Supporting Information

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Triterpenes and Saponins from Leaves of *Camellia nitidissima*, and Cytotoxic Activities Against Bel-7402 and SMMC-7721 Human Liver Cancer Cells

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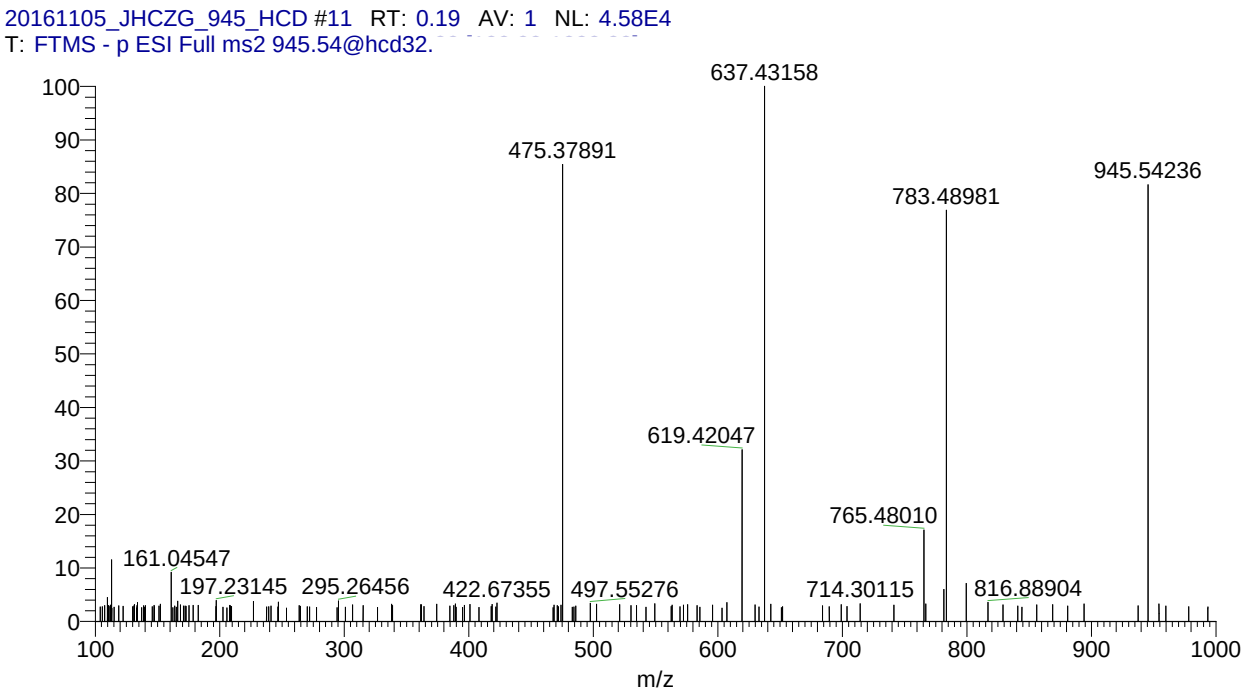

Figure S1: HR-ESI-MS spectrum of compound **12**

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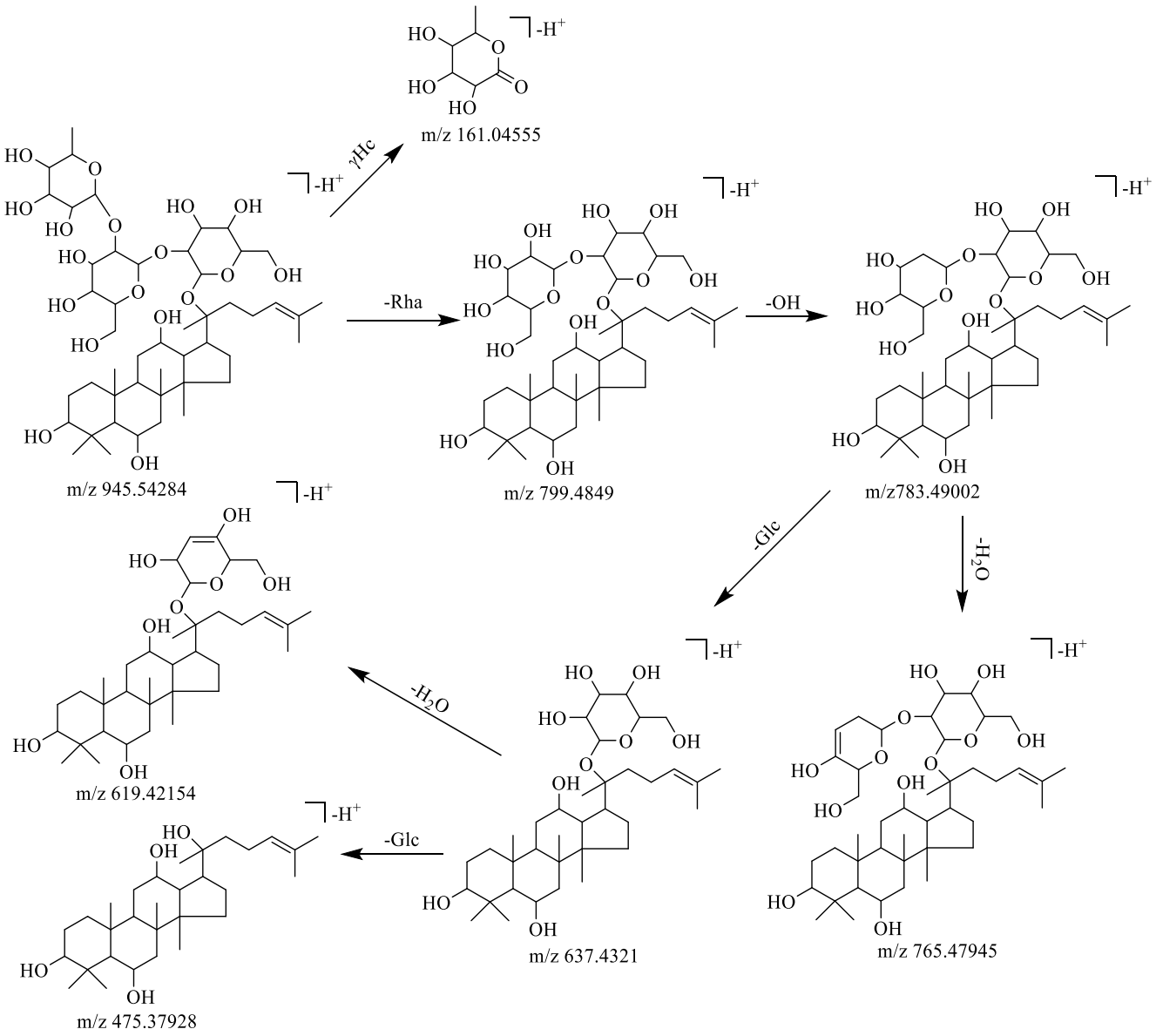

Figure S2:MS fragmentation pathway of compound **12**

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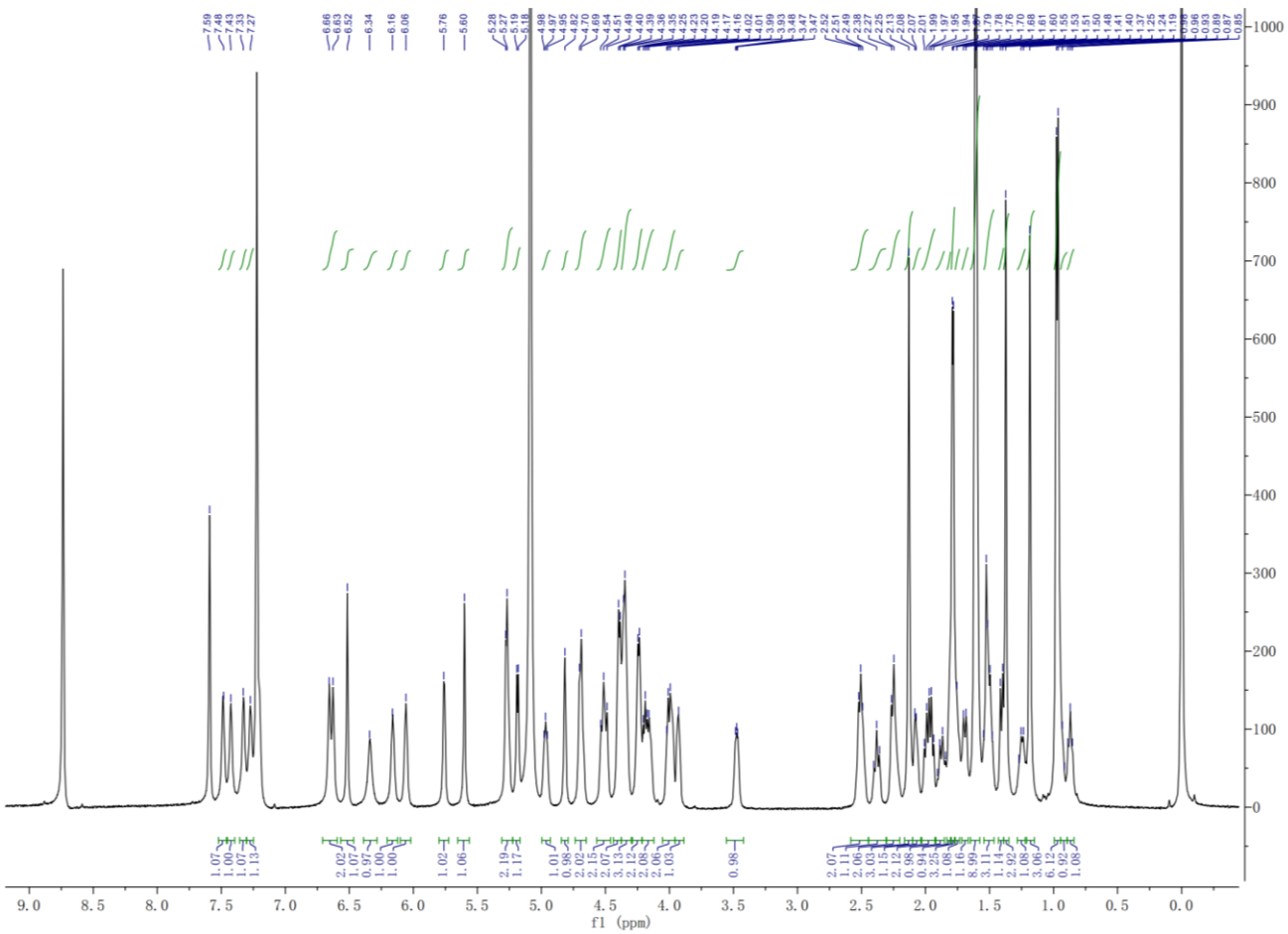

Figure S3: ^{1}H-NMR (600 MHz, Pyridine-d_5) spectrum of compound **12**

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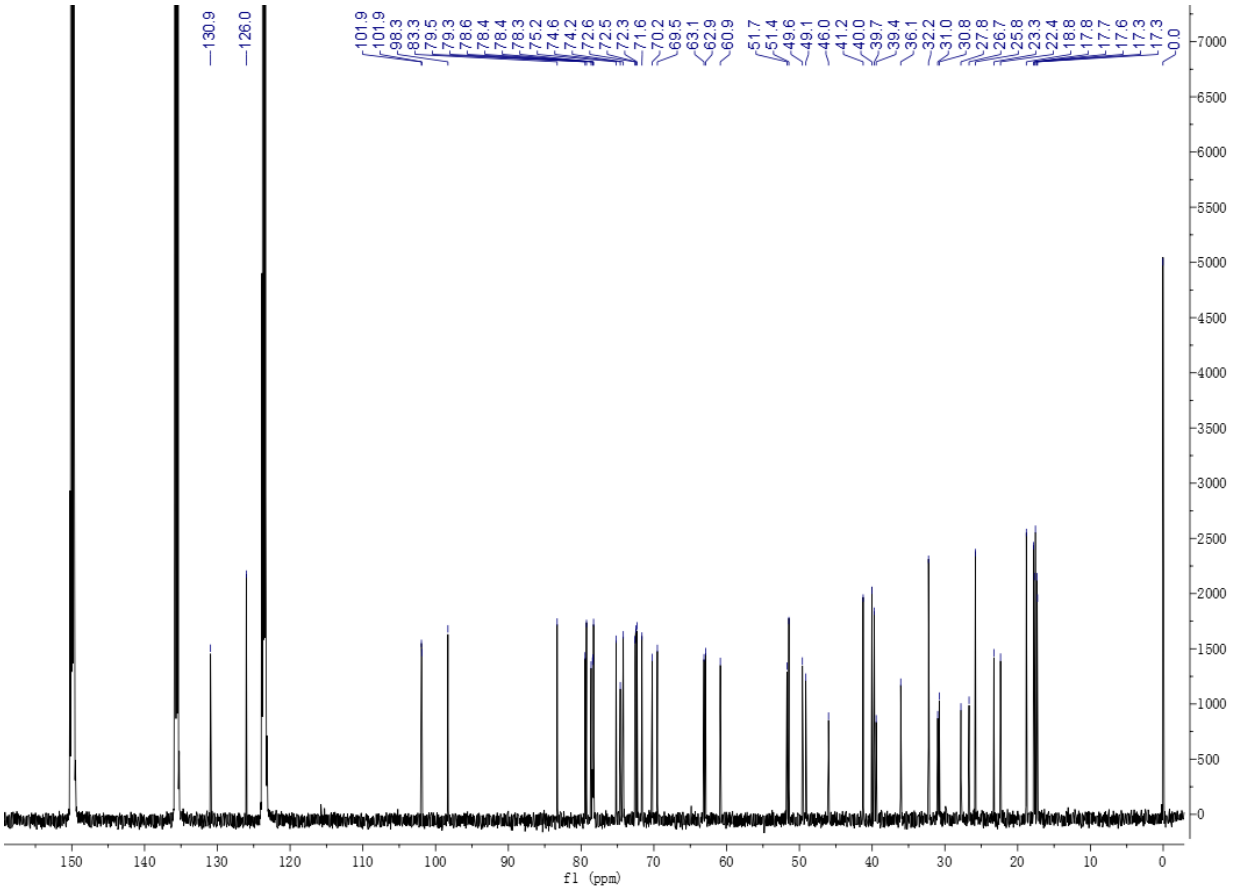

Figure S4: ^{13}C-NMR (150 MHz, Pyridine-d_5) spectrum of compound **12**

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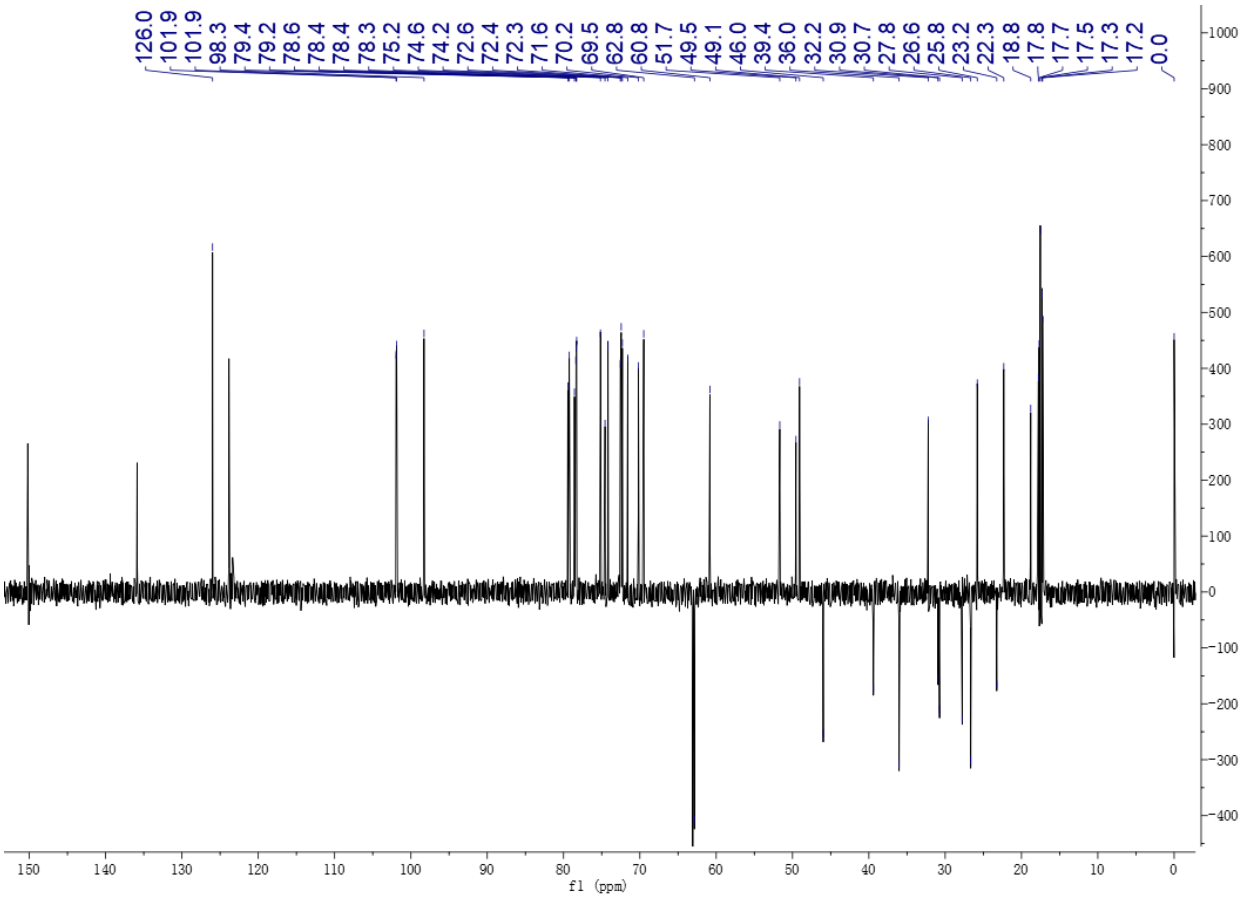

Figure S5: DEPT135 (150 MHz, Pyridine-d_5) spectrum of compound **12**

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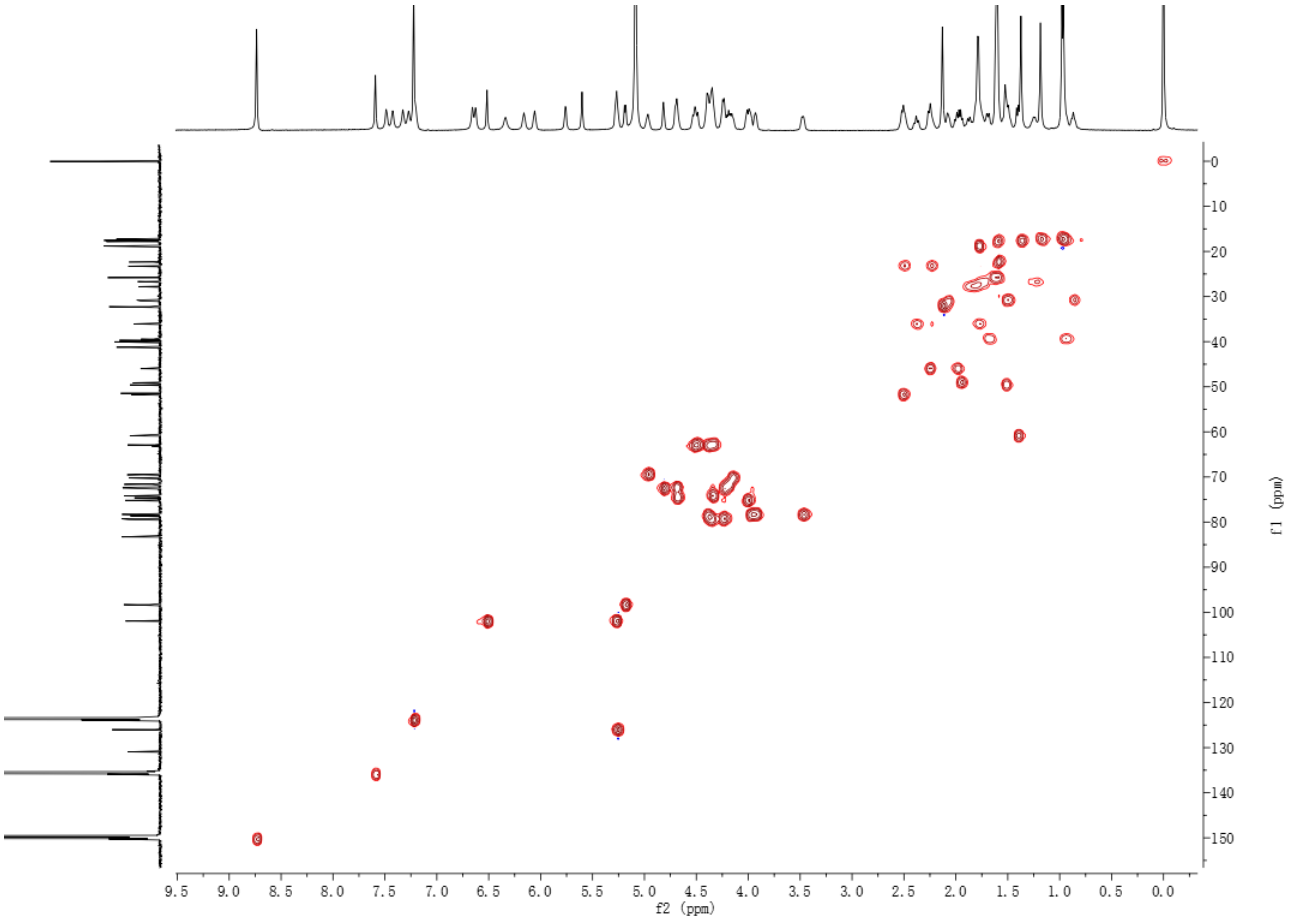

Figure S6: HSQC spectrum of compound **12**

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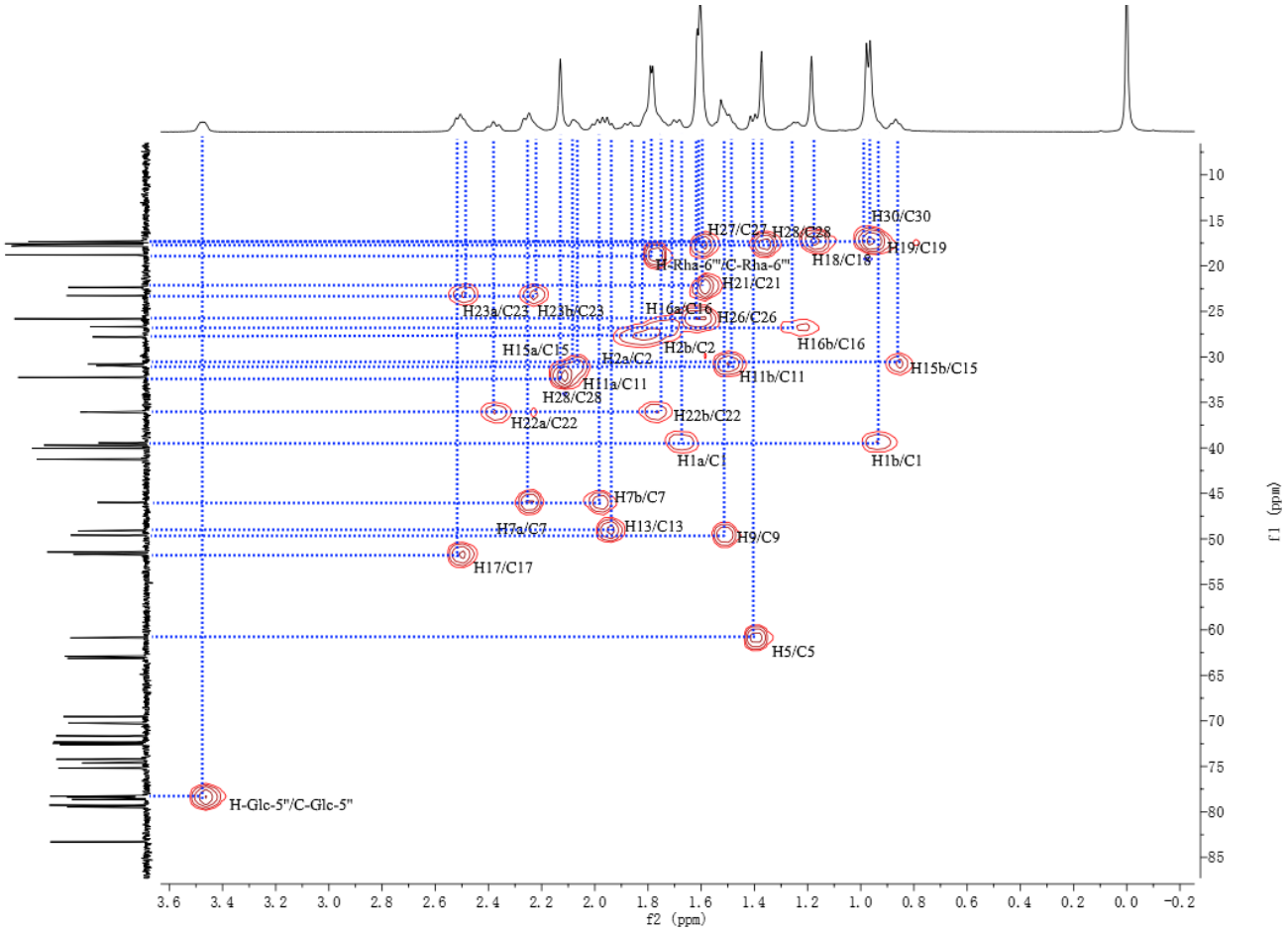

Figure S7: HSQC spectrum of compound **12** (From δ_C10 ppm to δ_C 85 ppm)

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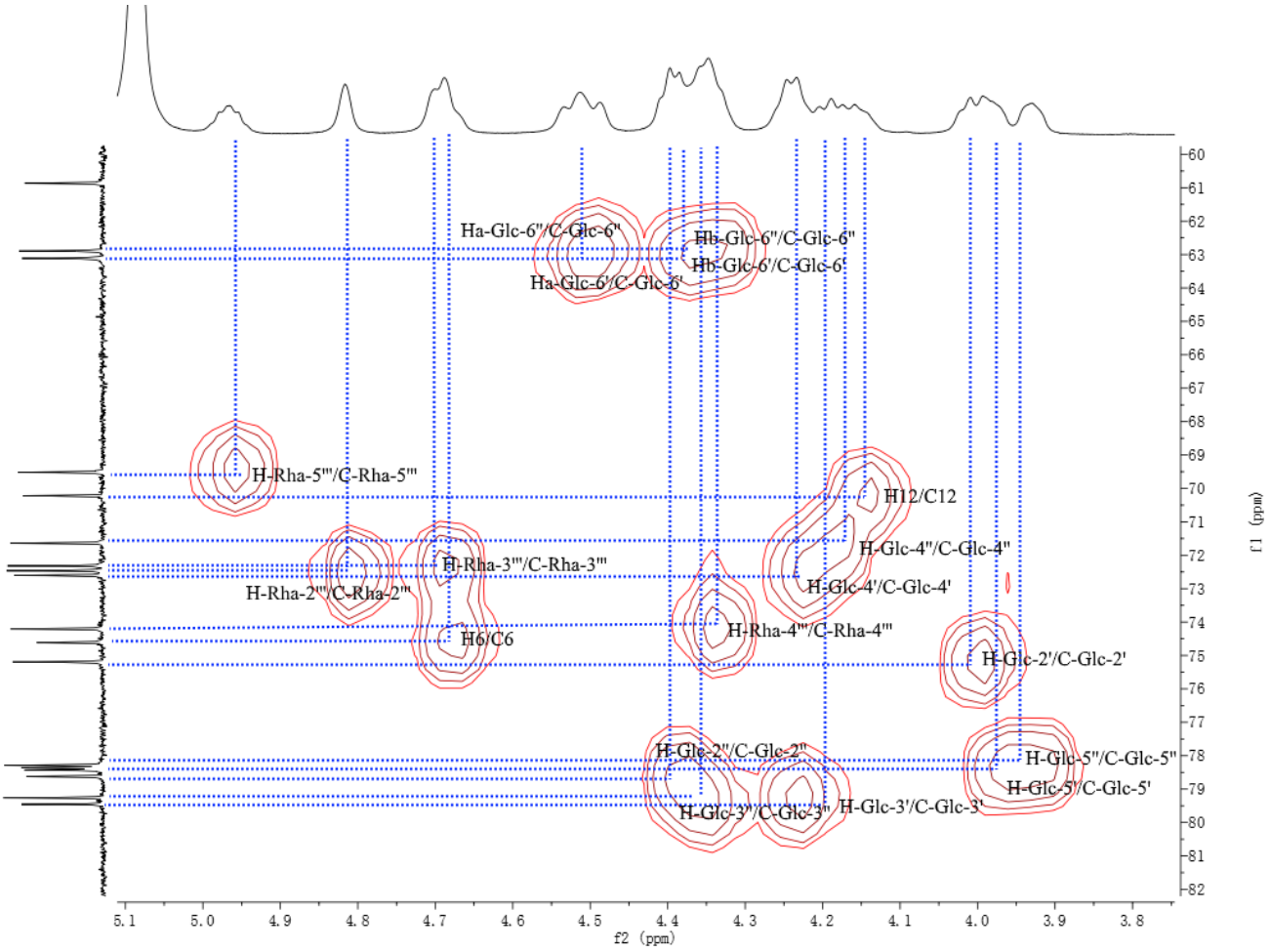

Figure S8: Enlarge HSQC spectrum of compound **12** (From δ_C 60 ppm to δ_C 82 ppm)

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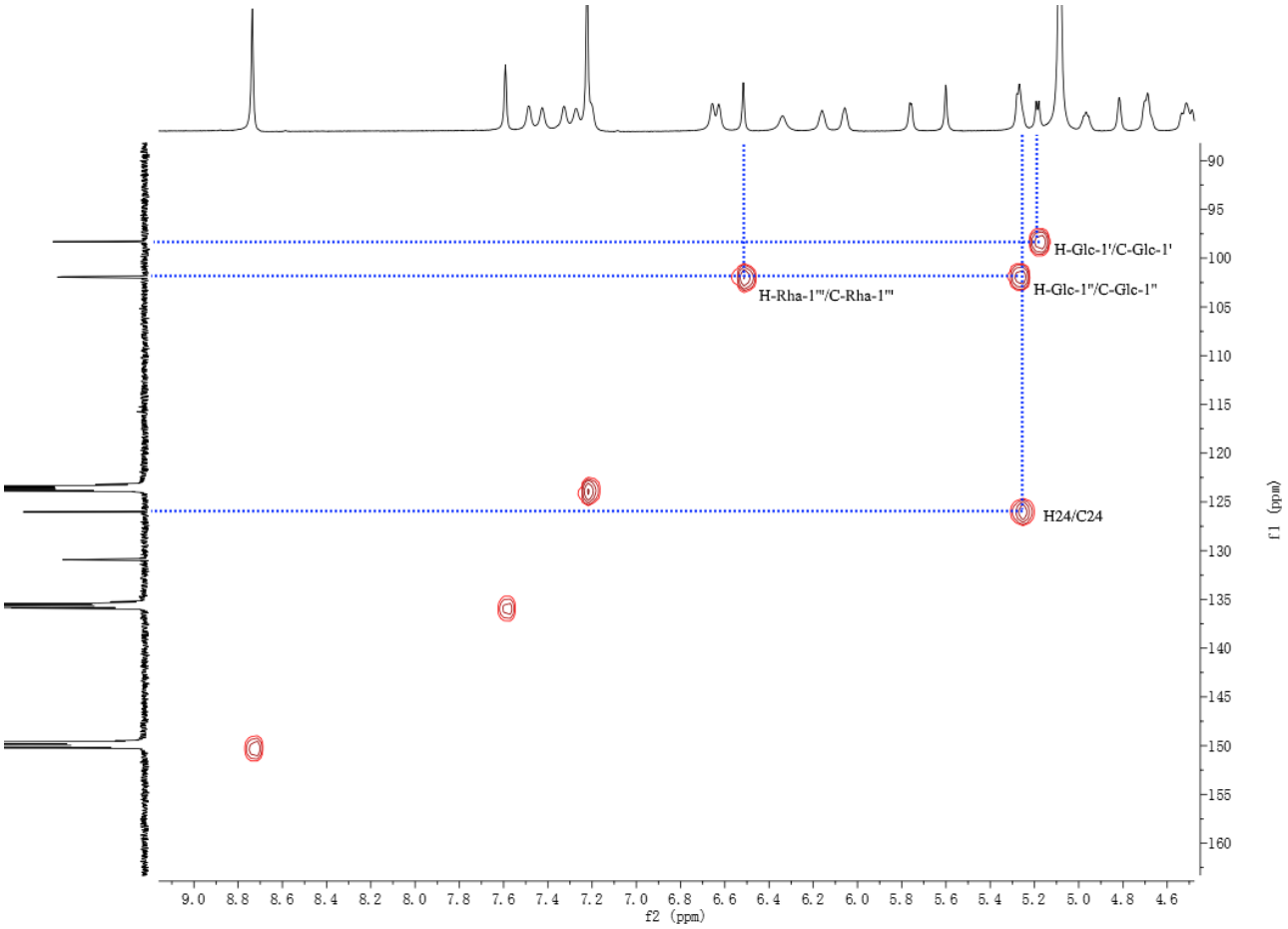

Figure S9: HSQC spectrum of compound **12** (From δ_C 90 ppm to δ_C 165 ppm)

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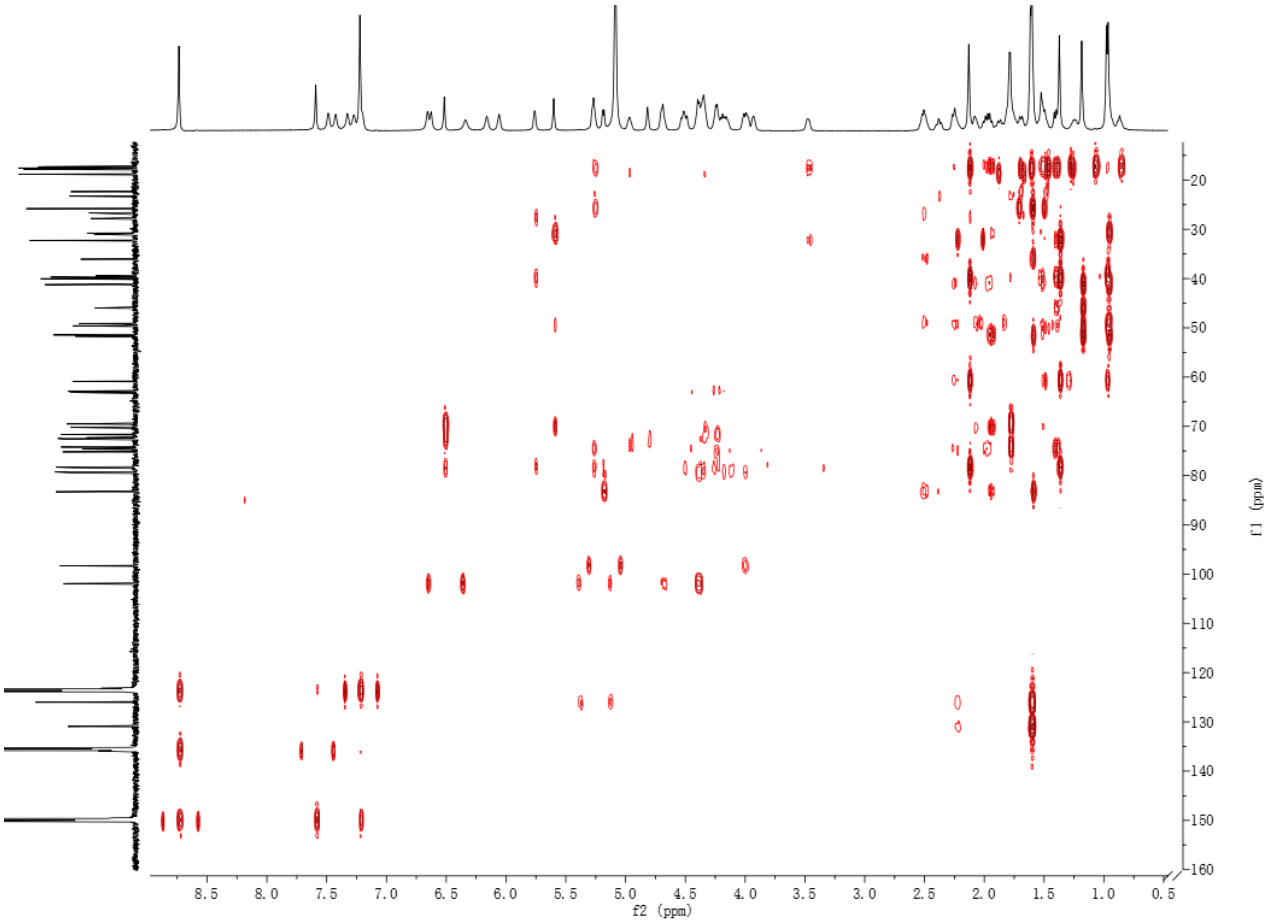

Figure S10: HMBC spectrum of compound **12**

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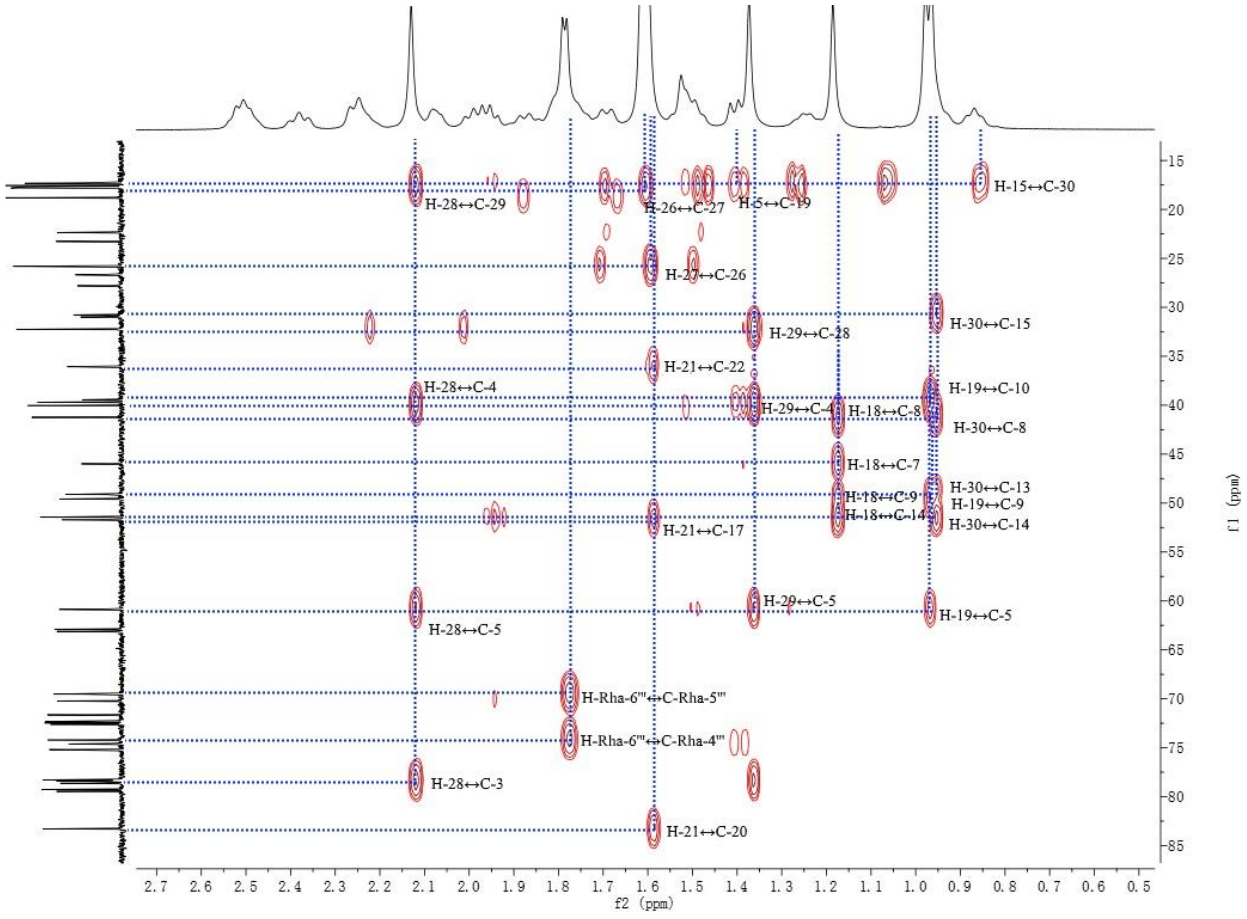

Figure S11: HMBC spectrum of compound **12** (From δ_H 0.5 ppm to δ_H 2.7 ppm)

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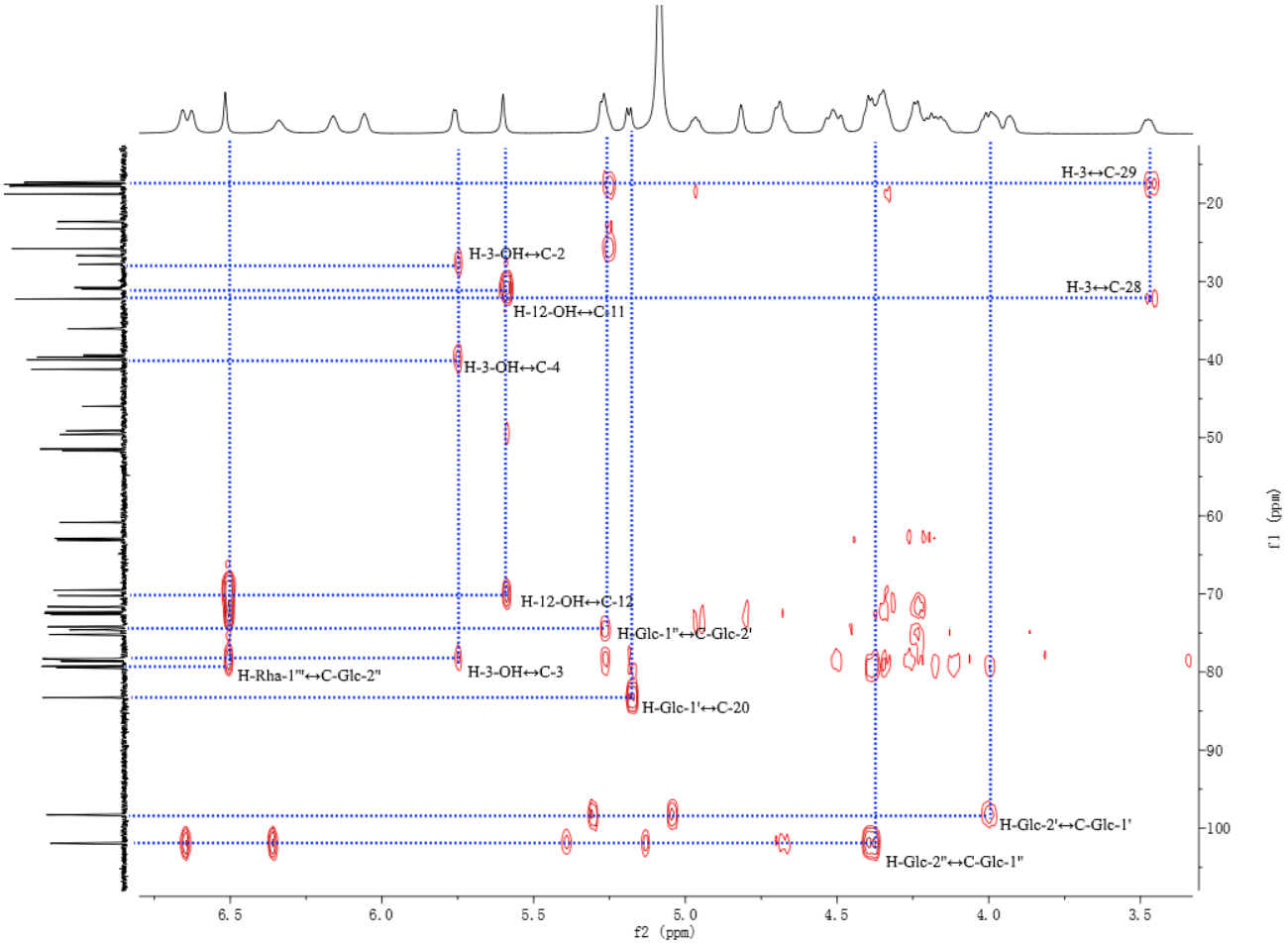

Figure S12: HMBC spectrum of compound **12** (From δ_H 3.5 ppm to δ_H 6.7 ppm)

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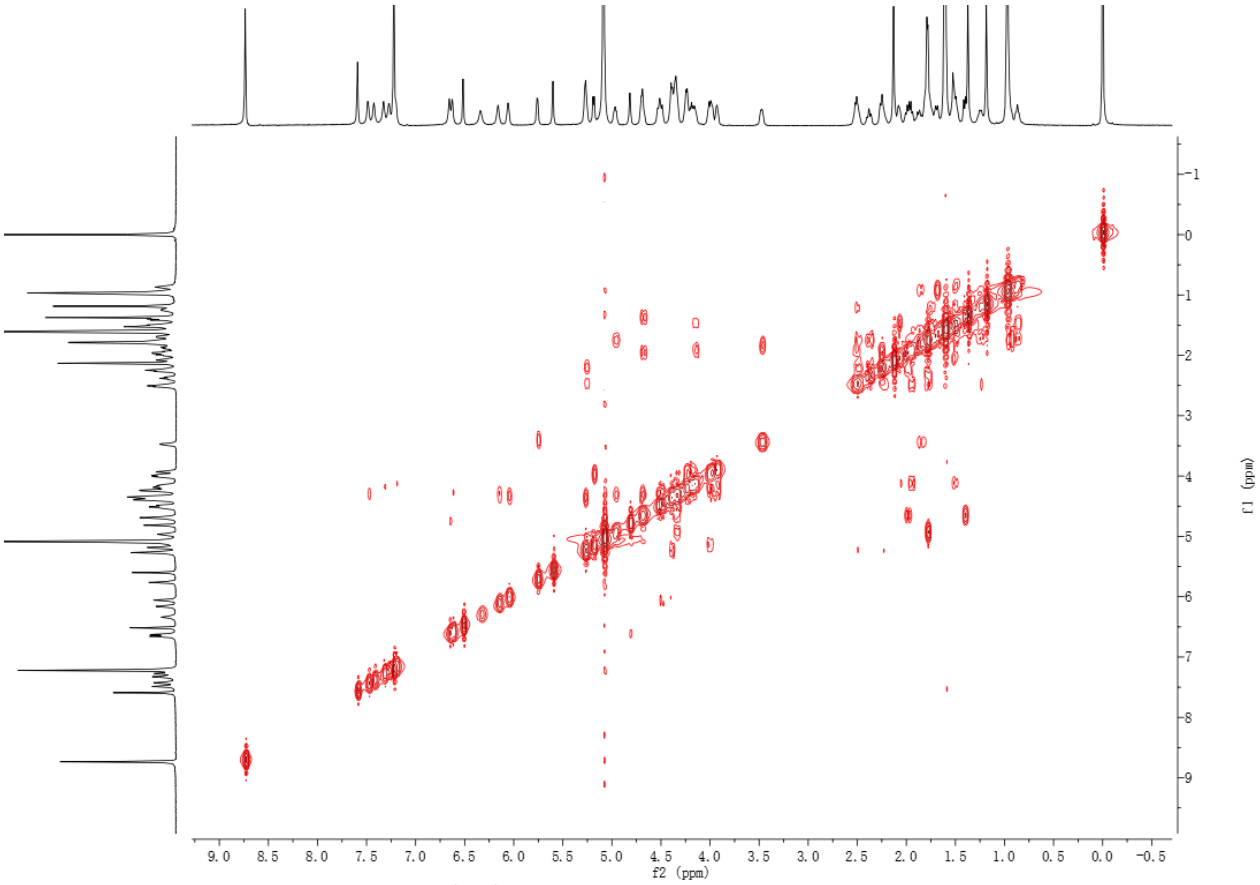

Figure S13: ^{1}H-^{1}H COSY spectrum of compound **12**

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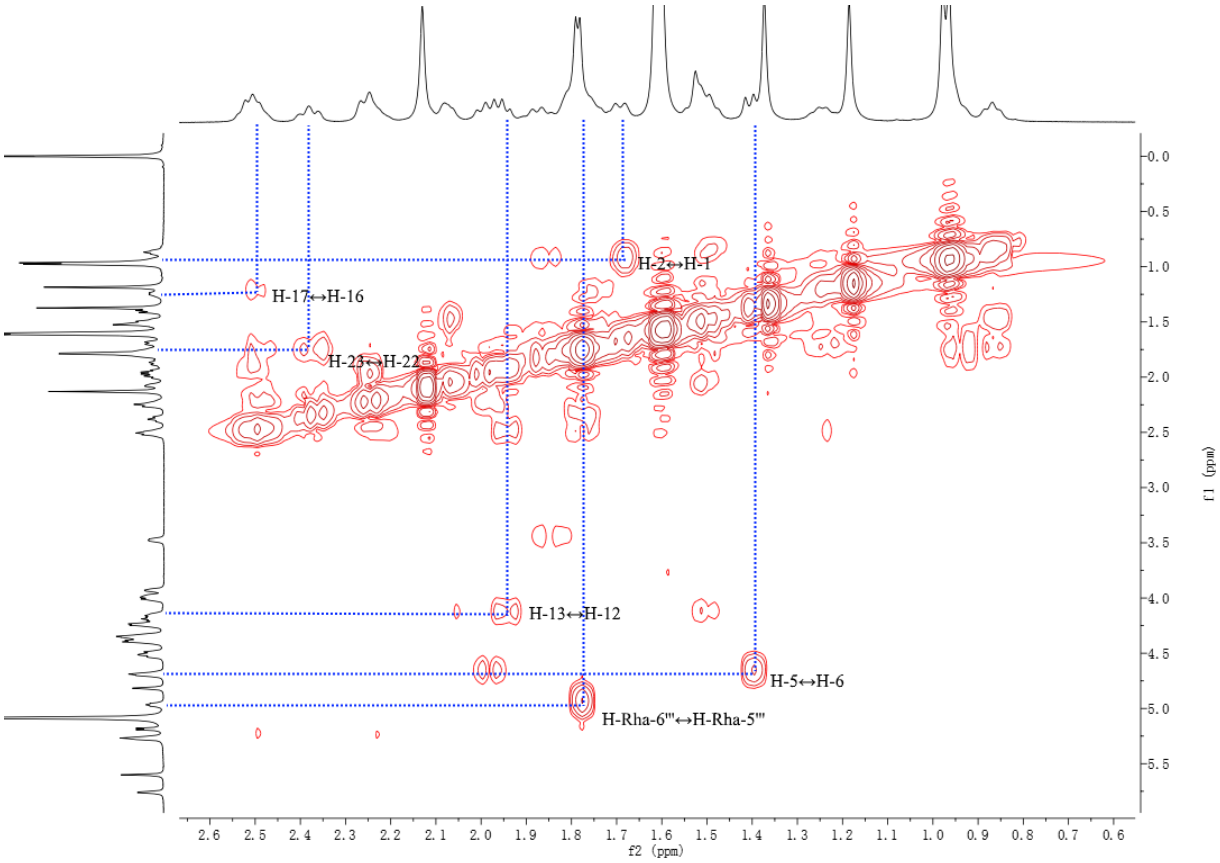

Figure S14: Enlarge ^{1}H-^{1}H COSY spectrum of compound **12** (From δ_H 0.6 ppm to δ_H 2.6 ppm)

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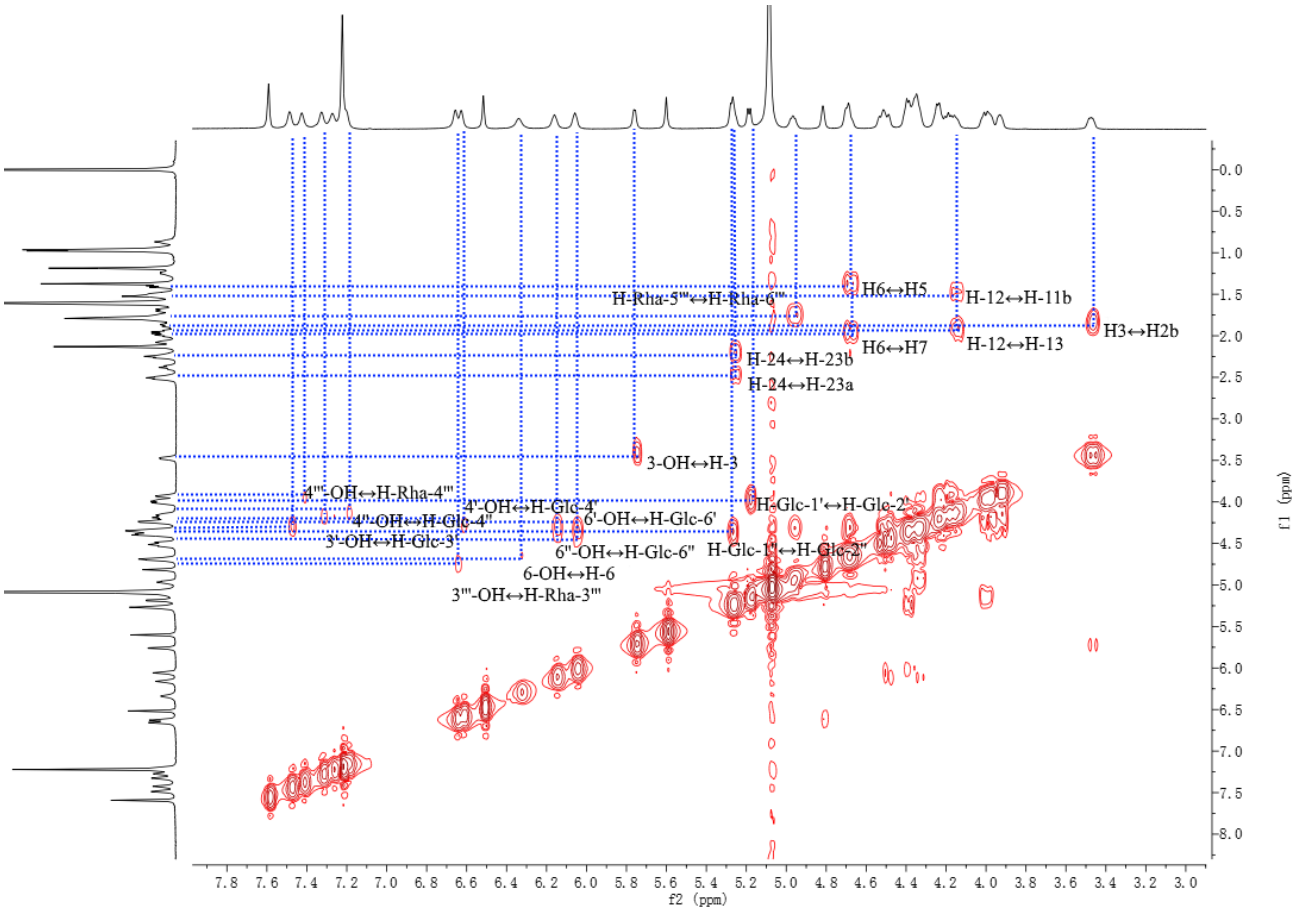

Figure S15: Enlarge ^{1}H-^{1}H COSY spectrum of compound **12** (From δ_H 3.0 ppm to δ_H 7.8 ppm)

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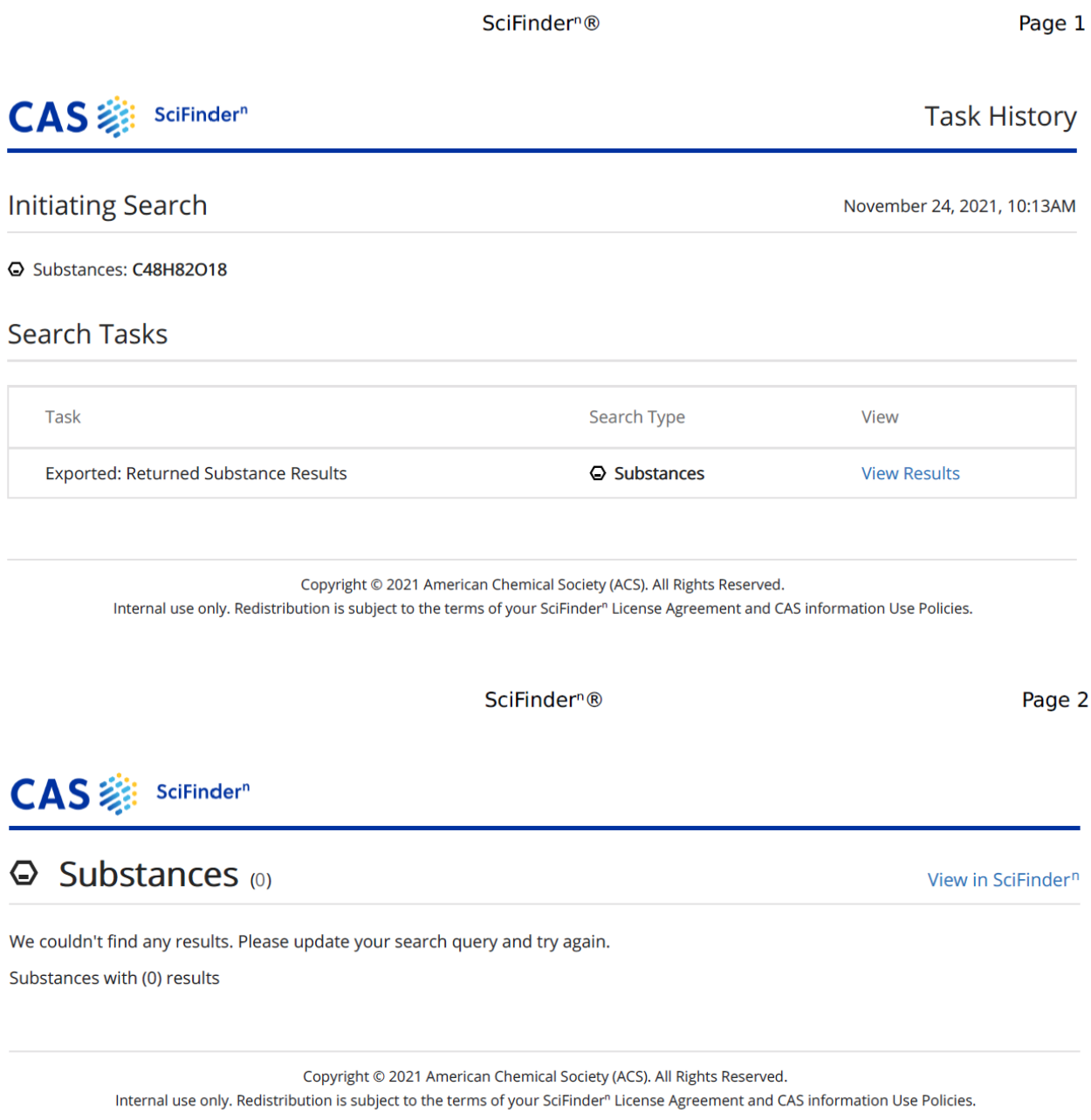

Figure S16: Scifinder search results of compound **12**

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S1: The ^{1}H and ^{13}C NMR data for compound 8-11

Compound **8**: white powder; ^{1}H NMR (Pyridine-d_5, 600 MHz) δ 5.24 (1H, t, J = 7.2 Hz, H-24), 5.18 (1H, d, J = 7.7 Hz, H-Glc-1''), 5.03 (1H, d, J = 7.8 Hz, H-Glc-1'), 2.07 (3H, s, H-28), 1.63(3H, s, H-21), 1.59 (6H, s, 2×-CH_3, H-26, H-27), 1.58 (3H, s, H-29), 1.51 (2H, m), 1.16 (3H, s, H-18), 1.03 (3H, s, H-19), 0.80 (3H, s, H-30); ^{13}C NMR (Pyridine-d_5, 150 MHz) δ 130.9 (C,C-25), 126.0 (CH,C-25), 106.0 (CHO_2, C-Glc-1'), 98.1 (CHO_2, C-Glc-1''), 83.3 (CO, C-20), 80.2 (CO, C-6), 79.7 (CHOH, C-Glc-3'), 79.4 (CHOH, C-Glc-3''), 78.7 (CHOH, C-3), 78.3 (COH, C-Glc-5''), 78.2 (COH, C-Glc-5'), 75.5 (CHOH, C-Glc-2'), 75.2 (CHOH, C-Glc-2''), 71.9 (CHOH, C-Glc-4''), 71.7 (CHOH, C-Glc-4'), 70.2 (CHOH, C-12), 63.1 (CH_2OH, C-Glc-6'), 62.9 (CH_2OH, C-Glc-6''), 61.4 (CH, C-5), 51.5 (CH, C-17), 51.4 (C, C-14), 50.0 (CH, C-9), 49.2 (CH, C-13), 45.1 (CH_2, C-7), 41.1 (C, C-8), 40.4 (C, C-4), 39.7 (C, C-10), 39.5 (CH_2, C-1), 36.2 (CH_2, C-22), 31.8 (CH_3, C-28), 31.0 (CH_2, C-11), 30.7 (CH_2, C-15), 28.0 (CH_2, C-2), 26.6 (CH_2, C-16), 25.8 (CH_3, C-26), 23.2 (CH_2, C-23), 22.3 (CH_3, C-21), 17.8 (CH_3, C-18), 17.6 (CH_3, C-19), 17.6 (CH_3, C-29), 17.2 (CH_3, C-27), 16.4 (CH_3, C-30); ESI-MS *m/z* 823.40 $[M+Na]^+$, 801.0 $[M+H]^+$.

Compound **9**: white powder; ^{1}H NMR (Pyridine-d_5, 600 MHz) δ 5.34 (1H, t, J = 12.7 Hz, H-24), 5.18 (1H, d, J = 7.7 Hz, H-Ara-1), 5.14 (1H, d, J = 7.8 Hz, H-Glc-1), 1.98 (3H, s, H-28), 1.66 (3H, s, H-26), 1.63 (6H, s, 2×-CH_3, H-27, H-21), 1.45 (3H, s, H-29), 1.09 (3H, s, H-18), 0.99 (3H, s, H-19), 0.95 (3H, s, H-29); ^{13}C NMR (Pyridine-d_5, 150 MHz) δ 131.1(C, C-25), 126.1(CH, C-24), 110.2 (CHO_2, C-Ara-1), 98.0 (CHO_2, C-glc-1), 86.0 (CHOH, C-Ara-4), 83.3 (CHOH, C-Ara-2), 83.3(CO, C-20), 79.2 (CHOH, C-glc-3), 79.2 (CHOH, C-Ara-3), 78.8 (CHOH, C-3), 76.5 (COH, C-glc-5), 75.0 (CHOH, C-glc-2), 72.1 (CHOH, C-glc-4), 70.2 (CHOH, C-12), 68.5 (CH_2OH, C-glc-6), 67.7 (CHOH, C-6), 62.5 (CH_2O, C-Ara-5), 61.7 (C, C-5), 51.6 (CHOH, C-17), 51.3 (C, C-14), 49.8 (CH, C-9), 49.0 (CH, C-13), 47.4 (CH_2, C-7), 41.1 (C, C-8), 40.3 (C, C-4), 39.5 (CH_2, C-1), 39.3 (C, C-10), 36.1 (CH_2, C-22), 31.9 (CH_3, C-28), 30.8 (CH_2, C-15), 30.7 (CH_2, C-11), 28.1 (CH_2, C-2), 26.6 (CH_2, C-16), 25.8 (CH_3, C-26), 23.1 (CH_2, C-23), 22.3 (CH_3, C-21), 17.8 (CH_3, C-27), 17.7 (CH_3, C-18), 17.6 (CH_3, C-30), 17.4 (CH_3, C-19), 16.5 (CH_3, C-29); ESIMS *m/z* 771.1$[M+H]^+$, 793.3$[M+Na]^+$.

Compound **10**: white powder; ^{1}H NMR (Pyridine-d_5, 600 MHz) δ 5.24 (1H, t, J = 6.9 Hz, H-24), 5.20 (1H, d, J = 7.8 Hz, H-Glc-1), 2.01 (3H, s, H-28), 1.64 (3H, s, H-26), 1.61 (3H, s, H-27), 1.60 (6H, s, 2×-CH_3, H-21, H-29), 1.11 (3H, s, H-18), 1.03 (3H, s, H-19), 0.99 (3H, s, H-30); ^{13}C NMR (Pyridine-d_5, 150 MHz) δ 130.9 (C, C-25), 126.0 (CH, C-24), 98.3 (CHO_2, C-Glc-1), 83.2 (CO, C-20), 79.4 (CHOH, C-Glc-3), 78.5 (CHOH, C-3), 78.3 (COH, C-Glc-5), 75.1 (CHOH, C-Glc-2), 71.7 (COH, C-Glc-4), 70.1 (CHOH, C-12), 67.7 (CHOH, C-6), 62.9 (CH_2OH, C-Glc-6), 61.8 (CH, C-5), 51.5 (CH, C-17), 51.3 (C, C-14), 49.9 (CH, C-9), 49.2 (CH, C-13), 47.5 (CH_2, C-7), 41.2 (C, C-8), 40.3 (C, C-4), 39.2 (CH_2, C-1), 39.4 (C, C-10), 36.1 (CH_2, C-22), 32.0 (CH_3,C-28), 30.9 (CH_2,C-11), 30.8 (CH_2, C-15), 28.1 (CH_2, C-2), 26.6 (CH_2, C-16), 25.7 (CH_3, C-26), 23.2 (CH_2, C-23), 22.3 (CH_3, C-21), 17.7 (CH_3, C-27), 17.6 (CH_3, C-18), 17.5 (CH_3, C-19), 17.4 (CH_3, C-30), 16.5 (CH_3, C-29); ESI-MS *m/z* 661.3$[M+Na]^+$, 638.9$[M+H]^+$.

Compound **11**: white powder; ^{1}H NMR (Pyridine-d_5, 600 MHz) δ 5.39 (1H, d, J = 7.6 Hz, H-Glc-1''), 5.25(1H, m, H-24), 5.21 (1H, d, J = 7.7 Hz, H-Glc-1'''), 4.93 (1H, d, J = 7.6 Hz, H-Glc-1'), 1.63 (3H, s, H-21), 1.60 (6H, s, 2×-CH_3, H-26, H-27), 1.29 (3H, s, H-28), 1.12 (3H, s, H-29), 0.96 (3H, s, H-18), 0.95 (3H, s, H-30), 0.81 (3H, s, H-19); ^{13}C NMR (Pyridine-d_5, 150 MHz) δ 130.9 (C, C-25), 125.9 (CH, C-24), 106.0 (CHO_2, C-Glc-1''), 105.1 (CHO_2, C-Glc-1'), 98.3 (CHO_2, C-Glc-1'''), 88.9 (CHO, C-3), 83.4 (C, C-20), 83.3 (CHO, C-Glc-2'), 79.8 (CHOH, C-Glc-3''), 78.3 (CHOH, C-Glc-3'), 78.3 (COH, C-Glc-5'), 78.2 (COH, C-Glc-5''), 78.1 (CHOH, C-Glc-3'''), 77.9 (COH, C-Glc-5'''), 77.1 (CHOH, C-Glc-2''), 75.1 (CHOH, C-Glc-2'''), 71.6 (CHOH, C-Glc-4'), 71.6 (CHOH, C-Glc-4''), 71.5 (CHOH, C-Glc-4'''),70.2 (CHOH, C-12), 62.9 (CH_2OH, C-Glc-6''), 62.8 (CH_2OH, C-Glc-6'), 62.7 (CH_2OH, C-Glc-6'''), 56.4 (CH, C-5), 51.6 (CH, C-17), 51.4 (C, C-14), 50.2 (CH, C-9), 49.4 (CH, C-13), 40.0 (C, C-8), 39.7 (C, C-4), 39.2 (CH_2,C-1), 36.9 (C, C-10), 36.1 (CH_2, C-22), 35.1 (CH_2, C-7), 30.9 (CH_2, C-15), 30.7 (CH_2, C-11), 28.1 (CH_3, C-28), 26.7 (CH_2, C-16), 26.6 (CH_2, C-2), 25.7 (CH_3,

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C-26), 23.2 (CH_2, C-23), 22.4 (CH_3, C-21), 18.4 (CH_2, C-6), 17.7 (CH_3, C-27), 17.3 (CH_3, C-30), 16.6 (CH_3, C-29), 16.2 (CH_3, C-18), 15.9 (CH_3, C-19); ESI-MS *m/z* 939.3$[M+Na]^+$, 917.5$[M+H]^+$.

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