Supplementary Information

Identification of four novel flavonoid adducts in *Arabidopsis thaliana* (L.) exposed to isobutyl S-2-diethylaminoethyl methylphosphonothiolate as potential plant exposure biomarkers

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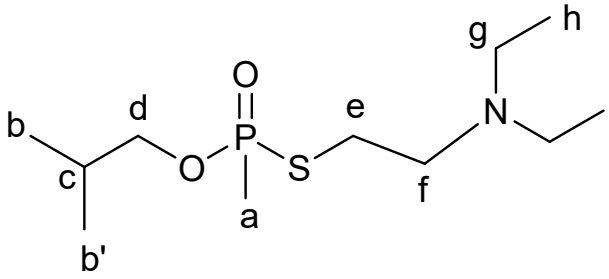

Fig. S1. Chemical structure of iBuVX

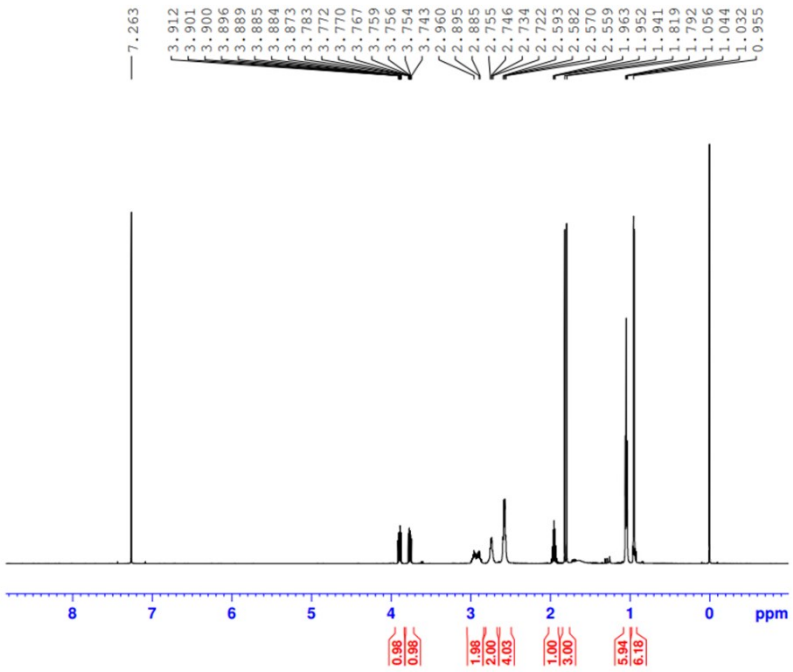

Fig. S2. ^{1}H NMR spectrum of iBuVX

Table S1. The assignment of ^{1}H NMR of iBuVX

Assignment	Chemical shift(ppm)	Coupling constant(Hz)
a	1.81	$^{3}J_{a\text{-}P}$=16.20
b	0.96	$^{3}J_{d\text{-}P}$=7.80
c	1.95	$^{3}J_{d'\text{-}P}$=7.20
d,d'	3.76,3.89	$^{3}J_{c\text{-}d}$=6.60
e	2.91	$^{3}J_{c\text{-}d'}$=6.60
f	2.74	$^{3}J_{h\text{-}g}$=7.20
g	2.58	$^{3}J_{d\text{-}d'}$=9.60
h	1.04	

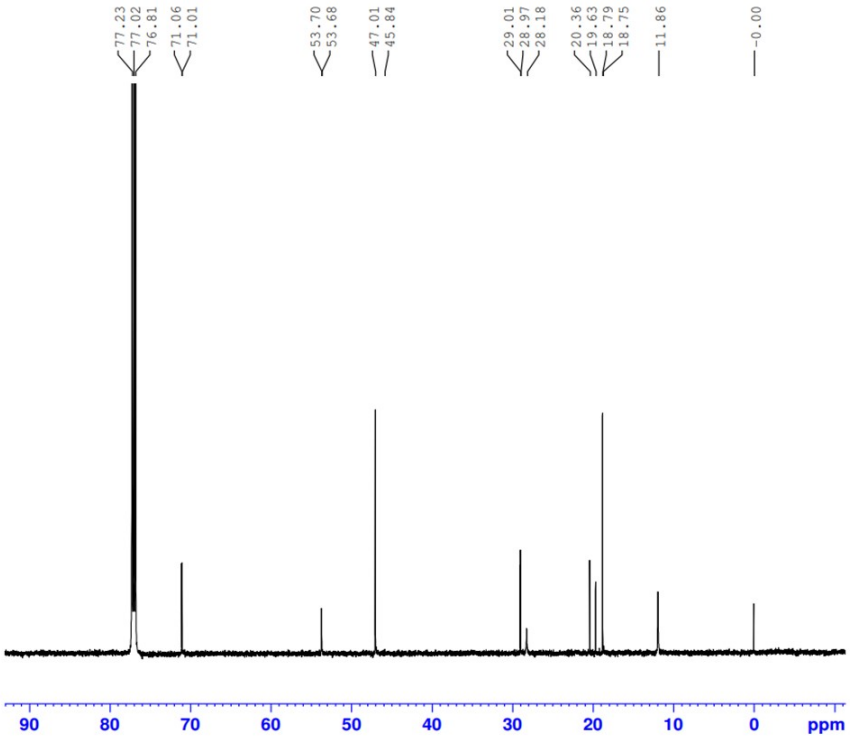

Fig. S3. ^{13}C NMR spectrum of iBuVX

Table S2. The assignment of ^{13}C NMR of iBuVX

Assignment	Chemical shift(ppm)	Coupling constant(Hz)
a	20.00	$J_{a\text{-}P}$=110.16
b,b'	18.79,18.75	$J_{c\text{-}P}$=6.04
c	28.99	$J_{d\text{-}P}$=7.54
d	71.04	$J_{f\text{-}P}$=3.02
e	28.18	
f	53.69	
g	47.01	
h	11.86	

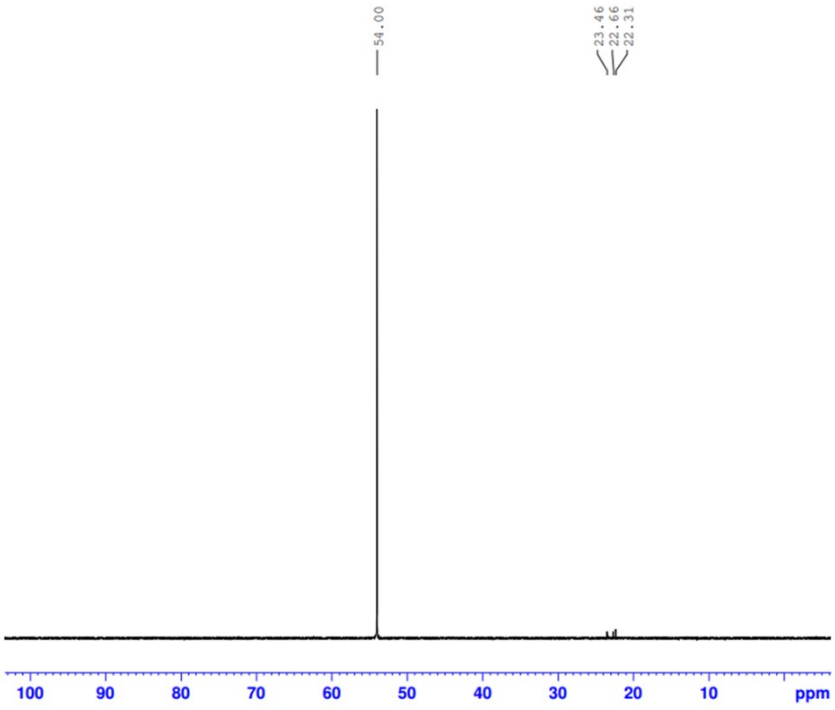

Fig. S4. ^{31}P NMR spectrum of iBuVX

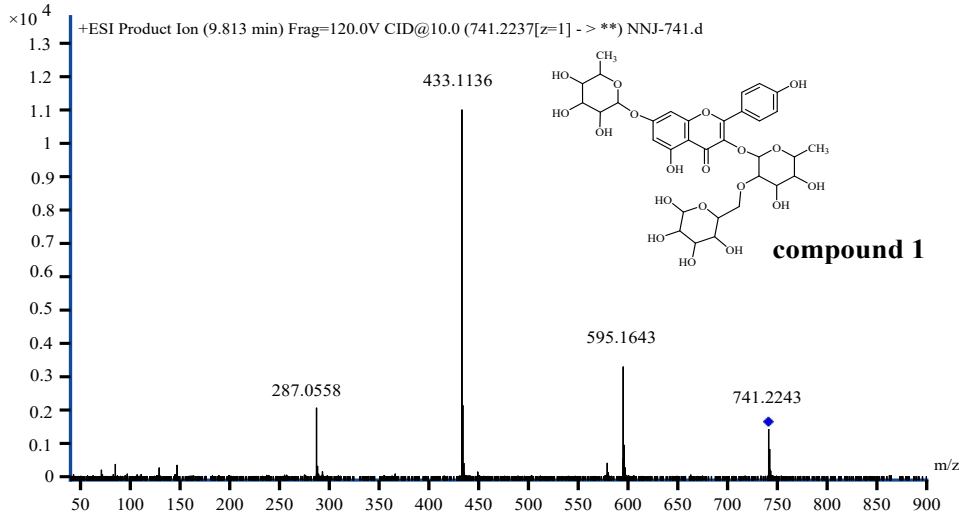

Fig. S5. Product ion mass spectrum of **compound 1**

Table S3. The deviations between calculated and observed m/z values of each fragment derived from **compound 1**

Fragment	Calculated m/z	Observed m/z	Deviation
$[M+H]^+$	741.2237	741.2243	0.87 ppm
$[M+H-C_6H_{10}O_4]^+$	595.1657	595.1643	-2.43 ppm
$[M+H-C_6H_{10}O_4-C_6H_{10}O_5]^+$	433.1129	433.1136	1.57 ppm
$[M+H-2C_6H_{10}O_4-C_6H_{10}O_5]^+$	287.0550	287.0558	2.75 ppm

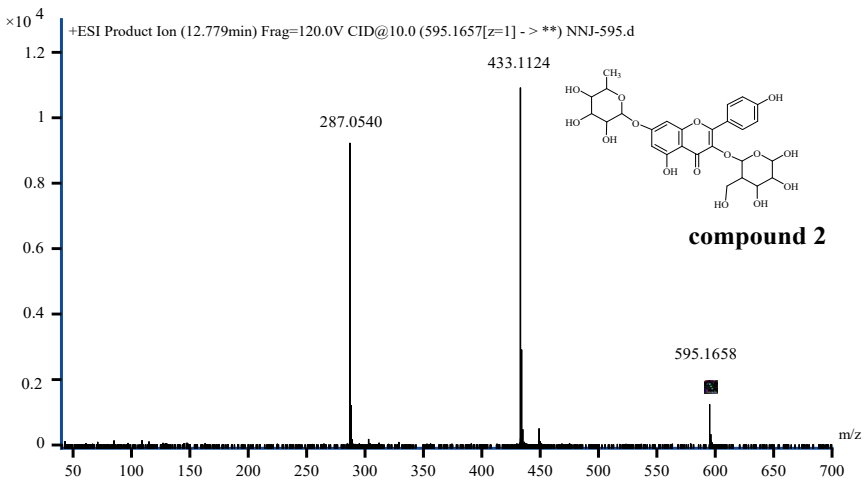

Fig. S6. Product ion mass spectrum of **compound 2**

Table S4. The deviations between calculated and observed m/z values of each fragment derived from **compound 2**

Fragment	Calculated m/z	Observed m/z	Deviation
$[M+H]^+$	595.1657	595.1658	0.09 ppm
$[M+H-C_6H_{10}O_4]^+$	433.1129	433.1124	-1.21 ppm
$[M+H-C_6H_{10}O_4-C_6H_{10}O_5]^+$	287.0550	287.0540	-3.55 ppm

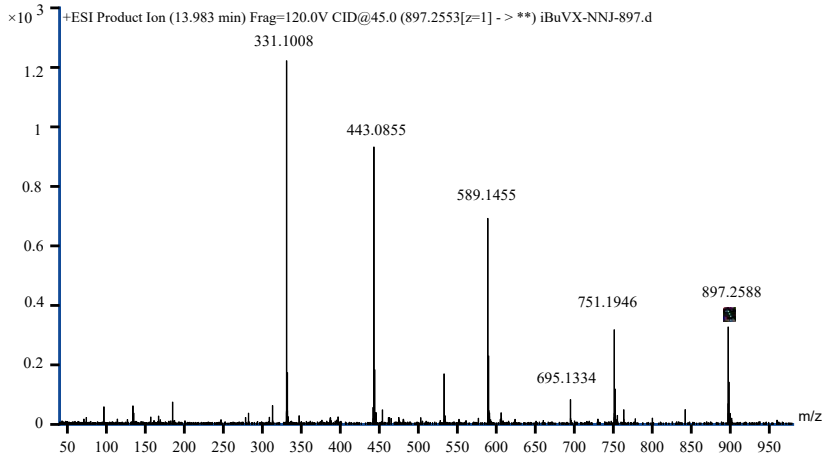

Fig. S7. Product ion mass spectrum of m/z 897.2553 (**compound 4**) in the extracts of leaves from *Arabidopsis thaliana* (L.) exposed to iBuVX

Table S5. The deviations between calculated and observed m/z values of each fragment derived from **compound 4** in the extract of leaves exposed to iBuVX

Fragment	Calculated m/z	Observed m/z	Deviation
$[M+Na]^+$	897.2553	897.2588	4.04 ppm
$[M+Na-C_6H_{10}O_4]^+$	751.1974	751.1946	-3.79 ppm
$[M+Na-C_6H_{10}O_4-C_4H_8]^+$	695.1348	695.1334	-2.02 ppm
$[M+Na-C_6H_{10}O_4-C_6H_{10}O_5]^+$	589.1445	589.1455	1.71 ppm
$[M+Na-2C_6H_{10}O_4-C_6H_{10}O_5]^+$	443.0866	443.0855	-2.68 ppm
$[M+Na-C_6H_{10}O_4-C_{20}H_{21}O_8P]^+$	331.1000	331.1008	2.75 ppm

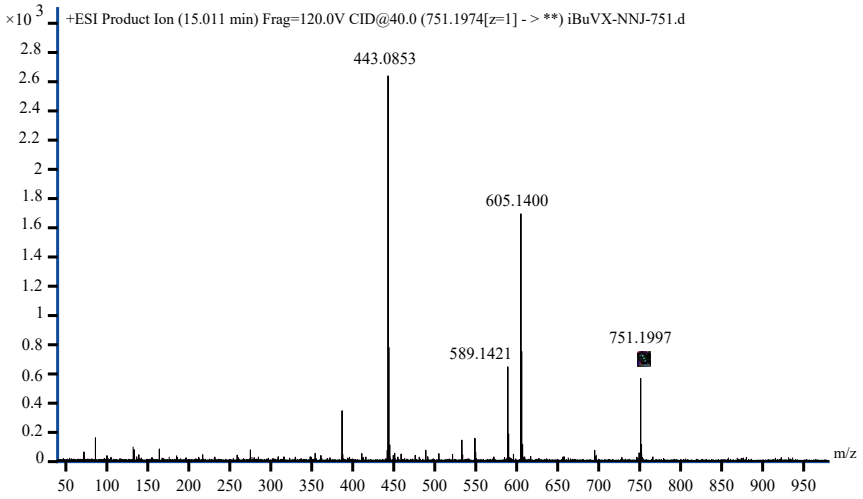

Fig. S8. Product ion mass spectrum of m/z 751.1974 (**compound 5**) in the extracts of leaves from *Arabidopsis thaliana* (L.) exposed to iBuVX

Table S6. The deviations between calculated and observed m/z values of each fragment derived from **compound 5** in the extract of leaves exposed to iBuVX

Fragment	Calculated m/z	Observed m/z	Deviation
$[M+Na]^+$	751.1974	751.1997	3.22 ppm
$[M+Na-C_6H_{10}O_4]^+$	605.1394	605.1400	0.95 ppm
$[M+Na-C_6H_{10}O_5]^+$	589.1445	589.1421	-4.30 ppm
$[M+Na-C_6H_{10}O_5-C_6H_{10}O_4]^+$	443.0866	443.0853	-3.15 ppm

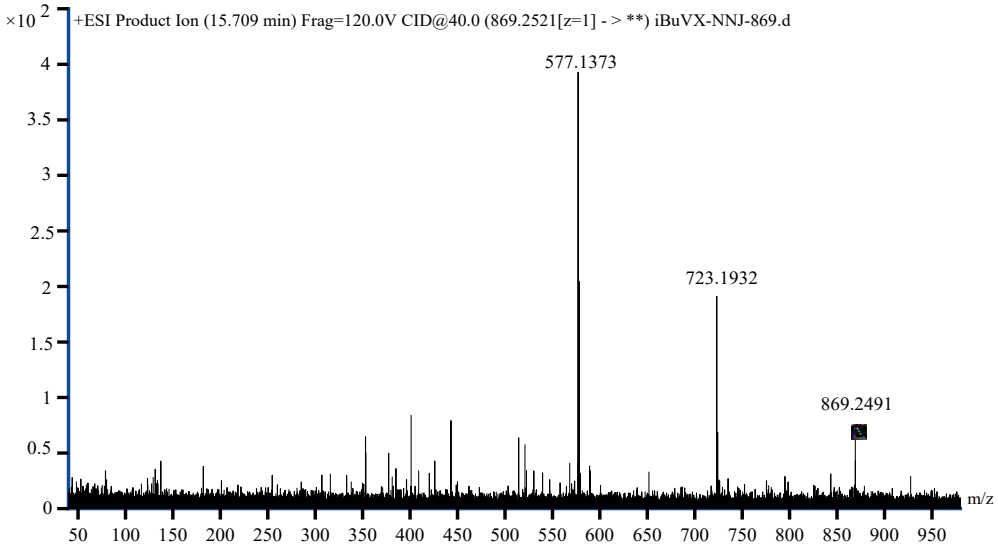

Fig. S9. Product ion mass spectrum of m/z 869.2521(**compound 7**) in the extracts of leaves from *Arabidopsis thaliana* (L.) exposed to iBuVX

Table S7. The deviations between calculated m/z and observed values of each fragment derived from **compound 7** in the extract of leaves exposed to iBuVX

Fragment	Calculated m/z	Observed m/z	Deviation
$[M+Na]^+$	869.2521	869.2491	-3.56 ppm
$[M+Na-C_6H_{10}O_4]^+$	723.1942	723.1932	-1.43 ppm
$[M+Na-2C_6H_{10}O_4]^+$	577.1363	577.1373	1.82 ppm

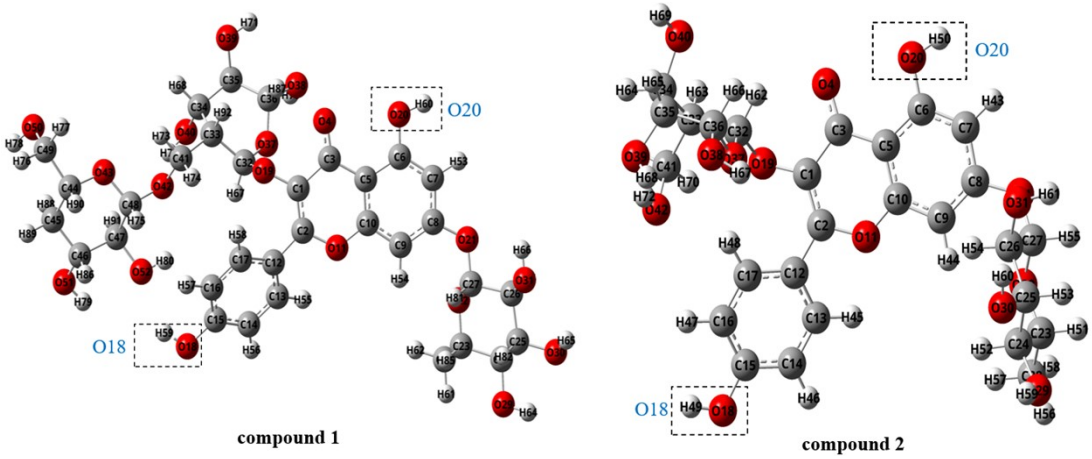

Fig. S10 The lowest energy conformations of **compound 1** and **compound 2**

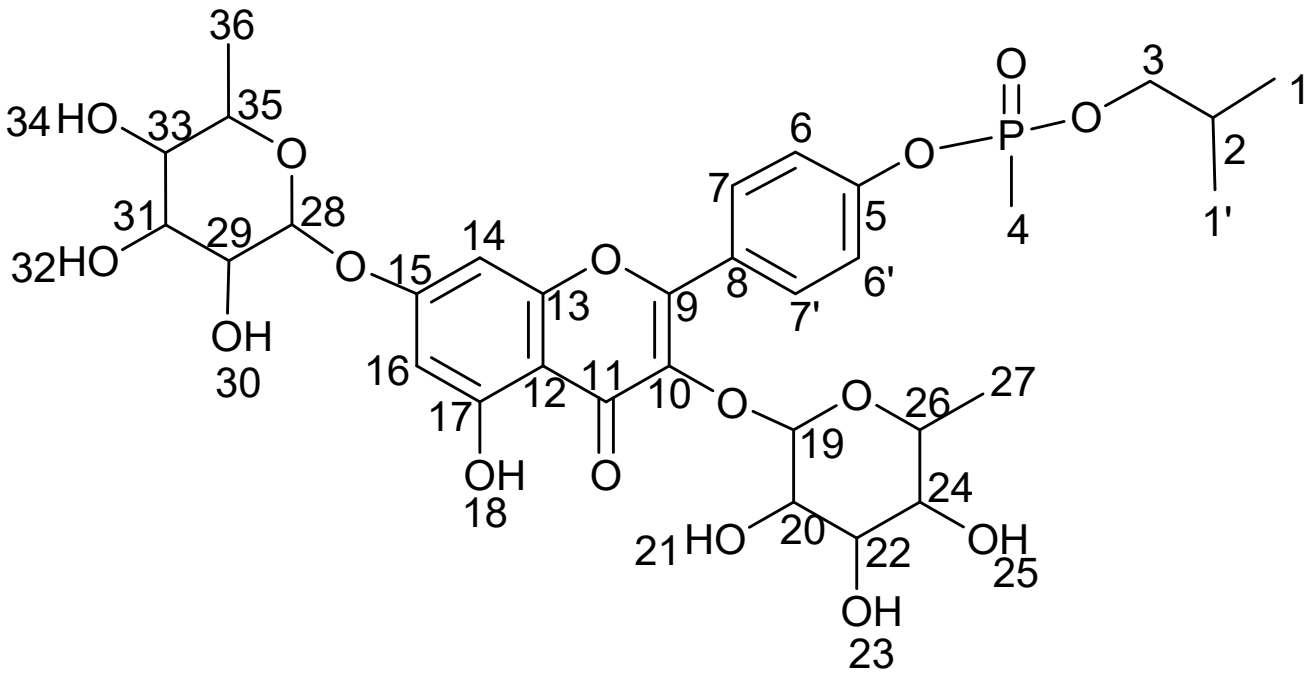

Fig. S11. Chemical structure of the synthesized **compound 6** with atoms numbering

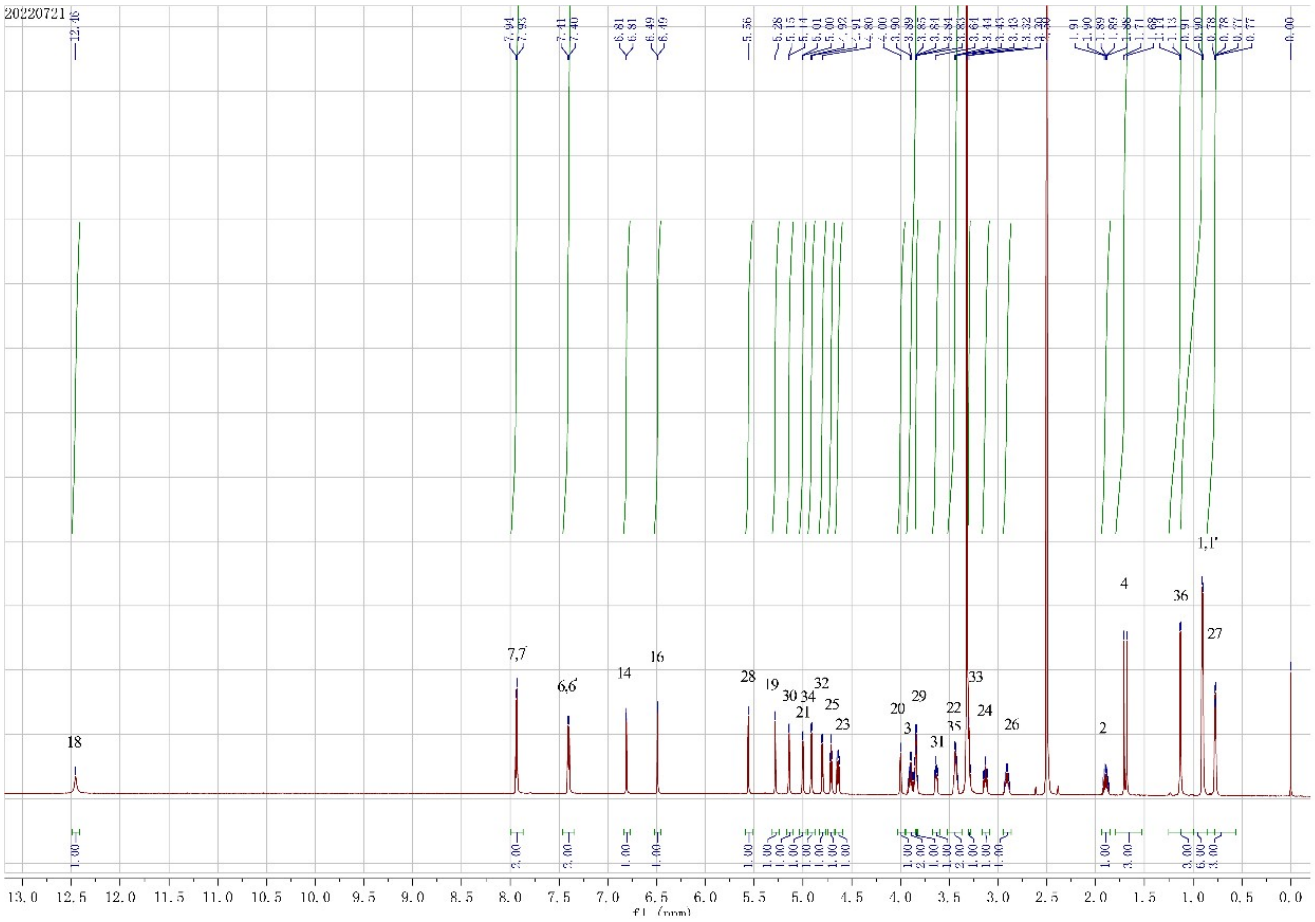

Fig. S12. ^{1}H NMR spectrum of the synthesized **compound 6**

Table S8. The assignment of ^{1}H NMR of the synthesized **compound 6**

Assignment	Chemical shift(ppm)	Assignment	Chemical shift(ppm)
1,1’	0.91	24	3.13
2	1.90	25	4.71
3	3.90	26	2.91
4	1.70	27	0.78
6,6’	7.40	28	5.56
7,7’	7.94	29	3.84
14	6.81	30	5.14
16	6.49	31	3.64
18	12.46	32	4.80
19	5.28	33	3.30
20	4.00	34	4.92
21	5.00	35	3.43
22	3.43	36	1.13
23	4.64		

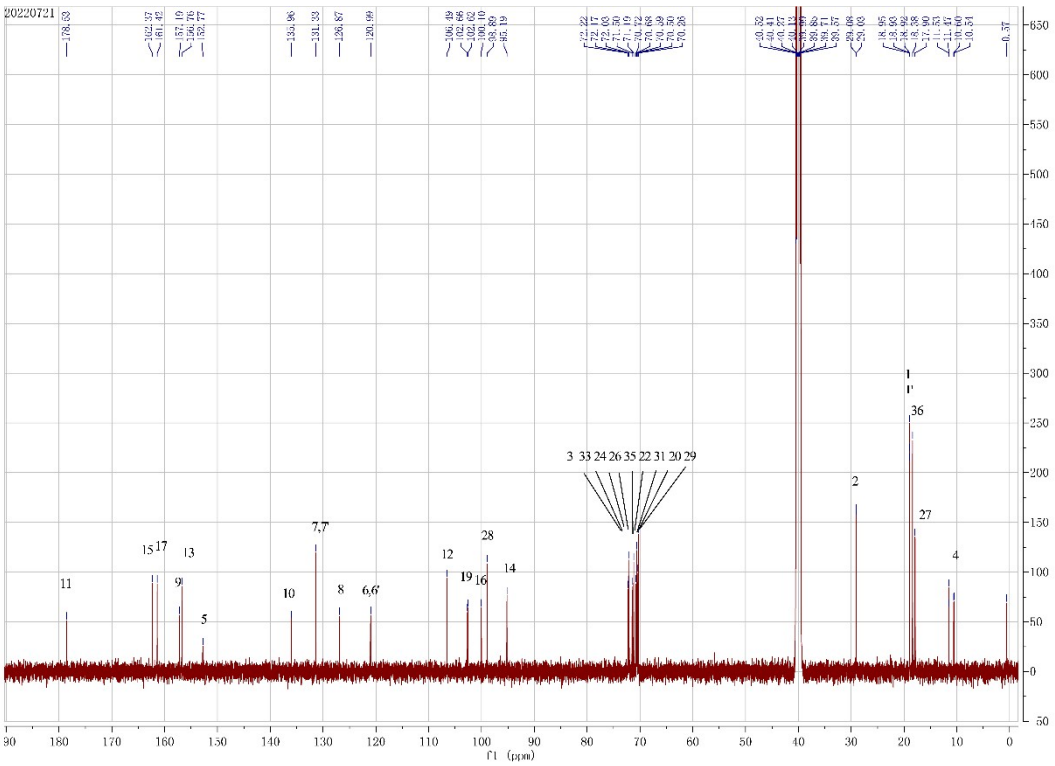

Fig. S13. ^{13}C NMR spectrum of the synthesized **compound 6**

Table S9. The assignment of ^{13}C NMR of the synthesized **compound 6**

Assignment	Chemical shift(ppm)	Assignment	Chemical shift(ppm)
1	18.93	16	100.10
2	29.06	17	161.42
3	72.20	19	102.64
4	11.04	20	70.50
5	152.77	22	70.68
6	120.99	24	71.50
7	131.33	26	71.19
8	126.87	27	17.90
9	157.19	28	98.89
10	135.96	29	70.26
11	178.53	31	70.59
12	106.49	33	72.03
13	156.76	35	70.72
14	95.19	36	18.38
15	162.37		

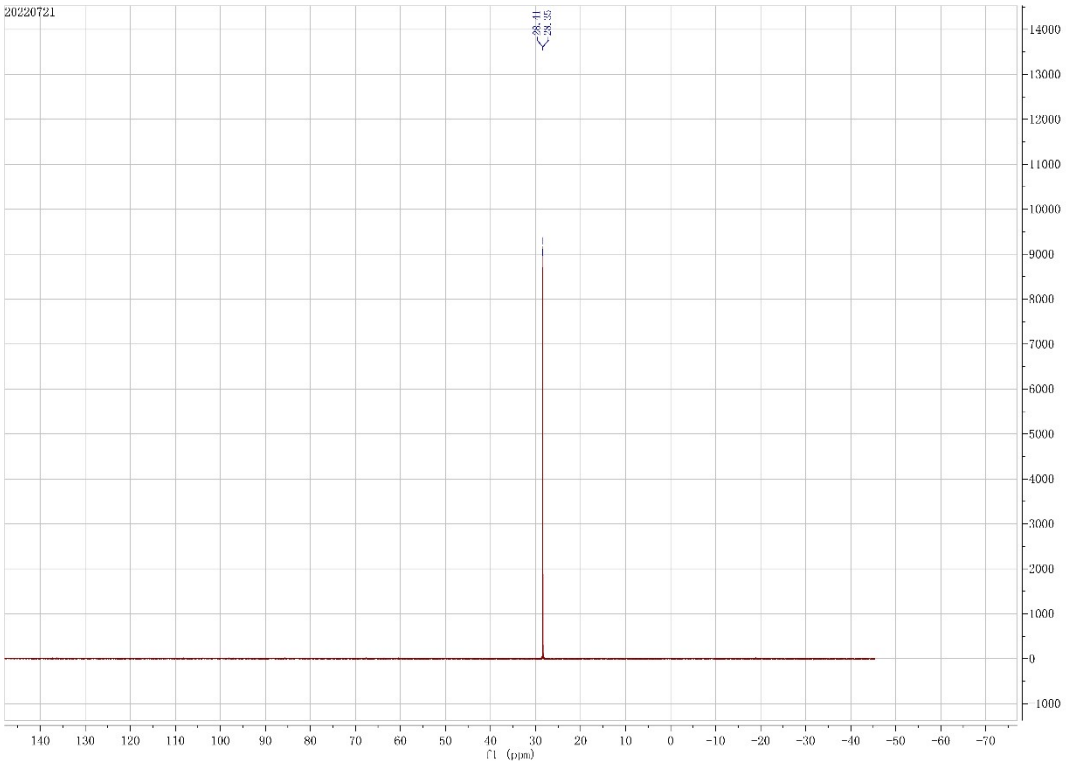

Fig. S14. ^{31}P NMR spectrum of the synthesized **compound 6**

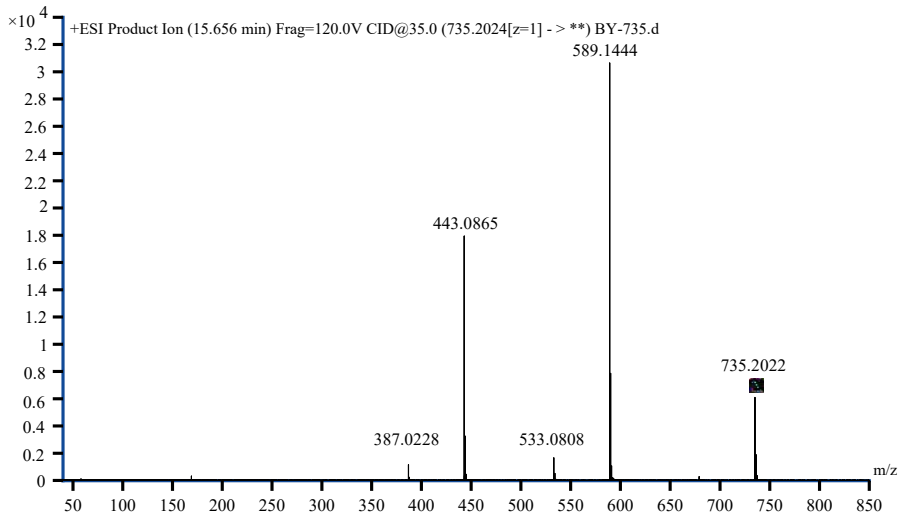

Fig. S15. Product ion mass spectrum of m/z 735.2024 from the synthesized **compound 6**

Table S10. The deviations between calculated and observed m/z values of each fragment from the synthesized **compound 6**

Fragment	Calculated m/z	Observed m/z	Deviation
$[M+Na]^+$	735.2024	735.2022	-0.34 ppm
$[M+Na-C_6H_{10}O_4]^+$	589.1445	589.1444	-0.24 ppm
$[M+Na-C_6H_{10}O_4-C_4H_8]^+$	533.0819	533.0808	-2.22 ppm
$[M+Na-2C_6H_{10}O_4]^+$	443.0866	443.0865	-0.30 ppm
$[M+Na-2C_6H_{10}O_4-C_4H_8]^+$	387.0240	387.0228	-3.36 ppm

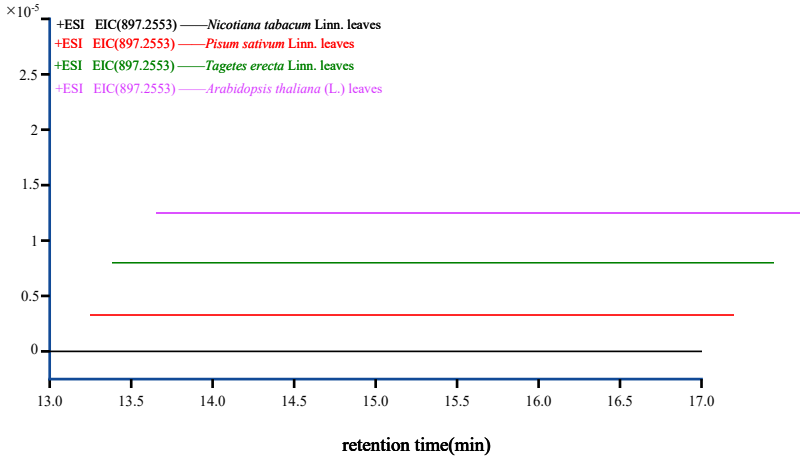

Fig. S16. EICs (m/z 897.2553) of the extracts of leaves from plants of *Nicotiana tabacum* Linn., *Pisum sativum* Linn., *Tagetes erecta* Linn. and *Arabidopsis thaliana* (L.) leaves with no exposure to iBuVX

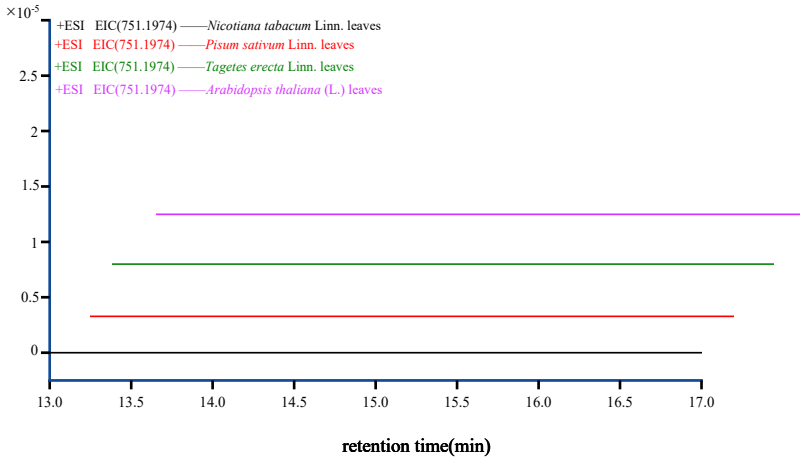

Fig. S17. EICs (m/z 751.1974) of the extracts of leaves from plants of *Nicotiana tabacum* Linn., *Pisum sativum* Linn., *Tagetes erecta* Linn. and *Arabidopsis thaliana* (L.) leaves with no exposure to iBuVX

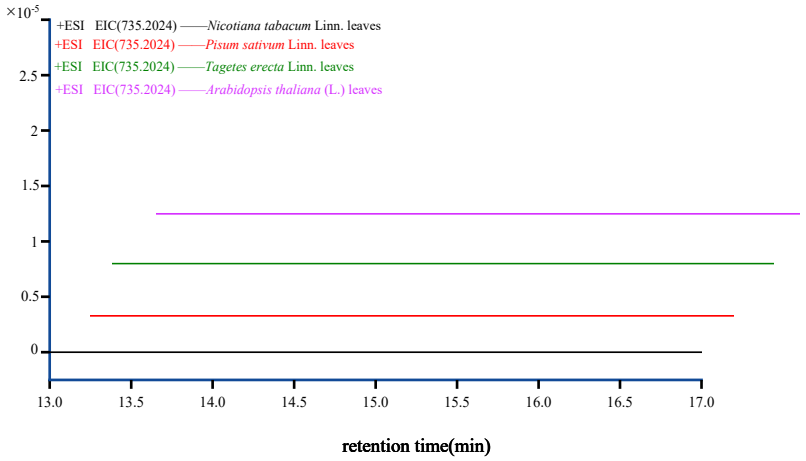

Fig. S18. EICs (m/z 735.2024) of the extracts of leaves from plants of *Nicotiana tabacum* Linn., *Pisum sativum* Linn., *Tagetes erecta* Linn. and *Arabidopsis thaliana* (L.) leaves with no exposure to iBuVX

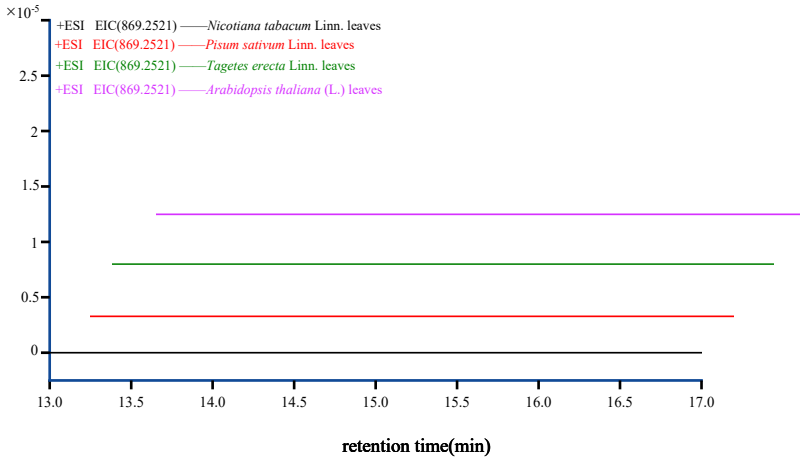

Fig. S19. EICs (m/z 869.2521) of the extracts of leaves from plants of *Nicotiana tabacum* Linn., *Pisum sativum* Linn., *Tagetes erecta* Linn. and *Arabidopsis thaliana* (L.) leaves with no exposure to iBuVX