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SUPPLEMENTARY MATERIAL TO

Three-component reaction of *β*-keto esters, aromatic aldehydes and urea/thiourea promoted by caffeine: A green and natural, biodegradable catalyst for eco-safe Biginelli synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones derivatives under solvent-free conditions

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*5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (**4a**, (Table II, entry 1).* Yield: 91 %; m.p.: 198–200 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.10 (3H, *t*, *J* = 7.2 Hz, C**H**$_3$CH$_2$), 2.26 (3H, *s*, CH$_3$), 3.99 (2H, *q*, *J* = 7.2 Hz, CH$_2$O), 5.15 (1H, *s*, benzylic H), 7.26 (3H, *d*, *J* = 7.2 Hz, Ar-H), 7.33 (2H, *t*, *J* = 7.2 Hz, Ar-H), 7.76 & 9.21 (2H, 2*s*, 2NH).

*4-(2-Chlorophenyl)-5-(ethoxycarbonyl)-6-methyl-3,4-dihydropyrimidin--2(1*H*)-one (**4b**, Table II, entry 2).* Yield: 82 %; m.p.: 221–223 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.00 (3H , *t*, *J* = 9.2 Hz, C**H**$_3$CH$_2$), 2.31 (3H, *s*, CH$_3$), 4.02 (2H, *q*, *J* = 9.2 Hz, CH$_2$O), 5.63 (1H, *s*, benzylic H), 7.25–7.34 (3H, *m*, Ar-H), 7.41 (1H, *d*, *J* = 8.8 Hz, Ar-H), 7.73 & 9.29 (2H, 2*s*, 2NH).

*5-(Ethoxycarbonyl)-4-(3-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin--2(1*H*)-one (**4d**, Table II, entry 4).* Yield: 84 %; m.p.: 203–205 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.13 (3H, *t*, *J* = 9.6 Hz, C**H**$_3$CH$_2$), 2.26 (3H, *s*, CH$_3$), 3.74 (3H, *s*, OCH$_3$), 4.01 (2H, *q*, *J* = 9.6 Hz, CH$_2$O), 5.13 (1H, *s*, benzylic H), 6.78–6.86 (3H, *m*, Ar-H), 7.26 (1H, *t*, *J* = 10.4 Hz, Ar-H), 7.76 & 9.20 (2H, 2*s*, 2NH).

*4-(3-Chlorophenyl)-5-(ethoxycarbonyl)-6-methyl-4-(3-chlorophenyl)-3,4--dihydropyrimidin-2(1*H*)-one (**4f**, Table II, entry 6).* Yield: 80 %; m.p.: 193–195 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 1.11 (3H, *t*, *J* = 9.6 Hz, C**H**$_3$CH$_2$), 2.26 (3H, *s*, CH$_3$), 4.01 (2H, *q*, *J* =9.6 Hz, CH$_2$O), 5.15 (1H, *s*, CHN), 7.19–7.26 (2H, *m*, Ar-H), 7.31–7.41 (2H, *m*, Ar-H), 7.83 & 9.30 (2H, 2*s*, 2NH).

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*5-(Ethoxycarbonyl)-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)--one (**4g**, Table II, entry 7)*. Yield: 84 %; m.p.: 209–210 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.10 (3H, *t*, *J* = 9.6 Hz, C**H**$_3$CH$_2$), 2.28 (3H, *s*, CH$_3$), 3.99 (2H, *q*, *J* = 9.6 Hz, CH$_2$O), 5.27 (1H, *s*, benzylic H), 7.50–7.53 (2H, *m*, Ar-H), 7.23 (2H, *d*, *J* = 9.2 Hz, Ar-H), 7.92 & 9.38 (2H, 2*s*, 2NH).

*5-(Ethoxycarbonyl)-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin--2(1*H*)-one (**4h**, Table II, entry 8)*. Yield: 87 %; m.p.: 200–202 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.11 (3H, *t*, *J* = 9.6 Hz, C**H**$_3$CH$_2$), 2.24 (3H, *s*, CH$_3$), 3.73 (3H, *s*, OCH$_3$), 3.99 (2H, *q*, *J* = 9.6 Hz, CH$_2$O), 5.09 (1H, *s*, benzylic H), 6.89 (2H, *d*, *J* = 8.4 Hz, Ar-H), 7.15 (2H, d, *J*= 8.8 Hz, Ar-H), 7.70 & 9.18 (2H, 2*s*, 2NH).

*5-(Ethoxycarbonyl)-4-(4-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin--2(1*H*)-one (**4i**, Table II, entry 9)*. Yield: 79 %; m.p.: 230–231 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.11 (3H , *t*, *J* = 9.6 Hz, C**H**$_3$CH$_2$), 2.50 (3H, *s*, CH$_3$), 3.98 (2H, *q*, *J* = 9.6 Hz, CH$_2$O), 5.04 (1H, *s*, benzylic H), 6.68–7.04 (4H, *m*, Ar-H), 7.64 & 9.13 (2H, 2*s*, 2NH), 9.35 (1H, *s*, OH).

*4-(4-Chlorophenyl)-5-(ethoxycarbonyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**4j**, Table II, entry 10)*. Yield: 81 %; m.p.: 215–217 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 1.10 (3H, *t*, *J* = 9.2 Hz, CH$_3$CH$_2$), 2.26 (3H, *s*, CH$_3$), 4.00 (2H, *q*, *J* =9.2 Hz, CH$_2$O), 5.14 (1H, *s*, CHN), 7.25 (2H, *d*, *J* = 11.2 Hz, Ar-H), 7.41 (2H, *d*, *J* = 11. 2 Hz, Ar-H), 7.79 & 9.27 (2H, 2*s*, 2NH).

*4-(Dimethylaminophenyl)-5-(ethoxycarbonyl)-6-methyl-3,4-dihydropyrimidin--2(1*H*)-one (**4k**, Table II, entry 11)*. Yield: 87 %; m.p.: 257–259 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 1.12 (3H, *t*, *J* = 9.2 Hz, C**H**$_3$CH$_2$), 2.26 (3H, *s*, CH$_3$), 2.85 (6H, *s*, 2CH$_3$), 3.99 (2H, *q*, *J* = 9.2 Hz, CH$_2$O), 5.04 (1H, *s*, CHN), 6.66 (2H, *d*, *J* = 11.6 Hz, Ar-H), 7.42 (2H, *d*, *J* = 11.6 Hz, Ar-H), 7.61 & 9.11 (2H, 2*s*, 2NH).

*5-(Ethoxycarbonyl)-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin--2(1*H*)-one (**4l**, Table II, entry 12)*. Yield: 88 %; m.p.: 204–206 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.11 (3H, *t*, *J* = 7.2 Hz, C**H**$_3$CH$_2$), 2.25 (3H, *s*, CH$_3$), 2.27 (3H, *s*, CH$_3$), 3.99 (2H, *q*, *J* = 7.2 Hz, CH$_2$O), 5.11 (1H, *s*, CHN), 7.13 (4H, *s*, Ar-H), 7.70 & 9.17 (2H, 2*s*, 2NH); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 14.0 (**C**H$_3$–CH$_2$O), 17.6 (**C**H$_3$–CH=CH), 21.1 (CH$_3$), 53.7 (Ar-CHN), 59.1 (CH$_3$–**C**H$_2$O), 99.2, 123.3 (CH$_3$–**C**H=**C**H), 126.8, 127.8, 128.2, 137.3, 144.7 & 148.0 (Ar-C), 151.9 (C=ONH), 165.3 (C=O ester).

*5-(Ethoxycarbonyl)-4-(4-fluorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)--one (**4m**, Table II, entry 13)*. Yield: 93 %; m.p.: 172–174 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 1.11 (3H , *t*, *J* = 9.6 Hz, C**H**$_3$CH$_2$), 2.25 (3H, *s*, CH$_3$), 3.99 (2H, *q*, *J* = 9.6 Hz, CH$_2$O), 5.14 (1H, *s*, CHN), 7.13–7.20 (2H, *m*, Ar-H), 7.24–7.29 (2H, *m*, Ar-H), 7.78 & 9.25 (2H, 2*s*, 2NH).

*4-(2-Chlorophenyl)-5-(methoxycarbonyl)-6-methyl-3,4-dihydropyrimidin--2(1*H*)-one (**4n**, Table II, entry 14).* Yield: 84 %; m.p.: 251–253 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 2.31 (3H, *s*, CH_3), 3.46 (3H, *s*, OCH_3), 5.62 (1H, *s*, benzylic H), 7.28–7.34 (3H, *m*, Ar-H), 7.42 (1H, *d*, *J* = 7.2 Hz, Ar-H), 7.72 & 9.36 (2H, 2*s*, 2NH).

*5-(Methoxycarbonyl)-6-methyl-4-(2-nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)--one (**4o**, Table II, entry 15).* Yield: 92 %; m.p.: 275–277 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 2.29 (3H, *s*, CH_3), 3.56 (3H, *s*, OCH_3), 5.29 (1H, *s*, benzylic H), 7.51–7.53 (2H, *m*, Ar-H), 8.21–8.24 (2H, *m*, Ar-H), 7.93 & 9.40 (2H, 2*s*, 2NH); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 17.7 (**C**H_3–CH=CH), 50.7 (Ar-CHN), 53.6 (CO_2-C**H**$_3$), 98.9, 123.2 (CH_3–**C**H=**C**H), 126.7, 127.9, 128.3, 137.4, 144.5 & 148.4 (Ar-C), 151.9 (C=ONH), 165.8 (C=O ester).

*4-(4-Chlorophenyl)-5-(methoxycarbonyl)-6-methyl-3,4-dihydropyrimidin--2(1*H*)-one (**4p**, Table II, entry 16).* Yield: 84 %; m.p.: 206–208 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 2.26 (3H, *s*, CH_3), 3.55 (3H, *s*, OCH_3), 5.15 (1H, *s*, benzylic H), 7.25 (1H, *d*, *J* = 11.2 Hz, Ar-H), 7.41 (1H, *d*, *J* = 11.2 Hz, Ar-H), 7.80 & 9.28 (2H, 2*s*, 2NH).

*5-Methoxycarbonyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)--one (**4q**, Table II, entry 17).* Yield: 89 %; m.p.: 215–217 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 2.28 (3H, *s*, CH_3), 3.55 (3H, *s*, OCH_3), 5.28 (1H, *s*, benzylic H), 7.52 (2H, *d*, *J* = 8.8Hz, Ar-H), 8.23 (2H, *d*, *J* = 8.8 Hz, Ar-H), 7.93 & 9.40 (2H, 2*s*, 2NH).

*5-(Methoxycarbonyl)-6-methyl-4-(4-hydroxyphenyl)-3,4-dihydropyrimidin--2(1*H*)-one (**4r**, Table II, entry 18).* Yield: 83 %; m.p.: 244–246 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 2.31 (3H, *s*, CH_3), 3.46 (3H, *s*, OCH_3), 5.04 (1H, *s*, CHN), 6.70 (2H, *d*, *J* =11.6 Hz, Ar-H), 7.02 (2H, *d*, *J* =11.6 Hz, Ar-H), 7.67 & 9.16 (2H, 2*s*, 2NH), 9.36 (1H, *s*, OH).

*4-(4-Fluorophenyl)-5-(methoxycarbonyl)-6-methyl-3,4-dihydropyrimidine--2(1*H*)-thione (**4s**, Table II, entry 19).* Yield: 92 %; m.p.: 210–212 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 2.31 (3H, *s*, CH_3), 3.57 (3H, *s*, OCH_3), 5.19 (1H, *s*, benzylic H), 7.17–7.44 (4H, *m*, Ar-H), 9.70 & 10.41 (2H, 2*s*, 2NH).

*5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidine-2(1*H*)-thione (**4u**)* (Table II, entry 21). Yield: 88 %; m.p.: 208–209 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.11 (3H , *t*, *J* = 7.2 Hz, C**H**$_3$CH$_2$), 2.31 (3H, *s*, CH_3), 4.02 (2H, *q*, *J* = 7.2 Hz, CH_2O), 5.19 (1H, *s*, benzylic H), 7.23 (2H, *d*, *J* = 7.2 Hz, Ar-H), 7.28 (1H, *t*, *J* = 7.2 Hz, Ar-H), 7.36 (2H, *t*, *J* = 7.2 Hz, Ar-H), 9.68 & 10.36 (2H, 2*s*, 2NH).

*5-(Ethoxycarbonyl)-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidine--2(1*H*)-thione (**4v**, Table II, entry 22).* Yield: 85 %; m.p.: 151–153 °C; ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 1.13 (3H, *t*, *J* = 9.6 Hz, C**H**$_3$CH$_2$), 2.29 (3H, *s*, CH_3), 3.74 (3H, *s*, OCH_3), 4.03 (2H, *q*, *J* = 9.6 Hz, CH_2O), 5.15 (1H, *s*, CHN),

6.77 (2H, *m*, Ar-H), 6.87 (1H, *m*, Ar-H), 7.28 (1H, *t*, *J* = 9.6 Hz, Ar-H), 9.66 & 10.37 (2H, 2*s*, 2NH).

*5-(Ethoxycarbonyl)-6-methyl-4-(3,4,5–trimethoxyphenyl)-3,4-dihydropyrimidine-2(1*H*)-thione (**4w**, Table II, entry 23).* Yield: 83 %; m.p.: 195–197 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.16 (3H, *t*, *J* = 7.2 Hz, C**H**$_3$CH$_2$), 2.30 (3H, *s*, CH$_3$), 3.65 (3H, *s*, OCH$_3$), 3.74 (6H, *s*, 2OCH$_3$), 4.07 (2H, *q*, *J* = 7.2 Hz, CH$_2$O), 5.16 (1H, *s*, CHN), 6.52 (2H, s, Ar-H), 9.65 & 10.37 (2H, 2*s*, 2NH); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 14.6 (**C**H$_3$–CH$_2$O), 17.6 (**C**H$_3$–CH=CH), 54.1 (Ar-CHN), 56.2, 60.1 & 60.4 (3OCH$_3$), 60.4 (CH$_3$–**C**H$_2$O), 101 & 103.8 (CH$_3$–**C**H=**C**H), 137.4, 139.5, 139.5, 145.4, 145.6 & 153.3 (Ar), 165.6 (C=O ester), 174.9 (C=SNH); MS (EI) [*m*/*z* (%)]: 366 (M, 118), 306 (10), 293 (77), 277 (17), 261 (12), 246 (17), 232 (12), 219 (9), 199 (100), 186 (5), 171 (47), 153 (49), 138 (4), 126 (19), 112 (18), 94 (12), 81 (11), 66 (18), 42 (32).