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Supplementary Information

Alum-Catalyzed One-Pot Synthesis of Dihydropyrano[3,2-*b*]chromenediones

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Experimental

IR spectra were determined on an FTS-40 infrared spectrometer; NMR spectra were determined on Bruker AV-400 spectrometer at room temperature using TMS as internal standard, coupling constants (*J*) were measured in Hz. Mass spectra were recorded on a Finnigan LCQ Advantage mass spectrometer. Elemental analyses were performed by a Vario-III elemental analyzer. Melting points were determined on a XT-4 binocular microscope and were uncorrected. Commercially available reagents were used throughout without further purification unless otherwise stated.

General procedure for the preparation of 2-(hydroxymethyl)-7,7-dimethyl-10-aryl- 7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-diones

A mixture of kojic acid (1 mmol), aldehyde (1 mmol), dimedone (1 mmol) and alum (0.1 mmol) was heated at 100 °C for an appropriate time (TLC). After completion of the reaction, the mixture was washed with water (15 mL) and the crude product was purified by column chromatography over silica gel using ethyl acetate-hexane (7:3) as eluent. The portions were combined and solvent evaporated under reduced pressure to provide compounds **4a**-**4k** as solids. The solids were recrystallized from EtOH to give pure **4a**-**4k** as white crystals. Aqueous washings were collected and evaporated under reduced pressure. After removal of the water, alum was recovered.

*2-(Hydroxymethyl)-7,7-dimethyl-10-phenyl-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4a**)*

IR (KBr) ν_{max}/cm^{-1}: 3362, 3080, 2952, 2890, 1667, 1637, 1441, 1378, 1219, 1193, 1078, 990, 950, 712; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.21 (m, 5H), 6.50 (s, 1H), 4.87 (s, 1H), 4.43-4.32 (m, 2H), 2.71-2.59 (m, 2H), 2.29-2.19 (m, 2H), 1.11 (s, 3H), 1.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.2, 171.3, 167.3, 163.9, 151.7, 140.5, 137.5, 128.8, 128.1, 127.8, 112.3, 112.2, 60.6, 50.4, 40.9, 38.4, 32.3, 29.0, 27.4. MS (ESI): *m/z* 353 $[M+H]^+$. Anal. Calc. for $C_{21}H_{20}O_5$: C 71.58, H 5.72; found: C 71.65, H 5.68.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(4-chlorophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4b**)*

IR (KBr) ν_{max}/cm^{-1}: 3325, 2961, 2930, 2870, 1672, 1640, 1600, 1490, 1442, 1377, 1218, 1190, 1076, 1014, 952, 850; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.18 (m, 4H), 6.52 (s, 1H), 4.87 (s, 1H), 4.41-4.37 (m, 2H), 2.66-2.60 (m, 2H), 2.30-2.21 (m, 2H), 1.11 (s, 3H), 1.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.3, 171.4, 168.3, 164.1, 151.2, 138.9, 137.5, 133.6, 129.4, 129.0, 112.0, 111.9, 60.4, 50.3, 40.8, 37.8, 32.3, 28.9, 27.4. MS (ESI): *m/z* 387 $[M+H]^+$. Anal. calc. for $C_{21}H_{19}ClO_5$: C 65.20, H 4.95; found: C 65.12, H 4.88.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(4-florophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4c**)*

IR (KBr) ν_{max}/cm^{-1}: 3363, 2953, 2930, 2853, 1675, 1638, 1601, 1509, 1443, 1378, 1219, 1192, 1157, 1075, 962, 845, 683; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24-7.20 (m, 2H), 6.99-6.95(m, 2H), 6.52 (s, 1H), 4.87 (s, 1H), 4.40-4.36 (m, 2H), 2.65-2.61 (m, 2H), 2.25-2.22 (m, 2H), 1.10 (s, 3H), 1.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.4, 171.5, 168.3, 164.0, 160.9, 151.5, 137.4, 136.2, 129.7, 129.6, 115.8, 115.6, 112.2, 112.0, 60.4, 50.3, 40.8, 37.7, 32.3, 28.9, 27.4; MS (ESI): *m/z* 371 $[M+H]^+$. Anal. calc. for $C_{21}H_{19}FO_5$: C 68.10, H 5.17; found: C 68.20, H 5.12.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(4-nitrophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4d**)*

IR (KBr) ν_{max}/cm^{-1}: 3334, 2960, 2928, 2855, 1675, 1633, 1596, 1520, 1375, 1347, 1216, 1123, 1058, 1003, 946, 867, 622. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, 2H, *J* 8.8 Hz), 7.47 (d, 2H, *J* 8.4 Hz), 6.53 (s, 1H), 5.03 (s, 1H), 4.42-4.37 (m, 2H), 2.69-2.65 (m, 2H), 2.27-2.23 (m, 2H), 1.13 (s, 3H), 1.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.0, 170.8, 167.0, 164.4, 150.0, 147.4, 137.9, 129.1, 124.1, 112.6, 111.5, 60.6, 50.3, 40.9, 38.4, 32.3, 28.9, 27.5.

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MS (ESI): *m/z* 398 $[M+H]^+$. Anal. calc. for $C_{21}H_{19}NO_7$: C 63.47, H 482, N 3.52; found: C 63.35, H 4.850, N 3.57.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(3-nitrophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4e**)*

IR (KBr) ν_{max}/cm^{-1}: 3393, 2955, 2922, 2851, 1669, 1637, 1599, 1530, 1448, 1377, 1350, 1213, 1143, 1080, 678. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.11-8.09 (m, 2H), 7.63 (d, 1H, *J* 8.0 Hz), 7.50 (t, 1H, *J* 8.0 Hz), 6.53 (s, 1H), 5.03 (s, 1H), 4.45-4.33 (m, 2H), 274-2.61 (m, 2H), 2.30-2.20 (m, 2H), 1.12 (s, 3H), 1.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.3, 171.3, 168.2, 164.7, 150.2, 148.4, 142.4, 137.7, 134.3, 129.8, 123.4, 122.9, 112.2, 111.3, 60.4, 50.3, 40.8, 38.3, 32.3, 28.9, 27.5. MS (ESI): *m/z* 398 $[M+H]^+$. Anal. calc. for $C_{21}H_{19}NO_7$: C 63.47, H 482, N 3.52; found: C 63.39, H 4.80, N 3.55.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(2-chlorophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4f**)*

IR (KBr) ν_{max}/cm^{-1}: 3291, 2956, 2931, 2860, 1673, 1634, 1600, 1468, 1445, 1378, 1221, 1116, 1080, 758. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36 (dd, 1H, *J* 0.8, 8.0 Hz), 7.20-7.16 (m, 3H), 6.49 (s, 1H), 5.44 (s, 1H), 4.40-4.34 (m, 2H), 2.67-2.64 (m, 2H), 2.26-2.22 (m, 2H), 1.12 (s, 3H), 1.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.1, 171.3, 168.0, 164.7, 150.9, 137.8, 137.5, 133.7, 130.1, 129.0, 127.3, 112.0, 111.5, 60.4, 50.3, 40.8, 35.7, 32.2, 29.0, 27.5; MS (ESI): *m/z* 387 $[M+H]^+$. Anal. calc. for $C_{21}H_{19}ClO_5$: C 65.20, H 4.95; found: C 65.30, H 4.82.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(2,4-dichlorophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4g**)*

IR (KBr) ν_{max}/cm^{-1}: 3296, 2952, 2863, 1676, 1637, 1600, 1445, 1376, 1221, 1101, 1079, 854. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39 (s, 1H), 7.21-7.18 (m, 1H), 7.14-7.12 (m, 1H), 6.50 (s, 1H), 5.39 (s, 1H), 4.41-4.37 (m, 2H), 2.71-2.65 (m, 2H), 2.26-2.22 (m, 2H), 1.13 (s, 3H), 1.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.0, 171.1, 167.6, 164.8, 150.3, 137.7, 134.4, 134.2, 130.9, 129.9, 127.7, 112.2, 111.2, 60.5, 50.3, 40.8, 37.5, 32.2, 28.9, 27.6. MS (ESI): *m/z* 422 $[M+H]^+$. Anal. calc. for $C_{21}H_{18}Cl_2O_5$: C 59.87, H 4.31; found: C 59.90, H 4.28.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(3,4,5-trimethoxyphenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H, 10H)-dione (**4h**)*

IR (KBr) ν_{max}/cm^{-1}: 3296, 2960, 2923, 2869, 1673, 1637, 1598, 1508, 1422, 1375, 1329, 1220, 1126, 1076, 956. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.50-6.44 (m, 3H), 4.81 (s, 1H), 4.45-4.37 (m, 2H), 3.80 (s, 6H), 3.79 (s, 3H), 2.68-2.63 (m, 2H), 2.28-2.27 (m, 2H), 1.14 (s, 3H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.3, 171.3, 167.7, 164.0, 153.4, 151.5, 137.3, 136.1, 112.1, 105.0, 60.8, 60.6, 56.1, 50.3, 40.9, 38.5, 32.2, 29.3, 27.1; MS (ESI): *m/z* 443 $[M+H]^+$. Anal. calc. for $C_{24}H_{26}O_8$: C 65.15, H 5.92; found: C 65.20, H 5.89.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(2,5-dimethoxyphenyl)-7,8-dihydropyrano[3,2-b]chromene- 4,9(6H, 10H)-dione (**4i**)*

IR (KBr) ν_{max}/cm^{-1}: 3284, 2950, 2930, 2854, 1672, 1636, 1594, 1503, 1449, 1379, 1226, 1194, 1148, 1080, 1047, 819, 709; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.77-6.74 (m, 3H), 6.47 (s, 1H), 5.17 (s, 1H), 4.40-4.35 (m, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 2.63-2.61 (m, 2H), 2.24-2.20 (m, 2H), 1.11 (s, 3H), 1.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.3, 171.3, 167.3, 164.6, 153.7, 151.7, 151.6, 137.8, 129.4, 116.1, 113.4, 112.7, 112.1, 111.4, 60.6, 56.6, 55.6, 50.4, 40.9, 33.8, 32.2, 29.2, 27.1; MS (ESI): *m/z* 413 $[M+H]^+$. Anal. calc. for $C_{23}H_{24}O_7$: C 66.98, H 5.87; found: C 67.05, H 5.80.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(4-methylphenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4j**)*

IR (KBr) ν_{max}/cm^{-1}: 3368, 2953, 2931, 2847, 1668, 1636, 1442, 1376, 1219, 1189, 1120, 1076, 950, 862, 624. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.13 (d, 2H, *J* 8.0 Hz), 7.08 (d, 2H, *J* 8.0 Hz), 6.50 (s, 1H), 4.83 (s, 1H), 4.38-4.34 (m, 2H), 2.64-2.61 (m, 2H), 2.28 (s, 3H), 2.23-2.20 (m, 2H), 1.10 (s, 3H), 1.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.4, 171.5, 168.2, 163.9, 152.0, 137.6, 137.5, 137.3, 129.5, 127.9, 112.4, 111.9, 60.4, 50.4, 40.8, 37.9, 32.2, 29.0, 27.4, 21.1; MS (ESI): *m/z* 367 $[M+H]^+$. Anal. calc. for $C_{22}H_{22}O_5$: C 72.12, H 6.05; found: C 72.20, H 6.00.

*2-(Hydroxymethyl)-7,7-dimethyl-10-(4-methoxyphenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4k**)*

IR (KBr) ν_{max}/cm^{-1}: 3355, 2958, 2922, 2836, 1672, 1637, 1511, 1443, 1377, 1219, 1193, 1120, 1029, 950, 860, 629; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.18-7.16 (m, 2H), 6.83-6.80 (m, 2H), 6.50 (s, 1H), 4.83 (s, 1H), 4.40-4.35 (m, 2H), 3.75 (s, 3H), 2.65-2.61 (m, 2H), 2.23-2.22 (m, 2H), 1.10 (s, 3H), 1.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.4, 171.5, 168.0, 16.7, 159.0, 152.0, 137.3, 132.7, 129.1, 114.2, 112.5, 129.1, 60.5, 55.2, 50.4, 40.8, 37.5, 32.2, 29.0, 27.4; MS (ESI): *m/z* 383 $[M+H]^+$. Anal. calc. for $C_{22}H_{22}O_6$: C 69.10, H 5.80; found: C 69.20, H5.72.

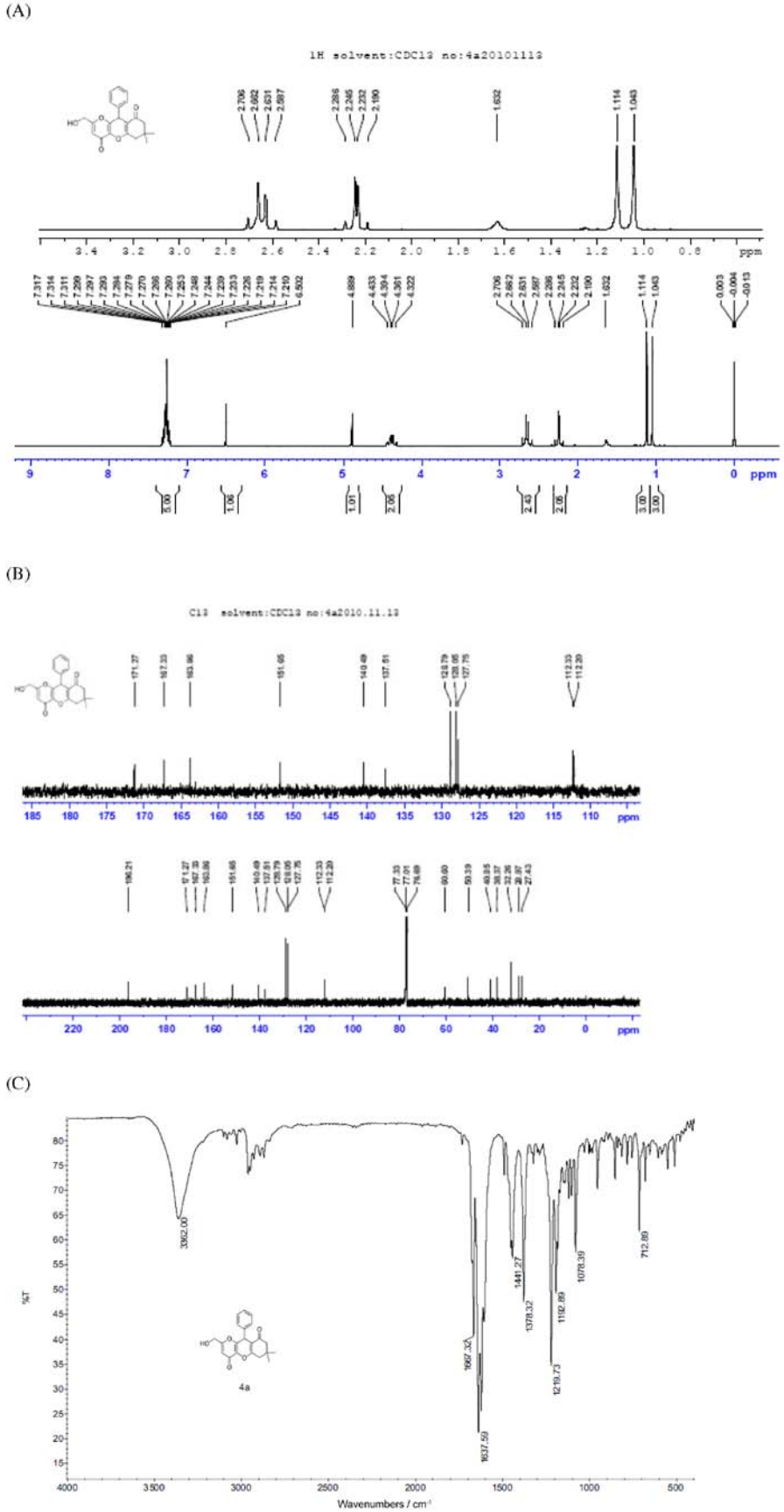

Figure S1. (A) ^{1}H NMR of **4a** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4a** (100 MHz, $CDCl_3$). (C) IR of **4a**.

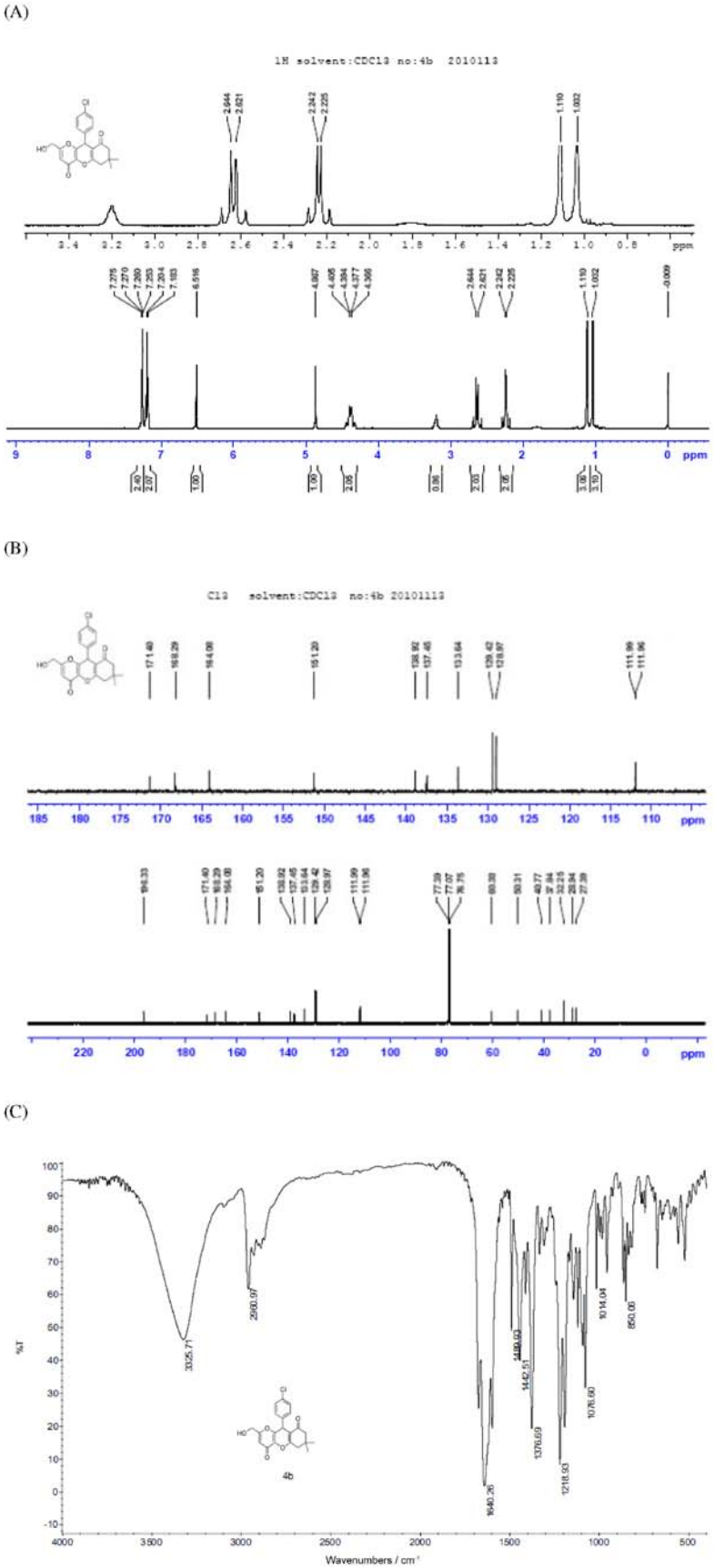

Figure S2. (A) ^{1}H NMR of **4b** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4b** (100 MHz, $CDCl_3$). (C) IR of **4b**.

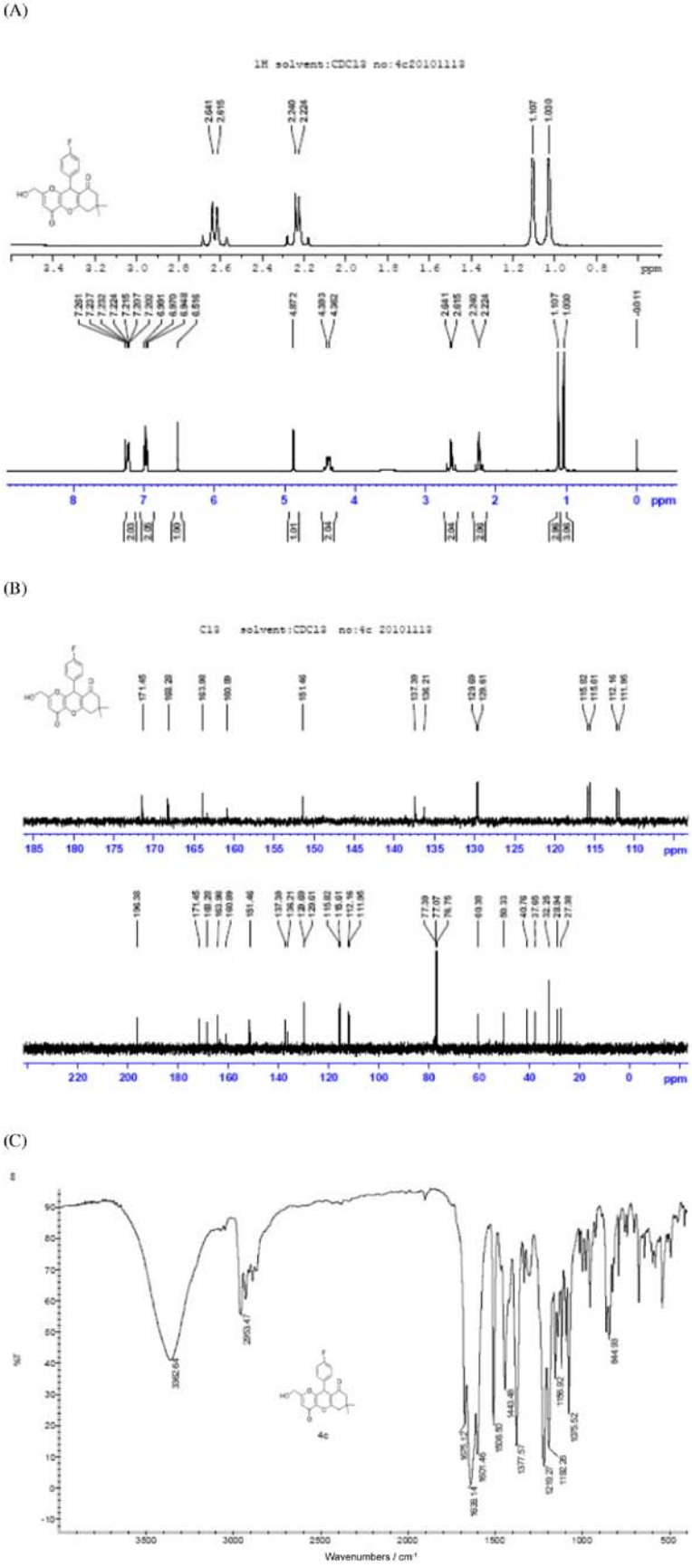

Figure S3. (A) ^{1}H NMR of **4c** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4c** (100 MHz, $CDCl_3$). (C) IR of **4c**.

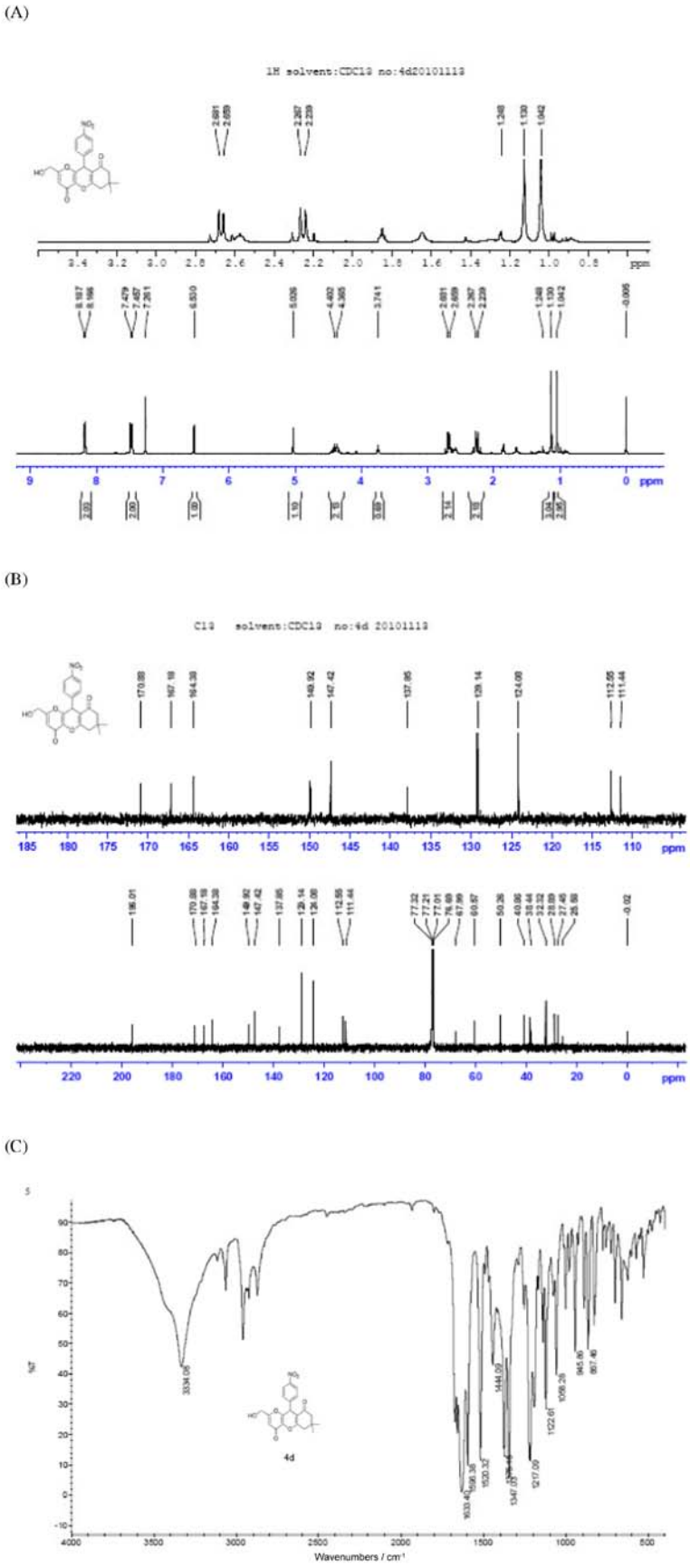

Figure S4. (A) ^{1}H NMR of **4d** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4d** (100 MHz, $CDCl_3$). (C) IR of **4d**.

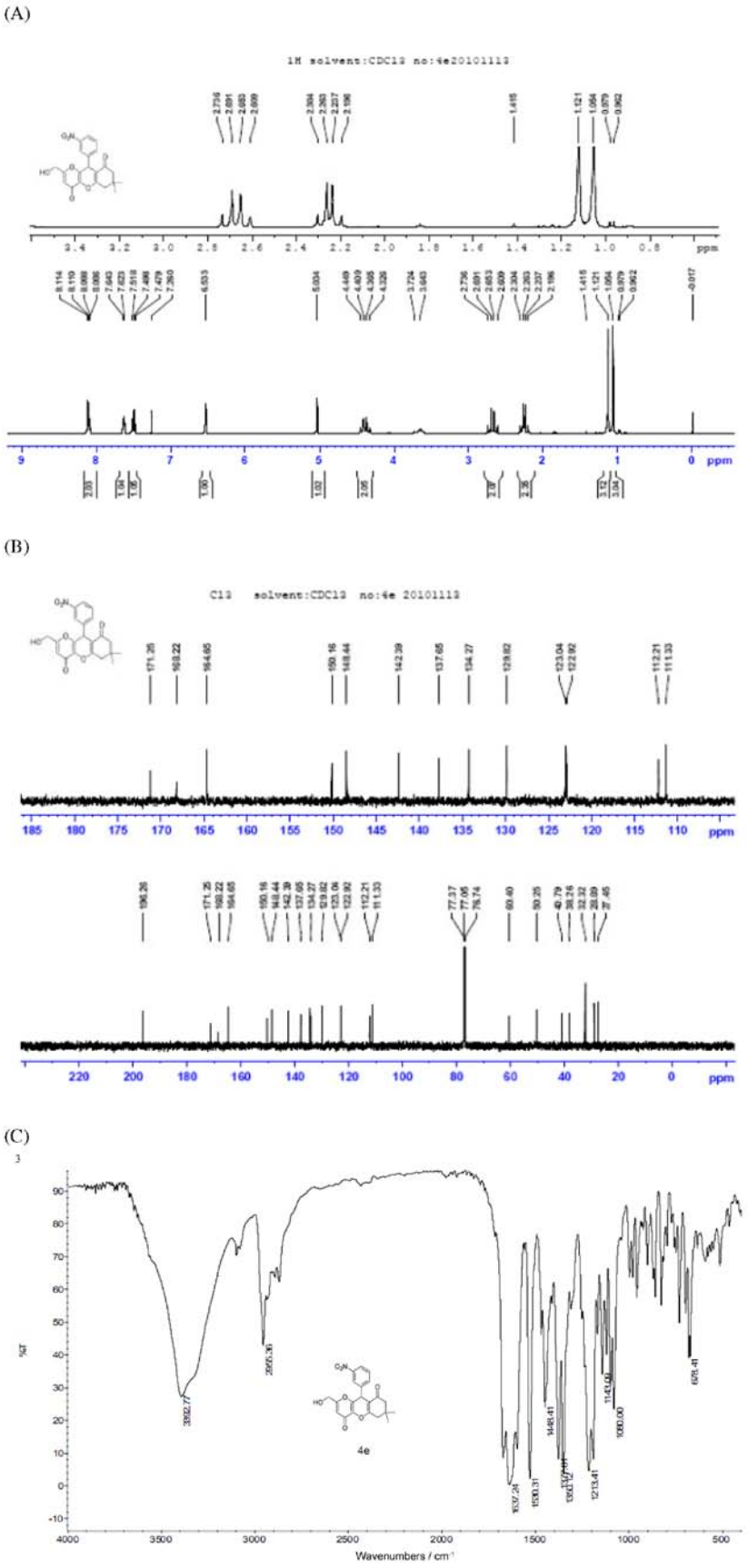

Figure S5. (A) ^{1}H NMR of **4e** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4e** (100 MHz, $CDCl_3$). (C) IR of **4e**.

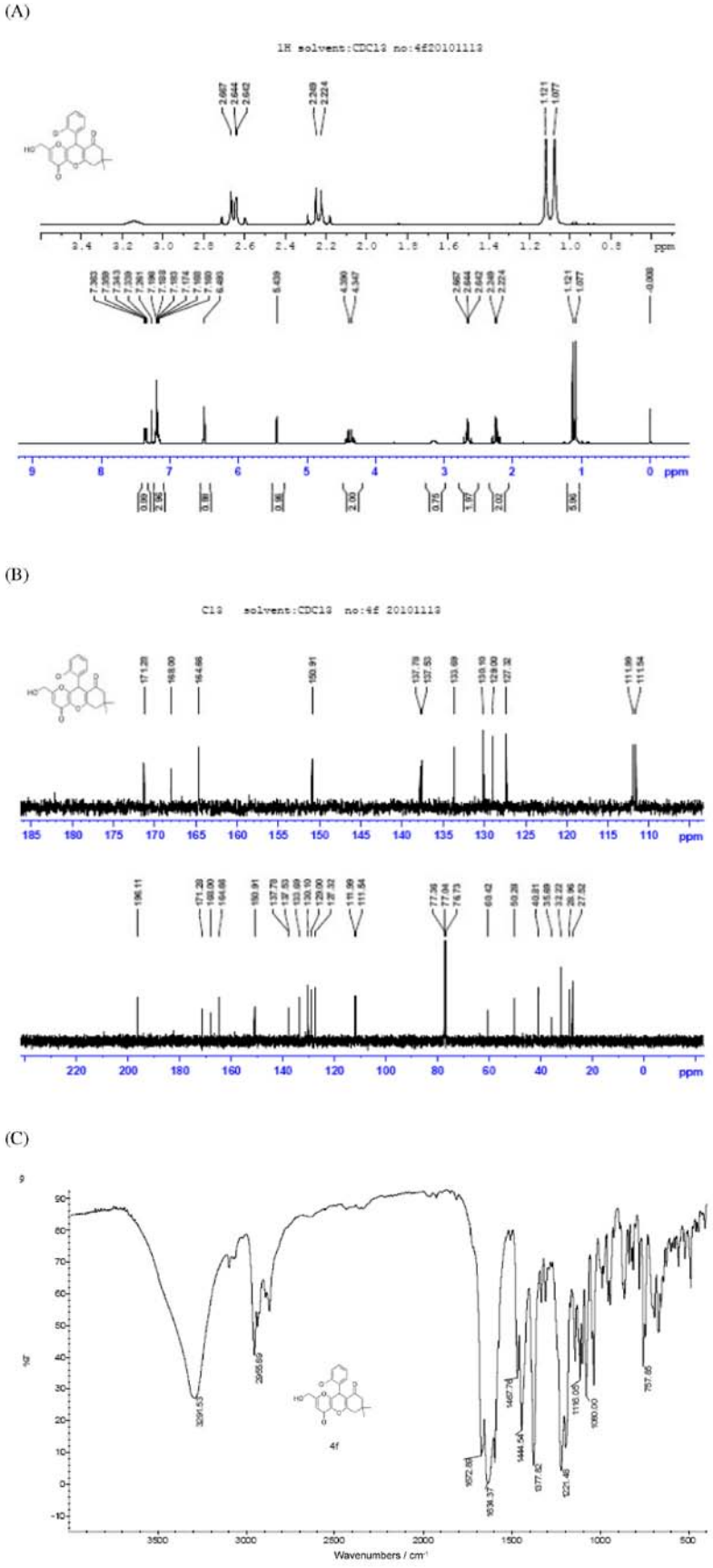

Figure S6. (A) ^{1}H NMR of **4f** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4f** (100 MHz, $CDCl_3$). (C) IR of **4f**.

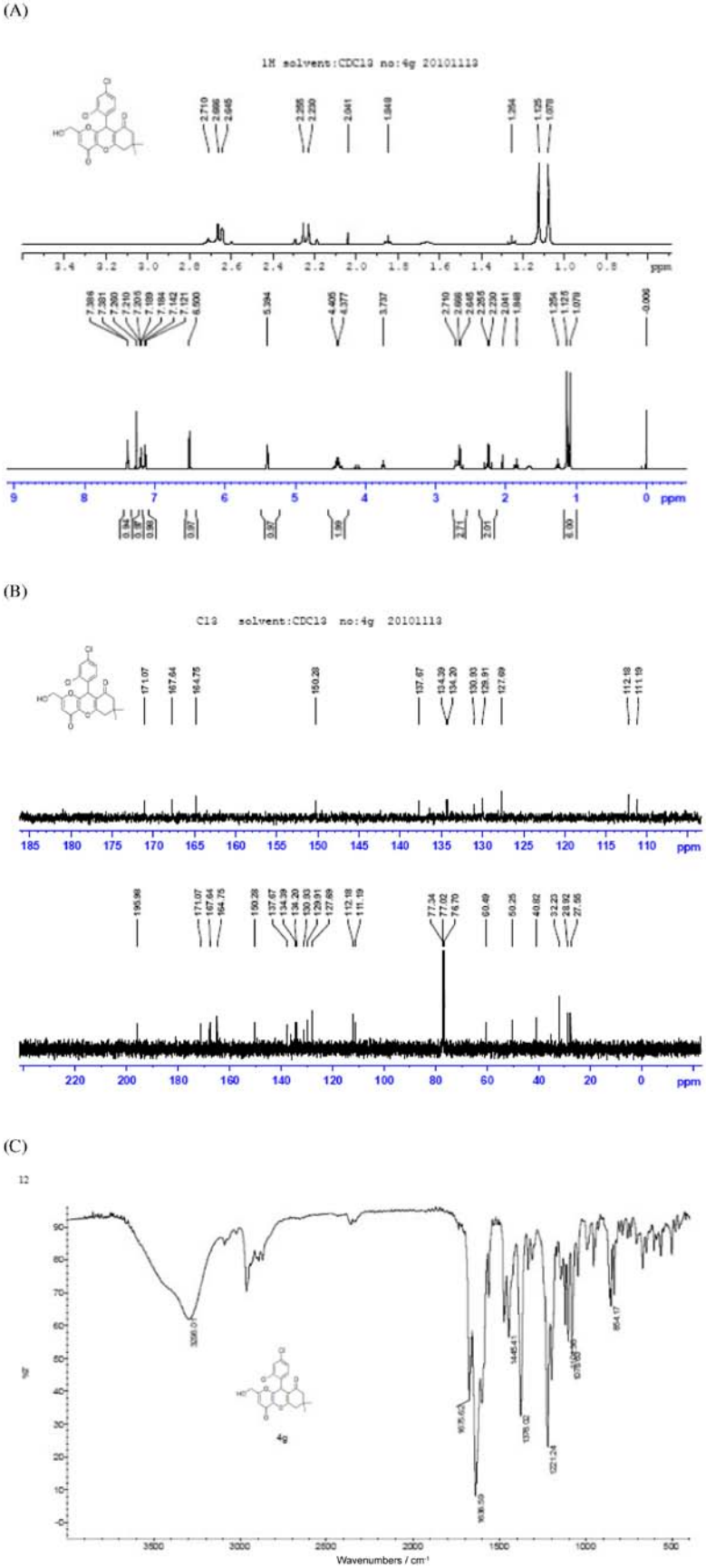

Figure S7. (A) ^{1}H NMR of **4g** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4g** (100 MHz, $CDCl_3$). (C) IR of **4g**.

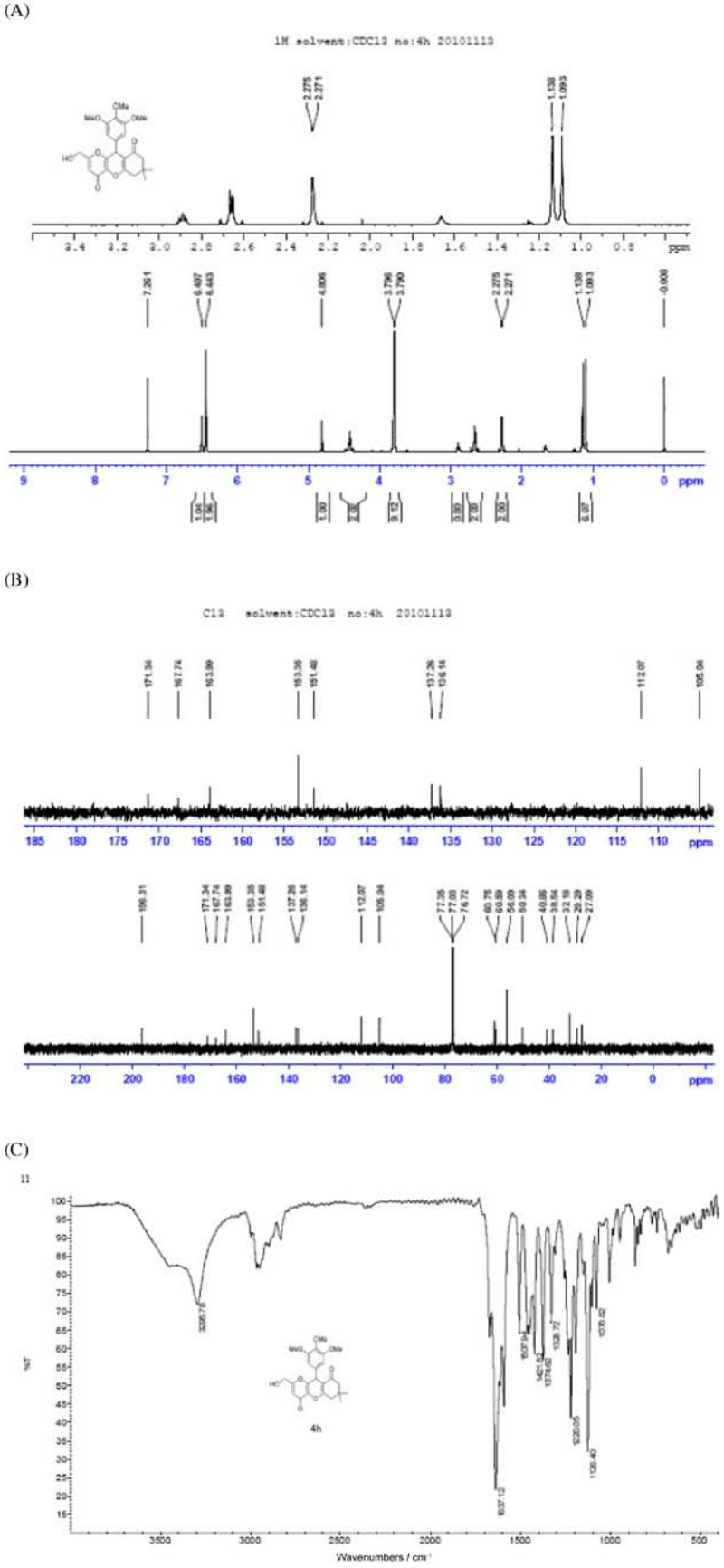

Figure S8. (A) ^{1}H NMR of **4h** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4h** (100 MHz, $CDCl_3$). (C) IR of **4h**.

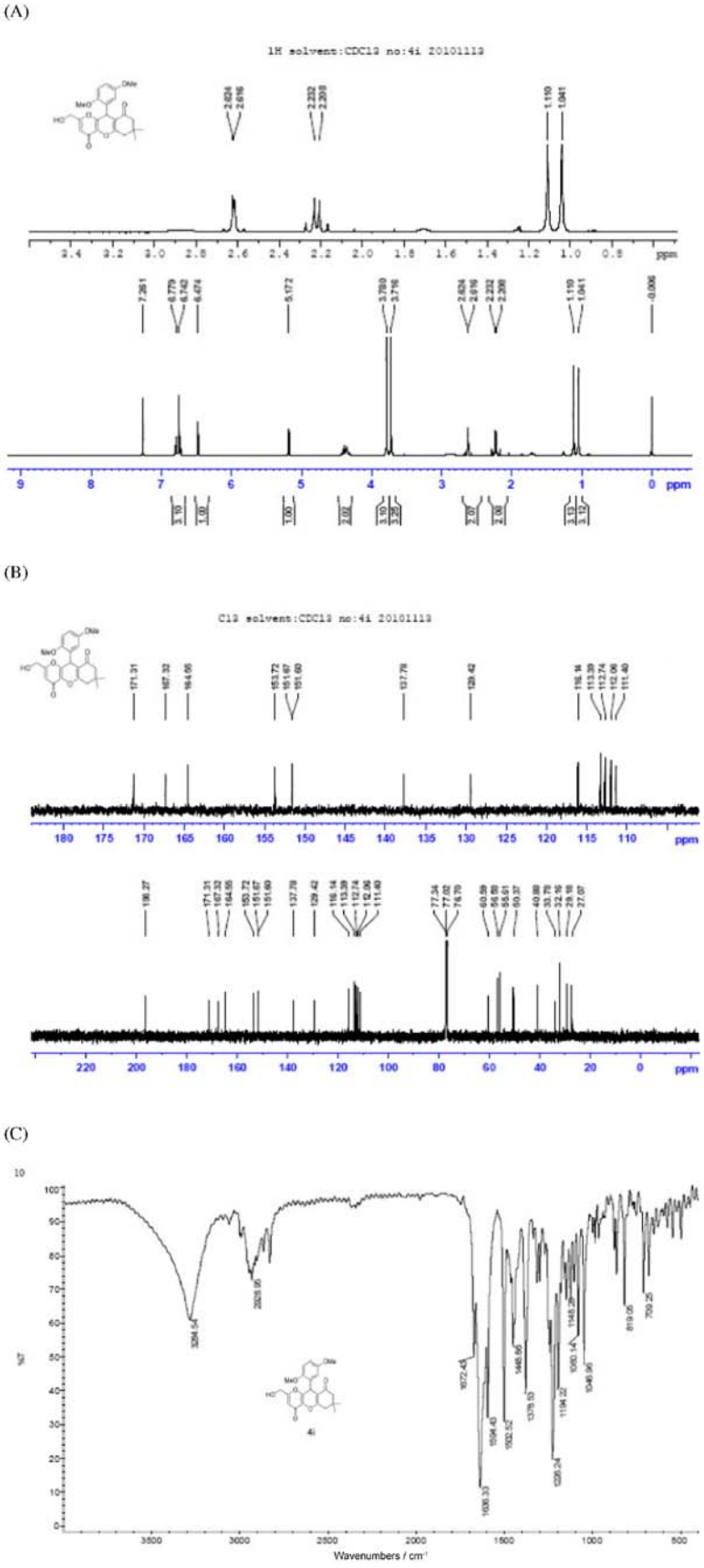

Figure S9. (A) ^{1}H NMR of **4i** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4i** (100 MHz, $CDCl_3$). (C) IR of **4i**.

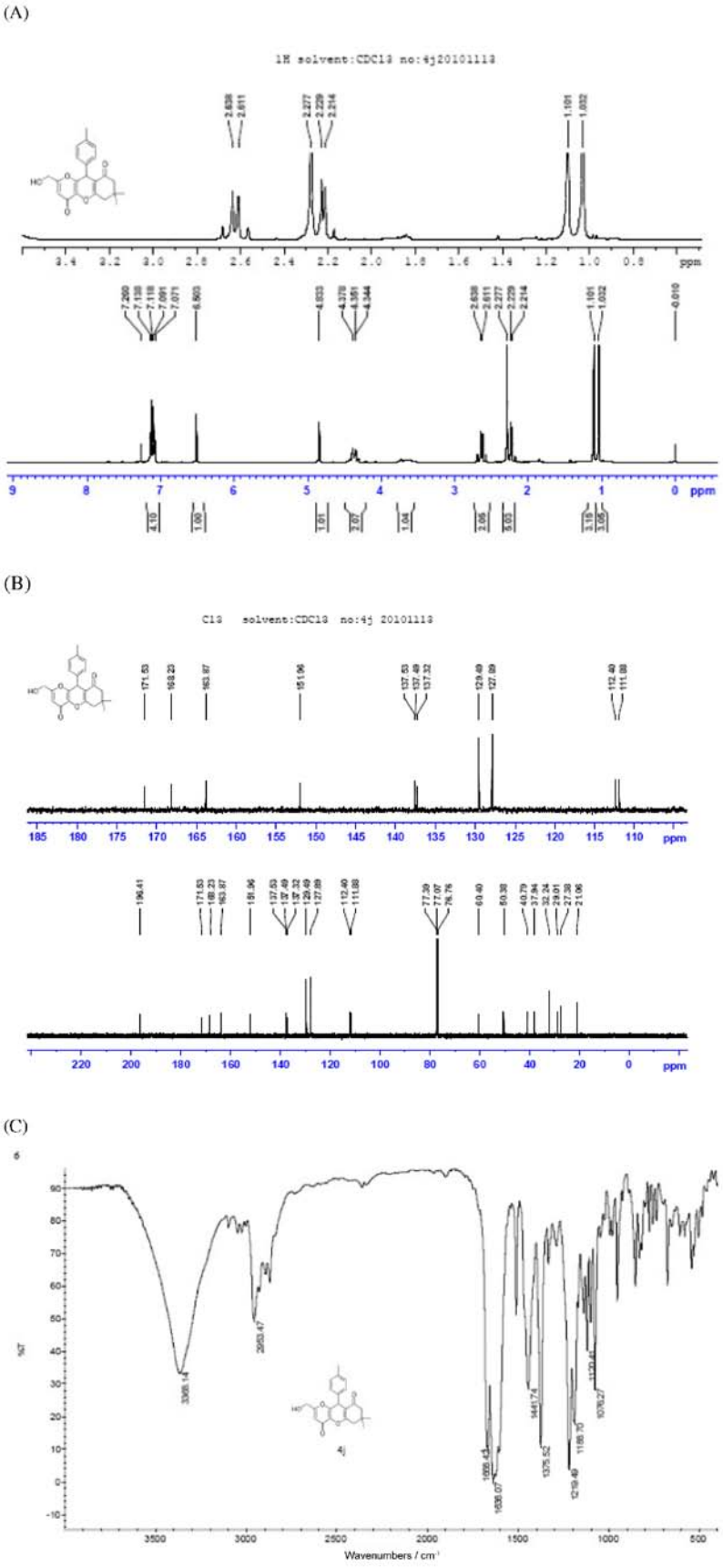

Figure S10. (A) ^{1}H NMR of **4j** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4j** (100 MHz, $CDCl_3$). (C) IR of **4j**.

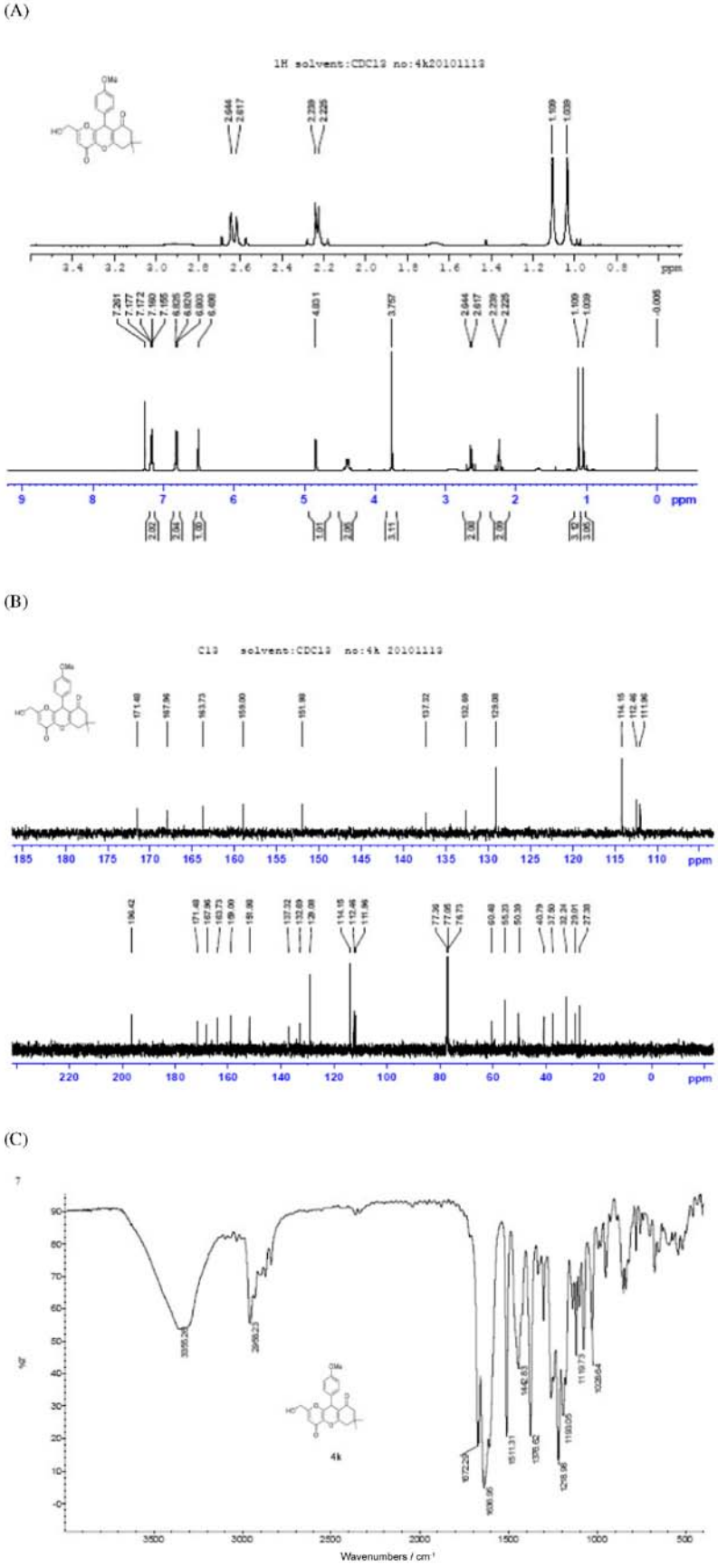

Figure S11. (A) ^{1}H NMR of **4k** (400 MHz, $CDCl_3$). (B) ^{13}C NMR of **4k** (100 MHz, $CDCl_3$). (C) IR of **4k**.