**Supporting Information for**

# Terpenoids from the Stems of *Fissistigma polyanthoides* and Their Anti-Inflammatory Activities

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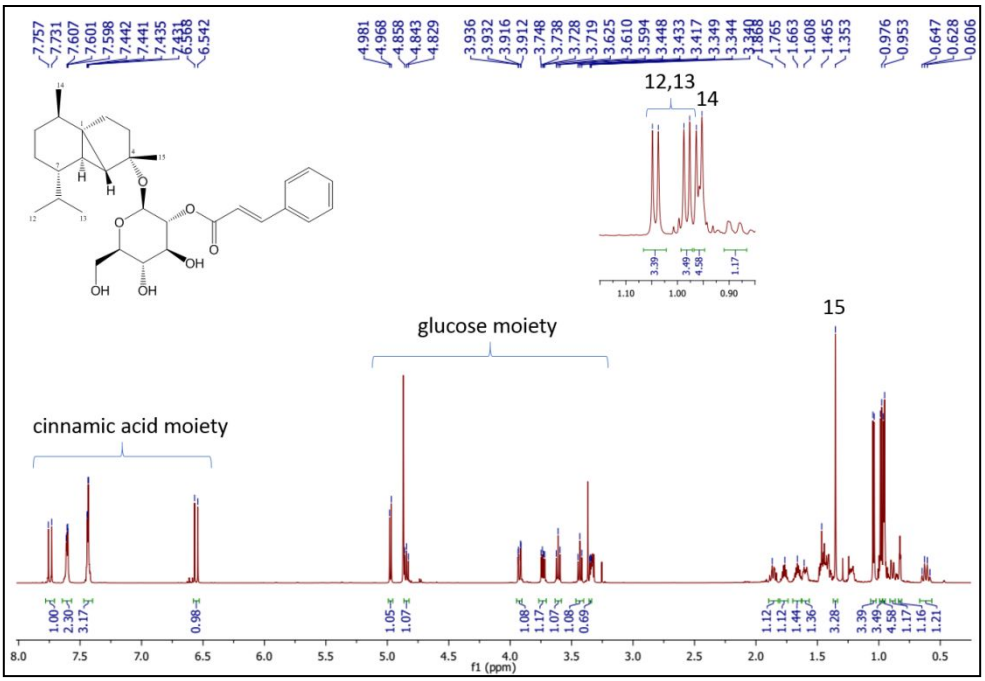



Figure S1.1. $^{1}$H NMR spectrum of compound **1** (600 MHz, in MeOH-$d_4$)

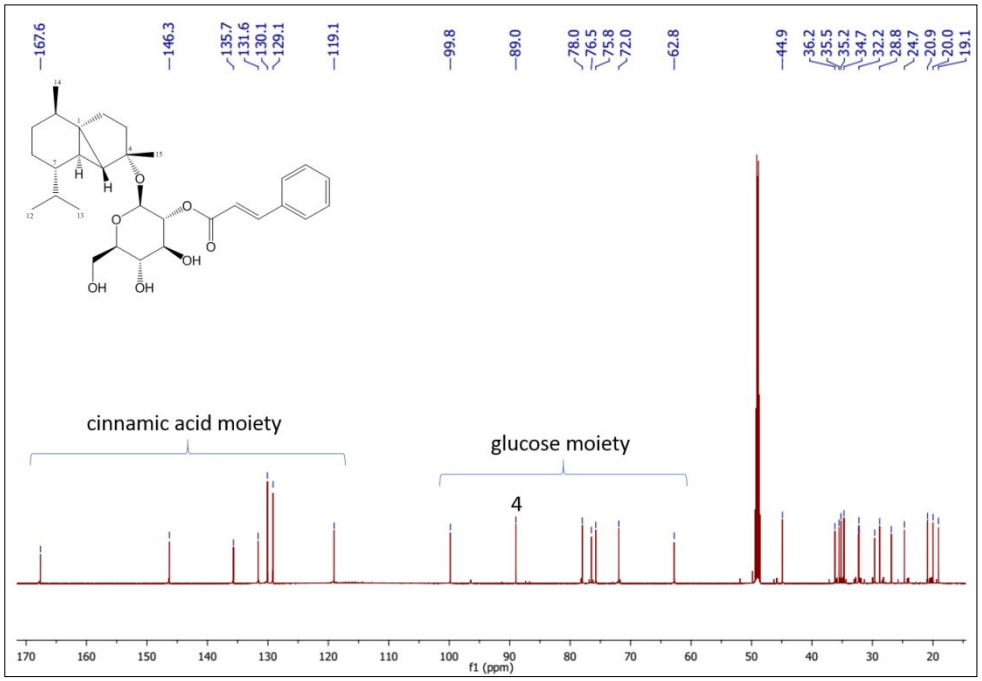



Figure S1.2. $^{13}$C NMR spectrum of compound **1** (150 MHz, in MeOH-$d_4$)

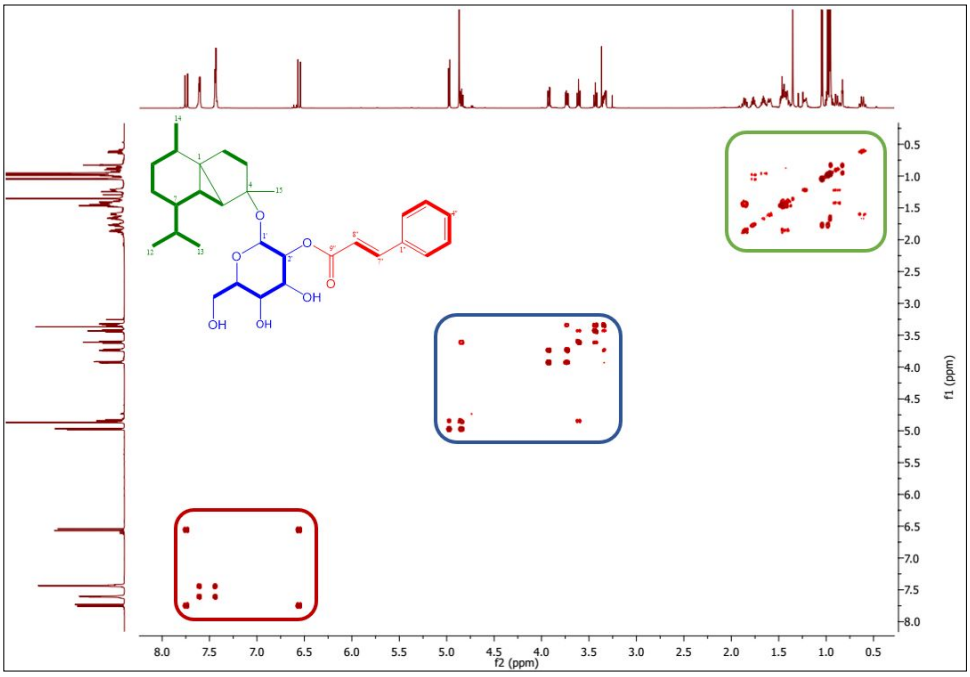



Figure S1.3. COSY spectrum of compound **1** (in MeOH-$d_4$)

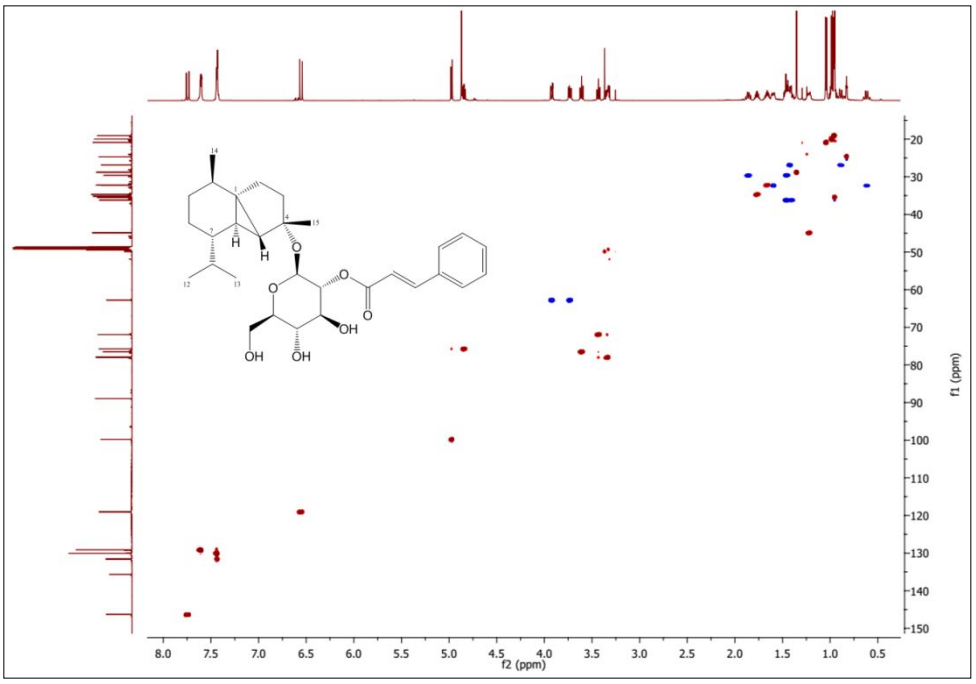



Figure S1.4. HSQC spectrum of compound **1** (in MeOH-$d_4$)

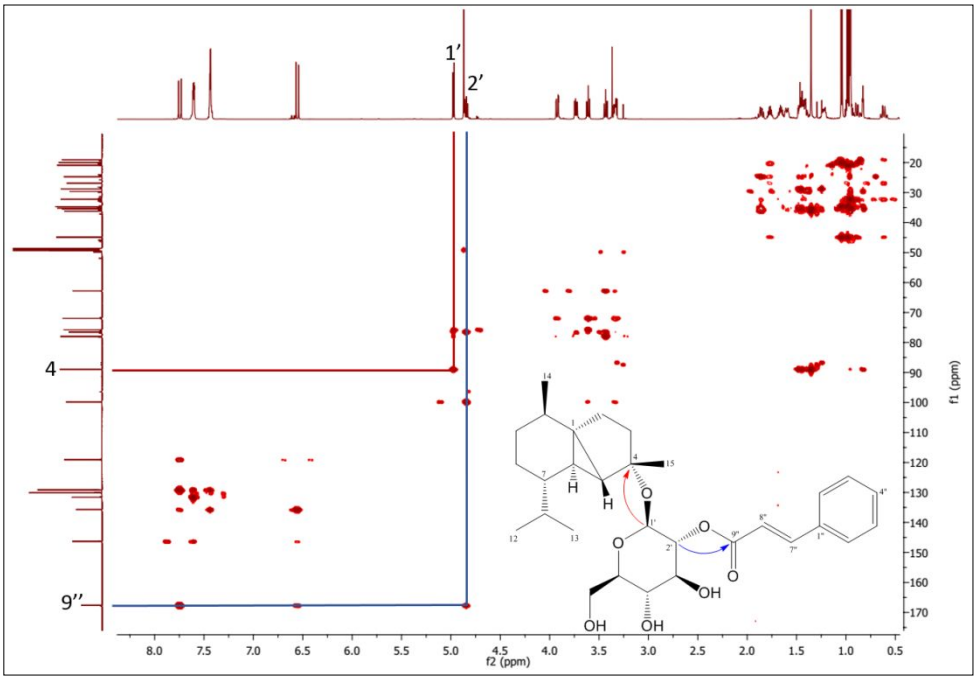



Figure S1.5. HMBC spectrum of compound **1** (in MeOH-$d_4$)

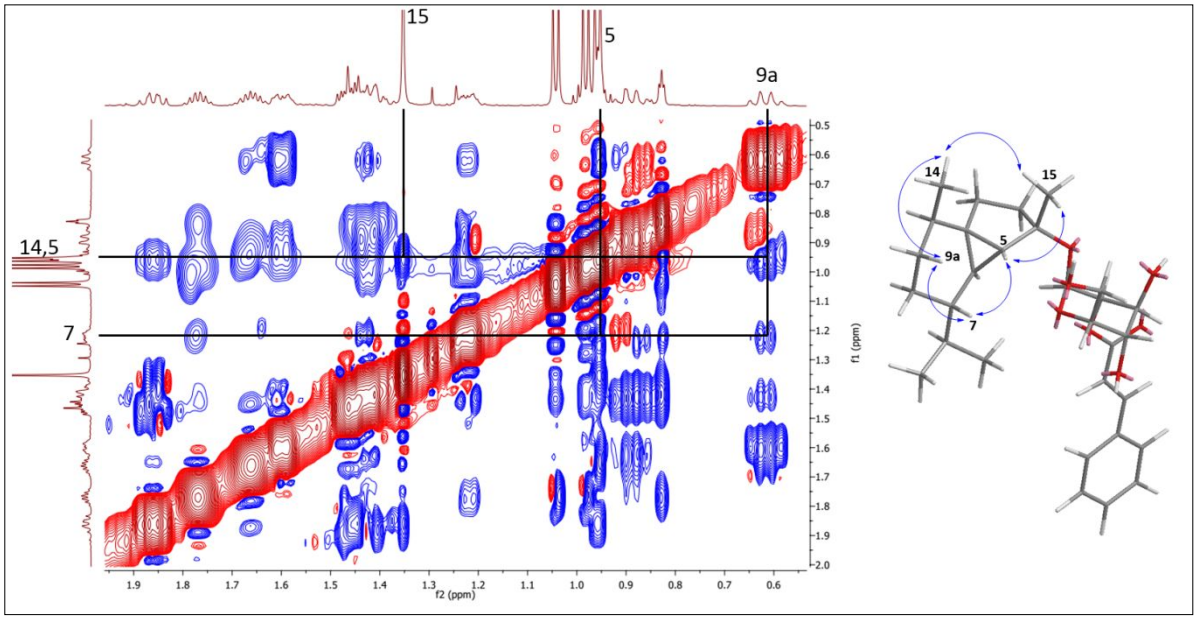



Figure S1.6.1. NOESY spectrum of compound **1** (aglycone, MeOH-$d_4$)

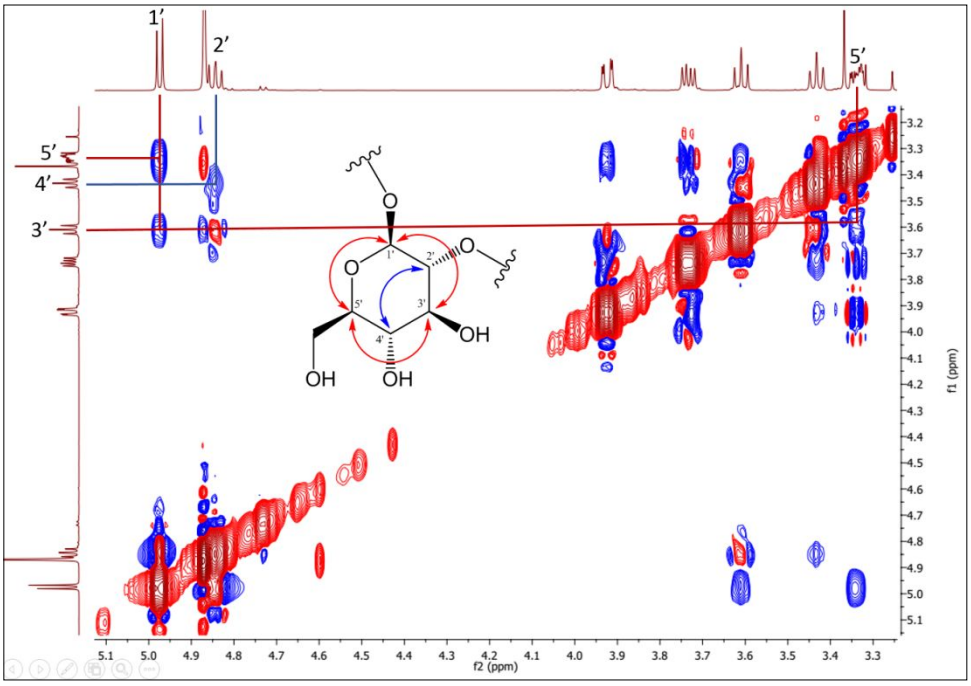



Figure S1.6.2. NOESY spectrum of compound **1** (sugar, MeOH-$d_4$)

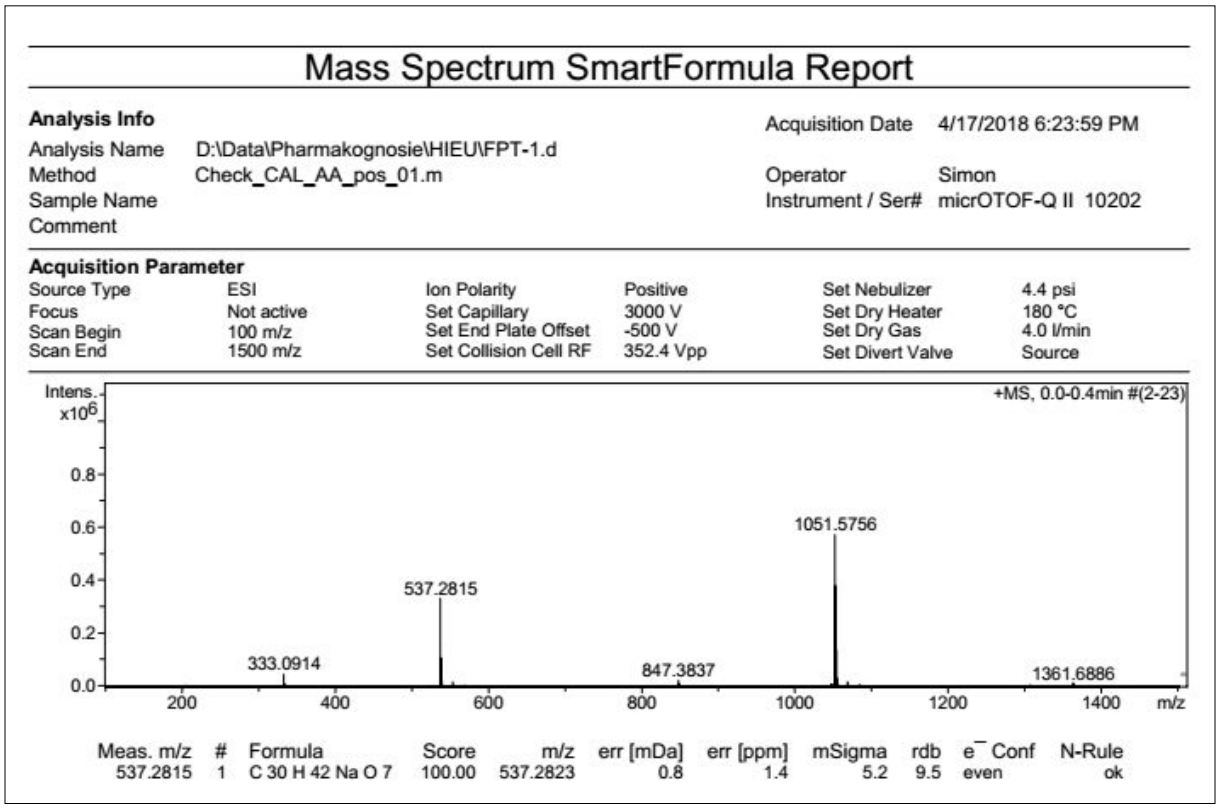



Figure S1.7. HRESIMS spectrum of compound **1**

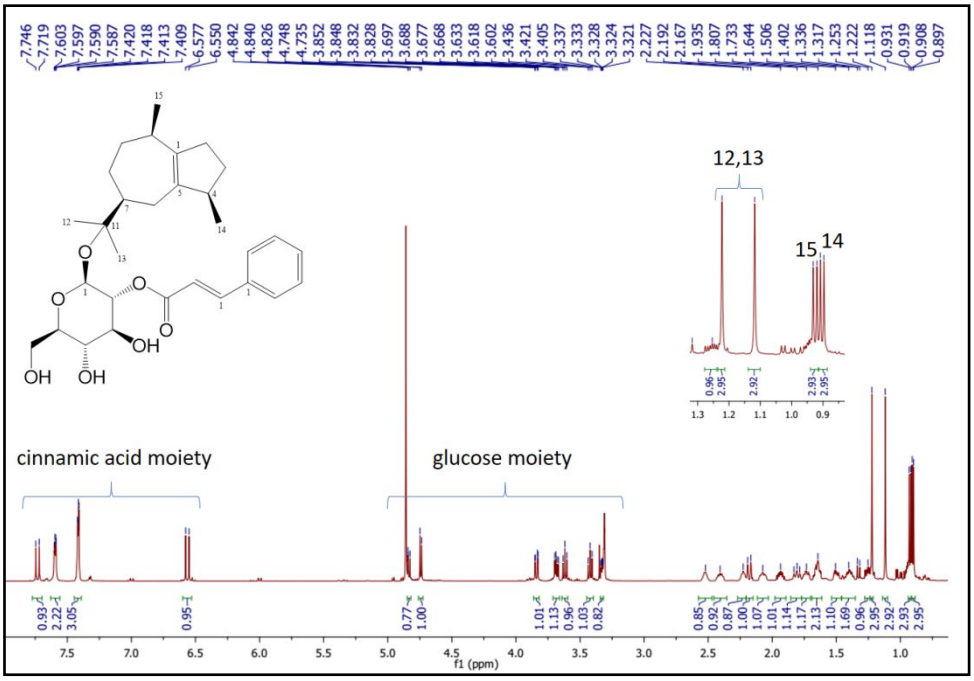



Figure S2.1. $^{1}$H NMR spectrum of compound **2** (600 MHz, in MeOH-$d_4$)

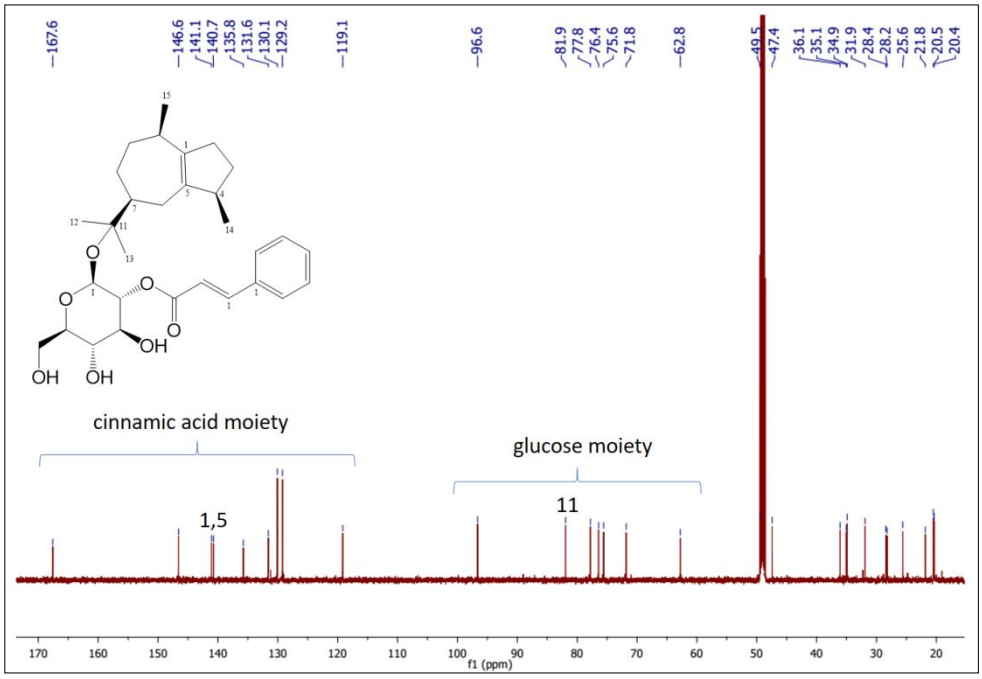



Figure S2.2. $^{13}$C NMR spectrum of compound **2** (150 MHz, in MeOH-$d_4$)

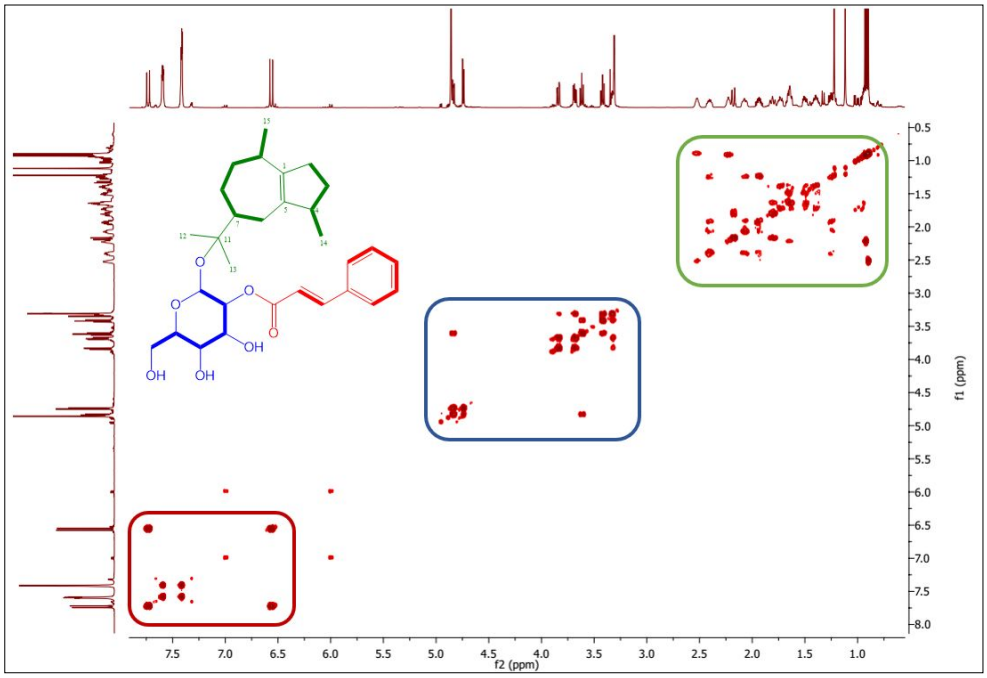



Figure S2.3. COSY spectrum of compound **2** (in MeOH-$d_4$)

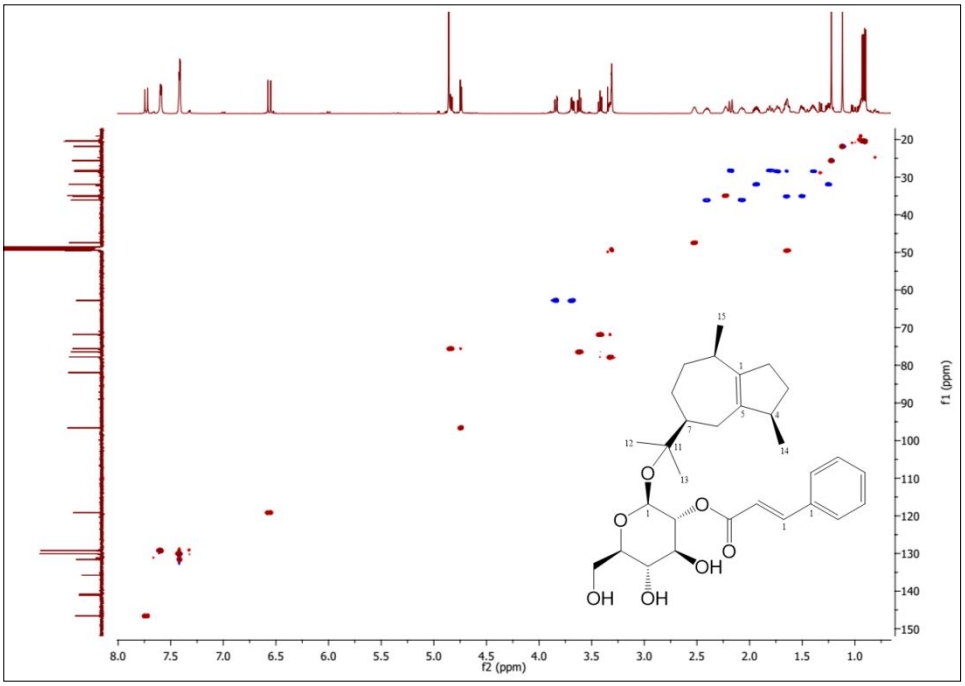



Figure S2.4. HSQC spectrum of compound **2** (in MeOH-$d_4$)

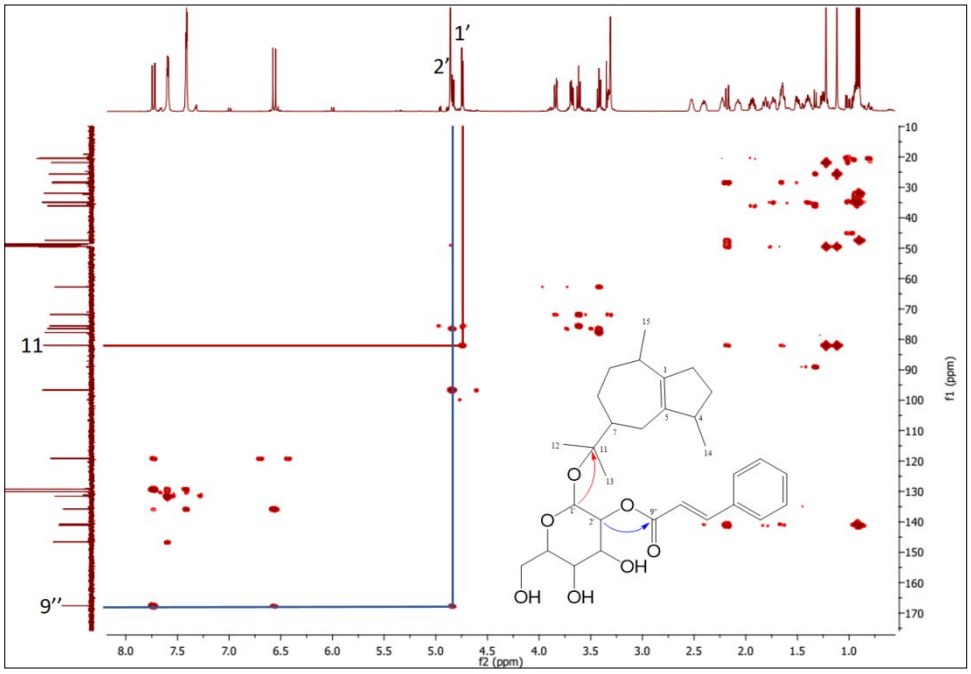



Figure S2.5. HMBC spectrum of compound **2** (in MeOH-$d_4$)

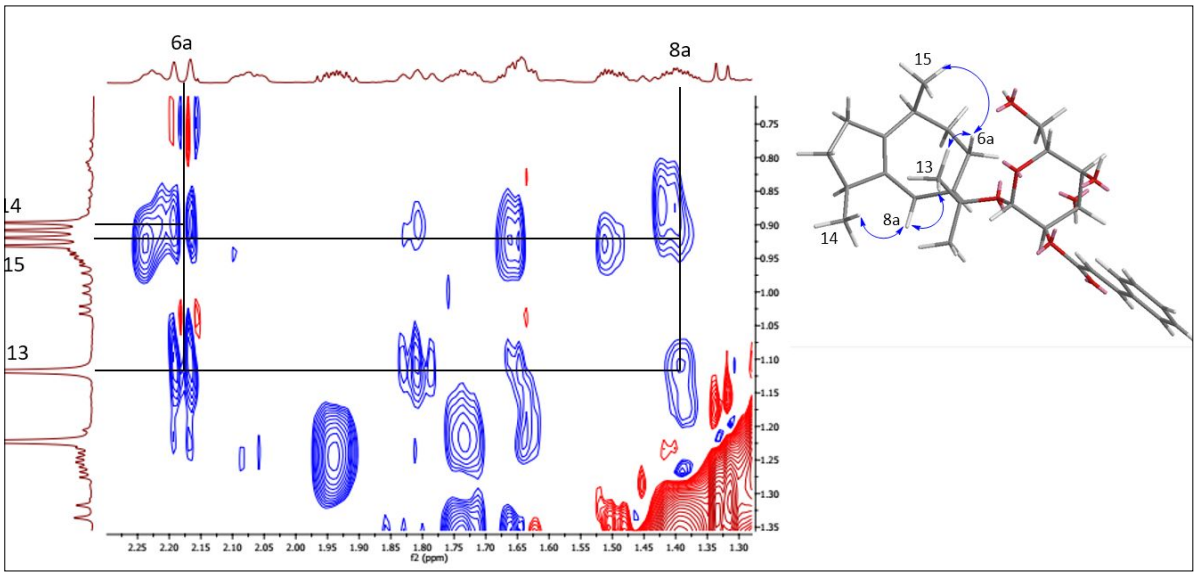



Figure S2.6. NOESY spectrum of compound **2** (aglycone, MeOH-$d_4$)

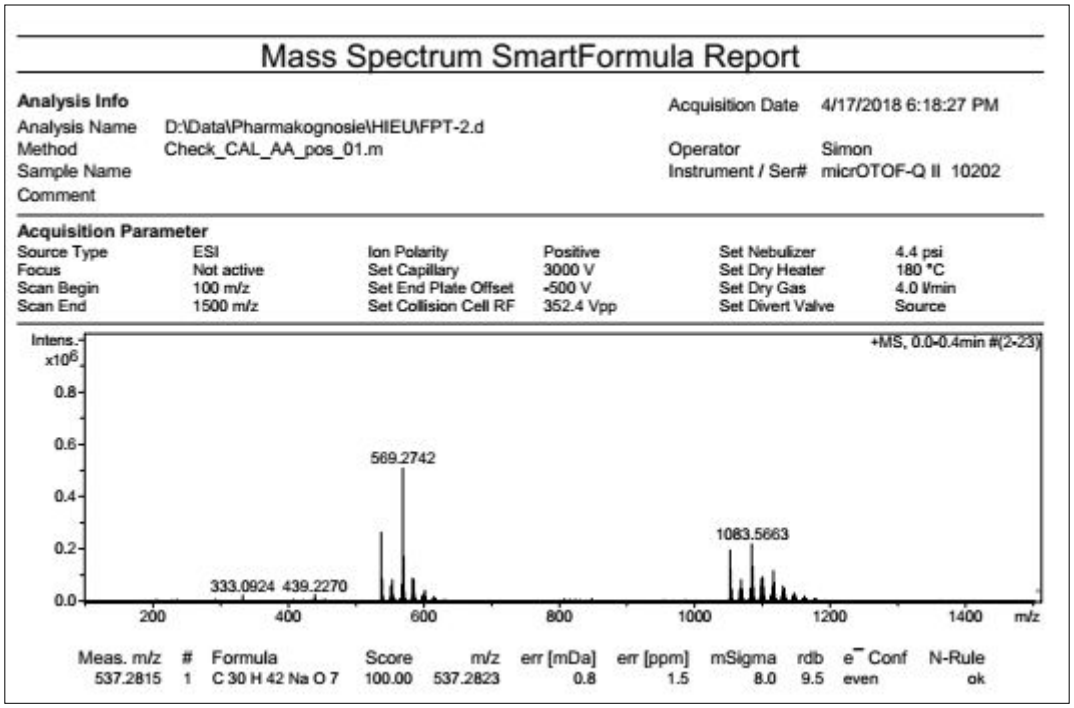



Figure S2.7. HRESIMS spectrum of compound **2**

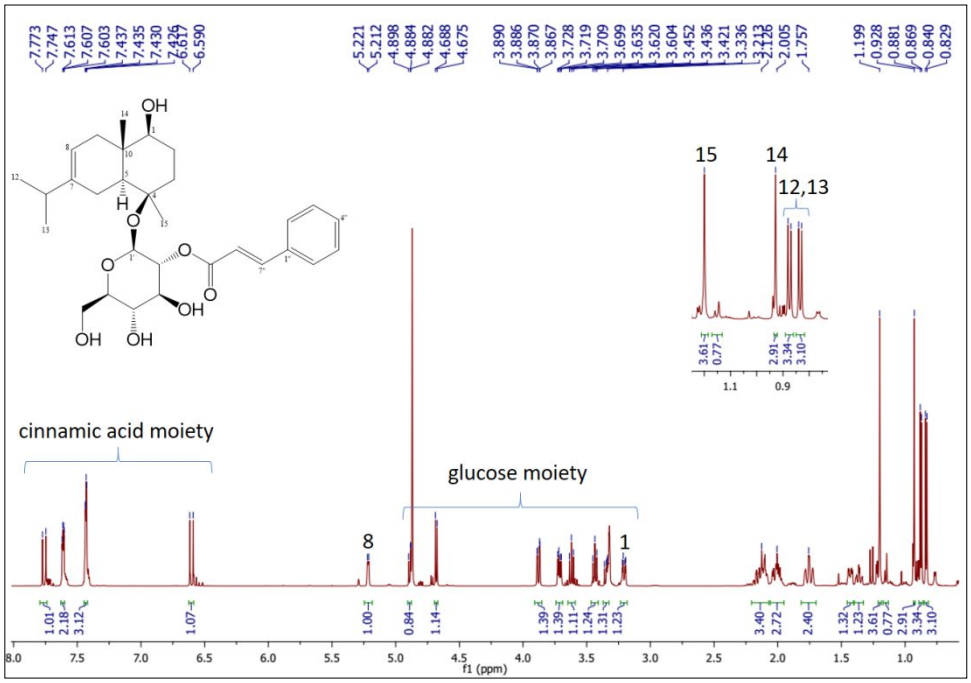



Figure S3.1. $^{1}$H NMR spectrum of compound **3** (600 MHz, in MeOH-$d_4$)

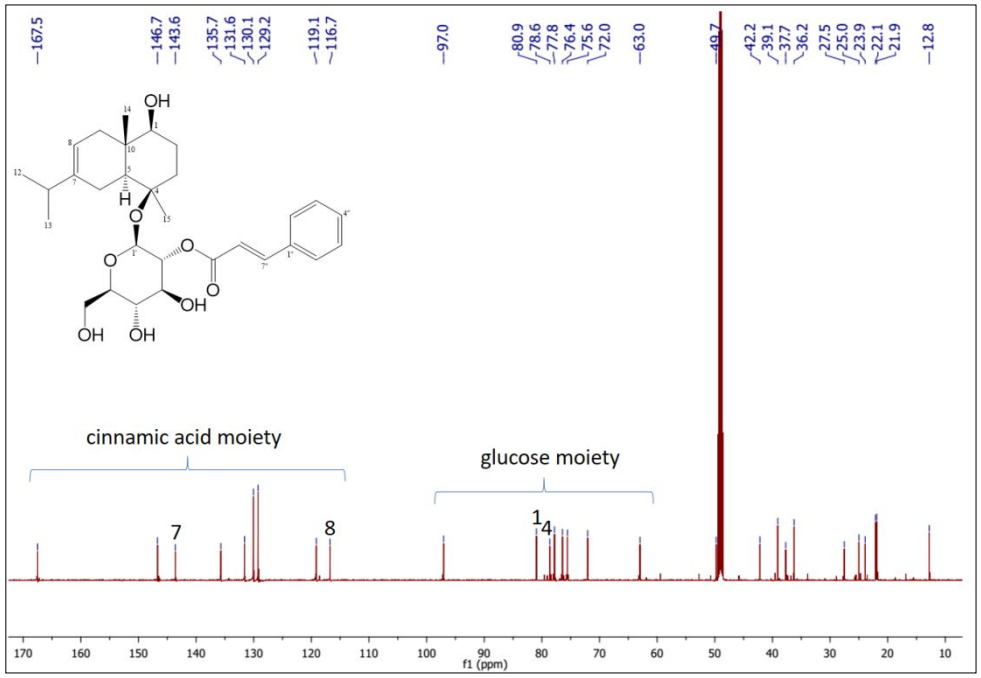



Figure S3.2. $^{13}$C NMR spectrum of compound **3** (150 MHz, in MeOH-$d_4$)

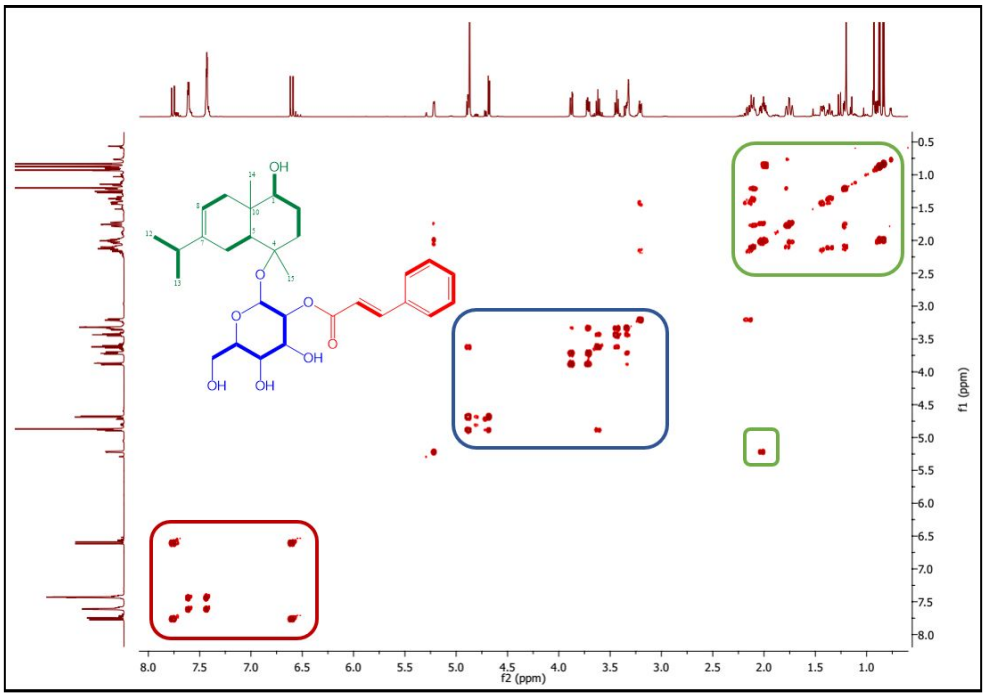



Figure S3.3. COSY spectrum of compound **3** (in MeOH-$d_4$)

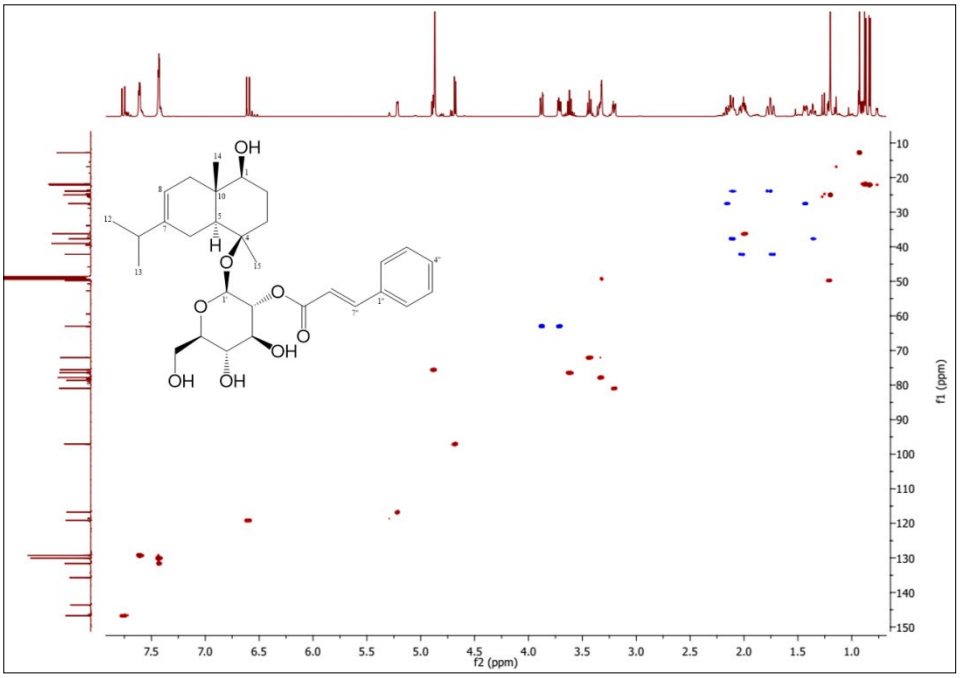



Figure S3.4. HSQC spectrum of compound **3** (in MeOH-$d_4$)

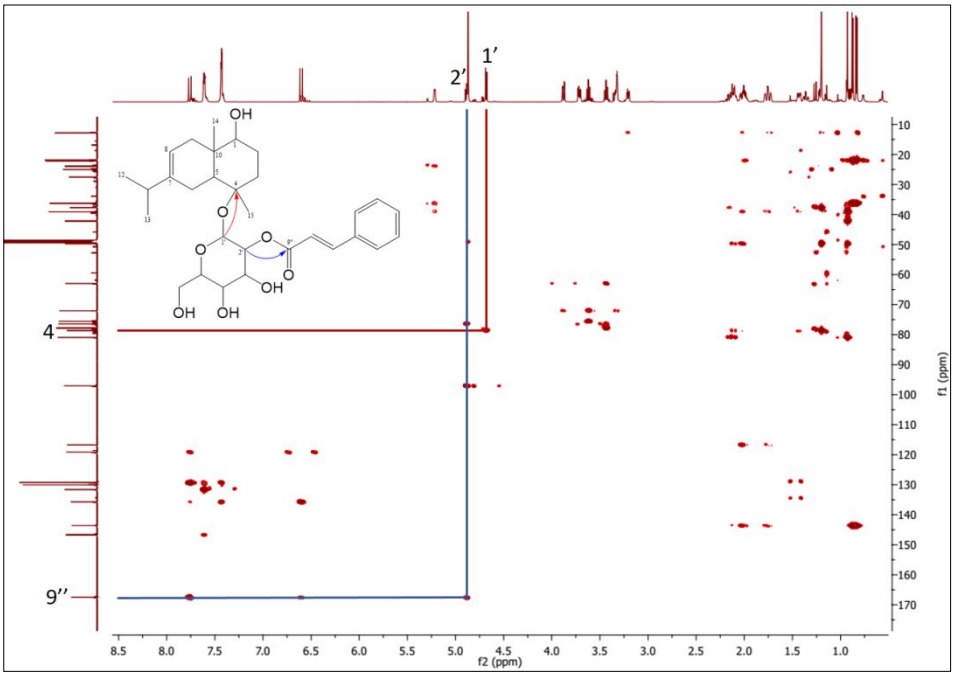



Figure S3.5. HMBC spectrum of compound **3** (in MeOH-$d_4$)

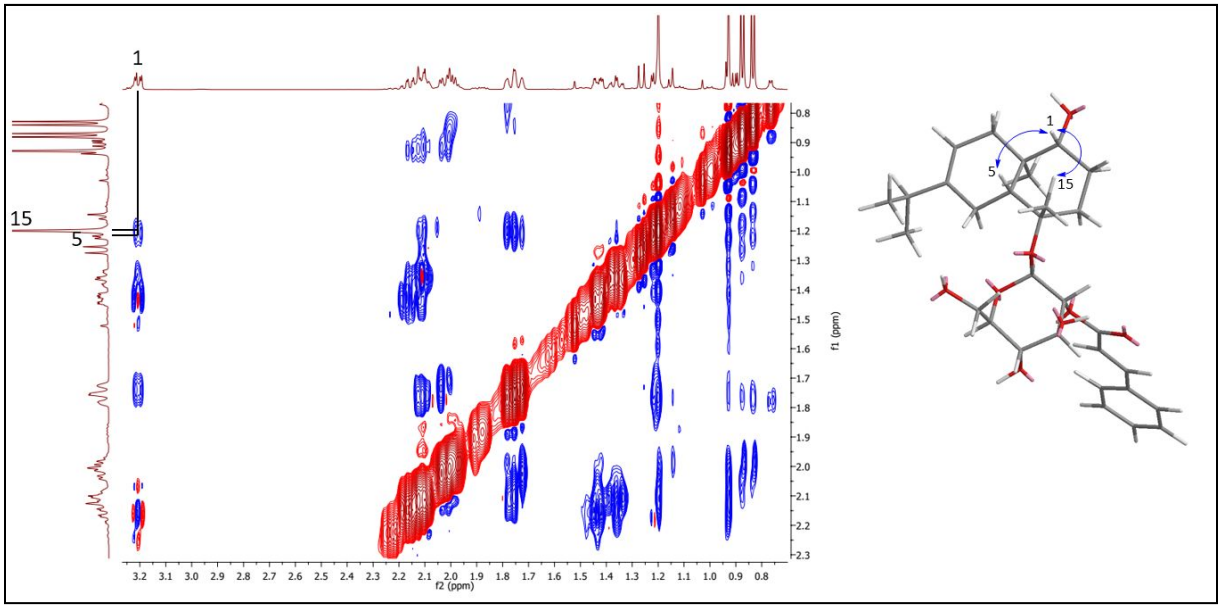



Figure S3.6.1. NOESY spectrum of compound **3** (aglycone, MeOH-$d_4$)

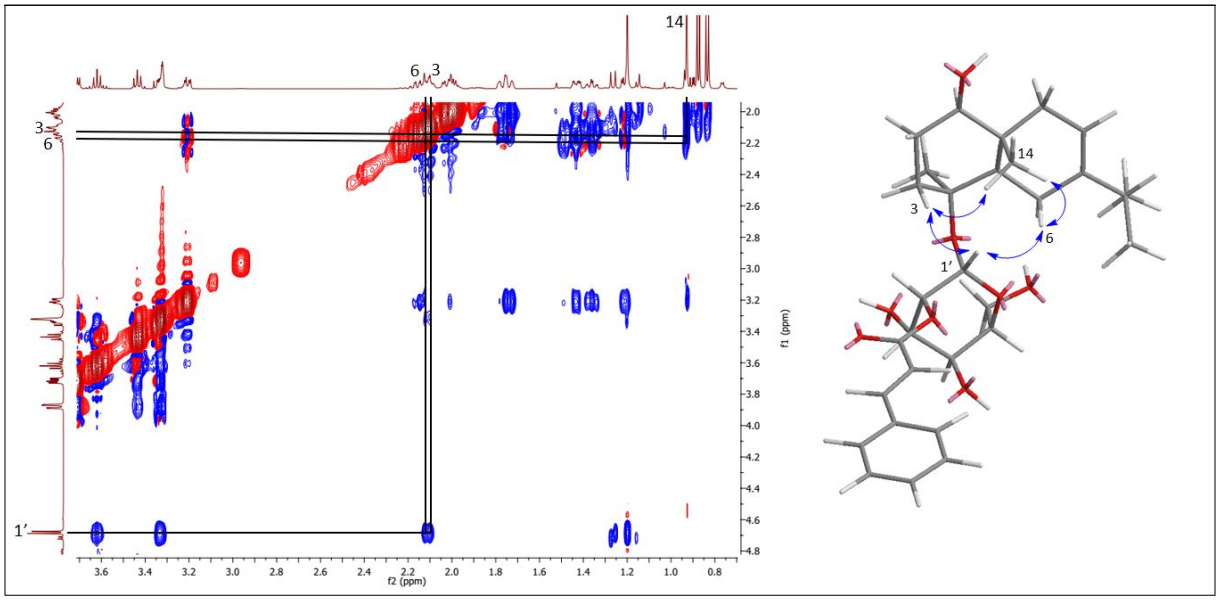



Figure S3.6.2. NOESY spectrum of compound **3** (aglycone, MeOH-$d_4$)

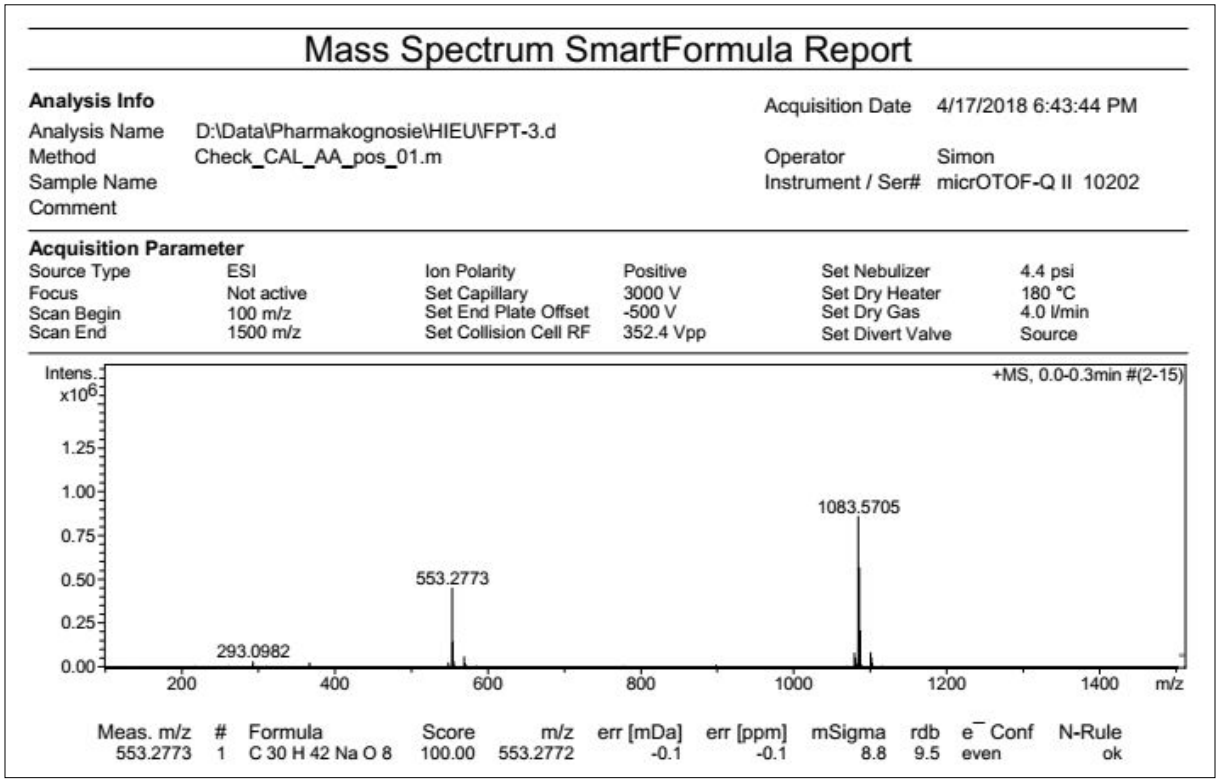



Figure S3.7. HRESIMS spectrum of compound **3**

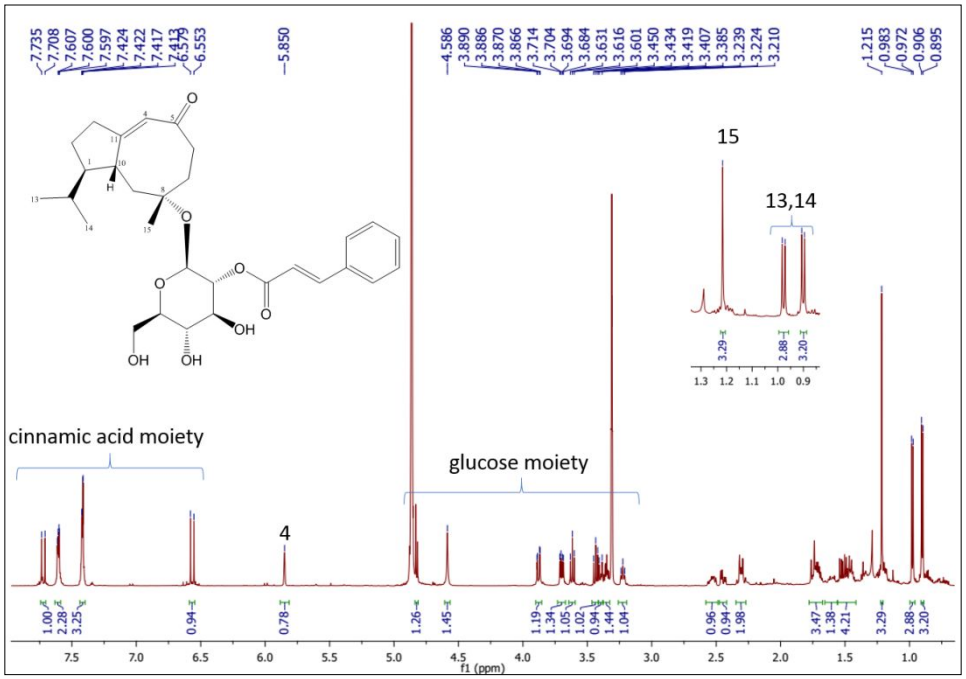



Figure S4.1. $^{1}$H NMR spectrum of compound **4** (600 MHz, in MeOH-$d_4$)

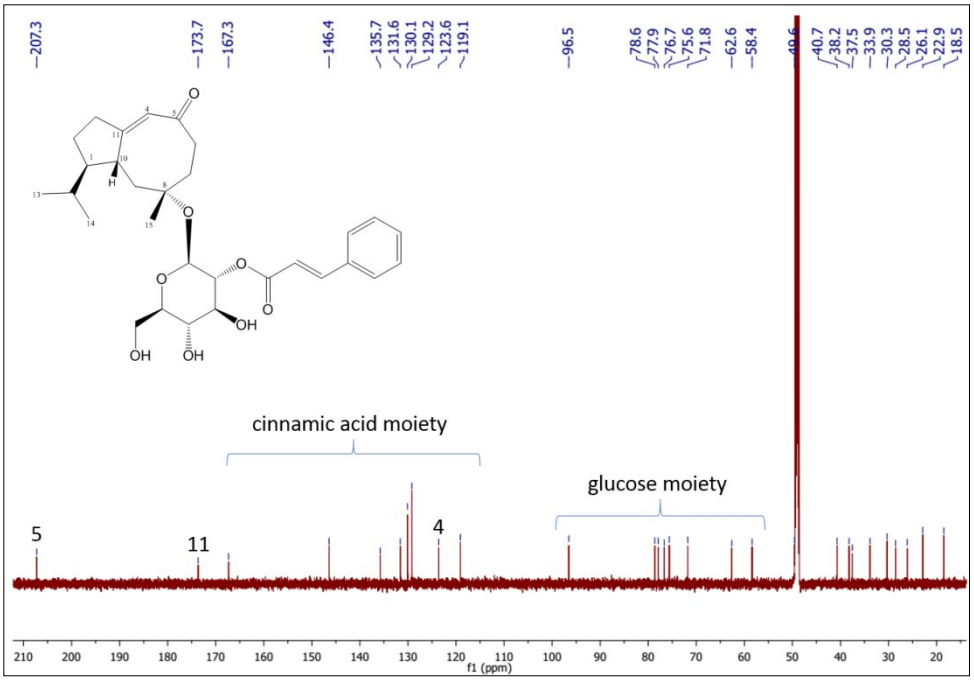



Figure S4.2. $^{13}$C NMR spectrum of compound **4** (150 MHz, in MeOH-$d_4$)

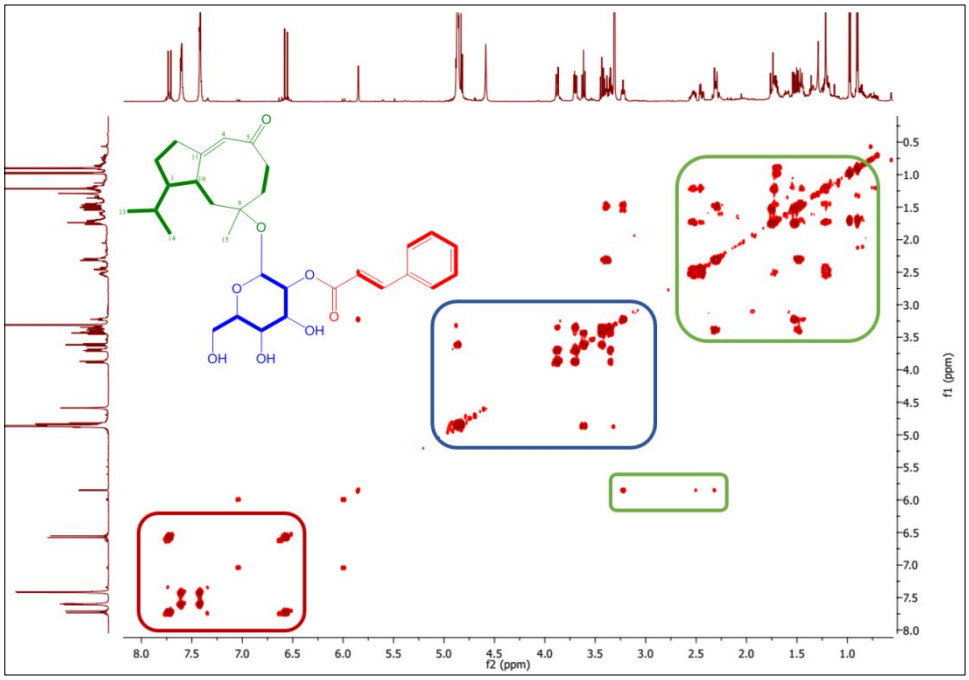



Figure S4.3. COSY spectrum of compound **4** (in MeOH-$d_4$)

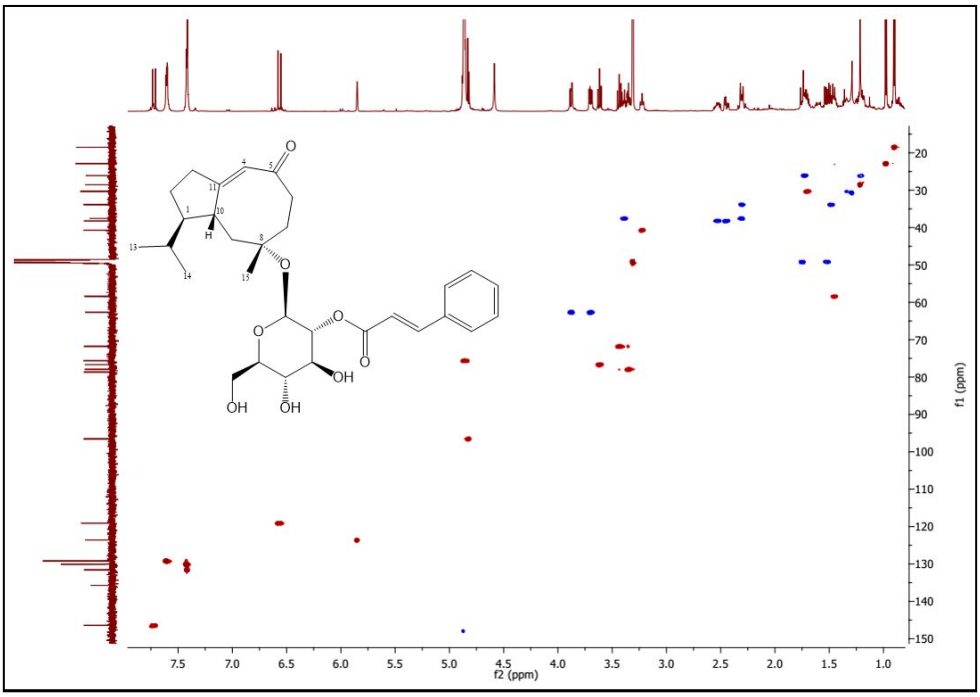



Figure S4.4. HSQC spectrum of compound **4** (in MeOH-$d_4$)

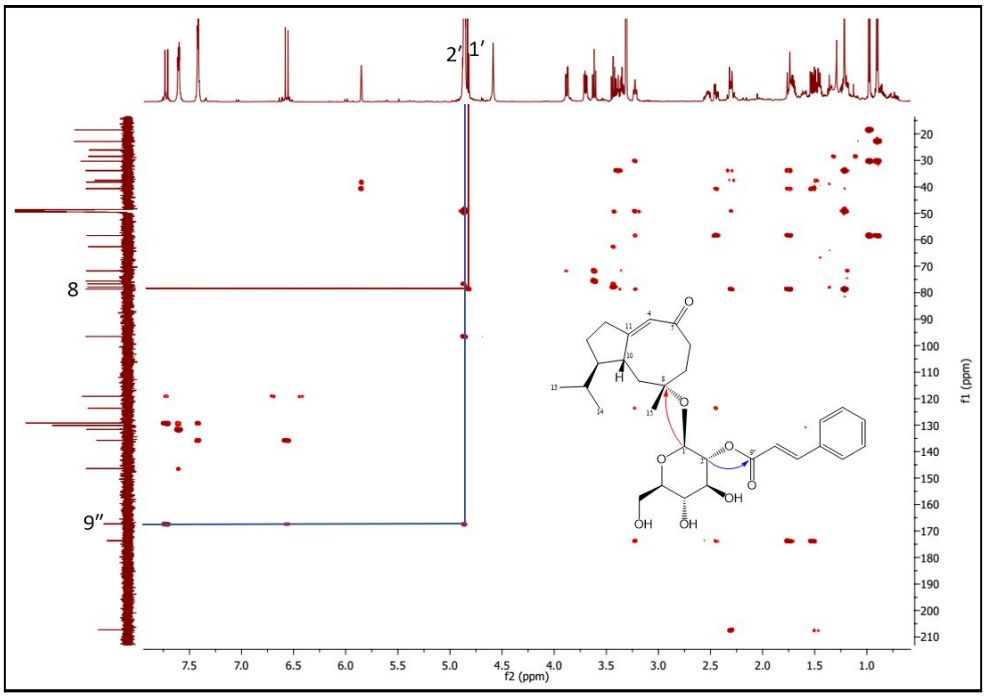



Figure S4.5. HMBC spectrum of compound **4** (in MeOH-$d_4$)

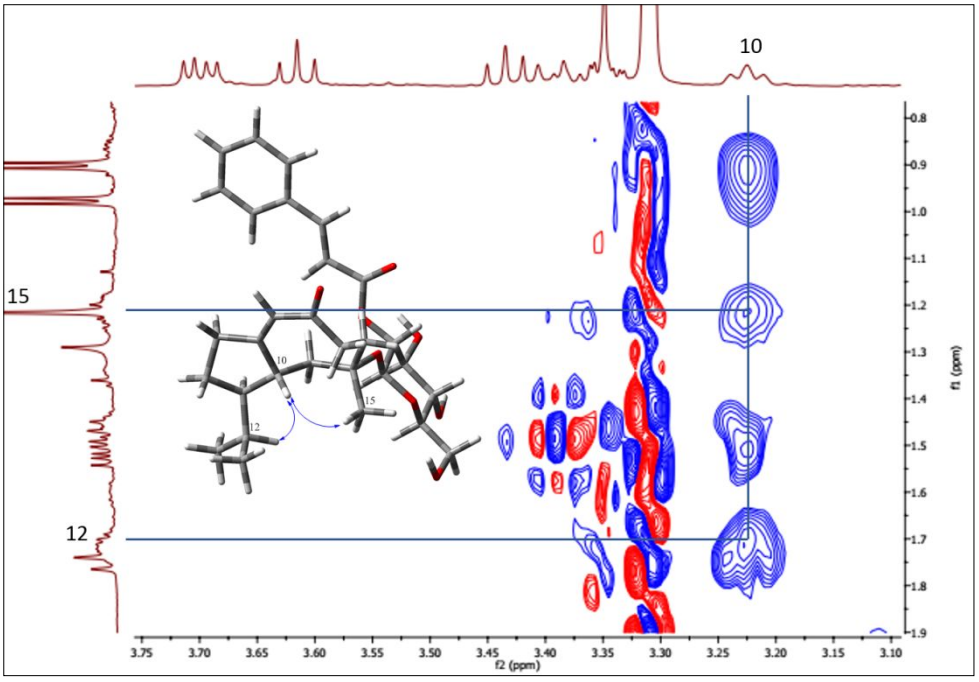



Figure S4.6.1. NOESY spectrum of compound **4** (aglycone, MeOH-$d_4$)

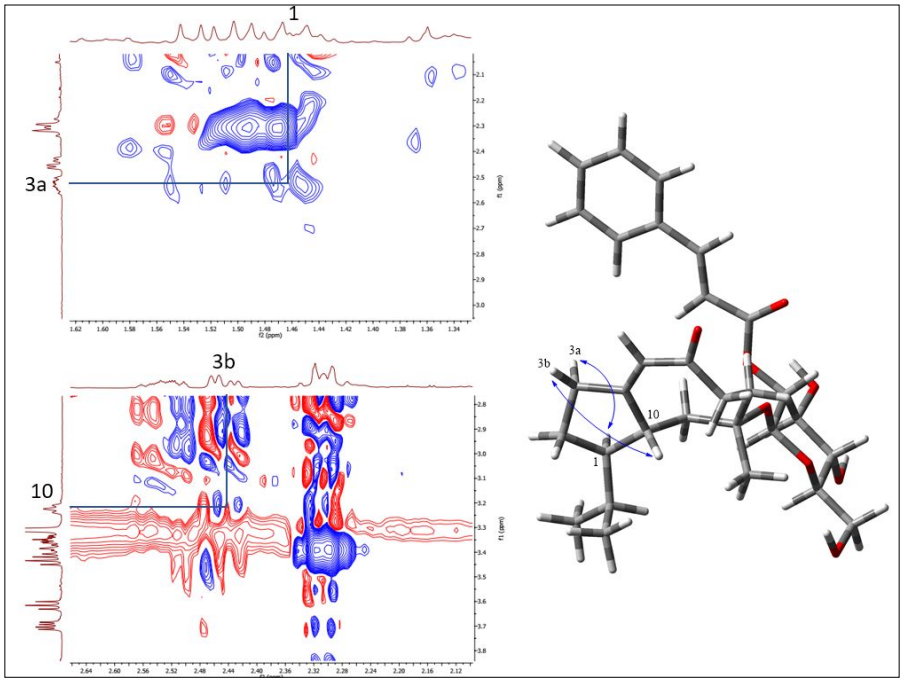



Figure S4.6.2. NOESY spectrum of compound **4** (aglycone, MeOH-$d_4$)

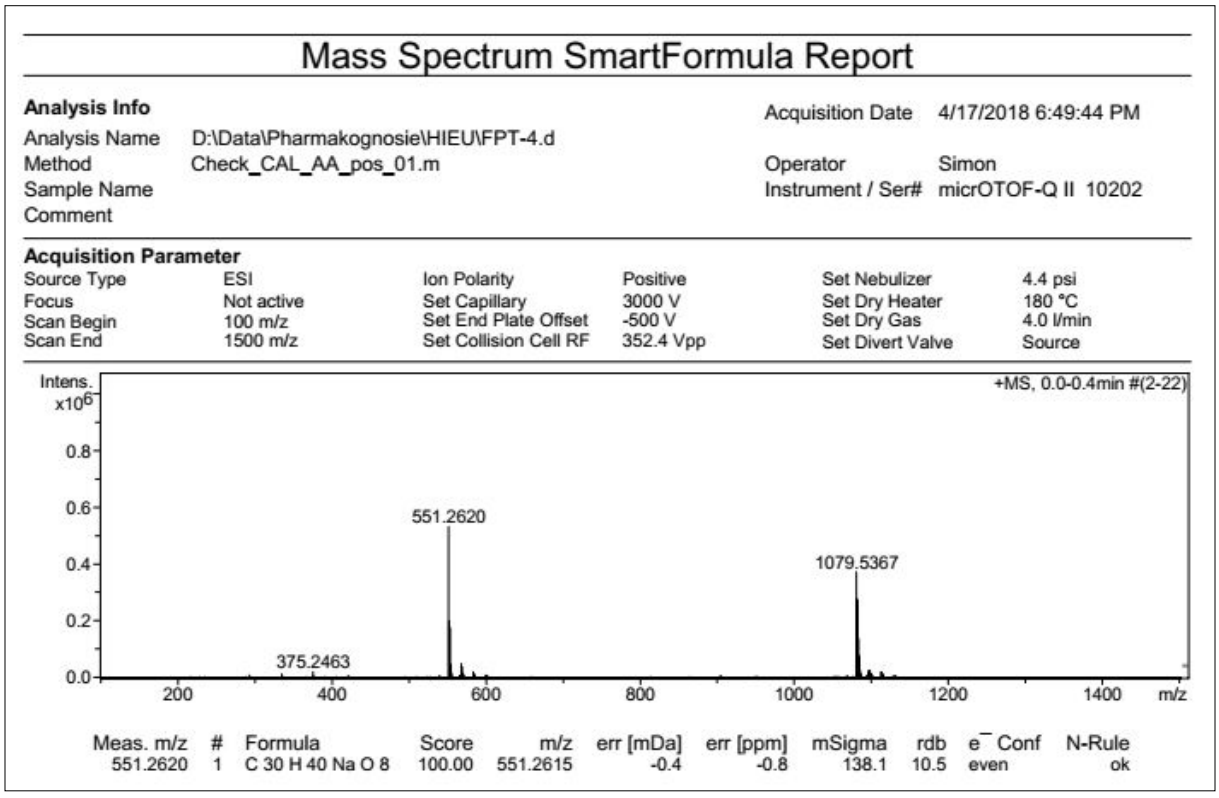



Figure S4.7. HRESIMS spectrum of compound **4**

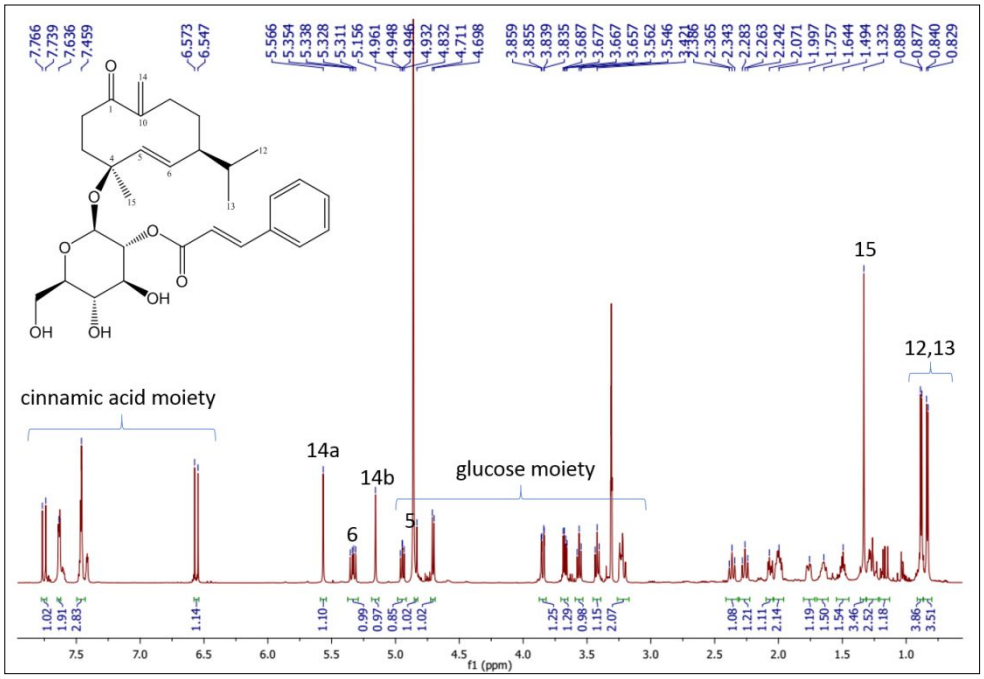



Figure S5.1. $^{1}$H NMR spectrum of compound **5** (600 MHz, in MeOH-$d_4$)

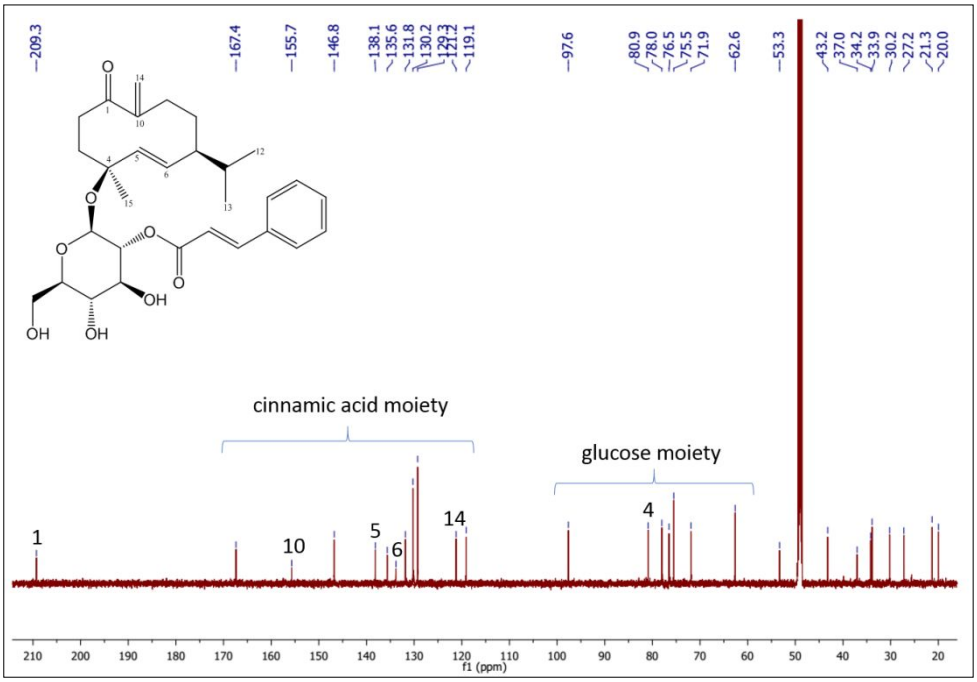



Figure S5.2. $^{13}$C NMR spectrum of compound **5** (150 MHz, in MeOH-$d_4$)

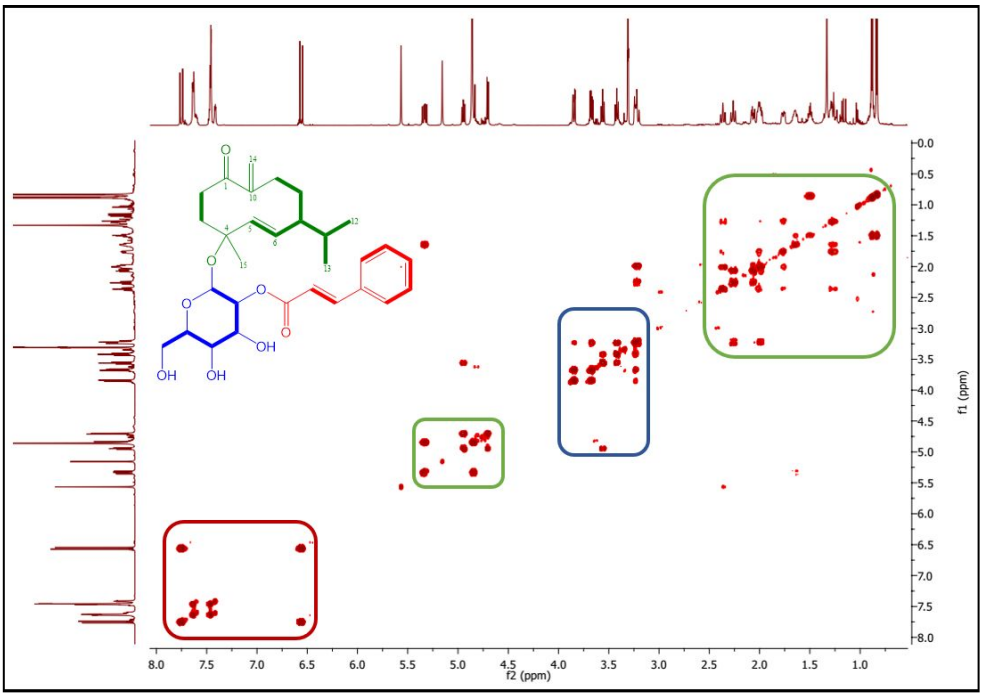



Figure S5.3. COSY spectrum of compound **5** (in MeOH-$d_4$)

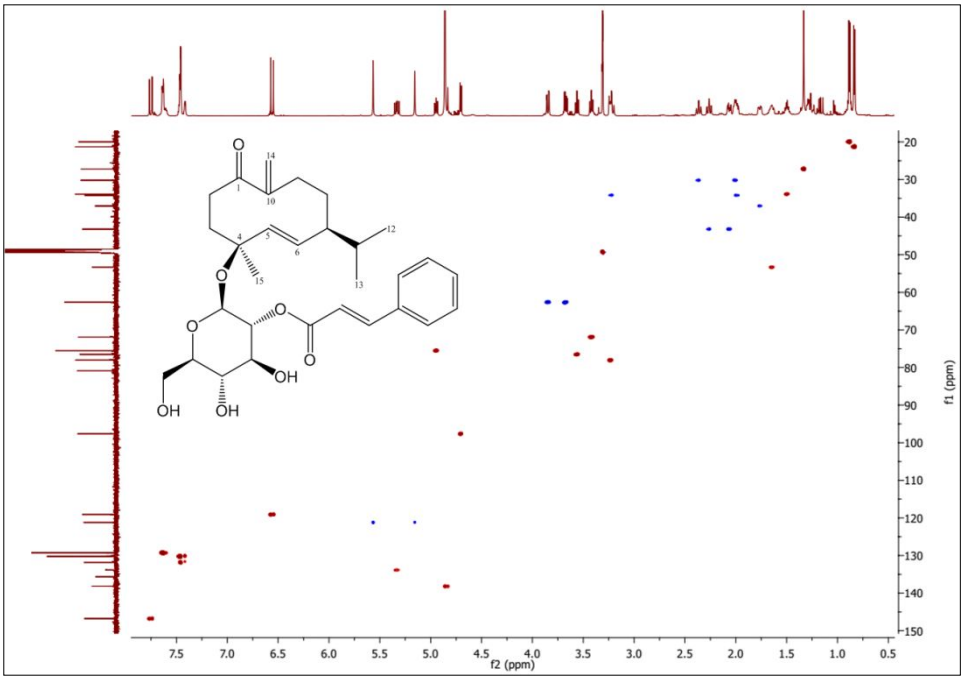



Figure S5.4. HSQC spectrum of compound **5** (in MeOH-$d_4$)

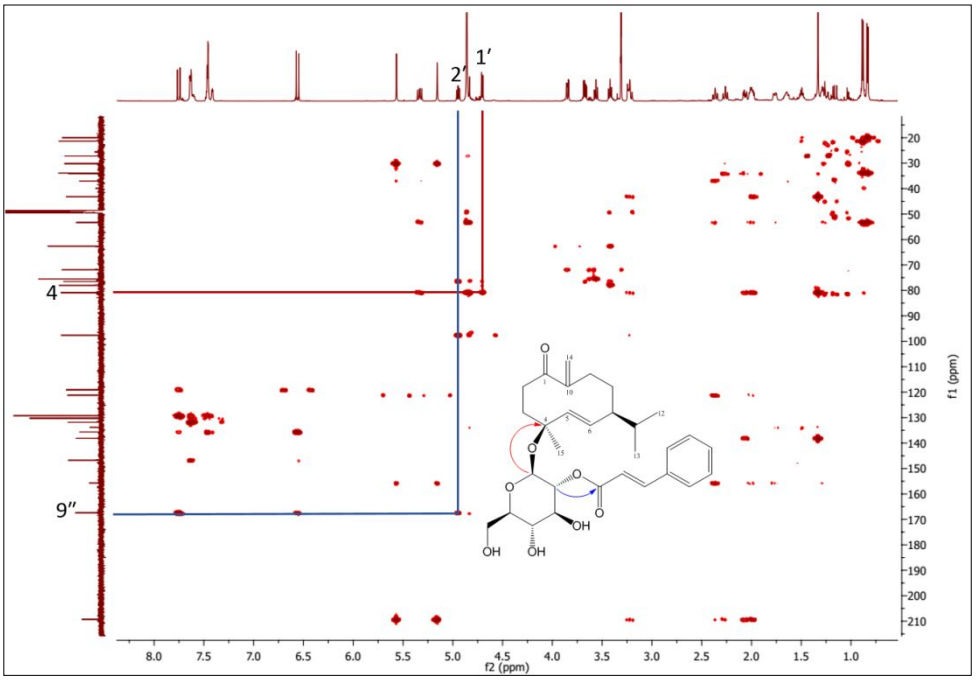



Figure S5.5. HMBC spectrum of compound **5** (in MeOH-$d_4$)

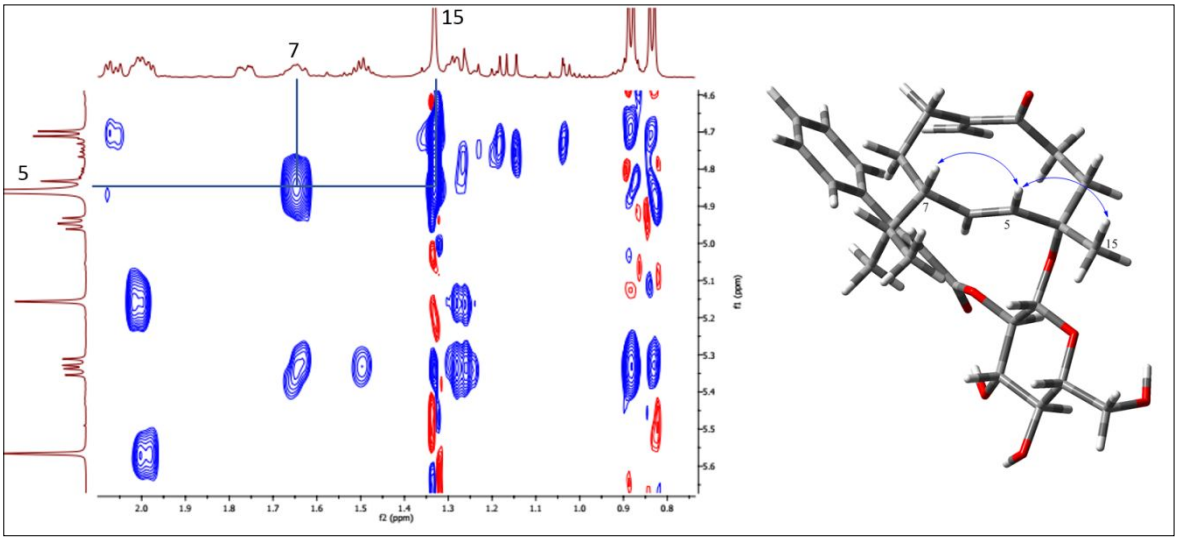



Figure S5.6. NOESY spectrum of compound **5** (aglycone, MeOH-$d_4$)

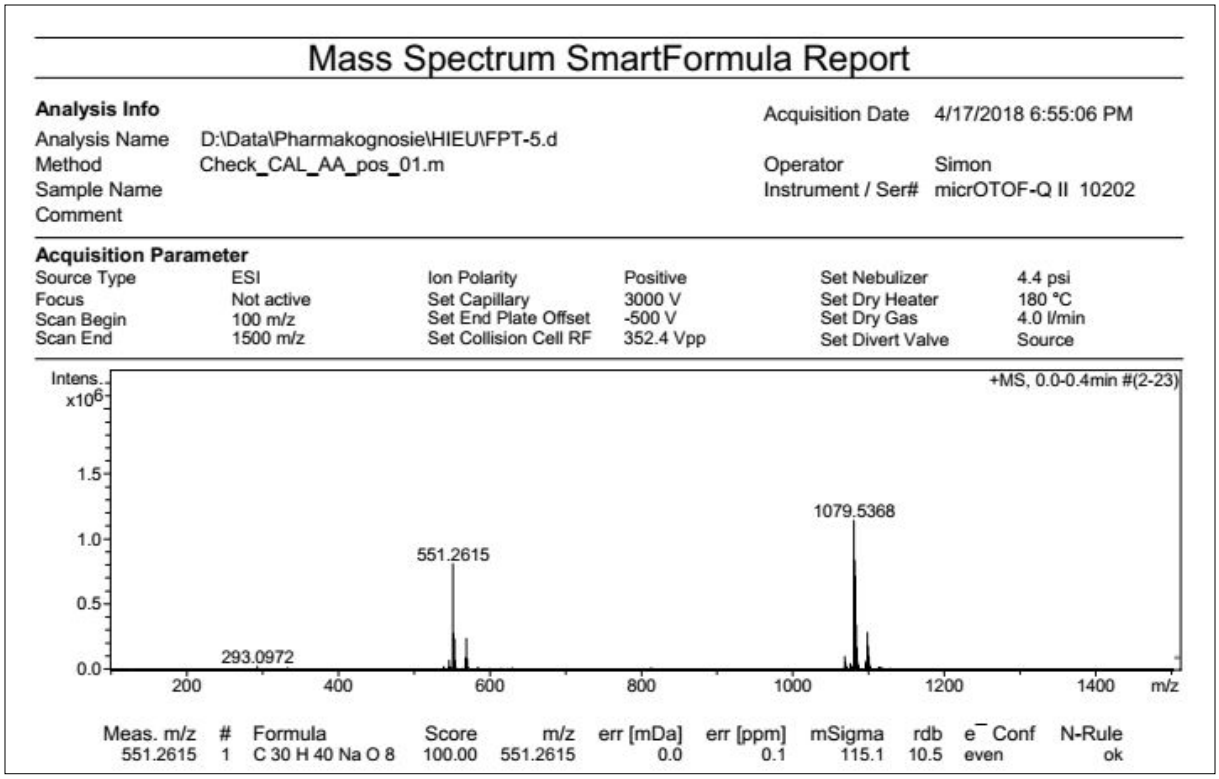



Figure S5.7. HRESIMS spectrum of compound **5**

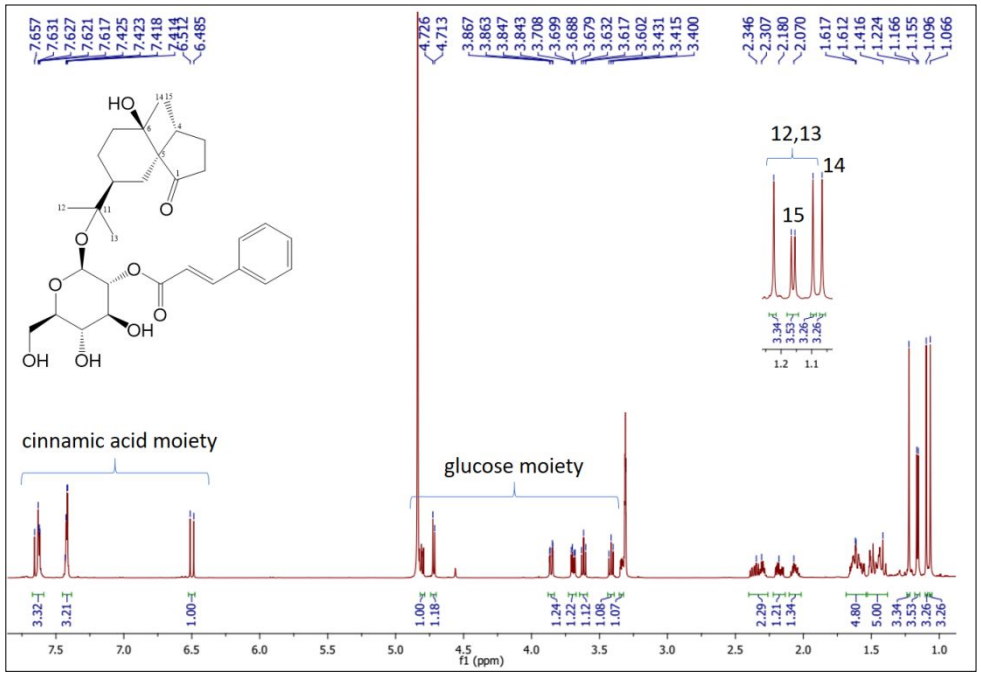



Figure S6.1. $^{1}$H NMR spectrum of compound **6** (600 MHz, in MeOH-$d_4$)

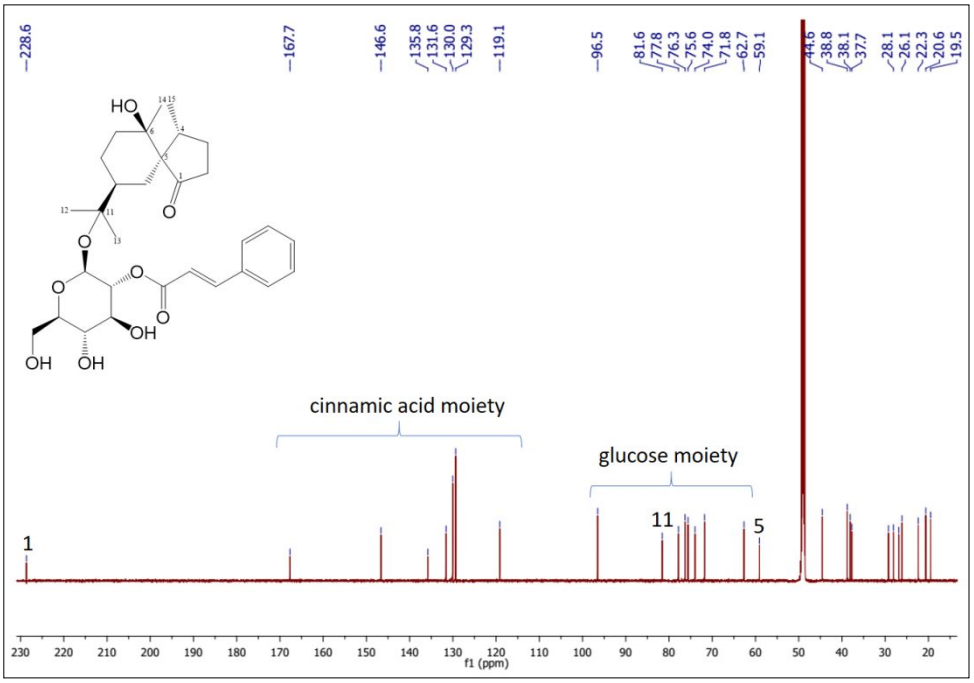



Figure S6.2. $^{13}$C NMR spectrum of compound **6** (150 MHz, in MeOH-$d_4$)

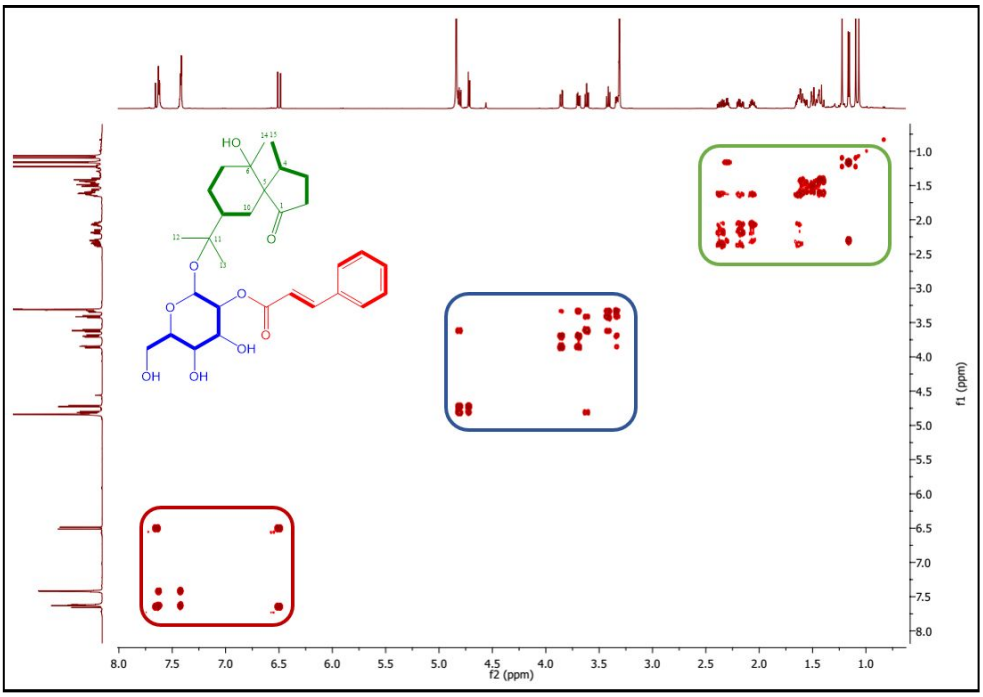



Figure S6.3. COSY spectrum of compound **6** (in MeOH-$d_4$)

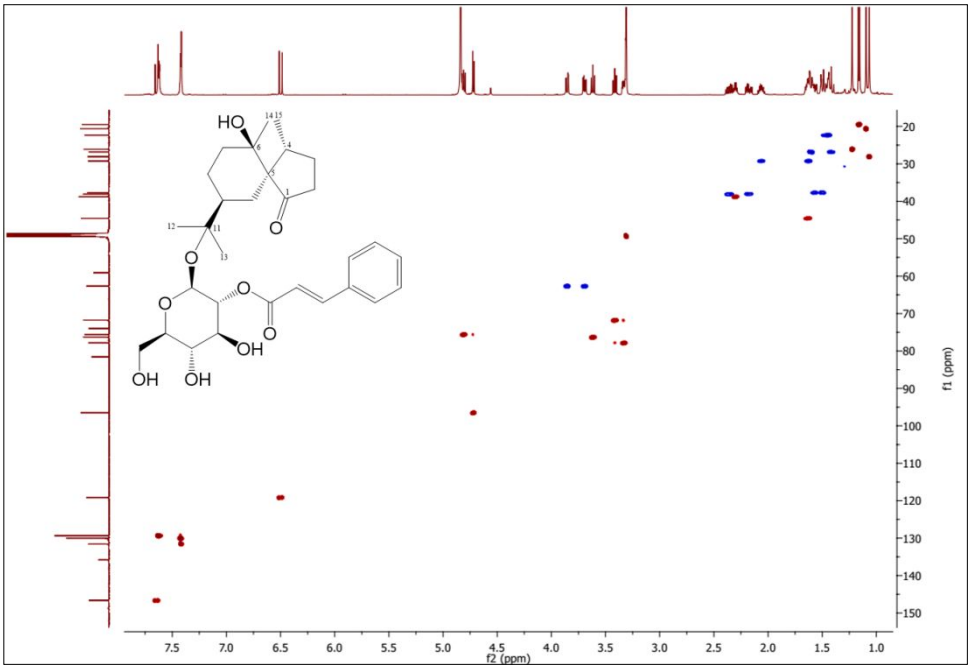



Figure S6.4. HSQC spectrum of compound **6** (in MeOH-$d_4$)

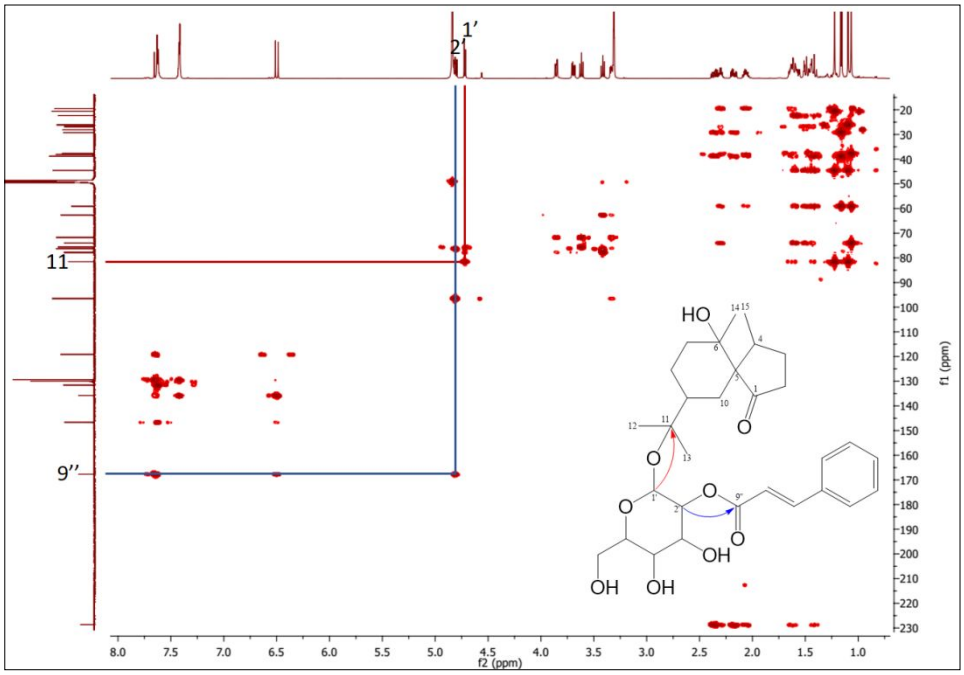
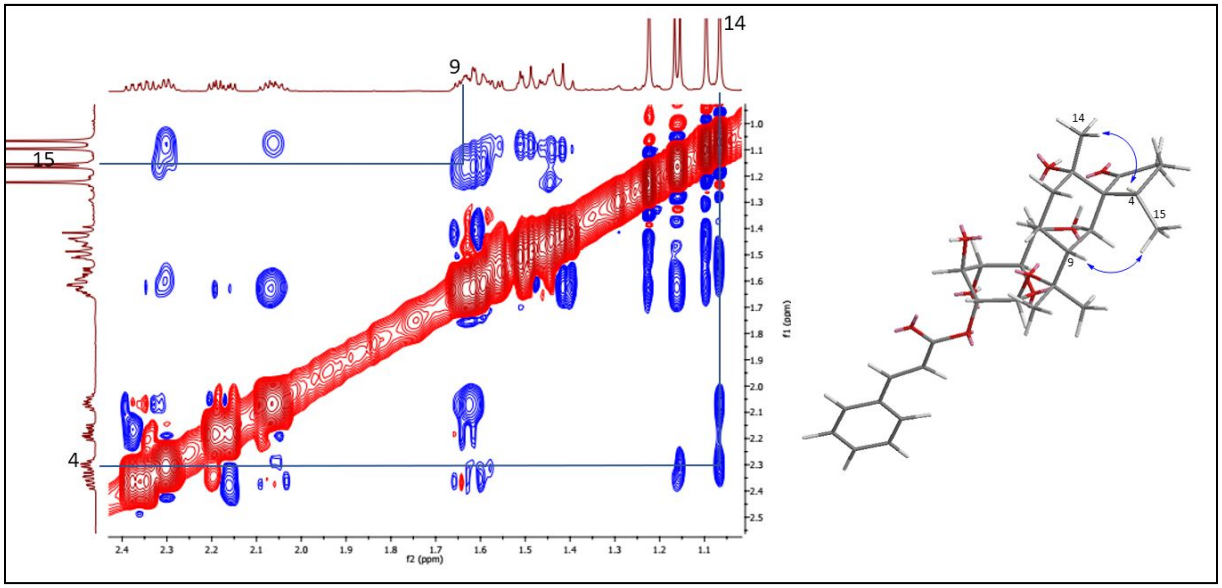



Figure S6.5. HMBC spectrum of compound **6** (in MeOH-$d_4$)

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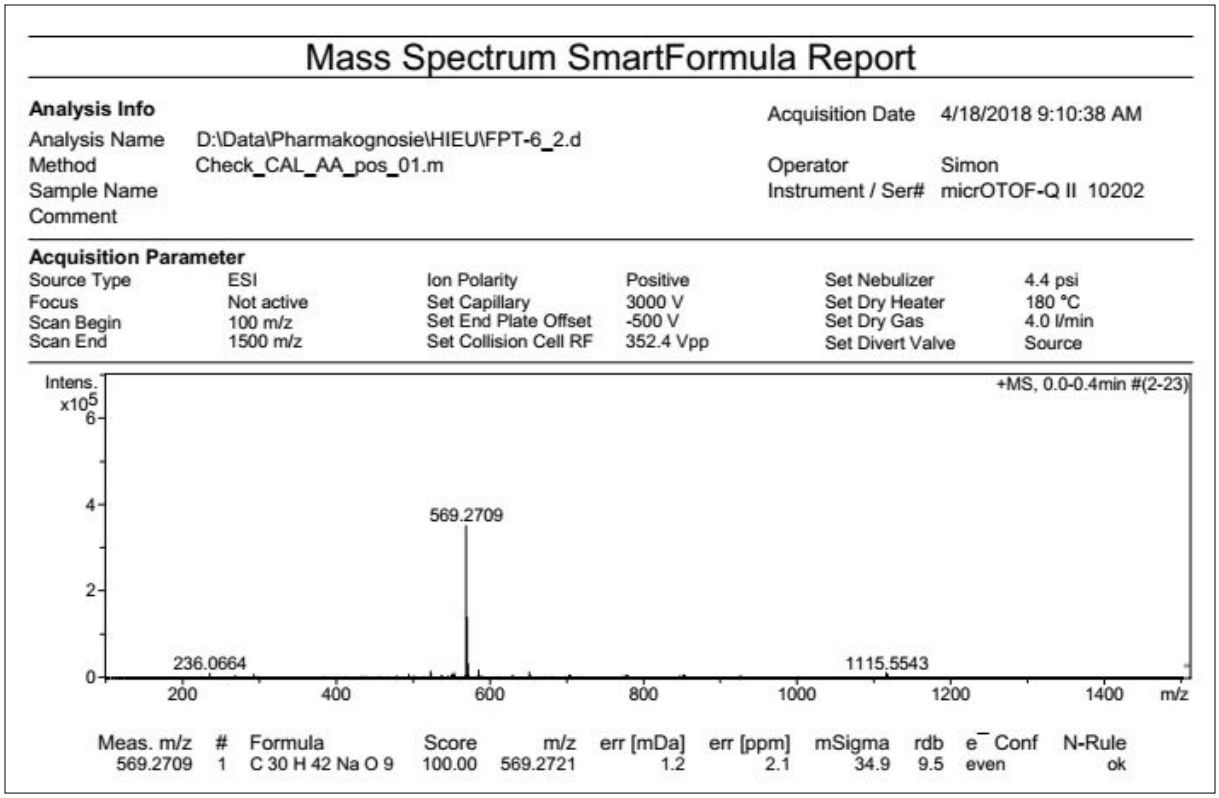



Figure S1.7. HRESIMS spectrum of compound **6**

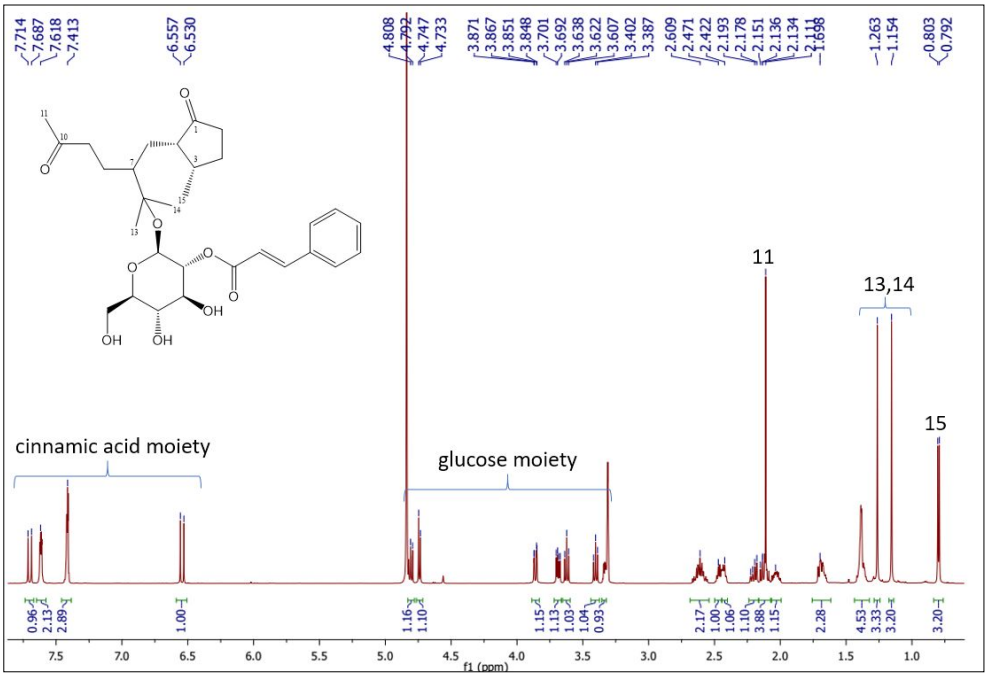



Figure S7.1.1. $^{1}$H NMR spectrum of compound **7** (600 MHz, in MeOH-$d_4$)

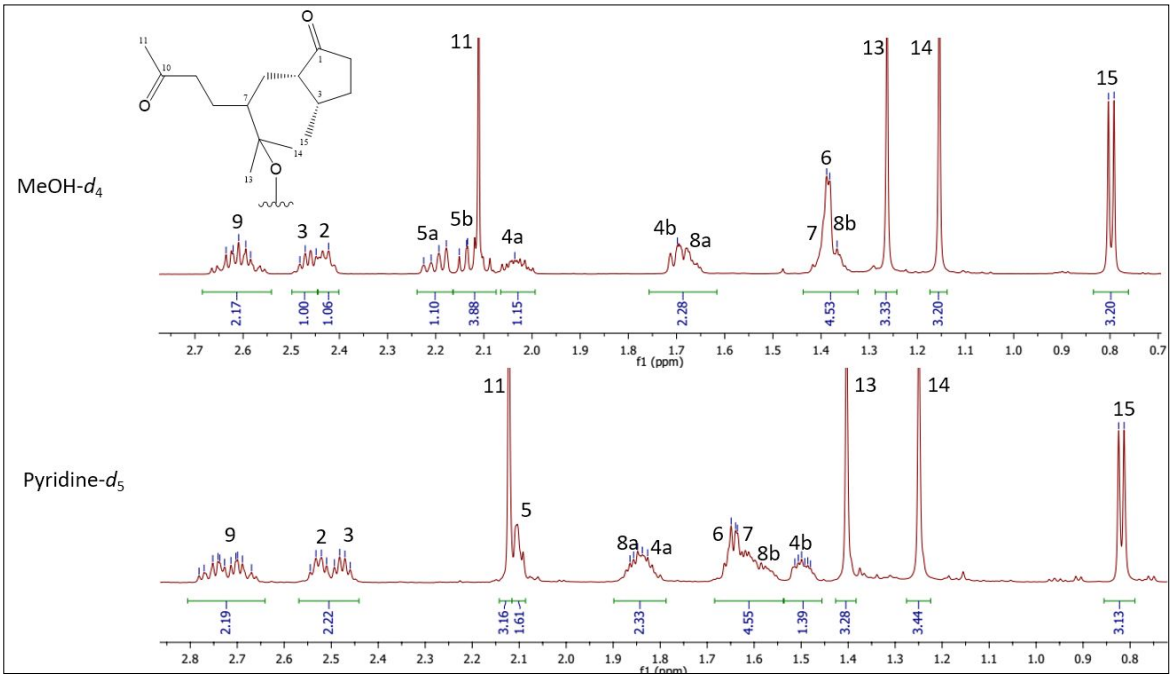



Figure S7.1.2. $^{1}$H NMR spectrum of compound **7** (600 MHz, in MeOH-$d_4$ and pyridine-$d_5$)

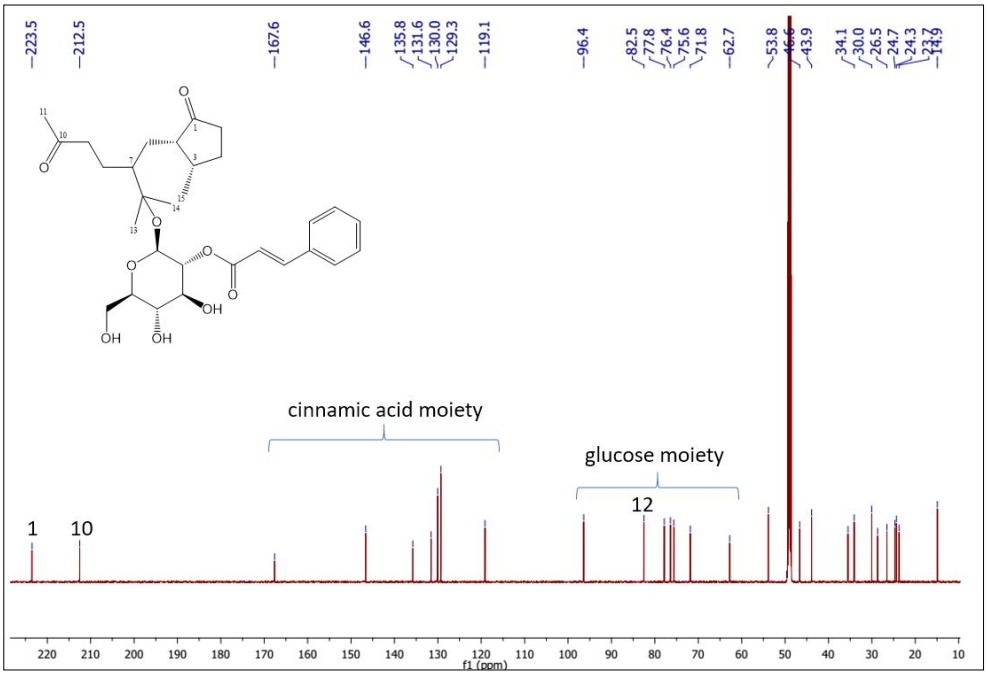



Figure S7.2. $^{13}$C NMR spectrum of compound **7** (150 MHz, in MeOH-$d_4$)

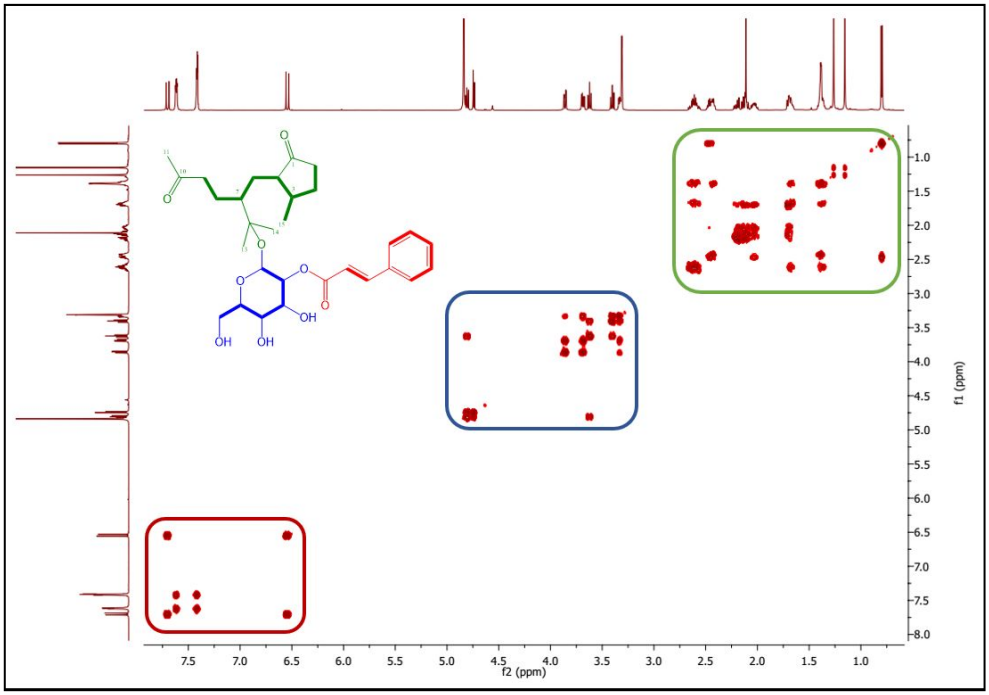



Figure S7.3. COSY spectrum of compound **7** (in MeOH-$d_4$)

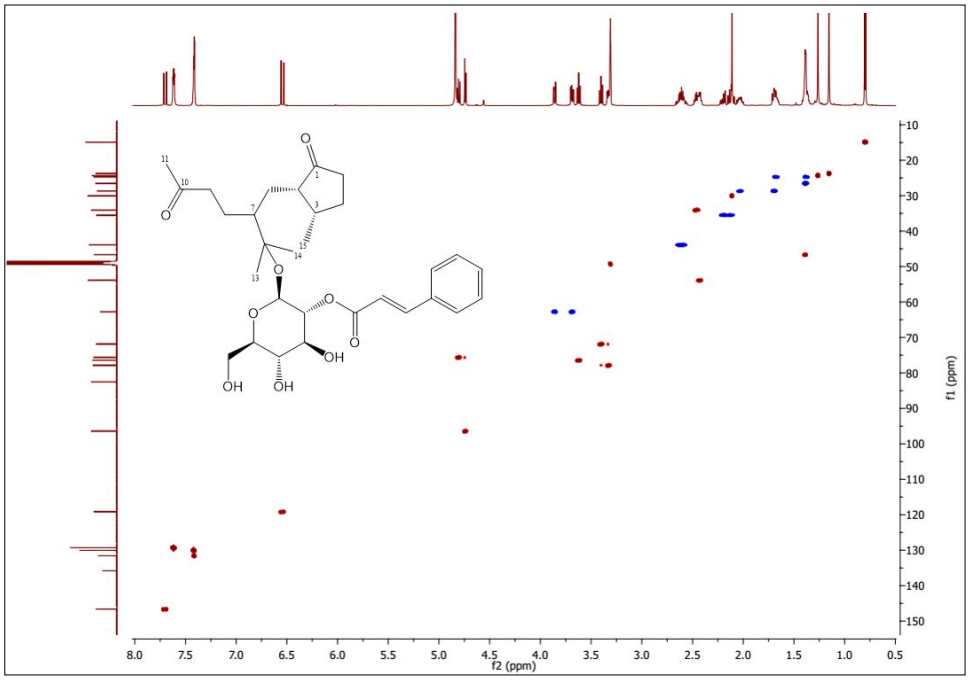



Figure S7.4. HSQC spectrum of compound **7** (in MeOH-$d_4$)

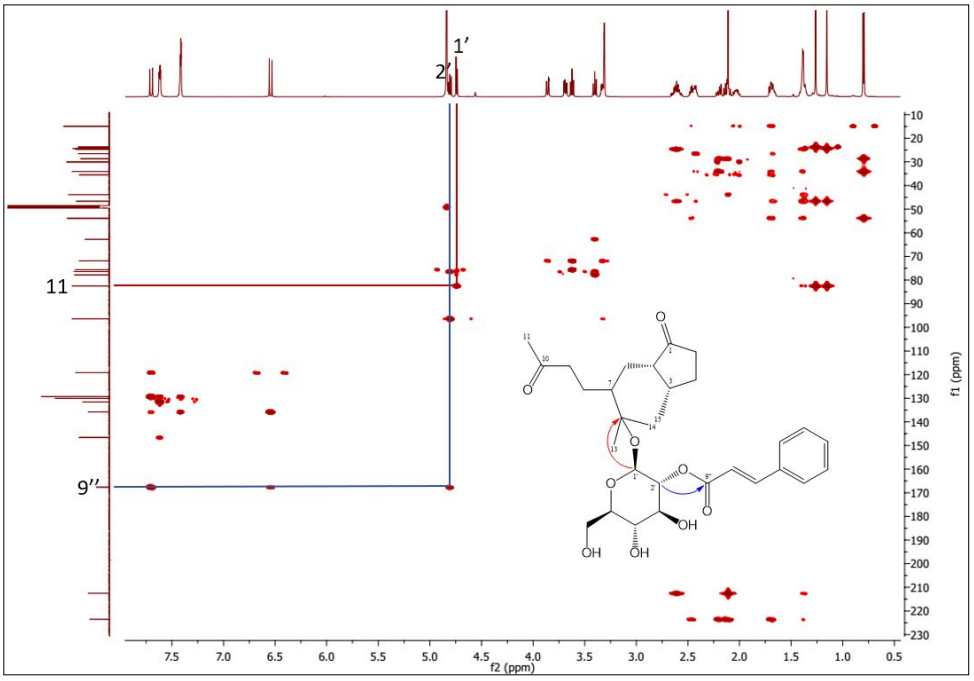



Figure S7.5. HMBC spectrum of compound **7** (in MeOH-$d_4$)

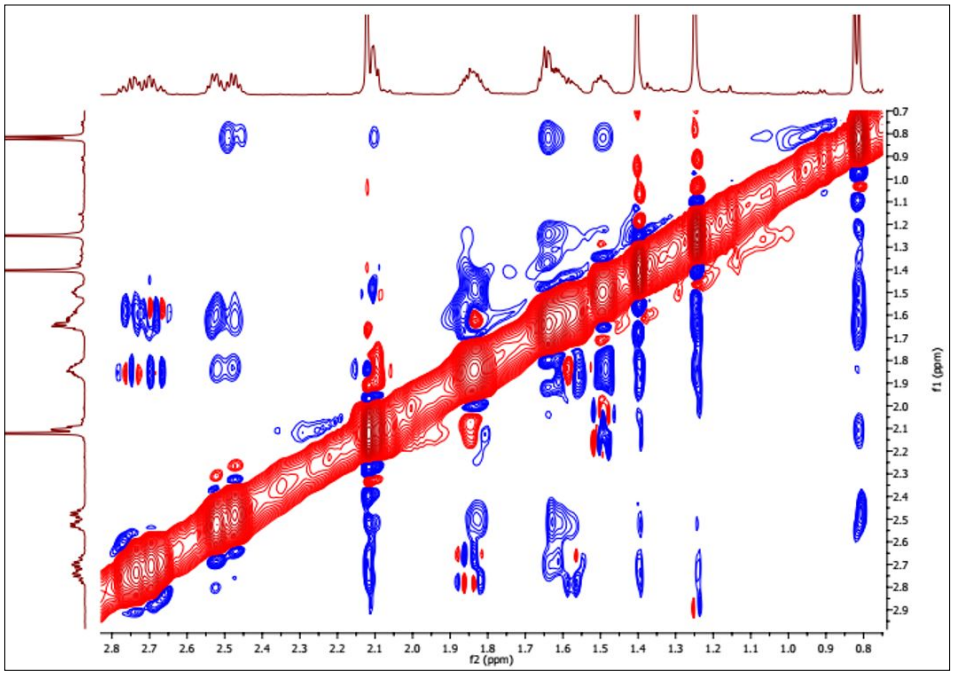



Figure S7.6. NOESY spectrum of compound **7** (aglycone, pyridine-$d_5$)

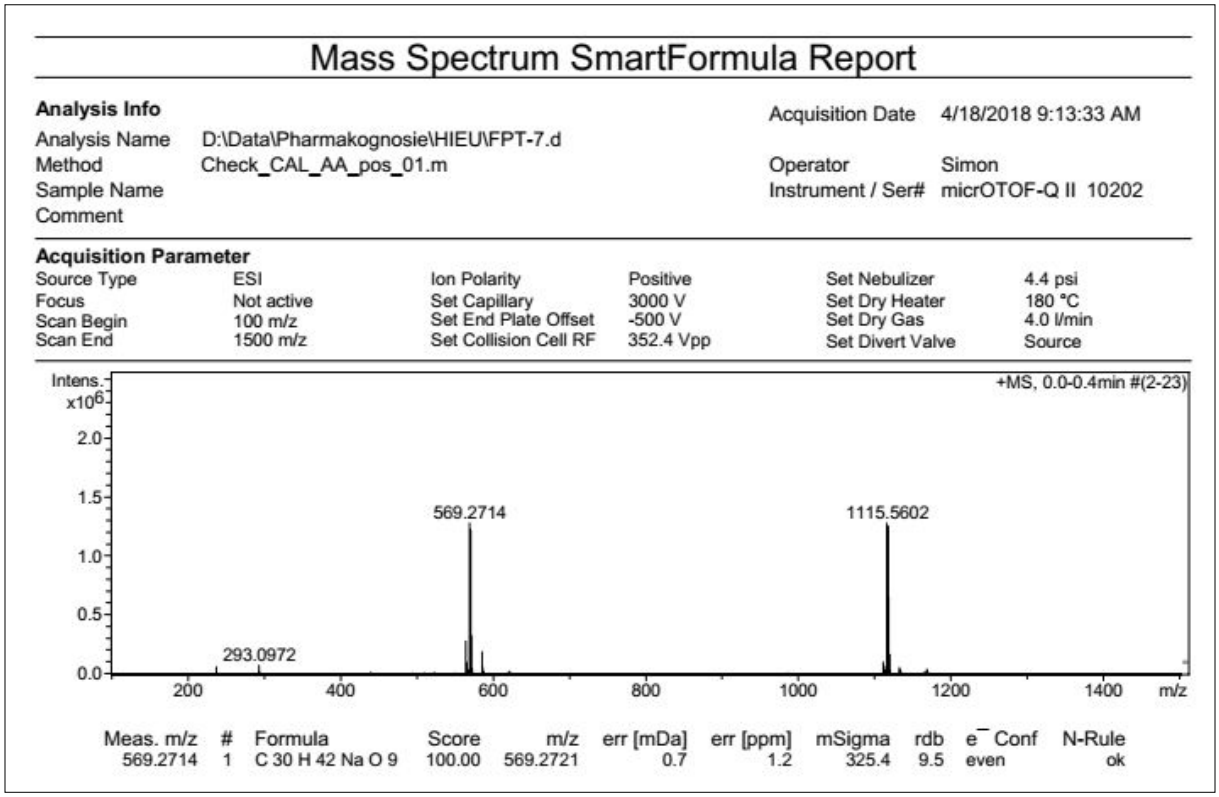



Figure S7.7. HRESIMS spectrum of compound **7**

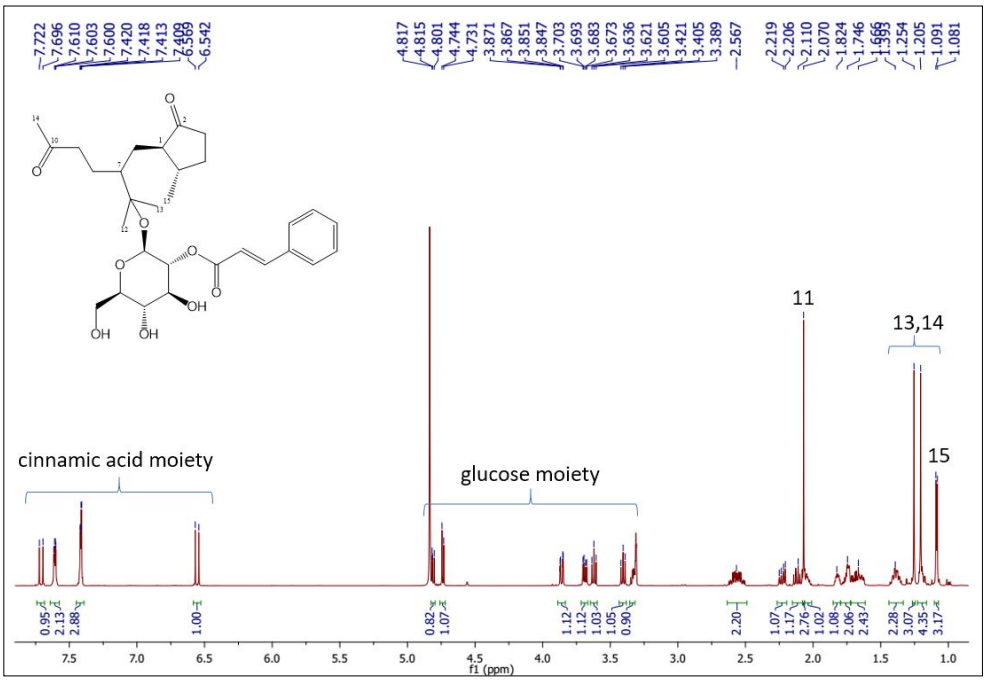



Figure S8.1.1. $^{1}$H NMR spectrum of compound **8** (600 MHz, in MeOH-$d_4$)

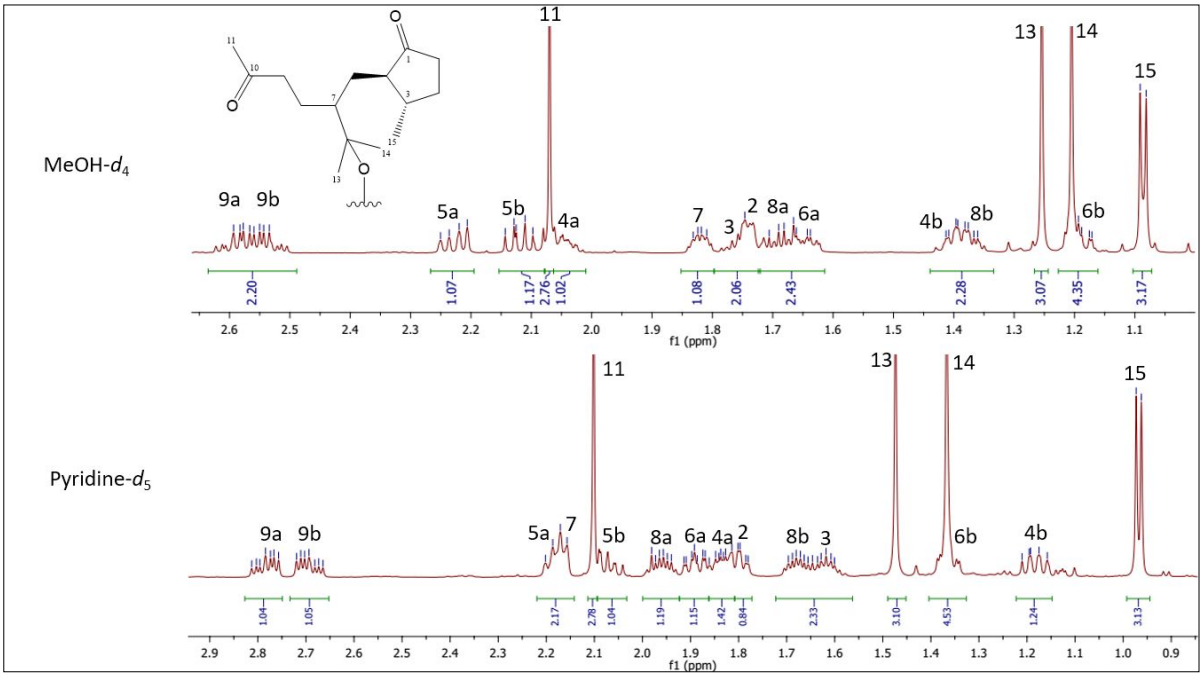



Figure S8.1.2. $^{1}$H NMR spectrum of compound **8** (600 MHz, in MeOH-$d_4$ and pyridine-$d_5$)

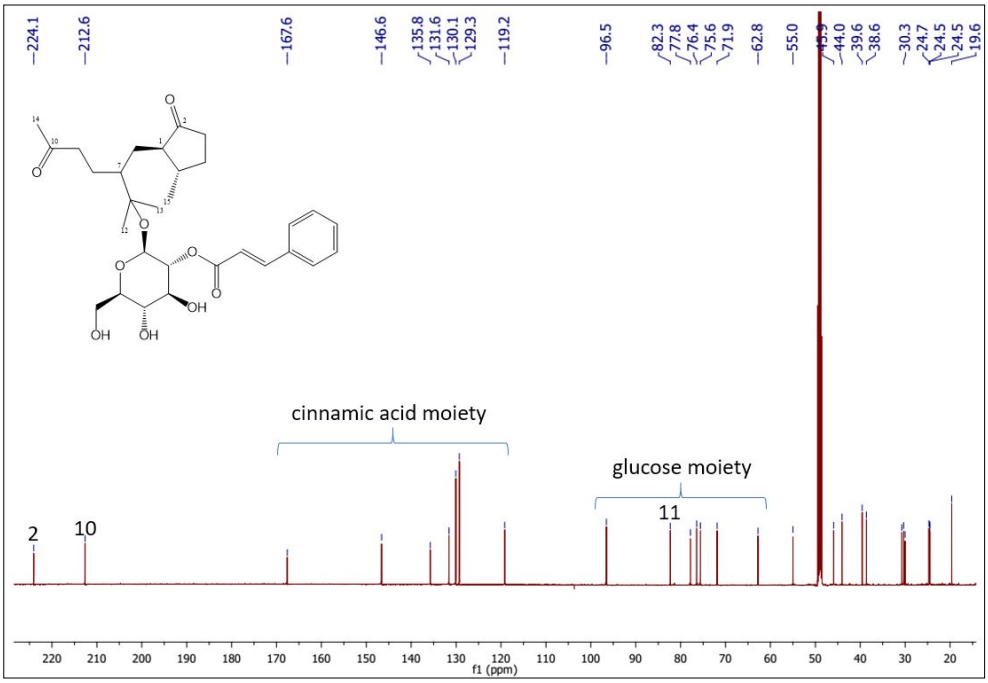



Figure S8.2. $^{13}$C NMR spectrum of compound **8** (150 MHz, in MeOH-$d_4$)

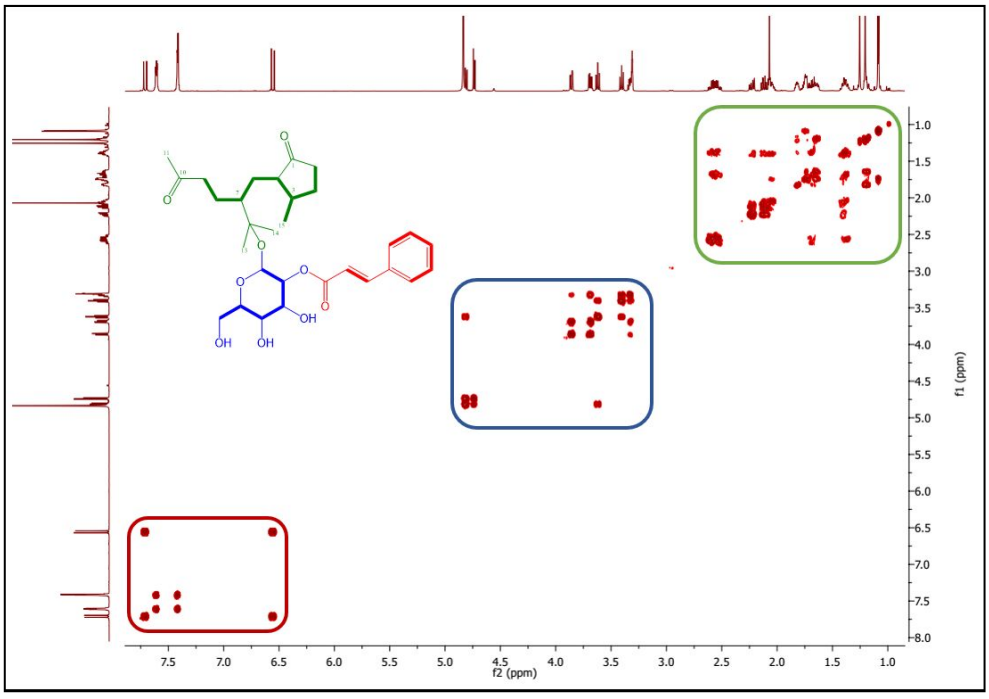



Figure S8.3. COSY spectrum of compound **8** (in MeOH-$d_4$)

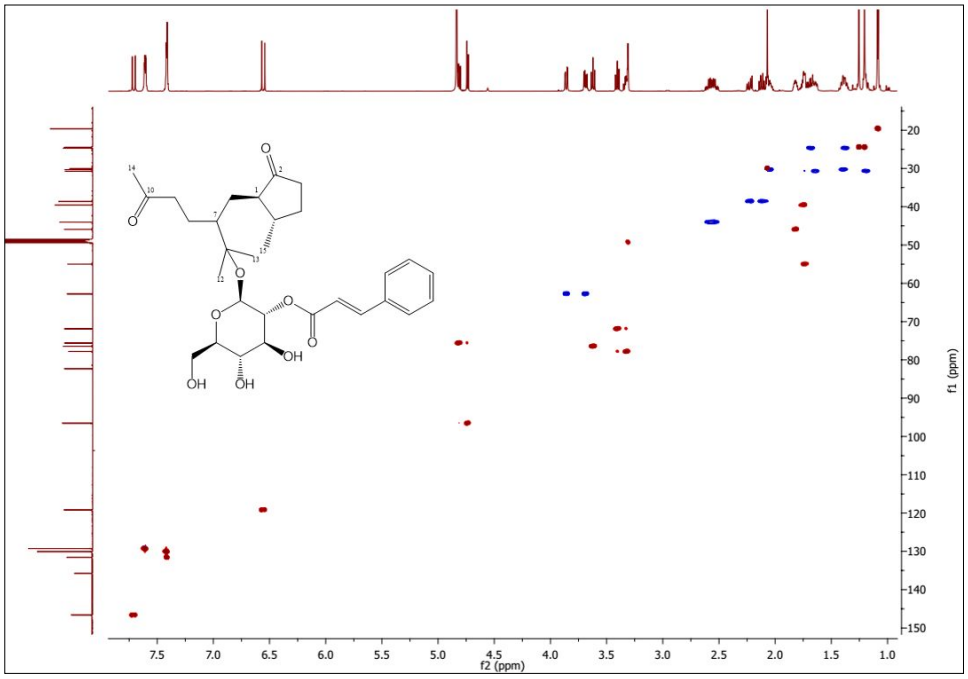



Figure S8.4. HSQC spectrum of compound **8** (in MeOH-$d_4$)

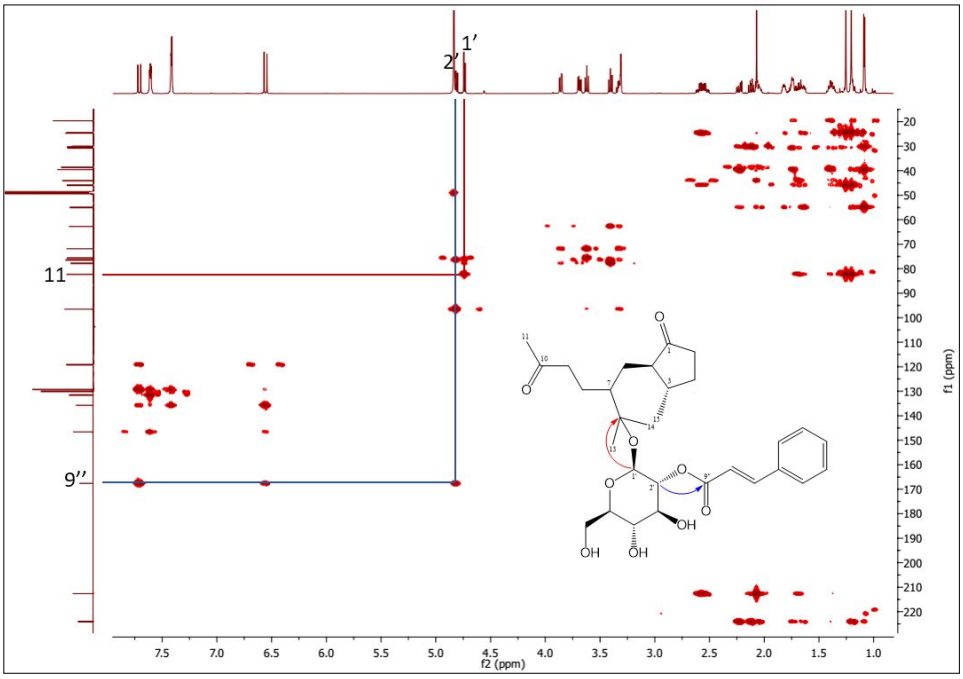



Figure S8.5. HMBC spectrum of compound **8** (in MeOH-$d_4$)

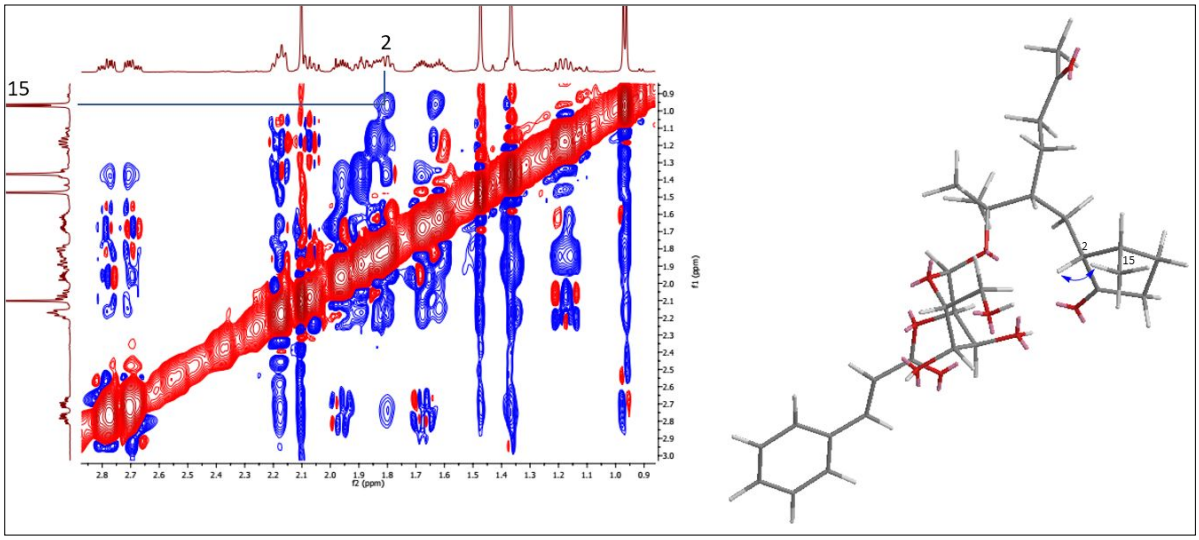



Figure S8.6. NOESY spectrum of compound **8** (aglycone, pyridine-$d_5$)

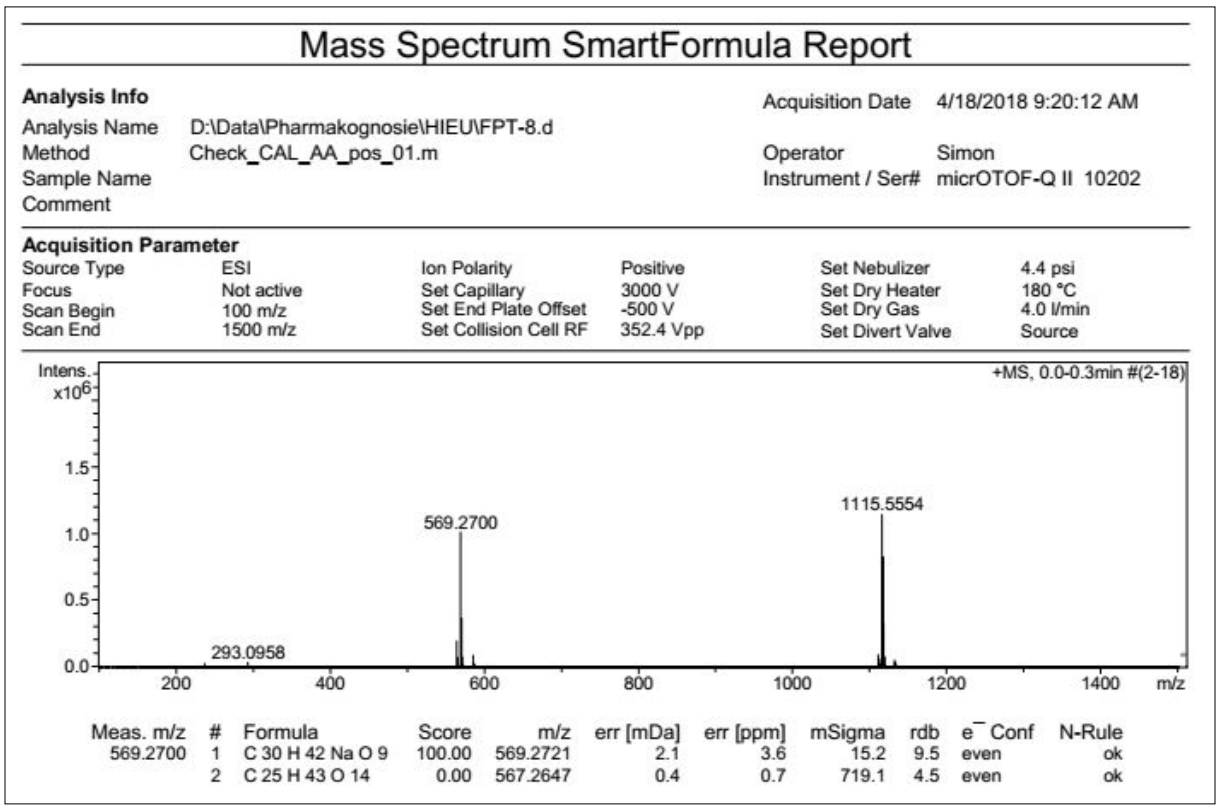



Figure S8.7. HRESIMS spectrum of compound **8**

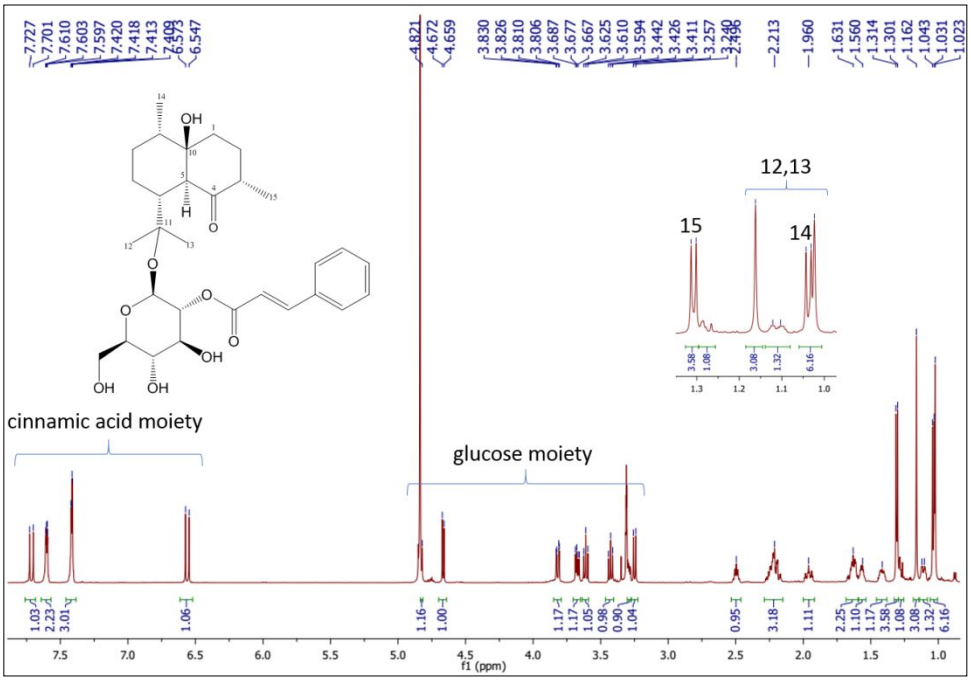



Figure S9.1. $^{1}$H NMR spectrum of compound **9** (600 MHz, in MeOH-$d_4$)

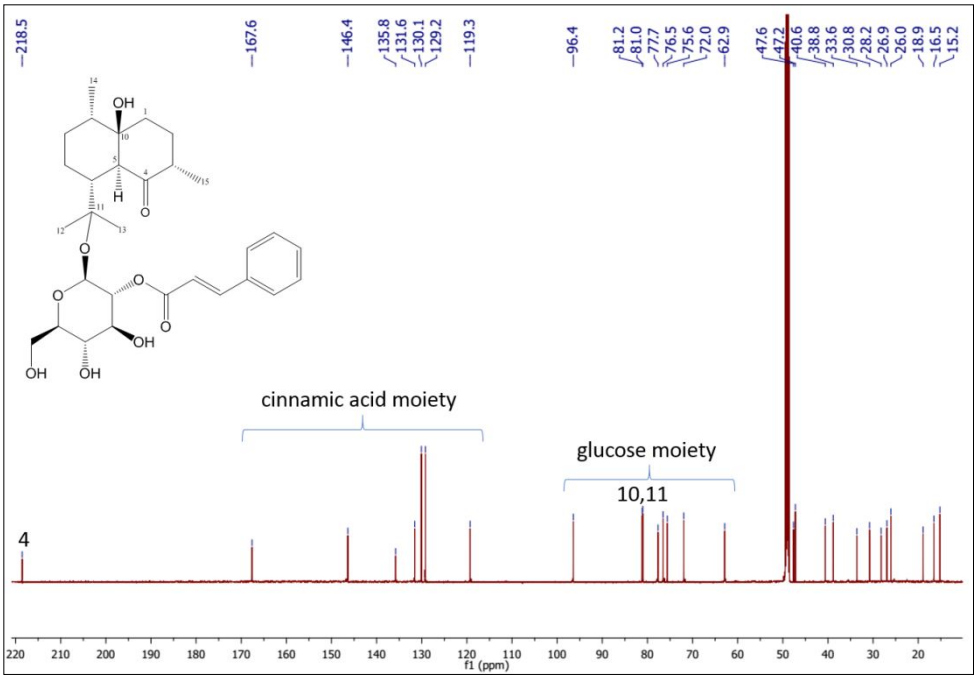



Figure S9.2. $^{13}$C NMR spectrum of compound **9** (150 MHz, in MeOH-$d_4$)

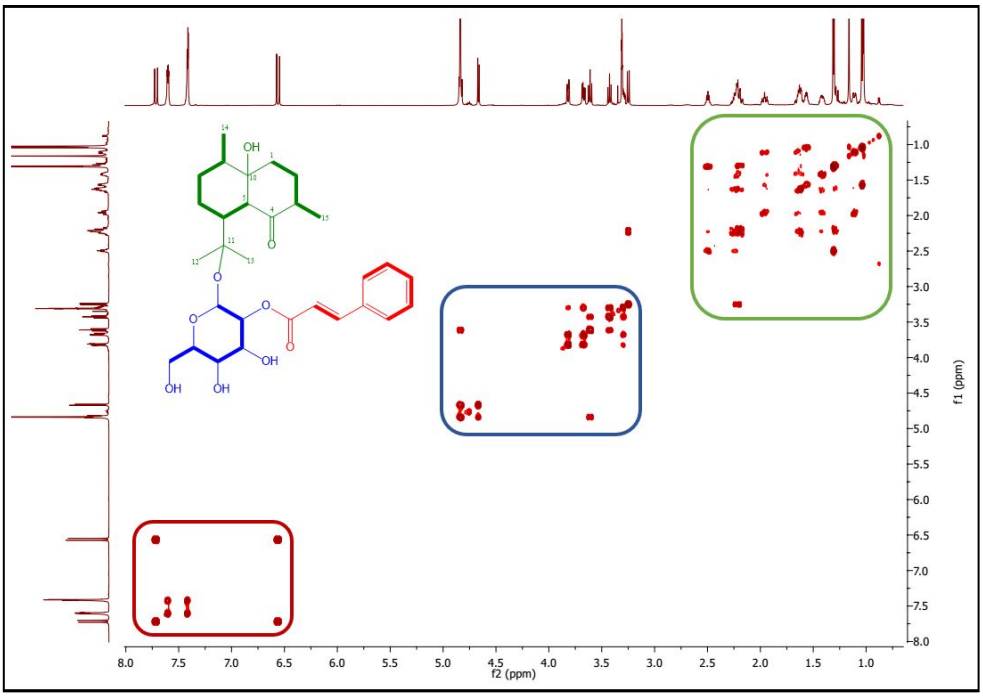



Figure S9.3. COSY spectrum of compound **9** (in MeOH-$d_4$)

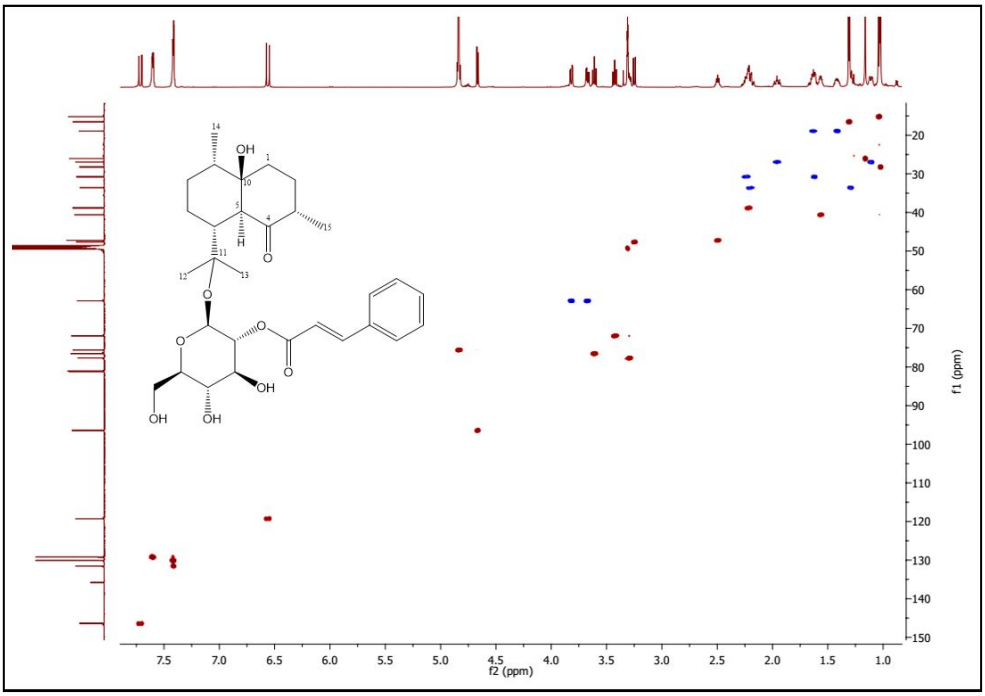



Figure S9.4. HSQC spectrum of compound **9** (in MeOH-$d_4$)

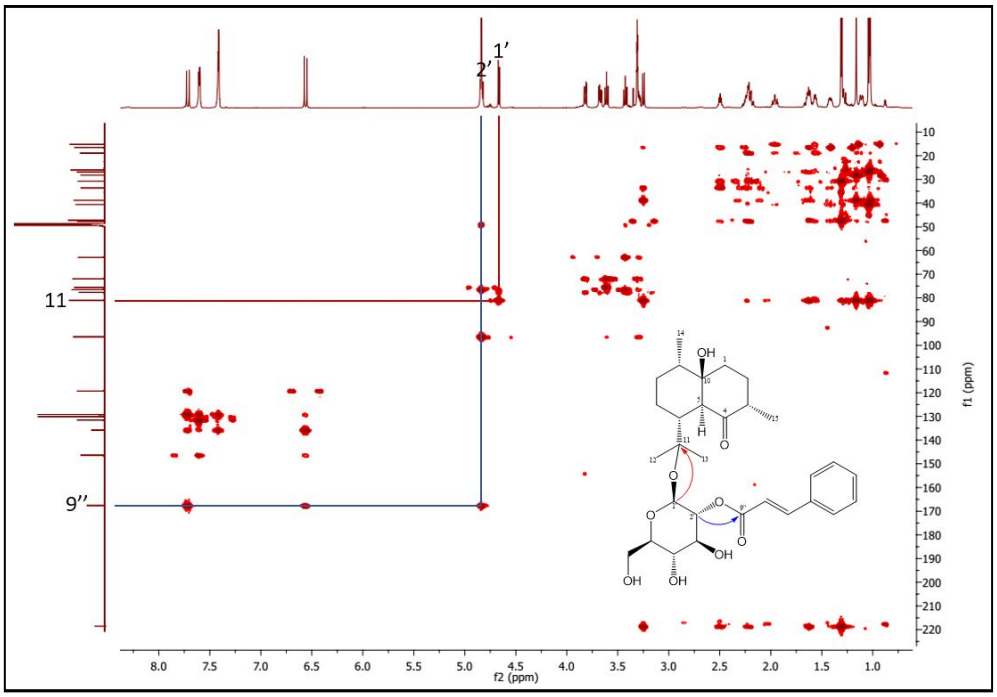



Figure S9.5. HMBC spectrum of compound **9** (in MeOH-$d_4$)

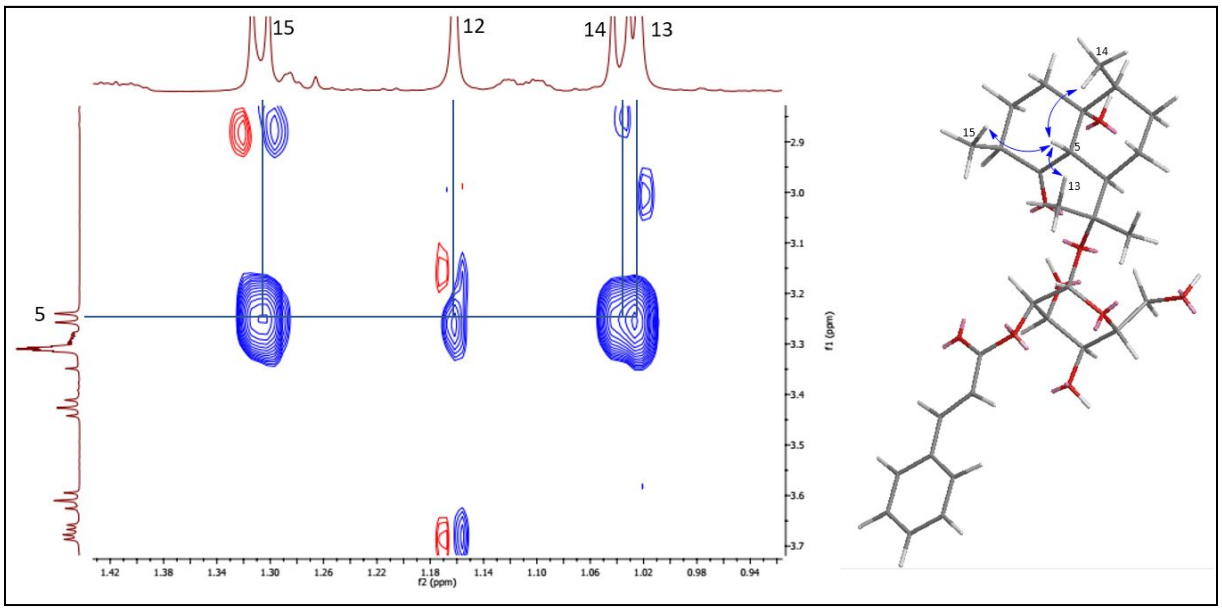



Figure S9.6. NOESY spectrum of compound **9** (aglycone, MeOH-$d_4$)

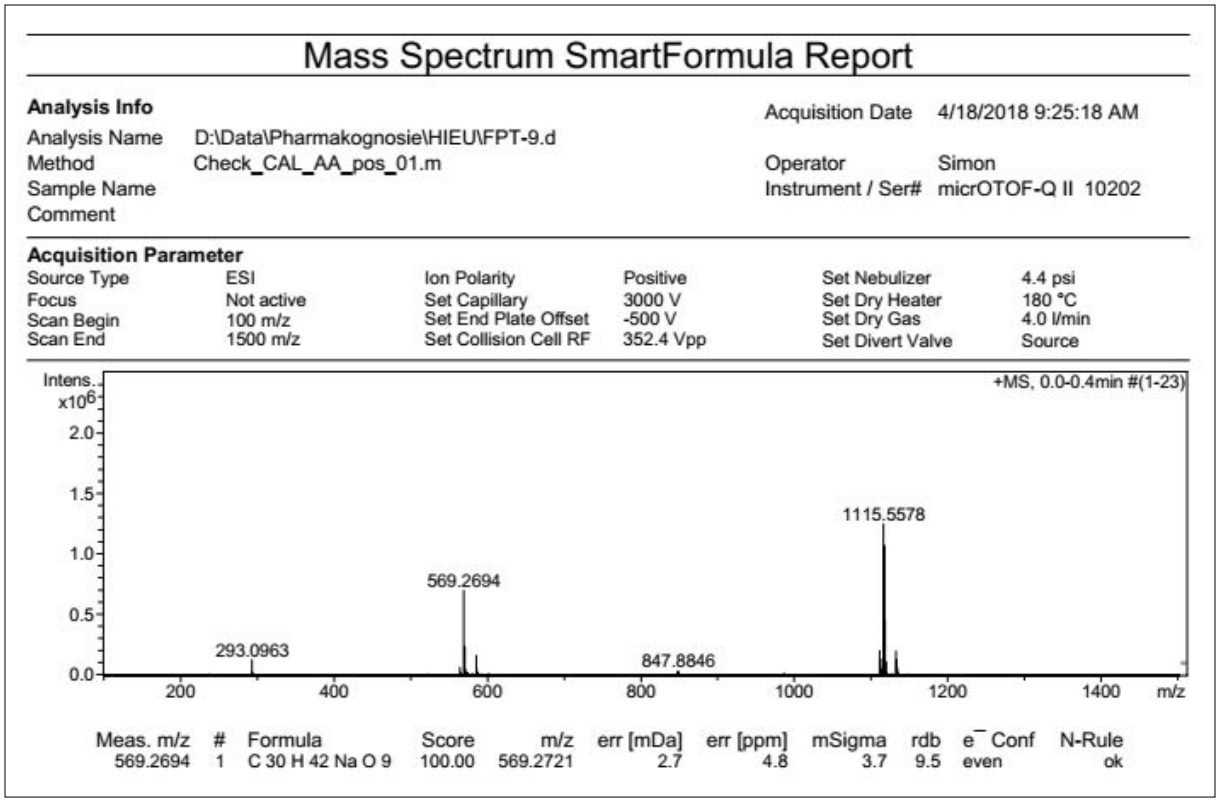



Figure S9.7. HRESIMS spectrum of compound **9**

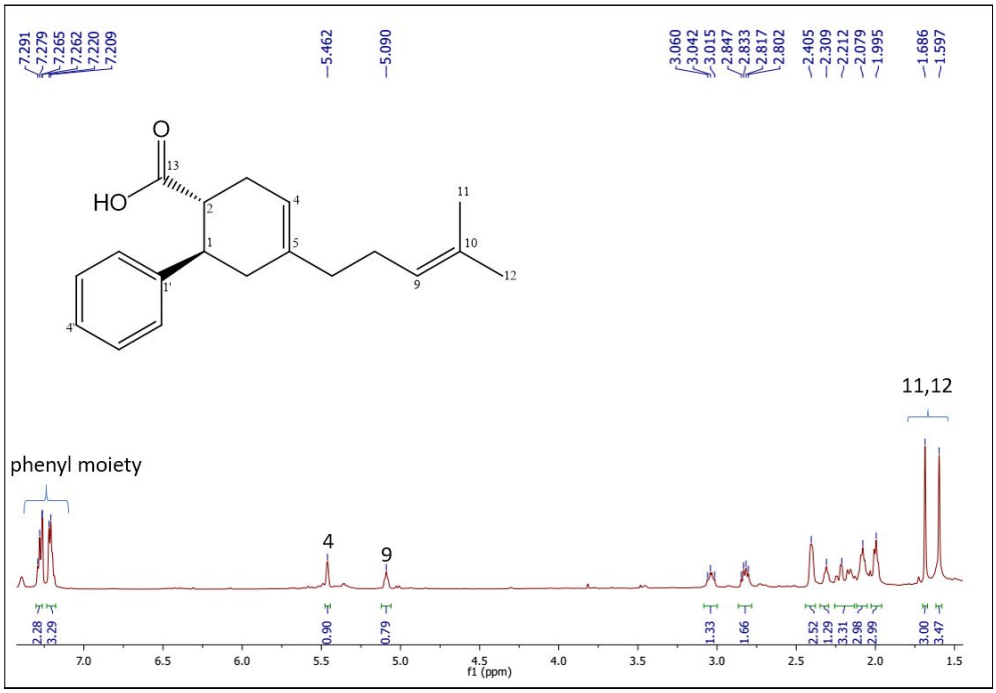



Figure S10.1. $^{1}$H NMR spectrum of compound **10** (600 MHz, in $CDCl_3$)

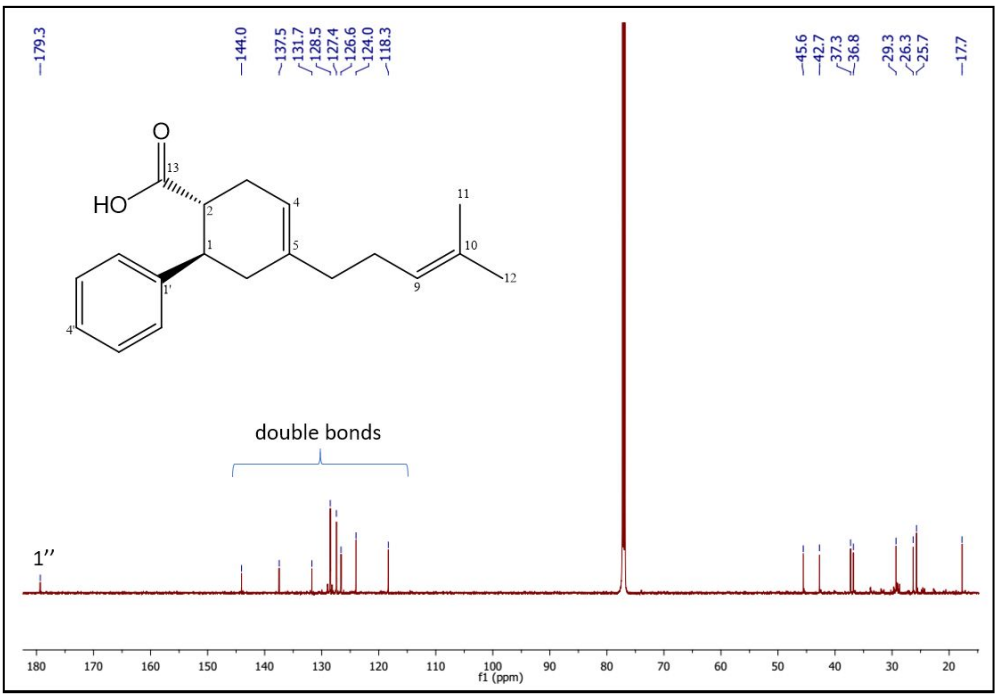



Figure S10.2. $^{13}$C NMR spectrum of compound **10** (150 MHz, in $CDCl_3$)

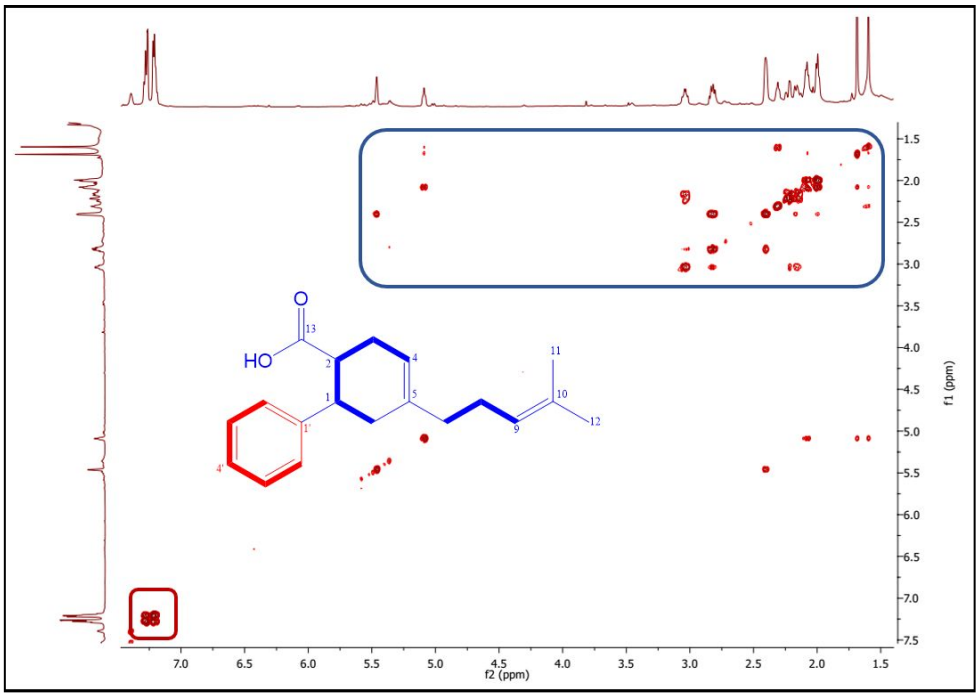



Figure S10.3. COSY spectrum of compound **10** (in $CDCl_3$)

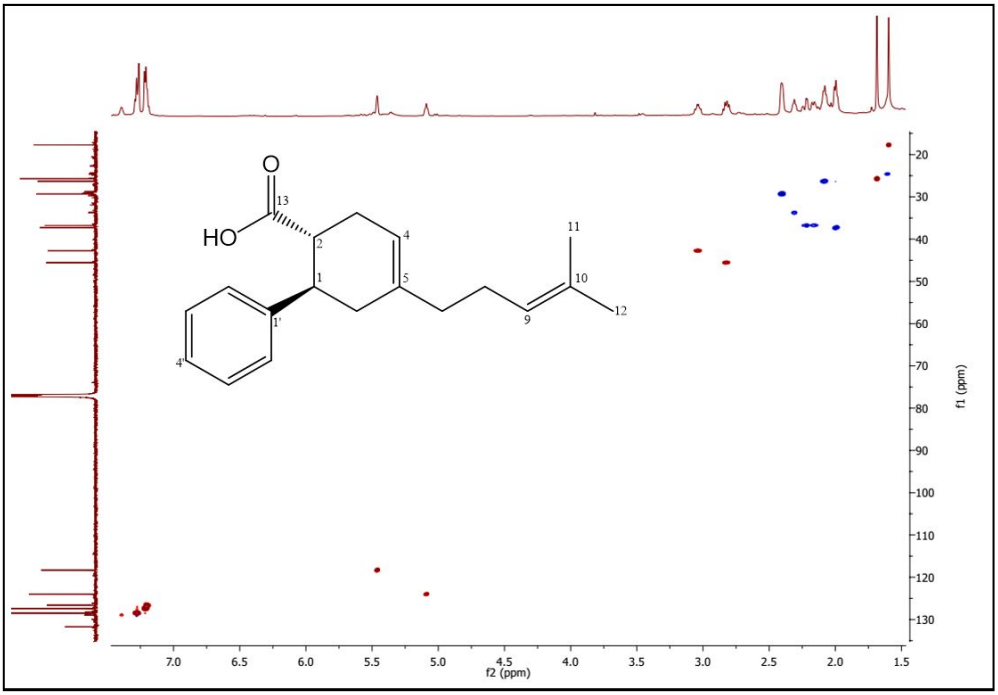



Figure S10.4. HSQC spectrum of compound **10** (in $CDCl_3$)

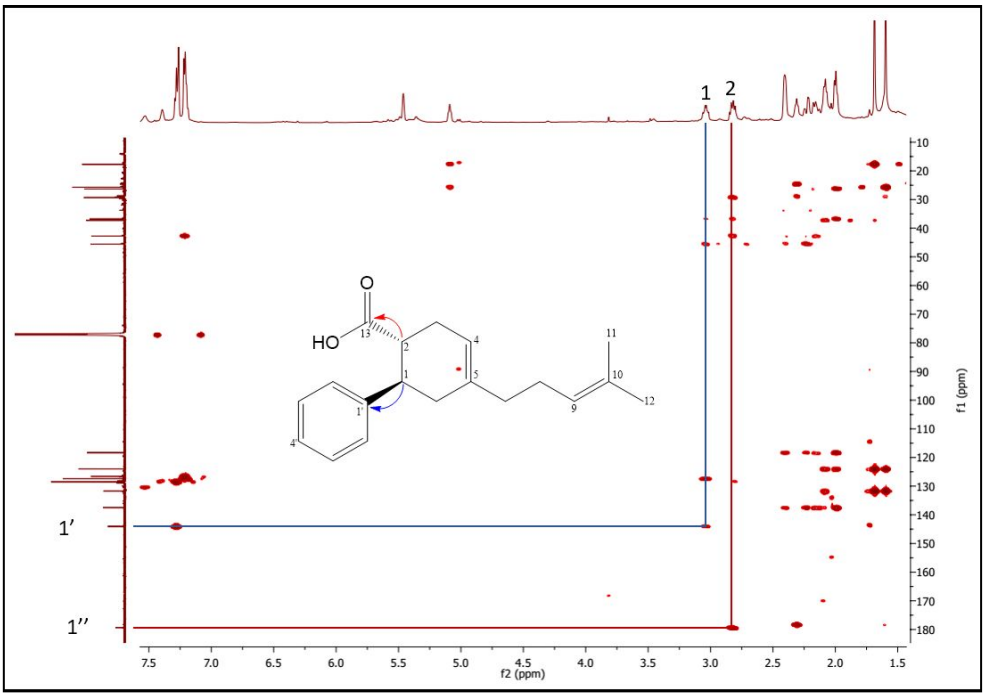



Figure S10.5. HMBC spectrum of compound **10** (in $CDCl_3$)

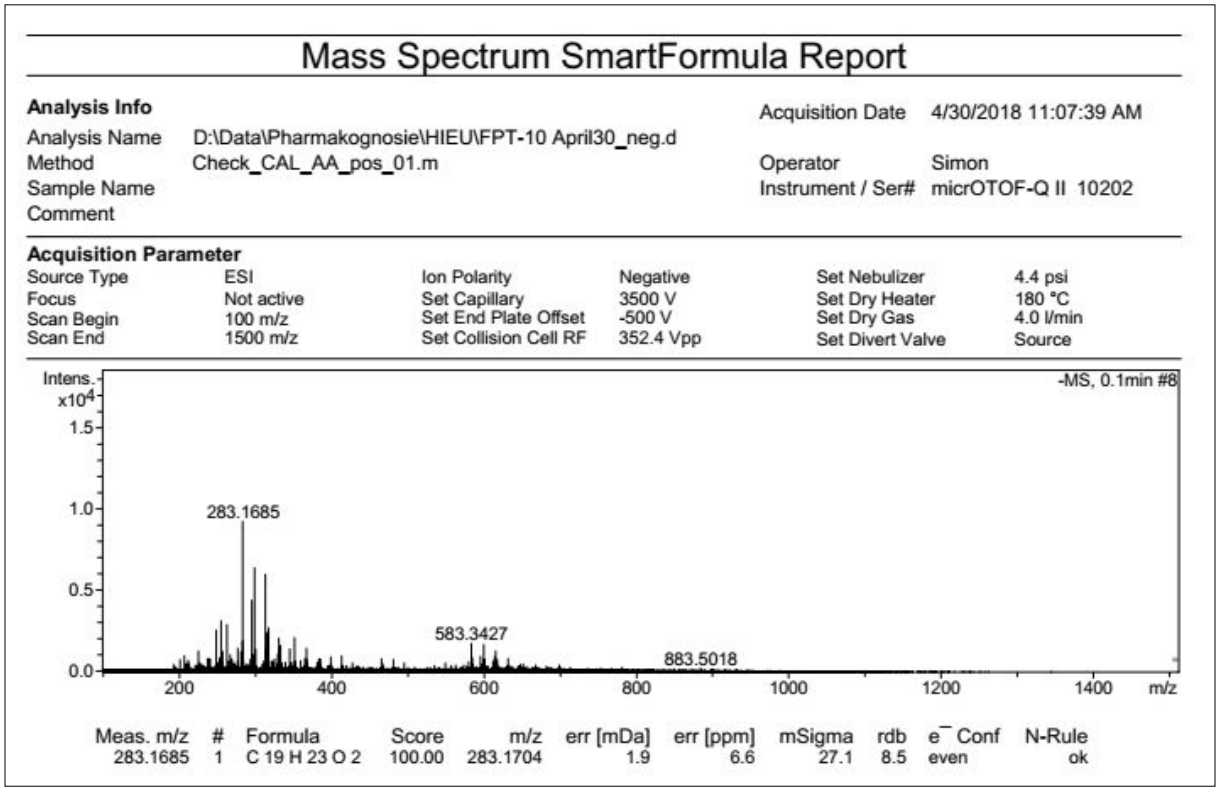



Figure S10.6. HRESIMS spectrum of compound **10**

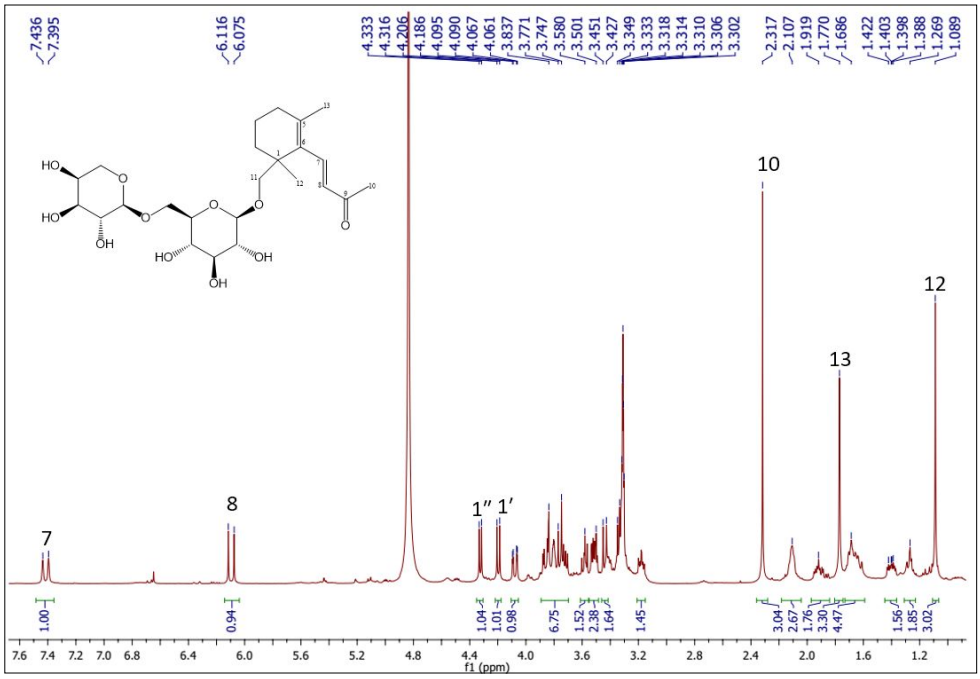



Figure S11.1. $^{1}$H NMR spectrum of compound **11** (400 MHz, in MeOH-$d_4$)

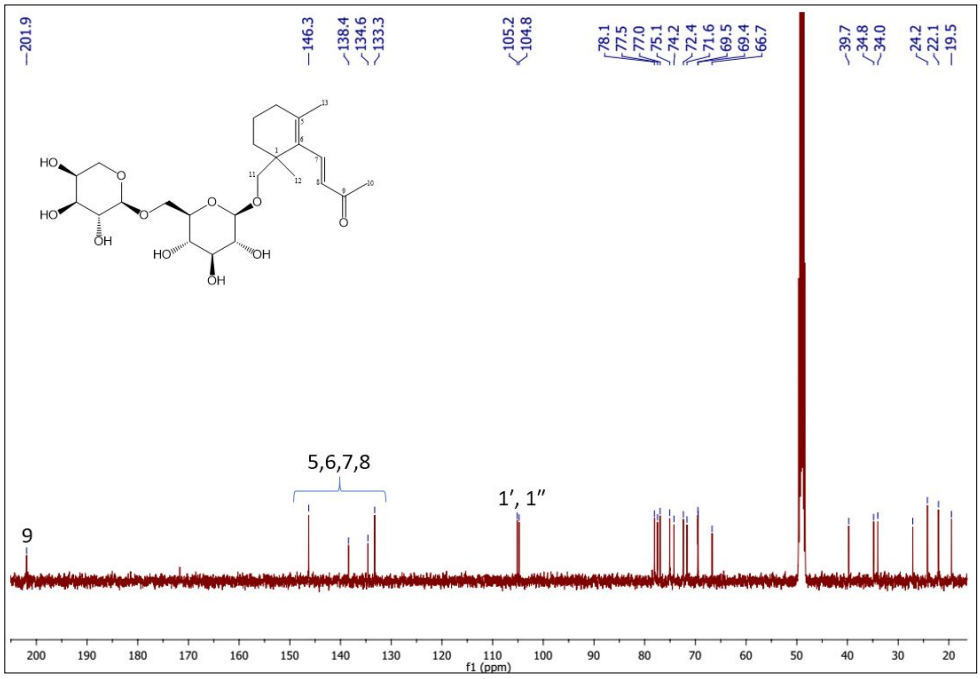



Figure S11.2. $^{13}$C NMR spectrum of compound **11** (100 MHz, in MeOH-$d_4$)

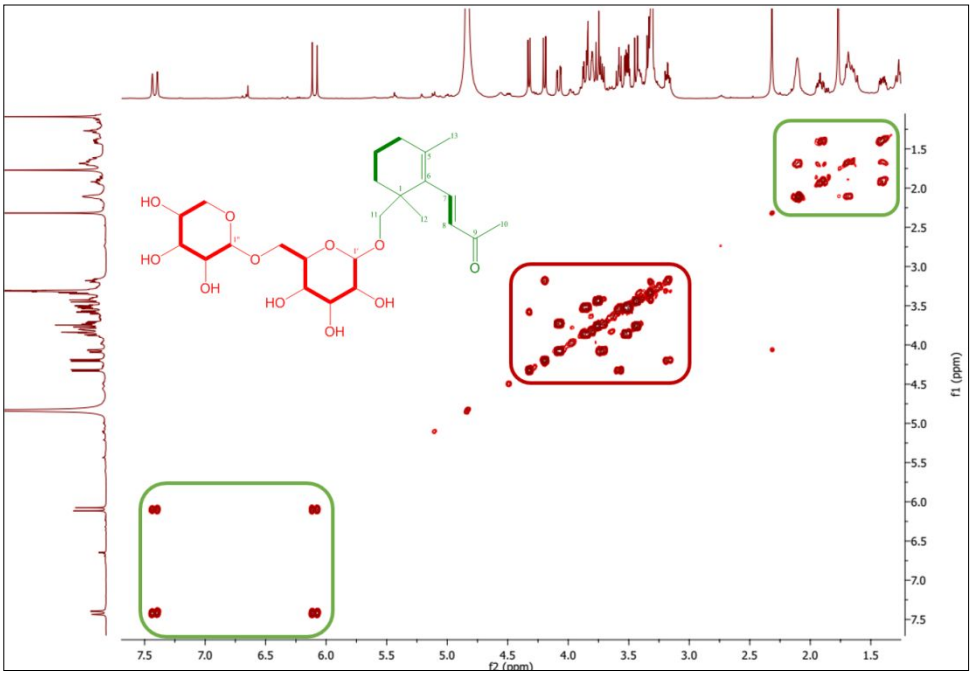



Figure S11.3. COSY spectrum of compound **11** (in MeOH-$d_4$)

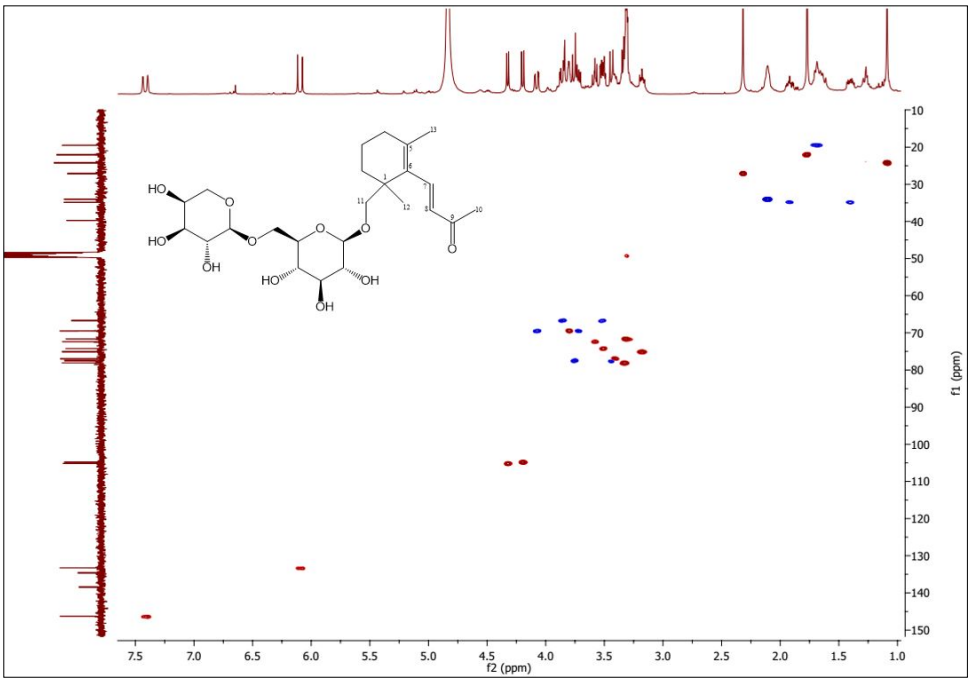



Figure S11.4. HSQC spectrum of compound **11** (in MeOH-$d_4$)

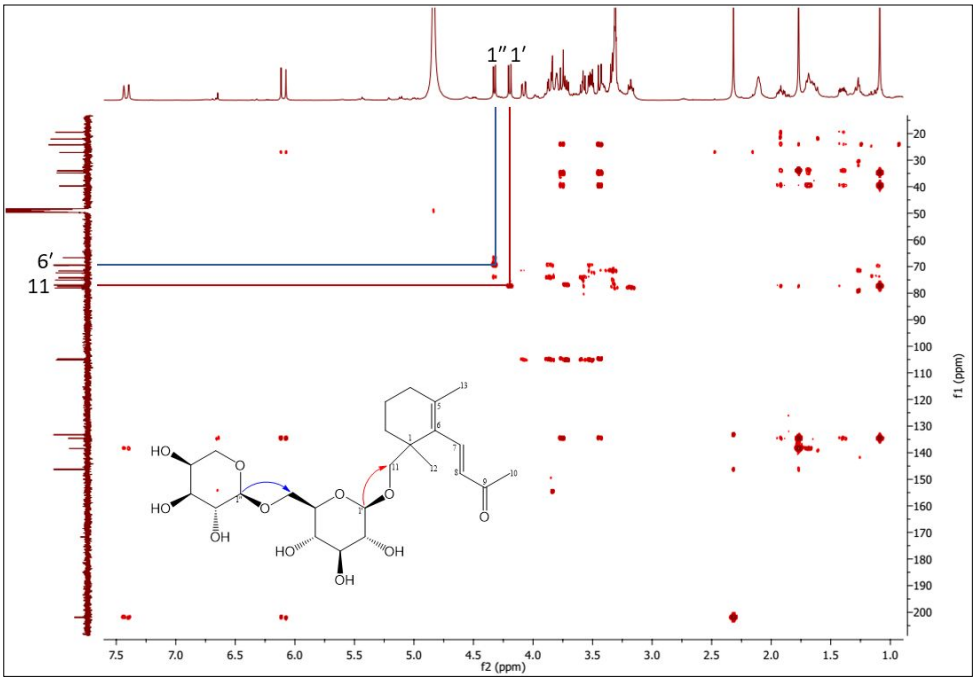



Figure S11.5. HMBC spectrum of compound **11** (in MeOH-$d_4$)

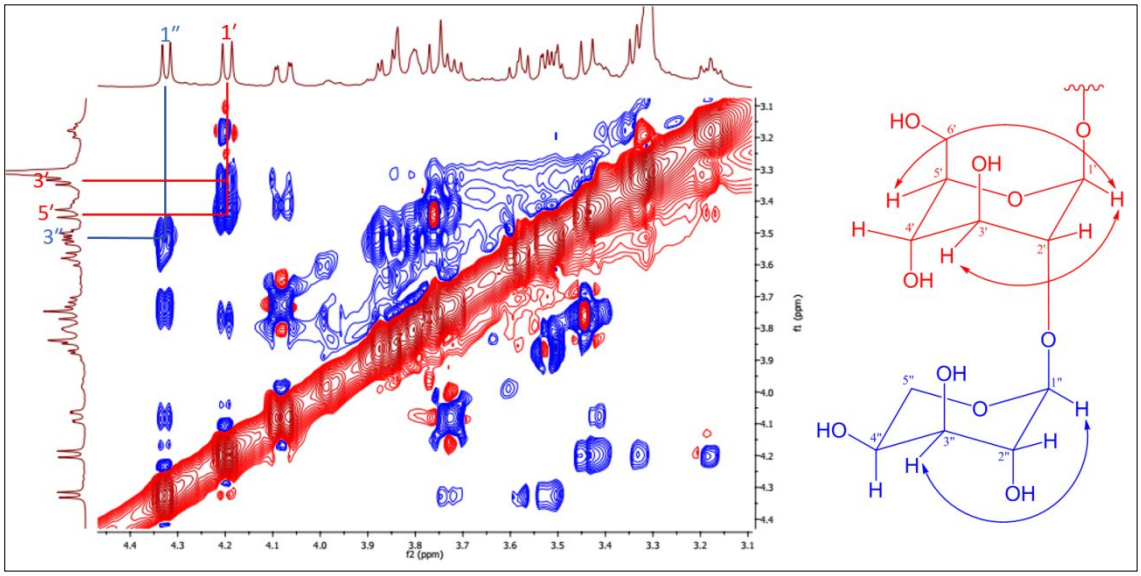



Figure S11.6. NOESY spectrum of compound **11** (in MeOH-$d_4$)

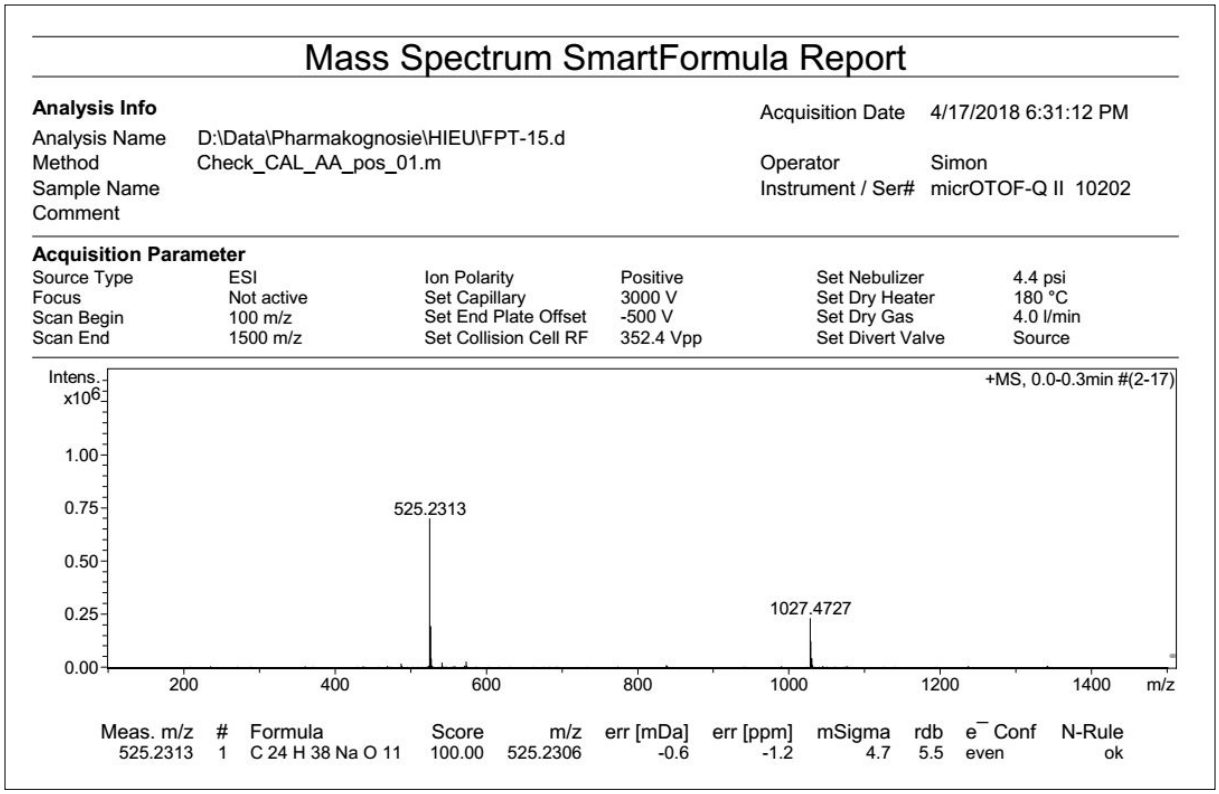



Figure S11.7. HRESIMS spectrum of compound **11**

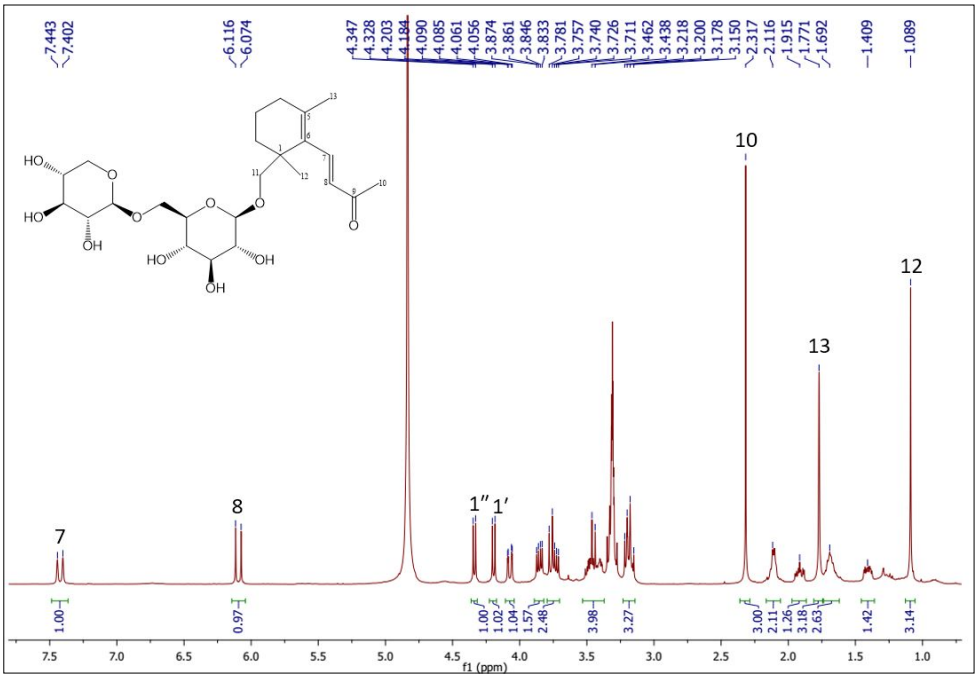



Figure S12.1. $^{1}$H NMR spectrum of compound **12** (400 MHz, in MeOH-$d_4$)

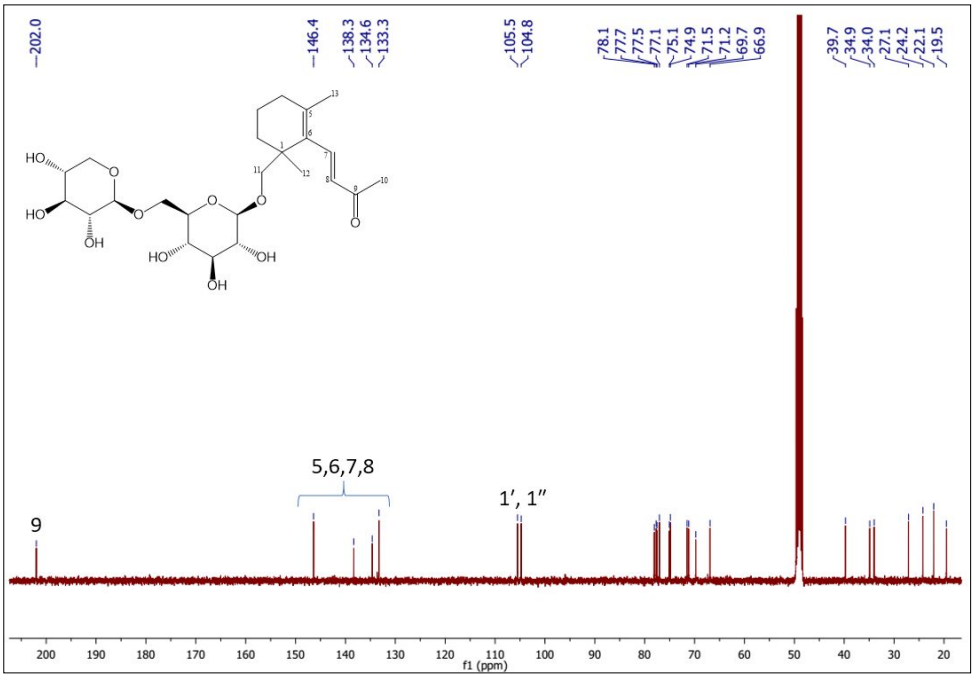



Figure S12.2. $^{13}$C NMR spectrum of compound **12** (100 MHz, in MeOH-$d_4$)

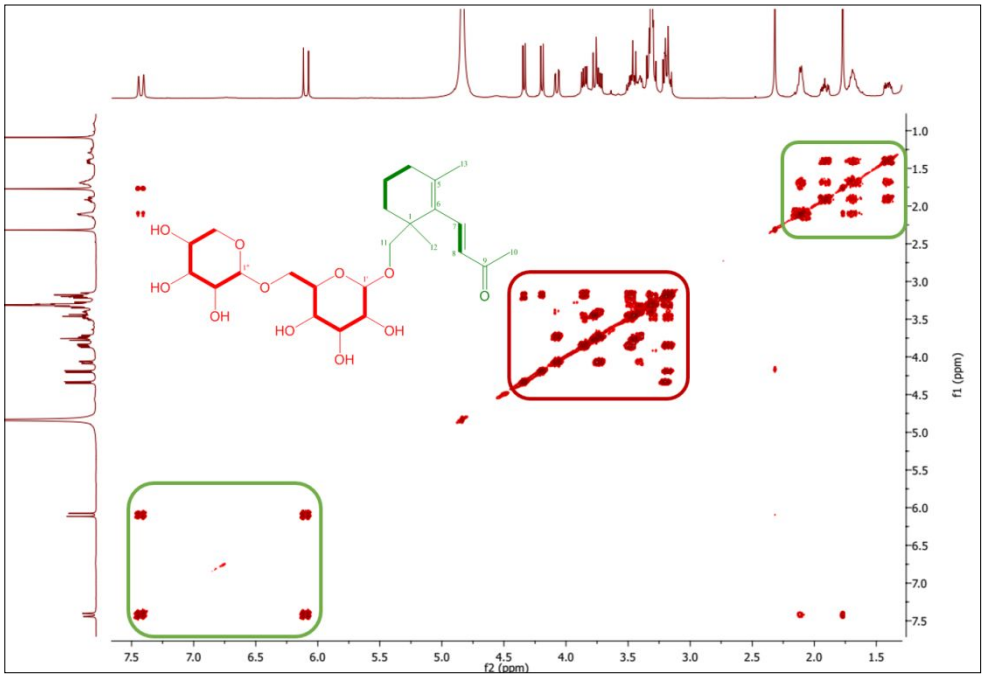



Figure S12.3. COSY spectrum of compound **12** (in MeOH-$d_4$)

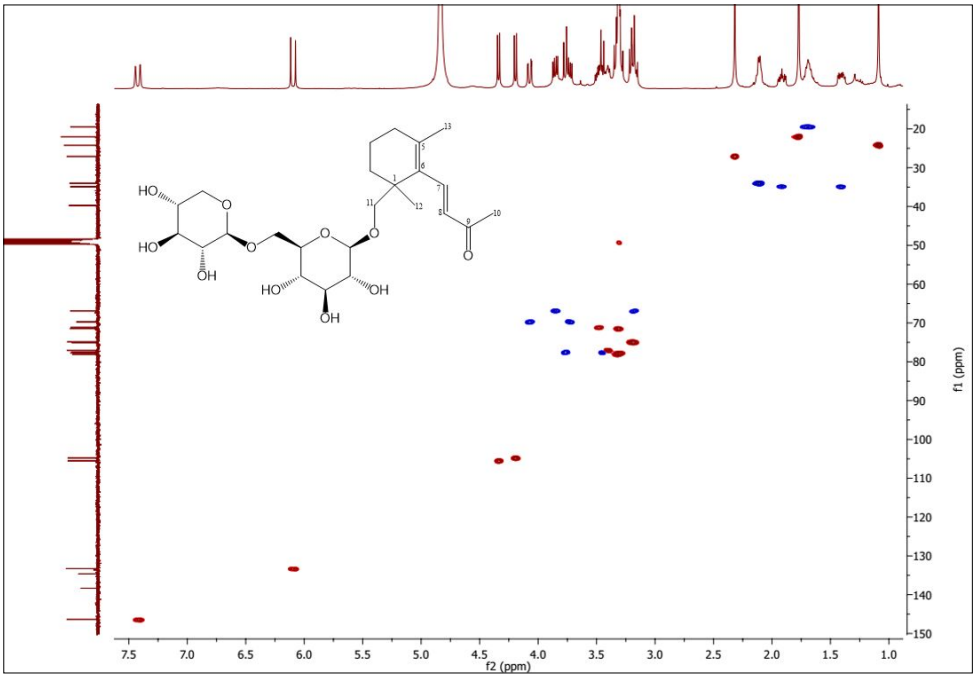



Figure S12.4. HSQC spectrum of compound **12** (in MeOH-$d_4$)

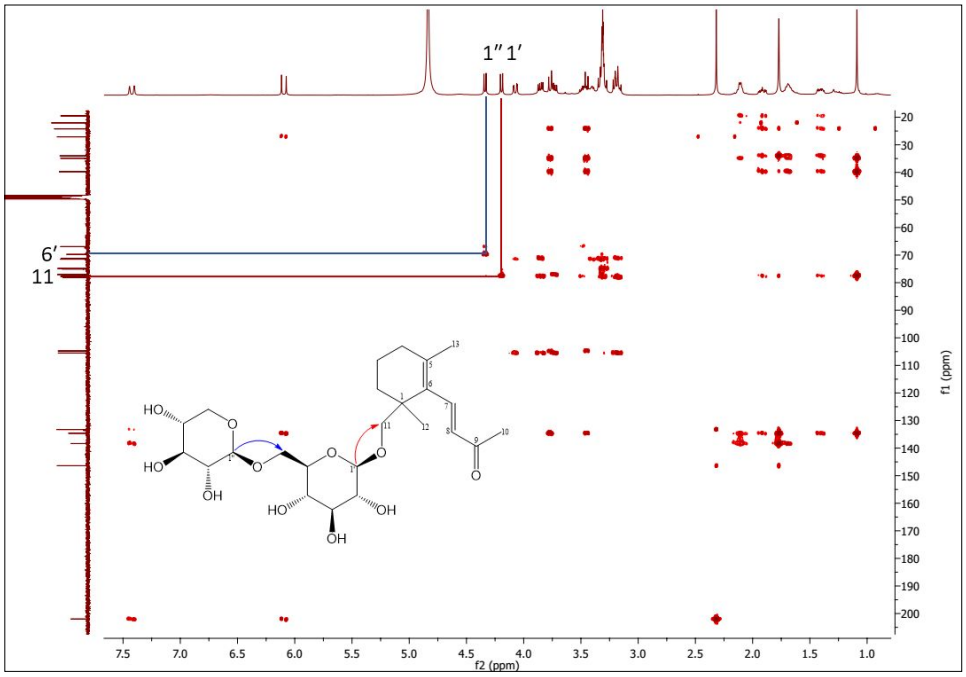



Figure S12.5. HMBC spectrum of compound **12** (in MeOH-$d_4$)

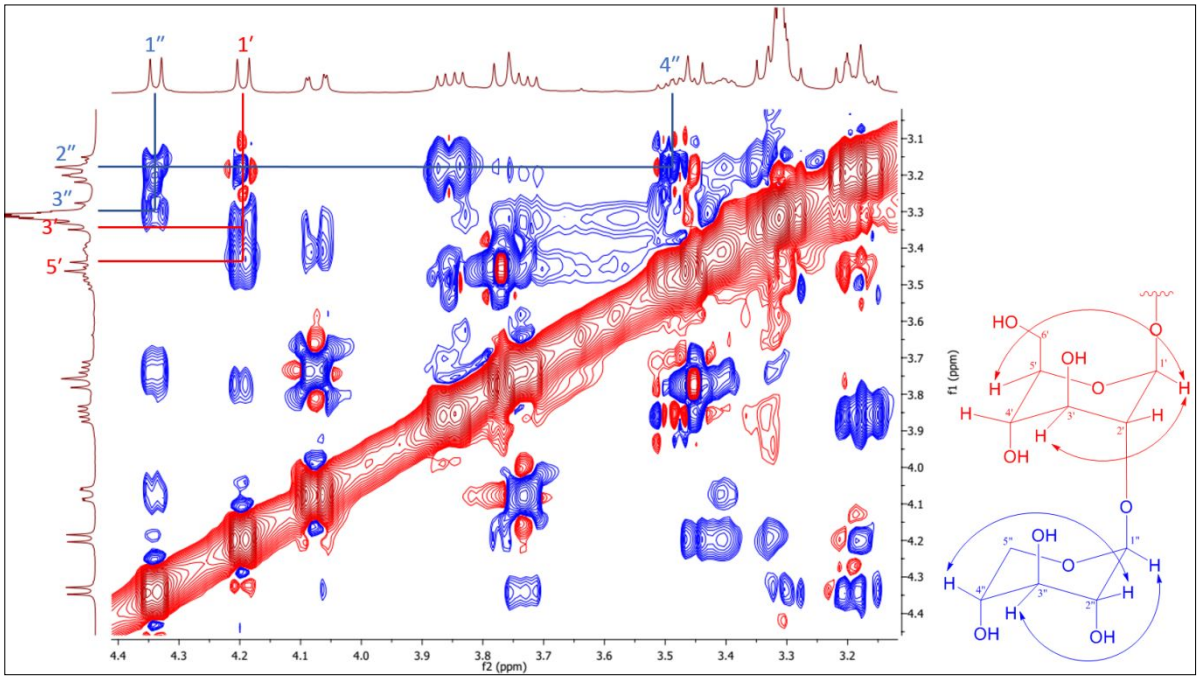



Figure S12.6. NOESY spectrum of compound **12** (in MeOH-$d_4$)

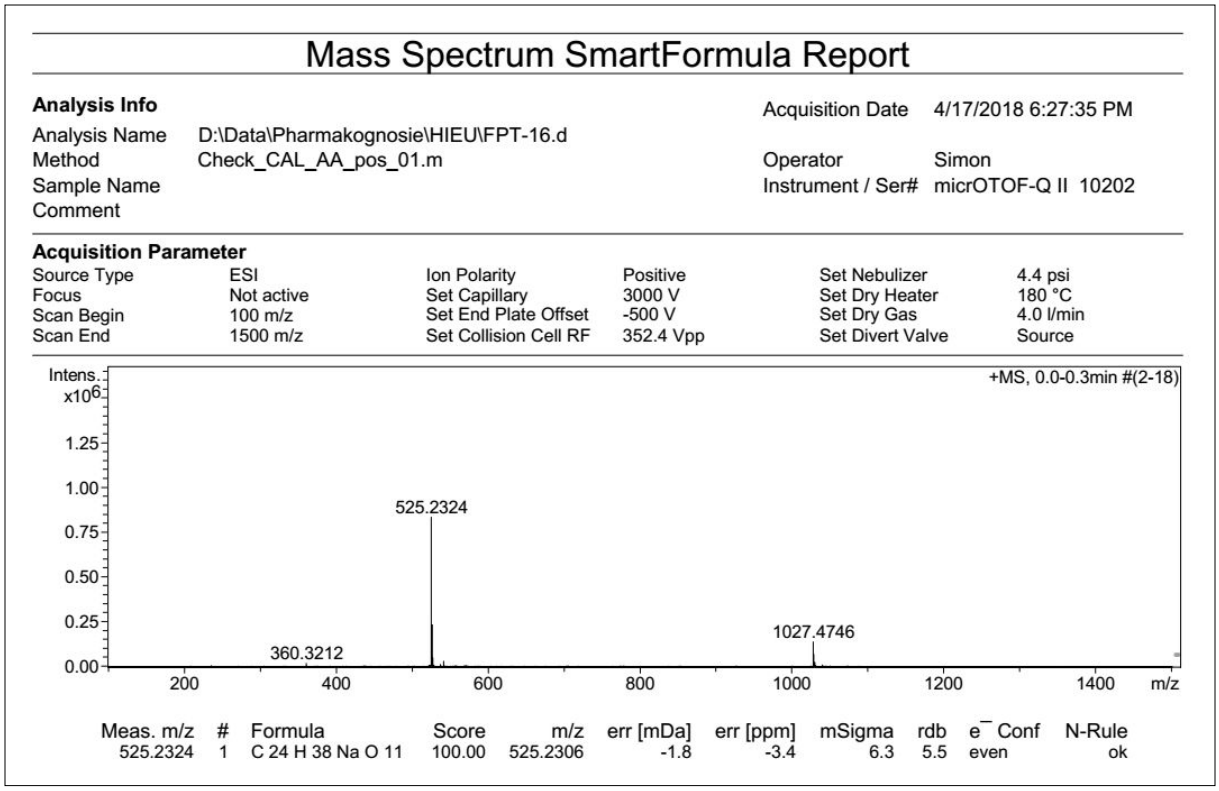
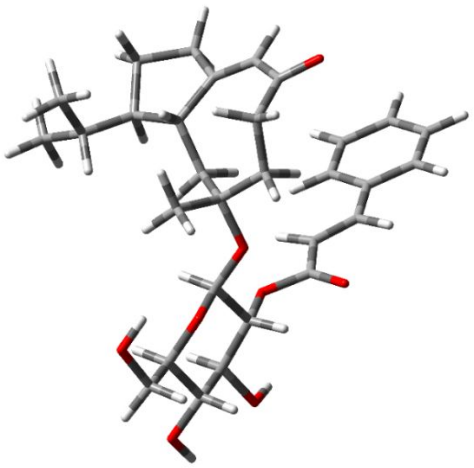



Figure S12.7. HRESIMS spectrum of compound **12**



C1-99.99%

Figure S13.1. Optimized conformer of compound **4** with DFT/B3LYP/6-31G in gas phase.

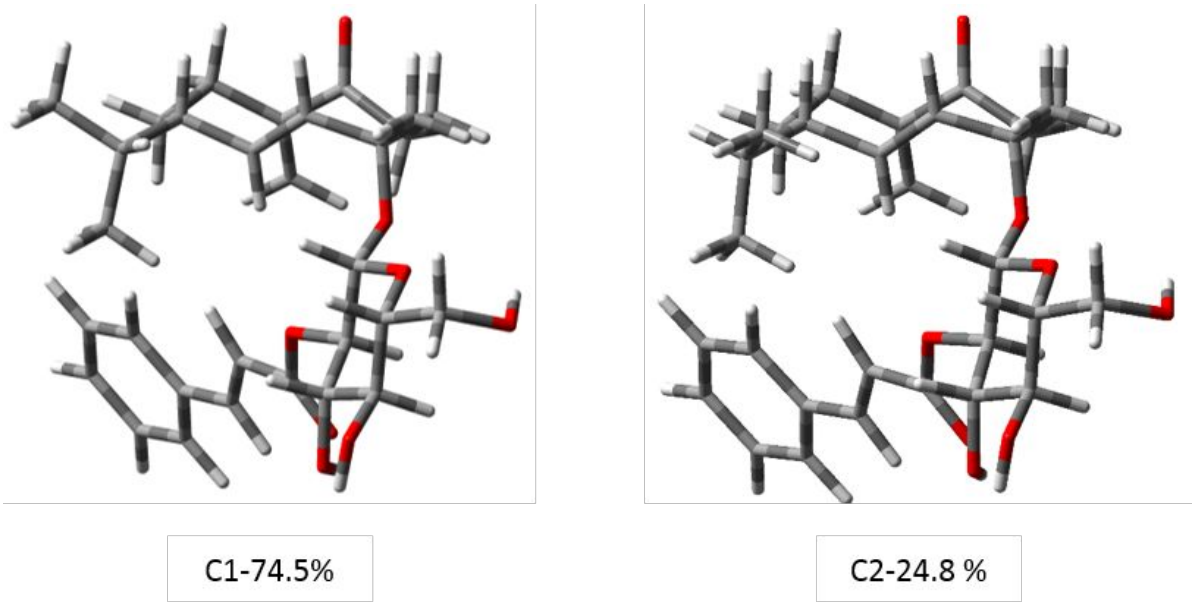



Figure S13.2. Optimized conformer of compound **5** with DFT/B3LYP/6-31G in gas phase.

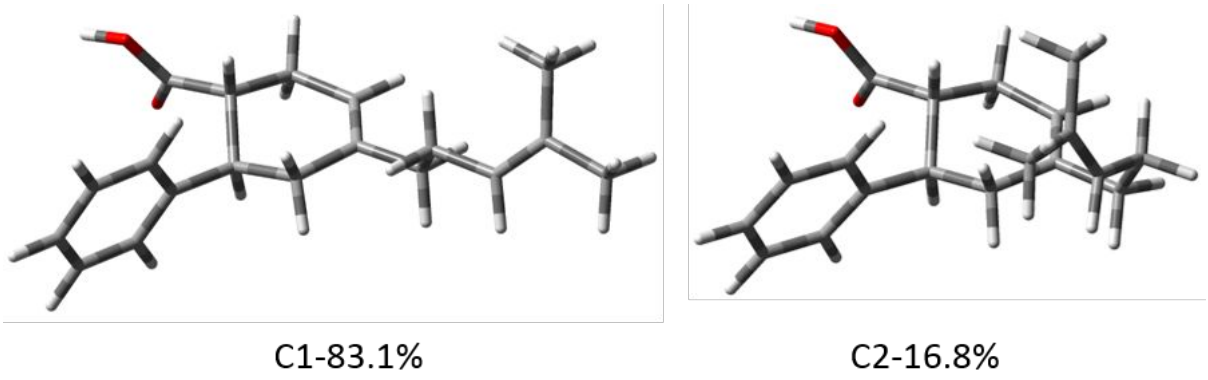



Figure S13.3. Optimized conformer of compound **10** with DFT/B3LYP/6-31G in gas phase.

F12 =Main!G11

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Unscaled Shifts | |
| 3 | | | | | | | | |
| 4 | | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
| 5 | sDP4+ (H data) | | 0.08% | 99.92% | - | - | - | - |
| 6 | sDP4+ (C data) | | 0.13% | 99.87% | - | - | - | - |
| 7 | sDP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |
| 8 | uDP4+ (H data) | | 97.52% | 2.48% | - | - | - | - |
| 9 | uDP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 10 | uDP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |
| 11 | DP4+ (H data) | | 2.95% | 97.05% | - | - | - | - |
| 12 | DP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 13 | DP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |

Figure S14.1. DP4+ probability results of **1**, chemical shifts calculated on using GIAO/mPW1PW91/6-311G+(d,p)/CPCM/methanol basis set and level of theory. Isomer 1 is 1*S*,4*R*,5*S*,6*S*,7*R*,9*S* and isomer 2 is 1*R*,4*S*,5*R*,6*R*,7*S*,9*R*.

Clipboard Font Alignment Numb

F12 =Main!G11

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Unscaled Shifts | |
| 3 | | | | | | | | |
| 4 | | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
| 5 | sDP4+ (H data) | | 84.74% | 15.26% | - | - | - | - |
| 6 | sDP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 7 | sDP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |
| 8 | uDP4+ (H data) | | 0.00% | 100.00% | - | - | - | - |
| 9 | uDP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 10 | uDP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |
| 11 | DP4+ (H data) | | 0.00% | 100.00% | - | - | - | - |
| 12 | DP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 13 | DP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |

Figure S14.2. DP4+ probability results of **2**, chemical shifts calculated on using GIAO/mPW1PW91/6-311G+(d,p)/CPCM/methanol basis set and level of theory. Isomer 1 is 4*S*,7*R*,10*S* and isomer 2 is 4*R*,7*S*,10*R*.

F12 =Main!G11

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Unscaled Shifts | |
| 3 | | | | | | | | |
| 4 | | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
| 5 | sDP4+ (H data) | | 98.39% | 1.61% | - | - | - | - |
| 6 | sDP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 7 | sDP4+ (all data) | | 0.02% | 99.98% | - | - | - | - |
| 8 | uDP4+ (H data) | | 97.48% | 2.52% | - | - | - | - |
| 9 | uDP4+ (C data) | | 3.36% | 96.64% | - | - | - | - |
| 10 | uDP4+ (all data) | | 57.30% | 42.70% | - | - | - | - |
| 11 | DP4+ (H data) | | 99.96% | 0.04% | - | - | - | - |
| 12 | DP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 13 | DP4+ (all data) | | 0.03% | 99.97% | - | - | - | - |

Figure S14.3. DP4+ probability results of **3**, chemical shifts calculated on using GIAO/mPW1PW91/6-311G+(d,p)/CPCM/methanol basis set and level of theory. Isomer 1 is 1*R*,4*S*,5*R*,10*R* and isomer 2 is 1*S*,4*R*,5*S*,10*S*.

F12 =Main!G11

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Unscaled Shifts | |
| 3 | | | | | | | | |
| 4 | | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
| 5 | sDP4+ (H data) | | 36.39% | 63.61% | - | - | - | - |
| 6 | sDP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 7 | sDP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |
| 8 | uDP4+ (H data) | | 3.43% | 96.57% | - | - | - | - |
| 9 | uDP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 10 | uDP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |
| 11 | DP4+ (H data) | | 1.99% | 98.01% | - | - | - | - |
| 12 | DP4+ (C data) | | 0.00% | 100.00% | - | - | - | - |
| 13 | DP4+ (all data) | | 0.00% | 100.00% | - | - | - | - |

Figure S14.4. DP4+ probability results of **6**, chemical shifts calculated on using GIAO/mPW1PW91/6-311G+(d,p)/CPCM/methanol basis set and level of theory. Isomer 1 is 4*S*,5*S*,6*S*,9*R* and isomer 2 is 4*R*,5*R*,6*R*,9*S* .

F12 =Main!G11

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Unscaled Shifts | |
| 3 | | | | | | | | |
| 4 | | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
| 5 | sDP4+ (H data) | | 0.01% | 99.99% | - | - | - | - |
| 6 | sDP4+ (C data) | | 99.94% | 0.06% | - | - | - | - |
| 7 | sDP4+ (all data) | | 8.48% | 91.52% | - | - | - | - |
| 8 | uDP4+ (H data) | | 0.00% | 100.00% | - | - | - | - |
| 9 | uDP4+ (C data) | | 99.92% | 0.08% | - | - | - | - |
| 10 | uDP4+ (all data) | | 0.56% | 99.44% | - | - | - | - |
| 11 | DP4+ (H data) | | 0.00% | 100.00% | - | - | - | - |
| 12 | DP4+ (C data) | | 100.00% | 0.00% | - | - | - | - |
| 13 | DP4+ (all data) | | 0.05% | 99.95% | - | - | - | - |

Figure S14.5. DP4+ probability results of **9**, chemical shifts calculated on using GIAO/mPW1PW91/6-311G+(d,p)/CPCM/methanol basis set and level of theory. Isomer 1 is 3*R*,5*R*,6*S*,9*R*,10*S*. and isomer 2 is 3*S*,5*S*,6*R*,9*S*,10*R*.

Table S1.1. Experimental and Boltzmann averaged calculated $^{1}$H and $^{13}$C NMR chemical shifts of compound **1**

| Atom | Exp. | Isomer 1 | Isomer 2 |
|---|---|---|---|
| C | 32.3 | 34.3 | 34.8 |
| C | 26.9 | 30.7 | 32.4 |
| C | 44.9 | 48.2 | 46.4 |
| C | 24.7 | 29.2 | 26.1 |
| C | 35.2 | 38.6 | 40.5 |
| C | 32.2 | 34.4 | 35.8 |
| C | 35.5 | 43.1 | 38.8 |
| C | 89.0 | 91.9 | 95.6 |
| C | 36.2 | 36.5 | 39.2 |
| C | 29.6 | 33.1 | 32.4 |
| C | 19.1 | 19.1 | 19.8 |
| C | 34.7 | 39.2 | 38.8 |
| C | 20.0 | 22.1 | 19.2 |
| C | 20.9 | 21.2 | 23.5 |
| C | 28.8 | 26.4 | 27.9 |
| C | 99.8 | 97.0 | 97.7 |
| C | 78.8 | 78.2 | 83.8 |
| C | 72.0 | 71.3 | 73.9 |
| C | 76.5 | 76.3 | 73.5 |

| | | | |
|---|---|---|---|
| C | 75.8 | 77.4 | 78.1 |
| C | 62.8 | 62.5 | 66.0 |
| C | 167.6 | 174.6 | 176.4 |
| C | 119.1 | 117.6 | 121.1 |
| C | 146.3 | 154.6 | 158.0 |
| C | 135.7 | 136.2 | 139.8 |
| C | 129.1 | 135.7 | 134.6 |
| C | 130.1 | 132.6 | 135.8 |
| C | 131.6 | 136.3 | 139.7 |
| C | 130.1 | 132.4 | 136.0 |
| C | 129.1 | 131.5 | 139.2 |
| H | 0.83 | 0.80 | 1.05 |
| H | 0.95 | 0.97 | 1.13 |
| H | 1.60 | 1.54 | 1.59 |
| H | 0.61 | 0.58 | 0.79 |
| H | 1.42 | 1.44 | 1.41 |
| H | 0.88 | 0.77 | 1.18 |
| H | 1.22 | 0.67 | 1.63 |
| H | 1.66 | 1.66 | 1.76 |
| H | 1.40 | 1.66 | 1.61 |
| H | 1.46 | 1.64 | 1.60 |
| H | 1.86 | 1.57 | 2.03 |
| H | 1.46 | 2.01 | 1.57 |
| H | 0.96 | 1.43 | 0.91 |
| H | 0.96 | 0.54 | 0.59 |
| H | 0.96 | 0.86 | 1.49 |
| H | 1.77 | 1.30 | 1.69 |
| H | 0.98 | 0.79 | 0.92 |
| H | 0.98 | 1.51 | 1.45 |
| H | 0.98 | 0.49 | 0.91 |
| H | 1.04 | 0.71 | 1.02 |
| H | 1.04 | 1.11 | 1.26 |
| H | 1.04 | 0.57 | 1.17 |
| H | 1.35 | 1.43 | 1.69 |
| H | 1.35 | 1.30 | 1.27 |
| H | 1.35 | 1.42 | 1.27 |
| H | 4.97 | 4.88 | 5.34 |
| H | 3.34 | 3.48 | 3.94 |
| H | 3.43 | 3.71 | 3.79 |
| H | 3.61 | 3.58 | 3.79 |
| H | 4.84 | 4.54 | 4.89 |
| H | 3.73 | 3.74 | 3.71 |
| H | 3.92 | 3.92 | 4.00 |

| | | | |
|---|---|---|---|
| H | 6.56 | 6.79 | 6.92 |
| H | 7.75 | 8.16 | 8.36 |
| H | 7.61 | 7.86 | 8.34 |
| H | 7.44 | 7.69 | 7.89 |
| H | 7.44 | 7.72 | 7.92 |
| H | 7.44 | 7.70 | 7.90 |
| H | 7.61 | 8.13 | 8.05 |

Table S1.2. Experimental and Boltzmann averaged calculated $^{1}H$ and $^{13}C$ NMR chemical shifts of compound **2**

| Atom | Exp. | Isomer 1 | Isomer 2 |
|---|---|---|---|
| C | 34.9 | 38.3 | 40.6 |
| C | 35.1 | 34.5 | 38.2 |
| C | 28.4 | 28.2 | 33.3 |
| C | 49.5 | 48.6 | 51.5 |
| C | 28.2 | 32.9 | 31.7 |
| C | 141.4 | 142.9 | 147.4 |
| C | 140.7 | 147.3 | 146.3 |
| C | 47.4 | 51.0 | 53.6 |
| C | 31.9 | 33.7 | 35.3 |
| C | 36.1 | 40.6 | 41.2 |
| C | 81.9 | 86.9 | 85.5 |
| C | 21.8 | 23.3 | 26.8 |
| C | 25.6 | 24.8 | 29.4 |
| C | 20.4 | 18.0 | 22.7 |
| C | 20.5 | 20.3 | 23.4 |
| C | 96.6 | 90.5 | 96.2 |
| C | 77.8 | 82.5 | 78.0 |
| C | 71.8 | 71.4 | 72.0 |
| C | 76.4 | 67.4 | 79.4 |
| C | 75.6 | 74.2 | 78.5 |
| C | 62.8 | 64.5 | 63.3 |
| C | 167.6 | 167.8 | 173.4 |
| C | 119.1 | 116.1 | 118.0 |
| C | 146.6 | 151.8 | 153.1 |
| C | 135.8 | 134.3 | 135.7 |
| C | 129.2 | 134.1 | 130.4 |
| C | 130.1 | 130.7 | 131.9 |
| C | 131.6 | 134.1 | 135.7 |
| C | 130.1 | 130.4 | 132.1 |
| C | 129.2 | 128.8 | 135.8 |
| H | 2.22 | 2.38 | 2.35 |

| | | | |
|---|---|---|---|
| H | 1.50 | 1.65 | 1.75 |
| H | 1.64 | 2.06 | 1.56 |
| H | 1.38 | 1.60 | 1.71 |
| H | 1.73 | 2.17 | 1.74 |
| H | 1.63 | 1.80 | 1.70 |
| H | 1.81 | 1.86 | 2.06 |
| H | 2.18 | 2.01 | 2.36 |
| H | 2.52 | 2.76 | 2.59 |
| H | 1.93 | 2.05 | 1.83 |
| H | 1.24 | 1.34 | 1.36 |
| H | 2.41 | 2.58 | 2.65 |
| H | 2.07 | 2.39 | 2.12 |
| H | 1.12 | 1.08 | 1.42 |
| H | 1.12 | 1.32 | 1.52 |
| H | 1.12 | 1.09 | 1.25 |
| H | 1.22 | 1.46 | 0.99 |
| H | 1.22 | 1.31 | 1.18 |
| H | 1.22 | 1.39 | 1.36 |
| H | 0.92 | 0.77 | 0.78 |
| H | 0.92 | 1.21 | 0.93 |
| H | 0.92 | 1.10 | 1.17 |
| H | 0.90 | 0.61 | 1.18 |
| H | 0.90 | 1.18 | 1.04 |
| H | 0.90 | 1.02 | 0.81 |
| H | 4.74 | 4.96 | 5.07 |
| H | 3.33 | 4.02 | 3.33 |
| H | 3.42 | 3.62 | 3.77 |
| H | 3.62 | 3.76 | 3.56 |
| H | 4.84 | 4.54 | 4.52 |
| H | 3.68 | 3.53 | 3.80 |
| H | 3.84 | 3.88 | 3.92 |
| H | 6.56 | 6.60 | 6.83 |
| H | 7.73 | 7.96 | 8.19 |
| H | 7.60 | 7.68 | 8.22 |
| H | 7.41 | 7.57 | 7.75 |
| H | 7.41 | 7.59 | 7.77 |
| H | 7.41 | 7.57 | 7.73 |
| H | 7.60 | 8.02 | 7.83 |

Table S1.3. Experimental and Boltzmann averaged calculated $^{1}H$ and $^{13}C$ NMR chemical shifts of compound **3**

| Atom | Exp. | Isomer 1 | Isomer 2 |
|---|---|---|---|
| C | 116.7 | 128.1 | 124.5 |
| C | 143.6 | 156.9 | 152.6 |
| C | 23.9 | 26.1 | 24.9 |
| C | 49.7 | 51.8 | 51.6 |
| C | 39.1 | 43.4 | 43.6 |
| C | 42.1 | 45.7 | 43.6 |
| C | 78.6 | 86.9 | 84.3 |
| C | 37.7 | 34.3 | 36.2 |
| C | 27.5 | 28.9 | 29.9 |
| C | 80.9 | 79.5 | 83.2 |
| C | 12.8 | 18.5 | 13.0 |
| C | 25.0 | 26.5 | 27.6 |
| C | 36.2 | 42.0 | 42.3 |
| C | 21.9 | 22.5 | 22.2 |
| C | 22.1 | 23.3 | 23.2 |
| C | 97.0 | 97.6 | 97.4 |
| C | 77.8 | 80.5 | 78.4 |
| C | 72.0 | 71.9 | 72.3 |
| C | 76.4 | 79.8 | 79.7 |
| C | 75.6 | 79.6 | 79.4 |
| C | 167.5 | 179.2 | 178.8 |
| C | 63.0 | 62.8 | 62.9 |
| C | 119.1 | 120.7 | 120.7 |
| C | 146.7 | 158.1 | 158.1 |
| C | 135.7 | 139.5 | 139.0 |
| C | 129.2 | 137.7 | 137.7 |
| C | 130.1 | 135.9 | 134.8 |
| C | 131.6 | 139.8 | 138.4 |
| C | 130.1 | 135.8 | 134.6 |
| C | 129.2 | 136.3 | 133.9 |
| H | 1.21 | 1.35 | 1.37 |
| H | 5.22 | 5.72 | 5.73 |
| H | 2.10 | 1.91 | 2.21 |
| H | 1.75 | 2.16 | 2.18 |
| H | 2.02 | 2.19 | 1.97 |
| H | 1.73 | 1.70 | 2.06 |
| H | 1.36 | 1.52 | 1.51 |
| H | 2.09 | 2.70 | 2.18 |
| H | 2.14 | 1.79 | 1.67 |
| H | 1.41 | 1.75 | 2.22 |

| | | | |
|---|---|---|---|
| H | 3.20 | 3.34 | 3.43 |
| H | 0.93 | 0.72 | 0.76 |
| H | 0.93 | 1.43 | 1.24 |
| H | 0.93 | 1.02 | 0.46 |
| H | 1.20 | 1.75 | 1.73 |
| H | 1.20 | 1.00 | 0.81 |
| H | 1.20 | 1.26 | 1.23 |
| H | 1.99 | 2.26 | 2.34 |
| H | 0.87 | 0.91 | 1.04 |
| H | 0.87 | 0.96 | 1.00 |
| H | 0.87 | 0.79 | 1.05 |
| H | 0.83 | 0.87 | 1.06 |
| H | 0.83 | 0.95 | 0.95 |
| H | 0.83 | 1.05 | 1.13 |
| H | 4.68 | 5.24 | 5.01 |
| H | 3.32 | 3.43 | 3.37 |
| H | 3.43 | 3.90 | 3.84 |
| H | 3.62 | 3.66 | 3.64 |
| H | 4.89 | 4.77 | 4.55 |
| H | 3.71 | 4.09 | 3.83 |
| H | 3.88 | 3.88 | 3.95 |
| H | 6.60 | 6.95 | 6.98 |
| H | 7.76 | 8.38 | 8.35 |
| H | 7.61 | 8.16 | 8.07 |
| H | 7.43 | 7.89 | 7.83 |
| H | 7.43 | 7.93 | 7.87 |
| H | 7.43 | 7.90 | 7.82 |
| H | 7.61 | 8.25 | 8.33 |

Table S1.4. Experimental and Boltzmann averaged calculated $^{1}H$ and $^{13}C$ NMR chemical shifts of compound **6**

| Atom | Exp. | Isomer 1 | Isomer 2 |
|---|---|---|---|
| C | 74.0 | 77.9 | 77.3 |
| C | 37.7 | 39.9 | 39.1 |
| C | 22.3 | 26.3 | 23.4 |
| C | 44.6 | 40.3 | 47.1 |
| C | 26.8 | 28.8 | 28.3 |
| C | 59.1 | 64.6 | 64.1 |
| C | 228.6 | 247.0 | 247.0 |
| C | 38.1 | 44.2 | 44.4 |
| C | 29.2 | 31.9 | 32.2 |
| C | 38.8 | 44.6 | 44.4 |

| | | | |
|---|---|---|---|
| C | 81.6 | 92.4 | 84.4 |
| C | 26.1 | 27.5 | 29.3 |
| C | 20.6 | 23.1 | 24.9 |
| C | 19.5 | 21.2 | 21.3 |
| C | 28.1 | 28.6 | 28.6 |
| C | 96.5 | 92.6 | 99.0 |
| C | 77.8 | 86.5 | 78.9 |
| C | 71.8 | 74.5 | 72.7 |
| C | 76.3 | 69.9 | 80.3 |
| C | 75.6 | 78.1 | 80.0 |
| C | 62.7 | 67.0 | 63.6 |
| C | 167.7 | 174.4 | 180.7 |
| C | 119.1 | 120.5 | 121.0 |
| C | 146.6 | 158.0 | 159.3 |
| C | 135.8 | 139.5 | 140.3 |
| C | 129.3 | 137.0 | 141.3 |
| C | 130.0 | 135.7 | 136.1 |
| C | 131.6 | 139.5 | 139.8 |
| C | 130.0 | 135.7 | 135.8 |
| C | 129.3 | 136.2 | 133.6 |
| H | 1.50 | 1.53 | 1.45 |
| H | 1.57 | 1.71 | 1.59 |
| H | 1.44 | 1.40 | 1.56 |
| H | 1.44 | 1.80 | 2.07 |
| H | 1.63 | 2.30 | 1.73 |
| H | 1.60 | 2.16 | 1.70 |
| H | 1.42 | 1.50 | 1.62 |
| H | 2.36 | 2.51 | 2.02 |
| H | 2.18 | 2.35 | 2.00 |
| H | 1.62 | 1.90 | 1.62 |
| H | 2.06 | 1.82 | 1.87 |
| H | 2.30 | 2.36 | 2.35 |
| H | 1.09 | 1.25 | 1.45 |
| H | 1.09 | 2.00 | 1.54 |
| H | 1.09 | 1.52 | 0.97 |
| H | 1.22 | 1.05 | 1.50 |
| H | 1.22 | 1.34 | 1.48 |
| H | 1.22 | 1.23 | 1.16 |
| H | 1.16 | 1.42 | 1.38 |
| H | 1.16 | 1.19 | 1.23 |
| H | 1.16 | 1.17 | 1.09 |
| H | 1.07 | 0.92 | 0.81 |
| H | 1.07 | 0.96 | 0.74 |

| | | | |
|---|---|---|---|
| H | 1.07 | 1.34 | 1.28 |
| H | 4.72 | 5.26 | 5.07 |
| H | 3.33 | 4.23 | 3.41 |
| H | 3.41 | 3.73 | 3.87 |
| H | 3.62 | 3.90 | 3.65 |
| H | 4.81 | 4.60 | 4.58 |
| H | 3.70 | 3.60 | 3.89 |
| H | 3.85 | 3.94 | 3.99 |
| H | 6.50 | 6.94 | 6.95 |
| H | 7.64 | 8.31 | 8.38 |
| H | 7.62 | 8.11 | 7.97 |
| H | 7.42 | 7.89 | 7.91 |
| H | 7.42 | 7.90 | 7.95 |
| H | 7.42 | 7.89 | 7.90 |
| H | 7.62 | 8.17 | 8.68 |

Table S1.5. Experimental and Boltzmann averaged calculated $^{1}H$ and $^{13}C$ NMR chemical shifts of compound **9**

| Atom | Exp. | Isomer 1 | Isomer 2 |
|---|---|---|---|
| C | 26.9 | 29.5 | 29.4 |
| C | 18.9 | 21.7 | 22.3 |
| C | 38.8 | 43.7 | 43.2 |
| C | 47.6 | 53.4 | 53.3 |
| C | 81.0 | 86.8 | 86.6 |
| C | 40.6 | 43.1 | 42.3 |
| C | 218.5 | 236.9 | 235.2 |
| C | 47.2 | 53.9 | 54.0 |
| C | 30.8 | 35.8 | 36.6 |
| C | 33.6 | 35.9 | 35.7 |
| C | 81.2 | 83.9 | 84.3 |
| C | 28.2 | 26.7 | 25.5 |
| C | 26.0 | 29.6 | 31.3 |
| C | 16.5 | 17.7 | 16.8 |
| C | 15.2 | 15.6 | 15.5 |
| C | 96.6 | 97.9 | 97.4 |
| C | 77.8 | 78.5 | 78.1 |
| C | 71.8 | 72.2 | 72.2 |
| C | 76.4 | 80.3 | 79.7 |
| C | 75.6 | 78.7 | 78.7 |
| C | 62.8 | 63.4 | 62.6 |
| C | 167.6 | 178.9 | 179.1 |
| C | 119.1 | 121.4 | 118.8 |

| | | | |
|---|---|---|---|
| C | 146.6 | 156.9 | 158.0 |
| C | 135.8 | 138.7 | 138.4 |
| C | 129.2 | 132.3 | 131.8 |
| C | 130.1 | 135.1 | 134.5 |
| C | 131.6 | 139.3 | 138.7 |
| C | 130.1 | 135.5 | 135.0 |
| C | 129.2 | 140.2 | 140.2 |
| H | 1.96 | 2.28 | 2.23 |
| H | 1.11 | 1.30 | 1.13 |
| H | 1.41 | 1.81 | 1.49 |
| H | 1.63 | 1.51 | 1.70 |
| H | 2.22 | 2.20 | 2.12 |
| H | 1.56 | 1.63 | 1.61 |
| H | 2.49 | 2.52 | 2.59 |
| H | 1.62 | 1.64 | 1.75 |
| H | 2.24 | 1.98 | 2.10 |
| H | 2.19 | 1.12 | 2.15 |
| H | 1.29 | 2.01 | 1.24 |
| H | 1.02 | 1.29 | 1.36 |
| H | 1.02 | 1.29 | 1.36 |
| H | 1.02 | 1.29 | 1.36 |
| H | 1.16 | 0.95 | 0.94 |
| H | 1.16 | 0.95 | 0.94 |
| H | 1.16 | 0.95 | 0.94 |
| H | 1.31 | 1.16 | 1.35 |
| H | 1.31 | 1.16 | 1.35 |
| H | 1.31 | 1.16 | 1.35 |
| H | 1.04 | 0.96 | 0.93 |
| H | 1.04 | 0.96 | 0.93 |
| H | 1.04 | 0.96 | 0.93 |
| H | 4.74 | 4.93 | 4.97 |
| H | 3.33 | 3.24 | 3.30 |
| H | 3.42 | 3.71 | 3.76 |
| H | 3.62 | 3.47 | 3.56 |
| H | 4.84 | 4.73 | 4.69 |
| H | 3.68 | 3.78 | 3.78 |
| H | 3.84 | 3.89 | 3.82 |
| H | 6.56 | 6.89 | 6.99 |
| H | 7.73 | 8.41 | 8.26 |
| H | 7.6 | 8.33 | 8.36 |
| H | 7.41 | 7.80 | 7.83 |
| H | 7.41 | 7.93 | 7.84 |
| H | 7.41 | 7.85 | 7.79 |

| | | | |
|---|---|---|---|
| H | 7.60 | 8.01 | 7.83 |
| H | 3.25 | 3.60 | 3.79 |

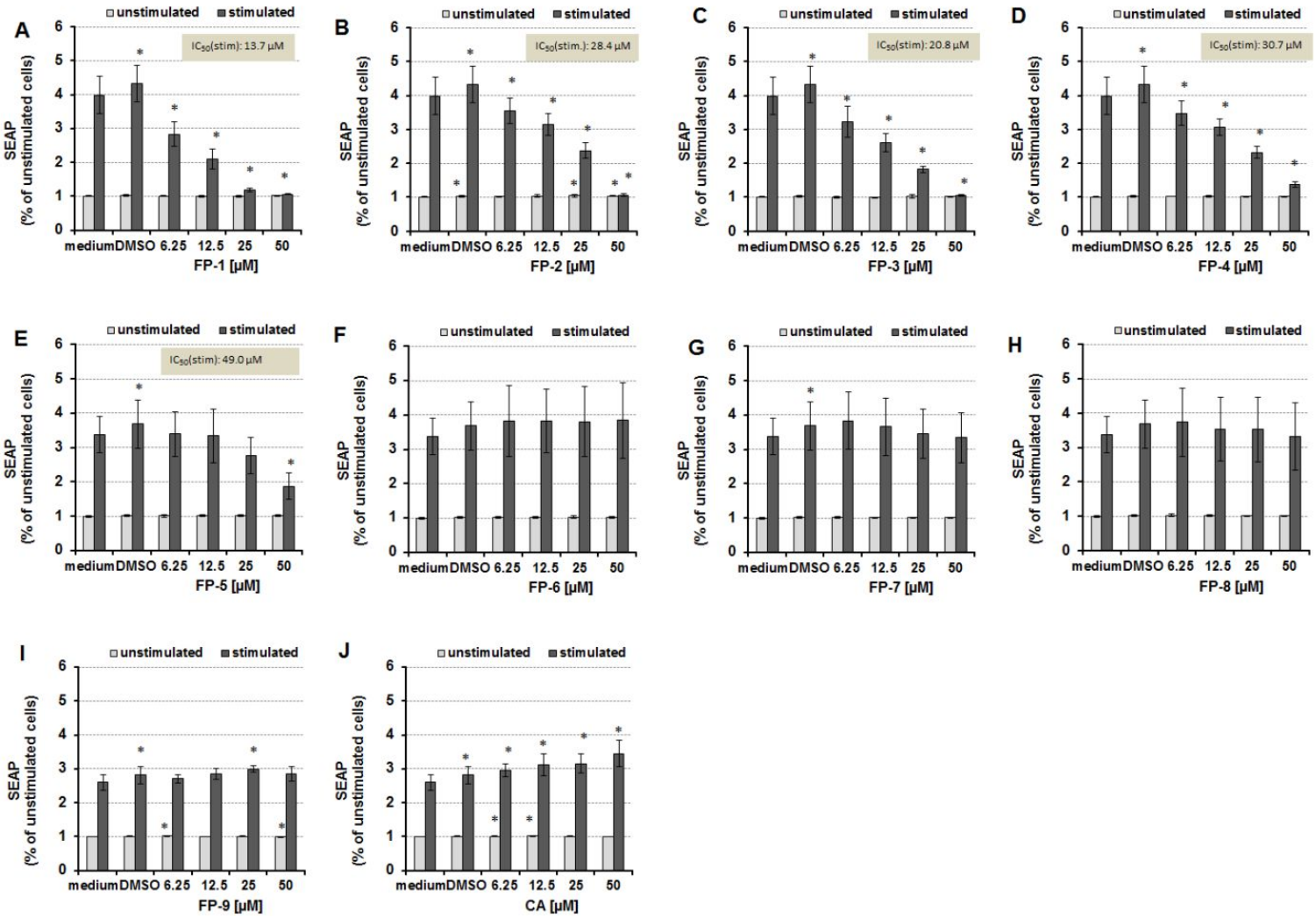



Figure S14.1. Effects of compounds **1**–**9** (FP-1 to FP-9) and cinnamic acid (CA) on NF-κB/AP-1 activation in unstimulated (light bars) and in lipopolysaccharide (LPS)-stimulated THP1-Blue-CD14 cells (dark bars). Activation NF-κB signaling was estimated by determining the activity of secreted embryonic alkaline phosphatase (SEAP) reporter. Cells were incubated with the respective compounds and stimulated or not with LPS for 24h. The results are shown in the mean values ± SEM of three independent experiments performed in duplicates (*$p<0.05$, compared to baseline = medium control with or without LPS). $IC_{50}$ = half maximal inhibitory concentration.

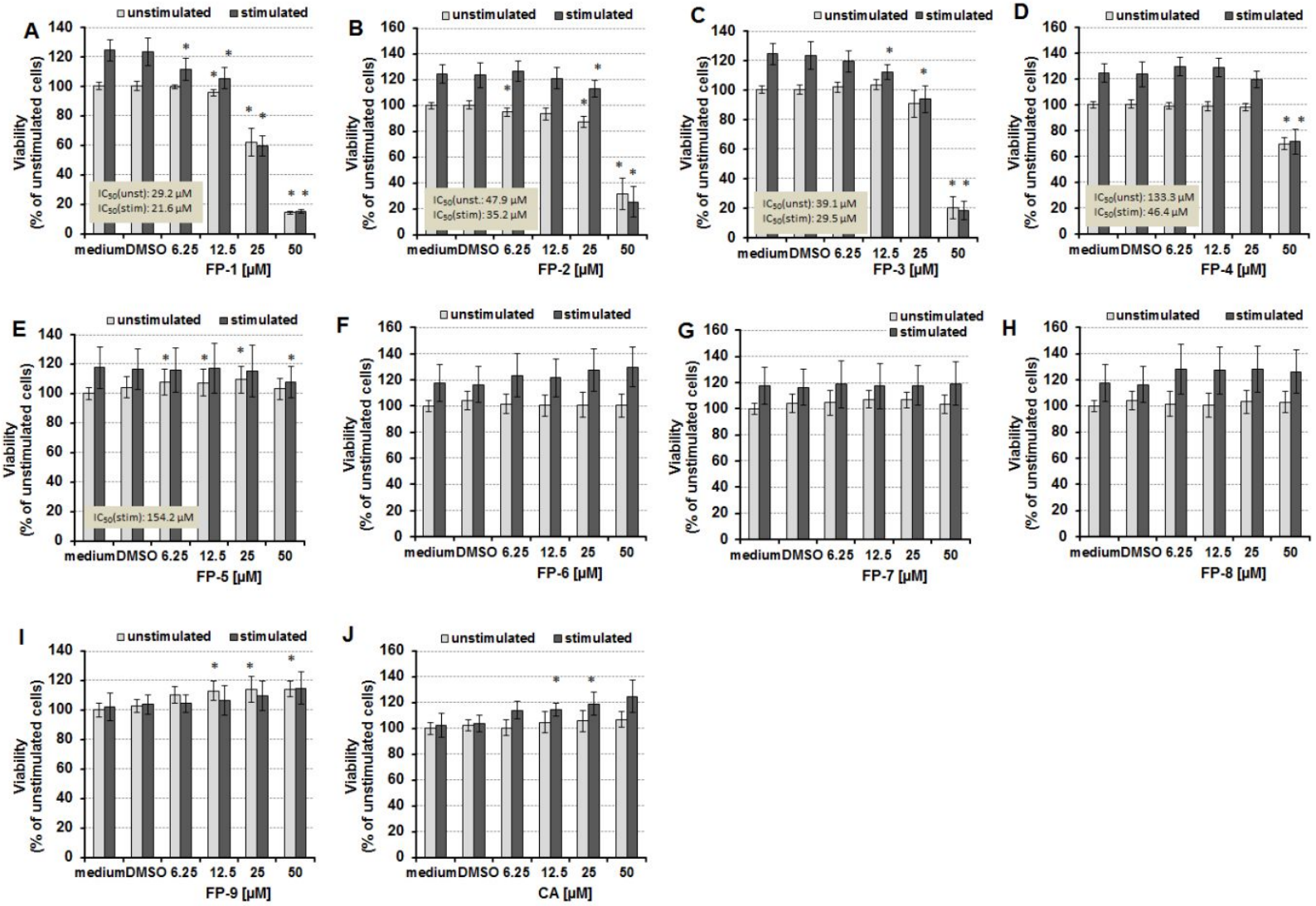



Figure S14.2. Effects of compounds **1**–**9** (FP-1 to FP-9) and cinnamic acid (CA) on cell viability, estimated by measuring resazurin reduction. THP1-Blue-CD14 cells were treated with or without additional stimulation with lipopolysaccharide (LPS) for 24h. Mean values ± SEM for three independent measurements in duplicates are shown (*$p<0.05$, compared to baseline = medium control with or without LPS). $IC_{50}$ = half maximal inhibitory concentration.