Suppl

Antioxidant Product Analysis of *Hulu Tea (Tadehagi triquetrum)*

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Note: This Supporting information provides the original data of **Table 1-2** in the main text.

Suppl. 1 Dose response curves

1. *DPPH•-scavenging assay*

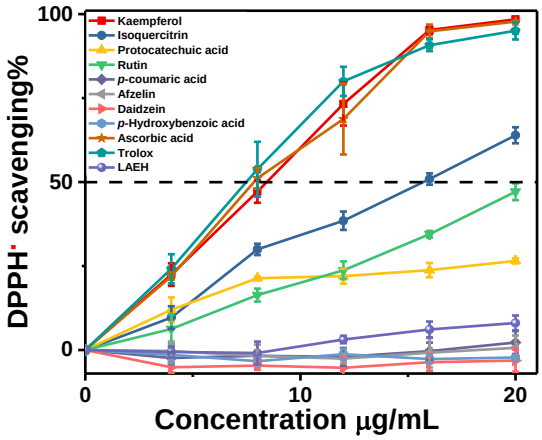


Figure S1.1: The dose response curves of kaempferol, isoquercitrin, protocatechuic acid, rutin, *p*-coumaric acid, afzelin, daidzein, *p*-hydroxybenzoic acid (pHBA), and LAEH in DPPH•-scavenging assay. Each value is expressed as mean ± SD (n = 3).

Tab. S1.1 The comparison of IC_{50} values of kaempferol, isoquercitrin, protocatechuic acid, rutin, *p*-coumaric acid, afzelin, daidzein, *p*-hydroxybenzoic acid (pHBA), and LAEH and positive control in DPPH•-scavenging assay.

	Mean±SD μg/mL	Mean±SD μM
kaempferol	8.5±0.6	29.8±2.3
isoquercitrin	15.5±0.3	33.4±0.6
protocatechuic acid	49.0±3.0	316.7±19.2
rutin	21.8±0.7	35.7±1.2
p-coumaric acid	145.4±34.2	885.9±208.4
afzelin	301.5±22.1	697.4±51.2
daidzein	272.6±34.7	1072.1±136.7
pHBA	6452.8±20.3	46718.0±146.7
LAEH	91.2±2.3	-
Ascorbic acid	8.5±0.6	48.5±3.6
Trolox	7.8±1.1	31.0±4.2

IC_{50} value was defined as the concentration of 50% superoxide anion radical inhibition and calculated by linear regression which was analyzed by Origin 6.0 professional software. Means values with different superscripts in the same column are significantly different ($p<0.05$).

2. PTIO•-scavenging assay

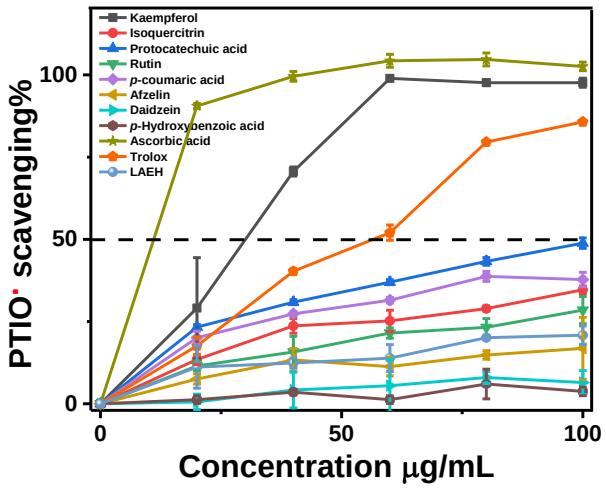


Figure S1.2: The dose response curves of kaempferol, isoquercitrin, protocatechuic acid, rutin, *p*-coumaric acid, afzelin, daidzein, *p*-hydroxybenzoic acid (pHBA), and LAEH in PTIO•-scavenging assay. Each value is expressed as mean ± SD (n = 3).

Tab. S1.2 The comparison of IC_{50} values of kaempferol, isoquercitrin, protocatechuic acid, rutin, *p*-coumaric acid, afzelin, daidzein, *p*-hydroxybenzoic acid (pHBA), and LAEH and positive control in PTIO•-scavenging assay.

	Mean±SD μg/mL	Mean±SD μM
kaempferol	30.0±4.8	104.9±16.7
isoquercitrin	164.7±8.3	354.7±18.0
protocatechuic acid	102.1±3.7	662.4±23.7
rutin	211.1±38.8	345.7±63.6
p-coumaric acid	141.5±11.1	862.3±67.5
afzelin	734.6±495.2	1699.0±1145.2
daidzein	689.4±249.2	2711.6±980.3
pHBA	3057.8±201.4	22138.5±1458.4
LAEH	328.4±72.6	-
Ascorbic acid	19.9±0.5	113.1±2.7
Trolox	54.2±1.4	216.6±5.5

IC_{50} value was defined as the concentration of 50% superoxide anion radical inhibition and calculated by linear regression which was analyzed by Origin 6.0 professional software. Means values with different superscripts in the same column are significantly different ($p<0.05$).

3. Fe^{2+}-reducing assay

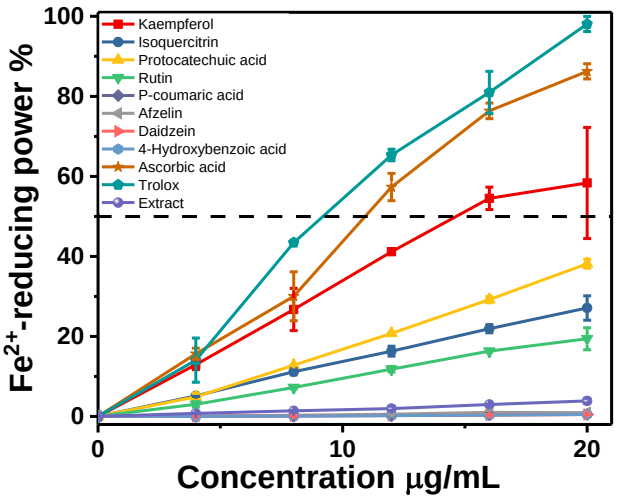


Figure S1.3: The dose response curves of kaempferol, isoquercitrin, protocatechuic acid, rutin, *p*-coumaric acid, afzelin, daidzein, *p*-hydroxybenzoic acid (pHBA), and LAEH in Fe^{2+}-reducing assay. Each value is expressed as mean ± SD (n = 3).

Tab. S1.3 The comparison of IC_{50} values of kaempferol, isoquercitrin, protocatechuic acid, rutin, *p*-coumaric acid, afzelin, daidzein, *p*-hydroxybenzoic acid (pHBA), and LAEH and positive control in Fe^{2+}-reducing assay.

	Mean±SD μg/mL	Mean±SD μM
kaempferol	15.9±1.6	55.6±5.7
isoquercitrin	36.8±3.0	79.3±6.4
protocatechuic acid	26.7±0.5	173.1±3.4
rutin	50.3±4.6	82.4±7.6
p-coumaric acid	1653.1±212.3	10070.2±1293.1
afzelin	963.0±156.9	2227.2±362.9
daidzein	2224.6±199.3	8749.8±784.1
*p*HBA	2177.0±184.9	15761.4±1338.9
LAEH	243.5±34.6	-
Ascorbic acid	11.3±0.4	63.9±2.1
Trolox	9.9±0.2	39.7±1.0

IC_{50} value was defined as the concentration of 50% superoxide anion radical inhibition and calculated by linear regression which was analyzed by Origin 6.0 professional software. Means values with different superscripts in the same column are significantly different ($p<0.05$).

4. Cu^{2+}-reducing assay

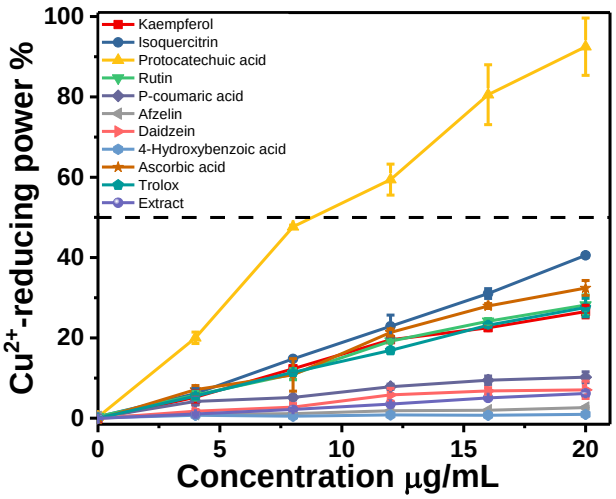


Figure S1.4: The dose response curves of kaempferol, isoquercitrin, protocatechuic acid, rutin, *p*-coumaric acid, afzelin, daidzein, *p*-hydroxybenzoic acid (pHBA), and LAEH in Cu^{2+}-reducing assay. Each value is expressed as mean ± SD (n = 3).

Tab. S1.4 The comparison of IC_{50} values of kaempferol, isoquercitrin, protocatechuic acid, rutin, *p*-coumaric acid, afzelin, daidzein, *p*-hydroxybenzoic acid (pHBA), and LAEH and positive control in Cu^{2+}-reducing assay.

	Mean±SD μg/mL	Mean±SD μM
kaempferol	36.0±1.2	125.7±4.2
isoquercitrin	25.1±0.3	54.1±0.6
protocatechuic acid	10.0±0.5	64.9±3.5
rutin	34.5±1.8	56.5±2.9
p-coumaric acid	100.6±12.6	612.8±76.5
afzelin	457.8±31.2	1058.9±72.2
daidzein	131.8±19.9	518.6±78.2
*p*HBA	1602.7±582.5	11603.6±4217.6
LAEH	189.4±15.7	-
Ascorbic acid	29.8±1.1	169.4±6.2
Trolox	35.7±2.1	142.7±8.4

IC_{50} value was defined as the concentration of 50% superoxide anion radical inhibition and calculated by linear regression which was analyzed by Origin 6.0 professional software. Means values with different superscripts in the same column are significantly different ($p<0.05$).

Suppl. 2 isoquercitrin-DPPH• adducts

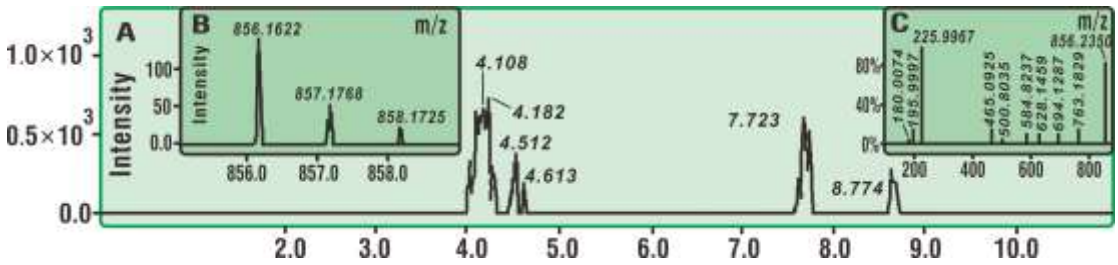


Figure S2.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (A) Chromatogram of isoquercitrin-DPPH adduct when the formula [$C_{39}H_{32}N_5O_{18}$-H] was extracted; (B) primary MS spectra of isoquercitrin-DPPH adduct; (C) secondary MS spectra of isoquercitrin-DPPH adduct.

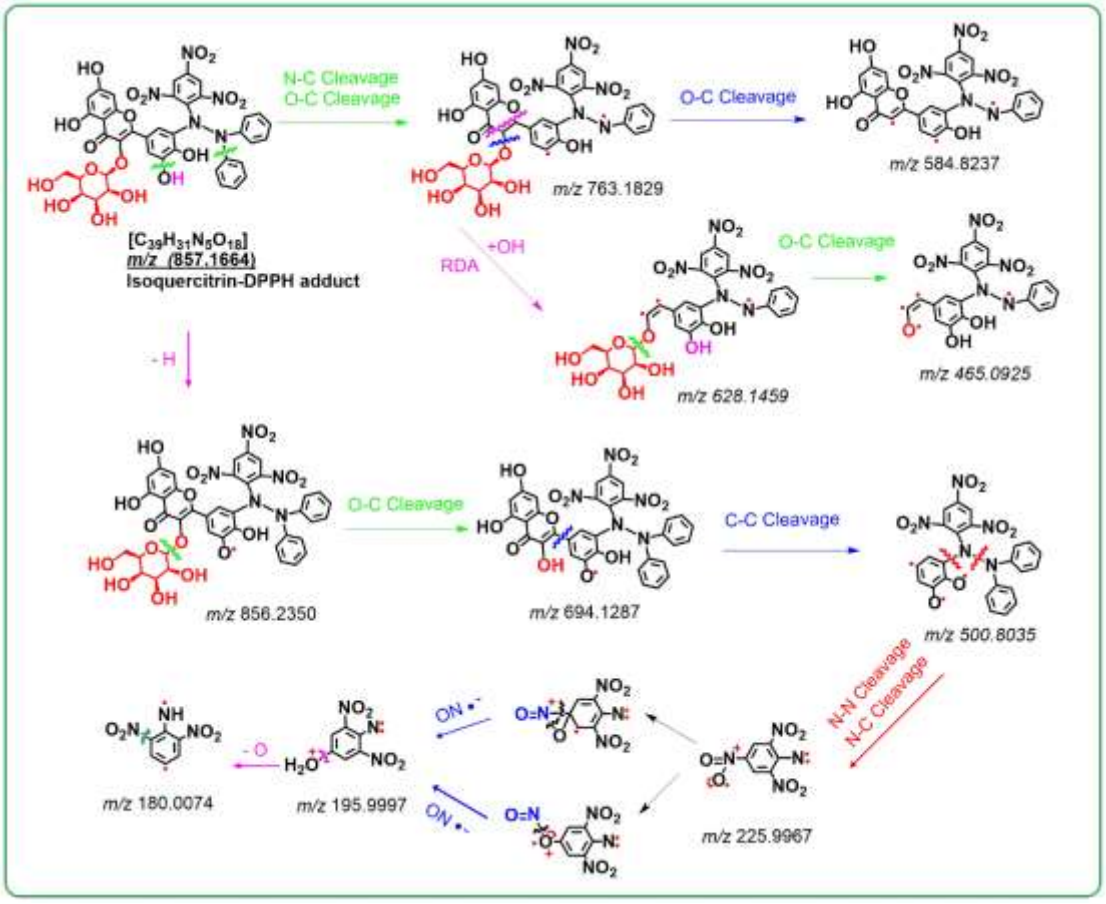


Figure S2.2 One of the possible interpretations of mass spectra of isoquercitrin-DPPH adduct (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 3 rutin-DPPH• adducts

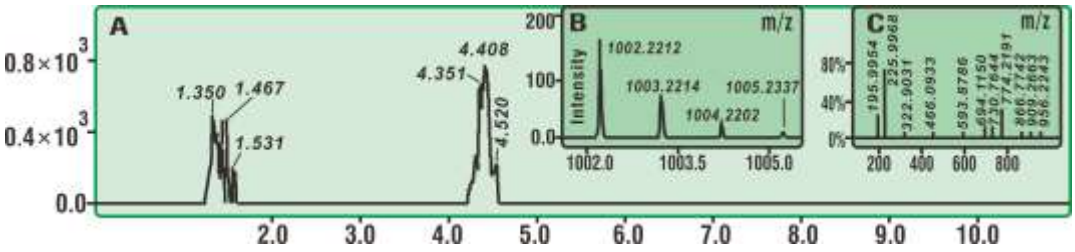


Figure S3.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (A) Chromatogram of rutin-DPPH adduct when the formula [$C_{45}H_{42}N_5O_{22}$-H] was extracted; (B) primary MS spectra of rutin-DPPH adduct; (C) secondary MS spectra of rutin-DPPH adduct.

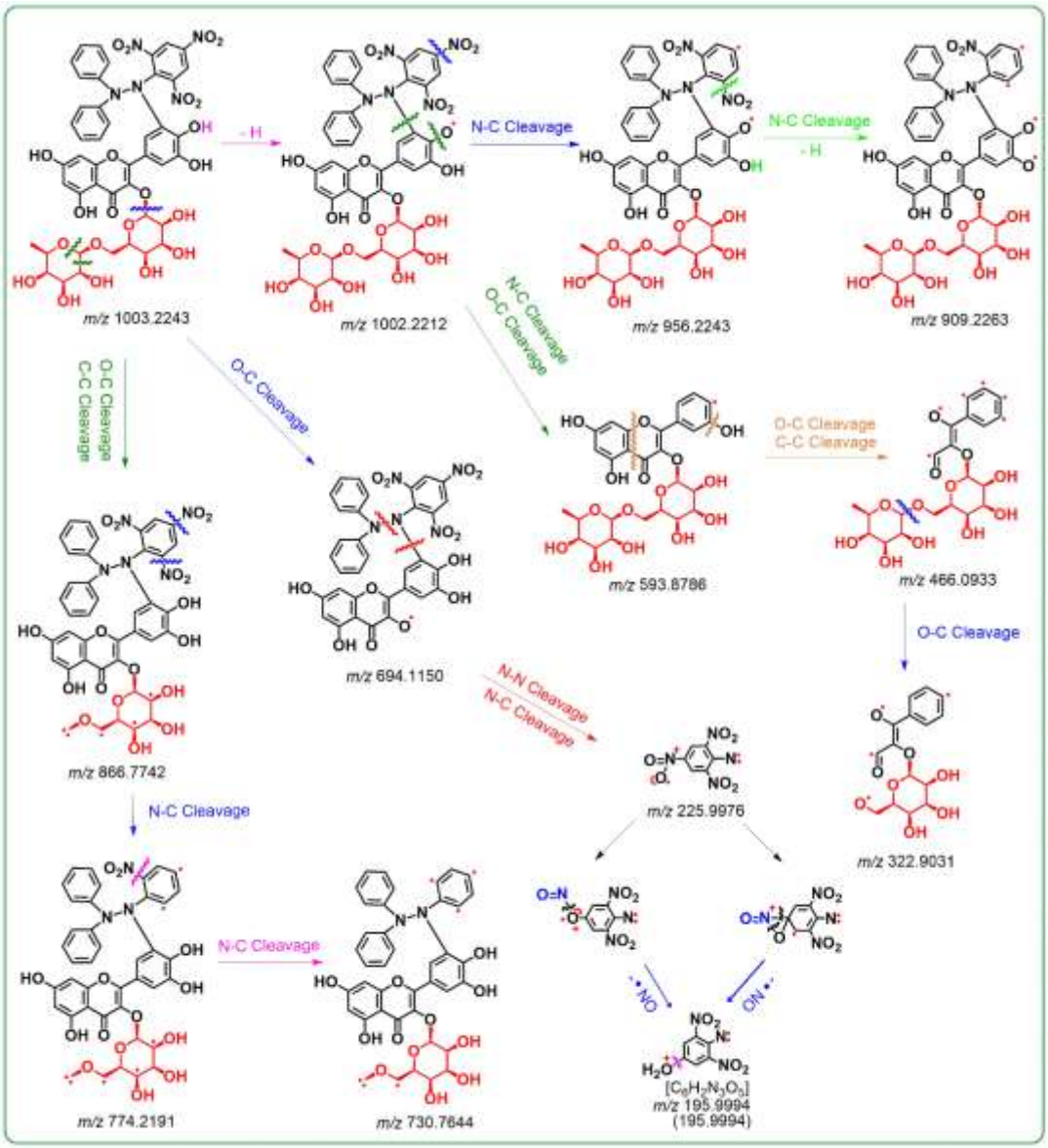


Figure S3.2 One of the possible interpretations of mass spectra of rutin-DPPH adduct (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 4 protocatechuic acid-DPPH• adducts

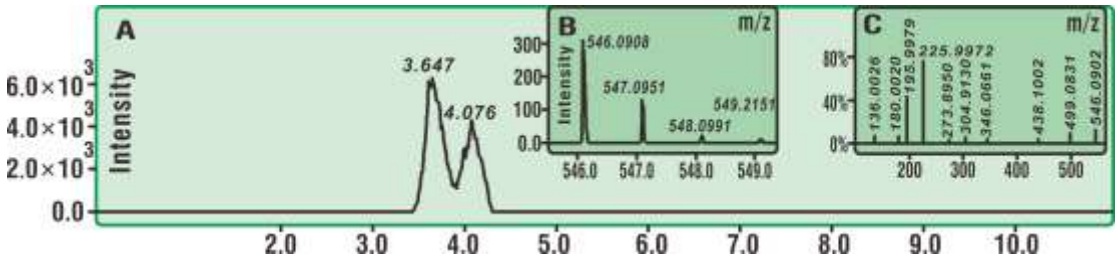


Figure S4.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (A) Chromatogram of protocatechuic acid-DPPH adduct when the formula [$C_{25}H_{18}N_5O_{10}$-H] was extracted; (B) primary MS spectra of protocatechuic acid-DPPH adduct; (C) secondary MS spectra of protocatechuic acid-DPPH adduct.

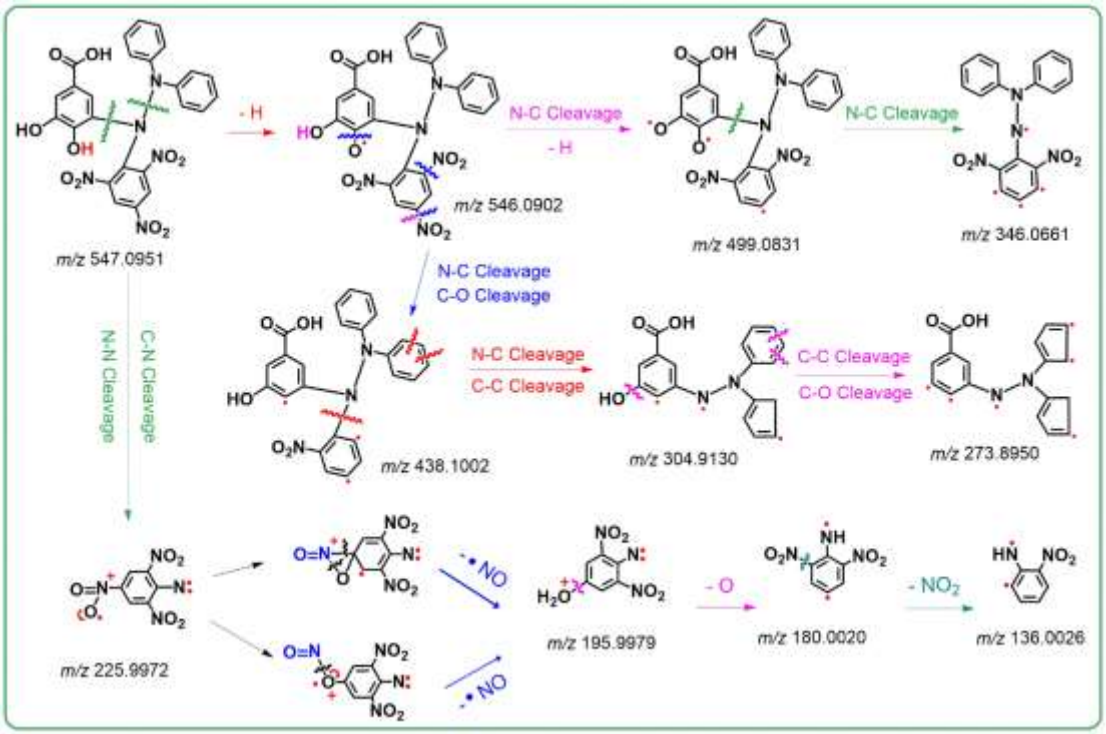


Figure S4.2 One of the possible interpretations of mass spectra of protocatechuic acid-DPPH adduct (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 5 daidzein-DPPH• adducts

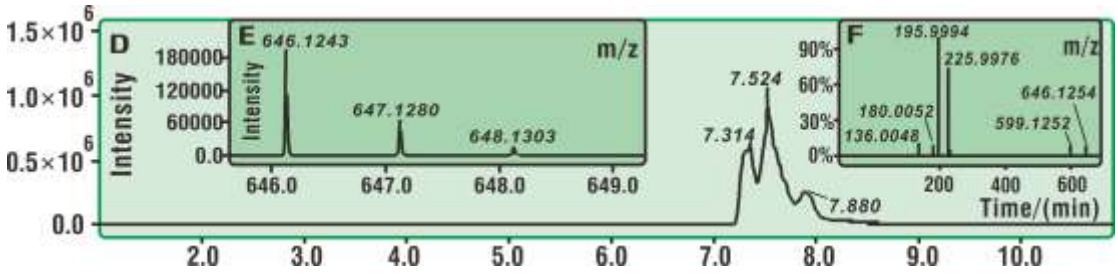


Figure S5.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (D) Chromatogram of daidzein-DPPH adduct when the formula [$C_{33}H_{22}N_5O_{10}$-H] was extracted; (E) primary MS spectra of daidzein-DPPH adduct; (F) secondary MS spectra of daidzein-DPPH adduct.

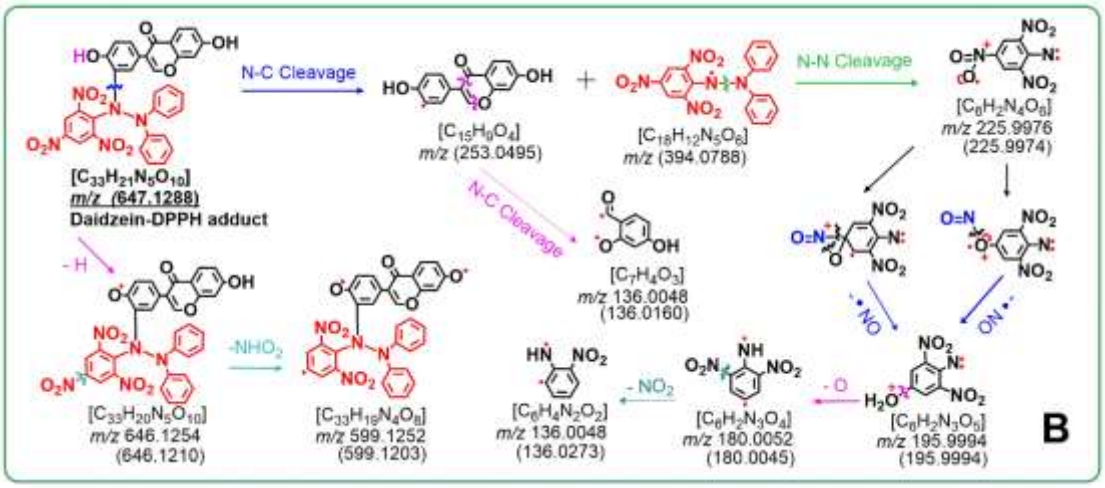


Figure S5.2 One of the possible interpretations of mass spectra of daidzein-DPPH adduct (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

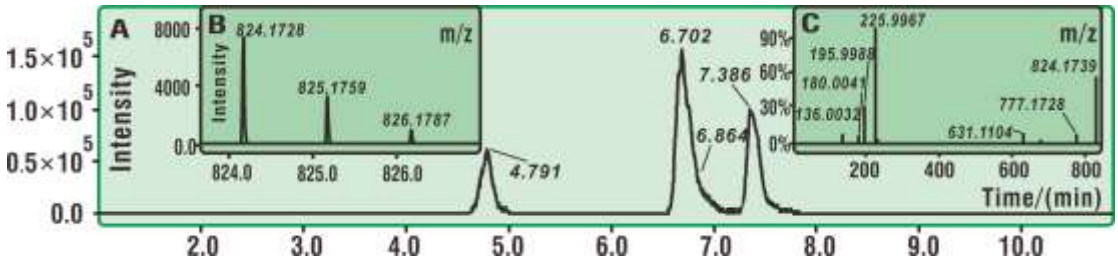


Figure S6.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (A) Chromatogram of afzelin-DPPH adduct when the formula [$C_{39}H_{32}N_5O_{16}$-H] was extracted; (B) primary MS spectra of afzelin-DPPH adduct; (C) secondary MS spectra of afzelin-DPPH adduct.

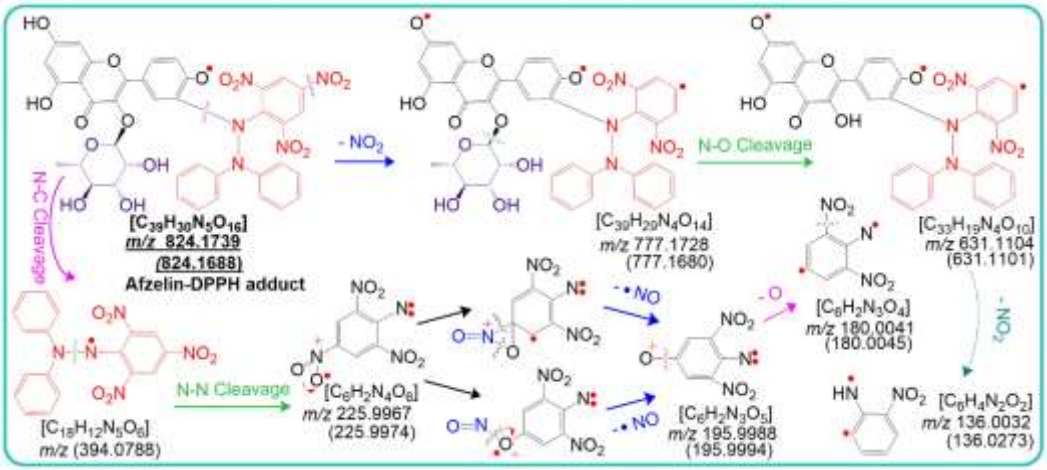


Figure S6.2 One of the possible interpretations of mass spectra of afzelin-DPPH adduct (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 7 p-coumaric acid-DPPH• adducts

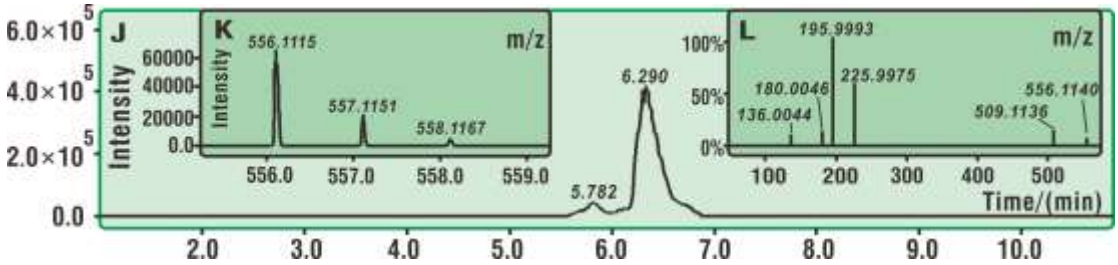


Figure S7.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (J) Chromatogram of *p*-coumaric acid-DPPH adduct when the formula [$C_{27}H_{20}N_5O_9$-H] was extracted; (K) primary MS spectra of *p*-coumaric acid-DPPH adduct; (L) secondary MS spectra of *p*-coumaric acid-DPPH adduct.

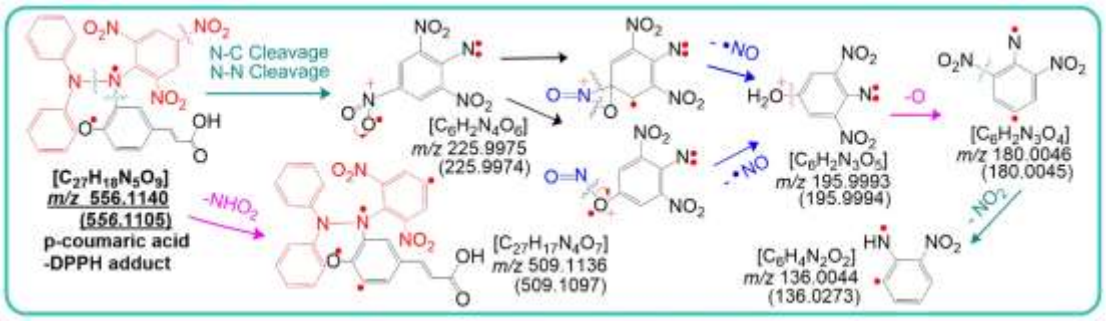


Figure S7.2 One of the possible interpretations of mass spectra of *p*-coumaric acid-DPPH adduct (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 8 pHBA-DPPH• adducts

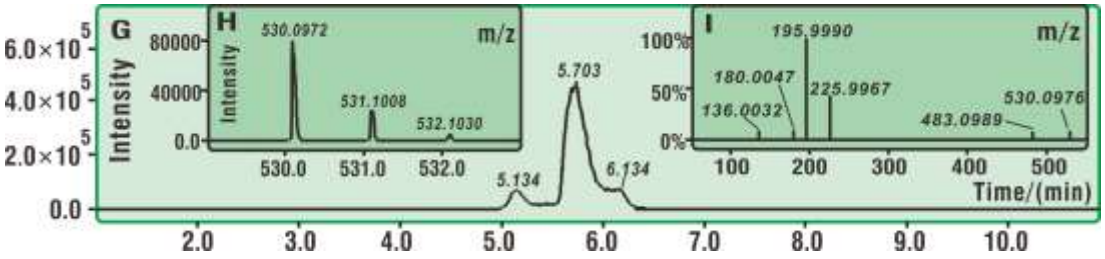


Figure S8.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (G) Chromatogram of pHBA-DPPH adduct when the formula [$C_{25}H_{18}N_5O_9$-H] was extracted; (H) primary MS spectra of pHBA-DPPH adduct; (L) secondary MS spectra of pHBA-DPPH adduct.

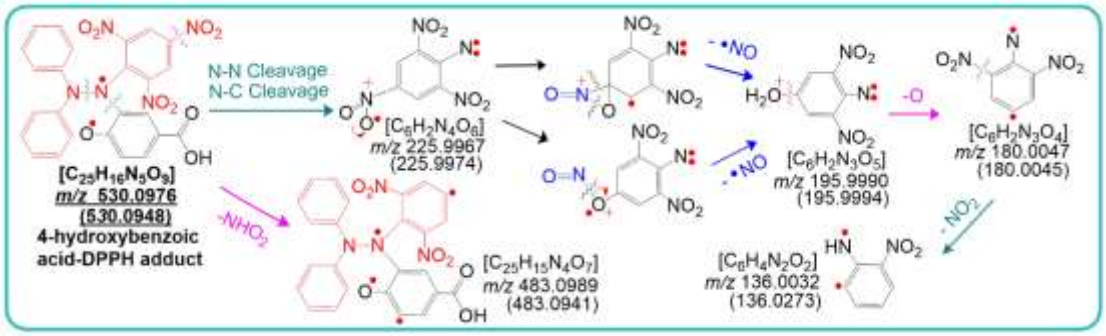


Figure S8.2 One of the possible interpretations of mass spectra of pHBA-DPPH adduct (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 9 kaempferol-kaempferol homodimers

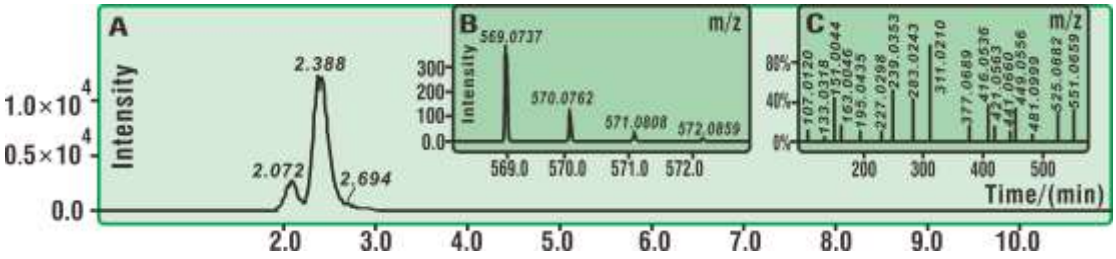


Figure S9.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (A) Chromatogram of kaempferol- kaempferol homodimers when the formula [$C_{30}H_{20}O_{12}$-2H] was extracted; (B) primary MS spectra of kaempferol- kaempferol homodimers; (C) secondary MS spectra of kaempferol- kaempferol homodimers.

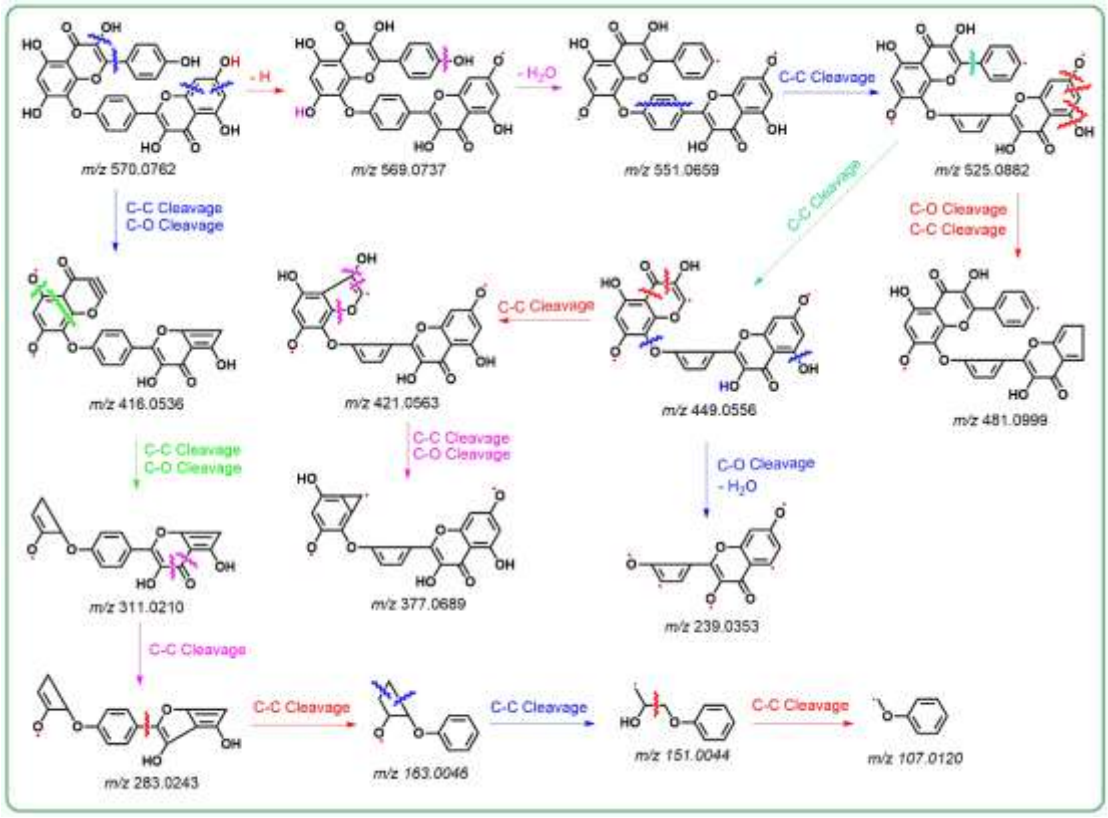


Figure S9.2 One of the possible interpretations of mass spectra of kaempferol- kaempferol homodimers (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

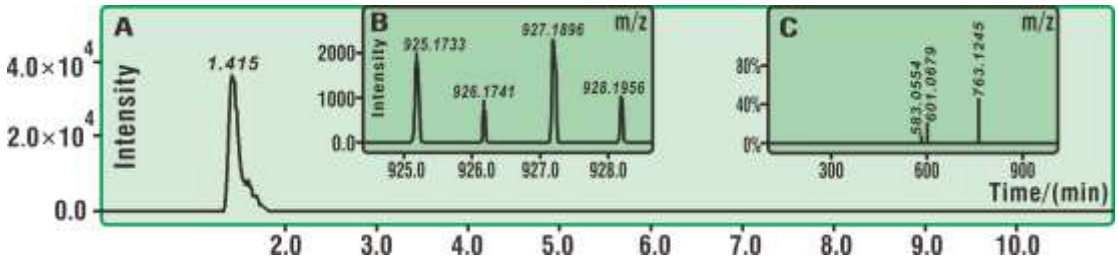


Figure S10.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (A) Chromatogram of isoquercitrin- isoquercitrin homodimers when the formula [$C_{42}H_{40}O_{24}$-2H] was extracted; (B) primary MS spectra of isoquercitrin- isoquercitrin homodimers; (C) secondary MS spectra of isoquercitrin- isoquercitrin homodimers.

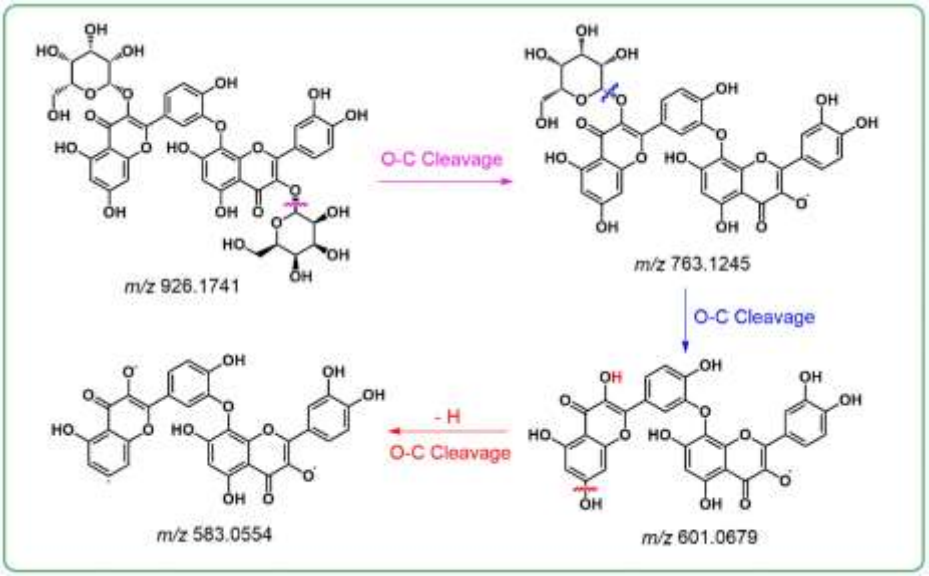


Figure S10.2 One of the possible interpretations of mass spectra of isoquercitrin- isoquercitrin homodimers (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 11 daidzein-daidzein homodimers

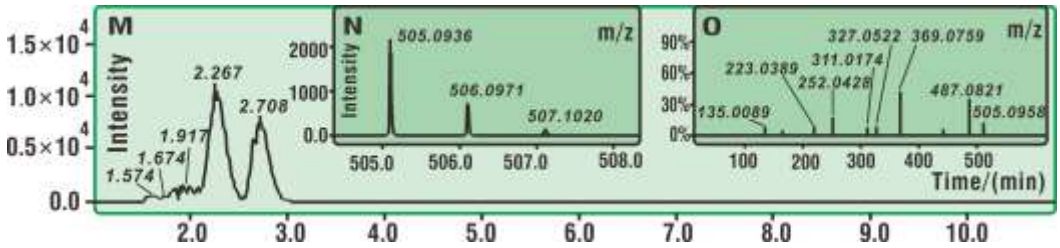


Figure S11.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (M) Chromatogram of daidzein- daidzein homodimers when the formula [$C_{30}H_{20}O_8$-2H] was extracted; (N) primary MS spectra of daidzein- daidzein homodimers; (O) secondary MS spectra of daidzein-daidzein homodimers.

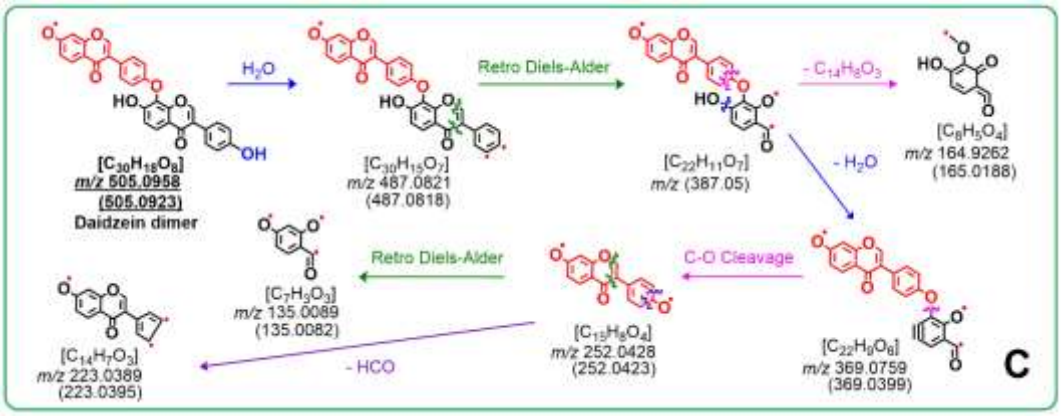


Figure S11.2 One of the possible interpretations of mass spectra of daidzein- daidzein homodimers (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 12 p-coumaric acid- p-coumaric acid homodimers

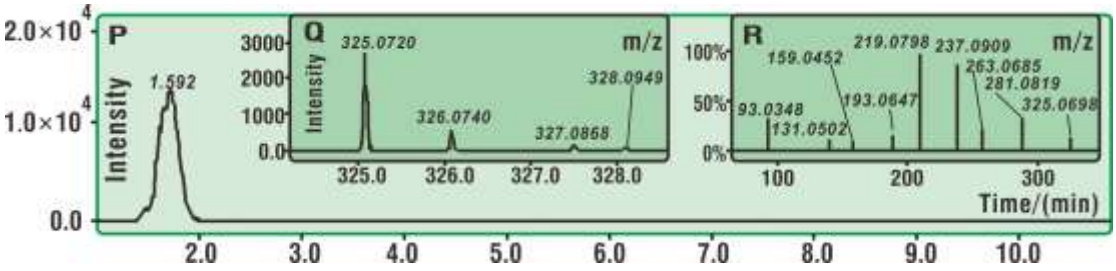


Figure S12.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (P) Chromatogram of *p*-coumaric acid- *p*-coumaric acid homodimers when the formula [$C_{18}H_{16}O_6$-2H] was extracted; (Q) primary MS spectra of *p*-coumaric acid- *p*-coumaric acid homodimers; (R) secondary MS spectra of *p*-coumaric acid- *p*-coumaric acid homodimers.

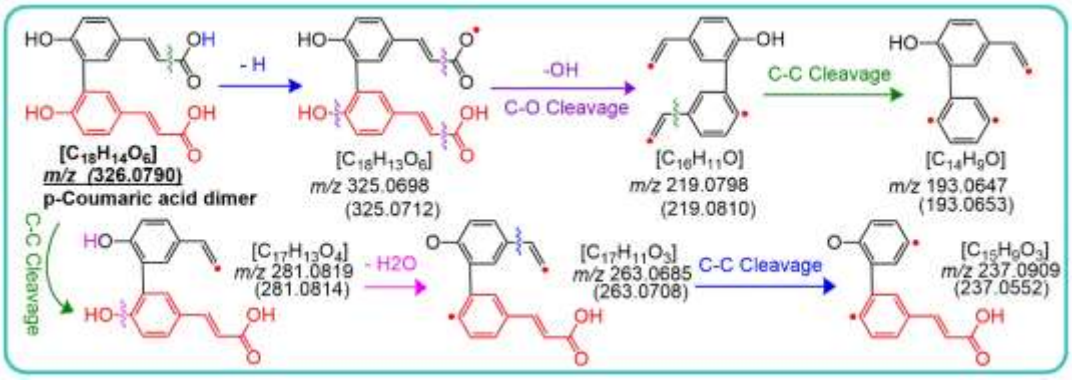


Figure S12.2 One of the possible interpretations of mass spectra of *p*-coumaric acid- *p*-coumaric acid homodimers (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Suppl. 13 p-coumaric acid plus pHBA heterodimers

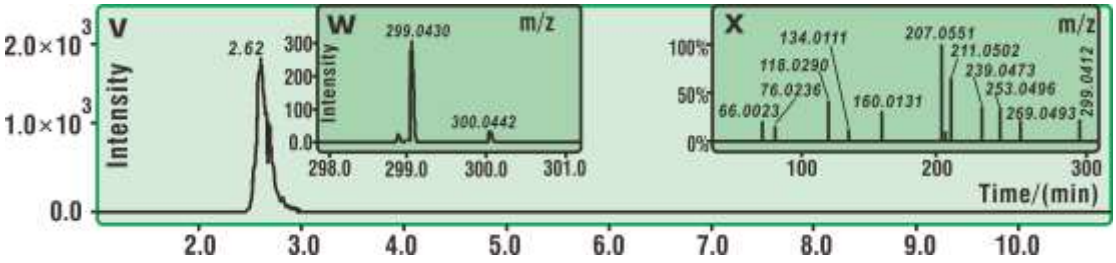


Figure S13.1: Typical results of the UPLC-ESI-Q-TOF-MS analysis: (V) Chromatogram of *p*-coumaric acid plus pHBA heterodimers when the formula [$C_{16}H_{12}O_6$-2H] was extracted; (W) primary MS spectra of *p*-coumaric acid plus pHBA heterodimers; (X) secondary MS spectra of *p*-coumaric acid plus pHBA heterodimers.

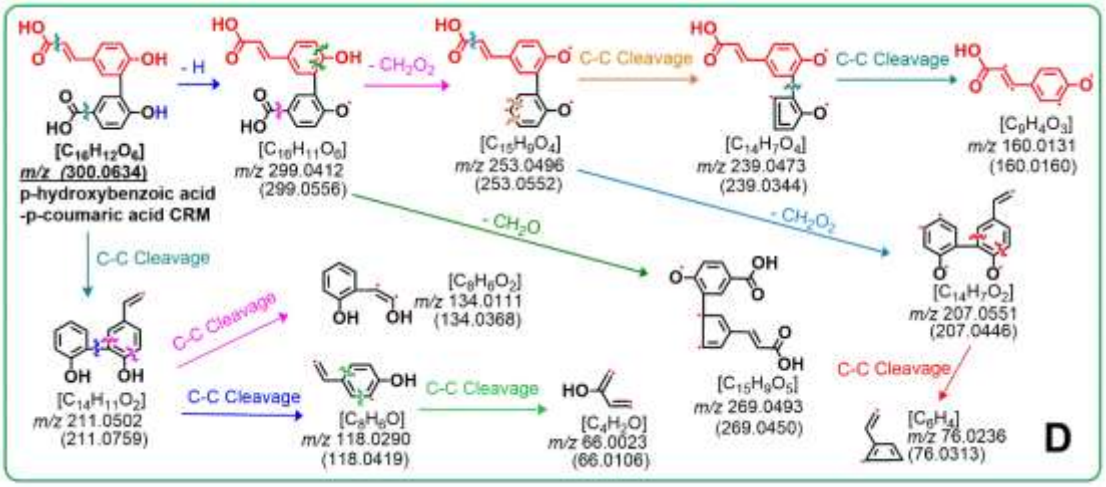
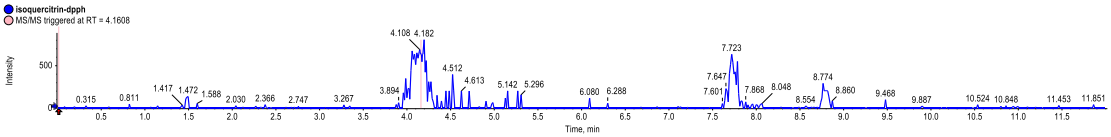
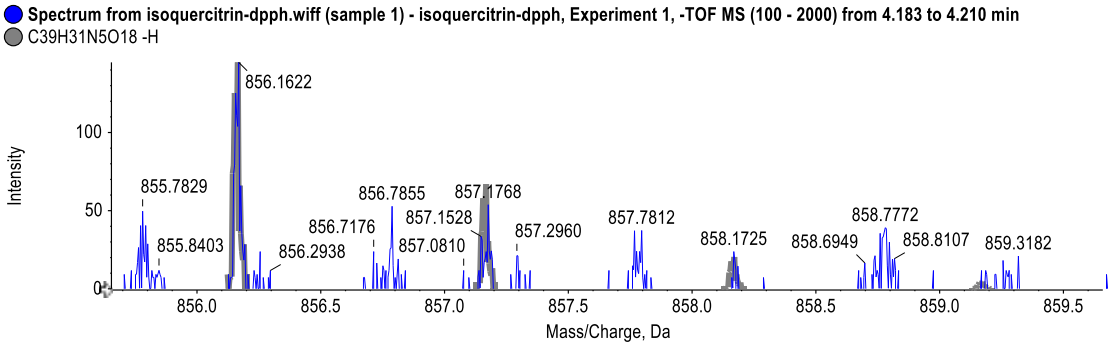


Figure S13.2 One of the possible interpretations of mass spectra of *p*-coumaric acid plus pHBA heterodimers (Other possible linking sites should not be excluded. The mass spectrogram was conducted under a negative ion model. The charge applied by the mass spectrogram is not shown. The relative atomic masses of C, H, O, and N were 12.0000, 1.007825, 15.994915, and 14.003074, respectively.)

Figure S2.1 (Raw figure)





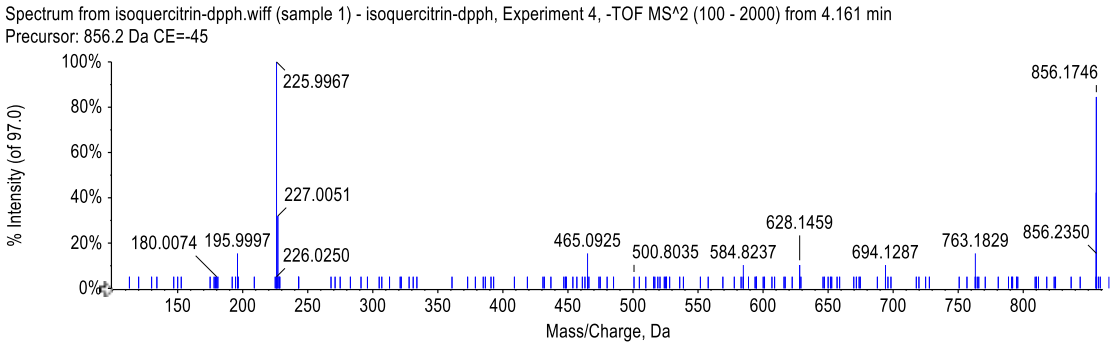
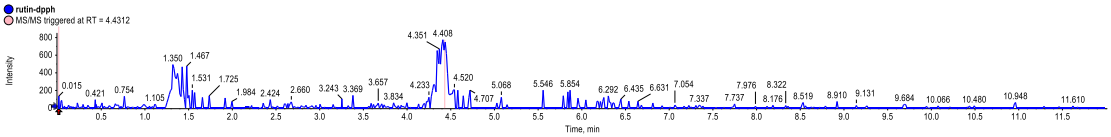
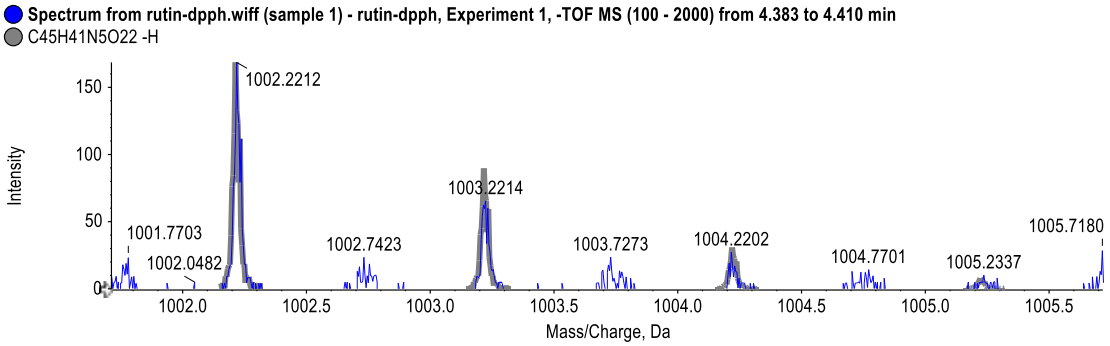


Figure S3.1 (Raw figure)





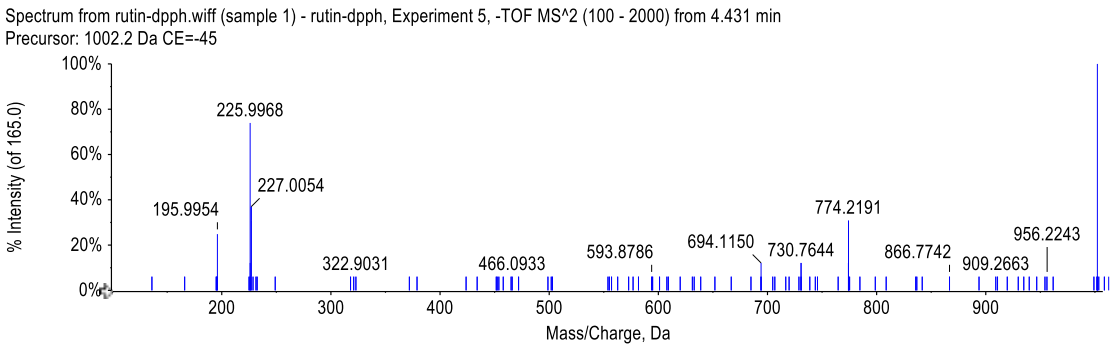
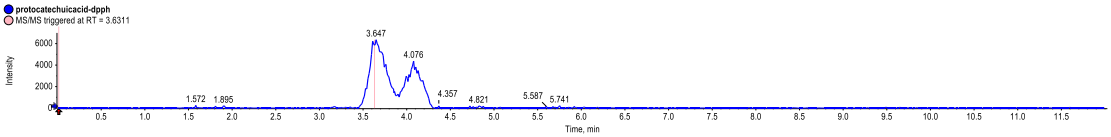
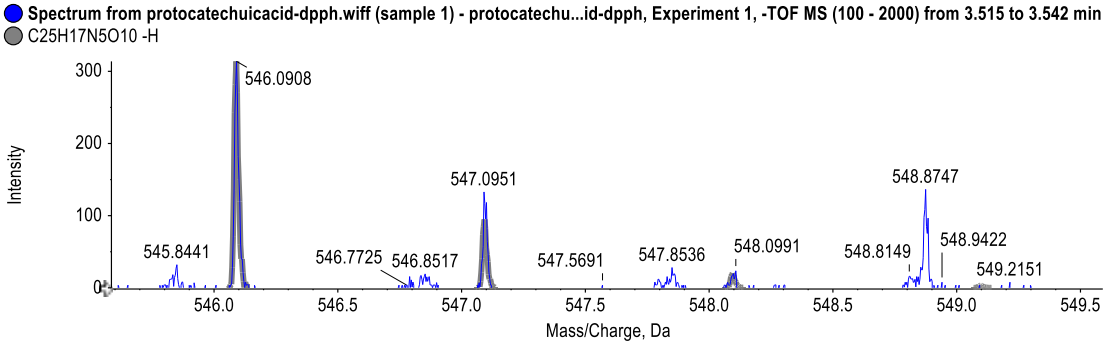


Figure S4.1 (Raw figure)





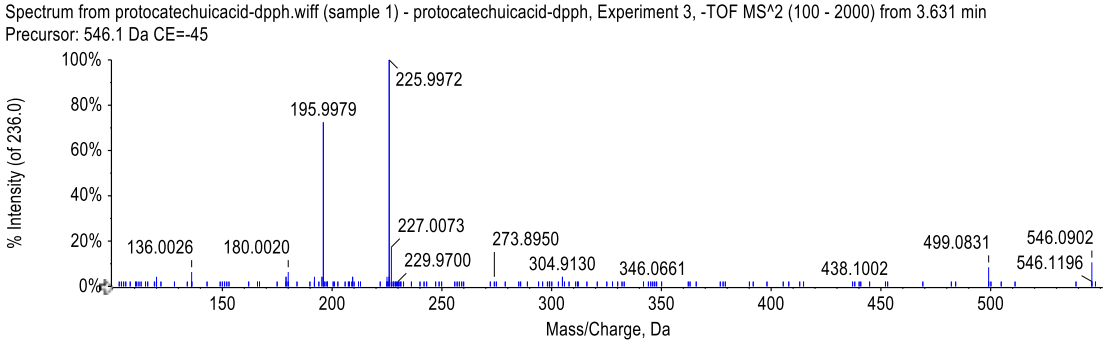


Figure S5.1 (Raw figure)

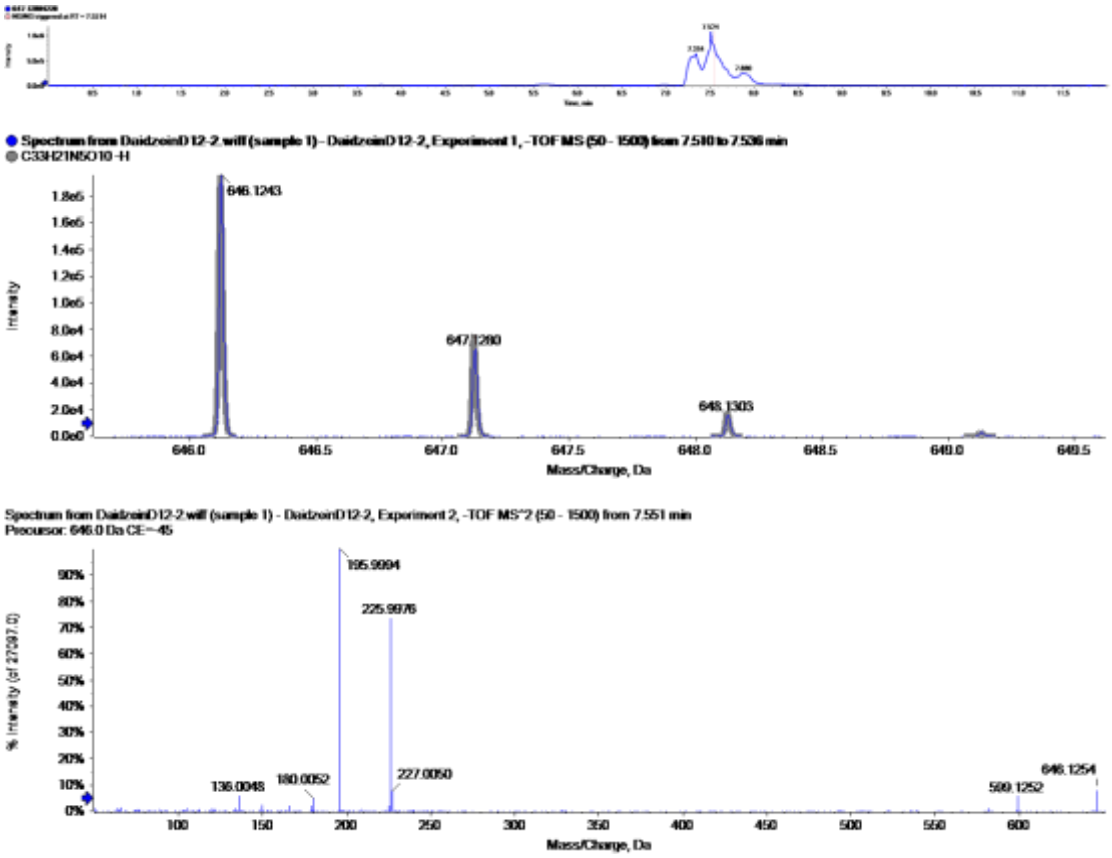


Figure S6.1 (Raw figure)

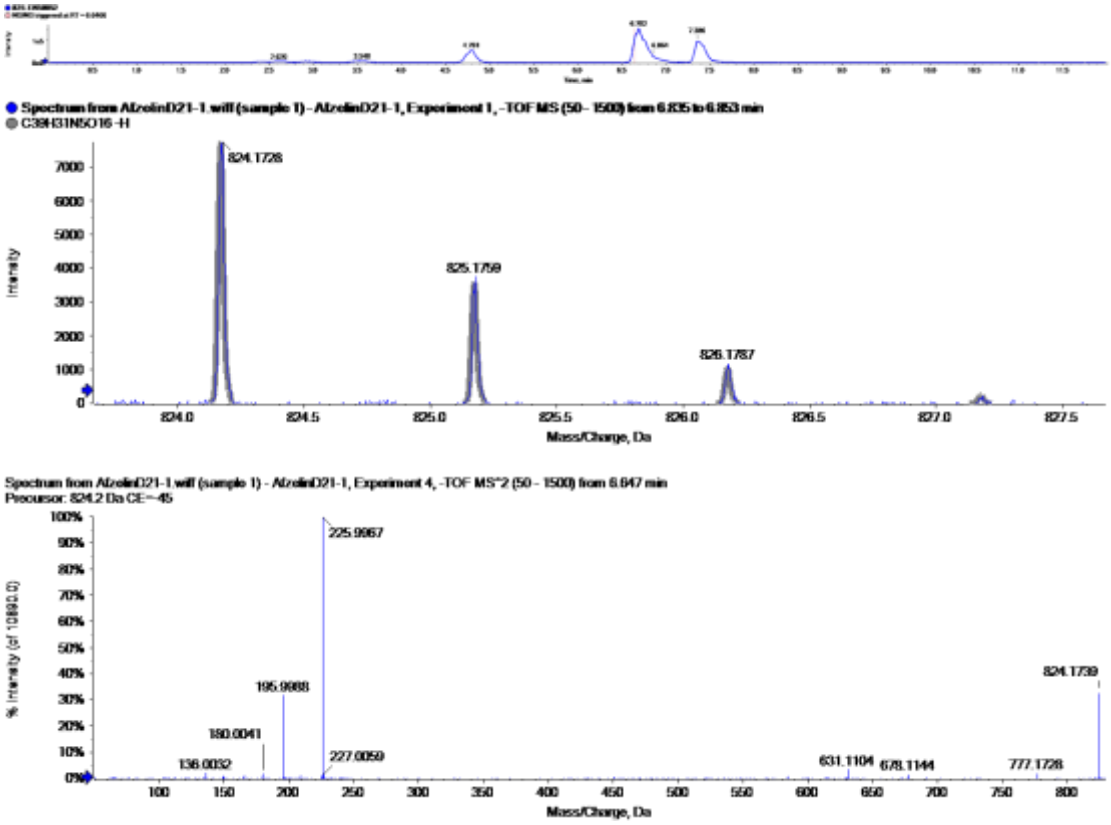
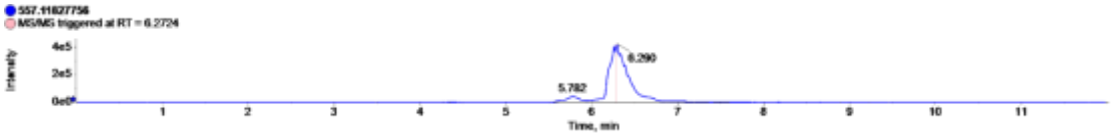
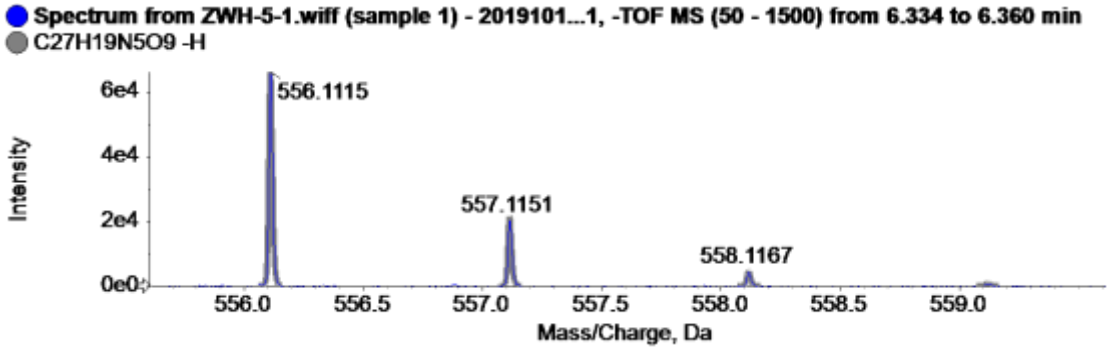


Figure S7.1 (Raw figure)





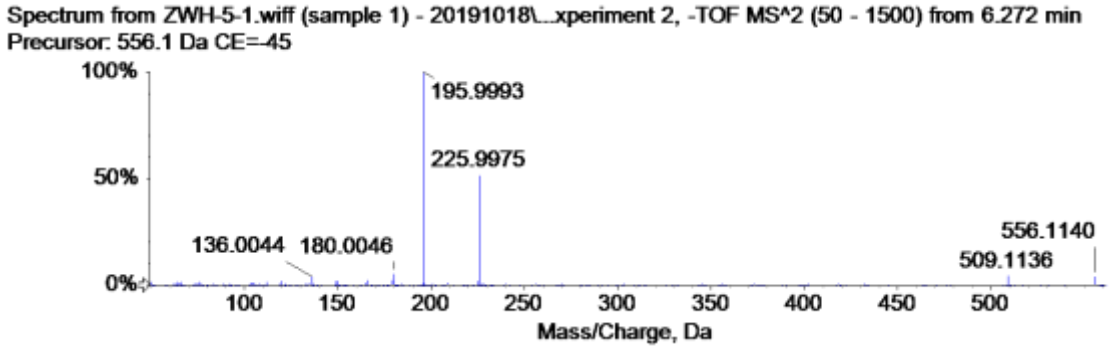
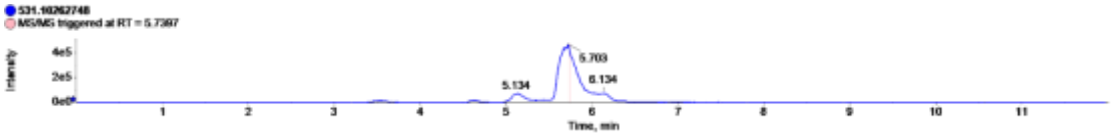
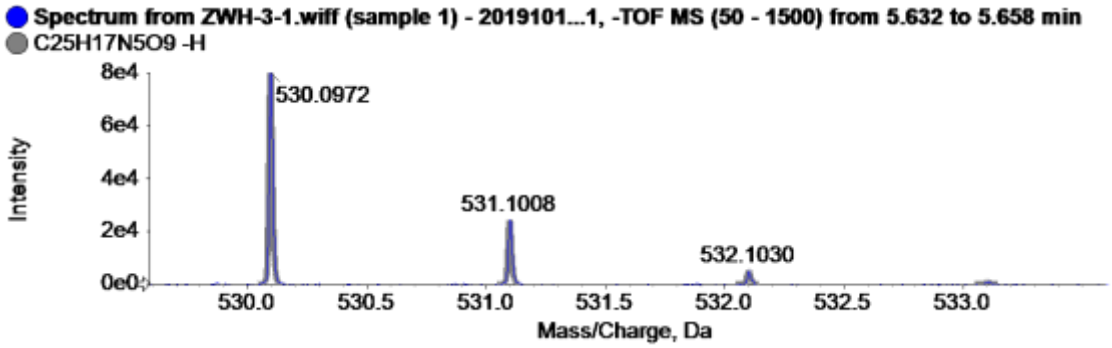
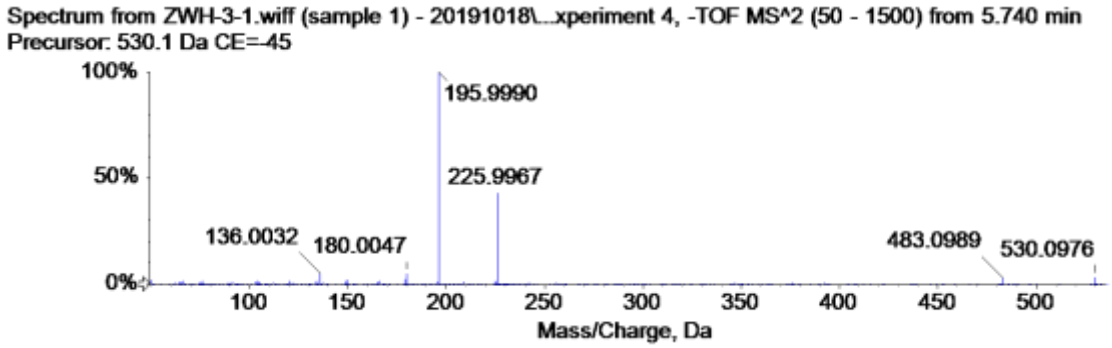


Figure S8.1 (Raw figure)







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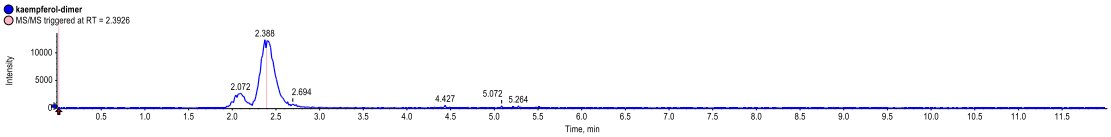
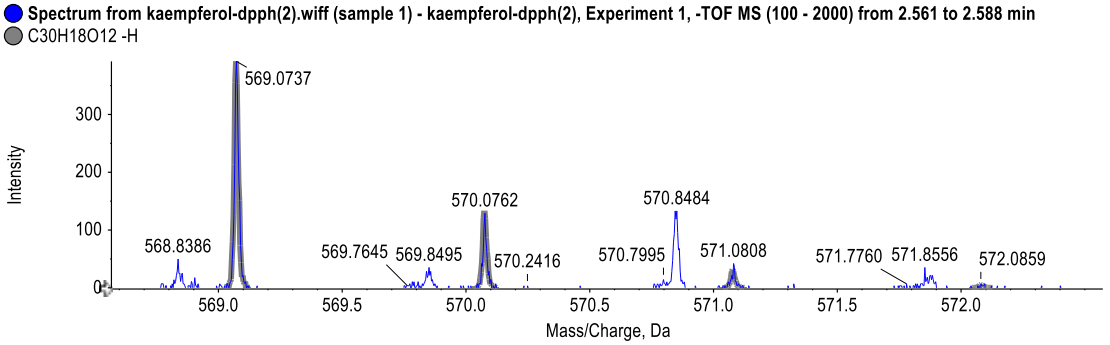




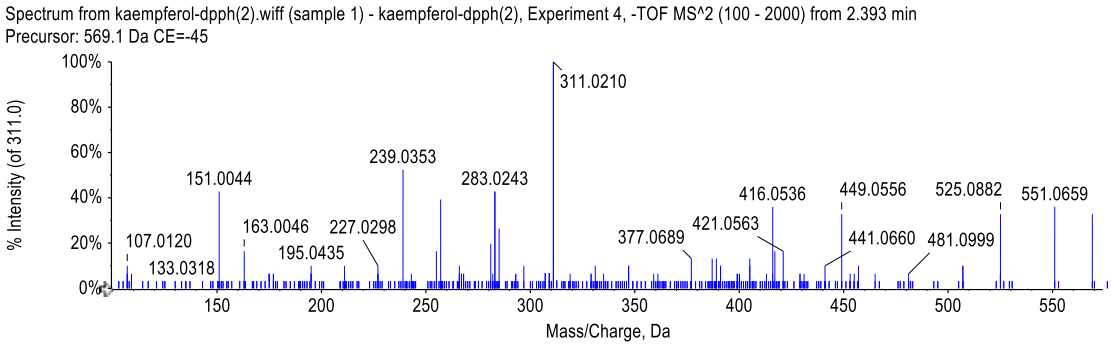
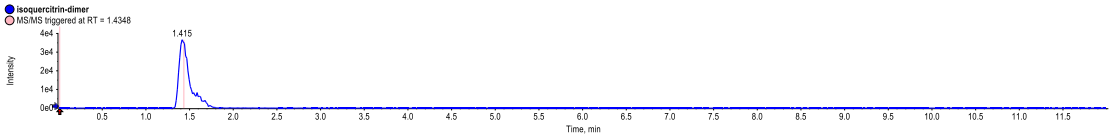
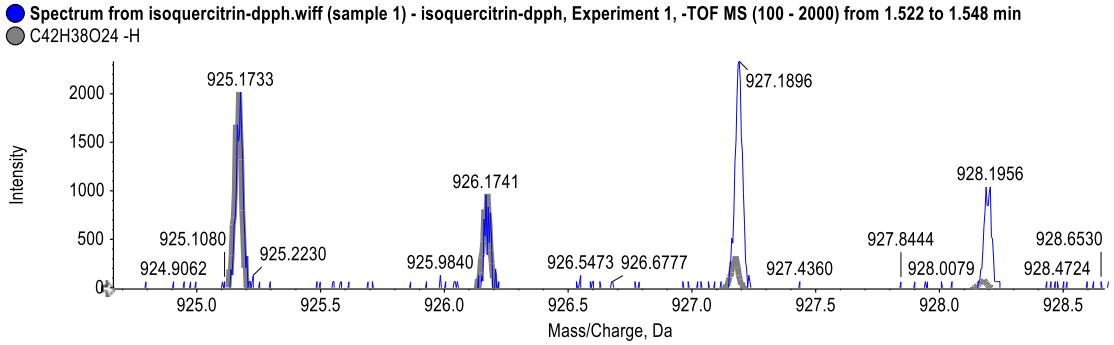
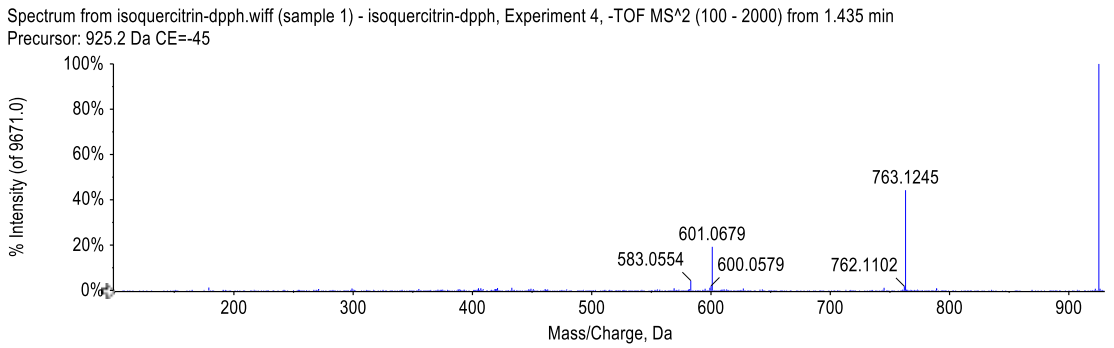


Figure S10.1 (Raw figure)







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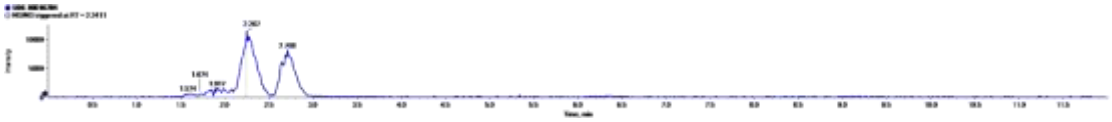

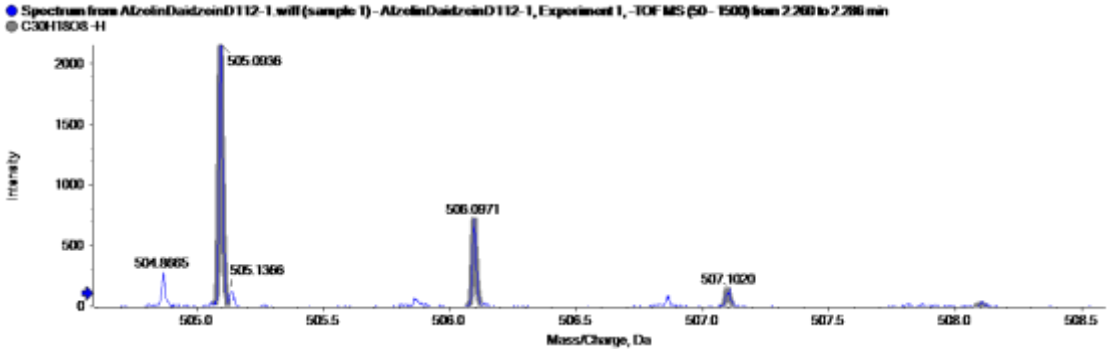

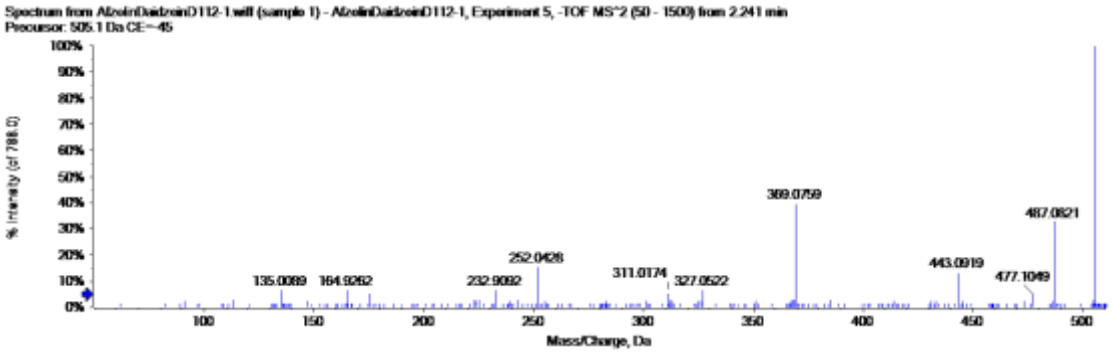

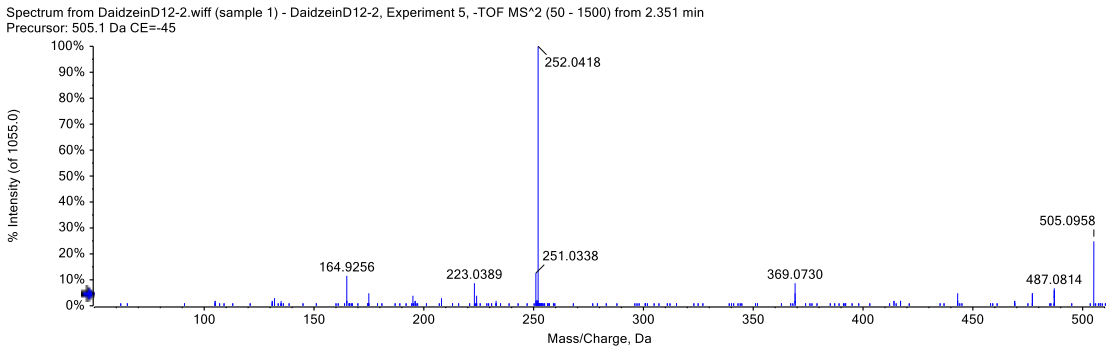

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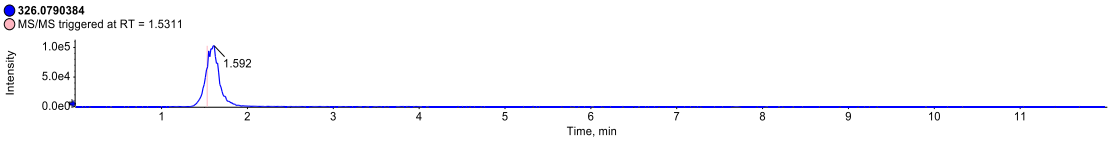

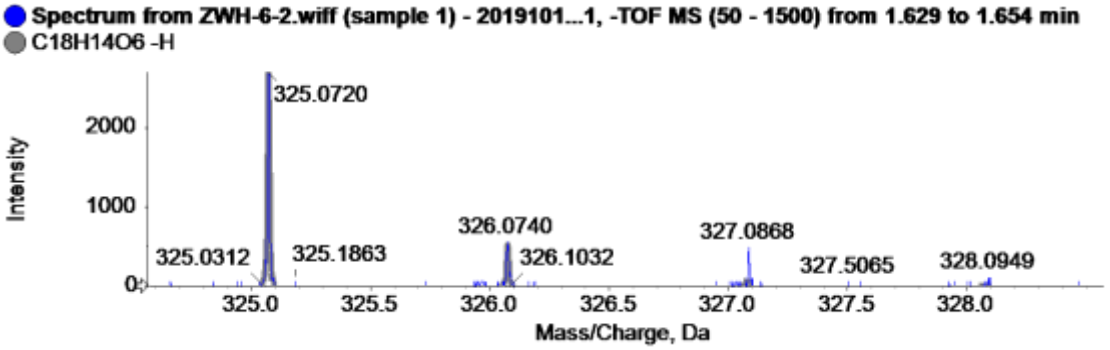

Spectrum from ZWH-5-1.wiff (sample 1) - 20191018\...xperiment 5, -TOF MS^2 (50 - 1500) from 1.531 min
Precursor: 325.1 Da CE=-45

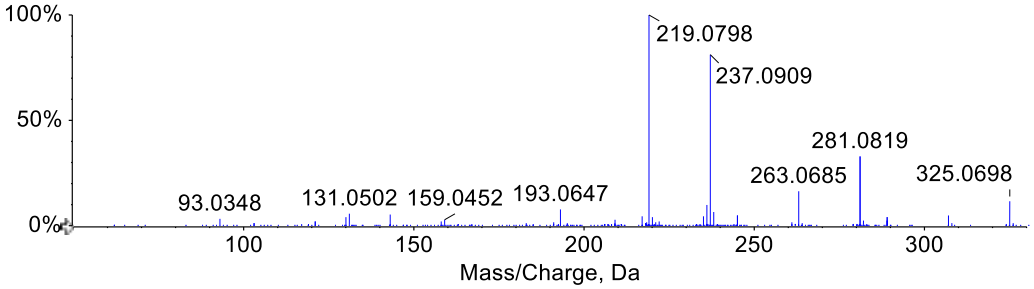

Figure S13.1 (Raw figure)