Synthesis of 3-(4-bromo-phenyl)-2-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3carbonyl)-6,6-dimethyl-3,5,6,7-tetrahydro-2H-benzofuran-4-one (4b). A mixture of 3-(2bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 4bromo benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 278-280 °C; IR (KBr) (v_{max}/cm^{-1}) : 3400, 1719, 1629; ¹H NMR (400 MHz, DMSO-d₆) 1.07 (s, 6H, 2xCH₃), 2.05-2.15 (m, 2H, CH₂), 2.27-2.39 (m, 5H, CH₂ & pyran CH_3), 4.21 (d, 1H, J = 4.8 Hz, furan C-3 proton), 4.80 (d, 1H, J = 4.4 Hz, furan C-2 proton), 6.15 (s, 1H, pyran proton), 7.21 (d, 2H, J = 8.0 Hz, ArH), 7.51 (d, 2H, J = 8.0 Hz, ArH); 13 C NMR (400 MHz, DMSO-d₆) 22.3, 27.9, 33.8, 36.2, 49.2, 51.6, 88.4, 99.4, 102.9, 112.7, 121.3, 130.9, 131.2, 136.1, 161.5, 164.6, 176.6, 185.4, 192.1, 199.9; Mass spectrum m/z: 475 $[M + 2]^+$. Anal. calcd. for $C_{23}H_{21}BrO_6$: C, 58.36; H, 4.47. Found: C, 58.31; H, 4.42.

3-(4-chloro-phenyl)-2-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-**Synthesis** carbonyl)-6,6-dimethyl 3,5,6,7-tetrahydro-2H-benzofuran-4-one (4c). A mixture of 3-(2bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 4chloro benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 271-273°C; IR (KBr) (v_{max}/cm^{-1}) : 3400, 1719, 1629; ¹H NMR (400 MHz, DMSO-d₆) 1.07 (s, 6H, 2xCH₃), 2.04-2.15 (m, 5H, CH₂ & pyran CH₃), 2.40-2.43 (m, 2H, CH_2), 4.01 (d, 1H, J = 4.8 Hz, furan C-3 proton), 4.81 (d, 1H, J = 4.0 Hz, furan C-2 proton), 6.16 (s, 1H, pyran proton), 7.27 (d, 2H, J = 8.4 Hz, ArH), 7.38 (d, 2H, J = 8.4 Hz, ArH); 13 C NMR (400 MHz, DMSO-d₆) 22.0, 27.9, 33.9, 36.2, 49.2, 51.6, 88.3, 100.0, 103.0, 112.8, 128.3, 130.6, 132.7, 135.7, 162.3, 164.4, 176.6, 185.2, 192.2, 198.9; Mass spectrum m/z: 429 $[M + H]^+$. Anal. calcd. for $C_{23}H_{21}ClO_6$: C, 64.41; H, 4.94. Found: C, 64.66; H, 4.87.

Synthesis of 2-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-carbonyl)-3-(4-hydroxy-phenyl)-6,6-dimethyl-3,5,6,7-tetrahydro-2H-benzofuran-4-one (4d). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 4-

hydroxy benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 310-312 °C; IR (KBr) (v_{max}/ cm^{-1}): 3379, 1720, 1630; ¹H NMR (400 MHz, DMSO-d₆) 1.07 (s, 6H, 2xCH₃), 2.04-2.14 (m, 2H, CH₂), 2.22 (s, 3H, CH₃), 2.40-2.48 (m, 2H, CH₂), 4.12 (d, 1H, J = 4.8 Hz, furan C-3 proton), 4.85 (d, 1H, J = 4.0 Hz, furan C-2 proton), 6.20 (s, 1H, pyran proton), 6.65 (d, 2H, J = 8.4 Hz, ArH), 7.02 (d, 2H, J = 8.0 Hz, ArH); ¹³C NMR (400 MHz, DMSO-d₆) 22.2, 27.7, 33.0, 36.1, 49.2, 51.6, 88.6, 99.7, 103.0, 112.8, 128.3, 130.6, 135.7, 156.1, 162.5, 163.7, 176.6, 186.2, 192.2, 198.9; Mass spectrum m/z: 411 [M +H]⁺. Anal. calcd. for C₂₃H₂₂O₇: C, 67.31; H, 5.40. Found: C, 67.38; H, 5.36.

Synthesis of 3-(4-Hydroxy-3-methoxy-phenyl)-2-(4-hydroxy-6-methyl-2-oxo-2Hpyran-3-carbonyl)-6,6 dimethyl-3,5,6,7-tetrahydro-2H-benzofuran-4-one (4e). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 4-hydroxy-3-methoxy benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 225-227 °C; IR (KBr) (v_{max}/ cm⁻¹): 3400, 1718, 1656; ¹H NMR (400 MHz, DMSO-d₆) 1.18 (s, 6H, 2xCH₃), 2.19-2.28 (m, 5H, CH₂ & pyran CH₃), 2.38-2.40 (m, 2H, CH₂), 3.84 (s, 3H, OCH₃), 4.12 (d, 1H, J = 4.8 Hz, furan C-3 proton), 4.96 (d, 1H, J = 4.4 Hz, furan C-2 proton), 6.17 (s, 1H, pyran proton), 7.09-7.12 (m, 2H, ArH), 7.55-7.59 (m, 1H, ArH); ¹³C NMR (400 MHz, DMSO-d₆) 22.2, 27.8, 33.7, 36.4, 49.1, 51.5, 55.5, 88.1, 99.6, 108.1, 115.3, 118.9, 121.0, 126.9, 144.9, 146.0, 152.9, 160.0, 162.7, 176.5, 184.0, 190.9, 198.0; Mass spectrum m/z: 441 [M +H]⁺. Anal. calcd. for C₂₄H₂₄O₈: C, 65.45; H, 5.49. Found: C, 65.49; H, 5.40.

Synthesis of 2-(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-carbonyl)-6,6-dimethyl-3-(4-nitro-phenyl)-3,5,6,7-tetrahydro-2H-benzofuran-4-one (4f). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 4-nitro

benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 181-183 °C; IR (KBr) (v_{max} / cm⁻¹): 3379, 1720, 1649; ¹H NMR (400 MHz, DMSO-d₆) 1.15 (s, 6H, 2xCH₃), 2.07-2.17 (m, 5H, CH₂ & pyran CH₃), 2.43-2.47 (m, 2H, CH₂), 4.17 (d, 1H, J = 5.2 Hz, furan C-3 proton), 5.00 (d, 1H, J = 4.4 Hz, furan C-2 proton), 6.15 (s, 1H, pyran proton), 7.55(d, 2H, J = 8.0 Hz, ArH), 8.19 (d, 2H, J = 8.4 Hz, ArH); ¹³C NMR (400 MHz, DMSO-d₆) 22.2, 27.8, 33.9, 36.2, 49.1, 51.4, 55.5, 88.5, 99.8, 102.8, 112.8, 122.6, 127.7, 144.2, 147.1, 162.2, 163.3, 177.0, 185.5, 192.1, 198.7. Anal. calcd. for C₂₃H₂₁NO₈: C, 62.86; H, 4.82; N, 3.19. Found: C, 62.82; H, 4.78; N, 3.24.

Synthesis of 2-(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-carbonyl)-6,6-dimethyl-3-(2,3,4-trimethoxy-phenyl)-3,5,6,7-tetrahydro-2H-benzofuran-4-one (4g). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 2,3,4-trimethoxy benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 191-193 °C; IR (KBr) (v_{max} / cm⁻¹): 3395, 1708, 1648; ¹H NMR (400 MHz, DMSO-d₆) 1.13 (s, 6H, 2xCH₃), 2.17-2.28 (m, 5H, CH₂ & pyran CH₃), 2.47-2.53 (m, 2H, CH₂), 3.84 (s, 3H, OCH₃), 3.85 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃), 4.28 (d, 1H, J = 5.2 Hz, furan C-3 proton), 5.09 (d, 1H, J = 4.8 Hz, furan C-2 proton), 6.18 (s, 1H, pyran proton), 7.26 (d, 1H, J = 7.2 Hz, ArH), 7.58 (d, 1H, J = 6.8 Hz, ArH). Anal. calcd. for C₂₆H₂₈O₉: C, 64.45; H, 5.83. Found: C, 64.48; H, 5.87.

Synthesis of 3-(2-Hydroxy-3-methoxy-phenyl)-2-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-carbonyl)-6,6-dimethyl-3,5,6,7-tetrahydro-2H-benzofuran-4-one (4h). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 2-hydroxy-3-methoxy benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was

filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 219-221 $^{\circ}$ C; IR (KBr) (ν_{max} / cm $^{-1}$): 3379, 1731, 1633; 1 H NMR (400 MHz, DMSO-d₆) 1.18 (s, 6H, 2xCH₃), 2.09-2.20 (m, 2H, CH₂), 2.28 (s, 3H, CH₃), 2.48-2.50 (m, 2H, CH₂), 3.84 (s, 3H, OCH₃), 4.26 (d, 1H, J = 4.4 Hz, furan C-3 proton), 5.10 (d, 1H, J = 4.4 Hz, furan C-2 proton), 6.15 (s, 1H, pyran proton), 7.22 (d, 1H, J = 9.2 Hz, ArH), 7.36-7.40 (m, 2H, ArH). Anal. calcd. for $C_{24}H_{24}O_8$: C, 65.43; H, 5.47. Found: C, 65.47; H, 5.49.

Synthesis of 2-(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-carbonyl)-3-(4-methoxy-phenyl)-6,6-dimethyl-3,5,6,7-tetrahydro-2H-benzofuran-4-one (**4i**). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 4-methoxy benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 221-223 °C; IR (KBr) (v_{max} / cm⁻¹): 3384, 1731, 1649; ¹H NMR (400 MHz, DMSO-d₆) 1.18 (s, 6H, 2xCH₃), 2.12-2.23 (m, 5H, CH₂ & pyran CH₃), 2.39-2.43 (m, 2H, CH₂), 3.71 (s, 3H, OCH₃), 4.22 (d, 1H, J = 4.8 Hz, furan C-3 proton), 5.00 (d, 1H, J = 4.4 Hz, furan C-2 proton), 6.19 (s, 1H, pyran proton), 6.70 (d, 2H, J = 8.4 Hz, ArH), 7.08 (d, 2H, J = 8.4 Hz, ArH); ¹³C NMR (400 MHz, DMSO-d₆) 22.5, 27.8, 33.9, 36.2, 49.1, 51.5, 56.1, 88.7, 100.1, 103.0, 112.8, 118.8, 130.6, 135.7, 159.9, 162.2, 163.8, 176.6, 185.7, 192.1, 200.0. Anal. calcd. for $C_{24}H_{24}O_7$: C, 67.91; H, 5.68. Found: C, 67.97; H, 5.63.

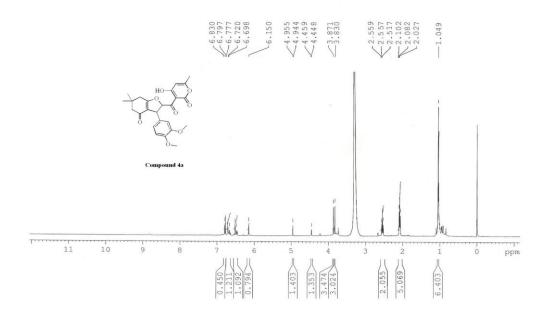
Synthesis of 2-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-carbonyl)-3-(2-hydroxy-naphthalen-1-yl)-6,6-dimethyl-3,5,6,7-tetrahydro-2H-benzofuran-4-one (4j). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 2-hydroxy-1-naphthaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 201-203 °C; IR (KBr) (v_{max}/ cm⁻¹): 3384, 1736, 1657; ¹H NMR (400 MHz, DMSO-d₆) 0.97 (s, 3H, CH₃), 1.07 (s, 3H, CH₃), 2.18-2.22 (m, 5H, CH₂ & pyran CH₃), 2.50-2.57 (m, 2H, CH₂), 4.40 (d, 1H, J = 4.8 Hz, furan C-3 proton), 4.85 (d,

1H, J = 4.4 Hz, furan C-2 proton), 6.18 (s, 1H, pyran proton), 7.36-7.43 (m, 2H, ArH), 7.75 (d, 1H, J = 8.8 Hz, ArH), 7.83 (d, 1H, J = 7.6 Hz, ArH), 8.09-8.12 (m, 2H, ArH); 13 C NMR (400 MHz, DMSO-d₆) 22.0, 25.8, 27.4, 31.6, 40.4, 50.5, 87.1, 99.6, 108.2, 116.6, 117.3, 123.5, 124.2, 126.2, 126.8, 127.6, 128.1, 130.4, 131.5, 147.9, 159.8, 162.7, 176.0, 183.8, 190.0, 195.8. Anal. calcd. for $C_{27}H_{24}O_7$: C, 70.42; H, 5.25. Found: C, 70.49; H, 5.29.

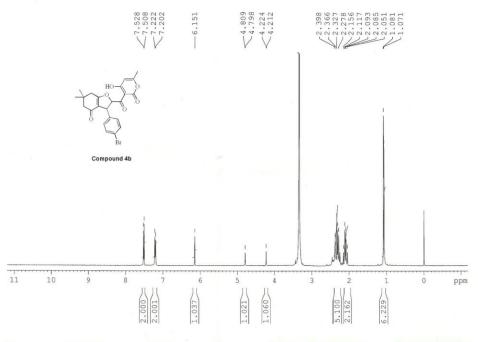
Synthesis of 2-(4-hydroxy-6-methyl-2-oxo-2H-pyrn-3-carbonyl)-3-(2-hydroxy-phenyl)-6,6-dimethyl-3,5,6,7-tetrahydro-2H-benzofuran-4-one (4k). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 2-hydroxy benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 210-212 °C; IR (KBr) (v_{max} / cm⁻¹): 3384, 1726, 1646; ¹H NMR (400 MHz, DMSO-d₆) 1.12 (s, 6H, 2xCH₃), 1.19-2.02 (m, 2H, CH₂), 2.22 (s, 3H, pyran CH₃), 2.44-2.47 (m, 2H, CH₂), 4.21 (d, 1H, J = 4.8 Hz, furan C-3 proton), 5.01 (d, 1H, J = 4.4 Hz, furan C-2 proton), 6.16 (s, 1H, pyran proton), 7.12-7.19 (m, 2H, ArH), 7.62-7.68 (m, 2H, ArH); ¹³C NMR (400 MHz, DMSO-d₆) 21.9, 27.4, 29.2, 31.6, 48.8, 51.1, 88.2, 99.6, 108.2, 116.6, 117.3, 123.5, 127.6, 128.1, 130.4, 150.2, 162.7, 164.4, 175.5, 183.8, 192.7, 199.3. Anal. calcd. for C₂₃H₂₂O₇: C, 67.30; H, 5.38. Found: C, 67.35; H, 5.32.

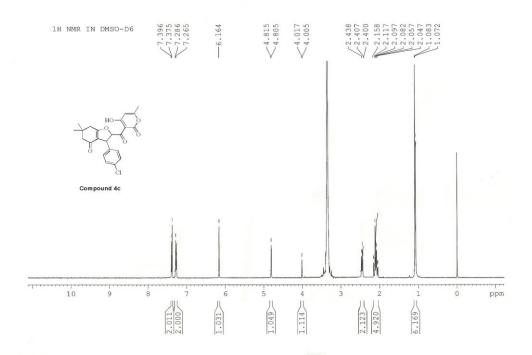
Synthesis of 2-(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-carbonyl)-6,6-dimethyl-3-(3-nitro-phenyl)-3,5,6,7-tetrahydro-2H-benzofuran-4-one (**4l**). A mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2H-pyran-2-one (1.1 mmol), dimedone (1 mmol), 3-nitro benzaldehyde (1 mmol) and pyridine (2 mmol) in acetonitrile (10 mL) was refluxed for 3hr. To the reaction mixture triethylamine (2.1 mmol) was added and the reaction mixture was refluxed for the appropriate time (Table 1). After cooling to room temperature, the solvent was distilled and neutralized with dil. HCl. The solid obtained was filtered washed with water and recrystallized from ethanol to give excellent yields of products (Table 1). Yellow solid; mp 208-210 °C; IR (KBr) (v_{max} / cm⁻¹): 3379, 1730, 1643; ¹H NMR (400 MHz, DMSO-d₆) 1.18 (s, 6H, 2xCH₃), 1.99-2.10 (m, 5H, CH₂ & pyran CH₃), 2.39-2.46 (m, 2H, CH₂), 4.20 (d, 1H, J = 4.8 Hz, furan C-3 proton), 5.12 (d, 1H, J = 4.4 Hz, furan C-2 proton), 6.16 (s, 1H, pyran proton), 7.57-7.61 (m, 2H, ArH), 8.09-8.13 (m, 2H, ArH); ¹³C NMR (400 MHz, DMSO-d₆) 22.2, 27.7, 31.1, 36.2, 45.7, 50.4, 88.4, 99.6, 108.1, 115.3, 123.5, 126.9, 130.1,

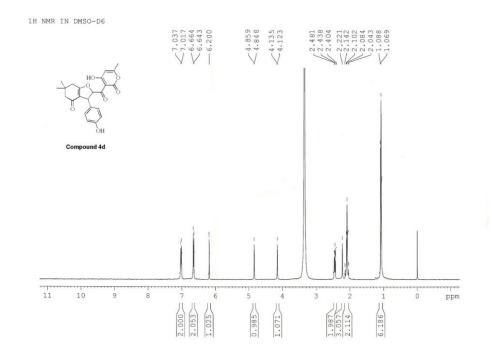
 $136.1,\,143.5,\,146.1,\,160.1,\,162.7,\,175.0,\,184.7,\,192.2,\,198.0.\,\,Anal.\,\,calcd.\,\,for\,\,C_{23}H_{21}NO_8:\,C,\\62.85;\,H,\,4.80;\,N,\,3.18.\,\,Found:\,C,\,62.80;\,H,\,4.75;\,N,\,3.22.$

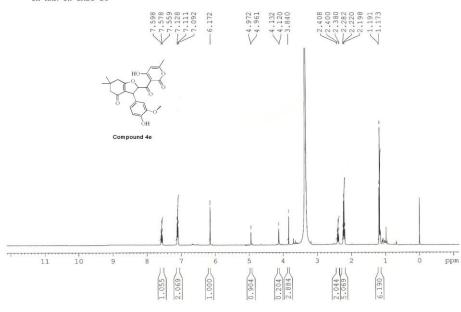




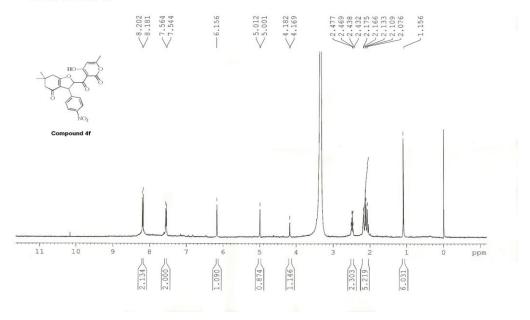




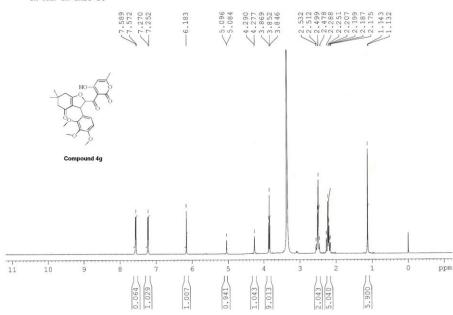


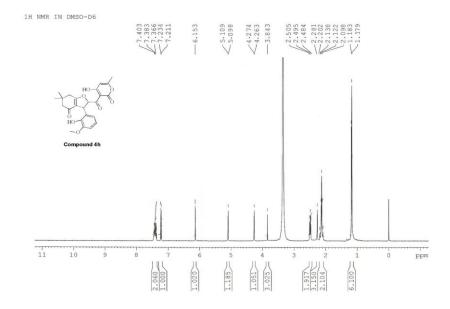


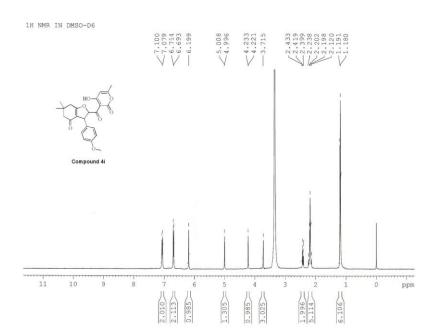




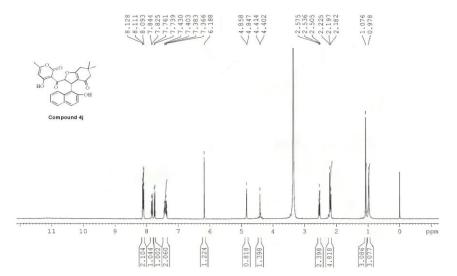


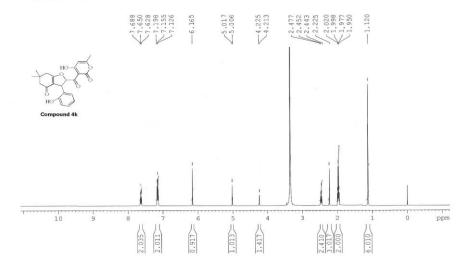




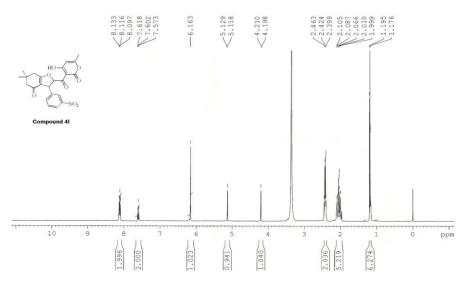


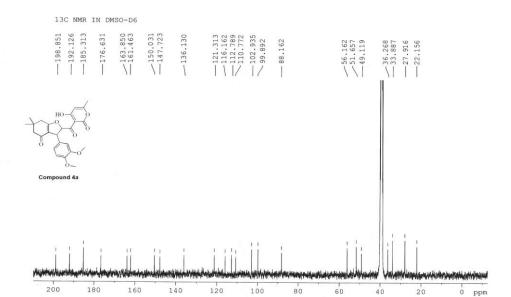


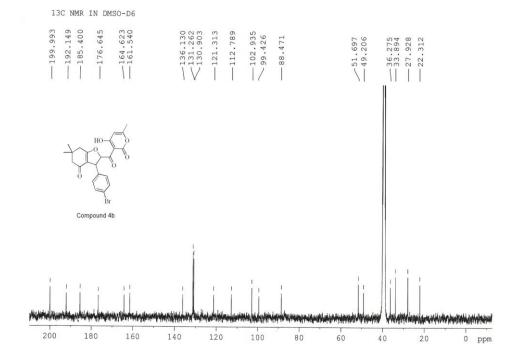


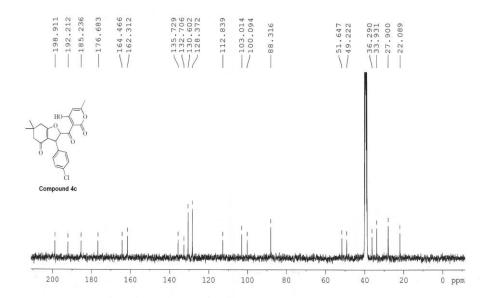


1H NMR IN DMSO-D6

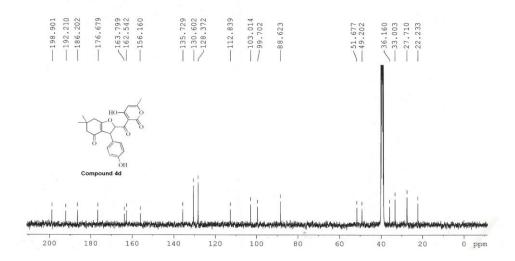


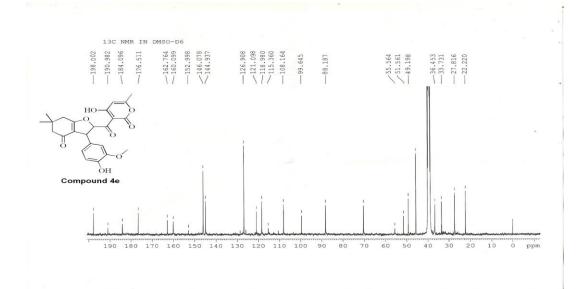


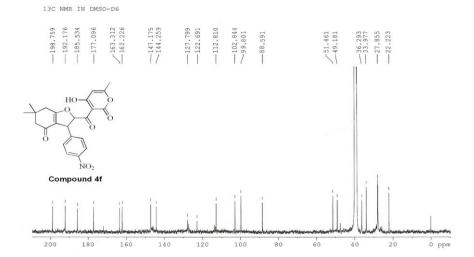


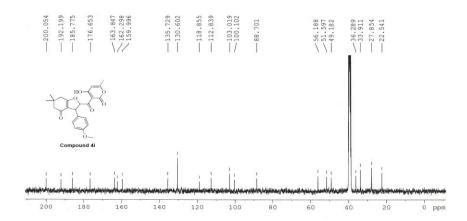












13C NMR IN DMSO-D6

