# Electronic Supplementary Information

## Identification of a Highly Promiscuous Glucosyltransferase from *Penstemon barbatus* for natural product glycodiversification

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## 1. Supplementary Tables

**Table S1.** Information of 10 candidates and 6His-MBP tag

| Name. | ORF (bp) | amino acids | Molecular weight(kDa) | enzyme activity |
|---|---|---|---|---|
| 45566 | 1374 | 457 | 50.9 | β1→3 rhamnosyltransferase |
| 43462 | 1455 | 484 | 54.2 | C-4'' OH glycosyltransferase |
| 51909 | 1338 | 445 | 50.4 | No activity |
| 54198 | 1428 | 475 | 54.4 | No activity |
| 43107 | 1371 | 456 | 50.8 | No activity |
| 57483 | 1365 | 454 | 51.3 | No activity |
| 56249 | 1371 | 456 | 51.5 | No activity |
| 56575 | 1425 | 474 | 52.1 | No activity |
| 49774 | 1377 | 458 | 51.8 | No activity |
| 50252 | 1284 | 427 | 47.3 | No activity |
| 6His-Mbp | 1188 | 396 | 43.5 | No activity |

**Table S2.** Primers used in this study

| Name | Sequences (5'-3') |
|---|---|
| MBP_45566_F | AATCCAATATTGGAAGTGGAATGCCTGAATTACAAAAGTCATCAAAAC |
| MBP_45566_R | GGCGCTCGAATTCGGATCCGCTACAATTCATACAAATTCTGAATAAAACTATCAATG |
| MBP_43462_F | AATCCAATATTGGAAGTGGAATGACCGCTGCAGAGAAAAAACAC |
| MBP_43462_R | GGCGCTCGAATTCGGATCCGCTAGATTATTGTATGATCGGTTCCTATCCGG |
| MBP_51909_F | AATCCAATATTGGAAGTGGAATGGAATCAAAATCTATTTTCAGAGTTCTAATG |
| MBP_51909_R | GGCGCTCGAATTCGGATCCGTCATTTCTTCATACAAATGTTTGACAACTGC |
| MBP_54198_F | AATCCAATATTGGAAGTGGAATGTTGATAATTGTAAAAAGAAAACTAGCAAAG |
| MBP_54198_R | GGCGCTCGAATTCGGATCCGCTACTTGTTCTTCATACAAAGTTTCATTAGC |
| MBP_43107_F | AATCCAATATTGGAAGTGGATGAATTTGATGATGAAGAAGAAGAAGAAAATAATTTTAATACC |
| MBP_43107_R | GGCGCTCGAATTCGGATCCGTCAAATAAATTGAGAGAAAGTAGACATTGCTGTAG |
| MBP_57483_F | AATCCAATATTGGAAGTGGAATGGATAATCAAGGTACAACATCTGTTCTGC |
| MBP_57483_R | GGCGCTCGAATTCGGATCCGTTAAGCAGTAGAAGATCTAAATGATGTAATAAAATCAACC |
| MBP_56249_F | AATCCAATATTGGAAGTGGAATGGATACGGTGATAAGAACCTACCC |
| MBP_56249_R | GGCGCTCGAATTCGGATCCGTCAATTAAATGATGAAATATCTTTCAAAAAAGAATCCAAG |
| MBP_56575_F | AATCCAATATTGGAAGTGGAATGTCAGACTCCGGCGCACACATC |
| MBP_56575_R | GGCGCTCGAATTCGGATCCGTCACATTAAACCTTTGTCCAATAAATCTTTGGTG |
| MBP_49774_F | AATCCAATATTGGAAGTGGAATGGACTACCATATTCTTCAAGTAACATTTCCAG |
| MBP_49774_R | GGCGCTCGAATTCGGATCCGTTACCCTTGACAATGCCCACCAAC |
| MBP_50252_F | AATCCAATATTGGAAGTGGAATGGGGATGGAATTGGCTCGAGGG |
| MBP_50252_R | GGCGCTCGAATTCGGATCCGTTACGCCTCAACCAGTTCAACCTTTC |
| T7 | TAATACGACTCACTATAGG |
| T7t | CAAAAAACCCCTCAAGACCCGTTTAGAGGCCCCAAGGGGTTATGCTAG |

**Table S3.** Information of all tested compounds catalyzed by UGT84A95.

| Type | No. | Name | Molecular formula | Molecular weight | CAS number |
|---|---|---|---|---|---|
| PhGs | **1** | Osmanthuside B | $C_{29}H_{36}O_{13}$ | 592.588 | 94492-23-6 |
| | **2** | Verbascoside | $C_{29}H_{36}O_{15}$ | 624.587 | 61276-17-3 |
| | **3** | Forsythoside A | $C_{29}H_{36}O_{15}$ | 624.587 | 79916-77-1 |
| | **4** | Forsythoside B | $C_{34}H_{44}O_{19}$ | 756.702 | 81525-13-5 |
| | **5** | Calceolarioside B | $C_{23}H_{26}O_{11}$ | 478.446 | 105471-98-5 |
| | **6** | Calceolarioside A | $C_{23}H_{26}O_{11}$ | 478.446 | 84744-28-5 |
| | **7** | Echinacoside | $C_{35}H_{46}O_{20}$ | 786.728 | 82854-37-3 |
| flavonoids | **8** | Rutin | $C_{27}H_{30}O_{16}$ | 610.518 | 153-18-4 |
| | **9** | Quercetin | $C_{15}H_{10}O_{7}$ | 302.236 | 117-39-5 |
| | **10** | Icariin | $C_{33}H_{40}O_{15}$ | 676.662 | 489-32-7 |
| | **11** | Orientin | $C_{21}H_{20}O_{11}$ | 448.377 | 28608-75-5 |
| | **12** | Kaempferol | $C_{15}H_{10}O_{6}$ | 286.236 | 520-18-3 |
| | **13** | Eriodictyol | $C_{15}H_{12}O_{6}$ | 288.252 | 552-58-9 |
| terpenoids | **14** | Picroside II | $C_{23}H_{28}O_{13}$ | 512.461 | 39012-20-9 |
| | **15** | Oleuropein | $C_{25}H_{32}O_{13}$ | 540.514 | 32619-42-4 |
| | **16** | Ginsenoside Re | $C_{48}H_{82}O_{18}$ | 947.154 | 52286-59-6 |
| | **17** | Ginsenoside Rg1 | $C_{42}H_{72}O_{14}$ | 801.013 | 22427-39-0 |
| | **18** | Paclitaxel | $C_{47}H_{51}NO_{14}$ | 853.906 | 33069-62-4 |
| Stilbene glycosides | **19** | 2,3,5,4'-Tetrahydroxy stilbene 2-O-β-D-glucoside | $C_{20}H_{22}O_{9}$ | 406.383 | 82373-94-2 |
| coumarins | **20** | alloisoimperatorin | $C_{16}H_{14}O_{4}$ | 270.280 | 35214-83-6 |
| | **21** | Umbelliferone | $C_{9}H_{6}O_{3}$ | 162.142 | 93-35-6 |
| | **22** | Scopoletin | $C_{10}H_{8}O_{4}$ | 192.168 | 92-61-5 |
| | **23** | Isoscopoletin | $C_{10}H_{8}O_{4}$ | 192.168 | 776-86-3 |
| | **24** | Esculetin | $C_{9}H_{6}O_{4}$ | 178.141 | 305-01-1 |
| | **25** | 7-demethylsuberosin | $C_{14}H_{14}O_{3}$ | 230.259 | 21422-04-8 |
| simple polyphenols | **26** | Caffeic acid | $C_{9}H_{8}O_{4}$ | 180.157 | 331-39-5 |
| | **27** | ferulic acid | $C_{10}H_{10}O_{4}$ | 194.184 | 1135-24-6 |
| | **28** | Resveratrol | $C_{14}H_{12}O_{3}$ | 228.243 | 501-36-0 |

**Table S4.** HPLC conditions used in this study.

| Method | Solvent A | Solvent B | Gradient Analysis | Substrates |
|---|---|---|---|---|
| A | $H_2O$ containing 0.1% formic acid | Acetonitrile | 5% B, 5min; 5-13.2%B, 13min; 18-21.6%B, 25min; 100%B, 7min; 5%B, 7min. | **1**, **2**, **6**, **7** |
| B | $H_2O$ containing 0.1% formic acid | Acetonitrile | 5% B, 5min; 5-52.5%B, 20min; 100%B, 7min; 5%B, 7min. | **3**, **4**, **5**, **8–28** |

**Table S5.** Information of large-scale reactions and purification.

| **Substrate (No)** | **reaction volumes** | **Reaction time(h)** | **gradient conditions** | **UV (nm)** | **product No. – Weight (mg)** |
|---|---|---|---|---|---|
| **1** | 1mL×15 | 5 | 18% B, 5 min; 18-19.5% B, 15 min;100 B, 10 min; 18% B, 10min; | 312 | **1a**–5.5<br>**1b**–3.2 |
| **2** | 1mL×20 | 5 | 17.5% B, 5 min; 17.5-19% B,15 min;100 B, 10 min; 17.5% B, 10min; | 312 | **2a**–4.5<br>**2b**–1.5 |
| **3** | 1mL×15 | 5 | 15% B, 12 min; 100% B, 8 min; 15% B, 8 min; | 312 | **3a**–3.7 |
| **4** | 1mL×20 | 24 | 15% B, 12 min; 100% B, 8 min; 15% B, 8 min; | 312 | **4a**–3.3 |
| **5** | 1mL×15 | 5 | 16% B, 10 min; 16-16.5% B, 5 min; 100% B, 8 min; 16% B, 8 min; | 312 | **5a**–3.9 |
| **8** | 1mL×15 | 5 | 15% B, 12 min; 100% B, 8 min; 15% B, 8 min; | 254 | **8a**–2.8 |
| **9** | 1mL×30 | 7 | 16% B, 7 min; 16-24% B, 20 min; 100% B, 8 min; 16% B, 8 min; | 254 | **9b**–4.5<br>**9c**–1.2<br>**9d**–3.4 |
| **14** | 1mL×15 | 5 | 14% B, 10 min; 100% B, 8 min; 14% B, 8 min; | 254 | **14a**–6.5 |
| **15** | 1mL×40 | 24 | 18.5% B, 8min; 19% B, 13 min; 100% B, 8 min;18.5% B, 8 min; | 254 | **15a**–6.0 |

**Table S6.** The sugar donor specificity of UGT84A95. Different substrates (**2**, **8**, **14**, **21**) were selected as acceptor substrates. " √ " means that the enzymatic reactions could be catalyzed by UGT84A95.

| | UDP-Glc | UDP-GlcA | UDP-Xyl | UDP-Rha | UDP-GlcNAc | UDP-Gal |
|---|---|---|---|---|---|---|
| **2** | √ | | | | | |
| **8** | √ | | √ | | | √ |
| **14** | √ | | | | | √ |
| **21** | √ | | √ | | | √ |

**Table S7.** Information of reported plant UGTs with characterized functions that are used for the phylogenetic analysis in this study.

| Name | Source | Genbank | Reference |
|---|---|---|---|
| FaGT2 | Fragaria anana | Q66PF4.1 | 1 |
| VLRSgt | Vitis labrusca | ABH03018.1 | 2 |
| UGT84A77 | Canarium album | QZM06937.1 | 3 |
| UGT84A23 | Punica granatum | ANN02875.1 | 4 |
| UGT84A34 | Nemophila menziesii | BBA68563.1 | 5 |
| DcUSAGT1 | Daucus carota | AMC33112.1 | 6 |
| UGT84A33 | Carthamus tinctorius | AYW01718.1 | 7 |
| UGT84A9a | Gentiana triflora | BAQ19550 .1 | 8 |
| UGT73A4 | Beta vulgaris | AAS94329 | 9 |
| UGT84F1 | Medicago truncatula | ABI94023.1 | 10 |
| UGT84F6 | Glycyrrhiza uralensis | QDM38904.1 | 11 |
| UGT84F9 | Medicago truncatula | XP_013470035.1 | 12 |
| GgSGT | Gomphrena globosa | BAG14302.1 | 13 |
| UGT84A9 | Brassica napus var. napus | CAS03354 .1 | 14 |
| UGT84A2 | Arabidopsis thaliana | NP_188793.1 | 15 |
| UGT84A1 | Arabidopsis thaliana | Q5XF20 | 15 |
| UGT84A57 | Eutrema japonicum | BBI55602.1 | 16 |
| UGT84B1 | Arabidopsis thaliana | NP_179907.1 | 17 |
| GAGT | Solanum lycopersicum | CAI62049.1 | 18 |
| UGT74M1 | Nicotiana tabacum | AAF61647.1 | 19 |
| UGT74F2 | Arabidopsis thaliana | NP_181910.1 | **20** |
| PgUGT8 | Panax ginseng | AIE12488.1 | 21 |
| UGT74M1 | Gypsophila vaccaria | ABK76266 | 22 |
| LOC542250 | Zea mays | AAA59054 | 23 |
| UGT74H5 | Avena strigosa | ACD03250 | 24 |
| UGT74F11 | Oryza sativa Japonica Group | 5TME | 25 |
| HvUGT13248 | Hordeum vulgare subsp. vulgare | ADC92550 | 26 |
| Bradi5g03300 | Brachypodium distachyon | PNT60691.1 | 27 |
| UGT723F9 | Crocus sativus | ACM66950.1 | 28 |
| UGT75C1 | Arabidopsis thaliana | AAL69494.1 | 29 |
| UGT75B1 | Arabidopsis thaliana | AEE27854 | 30 |
| UGT75D1 | Arabidopsis thaliana | AAB58497.1 | 15 |

## 2. Supplementary Figures

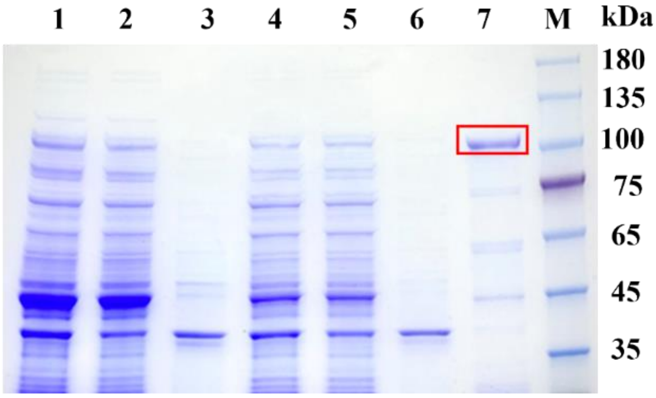


**Figure S1. SDS-PAGE analysis of expression of His-MBP-UGT84A95 fusion protein.**

Lane 1 ,2 and 3: Cell lysate, Supernatant and Precipitation of His-MBP.

Lane 4 ,5 and 6: Cell lysate, Supernatant and Precipitation of His-MBP-UGT84A95.

Lane 7: His-MBP-UGT84A95 purified by Ni-NTA affinity chromatography.

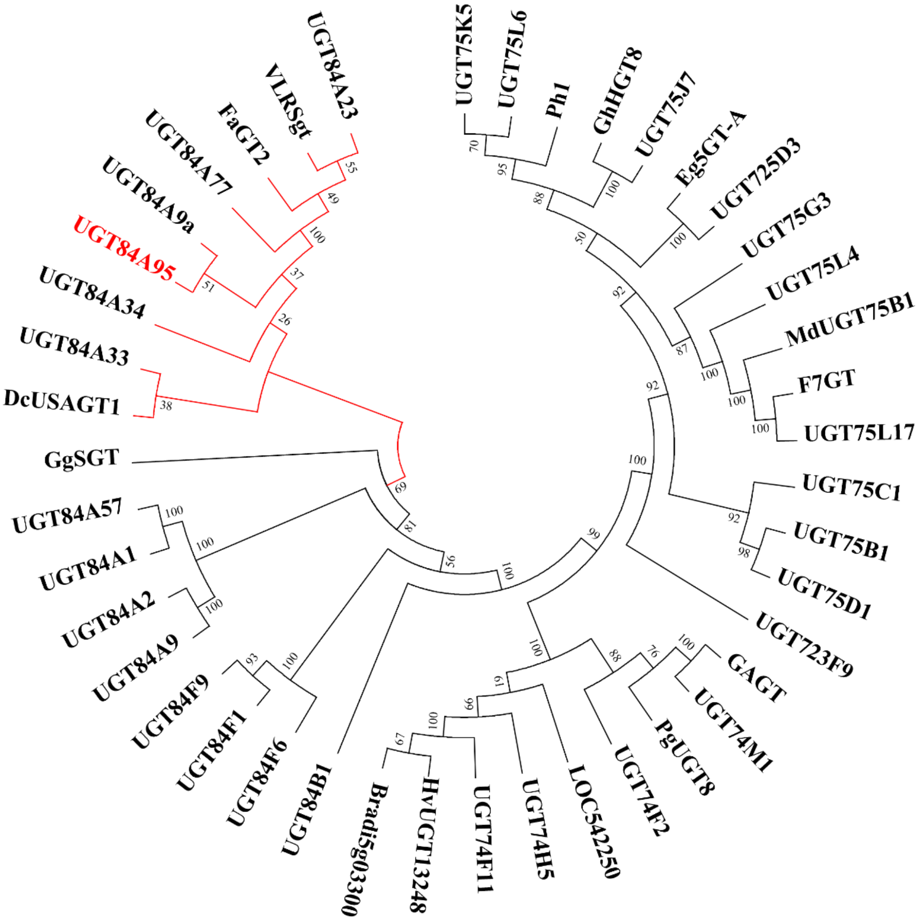


**Figure S2.** The phylogenetic relationships between UGT84A95 and the reported plant UGTs with characterized functions. The accession numbers of the sequences used in this study are shown in Table S6. The protein sequences were aligned using ClustalW. The neighbour-joining phylogenetic tree was drawn using MEGA 7. The bootstrap value was 1000, and the branch lengths represent the relative genetic distances.

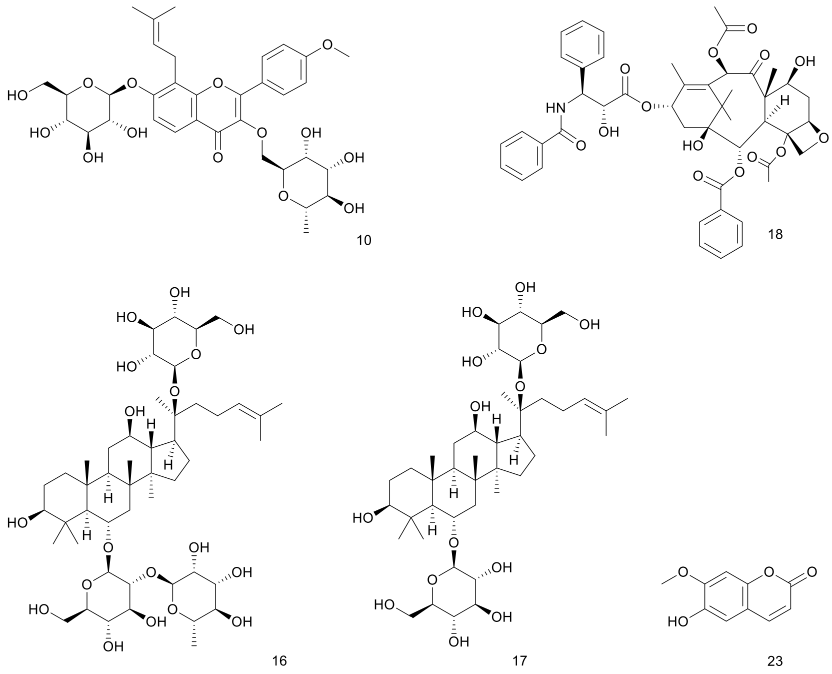


**Figure S3.** The compounds are not accepted by UGT84A95

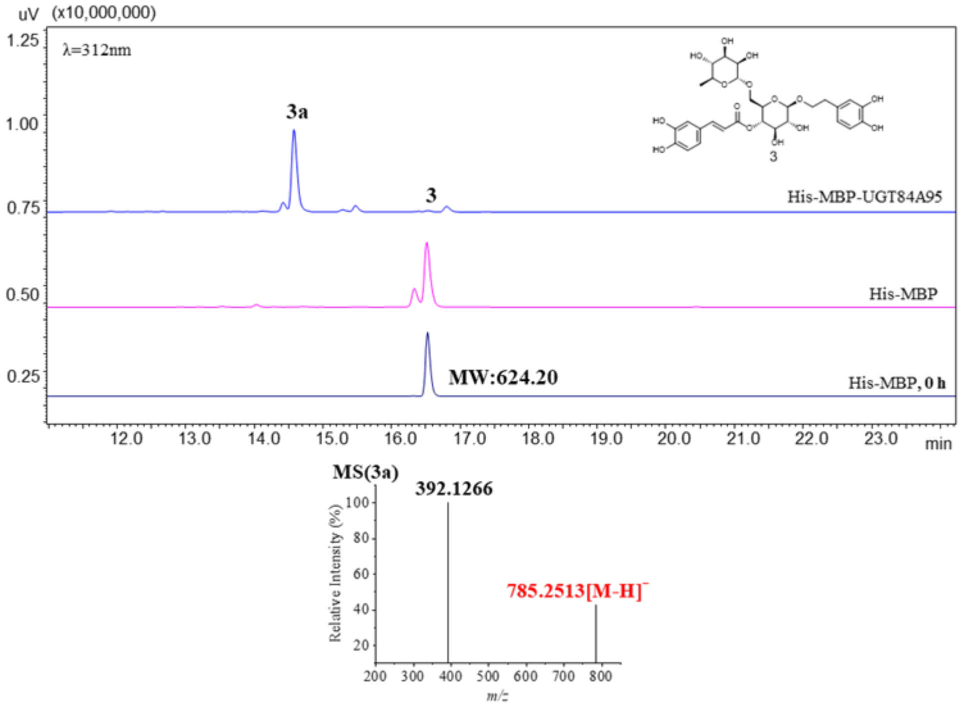


**Figure S4.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **3**.

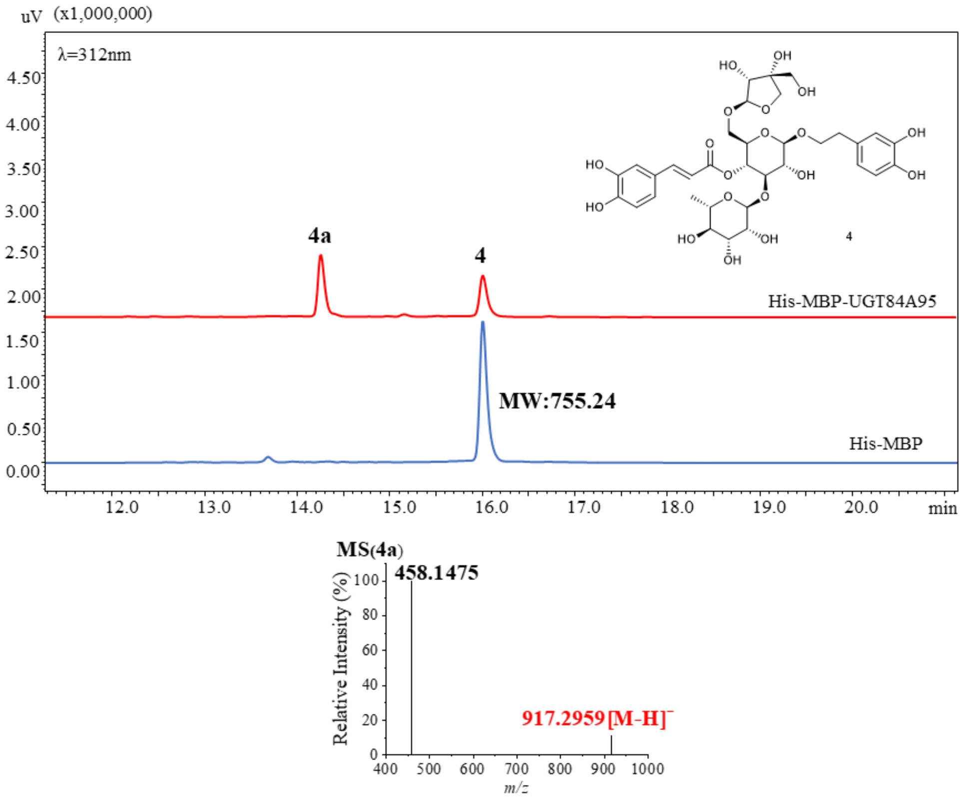


**Figure S5.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **4**.

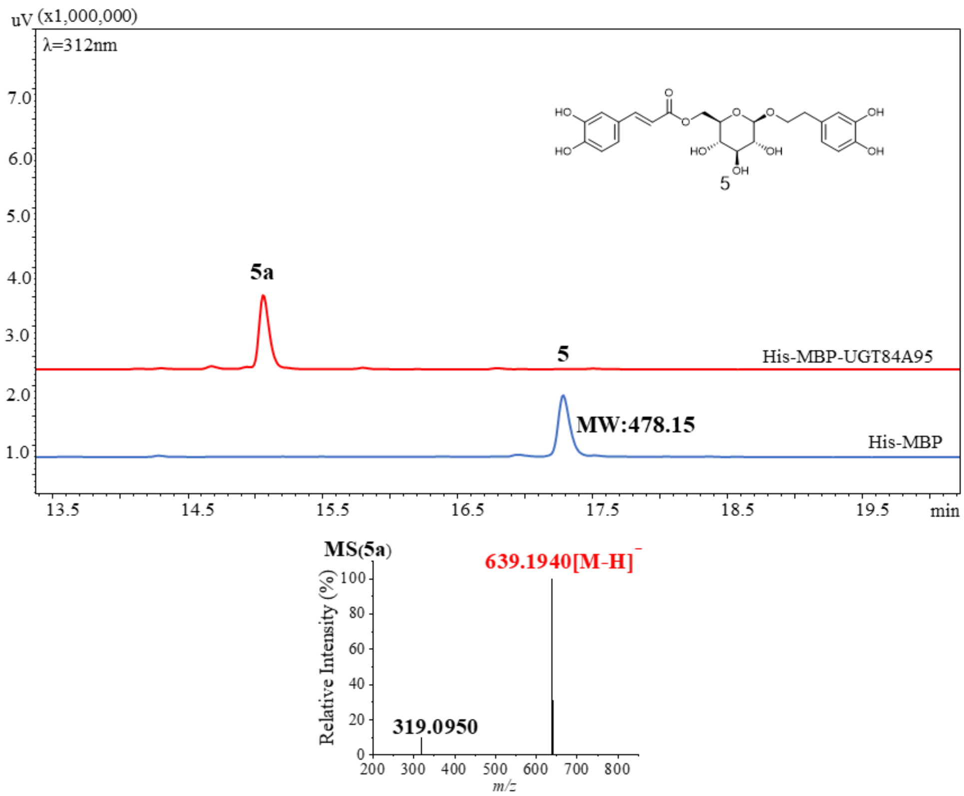


**Figure S6.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **5**.

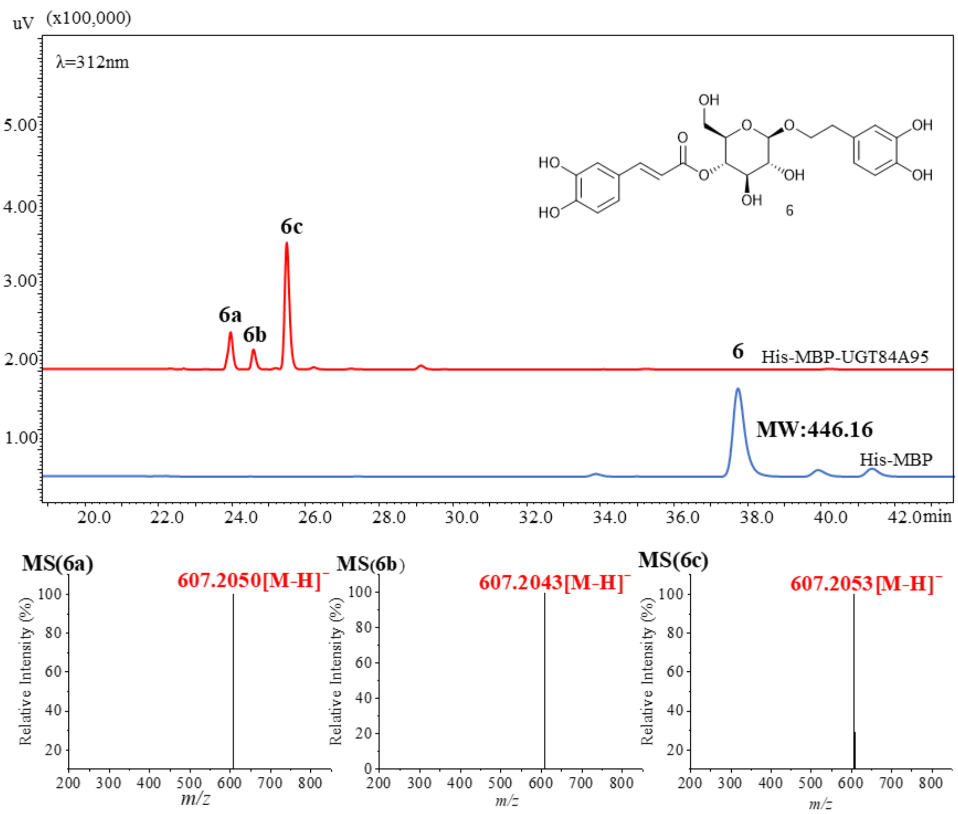


**Figure S7.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **6**.

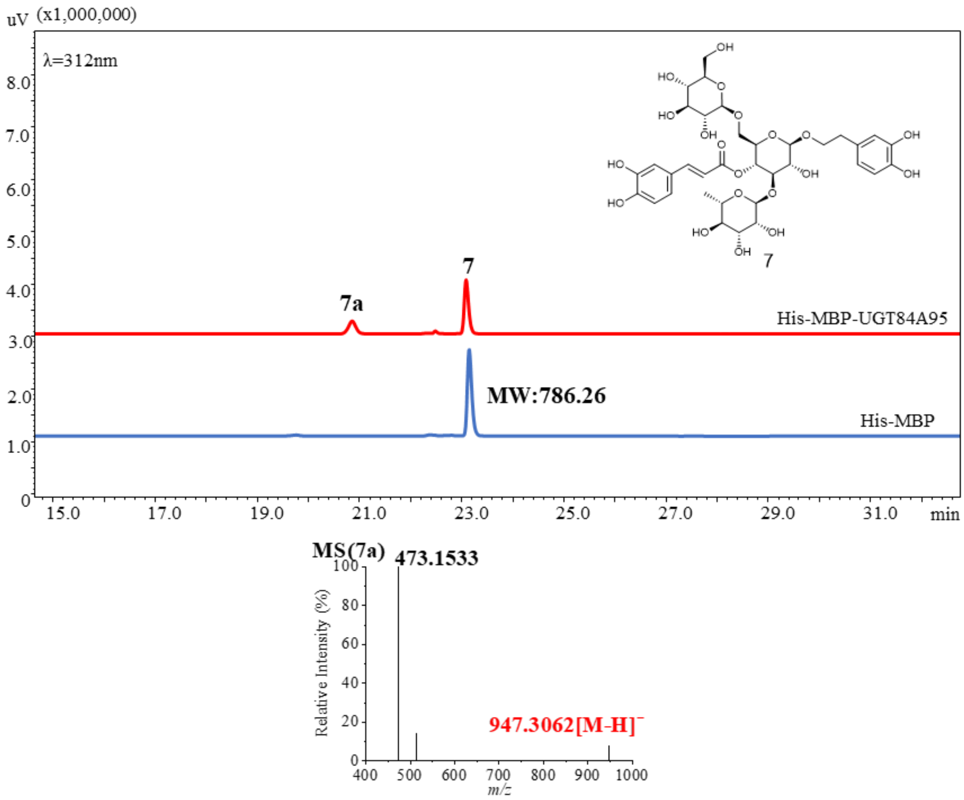


**Figure S8.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **7**.

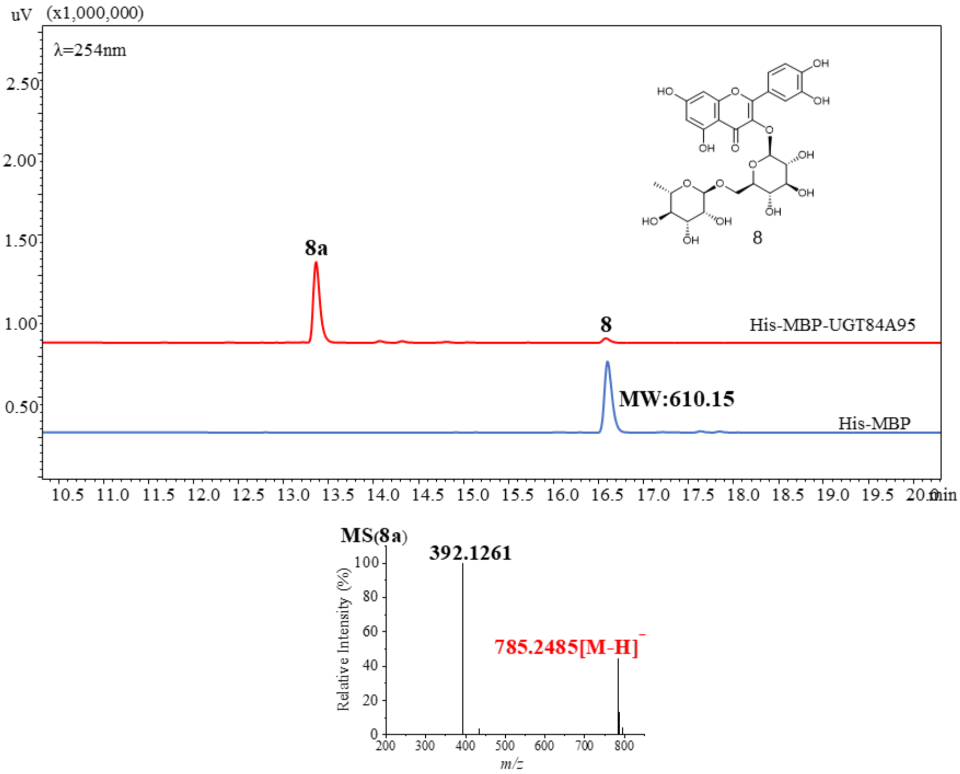


**Figure S9.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **8**.

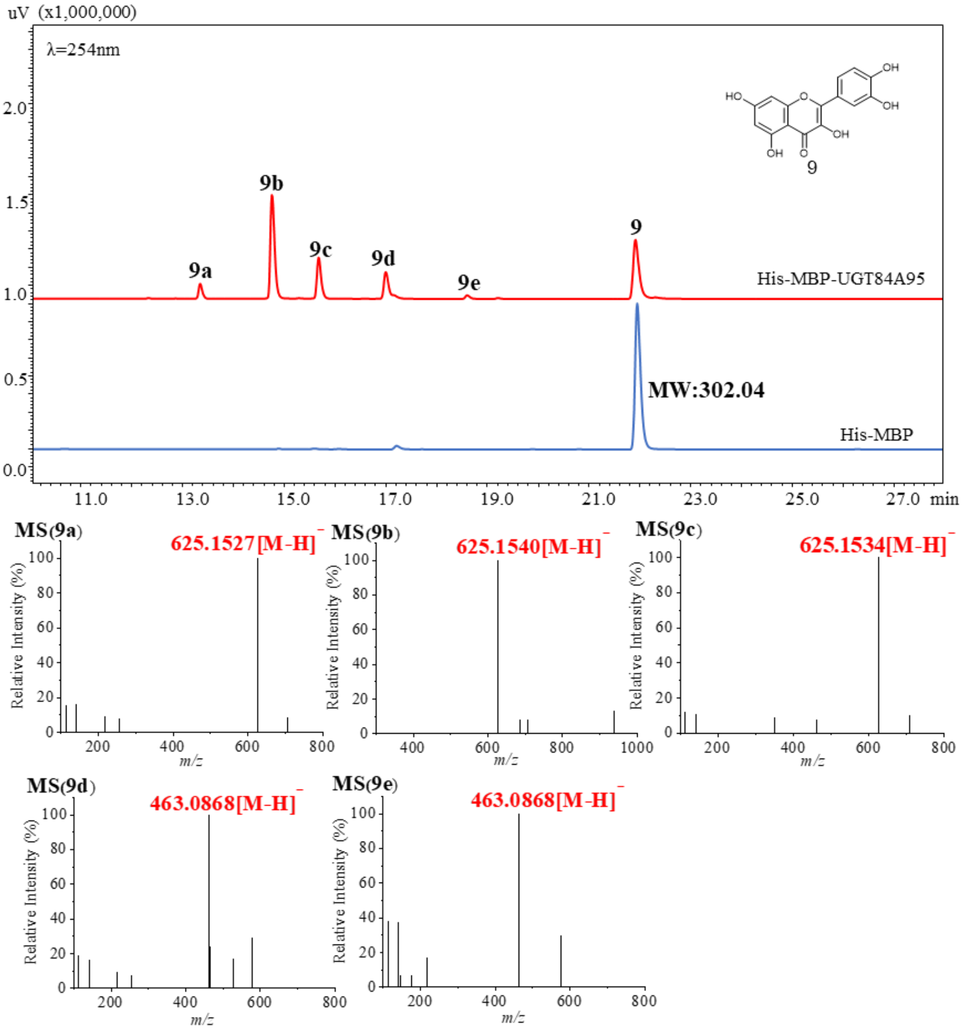


**Figure S10.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **9**.

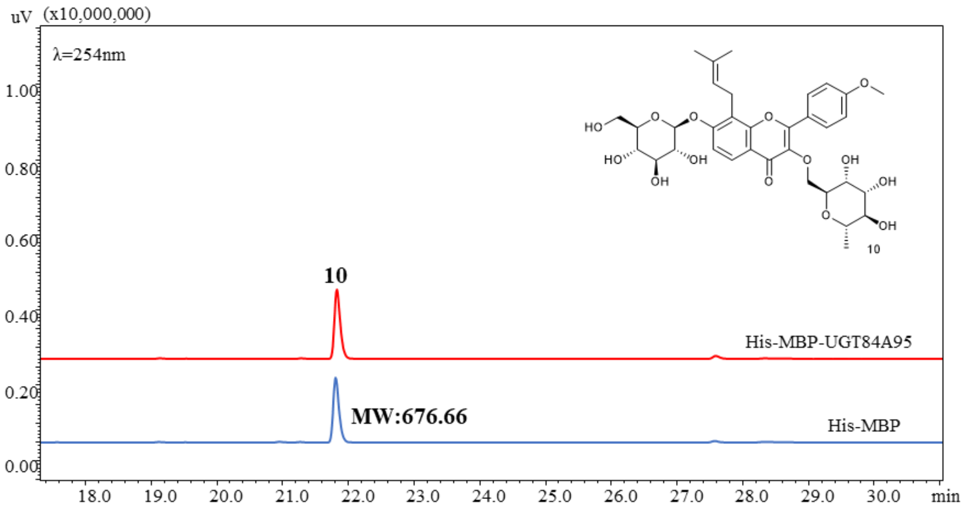


**Figure S11.** HPLC analysis of UGT84A95 catalytic reaction mixtures for compound **10**.

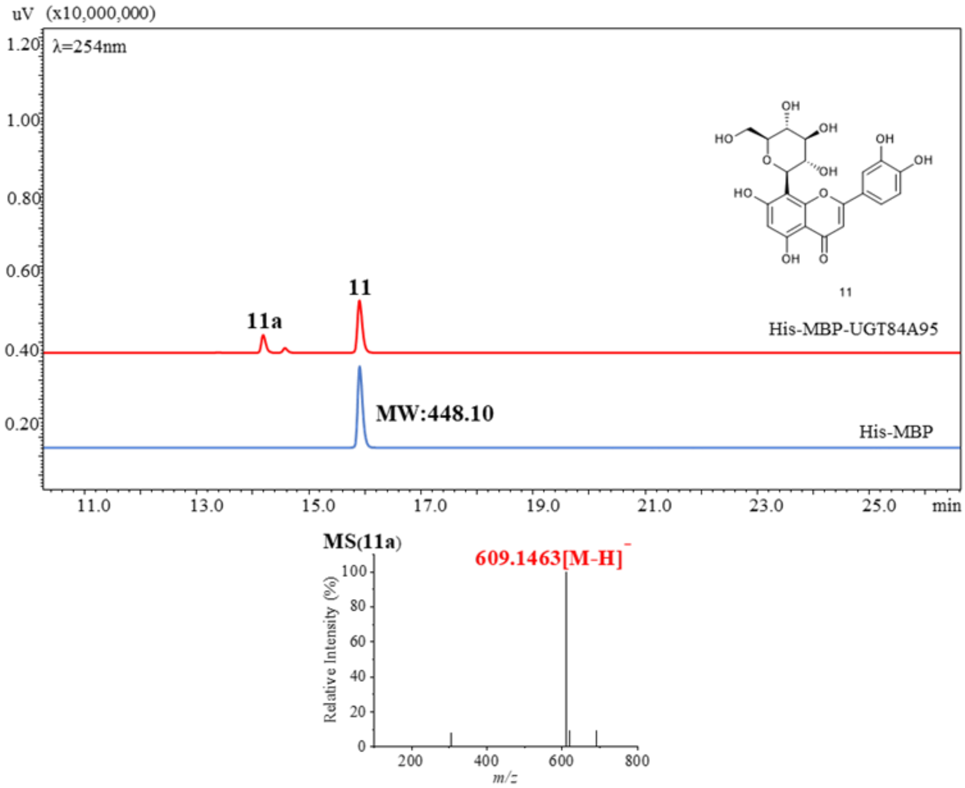


**Figure S12.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **11**.

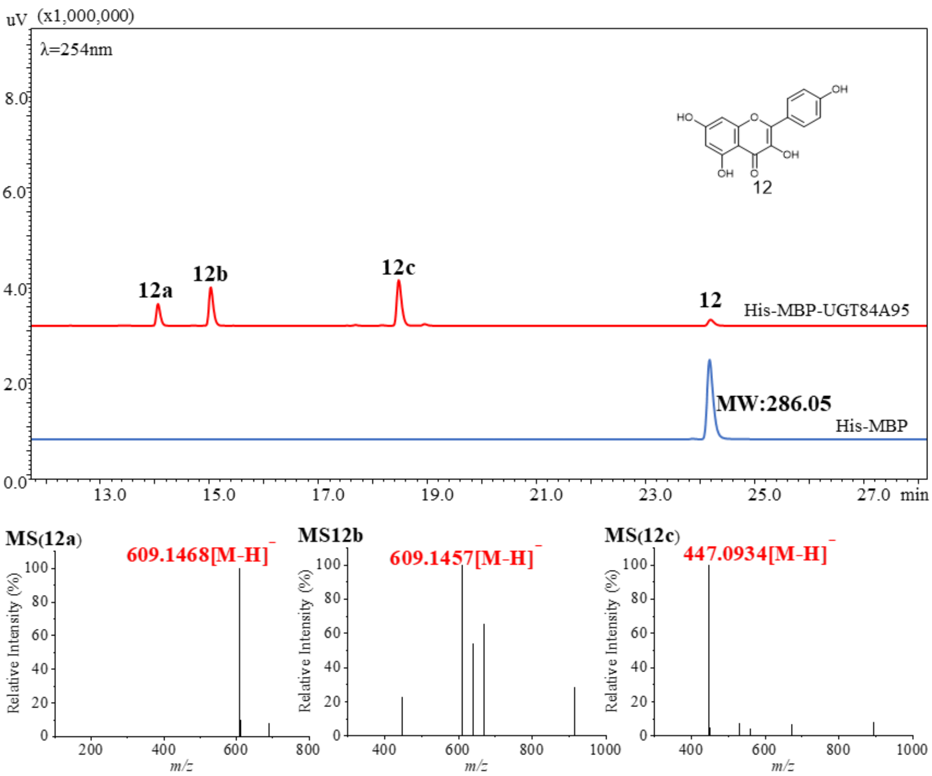


**Figure S13.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **12**.

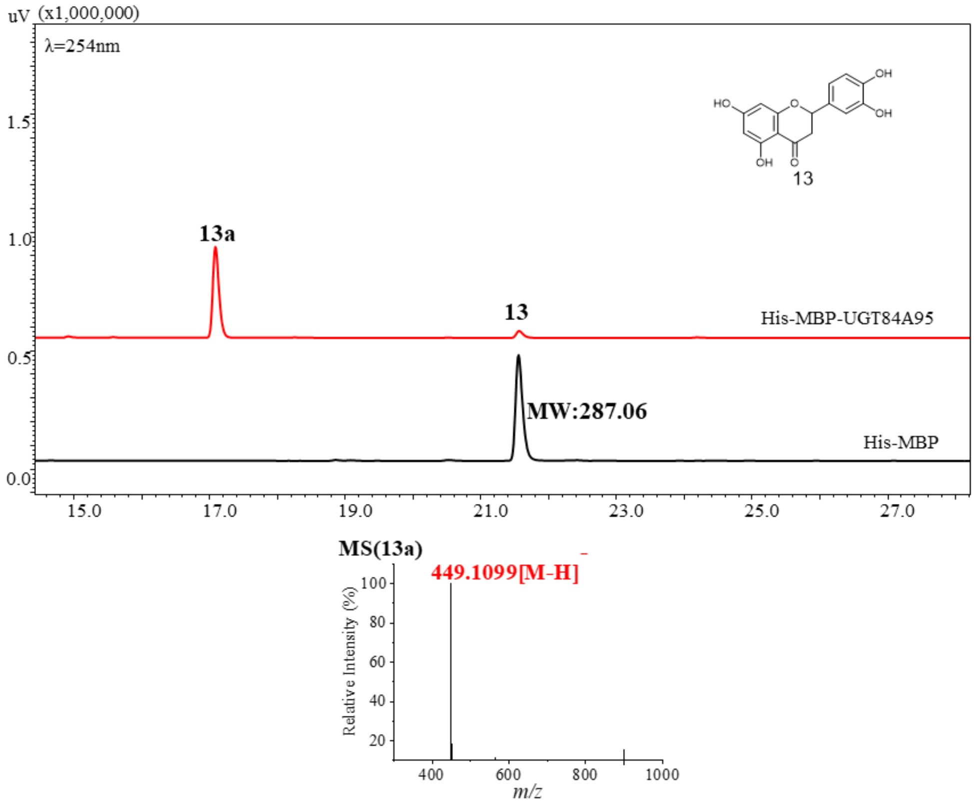


**Figure S14.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **13**.

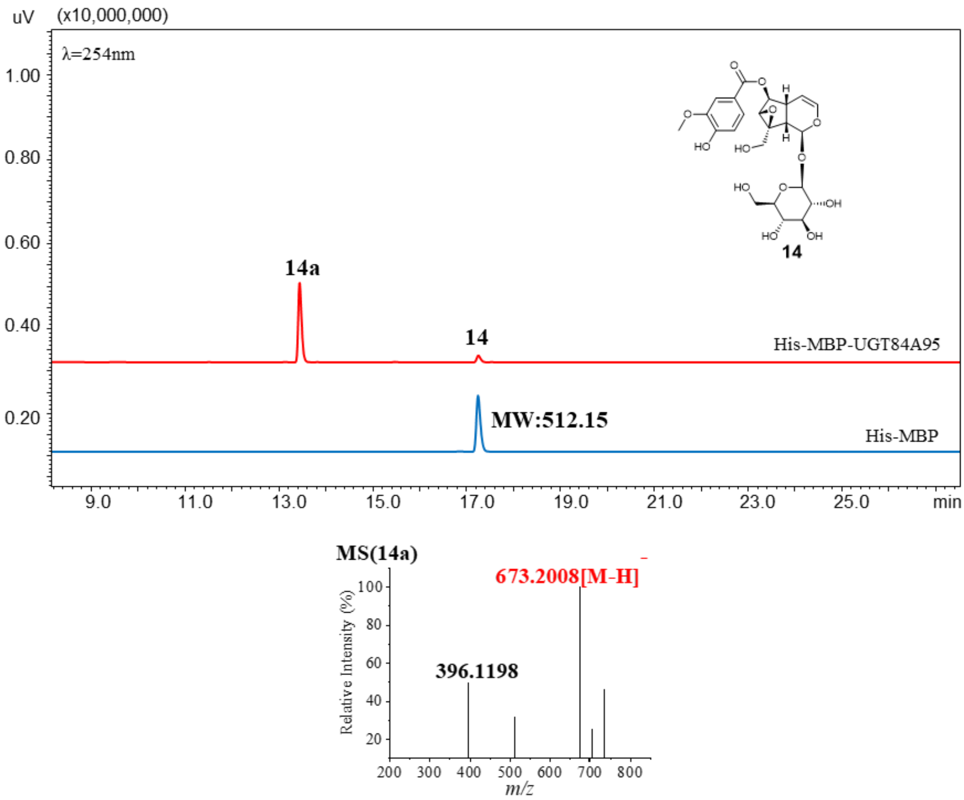


**Figure S15.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **14**.

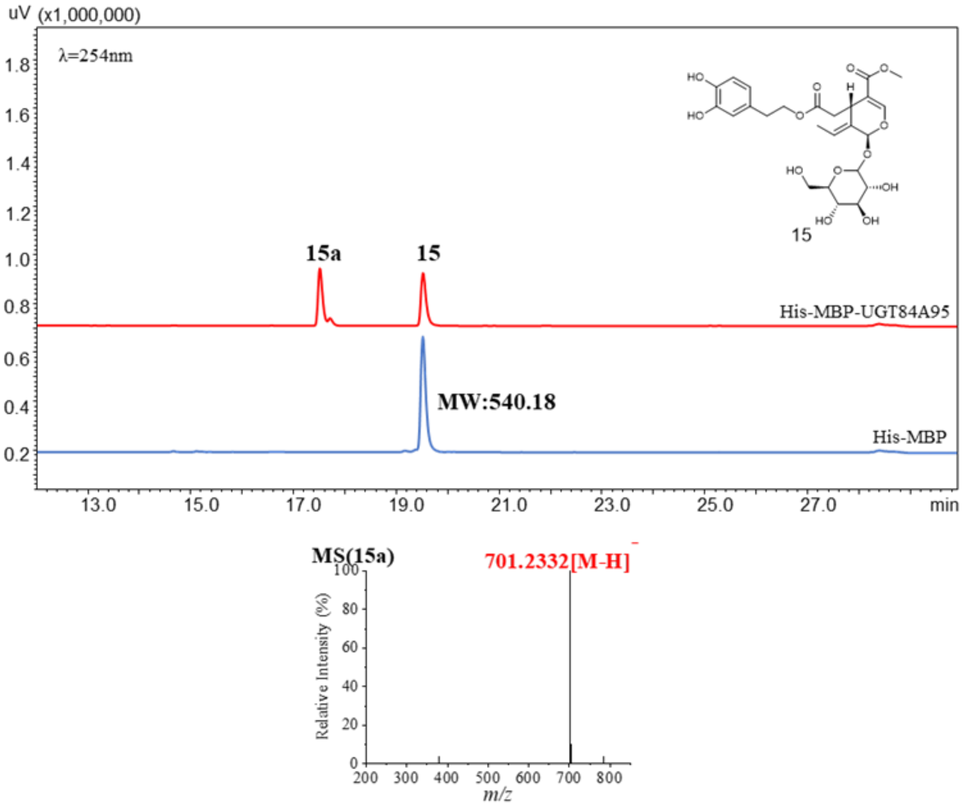


**Figure S16.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **15**.

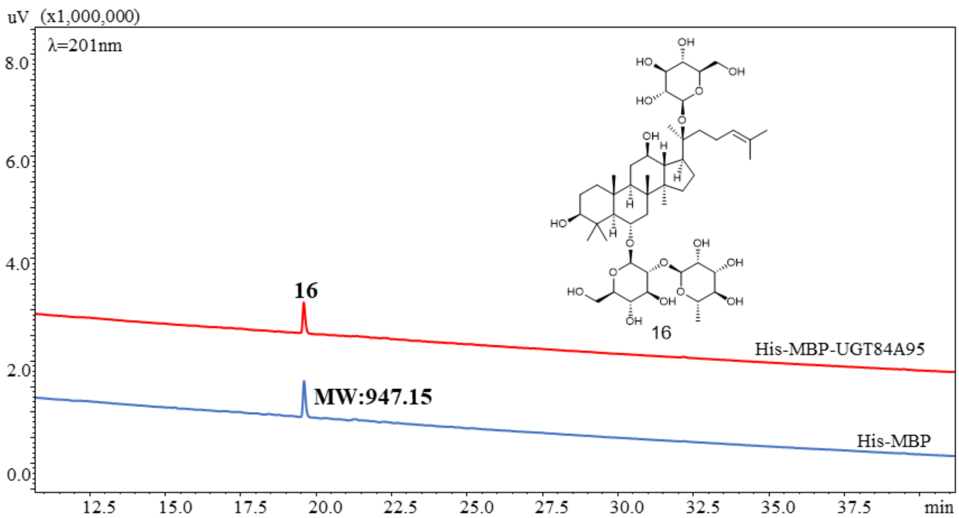


**Figure S17.** HPLC analysis of UGT84A95 catalytic reaction mixtures for compound **16**.

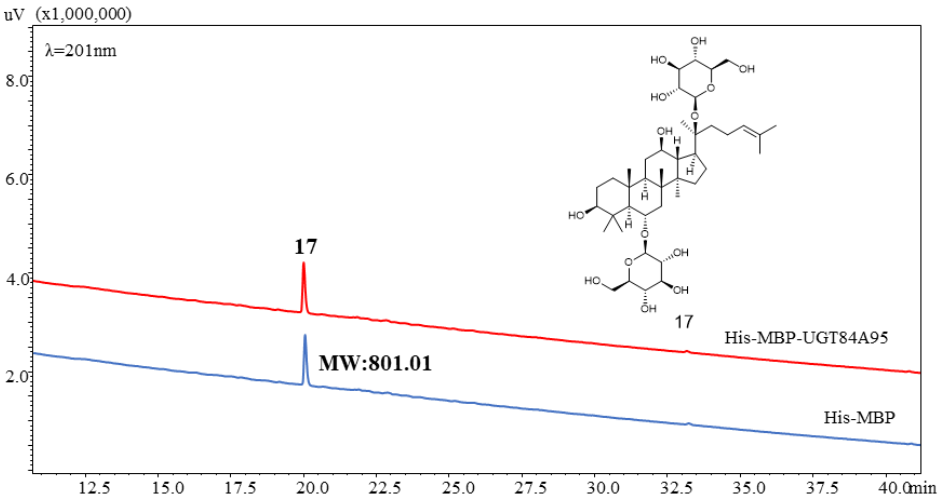


**Figure S18.** HPLC analysis of UGT84A95 catalytic reaction mixtures for compound **17**.

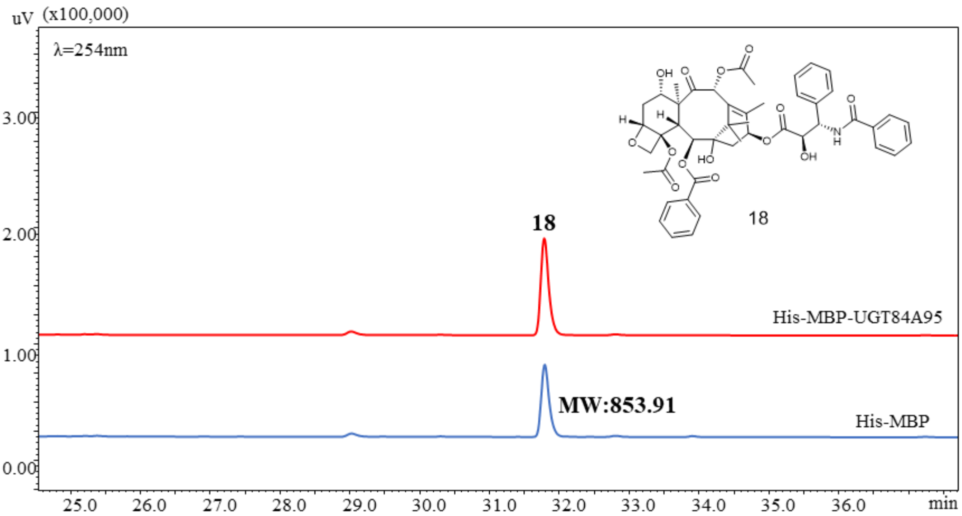


**Figure S19.** HPLC analysis of UGT84A95 catalytic reaction mixtures for compound **18**.

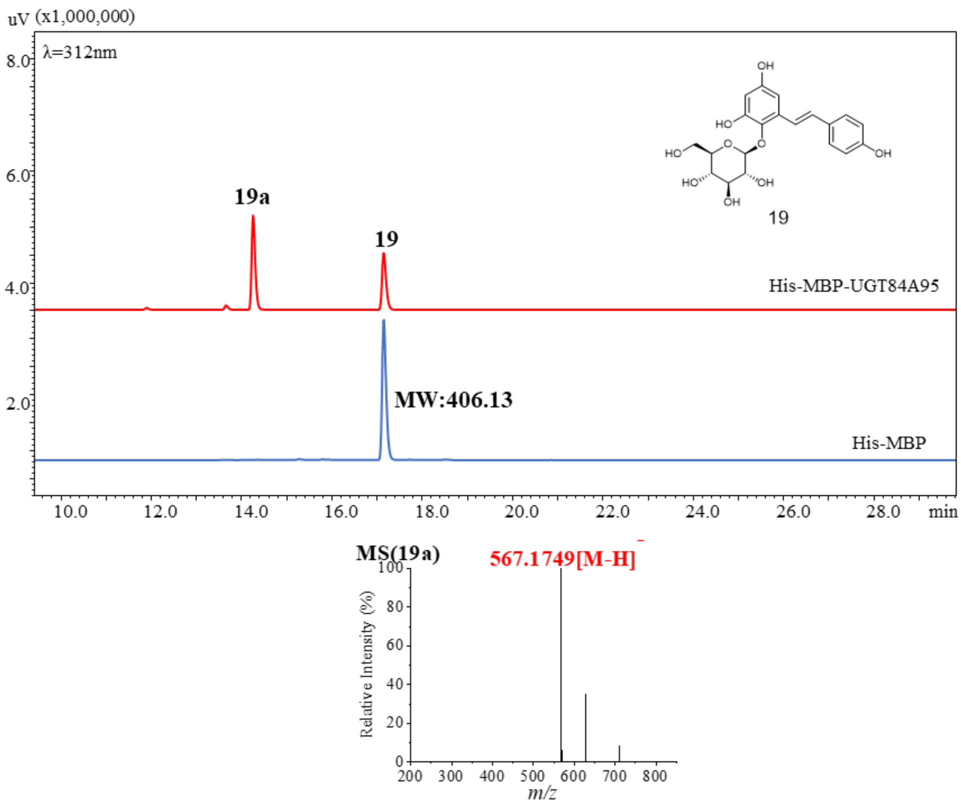


**Figure S20.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **19**.

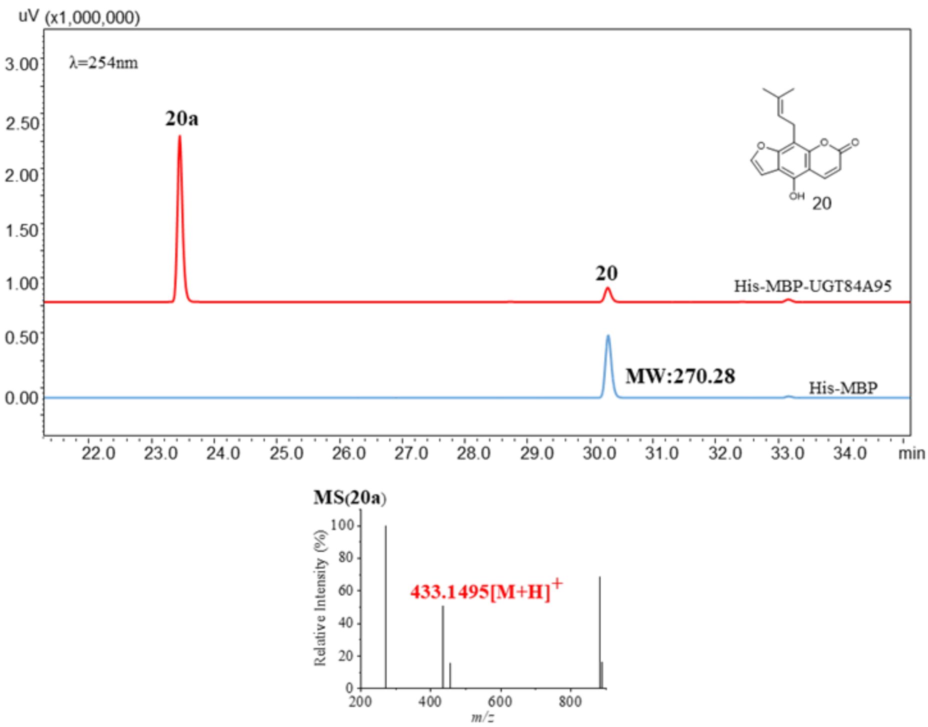


**Figure S21.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **20**.

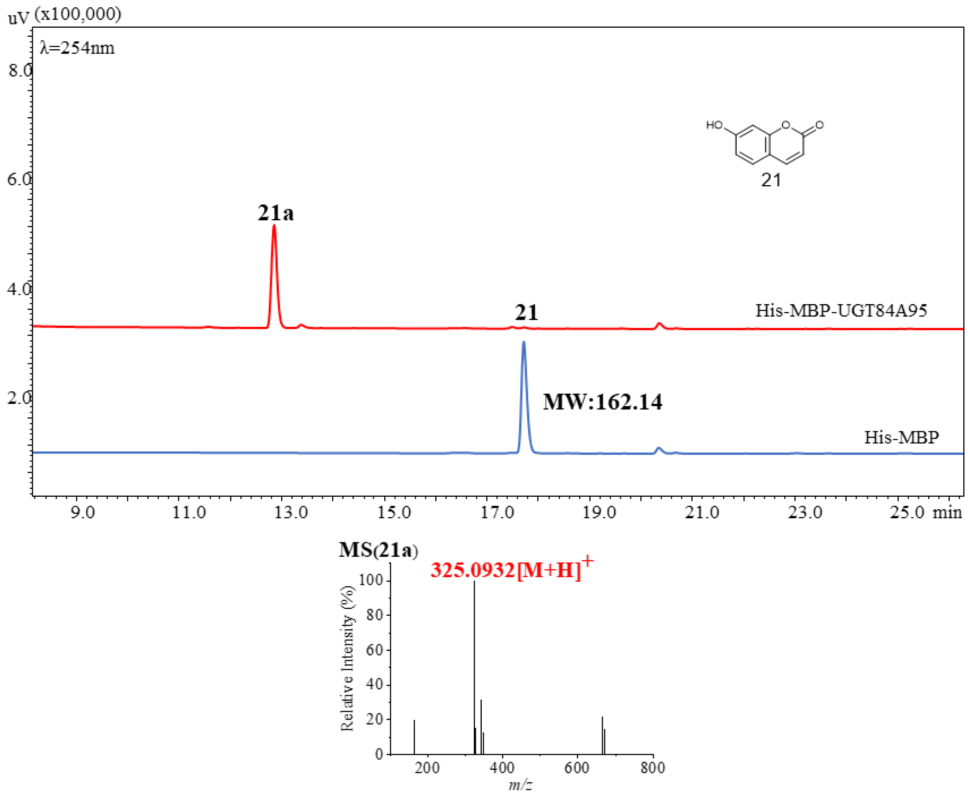


**Figure S22.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **21**.

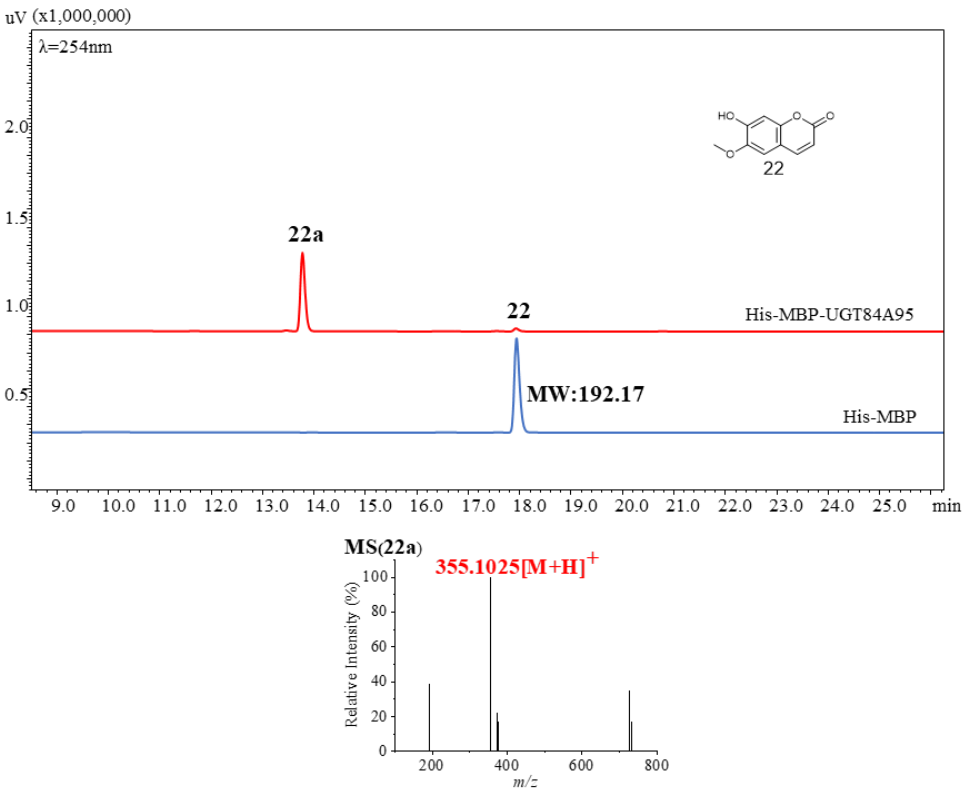


**Figure S23.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **22**.

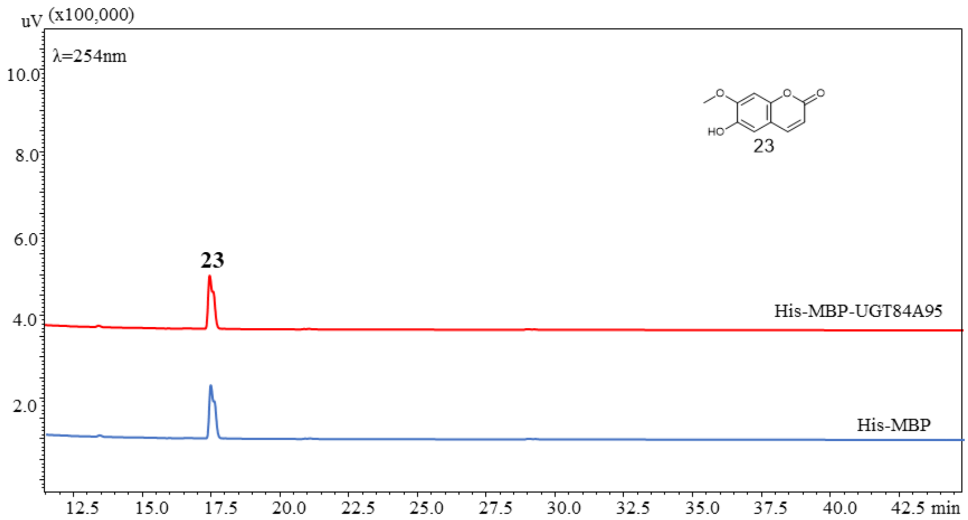


**Figure S24.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **23**.

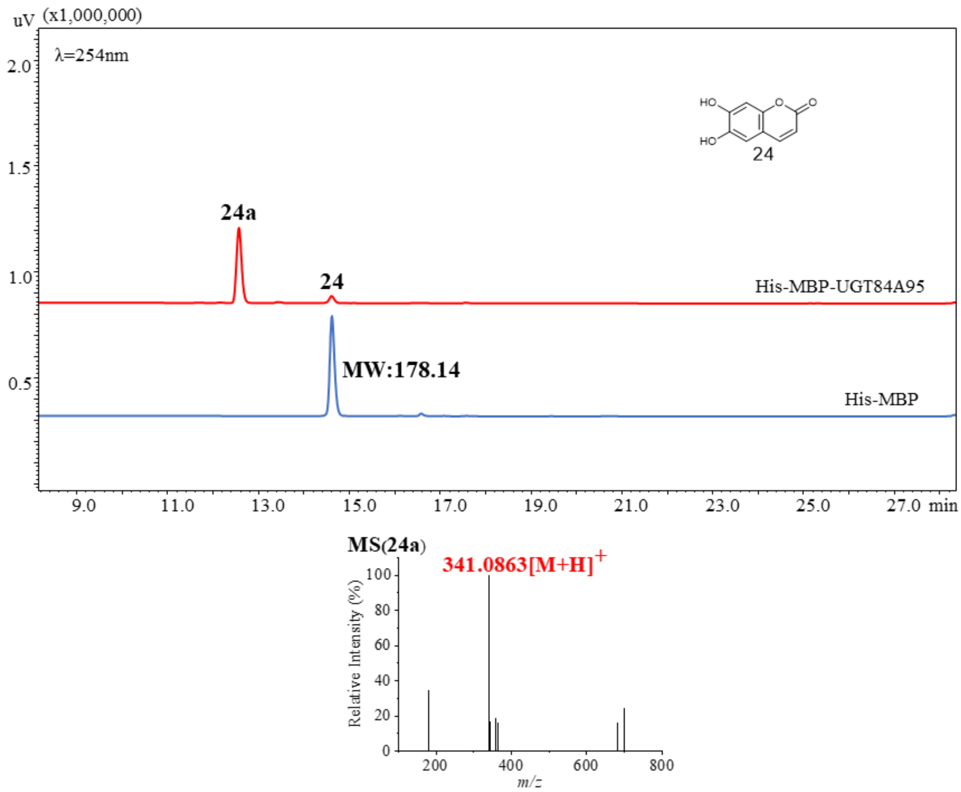


**Figure S25.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **24**.

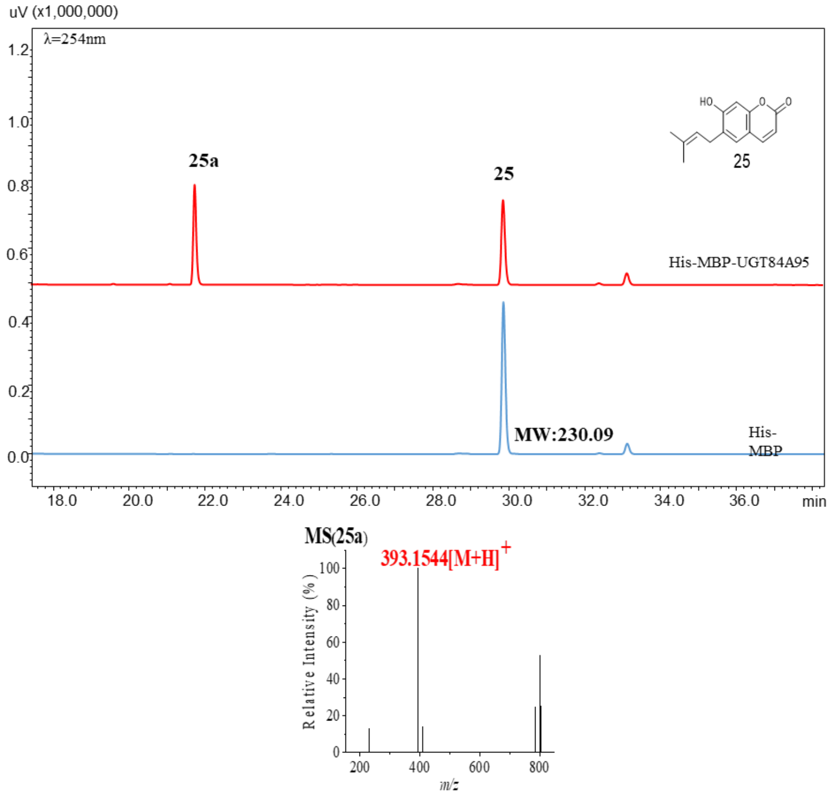


**Figure S26.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **25**.

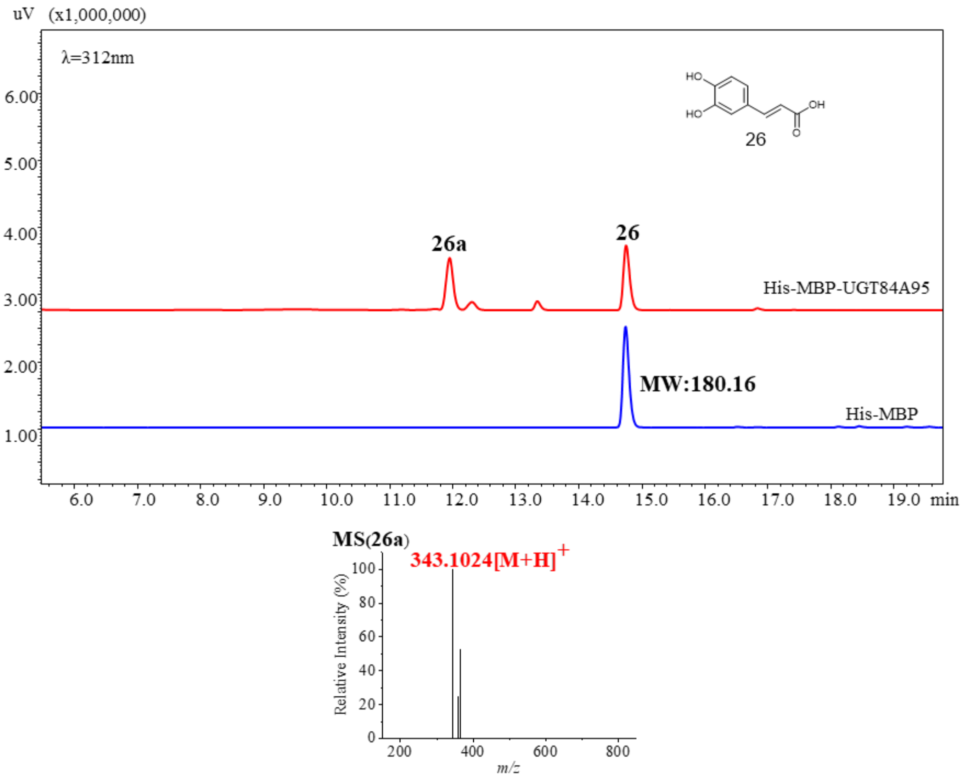


**Figure S27.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **26**.

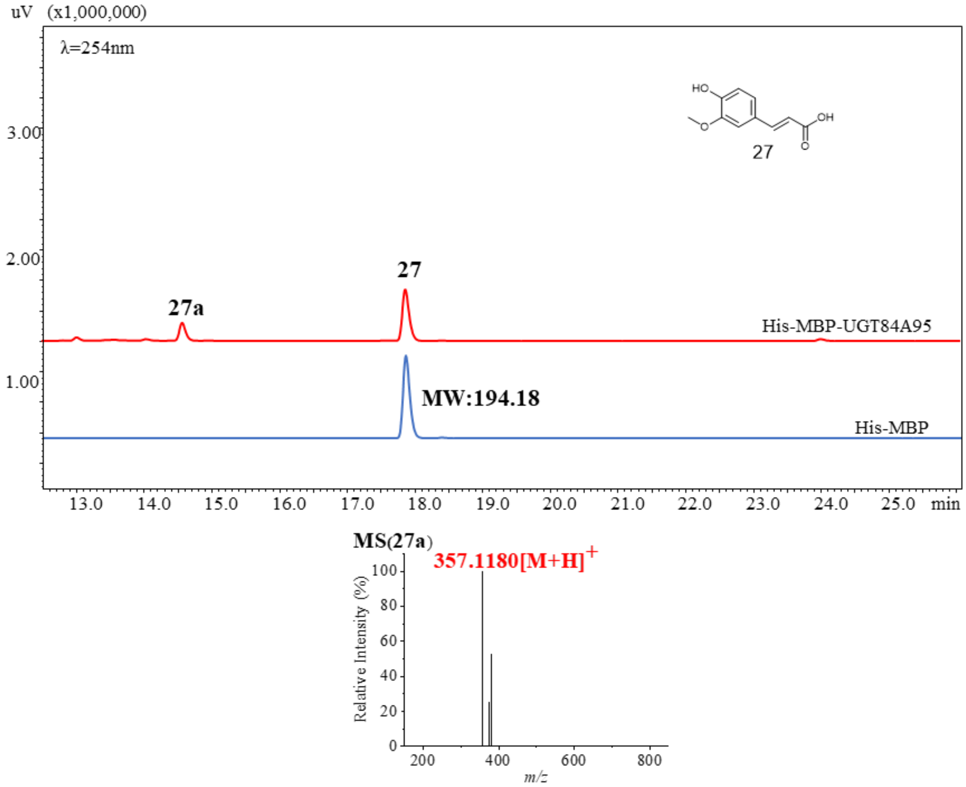


**Figure S28.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **27**.

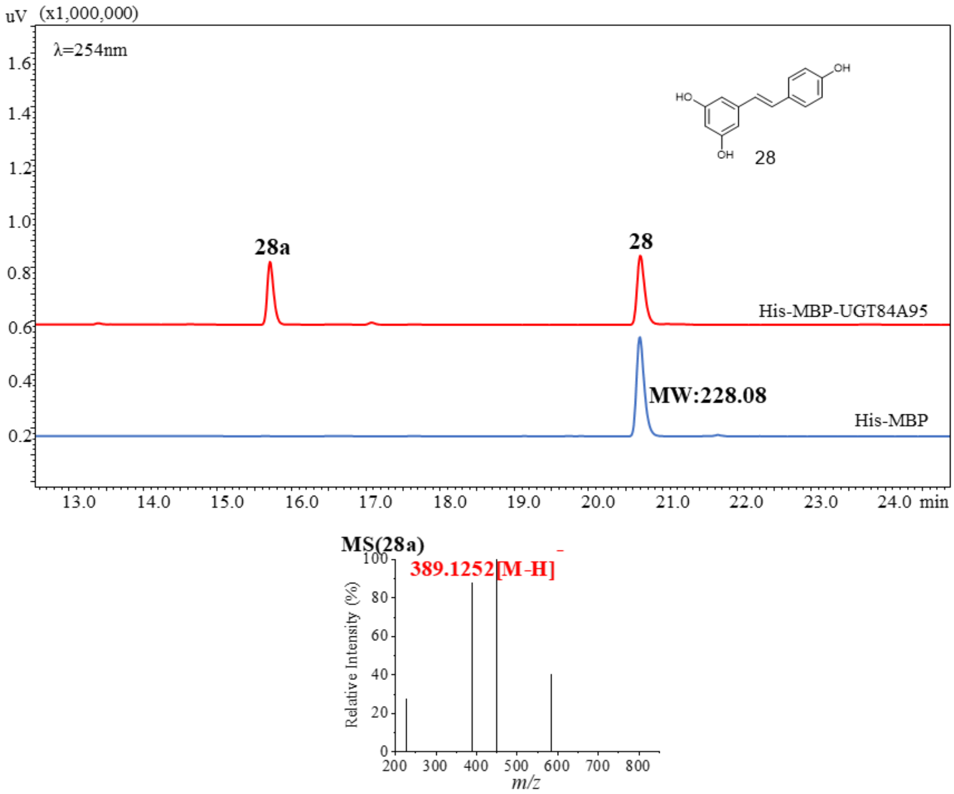


**Figure S29.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures for compound **28**.

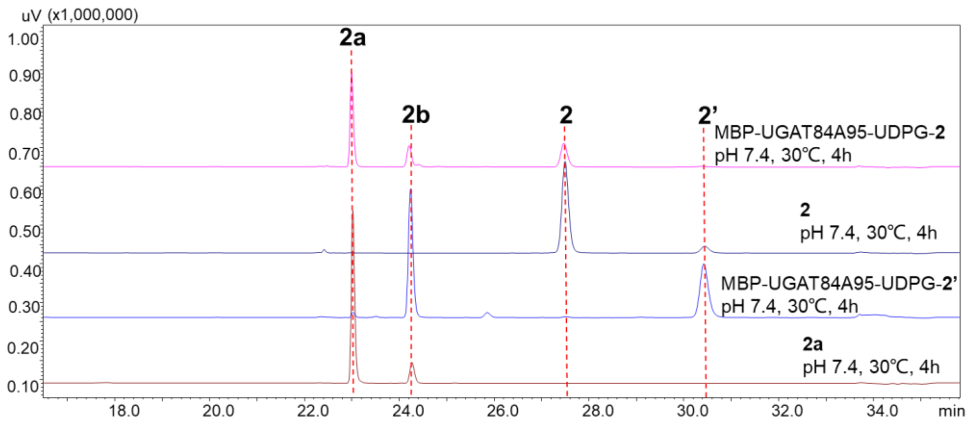


**Figure 30.** HPLC analysis of UGT84A95 catalytic reactions for compound **2** and **2'**.

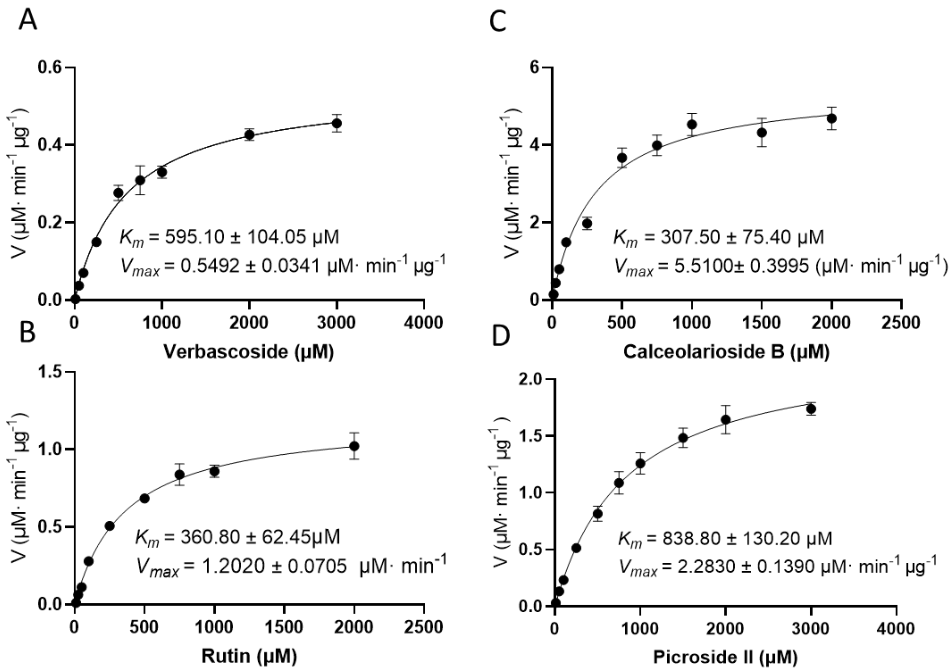


**Figure S31.** Determination of kinetic parameters ($K_m$ and $V_{max}$ values) for purified UGT71BD1 using UDP-Glc as a sugar donor and **2**, **5**, **8** and **14** as sugar acceptors, respectively.

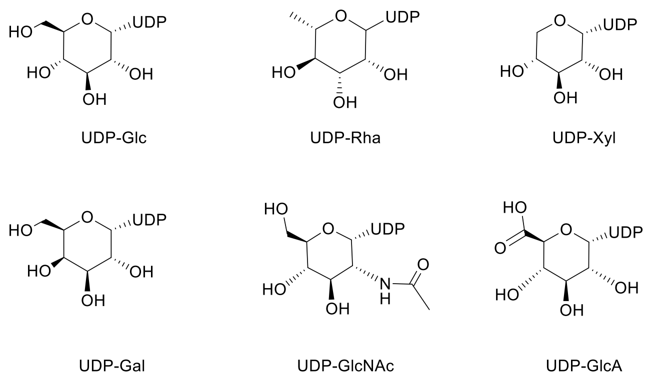


**Figure S32.** Structures of sugar donor in this study.

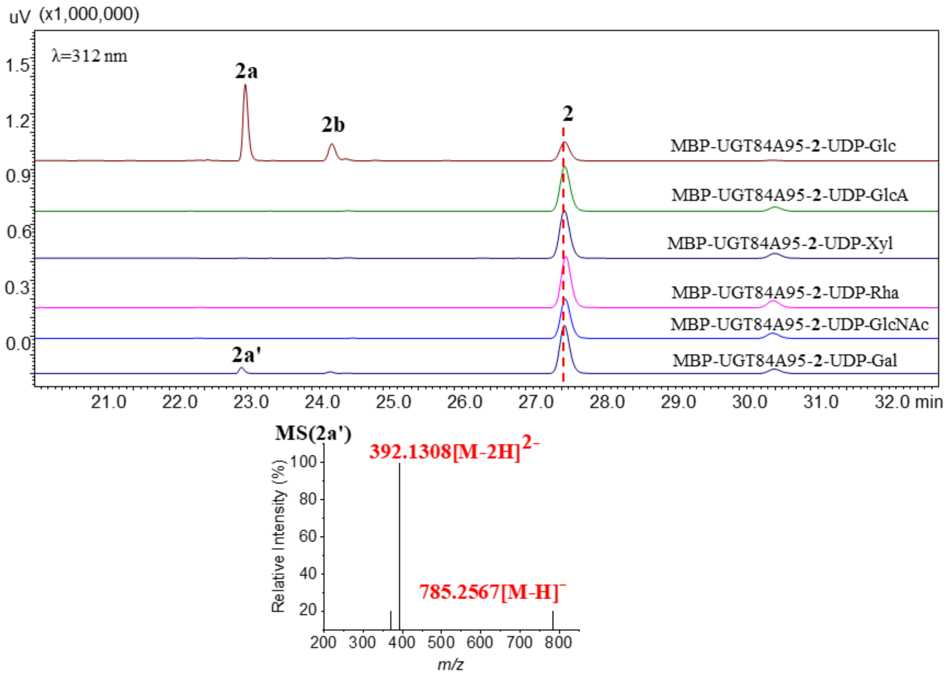


**Figure S33.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures using different sugar donors and using **2** as the acceptor.

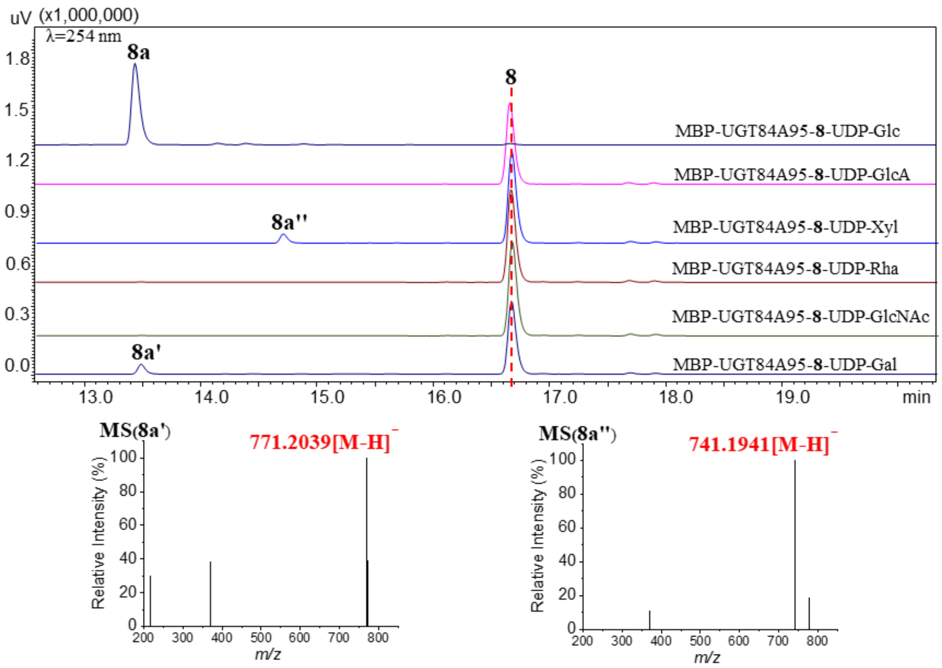


**Figure S34.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures using different sugar donors and using **8** as the acceptor.

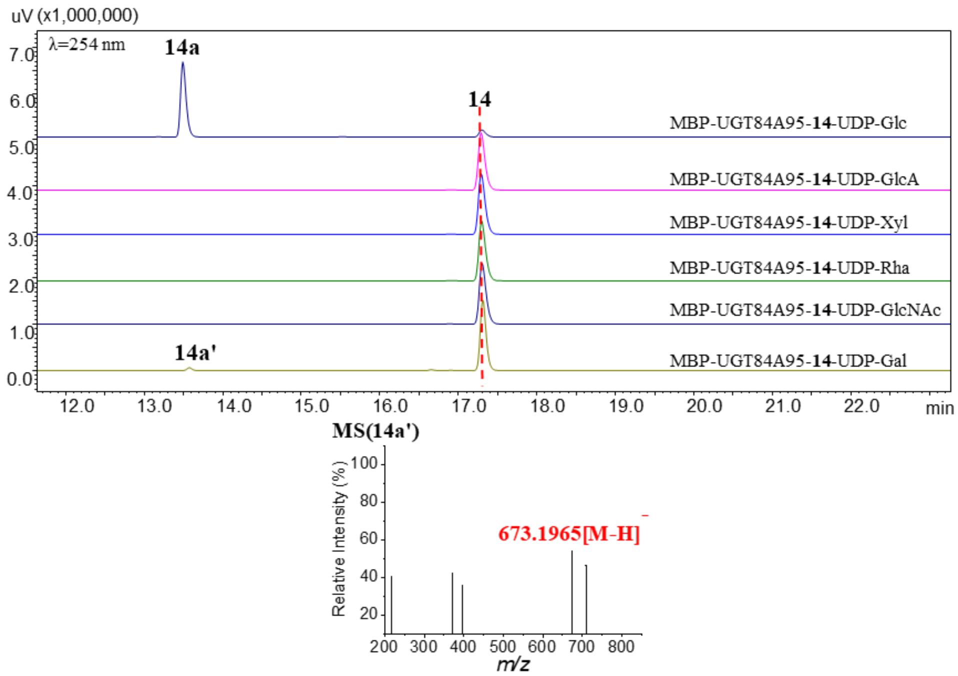


**Figure S35.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures using different sugar donors and using **14** as the acceptor

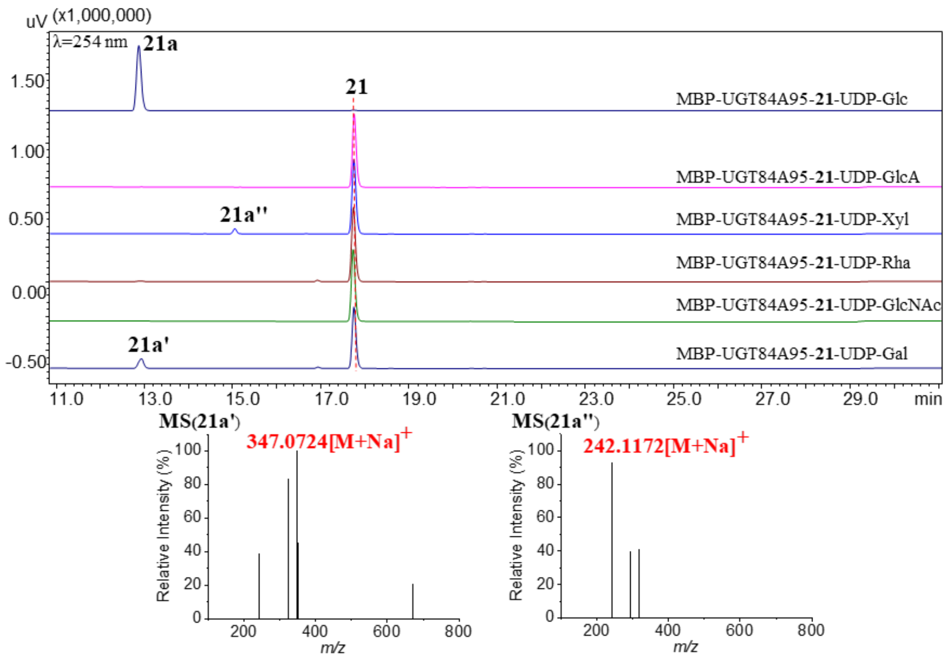


**Figure S36.** HPLC and LC-HRMS analysis of UGT84A95 catalytic reaction mixtures using different sugar donors and using **21** as the acceptor.

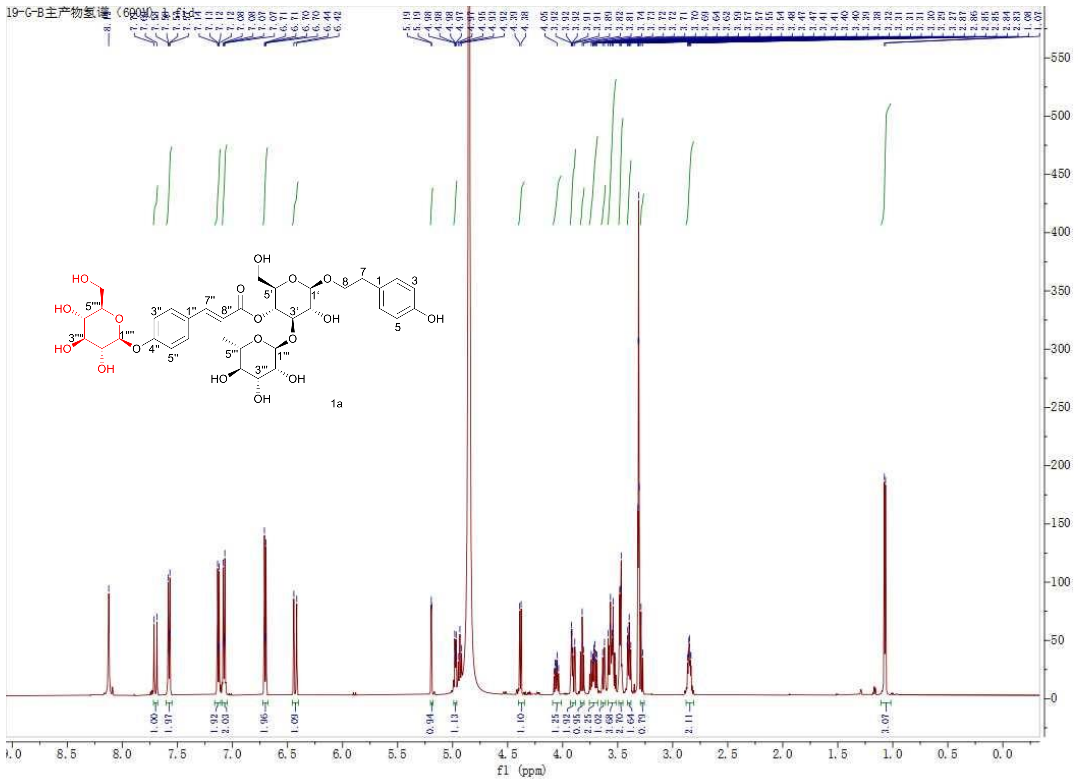


**Figure S37.** $^{1}H$ NMR spectrum of glycosylated product **1a** ($CD_3OD$, 600 MHz).

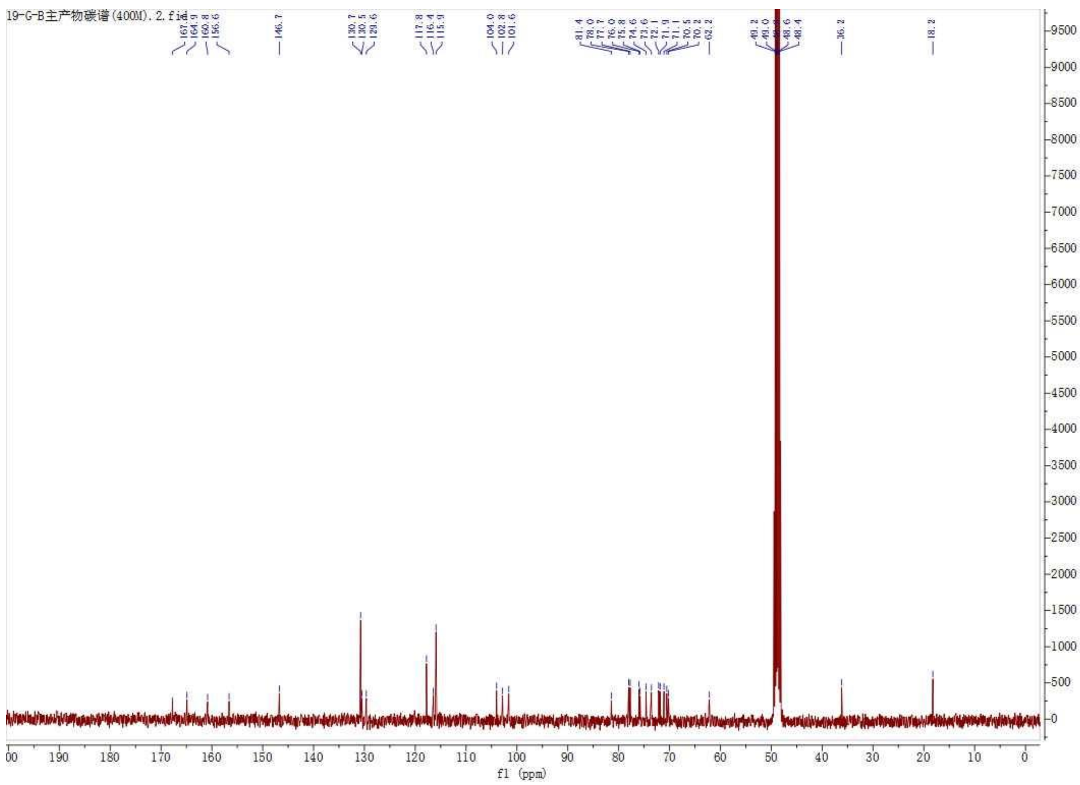


**Figure S38.** $^{13}C$ NMR spectrum of glycosylated product **1a** ($CD_3OD$, 400 MHz).

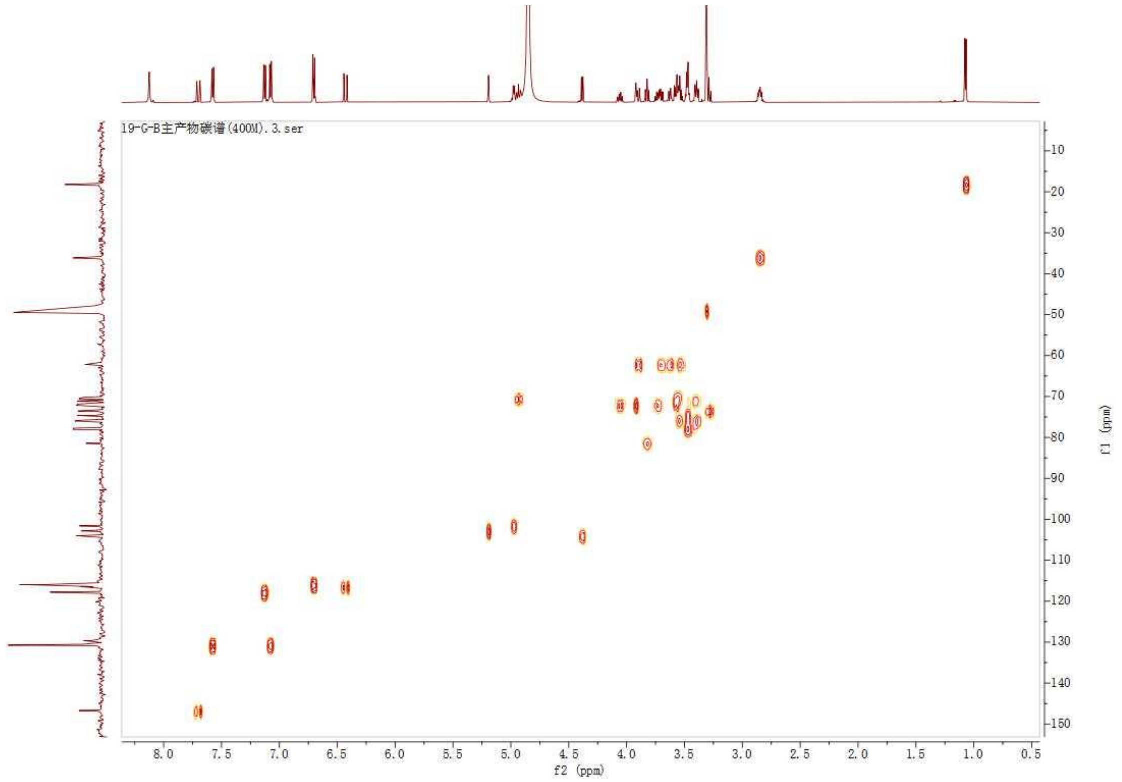


**Figure S39.** HSQC spectrum of glycosylated product **1a** ($CD_3OD$, 400 MHz).

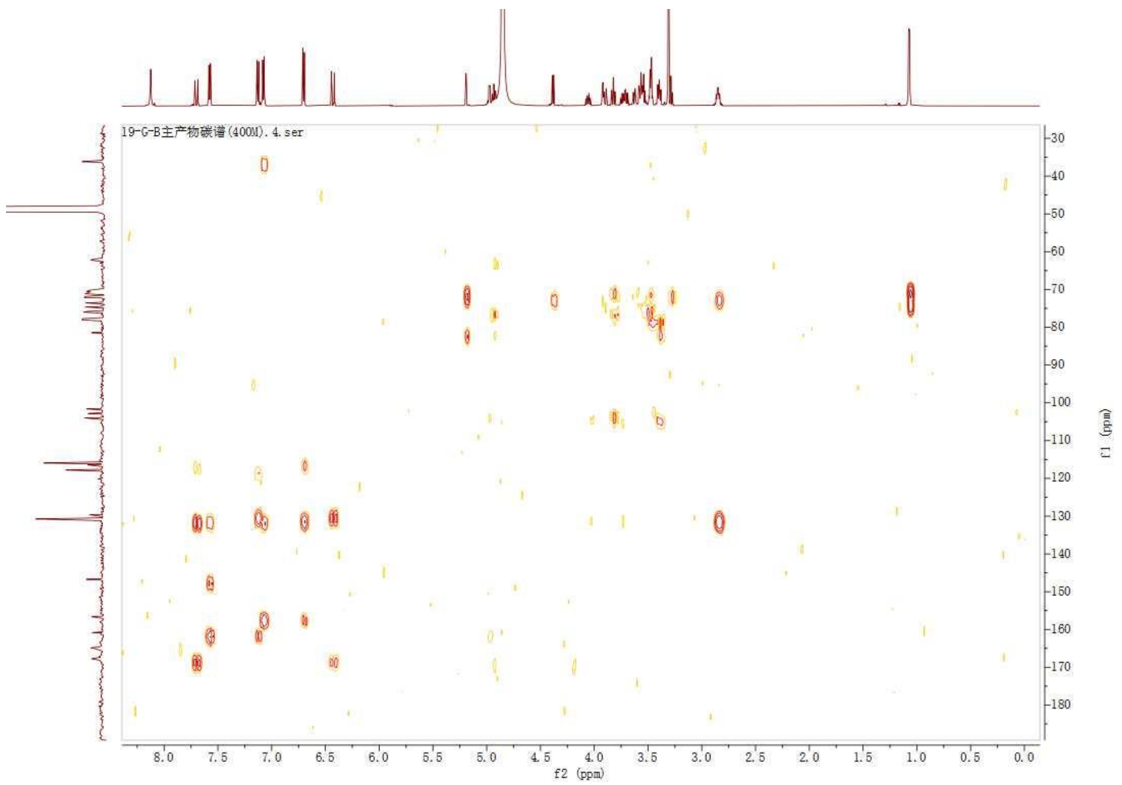


**Figure S40.** HMBC spectrum of glycosylated product **1a** ($CD_3OD$, 400 MHz).

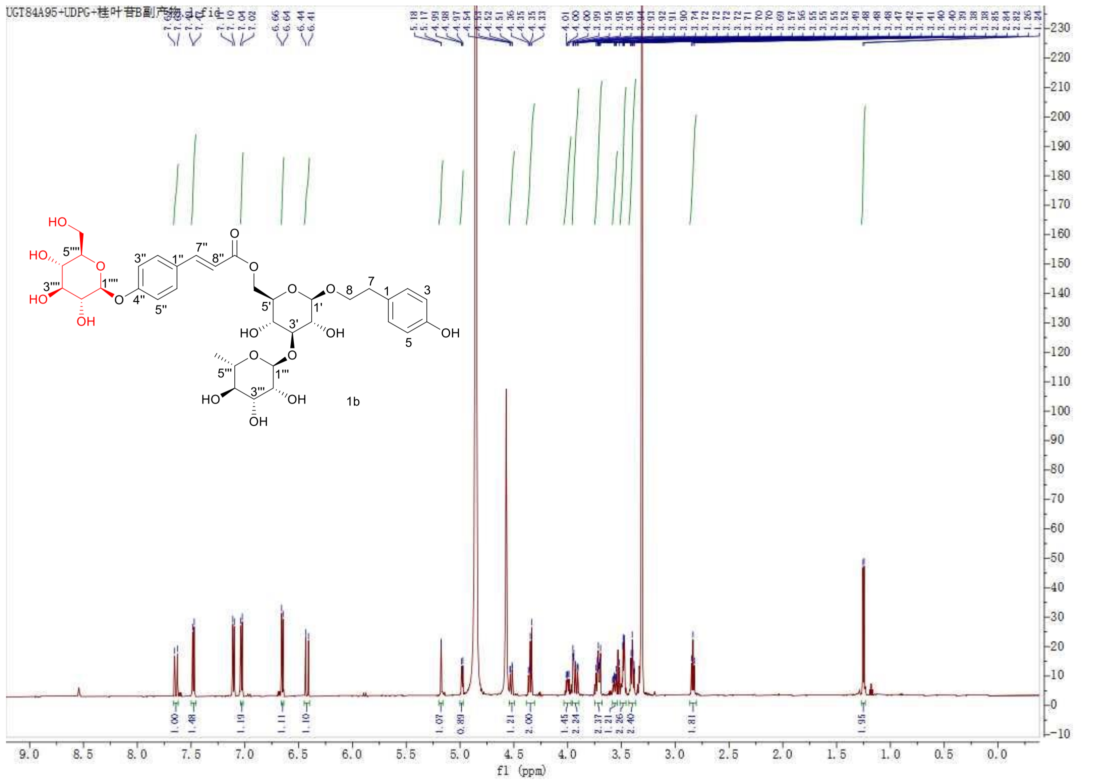

**Figure S41.** $^{1}H$ NMR spectrum of glycosylated product **1b** ($CD_3OD$, 600 MHz).

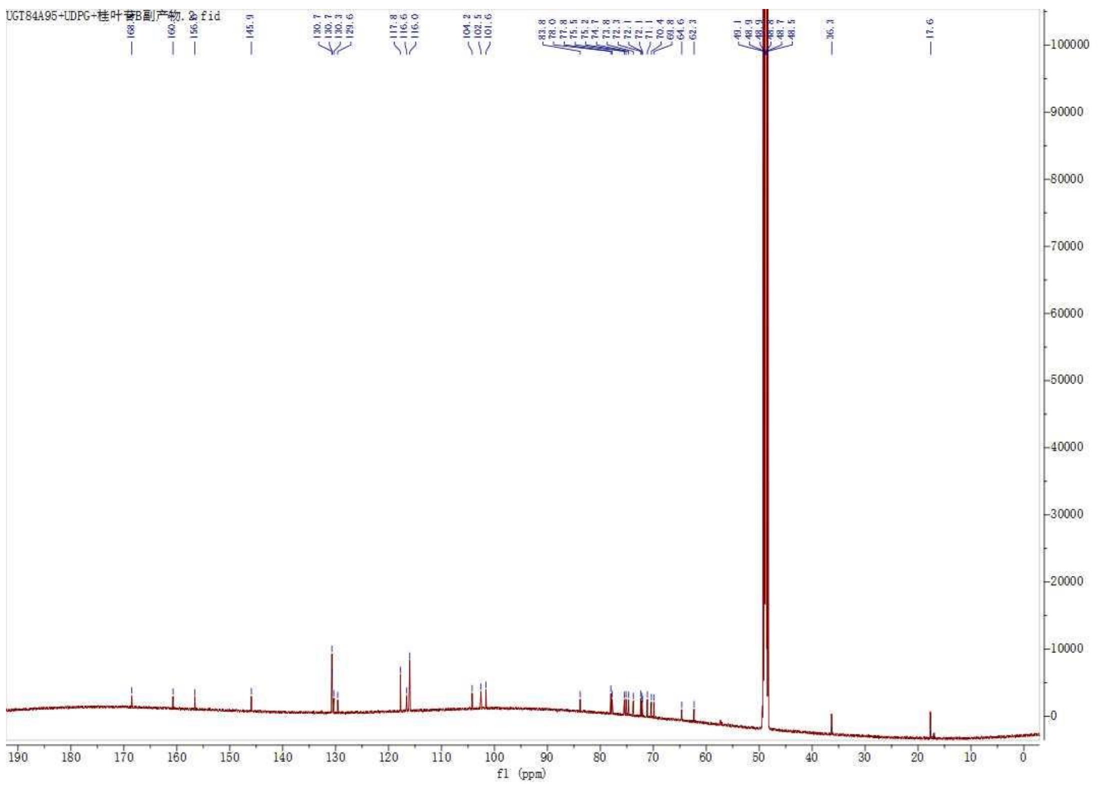

**Figure S42.** $^{13}C$ NMR spectrum of glycosylated product **1b** ($CD_3OD$, 600 MHz).

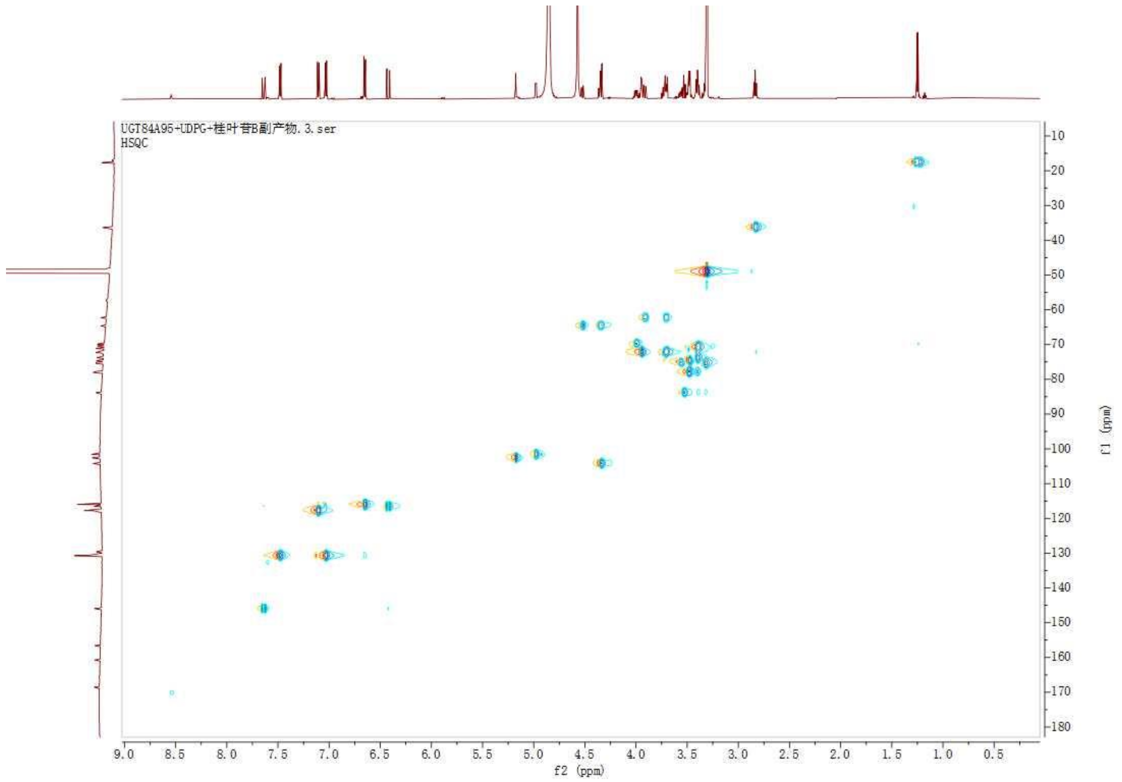


**Figure S43.** HSQC spectrum of glycosylated product **1b** ($CD_3OD$, 600 MHz).

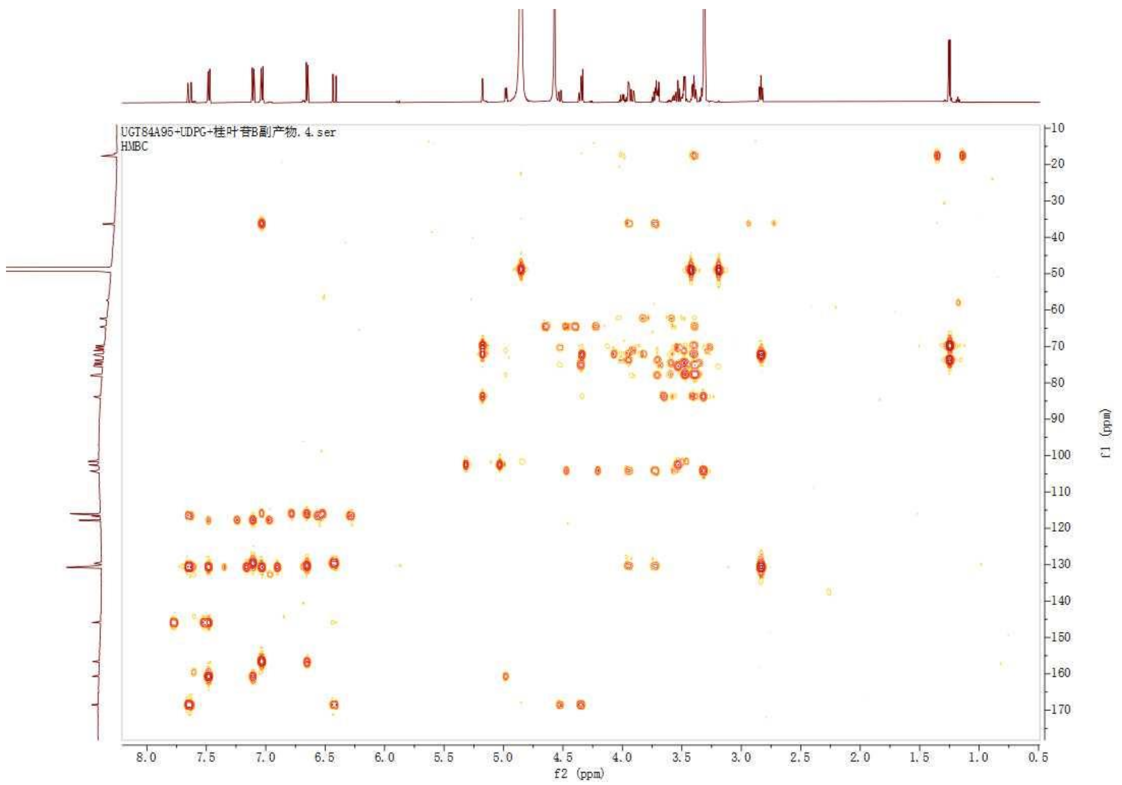


**Figure S44.** HMBC spectrum of glycosylated product **1b** ($CD_3OD$, 600 MHz).

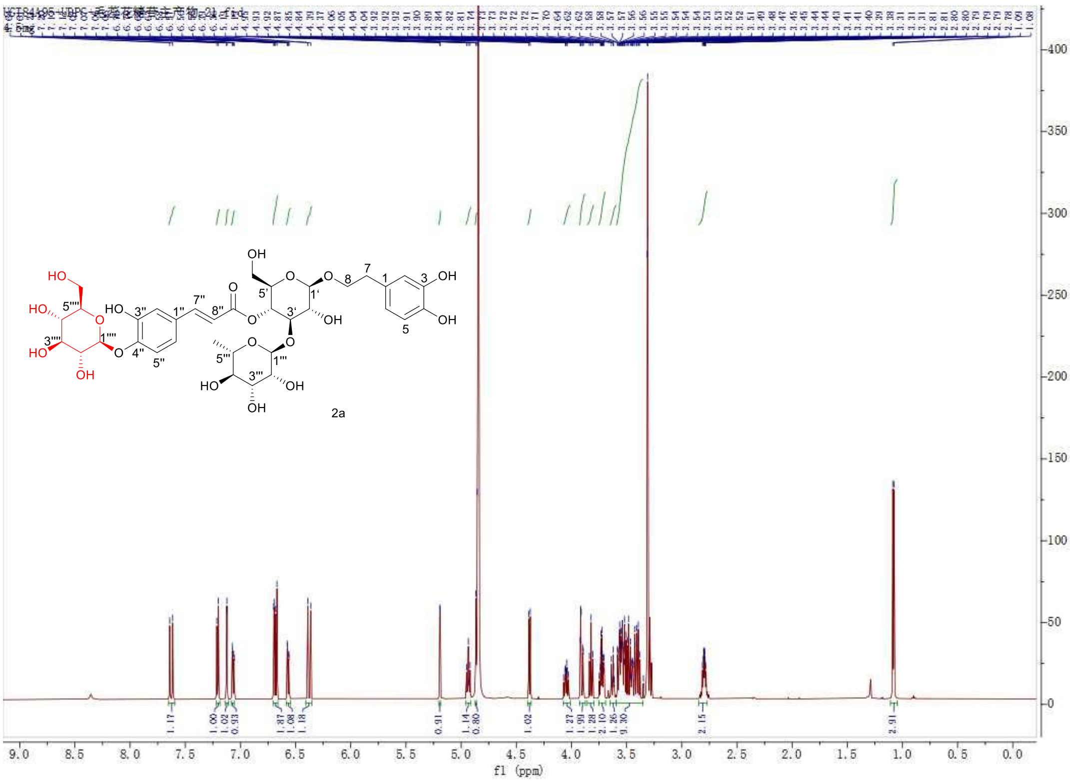

**Figure S45.** $^{1}H$ NMR spectrum of glycosylated product **2a** ($CD_3OD$, 600 MHz).

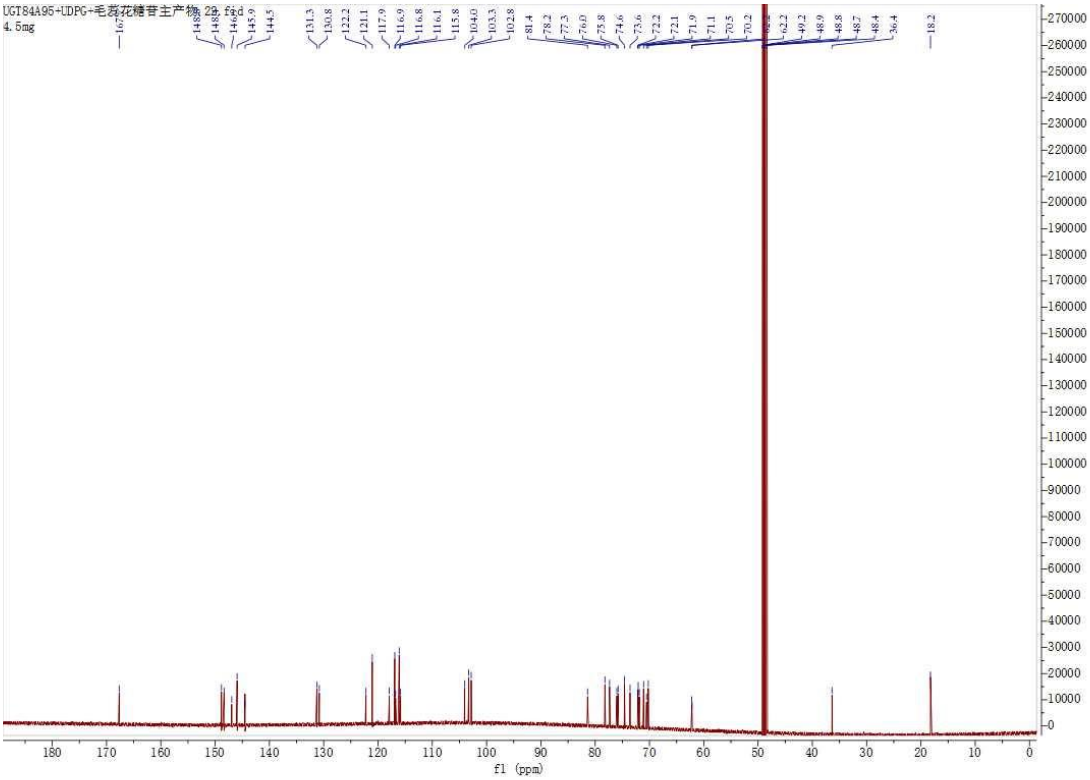

**Figure S46.** $^{13}C$ NMR spectrum of glycosylated product **2a** ($CD_3OD$, 600 MHz).

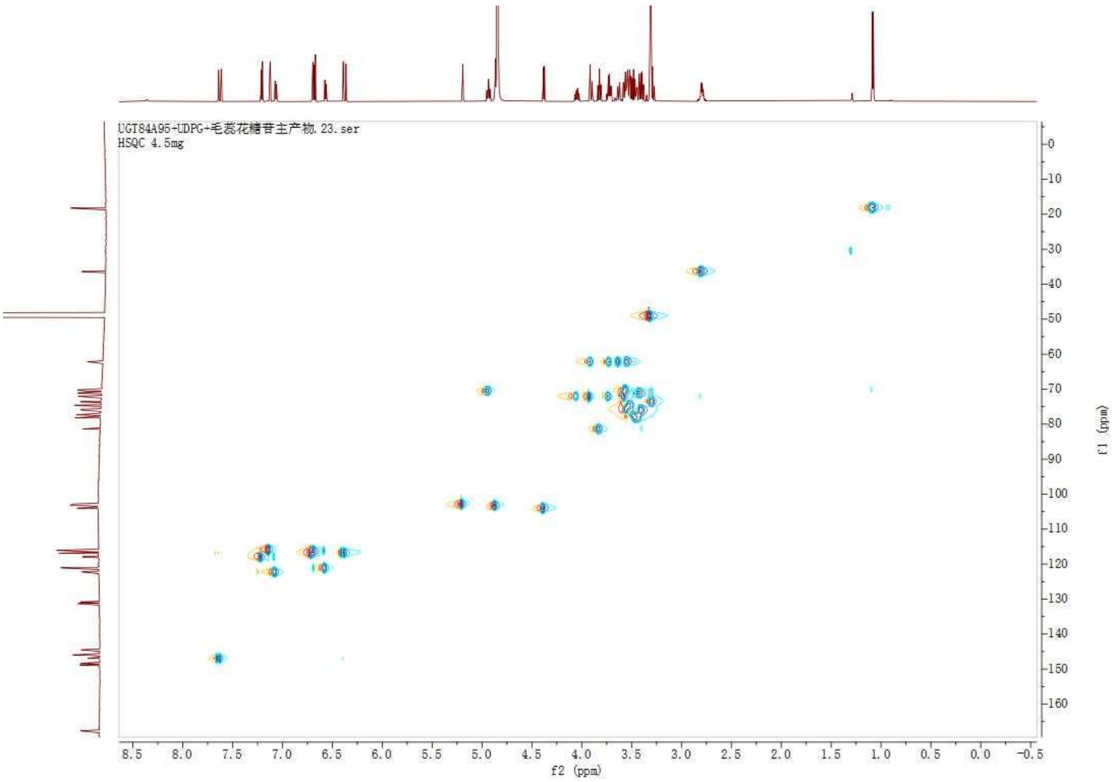


**Figure S47.** HSQC NMR spectrum of glycosylated product **2a** ($CD_3OD$, 600 MHz).

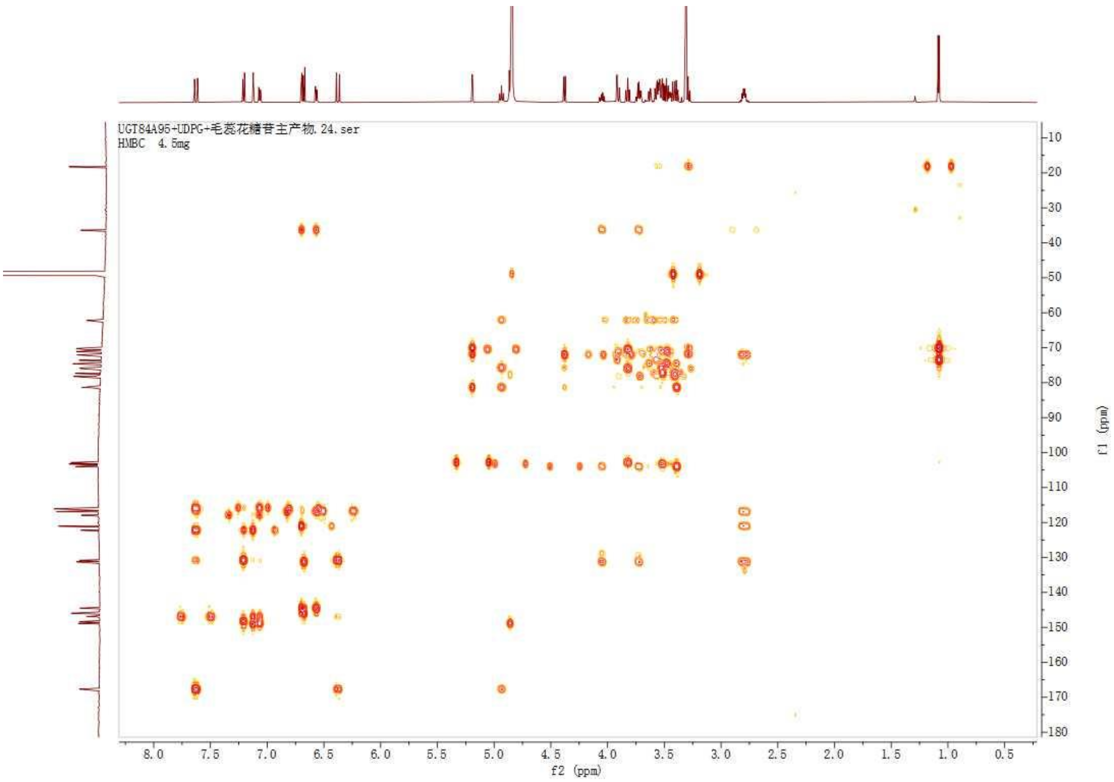


**Figure S48.** HMBC NMR spectrum of glycosylated product **2a** ($CD_3OD$, 600 MHz).

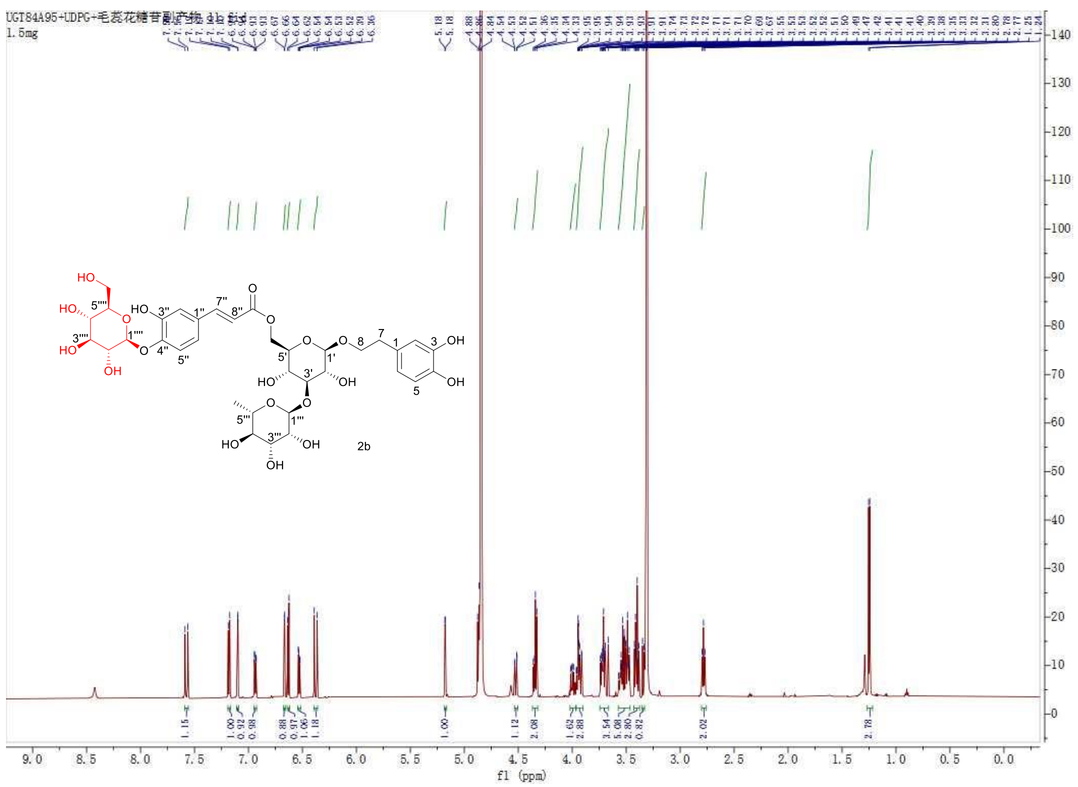

**Figure S49.** $^{1}H$ NMR spectrum of glycosylated product **2b** ($CD_3OD$, 600 MHz).

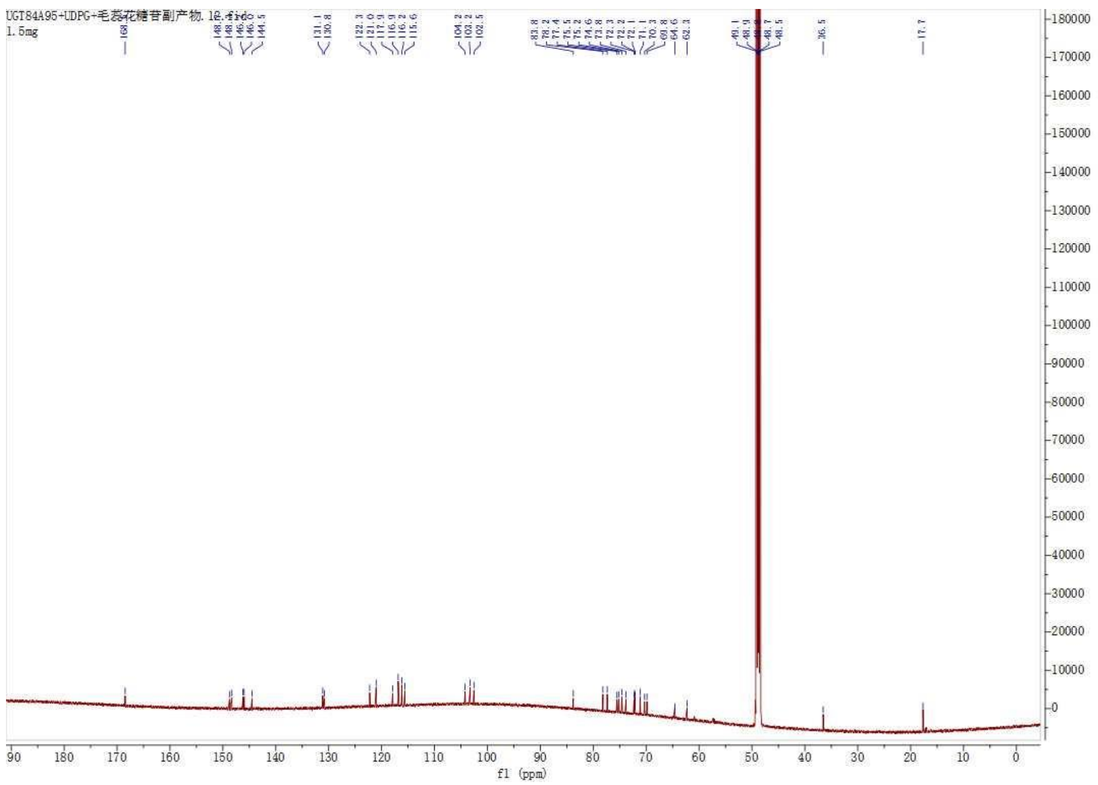

**Figure S50.** $^{13}C$ NMR spectrum of glycosylated product **2b** ($CD_3OD$, 600 MHz).

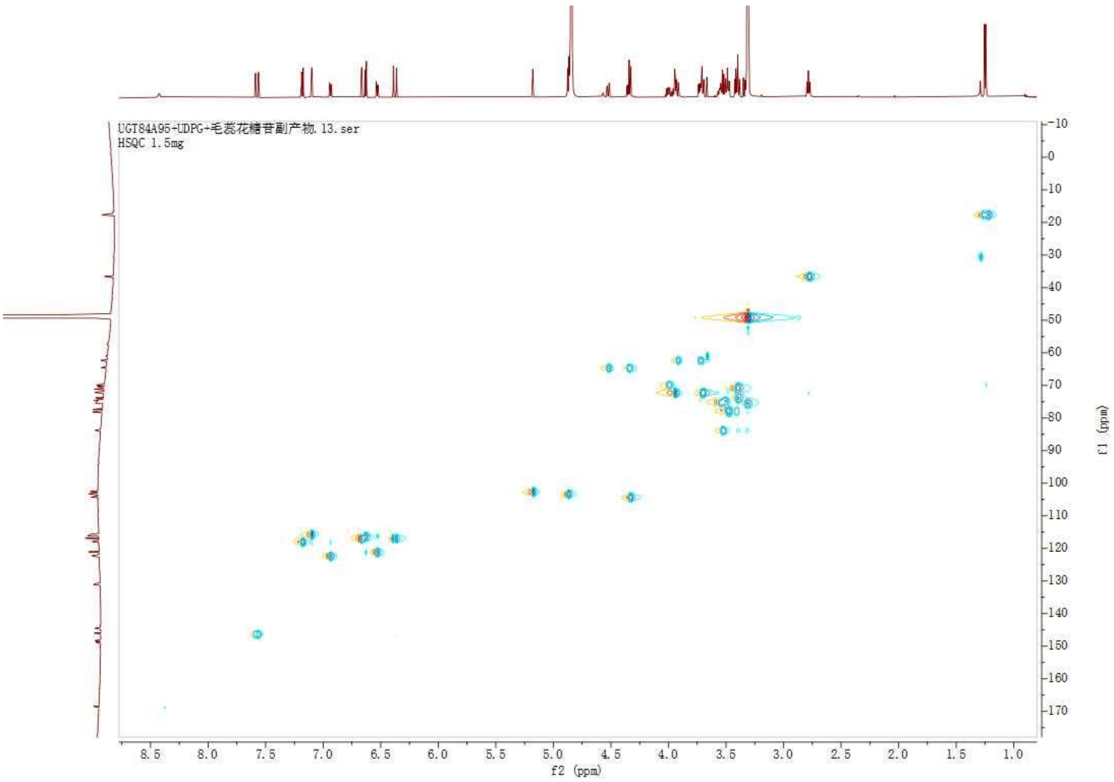


**Figure S51.** HSQC spectrum of glycosylated product **2b** ($CD_3OD$, 600 MHz).

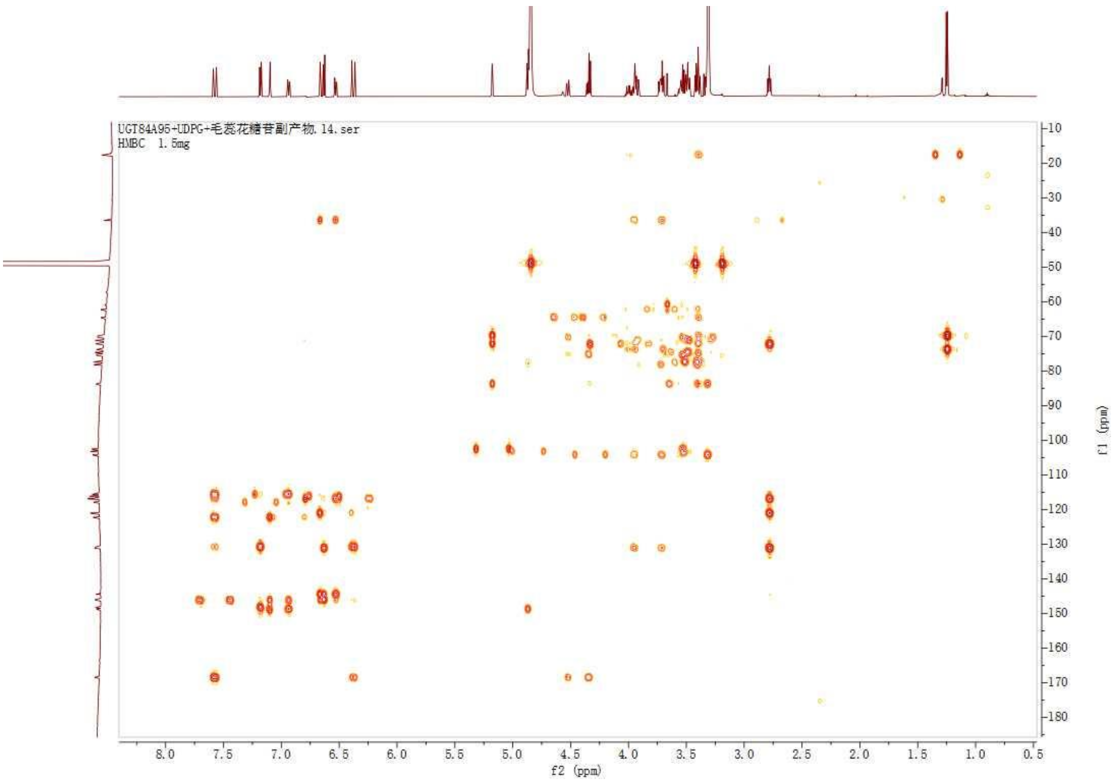


**Figure S52.** HMBC spectrum of glycosylated product **2b** ($CD_3OD$, 600 MHz).

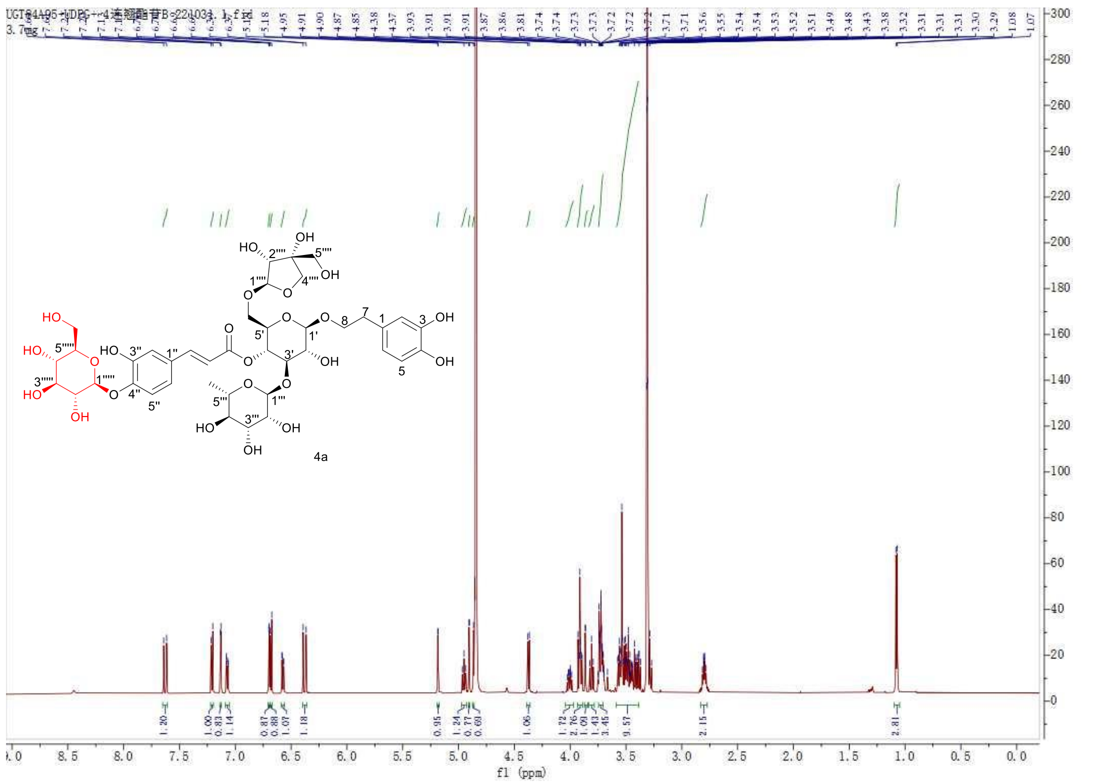

**Figure S53.** $^{1}$H NMR spectrum of glycosylated product **4a** ($CD_3OD$, 600 MHz).

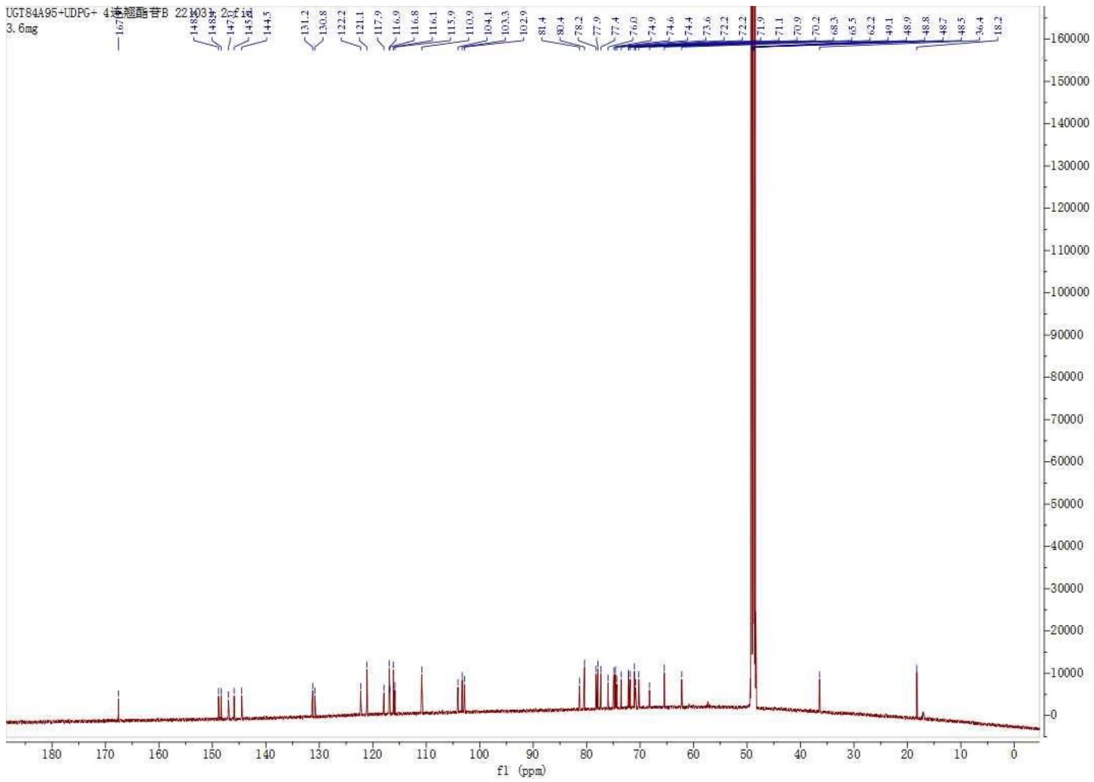

**Figure S54.** $^{13}$C NMR spectrum of glycosylated product **4a** ($CD_3OD$, 600 MHz).

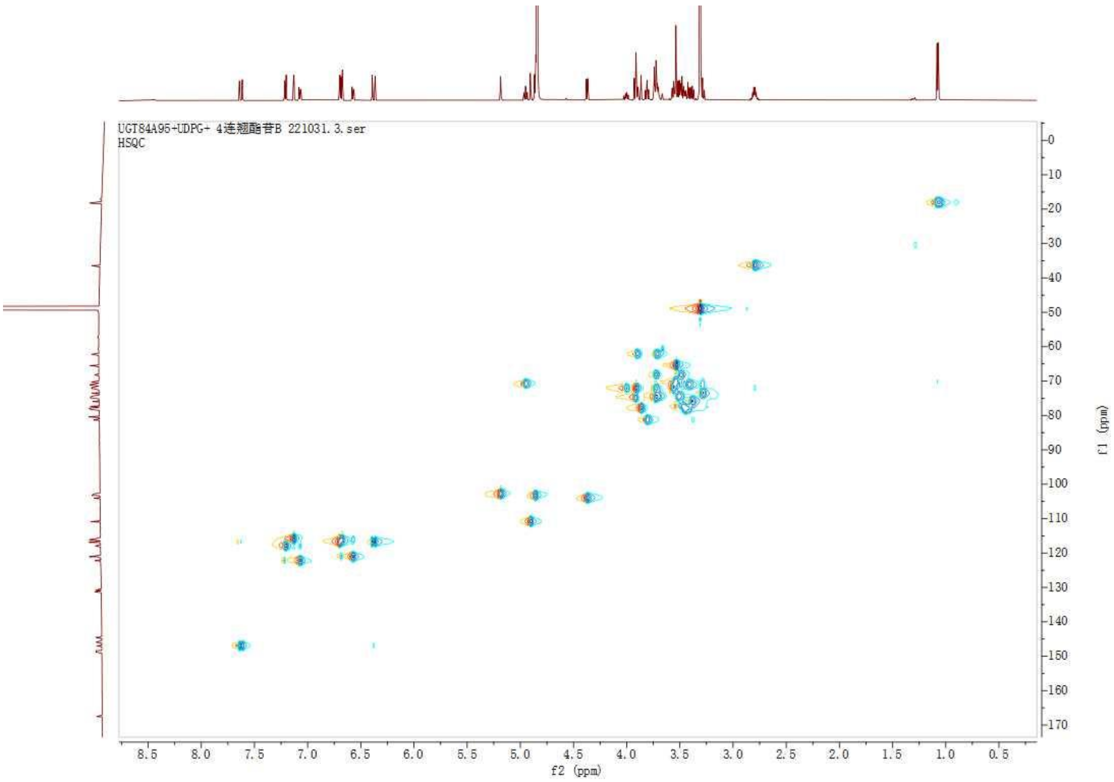


**Figure S55.** HSQC spectrum of glycosylated product **4a** ($CD_3OD$, 600 MHz).

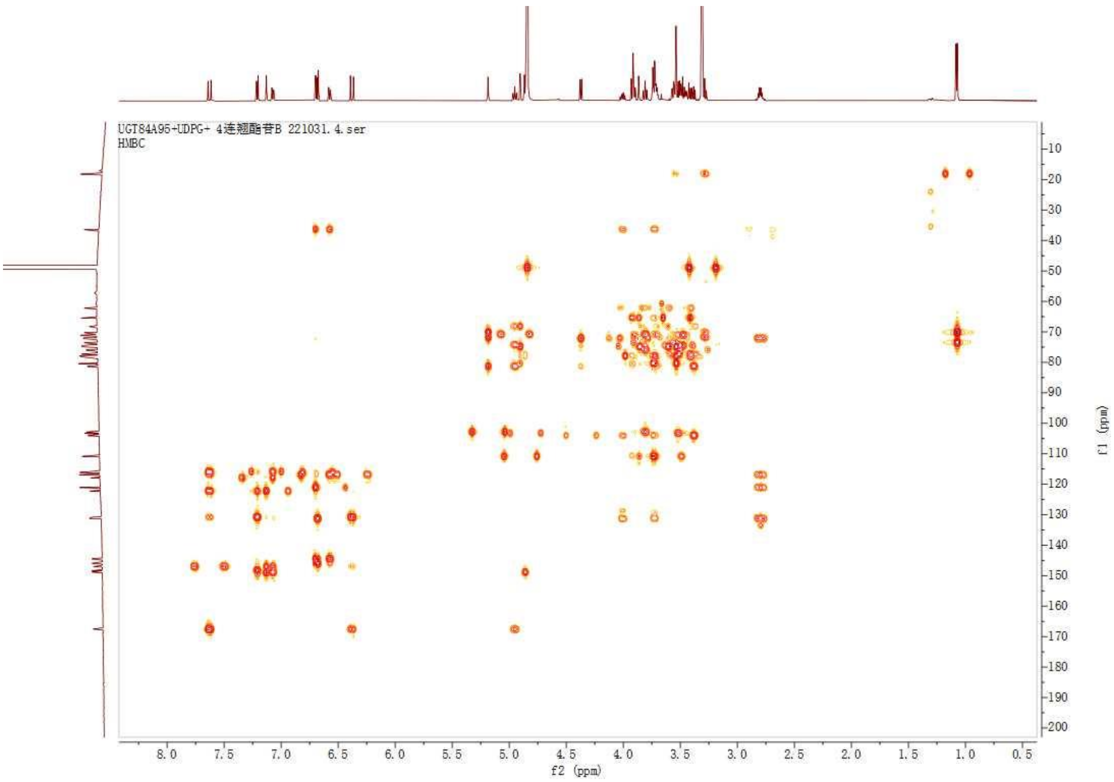


**Figure S56.** HMBC spectrum of glycosylated product **4a** ($CD_3OD$, 600 MHz).

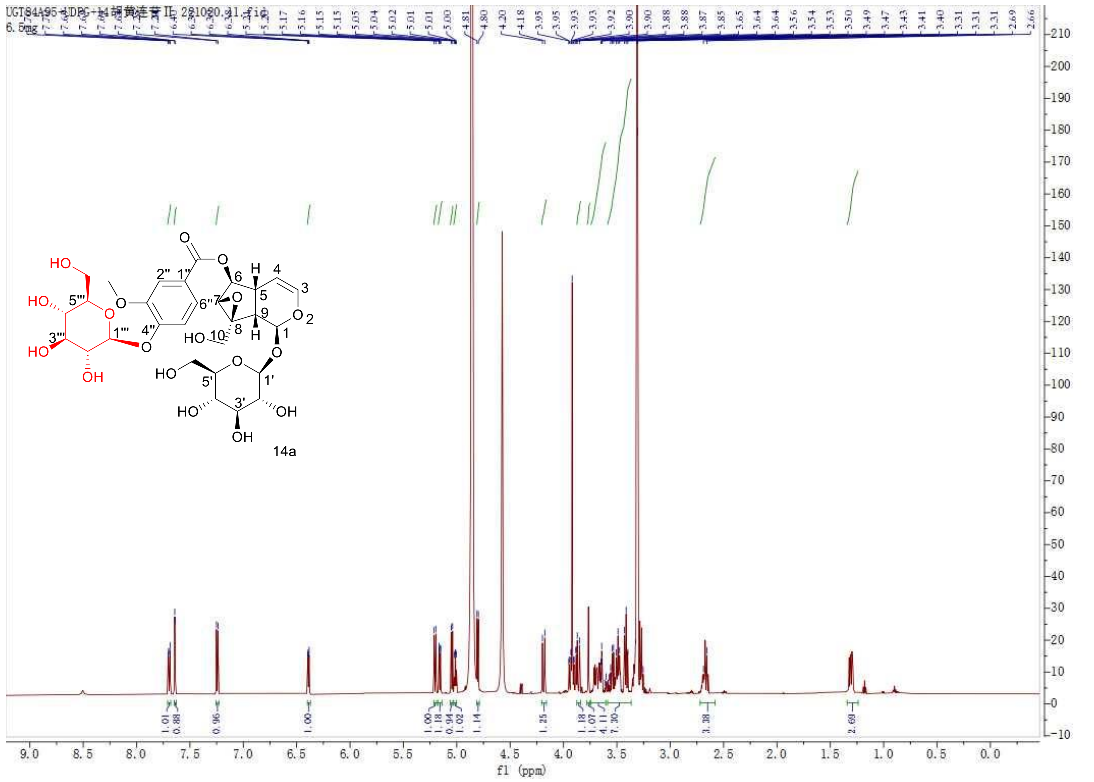

**Figure S57.** $^{1}H$ NMR spectrum of glycosylated product **14a** ($CD_3OD$, 600 MHz).

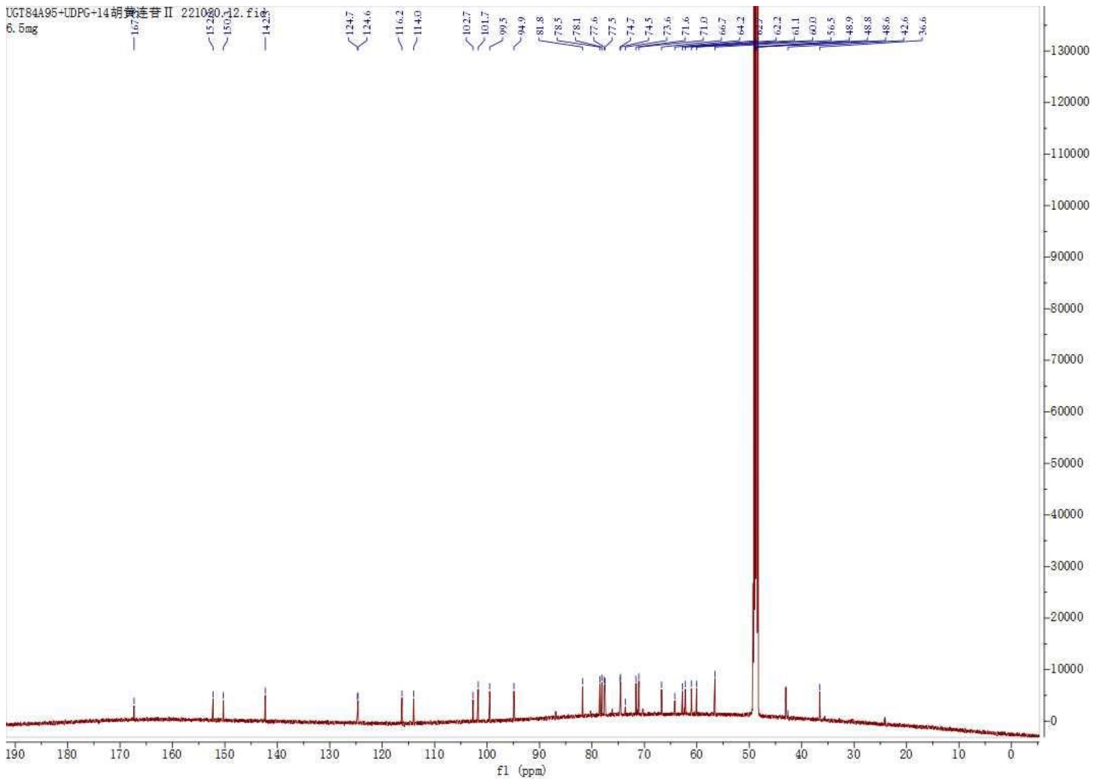

**Figure S58.** $^{13}C$ NMR spectrum of glycosylated product **14a** ($CD_3OD$, 600 MHz).

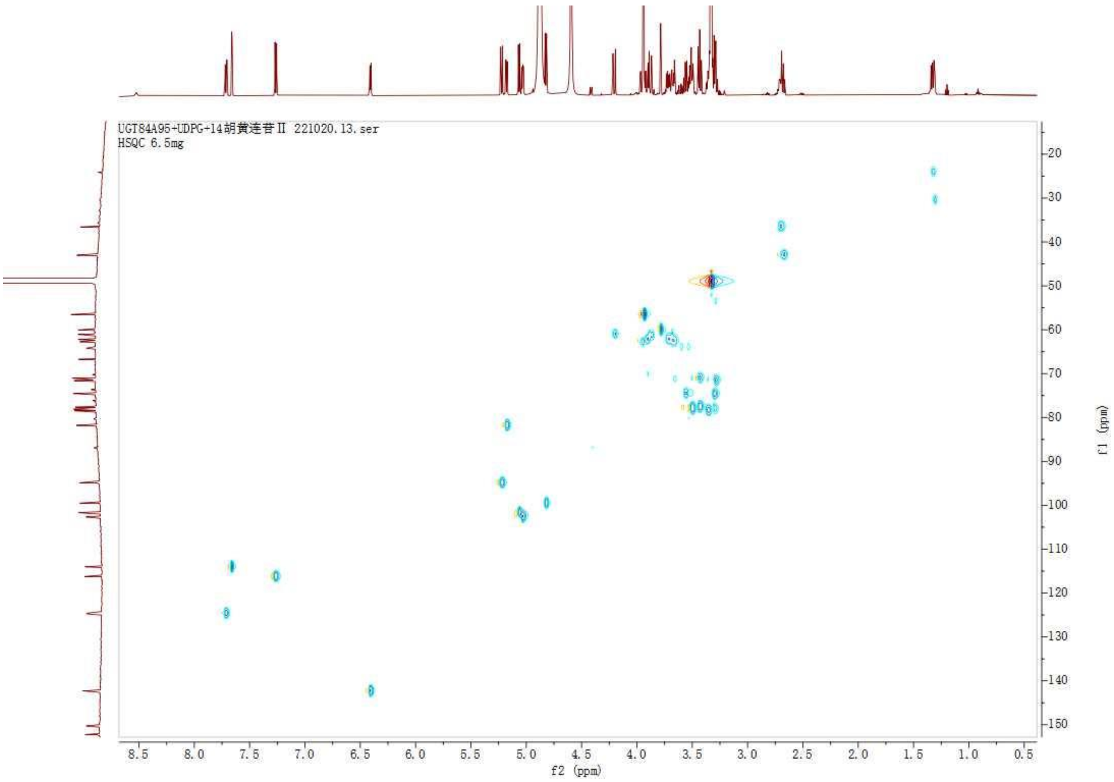


**Figure S59.** HSQC spectrum of glycosylated product **14a** ($CD_3OD$, 600 MHz).

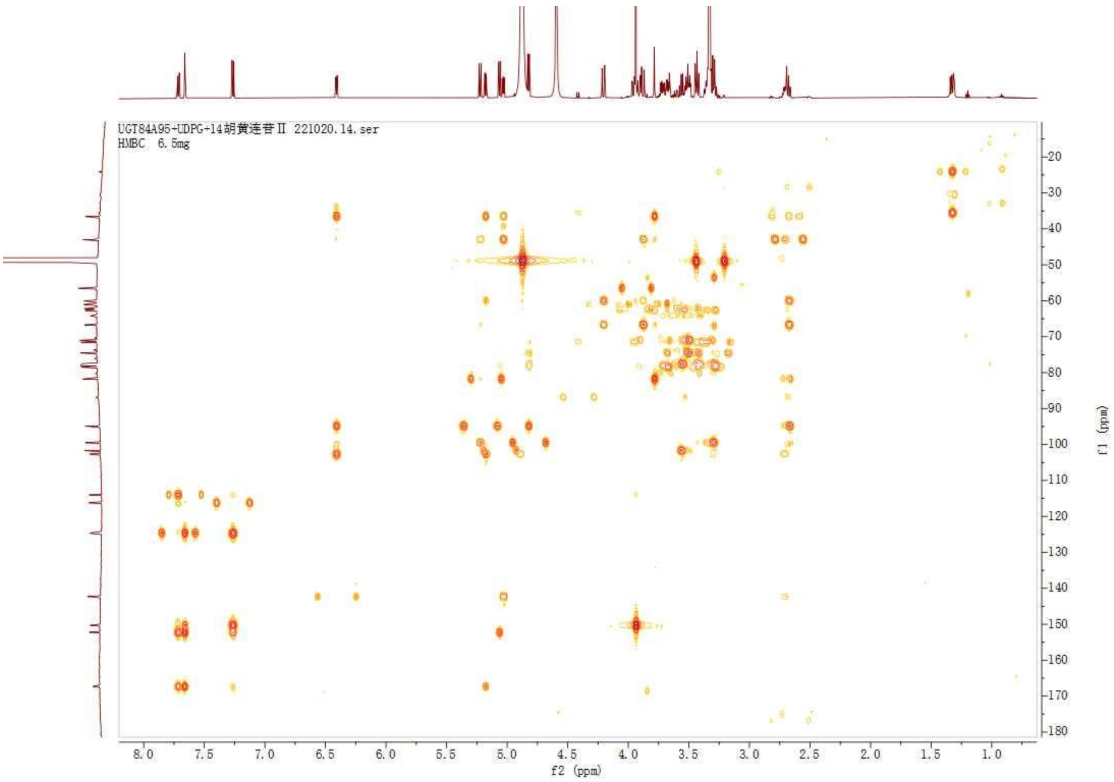


**Figure S60.** HMBC spectrum of glycosylated product **14a** ($CD_3OD$, 600 MHz).

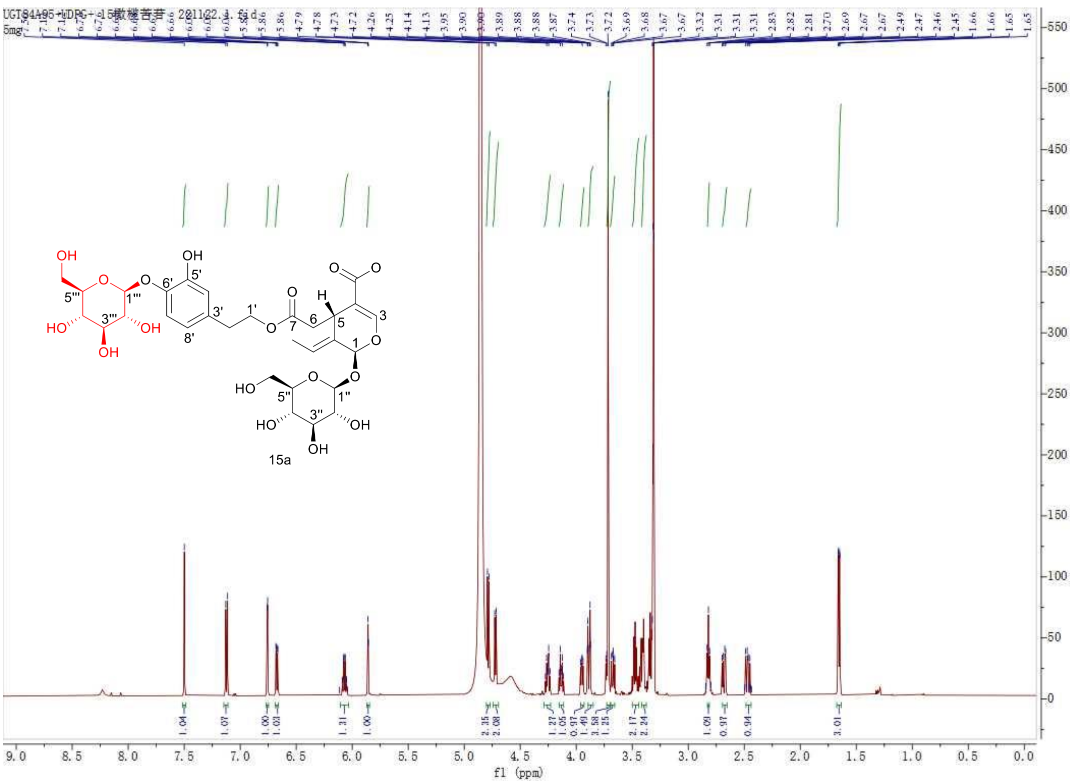

**Figure S61.** $^{1}H$ NMR spectrum of glycosylated product **15a** ($CD_3OD$, 600 MHz).

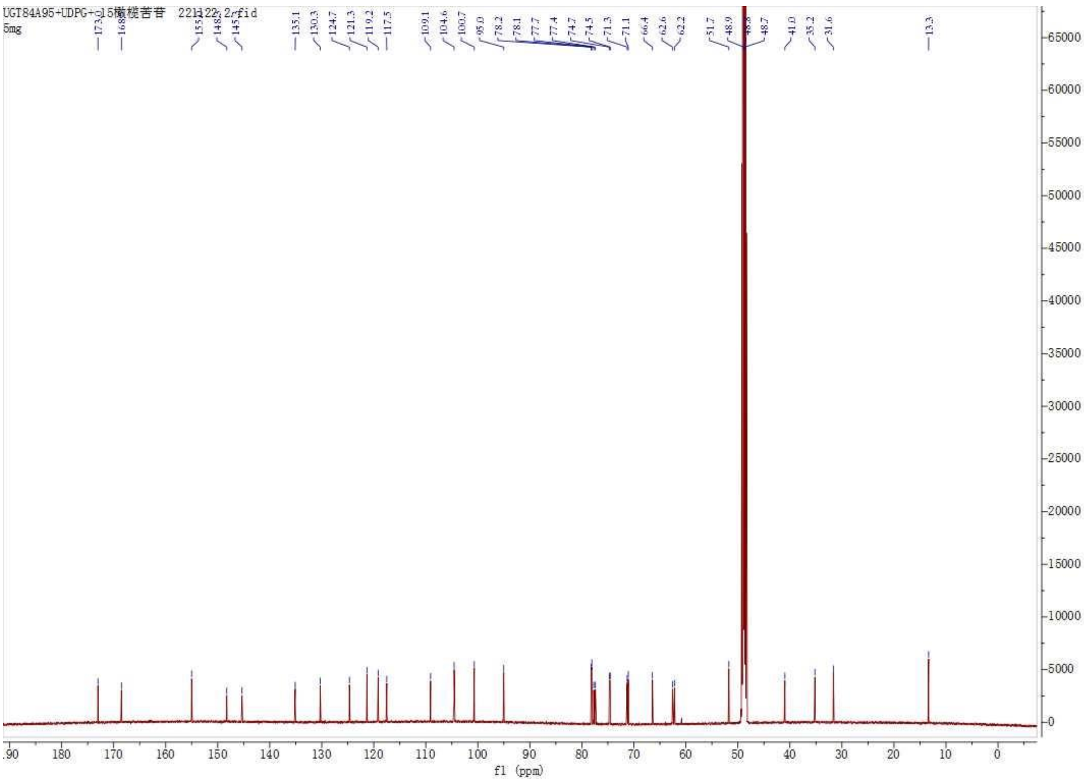

**Figure S62.** $^{13}C$ NMR spectrum of glycosylated product **15a** ($CD_3OD$, 600 MHz).

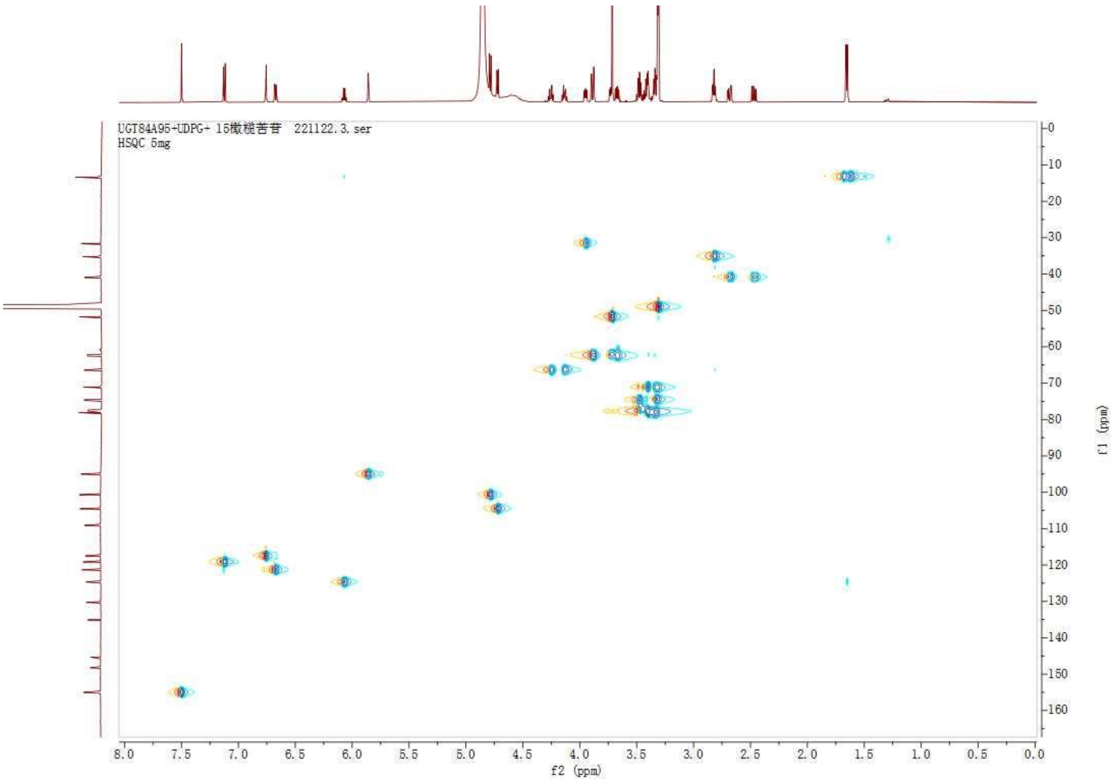


**Figure S63.** HSQC spectrum of glycosylated product **15a** ($CD_3OD$, 600 MHz).

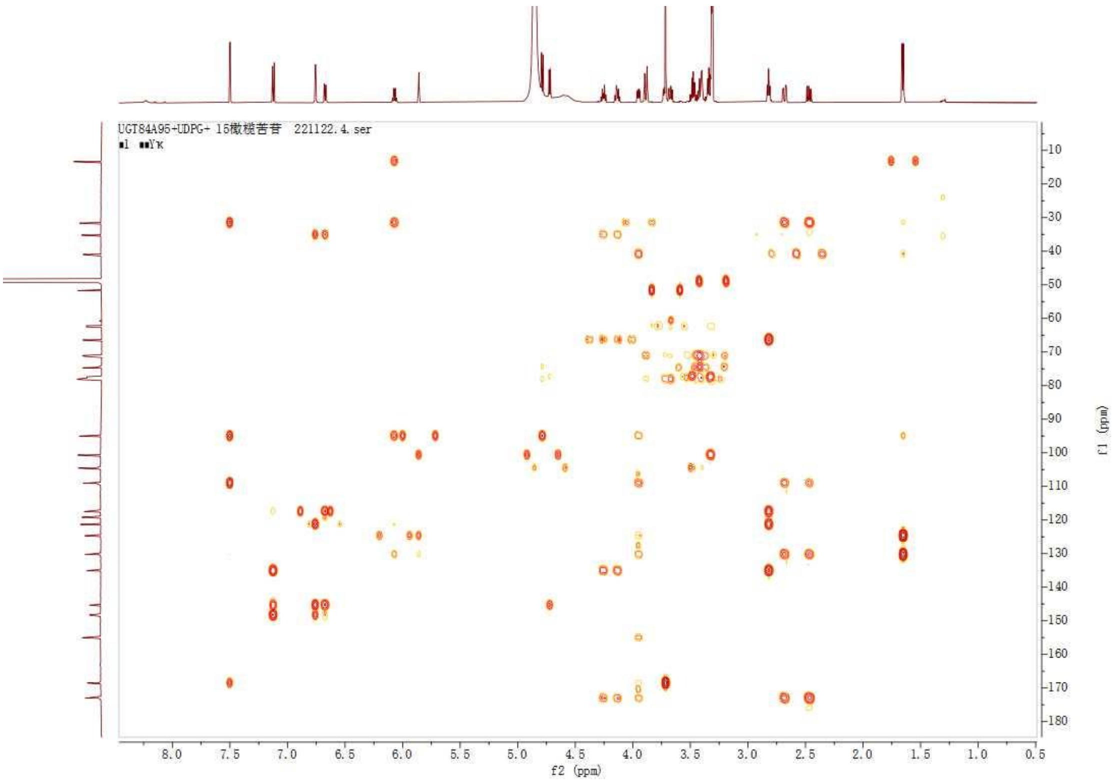


**Figure S64.** HMBC spectrum of glycosylated product **15a** ($CD_3OD$, 600 MHz).

## 3. Supplementary Note.

>UGT84A95

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