

Supplemental Materials

Stilbene epoxidation and detoxification in a *Photorhabdus luminescens*-nematode symbiosis

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Table S1. The major conformers of possible diastereomers A and B of compound **3**<sup>a</sup>

Conformers	Boltzmann population (%)	Relative energy (KJ/mol)
Diastereomer A_1	16.99561	0
Diastereomer A_2	16.796544	0.029
Diastereomer A_3	13.969961	0.486
Diastereomer A_4	13.012172	0.662
Diastereomer A_5	11.626486	0.941
Diastereomer A_6	6.890221	2.238
Diastereomer A_7	6.311961	2.455
Diastereomer A_8	4.674104	3.2
Diastereomer A_9	2.702416	4.558
Diastereomer A_10	2.654765	4.602
Diastereomer A_11	1.251053	6.467
Diastereomer A_12	1.13498	6.709
Diastereomer A_13	0.818636	7.518
Diastereomer A_14	0.586516	8.345
Diastereomer A_15	0.574573	8.396
Diastereomer B_1	15.456274	0
Diastereomer B_2	14.353578	0.183
Diastereomer B_3	11.025971	0.837
Diastereomer B_4	7.629023	1.75
Diastereomer B_5	7.555183	1.774
Diastereomer B_6	6.295617	2.226
Diastereomer B_7	6.206271	2.262
Diastereomer B_8	4.415255	3.106
Diastereomer B_9	3.46024	3.71
Diastereomer B_10	3.279239	3.843
Diastereomer B_11	3.103805	3.979
Diastereomer B_12	2.995462	4.068
Diastereomer B_13	2.755307	4.275
Diastereomer B_14	1.921398	5.168
Diastereomer B_15	1.830332	5.289
Diastereomer B_16	1.514783	5.758
Diastereomer B_17	1.217719	6.299
Diastereomer B_18	1.202138	6.331
Diastereomer B_19	1.199418	6.336
Diastereomer B_20	1.016044	6.748
Diastereomer B_21	0.788752	7.375
Diastereomer B_22	0.778191	7.409

<sup>a</sup>Conformers of possible diastereomers A and B (see Figure 6A in the main text) were elucidated by conformational searches in MMFF94 force field and the searches were achieved in the gas phase with a 50 kJ/mol energy limit.

Table S2. The major conformers of possible diastereomers A and B of compound **4**<sup>a</sup>

Conformers	Boltzmann population (%)	Relative energy (KJ/mol)
Diastereomer A_1	23.929334	0
Diastereomer A_2	23.663033	0.028
Diastereomer A_3	9.7899	2.215
Diastereomer A_4	7.908566	2.744
Diastereomer A_5	7.779933	2.785
Diastereomer A_6	7.646424	2.828
Diastereomer A_7	4.329456	4.238
Diastereomer A_8	3.649751	4.661
Diastereomer A_9	2.976641	5.167
Diastereomer A_10	1.910525	6.266
Diastereomer A_11	1.873444	6.314
Diastereomer A_12	1.341412	7.142
Diastereomer A_13	1.11643	7.598
Diastereomer A_14	1.10387	7.626
Diastereomer A_15	0.539609	9.4
Diastereomer A_16	0.441671	9.896
Diastereomer B_1	23.708086	0
Diastereomer B_2	23.048167	0.07
Diastereomer B_3	16.429826	0.909
Diastereomer B_4	12.912744	1.506
Diastereomer B_5	7.976771	2.7
Diastereomer B_6	3.860104	4.499
Diastereomer B_7	3.809869	4.532
Diastereomer B_8	0.875772	8.176
Diastereomer B_9	0.798784	8.404
Diastereomer B_10	0.697631	8.74
Diastereomer B_11	0.668061	8.847
Diastereomer B_12	0.64039	8.952
Diastereomer B_13	0.623508	9.018
Diastereomer B_14	0.561137	9.28
Diastereomer B_15	0.555323	9.306
Diastereomer B_16	0.531562	9.414
Diastereomer B_17	0.501356	9.559
Diastereomer B_18	0.469721	9.721
Diastereomer B_19	0.455625	9.796
Diastereomer B_20	0.442937	9.866
Diastereomer B_21	0.432627	9.924

<sup>a</sup>Conformers of possible diastereomers A and B (see Figure 6A in the main text) were elucidated by conformational searches in MMFF94 force field and the searches were achieved in the gas phase with a 50 kJ/mol energy limit.

Table S3. Calculated thermodynamic data and ZPVE (zero-point vibrational energy) of conformers of possible diastereomers A and B of compound **3** at the B3LYP/6-31G(d,p) level in the gas phase.

Conformers	Zero-Point Energy (ZPE)	Thermal Energies (U)	Thermal Enthalpies (H)	Thermal Free Energies (G)
Diastereomer A_1	-1285.106176	-1285.079023	-1285.078079	-1285.165206
Diastereomer A_2	-1285.106163	-1285.079016	-1285.078072	-1285.165155
Diastereomer A_3	-1285.105388	-1285.078283	-1285.077339	-1285.164452
Diastereomer A_4	-1285.104834	-1285.077491	-1285.076546	-1285.164277
Diastereomer A_5	-1285.105388	-1285.078283	-1285.077339	-1285.164452
Diastereomer A_6	-1285.107	-1285.080145	-1285.079201	-1285.165421
Diastereomer A_7	-1285.106466	-1285.07936	-1285.078416	-1285.165383
Diastereomer A_8	-1285.107	-1285.080145	-1285.079201	-1285.165421
Diastereomer A_9	-1285.107353	-1285.080415	-1285.079471	-1285.165956
Diastereomer A_10	-1285.107347	-1285.080407	-1285.079462	-1285.165926
Diastereomer A_11	-1285.10433	-1285.07734	-1285.076396	-1285.163169
Diastereomer A_12	-1285.103804	-1285.076563	-1285.075619	-1285.163183
Diastereomer A_13	-1285.10433	-1285.07734	-1285.076396	-1285.163169
Diastereomer A_14	-1285.104939	-1285.077872	-1285.076927	-1285.163916
Diastereomer A_15	-1285.104924	-1285.077859	-1285.076915	-1285.163919
Diastereomer B_1	-1285.105831	-1285.078842	-1285.077898	-1285.164893
Diastereomer B_2	-1285.105219	-1285.077974	-1285.07703	-1285.164831
Diastereomer B_3	-1285.105831	-1285.078842	-1285.077898	-1285.164893
Diastereomer B_4	-1285.104493	-1285.077241	-1285.076297	-1285.163918
Diastereomer B_5	-1285.1045	-1285.077231	-1285.076286	-1285.16409
Diastereomer B_6	-1285.106275	-1285.07923	-1285.078286	-1285.16546
Diastereomer B_7	-1285.106176	-1285.079135	-1285.078191	-1285.165336
Diastereomer B_8	-1285.103125	-1285.075823	-1285.074878	-1285.163119
Diastereomer B_9	-1285.103772	-1285.076574	-1285.075629	-1285.16326
Diastereomer B_10	-1285.103236	-1285.075784	-1285.07484	-1285.163296
Diastereomer B_11	-1285.103772	-1285.076574	-1285.075629	-1285.16326
Diastereomer B_12	-1285.103772	-1285.076574	-1285.075629	-1285.16326
Diastereomer B_13	-1285.103236	-1285.075784	-1285.07484	-1285.163296
Diastereomer B_14	-1285.103367	-1285.07637	-1285.075426	-1285.163239
Diastereomer B_15	-1285.102829	-1285.075593	-1285.074649	-1285.16296
Diastereomer B_16	-1285.103367	-1285.07637	-1285.075426	-1285.163239
Diastereomer B_17	-1285.104493	-1285.077241	-1285.076297	-1285.163918
Diastereomer B_18	-1285.102202	-1285.074961	-1285.074017	-1285.16215
Diastereomer B_19	-1285.1045	-1285.077231	-1285.076286	-1285.16409
Diastereomer B_20	-1285.101698	-1285.07418	-1285.073236	-1285.162346
Diastereomer B_21	-1285.103749	-1285.076692	-1285.075748	-1285.163708
Diastereomer B_22	-1285.103748	-1285.076691	-1285.075747	-1285.1636

Table S4. Calculated thermodynamic data and ZPVE (zero-point vibrational energy) of conformers of possible diastereomers of compound **4** at the B3LYP/6-31G(d,p) level in the gas phase.

Conformers	Zero-Point Energy (ZPE)	Thermal Energies (U)	Thermal Enthalpies (H)	Thermal Free Energies (G)
Diastereomer A_1	-1285.106353	-1285.079225	-1285.078281	-1285.165231
Diastereomer A_2	-1285.106452	-1285.079319	-1285.078375	-1285.16537
Diastereomer A_3	-1285.105057	-1285.07799	-1285.077045	-1285.163918
Diastereomer A_4	-1285.10446	-1285.077165	-1285.07622	-1285.163737
Diastereomer A_5	-1285.107496	-1285.08056	-1285.079615	-1285.166026
Diastereomer A_6	-1285.107512	-1285.080572	-1285.079628	-1285.166117
Diastereomer A_7	-1285.105057	-1285.07799	-1285.077046	-1285.163918
Diastereomer A_8	-1285.106399	-1285.079523	-1285.078579	-1285.16488
Diastereomer A_9	-1285.105867	-1285.078745	-1285.077801	-1285.164878
Diastereomer A_10	-1285.10473	-1285.07738	-1285.076436	-1285.164091
Diastereomer A_11	-1285.106399	-1285.079523	-1285.078579	-1285.16488
Diastereomer A_12	-1285.105167	-1285.078051	-1285.077107	-1285.164073
Diastereomer A_13	-1285.104895	-1285.077806	-1285.076862	-1285.16401
Diastereomer A_14	-1285.10489	-1285.077809	-1285.076865	-1285.163929
Diastereomer A_15	-1285.103821	-1285.076784	-1285.07584	-1285.162919
Diastereomer A_16	-1285.10331	-1285.076024	-1285.07508	-1285.162944
Diastereomer B_1	-1285.106937	-1285.07994	-1285.078995	-1285.165922
Diastereomer B_2	-1285.106931	-1285.079943	-1285.078999	-1285.165863
Diastereomer B_3	-1285.106256	-1285.079299	-1285.078355	-1285.165266
Diastereomer B_4	-1285.105724	-1285.078541	-1285.077596	-1285.165144
Diastereomer B_5	-1285.106256	-1285.079299	-1285.078355	-1285.165266
Diastereomer B_6	-1285.104365	-1285.077072	-1285.076128	-1285.164302
Diastereomer B_7	-1285.104417	-1285.077129	-1285.076184	-1285.164228
Diastereomer B_8	-1285.104417	-1285.077129	-1285.076184	-1285.164228
Diastereomer B_9	-1285.102898	-1285.075663	-1285.074719	-1285.162703
Diastereomer B_10	-1285.104106	-1285.077031	-1285.076087	-1285.164046
Diastereomer B_11	-1285.10403	-1285.076974	-1285.076029	-1285.163823
Diastereomer B_12	-1285.10229	-1285.074821	-1285.073877	-1285.162503
Diastereomer B_13	-1285.103485	-1285.076467	-1285.075523	-1285.163256
Diastereomer B_14	-1285.10333	-1285.07608	-1285.075136	-1285.162904
Diastereomer B_15	-1285.103485	-1285.076467	-1285.075523	-1285.163256
Diastereomer B_16	-1285.103005	-1285.075755	-1285.074811	-1285.163259
Diastereomer B_17	-1285.103005	-1285.075755	-1285.074811	-1285.16326
Diastereomer B_18	-1285.102766	-1285.075294	-1285.07435	-1285.162691
Diastereomer B_19	-1285.102898	-1285.075663	-1285.074719	-1285.162703
Diastereomer B_20	-1285.101769	-1285.074475	-1285.073531	-1285.162196
Diastereomer B_21	-1285.102898	-1285.075663	-1285.074719	-1285.162703

Table S5. The Boltzmann populations of the conformers of possible diastereomers A and B of compound **3** at the B3LYP/6-31G(d,p) level in the gas phase

Conformers	Zero-Point Energy (ZPE)	Thermal Energies (U)	Thermal Enthalpies (H)	Thermal Free Energies (G)
Diastereomer A_1	5.8%	4.8%	4.8%	9.1%
Diastereomer A_2	5.7%	4.7%	4.7%	10.5%
Diastereomer A_3	2.5%	2.2%	2.2%	2.2%
Diastereomer A_4	1.4%	0.9%	0.9%	1.8%
Diastereomer A_5	2.5%	2.2%	2.2%	21.2%
Diastereomer A_6	14.1%	15.8%	15.8%	23.4%
Diastereomer A_7	7.9%	6.8%	6.8%	2.2%
Diastereomer A_8	14.1%	15.8%	15.8%	6.2%
Diastereomer A_9	20.5%	21.1%	21.1%	6.2%
Diastereomer A_10	20.4%	21.0%	20.9%	2.7%
Diastereomer A_11	0.8%	0.8%	0.8%	6.2%
Diastereomer A_12	0.5%	0.3%	0.3%	2.6%
Diastereomer A_13	0.8%	0.8%	0.8%	2.5%
Diastereomer A_14	1.5%	1.4%	1.4%	2.3%
Diastereomer A_15	1.5%	1.4%	1.4%	0.8%
Diastereomer B_1	13.4%	14.8%	14.8%	9.9%
Diastereomer B_2	6.9%	5.8%	5.8%	9.3%
Diastereomer B_3	13.4%	14.8%	14.8%	9.9%
Diastereomer B_4	3.2%	2.7%	2.7%	3.5%
Diastereomer B_5	3.2%	2.6%	2.6%	4.2%
Diastereomer B_6	21.5%	22.4%	22.4%	18.2%
Diastereomer B_7	19.4%	20.2%	20.2%	15.9%
Diastereomer B_8	0.7%	0.6%	0.6%	1.5%
Diastereomer B_9	1.5%	1.3%	1.3%	1.7%
Diastereomer B_10	0.8%	0.6%	0.6%	1.8%
Diastereomer B_11	1.5%	1.3%	1.3%	1.7%
Diastereomer B_12	1.5%	1.3%	1.3%	1.7%
Diastereomer B_13	0.8%	0.6%	0.6%	1.8%
Diastereomer B_14	1.0%	1.0%	1.0%	1.7%
Diastereomer B_15	0.5%	0.5%	0.5%	1.3%
Diastereomer B_16	1.0%	1.0%	1.0%	1.7%
Diastereomer B_17	3.2%	2.7%	2.7%	3.5%
Diastereomer B_18	0.3%	0.2%	0.2%	0.5%
Diastereomer B_19	3.2%	2.6%	2.6%	4.2%
Diastereomer B_20	0.2%	0.1%	0.1%	0.6%
Diastereomer B_21	1.4%	1.5%	1.5%	2.8%
Diastereomer B_22	1.4%	1.5%	1.5%	2.5%

Table S6. The Boltzmann populations of the conformers of possible diastereomers A and B of compound **4** at the B3LYP/6-31G(d,p) level in the gas phase

Conformers	Zero-Point Energy (ZPE)	Thermal Energies (U)	Thermal Enthalpies (H)	Thermal Free Energies (G)
Diastereomer A_1	7.5%	6.5%	6.5%	9.0%
Diastereomer A_2	8.4%	7.1%	7.2%	10.4%
Diastereomer A_3	1.9%	1.7%	1.7%	2.2%
Diastereomer A_4	1.0%	0.7%	0.7%	1.8%
Diastereomer A_5	25.6%	27.0%	27.0%	21.1%
Diastereomer A_6	26.0%	27.3%	27.3%	23.2%
Diastereomer A_7	1.9%	1.7%	1.7%	2.2%
Diastereomer A_8	7.9%	8.9%	8.9%	6.2%
Diastereomer A_9	4.5%	3.9%	3.9%	6.2%
Diastereomer A_10	1.3%	0.9%	0.9%	2.7%
Diastereomer A_11	7.9%	8.9%	8.9%	6.2%
Diastereomer A_12	2.1%	1.8%	1.8%	2.6%
Diastereomer A_13	1.6%	1.4%	1.4%	2.4%
Diastereomer A_14	1.6%	1.4%	1.4%	2.2%
Diastereomer A_15	0.5%	0.5%	0.5%	0.8%
Diastereomer A_16	0.3%	0.2%	0.2%	0.8%
Diastereomer B_1	27.1%	27.8%	27.8%	22.0%
Diastereomer B_2	27.0%	27.9%	27.9%	20.6%
Diastereomer B_3	13.1%	14.0%	14.0%	10.9%
Diastereomer B_4	7.4%	6.2%	6.2%	9.6%
Diastereomer B_5	13.1%	14.0%	14.0%	10.9%
Diastereomer B_6	1.7%	1.3%	1.3%	3.9%
Diastereomer B_7	1.8%	1.4%	1.4%	3.6%
Diastereomer B_8	1.8%	1.4%	1.4%	3.6%
Diastereomer B_9	0.4%	0.3%	0.3%	0.7%
Diastereomer B_10	1.3%	1.2%	1.2%	3.0%
Diastereomer B_11	1.2%	1.2%	1.2%	2.3%
Diastereomer B_12	0.2%	0.1%	0.1%	0.6%
Diastereomer B_13	0.7%	0.7%	0.7%	1.3%
Diastereomer B_14	0.6%	0.4%	0.4%	0.9%
Diastereomer B_15	0.7%	0.7%	0.7%	1.3%
Diastereomer B_16	0.4%	0.3%	0.3%	1.3%
Diastereomer B_17	0.4%	0.3%	0.3%	1.3%
Diastereomer B_18	0.3%	0.2%	0.2%	0.7%
Diastereomer B_19	0.4%	0.3%	0.3%	0.7%
Diastereomer B_20	0.1%	0.1%	0.1%	0.4%
Diastereomer B_21	0.4%	0.3%	0.3%	0.7%

Table S7. Experimental (Exp.) and calculated (Cal.) NMR chemical shift values of compounds **3** and **4** with diastereomers A and B<sup>a</sup>

Compound <b>3</b>				Compound <b>4</b>			
Position	Exp.	Cal. A	Cal. B	Position	Exp.	Cal.A	Cal.B
C1	157.55	148.81	149.06	C1	157.57	149.53	148.29
C2	106.6	103.69	104.52	C2	110.83	107.12	107.87
C3	142.16	137.08	136.78	C3	133.86	135.89	134.16
C4	106.6	104.51	103.64	C4	110.83	106.66	108.71
C5	157.55	148.93	148.78	C5	157.57	148.41	148.85
C6	120.08	111.45	111.53	C6	121.45	113.04	113.04
C7	74.71	76.22	76.25	C7	73.82	75.71	80.37
C8	75.47	76.05	78.78	C8	74.35	76.47	76.8
C9	138.75	135.42	134.55	C9	143.39	136.06	135.67
C10	131.22	125.19	125.41	C10	127.5	122.45	121.5
C11	127.52	122.27	122.05	C11	128.2	122.37	122.01
C12	127.33	121.55	121.68	C12	127.4	120.8	121.14
C13	127.52	122.34	122.2	C13	128.2	121.97	122.6
C14	131.22	125	125.9	C14	127.5	121.68	122.62
C15	25.25	28.48	28.52	C15	25.33	28.55	28.54
C16	21.63	21.32	21.57	C16	21.59	21.18	21.28
C17	21.63	21.52	21.35	C17	21.59	21.28	21.24
C1'	178.67	169.22	169.23	C1'	175.93	169.55	170.24
C2'	65.3	63.62	63.49	C2'	65.59	63.63	64.45
C3'	30.87	29.49	29.98	C3'	29.98	29.48	29.72
C4'	24.15	24.97	26.16	C4'	23.9	25.05	27.5
C5'	52.71	49.07	51.44	C5'	52.44	49.01	52.54
H2	6.93	5.99	5.92	H2	7.12	5.85	6.2
H4	6.93	5.97	6.08	H4	7.12	6.2	5.77
H7	5.62	5.26	5.46	H7	4.52	4.01	3.2
H8	4.26	4.13	3.71	H8	5.77	5.37	5.5
H10	7.59	7.22	7.65	H10	7.55	7.38	7.24
H11	7.21	7.15	7.23	H11	7.2	7.17	7.24
H12	7.16	7.18	7.16	H12	7.11	7.1	7.12
H13	7.21	7.22	7.09	H13	7.2	7.22	7.18
H14	7.59	7.51	7	H14	7.55	7.28	7.4
H15	4.23	3.15	3.14	H15	4.25	3.3	3.24
H16	1.74	0.97	1.01	H16	1.75	0.96	0.97
H16	1.74	1.11	0.9	H16	1.75	1.16	1.35
H16	1.74	1.63	1.7	H16	1.75	1.57	1.32
H17	1.73	0.96	0.99	H17	1.74	0.97	0.96
H17	1.73	1.53	1.76	H17	1.74	1.61	1.81
H17	1.73	1.1	0.97	H17	1.74	1.09	0.92
H2'	3.92	3.61	3.66	H2'	4.29	3.7	3.44
H3'	2.2	2.18	2.05	H3'	2.23	2.17	1.93
H3'	2.06	1.97	1.98	H3'	2.11	2.01	1.87
H4'	1.5	1.91	1.79	H4'	1.55	1.91	1.79
H4'	1.72	1.95	2.06	H4'	1.74	1.95	2.15
H5'	2.59	2.91	2.57	H5'	3.01	2.92	2.47
H5'	3.19	3.3	3.13	H5'	3.52	3.29	3.43



Table S8. Minimum inhibitory concentrations (MIC) of the stilbene metabolites **1-4**.

Stilbene metabolites	Minimum Inhibitory Concentration (MIC) (µg/ml)		
	<i>Bacillus subtilis</i> NCIB3610	<i>Escherichia coli</i> Nissle1917	<i>Saccharomyces cerevisiae</i>
Prolbene A ( <b>3</b> )	>200	>200	>200
Prolbene B ( <b>4</b> )	>200	>200	>200
<i>trans</i> -Stilbene ( <b>1</b> )	3.125	12.5	12.5
Stilbene epoxide ( <b>2</b> )	12.5	25	50



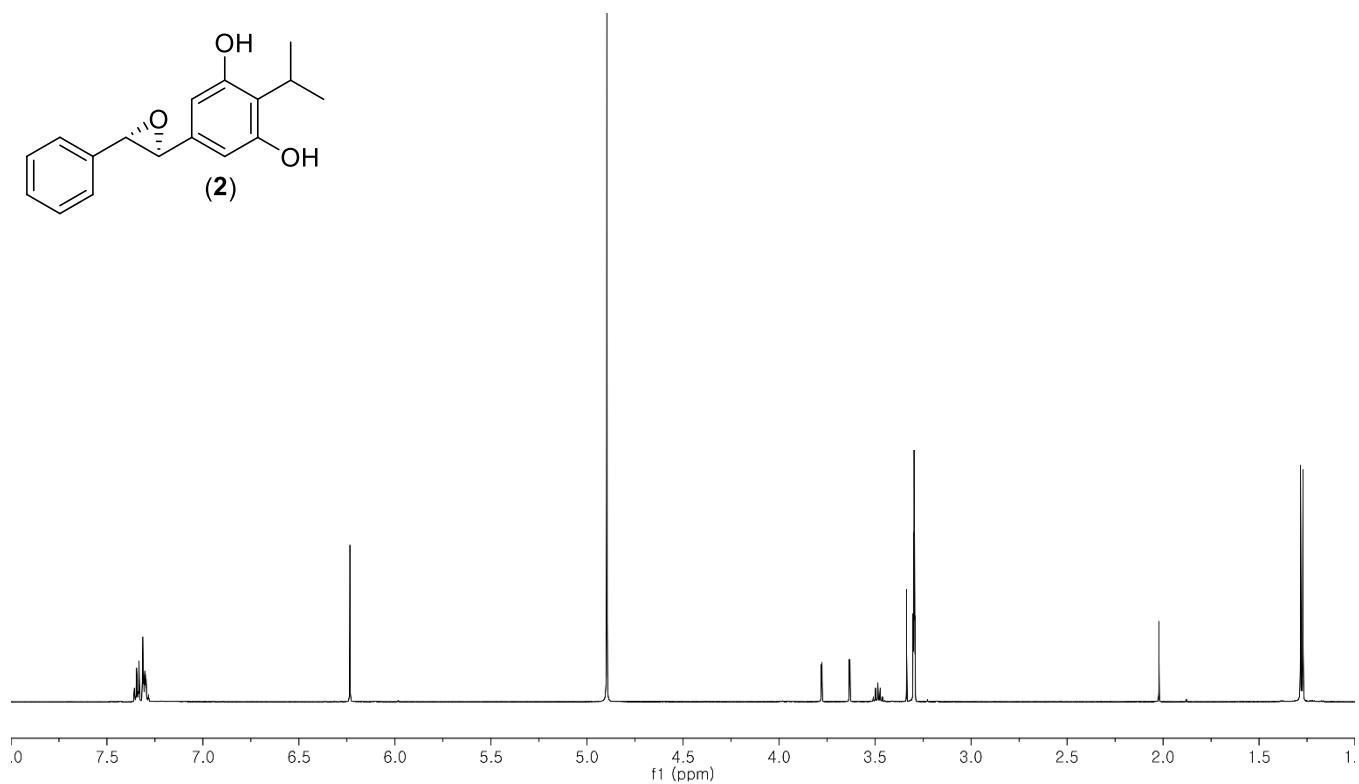


Figure S2. <sup>1</sup>H NMR spectrum of 2-isopropyl-5-(3-phenyl-oxiranyl)-benzene-1,3-diol (**2**)

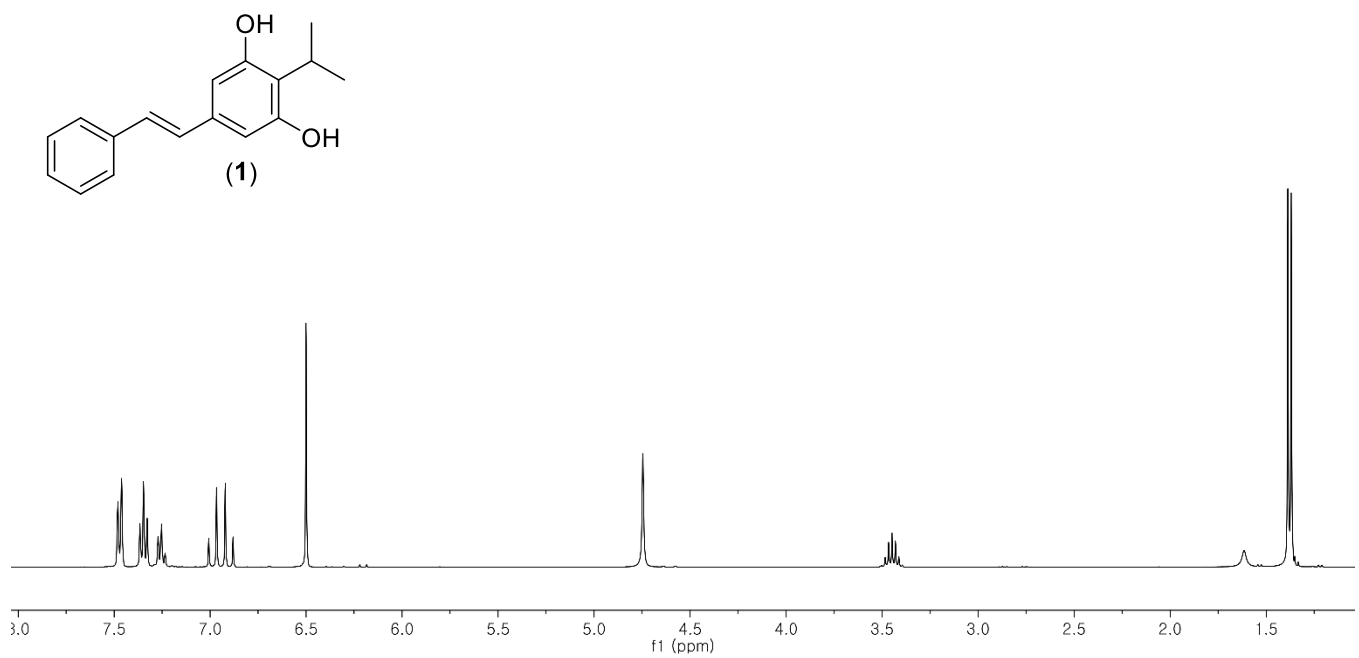


Figure S3. <sup>1</sup>H NMR spectrum of 3,5-dihydroxy-4-isopropyl-*trans*-stilbene (**1**)

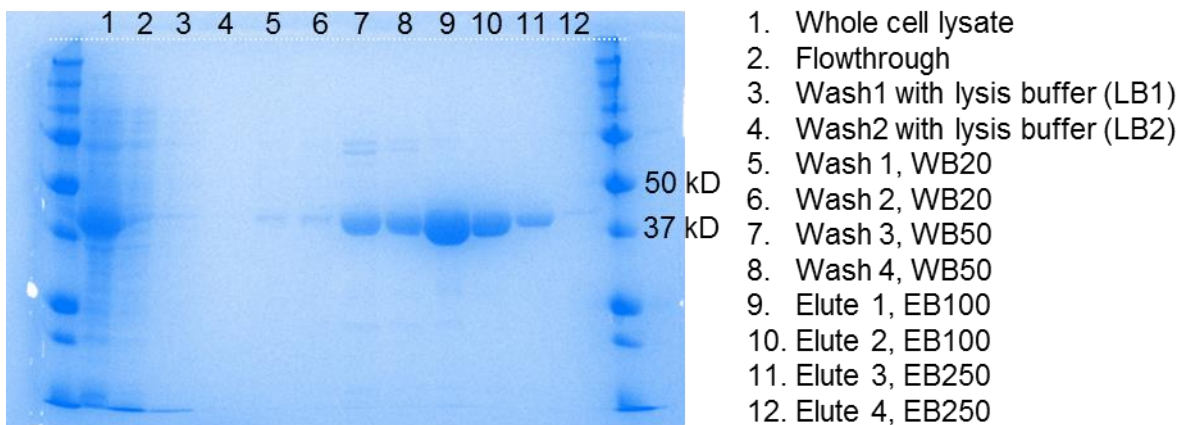


Figure S4. SDS-PAGE gel of fractions from the purification of 6xHis-Plu2236

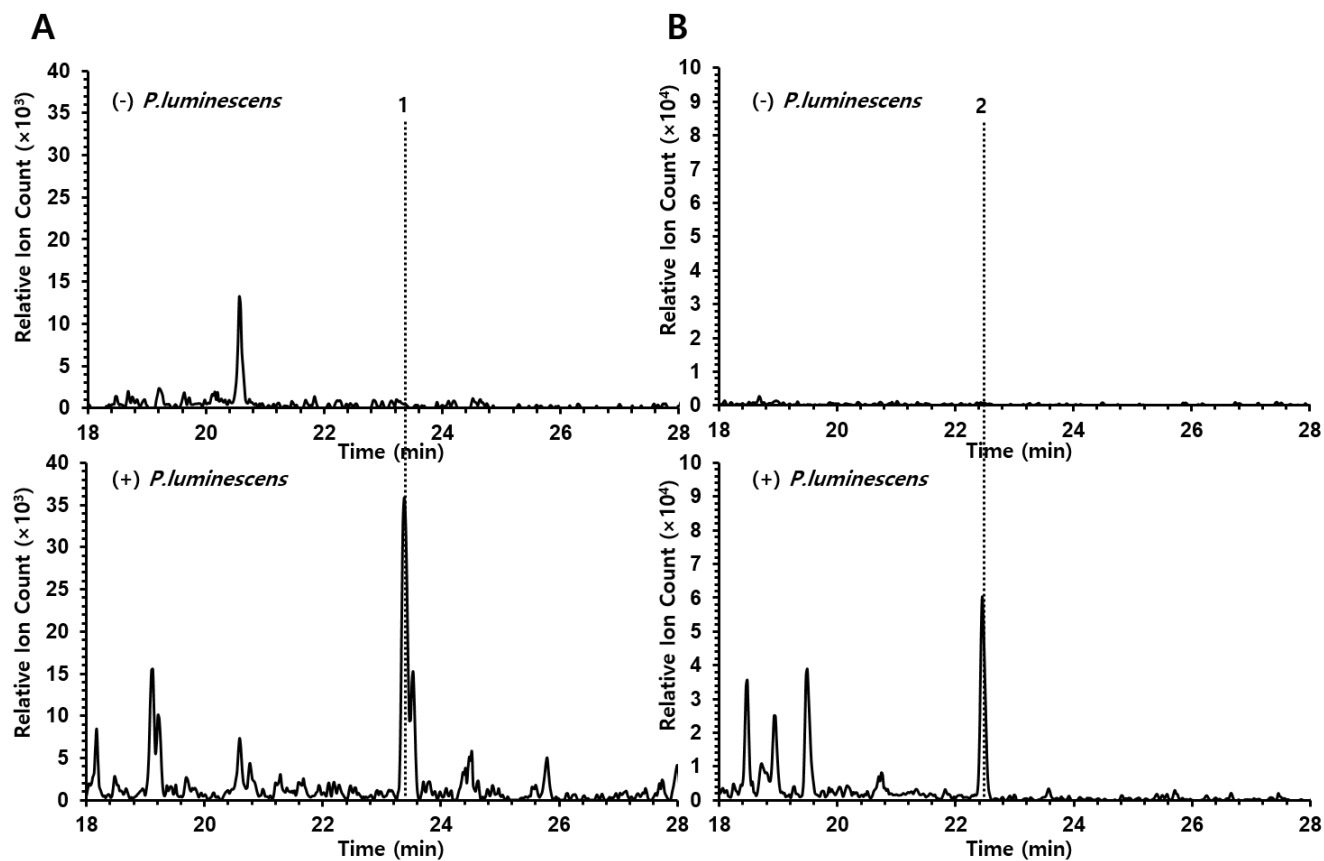


Figure S5. Extracted ion chromatograms for the production of stilbene **1** (A) and stilbene epoxide **2** (B) in *G. mellonella* larvae with (+) and without (-) *P. luminescens* TT01

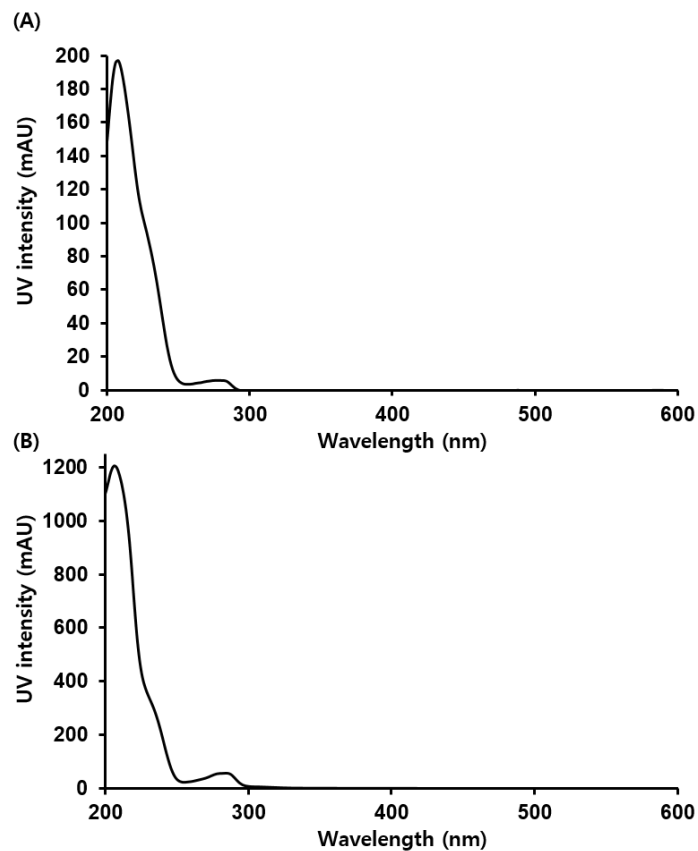


Figure S6. UV spectra of compounds **3** (A) and **4** (B)

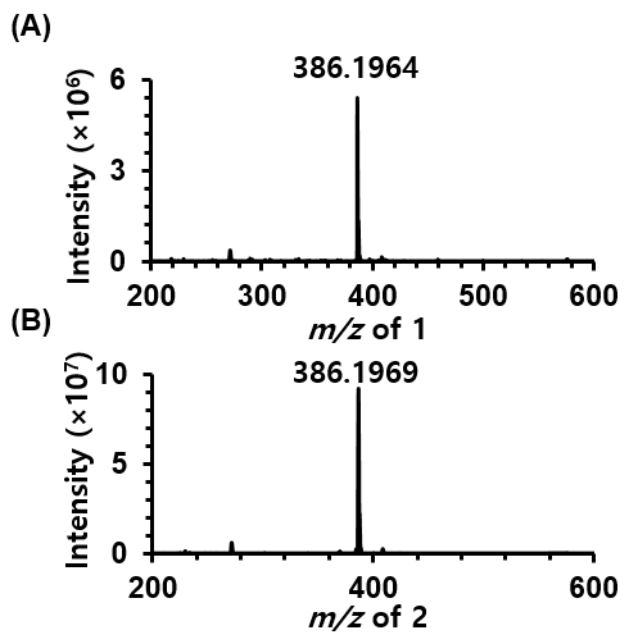


Figure S7. HRESIQTOFMS spectra of compounds **3** (A) and **4** (B)

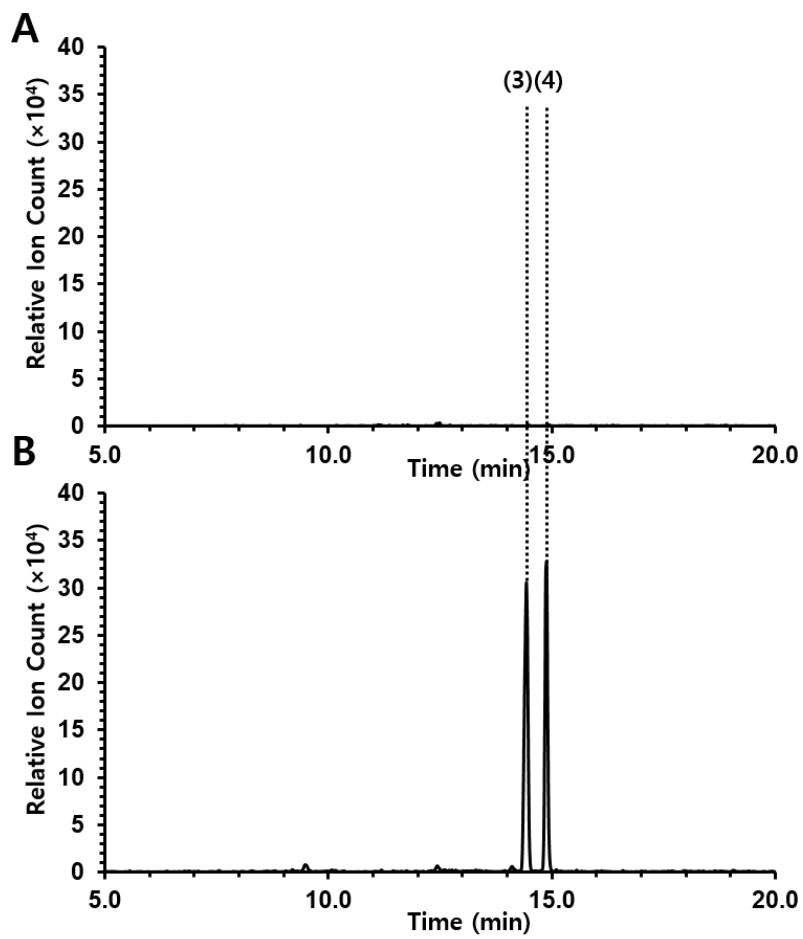


Figure S8. Extracted ion chromatograms for the detection of compounds **3** (A) and **4** (B) in hemolymph-mimetic medium

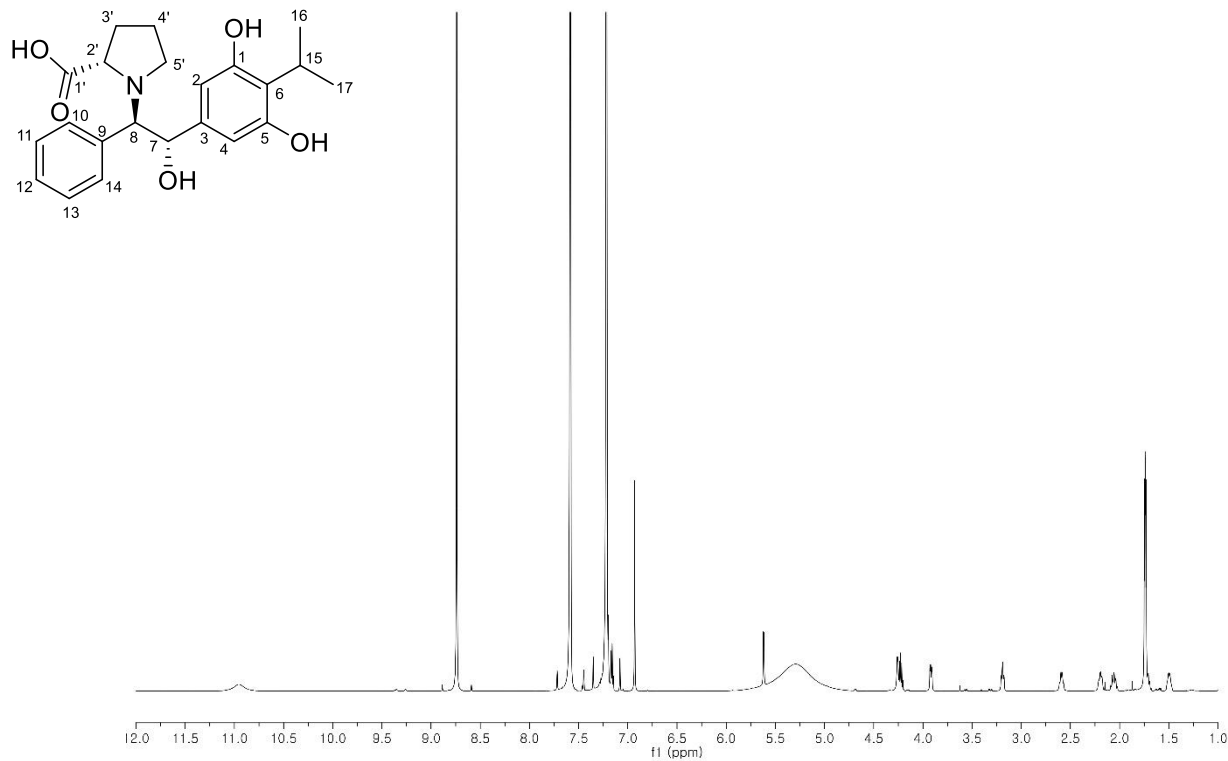


Figure S9.  $^1\text{H}$  NMR spectrum of compound **3**

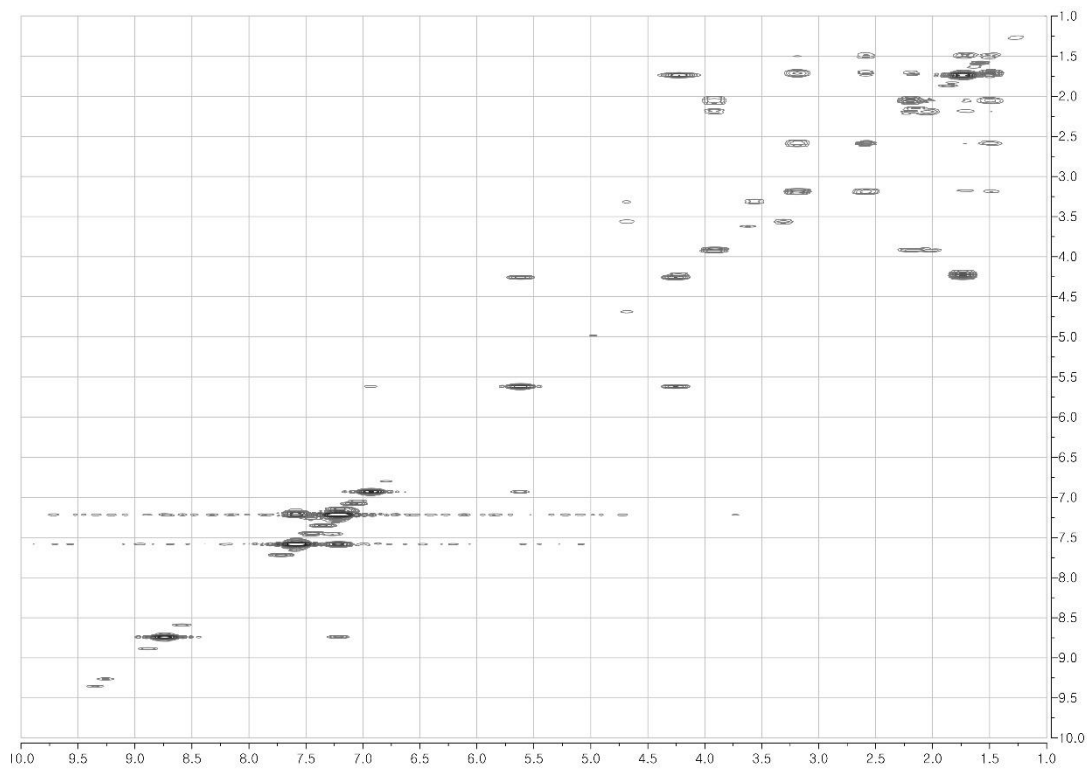


Figure S10. COSY NMR spectrum of compound **3**  
S16



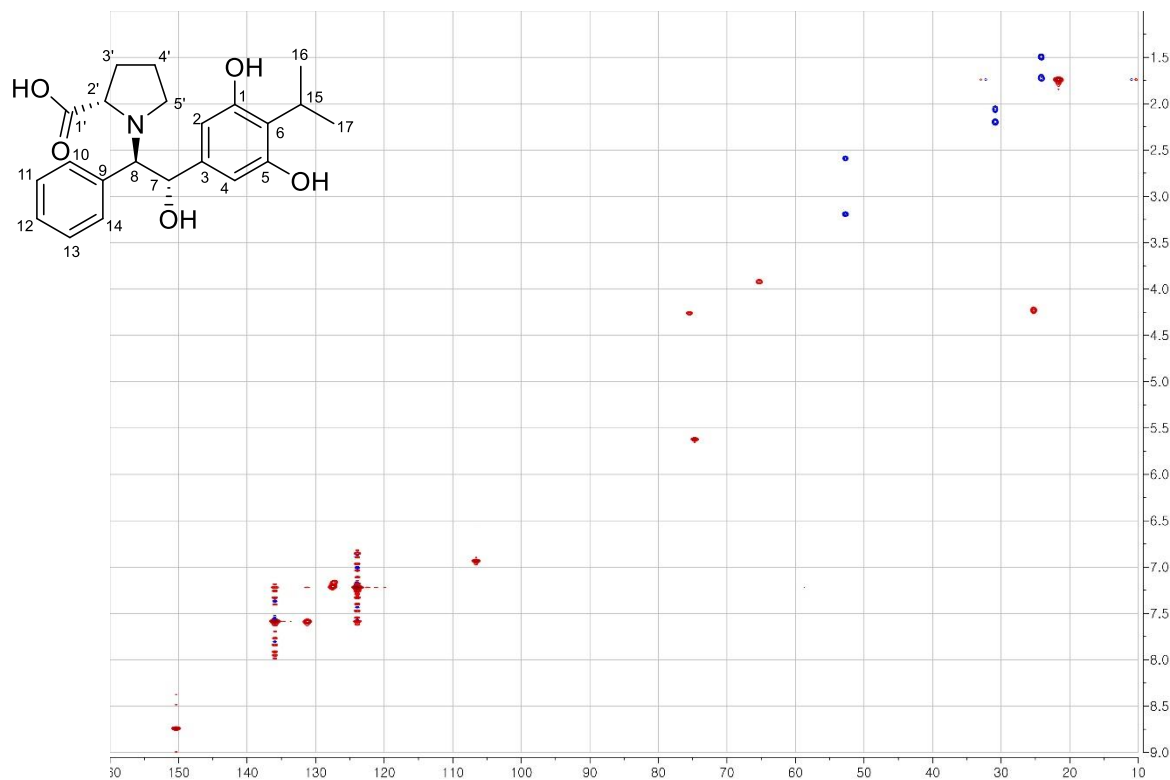


Figure S11. HSQC NMR spectrum of compound **3**

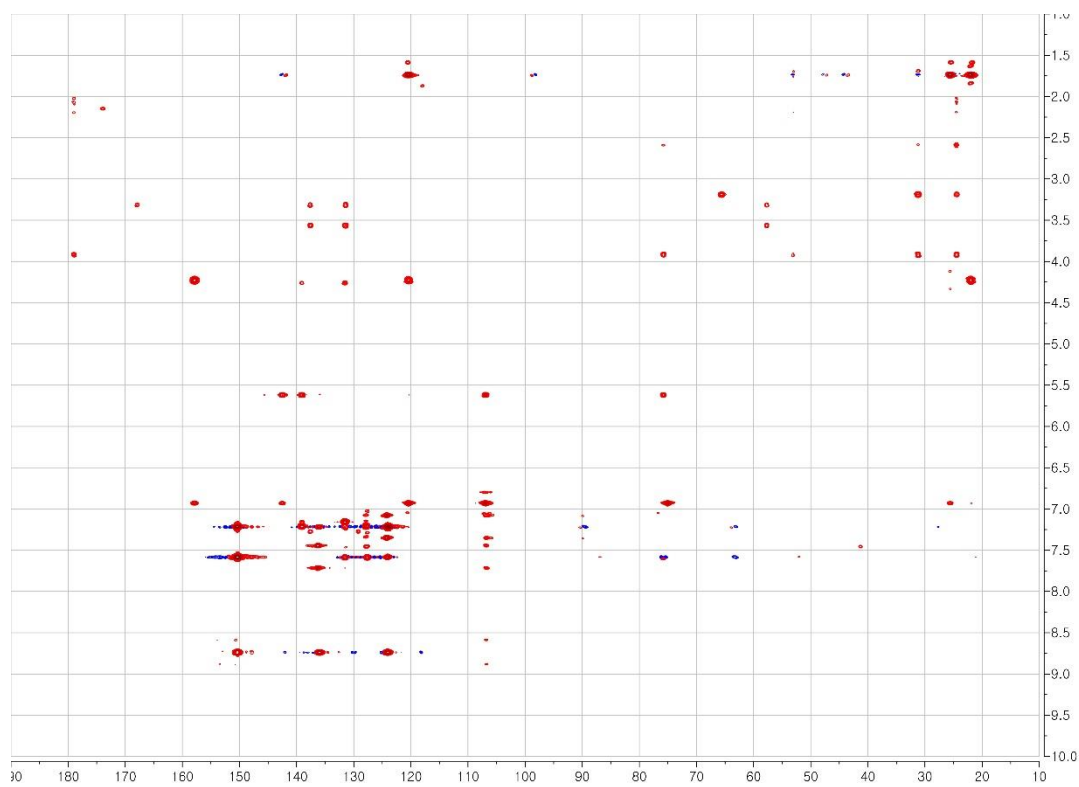


Figure S12. HMBC NMR spectrum of compound **3**

S17

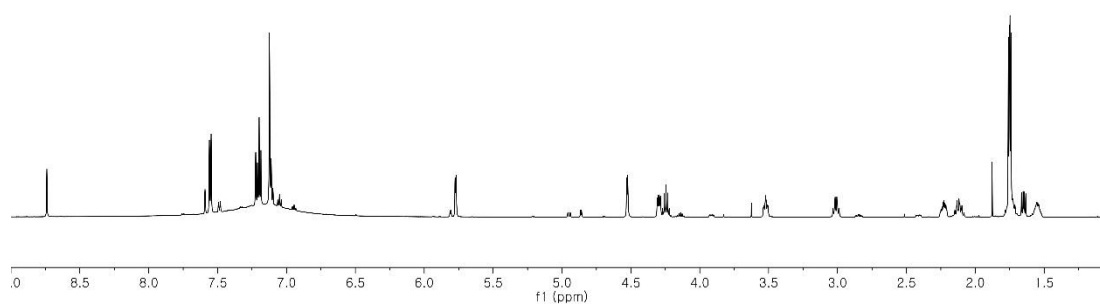
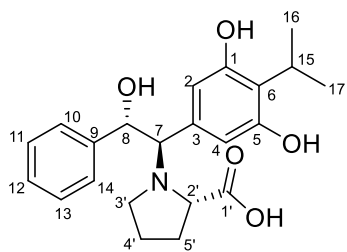


Figure S13. <sup>1</sup>H NMR spectrum of compound **4**

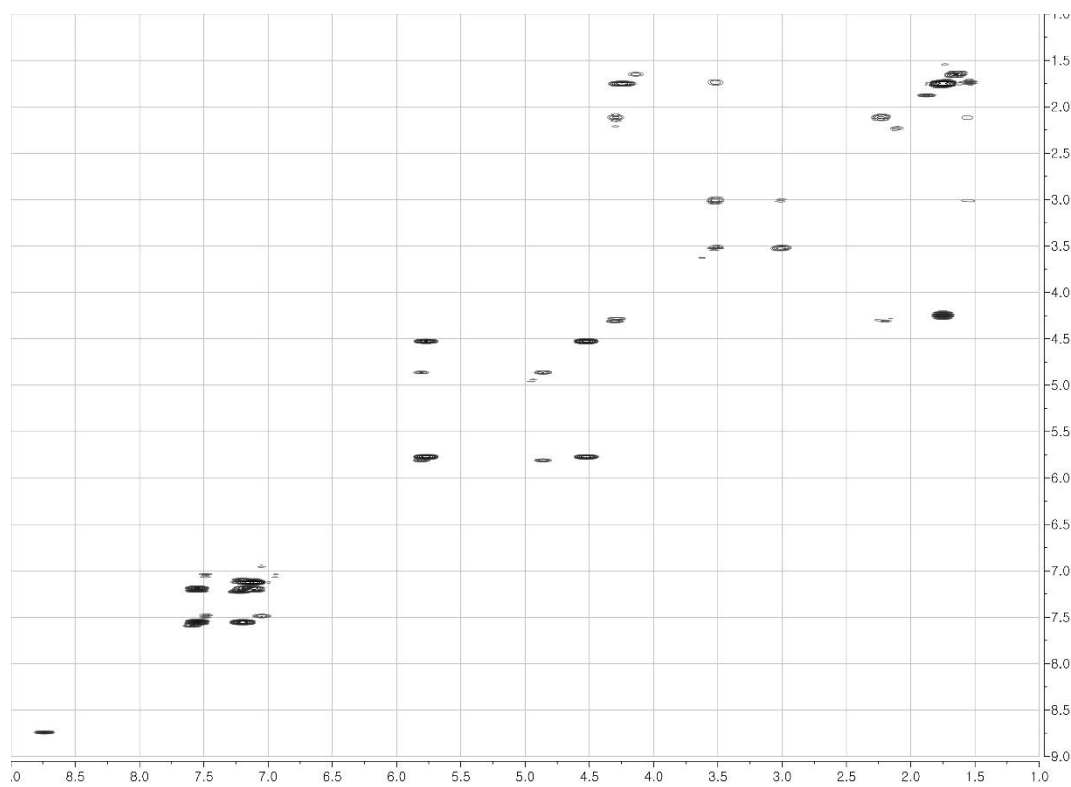


Figure S14. COSY NMR spectrum of compound **4**  
S18

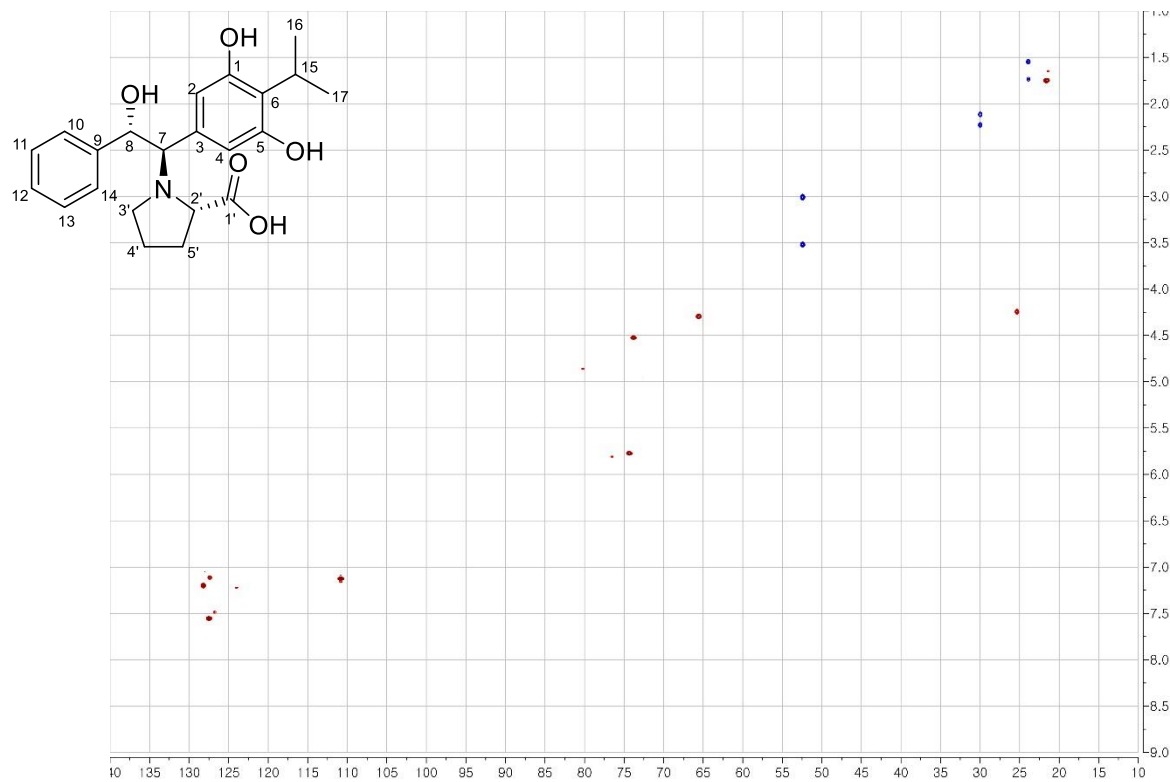


Figure S15. HSQC NMR spectrum of compound 4

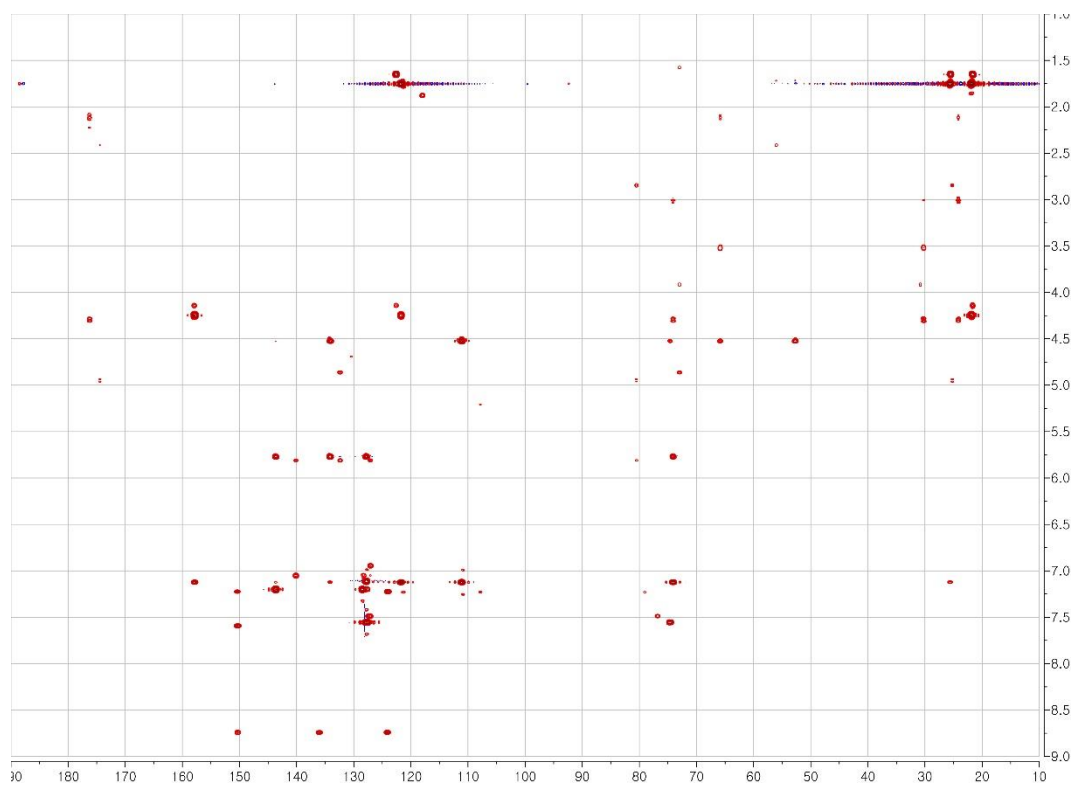


Figure S16. HMBC NMR spectrum of compound 4  
S19

Please select version of database to use:

DP4-original  
**DP4-database2**

Select probability distribution:

t distribution (recommended)  
 normal distribution

13C Calc:

C1,C2,C3,C4,C5,C6,C8,C11,C13,C14,C22,C23,C2  
 148.81,111.45,148.93,104.51,137.08,103.69,28.48  
 149.06,111.53,148.78,103.64,136.78,104.52,28.52

1H Calc:

H10,H12,H15,H16,H17,H18,H19,H20,H21,H29,H3  
 5.97,5.99,3.15,0.97,1.11,1.63,0.96,1.53,1.10,7.18,7  
 6.08,5.92,3.14,1.01,0.90,1.70,0.99,1.76,0.97,7.16,7

13C Expt:

157.55(C1),120.08(C2),157.55(C3),106.60(C4),14

1H Expt:

6.93(H10),6.93(H12),4.23(H15),1.74(H16),1.74(H1

Read Data Show Assignments Calculate Clear

This calculation will use the DP4-database2 version of the database and the t distribution.  
 (To change these options select the desired database and distribution from the menus at the top of the applet and then click Calculate).

Results of DP4 using both carbon and proton data:  
 Isomer 1: 95.1%  
 Isomer 2: 4.9%

Results of DP4 using the carbon data only:  
 Isomer 1: 47.4%  
 Isomer 2: 52.6%

Results of DP4 using the proton data only:  
 Isomer 1: 95.5%  
 Isomer 2: 4.5%

(c) Jonathan M Goodman and Steven G Smith

Figure S17. DP4 analysis of compound **3** with diastereomers A and B corresponding to isomers 1 and 2 in this figure

## Assignment of stereochemistry and structure using NMR and DP4

Please select version of database to use:

DP4-original  
**DP4-database2**

Select probability distribution:

t distribution (recommended)  
 normal distribution

**13C Calc:**

C1,C2,C3,C4,C5,C6,C8,C11,C13,C14,C22,C23,C2	H10,H12,H15,H16,H17,H18,H19,H20,H21,H29,H3
149.53,113.04,148.41,106.66,135.89,107.12,28.55	6.20,5.85,3.30,0.96,1.16,1.57,0.97,1.61,1.09,7.10,7
148.29,113.04,148.85,108.71,134.16,107.87,28.54	5.77,6.20,3.24,0.97,1.35,1.32,0.96,1.81,0.92,7.12,7

**1H Calc:**

**13C Expt:** 157.57(C1),121.45(C2),157.57(C3),110.83(C4),13:

**1H Expt:** 7.12(H10),7.12(H12),4.25(H15),1.75(H16),1.75(H1

Read Data Show Assignments Calculate Clear

This calculation will use the DP4-database2 version of the database and the t distribution. (To change these options select the desired database and distribution from the menus at the top of the applet and then click Calculate).

Results of DP4 using both carbon and proton data:  
 Isomer 1: 100.0%  
 Isomer 2: 0.0%

Results of DP4 using the carbon data only:  
 Isomer 1: 99.3%  
 Isomer 2: 0.7%

Results of DP4 using the proton data only:  
 Isomer 1: 100.0%  
 Isomer 2: 0.0%

Figure S18. DP4 analysis of compound **4** with diastereomers A and B corresponding to isomers 1 and 2 in this figure

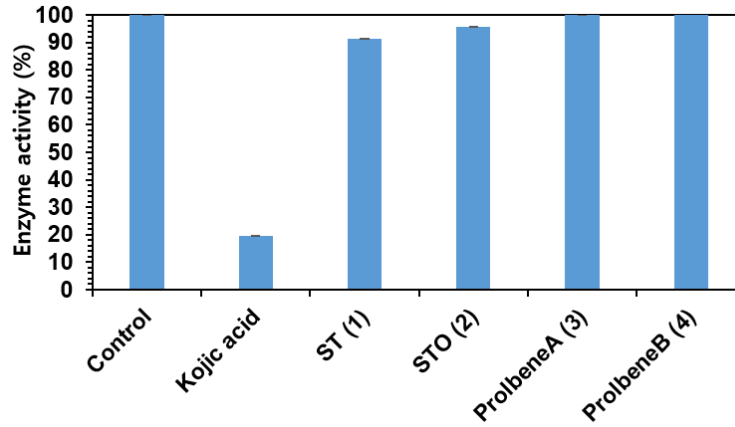
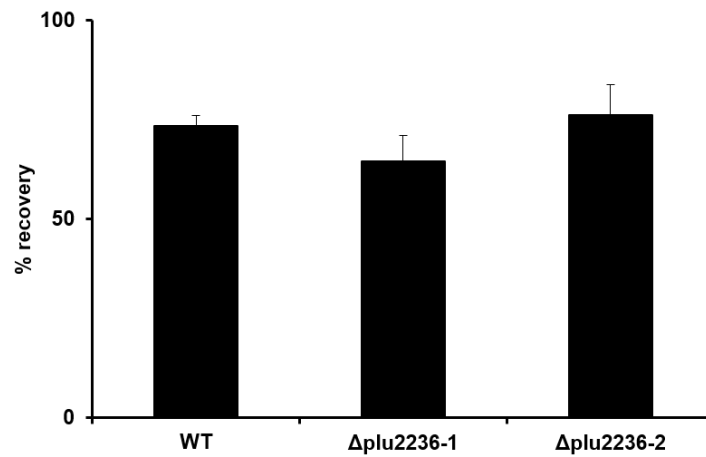


Figure S19. Mushroom tyrosinase inhibitory assay results of compounds **1-4**



Strain	% Recovery	n	SEM
WT	73.3	5	2.69
$\Delta plu2236-1$	64.5	5	6.32
$\Delta plu2236-2$	76.0	5	7.73

Figure S20. IJs recovery (in %) on *P. luminescens* WT and  $\Delta plu2236$ .  $\Delta plu2236-1$  and -2 indicate two independent isolates from mutagenesis

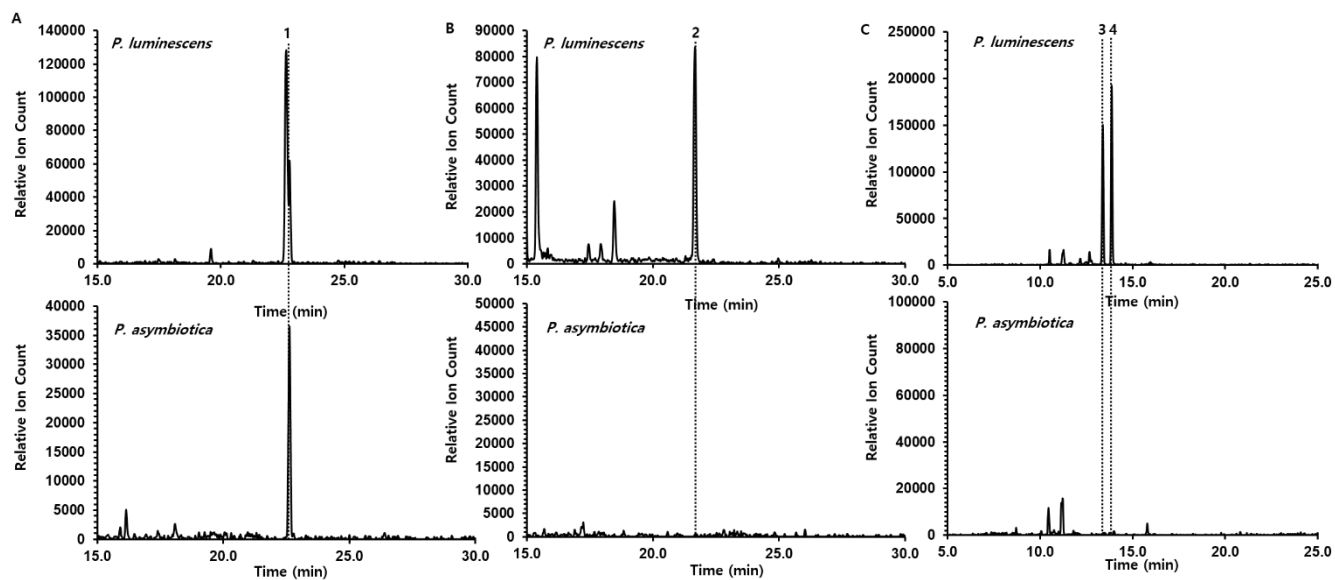


Figure S21. LC/MS comparisons for the production of stilbene **1**, stilbene epoxide **2**, and prolbene **3** and **4** from ethyl acetate extracts of *P. luminescens* (top) and *P. asymbiotica* (bottom) culture broth

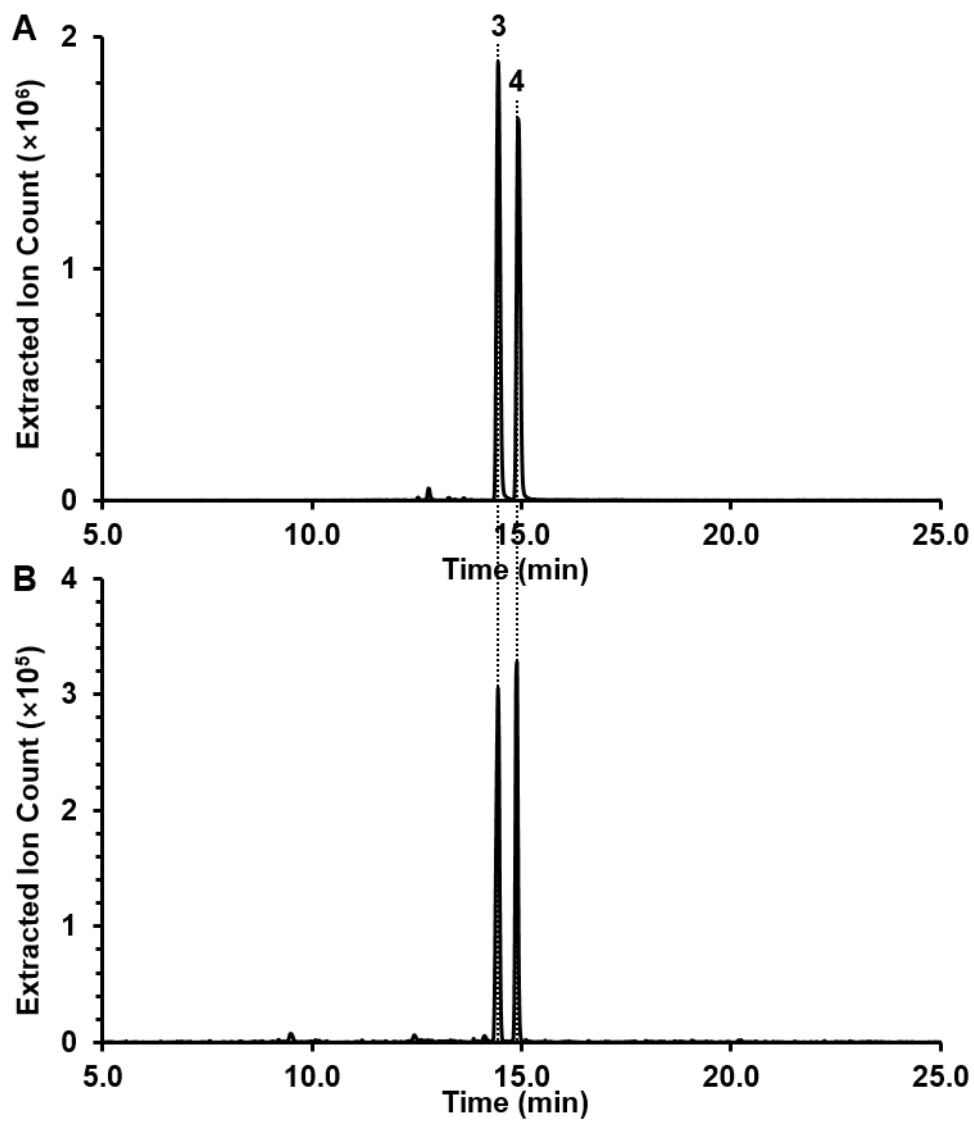


Figure S22. The production of prolbenes **3** and **4** from cell-free medium (B) supplemented with L-proline and stilbene epoxide **2**

#### Supplemental Reference

1. Robert, X., and Gouet, P. (2014) Deciphering key features in protein structures with the new ENDscript server. *Nucleic Acids Res.* **42(W1)**, W320-W324