

SUPPLEMENTARY MATERIAL

New aurone epoxide and auronolignan from the heartwood of *Cotinus coggygia* Scop.

Miroslav Novakovic^{1*}, Iris Djordjevic², Nina Todorovic¹, Snezana Trifunovic³, Boban Andjelkovic³, Boris Mandic³, Milka Jadranin¹, Ivan Vuckovic⁴, Vlatka Vajs¹, Slobodan Milosavljevic³ and Vele Tesevic³

¹*Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: mirnov76@yahoo.com; ninat@chem.bg.ac.rs; milkaj@chem.bg.ac.rs; vvajs@chem.bg.ac.rs)*

²*Faculty of Veterinary Medicine, University of Belgrade, Bulevar oslobođenja 18, 11000 Belgrade, Serbia (e-mail: iris@vet.bg.ac.rs)*

³*Faculty of Chemistry, University of Belgrade, Studentski trg 16, 11000 Belgrade, Serbia (snezanat@chem.bg.ac.rs; aboban@chem.bg.ac.rs; borism@chem.bg.ac.rs; smilo@chem.bg.ac.rs; vtesevic@chem.bg.ac.rs)*

⁴*Mayo Clinic, College of Medicine, Rochester, MN 55905, USA (vuckovic.ivan@mayo.edu)*

*Corresponding author, e-mail: mirnov76@yahoo.com

*Corresponding author, e-mail: mirnov76@yahoo.com

Abstract. From the methylene chloride/methanol extract of *Cotinus coggygia* Scop. heartwood one new aurone epoxide, 2,10-oxy-10-methoxysulfuretin (**14**), and one auronolignan (**15**), named cotinignan A, were isolated by silica gel column and semipreparative HPLC chromatography. In addition, thirteen known secondary metabolites namely sulfuretin, 2,3-*trans*-fustin, fisetin, butin, butein, taxifolin, eriodictyol, 3',5,5',7-tetrahydroxyflavanone, 3',4',7-trihydroxyflavone, 3-*O*-methyl-2,3-*trans*-fustin, 3-*O*-galloyl-

2,3-*trans*-fustin, β -resorcylic acid and 3-*O*- β -sitosterol glucoside were isolated as well. Their structures were elucidated by 1D and 2D NMR, HR-ESI-MS, IR and UV. Ten out of eleven isolated flavonoids possess 7, 3' and 4' hydroxy groups. These structural features could be considered as chemotaxonomic characteristic of flavonoids from *C. coggygia*. Cotinignan A (**15**) represents new subclass of secondary metabolites - auronolignans.

Keywords. *Cotinus coggygia* Scop, flavonoids, cotinignan A, semipreparative HPLC, NMR

Table S1. HPLC program for the quantification of the main compounds from the *C. coggygia* CH₂Cl₂/MeOH extract

Figure S1. UV spectra of **14** in MeOH, with addition of AlCl₃, and HCl

Figure S2. UV spectra of compound **14** in MeOH, with NaOAc, NaOAc+H₃BO₃ and with NaOMe

Figure S3. ¹H NMR spectrum of compound **14**

Figure S4. ¹³C NMR spectrum of compound **14**

Figure S5. Aromatic part of the COSY spectrum of **14**

Figure S6. Aromatic part of the NOESY spectrum of **14**

Figure S7. Aromatic part of the HSQC spectrum of **14**

Figure S8. Aromatic part of the HMBC spectrum of **14**

Figure S9. Key HMBC correlations of **14**

Table S2. ¹H, ¹³C NMR and HMBC data of **14** (CD₃OD, δ ppm, *J* in Hz)

Figure S10. Aromatic part of the ¹H NMR spectrum of **15**

Figure S11. Aliphatic part of the ¹H NMR spectrum of **15**

Figure S12. ¹³C NMR spectrum of **15**

Figure S13. HSQC spectrum of **15**

Figure S14. The first part of the HMBC spectrum of **15**

Figure S15. The second part of the HMBC spectrum of **15**

Figure S16. HMBC (4 Hz) correlation H-7''/C-4' (**15**)

Figure S17. The first part of the NOESY spectrum of **15**

Figure S18. The second part of the NOESY spectrum of **15**

Table S3. ^1H and ^{13}C NMR data of **15** (CD_3OD , δ ppm, J in Hz)

Figure S19. 3-Aryl-propanol moiety in **15**

Figure S20. Key HMBC correlations in **15**

Figure S21. UV spectrum of **15**

Figure S22. UV spectrum of **10**

Table S1. HPLC program for the quantification of the main compounds from the *C. coggygia* $\text{CH}_2\text{Cl}_2/\text{MeOH}$ extract

t (min)	A (water)	B (acetonitrile)	Flow (mL/min)
0	95	5	1.4
1.5	95	5	1.4
26	5	95	1.4
35	5	95	1.4
36	95	5	1.4
41	95	5	1.4

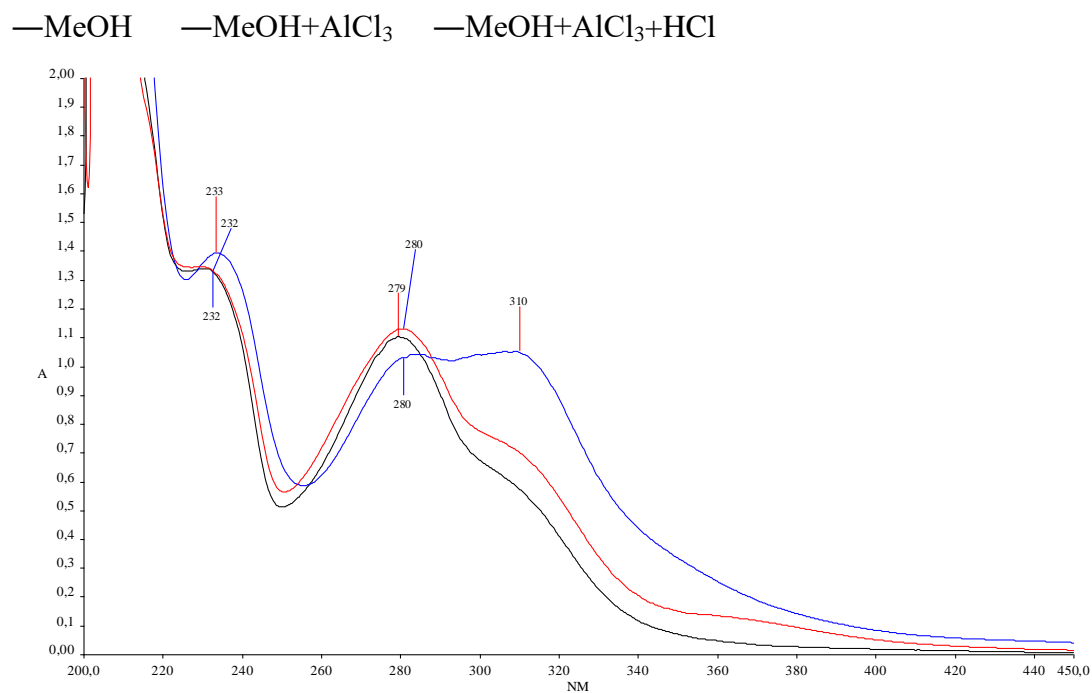


Figure S1. UV spectra of **14** in MeOH, with addition of AlCl₃, and HCl

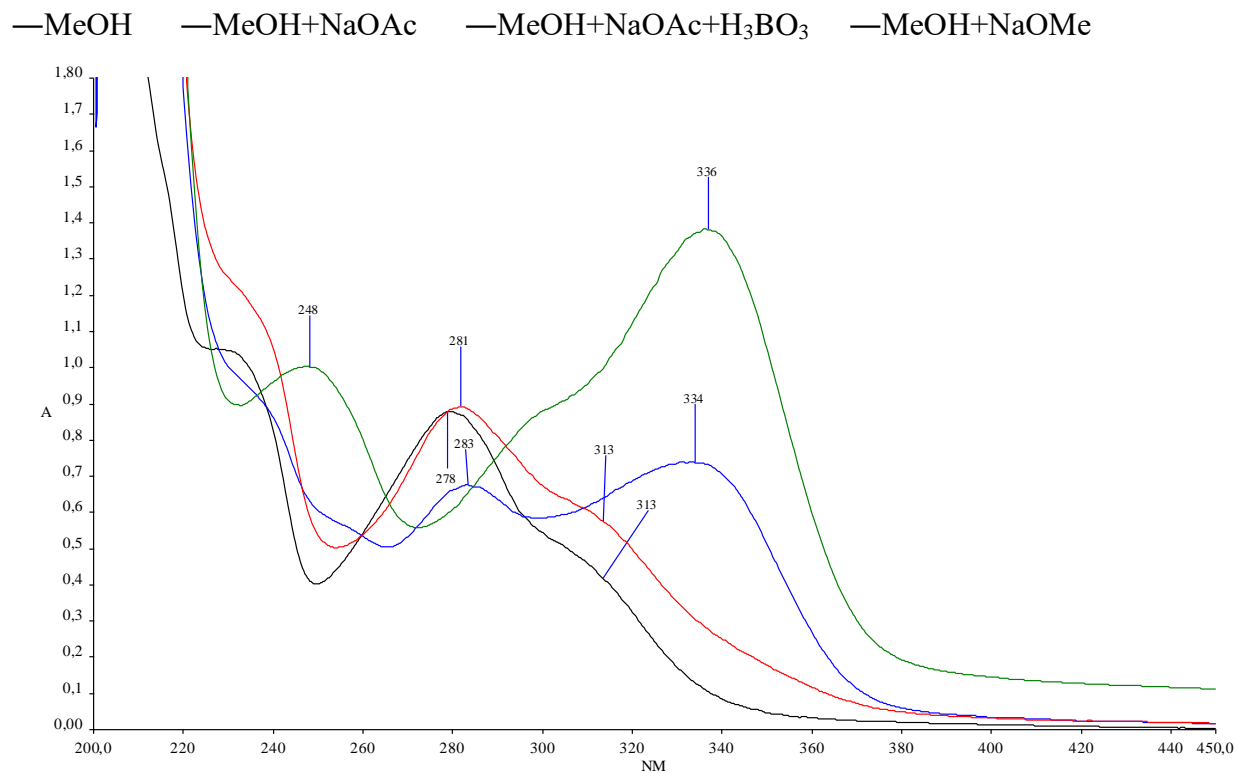


Figure S2. UV spectra of **14** in MeOH, with NaOAc, NaOAc+H₃BO₃ and with NaOMe

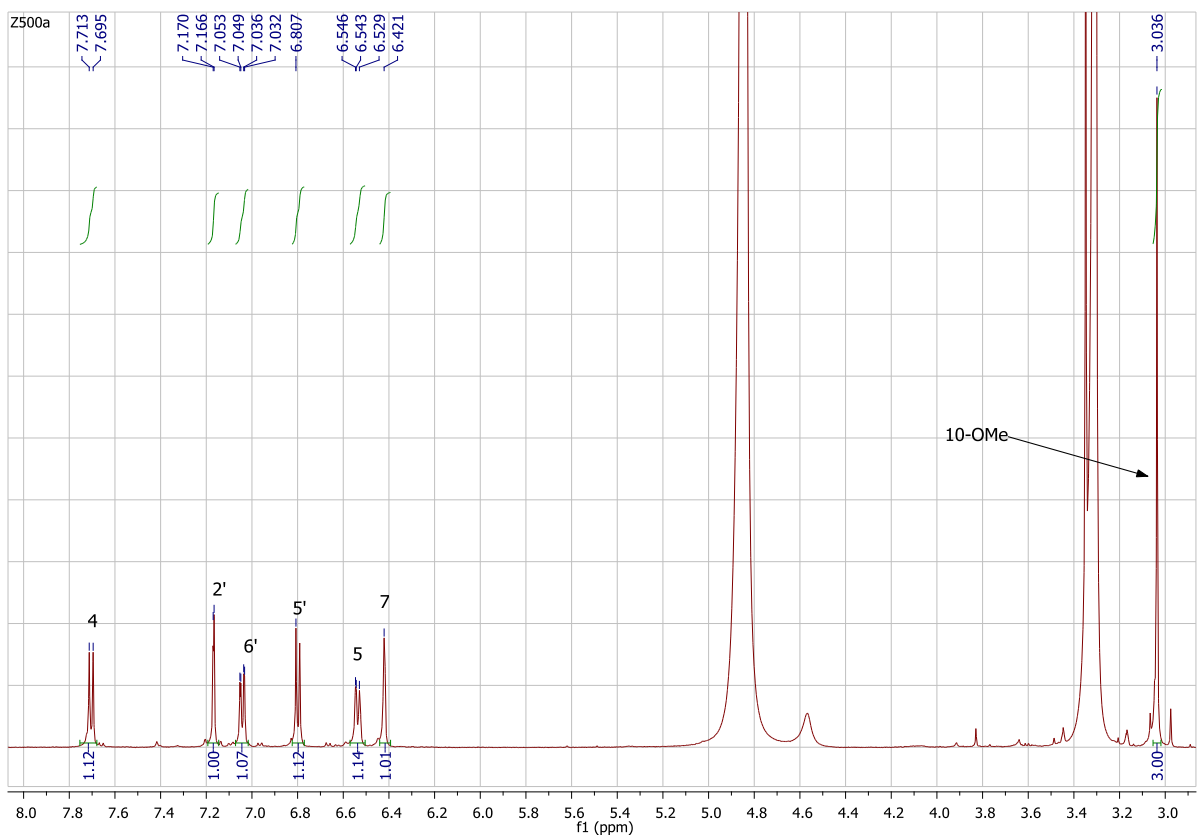


Figure S3. ¹H NMR spectrum of 14

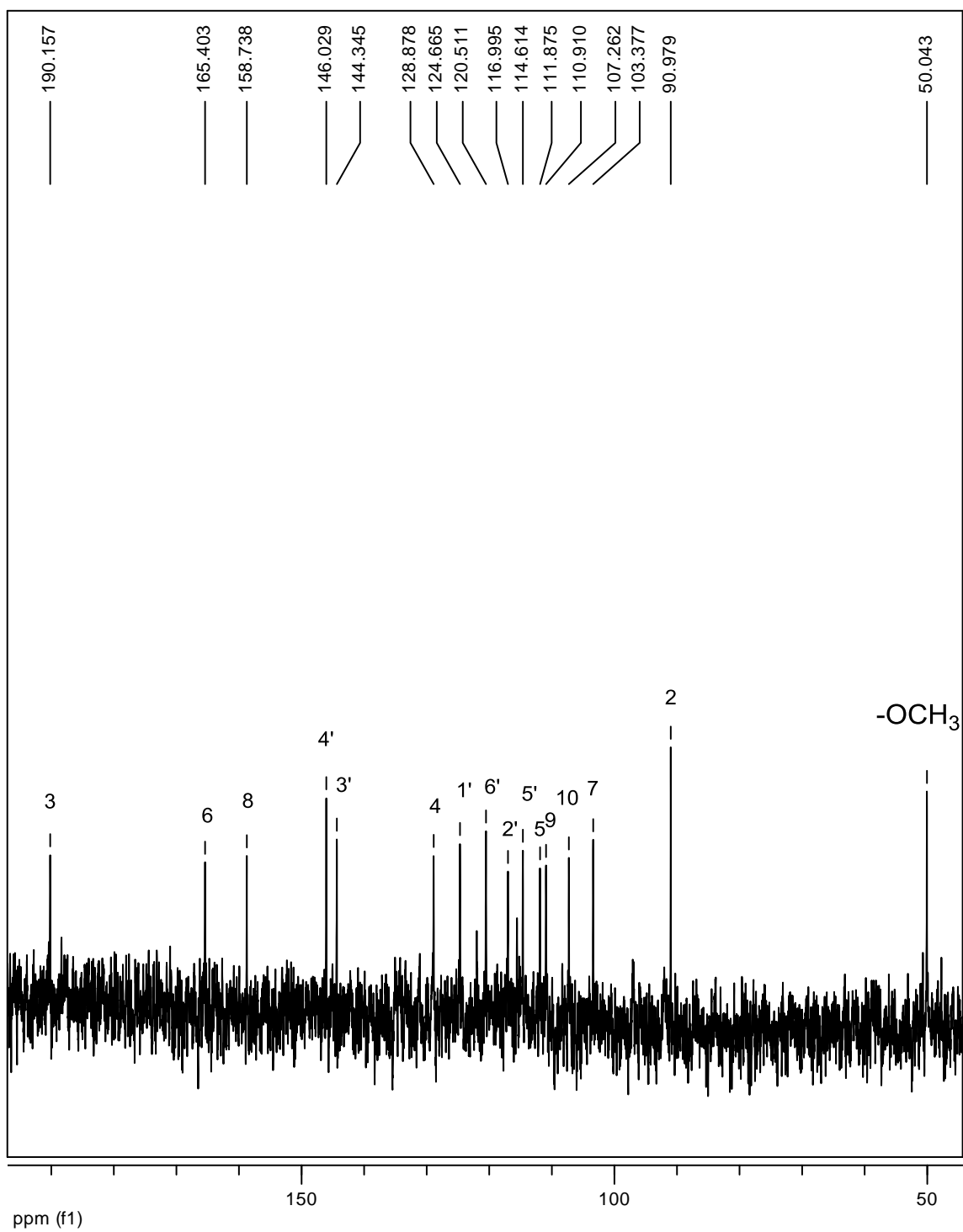


Figure S4. ¹³C NMR spectrum of **14**

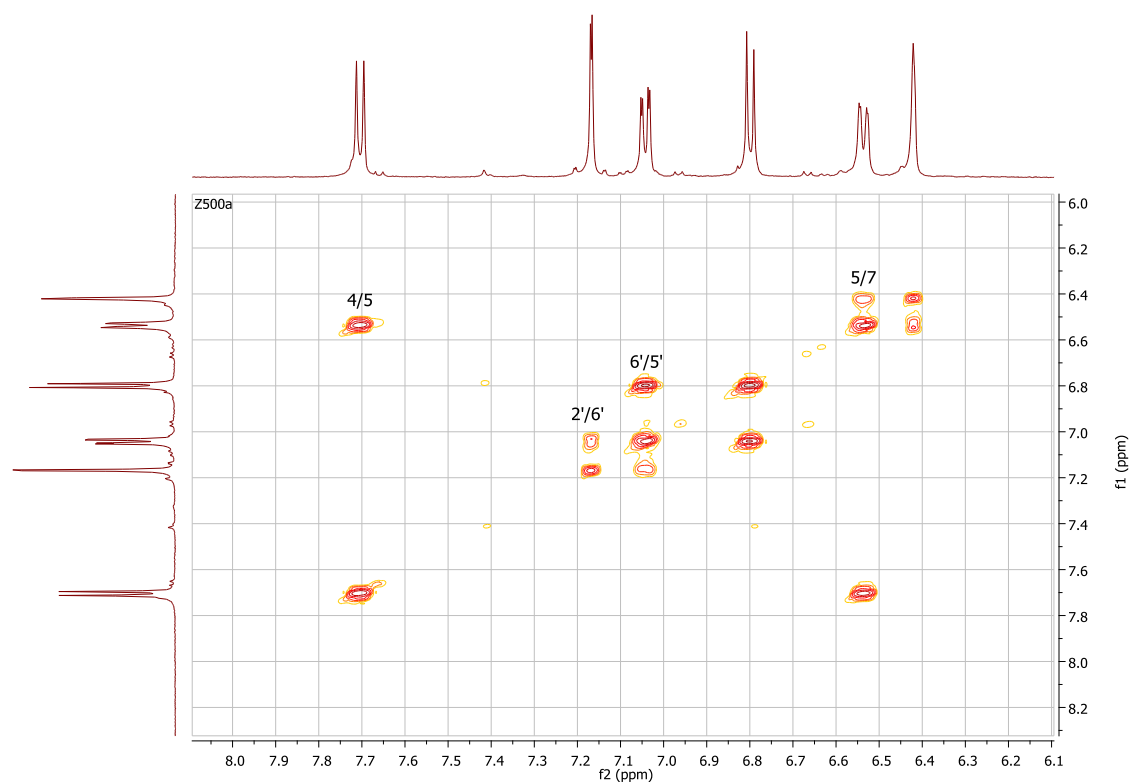


Figure S5. Aromatic part of the COSY spectrum of **14**

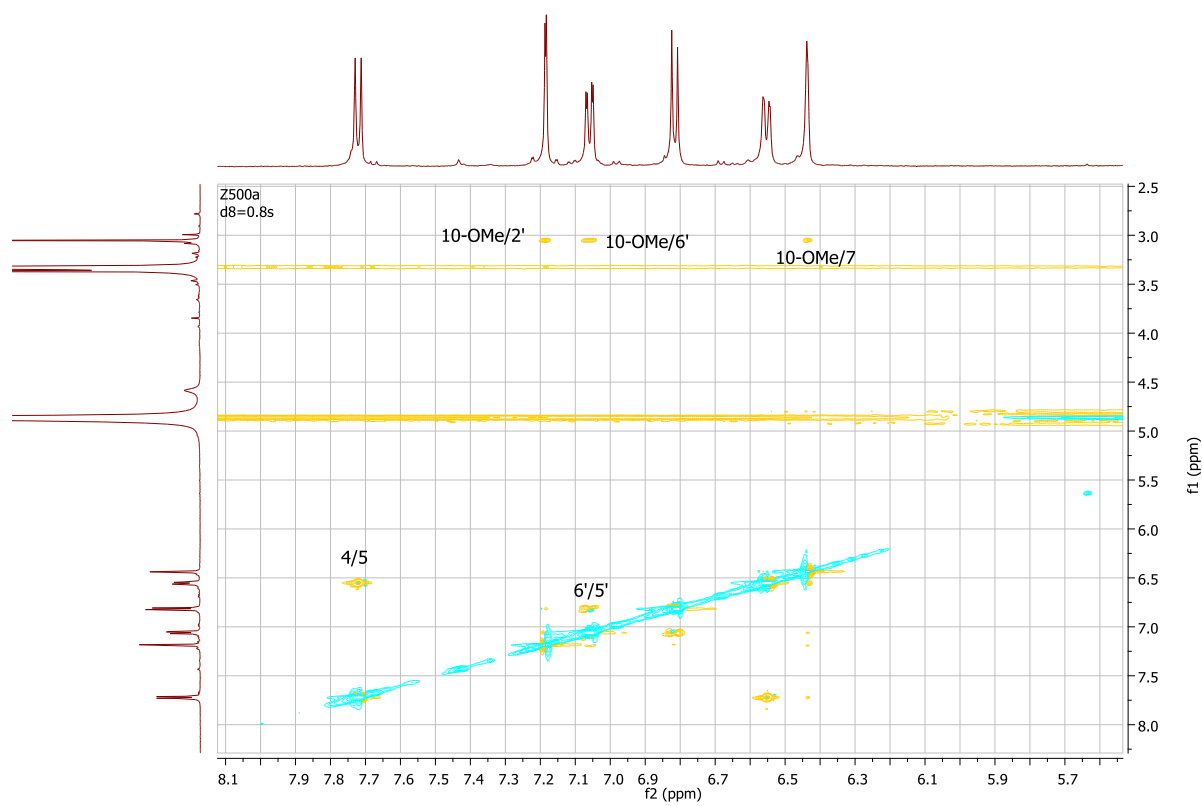


Figure S6. Aromatic part of the NOESY spectrum of **14**

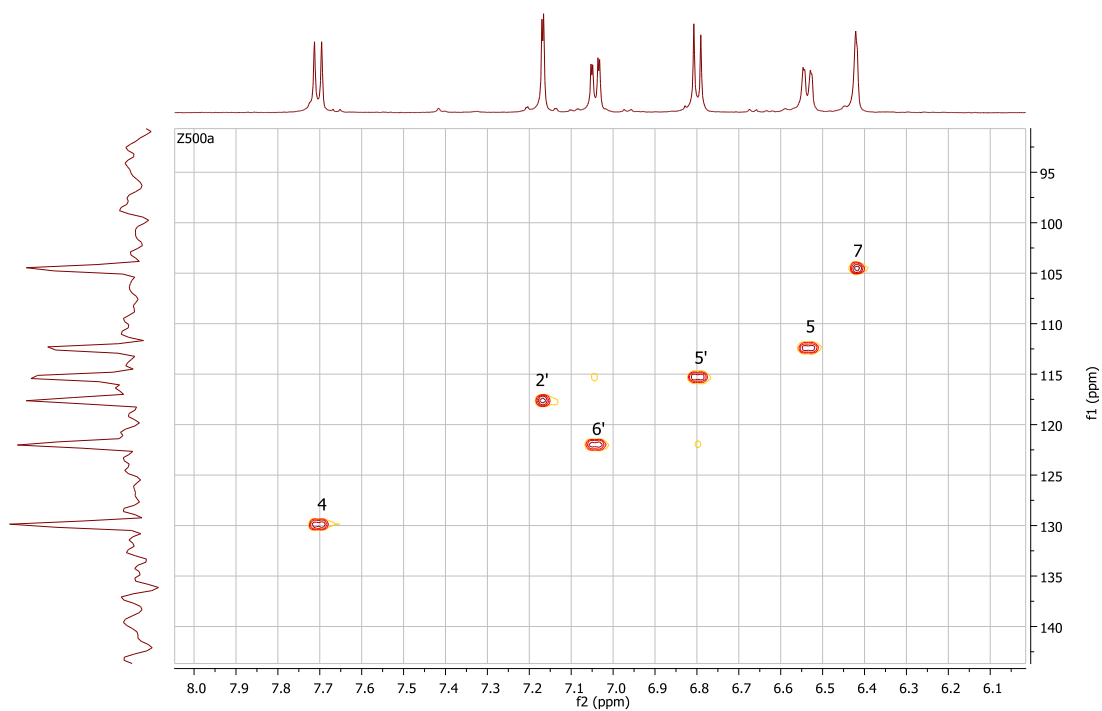


Figure S7. Aromatic part of the HSQC spectrum of **14**

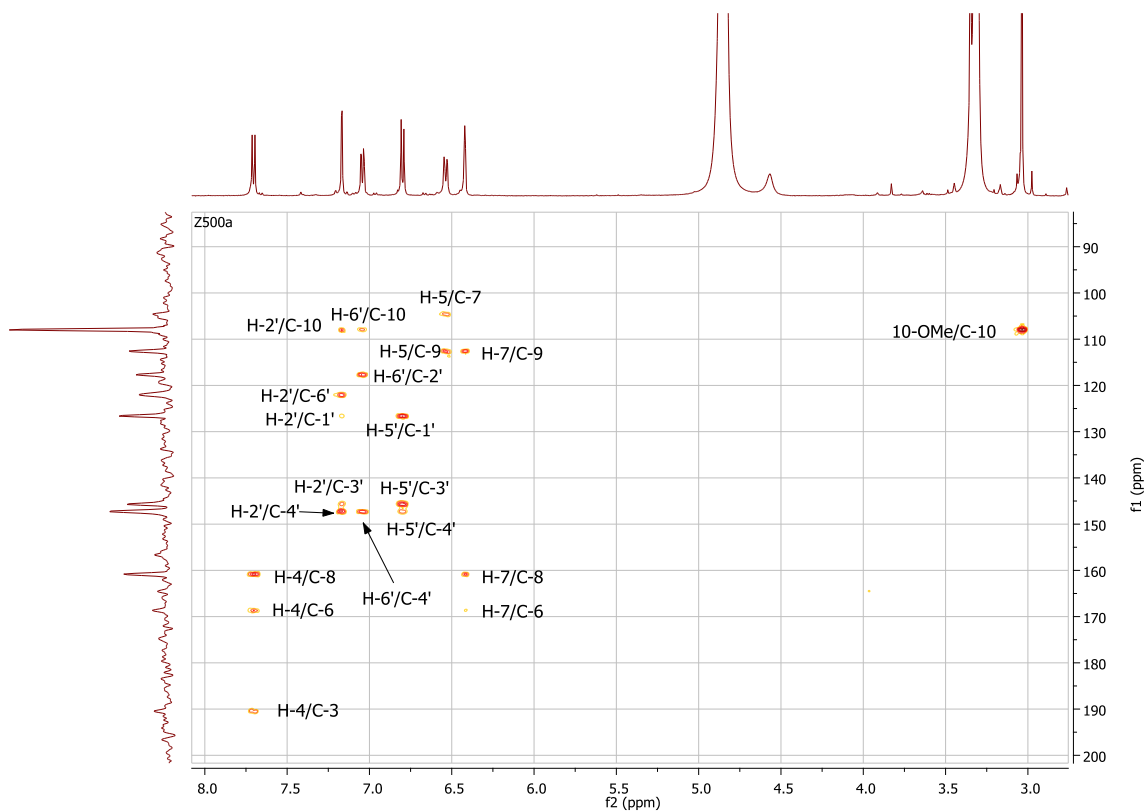


Figure S8. Aromatic part of the HMBC spectrum of **14**

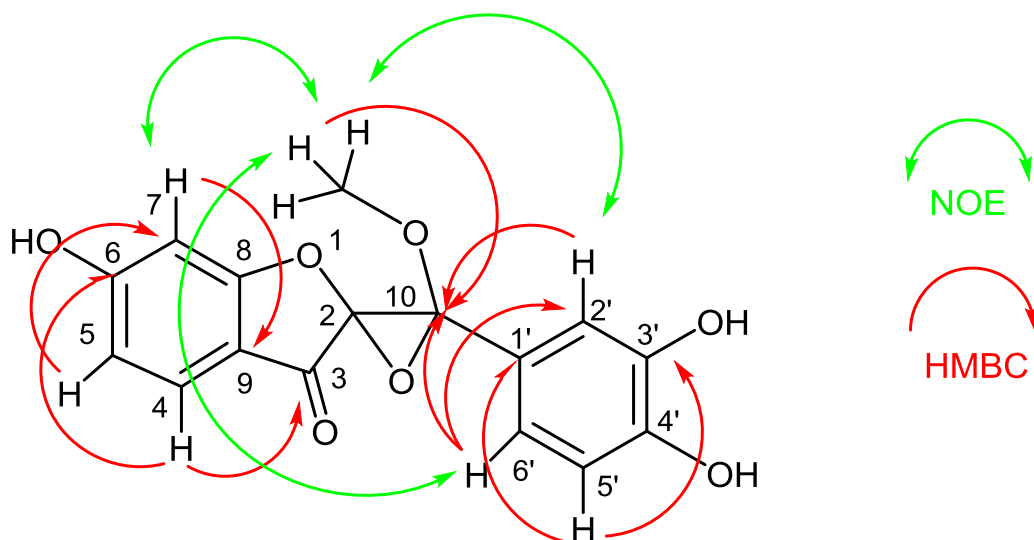


Figure S9. Key HMBC correlations of **14**

Table S2. ^1H , ^{13}C NMR and HMBC data of **14** (CD_3OD , δ ppm, J in Hz)

Position	δ_{H}	δ_{C}	HMBC $\text{H} \rightarrow \text{C}$
2		90.97	
3		190.16	
4	7.67 d (8.8 Hz)	128.88	8, 6
5	6.48 dd (8.8; 2.2 Hz)	110.91	7
6		165.40	
7	6.35 d (2.2 Hz)	103.37	9
8		158.74	
9		111.87	
10		107.26	
1'		124.66	
2'	7.17 d (2.0 Hz)	116.99	10, 4', 6'
3'		144.34	
4'		146.02	
5'	6.79 d (8.4 Hz)	114.61	1', 3'
6'	7.04 dd (8.4; 2.0 Hz)	120.51	2', 4'
10-OMe	3.03 s	50.04	10

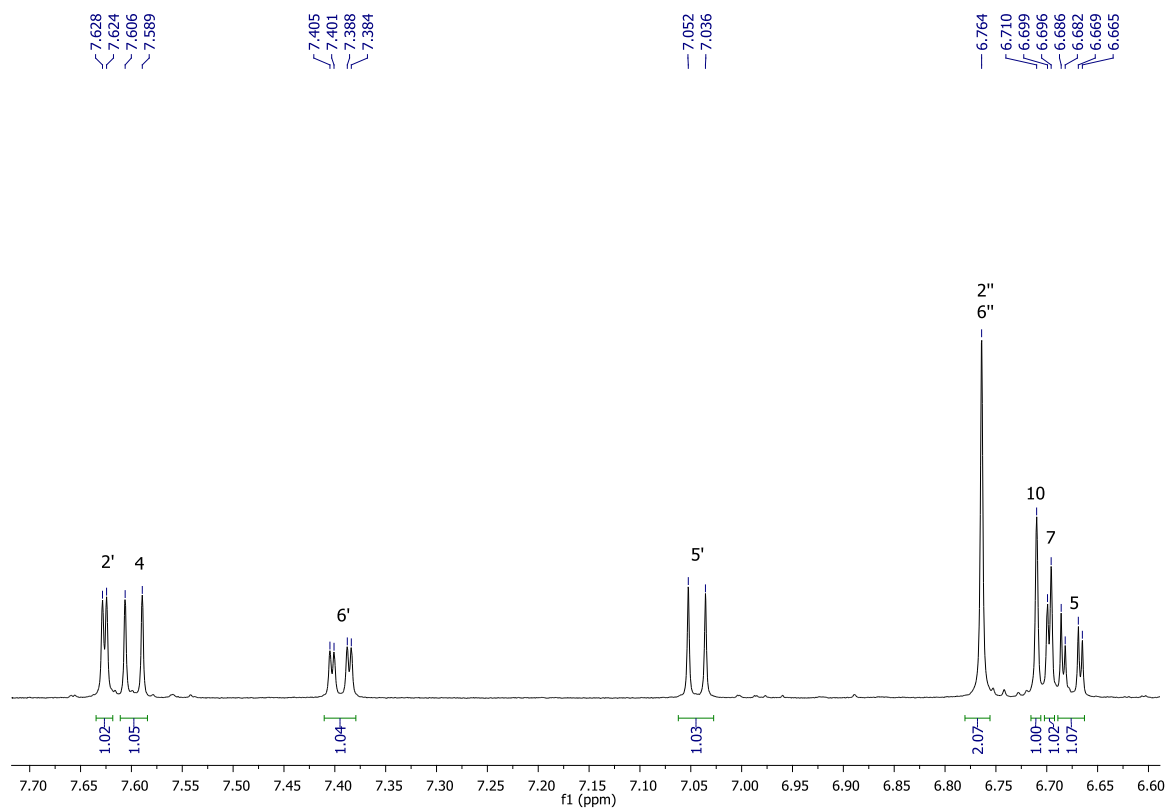


Figure S10. Aromatic part of the ^1H NMR spectrum of **15**

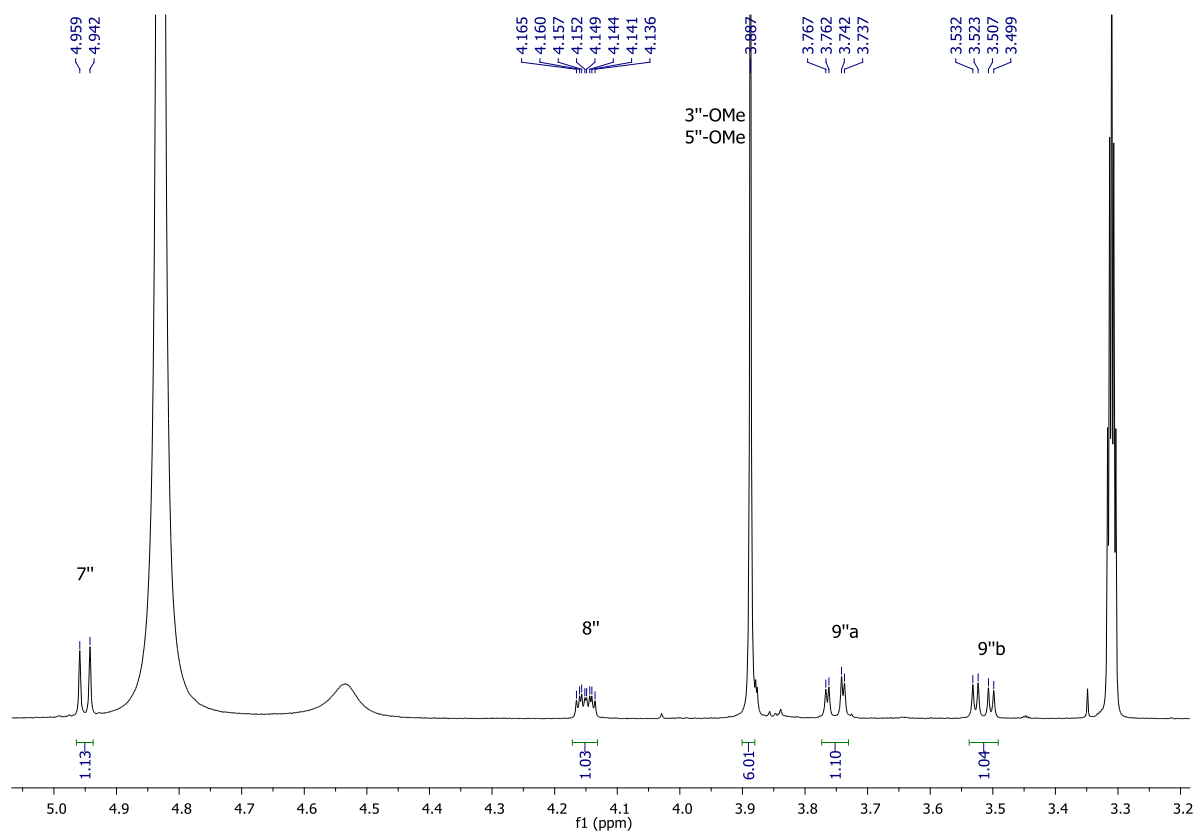


Figure S11. Aliphatic part of the ^1H NMR spectrum of **15**

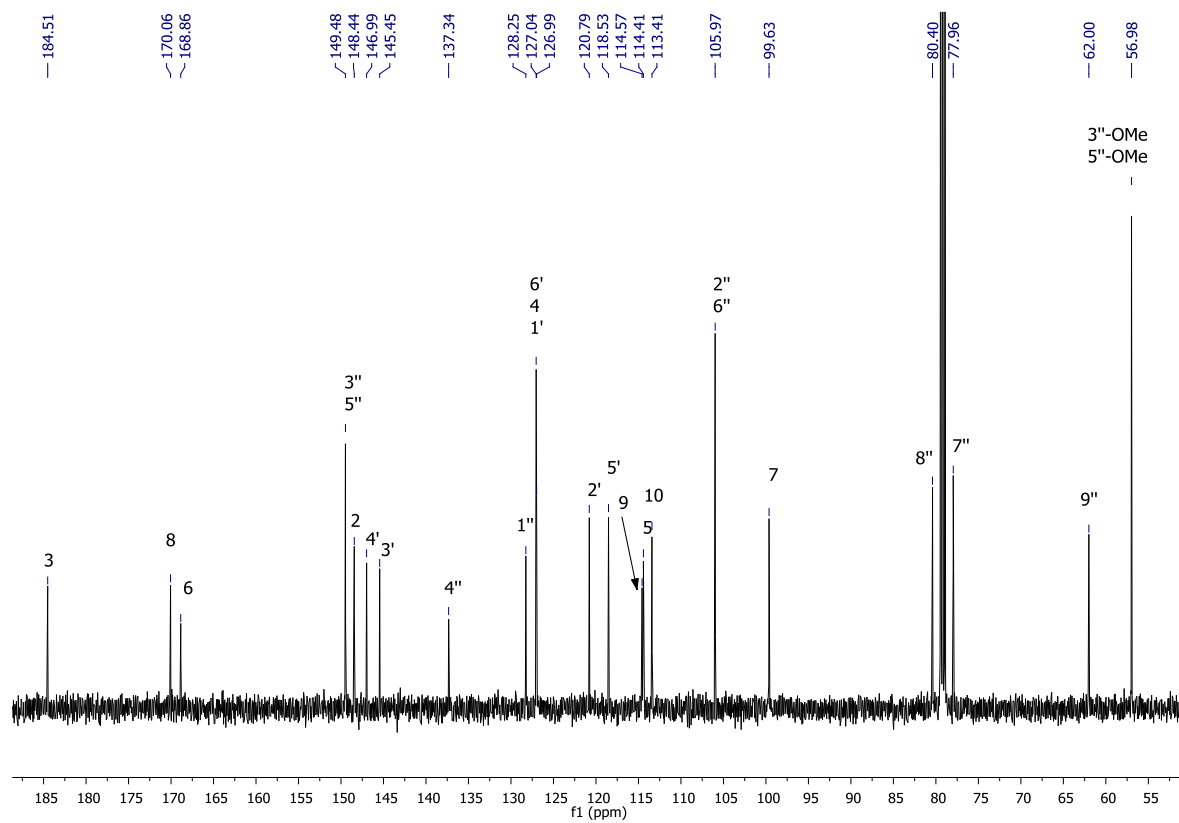


Figure S12. ^{13}C NMR spectrum of **15**

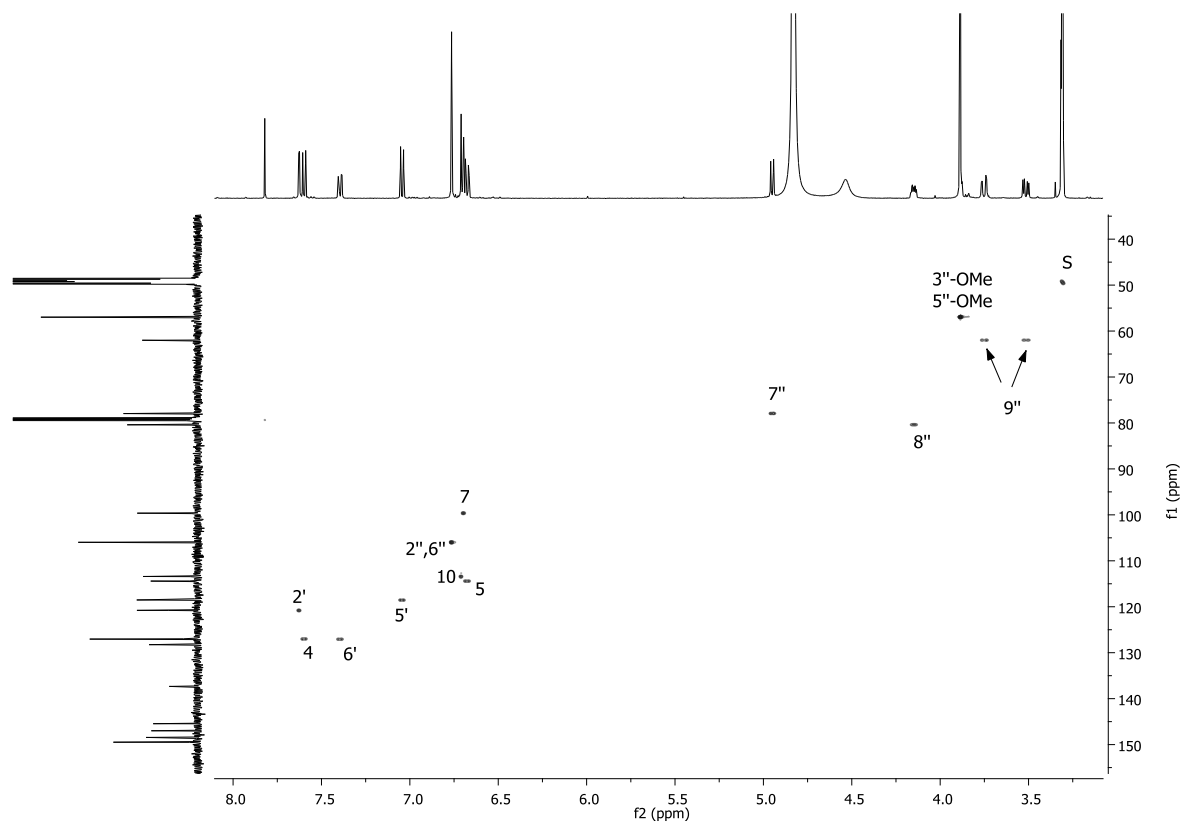


Fig. S13. HSQC spectrum of **15**

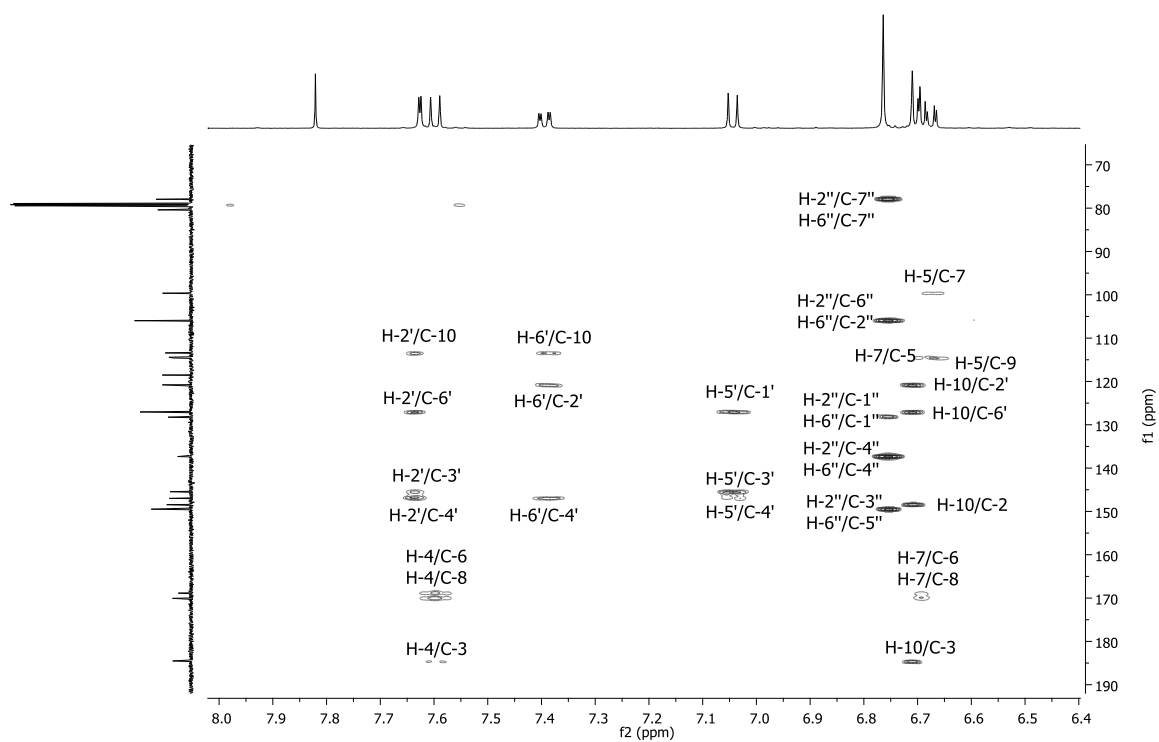


Figure S14. The first part of the HMBC spectrum of **15**

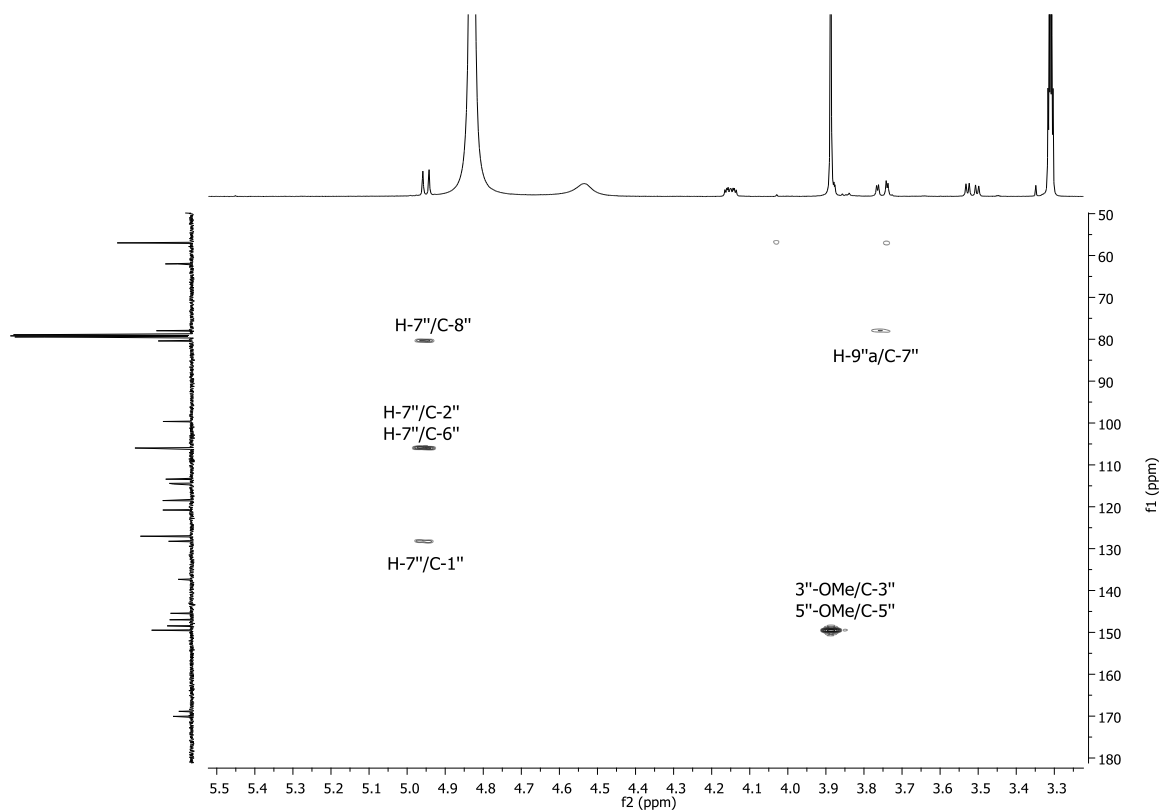


Figure S15. The second part of the HMBC spectrum of **15**

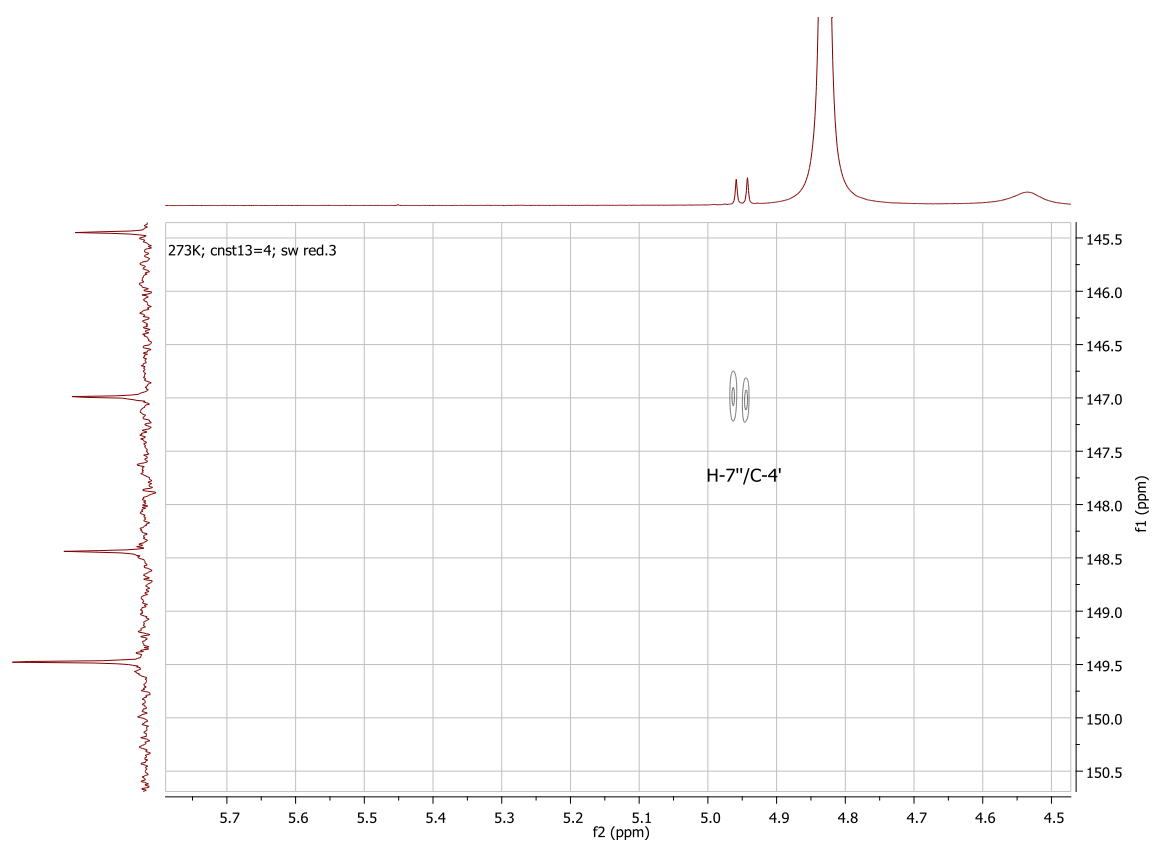


Figure S16. HMBC (4 Hz) correlation H-7''/C-4' (**15**)

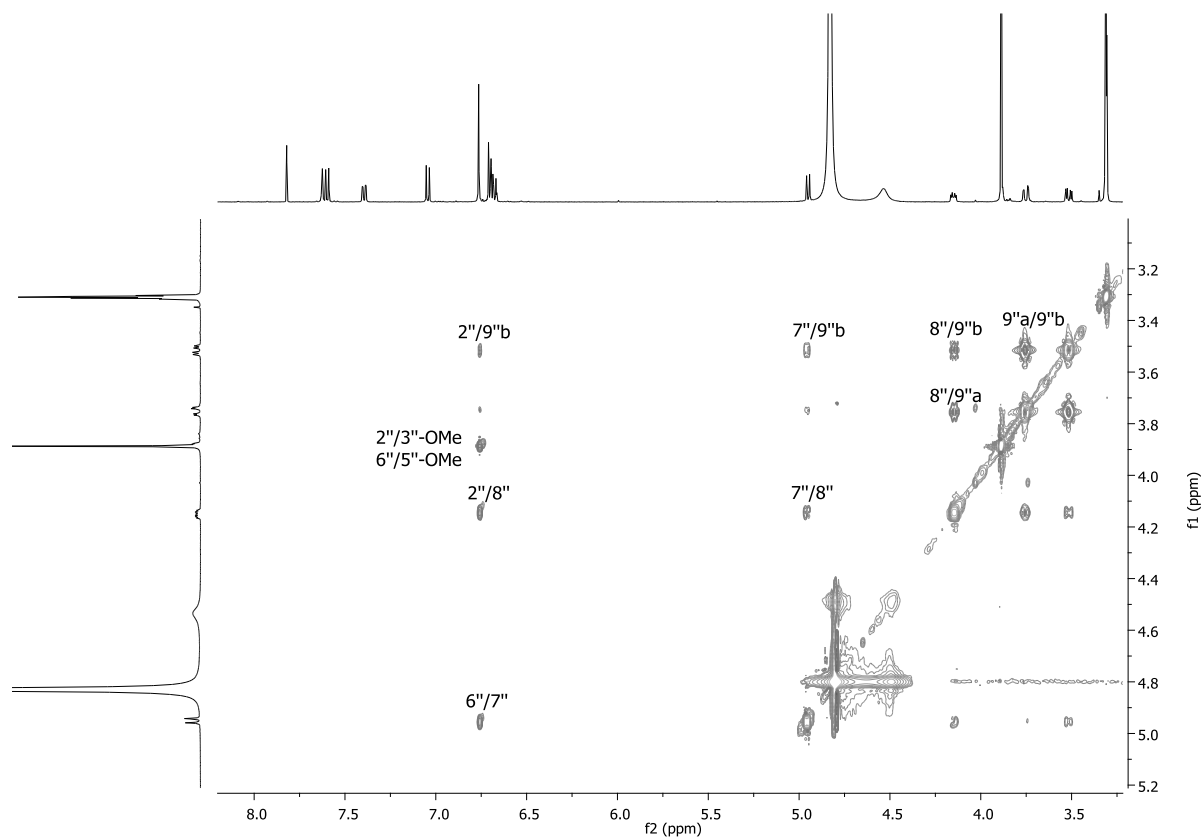


Figure S17. The first part of the NOESY spectrum of **15**

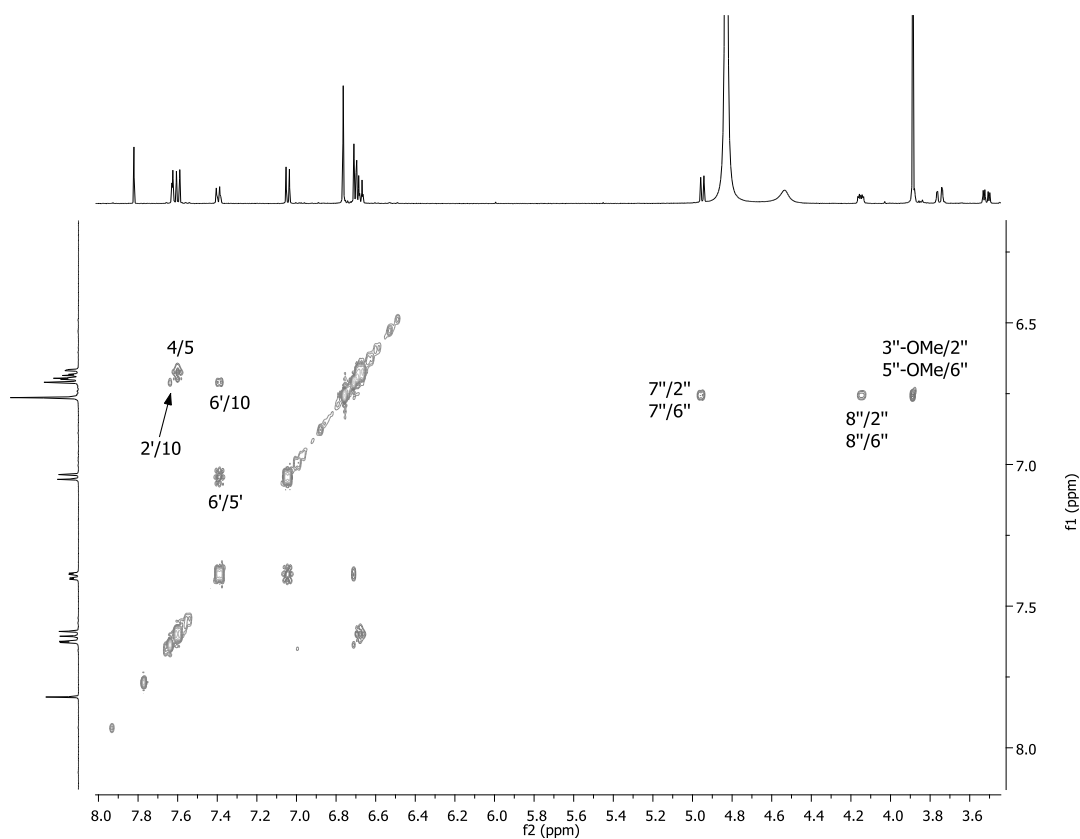


Figure S18. The second part of the NOESY spectrum of **15**

Table S3. ^1H and ^{13}C NMR data of compounds **15** (CD_3OD , δ ppm, J in Hz)

Compound	15	
Position	δ_{H}	δ_{C}
2	-	148.4
3	-	184.5
4	7.60 d (8.5)	128.2
5	6.68 dd (8.5; 2.0)	114.4
6	-	168.9
7	6.70 d (2.0)	99.6
8	-	170.1
9	-	114.6
10	6.71 s	113.4
1'	-	127.0
2'	7.62 d (2.0)	120.8
3'	-	145.5
4'	-	147.0
5'	7.04 d (8.5)	118.5
6'	7.39 dd (8.5; 2.0)	127.0

1"	-	128.3
2"	6.76 s	106.0
3"	-	149.5
4"	-	137.3
5"	-	149.5
6"	6.76 s	106.0
7"	4.95 d (8.0)	78.0
8"	4.15 ddd (8.0; 4.0; 2.5)	80.4
9"	3.75 dd (12.5; 2.5) 3.51 dd (12.5; 4.0)	62.0
3"-OMe	3.89 s	57.0
5"-OMe	3.89 s	57.0

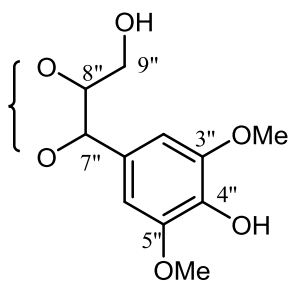


Figure S19. 3-Aryl-propanol moiety in **15**

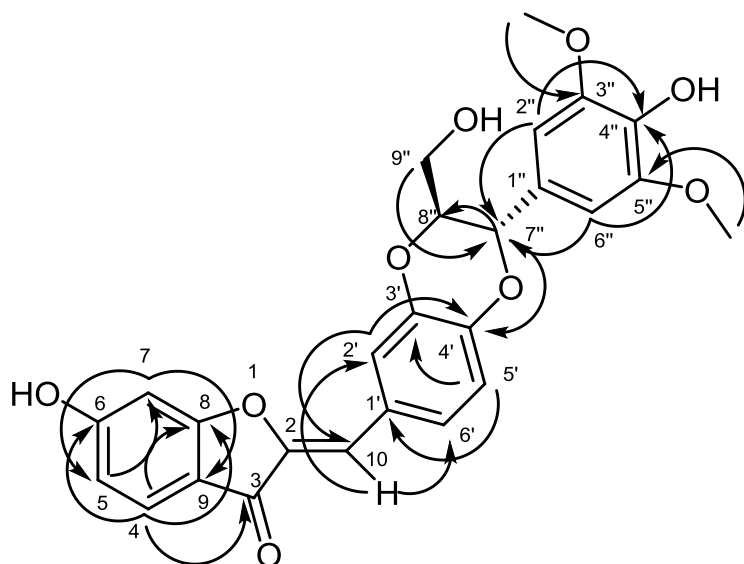


Figure S20. Key HMBC correlations in **15**

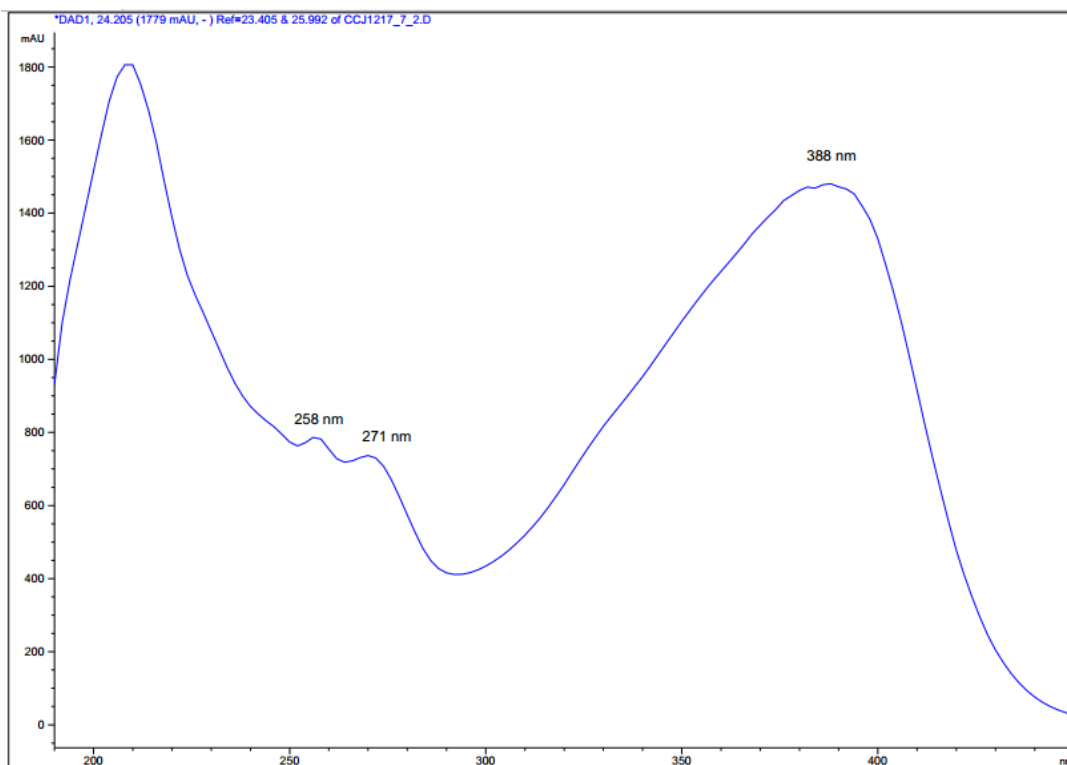


Figure S21. UV spectrum of 15

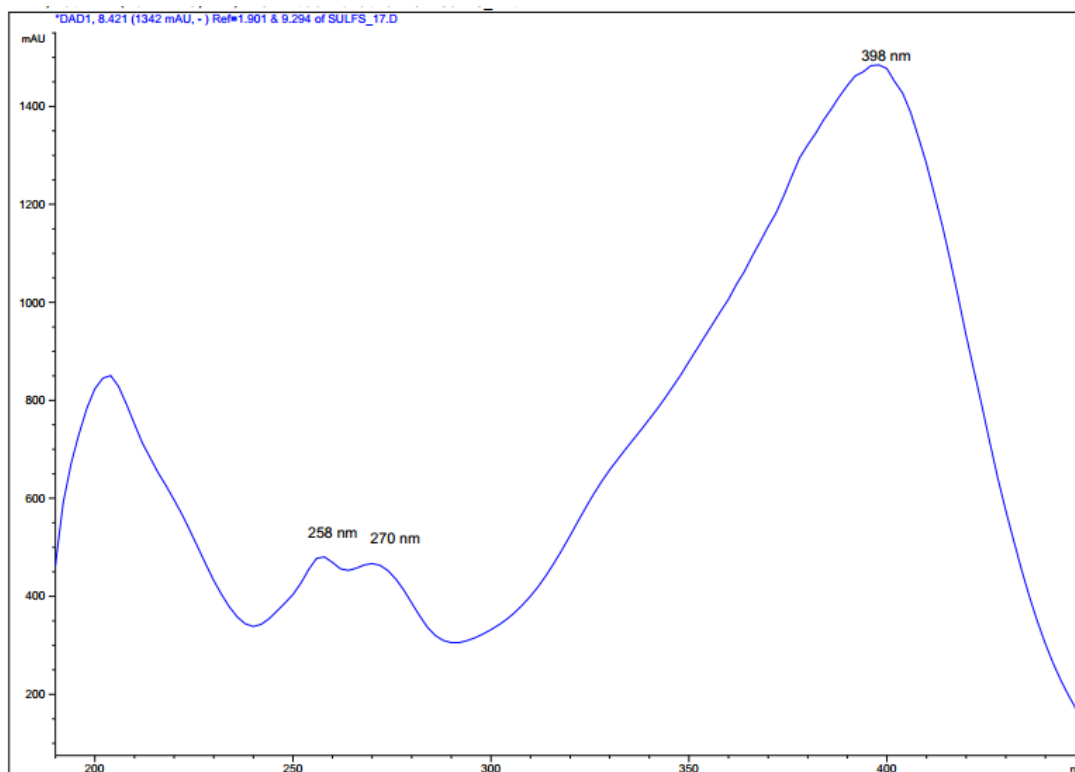


Figure S22. UV spectrum of 10