

Supplementary materials An investigation of the anti-depressive properties of phenylpropanoids and flavonoids in *Hemerocallis citrina* Baroni

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The NMR data about the known compounds

(E)-p-coumaric acid (1), yellow oil, C₉H₈O₃. HR-ESI-MS (negative) m/z 163.0400 [M-H]⁻ (calcd. for 163.0395). UV (MeOH) λ_{\max} 226, 310 nm. ¹H-NMR (600 MHz, CD₃OD): δ_{H} 6.28 (1H, d, J = 15.9, H-8), 6.79 (2H, d, J = 8.6 Hz, H-3, 5), 7.44 (2H, d, J = 8.6 Hz, H-2, 6), 7.59 (1H, d, J = 15.9 Hz, H-7). ¹³C-NMR (150 MHz, CD₃OD): δ_{C} 116.1 (C-8), 116.8 (C-3, 5), 127.3 (C-1), 131.0 (C-2, 6), 146.3 (C-7), 161.1 (C-4), 171.4 (C-9).

(Z)-p-coumaric acid (2), yellow oil, C₉H₈O₃. ESI-MS (negative) m/z 163.00 [M-H]⁻. UV (MeOH) λ_{\max} 296 nm. ¹H-NMR (600 MHz, CD₃OD): δ_{H} 5.81 (1H, d, J = 12.7 Hz, H-8), 6.60 (1H, d, J = 12.7 Hz, H-7), 6.71 (2H, d, J = 8.4 Hz, H-3, 5), 7.54 (2H, d, J = 8.4 Hz, H-2, 6). ¹³C-NMR (150 MHz, CD₃OD): δ_{C} 115.8 (C-3, 5), 116.8 (C-8), 128.4 (C-1), 132.7 (C-2, 6), 139.1 (C-7), 159.2 (C-4).

3-O-(E)-p-coumaroylquinic acid (3), colorless oil, C₁₆H₁₈O₈. HR-ESI-MS (negative) m/z 337.0938 [M-H]⁻ (calcd. for 337.0923). UV (MeOH) λ_{\max} 226, 312 nm. ¹H-NMR (600 MHz, CD₃OD): δ_{H} 1.95 (1H, dd, J = 13.5, 10.0 Hz, H-6ax), 2.14 (2H, m, H-2eq, H-6eq), 2.20 (1H, dd, J = 14.8, 3.4 Hz, H-2ax), 3.63 (1H, dd, J = 8.5, 3.4 Hz, H-4), 4.15 (1H, m, H-5), 5.35 (1H, dd, J = 7.6, 3.6 Hz, H-3), 6.36 (1H, d, J = 16.0 Hz, H-8'), 6.80 (2H, d, J = 8.6 Hz, H-3', 5'), 7.45 (2H, d, J = 8.6 Hz, H-2', 6'), 7.65 (1H, d, J = 16.0 Hz, H-7'). ¹³C-NMR (150 MHz, CD₃OD): δ_{C} 36.7 (C-2), 41.5 (C-6), 68.3 (C-5), 73.0 (C-3), 74.8 (C-4), 75.4 (C-1), 115.9 (C-8'), 116.8 (C-3', 5'), 127.4 (C-1'), 131.1 (C-2', 6'), 146.4 (C-7'), 161.1 (C-4'), 169.0 (C-9'), 178.3 (C-7).

3-O-(Z)-p-coumaroylquinic acid (4), colorless oil, C₁₆H₁₈O₈. HR-ESI-MS (negative) m/z 337.0935 [M-H]⁻ (calcd. for 337.0923). UV (MeOH) λ_{\max} 306 nm. ¹H-NMR (600 MHz, CD₃OD): δ_{H} 1.95-2.20 (4H, m, H-2, 6), 3.64 (1H, dd, J = 3.3, 8.2 Hz, H-4), 4.08 (1H, m, H-3), 5.31 (1H, dd, J = 7.9, 3.7 Hz, H-5), 5.83 (1H, d, J = 12.8 Hz, H-8'), 6.73 (2H, d, J = 8.7 Hz, H-3', 5'), 6.82 (1H, d, J = 12.9 Hz, H-7'), 7.68 (2H, d, J = 8.7 Hz, H-2', 6'). ¹³C-NMR (150 MHz, CD₃OD): δ_{C} 36.6 (C-6), 41.3 (C-2), 68.4 (C-3), 72.7 (C-4), 74.5 (C-5), 75.4 (C-1), 115.8 (C-3', 5'), 117.3 (C-8'), 127.7 (C-1'), 133.8 (C-2', 6'), 144.8 (C-7'), 160.0 (C-4'), 167.9 (C-9'), 178.4 (C-7).

3-O-(E)-p-coumaroylquinic acid methyl ester (5), white powder, C₁₇H₂₀O₈. UV (MeOH) λ_{\max} 226, 312 nm. ¹H-NMR (600 MHz, CD₃OD): δ_{H} 2.04 (1H, m, H-2ax), 2.10 (1H, m, H-2eq), 2.14 (1H, m, H-6eq), 2.24 (1H, dd, J = 14.0, 3.8 Hz, H-6ax), 3.70 (1H, dd, J = 7.7, 3.2 Hz, H-4), 3.75 (3H, s, H-8), 4.11 (1H, td, J = 8.2, 4.0 Hz, H-3), 5.35 (1H, m, H-5), 6.38 (1H, d, J = 15.9 Hz, H-8'), 6.82 (2H, d, J = 8.6 Hz, H-3', 5'), 7.48 (2H, d, J = 8.6 Hz, H-2', 6'), 7.67 (1H, d, J = 15.9 Hz, H-7'). ¹³C-NMR (150 MHz, CD₃OD): δ_{C} 36.4 (C-6), 40.8 (C-2), 52.9 (C-8), 68.6 (C-3), 72.6 (C-5), 73.8 (C-1), 75.3

(C-4), 115.8 (C-8'), 116.8 (C-3', 5'), 127.4 (C-1'), 131.1 (C-2', 6'), 146.5 (C-7'), 161.2 (C-4'), 168.9 (C-9'), 176.4 (C-7).

3-O-(Z)-p-coumaroylquinic acid methyl ester (6), white powder, C₁₇H₂₀O₈. ESI-MS (negative) *m/z* 351.16 [M-H]⁻. UV (MeOH) λ_{max} 210, 306 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 2.04 (1H, m, H-2ax), 2.10 (1H, m, H-2eq), 2.14 (1H, m, H-6eq), 2.24 (1H, dd, *J* = 14.0, 3.8 Hz, H-6ax), 3.69 (1H, dd, *J* = 7.3, 3.1 Hz, H-4), 3.73 (3H, s, H-8), 4.06 (1H, td, *J* = 7.7, 4.1 Hz, H-5), 5.32 (1H, m, H-3), 5.84 (1H, d, *J* = 12.8 Hz, H-8'), 6.74 (2H, d, *J* = 8.7 Hz, H-3', 5'), 6.84 (1H, d, 12.8, H-7'), 7.68 (2H, d, *J* = 8.7 Hz, H-2', 6'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 36.2 (C-6), 40.6 (C-2), 52.8 (C-8), 68.7 (C-5), 72.3 (C-3), 73.5 (C-1), 75.2 (C-4), 115.8 (C-8'), 117.2 (C-3', 5'), 127.7 (C-1'), 133.8 (C-2', 6'), 144.9 (C-7'), 160.0 (C-4'), 167.8 (C-9'), 176.4 (C-7).

3-O-(E)-p-coumaroylquinide (7), white powder, C₁₆H₁₆O₇. ESI-MS (negative) *m/z* 319.0821 [M-H]⁻ (calcd. for 319.0818). UV (MeOH) λ_{max} 228, 314 nm. ¹H-NMR (600 MHz, CD₃OD): 2.09 (1H, t, *J* = 11.6 Hz, H-2ax), 2.16 (1H, ddd, *J* = 2.6, 6.7, 11.5 Hz, H-2eq), 2.30 (1H, ddd, *J* = 2.7, 6.0, 11.5 Hz, H-6eq), 2.56 (1H, d, *J* = 11.6 Hz, H-6ax), 4.29 (1H, t, *J* = 4.6 Hz, H-4eq), 4.74 (1H, t, *J* = 5.4 Hz, H-5eq), 4.92 (1H, m, H-3ax), 6.36 (1H, d, *J* = 15.9 Hz, H-8'), 6.81 (2H, br d, *J* = 8.6 Hz, H-3', 5'), 7.47 (2H, br d, *J* = 8.6 Hz, H-2', 6'), 7.68 (1H, d, *J* = 16.0, H-7'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 36.9 (C-2), 37.8 (C-6), 64.8 (C-4), 70.2 (C-3), 73.0 (C-1), 77.6 (C-5), 114.8 (C-8'), 116.8 (C-3', 5'), 127.1 (C-1'), 131.2 (C-2', 6'), 147.2 (C-7'), 161.4 (C-4'), 168.0 (C-9'), 178.9 (C-7).

3-O-(Z)-p-coumaroylquinide (8), white powder, C₁₆H₁₆O₇. ESI-MS (negative) *m/z* 319.0824 [M-H]⁻ (calcd. for 319.0818). UV (MeOH) λ_{max} 310 nm. ¹H-NMR (600 MHz, CD₃OD): 2.03 (1H, t, *J* = 11.8 Hz, H-2ax), 2.12 (1H, ddd, *J* = 2.7, 6.9, 11.5 Hz, H-2eq), 2.29 (1H, ddd, *J* = 2.8, 6.0, 11.5 Hz, H-6eq), 2.53 (1H, d, *J* = 11.8 Hz, H-6ax), 4.28 (1H, t, *J* = 4.6 Hz, H-4eq), 4.72 (1H, t, *J* = 5.4 Hz, H-5eq), 4.88 (1H, m, H-3ax), 5.82 (1H, d, *J* = 12.8 Hz, H-8'), 6.76 (2H, br d, *J* = 8.7 Hz, H-3', 5'), 6.90 (1H, d, *J* = 12.8 Hz, H-7'), 7.68 (2H, br d, *J* = 8.4 Hz, H-2', 6'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 36.8 (C-2), 37.8 (C-6), 64.7 (C-4), 70.0 (C-3), 73.0 (C-1), 77.7 (C-5), 115.8 (C-3', 5'), 116.0 (C-8'), 127.5 (C-1'), 134.0 (C-2', 6'), 146.1 (C-7'), 160.3 (C-4'), 166.9 (C-9'), 178.9 (C-7).

4-O-(E)-p-coumaroylquinic acid (9), colorless oil, C₁₆H₁₈O₈. ESI-MS (negative) *m/z* 337.0931 [M-H]⁻ (calcd. for 337.0923). UV (MeOH) λ_{max} 228, 312 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 2.04 (1H, m, H-6eq), 2.05 (1H, m, H-2eq), 2.16 (1H, m, H-2ax), 2.18 (1H, m, H-6ax), 4.28 (1H, m, H-5), 4.30 (1H, m, H-3), 4.81 (1H, m, H-4), 6.45 (1H, d, *J* = 16.0 Hz, *J* H-8'), 6.83 (2H, d, = 8.5 Hz, H-3', 5'), 7.50 (2H, d, *J* = 8.4 Hz, H-2', 6'), 7.72 (1H, d, *J* = 15.9 Hz, H-7'). ¹³C-NMR (150 MHz, CD₃OD):

δ_c 38.7 (C-2), 42.4 (C-6), 65.9 (C-5), 69.5 (C-3), 77.0 (C-1), 79.2 (C-4), 115.5 (C-8'), 116.8 (C-3', 5'), 127.3 (C-1'), 131.2 (C-2', 6'), 146.7 (C-7'), 161.2 (C-4'), 169.0 (C-9'), 178.5 (C-7).

4-O-(Z)-p-coumaroylquinic acid (10), colorless oil, C₁₆H₁₈O₈. ESI-MS (negative) m/z 337.0928 [M-H]⁻ (calcd. for 337.0923). UV (MeOH) λ_{max} 308 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 2.00 (1H, dd, J = 10.8, 13.3 Hz, H-6ax), 2.05 (1H, m, H-2ax), 2.16 (1H, dd, J = 2.9, 14.5 Hz, H-2eq), 2.18 (1H, m, H-6eq), 4.24 (1H, m, H-3), 4.29 (1H, dd, J = 3.2, 7.0 Hz, H-5), 4.77 (1H, dd, J = 3.0 Hz, 9.3 Hz H-4), 5.91 (1H, d, J = 12.8 Hz, H-8'), 6.75 (2H, d, J = 8.7 Hz, H-3', 5'), 6.88 (1H, d, J = 12.8 Hz, H-7'), 7.70 (2H, d, J = 8.7 Hz, H-2', 6'). ¹³C-NMR (150 MHz, CD₃OD): δ_c 38.4 (C-2), 42.7 (C-6), 65.5 (C-5), 69.6 (C-3), 76.6 (C-1), 79.0 (C-4), 115.8 (C-3', 5'), 116.7 (C-8'), 127.6 (C-1'), 133.9 (C-2', 6'), 145.3 (C-7'), 160.1 (C-4'), 167.8 (C-9'), 177.3 (C-7).

5-O-(E)-p-coumaroylquinic acid (11), colorless oil, C₁₆H₁₈O₈. HR-ESI-MS (negative) m/z 337.0928 [M-H]⁻ (calcd. for 337.0923). UV (MeOH) λ_{max} 228, 312 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 1.95-2.22 (4H, m, H-2, 6), 3.72 (1H, dd, J = 2.2, 8.3 Hz, H-4), 4.17 (1H, brs, H-3), 5.35 (1H, m, H-5), 6.32 (1H, d, J = 16.0 Hz, H-8'), 6.80 (2H, d, J = 8.3 Hz, H-3', 5'), 7.46 (2H, d, J = 8.6 Hz, H-2', 6'), 7.62 (1H, d, J = 16.0 Hz, H-7'). ¹³C-NMR (150 MHz, CD₃OD): δ_c 38.3 (C-2), 39.2 (C-6), 71.8 (C-4), 72.1 (C-3), 73.8 (C-5), 76.8 (C-1), 115.4 (C-8'), 116.8 (C-3', 5'), 127.2 (C-1'), 131.2 (C-2', 6'), 146.6 (C-7'), 161.3 (C-4'), 168.8 (C-9').

Neochlorogenic acid (12), amorphous white powder, C₁₆H₁₈O₉. ESI-MS (negative) m/z 353.17 [M-H]⁻. UV (MeOH) λ_{max} 218, 240sh, 300sh, 326. ¹H-NMR (600 MHz, CD₃OD): δ_H 1.94-2.14 (4H, m, H-2ax, H-2eq, H-6ax, H-6eq), 3.69 (1H, m, H-4), 4.10 (1H, m, H-3), 5.37 (1H, m, H-5), 6.30 (1H, d, J = 15.8 Hz, H-7'), 6.77 (1H, d, J = 8.0 Hz, H-5'), 6.94 (1H, d, J = 7.7 Hz, H-6'), 7.05 (1H, s, H-2'), 7.56 (1H, d, J = 15.8 Hz, H-8'). ¹³C-NMR (150 MHz, CD₃OD): 36.9 (C-2), 40.8 (C-6), 68.8 (C-3), 72.8 (C-4), 74.3 (C-5), 75.7 (C-1), 115.1 (C-8'), 115.8 (C-2'), 116.5 (C-5'), 122.9 (C-6'), 128.0 (C-1'), 146.8 (C-7'), 146.8 (C-3'), 149.4 (C-4'), 168.9 (C-9'), 179.4 (COO-).

Crypto-chlorogenic acid (13), amorphous white powder, C₁₆H₁₈O₉. ESI-MS (negative) m/z 353.0875 [M-H]⁻ (calcd. for 353.0873). UV (MeOH) λ_{max} 218, 240, 302sh, 328 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 1.90-2.30 (4H, m, H-2ax, H-2eq, H-6ax, H-6eq), 4.29 (1H, m, H-5), 4.30 (1H, m, H-3), 4.80 (1H, dd, J = 2.8, 9.3 Hz, H-4), 6.36 (1H, d, J = 15.9 Hz, H-8'), 6.78 (1H, d, J = 8.2 Hz, H-5'), 6.96 (1H, dd, J = 1.6, 8.2 Hz, H-6'), 7.06 (1H, d, J = 1.6 Hz, H-2'), 7.64 (1H, d, J = 15.9 Hz, H-7'). ¹³C-NMR (150 MHz, CD₃OD): δ_c 38.4 (C-2), 42.7 (C-6), 65.6 (C-5), 69.6 (C-3), 76.7 (C-1), 79.3 (C-4), 115.2 (C-8'), 115.3 (C-2'), 116.5 (C-5'), 123.0 (C-6'), 127.8 (C-1'), 146.8 (C-3'), 147.1 (C-7'),

149.5 (C-4'), 169.0 (C-9'), 177.5(COO-).

chlorogenic acid (14), amorphous white powder, C₁₆H₁₈O₉. ESI-MS (negative) *m/z* 353.0883 [M-H]⁻ (calcd. for C₁₆H₁₇O₉, 353.0873). UV (MeOH) λ_{max} 218, 240sh, 300sh, 326 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 2.00-2.30 (4H, m, H-2ax, H-2eq, H-6ax, H-6eq), 3.73 (1H, dd, *J* = 3.0, 8.5 Hz, H-4), 4.17 (1H, m, H-3), 5.34 (1H, m, H-5), 6.26 (1H, d, *J* = 15.9 Hz, H-8'), 6.78 (1H, d, *J* = 8.2 Hz, H-5'), 6.95 (1H, dd, *J* = 1.9, 8.2 Hz, H-6'), 7.05 (1H, d, *J* = 1.9 Hz, H-2'), 7.56 (1H, d, *J* = 15.9 Hz, H-7'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 38.2 (C-2), 38.8 (C-6), 71.3 (C-3), 72.0 (C-5), 73.5 (C-4), 76.2 (C-1), 115.2 (C-2'), 115.2 (C-8'), 116.5 (C-5'), 123.0 (C-6'), 127.8 (C-1'), 146.8 (C-3'), 147.1 (C-7'), 149.5 (C-4'), 168.7 (C-9'), 177.1 (C-7).

3-O-(E)-feruloylquinic acid (15), amorphous white powder, C₁₇H₂₀O₉. ESI-MS (negative) *m/z* 367.25 [M-H]⁻. UV (MeOH) λ_{max} 218, 236, 324 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 1.95-2.18 (4H, m, H-2ax, H-2eq, H-6ax, H-6eq), 3.79 (1H, m, H-4), 3.88 (3H, s, H-8), 4.01 (1H, m, H-3), 5.42 (1H, m, H-5), 6.38 (1H, d, *J* = 15.8 Hz, H-8'), 6.80 (1H, d, *J* = 8.0 Hz, H-5'), 7.05 (1H, d, *J* = 8.0 Hz, H-6'), 7.17 (1H, s, H-2'), 7.65 (1H, d, *J* = 15.8 Hz, H-7'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 37.1 (C-2), 37.2 (C-6), 56.4 (-OCH₃), 69.9 (C-3), 72.4 (C-5), 73.4 (C-4), 76.6 (C-1), 111.8 (C-2'), 116.0 (C-8'), 116.5 (C-5'), 124.0 (C-6'), 127.9 (C-1'), 146.8 (C-3'), 149.3 (C-7'), 150.5 (C-4'), 168.7 (C-9').

Quercetin (16), amorphous yellow powder, C₁₅H₁₀O₇. ESI-MS (negative) *m/z* 301.0358 [M-H]⁻ (calcd. for 301.0348). UV (MeOH) λ_{max} 256, 372 nm. ¹H-NMR (600 MHz, DMSO-*d*₆): δ_H 6.19 (1H, s, H-6), 6.41 (1H, s, H-8), 6.88 (1H, d, *J* = 8.5, H-5'), 7.54 (1H, dd, *J* = 8.4, 2.0, H-6'), 7.68 (1H, d, *J* = 2.0, H-2'), 12.50 (1H, s, 5-OH). ¹³C-NMR (150 MHz, DMSO-*d*₆): δ_C 93.4 (C-8), 98.2 (C-6), 103.0 (C-10), 115.0 (C-2'), 115.6 (C-5'), 120.0 (C-6'), 122.0 (C-1'), 135.8 (C-3), 145.1 (C-3'), 146.8 (C-2), 147.7 (C-4'), 156.2 (C-9), 160.7 (C-5), 164.0 (C-7), 175.9 (C-4).

Quercetin-3-O-α-L-arabinopyranoside (17), amorphous yellow powder, C₂₀H₁₈O₁₁. ESI-MS (negative) *m/z* 433.0770 [M-H]⁻ (calcd. for 433.0771). UV (MeOH) λ_{max} 256, 356 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.45 (1H, dd, *J* = 2.7, 13.4 Hz, H-5), 3.66 (1H, dd, *J* = 3.0, 8.5 Hz, H-3''), 3.82 (1H, m, H-5''), 3.84 (1H, m, H-4''), 3.91 (1H, dd, *J* = 6.7, 8.3 Hz, H-2''), 5.13 (1H, d, *J* = 6.6 Hz, H-1''), 6.23 (1H, d, *J* = 2.0 Hz, H-6), 6.43 (1H, brs, H-8), 6.90 (1H, d, *J* = 8.5 Hz, H-5'), 7.58 (1H, dd, *J* = 2.0, 8.5 Hz, H-6'), 7.75 (1H, d, *J* = 2.0 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 67.0 (C-5''), 69.1 (C-4''), 72.8 (C-2''), 74.0 (C-3''), 94.8 (C-8), 100.0 (C-6), 104.5 (C-1''), 105.6 (C-10), 116.3 (C-5'), 117.5 (C-2'), 122.8 (C-1'), 123.1 (C-6'), 135.5 (C-3), 145.9 (C-3'), 149.9 (C-4'), 158.4 (C-2), 158.8 (C-9), 162.8 (C-5), 166.0 (C-7), 179.5 (C-4).

Quercetin-3-O-β-D-galactoside (18), amorphous yellow powder, C₂₁H₂₀O₁₂. HR-ESI-MS (positive) m/z 487.0827 [M+Na]⁺ (calcd. for 487.0852). UV (MeOH) λ_{max} 256, 354 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.47 (1H, t, J = 6.1 Hz, H-5''), 3.55 (2H, m, H-3'', 6''b), 3.64 (1H, dd, J = 6.0, 11.2 Hz, 6''a), 3.82 (1H, dd, J = 8.0, 9.5 Hz, H-2''), 3.85 (1H, d, J = 3.1 Hz, H-4''), 5.17 (1H, d, J = 7.8 Hz, H-1''), 6.20 (1H, d, J = 1.8 Hz, H-6), 6.40 (1H, d, J = 1.8 Hz, H-8), 6.86 (1H, d, J = 8.5 Hz, H-5'), 7.59 (H, dd, J = 8.5, 2.0 Hz, H-6'), 7.84 (1H, d, J = 2.0 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 61.9 (C-6''), 70.0 (C-4''), 73.2 (C-2''), 75.1 (C-3''), 77.2 (C-5''), 94.7 (C-8), 99.9 (C-6), 105.4 (C-1''), 105.6 (C-10), 116.1 (C-2'), 117.8 (C-5'), 122.9 (C-1', 6'), 135.8 (C-3), 145.8 (C-4'), 150.0 (C-3'), 158.5 (C-2), 158.8 (C-9), 163.0 (C-5), 166.1 (C-7), 179.5 (C-4).

Quercetin-3-O-β-D-glucoside (19), amorphous yellow powder, C₂₁H₂₀O₁₂. HR-ESI-MS (positive) m/z 487.0837 [M+Na]⁺ (calcd. for 487.0852). UV (MeOH) λ_{max} 256, 354 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.22 (1H, ddd, J = 2.1, 5.3, 9.4 Hz, H-5''), 3.34 (1H, t, J = 9.9 Hz, H-4''), 3.42 (1H, t, J = 8.9 Hz, H-3''), 3.47 (1H, dd, J = 7.9, 8.9 Hz, H-2''), 3.57 (1H, dd, J = 5.3, 11.9 Hz, H-6''b), 3.71 (1H, dd, J = 2.1, 11.9 Hz, H-6''a), 5.25 (1H, d, J = 7.7 Hz, H-1''), 6.20 (1H, s, H-6), 6.39 (1H, s, H-8), 6.86 (1H, d, J = 8.4 Hz, H-5'), 7.59 (H, dd, J = 8.4, 1.9 Hz, H-6'), 7.71 (1H, d, J = 1.9 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 62.5 (C-6''), 71.2 (C-4''), 75.7 (C-2''), 78.1 (C-3''), 78.4 (C-5''), 94.7 (C-8), 99.9 (C-6), 104.3 (C-1''), 105.7 (C-10), 116.0 (C-2'), 117.5 (C-5'), 123.1 (C-6'), 123.2 (C-1'), 135.6 (C-3), 145.9 (C-4'), 149.9 (C-3'), 158.5 (C-2), 159.0 (C-9), 163.1 (C-5), 166.1 (C-7), 179.5 (C-4).

Quercetin-3-O-rutinoside (20), amorphous yellow powder, C₂₇H₃₀O₁₆. ESI-MS (negative) m/z 609.1465 [M-H]⁻ (calcd. for 609.1456). UV (MeOH) λ_{max} 256, 354 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 1.12 (3H, d, J = 6.2 Hz, H-6''' CH₃), 3.27 (1H, m, H-4''), 3.29 (1H, m, H-4'''), 3.34 (1H, m, H-5''), 3.39 (1H, m, H-6''b), 3.40 (1H, m, H-3''), 3.45 (1H, m, H-5'''), 3.48 (1H, m, H-2''), 3.55 (1H, dd, J = 3.4, 9.5 Hz, H-3'''), 3.65 (1H, dd, J = 1.2, 2.9 Hz, H-2'''), 3.81 (1H, d, J = 11 Hz, H-6''a), 4.51 (1H, s, H-1'''), 5.10 (1H, d, J = 7.6 Hz, H-1''), 6.20 (1H, s, H-6), 6.38 (1H, s, H-8), 6.87 (1H, d, J = 8.4 Hz, H-5'), 7.62 (1H, dd, J = 2.0, 8.4 Hz, H-6'), 7.67 (1H, d, J = 2.0 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 17.9 (C-6'''), 68.5 (C-6''), 69.7 (C-5'''), 71.3 (C-4''), 72.1 (C-2'''), 72.2 (C-3'''), 73.9 (C-4'''), 75.7 (C-2''), 77.2 (C-5''), 78.1 (C-3''), 94.9 (C-8), 99.9 (C-6), 102.4 (C-1'''), 104.7 (C-1''), 105.6 (C-10), 116.0 (C-2'), 117.7 (C-5'), 123.1 (C-1'), 123.6 (C-6'), 135.6 (C-3), 145.8 (C-4'), 149.8 (C-3'), 158.5 (C-2), 159.3 (C-9), 162.9 (C-5), 166.0 (C-7), 179.3 (C-4).

Quercetin-3-O-α-L-rhamnopyranosyl-(1→6)-β-D-galactopyranoside (21), amorphous yellow

powder, C₂₇H₃₀O₁₆. ESI-MS (negative) m/z 609.44 [M-H]⁻. UV (MeOH) λ_{\max} 256, 354 nm. ¹H-NMR (600 MHz, CD₃OD): δ_{H} 1.19 (3H, d, J = 6.2 Hz, H-6'''), 3.29 (1H, m, H-4'''), 3.41 (1H, m, H-6'' b), 3.49 (1H, m, H-3'''), 3.53 (1H, dd, J = 9.5, 3.4 Hz, H-5'''), 3.56 (1H, m, H-3''), 3.58 (1H, m, H-2'''), 3.65 (1H, m, H-5''), 3.74 (1H, dd, J = 10.1, 5.7 Hz, H-6''a), 3.79 (1H, m, H-4''), 3.82 (1H, m, H-2''), 4.53 (1H, s, H-1'''), 5.07 (1H, d, J = 7.8 Hz, H-1''), 6.21 (1H, d, J = 1.8 Hz, H-6), 6.40 (1H, d, J = 1.8 Hz, H-8), 6.87 (1H, d, J = 8.4 Hz, H-5'), 7.59 (1H, dd, J = 8.4, 1.8 Hz, H-6'), 7.87 (1H, d, J = 1.9 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_{C} 18.0 (C-6'''), 67.3 (C-6''), 69.7 (C-5'''), 70.2 (C-4'''), 72.0 (C-2'''), 72.3 (C-3'''), 73.1 (C-2''), 73.9 (C-4'''), 75.1 (C-3''), 75.3 (C-5''), 94.8 (C-8), 100.0 (C-6), 101.9 (C-1'''), 105.5 (C-10), 106.0 (C-1''), 116.1 (C-5'), 117.9 (C-2'), 122.8 (C-1'), 123.0 (C-6'), 135.9 (C-3), 145.7 (C-3'), 150.0 (C-4'), 158.5 (C-2), 159.0 (C-9), 162.9 (C-5), 166.2 (C-7), 179.5 (C-4).

Quercetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside] (**22**), amorphous yellow powder, C₃₃H₄₀O₂₀. ESI-MS (negative) m/z 755.32 [M-H]⁻. UV (MeOH) λ_{\max} 256, 354 nm. ¹H-NMR (600 MHz, CD₃OD): δ_{H} 1.01 (3H, d, J = 6.2 Hz, H-6'''), 1.08 (3H, d, J = 6.2 Hz, H-6''''), 3.24 (1H, t, J = 9.5 Hz, H-4''''), 3.28 (1H, t, J = 9.5 Hz, H-4'''), 3.34 (1H, m, H-5'''), 3.35 (1H, m, H-4''), 3.40 (1H, m, H-6b''), 3.43 (1H, m, H-5''''), 3.49 (1H, dd, J = 9.5, 3.3 Hz, H-3''''), 3.54 (1H, t, J = 8.9 Hz, H-3''), 3.59 (1H, brs, H-2''''), 3.64 (1H, dd, J = 8.9, 7.9 Hz, H-2''), 3.80 (1H, m, H-3'''), 3.82 (1H, m, H-6a''), 4.00 (1H, brs, H-2'''), 4.08 (1H, dd, J = 9.3, 6.2 Hz, H-5'''), 4.51 (1H, brs, H-1''''), 5.22 (1H, brs, H-1'''), 5.59 (1H, d, J = 7.8 Hz, H-1''), 6.18 (1H, d, J = 1.8 Hz, H-6), 6.37 (1H, d, J = 1.8 Hz, H-8), 6.87 (1H, d, J = 8.2 Hz, H-5'), 7.59 (1H, dd, J = 8.2, 2.0 Hz, H-6'), 7.61 (1H, d, J = 2.0 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_{C} 17.5 (C-6'''), 17.9 (C-6''''), 68.3 (C-6''), 69.8 (C-5''''), 70.0 (C-5'''), 71.9 (C-4'''), 72.2 (C-2''''), 72.3 (C-3'''), 72.4 (C-2'''), 73.9 (C-4''''), 74.1 (C-4'''), 77.1 (C-5''), 78.9 (C-3''), 80.1 (C-2''), 94.7 (C-8), 99.8 (C-6), 100.5 (C-1''), 102.3 (C-1'''), 102.7 (C-1'''), 105.9 (C-10), 116.1 (C-5'), 117.4 (C-2'), 123.5 (C-1'), 123.6 (C-6'), 134.5 (C-3), 146.0 (C-3'), 149.6 (C-4'), 158.5 (C-9), 159.0 (C-2), 163.1 (C-5), 165.7 (C-7), 179.3 (C-4).

Quercetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-galactopyranoside] (**23**), amorphous yellow powder, C₃₃H₄₀O₂₀. ESI-MS (negative) m/z 755.35 [M-H]⁻. UV (MeOH) λ_{\max} 256, 354 nm. ¹H-NMR (600 MHz, CD₃OD): 0.95 (3H, d, J = 6.2 Hz, H-6'''), 1.18 (3H, d, J = 6.3 Hz, H-6''''), 3.22-4.10 (14H, sugar-H), 4.54 (1H, d, J = 1.2 Hz, H-1''''), 5.21 (1H, brs, H-1'''), 5.66 (1H, d, J = 7.8 Hz, H-1''), 6.18 (1H, brs, H-6), 6.37 (1H, brs, H-8), 6.87 (1H, d, J = 8.5 Hz, H-5'), 7.56 (1H, dd, J = 2.0, 8.5 Hz, H-6'), 7.69 (1H, d, J = 2.0 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_{C} 17.4 (C-6'''), 18.0 (C-6''''), 67.0 (C-6''), 69.7 (C-5''''), 69.8 (C-5'''), 70.9 (C-4''), 72.1 (C-

2'''), 72.3 (C-3'''), 72.3 (C-3'''), 72.4 (C-2'''), 73.9 (C-4'''), 74.1 (C-4'''), 75.3 (C-5''), 75.7 (C-3''), 77.5 (C-2''), 94.6 (C-8), 99.8 (C-6), 101.0 (C-1''), 101.9 (C-1'''), 102.6 (C-1'''), 105.8 (C-10), 116.1 (C-5'), 117.3 (C-2'), 123.0 (C-6'), 123.3 (C-1'), 134.5 (C-3), 145.9 (C-3'), 149.6 (C-4'), 158.4 (C-9), 158.4 (C-2), 163.1 (C-5), 165.8 (C-7), 179.3 (C-4).

Isorhamnetin (**24**), amorphous yellow powder, C₁₆H₁₂O₇. HR-ESI-MS (negative) *m/z* 315.0515 [M-H]⁻ (calcd. for 315.0505). UV (MeOH) λ_{max} 254, 372 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.94 (3H, s, -OCH₃), 6.19 (1H, d, *J* = 2.0 Hz, H-6), 6.43 (1H, d, *J* = 2.0 Hz, H-8), 6.93 (1H, d, *J* = 8.5 Hz, H-5'), 7.73 (1H, dd, *J* = 8.4, 2.0 Hz, H-6'), 7.86 (1H, d, *J* = 2.0 Hz, H-2'). ¹³C-NMR (150 MHz, DMSO-*d*₆): δ_C 55.8 (-OCH₃), 93.7 (C-8), 98.3 (C-6), 103.1 (C-10), 111.7 (C-2'), 115.6 (C-5'), 121.8 (C-6'), 122.0 (C-1'), 135.9 (C-3), 146.7 (C-4'), 147.5 (C-2), 148.9 (C-3'), 156.3 (C-9), 160.8 (C-5), 164.1 (C-7), 176.0 (C-4).

Isorhamnetin-3-O-β-D-galactopyranoside (**25**), amorphous yellow powder, C₂₂H₂₂O₁₂. ESI-MS (negative) *m/z* 477.23 [M-H]⁻. UV (MeOH) λ_{max} 256, 352 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.47 (1H, t, *J* = 6.3 Hz, H-5''), 3.56 (2H, m, H-3'', 6''a), 3.65 (1H, dd, *J* = 5.8, 11.2 Hz, H-6''b), 3.81 (1H, dd, *J* = 7.8, 9.7 Hz, H-2''), 3.84 (1H, d, *J* = 2.8 Hz, H-4''), 3.96 (3H, s, 3'-OCH₃), 5.33 (1H, d, *J* = 7.7 Hz, Gal H-1), 6.21 (1H, d, *J* = 2.0 Hz, H-6), 6.41 (1H, d, *J* = 2.0 Hz, H-8), 6.90 (1H, d, *J* = 8.5 Hz, H-5'), 7.58 (H, dd, *J* = 8.5, 2.0 Hz, H-6'), 8.03 (1H, d, *J* = 2.0 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 57.0 (-OCH₃), 62.2 (C-6''), 70.0 (C-4''), 73.2 (C-2''), 75.0 (C-3''), 77.3 (C-5''), 94.7 (C-8), 99.9 (C-6), 104.4 (C-1''), 105.8 (C-10), 114.5 (C-2'), 115.9 (C-5'), 123.0 (C-1'), 123.6 (C-6'), 135.4 (C-3), 148.4 (C-3'), 150.8 (C-4'), 158.5 (C-2), 158.6 (C-9), 163.1 (C-5), 166.0 (C-7), 179.5 (C-4).

Isorhamnetin-3-O-β-D-glucopyranoside (**26**), amorphous yellow powder, C₂₂H₂₂O₁₂. ESI-MS (negative) *m/z* 477.1054 [M-H]⁻ (calcd. for 477.1033). UV (MeOH) λ_{max} 254, 354 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.24 (1H, m, H-5''), 3.33 (1H, brs, H-4''), 3.44 (1H, m, H-3''), 3.46 (1H, m, H-2''), 3.56 (1H, dd, *J* = 5.5, 11.9 Hz, H-6''b), 3.74 (1H, dd, *J* = 2.0, 11.9 Hz, H-6''a), 3.94 (3H, s, 3'-OCH₃), 5.40 (1H, d, *J* = 7.3 Hz, H-1''), 6.19 (1H, s, H-6), 6.38 (1H, s, H-8), 6.89 (1H, d, *J* = 8.5 Hz, H-5'), 7.57 (1H, dd, *J* = 8.5, 1.0 Hz, H-6'), 7.92 (1H, d, *J* = 1.0 Hz, H-2'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 56.8 (-OCH₃), 62.5 (C-6''), 71.5 (C-4''), 75.9 (C-2''), 78.0 (C-5''), 78.5 (C-3''), 94.7 (C-8), 99.9 (C-6), 103.6 (C-1''), 105.8 (C-10), 114.3 (C-2'), 116.0 (C-5'), 123.1 (C-1'), 123.8 (C-6'), 135.3 (C-3), 148.4 (C-4'), 150.8 (C-3'), 158.4 (C-2), 158.6 (C-9), 163.1 (C-5), 166.0 (C-7), 179.4 (C-4).

Isorhamnetin-3-O-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (**27**), amorphous yellow powder, C₂₈H₃₂O₁₆. HR-ESI-MS (positive) *m/z* 647.1564 [M+Na]⁺ (calcd. for 647.1588). UV (MeOH)

λ_{\max} 254, 356 nm. $^1\text{H-NMR}$ (600 MHz, CD_3OD): δ_{H} 1.10 (3H, d, $J = 6.2$ Hz, H-6'''), 3.22-3.52 (8H, m, H-2'', 3'', 4'', 5'', 6b''), 3.63 (1H, brs, H-2'''), 3.81 (1H, d, $J = 11.0$, H-6a''), 3.94 (3H, s, 3'-OCH₃), 4.53 (1H, brs, H-1'''), 5.23 (1H, d, $J = 6.8$ Hz, H-1''), 6.19 (1H, s, H-6), 6.38 (1H, s, H-8), 6.90 (1H, d, $J = 7.4$ Hz, H-5'), 7.60 (1H, d, $J = 7.4$ Hz, H-6'), 7.94 (1H, s, H-2'). $^{13}\text{C-NMR}$ (150 MHz, CD_3OD): δ_{C} 17.9 (C-6'''), 56.7 (-OCH₃), 68.5 (C-6''), 69.7 (C-5'''), 71.6 (C-4''), 72.0 (C-3'''), 72.2 (C-2'''), 73.8 (C-4'''), 75.9 (C-2''), 77.3 (C-5''), 78.1 (C-3''), 94.9 (C-8), 99.9 (C-6), 102.5 (C-1'''), 104.4 (C-1''), 105.6 (C-10), 114.5 (C-2'), 116.0 (C-5'), 122.9 (C-6'), 123.9 (C-1'), 135.4 (C-3), 148.2 (C-3'), 150.8 (C-4'), 158.4 (C-2), 158.8 (C-9), 162.9 (C-5), 166.0 (C-7), 179.2 (C-4).

Isorhamnetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-galactopyranoside] (**28**), amorphous yellow powder, $\text{C}_{34}\text{H}_{42}\text{O}_{20}$. ESI-MS (positive) m/z 793.2132 $[\text{M}+\text{Na}]^+$ (calcd. for 793.2167). UV (MeOH) λ_{\max} 254, 354 nm. $^1\text{H-NMR}$ (600 MHz, CD_3OD): δ_{H} 0.88 (3H, d, $J = 6.2$ Hz, H-6'''), 1.17 (1H, d, $J = 6.3$ Hz, H-6'''), 3.00-4.10 (14H, m, H-2'', H-3'', H-4'', H-5'', H-6''a, H-6''b, H-2''', H-3''', H-4''', H-5''', H-2'''', H-3'''', H-4'''', H-5'''), 4.00 (3H, s, 3'-OCH₃), 4.56 (1H, d, $J = 1.5$ Hz, H-1'''), 5.16 (1H, s, H-1''), 5.79 (1H, d, $J = 7.8$ Hz, H-1'), 6.18 (1H, d, $J = 1.6$ Hz, H-6), 6.38 (1H, brs, H-8), 6.91 (1H, d, $J = 8.4$ Hz, H-5'), 7.52 (1H, dd, $J = 1.8, 8.4$ Hz, H-6'), 8.07 (1H, d, $J = 1.8$ Hz, H-2'). $^{13}\text{C-NMR}$ (150 MHz, CD_3OD): δ_{C} 17.4 (C-6'''), 18.0 (C-6'''), 57.2 (-OCH₃), 67.1 (C-6''), 69.7 (C-5'''), 69.8 (C-5'''), 70.5 (C-4''), 72.1 (C-2'''), 72.3 (C-3'''), 72.4 (C-3'''), 72.4 (C-2'''), 73.8 (C-4'''), 74.0 (C-4'''), 75.4 (C-5''), 75.6 (C-3''), 77.8 (C-2''), 94.6 (C-8), 99.7 (C-6), 100.8 (C-1''), 101.8 (C-1'''), 102.8 (C-1'''), 105.9 (C-10), 114.6 (C-2'), 115.9 (C-5'), 123.2 (C-6'), 123.3 (C-1'), 134.3 (C-3), 148.4 (C-3'), 150.5 (C-4'), 158.4 (C-2), 158.4 (C-9), 163.3 (C-5), 165.7 (C-7), 179.3 (C-4).

Isorhamnetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside] (**29**), amorphous yellow powder, $\text{C}_{34}\text{H}_{42}\text{O}_{20}$. ESI-MS (negative) m/z 769.2219 $[\text{M}-\text{H}]^-$ (calcd. for 769.2191). UV (MeOH) λ_{\max} 254, 354 nm. $^1\text{H-NMR}$ (600 MHz, CD_3OD): δ_{H} 0.92 (3H, d, $J = 6.2$ Hz, H-6'''), 1.07 (3H, d, $J = 6.3$ Hz, H-6'''), 3.32 (1H, brs, H-4'''), 3.24 (1H, t, $J = 9.4$ Hz, H-4'''), 3.25 (1H, m, H-4''), 3.39 (1H, m, H-5''), 3.40 (1H, m, H-5'''), 3.45 (1H, m, H-6''b), 3.52 (1H, m, H-3'''), 3.58 (1H, m, H-3''), 3.59 (1H, m, H-2'''), 3.64 (1H, m, H-2''), 3.78 (1H, m, H-3''), 3.83 (1H, m, H-6''a), 3.97 (3H, s, -OCH₃), 4.00 (1H, brs, H-2'''), 4.04 (1H, dd, $J = 6.2, 9.7$ Hz, H-5'''), 4.54 (1H, d, $J = 1.5$ Hz, H-1'''), 5.19 (1H, d, $J = 1.0$ Hz, H-1''), 5.73 (1H, d, $J = 7.7$ Hz, H-1'), 6.19 (1H, d, $J = 1.8$ Hz, H-6), 6.39 (1H, d, $J = 1.8$ Hz, H-8), 6.92 (1H, d, $J = 8.5$ Hz, H-5'), 7.58 (1H, dd, $J = 2.0, 8.4$ Hz, H-6'), 7.94 (1H, d, $J = 2.0$ Hz, H-2'). $^{13}\text{C-NMR}$ (150 MHz, CD_3OD): δ_{C} 17.4 (C-6'''), 17.8

(C-6'''), 57.0 (3'-OCH₃), 68.2 (C-6''), 69.8 (C-5'''), 69.9 (C-5''), 72.0 (C-4''), 72.1 (C-2'''), 72.3 (C-3'''), 72.3 (C-3''), 72.4 (C-2''), 73.8 (C-4'''), 73.9 (C-4''), 77.2 (C-5'), 78.8 (C-3''), 80.1 (C-2''), 94.7 (C-8), 99.8 (C-6), 100.5 (C-1''), 102.4 (C-1'''), 102.7 (C-1'), 105.9 (C-10), 114.5 (C-2'), 116.1 (C-5'), 123.3 (C-1'), 123.7 (C-6'), 134.3 (C-3), 148.4 (C-3'), 150.6 (C-4'), 158.4 (C-9), 158.5 (C-2), 163.2 (C-5), 165.7 (C-7), 179.2 (C-4).

Kaempferol (**30**), amorphous yellow powder, C₁₅H₁₀O₆. ESI-MS (negative) *m/z* 285.0404 [M-H]⁻ (calcd. for 285.0399). UV (MeOH) λ_{max} 266, 366 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 6.18 (1H, s, H-6), 6.40 (1H, s, H-8), 6.90 (2H, d, *J* = 8.5 Hz, H-3', 5'), 8.09 (2H, d, *J* = 8.5 Hz, H-2', 6'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 94.4 (C-8), 99.3 (C-6), 104.5 (C-10), 116.3 (C-3', 5'), 123.8 (C-1'), 130.7 (C-2', 6'), 137.4 (C-3), 148.1 (C-2), 158.3 (C-9), 160.5 (C-4'), 162.5 (C-5), 165.6 (C-7), 177.5 (C-4).

Kaempferol-3-O-α-L-arabinoside (**31**), amorphous yellow powder, C₂₀H₁₈O₁₀. HR-ESI-MS (negative) *m/z* 417.0821 [M-H]⁻ (calcd. for 417.0822). UV (MeOH) λ_{max} 266, 366 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.40 (1H, d, *J* = 11.0 Hz, H-5''a), 3.63 (1H, dd, *J* = 2.3, 8.1 Hz, H-3''), 3.78 (1H, m, H-5''b), 3.79 (1H, brs, H-4''), 3.89 (1H, dd, *J* = 6.7, 8.0 Hz, H-2''), 5.13 (1H, d, *J* = 6.3 Hz, H-1''), 6.20 (1H, s, H-6), 6.39 (1H, s, H-8), 6.88 (2H, d, *J* = 8.5 Hz, H-3', 5'), 8.05 (2H, d, *J* = 8.5 Hz, H-2', 6'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 66.8 (C-5''), 68.9 (C-4''), 72.8 (C-2''), 74.0 (C-3''), 94.7 (C-8), 99.9 (C-6), 104.4 (C-1''), 105.7 (C-10), 116.2 (C-3', C-5'), 122.6 (C-1'), 132.3 (C-2', C-6'), 135.6 (C-3), 158.4 (C-2), 158.8 (C-9), 161.6 (C-4'), 163.0 (C-5), 166.0 (C-7), 179.6 (C-4).

Kaempferol-3-O-β-D-galactopyranoside (**32**), amorphous yellow powder, C₂₁H₂₀O₁₁. ESI-MS (negative) *m/z* 447.22 [M-H]⁻. UV (MeOH) λ_{max} 264, 346 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.44 (1H, t, *J* = 6.1 Hz, H-5''), 3.52 (2H, m, H-3'', 6''b), 3.62 (1H, dd, *J* = 5.9, 11.2 Hz, H-6''a), 3.78 (1H, dd, *J* = 8.2, 9.3 Hz, H-2''), 3.82 (1H, d, *J* = 2.8 Hz, H-4''), 5.13 (1H, d, *J* = 7.7 Hz, H-1''), 6.20 (1H, s, H-6), 6.40 (1H, s, H-8), 6.87 (1H, d, *J* = 8.7 Hz, H-3', 5'), 8.08 (2H, d, *J* = 8.7 Hz, H-2', 6'). ¹³C-NMR (150 MHz, CD₃OD): δ_C 62.0 (C-6''), 70.0 (C-4''), 73.0 (C-2''), 75.0 (C-3''), 77.1 (C-5''), 94.8 (C-8), 99.9 (C-6), 105.0 (C-1''), 105.7 (C-10), 116.1 (C-3', 5'), 122.7 (C-1'), 132.4 (C-2', 6'), 135.6 (C-3), 158.5 (C-9), 159.1 (C-2), 161.6 (C-4'), 163.1 (C-5), 166.1 (C-7), 179.7 (C-4).

Kaempferol-3-O-β-D-glucopyranoside (**33**), amorphous yellow powder, C₂₁H₂₀O₁₁. HR-ESI-MS (negative) *m/z* 447.0931 [M-H]⁻ (calcd. for 447.0927). UV (MeOH) λ_{max} 264, 348 nm. ¹H-NMR (600 MHz, CD₃OD): δ_H 3.20 (1H, ddd, *J* = 2.1, 5.5, 9.1 Hz, H-5''), 3.34 (1H, brs, H-4''), 3.44 (1H, m, H-2''), 3.41 (1H, t, *J* = 9.2 Hz, H-3''), 3.52 (1H, dd, *J* = 5.5, 11.8 Hz, H-6''b), 3.69 (1H, dd, *J* = 2.1, 11.8

Hz, H-6''a), 5.25 (1H, d, $J = 7.3$ Hz, H-1''), 6.20 (1H, s, H-6), 6.40 (1H, s, H-8), 6.88 (2H, d, $J = 8.6$ Hz, H-3', 5'), 8.05 (2H, dd, $J = 8.6$ Hz, H-2', 6'). ^{13}C -NMR (150 MHz, CD_3OD): δ_{C} 62.6 (C-6''), 71.3 (C-4''), 75.7 (C-2''), 78.0 (C-3''), 78.4 (C-5''), 94.7 (C-8), 99.9 (C-6), 104.0 (C-1''), 105.7 (C-10), 116.1 (C-3', C-5'), 122.8 (C-1'), 132.3 (C-2', C-6'), 135.4 (C-3), 158.5 (C-2), 159.1 (C-9), 161.6 (C-4'), 163.1 (C-5), 166.0 (C-7), 179.5 (C-4).

Kaempferol-3-O-robinobioside (34), amorphous yellow powder, $\text{C}_{27}\text{H}_{30}\text{O}_{15}$. ESI-MS (negative) m/z 593.1534 $[\text{M}-\text{H}]^-$ (calcd. for 593.1507). UV (MeOH) λ_{max} 264, 346 nm. ^1H -NMR (600 MHz, CD_3OD): δ_{H} 1.18 (3H, d, $J = 6.2$ Hz, H-6'''), 3.38 (1H, dd, $J = 6.8, 10.1$ Hz, H-6''a), 3.49-3.79 (8H, H-2'', 3'', 4'', 5'', 2''', 3''', 4''', 5'''), 3.71 (1H, dd, $J = 5.7, 10.2$ Hz, H-6''b), 4.52 (1H, s, H-1'''), 5.04 (1H, d, $J = 7.8$ Hz, H-1''), 6.21 (1H, s, H-6), 6.40 (1H, s, H-8), 6.88 (2H, d, $J = 8.5$ Hz, H-3', 5'), 8.09 (2H, d, $J = 8.5$ Hz, H-2', H-6'). ^{13}C -NMR (150 MHz, CD_3OD): δ_{C} 18.0 (C-6'''), 67.4 (C-6''), 69.7 (C-5'''), 70.1 (C-4''), 72.0 (C-2''), 72.3 (C-3'''), 73.0 (C-2'''), 73.8 (C-4'''), 75.0 (C-3''), 75.3 (C-5''), 94.9 (C-8), 100.0 (C-6), 101.9 (C-1), 105.5 (C-1'), 105.6 (C-10), 116.1 (C-3', 5'), 122.6 (C-1'), 132.5 (C-2', 6'), 135.7 (C-3), 158.5 (C-2), 159.3 (C-9), 161.6 (C-4'), 163.0 (C-5), 166.1 (C-7), 179.6 (C-4).

Kaempferol-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (35), amorphous yellow powder, $\text{C}_{27}\text{H}_{30}\text{O}_{15}$. ESI-MS (negative) m/z 593.38 $[\text{M}-\text{H}]^-$. UV (MeOH) λ_{max} 264, 346 nm. ^1H -NMR (600 MHz, CD_3OD): δ_{H} 1.12 (3H, d, $J = 6.2$ Hz, H-6''' CH₃), 3.25 (1H, m, H-4''), 3.27 (1H, m, H-4'''), 3.32-3.46 (5H, m, H-2'', 3'', 5'', 6''b, H-5'''), 3.55 (1H, dd, $J = 3.4, 9.5$ Hz, H-3'''), 3.62 (1H, dd, $J = 1.6, 3.4$ Hz, H-2'''), 3.80 (1H, dd, $J = 1.5, 11$ Hz, H-6''a), 4.51 (1H, d, $J = 1.4$ Hz, H-1'''), 5.13 (1H, d, $J = 7.5$ Hz, H''-1), 6.21 (1H, d, $J = 2.0$ Hz, H-6), 6.41 (1H, d, $J = 2.0$ Hz, H-8), 6.89 (2H, d, $J = 9.0$ Hz, H-3', 5'), 8.06 (2H, d, $J = 9.0$ Hz, H-2', 6'). ^{13}C -NMR (150 MHz, CD_3OD): δ_{C} 18.0 (C-6'''), 68.6 (C-6''), 69.8 (C-5'''), 71.5 (C-4''), 72.1 (C-2'''), 72.3 (C-3'''), 73.9 (C-4'''), 75.8 (C-2''), 77.3 (C-5''), 78.2 (C-3''), 95.0 (C-8), 100.1 (C-6), 102.5 (C-1'''), 104.6 (C-1''), 105.7 (C-10), 116.2 (C-3', 5'), 122.8 (C-1'), 132.4 (C-2', 6'), 135.5 (C-3), 158.6 (C-2), 159.5 (C-9), 161.6 (C-5'), 163.1 (C-5), 166.3 (C-7), 179.5 (C-4).

Kaempferol-3-O-[α -L-rhamnopyranosyl-(1 \rightarrow 6)]-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-galactopyranoside (36), amorphous yellow powder, $\text{C}_{33}\text{H}_{40}\text{O}_{19}$. ESI-MS (negative): m/z 739.54 $[\text{M}-\text{H}]^-$. UV (MeOH) λ_{max} 264, 346 nm. ^1H -NMR (600 MHz, CD_3OD): δ_{H} 0.97 (3H, d, $J = 6.2$ Hz, H-6'''), 1.17 (3H, d, $J = 6.2$ Hz, H-6''''), 3.26 (1H, m, H-4''''), 3.49 (1H, m, H-3''''), 3.50 (1H, m, H-5''''), 3.34 (1H, m, H-4'''), 3.44 (1H, m, H-6''b), 3.55 (1H, m, H-2'''), 3.62 (1H, m, H-5''), 3.69 (1H, m, H-6''a), 3.72 (1H, m, H-3''), 3.76 (1H, m, H-3'''), 3.78 (1H, m, H-4''), 3.92 (1H, dd, $J = 7.9, 9.5$ Hz, H-2''),

3.99 (1H, m, H-2'''), 4.06 (1H, m, H-5'''), 4.52 (1H, s, H-1'''), 5.21 (1H, s, H-1'''), 5.60 (1H, d, $J = 7.7$ Hz, H-1''), 6.19 (1H, s, H-6), 6.38 (1H, s, H-8), 6.89 (2H, d, $J = 8.8$ Hz, H-3', 5'), 8.06 (2H, d, $J = 8.8$ Hz, H-2', 6'). ^{13}C -NMR (150 MHz, CD_3OD): δ_{C} 17.5 (C-6'''), 17.9 (C-6'''), 67.2 (C-6''), 69.7 (C-5'''), 69.8 (C-5''), 70.7 (C-4''), 72.1 (C-2'''), 72.3 (C-3'''), 72.3 (C-3''), 72.4 (C-2''), 73.9 (C-4'''), 74.1 (C-4''), 75.3 (C-5''), 75.7 (C-3''), 77.6 (C-2''), 94.7 (C-8), 99.8 (C-6), 100.9 (C-1''), 101.9 (C-1'''), 102.6 (C-1''), 105.9 (C-10), 116.2 (C-3', 5'), 123.0 (C-1'), 132.2 (C-2', 6'), 134.5 (C-3), 158.4 (C-9), 158.7 (C-2), 161.3 (C-4'), 163.2 (C-5), 165.7 (C-7), 179.4 (C-4).

Kaempferol-3-O-[\alpha-L-rhamnopyranosyl-(1→6)]-[\alpha-L-rhamnopyranosyl-(1→2)]-\beta-D-glucopyranoside (37), amorphous yellow powder, $\text{C}_{33}\text{H}_{40}\text{O}_{19}$. ESI-MS (negative): m/z 739.38 $[\text{M-H}]^-$. UV (MeOH) λ_{max} 264, 346 nm. ^1H -NMR (600 MHz, CD_3OD): δ_{H} 0.98 (3H, d, $J = 6.3$ Hz, H-6'''), 1.08 (3H, d, $J = 6.3$ Hz, H-6'''), 3.22-4.07 (15H, sugar-H), 4.50 (1H, brs, H-1'''), 5.20 (1H, brs, H-1'''), 5.60 (1H, d, $J = 7.6$ Hz, H-1''), 6.19 (1H, brs, H-6), 6.38 (1H, brs, H-8), 6.89 (2H, d, $J = 8.8$ Hz, H-3', 5'), 8.02 (2H, d, $J = 8.8$ Hz, H-2', 6'). ^{13}C -NMR (150 MHz, CD_3OD): δ_{C} 17.5 (C-6'''), 17.8 (C-6'''), 68.3 (C-6''), 69.7 (C-5'''), 69.9 (C-5''), 71.9 (C-4''), 72.1 (C-2'''), 72.3 (C-3'''), 72.3 (C-3''), 72.4 (C-2'''), 73.8 (C-4'''), 74.0 (C-4''), 77.1 (C-5''), 78.9 (C-3''), 79.9 (C-2''), 94.8 (C-8), 99.8 (C-6), 100.4 (C-1''), 102.3 (C-1''), 102.6 (C-1'''), 105.9 (C-10), 116.1 (C-3', 5'), 123.2 (C-1'), 132.1 (C-2', 6'), 134.3 (C-3), 158.5 (C-9), 159.0 (C-2), 161.2 (C-4'), 163.1 (C-5), 165.7 (C-7), 179.3 (C-4).

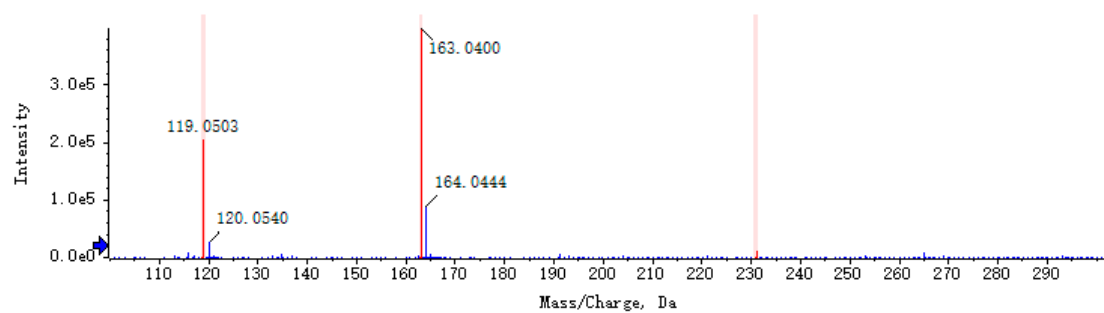


Figure S1. The HR-ESI-MS spectrum of compound 1

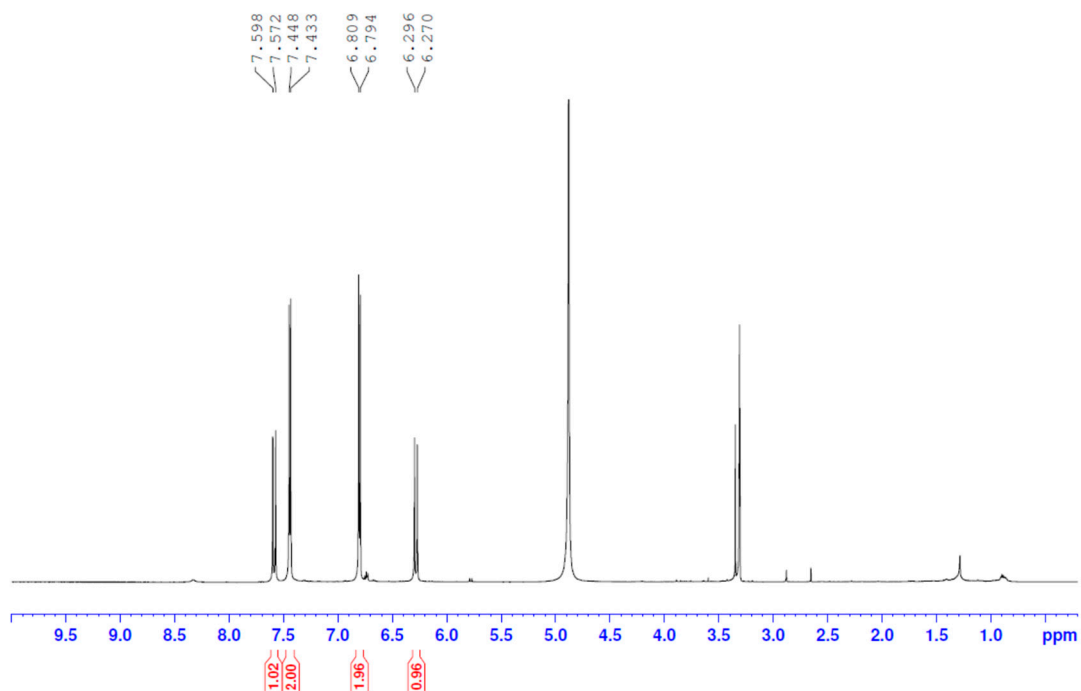


Figure S2. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 1

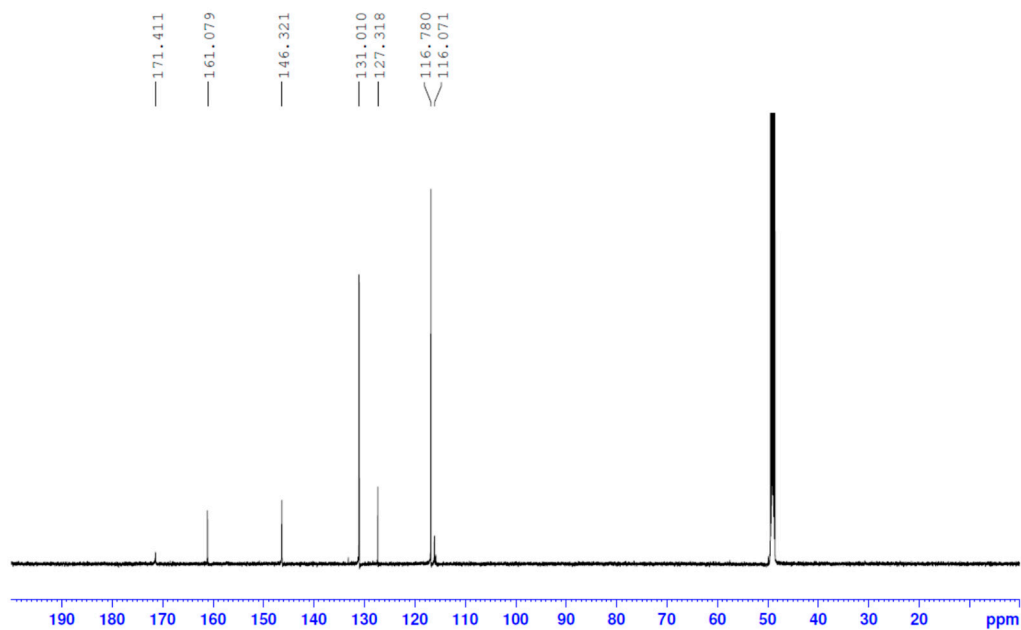


Figure S3. The ^{13}C -NMR (600MHz, CD_3OD) spectrum of compound 1

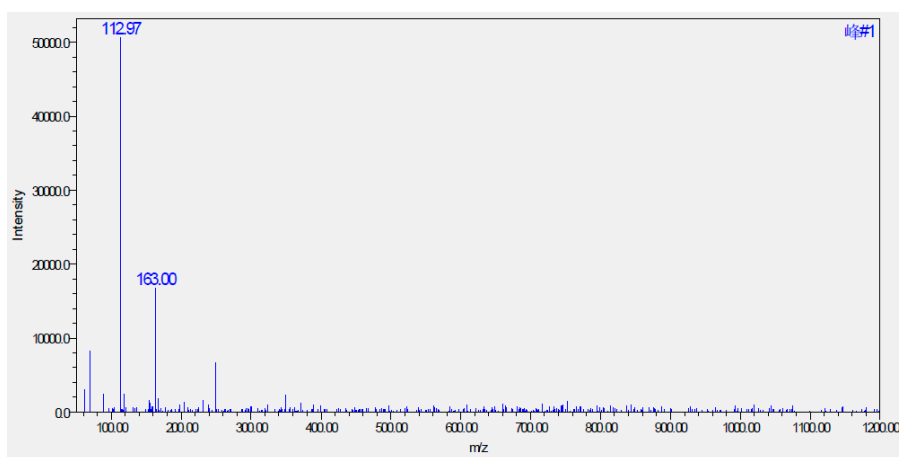


Figure S4. The ESI-MS spectrum of compound 2

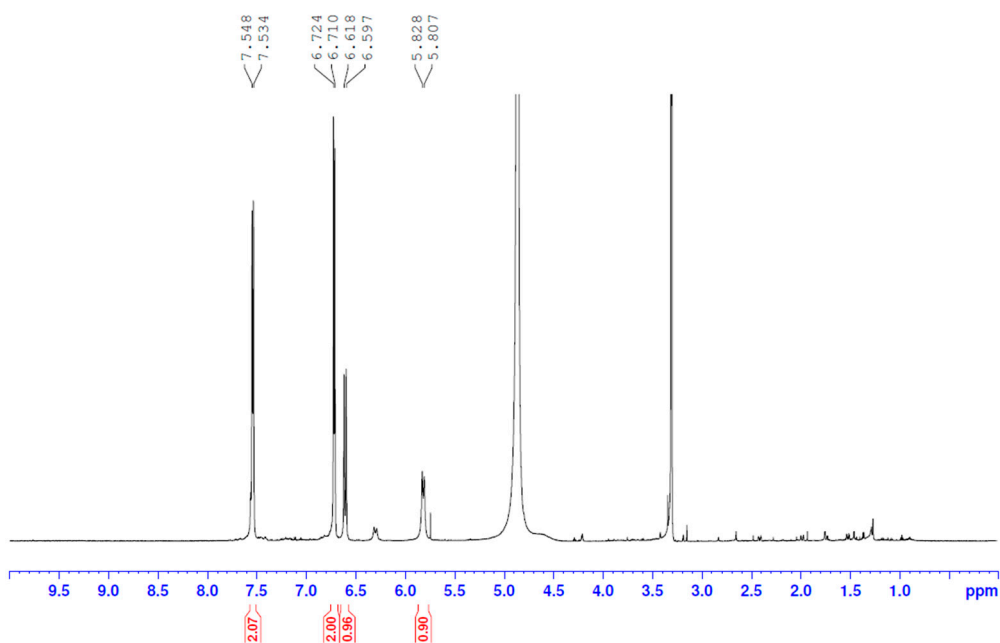


Figure S5. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 2

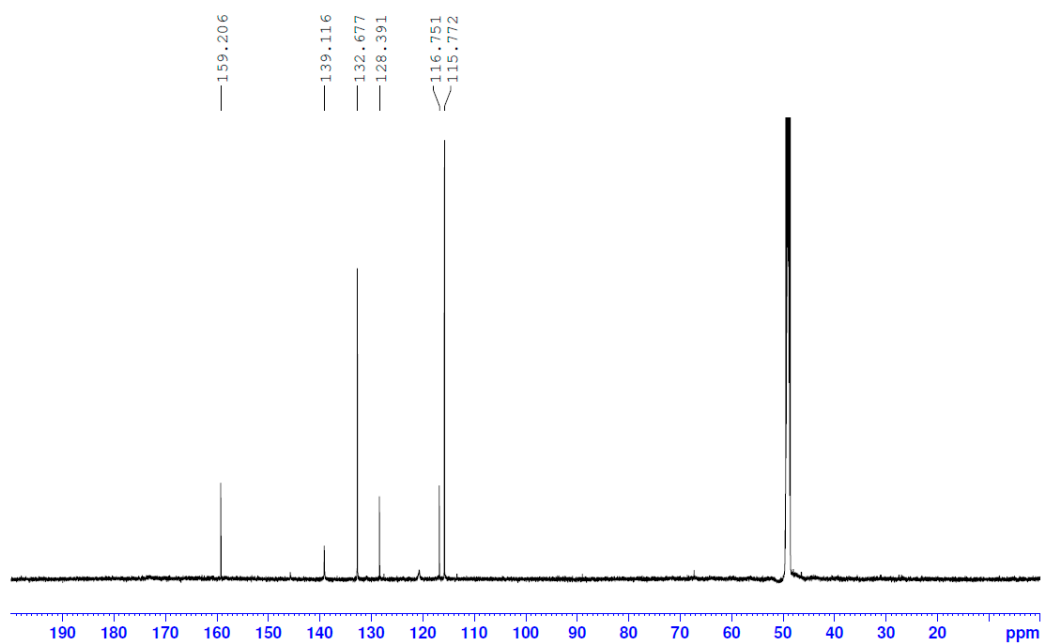


Figure S6. The ^{13}C -NMR (600MHz, CD_3OD) spectrum of compound 2

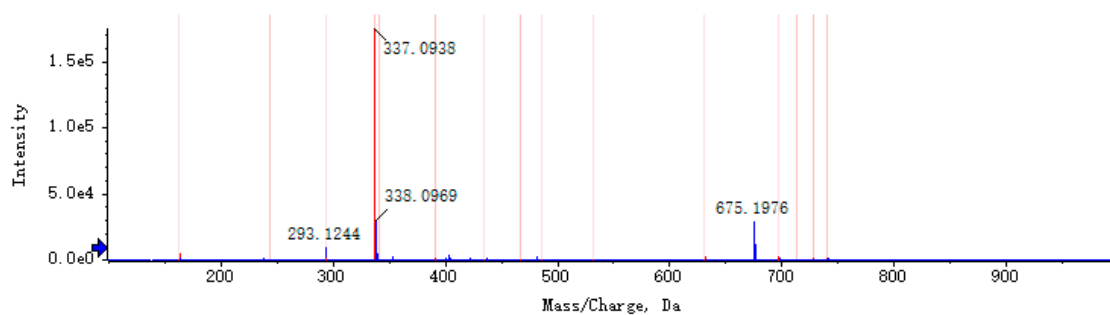


Figure S7. The HR-ESI-MS spectrum of compound 3

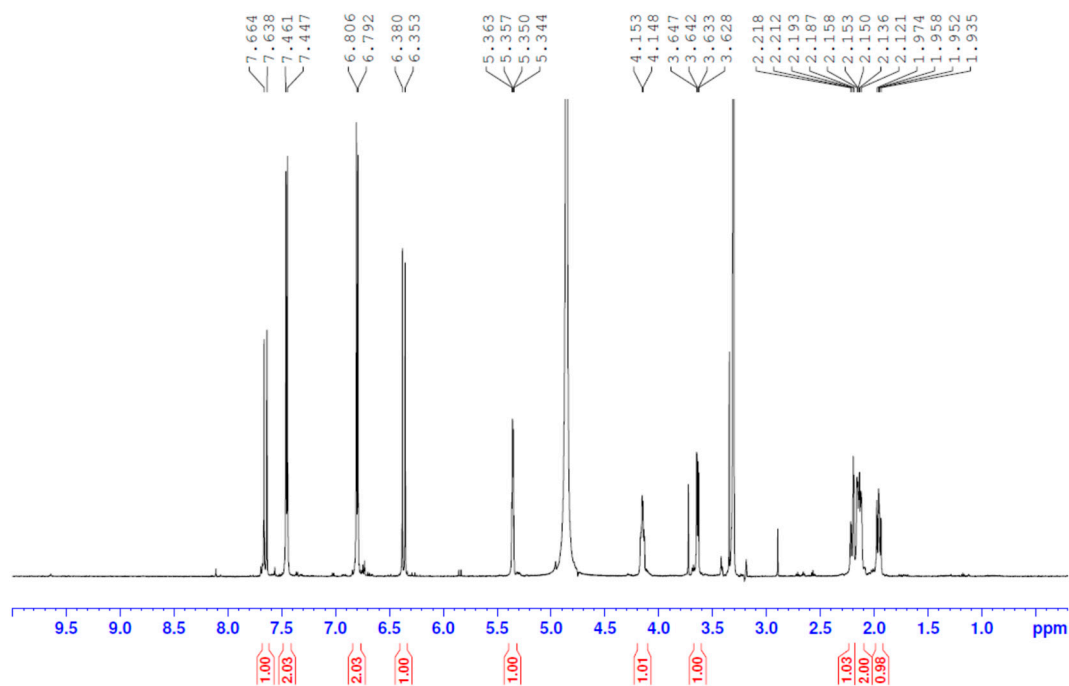


Figure S8. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 2

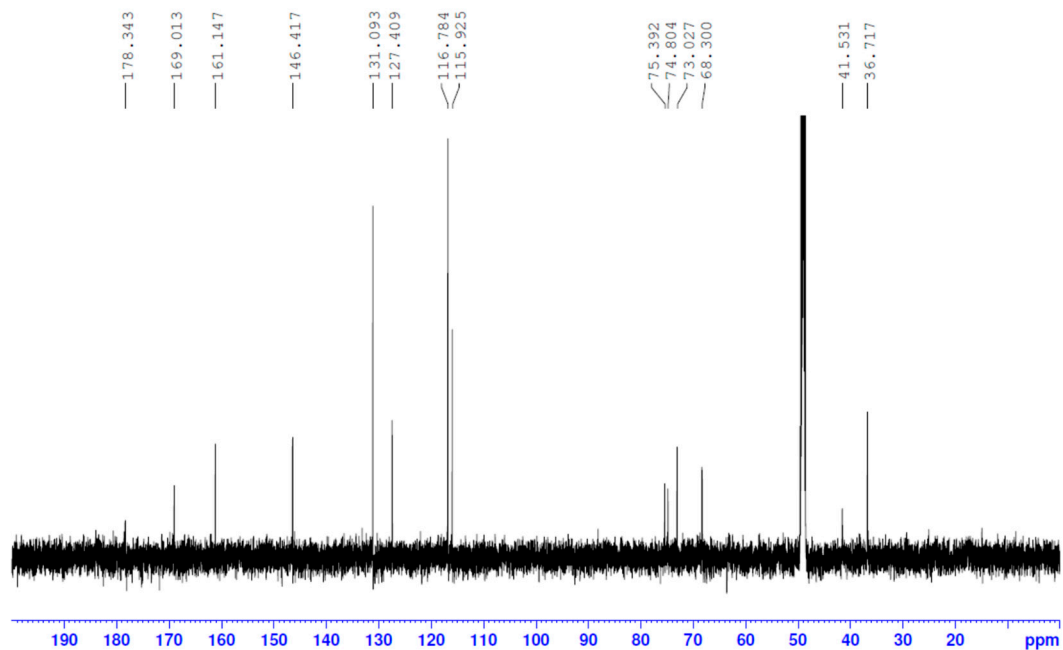


Figure S9. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 3

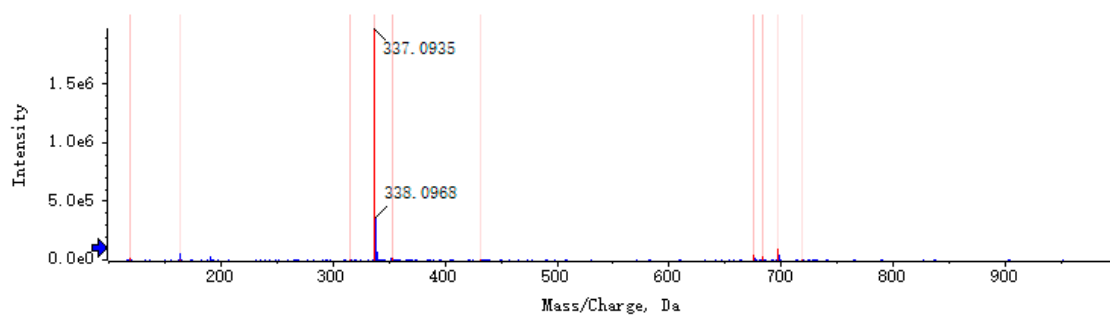


Figure S10. The HR-ESI-MS spectrum of compound 4

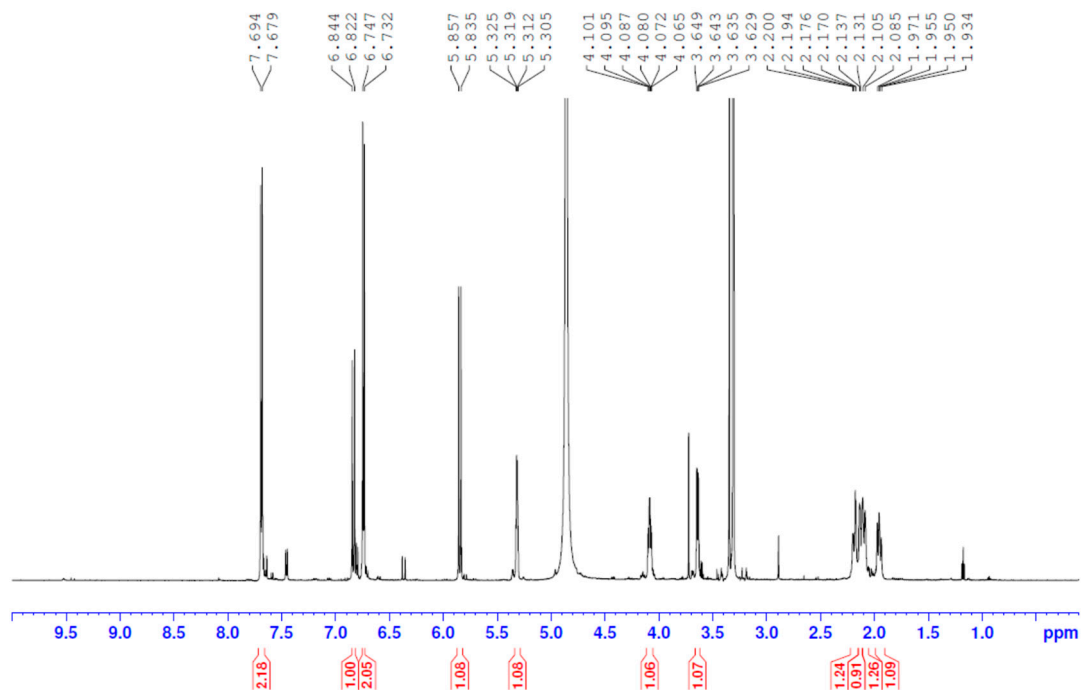


Figure S11. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 4

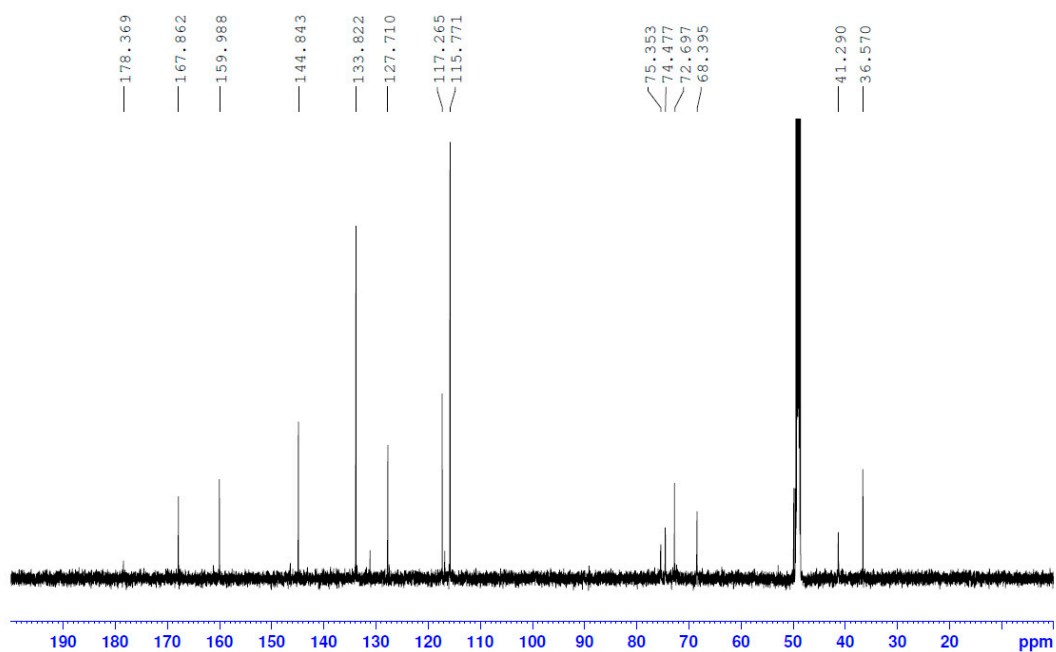


Figure S12. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 4

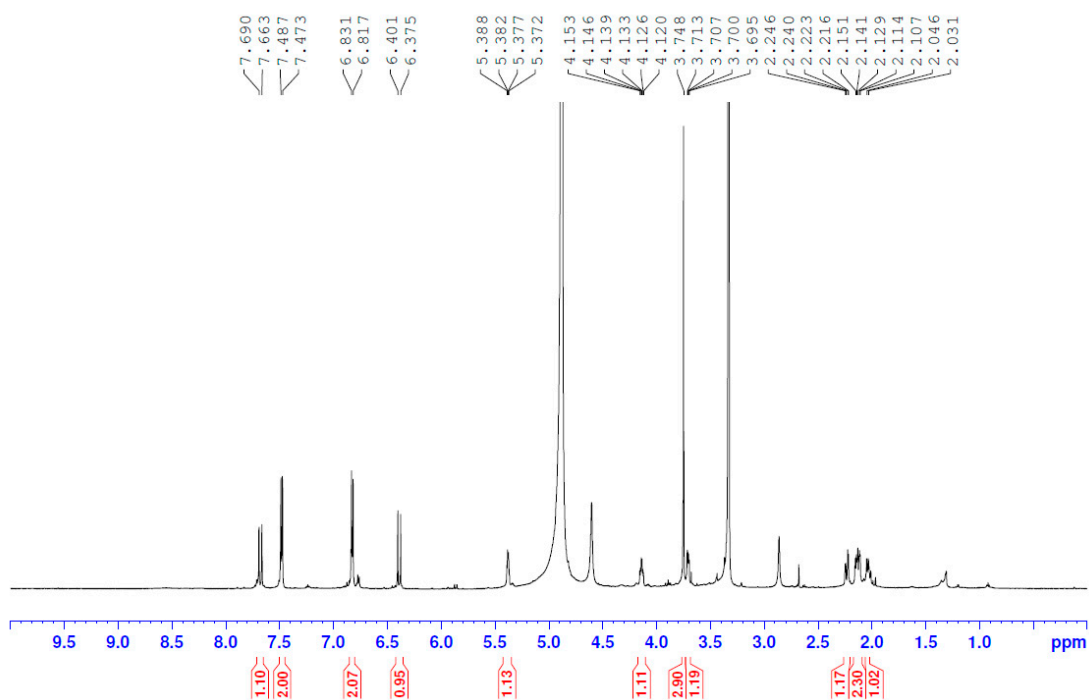


Figure S13. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 5

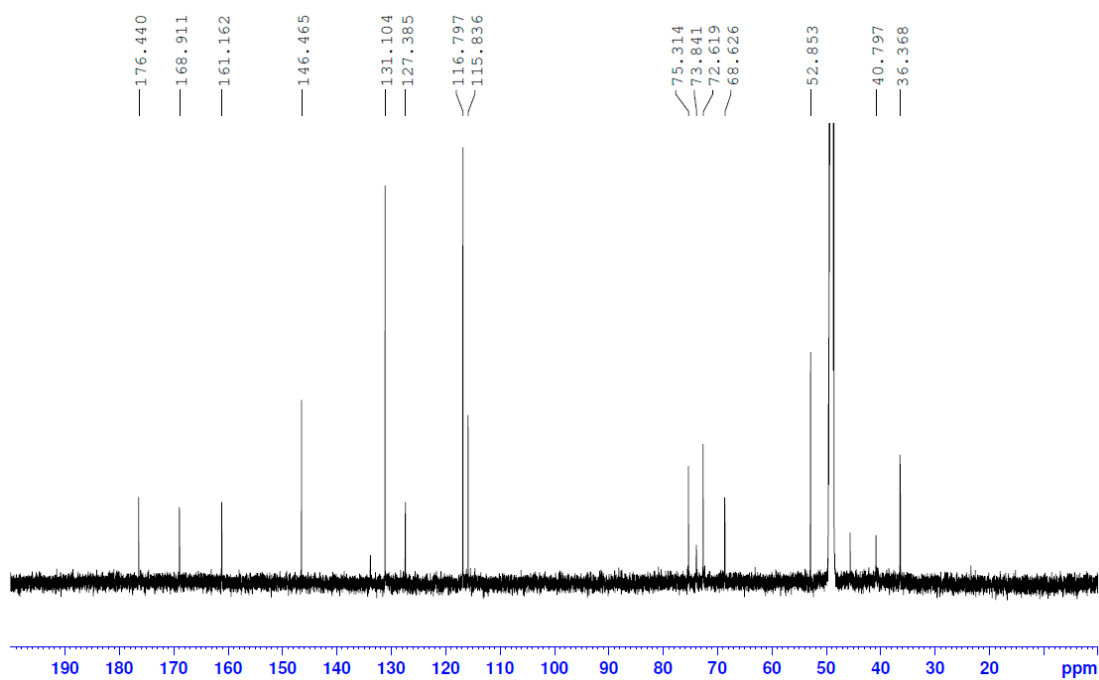


Figure S14. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 5

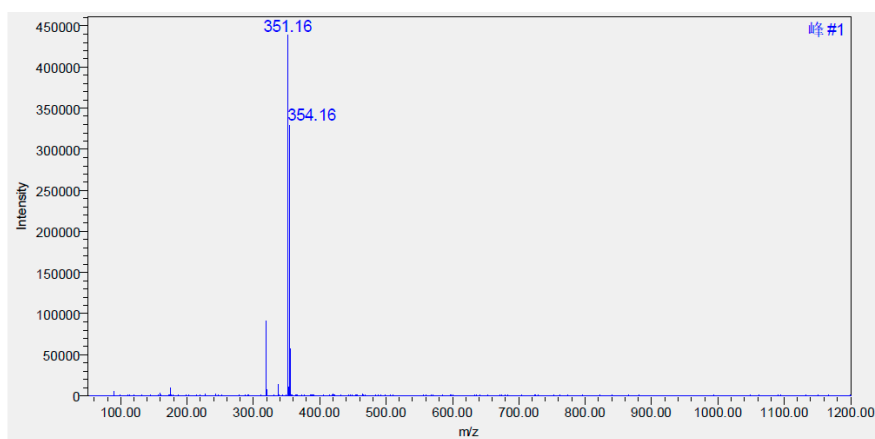


Figure S15. The ESI-MS spectrum of compound 6

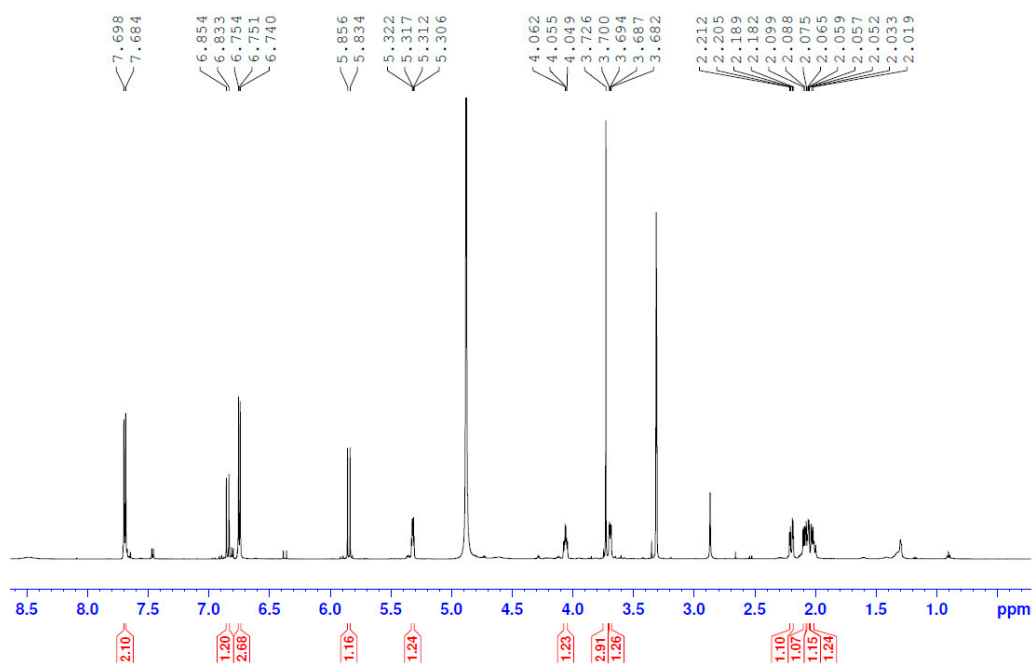


Figure S16. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 6

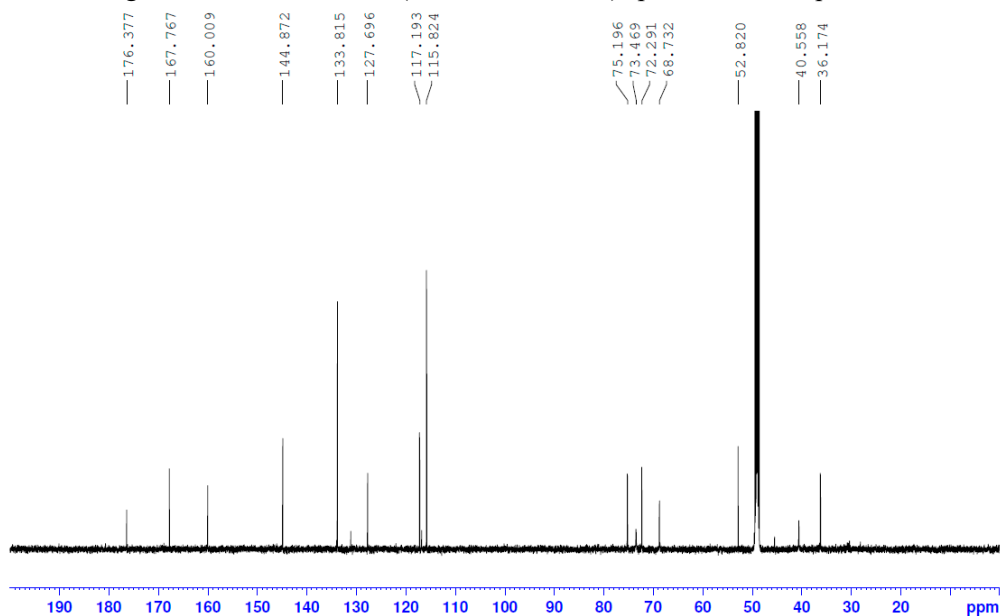


Figure S17. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 6

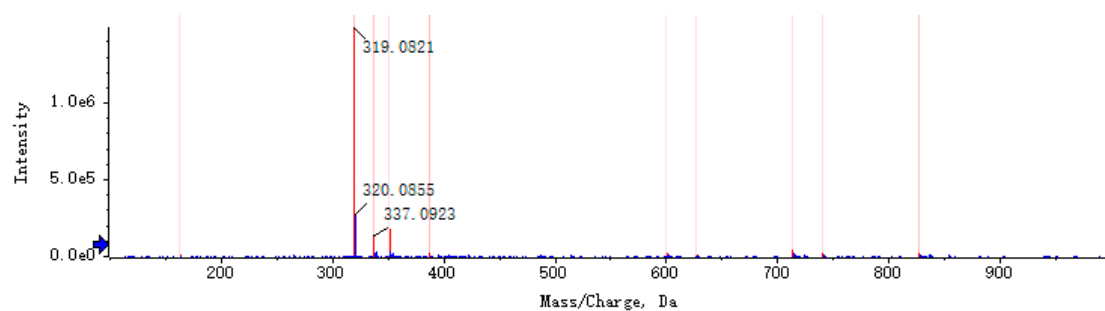


Figure S18. The HR-ESI-MS spectrum of compound 7

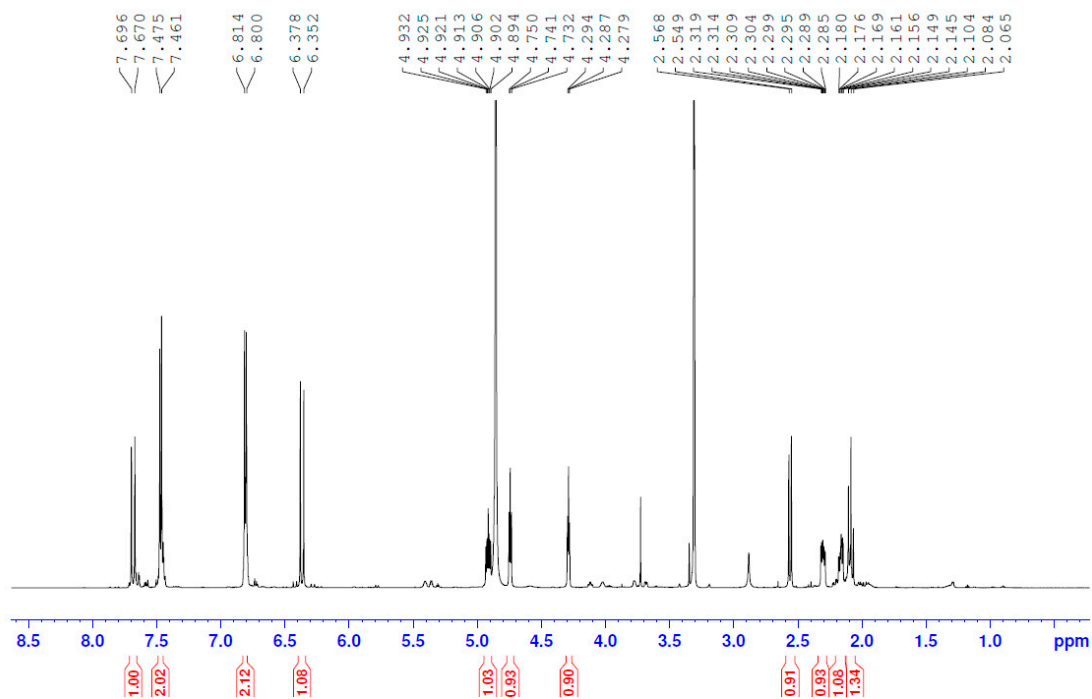


Figure S19. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 7

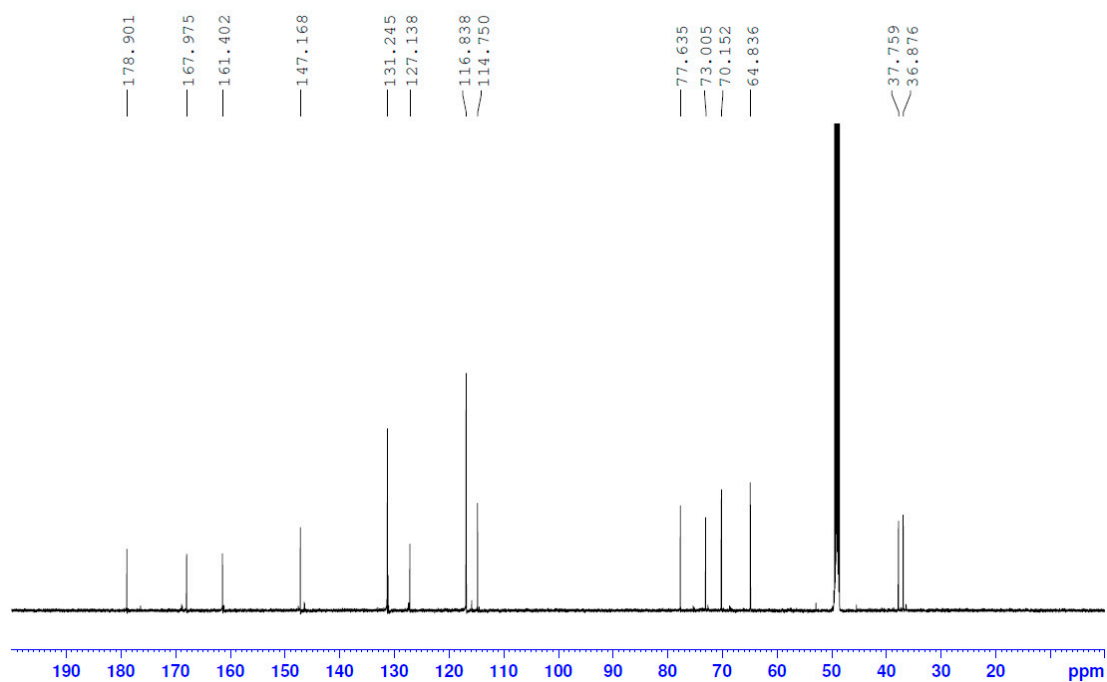


Figure S20. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 7

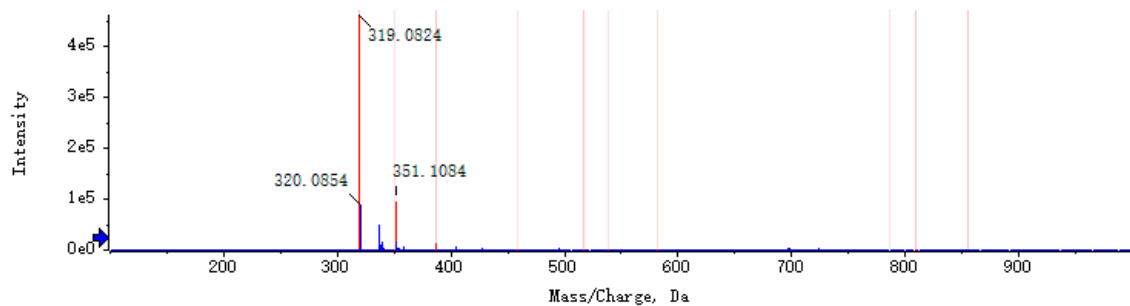


Figure S21. The HR-ESI-MS spectrum of compound 8

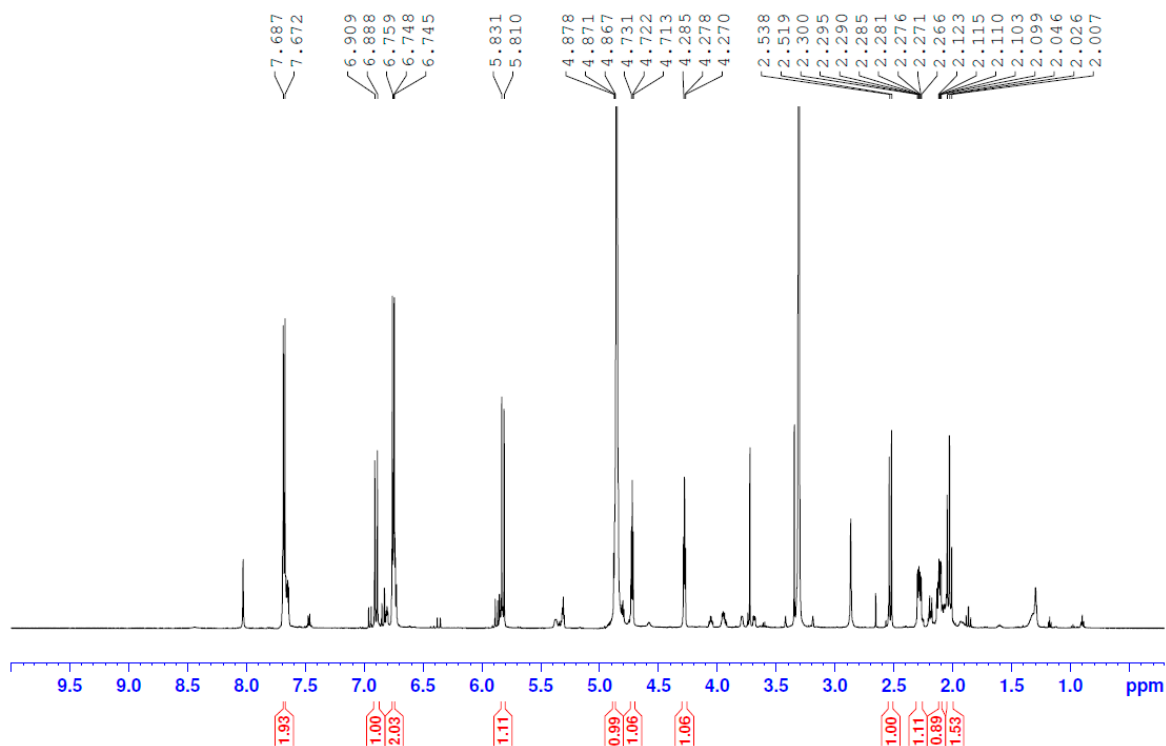


Figure S22. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 8

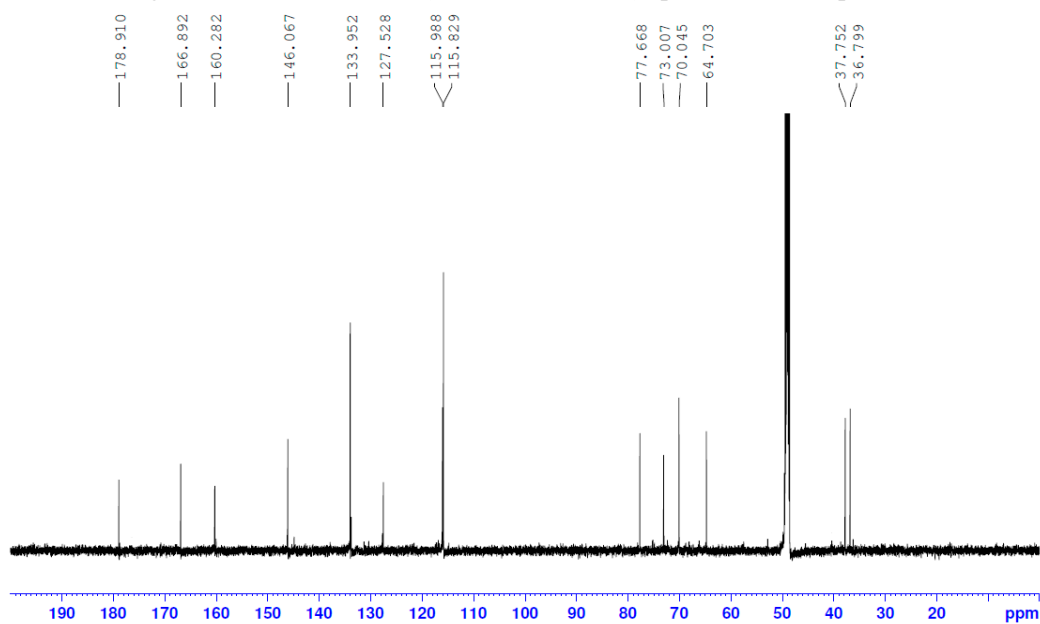


Figure S23. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 8

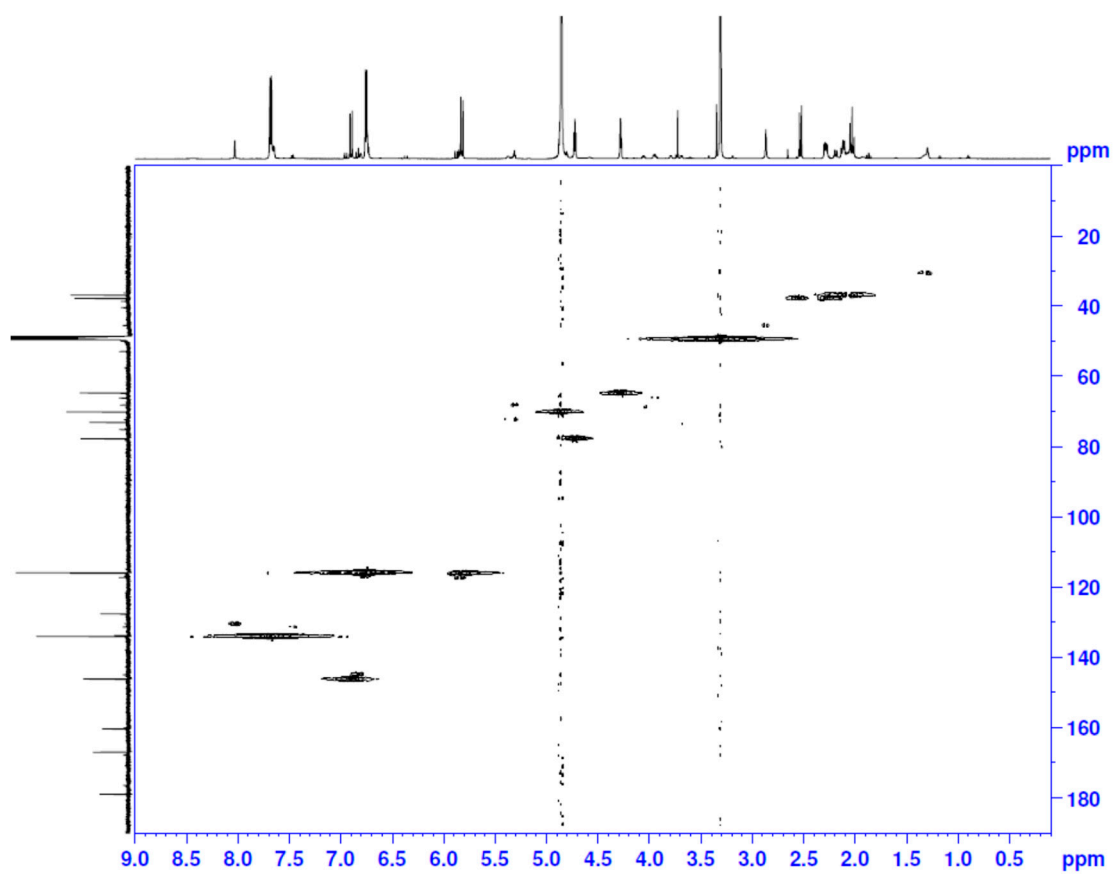


Figure S24. The HSQC spectrum of compound 8

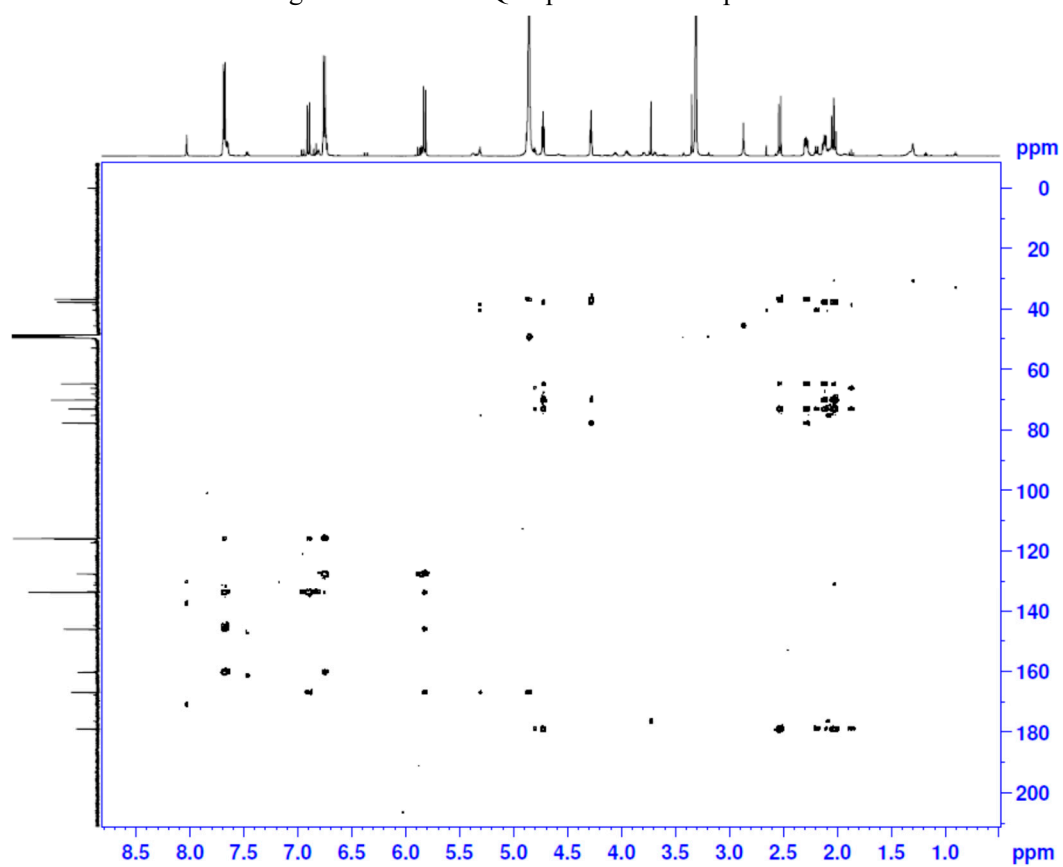


Figure S25. The HMBC spectrum of compound 8

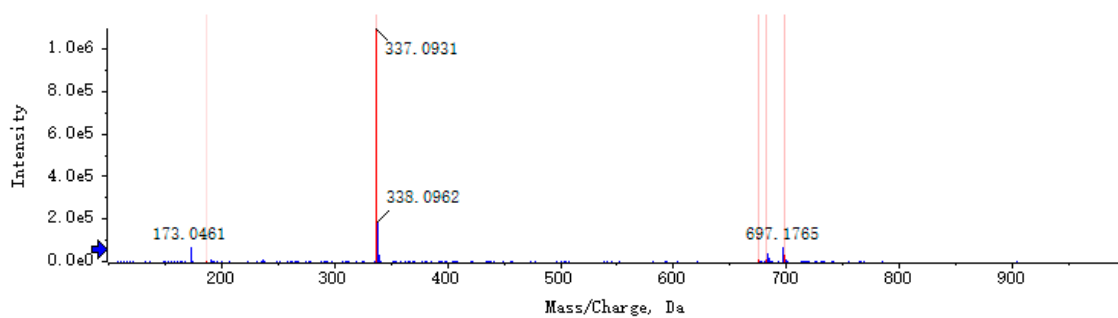


Figure S26. The HR-ESI-MS spectrum of compound 9

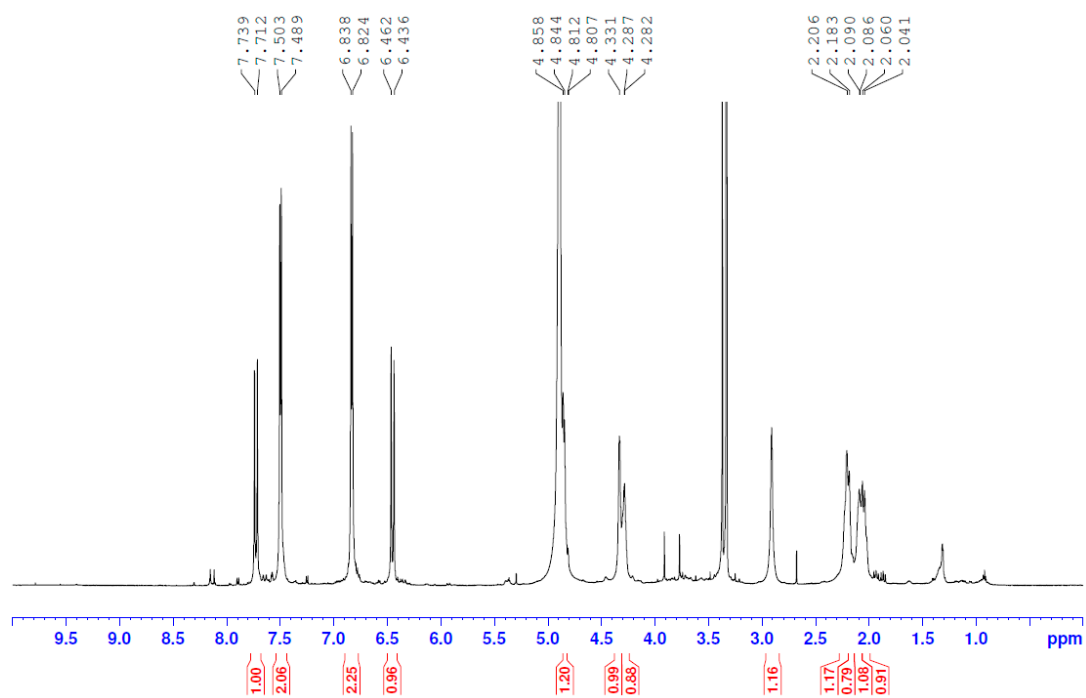


Figure S27. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 9

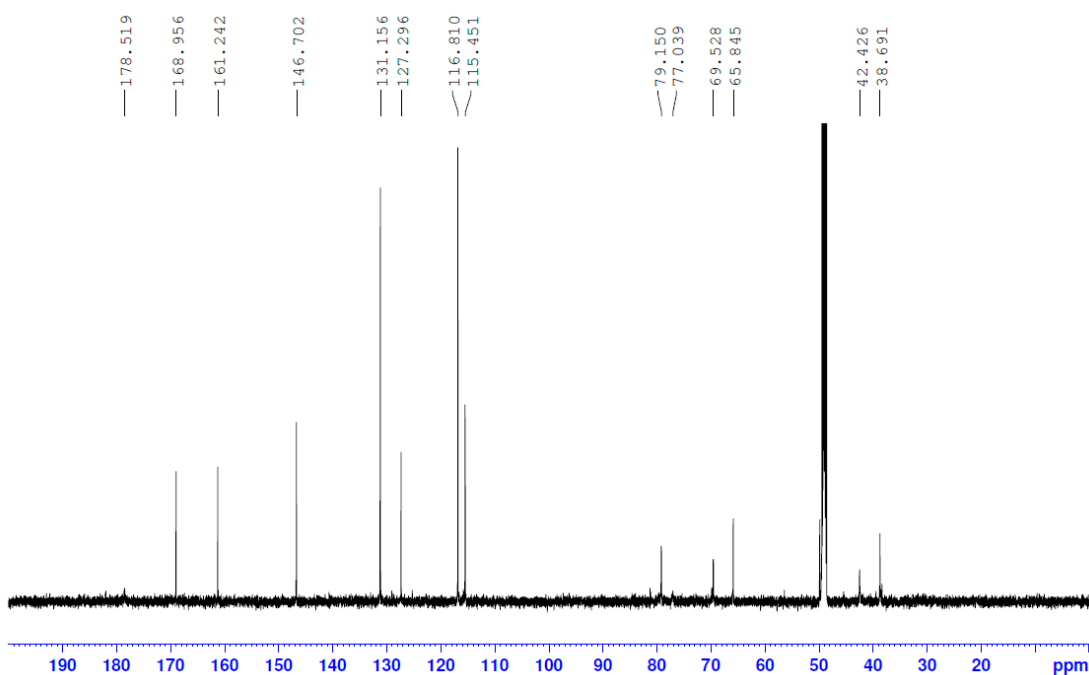


Figure S28. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 9

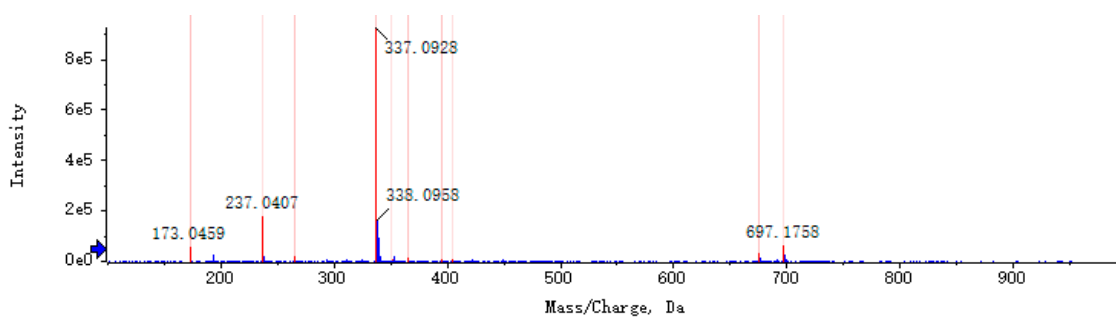


Figure S29. The HR-ESI-MS spectrum of compound 10

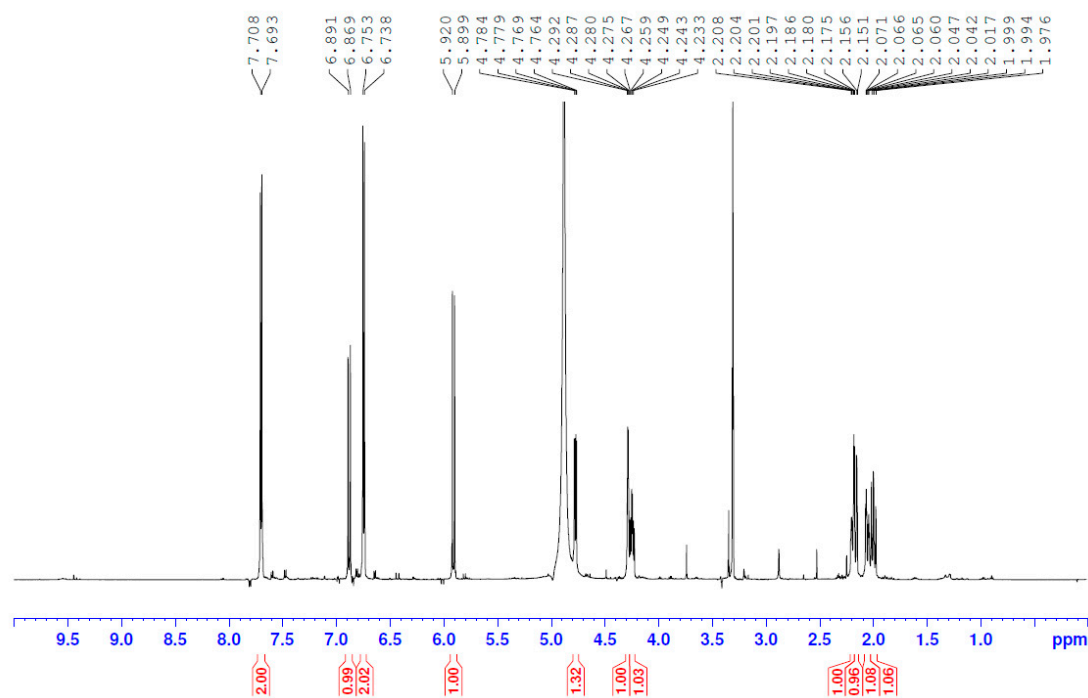


Figure S30. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 10

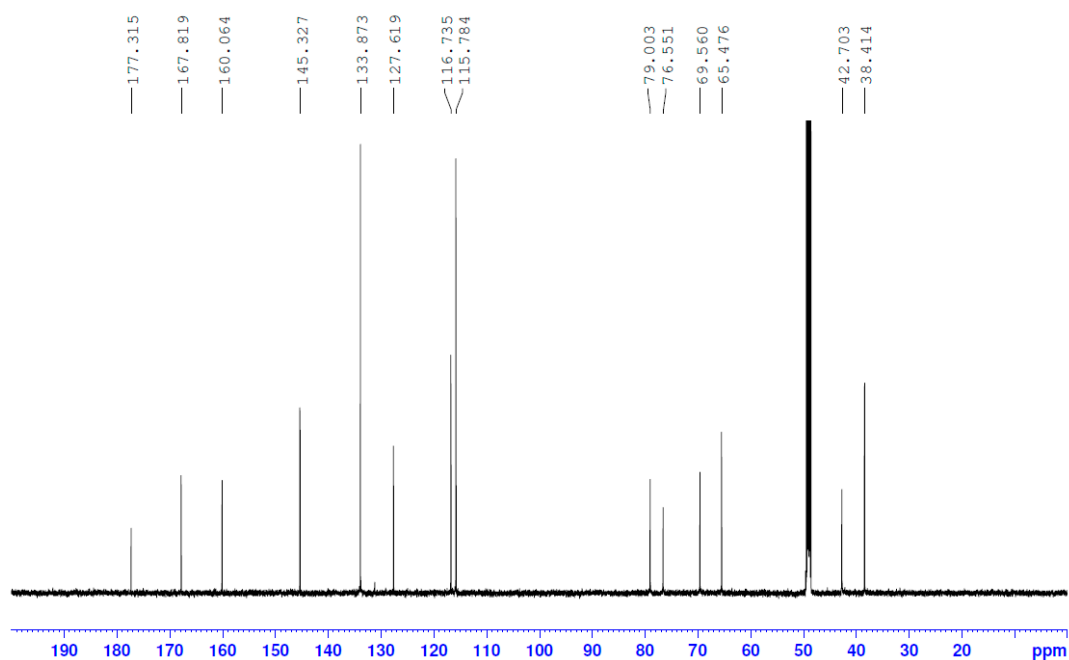


Figure S31. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 10

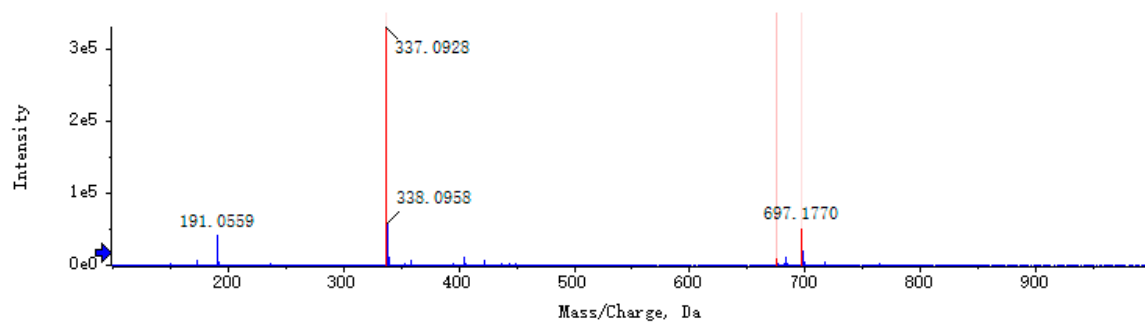


Figure S32. The HR-ESI-MS spectrum of compound 11

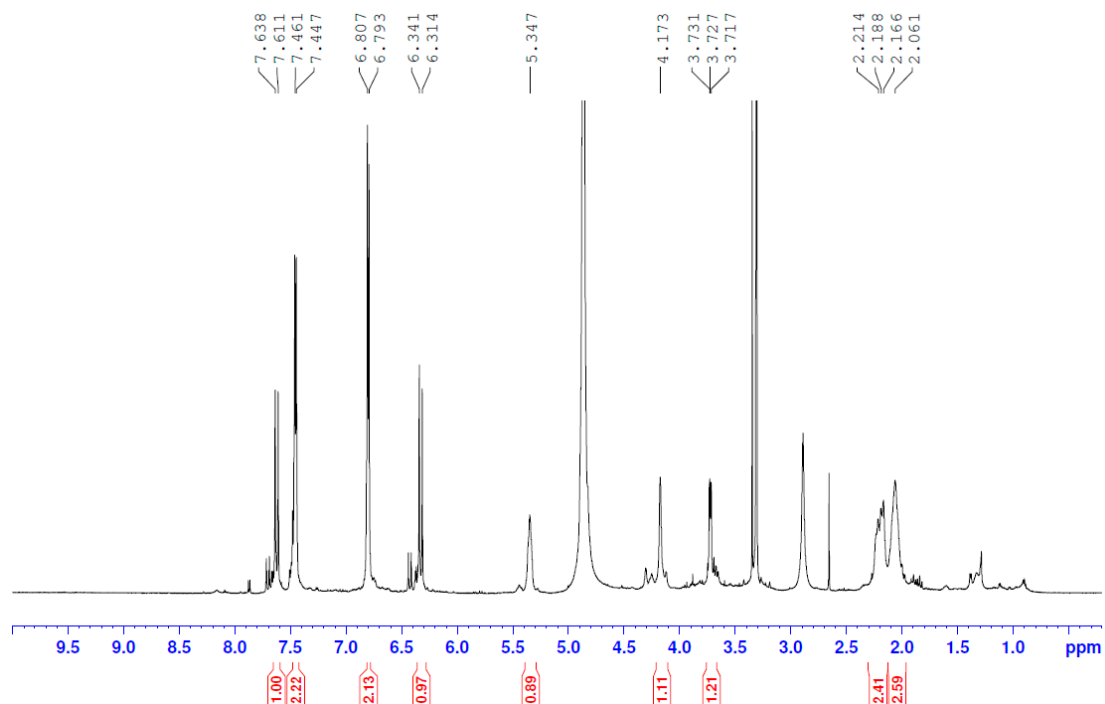


Figure S33. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 11

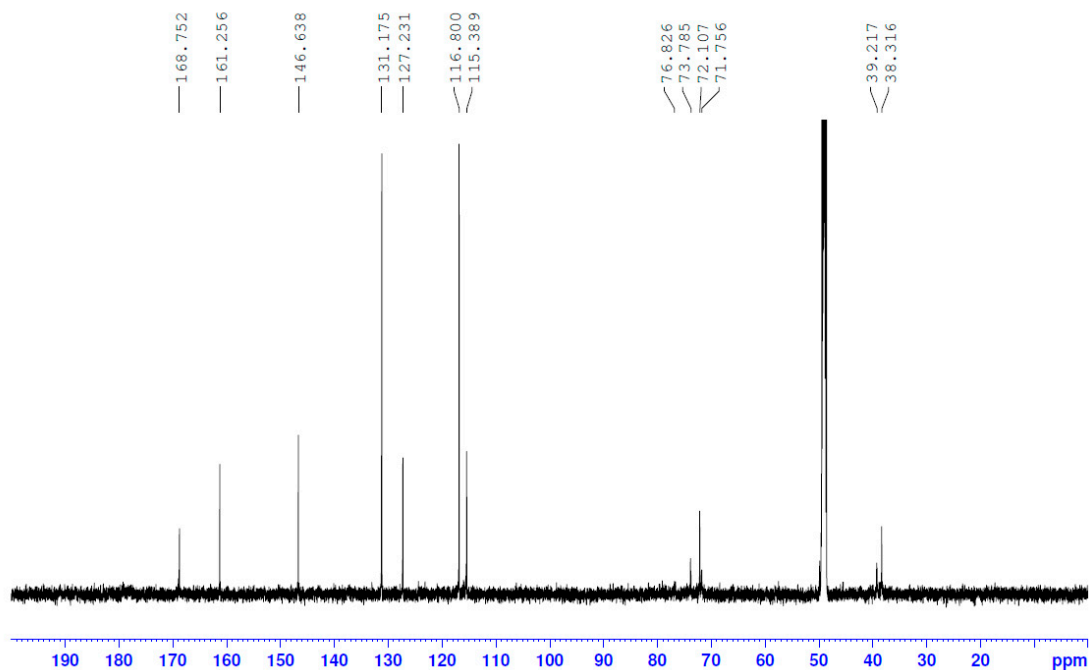


Figure S34. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 11

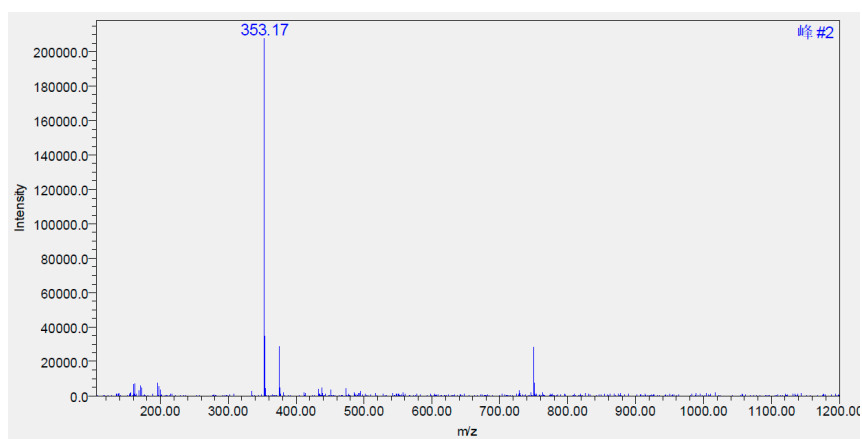


Figure S35. The ESI-MS spectrum of compound 12

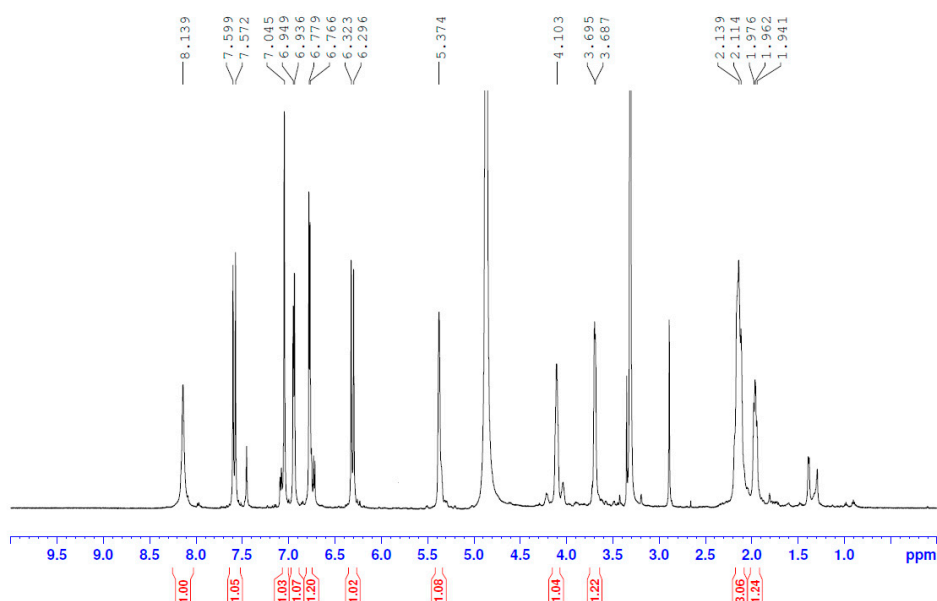


Figure S36. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 12

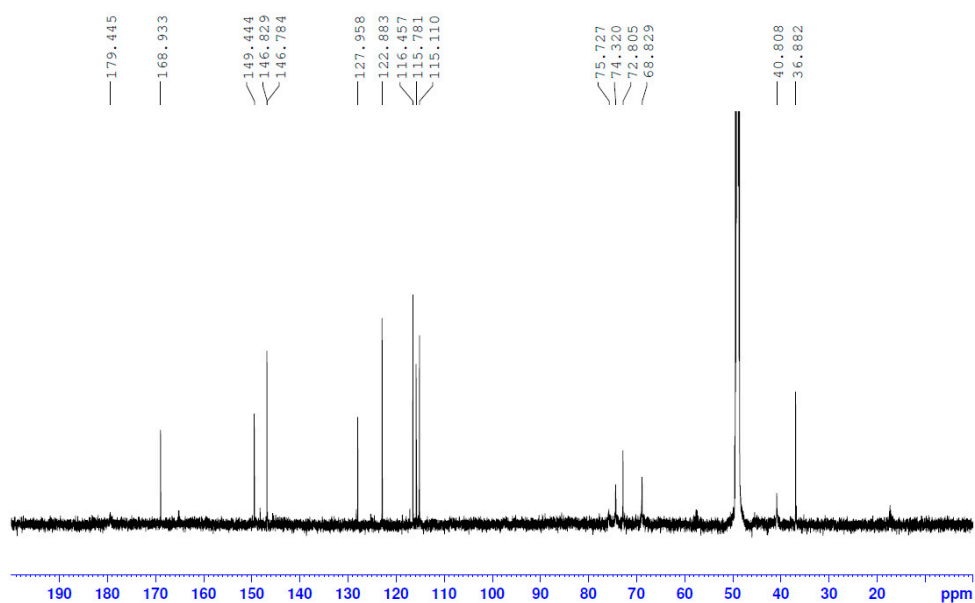


Figure S37. The ¹³C-NMR (150MHz, CD₃OD) spectrum of compound 12

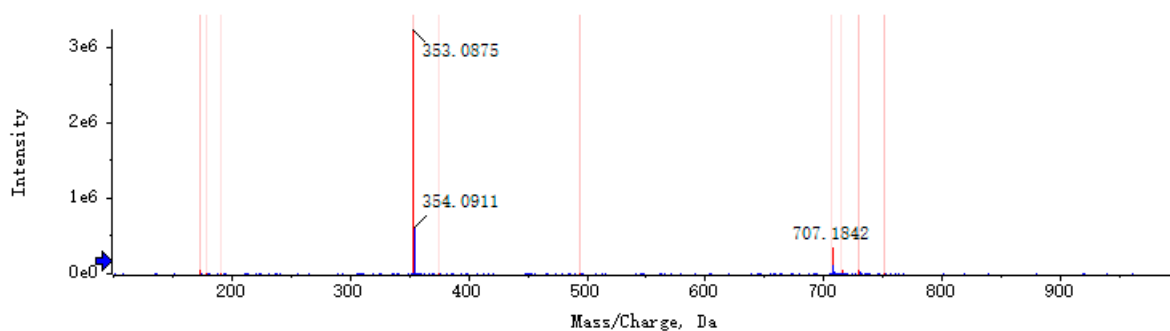


Figure S38. The ESI-MS spectrum of compound 13

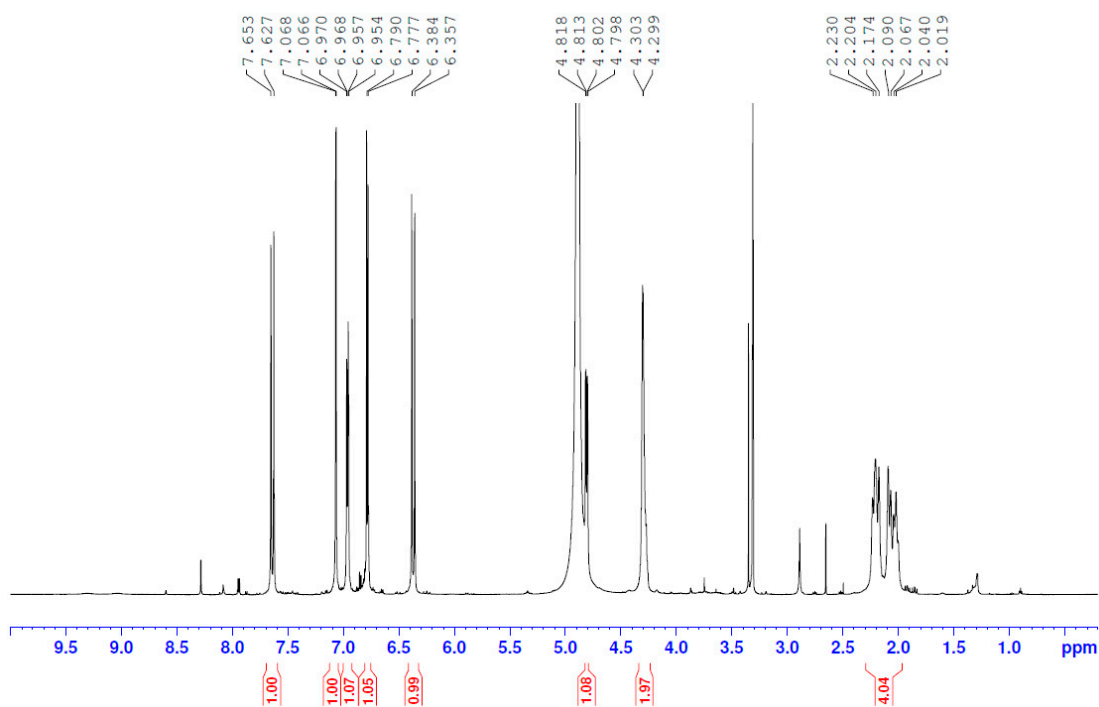


Figure S39. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 13

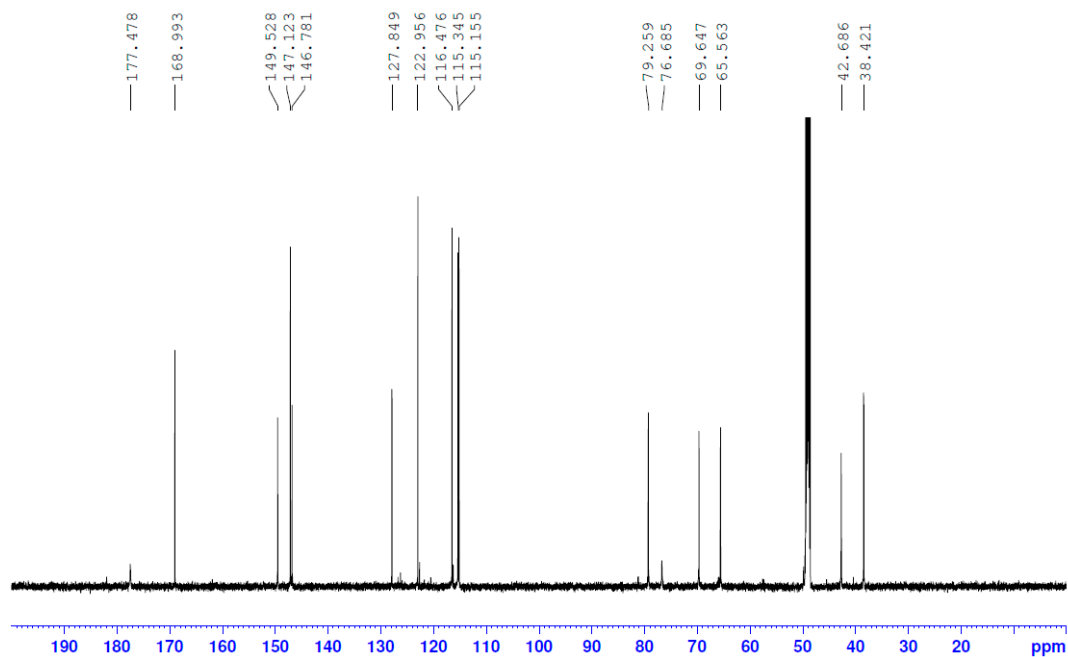


Figure S40. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 13

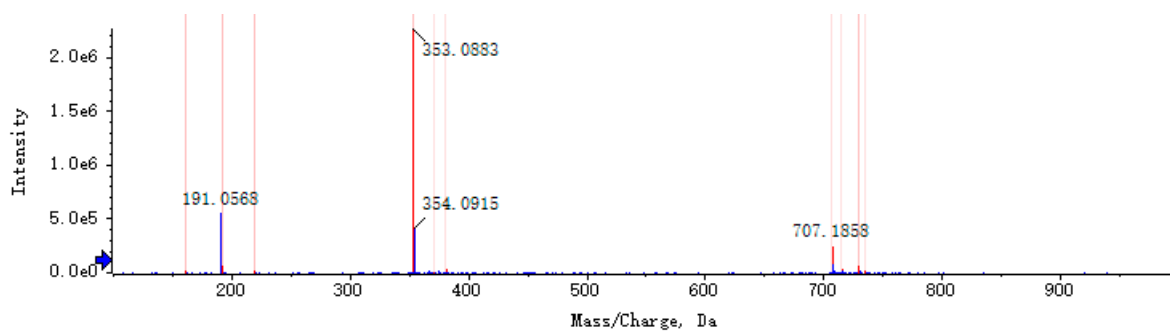


Figure S41. The HR-ESI-MS spectrum of compound 14

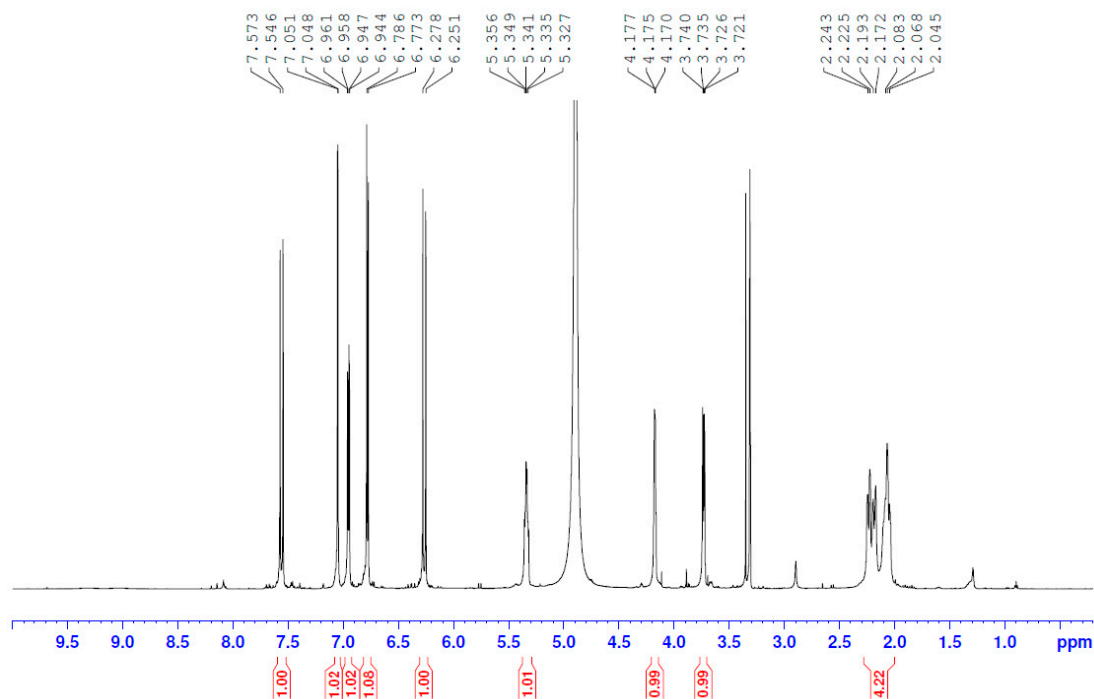


Figure S42. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 14

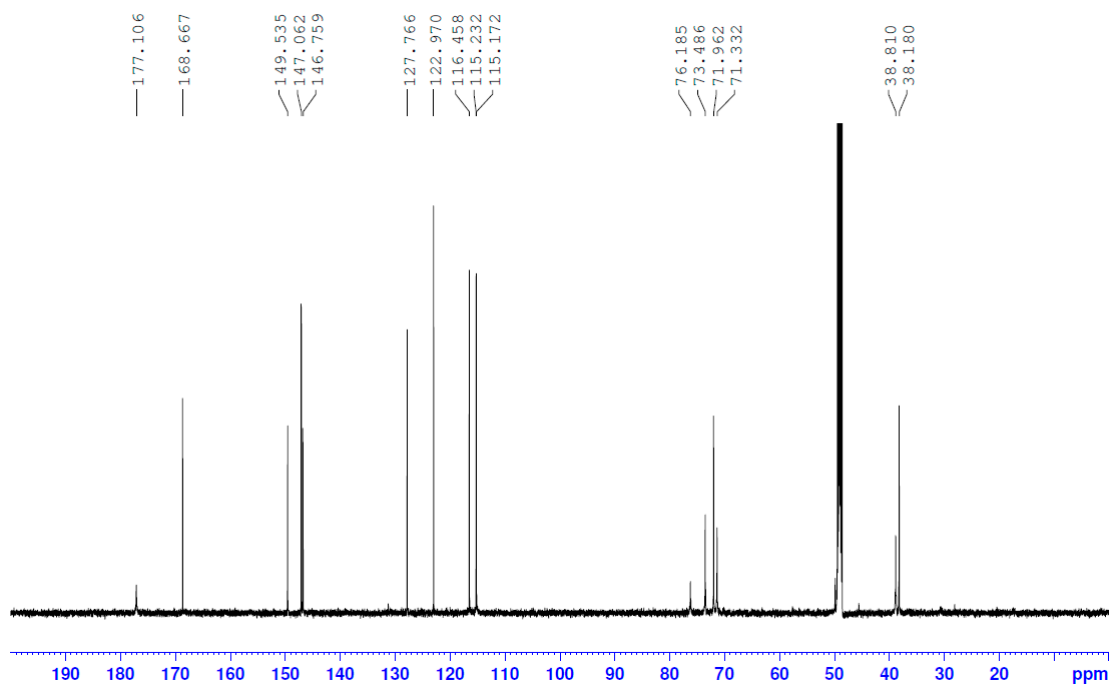
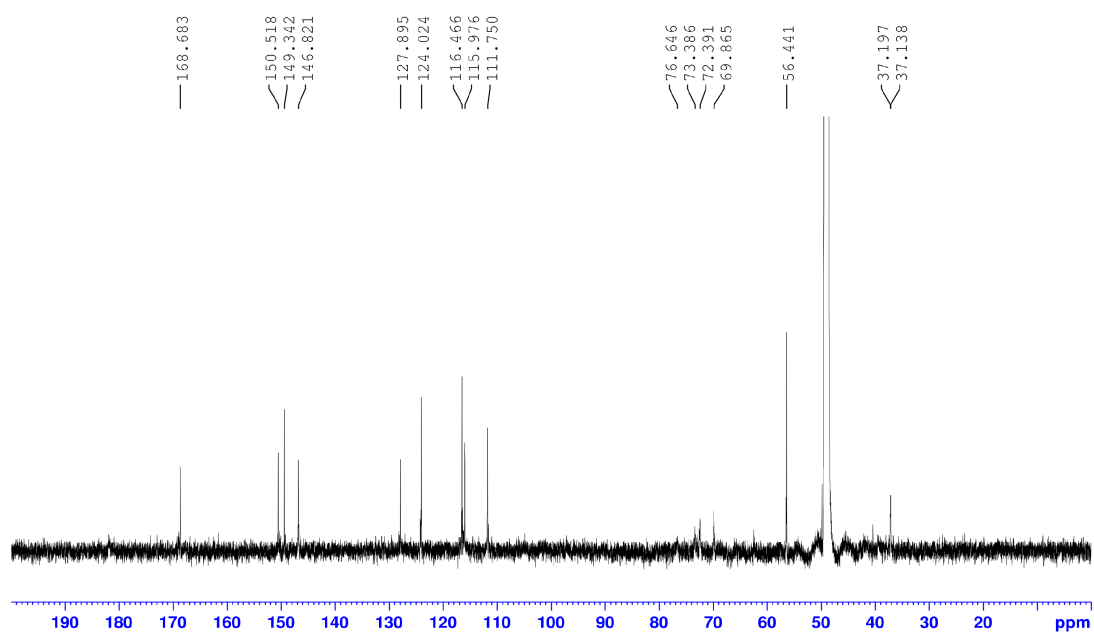
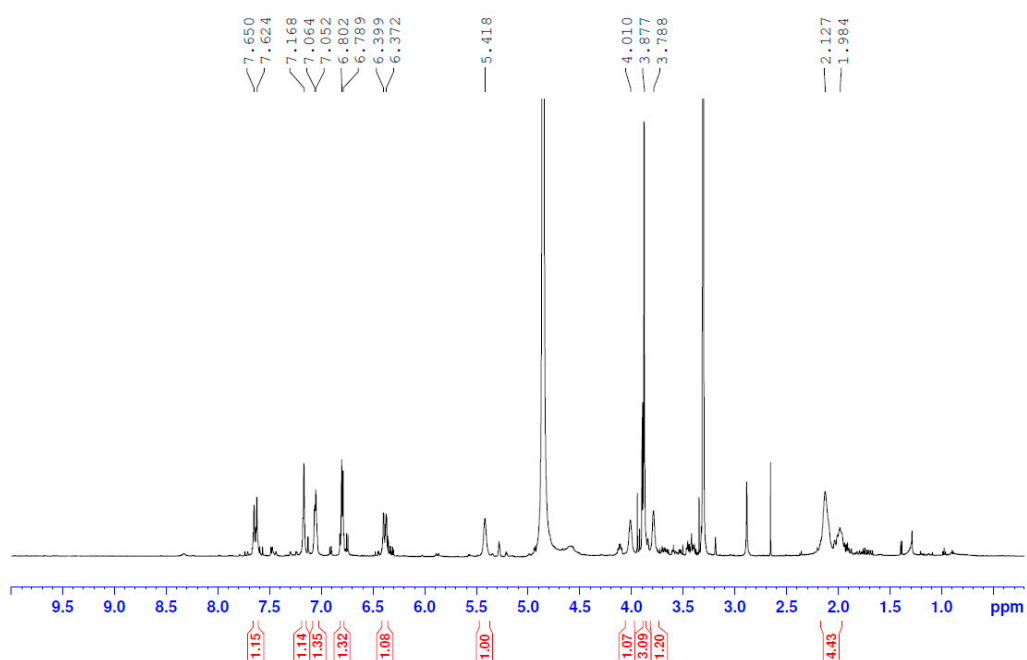
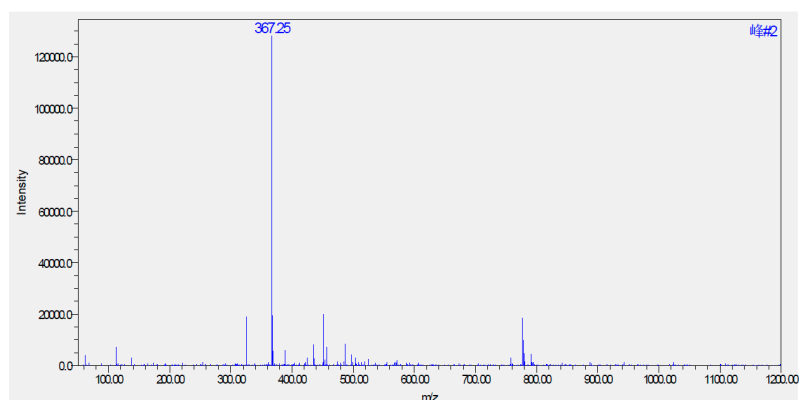


Figure S43. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 14



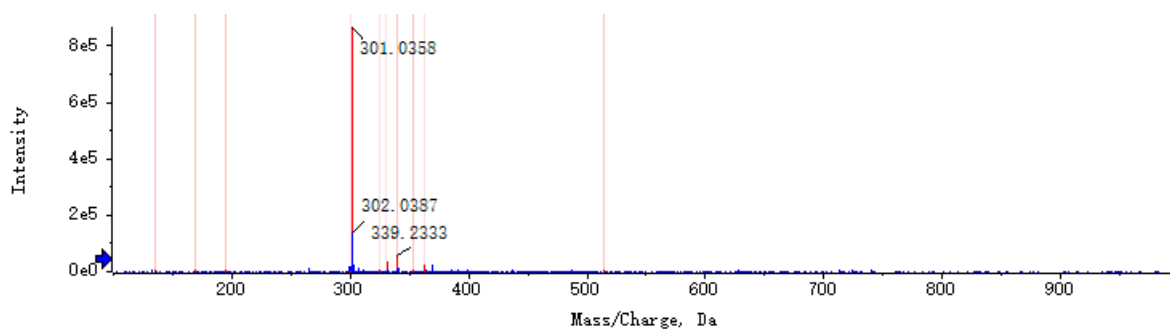


Figure S47. The HR-ESI-MS spectrum of compound 16

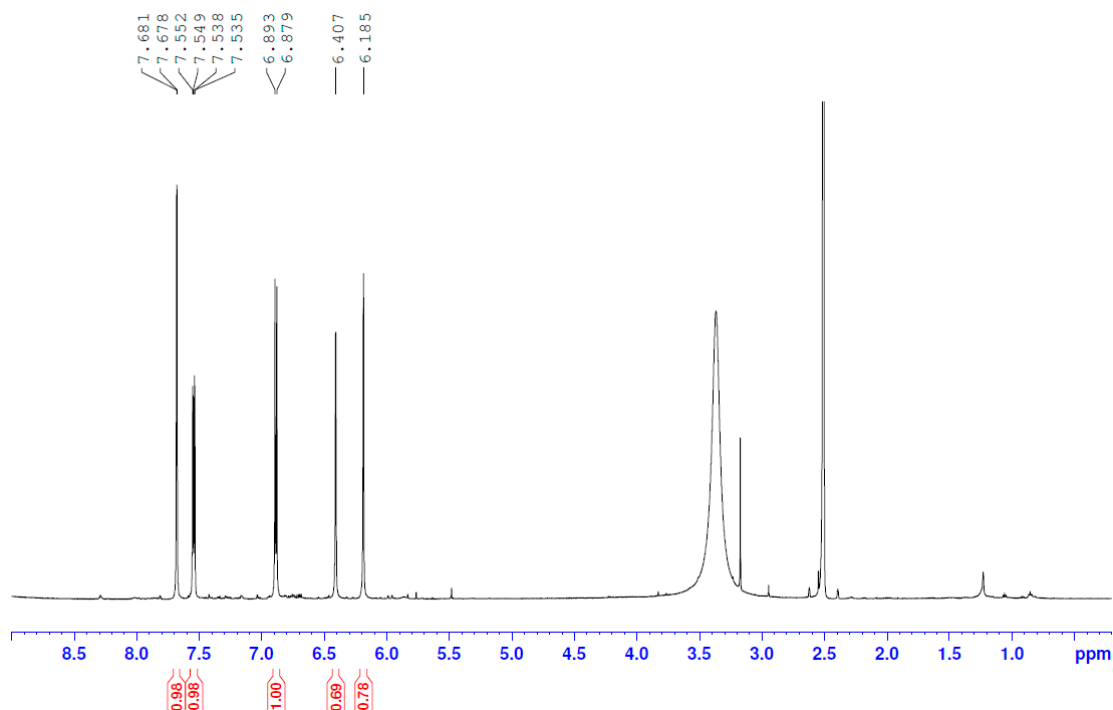


Figure S48. The ¹H-NMR (600MHz, DMSO-*d*₆) spectrum of compound 16

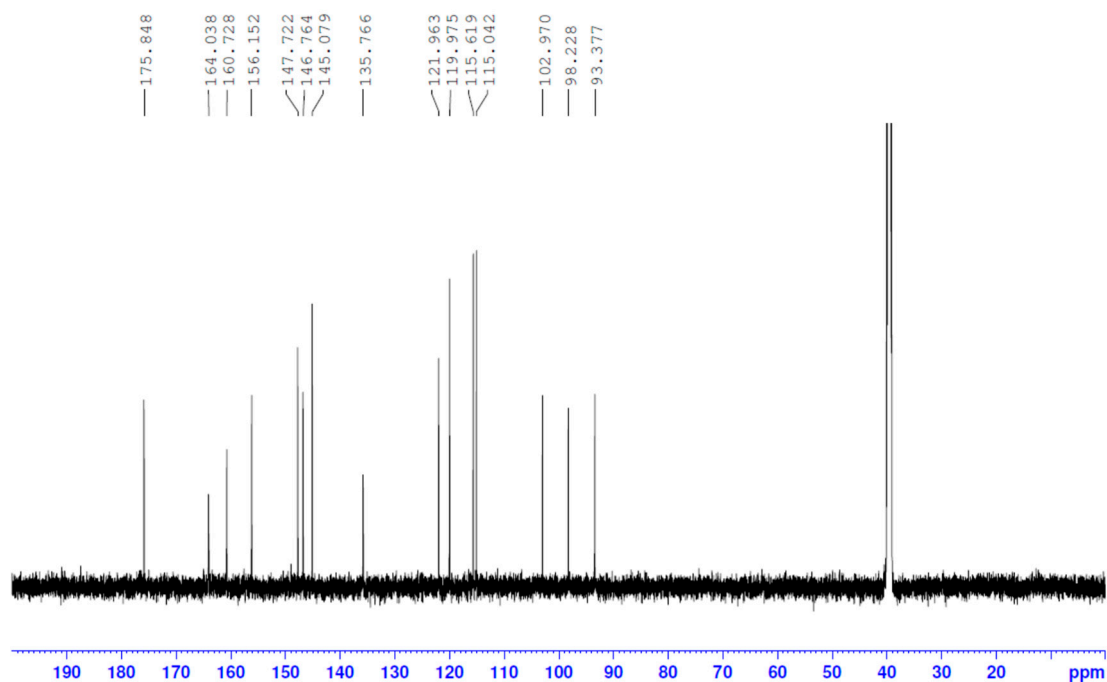


Figure S49. The ¹³C-NMR (150MHz, DMSO-*d*₆) spectrum of compound 16

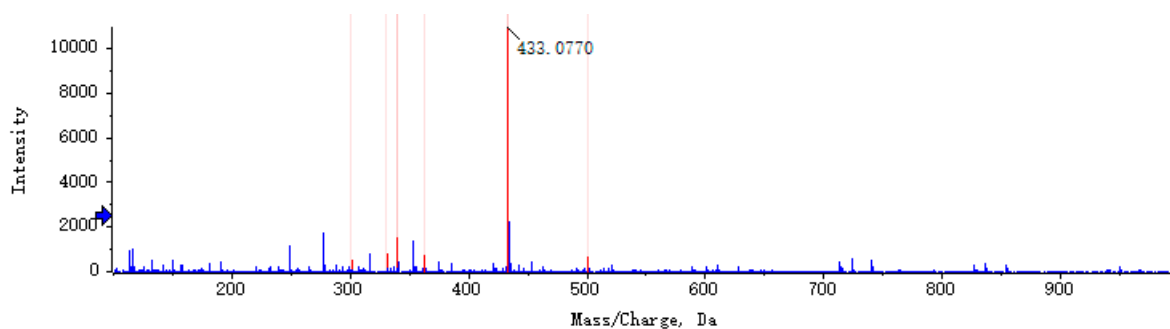


Figure S50. The HR-ESI-MS spectrum of compound 17

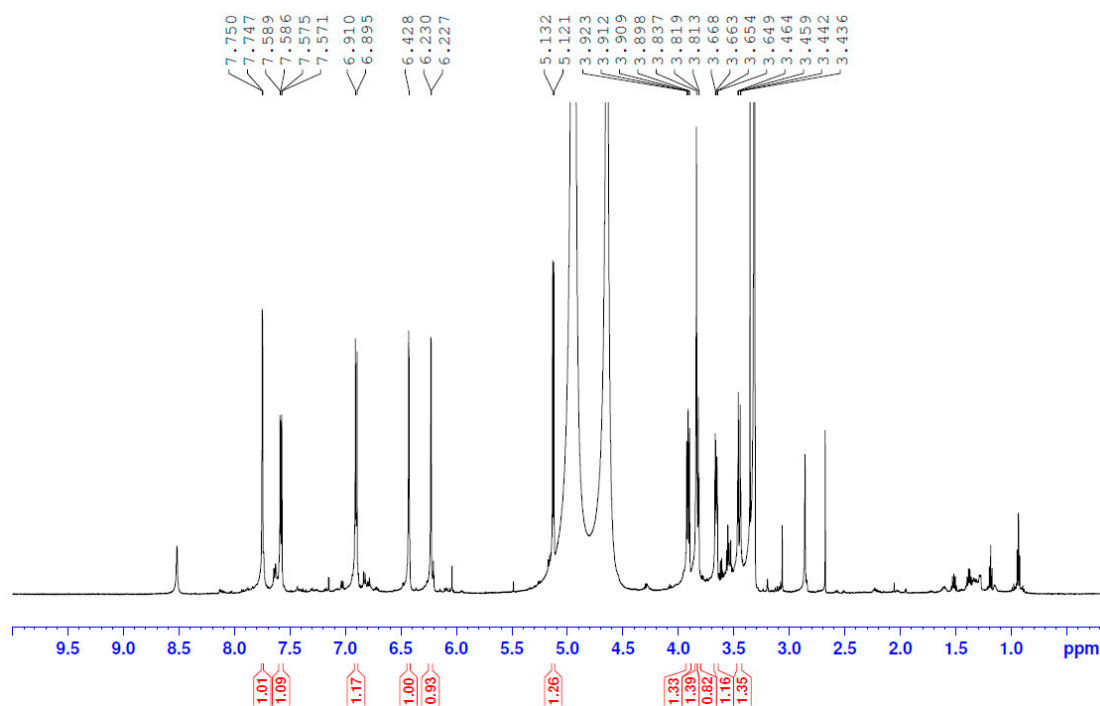


Figure S51. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 17

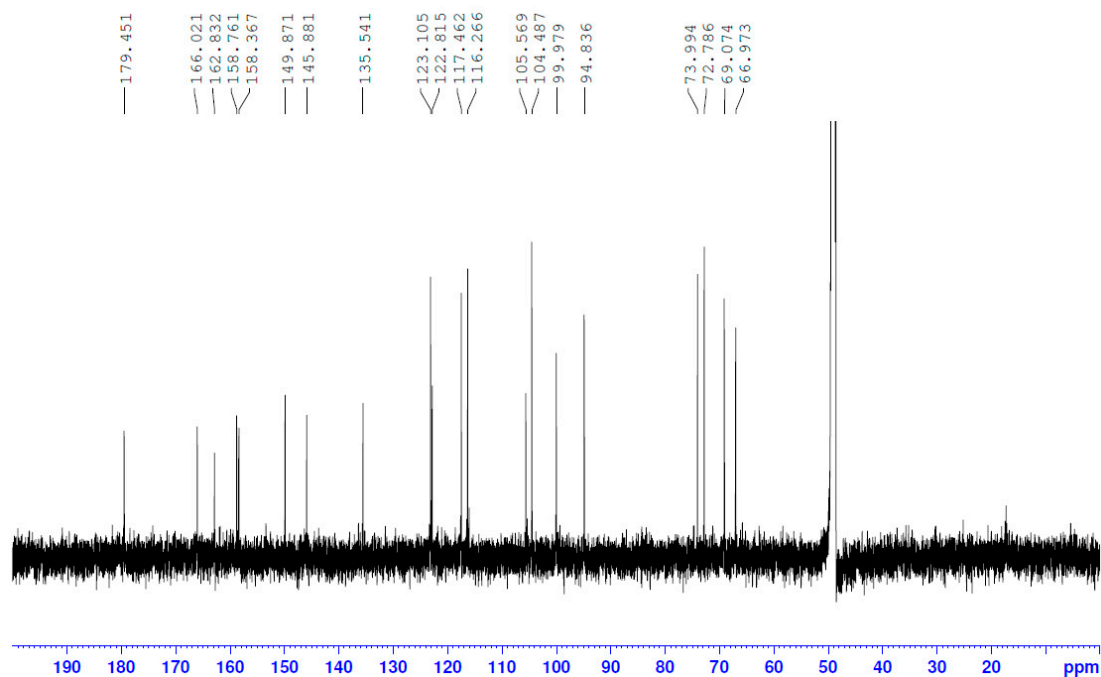


Figure S52. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 17

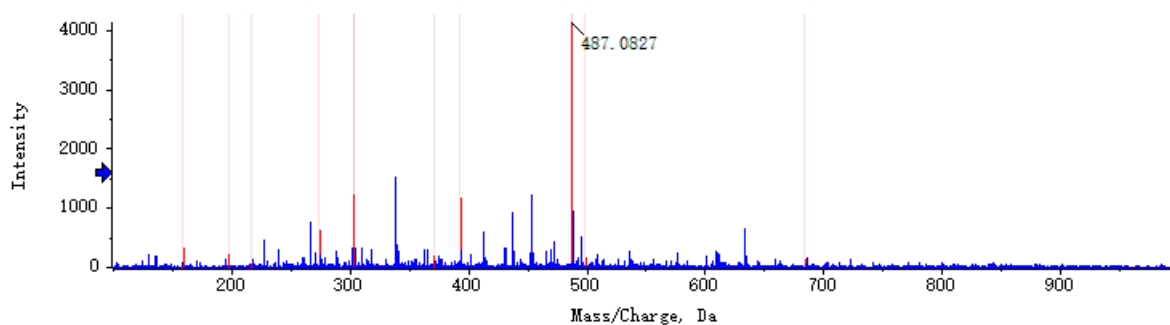


Figure S53. The HR-ESI-MS spectrum of compound 18

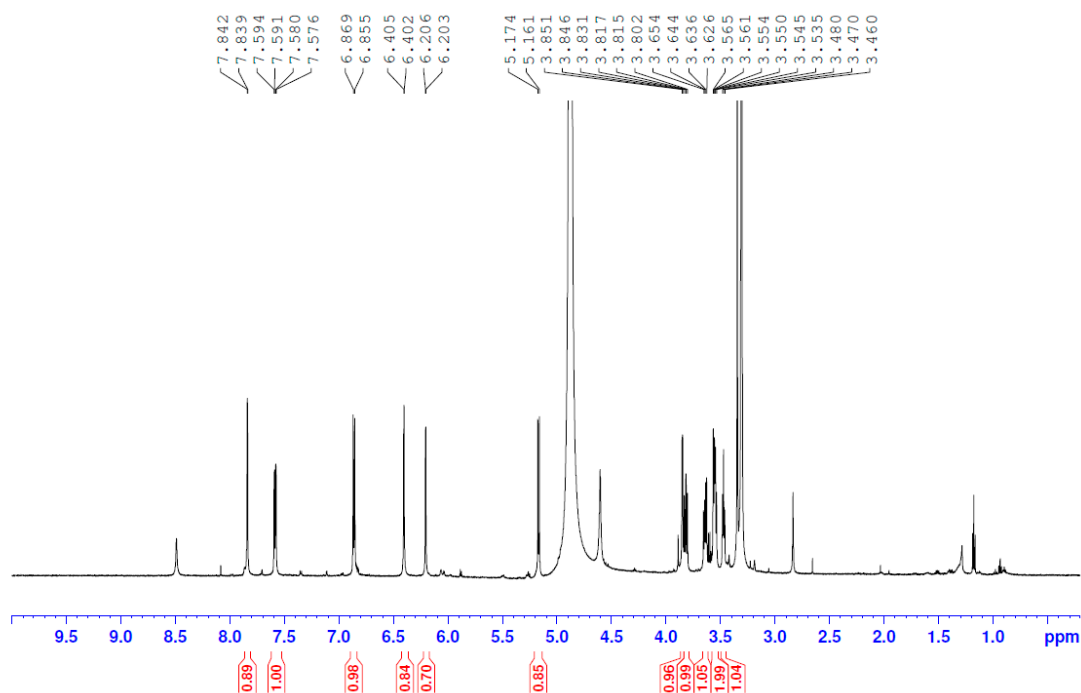


Figure S54. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 18

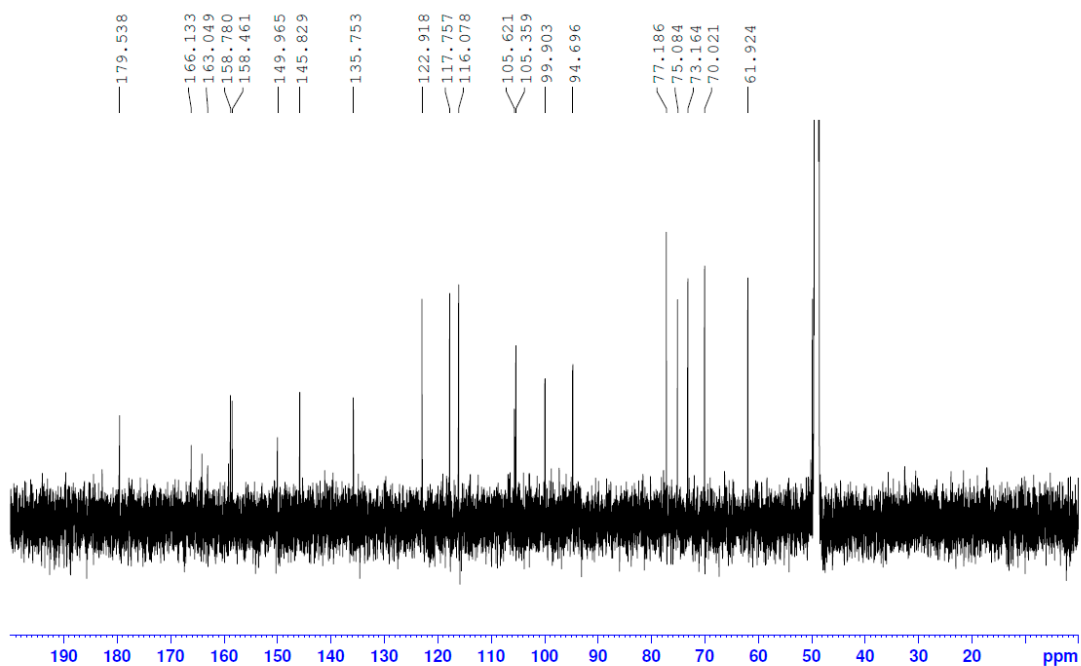


Figure S55. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 18

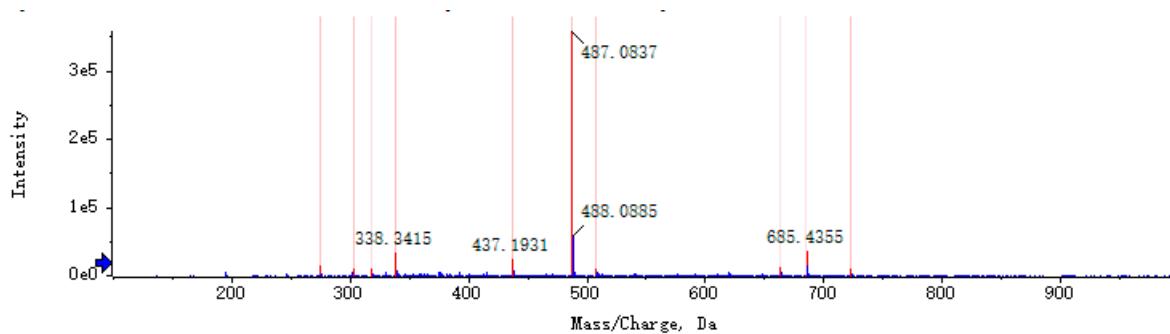


Figure S56. The HR-ESI-MS spectrum of compound 19

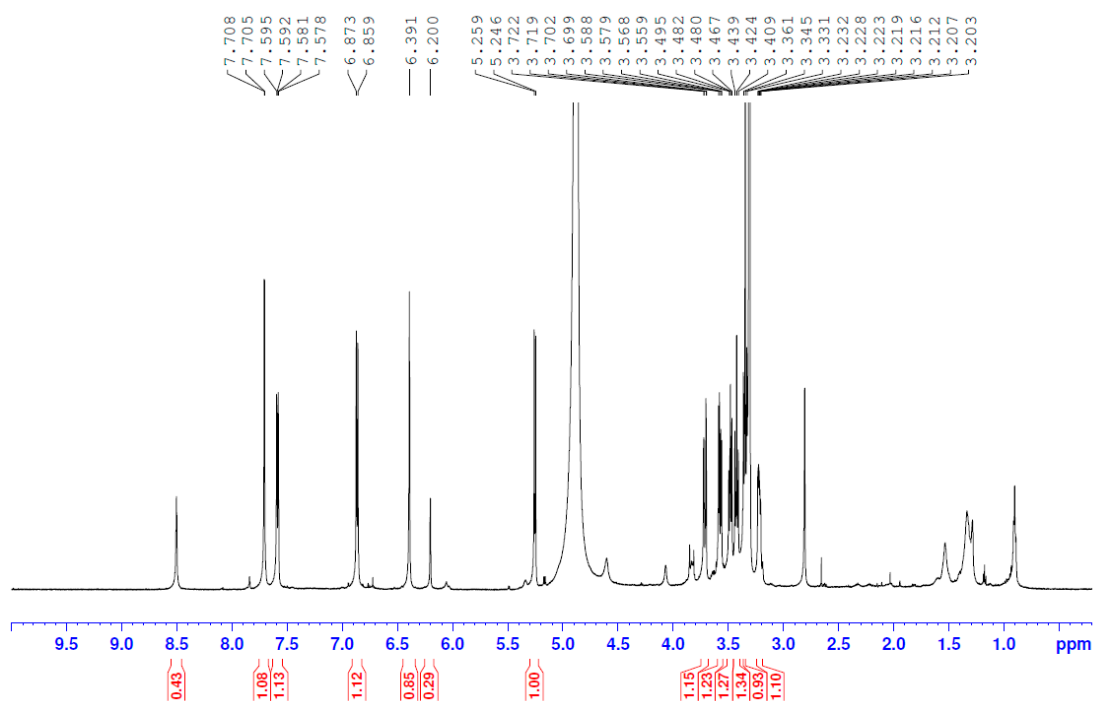


Figure S57. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 19

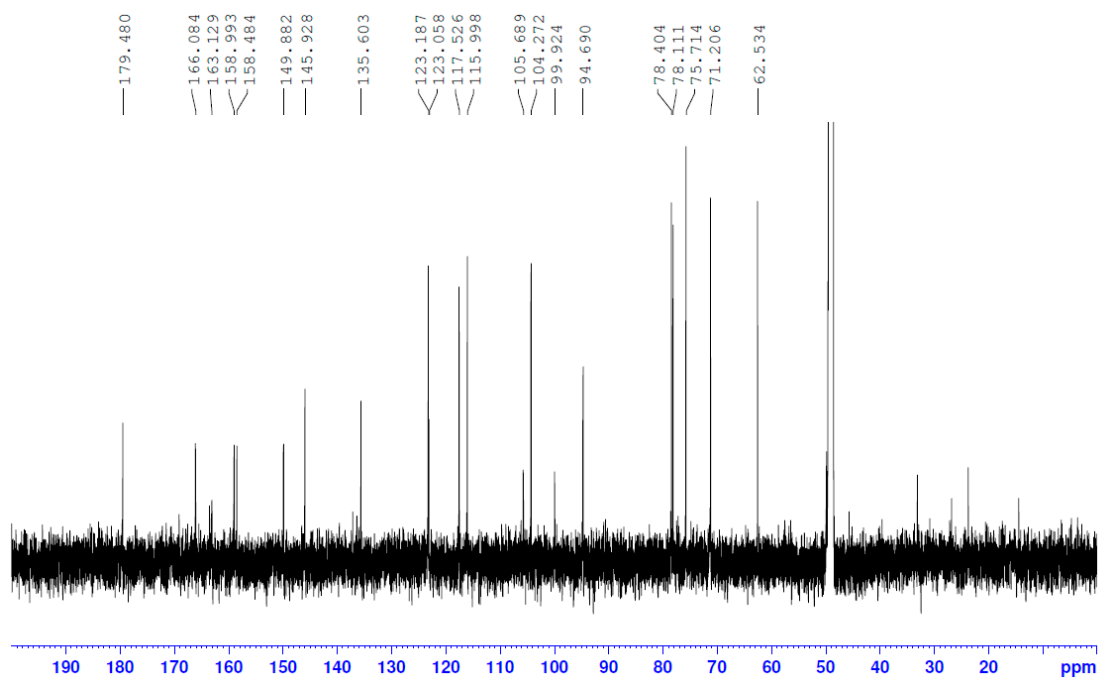


Figure S58. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 19

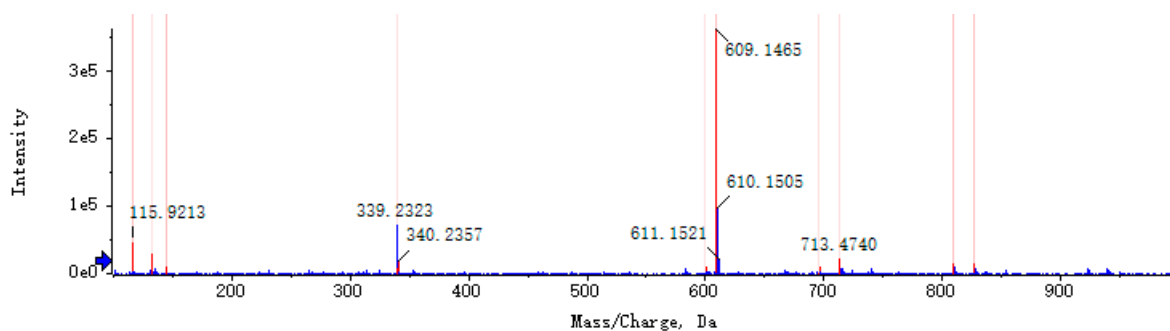


Figure S59. The HR-ESI-MS spectrum of compound 20

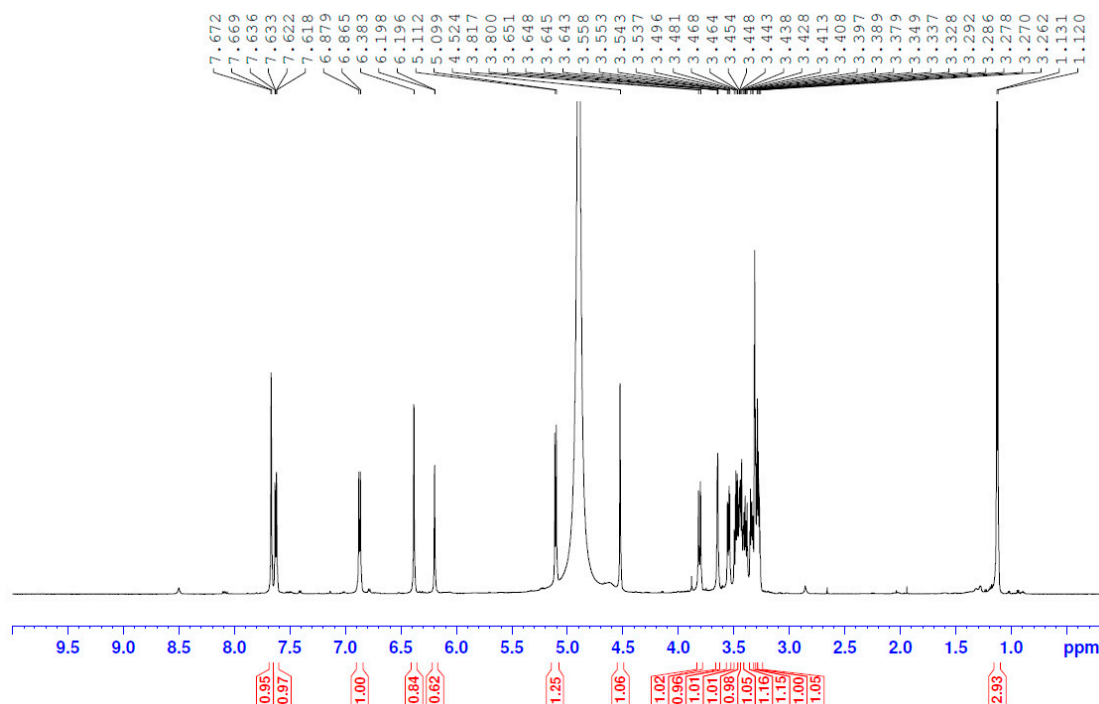


Figure S60. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 20

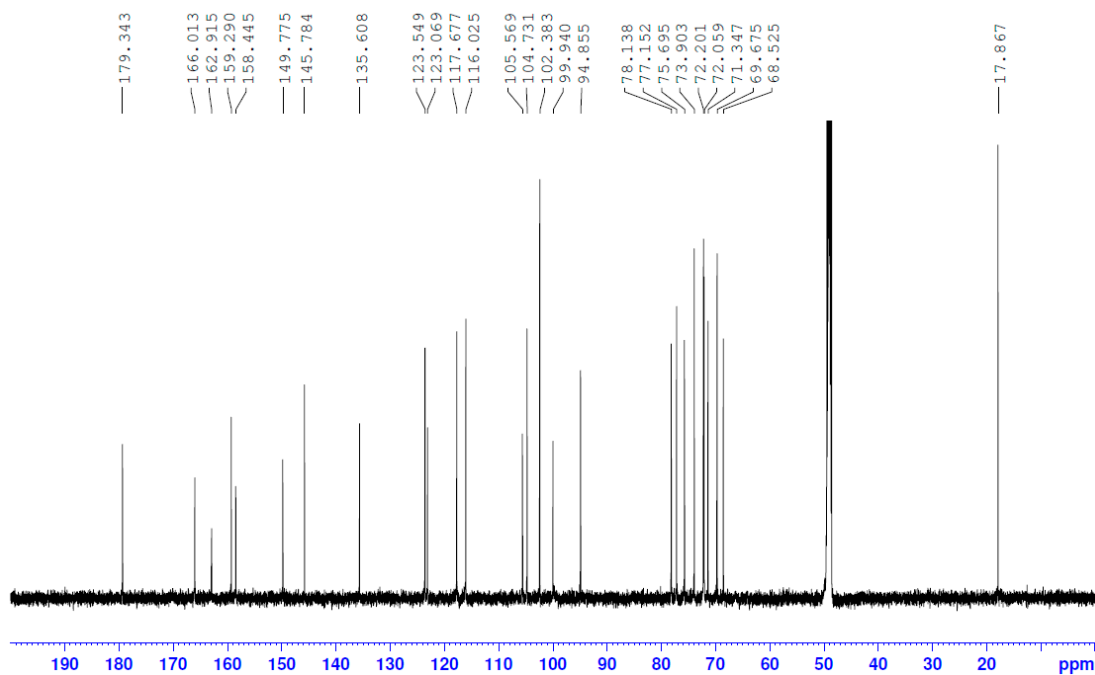


Figure S61. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 20

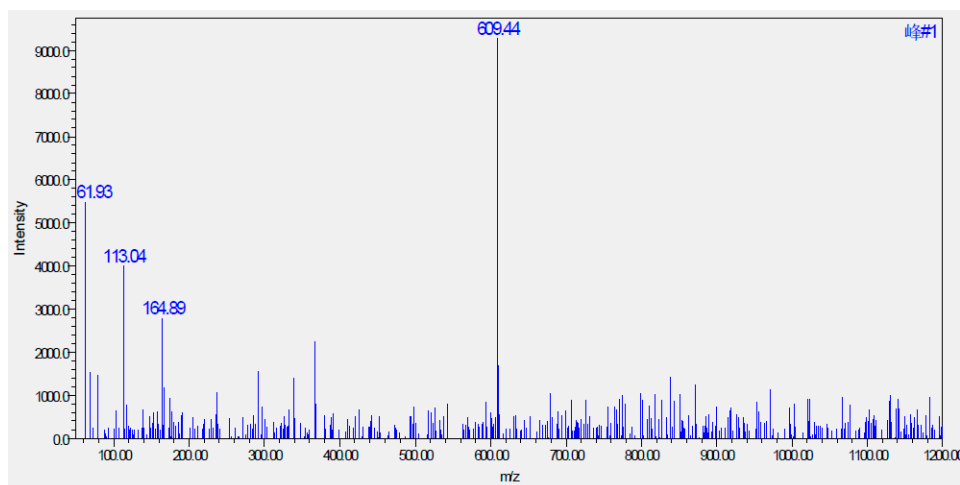


Figure S62. The ESI-MS spectrum of compound 21

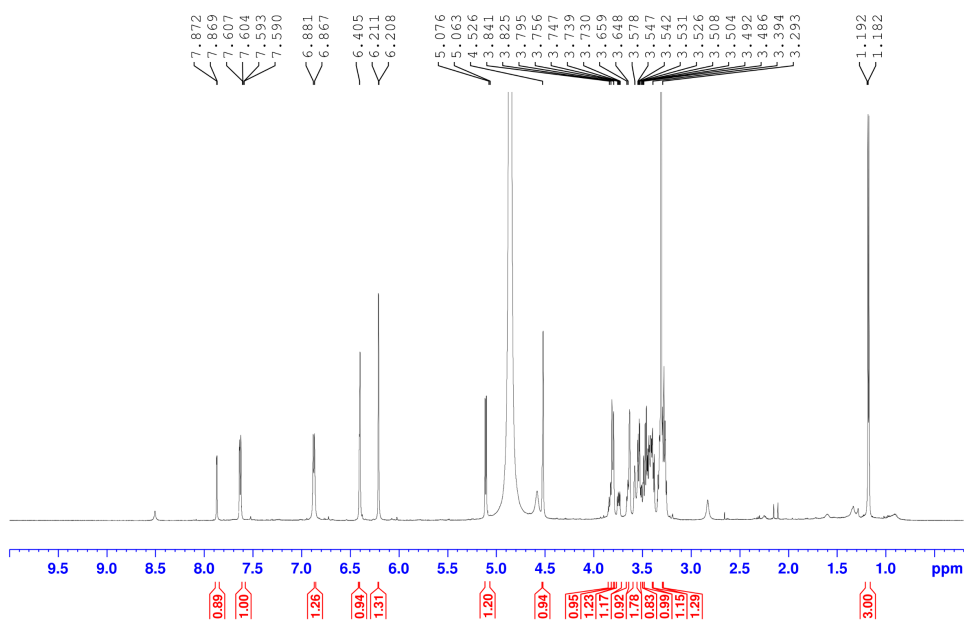


Figure S63. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 21

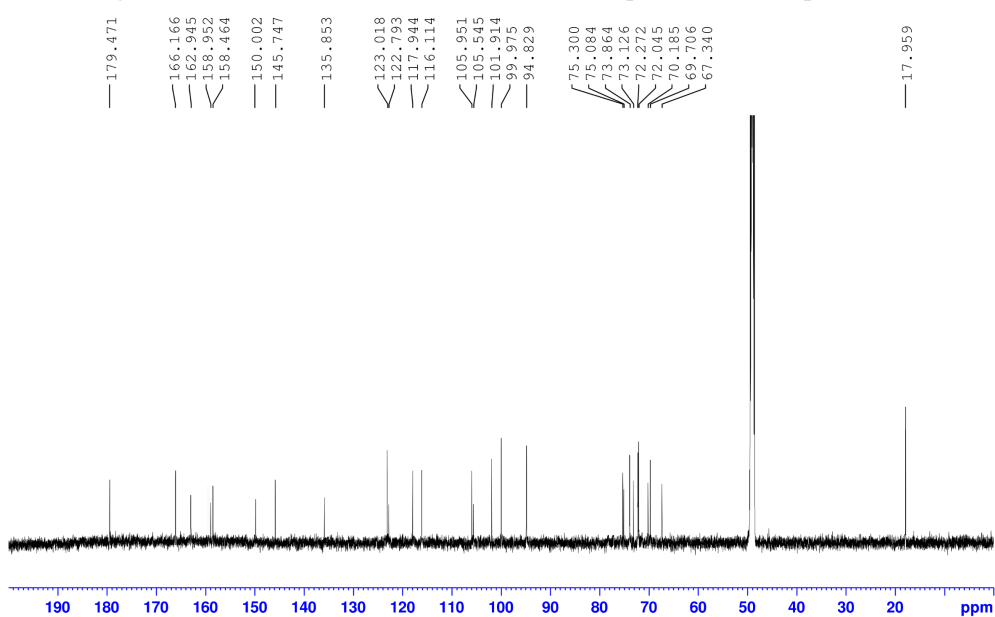


Figure S64. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 21

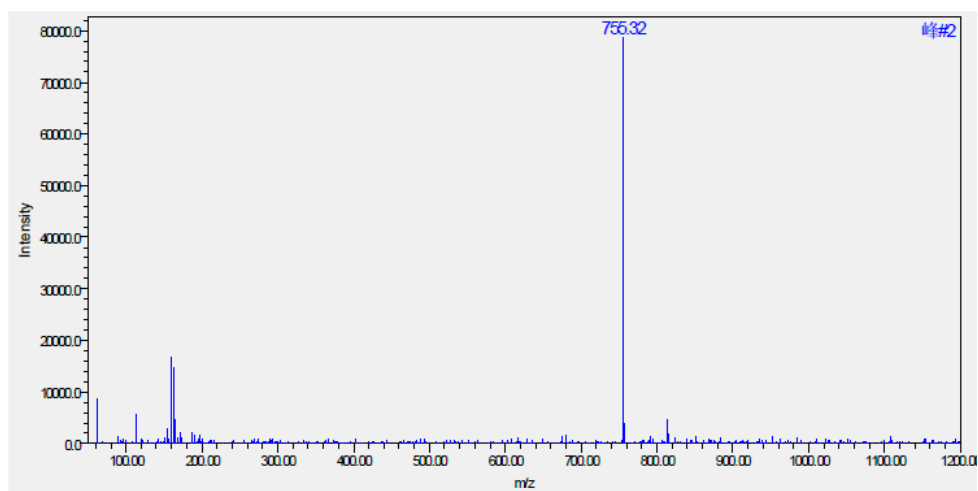


Figure S65. The ESI-MS spectrum of compound 22

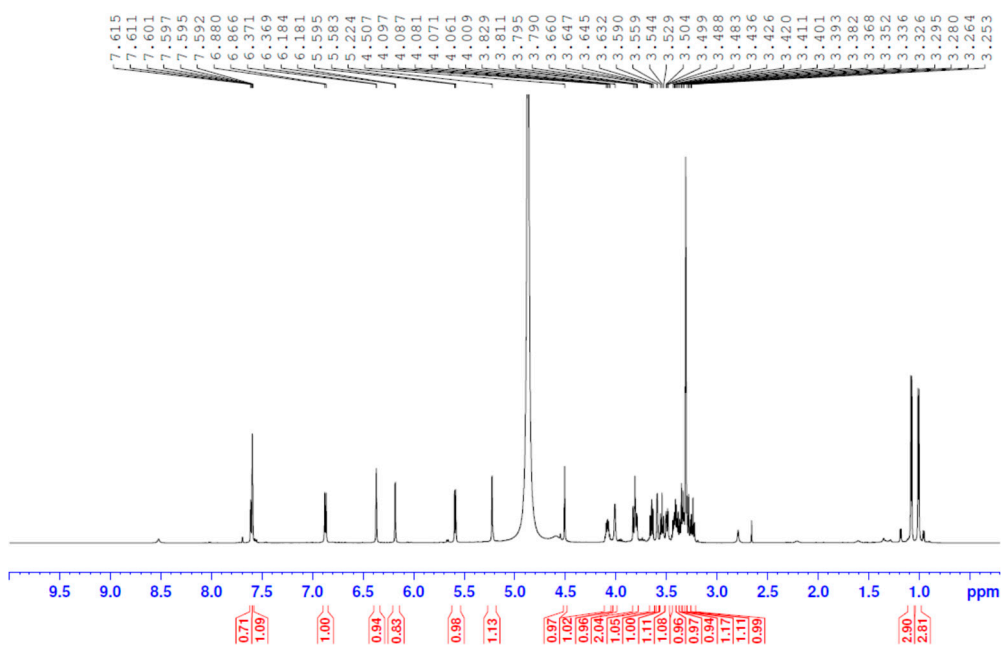


Figure S66. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 22

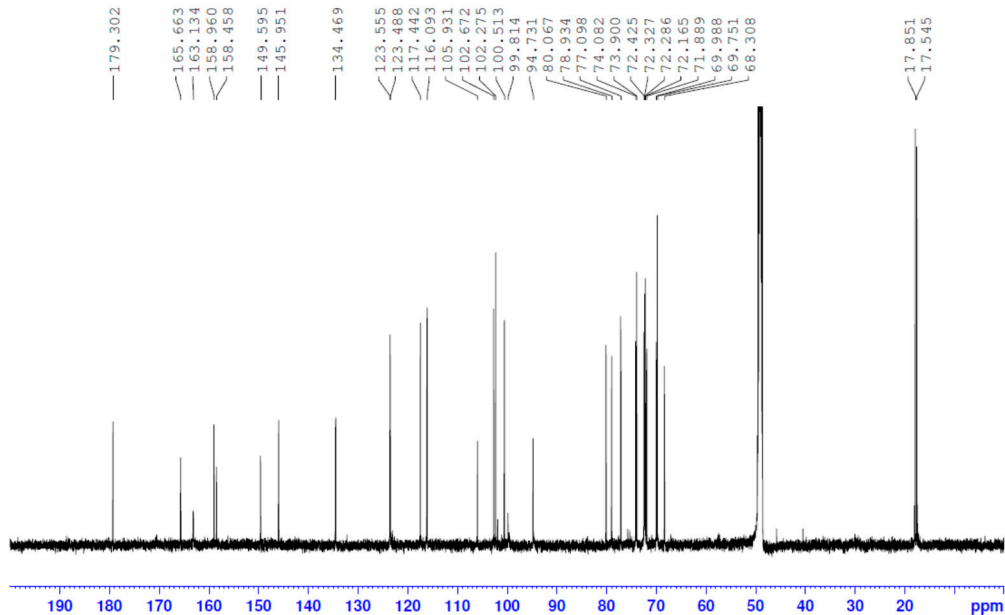


Figure S67. The ¹³C-NMR (150MHz, CD₃OD) spectrum of compound 22

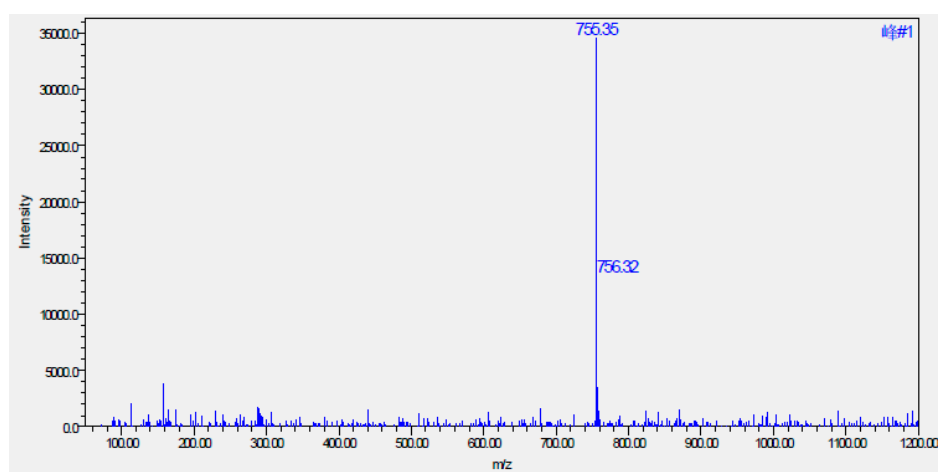


Figure S68. The ESI-MS spectrum of compound 23

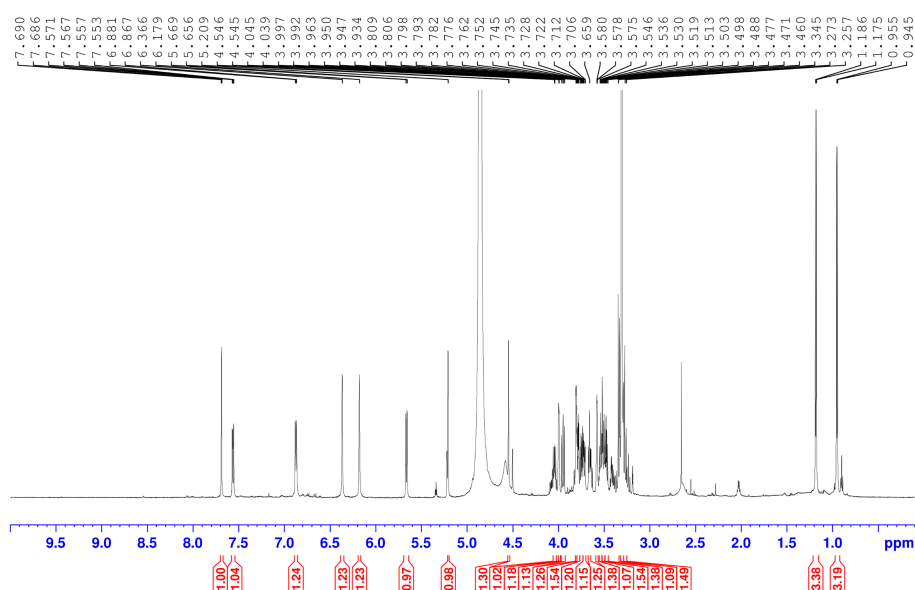


Figure S69. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 23

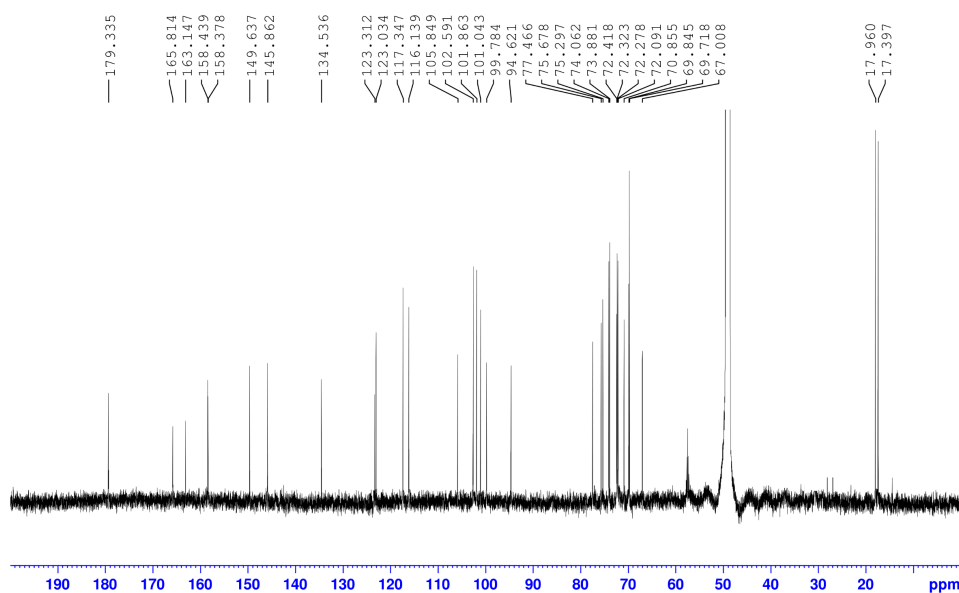


Figure S70. The ¹³C-NMR (150MHz, CD₃OD) spectrum of compound 23

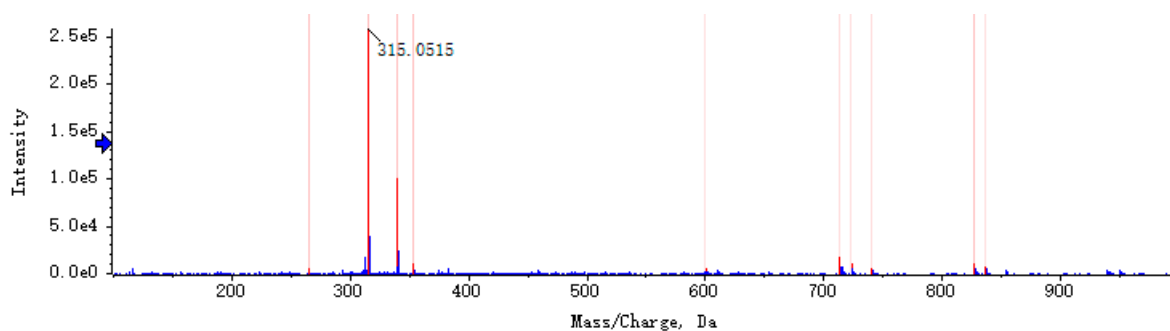


Figure S71. The ESI-MS spectrum of compound 24

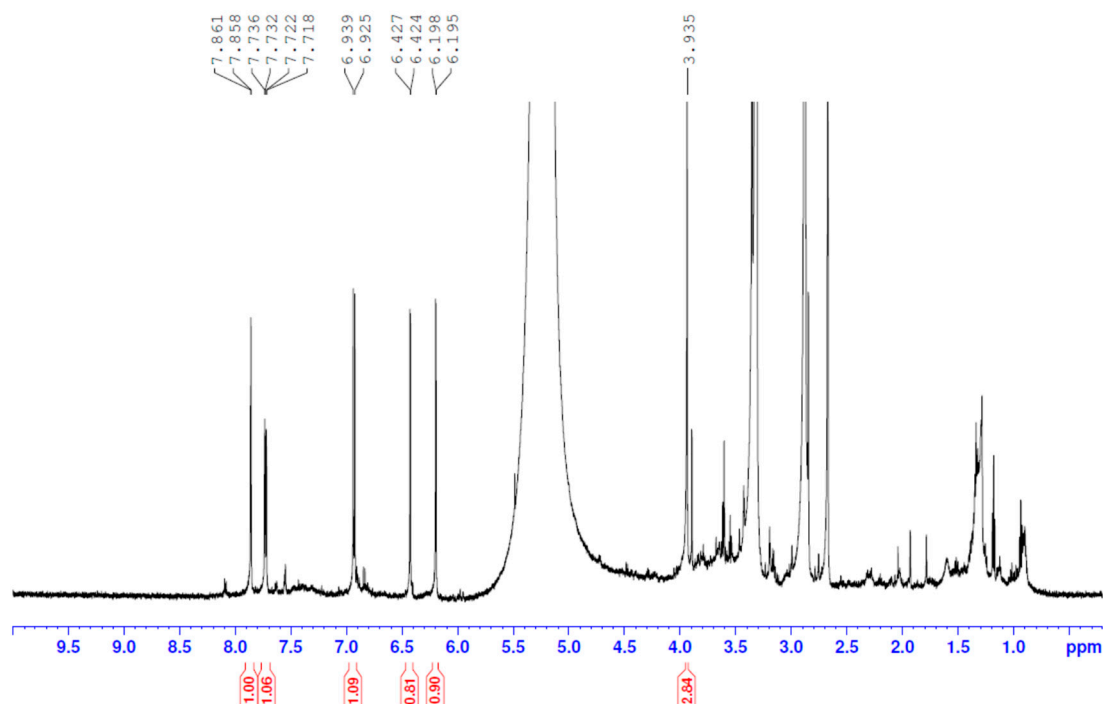


Figure S72. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 24

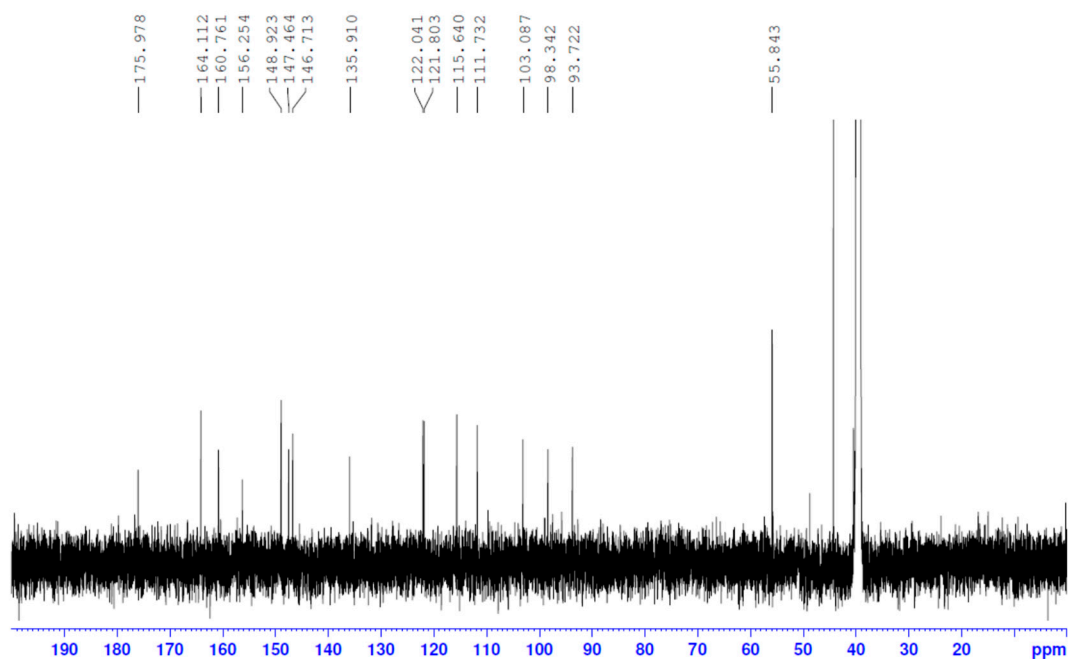


Figure S73. The ¹³C-NMR (150MHz, DMSO-*d*₆) spectrum of compound 24

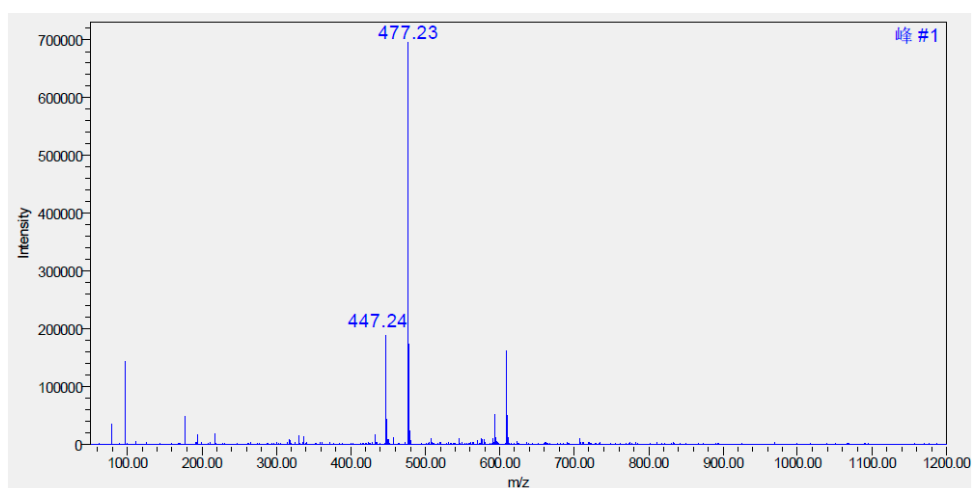


Figure S74. The ESI-MS spectrum of compound 25

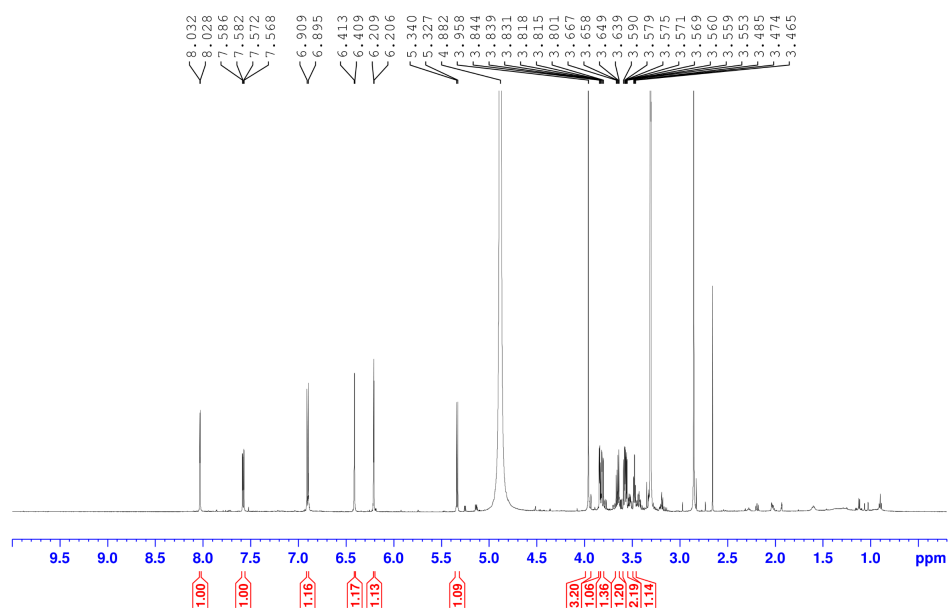


Figure S75. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 25

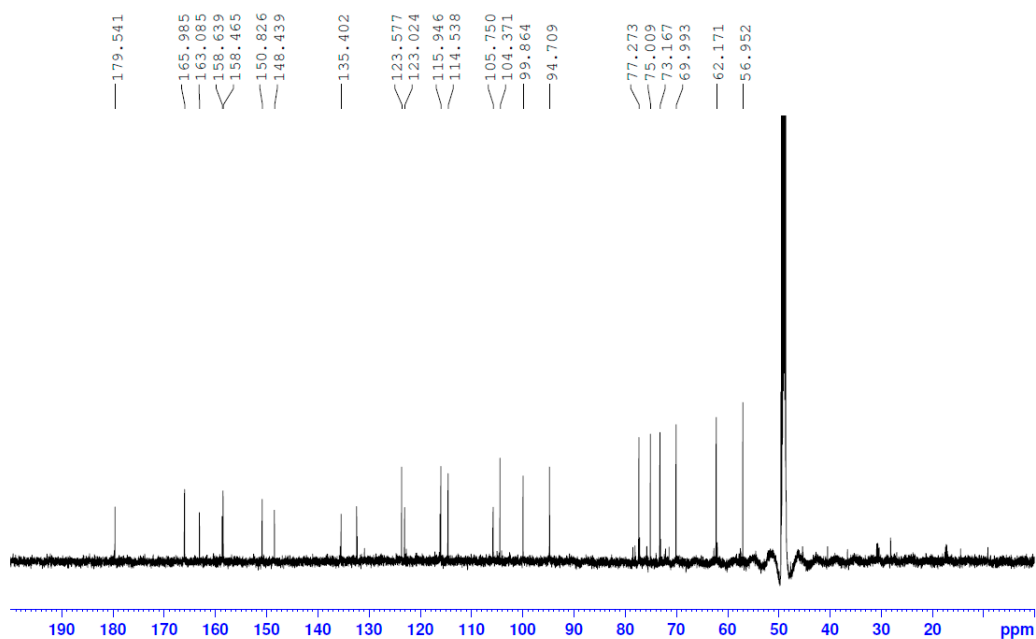


Figure S76. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 25

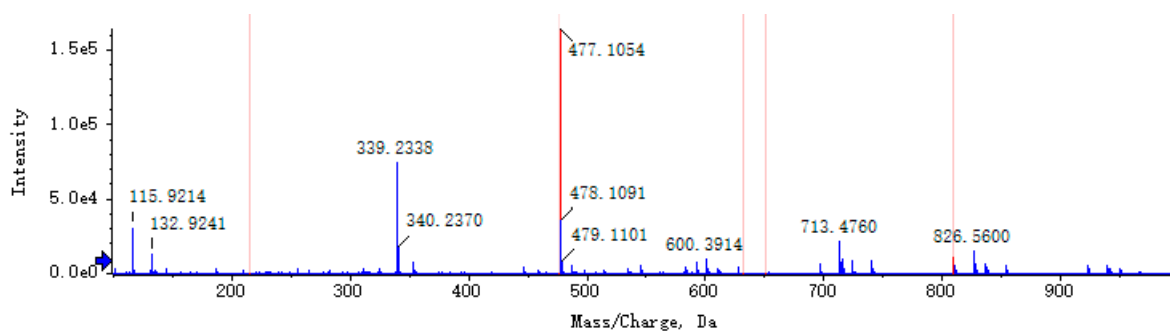


Figure S77. The ESI-MS spectrum of compound 26

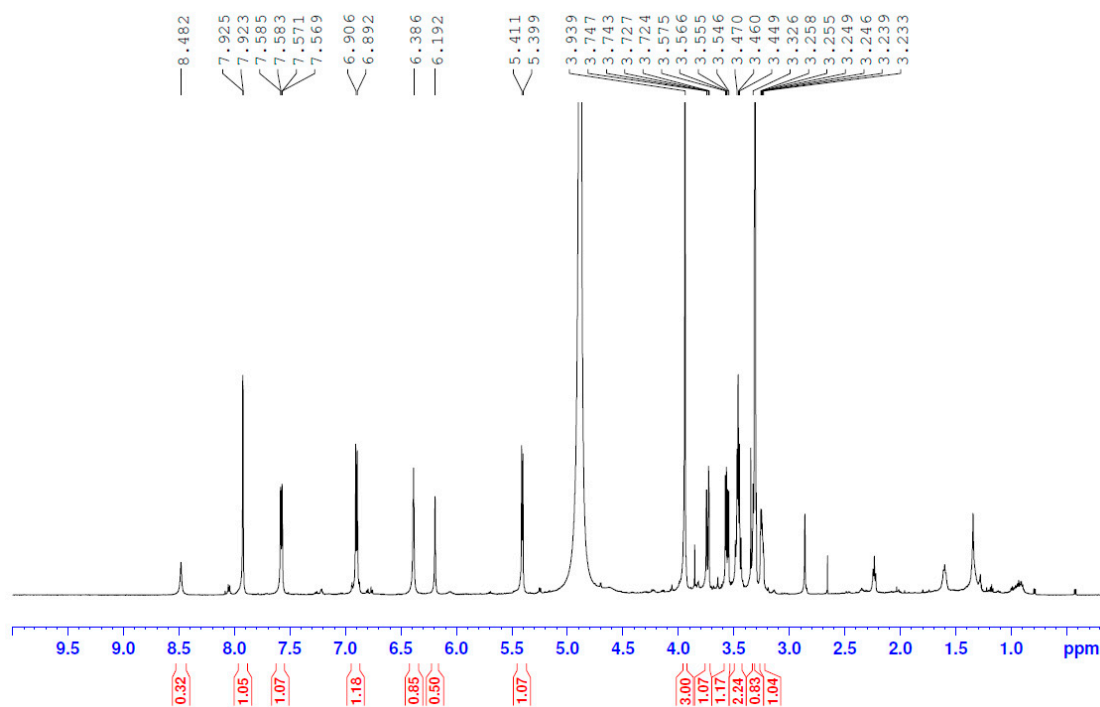


Figure S78. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 26

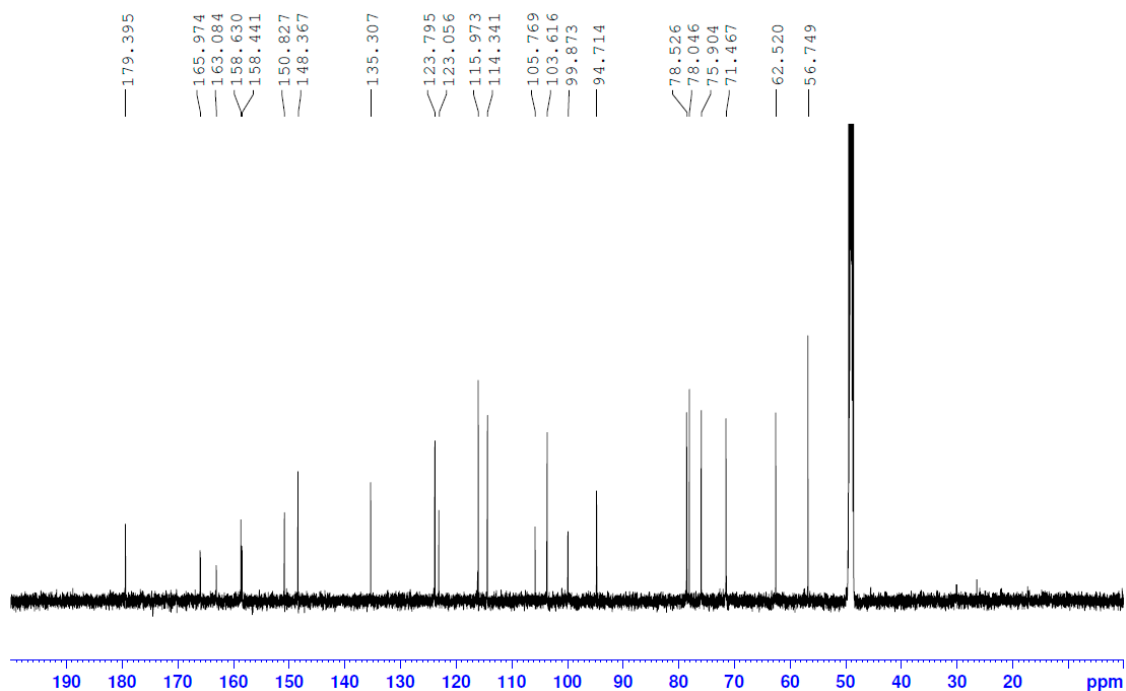


Figure S79. The ¹³C-NMR (150MHz, CD₃OD) spectrum of compound 26

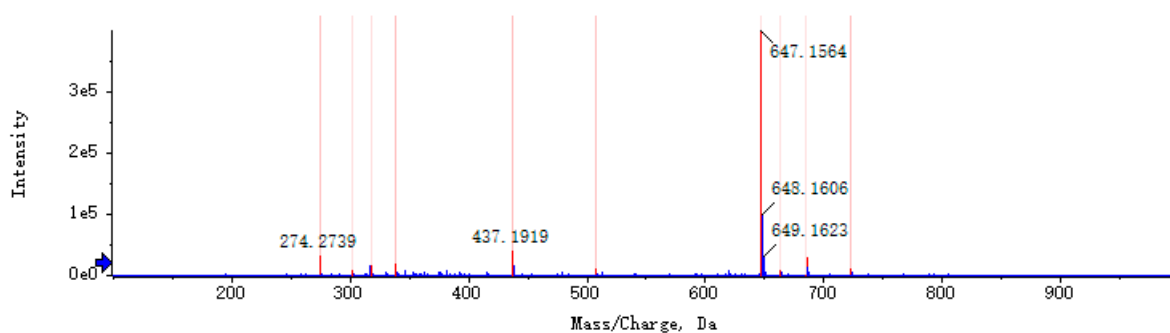


Figure S80. The ESI-MS spectrum of compound 27

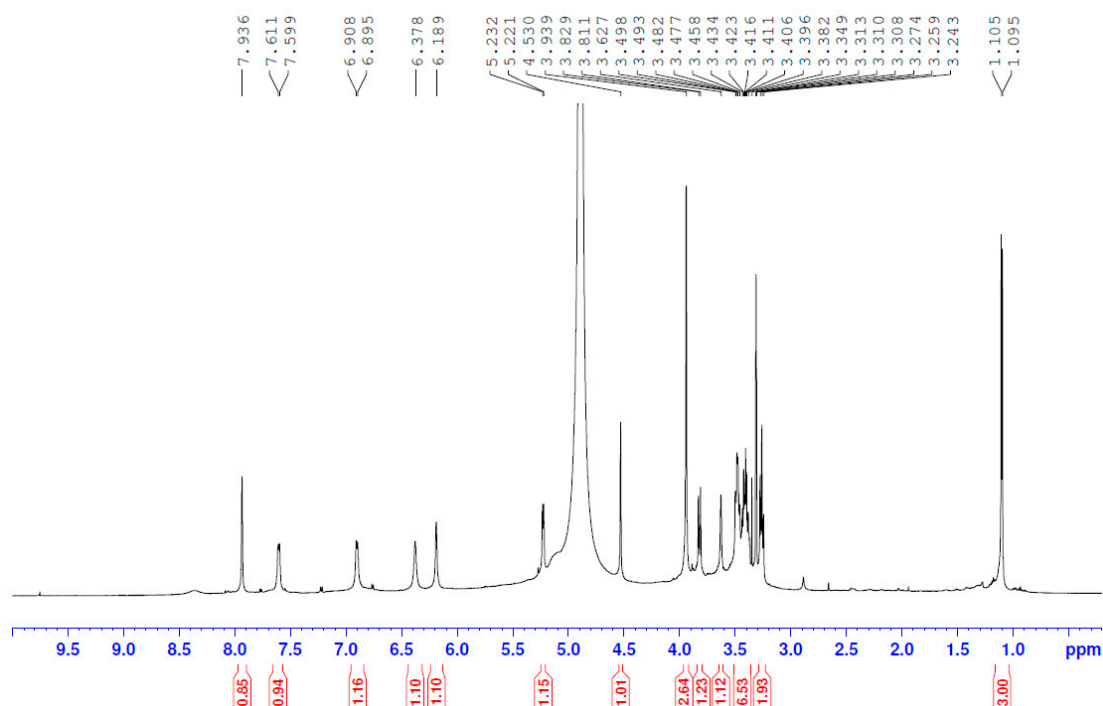


Figure S81. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 27

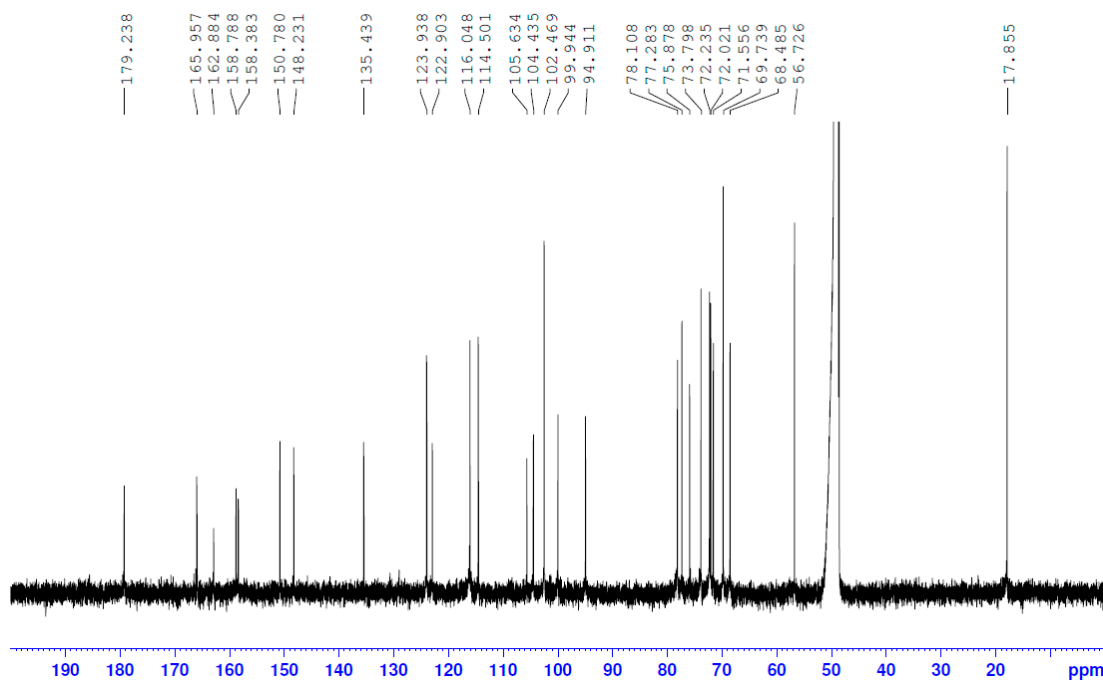


Figure S82. The ¹³C-NMR (150MHz, CD₃OD) spectrum of compound 27

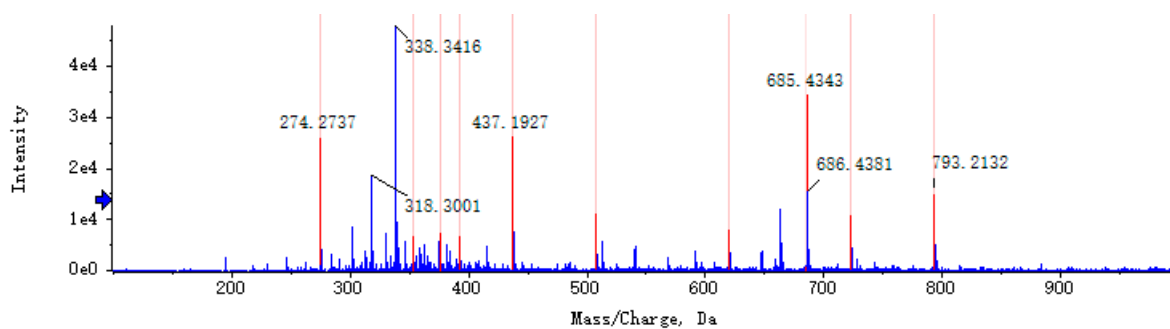


Figure S83. The HR-ESI-MS spectrum of compound 28

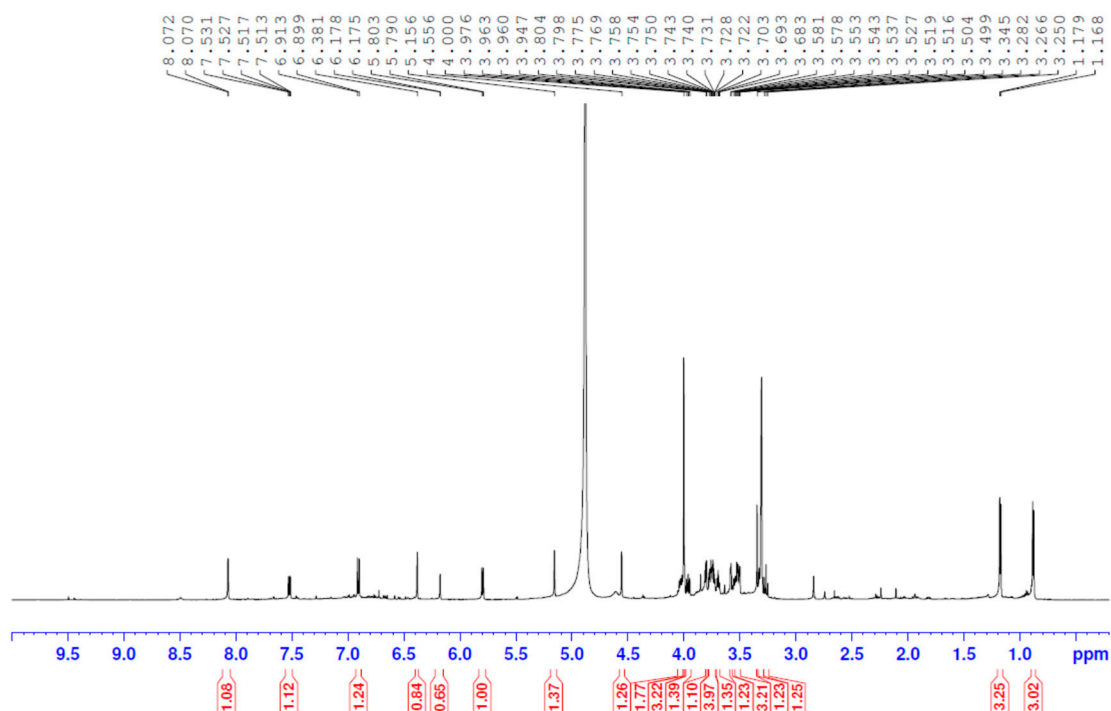


Figure S84. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 28

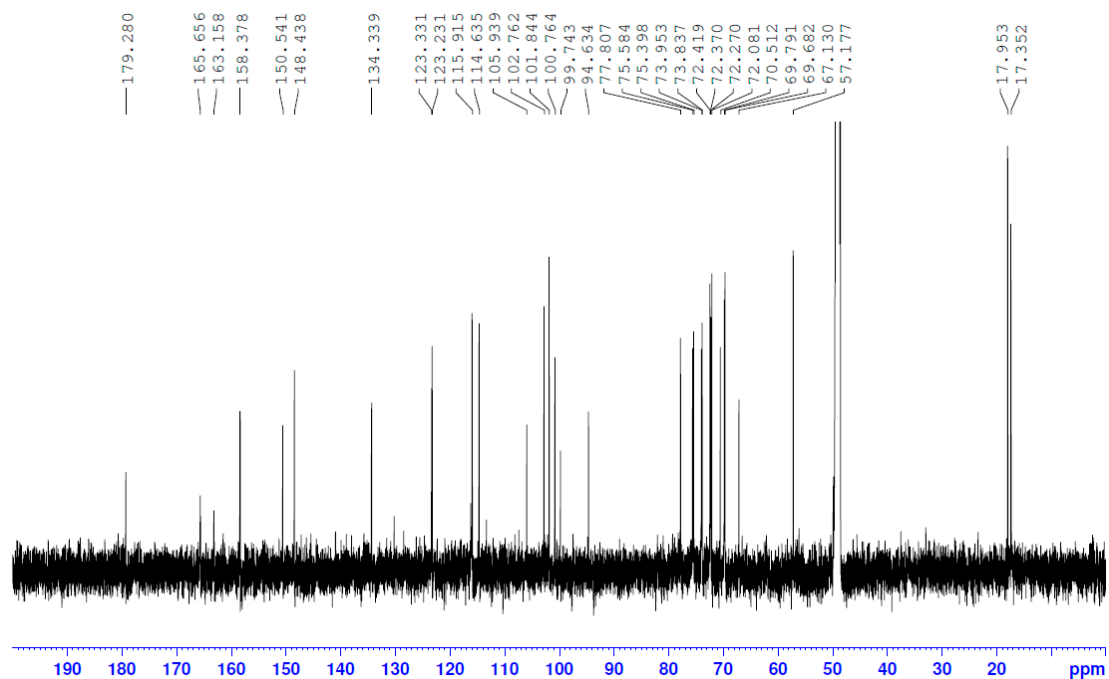


Figure S85. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 28

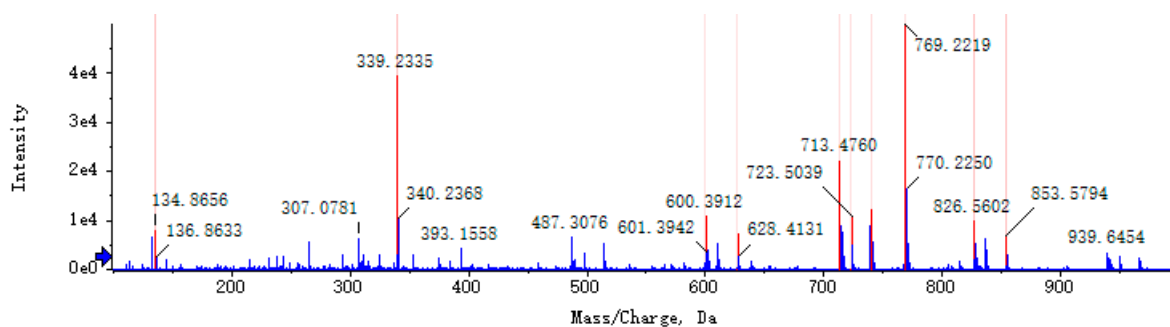


Figure S86. The HR-ESI-MS spectrum of compound 29

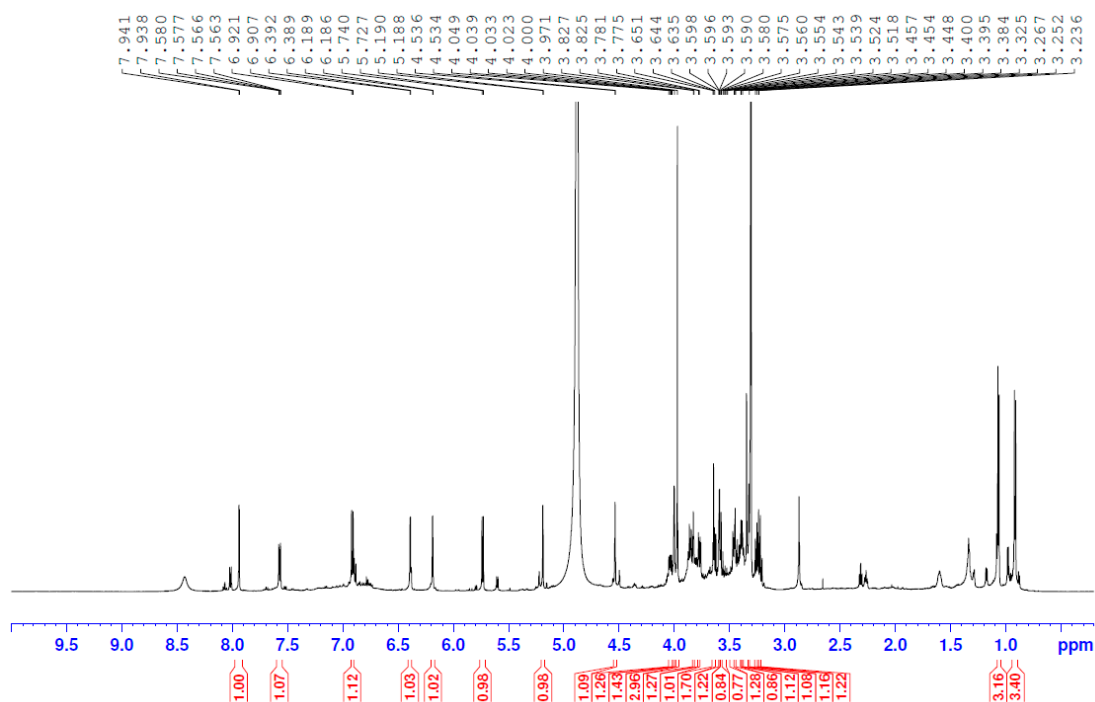


Figure S87. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 29

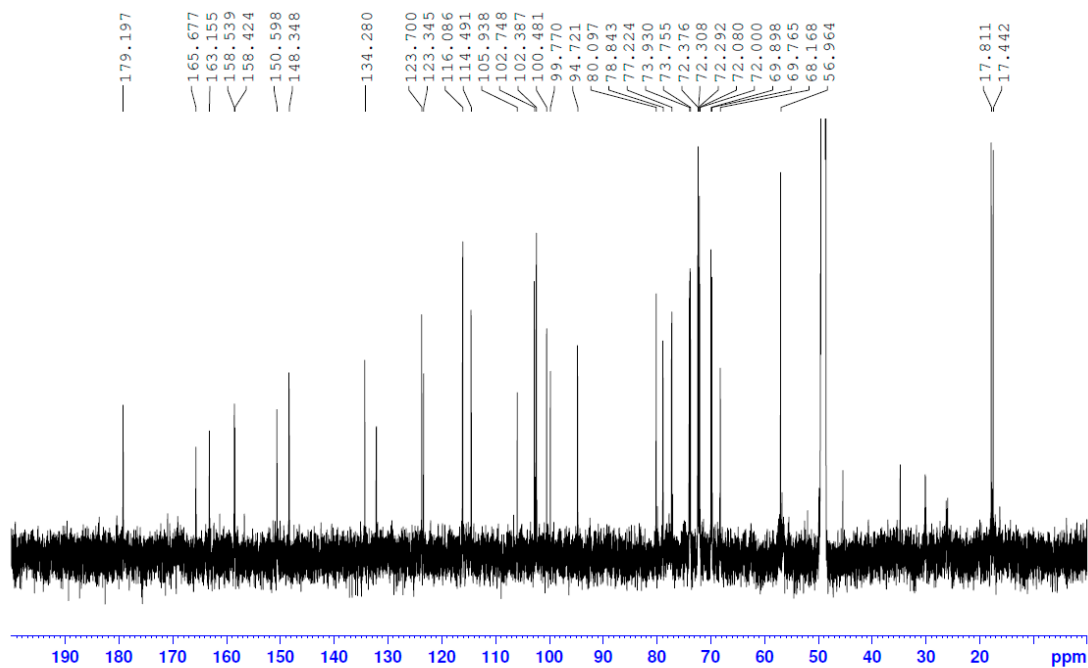


Figure S88. The ¹³C-NMR (150MHz, CD₃OD) spectrum of compound 29

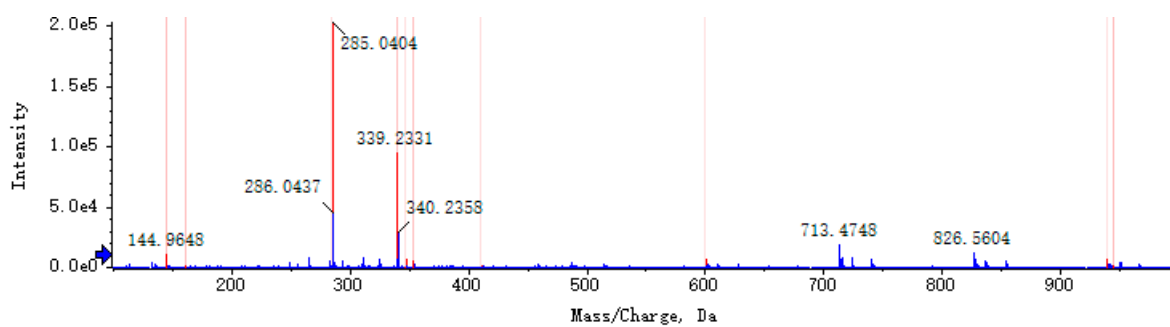


Figure S89. The HR-ESI-MS spectrum of compound 30

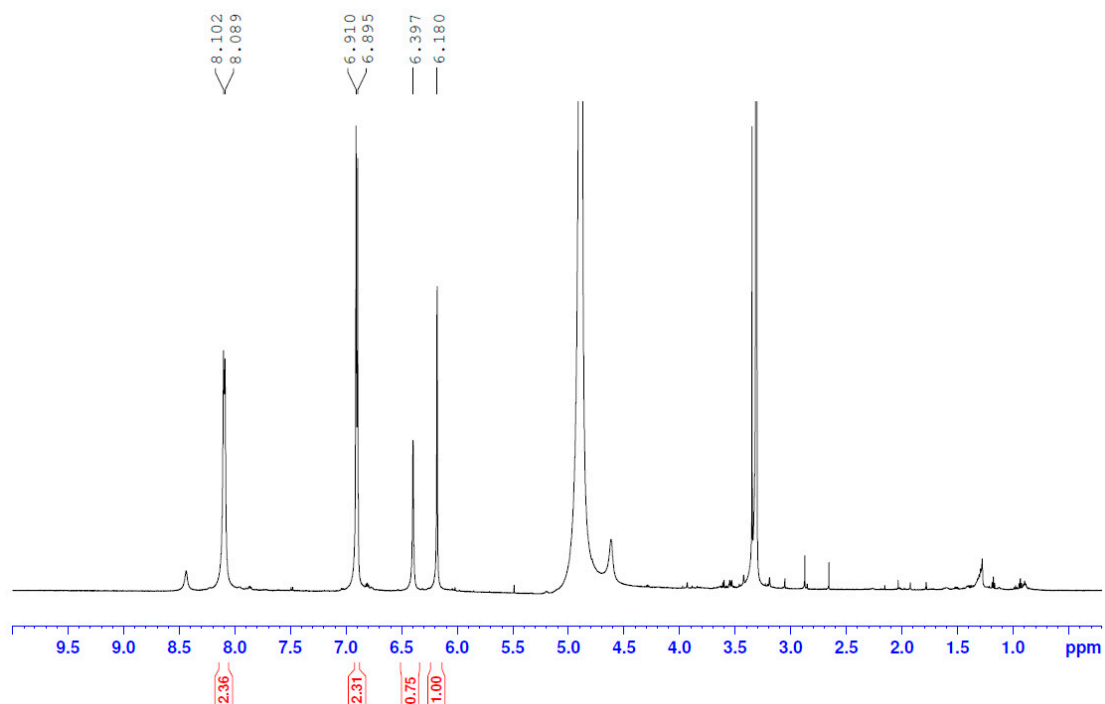


Figure S90. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 30

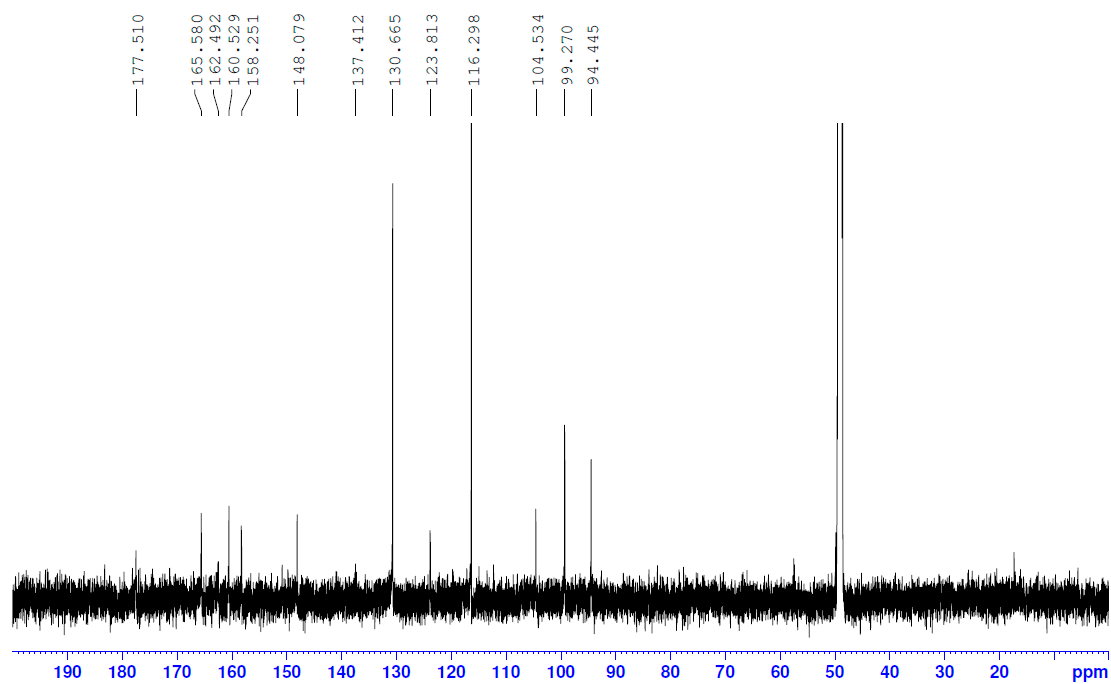


Figure S91. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 30

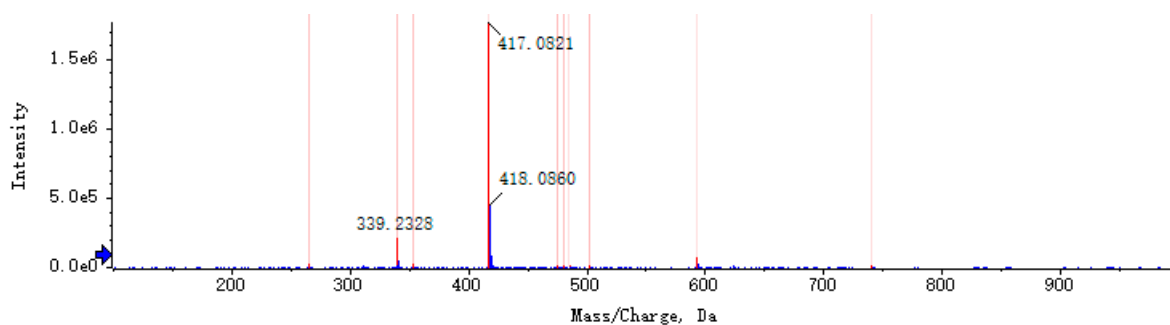


Figure S92. The HR-ESI-MS spectrum of compound 31

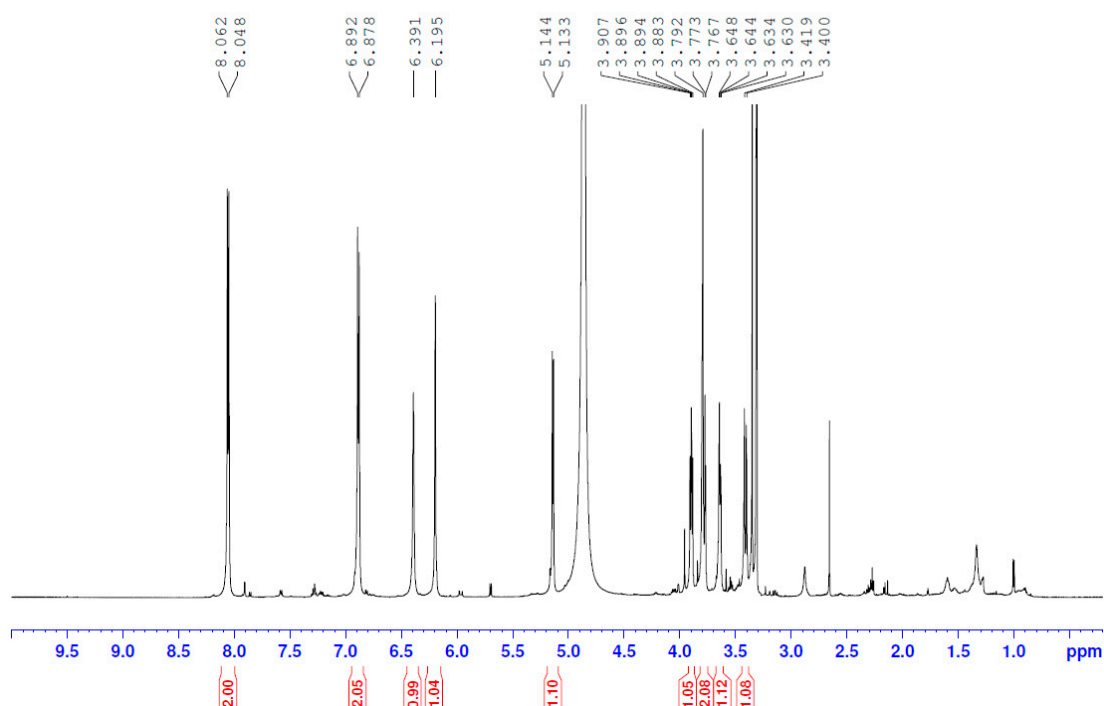


Figure S93. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 31

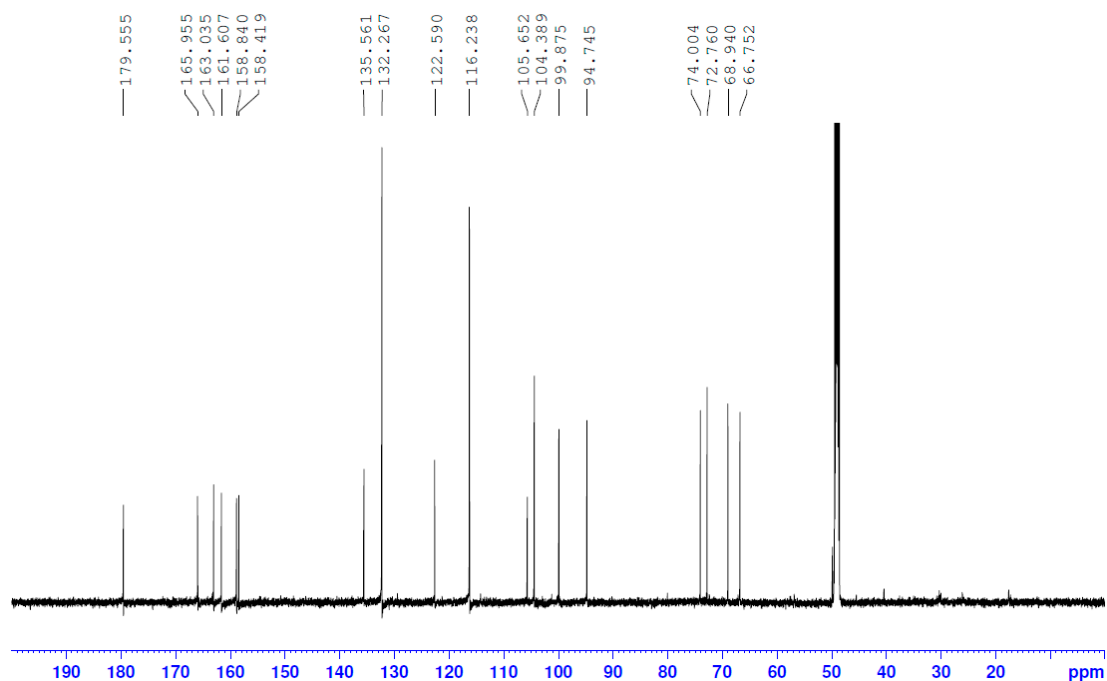


Figure S94. The ¹³C-NMR (150MHz, CD₃OD) spectrum of compound 31

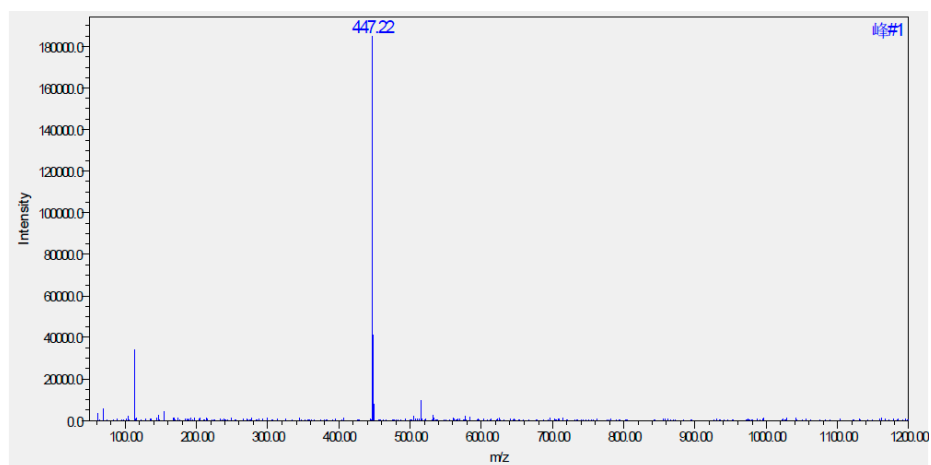


Figure S95. The ESI-MS spectrum of compound 32

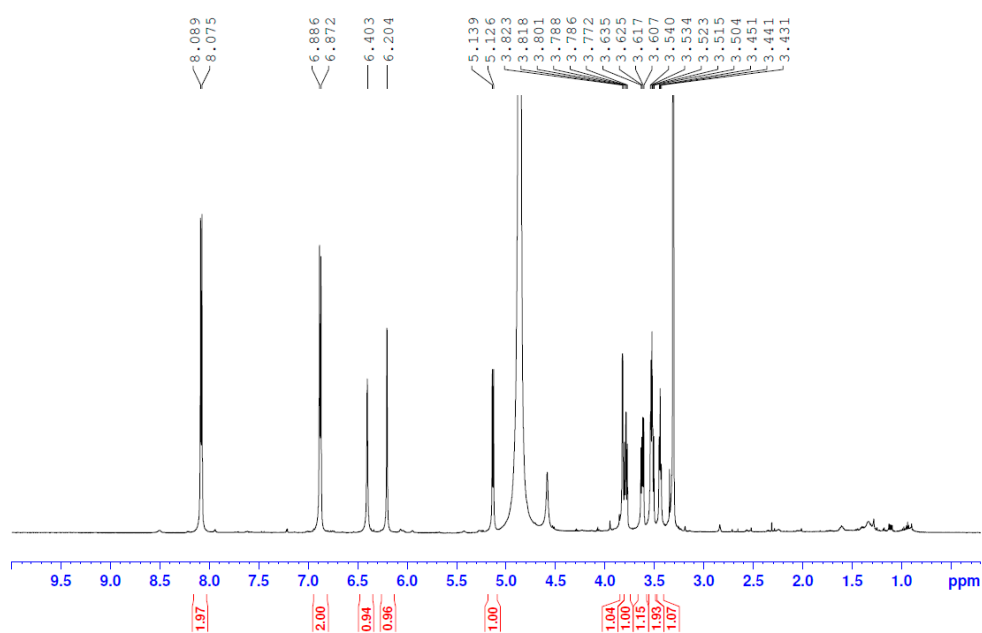


Figure S96. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 32

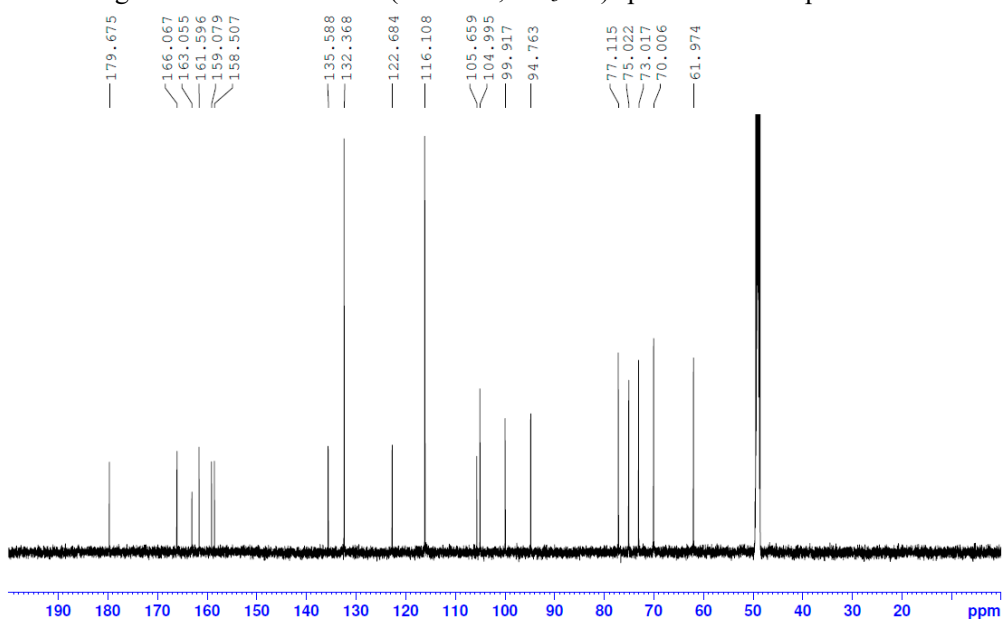


Figure S97. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 32

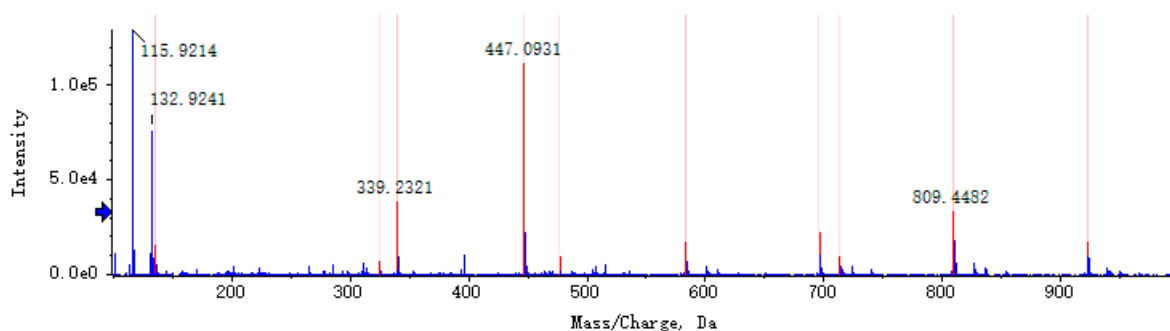


Figure S98. The ESI-MS spectrum of compound 33

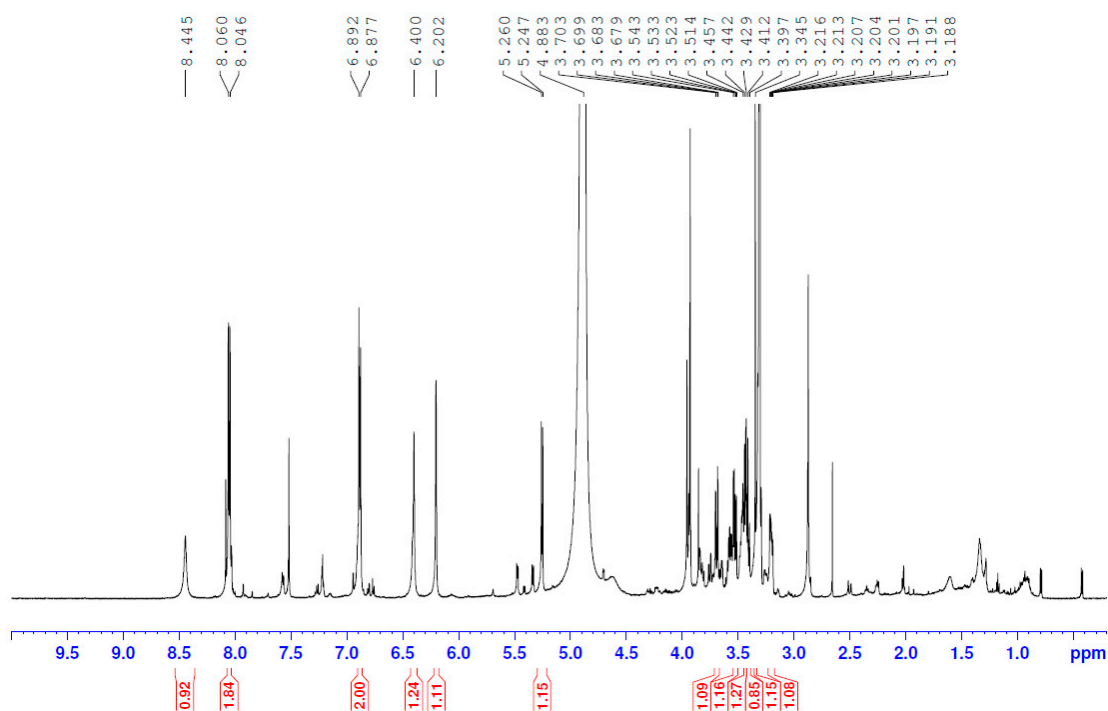


Figure S99. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 33

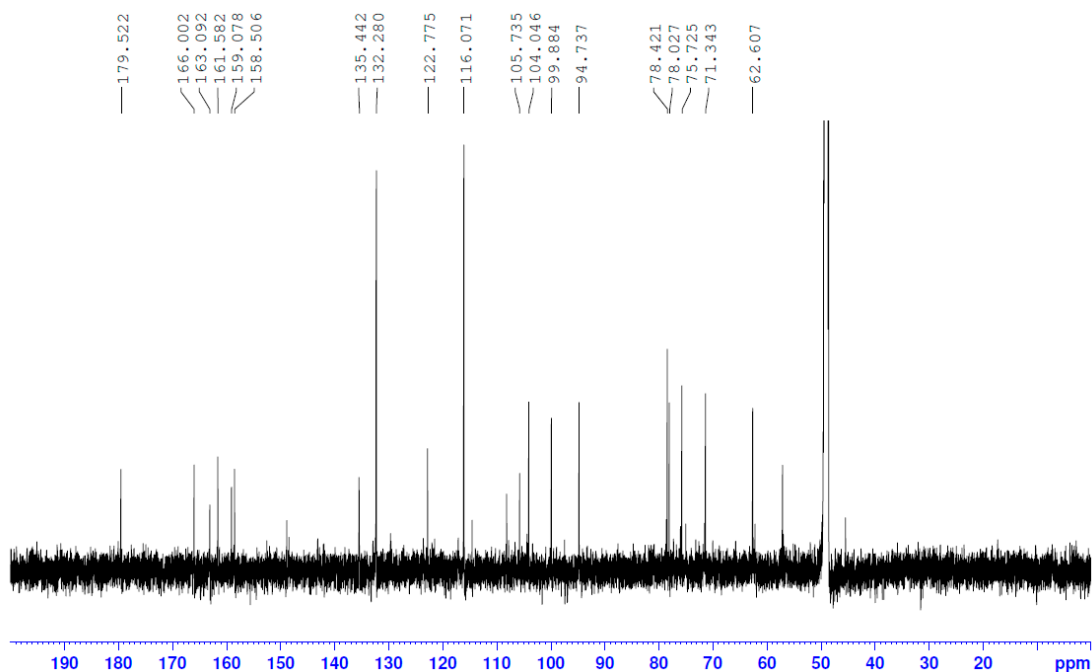


Figure S100. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 33

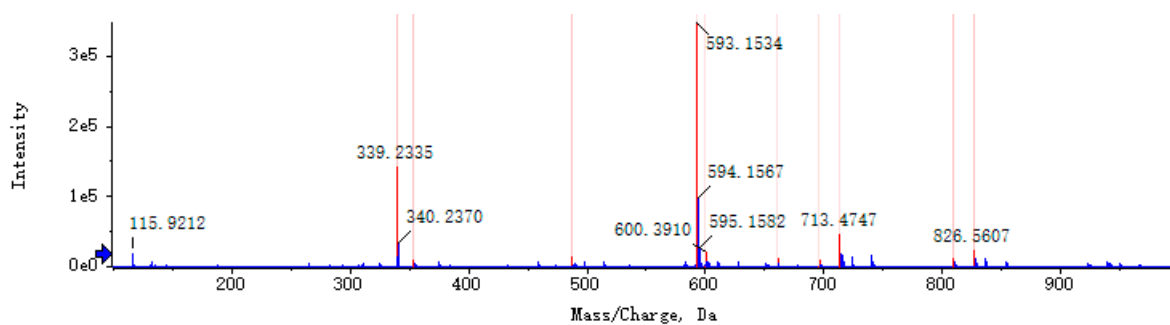


Figure S101. The ESI-MS spectrum of compound 34

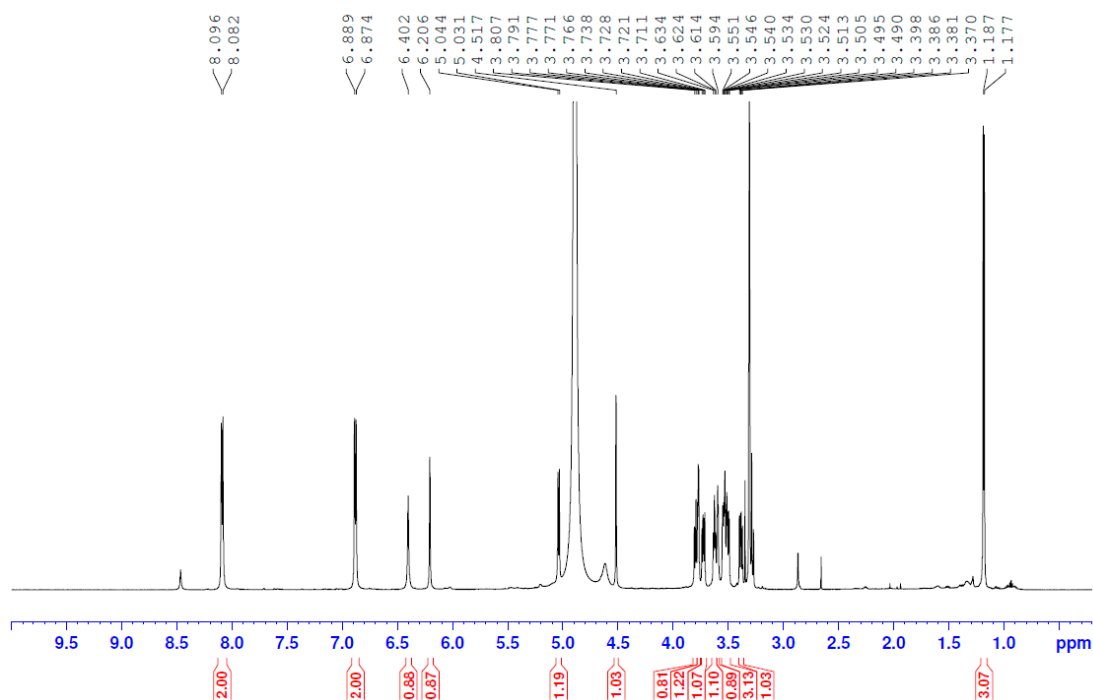


Figure S102. The ¹H-NMR (600MHz, CD₃OD) spectrum of compound 34

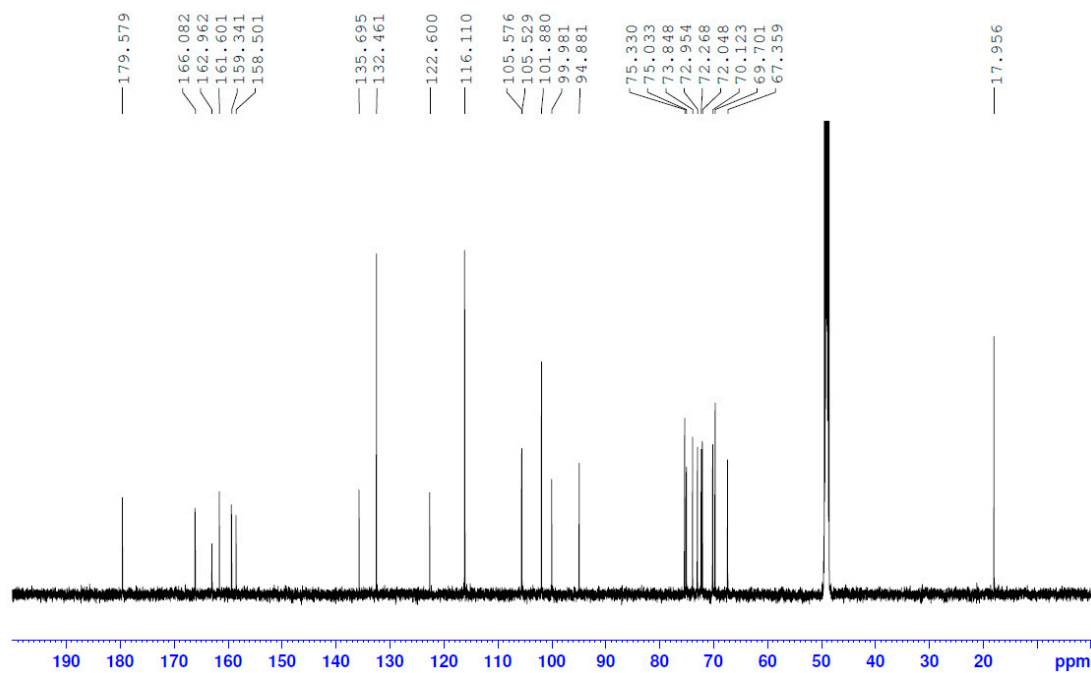


Figure S103. The ¹³C-NMR (150MHz, CD₃OD) spectrum of compound 34

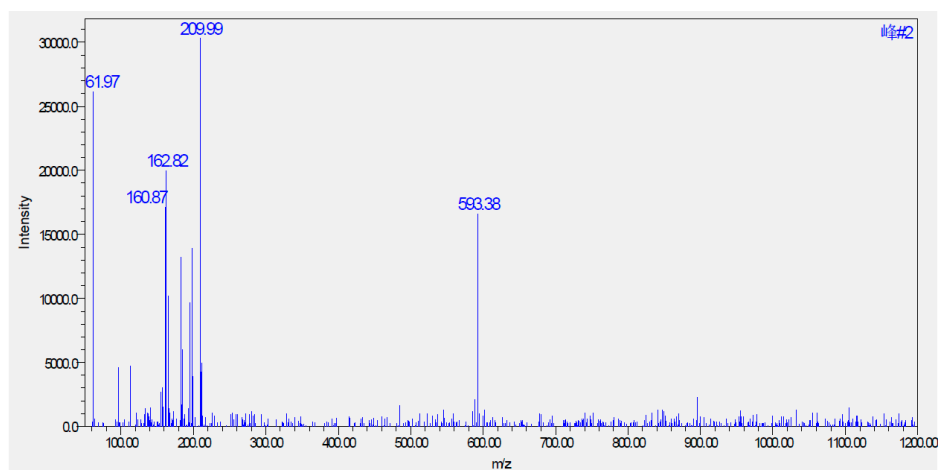


Figure S104. The ESI-MS spectrum of compound 35

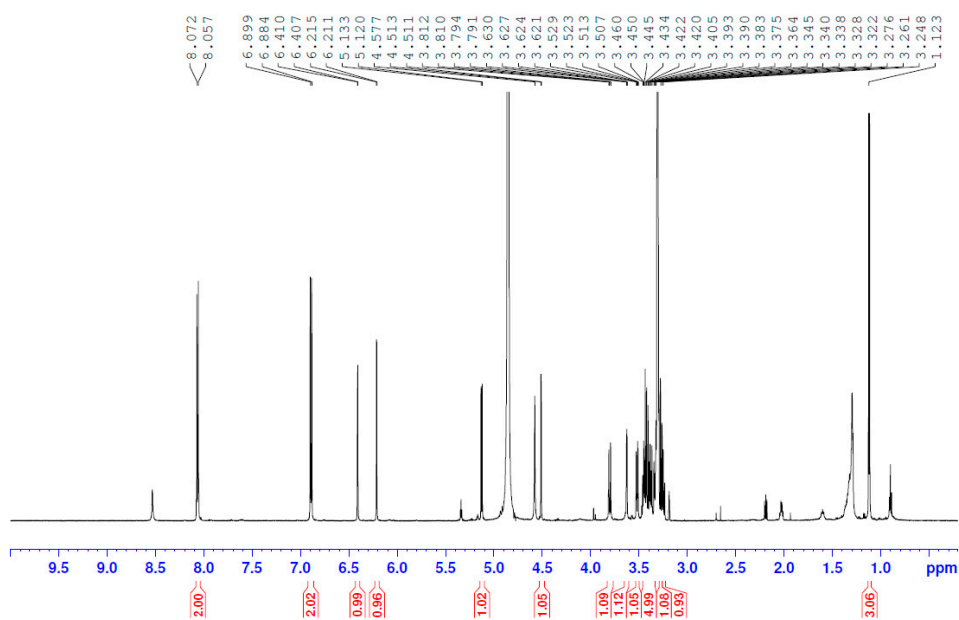


Figure S105. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 35

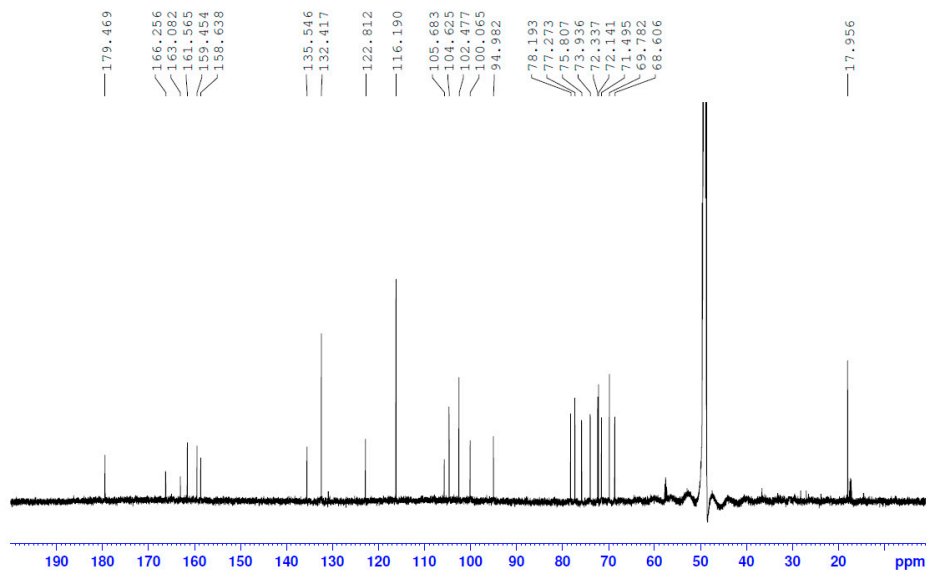


Figure S106. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 35

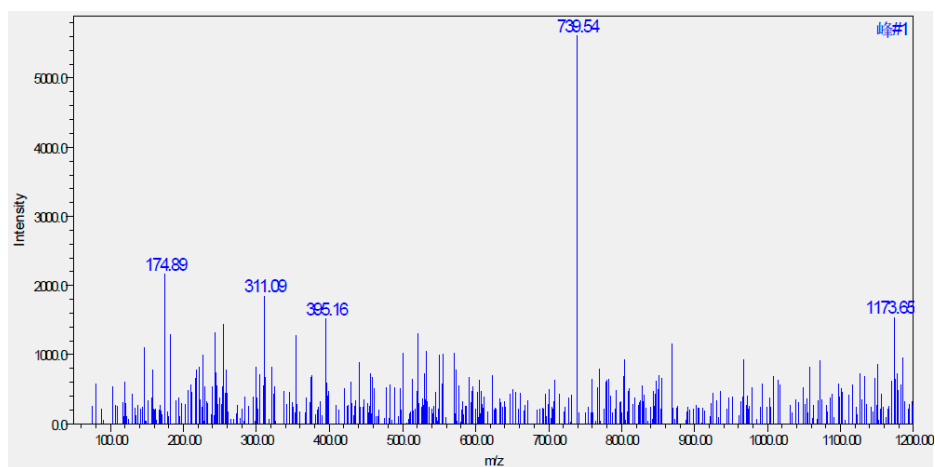


Figure S107. The ESI-MS spectrum of compound 36

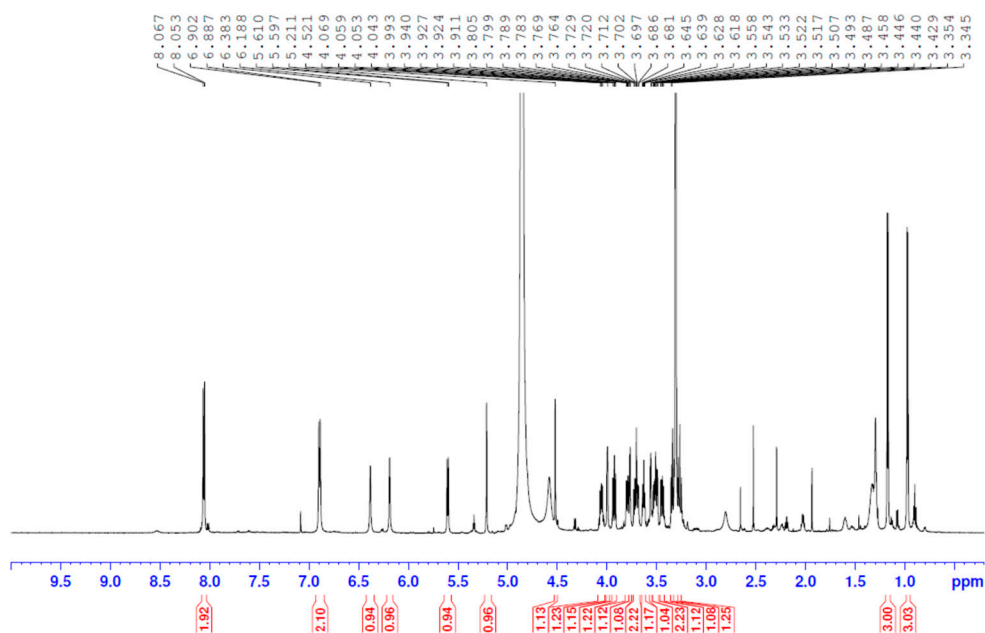


Figure S108. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 36

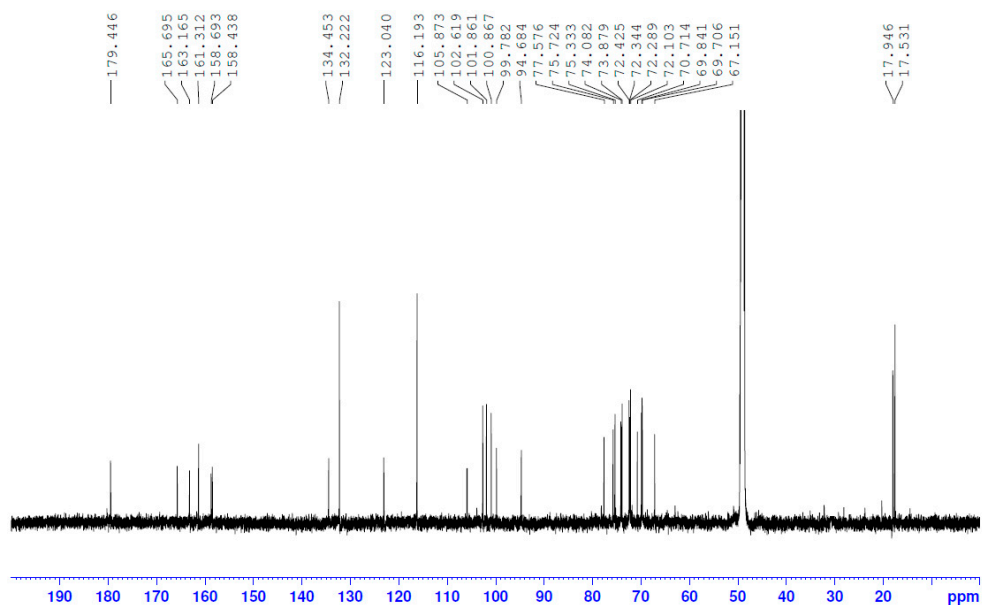


Figure S109. The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 36

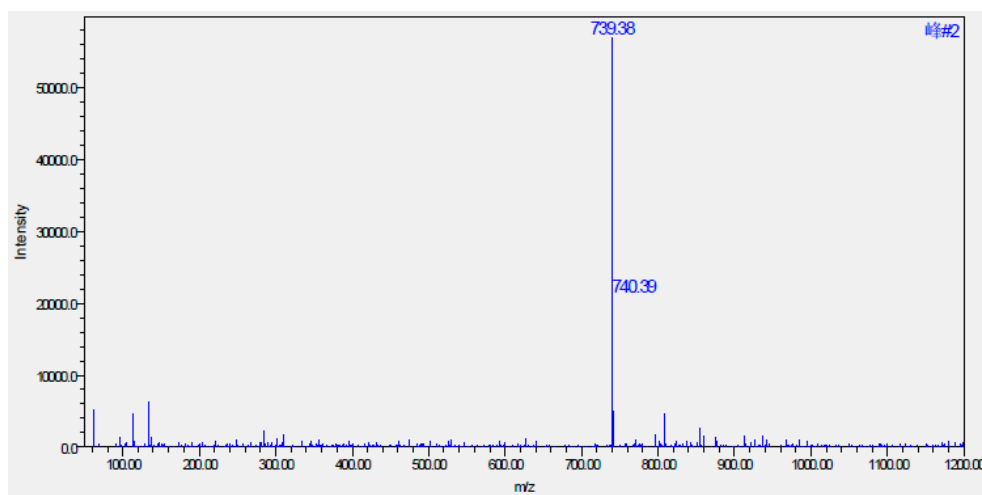


Figure S110. The ESI-MS spectrum of compound 37

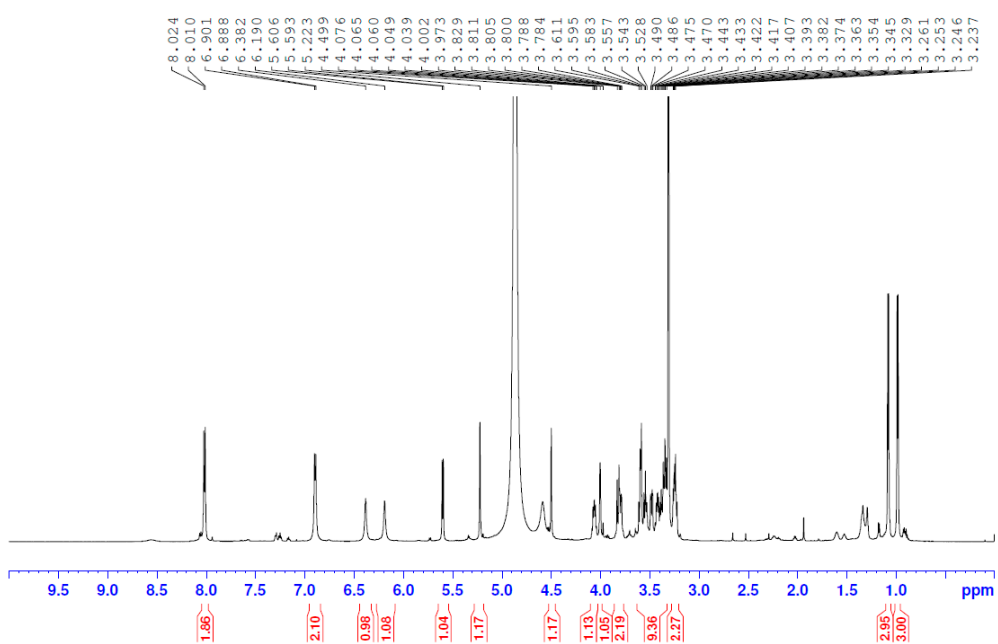


Figure S111. The ^1H -NMR (600MHz, CD_3OD) spectrum of compound 37

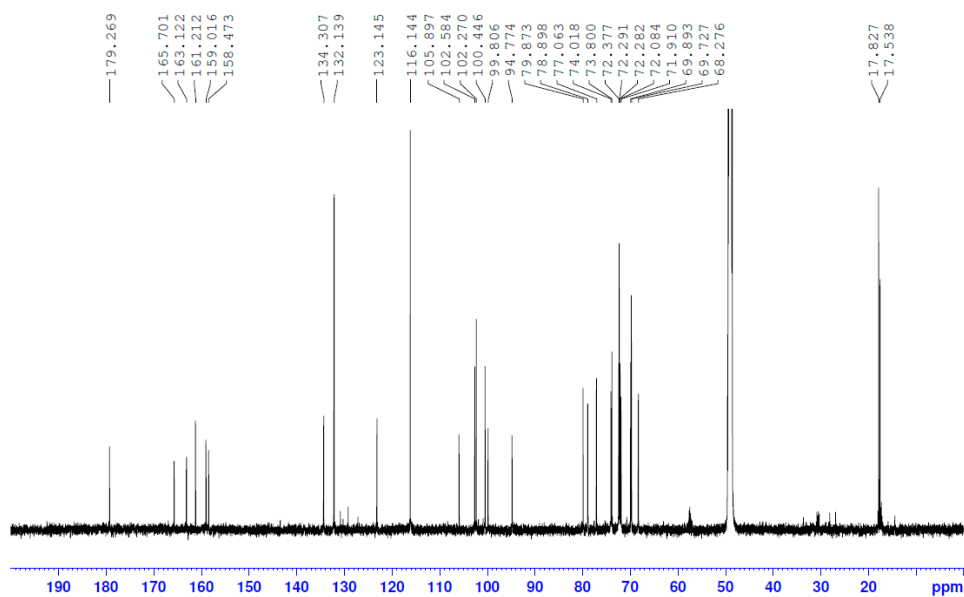


Figure S112 The ^{13}C -NMR (150MHz, CD_3OD) spectrum of compound 37

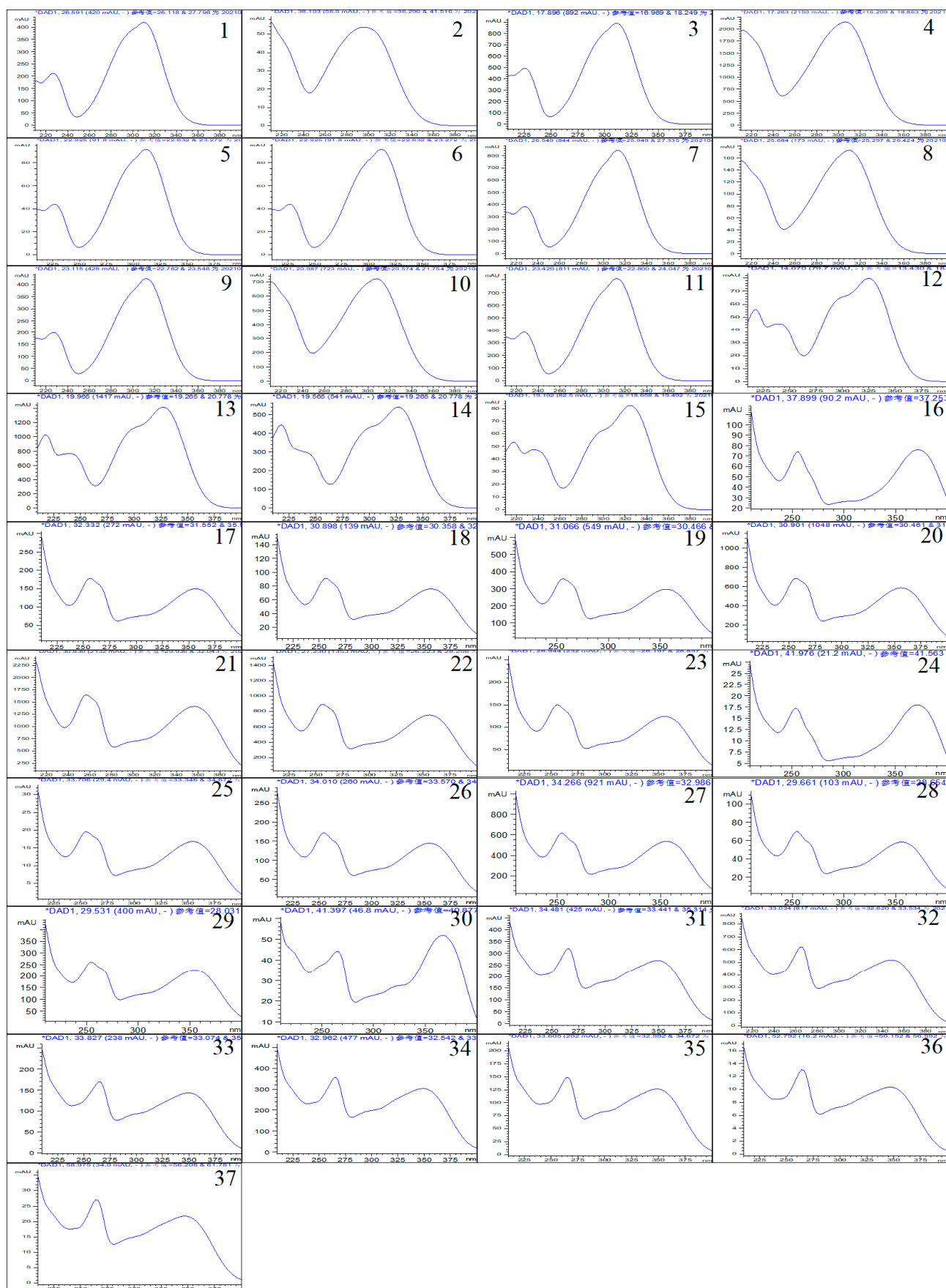


Figure S113 The UV spectrum of compound 1-37

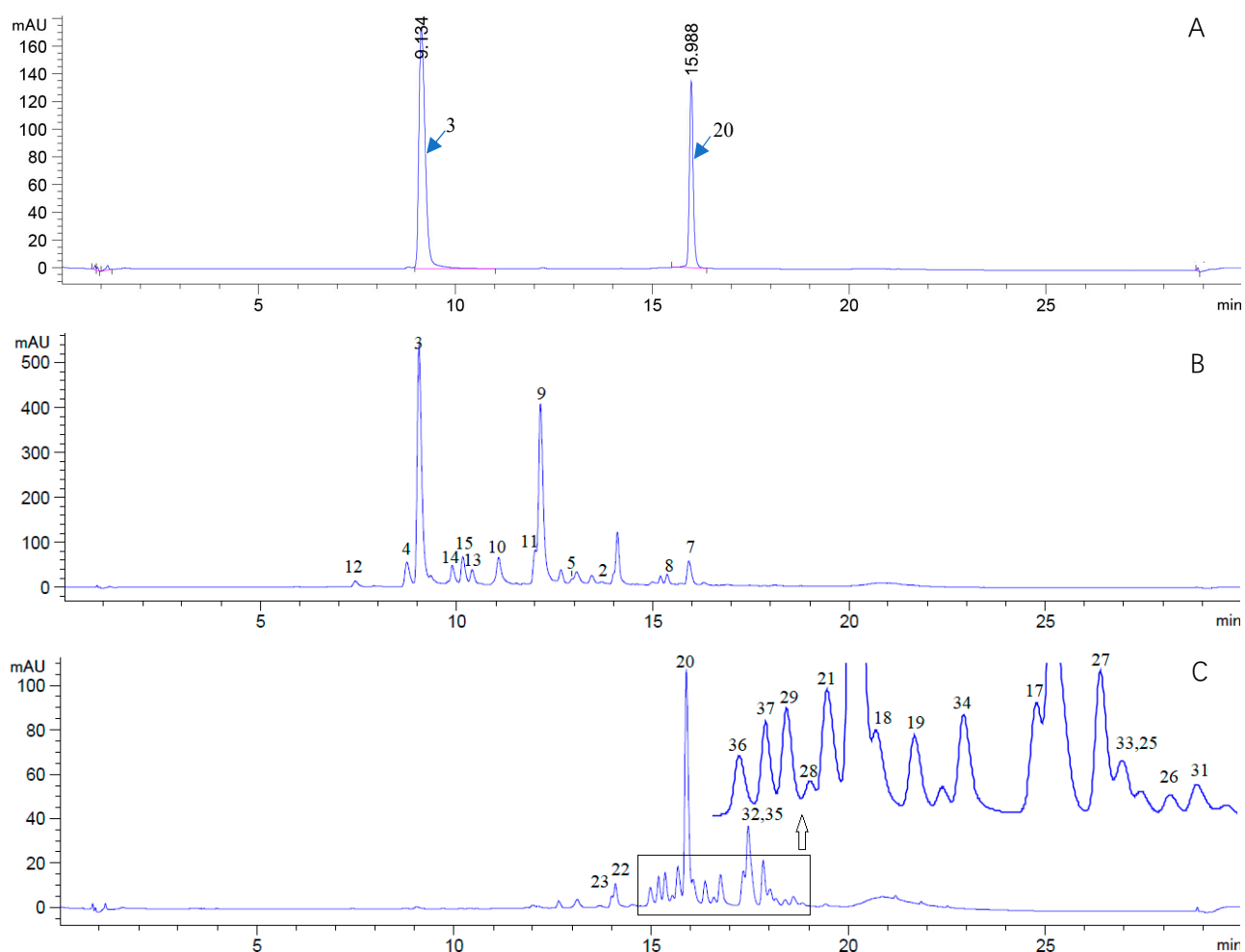


Figure S114 The UHPLC chromatogram of reference substance (A), HFPE(B) and HFPE(C). The analyses were performed by UHPLC system (Agilent, USA). The waters column (ACQUITY UPLC® HSS T3 1.7 μm , 2.1×100 mm) was used for separation. Mobile phases were water with 0.1% of formic acid (A) and acetonitrile with 0.1% of formic acid (B). Chromatographic separation was achieved using a gradient elution as follows: 0.01–2 min, 2%; 2–16 min, 2% to 20% B; 16–19 min, 20% to 23% B; 19–30 min, 23% to 100% B. A sample volume of 4 μL was injected and introduced to the column with 0.4 $\text{mL} \cdot \text{min}^{-1}$ of the solvent flow rate. The column temperature was set at 35°C.

Table S1 The phenylpropanoids compounds content in HFPE

Compound No.	Name	Retention time	Peak area	Content (mg/g)
12	neochlorogenic acid	7.420	118.59	2.62
4	3-O-(<i>Z</i>)- <i>p</i> -coumaroylquinic acid	8.736	441.09	9.75
3	3-O-(<i>E</i>)- <i>p</i> -coumaroylquinic acid	9.042	4482.65	99.13
14	chlorogenic acid	9.892	268.64	5.94
15	3-O-(<i>E</i>)-feruloylquinic acid	10.160	387.67	8.57
13	crypto-chlorogenic acid	10.396	217.97	4.82
10	4-O-(<i>Z</i>)- <i>p</i> -coumaroylquinic acid	11.069	618.46	13.68
11	5-O-(<i>E</i>)- <i>p</i> -coumaroylquinic acid	12.006	284.23	6.29
9	4-O-(<i>E</i>)- <i>p</i> -coumaroylquinic acid	12.138	3499.13	77.38
5	3-O-(<i>E</i>)- <i>p</i> -coumaroylquinic acid methyl ester	12.930	51.00	1.13
2	(<i>Z</i>)- <i>p</i> -coumaric acid	13.704	33.89	0.75
8	3-O-(<i>Z</i>)- <i>p</i> -coumaroylquinide	15.366	141.96	3.14
7	3-O-(<i>E</i>)- <i>p</i> -coumaroylquinide	15.920	418.99	9.27

Note: (*E*)-*p*-Coumaric acid (comp. 1) and 3-O-(*Z*)-*p*-coumaroyl quinic acid methyl ester (comp. 6) were not detected in UPLC, The content of each phenylpropanoids compound in HFPE was calculated by the external standard one point method using comp. 3 as reference substance.

Table S2 The flavonoids compounds content in HFFE

Compound No.	Compound name	Retention time	Peak area	Content (mg/g)
23	quercetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-galactopyranoside]	14.003	20.98	3.41
22	quercetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside]	14.098	65.48	10.63
36	kaempferol-3-O-[α -L-rhamnopyranosyl-(1 \rightarrow 6)]-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-galactopyranoside	14.983	46.37	7.53
37	kaempferol-3-O-[α -L-rhamnopyranosyl-(1 \rightarrow 6)]-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-glucopyranoside	15.190	62.97	10.22
29	isorhamnetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside]	15.359	68.85	11.18
28	isorhamnetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-galactopyranoside]	15.542	11.49	1.87
21	quercetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-galactopyranoside	15.682	99.15	16.10
20	quercetin-3-O-rutinoside	15.893	659.98	107.14
18	quercetin-3-O- β -D-galactopyranoside	16.070	56.70	9.20
19	quercetin-3-O- β -D-glucopyranoside	16.369	59.59	9.67
34	kaempferol-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-galactopyranoside	16.760	90.45	14.68
17	quercetin-3-O- α -L-arabinopyranoside	17.343	88.27	14.33
32, 35	kaempferol-3-O- β -D-galactopyranoside, kaempferol-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside	17.465	297.70	48.33
27	isorhamnetin-3-O-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside]	17.846	113.82	18.48
33, 25	kaempferol-3-O- β -D-glucopyranoside, isorhamnetin-3-O- β -D-galactopyranoside	18.016	34.52	5.60
26	isorhamnetin-3-O- β -D-glucopyranoside	18.397	14.09	2.29
31	kaempferol-3-O- α -L-arabinoside	18.613	28.72	4.66

Note: Quercetin (comp. 16), isorhamnetin (comp. 24) and kaempferol (comp. 30) were not detected in UPLC. The content of each flavonoid compound in HFFE was calculated by the external standard one point method using comp. 20 as reference substance. The two compounds of comp. 32 and comp. 35 were not separated by HPLC, their contents were calculated together. So as comp. 33 and comp. 25.

Determination of total phenolic

Both phenylpropanoids and flavonoids belong to total phenolic, so we measure total phenolic expressed phenylpropanoids and flavonoids. The total phenolic content of *H. citrina* was determined using Folin–Ciocalteu assay[1] with gallic acid as a standard. In brief, 1 mL sample methanolic solution was mixed with 0.5 mL Folin–Ciocalteu reagent (0.25 mol/L). After incubation for 3 min, 1.0 mL of Na₂CO₃ aqueous solution (15%, w/v) was added. After standing in dark for 30 min, the mixture was centrifuged at 3000 r/min for 5 min. The absorbance of the supernatant was measured at 760 nm (Aoxi UV1901PC, Shanghai, China). The total phenolic content of *H. citrina* was calculated based on a linear regression equation of Gallic acid ($y = 10.226x - 0.0773$, x for gallic acid concentration, y for absorbance at 760 nm, $r=0.9993$), and was expressed as gallic acid equivalents 9.58 mg/g in *H. citrina*.

References

1. Li, X.; Hu, Q.; Jiang, S.; Li, F.; Lin, J.; Han, L.; Hong, Y.; Lu, W.; Gao, Y.; Chen, D., Flos Chrysanthemi Indici protects against hydroxyl-induced damages to DNA and MSCs via antioxidant mechanism. *J. Saudi. Chem. Soc.* **2015**, *19*, 454-460.