

Electronic Supplementary Information

General solvent-free ionic liquid catalyzed C-N/C-C coupled cyclization to diverse dihydropyrimidinones and new organic materials: Langmuir-Blodgett film study[†]

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1. Materials and methods.

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Reported melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra (Bruker Advance 300) were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^1H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (Perkin Elmer Spectrum 100) in thin film using KBr. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadrupole mass spectrophotometer (Bruker).

2. General procedure for synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones

A mixture of aldehyde (10 mmol), dicarbonyl compound (10 mmol) and urea or thiourea (12 mmol) were taken in a round bottom flask and the reaction mixture was heated at 70 °C in an oil bath in the presence of a catalytic amount of protic ionic liquid **I** (5 mol%). Product was started to solidified within 2-10 min. The progress of the reaction was monitored by TLC (thin layer chromatography). Total consumption of starting materials were completed with in 10–300 min. depending upon the nature of substrates and reagents used. After completion of the reaction ice-water (50 gm) was added and the lump was crushed to obtained free flowing solid product. The product was then filtered, washed with cold water. Crystallization in ethanol was needed for few compounds. Large scale (100 mmol) reaction was also carried out without any difficulty. In case of amino acid and sugar-based chiral compounds the products were liquid and the diastereomeric ratio were reported according to the NMR method.

3. Characterization data of synthesized 3,4-dihydropyrimidin-2(1H)-ones/thiones

Ethyl-4-phenyl-6-methyl-2-oxo-1, 2, 3, 4-tetrahydropyrimidine-5-carboxylate (4a): Yield: 89%; m. p. 202-204°C (Lit.¹ m. p. 203-204°C); IR (KBr) 3435, 3248, 3118, 2980, 2933, 1701, 1648, 1461, 1291, 1222, 1094 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.16 (s, 1H); 7.71 (s, 1H), 7.33–7.21 (m, 5H), 5.13 (s, 1H), 3.98 (q, 2H), 2.24 (s, 3H), 1.08 (t, 3H).

Ethyl-4-(2-chlorophenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydropyrimidine-5-carboxylate (4b): Yield: 94%; m. p. 220-221°C (Lit.² m. p. 218-220°C); IR (KBr) 3353, 3229, 3114, 2978, 1696, 1640, 1455, 1370, 1298, 1227, 1096 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.25 (s, 1H); 7.68 (s, 1H), 7.40–7.22 (m, 4H), 5.62 (s, 1H), 3.88 (q, 2H), 2.29 (s, 3H), 0.98 (t, 3H).

Ethyl-4-(2-nitrophenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4c): Yield: 99%; m. p. 214-216°C (Lit.³ m. p. 216-218°C); IR (KBr) 3422, 3213, 3102, 2958, 1698, 1645, 1524, 1462, 1355, 1319, 1285, 1225, 1094 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.40 (s, 1H); 7.89 (d, *J* = 8.1 Hz, 1H); 7.70 (m, 2H), 7.52 (m, 2H), 5.80 (s, 1H), 3.82 (q, 2H); 2.27 (s, 3H); 0.91 (t, 3H).

Ethyl-4-(2-bromophenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4d): Yield: 90%; m. p. 204-206 °C; (Lit.⁴ m. p. 206-208°C); IR (KBr) 3346, 3230, 3113, 2978, 1694, 1639, 1458, 1371, 1318, 1228, 1097 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.28 (s, 1H), 7.70 (s, 1H), 7.56 (d, *J* = 9 Hz, 1H), 7.35-7.28 (m, 2H), 7.19-7.15 (m, 1H), 5.60 (d, *J* = 2.7 Hz, 1H), 3.92-3.84 (q, 2H), 2.29 (s, 3H), 0.98 (t, 3H); ¹³C NMR (DMSO-d₆, 75 MHz,) δ 165.4, 151.7, 149.7, 143.8, 133.0, 129.8, 129.2, 128.9, 122.7, 98.7, 59.5, 54.5, 18.1, 14.4; HRMS Calcd for C₁₄H₁₅N₂O₃Br 338.1845, Found: 338.0250

Ethyl-4-(3-nitrophenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4e): Yield: 98%; m. p. 228-230°C (Lit.⁵ m. p. 226-228°C); IR (KBr) 3332, 3225, 3108, 2966, 1708, 1689, 1629, 1526, 1457, 1346, 1317, 1224 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.35 (s, 1H); 8.10 (m, 2H), 7.88 (s, 1H), 7.66 (m, 2H), 5.29 (s, 1H), 3.96 (q, 2H); 2.26 (s, 3H); 1.10 (t, 3H).

Ethyl-4-(3-hydroxyphenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4f): Yield: 85%; m. p. 184-186°C (Lit.⁶ m. p. 167-170°C); IR (KBr) 3514, 3354, 3244, 3119, 2978, 1724, 1676, 1643, 1600, 1454, 1315, 1296 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.33 (s, 1H); 9.14 (s, 1H), 7.76 (s, 1H), 7.08 (t, 1H), 6.62 (m, 3H), 5.05 (s, 1H), 3.98 (q, 2H), 2.22 (s, 3H); 1.01 (t, 3H).

Ethyl-4-(4-chlorophenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4g): Yield: 96%; m. p. 212-214°C (Lit.⁷ m. p. 215-216°C); IR (KBr) 3245, 3117, 2980, 2953, 1702, 1648, 1490, 1461, 1367, 1323, 1291, 1221, 1170, 1089 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.22 (s, 1H); 7.74 (s, 1H); 7.38 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.13 (d, *J* = 3.3 Hz, 1H); 3.97 (q, 2H); 2.23 (s, 3H); 1.07 (t, 3H).

Ethyl-4-(4-nitrophenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4h): Yield: 98%; m. p. 208°C (Lit.⁸ m. p. 206-207°C); IR (KBr) 3447, 3239, 3120, 2987, 1729, 1699, 1646, 1521, 1464, 1349 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz,) δ 9.32 (s, 1H); 8.20 (d, *J* = 8.7 Hz, 2H), 7.86 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 5.26 (s, 1H), 3.97 (q, 2H); 2.25 (s, 3H); 1.08 (t, 3H).

Ethyl-4-(4-hydroxyphenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4i): Yield: 92%; m. p. 230°C (Lit.⁵ m. p. 226-228°C); IR (KBr) 3509, 3120, 2980, 2823, 1683, 1643, 1517, 1462, 1381, 1368, 1316, 1295, 1230, 1171, 1090 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.29 (s, 1H), 9.07 (s, 1H), 7.58 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 5.02 (d, *J* = 3.3 Hz, 1H), 3.96 (q, 2H), 2.21 (s, 3H), 1.05 (t, 3H).

Ethyl-4-(4-methoxyphenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4j): Yield: 90%; m. p. 200°C (Lit.⁷ m. p. 200-201°C); IR (KBr) 3243, 3111, 2985, 2956, 2933, 1705, 1650, 1516, 1279, 1221, 1088 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.12 (s, 1H); 7.63 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.08 (d, *J* = 3.0 Hz, 1H), 3.96 (q, 2H), 3.70 (s, 3H), 2.22 (s, 3H), 1.08 (t, 3H).

Ethyl-4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4k): Yield: 97%; m. p. 232-234°C (Lit.⁵ m. p. 231-233°C); IR (KBr) 3435, 3247, 3117, 2977, 2937, 1698, 1645, 1516, 1367, 1277 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.10 (s, 1H); 8.88 (s, 1H), 7.61 (s, 1H), 6.79 (d, *J* = 1.8 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.60 (dd, *J* = 8.1, 1.8 Hz, 1H), 5.08 (d, *J* = 3.0 Hz, 1H), 3.97 (q, 2H), 3.71 (s, 3H), 2.22 (s, 3H), 1.09 (t, 3H).

Ethyl-4-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4l). Yield: 95%; m. p. 174-176°C (Lit.⁹ m. p. 176-177°C); IR (KBr) 3434, 3256, 3122, 2933, 1707, 1682, 1654, 1518, 1462, 1236, 1139, 1095, 1027 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.13 (s, 1H); 7.65 (s, 1H), 6.88 (s, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.09 (d, *J* = 3.0 Hz, 1H), 3.97 (q, 2H), 3.70 (s, 3H), 2.23 (s, 3H), 1.01 (t, 3H).

Ethyl-4-(2-naphthyl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4m): Yield: 86%; m. p. 206-208 °C (Lit.¹ m. p. 210-211°C); IR (KBr) 3224, 3106, 2978, 2931, 1702, 1649, 1429, 1321, 1285, 1227, 1087 cm⁻¹; ¹H NMR (DMSO- d₆, 300 MHz) δ 9.27 (s, 1H), 7.90-7.85 (m, 4H), 7.67(s, 1H), 7.52-7.42 (m, 3H), 5.32 (s, 1H), 4.00-3.93 (q,2H), 2.29 (s,3H), 1.07 (t, 3H); ¹³C NMR (75 MHz, DMSO-d₆) δ 165.8, 152.5, 149.0, 142.6, 133.1, 132.8, 128.8, 128.3, 127.9, 126.7, 126.4, 125.4, 125.0, 99.5, 59.7, 54.7, 18.3, 14.5; HRMS Calcd for C₁₈H₁₈N₂O₃ 310.3471, Found: 310.1812

Ethyl-4-styryl-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4n): Yield: 84%; m. p. 232-234°C (Lit.¹⁰ m. p. 230-232°C); IR (KBr) 3436, 3253, 3121, 2929, 1722, 1708, 1652 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.14 (s, 1H); 7.54 (s, 1H), 7.39 -7.18 (m, 5H), 6.34 (d, *J*=15.6 Hz, 1H), 6.18 (dd, *J*=15.6, 6.3 Hz, 1H), 4.71 (t, *J*=4 Hz, 1H), 4.07 (q, 2H), 2.19 (s, 3H), 1.18 (t, 3H).

Ethyl-4-propyl-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4o): Yield: 85%; m. p. 176-178°C (Lit.¹¹ m. p. 168-170°C); IR (KBr) 3439, 3252, 3120, 2958, 2875, 1703, 1674, 1647, 1464, 1369, 1332, 1257, 1236, 1092 cm⁻¹; ¹H NMR (DMSO d₆, 300 MHz,) δ 8.91 (s, 1H), 7.30 (s, 1H), 4.04 (m, 3H), 2.14 (s, 3H), 1.33 (m, 4H), 1.19 (t, 3H), 0.85 (s, 3H).

Ethyl-4-isobutyl-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4p): Yield: 87%; m. p. 186°C (Lit.¹² m. p.185-186°C); IR (KBr) 3241, 3113, 2979, 2951, 2932, 1713, 1703, 1652, 1466, 1378, 1329, 1283, 1241, 1220, 1085 cm⁻¹; ¹H NMR (DMSO d₆, 300 MHz) δ 8.96 (s, 1H), 7.43 (s, 1H), 4.08-4.00 (q, 2H), 2.15 (s, 3H), 1.93-1.64(m, 1H), 1.40-1.31 (m, 1H), 1.20 (t, 3H), 1.17-1.03 (m, 1H), 0.85 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 165.8, 153.2, 148.7, 100.8, 59.5, 48.6, 46.5, 24.1, 23.2, 21.8, 18.1, 14.6; HRMS Calcd for C₁₂H₂₀N₂O₃ 240.2988, Found: 240.2014

Ethyl-4-n-heptyl-6-methyl-2-oxo-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (4q): Yield: 89%, m. p. 175-176°C (Lit¹ 178-179°C); IR (KBr) 3295, 3195, 3129, 2967, 2927, 1707, 1687, 1601, 1538, 1408, 1393, 1367, 1319, 1246, 1162, 1059 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.30 (s, 1H), 5.94 (s, 1H), 4.30 (s, 1H), 4.26-4.12 (q, 2H), 2.29 (s, 3H), 1.54-1.47 (m, 2H), 1.38-1.26 (m, 13H), 0.88 (t, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.9, 154.6, 146.6, 101.7, 59.9, 51.6, 36.9, 31.8, 29.2, 29.1, 24.4, 22.6, 18.5, 14.3, 14.1; HRMS Calcd for C₁₅H₂₆N₂O₃ 282.3785, Found: 282.2442

5-Acetyl-4-(4-hydroxyphenyl)-6-methyl-3, 4-dihydropyrimidin-2(1H)-one (4r): Yield: 92%; m. p. 253°C (Lit.¹³ m. p. 256-258°C); IR (KBr) 3268, 3111, 2960, 2819, 1699, 1649, 1598, 1566, 1412, 1251, 1233 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.40 (s, 1H); 9.12 (s, 1H), 7.71 (s, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 5.14 (d, *J* = 2.7 Hz, 1H), 2.26 (s, 3H), 2.04 (s, 3H).

5-Acetyl-4-(4-hydroxy-3-methoxyphenyl)-6-methyl-3, 4-dihydropyrimidin-2(1H)-one (4s): Yield: %; m. p. 236-238°C (Lit.¹³ m. p. 233-234°C); IR (KBr) 3346, 3294, 2968, 2939, 1688, 1637, 1610, 1526, 1442, 1381, 1361, 1254, 1238, 1212, 1030 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 8.45 (s, 1H); 8.31 (s, 1H), 7.05 (s, 1H), 6.17 (d, *J* = 1.8 Hz, 1H), 6.02 (d, *J* = 8.1 Hz, 1H), 5.91 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.49 (d, *J* = 3.0 Hz, 1H), 3.05 (s, 3H), 1.83 (s, 3H), 1.38 (s, 3H).

Ethyl-4-(1-*N*-Boc amino-3-methylbutane)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxaldehyde (4t): Yield: 83%; dr = 77:23; IR (neat) 3241, 3126, 2958, 2932, 2872, 1705 (br), 1645, 1392, 1228, 1169, 1089 cm⁻¹; diastereomeric ration was determined from the ratio of 6-methyl signals appeared in ¹H NMR spectrum

Ethyl-4-(3-*O*-allyl-1,2-*O*-isopropylidene- α -D-xylofuranoside)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxaldehyde (4u): Yield: 89%; [α]_D²³ +57.64° (1.44, CHCl₃); Chiral HPLC column: Column : chiralpak IB (1B00CE-LF003) semiprep column; Detection : Single Peak; Mobile Phase : hexane-ethylacetate; Temperature : 25 °C; IR (neat) 3410, 3231, 3117, 2981, 2872, 1703, 1681, 1644, 1453, 1373, 1222, 1091 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.49 (s, 1H), 5.85 (d, *J* = 3.6 Hz, 1H), 5.81-5.70 (m, 1H), 5.50 (s, 1H), 5.21-5.12 (m, 2H), 4.47 9s, 1H), 4.42 (d, *J* = 3.6 Hz, 1H), 4.16 (d, *J* = 4.5 Hz, 1H), 4.11-3.97 (m, 3H), 3.88 – 3.82 (m, 2H), 2.14 (s, 3H), 1.30 (s, 3H), 1.21 (s, 3H), 1.13 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 166.1, 155.0, 149.2, 133.3, 118.5, 111.7, 105.3, 97.2, 84.7, 82.6, 82.4, 71.0, 59.8, 51.6, 26.9, 26.4, 19.1, 14.4

5-Ethoxycarbonyl-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-thione (5b): Yield: 84%; m. p. 188-190°C (Lit.¹⁵ m. p. 190-192°C); IR (KBr) 3328, 3175, 2984, 1672, 1574, 1466, 1282, 1198, 1178, 1121 cm⁻¹. ¹H NMR (DMSO-d₆, 300 MHz) δ 10.40 (s, 1H), 9.68 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.16 (d, *J* = 3.6 Hz, 1H), 3.99 (q, 2H), 2.28 (s, 3H), 1.09 (t, 3H).

5-Ethoxycarbonyl-6-methyl-4-(3-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-thione (5c): Yield: 88%; m. p. 208-210°C (Lit.¹⁰ m. p. 205-207°C); IR (KBr) 3418, 3178, 2988, 2932, 1716, 1660, 1595, 1532, 1475, 1344, 1324, 1274, 1190, 1103 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 10.52 (s, 1H), 9.78 (s, 1H), 8.16 (m, 1H), 8.06 (s, 1H), 7.66 (m, 2H), 5.33 (d, *J* = 3.6 Hz, 1H), 3.99 (q, 2H), 2.29 (s, 3H), 1.09 (t, 3H).

5-Ethoxycarbonyl-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione (5d): Yield: 88%; m. p. 148-150°C (Lit.¹⁵ m. p. 150-152°C); IR (KBr) 3437, 3313, 3172, 3110, 2982, 2937, 1665, 1576, 1509, 1460, 1285, 1269, 1253, 1196, 1121 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 10.29 (s, 1H), 9.60 (s, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.10 (d, *J* = 3.3 Hz, 1H), 3.99 (q, 2H), 3.71 (s, 3H), 2.27 (s, 3H), 1.09 (t, 3H).

5-Ethoxycarbonyl-6-methyl-4-(2-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione (5e): Yield: 84%; m. p. 208-210°C (Lit.³ m. p. 206-208°C); IR (KBr) 3327, 3195, 3097, 3058, 2975, 1723, 1610, 1565, 1508, 1460, 1252, 1204, 1179, 1088 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 9.15 (s, 2H), 7.20 (m, 2H), 6.93 (t, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 1H), 4.57 (d, *J* = 2.4 Hz, 1H), 4.16 (q, 2H), 1.77 (s, 3H), 1.09 (t, 3H).

5f

Ethyl-4-(4-octadecyloxyphenyl)-6-methyl-2-thio-1, 2, 3, 4-tetrahydro- pyrimidine-5-carboxylate (5f): Yield: 80%, m. p. 100-101 °C; IR (KBr) 3183, 2918, 2850, 1709, 1695, 1651, 1573, 1467, 1314, 1182, 1109 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 8.38 (bs, 1H), 7.70 (bs, 1H), 7.08 (d, $J = 8.7$ Hz, 2H), 6.71 (d, $J = 8.7$ Hz, 2H), 5.22 (s, 1H), 4.00 – 3.94 (m, 2H), 2.25 (s, 3H), 1.74-1.62 (m, 2H), 1.32 – 1.04 (m, 33H), 0.78 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 174.1, 165.3, 159.1, 142.5, 134.6, 128.0, 114.7, 103.2, 68.3, 55.6, 31.9, 29.7, 29.4, 29.3, 29.2, 26.0, 22.7, 18.1, 14.1

4. ^1H and ^{13}C -NMR spectra of the compounds (**4a-v** & **5a-f**)

^1H NMR spectra of **4a** (300 MHz, DMSO-d_6)

4a

^1H NMR spectra of **4b** (300 MHz, DMSO- d_6)

4b

^1H NMR spectra of **4c** (300 MHz, DMSO- d_6)

4c

^1H NMR spectra of **4d** (300 MHz, DMSO- d_6)

4d

^1H NMR spectra of **4d** (300 MHz, DMSO- d_6)

4d

^1H NMR spectra of **4e** (300 MHz, DMSO- d_6)

^1H NMR spectra of **4f** (300 MHz, DMSO- d_6)

4f

^1H NMR spectra of **4g** (300 MHz, DMSO- d_6)

4g

^1H NMR spectra of **4h** (300 MHz, DMSO- d_6)

4h

^1H NMR spectra of **4i** (300 MHz, DMSO-d_6)

4i

^1H NMR spectra of **4j** (300 MHz, DMSO- d_6)

4j

^1H NMR spectra of **4k** (300 MHz, DMSO- d_6)

4k

^1H NMR spectra of **4I** (300 MHz, DMSO- d_6)

4I

^1H NMR spectra of **4m** (300 MHz, DMSO- d_6)

4m

^{13}C NMR spectra of **4m** (75 MHz, DMSO- d_6)

4m

^1H NMR spectra of **4n** (300 MHz, DMSO- d_6)

4n

^1H NMR spectra of **4o** (300 MHz, DMSO- d_6)

4o

^1H NMR spectra of **4p** (300 MHz, DMSO- d_6)

4p

S*

^{13}C NMR spectra of **4p** (75 MHz, DMSO- d_6)

4p

^1H NMR spectra of **4q** (300 MHz, DMSO- d_6)

4q

^1H NMR spectra of **4q** (75 MHz, DMSO- d_6)

4q

^1H NMR spectra of **4r** (300 MHz, DMSO- d_6)

4r

^1H NMR spectra of **4s** (300 MHz, DMSO- d_6)

4s

^1H NMR spectra of **4t** (300 MHz, CDCl_3)

^{13}C NMR spectra of **4t** (75 MHz, CDCl_3)

^1H NMR spectra of **4u** (300 MHz, CDCl_3)

^{13}C NMR spectra of **4u** (75 MHz, CDCl_3)

^1H NMR spectra of **4v** (200 MHz, CDCl_3)

4v

^{13}C NMR spectra of **4v** (50 MHz, CDCl_3)

4v

^1H NMR spectra of **5a** (300 MHz, DMSO- d_6)

5a

^1H NMR spectra of **5b** (300 MHz, DMSO- d_6)

5b

^1H NMR spectra of **5c** (300 MHz, DMSO- d_6)

5c

^1H NMR spectra of **5d** (300 MHz, DMSO- d_6)

5d

^1H NMR spectra of **5e** (300 MHz, DMSO- d_6)

5e

^1H NMR spectra of **5f** (300 MHz, CDCl_3)

^{13}C NMR spectra of **5f** (75 MHz, CDCl_3)

5. Experimental procedure for film preparation for physicochemical studies

Dihydropyrimidinones were synthesized in our laboratory and the molecular structures were confirmed by IR, NMR and mass spectrum analysis. Arachidonic acid (AA) used in this work was purchased from Aldrich Chemical Company (U.S.A.). Teflon-barrier type LB trough (model 2007DC, Apex Instruments Co., India) was used for studying the behavior of the pure monolayer of DHPM and AA and mixed monolayer of DHPM and AA at the air-water (A-W) interface. Deposition of the mono- and multi-layers of pure and mixed Langmuir-Blodgett films on quartz slides/silicon wafer was also performed with same LB trough. The sub phase used throughout this study was double distilled water. All the measurements were performed at room temperature (24 °C). Quartz slides cleaned by leaving them overnight in chromic acid were subsequently boiled in concentrated nitric acid to remove all the traces of organic material and then washed with distilled water, dried and stored in a vacuum oven till use.

Surface pressure isotherms of pure monolayer of DHPM (4v) and AA were obtained by spreading 150 μ l solutions of 4v and AA (concentration 0.5mg/ml) in chloroform on the air water interface. Surface pressure isotherms of mixed monolayers of 4v and AA were obtained by spreading the chloroform solution of 4v and AA mixed in a predetermined ratio. After evaporation of the solvent, the film at the (A-W) interface was compressed very slowly at a rate of about $5 \times 10^{-3} \text{ nm}^2 \text{ mol}^{-1} \text{ sec}^{-1}$ and a Wilhemy plate was used for measuring the surface pressure at (A-W) interface. Data was acquired by a DELL computer interfaced to Wilhemy balance that also controlled the compressing barrier maintaining the constant pressure of sub phase with an accuracy of 0.1mN/m. Y-type deposition of the pure LB film of DHPM and mixed LB film of DHPM and AA on quartz slides have been obtained at dipping speed of 5 mm/min at the surface pressure of 25 and 40 mN/m. A drying time of 15 minutes were allowed after each lift. For each mole-fraction of DHPM (4v), LB films of 10 bi-layers were deposited. The transfer ratios were found to be 0.96 ± 0.01 .

UV-Vis absorption and emission spectra of DHPM (4v) solution in quartz cell, microcrystal, pure DHPM LB film and mixed LB film of DHPM /AA on quartz slides were recorded by a Perkin Elmer Lamda 25 absorption spectrophotometer. Surface morphology of pure AA, pure DHPM (4v) and 4v/AA mixed monolayer film were studied by an AFM (Innova, Bruker Inc., USA). The AFM images were captured in tapping mode under ambient atmosphere.

6. Atomic force microscopic image of bare silicon wafer

7. Catalyst loading vs conversion plot

8. References

1. S. K. Kundu, A. Majee and A. Hajra, *Ind. J. Chem.* 2009, **48B**, 408.
2. K. Ananda Kumar, M. Kasthuraiah, C. Suresh Reddy and C. Devendranath Reddy, *Tetrahedron Lett.*, 2001, **42**, 7873.
3. B. Ahmed, A. R. Khan, Habibullah and M. Keshari, *Tetrahedron Lett.* 2009, **50**, 2889.
4. Y. Ma, C. Qian, L. wang and M. Yang, *J. Org. Chem.*, 2000, **65**, 3864.
5. R. Zheng, X. Wang, H. Xu and J. Du, *Synth. Commun.* 2006, **36**, 1503.
6. T. Y. Reddy, B. Rajitha, P. N. Reddy, B. S. Kumar and V. P. Rao, *Synth. Commun.* 2004, **34**, 3821.
7. E. H. Hu, D. R. Sidler and U.-H. Dolling, *J. Org. Chem.* 1998, **63**, 3454.
8. B. C. O'Reilly and K. S. Atwal, *Heterocycles* 1987, **26**, 1185.
9. B. Gangadasu, P. Narender, C. B. Raju and J. V. Rao, *Ind. J. Chem*, 2006, **45B**, 1259.
10. N. H. Karade, M. Sathe and P. M. Kaushik, *Molecules* 2007, **12**, 1341.
11. J. J. V. Eynde, N. Audiart, V. Conne, S. Micheal, Y. V. Haverbeke and C. O. Kappe, *Heterocycles* 1997, **45**, 1967.
12. S. S. Bahekar, S. A. Kotharkar and D. V. Shinde, *Mendeleev Commun.*, 2004, 210.
13. X. Jing, Z. Li, X. Pan, Y. Shi and C. Yan. *J. Iran. Chem. Soc.*, 2009, **6**, 514.
14. S. M. Sherif, M. M. Youssef, K. M. Mobarak and A.-S. M. Abdel-Fattah, *Tetrahedron* 1993, **49**, 9561.
15. Z. Wang, L. Xu, C. Xia and H. Wang, *Tetrahedron Lett.*, 2004, **45**, 7951.