A strategy based on isocratic and linear-gradient High-Speed Counter-Current Chromatography for comprehensive separation of platycosides from Platycodi Radix

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Supplementary material

1. NMR data for compounds 1-11 were given as follows:

Platycoside E (**1**): ^{1}H-NMR δ: 5.63 (1H, brs, H-12), 1.71 (3H, s, Me-25), 1.64 (3H, brs, Me-Rha), 1.07 (3H, s, Me-26), 1.40(3H, s, Me-27), 0.96(3H, s, Me-29), 1.04(3H, s, Me-30); ^{13}C-NMR δ: 45.1(C-1), 68.4(C-2), 88.7(C-3), 48.0(C-4), 47.3(C-5), 19.5(C-6), 33.5(C-7), 40.3(C-8), 45.1(C-9), 37.9(C-10), 24.1(C-11), 123.1(C-12), 144.1(C-13), 42.5(C-14), 36.0(C-15), 73.7(C-16), 49.8(C-17), 41.3 (C-18), 47.0 (C-19), 30.8(C-20), 35.8 (C-21), 32.1 (C-22), 63.8(C-23), 66.7 (C-24), 19.2(C-25), 17.5(C-26), 27.3(C-27), 175.7(C-28), 33.2(C-29), 24.6(C-30). Sugars linked at C-3:Glucose (inner) 105.9 (C-1), 74.6(C-2), 78.1(C-3), 72.0(C-4), 76.5(C-5), 70.8 (C-6); Glucose (center) 104.9 (C-1), 75.6(C-2), 78.1(C-3), 71.1(C-4), 77.5(C-5), 70.2 (C-6); Glucose (terminal) 105.7 (C-1), 75.2(C-2), 78.6(C-3), 71.0(C-4), 77.5(C-5), 62.6 (C-6); Sugars linked at C-28: Arabinose 93.4 (C-1), 74.6(C-2), 71.6(C-3), 66.5(C-4),

63.5(C-5); Rhamnose 100.9 (C-1), 71.2(C-2), 72.6(C-3), 83.6(C-4), 68.5(C-5), 18.1 (C-6); Xylose 106.4 (C-1), 76.6(C-2), 84.4(C-3), 69.5(C-4), 66.9(C-5); Apiose 110.8 (C-1), 77.6(C-2), 80.2(C-3), 74.6(C-4), 65.1(C-5).

Deapio-platycodin D_3 (**2**) : ^{1}H-NMR δ: 5.64 (1H, brs, H-12), 1.71 (3H, brs, Me-Rha), 1.67 (3H, s, Me-25), 1.10 (6H, s, Me-26, 30), 1.34(3H, s, Me-27), 0.97(3H, s, Me-29); ^{13}C-NMR δ: 45.5(C-1), 68.9(C-2), 88.8(C-3), 48.0(C-4), 47.5(C-5), 19.4(C-6), 33.5(C-7), 40.3(C-8), 45.0(C-9), 37.9(C-10), 24.0(C-11), 123.0(C-12), 144.1(C-13), 42.3(C-14), 36.0(C-15), 73.8(C-16), 49.6(C-17), 41.4 (C-18), 47.0 (C-19), 30.7(C-20), 35.9 (C-21), 32.1 (C-22), 63.3(C-23), 66.1 (C-24), 19.1(C-25), 17.5(C-26), 26.8(C-27), 175.8(C-28), 33.2(C-29), 24.6(C-30). Sugars linked at C-3:Glucose (inner) 106.4 (C-1), 74.7(C-2), 78.4(C-3), 71.3(C-4), 76.4(C-5), 70.4 (C-6); Glucose (terminal) 106.0 (C-1), 75.2(C-2), 77.8(C-3), 70.3(C-4), 77.7(C-5), 62.5 (C-6); Sugars linked at C-28: Arabinose 93.3 (C-1), 75.0(C-2), 71.8(C-3), 66.1(C-4), 63.1(C-5); Rhamnose 100.9 (C-1), 71.9(C-2), 72.6(C-3), 78.6(C-4), 68.4(C-5), 18.2 (C-6); Xylose 106.5 (C-1), 75.3(C-2), 84.0(C-3), 70.2(C-4), 66.9(C-5).

Platycodin D_3 (**3**): ^{1}H-NMR δ: 5.64 (1H, brs, H-12), 1.71 (6H, s, Me-25, Me-Rha), 1.10 (6H, s, Me-26, 30), 1.40(3H, s, Me-27), 0.97(3H, s, Me-29); ^{13}C-NMR δ: 45.1(C-1), 68.5(C-2), 88.5(C-3), 48.0(C-4), 47.3(C-5), 19.3(C-6), 33.2(C-7), 40.3(C-8), 44.5(C-9), 37.8(C-10), 23.7(C-11), 123.1(C-12), 144.1(C-13), 42.3(C-14), 36.0(C-15), 73.7(C-16), 49.5(C-17), 41.4 (C-18), 47.0 (C-19), 30.8(C-20), 35.7 (C-21), 32.0 (C-22), 63.3(C-23), 66.7 (C-24), 19.0(C-25), 17.5(C-26), 27.1(C-27), 175.7(C-28), 33.1(C-29), 24.6(C-30). Sugars linked at C-3:Glucose (inner) 105.8 (C-1), 74.6(C-2), 78.5(C-3), 71.6(C-4), 76.4(C-5), 70.5 (C-6); Glucose (terminal) 104.8 (C-1), 74.9(C-2), 78.3(C-3), 69.1(C-4), 77.5(C-5), 62.4 (C-6); Sugars linked at C-28: Arabinose 93.4 (C-1), 75.1(C-2), 71.2(C-3), 66.3(C-4), 63.0(C-5); Rhamnose 100.9 (C-1), 71.8(C-2), 72.6(C-3), 83.7(C-4), 68.5(C-5), 18.1 (C-6); Xylose 106.5 (C-1), 75.3(C-2), 84.5(C-3), 70.4(C-4), 67.1(C-5); Apiose 111.2 (C-1), 77.6(C-2), 80.2(C-3), 75.1(C-4), 65.3(C-5).

Deapio-platycodin D_2 (**4**) ^{1}H-NMR δ: 5.64 (1H, brs, H-12), 1.71 (6H, brs, Me-Rha, Me-25), 1.11 (6H, s, Me-26, 30), 1.47(3H, s, Me-27), 0.97(3H, s, Me-29); ^{13}C-NMR δ:

46.8(C-1), 69.1(C-2), 86.3(C-3), 47.8(C-4), 47.8(C-5), 19.1(C-6), 33.4(C-7), 40.2(C-8), 45.3(C-9), 37.3(C-10), 24.5(C-11), 122.8(C-12), 144.1(C-13), 42.1(C-14), 35.9(C-15), 73.8(C-16), 49.4(C-17), 41.2 (C-18), 46.8 (C-19), 30.7(C-20), 35.8 (C-21), 31.9 (C-22), 63.4(C-23), 66.0 (C-24), 18.2(C-25), 17.4(C-26), 26.9(C-27), 175.7(C-28), 33.0(C-29), 24.6(C-30). Sugars linked at C-3:Glucose (inner) 106.6 (C-1), 75.1(C-2), 88.3(C-3), 69.5(C-4), 78.3(C-5), 62.3 (C-6); Glucose (terminal) 106.0 (C-1), 75.5(C-2), 78.3(C-3), 72.4 (C-4), 78.5(C-5), 62.3 (C-6); Sugars linked at C-28: Arabinose 93.3 (C-1), 76.0(C-2), 70.0(C-3), 64.6(C-4), 63.0(C-5); Rhamnose 100.9 (C-1), 71.4(C-2), 72.4(C-3), 83.3(C-4), 68.4(C-5), 18.1 (C-6); Xylose 106.6 (C-1), 83.5(C-2), 84.0(C-3), 70.8(C-4), 67.2(C-5).

Platycodin D_2 (**5**) ^{1}H-NMR δ: 5.64 (1H, brs, H-12), 1.71 (3H, s, Me-25), 1.68 (3H, s, Me-Rha), 1.10 (6H, s, Me-26, 30), 1.44(3H, s, Me-27), 0.97(3H, s, Me-29); ^{13}C-NMR δ: 46.4(C-1), 69.2(C-2), 88.4(C-3), 48.0(C-4), 47.5(C-5), 19.1(C-6), 33.4(C-7), 40.2(C-8), 44.0(C-9), 37.2(C-10), 24.7(C-11), 123.1(C-12), 144.1(C-13), 42.3(C-14), 36.0(C-15), 73.8(C-16), 49.5(C-17), 41.5 (C-18), 47.0 (C-19), 30.7(C-20), 35.8 (C-21), 32.0 (C-22), 63.4(C-23), 66.1 (C-24), 18.1(C-25), 17.4(C-26), 27.0(C-27), 175.8(C-28), 33.0(C-29), 24.5(C-30). Sugars linked at C-3:Glucose (inner) 106.7 (C-1), 74.0(C-2), 88.7(C-3), 69.8(C-4), 78.3(C-5), 62.4 (C-6); Glucose (terminal) 105.7 (C-1), 75.6(C-2), 78.3(C-3), 71.9(C-4), 78.9(C-5), 62.4 (C-6); Sugars linked at C-28: Arabinose 93.4 (C-1), 75.6(C-2), 70.6(C-3), 65.6(C-4), 63.6(C-5); Rhamnose 101.0 (C-1), 71.6(C-2), 72.5(C-3), 83.6(C-4), 68.3(C-5), 18.1 (C-6); Xylose 106.5 (C-1), 75.0(C-2), 84.6(C-3), 69.4(C-4), 67.0(C-5); Apiose 111.2 (C-1), 77.5(C-2), 80.2(C-3), 75.0(C-4), 64.6(C-5).

Platycodin D (**6**) ^{1}H-NMR δ: 5.63 (1H, brs, H-12), 1.70 (3H, s, Me-25), 1.68 (3H, d, J = 4.4 Hz, Me-Rha), 1.09 (6H, s, Me-26, 30), 1.41(3H, s, Me-27), 0.96(3H, s, Me-29); ^{13}C-NMR δ: 46.0(C-1), 69.2(C-2), 86.4(C-3), 47.8(C-4), 47.7(C-5), 19.1(C-6), 33.3(C-7), 40.1(C-8), 44.8(C-9), 37.3(C-10), 24.0(C-11), 122.8(C-12), 144.1(C-13), 42.3(C-14), 35.9(C-15), 73.6(C-16), 49.4(C-17), 41.2 (C-18), 46.8 (C-19), 30.6(C-20), 35.8 (C-21), 31.8 (C-22), 63.3(C-23), 66.1 (C-24), 18.1(C-25), 17.4(C-26), 26.9(C-27), 175.8(C-28), 33.0(C-29), 24.5(C-30). Sugars linked at C-3:Glucose 106.4 (C-1),

75.1(C-2), 78.3(C-3), 71.6(C-4), 78.3(C-5), 62.2 (C-6); Sugars linked at C-28: Arabinose 93.3 (C-1), 75.1(C-2), 70.2(C-3), 65.0(C-4), 63.3(C-5); Rhamnose 100.9 (C-1), 71.3(C-2), 72.4(C-3), 83.5(C-4), 68.3(C-5), 18.1 (C-6); Xylose 106.4 (C-1), 74.9(C-2), 84.6(C-3), 69.2(C-4), 66.6(C-5); Apiose 110.9 (C-1), 77.5(C-2), 80.2(C-3), 74.9(C-4), 65.0(C-5).

Polygalacin D_2 (**7**) ^{1}H-NMR δ: 5.60 (1H, brs, H-12), 1.54 (3H, s, Me-24), 1.31 (3H, s, Me-25), 1.11 (3H, s, Me-26), 1.68 (3H, d, J = 6.0 Hz, Me-Rha), 1.73(3H, s, Me-27), 0.96(3H, s, Me-29), 1.12 (3H, s, Me-30); ^{13}C-NMR δ: 44.0(C-1), 69.5(C-2), 83.4(C-3), 42.6(C-4), 47.3(C-5), 17.8(C-6), 33.0(C-7), 40.0(C-8), 47.5(C-9), 36.7(C-10), 23.6(C-11), 122.8(C-12), 144.2(C-13), 42.0(C-14), 35.8(C-15), 73.7(C-16), 49.3(C-17), 41.0 (C-18), 46.7 (C-19), 30.6(C-20), 35.8 (C-21), 31.8 (C-22), 64.8(C-23), 14.8 (C-24), 17.4(C-25), 17.1(C-26), 27.0(C-27), 175.7(C-28), 33.0(C-29), 24.5(C-30). Sugars linked at C-3: Glucose (inner) 105.7 (C-1), 74.8(C-2), 88.6(C-3), 71.5(C-4), 76.3(C-5), 62.3 (C-6); Glucose (terminal) 105.2 (C-1), 75.0(C-2), 78.4(C-3), 69.4(C-4), 77.7(C-5), 62.3 (C-6); Sugars linked at C-28: Arabinose 93.2 (C-1), 73.8(C-2), 70.6(C-3), 65.8(C-4), 62.7(C-5); Rhamnose 100.9 (C-1), 71.7(C-2), 72.5(C-3), 82.5(C-4), 68.3(C-5), 18.1 (C-6); Xylose 106.4 (C-1), 75.3(C-2), 84.5(C-3), 69.2(C-4), 66.6(C-5); Apiose 110.9 (C-1), 78.0(C-2), 80.2(C-3), 73.8(C-4), 65.0(C-5).

Polygalacin D (**8**) ^{1}H-NMR δ: 5.60 (1H, brs, H-12), 1.54 (3H, s, Me-24), 1.31 (3H, s, Me-25), 1.11 (3H, s, Me-26), 1.68 (3H, d, J = 6.0 Hz, Me-Rha), 1.73(3H, s, Me-27), 0.96(3H, s, Me-29), 1.12 (3H, s, Me-30); ^{13}C-NMR δ: 44.0(C-1), 70.2(C-2), 83.4(C-3), 42.5(C-4), 49.3(C-5), 18.1(C-6), 33.0(C-7), 40.0(C-8), 49.3(C-9), 36.7(C-10), 23.8(C-11), 122.8(C-12), 144.1(C-13), 42.0(C-14), 35.8(C-15), 73.8(C-16), 49.3(C-17), 41.0 (C-18), 46.8 (C-19), 30.7(C-20), 35.9 (C-21), 31.8 (C-22), 66.7(C-23), 14.8 (C-24), 17.4(C-25), 17.1(C-26), 27.0(C-27), 175.7(C-28), 33.0(C-29), 24.5(C-30). Sugars linked at C-3: Glucose 105.4 (C-1), 75.2(C-2), 78.3(C-3), 71.6(C-4), 77.5(C-5), 62.3 (C-6); Sugars linked at C-28: Arabinose 93.2 (C-1), 75.2(C-2), 70.2(C-3), 65.8(C-4), 62.7(C-5); Rhamnose 100.9 (C-1), 71.6(C-2), 72.4(C-3), 83.4(C-4), 68.3(C-5), 18.1 (C-6); Xylose 106.4 (C-1), 75.2(C-2), 84.5(C-3), 69.6(C-4), 66.7(C-5); Apiose 110.9 (C-1), 78.0(C-2), 80.2(C-3), 73.8(C-4), 65.1(C-5).

2″-O-acetylplatycodin D (**9**) ^{1}H-NMR δ: 5.62 (1H, brs, H-12), 1.70 (3H, s, Me-25), 1.67 (3H, d, J = 6.0 Hz, Me-Rha), 1.08 (6H, s, Me-26, 30), 1.42(3H, s, Me-27), 0.96(3H, s, Me-29), 1.97 (3H, s, $\underline{CH_3}CO$); ^{13}C-NMR δ: 44.9(C-1), 69.2(C-2), 86.5(C-3), 47.8(C-4), 47.8(C-5), 19.1(C-6), 33.3(C-7), 40.1(C-8), 47.4(C-9), 37.2(C-10), 23.9(C-11), 122.8(C-12), 144.0(C-13), 42.1(C-14), 35.8(C-15), 73.6(C-16), 49.4(C-17), 41.2 (C-18), 46.7 (C-19), 30.6(C-20), 35.8 (C-21), 31.9 (C-22), 63.3(C-23), 66.2 (C-24), 18.1(C-25), 17.4(C-26), 26.9(C-27), 175.7(C-28), 33.0(C-29), 24.5(C-30). Sugars linked at C-3:Glucose 106.0 (C-1), 75.2(C-2), 78.5(C-3), 71.4(C-4), 78.4(C-5), 62.3 (C-6); Sugars linked at C-28: Arabinose 93.2 (C-1), 76.1(C-2), 70.0(C-3), 65.7(C-4), 63.4(C-5); Rhamnose 97.9 (C-1), 73.1(C-2), 70.0(C-3), 82.8(C-4), 68.5(C-5), 18.3 (C-6); Xylose 106.2 (C-1), 74.9(C-2), 84.5(C-3), 69.3(C-4), 66.7(C-5); Apiose 111.0 (C-1), 77.5(C-2), 80.2(C-3), 75.0(C-4), 65.1(C-5); $\underline{CH_3}CO$(20.6), $CH_3\underline{CO}$(170.5).

3″-O-acetylplatycodin D (**9′**) ^{1}H-NMR δ: 5.62 (1H, brs, H-12), 1.70 (3H, s, Me-25), 1.67 (3H, d, J = 6.0 Hz, Me-Rha), 1.10 (3H, s, Me-26), 1.42(3H, s, Me-27), 0.95(3H, s, Me-29), 1.07(3H, s, Me-30), 2.06 (3H, s, $\underline{CH_3}CO$); ^{13}C-NMR δ: 44.9(C-1), 69.2(C-2), 86.5(C-3), 47.8(C-4), 47.8(C-5), 19.1(C-6), 33.3(C-7), 40.1(C-8), 47.4(C-9), 37.2(C-10), 23.9(C-11), 122.8(C-12), 144.0(C-13), 42.1(C-14), 35.8(C-15), 73.6(C-16), 49.4(C-17), 41.2 (C-18), 46.7 (C-19), 30.6(C-20), 35.8 (C-21), 31.9 (C-22), 63.3(C-23), 66.2 (C-24), 18.1(C-25), 17.4(C-26), 26.9(C-27), 175.7(C-28), 33.0(C-29), 24.5(C-30). Sugars linked at C-3:Glucose 106.0 (C-1), 75.2(C-2), 78.5(C-3), 71.4(C-4), 78.4(C-5), 62.3 (C-6); Sugars linked at C-28: Arabinose 93.0 (C-1), 76.1(C-2), 70.0(C-3), 65.7(C-4), 63.4(C-5); Rhamnose 101.2 (C-1), 70.4(C-2), 75.6(C-3), 77.3(C-4), 68.1(C-5), 18.3 (C-6); Xylose 105.7 (C-1), 74.9(C-2), 84.5(C-3), 69.3(C-4), 66.7(C-5); Apiose 111.0 (C-1), 77.5(C-2), 80.2(C-3), 75.0(C-4), 65.1(C-5); $\underline{CH_3}CO$(21.1), $CH_3\underline{CO}$(170.2).

3″-O-acetylpolygalacin D_2 (**10**) ^{1}H-NMR δ: 5.60 (1H, brs, H-12), 1.56 (3H, s, Me-24), 1.33 (3H, s, Me-25), 1.13 (3H, s, Me-26), 1.69 (3H, d, J = 6.0 Hz, Me-Rha), 1.75(3H, s, Me-27), 0.97(3H, s, Me-29), 1.12 (3H, s, Me-30), 1.97 (3H, s, $\underline{CH_3}CO$); ^{13}C-NMR δ: 44.2 (C-1), 70.0(C-2), 83.7 (C-3), 42.7(C-4), 47.5(C-5), 18.0(C-6), 33.1(C-7), 40.0(C-

8), 47.6(C-9), 36.8(C-10), 23.9(C-11), 122.8(C-12), 144.2(C-13), 42.0(C-14), 35.8 (C-15), 73.9 (C-16), 49.4 (C-17), 41.1 (C-18), 46.9 (C-19), 29.8(C-20), 35.8 (C-21), 31.9 (C-22), 66.8 (C-23), 14.9 (C-24), 17.5(C-25), 17.2(C-26), 26.9 (C-27), 175.8(C-28), 33.1(C-29), 24.6 (C-30). Sugars linked at C-3: Glucose (inner) 105.7 (C-1), 74.1(C-2), 88.6(C-3), 70.0(C-4), 77.6(C-5), 62.4 (C-6); Glucose (terminal) 105.31 (C-1), 75.0 (C-2), 78.1(C-3), 71.4(C-4), 78.1(C-5), 62.2 (C-6); Sugars linked at C-28: Arabinose 93.0 (C-1), 75.8 (C-2), 70.7(C-3), 75.8 (C-4), 62.7(C-5); Rhamnose 98.0 (C-1), 73.3 (C-2), 70.7 (C-3), 82.6 (C-4), 69.1 (C-5), 18.4 (C-6); Xylose 106.2 (C-1), 75.1 (C-2), 84.54 (C-3), 69.5(C-4), 66.8(C-5); Apiose 111.1 (C-1), 78.1(C-2), 80.26 (C-3), 75.4(C-4), 65.9(C-5) ; $\underline{CH_3}CO$(20.7), $CH_3\underline{CO}$(170.3).

3″-O-acetylpolygalacin D_2 (**10′**) ^{1}H-NMR δ: 5.60 (1H, brs, H-12), 1.56 (3H, s, Me-24), 1.33/1.32 (3H, s, Me-25), 1.13 (3H, s, Me-26), 1.68 (3H, d, J = 6.0 Hz, Me-Rha), 1.75(3H, s, Me-27), 0.97(3H, s, Me-29), 1.12 (3H, s, Me-30), 2.06 (3H, s, $\underline{CH_3}CO$); ^{13}C-NMR δ: 44.1(C-1), 70.0(C-2), 83.6(C-3), 42.7(C-4), 47.5(C-5), 18.0(C-6), 33.1(C-7), 40.0(C-8), 47.6(C-9), 36.8(C-10), 23.9(C-11), 122.8(C-12), 144.2(C-13), 42.0(C-14), 35.9(C-15), 73.8(C-16), 49.5(C-17), 41.1 (C-18), 46.9 (C-19), 29.8(C-20), 35.9 (C-21), 31.9 (C-22), 66.6(C-23), 14.9 (C-24), 17.5(C-25), 17.2(C-26), 27.1 (C-27), 175.8(C-28), 33.1(C-29), 24.7(C-30). Sugars linked at C-3: Glucose (inner) 105.7 (C-1), 74.1(C-2), 88.6(C-3), 70.0(C-4), 77.6(C-5), 62.3 (C-6); Glucose (terminal) 105.33 (C-1), 74.9(C-2), 78.1(C-3), 71.4(C-4), 78.1(C-5), 62.1 (C-6); Sugars linked at C-28: Arabinose 93.1 (C-1), 76.0(C-2), 70.7(C-3), 75.9(C-4), 62.7(C-5); Rhamnose 101.1 (C-1), 70.0(C-2), 75.3(C-3), 77.6(C-4), 69.2(C-5), 18.3 (C-6); Xylose 105.8 (C-1), 75.0(C-2), 84.46(C-3), 69.5(C-4), 66.8(C-5); Apiose 111.1 (C-1), 78.1(C-2), 80.31(C-3), 75.4(C-4), 65.9(C-5) ; $\underline{CH_3}CO$(21.2), $CH_3\underline{CO}$(170.5).

2″-O-acetylpolygalacin D (**11**) ^{1}H-NMR δ: 5.60 (1H, brs, H-12), 1.53 (3H, s, Me-24), 1.30 (3H, s, Me-25), 1.11 (3H, s, Me-26), 1.68 (3H, d, J = 6.0 Hz, Me-Rha), 1.73(3H, s, Me-27), 0.96(3H, s, Me-29), 1.12 (3H, s, Me-30), 1.99 (3H, s, $\underline{CH_3}CO$); ^{13}C-NMR δ: 44.0(C-1), 70.2(C-2), 83.3(C-3), 42.6(C-4), 49.4(C-5), 18.1(C-6), 33.0(C-7), 40.0(C-8), 49.4(C-9), 36.8(C-10), 23.8(C-11), 122.8(C-12), 144.2(C-13), 42.0(C-14), 35.8(C-15), 73.8(C-16), 49.4(C-17), 41.1 (C-18), 46.9 (C-19), 30.7(C-20), 35.9 (C-21), 31.9

(C-22), 66.7(C-23), 14.9 (C-24), 17.4(C-25), 17.2(C-26), 27.0(C-27), 175.8(C-28), 33.0(C-29), 24.6(C-30). Sugars linked at C-3: Glucose 105.3 (C-1), 75.2 (C-2), 78.3(C-3), 71.7(C-4), 77.5(C-5), 62.3 (C-6); Sugars linked at C-28: Arabinose 93.2 (C-1), 75.3(C-2), 70.2(C-3), 65.8(C-4), 62.7(C-5); Rhamnose 97.9 (C-1), 73.2 (C-2), 70.2 (C-3), 83.3 (C-4), 68.4(C-5), 18.1 (C-6); Xylose 106.4/105.3 (C-1), 75.0(C-2), 84.6(C-3), 69.6(C-4), 66.7(C-5); Apiose 110.9 (C-1), 78.0(C-2), 80.2(C-3), 74.9(C-4), 65.8(C-5); $\underline{CH_3}CO$(20.7), $CH_3\underline{CO}$(170.4).

3″-O-acetylpolygalacin D (**11′**) ^{1}H-NMR δ: 5.60 (1H, brs, H-12), 1.53 (3H, s, Me-24), 1.30 (3H, s, Me-25), 1.11 (3H, s, Me-26), 1.68 (3H, d, J = 6.0 Hz, Me-Rha), 1.73(3H, s, Me-27), 0.96(3H, s, Me-29), 1.12 (3H, s, Me-30), 2.09 (3H, s, $\underline{CH_3}CO$); ^{13}C-NMR δ: 44.0(C-1), 70.2(C-2), 83.3(C-3), 42.6(C-4), 49.4(C-5), 18.1(C-6), 33.0(C-7), 40.0(C-8), 49.4(C-9), 36.8(C-10), 23.8(C-11), 122.8(C-12), 144.2(C-13), 42.0(C-14), 35.8(C-15), 73.8(C-16), 49.4(C-17), 41.1 (C-18), 46.9 (C-19), 30.7(C-20), 35.9 (C-21), 31.9 (C-22), 66.7(C-23), 14.9 (C-24), 17.4(C-25), 17.2(C-26), 27.0(C-27), 175.8(C-28), 33.0(C-29), 24.6(C-30). Sugars linked at C-3: Glucose 105.3 (C-1), 75.2 (C-2), 78.3(C-3), 71.7(C-4), 77.5(C-5), 62.3 (C-6); Sugars linked at C-28: Arabinose 93.2 (C-1), 75.3(C-2), 70.2(C-3), 65.8(C-4), 62.7(C-5); Rhamnose 101.0 (C-1), 70.2(C-2), 75.3(C-3), 77.5(C-4), 68.4(C-5), 18.1 (C-6); Xylose 105.3 (C-1), 75.0(C-2), 84.6(C-3), 69.6(C-4), 66.7(C-5); Apiose 110.9 (C-1), 78.0(C-2), 80.2(C-3), 74.9(C-4), 65.8(C-5); $\underline{CH_3}CO$(21.2), $CH_3\underline{CO}$(170.6).

2. Spectra for compounds 1-11 were given as follows:

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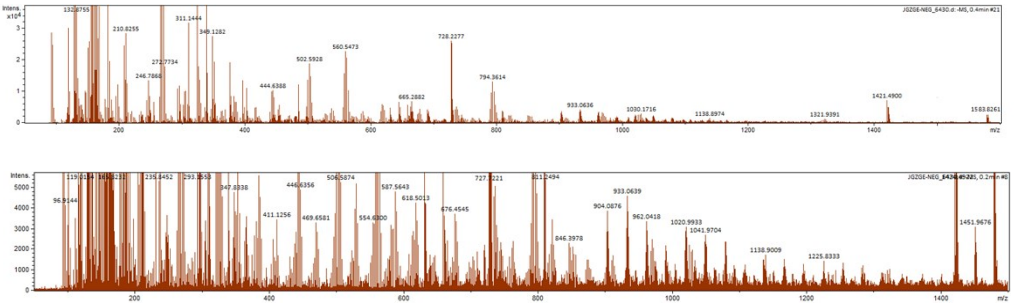


Figure S1. The HREIMS Spectroscopic Data of Compound **1**

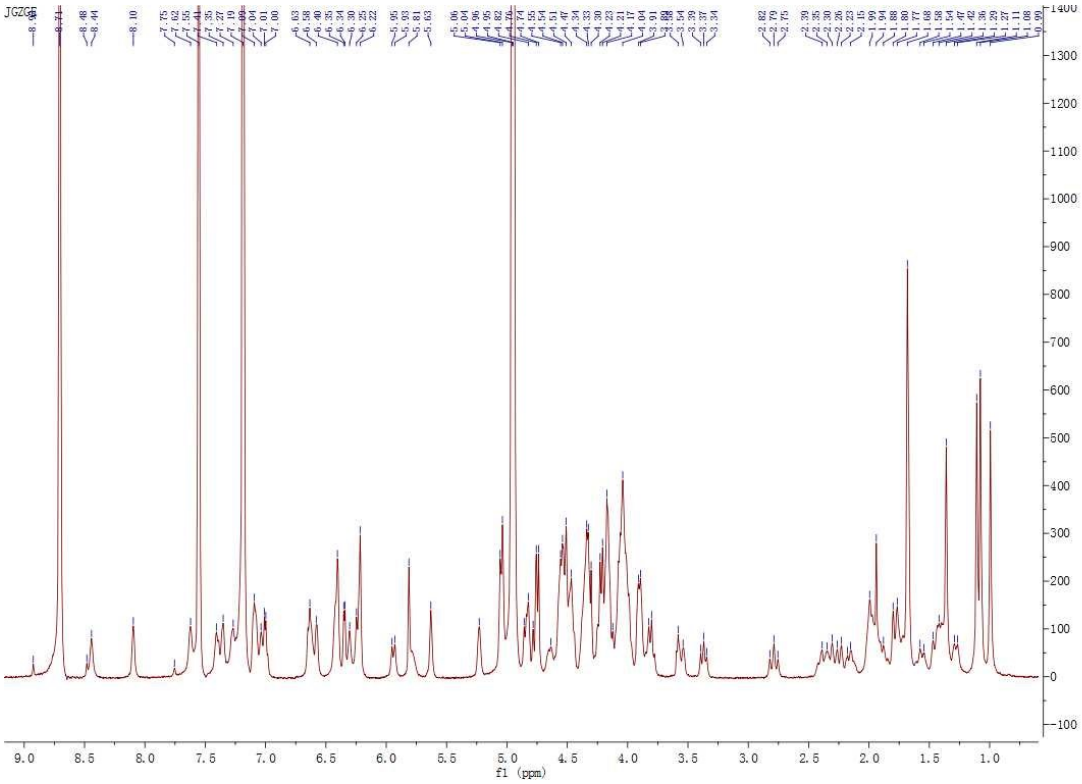


Figure S2. The ^{1}H NMR Spectrum of Compound **1** in CD_3OD (400 MHz)

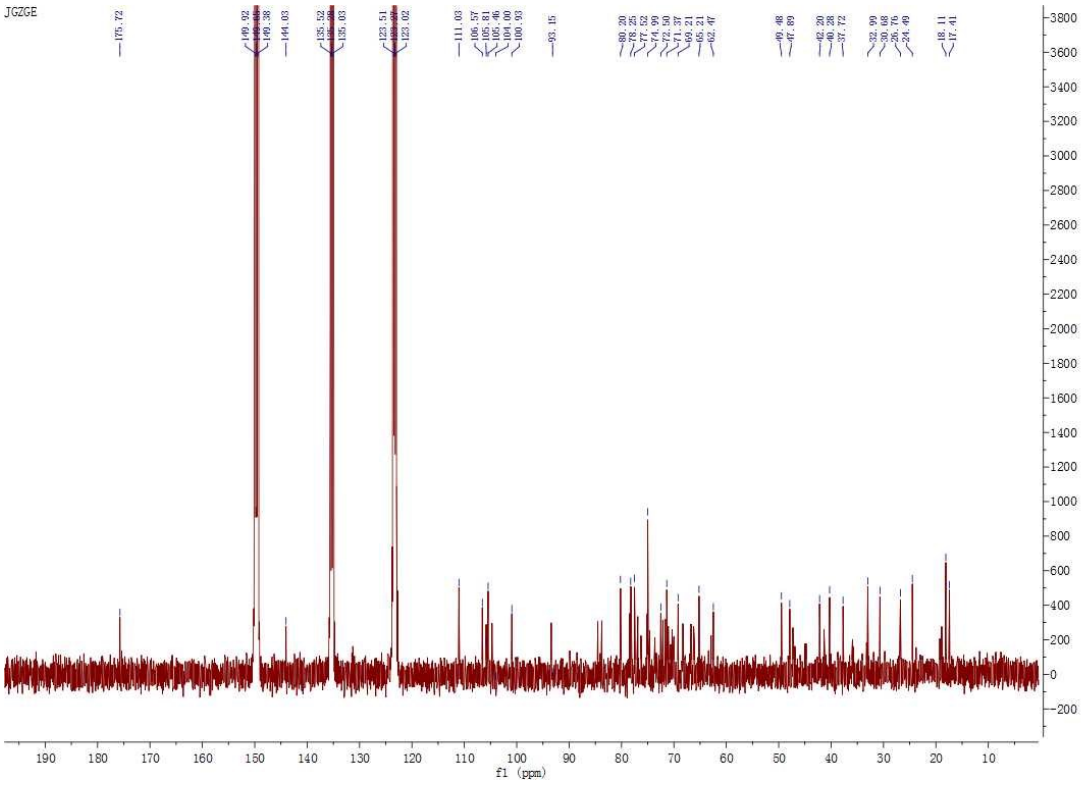


Figure S3. The ^{13}C NMR Spectrum of Compound **1** in CD_3OD (100 MHz)

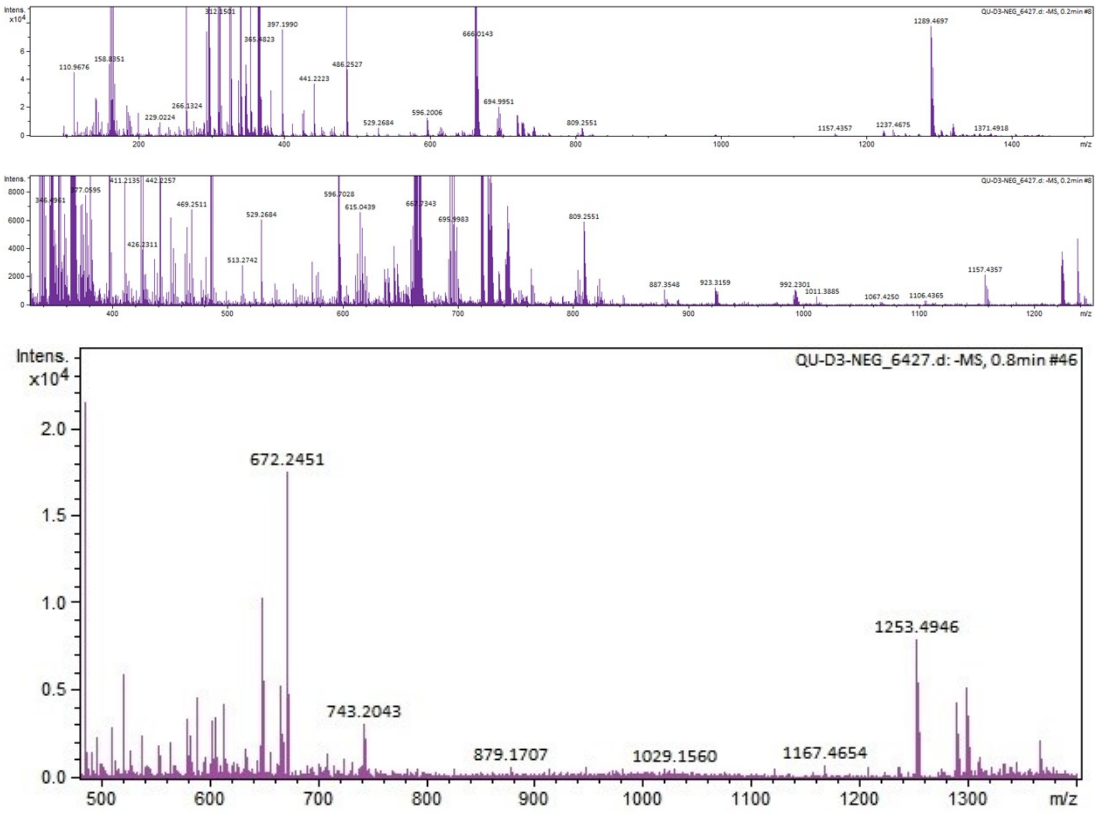


Figure S4. The HRESI-MS Spectroscopic Data of Compound **2**

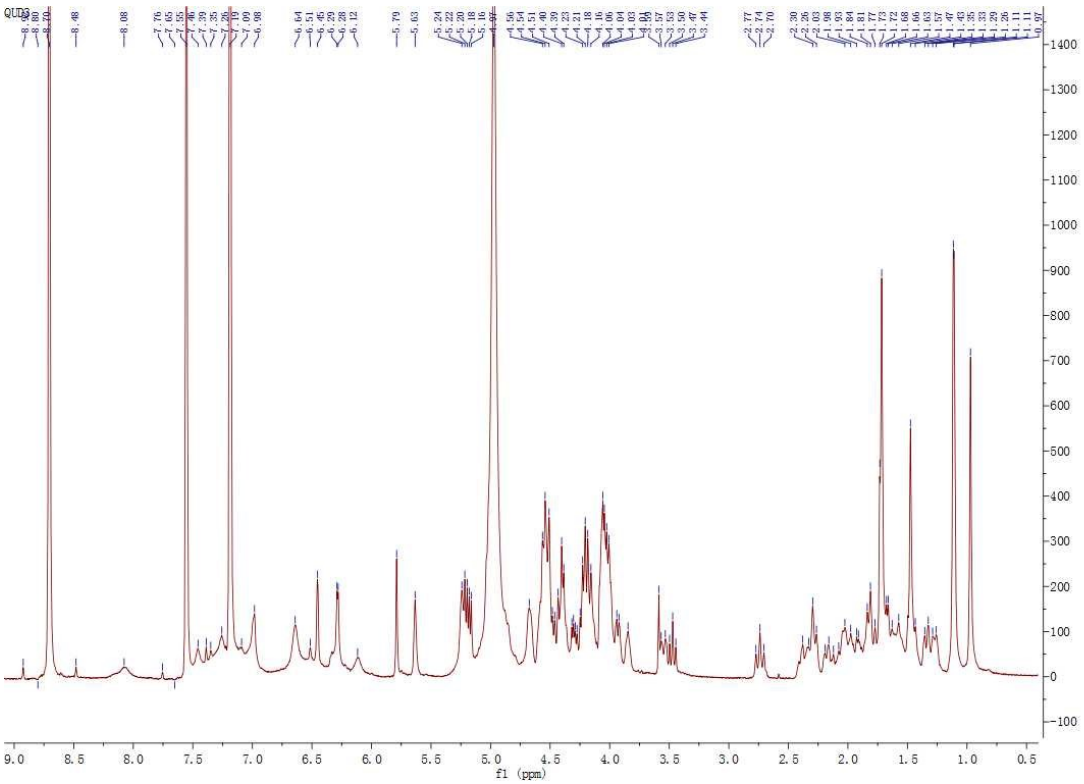


Figure S5. The ^{1}H NMR Spectrum of Compound **2** in CD_3OD (400 MHz)

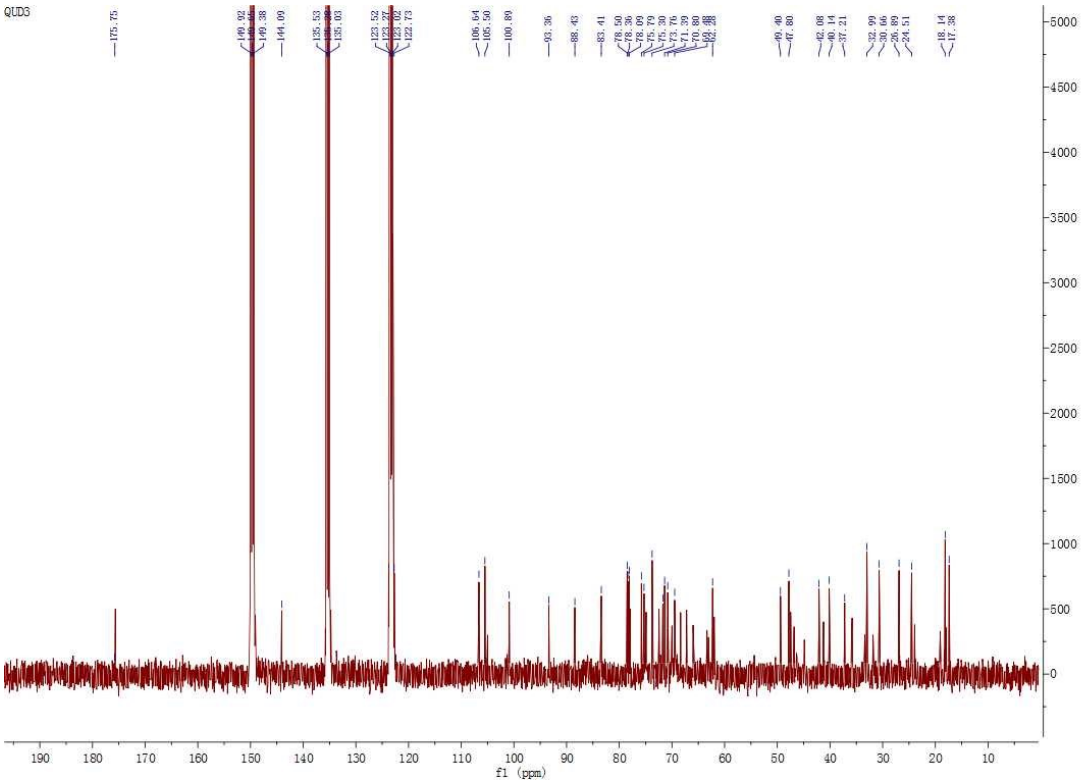


Figure S6. The ^{13}C NMR Spectrum of Compound **2** in CD_3OD (100 MHz)

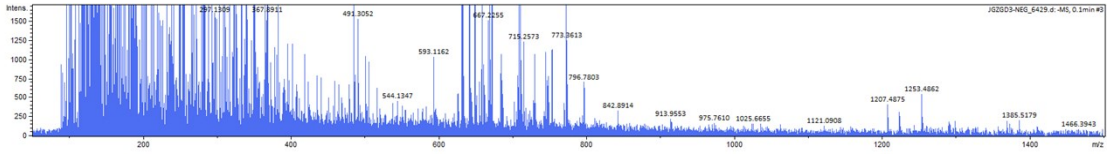


Figure S7. The HRESI-MS Spectroscopic Data of Compound **3**

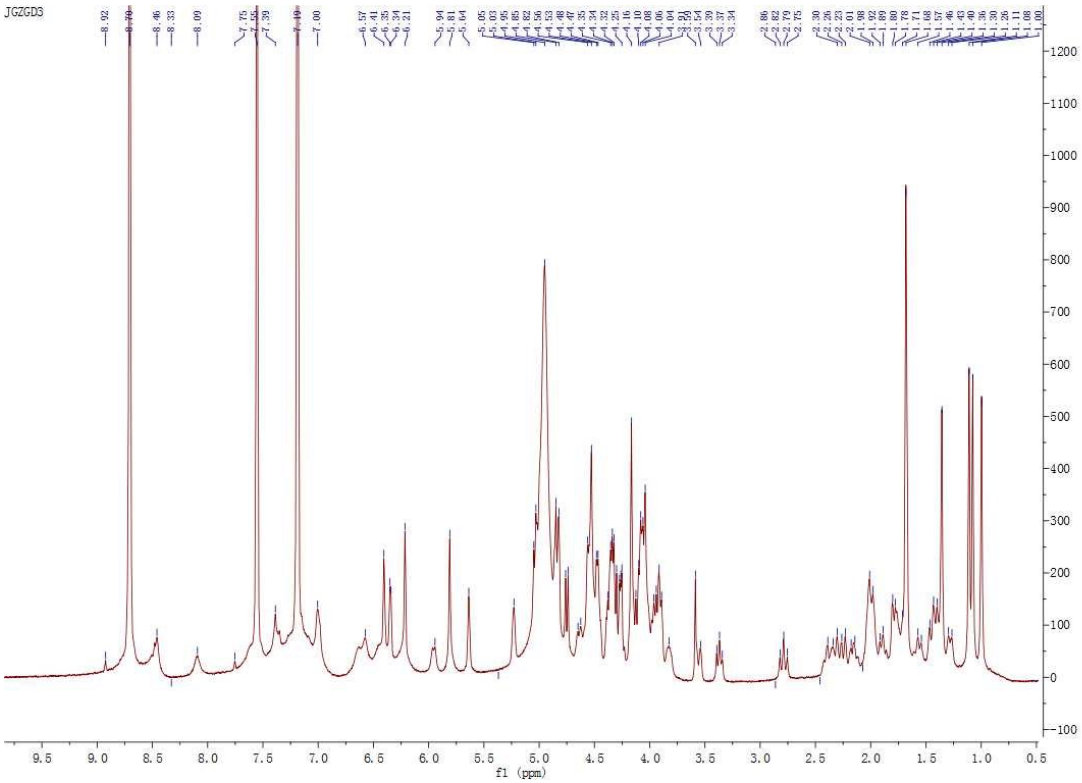


Figure S8. The ^{1}H NMR Spectrum of Compound **3** in CD_3OD (400 MHz)

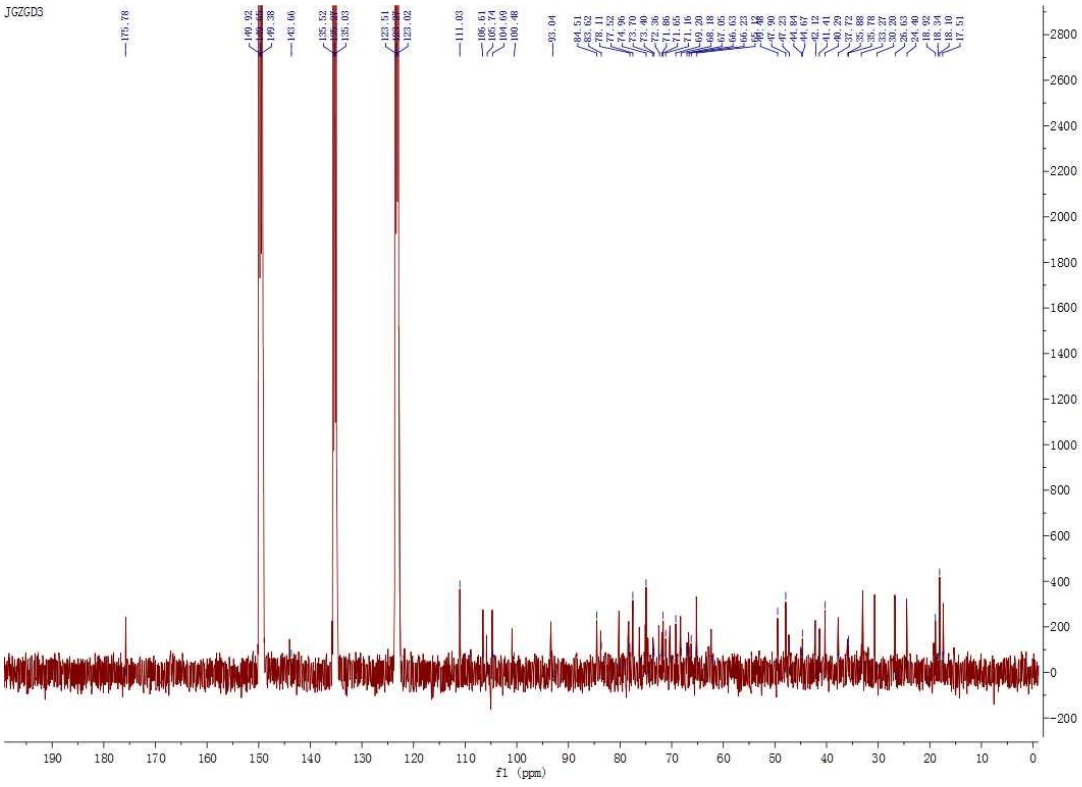


Figure S9. The ^{13}C NMR Spectrum of Compound **3** in CD_3OD (100 MHz)

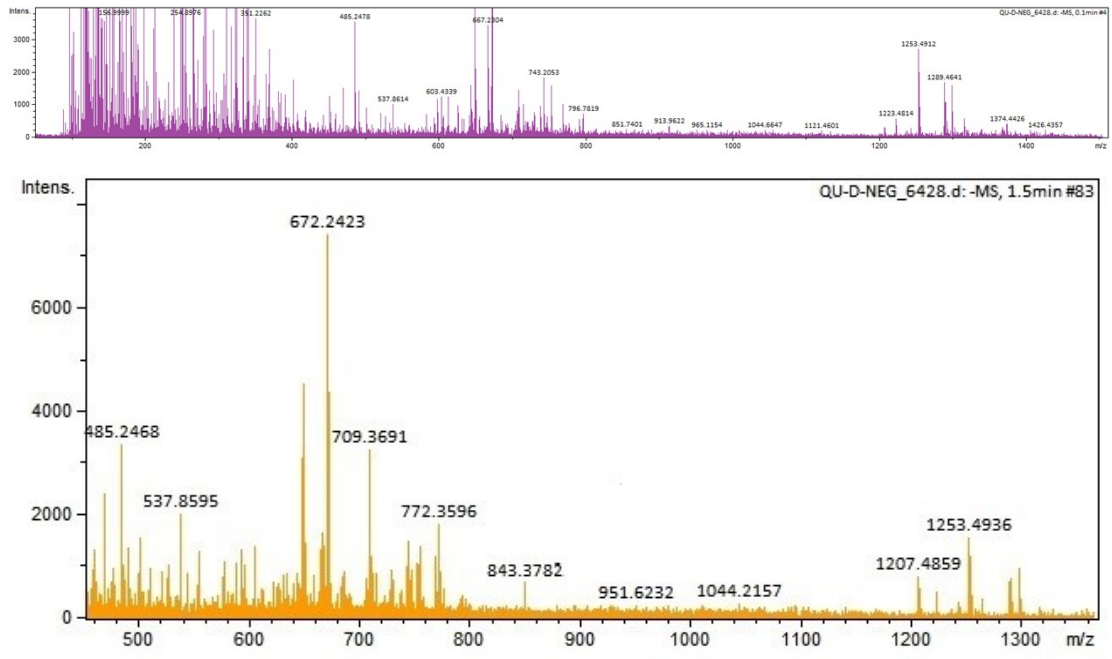


Figure S10. The HRES-IMS Spectroscopic Data of Compound **4**

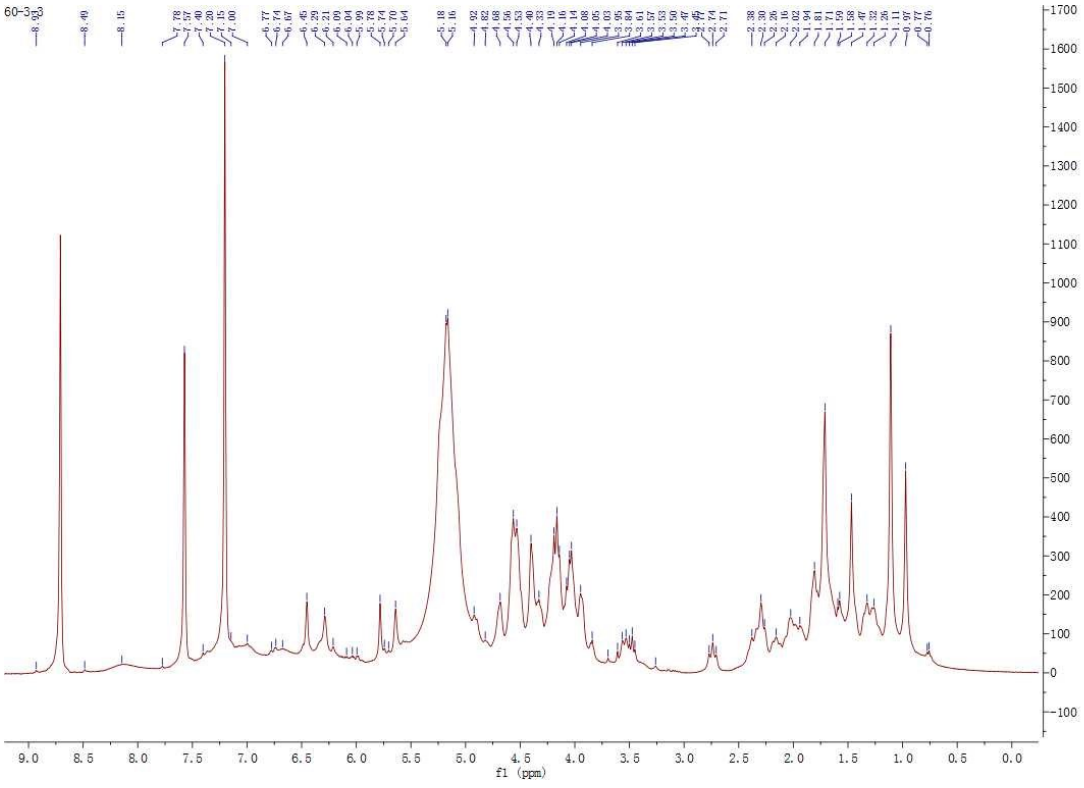


Figure S11. The ^{1}H NMR Spectrum of Compound **4** in CD_3OD (400 MHz)

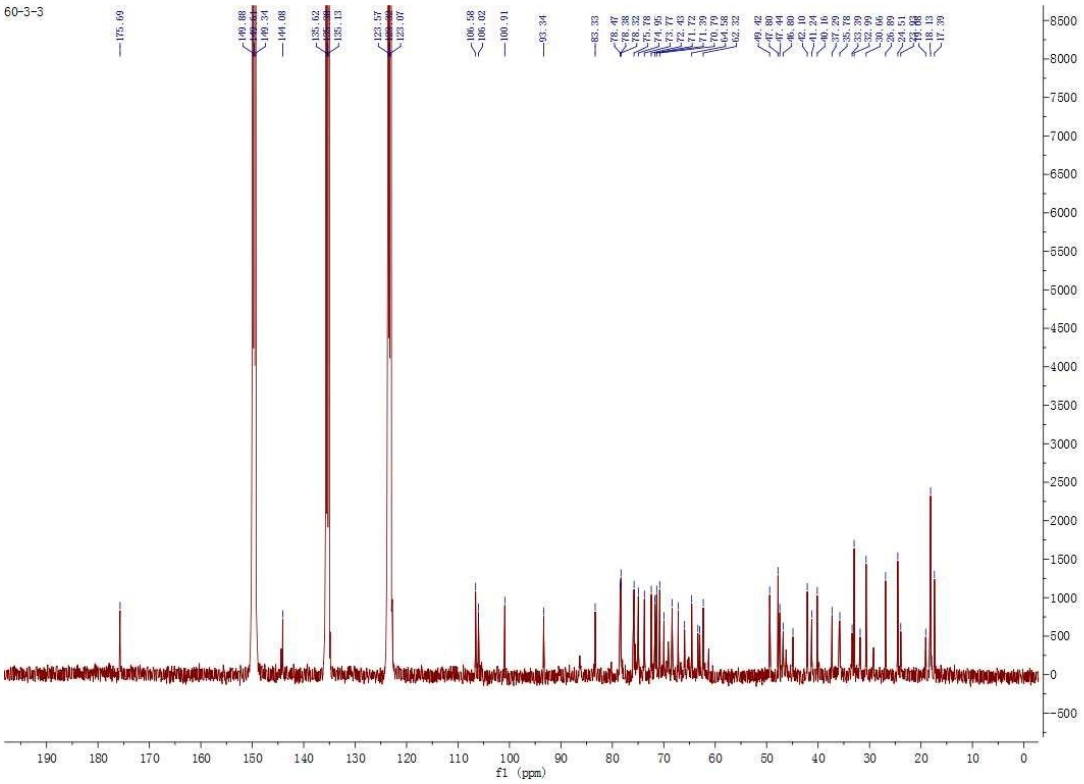


Figure S12. The ^{13}C NMR Spectrum of Compound **4** in CD_3OD (100 MHz)

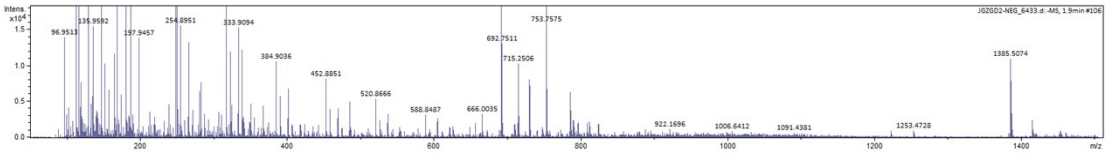


Figure S13. The HRESI-MS Spectroscopic Data of Compound **5**

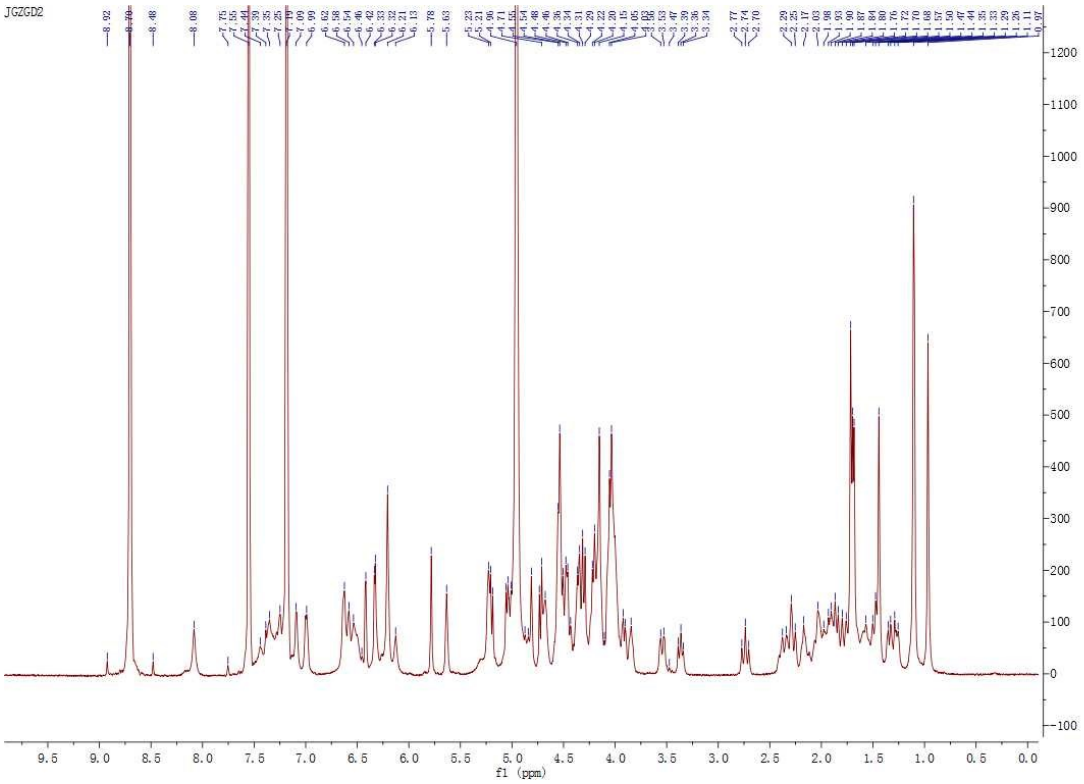


Figure S14. The ^{1}H NMR Spectrum of Compound **5** in CD_3OD (400 MHz)

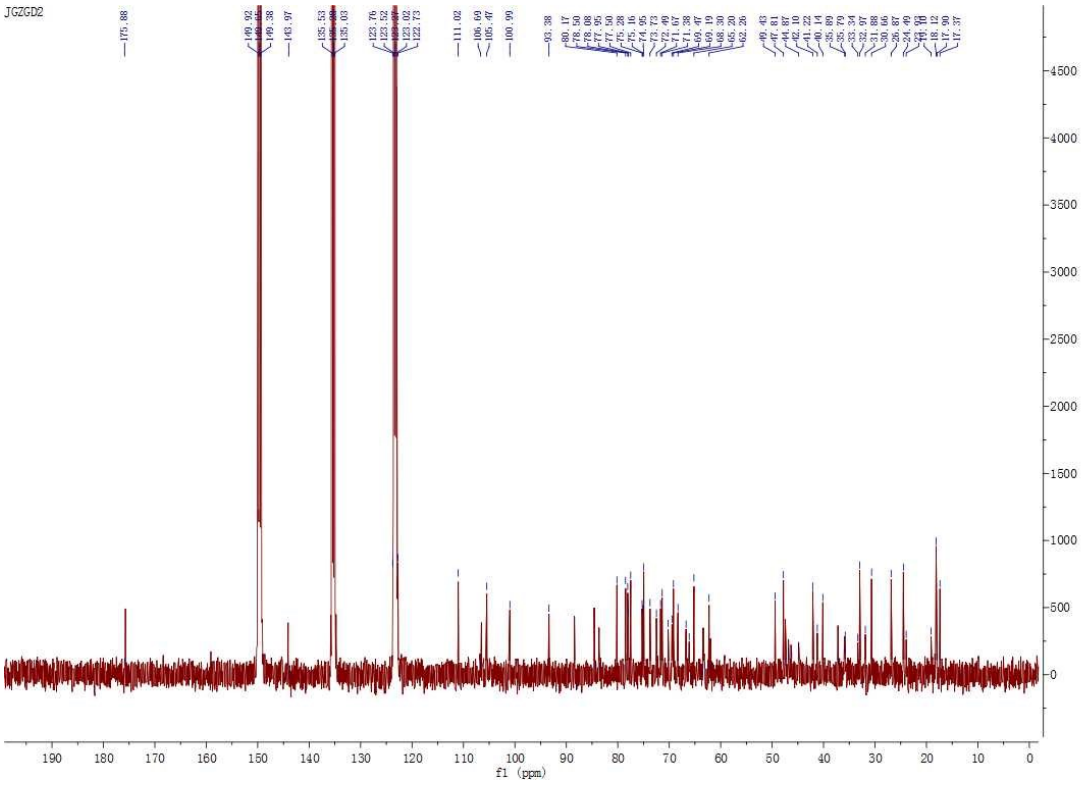


Figure S15. The ^{13}C NMR Spectrum of Compound **5** in CD_3OD (100 MHz)

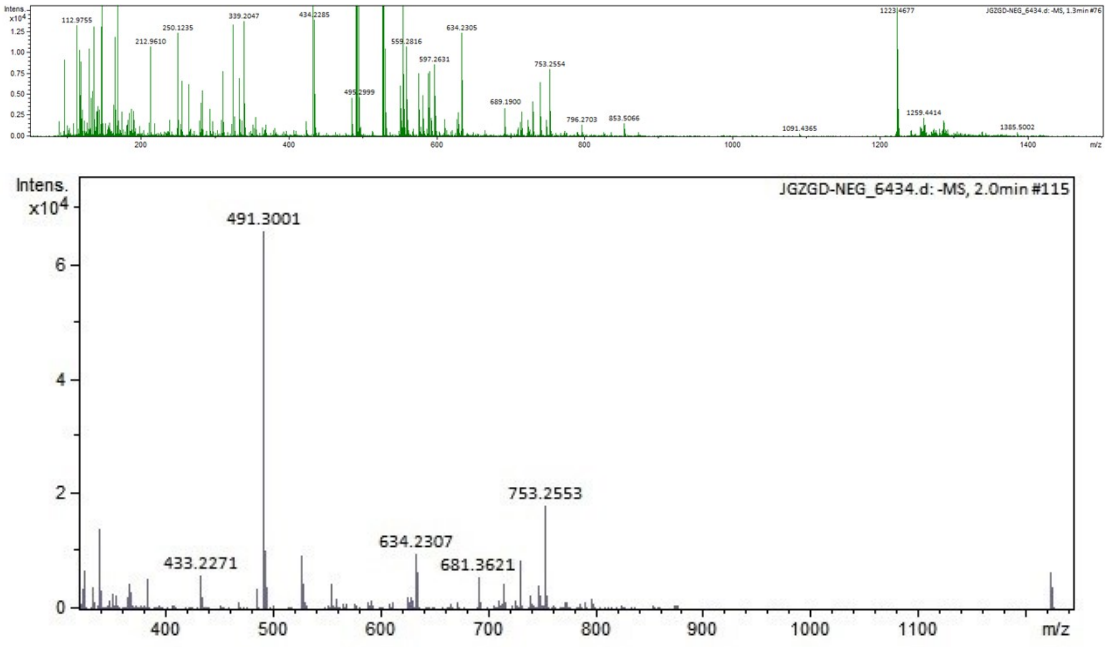


Figure S16. The HRESI-MS Spectroscopic Data of Compound **6**

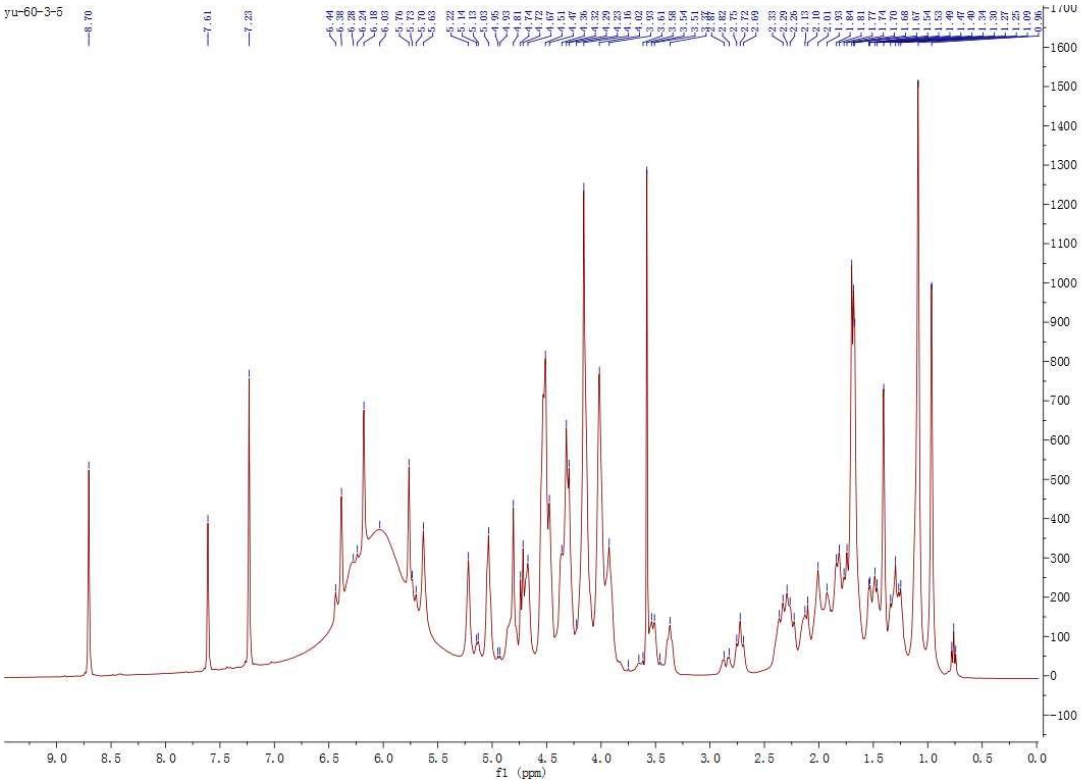


Figure S17. The ^{1}H NMR Spectrum of Compound **6** in CD_3OD (400 MHz)

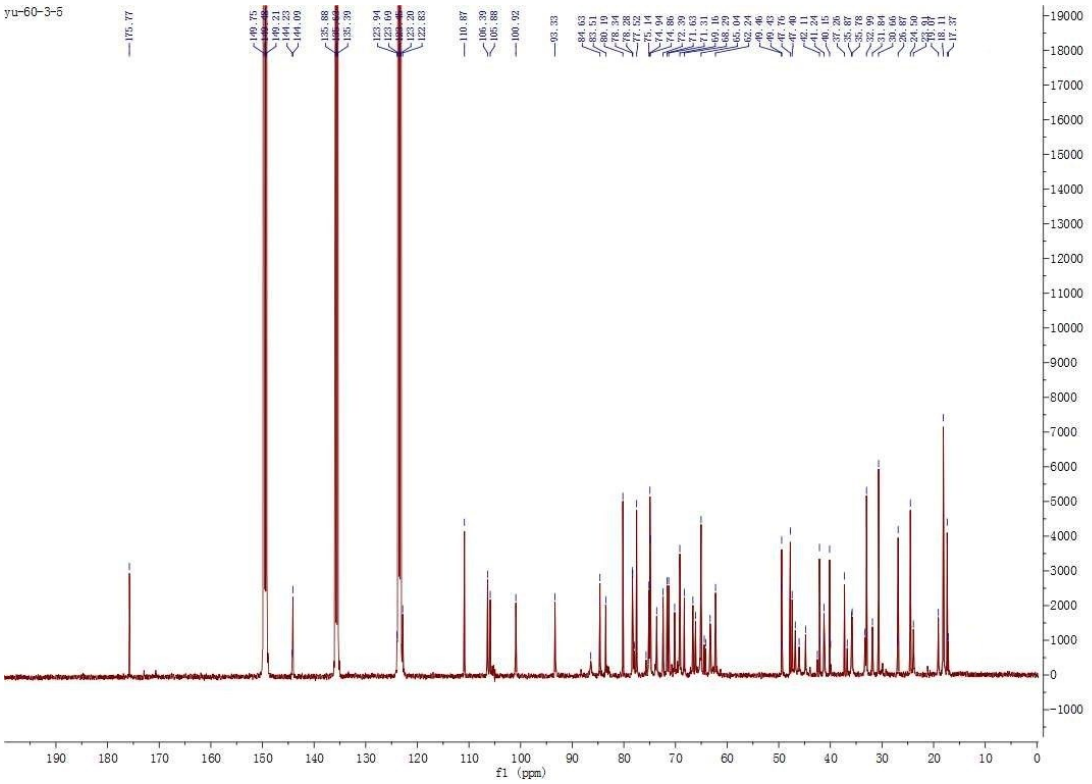


Figure S18. The ^{13}C NMR Spectrum of Compound **6** in CD_3OD (100 MHz)

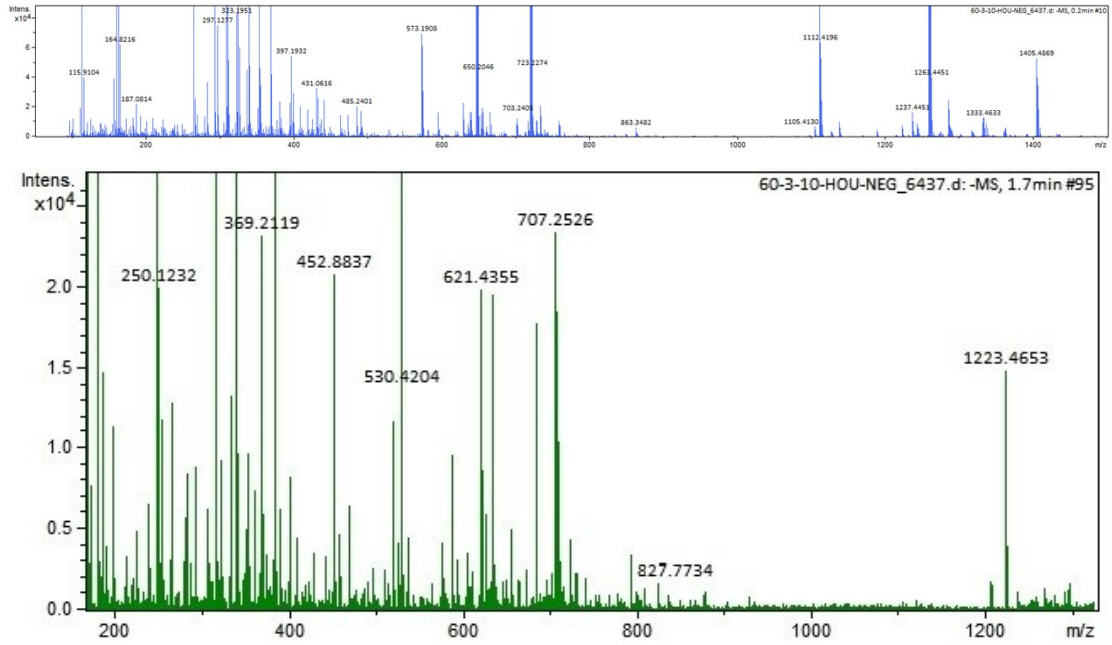


Figure S19. The HRESI-MS Spectroscopic Data of Compound **7**

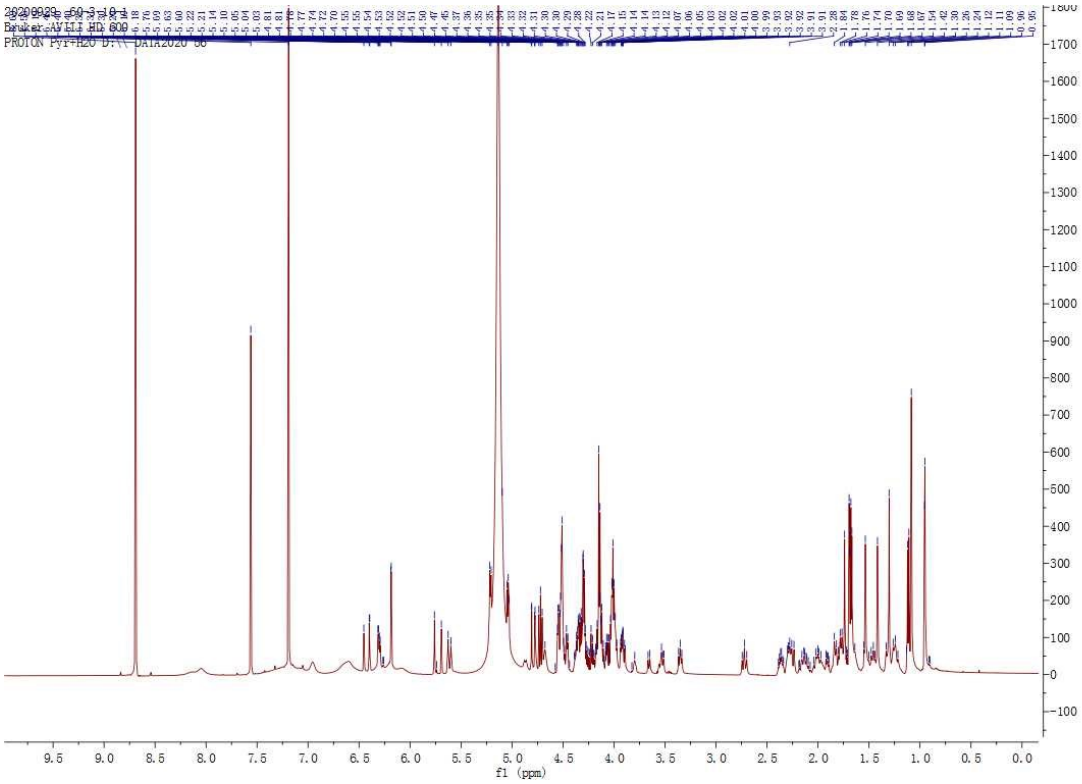


Figure S20. The ^{1}H NMR Spectrum of Compound **7** in C_5D_5N (400 MHz)

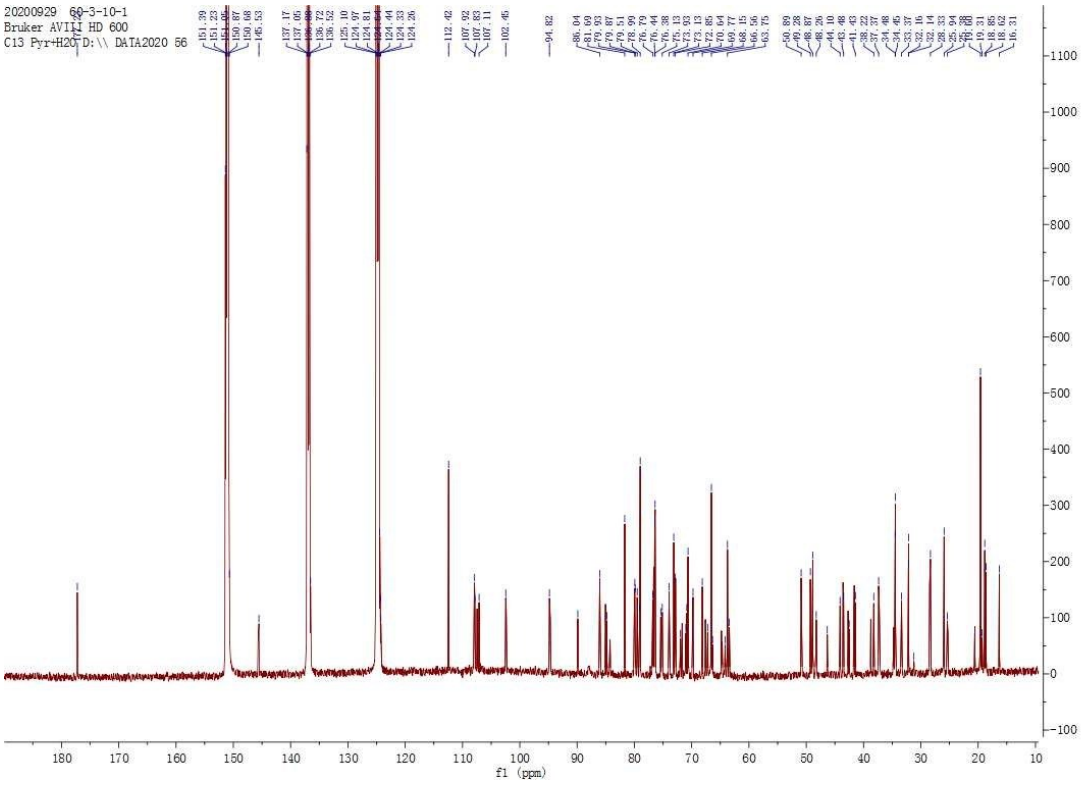


Figure S21. The ^{13}C NMR Spectrum of Compound **7** in C_5D_5N (100 MHz)

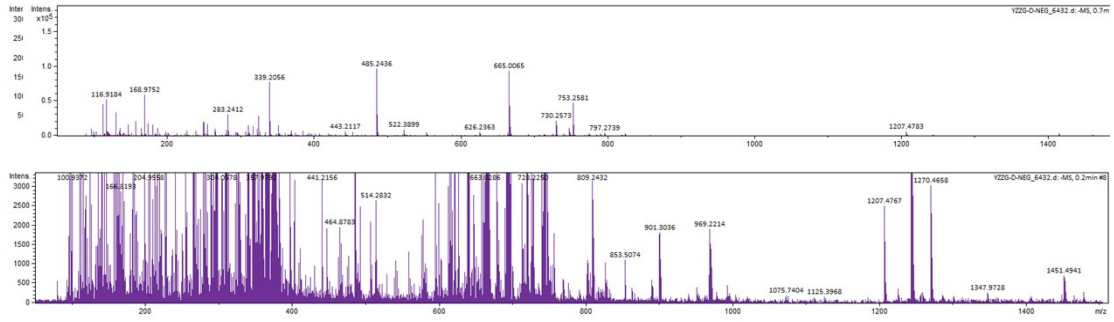


Figure S22. The HRESI-MS Spectroscopic Data of Compound **8**

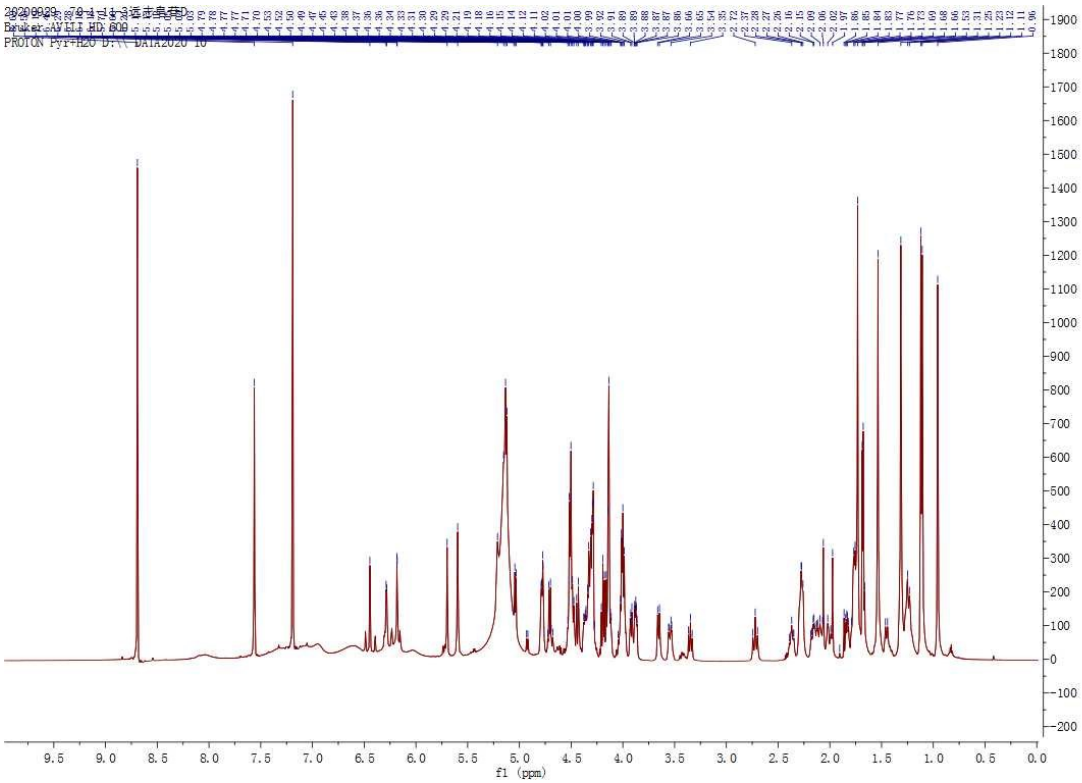


Figure S23. The ^{1}H NMR Spectrum of Compound **8** in C_5D_5N (400 MHz)

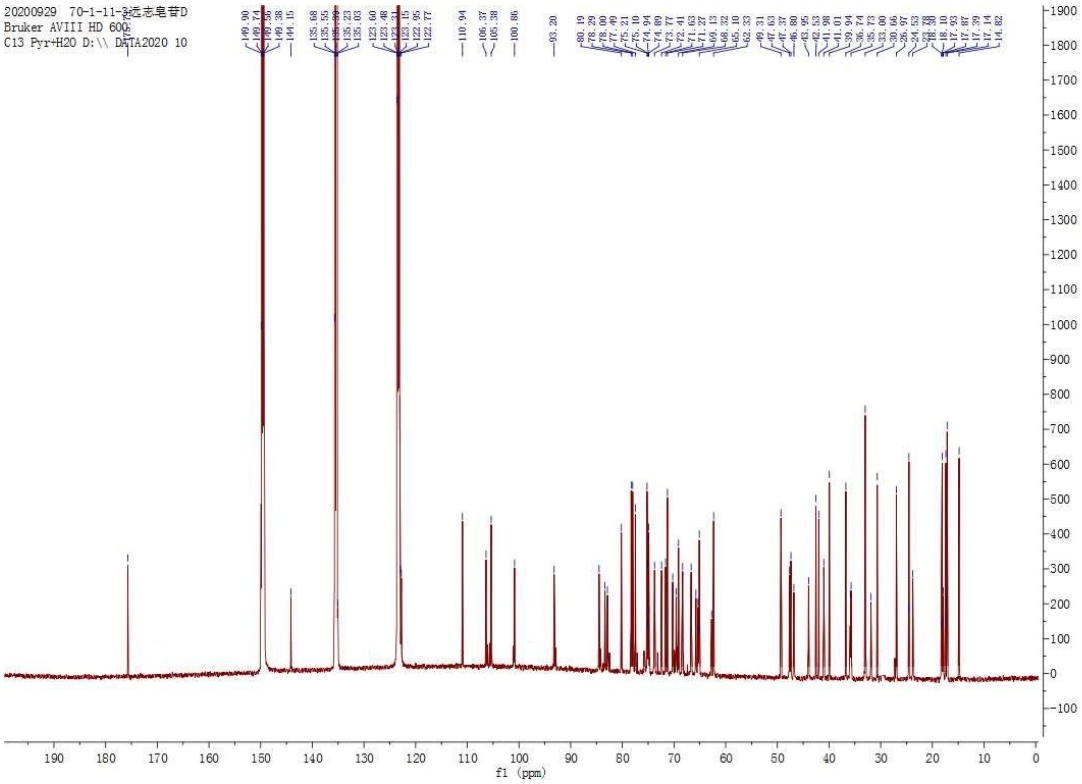


Figure S24. The ^{13}C NMR Spectrum of Compound **8** in C_5D_5N (100 MHz)

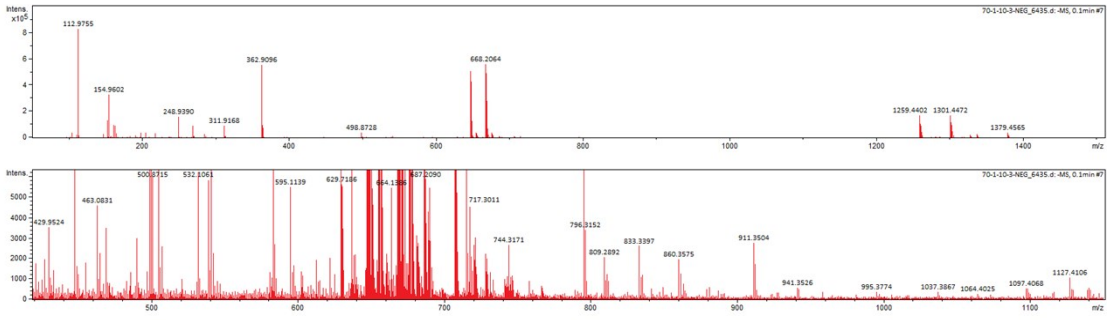


Figure S25. The HRESI-MS Spectroscopic Data of Compound **9**

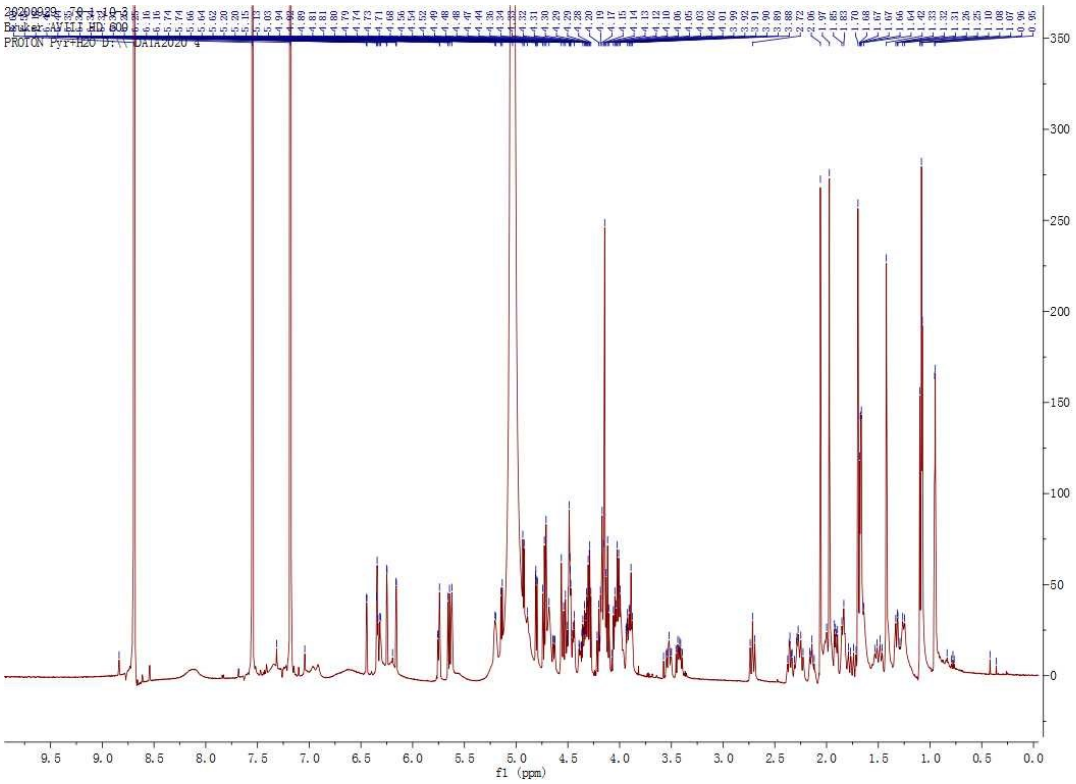


Figure S26. The ^{1}H NMR Spectrum of Compound **9** in C_5D_5N (600 MHz)

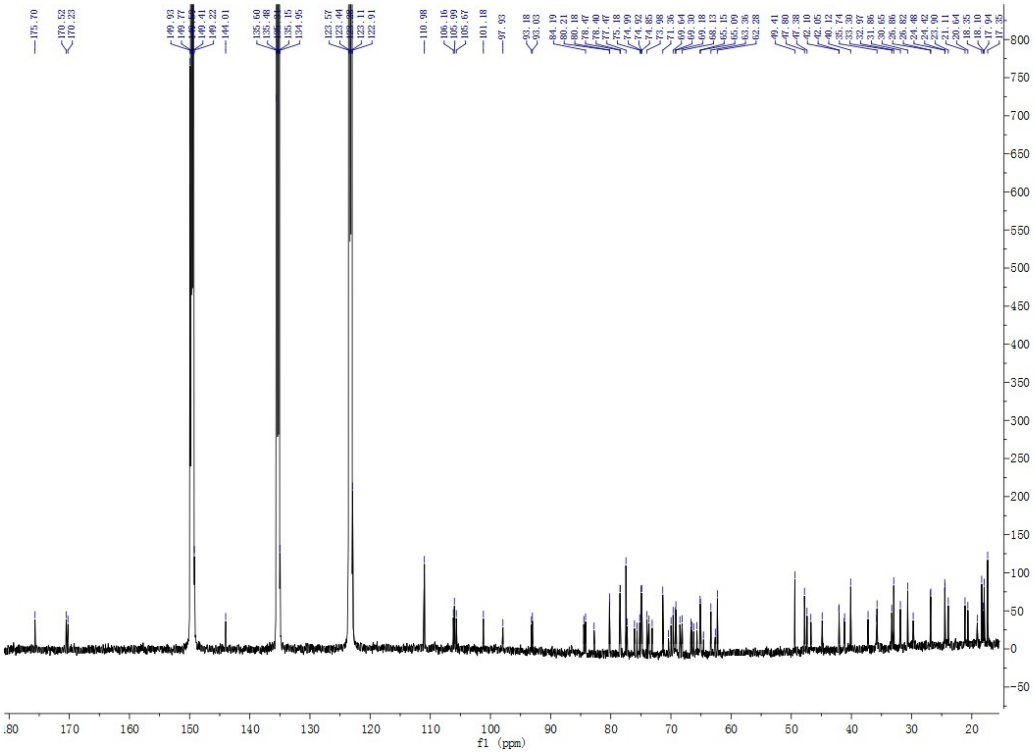
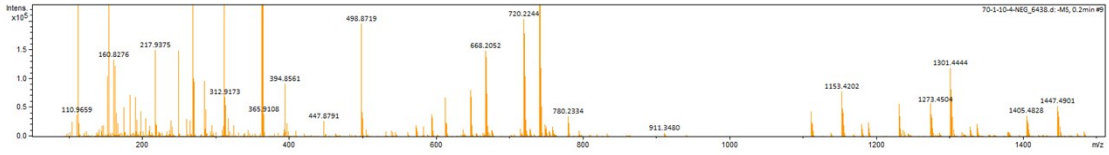


Figure S27. The ^{13}C NMR Spectrum of Compound **9** in C_5D_5N (150 MHz)



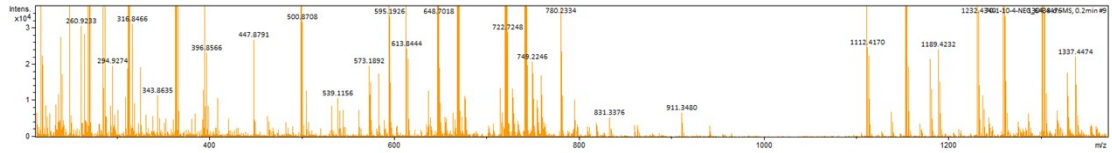


Figure S28. The HRESI-MS Spectroscopic Data of Compound **10**

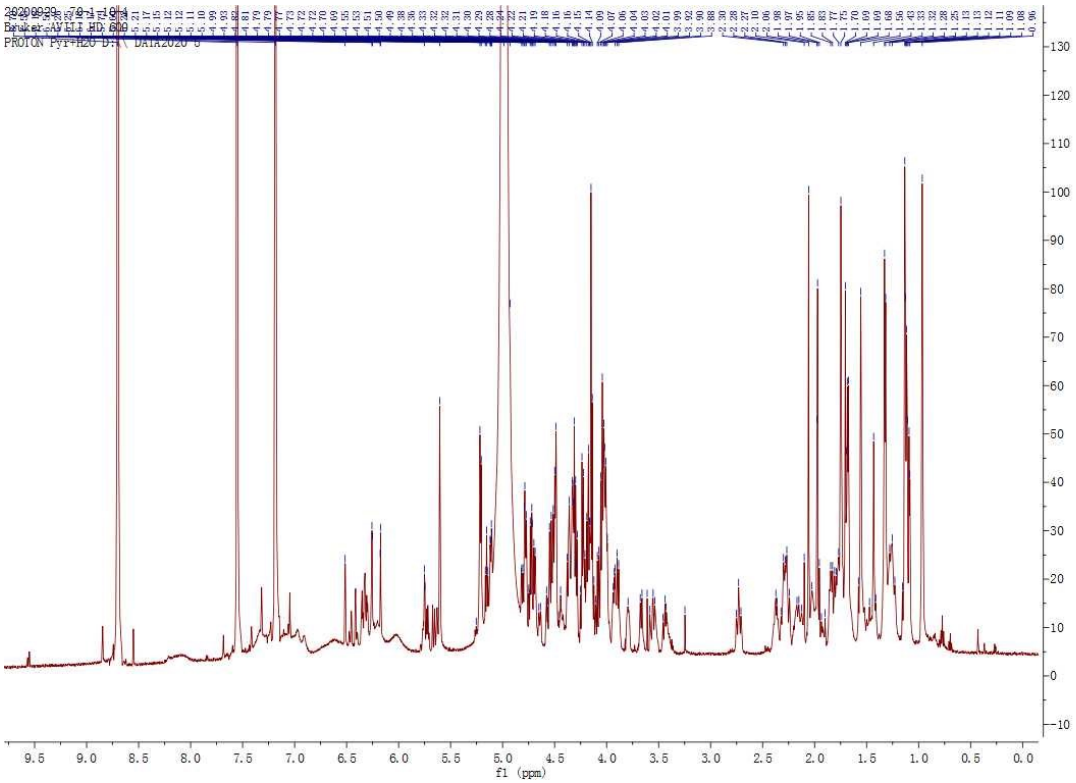


Figure S29. The ^{1}H NMR Spectrum of Compound **10** in C_5D_5N (600 MHz)

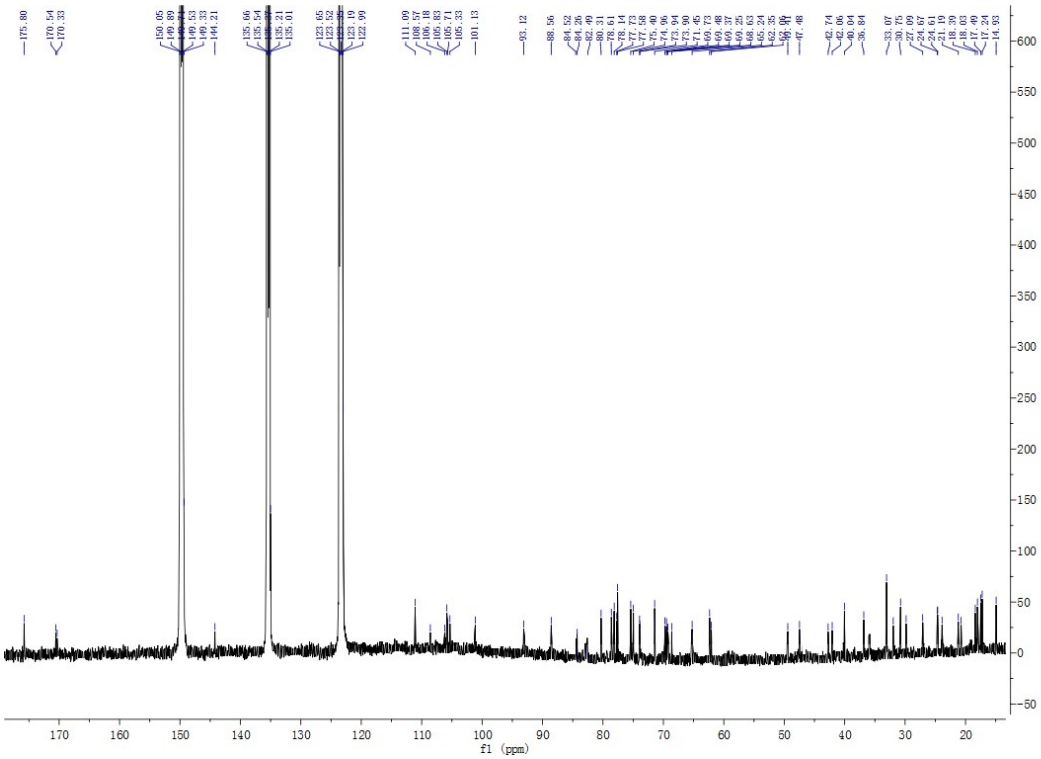


Figure S30. The ^{13}C NMR Spectrum of Compound **10** in C_5D_5N (150 MHz)

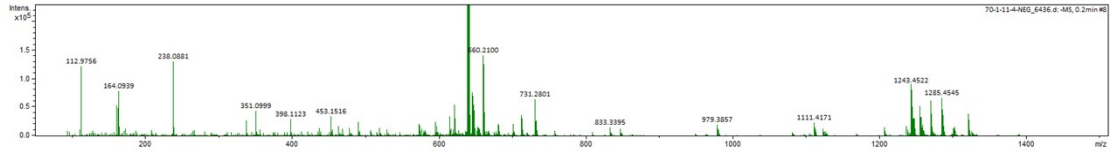


Figure S31. The HRESI-MS Spectroscopic Data of Compound **11**

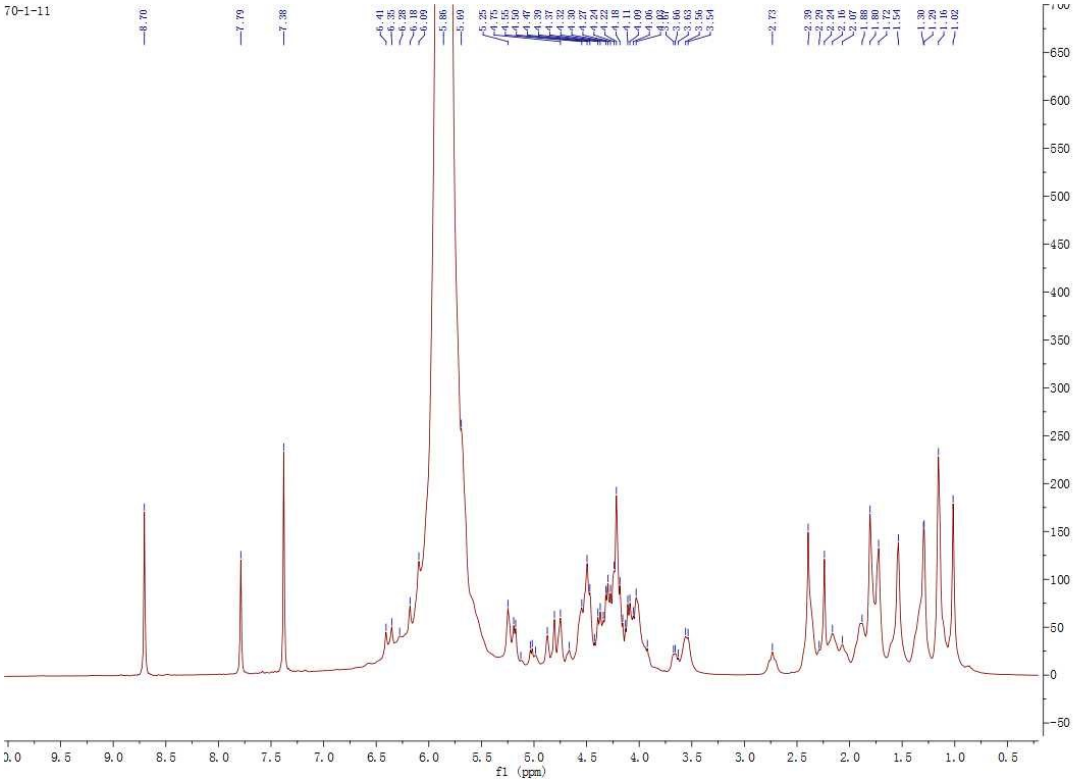


Figure S32. The ^{1}H NMR Spectrum of Compound **11** in C_5D_5N (600 MHz)

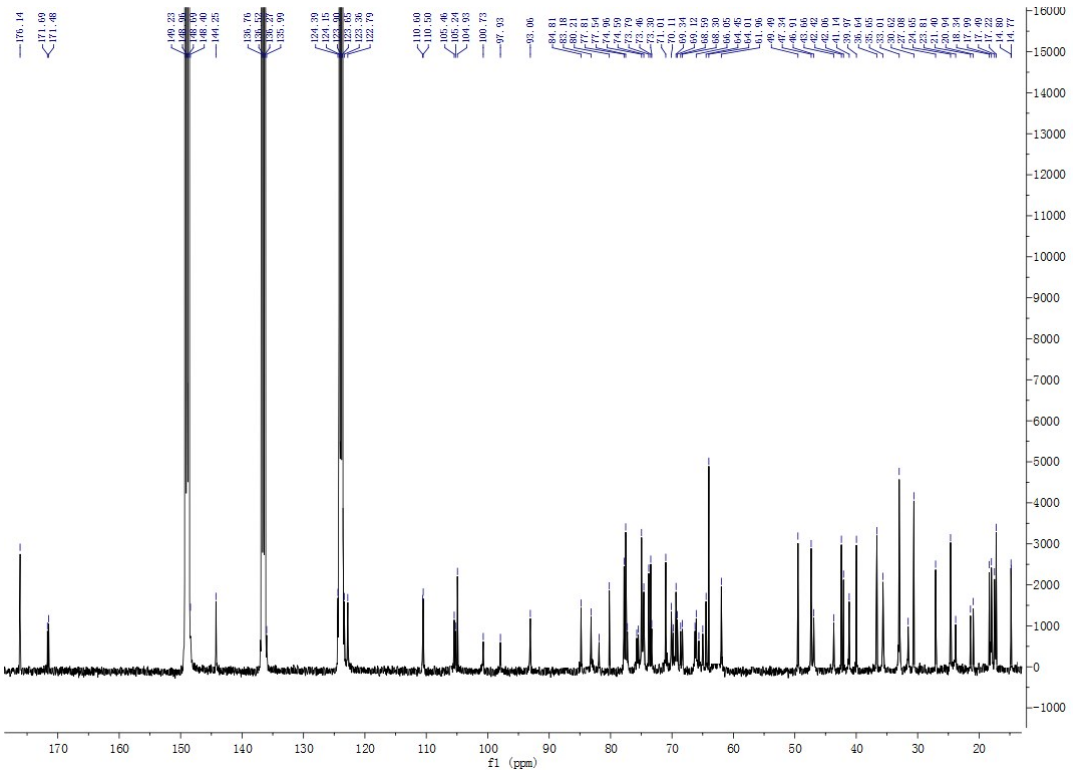


Figure S33. The ^{13}C NMR Spectrum of Compound **11** in C_5D_5N (150 MHz)