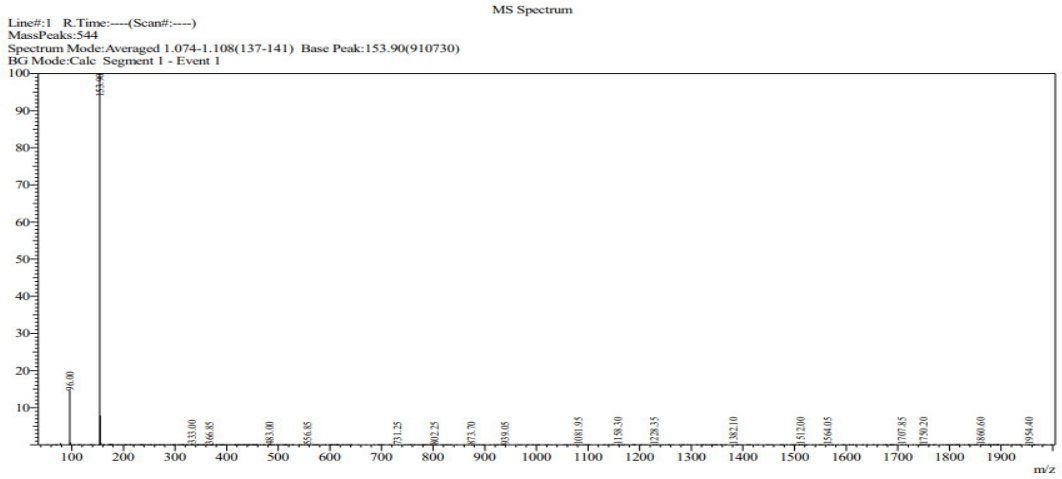
Supplementary data

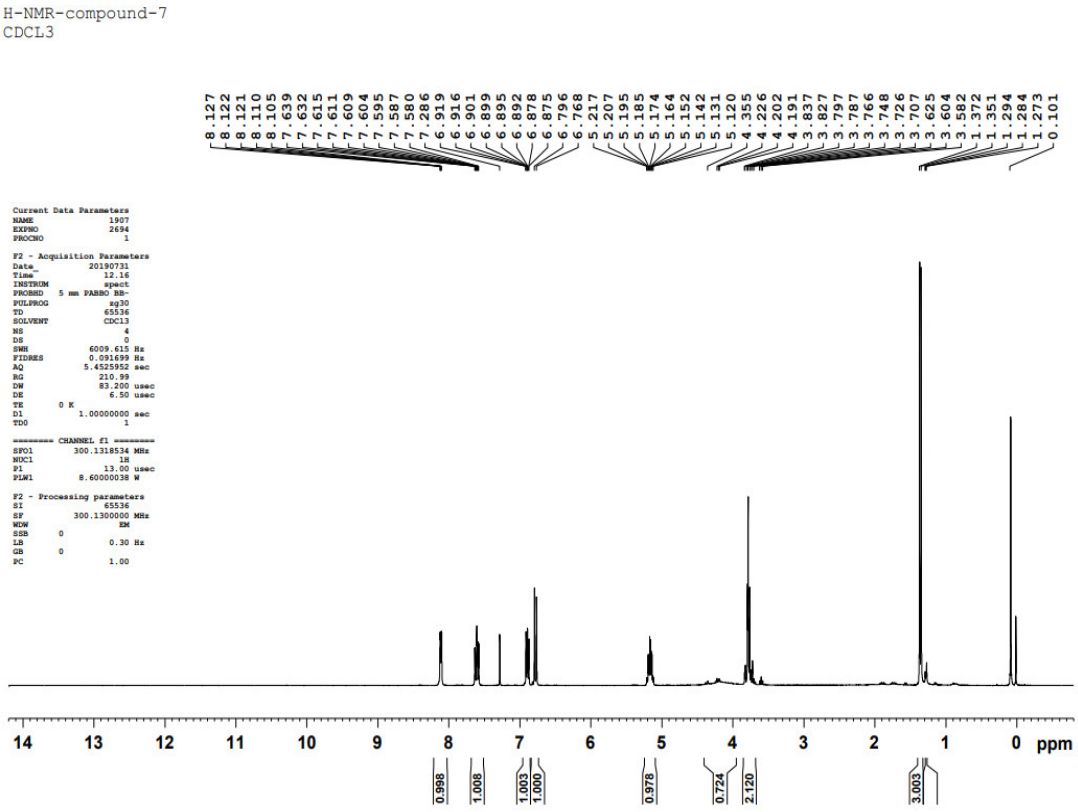
Table S1. The LC-MS and NMR information for metabolites PYPA, PYPAC, DPH-Pyr, 4'-OH-Pyr, and 5"-OH-Pyr.

Compound	LC-MS	^{1}H NMR
PYPA	(ES, *m*/*z*): $[M+H]^+$ = 154	(300 MHz, Chloroform-*d*): δ 1.36 (d, *J* = 6.5 Hz, 3H), 3.72 – 3.91 (m, 2H), 4.01 – 4.35 (m, 1H), 5.00 – 5.30 (m, 1H), 6.62 – 6.86 (m, 1H), 6.86 – 7.02 (m, 1H), 7.47 – 7.74 (m, 1H), 8.00 – 8.23 (m, 1H)
PYPAC	(ES, *m*/*z*): $[M+H]^+$ = 168	(300 MHz, DMSO-d_6): δ 1.50 (d, *J* = 7.0 Hz, 3H), 5.17 (q, *J* = 7.0 Hz, 1H), 6.68 – 6.91 (m, 1H), 6.91 – 7.12 (m, 1H), 7.53 – 7.88 (m, 1H), 8.00 – 8.24 (m, 1H), 12.71 (s, 1H)
DPH-Pyr	(ES, *m*/*z*): $[M+H]^+$ = 246	(400 MHz, Chloroform-*d*): δ 1.45 (d, *J* = 6.4 Hz, 3H), 3.92 – 4.04 (m, 1H), 4.07 – 4.16 (m, 1H), 5.16 – 5.66 (m, 1H), 6.62 – 6.86 (m, 5H), 6.80 – 7.01 (m, 1H), 7.47 – 7.65 (m, 1H), 8.06 – 8.36 (m, 1H)
4'-OH-Pyr	(ES, *m*/*z*): $[M+H]^+$ =338	(400 MHz, Chloroform-*d*): δ 1.50 (d, *J* = 6.4 Hz, 3H), 4.08 (dd, *J* = 9.9, 4.7 Hz, 1H), 4.18 (dd, *J* = 9.9, 5.4 Hz, 1H), 5.46 – 5.75 (m, 1H), 5.87 (s, 1H), 6.72 – 7.00 (m, 10H), 7.54 – 7.64 (m, 1H), 8.11 – 8.27 (m, 1H)
5"-OH-Pyr	(ES, *m*/*z*): $[M+H]^+$ =338	(400 MHz, Chloroform-d): δ 1.45 (d, J = 6.3 Hz, 3H), 4.01 – 4.09 (m, 1H), 4.11 – 4.19 (m, 1H), 5.35 – 5.46 (m, 1H), 6.63 – 6.71 (m, 1H), 6.86 – 7.00 (m, 6H), 7.00 – 7.09 (m, 1H), 7.14 – 7.22 (m, 1H), 7.24 – 7.34 (m, 2H), 7.72 – 7.79 (m, 1H)

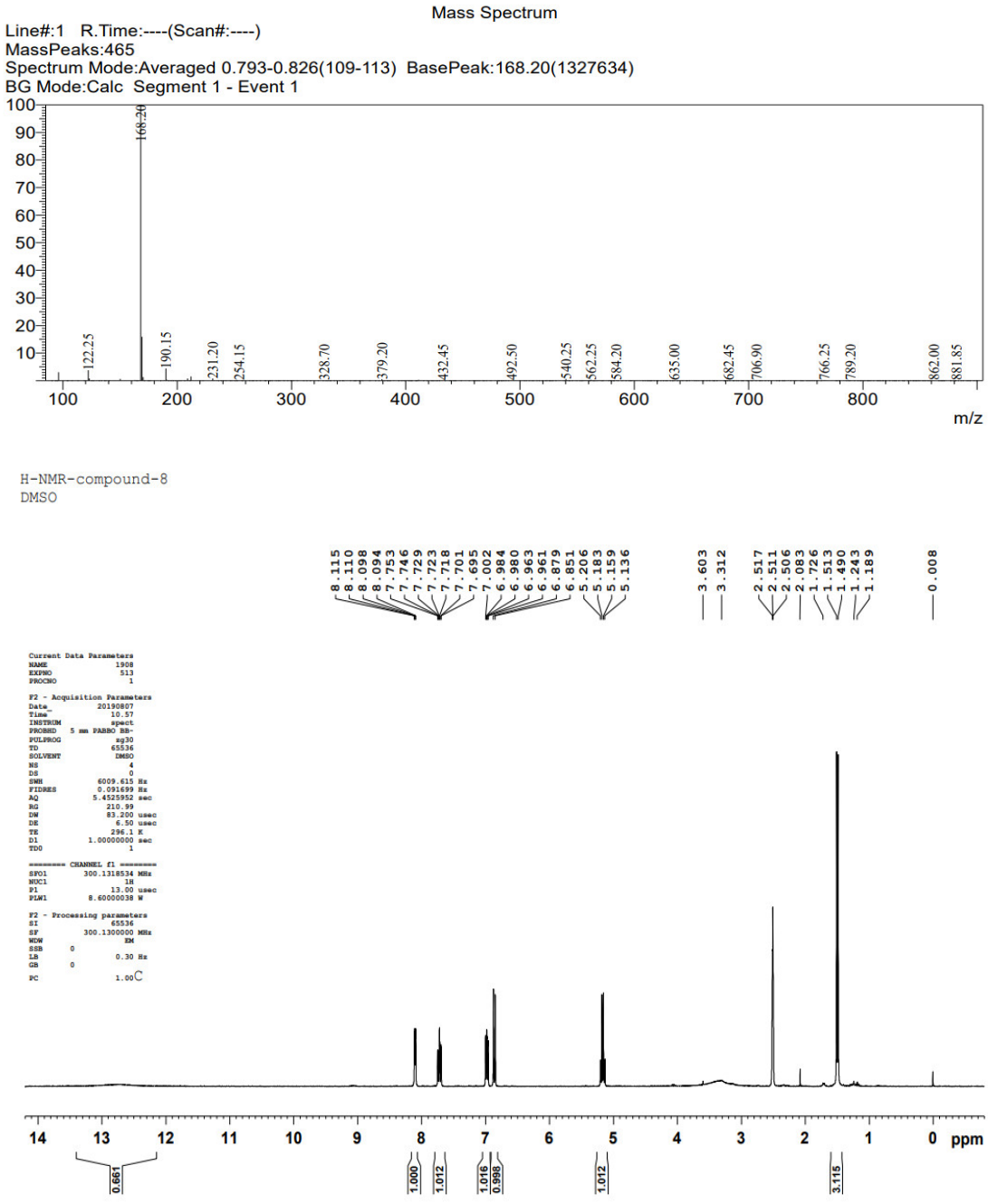
Table S2. Residue dissipation of pyriproxyfen and its metabolites on fresh tea leaves.

Time (d)	Pyriproxyfen		PYPA	PYPAC	DPH-Pyr	5"-OH-Pyr	4'-OH-Pyr
	Residues (mg/kg)	Dissipation rate (%)	Residues (mg/kg)	Residues (mg/kg)	Residues (mg/kg)	Residues (mg/kg)	Residues (mg/kg)
0 (2 h)	14.552±0.904	32.6	0.007±0.001	0.002±0.000	0.003±0.001	0.041±0.003	0.073±0.005
1	9.807±0.292	63.2	0.020±0.002	0.005±0.000	0.008±0.001	0.091±0.011	0.295±0.033
2	5.359±0.171	70.6	0.032±0.002	0.010±0.001	0.020±0.001	0.073±0.002	0.384±0.007
3	4.280±0.203	86.7	0.054±0.003	0.013±0.001	0.035±0.003	0.070±0.003	0.508±0.059
5	1.939±0.146	92.7	0.039±0.003	0.019±0.003	0.035±0.003	0.052±0.002	0.299±0.013
7	1.055±0.088	98.2	0.048±0.002	0.021±0.003	0.033±0.002	0.031±0.002	0.187±0.008
10	0.265±0.029	99.1	0.025±0.001	0.023±0.003	0.015±0.001	0.017±0.001	0.039±0.003
14	0.126±0.006	99.9	0.016±0.001	0.018±0.002	0.008±0.001	0.008±0.000	0.023±0.001
21	0.010±0.002	100.0	/	0.014±0.002	0.003±0.002	0.003±0.003	0.005±0.003
Dissipation equation	$C = 8.7121e^{-0.280t}$						
R^2	0.9587						
$t_{1/2}$ (d)	2.48						

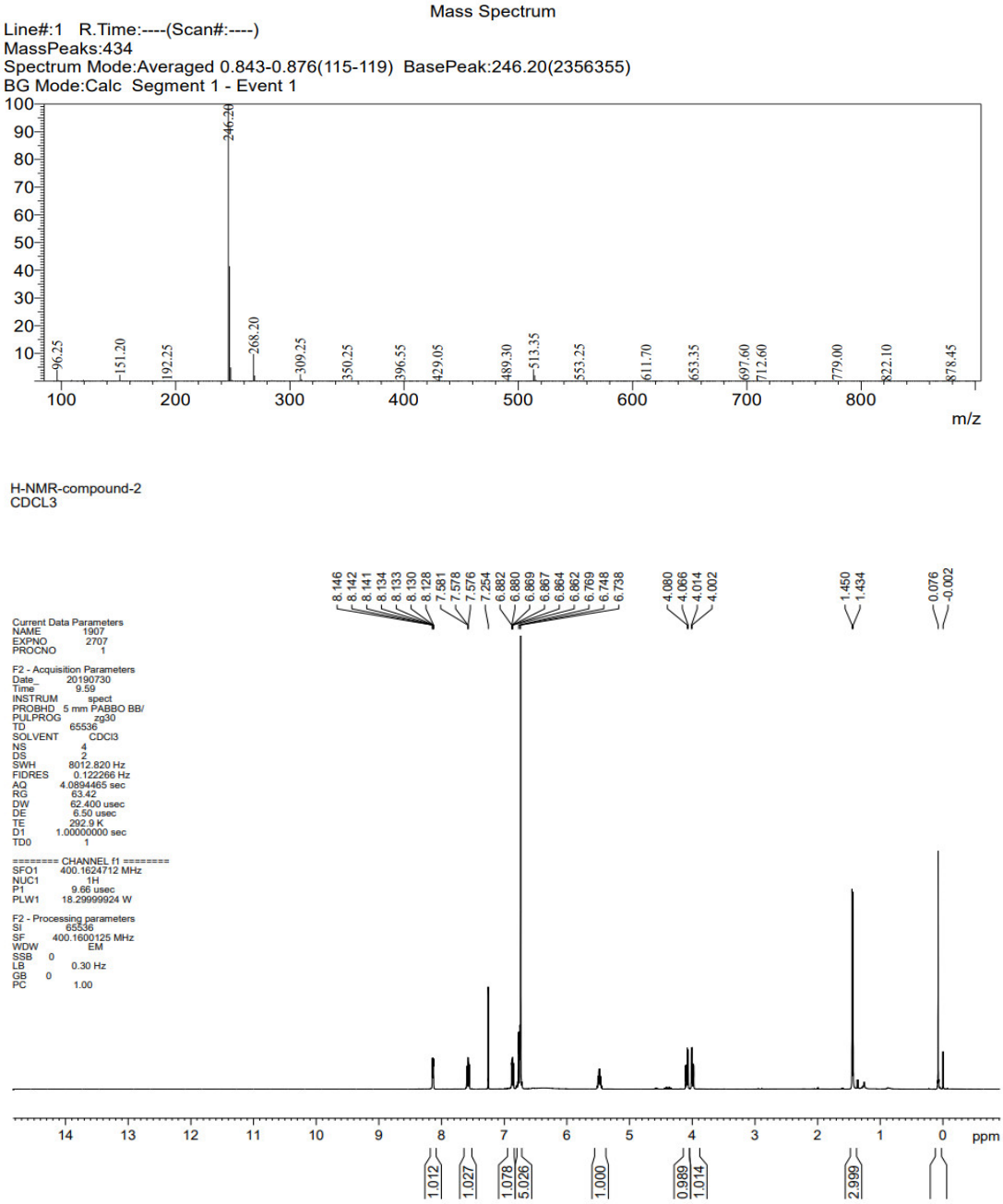




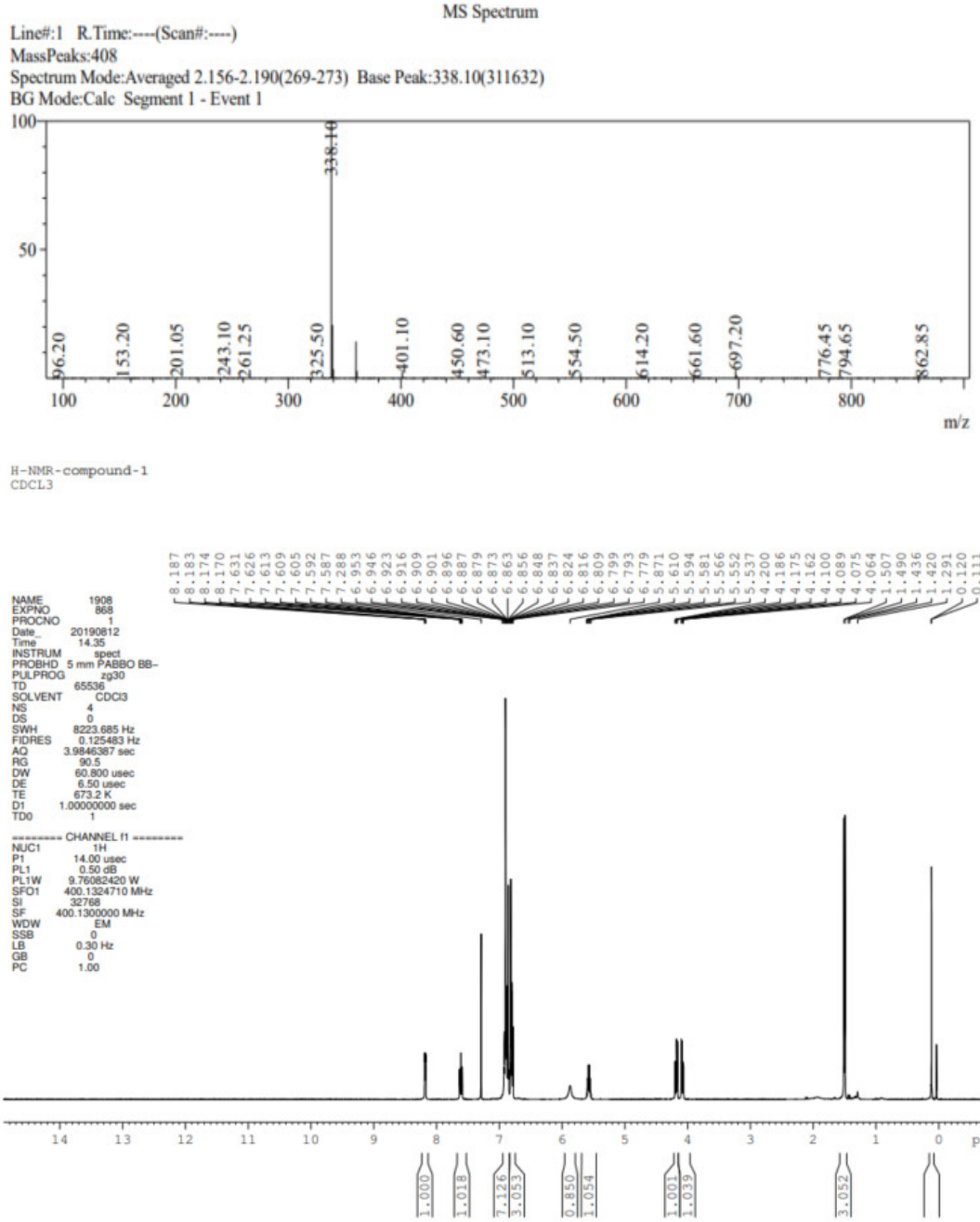
a. The LC-MS mass spectrum and ^{1}H NMR spectrum of PYPA



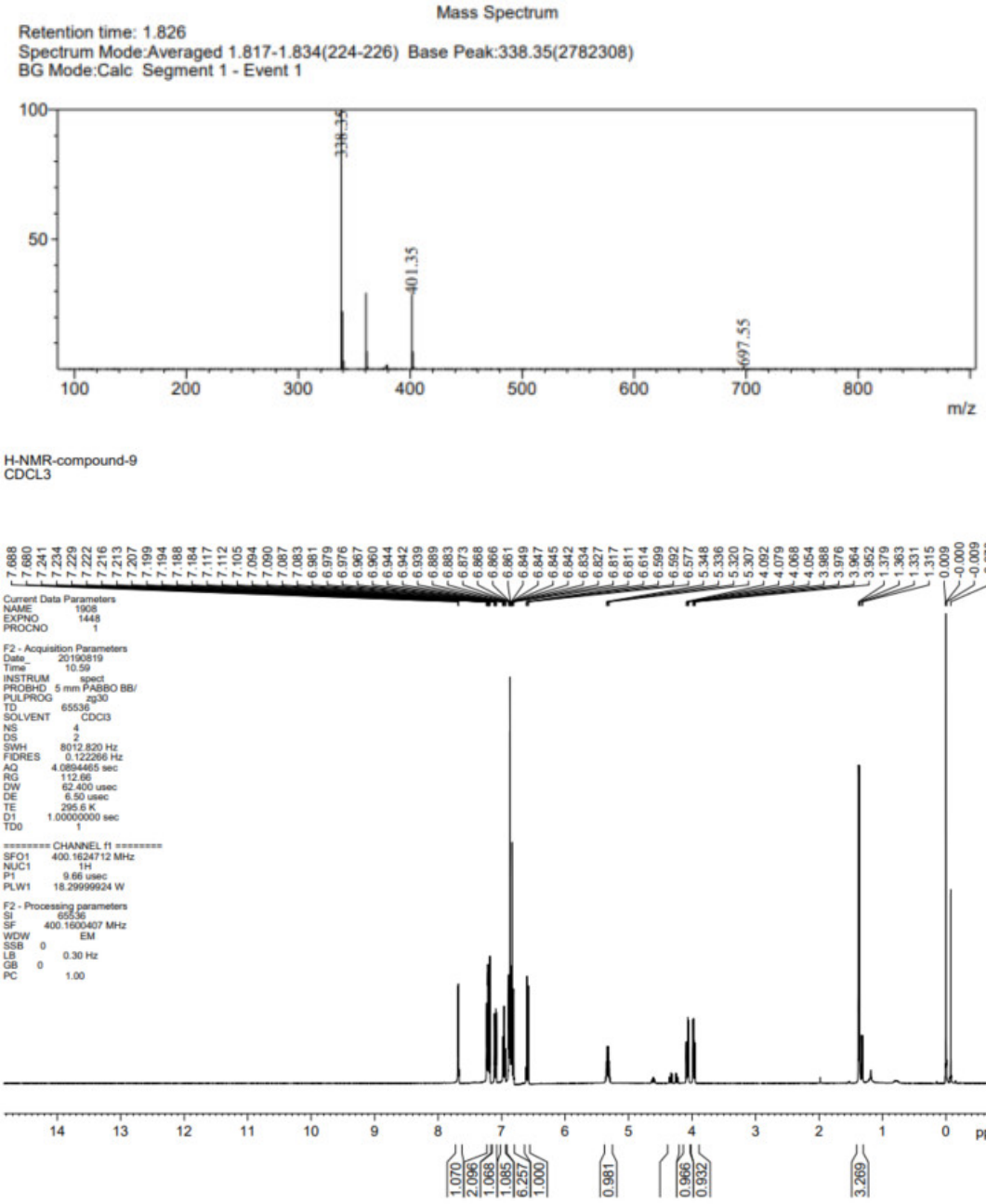
b. The LC-MS mass spectrum and ^{1}H NMR spectrum of PYPAC



c. The LC-MS mass spectrum and 1H NMR spectrum of DPH-Pyr



d. The LC-MS mass spectrum and ^{1}H NMR spectrum of 4'-OH-Pyr



e. The LC-MS mass spectrum and 1H NMR spectrum of 5"-OH-Pyr

Figure S1. The LC-MS and NMR spectrums of metabolites PYPA (a), PYPAC (b), DPH-Pyr (c), 4'-OH-Pyr (d), and 5"-OH-Pyr (e).

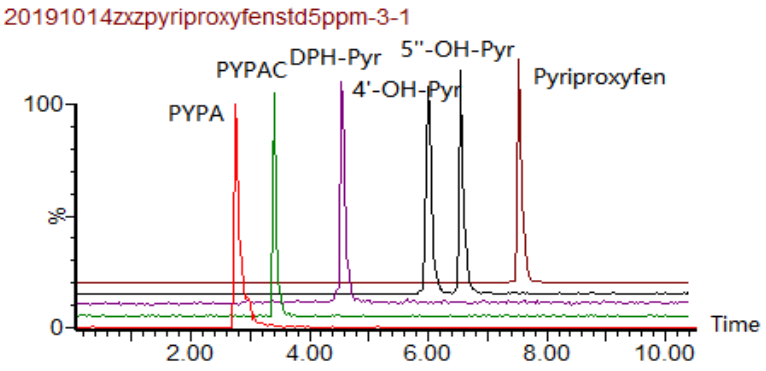


Figure S2. The chromatogram of pyriproxyfen and its metabolites under the optimized chromatographic conditions.

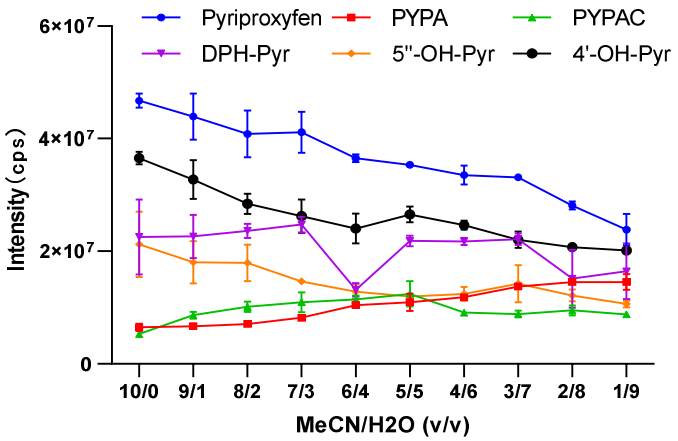


Figure S3. The responses of pyriproxyfen and its metabolites at different volume proportions of MeCN/H_2O as the injection solvents.

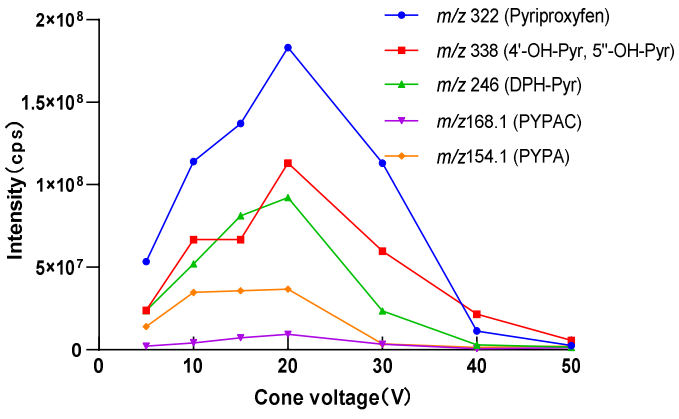


Figure S4. The responses of pyriproxyfen and its metabolites under different cone voltages.

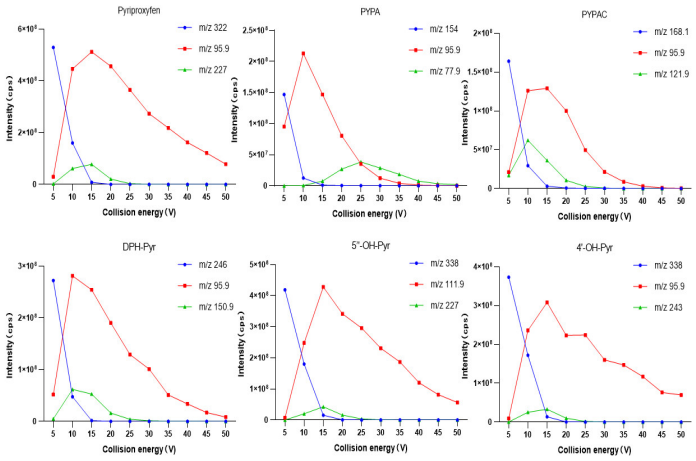


Figure S5. The responses of parent and daughter ions of pyriproxyfen and its metabolites under different collision energies.

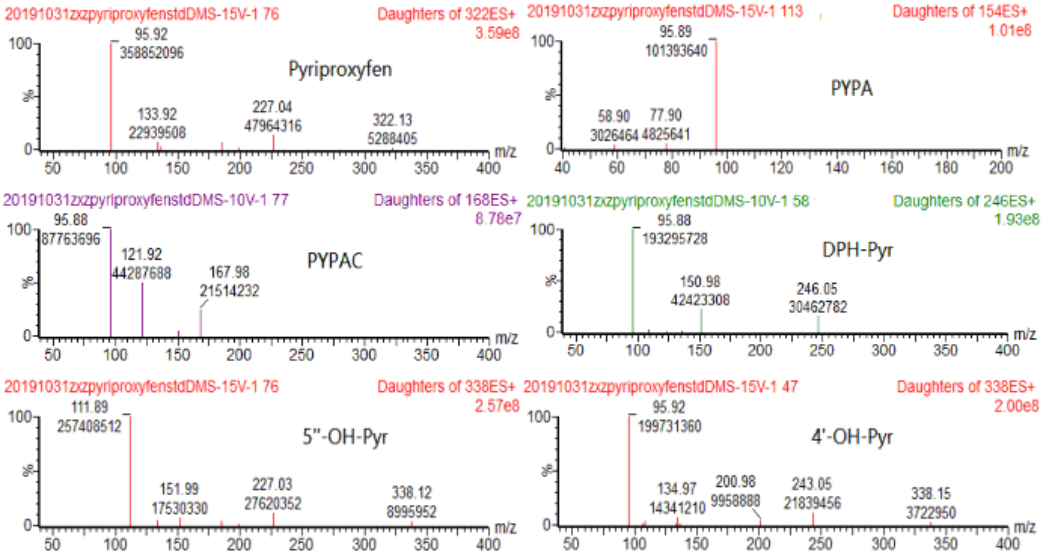


Figure S6. The fragmentation mass spectrometry of pyriproxyfen and its metabolites.

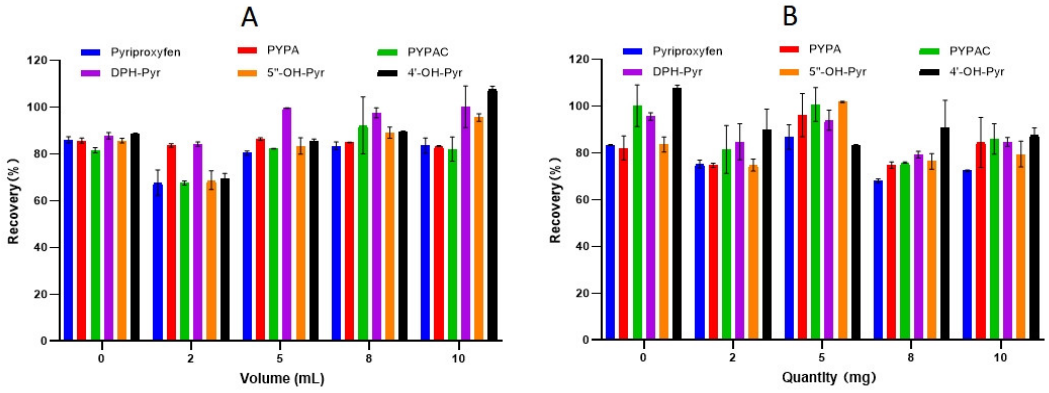


Figure S7. The recoveries of pyriproxyfen and its metabolites in different volumes of H_2O with 5% FA (A) and different quantities of $MgSO_4$ (B).

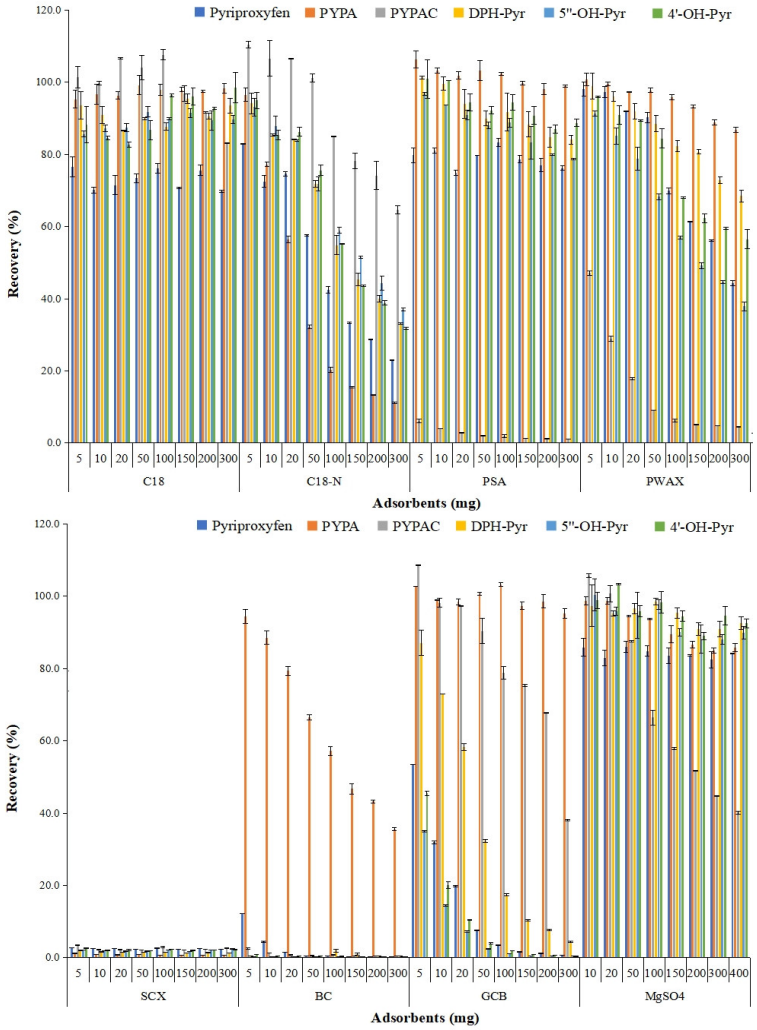


Figure S8. The recoveries of pyriproxyfen and its five metabolites under different types and different usages of purification adsorbents.