Supplementary Material (ESI) for Green Chemistry

Supporting information for

A Grinding-induced Catalyst- and Solvent-free Synthesis of Highly Functionalized 1,4-Dihydropyridines via a Domino Multicomponent Reaction

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General Consideration.

All the reactions were carried out at room temperature that is 28-32^{0}C. Unless otherwise specified, all the reagents were purchased from Sigma-Aldrich Chemical Co, Lancaster and were used directly without further any purification. NMR spectra were obtained using the Brucker DRX 300MHz spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR spectra were taken on VARIAN FT-IR spectrometer as KBr pellets. Reactions were monitored by thin layer chromatography. Elemental analyses were performed on a Carlo Erba's 108 or an Elementar's Vario EL III microanalyzer. The reactions under microwave heating were carried out in a Biotage initiator 2.5 microwave system. Thin layer chromatography (TLC) carried out on 0.25 mm silica gel plates visualized with UV light.

General procedure for synthesis of compounds 5(a-v), 6(a-e)

A mixture of the appropriate aldehyde (1 mmol), aniline (1 mmol), DEAD (1 mmol), and malanonitrile(1mmol) was ground in a mortar and pestle at room temperature for the appropriate time. After two minute syrupy solution was observed, which was solidify on completion of reaction. After completion of the reaction give solid product **5a** with high purity.

General procedure for synthesis of compounds 7 (a-e)

An oven dried microwave vial charged with Compound **5m**(1 mmol) and cyclohexanone (3 mmol), SDS (30 mol%), in 3 ml of water take in vial tube of microwave and irradiated at 150^0 C with stirring under microwave for 15 min. After the completion of the reaction were monitored by thin layer chromatography. The reaction was diluted with a 5 mL of ethyl acetate and washed with saturated aqueous NH_4Cl solution. The aqueous part was extracted with ether. The combined organic part was washed with brine and dried over Na_2SO_4. The solvent was evaporated to yield a crude residue, which upon purification via silica gel column chromatography using EtOAc/hexane gave pure product **7a**.

Diethyl 6-amino-5-cyano-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (5a). Pale yellow solid, Mp. 160-162^{0}C Reaction time- 15min, Yield 92%, ESI MS (m/z) = 418 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.52 (m, 3H, ArH), 7.40-7.39 (m, 5H, ArH), 7.28 (s, 2H, ArH), 4.71 (s, 1H, CH), 4.09-4.02 (m, 4H), 3.95-3.86 (m, 2H,), 1.13 (t, J = 7.11 Hz, 3H, CH_3), 0.98 (t, J = 7.14 Hz, 3H, CH_3). Analysis calculated for $C_{24}H_{23}N_3O_4$ C, 69.05; H, 5.55; N, 10.07; Found: C, 69.07; H, 5.58; N, 10.11. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 165.1, 163.0, 149.6, 144.9, 141.5, 135.3, 130.4, 129.8, 128.7, 127.1, 127.0, 120.5, 105.4, 62.8, 61.9, 60.8, 38.7, 13.8, 13.4.

Diethyl 6-amino-5-cyano-1,4-bis(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5b). Pale yellow solid, Mp. 168-170^{0}C. Reaction time- 8min, Yield 88%, ESI MS (m/z) = 478 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.28 (s, 4H, ArH), 6.99-6.90 (m, 4H, ArH), 4.64 (s, 1H, CH), 4.07-3.94 (m, 4H), 3.93-3.83 (m, 8H,), 1.15 (t, J = 6.93 Hz, 3H, CH_3), 1.04 (t, J = 6.96 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^\delta$C 165.5, 163.4, 160.9, 158.8, 150.0, 141.9, 137.7, 131.8, 128.4, 127.6, 121.0, 115.0, 114.2, 105.6, 63.0, 62.0, 60.9, 55.8, 55.4, 38.0, 14.1, 13.7. Analysis calculated for $C_{26}H_{27}N_3O_6$: C 65.40, H 5.70, N 8.80; Found: C 65.50, H 5.66, N 8.74.

Diethyl 6-amino-1-(4-chlorophenyl)-5-cyano-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5c). Pale yellow solid, Mp. 172-174^{0}C, Reaction time- 7min, Yield 84%, ESI MS (m/z) = 482 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.49 (d, J=8.58, 2H, ArH), 7.34-7.27 (m, 4H, ArH), 6.93 (d, J=8.58, 2H, ArH), 4.64 (s, 1H, CH), 4.09-4.02 (m, 5H), 3.99-3.82 (m, 4H,), 1.15 (t, J = 7.08 Hz, 3H, CH_3), 1.04 (t, J = 7.14 Hz, 3H, CH_3); Analysis calculated for $C_{25}H_{24}ClN_3O_5$: C, 62.31; H, 5.02; N, 8.72; Found: C 62.37, H 5.16, N 8.79. ^{13}C NMR (75 MHz; $CDCl_3$) $^\delta$C 164.5, 162.3, 158.2, 150.5, 140.9, 137.6, 134.6, 134.3, 132.3, 129.5, 127.9, 120.9, 114.0, 105.1, 61.4, 60.4, 59.9, 55.0, 37.9, 13.7, 13.0.

Diethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-1-p-tolyl-1,4-dihydropyridine-2,3-dicarboxylate (5d). Pale yellow solid. Mp. 140-142 ^{0}C. Reaction time- 10min, Yield 92%, ESI MS (m/z) = 462 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.32-7.23 (m, 6H, ArH), 6.92 (d, J = 8.43 Hz, 2H, ArH), 4.64 (s, 1H, CH), 4.09-4.02 (m, 4H), 3.96-3.82 (m, 5H,), 2.42 (s, 3H, CH_3), 1.15 (t, J = 6.93 Hz, 3H, CH_3), 1.01 (t, J =7.11 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^\delta$C 165.5, 163.3, 158.8, 149.8, 141.6, 141.0, 137.7, 132.7, 130.6, 130.3, 128.5, 120.9, 114.2, 105.7, 63.1, 62.0, 60.9, 55.4, 38.1, 21.4, 14.1, 13.6. Analysis calculated for $C_{26}H_{27}N_3O_5$: C, 67.66; H, 5.90; N, 9.10; Found: C, 67.69; H, 5.81; N, 8.93.

Diethyl 6-amino-5-cyano-1-(4-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5e). Pale yellow solid, Mp. 162-164^{0}C, Reaction time- 13min, Yield 99%, ESI MS (m/z) = 538 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.26 (d, J= 8.8, 2H, ArH), 6.98 (d, J = 8.8Hz, 2H, ArH), 6.62 (s, 2H,

ArH), 4.63 (s, 1H, CH), 4.10-4.3.85 (m, 18H), 1.17 (t, J = 7.08 Hz, 3H, CH_3), 1.04 (t, J =7.14 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^{\delta}$C 165.3, 163.2, 161.0, 153.5, 150.2, 142.3, 140.9, 137.2, 131.7, 127.5, 120.9, 115.1, 105.0, 104.0, 62.7, 62.1, 61.07, 61.02, 55.8, 38.7, 14.1, 13.7.. Analysis calculated for $C_{28}H_{31}N_3O_8$: C, 62.56; H, 5.81; N, 7.82; Found: C, 62.58; H, 5.88; N, 7.83.

Diethyl 6-amino-1-(4-chlorophenyl)-5-cyano-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5f). Pale yellow solid, Mp. 185-187^{0}C, Reaction time- 12min, Yield 84%, ESI MS (m/z) = 542 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.50 (s, J = 8.55 Hz, 2H, ArH), 7.30 (s, 2H, ArH), 6.60 (s, 2H, ArH), 4.64 (s, 1H, CH), 4.11-4.04 (m, 4H), 3.98-3.95 (m, 2H,), 3.90-3.86 (m, 9H, OCH_3), 1.17 (t, J = 7.08 Hz, 3H, CH_3), 1.06 (t, J =7.11 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^{\delta}$C 165.3, 163.1, 153.7, 149.4, 141.5, 140.5, 137.3, 137.0, 134.0, 131.8, 130.4, 120.5, 105.8, 104.1, 63.7, 62.3, 61.2, 61.0, 56.2, 38.7, 14.2, 13.7. Analysis calculated for $C_{27}H_{28}ClN_3O_7$: C, 59.83; H, 5.21; N, 7.75; Found: C, 59.77; H, 5.14; N, 7.86.

Diethyl 6-amino-5-cyano-1,4-bis(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5g). Pale yellow solid, Mp. 196-198^{0}C Reaction time- 11min, Yield 84%, ESI MS (m/z) = 598 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 6.63 (s, 2H, ArH), 6.54 (s, 2H, ArH), 4.65 (s, 1H, CH), 4.22(s, 2H), 4.11-4.00 (m, 4H), 3.91-3.86 (m, 18H,), 1.18 (t, J = 6.99 Hz, 3H, CH_3), 1.06 (t, J =6.99 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^{\delta}$C 165.3, 163.2, 153.9, 153.6, 149.9, 141.8, 140.8, 139.8, 137.3, 130.5, 120.8, 107.8, 105.5, 104.2, 62.8, 62.1, 61.2, 61.1, 61.0, 56.5, 56.2, 38.6, 14.1, 13.8. Analysis calculated for $C_{30}H_{35}N_3O_{10}$: C, 60.29; H, 5.90; N, 7.03; Found: C, 60.34; H, 6.01; N, 7.09.

Diethyl 6-amino-5-cyano-1-p-tolyl-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (**5h**). Pale yellow solid, Mp. 175-177^{0}C, Reaction time- 17min, Yield 96%, ESI MS (m/z) = 522 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.30-7.28 (m, 2H, ArH), 7.22 (d, J = 8.1 Hz, 2H, ArH), 6.62 (s, 2H, ArH), 4.63 (s, 1H, CH), 4.10-4.08 (m, 4H, $2CH_2$), 3.94-3.86 (m, 11H), 2.42 (s, 3H, CH_3), 1.17 (t, J = 7.1 Hz, 3H, CH_3), 1.02 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^{\delta}$C 165.4, 163.2, 153.6, 150.0, 142.1, 141.1, 140.9, 137.2, 132.7, 130.7, 130.2, 120.8, 105.2, 104.1, 62.9, 62.1, 61.1, 61.0, 56.2, 38.7, 21.4, 14.2, 13.6. Analysis calculated for $C_{28}H_{31}N_3O_7$: C 64.48, H 5.99, N 8.06; Found: C 64.50, H 5.95, N 8.10.

Diethyl 6-amino-5-cyano-1-(2,4-dimethylphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5i). Pale yellow solid, Mp. 153-155^{0}C, Reaction time- 13min, Yield 92%, ESI MS (m/z) = 536 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.28 (s, 2H, ArH), 7.21 (s, 2H, ArH), 6.62 (s, 2H), 4.71(s, 1H, CH), 4.08-4.03 (m, 4H), 3.93-3.85 (m, 10H,), 2.35 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.14 (t, J = 7.11 Hz, 3H, CH_3), 0.99 (t, J =7.14 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^{\delta}$C 165.3, 162.8, 153.3, 149.1, 141.4, 141.1, 137.2,

136.8, 136.0, 133.6, 131.6, 131.4, 131.2, 131.0, 120.9, 104.4, 104.3, 104.1, 62.0, 61.8, 60.7, 55.9, 39.1, 38.8, 20.6, 17.4, 17.1, 13.9, 13.3. Analysis calculated for $C_{29}H_{33}N_3O_7$: C, 65.03; H, 6.21; N, 7.85; Found: C, 65.09; H, 6.17; N, 7.67.

Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5j). Yield 95%, Mp. 187-189^{0}C, Reaction time- 6min, ESI MS (m/z) = 586 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.65 (d, J = 8.52 Hz, 2H, ArH), 7.23 (d, J = 8.49 Hz, 2H, ArH), 6.60 (s, 2H), 4.64 (s, 1H, CH), 4.11-4.04 (m, 4H), 3.98-3.95 (m, 2H,), 3.90-3.86 (m, 9H, OCH_3), 1.17 (t, J = 7.08 Hz, 3H, CH_3), 1.06 (t, J =7.11 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^{\delta}$C 165.2, 163.1, 153.6, 149.4, 141.4, 140.5, 137.3, 134.5, 133.4, 132.1, 125.0, 120.5, 105.8, 104.0, 63.6, 62.3, 61.2, 61.0, 56.2, 38.7, 14.1, 13.6. Analysis calculated for $C_{27}H_{28}BrN_3O_7$: C, 55.30; H, 4.81; N, 7.17; Found: C, 55.42; H, 4.85; N, 7.14.

Diethyl 6-amino-5-cyano-1-phenyl-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5k). Yellow solid, Mp. 146-148^{0}C. Reaction time- 18min, Yield 91 %, ESI MS (m/z) = 508 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.52-7.50 (m, 3H, ArH), 7.36-7.33 (m, 2H, ArH), 6.63 (s, 2H, ArH), 4.65 (s, 1H, CH), 4.11-4.08 (m, 4H, $2CH_2$), 3.91-3.87 (m, 11H), 1.17 (t, J = 7.1 Hz, 3H, CH_3), 0.98 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 165.2, 163.1, 153.5, 149.8, 141.8, 140.8, 137.1, 135.4, 130.6, 120.7, 105.3, 104.0, 74.8, 74.6, 62.9, 62.1, 61.0, 60.9, 56.1, 38.7, 14.1, 13.5. Analysis calculated for $C_{27}H_{29}N_3O_7$: C 63.89, H 5.76, N 8.28; Found: C 63.90, H 5.80, N 8.25.

Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(3,4-dimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5l). Yellow solid, Mp. 183-185^{0}C, Reaction time- 14min, Yield 94%, ESI MS (m/z) = 557 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.65 (d, J = 8.5 Hz, 2H, ArH), 7.28-7.22 (m, 2H, ArH), 6.92-6.90 (m, 3H, ArH), 4.64 (s, 1H, CH), 4.08-4.02 (m, 4H, $2CH_2$), 3.98-3.89 (m, 8H), 1.16 (t, J = 7.1 Hz, 3H, CH_3), 1.05 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 165.3, 163.2, 149.2, 148.3, 141.1, 137.7, 134.6, 133.3, 132.2, 125.0, 120.5, 119.2, 111.7, 110.7, 106.2, 63.9, 62.3, 61.1, 56.0, 38.2, 14.1, 13.7. Analysis calculated for $C_{26}H_{26}BrN_3O_6$: C 56.12, H 4.71, N 7.55; Found: C 56.10, H 4.75, N 7.60.

Diethyl 6-amino-1-(4-chlorophenyl)-5-cyano-4-(3,4-dimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5m).

Yield 84%, Mp. 177-178^{0}C, Reaction time- 8min, ESI MS (m/z) = 512 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.48 (d, J = 8.58 Hz, 2H, ArH), 7.31-7.28 (m, 2H, ArH), 6.91-6.90 (m, 3H, ArH), 4.63 (s, 1H, CH), 4.10-4.04 (m, 4H), 4.01-3.89 (m, 8H), 1.15 (t, J = 7.08 Hz, 3H, CH_3), 1.04 (t, J =7.14 Hz, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$) $^{\delta}$C 165.2, 163.1, 149.4, 149.1, 148.2, 141.2, 137.7, 136.8, 134.0, 131.9, 130.2, 120.5, 119.1, 115.0,

111.7, 110.7, 106.1, 63.6, 62.2, 61.1, 56.0, 38.2, 14.1, 13.6. Analysis calculated for $C_{26}H_{26}ClN_3O_6$ C, 61.00; H, 5.12; N, 8.21; Found: C, 61.12; H, 5.14; N, 8.14.

Diethyl 6-amino-5-cyano-4-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5n). Yield 82%, Mp. 168-170^{0}C, Reaction time- 11min ESI MS (m/z) = 508 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.28-7.25 (m, 2H, ArH), 6.97-6.90 (m, 5H, ArH), 4.63 (s, 1H, CH), 4.07-4.03 (m, 4H), 3.97-3.85 (m, 11H), 1.15 (t, J = 7.08 Hz, 3H, CH_3), 1.03 (t, J =7.14 Hz, 3H, CH_3); Analysis calculated for $C_{27}H_{29}N_3O_7$ C, 63.89; H, 5.76; N, 8.28; Found: C, 63.94; H, 5.85; N, 8.31. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 165.2, 163.1, 160.7, 149.8, 148.9, 148.0, 141.8, 138.0, 131.5, 127.4, 120.7, 119.0, 114.8, 111.4, 110.4, 105.1, 62.7, 61.8, 60.8, 55.9, 55.8, 55.6, 38.0, 13.9, 13.5.

Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5o). Yield 88%, Mp. 175-177^{0}C, Reaction time- 5min, ESI MS (m/z) = 526 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.65 (m, 2H, ArH), 7.33-7.26 (m, 4H, ArH), 6.95-6.91 (m, 2H, ArH), 4.66(s, 1H, CH), 4.13-3.94 (m, 6H, CH), 3.84 (s, 3H, OCH_3), 1.18 (t, J = 10.6 Hz, 3H, CH_3), 1.07 (t, J =10.7 Hz, 3H, CH_3); Analysis calculated for $C_{25}H_{24}BrN_3O_5$ C, 57.04; H, 4.60; N, 7.98; Found: C, 57.08; H, 4.76; N, 8.26. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 164.9, 162.8, 158.6, 150.8, 141.2, 138.0, 135.1, 132.8, 128.3, 123.8, 121.2, 114.3, 105.7, 61.8, 60.8, 60.7, 55.3, 14.1, 13.5.

Diethyl 6-amino-5-cyano-1-(4-ethoxyphenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5p). Yield 92%, Mp. 166-167^{0}C, Reaction time- 16min ESI MS (m/z) = 492 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.34-7.27 (m, 4H, ArH), 6.99-6.90 (m, 4H, ArH), 4.65 (s, 1H, CH), 4.13-3.86 (m, 8H), 3.84 (s, 3H, OCH_3), 1.51 (t, J = 10.4 Hz, 3H, CH_3), 1.18 (t, J = 10.6 Hz, 3H, CH_3), 1.06 (t, J =10.7 Hz, 3H, CH_3); Analysis calculated for $C_{27}H_{29}N_3O_6$ C, 65.97; H, 5.95; N, 8.55; Found: C, 66.13; H, 6.00; N, 8.43. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 165.3, 163.2, 160.1, 158.6, 149.8, 141.7, 137.6, 131.6, 128.3, 127.1, 120.8, 115.3, 114.0, 105.3, 63.9, 62.7, 61.8, 60.7, 55.2, 37.8, 14.6, 13.9, 13.5.

Diethyl 6-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (5q). Yield 93%, Mp. 183-185^{0}C, Reaction time- 6min ESI MS (m/z) = 530 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.69 (dd, J= 9.99, 3.0 Hz, 2H, ArH), 7.40-7.25 (m, 6H, ArH), 4.69 (s, 1H, CH), 4.13-3.94 (m, 6H), 1.17 (t, J = 10.6 Hz, 3H, CH_3), 1.08 (t, J = 10.7 Hz, 3H, CH_3); Analysis calculated for $C_{24}H_{21}BrClN_3O_4$ C, 54.31; H, 3.99; 6.68; N, 7.92; Found: C, 54.37; H, 4.13; 6.74; N, 8.14. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 164.8, 162.7, 149.3, 143.2, 141.3, 134.1, 133.2, 132.9, 132.0, 128.9, 128.5, 125.0, 120.1, 105.4, 62.9, 62.2, 61.0, 38.2, 13.8, 13.4.

Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(2,4-dichlorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5r). Yield 98%, Mp. 180-181^{0}C, Reaction time- 8min, ESIMS (m/z) = 564 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.66 (d, J= 8.49 Hz, 2H, ArH), 7.42-7.26 (m, 5H, ArH), 5.26 (s, 1H, CH), 4.07-3.90 (m, 6H), 1.10-1.01 (m, 6H, CH_3); Analysis calculated for $C_{24}H_{20}BrCl_2N_3O_4$ C, 51.00; H, 3.57; N, 7.43; Found: C, 51.04; H, 3.51; N, 7.52. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 169.2, 167.2, 155.6, 147.6, 146.9, 139.3, 137.68, 137.60, 137.3, 136.0, 133.7, 132.9, 128.9, 125.2, 108.4, 66.6, 65.5, 64.0, 40.5, 18.7, 18.2.

Diethyl 6-amino-4-(4-(benzyloxy)phenyl)-1-(4-bromophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (5s). Yield 95%, Mp. 173-174^{0}C, Reaction time- 15min, ESI MS (m/z) = 602 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.93 (d, J= 8.8 Hz, 3H, ArH), 7.65(d, J= 9.03, 4H), 7.25-6.97 (m, 6H), 5.08 (s, 2H, -OCH_2), 4.65 (s, 1H, CH), 4.10-3.93 (m, 6H), 1.14 (t, J = 7.11 Hz, 3H, CH_3), 1.05 (t, J = 7.11 Hz, 3H, CH_3); Analysis calculated for $C_{31}H_{28}BrN_3O_5$ C, 61.80; H, 4.68; N, 6.97; Found: C, 61.88; H, 4.73; N, 6.91. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 165.1, 163.9, 162.9, 158.8, 149.1, 140.8, 137.4, 135.4, 132.1, 128.59, 128.53, 128.3, 127.9, 124.8, 120.3, 115.0, 114.4, 113.3, 106.2, 63.7, 62.1, 60.9, 37.9, 13.9, 13.4.

Diethyl 6-amino-5-cyano-4-(4-nitrophenyl)-1-p-tolyl-1,4-dihydropyridine-2,3-dicarboxylate (5t). Yield 96%, Mp. 170-172^{0}C Reaction time- 7min, ESI MS (m/z) = 477 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.28 (d, J= 8.4 Hz, 2H, ArH), 7.58 (d, J= 8.49, 2H), 7.33-7.24 (m, 4H), 4.83 (s, 1H, CH), 4.17 (s, 2H, NH_2), 4.09-3.89 (m, 4H), 2.43 (s, 3H, CH_3), 1.13 (t, J = 7.08 Hz, 3H, CH_3), 1.03 (t, J = 7.11 Hz, 3H, CH_3); Analysis calculated for $C_{25}H_{24}N_4O_6$ C, 63.02; H, 5.08; N, 11.76; Found: C, 63.05; H, 5.14; N, 11.81. ^{13}C NMR (50 MHz; $CDCl_3$) δ_C 164.1, 162.1, 152.1, 150.3, 146.3, 142.3, 140.4, 131.6, 129.9, 129.7, 127.6, 123.5, 102.9, 61.4, 60.4, 59.1, 20.7, 13.4, 12.8.

Triethyl 6-amino-1-(4-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6a). Yield 91%, Mp. 184-186^{0}C, Reaction time- 18min, ESI MS (m/z) = 485 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.28 (d, J= 8.7 Hz, 2H, ArH), 6.98 (d, J= 8.88, 2H), 6.69 (s, 2H), 6.23 (s, 2H, NH_2), 5.01 (s, 1H, CH), 4.17-4.11 (m, 4H), 3.95-3.84 (m, 14H), 1.32 (t, J = 7.08 Hz, 3H, CH_3), 1.23 (t, J = 7.11 Hz, 3H, CH_3), 1.03 (t, J = 7.17 Hz, 3H, CH_3); Analysis calculated for $C_{30}H_{36}N_2O_{10}$ C, 61.63; H, 6.21; N, 4.79; Found: C, 61.72; H, 6.28; N, 4.83. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 169.5, 165.6, 163.5, 160.6, 153.4, 152.7, 151.6, 142.7, 141.7, 136.3, 131.6, 129.0, 127.6, 114.8, 114.6, 107.2, 104.7, 79.9, 63.2, 61.6, 60.9, 60.7, 60.6, 59.2, 56.3, 55.8, 55.5, 36.8, 14.6, 14.0, 13.5, 13.4.

Triethyl 6-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6b). Yield 93%, Mp. 115-117^{0}C, Reaction time- 12min, ESI MS (m/z) = 577 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$)

δ_H 7.61 (d, J= 8.5 Hz, 2H, ArH), 7.35-7.25 (m, 6H, ArH), 6.18 (s, 2H, NH_2), 5.00 (s, 1H, -CH), 4.13-4.06 (m, 4H), 3.97-3.89 (m, 2H), 1.27-1.16 (m, 6H, CH_3), 1.03 (t, J = 7.11 Hz, 3H, CH_3). Analysis calculated for $C_{26}H_{26}BrClN_2O6$ C, 54.04; H, 4.54; N, 4.85; Found: C, 54.08; H, 4.59; N, 5.07. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 169.3, 165.3, 163.2, 150.8, 145.5, 140.8, 134.4, 133.1, 132.6, 131.8, 129.3, 128.0, 124.6, 107.8, 80.1, 61.9, 60.8, 59.4, 36.7, 14.3, 13.9, 13.4.

Triethyl 6-amino-4-(4-nitrophenyl)-1-p-tolyl-1,4-dihydropyridine-2,3,5-tricarboxylate (6c). Yield 91%, Mp. 191-192^{0}C, Reaction time- 20min, ESI MS (m/z) = 524 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.81 (d, J= 8.2 Hz, 2H, ArH), 7.65 (d, J= 8.2, 2H, ArH), 7.23-7.17 (m, 4H), 4.75 (s, 1H, -CH), 4.11-3.83 (m, 6H), 3.45-3.39 (m, 2H), 2.36(s, 3H, Ar$\underline{CH_3}$), 1.17 (t, J = 6.9 Hz, 3H, CH_3), 1.05 (t, J = 6.9 Hz, 3H, CH_3), 0.95 (t, J = 6.9 Hz, 3H, CH_3); Analysis calculated for $C_{27}H_{29}N_3O_8$ C, 61.94; H, 5.58; N, 8.03; Found: C, 61.97; H, 5.65; N, 8.07. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 163.4, 161.3, 151.7, 149.9, 145.7, 141.7, 139.5, 131.1, 129.1, 127.0, 122.8, 119.5, 102.2, 60.7, 59.7, 58.1, 20.1, 12.8, 12.2.

Triethyl 6-amino-1,4-bis(4-chlorophenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6d). Yield 84%, Mp. 176-178^{0}C, Reaction time- 10min, ESI MS (m/z) = 533 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.51(d, J= 8.6 Hz, 2H, ArH), 7.36-7.25 (m, 6H), 6.18 (s, 2H, NH_2) 5.0 (s, 1H, -CH), 4.14-4.10 (m, 4H), 3.53 (q, J=7.0, 2H), 1.27-0.98(m, 9H). Analysis calculated for $C_{26}H_{26}Cl_2N_2O_6$ C, 58.54; H, 4.91; N, 5.25; Found: C, 58.57; H, 4.94; N, 5.22. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 169.3, 165.3, 163.3, 150.9, 145.5, 140.9, 136.5, 133.8, 132.0, 131.8, 130.0, 129.3, 128.0, 107.8, 80.1, 61.9, 60.8, 59.4, 50.7, 36.7, 14.3, 13.9, 13.4.

Diethyl 6-amino-5-carbamoyl-1,4-bis(4-chlorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (6e). Yield 79%, Mp. 218-220^{0}C Reaction time- 20min, ESI MS (m/z) = 504 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.66(d, J= 8.5 Hz, 2H, ArH), 7.38-7.28 (m, 4H), 7.01(t, J= 8.7 Hz, 2H, ArH), 6.68 (s, 2H, $CONH_2$), 6.1 (s, 2H, NH_2), 5.0 (s, 1H, -CH), 4.16-3.98 (m, 4H), 1.28-1.16 (m, 6H). Analysis calculated for $C_{24}H_{23}Cl_2N_3O_5$ C, 57.15; H, 4.60; N, 8.33; Found: C, 57.15; H, 4.60; N, 8.33. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 169.4, 165.4, 163.3, 163.0, 159.7, 150.7, 142.8, 140.6, 134.5, 133.0, 132.4, 129.5, 129.4, 124.6, 114.8, 114.5, 108.1, 80.4, 61.9, 60.7, 59.4, 36.6, 14.3, 13.9, 13.4.

Diethyl 5-amino-1-(4-chlorophenyl)-4-(3,4-dimethoxyphenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7a). White solid. Yield 65%, Mp. 197-199^{0}C, ESI MS (m/z) = 592 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.52 (d, J = 8.4 Hz, 2H, ArH), 7.24 (d, 2H, J=8.4, ArH), 6.93-6.85 (m, 3H, ArH), 5.26 (s, 2H, NH_2), 4.68 (s, 1H, CH), 4.09-3.81 (m, 10H), 2.42-2.08 (m, 4H), 1.79 (m, 4H), 1.12 (t, J = 7.08 Hz, 3H, CH_3), 1.03 (t, J =7.14 Hz, 3H, CH_3). Analysis calculated for $C_{32}H_{34}ClN_3O_6$ C,

64.91; H, 5.79; N, 7.10; Found: C, 64.94; H, 5.85; N, 7.23. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 167.8, 166.7, 161.5, 159.5, 156.1, 149.3, 145.5, 142.2, 140.2, 135.5, 130.3, 128.7, 124.1, 119.4, 115.5, 113.6, 109.8, 108.6, 100.3, 62.8, 62.3, 55.6, 55.1, 38.1, 28.6, 26.5, 22.6, 14.1, 13.8.

Diethyl 5-amino-1-(4-ethoxyphenyl)-4-(4-methoxyphenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7b). White solid. Yield 52%, Mp. 191-192^{0}C, ESI MS (m/z) = 572 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.36-7.23(m, 4H), 5.41(s, 2H, NH_2), 4.68(s, 1H, CH), 4.18-3.77(m, 9H), 2.38-1.94 (m, 4H), 1.78-1.64 (m, 4H), 7.04-6.92 (m, 4H, ArH), 1.52 (t, J = 10.3 Hz, 3H, CH_3), 1.12 (t, J = 10.6 Hz, 3H, CH_3), 0.98 (t, J =10.7 Hz, 3H, CH_3); Analysis calculated for $C_{33}H_{37}N_3O_6$ C, 69.33; H, 6.52; N, 7.35; Found: C, 69.36; H, 6.58; N, 7.43. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 167.8, 166.7, 158.9, 156.9, 154.5, 152.2, 142.8, 136.3, 132.6, 127.8, 127.4, 116.9, 116.4, 116.1, 114.4, 110.8, 101.2, 64.4, 62.3, 61.9, 55.1, 37.9, 28.6, 26.6, 21.5, 14.2, 13.8.

Diethyl 5-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7c). White solid. Yield 68%, Mp. 203-205^{0}C, ESI MS (m/z) = 610 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.64 (dd, J= 10.01, 3.0 Hz, 2H, ArH), 7.37-7.15 (m, 6H, ArH), 6.39 (s, 2H, NH_2), 4.68 (s, 1H, CH), 4.13-3.98 (m, 4H), 2.39-2.12(m, 4H), 1.68(m, 4H), 1.17 (t, J = 10.6 Hz, 3H, $CH_2\underline{CH_3}$), 1.08 (t, J = 10.7 Hz, 3H, $CH_2\underline{CH_3}$); Analysis calculated for $C_{30}H_{29}BrClN_3O_4$ C, 58.98; H, 4.78; N, 6.88; Found: C, 59.05; H, 4.88; N, 6.91. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 167.5, 166.8, 161.8, 160.1, 158.3, 146.5, 144.7, 135.0, 132.3, 128.5, 124.1, 120.3, 116.9, 116.1, 113.9, 109.5, 108.7, 102.4, 62.4, 38.3, 28.7, 26.6, 22.6, 14.1.

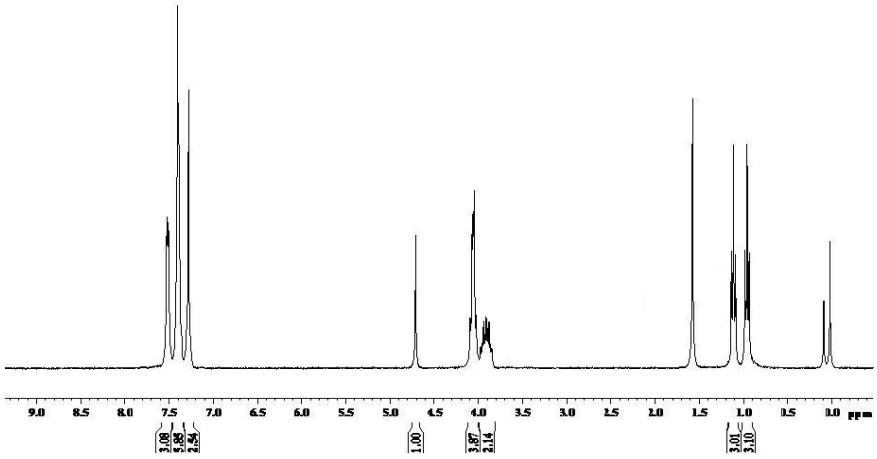
Diethyl 5-amino-1-(4-bromophenyl)-4-(2,4-dichlorophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7d). White solid. Yield 79%, Mp. 227-228^{0}C, ESI MS (m/z) = 644 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.64(d, J= 8.50 Hz, 2H, ArH), 7.33-7.17 (m, 5H, ArH), 5.82(s, 2H, NH_2), 4.61(s, 1H, CH), 4.04-3.78 (m, 4H), 2.69-2.42 (m, 4H), 1.82-1.59 (m, 4H), 1.15 (t, J = 8.89 Hz, 3H, $CH_2\underline{CH_3}$), 1.04 (t, J = 8.98 Hz, 3H, $CH_2\underline{CH_3}$); Analysis calculated for $C_{30}H_{28}BrCl_2N_3O_4$ C, 55.83; H, 4.37; N, 6.51; Found: C, 55.85; H, 4.40; N, 6.53. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 168.0, 167.0, 161.9, 160.2, 150.1, 146.7, 144.8, 135.3, 133.0, 129.0, 124.6, 117.7, 116.6, 120.3, 114.3, 109.8, 102.7, 62.7, 49.5, 28.9, 26.7, 22.9, 14.3.

Diethyl 5-amino-4-(4-(benzyloxy)phenyl)-1-(4-bromophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7e).

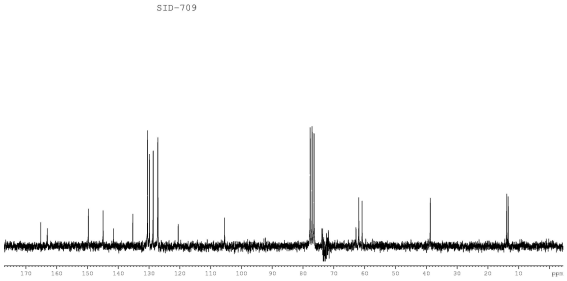
White solid. Yield 61%, Mp. 232-234^{0}C, ESI MS (m/z) = 682 $(M+H)^+$. ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 7.91 (d, J= 8.8 Hz, 3H, ArH), 7.63(d, J= 9.05, 4H), 7.41-7.21 (m, 6H), 6.16 (s, 2H, NH_2), 5.02 (s, 2H, -OCH_2), 4.58 (s,

1H, CH), 4.10-3.93 (m, 4H), 2.43-2.38 (m, 2H), 2.22-2.18 (m, 2H), 2.64-2.49 (m, 4H), 1.14 (t, J = 7.10 Hz, 3H, CH_3), 0.98 (t, J = 7.11 Hz, 3H, CH_3); Analysis calculated for $C_{37}H_{36}BrN_3O_5$ **C**, 65.10; H, 5.32; N, 6.16; Found: C, 65.04; H, 5.37; N, 6.19. ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 167.8, 166.8, 160.7, 158.8, 156.1, 154.1, 142.7, 142.4, 136.5, 133.3, 132.5, 131.0, 129.1, 127.9, 127.5, 116.9, 116.4, 115.1, 114.5, 110.8, 101.3, 71.6, 62.6, 62.4, 38.0, 28.7, 26.6, 21.5, 14.0.

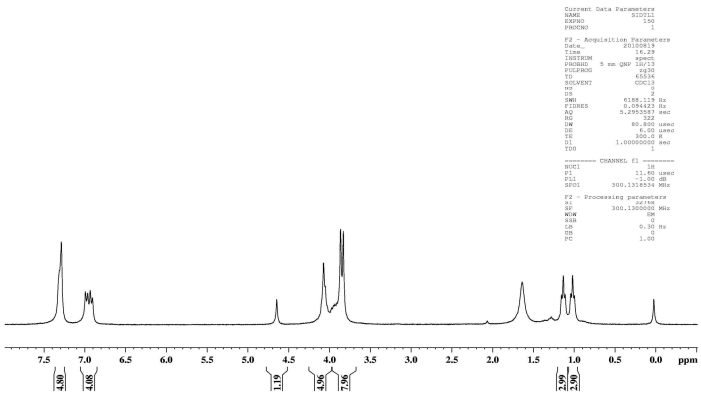
Diethyl 2-(4-methoxyphenylamino)maleate (Intermediate). Oil, ESI MS (m/z) = 294 $(M+H)^+$. ^1H NMR (300 MHz; $CDCl_3$) δ_H 9.58 (s, 1H, NH), 6.92 (d, 2H, J=8.9 Hz, ArH), 6.84 (d, 2H, J=8.9 Hz), 5.30 (s, 1H), 4.23-4.10 (m, 4H), 3.79 (s, 3H), 1.37 (t, 3H, J= 7.14Hz), 1.10(t, 3H, J= 7.14 Hz).



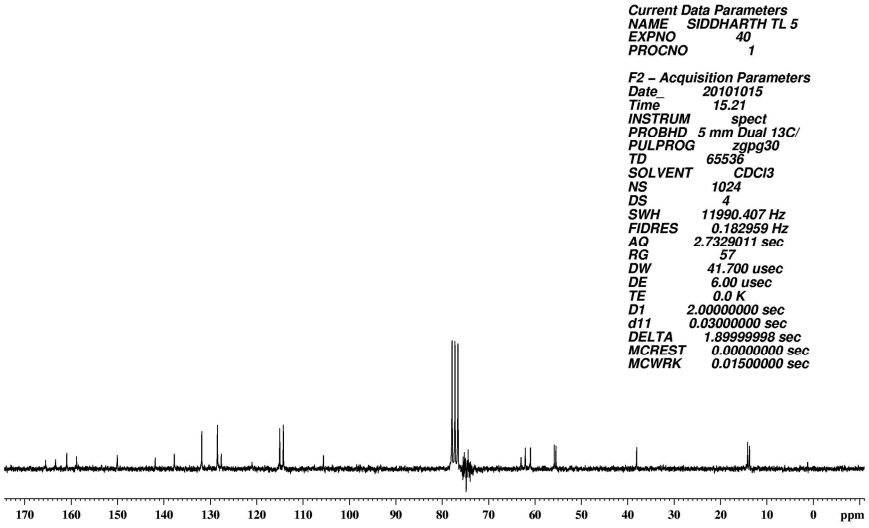
Diethyl 6-amino-5-cyano-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (5a).



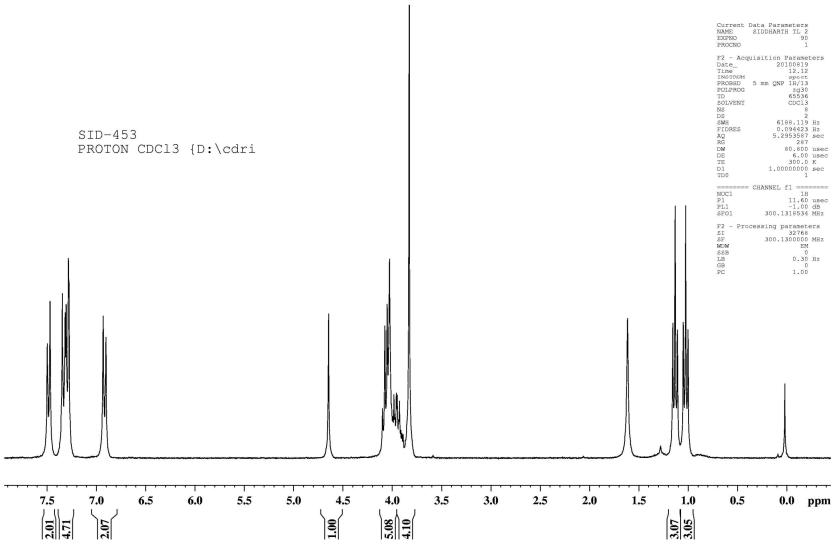
Diethyl 6-amino-5-cyano-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (5a).



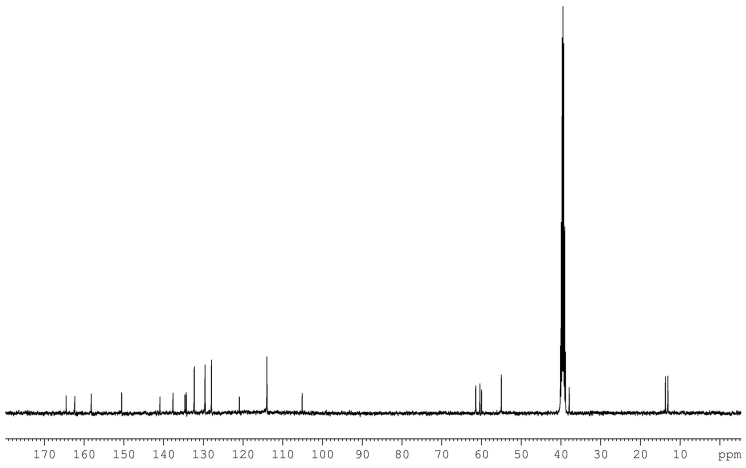
Diethyl 6-amino-5-cyano-1,4-bis(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5b).



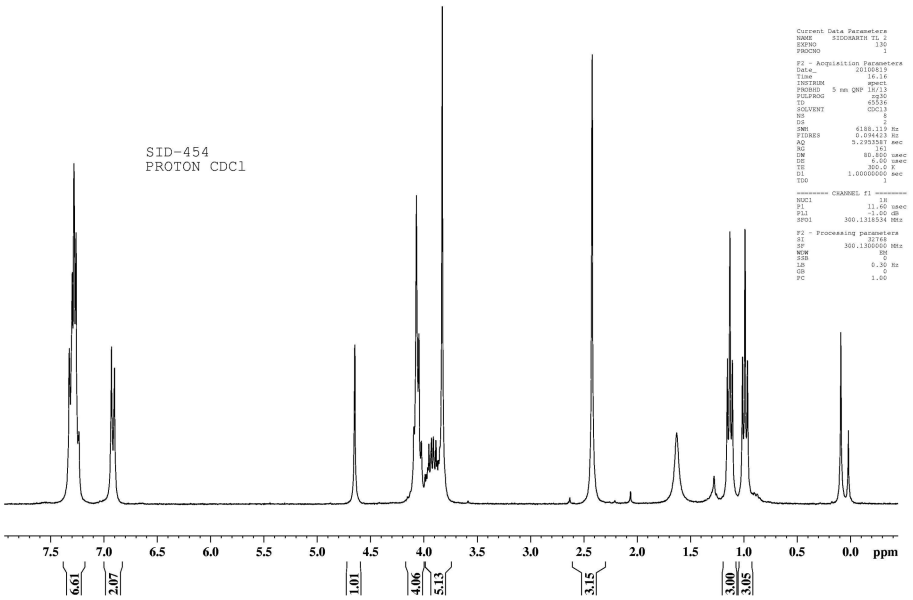
Diethyl 6-amino-5-cyano-1,4-bis(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5b).



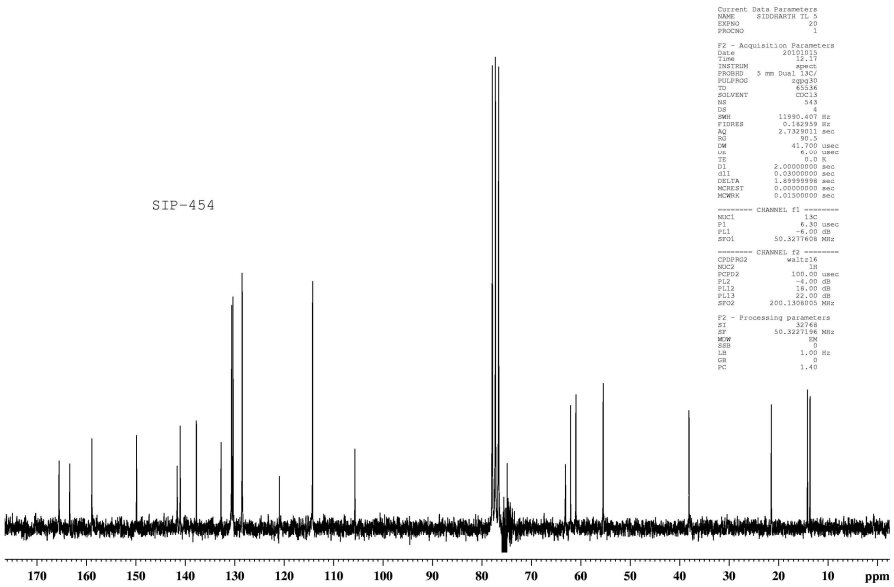
Diethyl 6-amino-1-(4-chlorophenyl)-5-cyano-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5c).



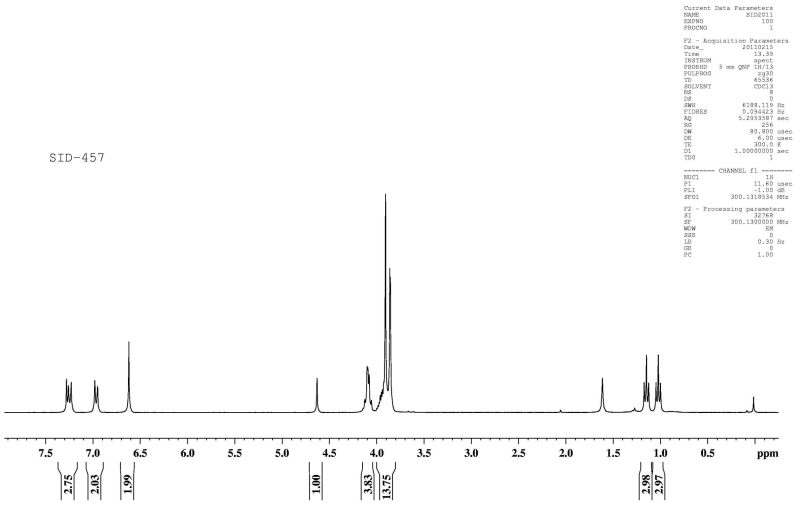
Diethyl 6-amino-1-(4-chlorophenyl)-5-cyano-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5c).



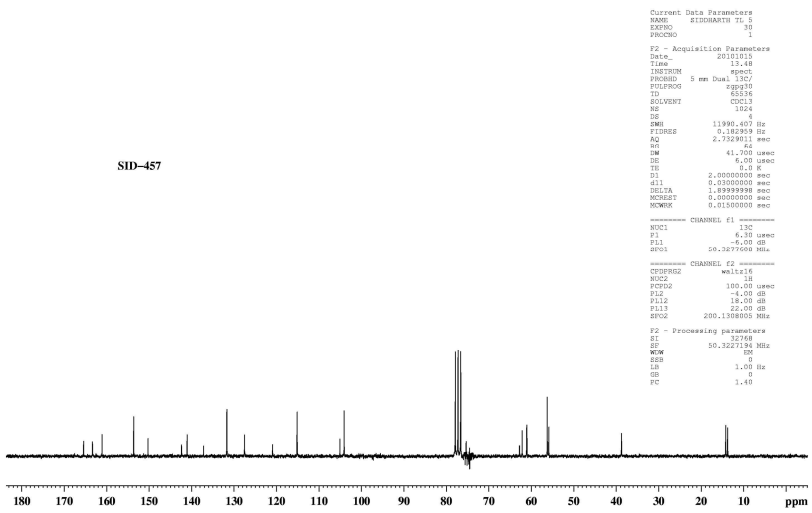
Diethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-1-p-tolyl-1,4-dihydropyridine-2,3-dicarboxylate (5d).



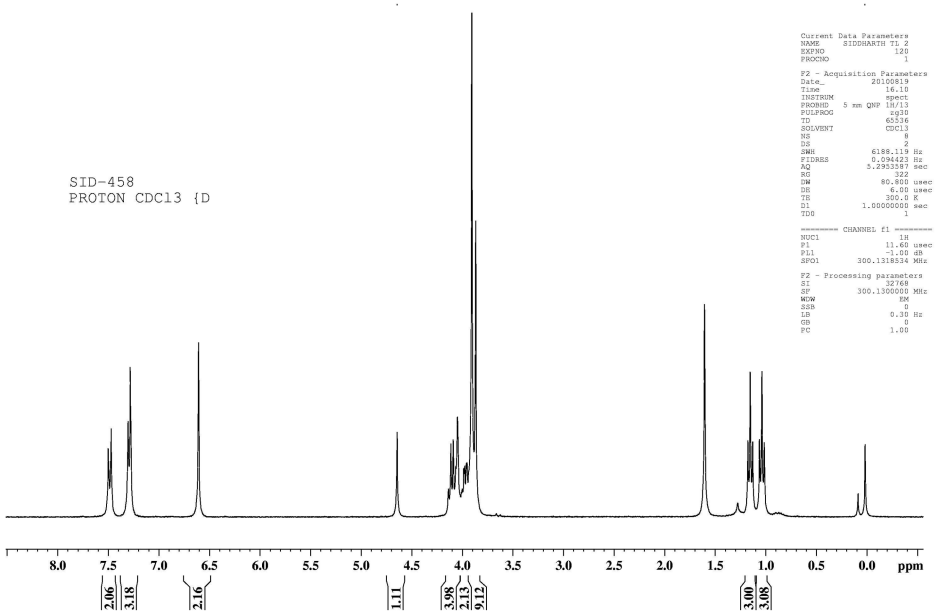
Diethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-1-p-tolyl-1,4-dihydropyridine-2,3-dicarboxylate (5d).



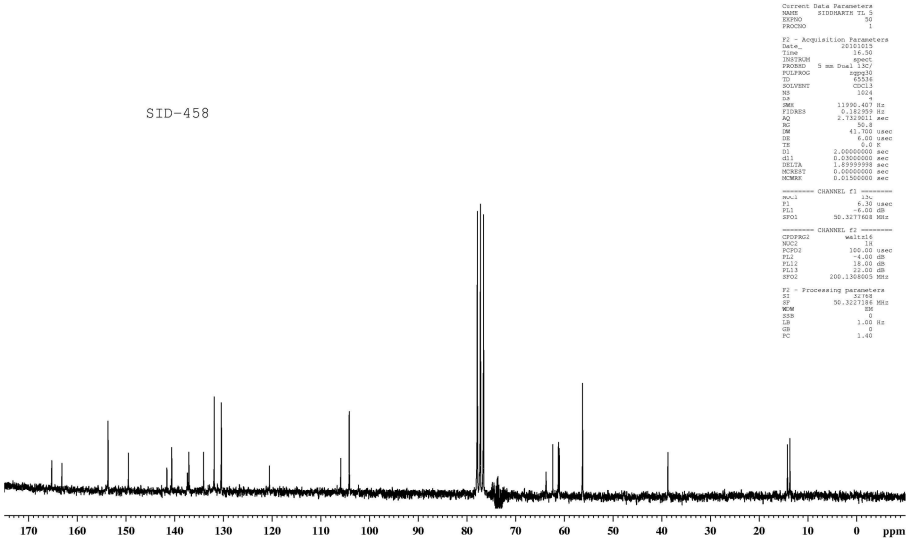
Diethyl 6-amino-5-cyano-1-(4-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5e).



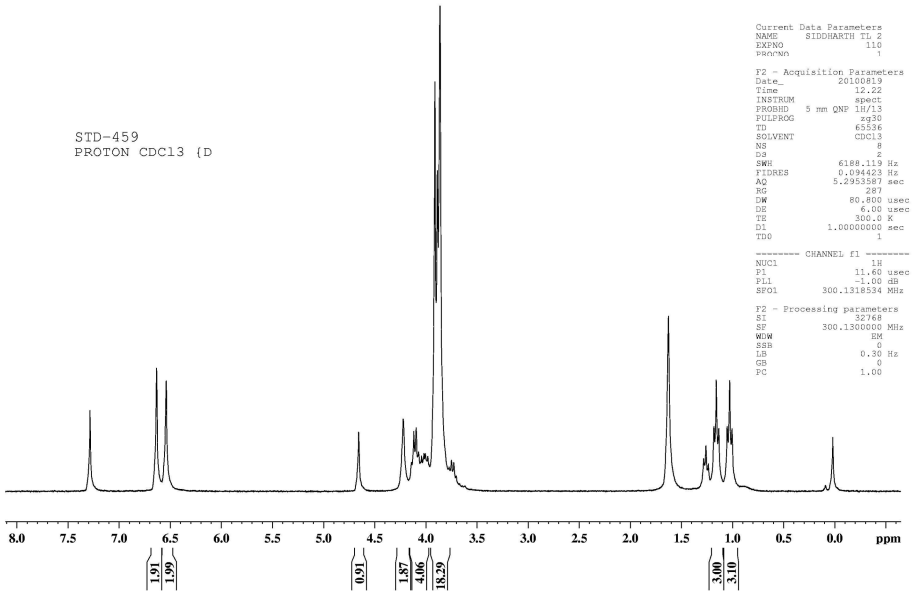
Diethyl 6-amino-5-cyano-1-(4-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5e)



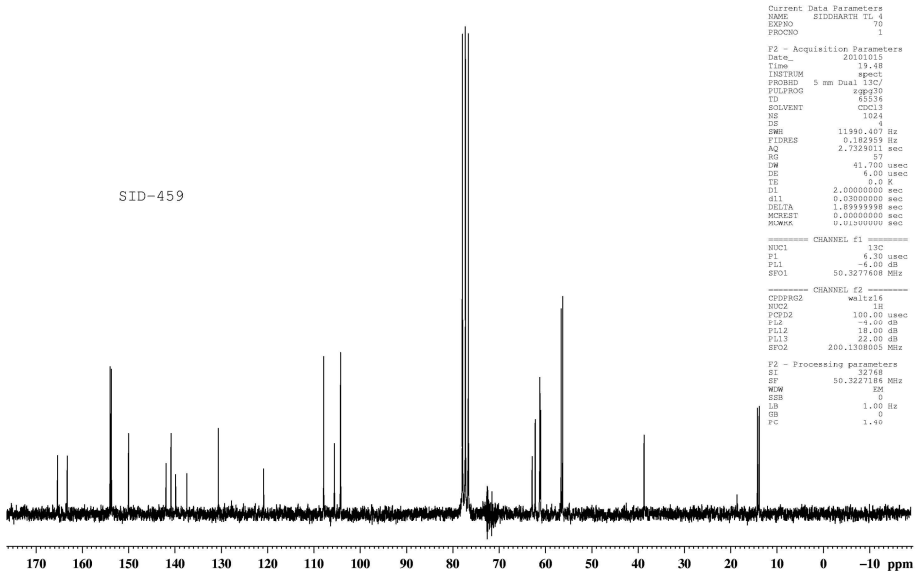
Diethyl 6-amino-1-(4-chlorophenyl)-5-cyano-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5f).



Diethyl 6-amino-1-(4-chlorophenyl)-5-cyano-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5f).



Diethyl 6-amino-5-cyano-1,4-bis(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5g).



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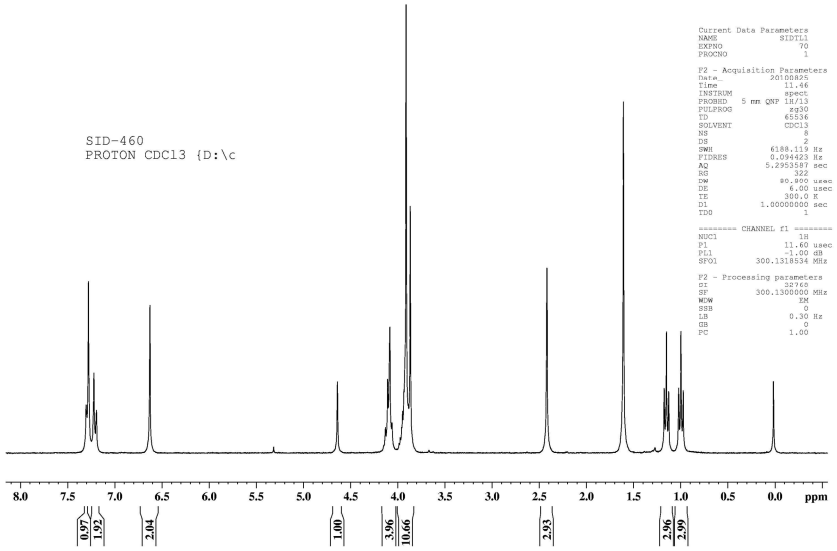
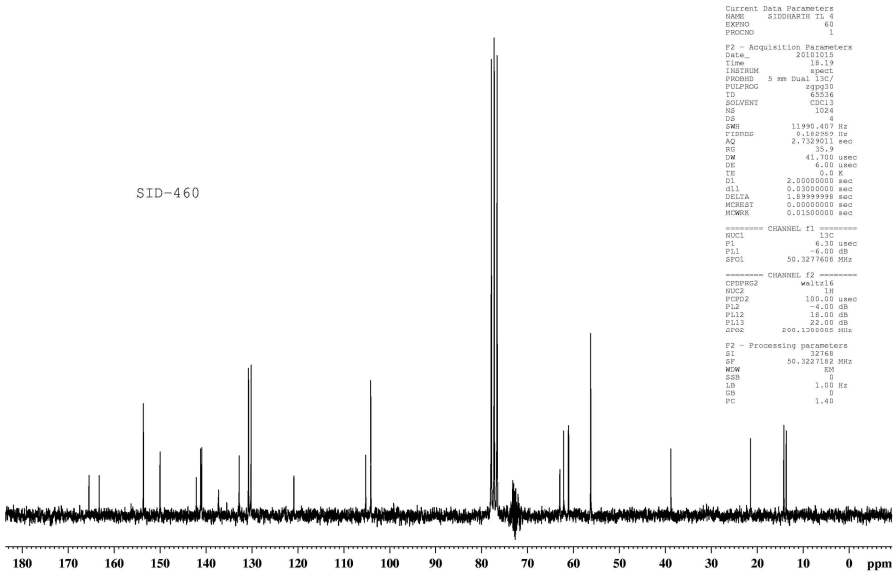


Diethyl 6-amino-5-cyano-1-p-tolyl-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5h)



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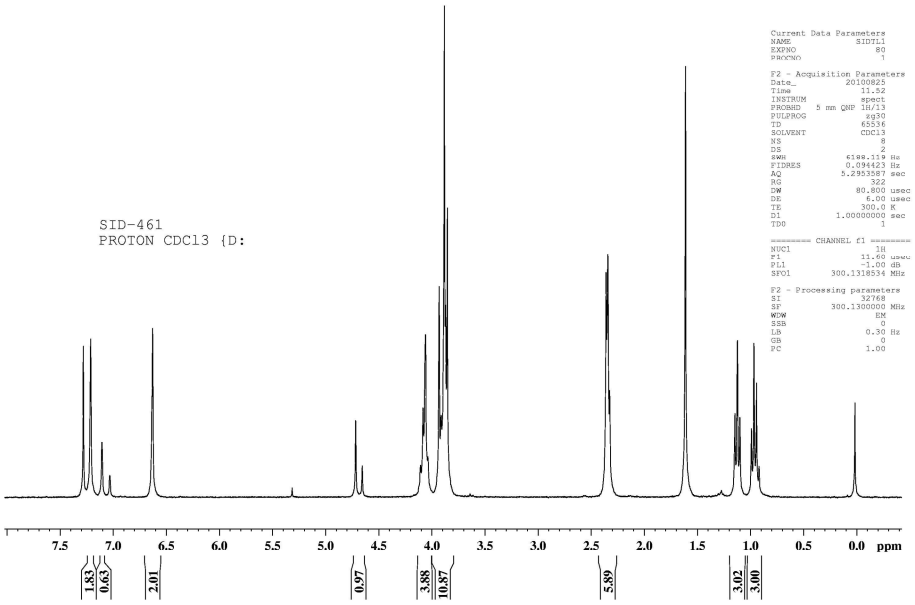
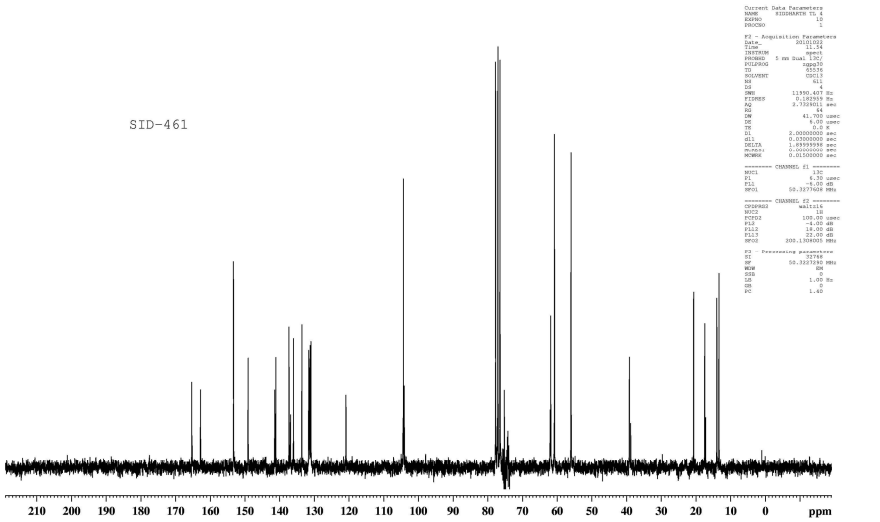
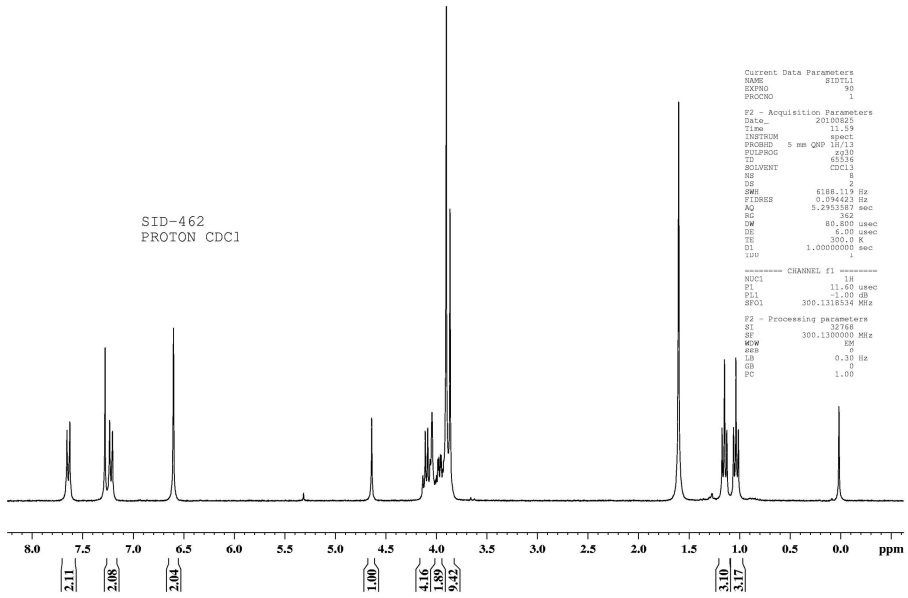


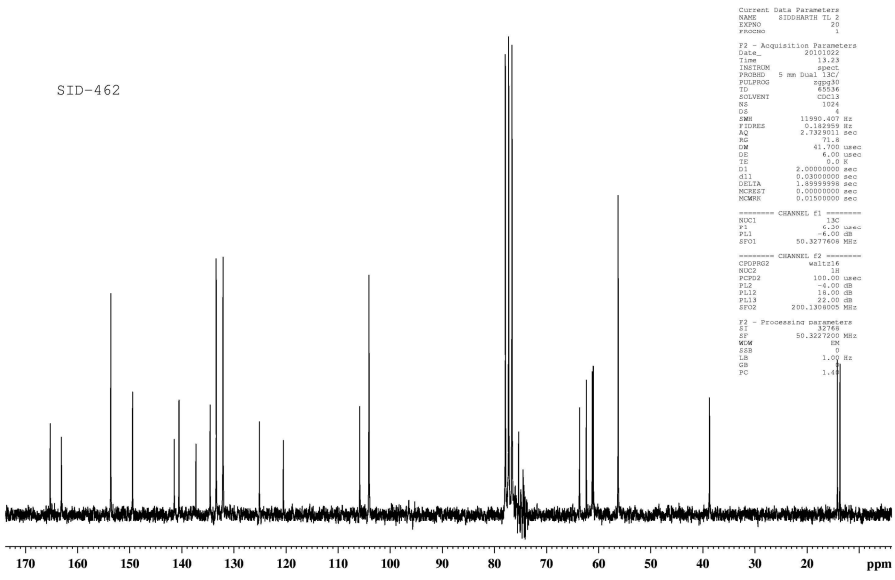
Diethyl 6-amino-5-cyano-1-(2,4-dimethylphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5i).



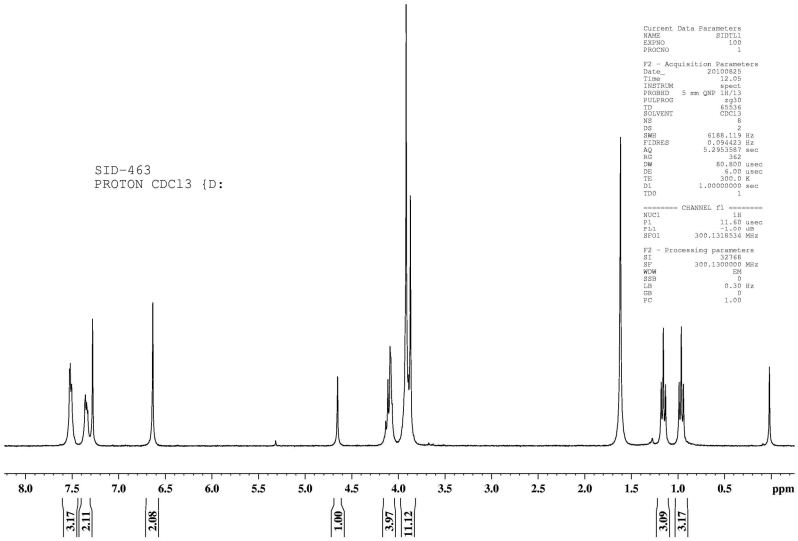
Diethyl 6-amino-5-cyano-1-(2,4-dimethylphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5i).



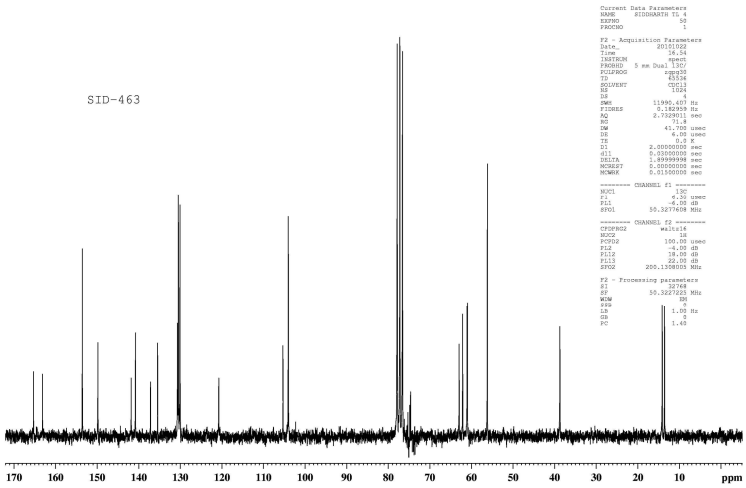
Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5j).



Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5j).



Diethyl 6-amino-5-cyano-1-phenyl-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5k).



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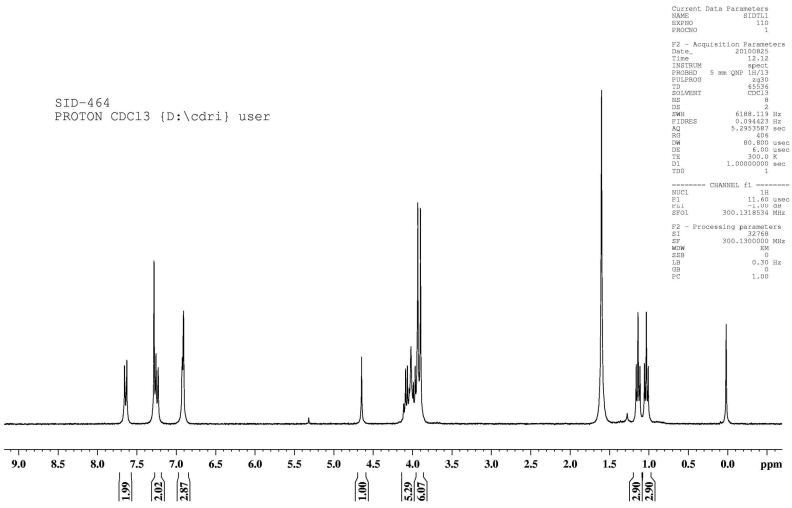
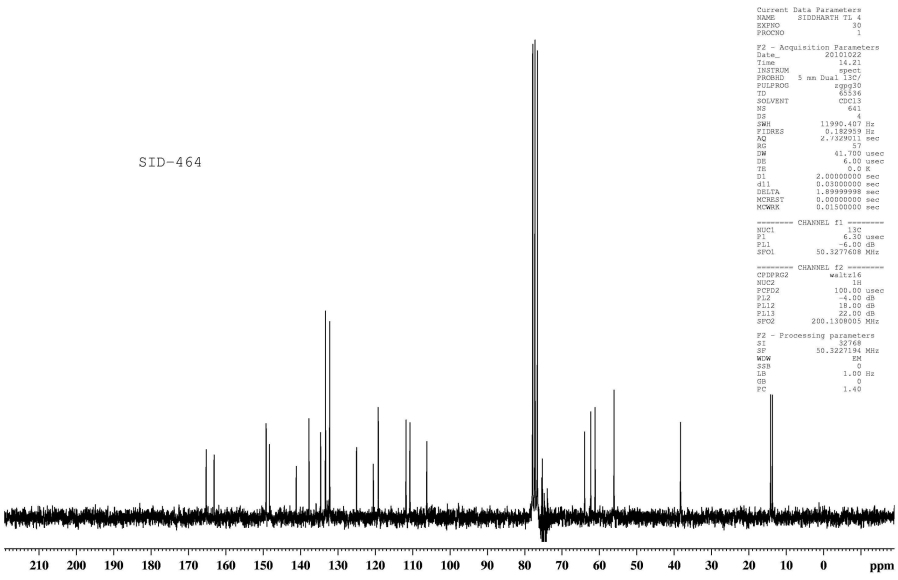


Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(3,4-dimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5l).



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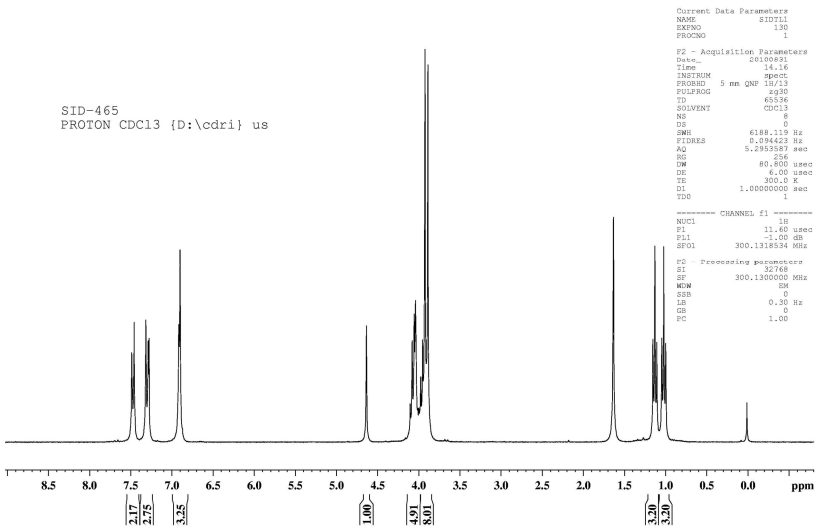
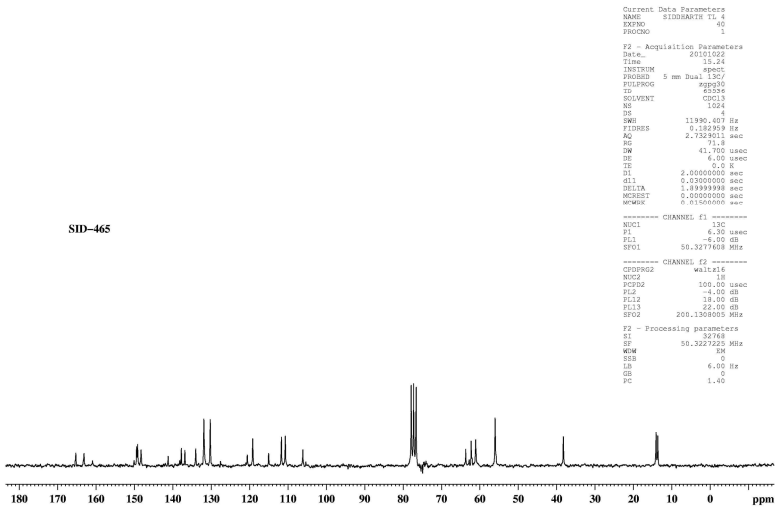


Diethyl 6-amino-1-(4-chlorophenyl)-5-cyano-4-(3,4-dimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5m).



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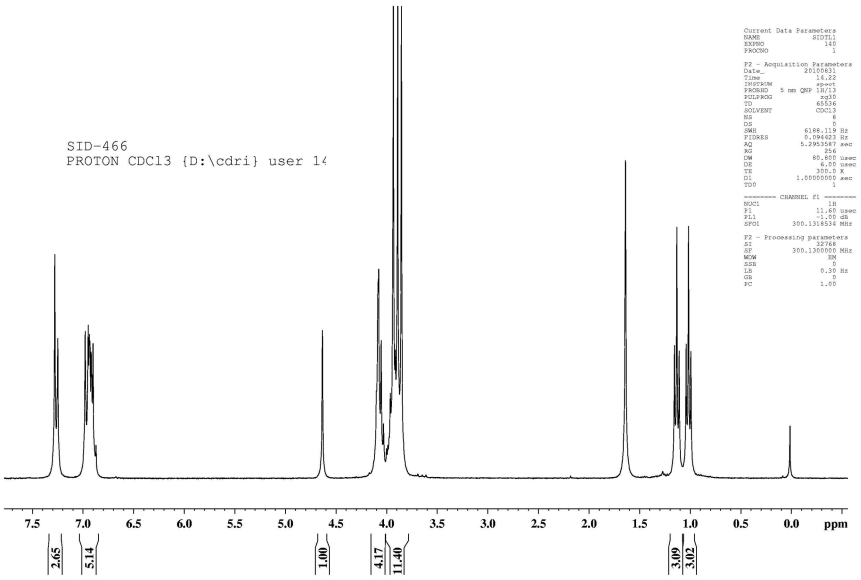
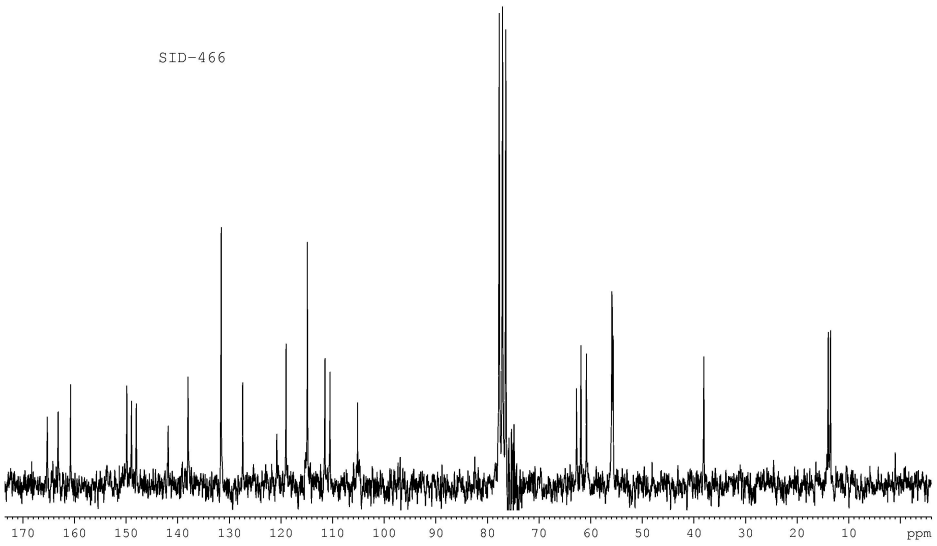
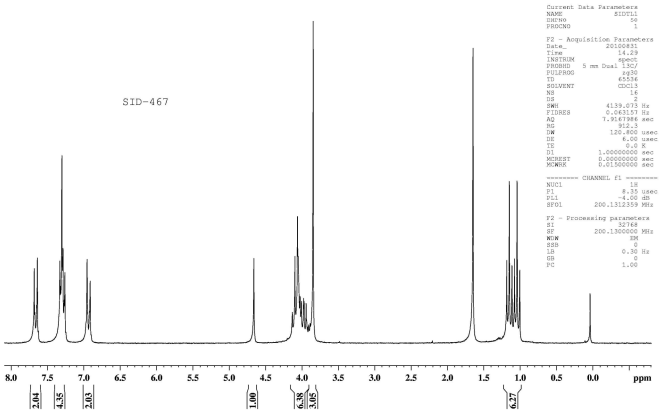


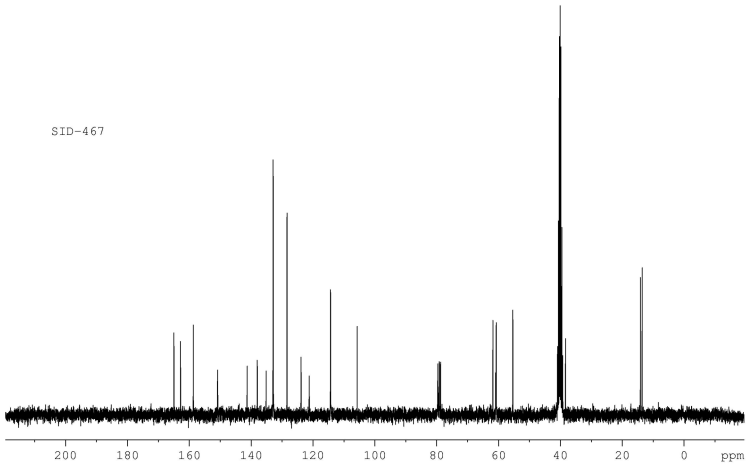
Diethyl 6-amino-5-cyano-4-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5n).



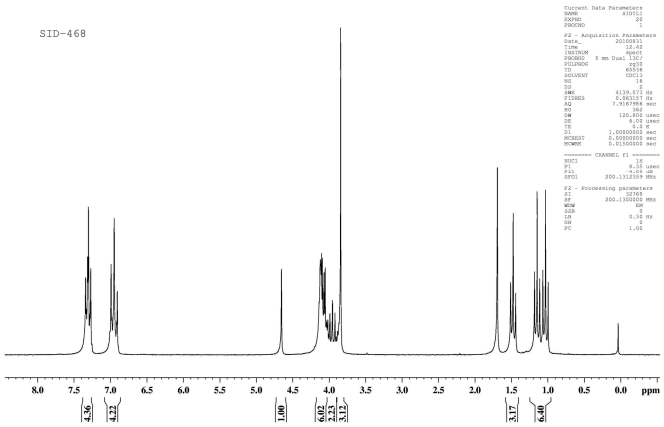
Diethyl 6-amino-5-cyano-4-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5n).



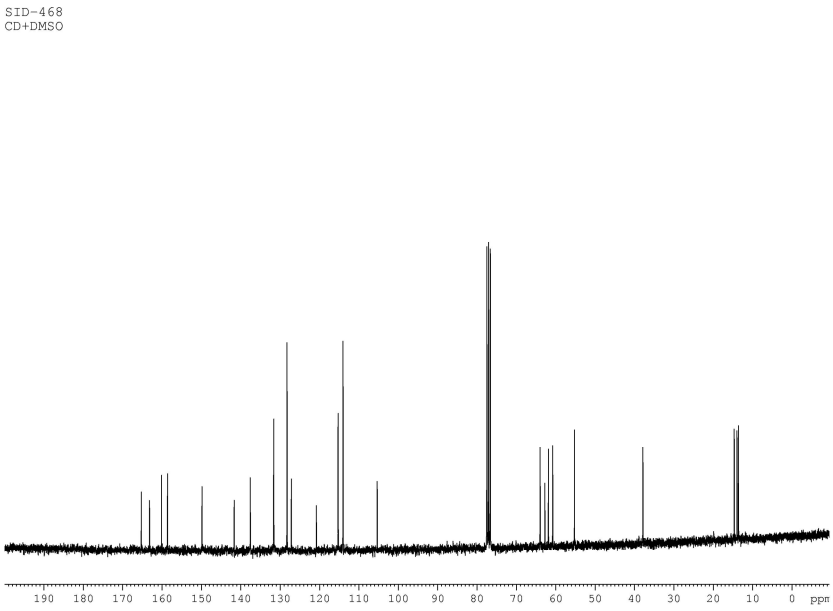
Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5o).



Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5o).



Diethyl 6-amino-5-cyano-1-(4-ethoxyphenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5p).



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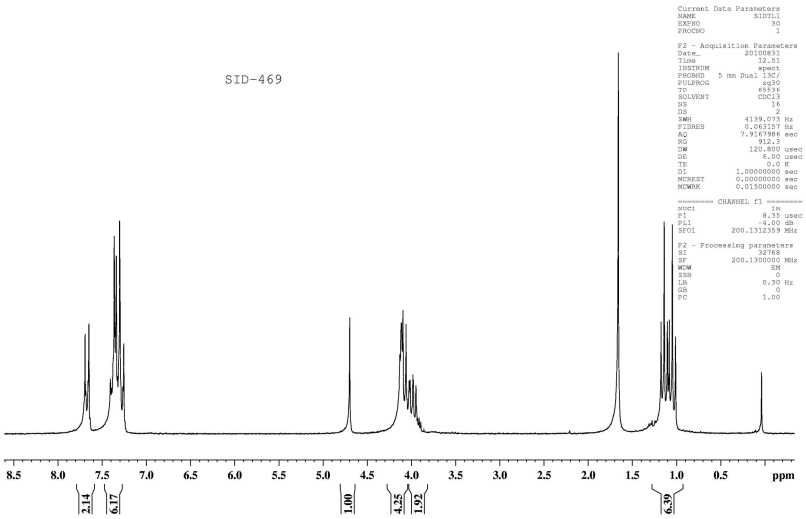
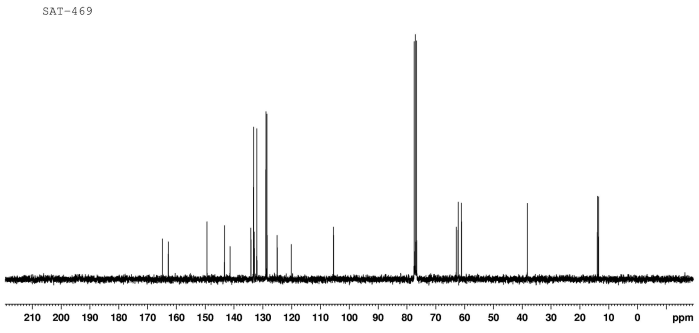


Diethyl 6-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (5q)



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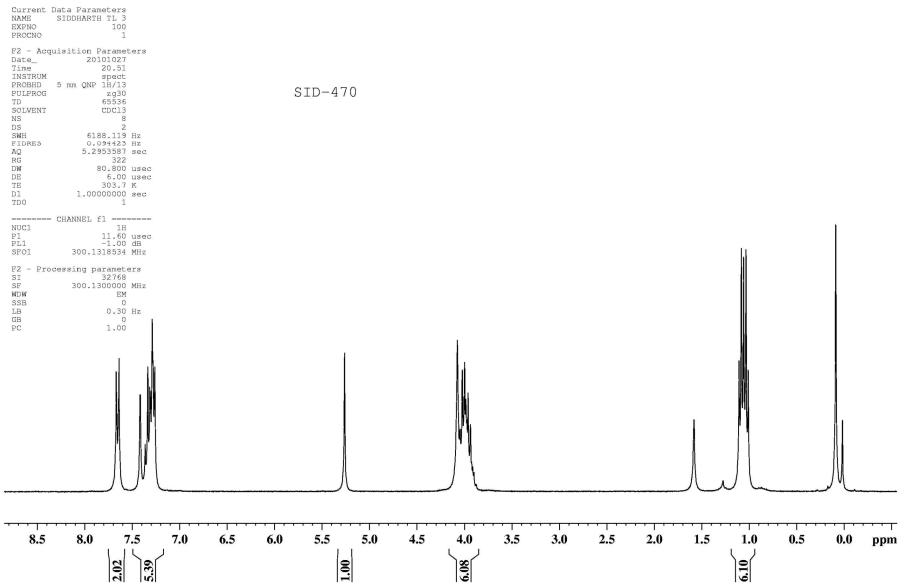
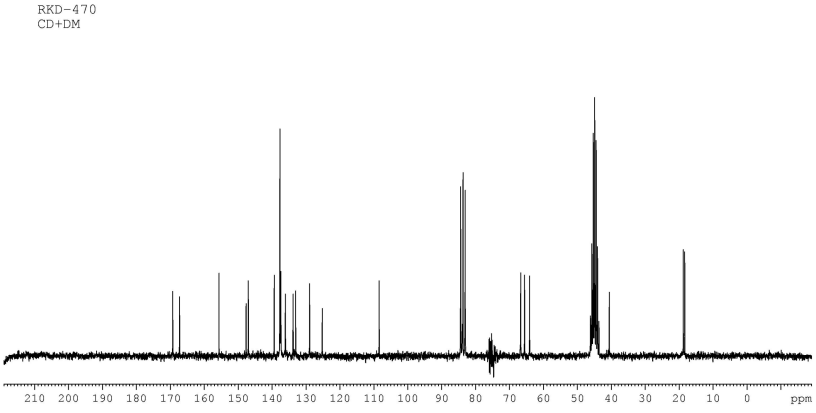
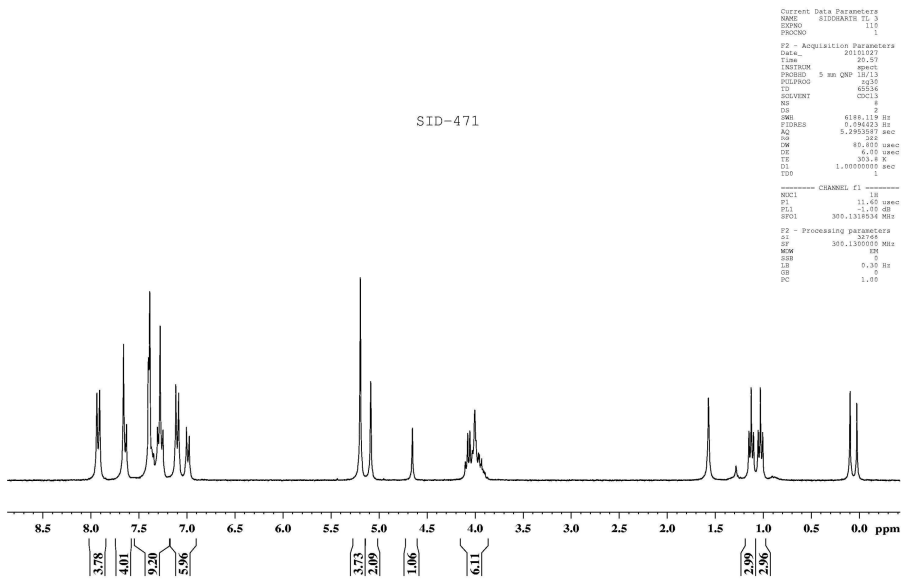


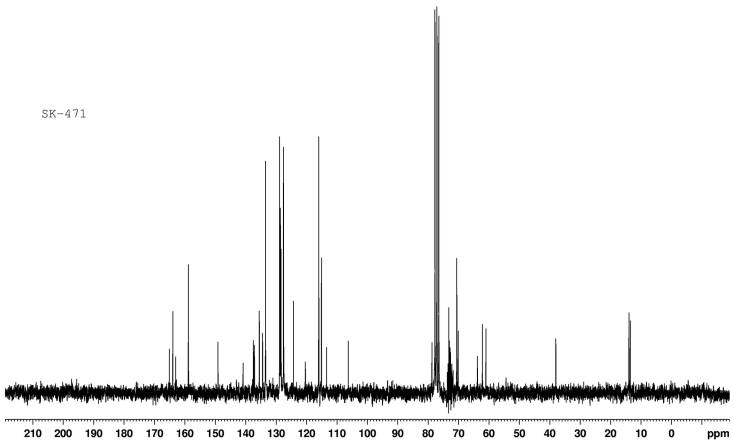
Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(2,4-dichlorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5r).



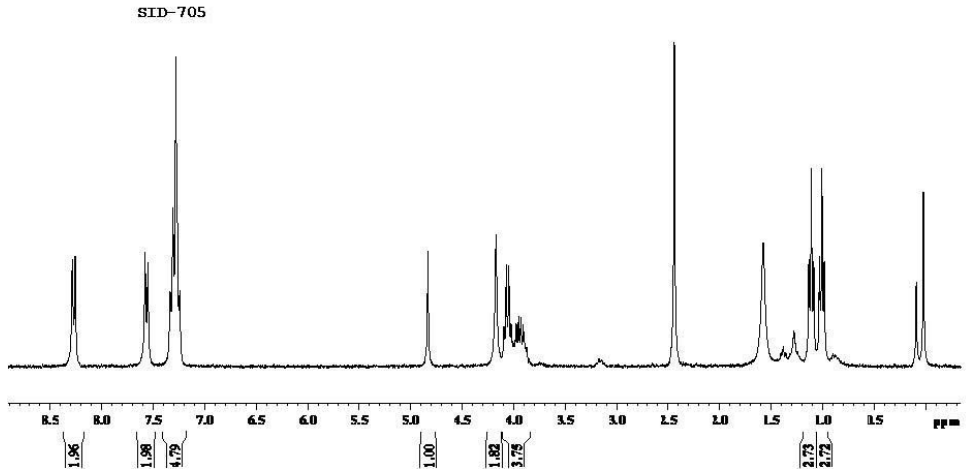
Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(2,4-dichlorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (5r).



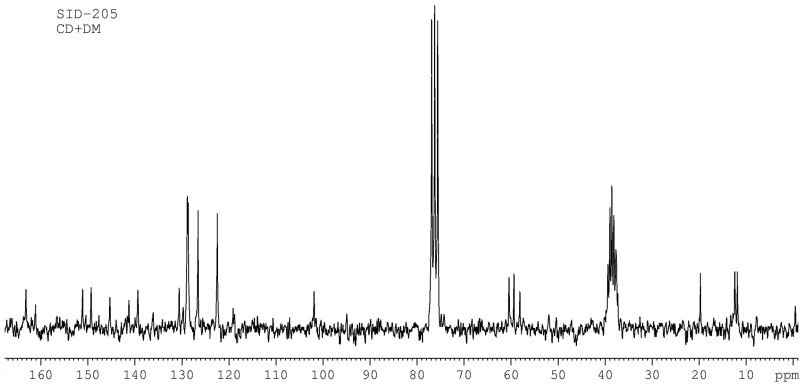
Diethyl 6-amino-4-(4-(benzyloxy)phenyl)-1-(4-bromophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (5s).



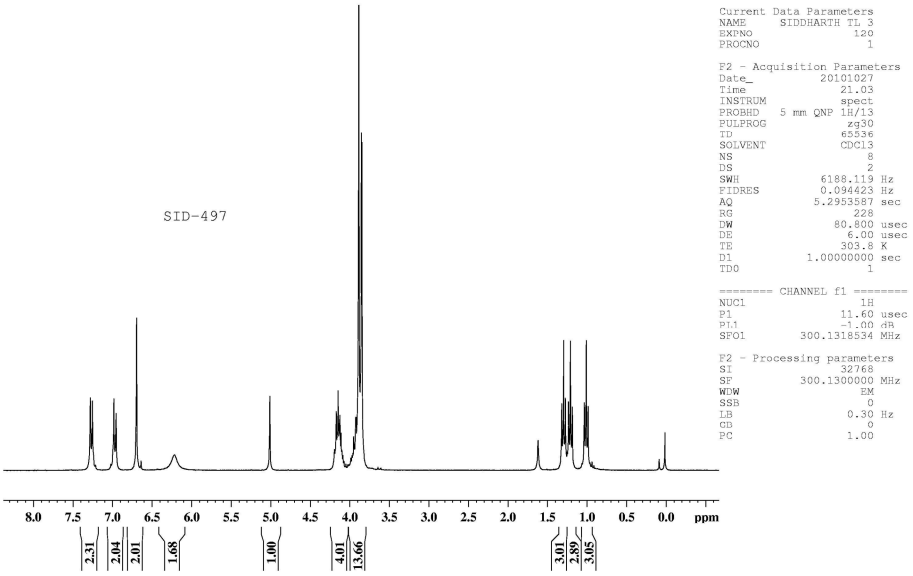
Diethyl 6-amino-4-(4-(benzyloxy)phenyl)-1-(4-bromophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (5s).



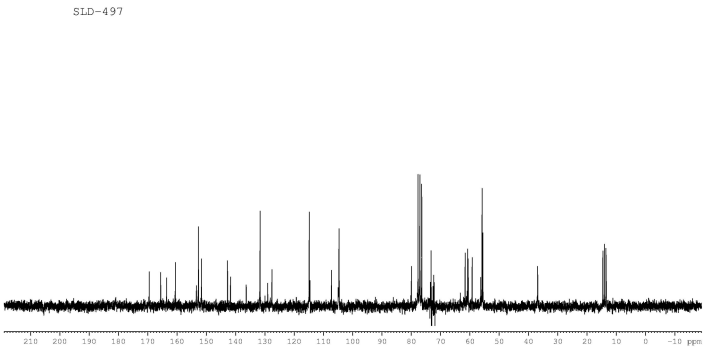
Diethyl 6-amino-5-cyano-4-(4-nitrophenyl)-1-p-tolyl-1,4-dihydropyridine-2,3-dicarboxylate (5t).



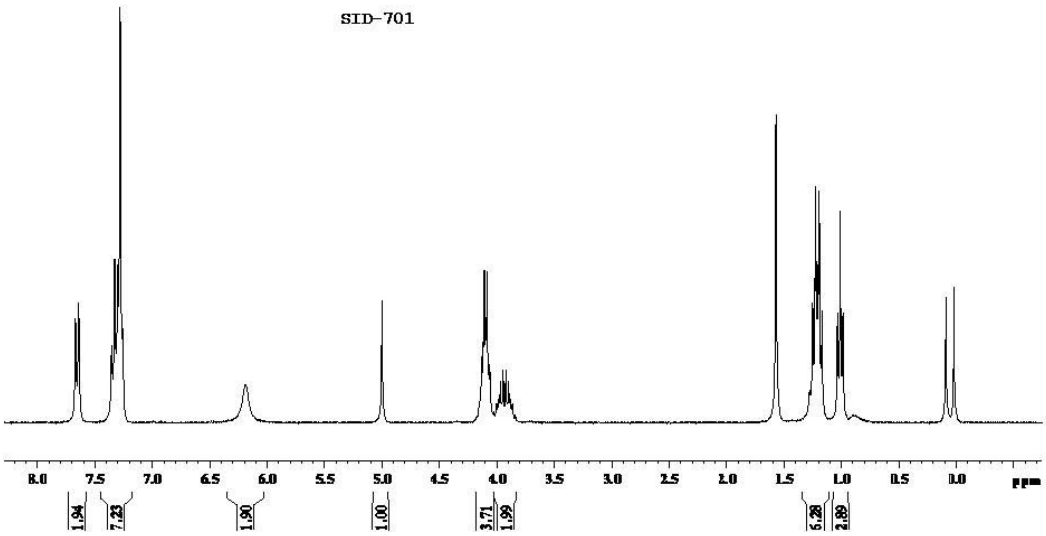
Diethyl 6-amino-5-cyano-4-(4-nitrophenyl)-1-p-tolyl-1,4-dihydropyridine-2,3-dicarboxylate (5t).



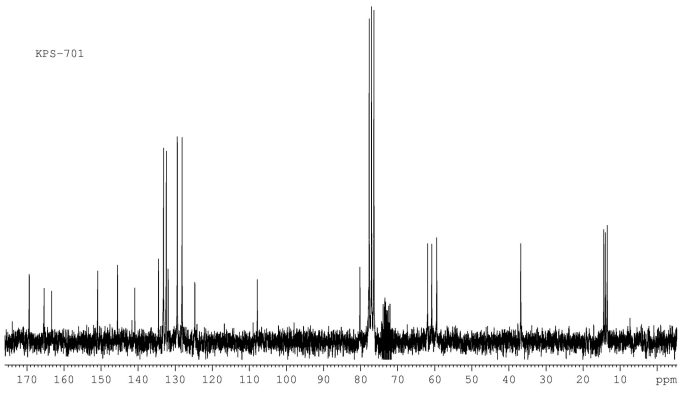
Triethyl 6-amino-1-(4-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6a).



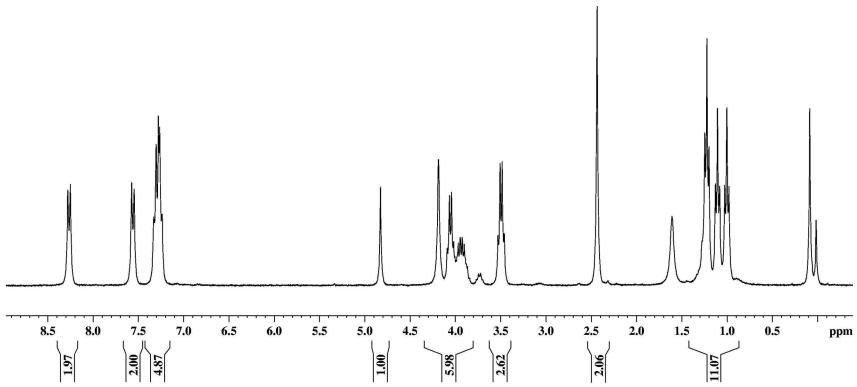
Triethyl 6-amino-1-(4-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6a).



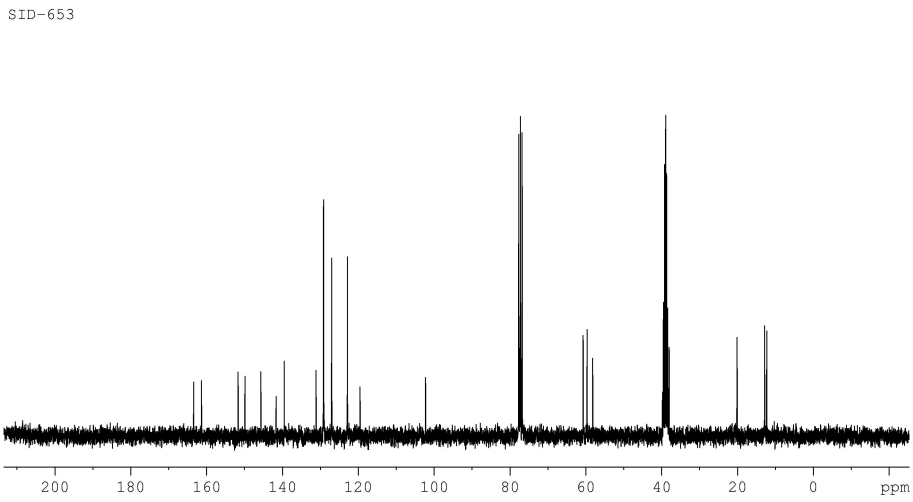
Triethyl 6-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6b).



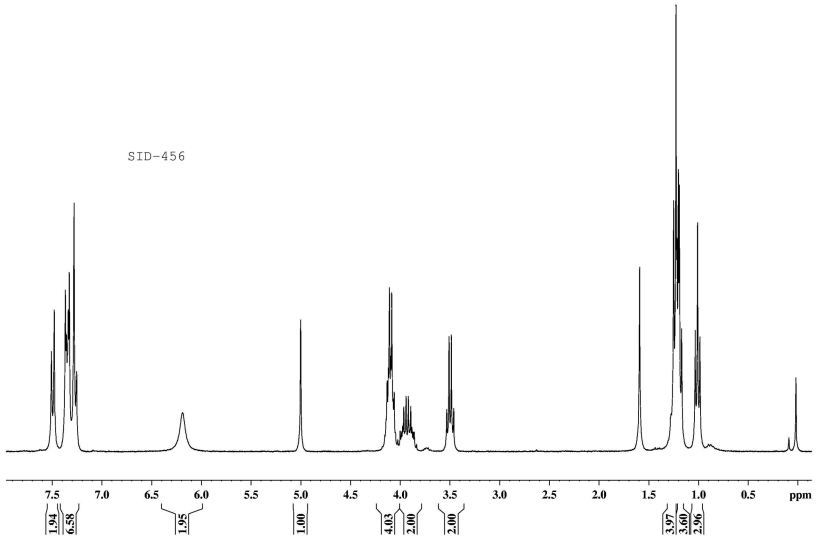
Triethyl 6-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6b).



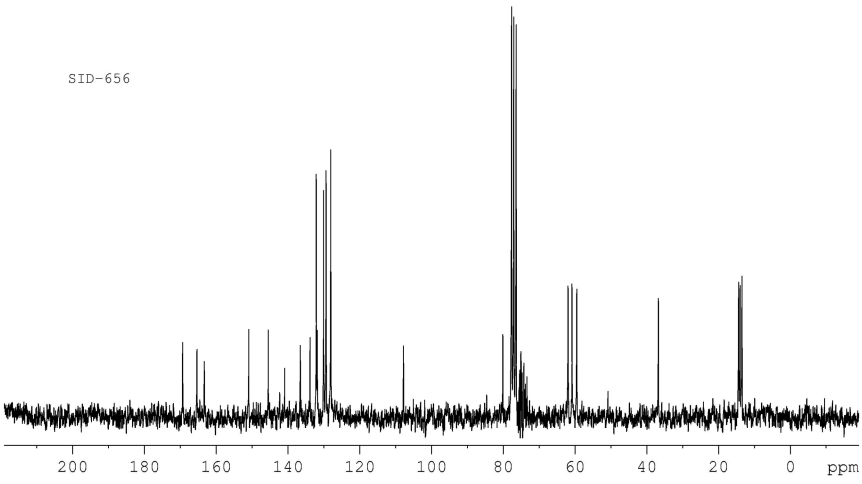
Triethyl 6-amino-4-(4-nitrophenyl)-1-p-tolyl-1,4-dihydropyridine-2,3,5-tricarboxylate (6c).



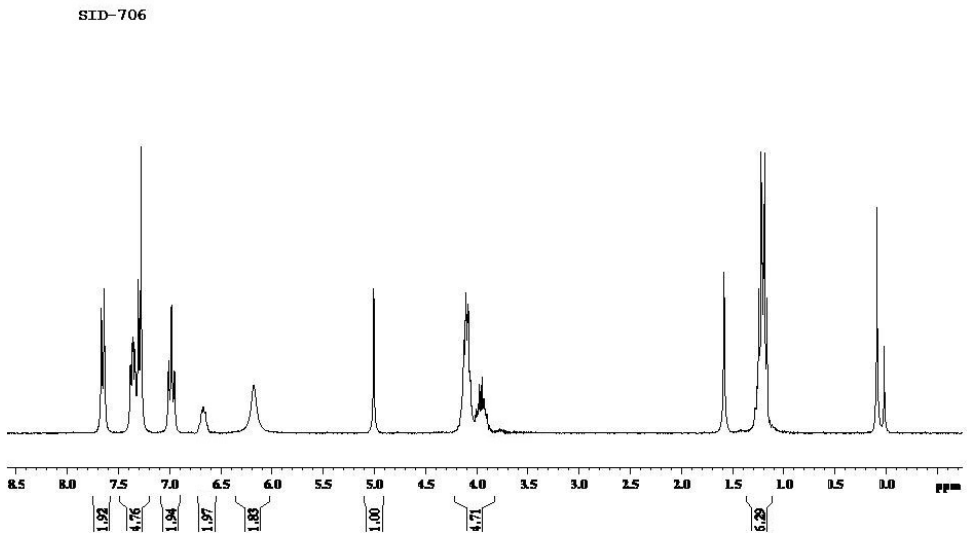
Triethyl 6-amino-4-(4-nitrophenyl)-1-p-tolyl-1,4-dihydropyridine-2,3,5-tricarboxylate (6c).



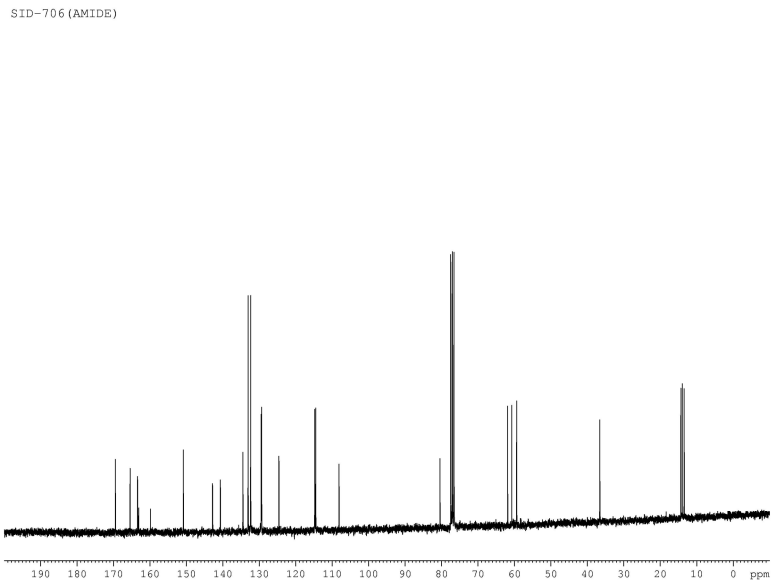
Triethyl 6-amino-1,4-bis(4-chlorophenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6d).



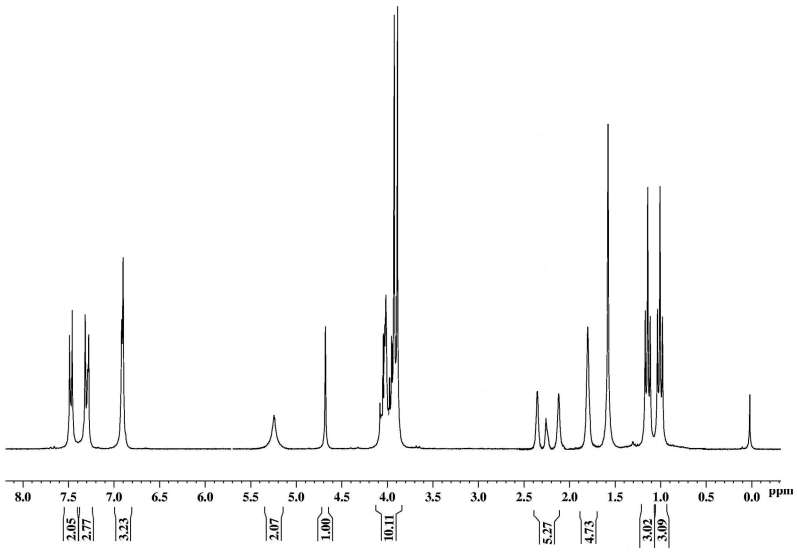
Triethyl 6-amino-1,4-bis(4-chlorophenyl)-1,4-dihydropyridine-2,3,5-tricarboxylate (6d).



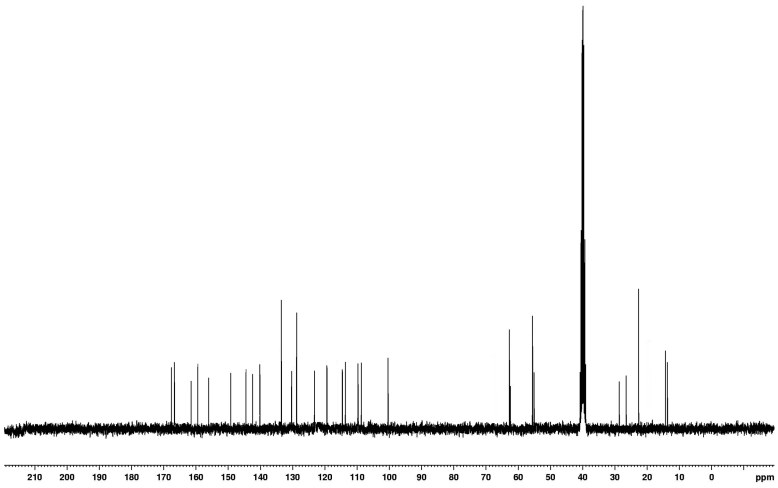
Diethyl 6-amino-5-carbamoyl-1,4-bis(4-chlorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (6e).



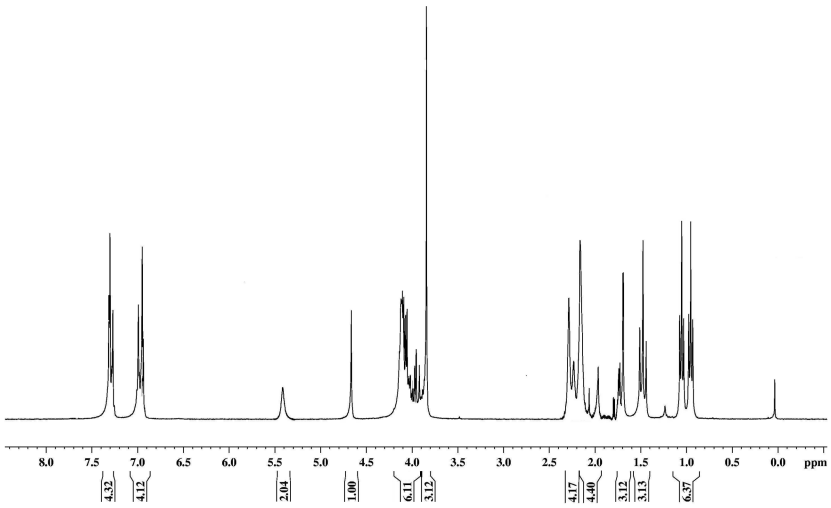
Diethyl 6-amino-5-carbamoyl-1,4-bis(4-chlorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (6e).



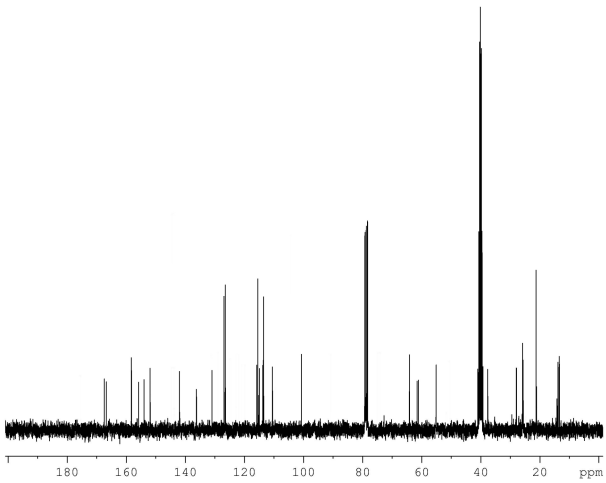
Diethyl 5-amino-1-(4-chlorophenyl)-4-(3,4-dimethoxyphenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7a).



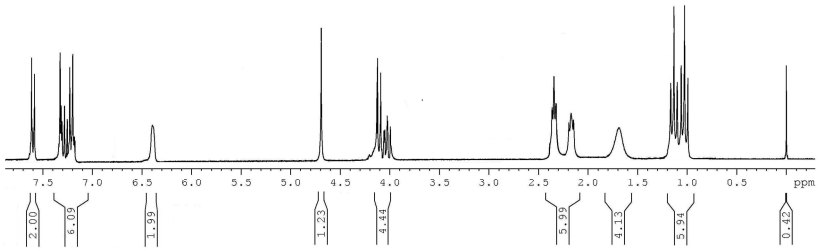
Diethyl 5-amino-1-(4-chlorophenyl)-4-(3,4-dimethoxyphenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7a).



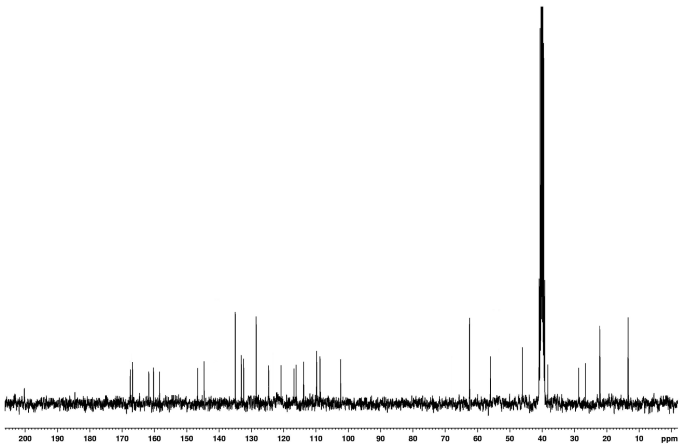
Diethyl 5-amino-1-(4-ethoxyphenyl)-4-(4-methoxyphenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7b).



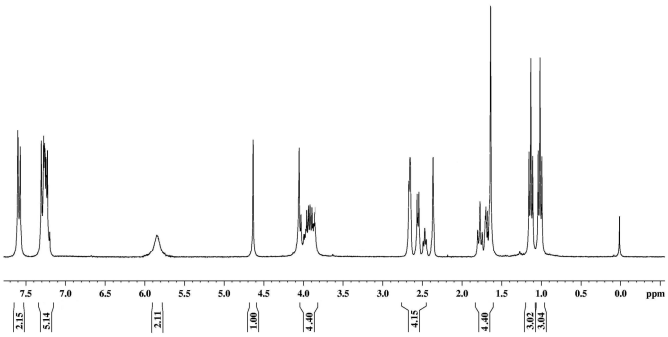
Diethyl 5-amino-1-(4-ethoxyphenyl)-4-(4-methoxyphenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7b).



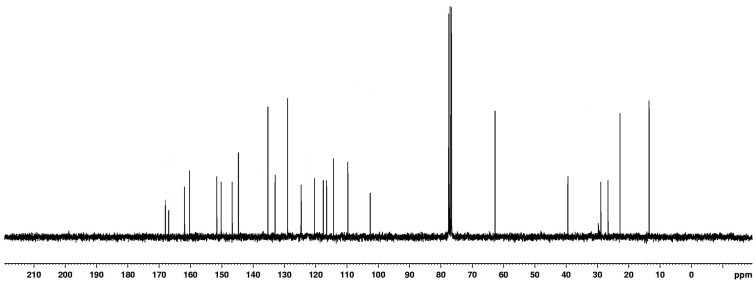
Diethyl 5-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7c).



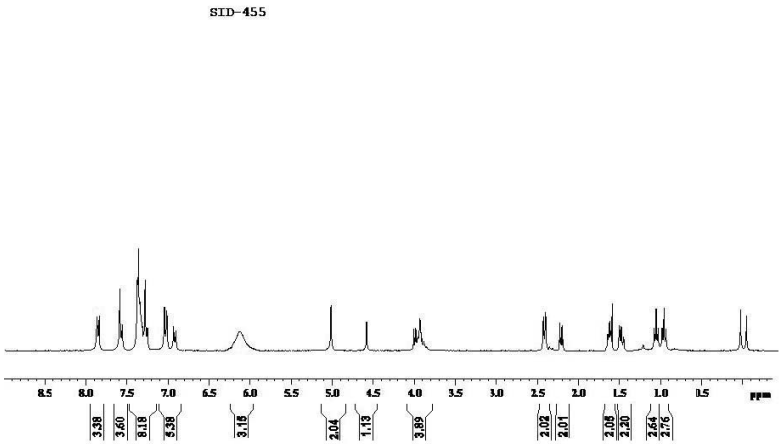
Diethyl 5-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7c).



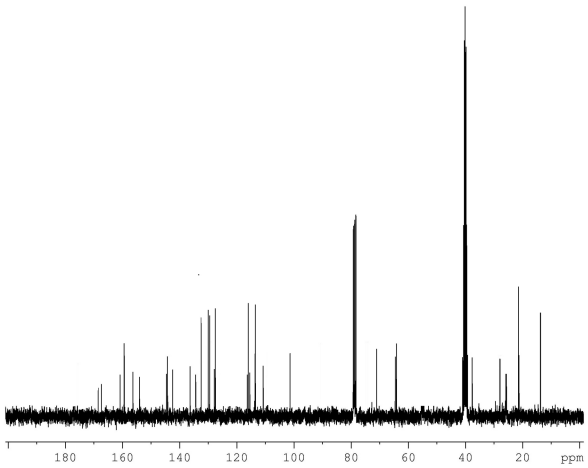
Diethyl 5-amino-1-(4-bromophenyl)-4-(2,4-dichlorophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7d).



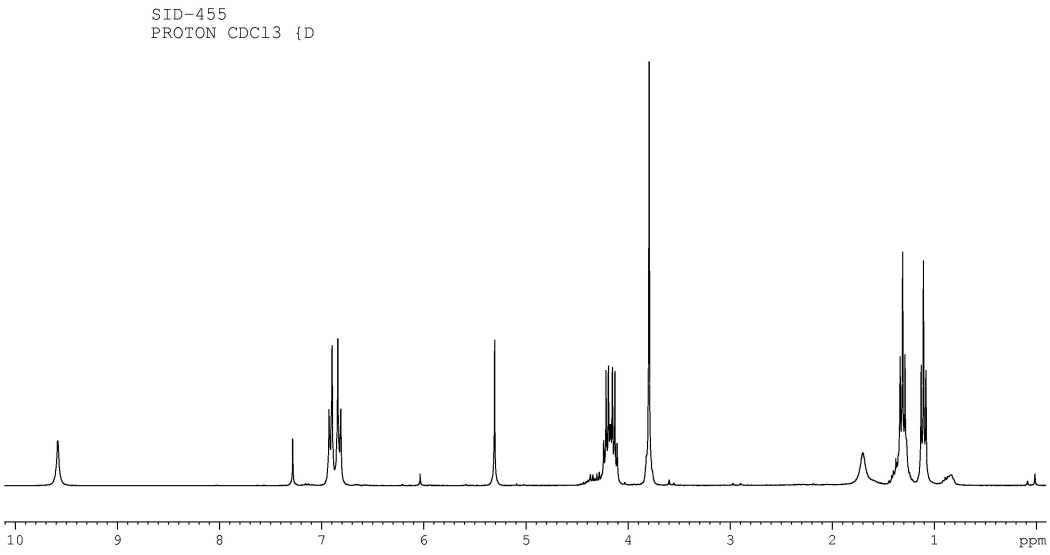
Diethyl 5-amino-1-(4-bromophenyl)-4-(2,4-dichlorophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7d).



Diethyl 5-amino-4-(4-(benzyloxy)phenyl)-1-(4-bromophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7e).



Diethyl 5-amino-4-(4-(benzyloxy)phenyl)-1-(4-bromophenyl)-1,4,6,7,8,9-hexahydrobenzo[b][1,8]naphthyridine-2,3-dicarboxylate (7e).



Diethyl 2-(4-methoxyphenylamino)maleate ((Intermediate).