

Supporting Information

New Fusaric Acid Derivatives from the Endophytic Fungus *Fusarium oxysporum* and Their Phytotoxicity to Barley Leaves

Shuai Liu,[†] Haofu Dai,[‡] Raha S. Orfali,[§] Wenhan Lin,[‡] Zhen Liu,^{*,†} Peter Proksch^{*,†}

[†]Institute of Pharmaceutical Biology and Biotechnology, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, 40225 Düsseldorf, Germany

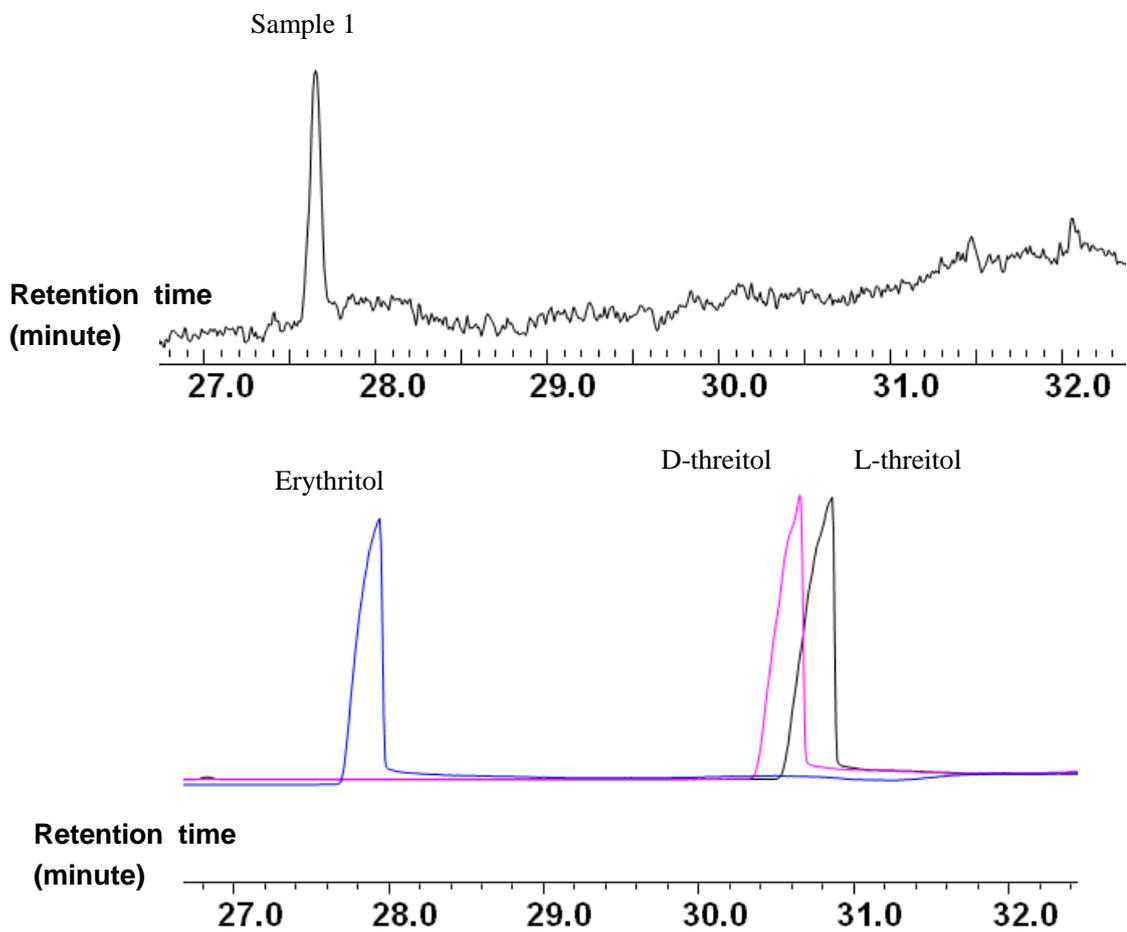
[‡]Key Laboratory of Biology and Genetic Resources of Tropical Crops, Ministry of Agriculture, Institute of Tropical Bioscience and Biotechnology, Chinese Academy of Tropical Agricultural Sciences, Haikou 571101, China

[§]Department of Pharmacognosy, Faculty of Pharmacy, King Saud University, Riyadh, Saudi Arabia

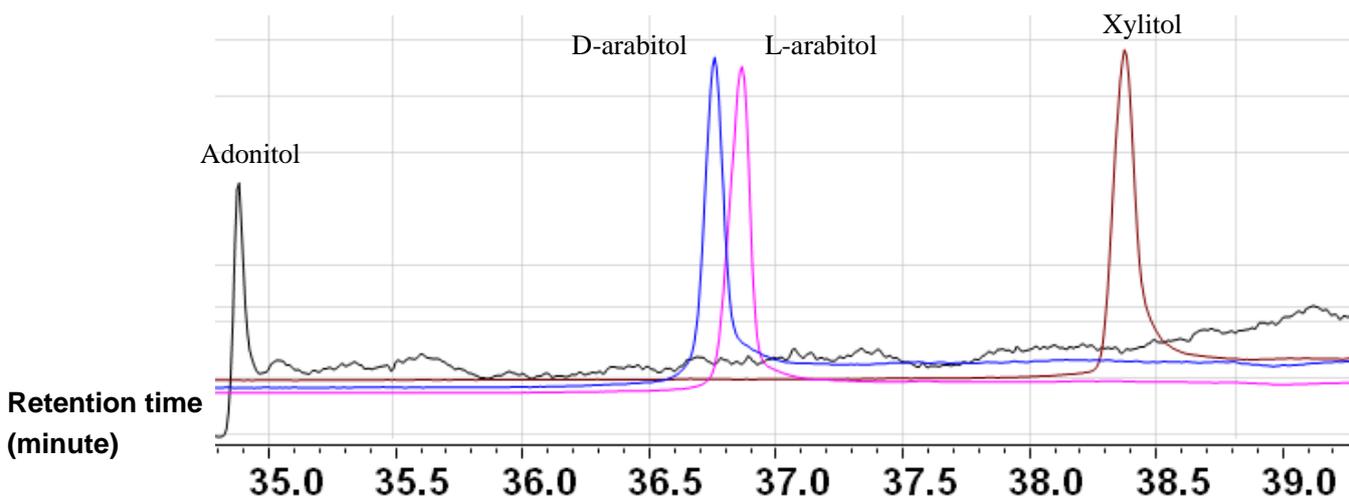
[‡]State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100191, China

Figures	Page
S1-A. Analysis of trifluoroacetyl sample 1 (degraded from compound 3) and trifluoroacetyl tetritol standards by gas chromatography.	4
S1-B. Analysis of trifluoroacetyl pentitol standards by gas chromatography.	5
S1-C. Analysis of trifluoroacetyl sample 2 (degraded from mixture of compounds 4 and 5) by gas chromatography.	5
S1-D. Analysis of trifluoroacetyl sample 2 (degraded from mixture of compounds 4 and 5) and L-arabitol in one injection by gas chromatography.	6
S1-E. Analysis of trifluoroacetyl sample 2 (degraded from mixture of compounds 4 and 5) and D-arabitol in one injection by gas chromatography.	6
S2. UV spectrum of compound 1 .	7
S3. HRESIMS spectrum of compound 1 .	7
S4. ¹ H NMR (600 MHz, CD ₃ OD) spectrum of compound 1 .	8
S5. ¹³ C NMR (150 MHz, CD ₃ OD) spectrum of compound 1 .	8
S6. ¹ H- ¹ H COSY (600 MHz, CD ₃ OD) spectrum of compound 1 .	9
S7. HSQC (600 and 150 MHz, CD ₃ OD) spectrum of compound 1 .	9
S8. HMBC (600 and 150 MHz, CD ₃ OD) spectrum of compound 1 .	10
S9. UV spectrum of compound 2 .	10
S10. HRESIMS spectrum of compound 2 .	11
S11. ¹ H NMR (600 MHz, CD ₃ OD) spectrum of compound 2 .	11
S12. ¹³ C NMR (150 MHz, CD ₃ OD) spectrum of compound 2 .	12
S13. ¹ H- ¹ H COSY (600 MHz, CD ₃ OD) spectrum of compound 2 .	12
S14. HMBC (600 and 150 MHz, CD ₃ OD) spectrum of compound 2 .	13
S15. UV spectrum of compound 3 .	13
S16. HRESIMS spectrum of compound 3 .	14
S17. ¹ H NMR (600 MHz, CD ₃ OD) spectrum of compound 3 .	14

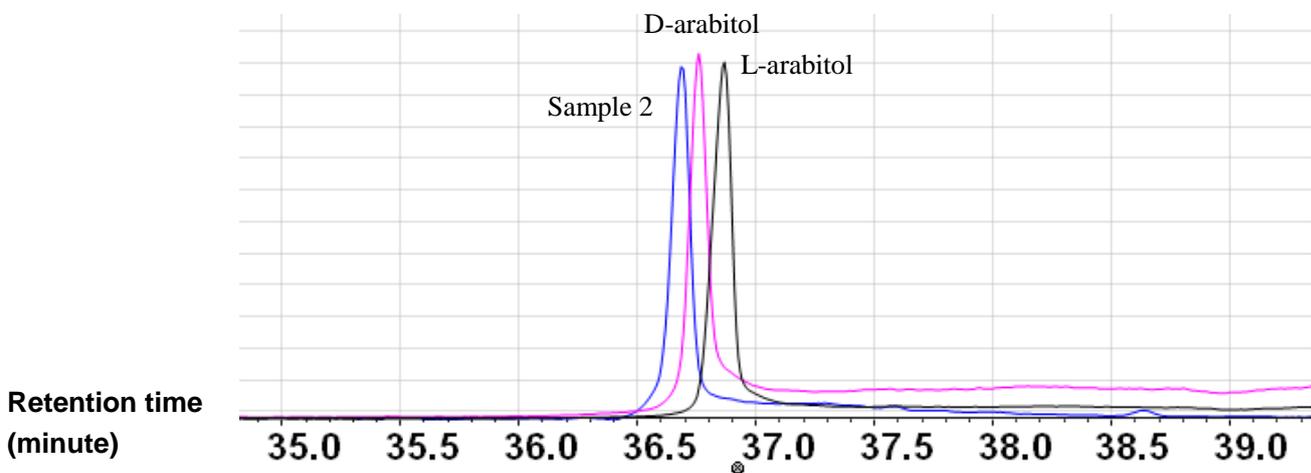
S18. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of compound 3 .	15
S19. HSQC (600 and 150 MHz, CD_3OD) spectrum of compound 3 .	15
S20. HMBC (600 and 150 MHz, CD_3OD) spectrum of compound 3 .	16
S21. UV spectrum of mixture of 4 and 5 .	16
S22. HRESIMS spectrum of mixture of 4 and 5 .	17
S23. ^1H NMR (600 MHz, CD_3OD) spectrum of mixture of 4 and 5 .	17
S24. ^{13}C NMR (150 MHz, CD_3OD) spectrum of mixture of 4 and 5 .	18
S25. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of mixture of 4 and 5 .	18
S26. HSQC (600 and 150 MHz, CD_3OD) spectrum of mixture of 4 and 5 .	19
S27. HMBC (600 and 150 MHz, CD_3OD) spectrum of mixture of 4 and 5 .	19
S28. UV spectrum of mixture of 6 and 7 .	20
S29. HRESIMS spectrum of mixture of 6 and 7 .	20
S30. ^1H NMR (600 MHz, CD_3OD) spectrum of mixture of 6 and 7 .	21
S31. ^{13}C NMR (150 MHz, CD_3OD) spectrum of mixture of 6 and 7 .	21
S32. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of mixture of 6 and 7 .	22
S33. HSQC (600 and 150 MHz, CD_3OD) spectrum of mixture of 6 and 7 .	22
S34. HMBC (600 and 150 MHz, CD_3OD) spectrum of mixture of 6 and 7 .	23
S35. UV spectrum of compound 8 .	23
S36. HRESIMS spectrum of compound 8 .	24
S37. ^1H NMR (600 MHz, CD_3OD) spectrum of compound 8 .	24
S38. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of compound 8 .	25
S39. HSQC (600 and 150 MHz, CD_3OD) spectrum of compound 8 .	25
S40. HMBC (600 and 150 MHz, CD_3OD) spectrum of compound 8 .	26
S41. Phytotoxic bioassay for fusaric acid derivatives	27



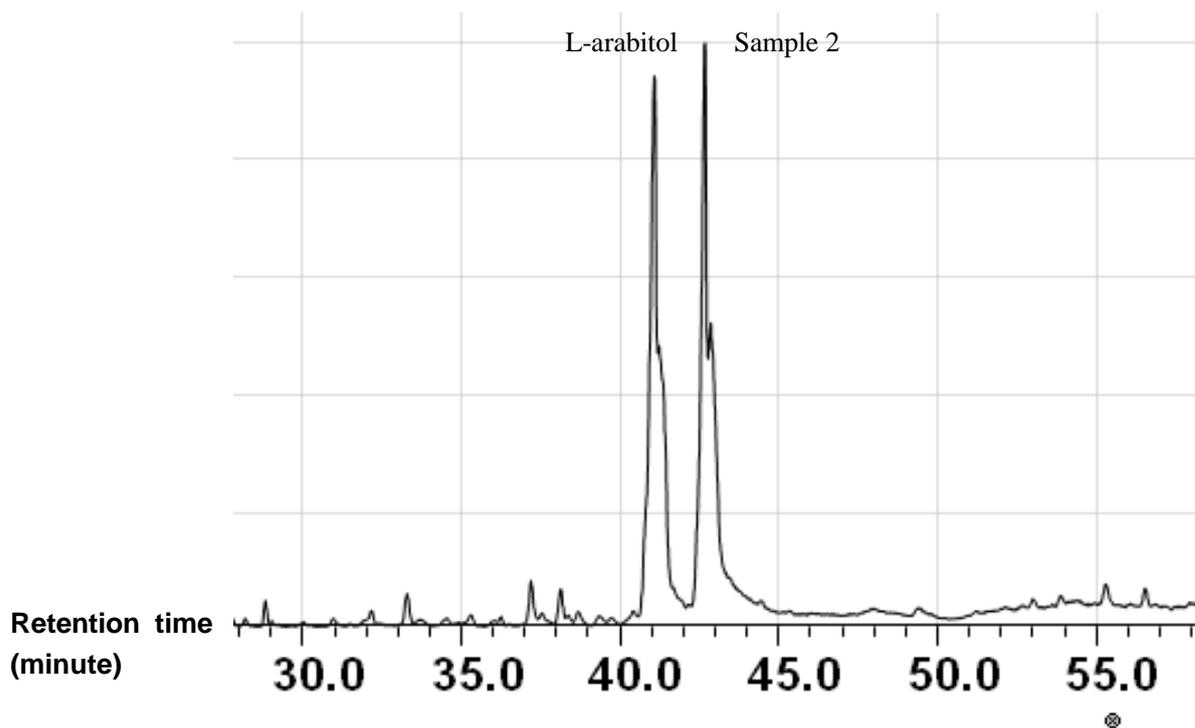
S1-A. Analysis of trifluoroacetyl sample 1 (degraded from compound **3**) and trifluoroacetyl tetritol standards by gas chromatography.



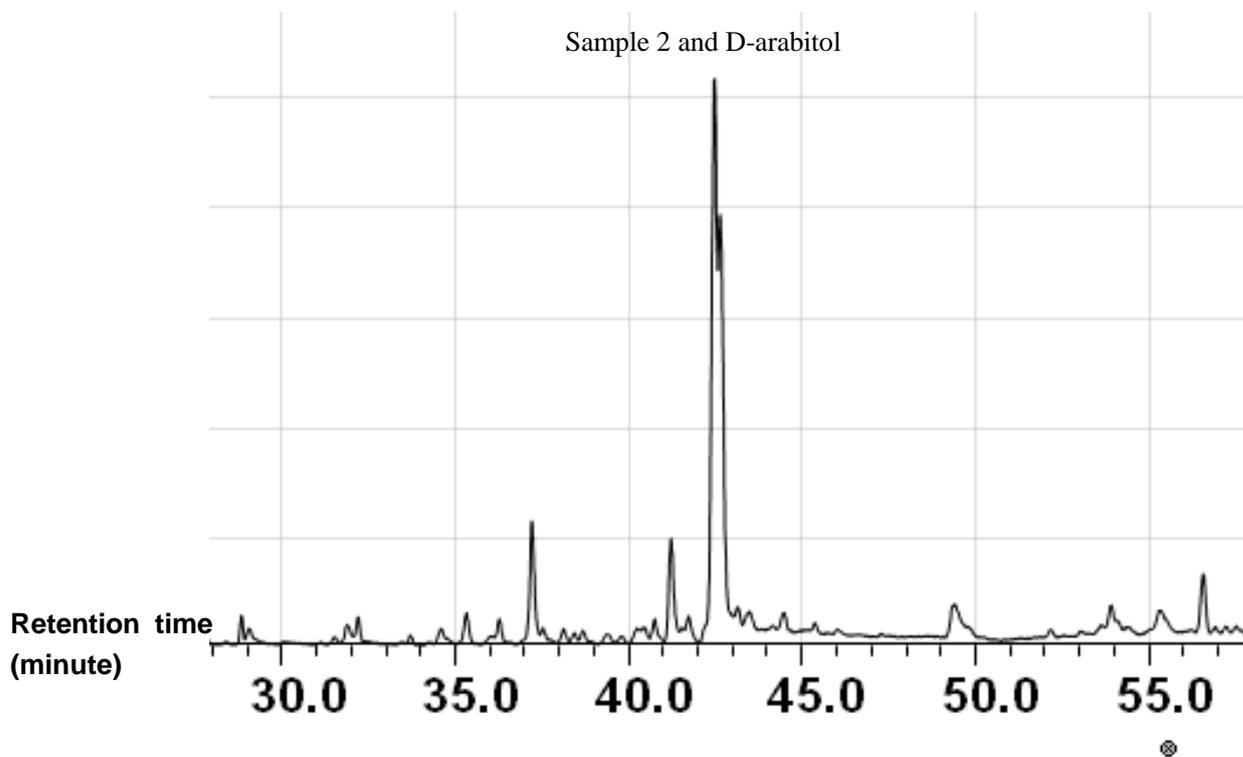
S1-B. Analysis of trifluoroacetyl pentitol standards by gas chromatography.



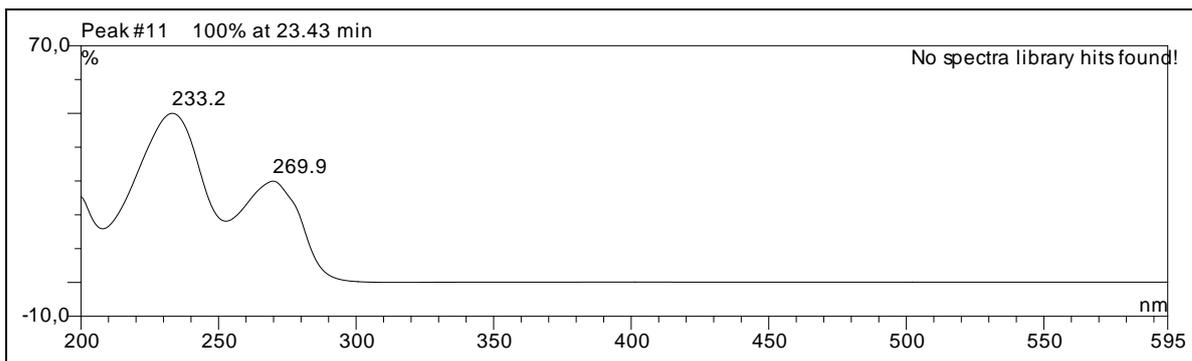
S1-C. Analysis of trifluoroacetyl sample 2 (degraded from mixture of compounds 4 and 5) by gas chromatography.



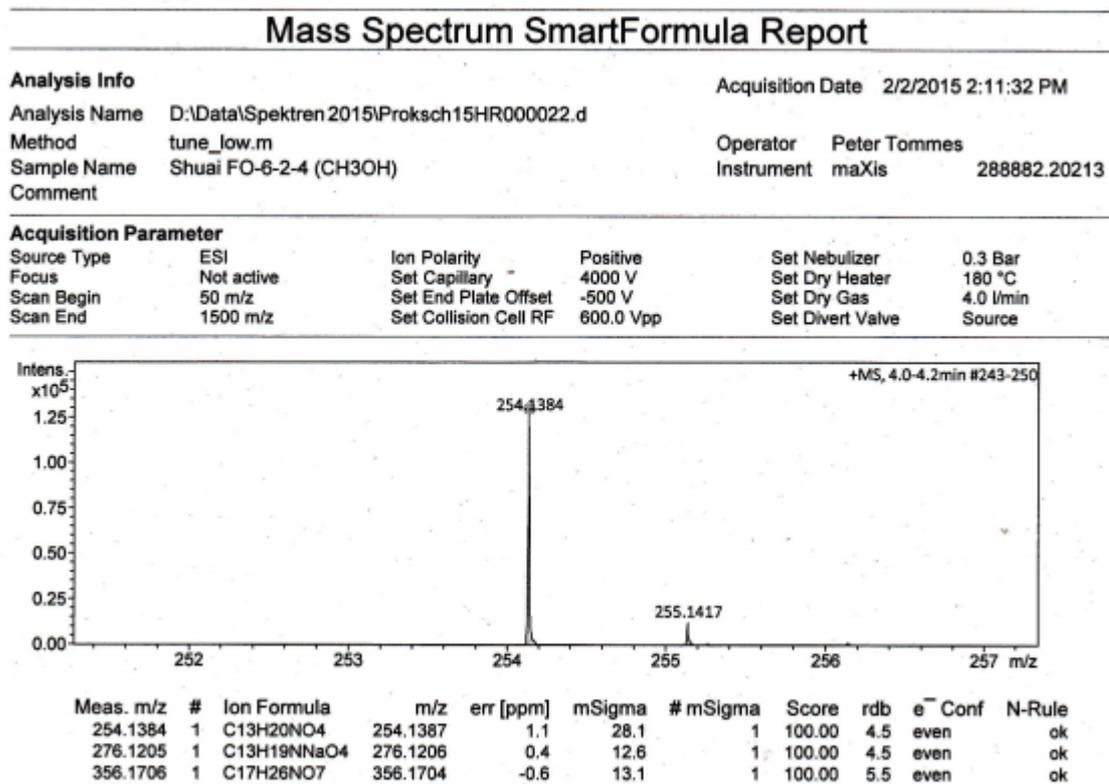
S1-D. Analysis of trifluoroacetyl sample 2 (degraded from mixture of compounds 4 and 5) and L-arabitol in one injection by gas chromatography.



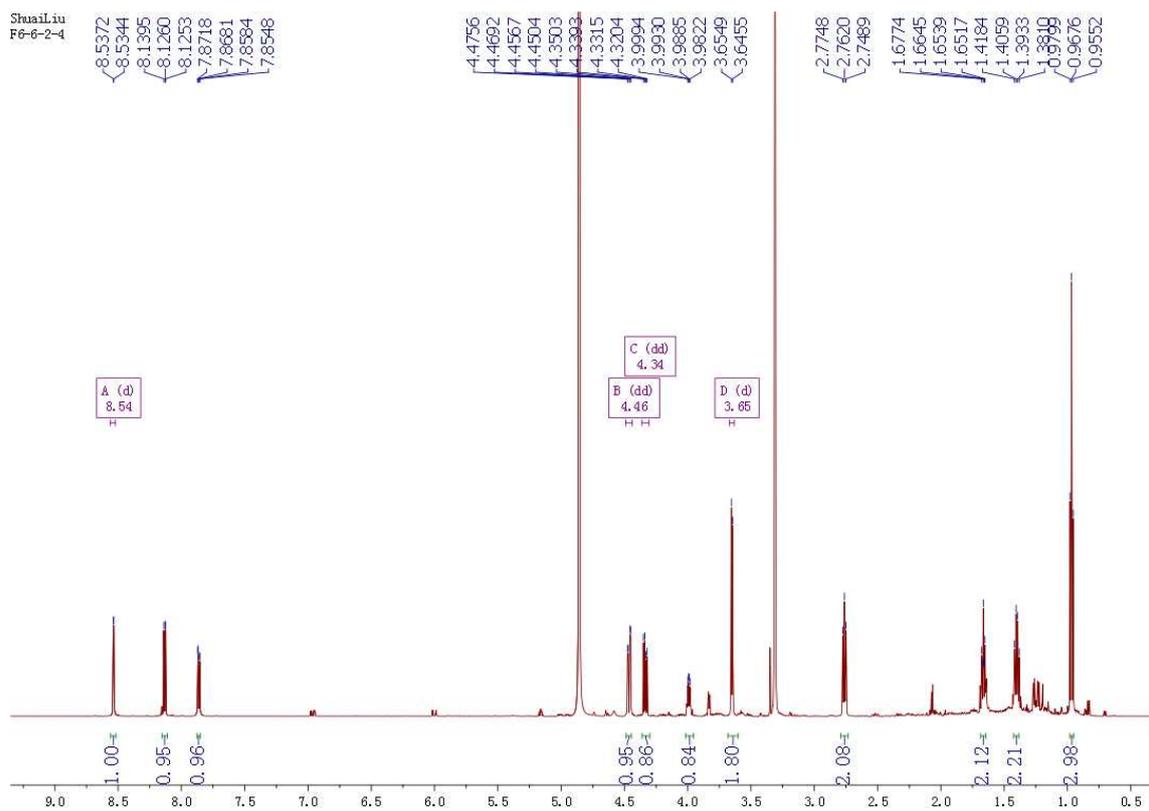
S1-E. Analysis of trifluoroacetyl sample 2 (degraded from mixture of compounds 4 and 5) and D-arabitol in one injection by gas chromatography.



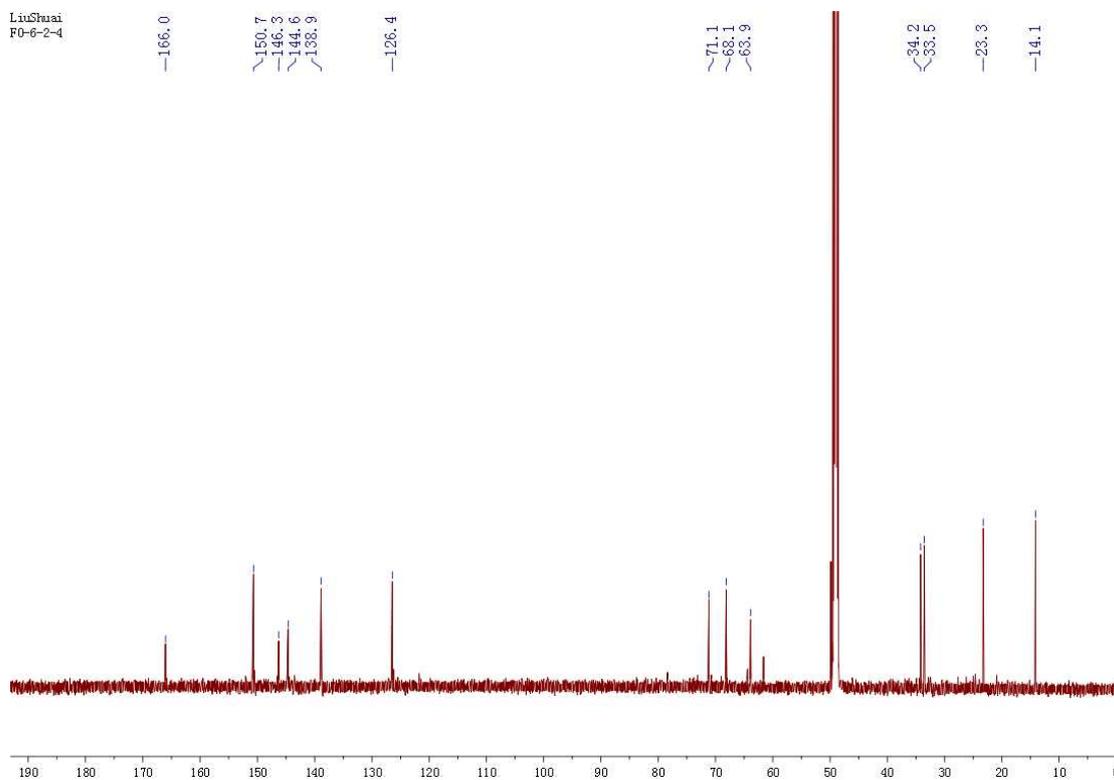
S2. UV spectrum of compound 1.



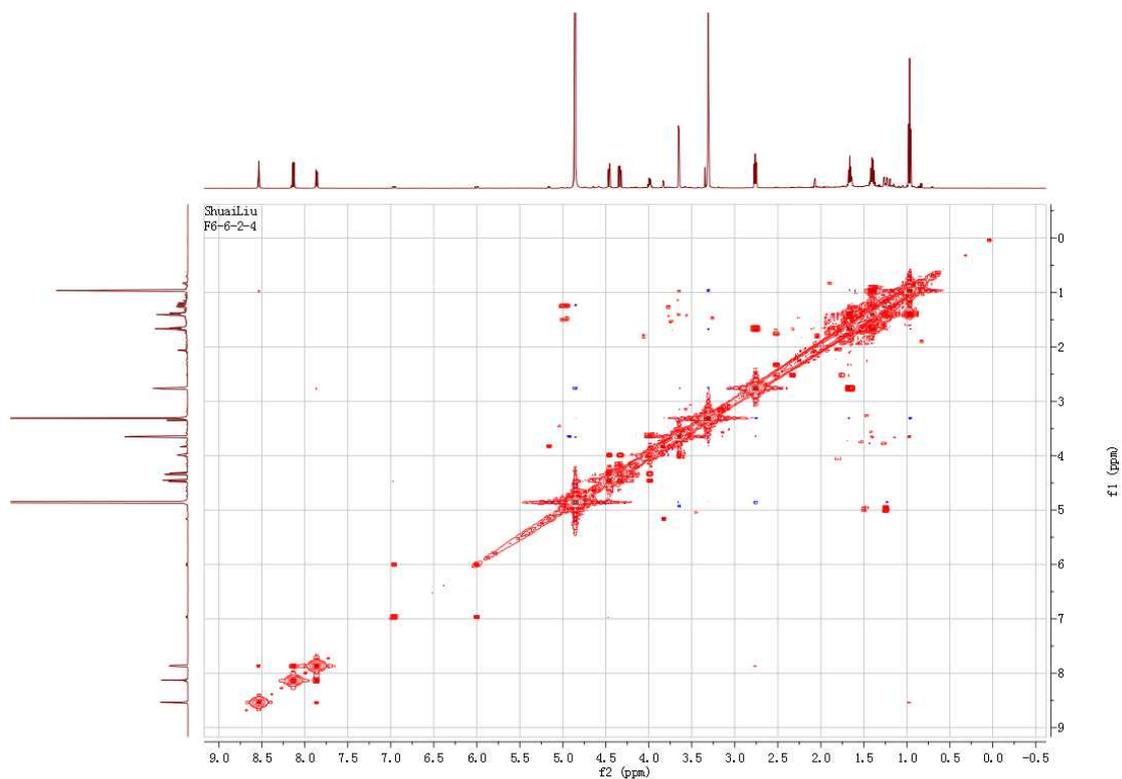
S3. HRESIMS spectrum of compound 1.



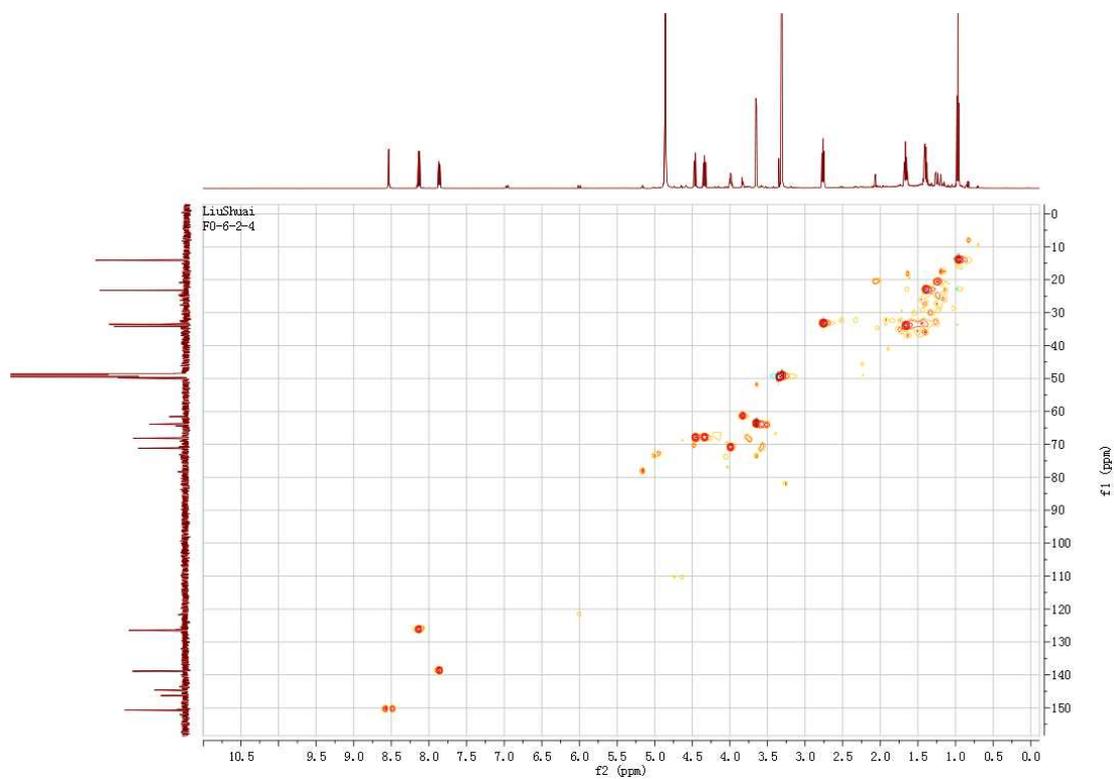
S4. ^1H NMR (600 MHz, CD_3OD) spectrum of compound **1**.



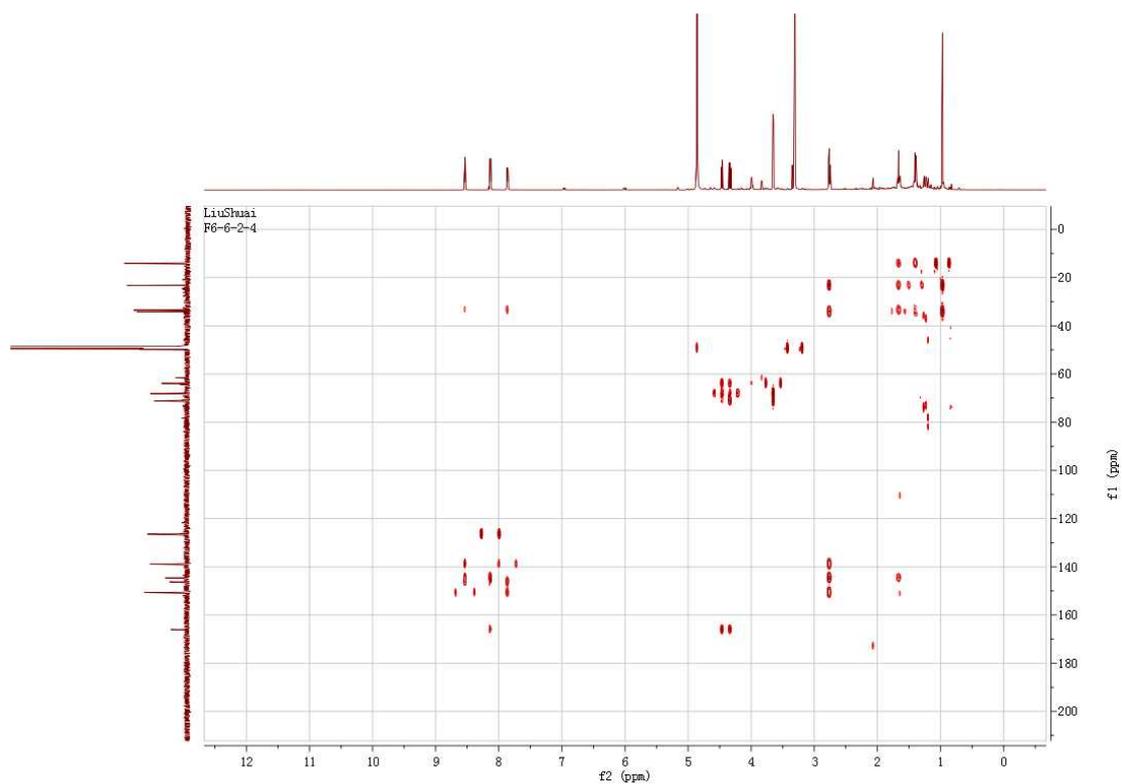
S5. ^{13}C NMR (150 MHz, CD_3OD) spectrum of compound **1**.



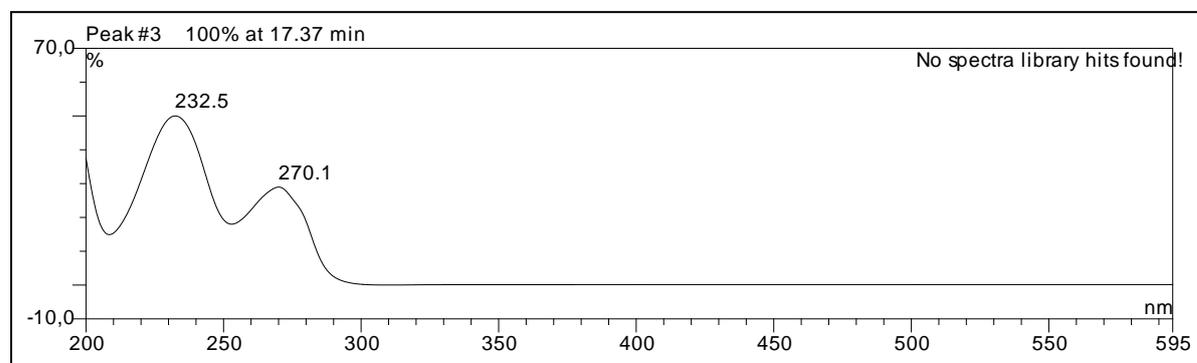
S6. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of compound **1**.



S7. HSQC (600 and 150 MHz, CD_3OD) spectrum of compound **1**.



S8. HMBC (600 and 150 MHz, CD₃OD) spectrum of compound **1**.

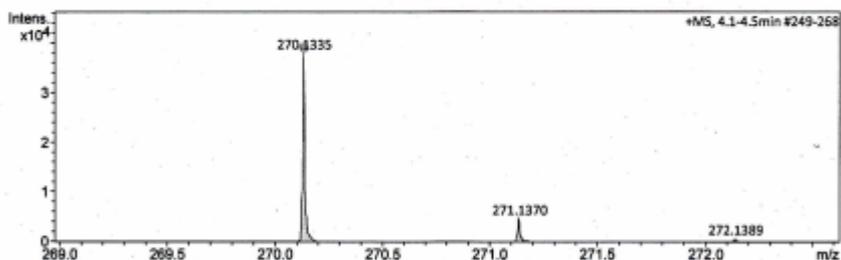


S9. UV spectrum of compound **2**.

Mass Spectrum SmartFormula Report

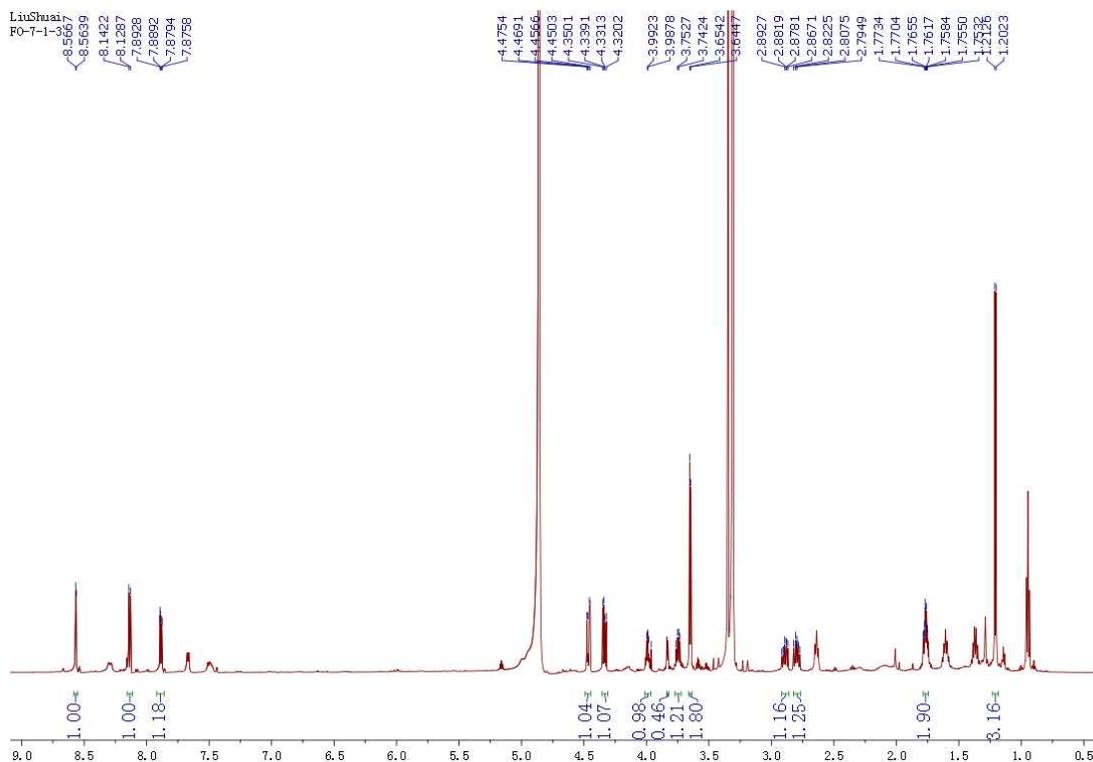
Analysis Info		Acquisition Date 2/17/2015 1:42:14 PM
Analysis Name	D:\Data\Spektren 2015\Proksch15HR000039.d	
Method	tune_low.m	Operator Peter Tommes
Sample Name	Shuai Liu FO-7-1-3 (CH3OH)	Instrument maXis 268882.20213
Comment		

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



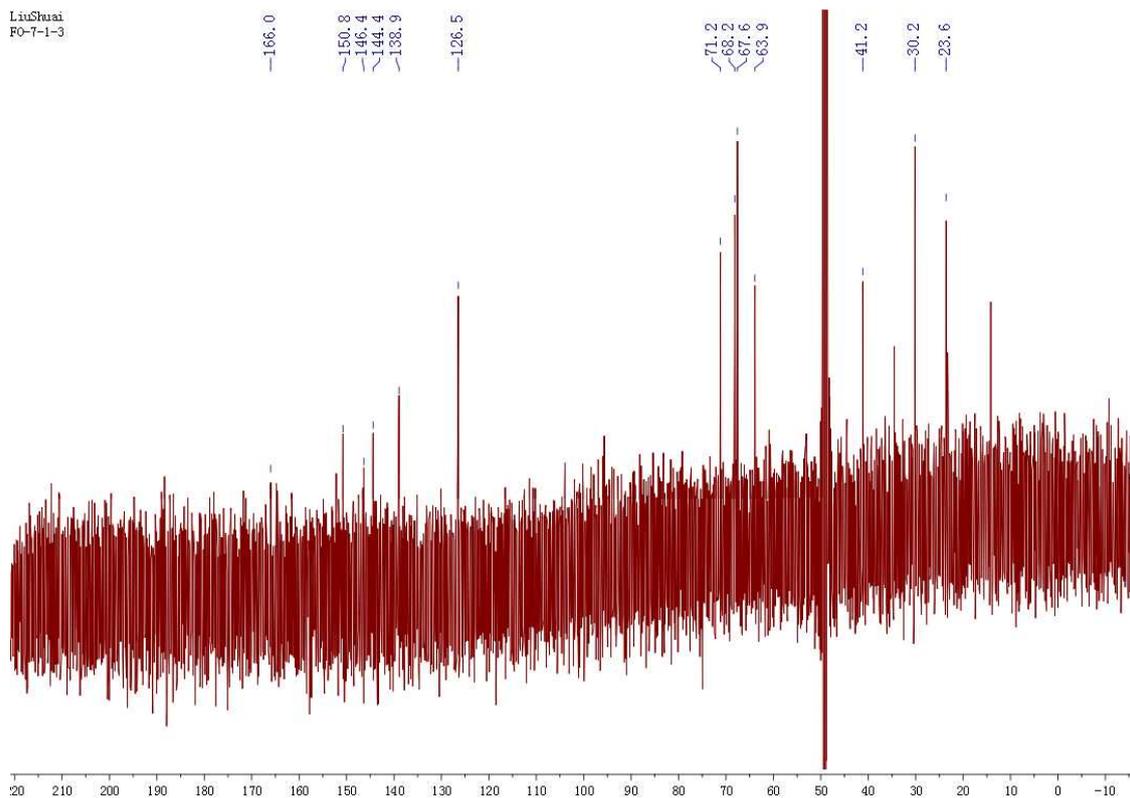
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻	Conf	N-Rule
270.1335	1	C13H20NO5	270.1336	0.4	16.2	1	100.00	4.5	even		ok
292.1155	1	C13H19NNaO5	292.1155	0.2	2.4	1	100.00	4.5	even		ok

S10. HRESIMS spectrum of compound **2**.

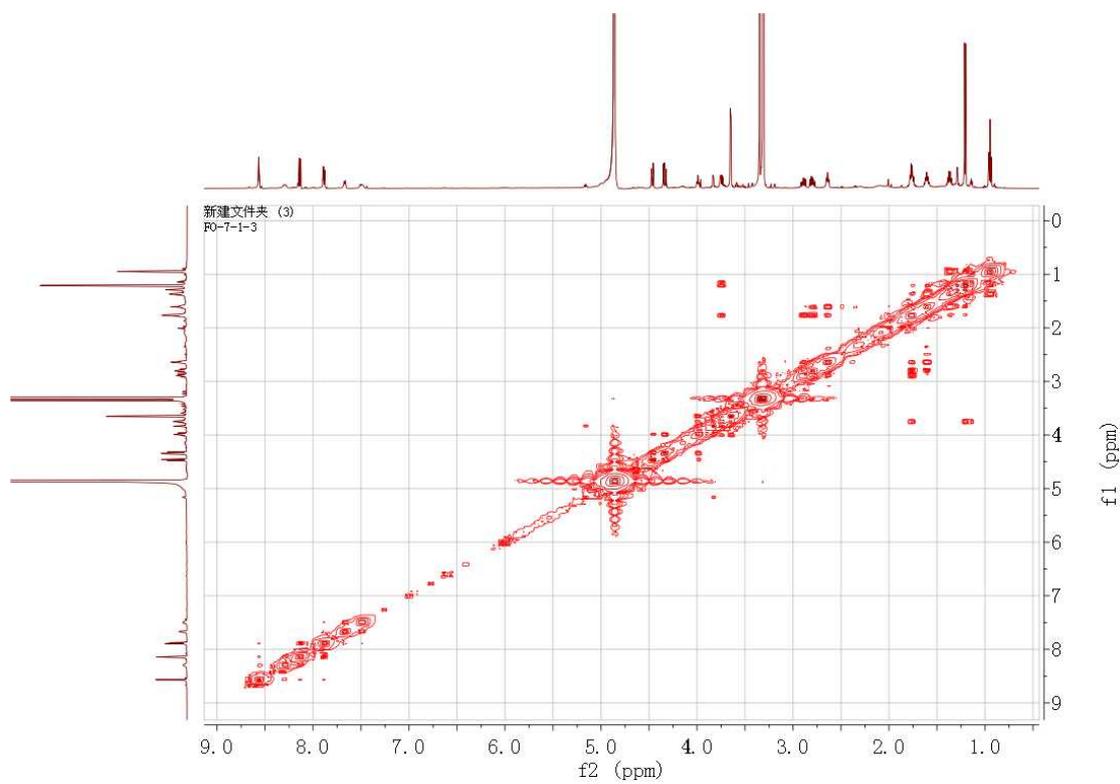


S11. ¹H NMR (600 MHz, CD₃OD) spectrum of compound **2**.

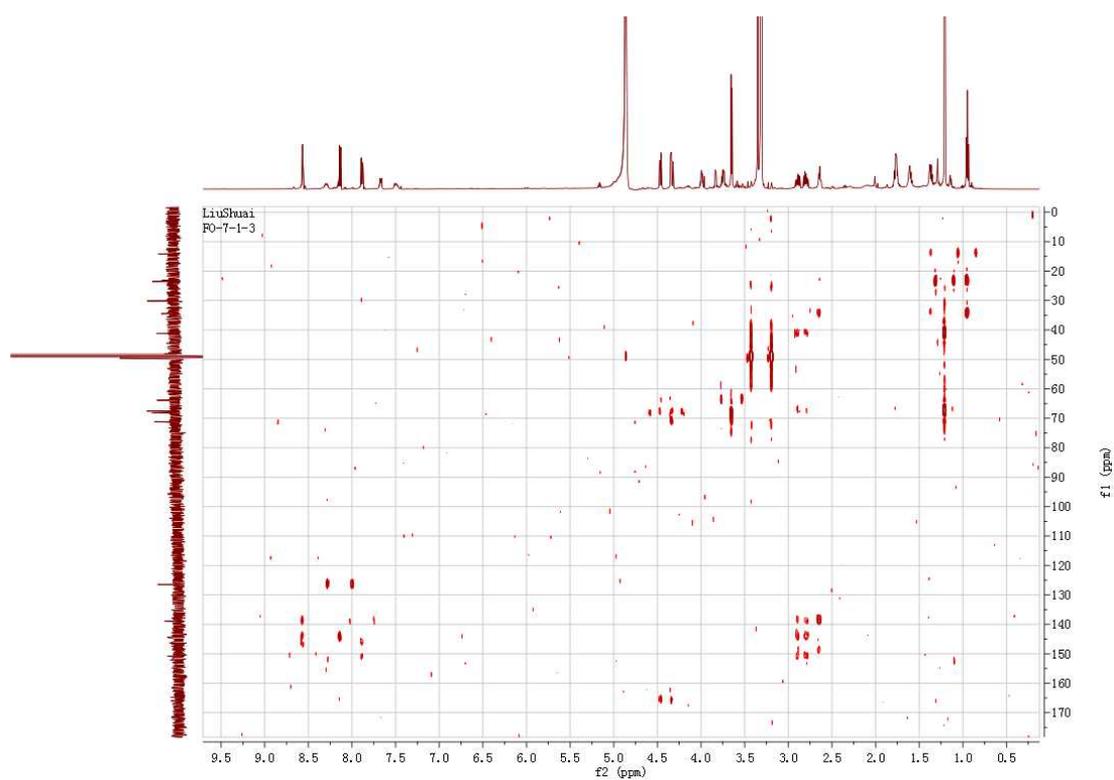
LiuShuai
FO-7-1-3



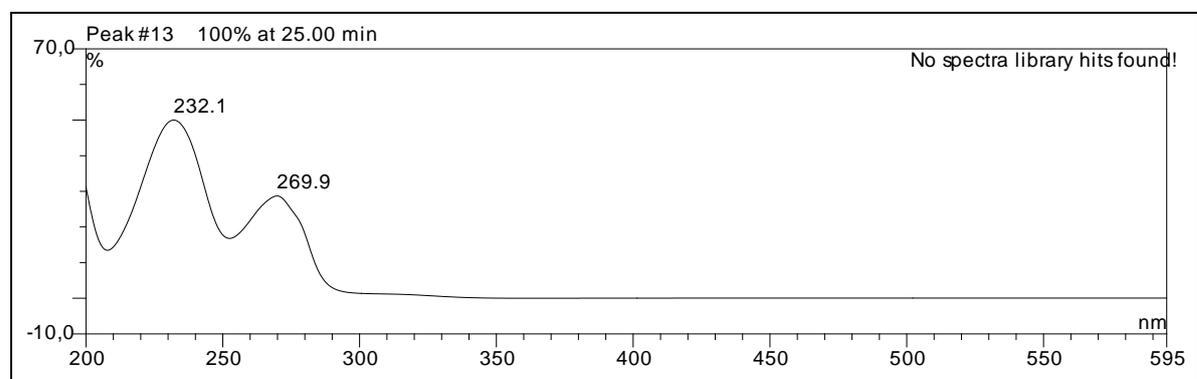
S12. ^{13}C NMR (150 MHz, CD_3OD) spectrum of compound **2**.



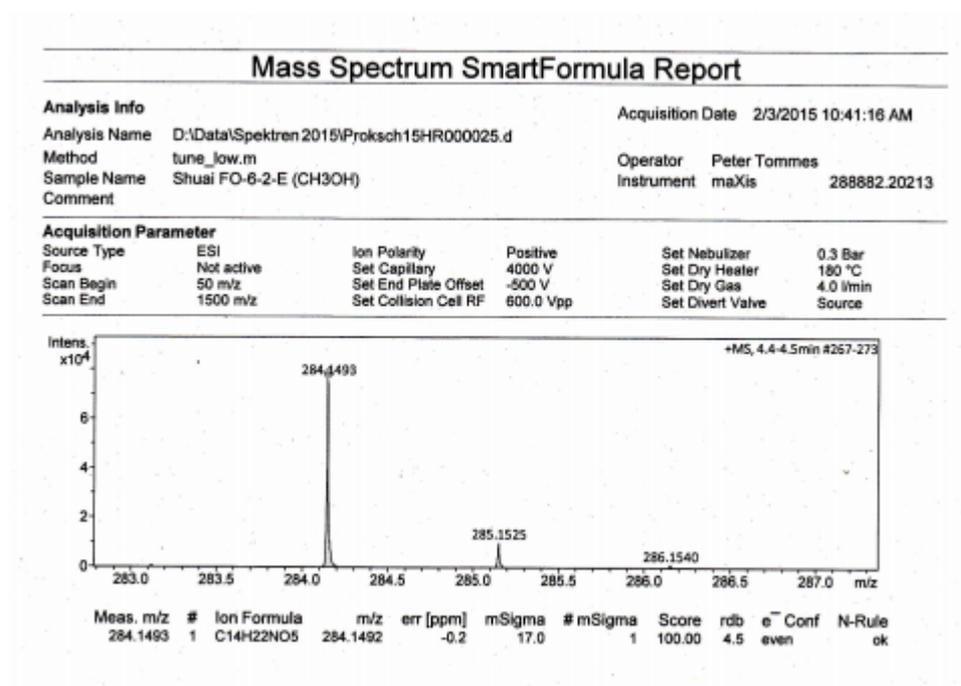
S13. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of compound **2**.



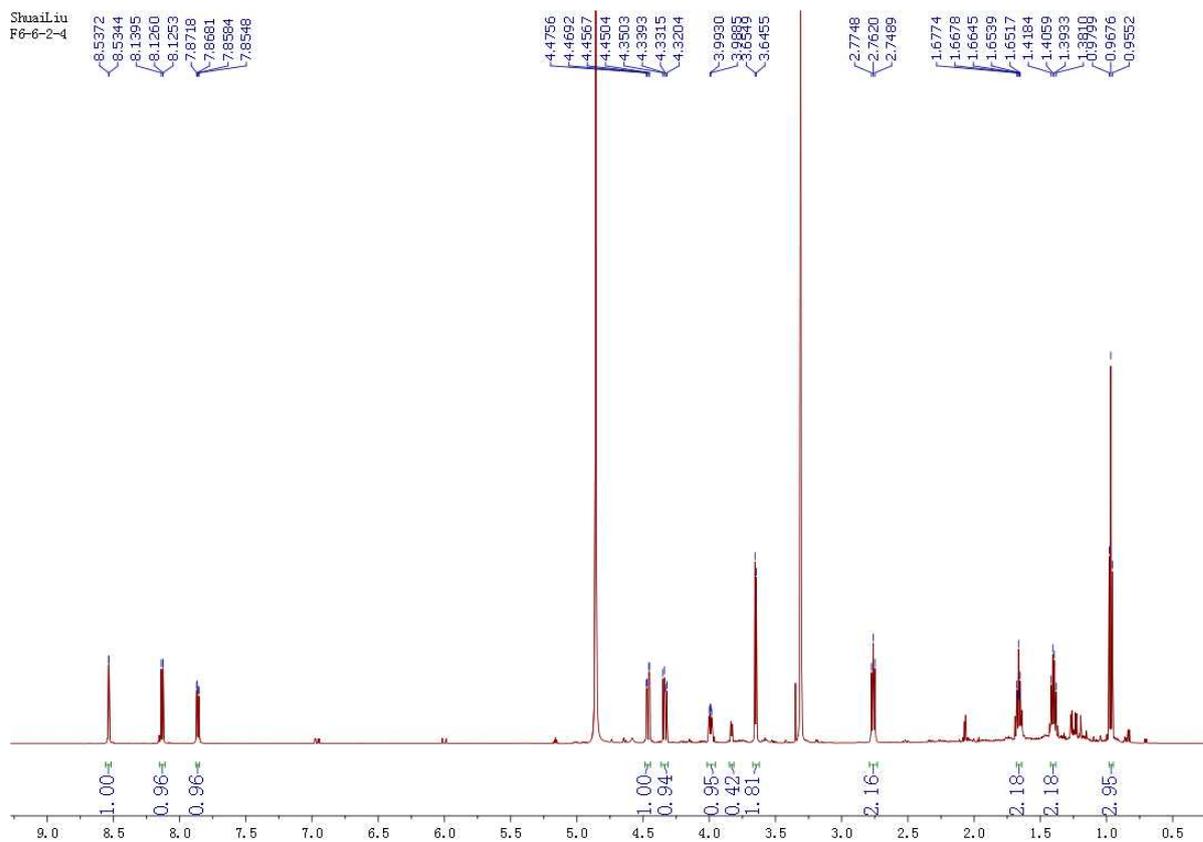
S14. HMBC (600 and 150 MHz, CD₃OD) spectrum of compound **2**.



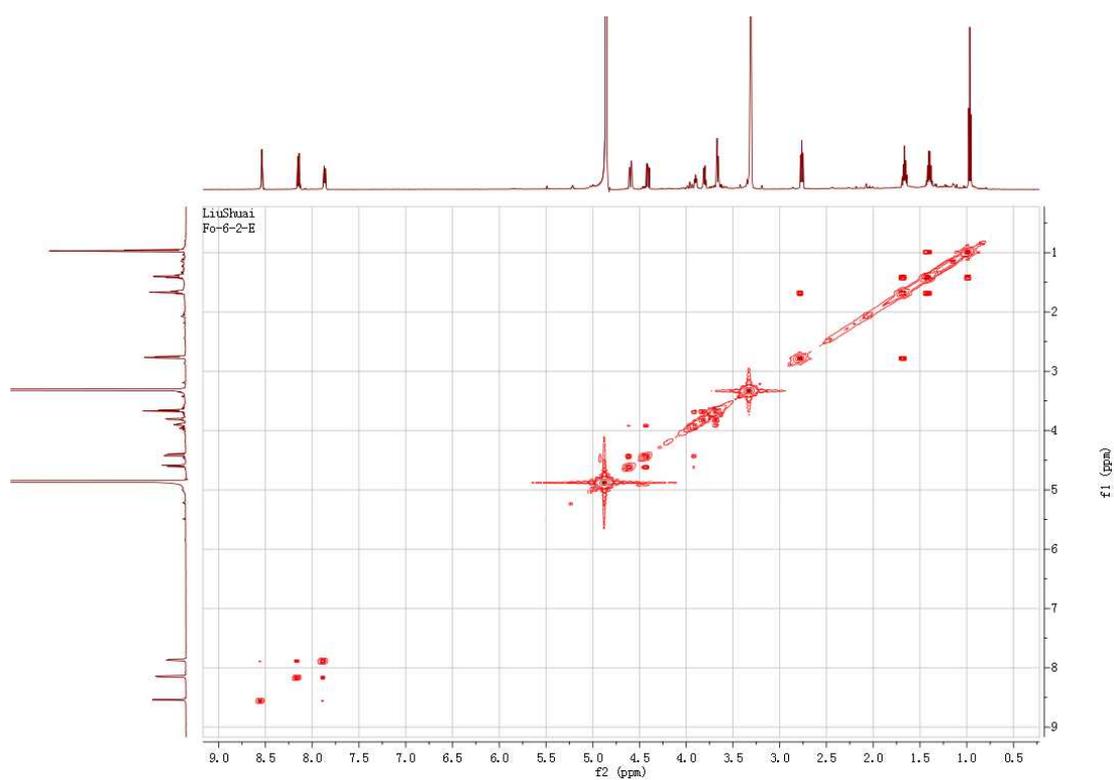
S15. UV spectrum of compound **3**.



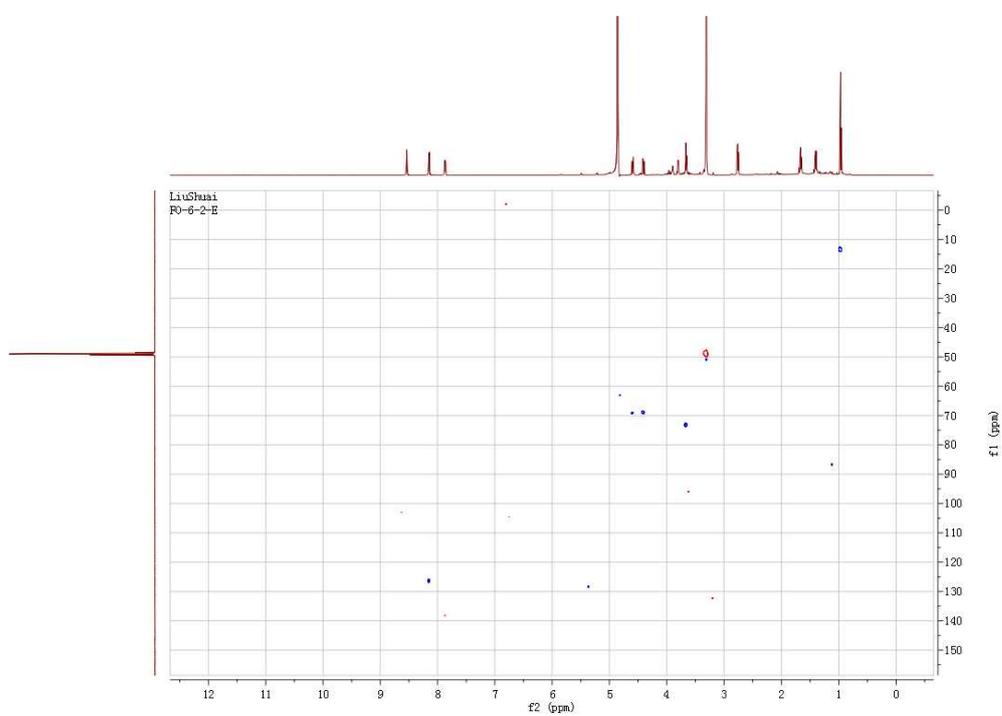
S16. HRESIMS spectrum of compound **3**.



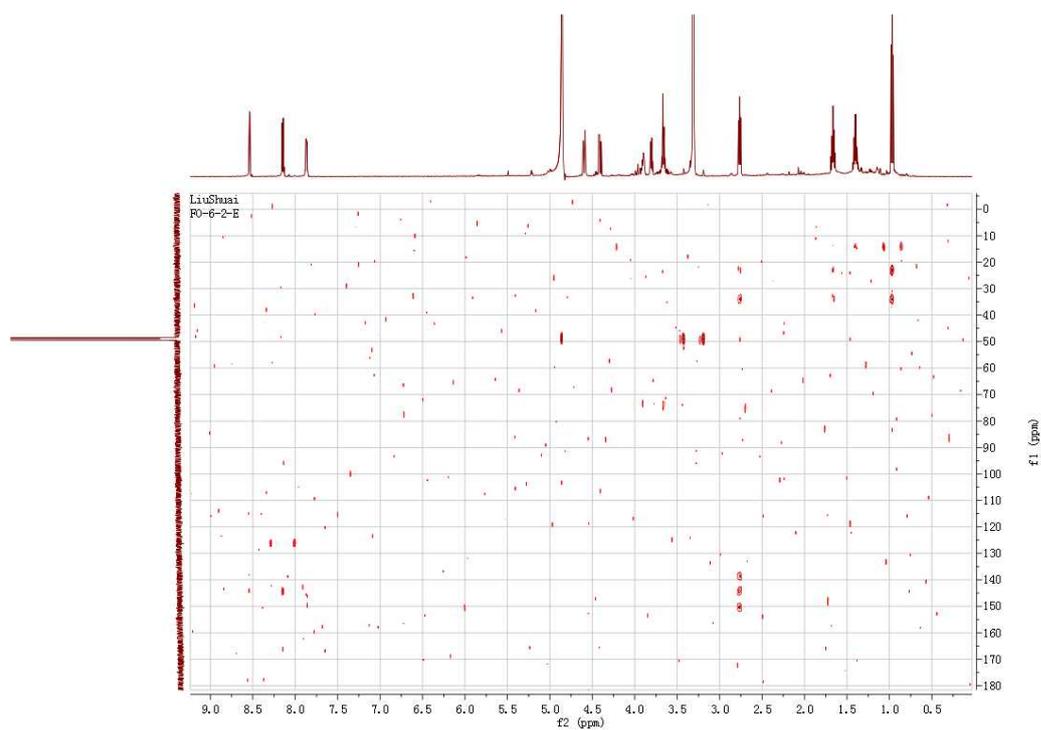
S17. ¹H NMR (600 MHz, CD₃OD) spectrum of compound **3**.



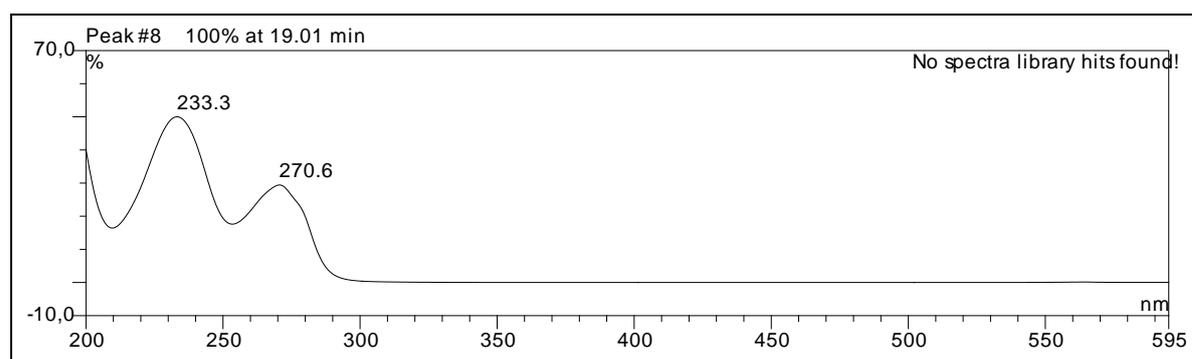
S18. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of compound **3**.



S19. HSQC (600 and 150 MHz, CD_3OD) spectrum of compound **3**.



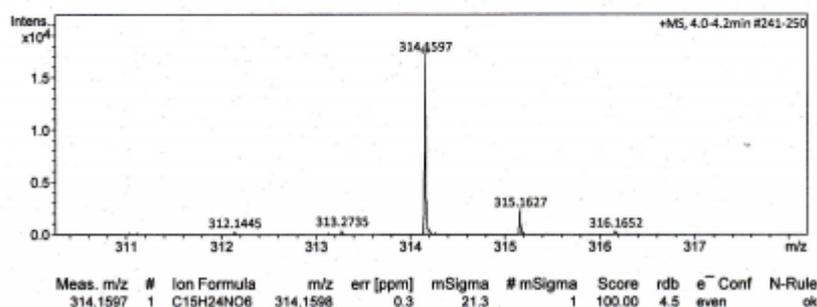
S20. HMBC (600 and 150 MHz, CD₃OD) spectrum of compound **3**.



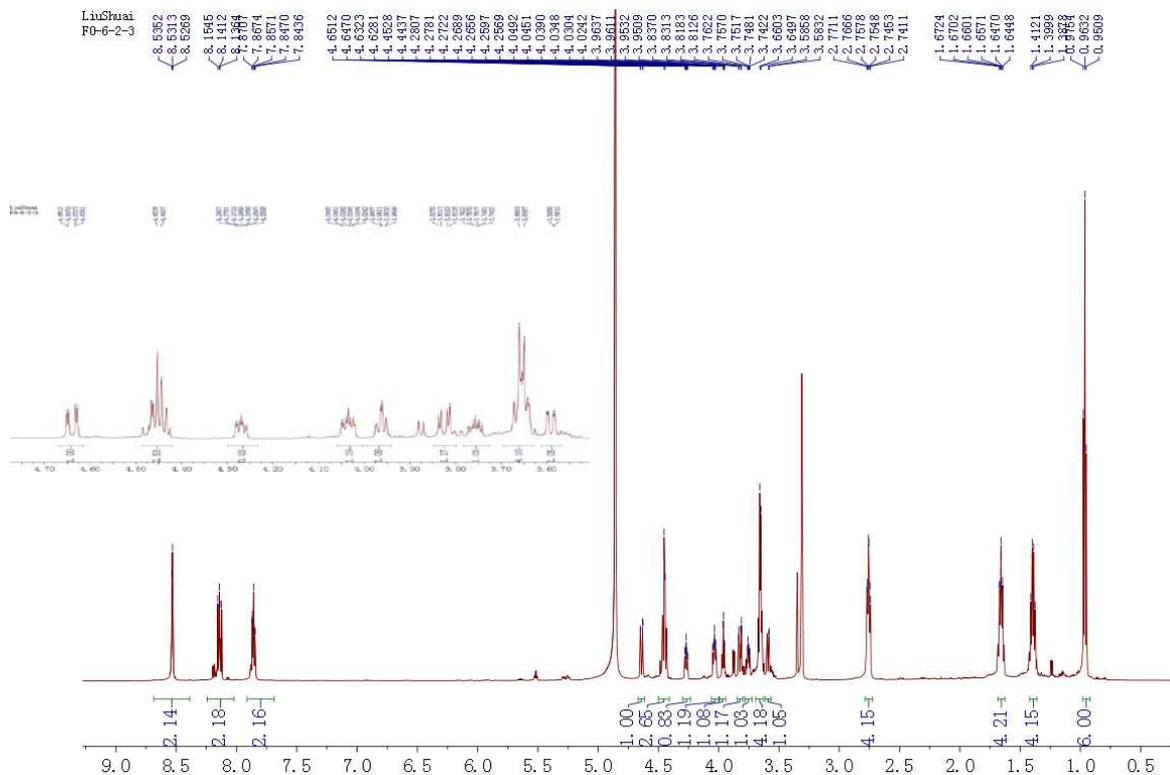
S21. UV spectrum of mixture of **4** and **5**.

Mass Spectrum SmartFormula Report

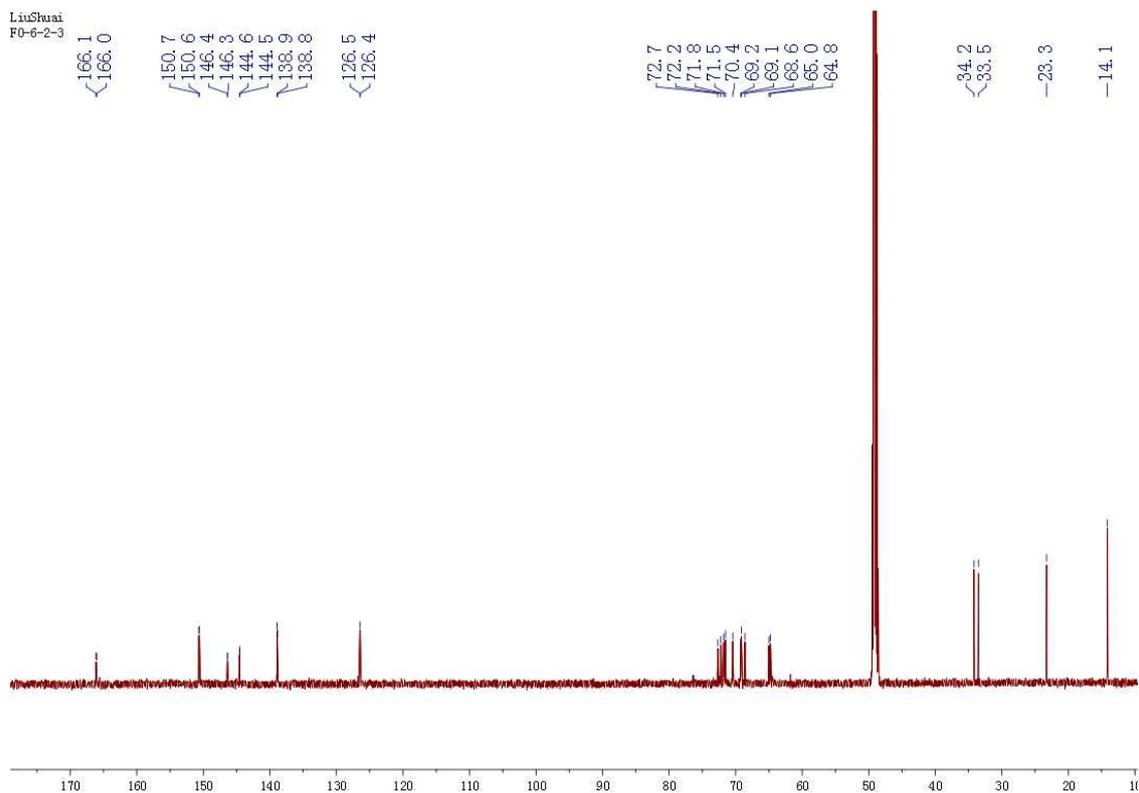
Analysis Info		Acquisition Date	
Analysis Name	D:\Data\Spektren 2015\Proksch15HR000021.d	2/2/2015 1:55:51 PM	
Method	tune_low.m	Operator	Peter Tommes
Sample Name	Shuai FO-6-2-3 (CH3OH)	Instrument	maXis 288882.20213
Comment			
Acquisition Parameter			
Source Type	ESI	Ion Polarity	Positive
Focus	Not active	Set Capillary	4000 V
Scan Begin	50 m/z	Set End Plate Offset	-500 V
Scan End	1500 m/z	Set Collision Cell RF	600.0 Vpp
		Set Nebulizer	0.3 Bar
		Set Dry Heater	180 °C
		Set Dry Gas	4.0 l/min
		Set Divert Valve	Source



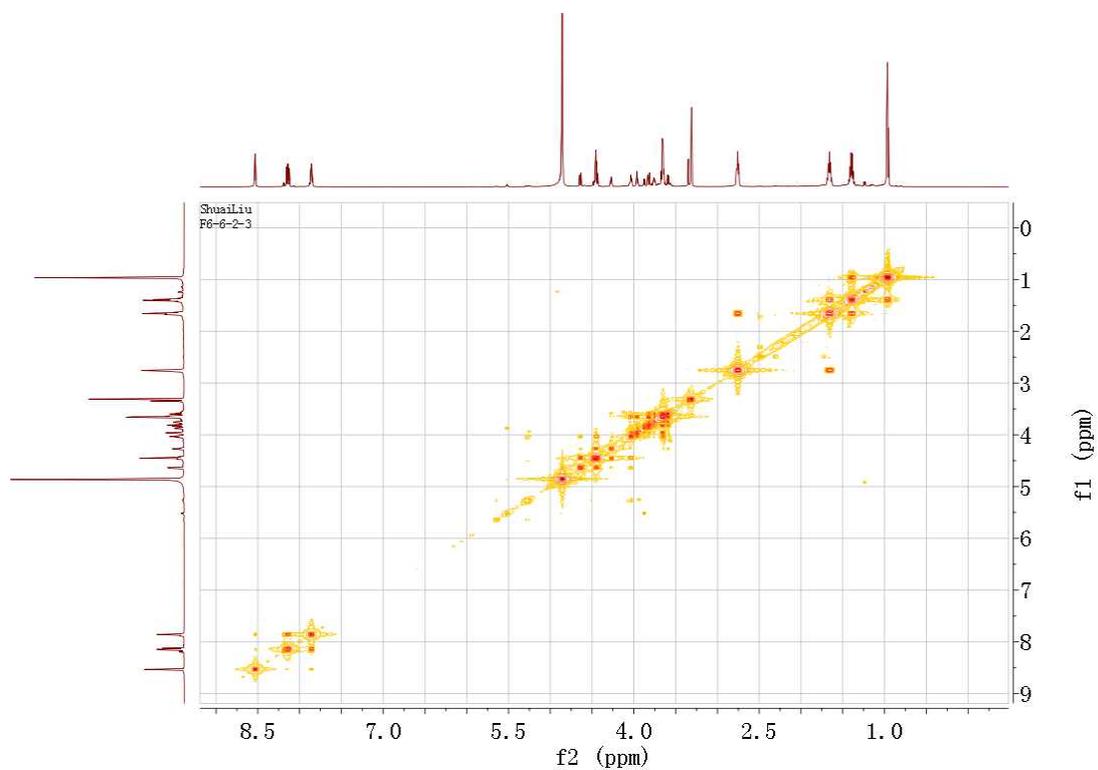
S22. HRESIMS spectrum of mixture of 4 and 5.



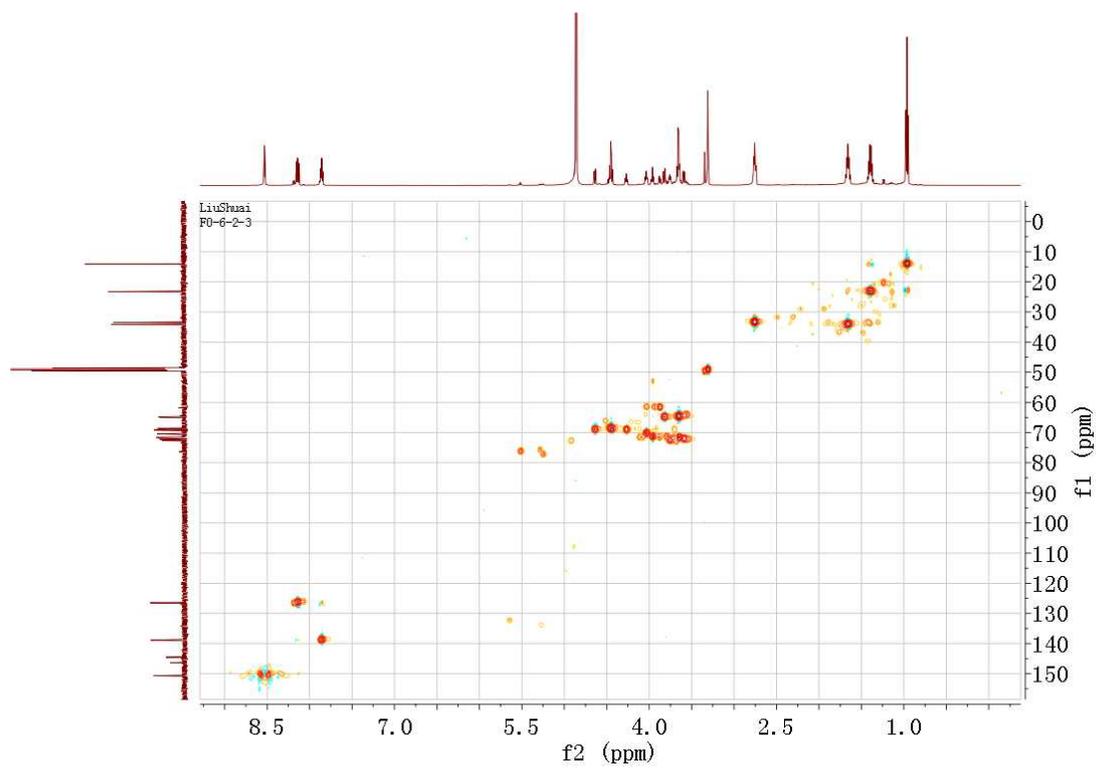
S23. ¹H NMR (600 MHz, CD₃OD) spectrum of mixture of 4 and 5.



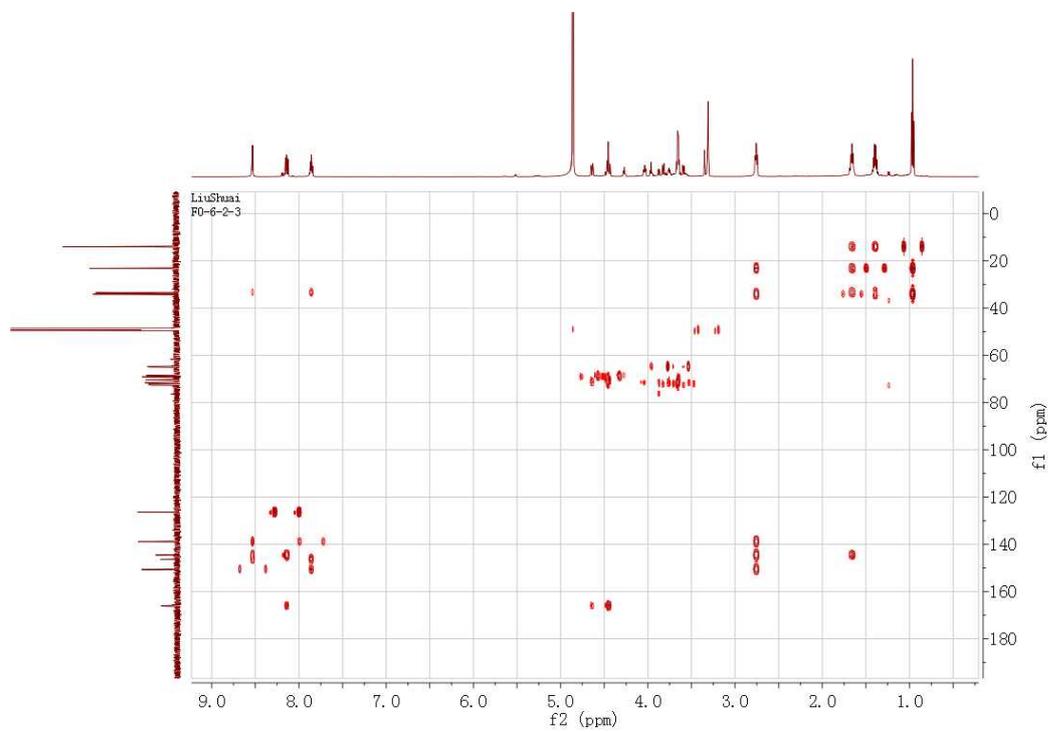
S24. ^{13}C NMR (150 MHz, CD_3OD) spectrum of mixture of **4** and **5**.



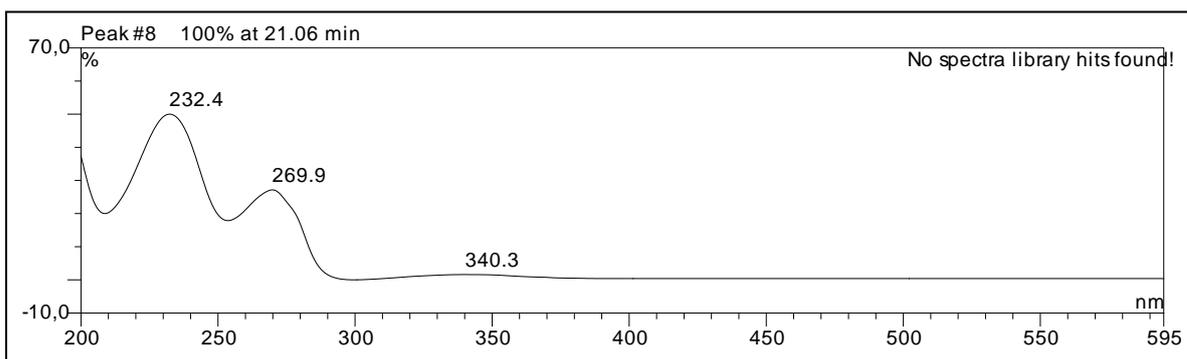
S25. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of mixture of **4** and **5**.



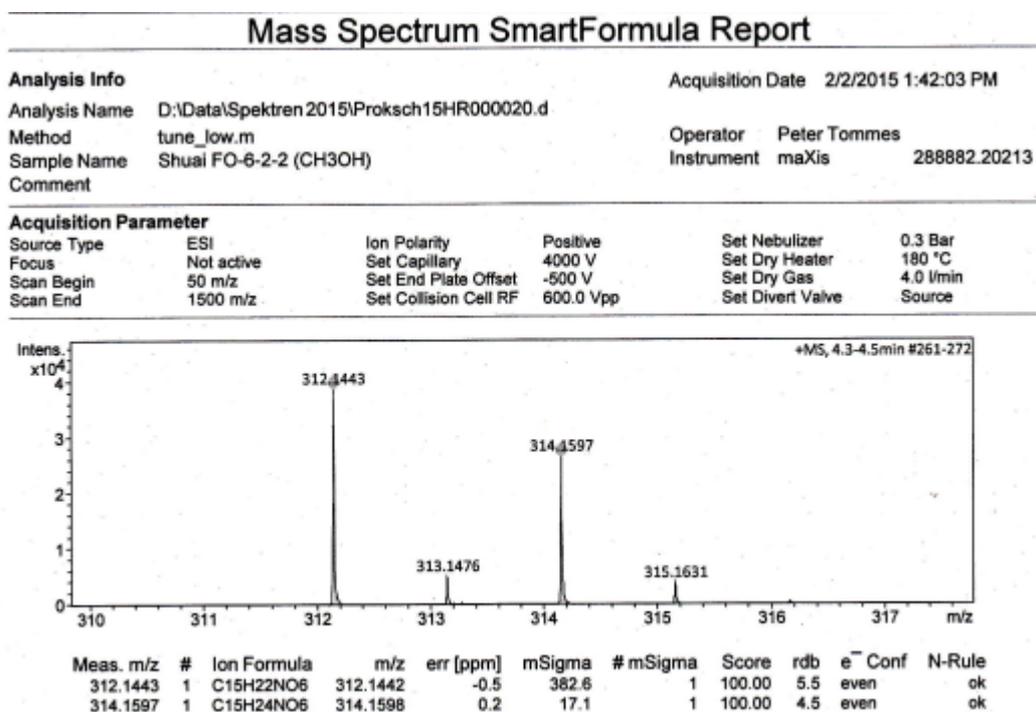
S26. HSQC (600 and 150 MHz, CD₃OD) spectrum of mixture of **4** and **5**.



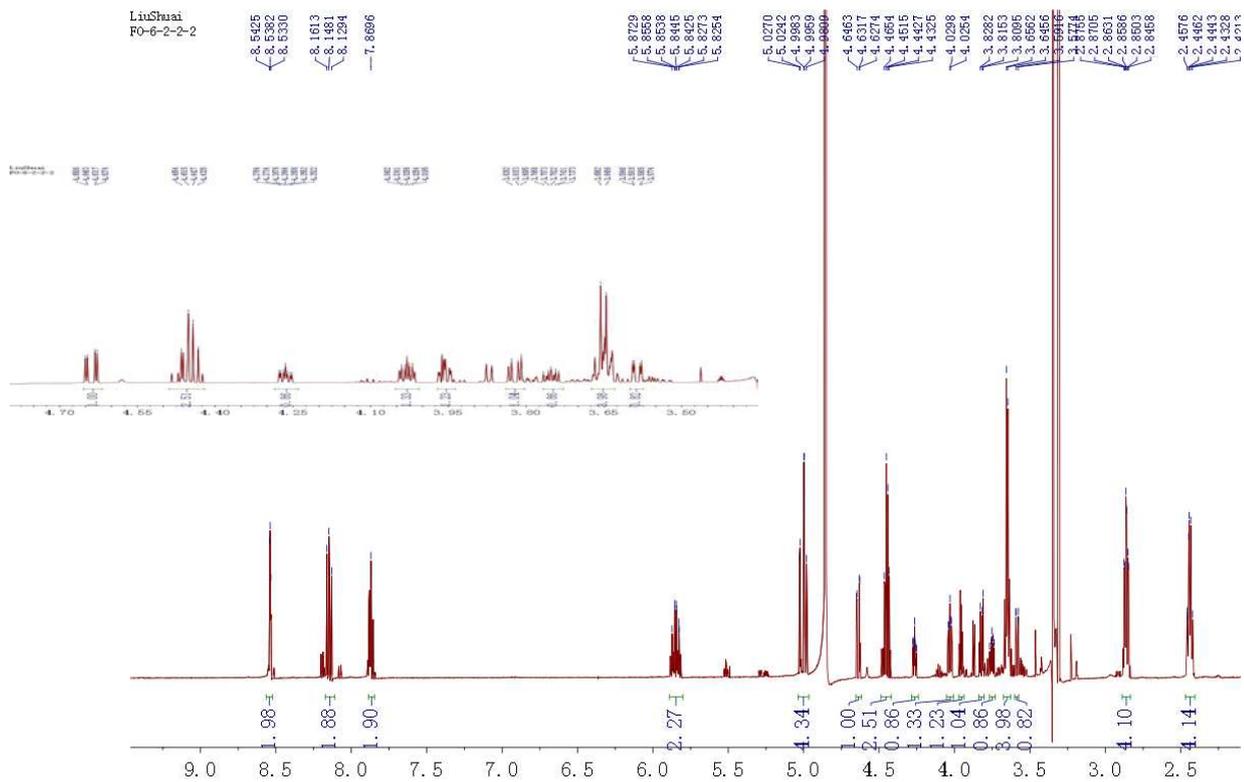
S27. HMBC (600 and 150 MHz, CD₃OD) spectrum of mixture of **4** and **5**.



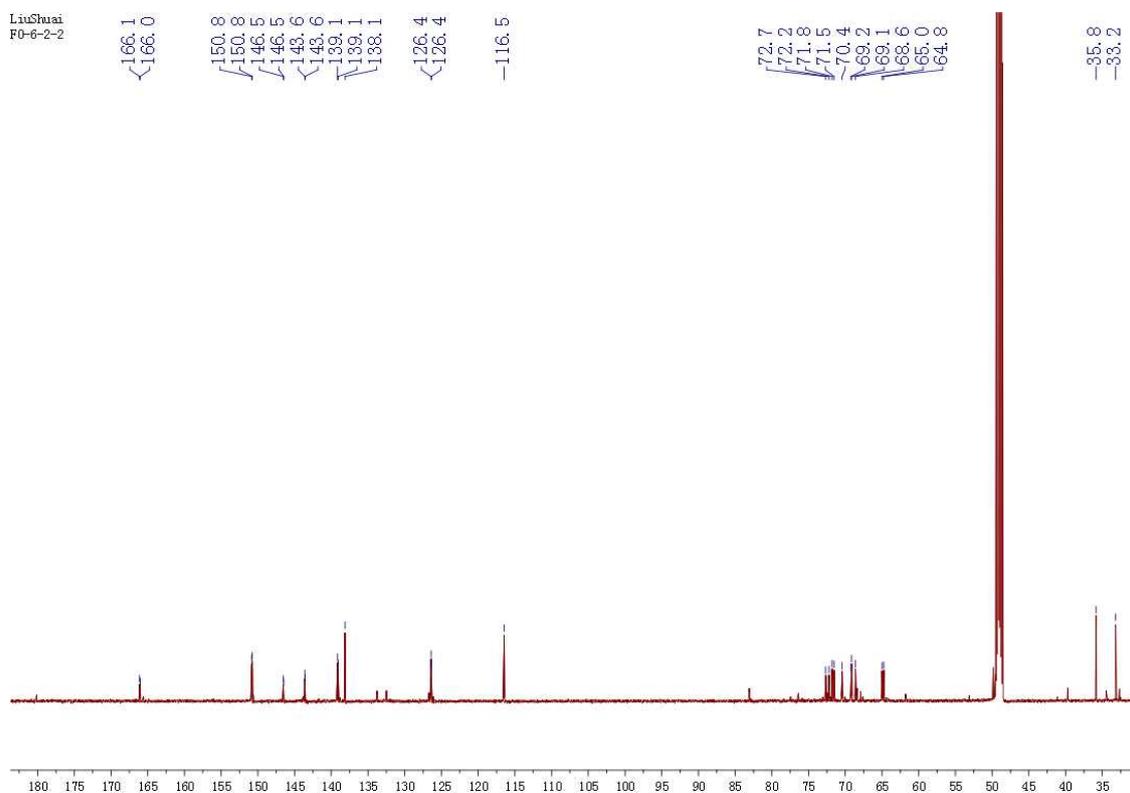
S28. UV spectrum of mixture of 6 and 7.



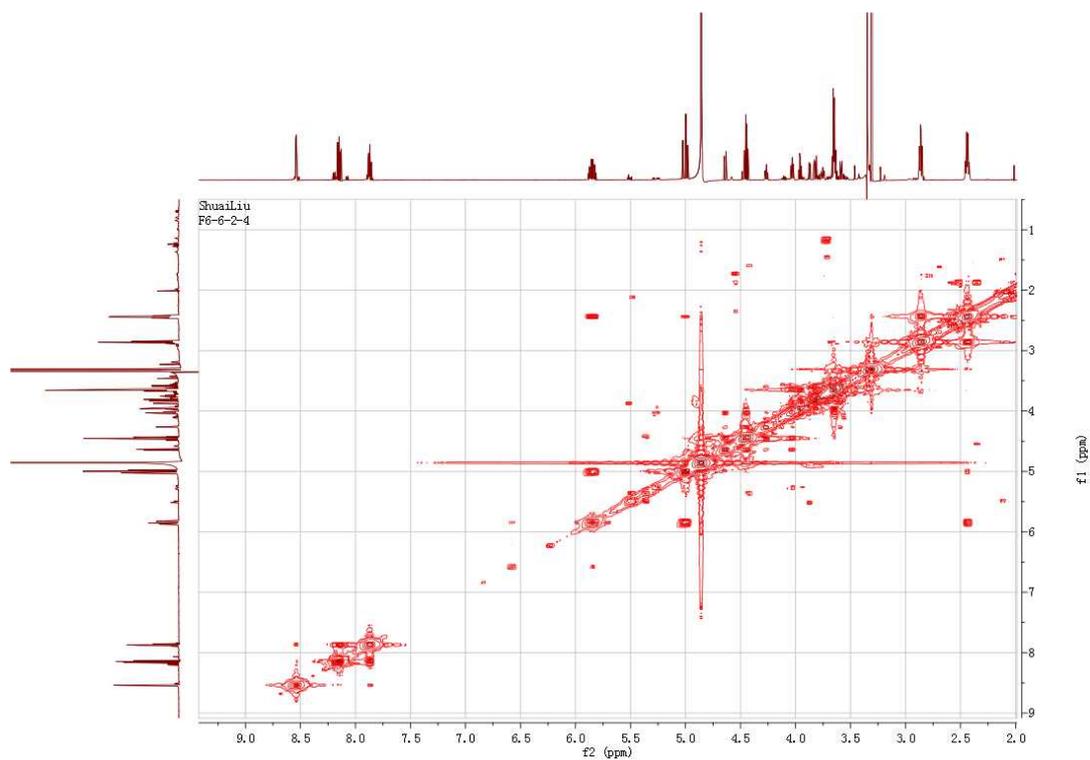
S29. HRESIMS spectrum of mixture of 6 and 7.



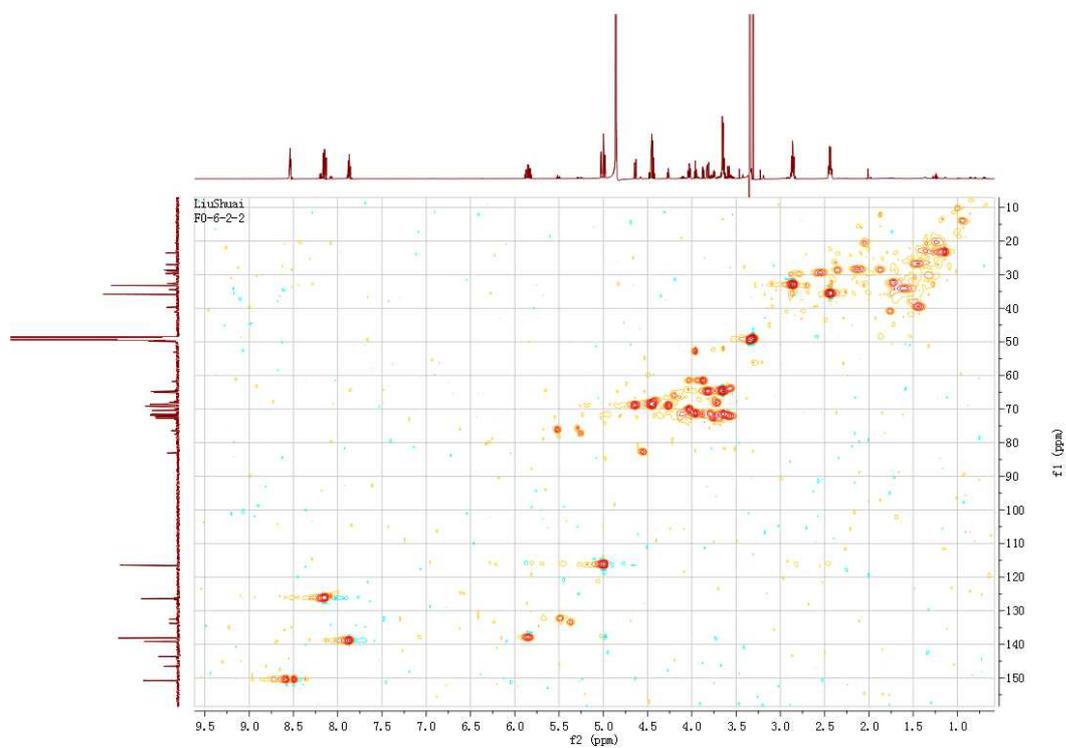
S30. ^1H NMR (600 MHz, CD_3OD) spectrum of mixture of **6** and **7**.



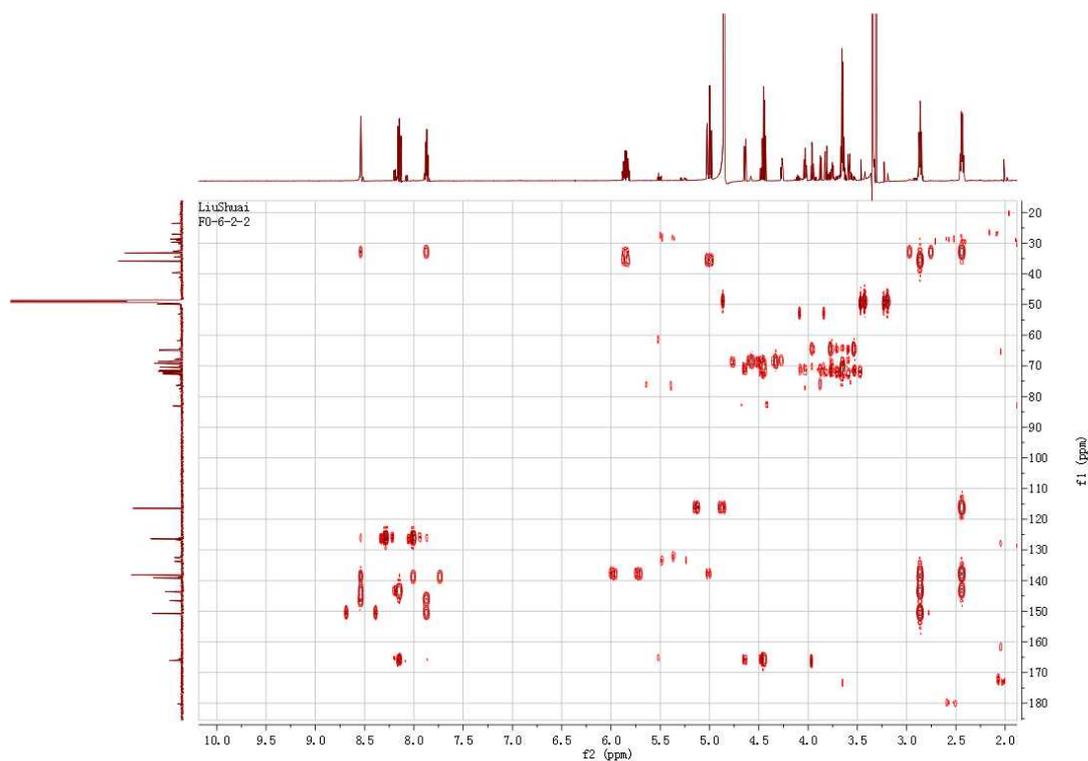
S31. ^{13}C NMR (150 MHz, CD_3OD) spectrum of mixture of **6** and **7**.



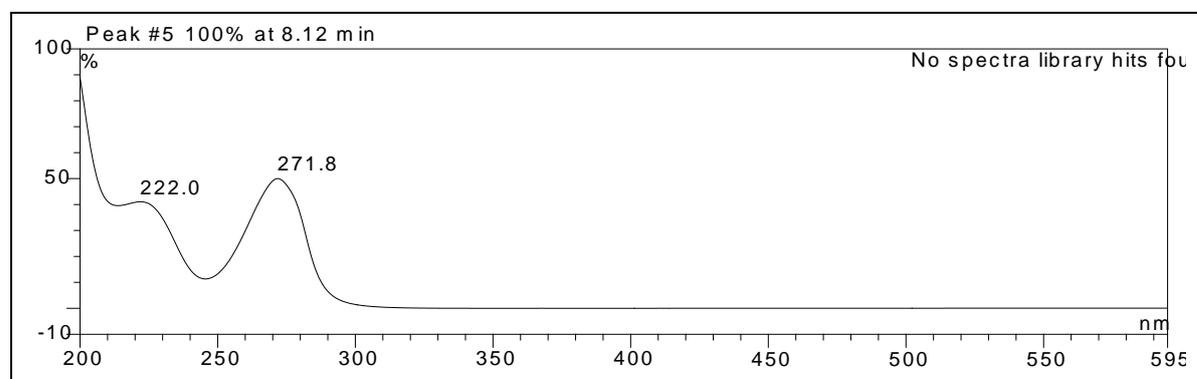
S32. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of mixture of **6** and **7**.



S33. HSQC (600 and 150 MHz, CD_3OD) spectrum of mixture of **6** and **7**.



S34. HMBC (600 and 150 MHz, CD₃OD) spectrum of mixture of **6** and **7**.



S35. UV spectrum of compound **8**.

Mass Spectrum SmartFormula Report

Analysis Info

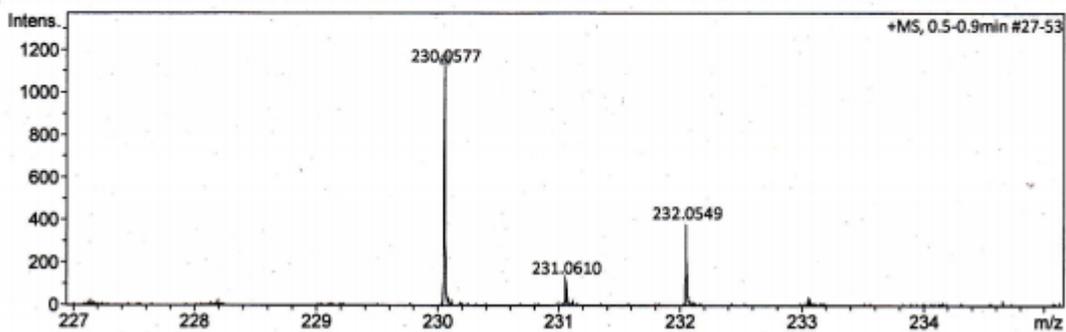
Analysis Name D:\Data\Spekren 2015\Proksch15HR000024.d
 Method tune_low.m
 Sample Name Shuai FO-7-1-1 (CH3OH)
 Comment

Acquisition Date 2/2/2015 3:41:04 PM

Operator Peter Tommes
 Instrument maXis 288882.20213

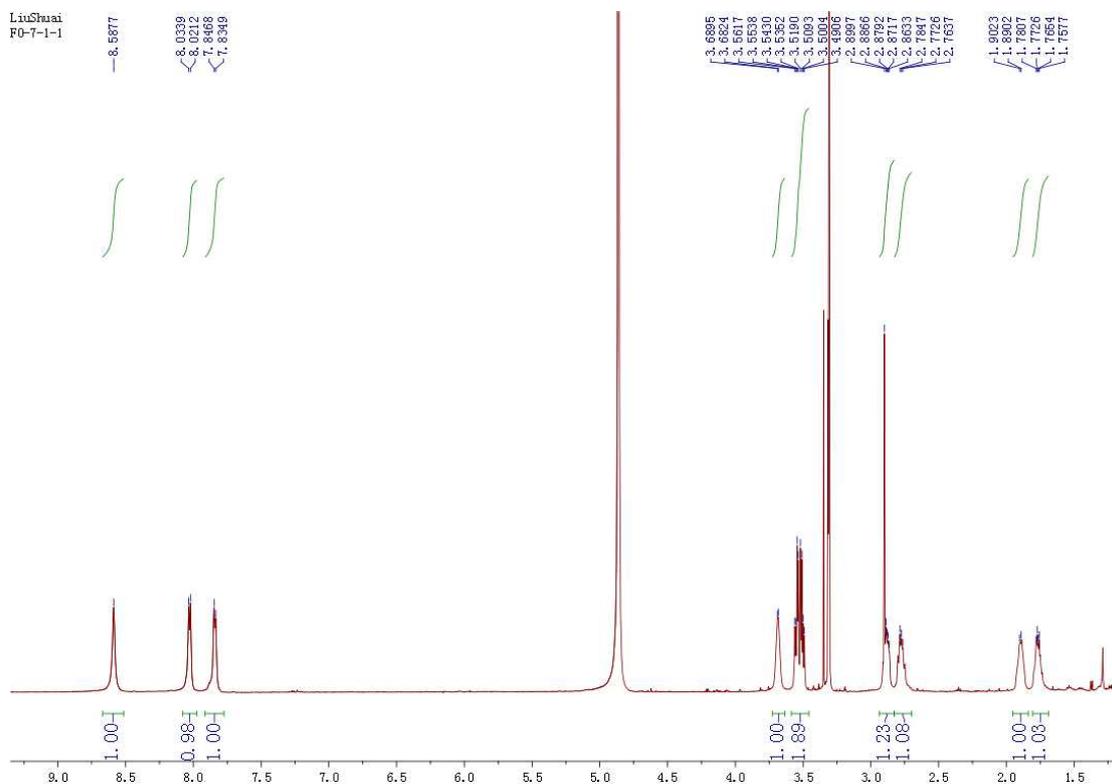
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

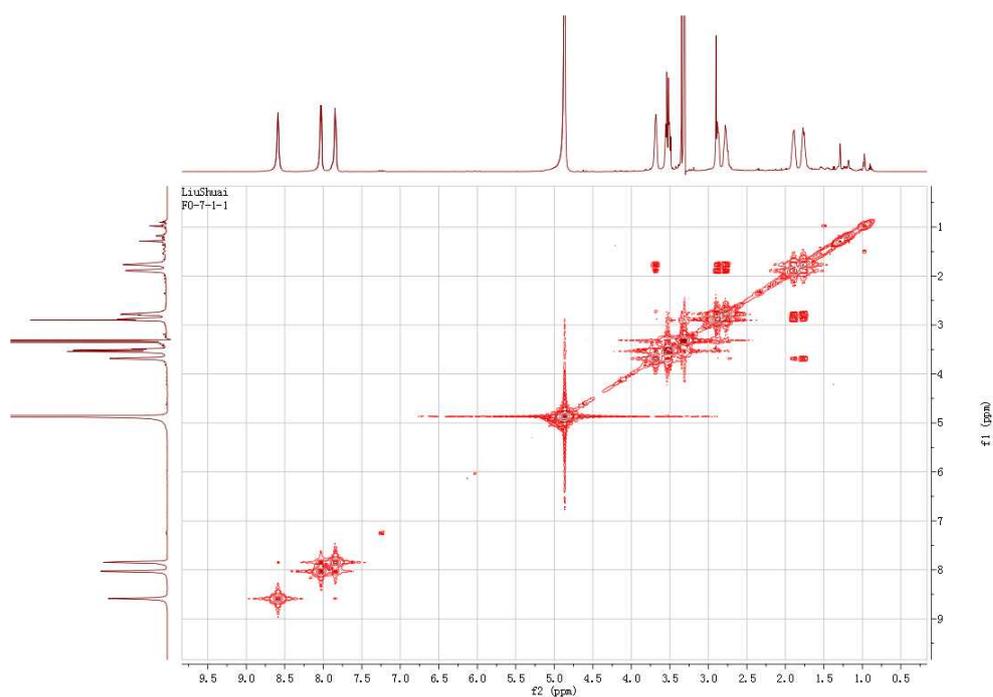


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
230.0577	1	C10H13CINO3	230.0578	0.8	19.4	1	100.00	4.5	even	ok

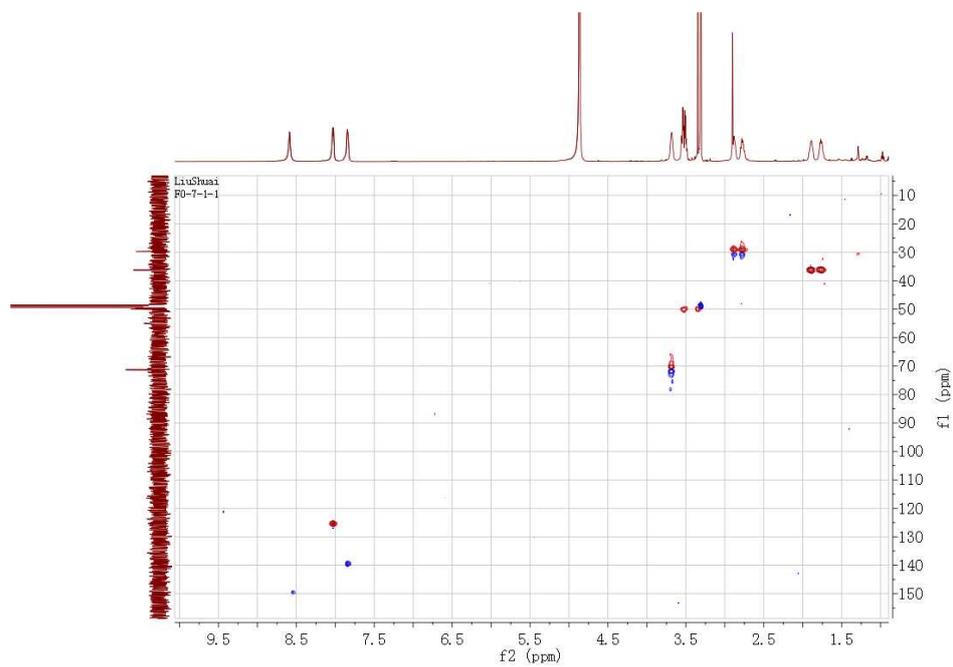
S36. HRESIMS spectrum of compound 8.



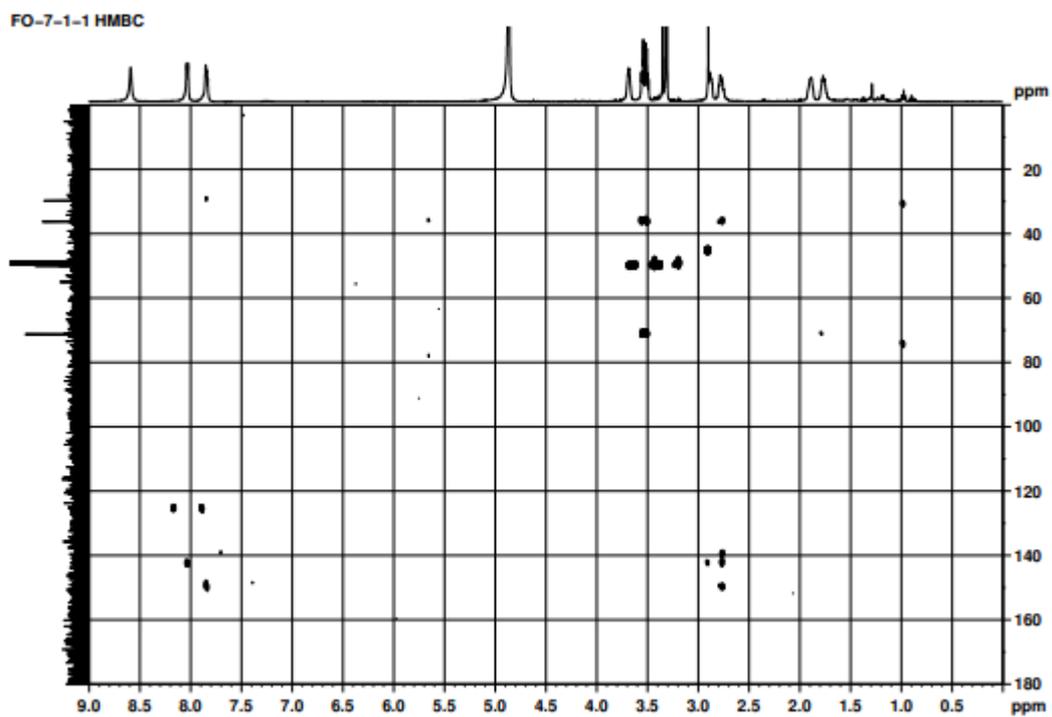
S37. ¹H NMR (600 MHz, CD₃OD) spectrum of compound 8.



S38. ^1H - ^1H COSY (600 MHz, CD_3OD) spectrum of compound **8**.

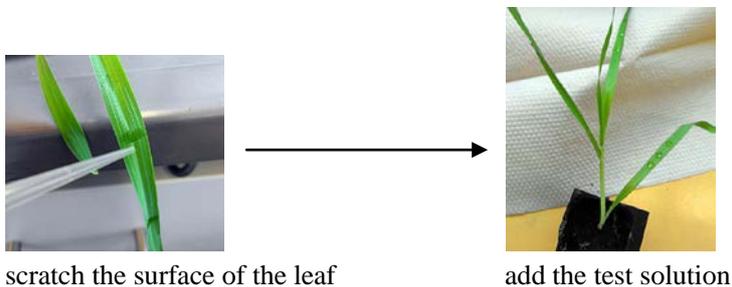


S39. HSQC (600 and 150 MHz, CD_3OD) spectrum of compound **8**.



S40. HMBC (600 and 150 MHz, CD₃OD) spectrum of compound **8**.

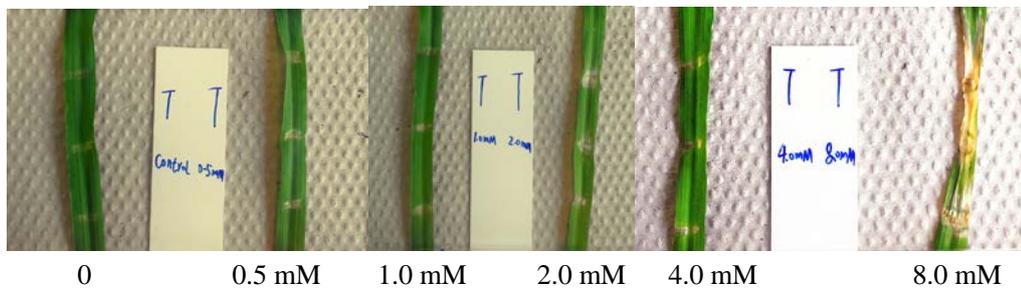
S41. Phytotoxic bioassay for fusaric acid derivatives (20 μ L at three locations on barley leaf).



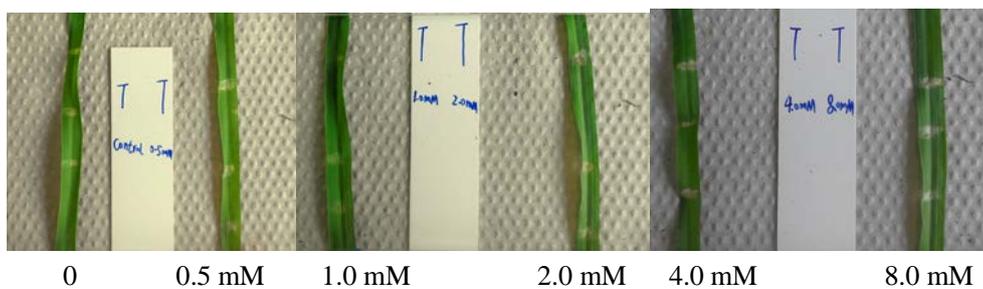
Score 0 1 2 3 4 5

Visual rating: 0 = no necrosis (negative control); 5 = severe necrosis.

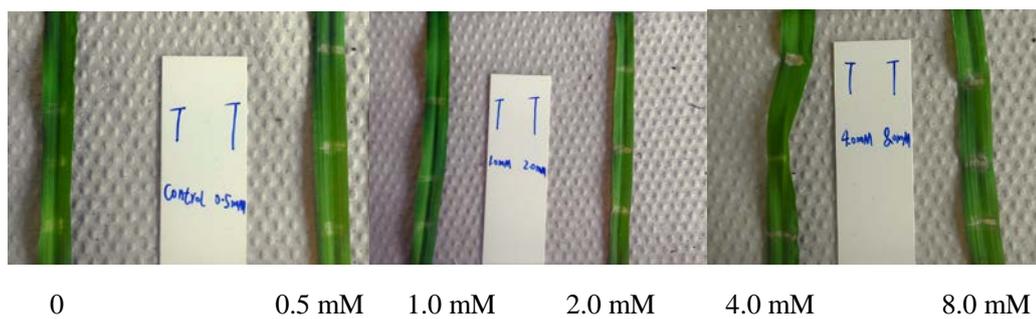
Compound 1



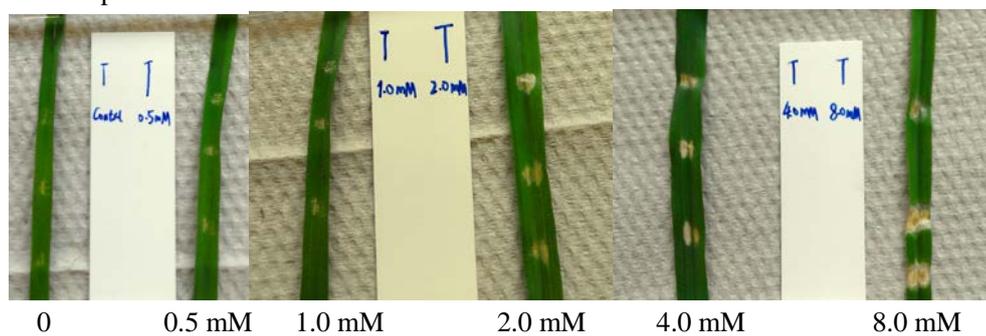
Compound 2



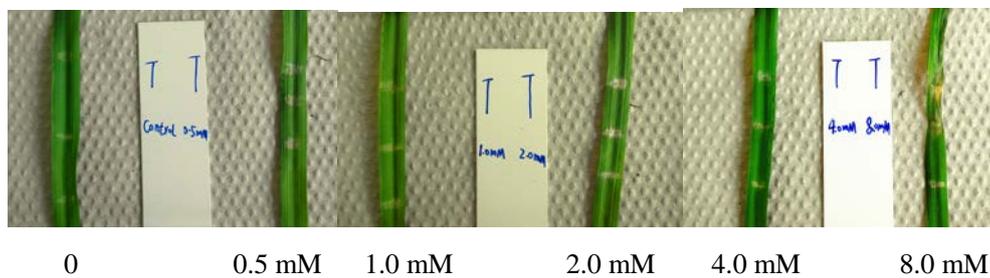
Compound 3



Mixture of compounds 4 and 5



Mixture of compounds 6 and 7



Compound 8

