

Novel phenolic constituents of *Pulmonaria officinalis* L. LC-MS/MS comparison of spring and autumn metabolite profiles

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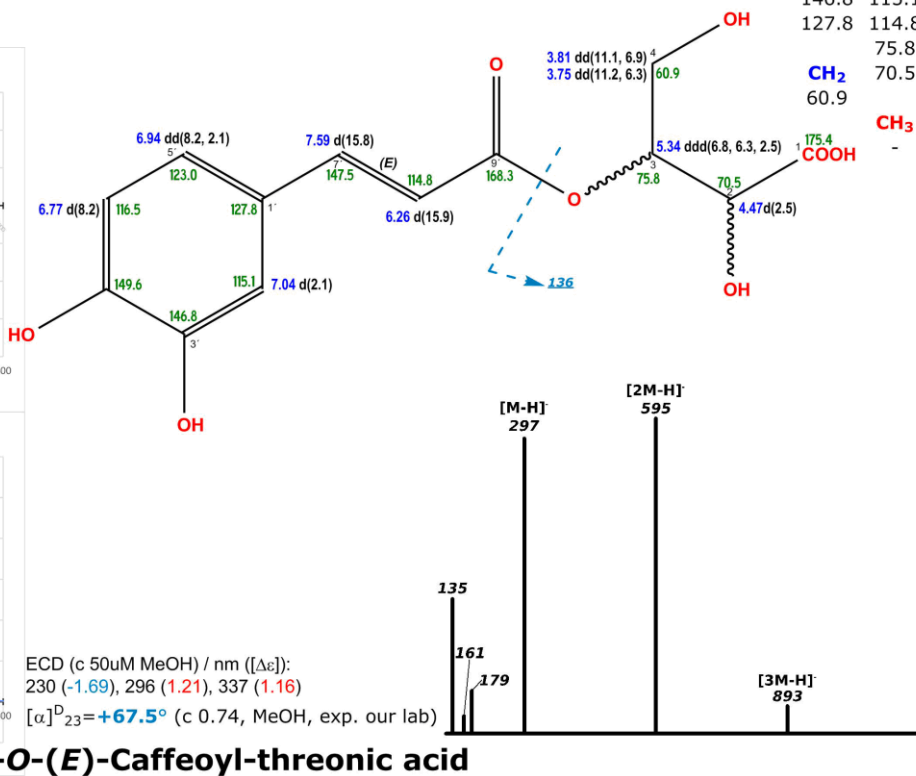
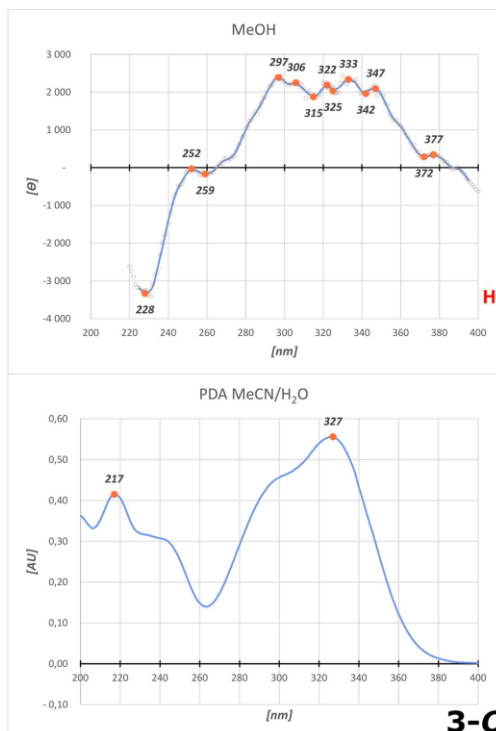
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POAmz297Fr_II_p15-28_flash_4-2

Chemical Formula: $C_{13}H_{14}O_8$
Exact Mass: 298,0689

NEW!

MeOH- d_4 , 25°C



Quat	CH
175.4	147.5
168.3	123.0
149.6	116.5
146.8	115.1
127.8	114.8
	75.8
	70.5
	60.9
	CH ₃
	-

Figure 3S. ¹H (500 MHz) and ¹³C (125 MHz) NMR data of compound 3 in CD₃OD, 25°C; on-line PDA UV spectrum in MeCN/H₂O, ECD spectrum in MeOH

¹H NS16 CD3OD 25°C - NS=16

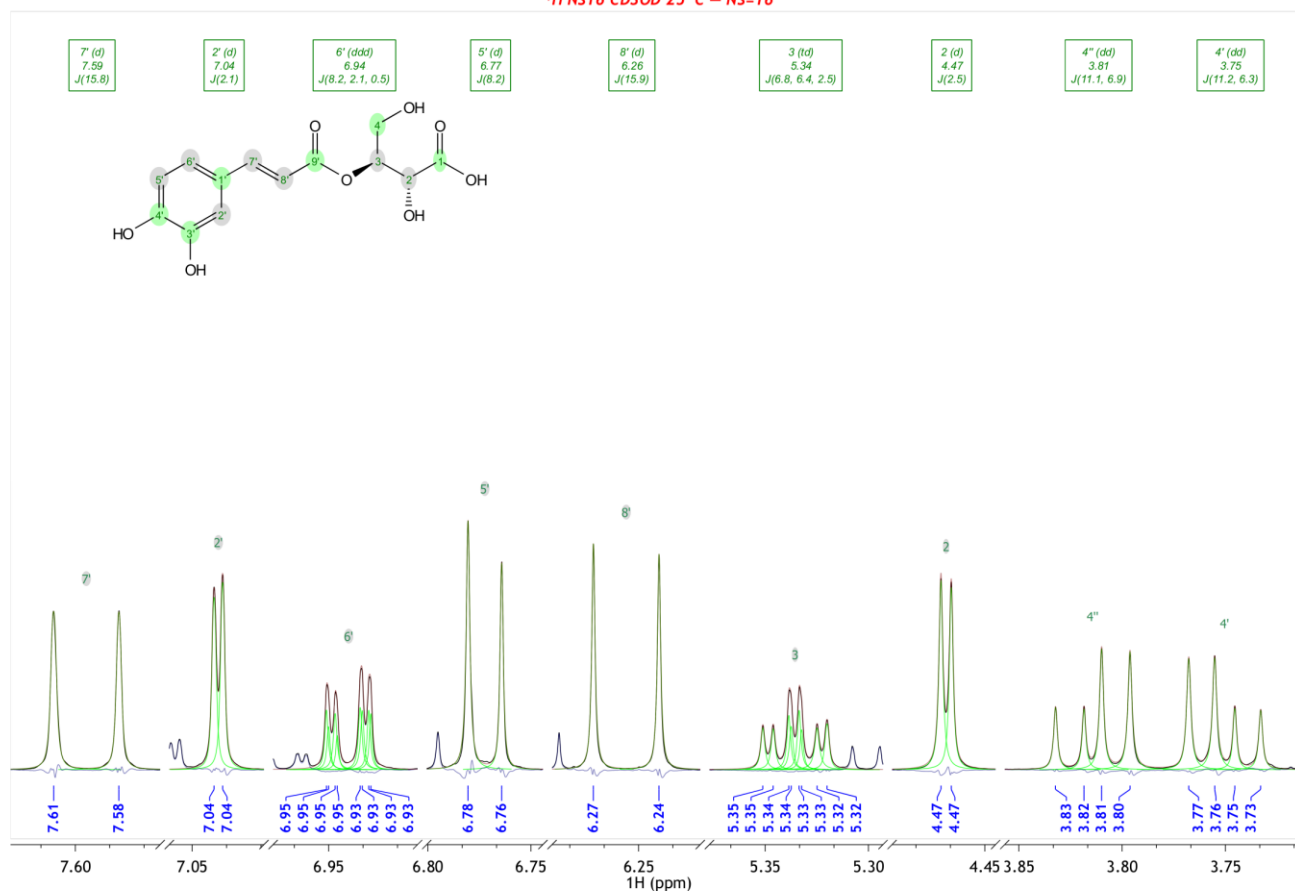


Figure 4S. ¹H NMR spectrum of compound 3

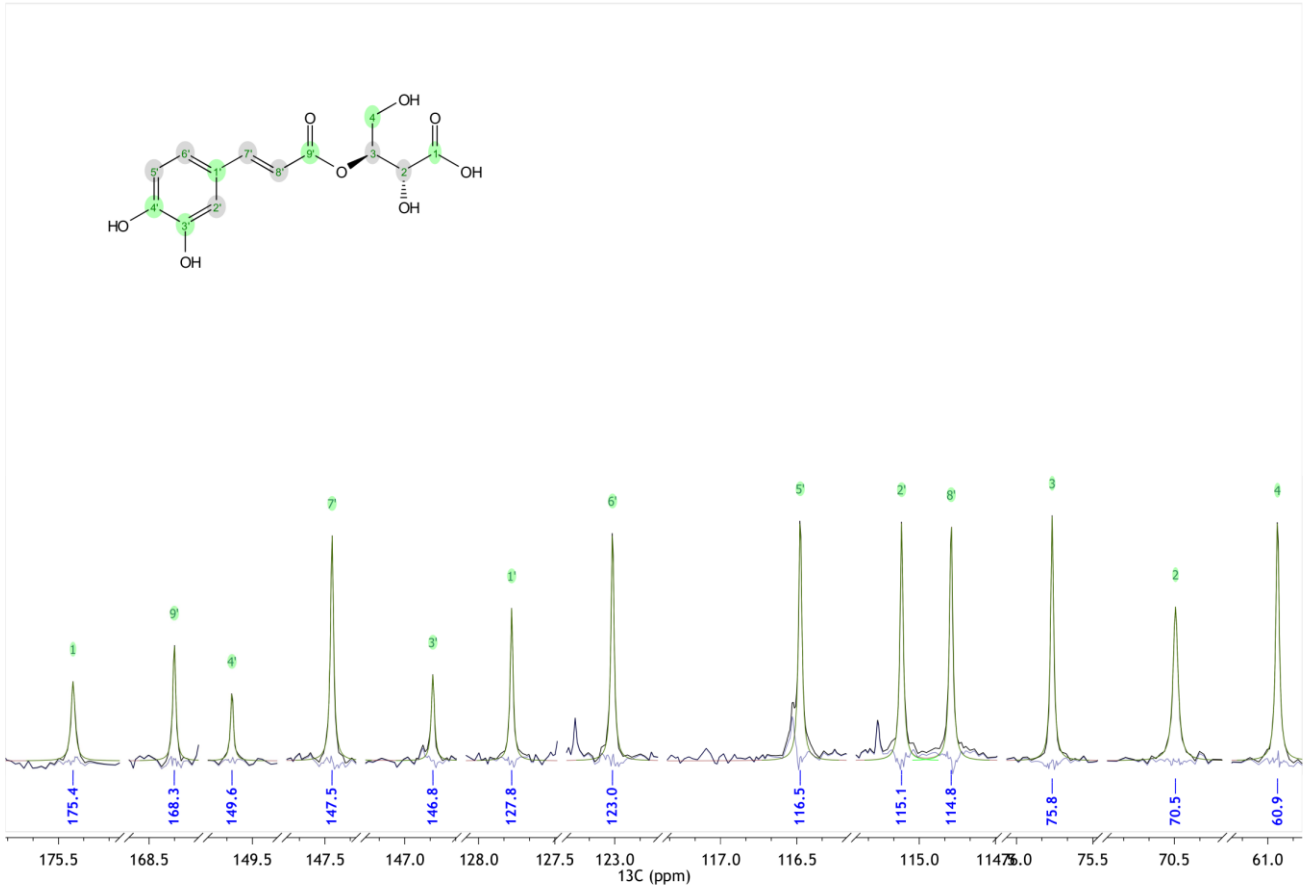


Figure 5S. ¹³C UDEFT NMR spectrum of compound 3

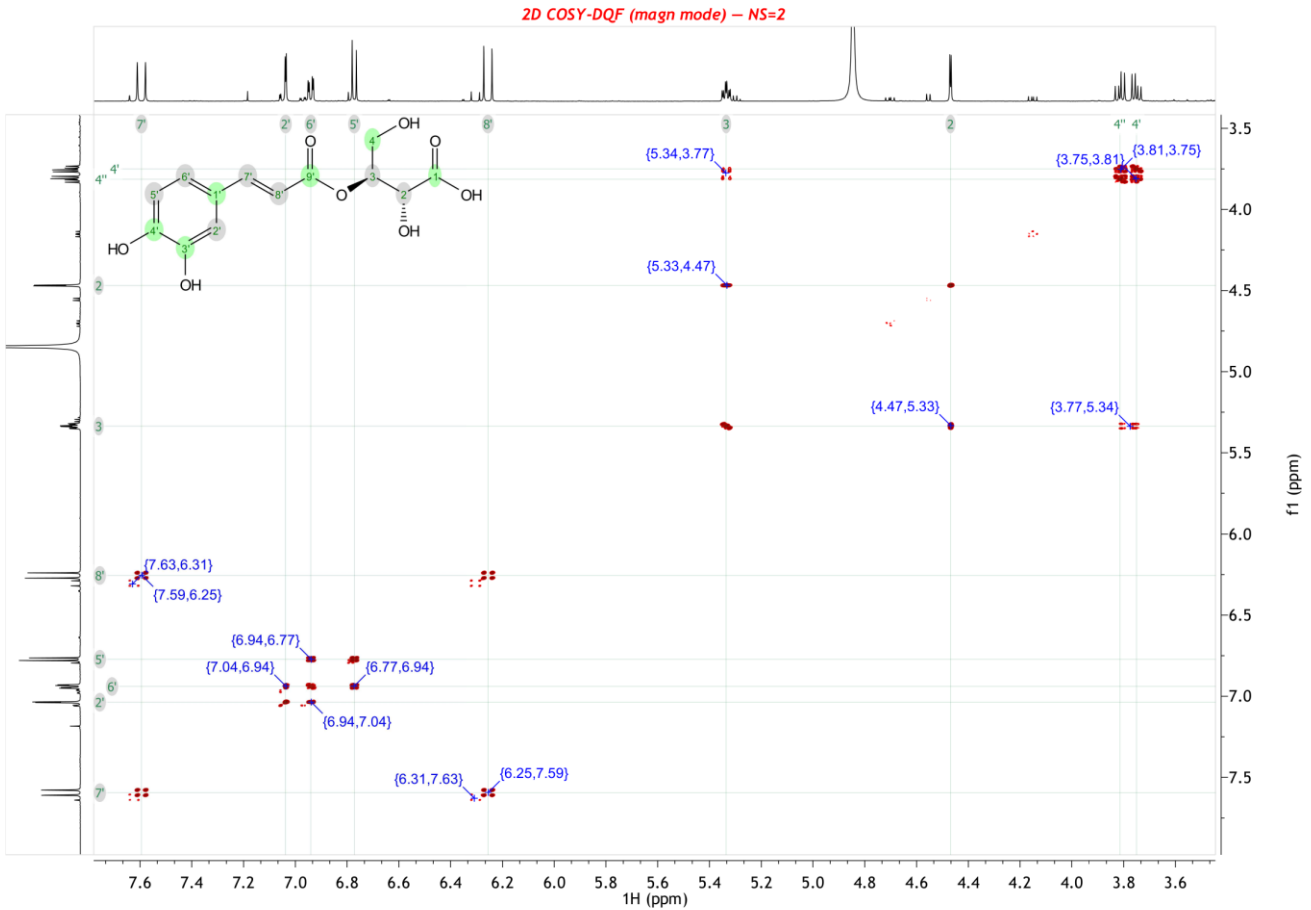


Figure 6S. ¹H-¹H COSY NMR spectrum of compound 3

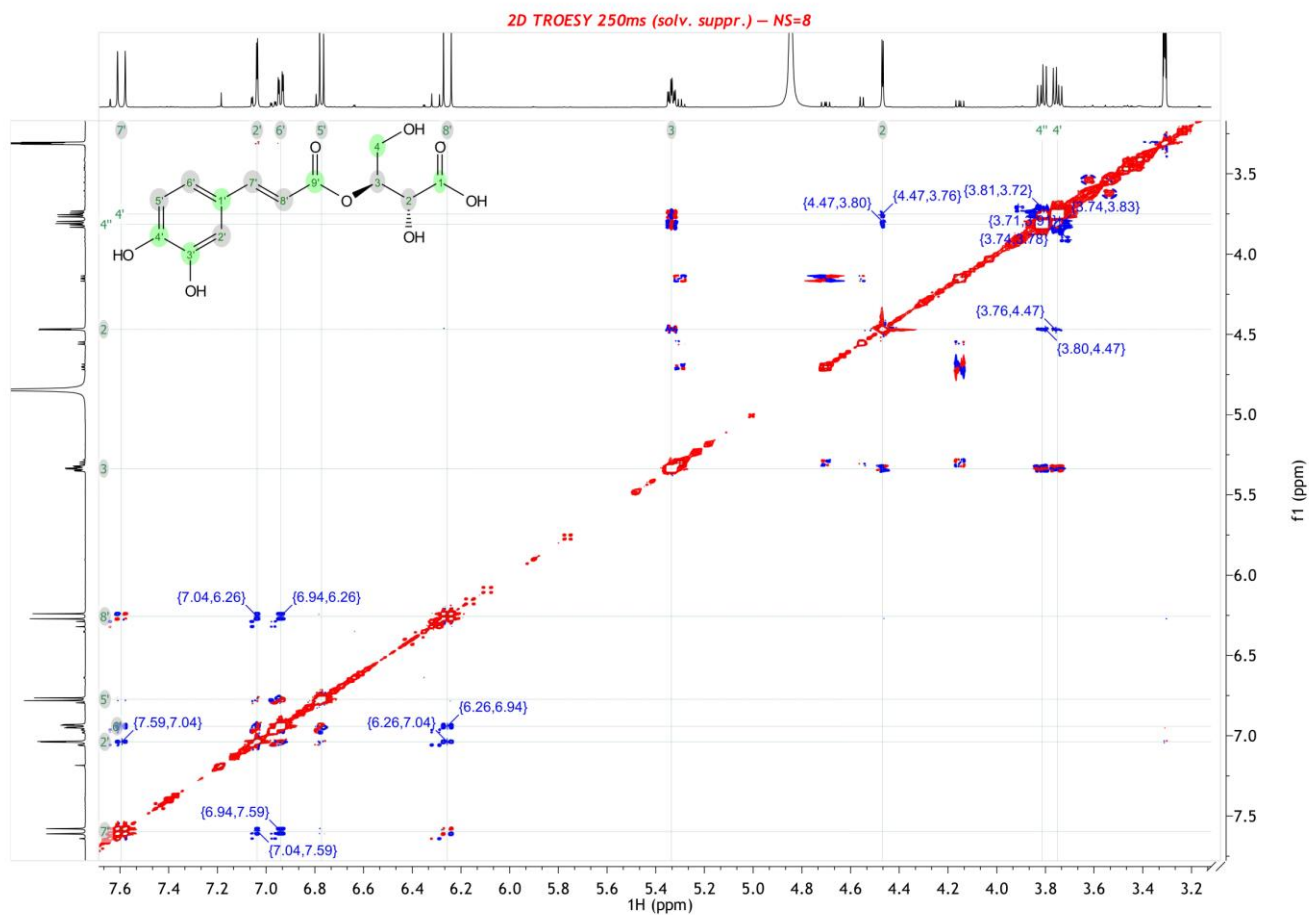


Figure 7S. ^1H - ^1H TROESY (250 ms) NMR spectrum of compound 3

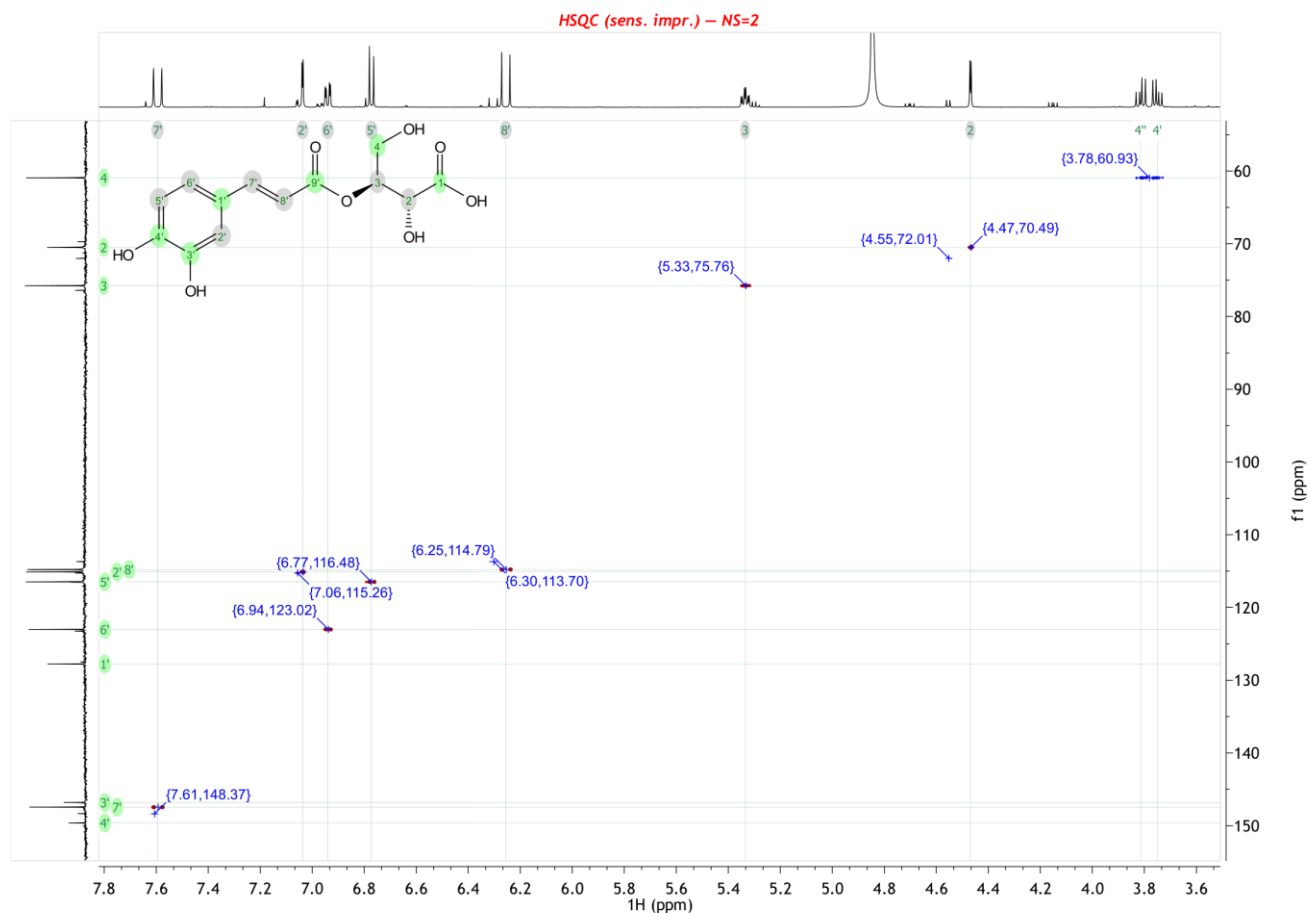


Figure 8S. ^1H - ^{13}C HSQC NMR spectrum of compound 3

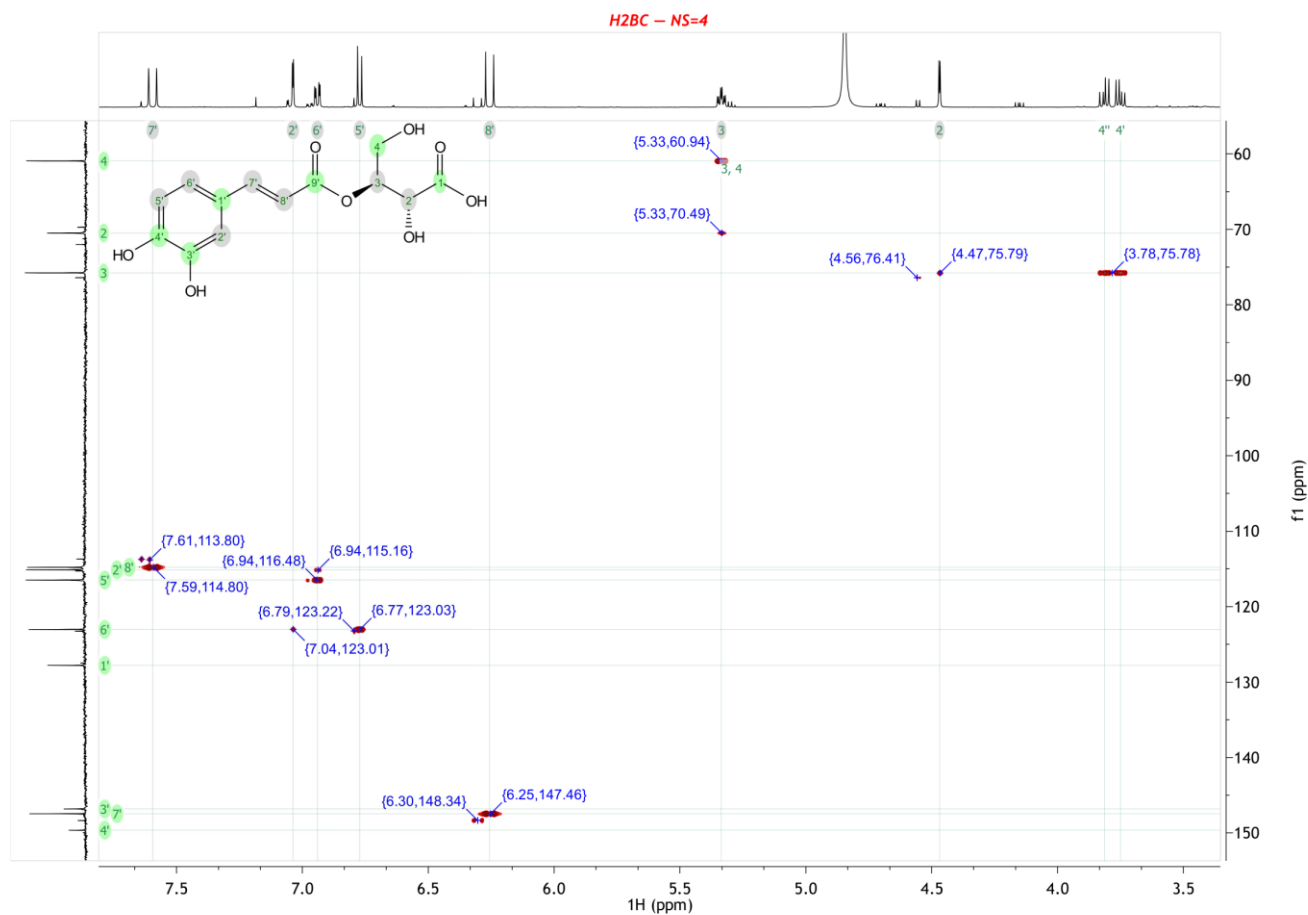


Figure 9S. ^1H - ^{13}C H2BC NMR spectrum of compound 3

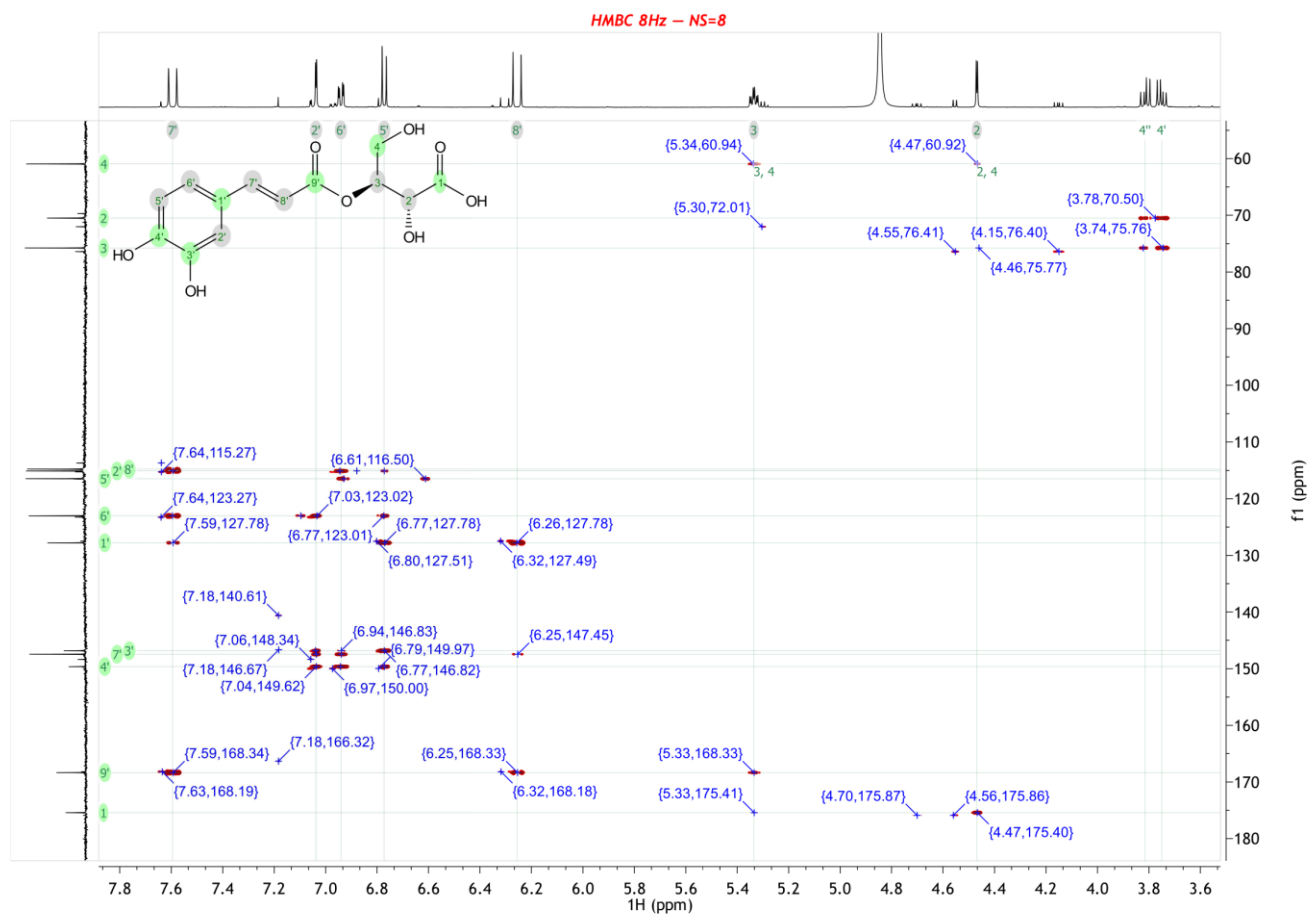


Figure 10S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 3

POAmz297Fr_II_p15-28_flash_4-3

Chemical Formula: $C_{13}H_{14}O_8$
Exact Mass: 298.0689

KNOWN

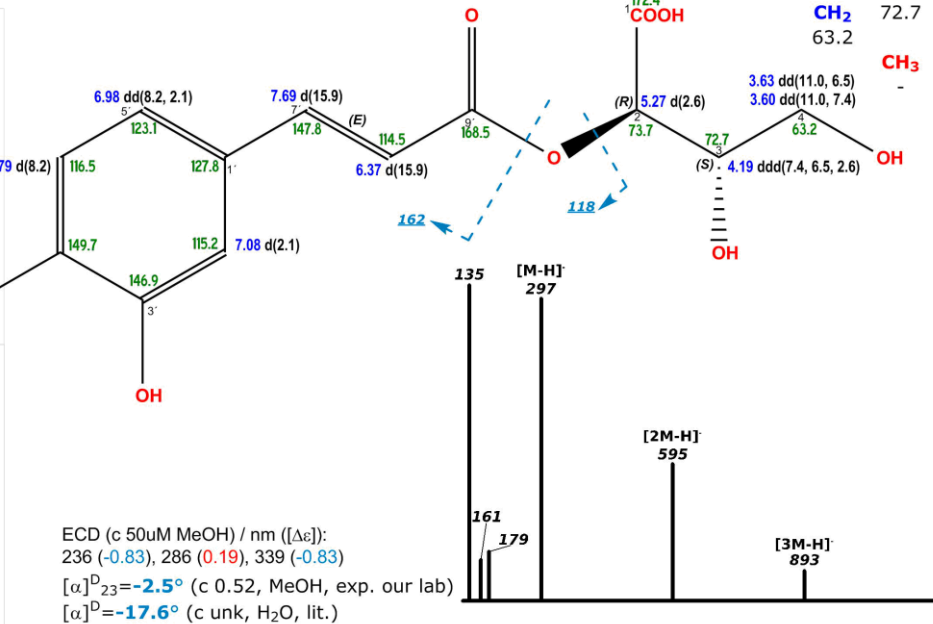
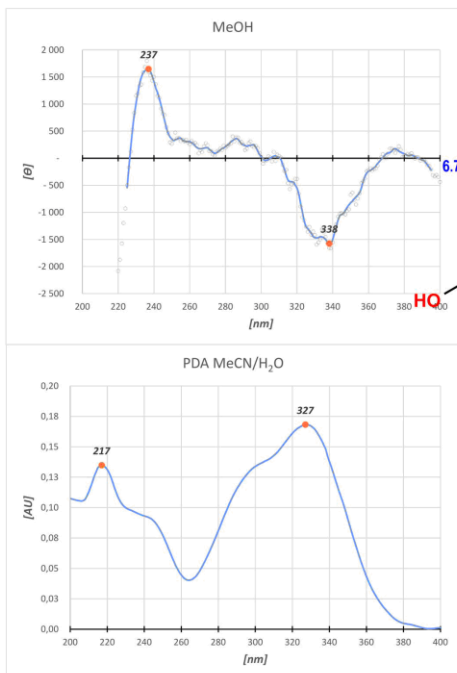
MeOH- d_4 , 25°C

Quat	CH
172.4	147.8
168.5	123.1
149.7	116.5
146.9	115.2
127.8	114.5
	73.7
	72.7
	63.2

CH₂ 72.7

63.2

CH₃ -



2-O-(E)-Caffeoyl-L-threonic acid

1. Kuczkowiak, U., Petereit, F., Nahrstedt, A., 2014. Hydroxycinnamic Acid Derivatives Obtained from a Commercial Crataegus Extract and from Authentic Crataegus spp. Sci. Pharm. 82, 835-846. doi:10.3797/scipharm.1404-02
2. Parveen, I., Winters, A., Threadgill, M.D., Hauck, B., Morris, P., 2008. Extraction, structural characterisation and evaluation of hydroxycinnamate esters of orchard grass (Dactylis glomerata) as substrates for polyphenol oxidase. Phytochemistry 69, 2799-2806. doi:10.1016/j.phytochem.2008.08.019

Figure 11S. ¹H (500 MHz) and ¹³C (125 MHz) NMR data of compound 4 in CD₃OD, 25°C; on-line PDA UV spectrum in MeCN/H₂O, ECD spectrum in MeOH

POAmz215Fr_II_p19-33_F2-1

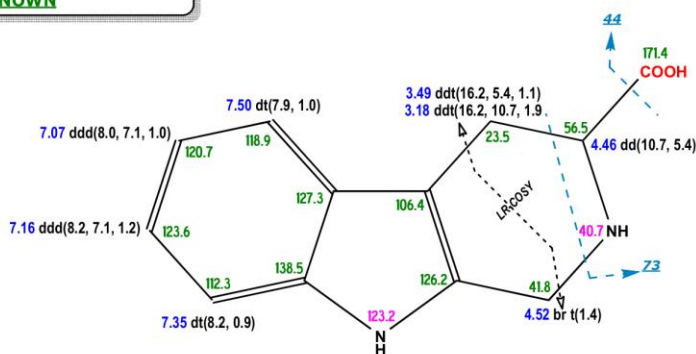
Chemical Formula: $C_{12}H_{12}N_2O_2$
Molecular Weight: 216.2400

KNOWN

MeOH- d_4 +TFA, 25°C

Quat	CH
171.4	123.6
138.5	120.7
127.3	118.9
126.2	112.3
106.4	56.5

CH₂ 41.8
CH₃ -
23.5



MeOH, 25°C

$[\alpha] =$ (exp. our lab)

-° (exp. data, H₂O)

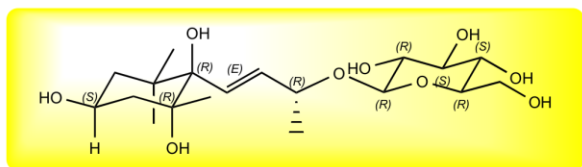
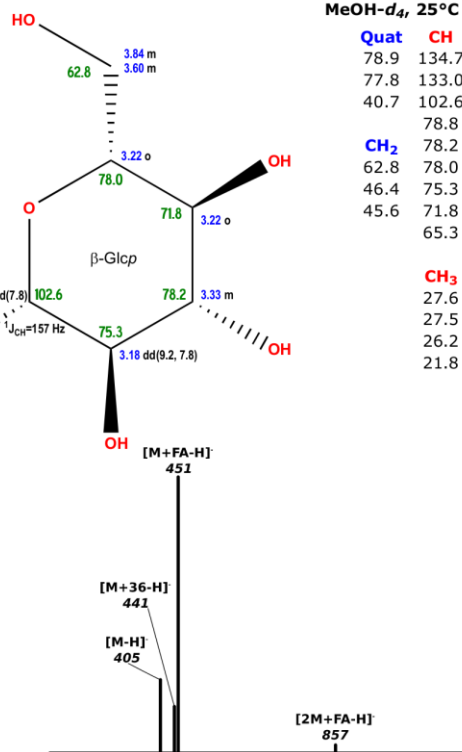
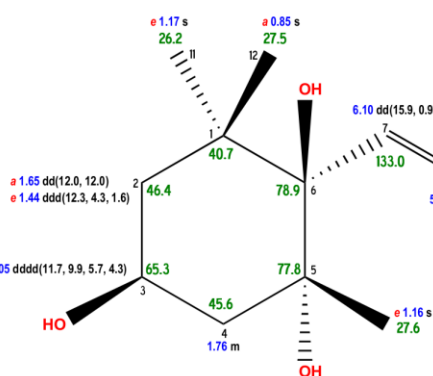
Lycoperodine-1

Figure 12S. ¹H (500 MHz) ¹³C (125 MHz) and ¹⁵N (50 MHz) NMR data of compound 5 in CD₃OD, 25°C

POAmz405Fr_I_p41-46_flash_3-1

Chemical Formula: C₁₉H₃₄O₉
Molecular Weight: 406,4720

KNOWN



Actinidioionoside

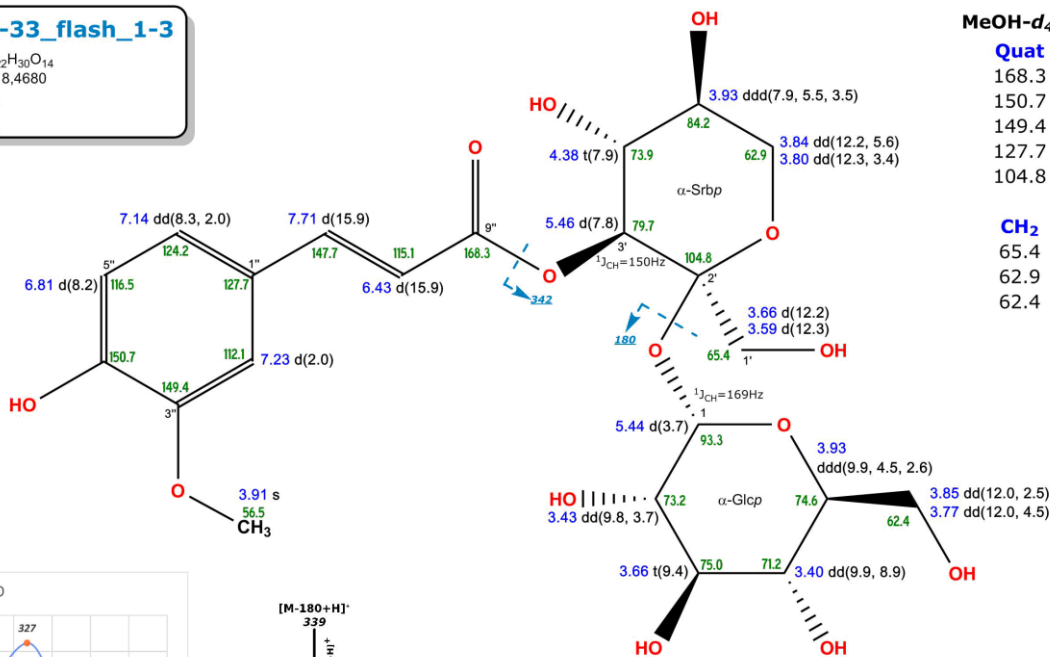
1. Murai, F., Tagawa, M., 1989. Relationship between ionone glycosides and terpenoids in Actinidia polygama, in: Abstract Papers of the 33rd Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics (TEAC), Sendai, pp. 68-70.
2. Otsuka, H., Hirata, E., Shinzato, T., Takeda, Y., 2003. Stereochemistry of megastigmane glycosides from Glochidion zeylanicum and Alangium premmifolium. Phytochemistry 62, 763-768. doi:10.1016/S0031-9422(02)00614-3

Figure 13S. ¹H (500 MHz) and ¹³C (125 MHz) NMR data of compound 7 in CD₃OD, 25°C

POAmz517Fr_II_p19-33_flash_1-3

Chemical Formula: C₂₂H₃₀O₁₄
Molecular Weight: 518,4680

NEW!



¹H NS16 CD3OD 25°C – NS=16

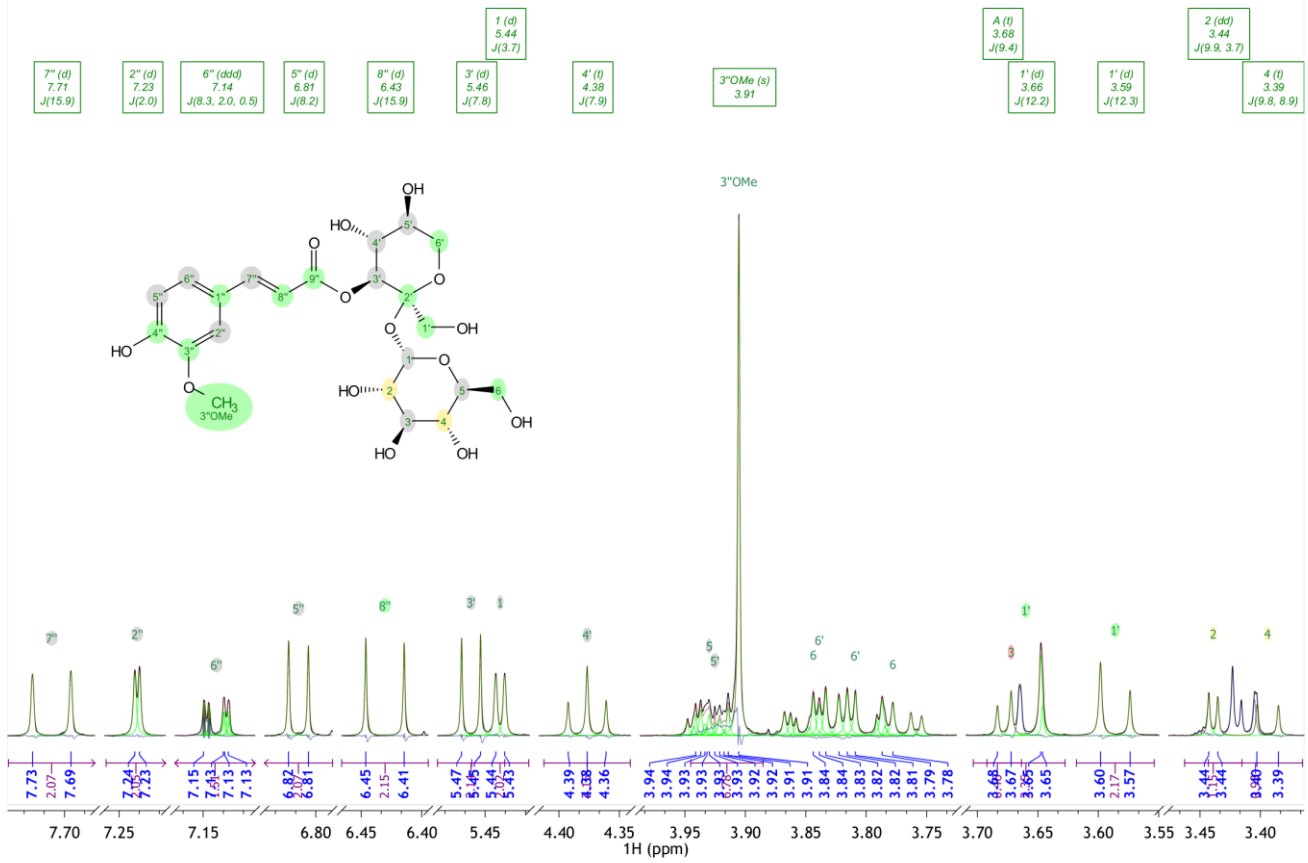


Figure 15S. ¹H NMR spectrum of compound 10

¹³C dec UDEFT – NS=2048

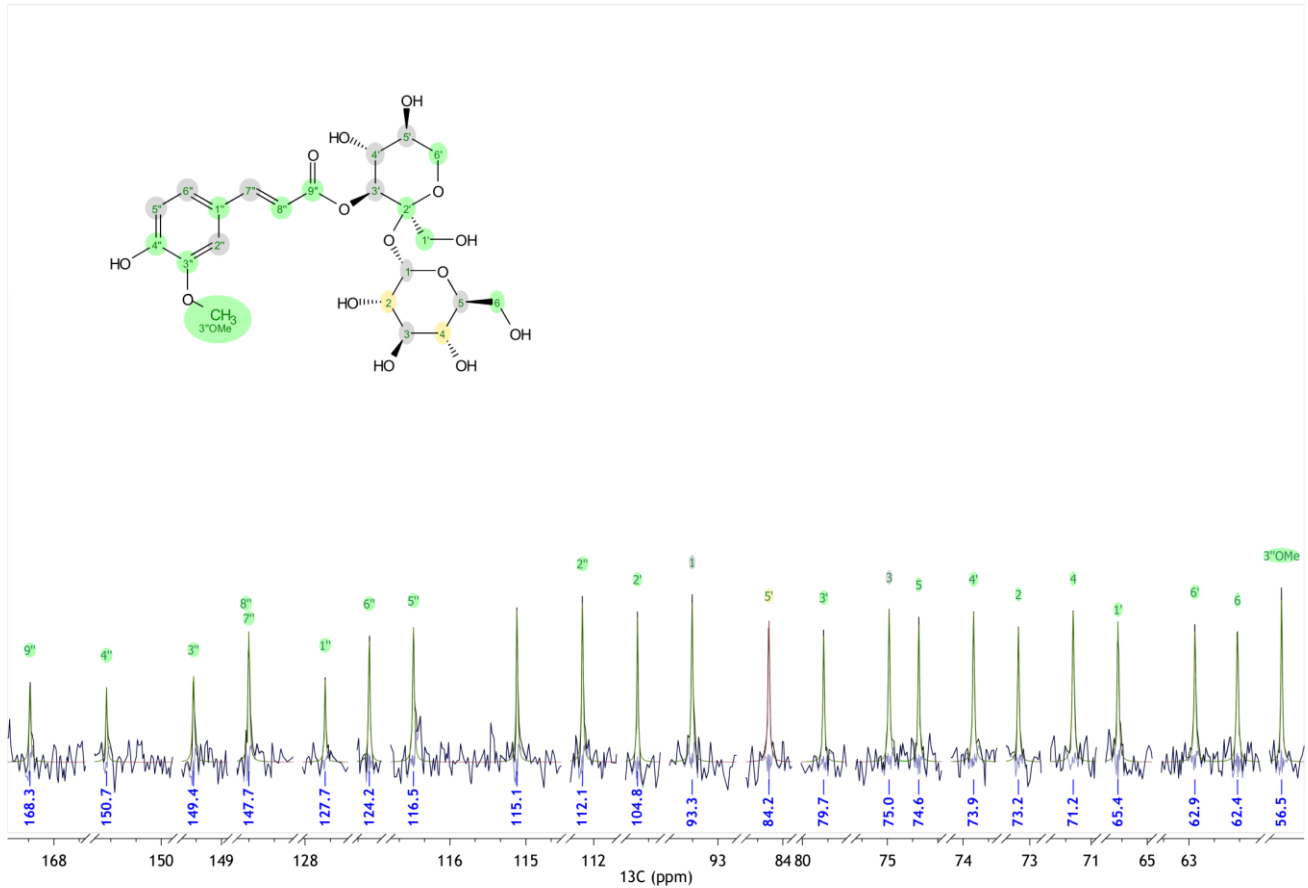


Figure 16S. ¹³C DEPTQ NMR spectrum of compound 10

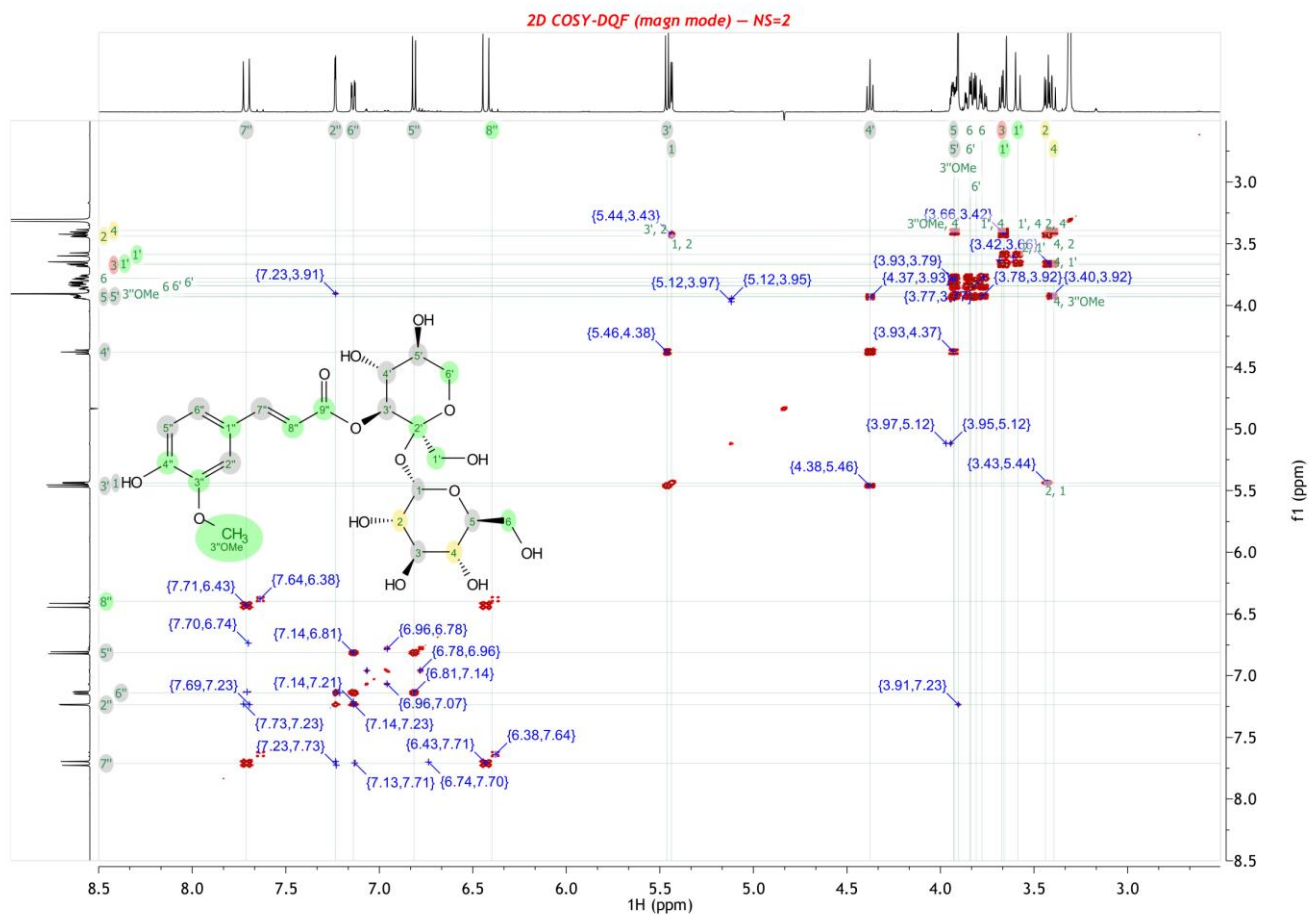


Figure 17S. ^1H - ^1H COSY NMR spectrum of compound 10

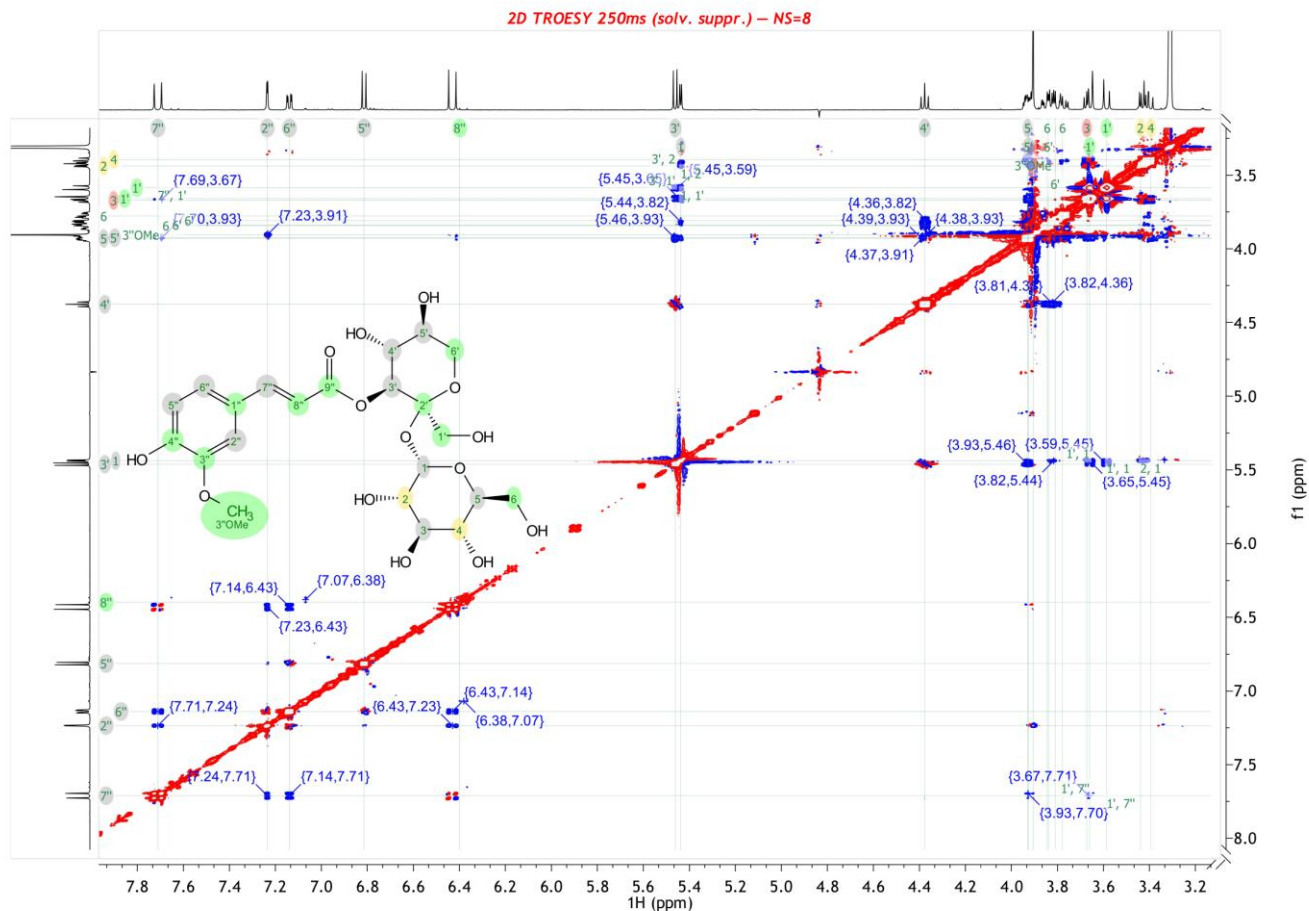


Figure 18S. ^1H - ^1H TROESY (250 ms) NMR spectrum of compound 10

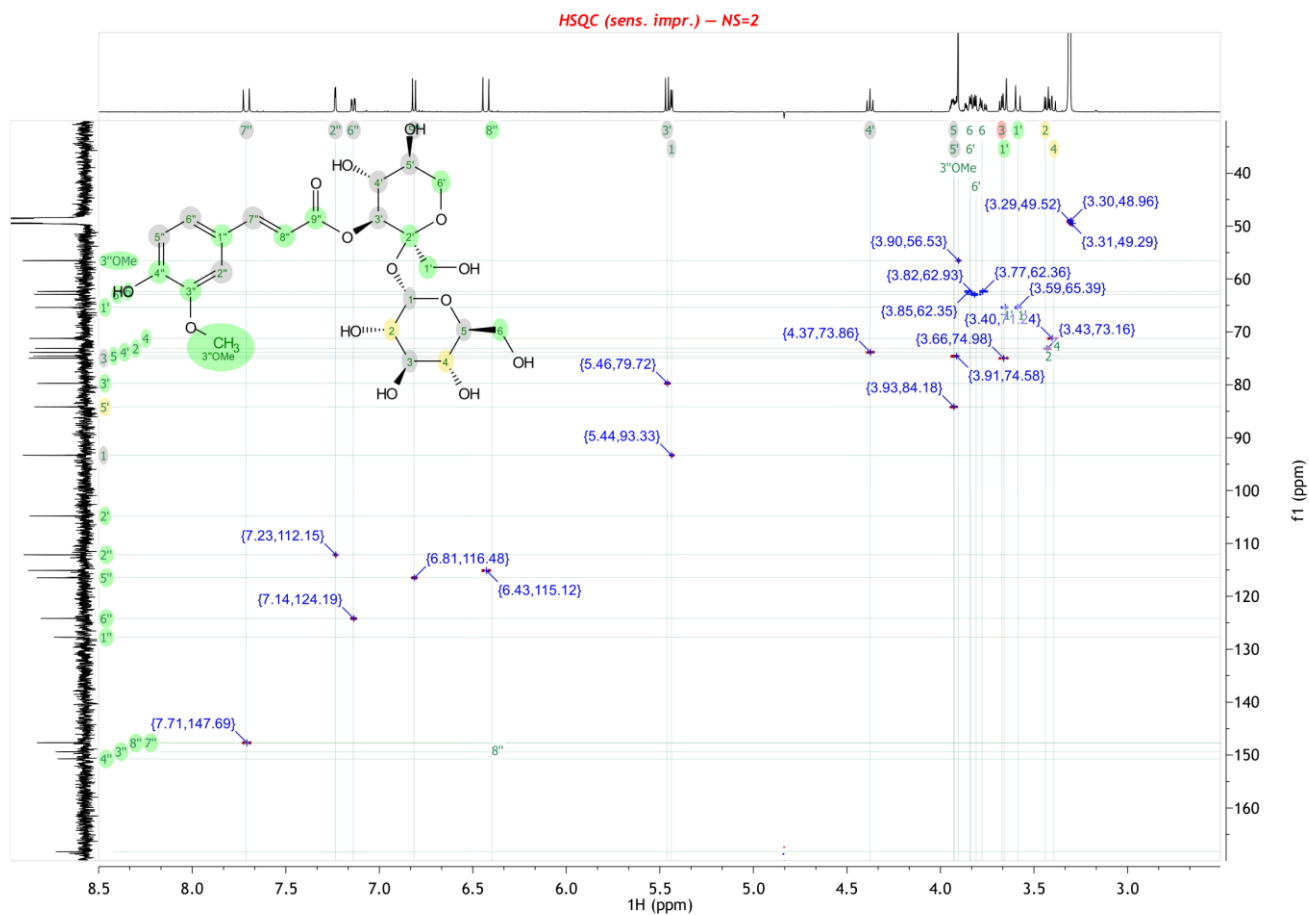


Figure 19S. ^1H - ^{13}C HSQC NMR spectrum of compound 10

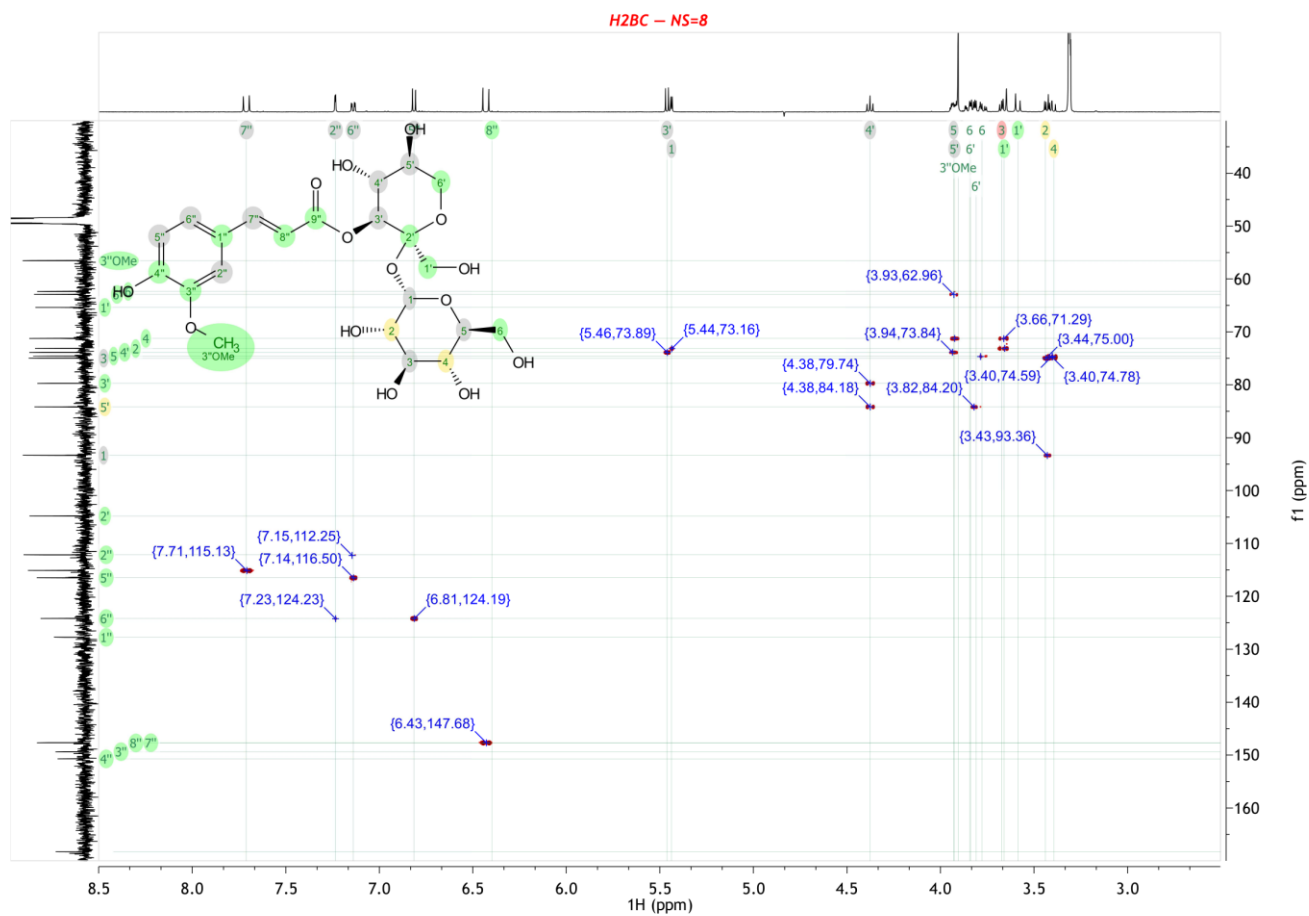


Figure 20S. ^1H - ^{13}C H2BC NMR spectrum of compound 10

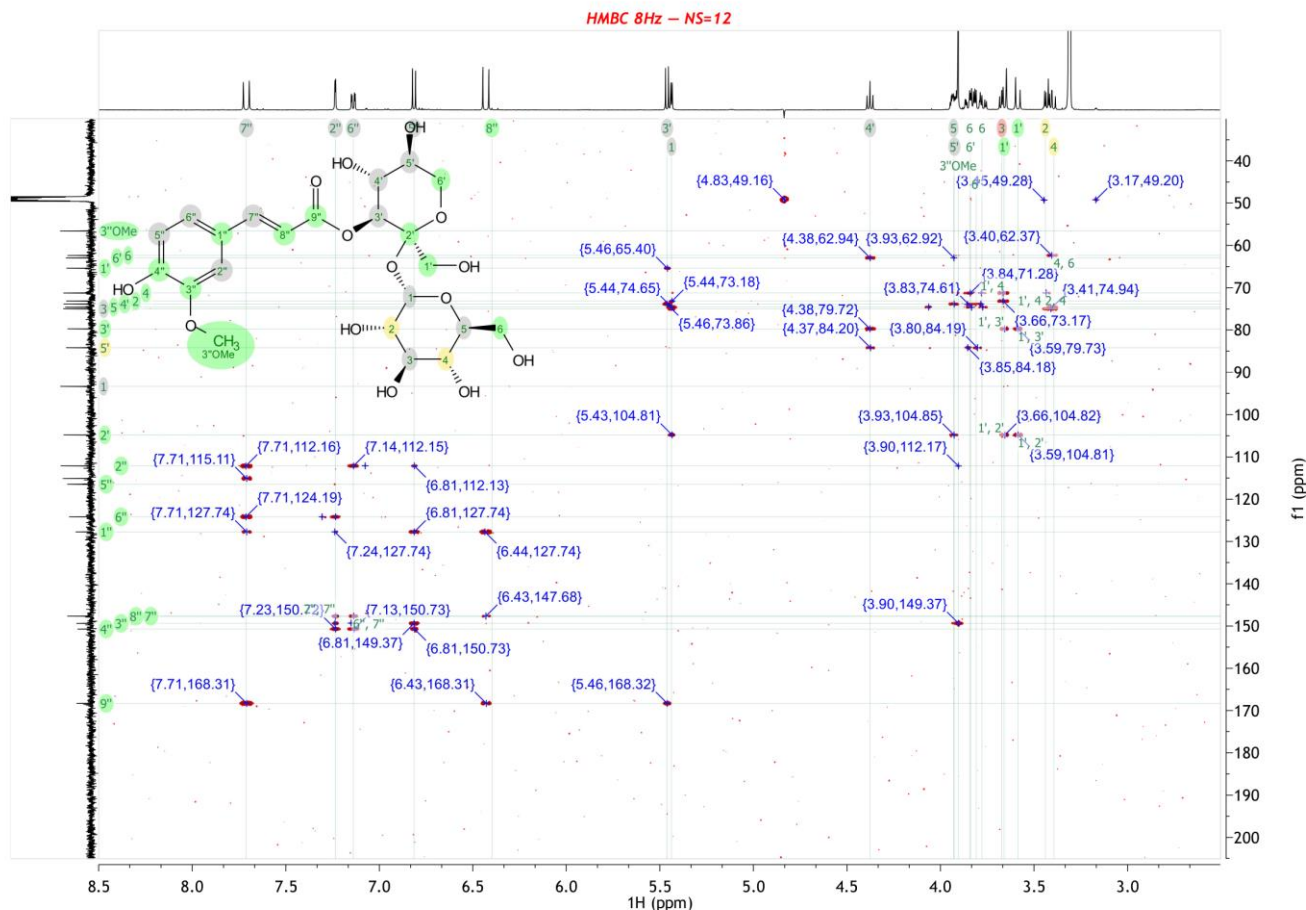
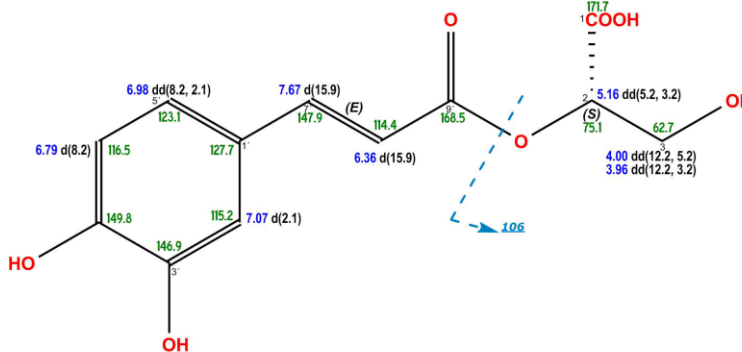
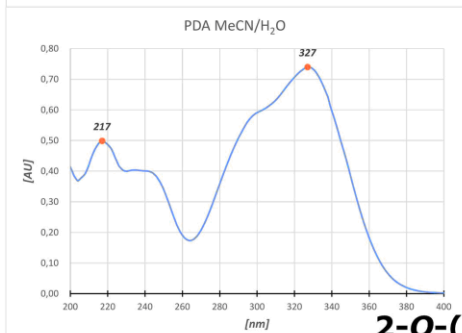
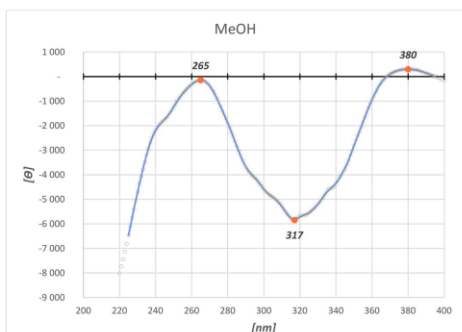


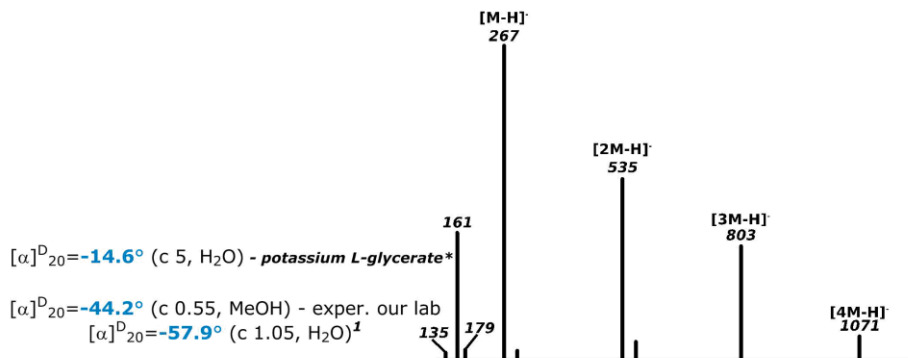
Figure 21S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 10

POAmz267Fr_II_p15-28_flush_6
 Chemical Formula: $\text{C}_{12}\text{H}_{12}\text{O}_7$
 Exact Mass: 268.0583
KNOWN



MeOH- d_4 , 25°C

Quat	CH
171.7	147.9
168.5	123.1
149.8	116.5
146.9	115.2
127.7	114.4
	75.1
CH ₂	CH ₃
62.7	-



2-O-(E)-Caffeoyl-L-glyceric acid

$[\alpha]_{20}^D = -14.6^\circ$ (c 5, H_2O) - *potassium L-glycerate**
 $[\alpha]_{20}^D = -44.2^\circ$ (c 0.55, MeOH) - exper. our lab
 $[\alpha]_{20}^D = -57.9^\circ$ (c 1.05, H_2O)¹

1. Hahn, R., Nahrstedt, A., 1993. Hydroxycinnamic acid derivatives, caffeoylmalic and new caffeoylaldonic acid esters, from *Chelidonium majus*. *Planta Med.* 59, 71-75. doi:10.1055/s-2006-959608
 * <http://www.drugfuture.com/chemdata/glyceric-acid.html>

Figure 22S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 11 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O ; ECD spectrum in MeOH

POAmz297Fr_II_p19-34_flash_2-p23

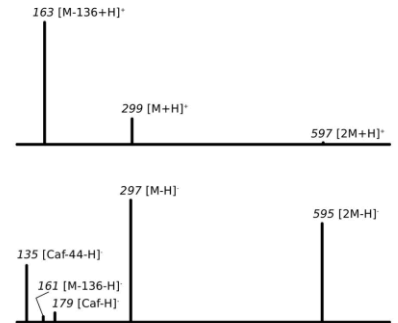
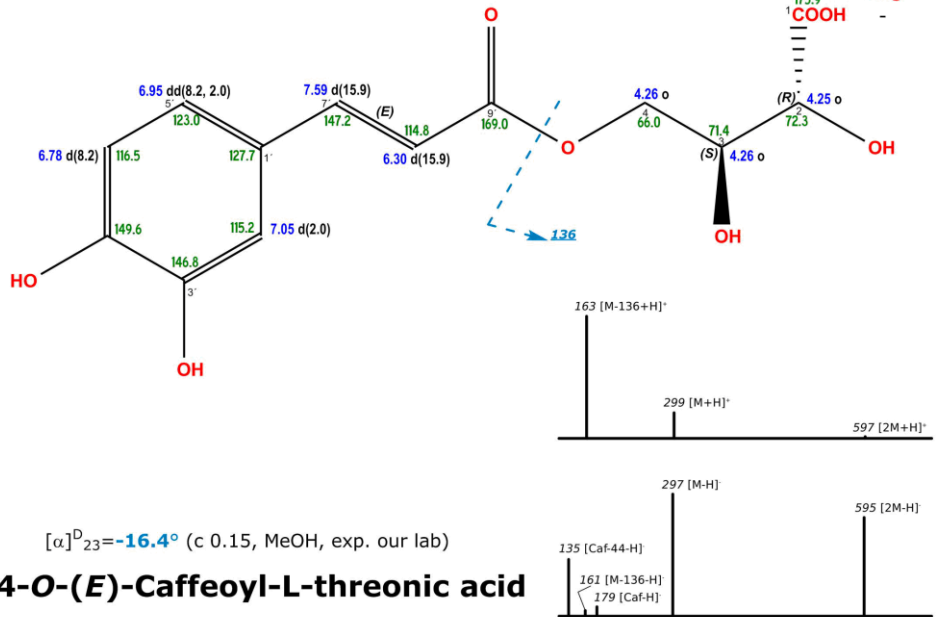
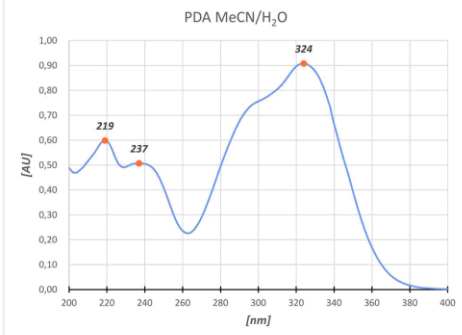
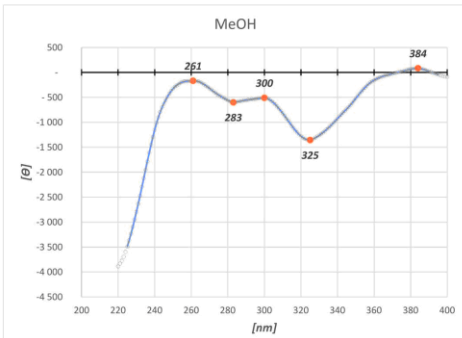
Chemical Formula: $C_{13}H_{14}O_8$
Exact Mass: 298,0689

KNOWN

MeOH- d_4 , 25°C

Quat	CH
175.9	147.2
169.0	123.0
149.6	116.5
146.8	115.2
127.7	114.8
	72.3
CH₂	71.4
66.0	

CH₃
-



Hahn, R., Nahrstedt, A., 1993. Hydroxycinnamic acid derivatives, caffeoylmalic and new caffeoylalonic acid esters, from *Chelidonium majus*. *Planta Med.* 59, 71–75. doi:10.1055/s-2006-959608

Figure 23S. 1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 12 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O ; ECD spectrum in MeOH

POAmz267Fr_II_p19-33_2-3-1

Chemical Formula: $C_{12}H_{12}O_7$
Exact Mass: 268,0583

NEW!

MeOH- d_4 , 25°C

Quat	CH
174.8	147.4
168.9	123.0
149.7	116.5
146.8	115.1
127.7	114.6
	70.3
CH₂	66.9
66.9	

CH₃
-

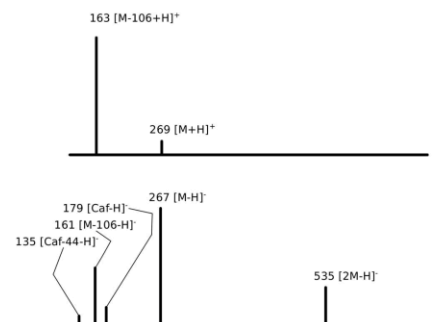
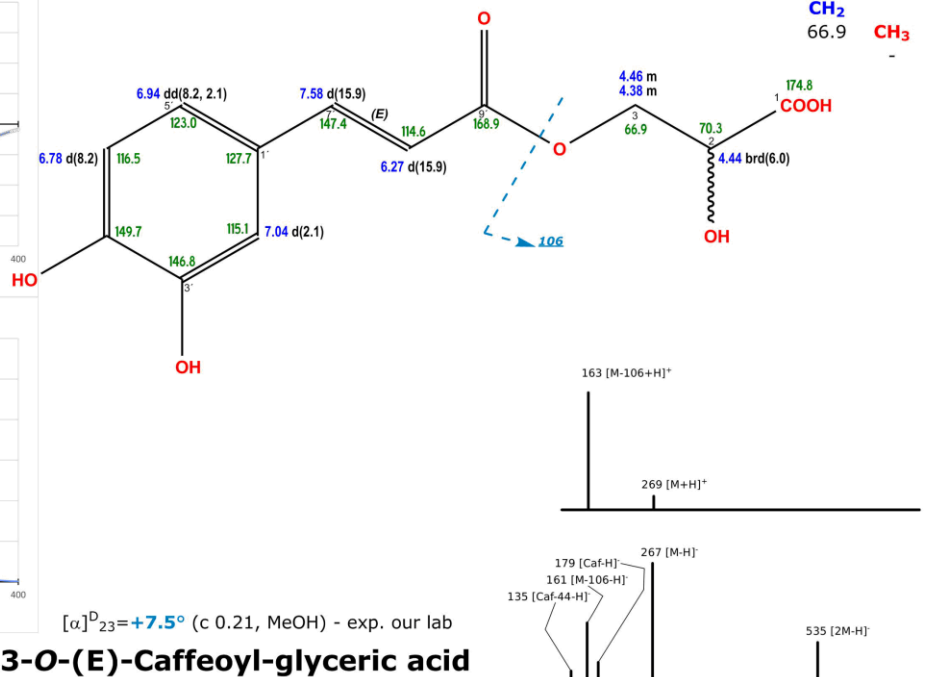
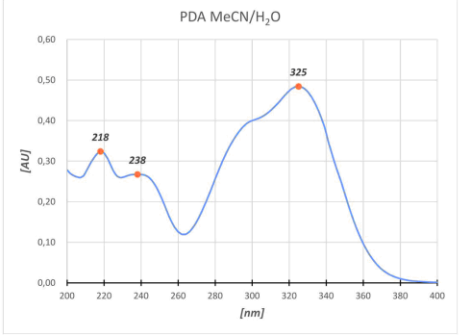
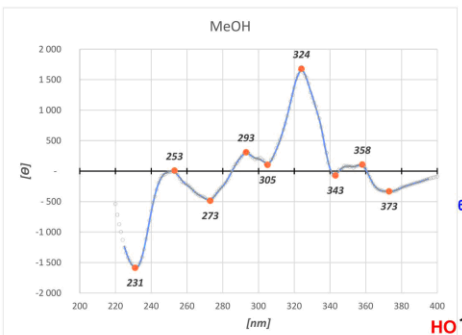


Figure 24S. 1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 14 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O ; ECD spectrum in MeOH

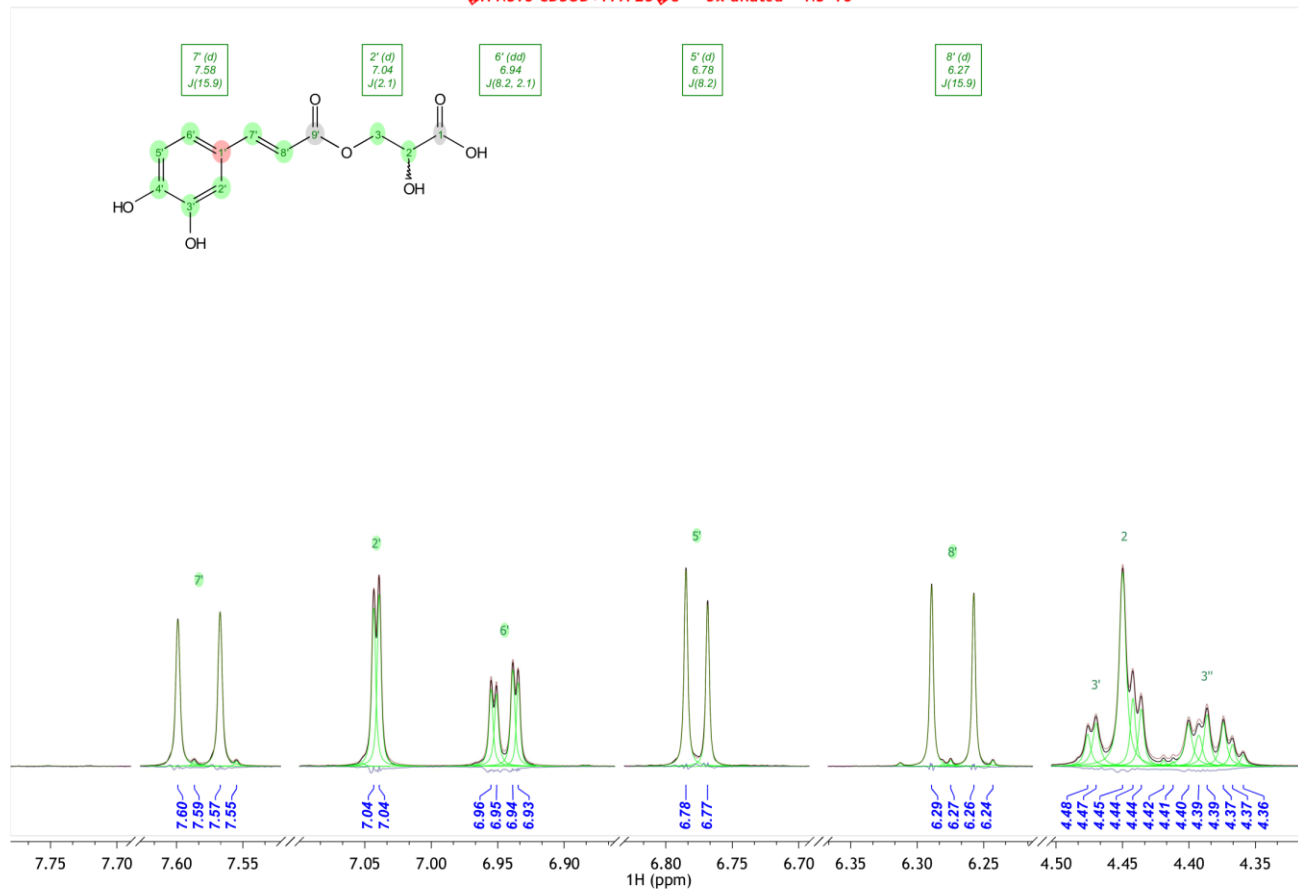


Figure 25S. ^1H NMR spectrum of compound 14

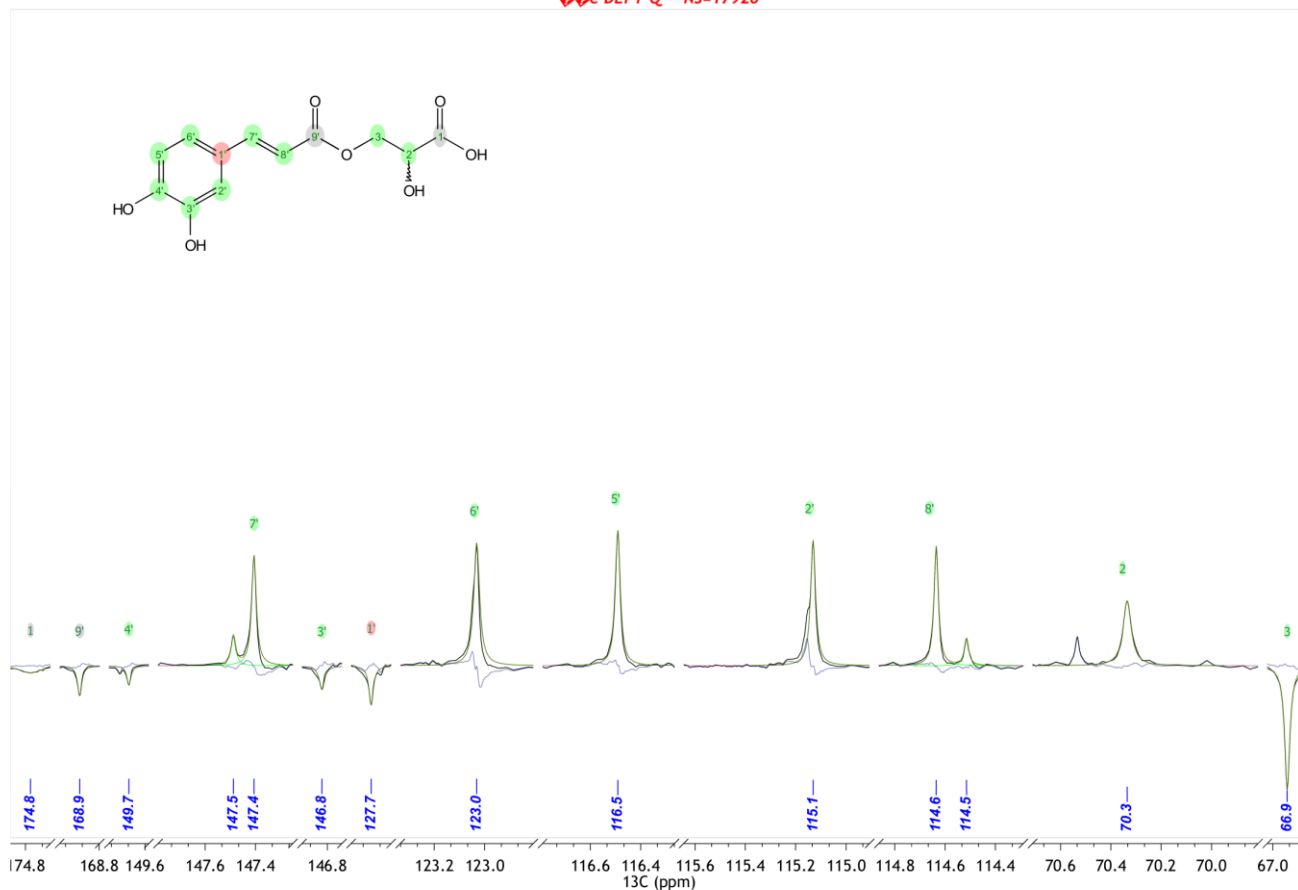


Figure 26S. ^{13}C DEPTQ NMR spectrum of compound 14

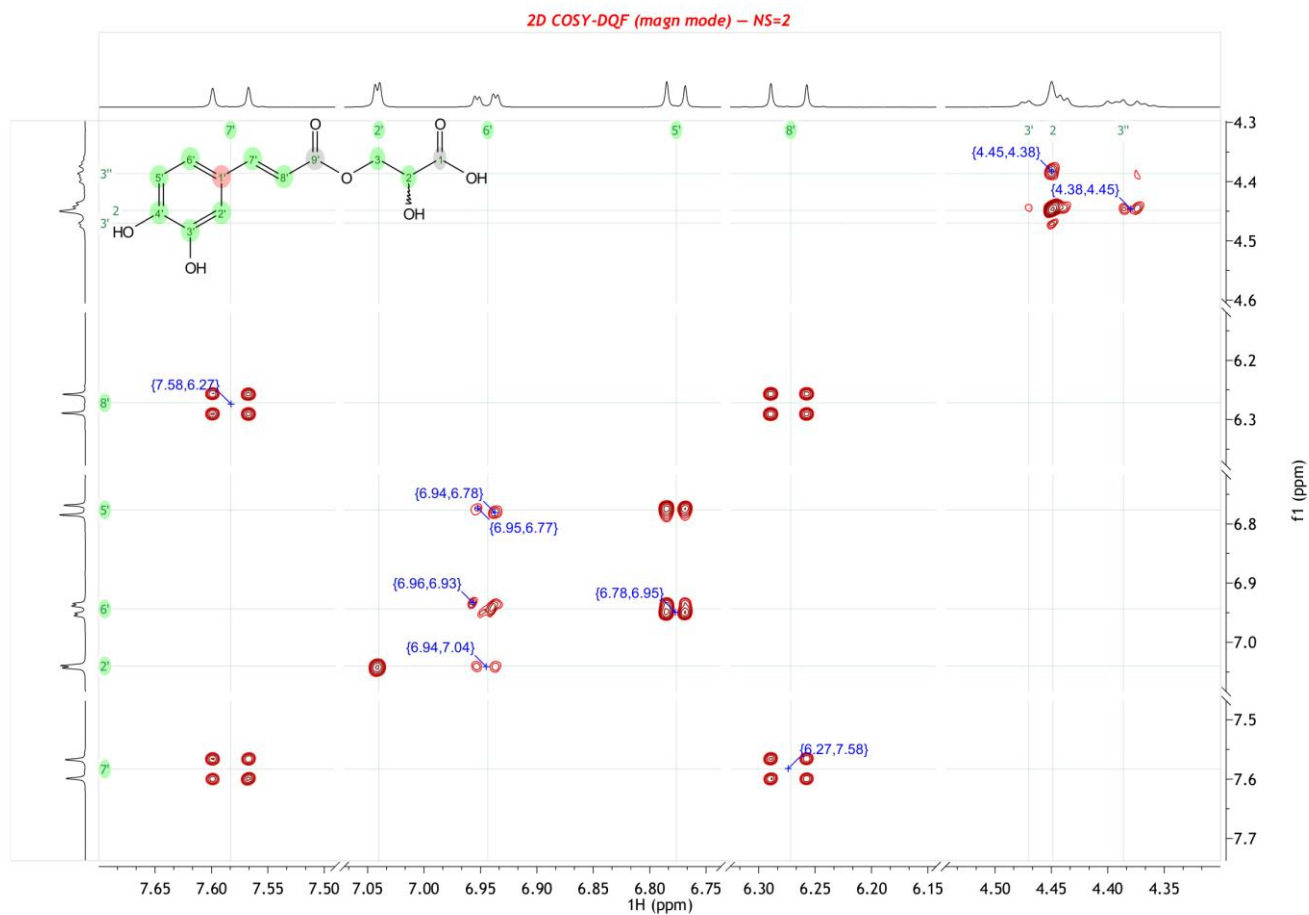


Figure 27S. ^1H - ^1H COSY NMR spectrum of compound 14

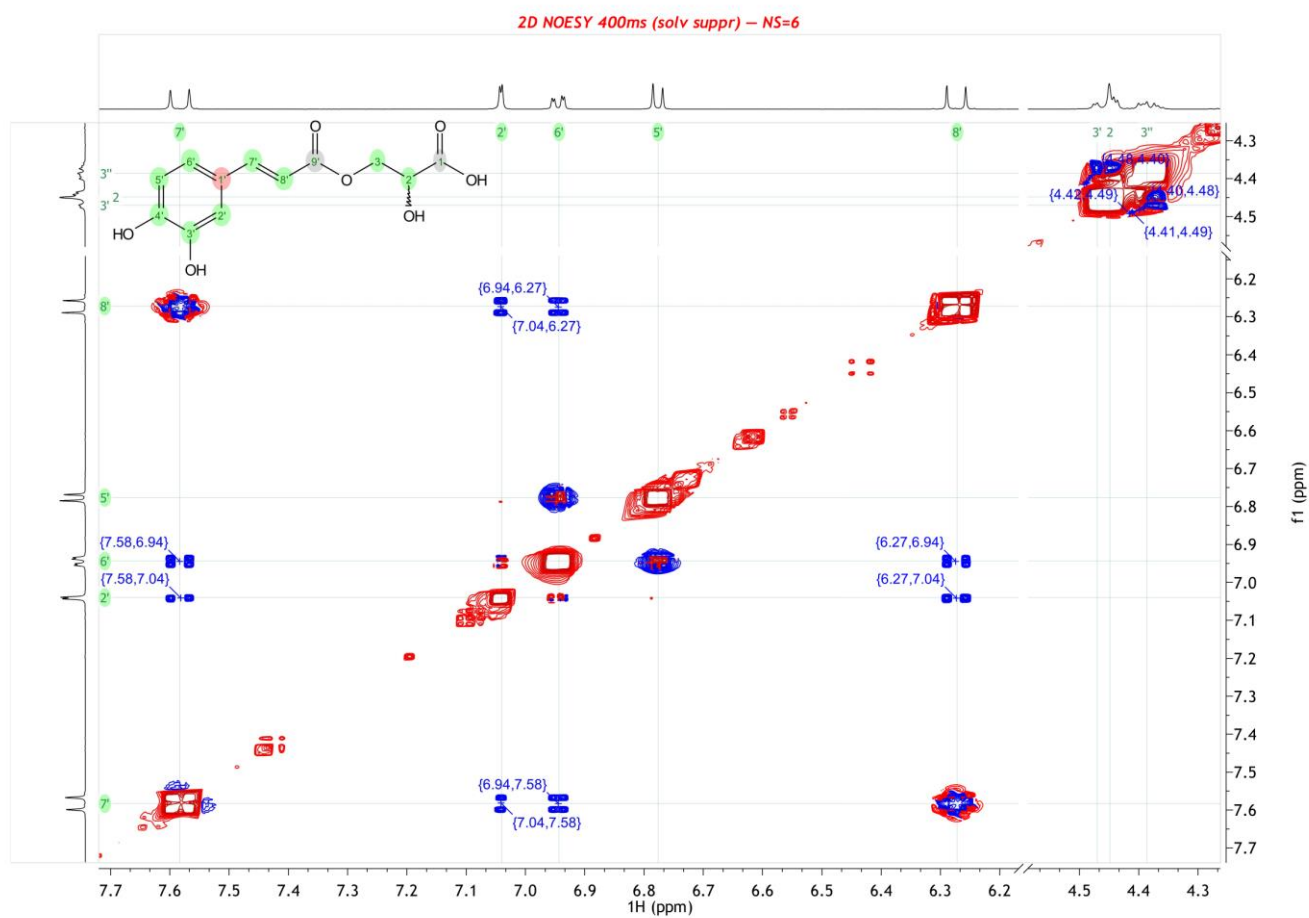


Figure 28S. ^1H - ^1H NOESY (400 ms) NMR spectrum of compound 14

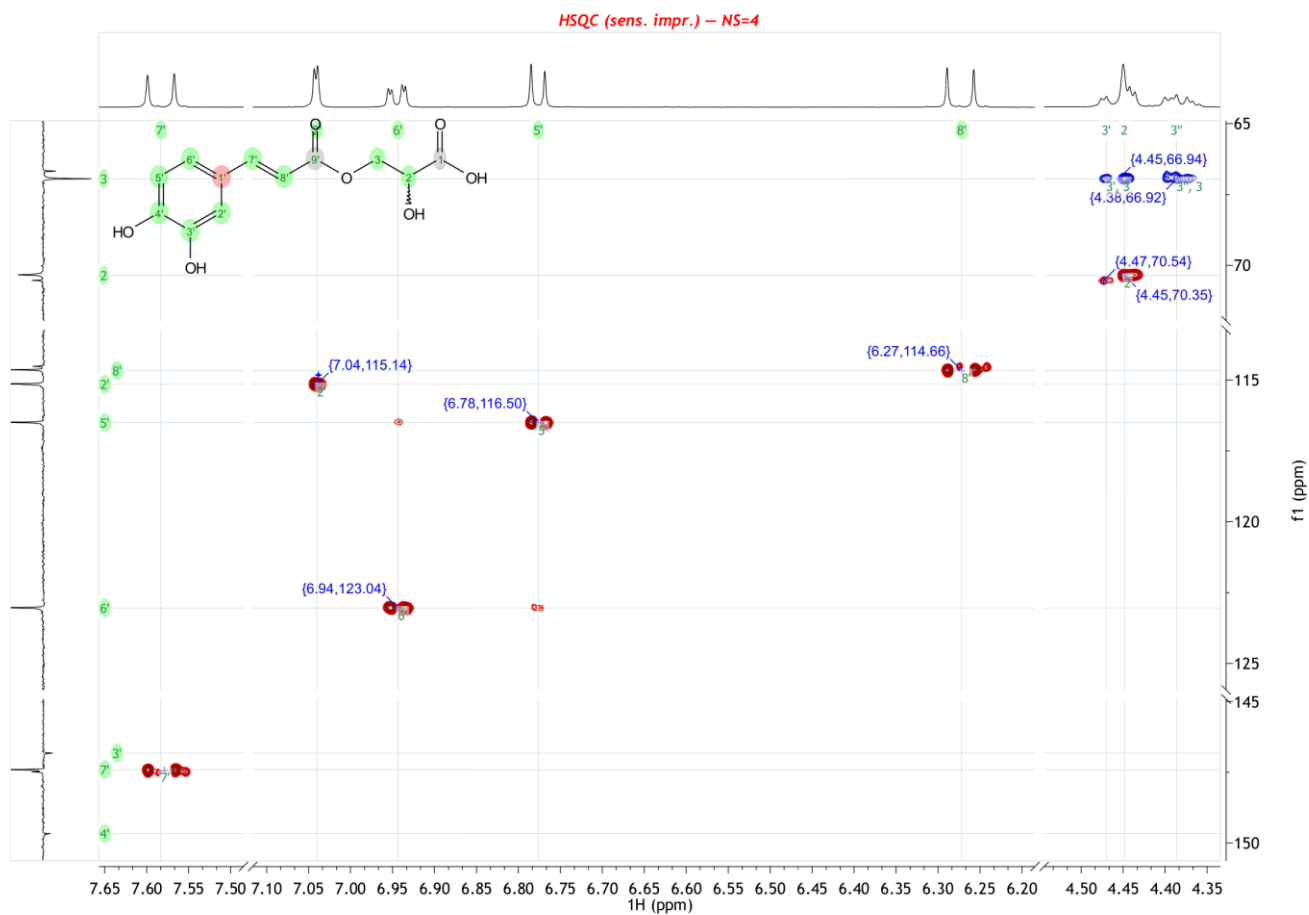


Figure 29S. ^1H - ^{13}C HSQC NMR spectrum of compound 14

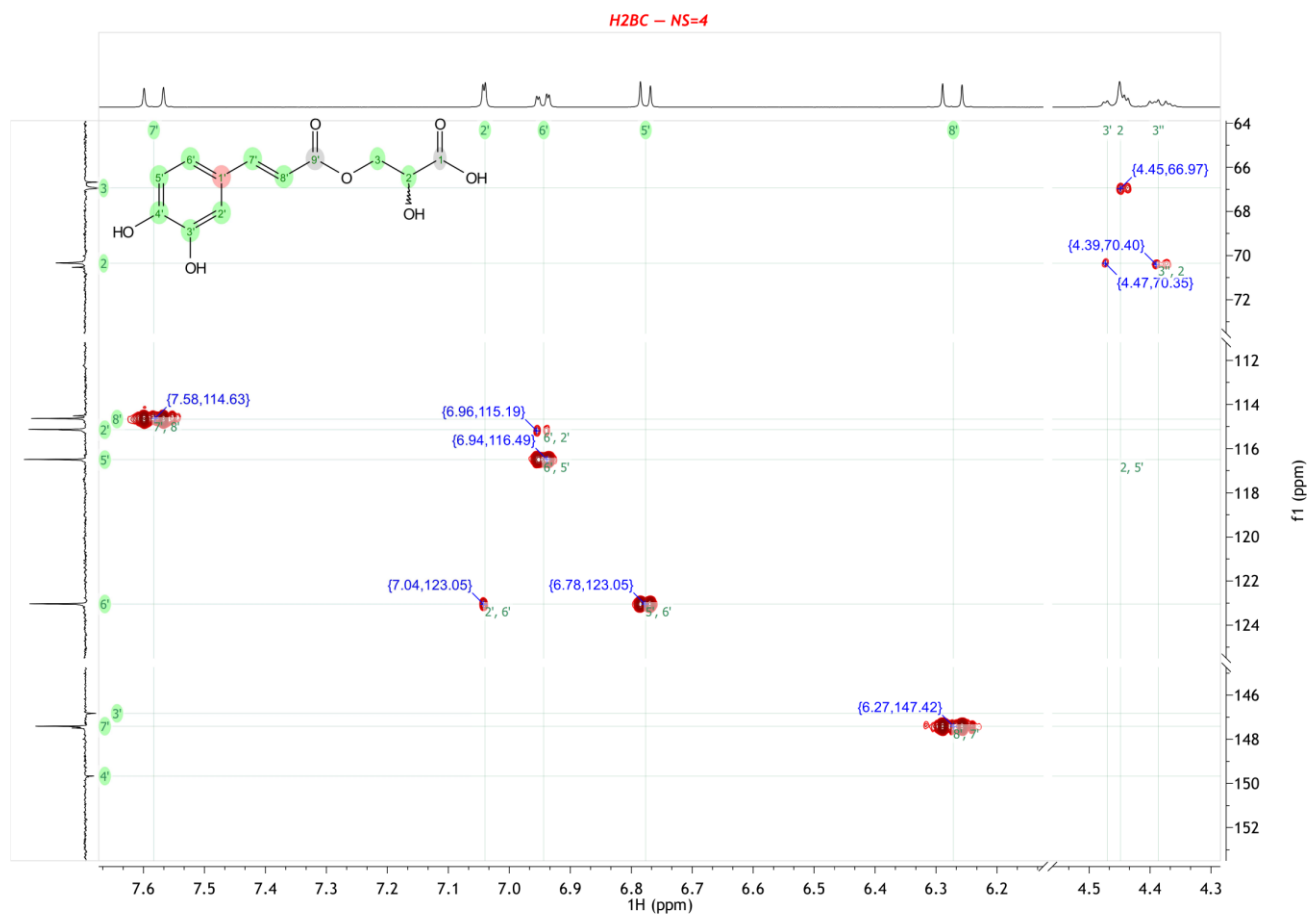


Figure 30S. ^1H - ^{13}C H2BC NMR spectrum of compound 14

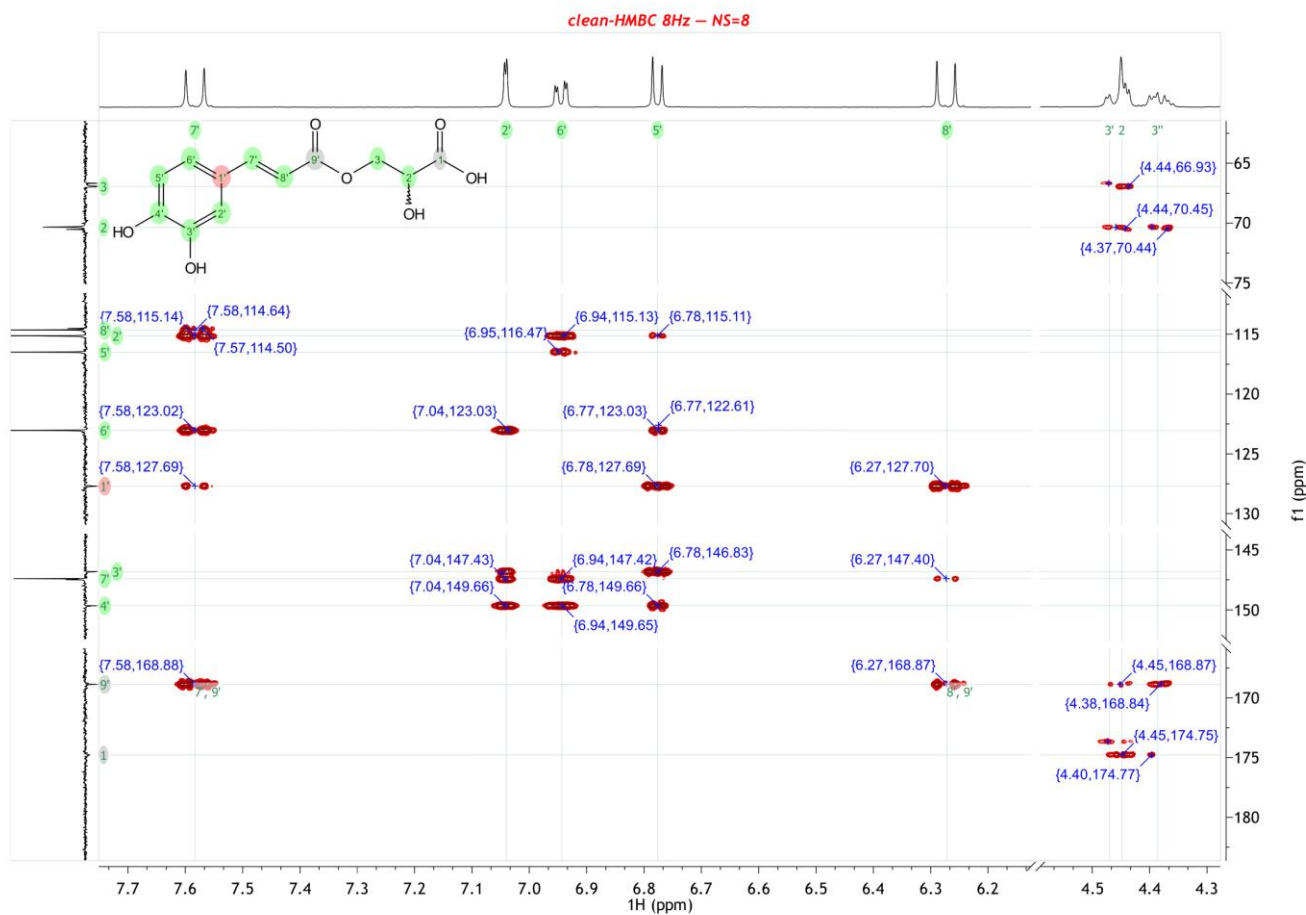
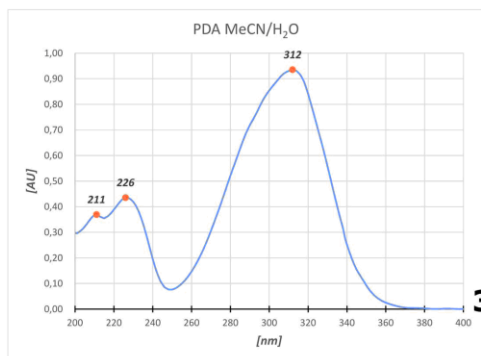
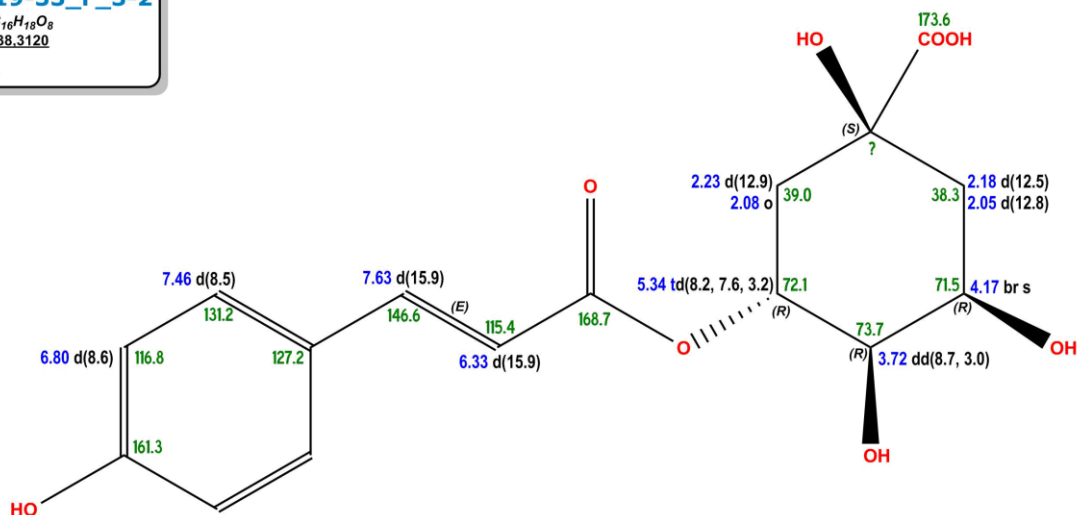


Figure 31S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 14

POAmz337Fr_II_p19-33_F_3-2
 Chemical Formula: $\text{C}_{16}\text{H}_{18}\text{O}_8$
 Molecular Weight: **338.3120**
KNOWN



$[\alpha]_{23}^{\text{D}} = -28.5^\circ$ (c 0.23, MeOH, exp. our lab)
3-O-p-Coumaroylquinic acid

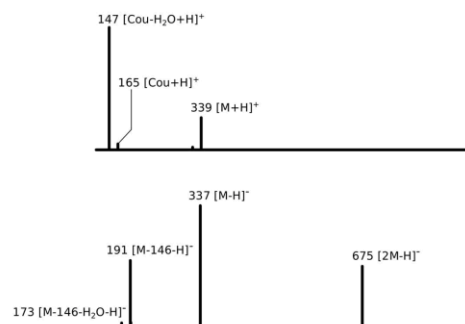
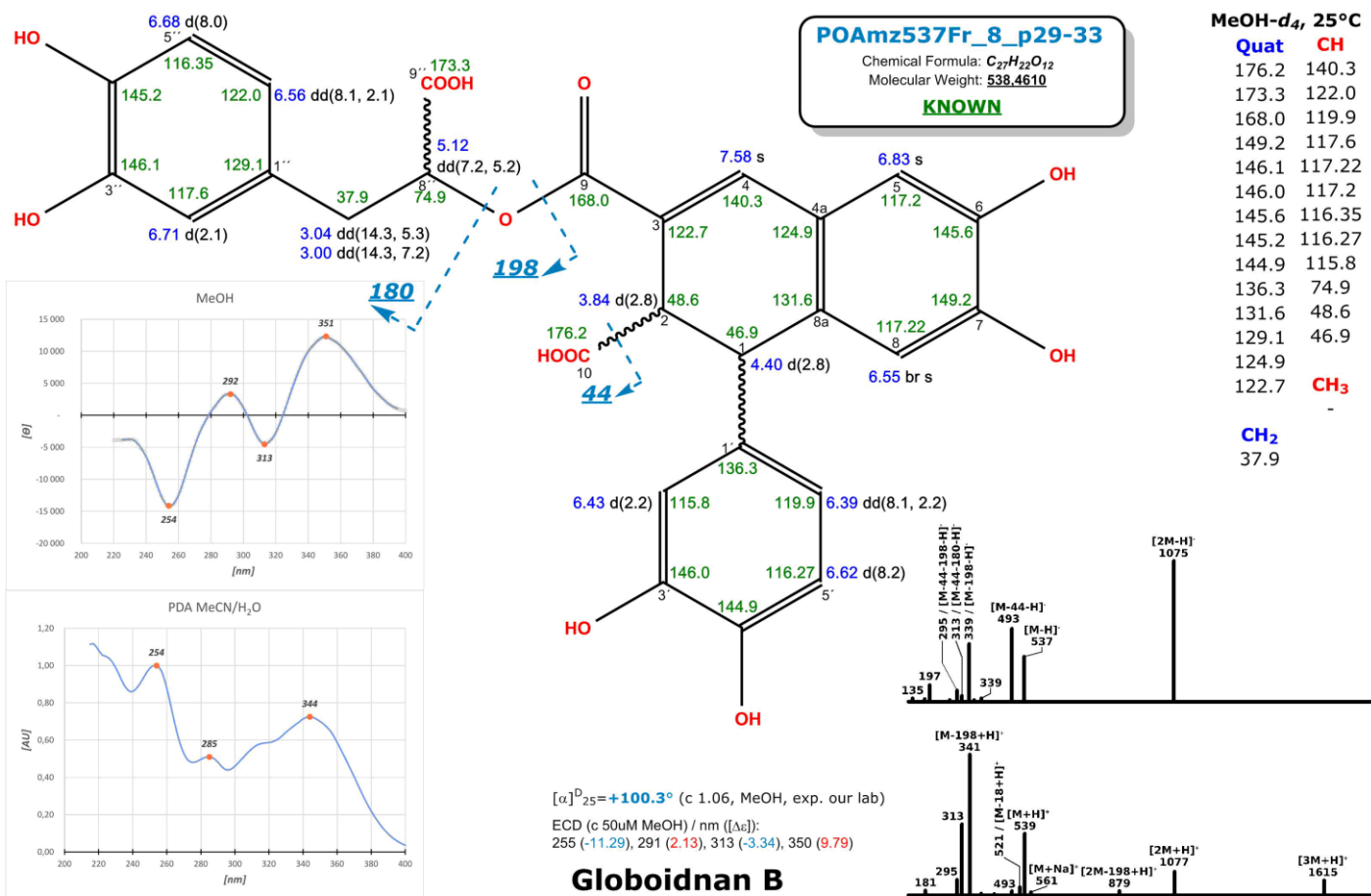


Figure 32S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 15 in CD_3OD , 25°C ; on-line PDA UV spectrum in MeCN/H₂O



1. Basli, A., Delaunay, J.-C., Pedrot, E., Bernillon, S., Madani, K., Monti, J.-P., Mérlion, J.M., Chibane, M., Richard, T., 2014. New Cycloignans from *Origanum glandulosum* Active Against β -amyloid Aggregation. *Rec. Nat. Prod.* 8, 208–216.
 2. Assoumatine, T., Datta, P.K., Hooper, T.S., Yvon, B.L., Charlton, J.L., 2004. A Short Asymmetric Synthesis of (+)-Lyoniresinol Dimethyl Ether. *J. Org. Chem.* 69, 4140–4144. doi:10.1021/jo0497454

Figure 33S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 18 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O ; ECD spectrum in MeOH

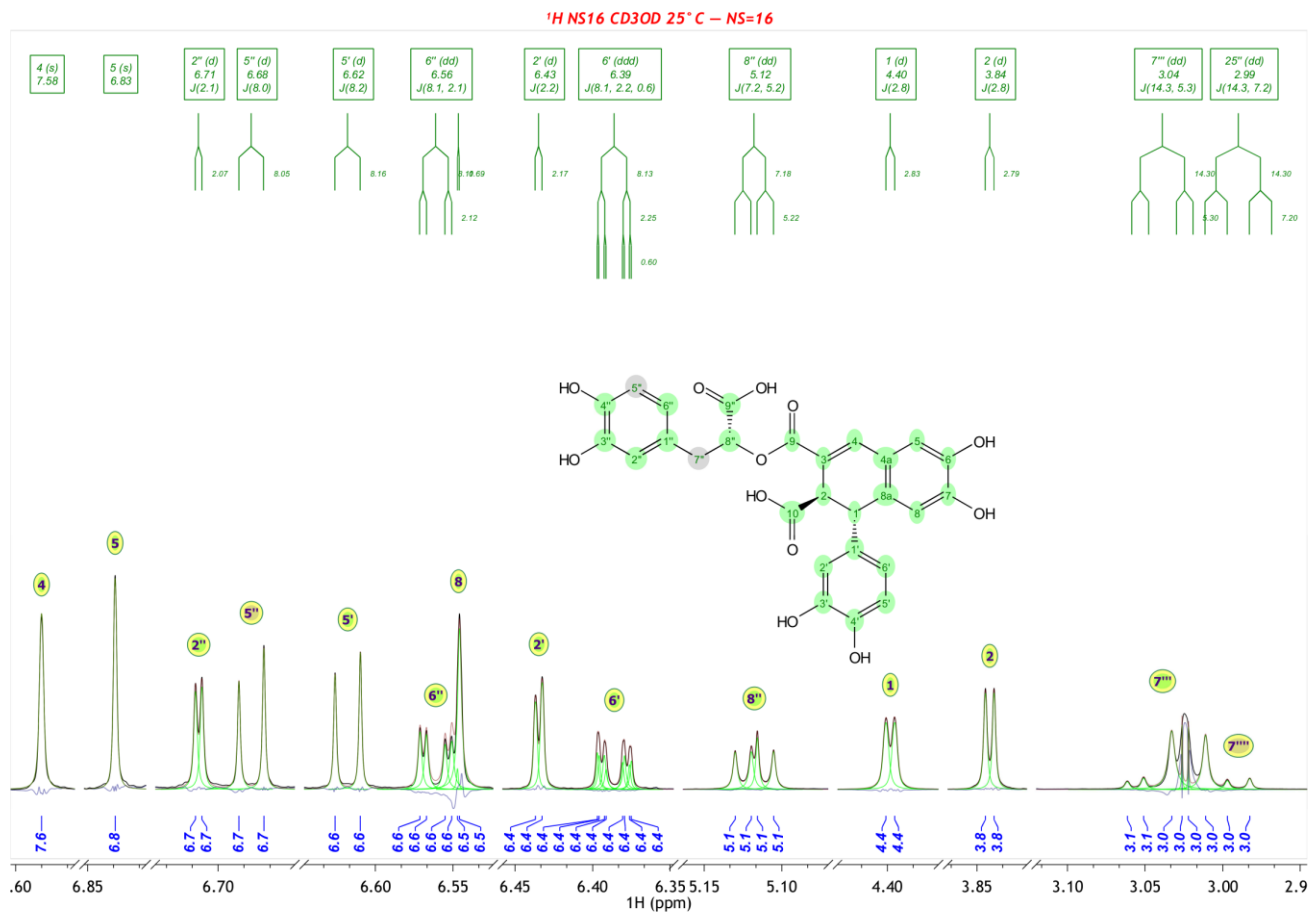


Figure 34S. ^1H NMR spectrum of compound 18

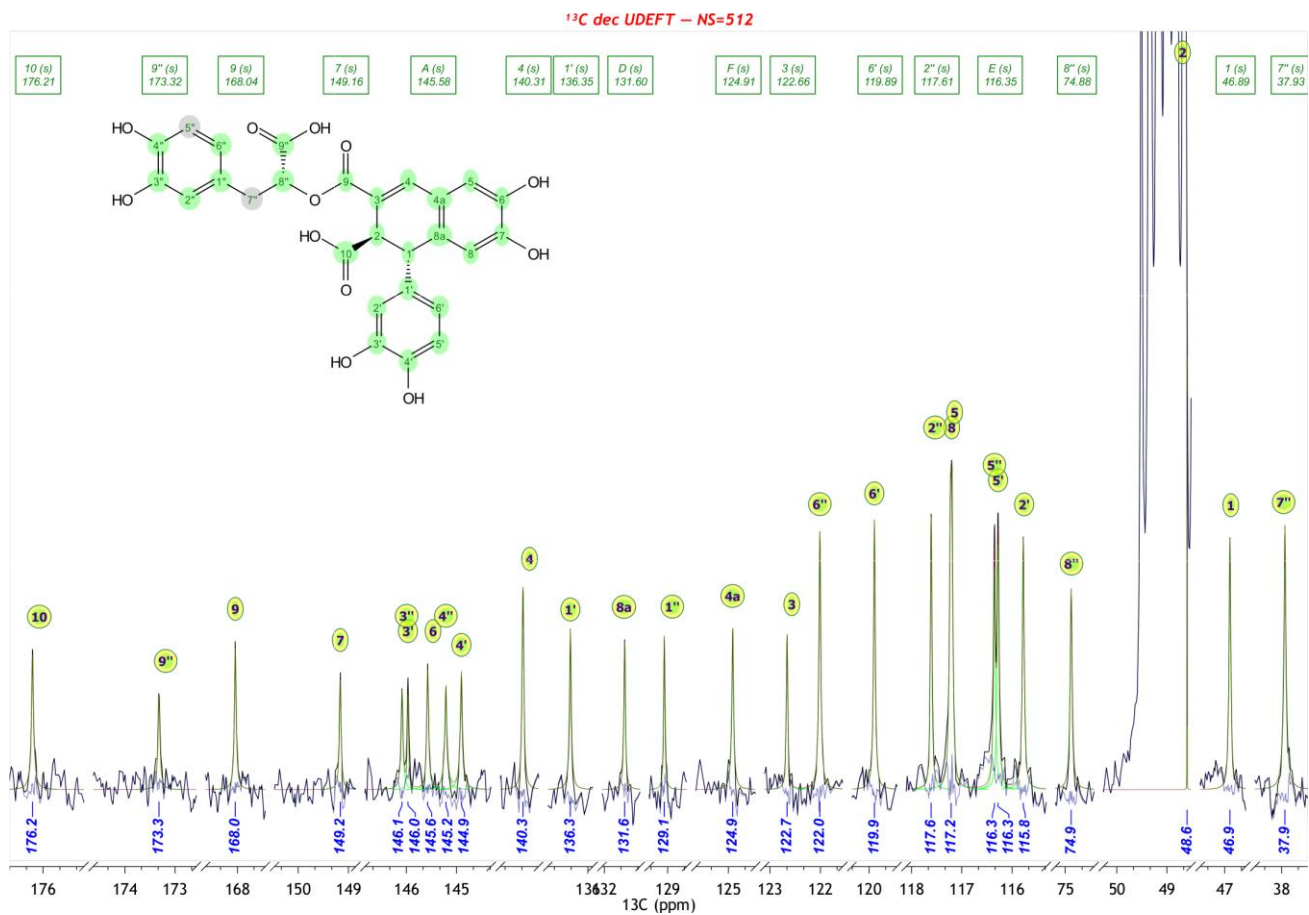


Figure 35S. ¹³C DEPTQ NMR spectrum of compound 18

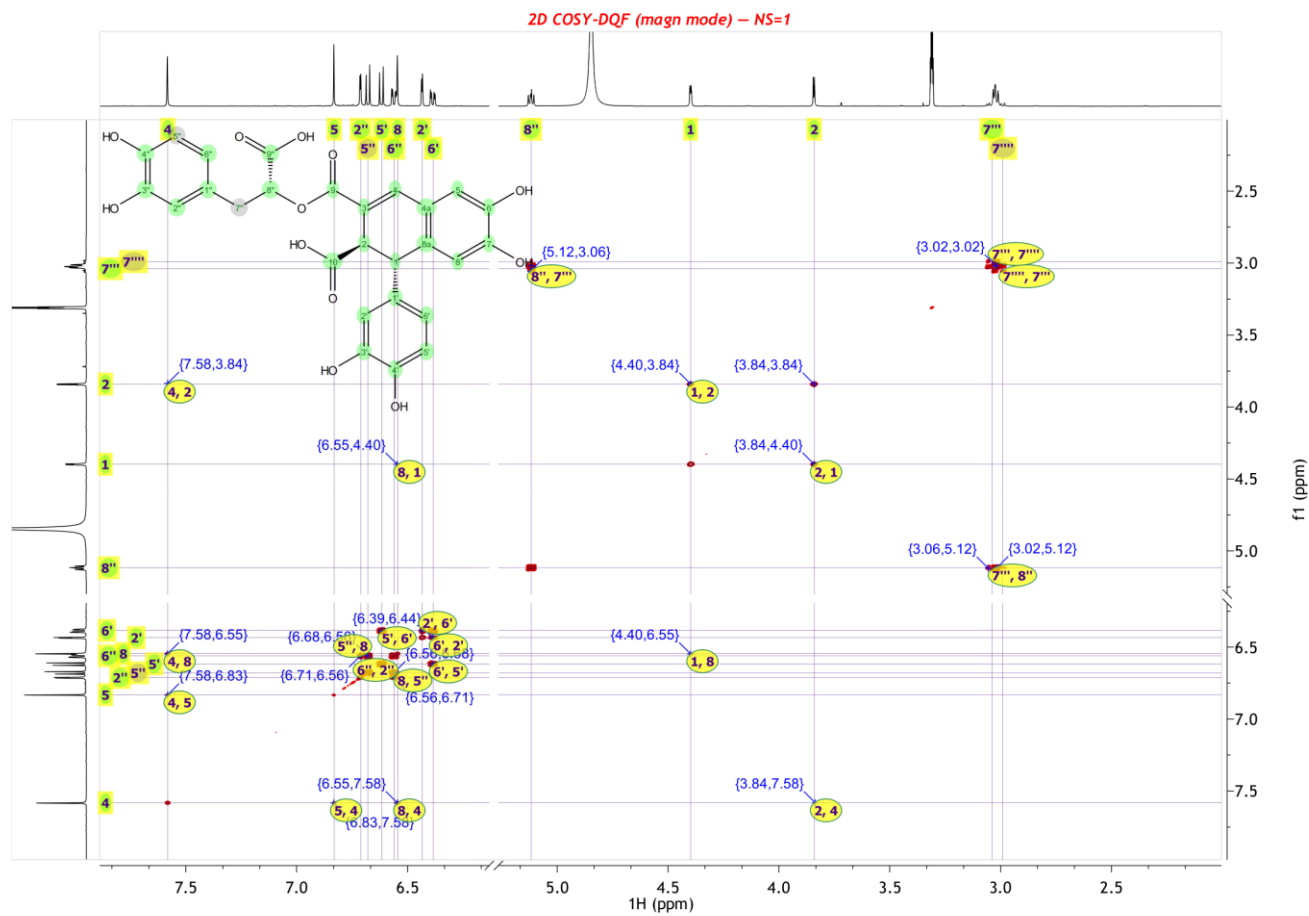


Figure 36S. ¹H-¹H COSY NMR spectrum of compound 18

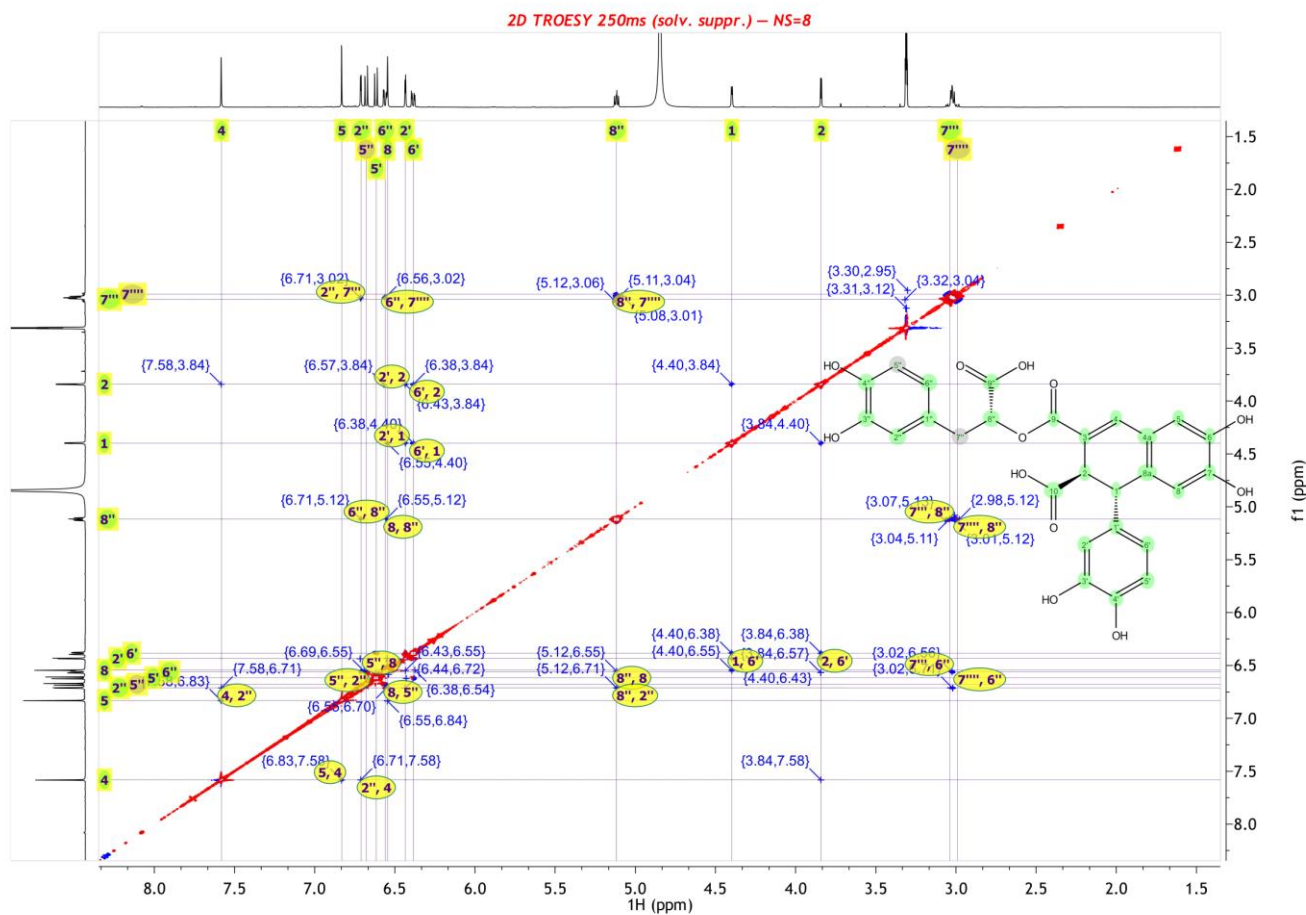


Figure 37S. ^1H - ^1H TROESY (250 ms) NMR spectrum of compound 18

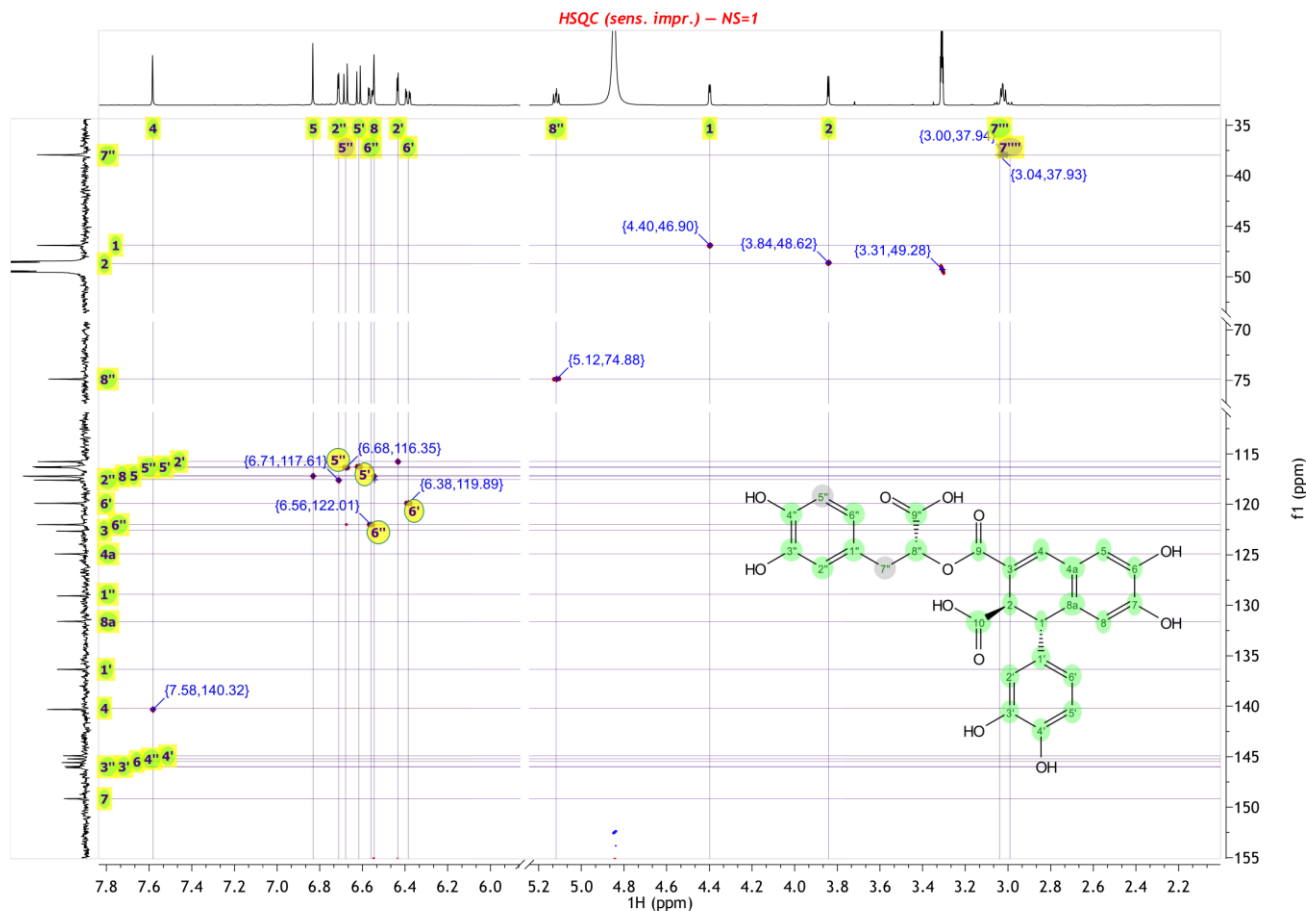


Figure 38S. ^1H - ^{13}C HSQC NMR spectrum of compound 18

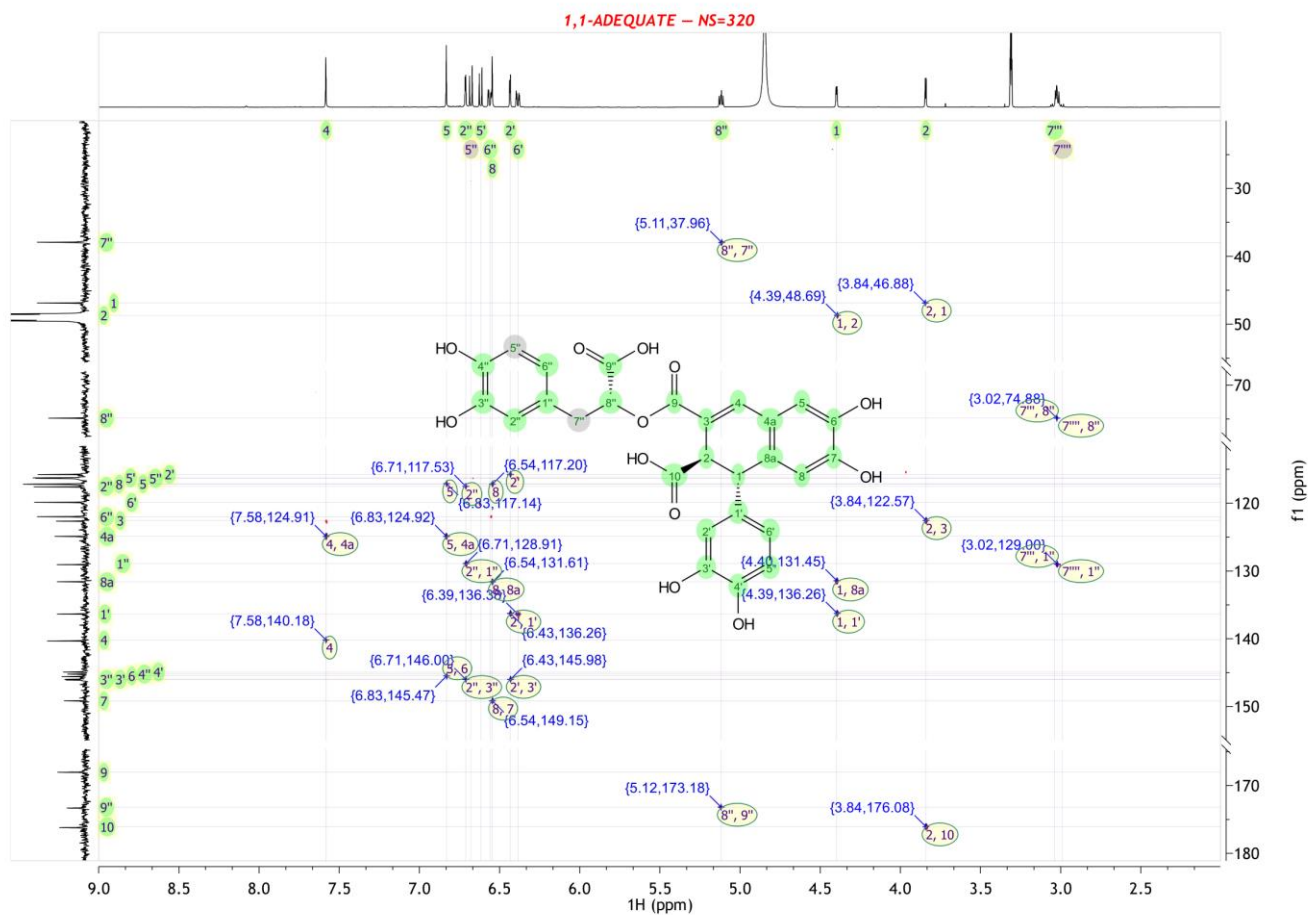


Figure 39S. ^1H - ^{13}C 1,1-ADEQUATE NMR spectrum of compound 18

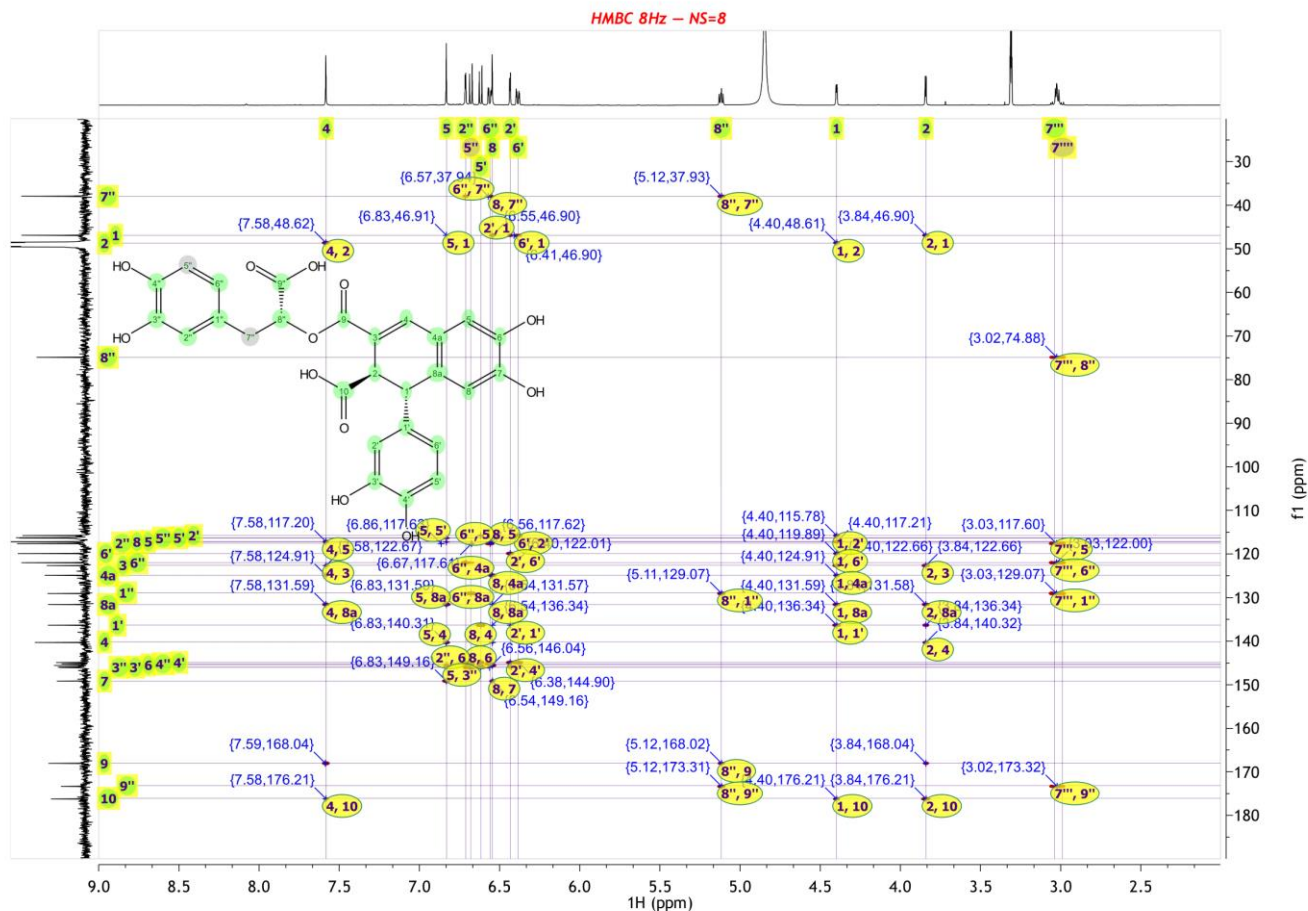
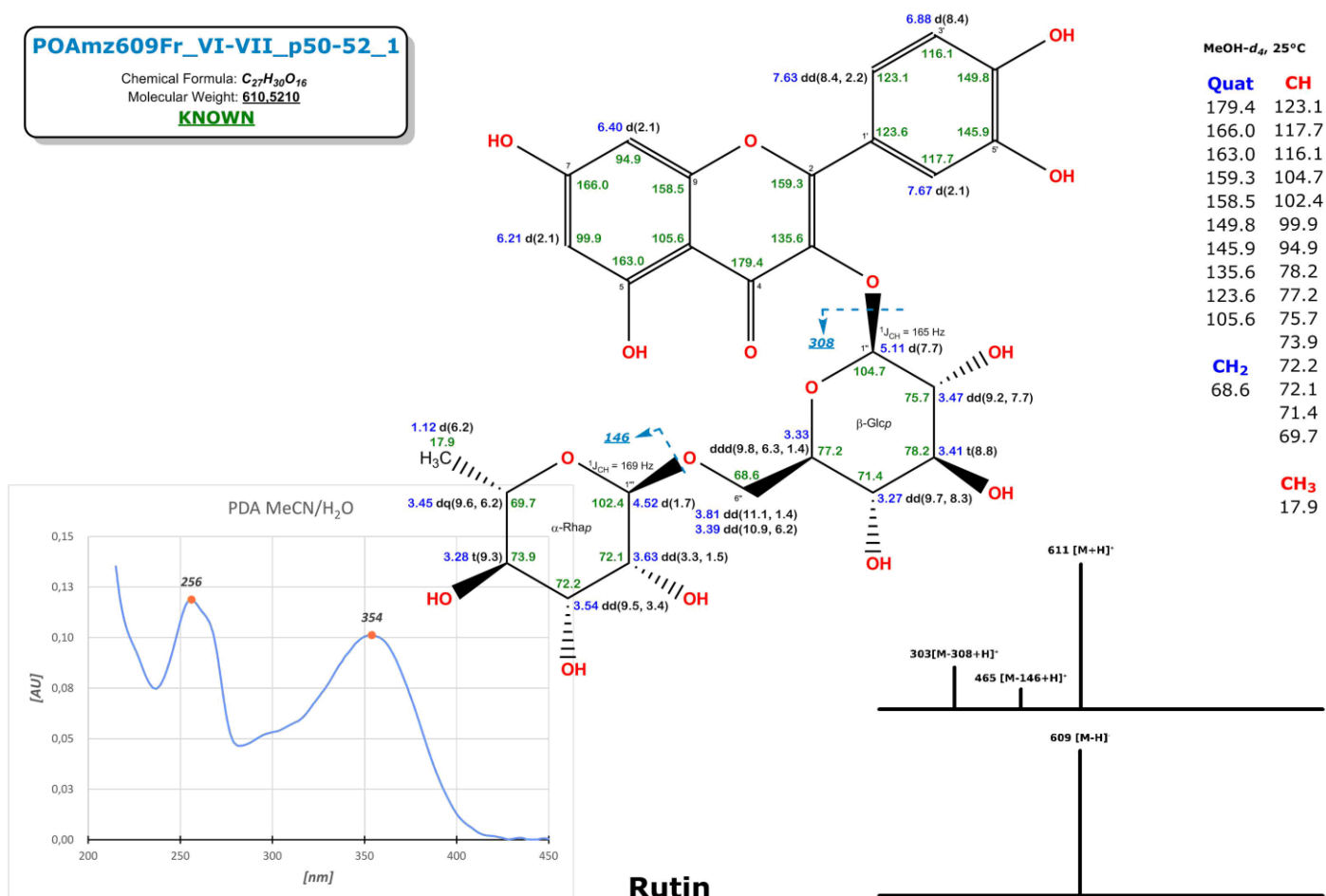


Figure 40S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 18

POAmz609Fr_VI-VII_p50-52_1

Chemical Formula: $C_{27}H_{30}O_{16}$
Molecular Weight: **610.5210**

KNOWN



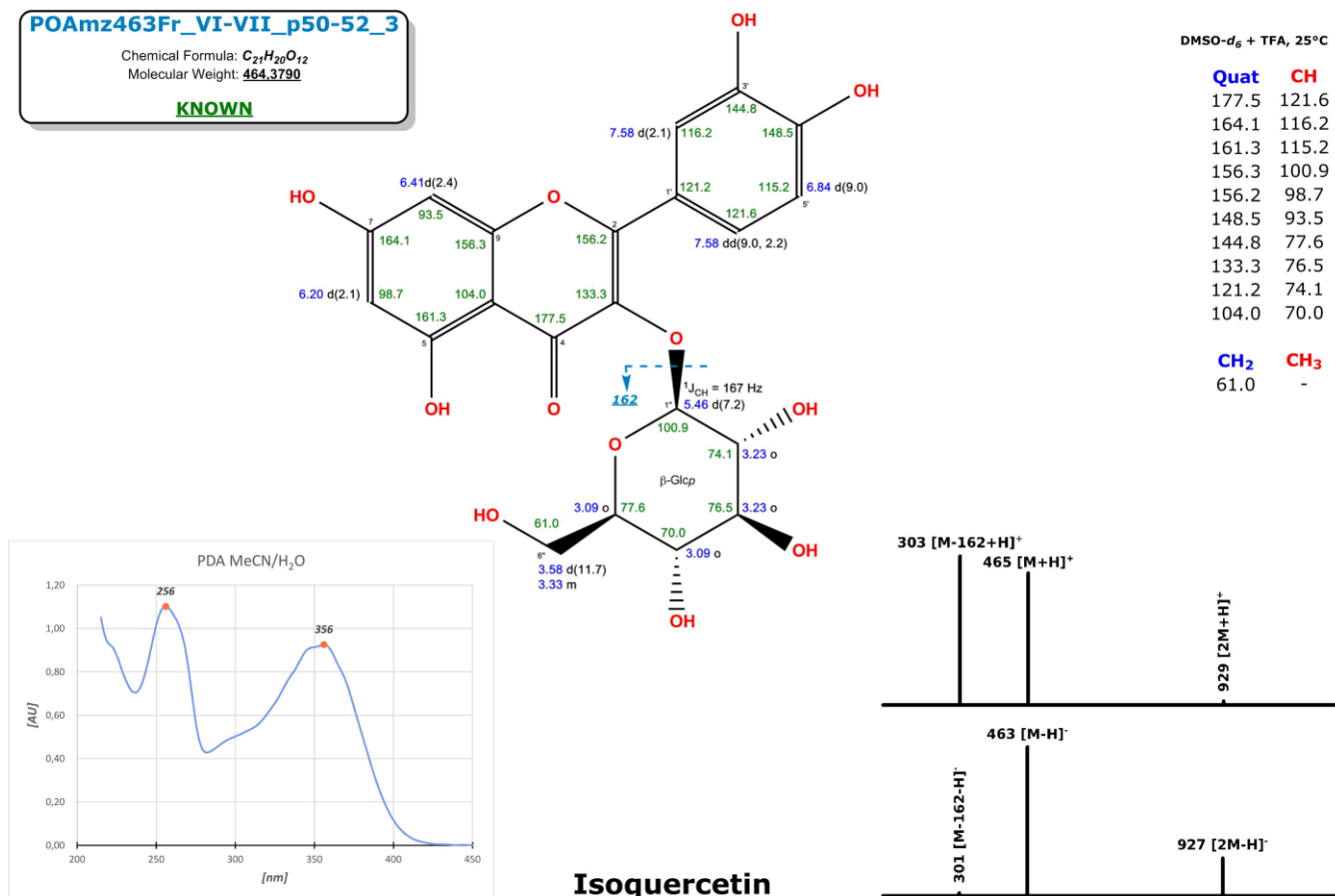
Rutin

Figure 41S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 19 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/H₂O

POAmz463Fr_VI-VII_p50-52_3

Chemical Formula: $C_{21}H_{20}O_{12}$
Molecular Weight: **464.3790**

KNOWN



Isoquercetin

Figure 42S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 21 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/H₂O

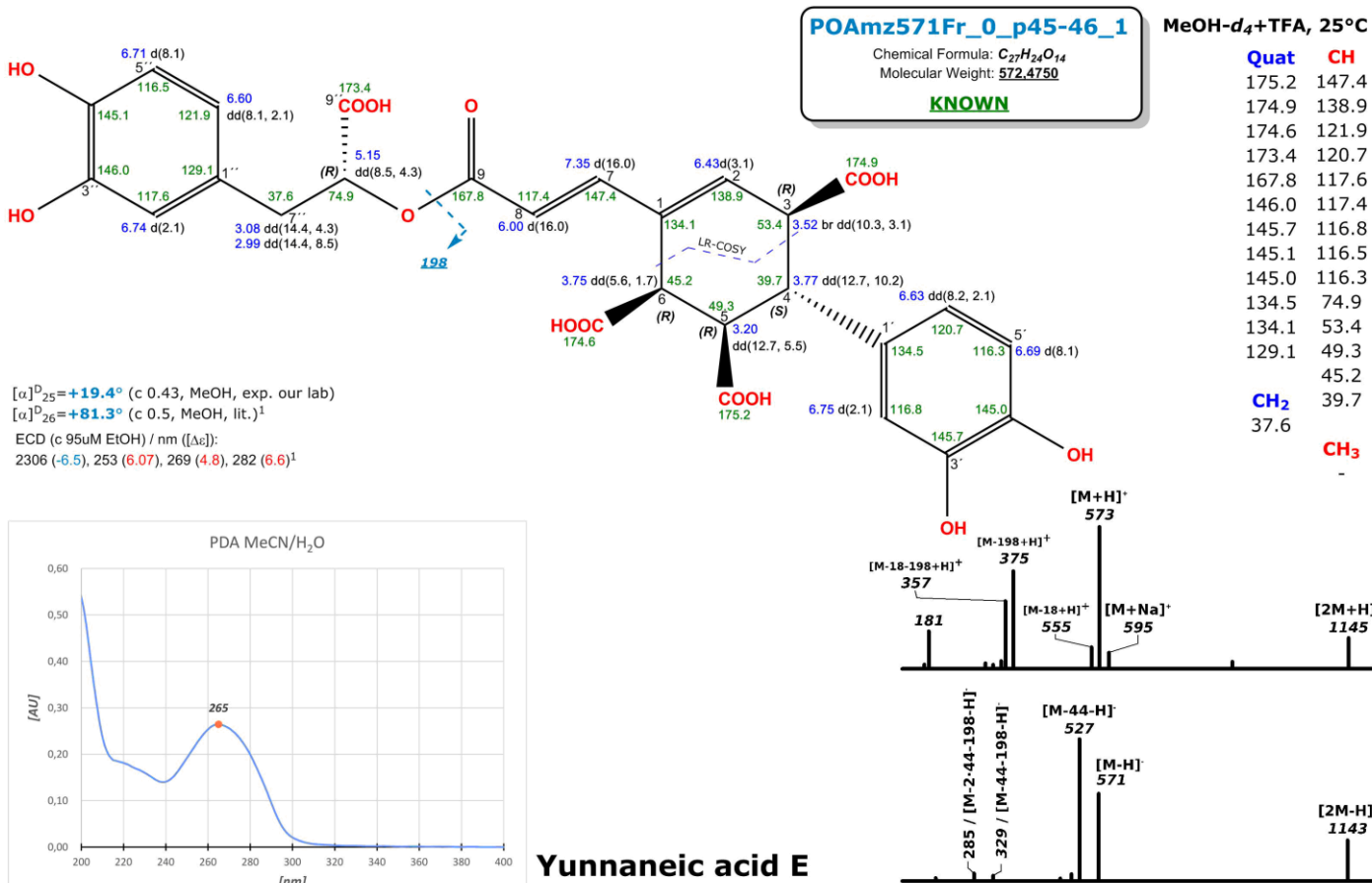


Figure 43S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 22 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O

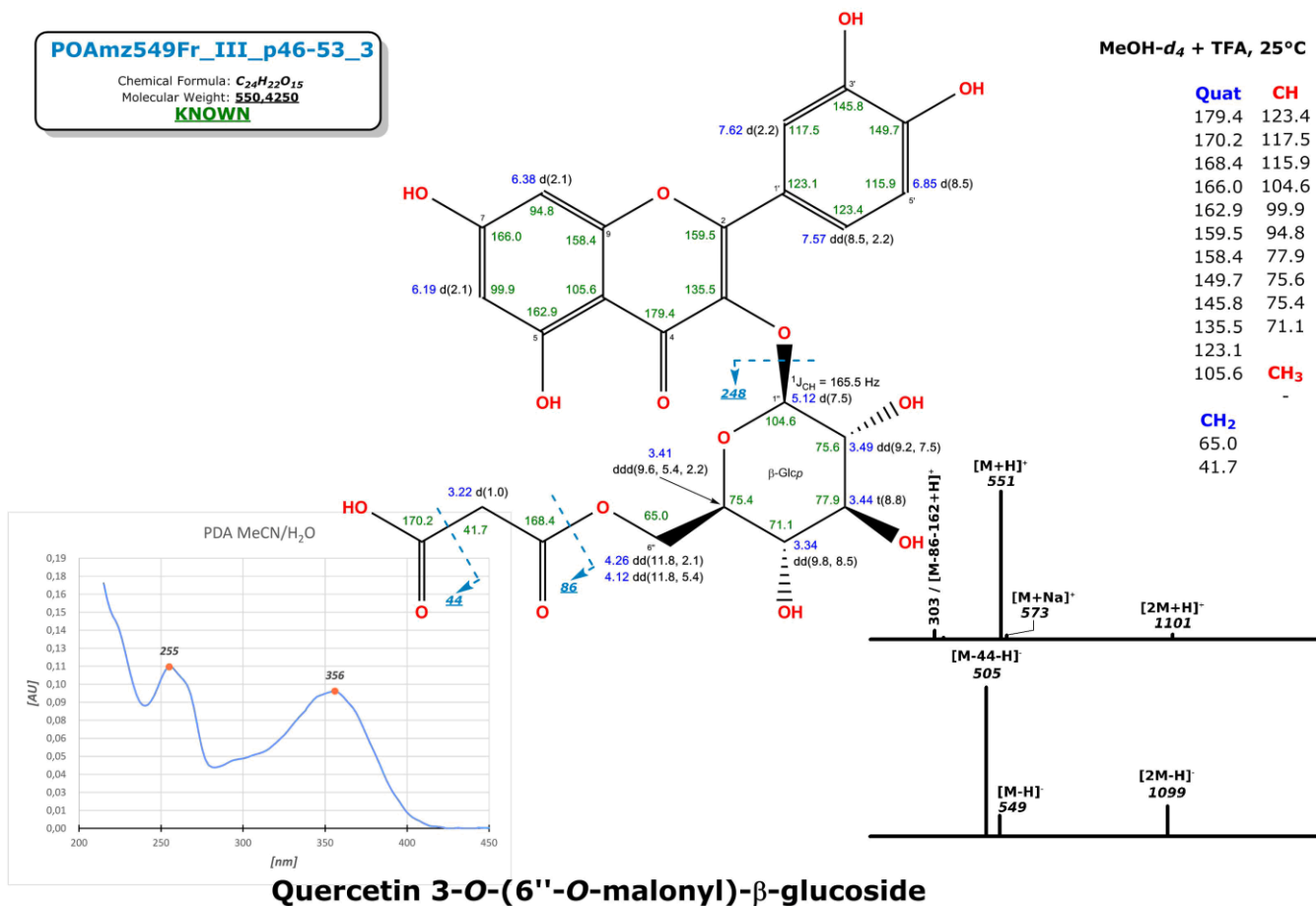
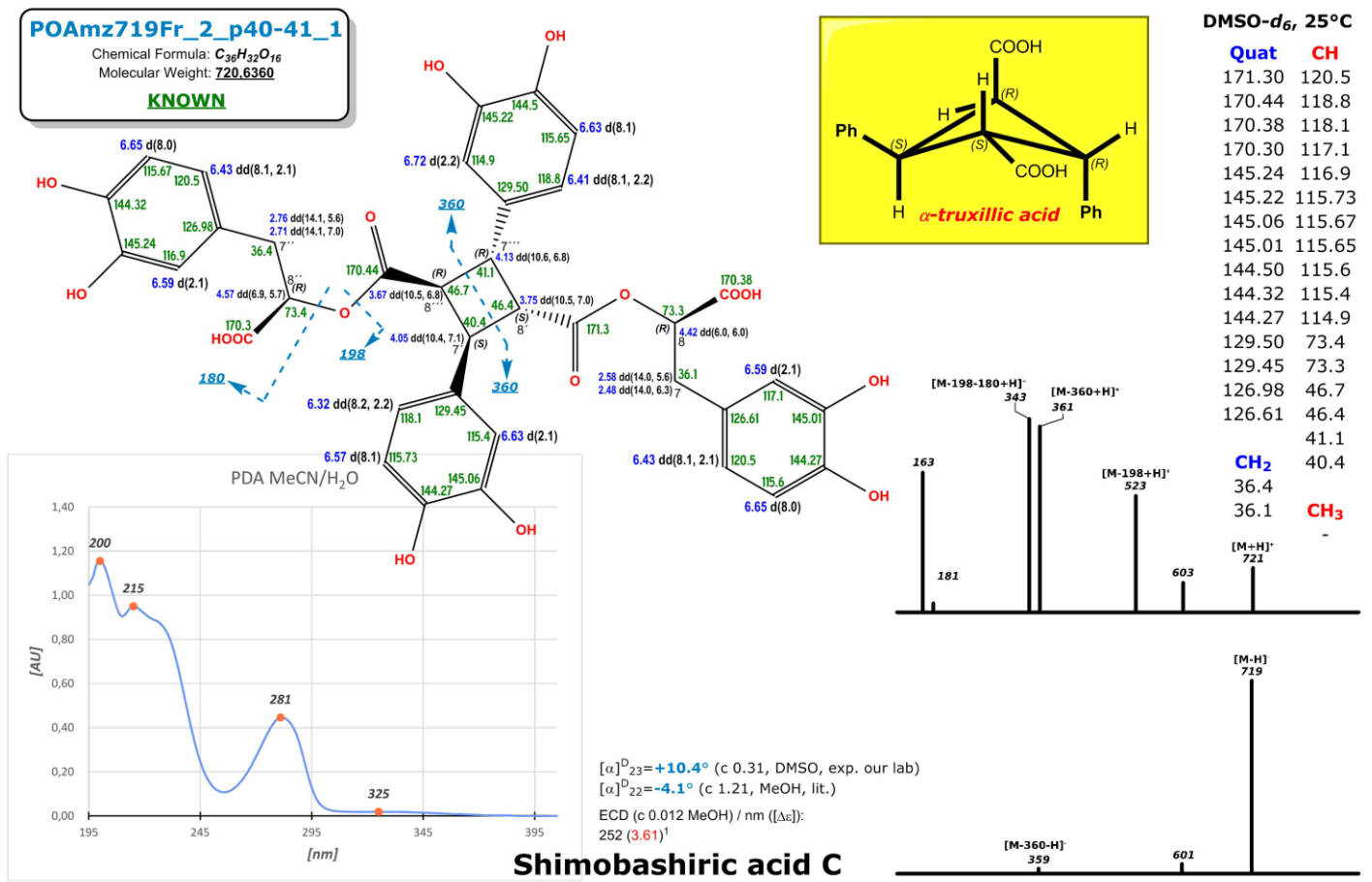
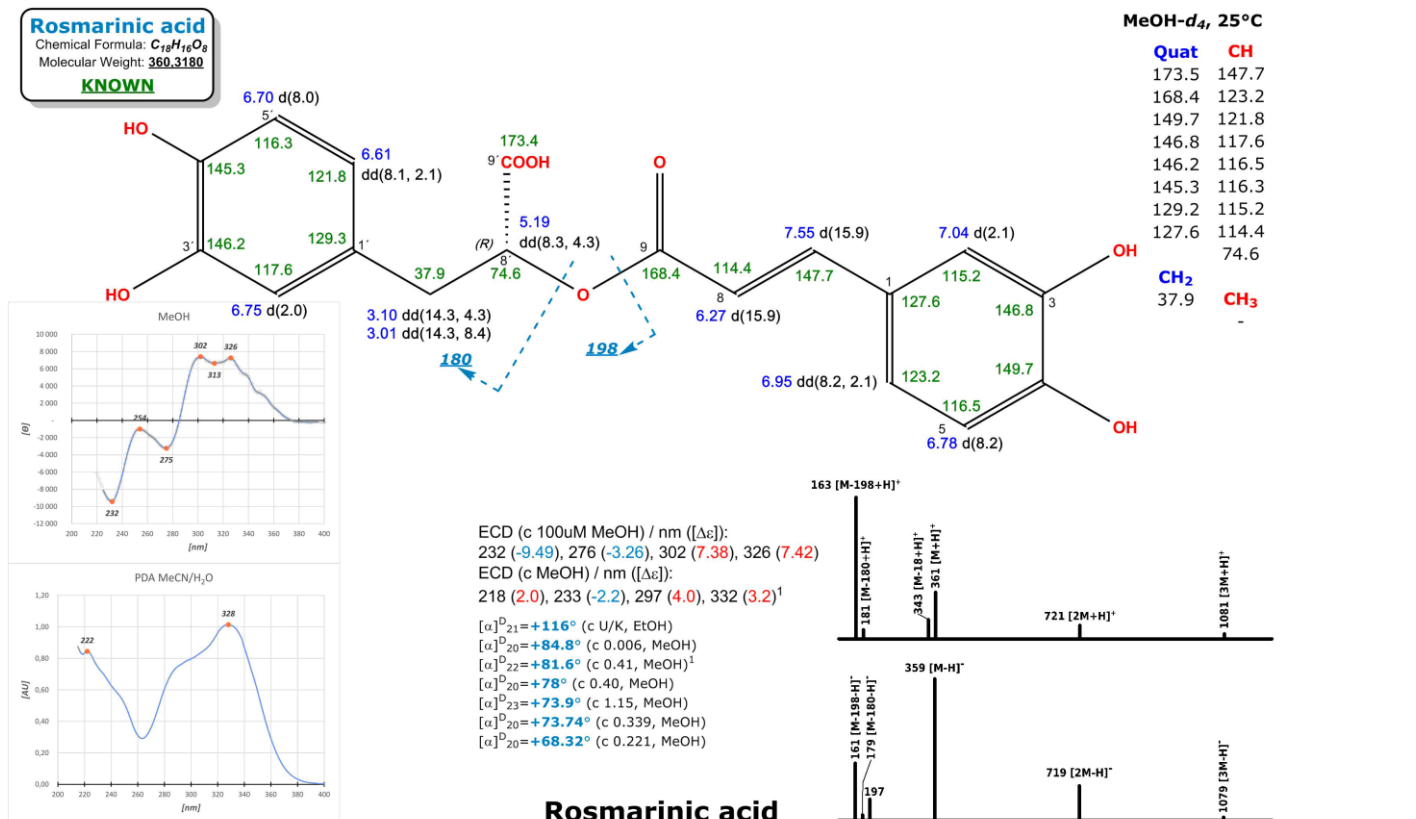


Figure 44S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 23 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O



1. Murata, T., Miyase, T., Yoshizaki, F., 2012. Hyaluronidase Inhibitors from Keiskeia japonica. Chem. Pharm. Bull. (Tokyo). 60, 121–128. doi:10.1248/cpb.60.121
 2. Chen, Y.-S., Yu, H.-M., Shie, J.-J., Cheng, T.-J.R., Wu, C.-Y., Fang, J.-M., Wong, C.-H., 2014. Chemical constituents of Plectranthus amboinicus and the synthetic analogs possessing anti-inflammatory activity. Bioorg. Med. Chem. 22, 1766–1772. doi:10.1016/j.bmc.2014.01.009



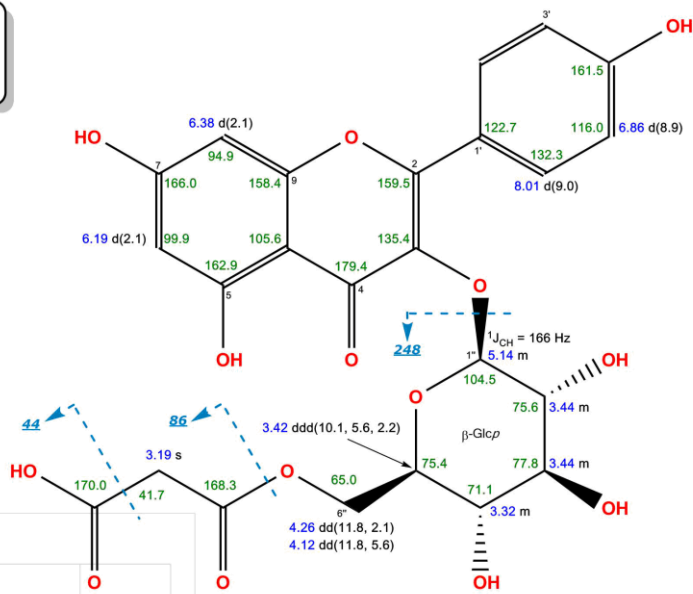
1. Dapkevicius, A., van Beek, T.A., Lelyveld, G.P., van Veldhuizen, A., de Groot, A., Linssen, J.P.H., Venskutonis, R., 2002. Isolation and Structure Elucidation of Radical Scavengers from Thymus vulgaris Leaves. J. Nat. Prod. 65, 892–896. doi:10.1021/np01063j

POAmz533Fr_II_p56-57_2

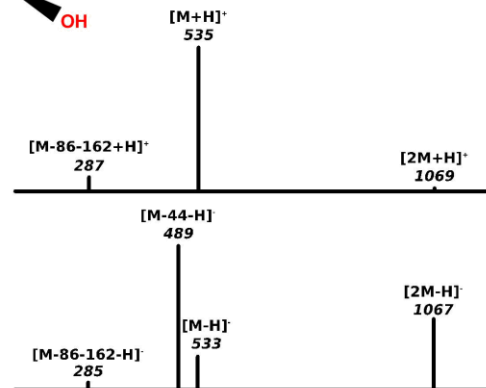
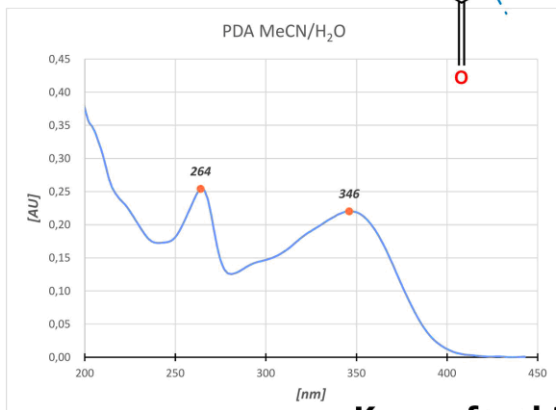
Chemical Formula: $C_{24}H_{22}O_{14}$
Molecular Weight: 534.4260

KNOWN

MeOH- d_4 +TFA, 25°C



Quat	CH
179.4	132.3
170.0	116.0
168.3	104.5
166.0	99.9
162.9	94.9
161.5	77.8
159.5	75.6
158.4	75.4
135.4	71.1
122.7	
105.6	CH ₃
	-
	CH ₂
65.0	
41.7	



Kaempferol 3-O-(6''-O-malonyl)-β-glucoside

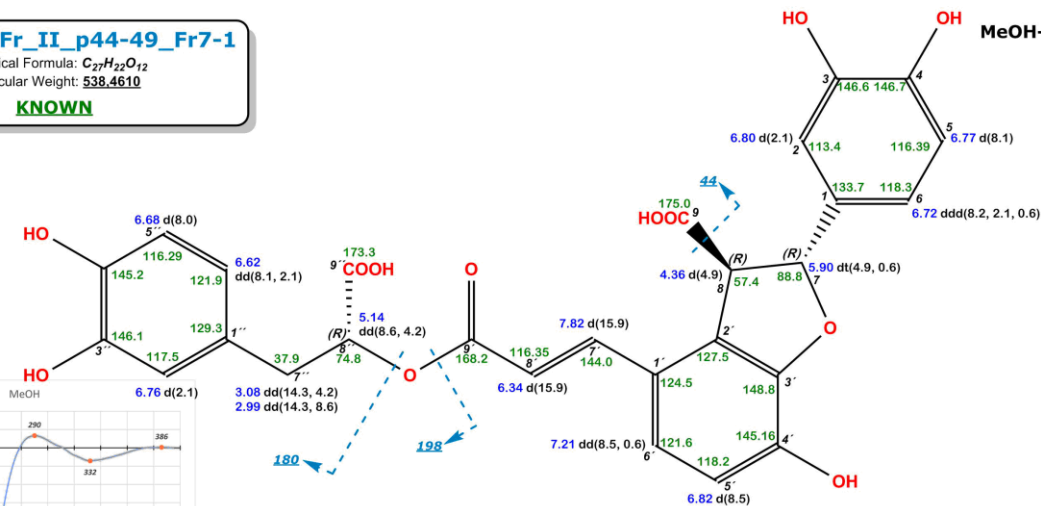
Figure 49S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 28 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O

POAmz537Fr_II_p44-49_Fr7-1

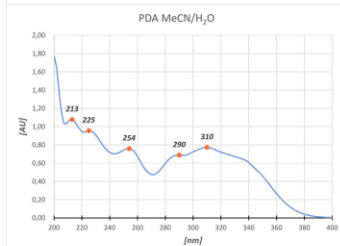
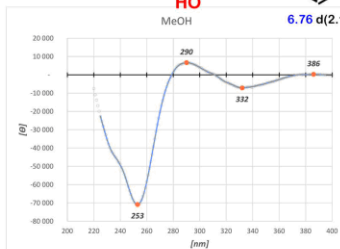
Chemical Formula: $C_{27}H_{22}O_{12}$
Molecular Weight: 538.4610

KNOWN

MeOH- d_4 +TFA, 25°C

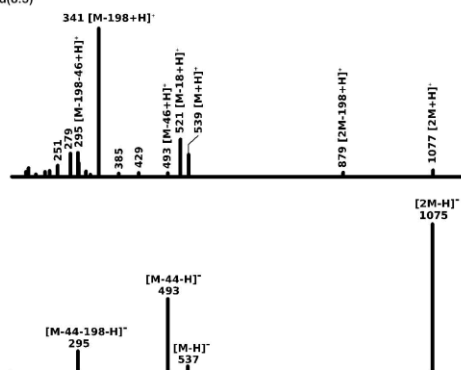


Quat	CH
175.0	144.0
173.3	121.9
168.2	121.6
148.8	118.3
146.7	118.2
146.6	117.5
145.20	116.39
145.16	116.35
133.7	116.29
129.3	113.4
127.5	88.8
124.5	74.8
57.4	
	CH ₂
37.9	
	CH ₃
	-



$[\alpha]_{23}^D = -120.9^\circ$ (c 0.78, MeOH, exp. our lab)
 $[\alpha]_{23}^D = -86.2^\circ$ (c unk, MeOH, lit.)
ECD (c 0.05 MeOH) / nm ($[\Delta\epsilon]$):
230 (-15.98), 252 (-22.77), 288 (1.73), 333 (-1.64)

Monardic acid A



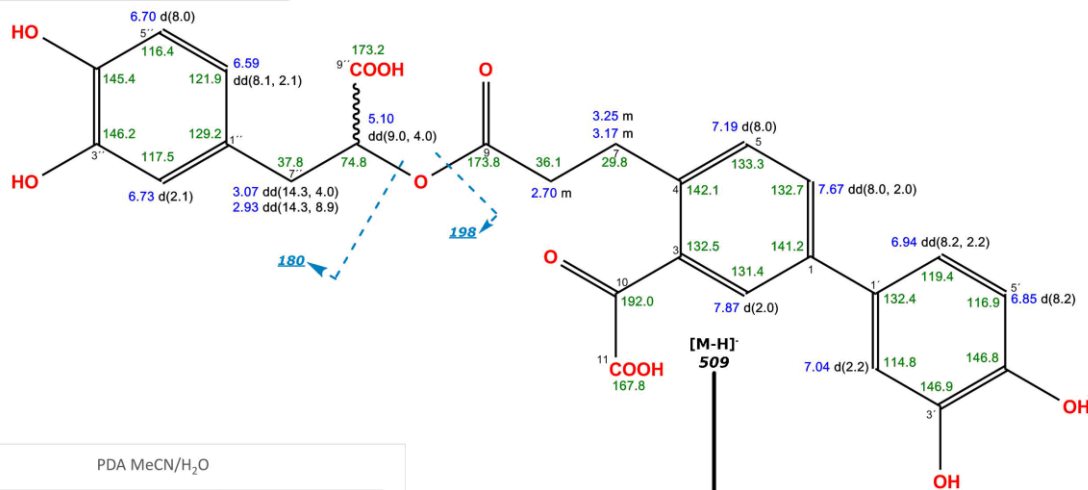
1. Murata, T., Oyama, K., Fujiyama, M., Oobayashi, B., Umehara, K., Miyase, T., Yoshizaki, F., 2013. Diastereomers of lithospermic acid and lithospermic acid B from *Monarda fistulosa* and *Lithospermum erythrorhizon*. *Fitoterapia* 91, 51–59. doi:10.1016/j.fitote.2013.08.009

Figure 50S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 29 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O ; ECD spectrum in MeOH

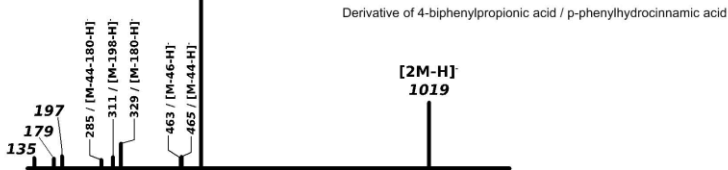
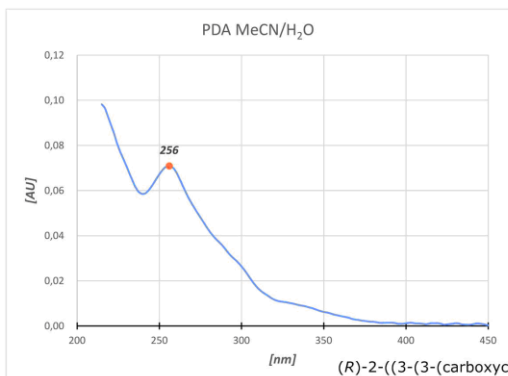
POAmz509Fr_II_p44-49_Fr5
 Chemical Formula: $C_{26}H_{22}O_{11}$
 Molecular Weight: 510.4510
NEW!

MeOH- d_4 +TFA, 25°C

Quat	CH
192.0	133.3
173.8	132.7
173.2	131.4
167.8	121.9
146.9	114.4
146.8	117.5
146.2	116.9
145.4	116.4
142.1	114.8
141.2	74.8
132.5	
132.4	CH ₃
129.2	-



CH ₂
37.8
36.1
29.8



Yunnaneic acid E-1

(R)-2-((3-(3-(carboxycarbonyl)-3',4'-dihydroxy-[1,1'-biphenyl]-4-yl)propanoyl)oxy)-3-(3,4-dihydroxyphenyl)propanoic acid

Figure 51S. ¹H (500 MHz) and ¹³C (125 MHz) NMR data of compound 30 in CD₃OD, 25°C; on-line PDA UV spectrum in MeCN/H₂O

¹H NS16 CD3OD+TFA (0.1%) 25°C - NS=16

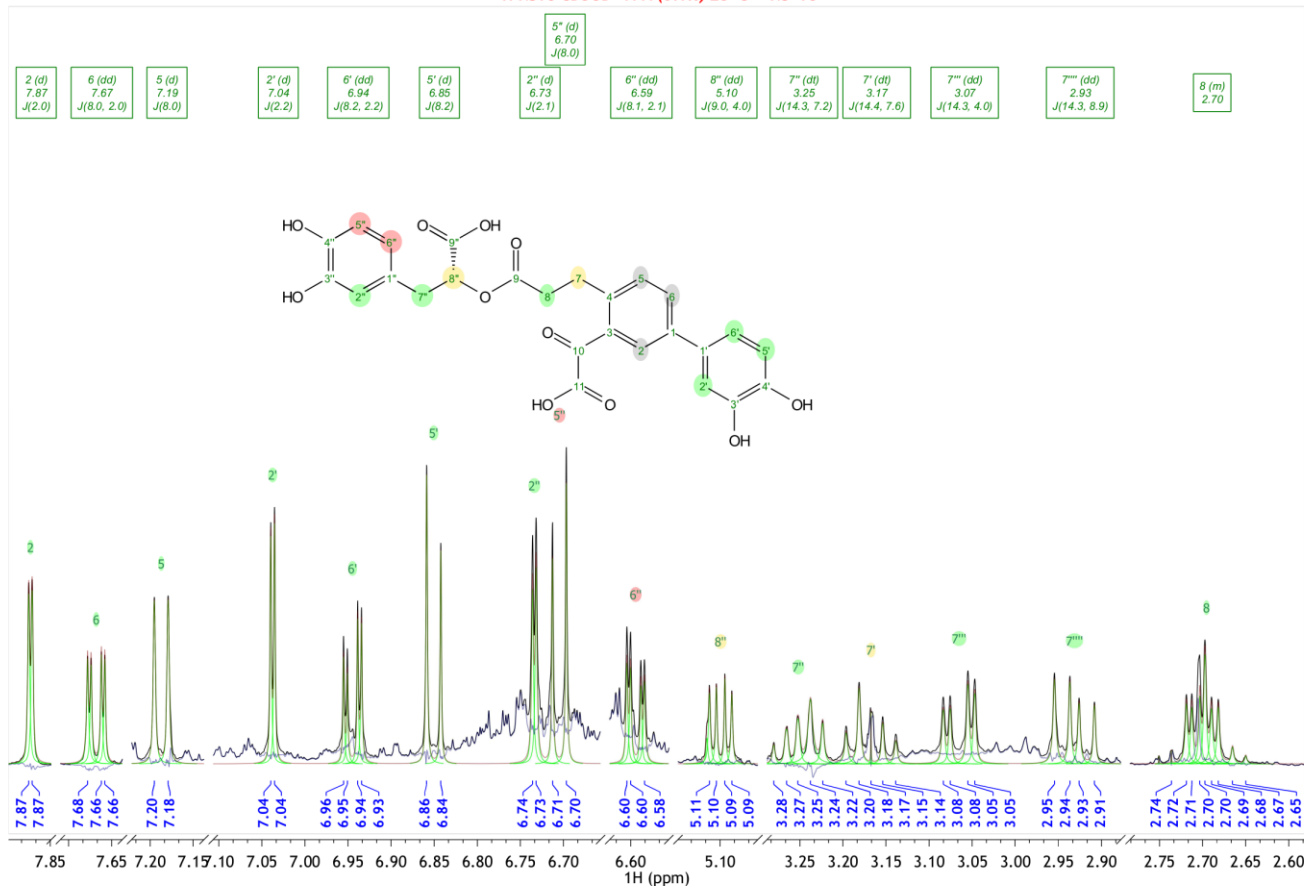


Figure 52S. ¹H NMR spectrum of compound 30

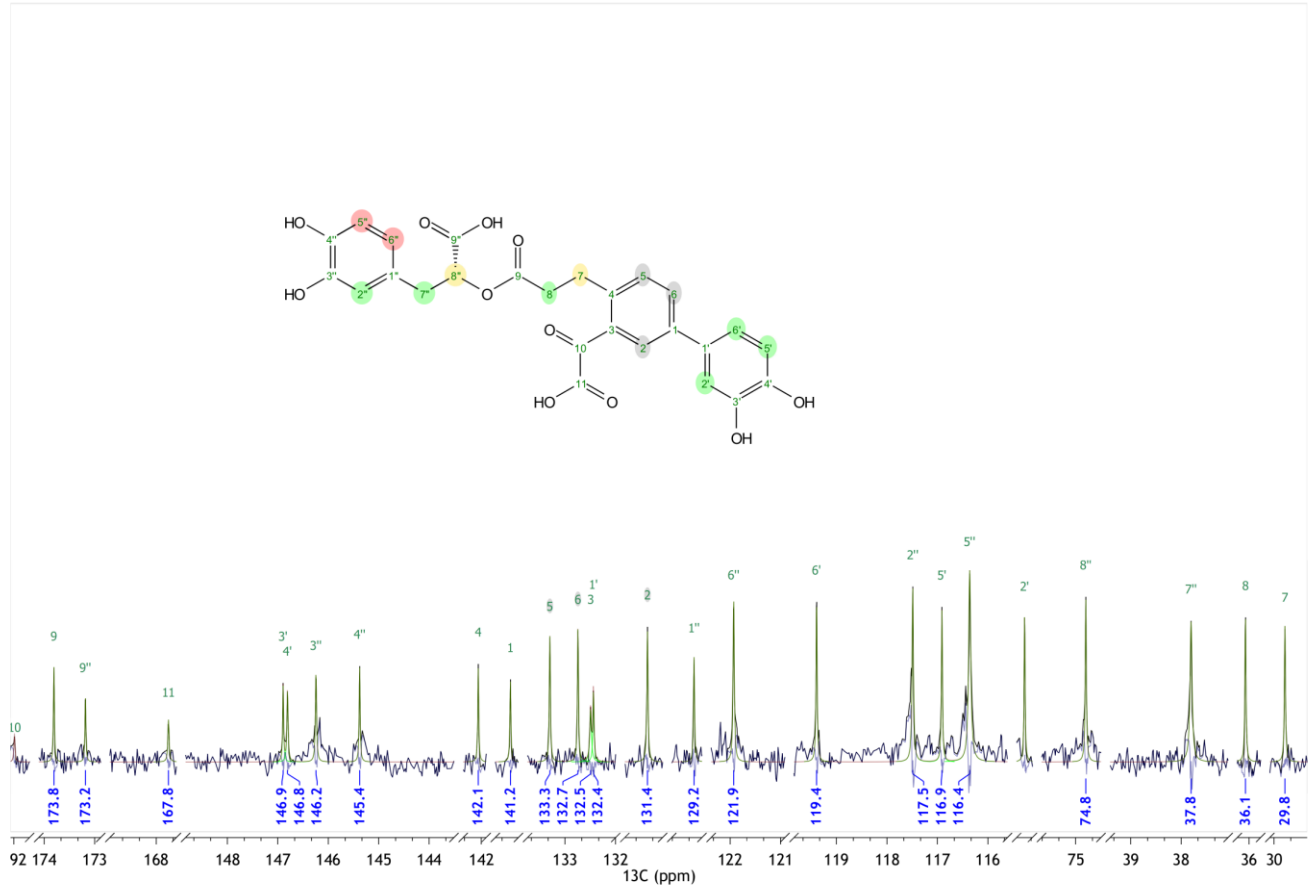


Figure 53S. ¹³C DEPTQ NMR spectrum of compound 30

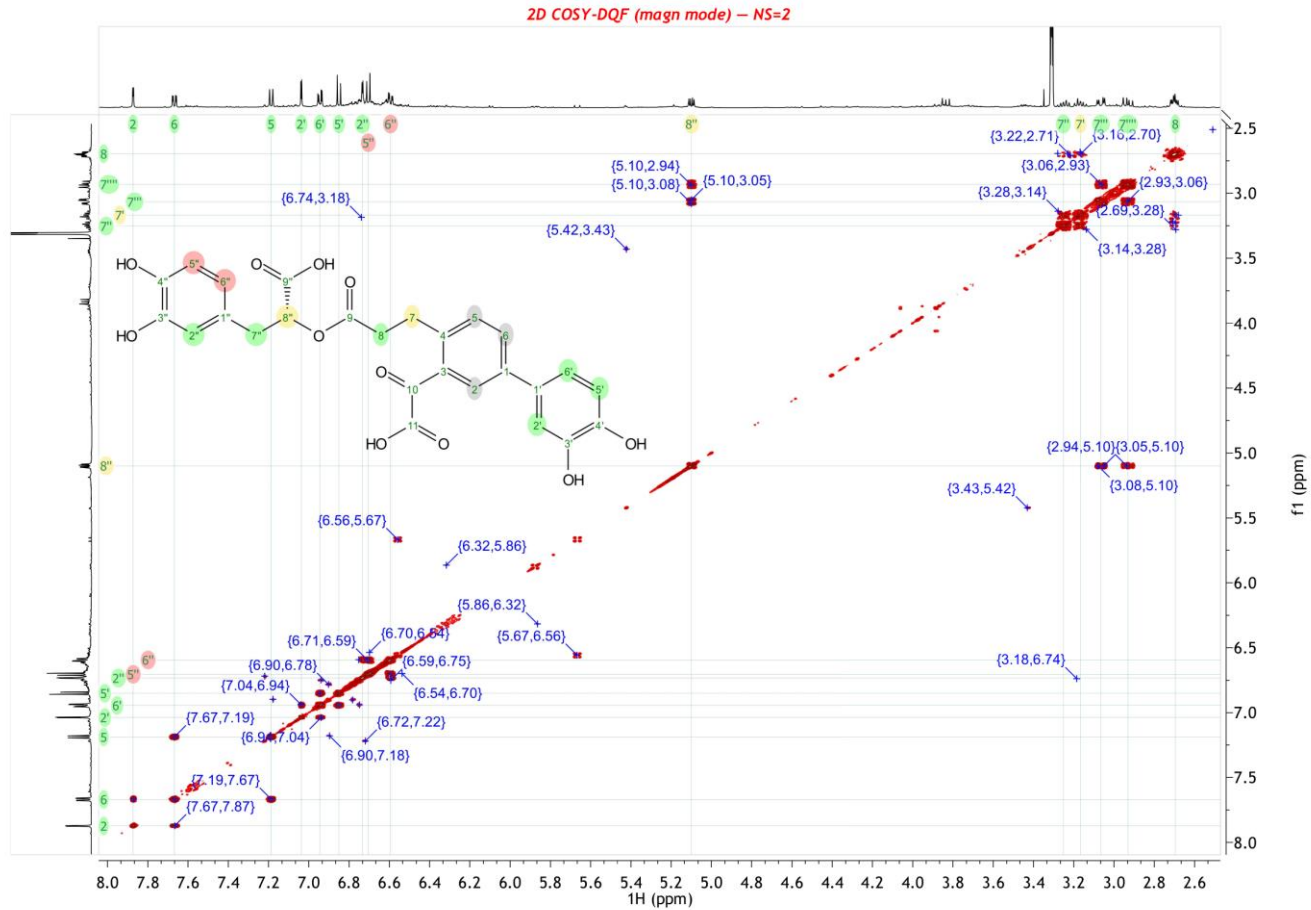


Figure 54S. ¹H-¹H COSY NMR spectrum of compound 30

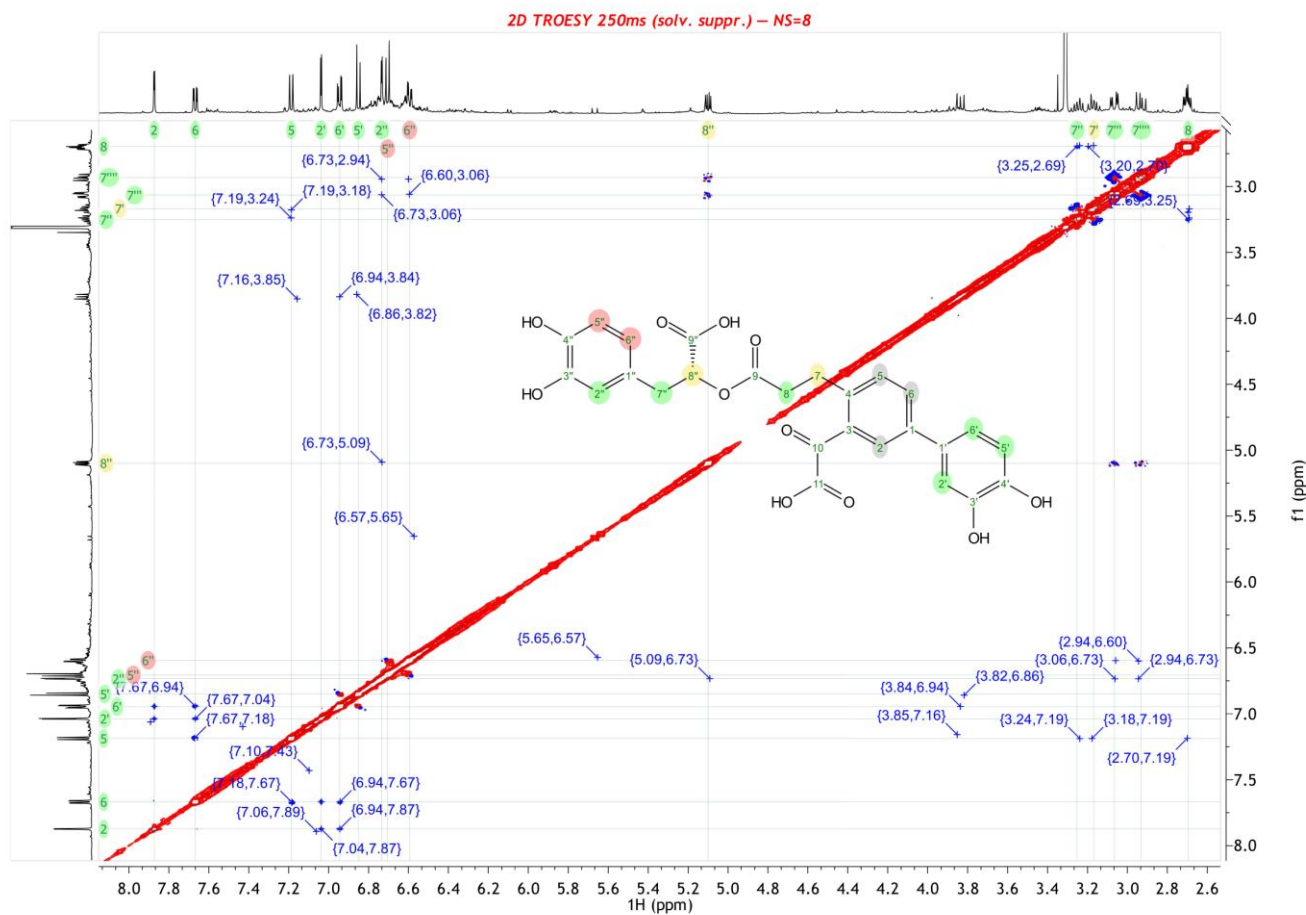


Figure 55S. ^1H - ^1H TROESY (250 ms) NMR spectrum of compound 30

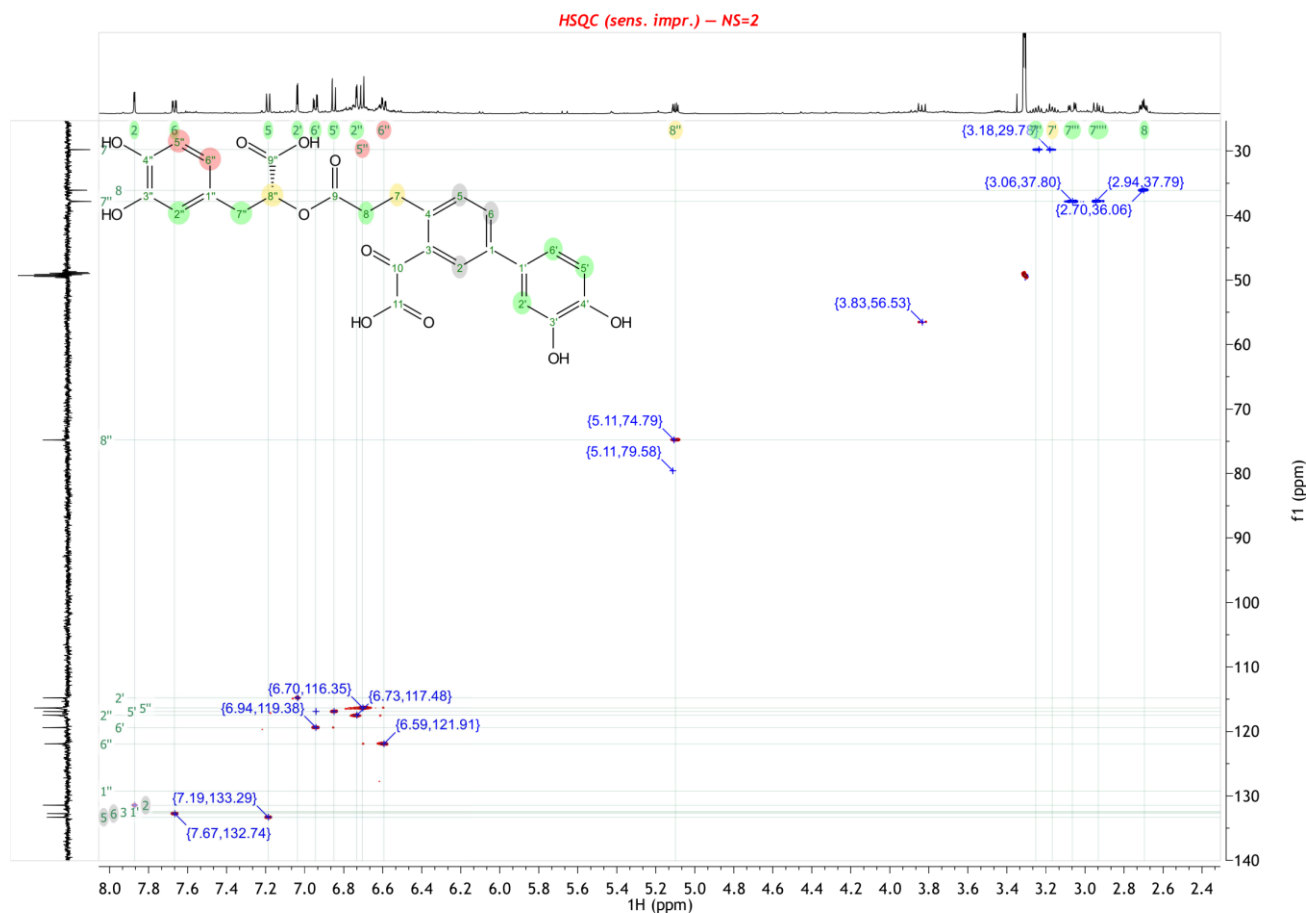


Figure 56S. ^1H - ^{13}C HSQC NMR spectrum of compound 30

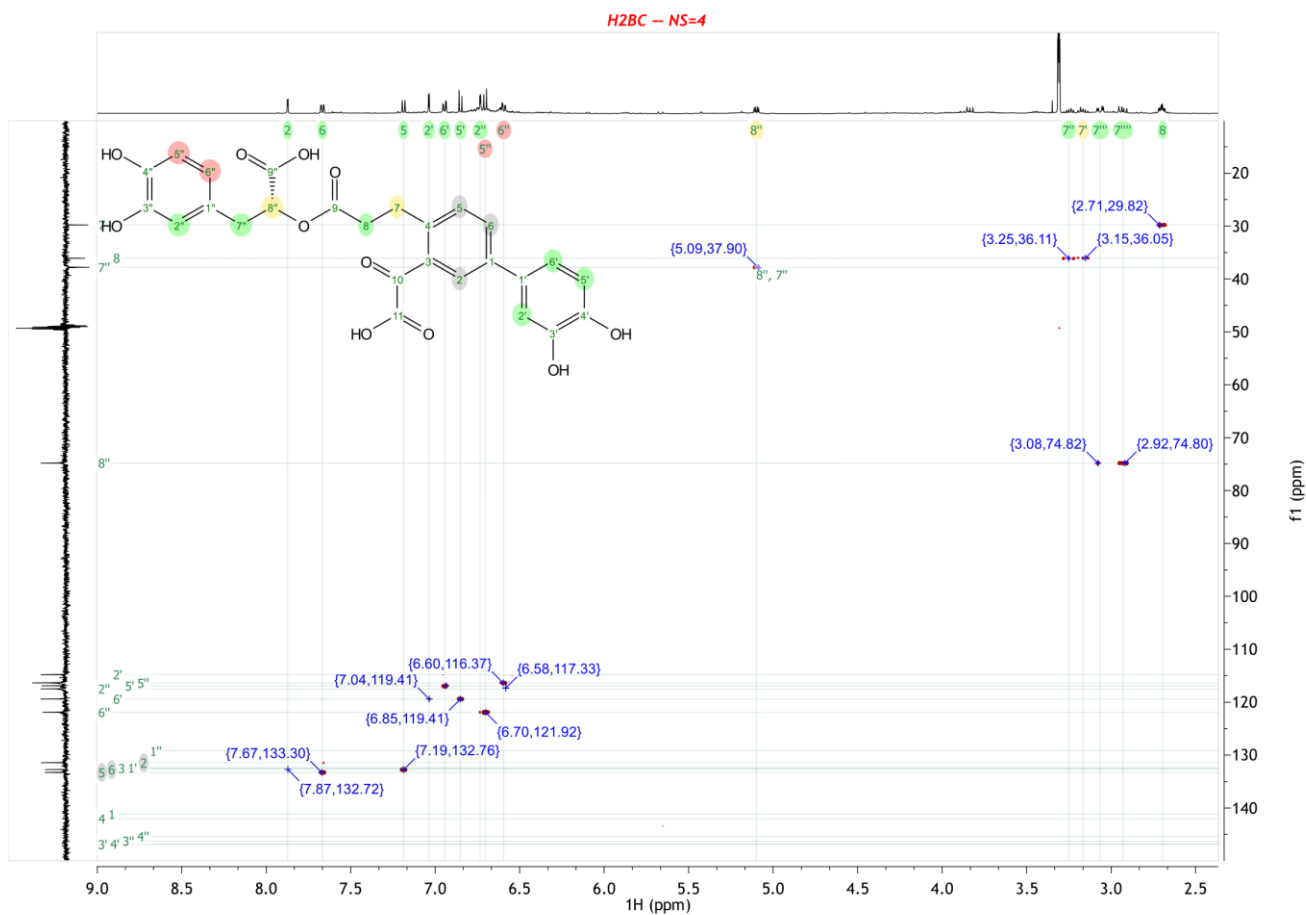


Figure 57S. ^1H - ^{13}C H2BC NMR spectrum of compound 30

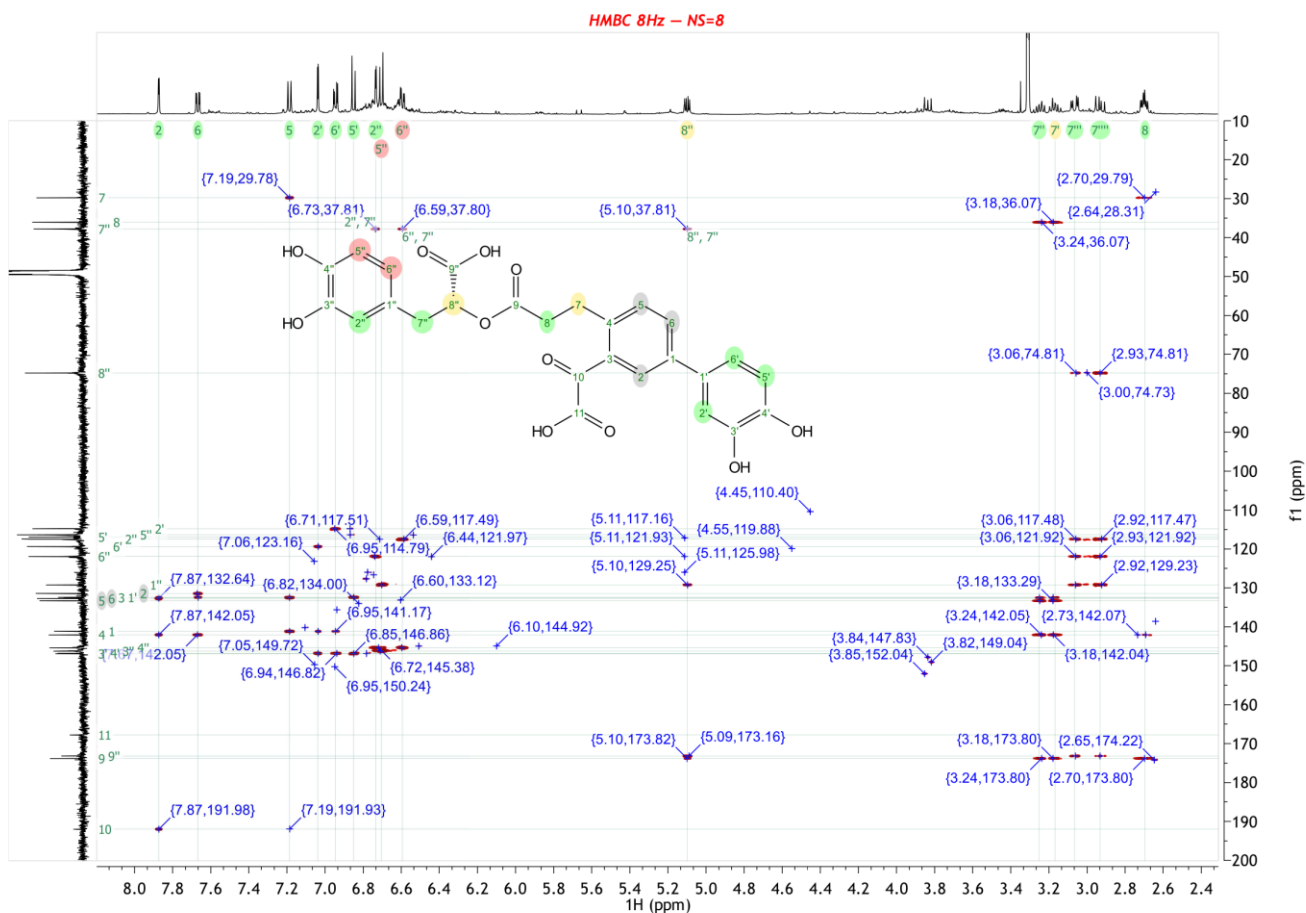


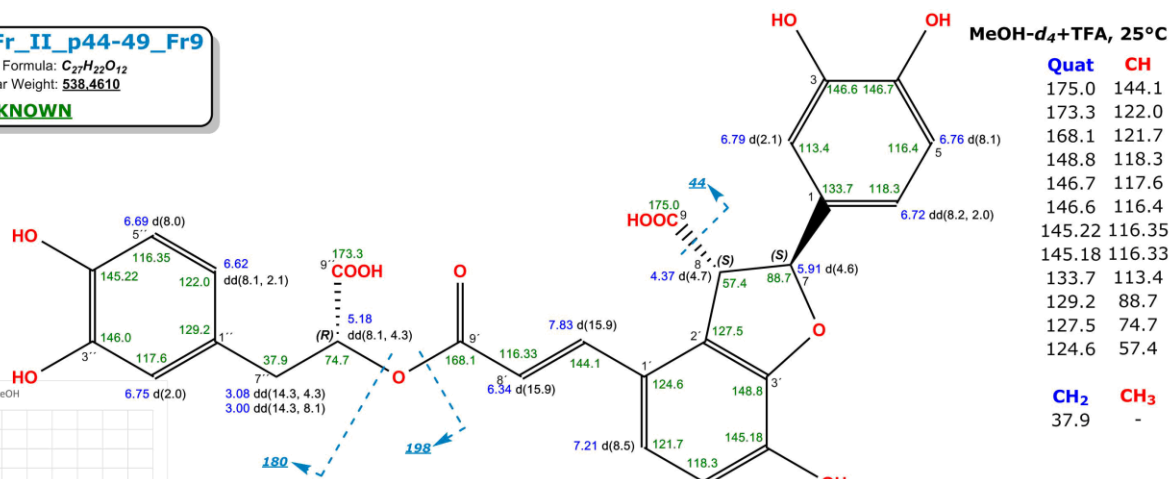
Figure 58S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 30

POAmz537Fr_II_p44-49_Fr9

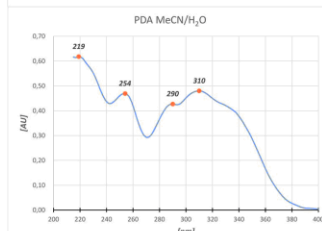
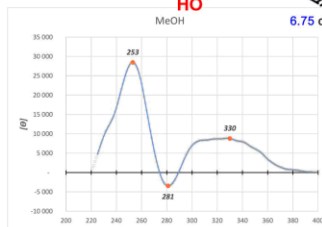
Chemical Formula: $C_{27}H_{22}O_{12}$
Molecular Weight: **538.4610**

KNOWN

MeOH- d_4 +TFA, 25°C



Quat	CH
175.0	144.1
173.3	122.0
168.1	121.7
148.8	118.3
146.7	117.6
146.6	116.4
145.22	116.35
145.18	116.33
133.7	113.4
129.2	88.7
127.5	74.7
124.6	57.4
	CH₂
	CH₃
	37.9



$[\alpha]_{25}^D = +154.9^\circ$ (c 0.90, MeOH, exp. our lab)
 $[\alpha]_D = +78^\circ$
 $[\alpha]_D = +68.3^\circ$
 $[\alpha]_D = +56.5^\circ$
 $[\alpha]_D = +136.9^\circ$ (c unk, MeOH, total synth)¹

(+)-Lithospermic acid A

1. O'Malley, S.J., Tan, K.L., Watzke, A., Bergman, R.G., Ellman, J.A., 2005. Total Synthesis of (+)-Lithospermic Acid by Asymmetric Intramolecular Alkylation via Catalytic C-H Bond Activation. *J. Am. Chem. Soc.* 127, 13496-13497. doi:10.1021/ja052680h
2. Murata, T., Oyama, K., Fujiyama, M., Oobayashi, B., Umehara, K., Miyase, T., Yoshizaki, F., 2013. Diastereomers of lithospermic acid and lithospermic acid B from *Monarda fistulosa* and *Lithospermum erythrorhizon*. *Fitoterapia* 91, 51-59. doi:10.1016/j.fitote.2013.08.009

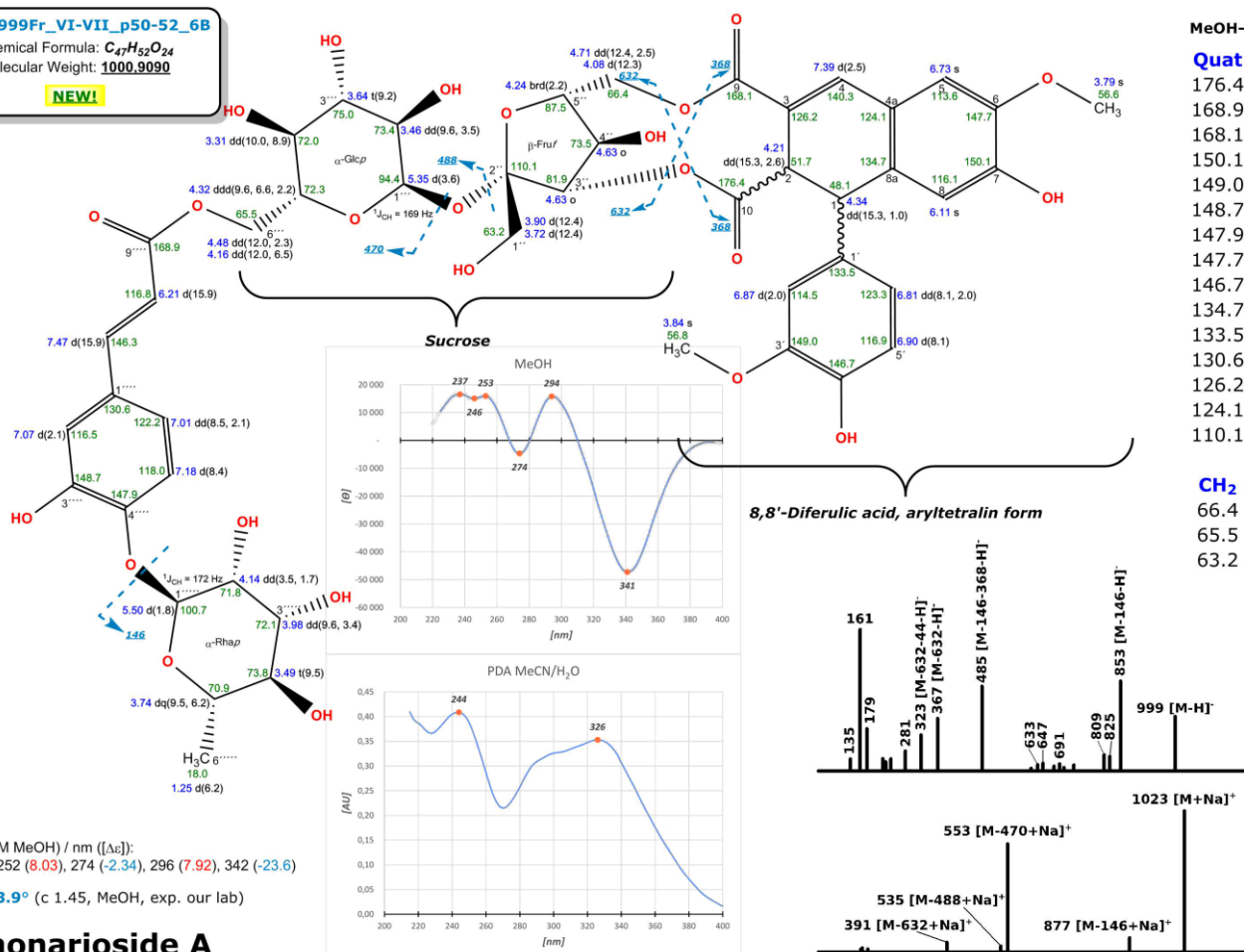
Figure 59S. 1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 31 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O

POAmz999Fr_VI-VII_p50-52_6B

Chemical Formula: $C_{47}H_{52}O_{24}$
Molecular Weight: **1000.9090**

NEW!

MeOH- d_4 , 25°C



Quat	CH
176.4	146.3
168.9	140.3
168.1	123.3
150.1	122.2
149.0	118.0
148.7	116.9
147.9	116.8
147.7	116.5
146.7	116.1
134.7	114.5
133.5	113.6
130.6	100.7
126.2	94.4
124.1	87.5
124.1	87.5
110.1	81.9
	75.0
	CH₂
	73.8
	73.5
	73.4
	72.3
	72.1
	72.0
	71.8
	70.9
	51.7
	48.1
	CH₃
	56.8
	56.6
	18.0

ECD (c 50μM MeOH) / nm ($[\Delta\epsilon]$):
234 (8.38), 252 (8.03), 274 (-2.34), 296 (7.92), 342 (-23.6)

$[\alpha]_{23}^D = -73.9^\circ$ (c 1.45, MeOH, exp. our lab)

Pulmonarioside A

Figure 60S. 1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 32 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O

¹H solv suppr – NS=16

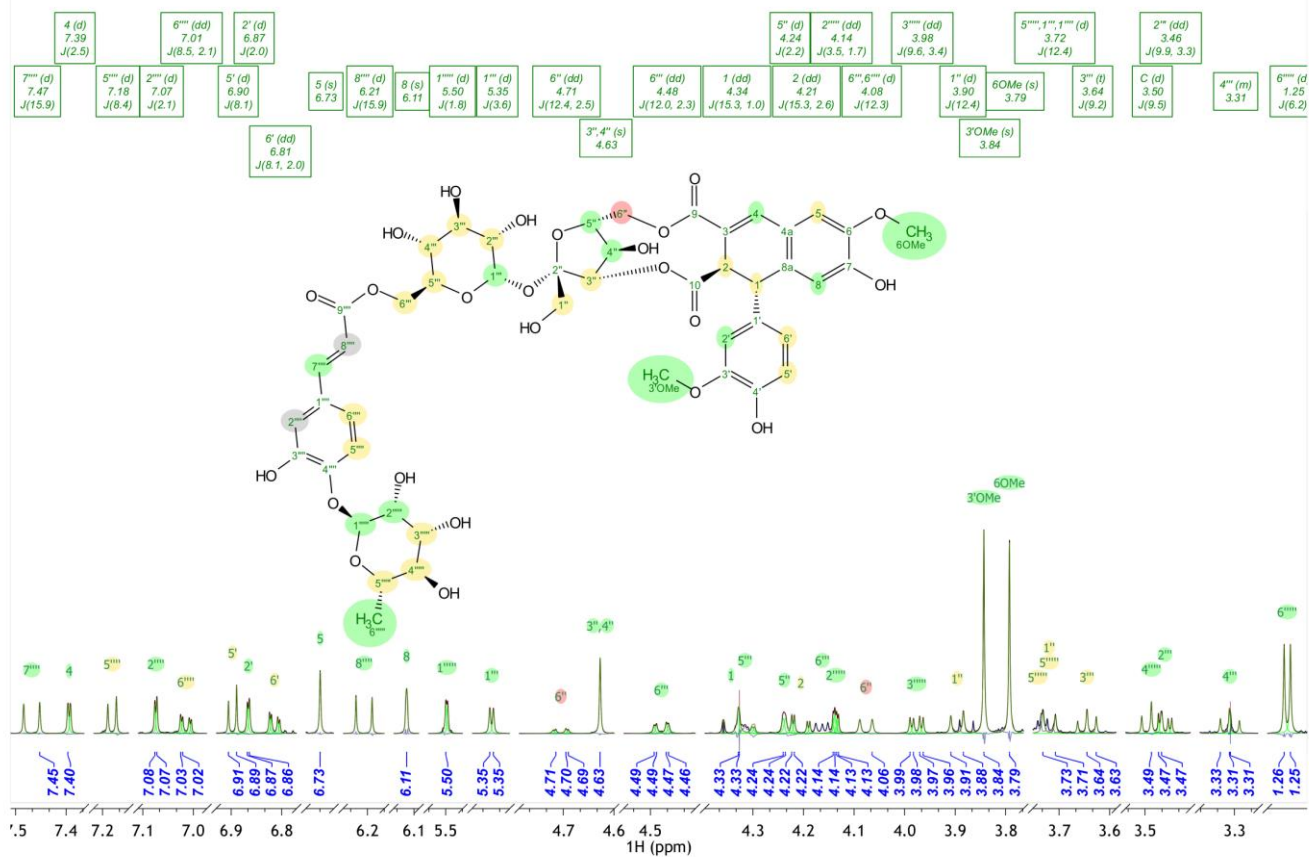


Figure 61S. ¹H NMR spectrum of compound 32

¹³C DEPT Q – NS=1024

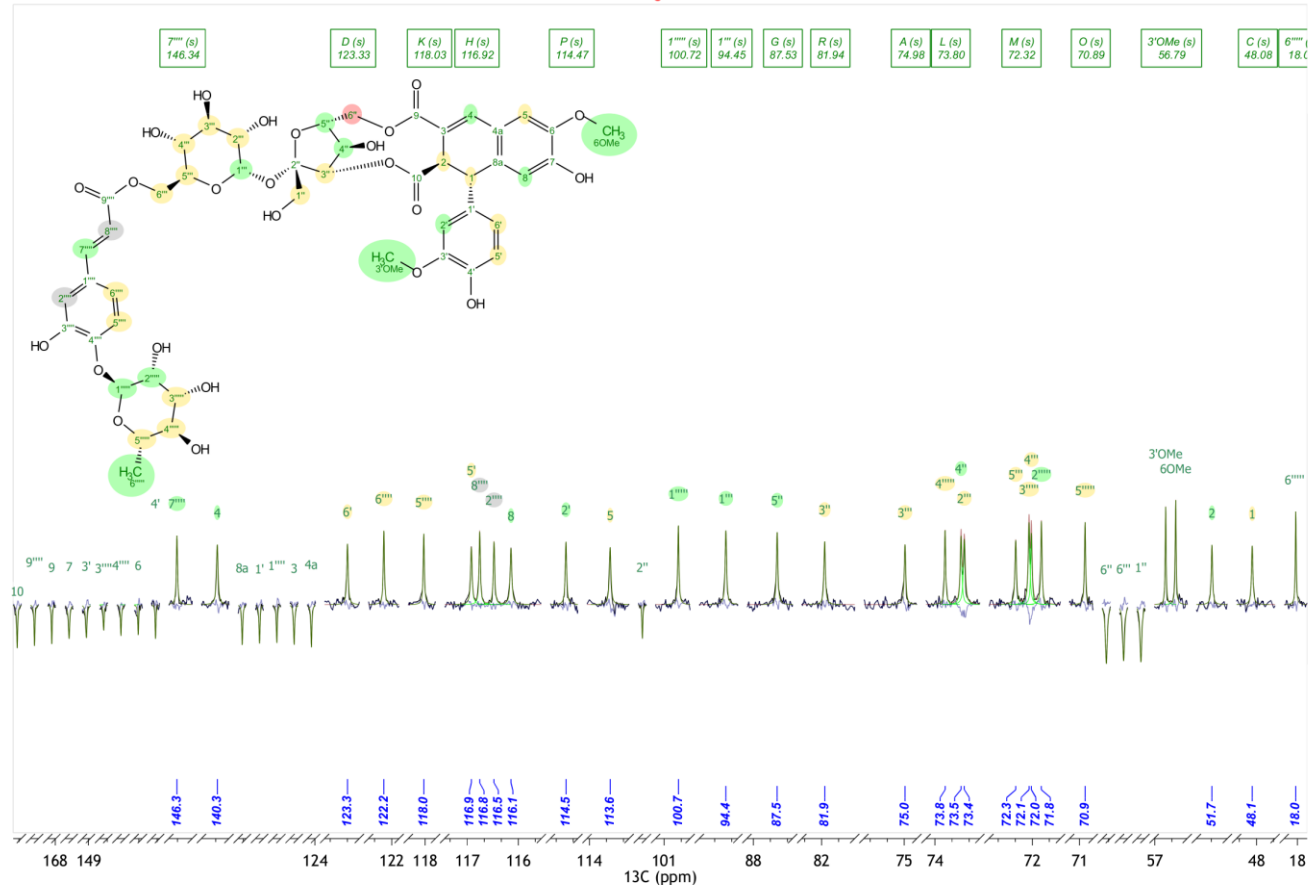


Figure 62S. ¹³C DEPTQ NMR spectrum of compound 32

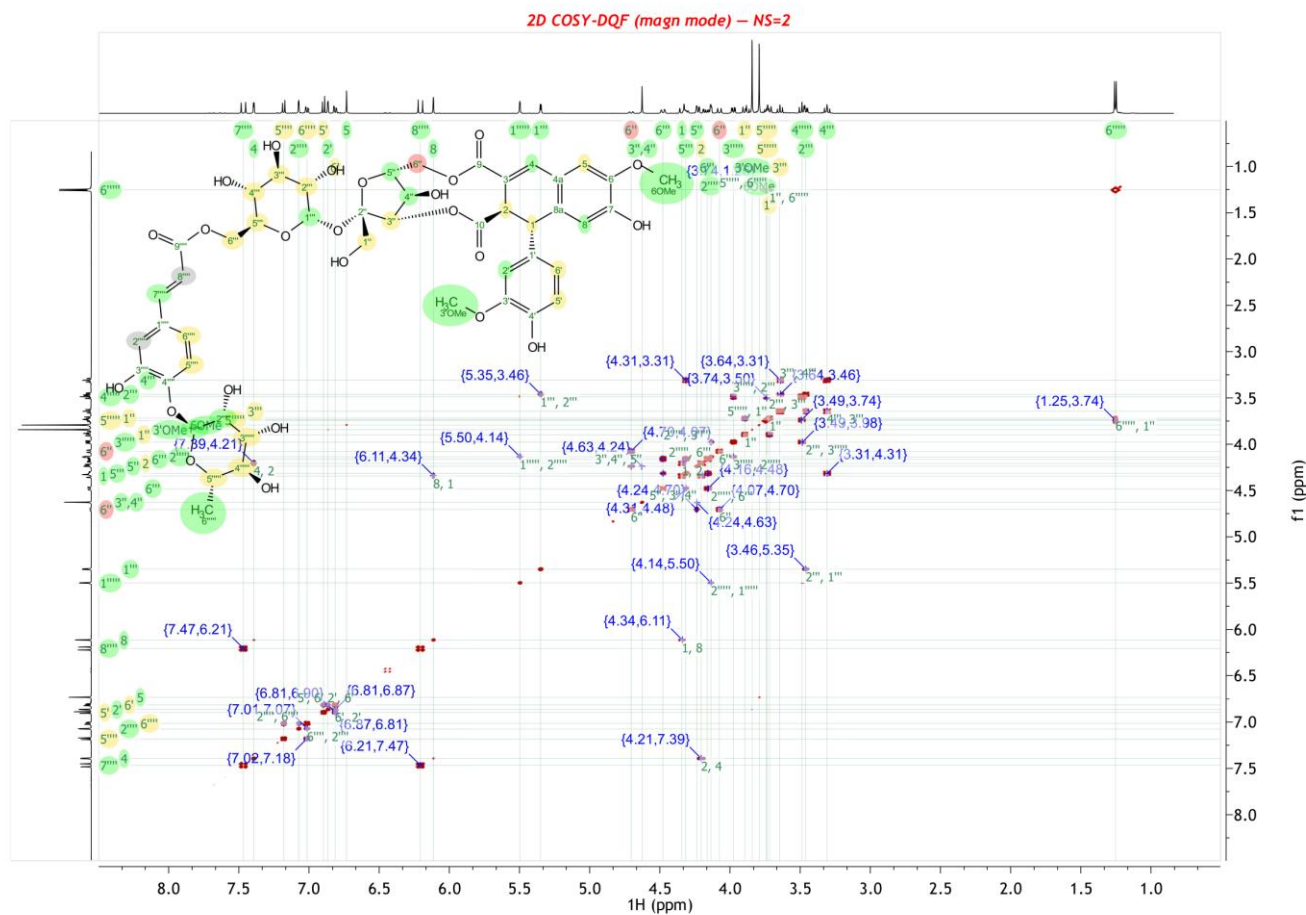


Figure 63S. ^1H - ^1H COSY NMR spectrum of compound 32

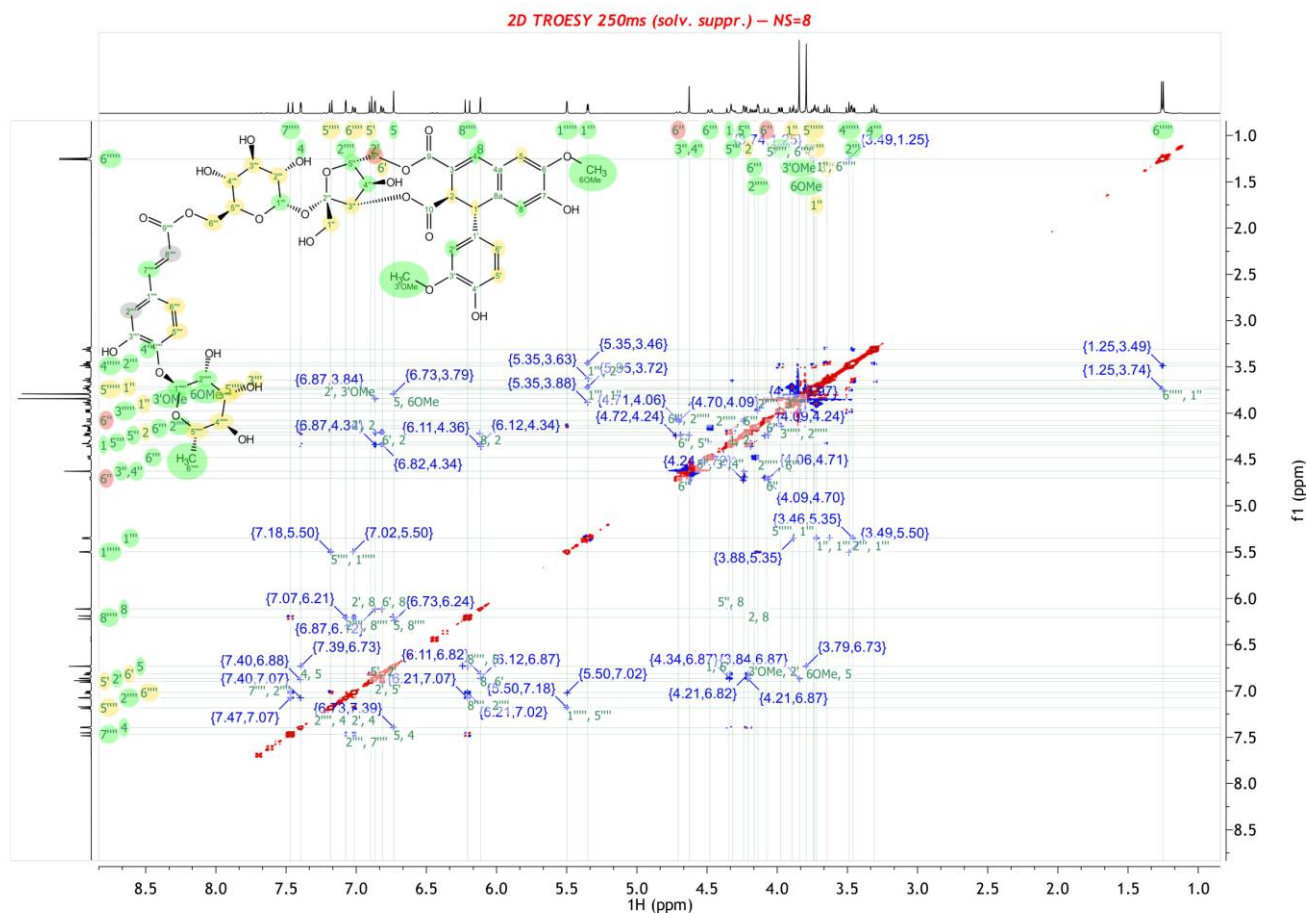


Figure 64S. ^1H - ^1H TROESY (250 ms) NMR spectrum of compound 32

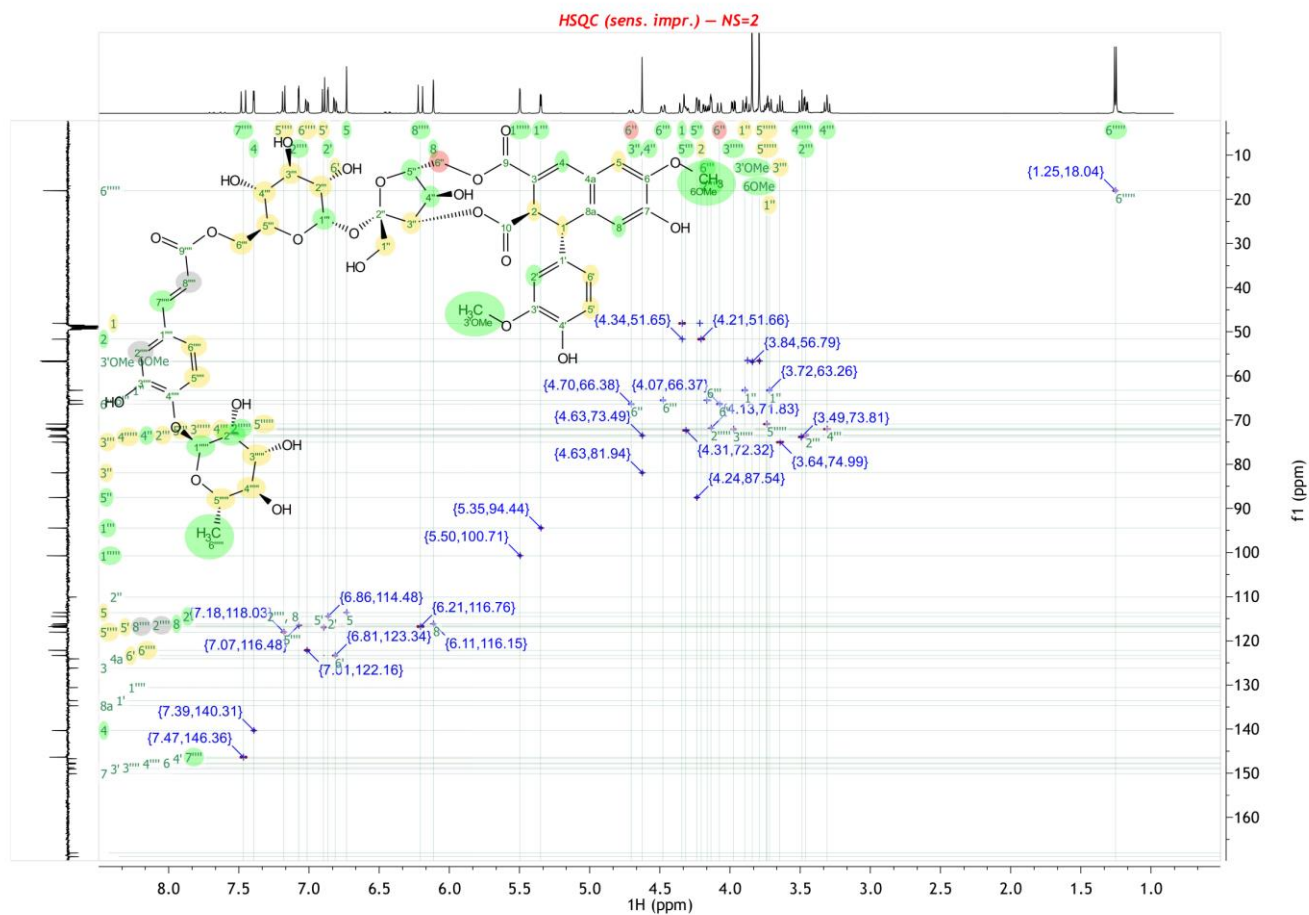


Figure 65S. ^1H - ^{13}C HSQC NMR spectrum of compound 32

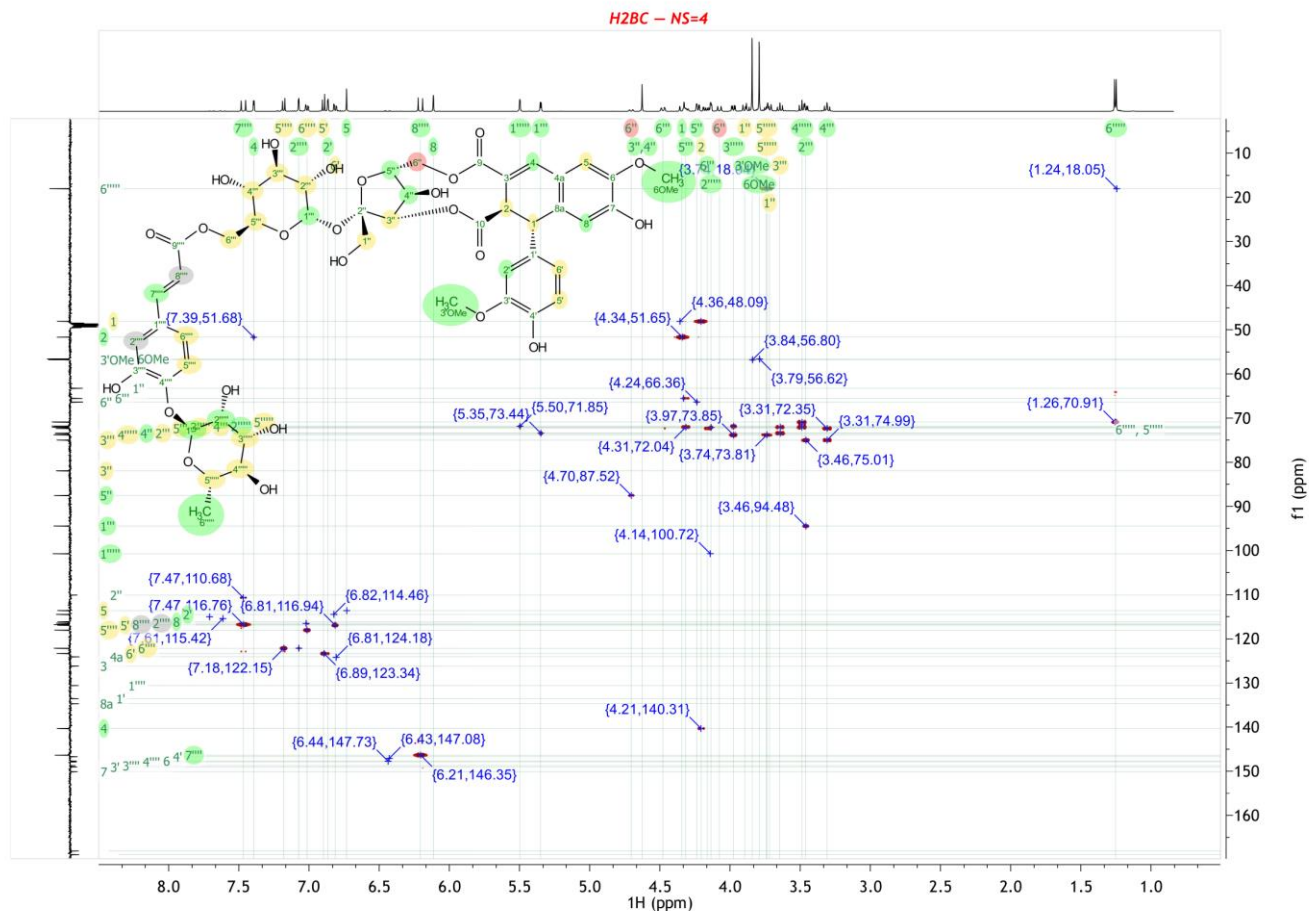


Figure 66S. ^1H - ^{13}C H2BC NMR spectrum of compound 32

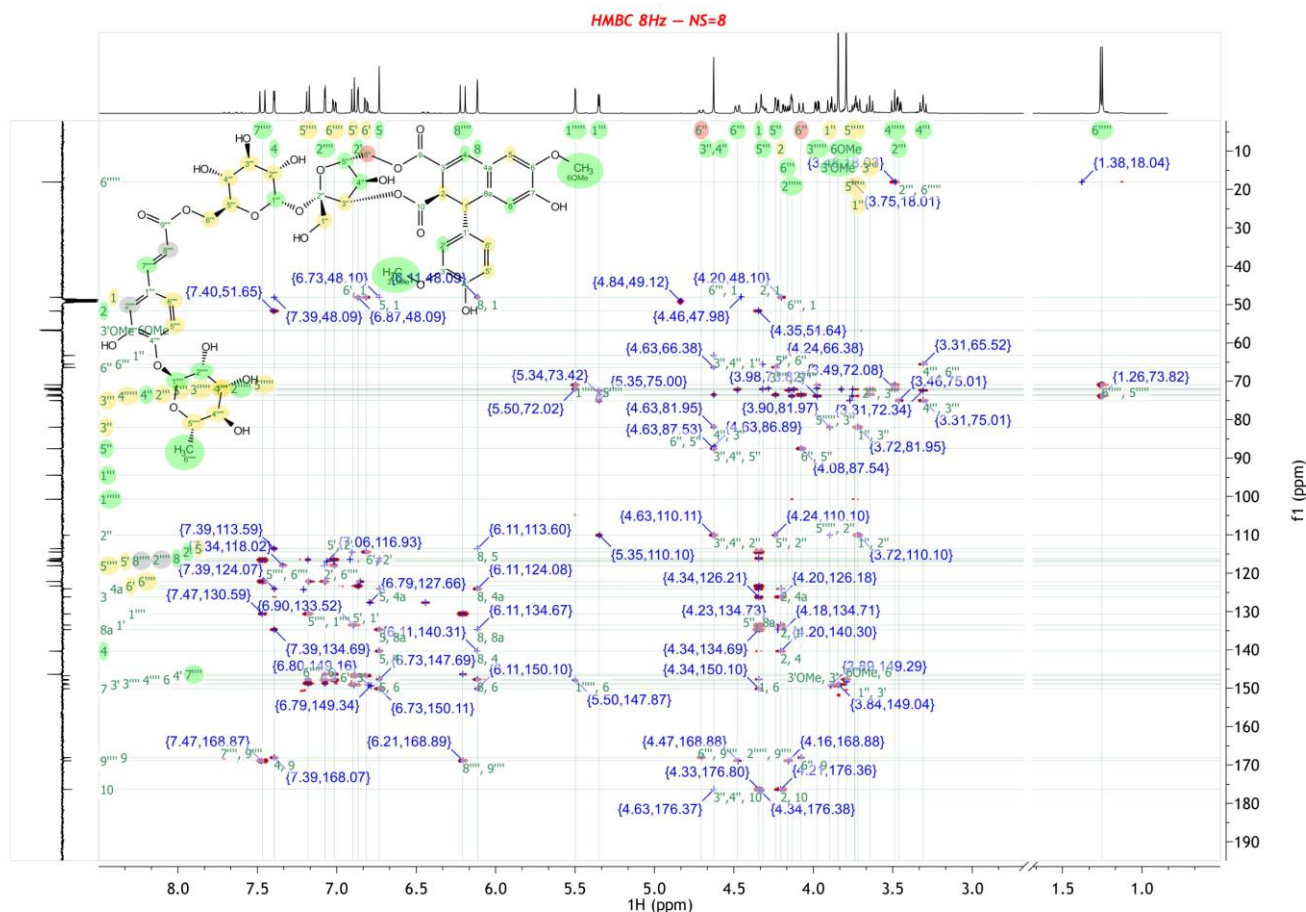
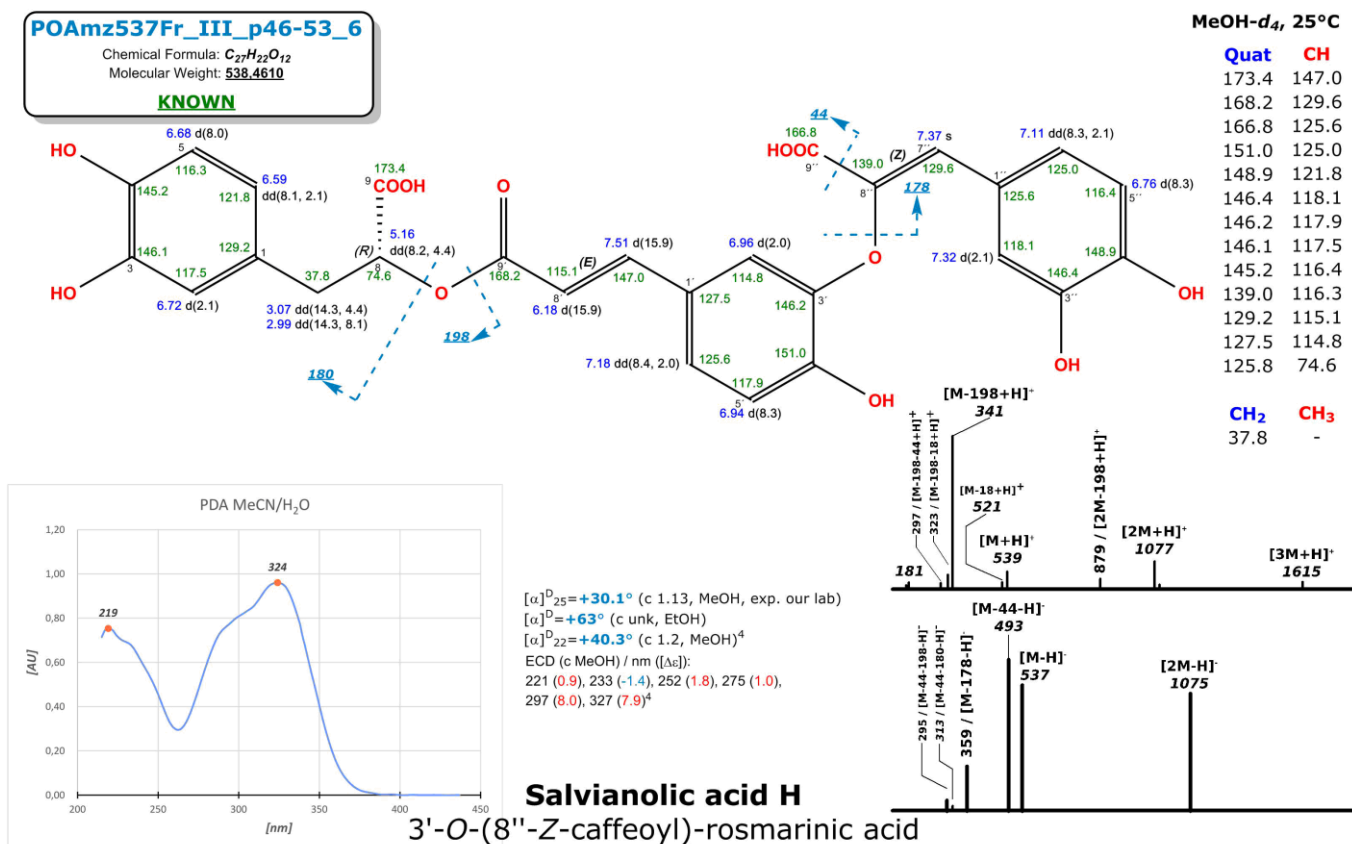


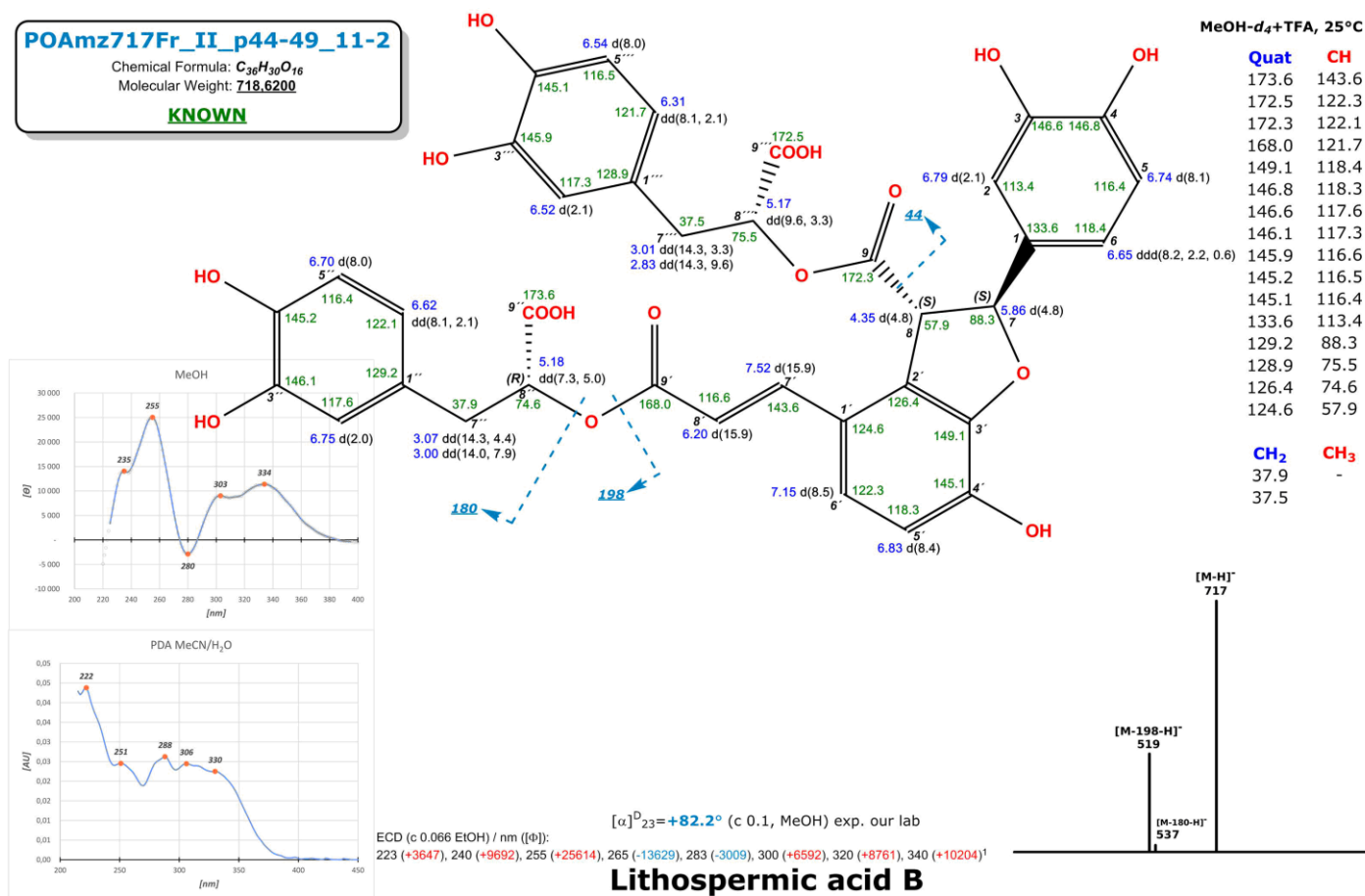
Figure 67S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 32



1. Zhang, H.J., Li, L.N., 1993. Salviannolic acid H, a new depside from *Salvia cavalerieri* var. *simplicifolia*. Chinese Chem. Lett. 4, 501-504.
 2. Yan, X., 2015. Dan Shen (*Salvia miltiorrhiza*) in Medicine. Springer Netherlands, Dordrecht. doi:10.1007/978-94-017-9463-3
 3. AGATA, I., KUSAKABE, H., HATANO, T., NISHIBE, S., OKUDA, T., 1993. Melitric Acids A and B, New Trimeric Caffeic Acid Derivatives from *Melissa officinalis*. Chem. Pharm. Bull. (Tokyo). 41, 1608-1611. doi:10.1248/cpb.41.1608
 4. Dapkevicius, A., van Beek, T.A., Lelyveld, G.P., van Veldhuizen, A., de Groot, A., Linssen, J.P.H., Venskutonis, R., 2002. Isolation and Structure Elucidation of Radical Scavengers from *Thymus vulgaris* Leaves. J. Nat. Prod. 65, 892-896. doi:10.1021/np010636j

Figure 68S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 33 in CD_3OD , 25°C; on-line PDA UV spectrum in $\text{MeCN}/\text{H}_2\text{O}$

POAmz717Fr_II_p44-49_11-2
 Chemical Formula: $C_{36}H_{30}O_{16}$
 Molecular Weight: **718,6200**
KNOWN



Anja Watzke, Steven J. O'Malley, Robert G. Bergman, * and, Eilman*, J.A., 2006. Reassignment of the Configuration of Salvianolic Acid B and Establishment of Its Identity with Lithospermic Acid B. doi:10.1021/NP060136W

Figure 69S. ¹H (500 MHz) and ¹³C (125 MHz) NMR data of compound 34 in CD₃OD, 25°C; on-line PDA UV spectrum in MeCN/H₂O; ECD spectrum in MeOH

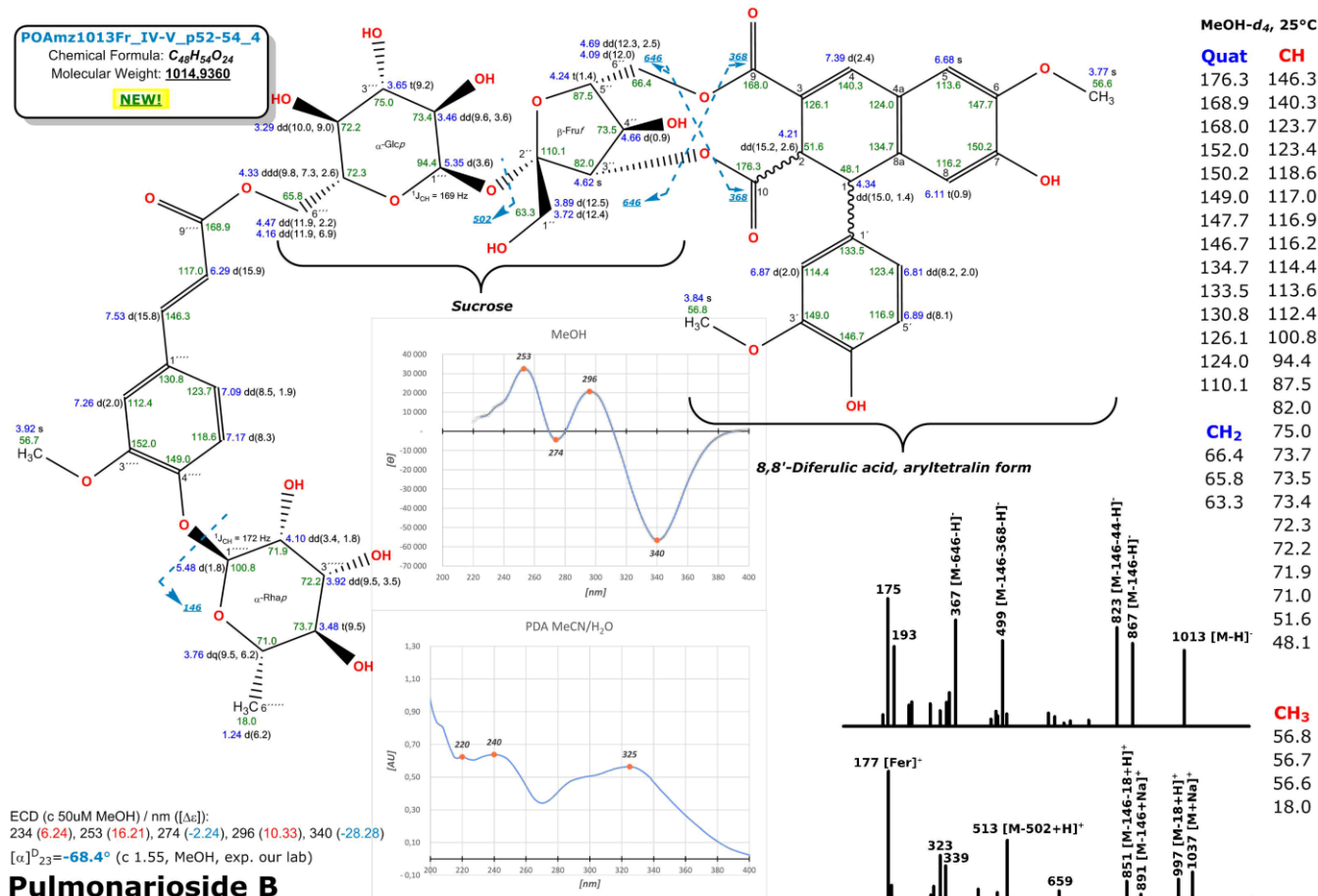


Figure 70S. ¹H (500 MHz) and ¹³C (125 MHz) NMR data of compound 35 in CD₃OD, 25°C; on-line PDA UV spectrum in MeCN/H₂O; ECD spectrum in MeOH

¹H NS16 CD3OD 25°C – NS=16

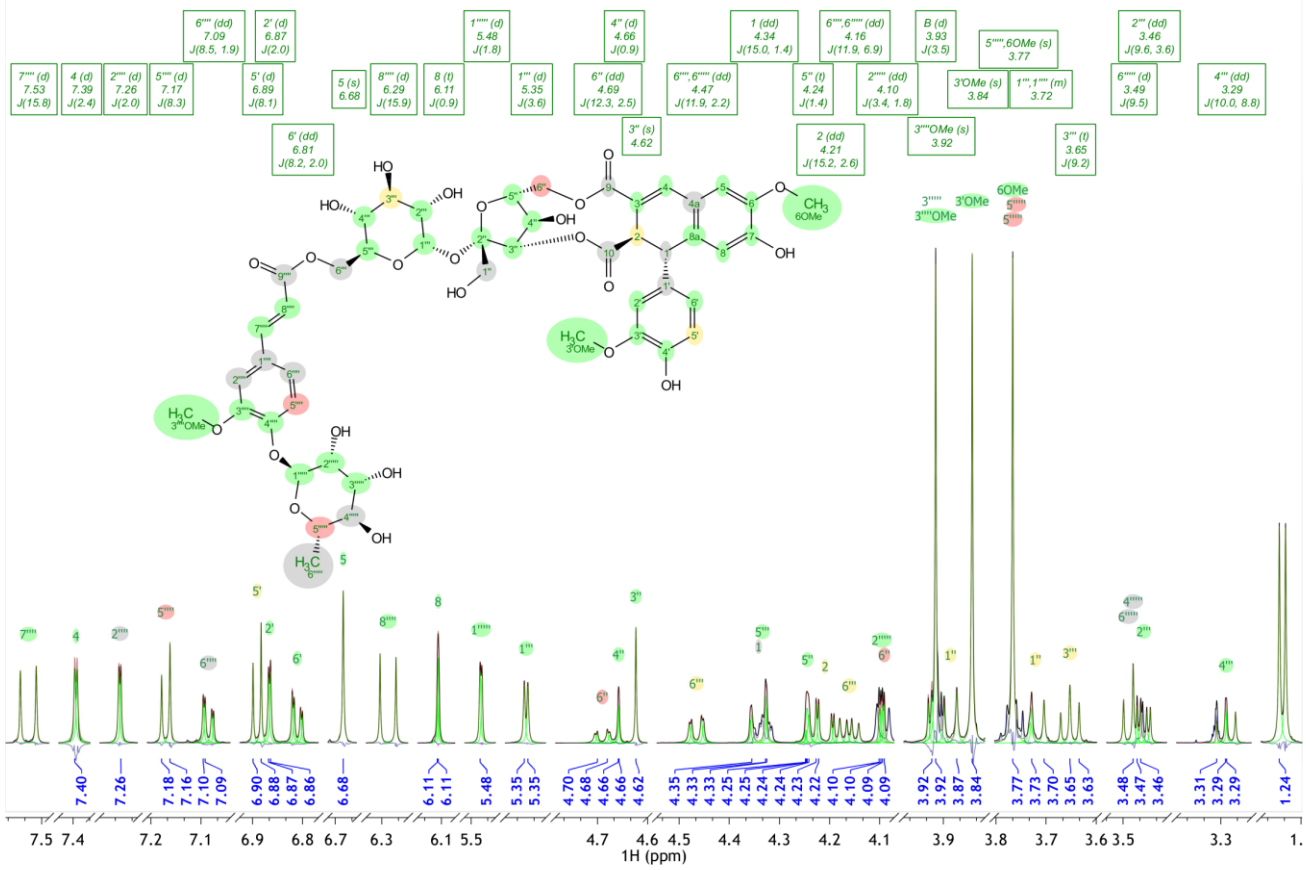


Figure 71S. ¹H NMR spectrum of compound 35

¹³C DEPT Q – NS=1024

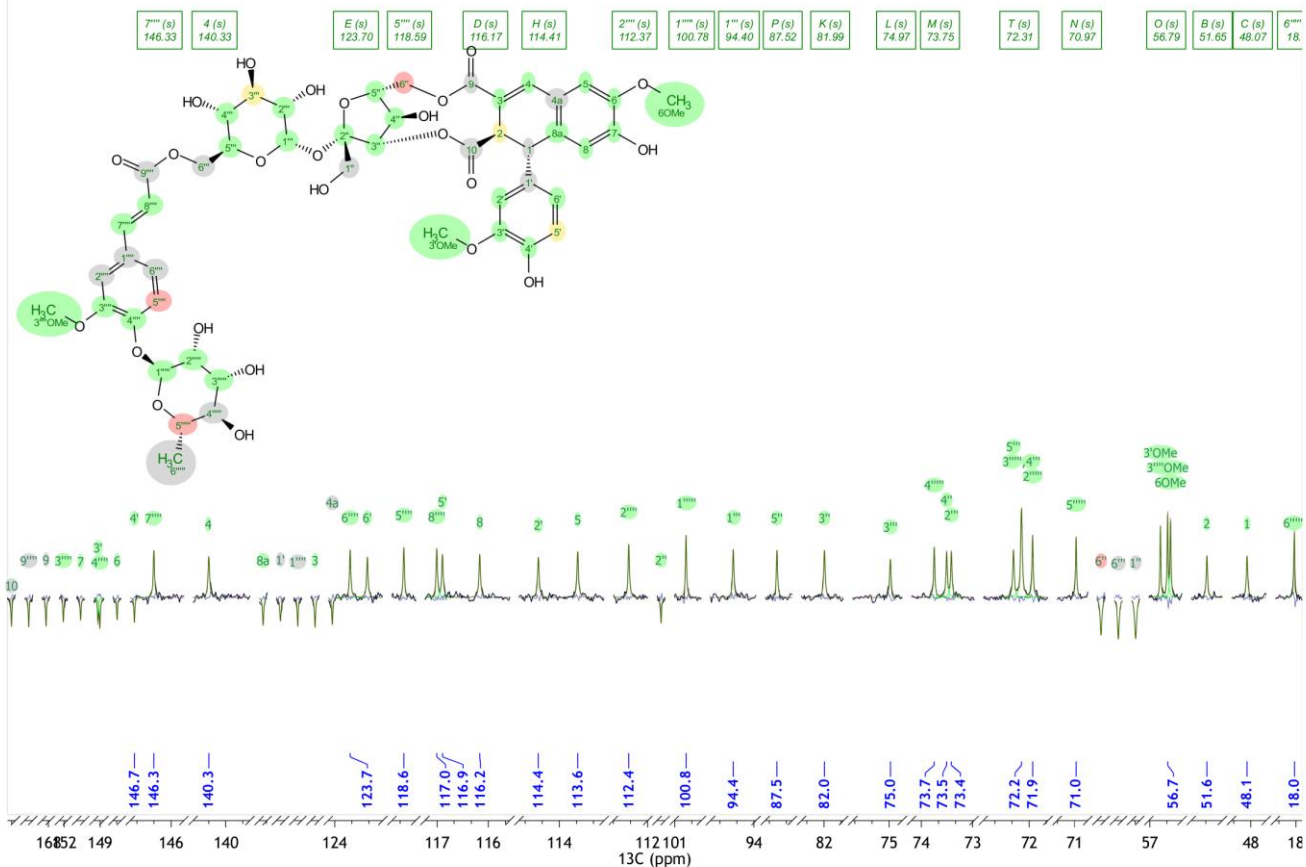


Figure 72S. ¹³C DEPTQ NMR spectrum of compound 35

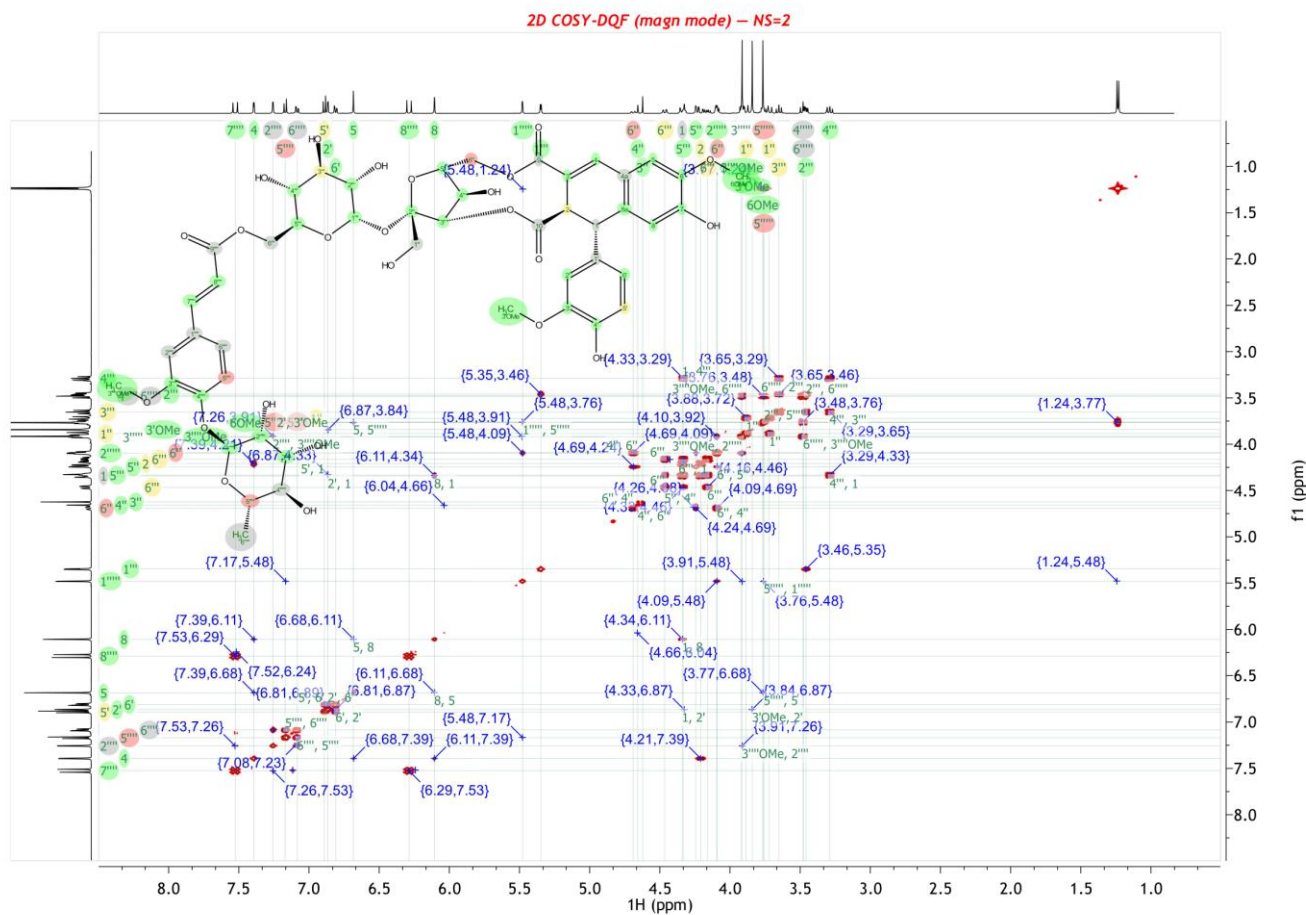


Figure 73S. ^1H - ^1H COSY NMR spectrum of compound 35

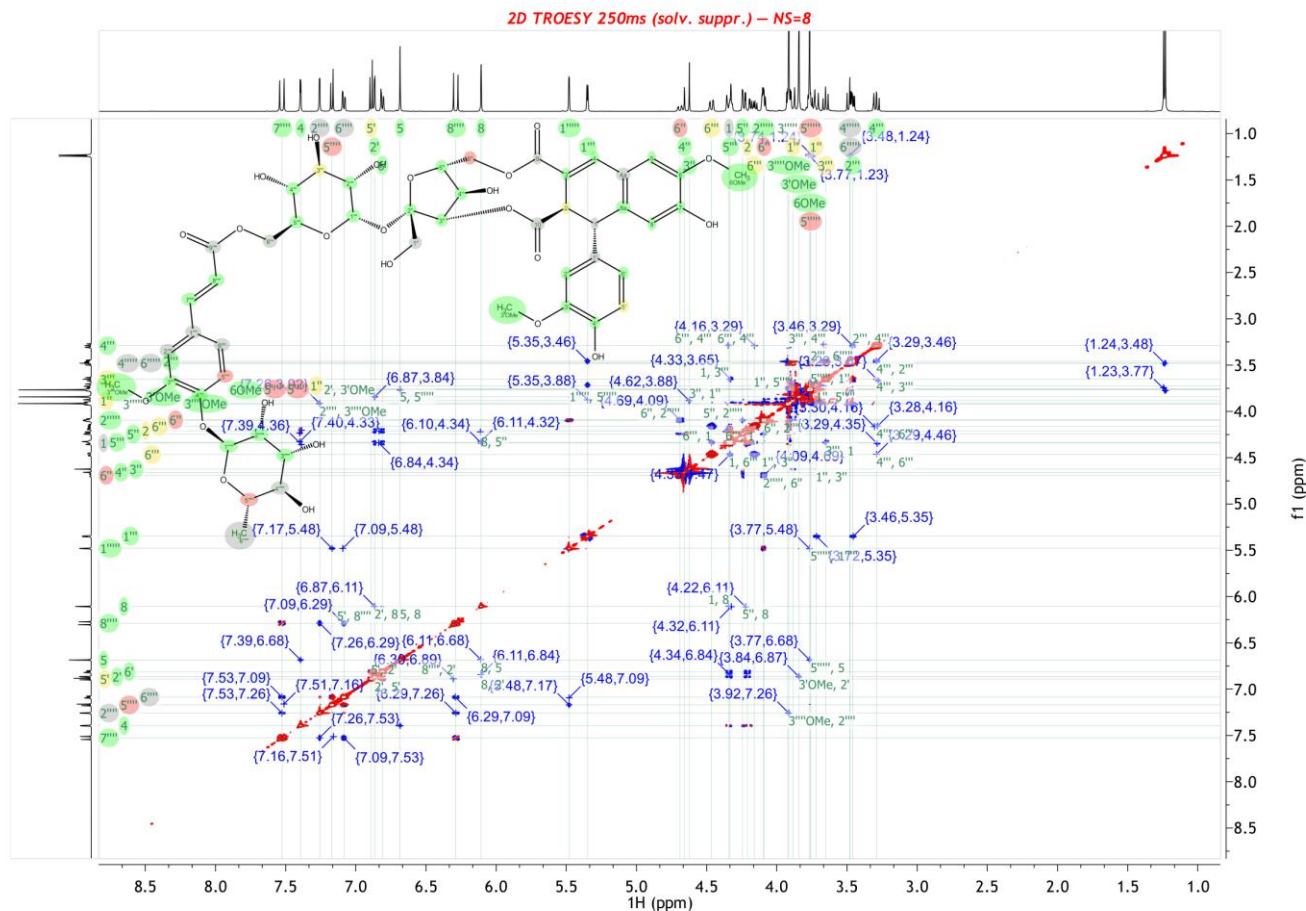


Figure 74S. ^1H - ^1H TROESY (250 ms) NMR spectrum of compound 35

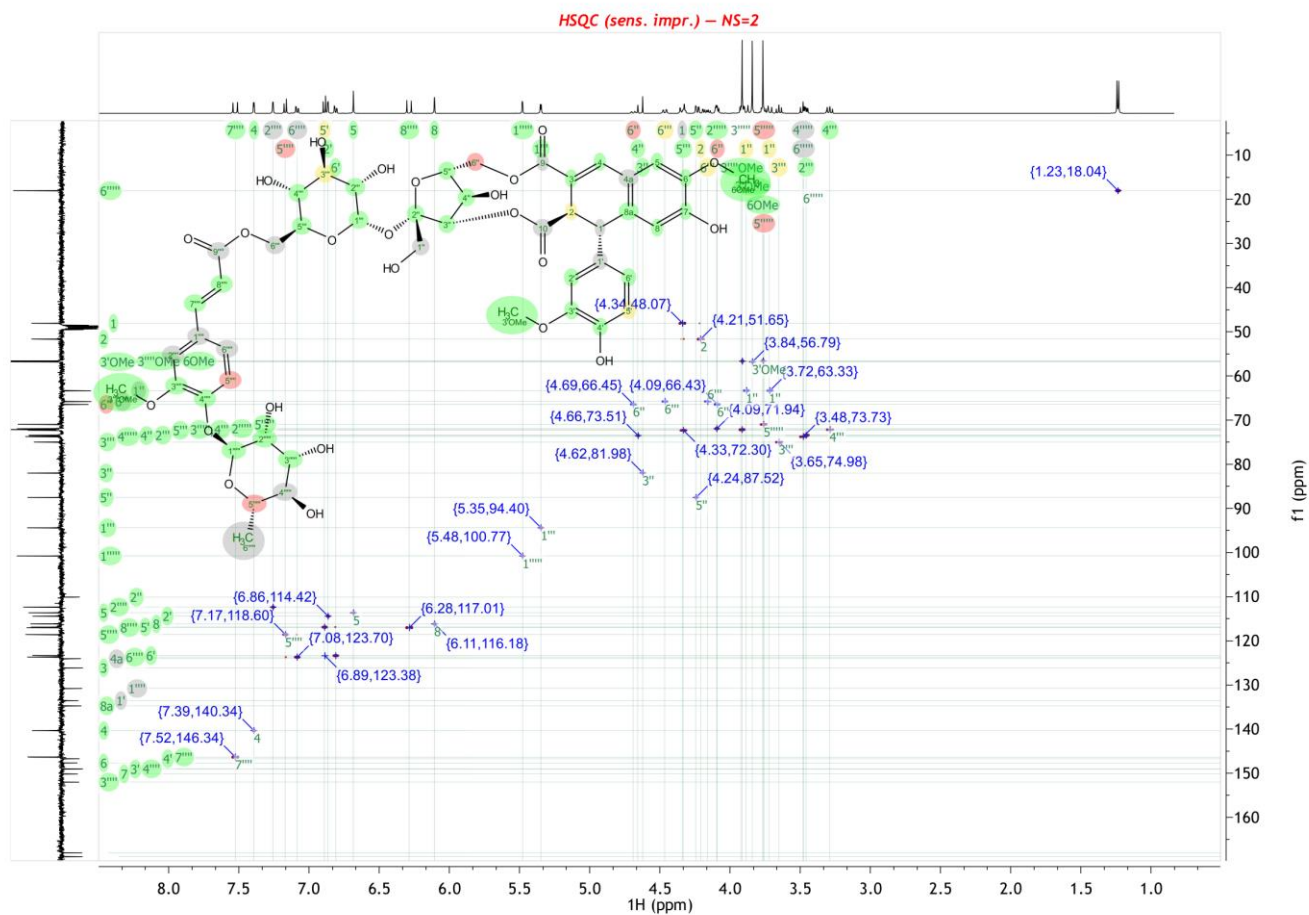
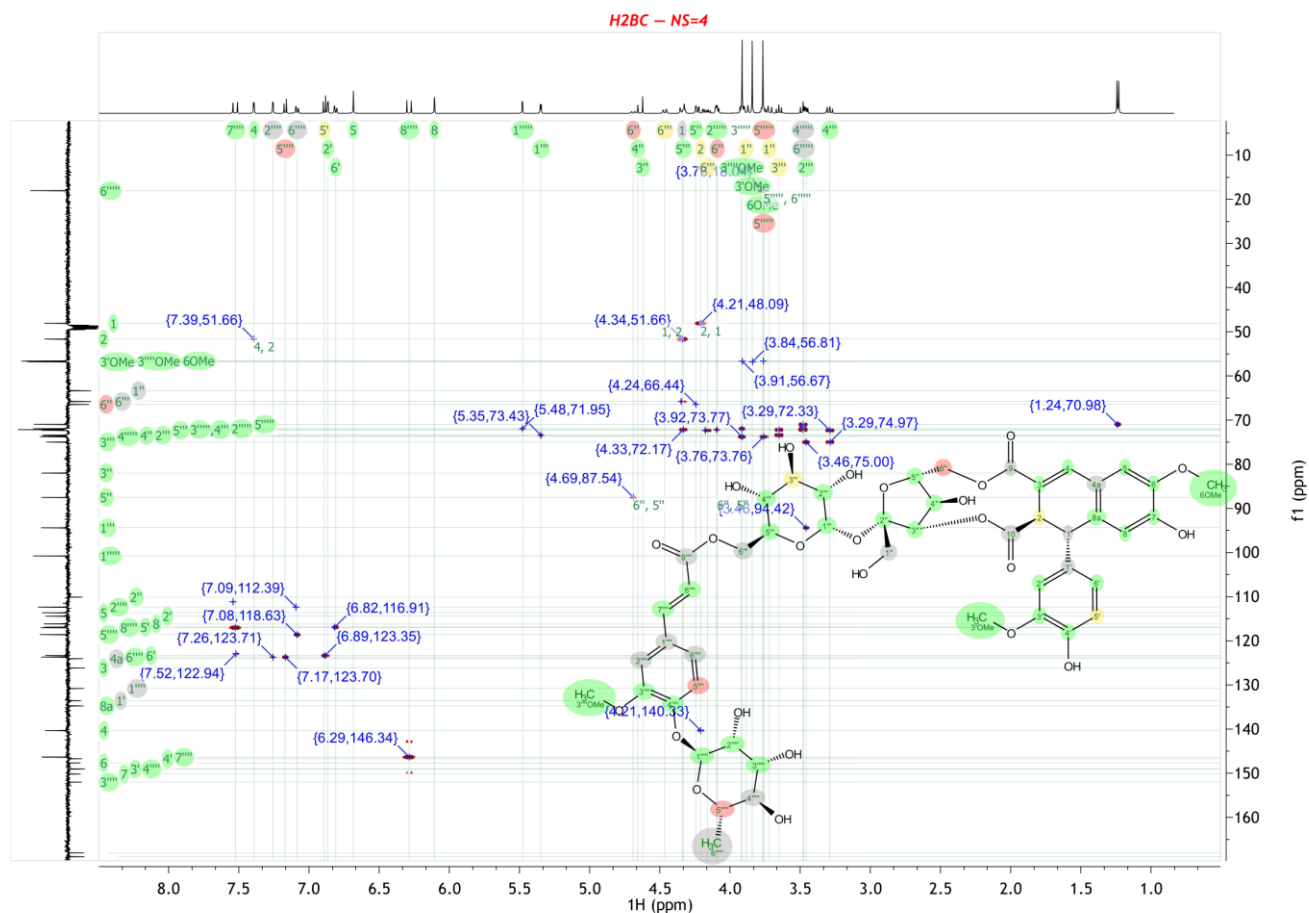


Figure 75S. ^1H - ^{13}C HSQC NMR spectrum of compound 35



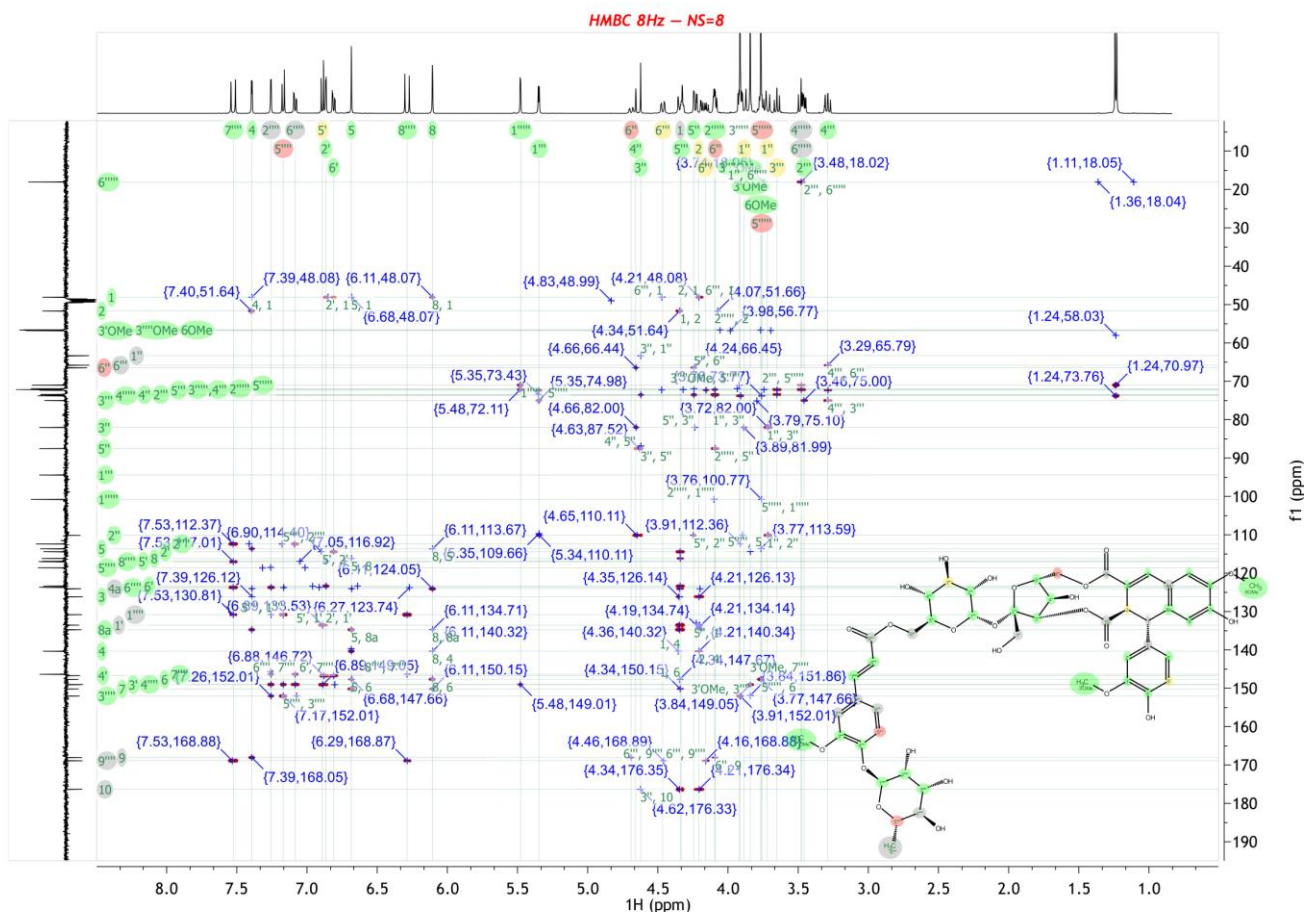
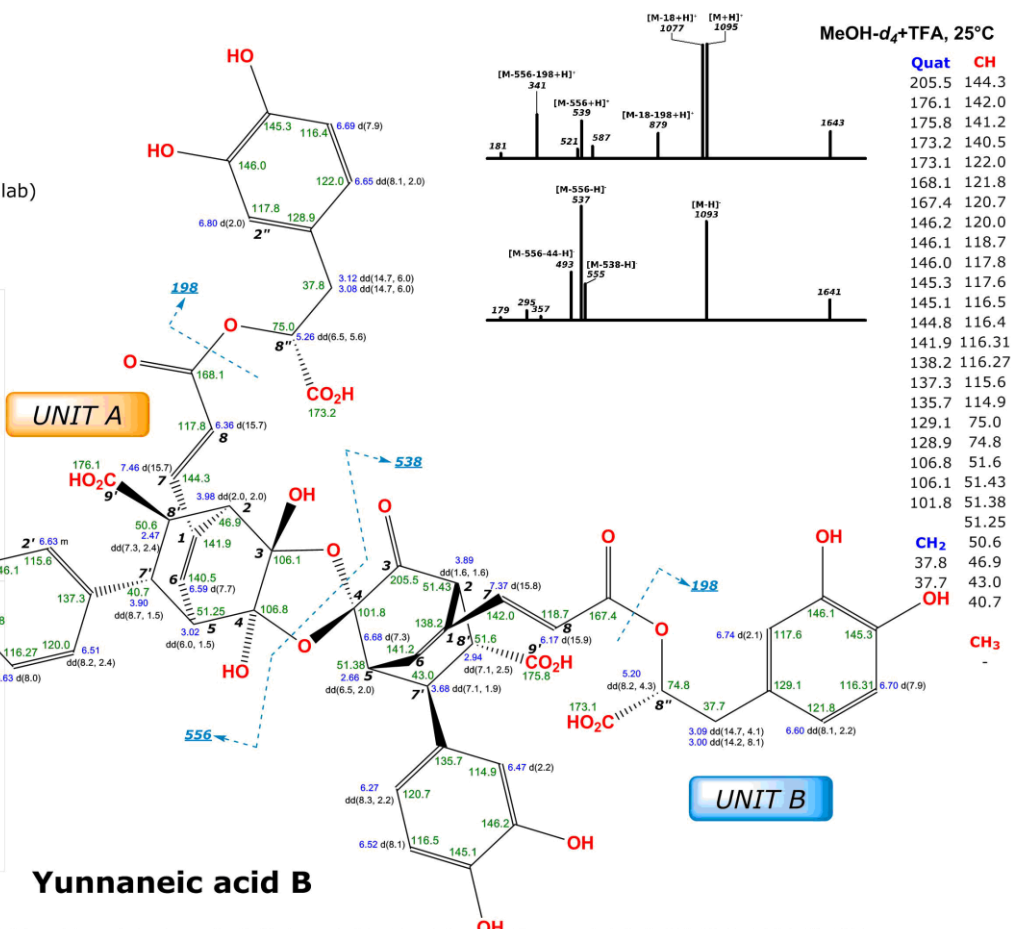
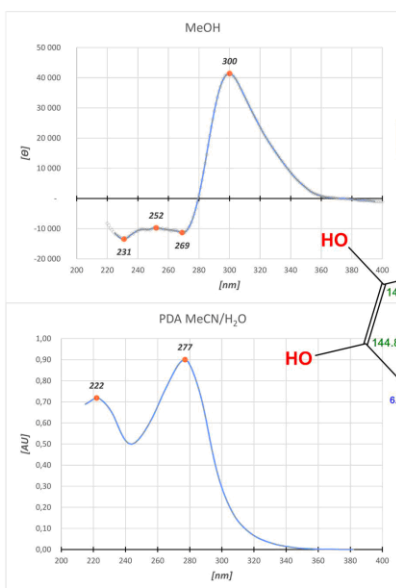


Figure 77S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 35

POAmz1093Fr_I_537czyste_3
 Chemical Formula: $\text{C}_{24}\text{H}_{46}\text{O}_{25}$
 Molecular Weight: 1094.9370
KNOWN

$[\alpha]_{25}^{\text{D}} = +92.7^\circ$ (c 1.22, MeOH, exp. our lab)
 $[\alpha]_{\text{D}}^{\text{D}} = +80.5^\circ$ (c unk, MeOH)



1. Tanaka, T., Nishimura, A., Kouno, I., Nonaka, G.I., Young, T.J., 1996. Isolation and characterization of yunnaneic acids A-D, four novel caffeic acid metabolites from *Salvia yunnanensis*. *J. Nat. Prod.* 59, 843-849. doi:10.1021/np960425s
 2. Yan, X., 2015. Dan Shen (*Salvia miltiorrhiza*) in Medicine. Springer Netherlands, Dordrecht. doi:10.1007/978-94-017-9463-3

Figure 78S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 36 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/ H_2O ; ECD spectrum in MeOH

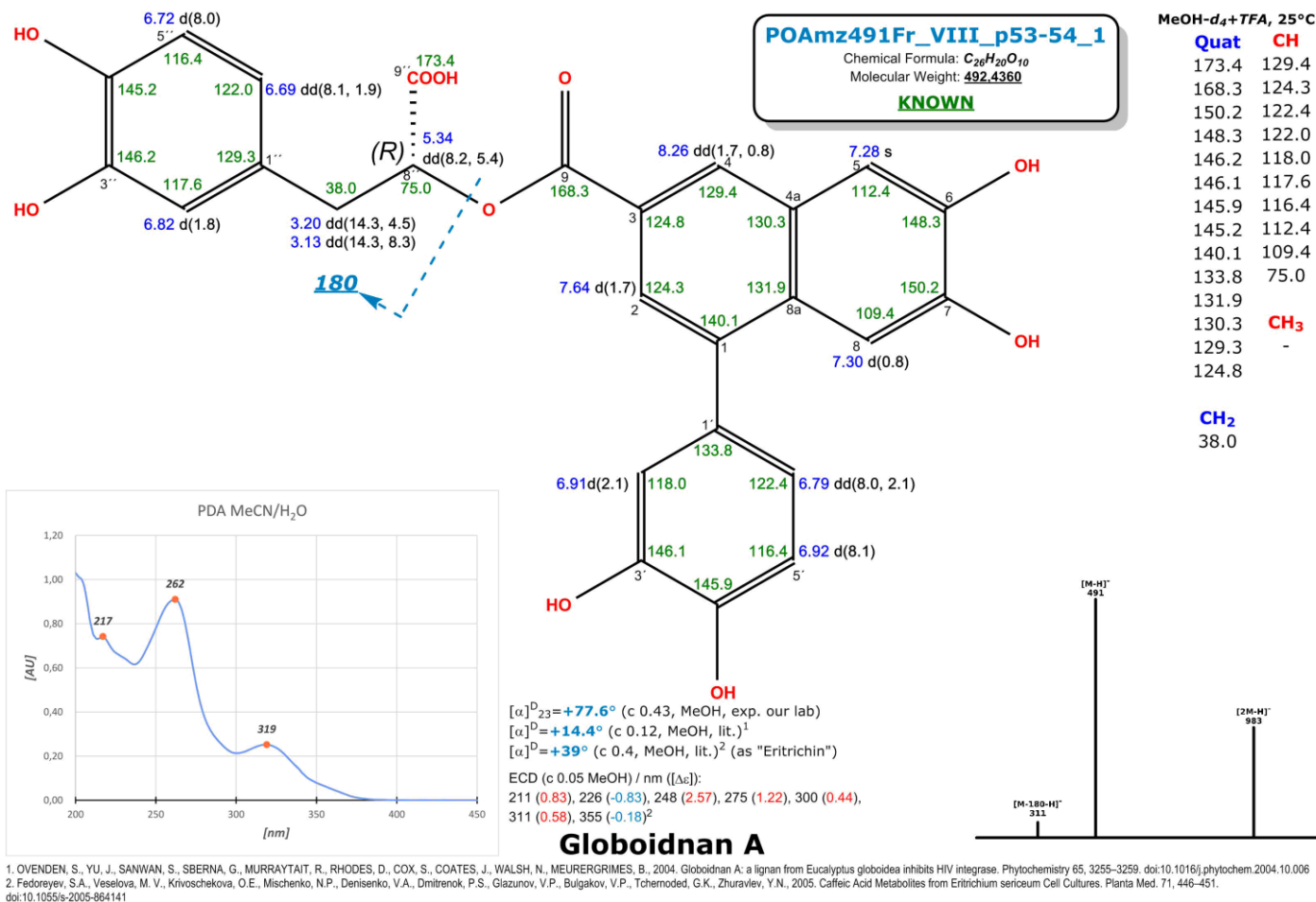


Figure 79S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 37 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/H₂O

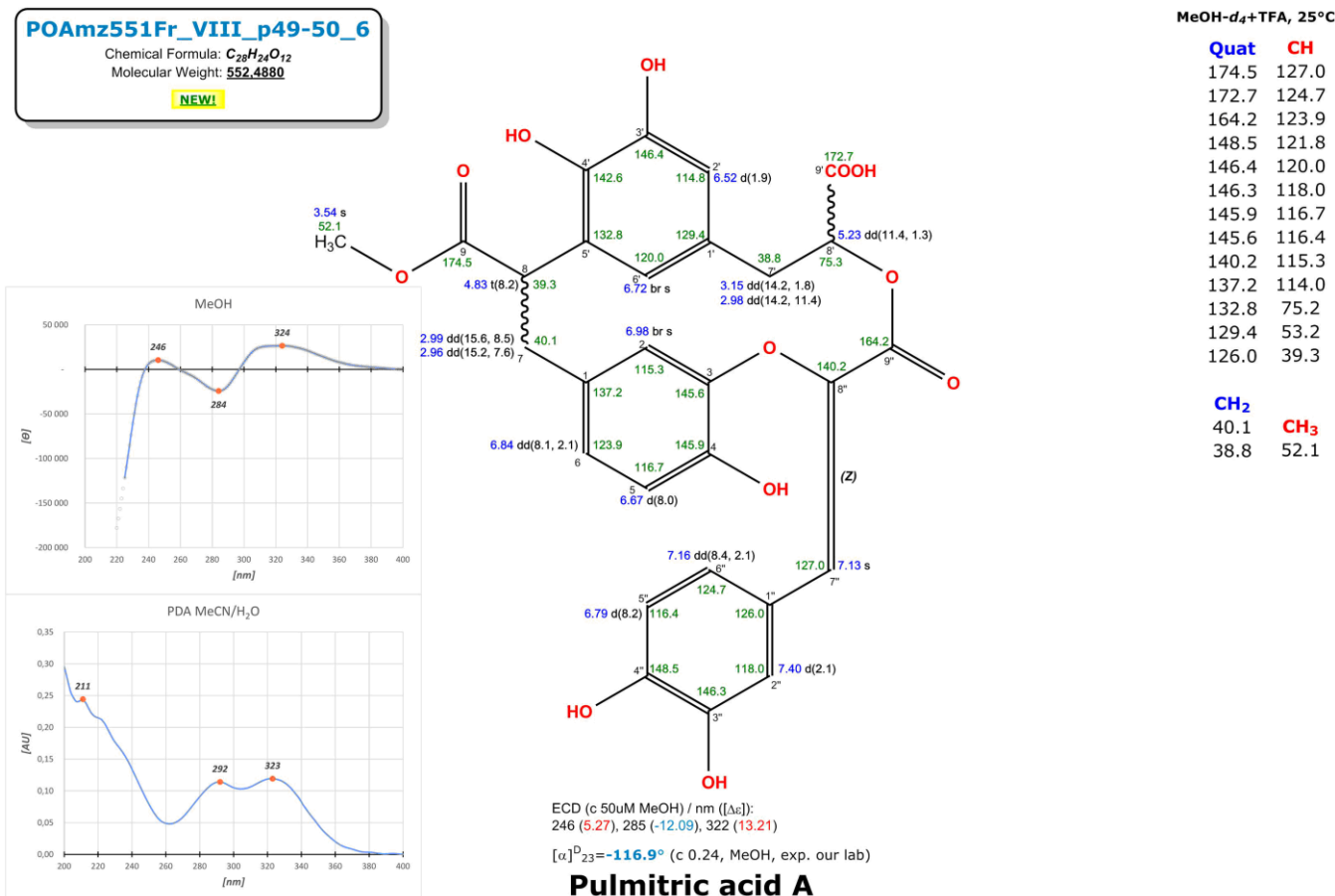


Figure 80S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 38 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/H₂O

- NS=8

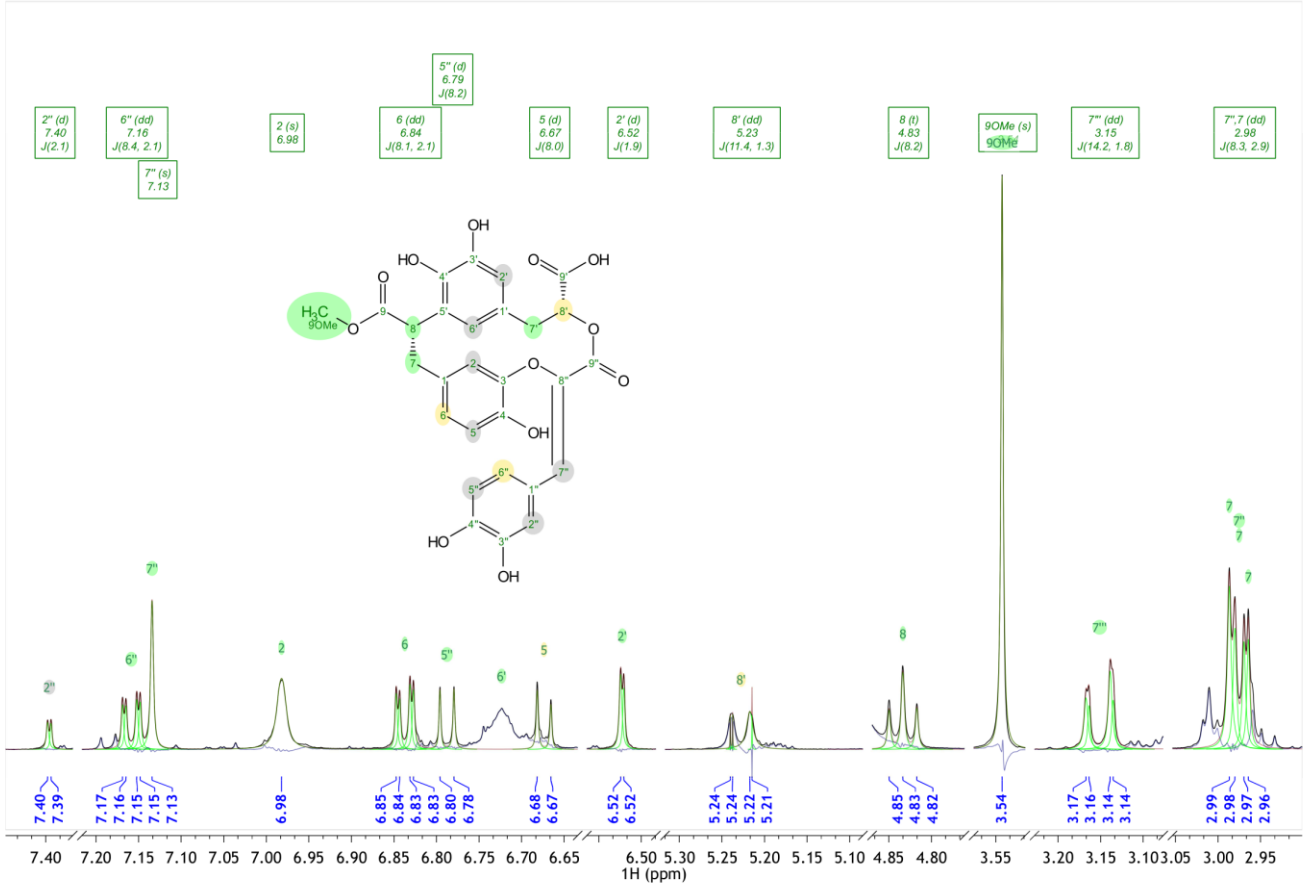


Figure 81S. ¹H NMR spectrum of compound 38

¹³C DEPT Q - NS=8192

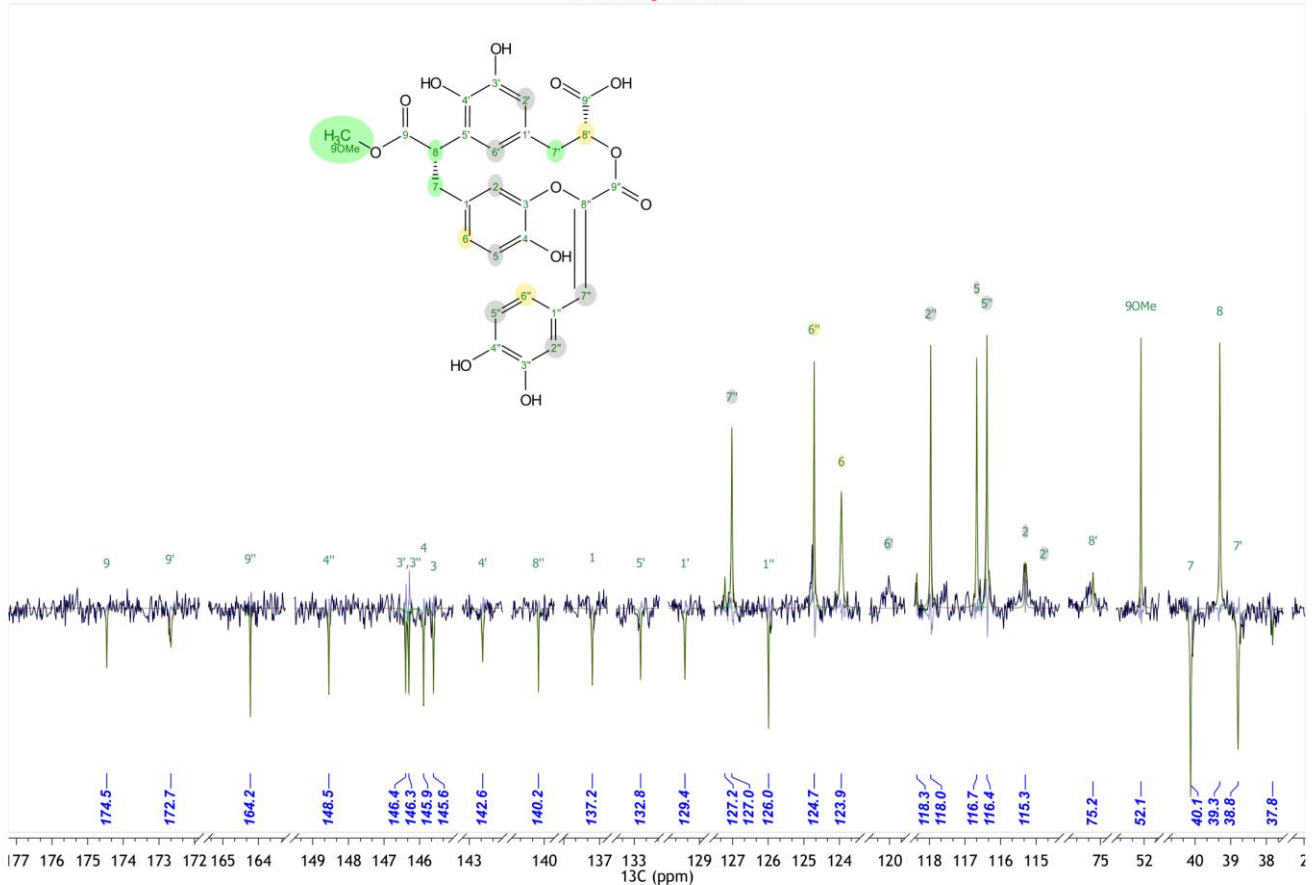


Figure 82S. ¹³C DEPTQ NMR spectrum of compound 38

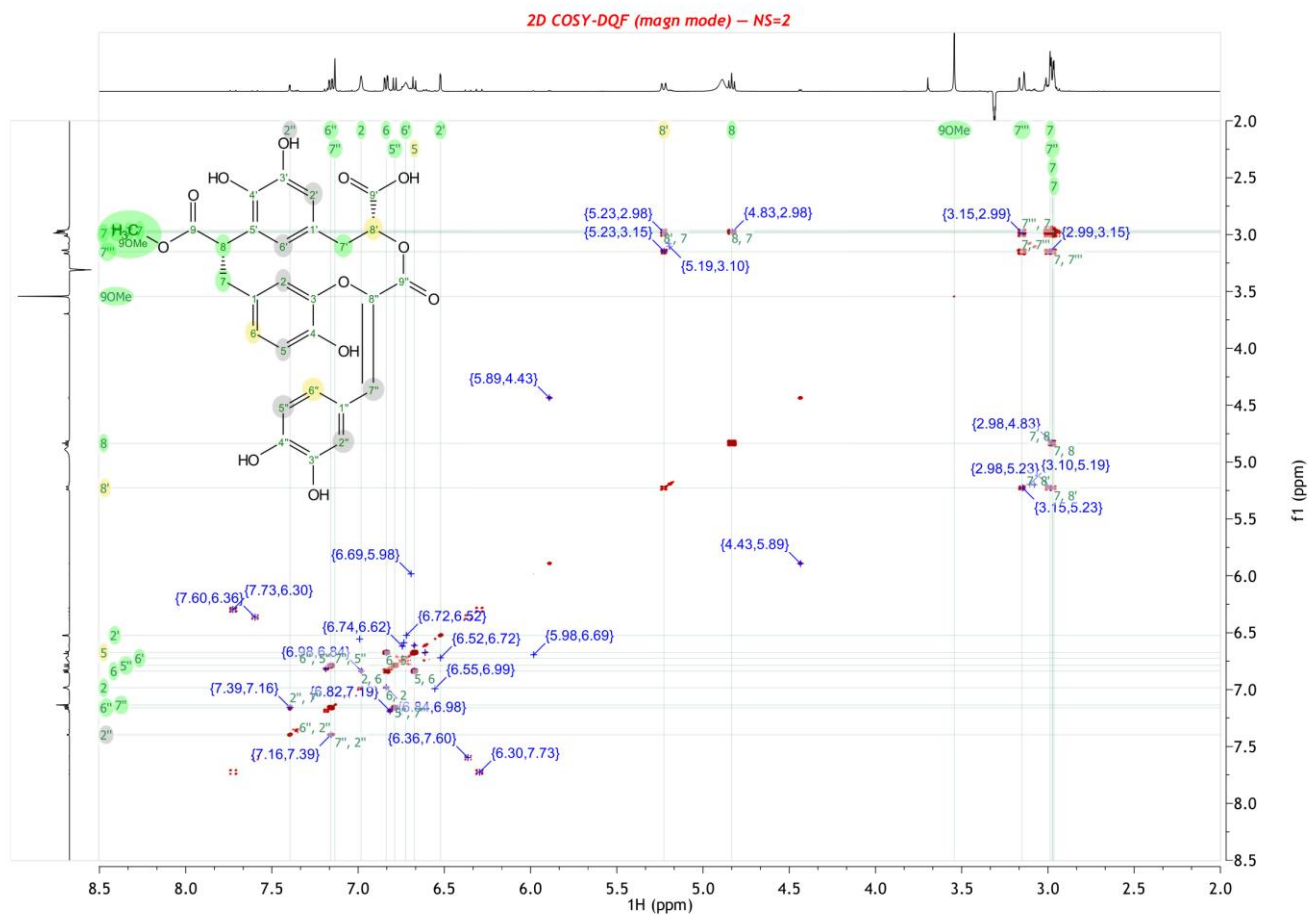


Figure 83S. ^1H - ^1H COSY NMR spectrum of compound 38

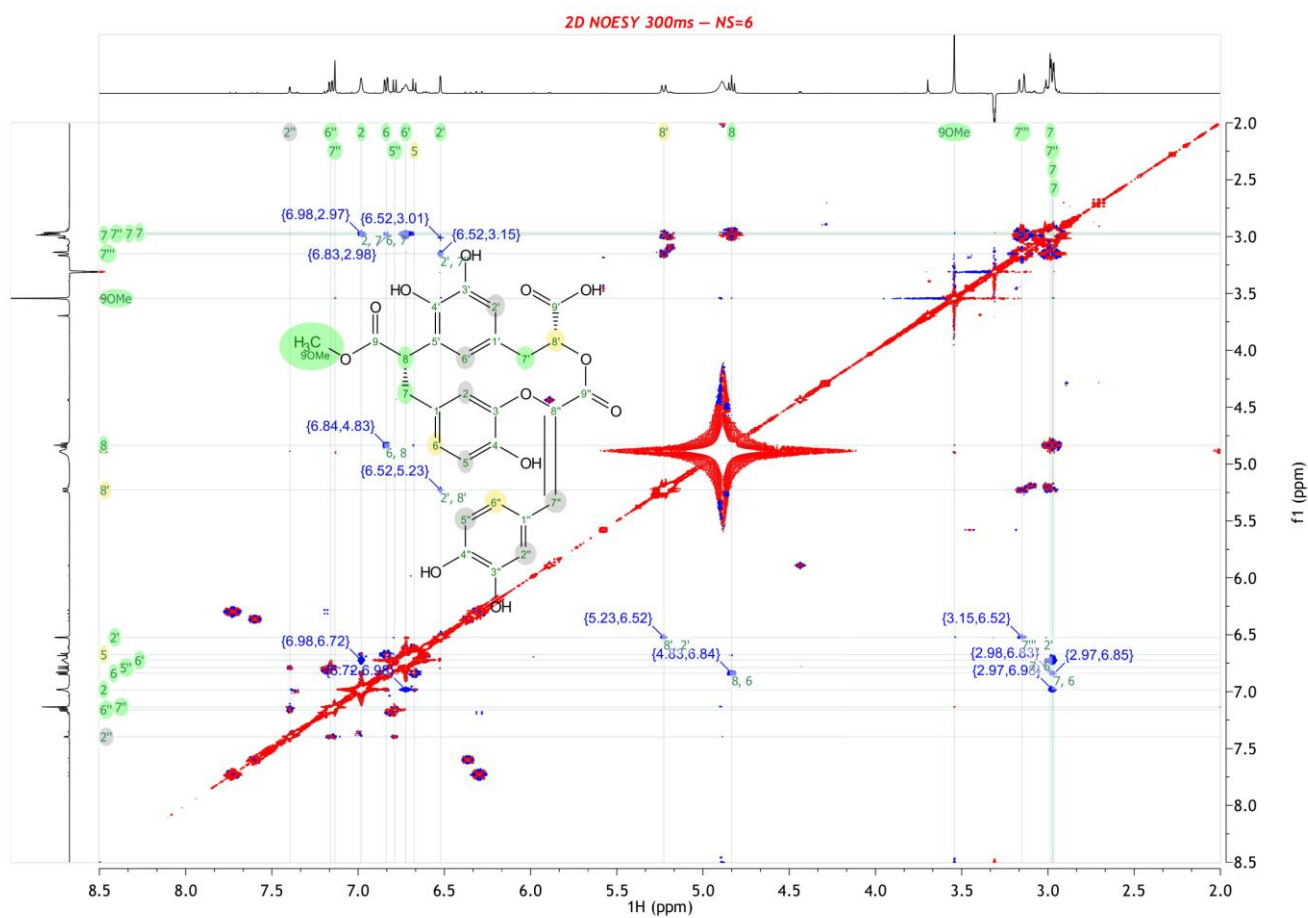


Figure 84S. ^1H - ^1H NOESY (300 ms) NMR spectrum of compound 38

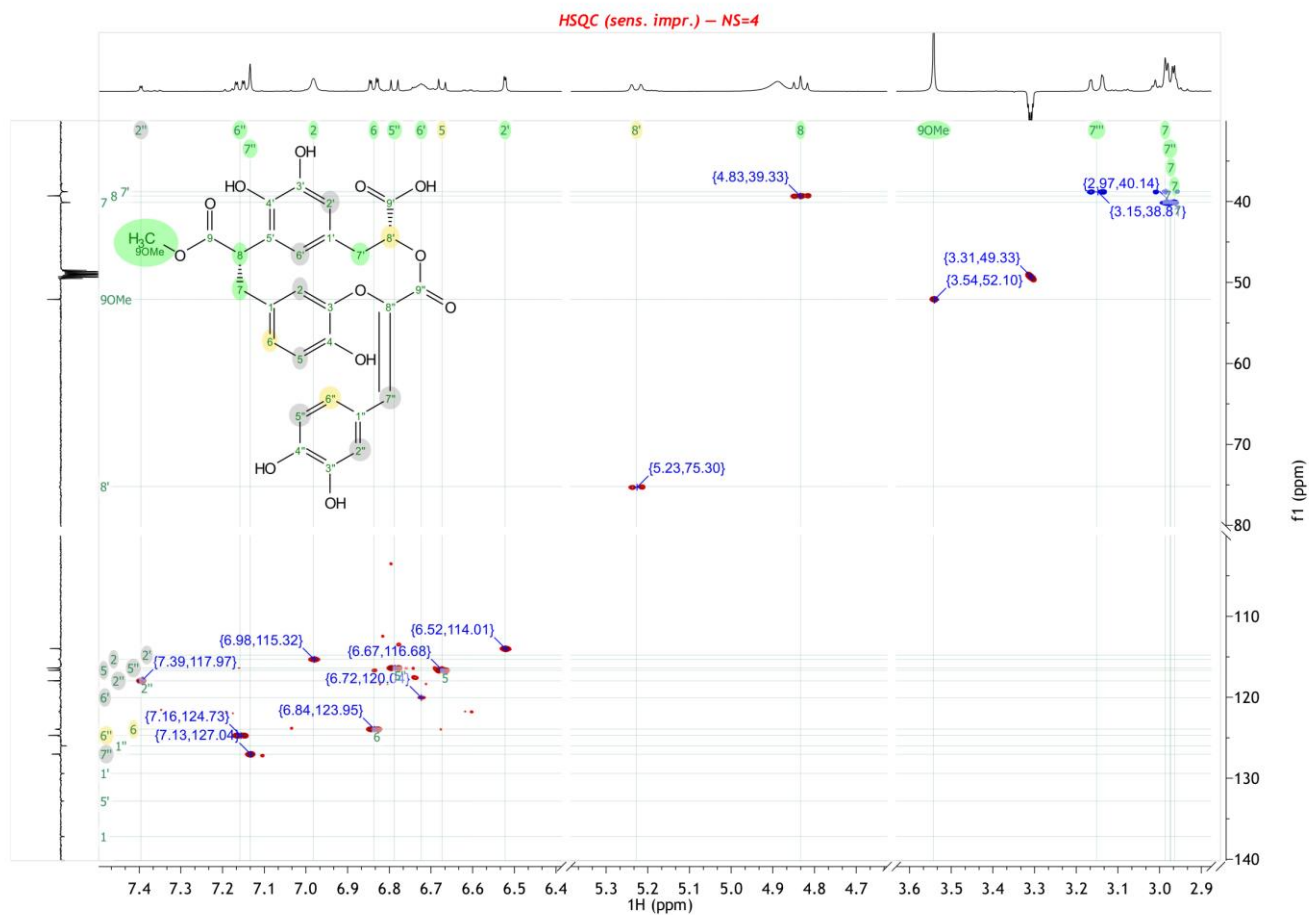


Figure 85S. ^1H - ^{13}C HSQC NMR spectrum of compound 38

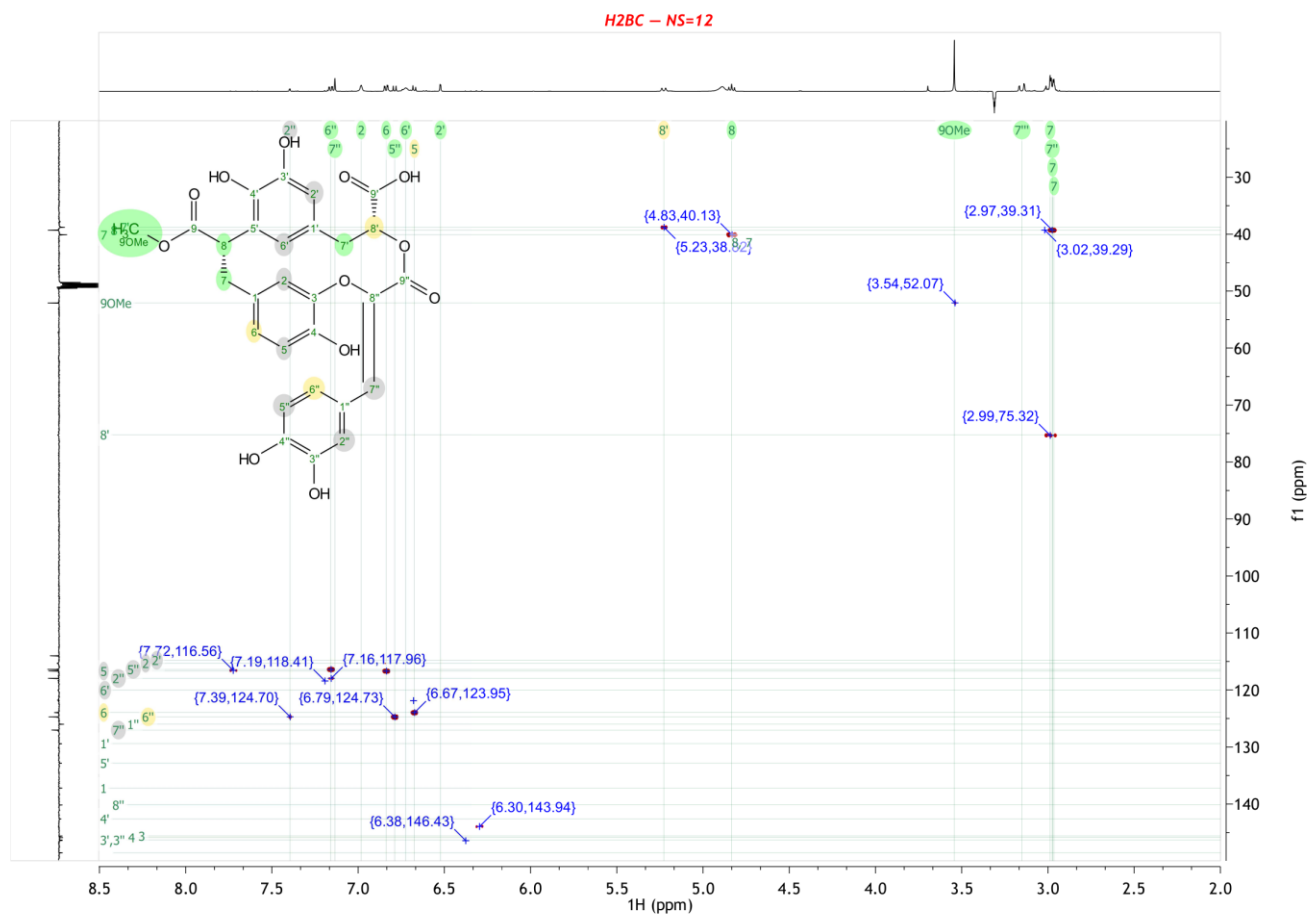


Figure 86S. ^1H - ^{13}C H2BC NMR spectrum of compound 38

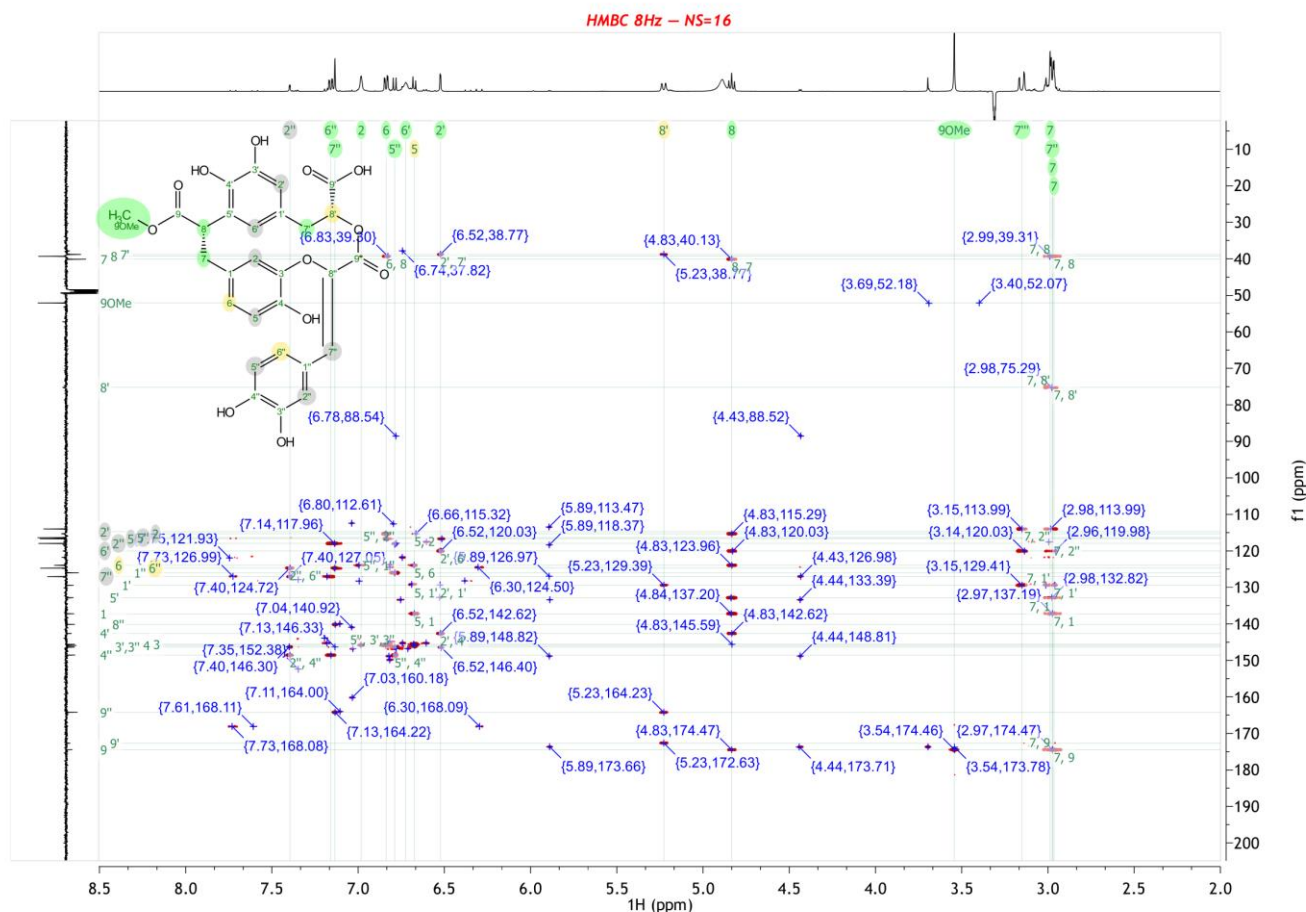
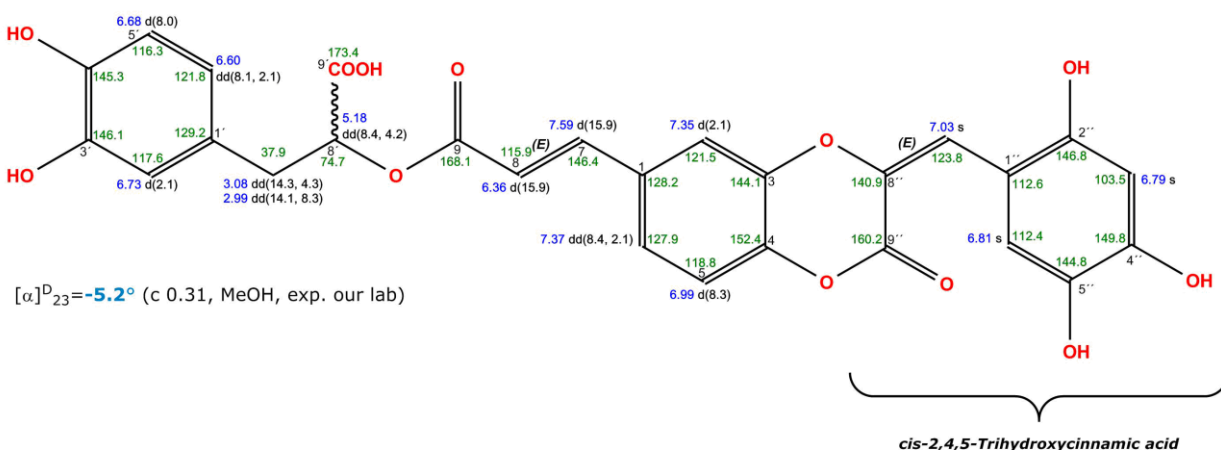


Figure 87S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 38

POAmz535Fr_VIII_p51-52_2
 Chemical Formula: $\text{C}_{27}\text{H}_{20}\text{O}_{12}$
 Molecular Weight: **536.4450**
NEW!

MeOH- d_4 +TFA, 25°C



Quat	CH
173.4	146.4
168.1	127.9
160.2	123.8
152.4	121.8
149.8	121.5
146.8	118.8
146.1	117.6
145.3	116.3
144.8	115.9
144.1	112.4
140.9	103.5
129.2	74.7
128.2	
112.6	
	CH₃
	CH₂
37.9	-

$[\alpha]_{23}^D = -5.2^\circ$ (c 0.31, MeOH, exp. our lab)

Pulmitric acid B

1. Murata, T., Watahiki, M., Tanaka, Y., Miyase, T., Yoshizaki, F., 2010. Hyaluronidase Inhibitors from Takuran, *Lycopus lucidus*. Chem. Pharm. Bull. (Tokyo). 58, 394-397. doi:10.1248/cpb.58.394

Figure 88S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 39 in CD_3OD , 25°C

¹H solv sup – NS=16

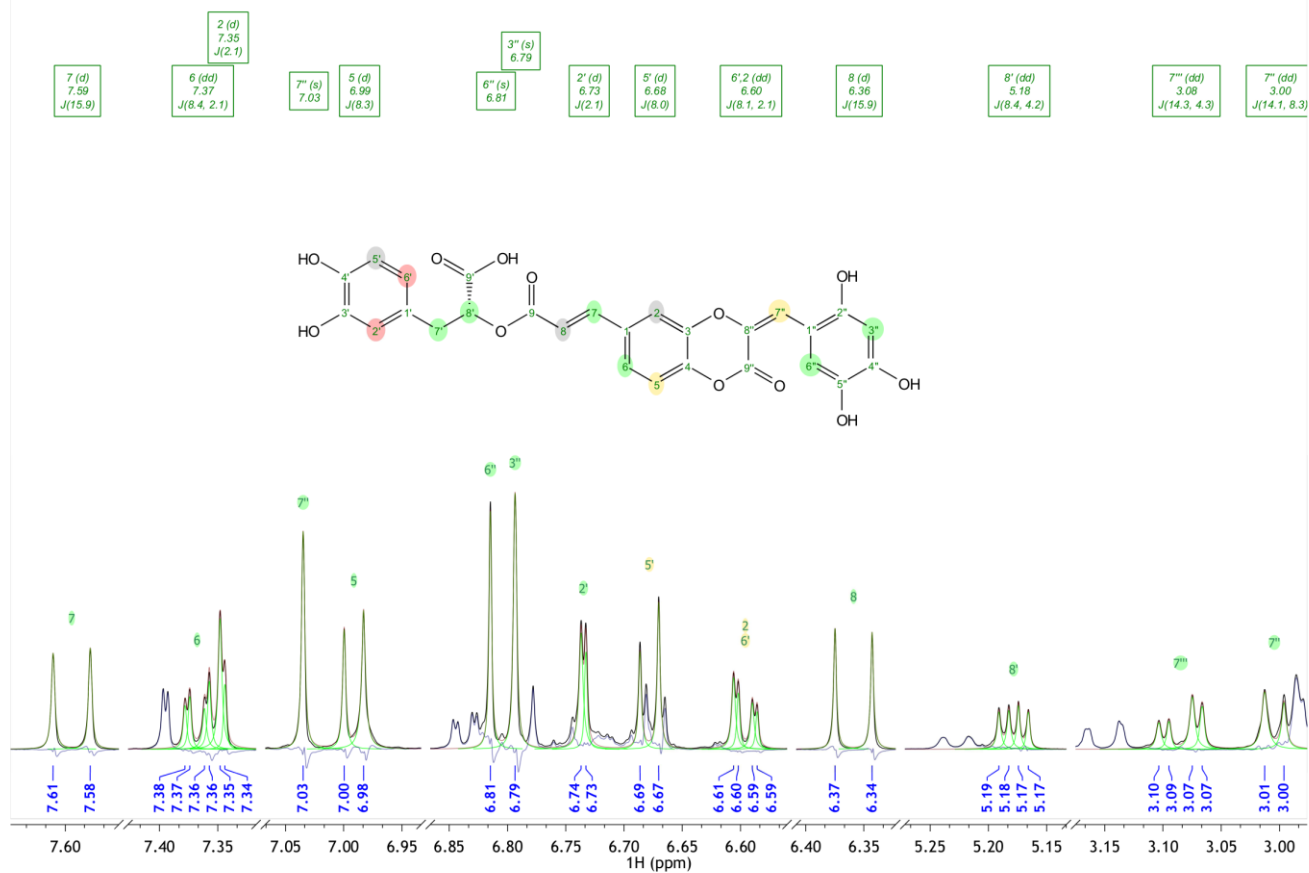


Figure 89S. ¹H NMR spectrum of compound 39

¹³C DEPT Q – NS=4096

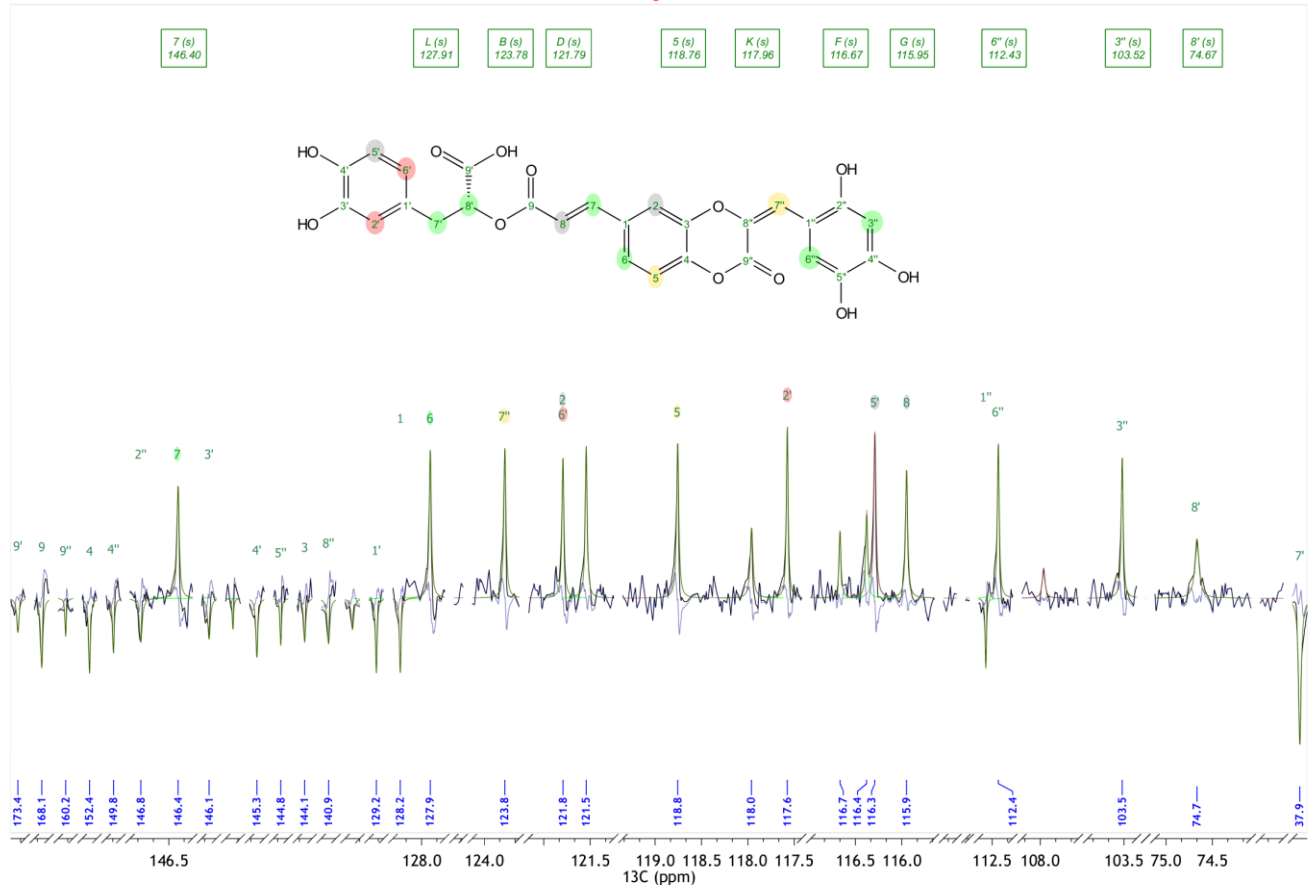


Figure 90S. ¹³C DEPTQ NMR spectrum of compound 39

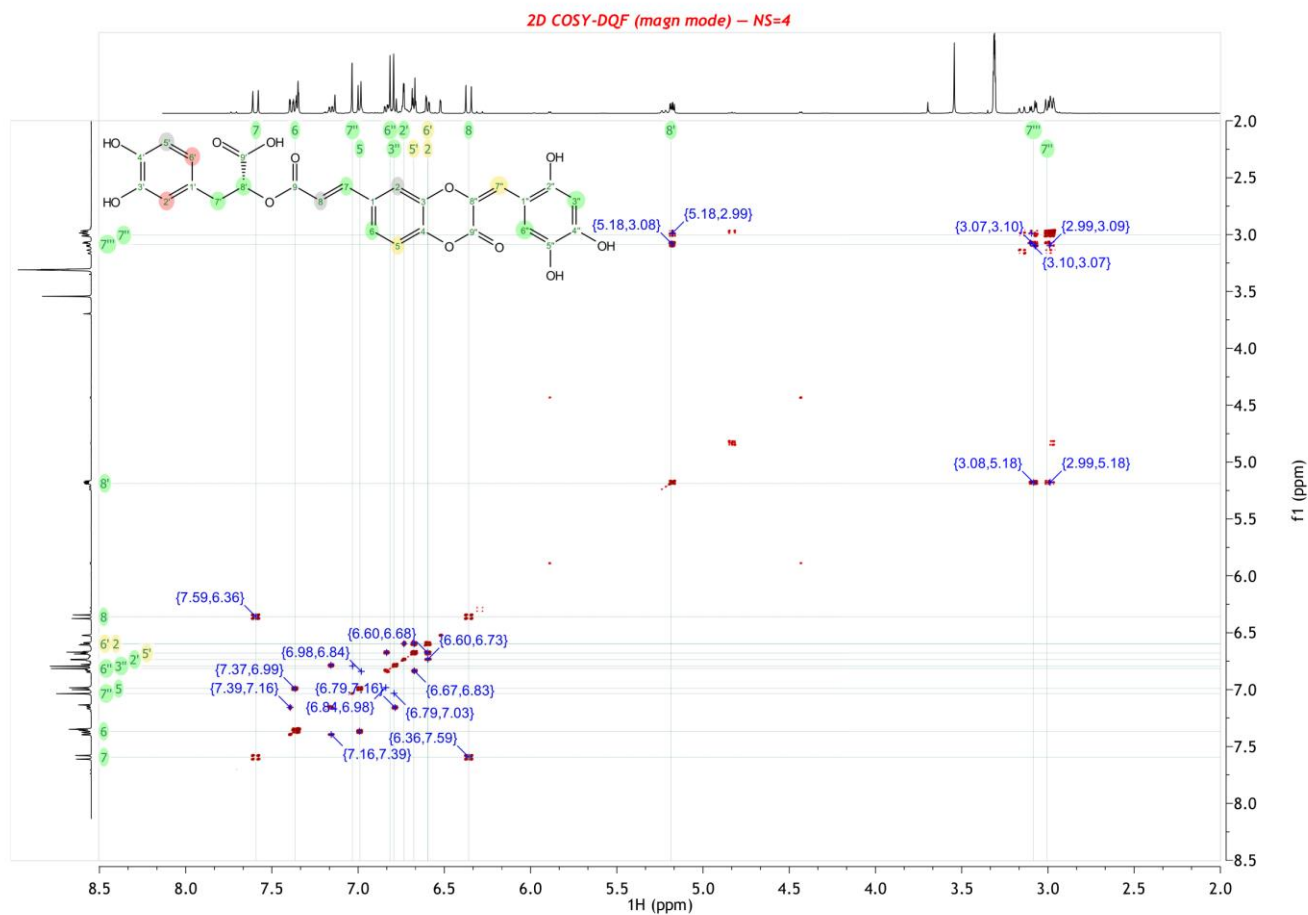


Figure 91S. ^1H - ^1H COSY NMR spectrum of compound 39

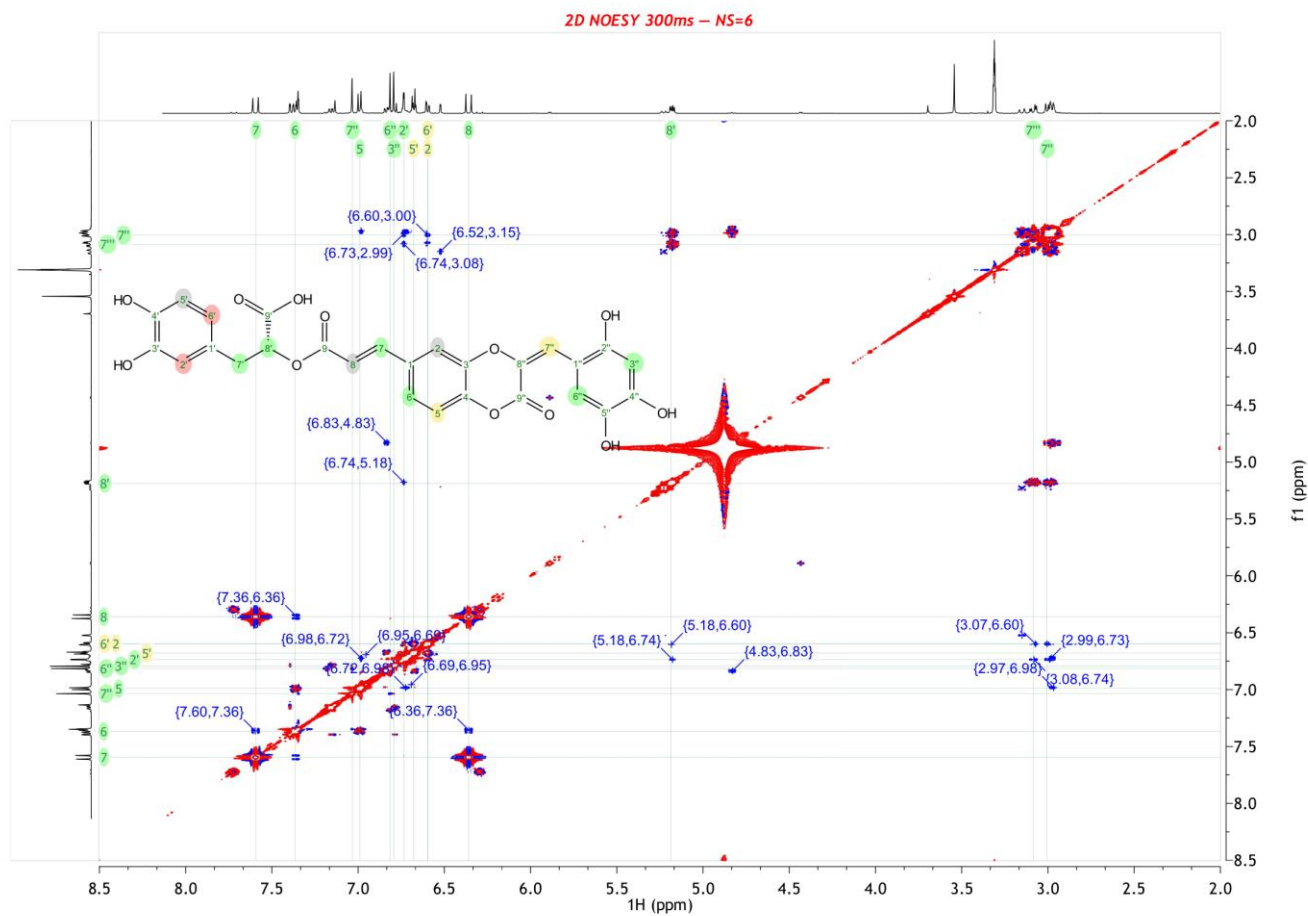


Figure 92S. ^1H - ^1H NOESY (300 ms) NMR spectrum of compound 39

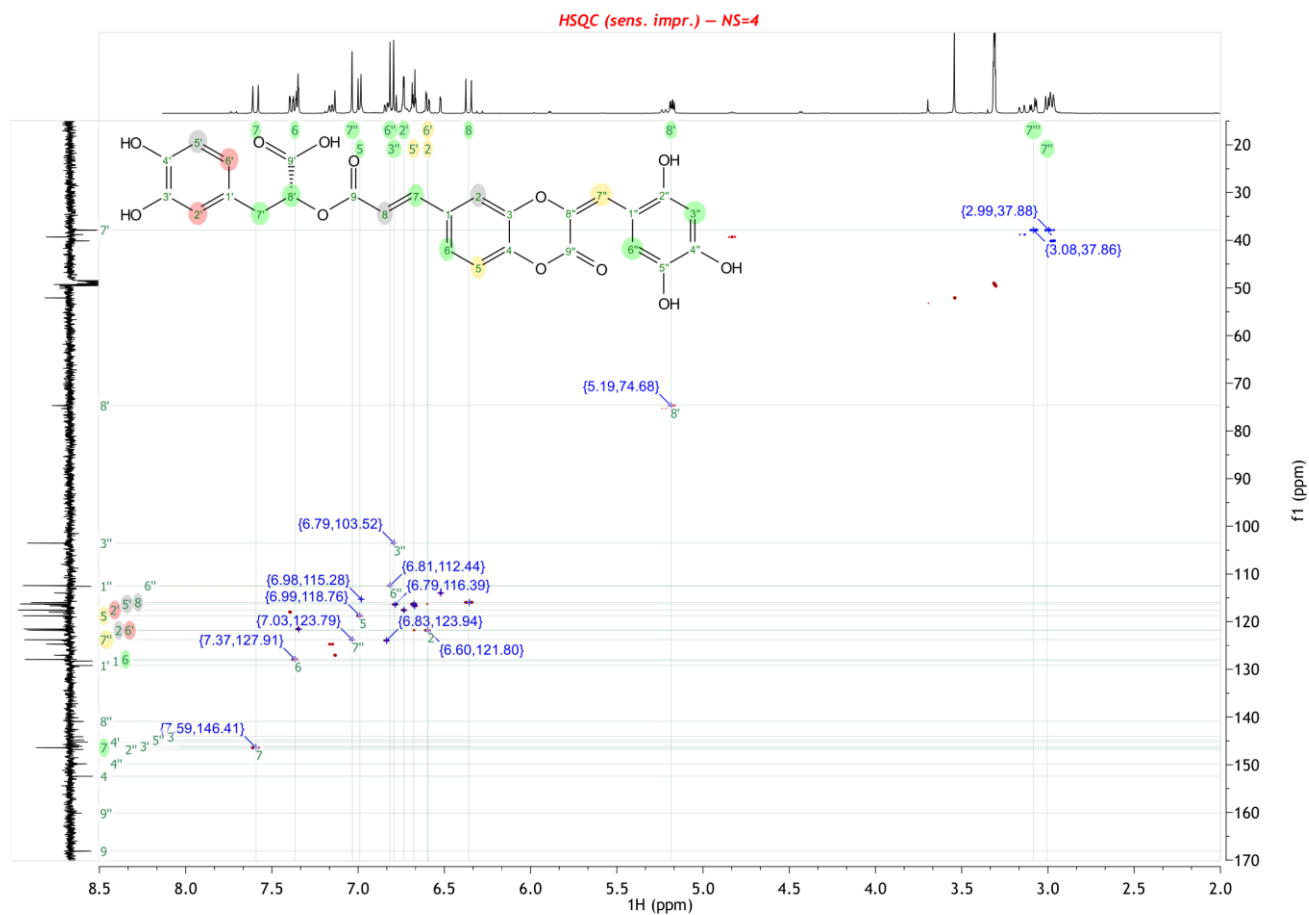


Figure 93S. ^1H - ^{13}C HSQC NMR spectrum of compound 39

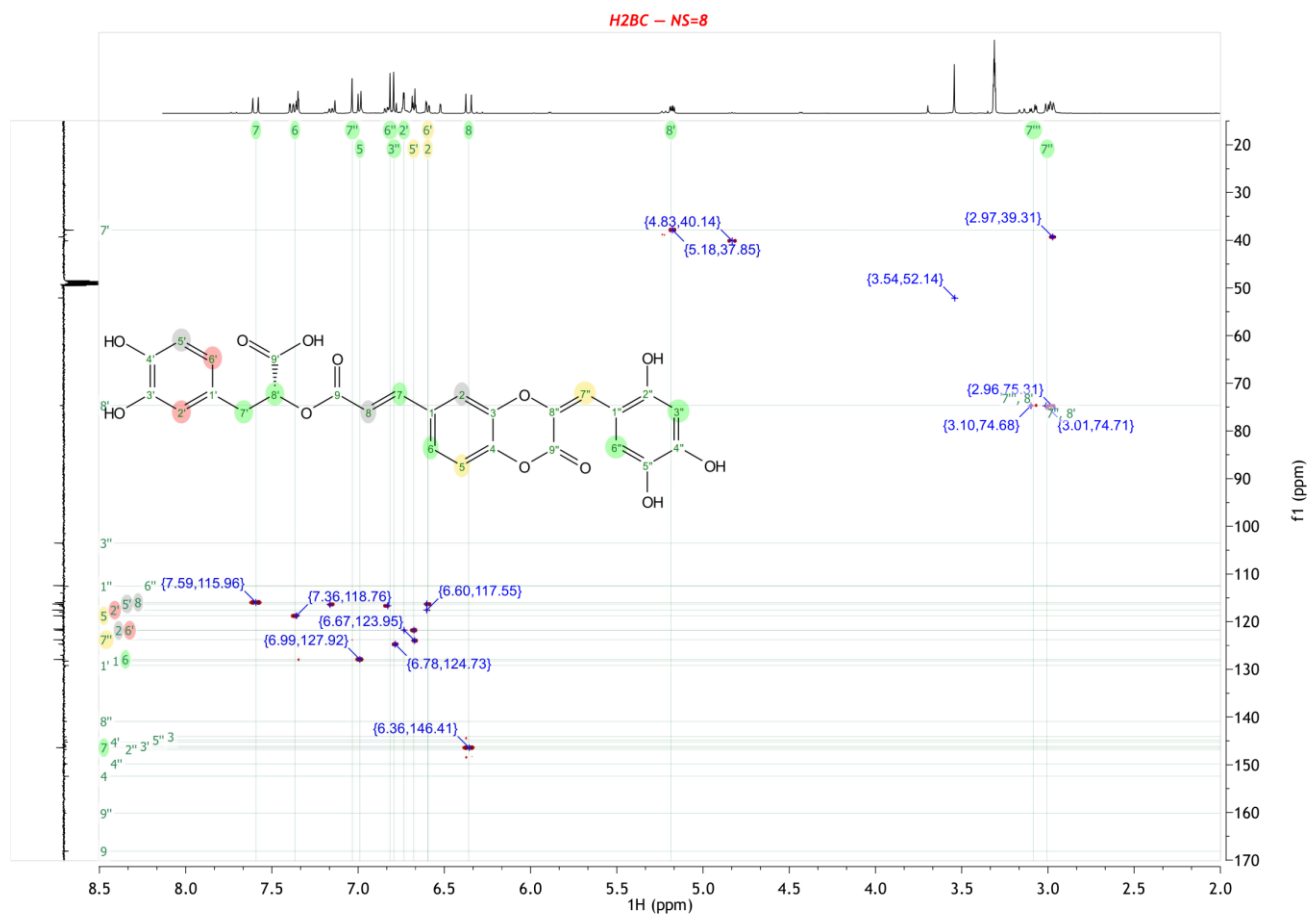


Figure 94S. ^1H - ^{13}C H2BC NMR spectrum of compound 39

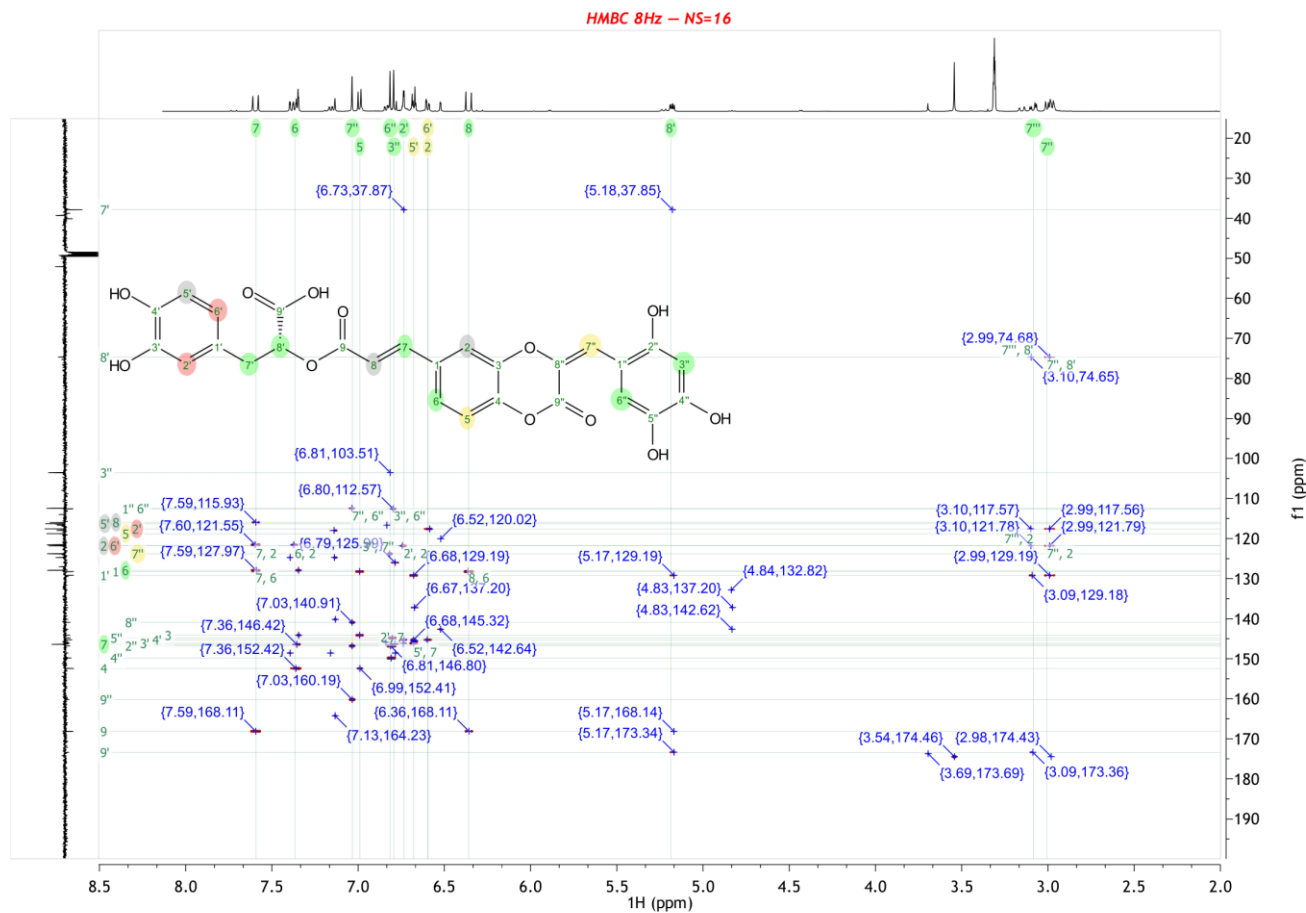
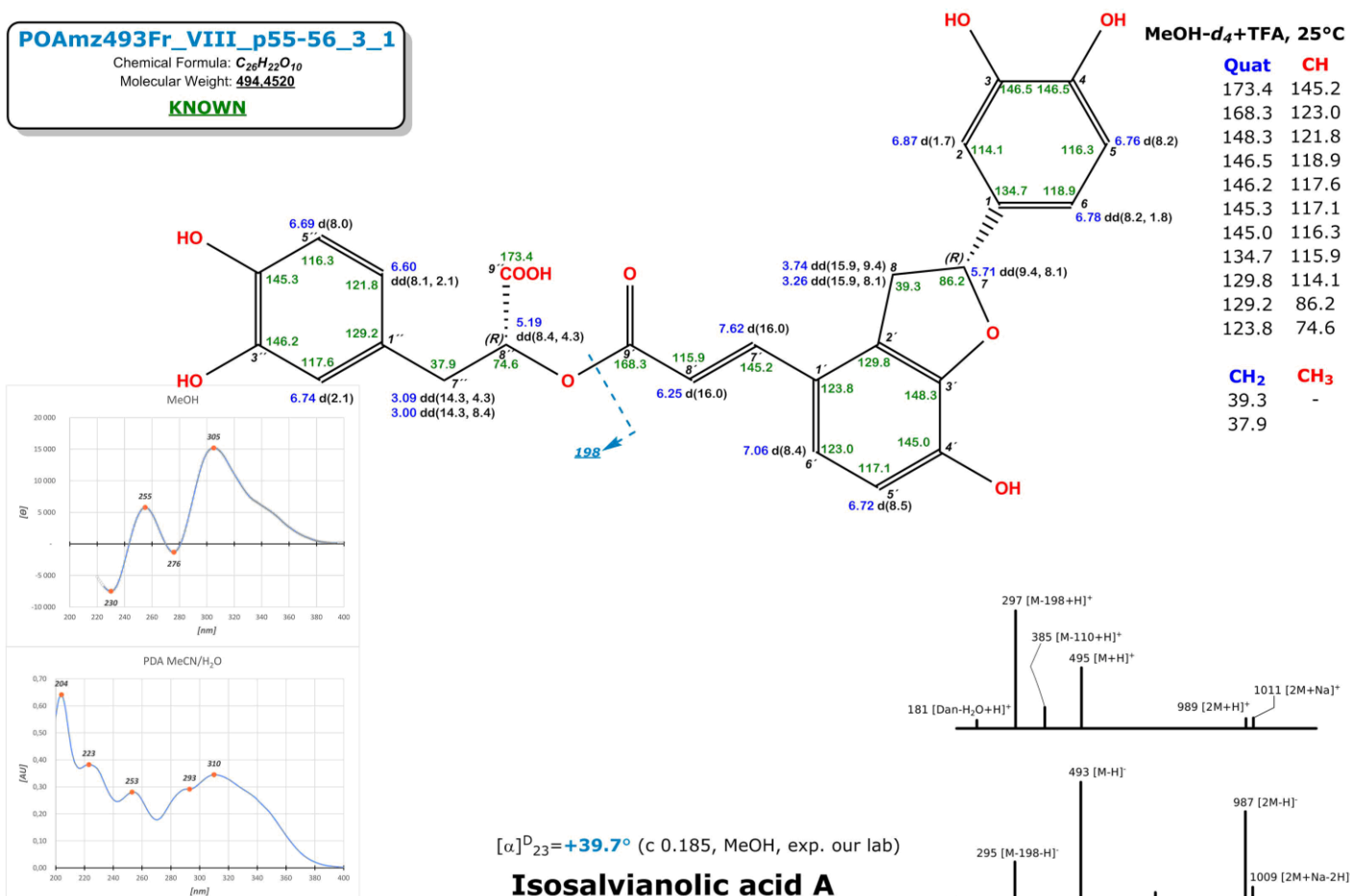


Figure 95S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 39

POAmz493Fr_VIII_p55-56_3_1
 Chemical Formula: $\text{C}_{26}\text{H}_{22}\text{O}_{10}$
 Molecular Weight: 494.4520
KNOWN



1. Lee, H. J.; Cho, J.-Y.; Moon, J.-H. Chemical conversions of salvianolic acid B by decouction in aqueous solution. *Fitoterapia* 2012, 83, 1196–1204, doi:10.1016/j.fitote.2012.06.015.

Figure 96S. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 40 in CD_3OD , 25°C; on-line PDA UV spectrum in $\text{MeCN}/\text{H}_2\text{O}$; ECD spectrum in MeOH

POAmz493Fr_VIII_p55-56_3_2
 Chemical Formula: $C_{26}H_{22}O_{10}$
 Molecular Weight: 494.4520
NEW!

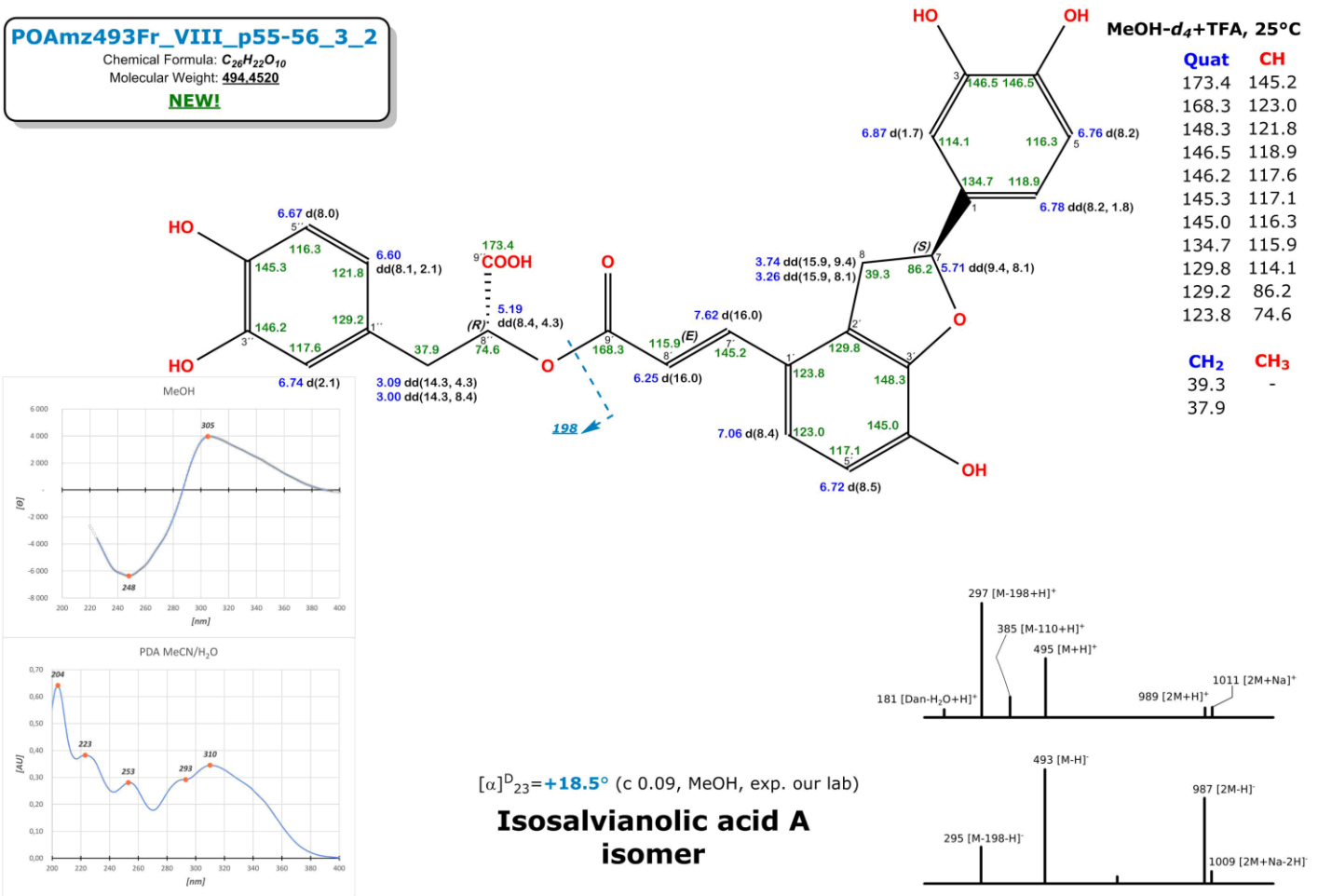
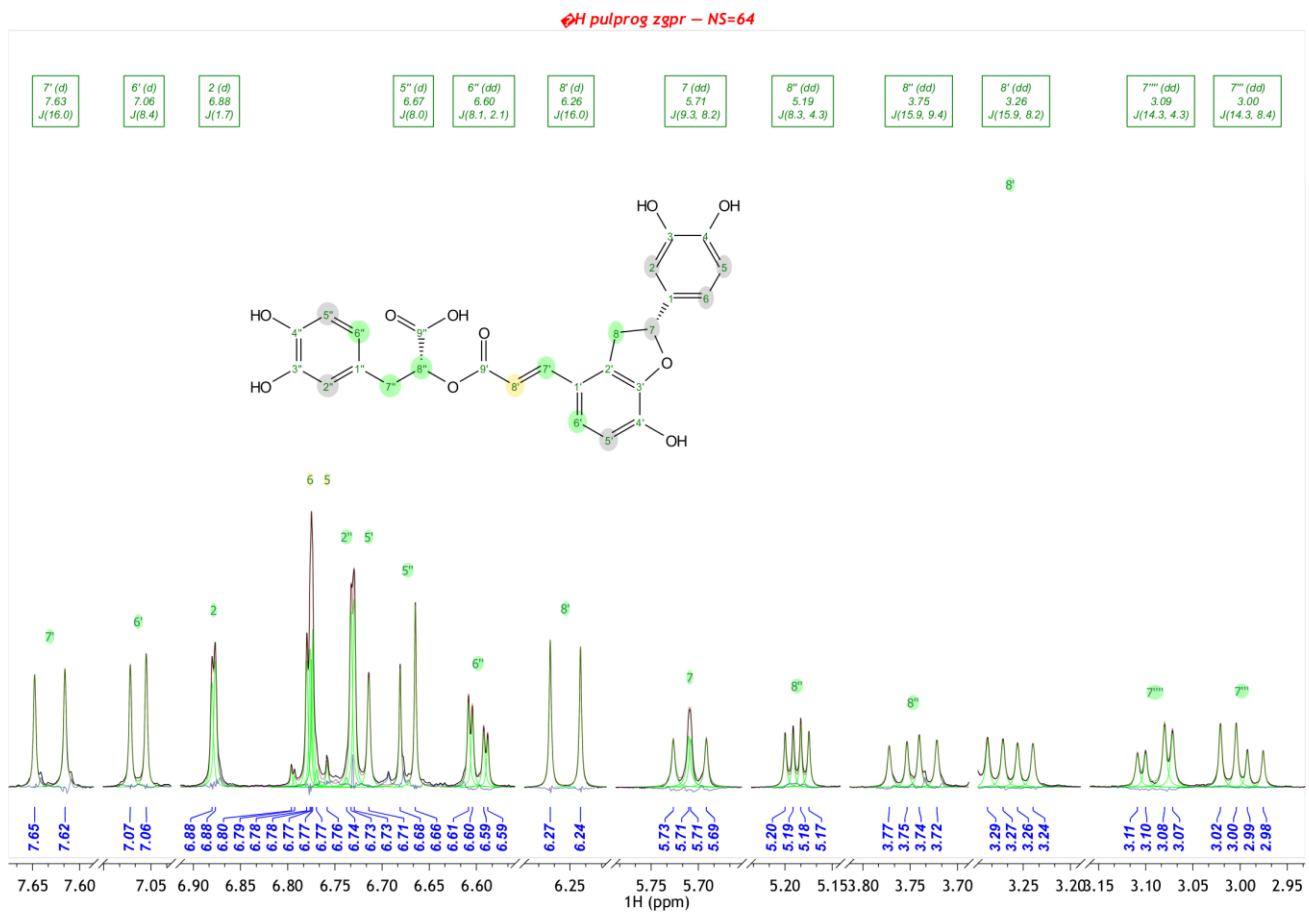


Figure 97S. 1H (500 MHz) and ^{13}C (125 MHz) NMR data of compound 41 in CD_3OD , 25°C; on-line PDA UV spectrum in MeCN/H₂O; ECD spectrum in MeOH



DEPT Q - NS=8192

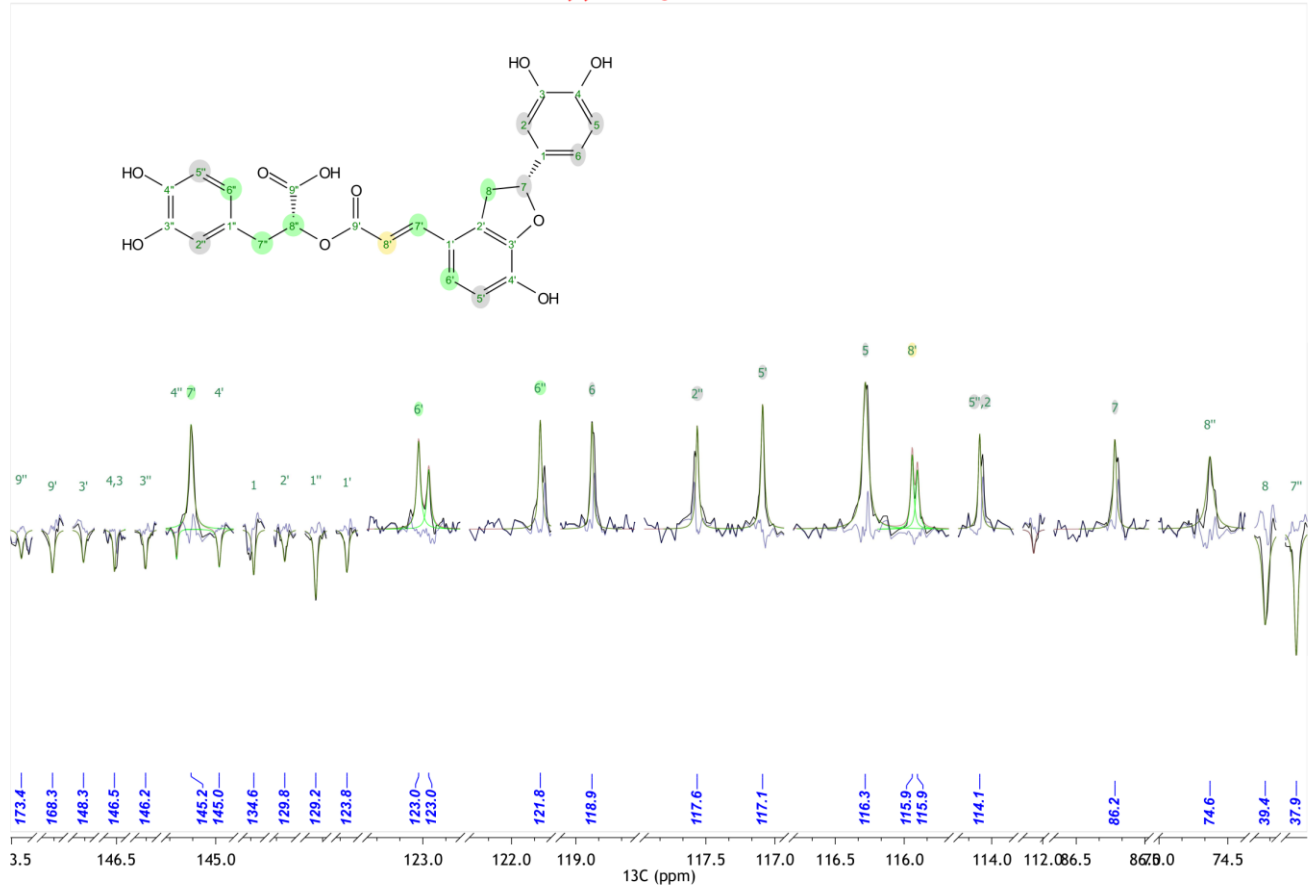


Figure 99S. ¹³C DEPTQ NMR spectrum of compound 41

2D COSY-DQF (magn mode) - NS=4

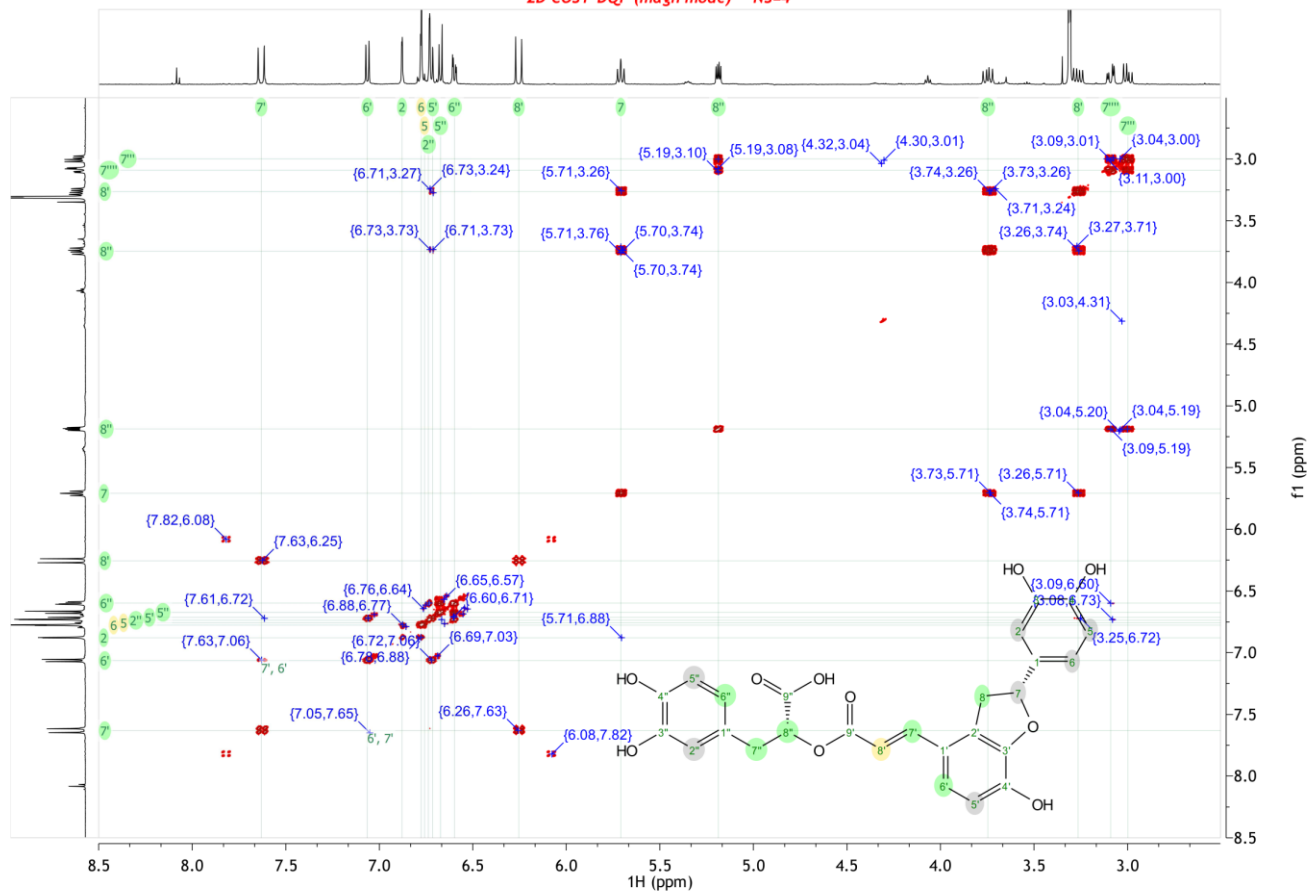


Figure 100S. ¹H-¹H COSY NMR spectrum of compound 41

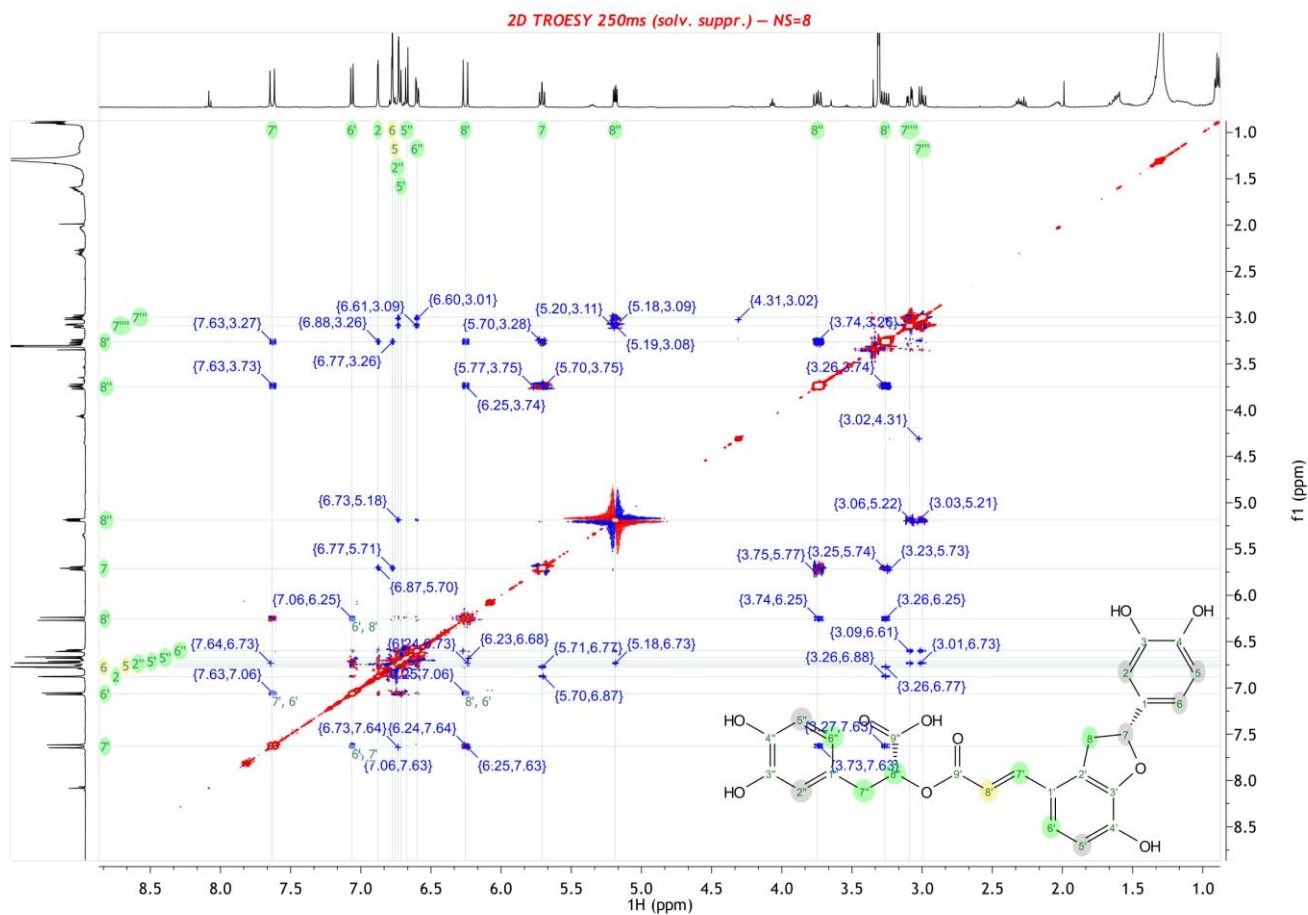


Figure 101S. ^1H - ^1H TROESY (250 ms) NMR spectrum of compound 41

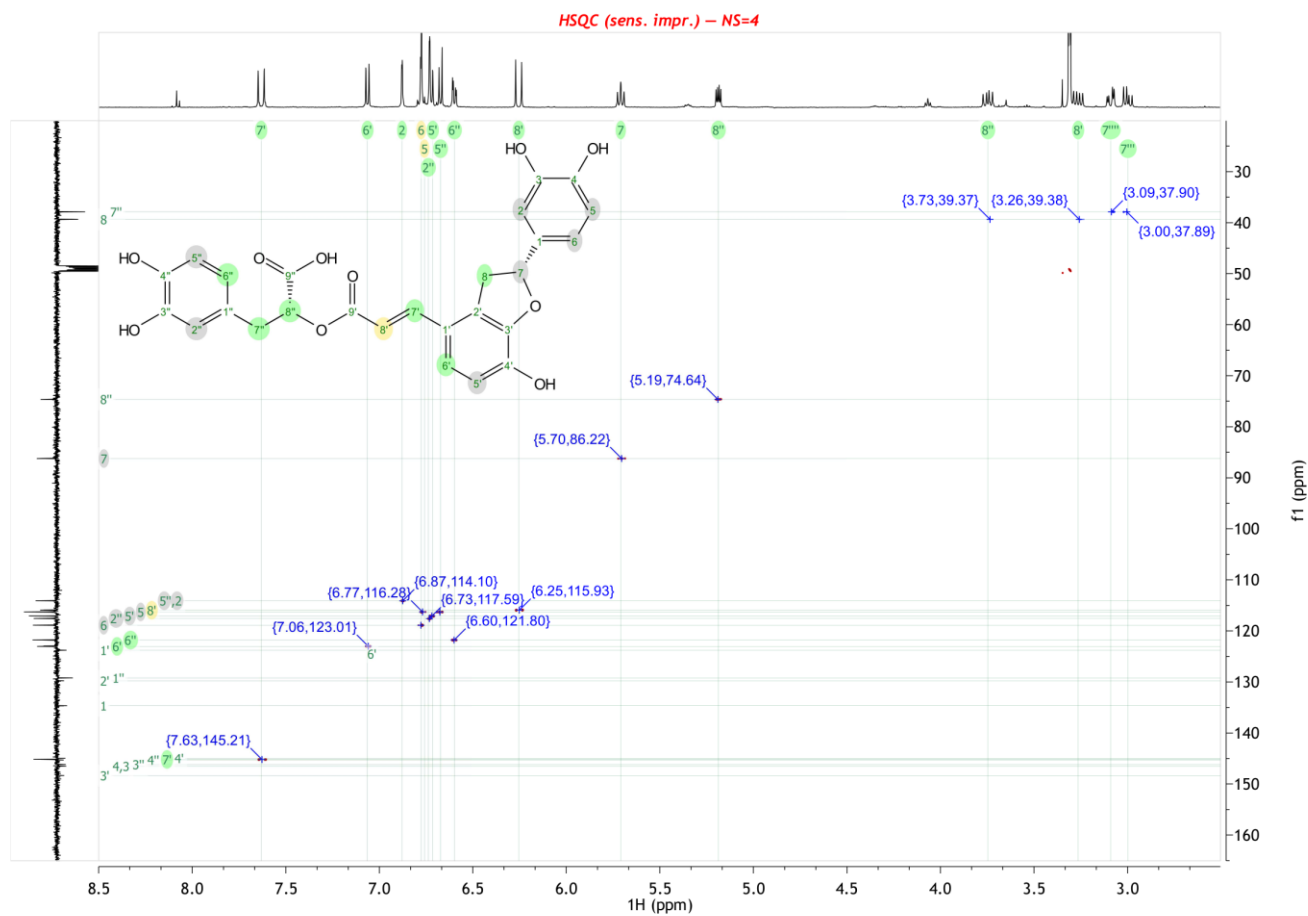


Figure 102S. ^1H - ^{13}C HSQC NMR spectrum of compound 41

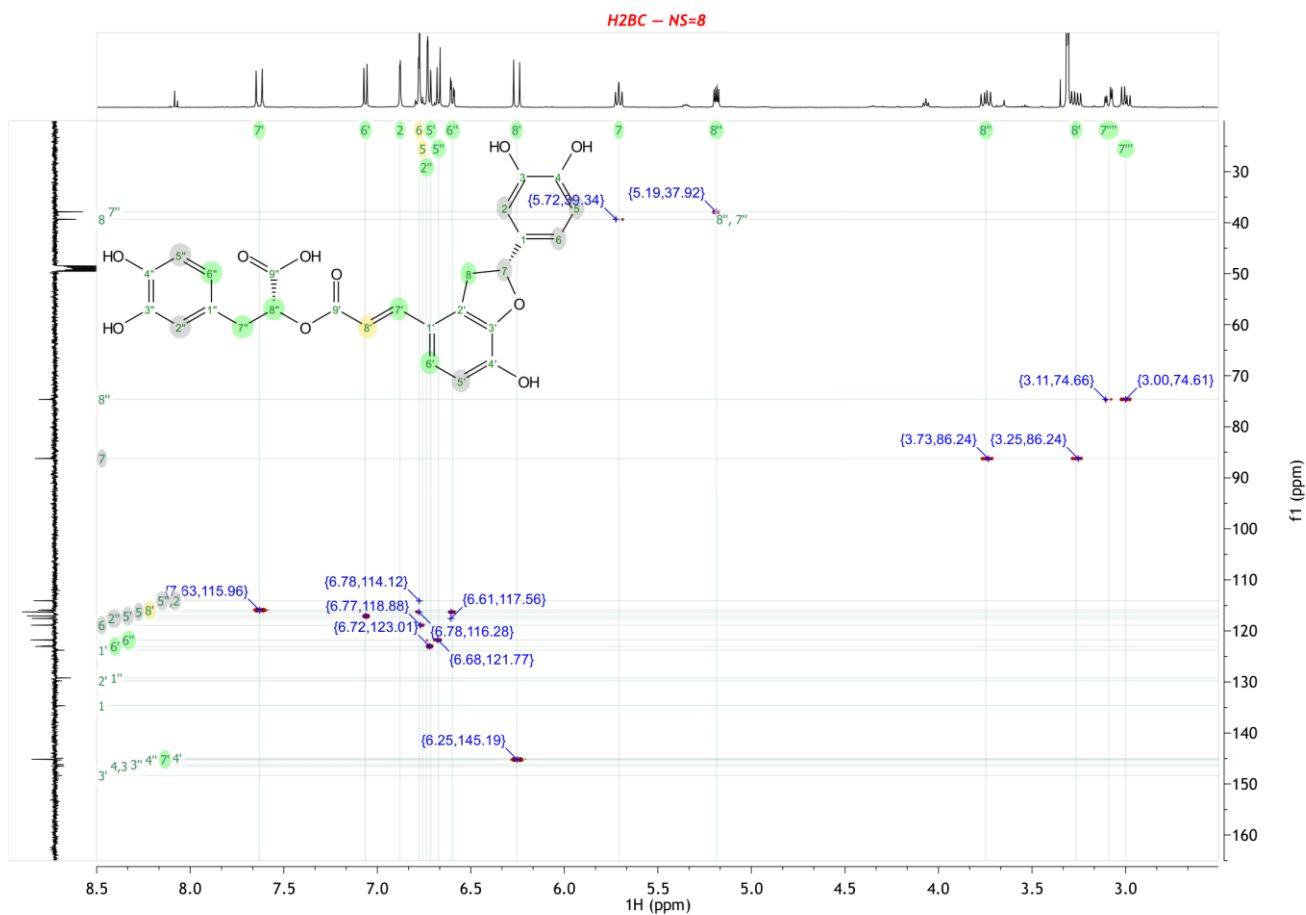


Figure 103S. ^1H - ^{13}C H2BC NMR spectrum of compound 41

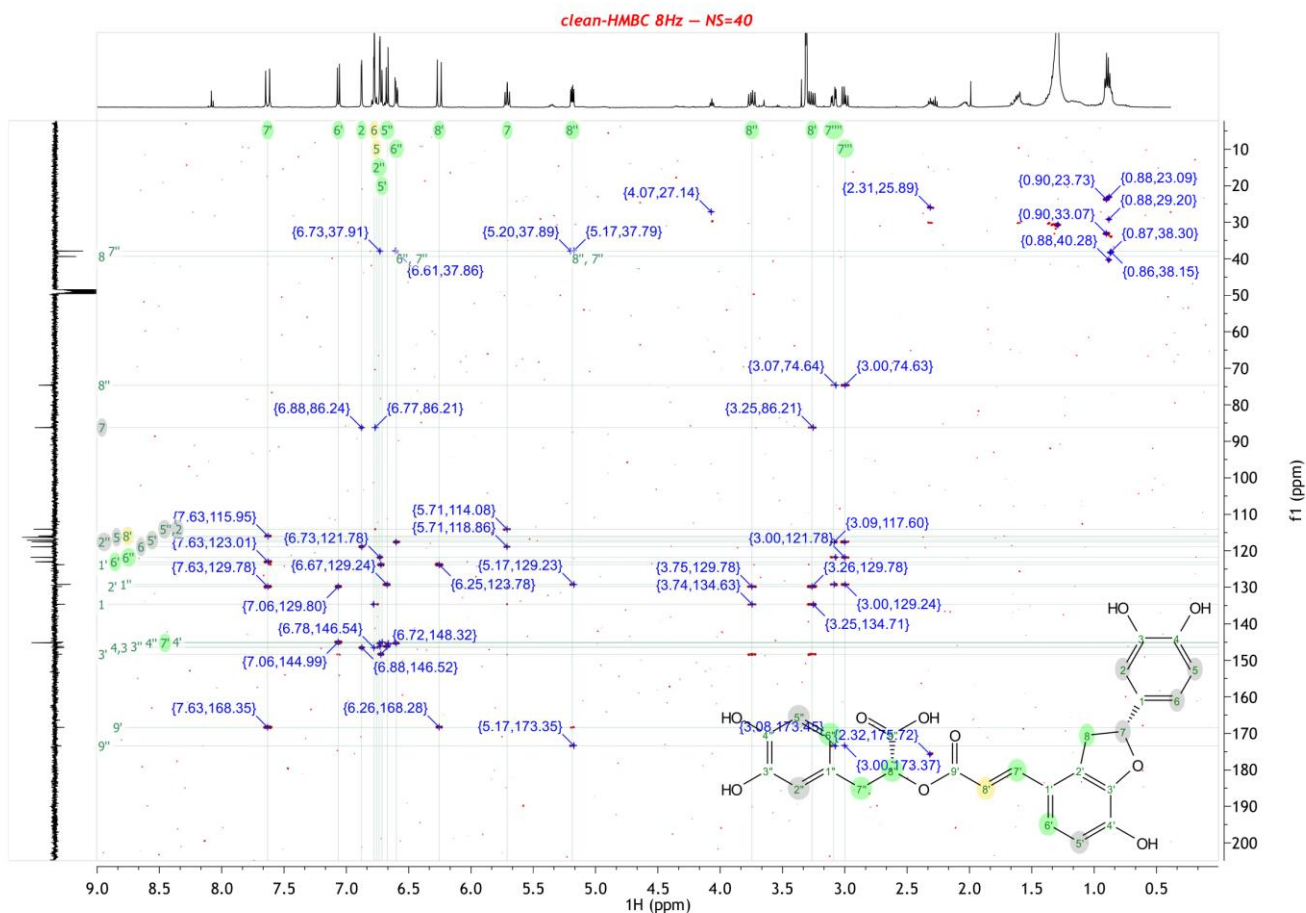
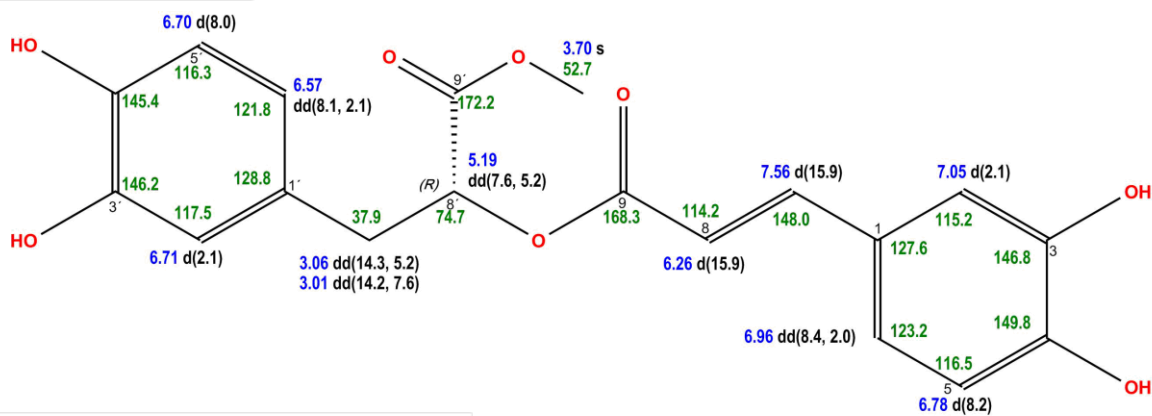
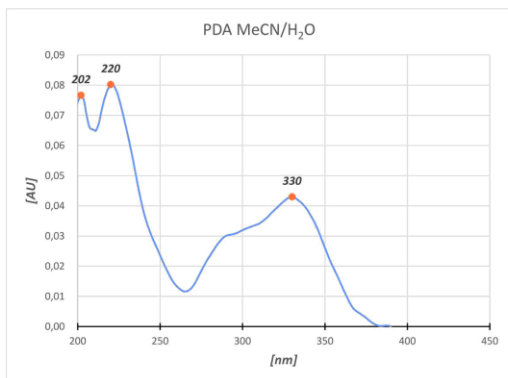


Figure 104S. ^1H - ^{13}C HMBC (8 Hz) NMR spectrum of compound 41

POAmz373Fr_VIII_p45-48_4-5
 Chemical Formula: $C_{19}H_{18}O_8$
 Molecular Weight: 374.3450
KNOWN



CH
 148.0
 123.2
 121.8
 117.5
 116.5
 116.3
 115.2
 114.2
 74.7
CH₃
 52.7



$[\alpha]_{23}^D = +26.6^\circ$ (c 0.26, MeOH, exp. our lab)

Rosmarinic acid methyl ester

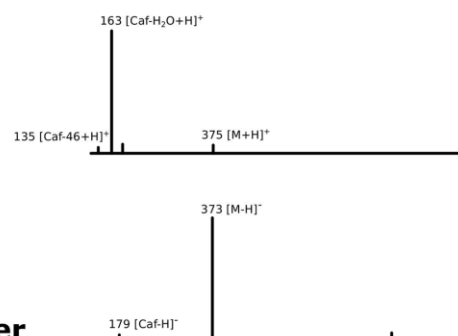
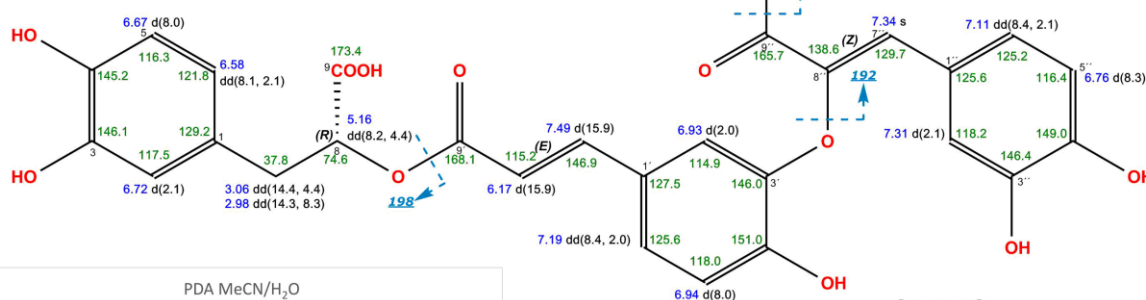


Figure 105S.
 in MeCN/H₂O

¹H (500 MHz) and ¹³C (125 MHz) NMR data of compound 43 in CD₃OD, 25°C; on-line PDA UV spectrum

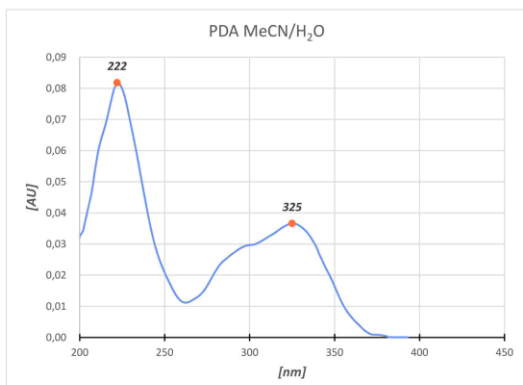
POBmz551Fr_10
 Chemical Formula: $C_{28}H_{32}O_{12}$
 Molecular Weight: 552.4880
KNOWN



MeOH-*d*₄, 25°C

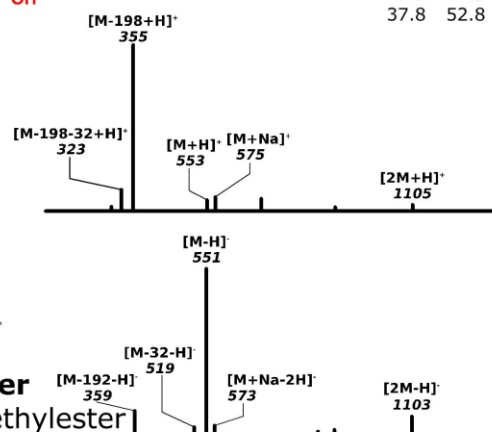
Quat CH
 173.4 146.9
 168.1 129.7
 165.7 125.6
 151.0 125.2
 149.0 121.8
 146.4 118.2
 146.1 118.0
 146.0 117.5
 145.2 116.4
 138.6 116.3
 129.2 115.2
 127.5 114.9
 125.6 74.6

CH₂ CH₃
 37.8 52.8



$[\alpha]_{21}^D = +65.5^\circ$ (c 0.55, MeOH)¹
 ECD (c 0.033 MeOH) / nm ([Δε]):
 206 (-3.94), 251 (6.58), 280 (2.70), 297 (6.34),
 328 (6.67)¹

Salvianolic acid H-9''-methyl ester
 3'-O-(8''-Z-caffeoyl)rosmarinic acid-9''-methyl ester



1. Murata, T., Watahiki, M., Tanaka, Y., Miyase, T., Yoshizaki, F., 2010. Hyaluronidase Inhibitors from Takuran, *Lycopus lucidus*. Chem. Pharm. Bull. (Tokyo). 58, 394-397. doi:10.1248/cpb.58.394

Figure 106S.
 in MeCN/H₂O

¹H (500 MHz) and ¹³C (125 MHz) NMR data of compound 44 in CD₃OD, 25°C; on-line PDA UV spectrum

Table S1.

No.	Compound name	Regression equation	R ²	Calibration range [µg/mL]	LOD [µg/mL]	LOQ [µg/mL]
1	Danshensu	$y=-0.0002x^2+0.0194x+0.0045$	0.9977	0.2-35	0.1	0.4
2	Menisdaurin	$y=-0.0004x^2+0.0374x+0.0067$	0.9987	0.2-35	0.1	0.4
3	3- <i>O</i> -(<i>E</i>)-caffeoyl-L-threonic acid	$y=-0.0024x^2+0.0577x+0.0053$	0.9995	0.2-12	0.1	0.3
4	2- <i>O</i> -(<i>E</i>)-caffeoyl-L-threonic acid	$y=-0.0004x^2+0.0400x+0.0074$	0.9989	0.2-35	0.1	0.4
5	Lycoperodine-1	$y=-0.0006x^2+0.0387x+0.0114$	0.9971	0.2-35	0.1	0.4
6	Chlorogenic acid	$y=-0.0109x^2+0.2568x+0.0126$	0.9998	0.2-12	0.1	0.3
7	Actinidioionoside	$y=-0.0013x^2+0.0762x+0.0342$	0.9937	0.2-12	0.1	0.3
8	Caffeic acid	$y=-0.0003x^2+0.0447x+0.0229$	0.9982	0.2-60	0.1	0.3
9	Cryptochlorogenic acid		Calibrated using compound 6 curve.			
10	3'- <i>O</i> -(<i>E</i>)-Feruoyl- α -sorbopyranosyl-(2' \rightarrow 1)- α -glucopyranoside	$y=-0.004x^2+0.0902x+0.0113$	0.9988	0.2-12	0.1	0.4
11	2- <i>O</i> -(<i>E</i>)-caffeoyl-D-glyceric acid	$y=-0.0004x^2+0.0477x+0.021$	0.9979	0.3-60	0.2	0.6
12	4- <i>O</i> -(<i>E</i>)-caffeoyl-L-threonic acid	$y=-0.005x^2+0.1131x+0.0107$	0.9992	0.2-12	0.1	0.3
13	Neochlorogenic acid	$y=-0.0109x^2+0.2568x+0.0126$	0.9998	0.2-12	0.1	0.3
14	3- <i>O</i> -(<i>E</i>)-caffeoyl-D-glyceric acid	$y=-0.0006x^2+0.0717x+0.0267$	0.9986	0.2-60	0.1	0.3
15	3- <i>O</i> - <i>p</i> -coumaroyl-quinic acid	$y=-0.0015x^2+0.0967x+0.0358$	0.9959	0.2-35	0.1	0.4
16	4- <i>O</i> - <i>p</i> -coumaroyl-quinic acid		Calibrated using compound 15 curve.			
17	5- <i>O</i> - <i>p</i> -coumaroyl-quinic acid		Calibrated using compound 15 curve.			
18	Globoidnan B	$y=-0.0003x^2+0.0489x+0.0157$	0.9989	0.4-60	0.3	0.9
19	Rutin	$y=-0.0012x^2+0.0739x+0.0261$	0.9948	0.2-35	0.1	0.3
20	Nicotiflorin isomer		Calibrated using compound 24 curve.			
21	Quercetin 3- <i>O</i> - β -glucoside	$y=-0.0064x^2+0.1414x+0.0189$	0.9984	0.2-12	0.1	0.3
22	Yunnaneic acid E	$y=-0.0001x^2+0.0077x-0.001$	0.9984	0.5-60	0.4	1.2
23	Quercetin 3- <i>O</i> -(6''- <i>O</i> -malonyl)- β -glucoside	$y=-0.0004x^2+0.0265x+0.009$	0.9944	0.2-35	0.1	0.3
24	Nicotiflorin	$y=-0.0018x^2+0.1125x+0.0327$	0.9966	0.2-35	0.1	0.4
25	Astragaln	$y=-0.002x^2+0.1069x+0.0483$	0.9933	0.2-35	0.1	0.3
26	Shimobashiric acid C	$y=-0.0001x^2+0.0509x+0.0116$	0.9993	0.3-60	0.2	0.9
27	Rosmarinic acid	$y=-0.0001x^2+0.0509x+0.0116$	0.9993	0.2-12	0.1	0.3
28	Kaempferol 3- <i>O</i> -(6''- <i>O</i> -malonyl)- β -glucoside	$y=-0.0004x^2+0.0284x+0.0073$	0.9968	0.2-35	0.1	0.3
29	Monardic acid A	$y=-0.0001x^2+0.0017x+0.0032$	0.9858	0.5-60	0.5	1.5
30	Yunnaneic acid E-1		Not measured			
31	Lithospermic acid A	$y=-0.0001x^2+0.0095x+0.0059$	0.9997	0.2-60	0.3	0.9
32	Pulmonarioside A	$y=-0.0003x^2+0.0331x+0.0145$	0.9975	0.2-60	0.2	0.6
33	Salvianolic acid H	$y=-0.0005x^2+0.0683x+0.0135$	0.9991	0.2-60	0.1	0.3
34	Lithospermic acid B		Not measured			
35	Pulmonarioside B	$y=-0.0002x^2+0.0291x+0.0105$	0.9982	0.2-60	0.1	0.3
36	Yunnaneic acid B	$y=-0.0001x^2+0.0024x-0.0017$	0.9988	0.2-60	0.1	0.3
37	Globoidnan A	$y=-0.0072x^2+0.1572x+0.0108$	0.9995	0.2-12	0.1	0.3
38	Pulmitric acid A	$y=-0.0128x^2+0.2597x+0.0201$	0.9994	0.2-12	0.1	0.3
39	Pulmitric acid B	$y=-0.0026x^2+0.2597x+0.0201$	0.9954	0.2-35	0.1	0.3
40	Isosalvianolic acid A	$y=-0.0117x^2+0.2729x+0.0298$	0.9986	0.2-12	0.1	0.3
41	Isosalvianolic acid A-1		Calibrated using compound 40 curve.			
42	Isosalvianolic acid A isomer		Calibrated using compound 40 curve.			
43	Rosmarinic acid methyl ester	$y=-0.0154x^2+0.3333x+0.0683$	0.9973	0.2-12	0.1	0.3
44	Salvianolic acid H-9''-methyl ester	$y=-0.001x^2+0.0691x+0.0125$	0.9984	0.2-35	0.1	0.3
45	Lycopic acid C		Not measured			

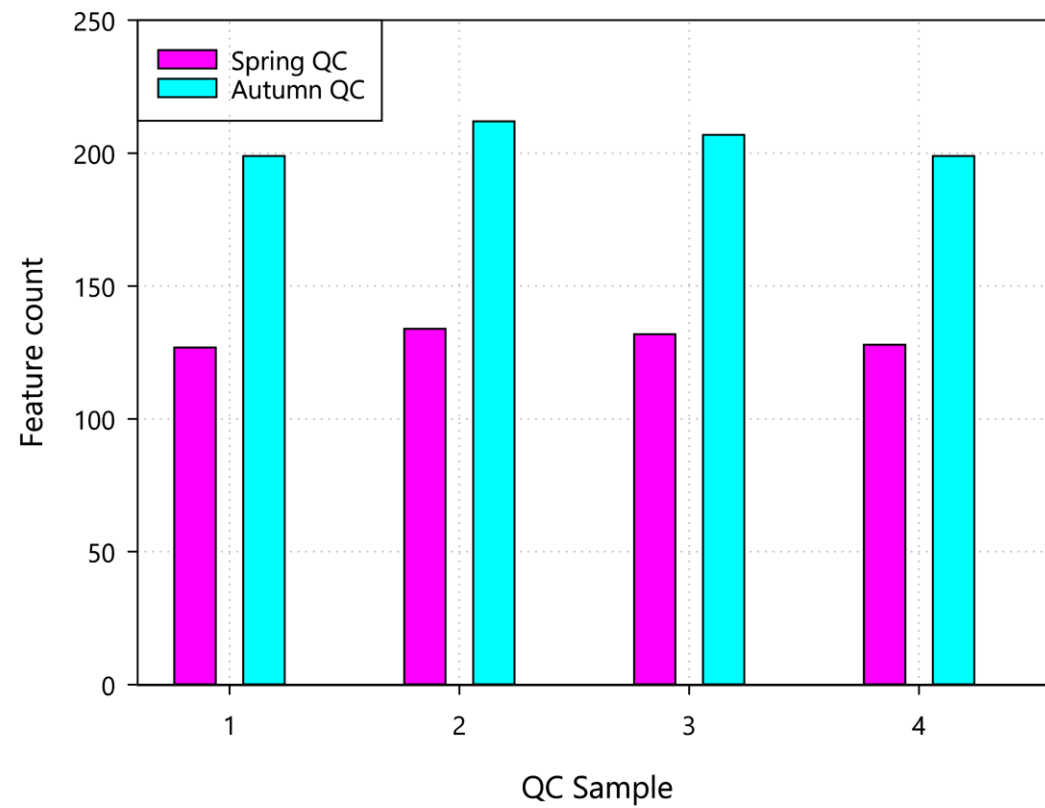
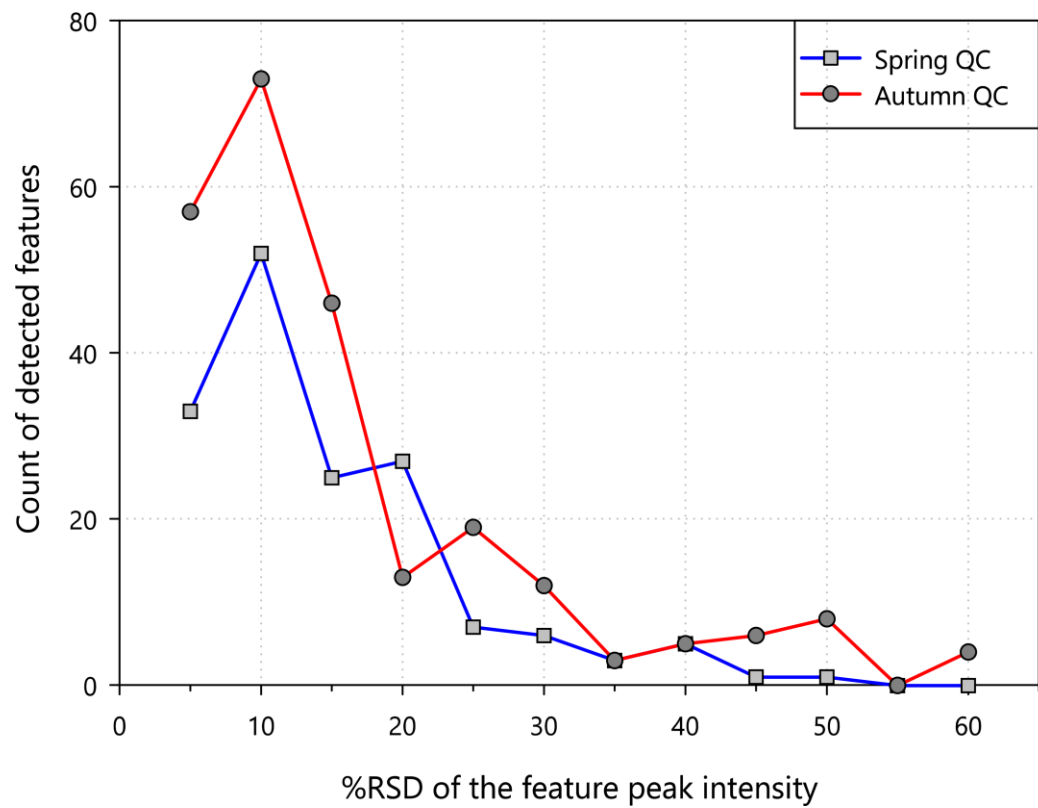


Figure 107S. Frequency distribution of the relative standard deviation for the peak intensities and peak numbers in QC samples