Supporting Information for

Comprehensive mass spectrometry-guided plant specialized metabolite phenotyping reveals metabolic diversity in the cosmopolitan plant family Rhamnaceae

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Result S1. Inspection on putative annotation of molecular families C and E.

Based on Mass2Motifs, two flavonoid aglycone substructures, quercetin and kaempferol, could be distinguished in **C**. Supplementary Figure 1(a) visualizes Mass2Motif-mapped molecular family **C**. Three Mass2Motifs 86, 130, and 149 were extracted from MS/MS spectra in **C**; these Mass2Motifs explained MS/MS features which are commonly observed in plant metabolomics dataset, so they could be easily annotated. Mass2Motif 130 was annotated as a kaempferol-related motif, while Mass2motif 86 as a quercetin-related motif. Mass2Motif 149 contained MS/MS fragments which are commonly observed in collision-induced dissociation (CID) fragmentation spectra of flavonol aglycones, such as quercetin or myricetin (Fabre *et al.*, 2001). As shown in Figure S1(a), spectral node in **C** could be grouped into two subfamilies regarding to their Mass2Motifs. Nodes with Mass2Motifs 130 were suggested to be 3-*O*-glycoside derivatives of kaempferol, while the others were annotated to be quercetin 3-*O*-glycosides. These annotations were supported by spectral library matching and the NAP *in silico* identification results, and confirmed by chromatographic validation for nodes **14** (nicotiflorin) and **15** (kaempferol 3-*O*-neohesperidoside) using reference standards (Figures S4 and S5). Flavonol 3-*O*-glycosides are commonly observed plant secondary metabolites, and the taxonomical mapping of cluster **C** corresponds to the universal distribution of this class of metabolites.

A 22 spectra containing molecular family **E** shows how NAP works in network clusters for which library matches are not present. In MetFrag *in silico* library matching for cluster **E**, some nodes were annotated as "unnatural" compounds; for example, the best MetFrag candidates for nodes **16** (*m/z* 533.277) and **17** (*m/z* 485.313) were synthetic compounds. However, consensus scoring perceived that most nodes in this cluster contain a similar chemical scaffold; so the candidates were re-ranked and we can see that the best candidates in final NAP result are compounds of similar structures (Figure S1(b)). This type of chemical scaffold, called

cyclopeptide alkaloid, is a subclass of plant cyclopeptides of which most derivatives have been mostly reported from Rhamnaceae species (Tuenter *et al.*, 2017a). The NAP identification for the node **18** (*m/z* 499.329), adouetine X, was confirmed by chromatographic comparison with the previously purified compound (Figure S9); so chemical annotations for this cluster as cyclopeptide alkaloids were validated. One of remarkable points in this cluster was that some nodes were labeled with an orange color, which represents *Berchemia* species. There has not been any report of cyclopeptide alkaloids from this genus, but now our result suggests the presence of cyclopeptide alkaloids in *B. lineata*, a hardly investigated species for its metabolites. This suggests that MS/MS spectral network enhanced by the NAP can also be an efficient sample prioritization strategy for natural products discovery.

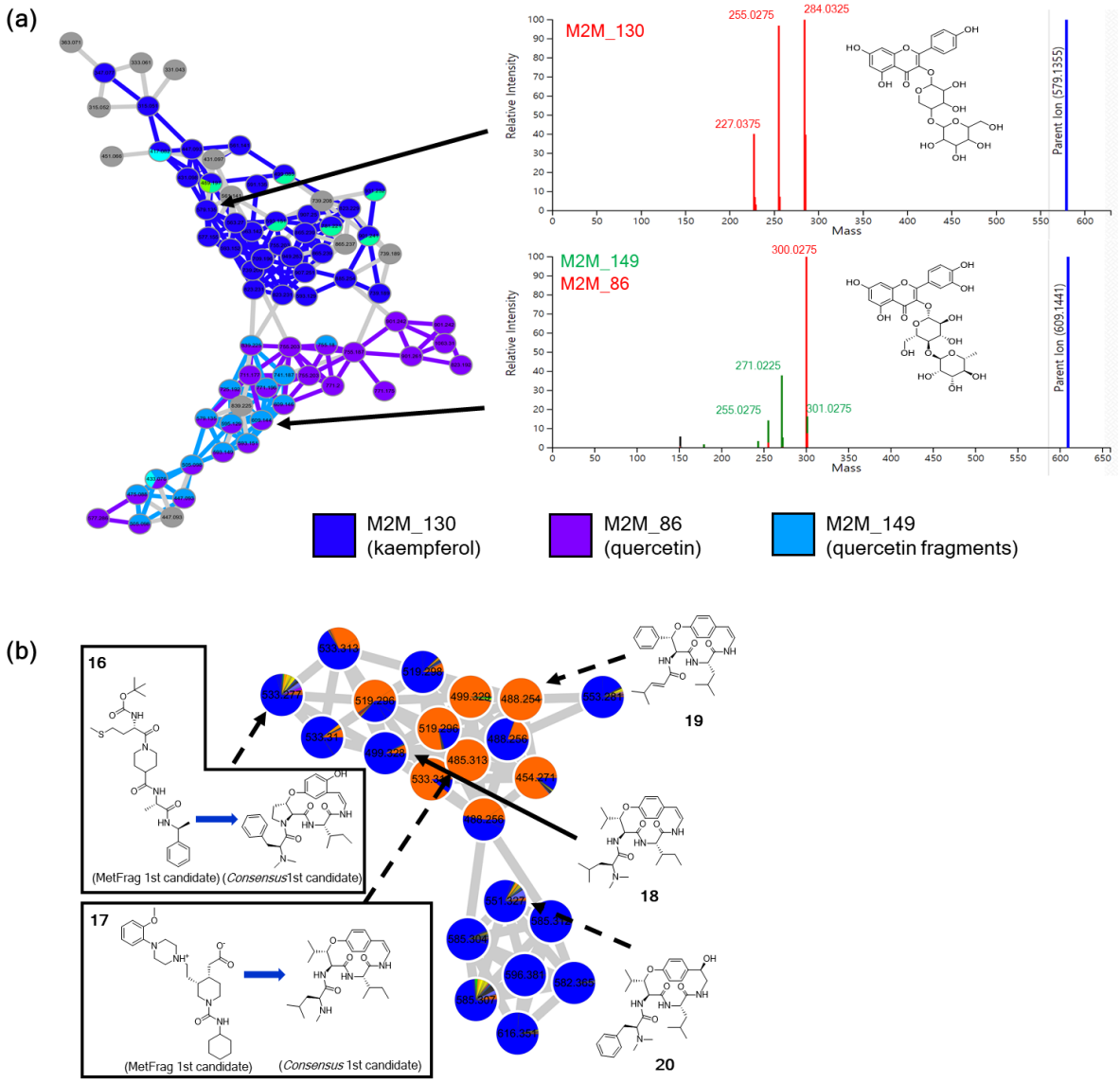

Figure S1. NAP/MS2LDA-driven metabolite annotation of (a) flavonol 3-*O*-glycosides (molecular family **C**) and (b) cyclopeptide alkaloids (molecular family **E**).

Result S2. Validation of spectral identification using reference standards

Identifications were confirmed by comparing chromatographic t_R and MS/MS spectra as Figures S2–9. Reference standards were acquired as described below.

Emodin-8-*O*-β-D-glucopyranoside (**9**): The reference standard was isolated and identified in our previous study (Kim *et al.*, 2009a). MS/MS spectrum is deposited in the GNPS spectral library, https://gnps.ucsd.edu/ProteoSAFe/gnpslibraryspectrum.jsp?SpectrumID=CCMSLIB00004679279#%7B%7D.

3-*O*-Protocatechuoylceanothic acid 2-methyl ester (**10**): The reference standard was isolated and identified in our previous study (Kang *et al.*, 2016). MS/MS spectrum is deposited in the GNPS spectral library, https://gnps.ucsd.edu/ProteoSAFe/gnpslibraryspectrum.jsp?SpectrumID=CCMSLIB00004679282#%7B%7D.

3-*O*-Vanilloylceanothic acid (**11**): The reference standard was isolated and identified in our previous study (Kang *et al.*, 2016). MS/MS spectrum is deposited in the GNPS spectral library, https://gnps.ucsd.edu/ProteoSAFe/gnpslibraryspectrum.jsp?SpectrumID=CCMSLIB00004679281#%7B%7D.

3-*O*-Protocatechuoylceanothic acid (**12**): The reference standard was isolated and identified in our previous study (Kang *et al.*, 2016). MS/MS spectrum is deposited in the GNPS spectral library, https://gnps.ucsd.edu/ProteoSAFe/gnpslibraryspectrum.jsp?SpectrumID=CCMSLIB00004679284#%7B%7D.

Nicotiflorin (**14**): The reference standard, which was isolated and identified by (Yoo *et al.*, 2015) was kindly provided by S. H. Kim (Yonsei University, Korea). MS/MS spectrum is deposited in the GNPS spectral library,

https://gnps.ucsd.edu/ProteoSAFe/gnpslibraryspectrum.jsp?SpectrumID=CCMSLIB00004679287#%7B%7D.

Quercetin 3-*O*-neohesperidoside (**15**): The reference standard was isolated and identified in our previous study (Sung, 1998; Kim *et al.*, 2009b). MS/MS spectrum is deposited in the GNPS spectral library, https://gnps.ucsd.edu/ProteoSAFe/gnpslibraryspectrum.jsp?SpectrumID=CCMSLIB00004679290#%7B%7D.

Adouetine X (**18**): The reference standard was isolated and identified in our previous study (Tuenter *et al.*, 2017b). MS/MS spectrum is deposited in the GNPS spectral library, https://gnps.ucsd.edu/ProteoSAFe/gnpslibraryspectrum.jsp?SpectrumID=CCMSLIB00004679280#%7B%7D.

Emodin (**21**): The reference standard was isolated and identified in our previous study (Kim *et al.*, 2009a). MS/MS spectrum is deposited in the GNPS spectral library, https://gnps.ucsd.edu/ProteoSAFe/gnpslibraryspectrum.jsp?SpectrumID=CCMSLIB00004679278#%7B%7D.

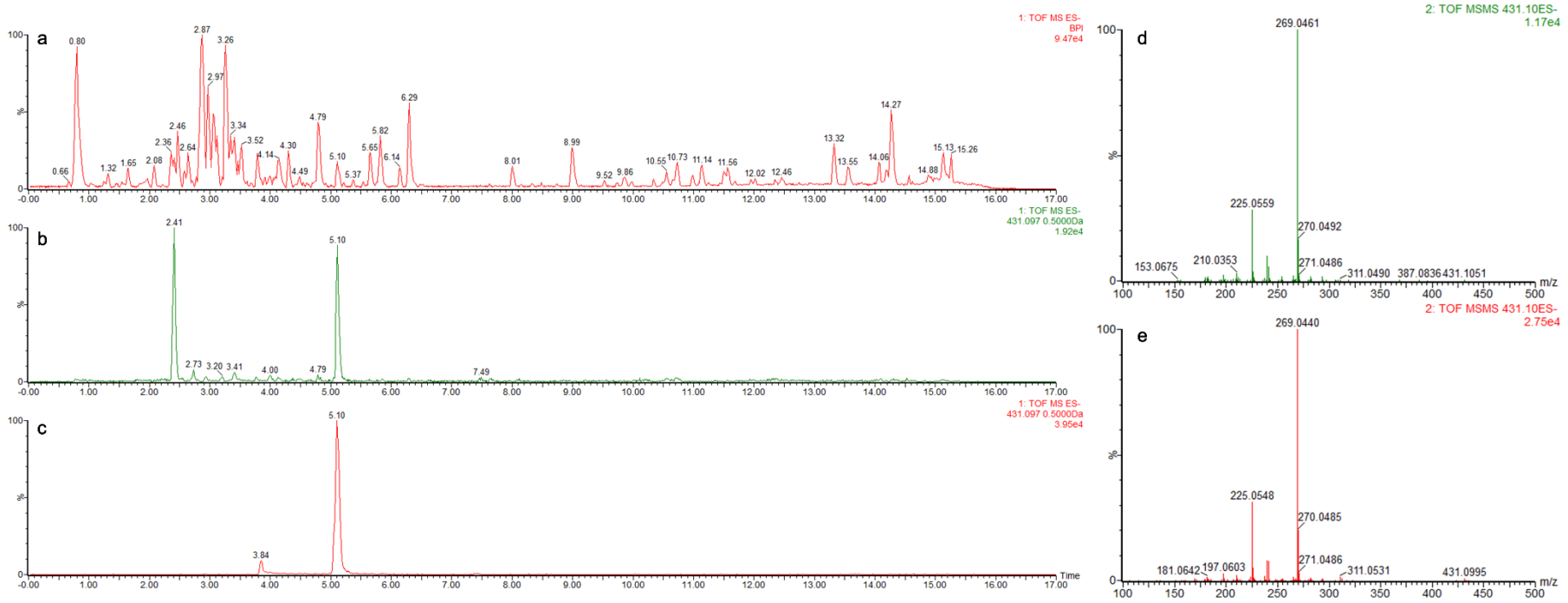

Figure S2. Chromatographic validation for emodin-8-*O*-β-D-glucopyranoside (**9**). BPI (**a**) and XIC (*m/z* 431.097, **b**) chromatograms of *Berchemia yunnanensis*, XIC (*m/z* 431.097, **c**) chromatogram of the reference standard, MS/MS spectra of emodin-8-*O*-β-D-glucopyranoside from *B. yunnanensis* (**d**) and the reference (**e**).

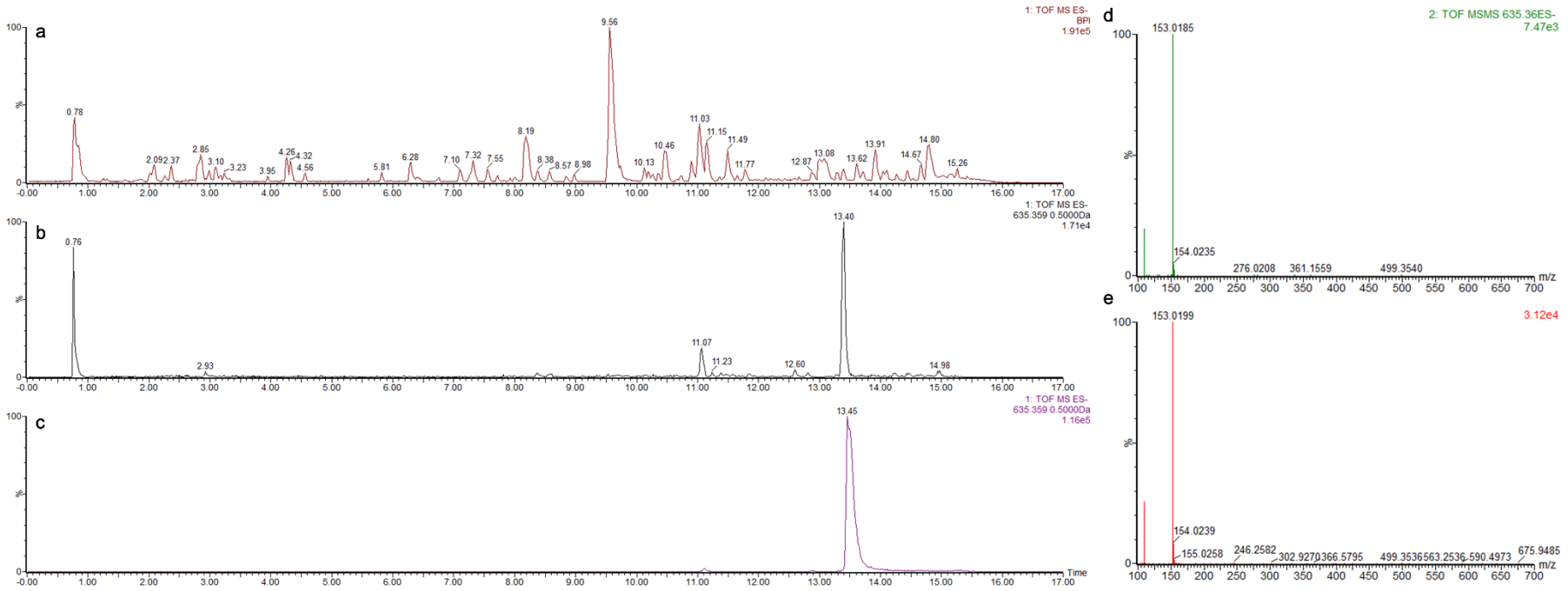

Figure S3. Chromatographic validation for 3-*O*-protocatechuoylceanothic acid 2-methyl ester (**10**). BPI (**a**) and XIC (*m/z* 635.359, **b**) chromatograms of *Ziziphus apelata*, XIC (*m/z* 635.359, **c**) chromatogram of the reference standard, MS/MS spectra of 3-*O*-protocatechuoylceanothic acid 2-methyl ester from *Z. apelata* (**d**) and the reference (**e**).

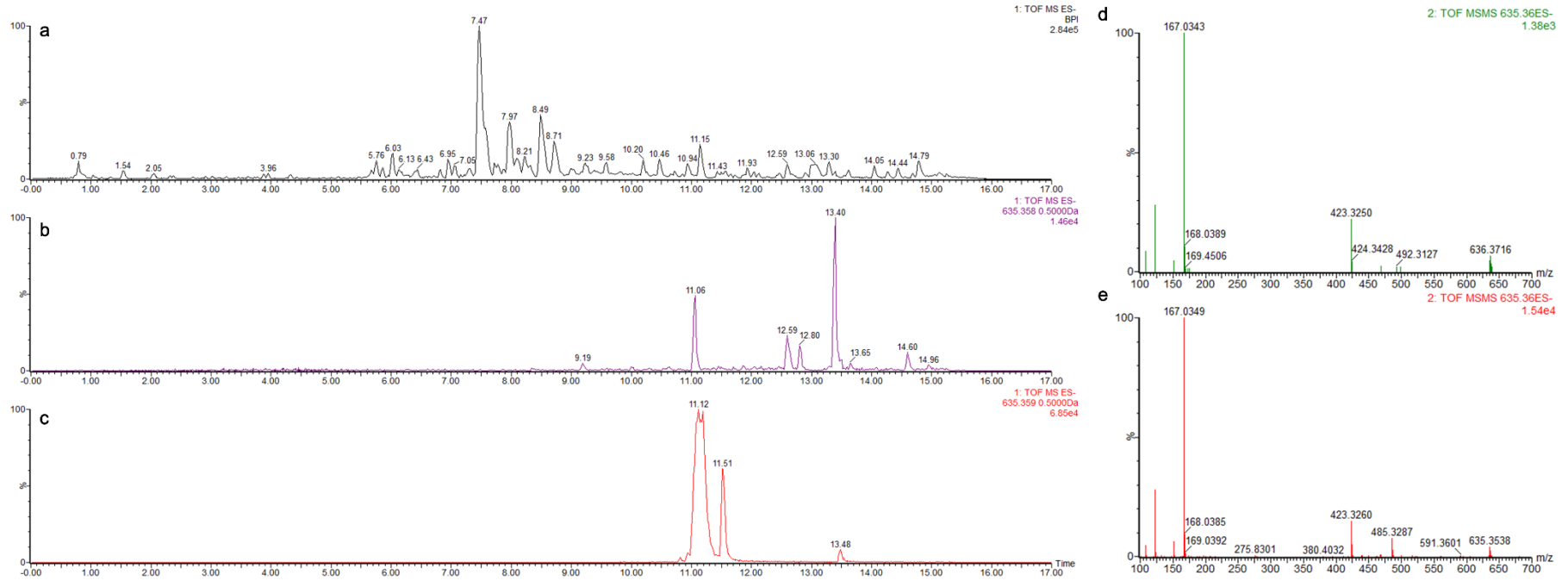

Figure S4. Chromatographic validation for 3-*O*-vanilloylceanothic acid (**11**). BPI (**a**) and XIC (*m/z* 635.359, **b**) chromatograms of *Ziziphus guatemalensis*, XIC (*m/z* 635.359, **c**) chromatogram of the reference standard, MS/MS spectra of 3-*O*-vanilloylceanothic acid from *Z. guatemalensis* (**d**) and the reference (**e**). The other peak at 13.40 min was identified as 3-*O*-vanilloylepiceanothic acid, an epimeric isomer (Kang *et al.*, 2016).

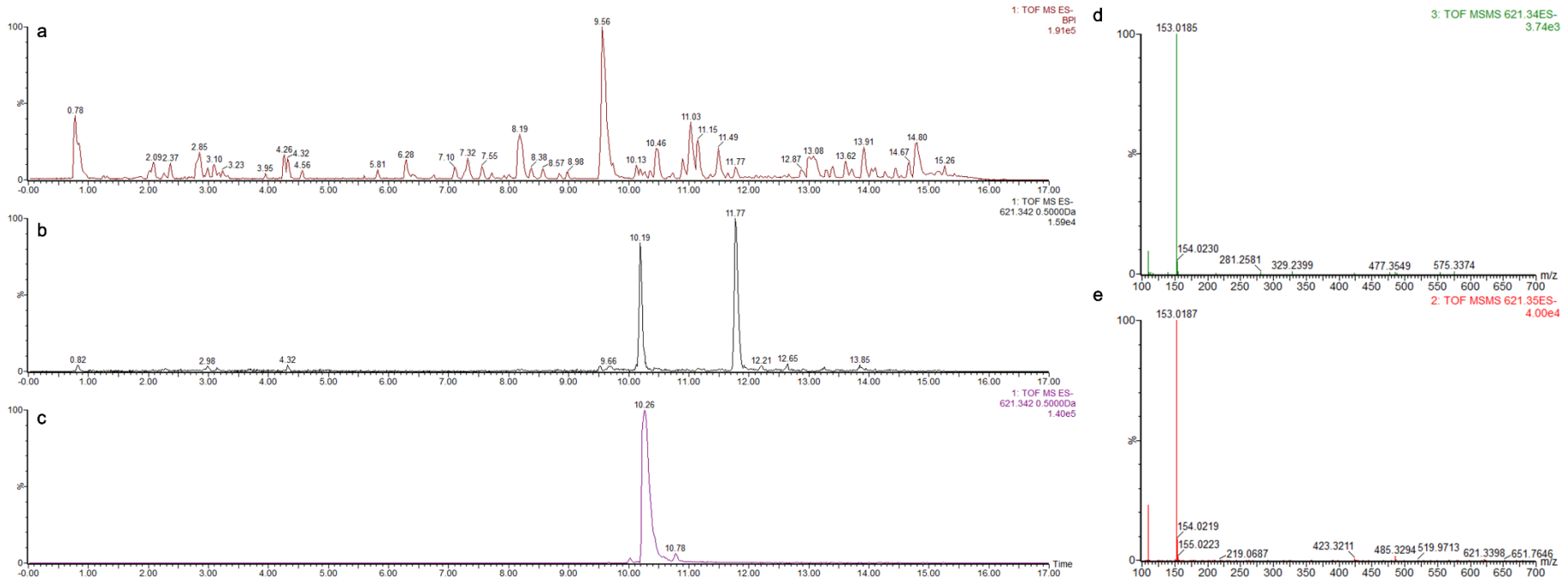

Figure S5. Chromatographic validation for 3-*O*-protocatechuoylceanothic acid (**12**). BPI (**a**) and XIC (*m/z* 621.342, **b**) chromatograms of *Ziziphus apelata*, XIC (*m/z* 621.342, **c**) chromatogram of the reference standard, MS/MS spectra of 3-*O*-protocatechuoylceanothic acid from *Z. apelata* (**d**) and the reference (**e**). The other peak at 11.77 min was identified as 2-*O*-vanilloylalphitolic acid (Kang *et al.*, 2016).

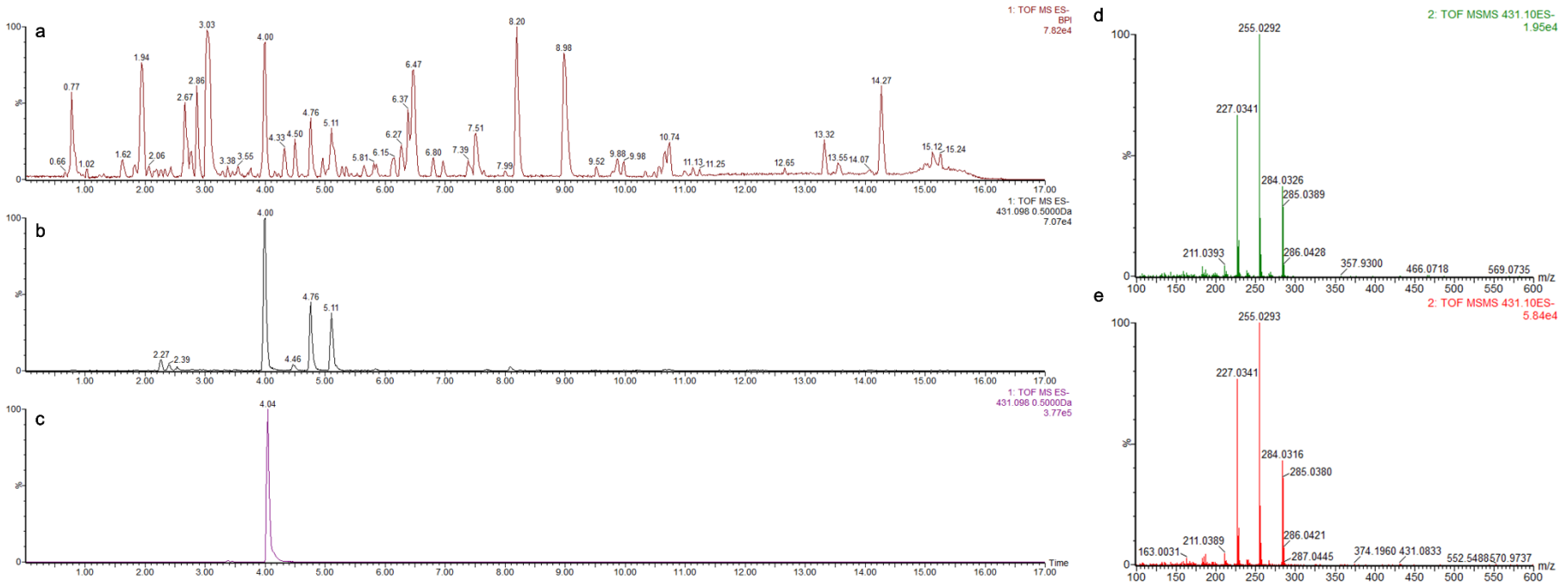

Figure S6. Chromatographic validation for nicotiflorin (**14**). BPI (**a**) and XIC (*m/z* 593.151, **b**) chromatograms of *Berchemia lineata*, XIC (*m/z* 593.151, **c**) chromatogram of the reference standard, MS/MS spectra of nicotiflorin from *B. lineata* (**d**) and the reference (**e**).

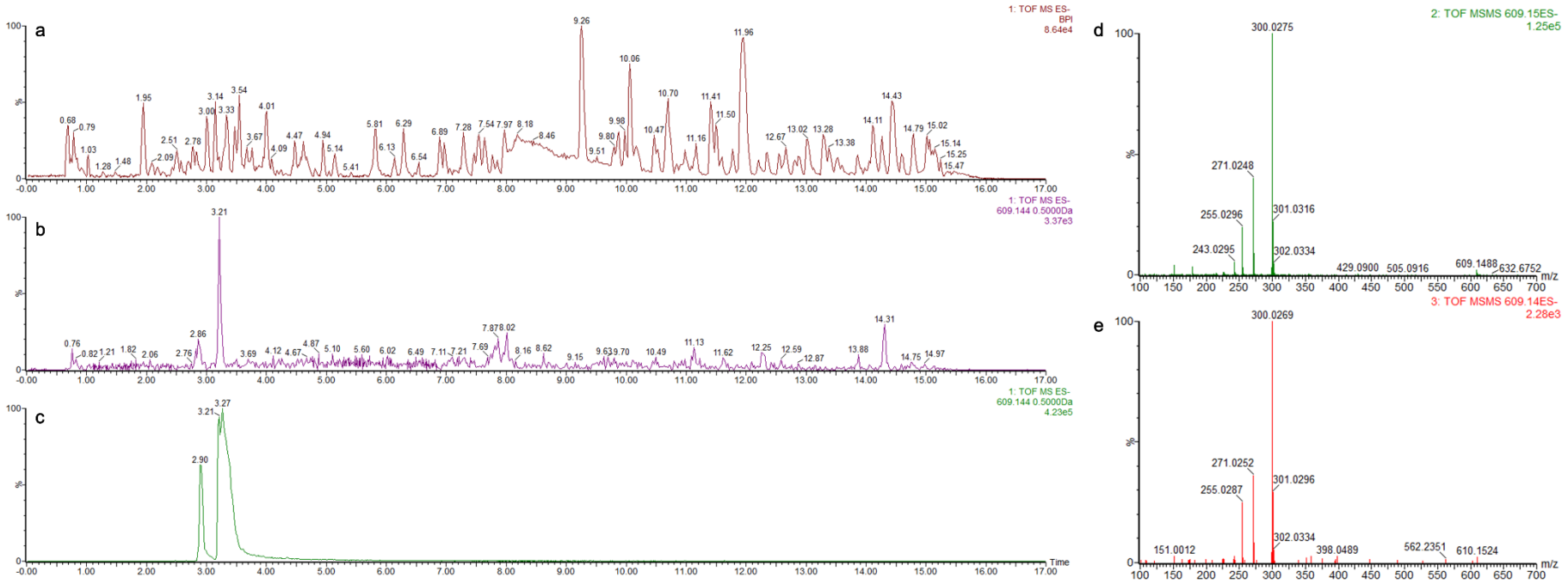

Figure S7. Chromatographic validation for quercetin 3-*O*-neohesperidoside (**15**). BPI (**a**) and XIC (*m/z* 609.144, **b**) chromatograms of *Ziziphus thyrsiflora*, XIC (*m/z* 609.144, **c**) chromatogram of the reference standard, MS/MS spectra of quercetin 3-*O*-neohesperidoside from *Z. thyrsiflora* (**d**) and the reference (**e**).

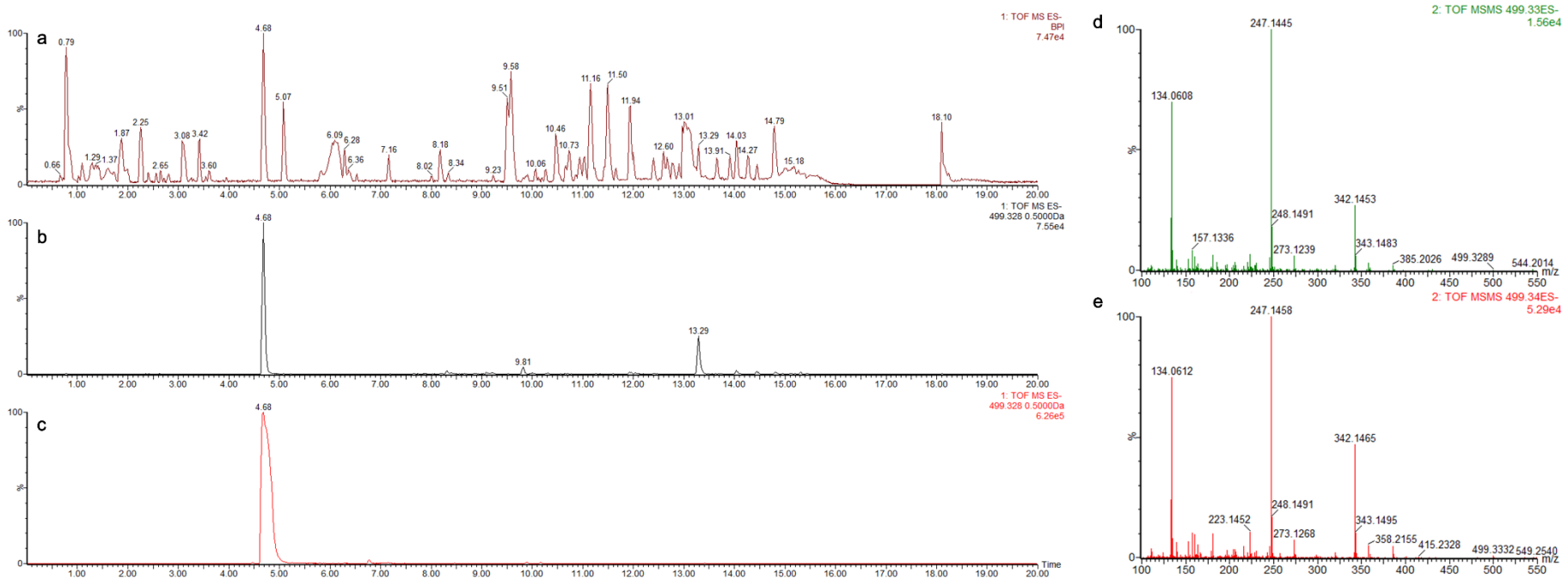

Figure S8. Chromatographic validation for adouetine X (**18**). BPI (**a**) and XIC (*m/z* 499.328, **b**) chromatograms of *Ziziphus incurva*, XIC (*m/z* 499.328, **c**) chromatogram of the reference standard, MS/MS spectra of adouetine X from *Z. incurva* (**d**) and the reference (**e**).

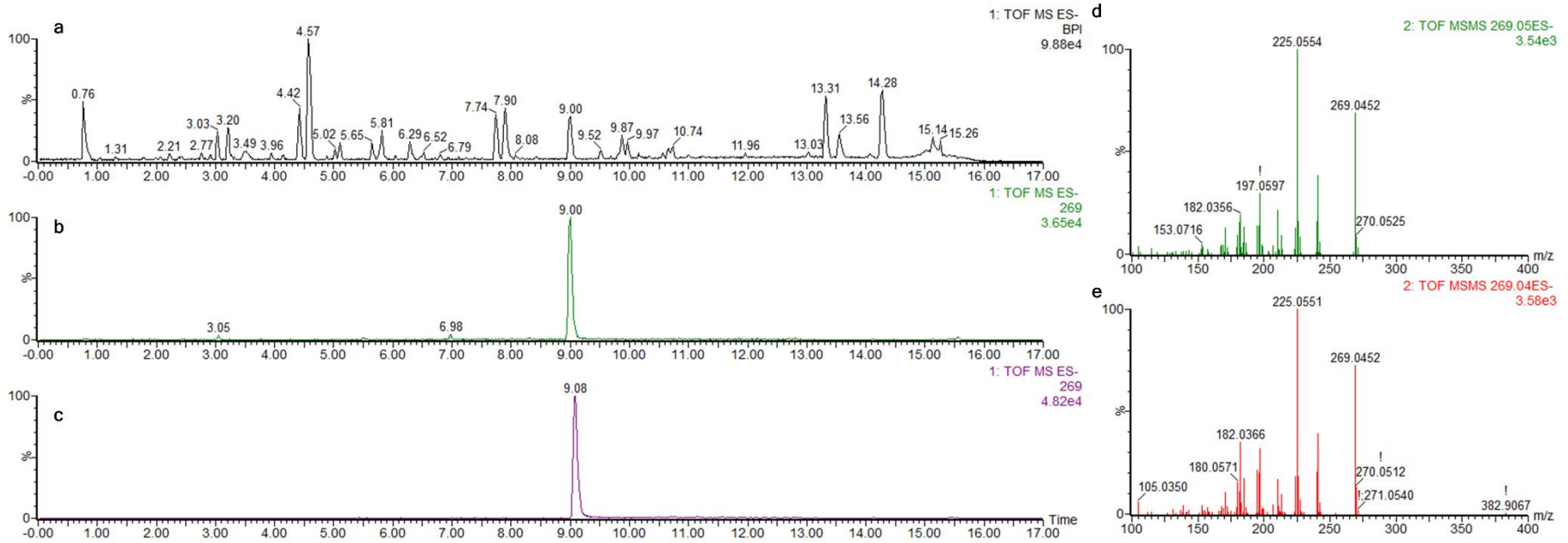

Figure S9. Chromatographic validation for emodin (**21**). BPI (**a**) and XIC (*m/z* 269.043, **b**) chromatograms of *Rhamnus oreodendron*, XIC (*m/z* 269.043, **c**) chromatogram of the reference standard, MS/MS spectra of emodin from *R. oreodendron* (**d**) and the reference (**e**).

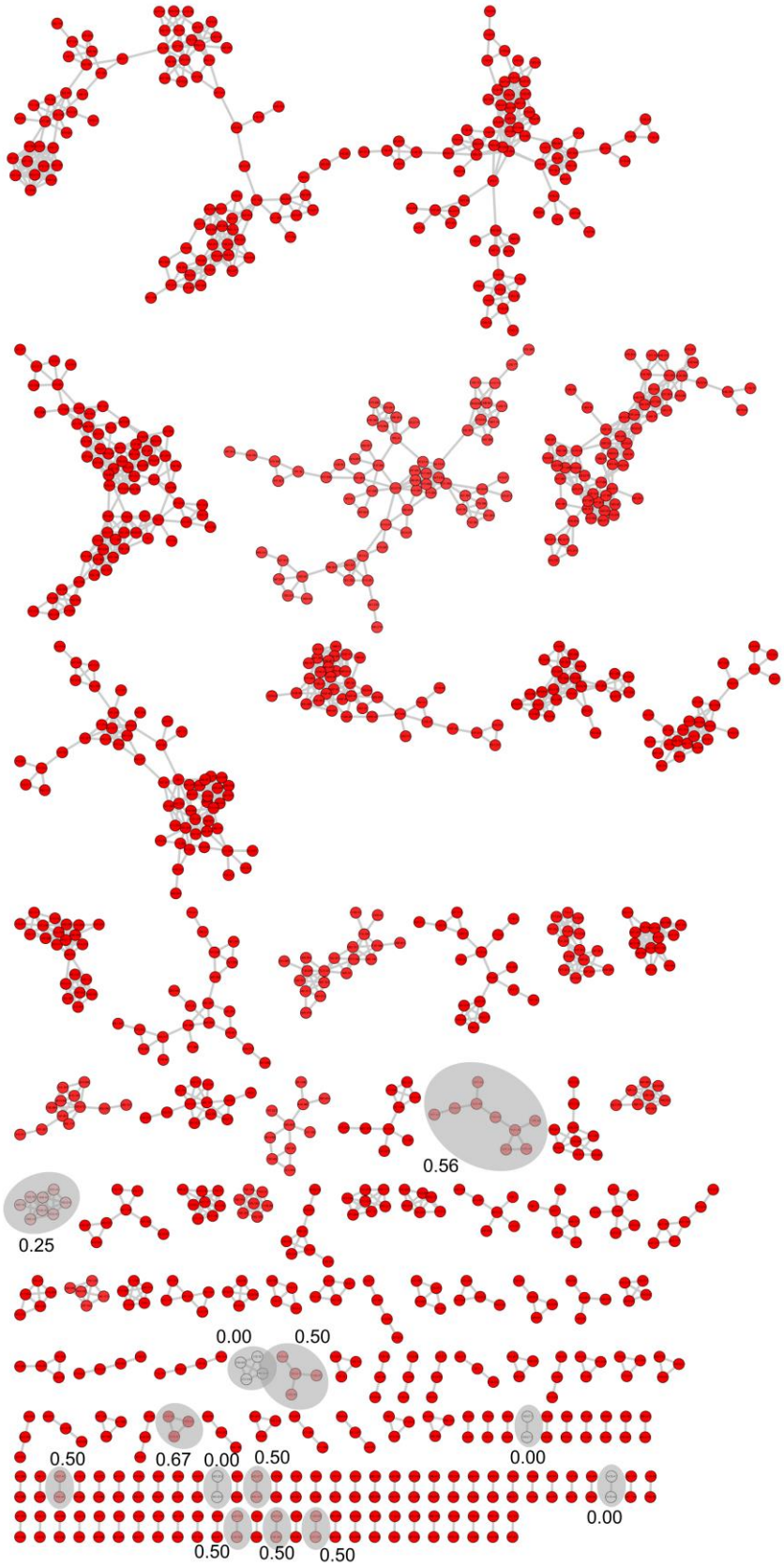

Figure S10. ClassyFire consistency scores for the Rhamnaceae molecular network. Molecular families with scores < 0.70 were marked with their scores.

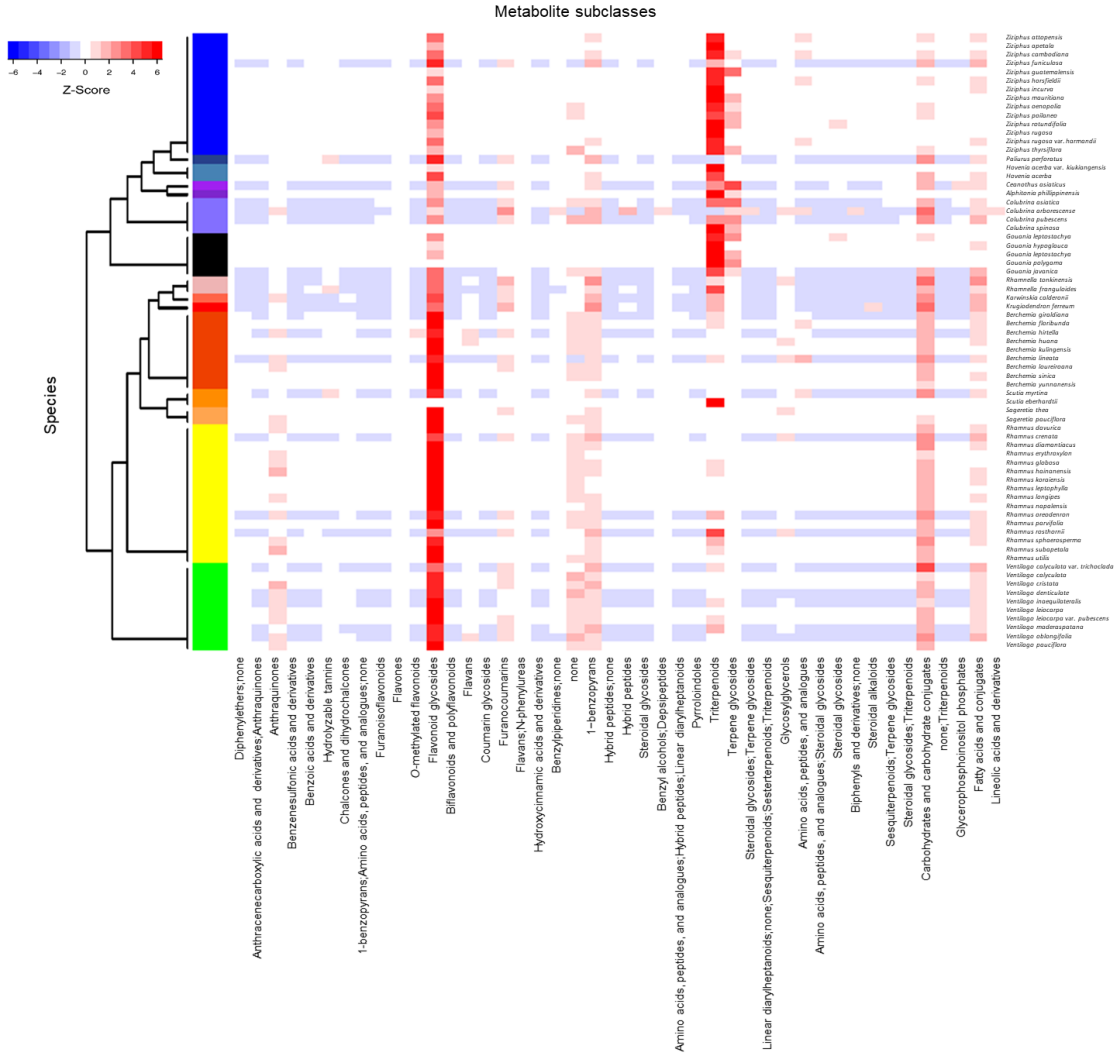

Figure S11. The complete chemical subclass distribution heatmap.

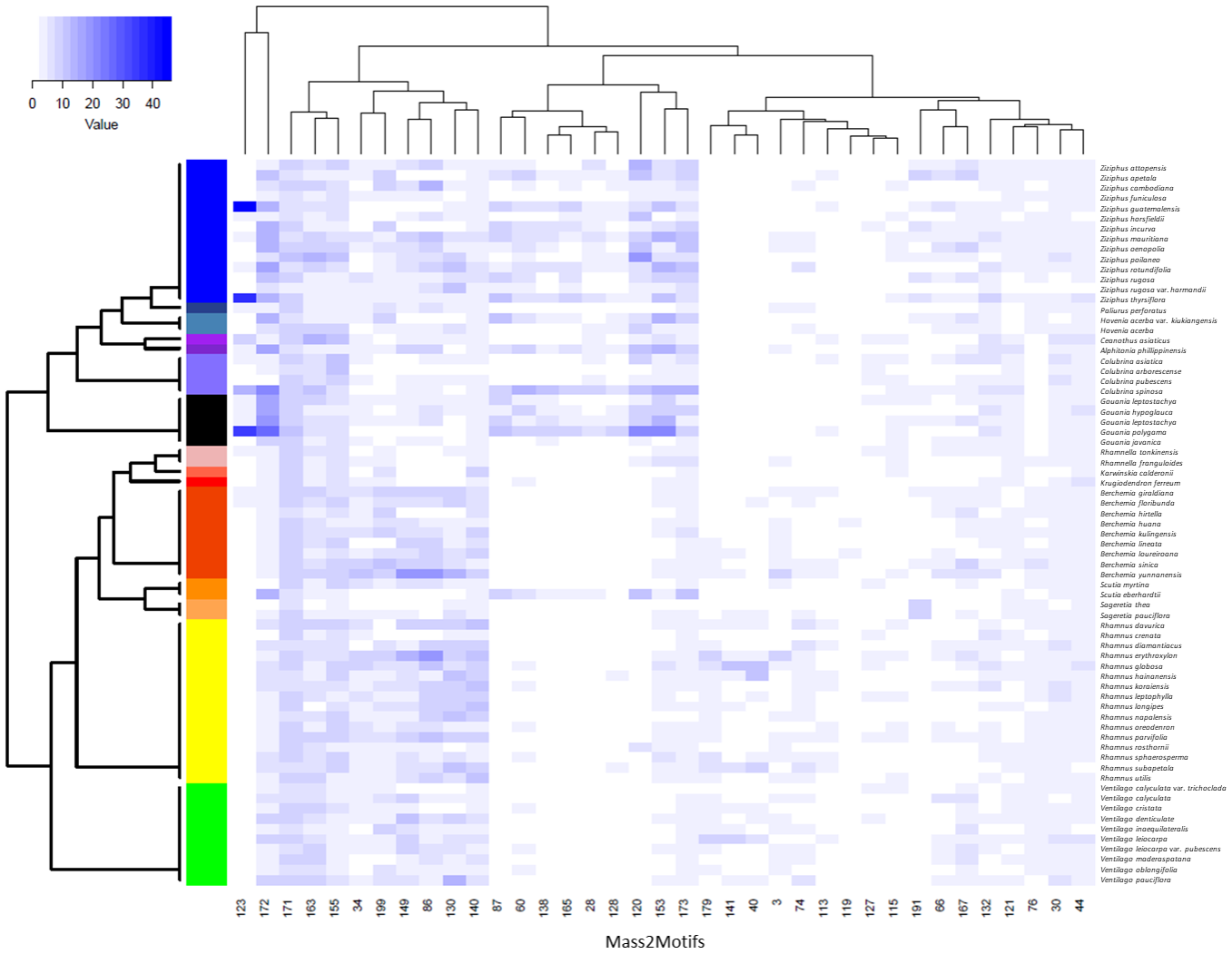

Figure S12. The complete Mass2Motif distribution heatmap.

Table S1. Detailed information about Rhamnaceae plant samples.

No.	Scientific names	Voucher No.	Extract Code	Extraction solvent	Collection	
					Date	Site
1	*Alphitonia philippinensis* Braid	#N/A	FBM072-017	MeOH	#N/A	Vietnam
2	*Berchemia floribunda* (Wall.) Brongn.	KRIB 0027008	FBM073-082	MeOH	2009-03-31	Kon Tum prov., Dak Glei distr., Muong Hoong comm., Vietnam
3	*Berchemia giraldiana* C.K. Schneid.	KRIB 0041278	FBM151-052	MeOH	2012-03-20	Lam Dong prov., Lac Duong distr., Lat comm., Vietnam
4	*Berchemia hirtella* Tsai & K.M. Feng	KRIB 0063332	FBM021-009	95% EtOH	2006-08-30	Mengla, Menghai, Yunnan Prov., China
5	*Berchemia huana* Rehder	#N/A	FBM085-005	95% EtOH	#N/A	China
6	*Berchemia kulingensis* Schneid.	KRIB 0054196	FBM217-027	MeOH	2014-05-20	Xiping, Jinggangshan, Jiangxi Province, China
7	*Berchemia lineata* (L.) DC.	KRIB 0042028	FBM150-010	95% EtOH	2012-05-25	Zhaoqing, Guangdong Prov., China
8	*Berchemia loureiroana* DC.	KRIB 0016870	FBM032-033	MeOH	2007-12-01	Lang Son, Huu Lien Reserve, Vietnam
9	*Berchemia sinica* C. K. Schneid.	KRIB 0042529	FBM166-058	MeOH	#N/A	Gansu Province, China
10	*Berchemia yunnanensis* Franch.	KRIB 0061158	FBM059-037	95% EtOH	#N/A	Luquan, Yunnan Prov., China
11	*Ceanothus asiaticus* L.	KRIB 0041714	FBM151-028	MeOH	2012-04-08	Phu Yen prov., Song Cau distr., Xuan Loc comm., Vietnam
12	*Colubrina arborescens* (Mill.) Sarg.	KRIB 0063798	FBM123-083	95% EtOH	#N/A	Yunnan Prov., China
13	*Colubrina asiatica* (L.) Brongn.	KRIB 0035940	FBM122-078	MeOH	2011-01-08	An Giang prov., Tinh Bien distr., An Hao comm., Vietnam
14	*Colubrina pubescens* Kurz.	KRIB 0045827	FBM169-088	MeOH	2012-09-12	Ban Veun Village, Moun District, Champasak Province, Laos
15	*Colubrina spinosa* Donn. Sm.	KRIB 0019866	FBM040-072	95% EtOH	2008-03-11	Costa Rica
16	*Gouania javanica* Miq.	KRIB 0036193	FBM126-044	MeOH	2011-01-23	Binh Phuoc prov., Phuoc Long distr., Son Giang comm., Vietnam
17[a]	*Gouania leptostachya* DC.	KRIB 0012626	FBM018-045	MeOH	2007-04-07	Ngoc Thanh, Me Linh district, Vinh Phuc province, Vietnam
		KRIB 0062079	FBM085-041	95% EtOH	#N/A	Mengla, Yunnan Prov., China
18	*Gouania hypoglauca* Standl.	KRIB 0042922	FBM154-017	95% EtOH	2012-08-10	Guanacaste, Guanacaste National Park, Costa Rica
19	*Gouania polygama* (Jacq.) Urb.	KRIB 0032495	FBM096-071	95% EtOH	#N/A	Guanacaste, Guanacaste National Park, Costa Rica
20	*Hovenia acerba* Lindl.	KRIB 0050080	FBM183-079	MeOH	2012-09-30	Zheshang Park, Wuhu City, Anhui Province, China
21	*Hovenia acerba* var. *kiukiangensis* (Hu & W.C. Cheng) C.Y. Wu ex Y.L. Chen & P.K. Chou	KRIB 0064069	FBM006-040	95% EtOH	2005-07-12	Mengla, Jinghong, Yunnan Prov., China
22	*Karwinskia calderonii* Standl.	KRIB 0056245	FBM213-017	95% EtOH	2014-02-21	Guanacaste Conservation Area, Santa Rosa National Park, Costa Rica

23	*Krugiodendron ferreum* (Vahl) Urb.	KRIB 0043036	FBM158-013	95% EtOH	2012-03-16	Guanacaste Conservation Area, Santa Rosa National Park, Costa Rica
24	*Paliurus perforatus* Blanco	KRIB 0041920	FBM153-046	MeOH	2009-03-03	Khanh Hoa province, Hon Ba Natural Reserve, Vietnam
25	*Rhamnella franguloides* (Maxim.) Weberb.	KRIB 0050128	FBM189-042	MeOH	2013-06-02	Dongdianhoucun, Longquanzhen, Kunyuqu, Yantai City, Shandong Province, China
26	*Rhamnella tonkinensis* (Pit.) T.Yamaz.	KRIB 0038948	FBM139-020	MeOH	2011-08-16	Gia Lai prov., Kbang distr., So Pai comm., Vietnam
27	*Rhamnus crenata* Siebold & Zucc.	#N/A	FBM010-079	MeOH	#N/A	China
28	*Rhamnus davurica* Pall.	KRIB 0037275	FBM136-009	95% EtOH	2011-06-29	Sandao, Yanji, Jilin Prov., China
29	*Rhamnus diamantiaca* Nakai	KRIB 0050134	FBM186-021	MeOH	2013-06-02	Dongdianhoucun, Longquanzhen, Kunyuqu, Yantai City, Shandong Province, China
30	*Rhamnus erythroxylon* Pall.	KRIB 0050051	FBM188-047	MeOH	2013-09-20	Selenge aimag, Dulaanhaan soum, Delgerkhaan uul, Mongolia
31	*Rhamnus globosa* Bunge	KRIB 0042549	FBM166-018	MeOH	#N/A	Gansu Province, China
32	*Rhamnus hainanensis* Merr. & Chun	KRIB 0036872	FBM122-097	MeOH	2011-03-18	Kon Tum prov., Kon Plong distr., Mang Canh comm., Vietnam
33	*Rhamnus koraiensis* Schneid.	KRIB 0050198	FBM189-007	MeOH	2013-06-04	Huanshanlu, Longquanzhen,Kunyuqu, Yantai City, Shandong Province, China
34	*Rhamnus leptophylla* C.K. Schneid.	#N/A	FBM071-009	95% EtOH	#N/A	China
35	*Rhamnus longipes* Merr. & Chun	KRIB 0018920	FBM046-085	MeOH	2008-06-21	Bac Kan, Cho Don, Bang Lung, Vietnam
36	*Rhamnus napalensis* (Wall.) M.A. Lawson	KRIB 0016963	FBM030-061	MeOH	2007-12-01	Lang Son, Huu Lien Reserve, Vietnam
37	*Rhamnus oreodendron* L.O. Williams	KRIB 0019642	FBM040-049	95% EtOH	2008-03-11	Costa Rica
38	*Rhamnus parvifolia* Bunge	KRIB 0041050	FBM148-007	MeOH	2012-05-23	Eastern Tai, Xiaowutai Mt. Yu Xian, Hebei Province, China
39	*Rhamnus rosthornii* Pritz.	#N/A	FBM189-082	95% EtOH	#N/A	China
40	*Rhamnus sphaerosperma* Sw.	KRIB 0038090	FBM140-040	95% EtOH	#N/A	Bosque del Nino. Station surroundings, Grecia Forest Reserve, Coordillera Volcanica Central, Costa Rica
41	*Rhamnus subapetala* Merr.	KRIB 0039344	FBM142-012	MeOH	2011-08-11	Gia Lai prov., Kbang distr., So Pai comm., Vietnam
42	*Rhamnus utilis* Decne.	#N/A	FBM190-013	95% EtOH	#N/A	China
43	*Sageretia pauciflora*	KRIB 0062983	FBM127-030	95% EtOH	#N/A	Yunnan Prov., China
44	*Sageretia thea* (Osbeck) M.C. Johnst.	KRIB 0045154	FBM145-050	95% EtOH	2011-07-31	Guangdong liannan, China
45	*Scutia eberhardtii* Tard.-Blot	#N/A	FBM168-080	MeOH	#N/A	Laos
46	*Scutia myrtina* (Burm. f.) Kurz	KRIB 0016994	FBM030-064	MeOH	2007-12-01	Lang Son, Huu Lien Reserve, Vietnam
47	*Ventilago calyculata* Tul.	#N/A	FBM004-096	95% EtOH	#N/A	China
48	*Ventilago calyculata* var. *trichoclada*	KRIB 0062082	FBM070-051	95% EtOH	#N/A	Mengla, Yunnan Prov., China

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49	V*entilago cristata* Pierre	KRIB 0032044	FBM163-032	MeOH	2010-04-17	Kampong Chhnang province, Roleaba-ear district, Svay Chrom commune, Dambok Kokoh village, Vietnam
50	*Ventilago denticulate* Willdenow	KRIB 0029017	FBM097-016	MeOH	#N/A	Laos
51	*Ventilago inaequilateralis* Merr. & Chun	#N/A	FBM063-029	95% EtOH	#N/A	China
52	*Ventilago leiocarpa* Benth.	KRIB 0036436	FBM122-027	MeOH	2011-03-05	Gia Lai prov., Krong Pa distr., Ia Rbol comm., Vietnam
53	*Ventilago leiocarpa* var. *pubescens* Y.L. Chen & P.K. Chou	KRIB 0061969	FBM058-049	95% EtOH	#N/A	Mengla, Yunnan Prov., China
54	*Ventilago maderaspatana* Gaertn.	#N/A	FBM060-074	95% EtOH	#N/A	China
55	*Ventilago oblongifolia* Blume	KRIB 0063851	FBM127-061	95% EtOH	#N/A	Yunnan Prov., China
56	*Ventilago pauciflora* Pit.	KRIB 0026610	FBM076-056	MeOH	2009-03-02	Lao Cai prov., Van Ban distr., Liem Phu comm., Vietnam
57	*Ziziphus apetala* Hook.f.	KRIB 0064121	FBM007-100	95% EtOH	2006-08-17	Jinghong, Yunnan Prov., China
58	*Ziziphus attopensis* Pierre	KRIB 0062056	FBM085-044	95% EtOH	#N/A	Mengla, Yunnan Prov., China
59	*Ziziphus cambodiana* Pierre	KRIB 0035058	FBM114-016	MeOH	2010-08-02	Ninh Thuan prov., Bac Ai distr., Phuoc Tien comm., Vietnam
60	*Ziziphus funiculosa* Buch.-Ham. ex Wall.	KRIB 0031771	FBM109-037	MeOH	2010-01-09	Binh Phuoc prov., Bu Gia Map distr., Bu Gia Map comm., Vietnam
61	*Ziziphus guatemalensis* Hemsl.	KRIB 0043014	FBM154-064	95% EtOH	2012-03-13	Guanacaste Conservation Area, Santa Rosa National Park, Costa Rica
62	*Ziziphus horsfieldii* Miq.	KRIB 0038608	FBM090-055	MeOH	2009-06-29	Pangandaran Nature Reserve, West Java, Indonesia
63	*Ziziphus incurva* Roxb.	KRIB 0051035	FBM198-002	MeOH	2013-09-18	Makwanpur, Bhimphedi, Suping, Ward-6, Nepal
64	*Ziziphus mauritiana* Lam.	KRIB 0027779	FBM072-087	MeOH	2009-06-11	Thanh Hoa prov., Thuong Xuan distr., Van Xuan comm., Vietnam
65	*Ziziphus oenopolia* (L.) Mill.	KRIB 0016864	FBM032-031	MeOH	2007-12-01	Lang Son, Huu Lien Reserve, Vietnam
66	*Ziziphus poilaneo* Tardieu	KRIB 0019300	FBM051-097	MeOH	2008-08-15	Quang Binh, Quang Ninh, Truong Son, Vietnam
67	*Ziziphus rotundifolia* Lam.	KRIB 0035218	FBM121-011	MeOH	2010-05-30	Baluran, Java, Indonesia
68	*Ziziphus rugosa* Lam.	KRIB 0061514	FBM053-022	95% EtOH	#N/A	Mengla, Yunnan Prov., China
69	*Ziziphus rugosa* var. *harmandii* Pierre	KRIB 0048593	FBM201-085	MeOH	2013-06-03	Lake 11 Village, Songkhon District(Xebengnouan NBCA), Laos
70	*Ziziphus thyrsiflora* Benth.	KRIB 0052309	FBM206-061	MeOH	2013-06-03	Mutile city, Esmeraldas Province, Ecuador

[a] Two samples of *Gouania leptostachya* (from different places) were applied for validating the comparative analysis.

Table S2. The list of 200 Mass2Motifs extracted from Rhamnaceae dataset.

Name	Degree	Features	Probability[a]	Annotation
motif_123	82	fragment_241.0025	0.740	
motif_163	58	fragment_101.0225	0.924	Glucosyl moiety
motif_120	53	fragment_145.0275	0.653	Coumaric acid - H_2O loss
		fragment_119.0525	0.054	
motif_130	51	fragment_284.0325	0.412	Kaempferol
		fragment_285.0375	0.177	
		fragment_255.0275	0.163	
motif_172	44	loss_43.9875	0.673	CO_2 loss
		loss_42.9825	0.058	
		fragment_749.4425	0.054	
motif_86	43	fragment_300.0275	0.509	Quercetin related motif
		fragment_301.0325	0.161	
motif_153	38	loss_43.9925	0.567	CO_2 loss
motif_149	35	fragment_271.0225	0.552	core flavonol fragments (quercetin and myricetin)
		fragment_255.0275	0.080	
motif_155	35	fragment_113.0225	0.802	
motif_167	31	fragment_152.0125	0.586	
		fragment_108.0225	0.106	
		fragment_109.0275	0.055	
motif_34	30	loss_162.0525	0.666	hexose (Glc) loss
		fragment_128.0375	0.056	
		loss_161.0475	0.051	
motif_87	29	fragment_485.3275	0.463	(epi)ceanothic acid-related
		fragment_486.3325	0.076	
		fragment_486.3275	0.062	
motif_199	27	fragment_125.0225	0.590	
		fragment_471.3475	0.115	
motif_140	26	fragment_151.0025	0.602	
		fragment_107.0125	0.103	
		fragment_191.0525	0.062	
		loss_196.0375	0.062	
motif_92	26	fragment_161.0475	0.601	
motif_60	25	loss_62.0025	0.617	CO_2/H_2O loss
		loss_60.9975	0.072	
motif_148	24	fragment_264.1025	0.259	Cyclopeptide alkaloids-related
		fragment_134.0625	0.090	
		fragment_281.1275	0.061	
		fragment_189.0675	0.056	

		fragment_133.0525	0.053	
motif_33	24	fragment_131.0325	0.604	Xyl or Ara moiety
		fragment_101.0225	0.084	
motif_191	23	fragment_167.0325	0.377	vanilloyl-related
		fragment_134.0375	0.123	
		fragment_123.0425	0.119	
motif_74	23	fragment_285.0425	0.399	
motif_28	21	fragment_163.0375	0.39	coumaric acid-related
		fragment_255.0275	0.147	
		fragment_119.0475	0.129	
motif_117	20	fragment_153.0175	0.531	protocatechuoyl-related
		fragment_109.0275	0.062	
		fragment_154.0225	0.056	
motif_173	20	loss_18.0125	0.449	
		fragment_423.3225	0.112	
		fragment_467.3125	0.053	
motif_196	19	fragment_161.0425	0.432	
		fragment_101.0225	0.158	
		fragment_143.0325	0.054	
motif_40	18	fragment_269.0425	0.388	Emodin-related
		fragment_191.0825	0.135	
		fragment_112.9825	0.078	
motif_66	18	fragment_108.0225	0.454	
		fragment_425.3025	0.095	
motif_104	18	fragment_285.0375	0.319	
		fragment_167.0375	0.206	
		fragment_825.4975	0.057	
motif_141	18	fragment_269.0475	0.403	Emodin-related
		fragment_251.0525	0.119	
motif_30	18	fragment_101.0275	0.430	
		loss_67.9875	0.244	
		fragment_191.0325	0.079	
motif_179	16	fragment_314.0425	0.293	Rhamnetin (=7-methylquercetin)
		fragment_299.0175	0.160	
		fragment_315.0475	0.109	
		fragment_315.0525	0.086	
motif_171	16	fragment_116.9275	0.445	
		fragment_471.3425	0.061	
		loss_99.9275	0.059	
		fragment_99.9275	0.055	
motif_165	15	fragment_423.3275	0.394	ceanothic acid A-ring CO_2 loss

		loss_92.0475	0.065	
motif_145	15	loss_60.0225	0.355	
		loss_59.0175	0.058	
motif_108	15	loss_46.0075	0.556	
motif_181	15	fragment_131.0375	0.348	
		fragment_125.0275	0.234	
		loss_44.0275	0.118	
motif_64	14	fragment_256.0375	0.445	norrubrofusarin-related
		fragment_117.0175	0.078	
motif_51	14	fragment_247.1475	0.284	cyclopeptide alkaloids-related
		fragment_134.0625	0.179	
motif_152	14	fragment_241.0025	0.144	
		fragment_152.9875	0.065	
		loss_59.0175	0.052	
motif_128	14	loss_60.0175	0.410	
		fragment_101.0225	0.090	
		loss_104.0075	0.052	
motif_121	13	loss_46.0025	0.483	
		fragment_255.0325	0.218	
motif_132	13	fragment_171.1025	0.336	
		fragment_133.0275	0.092	
		fragment_300.0325	0.075	
motif_138	13	fragment_439.3225	0.290	
		fragment_279.2325	0.102	
motif_76	13	fragment_124.0175	0.393	
		fragment_268.0425	0.069	
		loss_41.1675	0.069	
motif_88	12	fragment_337.0725	0.228	
		fragment_217.0125	0.072	
		fragment_319.0625	0.057	
motif_3	12	fragment_316.0225	0.294	myricetin-related motif
		fragment_287.0225	0.055	
		loss_150.0275	0.055	
motif_134	12	fragment_137.0225	0.415	
		loss_76.0175	0.220	
motif_169	11	fragment_163.0425	0.342	coumaric acid related
		fragment_508.2825	0.058	
		fragment_119.0475	0.057	
motif_48	10	fragment_247.1425	0.202	cyclopeptide alkaloids-related
		fragment_134.0625	0.106	
		fragment_233.0425	0.081	

motif_113	10	loss_59.0125	0.401	
		fragment_161.0275	0.089	
		fragment_927.4925	0.071	
motif_133	10	fragment_165.0575	0.256	
		fragment_150.0325	0.117	
motif_178	10	fragment_409.3125	0.274	
		fragment_501.3225	0.102	
		fragment_471.3125	0.051	
motif_69	9	fragment_300.9975	0.288	
		fragment_299.9925	0.108	
		loss_108.0575	0.053	
motif_127	9	fragment_179.0575	0.241	
		fragment_341.1075	0.054	
motif_164	8	fragment_283.0225	0.198	rhamnocitrin-related
		fragment_298.0475	0.114	
		fragment_299.0575	0.089	
		fragment_169.0175	0.06	
		fragment_210.9875	0.052	
motif_59	8	fragment_487.3425	0.279	
		fragment_281.2475	0.116	
		fragment_839.5125	0.100	
		fragment_488.3475	0.053	
motif_101	8	fragment_123.0475	0.334	
		fragment_111.0475	0.154	
		fragment_437.3425	0.104	
		fragment_524.2775	0.064	
motif_115	8	fragment_113.0275	0.392	
		fragment_431.0975	0.090	
motif_44	7	fragment_183.0125	0.280	
		fragment_165.0225	0.205	
		fragment_119.0475	0.174	
motif_109	7	loss_58.0425	0.185	side group (loss based)
		loss_30.0475	0.111	
motif_19	6	fragment_509.3125	0.287	
		fragment_160.0375	0.099	
motif_14	6	loss_42.9875	0.371	
		fragment_134.0575	0.205	
		fragment_107.0125	0.063	
motif_67	6	fragment_241.0075	0.324	
		fragment_301.0025	0.185	
motif_68	6	fragment_193.0525	0.236	

		fragment_134.0375	0.099
		fragment_395.3325	0.084
		loss_118.0275	0.077
motif_142	6	fragment_749.4475	0.153
		fragment_895.5025	0.054
		fragment_225.0575	0.054
motif_151	6	fragment_351.1275	0.163
		fragment_209.0425	0.100
		fragment_205.0725	0.079
		fragment_284.0275	0.070
		fragment_143.0375	0.061
		fragment_127.0425	0.060
		fragment_115.0375	0.057
		fragment_145.0525	0.053
motif_35	6	fragment_165.0525	0.213
		loss_146.0575	0.064
		fragment_195.0675	0.053
		fragment_150.0325	0.052
		loss_162.0875	0.050
motif_80	5	fragment_121.0275	0.288
		fragment_245.0475	0.147
		loss_122.0375	0.098
motif_85	5	fragment_453.3375	0.255
		fragment_199.1325	0.070
motif_8	5	fragment_603.3875	0.198
		fragment_749.4525	0.073
motif_55	5	fragment_271.0625	0.284
motif_174	5	fragment_255.2325	0.270
		fragment_151.0375	0.221
		loss_172.1075	0.063
motif_27	5	fragment_251.0575	0.117
		fragment_209.0475	0.107
motif_112	4	loss_43.0175	0.258
motif_62	4	fragment_147.0425	0.250
		fragment_183.1025	0.059
		loss_112.1225	0.059
		loss_124.1275	0.054
motif_146	4	fragment_451.3175	0.125
		fragment_354.2525	0.096
		loss_115.0775	0.070
		loss_18.0125	0.055

motif_182	4	fragment_189.0575	0.214	
		fragment_765.4475	0.163	
motif_105	4	fragment_793.4675	0.074	
		loss_46.0025	0.063	
motif_119	4	loss_152.0125	0.264	
motif_90	4	fragment_210.9925	0.147	
		fragment_152.9875	0.128	
		fragment_150.9675	0.074	
		fragment_152.9825	0.061	
		fragment_845.3975	0.060	
		fragment_815.3825	0.059	
		fragment_180.9775	0.055	
motif_97	4	fragment_457.3325	0.236	
motif_154	4	fragment_671.3625	0.152	
		fragment_161.0425	0.123	
		fragment_509.3125	0.054	
		fragment_255.0625	0.053	
motif_156	4	fragment_271.0275	0.271	
		fragment_144.0675	0.064	
motif_21	4	loss_167.0325	0.106	
		fragment_283.0625	0.083	
		fragment_164.0125	0.076	
motif_168	3	fragment_245.0825	0.231	torachrysone-related
		loss_64.0175	0.114	
		fragment_230.0575	0.097	
motif_110	3	fragment_187.0525	0.154	
		fragment_225.0075	0.131	
		fragment_467.3175	0.102	
		fragment_164.9875	0.073	
motif_9	3	fragment_242.0225	0.078	
		loss_71.0125	0.063	
		fragment_214.0275	0.058	
		loss_99.0075	0.051	
motif_7	3	loss_30.0125	0.156	
		loss_74.0025	0.088	
		fragment_123.0025	0.068	
		fragment_172.0475	0.068	
		fragment_443.3125	0.068	
		fragment_187.0725	0.063	
motif_139	3	fragment_125.0225	0.155	
		fragment_149.0575	0.108	

		fragment_177.0225	0.076
		fragment_259.0575	0.067
motif_177	3	fragment_423.3275	0.201
		fragment_407.3325	0.068
		fragment_424.3325	0.054
motif_183	3	fragment_103.9275	0.087
		loss_68.1375	0.087
		loss_146.0575	0.063
		fragment_108.0175	0.260
motif_106	3	loss_109.9975	0.096
		fragment_259.0975	0.059
		fragment_329.0675	0.058
		fragment_345.2775	0.058
motif_73	3	fragment_100.9325	0.122
		fragment_423.2925	0.118
		loss_78.0275	0.056
motif_84	2	fragment_189.0525	0.159
		fragment_300.0225	0.065
		fragment_471.3175	0.057
motif_89	2	loss_29.0025	0.067
		fragment_240.0375	0.063
motif_10	2	fragment_469.3275	0.097
		loss_136.0525	0.051
motif_11	2	fragment_165.0175	0.238
motif_63	2	fragment_179.0525	0.111
		fragment_139.0375	0.083
		fragment_127.0375	0.076
motif_65	2	fragment_114.9875	0.156
		fragment_181.0575	0.088
		fragment_158.9775	0.076
motif_0	2	fragment_175.0375	0.211
		loss_110.0025	0.053
motif_2	2	fragment_138.0325	0.175
		fragment_123.0075	0.068
motif_50	2	fragment_501.3575	0.163
		fragment_779.4575	0.058
motif_58	2	loss_43.9825	0.206
motif_135	2	fragment_113.0975	0.075
		loss_180.1125	0.075
motif_42	2	fragment_261.0425	0.135
		fragment_291.0525	0.084

		fragment_205.0525	0.079
		fragment_281.0375	0.067
motif_49	2	fragment_335.1475	0.164
		loss_44.9975	0.130
motif_124	2	loss_163.0625	0.172
		fragment_164.0725	0.104
		fragment_270.0525	0.078
motif_186	2	fragment_275.0575	0.131
		fragment_451.3225	0.108
		loss_18.0125	0.082
		loss_115.0725	0.052
		fragment_354.2575	0.052
motif_103	2	fragment_179.0325	0.257
		fragment_283.2625	0.123
motif_100	2	loss_192.0625	0.273
		fragment_749.4475	0.066
motif_78	2	fragment_152.0075	0.227
		fragment_301.0325	0.076
motif_197	2	fragment_299.0225	0.127
		fragment_441.3375	0.170
motif_26	2	fragment_411.3275	0.101
		fragment_205.0725	0.076
		fragment_347.2525	0.076
		fragment_115.0425	0.068
		fragment_143.0325	0.057
		fragment_127.0375	0.056
motif_83	1	loss_84.0225	0.087
		fragment_425.3075	0.075
		fragment_171.0975	0.074
		loss_42.0125	0.063
motif_82	1	fragment_99.9275	0.097
		loss_158.1325	0.062
motif_81	1	fragment_134.0325	0.156
		loss_128.1575	0.134
		fragment_230.0225	0.125
		fragment_245.0425	0.119
motif_18	1	loss_45.9975	0.207
		fragment_177.0575	0.052
motif_12	1	fragment_148.0125	0.078
motif_111	1	fragment_183.0425	0.052
motif_126	1	fragment_655.3675	0.119

		fragment_515.3375	0.076
motif_1	1	loss_71.9825	0.119
		fragment_171.1225	0.063
		loss_122.0925	0.063
motif_57	1	loss_166.0275	0.096
motif_189	1	fragment_176.9625	0.090
		loss_181.2975	0.090
		loss_48.0175	0.074
motif_46	1	loss_30.0075	0.192
		fragment_213.0575	0.064
motif_45	1	loss_88.0175	0.152
		loss_147.0675	0.086
		loss_176.0675	0.080
		fragment_227.0325	0.068
motif_147	1	fragment_215.0725	0.266
motif_144	1	fragment_619.3825	0.086
		fragment_353.0675	0.071
motif_143	1	fragment_164.9875	0.128
		fragment_283.0125	0.070
		fragment_216.0375	0.063
motif_17	1	loss_134.0525	0.094
motif_166	1	loss_146.0375	0.219
		fragment_367.1175	0.069
		loss_112.2125	0.069
motif_176	1	loss_177.0725	0.118
		fragment_851.3375	0.052
motif_102	1	fragment_109.0275	0.181
motif_75	1	fragment_191.0575	0.218
motif_72	1	fragment_411.3225	0.10
		fragment_529.3525	0.10
		loss_192.0525	0.054
		fragment_121.0625	0.050
		fragment_267.0575	0.050
		fragment_269.1125	0.050
		fragment_483.3475	0.050
		loss_190.1575	0.050
		loss_28.0625	0.050
motif_194	1	loss_138.0325	0.109
motif_195	1	fragment_391.3025	0.052
motif_190	1	fragment_469.3325	0.212
		fragment_109.0325	0.103

		fragment_793.4725	0.074
motif_192	1	fragment_162.0275	0.077
		fragment_430.0925	0.061
motif_36	1	loss_27.9975	0.099
motif_38	1	fragment_617.3825	0.141
		loss_46.0225	0.055
motif_94	1	loss_48.0225	0.097
		fragment_393.3175	0.054
		fragment_279.2375	0.052
		fragment_453.2975	0.052
motif_96	1	fragment_149.0225	0.236
motif_98	1	loss_178.0825	0.193
		fragment_763.4625	0.125
		fragment_283.0275	0.061
motif_99	1	loss_116.0125	0.113
		fragment_109.0675	0.056
		fragment_201.1125	0.059
		loss_112.1275	0.059
motif_161	0	fragment_471.3075	0.107
		fragment_135.0825	0.055
motif_160	0	loss_176.0325	0.095
		loss_78.0325	0.061
		fragment_225.0525	0.050
motif_162	0	fragment_145.0325	0.099
		fragment_150.0575	0.066
		fragment_173.0725	0.066
motif_13	0	loss_105.9925	0.069
		fragment_393.3125	0.064
		loss_67.9825	0.061
		fragment_309.0775	0.058
		fragment_437.3025	0.050
motif_61	0		
motif_187	0	fragment_801.4225	0.114
motif_122	0	fragment_240.0425	0.219
		fragment_240.9975	0.208
		fragment_150.9975	0.062
motif_4	0	fragment_809.4725	0.070
		loss_138.1025	0.070
		fragment_225.0025	0.054
motif_5	0	fragment_241.0525	0.250
		fragment_119.0525	0.128

		fragment_135.0475	0.053
		loss_61.0175	0.053
motif_6	0	fragment_300.0875	0.067
		loss_151.2325	0.067
		fragment_223.0025	0.055
motif_54	0	loss_87.0125	0.093
		fragment_116.9325	0.055
motif_56	0		
motif_52	0	fragment_161.0225	0.230
		fragment_347.2575	0.073
motif_53	0	loss_188.0675	0.078
		fragment_142.6525	0.052
		fragment_697.3775	0.052
		fragment_797.5025	0.052
motif_131	0	fragment_322.9825	0.054
motif_136	0	fragment_162.8425	0.064
		loss_188.1025	0.140
motif_137	0	fragment_112.9875	0.164
		fragment_487.3475	0.056
motif_47	0	fragment_277.2175	0.251
		fragment_264.0925	0.069
motif_43	0	fragment_293.0425	0.072
		fragment_135.0475	0.061
motif_41	0	fragment_391.3025	0.069
		fragment_259.0625	0.067
motif_15	0	fragment_451.2825	0.093
		loss_180.0425	0.090
		fragment_295.2225	0.058
motif_16	0	fragment_257.0425	0.219
		fragment_453.3025	0.124
		fragment_281.2525	0.074
motif_175	0		
motif_170	0	fragment_164.0475	0.264
		fragment_271.0575	0.173
		fragment_537.3425	0.051
motif_125	0	loss_87.9775	0.109
		fragment_279.2275	0.057
		loss_178.0275	0.057
motif_180	0	fragment_151.0075	0.123
		fragment_175.0425	0.082
		fragment_337.3475	0.063

motif_158	0	fragment_151.0425	0.151
		fragment_133.0575	0.079
		fragment_149.0625	0.058
motif_185	0	fragment_241.0475	0.173
motif_184	0	fragment_193.0475	0.131
		fragment_185.1225	0.072
		fragment_187.0375	0.072
		loss_106.0725	0.072
		fragment_159.0325	0.063
motif_159	0	loss_18.0075	0.154
		fragment_469.2975	0.065
motif_188	0	fragment_215.0325	0.250
		loss_43.9975	0.085
		fragment_264.0975	0.072
motif_129	0		
motif_107	0		
motif_79	0	loss_162.0325	0.088
		fragment_273.1475	0.065
motif_77	0	loss_87.0075	0.186
		fragment_483.3125	0.137
motif_70	0	fragment_499.3025	0.077
motif_71	0	fragment_255.2275	0.174
		fragment_149.0275	0.101
motif_150	0	fragment_499.3425	0.197
		fragment_413.3425	0.057
		fragment_118.9625	0.056
		loss_55.9925	0.056
		fragment_500.3475	0.055
motif_193	0	fragment_329.0275	0.077
		loss_62.0075	0.065
		fragment_345.0625	0.055
		fragment_344.0525	0.053
motif_198	0	fragment_192.0075	0.136
		fragment_193.0125	0.069
		fragment_359.1125	0.054
motif_118	0	loss_148.0375	0.114
		fragment_153.0225	0.093
		fragment_205.0525	0.072
		fragment_378.2475	0.058
		loss_171.0975	0.058
motif_114	0	fragment_121.0325	0.103

		fragment_197.0475	0.064
		loss_156.1125	0.064
motif_116	0	fragment_501.3175	0.126
		fragment_293.0475	0.091
motif_32	0	loss_73.0275	0.070
motif_31	0	fragment_183.0325	0.134
		loss_140.0325	0.058
motif_37	0	fragment_137.0275	0.236
motif_39	0	fragment_455.3525	0.088
motif_91	0	fragment_181.0525	0.132
		fragment_373.0425	0.114
		loss_163.0575	0.085
		fragment_417.1575	0.070
motif_93	0		
motif_95	0	fragment_111.0075	0.109
		fragment_423.3325	0.063
motif_157	0	fragment_181.0475	0.110
		fragment_264.1075	0.098
		fragment_765.4425	0.094
		fragment_337.0675	0.068
motif_25	0	fragment_647.4175	0.084
		loss_163.2075	0.067
motif_24	0	loss_136.0175	0.071
motif_20	0	fragment_469.2925	0.111
		fragment_255.0675	0.088
motif_23	0	loss_177.0775	0.170
		fragment_177.0175	0.102
		fragment_160.0425	0.099
motif_22	0	fragment_155.1075	0.068
		fragment_781.4375	0.068
motif_29	0	fragment_135.0425	0.159
		loss_178.0475	0.140
		fragment_207.0875	0.064

[a] Only MS/MS features which can be explained by any inferred Mass2Motif with probability > 0.05 are shown in this table.

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