	2.15 (m)	35.5d	H-33	
22	4.55 (d, 9.8)	71.0d	H-23	C-20, C-23, C-24, C-33
23	1.92 (m)	39.3d	H-22, H-34	C-22
24	4.22 (d, 8.6)	74.5d	H-25	C-22, C-25, C-26, C-34, C-35
25	2.88 (m)	37.8d	H-24, H-26, H-35	C-24, C-26, C-27, C-35
26	6.49 (d, 9.3)	150.3d		C-24, C-28, C-36
27		139.4s		
28		198.4s		
29	2.28 (s)	15.5q		C-2, C-3, C-4
30	2.12 (s)	13.1q		C-12, C-13, C-14
31	1.25 (d, 5.4)	22.0q	H-17	C-16, C-17, C-18
32	1.05 (m)	15.2q	H-19	C18, C-19, C-20
33	1.25 (d, 5.4)	11.4q	H-21	C-20, C-21, C-22
34	1.05 (m)	9.5q	H-23	C-22,C-23, C-24
35	0.73 (d, 6.9)	16.3q	H-25	C-24, C-25, C-26
36	2.08 (s)	12.6q		C-26, C-27, C-28

 Table S8. NMR spectroscopy data (pyridine-d5) for compound 8.



Figure S1. Key <sup>1</sup>H-<sup>1</sup>H COSY, HMBC and ROESY correlations for 1.







Figure S3. Key <sup>1</sup>H-<sup>1</sup>H COSY, HMBC and ROESY correlations for 3.



#### Figure S4. Key <sup>1</sup>H-<sup>1</sup>H COSY, HMBC and ROESY correlations for 4.







Figure S6. Key <sup>1</sup>H-<sup>1</sup>H COSY and HMBC correlations for 6.



Figure S7. Key <sup>1</sup>H-<sup>1</sup>H COSY and HMBC correlations for 7.



Figure S8. Key <sup>1</sup>H-<sup>1</sup>H COSY and HMBC correlations for 8.



- COSY A HMBC



#### Figure S9. <sup>1</sup>H NMR (600 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 1







Figure S11. <sup>1</sup>H-<sup>1</sup>H COSY spectrum for compound 1

Figure S12. HSQC spectrum for compound 1







Figure S14. ROESY spectrum for compound 1



#### Figure S15. <sup>1</sup>H NMR (600 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 2









Figure S17. <sup>1</sup>H-<sup>1</sup>H COSY spectrum for compound 2

Figure S18. HSQC spectrum for compound 2







Figure S20. ROESY spectrum for compound 2





#### Figure S21. <sup>1</sup>H NMR (600 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 3





Figure S23. <sup>1</sup>H-<sup>1</sup>H COSY spectrum for compound 3



9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f2 (ppm)

-150

Figure S25. HMBC spectrum for compound 3



Figure S26. ROESY (acetone-d<sub>6</sub>) spectrum for compound 3





## Figure S27. <sup>1</sup>H NMR (400 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 4







Figure S29. <sup>1</sup>H-<sup>1</sup>H COSY spectrum for compound 4







f2 (ppm)



Figure S33. <sup>1</sup>H NMR (600 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 5

Figure S34. <sup>13</sup>C NMR (151 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 5







Figure S37. HMBC spectrum for compound 5







#### Figure S39. <sup>1</sup>H NMR (600 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 6









7.0

11.0

10.0

9.0

8.0

6.0 f2 (ppm)

5.0

4.0

3.0

2.0

1.0





Figure S44. ROESY spectrum for compound 6







Figure S46. <sup>13</sup>C NMR (151 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 7





Figure S47. <sup>1</sup>H-<sup>1</sup>H COSY spectrum for compound 7

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 f2 (ppm)

Figure S49. HMBC spectrum for compound 7



Figure S50. ROESY spectrum for compound 7





#### Figure S51. <sup>1</sup>H NMR (400 MHz, pyridine-*d*<sub>5</sub>) spectrum for compound 8





Figure S53. <sup>1</sup>H-<sup>1</sup>H COSY spectrum for compound 8



9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f2 (ppm)

Figure S55. HMBC spectrum for compound 8



Figure S56. ROESY spectrum for compound 8















Figure S60. High-resolution ESIMS spectrum for compound 4







Figure S62. High-resolution ESIMS spectrum for compound 6



#### Figure S63. High-resolution ESIMS spectrum for compound 7







#### Figure S65. The proposed streptovaricin biosynthetic logic

