Metal free, one-pot rapid synthesis of tetrahydropyridines using dual role of acetic acid as solvent and catalyst at room temperature

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SUPPLEMENTARY MATERIAL

Experimental section

General information:

All the solvents and chemicals were received commercially. Melting points were determined by using GUNA melting point apparatus and are uncorrected. FTIR spectra were recorded using JASCO-4100 spectrometer instrument. NMR spectra were taken with a BRUKER AV III spectrometer at 500 MHz (¹H and ¹³C) and BRUKER at 400 MHz (¹H and ¹³C) using CDCl₃ as the solvent with TMS as internal standard. HRMS analysis was obtained from JEOL GC Mate.

General procedure for the preparation of functionalized tetrahydropyridines.

A mixture of β-keto ester (1 mmol), amine (2mmol) and 3 ml glacial acetic acid was stirred at room temperature for 5 min followed by the addition of aldehyde (2 mmol) was allowed to stirr for an appropriate time (Table 1). Completion of the reaction was monitored by TLC using 1:9 ratio of ethylacetate and hexane. The solid product formed

in reaction mixture was filtered, washed with methanol and recrystallized using Ethanol and THF (1:1 ratio).

4a. Methyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate

White yellow solid; Melting point: 192-194 °C: IR (KBr): 3250, 3024, 2949, 2867, 1815, 1661, 1606, 1504, 1449, 1375, 1321, 1245, 1183, 1070, 978, 920, 748, 646 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.78-2.74 (dd, *J*=32.0, 4 Hz, 1H), 2.89-2.84 (dd, *J*=32.0, 4.0 Hz, 1H), 3.93 (s, 3H), 5.14 (s, 1H), 6.28-6.26 (d, *J*=8.0 Hz, 2H), 6.45 (s, 1H), 6.53-6.51 (d, *J*=8.0 Hz, 2H), 6.61-6.57 (t, *J*=8.0 Hz, 1H), 7.33-7.03 (m, 15H), 10.25 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) ppm: 33.6, 51.0, 55.1, 58.2, 97.9, 112.9, 116.2, 125.8, 125.9, 126.4, 126.4, 126.6, 127.2, 128.3, 128.7, 128.9, 128.9, 137.8, 142.7, 143.9, 146.9, 156.3, 168.6;

4b. Methyl 1,2,5,6-tetrahydro-2,6-bis(2-methoxyphenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

White solid; Melting point: 199-200 °C: IR (KBr): 3234, 3068, 2940, 2835, 1666, 1591, 1503, 1460, 1369, 1322, 1286, 1239, 1069, 1027, 979, 770, 690 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.87-2.82 (dd, *J*=32.0, 4.0 Hz, 1H), 3.02-2.97 (dd, *J*=32.0, 4.0 Hz, 1H), 3.58 (s, 3H), 3.83 (s, 3H), 3.89 (s, 3H), 5.43 (s, 1H), 6.26-6.24 (d, *J*=8.0 Hz, 2H), 6.45-6.41 (t, *J*=8.0 Hz, 3H), 6.58-6.54 (t, *J*=8.0 Hz, 1H), 6.83-6.76 (m, 3H), 6.92-6.90 (d, *J*=8.0 Hz, 1H), 7.08-7.01 (m, 6H), 7.16-7.13 (m, 3H), 9.85 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) ppm: 29.3, 50.9, 53.2, 53.3, 54.8, 55.5, 97.8, 109.9, 111.2, 112.6, 115.8, 119.7, 120.7, 125.1, 125.9, 127.6, 128.0, 128.3, 128.2, 128.6, 128.8, 129.5, 130.5, 138.6, 146.8, 154.9, 156.1, 157.5, 169.2;

4c. Methyl 1,2,5,6-tetrahydro-2,6-bis(3-nitrophenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

White yellow solid; Melting point: 179-180 °C: IR (KBr): 3212, 3084, 2954, 2860, 1657, 1595, 1530, 1450, 1369, 1325, 1263, 1066, 907, 781, 725, 689 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.89-2.88 (d, *J* = 4.0 Hz, 2H), 3.98 (s, 3H), 5.34 (s, 1H), 6.42-6.39 (m, 2H), 6.46-6.44 (d, *J* = 8.0 Hz, 2H), 6.49 (s, 1H), 6.71-6.67 (t, *J* = 8.0 Hz, 1H), 7.15-7.07 (m, 5H), 7.49-7.45 (m, 3H), 7.67-7.65 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 8.13-8.08 (m, 2H), 10.30 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) ppm: 25.6, 33.8, 51.5, 55.2, 57.0, 67.9, 96.8, 117.7, 121.4, 121.5, 121.9, 122.5, 125.7, 126.6, 129.2, 129.4, 129.7, 132.6, 132.6, 137.2, 144.5, 145.8, 146.3, 148.6, 148.6, 155.6, 168.0;

4d. Methyl 2,6-bis(4-cyanophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

Yellow solid; Melting point: 152-154 °C: IR (KBr): 3236, 3063, 2949, 2857, 2226, 1928, 1660, 1592, 1498, 1445, 1317, 1255, 1189, 1076, 1017, 862, 788, 762, 691 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.82-2.81 (s, 2H), 3.94 (s, 3H), 5.19 (s, 1H), 6.47-6.75 (m, 5H), 6.70-6.64 (t, *J* = 12.0 Hz, 1H), 7.11-7.05 (m, 2H), 7.26-7.15 (m, 4H), 7.44-7.42 (d, *J* = 8.0 Hz, 2H), 7.59-7.54 (m, 5H), 10.26 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) ppm: 25.6, 33.6, 51.5, 55.2, 57.3, 67.9, 96.7, 112.9, 117.7, 123.7, 123.8, 123.9, 124.0, 125.5, 126.5, 127.4, 127.4, 127.6, 127.8, 129.1, 129.2, 129.4, 137.1, 145.8, 146.8, 147.3, 149.8, 151.6, 155.5, 167.9; HRMS (ESI): found: 510.2029. C₃₃H₂₆N₄O₂ Calc. 510.2056

4e. Methyl 2,6-bis(4-bromophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

White yellow solid; Melting point: 194-196 °C: IR (KBr): 3212, 3064, 2946, 2864, 1660, 1589, 1485, 1399, 1288, 1230, 1185, 1071, 1010, 790, 697 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.75-2.71 (dd, *J* = 24.0, 4.0 Hz, 1H), 2.84-2.79 (dd, *J* = 32.0, 4.0 Hz, 1H), 3.91 (s, 3H), 5.07 (s, 1H), 6.33 (s, 1H), 6.41-6.39 (d, *J* = 8.0 Hz, 2H), 6.46-6.43 (d, *J* = 12.0 Hz, 2H), 6.66-6.62 (t, *J* = 8.0 Hz, 1H), 7.00-6.98 (d, *J* = 8.0 Hz, 2H), 7.18-7.05 (m, 7H), 7.40-7.37 (m, 4H), 10.24 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) ppm: 33.6, 51.2, 54.8, 57.4, 97.5, 112.9, 116.8, 120.3, 120.9, 125.8, 126.0, 128.1, 128.4, 129.0, 129.0, 131.3, 131.7, 137.6, 141.5, 142.9, 146.4, 156.0, 168.3;

4f. Methyl 1,2,5,6-tetrahydro-2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

Yellow solid; Melting point: 236-238 °C: IR (KBr): 3239, 3041, 2951, 2856, 1930, 1667, 1615, 1530, 1178, 1070, 978, 853, 729, 698 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.87 (s, 2H), 3.97 (s, 3H), 5.27 (s, 1H), 6.44-6.39 (t, *J* = 10.0 Hz, 3H), 6.48 (s, 1H), 6.71-6.68 (t, *J* = 6.0 Hz, 1H), 7.13-7.04 (t, *J* = 18.0 Hz, 2H), 7.16 (s, 3H), 7.30-7.26 (m, 2H), 7.51-7.49 (d, *J* = 8.0 Hz, 2H), 8.17-8.12 (t, *J* = 10.0 Hz, 5H), 10.28 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) ppm: 25.6, 33.6, 51.5, 55.2, 57.3, 67.9, 96.7, 112.9, 117.7, 123.7, 123.8, 123.9, 124.0, 125.5, 126.5, 127.4, 127.4, 127.6, 127.8, 129.1, 129.2, 129.4, 137.1, 145.8, 146.8, 147.3, 149.8, 151.6, 155.5, 167.9;

4g. Methyl 1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)-2,6-dip-tolylpyridine-3-carboxylate

White solid; Melting point: 210-212 °C: IR (KBr): 3225, 3024, 2949, 2862, 1655, 1607, 1591, 1496, 1250, 1186, 1071, 926, 785, 750, 695 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.37 (s, 3H), 2.33 (s, 3H), 2.77-2.73 (d, *J* = 16.0 Hz, 1H), 2.88-2.83 (dd, *J* = 32.0,

4.0 Hz, 1H), 3.89 (s, 3H), 5.10 (s, 1H), 6.30-6.29 (d, $J = 4.0$ Hz, 2H), 6.39 (s, 1H), 6.53-6.51 (d, $J = 8.0$ Hz, 2H), 6.60-6.57 (t, $J = 6.0$ Hz, 1H), 7.08-7.05 (m, 11H), 7.20-7.18 (d, $J = 8.0$ Hz, 2H), 10.24 (br s, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3) ppm: 21.0, 21.1, 33.6, 50.9, 54.9, 57.9, 98.1, 112.9, 115.9, 125.6, 125.8, 126.3, 126.5, 128.8, 128.8, 128.9, 129.3, 135.8, 136.6, 137.9, 139.6, 140.9, 147.0, 156.3, 168.6.

4h. Methyl 1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

Yellow solid; Melting point: 188-190 $^{\circ}\text{C}$: IR (KBr): 3222, 3062, 2948, 2837, 1653, 1610, 1592, 1508, 1455, 1301, 1245, 1174, 1070, 1034, 829, 742, 698 cm^{-1} : ^1H NMR (400 MHz, CDCl_3) ppm 2.76-2.73 (d, $J = 12.0$ Hz, 1H), 2.87-2.82 (dd, $J = 32.0, 4.0$ Hz, 1H), 3.77 (s, 3H), 3.78 (s, 3H), 3.91 (s, 3H), 5.08 (s, 1H), 6.36-6.34 (d, $J = 8.0$ Hz, 3H), 6.53-6.51 (d, $J = 8.4$ Hz, 2H), 6.61-6.57 (t, $J = 8.0$ Hz, 1H), 6.81-6.79 (d, $J = 8.0$ Hz, 4H), 7.13-7.05 (m, 7H), 7.24-7.20 (t, $J = 8.0$ Hz, 2H), 10.27 (br s, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3) ppm: 33.7, 51.0, 54.7, 55.2, 55.3, 57.5, 98.1, 112.9, 113.6, 114.0, 116.1, 125.7, 125.8, 127.5, 127.7, 128.9, 134.6, 135.8, 137.9, 147.0, 156.4, 158.1, 158.7, 168.6.

4i. Methyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenyl pyridine-3-carboxylate

Yellow solid; Melting point: 218-220 $^{\circ}\text{C}$: IR (KBr): 3258, 3085, 2943, 2867, 1650, 1600, 1591, 1504, 1451, 1375, 1318, 1250, 1077, 978, 929, 852, 781, 690 cm^{-1} : ^1H NMR (400 MHz, CDCl_3) ppm: 2.71-2.67 (d, $J = 16.0$ Hz, 1H), 2.87-2.82 (dd, $J = 32.0, 4.0$ Hz, 1H), 3.94 (s, 3H), 5.10 (s, 1H), 6.18-6.14 (d, $J = 16.0$ Hz, 2H), 6.38 (s, 1H), 6.44-6.40 (d, $J = 16.0$ Hz, 2H), 7.00-6.96 (d, $J = 16.0$ Hz, 2H), 7.06-7.03 (d, $J = 12.0$ Hz, 2H), 7.15-7.17 (d, $J = 8.0$ Hz, 2H), 7.32-7.20 (m, 8H), 10.19 (br s, 1H, NH); ^{13}C NMR (100 MHz,

CDCl₃) ppm: 33.5, 51.2, 55.3, 58.3, 98.4, 114.0, 121.2, 126.3, 126.5, 126.6, 127.1, 127.5, 128.4, 128.7, 128.8, 129.0, 131.5, 136.3, 142.2, 143.2, 145.5, 155.6, 168.5.

4j. Methyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate

White solid; Melting point: 170-172 °C; IR (KBr): 3237, 3067, 2951, 2888, 1898, 1777, 1673, 1454, 1128, 1088, 924, 855, 860, 765, 613 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) ppm: 2.70-2.66 (d, *J* = 16.0 Hz, 1H), 2.84-2.79 (dd, *J* = 32.0, 4.0 Hz, 1H), 3.92 (s, 3H), 5.07 (s, 1H), 6.39-6.29 (m, 5H), 7.01-6.94 (m, 6H), 7.12-6.08 (m, 4H), 7.21 (s, 2H), 10.22 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) ppm: 51.3, 54.7, 57.4, 98.2, 114.1, 115.1, 115.3, 115.6, 115.8, 117.7, 126.9, 127.8, 127.8, 127.9, 128.0, 128.8, 129.2, 131.7, 136.2, 138.6, 145.1, 155.4, 168.3.

4k. Methyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-dip-tolylpyridine-3-carboxylate

White yellow solid; Melting point: 198-200 °C; IR (KBr): 3228, 3085, 2978, 2863, 1905, 1644, 1604, 1504, 1369, 1246, 1184, 1012, 933, 758, 652 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) ppm: 2.32 (s, 3H), 2.34 (s, 3H), 2.70-2.66 (dd, *J* = 28.0, 4 Hz, 1H), 2.86-2.81 (dd, *J* = 32.0, 4.0 Hz, 1H), 3.93 (s, 3H), 5.06 (s, 1H), 6.20-6.17 (d, *J* = 12.0 Hz, 2H), 6.32 (s, 1H), 6.44-6.40 (d, *J* = 16.0 Hz, 2H), 7.13-6.96 (m, 12H), 10.19 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃) ppm: 21.0, 21.1, 33.5, 51.1, 55.1, 58.0, 98.6, 113.9, 121.0, 126.2, 126.4, 127.0, 128.7, 128.9, 129.0, 129.4, 131.3, 136.1, 136.5, 137.0, 139.2, 140.1, 145.6, 155.6, 168.5; HRMS (ESI): found: 556.1684 C₃₃H₃₀Cl₂N₂O₂ Calc. 556.1684.

5a. Ethyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate

White yellow solid; Melting point: 174-175 °C: IR (KBr): 3245, 3057, 2980, 2873, 1651, 1599, 1503, 1448, 1375, 1328, 1243, 1170, 1069, 1028, 943, 835, 729, 723, 697 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.48-1.44 (t, *J* = 8.0 Hz, 3H), 2.78-2.74 (d, *J* = 16.0 Hz, 1H), 2.90-2.84 (dd, *J* = 32.0, 4.0 Hz, 1H), 4.35- 4.30 (m, 1H), 4.49-4.43 (m, 1H), 5.14 (s, 1H), 6.28-6.26 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 6.54-6.52 (d, *J* = 8.0 Hz, 2H), 6.61-6.58 (m, 1H), 7.08-7.03 (m, 5H), 7.21-7.16 (m, 3H), 7.29-7.25 (m, 5H), 7.36-7.34 (d, *J* = 8.0 Hz, 2H), 10.31 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.9, 33.7, 55.2, 58.3, 59.8, 98.3, 113.0, 116.2, 125.8, 125.9, 126.4, 126.5, 126.7, 127.2, 128.3, 128.7, 128.9, 128.9, 137.9, 142.9, 144.1, 147.0, 156.2, 168.3.

5b. Ethyl 2,6-bis(2-fluorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

Yellow solid; Melting point: 128-130 °C: IR (KBr): 3229, 3066, 2979, 2868, 1649, 1608, 1591, 1502, 1455, 1376, 1321, 1253, 1176, 1092, 1066, 996, 933, 763, 690 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.42-1.39 (t, *J* = 6.0 Hz, 3H), 2.92-2.91 (s, 2H), 4.31- 4.23 (m, 1H), 4.45-4.37 (m, 1H), 5.44 (s, 1H), 6.39-6.37 (s, 2H), 6.50-6.48 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 1H), 6.66-6.63 (t, *J* = 6.0 Hz, 1H), 7.24-6.96 (m, 13H), 10.20 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.0, 31.1, 52.1, 52.3, 59.8, 96.9, 113.1, 115.0, 115.3, 116.3, 116.5, 117.0, 123.4, 123.4, 124.4, 124.4, 125.7, 125.8, 128.3, 128.4, 128.8, 128.9, 128.9, 129.0, 129.1, 129.1, 129.8, 129.9, 138.0, 146.4, 155.4, 158.8, 159.5, 161.2, 161.9, 168.1; HRMS (ESI): found: 510.2069 C₃₂H₂₈F₂N₂O₂ Calc. 510.2119.

5c. Ethyl 2,6-bis(3-fluorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

White yellow solid; Melting point: 154-156 °C: IR (KBr): 3225, 3068, 2972, 2927, 1649, 1590, 1504, 1447, 1320, 1250, 1178, 1091, 1031, 947, 882, 781, 678 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.48-1.45 (t, *J* = 6.0 Hz, 3H), 2.79-2.76 (d, *J* = 12.0 Hz, 1H), 2.91-2.86 (dd, *J* = 28.0, 4.0 Hz, 1H), 4.37- 4.29 (m, 1H), 4.50-4.42 (m, 1H), 5.13 (s, 1H), 6.39-6.37 (d, *J* = 8.0 Hz, 2H), 6.41 (s, 1H), 6.50-6.48 (d, *J* = 8.0 Hz, 2H), 6.66-6.62 (t, *J* = 8.0 Hz, 1H), 6.96-6.83 (m, 4H), 7.16-7.06 (m, 7H), 7.23-7.22 (d, *J* = 4.0 Hz, 2H), 10.33 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.8, 33.5, 54.9, 57.6, 59.9, 97.6, 112.9, 113.3, 113.3, 113.5, 113.6, 113.8, 114.1, 114.3, 116.8, 122.0, 122.0, 122.1, 122.2, 125.8, 126.0, 128.9, 129.1, 129.7, 129.8, 130.2, 130.3, 137.7, 145.5, 145.6, 146.5, 146.9, 147.0, 155.8, 161.8; HRMS (ESI): found: 510.2110 C₃₂H₂₈F₂N₂O₂ Calc. 510.2119.

5d. Ethyl 2,6-bis(3-bromophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

White yellow solid; Melting point: 158-160 °C: IR (KBr): 3255, 3060, 2971, 2883, 1879, 1645, 1589, 1498, 1471, 1372, 1318, 1246, 1169, 1091, 995, 942, 779, 760, 694, 658 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.49-1.45 (t, *J* = 8.0 Hz, 3H), 2.76-2.74 (d, *J* = 8.0 Hz, 1H), 2.82-2.80 (d, *J* = 8.0 Hz, 1H), 4.36- 4.28 (m, 1H), 4.53-4.45 (m, 1H), 5.10 (s, 1H), 6.37-6.35 (d, *J* = 8.0 Hz, 3H), 6.48-6.45 (d, *J* = 12.0 Hz, 2H), 6.67-6.63 (t, *J* = 8.0 Hz, 1H), 7.20-7.05 (m, 9H), 7.23 (s, 1H), 7.35-7.33 (d, *J* = 8.0 Hz, 1H), 7.39-7.37 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 10.29 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃)TM ppm: 14.9, 33.5, 54.9, 57.5, 59.9, 97.3, 113.0, 116.9, 122.7, 125.0, 125.2, 126.1, 126.2, 129.0, 129.1, 129.6, 129.7, 129.8, 130.3, 130.4, 137.6, 145.0, 146.3, 146.6, 155.8, 167.8; HRMS (ESI): found: 630.0518 C₃₂H₂₈Br₂N₂O₂ Calc. 630.0518.

5e. Ethyl 1,2,5,6-tetrahydro-2,6-bis(3-nitrophenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

Yellow solid; Melting point: 188-189 °C: IR (KBr): 3233, 3078, 2979, 2865, 1958, 1659, 1504, 1493, 1292, 1248, 1171, 1092, 1063, 914, 862, 781, 634 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) ppm: 1.57-1.54 (t, *J* = 6.0 Hz, 3H), 2.92-2.92 (s, 2H), 4.41- 4.37 (m, 1H), 4.59-4.55 (m, 1H), 5.36 (s, 1H), 6.44-6.42 (m, 2H), 6.48-6.46 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 1H), 6.74-6.71 (t, *J* = 6.0 Hz, 1H), 7.19-7.11 (m, 5H), 7.51-7.46 (m, 3H), 7.68-7.66 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 8.17-8.12 (m, 2H), 8.35 (s, 1H), 10.38 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃) ppm: 14.8, 25.6, 33.8, 55.2, 57.0, 60.3, 67.9, 97.0, 113.1, 117.7, 121.4, 121.7, 121.8, 122.5, 125.6, 126.5, 129.1, 129.3, 129.4, 129.7, 132.3, 132.6, 137.2, 144.5, 145.8, 146.4, 148.6, 148.7, 155.3, 167.7.

5f. Ethyl 1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)-2,6-dim-tolylpyridine-3-carboxylate

White solid; Melting point: 140-142 °C: IR (KBr): 3227, 3057, 2928, 2882, 1953, 1644, 1599, 1503, 1463, 1369, 1324, 1257, 1069, 1035, 947, 805, 743, 665 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) ppm: 1.48-1.44 (t, *J* = 8.0 Hz, 3H), 2.29 (s, 3H), 2.31 (s, 3H), 2.76-2.72 (d, *J* = 16.0 Hz, 1H), 2.89-2.85 (dd, *J* = 32.0, 4.0 Hz, 1H), 4.36- 4.28 (m, 1H), 4.51-4.43 (m, 1H), 5.09 (s, 1H), 6.27-6.25 (s, 2H), 6.27-6.25 (s, 2H), 6.41 (s, 1H), 6.53-6.51 (d, *J* = 8.0 Hz, 2H), 6.61-6.57 (t, *J* = 8.0 Hz, 1H), 6.99-6.93 (d, *J* = 24.0 Hz, 2H), 7.16-7.00 (m, 11H), 10.26 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.9, 21.6, 21.8, 33.6, 55.2, 58.3, 59.6, 98.2, 112.9, 115.9, 123.6, 123.7, 125.7, 126.0, 126.9, 127.1, 127.3, 127.9, 128.0, 128.5, 128.7, 128.8, 137.8, 137.9, 138.1, 142.8, 144.2, 147.1, 156.2, 168.3; HRMS (ESI): found: 502.2620. C₃₄H₃₄N₂O₂ Calc. 502.2620.

5g. Ethyl 1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)-2,6-dip-tolylpyridine-3-carboxylate

White solid; Melting point: 226.5-227.5 °C: IR (KBr): 3234, 3034, 2980, 2869, 1911, 1803, 1651, 1614, 1504, 1456, 1372, 1240, 1171, 1068, 1020, 950, 897, 740, 691 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.47-1.43 (t, *J* = 8.0 Hz, 3H), 2.31 (s, 3H), 2.32 (s, 3H), 2.78-2.73 (d, *J* = 16.0 Hz, 1H), 2.88-2.83 (dd, *J* = 24.0, 4.0 Hz, 1H), 4.35- 4.27 (m, 1H), 4.48-4.39 (m, 1H), 5.10 (s, 1H), 6.30-6.28 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 6.53-6.51 (d, *J* = 8.0 Hz, 2H), 6.60-6.57 (t, *J* = 6.0 Hz, 1H), 7.10-7.03 (m, 10H), 7.23-7.20 (d, *J* = 12.0 Hz, 2H), 10.28 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.8, 21.0, 33.7, 54.9, 57.9, 59.6, 98.4, 112.9, 115.9, 125.5, 125.7, 126.3, 126.6, 128.8, 128.8, 128.9, 129.3, 135.7, 136.6, 138.0, 139.7, 141.0, 147.1, 156.1, 168.3; HRMS (ESI): found: 530.2934. C₃₆H₃₈N₂O₂ Calc. 530.2993.

5h. Ethyl 2,6-bis(4-ethylphenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

White solid; Melting point: 181-182 °C: IR (KBr): 3230, 3055, 2969, 2861, 1650, 1608, 1503, 1456, 1370, 1327, 1244, 1173, 1069, 898, 830, 749, 692 cm⁻¹: ¹H NMR (500 MHz, CDCl₃) ppm: 1.31-1.26 (m, 6H), 1.53-1.50 (t, *J* = 7.5 Hz, 3H), 2.71-2.65 (m, 4H), 2.80-2.77 (d, *J* = 15.0 Hz, 1H), 2.93-2.89 (dd, *J* = 32.0, 4.0 Hz, 1H), 4.39- 4.36 (m, 1H), 4.54-4.50 (m, 1H), 5.17 (s, 1H), 6.30-6.28 (d, *J* = 10.0 Hz, 2H), 6.49 (s, 1H), 6.62-6.60 (d, *J* = 10.0 Hz, 2H), 6.66-6.63 (t, *J* = 7.5 Hz, 1H), 7.17-7.11 (m, 11H), 7.30-7.28 (d, *J* = 10.0 Hz, 7H), 10.35 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃) ppm: 14.8, 15.5, 15.9, 28.4, 28.6, 33.7, 54.9, 58.1, 59.6, 98.4, 112.9, 115.9, 125.6, 125.9, 126.4, 126.6, 127.7, 128.1, 128.9, 138.0, 140.2, 141.2, 142.1, 143.2, 147.1, 156.2, 168.3.

5i. Ethyl 2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

White solid; Melting point: 232-233 °C: IR (KBr): 3242, 3024, 2977, 2871, 1933, 1660, 1505, 1371, 1294, 1066, 949, 898, 792, 744, 658 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) ppm: 1.49-1.46 (t, *J* = 7.5 Hz, 3H), 2.79-2.75 (d, *J* = 20 Hz, 1H), 2.88-2.83 (dd, *J* = 24.0, 4.0 Hz, 1H), 4.37- 4.34 (m, 1H), 4.50-4.46 (m, 1H), 5.11 (s, 1H), 6.38 (s, 1H), 6.45-6.43 (d, *J* = 10.0 Hz, 2H), 6.50-6.48 (d, *J* = 10.0 Hz, 2H), 6.69-6.66 (t, *J* = 7.5 Hz, 1H), 7.04-7.02 (d, *J* = 10.0 Hz, 2H), 7.24-7.10 (m, 7H), 7.44-7.41 (t, *J* = 7.5 Hz, 4H), 10.32 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃) ppm: 14.8, 33.6, 54.8, 57.4, 59.9, 97.7, 112.9, 116.8, 120.2, 120.9, 125.7, 125.9, 128.2, 128.4, 129.0, 129.1, 131.3, 131.7, 137.7, 141.5, 143.0, 146.5, 155.8, 167.9; HRMS (ESI): found: 510.2119 C₃₂H₂₈F₂N₂O₂ Calc. 510.2119.

5j. Ethyl 2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate

White solid; Melting point: 220-222 °C: IR (KBr): 3235, 3038, 2979, 2870, 1649, 1596, 1500, 1405, 1368, 1320, 1254, 1174, 1067, 1011, 859, 782, 747, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) ppm: 1.47-1.43 (t, *J* = 12.0 Hz, 3H), 2.76-2.72 (d, *J* = 16.0 Hz, 1H), 2.85-2.80 (dd, *J* = 32.0, 4.0 Hz, 1H), 4.36- 4.28 (m, 1H), 4.48-4.40 (m, 1H), 5.09 (s, 1H), 6.36 (s, 1H), 6.41-6.39 (d, *J* = 8.0 Hz, 2H), 6.46-6.44 (d, *J* = 8.0 Hz, 2H), 6.66-6.62 (t, *J* = 8.0 Hz, 1H), 7.17-7.04 (m, 7H), 7.27-7.22 (m, 6H), 10.29 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.8, 33.7, 54.7, 57.4, 59.9, 97.8, 112.9, 116.7, 125.7, 125.9, 127.8, 128.0, 128.4, 128.8, 129.0, 129.1, 132.1, 132.9, 137.7, 140.9, 142.5, 146.5, 155.8, 167.9.

5k. Ethyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenyl pyridine-3-carboxylate

Yellow solid; Melting point: 214-216 °C: IR (KBr): 3241, 3060, 2972, 2857, 1644, 1585, 1493, 1451, 1319, 1227, 1070, 941, 849, 802, 777, 697 cm⁻¹: ¹H NMR (500 MHz, CDCl₃) ppm: 1.52-1.49 (t, *J*=6.0 Hz, 3H), 2.75-2.72 (d, *J*=12.0 Hz, 1H), 2.91-2.87 (dd, *J*=24.0, 4.0 Hz, 1H), 4.39- 4.35 (m, 1H), 4.52-4.49 (m, 1H), 5.14-5.13 (s, 1H), 6.21-6.19 (d, *J*=8.0 Hz, 2H), 6.43 (s, 1H), 6.48-6.46 (d, *J*=8.0 Hz, 2H), 7.04-7.02 (d, *J*=8.0 Hz, 2H), 7.09-7.07 (d, *J*=8.0 Hz, 2H), 7.19-7.17 (d, *J*= 8.0 Hz, 2H), 7.31-7.27 (m, 8H), 10.27 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃) ppm: 14.8, 33.5, 55.3, 58.3, 59.9, 98.7, 114.0, 121.2, 126.3, 126.5, 126.6, 127.0, 127.5, 128.4, 128.7, 128.8, 129.0, 131.4, 136.4, 142.3, 143.3, 145.5, 155.4, 168.1.

5l. Ethyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-dip-tolylpyridine-3-carboxylate

White yellow solid; Melting point: 232-234 °C: IR (KBr): 3249, 3087, 2948, 2854, 1650, 1604, 1493, 1454, 1320, 1257, 1076, 853, 790, 755, 682 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.48-1.44 (t, *J*= 8.0 Hz, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 2.70-2.66 (d, *J*=16.0 Hz, 1H), 2.87-2.81 (dd, *J*=24, 4.0 Hz, 1H), 4.36- 4.28 (m, 1H), 4.49-4.41 (m, 1H), 5.05 (s, 1H), 6.19-6.17 (d, *J*=8.0 Hz, 2H), 6.33 (s, 1H), 6.44-6.42 (d, *J*=8.0 Hz, 2H), 7.10-6.97 (m, 10H), 7.17-7.15 (d, *J*=8.0 Hz, 2H), 10.26 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.8, 21.0, 21.1, 33.5, 55.0, 58.0, 59.8, 98.9, 114.0, 121.0, 126.2, 126.4, 126.9, 128.7, 128.9, 129.0, 129.4, 131.2, 136.1, 136.5, 137.0, 139.2, 140.3, 145.6, 155.4, 168.2; HRMS (ESI): found: 570.1849 C₃₄H₃₂Cl₂N₂O₂ Calc. 570.1841.

5m. Ethyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-2,6-bis(4-ethylphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate

Yellow solid; Melting point: 198-200 °C: IR (KBr): 3234, 3087, 2966, 2853, 1644, 1603, 1589, 1492, 1319, 1251, 1070, 1013, 938, 850, 801, 749 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.25-1.20 (t, *J* = 10.0 Hz, 6H), 1.48-1.44 (t, *J* = 8.0 Hz, 3H), 2.67-2.59 (m, 5H), 2.86-2.80 (dd, *J* = 32.0, 8.0 Hz, 1H), 4.34- 4.30 (m, 1H), 4.48-4.42 (m, 1H), 5.06 (s, 1H), 6.14-6.11 (d, *J* = 12.0 Hz, 2H), 6.35 (s, 1H), 6.46-6.43 (d, *J* = 12.0 Hz, 2H), 7.17-6.98 (m, 12H), 10.26 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.7, 15.5, 15.9, 28.3, 28.3, 33.5, 55.0, 58.2, 59.8, 98.8, 113.9, 120.9, 126.2, 126.4, 127.1, 127.8, 128.2, 128.6, 128.9, 131.2, 136.5, 139.6, 140.4, 142.4, 143.6, 145.6, 155.5, 168.2; HRMS (ESI): found: 598.2158 C₃₆H₃₆Cl₂N₂O₂ Calc. 598.2154.

5n. Ethyl 4-(p-tolylamino)-1,2,5,6-tetrahydro-2,6-diphenyl-1-p-tolylpyridine-3-carboxylate

White solid; Melting point: 166-168 °C: IR (KBr): 3429, 3169, 3024, 2980, 2922, 1651, 1597, 1516, 1448, 1317, 1251, 1072, 1031, 947, 800, 700 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.47-1.43 (t, *J* = 8 Hz, 3H), 2.14 (s, 3H), 2.25 (s, 3H), 2.75-2.70 (dd, *J* = 29.6, 2.0 Hz, 1H), 2.85-2.80 (dd, *J* = 32.0, 4.0 Hz, 1H), 4.39- 4.28 (m, 1H), 4.47-4.39 (m, 1H), 5.10 (s, 1H), 6.15-6.13 (d, *J* = 8.0 Hz, 2H), 6.43-6.41 (d, *J* = 8.0 Hz, 3H), 6.88-6.85 (m, 4H), 7.27-7.15 (m, 8H), 7.32-7.29 (d, *J* = 12.0 Hz, 2H), 10.20 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.8, 20.1, 20.8, 33.5, 55.1, 58.2, 59.5, 97.6, 112.9, 125.0, 125.9, 126.1, 126.4, 126.6, 127.0, 128.2, 128.6, 129.4, 129.4, 135.2, 135.5, 143.0, 144.3, 144.8, 156.4, 168.3.

5o. Ethyl 4-(p-tolylamino)-1,2,5,6-tetrahydro-1,2,6-trip-tolylpyridine-3-carboxylate

White solid; Melting point: 196-198 °C: IR (KBr): 3236, 3024, 2978, 2918, 2864, 1654, 1517, 1448, 1409, 1371, 1323, 1246, 1070, 1018, 954, 848 cm⁻¹: ¹H NMR (400 MHz,

CDCl₃) ppm: 1.45-1.41 (t, *J* = 8.0 Hz, 3H), 2.14 (s, 3H), 2.24 (s, 3H), 2.30 (s, 3H), 2.32 (s, 3H), 2.74-2.70 (dd, *J* = 32.0, 4.0 Hz, 1H), 2.84-2.79 (dd, *J* = 32.0, 4.0 Hz, 1H), 4.34-4.26 (m, 1H), 4.46-4.38 (m, 1H), 5.06 (s, 1H), 6.17-6.15 (d, *J* = 8.0 Hz, 2H), 6.36 (s, 1H), 6.44-6.42 (d, *J* = 8.0 Hz, 2H), 6.88-6.84 (t, *J* = 8.0 Hz, 4H), 7.08-7.02 (m, 6H), 7.22-7.20 (d, *J* = 8.0 Hz, 2H), 10.23 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 13.3, 13.4, 13.9, 13.9, 16.5, 16.7, 43.8, 45.4, 56.3, 61.6, 61.8, 63.7, 64.9, 113.8, 113.8, 113.9, 114.5, 114.7, 115.1, 118.2, 118.2, 120.8, 122.5, 122.6, 122.6, 126.3, 129.2, 129.2, 129.3, 130.2, 130.2, 130.2, 130.3, 142.8, 142.9, 146.1, 146.2, 167.4, 168.5, 202.8; HRMS (ESI): found: 530.2930 C₃₆H₃₆Cl₂N₂O₂ Calc. 530.2933.

5p. Ethyl 4-(p-tolylamino)-2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydro-1-p-tolylpyridine-3-carboxylate

White solid; Melting point: 208-210-200 °C: IR (KBr): 3246, 3093, 3032, 2978, 2918, 1970, 1653, 1517, 1367, 1174, 1072, 802, 682 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 1.45-1.41 (t, *J* = 8.0 Hz, 3H), 2.16 (s, 3H), 2.27 (s, 3H), 2.80-2.69 (m, 2H), 4.38-4.27 (m, 2H), 5.05 (s, 1H), 6.29-6.27 (d, *J* = 8.0 Hz, 2H), 6.32 (s, 1H), 6.37-6.35 (d, *J* = 8.0 Hz, 2H), 6.89-6.87 (d, *J* = 8.0 Hz, 2H), 6.95-6.93 (d, *J* = 8.0 Hz, 2H), 7.07-7.05 (d, *J* = 8.0 Hz, 2H), 7.26-7.3 (m, 6H), 10.21 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 14.8, 20.1, 20.9, 33.6, 54.8, 57.3, 59.7, 97.2, 112.9, 125.7, 125.8, 127.8, 128.0, 128.3, 128.7, 129.5, 131.9, 132.7, 134.9, 135.8, 141.2, 142.7, 144.3, 156.1, 167.9.

5q. Ethyl 4-(4-nitrophenylamino)-1,2,5,6-tetrahydro-1-(4-nitrophenyl)-2,6-dip-tolylpyridine-3-carboxylate

Yellow solid; Melting point: 204-206 °C: IR (KBr): 3163, 3086, 2980, 2922, 2854, 1901, 1656, 1593, 1502, 1342, 1313, 1112, 1068, 854, 758 cm⁻¹: ¹H NMR (400 MHz, CDCl₃)

ppm: 1.52-1.48 (t, J = 8.0 Hz, 3H), 2.34 (s, 6H), 2.98-2.93 (dd, J = 24.0, 4.0 Hz, 1H), 3.10-3.04 (dd, J = 24.0, 4.0 Hz, 1H), 4.42- 4.34 (m, 1H), 4.54-4.48 (m, 1H), 5.28 (s, 1H), 6.46-6.42 (d, J = 16.0 Hz, 2H), 6.49 (s, 1H), 6.56-6.53 (d, J = 12.0 Hz, 2H), 7.03-7.01 (d, J = 8.0 Hz, 2H), 7.17-7.11 (m, 6H), 8.00-7.95 (m, 4H), 10.65 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) ppm: 14.6, 20.9, 21.1, 25.6, 33.6, 55.6, 58.4, 60.7, 102.2, 112.1, 122.8, 124.9, 125.8, 125.9, 126.0, 129.5, 129.8, 137.0, 137.4, 137.7, 137.9, 138.3, 143.9, 144.0, 151.7, 152.9, 167.7.

6a. Ethyl 5-ethyl-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenyl amino) pyridine-3-carboxylate

White solid; Melting point: 172-174 $^{\circ}\text{C}$: IR (KBr): 3228, 3143, 3035, 2929, 2873, 1658, 1579, 1371, 1300, 1265, 1068, 991, 835, 794, 694 cm^{-1} : ^1H NMR (400 MHz, CDCl_3) ppm: 0.73-0.69 (t, J = 8.0 Hz, 3H), 1.33-1.23 (m, 1H), 1.41-1.37 (t, J = 8.0 Hz, 3H), 1.49-1.43 (m, 1H), 2.79 (s, 1H), 4.33- 4.25 (m, 1H), 4.45-4.37 (m, 1H), 5.08 (s, 1H), 6.27 (s, 1H), 6.37-6.27 (m, 2H), 6.61-6.59 (d, J = 8.0 Hz, 2H), 6.68-6.64 (t, J = 8.0 Hz, 1H), 6.99-6.88 (m, 4H), 7.15-7.03 (m, 7H), 7.28-7.25 (m, 2H), 10.45 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) ppm: 12.0, 14.7, 24.9, 45.8, 54.8, 59.7, 59.9, 96.5, 114.4, 114.6, 115.2, 115.5, 117.1, 126.3, 127.1, 128.5, 128.5, 128.8, 128.9, 129.0, 138.1, 139.0, 139.0, 140.0, 140.0, 147.2, 159.3, 160.2, 160.5, 162.6, 162.9, 168.9; HRMS (ESI): found: 538.2434 $\text{C}_{36}\text{H}_{36}\text{Cl}_2\text{N}_2\text{O}_2$ Calc. 538.2434.

6b. Ethyl 2,6-bis(4-chlorophenyl)-5-ethyl-1,2,5,6-tetrahydro-1-phenyl-4-(phenyl amino) pyridine-3-carboxylate

White solid; Melting point: 178-180 $^{\circ}\text{C}$: IR (KBr): 3219, 3147, 3063, 2958, 2872, 1654, 1591, 1489, 1301, 1172, 1010, 954, 835, 746, 696 cm^{-1} : ^1H NMR (400 MHz, CDCl_3)

ppm: 0.74-0.700 (t, $J = 8.0$ Hz, 3H), 1.31-1.21 (m, 1H), 1.41-1.37 (t, $J = 8.0$ Hz, 3H), 1.49-1.42 (m, 1H), 2.78-2.74 (m, 1H), 4.33- 4.27 (m, 1H), 4.45-4.37 (m, 1H), 5.07 (s, 1H), 6.25 (s, 1H), 6.38-6.36 (m, 2H), 6.59-6.56 (d, $J = 12.0$ Hz, 2H), 6.69-6.65 (t, $J = 6.0$ Hz, 1H), 7.02-7.00 (d, $J = 8.0$ Hz, 2H), 7.18-7.08 (m, 6H), 7.25-7.23 (m, 1H), 10.45 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) ppm: 12.0, 14.7, 25.0, 25.6, 45.7, 54.9, 59.7, 59.9, 67.9, 96.1, 114.6, 117.3, 126.4, 127.1, 127.9, 128.4, 128.6, 128.9, 128.9, 131.9, 132.5, 138.0, 141.9, 142.9, 147.1, 159.3, 168.8.

6c. Ethyl 2,6-bis(4-cyanophenyl)-5-ethyl-1,2,5,6-tetrahydro-1-phenyl-4-(phenyl amino) pyridine-3-carboxylate

Yellow solid; Melting point: 224-226 $^{\circ}\text{C}$: IR (KBr): 3221, 3062, 2970, 2872, 2225, 1651, 1589, 1498, 1301, 1247, 1068, 952, 744, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) ppm: 0.77-0.73 (t, $J = 8.0$ Hz, 3H), 1.34-1.21 (m, 1H), 1.41-1.37 (t, $J = 8.0$ Hz, 3H), 1.47-1.44 (m, 1H), 2.77 (s, 1H), 4.45- 4.28 (m, 2H), 5.14 (s, 1H), 6.31 (s, 1H), 6.39 (s, 2H), 6.55-6.53 (d, $J = 8.0$ Hz, 2H), 6.73-6.70 (t, $J = 6.0$ Hz 1H), 7.13-7.09 (t, $J = 8.0$ Hz, 2H), 7.20-7.18 (m, 5H), 7.45-7.43 (d, $J = 8.0$ Hz, 2H), 7.60-7.52 (m, 4H), 10.49 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) ppm: 12.0, 14.6, 25.1, 25.6, 45.3, 55.3, 60.1, 60.2, 67.9, 95.1, 110.2, 110.9, 114.8, 118.2, 118.7, 119.0, 126.9, 127.0, 127.8, 128.3, 131.8, 132.4, 137.6, 146.6, 148.9, 150.0, 159.2, 168.5; HRMS (ESI): found: 552.2525 $\text{C}_{36}\text{H}_{36}\text{Cl}_2\text{N}_2\text{O}_2$ Calc. 552.2525.

7a. Allyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenylpyridine-3-carboxylate

Yellow solid; Melting point: 166-168 $^{\circ}\text{C}$: IR (KBr): 3242, 3084, 3026, 2978, 2924, 2858, 1735, 1649, 1600, 1494, 1450, 1321, 1251, 1066, 970, 802, 729, 698 cm^{-1} ; ^1H NMR (400

MHz, CDCl₃) ppm: 2.72-2.70 (d, *J* = 8.0 Hz, 1H), 2.85-2.84 (d, *J* = 4.0 Hz, 1H), 4.92-4.79 (m, 2H), 5.11 (s, 1H), 5.35-5.32 (d, *J* = 12.0 Hz, 1H), 5.48-5.44 (d, *J* = 12.0 Hz, 1H), 6.19-6.09 (m, 3H), 6.45-6.41 (d, *J* = 16.0 Hz, 3H), 6.70-6.97 (d, *J* = 12.0 Hz, 2H), 7.15-7.00 (m, 4H), 7.31-7.19 (m, 8H), 10.21 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 33.5, 55.2, 58.2, 64.6, 98.3, 114.0, 117.9, 121.2, 126.2, 126.5, 126.6, 127.1, 127.5, 128.4, 128.7, 128.8, 129.0, 131.5, 132.9, 136.3, 142.1, 143.1, 145.4, 155.9, 167.6; HRMS (ESI): found: 554.1528 C₃₆H₃₆Cl₂N₂O₂ Calc. 554.1501.

7b. Allyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-bis(3-nitrophenyl)pyridine-3-carboxylate

Yellow solid; Melting point: 190-192 °C: IR (KBr): 3221, 3155, 3076, 2926, 2862, 1734, 1658, 1598, 1526, 1494, 1350, 1251, 1091, 978, 800, 729 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.94-2.82 (m, 2H), 4.86-4.84 (d, *J* = 8.0 Hz, 1H), 4.98-4.93 (m, 1H), 5.31 (s, 1H), 5.41-5.38 (d, *J* = 12.0 Hz, 1H), 5.51-5.46 (d, *J* = 20.0 Hz, 1H), 6.18-6.11 (m, 1H), 6.41-6.33 (m, 4H), 6.44 (s, 1H), 7.05-7.01 (d, *J* = 16.0 Hz, 2H), 7.14-7.11 (d, *J* = 12.0 Hz, 2H), 7.53-7.44 (m, 3H), 7.64-7.62 (d, *J* = 8.0 Hz, 1H), 7.95 (s, 1H), 8.10-8.09 (m, 2H), 10.31 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 33.7, 55.3, 57.0, 65.2, 97.2, 114.3, 118.9, 121.3, 121.5, 122.1, 122.7, 122.9, 126.7, 129.2, 129.4, 129.5, 129.9, 132.2, 132.3, 132.4, 135.6, 143.8, 144.2, 145.6, 148.6, 148.7, 155.0, 167.1; HRMS (ESI): found: 664.1229 C₃₆H₃₆Cl₂N₂O₂ Calc. 664.1221.

7c. Allyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-dip-tolylpyridine-3-carboxylate

Yellow solid; Melting point: 192-194 °C: IR (KBr): 3236, 3088, 3020, 2981, 2920, 2878, 1737, 1649, 1602, 1498, 1321, 1249, 1064, 931, 794, 758 cm⁻¹: ¹H NMR (400 MHz,

CDCl₃) ppm: 2.31 (s, 3H), 2.34 (s, 3H), 2.71-2.67 (d, $J = 16.0$ Hz, 1H), 2.88-2.83 (d, $J = 20.0$ Hz, 1H), 4.90- 4.79 (m, 2H), 5.06 (s, 1H), 5.34-5.31 (d, $J = 12.0$ Hz, 1H), 5.47-5.43 (d, $J = 16.0$ Hz, 1H), 6.16-6.07 (m, 1H), 6.20-6.18 (d, $J = 8.0$ Hz, 2H), 6.31 (s, 1H), 6.44-6.41 (d, $J = 12.0$ Hz, 2H), 7.10-6.90 (m, 10H), 7.22-7.18 (d, $J = 16.0$ Hz, 2H), 10.21 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 20.9, 21.1, 33.5, 55.0, 57.9, 64.5, 98.4, 113.9, 117.8, 121.0, 126.2, 126.4, 127.0, 128.6, 128.9, 129.0, 129.4, 131.3, 132.9, 136.1, 136.4, 137.0, 139.1, 140.1, 145.5, 155.9, 167.7; HRMS (ESI): found: 582.1841 C₃₆H₃₆Cl₂N₂O₂ Calc. 582.1836.

8a. Benzyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate

Yellow solid; Melting point: 224-226 °C: IR (KBr): 3236, 3057, 3030, 2887, 2368, 1643, 1593, 1500, 1450, 1278, 1236, 1039, 968, 914, 746 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.53-2.40 (m, 1H), 2.83-2.79 (d, $J = 24.0, 4.0$ Hz, 1H), 4.57- 4.53 (dd, $J = 24.0, 4.0$ Hz, 1H), 5.19-5.16 (d, $J = 12.0$ Hz, 1H), 5.27-5.24 (d, $J = 12.0$ Hz, 1H), 6.30 (s, 1H), 6.74-6.70 (t, $J = 8.0$ Hz, 1H), 6.87-6.85 (d, $J = 8.0$ Hz, 2H), 6.97-6.95 (d, $J = 8.0$ Hz, 2H), 7.14-7.09 (m, 4H), 7.21-7.17 (t, $J = 8.0$ Hz, 2H), 7.30-6.23 (m, 10H), 7.40-7.36 (t, $J = 8.0$ Hz, 2H), 7.64-7.62 (d, $J = 8.0$ Hz, 2H), 10.66 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 36.4, 60.5, 61.5, 65.3, 97.4, 115.5, 118.2, 123.9, 125.0, 126.8, 126.8, 127.1, 127.5, 127.8, 128.5, 128.7, 128.8, 129.3, 136.9, 138.5, 143.4, 146.0, 150.5, 158.0, 168.0; HRMS (ESI): found: 536.2464 C₃₆H₃₆Cl₂N₂O₂ Calc. 536.2469.

8b. Benzyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenylpyridine-3-carboxylate

Yellow solid; Melting point: 230-232 °C: IR (KBr): 3232, 3028, 2924, 2852, 1643, 1593, 1500, 1379, 1278, 1236, 1037, 914, 844, 700 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 2.53-2.40 (m, 1H), 2.84-2.79 (dd, *J* = 24.0, 4.0 Hz 1H), 4.57- 4.53 (dd, *J* = 24.0, 4.0 Hz, 1H), 5.19-5.16 (d, *J* = 12.0 Hz, 1H), 5.27-5.24 (d, *J* = 12.0 Hz, 1H), 6.30 (s, 1H), 6.74-6.71 (t, *J* = 6.0 Hz, 1H), 6.87-6.85 (d, *J* = 8.0 Hz, 2H), 6.97-6.95 (d, *J* = 8.0 Hz, 2H), 7.21-7.10 (m, 6H), 7.31-6.25 (m, 9H), 7.40-7.36 (t, *J* = 8.0 Hz, 2H), 7.64-7.62 (d, *J* = 8.0 Hz, 2H), 10.62 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) ppm: 36.4, 60.5, 61.5, 65.2, 97.4, 115.5, 118.2, 123.9, 124.9, 126.8, 126.8, 127.1, 127.5, 127.8, 128.4, 128.7, 128.8, 129.3, 136.9, 138.5, 143.4, 146.1, 150.5, 158.0, 168.0; HRMS (ESI): found: 604.1684 C₃₆H₃₆Cl₂N₂O₂ Calc. 604.1684.

9. Ethyl 2-((phenylamino)(phenyl)methyl)-3-oxohexanoate

White solid; Melting point: 78-80 °C: IR (KBr): 3379, 3020, 2966, 2872, 2372, 1737, 1710, 1602, 1514, 1494, 1303, 1282, 1029, 750, 700 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) ppm: 0.83-0.77 (t, *J* = 12.0 Hz, 3H), 1.16-1.10 (t, *J* = 12.0 Hz, 3H), 1.58-1.45 (m, 2H), 2.40-2.22 (m, 1H), 2.55-2.46 (m, 1H), 3.97-3.89 (dd, *J* = 24.0, 4.0 Hz, 1H), 4.16- 4.05 (m, 2H), 5.20 (s, 1H), 6.57-6.55 (d, *J* = 8.0 Hz, 2H), 6.69-6.65 (t, *J* = 12.0 Hz, 1H), 6.92-6.87 (t, *J* = 10.0 Hz, 1H), 7.42-7.03 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) ppm: 13.3, 13.9, 16.5, 43.8, 45.4, 56.3, 61.6, 63.7, 64.9, 113.8, 114.7, 115.1, 118.2, 120.8, 122.5, 126.3, 129.1, 129.3, 130.2, 142.8, 146.2, 168.5, 202.8; HRMS (ESI): found: 339.1834 C₃₆H₃₆Cl₂N₂O₂ Calc. 339.1833.

Supporting information

¹H-NMR spectrum of 4a

¹³C-NMR spectrum of 4a

¹H-NMR spectrum of 4b

¹³C-NMR spectrum of 4b

¹H-NMR spectrum of 4c

¹³C-NMR spectrum of 4c

¹H-NMR spectrum of 4d

¹³C-NMR spectrum of 4d

¹H-NMR spectrum of 4e

¹³C-NMR spectrum of 4e

¹H-NMR spectrum of 4f

^{13}C -NMR spectrum of 4f

¹H-NMR spectrum of 4g

¹³C-NMR spectrum of 4g

¹H-NMR spectrum of 4h

¹³C-NMR spectrum of 4h

¹H-NMR spectrum of 4i

¹³C-NMR spectrum of 4i

¹H-NMR spectrum of 4j

^{13}C -NMR spectrum of 4j

¹H-NMR spectrum of 4k

```

NAME      NAAA4CLAMC
EXPNO     1
PROCNO    1
Date_     20110922
Time      19.42
INSTRUM    spect
PROBHD     5 mm BBO BB-1H
PULPROG    zgpg30
TD         32768
SOLVENT    CDCl3
NS         14
DS         4
SWH         8012.828 Hz
FIDRES     0.244622 Hz
AQ         2.0447731 sec
RG          645
DM          42.450 usec
DE          6.50 usec
TE         296.4 K
D1         2.00000000 sec
D11        1
===== CHANNEL f1 =====
NUC1       1H
P1         14.00 usec
PL1        0.20 dB
PLRM       10.31496146 M
SFO1       400.1526910 MHz
SI         16384
SF         400.1510134 MHz
MCW        0
SSB         0
LB          0.20 Hz
GB          0
PC          1.00
  
```

¹³C-NMR spectrum of 4k

```

NAME      NAAA4CLAMC C13
EXPNO     1
PROCNO    1
Date_     20110922
Time      19.42
INSTRUM    spect
PROBHD     5 mm BBO BB-1H
PULPROG    zgpg30
TD         32768
SOLVENT    CDCl3
NS         4
DS         4
SWH         24039.461 Hz
FIDRES     0.346798 Hz
AQ         1.3431999 sec
RG          645
DM          20.800 usec
DE          6.50 usec
TE         296.4 K
D1         2.00000000 sec
D11        0.05000000 sec
TD4        1
===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        -0.10 dB
PLRM       44.09128223 M
SFO1       100.6270593 MHz
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      90.00 usec
PL2        0.20 dB
PL12       14.20 dB
PL13       14.20 dB
PLRM       10.31496146 M
PL12M      0.25910059 M
PL13M      0.25910059 M
SFO2       400.1510134 MHz
SF         400.1510134 MHz
MCW        0
SSB         0
LB          1.00 Hz
GB          0
PC          1.40
  
```

¹H-NMR spectrum of 5a

¹³C-NMR spectrum of 5a

¹H-NMR spectrum of 5b

¹³C-NMR spectrum of 5b

¹H-NMR spectrum of 5c

¹³C-NMR spectrum of 5c

¹H-NMR spectrum of 5d

^{13}C -NMR spectrum of 5d

¹H-NMR spectrum of 5e

^{13}C -NMR spectrum of 5e

¹H-NMR spectrum of 5f

¹³C-NMR spectrum of 5f

¹H-NMR spectrum of 5g

¹³C-NMR spectrum of 5g

¹H-NMR spectrum of 5h

¹³C-NMR spectrum of 5h

¹H-NMR spectrum of 5i

¹³C-NMR spectrum of 5i

¹H-NMR spectrum of 5j

¹³C-NMR spectrum of 5j

¹H-NMR spectrum of 5k

¹³C-NMR spectrum of 5k

¹H-NMR spectrum of 5l

```

NAME      ZAA4CLANC
EXPNO     1
PROCNO    1
Date_     20110923
Time      9.24
INSTRUM    spect
PROBHD     5 mm BBO BB-1H
PULPROG    zgpg30
TD         32768
SOLVENT    CDCl3
NS         16
DS         0
SWH         6012.820 Hz
FIDRES     0.244533 Hz
AQ         2.0447731 sec
RG         256
IN         62.4850 usec
DE         6.50 usec
TE         296.7 K
D1         2.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.20 usec
PL1        0.20 dB
PL12M      10.31499146 M
SFO1       400.1500146 MHz
SI         16384
SF         400.1500146 MHz
MDM        0
SGB         0
LB         0.30 Hz
GB         0
PC         1.00
  
```

¹³C-NMR spectrum of 5l

```

NAME      ZAA4CLANC
EXPNO     1
PROCNO    1
Date_     20110923
Time      9.54
INSTRUM    spect
PROBHD     5 mm BBO BB-1H
PULPROG    zgpg30
TD         32768
SOLVENT    CDCl3
NS         4
DS         4
SWH         24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631998 sec
RG         256
IN         20.800 usec
DE         4.50 usec
TE         296.7 K
D1         2.00000000 sec
D11        0.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.88 usec
PL1        0.00 dB
PL12M      44.08129323 M
SFO1       100.6278693 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      90.00 usec
PL2        0.20 dB
PL12       16.20 dB
PL13       16.20 dB
PL12M      10.31499146 M
PL13M      0.259910669 M
SFO2       400.1500146 MHz
SI         32768
SF         100.6278693 MHz
MDM        0
SGB         0
LB         1.00 Hz
GB         0
PC         1.40
  
```

¹H-NMR spectrum of 5m

```

NAME      EAA4CL4 ac
EXPNO     1
PROCNO    1
Date_     20110923
Time      10.30
INSTRUM    spect
PROBHD     5 mm BBO BB-1H
PULPROG    zgpg30
TD         65536
SOLVENT    CDCl3
NS         16
DS         4
SWH         8012.420 Hz
FIDRES     0.244532 Hz
AQ         2.0447722 sec
RG         640
IN         62.400 usec
DE         6.50 usec
TE         296.7 K
D1         2.00000000 sec
DEL        1
===== CHANNEL f1 =====
NUC1       1H
P1         14.20 usec
PL1        0.20 dB
PL1M       10.21499146 M
SFO1       400.1514000 MHz
SI         32768
SF         400.1514000 MHz
MAGN       1H
GB         0
GB2         0
GB3         0
PC         1.00

```

¹³C-NMR spectrum of 5m

```

NAME      EAA4CL4 ac CD3
EXPNO     1
PROCNO    1
Date_     20110923
Time      10.30
INSTRUM    spect
PROBHD     5 mm BBO BB-1H
PULPROG    zgpg30
TD         65536
SOLVENT    CDCl3
NS         16
DS         4
SWH         24038.461 Hz
FIDRES     0.344788 Hz
AQ         1.3631998 sec
RG         2560
IN         20.000 usec
DE         6.50 usec
TE         296.7 K
D1         2.00000000 sec
DEL        1
===== CHANNEL f1 =====
NUC1       13C
P1         9.99 usec
PL1        0.80 dB
PL1M       44.09129222 M
SFO1       100.6274500 MHz
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      90.00 usec
PL2        0.20 dB
PL12       14.20 dB
PL13       14.20 dB
PL1M       10.21499146 M
PL12M      0.25910000 M
PL13M      0.25910000 M
SFO2       400.1514000 MHz
SI         32768
SF         100.6177990 MHz
MAGN       1H
GB         0
GB2         1.00 Hz
GB3         0
PC         1.40

```

¹H-NMR spectrum of 5n

¹³C-NMR spectrum of 5n

¹H-NMR spectrum of 5o

¹³C-NMR spectrum of 5o

¹H-NMR spectrum of 5p

^{13}C -NMR spectrum of 5p

¹H-NMR spectrum of 5q

¹³C-NMR spectrum of 5q

¹H-NMR spectrum of 6a

¹³C-NMR spectrum of 6a

¹H-NMR spectrum of 6b

¹³C-NMR spectrum of 6b

¹H-NMR spectrum of 6c

¹³C-NMR spectrum of 6c

¹H-NMR spectrum of 7a

¹³C-NMR spectrum of 7a

¹H-NMR spectrum of 7b

¹³C-NMR spectrum of 7b

¹H-NMR spectrum of 7c

^{13}C -NMR spectrum of 7c

¹H-NMR spectrum of 8a

¹³C-NMR spectrum of 8a

¹H-NMR spectrum of 8b

¹³C-NMR spectrum of 8b

¹H-NMR spectrum of 9a

¹³C-NMR spectrum of 9a

SI Figure 1: ORTEP X-ray structure of 4a

SI Figure 2: ORTEP X-ray structure of 5a

Table 1. Crystal data and structure refinement for 5a.

Identification code	5a	
Empirical formula	$C_{32} H_{30} N_2 O_2$	
Formula weight	474.58	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 9.7807(9) Å	α = 106.192(6)°.
	b = 11.0044(8) Å	β = 108.601(7)°.
	c = 13.9138(9) Å	γ = 99.996(7)°.
Volume	1305.09(17) Å ³	
Z	2	
Density (calculated)	1.208 Mg/m ³	
Absorption coefficient	0.075 mm ⁻¹	
F(000)	504	
Theta range for data collection	2.97 to 29.31°.	
Index ranges	-13 ≤ h ≤ 12, -13 ≤ k ≤ 14, -	
	19 ≤ l ≤ 17	
Reflections collected	14187	
Independent reflections	6135 [R(int) = 0.0456]	
Completeness to theta = 25.00°	99.9 %	
Refinement method	Full-matrix least-squares on	
	F ²	
Data / restraints / parameters	6135 / 0 / 330	
Goodness-of-fit on F ²	0.916	
Final R indices [I > 2σ(I)]	R1 = 0.0556, wR2 = 0.1383	

R indices (all data)

$R1 = 0.0977$, $wR2 = 0.1534$

Largest diff. peak and hole

0.209 and -0.207 e.Å⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)**for 5a. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.**

Atoms	x	y	z	U(eq)
O(1)	4408(1)	6425(1)	4802(1)	60(1)
O(2)	2846(1)	5290(1)	5339(1)	57(1)
C(3)	4698(2)	7188(1)	6646(1)	41(1)
N	3862(1)	8108(1)	8111(1)	43(1)
C(5)	2691(2)	7987(2)	8473(1)	42(1)
C(6)	4180(2)	6935(1)	7506(1)	42(1)
N(0AA)	6319(2)	8764(1)	6286(1)	52(1)
C(8)	5766(2)	8364(2)	6955(1)	42(1)
C(9)	4025(2)	6302(2)	5535(1)	45(1)
C(10)	4746(2)	9408(1)	8264(1)	42(1)
C(11)	7399(2)	10004(2)	6603(1)	45(1)
C(12)	3918(2)	10068(2)	7526(1)	45(1)
C(13)	5271(2)	6425(1)	8255(1)	44(1)
C(14)	1935(2)	6780(2)	8452(1)	54(1)
C(15)	2231(2)	9088(2)	8884(1)	48(1)
C(16)	6199(2)	9284(2)	8091(1)	45(1)
C(17)	5626(2)	6845(2)	9363(1)	59(1)
C(18)	745(2)	6673(2)	8792(2)	67(1)
C(19)	1048(2)	8963(2)	9226(1)	60(1)
C(20)	2695(2)	9349(2)	6563(1)	54(1)
C(21)	5887(2)	5482(2)	7818(2)	56(1)
C(22)	4421(2)	11417(2)	7795(2)	65(1)
C(23)	6959(2)	11025(2)	6346(2)	65(1)
C(24)	294(2)	7755(2)	9173(2)	69(1)
C(25)	8899(2)	10166(2)	7157(2)	67(1)

C(26)	2077(2)	4352(2)	4232(2)	68(1)
C(27)	6568(2)	6331(2)	10013(2)	73(1)
C(28)	2016(2)	9954(2)	5873(2)	73(1)
C(29)	760(3)	3429(2)	4189(2)	85(1)
C(30)	7165(2)	5399(2)	9565(2)	76(1)
C(31)	6835(2)	4978(2)	8473(2)	72(1)
C(32)	2536(3)	11287(3)	6145(2)	86(1)
C(33)	8043(3)	12214(2)	6658(2)	86(1)
C(34)	9938(2)	11351(2)	7460(2)	89(1)
C(35)	9526(3)	12361(2)	7219(2)	89(1)
C(36)	3724(3)	12023(2)	7100(2)	87(1)

Table 3. Bond lengths [Å] and angles [°] for 5a.

ATOMS	Distance	ATOMS	Distance
O(1)-C(9)	1.2256(18)	C(22)-C(36)	1.393(3)
O(2)-C(9)	1.3525(19)	C(23)-C(33)	1.390(3)
O(2)-C(26)	1.452(2)	C(25)-C(34)	1.367(3)
C(3)-C(8)	1.373(2)	C(26)-C(29)	1.468(3)
C(3)-C(9)	1.436(2)	C(27)-C(30)	1.365(3)
C(3)-C(6)	1.514(2)	C(28)-C(32)	1.365(3)
N-C(5)	1.3909(19)	C(30)-C(31)	1.367(3)
N-C(10)	1.4568(18)	C(32)-C(36)	1.364(3)
N-C(6)	1.4742(19)	C(33)-C(35)	1.365(4)
C(5)-C(14)	1.391(2)	C(12)-C(22)	1.380(2)
C(5)-C(15)	1.401(2)	C(12)-C(20)	1.382(2)
C(6)-C(13)	1.538(2)	C(13)-C(21)	1.382(2)
N(0AA)-C(8)	1.3489(19)	C(13)-C(17)	1.383(2)

N(0AA)-C(11)	1.428(2)	C(14)-C(18)	1.388(2)
C(8)-C(16)	1.494(2)	C(15)-C(19)	1.384(2)
C(10)-C(12)	1.525(2)	C(17)-C(27)	1.387(2)
C(10)-C(16)	1.537(2)	C(18)-C(24)	1.369(3)
C(11)-C(23)	1.367(2)	C(19)-C(24)	1.374(3)
C(11)-C(25)	1.375(2)	C(20)-C(28)	1.382(2)
C(34)-C(35)	1.338(3)	C(21)-C(31)	1.386(3)

ATOMS	Angle	ATOMS	Angle
C(9)-O(2)-C(26)	117.13(13)	C(14)-C(5)-C(15)	117.14(14)
C(8)-C(3)-C(9)	120.80(14)	N-C(6)-C(3)	110.86(11)
C(8)-C(3)-C(6)	116.83(13)	N-C(6)-C(13)	112.72(12)
C(9)-C(3)-C(6)	122.16(13)	C(3)-C(6)-C(13)	112.60(12)
C(5)-N-C(10)	120.35(12)	C(8)-N(0AA)-C(11)	124.48(14)
C(5)-N-C(6)	121.31(12)	N(0AA)-C(8)-C(3)	124.61(14)
C(10)-N-C(6)	118.23(11)	N(0AA)-C(8)-C(16)	119.80(13)
N-C(5)-C(14)	121.84(14)	C(3)-C(8)-C(16)	115.31(13)
N-C(5)-C(15)	121.02(14)	O(1)-C(9)-O(2)	121.08(14)
O(1)-C(9)-C(3)	125.77(14)	C(17)-C(13)-C(6)	122.13(14)
O(2)-C(9)-C(3)	113.13(14)	C(18)-C(14)-C(5)	121.02(17)
N-C(10)-C(12)	114.39(12)	C(19)-C(15)-C(5)	120.99(16)
N-C(10)-C(16)	108.89(12)	C(8)-C(16)-C(10)	108.07(12)
C(12)-C(10)-C(16)	109.64(12)	C(13)-C(17)-C(27)	120.90(18)
C(23)-C(11)-C(25)	119.65(16)	C(24)-C(18)-C(14)	121.01(17)
C(23)-C(11)-N(0AA)	120.70(16)	C(24)-C(19)-C(15)	120.85(18)
C(25)-C(11)-N(0AA)	119.64(15)	C(28)-C(20)-C(12)	121.18(17)
C(22)-C(12)-C(20)	118.08(16)	C(13)-C(21)-C(31)	120.77(17)
C(22)-C(12)-C(10)	119.91(15)	C(12)-C(22)-C(36)	120.47(19)

C(20)-C(12)-C(10)	121.97(14)	C(11)-C(23)-C(33)	119.11(19)
C(21)-C(13)-C(17)	118.04(15)	C(18)-C(24)-C(19)	118.96(17)
C(21)-C(13)-C(6)	119.80(14)	C(34)-C(25)-C(11)	119.88(18)
O(2)-C(26)-C(29)	107.61(17)	C(36)-C(32)-C(28)	120.0(2)
C(30)-C(27)-C(17)	120.16(19)	C(35)-C(33)-C(23)	120.4(2)
C(32)-C(28)-C(20)	120.0(2)	C(35)-C(34)-C(25)	121.2(2)
C(27)-C(30)-C(31)	119.80(18)	C(34)-C(35)-C(33)	119.7(2)
C(30)-C(31)-C(21)	120.33(19)	C(32)-C(36)-C(22)	120.25(19)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	58(1)	68(1)	42(1)	11(1)	20(1)	5(1)
O(2)	44(1)	61(1)	45(1)	5(1)	12(1)	-3(1)
C(3)	31(1)	49(1)	38(1)	12(1)	11(1)	9(1)
N	36(1)	48(1)	47(1)	16(1)	19(1)	10(1)
C(5)	31(1)	58(1)	35(1)	18(1)	11(1)	10(1)
C(6)	33(1)	46(1)	40(1)	11(1)	14(1)	6(1)
N(0AA)	45(1)	59(1)	41(1)	10(1)	18(1)	-1(1)
C(8)	29(1)	55(1)	39(1)	14(1)	12(1)	10(1)
C(9)	36(1)	51(1)	44(1)	14(1)	13(1)	12(1)
C(10)	35(1)	48(1)	36(1)	7(1)	14(1)	6(1)
C(11)	38(1)	53(1)	45(1)	16(1)	21(1)	11(1)
C(12)	42(1)	49(1)	49(1)	17(1)	25(1)	13(1)
C(13)	33(1)	46(1)	48(1)	16(1)	16(1)	5(1)
C(14)	45(1)	66(1)	62(1)	30(1)	26(1)	18(1)
C(15)	38(1)	61(1)	43(1)	14(1)	15(1)	11(1)
C(16)	30(1)	56(1)	41(1)	12(1)	12(1)	4(1)
C(17)	52(1)	73(1)	47(1)	18(1)	16(1)	22(1)
C(18)	50(1)	79(1)	82(1)	40(1)	34(1)	13(1)
C(19)	48(1)	79(1)	56(1)	18(1)	26(1)	23(1)
C(20)	47(1)	61(1)	51(1)	18(1)	17(1)	18(1)
C(21)	57(1)	56(1)	60(1)	21(1)	27(1)	16(1)
C(22)	54(1)	54(1)	88(1)	20(1)	34(1)	9(1)
C(23)	62(1)	68(1)	65(1)	24(1)	21(1)	27(1)
C(24)	49(1)	96(2)	77(1)	34(1)	38(1)	22(1)

C(25)	40(1)	67(1)	83(1)	25(1)	14(1)	12(1)
C(26)	56(1)	65(1)	50(1)	-1(1)	6(1)	-1(1)
C(27)	62(1)	96(2)	57(1)	32(1)	12(1)	26(1)
C(28)	69(1)	101(2)	64(1)	37(1)	27(1)	43(1)
C(29)	68(1)	72(1)	76(1)	14(1)	3(1)	-6(1)
C(30)	56(1)	92(2)	90(2)	52(1)	18(1)	29(1)
C(31)	64(1)	72(1)	101(2)	41(1)	41(1)	34(1)
C(32)	85(2)	111(2)	113(2)	76(2)	56(2)	56(2)
C(33)	124(2)	58(1)	83(2)	31(1)	44(2)	31(1)
C(34)	44(1)	83(2)	113(2)	18(1)	23(1)	-1(1)
C(35)	89(2)	66(1)	97(2)	16(1)	44(2)	-9(1)
C(36)	85(2)	65(1)	144(2)	56(2)	67(2)	31(1)

Table 5. Torsion angles [°] for 5a.

ATOMS	Angle	ATOMS	Angle
C(10)-N-C(5)-C(14)	-172.67(13)	C(5)-N-C(10)-C(16)	164.34(13)
C(6)-N-C(5)-C(14)	11.3(2)	C(6)-N-C(10)-C(16)	-19.50(16)
C(10)-N-C(5)-C(15)	6.8(2)	C(8)-N(0AA)-C(11)-C(23)	-101.4(2)
C(6)-N-C(5)-C(15)	-169.19(13)	C(8)-N(0AA)-C(11)-C(25)	79.7(2)
C(5)-N-C(6)-C(3)	144.31(13)	N-C(10)-C(12)-C(22)	160.42(14)
C(10)-N-C(6)-C(3)	-31.80(16)	C(16)-C(10)-C(12)-C(22)	-76.94(18)
C(5)-N-C(6)-C(13)	-88.43(15)	N-C(10)-C(12)-C(20)	-22.0(2)
C(10)-N-C(6)-C(13)	95.45(14)	C(16)-C(10)-C(12)-C(20)	100.61(17)
C(8)-C(3)-C(6)-N	45.97(18)	N-C(6)-C(13)-C(21)	-168.79(13)
C(9)-C(3)-C(6)-N	-128.83(14)	C(3)-C(6)-C(13)-C(21)	-42.46(18)
C(8)-C(3)-C(6)-C(13)	-81.36(16)	N-C(6)-C(13)-C(17)	13.5(2)
C(9)-C(3)-C(6)-C(13)	103.85(16)	C(3)-C(6)-C(13)-C(17)	139.81(15)

C(11)-N(0AA)-C(8)-C(3)	178.17(15)	N-C(5)-C(14)-C(18)	-178.43(15)
C(11)-N(0AA)-C(8)-C(16)	4.5(2)	C(15)-C(5)-C(14)-C(18)	2.0(2)
C(9)-C(3)-C(8)-N(0AA)	-3.1(2)	N-C(5)-C(15)-C(19)	178.86(14)
C(6)-C(3)-C(8)-N(0AA)	-177.96(14)	C(14)-C(5)-C(15)-C(19)	-1.6(2)
C(9)-C(3)-C(8)-C(16)	170.85(13)	N(0AA)-C(8)-C(16)-C(10)	124.75(15)
C(6)-C(3)-C(8)-C(16)	-4.0(2)	C(3)-C(8)-C(16)-C(10)	-49.51(18)
C(26)-O(2)-C(9)-O(1)	0.9(2)	N-C(10)-C(16)-C(8)	60.80(15)
C(26)-O(2)-C(9)-C(3)	179.12(14)	C(12)-C(10)-C(16)-C(8)	-65.04(15)
C(8)-C(3)-C(9)-O(1)	7.3(3)	C(21)-C(13)-C(17)-C(27)	-0.3(3)
C(6)-C(3)-C(9)-O(1)	-178.11(15)	C(6)-C(13)-C(17)-C(27)	177.51(16)
C(8)-C(3)-C(9)-O(2)	-170.80(13)	C(5)-C(14)-C(18)-C(24)	-1.0(3)
C(6)-C(3)-C(9)-O(2)	3.8(2)	C(5)-C(15)-C(19)-C(24)	0.1(3)
C(5)-N-C(10)-C(12)	-72.61(17)	C(22)-C(12)-C(20)-C(28)	1.6(3)
C(6)-N-C(10)-C(12)	103.54(15)	C(10)-C(12)-C(20)-C(28)	-175.97(16)

ATOMS	Angle	ATOMS	Angle
C(17)-C(13)-C(21)-C(31)	-0.1(2)	C(12)-C(20)-C(28)-C(32)	-1.0(3)
C(6)-C(13)-C(21)-C(31)	-177.94(15)	C(17)-C(27)-C(30)-C(31)	0.3(3)
C(20)-C(12)-C(22)-C(36)	-1.0(3)	C(27)-C(30)-C(31)-C(21)	-0.6(3)
C(10)-C(12)-C(22)-C(36)	176.63(17)	C(13)-C(21)-C(31)-C(30)	0.6(3)
C(25)-C(11)-C(23)-C(33)	-0.5(3)	C(20)-C(28)-C(32)-C(36)	-0.2(3)
N(0AA)-C(11)-C(23)-C(33)	-179.38(17)	C(11)-C(23)-C(33)-C(35)	-0.3(3)
C(14)-C(18)-C(24)-C(19)	-0.6(3)	C(11)-C(25)-C(34)-C(35)	-0.7(3)
C(15)-C(19)-C(24)-C(18)	1.1(3)	C(25)-C(34)-C(35)-C(33)	0.0(4)
C(23)-C(11)-C(25)-C(34)	1.0(3)	C(23)-C(33)-C(35)-C(34)	0.6(4)
N(0AA)-C(11)-C(25)-C(34)	179.90(18)	C(28)-C(32)-C(36)-C(22)	0.8(3)
C(9)-O(2)-C(26)-C(29)	-174.41(15)	C(12)-C(22)-C(36)-C(32)	-0.2(3)

C(13)-C(17)-C(27)-C(30) 0.2(3)

SI Table 1

Screening of catalysts and solvents for the one-pot synthesis of tetrahydropyridine **5a**^a

Entry	Catalyst (mol %)	Solvent	Time/h	Yield (%) ^b
1	FeCl ₃ (10 mol %)	MeOH	12	46
2	LaCl ₃ (10 mol %)	MeOH	4	80
3	AlCl ₃ (10 mol %)	MeOH	12	28
4	NiCl ₂ (10 mol %)	MeOH	12	38
5	CuCl ₂ (10 mol %)	MeOH	12	40
6	ZnCl ₂ (10 mol %)	MeOH	12	55
7	Al ₂ O ₃ basic (10 mol %)	MeOH	12	19
8	Li ₂ O ₃ + L-proline (10+5 mol %)	MeOH	12	41
9	Triethyl amine (10 mol %)	MeOH	12	None
10	La ₂ O ₃ (10 mol %)	MeOH	8	65
11	SiO ₂ Cl (10 mol %)	MeOH	3.5	78
12	SiO ₂ Cl (10 mol %)	EtOH	3.5	70
13	SiO ₂ Cl (10 mol %)	CH ₃ CN	3.5	75
14	SiO ₂ Cl (10 mol %)	CH ₂ Cl ₂	3.5	62
15	SiO ₂ Cl (10 mol %)	CHCl ₃	3.5	63

16	SiO ₂ Cl (10 mol %)	i-PrOH	4	58
17	SiO ₂ Cl (10 mol %)	n-BuOH	12	None
18	SiO ₂ Cl (10 mol %)	THF	4	60
19	SiO ₂ Cl (10 mol %)	Ethyl acetate	12	21
20	SiO ₂ Cl (10 mol %)	Acetone	3.5	46
21	SiO ₂ Cl (10 mol %)	Toluene	12	None
22	SiO ₂ Cl (10 mol %)	Water	12	None
23	SiO ₂ Cl (10 mol %)	AcOH	0.5	93
24	LaCl ₃ (10 mol %)	AcOH	0.5	93
25	CuCl ₂ (10 mol %)	AcOH	0.5	91
26	ZnCl ₂ (10 mol %)	AcOH	0.5	93
27	La ₂ O ₃ (10 mol %)	AcOH	0.5	93
28	1 N, Con HCl (10 mol %)	MeOH	2.5, 2	58, 60
29	1 N, Con H ₂ SO ₄ (10 mol %)	MeOH	12	None
30	1 N, Con HNO ₃ (10 mol %)	MeOH	12	None

a. Conditions: Ethyl acetoacetate (0.5 mmol), benzaldehyde (1 mmol), aniline (1 mmol) and 10 mol % catalyst in solvent (3ml), stirring in room temperature. b Isolated yields.