Supporting Information

L-Proline-Catalyzed Synthesis of Highly Functionalized Multisubstituted 1,4-Dihydropyridines

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General

Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, of the chloroform solvent with TMS as the internal standard. IR spectra were obtained either 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 spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. The alkynones were prepared by the Sonagashira couplings between acyl chlorides and terminal alkynes. All the other chemicals were purchased from Aldrich Chemicals.

General procedure for the synthesis of 1,4-Dihydropyridine 5 (A).

Amine **2** (1.0 mmol) was added to a stirring solution of alkyne **1** (1.0 mmol) in ethanol (3 mL). After the mixture was stirred at room temperature for 30 min, *β*-dicarbonyl compound **3** (1.5 mmol), aldehyde **4** (1.2 mmol) and L-proline (12 mg, 10 mol%) were added successively, and continued stirring for another

12h. The progress of the reaction was followed by TLC. After completion of the reaction, the solvent was removed under reduced pressure, then the mixture was diluted with water and extracted with diethyl ether (15 mL × 3). The organic phase was washed with saturated brine, and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by silica gel chromatography (petroleum ether / ethyl acetate = 2:1) to afford the products **5aaaa-5ajaa, 5baaa-5gkaa, 5bkca** and **5bkab** in 62-86% yields.

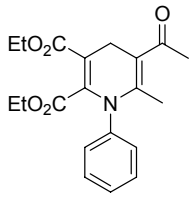
General procedure for the synthesis of 1,4-Dihydropyridine 5 (B).

Amine **2** (1.0 mmol) was added to a stirring solution of alkyne **1** (1.0 mmol) in ethanol (3 mL). After the mixture was stirred at room temperature for 30 min, ethyl acetoacetate **3b** (260mg, 2.0 mmol), 35% formaldehyde **4a** (103 mg, 1.2 mmol) and L-proline (12 mg, 10 mol%) were added successively, and continued stirring for another 12h. The progress of the reaction was followed by TLC. After completion of the reaction, the solvent was removed under reduced pressure, then the mixture was diluted with water and extracted with diethyl ether (15 mL × 3). The organic phase was washed with saturated brine, and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by silica gel chromatography (petroleum ether / ethyl acetate = 4:1) to afford the products **5aaba, 5acba, 5alba** and **5bkba** in 64-71% yields.

General procedure for the synthesis of 1,4-Dihydropyridine 5 (C).

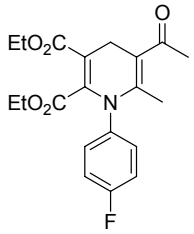
30% methanamine **2k** (103mg, 1.0 mmol) was added to a stirring solution of alkynone **1b** (206mg, 1.0 mmol) in ethanol (3 mL). After the mixture was stirred at room temperature for 30 min, acetylacetone **3a** (150mg, 1.5 mmol), 4-nitrobenzaldehyde **4c** (181 mg, 1.2 mmol) and L-proline (12 mg, 10 mol%) were added successively, and continued stirring for another 24h at 50℃. The progress of the reaction was followed by TLC. After completion of the reaction, the solvent was removed under reduced pressure, then the mixture was diluted with water and extracted with diethyl ether (15 mL × 3).The organic phase was washed with saturated brine, and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by silica gel chromatography (petroleum ether / ethyl acetate = 2:1) to afford the product **5bkac** in 67% yield.

(1) Diethyl 5-acetyl-1,4-dihydro-6-methyl-1-phenylpyridine-2,3-dicarboxylate (5aaaa)



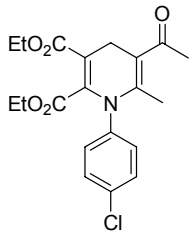
Yellow oil; IR (KBr): V_{max} = 2992, 1765, 1699, 1458, 1376, 1243, 1107, 1055 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$):δ = 7.32-7.30(m, 3H), 7.18-7.16(m, 2H), 4.11(q, *J* = 7.2Hz, 2H), 3.75(q, *J* = 7.2Hz, 2H), 3.43(s, 2H), 2.19(s, 3H), 1.78(s, 3H), 1.18 (t, *J* = 7.2Hz, 3H), 0.87 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 165.9, 163.8, 145.9, 143.7, 138.6, 130.9, 129.1, 129.0, 110.0, 101.5, 61.5, 60.6, 30.0, 24.9,18.0, 14.2,13.4; EI-MS: m/z = 357(M^+, 8), 314(37), 268(45), 240(61), 168(34), 28(100); Anal. Calcd for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49; N, 3.92; Found: C, 67.43; H, 6.58; N, 4.01.

(2) Diethyl 5-acetyl-1-(4-fluorophenyl)-1,4-dihydro-6-methylpyridine-2,3-dicarboxylate (5abaa)



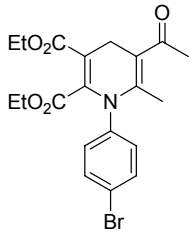
Yellow oil; IR (KBr): V_{max} = 2991, 1740, 1699, 1456, 1372, 1245, 1114, 1053 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.14(m, 2H), 7.02-6.98(m, 2H), 4.11(q, *J* = 7.2Hz, 2H), 3.80(q, *J* = 7.2Hz, 2H), 3.41(s, 2H), 2.19(s, 3H), 1.77(s, 3H), 1.18 (t, *J* = 7.2Hz, 3H), 0.93 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 165.7, 163.7, 161.3, 145.4, 143.6, 134.6, 132.8,132.7, 116.1, 115.9, 110.4, 101.9, 61.7, 60.7, 29.9, 24.9, 17.9, 14.2,13.4; EI-MS: m/z = 375(M^+, 18), 332(62), 286(73), 258(100), 186(56); Anal. Calcd for $C_{20}H_{22}FNO_5$: C, 63.99; H, 5.91; N, 3.73; Found: C, 63.82; H, 6.03; N, 3.68.

(3) Diethyl 5-acetyl-1-(4-chlorophenyl)-1,4-dihydro-6-methylpyridine-2,3-dicarboxylate (5acaa)



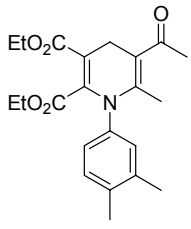
Yellow oil; IR (KBr): V_{max} = 2984, 1766, 1698, 1489, 1373, 1244, 1112, 1053 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.28(m, 2H), 7.13-7.11(m, 2H), 4.11(q, *J* = 7.2Hz, 2H), 3.81(q, *J* = 7.2Hz, 2H), 3.41(s, 2H), 2.19(s, 3H), 1.77(s, 3H), 1.19 (t, *J* = 7.2Hz, 3H), 0.93 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 165.7, 163.7, 145.2, 143.3, 137.1, 135.2, 132.2, 129.3, 110.4, 101.9, 61.7, 60.7, 30.0, 24.8, 18.0, 14.2, 13.4; EI-MS: m/z = 391(M^+, 14), 348(28), 302(23), 274(24), 202(17), 28(100); Anal. Calcd for $C_{20}H_{22}ClNO_5$: C, 61.30; H, 5.66; N, 3.57; Found: C, 61.08; H, 5.81; N, 3.49.

(4) Diethyl 5-acetyl-1-(4-bromophenyl)-1,4-dihydro-6-methylpyridine-2,3-dicarboxylate (5adaa)



Yellow oil; IR (KBr): V_{max} = 2991, 1765, 1699, 1458, 1375, 1244, 1108, 1054 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.44(m, 2H), 7.06-7.04(m, 2H), 4.11(q, *J* = 7.2Hz, 2H), 3.81(q, *J* = 7.2Hz, 2H), 3.41(s, 2H), 2.19(s, 3H), 1.77(s, 3H), 1.18 (t, *J* = 7.2Hz, 3H), 0.93 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.4, 165.7, 163.7, 145.1, 143.3, 137.7, 132.5, 132.3, 123.3, 110.5, 102.0, 61.7, 60.7, 29.9, 24.9, 18.0, 14.2, 13.4; EI-MS: m/z = 435(M^+, 17), 392(41), 318(62), 246(21), 28(100); Anal. Calcd for $C_{20}H_{22}BrNO_5$: C, 55.06; H, 5.08; N, 3.21; Found: C, 55.24; H, 5.16; N, 3.07.

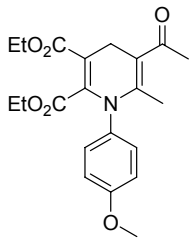
(5) Diethyl 5-acetyl-1,4-dihydro-6-methyl-1-(3,4-dimethylphenyl)pyridine-2,3-dicarboxylate (5aeaa)



Yellow oil; IR (KBr): V_{max} = 2992, 1766, 1699, 1457, 1376, 1244, 1108, 1057 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05-7.03(d, *J* = 8Hz, 1H), 6.92-6.86(m, 2H), 4.10(q, *J* = 7.2Hz, 2H), 3.79(q, *J* = 7.2Hz, 2H), 3.41(s, 2H), 2.18(s, 6H), 2.17(s, 3H), 1.79(s, 3H), 1.18 (t, *J* = 7.2Hz, 3H), 0.90 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 165.9, 163.8, 146.4, 143.9, 137.8, 137.5, 136.0,

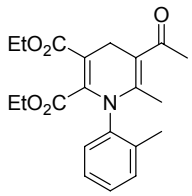
131.5, 130.0, 127.9, 109.7, 101.2, 61.4, 60.6, 30.0, 24.9, 19.6, 19.4, 18.0, 14.2,13.4; EI-MS: m/z = 385(M^+, 25), 342(17), 296(12), 268(34), 196(9), 28(100); Anal. Calcd for $C_{22}H_{27}NO_5$: C, 68.55; H, 7.06; N, 3.63; Found: C, 68.42; H, 7.12; N, 3.56.

(6) Diethyl 5-acetyl-1,4-dihydro-1-(4-methoxyphenyl)-6-methylpyridine-2,3-dicarboxylate (5afaa)



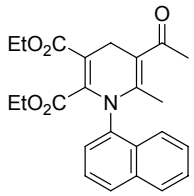
Yellow oil; IR (KBr): V_{max} = 2992, 1767, 1698, 1472, 1376, 1243, 1107, 1054 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.13-7.11(m, 2H), 6.86-6.84(m, 2H), 4.15(q, *J* = 7.2Hz, 2H), 3.85(q, *J* = 7.2Hz, 2H), 3.79(s, 3H), 3.47(s, 2H), 2.24(s, 3H), 1.83(s, 3H), 1.23 (t, *J* = 7.2Hz, 3H), 0.98 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 165.9, 163.8, 159.8, 146.5, 144.1, 131.9, 131.1, 114.1, 110.0, 101.4, 61.5, 60.6, 55.5, 29.5, 24.9, 17.9, 14.2,13.5; EI-MS: m/z = 387(M^+, 22), 344(46), 298(73), 270(100), 198(33); Anal. Calcd for $C_{21}H_{25}NO_6$: C, 65.10; H, 6.50; N, 3.62; Found: C, 65.36; H, 6.64; N, 3.51.

(7) Diethyl 5-acetyl-1,4-dihydro-6-methyl-1-*o*-tolylpyridine-2,3-dicarboxylate (5agaa)



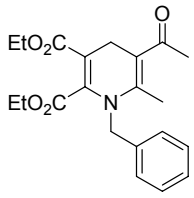
Yellow oil; IR (KBr): V_{max} = 2991, 1766, 1698, 1458, 1375, 1244, 1108, 1056 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.15(m, 4H), 4.18(q, *J* = 7.2Hz, 2H), 3.85-3.75(m, 2H), 3.53(q, *J* = 17.6Hz, 2H), 2.31(s, 3H), 1.81(s, 3H), 2.27(s, 3H), 1.26 (t, *J* = 7.2Hz, 3H), 0.92 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 166.0, 163.6, 145.9, 143.4, 138.9, 137.3, 131.3, 130.8, 129.5, 126.5, 109.7, 101.6, 61.5, 60.7, 30.1, 25.0, 17.7, 17.3, 14.2,13.4; EI-MS: m/z = 371(M^+, 32), 328(37), 282(87), 254(100), 182(31); Anal. Calcd for $C_{21}H_{25}NO_5$: C, 67.91; H, 6.78; N, 3.77; Found: C, 68.06; H, 6.64; N, 3.85.

(8) Diethyl 5-acetyl-1,4-dihydro-6-methyl-1-(naphthalen-1-yl)pyridine-2,3-dicarboxylate (5ahaa)



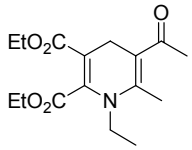
Yellow oil; IR (KBr): V_{max} = 2991, 1764, 1698, 1457, 1375, 1244, 1111, 1053 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02-8.00(d, *J* = 8Hz, 1H), 7.90-7.87(m, 2H), 7.62-7.42(m, 4H), 4.18(q, *J* = 7.2Hz, 2H), 3.64(q, *J* = 17.6Hz, 2H), 3.62-3.51(m, 2H), 2.31(s, 3H), 1.79(s, 3H), 1.24 (t, *J* = 7.2Hz, 3H), 0.48 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 165.9, 163.6, 146.5, 144.1, 134.9, 134.0, 132.3, 129.9, 129.5, 128.2, 127.6, 126.8, 124.9, 123.0, 109.9, 101.8, 61.2, 60.7, 30.2, 25.1, 17.3, 14.2,12.9; EI-MS: m/z = 407(M^+, 14), 364(29), 318(32), 290(25), 218(53), 28(100); Anal. Calcd for $C_{24}H_{25}NO_5$: C, 70.74; H, 6.18; N, 3.44; Found: C, 70.98; H, 6.27; N, 3.35.

(9) Diethyl 5-acetyl-1-benzyl-1,4-dihydro-6-methylpyridine-2,3-dicarboxylate (5aiaa)



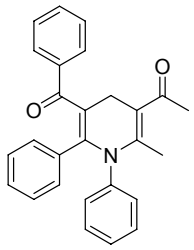
Yellow oil; IR (KBr): V_{max} = 2992, 1765, 1698, 1459, 1376, 1243, 1112, 1056 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.22(m, 5H), 4.62(s, 2H), 4.20-4.13(m, 4H), 3.36(s, 2H), 2.23(s, 3H), 2.19(s, 3H), 1.26 (t, *J* = 7.2Hz, 3H), 1.13 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.4, 165.7, 164.8, 146.4, 144.5, 137.2, 128.8, 127.6, 126.0, 111.7, 102.7, 62.1, 60.7, 50.4, 30.0, 24.6, 15.9, 14.2, 13.5; EI-MS: m/z = 371(M^+, 12), 328(39), 282(32), 254(46), 192(45), 28(100); Anal. Calcd for $C_{21}H_{25}NO_5$: C, 67.91; H, 6.78; N, 3.77; Found: C, 67.82; H, 6.85; N, 3.84.

(10) Diethyl 5-acetyl-1-ethyl-1,4-dihydro-6-methylpyridine-2,3-dicarboxylate (5ajaa)



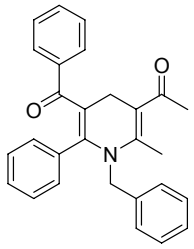
Yellow oil; IR (KBr): V_{max}= 2992, 1766, 1700, 1457, 1376, 1243, 1099, 1056 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.34(q, *J* = 7.2Hz, 2H), 4.16(q, *J* = 7.2Hz, 2H), 3.42(q, *J* = 17.6Hz, 2H), 3.29(s, 2H), 2.24(s, 3H), 2.22(s, 3H), 1.36 (t, *J* = 7.2Hz, 3H), 1.25 (t, *J* = 7.2Hz, 3H), 1.20 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 165.8, 165.0, 145.6, 144.0, 111.5, 102.3, 62.2, 60.6, 42.0, 30.0, 24.5, 16.0, 15.5, 14.2, 13.8; EI-MS: m/z = 309(M^+, 19), 266(44), 220(41), 192(61), 120(22), 28(100); Anal. Calcd for $C_{16}H_{23}NO_5$: C, 62.12; H, 7.49; N, 4.53; Found: C, 62.29; H, 7.62; N, 4.45.

(11) 5-Acetyl-3-benzoyl-1,4-dihydro-1, 2-diphenyl-6-methylpyridine (5baaa)



Reddish brown oil; IR (KBr): V_{max} = 2923, 2852, 1740, 1640, 1457, 1108, 939, 533 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.50(m, 2H), 7.27-7.01(m, 8H), 6.86-6.77(m, 5H), 3.70(s, 2H), 2.30(s, 3H), 2.07(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 198.0, 148.6, 147.3, 140.7, 138.9, 134.3, 131.3, 131.1, 131.0, 128.7, 128.6, 128.1, 127.6, 127.2, 114.2, 110.1, 30.1, 28.0, 18.7; EI-MS: m/z = 393(M^+, 21), 350(9), 316(14), 288(12), 245(11) 28(100); Anal. Calcd for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56; Found: C, 82.23; H, 5.99; N, 3.48.

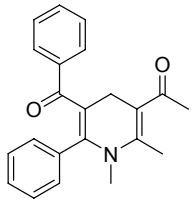
(12) 5-Acetyl-3-benzoyl-1-benzyl-1,4-dihydro-6-methyl-2-phenylpyridine (5biaa)



Reddish brown oil; IR (KBr): V_{max} = 2921, 2853, 1739, 1649, 1459, 1103, 941, 530 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.41(m, 2H), 7.29-7.03(m, 13H), 4.54(s, 2H), 3.45(s, 2H), 2.42(s, 3H), 2.27(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.1, 197.0, 151.2, 149.3, 139.2, 138.2, 133.8, 131.0, 130.6, 129.4, 128.9, 128.8, 128.2, 127.5, 126.2, 113.3, 50.8, 30.2, 27.3,16.2; EI-MS: m/z = 407(M^+, 6),

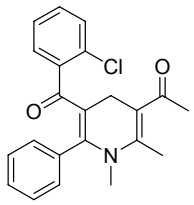
364(12), 316(42), 269(33), 91(100); Anal. Calcd for $C_{28}H_{25}NO_2$: C, 82.53; H, 6.18; N, 3.44; Found: C, 82.74; H, 6.33; N, 3.37.

(13) 5-Acetyl-3-benzoyl-1,4-dihydro-1,6-dimethyl-2-phenylpyridine (5bkaa)



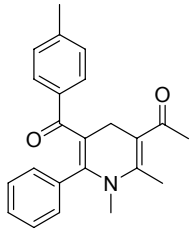
Reddish brown oil; IR (KBr): V_{max} = 2923, 2853, 1740, 1645, 1456, 1110, 938, 530 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.32(m, 2H), 7.11-6.96(m, 8H), 3.34(s, 2H), 2.86(s, 3H), 2.43(s, 3H), 2.22(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 196.5, 151.2, 150.1, 139.3, 133.6, 130.7, 130.3, 129.1, 128.7, 127.9, 127.3, 111.8, 110.5, 36.3, 29.9, 27.0, 15.9; EI-MS: m/z = 331(M^+, 26), 288(21), 254(37), 226(25), 183(17), 28(100); Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23; Found: C, 79.87; H, 6.46; N, 4.19.

(14) 5-Acetyl-1,4-dihydro-1,6-dimethyl-3-(2-chlorobenzoyl)-2-phenylpyridine (5ckaa)



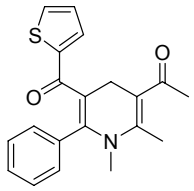
Reddish brown solid; m.p.:145-147℃; IR (KBr): V_{max} = 2921, 2851, 1738, 1652, 1466, 1088, 941, 528 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.06-6.84(m, 9H), 3.47(s, 2H), 2.82(s, 3H), 2.43(s, 3H), 2.35(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.2, 193.4, 155.5, 147.9, 141.0, 133.5, 130.8, 129.8, 129.4, 129.2, 128.1, 125.5, 112.4, 111.5, 36.3, 30.0, 25.3, 15.8; EI-MS: m/z = 365(M^+, 10), 322(8), 288(16), 139(15), 28(100); Anal. Calcd for $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51; N, 3.83; Found: C, 72.31; H, 5.56; N, 3.76.

(15) 5-Acetyl-1,4-dihydro-1,6-dimethyl-3-(4-methylbenzoyl)-2-phenylpyridine (5dkaa)



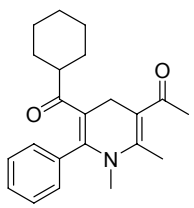
Reddish brown oil; IR (KBr): V_{max} = 2928, 2851, 1742, 1650, 1460, 1106, 940, 529 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.34(d, *J* = 8Hz, 2H), 7.10-7.06(m, 5H), 6.88-6.86(d, *J* = 8Hz, 2H), 3.37(s, 2H), 2.92(s, 3H), 2.49(s, 3H), 2.26(s, 3H), 2.20(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 196.2, 150.6, 150.0, 141.4, 136.2, 133.6, 130.2, 129.0, 128.9, 128.1, 127.9, 112.2, 110.0, 36.2, 30.0, 27.3, 21.2,16.0; EI-MS: m/z = 345(M^+, 40), 302(46), 268(39), 226(42), 28(100); Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05; Found: C, 79.80; H, 6.82; N, 3.99.

(16) 5-Acetyl-1,4-dihydro-1,6-dimethyl-2-phenyl-3-(thiophene-2-carbonyl)pyridine (5ekaa)



Reddish brown oil; IR (KBr): V_{max} = 2924, 2851, 1739, 1647, 1465, 1109, 939, 530 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.31(m, 1H), 7.18-7.14(m, 6H), 6.72-6.70(m, 1H), 3.40(s, 2H), 2.96(s, 3H), 2.48(s, 3H), 2.26(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 187.9, 150.7, 149.1, 144.6, 133.7, 132.7, 132.2, 130.1, 129.2, 128.2, 126.8, 112.6, 110.2, 36.3, 30.0, 27.5,16.1; EI-MS: m/z = 337(M^+, 62), 294(55), 260(52), 226(56), 111(100); Anal. Calcd for $C_{20}H_{19}NO_2S$: C, 71.19; H, 5.68; N, 4.15; Found: C, 71.43; H, 5.78; N, 4.04.

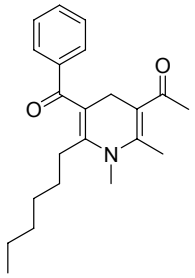
(17) 5-Acetyl-1,4-dihydro-1,6-dimethyl-3-cyclohexanecarbonyl-2-phenylpyridine (5fkaa)



Reddish brown oil; IR (KBr): V_{max} = 2927, 2853, 1742, 1655, 1448, 1112, 940, 530 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.43(m, 3H), 7.26-7.24(m, 2H), 3.23(s, 2H), 2.89(s, 3H), 2.42(s, 3H), 2.28(s,

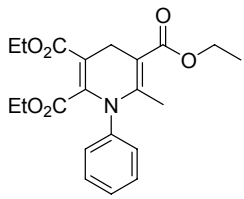
3H), 1.62-0.94(m, 8H), 0.67-0.57(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.5, 198.9, 150.6, 149.3, 135.0, 129.7, 128.7, 112.2, 110.9, 48.3, 36.1, 30.0, 29.5, 26.0, 25.7, 25.6,15.9; EI-MS: m/z = 337(M^+,65), 294(63), 260(100), 226(79), 212(87); Anal. Calcd for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.06; N, 4.15; Found: C, 78.21; H, 8.13; N, 4.10.

(18) 5-Acetyl-3-benzoyl-1,4-dihydro-2-hexyl-1,6-dimethylpyridine (5gkaa)



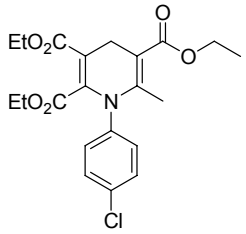
Reddish brown oil; IR (KBr): V_{max} = 2925, 2852, 1744, 1649, 1461, 1101, 938, 529 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75-7.40(m, 5H), 3.25(s, 3H), 3.05(s, 2H), 2.44(s, 3H), 2.13(s, 3H), 1.41-0.80(m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 197.6, 151.5, 150.8, 139.4, 131.9, 128.7, 128.4, 111.3, 108.9, 33.4, 31.3, 30.0, 29.1, 29.0, 28.9, 27.6, 22.5, 16.1, 13.9; EI-MS: m/z = 339(M^+, 14), 296(23), 254(21), 234(16), 28(100); Anal. Calcd for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13; Found: C, 78.06; H, 8.78; N, 4.01.

(19) Triethyl 1,4-dihydro-6-methyl-1-phenylpyridine-2,3,5-tricarboxylate (5aaba)



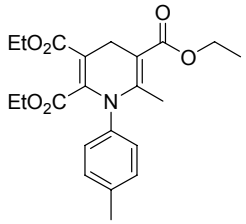
Yellow oil; IR (KBr): V_{max} = 2994, 1765, 1699, 1459, 1375, 1243, 1108, 1056 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.21(m, 5H), 4.20-4.11(m, 4H), 3.80(q, *J* = 7.2Hz, 2H), 3.41(s, 2H), 1.91(s, 3H), 1.28 (t, *J* = 7.2Hz, 3H), 1.23 (t, *J* = 7.2Hz, 3H), 0.92 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 166.1, 164.0, 147.3, 143.6, 138.9, 131.0, 129.0, 102.1, 101.7, 61.5, 60.5, 60.0, 23.9, 17.7, 14.3, 14.2, 13.4; EI-MS: m/z = 387(M^+, 23), 342(25), 314(100), 268(45), 240(97), 196(77); Anal. Calcd for $C_{21}H_{25}NO_6$: C, 65.10; H, 6.50; N, 3.62; Found: C, 65.38; H, 6.66; N, 3.50.

(20) Triethyl 1-(4-chlorophenyl)-1,4-dihydro-6-methylpyridine-2,3,5-tricarboxylate (5acba)



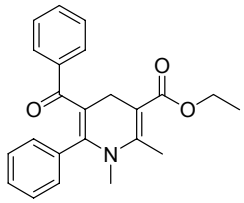
Yellow oil; IR (KBr): V_{max} = 2992, 1766, 1698, 1486, 1375, 1244, 1110, 1053 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.35(m, 2H), 7.21-7.08(m, 2H), 4.23-4.15(m, 4H), 3.88(q, *J* = 7.2Hz, 2H), 3.41(s, 2H), 1.93(s, 3H), 1.30 (t, *J* = 7.2Hz, 3H), 1.25 (t, *J* = 7.2Hz, 3H), 1.00 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 165.9, 163.9, 146.7, 143.1, 137.3, 135.1, 132.3, 129.2, 102.6, 102.1, 61.7, 60.6, 60.2, 23.8, 17.7, 14.3, 14.2, 13.4; EI-MS: m/z = 421(M^+, 11), 376(10), 348(32), 302(13), 274(26), 230(17), 28(100); Anal. Calcd for $C_{21}H_{24}ClNO_6$: C, 59.79; H, 5.73; N, 3.32; Found: C, 59.56; H, 5.89; N, 3.23.

(21) Triethyl 1,4-dihydro-6-methyl-1-*p*-tolylpyridine-2,3,5-tricarboxylate (5alba)



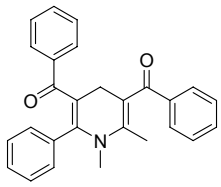
Yellow oil; IR (KBr): V_{max} = 2991, 1766, 1699, 1460, 1375, 1243, 1108, 1056 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.10(m, 4H), 4.22-4.14(m, 4H), 3.85(q, *J* = 7.2Hz, 2H), 3.42(s, 2H), 2.36(s, 3H), 1.93(s, 3H), 1.30 (t, *J* = 7.2Hz, 3H), 1.25 (t, *J* = 7.2Hz, 3H), 0.97 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 166.1, 164.0, 147.6, 143.7, 139.1, 136.1, 130.6, 129.5, 101.9, 101.4, 61.4, 60.5, 60.0, 23.8, 21.1, 17.6, 14.3, 14.2, 13.4; EI-MS: m/z = 401(M^+, 7), 356(5), 328(24), 282(12), 254(17), 210(20), 28(100); Anal. Calcd for $C_{22}H_{27}NO_6$: C, 65.82; H, 6.78; N, 3.49; Found: C, 65.62; H, 6.93; N, 3.38.

(22) Ethyl 3-benzoyl-1,4-dihydro-1,6-dimethyl-2-phenylpyridine-5-carboxylate (5bkba)



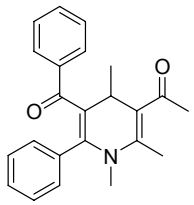
Reddish brown oil; IR (KBr): V_{max} = 2995, 2852, 1764, 1650, 1458, 1370, 1242, 1105, 939, 529 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.03(m, 10H), 4.19(q, *J* = 7.2Hz, 2H), 3.38(s, 2H), 2.90 (s, 3H), 2.53(s, 3H), 1.28 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8, 167.7, 151.4, 150.7, 139.4, 134.0, 130.8, 130.4, 129.0, 128.9, 128.0, 127.3, 112.1, 102.3, 59.8, 36.4, 26.0, 15.9, 14.3; EI-MS: m/z = 361(M^+, 48), 332(43), 284(64), 256(100), 212(47); Anal. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88; Found: C, 76.60; H, 6.54; N, 3.78.

(23) 3,5-Dibenzoyl-1,4-dihydro-1,6-dimethyl-2-phenylpyridine (5bkca)



Reddish brown solid; m.p.:120-122 ^oC; IR (KBr): V_{max} = 2992, 2854, 1743, 1652, 1458, 1108, 940, 529 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74(d, *J* = 8Hz, 2H), 7.45-7.33(m, 5H), 7.13-7.01(m, 8H), 3.32(s, 2H), 2.95(s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.9, 196.2, 152.0, 148.1, 139.5, 139.2, 133.8, 131.8, 130.7, 130.5, 129.2, 128.7, 128.6, 128.4, 128.3, 128.1, 127.4, 111.0, 110.6, 36.2, 28.3, 16.7; EI-MS: m/z = 393(M^+, 6), 377(32), 348(55), 300(18), 105(100); Anal. Calcd for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56; Found: C, 82.60; H, 5.95; N, 3.50.

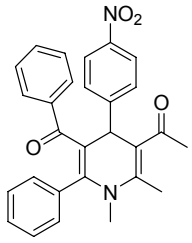
(24) 5-acetyl-3-benzoyl-1,4-dihydro-2-phenyl-1,4,6-trimethylpyridine (5bkab)



Yellowish green solid; m.p.: 109-110 ^oC; IR (KBr): V_{max} = 2991, 2836, 1765, 1606, 1445, 1367, 1243, 1057, 868, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.30(m, 2H), 7.11-6.96(m, 8H), 3.68 (t, *J* =

6.8Hz, 1H), 2.94(s, 3H), 2.52(s, 3H), 2.32(s, 3H), 1.18 (d, *J* = 6.8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.0, 196.7, 150.1, 148.6, 139.8, 133.8, 130.8, 130.5, 129.3, 128.8, 128.0, 127.2, 117.5, 116.9, 36.5, 31.3, 29.5, 21.8, 16.5; EI-MS: m/z = 345(M^+, 5), 330(100), 302(13), 268(4), 240(12); Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05; Found: C, 80.08; H, 6.78; N, 4.01.

(25) 5-acetyl-3-benzoyl-1,4-dihydro-1,6-dimethyl-4-*p*-nitrophenyl-2-phenylpyridine (5bkac)



Yellowish green oil; IR (KBr): V_{max} = 2835, 1707, 1616, 1453, 1345, 1236, 1164, 781, 589cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14(d, *J* = 8.8Hz, 2H), 7.61(d, *J* = 8.8Hz, 2H), 7.25(d, *J* = 8.8Hz, 2H), 7.09-6.95(m, 8H), 5.08(s, 1H), 2.87(s, 3H), 2.65(s, 3H), 2.28(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 196.5, 152.7, 152.3, 149.6, 146.4, 139.8, 132.8, 130.5, 129.8, 128.6, 128.1, 127.8, 127.2, 123.5, 114.4, 114.3, 40.1,16.5, 36.6, 29.8; EI-MS: m/z = 452(M^+, 4), 409(9), 375(13), 347(8), 28(100); Anal. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19; Found: C, 74.41; H, 5.39; N, 6.11.