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**Development, Scope, and Mechanisms of Multicomponent Reactions  
of Asymmetric electron-deficient alkyne with Amines and  
Formaldehyde**

Hua Cao, Xiujun Wang, Huanfeng Jiang\*<sup>[a]</sup>, Qiuhua Zhu, Min Zhang and Haiyang Liu

<sup>[a]</sup>*School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou  
510640, P. R. China*

**General** All reactions were performed at the room temperature under air atmosphere in a round bottom flask equipped with magnetic stir bar.  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer and referenced to 7.24 ppm and 77.0 ppm for chloroform solvent respectively with TMS as internal standard. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP5050A at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). Elemental analysis was performed on a Vario EL elemental analyzer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF<sub>254</sub>), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals.

**General procedure for synthesis of ethyl 1,3-dibenzyl-6-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate via four-component reactions:**

To a stirring mixture of ethyl phenylpropiolate **1a** (1 mmol), benzylamine (2.2 mmol), and 3 mL DMF were added successively. The mixture was stirred at room temperature for 6 hours. And then, formaldehyde (4 mmol) was added. After completion of the reaction (monitored by TLC), the solution was evaporated to dryness under reduced pressure, and 8 mL of water was added. The aqueous solution was extracted with diethyl ether (3×15 mL), and the combined extract was dried with anhydrous  $\text{MgSO}_4$ . Solvent was removed, and the crude product was separated by column chromatography to give a pure sample **4a**.

**Ethyl 1,3-dibenzyl-6-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4a).** Yellowish viscous oil; IR (KBr) 3029, 2978, 1670, 1571, 1287, 1099, 763, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23–7.37 (m, 13H), 7.06 (d,  $J = 3.2$  Hz, 2H), 3.98 (s, 2H), 3.86 (q,  $J = 7.2$  Hz, 2H), 3.80 (s, 2H), 3.74 (s, 2H), 3.68 (s, 2H), 0.87 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 156.2, 137.9, 137.0, 128.9, 128.7, 128.4, 128.3, 128.21, 127.6, 127.2, 98.7, 67.2, 58.9, 57.8, 53.9, 52.1, 13.8; MS (EI)  $m/z$  (%): 412 ( $\text{M}^+$ ), 383, 367, 339, 321, 220, 119, 91, 65;  $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_2$ : Calcd. C, 78.61; H, 6.84; N, 6.79; Found: C, 78.22; H, 6.86; N, 6.81.

**Ethyl 1,3-dibutyl-6-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4b).** Yellowish viscous oil; IR (KBr) 3044, 2961, 1665, 1572, 1371, 1288, 1080, 914, 762  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.33 (m, 3H), 7.17–7.20 (m, 2H), 3.89 (s, 2H), 3.76 (q,  $J = 7.2$  Hz, 2H), 3.52 (s, 2H), 2.77 (t,  $J = 7.6$  Hz, 2H), 2.54 (t,  $J = 7.6$  Hz, 2H), 1.55–1.58 (m, 2H), 1.33–1.39 (m, 4H), 1.01–1.03 (m, 2H), 0.93 (t,  $J = 7.2$  Hz, 3H), 0.79 (t,  $J = 6.8$  Hz, 3H), 0.71 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 156.1, 137.0, 132.4, 128.5, 128.1, 127.9, 95.7, 68.5, 58.6, 53.3, 51.5, 50.4, 31.6, 29.7, 20.6, 20.0, 19.8, 14.0, 13.8, 13.6; MS (EI)  $m/z$  (%): 344, 315, 267, 258, 173, 114, 29;  $\text{C}_{21}\text{H}_{32}\text{N}_2\text{O}_2$ : Calcd. C, 73.22; H, 9.36; N, 8.13; Found: C, 72.91; H, 9.39; N, 8.15.

**Ethyl 1,3-diallyl-6-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4c).** Yellowish viscous oil; IR (KBr) 3034, 2980, 2896, 1669, 1556, 1267, 1115, 832  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.33 (m, 3H), 7.20–7.22 (m, 2H), 5.88–5.93 (m, 1H), 5.578–5.60 (m, 1H), 5.06–5.25 (m, 4H), 3.86 (s, 2H), 3.77 (q,  $J = 7.2$  Hz, 2H), 3.56 (s, 2H), 3.38 (d,  $J = 5.6$  Hz, 2H), 3.21 (d,  $J = 6.4$  Hz, 2H), 0.79 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 155.9, 136.8, 134.7, 134.5, 128.4, 128.4, 128.0, 118.4, 117.1, 97.0, 67.2, 58.8, 56.6, 53.1, 51.7, 13.8; MS (EI)  $m/z$  (%): 312, 283, 271, 198, 170, 114, 56, 41, 28;  $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$ : Calcd. C, 73.05; H, 7.74; N, 8.97; Found: C, 72.71; H, 7.76; N, 8.90.

**Ethyl 1,3-dicyclohexyl-6-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4d).** Yellowish viscous oil; IR (KBr) 3026, 2977, 2893, 1672, 1544, 1357, 1100, 700  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.33 (m, 3H), 7.16–7.18 (m, 2H), 3.88 (s, 2H), 3.75 (q,  $J = 7.2$  Hz, 2H), 3.55 (s, 2H), 2.83–2.87 (m, 1H), 2.47–2.49 (m, 1H), 1.21–2.02 (m, 20H), 0.78 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 156.3, 137.5, 128.1, 127.9, 97.4, 60.7, 60.2, 58.4, 57.6, 48.8, 31.3, 29.8, 26.1, 25.7, 25.6, 25.3, 13.8; MS (EI)  $m/z$  (%): 396 ( $\text{M}^+$ ), 367, 323, 313, 298, 212, 158, 104, 55, 41;  $\text{C}_{25}\text{H}_{36}\text{N}_2\text{O}_2$ : Calcd. C, 75.72; H, 9.15; N, 7.06; Found: C, 76.10; H, 9.11; N, 7.04.

**Ethyl 1-benzyl-3-(4-fluorophenyl)-6-phenyl-1,2,3,4-tetrahydropyrimidine -5-carboxylate (4e).** Yellowish viscous oil; IR (KBr) 3062, 2977, 1674, 1549, 1273, 732  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26–7.34 (m, 8H), 7.14 (d,  $J = 3.2$  Hz, 2H), 6.91 (d,  $J = 4.4$  Hz, 2H), 6.83–6.85 (m, 2H), 4.37 (s, 2H), 4.22 (s, 2H), 3.97 (s, 2H), 3.86 (q,  $J = 7.2$  Hz, 2H), 0.85 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 158.6, 157.0, 156.2, 145.0, 137.6, 136.7, 128.9, 128.6, 128.3, 128.2, 127.4, 119.3, 118.7, 116.0, 115.7, 115.5, 100.5, 66.8, 59.2, 54.0, 49.1, 13.8; MS (EI)  $m/z$  (%) 416 ( $\text{M}^+$ ), 387, 343, 325, 294, 220, 123, 105, 91, 77, 65;  $\text{C}_{26}\text{H}_{25}\text{FN}_2\text{O}_2$ : Calcd. C, 74.98; H, 6.05; N, 6.73; Found: C, 75.32; H, 6.02; N, 6.76.

**Ethyl 1-benzyl-6-phenyl-3-p-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4f).** Yellowish viscous oil; IR (KBr) 3036, 2988, 1668, 1543, 1287, 1104, 760  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26–7.34 (m, 8H), 7.19 (d,  $J = 6.8$  Hz, 2H), 7.05 (d,  $J = 8.0$  Hz, 2H), 6.83 (d,  $J = 8.4$  Hz, 2H), 4.41 (s, 2H), 4.16 (s, 2H), 3.92 (s, 2H), 3.89 (q,  $J = 7.2$  Hz, 2H), 2.28 (s, 3H), 0.87 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 157.0, 146.3, 137.8, 136.9, 129.8, 129.7, 128.7, 128.6, 128.4, 128.1, 127.5, 127.4, 117.1, 101.3, 66.4, 59.1, 54.1, 48.8, 20.4, 13.7; MS (EI)  $m/z$  (%) 412 ( $\text{M}^+$ ), 383, 321, 294, 237, 208, 119, 105, 91, 77, 65, 55;  $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_2$ : Calcd. C, 78.61; H, 6.84; N, 6.79; Found: C, 79.00; H, 6.81; N, 6.82.

**Methyl 1,3-dibenzyl-6-pentyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4g).** Yellowish viscous oil; IR (KBr) 3022, 2950, 1680, 1561, 1457, 1245, 1123, 736  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14–7.32 (m, 10H), 4.36 (s, 2H), 3.82 (s, 2H), 3.65 (s, 2H), 3.63 (s, 2H), 3.57 (s, 2H), 2.89 (t,  $J = 8.4$  Hz, 2H), 1.56–1.58 (m, 2H), 1.31–1.35 (m, 4H), 0.87 (t,  $J = 7.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 158.9, 138.3, 137.8, 128.8, 128.6, 128.2, 128.1, 127.3, 127.1, 126.9, 126.5, 91.2, 68.2, 57.2, 52.2, 51.1, 50.3, 32.0, 29.0, 22.4, 13.9; MS (EI)  $m/z$  (%) 392 ( $\text{M}^+$ ), 377, 357, 321, 301, 120, 91;  $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_2$ : Calcd. C, 76.49; H, 8.22; N, 7.14; Found: C, 76.16; H, 8.19; N, 7.16.

**Methyl 1,3-dibutyl-6-pentyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4h).** Yellowish viscous oil; IR (KBr) 2963, 2894, 1654, 1558, 1457, 1049, 880  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.84 (s, 2H), 3.60 (s, 3H), 3.13 (s, 2H), 3.11 (t,  $J = 8.0$  Hz, 2H), 2.76 (t,  $J = 8.4$  Hz, 2H), 2.42 (t,  $J = 7.2$  Hz, 2H), 1.44–1.49 (m, 6H), 1.26–1.34 (m, 8H), 0.86–0.93 (m, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 158.9, 90.0, 69.0, 52.8, 51.1, 50.2, 48.9, 32.2, 31.8, 29.9, 28.8, 28.6, 22.4, 20.6, 20.1, 14.0, 13.8; MS (EI)  $m/z$  (%): 324, 268, 211, 128, 84;  $\text{C}_{19}\text{H}_{36}\text{N}_2\text{O}_2$ : Calcd. C, 70.32; H, 11.18; N, 8.63; Found: C, 70.67; H, 11.13; N, 8.59.

**Methyl 1,3-diallyl-6-pentyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4i).** Yellowish viscous oil; IR (KBr) 2957, 2862, 1673, 1552, 1409, 1239, 728  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.70–5.85 (m, 2H), 5.09–5.17 (m, 4H), 3.81 (s, 2H), 3.75 (d,  $J = 4.8$  Hz, 2H), 3.58 (s, 3H), 3.46 (s, 2H), 3.10 (d,  $J = 6.8$  Hz, 2H), 2.76 (t,  $J = 8.0$  Hz, 2H), 1.46–1.50 (m, 2H), 1.27–1.36 (m, 4H), 0.85 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.8, 158.8, 135.2, 135.0, 134.5, 134.0, 118.0, 117.7, 116.8, 90.8, 67.8, 58.4, 56.1, 55.8, 55.3, 51.2, 51.0, 50.3, 32.1, 28.9, 28.6, 22.4, 14.0, 13.9; MS (EI)  $m/z$  (%): 292, 277, 233, 147, 57, 43;  $\text{C}_{17}\text{H}_{28}\text{N}_2\text{O}_2$ : Calcd. C, 69.83; H, 9.65; N, 9.58; Found: C, 69.59; H, 9.69; N, 9.55.

**Methyl 1,3-dicyclohexyl-6-pentyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4j).** Yellowish viscous oil; IR (KBr) 2963, 2871, 1681, 1565, 1119, 736  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.79 (s, 2H), 3.59 (s, 3H), 3.44 (s, 2H), 2.81 (s, 1H), 2.35 (s, 1H), 1.67–1.90 (m, 10H), 1.18–1.43 (m, 18H), 0.86 (t,  $J = 3.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 159.0, 92.1, 60.5, 59.6, 55.9, 50.2, 48.5, 32.0, 31.5, 30.0, 28.4, 26.0, 25.6, 25.4, 22.3, 14.0; MS (EI)  $m/z$  (%): 376 ( $\text{M}^+$ ), 361, 317, 305, 278, 264, 150, 122, 98, 83, 55, 41;  $\text{C}_{23}\text{H}_{40}\text{N}_2\text{O}_2$ : Calcd. C, 73.36; H, 10.71; N, 7.44; Found: C, 73.01; H, 10.66; N, 7.47.

**Ethyl 1,3-dibenzyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4k).** Yellowish viscous oil; IR (KBr) 2950, 2862, 1680, 1551, 1440, 1278, 755  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (s, 1H), 7.16–7.32 (m, 10H), 4.21 (s, 2H), 4.13 (q,  $J = 7.2$  Hz, 2H), 3.80 (s, 2H), 3.57 (s, 2H), 3.52 (s, 2H), 1.24 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 144.6, 138.1, 136.6, 128.9, 128.8, 128.6, 128.3, 127.9, 127.6, 127.2, 93.1, 65.2, 59.0, 57.7, 57.1, 47.9, 14.6; MS (EI)  $m/z$  (%): 336, 282, 207, 148, 133, 105, 91, 65, 29;  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$ : Calcd. C, 74.97; H, 7.19; N, 8.33; Found: C, 75.30; H, 7.21; N, 8.37.

**Ethyl 1,3-dibutyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4l).** Yellowish viscous oil; IR (KBr) 2958, 2855, 1682, 1580, 1456, 1074, 901, 751  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (s, 1H), 4.09 (q,  $J = 7.2$  Hz, 2H), 3.87 (s, 2H), 3.43 (s, 2H), 3.06 (t,  $J = 3.6$  Hz, 2H), 2.46 (t,  $J = 7.6$  Hz, 2H), 1.29–1.49 (m, 8H), 1.22 (t,  $J = 6.8$  Hz, 3H), 0.89 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 144.5, 91.9, 66.6, 58.9, 53.7, 52.7, 47.8, 31.2, 30.0, 20.5, 19.8, 14.6, 14.0, 13.7; MS (EI)  $m/z$  (%): 268, 240, 183, 154, 109, 95, 80, 42, 28;  $\text{C}_{15}\text{H}_{28}\text{N}_2\text{O}_2$ : Calcd. C, 67.13; H, 10.52; N, 10.44; Found: C, 66.87; H, 10.56; N, 10.39.

**Ethyl 1,3-diallyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4m).** Yellowish viscous oil; IR (KBr) 2972, 2876, 1680, 1566, 1476, 1208, 1117, 750  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (s, 1H), 5.82–5.89 (m, 1H), 5.70–5.76 (m, 1H), 5.12–5.22 (m, 4H), 4.09 (q,  $J = 7.2$  Hz, 2H), 3.85 (s, 2H), 3.64 (d,  $J = 6.0$  Hz, 2H), 3.44 (s, 2H), 3.10 (d,  $J = 6.4$  Hz, 2H), 1.21 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 143.4, 134.3, 132.4, 117.6, 117.2, 92.2, 64.4, 58.1, 55.3, 55.2, 46.9, 13.7; MS (EI)  $m/z$  (%): 236 ( $\text{M}^+$ ), 235, 207, 163, 122, 94, 57, 41;  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2$ : Calcd. C, 66.07; H, 8.53; N, 11.85; Found: C, 65.84; H, 8.55; N, 11.80.

**Ethyl 1,3-dicyclohexyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4n).** Yellowish viscous oil; IR (KBr) 2976, 2863, 1681, 1563, 1402, 1254, 1102, 733  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (s, 1H), 4.08 (q,  $J = 7.2$  Hz, 2H), 3.99 (s, 2H), 3.51 (s, 2H), 2.85–2.83 (m, 1H), 2.39–2.41 (m, 1H), 1.60–1.88 (m, 10H), 1.09–1.36 (m, 13H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 142.4, 92.1, 61.4, 57.8, 57.5, 57.3, 44.2, 31.0, 30.0, 29.6, 28.3, 25.1, 24.8, 24.6, 24.4, 17.5, 13.8; MS (EI)  $m/z$  (%): 320 ( $\text{M}^+$ ), 276, 248, 166, 126, 57, 28;  $\text{C}_{19}\text{H}_{32}\text{N}_2\text{O}_2$ : Calcd. C, 71.21; H, 10.06; N, 8.74; Found: C, 70.91; H, 10.10; N, 8.71.

**Ethyl 1,3-di-*tert*-butyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4o).** Yellowish viscous oil; IR (KBr) 2975, 2864, 1682, 1569, 1469, 1204, 730  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (s, 1H), 4.11 (q,  $J = 7.2$  Hz, 2H), 3.85 (s, 2H), 3.39 (s, 2H), 1.27 (s, 9H), 1.21 (t,  $J = 7.2$  Hz, 3H), 1.16 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 140.4, 94.8, 57.9, 57.4, 55.2, 52.9, 42.4, 27.4, 25.5, 17.5, 13.8; MS (EI)  $m/z$  (%): 268 ( $\text{M}^+$ ), 213, 157, 128, 70, 57, 41;  $\text{C}_{15}\text{H}_{28}\text{N}_2\text{O}_2$ : Calcd. C, 67.13; H, 10.52; N, 10.44; Found: C, 67.43; H, 10.48; N, 10.39.

**(1,3-Dibenzyl-1,2,3,4-tetrahydro-6-phenylpyrimidin-5-yl)(phenyl)methanone (4p).** IR (KBr) 3042, 2895, 1601, 1505, 734  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22–7.36 (m, 13H), 7.01–7.07 (m, 7H), 4.00 (s, 2H), 3.84 (s, 2H), 3.81 (s, 2H), 3.79 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.9, 157.4, 141.2, 137.8, 137.7, 135.7, 130.5, 130.0, 129.8, 129.1, 129.0, 128.6, 128.4, 128.3, 127.9, 127.7, 127.2, 127.1, 113.7, 69.6, 58.1, 54.9, 53.7; MS (EI)  $m/z$  (%): 444, 353, 105, 91, 77, 65;  $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}$ : Calcd. C, 83.75; H, 6.35; N, 6.30; Found: C, 83.59; H, 6.41; N, 6.33.

**(1,3-Dibutyl-1,2,3,4-tetrahydro-6-phenylpyrimidin-5-yl)(phenyl)methanone (4q).** IR (KBr) 3042, 2917, 1610, 724  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (d,  $J = 8.4$  Hz, 2H), 7.06 (d,  $J = 8.0$  Hz, 2H), 6.95–7.02 (m, 6H), 3.95 (s, 2H), 3.69 (s, 2H), 2.86 (t,  $J = 7.6$  Hz, 2H), 2.60 (t,  $J = 7.6$  Hz, 2H), 1.60–1.65 (m, 2H), 1.42–1.47 (m, 4H), 1.09–1.12 (m, 2H), 0.97 (t,  $J = 7.2$  Hz, 3H), 0.75 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 158.2, 142.1, 135.6, 130.5, 129.1, 128.8, 128.4, 127.6, 127.0, 111.2, 53.8, 53.1, 51.6, 31.7, 29.8, 25.3, 20.6, 19.8, 13.9, 13.6; MS (EI)  $m/z$  (%): 376, 305, 105, 77, 57, 43;  $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}$ : Calcd. C, 79.75; H, 8.57; N, 7.44; Found: C, 80.02; H, 8.73; N, 7.39.

**(1,3-Dibenzyl-1,2,3,4-tetrahydro-6-phenylpyrimidin-5-yl)(thiophen-2-yl)methanone (4r).** IR (KBr) 3026, 2911, 1604, 1450, 739, 700  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.07–7.39 (m, 17H), 6.65–6.67 (m, 1H), 4.00 (s, 2H), 3.76 (s, 2H), 3.74 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.6, 155.1, 145.9, 138.0, 136.2, 132.1, 131.1, 130.2, 129.2, 129.0, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.3, 127.2, 126.5, 115.6, 67.5, 58.2, 54.8, 53.9; MS (EI)  $m/z$  (%): 450, 359, 91, 65;  $\text{C}_{29}\text{H}_{26}\text{N}_2\text{O}$ : Calcd. C, 77.30; H, 5.82; N, 6.22; Found: C, 77.46; H, 5.80; N, 6.23.

**(1,3-Dibutyl-1,2,3,4-tetrahydro-6-phenylpyrimidin-5-yl)(thiophen-2-yl)methanone (4s).** IR (KBr) 3009, 2936, 1614, 1524, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12–7.24 (m, 6H), 6.97–6.98 (m, 1H), 6.60–6.62 (m, 1H), 3.96 (s, 2H), 3.70 (s, 2H), 2.92 (t,  $J = 7.6$  Hz, 2H), 2.62 (t,  $J = 7.6$  Hz, 2H), 1.63–1.65 (m, 2H), 1.50–1.52 (m, 2H), 1.40–1.44 (m, 2H), 1.15–1.17 (m, 2H), 0.97 (t,  $J = 7.6$  Hz, 3H), 0.79 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  187.9, 156.1, 146.2, 135.9, 131.4, 130.3, 128.9, 127.8, 126.2, 112.3, 69.2, 53.8, 51.5, 31.6, 29.5, 20.5, 19.8, 13.9, 13.6; MS (EI)  $m/z$  (%): 382, 361, 105, 91, 77, 65, 43;  $\text{C}_{23}\text{H}_{30}\text{N}_2\text{OS}$ : Calcd. C, 72.21; H, 7.90; N, 7.32; Found: C, 72.36; H, 7.85; N, 7.37.

**(1,3-Dibenzyl-1,2,3,4-tetrahydro-6-phenylpyrimidin-5-yl)(*p*-tolyl)methanone (4t).** IR (KBr) 3028, 2889, 1606, 1561, 706  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25–7.37 (m, 12H), 7.04–7.07 (m, 5H), 6.82 (d,  $J = 7.6$  Hz, 2H), 3.98 (s, 2H), 3.80 (s, 2H), 3.77 (s, 4H), 2.19 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.4, 156.3, 140.3, 138.1, 138.0, 137.8, 136.0, 130.4, 129.0, 128.9, 128.3, 127.9, 127.2, 114.4, 67.5, 58.2, 54.9, 53.9, 21.2; MS (EI)  $m/z$  (%):  $\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}$ : Calcd. C, 83.81; H, 6.59; N, 6.11; Found: C, 84.02; H, 6.52; N, 6.21.

**(1,3-Dibenzyl-1,2,3,4-tetrahydro-6-pentylpyrimidin-5-yl)(phenyl)methanone (4u).** IR (KBr) 3014, 2934, 1627, 727  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17–7.49 (m, 15H), 4.40 (s, 2H), 3.92 (s, 2H), 3.66 (s, 2H), 3.59 (s, 2H), 2.64 (t,  $J = 8.4$  Hz, 2H), 1.57–1.60 (m, 2H), 1.18–1.21 (m, 4H), 0.81 (t,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.0, 159.2, 143.2, 137.8, 137.4, 129.7, 128.9, 128.8, 128.3, 128.1, 128.0, 127.5, 127.4, 127.2, 126.9, 126.6, 102.3, 68.5, 56.7, 52.8, 52.2, 31.3, 29.9, 29.3, 22.5, 13.9; MS (EI)  $m/z$  (%): 438, 377, 356, 120, 91, 65, 43;  $\text{C}_{30}\text{H}_{33}\text{N}_3\text{O}_3$ : Calcd. C, 82.15; H, 7.81; N, 6.39; Found: C, 82.29; H, 7.79; N, 6.34.

**1-(3,5-Dibenzyl-2-pentylcyclohex-1-enyl)-2-(4-nitrophenyl)ethanone (4v).** IR (KBr) 3023, 2936, 1606, 1560, 712  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (d,  $J = 8.4$  Hz, 2H), 7.53 (d,  $J = 8.8$  Hz, 2H), 7.22–7.42 (m, 10H), 4.50 (s, 2H), 4.03 (s, 2H), 3.66 (s, 2H), 3.48 (s, 2H), 2.86 (t,  $J = 8.0$  Hz, 2H), 1.64–1.66 (m, 2H), 1.27–1.29 (m, 4H), 0.87 (t,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.0, 162.1, 149.5, 147.9, 137.3, 136.5, 129.0,

128.8, 128.3, 127.8, 127.7, 127.4, 126.5, 123.4, 99.5, 69.0, 56.6, 52.1, 31.4, 30.0, 29.4, 29.1, 22.5, 13.9; MS (EI) *m/z* (%): 483, 377, 91, 65, 42; C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>: Calcd. C, 74.51; H, 6.88; N, 8.69; Found: C, 74.29; H, 6.43; N, 8.73.

**General procedure for synthesis of ethyl 1,3,6-triphenyl-1,2,3,4- tetrahydropyrimidine-5-carboxylate via three-component reactions:**

To a stirring mixture of ethyl phenylpropiolate **1a** (1 mmol), aniline (2.4 mmol), AgBF<sub>4</sub> (5% mmol), *L*-proline (5% mmol) and 3 mL DMF were added successively. The mixture was stirred at room temperature for 5 hours. And then, formaldehyde (4 mmol) was added. After completion of the reaction (monitored by TLC), the solution was evaporated to dryness under reduced pressure, and 8 mL of water was added. The aqueous solution was extracted with diethyl ether (3×15 mL), and the combined extract was dried with anhydrous MgSO<sub>4</sub>. Solvent was removed, and the crude product was separated by column chromatography to give a pure sample of **4aj**.

**Ethyl 1,3-bis(4-fluorophenyl)-6-phenyl-1,2,3,4- tetrahydropyrimidine-5- carboxylate (4af).** White solid; m.p. 130–132 °C; IR (KBr) 3053, 2983, 1677, 1580, 1507, 1290, 1103, 833, 766 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 7.12–7.15 (m, 5H), 6.84–6.88 (m, 4H), 6.63–6.68 (m, 4H), 4.86 (s, 2H), 4.27 (s, 2H), 3.90 (q, *J* = 7.2 Hz, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 167.6, 160.9, 158.7, 158.5, 156.3, 154.1, 144.6, 141.9, 136.1, 129.7, 128.4, 128.1, 128.0, 118.9, 118.9, 115.8, 115.5, 115.3, 104.0, 71.5, 49.4, 13.7; MS (EI) *m/z* (%): 421 (M<sup>+</sup>), 391, 297, 224, 198, 95; C<sub>25</sub>H<sub>22</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: Calcd. C, 71.42; H, 5.27; N, 6.66; Found: C, 71.06; H, 5.48; N, 6.63.

**Ethyl 6-phenyl-1,3-di-*p*-tolyl-1,2,3,4- tetrahydropyrimidine-5-carboxylate (4ag).** White solid; m.p. 107–110 °C; IR (KBr) 3062, 2923, 1671, 1565, 1510, 1291, 1105, 819, 763 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 7.11–7.18 (m, 5H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.78–6.84 (m, 4H), 6.60–6.62 (d, *J* = 8.4 Hz, 2H), 4.88 (s, 2H), 4.27 (s, 1H), 3.87 (q, *J* = 7.2 Hz, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 167.8, 154.4, 151.5, 145.9, 136.5, 129.8, 129.6, 129.1, 128.8, 128.3, 128.2, 127.7, 126.3, 117.6, 117.2, 117.0, 103.5, 60.0, 49.2, 20.8, 20.4, 13.6; MS (EI) *m/z* (%): 412 (M<sup>+</sup>), 383, 293, 220, 194, 91, 77, 65, 32; C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: Calcd. C, 78.61; H, 6.84; N, 6.79; Found: C, 79.10; H, 5.48; N, 4.37.

**Ethyl 1,3-bis(4-chlorophenyl)-6-phenyl-1,2,3,4-tetrahydropyrimidine-5- carboxylate (4ah).** White solid; m.p. 153–155 °C; IR (KBr) 3049, 2921, 1679, 1593, 1490, 1286, 1100, 822 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 7.13–7.21 (m, 9H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.59–6.61 (m, 2H), 4.91 (s, 2H), 4.28 (s, 2H), 3.90 (q, *J* = 7.2 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 166.6, 152.6, 145.7, 143.5, 134.9, 129.4, 128.9, 128.2, 127.9, 127.8, 126.8, 126.4, 124.3, 117.0, 104.5, 69.1, 58.9, 48.1, 12.8; MS (EI) *m/z* (%): 452 (M<sup>+</sup>), 423, 313, 267, 240, 214, 206, 138, 111, 75, 65, 51, 32; C<sub>25</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: Calcd. C, 66.23; H, 4.89; N, 6.18; Found: C, 66.56; H, 4.91; N, 6.21.

**Ethyl 1,3-bis(4-bromophenyl)-6-phenyl-1,2,3,4-tetrahydropyrimidine-5- carboxylate (4ai).** White solid; m.p. 143–145 °C; IR (KBr) 3054, 2924, 1685, 1590, 1489, 1379, 1272, 1003, 805, 763 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 7.12–7.21 (m, 7H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 9.2 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 4.91 (s, 2H), 4.28 (s, 2H), 3.93 (q, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 167.4, 153.4, 146.9, 144.9, 135.7, 132.1, 132.0, 131.8, 129.8, 128.8, 128.6, 127.7, 127.6, 118.2, 114.6, 112.4, 105.6, 69.7, 59.8, 48.9, 13.7; MS (EI) *m/z* (%): 542, 540 (M<sup>+</sup>), 357, 286, 260, 206, 184, 155, 115, 77, 55, 32; C<sub>25</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: Calcd. C, 55.37; H, 4.09; N, 5.17; Found: C, 55.09; H, 4.08; N, 5.19.

**Ethyl 1, 3, 6-triphenyl-1, 2, 3, 4-tetrahydropyrimidine-5-carboxylate (4aj).** White solid; m.p. 125–127 °C; IR (KBr) 3059, 2979, 1686, 1595, 1497, 1381, 1033, 753, 695; cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 7.12–7.20 (m, 7H), 6.99–7.03 (m, 2H), 6.83–6.91 (m, 4H), 6.72–6.75 (m, 2H), 4.98 (s, 2H), 4.33 (s, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 167.7, 154.1, 148.1, 145.8, 136.3, 129.9, 129.1, 128.8, 128.6, 128.4, 127.6, 126.3, 124.7, 120.1, 116.7, 104.6, 70.0, 49.0, 13.7; MS (EI) *m/z* (%): 384 (M<sup>+</sup>), 355, 279, 206, 180, 77; C<sub>25</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: Calcd. C, 78.10; H, 6.29; N, 7.29; Found: C, 78.35; H, 6.26; N, 7.32.

**Ethyl 6-phenyl-1,3-bis(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydropyrimidine -5-carboxylate (4ak).** White solid; m.p. 158–160 °C; IR (KBr) 3059, 2988, 1687, 1614, 1326, 1114, 848, 763 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 7.38 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.18–7.23 (m, 5H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.06 (s, 2H), 4.36 (s, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 167.3, 152.7, 150.0, 148.7, 135.4, 129.8, 129.1, 128.9, 128.6, 127.9, 126.8, 126.5, 126.0, 125.2, 114.8,

107.9, 68.2, 60.1, 48.5, 13.7; MS (EI)  $m/z$  (%): 520, 491, 347, 274, 248, 173, 145, 77, 29;  $C_{27}H_{22}N_2O_2$ : Calcd. C, 62.31; H, 4.26; N, 5.38; Found: C, 62.08; H, 4.25; N, 5.36.

**Ethyl 1,3-bis(4-methoxyphenyl)-6-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4al).** White solid; m.p. 114–116 °C; IR (KBr) 3053, 2928, 1666, 1574, 1505, 1366, 1279, 1232, 1114, 826  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.13 (s, 5H), 6.91 (d,  $J = 7.2$  Hz, 2H), 6.78 (d,  $J = 8.8$  Hz, 2H), 6.62 (d,  $J = 9.2$  Hz, 2H), 6.52 (d,  $J = 8.8$  Hz, 2H), 4.84 (s, 2H), 4.27 (s, 2H), 3.89 (q,  $J = 7.2$  Hz, 2H), 3.75 (s, 3H), 3.64 (s, 3H), 0.86 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.9, 155.8, 153.9, 153.3, 141.5, 138.0, 135.7, 128.8, 127.1, 126.5, 118.4, 113.6, 112.8, 101.4, 58.4, 54.7, 54.3, 48.7, 12.9; MS (EI)  $m/z$  (%): 444 ( $M^+$ ), 309 (100), 294, 248, 236, 210, 135, 120, 92, 77, 43, 32;  $C_{27}H_{28}N_2O_2$ : Calcd. C, 72.95; H, 6.35; N, 6.30; Found: C, 73.29; H, 6.38; N, 6.28.

**Ethyl 6-phenyl-1,3-di-*o*-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4am).** White solid; m.p. 141–154 °C; IR (KBr) 3055, 2978, 1689, 1604, 1490, 1369, 1100, 761, 731  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  6.95–7.21 (m, 10H), 6.80–6.82 (m, 1H), 6.72–6.74 (m, 1H), 6.56–6.58 (m, 1H), 4.58 (d,  $J = 7.2$  Hz, 1H), 4.36 (d,  $J = 7.2$  Hz, 1H), 4.24 (d,  $J = 16.0$  Hz, 1H), 4.05 (d,  $J = 16.0$  Hz, 1H), 3.89 (q,  $J = 7.2$  Hz, 2H), 2.24 (s, 3H), 2.11 (s, 3H), 0.86 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  167.6, 155.1, 148.1, 144.2, 136.7, 134.3, 132.8, 131.2, 130.4, 129.3, 129.1, 128.2, 127.6, 127.4, 127.2, 126.5, 125.9, 125.7, 123.9, 120.5, 103.4, 70.6, 59.3, 51.3, 18.2, 18.0, 13.8; MS (EI)  $m/z$  (%): 412 ( $M^+$ ), 383, 293, 264, 220, 194, 118, 91, 65, 32;  $C_{27}H_{28}N_2O_2$ : Calcd. C, 78.61; H, 6.84; N, 6.79; Found: C, 79.09; H, 6.87; N, 6.81.

**Methyl 6-pentyl-1,3-di-*o*-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4bm).** Yellowish viscous oil; IR (KBr) 3047, 2928, 1672, 1612, 1529, 1360, 1237, 763  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  6.98–7.18 (m, 7H), 6.73 (d,  $J = 7.6$  Hz, 1H), 4.41 (d,  $J = 11.6$  Hz, 1H), 4.31 (d,  $J = 11.6$  Hz, 1H), 4.07 (d,  $J = 3.2$  Hz, 2H), 3.69 (s, 3H), 2.74–2.78 (m, 1H), 2.20–2.47 (m, 1H), 2.18 (s, 3H), 2.05 (s, 3H), 1.33–1.39 (m, 2H), 1.02–1.09 (m, 4H), 0.71 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  167.5, 159.7, 148.7, 142.7, 136.2, 132.3, 131.1, 130.9, 128.8, 127.3, 126.7, 126.4, 123.7, 121.0, 95.1, 50.6, 50.5, 31.8, 30.2, 28.4, 22.0, 18.1, 17.7, 13.8; MS (EI)  $m/z$  (%): 392, 377, 273, 202, 186, 118, 91, 65;  $C_{25}H_{32}N_2O_2$ : Calcd. C, 76.49; H, 8.22; N, 7.14; Found: C, 76.82; H, 8.19; N, 6.92.

**Ethyl 1,3-bis(4-fluorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4cf).** White solid; m.p. 115–116 °C; IR (KBr) 3049, 2973, 1666, 1621, 1510, 1239, 1102, 816  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.72 (s, 1H), 6.87–7.05 (m, 8H), 4.91 (s, 2H), 4.15–4.20 (m, 4H), 1.26 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.8, 160.0, 159.0, 158.156.6, 145.1, 140.7, 140.5, 120.0, 119.9, 119.8, 116.6, 116.3, 115.8, 115.6, 99.7, 66.0, 59.7, 47.8, 14.5; MS (EI)  $m/z$  (%): 344, 315, 221, 192, 148, 122, 95, 55, 29;  $C_{19}H_{18}F_2N_2O_2$ : Calcd. C, 66.27; H, 5.27; N, 8.14; Found: C, 65.96; H, 5.29; N, 8.18.

**Ethyl 1,3-dip-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4cg).** White solid; m.p. 114–116 °C; IR (KBr) 3024, 2918, 1673, 1620, 1514, 1243, 1102, 803  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.79 (s, 1H), 7.15 (d,  $J = 8.0$  Hz, 2H), 7.01 (d,  $J = 8.0$  Hz, 2H), 6.90 (d,  $J = 8.8$  Hz, 2H), 6.84 (d,  $J = 8.0$  Hz, 2H), 4.97 (s, 2H), 4.22 (s, 2H), 4.15–4.22 (m, 4H), 2.33 (s, 3H), 2.34 (s, 3H), 1.27 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.0, 145.6, 141.0, 139.6, 132.4, 129.6, 129.2, 128.8, 117.2, 117.1, 98.2, 64.1, 58.5, 46.8, 19.8, 19.6, 13.7; MS (EI)  $m/z$  (%): 336, 307, 217, 188, 144, 118, 91, 65, 29;  $C_{21}H_{24}N_2O_2$ : Calcd. C, 74.97; H, 7.19; N, 8.33; Found: C, 75.31; H, 7.23; N, 8.37.

**Ethyl 1,3-bis(4-chlorophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4ch).** White solid; m.p. 132–134 °C; IR (KBr) 3059, 2975, 1683, 1606, 1489, 1233, 1103, 810  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.74 (s, 1H), 7.29–7.32 (m, 2H), 7.14–7.16 (m, 2H), 6.89–6.91 (m, 2H), 6.80–6.82 (m, 2H), 4.96 (s, 2H), 4.17–4.23 (m, 4H), 1.28 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  165.6, 146.3, 141.8, 138.7, 128.9, 128.6, 128.3, 128.1, 125.3, 118.2, 118.0, 99.8, 63.7, 58.9, 46.6, 13.6; MS (EI)  $m/z$  (%): 376 ( $M^+$ ), 347, 237 (100), 208, 164, 138, 111, 75, 55;  $C_{19}H_{18}Cl_2N_2O_2$ : Calcd. C, 60.49; H, 4.81; N, 7.43; Found: C, 60.18; H, 4.79; N, 7.46.

**Ethyl 1,3-bis(4-bromophenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4ci).** White solid; m.p. 133–135 °C; IR (KBr) 3043, 2963, 1682, 1610, 1490, 1231, 1103, 811  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.73 (s, 1H), 7.45 (d,  $J = 8.8$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 6.84 (d,  $J = 8.8$  Hz, 2H), 6.75 (d,  $J = 8.8$  Hz, 2H), 4.95 (s, 2H), 4.17–4.22 (m, 4H), 1.28 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.5, 147.7, 143.1, 139.5, 132.7, 132.1, 119.5, 119.1, 116.5, 113.5, 100.9, 64.4, 59.8, 47.5, 14.6; MS (EI)  $m/z$  (%): 466, 464 ( $M^+$ ), 437, 281, 252, 210, 182, 157, 130, 76, 55, 29;  $C_{19}H_{18}Br_2N_2O_2$ : Calcd. C, 48.95; H, 3.89; N, 6.01; Found: C, 49.71; H, 3.90; N, 6.04.

**Ethyl 1,3-diphenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4cj).** White solid; m.p. 100–103 °C; IR (KBr) 3062, 2976, 1680, 1623, 1594, 1497, 1245, 1101, 749  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.83 (s, 1H),

7.44–7.36 (m, 10H), 5.04 (s, 2H), 4.26 (s, 2H), 4.20 (q,  $J = 7.2$  Hz, 2H), 1.28 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  166.0, 147.9, 143.3, 139.3, 128.8, 128.3, 122.7, 120.2, 116.9, 116.8, 99.2, 63.6, 58.7, 46.6, 13.7; MS (EI)  $m/z$  (%): 308, 280, 241, 203, 174, 130, 104, 77, 55;  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$ : Calcd. C, 74.00; H, 6.54; N, 9.08; Found: C, 74.37; H, 6.51; N, 9.12.

**Ethyl 1,3-bis(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4ck).** White solid; m.p. 127–129 °C; IR (KBr) 3051, 2986, 1704, 1609, 1524, 1331, 1232, 1114, 826  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  7.81 (s, 1H), 7.63 (d,  $J = 8.4$  Hz, 2H), 7.43 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 5.10 (s, 2H), 4.31 (s, 2H), 4.20 (q,  $J = 7.2$  Hz, 2H), 1.28 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  166.2, 151.0, 146.3, 138.7, 127.2, 126.7, 116.7, 102.7, 63.1, 60.1, 47.3, 14.5; MS (EI)  $m/z$  (%): 444 ( $\text{M}^+$ ), 415, 371, 271, 242, 226, 198, 172, 145, 130, 95, 55, 29;  $\text{C}_{21}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_2$ : Calcd. C, 56.76; H, 4.08; N, 6.30; Found: C, 56.48; H, 4.09; N, 6.32.

**(1,2,3,4-Tetrahydro-1,3,6-triphenylpyrimidin-5-yl)(phenyl)methanone (4dj).** IR (KBr) 3028, 1602, 1527, 726  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  7.43 (d,  $J = 7.2$  Hz, 2H), 6.78–7.16 (m, 13H), 5.13 (s, 2H), 4.48 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  197.0, 153.9, 147.9, 146.3, 140.1, 135.5, 131.1, 130.5, 129.1, 128.9, 128.6, 127.5, 127.3, 125.9, 124.5, 119.8, 116.6, 116.2, 70.3, 49.5; MS (EI)  $m/z$  (%): 416, 341, 105, 77, 65;  $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}$ : Calcd. C, 83.63; H, 5.81; N, 6.73; Found: C, 83.75; H, 5.78; N, 6.71.

**(1,3-Bis(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-6-phenylpyrimidin-5-yl)(phenyl)methanone (4do).** IR (KBr) 3027, 1576, 1482, 721  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  7.48 (d,  $J = 7.6$  Hz, 2H), 7.09 (d,  $J = 4.4$  Hz, 1H), 6.62–7.08 (m, 13H), 5.07 (s, 2H), 4.43 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  196.6, 151.7, 147.0, 145.7, 139.0, 134.6, 133.0, 131.2, 130.7, 130.6, 130.4, 129.5, 129.2, 128.9, 128.5, 128.1, 128.0, 127.9, 127.5, 127.1, 124.8, 118.0, 117.5, 115.3, 69.4, 49.4; MS (EI)  $m/z$  (%): 554, 552, 350, 352, 105, 77, 51;  $\text{C}_{29}\text{H}_{20}\text{Cl}_4\text{N}_2\text{O}$ : Calcd. C, 62.84; H, 3.64; N, 5.05; Found: C, 62.42; H, 3.65; N, 5.09.

**(1,3-Bis(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-6-phenylpyrimidin-5-yl)(thiophen-2-yl)methanone (4eo).** IR (KBr) 3035, 1598, 1507, 736  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  6.50–7.33 (m, 14H), 5.03 (s, 2H), 4.38 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  188.5, 149.4, 147.0, 145.7, 144.6, 134.8, 133.2, 133.0, 132.9, 132.7, 130.6, 130.4, 129.5, 128.4, 128.3, 127.1, 126.9, 124.7, 123.0, 119.3, 117.4, 115.3, 69.56, 49.2; MS (EI)  $m/z$  (%): 558, 345, 174, 161, 111, 77, 63;  $\text{C}_{27}\text{H}_{18}\text{Cl}_4\text{N}_2\text{OS}$ : Calcd. C, 57.88; H, 3.24; N, 5.00; Found: C, 57.69; H, 3.28; N, 5.10.

**(Z)-Ethyl 3-(benzylamino)-3-phenylacrylate (3a).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  8.91 (s, 1H), 7.16–7.40 (m, 10H), 4.67 (s, 1H), 4.26 (d,  $J = 6.4$  Hz, 2H), 4.15 (q,  $J = 7.2$  Hz, 2H), 1.27 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  170.3, 164.7, 139.2, 135.9, 129.3, 128.6, 128.4, 127.9, 127.2, 126.8, 86.2, 58.8, 48.3, 14.6.

**(Z)-Ethyl 3-phenyl-3-(phenylamino)acrylate (3c).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  10.32 (s, 1H), 7.26–7.36 (m, 5H), 7.07 (t,  $J = 6.0$  Hz, 2H), 6.91 (t,  $J = 4.0$  Hz, 1H), 6.67 (d,  $J = 8.0$  Hz, 2H), 5.01 (s, 1H), 4.22 (q,  $J = 8.0$  Hz, 2H), 1.32 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  170.1, 159.1, 140.5, 136.0, 131.6, 129.4, 129.0, 128.7, 128.6, 128.4, 128.2, 122.9, 122.2, 115.2, 92.1, 59.3, 14.5; MS (EI)  $m/z$  (%): 267, 222, 193, 180, 165, 105, 77.

**(Z)-Ethyl 3-(4-chlorophenylamino)-3-phenylacrylate (3d).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  10.25 (s, 1H), 7.28–7.34 (m, 5H), 7.00 (d,  $J = 8.0$  Hz, 2H), 6.55 (d,  $J = 8.0$  Hz, 2H), 5.00 (s, 1H), 4.19 (q,  $J = 8.0$  Hz, 2H), 1.30 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  170.1, 158.6, 139.1, 135.5, 129.6, 128.7, 128.6, 128.1, 123.2, 91.9, 59.4, 14.5; MS (EI)  $m/z$  (%): 301, 299, 297, 270, 214, 77.

**(Z)-Ethyl 3-(4-fluorophenylamino)-3-phenylacrylate (3e).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  10.22 (s, 1H), 7.26–7.33 (m, 5H), 6.74–6.78 (m, 4H), 6.60–6.64 (m, 4H), 4.98 (s, 1H), 4.19 (q,  $J = 8.0$  Hz, 2H), 1.29 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  170.2, 160.1, 159.3, 136.5, 135.6, 129.4, 128.7, 128.2, 124.0, 115.4, 115.2, 90.9, 59.3, 14.5; MS (EI)  $m/z$  (%): 285, 211, 198, 95, 77.

**(Z)-Ethyl 3-(*p*-tolylamino)-3-phenylacrylate (3f).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  10.25 (s, 1H), 7.26–7.33 (m, 5H), 6.85–6.87 (d,  $J = 8.0$  Hz, 2H), 6.54–6.56 (d,  $J = 8.0$  Hz, 2H), 4.95 (s, 1H), 4.19 (q,  $J = 8.0$  Hz, 2H), 2.19 (s, 3H), 1.30 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  170.1, 159.4, 137.7, 136.0, 132.6, 129.3, 129.1, 128.5, 128.3, 128.2, 122.3, 90.3, 59.2, 20.6, 14.5; MS (EI)  $m/z$  (%): 281, 235, 223, 105, 77.

**(Z)-Ethyl 3-(4-bromophenylamino)-3-phenylacrylate (3g).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $d$  10.24 (s, 1H), 7.28–7.34 (m, 5H), 7.15 (d,  $J = 8.0$  Hz, 2H), 6.49 (d,  $J = 8.0$  Hz, 2H), 5.01 (s, 1H), 4.19 (q,  $J = 8.0$  Hz, 2H), 1.30 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $d$  170.0, 158.5, 139.5, 135.5, 133.7, 132.0, 131.6, 129.6, 128.7, 128.1, 123.5, 92.1, 59.4, 14.5; MS (EI)  $m/z$  (%): 345, 285, 205, 204, 105, 77.



**(Z)-Ethyl 3-(4-(trifluoromethyl)phenylamino)-3-phenylacrylate (3h).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 10.37 (s, 1H), 7.28–7.39 (m, 7H), 6.65 (d, *J* = 8.0 Hz, 2H), 5.09 (s, 1H), 4.20 (q, *J* = 8.0 Hz, 2H), 1.31 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 169.8, 157.7, 143.6, 135.4, 129.3, 128.5, 128.2, 126.6, 125.8, 124.5, 93.7, 60.3, 46.0, 14.3; MS (EI) *m/z* (%): 335, 290, 261, 248, 161, 105, 77.

**(Z)-Ethyl 3-(4-methoxyphenylamino)-3-phenylacrylate (3i).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 10.20 (s, 1H), 7.22–7.30 (m, 5H), 6.61 (s, 4H), 4.92 (s, 1H), 4.18 (q, *J* = 8.0 Hz, 2H), 3.68 (s, 3H) 1.30 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 170.3, 159.9, 155.8, 136.0, 133.4, 129.2, 128.3, 124.2, 113.8, 89.5, 59.1, 55.3, 14.5; MS (EI) *m/z* (%): 297, 281, 207, 105, 77.

**(Z)-Ethyl 3-(*o*-tolylamino)-3-phenylacrylate (3j).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 10.13 (s, 1H), 7.25–7.29 (m, 5H), 7.11(d, *J* = 8.0 Hz, 1H), 6.77–6.84 (m, 2H), 6.31(d, *J* = 8.0 Hz, 1H), 5.02 (s, 1H), 4.20 (q, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.31 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 170.3, 159.8, 139.0, 136.1, 130.4, 129.3, 128.5, 128.3, 128.

**(Z)-Ethyl 3-(naphthalen-1-ylamino)-3-phenylacrylate (3k).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 10.07 (s, 1H), 8.34 (d, *J* = 12.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.47–7.60 (m, 3H), 7.17–7.33 (m, 5H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.51(d, *J* = 8.0 Hz, 1H), 5.20 (s, 1H), 4.26 (q, *J* = 8.0 Hz, 2H), 1.36 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 170.4, 160.4, 136.3, 136.1, 134.1, 129.3, 128.4, 128.3, 127.9, 126.3, 125.1, 124.0, 122.0, 121.1, 91.8, 59.4, 14.5; MS (EI) *m/z* (%): 317, 281, 249, 207, 143, 115, 105, 77.

**(Z)-Ethyl 3-(4-bromophenylamino)acrylate (3l).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 9.87–9.90 (d, *J* = 12 Hz, 1H), 7.34–7.38 (m, 2H), 7.12–7.17 (m, 1H), 4.84 (d, *J* = 8.4 Hz, 1H), 4.15 (q, *J* = 6.8 Hz, 2H), 1.27 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 170.3, 142.4, 139.8, 132.5, 116.8, 114.7, 88.3, 59.4, 14.4; MS (EI) *m/z* (%): 269, 223, 225, 145, 116, 76, 63.

**(Z)-3-(3,4-Dichlorophenylamino)-3-phenyl-1-*p*-tolylprop-2-en-1-one (3m).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *d* 12.78 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.38–7.41 (m, 5H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.53–6.56 (m, 1H), 6.13 (s, 1H), 2.41 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) *d* 190.1, 160.1, 142.3, 139.4, 136.8, 135.2, 132.5, 130.1, 130.0, 129.1, 128.8, 128.2, 127.4, 127.2, 124.2, 121.9, 98.2, 21.5.