Supporting information

For

Cascade [4+1] annulation via greener nitrogen ylide in water: Synthesis of bicyclic and tricyclic fused dihydrofuran

Atul Kumar*, Suman Srivastava, Garima Gupta

*Medicinal and Process Chemistry Division, Central Drug Research Institute, Lucknow, India,
Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi

Contents

• General remarks
• General experimental procedure
• Characterization data for compounds
• Copies of $^1$H and $^{13}$C NMR
General remarks
Commercially available N-methylimidazole from Aldrich was used. Progress of reactions was monitored by thin layer chromatography (TLC). NMR spectra were recorded in $d_6$-DMSO or CDCl$_3$ at 300 and 200 MHz (based on availability of instruments) 75 and 50 MHz (for $^{13}$C) respectively on Bruker Avance DPX-300 MHz and Bruker Avance DPX-200 MHz. Chemical shifts are reported in $\delta$ (ppm) relative to TMS ($^1$H) or CDCl$_3$ ($^{13}$C) as internal standards. Integrals are in accordance with assignments; coupling constants are given in Hz. Yields refer to quantities obtained after chromatography.

General experimental procedure

Typical procedure for the preparation of 1-methyl-3-phenacylimidazolium bromide (3):
A solution of 8.2 g (0.1 mol) of N-methylimidazole and 20.0 g (0.1 mol) of phenacylbromide in 300 ml of ether was allowed to stand at room temperature for 16h. The solids, which separated, was collected and then recrystallized from acetonitrile to give 27.0 g (95%) of 1-Methyl-3-phenacylimidazolium bromide as white powder.

Representative one pot procedure for the synthesis of 6a-h, 8a-d, 10a-j:
A mixture of substituted aldehyde (1 mmol), 4-hydroxy coumarin / 5, 5 dimethyl, 1, 3-cyclohexanedione / 1, 3-cyclohexanedione / 4-hydroxy-6-methyl-2$H$-pyran-2-one (1 mmol) and N-methyl imidazole (0.5 mmol) in water (5 ml) was allowed to reflux for 1h at 100ºC. After that 1-methyl-3-phenacylimidazolium bromide (1 mmol) was added and stirring was continued for 1h at 100ºC. After completion of reaction as indicated on TLC, the reaction mixture was extracted with ethyl acetate and water. Organic layer was dried over anhydrous sodium sulphate and concentrated in vacuo. The crude product was chromatographed on a silica gel column with a hexane-ethyl acetate mixture to afford dihydrofuran derivatives 6a-h, 8a-d, and 10a-j in good to excellent yield.
Characterisation data of all the compounds

**N-Methyl-3-phenacylimidazolium bromide (3):**

\[
\text{m.p:153-155°C; 95% as white solid; } ^1\text{H NMR (DMSO-}\text{d}_6, 300 \text{ MHz) } \delta = 9.11 \text{ (s, 1H, CH), 8.07 (d, } J = 7.3 \text{Hz, 2H, ArH), 7.80-7.73 (m, 3H, Ar-H), 7.66 (t, } J = 7.7 \text{Hz, 2H, CH), 6.10 (s, 2H, CH}_2, 3.96 (s, 3H, N-CH}_3); \text{ } ^{13}\text{C NMR (DMSO-}\text{d}_6, 50 \text{ MHz) } \delta = 191.4, 137.7, 134.5, 133.7, 129.1, 128.2, 123.9, 123.3, 55.4, 36.0; \text{ Ana. Calcd for } C_{12}H_{13}N_2OBr: C, 51.26; H, 4.66; N, 9.96. \text{ Found: C, 51.11; H, 4.58; N, 10.02.}
\]

**2-(4-Bromobenzoyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one (6a):**

\[
\text{m.p: 152-155°C; White solid; yield: 95% } ^1\text{H NMR (CDCl}_3, 300\text{MHz) } \delta = 7.72 (d, } J = 8.9 \text{Hz, 2H, Ar-H), 7.63 (d, } J = 7.1 \text{Hz, 2H, ArH), 7.37 (d, } J = 7.3 \text{Hz, 3H, ArH), 7.25 (d, } J = 8.8 \text{Hz, 2H, ArH), 6.14 (s 1H, CH), 5.93 (d, } J = 4.8 \text{Hz, 1H, CH), 4.63 (d, } J = 4.6 \text{Hz, 1H, CH), 2.29 (s, 3H, CH}_3); \text{ } ^{13}\text{C NMR (CDCl}_3, 50\text{MHz) } \delta = 191.5, 170.9, 166.8, 160.7, 139.7, 132.4, 130.5, 129.3, 128.2, 127.5, 102.5, 95.5, 92.2, 48.3, 20.6; \text{ MS (ESI+) } m/z: 411.0 (M+H)^{+}\text{ Ana. Calcd for } C_{21}H_{15}BrO_4: C, 61.33; H, 3.68; \text{ Found: C, 61.38; H, 3.60.}
\]

**2-Benzoyl-3-(4-fluorophenyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one (6b):**

\[
\text{m.p:135-140°C; White solid; yield: 86%; } ^1\text{H NMR (CDCl}_3, 300\text{MHz) } \delta = 7.85 (d, } J = 7.1 \text{Hz, 2H, Ar-H), 7.64 (d, } J = 6.5 \text{Hz, 1H, ArH), 7.51 (d, } J = 7.4 \text{Hz, 2H, ArH), 7.24 (dd, } J = 5.4 \text{Hz, 2H, ArH), 7.08 (m, 2H, ArH), 6.16 (s, 1H, CH), 5.96 (d, } J = 4.9 \text{Hz, 1H, CH), 4.63 (d, } J = 4.7 \text{Hz, 1H, CH), 2.30 (s, 3H, CH}_3); \text{ } ^{13}\text{C NMR (CDCl}_3, 50\text{MHz) } \delta = 192.3, 171.1, 166.9, 164.9, 160.8, 160.0, 135.6, 134.5, 133.2, 129.3, 129.1, 116.4, 116.0, 102.4, 95.6, 92.3, 47.7, 20.6; \text{ MS (ESI+) } m/z: 351.1 (M+H)^{+}\text{ Ana. Calcd for } C_{21}H_{15}FO_4: C, 71.99; H, 4.32; \text{ Found: C, 71.91; H, 4.38.}
\]

**3-(4-Chlorophenyl)-2-(4-methoxybenzoyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one (6c):**

\[
\text{m.p:147-150°C; white solid; yield: 82%; } ^1\text{H NMR (CDCl}_3, 300\text{MHz) } \delta = 7.82 (d, } J = 8.6 \text{Hz, 2H, Ar-H), 7.35 (d, } J = 8.4 \text{Hz, 2H, ArH), 7.20 (d, } J = 8.4 \text{Hz, 2H, ArH), 6.95 (d, } J = 8.9 \text{Hz, 2H, Ar-H), 6.15 (s, 1H, CH), 5.90 (d, } J = 5.0 \text{Hz, 1H, CH), 4.62 (d, } J = 4.8 \text{Hz, 1H, CH), 3.88 (s, 3H, OCH}_3, 2.29 (s, 3H, CH}_3); \text{ } ^{13}\text{C NMR (CDCl}_3, 50\text{MHz) } \delta = 190.6, 171.2, 166.9, 164.6, 160.8, 138.5,
2-(Biphenylcarbonyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one (6d): m.p: 155-160°C; white solid; yield: 91%; 1H NMR (CDCl3, 300 MHz) δ = 7.85 (d, J = 8.3 Hz, 2H, Ar-H), 7.64 (d, J = 8.2 Hz, 2H, Ar-H), 7.56 (d, J = 6.9 Hz, 2H, Ar-H), 7.43-7.34 (m, 3H, Ar-H), 7.29 (s, 2H, Ar-H), 7.18 (t, J = 7.9 Hz, 3H, Ar-H), 6.09 (s, 1H, CH), 5.90 (d, J = 5.0 Hz, 1H, CH), 4.60 (d, J = 4.8 Hz, 1H, CH), 2.23 (s, 3H, CH3); 13C NMR (CDCl3, 50 MHz) δ = 191.8, 171.2, 167.0, 160.8, 147.8, 139.4, 138.4, 134.0, 131.8, 129.7, 129.5, 129.2, 128.8, 127.7, 127.4, 102.3, 95.6, 92.2, 47.9, 20.7; MS (ESI+) m/z: 443.1 (M+H)+ Ana. Calcd for C27H20O4: C, 79.40; H, 4.94; Found: C, 79.45; H, 4.97.

2-(Biphenylcarbonyl)-3-(furan-2-yl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one (6e): m.p: 125-130°C; as white solid; Yield: 90% 1H NMR (CDCl3, 300 MHz) δ = 8.05 (d, J = 8.3 Hz, 2H, Ar-H), 7.74 (d, J = 8.3 Hz, 2H, Ar-H), 7.65 (d, J = 7.0 Hz, 2H, Ar-H), 7.51-7.43 (m, 4H, Ar-H), 6.38 (s, 1H, Ar-H), 6.31 (d, J = 2.8 Hz, 1H, Ar-H), 6.20 (d, J = 4.6 Hz, 1H, CH), 6.14 (s, 1H, CH), 4.86 (d, J = 4.4 Hz, 1H, CH), 2.30 (s, 3H, CH3); 13C NMR (CDCl3, 50 MHz) δ = 191.6, 171.6, 167.0, 160.8, 151.3, 147.2, 142.8, 139.5, 131.8, 129.8, 129.1, 128.7, 127.7, 127.4, 111.0, 108.2, 99.6, 95.7, 88.9, 41.9, 20.7; MS (ESI+) m/z: 399.1 (M+H)+ Ana. Calcd for C25H18O5: C, 75.37; H, 4.55; Found: C, 75.39; H, 4.50.

2-(4-Methoxybenzoyl)-6-methyl-3-(naphthalen-1-yl)-2H-furo[3,2-c]pyran-4(3H)-one (6f): m.p: 160-165°C; White solid; yield: 80%; 1H NMR (CDCl3, 300 MHz) δ = 7.96 (d, J = 8.0 Hz, 1H, Ar-H), 7.86-7.79 (m, 4H, Ar-H), 7.47-7.41 (m, 3H, Ar-H), 7.33 (d, J = 6.9 Hz, 1H, Ar-H), 6.87 (d, J = 8.8 Hz, 2H, Ar-H), 6.12 (s, 1H, CH), 5.90 (s, 1H, CH), 5.73 (s, 1H, CH), 3.84 (s, 3H, OCH3), 2.30 (s, 3H, CH3); 13C NMR (CDCl3, 50 MHz) δ = 190.8, 170.9, 166.5, 164.5, 161.0, 135.9, 134.2, 131.9, 131.3, 129.0, 128.5, 126.6, 125.9, 125.7, 123.2, 114.1, 102.3, 95.5, 91.8, 60.4, 55.6, 42.6, 20.6, 14.2;
MS (ESI+) m/z: 413.1 (M+H)+ Ana. Calcd for C$_{26}$H$_{20}$O$_{5}$: C, 75.72; H, 4.89; Found: C, 75.78; H, 4.85.

2-(4-Bromobenzoyl)-3-ferrocenyl-6-methyl-2$H$-furo[3,2-c]pyran-4(3$H$)-one (6g): m.p: 142-145°C; yellow solid; yield: 89%; $^1$H NMR (CDCl$_3$, 300MHz) \( \delta = 7.95 \) (d, \( J = 8.5Hz, 2H, Ar-H \)), 7.71 (d, \( J = 8.4Hz, 2H, ArH \)), 6.08 (d, \( J = 3.9Hz, 1H, CH \)), 6.01 (s, 1H, CH), 4.67 (d, \( J = 3.7Hz, 1H, CH \)), 4.26 (s, 1H, Fc-H), 4.21-4.12 (m, 8H, Fc-H), 2.27 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) \( \delta = 192.3 \), 169.8, 166.3, 161.0, 132.8, 132.4, 130.7, 129.6, 102.8, 95.4, 91.3, 89.6, 69.6, 69.2, 68.8, 68.5, 67.0, 41.0, 20.6; MS (ESI+) m/z: 519.2 (M+H)+ Ana.

Calcd for C$_{25}$H$_{19}$FeO$_4$Br: C, 57.84; H, 3.69; Found: C, 57.75; H, 3.78.

2-(Biphenylcarbonyl)-3-ferrocenyl-6-methyl-2$H$-furo[3,2-c]pyran-4(3$H$)-one (6h): m.p: 175-180°C; yellow solid; yield: 86%; $^1$H NMR (CDCl$_3$, 300MHz) \( \delta = 8.07 \) (d, \( J = 8.4Hz, 2H, Ar-H \)), 7.70 (d, \( J = 8.3Hz, 2H, ArH \)), 7.64-7.33 (m, 3H, ArH), 6.11 (d, \( J = 3.8Hz, 1H, CH \)), 5.96 (s, 1H, CH), 4.61 (d, \( J = 3.7Hz, 1H, CH \)), 4.22-4.05 (m, 9H, Fc-H), 2.18 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) \( \delta = 192.7 \), 170.2, 166.3, 161.3, 147.0, 139.6, 132.7, 129.9, 129.2, 128.7, 127.7, 127.4, 103.0, 95.6, 91.4, 89.1, 68.9, 68.4, 68.1, 67.7, 66.4, 41.3, 20.6; MS (ESI+) m/z: 516.1 (M+H)+ Ana. Calcd for C$_{31}$H$_{24}$FeO$_4$: C, 72.11; H, 4.68; Found: C, 72.24; H, 4.58.

2-Benzoyl-3-isopropyl-2$H$-furo[3,2-c]chromen-4(3$H$)-one (8a): m.p: 98-100°C; white solid; yield: 92%; $^1$H NMR (CDCl$_3$, 300MHz) \( \delta = 8.04 \) (d, \( J = 7.3Hz, 2H, Ar-H \)), 7.69-7.51 (m, 4H, ArH), 7.39 (d, \( J = 8.3Hz, 1H, ArH \)), 7.30 (t, \( J = 7.3Hz, 2H, ArH \)), 5.94 (d, \( J = 4.6Hz, 1H, CH \)), 3.90 (t, \( J = 3.9Hz, 1H, CH \)), 2.54-2.46 (m, 1H, CH), 1.01-0.98 (m, 6H, 2xCH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) \( \delta = 193.7 \), 166.2, 160.1, 155.0, 134.1, 133.9, 132.6, 129.1, 128.9, 124.0, 122.8, 116.8, 112.0, 103.8, 86.6, 49.0, 29.3, 19.9, 18.1; MS (ESI+) m/z: 335.1 (M+H)+ Ana. Calcd for C$_{21}$H$_{18}$O$_4$: C, 75.43; H, 5.43; Found: C, 75.40; H, 5.49.
2-(4-Methoxybenzoyl)-3-phenyl-2H-furo[3,2-c]chromen-4(3H)-one (8b): m.p : 175-180°C; white solid; yield: 87%; $^1$H NMR (CDCl$_3$, 300MHz) $\delta =$ 7.89 (t, $J =$ 8.9Hz, 3H, Ar-H), 7.62 (t, $J =$ 7.1Hz, 1H, Ar-H), 7.40-7.32 (m, 7H, ArH), 6.97 (d, $J =$ 8.8Hz, 2H, Ar-H), 6.13 (d, $J =$ 4.9Hz, 1H, CH), 4.81(d, $J =$ 4.9Hz, 1H, CH), 3.89 (s, 3H, OCH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) $\delta =$ 190.7, 166.6, 164.6, 159.5, 155.5, 139.8, 133.0, 131.6, 130.2, 129.3, 128.2, 127.7, 126.1, 124.2, 123.3, 117.1, 114.4, 112.3, 105.5, 92.6, 55.7, 49.6; MS (ESI+) $m/z$: 399.1 (M+H)$^+$ Ana. Calcd for C$_{25}$H$_{18}$O$_5$: C, 75.37; H, 4.55; Found: C, 75.45; H, 4.39.

3-(2,4-Dichlorophenyl)-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one (8c): m.p:150-154°C; white solid; yield: 89%; $^1$H NMR (CDCl$_3$, 300MHz) $\delta =$ 7.99 (d, $J =$ 8.8Hz, 2H, Ar-H), 7.76 (d, $J =$ 6.8Hz, 1H, Ar-H), 7.63-7.58 (m, 1H, ArH), 7.42 (d, $J =$ 8.4Hz, 2H, ArH), 7.34-7.18 (m, 3H, ArH), 6.99 (d, $J =$ 8.8Hz, 2H, Ar-H), 6.07 (d, $J =$ 5.1Hz, 1H, CH), 5.45 (d, $J =$ 5.0Hz, 1H, CH), 3.90 (s, 3H, OCH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) $\delta =$ 189.6, 166.8, 164.6, 159.1, 155.4, 135.7, 134.4, 134.3, 133.1, 131.6, 130.4, 130.0, 127.9, 126.5, 124.2, 123.1, 117.1, 114.3, 112.0, 103.9, 90.6, 55.6, 45.3; MS (ESI+) $m/z$: 467.1 (M+H)$^+$ Ana. Calcd for C$_{25}$H$_{16}$Cl$_2$O$_5$: C, 64.26; H, 3.45; Found: C, 64.32; H, 3.22.

3-Ferrocenyl,2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one (8d):

m.p :150-155°C; yellow solid; yield: 88%; $^1$H NMR (CDCl$_3$, 300MHz) $\delta =$ 8.16 (d, $J =$ 8.6Hz, 2H, Ar-H), 7.71 (d, $J =$ 7.6Hz, 1H, Ar-H), 7.58 (t, $J =$ 7.5Hz, 1H, Ar-H), 7.38 (d, $J =$ 8.3Hz, 1H, Ar-H), 7.29 (d, $J =$ 7.9Hz, 1H, Ar-H), 7.06 (d, $J =$ 8.6Hz, 2H, Ar-H), 6.31 (d, $J =$ 3.9Hz, 1H, CH), 4.89 (d, $J =$ 3.9Hz, 1H, CH), 4.36 (s, 1H, Fc-H), 4.23-4.11 (m, 8H, Fc-H), 3.92 (s, 3H, OCH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) $\delta =$ 191.2, 165.1, 164.6,159.8, 155.2, 132.7, 131.8, 127.1, 124.1, 123.0, 117.0, 114.4, 112.4, 106.0, 91.5, 88.7, 68.8, 68.4, 68.3, 66.2, 55.8, 42.1; MS (ESI+) $m/z$: 507.1 (M+H)$^+$ Ana. Calcd for C$_{29}$H$_{22}$FeO$_5$: C, 68.79; H, 4.38; Found: C, 68.85; H, 4.25.
2-Benzoyl-3-(3-nitrophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10a):

m.p: 145-150°C; 88% as white solid; $^1$H NMR (CDCl$_3$, 300 MHz) δ = 8.13 (t, $J = 7.9$ Hz, 2H, ArH), 7.86 (d, $J = 7.4$ Hz, 2H, Ar-H), 7.66-7.45 (m, 5H, Ar-H), 5.85 (d, $J = 5.1$ Hz, 1H, CH), 4.68 (d, $J = 4.4$ Hz, 1H, CH), 2.72 (s, 2H, CH$_2$), 2.34-2.32 (m, 2H, CH$_2$), 2.16-2.12 (m, 2H, CH$_2$); $^{13}$C NMR (CDCl$_3$, 50MHz) δ = 194.2, 192.2, 148.6, 143.1, 134.4, 134.0, 133.2, 129.9, 129.0, 122.6, 122.1, 115.5, 90.9, 47.8, 36.6, 23.8, 21.6; MS (ESI+) m/z: 364.1 (M+H)+

Ana. Calcd for C$_{21}$H$_{17}$NO$_5$: C, 69.41; H, 4.72; N, 3.85; Found: C, 69.26; H, 4.65; N, 3.79.

2-Benzoyl-3-(4-methoxyphenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10b):

m.p: 115-120°C; 85% as white solid; $^1$H NMR (CDCl$_3$, 300 MHz) δ = 7.83 (d, $J = 7.3$ Hz, 2H, ArH), 7.62 (t, $J = 7.1$ Hz, 1H, Ar-H), 7.47 (t, $J = 7.7$ Hz, 2H, ArH), 7.16 (d, $J = 8.5$ Hz, 2H, ArH), 6.89 (d, $J = 8.6$ Hz, 2H, ArH), 5.83 (d, $J = 4.6$ Hz, 1H, CH), 4.36 (d, $J = 3.8$ Hz, 1H, CH), 3.79 (s, 3H, OCH$_3$), 2.70 (s, 2H, CH$_2$), 2.34-2.29 (m, 2H, CH$_2$), 2.12-2.08 (m, 2H, CH$_2$); $^{13}$C NMR (CDCl$_3$, 50MHz) δ = 194.5, 193.1, 177.3, 159.1, 134.2, 133.4, 129.0, 128.5, 116.7, 114.5, 91.8, 55.4, 48.5, 36.9, 29.8, 24.0, 21.8; MS (ESI+) m/z: 349.1 (M+H)+ Ana. Calcd for C$_{22}$H$_{20}$O$_4$: C, 75.84; H, 5.79; Found:C, 75.85; H, 5.70.

2-Benzoyl-3-(4-chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10c):

m.p: 160-165°C; 89% as white solid; $^1$H NMR (CDCl$_3$, 300 MHz) δ = 7.82 (d, $J = 7.6$ Hz, 2H, ArH), 7.63 (t, $J = 7.0$ Hz, 1H, Ar-H), 7.47 (t, $J = 7.2$ Hz, 2H, ArH), 7.31 (d, $J = 7.6$ Hz, 2H, ArH), 7.17 (d, $J = 7.8$ Hz, 2H, ArH), 5.81 (d, $J = 4.6$ Hz, 1H, CH), 4.43 (d, $J = 3.6$ Hz, 1H, CH), 2.69 (s, 2H, CH$_2$), 2.33-2.29 (m, 2H, CH$_2$), 2.14-2.12 (m, 2H, CH$_2$); $^{13}$C NMR (CDCl$_3$, 50MHz) δ = 194.06, 192.48, 177.38, 139.59, 134.13, 133.12, 128.98, 128.80, 128.65, 115.92, 91.12, 48.01, 36.55, 23.70, 21.53; MS (ESI+) m/z: 353.1(M+H)+ Ana. Calcd for C$_{21}$H$_{17}$ClO$_3$: C, 71.49; H, 4.86; Found:C, 71.55; H, 4.81.
2-Benzoyl-3-(biphenyl-4-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10d): m.p: 155-158°C; 82% as white solid; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 7.82 (d, $J$ = 7.4Hz, 2H, ArH), 7.63 (t, $J$ = 7.3Hz, 1H, Ar-H), 7.47-7.32 (m, 7H, ArH), 7.16 (d, $J$ = 8.5Hz, 2H, ArH), 6.96 (d, $J$ = 8.5Hz, 2H, ArH), 5.83 (d, $J$ = 4.6Hz, 1H, CH), 4.37 (d, $J$ = 4.0Hz, 1H, CH), 2.70 (s, 2H, CH$_2$), 2.34-2.30 (m, 2H, CH$_2$), 2.12-2.08 (m, 2H, CH$_2$); $^{13}$C NMR (CDCl$_3$, 50MHz) $\delta$ = 194.4, 193.0, 177.3, 158.3, 137.0, 134.2, 133.6, 133.3, 129.0, 128.7, 128.5, 128.1, 127.6, 116.6, 115.4, 91.8, 70.1, 48.4, 36.8, 23.9, 21.8; MS (ESI+) m/z: 395.2 (M+H)$^+$ Ana. Calcd for C$_{27}$H$_{22}$O$_3$: C, 82.21; H, 5.62; Found: C, 82.25; H, 5.60.

2-Benzoyl-6,6-dimethyl-3-propyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10e): m.p: 94-96°C; White solid; yield: 94%; $^1$H NMR (CDCl$_3$, 300MHz) $\delta$ = 7.93 (d, $J$ = 7.3Hz, 2H, ArH), 7.64 (t, $J$ = 7.3Hz, 1H, Ar-H), 7.52 (t, $J$ = 7.7Hz, 2H, Ar-H), 5.63 (d, $J$ = 4.3Hz, 1H, CH), 3.43 (s, 1H, CH), 2.50-2.33 (m, 2H, CH$_2$), 2.22 (s, 2H, CH$_2$), 1.88-1.63 (m, 2H, CH), 1.42-1.30 (m, 2H, CH$_2$), 1.12 (s, 6H, 2xCH$_3$), 0.95 (t, $J$ = 7.2Hz, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) $\delta$ = 193.4, 194.1, 176.2, 133.8, 128.8, 128.7, 88.8, 51.2, 42.9, 37.5, 35.2, 34.1, 28.9, 28.3, 19.4, 14.1; MS (ESI+) m/z: 313.2(M+H)$^+$ Ana. Calcd for C$_{20}$H$_{24}$O$_3$: C, 76.89; H, 7.74; Found: C, 76.67; H, 7.65.

2-(4-Bromobenzoyl)-3-(2,5-dimethoxyphenyl)-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10f): m.p: 147-150°C; 87% as white solid; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 7.73 (d, $J$ = 8.5Hz, 2H, ArH), 7.59 (d, $J$ = 8.4Hz, 2H, Ar-H), 6.76 (s, 2H, ArH), 6.66 (s, 1H, Ar-H), 5.72 (d, $J$ = 5.1Hz, 1H, CH), 4.81 (d, $J$ = 4.4Hz, 1H, CH), 3.72 (s, 3H, OCH$_3$), 3.55 (s, 3H, OCH$_3$), 2.57-2.43 (m, 2H, CH$_2$), 2.25 (m, 2H, CH$_2$), 1.19 (s, 3H, CH$_3$), 1.15 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) $\delta$ = 193.7, 192.4, 176.8, 153.8, 150.9, 132.8, 132.0, 129.2, 115.0, 113.5, 112.7, 111.9, 90.2, 55.7, 51.3, 43.1, 37.8, 34.3, 29.2, 28.4; MS (ESI+) m/z: 485.1 (M+H)$^+$ Ana. Calcd for C$_{25}$H$_{25}$BrO$_5$: C, 61.86; H, 5.19; Found: C, 61.88; H, 5.11.
2-Benzoyl-6,6-dimethyl-3-(naphthalen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10g): m.p: 175-179°C; 84% as white solid; $^1$H NMR (CDCl$_3$, 300 MHz) δ = 7.94-7.77 (m, 5H, ArH), 7.59-7.32 (m, 7H, Ar-H), 5.86 (s, 1H, CH), 5.45 (s, 1H, CH), 2.56 (s, 2H, CH$_2$), 2.27 (m, 2H, CH$_2$), 1.22 (s, 3H, CH$_3$), 1.17 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) δ = 193.7, 193.0, 176.0, 134.2, 133.8, 131.3, 129.4, 128.9, 128.3, 126.4, 125.9, 125.7, 123.4, 115.2, 91.5, 51.4, 37.9, 34.4, 29.2, 28.7; MS (ESI+) m/z: 397.1; (M+H)$^+$ Ana. Calcd for C$_{27}$H$_{24}$O$_3$: C, 81.79; H, 6.10; Found: C, 81.81; H, 6.14.

2-(4-Bromobenzoyl)-6,6-dimethyl-3-(thiophen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10h): m.p: 145-150°C; White solid; Yield, 86% $^1$H NMR (CDCl$_3$, 300 MHz) δ = 7.79 (d, $J$ = 8.5Hz, 2H, ArH), 7.65 (d, $J$ = 8.4Hz, 2H, Ar-H), 7.23 (d, $J$ = 4.8Hz, 1H, ArH), 6.98 (dd, $J$ = 3.4, 4.5Hz, 2H, ArH), 5.84 (d, $J$ = 4.2Hz, 1H, CH), 4.78 (s, 1H, CH), 2.61-2.46 (m, 2H, CH$_2$), 2.24 (m, 2H, CH$_2$), 1.19 (s, 3H, CH$_3$), 1.15 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) δ = 193.4, 191.6, 176.4, 144.7, 132.4, 132.0, 130.5, 129.8, 127.4, 125.3, 124.9, 114.5, 91.4, 51.2, 43.8, 37.7, 34.3, 29.2, 28.2; MS (ESI+) m/z: 431.0 (M+H)$^+$ Ana. Calcd for C$_{21}$H$_{19}$BrO$_3$S: C, 58.47; H, 4.44; Found: C, 58.41; H, 4.46.

2-Benzoyl-3-ferrocenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10i): m.p: 120-125°C; 88% as yellow solid; $^1$H NMR (CDCl$_3$, 300 MHz) δ = 8.08 (d, $J$ = 7.4Hz, 2H, ArH), 7.67-7.52 (m, 3H, Ar-H), 6.07 (d, $J$ = 3.6Hz, 1H, CH), 4.47 (d, $J$ = 3.3Hz, 1H, CH), 4.26 (s, 1H, Fe-H), 4.27-4.10 (m, 8H, Fe-H), 2.58-2.56 (m, 2H, CH$_2$), 2.43-2.26 (m, 2H, CH$_2$), 2.10-2.01(m, 2H, CH$_2$); $^{13}$C NMR (CDCl$_3$, 50MHz) δ = 194.5, 193.8, 176.1, 134.4, 134.1, 129.2, 129.0, 117.0, 90.5, 90.1, 68.7, 68.0, 66.6, 41.4, 37.0, 24.0, 21.6; MS (ESI+) m/z: 427.1 (M+H)$^+$ Ana. Calcd for C$_{25}$H$_{22}$FeO$_3$: C, 70.44; H, 5.20; Found: C, 70.24; H, 5.29.
6,6-Dimethyl-3-ferrocenyl-2-(4-methoxybenzoyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10j): m.p: 124-128°C; yellow solid; yield: 87%; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 8.07 (d, $J = 8.8$ Hz, 2H, ArH), 7.03 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.05 (d, $J = 3.7$ Hz, 1H, CH), 4.43 (d, $J = 2.6$ Hz, 1H, CH), 4.20-4.09 (m, 9H, Fc-H), 3.90 (s, 3H, OCH$_3$), 2.50-2.36 (m, 2H, CH$_2$), 2.24 (s, 2H), 1.15 (s, 3H, CH$_3$), 1.12 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 50MHz) $\delta$ = 193.9, 192.1, 175.5, 164.3, 131.5, 127.2, 115.4, 114.3, 91.2, 90.5, 68.7, 67.9, 67.8, 66.7, 55.7, 51.5, 41.4, 37.9, 34.1, 29.1, 28.3; MS (ESI+) $m/z$: 485.0 (M+H$^+$) Ana.

Calcd. for C$_{28}$H$_{28}$FeO$_4$: C, 69.43; H, 5.83; Found: C, 69.23; H, 5.78;

$^1$H and $^{13}$C spectra of all the compounds:
Fig. 1: $^1$H spectra of N-Methyl-3-phenacylimidazolium bromide:

Current Data Parameters

NAME  imidazole ne
EXPNO  40
PROCNO  1

F2 – Acquisition Param
Data  20111291
Time  12:57
INSTRUM  spect
PROBNO  5 mm QNP
PULPROG  zgX
TD  65536
SOLVENT  DMS
NS  8
DS  8
SWH  6188.119
FINRES  6.064421
AQ  5.293587
R0  80.300 us
DE  6.00 use
TE  300.5 K
TD1  1.00000000
TDO  1

%%%%%%%%%%%%%%%% CHANNEL
NUC1  $^1$H
P1  11.80 use
PL1  -1.00 dB
SF01  300.121853

F2 – Processing param
SI  32798
SP  300.130000
WOW  EM
DSB  0
LB  0.30 Hz
GB  0
PC  1.00
Fig 2: $^{13}$C spectra of N-Methyl-3-phenacylimidazolium bromide:
Fig 3: $^1$H spectra of 2-(4-bromobenzoyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one:
Fig 4: $^{13}$C spectra of 2-(4-bromobenzoyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one:
Fig 5: $^1$H spectra of 2-benzoyl-3-(4-fluorophenyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-
Fig 6: 13C spectra of 2-benzoyl-3-(4-fluorophenyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-
Fig 7: $^1$H spectra of 3-(4-chlorophenyl)-2-(4-methoxybenzoyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one
Fig 8. 13C spectra of 3-(4-chlorophenyl)-2-(4-methoxybenzoyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one.
Fig 9: $^1$H spectra of 2-(biphenylcarbonyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one:
Fig 10: $^{13}$C spectra of 2-(biphenylcarbonyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one
Fig 11: $^1$H spectra of 2-(biphenylcarbonyl)-3-(furan-2-yl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one
Fig 12: $^{13}$C spectra of (2-(biphenylcarbonyl)-3-(furan-2-yl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one:
Fig. 13: $^1$H spectra of 2-(4-methoxybenzoyl)-6-methyl-3-(naphthalen-1-yl)-2H-furo[3,2-c]pyran-4(3H)-one.
Fig 14: $^{13}$C spectra of 2-(4-methoxybenzoyl)-6-methyl-3-(naphthalen-1-yl)-2H-furo[3,2-c]pyran-4(3H)-one:
Fig 15: $^1$H spectra of 2-(4-bromobenzoyl)-3-ferrocenyl-6-methyl- 2H-furo[3,2-c]pyran-4(3H)-one
Fig 16: $^{13}$C spectra of 2-(4-bromobenzoyl)-3-ferrocenyl-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one
Fig 17: $^1$H spectra of 2-(biphenylcarbonyl)-3-ferrocenyl-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one
Fig. 18: $^{13}$C spectra of 2-(biphenylcarbonyl)-3-ferrocenyl-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one.
Fig 19: $^1$H spectra of 2-benzoyl-3-isopropyl-2H-furo[3,2-c]chromen-4(3H)-one:
Fig 20: $^{13}$C spectra of 2-benzoyl-3-isopropyl-2H-furo[3,2-c]chromen-4(3H)-one:
Fig 21: $^1$H spectra of 2-(4-methoxybenzoyl)-3-phenyl-2H-furo[3,2-c]chromen-4(3H)-one
Fig 22: $^{13}$C spectra of 2-(4-methoxybenzoyl)-3-phenyl-2H-furo[3,2-c]chromen-4(3H)-one
Fig 23: $^1$H spectra of 3-(2,4-dichlorophenyl)-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one:
Fig 24: $^{13}$C spectra of 3-(2,4-dichlorophenyl)-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one
Fig 25: COSY spectra of 3-(2,4-dichlorophenyl)-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one:
Fig. 27: HMBC spectra of 3-(2,4-dichlorophenyl)-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one.

Electronic Supplementary Material (ESI) for Green Chemistry

This journal is © The Royal Society of Chemistry 2012
Fig 28: $^1$H spectra of 3-ferroceny1-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one:
Fig 29: $^{13}$C spectra of 3-ferrocenyl-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one:
Fig 30: $^1$H spectra of 2-benzoyl-3-(3-nitrophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 31: $^{13}$C spectra of 2-benzoyl-3-(3-nitrophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 32. $^1$H spectra of 2-benzoyl-3-(4-methoxyphenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 33: $^{13}$C spectra of 2-benzoyl-3-(4-methoxyphenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 34: 1H spectra of 2-benzoyl-3-(4-chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one.
Fig 35: $^{13}$C spectra of 2-benzoyl-3-(4-chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 36: 1H spectra of 2-benzoyl-3-(4-biphenyl-4-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 37: $^{13}$C spectra of 2-benzoyl-3-(biphenyl-4-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-
Fig 38: $^1$H spectra of 2-benzoyl-6,6-dimethyl-3-propyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 39: $^{13}$C spectra of 2-benzoyl-6,6-dimethyl-3-propyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 40: 1H spectra of 2-(4-bromobenzoyl)-3-(2,5-dimethoxyphenyl)-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one.

Current Data Parameters
NAME: SUMAN IMIDA
EXPN: 1
PROCNO: 1

F2 – Acquisition Parameters
Date: 20130607
Time: 13:03
INSTRUM: spect
PROBHD: 1 mm QNP 1H
E: 90°
TD: 6000000 Hz
SWH: 6136119 Hz
FIDRES: 0.056429 H
AQ: 5.286587 sec
R: 101
DW: 80000 usec
DE: 0.0 usec
TE: 300.0 K
D1: 1.000000 sec
D2: 1.0

– CHANNEL 1
N: 0.1
I: 1H
P: 11.0 usec
PL1: -1.00 dB
SPO1: 300.1318534 H

F2 – Processing parameters
S: 1024
S: 32768
S: 200.1300000 MHz
W: 0.0
L: 0.0 Hz
G: 0
P: 1.0

Electronic Supplementary Material (ESI) for Green Chemistry
This journal is © The Royal Society of Chemistry 2012
Fig 41: $^{13}$C spectra of 2-(4-bromobenzoyl)-3-(2,5-dimethoxyphenyl)-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 42: $^1$H spectra of 2-benzoyl-6,6-dimethyl-3-(naphthalen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 43: $^{13}$C spectra of 2-benzoyl-6,6-dimethyl-3-(naphthalen-2-yl)-2,3,6,7-
tetrahydronaphtho[4,3-b]furan-4(5H)-one:

Electronic Supplementary Material (ESI) for Green Chemistry
This journal is © The Royal Society of Chemistry 2012
Fig 44: $^1$H spectra of 2-(4-bromobenzoyl)-6,6-dimethyl-3-(thiophen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one.
Fig 45: $^{13}$C spectra of 2-(4-bromobenzoyl)-6,6-dimethyl-3-(thiophen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 46: $^1$H spectra of 2-benzoyl-3-ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one:
Fig 47: 13C spectra of 2-benzoyl-3-ferroceny1 2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-
Fig 48: $^1$H spectra of 6,6-dimethyl-3-ferrocenyl-2-(4-methoxybenzoyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one:
Fig 49: $^{13}$C spectra of 6,6-dimethyl, 3-ferrocenyl 2-(4-methoxybenzoyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one.