

Supporting Information

A highly efficient ultrasound-promoted synthesis of 2,3-disubstituted benzo[*b*]furans *via* intramolecular C-C bond formation in ionic liquid[bmim]BF₄ at room temperature

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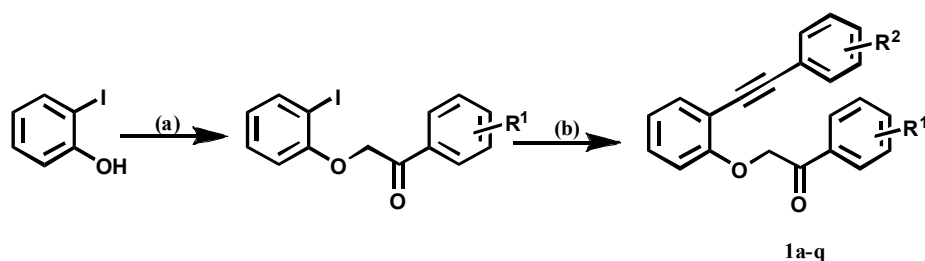
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General Considerations

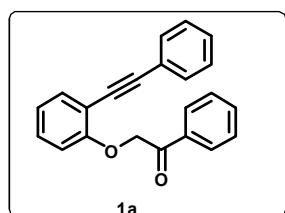
Reagent grade solvents were used for extraction and column chromatography. All the reagents and chemicals were purchased from Sigma–Aldrich and Merck and were used directly without further purification. The progress of reactions was checked by analytical thin-layer chromatography (TLC, Merck silica gel 60 F-254 plates). The plates were visualized first with UV illumination followed by iodine. Column chromatography was performed using silica gel (100-200 mesh). The solvent compositions reported for all chromatographic separations are on a volume/volume (v/v) basis. ^1H -NMR spectra were recorded at either 200 or 300 MHz and are reported in parts per million (ppm) on the δ scale relative to tetramethylsilane as an internal standard. ^{13}C -NMR spectra were recorded at either 50 or 75 MHz and are reported in parts per million (ppm) on the δ scale relative to CDCl_3 (δ 77.00). Mass spectra were obtained using JEOL SX-102 (ESI) instrument. Melting points were determined on a Mel Temp II melting point apparatus and are uncorrected.

Experimental procedure

General procedure for the synthesis of compounds 1a-q



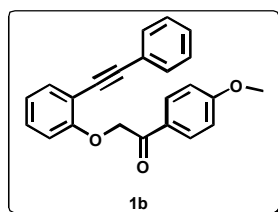
Scheme 1 (a) K_2CO_3 , dry acetone, phenacyl bromide derivatives, reflux, 2-3hr (b) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , Et_3N , room temperature, 3 hr.



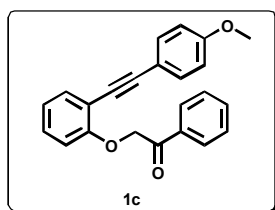
1-phenyl 2-(2-(phenylethynyl) phenoxy) ethanone (**1a**)¹

To a solution of 2-(2-iodophenoxy)-1-phenylethanone (3.40g, 10mmole) in 20 ml of Et_3N $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (2 mole %) and CuI (1mole %) were added and reaction mixture was stirred at room temperature under N_2 atmosphere for 10 minutes. Phenyl acetylene (1.3 ml, 12 mmole)

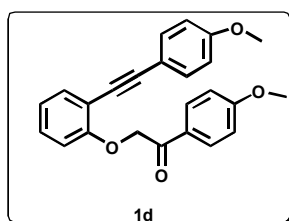
was then added drop wise and stirring was continued at rt for 3 hr. Progress of the reaction was monitored by TLC. After completion, it was quenched with aqueous NH_4Cl solution, extracted with EtOAc, dried over Na_2SO_4 and concentrated under reduced pressure to afford dark brown solid. The crude product was purified by silica gel column chromatography (EtOAc/hexane) to afford the pure compound **1a** as white solid (2.4 g, (80%), mp 65-66 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 8.11-8.08 (d, $J=7.2$ Hz, 2H), 7.60-7.46 (m, 6H), 7.34-7.32 (m, 4H), 7.03-6.98 (t, $J=6.8$ Hz, 1H), 6.91-6.88 (d, $J=8.3$ Hz, 1H), 5.36 (s, CH_2 , 2H). ESI-MS: (m/z) = 313 [$\text{M}+\text{H}$]. $^+$



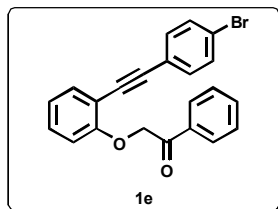
1-(4-methoxyphenyl)-2-(2-(phenylethynyl)phenoxy) ethanone (**1b**). Yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 8.13-8.10 (d, $J=8.8$ Hz, 2H), 7.54-7.46 (m, 3H), 7.34-7.25 (m, 4H), 7.02-6.97 (t, $J=7.0$ Hz, 1H), 6.93-6.88 (m, 3H), 5.28 (s, CH_2 , 2H), 3.82 (s, OCH_3 , 3H). ESI-MS: (m/z) = 343 [$\text{M}+\text{H}$]. $^+$



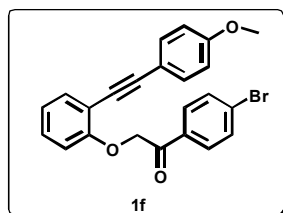
2-(2-(4-methoxyphenyl) ethynyl) phenoxy)-1-phenyl ethanone (**1c**). Yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 8.13-8.10 (d, $J=8.8$ Hz, 2H), 7.54-7.46 (m, 3H), 7.34-7.25 (m, 4H), 7.02-6.97 (t, $J=7.0$ Hz, 1H), 6.93-6.88 (m, 3H), 5.28 (s, CH_2 , 2H), 3.82 (s, OCH_3 , 3H). ESI-MS: (m/z) = 343 [$\text{M}+\text{H}$]. $^+$



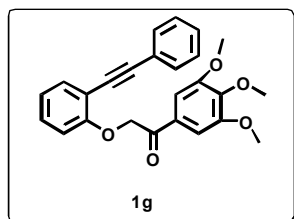
1-(4-methoxyphenyl)-2-(2-((4-methoxyphenyl) ethynyl)phenoxy) ethanone (**1d**). White solid: mp 98-99 °C; ¹H NMR(300 MHz, CDCl₃) δ 8.13-8.10 (d, J=8.8Hz, 2H), 7.51-7.49 (d, J=7.2 Hz, 1H), 7.42-7.39 (d, J=8.7 Hz, 2H), 7.26-7.24 (d, J=7.2 Hz, 1H), 7.01-6.85 (m, 6H), 5.27 (s, CH₂, 2H), 3.84 (s, OCH₃, 6H). ESI-MS: (m/z) = 373 [M+H].⁺



2-(2-((4-bromophenyl)ethynyl)phenoxy)-1-phenyl ethanone (**1e**). White solid: mp 74-75 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.00-7.97 (d, J=6.9 Hz, 2H), 7.60-7.58 (d, J=7.3 Hz, 2H), 7.54-7.52 (d, J=6.1 Hz, 1H), 7.44-7.29 (m, 6H), 7.02-6.99 (d, J=7.4 Hz, 1H), 6.91-6.88 (d, J=7.9 Hz, 1H), 5.27 (s, CH₂, 2H). ESI-MS: (m/z) =391 [M+H].⁺

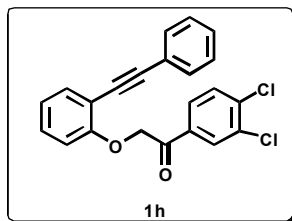


1-(4-bromophenyl)-2-(2-((4-methoxyphenyl)ethynyl)phenoxy) ethanone (**1f**). Colourless oil; ¹H NMR (300 MHz, CDCl₃) δ 7.99-7.97 (d, J=6.9 Hz, 2H), 7.60-7.57 (d, J=8.6 Hz, 2H), 7.52-7.50 (d, J=6.0 Hz, 1H), 7.37-7.35 (d, J=6.9 Hz, 2H), 7.30-7.24 (m, 1H), 7.03-6.97 (m, 1H), 6.89-6.87 (d, J=6.9 Hz, 3H), 5.28 (s, CH₂, 2H), 3.85 (s, OCH₃, 3H). ESI-MS: (m/z) = 421 [M+H].⁺

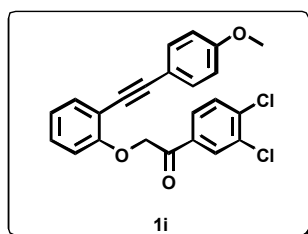


2-(2-(phenylethynyl) phenoxy)-1-(3,4,5-trimethoxyphenyl) ethanone (**1g**). White solid: mp 91-92 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.54-7.52 (d, J=7.5 Hz, 1H), 7.45-7.41 (m, 2H), 7.36-7.34 (d, J=6.6 Hz, 2H), 7.33-7.29 (m, 4H), 7.03-6.98 (t, J=7.5 Hz, 1H), 6.92-6.89 (d,

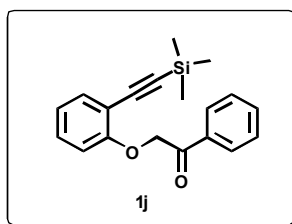
J=8.2 Hz, 1H), 5.29 (s, CH₂, 2H), 3.91 (s, OCH₃, 3H), 3.88 (s, OCH₃, 6H). ESI-MS: (m/z) = 403 [M+H].⁺



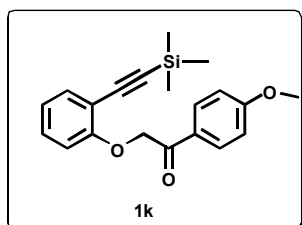
1-(3,4-dichlorophenyl)-2-(2-(phenylethynyl)phenoxy) ethanone(**1h**). Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.73 (s, 2H), 7.49-7.43 (m, 2H), 7.30-7.22 (m, 2H), 7.20-7.16 (m, 2H), 6.91-6.87 (t, J=6.9 Hz, 2H), 6.75-6.72 (d, J=8.2 Hz, 2H), 4.73 (s, CH₂, 2H). ESI-MS: (m/z) = 381[M+H].⁺



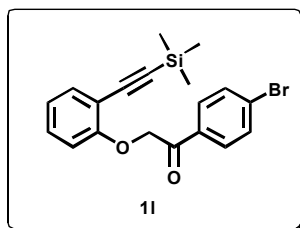
1-(3,4-dichlorophenyl)-2-(2-((4-methoxyphenyl)ethynyl)phenoxy) ethanone (**1i**). Yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.77 (s, 1H), 7.50-7.43 (m, 4H), 7.30-7.28 (d, J=8.2 Hz, 1H), 7.22 (s, 1H), 6.94-6.86 (m, 3H), 6.77-6.74 (d, J=8.2 Hz, 1H), 4.77 (s, CH₂, 2H), 3.80 (s, OCH₃, 3H). ESI-MS: (m/z) = 411 [M+H].⁺



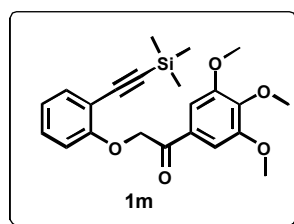
1-phenyl-2-(2-((trimethylsilyl)ethynyl)phenoxy) ethanone (**1j**). Colourless oil; ¹H NMR (300 MHz, CDCl₃) δ 8.07 (s, 2H), 7.62-7.50 (m, 3H), 7.25-6.90 (m, 2H), 6.87-6.76 (m, 2H), 5.32 (s, CH₂, 2H), 0.23 (s, CH₃, 9H). ESI-MS: (m/z) = 237 [M+H].⁺



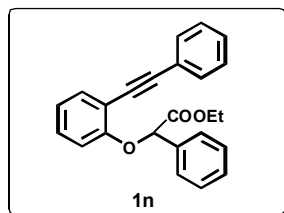
1-(4-methoxyphenyl)-2-(2-((trimethylsilyl)ethynyl)phenoxy) ethanone (**1l**). White solid: mp 79-80 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.10-8.07 (d, J=8.9 Hz, 2H), 7.46-7.744 (d, J=7.6 Hz, 1H), 7.27-7.24 (d, J=7.6 Hz, 1H), 6.98-6.95 (d, 8.9 Hz, 3H), 6.87-6.84 (m, J=8.3 Hz, 1H), 5.25 (s, CH₂, 2H), 3.89 (s, OCH₃, 3H), 0.24 (s, CH₃, 9H). ESI-MS: (m/z) = 267 [M+H].⁺



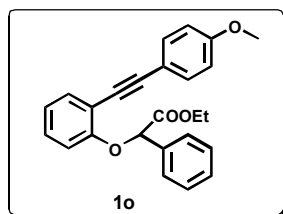
1-(4-bromophenyl)-2-(2-((trimethylsilyl)ethynyl)phenoxy) ethanone (**1l**). Off white solid: mp 85-86 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.98-7.95 (d, J=8.4 Hz, 2H), 7.65-7.63 (d, J=8.5 Hz, 2H), 7.47-7.45 (d, J=7.6 Hz, 1H), 7.29-7.24 (m, 1H), 6.99-6.94 (t, J=7.5 Hz, 1H), 6.87-6.84 (d, J=8.3 Hz, 1H), 5.24 (s, CH₂, 2H), 0.23 (s, CH₃, 9H). ESI-MS: (m/z) = 315 [M+H].⁺



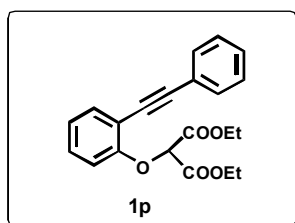
1-(3,4,5-trimethoxyphenyl)-2-(2-((trimethylsilyl)ethynyl)phenoxy) ethanone (**1m**). Light yellow solid: mp 74-76 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.48-7.45 (d, J=7.2 Hz, 1H), 7.38 (s, 2H), 7.28-7.23 (t, J=7.6 Hz, 1H), 6.97-7.92 (t, J=7.4 Hz, 1H), 6.86-6.84 (d, J=8.4 Hz, 1H), 5.24 (s, CH₂, 2H), 3.93 (s, OCH₃, 9H), 0.21 (s, CH₃, 9H). ESI-MS: (m/z) = 327 [M+H].⁺



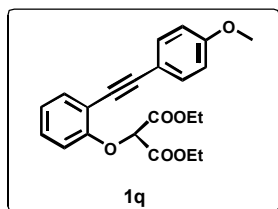
Ethyl 2-phenyl-2-(2-(phenylethynyl)phenoxy) acetate (**1n**). Yellow solid: mp 70-71 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.74-7.72 (d, J=7.4 Hz, 2H), 7.56-7.53 (d, J=7.5 Hz, 3H), 7.41-7.35 (m, 7H), 7.04-6.99 (t, J=7.5 Hz, 1H), 6.92-6.89 (d, J=8.4 Hz, 1H), 5.78 (s, CH, 1H), 4.24-4.17 (m, CH₂, 2H), 1.23-1.18 (t, J=7.1 Hz, CH₃, 3H). ESI-MS: (m/z) = 357 [M+H].⁺



Ethyl 2-(2-((4-methoxyphenyl)ethynyl)phenoxy)-2-phenyl acetate (**1o**). Off white solid: mp 76-77 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.73-7.71 (d, J=5.5 Hz, 2H), 7.53-7.44 (m, 6H), 7.39-7.28 (m, 1H), 7.03-7.01 (m, 1H), 6.90-6.88 (d, J=7.4 Hz, 3H), 5.78 (s, CH, 1H), 4.24-4.17 (m, CH₂, 2H), 3.86 (s, OCH₃, 3H), 1.23-1.20 (t, J=5.5 Hz, CH₃, 3H). ESI-MS: (m/z) = 387 [M+H].⁺

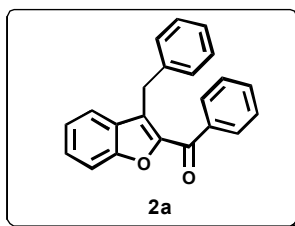


Diethyl 2-(2-(phenylethynyl)phenoxy) malonate (**1p**). Brown solid: mp 60-61 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.58-7.55 (m, 3H), 7.36-7.10 (m, 4H), 7.08-7.02 (m, 2H), 5.40 (s, CH, 1H), 4.35-4.28 (m, CH₂, 4H), 1.31-1.26 (t, J=7.4 Hz, CH₃, 6H). ESI-MS: (m/z) = 353 [M+H].⁺

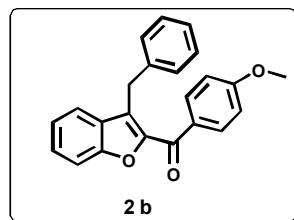


Diethyl 2-(2-((4-methoxyphenyl)ethynyl)phenoxy) malonate (**1q**). Brown solid: mp 69-71 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.54-7.50 (m, 3H), 7.26-7.24 (d, J=6.6 Hz, 1H), 7.10-7.02 (m, 2H), 6.91-6.88 (d, J=8.7 Hz, 2H), 5.41 (s, CH, 1H), 4.33-4.26 (m, CH₂, 4H), 3.85 (s, OCH₃, 3H), 1.32-1.27 (t, J=7.1 Hz, CH₃, 6H). ESI-MS: (m/z) = 383 [M+H].⁺

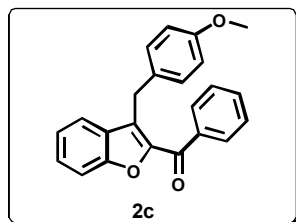
Characterization data of 2,3-disubstituted benzo[*b*]furans 2a-q



(3-Benzylbenzofuran-2-yl) phenyl methanone (**2a**). White solid: mp 110-111 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.15-8.13 (d, J=7.1Hz, 2H), δ 7.66-7.48 (m, 6H), 7.40-7.38 (d, J=7.1Hz, 2H), 7.31-7.18 (m, 4H), 4.57 (s, CH₂, 2H). ¹³C NMR (50 MHz, CDCl₃) δ 185.9, 154.5, 148.4, 139.7, 137.8, 132.8, 129.2, 128.8, 128.6, 128.5, 128.4, 128.2, 126.4, 123.6, 122.2, 112.4, 30.5. IR (KBr, cm⁻¹): 1641, 1550, 1262, 1218, 1018, 769. ESI-MS: (m/z) = 313 [M+H].⁺

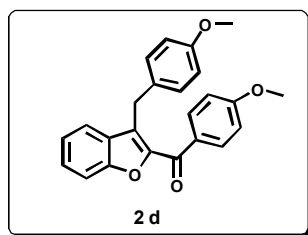


(3-Benzylbenzofuran-2-yl) (4-methoxyphenyl) methanone (**2b**). White solid: mp 78-80 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.22-8.19 (d, J=8.8 Hz, 2H), 7.59-7.56 (d, J=9.2 Hz, 2H), 7.49-7.44 (t, J=7.8Hz, 1H), 7.40-7.38 (d, J=7.0 Hz, 2H), 7.31-7.26 (t, J=7.6 Hz, 4H), 7.05-7.02 (d, J=8.8 Hz, 2H), 4.56 (s, CH₂, 2H), 3.93 (s, OCH₃, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 184.2, 163.5, 154.3, 148.8, 139.3, 132.5, 128.8, 128.5, 127.9, 126.4, 123.5, 122.1, 113.7, 112.2, 55.5, 30.5. IR (KBr, cm⁻¹): 1635, 1218, 1166, 1068, 769. ESI-MS: (m/z) = 343 [M+H].⁺

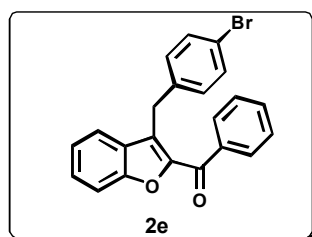


(3-(4-Methoxybenzyl) benzofuran-2-yl)phenyl methanone (**2c**). White solid: mp 115-116 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.15-8.13 (d, J=7.2 Hz, 2H), 7.64-7.45 (m, 6H), 7.33-7.26 (m, 3H), 6.84-6.82 (d, J=8.4 Hz, 2H), 4.50 (s, CH₂, 2H), 3.78 (s, OCH₃, 3H). ¹³C NMR (50 MHz,

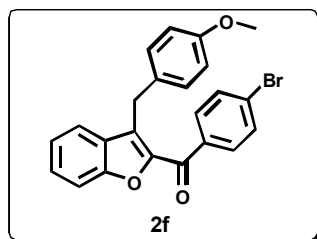
CDCl_3), δ 185.8, 158.1, 154.5, 148.2, 137.7, 132.7, 131.2, 130.9, 129.8, 128.3, 128.0, 123.4, 122.1, 113.9, 112.3, 55.2, 31.9, 29.7, 22.7. IR (KBr, cm^{-1}): 1642, 1511, 1217, 1065, 766. ESI-MS: (m/z) = 343 $[\text{M}+\text{H}]^+$.



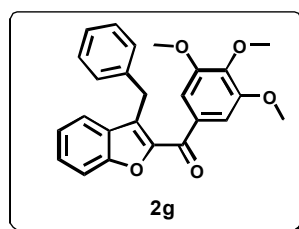
(3-(4-Methoxybenzyl)benzofuran-2-yl)(4-methoxyphenyl) methanone (**2d**). White solid: mp 101-102 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 8.21-8.19 (d, $J=8.8$ Hz, 2H), 7.70-7.55 (t, $J=7.1$ Hz, 2H), 7.49-7.44 (t, $J=7.4$ Hz, 1H), 7.33-7.25 (m, 3H), 7.05-7.02 (d, $J=8.8$ Hz, 2H), 6.84-6.81 (d, $J=8.5$ Hz, 2H), 4.49 (s, CH_2 , 2H), 3.93 (s, OCH_3 , 3H), 3.77 (s, OCH_3 , 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 184.2, 163.5, 158.1, 154.3, 148.6, 132.4, 131.4, 129.7, 127.8, 123.4, 122.1, 113.9, 112.2, 55.5, 55.2, 29.6. IR (KBr, cm^{-1}): 1727, 1597, 1257, 1029, 769. ESI-MS: (m/z) = 373 $[\text{M}+\text{H}]^+$.



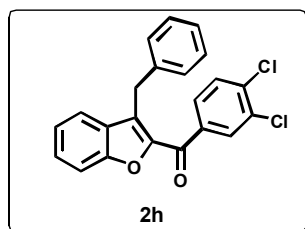
(3-(4-bromobenzyl)benzofuran-2-yl)(phenyl) methanone (**2e**). White solid: mp 102-103 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 8.05-8.02 (d, $J=8.5$ Hz, 2H), 7.71-7.68 (d, $J=8.5$ Hz, 2H), 7.62-7.47 (m, 3H), 7.40-7.38 (d, $J=7.0$ Hz, 2H), 7.32-7.22 (m, 4H), 4.58 (s, CH_2 , 2H). ^{13}C NMR (50 MHz, CDCl_3) δ 184.5, 154.5, 148.1, 139.0, 136.4, 131.7, 131.5, 128.7, 128.6, 128.4, 126.5, 123.7, 122.2, 112.3, 30.5. IR (KBr, cm^{-1}): 1636, 1553, 1288, 1070, 746. ESI-MS: (m/z) = 391 $[\text{M}+\text{H}]^+$.



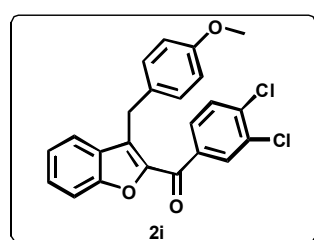
(4-Bromophenyl) (3-(4-methoxy benzyl) benzofuran- 2-yl) methanone (**2f**). White solid: mp 128-130 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.04- 8.01 (d, J=8.5 Hz, 2H), 7.71-7.68 (d, J=8.5 Hz, 2H), 7.62-7.47 (m, 3H), 7.32-7.30 (d, J=8.4 Hz, 3H), 6.85-6.82 (d, J=8.5 Hz, 2H), 4.50 (s, CH₂, 2H), 3.78 (s, OCH₃, 3H). ¹³C NMR (50MHz, CDCl₃) δ 184.5, 158.2, 154.5, 147.9, 136.4, 131.6, 131.4, 131.1, 130.3, 129.7, 128.4, 123.6, 122.2, 114.0, 112.3, 55.2, 29.7. IR (KBr, cm⁻¹): 1641, 1217, 1031, 928, 767. ESI-MS: (m/z) = 421 [M+H].⁺



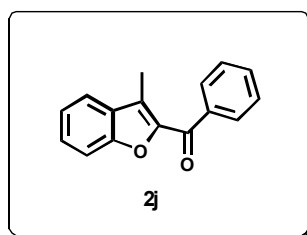
(3-Benzylbenzofuran-2-yl) (3,4,5-trimethoxyphenyl) methanone (**2g**). White solid: mp 103-104 °C; ¹H NMR (300MHz, CDCl₃) δ 7.63-7.45 (m, 5H), 7.40-7.38 (d, J=7.0 Hz, 2H), 7.32-7.27 (m, 4H) 4.5 (s, CH₂, 2H), 3.98 (s, OCH₃, 3H), 3.93 (s, OCH₃, 6H). ¹³C NMR (50 MHz, CDCl₃) δ 184.4, 154.4, 152.9, 148.4, 142.5, 139.1, 132.6, 129.1, 128.7, 128.5, 126.4, 123.6, 122.2, 112.2, 107.6, 61.0, 56.3, 30.5. IR (KBr, cm⁻¹): 1632, 1232, 1127, 994, 745. ESI-MS: (m/z) = 403 [M+H].⁺



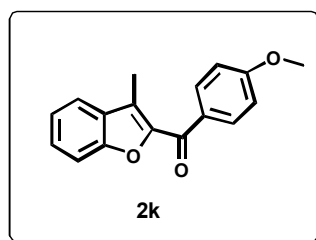
(3-Benzylbenzofuran-2-yl) (3,4-dichlorophenyl) methanone (**2h**). White solid: mp 111-112 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.27 (s, 1H), 8.04-8.01 (m, 1H), 7.65-7.52 (m, 4H), 7.39-7.22 (m, 6H), 4.58 (s, CH₂, 2H). ¹³C NMR (50 MHz, CDCl₃) δ 182.9, 154.5, 147.7, 138.9, 137.2, 132.9, 131.9, 130.5, 129.0, 128.7, 128.6, 128.3, 126.5, 123.8, 122.3, 112.4, 30.5. IR (KBr, cm⁻¹): 1631, 1293, 1022, 896, 740. ESI-MS: (m/z) = 381[M+H].⁺



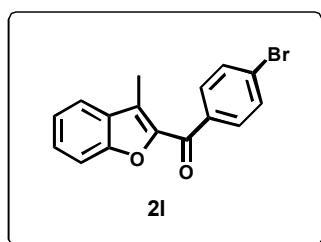
(3,4-Dichlorophenyl) (3-(4-methoxybenzyl) benzofuran-2-yl) methanone (**2i**). White solid: mp 126-128 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.26 (s, 1H), 8.03-8.00 (m, 1H), 7.64-7.49 (m, 4H), 7.31-7.29 (m, 3H), 6.85-6.82 (d, J= 8.6 Hz, 2H), 4.5 (s, CH₂, 2H), 3.78 (s, OCH₃, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 182.9, 158.2, 154.5, 147.6, 137.2, 132.9, 131.9, 130.9, 130.4, 129.7, 129.0, 128.6, 128.3, 123.8, 122.3, 114.0, 112.9, 55.2, 29.7. IR (KBr, cm⁻¹): 1623, 1547, 1295, 1253, 1031, 906, 744. ESI-MS: (m/z) = 411 [M+H].⁺



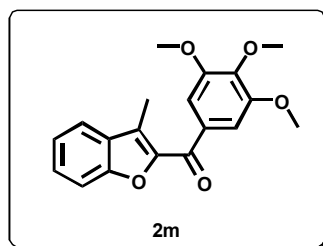
(3-Methyl benzofuran-2-yl)phenyl methanone (**2j**). Colourless oil; ¹H NMR (300MHz, CDCl₃) δ 8.13-8.10 (d, J=7.1 Hz, 2H), 7.75-7.72 (d, J=7.8 Hz, 1H), 7.64-7.50 (m, 5H), 7.39-7.34 (t, J=6.7 Hz, 1H), 2.67 (s, CH₃, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 185.9, 154.3, 148.3, 138.4, 137.9, 132.6, 129.8, 129.2, 128.3, 128.2, 126.9, 124.0, 123.3, 121.4, 112.2, 30.2, 10.0. IR (neat, cm⁻¹): 2925, 1641, 1565, 1219, 936, 769. ESI-MS: (m/z) = 237 [M+H].⁺



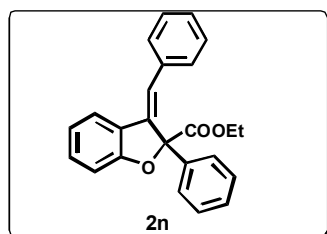
(4-Methoxyphenyl) (3-methylbenzofuran-2-yl) methanone (**2k**). White solid: mp 77-78 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.20-8.17 (d, J=8.8 Hz, 2H), 7.73-7.71 (d, J=7.7 Hz, 1H), 7.58-7.50 (m, 2H), 7.38-7.33 (t, J=7.1 Hz, 1H), 7.05-7.02 (d, J=8.8 Hz, 2H), 3.93 (s, OCH₃, 3H), 2.66 (s, CH₃, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 184.4, 163.3, 154.1, 148.6, 132.3, 130.5, 129.3, 127.9, 126.1, 123.2, 121.3, 113.6, 112.1, 55.5, 10.0. IR (KBr, cm⁻¹): 2923, 1637, 1508, 1258, 1029, 841, 770. ESI-MS: (m/z) = 267 [M+H].⁺



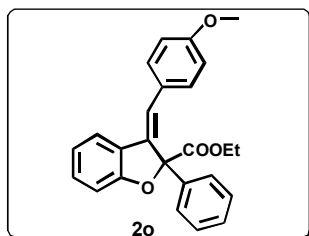
(3-Bromobenzyl) (3-methylbenzofuran-2-yl) methanone (**2l**). White solid: mp 92-94 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.03-8.00 (d, J=8.5 Hz, 2H), 7.45-7.68 (m, 3H), 7.57- 7.53 (t, J=7.5Hz, 2H), 7.40-7.32 (m, 1H), 2.68 (s, CH₃, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 184.5, 154.3, 148.0, 136.5, 131.6, 131.3, 129.1, 128.4, 127.7, 123.5, 121.5, 112.2, 10.0. IR (KBr, cm⁻¹): 2926, 1637, 1281, 1069, 769. ESI-MS: (m/z) = 315 [M+H].⁺



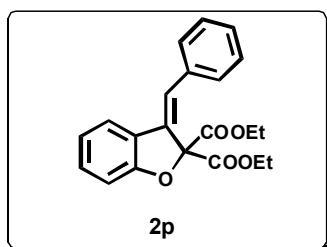
(3-Methylbenzofuran-2-yl) (3,4,5-trimethoxyphenyl) methanone (**2m**). White solid: mp 103-104 °C; ¹H NMR (300MHz, CDCl₃) δ 7.75-7.73 (d, J=7.7 Hz, 1H), 7.58-7.45 (m, 2H), 7.40-7.35 (m, 3H), 3.98 (s, OCH₃, 3H), 3.95 (s, OCH₃, 6H), 2.66 (s, CH₃, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 184.5, 154.2, 152.9, 148.3, 142.4, 132.7, 129.2, 128.2, 126.8, 123.4, 121.4, 112.1, 107.5, 61.0, 56.3, 10.1. IR (KBr, cm⁻¹): 2929, 1644, 1233, 1116, 995, 757. ESI-MS: (m/z) = 327 [M+H].⁺



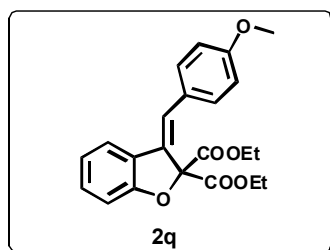
Ethyl-3-benzylidene-2-phenyl, 2,3-dihydrobenzofuran-2-carboxylate (**2n**) Semisolid; ¹H NMR (300MHz, CDCl₃) δ 7.62-7.60 (d, J=6.0Hz, 2H), 7.37-7.16(m, 10H), 7.03-7.01(d, J=7.4 Hz, 1H), 6.92-6.90 (d, J=8.00 Hz, 1H), 4.17-4.0(m, 2H), 1.01-0.96 (t, J=7.0 Hz, 3H). ¹³C NMR (50MHz, CDCl₃) δ 168.5, 159.7, 137.1, 135.8, 134.8, 129.7, 128.8, 128.3, 128.0, 127.6, 123.2, 121.6, 120.2, 110.7, 93.3, 63.3, 29.8, 13.7. IR (neat, cm⁻¹): 2133, 1642, 1464, 1218, 1025, 769. ESI-MS: (m/z) = 357 [M+H].⁺



Ethyl 3-(4-methoxybenzylidene)-2-phenyl 2,3-dihydrobenzofuran-2-carboxylate (**2o**). White solid: mp 95-96 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.61 (m, 3H), 7.58-7.55 (d, J = 7.6 Hz, 3H), 7.38-7.20 (m, 4H), 7.03-6.99 (t, J =7.4 Hz, 1H), 6.90-6.87 (d, J =8.0 Hz, 1H), 6.71-6.68 (d, J =8.7 Hz, 2H), 4.19-4.11 (m, CH_2 , 2H), 3.76 (s, OCH_3 , 3H), 1.05-1.00 (t, J =7.0 Hz, CH_3 , 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 168.7, 159.5, 159.1, 131.4, 129.9, 129.1, 128.8, 128.3, 122.8, 121.5, 119.8, 113.4, 110.5, 93.3, 62.2, 55.2, 29.7, 22.7, 13.7. IR (KBr, cm^{-1}): 2359, 1640, 1464, 1219, 1028, 769. ESI-MS: (m/z) = 387 $[\text{M}+\text{H}]^+$.



Diethyl 3-benzylidene benzofuran 2,2 (3H)-dicarboxylate (**2p**). Colourless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.79-7.54 (m, 3H), 7.47-7.44 (t, J =7.2 Hz, 1H), 7.31-7.22 (m, 6H), 4.52-4.46 (m, CH_2 , 4H), 1.45-1.43 (t, J =7.1 Hz, CH_3 , 6H). ^{13}C NMR (50 MHz, CDCl_3) δ 160.4, 154.6, 141.2, 139.0, 128.6, 128.5, 127.7, 126.4, 123.3, 121.8, 112.3, 61.3, 29.7, 14.4. IR (neat, cm^{-1}): 2309, 2109, 1726, 1626, 1457, 1257, 1030, 771. ESI-MS: (m/z) = 353 $[\text{M}+\text{H}]^+$.



Diethyl 3-(4-methoxybenzylidene) benzofuran 2,2-(3H) dicarboxylate (**2q**). Colourless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.46 (m, 2H), 7.45-7.41 (t, J =7.3 Hz, 1H), 7.26-7.23 (m, 4H), 6.84-6.81 (d, J =8.5 Hz, 2H), 4.53-4.45 (m, CH_2 , 4H), 3.78 (s, OCH_3 , 3H), 1.45-1.43 (t, J =7.0 Hz, CH_3 , 6H). ^{13}C NMR (50 MHz, CDCl_3) δ 158.2, 154.6, 131.0, 129.5, 128.5, 127.7, 123.3, 121.8, 113.9, 112.3, 61.3, 55.2, 29.7, 14.4. IR (neat, cm^{-1}): 2360, 1717, 1615, 1457, 1292, 1032, 749. 383. ESI-MS: (m/z) = 383 $[\text{M}+\text{H}]^+$.

Synthesis of (3-benzyl-6-methoxy-2,3-dihydrobenzofuran-2-yl)(phenyl) methanone **4**

To a mixture of 2-(5-methoxy-2-styrylphenoxy)-1-phenylethanone (0.5mmol) in 0.6 ml of (bmim)BF₄, anhydrous potassium phosphate (0.75 mmol) was added and the reaction mixture was kept under sonication for 4 hr. After completion of reaction, the product was extracted with anhydrous diethyl ether (50mlx3), dried over Na₂SO₄ and concentrated at reduced pressure to give a brown residue. The crude product was purified through column chromatography using hexane/EtOAc (25:1) to afford **4** as off white solid (80%), mp 105-107 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.65 (d, J = 7.17 Hz, 2H), 7.63-7.51 (m, 1H), 7.37-7.30 (m, 5H), 7.25-7.23 (m, 2H), 6.80 (d, J = 8.16 Hz, 1H), 6.55 (d, J = 2.04 Hz, 1H), 6.42 (dd, J = 8.19, 2.19 Hz, 1H), 5.68 (d, J = 3.84 Hz, CH, 1H), 3.93-3.87 (m, CH, 1H), 3.79 (s, OCH₃, 3H), 3.13-2.99 (m, CH₂, 2H). ¹³C NMR (CDCl₃, 50 MHz) δ 195.55, 160.89, 160.52, 138.40, 134.11, 133.40, 129.53, 128.82, 128.61, 126.81, 124.82, 120.60, 106.98, 96.32, 87.44, 55.48, 46.41, 42.03. IR (KBr, cm⁻¹); 3317, 2967, 1684, 1622, 1495, 1338, 1146, 1105, 969, 835, 748. ESI-MS (m/z) = 345 [M+H]⁺ and 5-methoxy-2-styrylphenol **5** as white solid (15%), mp 118-119 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.84 (brs, OH, 1H), 7.51-7.49 (m, 3H), 7.37-7.31 (m, 3H), 7.23-7.18 (m, 1H), 7.09-7.03 (d, J = 16.50 Hz, 1H), 6.45-6.42 (d, 7.41 Hz, 1H), 3.72 (s, OCH₃, 3H).

References

- [1] J. Hu, L.Y. Wu, X.C. Wang, Y.Y. Hu, Y.N. Niu, X.Y. Liu, S. Yang, Y.M. Liang, *Adv. Synth. Catal.* **2010**, 352, 351.

