Supporting Information

Green and Sustainable One-Pot Synthesis of Novel Tetrahydropyridines Using [Et3NH][HSO4] as an Ionic Liquid Catalyst

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1.General Consideration

All the experiments were performed in an oven dried glass apparatus. All the commercially available reagents were purchased from Sigma-Aldrich and were used without further purification. Melting points (^{0}C) were measured in open glass capillaries using Labtronics digital melting point apparatus and are uncorrected. The progress of reaction was monitored using thin layer chromatography (TLC) using silica gel pre-coated aluminum sheets (60 F254, Merck). The crude products were purified by recrystallization with ethanol: ethylacetate. Visualization of spots was effected by exposure to ultraviolet light (UV) at 362nm and 256nm, iodine vapors and 3% 2,4-dinitrophenylhydrazine in methanol containing few drops of H_2SO_4, draggendroff reagent, and anisaldehyde reagent. Solvents used in purification were distilled prior to use. IR spectra were recorded on Bruker Alpha II FTIR-spectrometer, ^{1}H and ^{13}C NMR were recorded on Bruker AC400 spectrometer operating at 400MHz for ^{1}H and 100MHz for ^{13}C with tetramethylsilane (TMS) as an internal standard. The chemical shifts are expressed in d (ppm) downfield from TMS. All the ^{13}C NMR spectra are proton decoupled. J values are given in Hertz (Hz). The

abbreviations s, d, dd, t, q, and m in ^{1}H NMR spectra refer to singlet, doublet, doublet of doublet, triplet, quartet, and multiplet, respectively. Solvents were removed using Buchi rotavapor R-300.

2.General procedure for the preparation and characterization of [Et3NH][HSO4] ionic liquid catalyst

[Et3NH][HSO4] was synthesized according to the reported method. The synthesized IL was characterized by melting point, FT-IR,^{1}H and ^{13}C NMR spectrum and its acidity was determined by pH. **[Fig. S2-S4].**

[Et3NH][HSO4] Spectral data: Brownish orange solid, Yield 99%, pH= 4.1 of its 0.1 mM solution in H2O, m.p. 82.5-83.5 ^{o}C, **FT-IR (KBr, cm-1)** 845, 1026.85, 1153.48, 1397.13, 1469.35, 2512.48, 3037.53, 3410.07; **^{1}H NMR (400 MHz, DMSO d6)** δ 1.13 (t, *J* = 7.3 Hz, 9H, 3 CH3), 3.03-3.04 (m, 6H, 3 CH2),8.95 (s, 1H, OH); **^{13}C NMR (100 MHz, DMSO d6);** δ 9.0, 46.2.

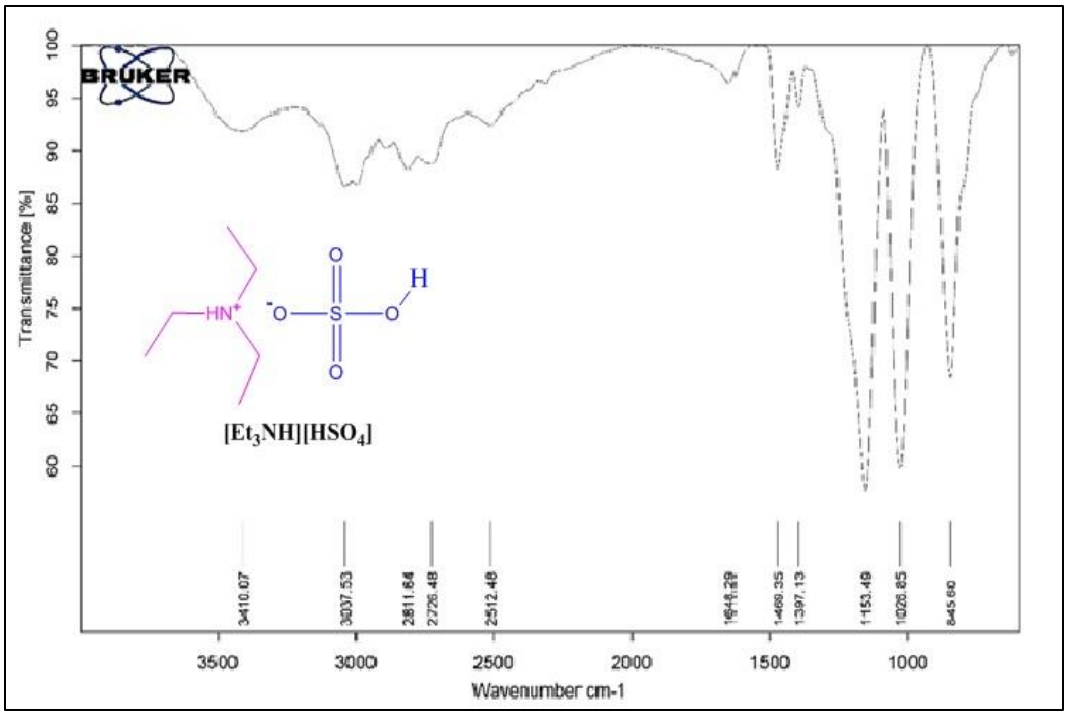


Figure.S1: FT-IR spectrum of [Et3NH][HSO4] Ionic liquid

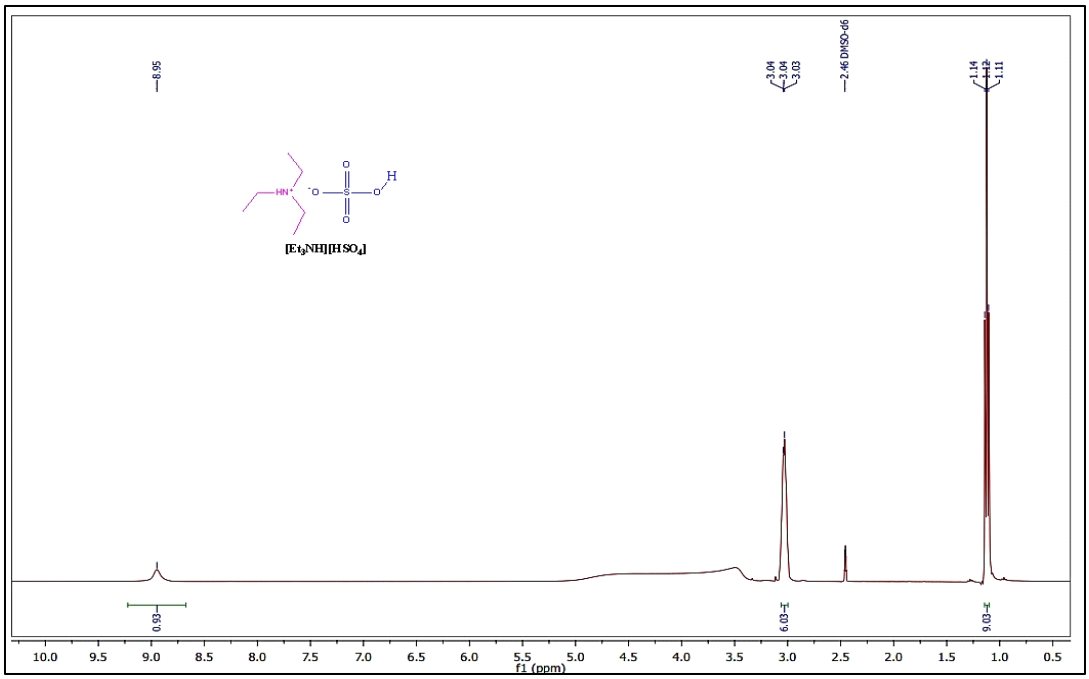


Figure.S2: 1H NMR spectrum of [Et3NH][HSO4] Ionic liquid

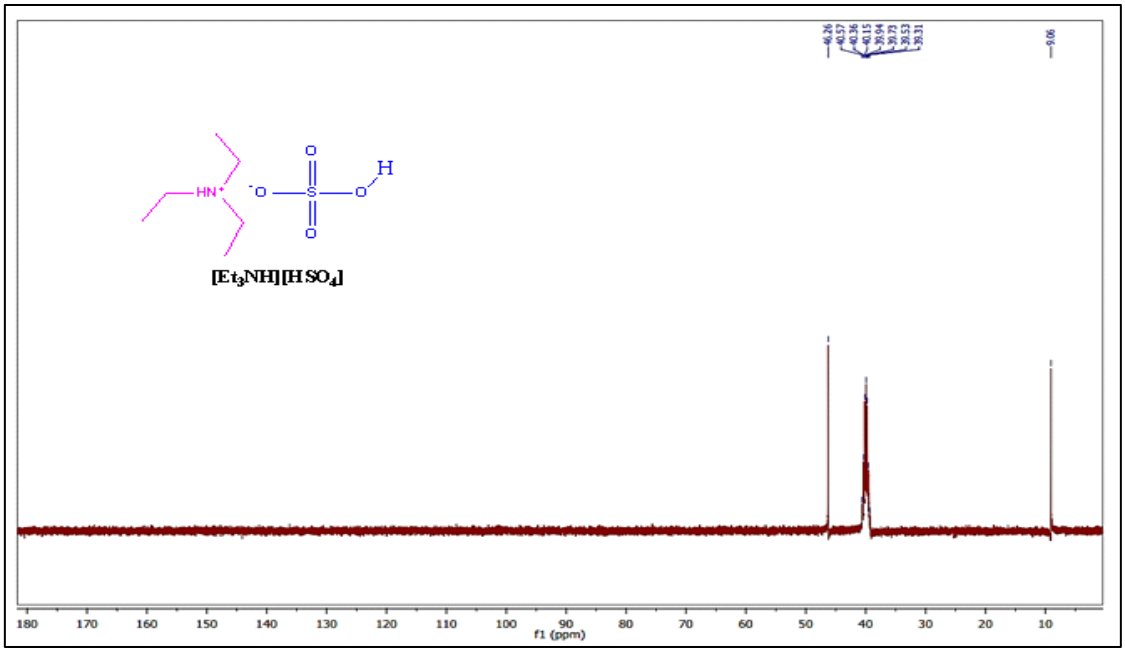


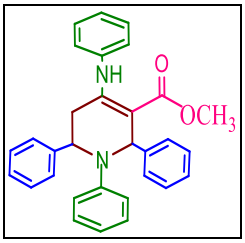
Figure.S3: 13C NMR spectrum of [Et3NH][HSO4] Ionic liquid

1. *General procedure for the Synthesis of 1,2,5,6-tetrahydropiridines derivatives 4a-o*

A mixture of various aromatic amines **2** (2 mmol), various aromatic aldehydes **1**(2 mmol), methyl acetoacetate **3**(1 mmol), Ethanol: water (1:1) 10 ml and [Et3NH][HSO_4] (10 mol%), at 60°C temperature was stirred for the appropriate reaction time (Table 2, entry 1-15). After completion of the reaction, which was monitored by TLC (n-hexane/acetone, 10:1), the solid product was collected by filtration (after evaporation of the ethanol, cool methylene dichloride (5 mL) was added, and the catalyst was recovered), washed with ethanol and purified by recrystallization from ethanol: ethyl acetate (2:1), to obtain the final 1, 2, 5, 6-tetrahydropiridines derivatives.

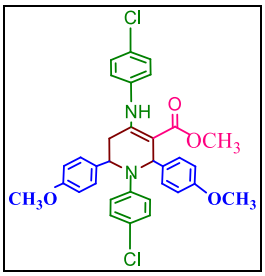
2. Physical and Chemical Data of final derivatives

Methyl-1, 2, 6-triphenyl-4- (phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4a)



white crystalline solid, Yield = 94%, M.P:112-113 °C, FTIR (KBr) *v*, cm^{-1}: 3347 (NH), 1653 (C=O),^{1}H-NMR (400 MHz, CDCl3) δ: 2.73-2.78 (d, *J*=15 Hz, 1H), 2.85-2.88 (dd, *J*=15, 6 Hz, 1H), 3.92 (s, 3H), 5.15 (br s, 1H), 6.26 (d, *J*=7.6 Hz, 2H), 6.44 (s, 1H), 6.51-6.56 (d, *J* = 8.0 Hz, 2H), 6.59-6.61 (t, *J*=7.0 Hz, 1H), 7.04-7.33(m,15H), 10.25 (s, 1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): *δ*H=13.4 (O<u>C</u>H3), 33.6 (C^5), 55.1 (C^6), 58.2 (C^2), 98.2 (C^3), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^4, C-Ar), 168.2 (CO).

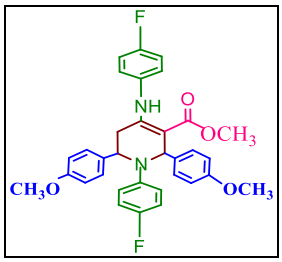
Methyl-1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4- methoxyphenyl)-1,2,5,6- tetrahydropyridine-3-carboxylate(4b)



White solid. Mp: 170– 172 °C. Yield: 91%. IR (KBr, cm_1): 3250 (N–H), 1651 (C=O), 1257 (C–O),^{1}H-NMR (400 MHz, CDCI3):
δ 2.68-2.71 (m, 1H), 2.81-2.85(m, 1H), 3.79 (s, 6H), 3.91 (s, 3H), 5.03(br s,1H), 6.20-6.35 (m, 5H), 6.80-6.82(m, 3H), 7.13-7.26

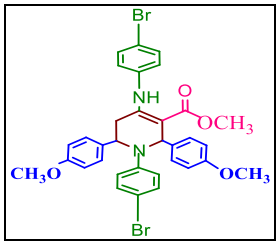
(m,9H), 10.20 (s, 1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): δH=13.4 (OCH3), 33.6 (C^5), 55.1 (C^6), 58.2 (C^2), 98.2 (C^3), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^4, C-Ar), 168.2 (CO).

Methyl-1-(4-fluorophenyl)-4-((4-fluorophenyl)amino)-2,6-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate(4c)



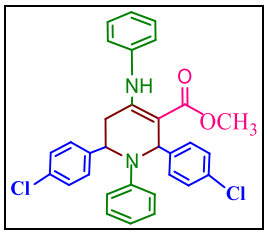
Light brown solid. Mp: 152– 154 °C. Yield: 94%.FIR (KBr, cm_1): 3250 (N–H), 1651 (C=O), 1257 (C–O). Yield=91%, ^{1}H NMR (400 MHz,CDCl3): δ 2.68-2.71 (m, 1H), 2.81-2.84(m, 1H), 3.78 (s, 6H), 3.92 (s, 3H), 5.03(br s,1H), 6.20-6.38 (m, 5H), 6.80-6.81(m, 3H), 7.12-7.26 (m,9H), 10.20 (s, 1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): δH=13.4 (OCH3), 33.6 (C^5), 55.1 (C^6), 58.2 (C^2), 96.7 (C^3), 113.0, 116.1, 125.9, 125.8, 126.3, 126.4,126.6, 127.2, 128.2, 128.3, 128.2, 128.1, 137.9, 142.8, 144.1, 147.0, 156.7 (C^4, C-Ar), 168.4 (CO).

Methyl-1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate(4d)



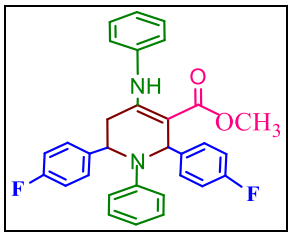
Light yellow solid. Mp: 158– 160 °C. Yield: 89%. IR (KBr, cm_1): 3250 (N–H), 1651 (C=O), 1257 (C–O). Yield=91%, ^{1}H NMR(400MHz,CDCl3): δ 2.68-2.71 (m, 1H), 2.81-2.84(m, 1H), 3.78 (s, 6H), 3.92 (s, 3H), 5.03(br s,1H), 6.20-6.38 (m, 5H), 6.80-6.81(m, 3H), 7.12-7.26 (m,9H), 10.20 (s, 1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): δH=13.4 (OCH3), 33.6 (C^5), 55.1 (C^6), 58.2 (C^2), 98.2 (C^3), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^4, C-Ar), 168.2 (CO).

Methyl-2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4e)



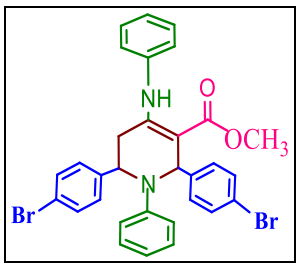
Light brown solid. Mp: 171– 172 ºC. Yield: 96%. IR (KBr, cm_1): 3250 (N–H), 1651 (C=O), 1257 (C–O),^{1}H NMR (500 MHz, CDCl3) δ: 2.74 (dd, *J*=15.0, 2.5, 1H), 2.82 (dd, *J*=15.0, 5.5, 1H), 3.91 (s, 3H),5.07 (br s, 1H), 6.32 (s, 1H), 6.41 (d, *J*=7.0, 2H), 6.45 (d, *J*=8.5, 2H), 6.65 (t, *J*=7.3, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 7.06-7.18 (m, 7H), 7.37-7.40 (m, 4H), 10.23 (s,1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): *δ*H=13.4 (OCH3), 33.6 (C^{5}), 55.1 (C^{6}), 58.2 (C^{2}), 98.2 (C^{3}), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^{4}, C-Ar), 168.2 (CO).

Methyl-2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4f)



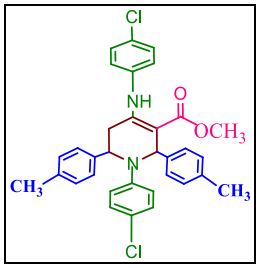
Dark brown solid. Mp: 142– 143 ºC. Yield: 96%. IR (KBr, cm_1): 3250 (N–H), 1651 (C=O), 1257 (C–O),^{1}H NMR (500 MHz, CDCl3) δ: 2.74 (dd, *J*=15.0, 2.5, 1H), 2.82 (dd, *J*=15.0, 5.5, 1H), 3.91 (s, 3H),5.07 (br s, 1H), 6.32 (s, 1H), 6.41 (d, *J*=7.0, 2H), 6.45 (d, *J*=8.5, 2H), 6.65 (t, *J*=7.3, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 7.06-7.18 (m, 7H), 7.37-7.40 (m, 4H), 10.23 (s,1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): *δ*H=13.4 (OCH3), 33.6 (C^{5}), 55.1 (C^{6}), 58.2 (C^{2}), 98.2 (C^{3}), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^{4}, C-Ar), 168.2 (CO).

Methyl-2,6-bis(4-bromophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4g)



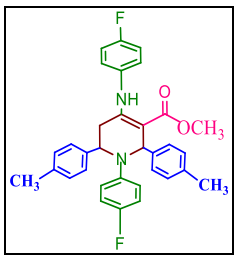
Dark brown solid. Mp: 164– 165 °C. Yield: 94%. IR (KBr, cm_1): 3250 (N–H), 1651 (C=O), 1257 (C–O), ^{1}H NMR (500 MHz, CDCl3) δ: 2.73 (dd, *J*=15.0, 2.5, 1H), 2.81 (dd,*J*=15.0, 5.5, 1H), 3.91 (s, 3H), 5.06 (br s,1H), 6.32 (s, 1H), 6.40 (d, *J*=7.0, 1H),6.45 (d, *J*=8.5, 2H), 6.64 (t, *J*=7.3, 1H),7.0 (d, *J* =8.5 Hz, 2H), 7.05-7.17 (m, 7H), 7.37-7.39 (m, 4H), 10.23 (s, 1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): *δ*H=13.4 (O<u>C</u>H3), 33.6 (C^{5}), 55.1 (C^{6}), 58.2 (C^{2}), 98.2 (C^{3}), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^{4}, C-Ar), 168.2 (CO).

Methyl-1-(4-chlorophenyl)-4-(4-chlorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4h)



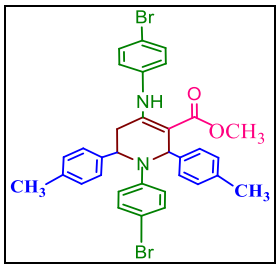
Grey solid. Mp: 178– 179 °C. Yield: 93%. IR (KBr, cm_1): 3250 (N–H), 1651 (C=O), 1257 (C–O). ^{1}H NMR (500 MHz, CDCl3) δ:2.31 (s, 3H), 2.34 (s, 3H), 2.66-2.70 (m, 1H),2.81-2.86 (m, 1H), 3.92 (s, 3H), 5.05 (br s,1H), 6.19 (d, *J* = 10.5 Hz, 2H), 6.31 (s, 1H),6.40 (d, *J* = 11.0 Hz, 2H), 6.60 (d, *J*=8.5,1H) 7.01-7.14 (m, 12H), 10.18 (s, 1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): *δ*H=13.4 (O<u>C</u>H3), 33.6 (C^{5}), 55.1 (C^{6}), 58.2 (C^{2}), 98.2 (C^{3}), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^{4}, C-Ar), 168.2 (CO).

Methyl-1-(4-fluorophenyl)-4-(4-fluorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4i)



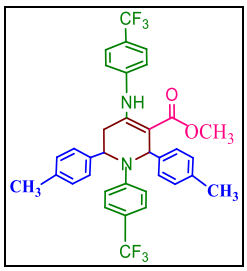
Light orange solid. Mp: 148– 149 ºC. Yield: 91%. IR (KBr, cm_1): 3250 (N–H), 1651 (C=O), 1257 (C–O). ^{1}H NMR (500 MHz, CDCl3) δ:2.31 (s, 3H), 2.34 (s, 3H), 2.66-2.70 (m, 1H),2.81-2.86 (m, 1H), 3.92 (s, 3H), 5.05 (br s,1H), 6.19 (d, *J* = 10.5 Hz, 2H), 6.31 (s, 1H),6.40 (d, *J* = 11.0 Hz, 2H), 6.60 (d, *J*=8.5,1H) 7.01-7.14 (m, 12H), 10.18 (s, 1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): *δ*H=13.4 (O<u>C</u>H3), 33.6 (C^{5}), 55.1 (C^{6}), 58.2 (C^{2}), 98.2 (C^{3}), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^{4}, C-Ar), 168.2 (CO).

Methyl-1-(4-bromophenyl)-4-(4-bromophenyl)amino)-2,6-di-p-tolyl- 1,2,5,6-tetrahydropyridine-3-carboxylate(4j)



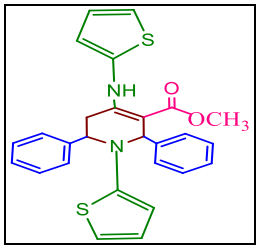
Light orange solid. Mp: 153– 154 ºC. Yield: 90%. IR (KBr, cm_1): 3250 (N–H), 1651 (C=O), H^{1}NMR (500 MHz,CDCl3) δ: 2.32 (s, 3H), 2.34 (s, 3H), 2.64(d, *J*=17.5, 1H), 2.84 (dd, *J*=19.0, 7.5,1H), 3.93 (s, 3H), 5.06 (d, *J*=6.5, 1H),6.12 (d, *J*= 10.0, 2H), 6.31 (s, 1H), 6.38 (d, *J*=11.0, 2H), 7.02 (d, *J=10.0*, 2H),7.09(d, *J*=9.0,2H), 7.14 (d, *J*=15.0, 2H), 7.20 (d, *J=10.5*, 2H), 7.26 (s, 2H), 10.19 (s, 1H). ^{13}C NMR (100 MHz, CDCl3, 25°C): *δ*H=13.4 (O<u>C</u>H3), 33.6 (C^{5}), 55.1 (C^{6}), 58.2 (C^{2}), 98.2 (C^{3}), 113.0, 116.1, 125.7, 125.8, 126.3, 126.4,126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 137.9, 142.8, 144.1, 147.0, 156.1 (C^{4}, C-Ar), 168.2 (CO).

Methyl-1-(4-trifluoromethylphenyl)-4-(4-trifluoromethylphenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4k)



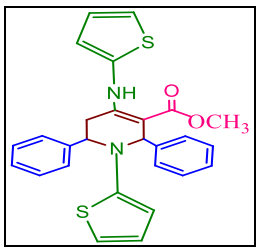
Pink solid. Mp: 153–154 8C. Yield: 84%. IR (KBr, cm_1): 3235 (N–H), 1651 (C5O), 1262 (C–O). 1H-NMR (FT-300 MHz, CDCl3): d (ppm) 2.36 (s, CH3, 6H), 2.80 (d, CH2, J = 11.1 Hz, 2H), 3.99 (s, CH3, 3H), 5.17 (s, CH, H), 6.42–7.38 (m, aromatic, 16H, s, CH, 1H), 10.44 (s, NH, 1H). 13C-NMR (FT-300 MHz, CDCl3): d (ppm) 21.0, 33.4, 51.3, 55.2, 58.1, 99.0, 109.2, 112.7, 115.9, 122.4, 126.0, 126.4, 129.2, 129.5, 131.3, 136.4, 137.4, 138.5, 155.3, 168.5.

Methyl-2,6-bis(phenyl)-1-thiophene-2-yl-4-(thiophene-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4l)



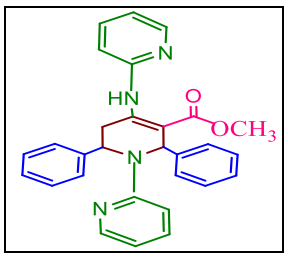
White crystalline solid; Yield: 86%; m.p. 205-206 °C.FTIR (KBr) *v*, cm^{-1}: 3240 (NH), 1656 (C=O). ^{1}H NMR (400 MHz, CDCl3, 25°C): δH=1.37 (t, *J*(H,H)=7.1 Hz, 3H; OCH2CH3), 2.97 (dd, *J*(H,H)=15.4, 11.4 Hz, 1H; C^{5}H*A*H*B*), 3.03 (dd, *J*(H,H)=15.4, 4.6 Hz, 1H; C^{5}H*A*H*B*), 4.23 (dq, *J*(H,H)=10.8, 7.1Hz, 1H; OCH*A*H*B*CH3), 4.39 (dq, *J*(H,H)=10.8, 7.1 Hz, 1H; OCH*A*H*B*CH3), 4.97 (dd, *J*(H,H)=11.3, 4.5 Hz, 1H; C^{6}H), 6.26 (s,1H; C^{2}H), 6.82-6.90 (m, 2H; Ar-2CH), 7.01-7.13 (m, 7H; Ar-7CH), 7.17-7.25 (m, 3H; Ar-3CH), 7.29 (dd, *J*(H,H)=3.5, 1.9 Hz, 2H; Ar-2CH), 7.34-7.38 (m,2H; Ar-2CH), 10.68 (s, 1H; NH). ^{13}C NMR (100 MHz, CDCl3, 25°C): δH=14.1 (OCH2CH3), 36.5 (C^{5}), 55.7 (C^{6}), 59.1 (C^{2}), 59.3 (OCH2CH3), 98.5 (C^{3}), 116.1, 118.9, 123.5, 123.5, 123.5, 123.6,124.1, 124.6, 126.0, 126.5, 128.2, 128.9, 138.0, 148.0, 149.6, 152.3, 156.6 (C^{4}, C-Ar), 167.3(CO).

Methyl-2,6-bis(phenyl)-1-thizole-2-yl-4-(thizole-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4m)



White crystalline solid; Yield: 86%; m.p. 205-206 °C.FTIR (KBr) *v*, cm^{-1}: 3240 (NH), 1656 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δH=1.37 (t, *J*(H,H)=7.1 Hz, 3H; $OCH_2\underline{CH_3}$), 2.97 (dd, *J*(H,H)=15.4, 11.4 Hz, 1H; $C^5\underline{H}\underline{\textit{A}}H\underline{\textit{B}}$), 3.03 (dd, *J*(H,H)=15.4, 4.6 Hz, 1H; $C^5H\underline{\textit{A}}\underline{\textit{B}}$), 4.23 (dq, *J*(H,H)=10.8, 7.1Hz, 1H; $OC\underline{H}\underline{\textit{A}}H\underline{\textit{B}}CH_3$), 4.39 (dq, *J*(H,H)=10.8, 7.1 Hz, 1H; $OCH\underline{\textit{A}}H\underline{\textit{B}}CH_3$), 4.97 (dd, *J*(H,H)=11.3, 4.5 Hz, 1H; C^6H), 6.26 (s,1H; C^2H), 6.82-6.90 (m, 2H; Ar-2C<u>H</u>), 7.01-7.13 (m, 7H; Ar-7C<u>H</u>), 7.17-7.25 (m, 3H; Ar-3C<u>H</u>), 7.29 (dd, *J*(H,H)=3.5, 1.9 Hz, 2H; Ar-2C<u>H</u>), 7.34-7.38 (m,2H; Ar-2C<u>H</u>), 10.68 (s, 1H; NH). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δH=14.1 ($OCH_2\underline{C}H_3$), 36.5 (C^5), 55.7 (C^6), 59.1 (C^2), 59.3 ($O\underline{C}H_2CH_3$), 98.5 (C^3), 116.1, 118.9, 123.5, 123.5, 123.5, 123.6,124.1, 124.6, 126.0, 126.5, 128.2, 128.9, 138.0, 148.0, 149.6, 152.3, 156.6 (C^4, C-Ar), 167.3(CO).

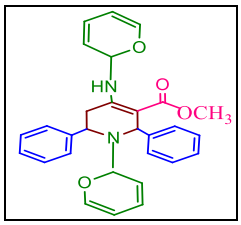
Methyl-2,6-bis(phenyl)-1-pyridine-2-yl-4-(pyridine-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4n)



Light yellow crystalline solid; Yield: 89%; m.p. 192-193 °C.FTIR (KBr) *v*, cm^{-1}: 3240 (NH), 1656 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δH=1.37 (t, *J*(H,H)=7.1 Hz, 3H; $OCH_2\underline{CH_3}$), 2.97 (dd, *J*(H,H)=15.4, 11.4 Hz, 1H; $C^5\underline{H}\underline{\textit{A}}H\underline{\textit{B}}$), 3.03 (dd, *J*(H,H)=15.4, 4.6 Hz, 1H; $C^5H\underline{\textit{A}}\underline{\textit{B}}$), 4.23 (dq, *J*(H,H)=10.8, 7.1Hz, 1H; $OC\underline{H}\underline{\textit{A}}H\underline{\textit{B}}CH_3$), 4.39 (dq, *J*(H,H)=10.8, 7.1 Hz, 1H; $OCH\underline{\textit{A}}H\underline{\textit{B}}CH_3$), 4.97 (dd, *J*(H,H)=11.3, 4.5 Hz, 1H; C^6H), 6.26 (s,1H; C^2H), 6.82-6.90 (m, 2H; Ar-2C<u>H</u>), 7.01-7.13 (m, 7H; Ar-7C<u>H</u>), 7.17-7.25 (m, 3H; Ar-3C<u>H</u>), 7.29 (dd, *J*(H,H)=3.5, 1.9 Hz, 2H; Ar-2C<u>H</u>), 7.34-7.38 (m,2H; Ar-2C<u>H</u>), 10.68 (s, 1H; NH). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δH=14.1 ($OCH_2\underline{C}H_3$), 36.5 (C^5),

55.7 (C^6), 59.1 (C^2), 59.3 (O<u>C</u>H2CH3), 98.5 (C^3), 116.1, 118.9, 123.5, 123.5, 123.5, 123.6,124.1, 124.6, 126.0, 126.5, 128.2, 128.9, 138.0, 148.0, 149.6, 152.3, 156.6 (C^4, C-Ar), 167.3(CO).

Methyl-2,6-bis(phenyl)-1-pyran-2-yl-4-(pyran-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4o)



Light brown crystalline solid; Yield: 85%; m.p. 197-198 °C.FTIR (KBr) *v*, cm^{-1}: 3240 (NH), 1656 (C=O). ^{1}H NMR (400 MHz, CDCl3, 25°C): *δ*H=1.37 (t, *J*(H,H)=7.1 Hz, 3H; OCH2<u>CH3</u>), 2.97 (dd, *J*(H,H)=15.4, 11.4 Hz, 1H; C^{5}H<u>*A*</u>H*B*), 3.03 (dd, *J*(H,H)=15.4, 4.6 Hz, 1H; C^{5}H*A*<u>H*B*</u>), 4.23 (dq, *J*(H,H)=10.8, 7.1Hz, 1H; OC<u>H*A*</u>H*B*CH3), 4.39 (dq, *J*(H,H)=10.8, 7.1 Hz, 1H; OCH*A*<u>H*B*</u>CH3), 4.97 (dd, *J*(H,H)=11.3, 4.5 Hz, 1H; C^{6}H), 6.26 (s,1H; C^{2}H), 6.82-6.90 (m, 2H; Ar-2C<u>H</u>), 7.01-7.13 (m, 7H; Ar-7C<u>H</u>), 7.17-7.25 (m, 3H; Ar-3C<u>H</u>), 7.29 (dd, *J*(H,H)=3.5, 1.9 Hz, 2H; Ar-2C<u>H</u>), 7.34-7.38 (m,2H; Ar-2C<u>H</u>), 10.68 (s, 1H; NH). ^{13}C NMR (100 MHz, CDCl3, 25°C): *δ*H=14.1 (OCH2<u>C</u>H3), 36.5 (C^5), 55.7 (C^6), 59.1 (C^2), 59.3 (O<u>C</u>H2CH3), 98.5 (C^3), 116.1, 118.9, 123.5, 123.5, 123.5, 123.6,124.1, 124.6, 126.0, 126.5, 128.2, 128.9, 138.0, 148.0, 149.6, 152.3, 156.6 (C^4, C-Ar), 167.3(CO).

^{1}H-NMRspectrumofMethyl-1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4a)

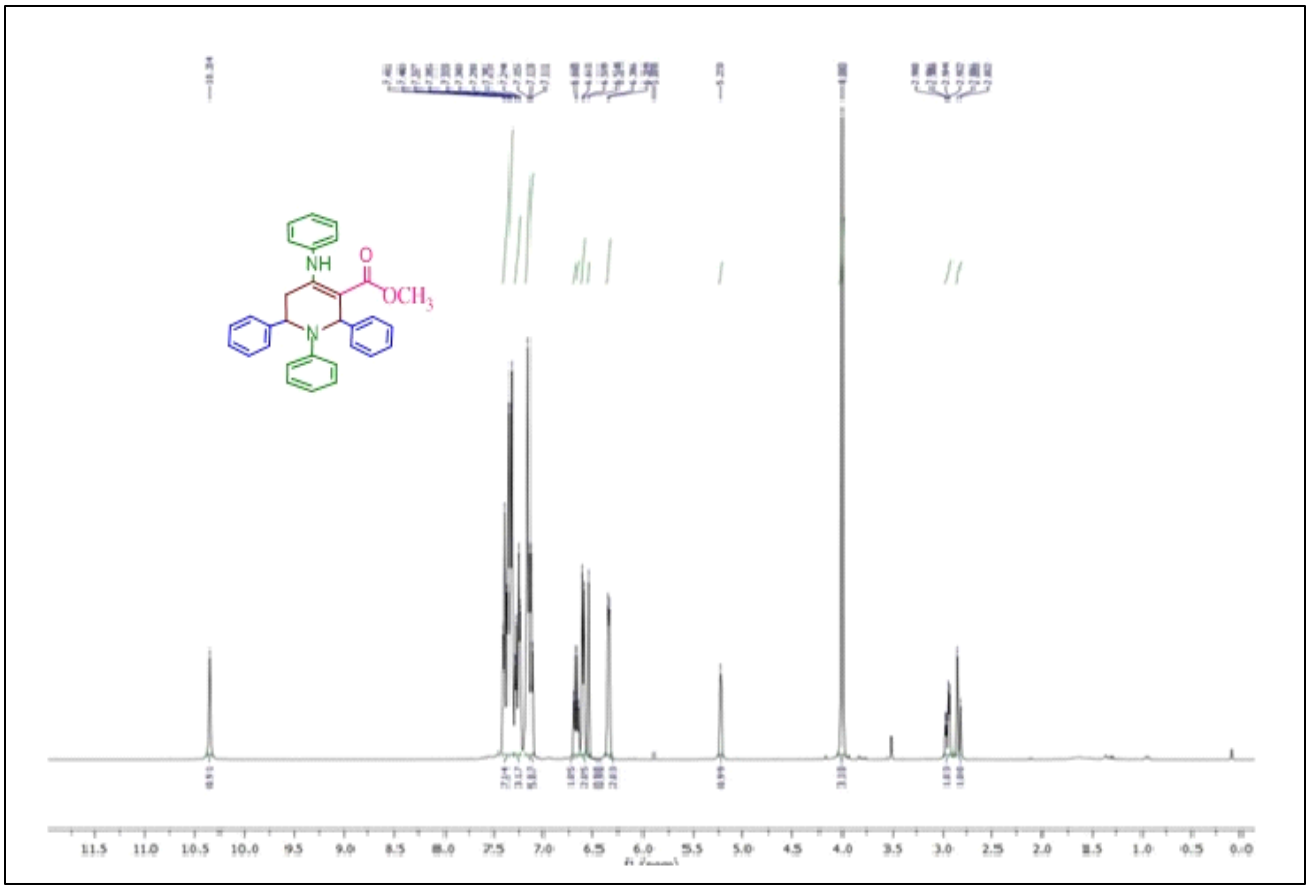


Figure S4. ^{1}H NMR spectrum of compound **4a** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4a)

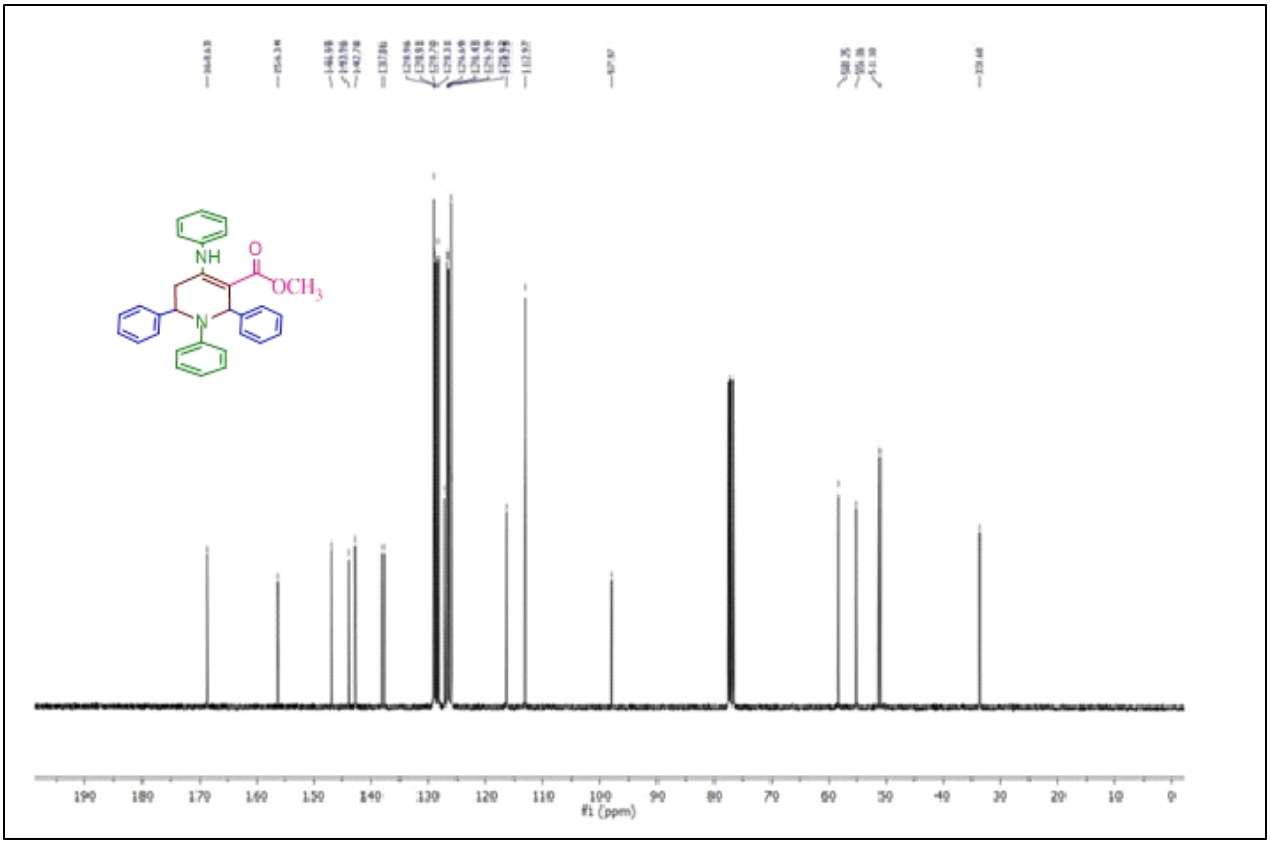


Figure S5. ^{13}C NMR spectrum of compound **4a** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate(4b)

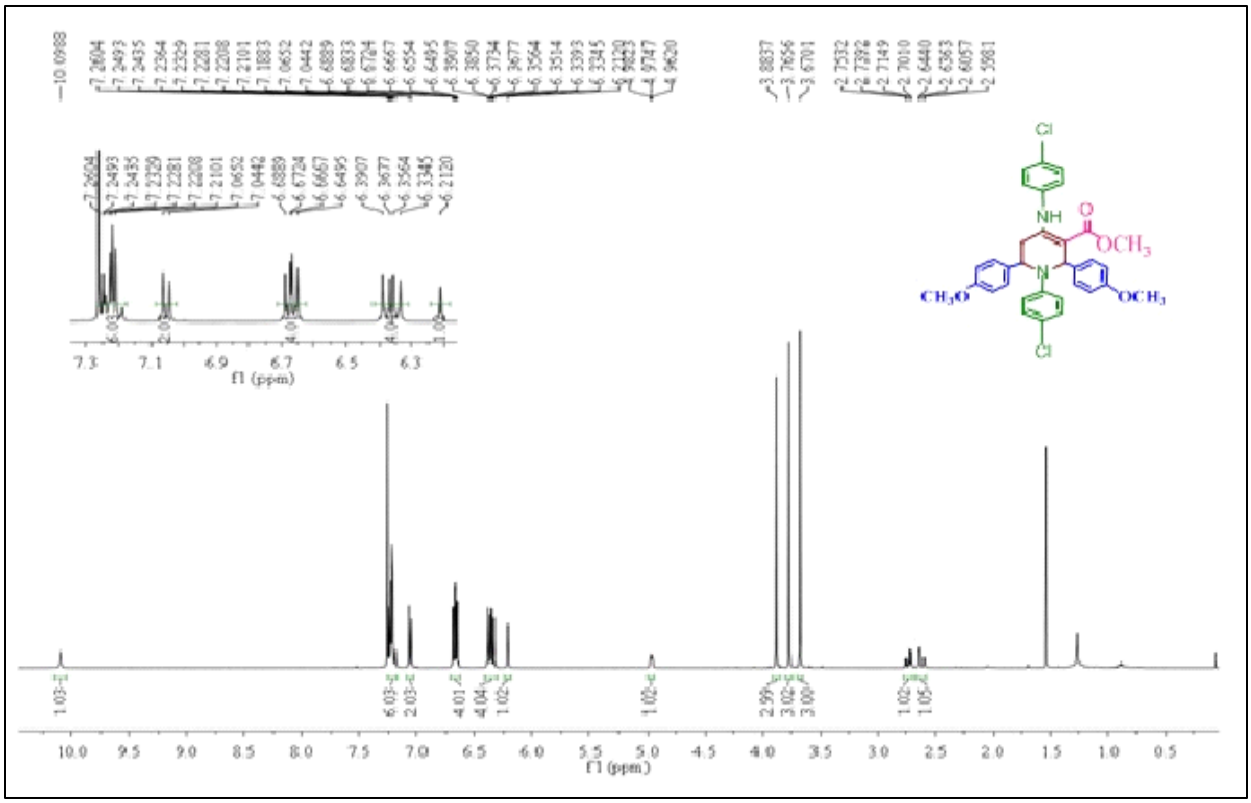


Figure S6. ^{1}H NMR spectrum of compound **4b** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate(4b)

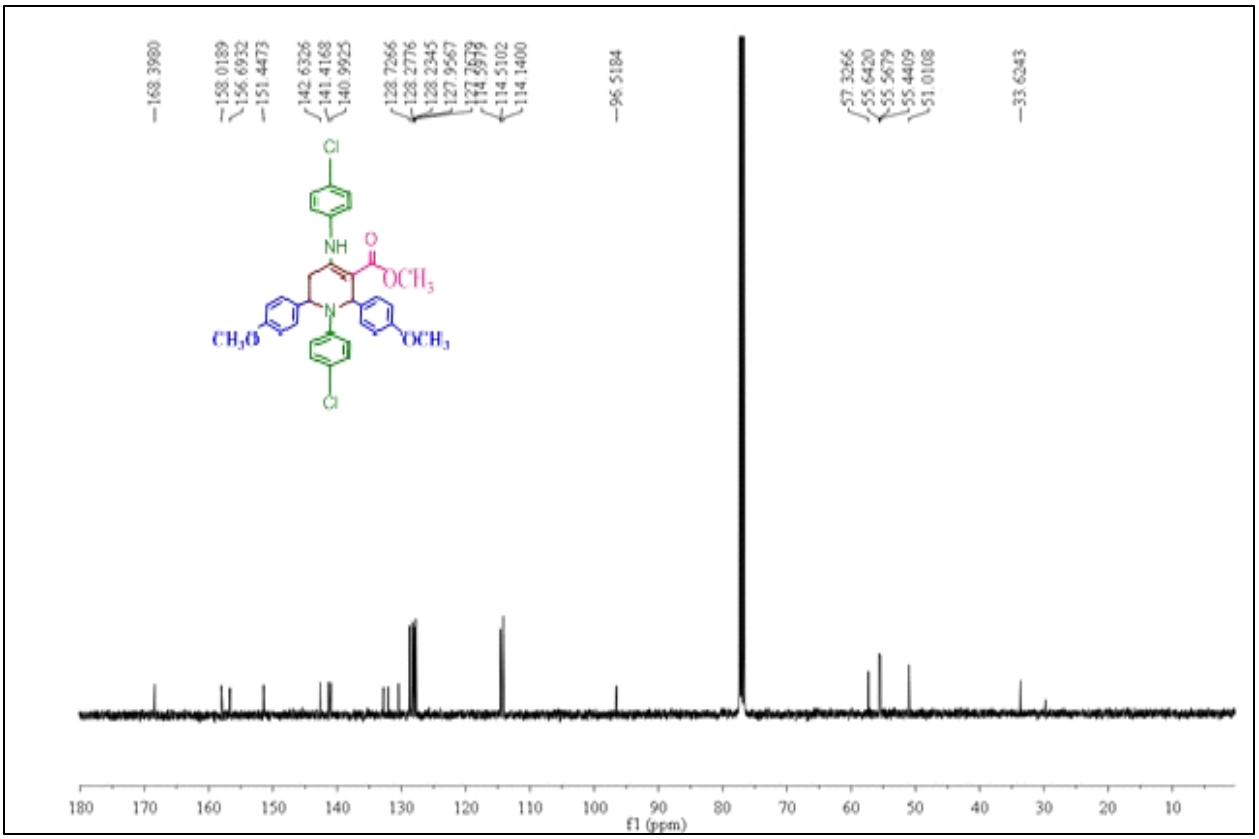


Figure S7. ^{13}C NMR spectrum of compound **4b** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-1-(4-fluorophenyl)-4-((4-fluorophenyl)amino)-2,6-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate(4c)

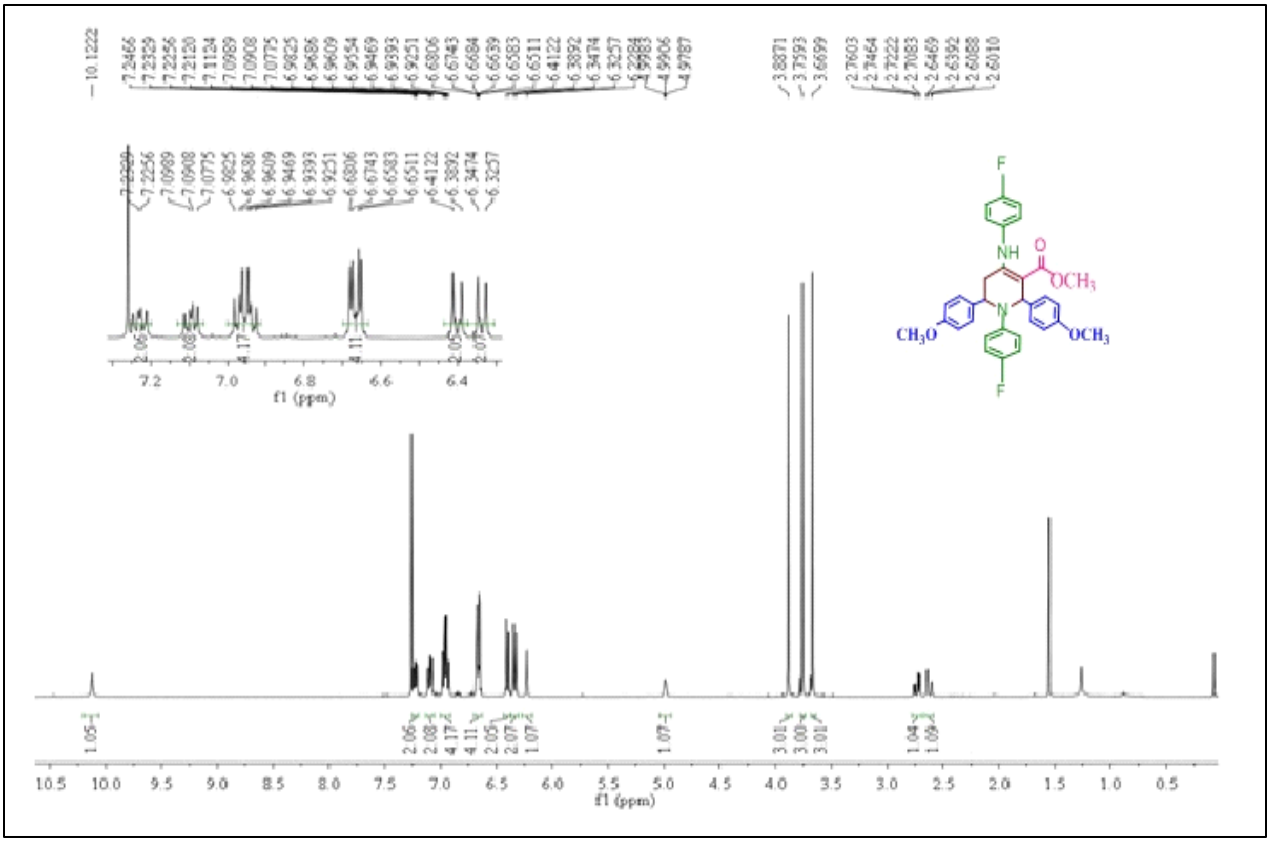


Figure S8. ^{1}H NMR spectrum of compound **4c** (400 MHz, CDCl3)

^{13}C-NMRspectrumofMethyl-1-(4-fluorophenyl)-4-((4-fluorophenyl)amino)-2,6-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate(4c)

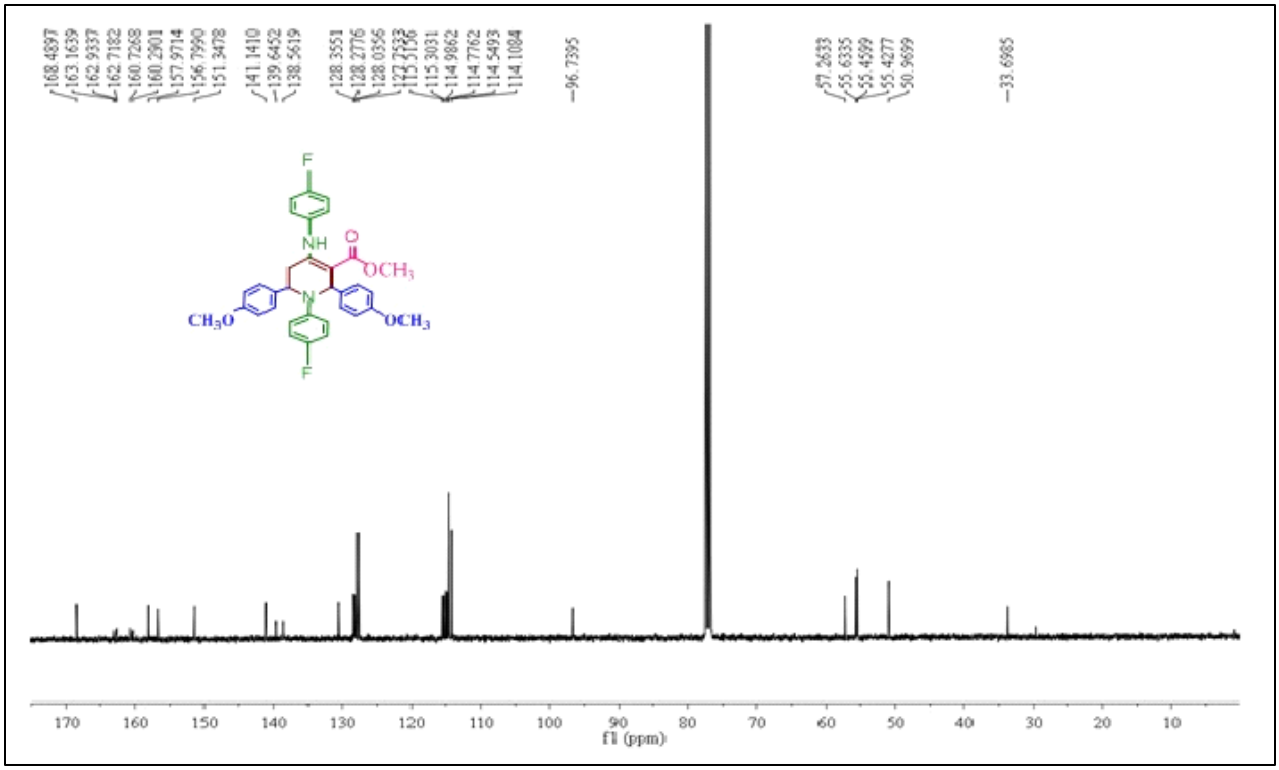


Figure S9. ^{13}C NMR spectrum of compound **4c** (100 MHz, CDCl3)

^{1}H-NMRspectrumofMethyl-1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate(4d)

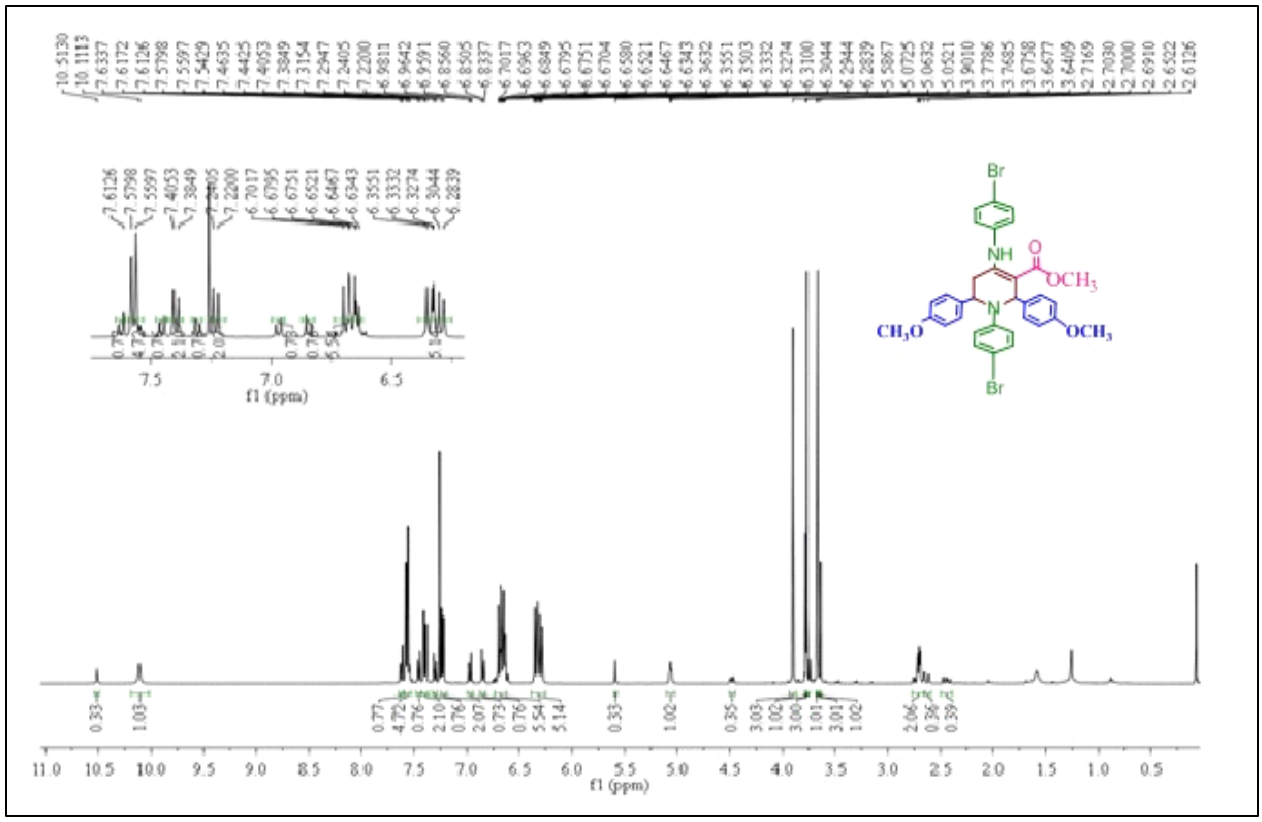


Figure S10. ^{1}H NMR spectrum of compound **4d** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-bis(4-methoxyphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate(4d)

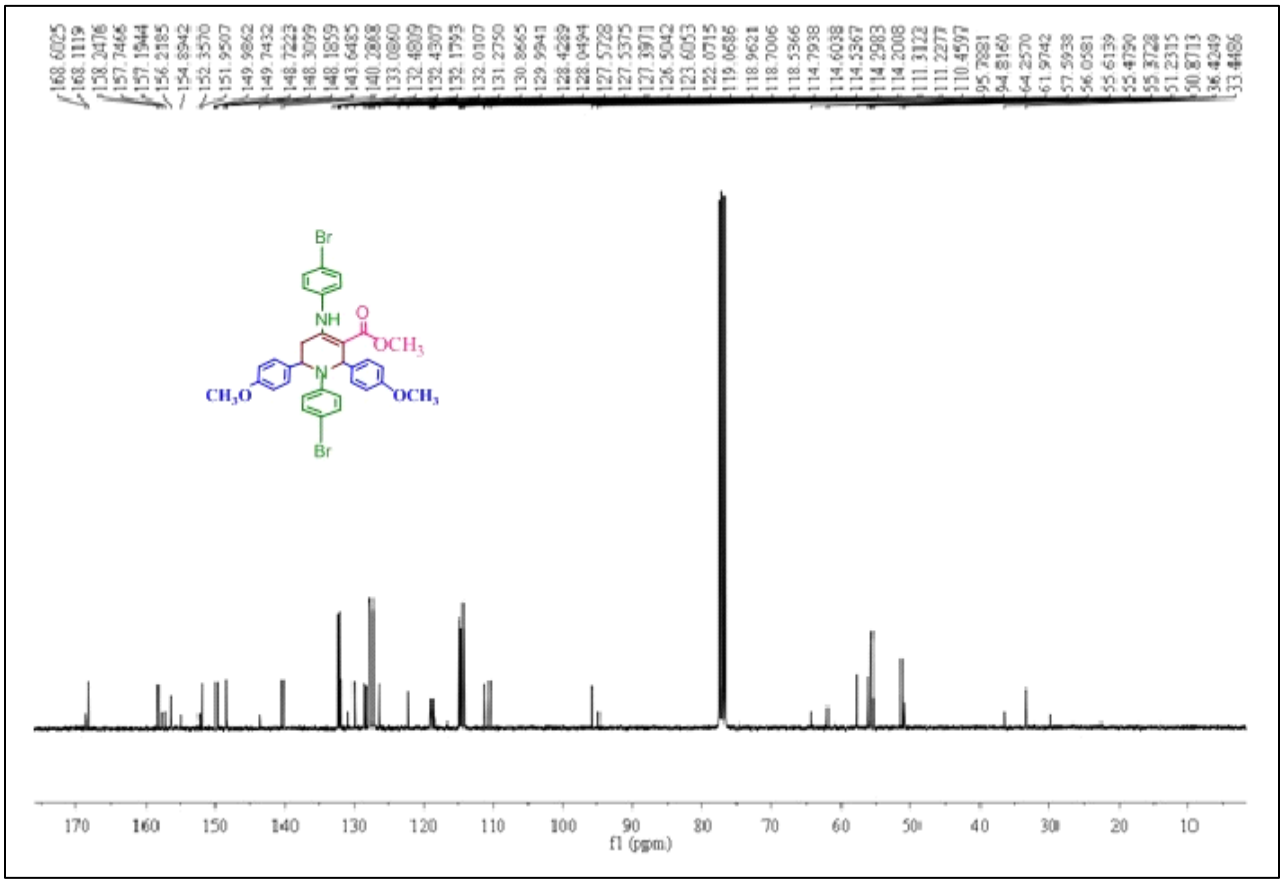


Figure S11. ^{13}C NMR spectrum of compound **4d** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4e)

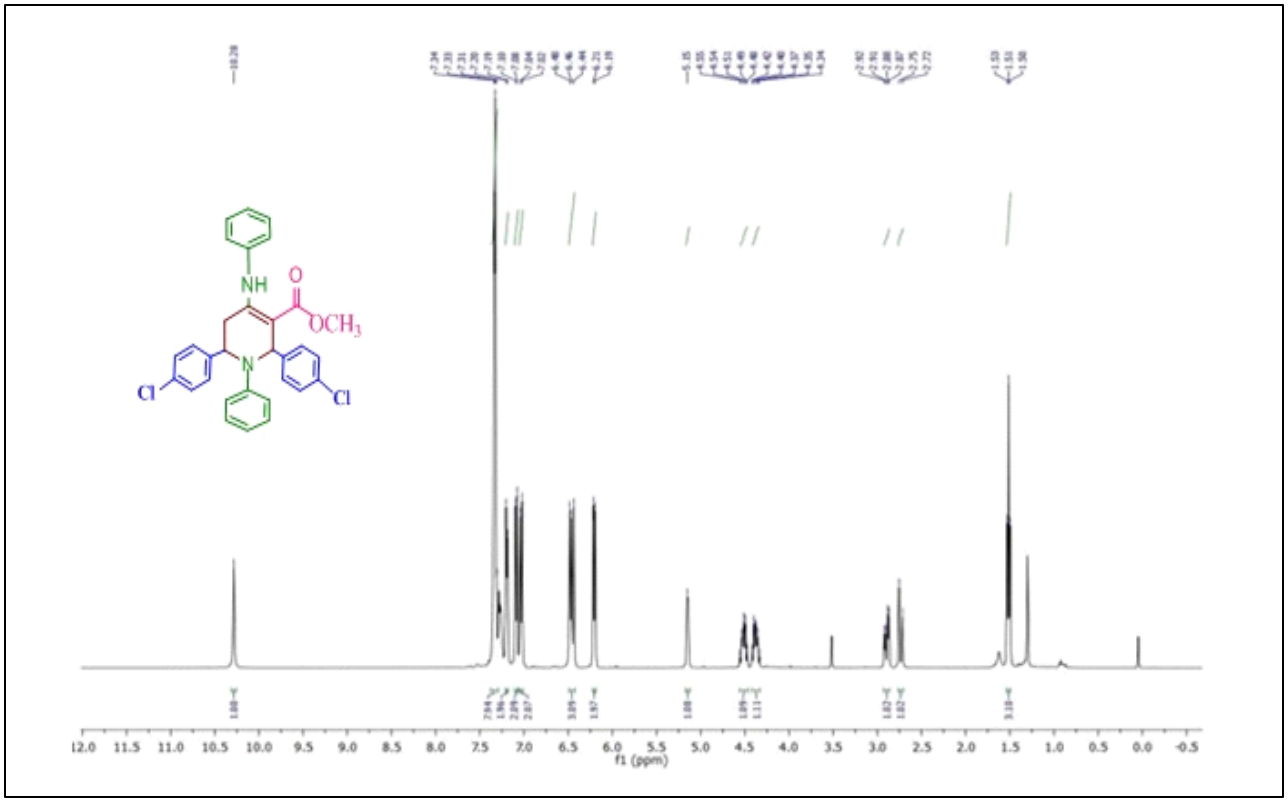


Figure S12. ^{1}H NMR spectrum of compound **4e** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4e)

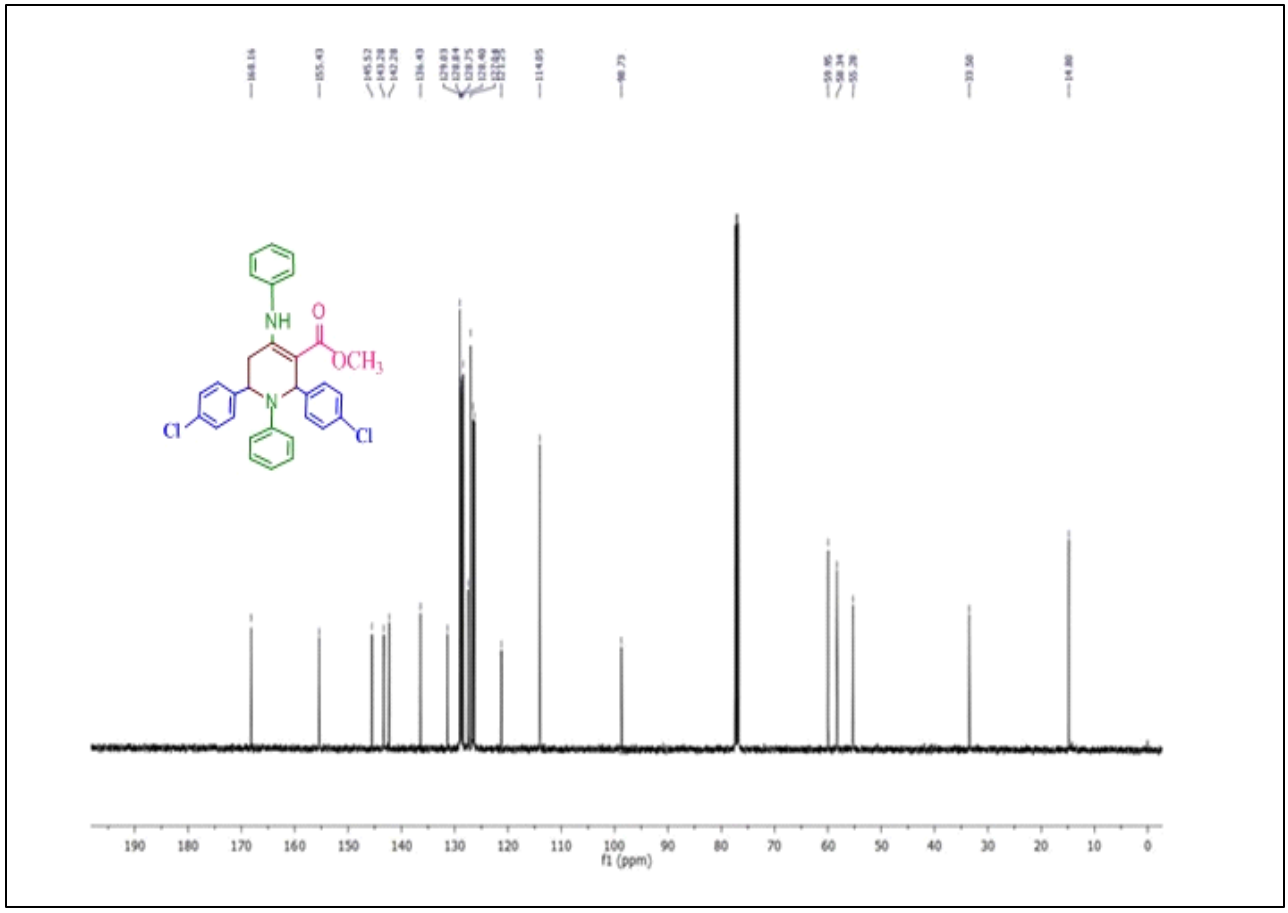


Figure S13. ^{13}C NMR spectrum of compound **4e** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4f)

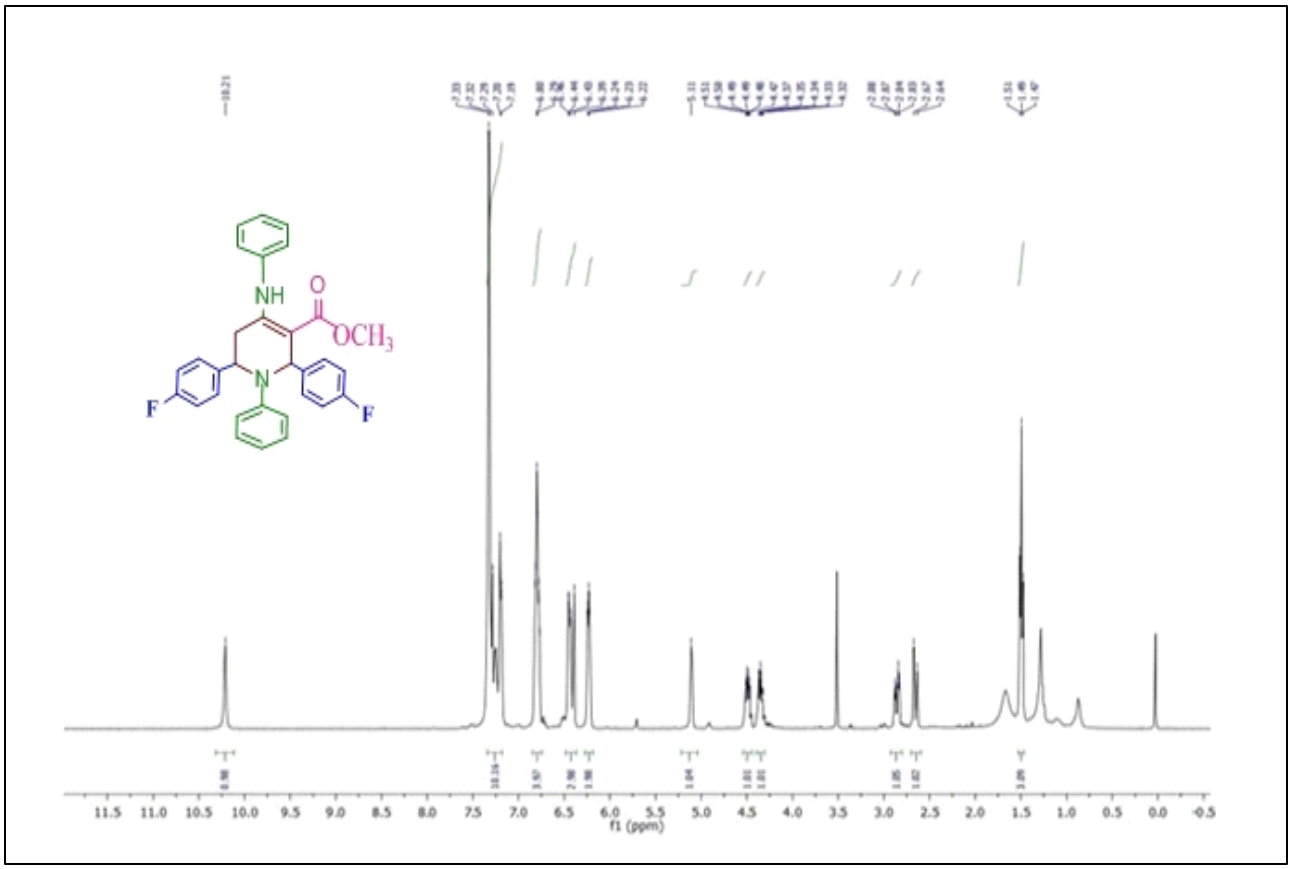


Figure S14. ^{1}H NMR spectrum of compound **4f** (100 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4f)

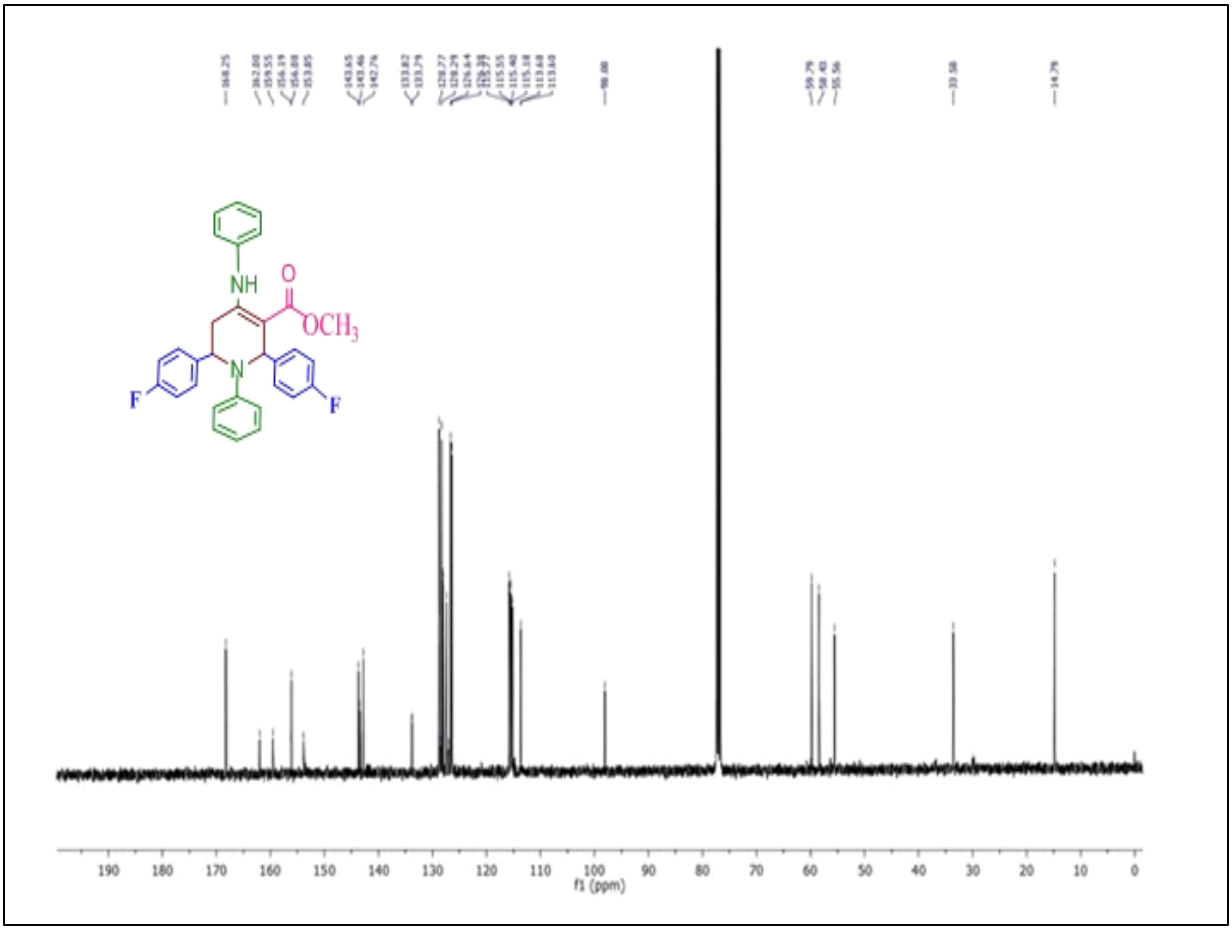


Figure S15. ^{13}C NMR spectrum of compound **4f** (100 MHz, $CDCl_3$)

[1]H-NMRspectrumofMethyl-2,6-bis(4-bromophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4g)

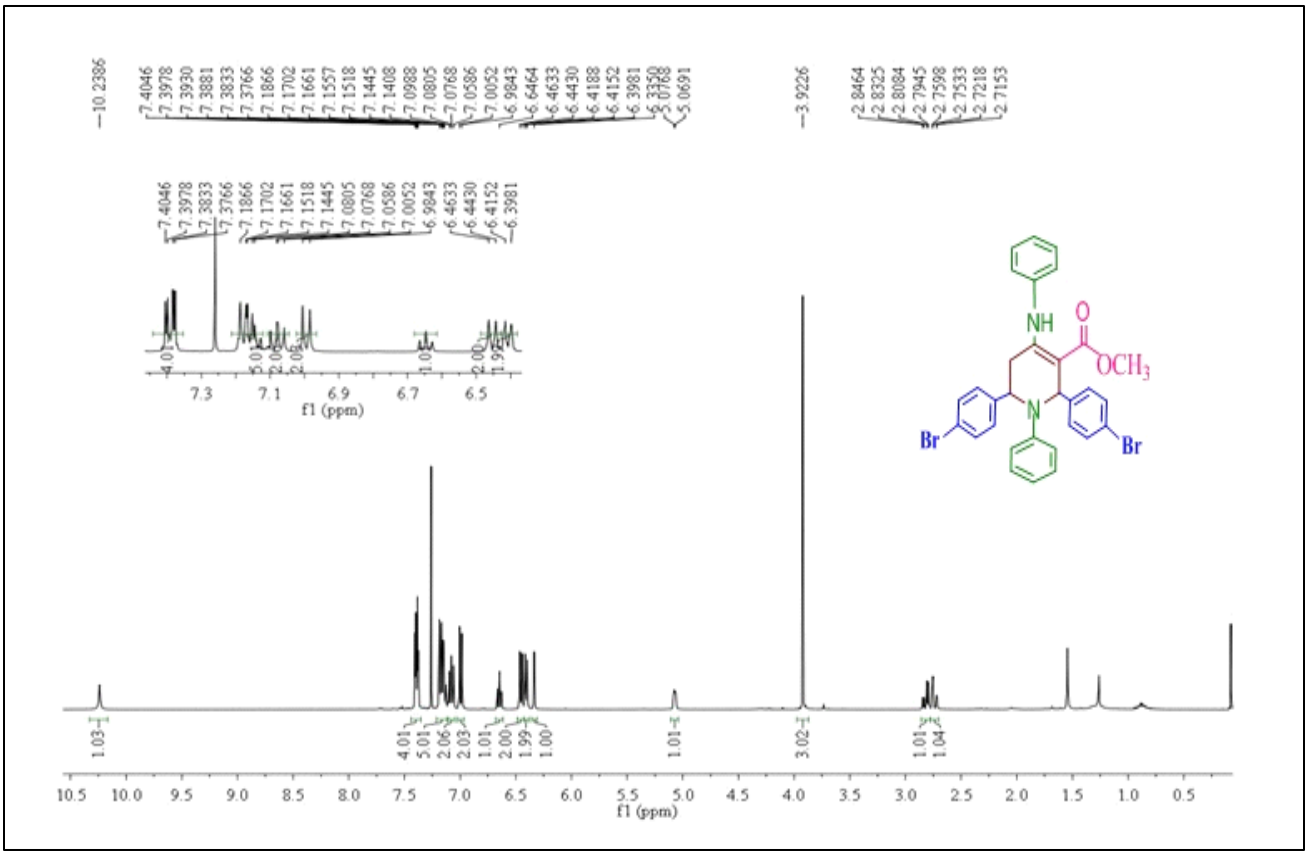


Figure S16. ^{1}H NMR spectrum of compound **4g** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-2,6-bis(4-bromophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4g)

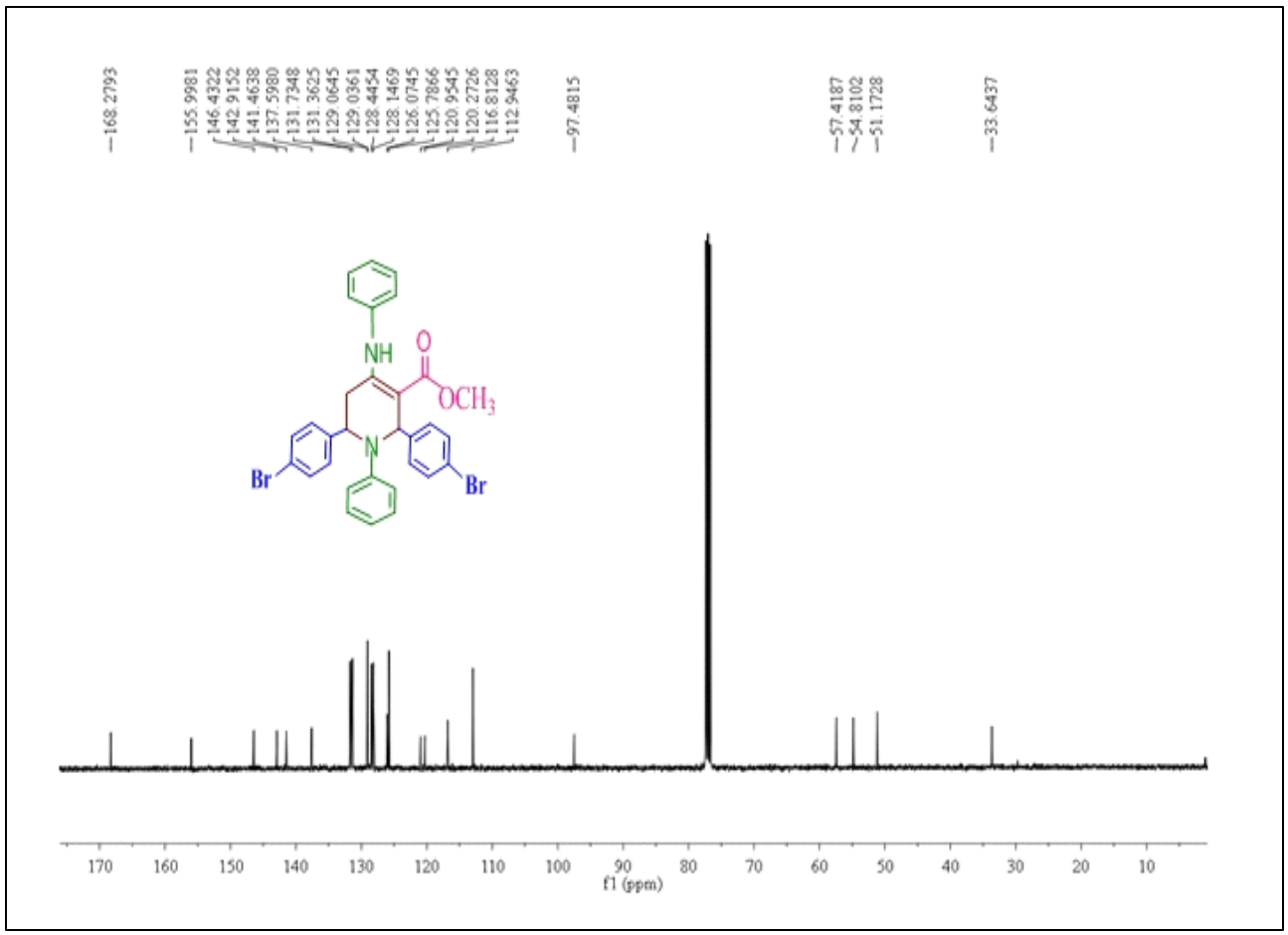


Figure S17. ^{13}C NMR spectrum of compound **4g** (100 MHz, $CDCl_3$)

[1]H-NMRspectrumofMethyl-1-(4-chlorophenyl)-4-(4-chlorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4h)

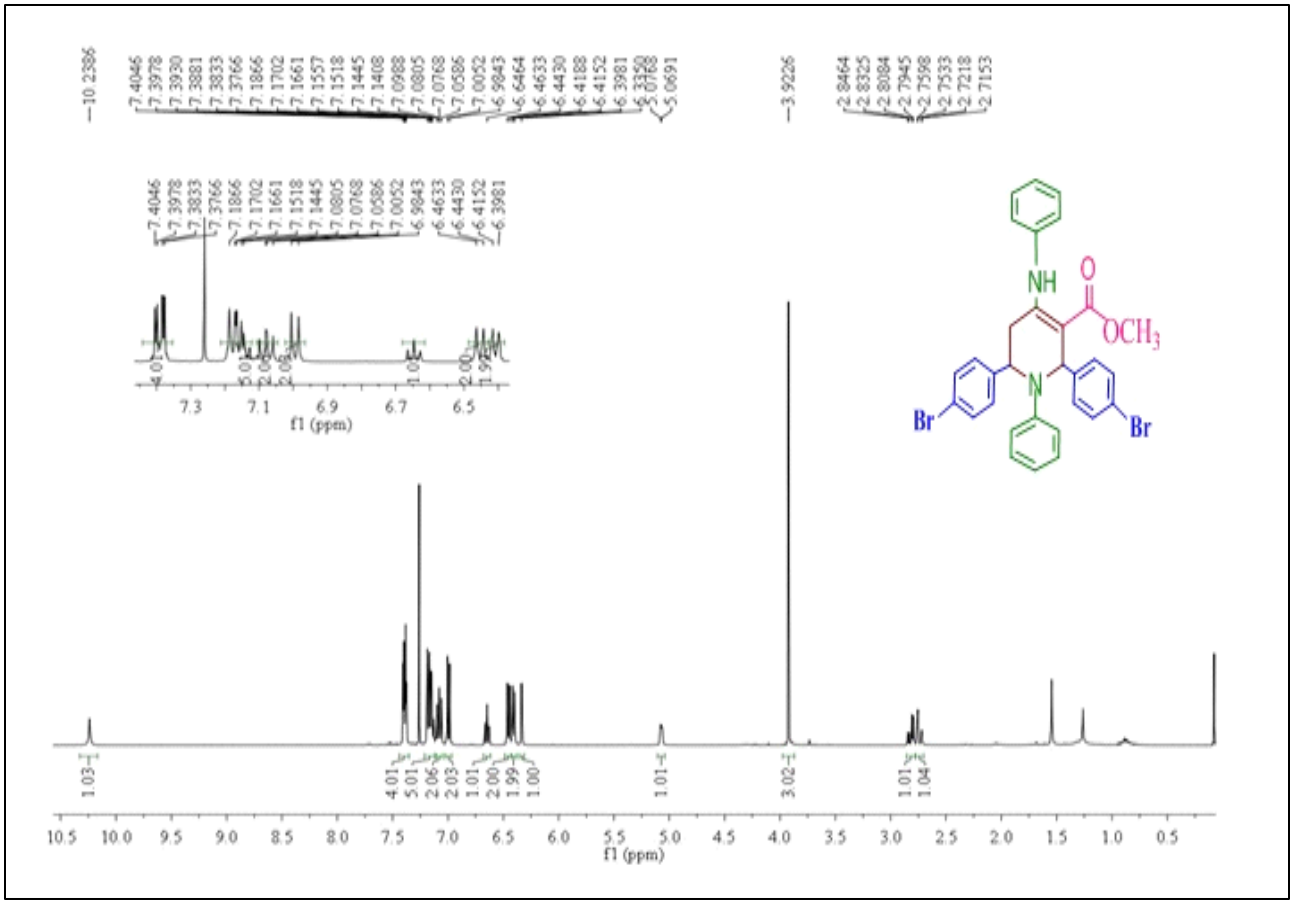


Figure S18. [1]H NMR spectrum of compound **4h** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-1-(4-chlorophenyl)-4-(4-chlorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4h)

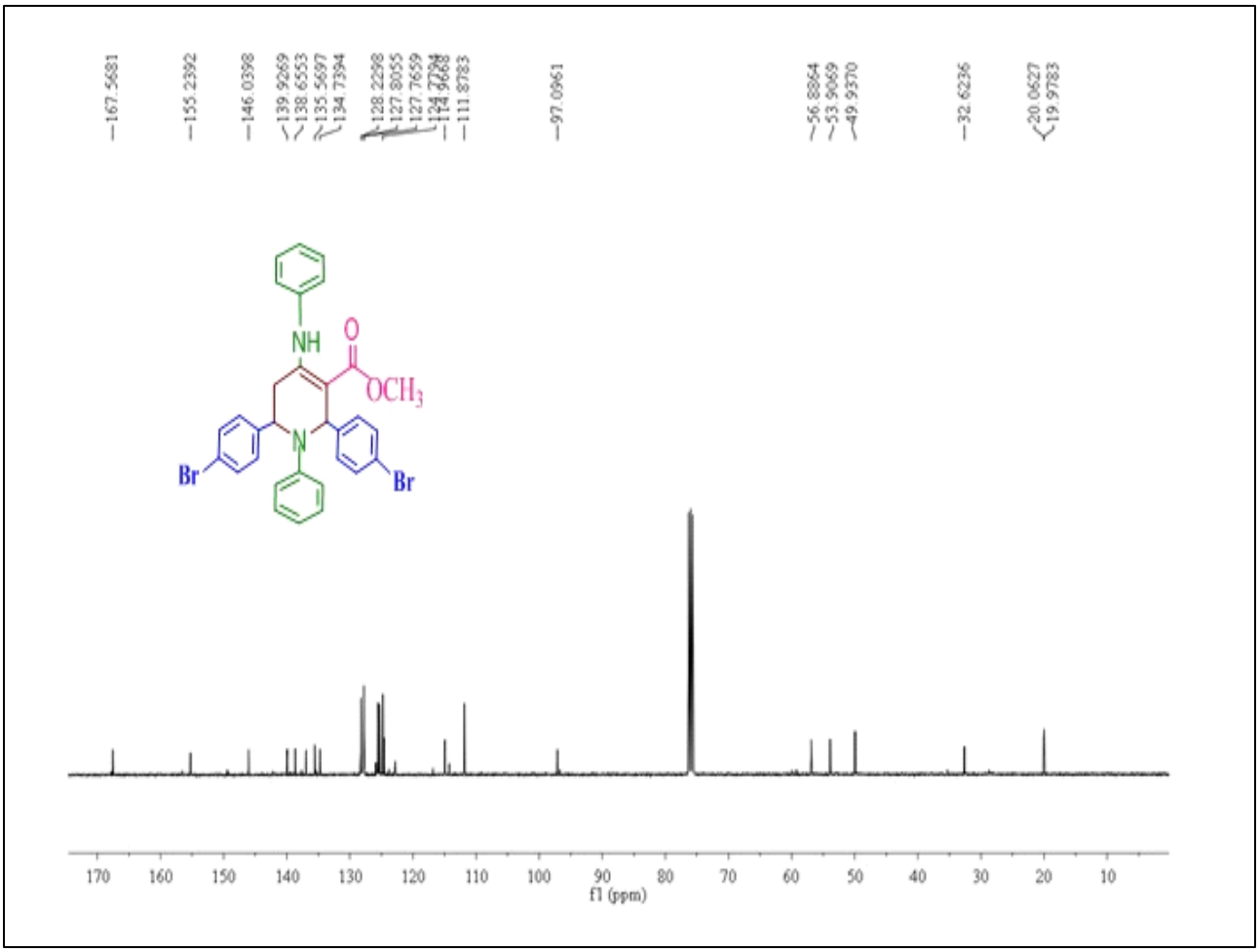


Figure S19. ^{13}C NMR spectrum of compound **4h** (100 MHz, $CDCl_3$)

[1]H-NMRspectrumofMethyl-1-(4-fluorophenyl)-4-(4-fluorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4i)

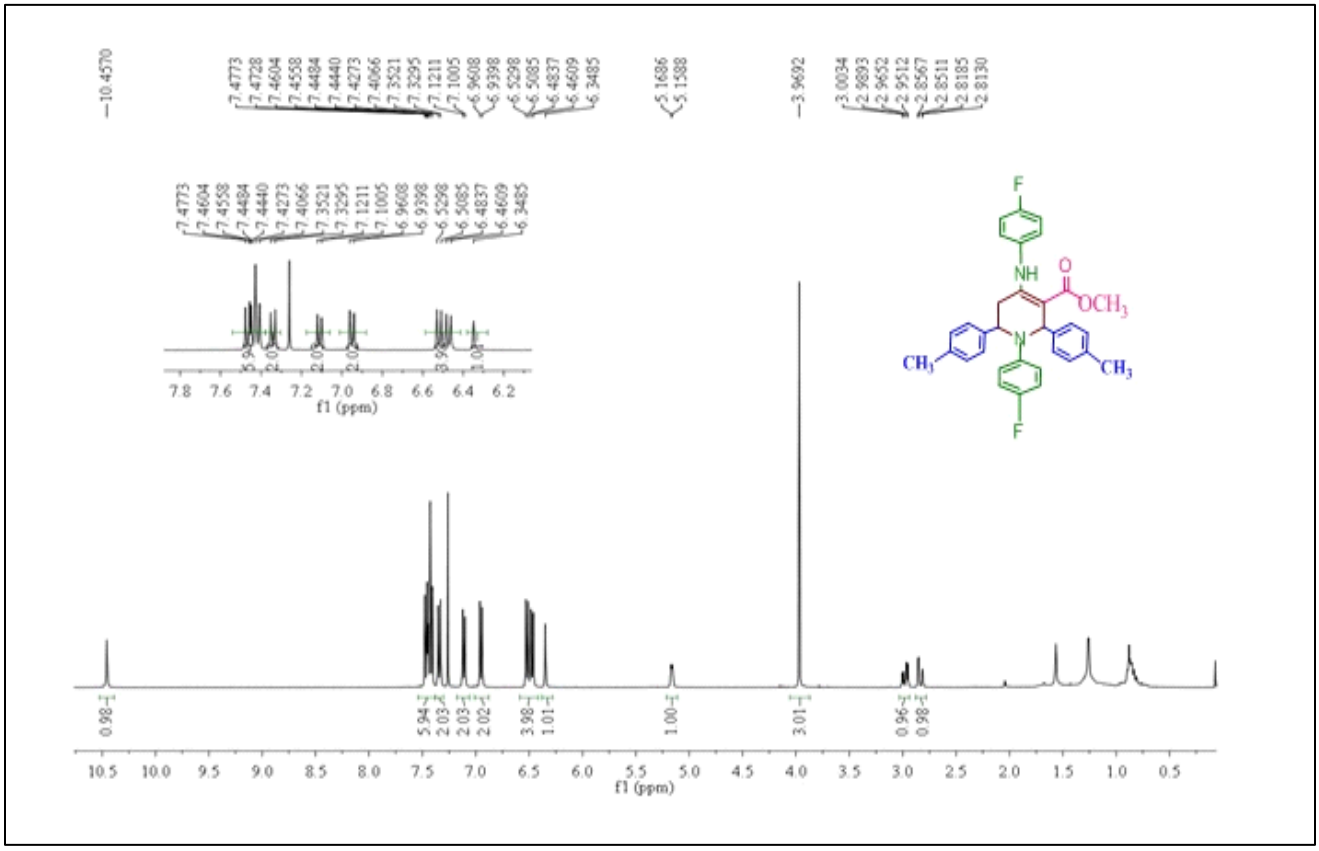


Figure S20. 1H NMR spectrum of compound **4i** (400 MHz, CDCl3)

^{13}C-NMRspectrumofMethyl-1-(4-fluorophenyl)-4-(4-fluorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4i)

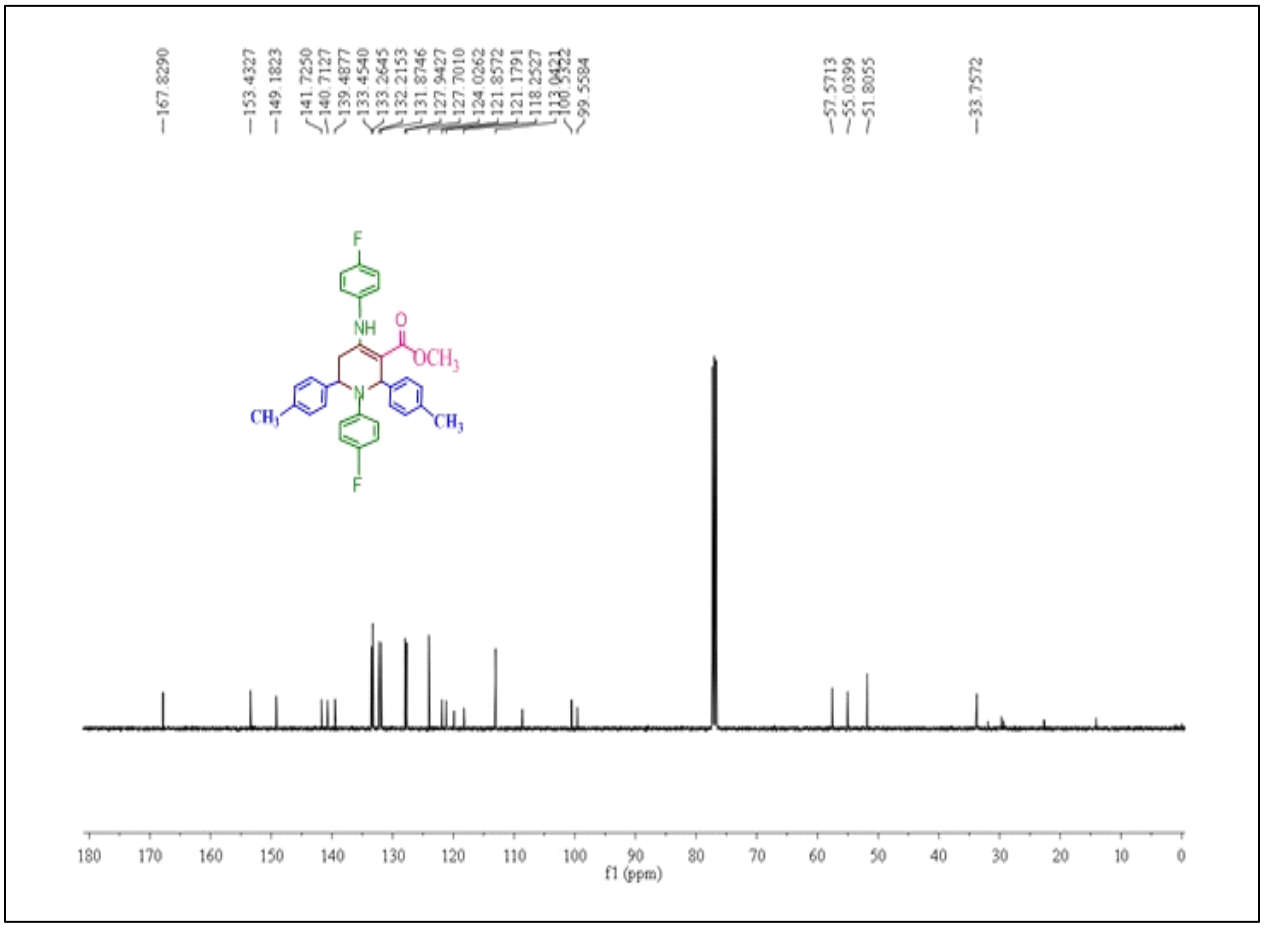


Figure S21. ^{13}C NMR spectrum of compound **4i** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-1-(4-bromophenyl)-4-(4-bromophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4j)

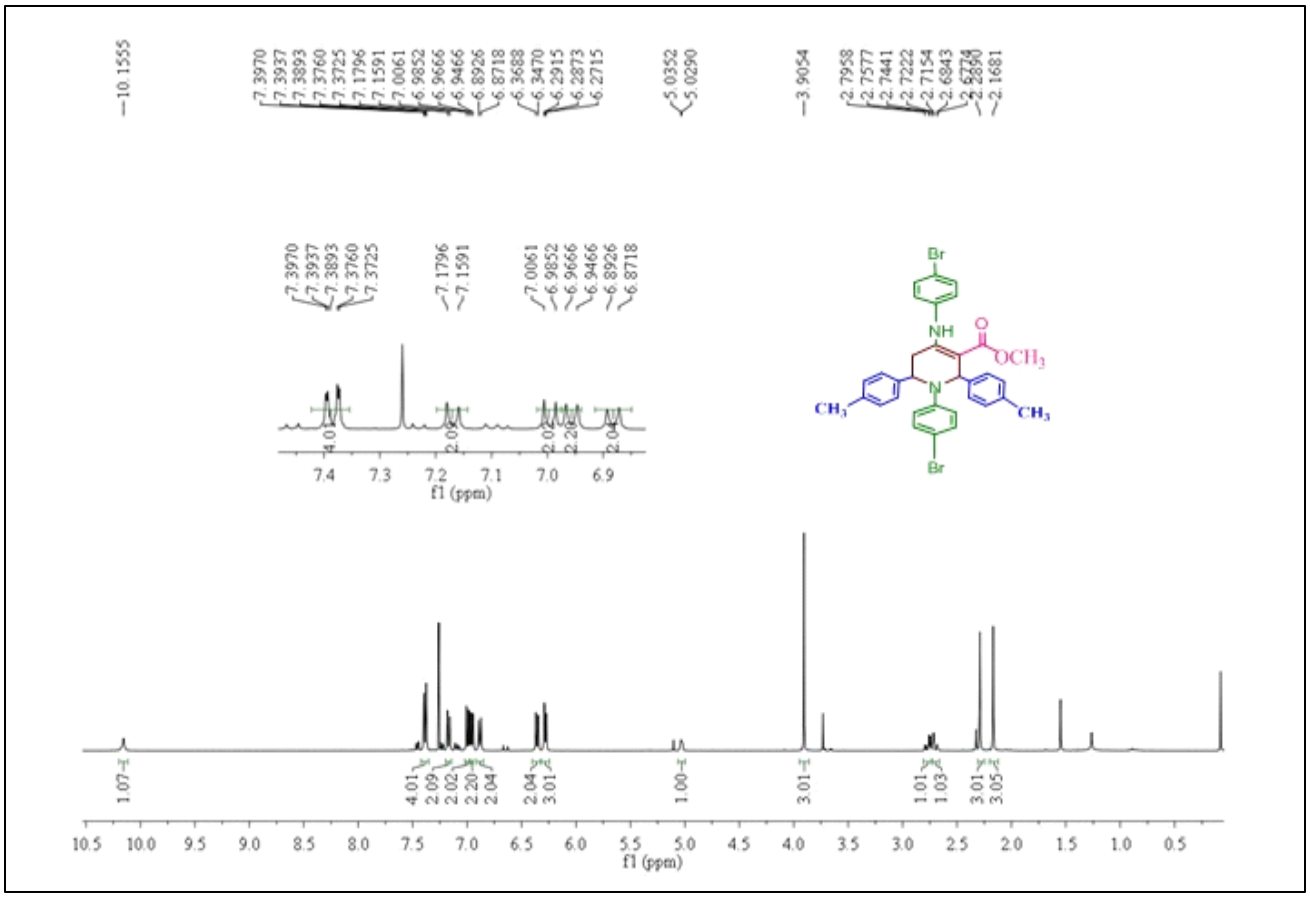


Figure S22. ^{1}H NMR spectrum of compound **4j** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-1-(4-bromophenyl)-4-(4-bromophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4j)

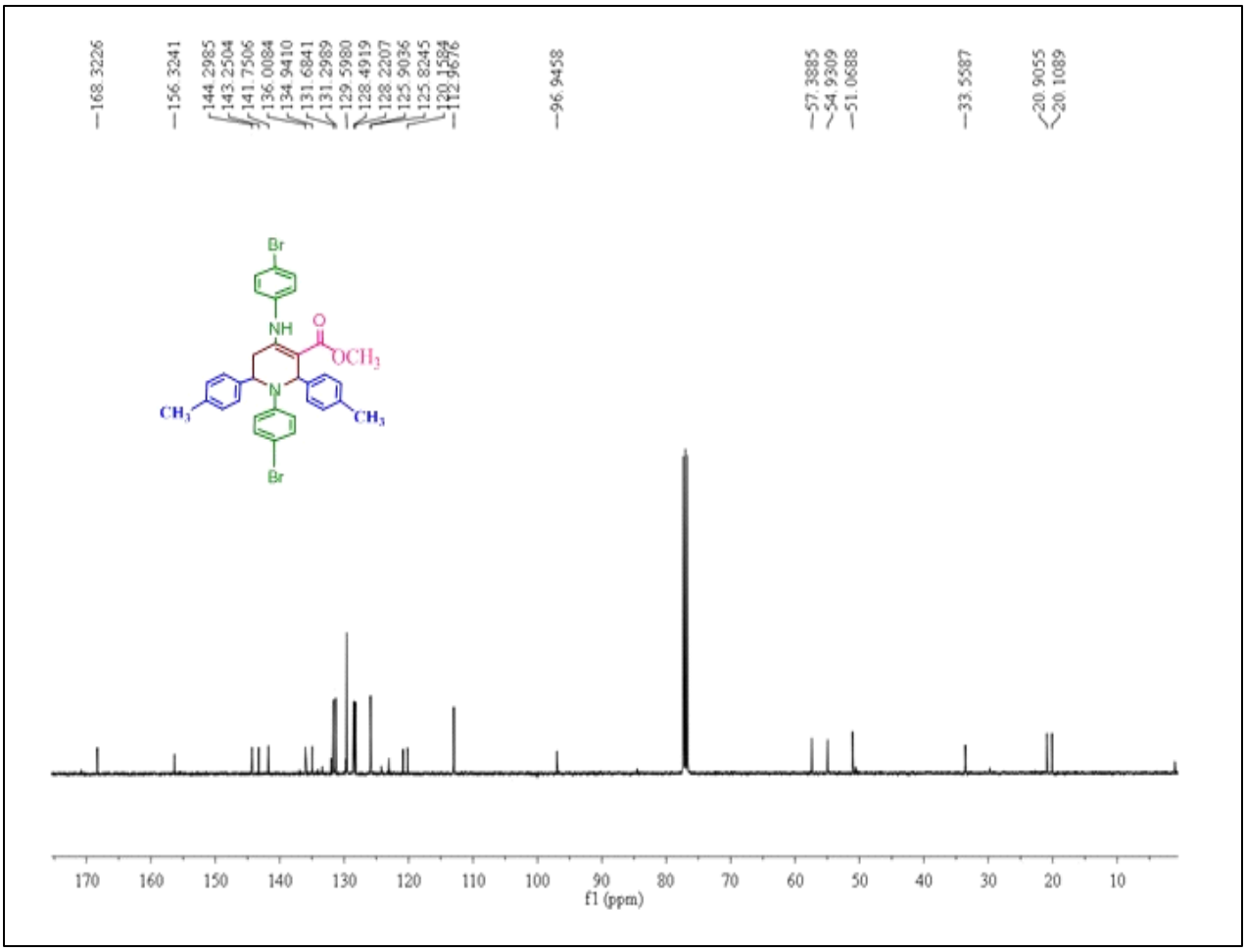


Figure S23. ^{13}C NMR spectrum of compound **4j** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-1-(4-trifluoromethylphenyl)-4-(4-trifluoromethylphenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4k)

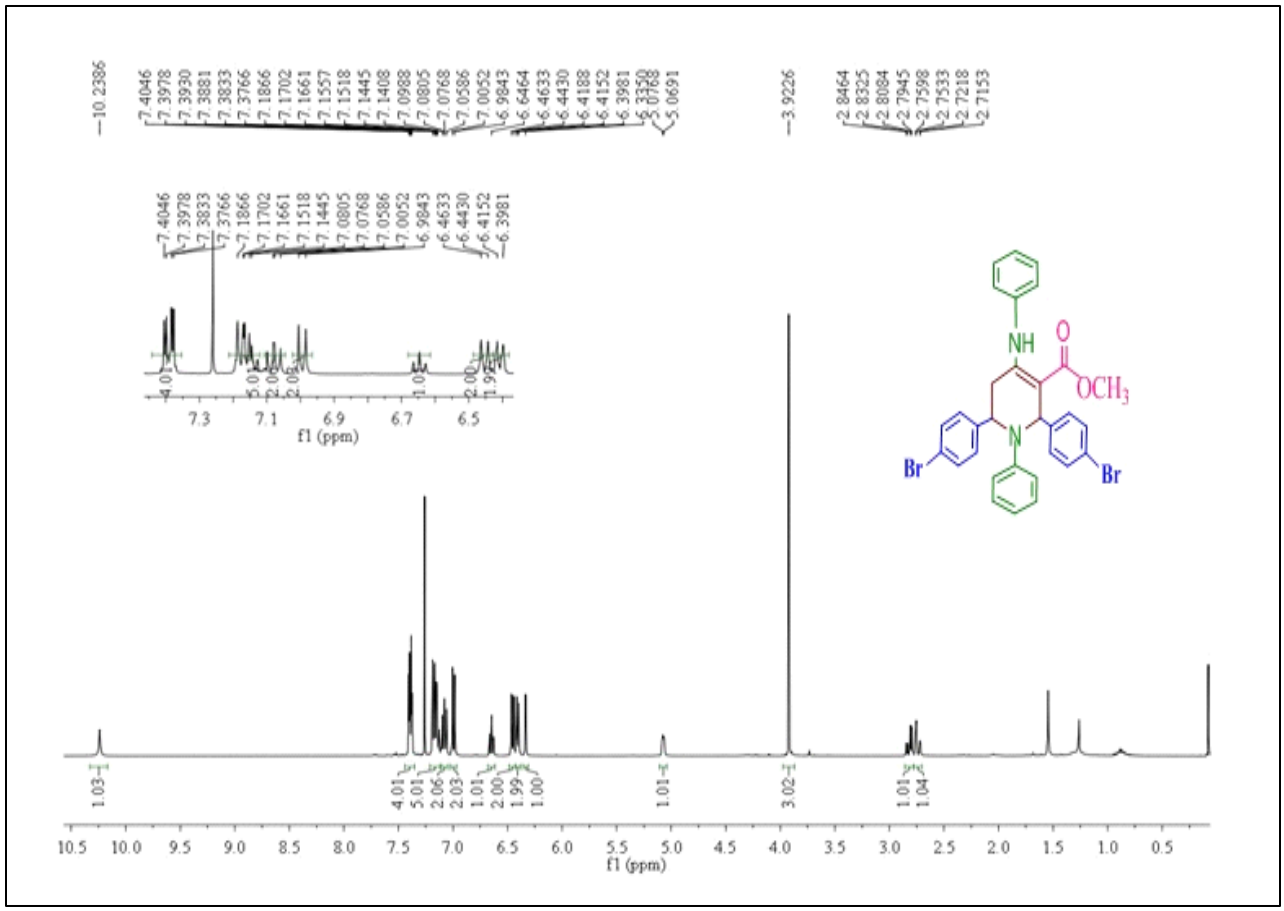


Figure S24. ^{1}H NMR spectrum of compound **4k** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-1-(4-trifluoromethylphenyl)-4-(4-trifluoromethylphenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate(4k)

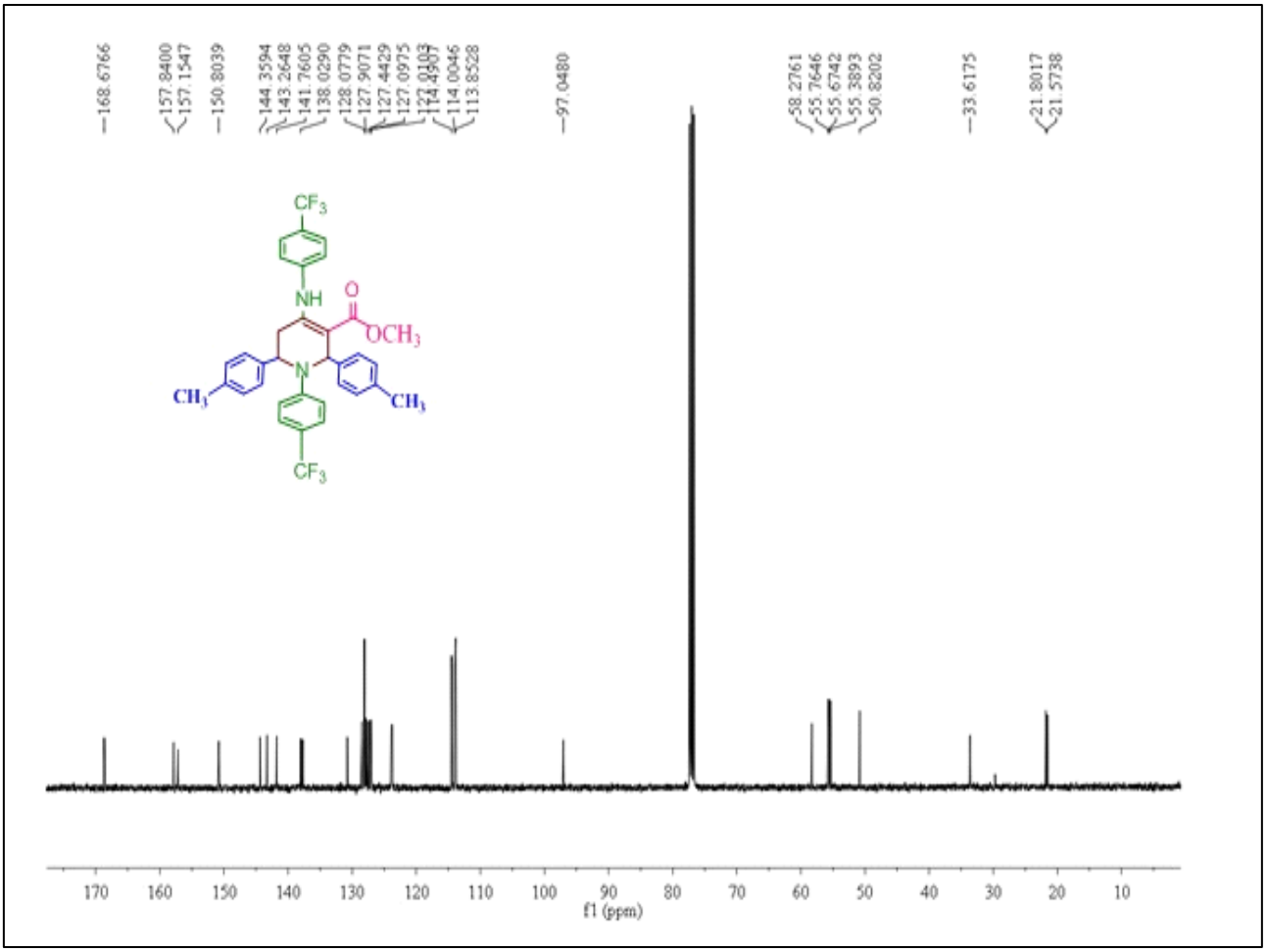


Figure S25. ^{13}C NMR spectrum of compound **4k** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-2,6-bis(phenyl)-1-thiophene-2-yl-4-(thiophene-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4l)

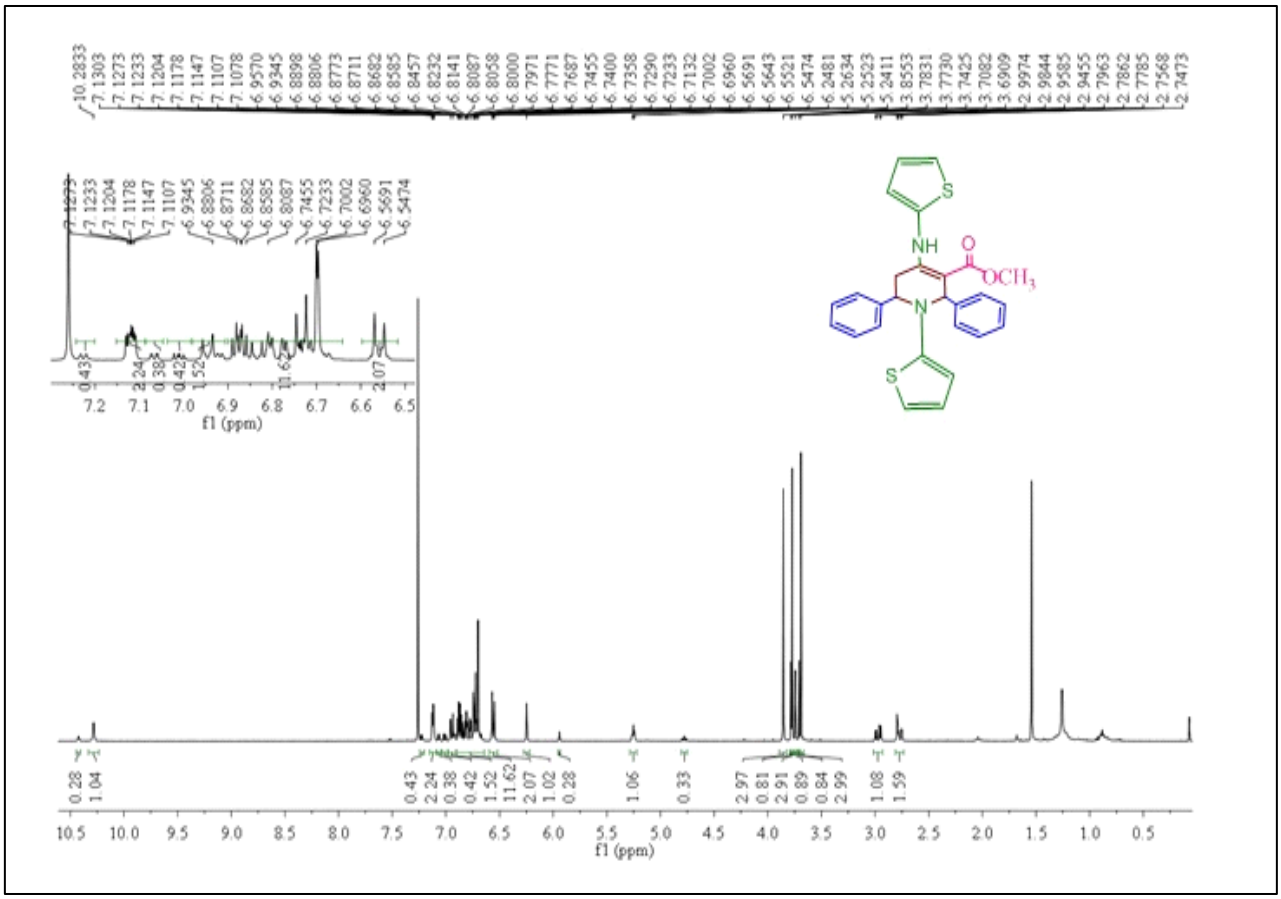


Figure S26. ^{1}H NMR spectrum of compound **4l** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-2,6-bis(phenyl)-1-thiophene-2-yl-4-(thiophene-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4l)

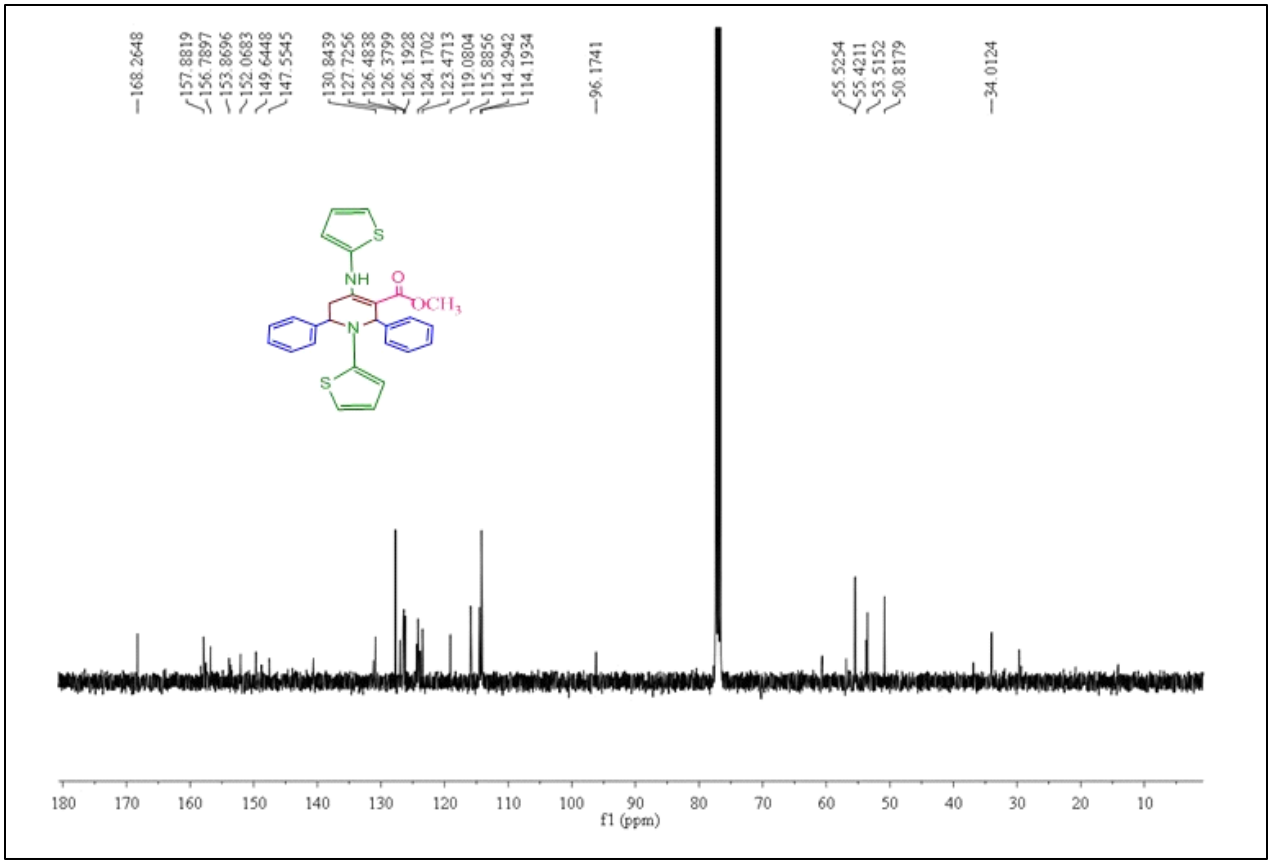


Figure S27. ^{13}C NMR spectrum of compound **4l** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-2,6-bis(phenyl)-1-thizole-2-yl-4-(thizole-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4m)

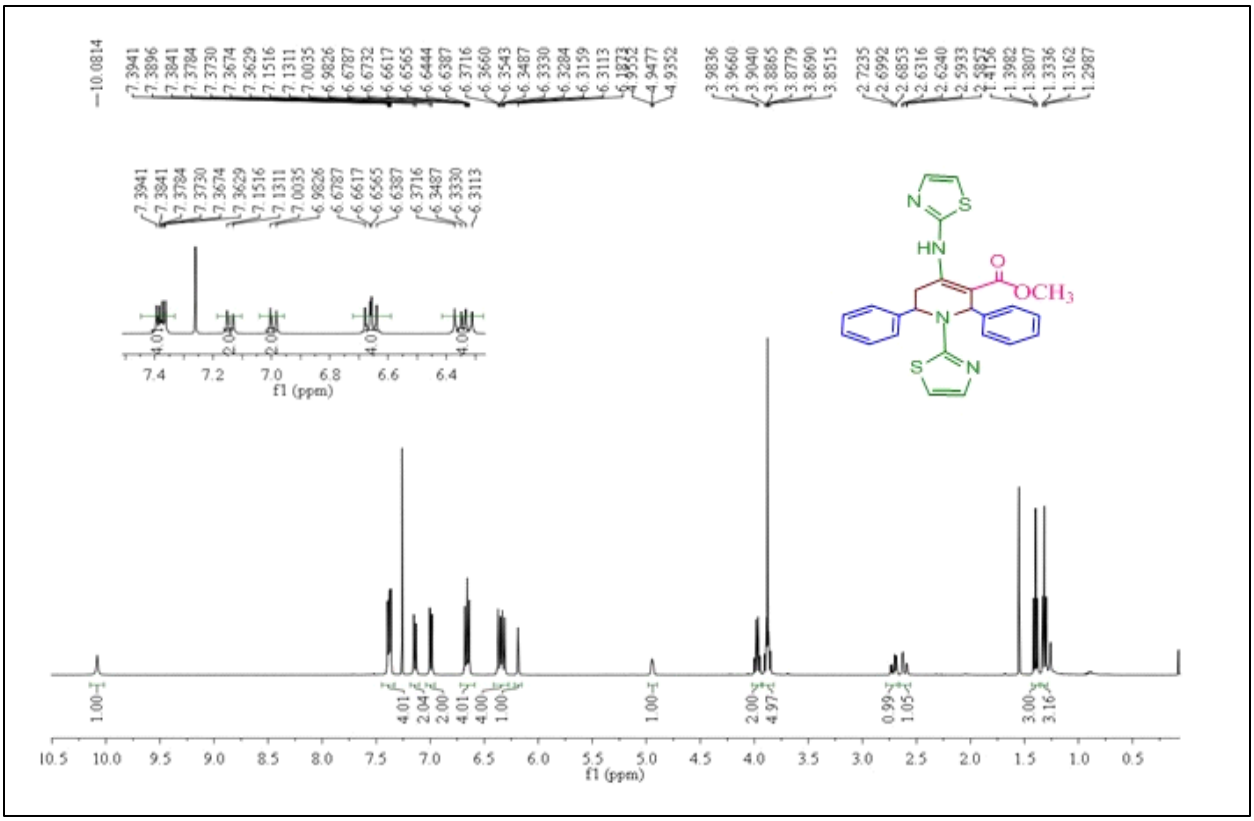


Figure S28. ^{1}H NMR spectrum of compound **4m** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-2,6-bis(phenyl)-1-thizole-2-yl-4-(thizole-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4m)

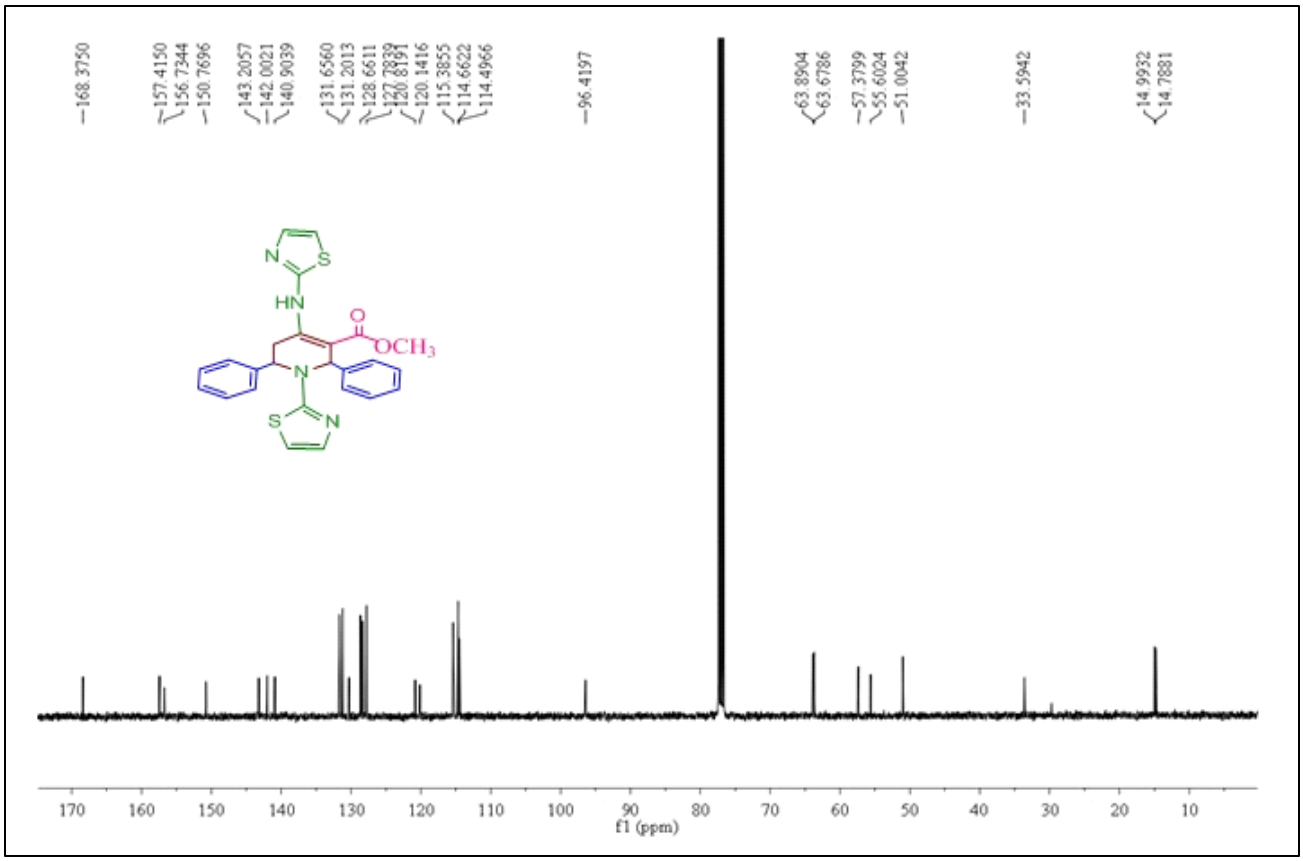


Figure S29. ^{13}C NMR spectrum of compound **4m** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-2,6-bis(phenyl)-1-pyridine-2-yl-4-(pyridine-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4n)

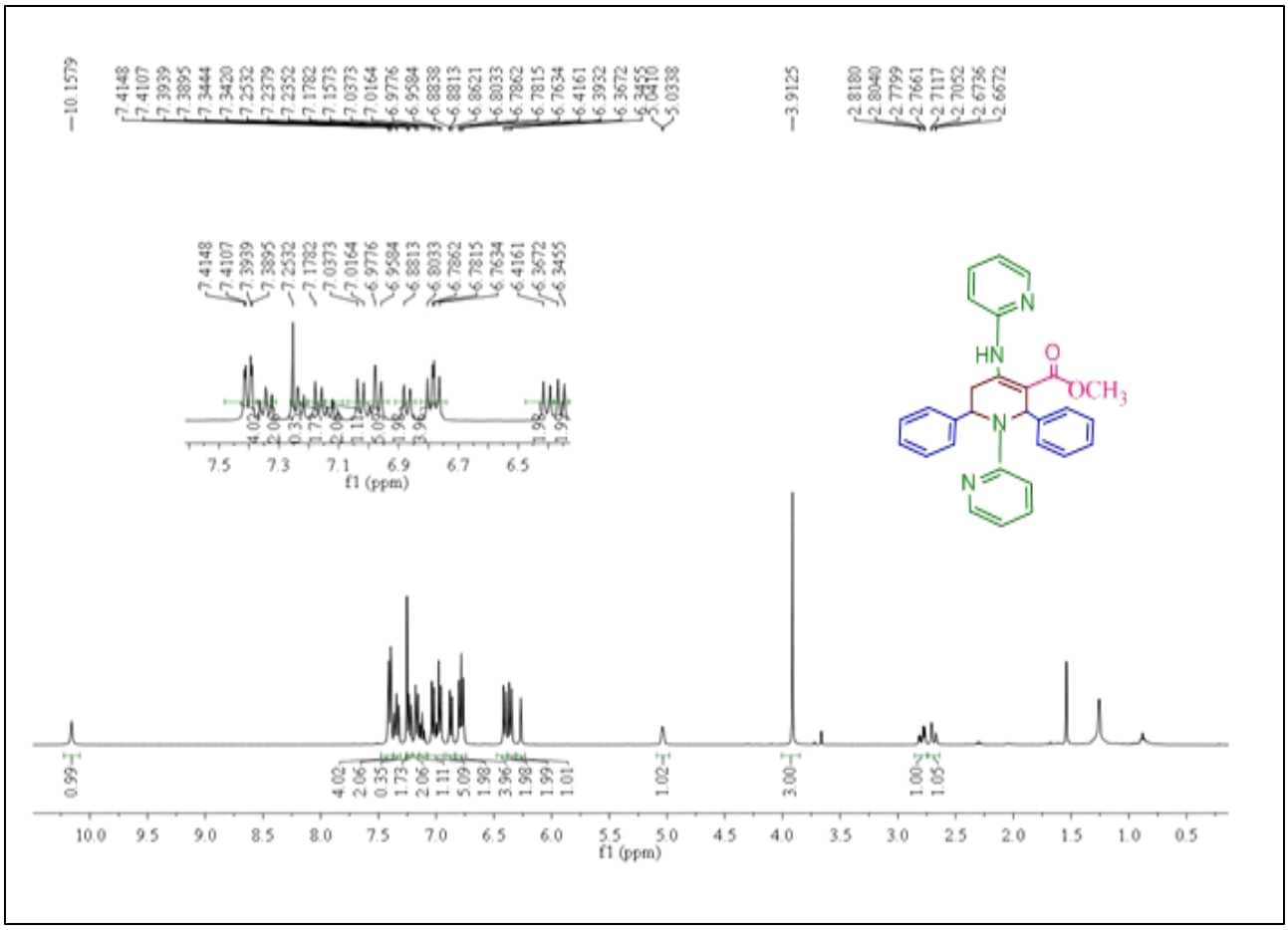


Figure S30. ^{1}H NMR spectrum of compound **4n** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-2,6-bis(phenyl)-1-pyridine-2-yl-4-(pyridine-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4n)

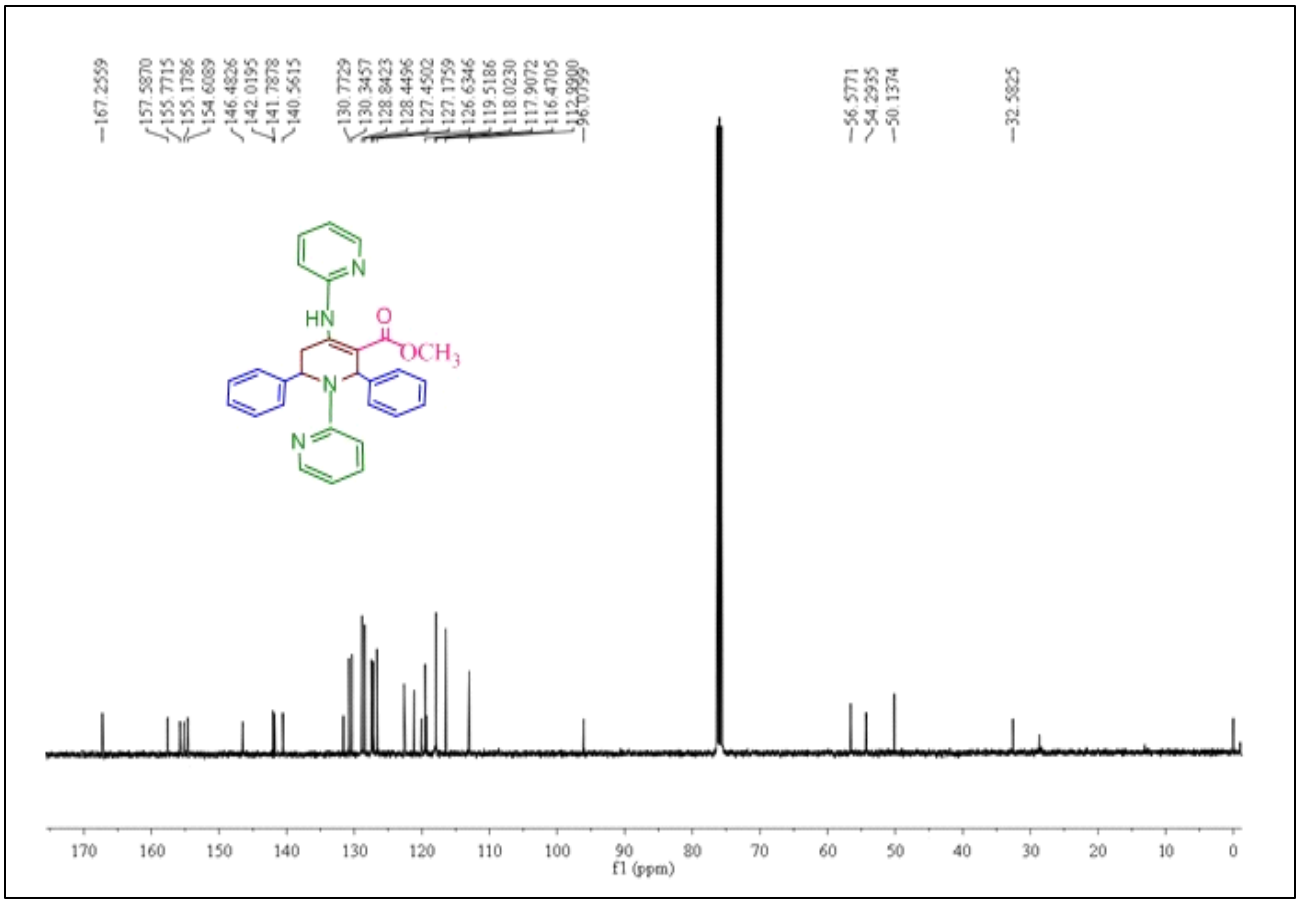


Figure S31. ^{13}C NMR spectrum of compound **4n** (100 MHz, $CDCl_3$)

^{1}H-NMRspectrumofMethyl-2,6-bis(phenyl)-1-pyran-2-yl-4-(pyran-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4o)

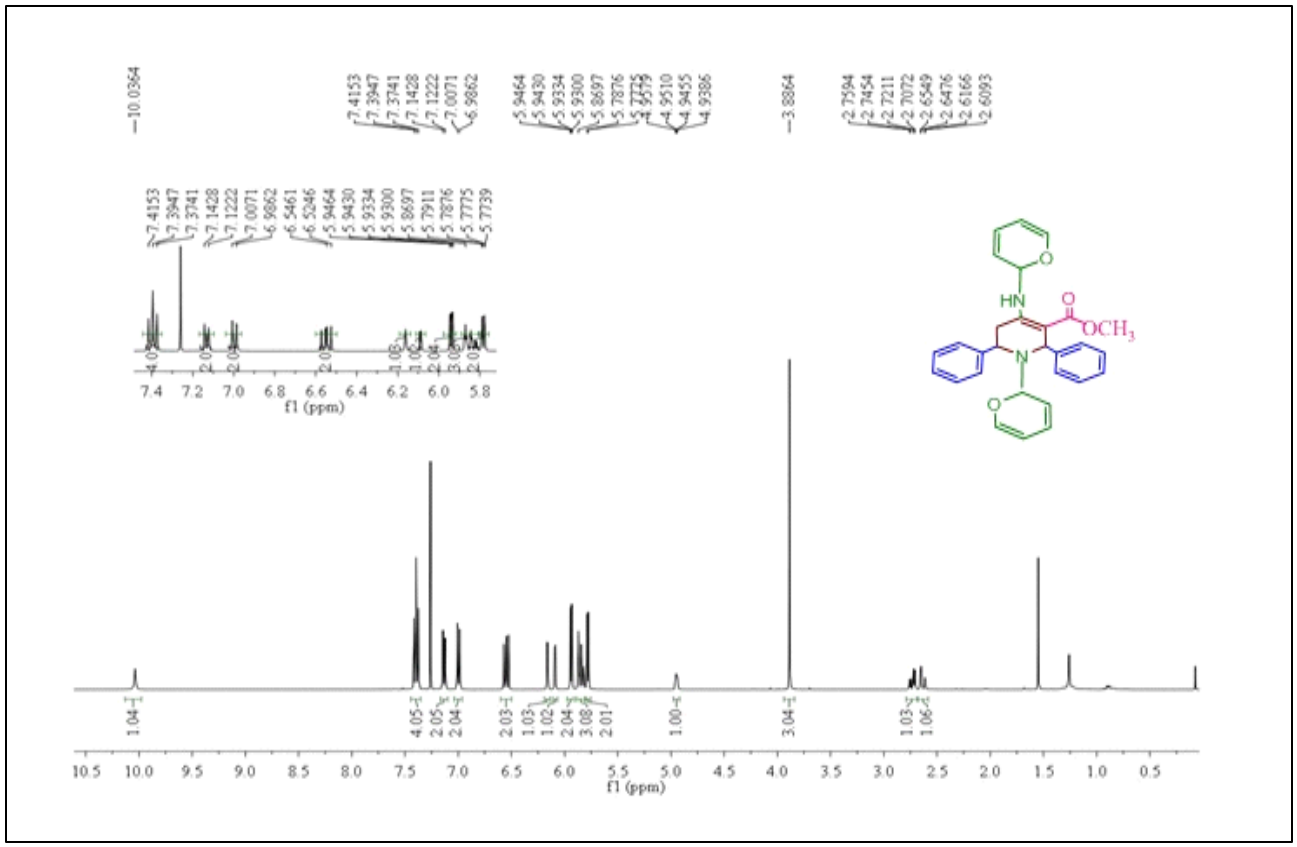


Figure S32. ^{1}H NMR spectrum of compound **4o** (400 MHz, $CDCl_3$)

^{13}C-NMRspectrumofMethyl-2,6-bis(phenyl)-1-pyran-2-yl-4-(pyran-2-yl-amino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4o)

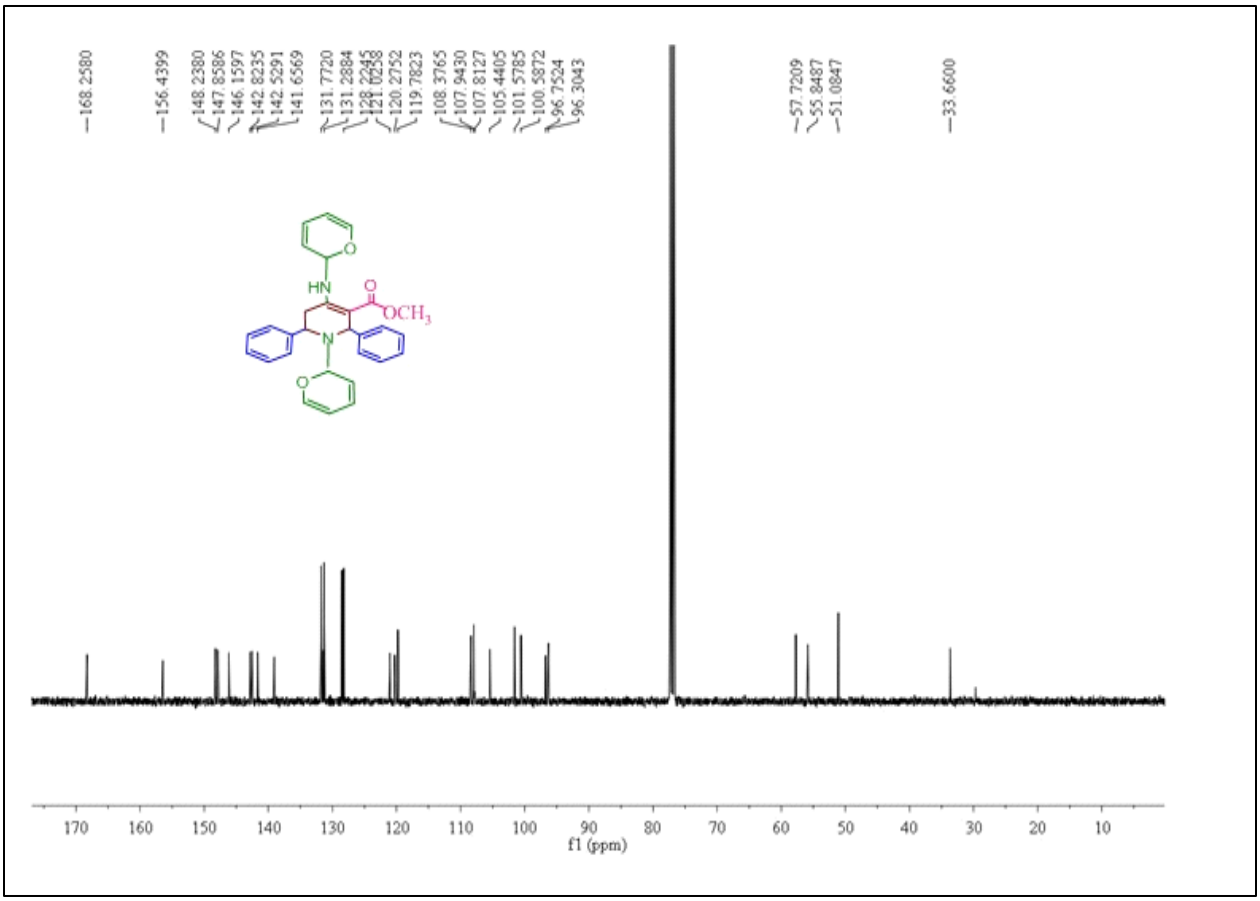


Figure S33. ^{13}C NMR spectrum of compound **4o** (100 MHz, $CDCl_3$)