Supporting Information

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Chemical Constituents and Antioxidant Activity of *Teucrium barbeyanum* Aschers.

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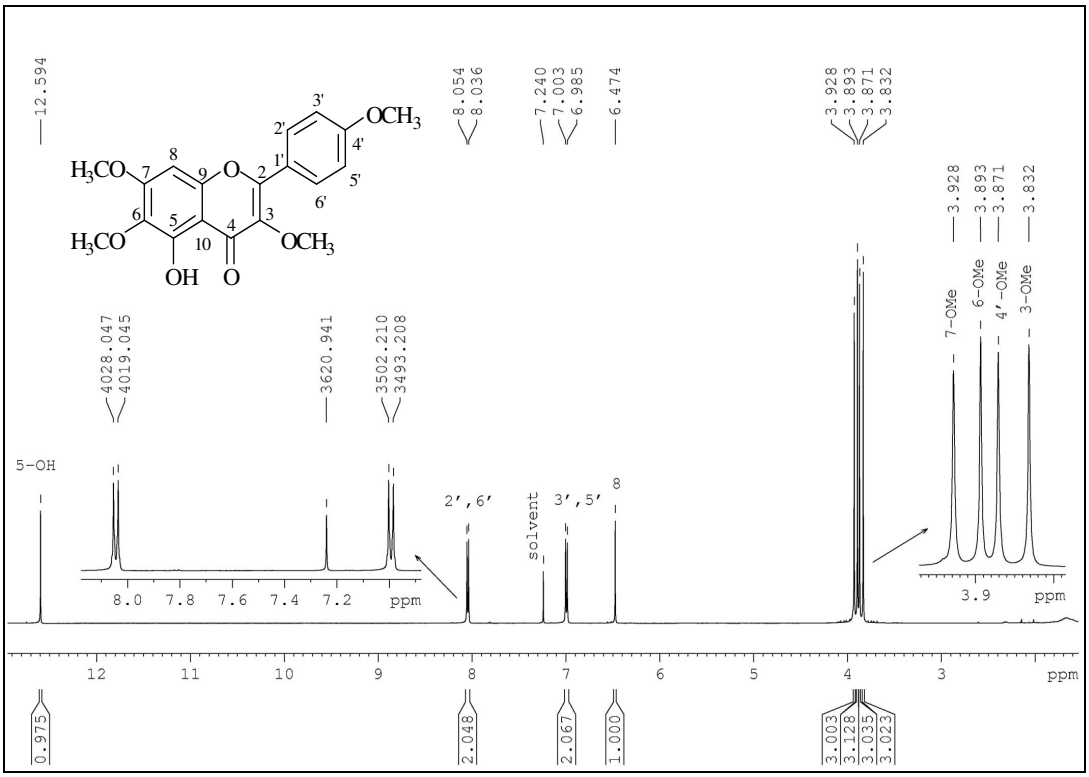
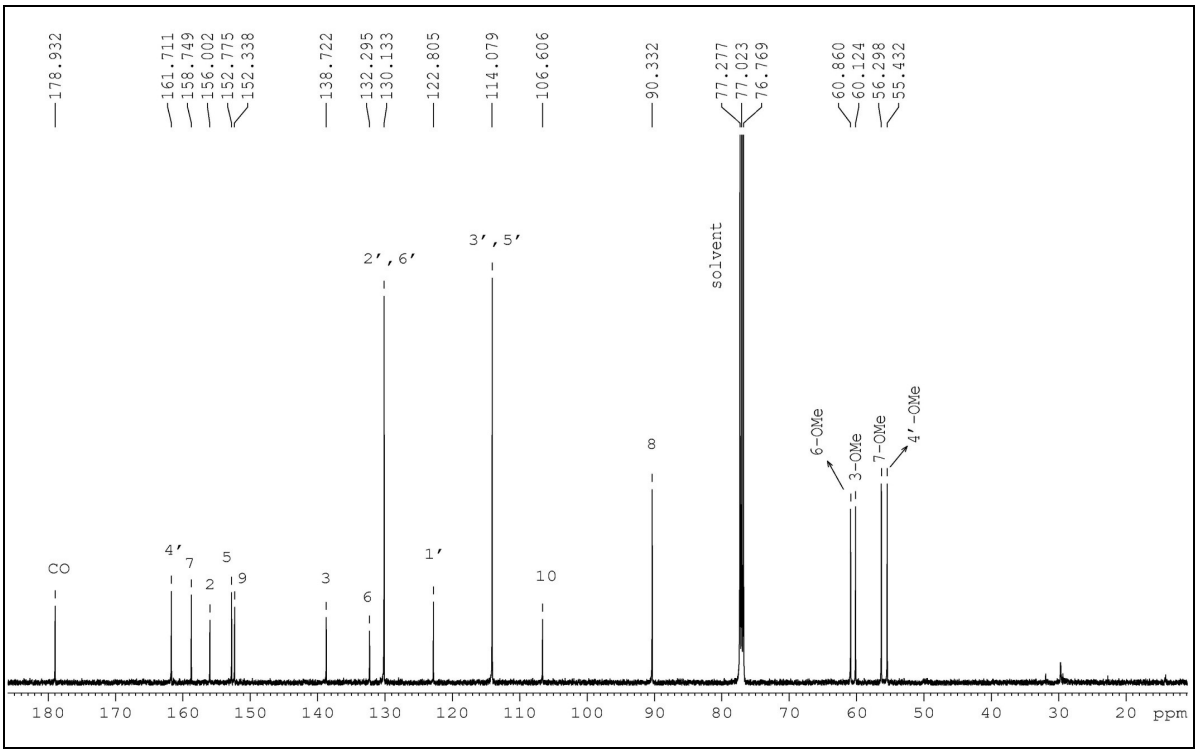
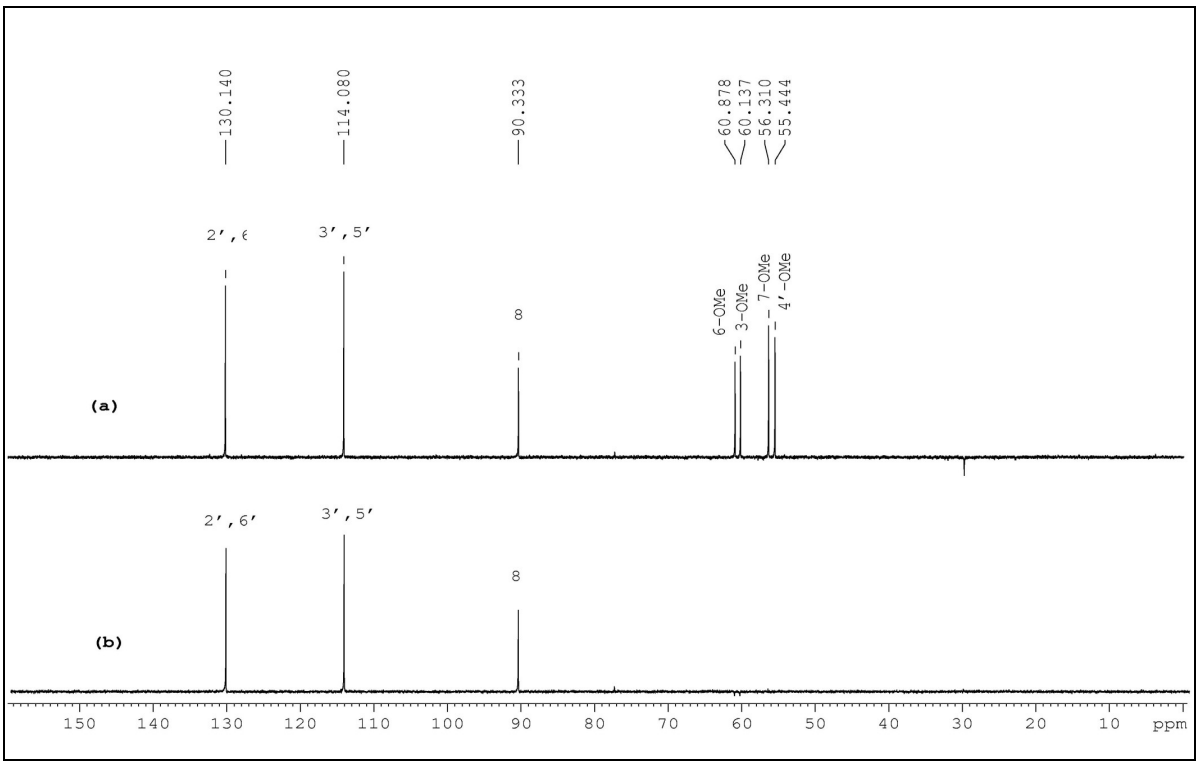


S1: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **1** (5-hydroxy-3,6,7,4′-tetramethoxyflavone)

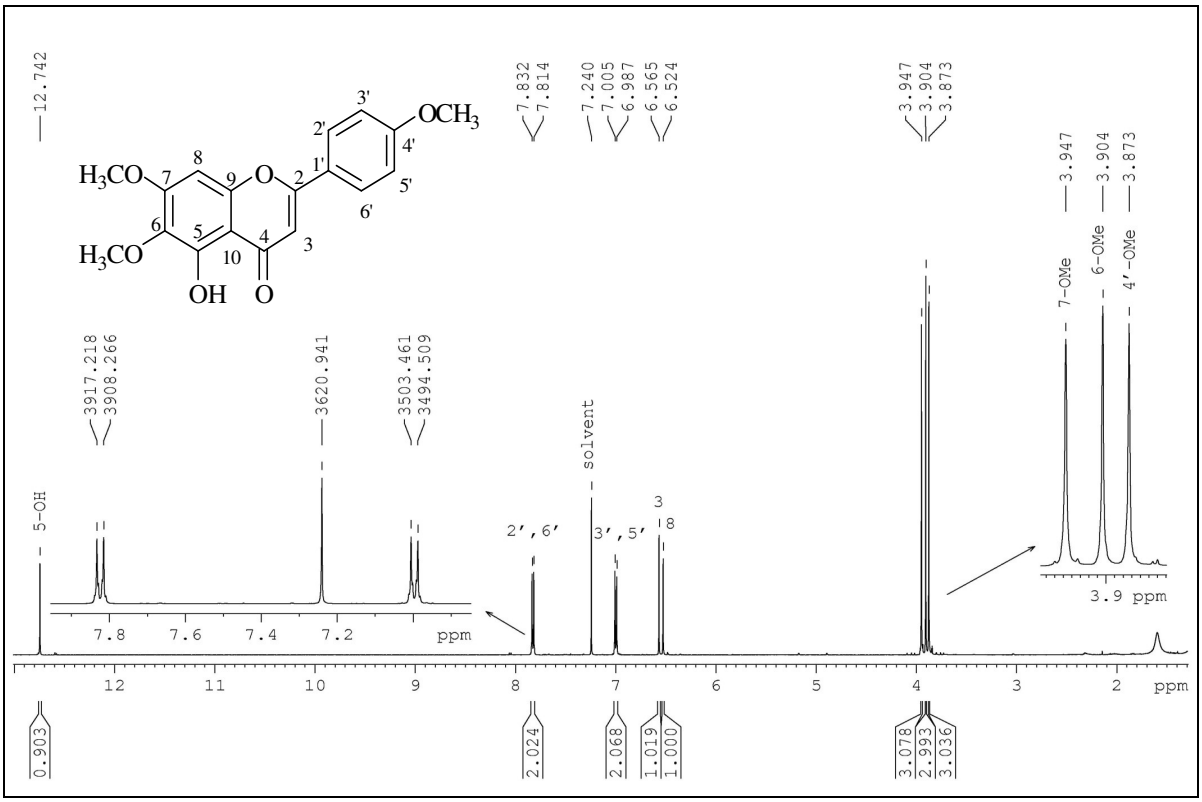
Compound **1** (5-hydroxy-3,6,7,4′-tetramethoxyflavone), yellow wax: -ESI-MS *m/z*: 357.1 $[M–H]^-$; UVλ_{max} (nm): (MeOH) 234 (sh), 273, 335, (NaOMe) 291, 366 (sh), ($AlCl_3$) 233 (sh), 283, 299 (sh), 363, ($AlCl_3$/HCl) 235, 285, 299 (sh), 357, (NaOAc) 294, 320 (sh), (NaOAc/H_3BO_3) 272, 336; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.59 (s, 1 H, 5-OH), 8.04 (d, J = 9.0 Hz, 2 H, H-2′, 6′), 7.00 (d, J = 9.0 Hz, 2 H, H-3′, 5′), 6.47 (s, 1 H, H-8), 3.93 (s, 3 H, 7-OMe), 3.89 (s, 3 H, 6-OMe), 3.87 (s, 3 H, 4′-OMe), 3.83 (s, 3 H, 3-OMe); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.93 (C-4), 161.71 (C-4′), 158.75 (C-7), 156.00 (C-2), 152.78 (C-5), 152.34 (C-9), 138.72 (C-3), 132.30 (C-6), 130.13 (C-2′, 6′), 122.81 (C-1′), 114.08 (C-3′, 5′), 106.61 (C-10), 90.33 (C-8), 60.86 (6-OMe), 60.12 (3-OMe), 56.43 (4′-OMe), 56.30 (7-OMe).



S2: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of compound **1** (5-hydroxy-3,6,7,4′-tetramethoxyflavone)

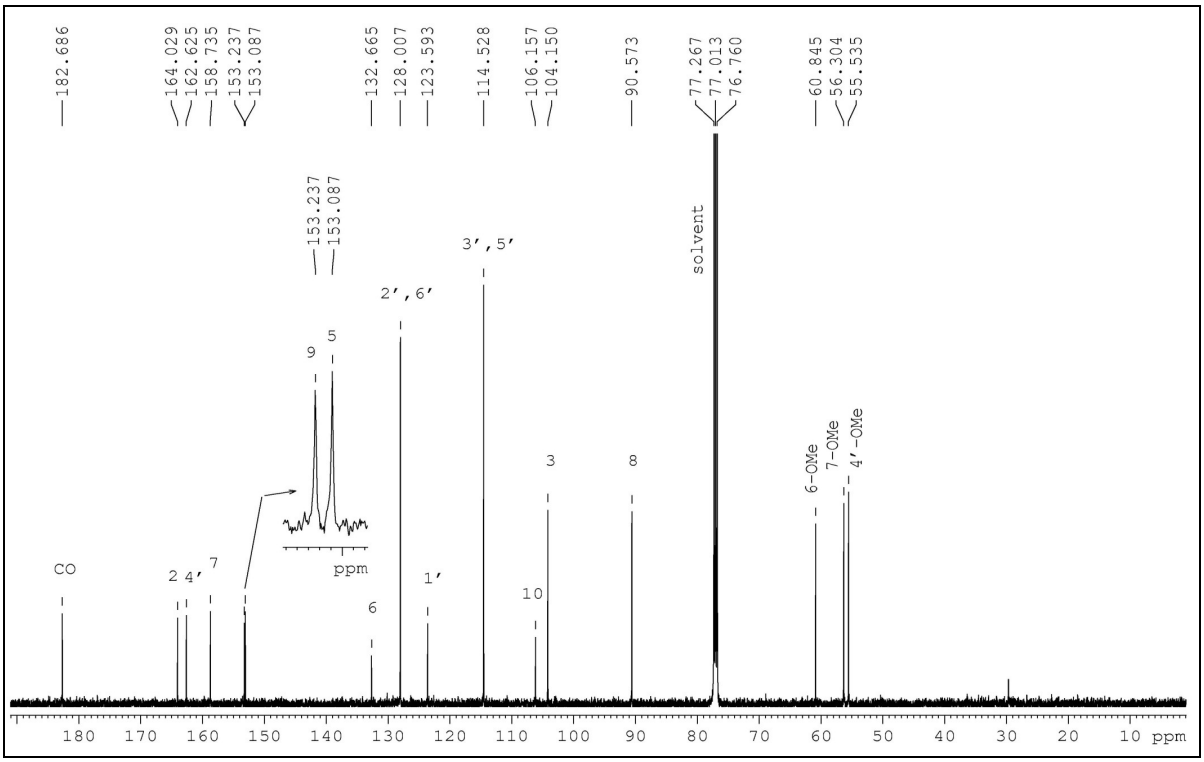


S3: (a) DEPT 135 and **(b)** DEPT 90 NMR ($CDCl_3$, 125 MHz) spectra of compound **1** (5-hydroxy-3,6,7,4′-tetramethoxyflavone)

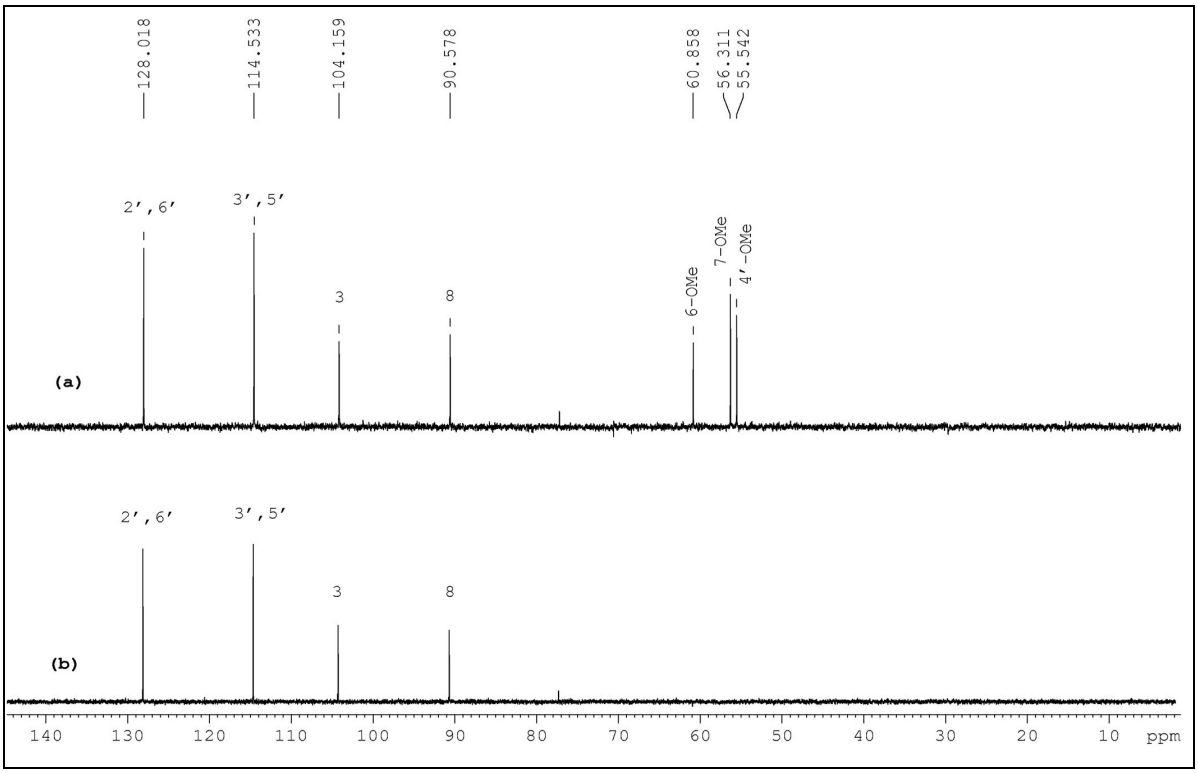


S4: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **2** (Salvigenin)

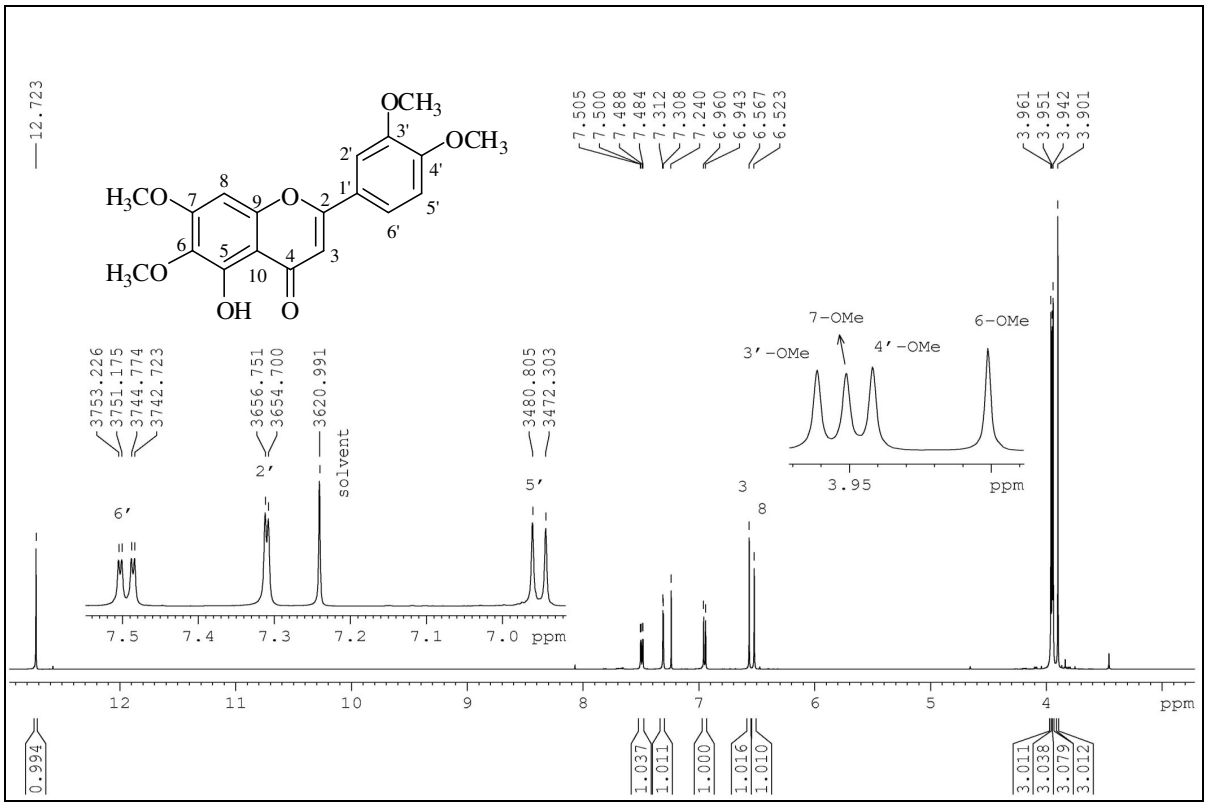
Compound **2** (Salvigenin), yellow wax: -ESI-MS *m*/*z*: 327.1 $[M–H]^-$; UV λ_{max} (nm): (MeOH) 275, 333, (NaOMe) 295, 369 (sh), ($AlCl_3$) 263, 289 (sh), 301, 357, ($AlCl_3$/HCl) 261, 289 (sh), 300, 354, (NaOAc) 280, 328, (NaOAc/H_3BO_3) 275, 332; ^{1}H NMR (500 MHz, $CDCyl_3$): δ 12.74 (s, 1 H, 5-OH), 7.82 (d, J = 8.9 Hz, 2 H, H-2′, 6′), 6.99 (d, J = 8.9 Hz, 2 H, H-3′, 5′), 6.57 (s, 1 H, H-3), 6.52 (s, 1 H, H-8) 3.95 (s, 3 H, 7-OMe), 3.90 (s, 3 H, 6-OMe), 3.87 (s, 3 H, 4′-OMe); ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.69 (C-4), 164.03 (C-2), 162.63 (C-4′), 158.74 (C-7), 153.24 (C-9), 153.09 (C-5), 132.67 (C-6), 128.01 (C-2′, 6′), 123.59 (C-1′), 114.53 (C-3′, 5′), 106.16 (C-10), 104.15 (C-3), 90.57 (C-8), 60.85 (6-OMe), 56.30 (7-OMe), 55.54 (4′-OMe).



S5: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of compound **2** (Salvigenin)

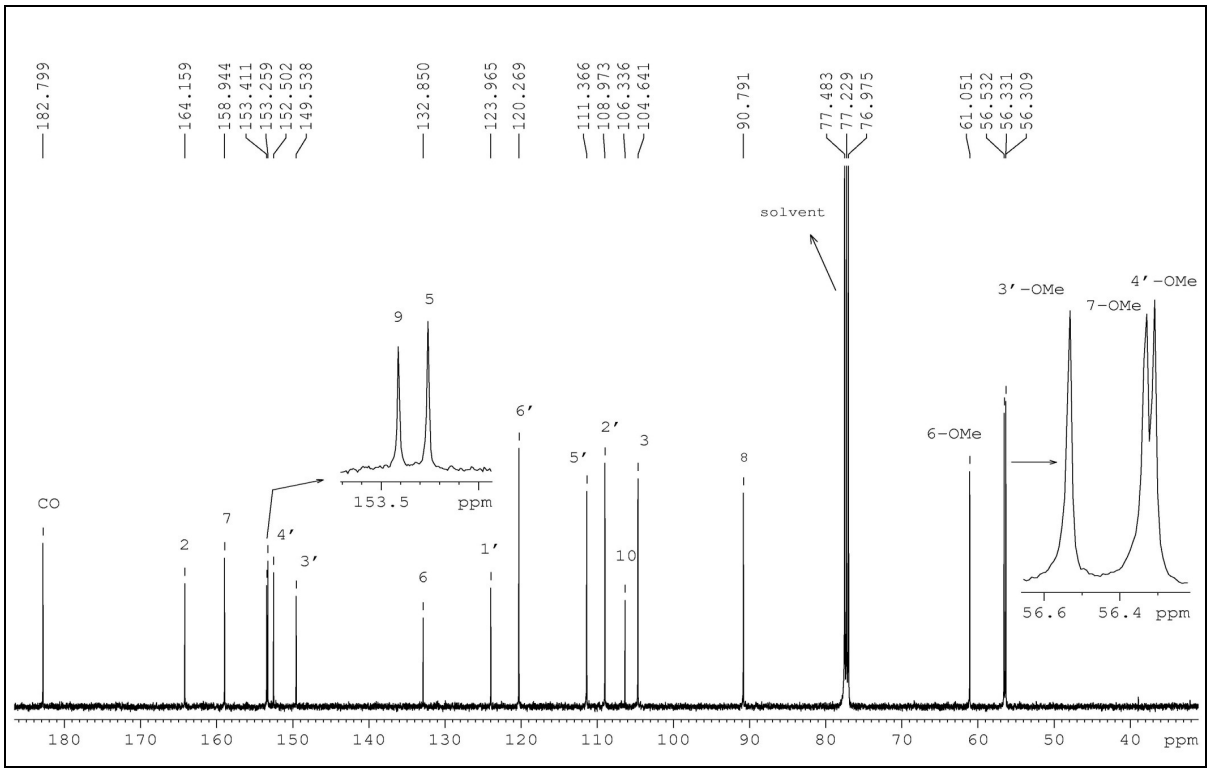


S6: (a) DEPT 135 and **(b)** DEPT 90 NMR ($CDCl_3$, 125 MHz) spectra of compound **2** (Salvigenin)

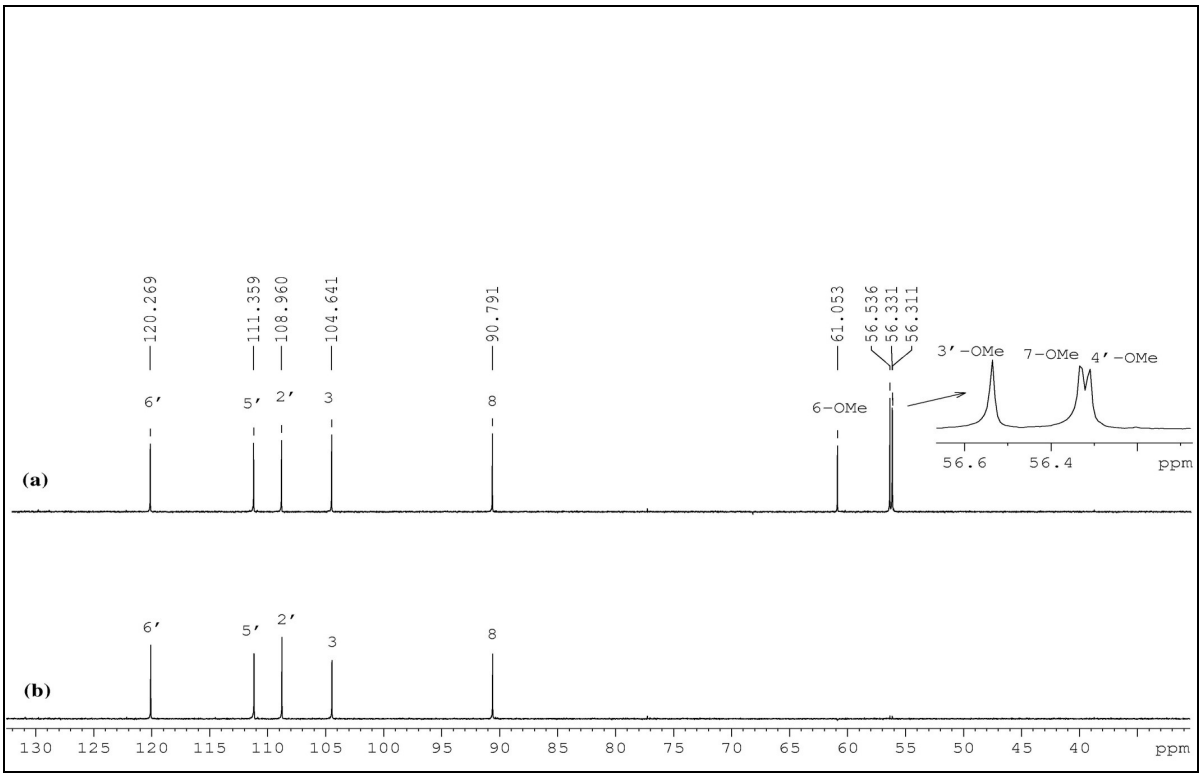


S7: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3** (5-hydroxy-6,7,3′,4′-tetramethoxyflavone)

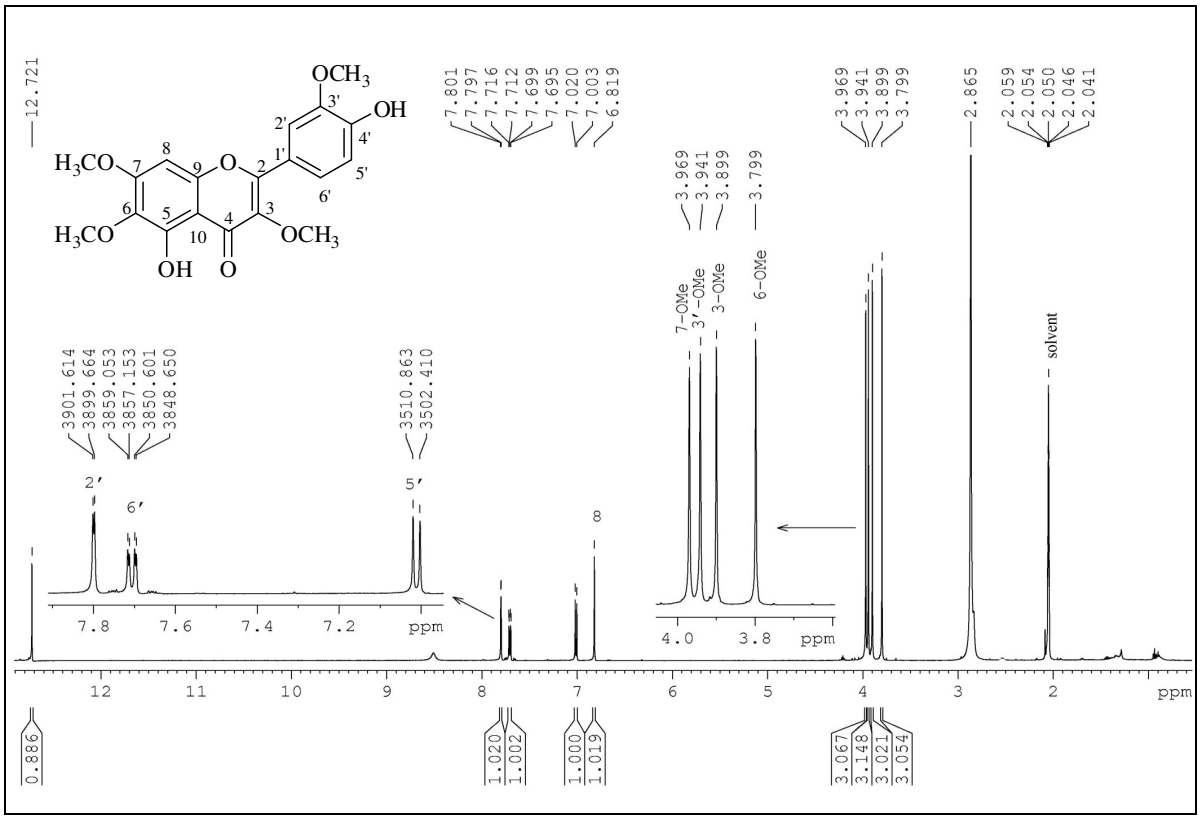
Compound **3** (5-hydroxy-6,7,3′,4′-tetramethoxyflavone), yellow needles: -ESI-MS *m*/*z*: 357.1 $[M–H]^-$; UV λ_{max} (nm): (MeOH) 276, 337, (NaOMe) 291, 371 (sh), ($AlCl_3$) 257 (sh), 285, 364, ($AlCl_3$/HCl) 257 (sh), 287, 359, (NaOAc) 282, 325, (NaOAc/H_3BO_3) 275, 338; ^{1}H NMR (500 MHz, acetone-d_6): δ 12.95 (s, 1 H, 5-OH), 7.71 (dd, J = 8.5, 2.2 Hz, 1 H, H-6′), 7.63 (d, J = 2.2 Hz, 1 H, H-2′), 7.15 (d, J = 8.5 Hz, 1 H, H-5′), 6.87 (s, 1 H, H-8), 6.78 (s, 1 H, H-3), 3.98 (s, 1 H, 7-OMe), 3.96 (s, 1 H, 3′-OMe), 3.93 (s, 1 H, 4′-OMe), 3.80 (s, 1 H, 6-OMe); ^{13}C NMR (125 MHz, acetone-d_6): δ 183.63 (C-4), 165.13 (C-2), 160.22 (C-7), 154.19 (C-5), 154.03 (C-9), 153.89 (C-4′), 150.76 (C-3′), 133.63 (C-6), 124.48 (C-1′), 121.04 (C-6′), 112.58 (C-5′), 110.50 (C-2′), 106.62 (C-10), 104.68 (C-3), 92.05 (C-8), 60.61 (6-OMe), 56.90 (7-OMe), 56.50 (3′-OMe), 56.35 (4′-OMe).



S8: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of compound **3** (5-hydroxy-6,7,3′,4′-tetramethoxyflavone)

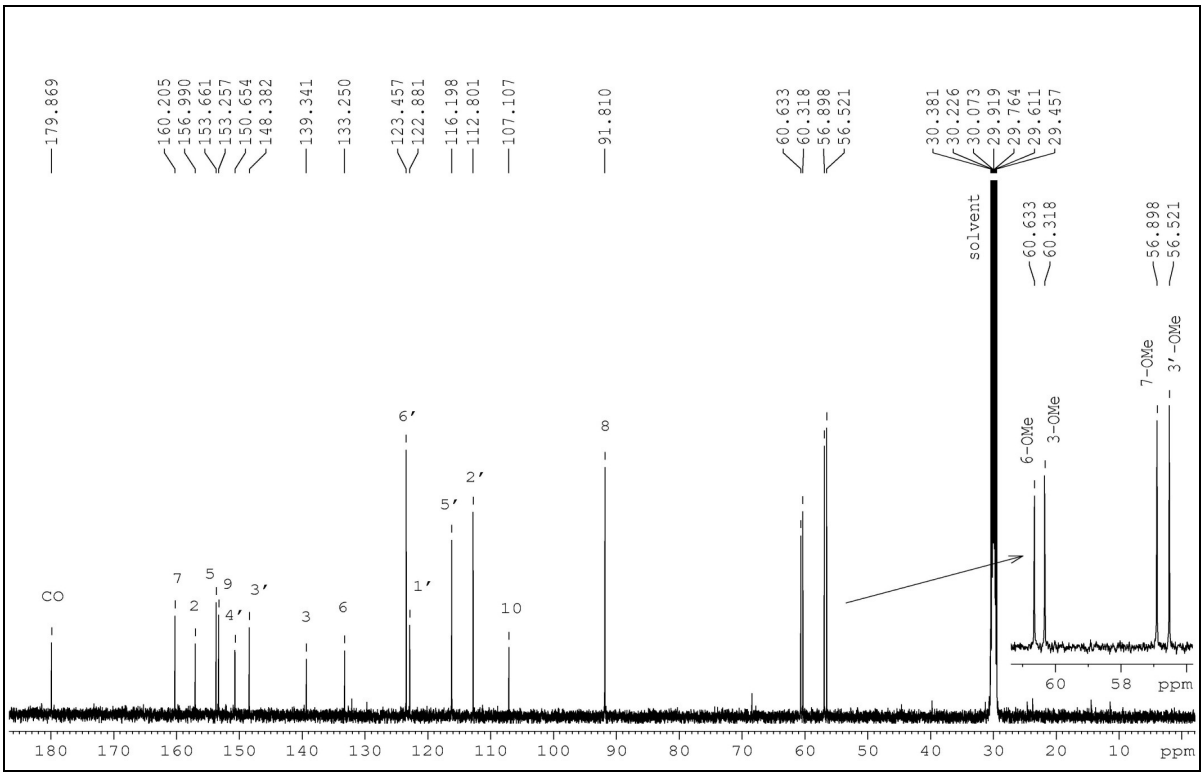


S9: (**a**) DEPT 135 and (**b**) DEPT 90 NMR ($CDCl_3$, 125 MHz) spectra of compound **3** (5-hydroxy-6,7,3′,4′-tetramethoxyflavone)

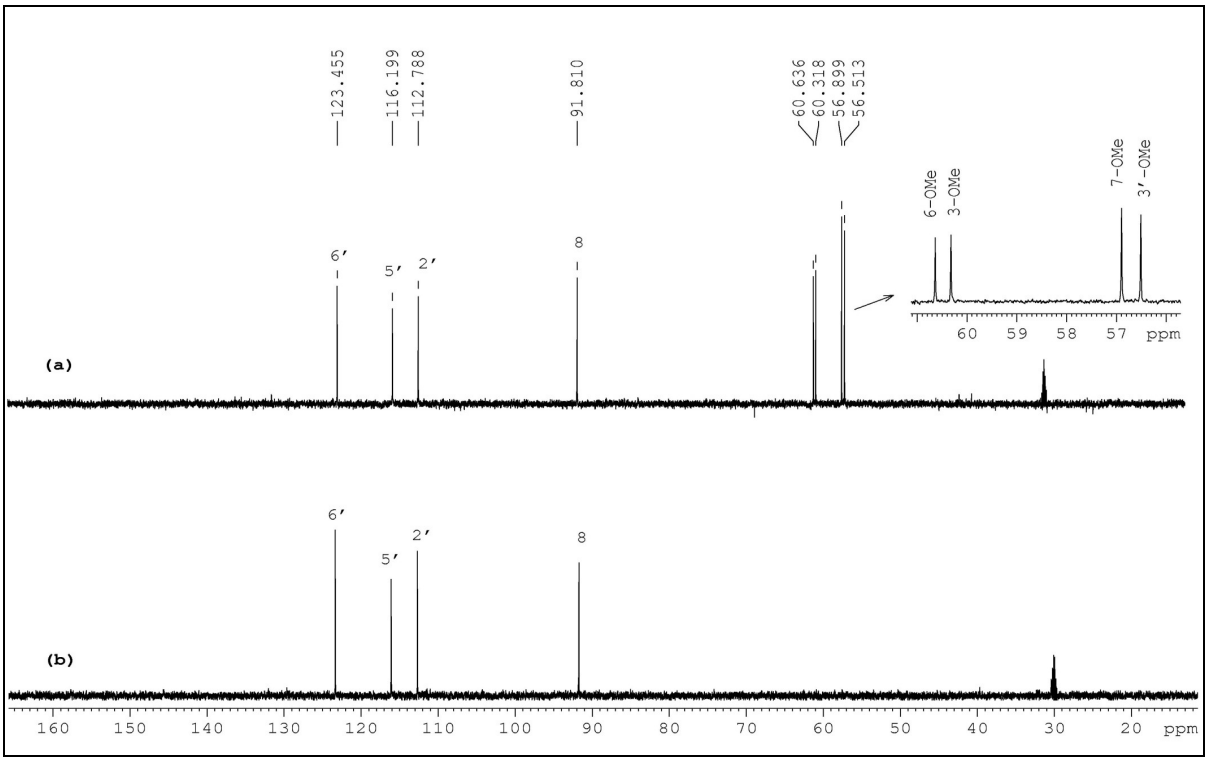


S10: ^{1}H NMR (Acetone-d_6, 500 MHz) spectrum of compound **4** (Chrysosplenetin)

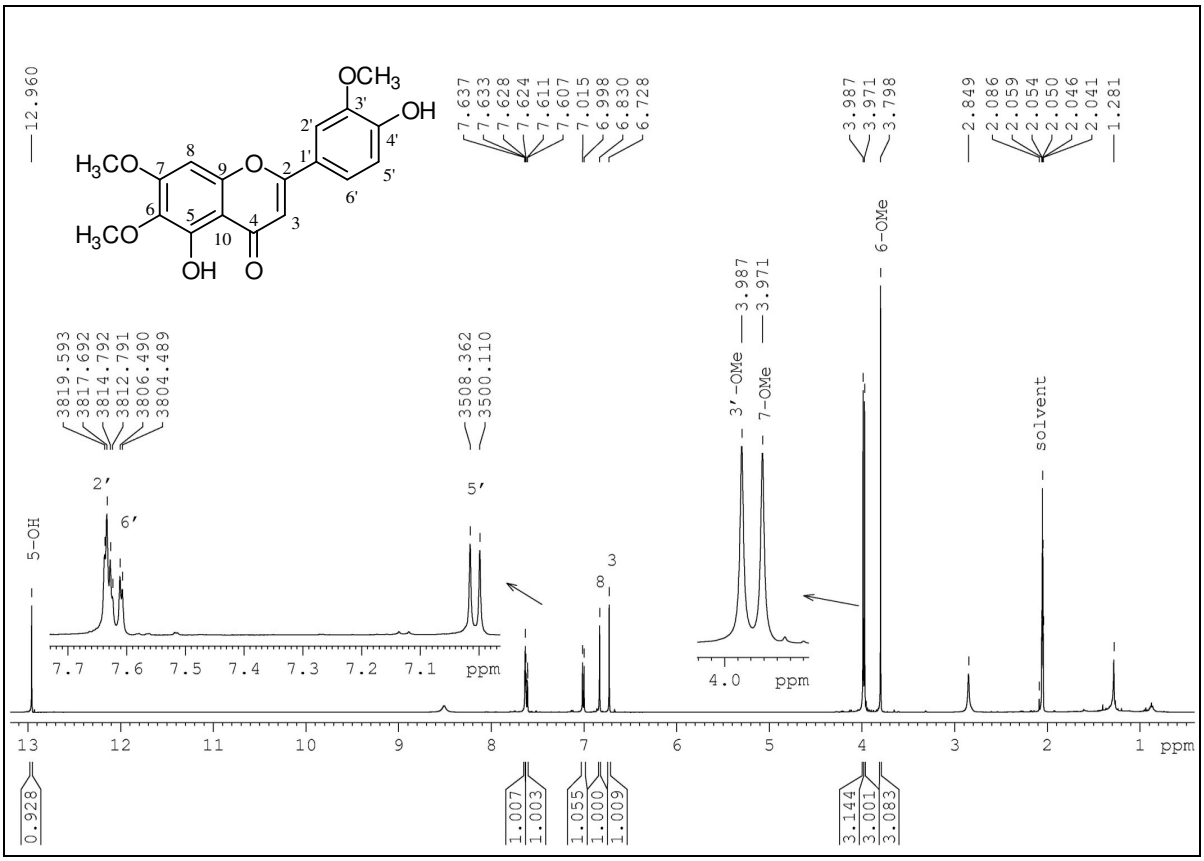
Compound **4** (Chrysosplenetin), yellow solid: EI-MS *m/z*: 374.1 $[M]^+$; UV λ_{max} (nm): (MeOH) 257, 269 (sh), 351, (NaOMe) 268, 405, ($AlCl_3$) 268, 379, ($AlCl_3$/HCl) 265, 279 (sh), 366, (NaOAc) 268, 292 (sh), 413, (NaOAc/H_3BO_3) 257, 268 (sh), 354; ^{1}H NMR (500 MHz, acetone-d_6): δ 12.72 (s, 1 H, 5-OH), 7.80 (d, J = 2.0 Hz, 1 H, H-2′), 7.72 (dd, J = 2.0, 8.5 Hz, 1 H, H-6′), 7.01 (d, J = 8.5 Hz, 1 H, H-5′), 6.82 (s, 1 H, H-8), 3.97 (s, 3 H, 7-OMe), 3.94 (s, 3 H, 3′-OMe), 3.90 (s, 3 H, 3-OMe), 3.80 (s, 3 H, 6-OMe); ^{13}C NMR (125 MHz, acetone-d_6): δ 179.87 (C-4), 156.99 (C-2), 160.21 (C-7), 153.66 (C-5), 153.26 (C-9), 150.65 (C-4′), 148.38 (C-3′), 139.34 (C-3), 133.25 (C-6), 123.46 (C-6′), 122.88 (C-1′), 116.20 (C-5′), 112.80 (C-2′), 107.11 (C-10), 91.81 (C-8), 60.63 (6-OMe), 60.32 (3-OMe), 56.90 (7-OMe), 56.52 (3′-OMe).



S11: ^{13}C NMR (Acetone-d_6, 125 MHz) spectrum of compound **4** (Chrysosplenetin)

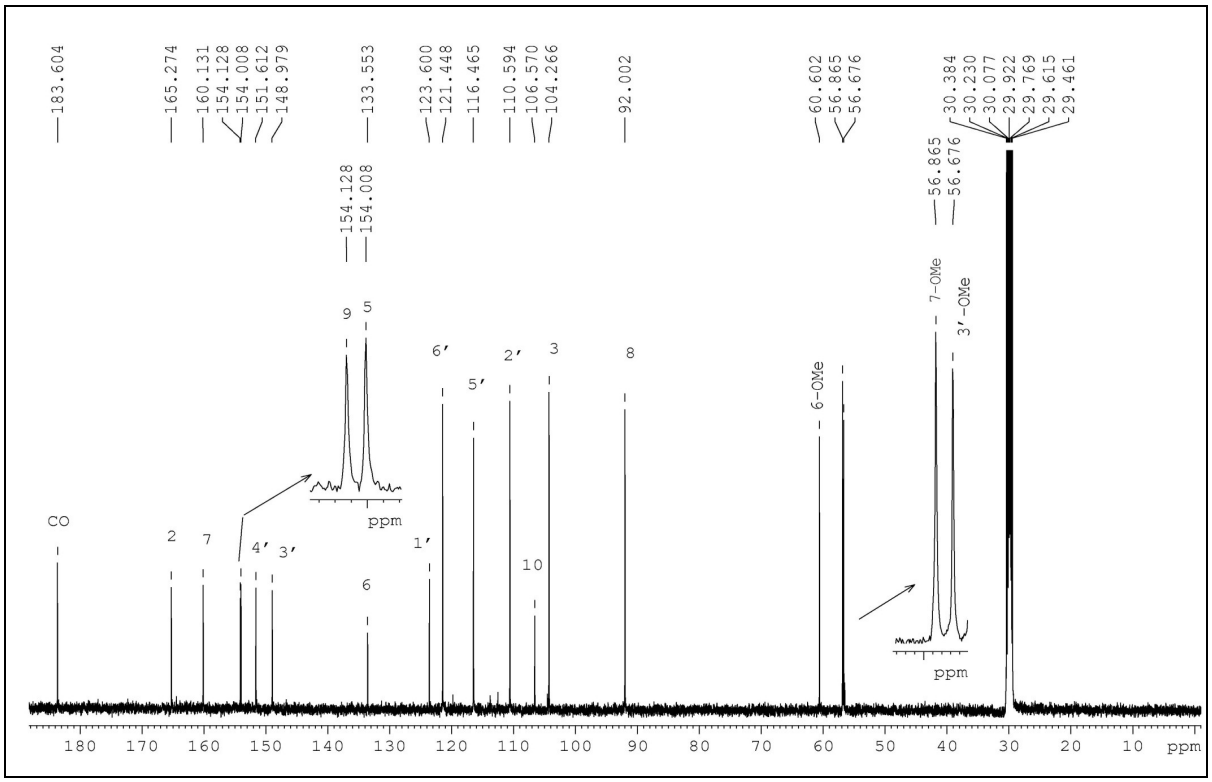


S12: (a) DEPT 135 and **(b)** DEPT 90 NMR (Acetone-d_6, 125 MHz) spectra of compound **4** (Chrysosplenetin)

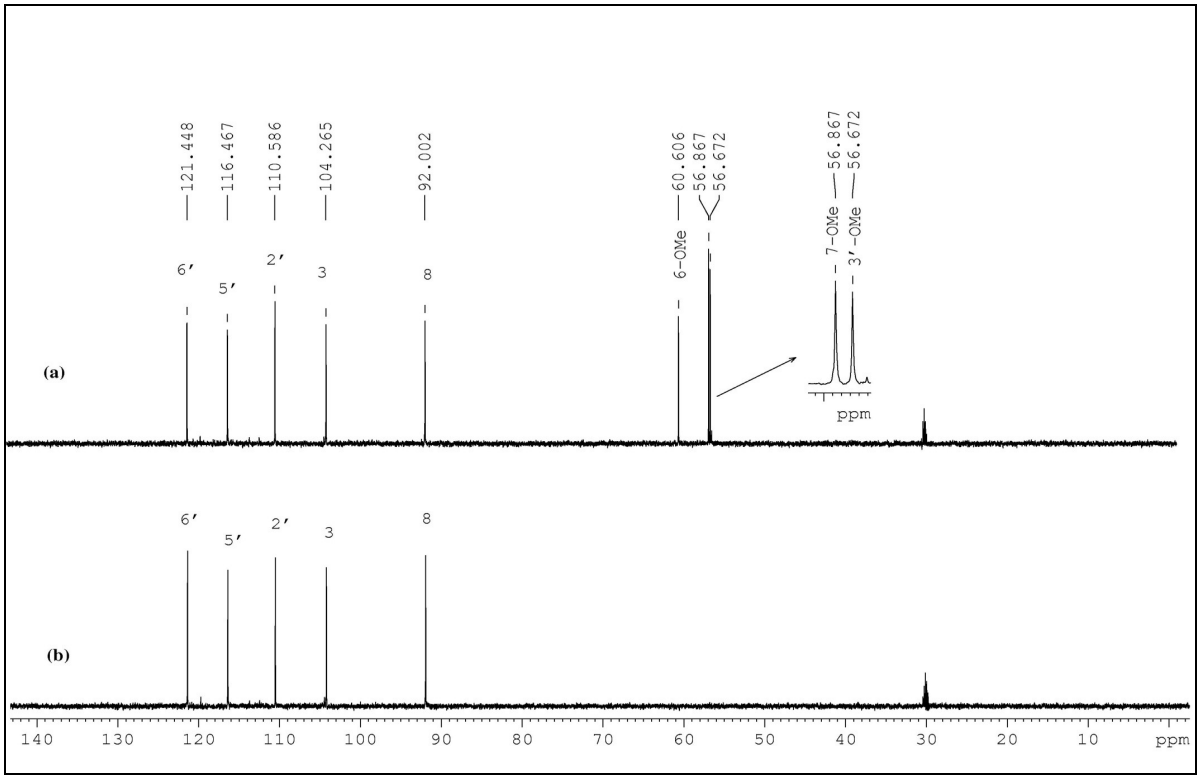


S13: ^{1}H NMR (Acetone-d_6, 500 MHz) spectrum of compound **5** (Cirsilineol)

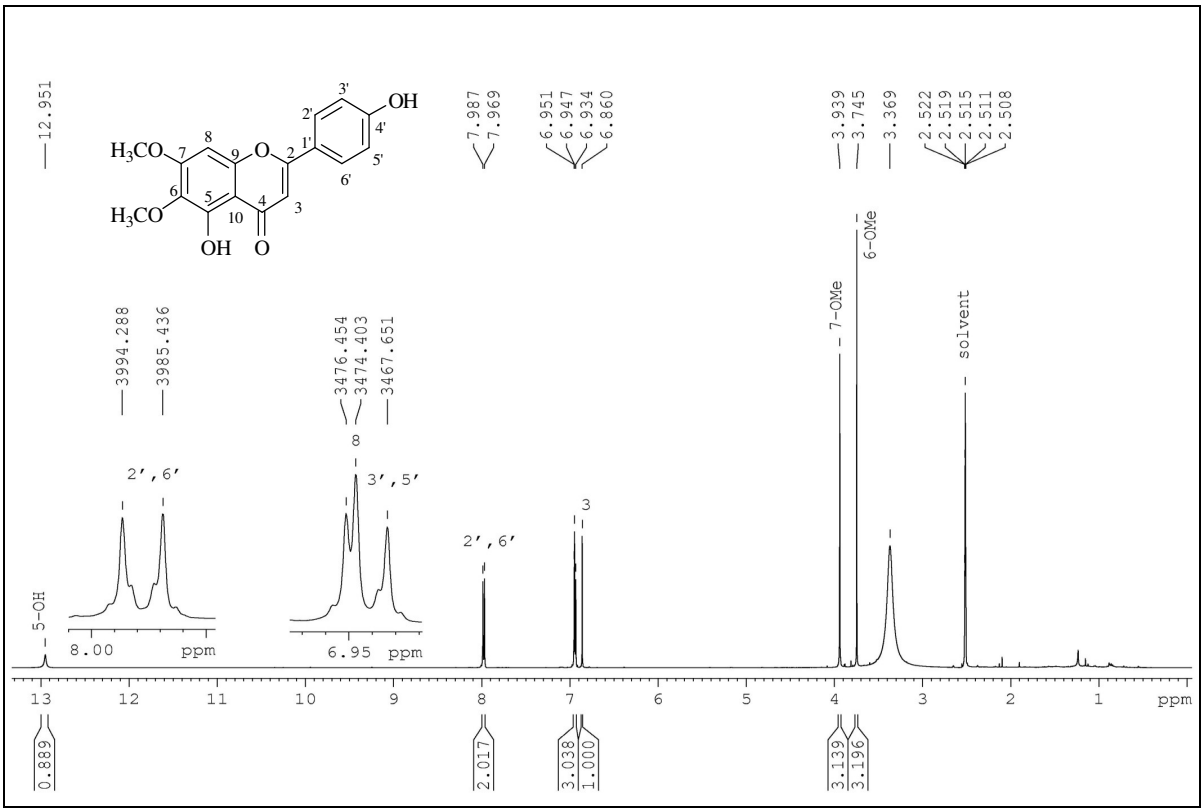
Compound **5** (Cirsilineol), yellow amorphous: EI-MS *m*/*z*: 344.1 $[M]^+$; UV λ_{max} (nm): (MeOH) 241, 275, 343, (NaOMe) 266, 402, ($AlCl_3$) 261, 285, 373, ($AlCl_3$/HCl) 259, 289, 365, (NaOAc) 271, 416, (NaOAc/H_3BO_3) 275, 347; ^{1}H NMR (500 MHz, acetone-d_6): δ 12.96 (s, 1 H, 5-OH), 7.63 (m, 2 H, H-2′, 6′), 7.08 (d, J = 8.2 Hz, 1 H, H-5′), 6.84 (s, 1 H, H-8), 6.74 (s, 1 H, H-3), 3.99 (s, 3 H, 3′-OMe), 3.97 (s, 3 H, 7-OMe), 3.80 (s, 3 H, 6-OMe); ^{13}C NMR (125 MHz, acetone-d_6): δ 183.60 (C-4), 165.27 (C-2), 160.13 (C-7), 154.13 (C-5), 154.01 (C-9), 151.61 (C-4′), 148.98 (C-3′), 133.55 (C-6), 123.60 (C-1′), 121.45 (C-6′), 116.47 (C-5′), 110.59 (C-2′), 106.57 (C-10), 104.26 (C-3), 92.00 (C-8), 60.60 (6-OMe), 56.87 (7-OMe), 56.68 (3′-OMe).



S14: ^{13}C NMR (Acetone-d_6, 125 MHz) spectrum of compound **5** (Cirsilineol)

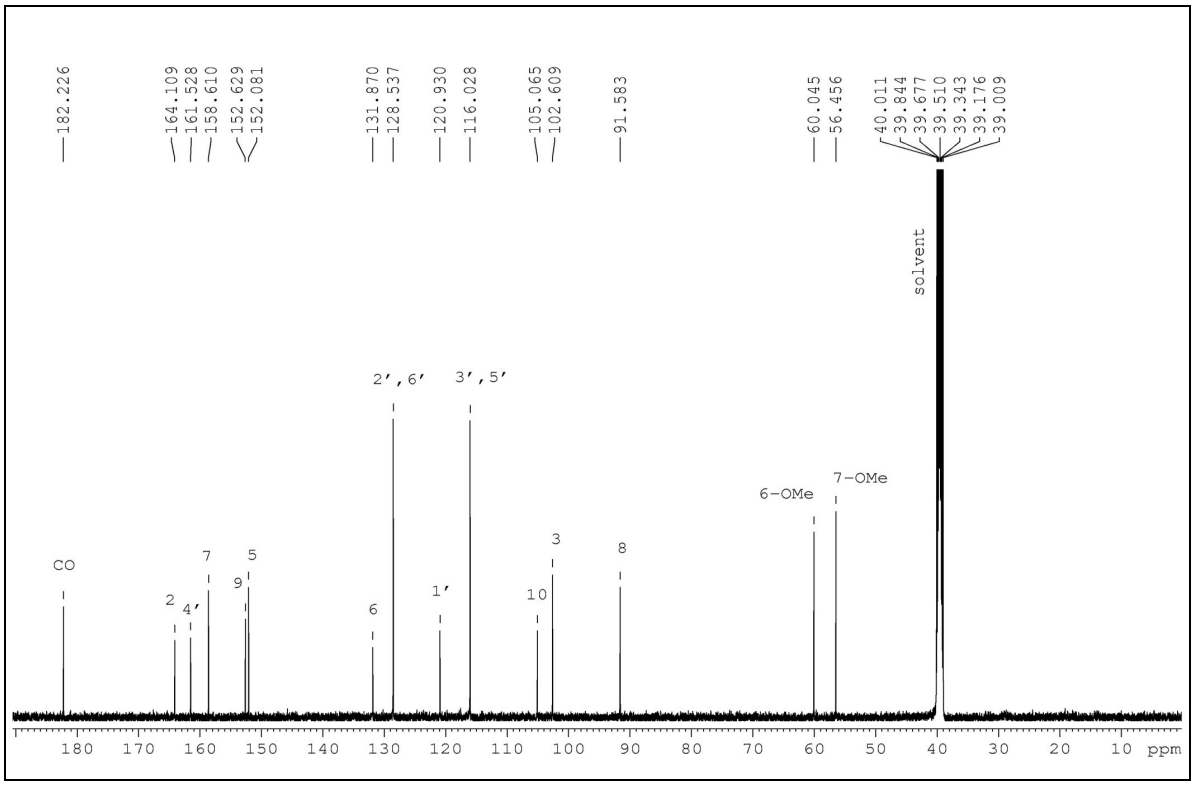


S15: (a) DEPT 135 and **(b)** DEPT 90 NMR (Acetone-d_6, 125 MHz) spectra of compound **5** (Cirsilineol)

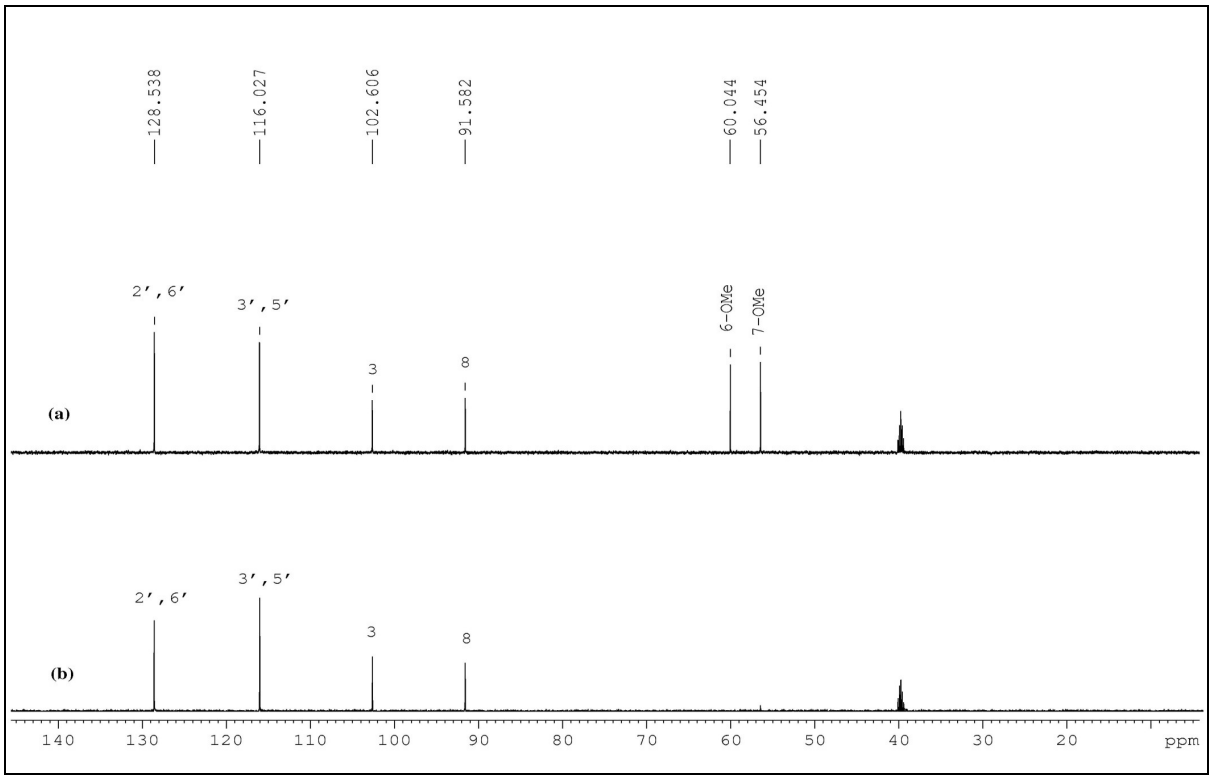


S16: ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **6** (Cirsimaritin)

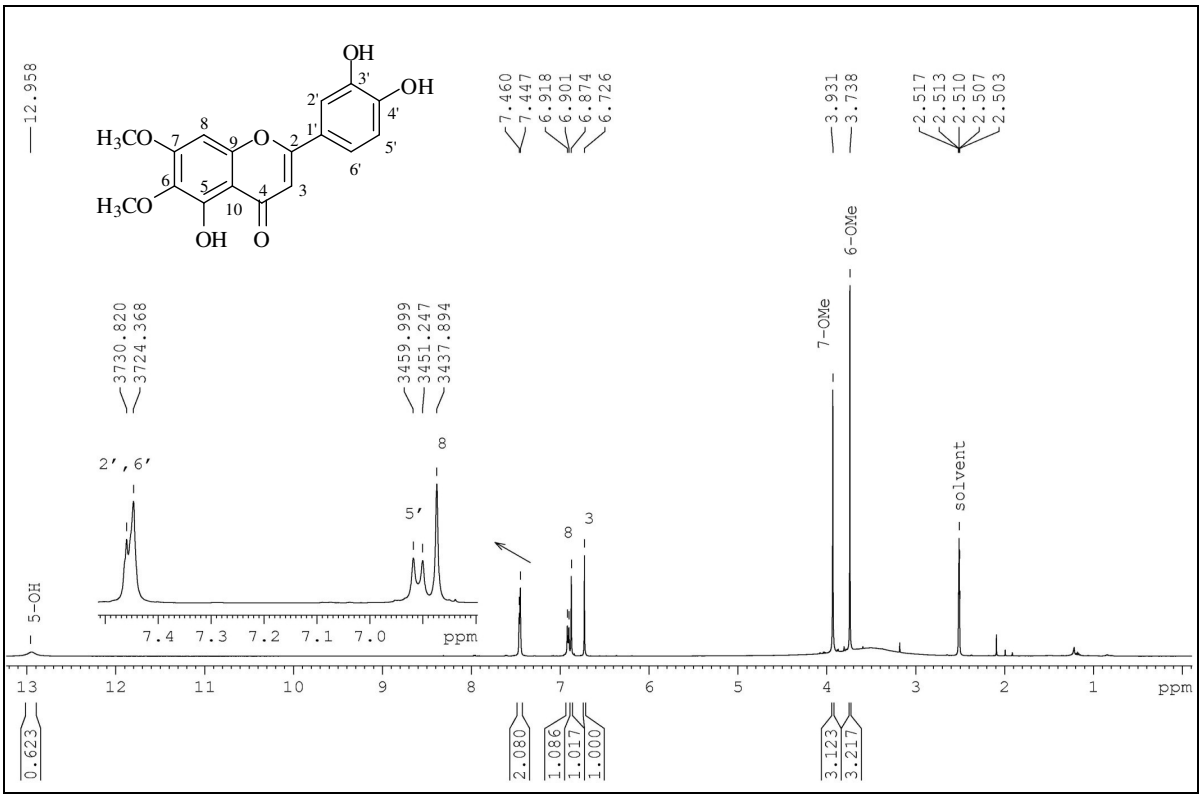
Compound **6** (Cirsimaritin), yellow crystal: EI-MS *m/z*: 314.1 $[M]^+$; UV λ_{max} (nm): (MeOH) 276, 332, (NaOMe) 274, 383, ($AlCl_3$) 265 (sh), 290 (sh), 301, 361, ($AlCl_3$/HCl) 265 (sh), 290 (sh), 300, 354, (NaOAc) 273, 388, (NaOAc/H_3BO_3) 275, 337; ^{1}H NMR (500 MHz, acetone-d_6): δ 12.94 (s, 1 H, 5-OH), 7.95 (d, J = 8.8 Hz, 2 H, H-2′, 6′), 7.02 (d, J = 8.8 Hz, 2 H, H-3′, 5′), 6.85 (s, 1 H, H-8), 6.68 (s, 1 H, H-3), 3.98 (s, 3 H, 7-OMe), 3.79 (s, 3 H, 6-OMe); ^{13}C NMR (125 MHz, acetone-d_6): δ 183.61 (C-4), 165.49 (C-2), 162.33 (C-4′) 160.13 (C-7), 154.13 (C-9), 153.94 (C-5), 133.53 (C-6), 129.33 (C-2′, 6′), 123.05 (C-1′), 116.97 (C-3′, 5′), 106.51 (C-10), 103.84 (C-3), 92.02 (C-8), 60.62 (6-OMe), 56.89 (7-OMe).



S17: ^{13}C NMR (DMSO-d_6, 125 MHz) spectrum of compound **6** (Cirsimaritin)

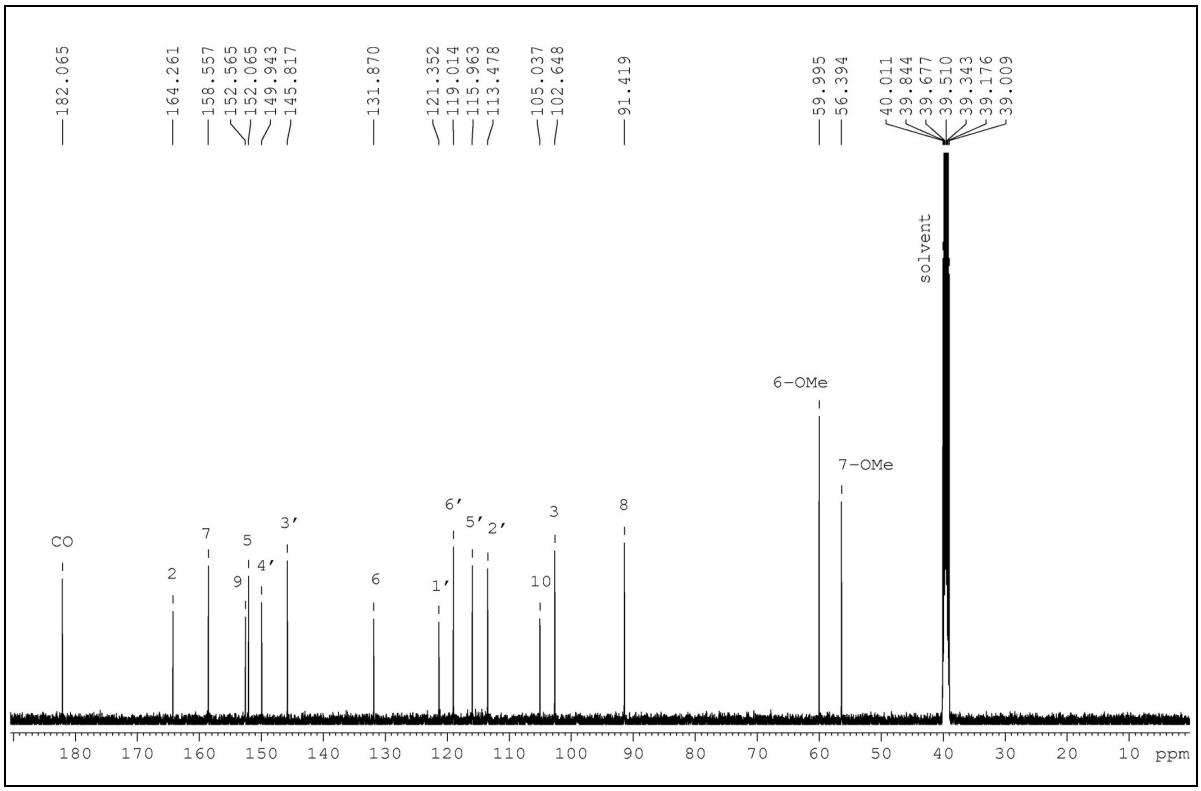


S18: (a) DEPT 135 and **(b)** DEPT 90 NMR (DMSO-d_6, 125 MHz) spectra of compound **6** (Cirsimaritin)

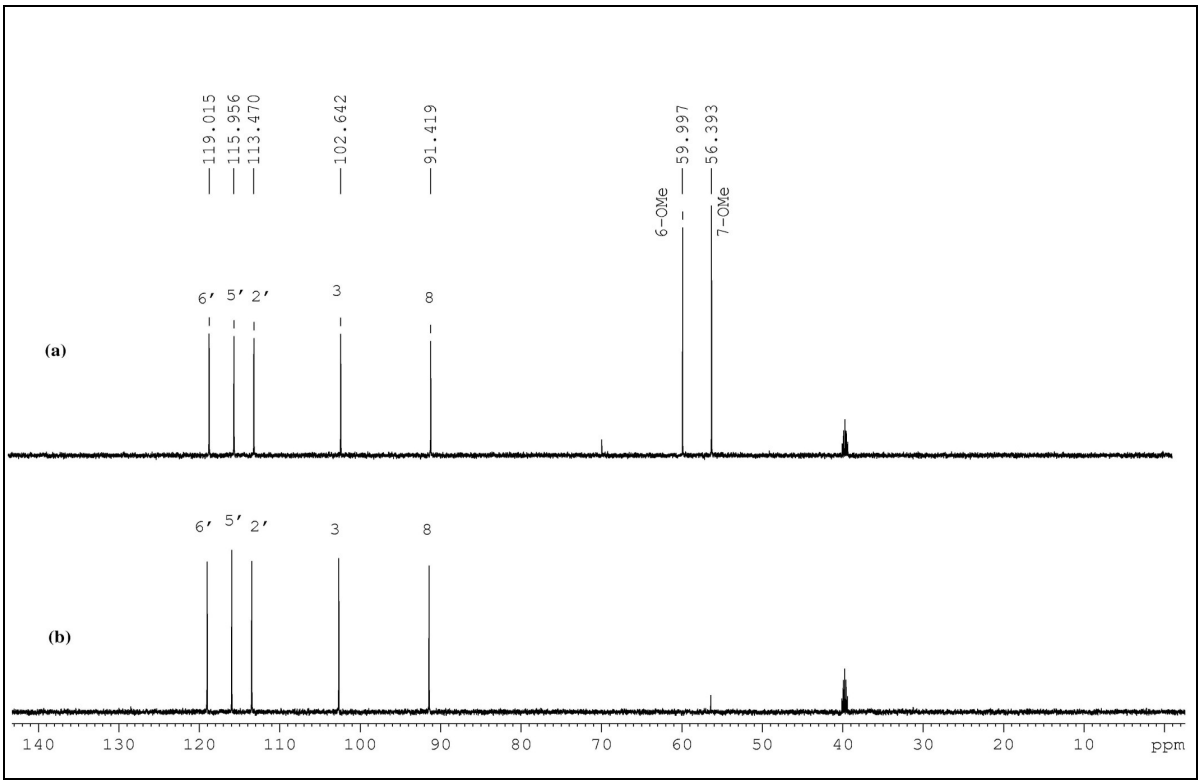


S19: ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **7** (Cirsiliol)

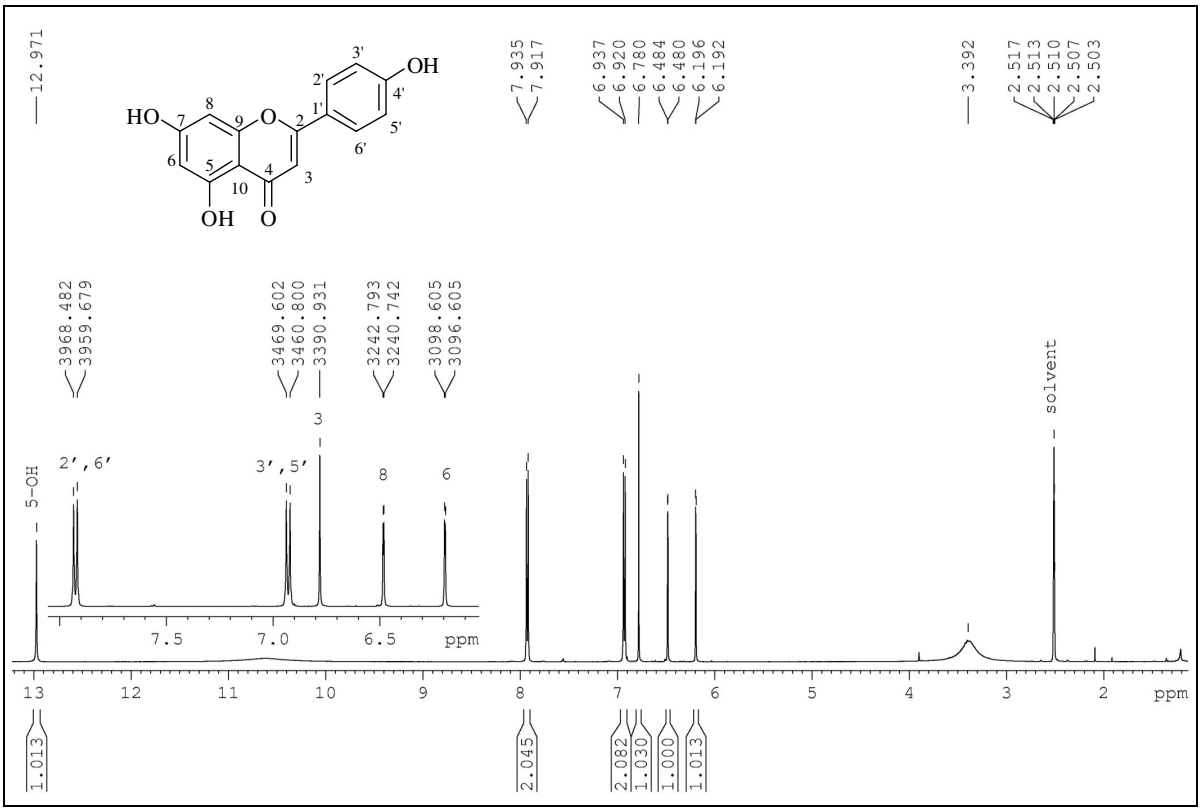
Compound **7** (Cirsiliol), yellow powder: EI-MS *m*/*z*: 330.1 $[M]^+$; UV λ_{max} (nm): (MeOH) 255, 273, 345, (NaOMe) 239 (sh), 268, 400, ($AlCl_3$) 240 (sh), 275, 300 (sh), 342 (sh), 423, ($AlCl_3$/HCl) 262, 284, 366, (NaOAc) 269, 402, (NaOAc/H_3BO_3) 263, 370; ^{1}H NMR (500 MHz, acetone-d_6): δ 12.96 (s, 1 H, 5-OH), 7.45 (m, 2 H, H-2′, 6′), 6.91 (d, J = 8.8 Hz, 1 H, H-5′), 6.87 (s, 1 H, H-8), 6.73 (s, 1 H, H-3),3.93 (s, 3 H, 7-OMe), 3.74 (s, 3 H, 6-OMe); ^{13}C NMR (125 MHz, DMSO-d_6): δ 182.07 (C-4), 164.26 (C-2), 158.56 (C-7), 152.57 (C-9), 152.07 (C-5), 149.94 (C-4′), 145.82 (C-3′), 131.87 (C-6), 121.35 (C-1′), 119.01 (C-6′), 115.96 (C-5′), 113.48 (C-2′), 105.04 (C-10), 102.65 (C-3), 91.42 (C-8), 60.00 (6-OMe), 56.40 (7-OMe).



S20: ^{13}C NMR (DMSO-d_6, 125 MHz) spectrum of compound **7** (Cirsiliol)

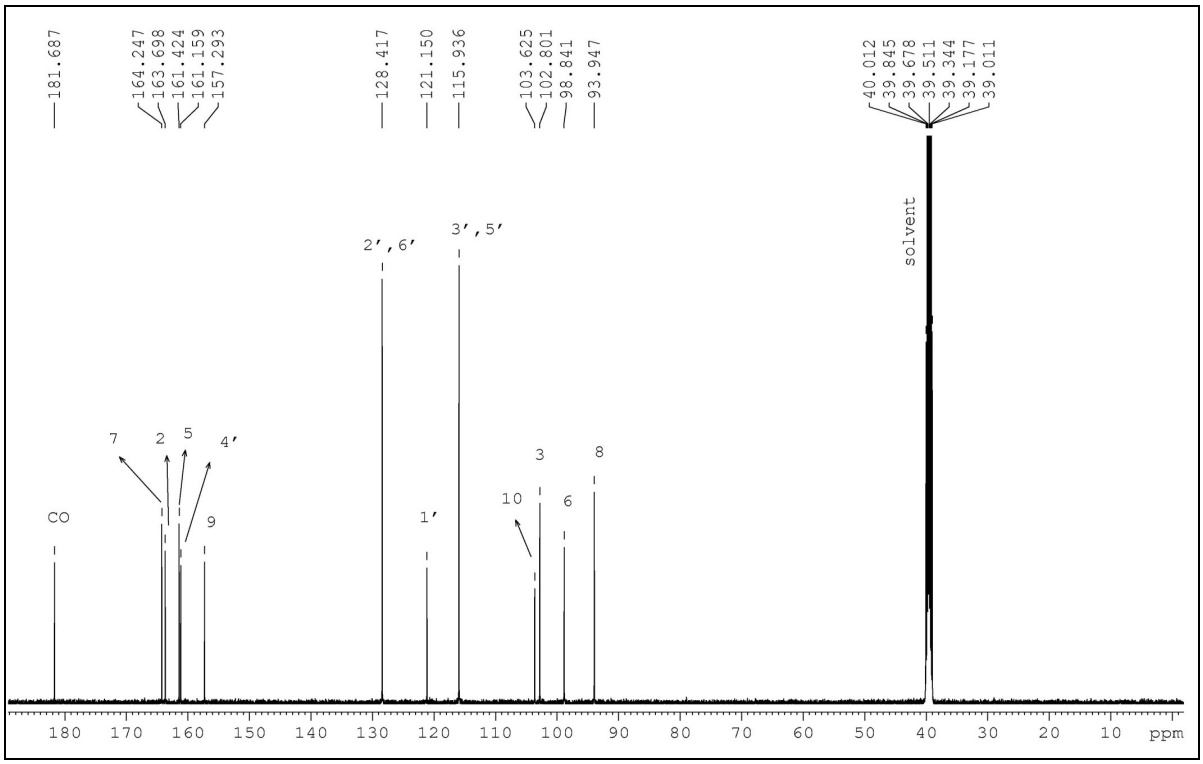


S21: (a) DEPT 135 and **(b)** DEPT 90 NMR (DMSO-d_6, 125 MHz) spectra of compound **7** (Cirsiliol)

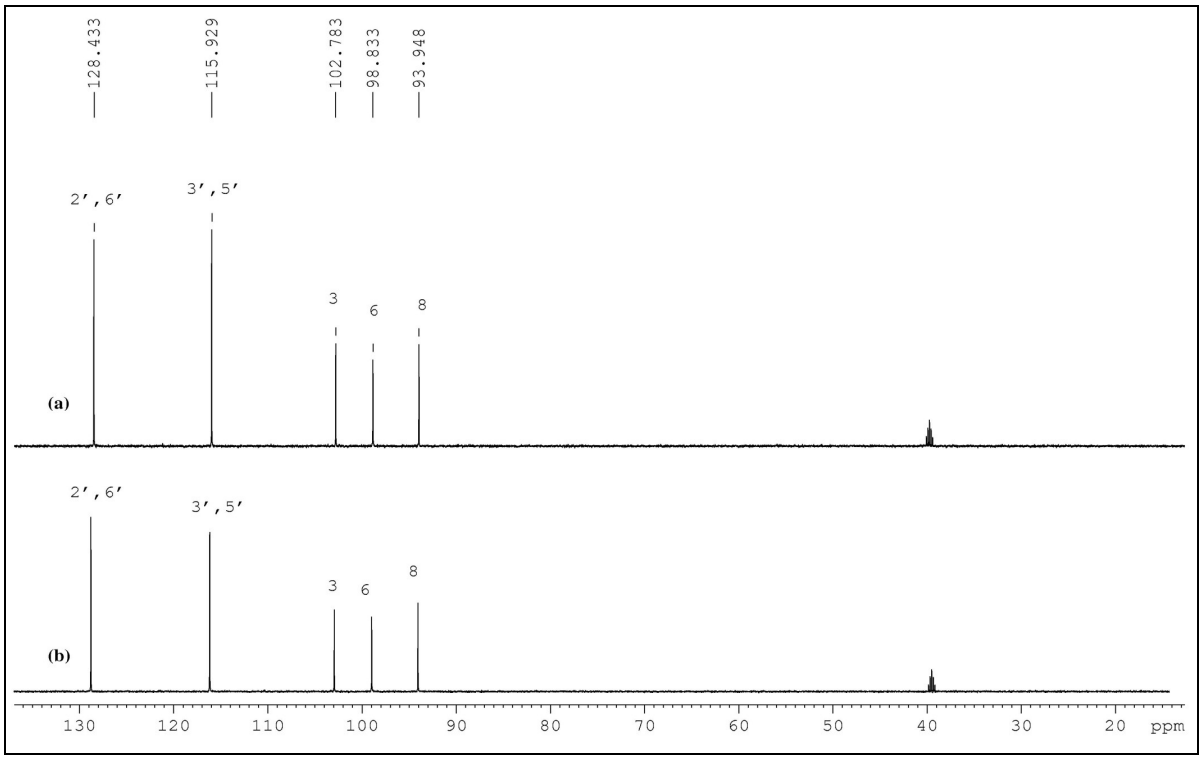


S22: ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **8** (Apigenin)

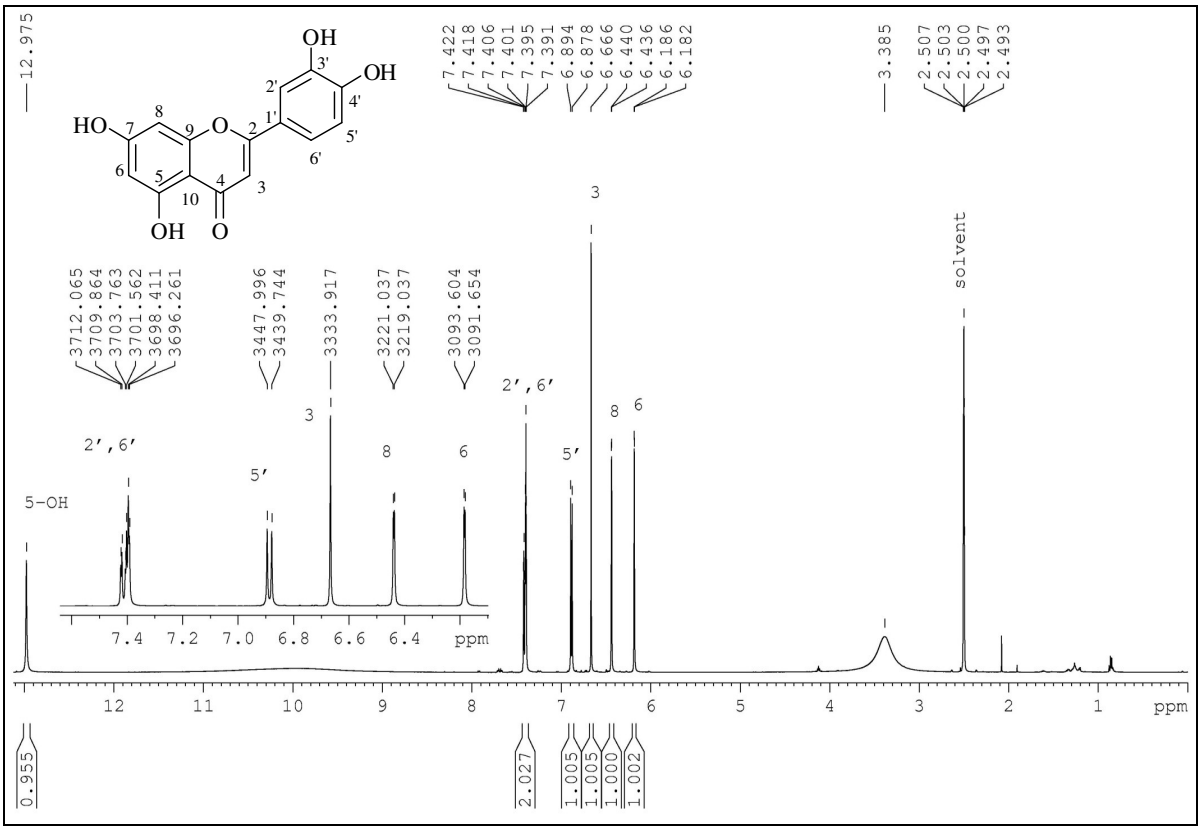
Compound **8** (Apigenin), yellow powder: EI-MS *m/z*: 270.1 $[M]^+$; UV λ_{max} (nm): (MeOH) 268, 336, (NaOMe) 275, 325, 393, ($AlCl_3$) 275, 302, 349, 379, ($AlCl_3$/HCl) 277, 300, 340, 374, (NaOAc) 275, 312, 389, (NaOAc/H_3BO_3) 269, 343; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.97 (s, 1 H, 5-OH), 7.93 (d, J = 8.8 Hz, 2 H, H-2′, 6′), 6.93 (d, J = 8.8 Hz, 2 H, H-3′, 5′), 6.78 (s, 1 H, H-3), 6.48 (d, J = 2.0 Hz, 1 H, H-8), 6.19 (d, J = 2.0 Hz,1 H, H-6); ^{13}C NMR (125 MHz, DMSO-d_6): δ 181.75 (C-4), 164.29 (C-7), 163.72 (C-2), 161.46 (C-5), 161.20 (C-4′), 157.33 (C-9), 128.48 (C-2′, 6′), 121.17 (C-1′), 115.97 (C-3′, 5′), 103.65 (C-10), 102.82 (C-3), 98.87 (C-6), 93.99 (C-8).



S23: ^{13}C NMR (DMSO-d_6, 125 MHz) spectrum of compound **8** (Apigenin)

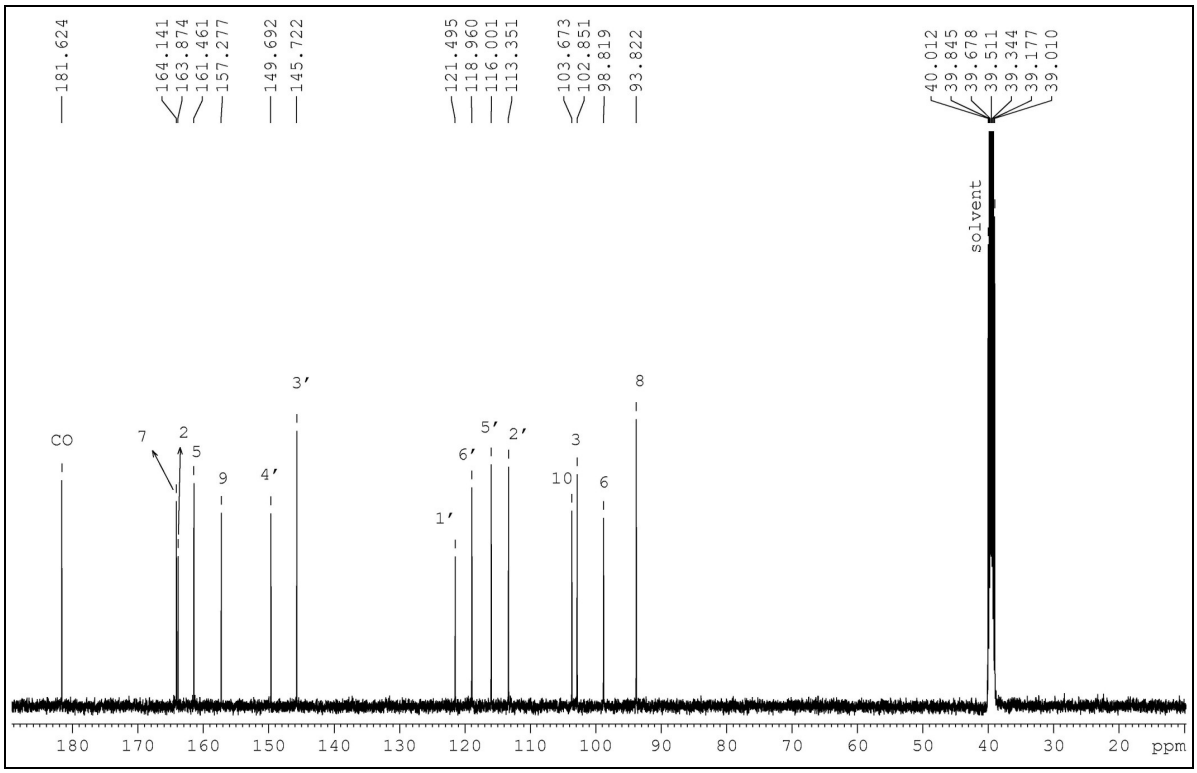


S24: (a) DEPT 135 and **(b)** DEPT 90 NMR (DMSO-d_6, 125 MHz) spectra of compound **8** (Apigenin)

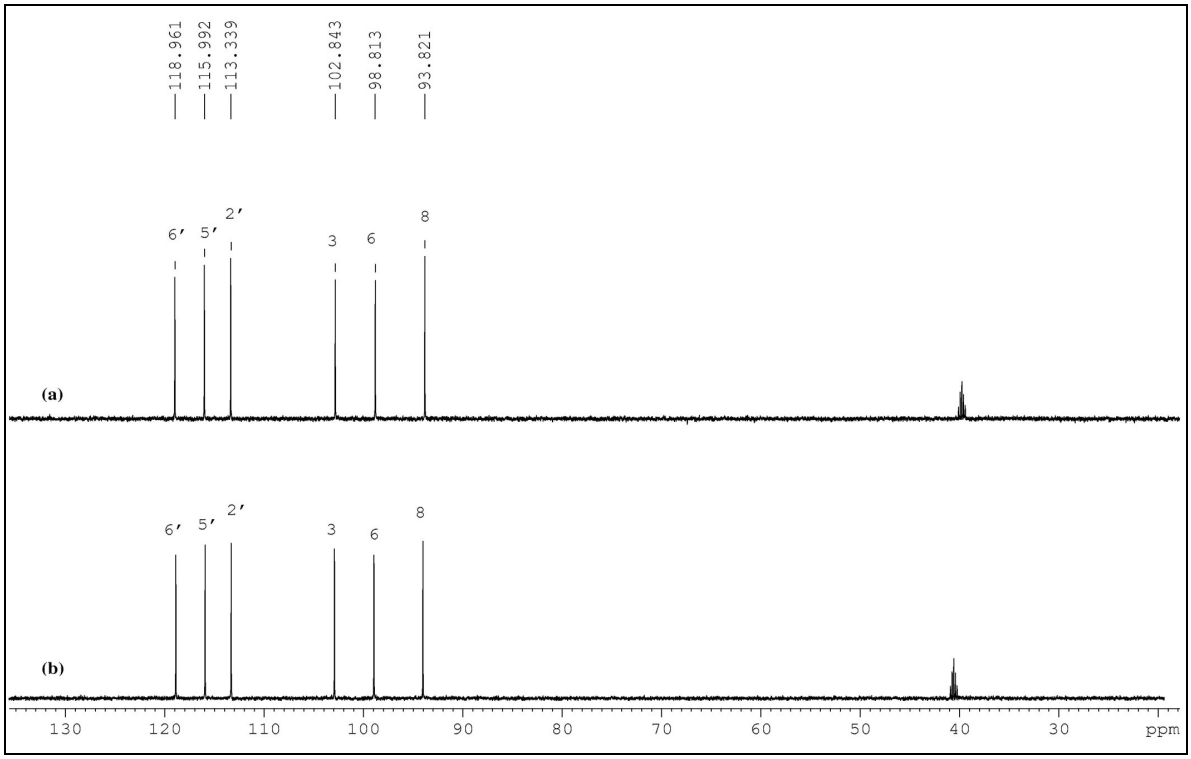


S25: ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **9** (Luteolin)

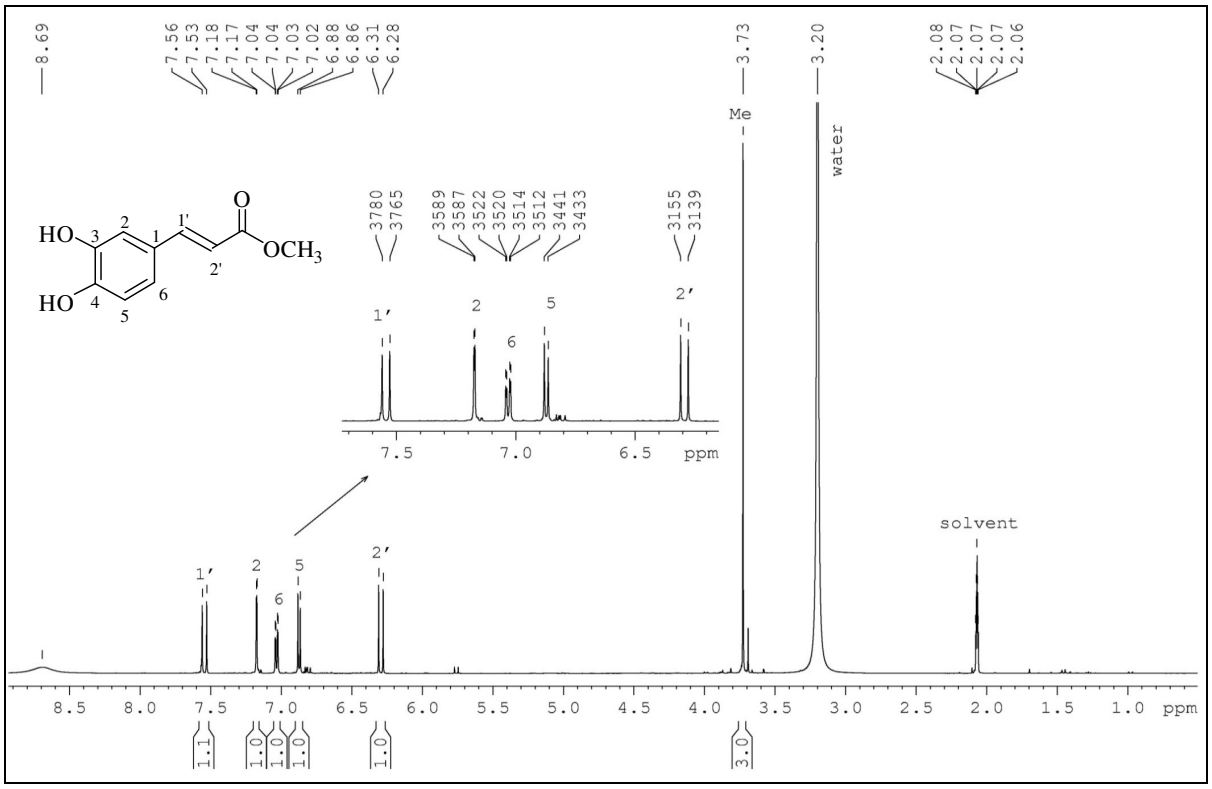
Compound **9** (Luteolin), yellow powder: EI-MS *m/z*: 286.1 $[M]^+$; UV λ_{max} (nm): (MeOH) 254, 265, 295 (sh), 348, (NaOMe) 267, 333, 403, ($AlCl_3$) 273, 300 (sh), 333, 424, ($AlCl_3$/HCl) 263, 275, 295 (sh), 357, 381, (NaOAc) 270, 326, 399, (NaOAc/H_3BO_3) 262, 300 (sh), 374, 422 (sh); ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.98 (s, 1 H, 5-OH), 7.42 (m, 2 H, H-2′, 6′), 6.90 (d, J = 8.0 Hz, 1 H, H-5′), 6.67 (s, 1 H, H-3), 6.45 (d, J = 2.0 Hz, 1 H, H-8), 6.19 (d, J = 2.0 Hz, 1 H, H-6); ^{13}C NMR (125 MHz, DMSO-d_6): δ 181.70 (C-4), 164.16 (C-7), 163.92 (C-2), 161.52 (C-5), 157.32 (C-9), 149.73 (C-4′), 145.77 (C-3′), 121.56 (C-1′), 119.02 (C-6′), 116.05 (C-5′), 113.40 (C-2′), 103.74 (C-10), 102.91 (C-3), 98.87 (C-6), 93.88 (C-8).



S26: ^{13}C NMR (DMSO-d_6, 125 MHz) spectrum of compound **9** (Luteolin)

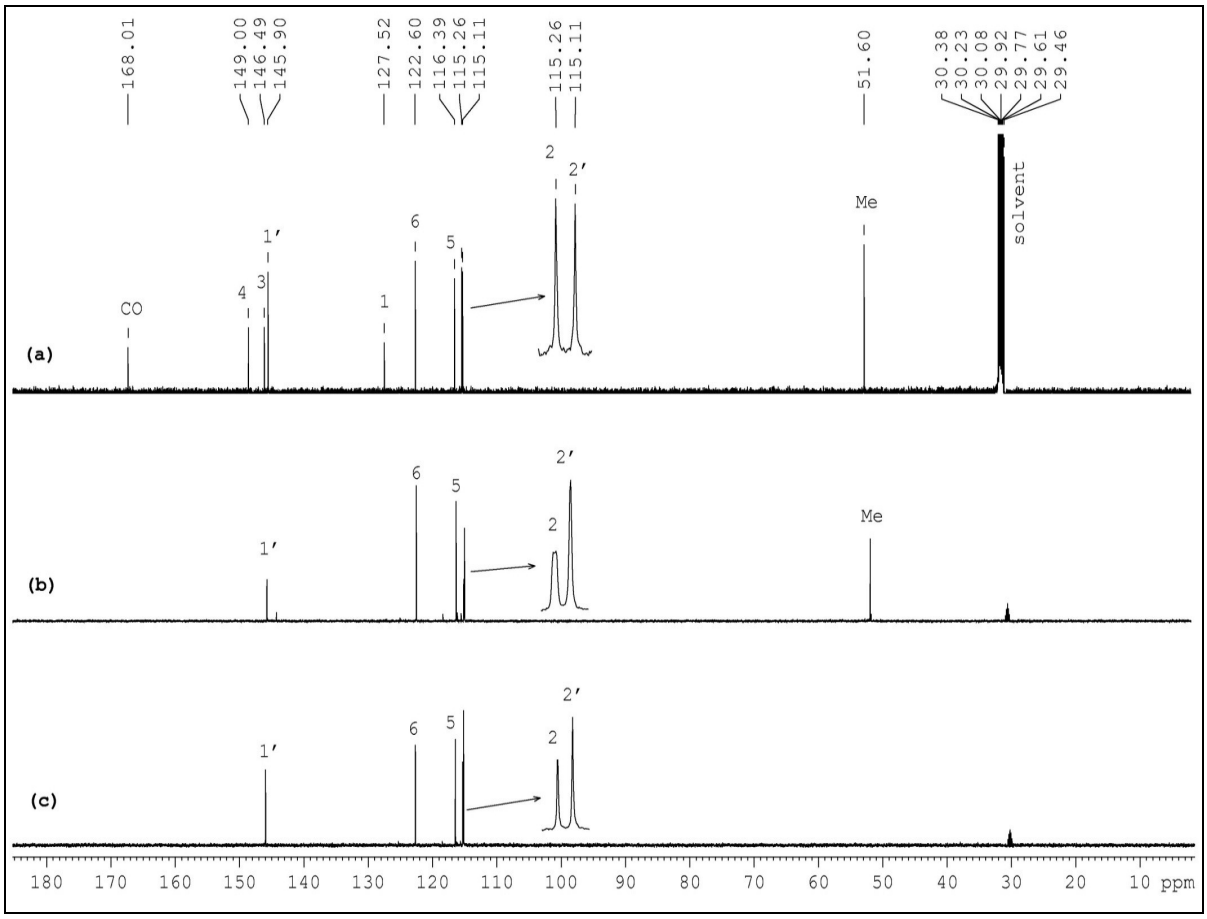


S27: (a) DEPT 135 and **(b)** DEPT 90 NMR (DMSO-d_6, 125 MHz) spectra of compound **9** (Luteolin)

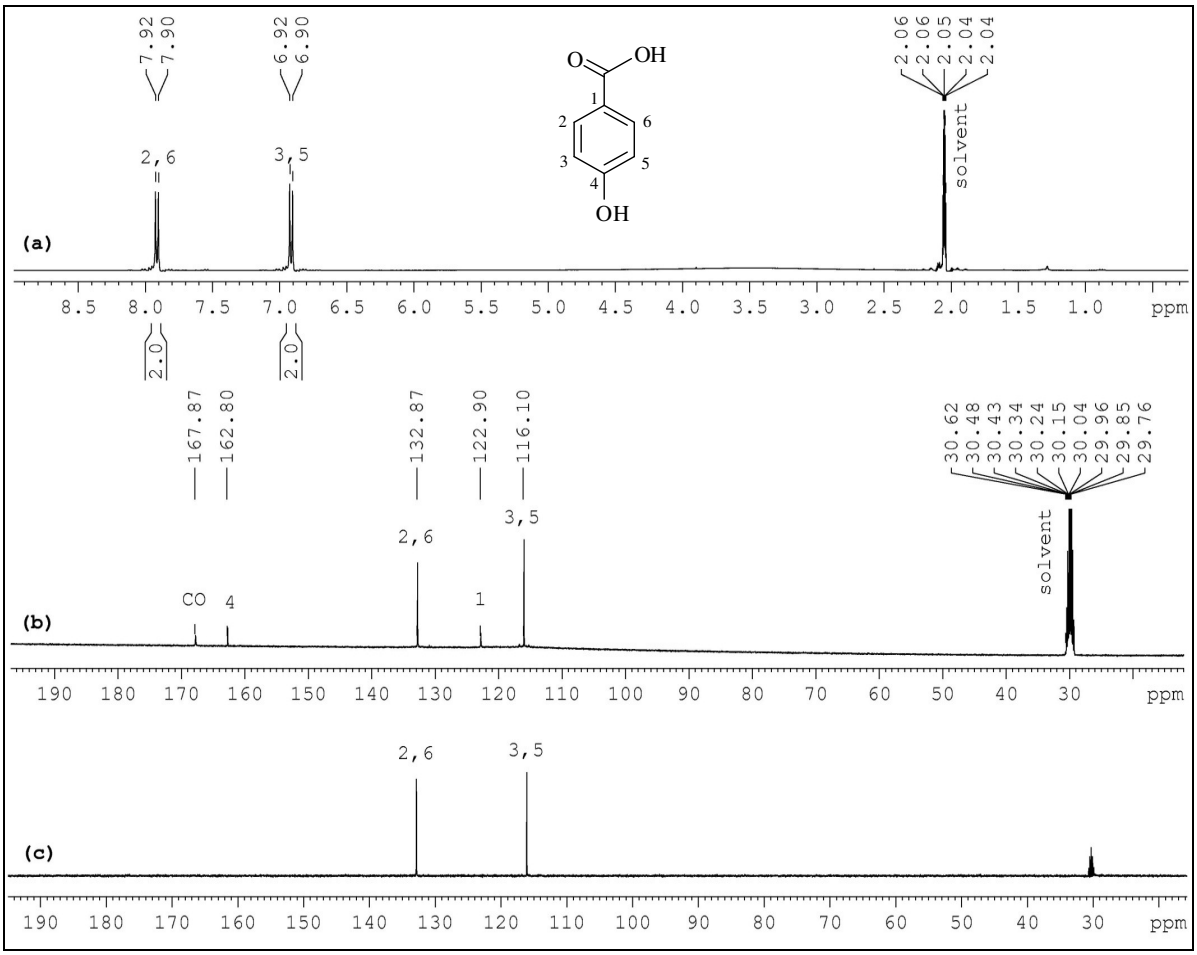


S28: ^{1}H NMR (acetone-d_6, 500 MHz) spectrum of compound **10** (methyl caffeate)

Compound **10** (methyl caffeate), brown solid: EI-MS *m*/*z*: 194.0 $[M]^+$; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.54 (d, J = 15.9 Hz, 1 H, H-1′), 7.17 (d, J = 2.0 Hz, 1 H, H-2), 7.03 (dd, J = 8.2, 2.0 Hz, 1 H, H-6), 6.87 (d, J = 8.2 Hz, 1 H, H-5), 6.29 (d, J = 15.9 Hz, 1 H, H-2′), 3.73 (s, 3 H, -O<u>Me</u>); ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.01 (CO), 149.00 (C-4),), 146.49 (C-3), 145.90 (C-1′), 127.52 (C-1), 122.60 (C-6), 116.39 (C-5), 115.26 (C-2), 115.11 (C-2′), 51.60 (-O<u>Me</u>).

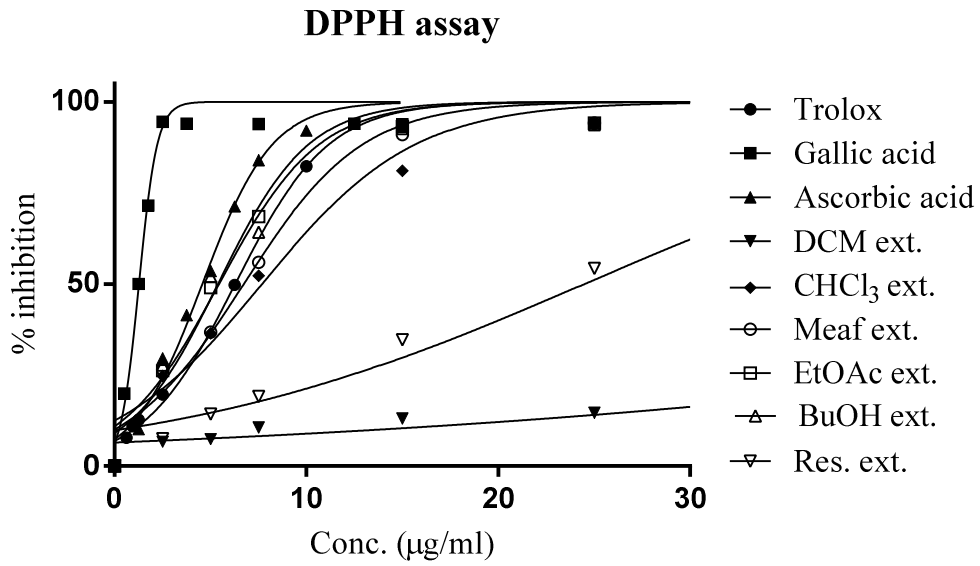


S29: (a) ^{13}C, **(b)** DEPT 135 and **(c)** DEPT 90 NMR (acetone-d_6, 125 MHz) spectra of compound **10** (methyl caffeate)

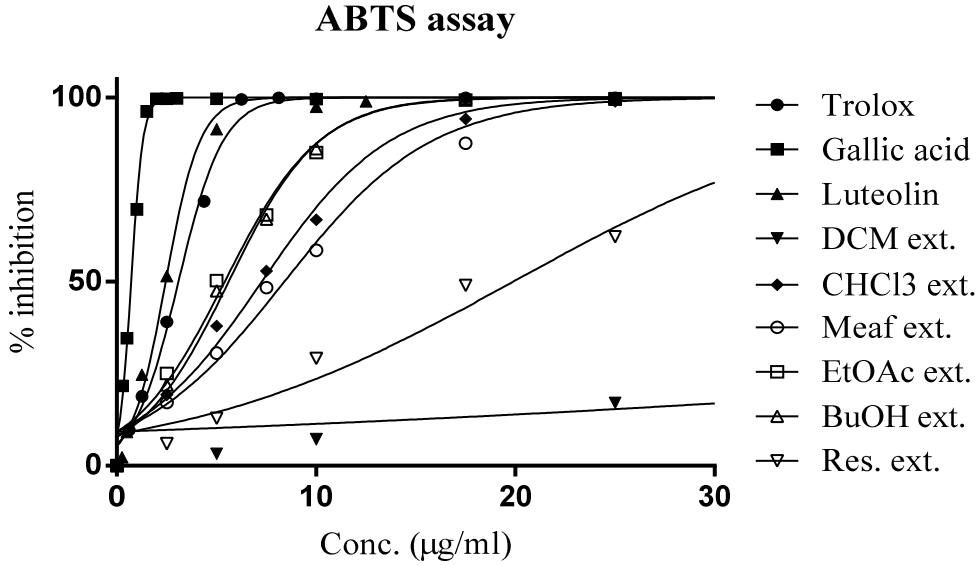


S30: (a) ^{1}H, **(b)** ^{13}C and **(c)** DEPT 90 NMR (acetone-d_6, 500/125 MHz) spectra of compound **11 (**4-hydroxybenzaoic acid**)**

Compound **11** (4-hydroxybenzaoic acid), brown solid: -ESI-MS *m/z*: 137.0 $[M–H]^-$;^{1}H NMR (500 MHz, acetone-d_6): δ 7.91 (d, J = 8.7 Hz, 2 H, H-2, 6), 6.91 (d, J = 8.7 Hz, 2 H, H-3, 5); ^{13}C NMR (125 MHz, DMSO-d_6): δ 167.87 (CO), 162.80 (C-4), 132.87 (C-2, 6), 122.90 (C-1), 116.10 (C-3, 5).



S31: Inhibition effect at various concentrations of extracts and standards (trolox, gallic acid and ascorbic acid) on DPPH radical.



S32: Inhibition effect at various concentrations of extracts and standards (trolox, gallic acid and luteolin) on ABTS radical.

Table S33: Correlation (Pearson's correlation coefficients).

Extract	TFC (QE)	DPPH (IC_{50})	ABTS (TEAC)	ABTS (IC_{50})	FRAP (TE)
TPC (GAE)	0.785	-0.785	0.935	-0.769	0.839
TFC (QE)		-0.677	0.915	-0.638	0.986
DPPH (IC_{50})			-0.81	0.982	-0.74
ABTS (TEAC)				-0.788	0.953
ABTS (IC_{50})					-0.701

Correlation is significant at the 0.01 level.