

SUPPLEMENTARY MATERIAL

Methylenebisnicotiflorin: A Rare Methylene-bridged Bisflavonoid Glycoside from Ripe Pu-er Tea

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ABSTRACT

A new methylene-bridged dimeric flavonol glycoside, methylenebisnicotiflorin (**1**), was isolated from ripe Pu-er tea, along with 10 known flavonoids (**2-11**) and seven known phenolic compounds (**12-18**). The structure elucidation was based on spectroscopic analysis. Among them, 1,3-dihydroxyphenyl-2-*O*-sulfate (**13**), 2,3,4-trihydroxybenzoic acid (**16**) and 3,3',4,4'-tetrahydroxybiphenyl (**18**) are reported from tea plants for the first time.

Keywords: ripe Pu-er tea; bisflavonoid glycoside; methylenebisnicotiflorin;
methylene-bridged

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1. Identification of Compounds 2-18

The known compounds **2-18** were identified as 10 flavonoids, kaempferol-3-*O*- α -L-rhamnopyranosyl-(1 \rightarrow 3)-(4'''-*O*-acetyl)- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (**2**) (Lakenbrink et al. 2000), kaempferol-3-*O*-robinobioside (**3**) (Brasseur & Angenot 1986), nicotiflorin (**4**) (Zhou & Yang 2000), quercetin-3-*O*-robinobioside (**5**) (Brasseur & Angenot 1986), rutin (**6**) (Zhou & Yang 2000), kaempferol (**7**) (Zhou & Yang 2000), quercetin (**8**) (Zhou & Yang 2000), isovitexin (**9**) (Tao et al. 2014), (2*R*)-isohemiphloin (**10**) (Veloza et al. 1999) and (2*S*)-isohemiphloin (**11**) (Veloza et al. 1999), and seven simple phenolics, 4-*O*-*p*-trans-coumaroyl quinic acid (**12**) (Wu et al. 2005), 1,3-dihydroxyphenyl-2-*O*-sulfate (**13**) (Daykin et al. 2005), pyrogallol (**14**) (Wang et al. 2005), protocatechuic acid (**15**) (Wang et al. 2005), 2,3,4-trihydroxybenzoic acid (**16**) (Zhai et al. 2010), gallic acid (**17**) (Zhou & Yang 2000) and 3,3',4,4'-tetra-hydroxybiphenyl (**18**) (Fu et al. 2011), respectively.

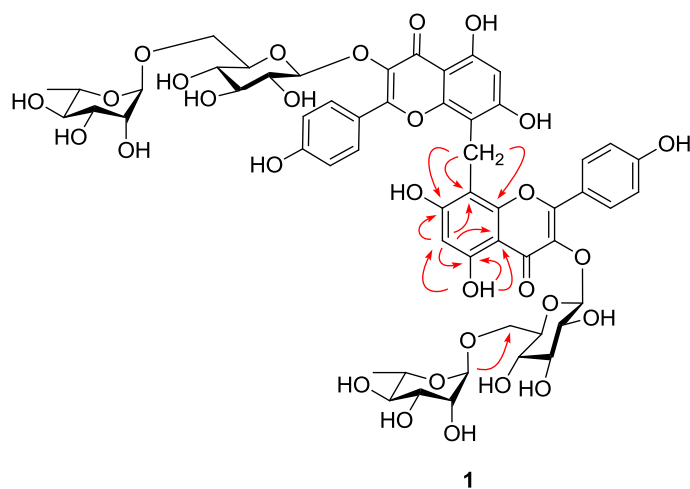


Figure S1. Key HMBC correlations (H \rightarrow C) of **1**.

Figure S2. ^1H NMR spectrum of compound **1** (DMSO- d_6 , 600 MHz)

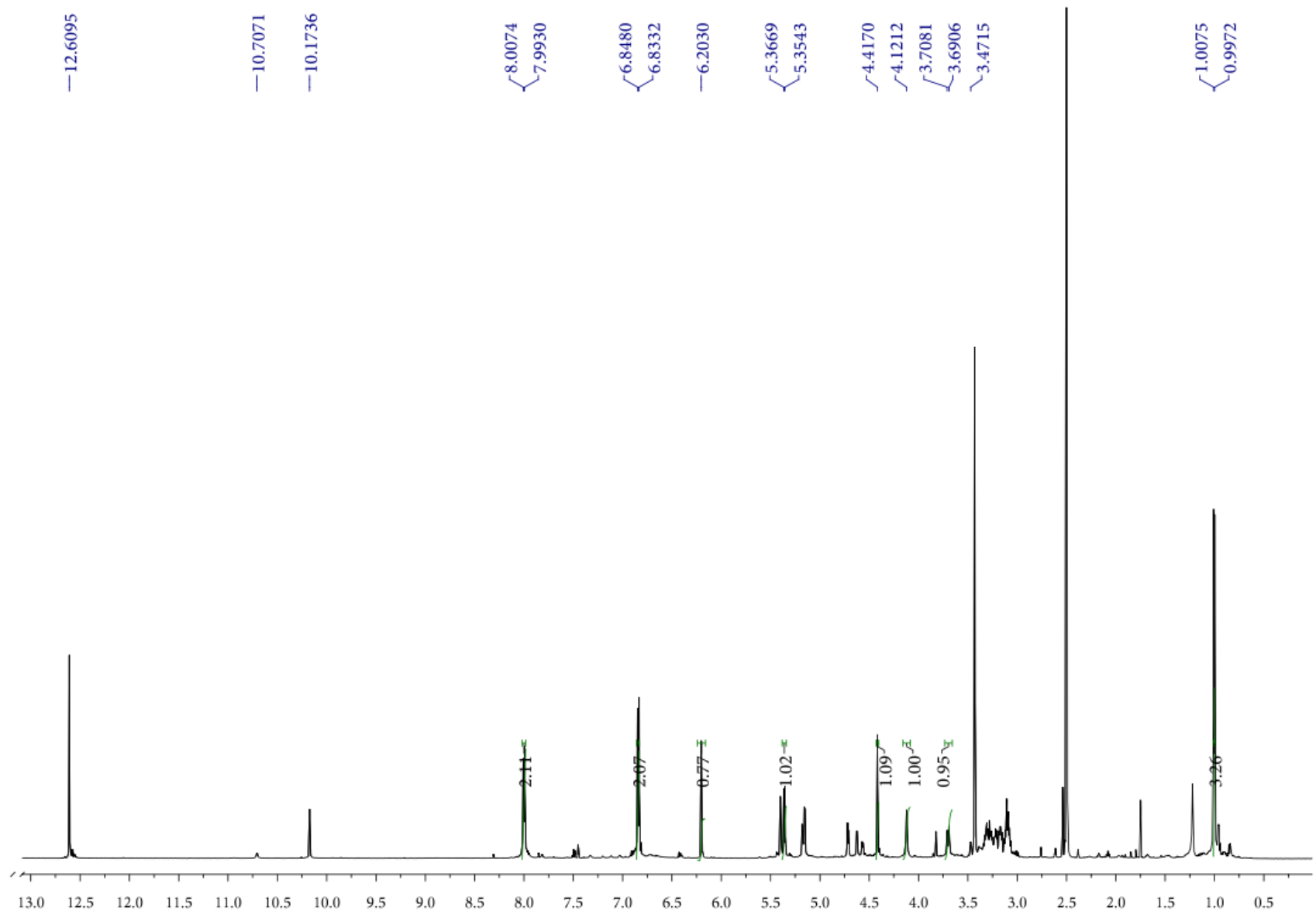


Figure S3. ^{13}C NMR and DEPT spectra of compound 1 (DMSO- d_6 , 150 MHz)

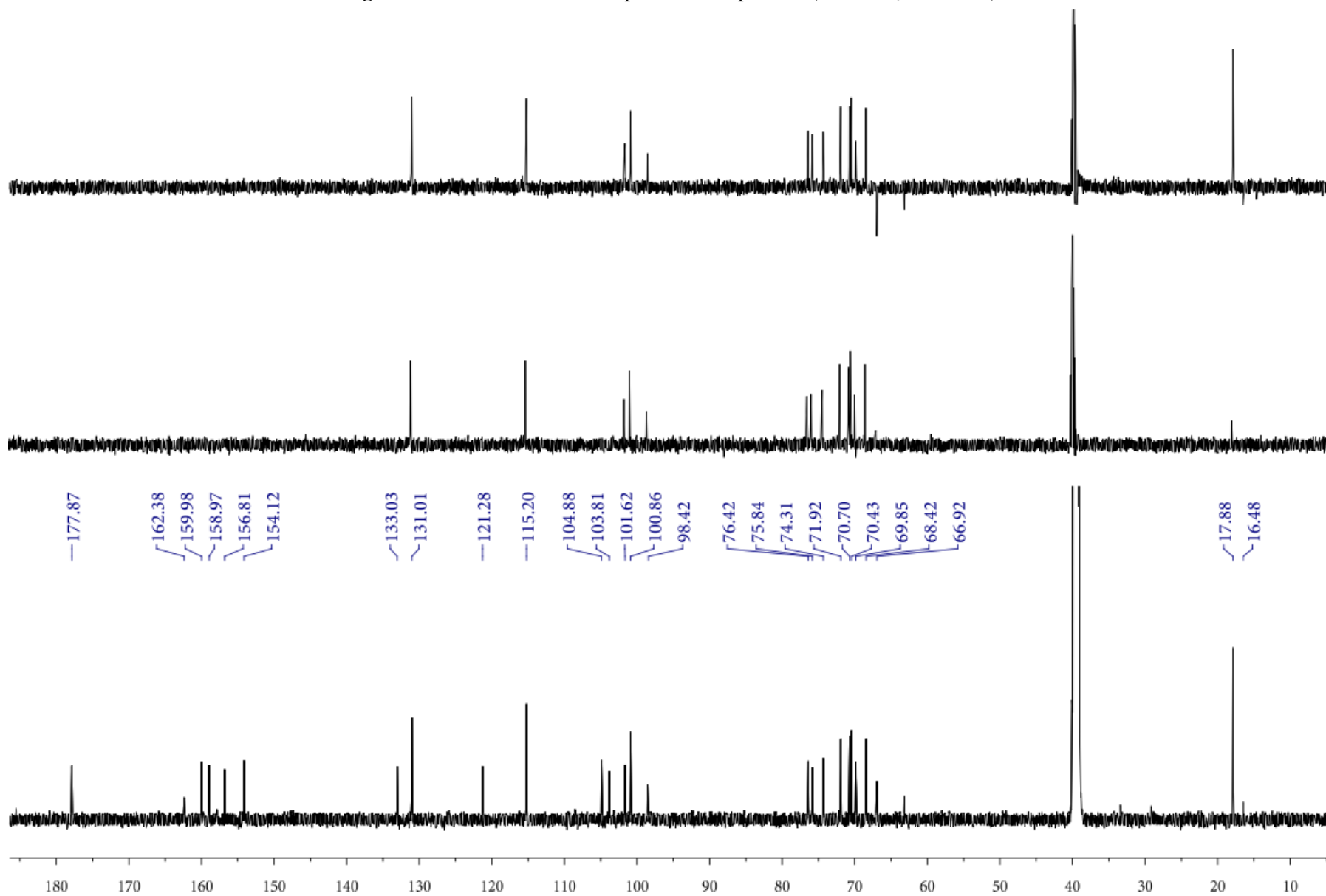


Figure S4. HSQC spectrum of compound 1 (DMSO-*d*₆, 150 MHz)

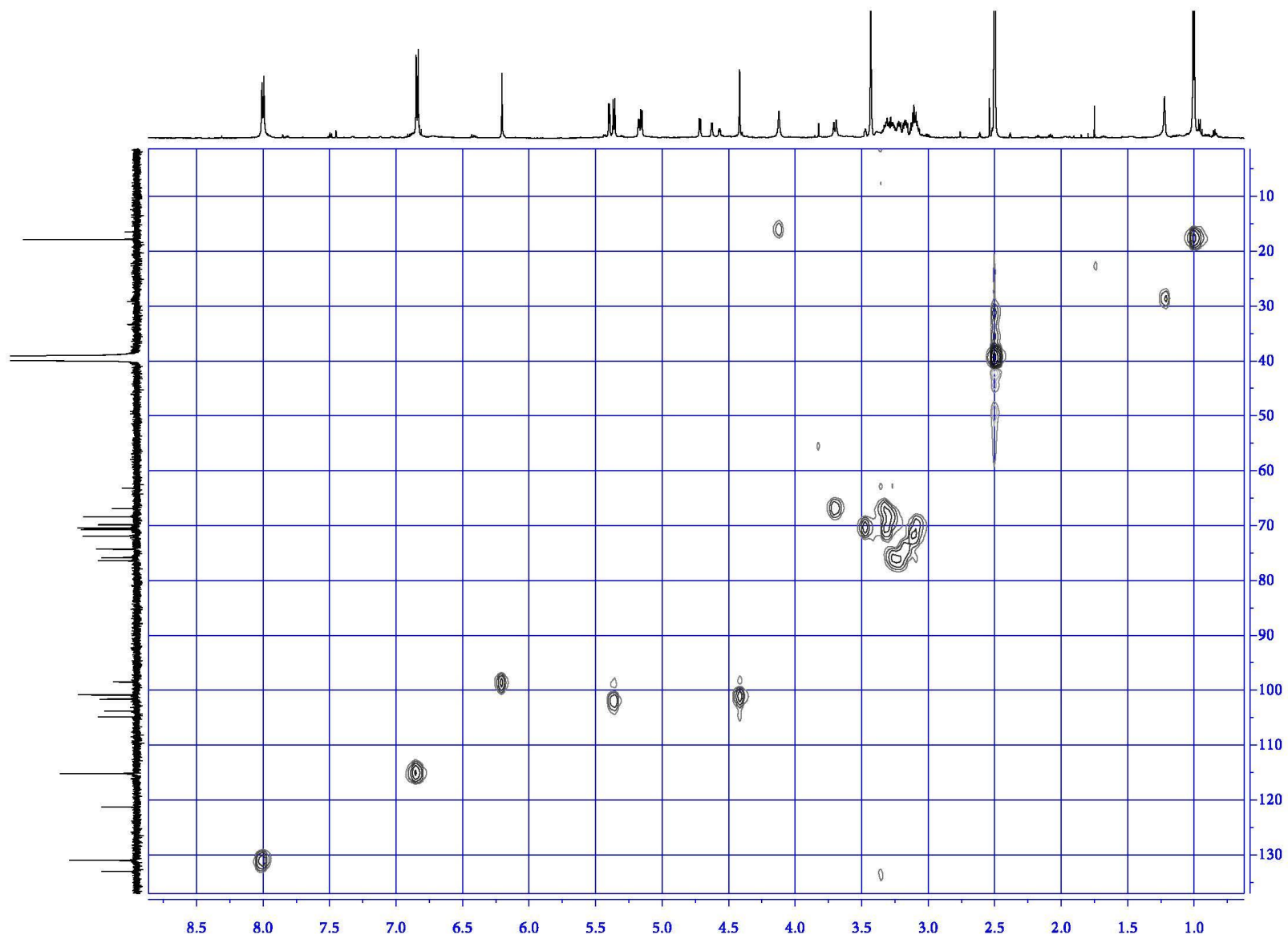


Figure S5. HMBC spectrum of compound 1 (DMSO-*d*₆, 150 MHz)

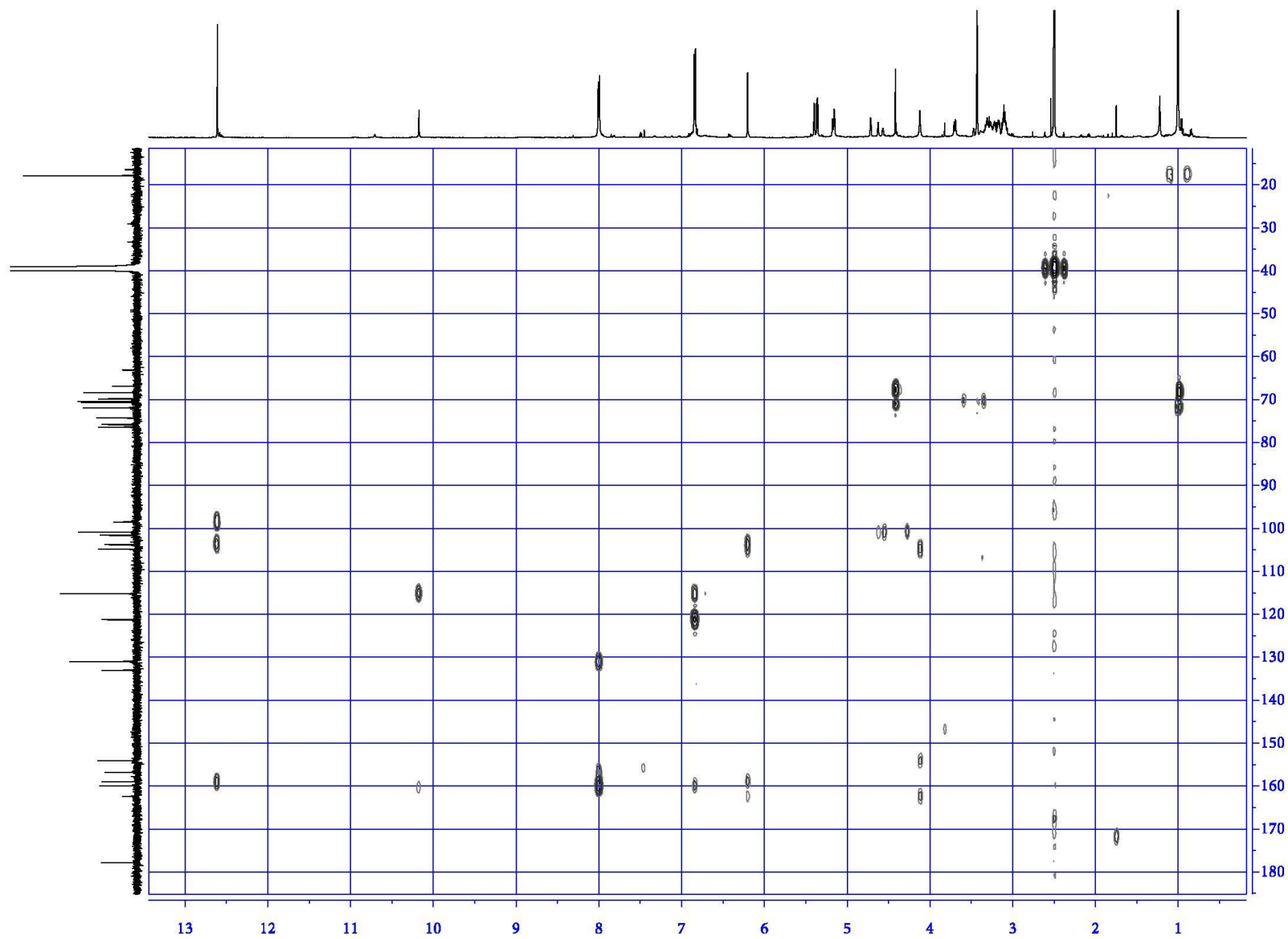


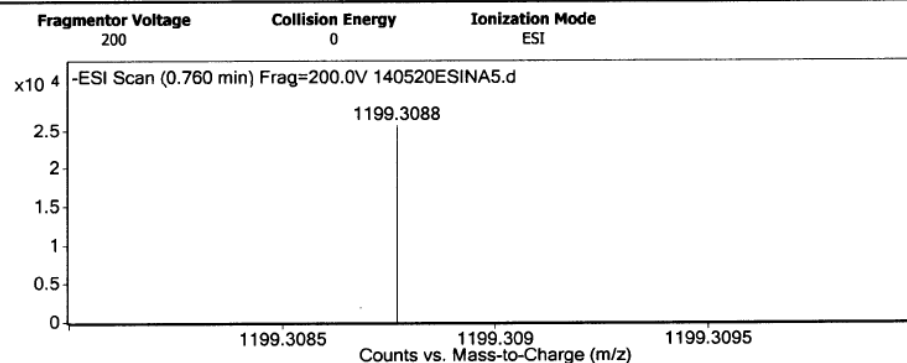
Figure S6. HR-ESI-MS of compound 1

Qualitative Analysis Report

Data Filename	140520ESINA5.d	Sample Name	yt6105
Sample Type	Sample	Position	
Instrument Name	Agilent G6230 TOF MS	User Name	KIB
Acq Method	ESIN.m	Acquired Time	5/20/2014 7:51:27 PM
IRM Calibration Status	XXXXXXXXXX	DA Method	ESIN.m
Comment			

Sample Group	Info.
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)

User Spectra



Peak List

m/z	z	Abund
1033.9881	1	53046.36

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	20	34

Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C55 H59 O30	1199.3091	1199.3088	0.3	0.3	26.5

--- End Of Report ---

Reference

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