Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supplementary Information

$[Ru(bpy)_3]^{2+}$ Aided Photocatalytic Synthesis of 2-Arylpyridines via Hantzsch Reaction under the Visible Irradiation and Oxygen Atmosphere

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General

All chemicals and solvents used in this study were of analytical reagent grade, and they were used without further purification. The degradation study was analyzed by absorption spectroscopic technique using a high precision double beam UV-Visible Spectrophotometer (UV-1601 SHIMADZU). Milli-Q water and acetonitrile of HPLC grade were used for the preparation of all solutions for the degradation study. The complex $[Ru(C_{10}H_8N_2)_3]Cl_2$. $6H_2O$ used in the present work was synthesized with the help of standard literature procedure[1]. All the ^1H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz respectively.

General procedure for the preparation of 1,2-dihydropyridine (dimethyl 2-(4-chlorophenyl)-1,2-dihydro-4,6-dimethylpyridine-3,5-dicarboxylate):

In a 50 ml round-bottomed flask 4-chlorobenzaldehyde (2 mmol), methyl acetoacetate (4.8 mmol) and ammonium acetate (2.4 mmol) were taken, and the mixture was stirred at room temperature under nitrogen atmosphere. The progress of the reaction was monitored by TLC. After 8 h of stirring the aldehyde was found to be consumed, and the reaction was stopped. The mixture was treated with a brine solution; the organic part was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and then filtered. The crude product was obtained after the evaporation of the filtrate by rotary evaporator. The pure yellow product-1,2-dihydropyridine (80 %) was isolated by chromatography over a silica gel column. Again, the isomeric compound of 1,2-dihydropyridine, i.e. 1,4-dihydropyridine (Dimethyl 4-(4-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate) was synthesized by the reported literature procedure.[2]

General procedure for the photooxidation of the substrate 1,2-dihydropyridine [dimethyl 2-(4-chlorophenyl)-1,2-dihydro-4,6-dimethylpyridine-3,5-dicarboxylate] under the visible light:

The photooxidation of the above 1,2-dihydropyridine was carried out in the presence of a catalytic amount of the complex $[Ru(C_{10}H_8N_2)_3]Cl_2$. $6H_2O$ in a mixed solvent system- MeCN-H_2O (2:3 ratio) under the visible irradiation. In a typical procedure, the compound 1,2 DHP (1.19×10^{-4} M), and the photocatalyst, $[Ru(C_{10}H_8N_2)_3]Cl_2 . 6H_2O$ (5 mol%), in $MeCN\text{-}H_2O$ solvent system were taken in a 30 ml of pyrex glass vessel. The reaction vessel was placed 10 cm away from the visible light source (500 W halogen lamp of Philips with light filter (15 % of aqueous solution of $NaNO_2$, which allows only the visible light of $\lambda > 400$ nm) with a water circulation by a pyrex glass jacket (inner diameter: 5 cm and outer diameter: 8 cm) to cool the lamp. The reaction mixture was saturated with molecular oxygen by oxygen bubbling (1 atm) before irradiation (30 min) and also the bubbling with oxygen was continued during the irradiation. After a regular interval of the irradiation time, a certain volume (4 ml) of the aliquot was taken from the reaction vessel and the absorption spectrum of the aliquot was recorded. It is observed that the absorbance at 356 nm was decreasing gradually with the increase of irradiation time. From the absorption spectra of the aliquots at different irradiation time, the extend of the degradation of 1,2 DHP was calculated at wavelength 356 nm. Further, the reaction mixture after complete degradation of 1,2-DHP, was made free from the catalyst, $[Ru(bpy)_3]^{2+}$, by using cation exchange resin-amberlite CG-120, 200-400 mesh. Then the solution was analyzed using LC-MS (Waters 2695 separation module with P.D.A. detector) for identifying the different photodegradation products.

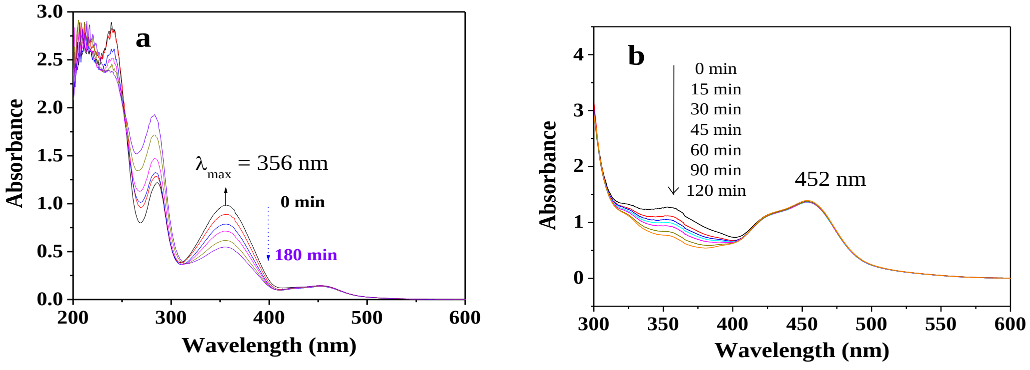


Figure S1: The change in absorption spectra during visible irradiation of the reaction mixture containing (**a**) 1,2-DHP (1.19×10^{-4} M), the photocatalyst, $[Ru(C_{10}H_8N_2)_3]Cl_2 . 6H_2O$ (5 mol%) in $MeCN\text{-}H_2O$ (2:3) solvent system, (**b**) 1,2-DHP (1.0×10^{-4} M), stoichiometric amount of the photocatalyst, $[Ru(C_{10}H_8N_2)_3]Cl_2 . 6H_2O$ (1.0×10^{-4} M) in $DMSO\text{-}H_2O$ (1:4) solvent system.

Effect of Fe^{2+} ions on the photooxidation of 1,2-DHP and 1,4-DHP:

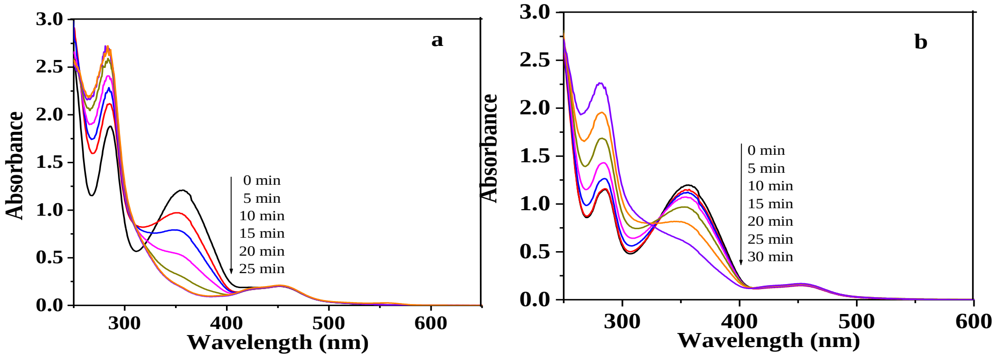


Figure S2: The change in absorption spectra during visible irradiation of the reaction mixture containing (a) 1,2-DHP (**A**) (1.19 × 10^{-4} M), the photocatalyst, $[Ru(C_{10}H_8N_2)_3]Cl_2$. $6H_2O$ (10 mol%) and Fe^{2+} ions (1.66 × 10^{-4} M) in MeCN-H_2O (2:3) solvent system. (b) 1,4-DHP (**A**) (1.19 × 10^{-4} M), the photocatalyst, $[Ru(C_{10}H_8N_2)_3]Cl_2$. $6H_2O$ (10 mol%) and Fe^{2+} ions (1.66 × 10^{-4} M) in MeCN-H_2O (2:3) solvent system.

Detection of total number of products after complete consumption of the substrate 1,2-DHP namely, dimethyl 2-(4-chlorophenyl)-1,2-dihydro-4,6-dimethylpyridine-3,5-dicarboxylate with corresponding mass by LC-MS study:

After complete consumption of the 1,2-dihydropyridine, the reaction solution was made free from the catalyst, $[Ru(bpy)_3]^{2+}$, by using cation exchange resin-amberlite CG-120, 200-400 mesh. Then the solution was subjected for the detection of the degradation products by the LC-MS study (Waters 2695 separation module with P.D.A. detector).

There are five products detected by the LC when the substrate 1,2-DHP was subjected for photooxidation with 10 mol% $[Ru(bpy)_3]^{2+}$, and molecular oxygen. One of the products identified is the corresponding 2-arylpyridine, i.e. Dimethyl 2-(4-chlorophenyl)-4,6-dimethylpyridine-3,5-dicarboxylate (retention time 9.54 min and m/z value 334.11 $[M+H]^+$).

But, only one product (retention time 9.62 min and m/z value 334.11 $[M+H]^+$) was detected by the LC, when the substrate 1,2-DHP was subjected for photooxidation in the presence of 20 mol% $[Ru(bpy)_3]^{2+}$, and molecular oxygen.

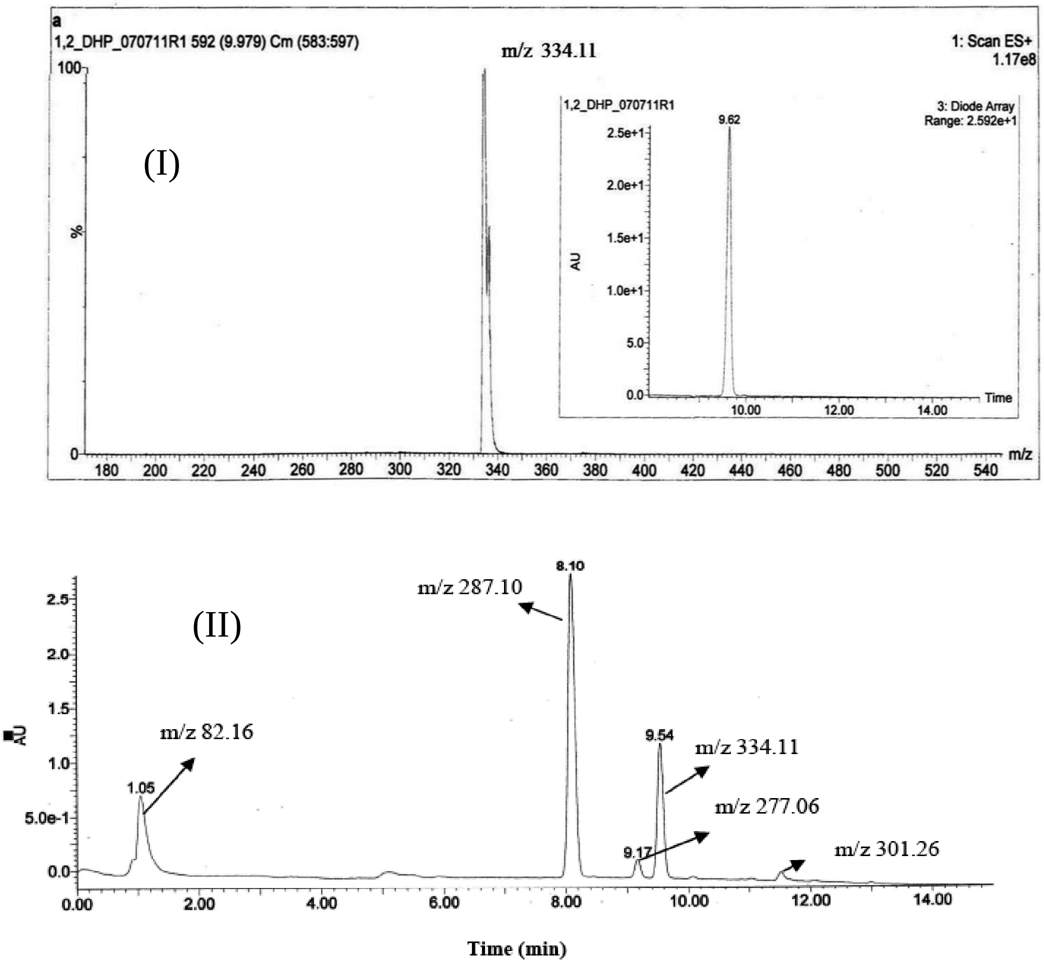
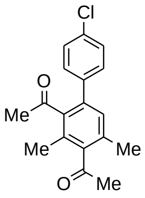
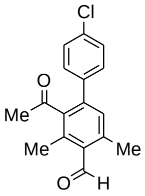
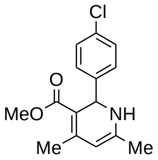
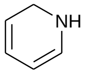


Figure S4: The oxidation products (retention time and m/z value) of 1,2-dihydropyridine detected by LC-MS after photodegradation **(I)** in the presence of 20 mol% $[Ru(bpy)_3]^{2+}$, and molecular oxygen and (**II**) in the presence of 10 mol% $[Ru(bpy)_3]^{2+}$, molecular oxygen and Fe^{2+} ions.

Table S1. Hypothetical structures with mass values of the products detected by LC-MS

Entry	Hypothetical Structure	Exact Mass (M/Z)	Observed Mass
1		301.0870	301.26
2		287.0713	287.10
3		277.0870	277.06
4		81.0578	82.16

Detection of superoxide radical anion by benzoquinone used as the scavenger:

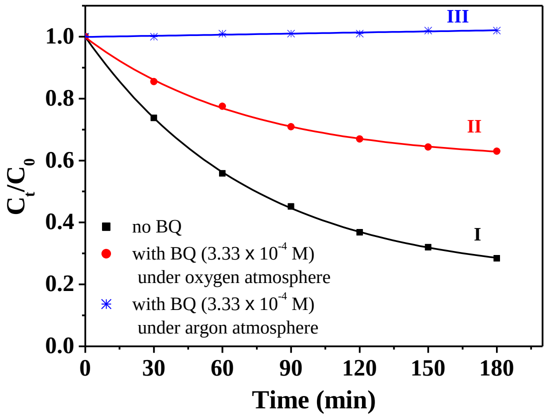
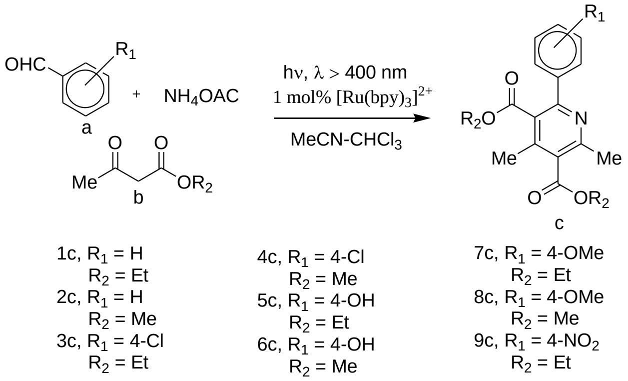


Figure S3: Plot of C_t/C_0 *versus* irradiation time during visible irradiation of the reaction mixture containing 1,2-DHP-**A** (1.19×10^{-4} M), the photocatalyst, $[Ru(C_{10}H_8N_2)_3]Cl_2$. $6H_2O$ (10 mol%) in MeCN-DMSO (2:3) solvent system (I) in the absence of superoxide radical anion quencher-benzoquinone and (II) in the presence of superoxide radical anion quencher-benzoquinone (3.33×10^{-4} M).

General procedure for the photocatalytic synthesis of 2-arylpyridine under the visible irradiation:



In the present study, 2-arylpyridine was synthesized photocatalytically in the presence of a catalytic amount of the complex $[Ru(C_{10}H_8N_2)_3]Cl_2$. $6H_2O$ under the visible irradiation taking aldehyde, β-kitoester and ammonium acetate in one pot. In a typical experimental procedure, aldehyde (1 mmol), ethyl/methyl acetoacetate (2.4 mmol) and ammonium acetate (1.2 mmol) were taken in a 50 ml pyrex glass vessel. The reaction mixture was stirred for 8 h in the dark at room temperature under nitrogen atmosphere. The reaction mixture turned into yellow colour, which indicates the formation of 1,2-dihydropyridine. The organic part was extracted with dichloromethane and the solvent was evaporated by rotary evaporator. Now, the photocatalyst (1 mol%, 0.01 mmol) and 20 ml of acetonitrile was added to the reaction mixture [mixed solvent, MeCN-$CHCl_3$ (2:1) was used for the Hantzsch reaction under inert condition]. The reaction mixture was irradiated under the visible light and oxygen atmosphere. The progress of the reaction was monitored by TLC. After 4-6 h of irradiation the yellow colored compound was found to be consumed. Then the irradiation was stopped. The organic solvent was evaporated by rotary evaporator. The crude thus obtained was treated with a brine solution; the organic part was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and then filtered. The crude product was obtained after the evaporation of the filtrate by rotary evaporator. The pure product of moderate to good yield was isolated by chromatography over a silica gel column.

General procedure for the photoaromatization of 1,2-dihydropyridine (dimethyl 2-(4-chlorophenyl)-1,2-dihydro-4,6-dimethylpyridine-3,5-dicarboxylate) under the visible irradiation:

The photoaromatization of 1,2-dihydropyridine was carried out in the presence of a catalytic amount of the complex $[Ru(C_{10}H_8N_2)_3]Cl_2$. $6H_2O$ under the visible irradiation in a mixed solvent system- MeCN-$CHCl_3$ (2:1) in inert atmosphere or in neat acetonitrile under oxygen atmosphere. In a typical experimental procedure, the compound 1,2 DHP (A) (2 mmol), the photocatalyst, $[Ru(C_{10}H_8N_2)_3]Cl_2$. $6H_2O$ (1 mol%) were taken in a 50 ml pyrex glass vessel. Then to the reaction vessel 20 ml solvent (MeCN-$CHCl_3$ (2:1)) was added. The reaction mixture was purged with nitrogen gas. The reaction vessel was placed 5 cm away from the visible light source (45 W household of Philips CFL white lamp. The reaction mixture was saturated with nitrogen gas by nitrogen bubbling (1 atm) before irradiation (30 min) and also the nitrogen bubbling was continued during the irradiation. The mixture was irradiated under the visible light and stirred at room temperature under nitrogen atmosphere. The progress of the reaction was monitored by TLC. After 3 h of irradiation the yellow colored compound was found to be consumed. The reaction was stopped. The organic solvent was evaporated by rotary evaporator. The crude thus obtained was treated with a brine solution; the organic part was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and then filtered. The crude product was obtained after the evaporation of the filtrate by rotary evaporator. The pure white solid product (97 %) was isolated by chromatography over a silica gel column (under oxygen atmosphere the yield was 95%).

Crystal Data of compound 6c: The compound **6c** obtained by the above procedure was recrystalized from ethyl acetate –hexane solvent mixture.

$C_{17}H_{17}NO_5$, *M*r = 315.32, *T* = 293 K, orthorombic, space group Pcab, *a* = 8.8191(6), *b* = 17.5507(11), *c* = 20.7531(13). Final indices R_1 = 0.0520, wR_2 = 0.1682. **CCDC: 818065** .

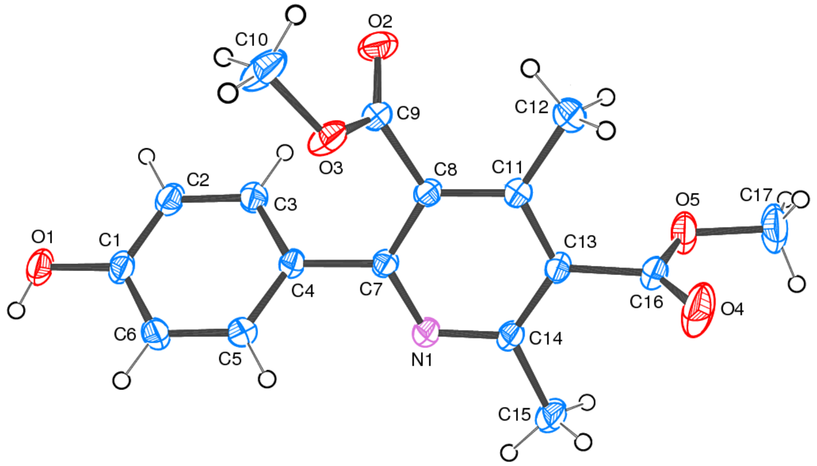
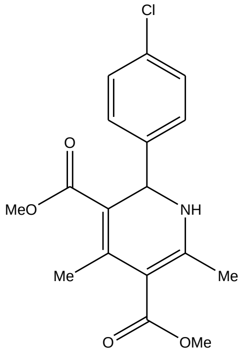


Figure S5: ORTEP diagram (with atom numbering) of compound **6c**.

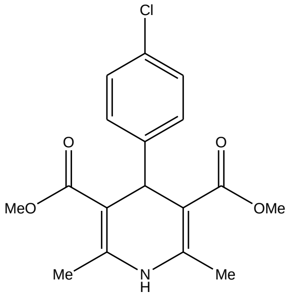
^{1}H and ^{13}C NMR spectral data:

(1,2-DHP) Dimethyl 2-(4-chlorophenyl)-1,2-dihydro-4,6-dimethylpyridine-3,5-dicarboxylate



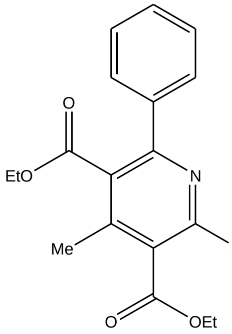
Yield 80%; yellow solid; δ_H (200 MHz, $CDCl_3$): 7.16 (4H, PhH), 6.44 (1H, d, *J* = 4.2 Hz, -NH), 5.53 (1H, d, *J* = 4.2 Hz, -CH), 3.65 (3H, s, 3-CO_2CH_3), 3.62 (3H, s, 5-CO_2CH_3), 2.37 (3H, s, 6-CH_3), 2.17 (3H, s, 4-CH_3); δ_c (50 MHz, $CDCl_3$): 168.3 (C=O), 167.3 (C=O), 155.4 (C-6), 147.5 (C-Cl), 141.3 (C-2), 133.4 (C-4), 128.6 (Ph-C), 127.7 (Ph-C), 108.9 (C-3), 103.3 (C-5), 53.9 (Ph-CH), 51.3 (-OCH_3), 50.8 (-OCH_3), 21.1 (6-CH_3), 19.5 (4-CH_3).

(1,4-DHP) Dimethyl 4-(4-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate [2]



Yield 80%; light yellow solid; δ_H (200 MHz, $CDCl_3$): 7.16 (4H, PhH), 6.10 (1H, s, -NH), 4.96 (1H, s, -CH), 3.62 (6H, s, -2CO_2CH_3), 2.29 (6H, s, -2CH_3); δ_c (50 MHz, $CDCl_3$): 167.9 (2C=O), 146.0 (C-2, C-6), 144.6 (Ph-C), 131.8 (Ph-C), 129.0 (2Ph-CH), 128.1 (2Ph-CH), 103.4 (C-3, C-5), 51.0 (-2OCH_3), 38.9 (C-4), 19.4 (-2CH_3); Elemental analysis of $C_{17}H_{18}ClNO_4$: Calculated: C, 60.81; H, 5.40; N, 4.17; Found: C, 60.80; H, 5.38; N, 4.20.

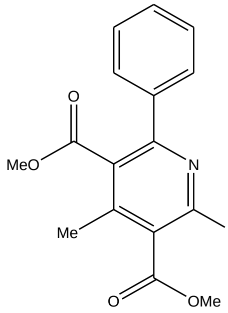
(1c) Diethyl 2,4-dimethyl-6-phenylpyridine-3,5-dicarboxylate [3]



R_f (20% EtOAc) = 0.39, λ_{max} (MeCN)/nm 251 (ε/dm^{-3} mol^{-1} cm^{-1} 13 980)

Yield 77%; colorless oil; δ_H (200 MHz, $CDCl_3$): 7.58-7.55 (2H, m, PhH), 7.43-7.33 (3H, m, PhH), 4.46 (2H, q, *J* = 7.0, 3-$CO_2CH_2CH_3$), 4.11 (2H, q, *J* = 7.0, 5-$CO_2CH_2CH_3$), 2.63 (3H, s, 2-CH_3), 2.38 (3H, s, 4-CH_3), 1.42 (3H, t, *J* = 7.0, 3-$CO_2CH_2CH_3$), 0.99 (3H, t, *J* = 7.0, 5-$CO_2CH_2CH_3$); δ_c (50 MHz, $CDCl_3$): 168.3 (C=O), 168.3 (C=O), 156.4 (C-2), 155.2 (C-6), 142.8 (C-4), 139.6 (Ph-C), 128.8 (Ph-C), 128.8 (Ph-C), 128.3 (Ph-C), 128.2 (C-3), 127.2 (C-5), 61.7 (-OCH_2CH_3), 61.5 (-OCH_2CH_3), 23.1 (2-CH_3), 16.9 (4-CH_3), 14.2 (-OCH_2CH_3), 13.6 (-OCH_2CH_3).

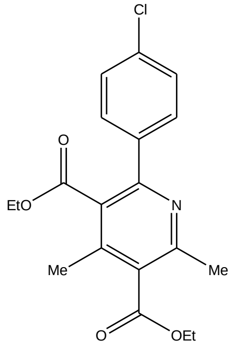
(2c) Dimethyl 2,4-dimethyl-6-phenylpyridine-3,5-dicarboxylate [3]



R_f (20% EtOAc) = 0.35, λ_{max} (MeCN)/nm 252 (ε/dm^{-3} mol^{-1} cm^{-1} 12 770)

Yield 75%; white solid; mp: 85-86 ^{0} C; δ_H (200 MHz, $CDCl_3$): 7.58-7.54 (2H, m, PhH), 7.42-7.38 (3H, m, PhH), 3.95 (3H, s, 3-CO_2CH_3), 3.62 (3H, s, 5-CO_2CH_3), 2.59 (3H, s, 2-CH_3), 2.33 (3H, s, 4-CH_3); δ_c (50 MHz, $CDCl_3$): 169.0 (C=O), 168.8 (C=O), 155.5 (C-2), 155.6 (C-6), 143.1 (C-4), 139.6 (Ph-C), 129.0 (Ph-C), 128.5 (Ph-C), 128.2 (C-3), 127.0 (C-5), 52.6 (-OCH_3), 52.4 (-OCH_3), 23.3 (2-CH_3), 17.1 (4-CH_3); Elemental analysis of $C_{17}H_{17}NO_4$: Calculated: C, 68.21; H, 5.72; N, 4.68; Found: C, 68.19; H, 5.73; N, 4.70.

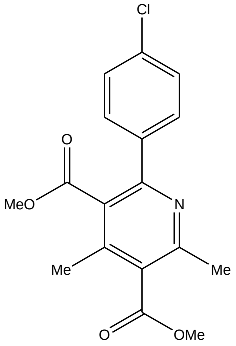
(3c) Diethyl 2-(4-chlorophenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



R_f (20% EtOAc) = 0.46, λ_{max} (MeCN)/nm 254 (ε/dm^{-3} mol^{-1} cm^{-1} 16 310)

Yield 76%; light yellow oil; δ_H (200 MHz, CDCl$_3$): 7.51 (2H, d, *J* = 8.4 Hz, PhH), 7.38 (2H, d, *J* = 8.4 Hz, PhH), 4.44 (2H, q, *J* = 7.2, 3-CO$_2$CH$_2$CH$_3$), 4.13 (2H, q, *J* = 7.2, 5-CO$_2$CH$_2$CH$_3$), 2.59 (3H, s, 6-CH$_3$), 2.34 (3H, s, 4-CH$_3$), 1.40 (3H, t, *J* = 7.2, 3-CO$_2$CH$_2$CH$_3$), 1.05 (3H, t, *J* = 7.2, 5-CO$_2$CH$_2$CH$_3$); δ_c (50 MHz, CDCl$_3$): 168.3 (C=O), 168.3 (C=O), 155.5 (C-6), 155.1 (C-2), 143.2 (C-4), 138.1 (Ph-C), 135.3 (Ph-C), 129.8 (Ph-C), 128.9 (C-3), 128.7 (Ph-C), 127.4 (C-5) 61.9 (-OCH$_2$CH$_3$), 61.8 (-OCH$_2$CH$_3$), 23.1 (6-CH$_3$), 16.9 (4-CH$_3$), 14.3 (-OCH$_2$CH$_3$), 13.8 (-OCH$_2$CH$_3$); HRMS (ES+) m/z calculated for $C_{19}H_{21}ClNO_4$ [M+H]$^+$: 362.1159: found: 362.1157.

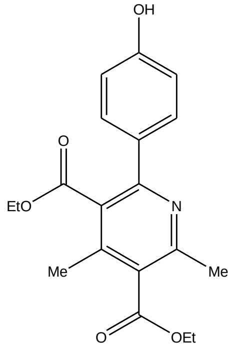
(4c) Dimethyl 2-(4-chlorophenyl)-4,6-dimethylpyridine-3,5-dicarboxylate [3]



R_f (20% EtOAc) = 0.42, λ_{max} (MeCN)/nm 256 (ε/dm^{-3} mol^{-1} cm^{-1} 17 540)

Yield 75%; white solid; mp: 89-90 ^{0} C; δ_H (200 MHz, CDCl$_3$): 7.50 (2H, d, *J* = 8 Hz, PhH), 7.37 (2H, d, *J* = 8 Hz, PhH), 3.94 (3H, s, 3-CO$_2$CH$_3$), 3.64 (3H, s, 5-CO$_2$CH$_3$), 2.57 (3H, s, 6-CH$_3$), 2.31 (3H, s, 4-CH$_3$); δ_c (50 MHz, CDCl$_3$): 168.6 (C=O), 168.5 (C=O), 155.5 (C-6), 154.9 (C-2), 143.2 (C-4), 137.9 (Ph-C), 135.1 (Ph-C), 129.5 (Ph-C), 128.5 (Ph-C), 128.3 (C-3), 126.8 (C-5) 52.5 (-OCH$_3$), 52.4 (-OCH$_3$), 23.1 (6-CH$_3$), 16.9 (4-CH$_3$); Elemental analysis of $C_{17}H_{16}ClNO_4$: Calculated: C, 68.18; H, 4.83; N, 4.20; Found: C, 68.21; H, 4.82; N, 4.18; HRMS (ES+) m/z calculated for $C_{17}H_{17}ClNO_4$ [M+H]$^+$: 334.0846: found: 334.0845.

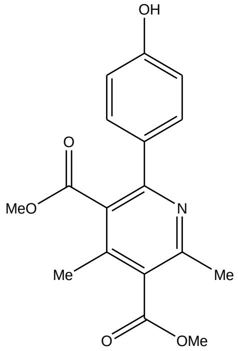
(5c) Diethyl 2-(4-hydroxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



R$_f$ (20% EtOAc) = 0.17, λ_{max} (MeCN)/nm 286 (ε/dm^{-3} mol^{-1} cm^{-1} 24 490)

Yield 72%; light yellow oil; δ_H (200 MHz, CDCl$_3$): 7.31 (2H, d, *J* = 8.4 Hz, PhH), 6.60 (2H, d, *J* = 8.4 Hz, PhH), 4.44 (2H, q, *J* = 7.0, 3-CO$_2$CH$_2$CH$_3$), 4.10 (2H, q, *J* = 7.0, 5-CO$_2$CH$_2$CH$_3$), 2.59 (3H, s, 6-CH$_3$), 2.34 (3H, s, 4-CH$_3$), 1.40 (3H, t, *J* = 7.0, 3-CO$_2$CH$_2$CH$_3$), 1.04 (3H, t, *J* = 7.0, 5-CO$_2$CH$_2$CH$_3$); δ_c (50 MHz, CDCl$_3$): 168.7 (C=O), 168.3 (C=O), 157.6 (C-6), 156.4 (C-2), 155.2 (C-4), 143.4 (Ph-C), 130.6 (Ph-C), 129.8 (Ph-C), 128.4 (C-3), 127.6 (C-5), 115.8 (Ph-C) 61.9 (-OCH$_2$CH$_3$), 61.9 (-OCH$_2$CH$_3$), 22.5 (6-CH$_3$), 17.1 (4-CH$_3$), 14.3 (-OCH$_2$CH$_3$), 13.8 (-OCH$_2$CH$_3$); HRMS (ES+) m/z calculated for $C_{19}H_{22}NO_5$ [M+H]$^+$: 344.1498: found: 316.1192

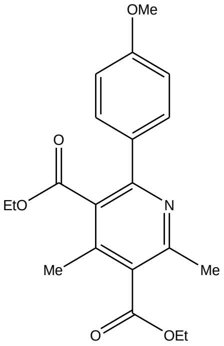
(6c) Dimethyl 2-(4-hydroxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



R$_f$ (20% EtOAc) = 0.15, λ_{max} (MeCN)/nm 287 (ε/dm^{-3} mol^{-1} cm^{-1} 19 100)

Yield 74%; colorless crystal; mp: 140-141 ^{0} C; δ_H (200 MHz, CDCl$_3$): 7.43 (2H, d, *J* = 8.6 Hz, PhH), 6.81 (2H, d, *J* = 8.6 Hz, PhH), 3.97 (3H, s, 3-CO$_2$CH$_3$), 3.67 (3H, s, 5-CO$_2$CH$_3$), 2.67 (3H, s, 6-CH$_3$), 2.34 (3H, s, 4-CH$_3$); δ_c (50 MHz, CDCl$_3$): 169.2 (C=O), 168.7 (C=O), 157.7 (C-6), 156.3 (C-2), 155.6 (C-4), 143.8 (Ph-C), 130.4 (Ph-C), 129.7 (Ph-C), 128.1 (C-3), 127.2 (C-5), 115.9 (Ph-C) 52.7 (-OCH$_3$), 22.7 (6-CH$_3$), 17.3 (4-CH$_3$); Elemental analysis of $C_{17}H_{17}NO_5$: calcd: C, 64.75; H, 5.43; N, 4.44; found: C, 64.70; H, 5.46; N, 4.46; HRMS (ES+) m/z calculated for $C_{17}H_{18}NO_5$ [M+H]$^+$: 316.1185: found: 316.1177

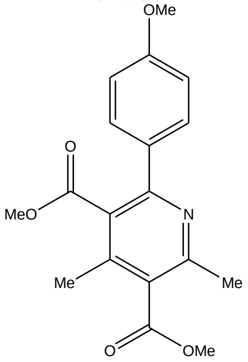
(7c) Diethyl 2-(4-methoxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



R_f (20% EtOAc) = 0.18, λ_{max} (MeCN)/nm 287 (ε/dm^{-3} mol^{-1} cm^{-1} 21 790)

Yield 70%; light yellow oil; δ_H (200 MHz, CDCl$_3$): 7.50 (2H, d, *J* = 8.8 Hz, PhH), 6.89 (2H, d, *J* = 8.8 Hz, PhH), 4.38 (2H, q, *J* = 7.0, 3-CO$_2$CH$_2$CH$_3$), 4.10 (2H, q, *J* = 7.0, 5-CO$_2$CH$_2$CH$_3$), 3.75 (3H, s, Ph-OCH$_3$), 2.55 (3H, s, 6-CH$_3$), 2.30 (3H, s, 4-CH$_3$), 1.34 (3H, s, 3-CO$_2$CH$_2$CH$_3$), 1.01 (3H, s, 5-CO$_2$CH$_2$CH$_3$); δ_c (50 MHz, CDCl$_3$): 168.6 (C=O), 168.3 (C=O), 160.3 (C-6), 155.8 (C-OCH$_3$), 155.1 (C-2), 142.6 (C-4), 132.1 (Ph-C), 129.7 (Ph-C), 127.9 (C-3), 126.9 (C-5), 113.8 (Ph-C), 61.6 (-OCH$_2$CH$_3$), 61.5 (-OCH$_2$CH$_3$), 55.2 (-OCH$_3$), 23.1 (6-CH$_3$), 16.8 (4-CH$_3$), 14.1 (-OCH$_2$CH$_3$), 13.7 (-OCH$_2$CH$_3$); HRMS (ES+) m/z calculated for $C_{20}H_{24}NO_5$ [M+H]$^+$: 358.1654: found: 358.1647

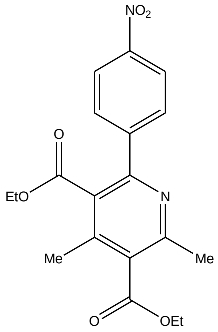
(8c) Dimethyl 2-(4-methoxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate [3]



R_f (20% EtOAc) = 0.18, λ_{max} (MeCN)/nm 251 (ε/dm^{-3} mol^{-1} cm^{-1} 19 830)

Yield 73%; light yellow solid; mp: 62-63 ^{0} C; δ_H (200 MHz, CDCl$_3$): 7.50 (2H, d, *J* = 8 Hz, PhH), 6.89 (2H, d, *J* = 8 Hz, PhH), 3.92 (3H, s, 3-CO$_2$CH$_3$), 3.79 (3H, s, PhOCH$_3$), 3.64 (3H, s, 5-CO$_2$CH$_3$), 2.55 (3H, s, 6-CH$_3$), 2.28 (3H, s, 4-CH$_3$); δ_c (50 MHz, CDCl$_3$): 169.3 (C=O), 168.9 (C=O), 160.3 (C-6), 155.8 (C-OCH$_3$), 155.5 (C-2), 143.0 (C-4), 131.9 (Ph-C), 129.6 (Ph-C), 127.6 (C-3), 126.5 (C-5), 113.9 (Ph-C), 55.3 (Ph-OCH$_3$), 52.5 (-OCH$_3$), 52.4 (-OCH$_3$), 23.2 (6-CH$_3$), 17.0 (4-CH$_3$); Elemental analysis of $C_{18}H_{19}NO_5$: Calculated: C, 65.64; H, 5.81; N, 4.25; Found: C, 65.65; H, 5.84; N, 4.21

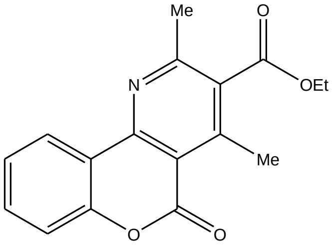
(9c) Diethyl 2,4-dimethyl-6-(4-nitrophenyl)pyridine-3,5-dicarboxylate [3]



R$_f$ (20% EtOAc) = 0.22, λ_{max} (MeCN)/nm 292 (ε/dm^{-3} mol^{-1} cm^{-1} 12 110)

Yield 58%; colorless oil; δ_H (200 MHz, $CDCl_3$): 8.30 (2H, d, *J* = 8.8 Hz, PhH), 7.77 (2H, d, *J* = 8.8 Hz, PhH), 4.48 (2H, q, *J* = 7.2, 3-$CO_2CH_2CH_3$), 4.16 (2H, q, *J* = 7.2, 5-$CO_2CH_2CH_3$), 2.63 (3H, s, 6-CH_3), 2.40 (3H, s, 4-CH_3), 1.44 (3H, t, *J* = 7.0, 3-$CO_2CH_2CH_3$), 1.07 (3H, t, *J* = 7.0, 5-$CO_2CH_2CH_3$); δ_c (50 MHz, $CDCl_3$): 167.8 (C=O), 167.7 (C=O), 157.7 (C-6), 153.8 (C-2), 148.0 (C-4), 145.8 (Ph-C), 143.3 (Ph-C), 129.6 (Ph-C), 129.4 (C-3), 127.5 (C-5), 123.5 (Ph-C) 61.9 (-OCH_2CH_3), 61.9 (-OCH_2CH_3), 23.0 (6-CH_3), 16.9 (4-CH_3), 14.2 (-OCH_2CH_3), 13.7 (-OCH_2CH_3).

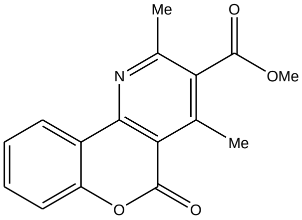
(10c) Ethyl 2,4-dimethyl-5-oxo-5H-chromeno[4,3-*b*]pyridine-3-carboxylate [4]



R$_f$ (20% EtOAc) = 0.37, λ_{max} (MeCN)/nm 304 and 271 (ε/dm^{-3} mol^{-1} cm^{-1} 11 490 and 16 050)

Yield 75%; white solid; mp: 93-94 ^{0} C; δ_H (200 MHz, $CDCl_3$): 8.37 (1H, d, *J* = 8 Hz, PhH), 7.47-7.39 (1H, m, PhH), 7.24-7.14 (2H, m, PhH), 4.37 (2H, q, *J* = 7.0, -$CO_2CH_2CH_3$), 2.67 (3H, s, 2-CH_3), 2.55 (3H, s, 4-CH_3), 1.37 (3H, t, *J* = 7.0, -$CO_2CH_2CH_3$); δ_c (50 MHz, $CDCl_3$): 167.9 (C=O), 160.3 (C=O), 159.9 (C-2), 152.4 (C-6), 152.0 (C-4), 149.7 (Ph-C), 132.2 (Ph-C), 131.5 (Ph-C), 125.3 (Ph-C), 124.4 (Ph-C), 118.8 (Ph-C) 116.4 (C-5), 113.6 (C-3), 62.0 (-OCH_2CH_3), 23.6 (2-CH_3), 19.3 (4-CH_3), 14.1 (-OCH_2CH_3); Elemental analysis of $C_{17}H_{15}NO_4$: Calculated: C, 68.68; H, 5.09; N, 4.71; Found: C, 68.65; H, 5.11; N, 4.72.

(11c) Methyl 2,4-dimethyl-5-oxo-5H-chromeno[4,3-*b*]pyridine-3-carboxylate [4]



R_f (20% EtOAc) = 0.33, λ_{max} (MeCN)/nm 304 and 272 (ε/dm^{-3} mol^{-1} cm^{-1} 11 480 and 16 120)

Yield 70%; white solid; mp: 115-116 ^{0} C; δ_H (200 MHz, $CDCl_3$): 8.55 (1H, d, *J* = 8 Hz, PhH), 7.58-7.50 (1H, m, PhH), 7.37-7.25 (2H, m, PhH), 3.99 (3H, s, $-OCH_3$), 2.76 (3H, s, 2-CH_3), 2.64 (3H, s, 4-CH_3); δ_c (50 MHz, $CDCl_3$): 168.7 (C=O), 160.8 (C=O), 160.2 (C-2), 152.8 (C-6), 152.6 (C-4), 150.2 (Ph-C), 132.5 (Ph-C), 131.6 (Ph-C), 125.7 (Ph-C), 124.7 (Ph-C), 119.1 (Ph-C) 116.7 (C-5), 113.9 (C-3), 52.9 ($-OCH_3$), 24.0 (2-CH_3), 19.7 (4-CH_3); Elemental analysis of $C_{16}H_{13}NO_4$: Calculated: C, 67.84; H, 4.63; N, 4.94; Found: C, 67.87; H, 4.64; N, 4.90

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1. J. A. Broomhead, C. G. Young and P. Hood, *Inorg. Synth.*, 1990, **28**, 338-340.

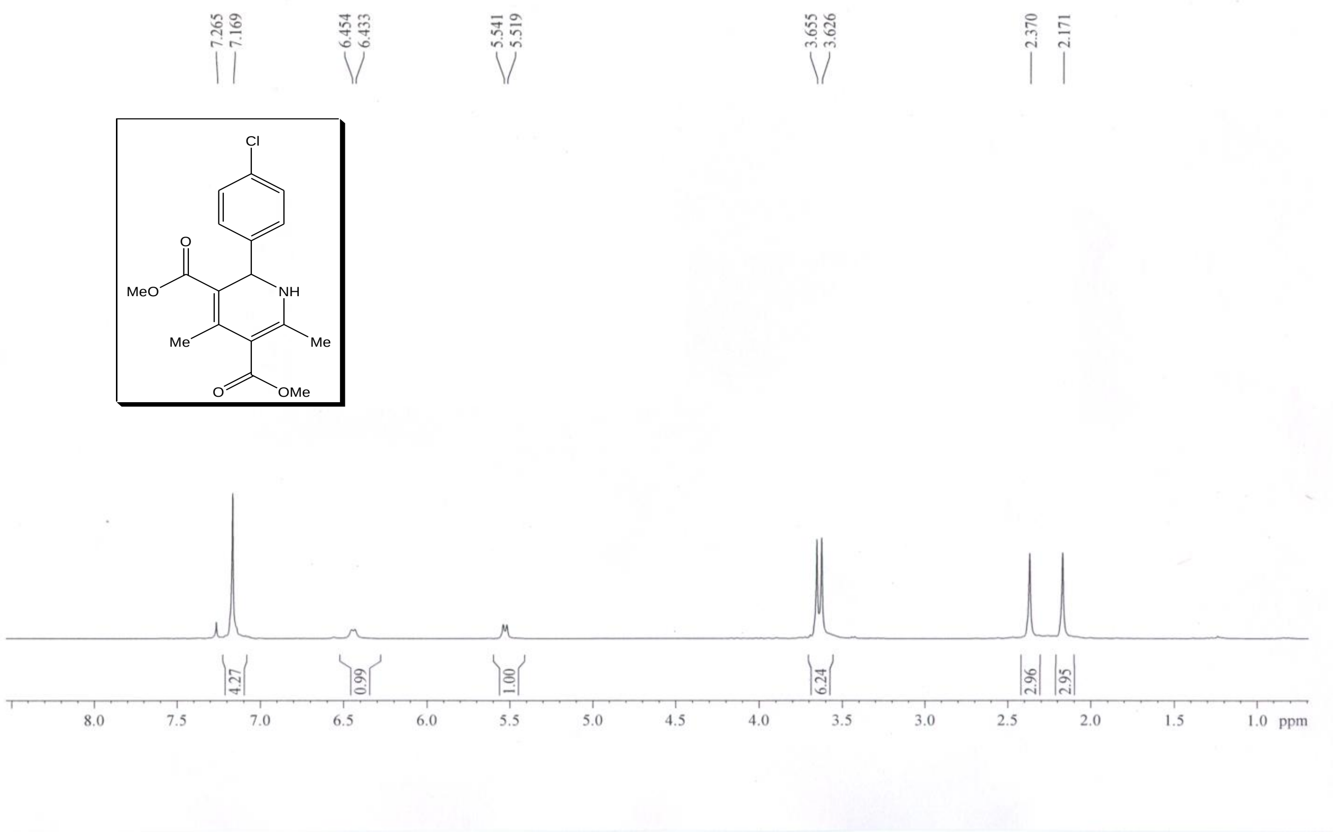
2. A. Debache, W. Ghalem, R. Boulcina, A. Belfaitah, S. Rhouati and B. Carboni, *Tetrahedron Lett.*, 2009, **50**, 5248-5250.

3. L. Shen, S. Cao, J. Wu, J. Zhang, H. Li, N. Liu and X. Qian, *Green Chem.*, 2009, **11**, 1414-1420.

4. C. N. O'Callaghan, *Synthesis.*, 1987, **5**, 499-503.

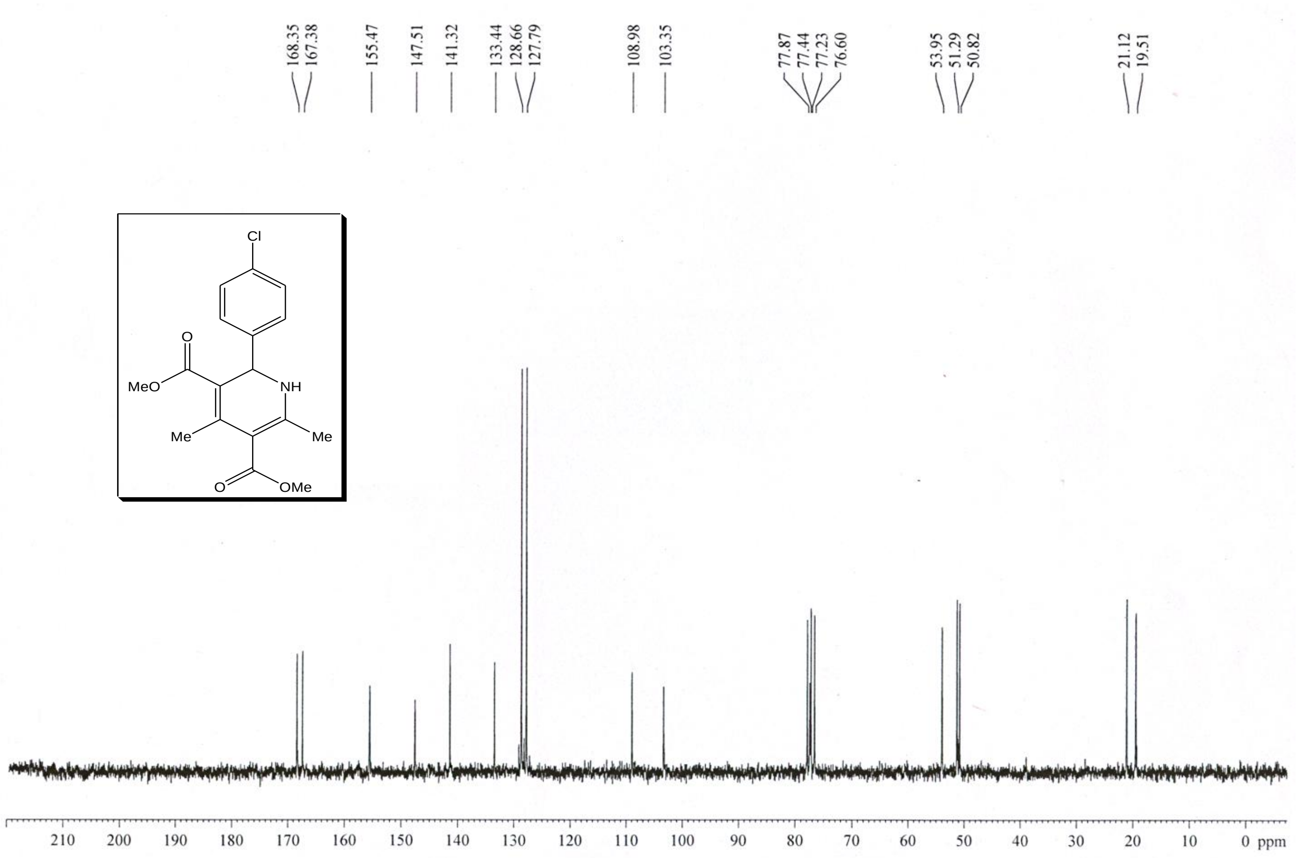
(1,2-DHP-A)

Dimethyl 2-(4-chlorophenyl)-1,2-dihydro-4,6-dimethylpyridine-3,5-dicarboxylate



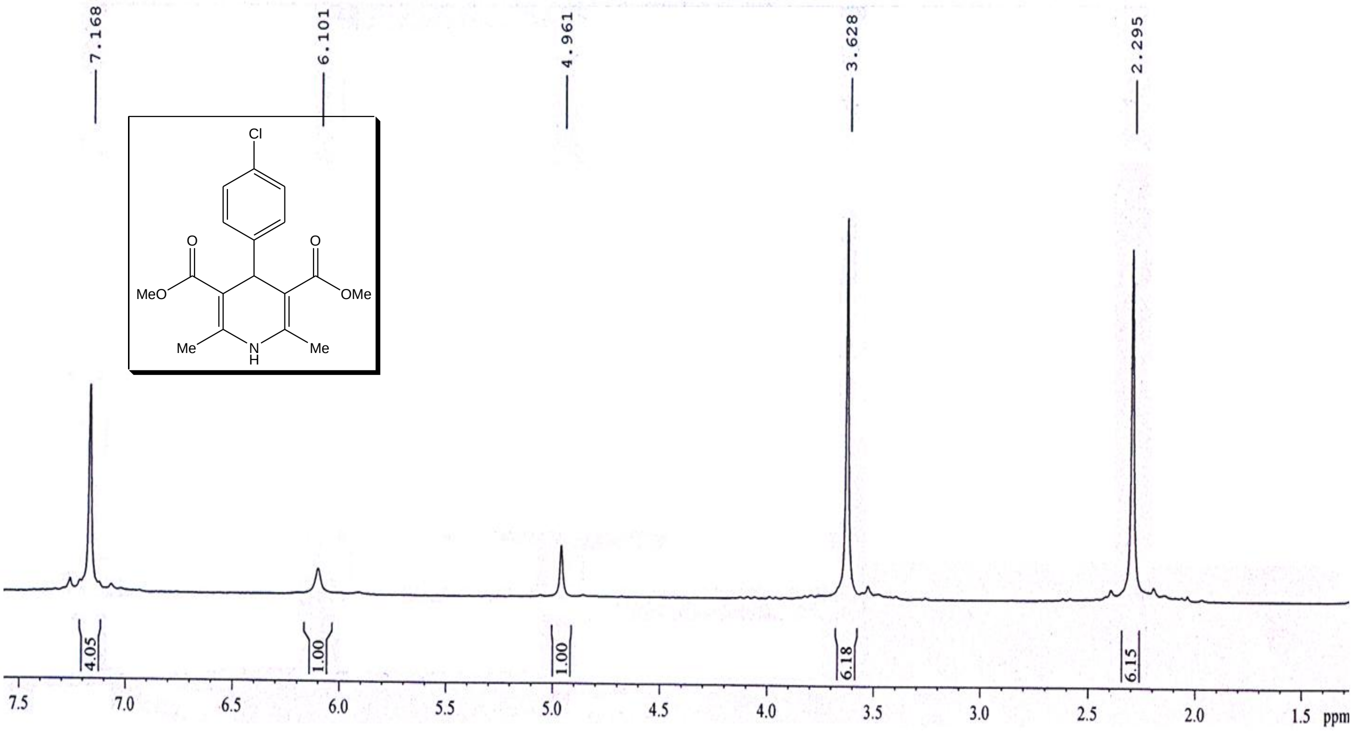
(1,2-DHP-A)

Dimethyl 2-(4-chlorophenyl)-1,2-dihydro-4,6-dimethylpyridine-3,5-dicarboxylate



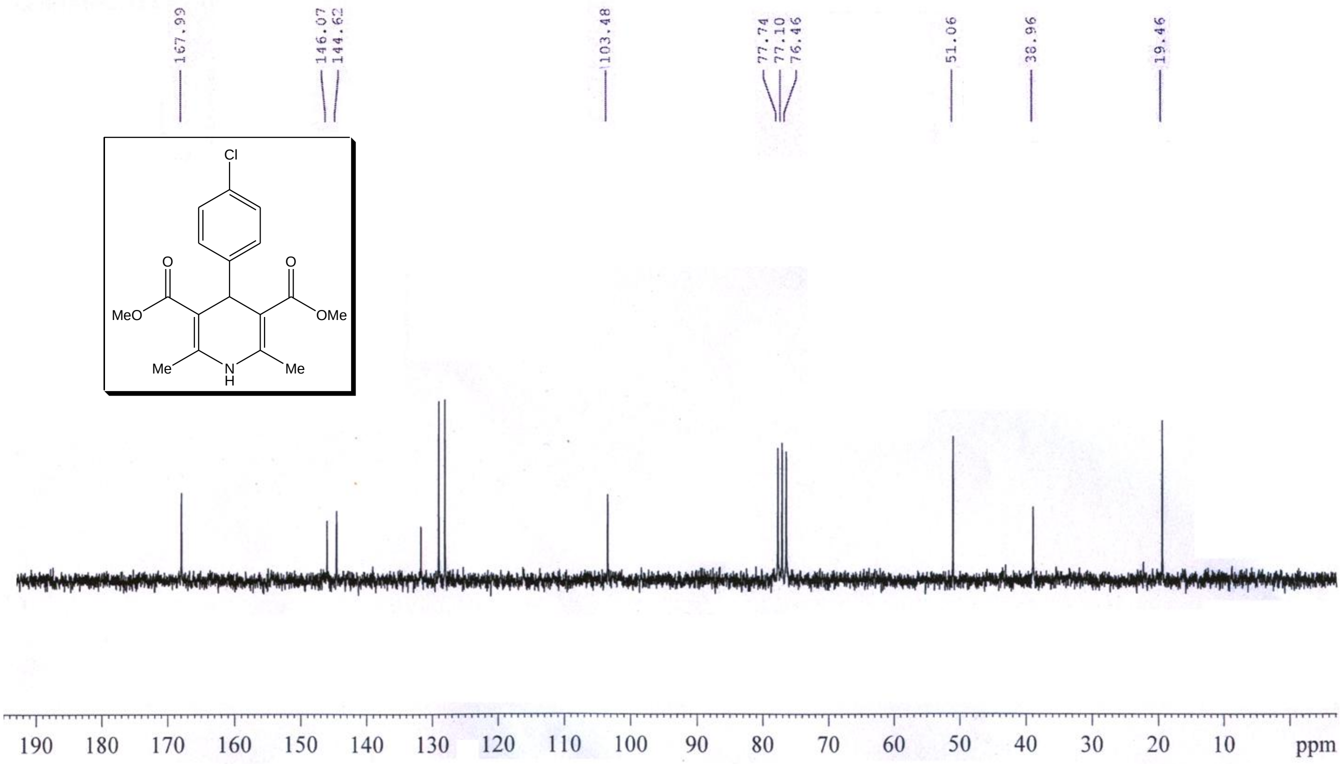
(1,4-DHP-A)

Dimethyl 4-(4-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate



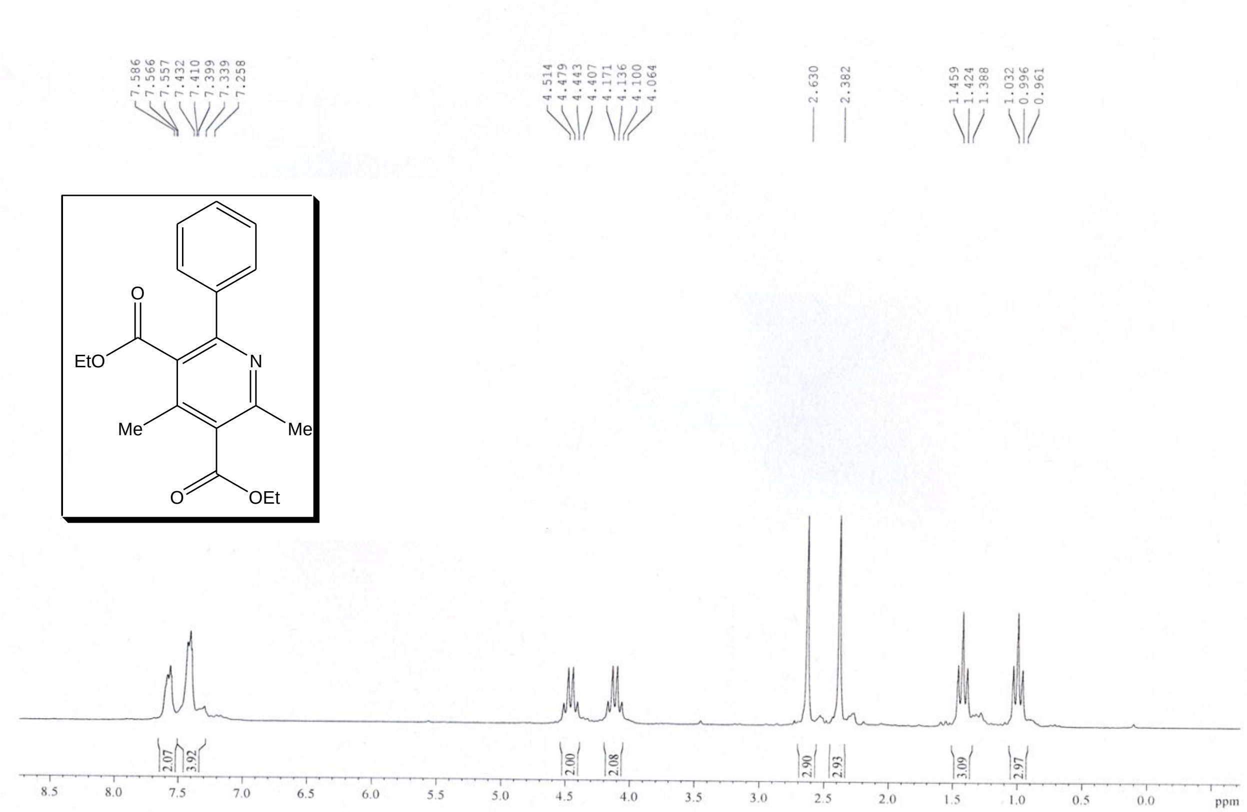
(1,4-DHP-A)

Dimethyl 4-(4-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate



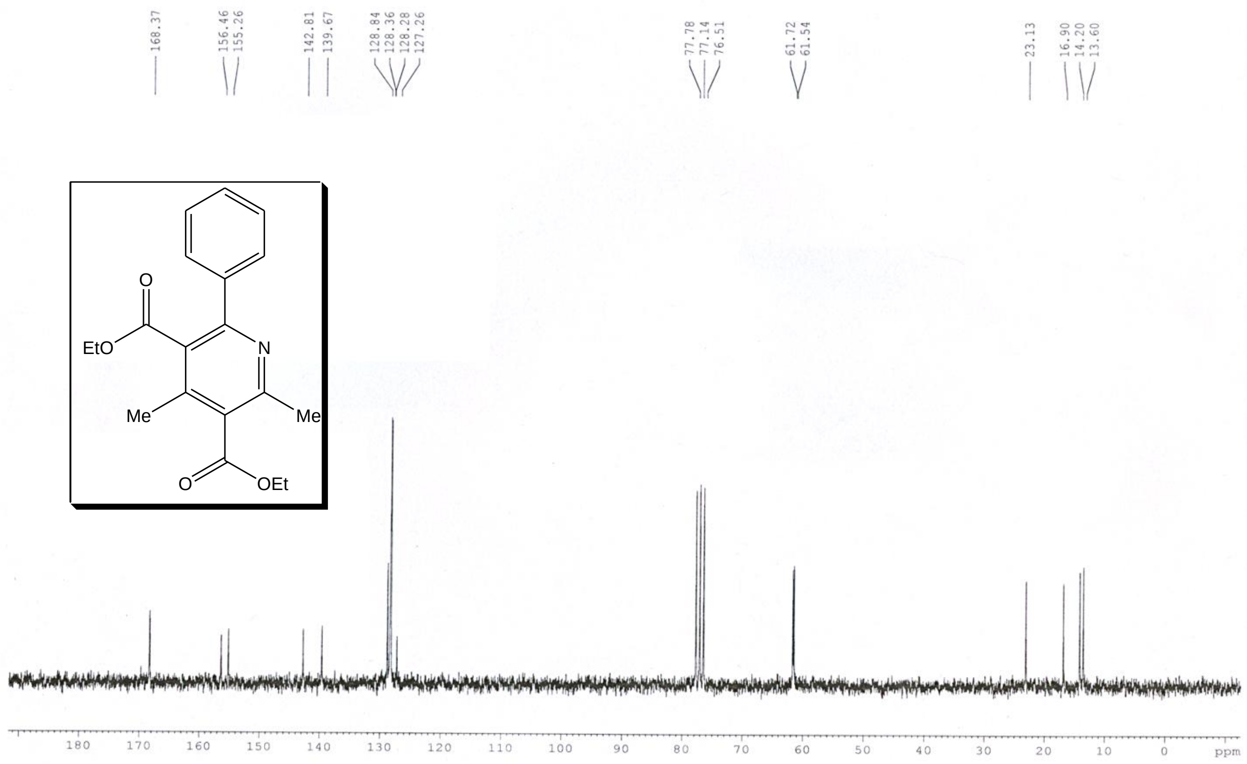
(1c)

Diethyl 2,4-dimethyl-6-phenylpyridine-3,5-dicarboxylate



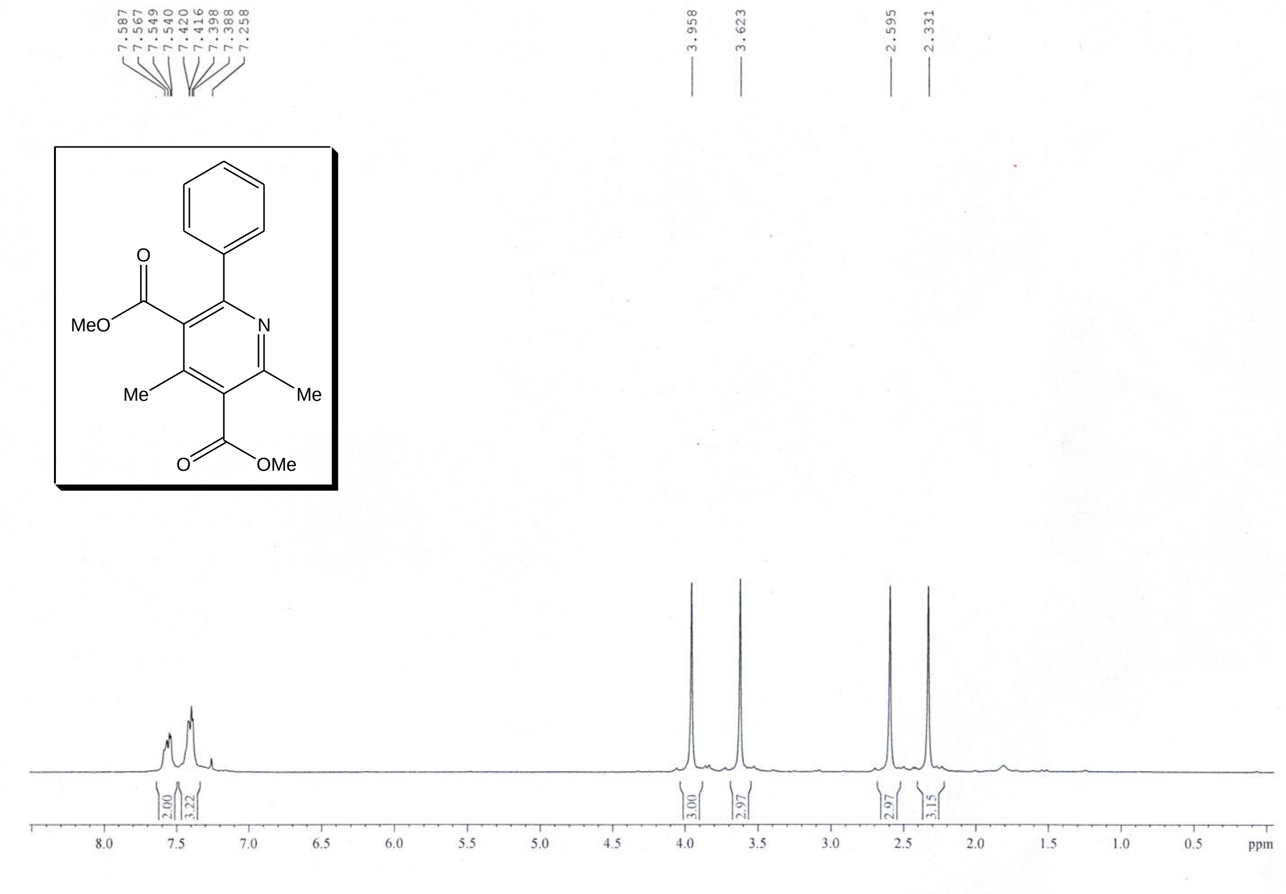
(1c)

Diethyl 2,4-dimethyl-6-phenylpyridine-3,5-dicarboxylate



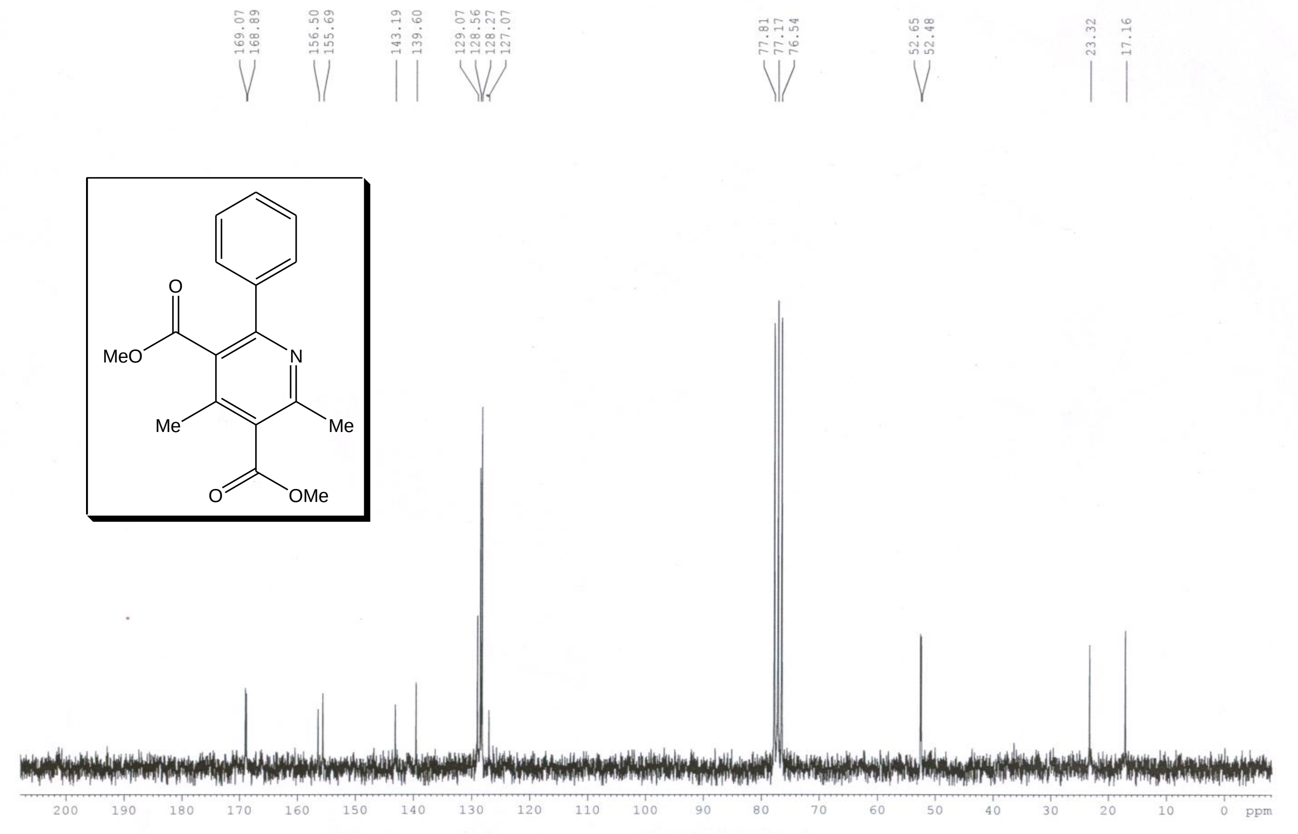
(2c)

Dimethyl 2,4-dimethyl-6-phenylpyridine-3,5-dicarboxylate



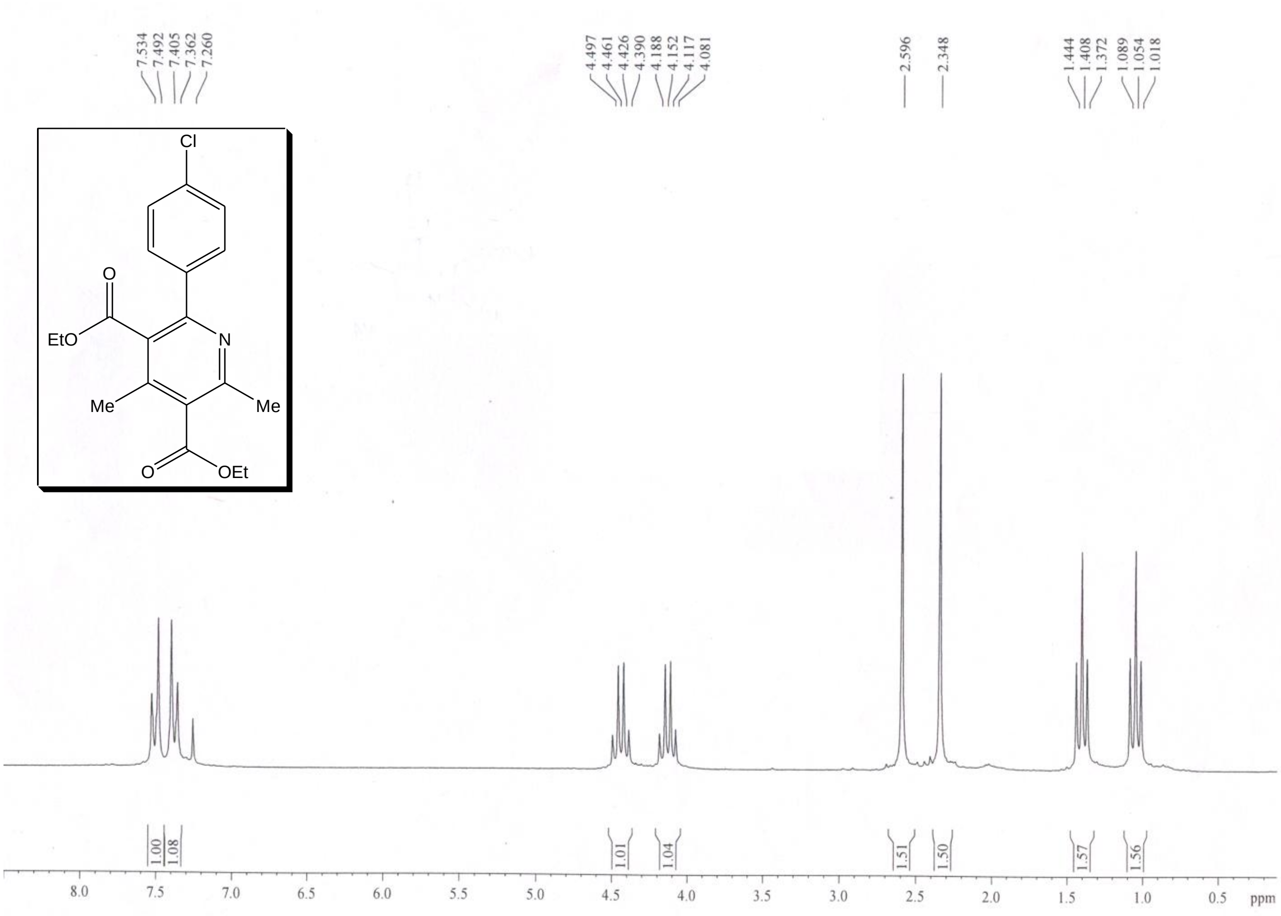
(2c)

Dimethyl 2,4-dimethyl-6-phenylpyridine-3,5-dicarboxylate



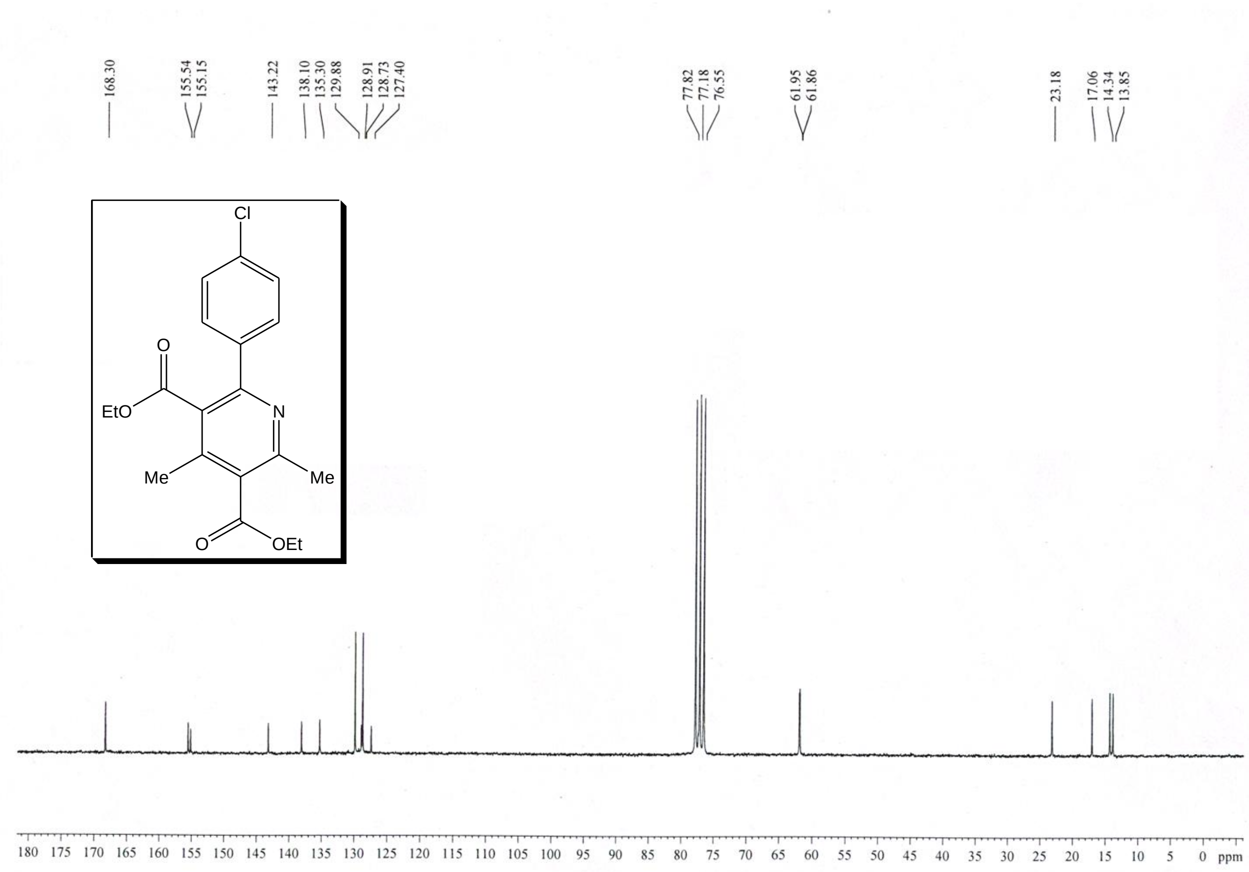
(3c)

Diethyl 2-(4-chlorophenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



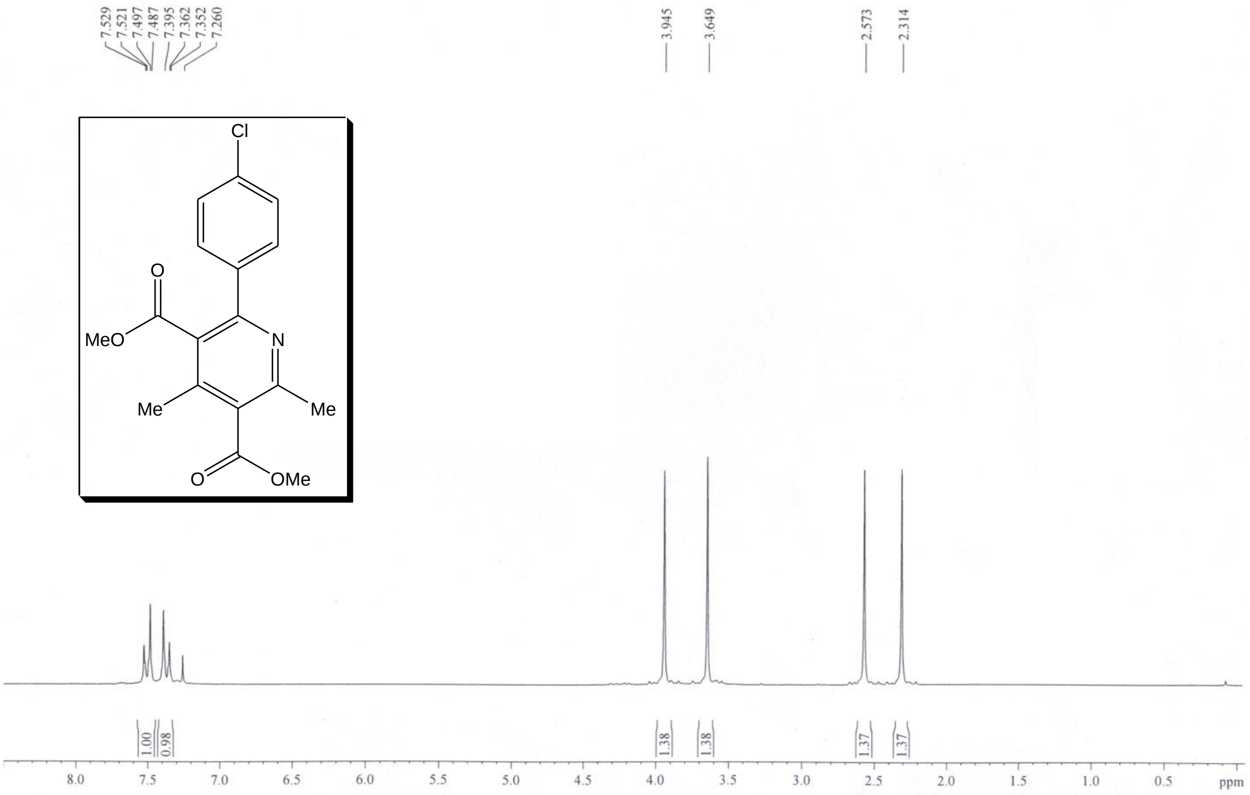
(3c)

Diethyl 2-(4-chlorophenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



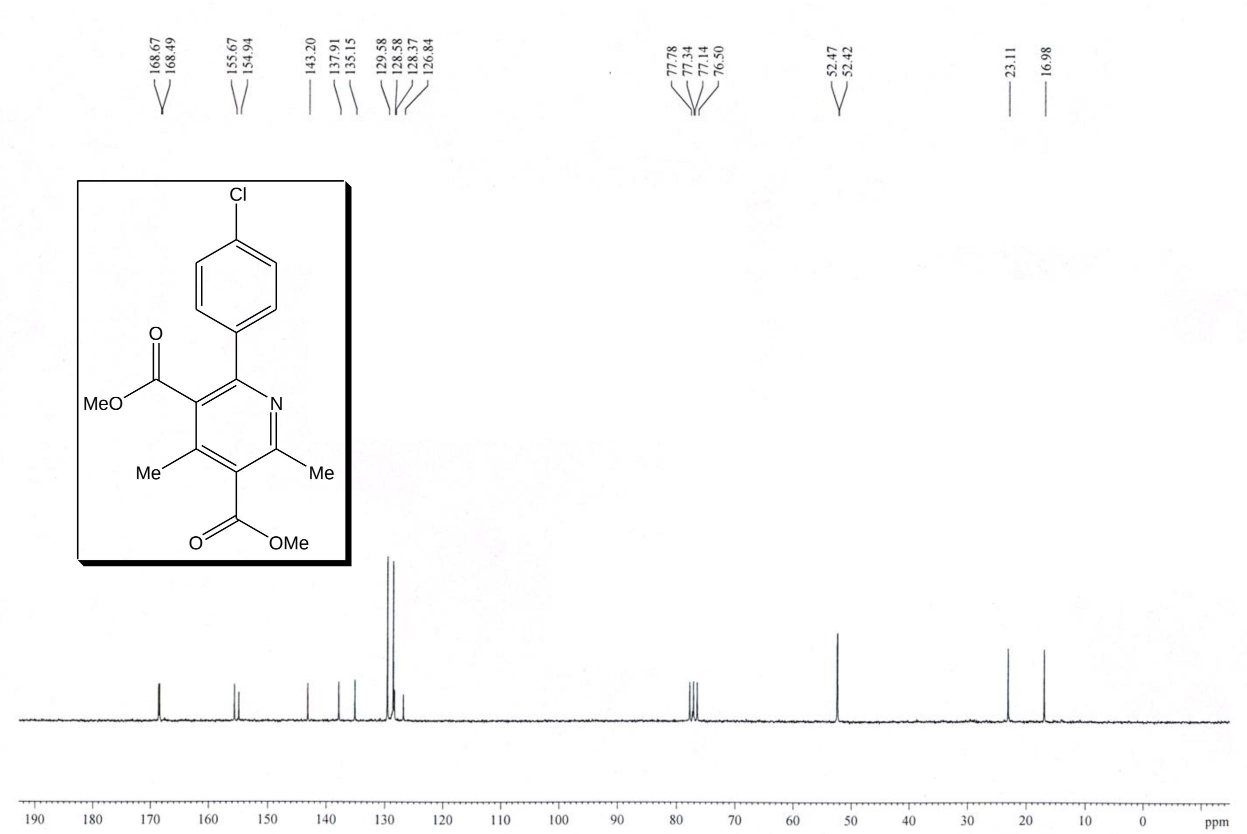
(4c)

Dimethyl 2-(4-chlorophenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



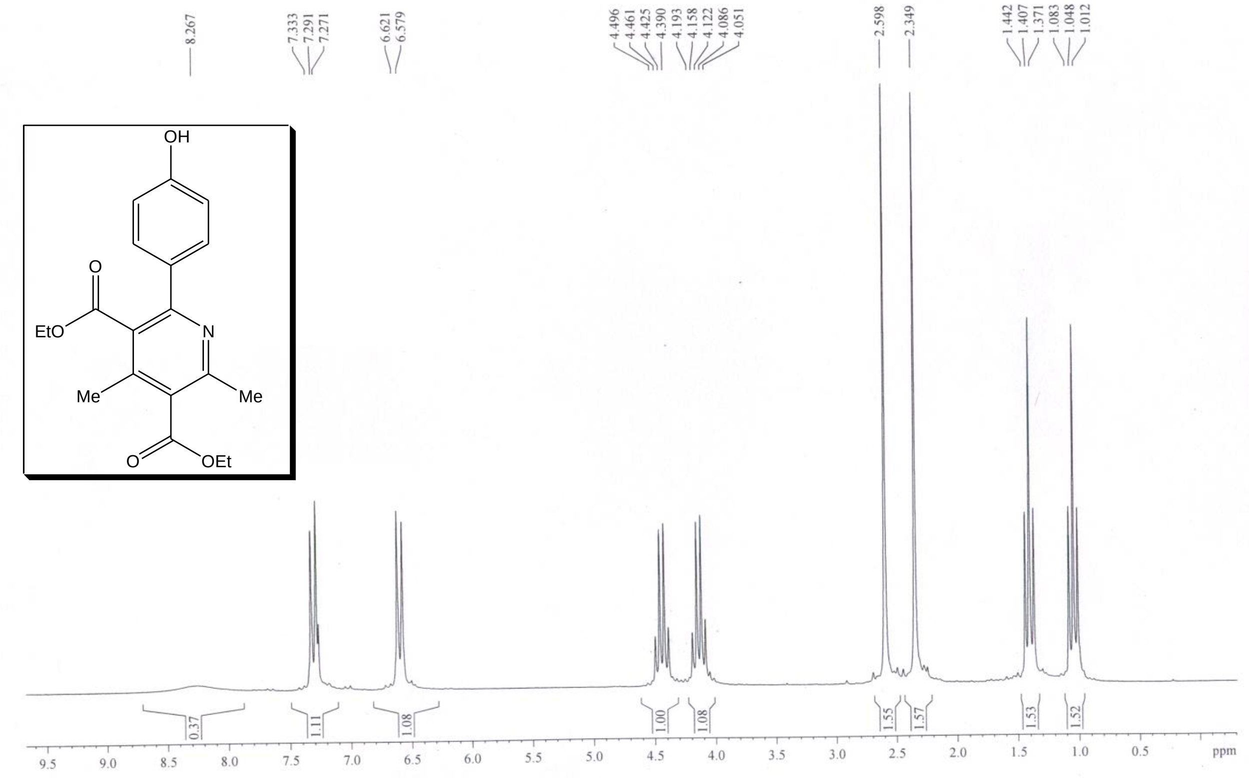
(4c)

Dimethyl 2-(4-chlorophenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



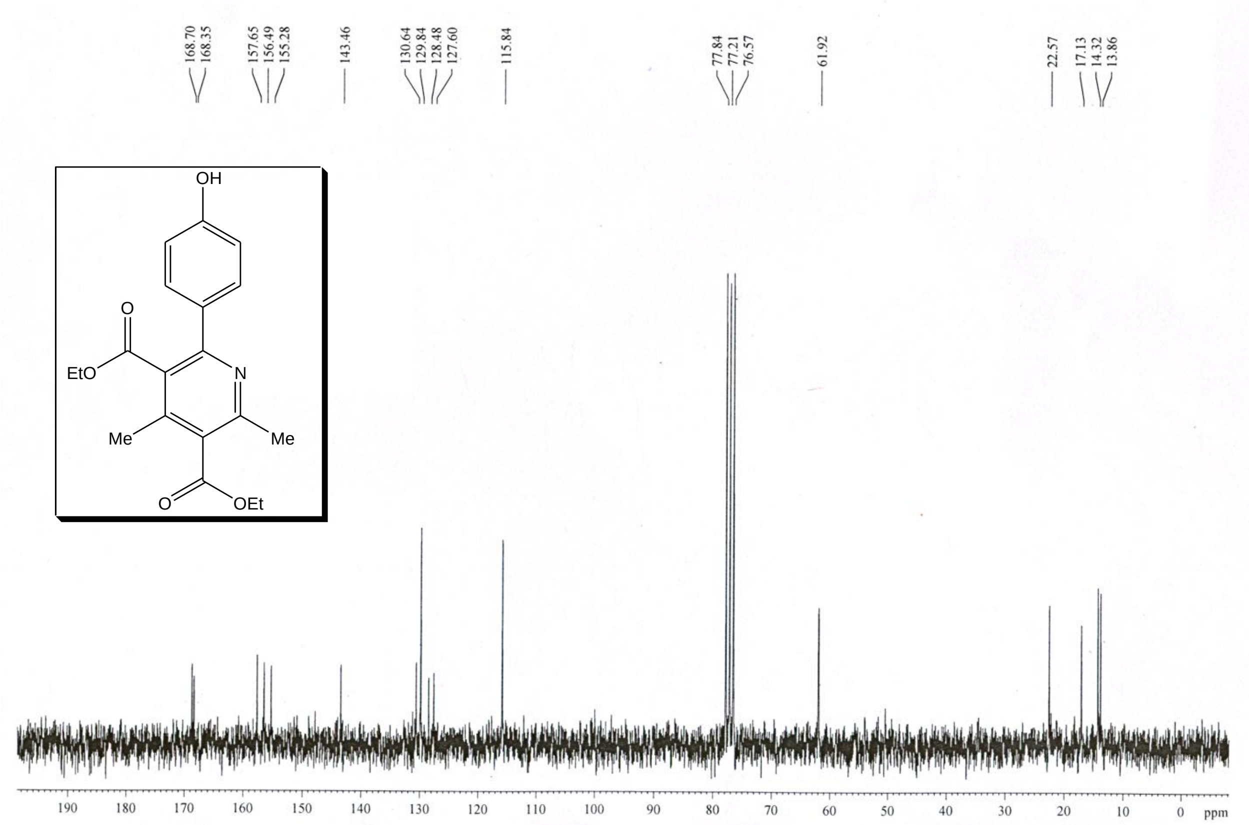
(5c)

Diethyl 2-(4-hydroxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



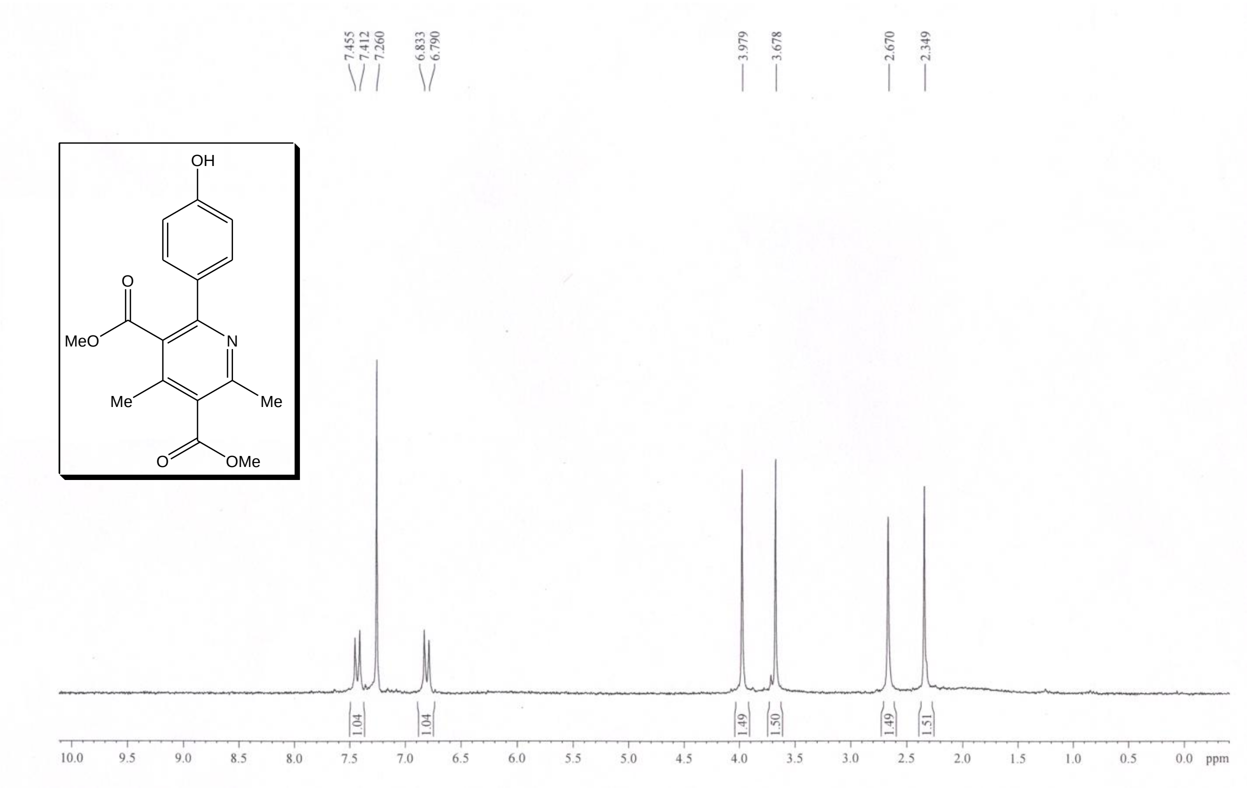
(5c)

Diethyl 2-(4-hydroxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



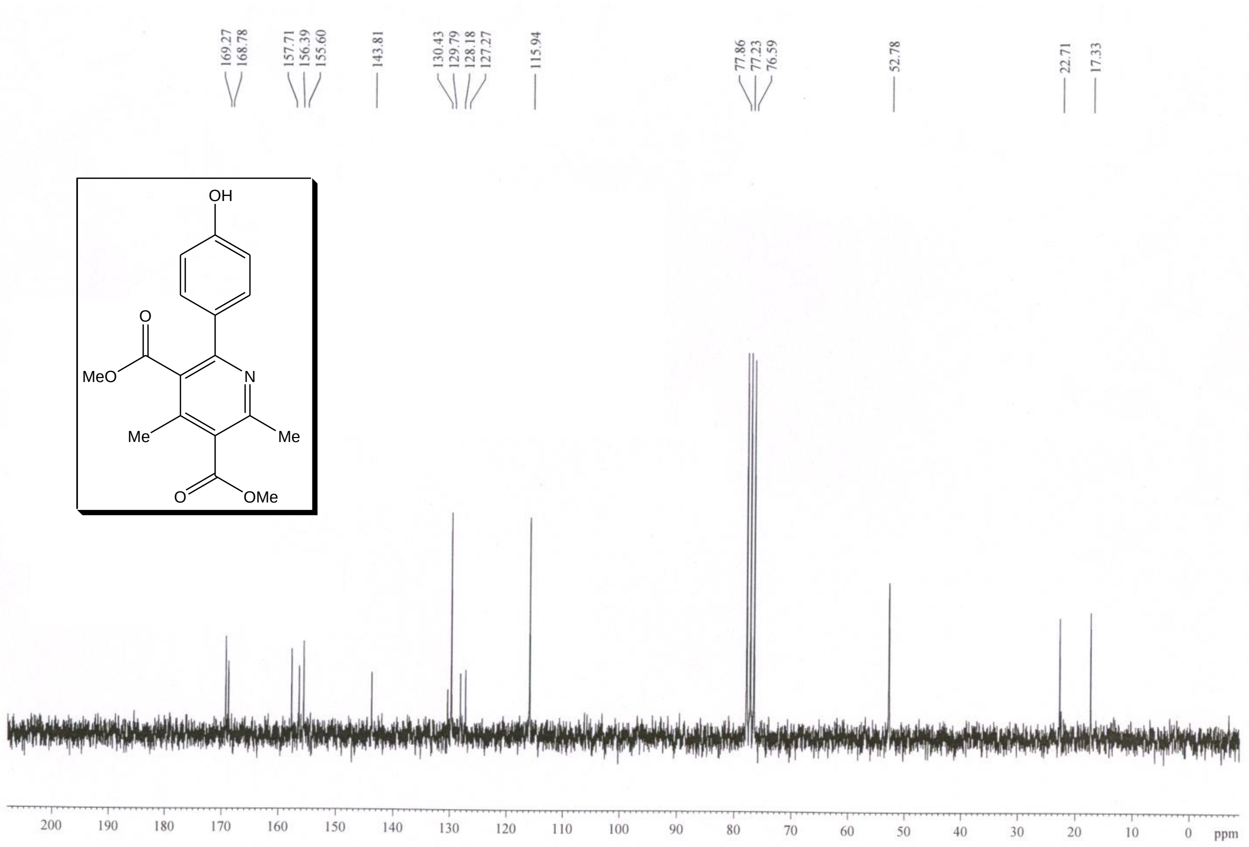
(6c)

Dimethyl 2-(4-hydroxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



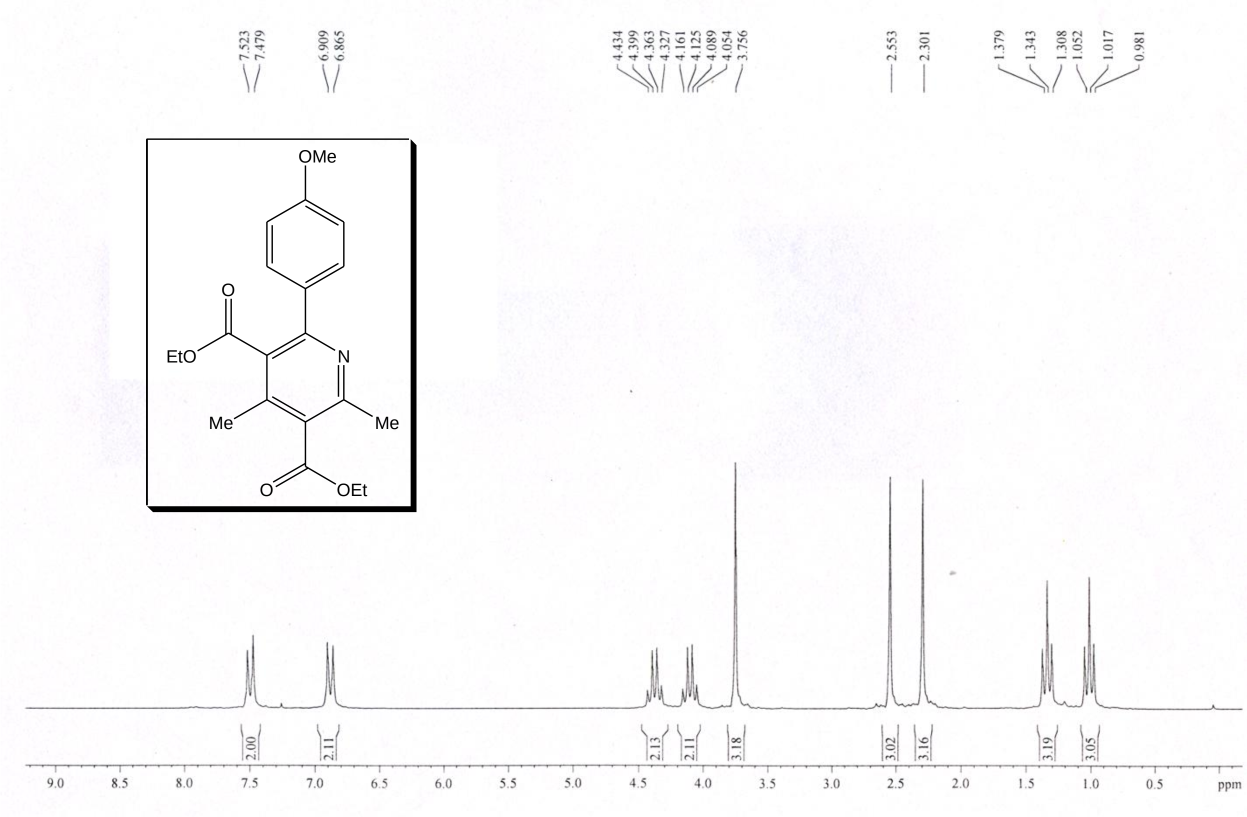
(6c)

Dimethyl 2-(4-hydroxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



(7c)

Diethyl 2-(4-methoxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



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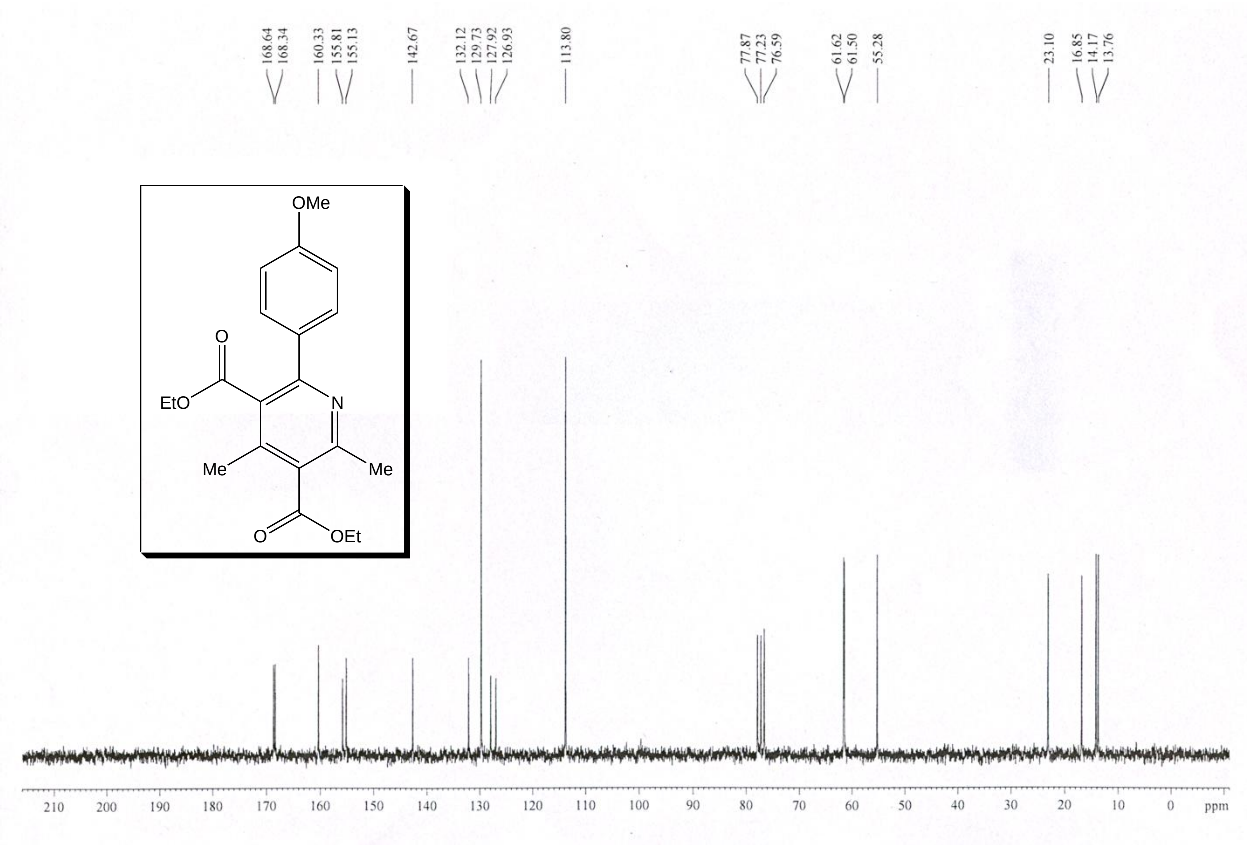
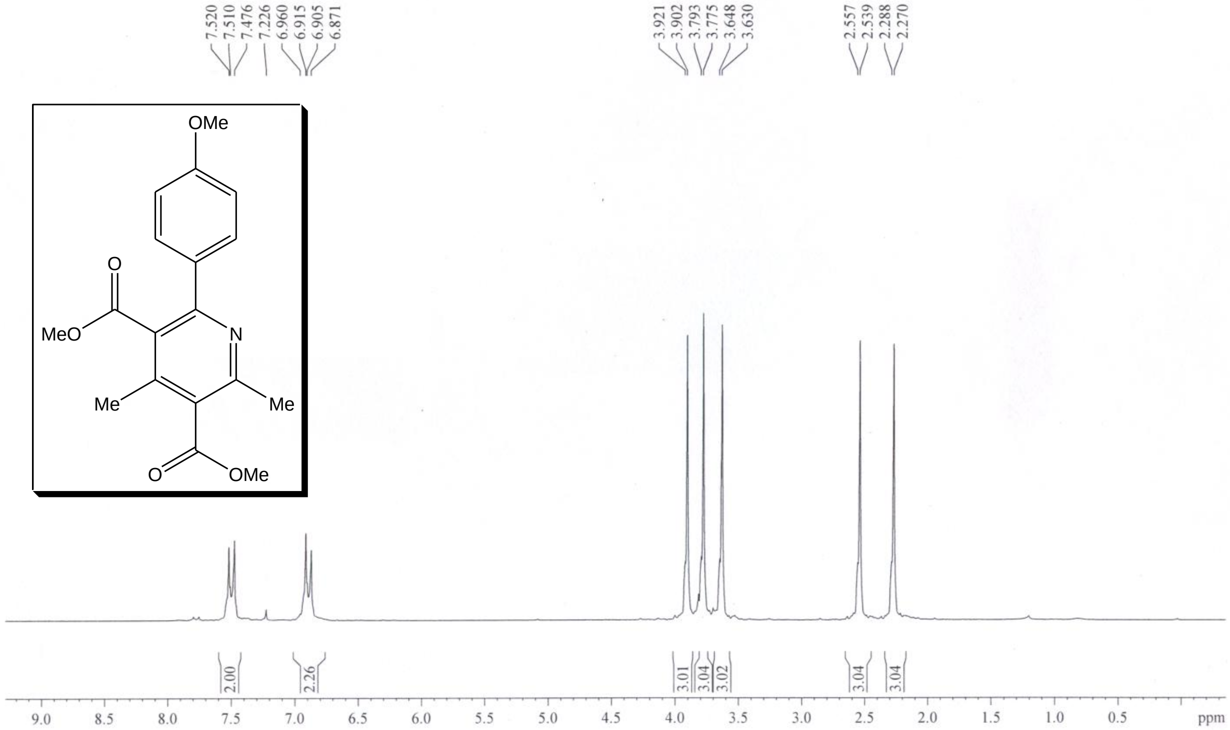
Diethyl 2-(4-methoxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



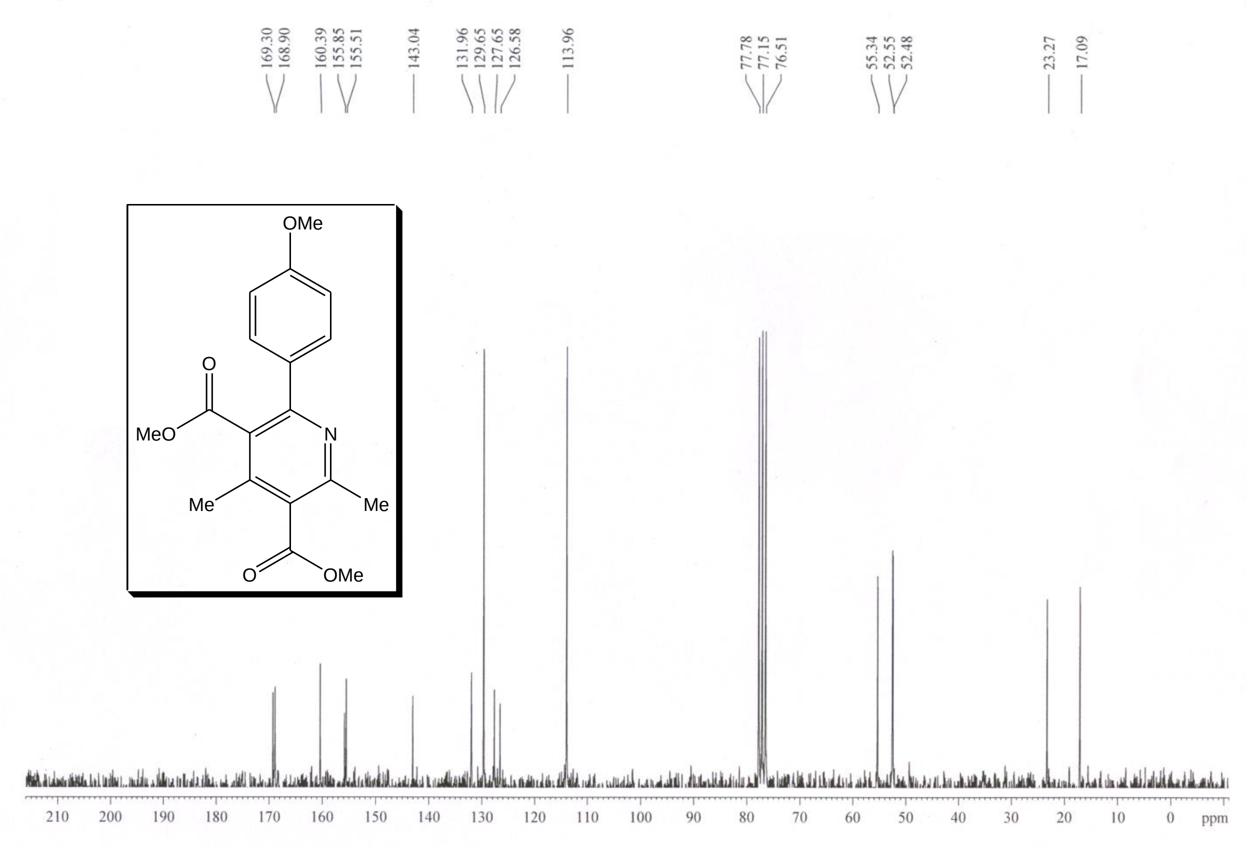
(8c)

Dimethyl 2-(4-methoxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



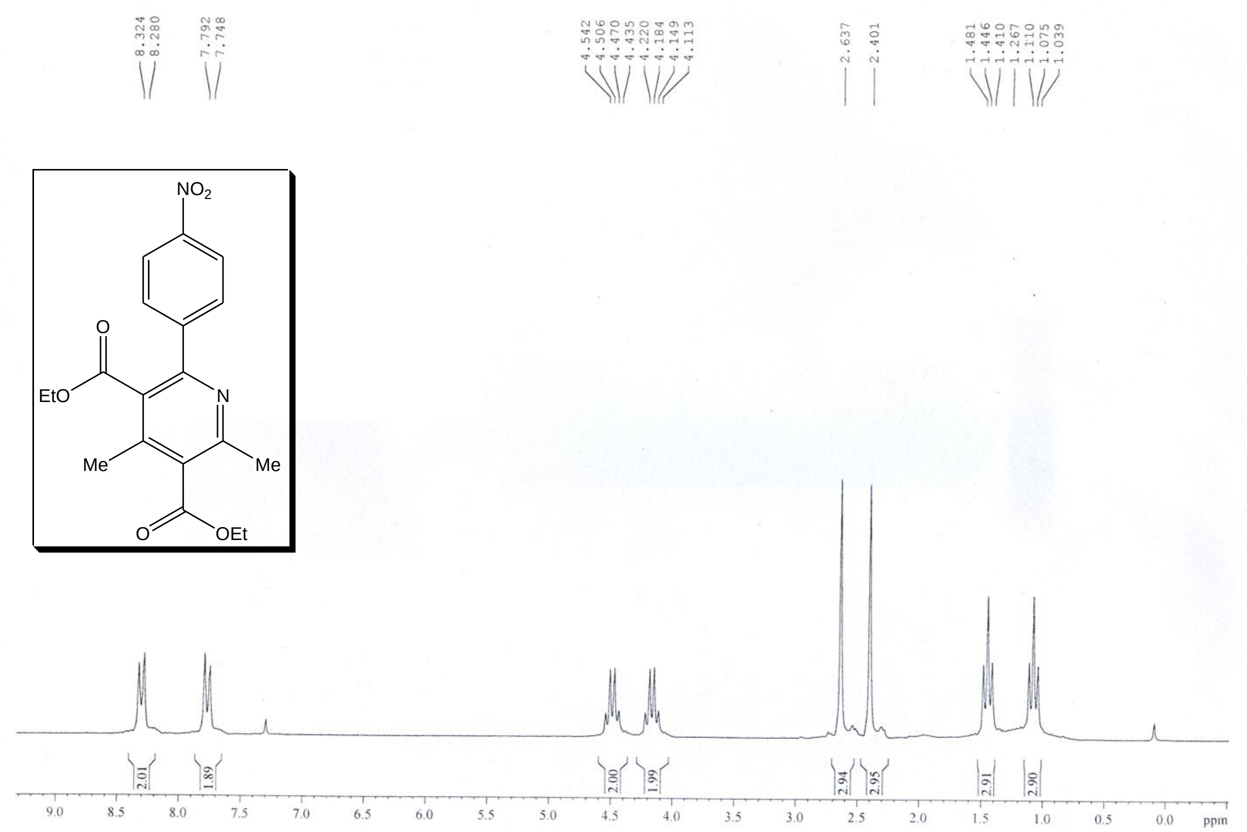
(8c)

Dimethyl 2-(4-methoxyphenyl)-4,6-dimethylpyridine-3,5-dicarboxylate



(9c)

Diethyl 2,4-dimethyl-6-(4-nitrophenyl)pyridine-3,5-dicarboxylate



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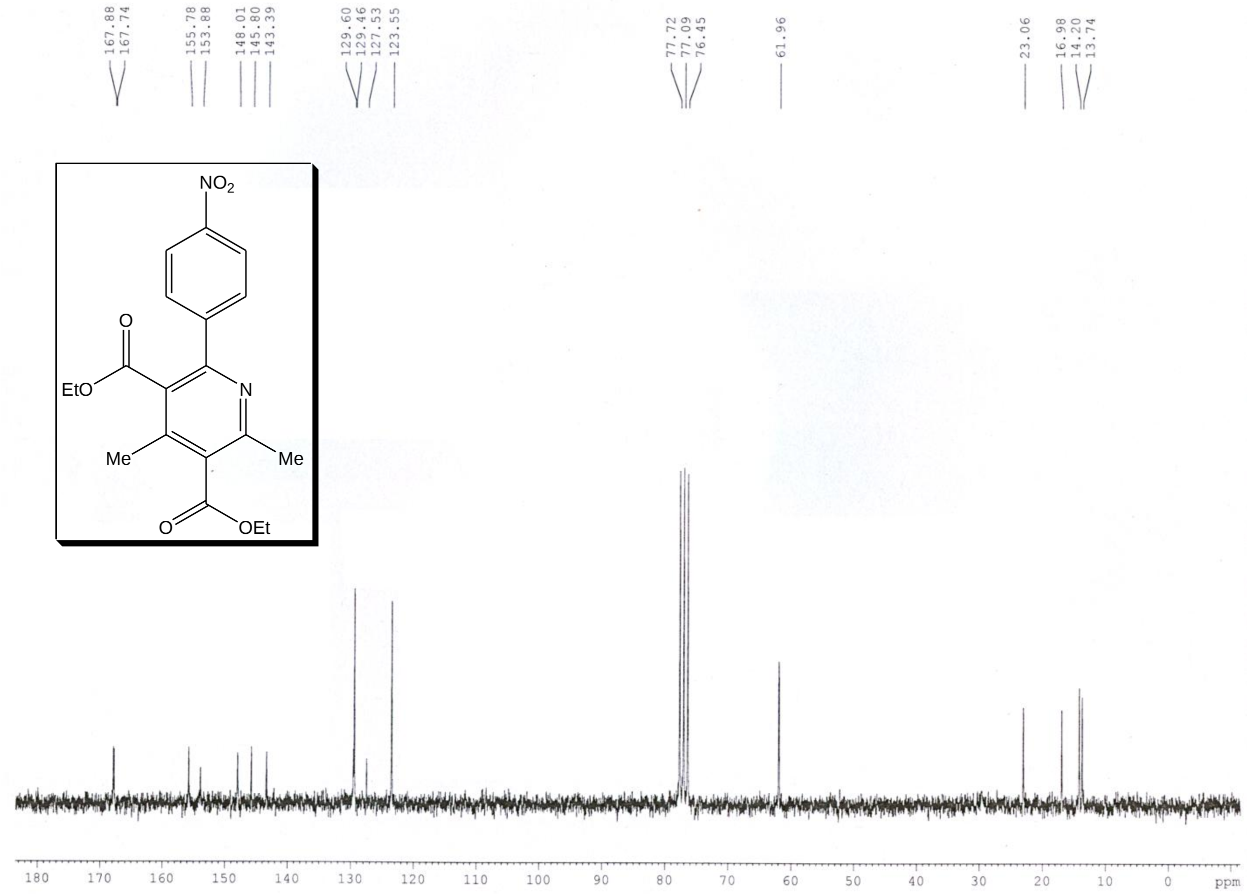
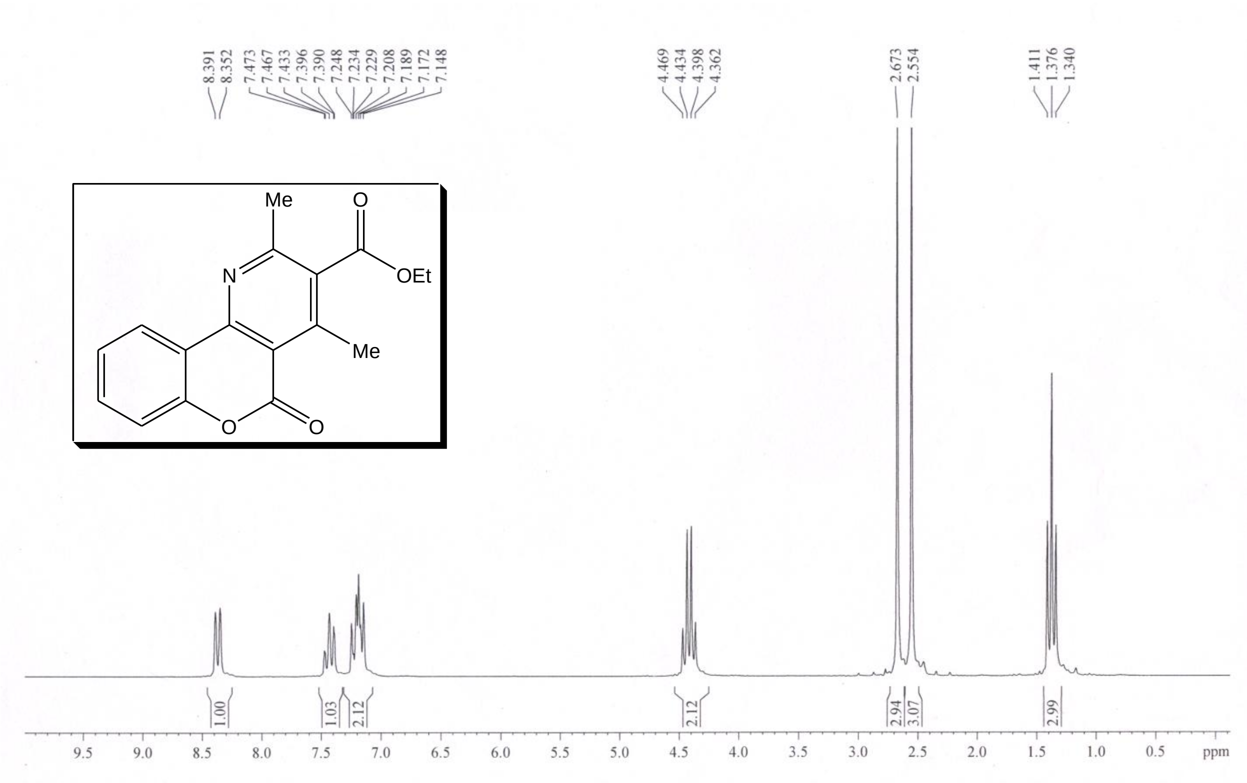
Diethyl 2,4-dimethyl-6-(4-nitrophenyl)pyridine-3,5-dicarboxylate



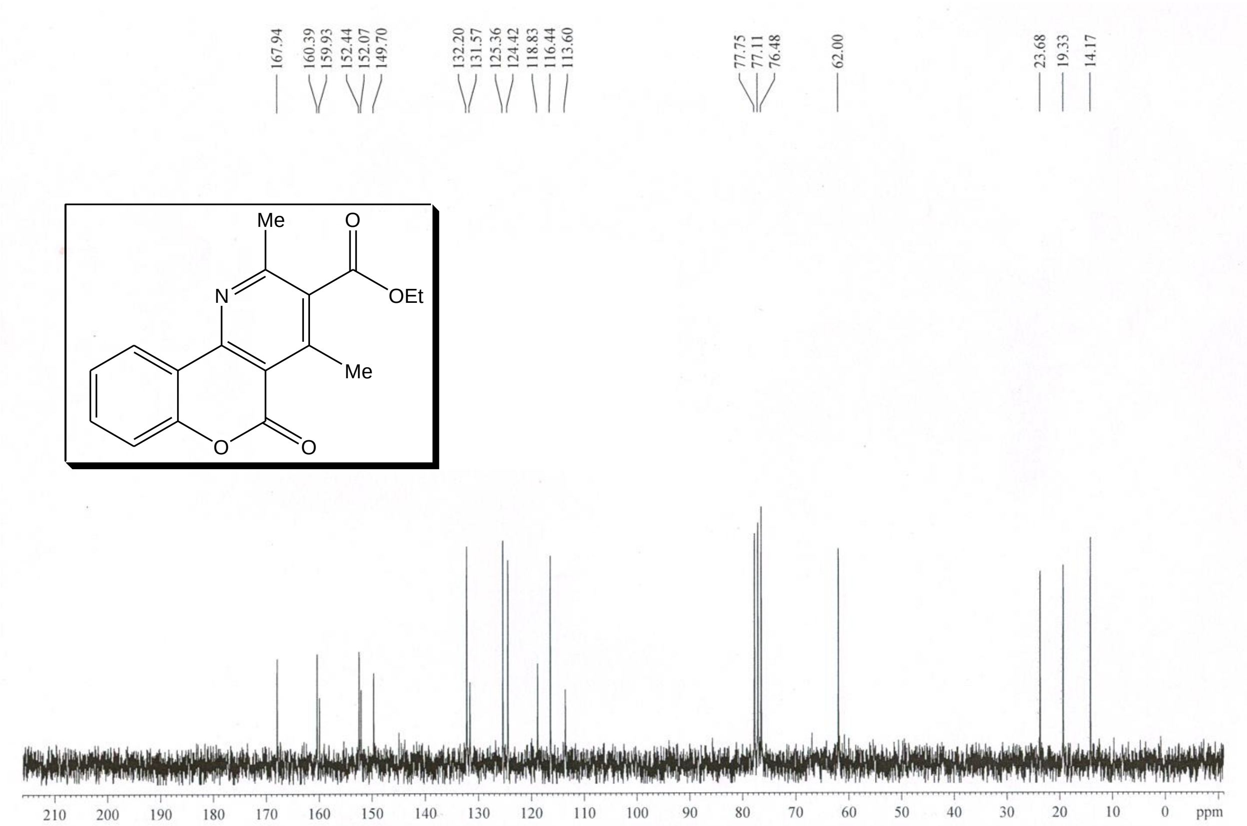
(10c)

Ethyl 2,4-dimethyl-5-oxo-5H-chromeno[4,3-*b*]pyridine-3-carboxylate



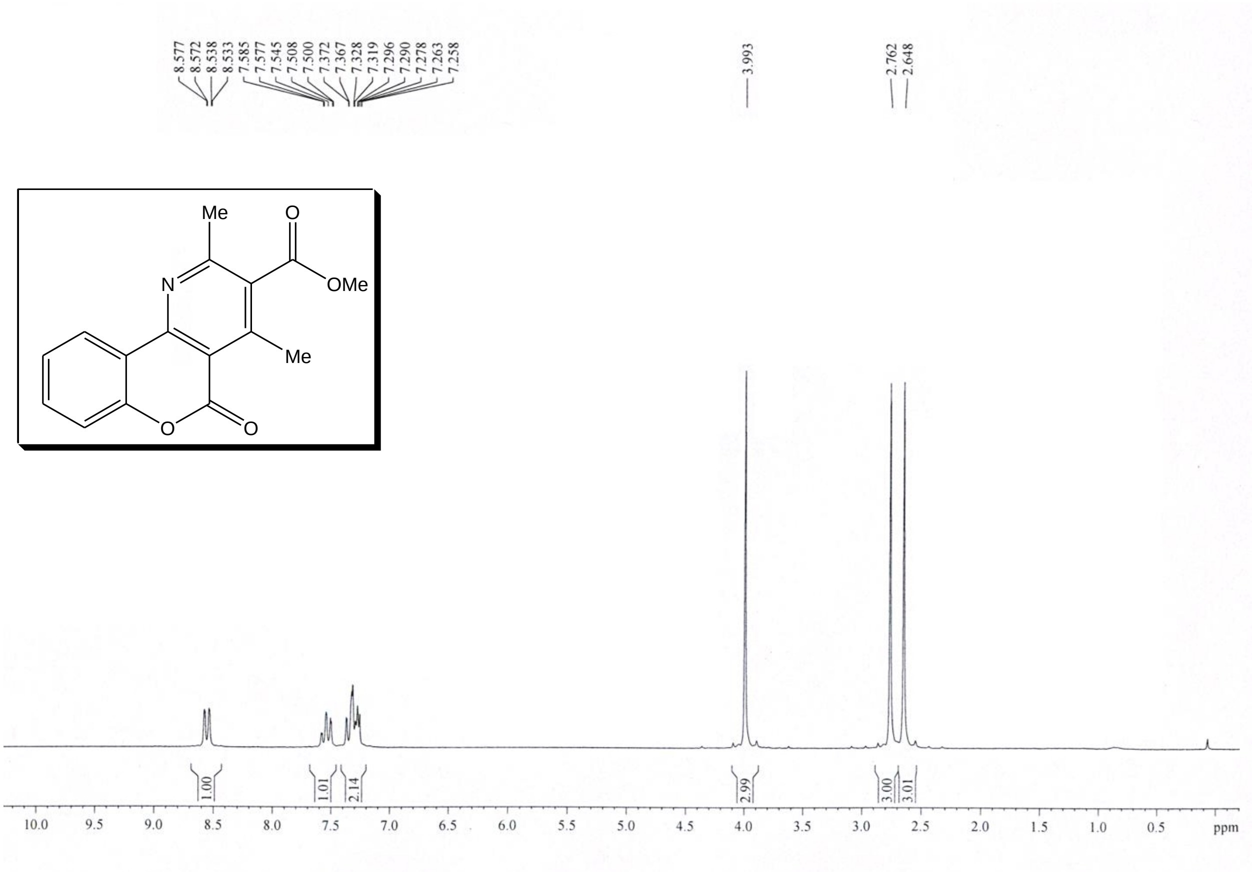
(10c)

Ethyl 2,4-dimethyl-5-oxo-5H-chromeno[4,3-*b*]pyridine-3-carboxylate



(11c)

Methyl 2,4-dimethyl-5-oxo-5H-chromeno[4,3-*b*]pyridine-3-carboxylate



(11c)

Methyl 2,4-dimethyl-5-oxo-5H-chromeno[4,3-*b*]pyridine-3-carboxylate