Supplementary information

Monapinone coupling enzyme produces non-natural heterodimers

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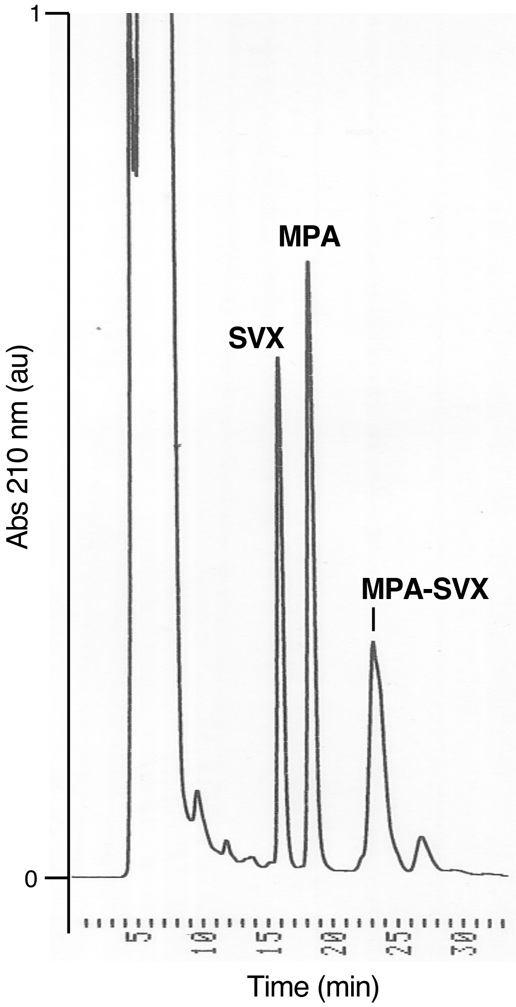
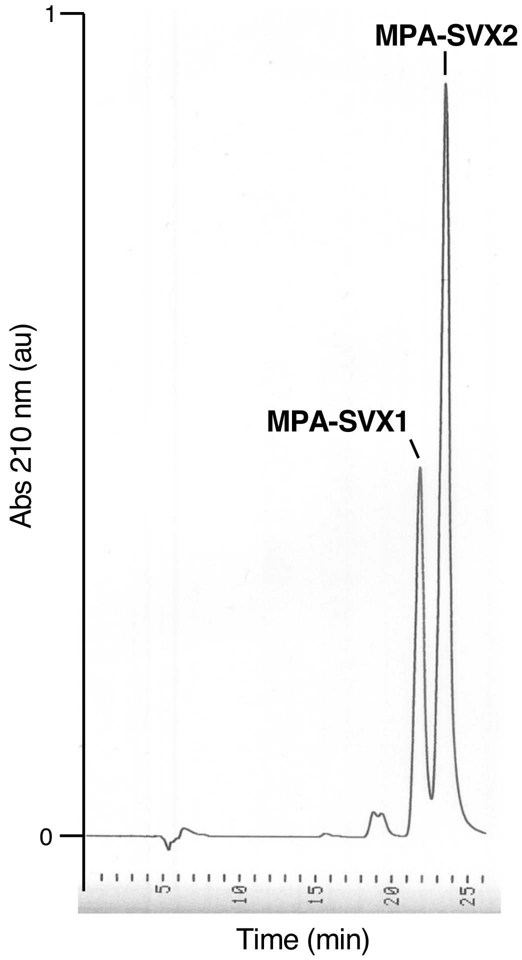


Supplementary Figure S1. Isolation of atropmixture of MPA-SVX by preparative HPLC (column, PEGASIL ODS SP100, i.d. 20 x 250 mm); mobile phase, 75% aqCH_3CN-0.05% TFA isocratic; detection, UV at 210 nm; flow rate, 8.0 ml min^{-1}).

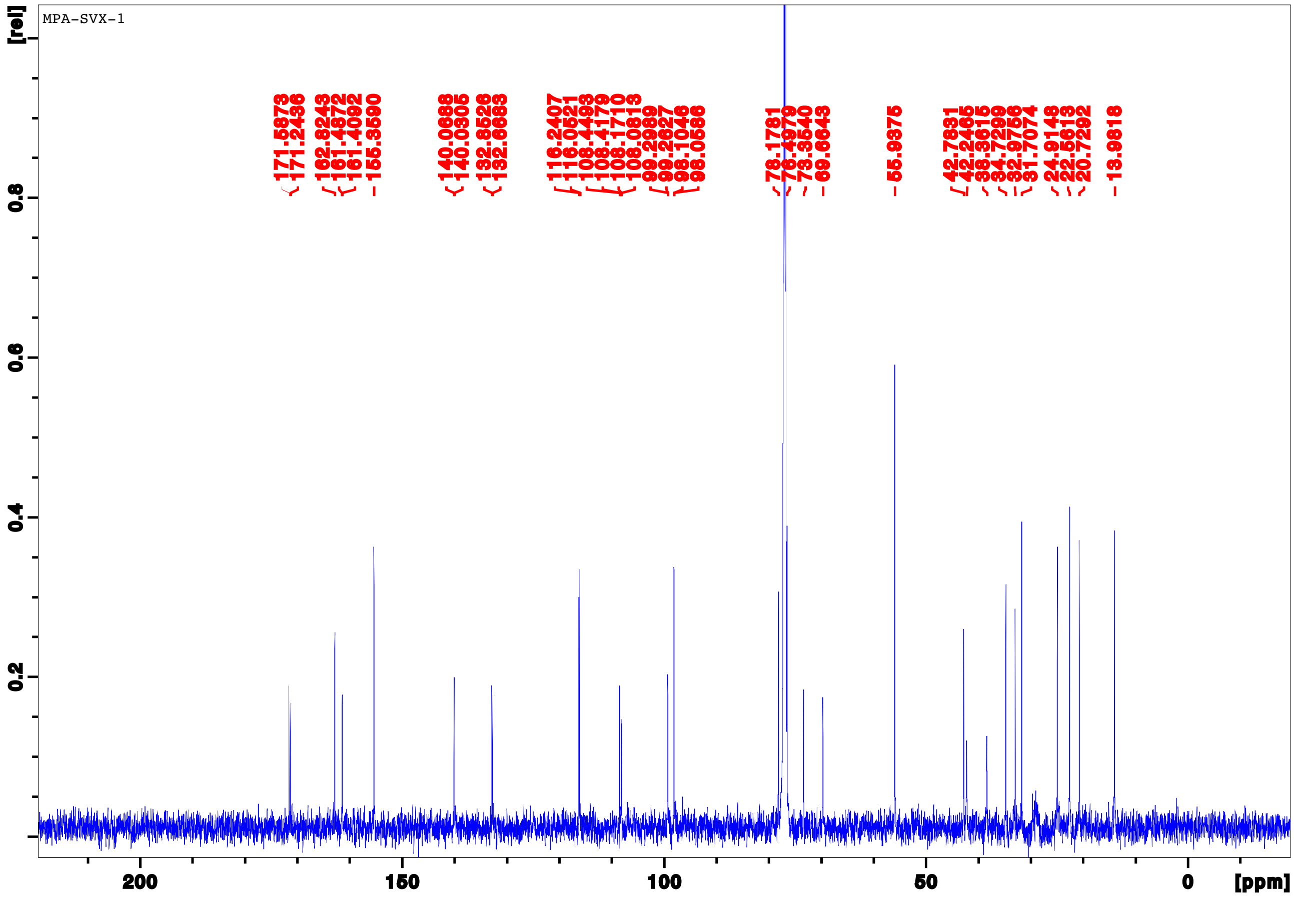


Supplementary Figure S2. Isolation of MPA-SVX1 and MPA-SVX2 by preparative HPLC (column, Develosil C30 column, i.d. 20 x 250 mm); mobile phase, 80% aqCH_3CN-0.05% TFA isocratic; detection, UV at 210 nm; flow rate, 8.0 ml min^{-1}).

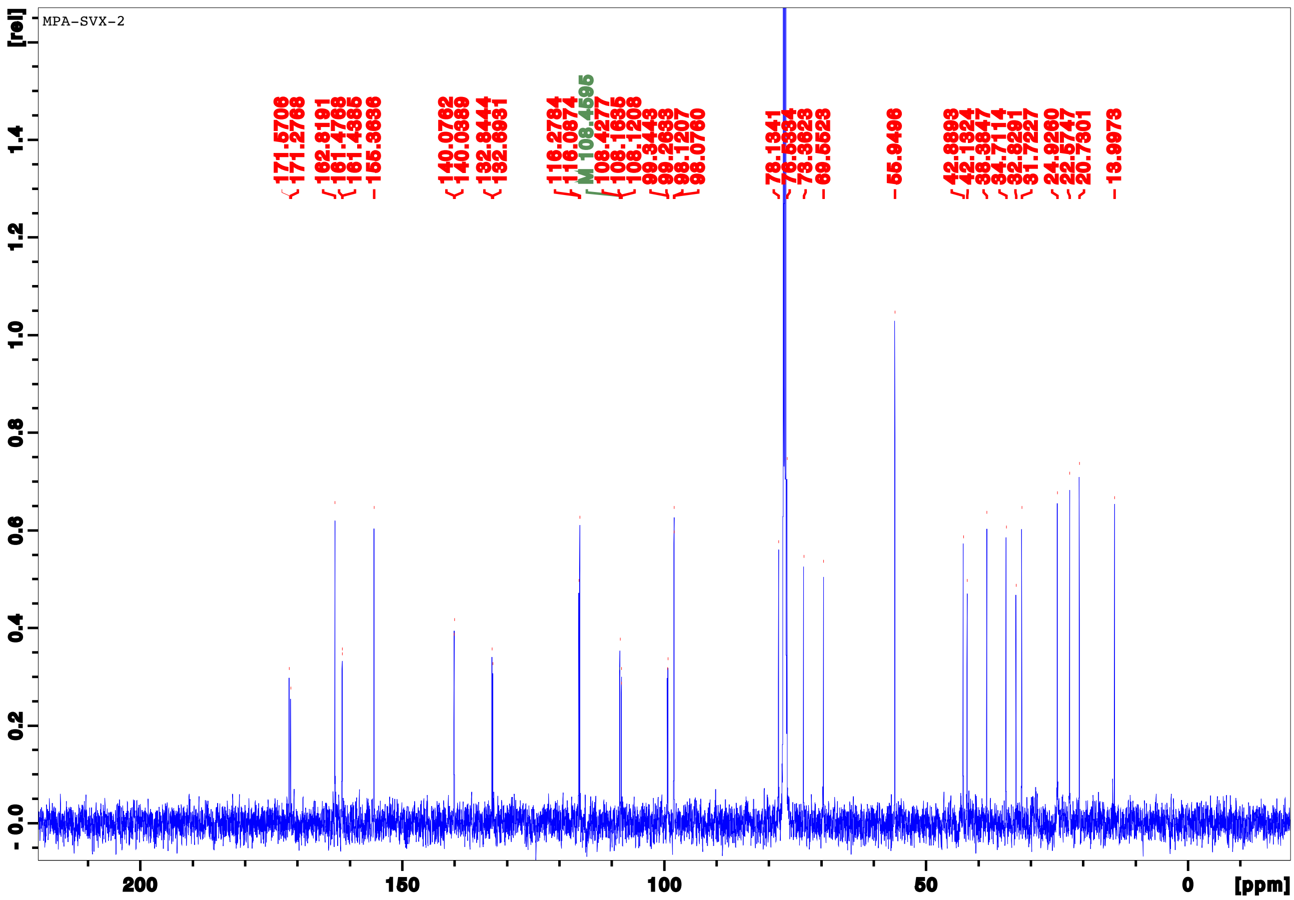
Supplementary Table S1. NMR chemical shifts of MPA-SVX-1 (**1**) and MPA-SVX-2 (**2**) in $CDCl_3$.

	1					**2**				
Position	δ_C	δ_H (multi, *J* Hz)				δ_C	δ_H (multi, *J* Hz)			
1	171.59 [a]					171.57 [a]				
2										
3	78.13	4.88	1H	brs		78.13	4.88			
4	32.98	3.12	2H	brm		32.83	3.12			
4a	132.67 [b]					132.84 [b]				
5	116.24 [c]	6.96	1H	s		116.28 [c]	6.96			
5a	140.07 [d]					140.08 [d]				
6	98.10 [e]	6.71	1H	s		98.12 [e]	6.71			
7	161.49 [f]					161.48 [f]				
8	108.17 [g]					108.16 [g]				
9	155.36 [#]					155.36 [#]				
9-OH		9.71	1H	s			9.70			
9a	108.45 [h]					108.46 [h]				
10	162.82 [##]					162.82 [##]				
10-OH		13.80	1H	s			13.81			
10a	99.30 [i]					99.34 [i]				
11	55.94 [###]	3.85	3H	s		55.95 [###]	3.85			
12	42.25	1.90	1H	brm		42.13	1.88			
		2.15	1H	brm			2.14			
13	69.66	4.23	1H	brs		69.55	4.20			
14	42.78	1.66	2H	m		42.89	1.65			
15	73.35	3.94	1H	brs		93.36	3.92			
16	38.36	1.56	2H	m		38.38	1.49			
17	24.91	1.33	1H	m		24.93	1.32			
		1.40	1H	m			1.41			
18	31.71	1.33	2H	m		31.71	1.31			
19	22.56	1.31	2H	m		22.57	1.32			
20	13.98	0.90	3H	t	6.7	14.00	0.90	3H	t	6.7
1'	171.24 [a]					171.28 [a]				
2'										
3'	76.50	4.78	1H	brs		76.53	4.76			
4'	34.73	3.02	2H	brm		34.71	3.02	2H	brm	
4a'	132.85 [b]					132.69 [b]				
5'	116.05 [c]	6.96	1H	s		116.09 [c]	6.96			
5a'	140.23 [d]					140.04 [d]				
6'	98.06 [e]	6.71	1H	s		98.08 [e]	6.71			
7'	161.41 [f]					161.44 [f]				
8'	108.08 [g]					108.12 [g]				
9'	155.36 [#]					155.36 [#]				
9-OH'		9.67	1H	s			9.68			
9a'	108.42 [h]					108.43 [h]				
10'	162.82 [##]					162.82 [##]				
10-OH'		13.70	1H	s			13.71			
10a'	99.26 [i]					99.26 [i]				
11'	55.94 [###]	3.85	3H	s		55.95 [###]	3.85			
12'	20.73	1.56	3H	d	6.2	20.73	1.56	3H	d	6.2

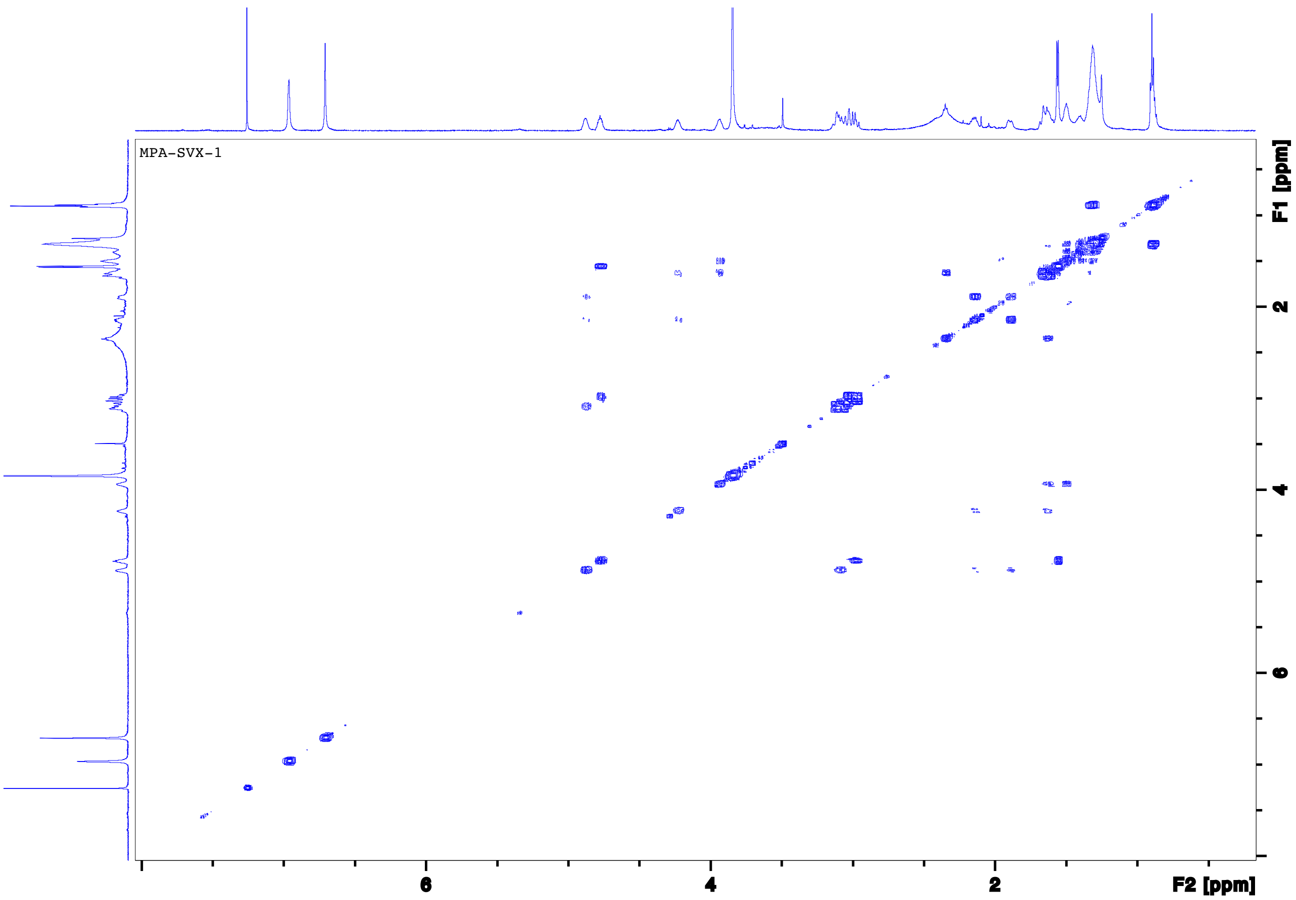
Chemical shifts are shown with reference to $CDCl_3$ as 77.0 ppm for ^{13}C and 7.26 ppm for ^{1}H.
a, b, c, d, e, f, g, h, i: Chemical shifts are exchangeable. #, ##, ###: Overlapped



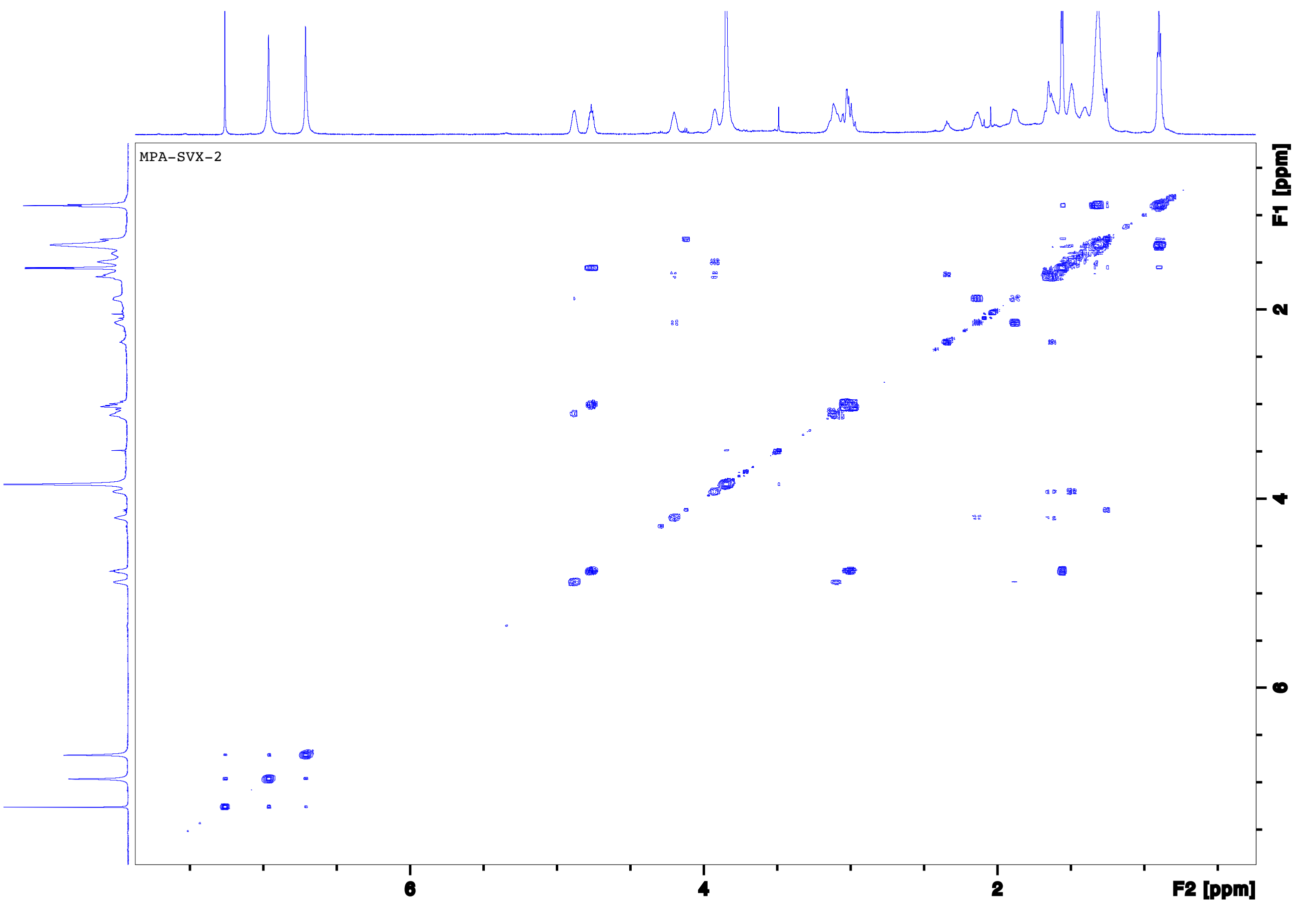
Supplementary Figure S3. ^{13}C NMR spectrum of compound **1** (150 MHz, $CDCl_3$)



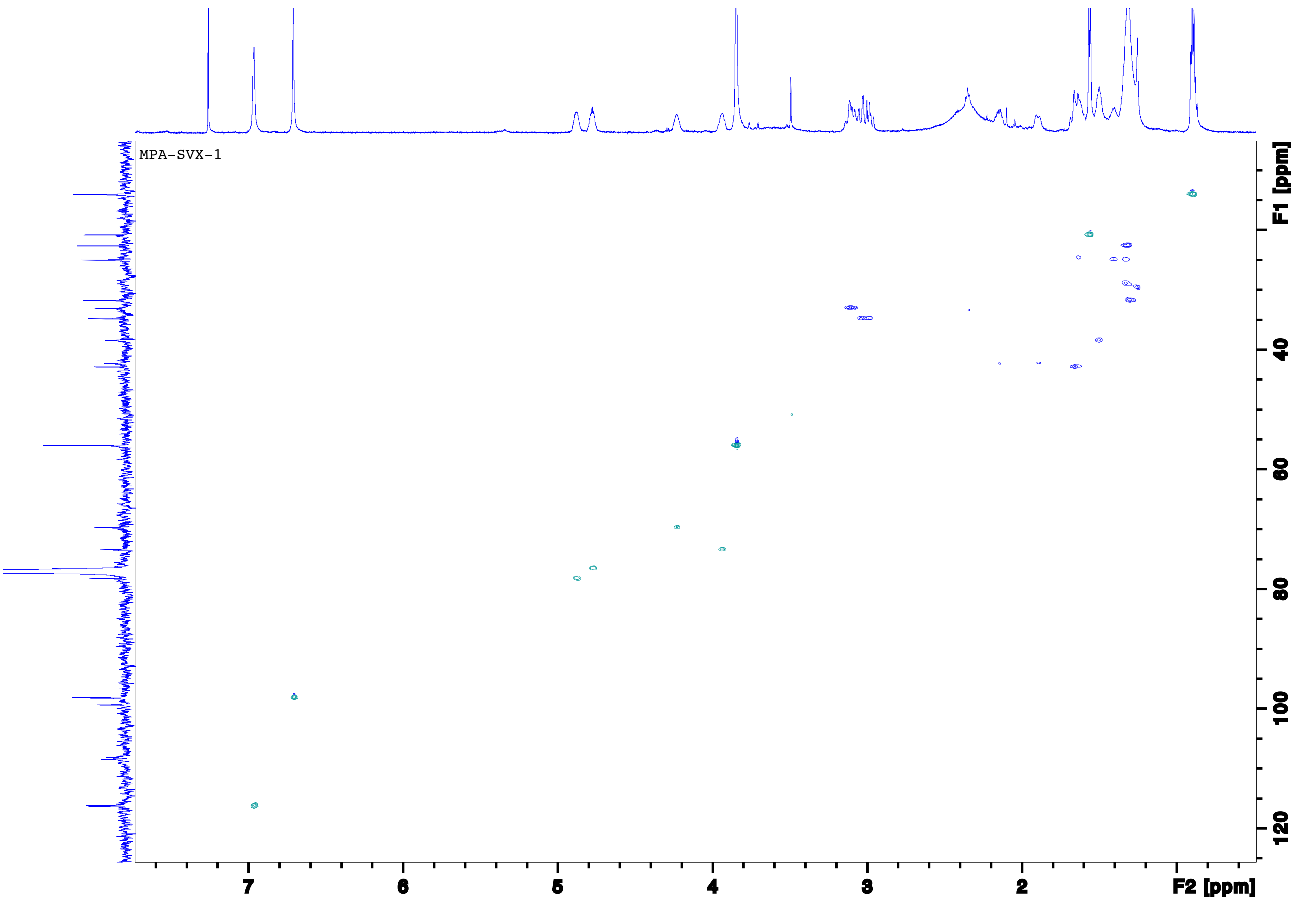
Supplementary Figure S4. ^{13}C NMR spectrum of compound **2** (150 MHz, $CDCl_3$)



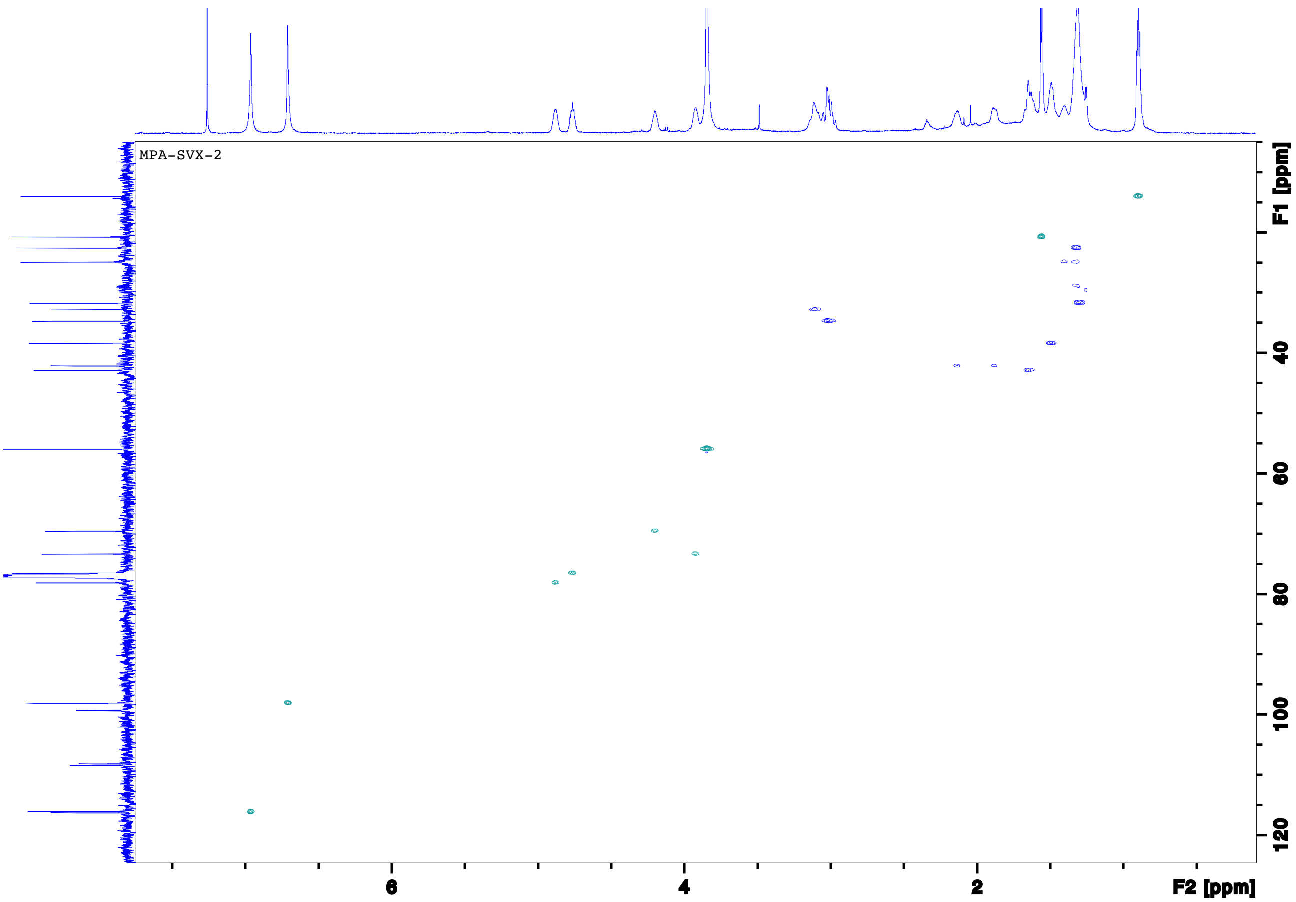
Supplementary Figure S5. ^{1}H-^{1}H COSY spectrum of compound **1** (600 MHz, $CDCl_3$)



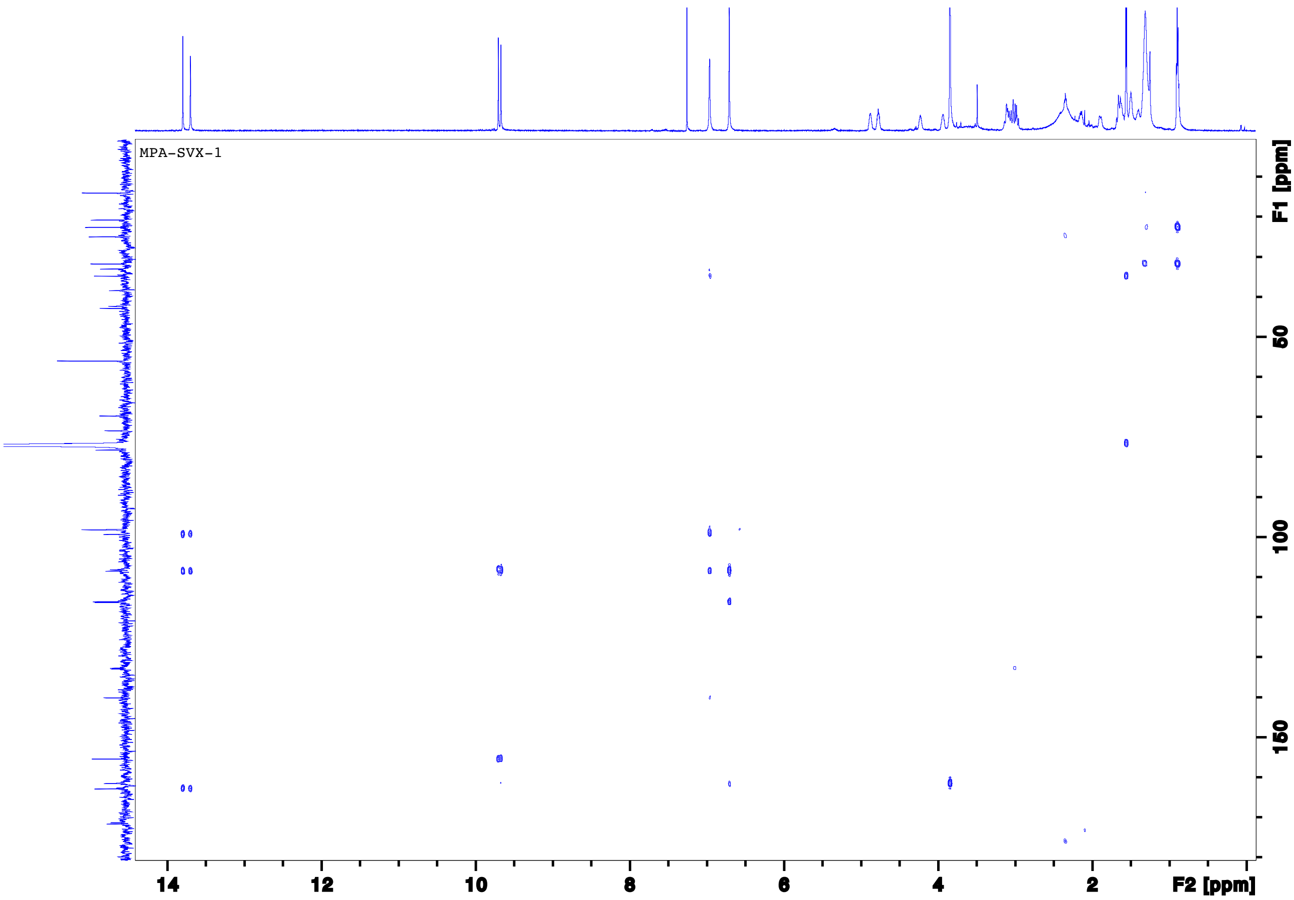
Supplementary Figure S6. ^{1}H-^{1}H COSY spectrum of compound **2** (600 MHz, $CDCl_3$)



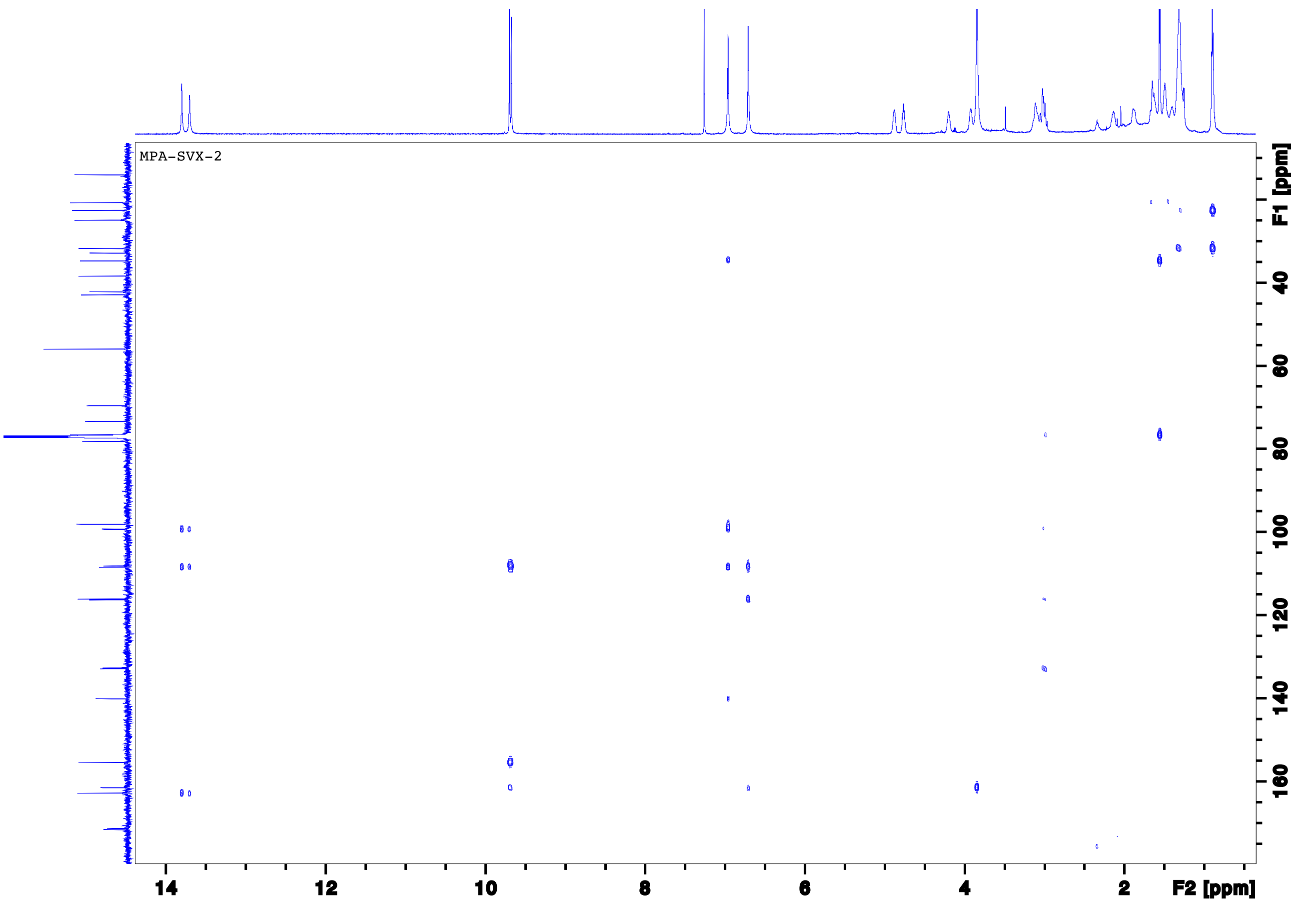
Supplementary Figure S7. HSQC spectrum of compound **1** (600 MHz, 150 MHz, $CDCl_3$)



Supplementary Figure S8. HSQC spectrum of compound **2** (600 MHz, 150 MHz, $CDCl_3$)

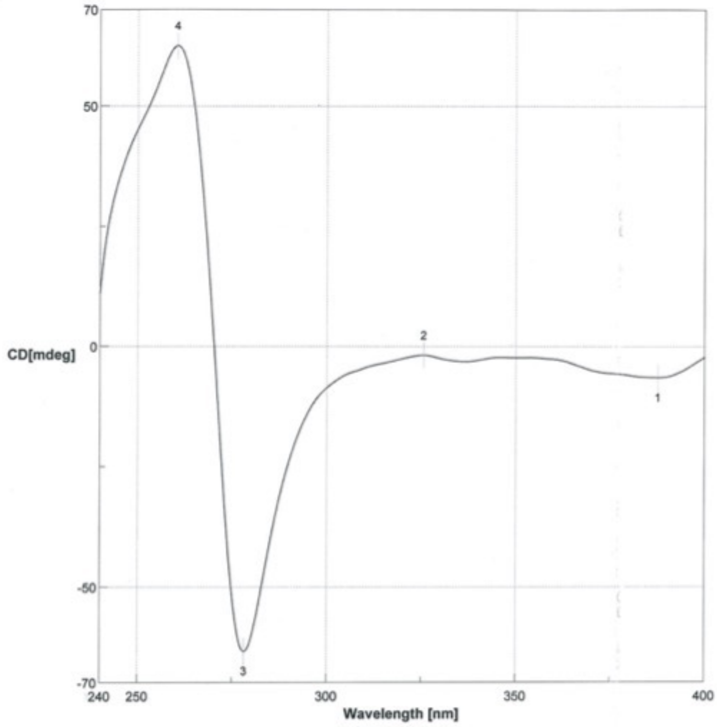


Supplementary Figure S9. HMBC spectrum of compound **1** (600 MHz, 150 MHz, $CDCl_3$)

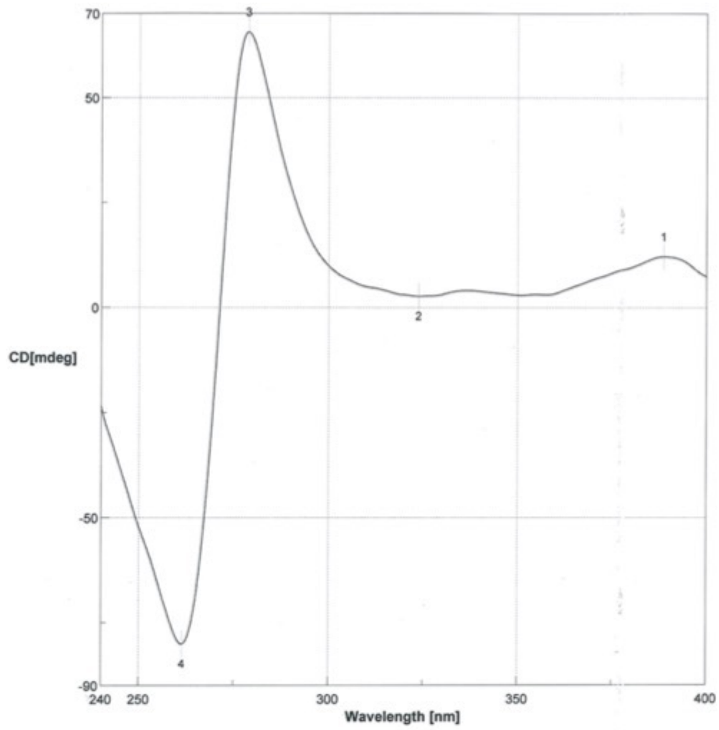


Supplementary Figure S10. HMBC spectrum of compound **2** (600 MHz, 150 MHz, $CDCl_3$)

MPA-SVX1 **(1)**



MPA-SVX2 **(2)**



Supplementary Figure S11. CD spectrum of compounds **1** and **2**.