

# Supplementary Information

## Nano Aluminium Nitride as a Solid Source of Ammonia for the Preparation of Hantzsch 1,4-Dihydropyridines and Bis-(1,4-dihydropyridines) in Water via One Pot Multicomponent Reaction

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### General methods

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded 400 MHz (<sup>1</sup>H) or 100.6 MHz (<sup>13</sup>C). Chemical shifts are reported in ppm ( $\delta$ ) and are referenced to the solvent, i.e., 7.26/77.1 for CDCl<sub>3</sub> and 2.49/39.5 for DMSO-d<sub>6</sub>. Multiplicities are described as br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants ( $J$ ) are reported in Hertz (Hz). IR spectra were measured with a FT-IR spectrometer. Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 TLC plates. Purity and homogeneity of all materials was determined from TLC, <sup>1</sup>H NMR, and <sup>13</sup>C NMR.

### General procedure for the synthesis of 1,4-dihydropyridines

Aluminium nitride (0.123 g, 3 mmol) was added to a stirring mixture of 3-nitrobenzaldehyde (0.151 g, 1 mmol) and methyl acetoacetate (0.348 g, 3 mmol) at room temperature. The reaction vessel was sealed and allowed to warm to 80 °C over 6 h. Then reaction mixture cooled down to room temperature and the crude product extracted by dichloromethane. Dichloromethane was removed by simple evaporation. Finally crude product (0.343 g, 99%) recrystallized from EtOH/H<sub>2</sub>O to afford pure 1,4-dihydropyridine.

### Synthesis of 2,6-dimethyl-4-(3-nitrophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3j): as a typical procedure

Aluminium nitride (0.123 g, 3 mmol) was added to the stirring mixture of 3-nitrobenzaldehyde (0.151 g, 1 mmol), methyl acetoacetate (0.348 g, 3 mmol) at room temperature. The reaction vessel was sealed and allowed to warm to 80 °C over 6 h. Then reaction mixture cooled down

to room temperature and the crude product extracted by dichloromethane. Dichloromethane was removed by simple evaporation. Finally crude product (0.343 g, 99%) recrystallized from EtOH/H<sub>2</sub>O to afford pure 2,6-dimethyl-4-(3-nitrophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine in 60% yield (0.207 g) as yellow crystalline solid; mp 204.1–205.9 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3349 (N-H), 1704 (C=O), 1650, 1641, 1529, 1464, 1377, 1344, 1219; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.11 (s, 1H), 8.00–8.02 (d, 1H,  $J$  8.8 Hz), 7.63–7.65 (d, 1H,  $J$  8.0 Hz), 7.39–7.41 (t, 1H,  $J$  8.0 Hz), 5.72 (s, 1H), 5.11 (s, 1H), 3.66 (s, 6H), 2.38 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  167.5, 149.6, 148.4, 145.0, 134.2, 128.7, 122.7, 121.4, 103.1, 52.9, 39.6, 19.6 ppm.

### 2,6-Dimethyl-4-(iso-propyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3a)

Pale yellow crystalline solid; mp 162.2–163.4 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3336 (N-H), 1706 (C=O), 1652, 1463, 1435, 1377, 1219; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.64 (s, 1H), 3.90–3.89 (d, 1H,  $J$  5.2 Hz), 3.71 (s, 6H), 2.31 (s, 6H), 1.58–1.62 (sep, 1H,  $J$  6.8 Hz), 0.75–0.73 (d, 6H,  $J$  6.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.2, 145.1, 101.3, 50.8, 38.8, 35.4, 19.2, 18.2 ppm.

### 2,6-Dimethyl-4-(n-propyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3b)

Pale yellow crystalline solid; mp 133–135 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3343 (N-H), 1703 (C=O), 1650, 1492, 1435, 1329, 1218; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.54 (s, 1H), 3.92 (m, 1H), 3.72 (s, 6H), 2.29 (s, 6H), 1.28–1.20 (m, 4H), 0.85–0.83 (t, 3H,  $J$  6.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.6, 145.0, 103, 50.9, 39.2, 32.8, 19.4, 17.9, 14.3 ppm.

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**2,6-Dimethyl-4-(2-phenylethylene)-3,5-dicarbomethoxy-1,4-dihydropyridine (3c)**

Pale yellow crystalline solid; mp 172-173.5 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3335 (N-H), 1698 (C=O), 1647, 1489, 1465, 1377, 1226; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.34-7.17 (m, 5H), 6.20-6.17 (m, 2H), 5.67 (s, 1H), 4.63-4.62 (d, 1H, J 5.2 Hz), 3.74 (s, 6H), 2.35 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.0, 145.4, 137.7, 131.8, 128.4, 128.0, 126.9, 126.3, 101.2, 51.2, 36.2, 19.4 ppm.

**2,6-Dimethyl-4-(phenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3d)**

Pale yellow crystalline solid; mp: 195.5-196.5 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3342 (N-H), 1699 (C=O), 1649, 1464, 1377, 1344, 1220; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.26-7.14 (m, 5H), 5.64 (s, 1H), 5.02 (s, 1H), 3.66 (s, 6H), 2.35 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.1, 147.4, 144.3, 128.0, 127.6, 126.2, 103.8, 51.0, 39.3, 19.5 ppm.

**2,6-Dimethyl-4-(4-chlorophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3e)**

Pale yellow crystalline solid; mp 192.8-194.0 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3323 (N-H), 1702 (C=O), 1650, 1488, 1465, 1377, 1219 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.26-7.19 (m, 4H), 5.64 (s, 1H), 4.98 (s, 1H), 3.65 (s, 6H), 2.35 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.9, 146.0, 144.4, 131.8, 129.1, 128.1, 103.6, 51.1, 39.0, 19.5 ppm.

**2,6-Dimethyl-4-(4-bromophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3f)**

Pale yellow crystalline solid; mp 197.8-198.9 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3319 (N-H), 1698 (C=O), 1650, 1483, 1462, 1435, 1215; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.35-7.33 (d, 2H, J 8.4), 7.16-7.14 (d, 2H, J 8.4), 5.71 (s, 1H), 4.97 (s, 1H), 3.65 (s, 6H), 2.34 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.9, 146.5, 144.4, 131.1, 129.5, 120.0, 103.5, 51.1, 39.0, 19.6 ppm.

**2,6-Dimethyl-4-(4-methoxyphenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3g)**

Pale yellow crystalline solid; mp 187.0-187.6 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3346 (N-H), 1697 (C=O), 1649, 1606, 1465, 1377, 1302, 1216; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.20-7.18 (d, 2H, J 8.8), 6.77-6.75 (d, 2H, J 8.8), 5.58 (s, 1H), 4.95 (s, 1H), 3.76 (s, 3H), 3.66 (s, 6H), 2.35 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.1, 158.0, 143.9, 139.9, 128.6, 113.4, 104.2, 55.1, 51.0, 38.4, 19.6 ppm.

**2,6-Dimethyl-4-(4-fluorophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3h)**

Pale yellow crystalline solid; mp 171.0-172.0 °C; IR

(KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3349 (N-H), 1707 (C=O), 1650, 1465, 1435, 1377, 1343, 1218; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.24-7.21 (m, 2H), 6.92-6.88 (m, 2H), 5.62 (s, 1H), 4.99 (s, 1H), 3.66 (s, 6H), 2.35 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.0, 162.6, 160.2, 144.3, 143.4, 143.3, 129.1, 129, 114.8, 114.6, 103.8, 51.0, 38.7, 19.5 ppm.

**2,6-Dimethyl-4-(3,4-dimethoxyphenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine (3i)**

Pale yellow crystalline solid; mp 148.5-149.5 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3313 (N-H), 1698 (C=O), 1649, 1492, 1463, 1377, 1267, 1213; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.88 (s, 1H), 6.79-6.72 (q, 2H, J 8 Hz), 5.62 (s, 1H), 4.97 (s, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.67 (s, 6H), 2.35 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.1, 148.4, 147.4, 144.0, 140.3, 119.4, 111.5, 111.0, 77.3, 55.8, 50.98, 38.8, 19.6 ppm.

**2,6-Dimethyl-4-(iso-propyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3k)**

Pale yellow crystalline solid; mp 97.0-99.0 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3341 (N-H), 1696 (C=O), 1652, 1464, 1377, 1216; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.55 (s, 1H), 4.25-4.12 (m, 4H), 3.94-3.92 (d, 1H, J 5.6 Hz), 2.31 (s, 6H), 1.32-1.29 (t, 6H, J 7.2 Hz), 0.77-0.75 (d, 6H, J 6.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.2, 144.6, 101.7, 59.5, 38.8, 35.5, 19.3, 18.5, 14.4 ppm.

**2,6-Dimethyl-4-(n-propyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3l)**

Pale yellow crystalline solid; mp 125.2-126.3 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3350 (N-H), 1699 (C=O), 1465, 1378, 1299, 1213; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.49 (s, 1H), 4.25-4.12 (m, 4H), 3.96-3.93 (t, 1H, J 5.2 Hz), 2.29 (s, 6H), 1.32-1.29 (t, 6H, J 7.2 Hz), 1.25-1.23 (m, 4H), 0.87-0.83 (t, 3H, J 7.2 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.2, 144.7, 103.4, 59.6, 39.3, 32.7, 19.4, 18.0, 14.4, 14.3 ppm.

**2,6-Dimethyl-4-(phenyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3m)**

Pale yellow crystalline solid; mp 157.3-158.3 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3340 (N-H), 1687 (C=O), 1650, 1486, 1464, 1374, 1247, 1211; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.30-7.13 (m, 5H), 5.57 (s, 1H), 5.00 (s, 1H), 4.13-4.08 (q, 4H, J 7.2 Hz), 2.34 (s, 6H), 1.25-1.21 (t, 6H, J 7.2 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.7, 147.8, 144.0, 128.0, 127.8, 126.1, 104.0, 59.7, 39.6, 19.5, 14.3 ppm.

**2,6-Dimethyl-4-(4-chlorophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3n)**

Pale yellow crystalline solid; mp 149.5-151.0 °C; IR

(KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3357 (N-H), 1695 (C=O), 1652, 1486, 1463, 1377, 1214; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.23-7.21 (d, 2H, *J* 6.8 Hz), 7.18-7.16 (d, 2H, *J* 8 Hz), 5.56 (s, 1H), 4.96 (s, 1H), 4.10 (m, 4H), 2.34 (s, 6H), 1.24-1.21 (t, 6H, *J* 6.4 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  167.5, 146.4, 144.1, 131.7, 129.4, 127.9, 103.8, 59.8, 39.3, 19.5, 14.3 ppm.

**2,6-Dimethyl-4-(4-bromophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3o)**

Pale yellow crystalline solid; mp 165.5-166.5 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3360 (N-H), 1693 (C=O), 1652, 1486, 1463, 1377, 1214; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34-7.32 (d, 2H, *J* 8.4 Hz), 7.18-7.15 (d, 2H, *J* 8.4 Hz), 5.61 (s, 1H), 4.95 (s, 1H), 4.11-4.08 (q, 4H, *J* 4.8 Hz), 2.33 (s, 6H), 1.25-1.21 (t, 6H, *J* 7.2 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  167.4, 146.9, 144.1, 130.9, 129.8, 119.9, 103.7, 59.8, 39.3, 19.5, 14.3 ppm.

**2,6-Dimethyl-4-(4-methoxyphenyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3p)**

Pale yellow crystalline solid; mp 158.0-159.0 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3340 (N-H), 1689 (C=O), 1649, 1488, 1464, 1373, 1301, 1211; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.22-7.19 (d, 2H, *J* 8.8 Hz), 6.77-6.75 (d, 2H, *J* 8.4 Hz), 5.60 (s, 1H), 4.94 (s, 1H), 4.13-4.06 (q, 4H, *J* 5.2 Hz), 3.76 (s, 3H), 2.33 (s, 6H), 1.25-1.22 (t, 6H, *J* 6.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  167.8, 143.7, 140.4, 128.9, 113.2, 104.3, 59.7, 55.1, 38.8, 19.5, 14.3 ppm.

**2,6-Dimethyl-4-(4-fluorophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3q)**

Pale yellow crystalline solid; mp 149.0-150.5 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3342 (N-H), 1686 (C=O), 1650, 1488, 1461, 1373, 1299, 1211; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.82 (s, 1H), 7.16-7.00 (m, 4H), 4.83 (s, 1H), 3.99-3.96 (q, 4H, *J* 7.2 Hz), 2.24 (s, 6H), 1.13-1.10 (t, 6H, *J* 7.2 Hz) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.3, 162.2, 159.8, 145.9, 144.9, 144.8, 129.6, 129.5, 115.0, 114.7, 102.3, 59.4, 38.8, 18.6, 14.5 ppm.

**2,6-Dimethyl-4-(3,4-dimethoxyphenyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3r)**

Pale yellow crystalline solid; mp 132.0-133.0 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3352 (N-H), 1692 (C=O), 1644, 1623, 1463, 1377, 1304, 1122; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  6.89-6.72 (m, 3H), 5.57 (s, 1H), 4.95 (s, 1H), 4.15-4.08 (m, 4H), 3.84 (s, 3H), 3.83 (s, 3H), 2.34 (s, 6H), 1.26-1.23 (t, 6H, *J* 6.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.7, 148.1, 147.3, 143.8, 140.8, 119.8, 111.8, 110.9, 104.1, 59.7, 55.8, 55.7, 39.0, 19.5, 14.3 ppm.

**2,6-Dimethyl-4-(3-nitrophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine (3s)**

Pale yellow crystalline solid; mp 160.0-161.0 °C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3342 (N-H), 1699 (C=O), 1652, 1464, 1376, 1348, 1211; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.13 (s, 1H), 8.02-8.00 (d, 1H, *J* 8.4 Hz), 5.68 (s, 1H), 5.10 (s, 1H), 4.14-4.06 (q, 4H, *J* 7.2 Hz), 2.38 (s, 6H), 1.25-1.21 (t, 6H, *J* 7.2 Hz) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.1, 149.9, 148.2, 144.8, 134.5, 128.6, 123.1, 121.3, 103.3, 60.0, 40.0, 19.6, 14.2 ppm.

**1,3-Bis-(2,6-diethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene (3'a)**

Pale yellow crystalline solid; mp 181-185 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.75 (s, 2H), 6.85-7.00 (m, 4H), 4.79 (s, 2H), 3.93-3.98 (q, 8H, *J* 6.8 Hz), 2.23 (s, 12H), 1.08-1.12 (t, 12H, *J* 6.8 Hz) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.4, 147.9, 145.7, 127.7, 126.7, 125.3, 102.3, 59.3, 18.6, 14.6 ppm.

**1,4-Bis-(2,6-diethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene (3'b)**

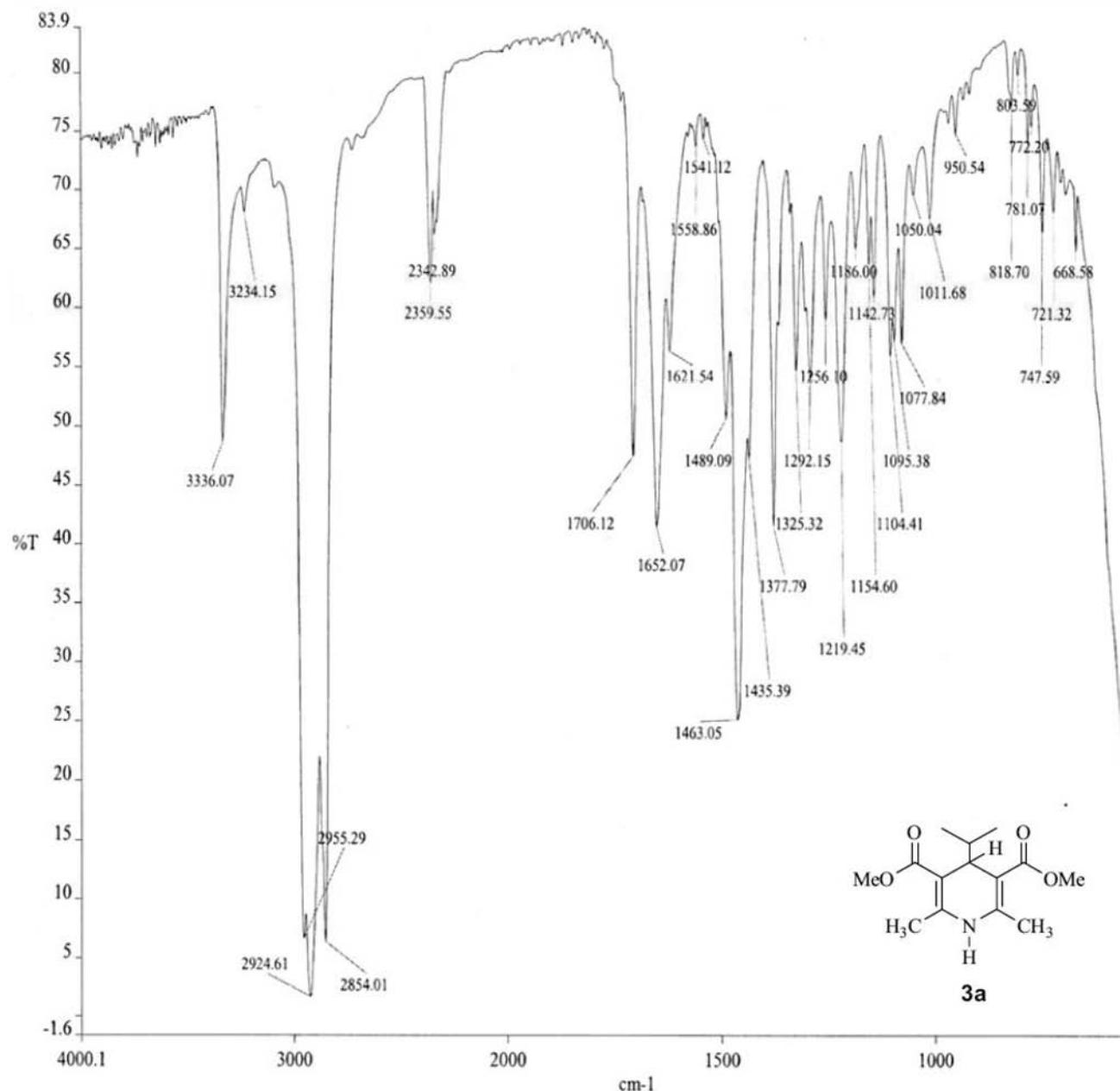
Pale yellow crystalline solid; mp 289-293 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.75 (s, 2H), 6.95 (s, 4H), 4.76 (s, 2H), 3.93-4.00 (q, 8H, *J* 7.2 Hz), 2.22 (s, 12H), 1.07-1.11 (t, 12H, *J* 7.2 Hz) ppm. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.5, 147.9, 146.1, 145.7, 127.3, 102.3, 59.4, 18.7, 14.6 ppm.

**1,3-Bis-(2,6-dimethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene (3'c)**

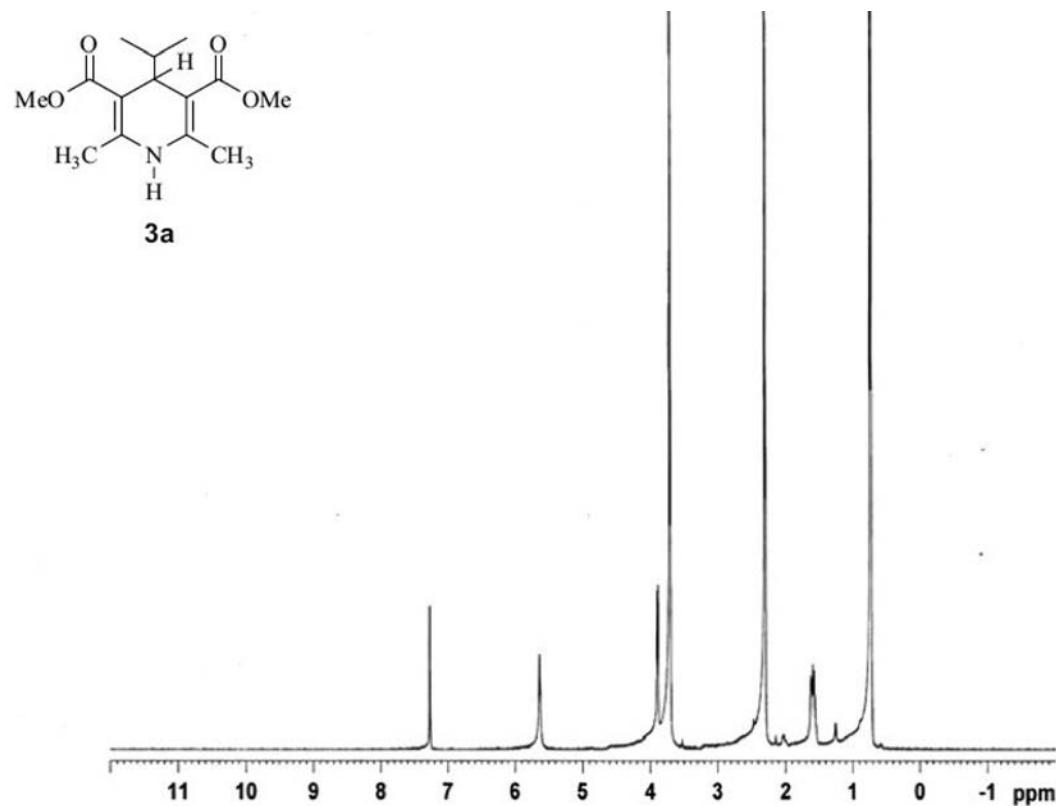
Pale yellow crystalline solid; mp 118-121 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.86 (s, 2H), 6.84-7.01 (m, 4H), 4.78 (s, 2H), 3.51 (s, 12H), 2.24 (s, 12H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.9, 147.8, 146.1, 128.1, 126.3, 125.0, 102.0, 51.0, 18.6 ppm.

**1,4-Bis-(2,6-dimethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene (3'd)**

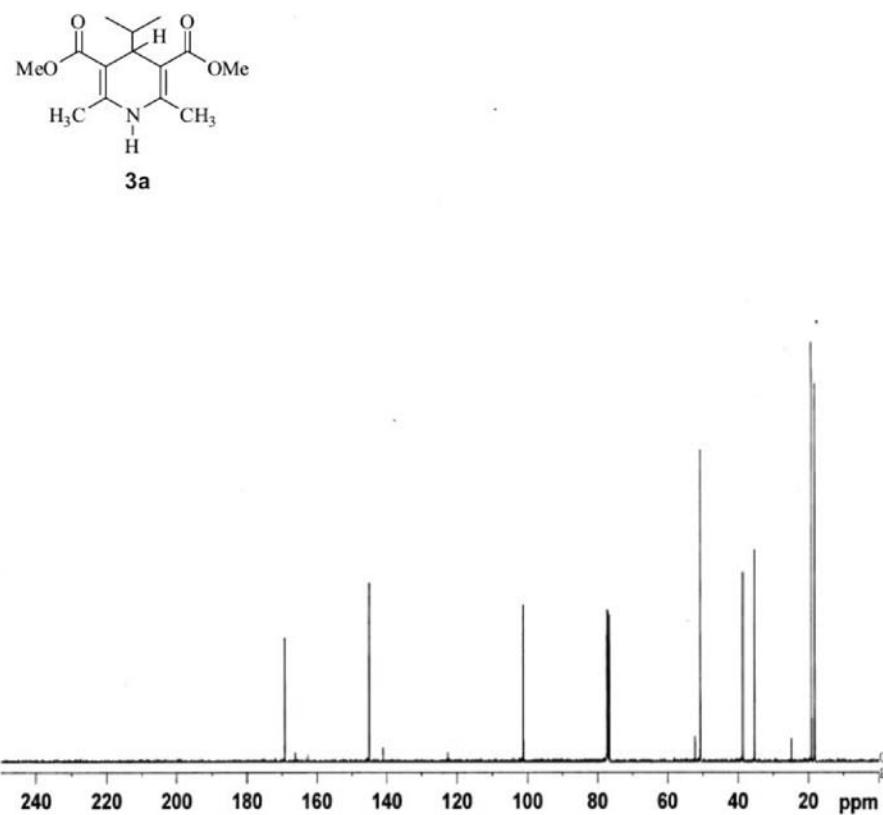
Pale yellow crystalline solid; mp 175-179 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.88 (s, 2H), 6.93-7.12 (m, 4H), 4.86 (s, 2H), 3.54 (s, 12H), 2.24 (s, 12H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.9, 146.3, 145.6, 127.1, 101.8, 51.1, 18.7 ppm.



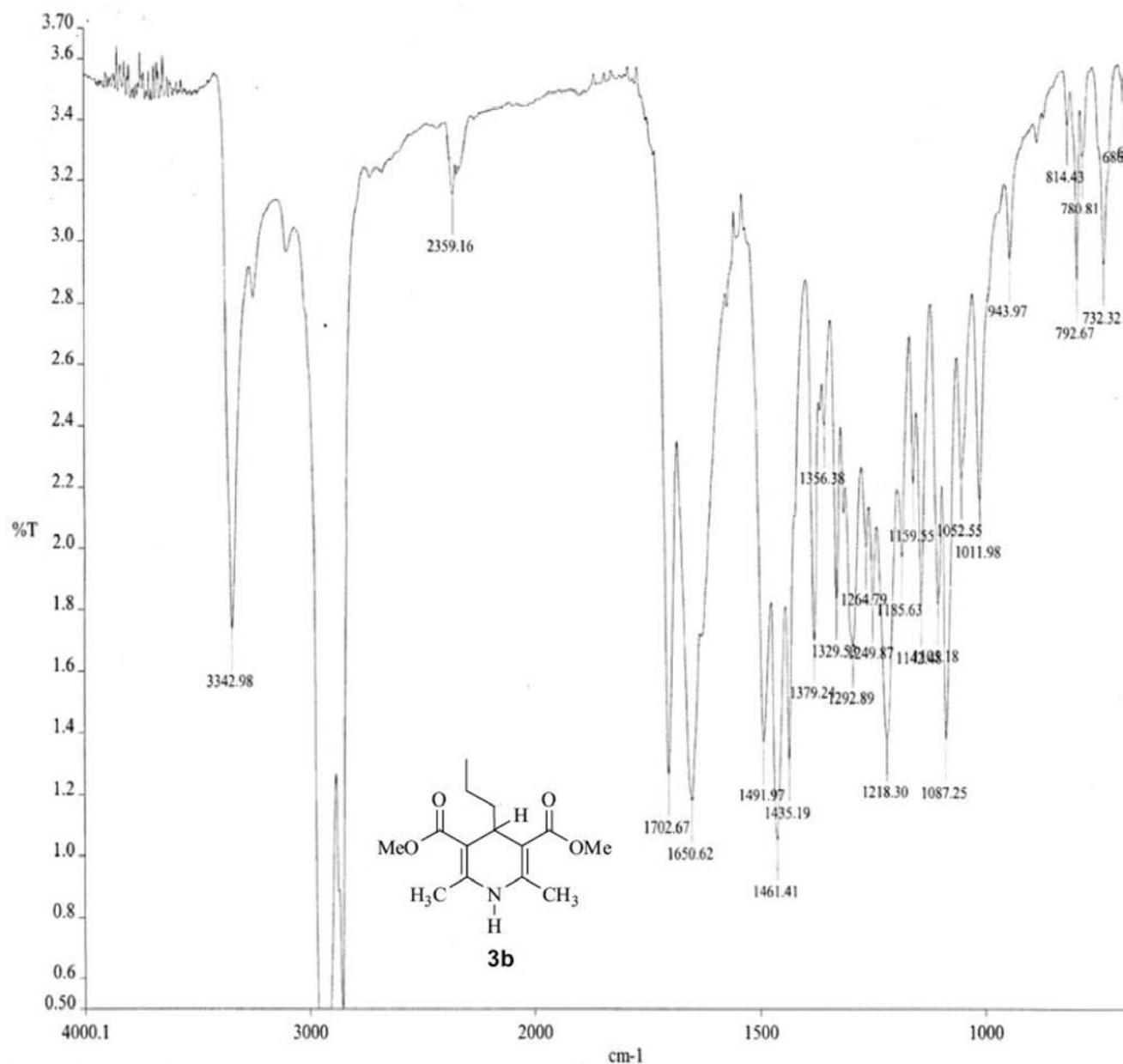
**Figure S1.** IR spectrum of 2,6-dimethyl-4-(iso-propyl)-3,5-dicarbomethoxy-1,4-dihdropyridine.



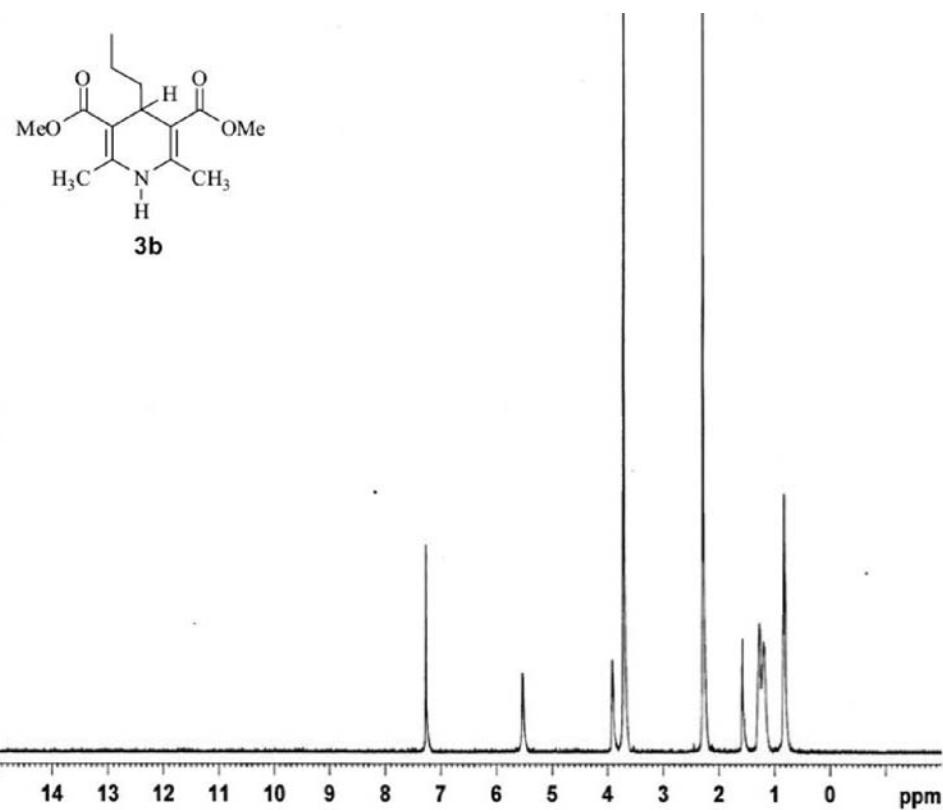
**Figure S2.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(iso-propyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



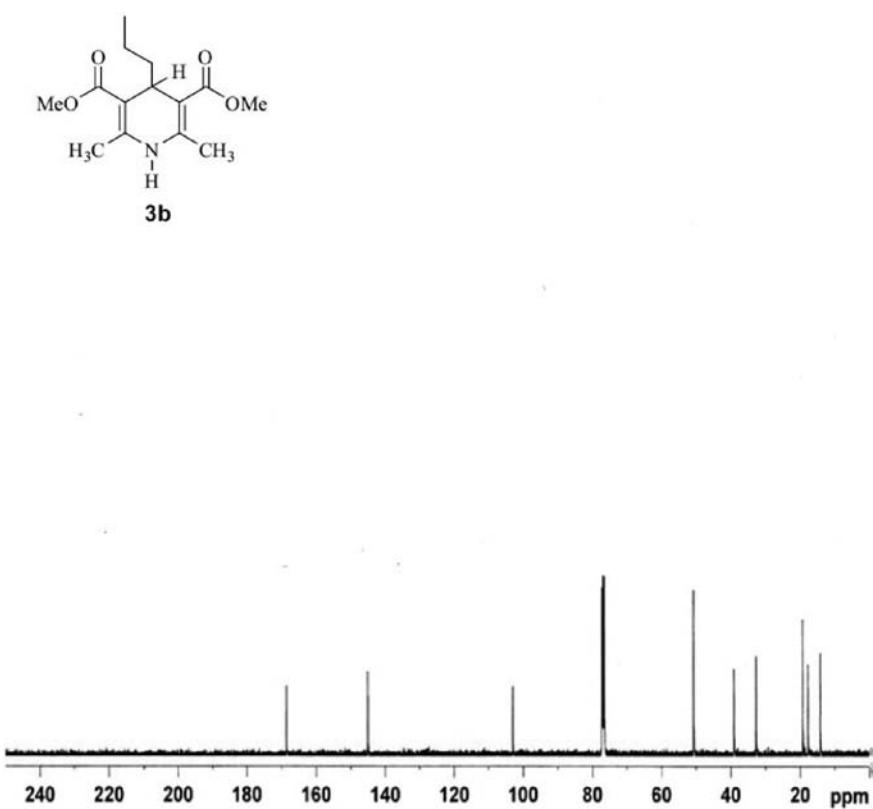
**Figure S3.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(iso-propyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



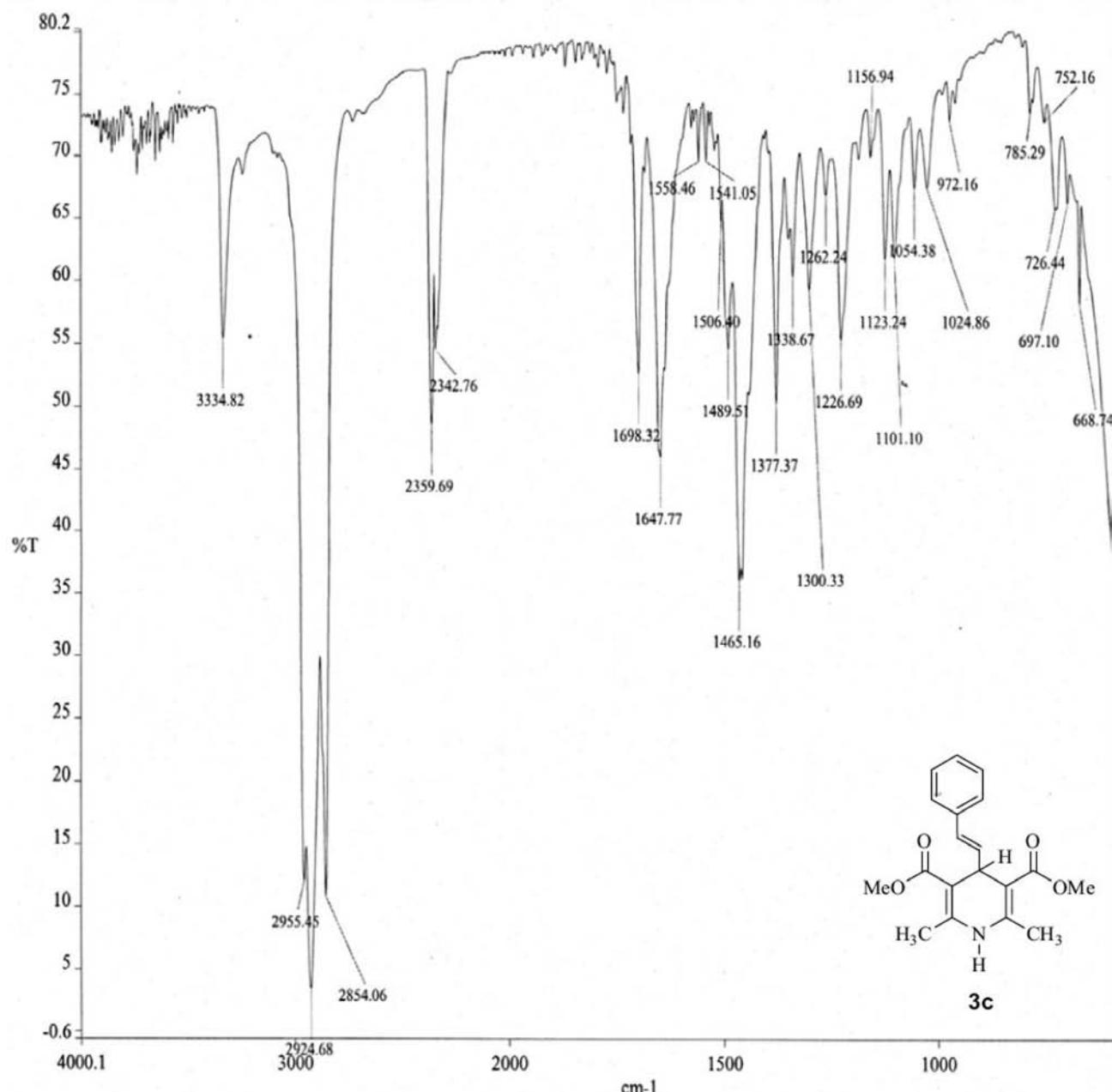
**Figure S4.** IR spectrum of 2,6-dimethyl-4-(n-propyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



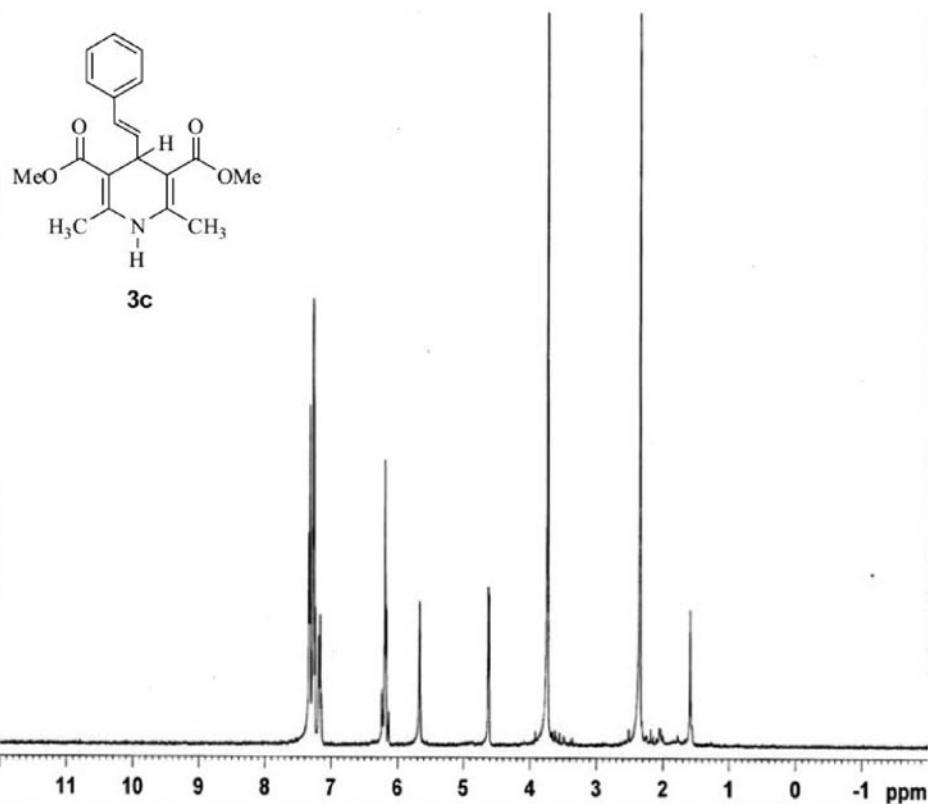
**Figure S5.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(n-propyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



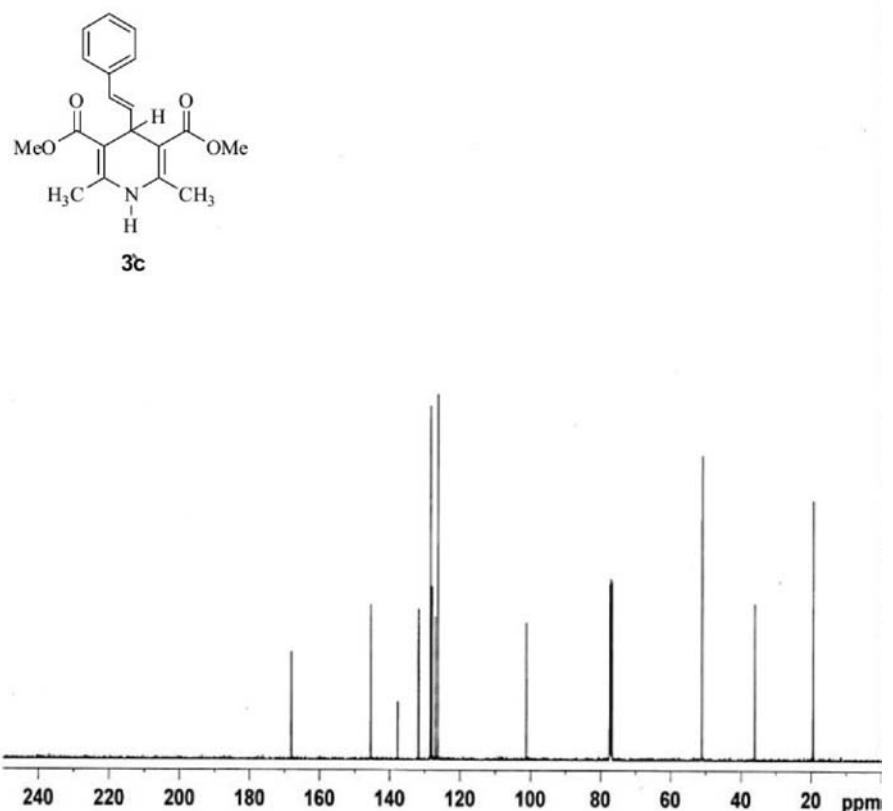
**Figure S6.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(n-propyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



**Figure S7.** IR spectrum of 2,6-dimethyl-4-(2-phenylethylene)-3,5-dicarbomethoxy-1,4-dihydropyridine.



**Figure S8.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(2-phenylethylene)-3,5-dicarbomethoxy-1,4-dihydropyridine.



**Figure S9.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(2-phenylethylene)-3,5-dicarbomethoxy-1,4-dihydropyridine.

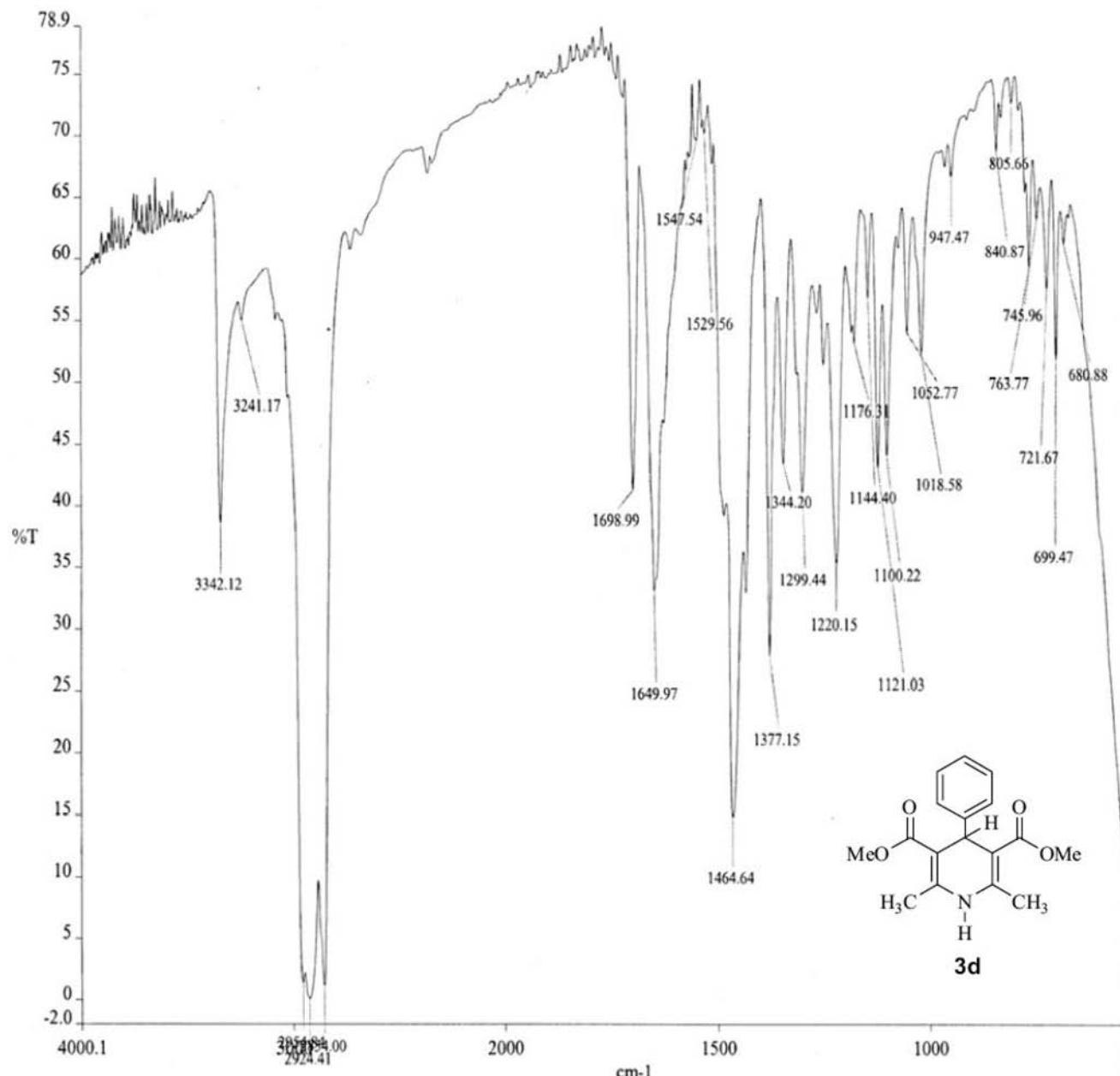
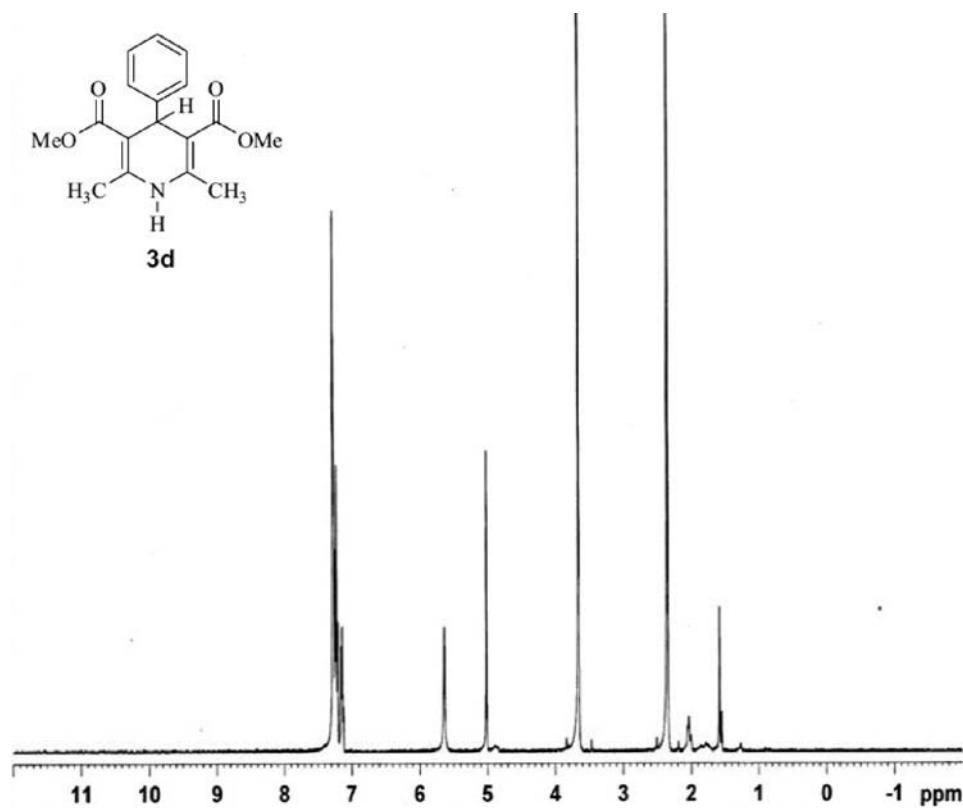
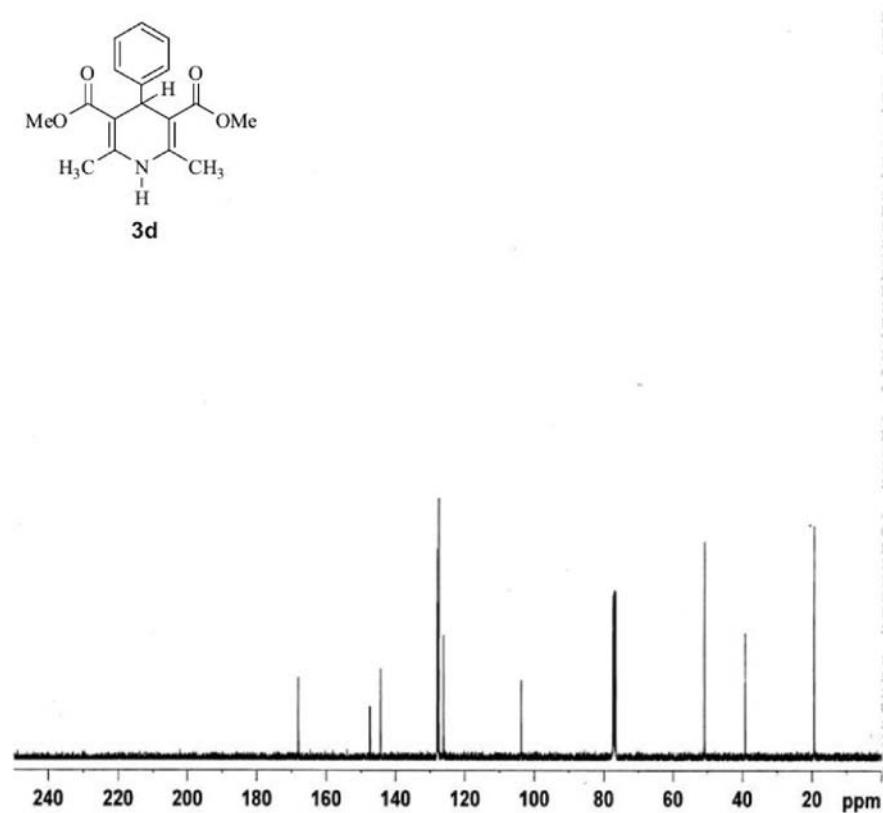


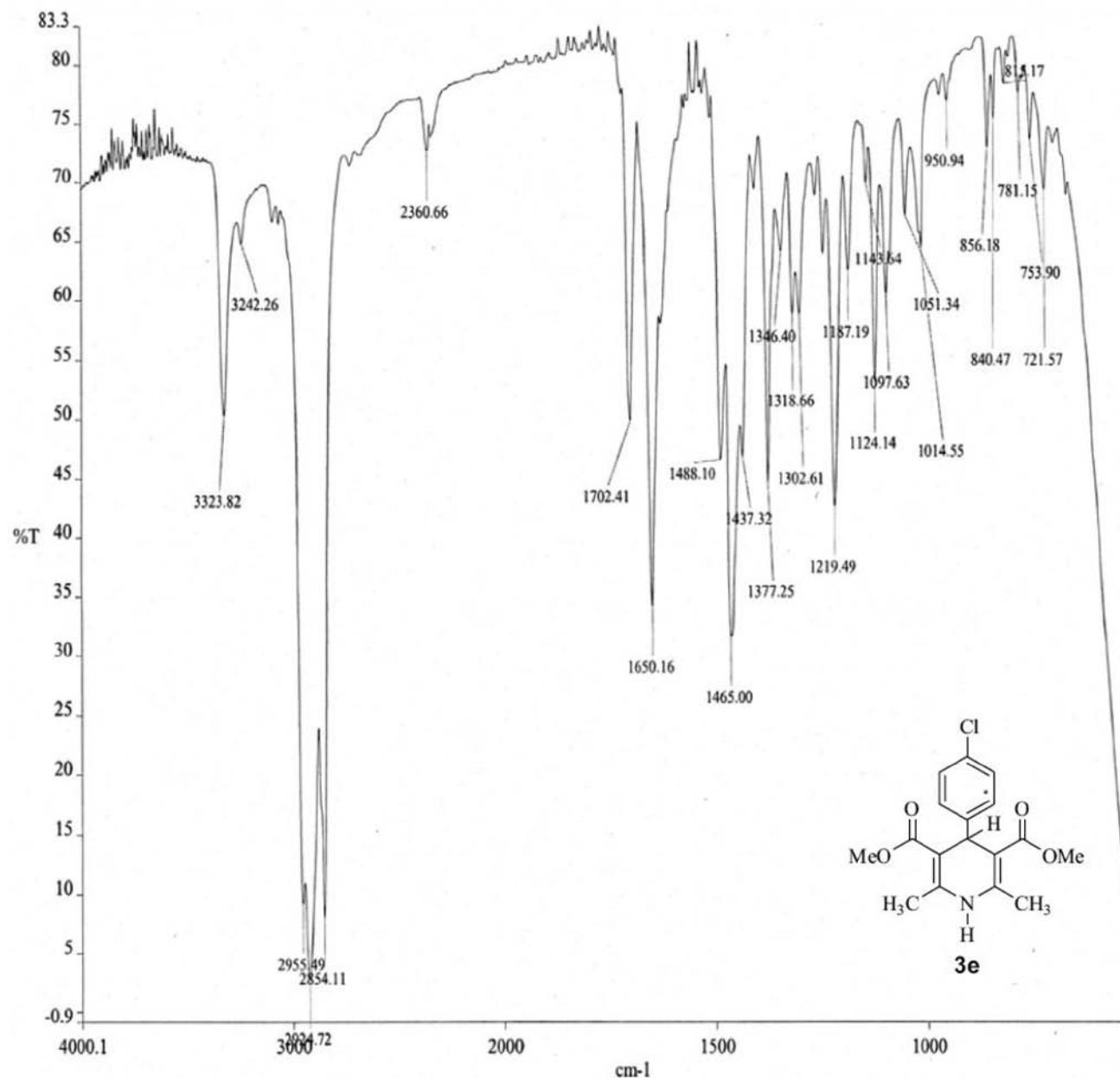
Figure S10. IR spectrum of 2,6-dimethyl-4-(phenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



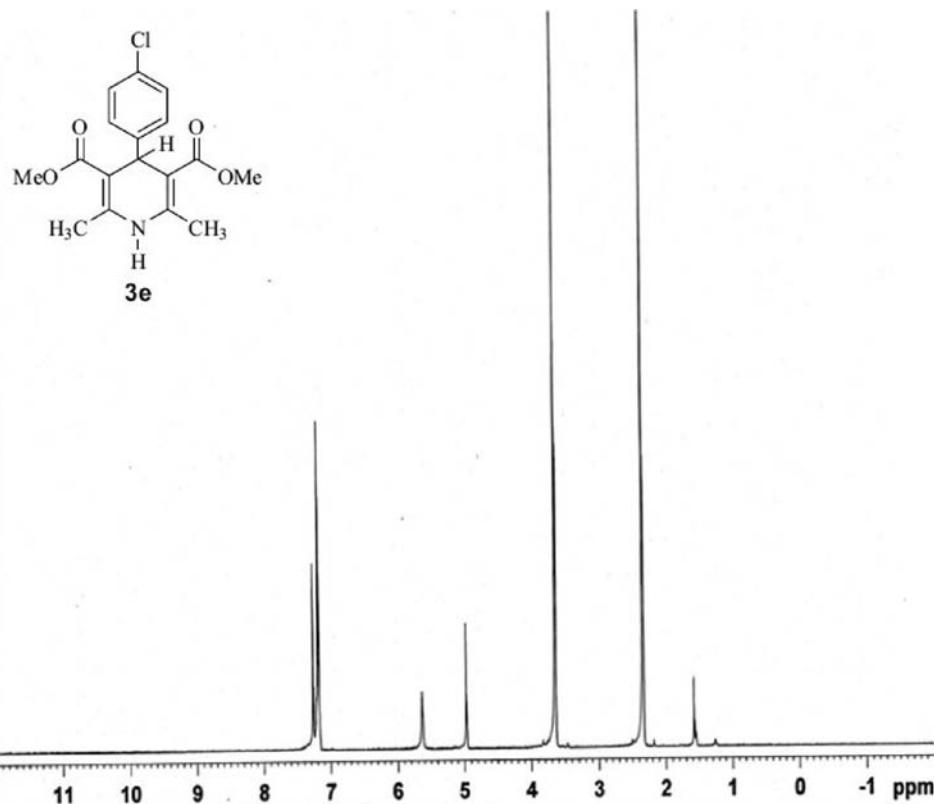
**Figure S11.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(phenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



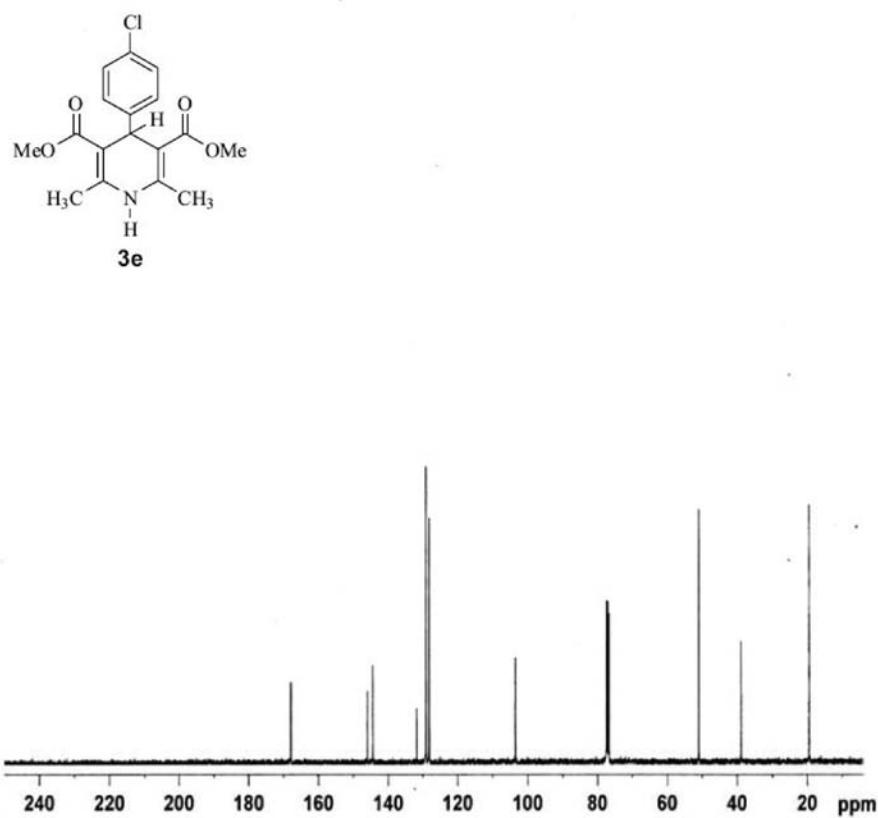
**Figure S12.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(phenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



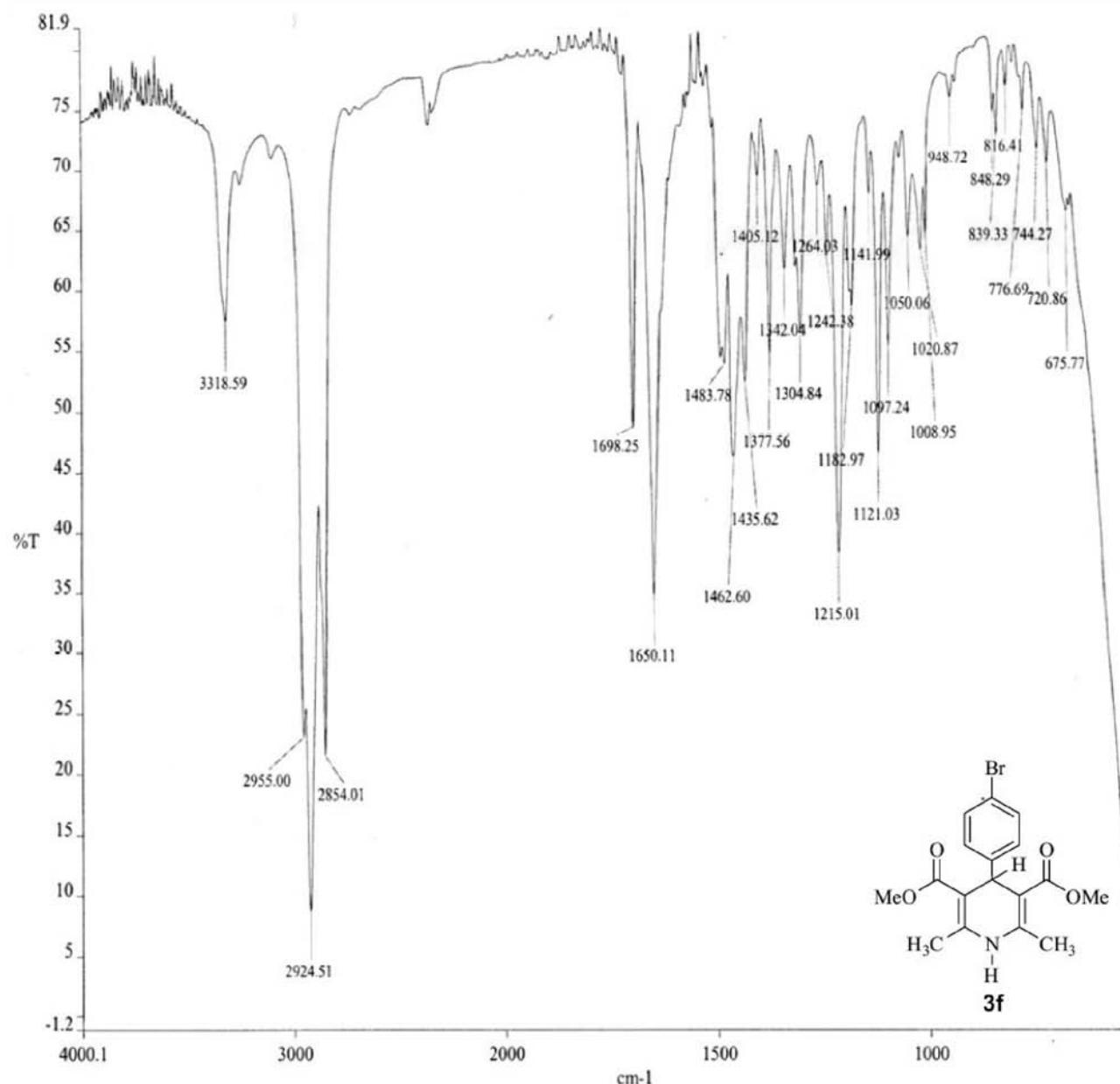
**Figure S13.** IR spectrum of 2,6-dimethyl-4-(4-chlorophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



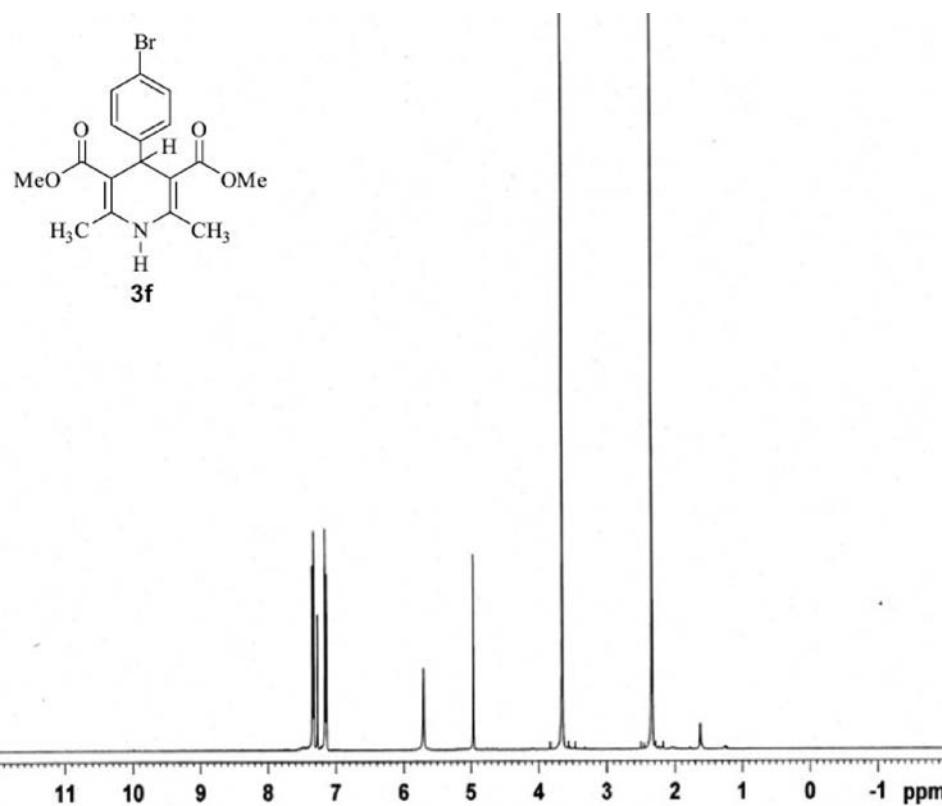
**Figure S14.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-chlorophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



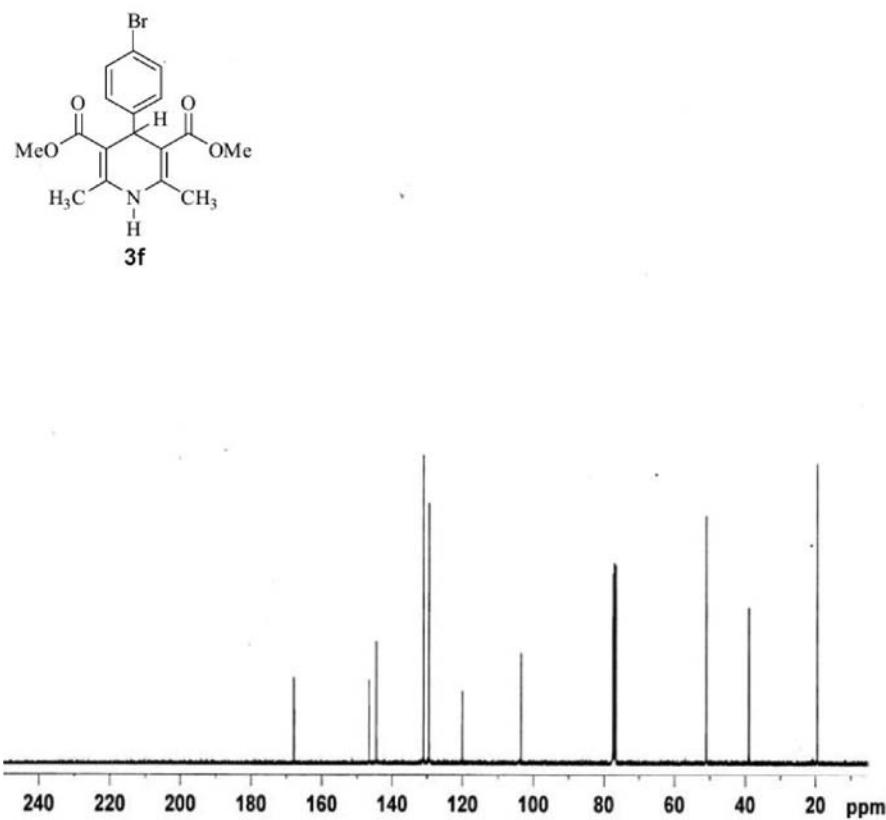
**Figure S15.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-chlorophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



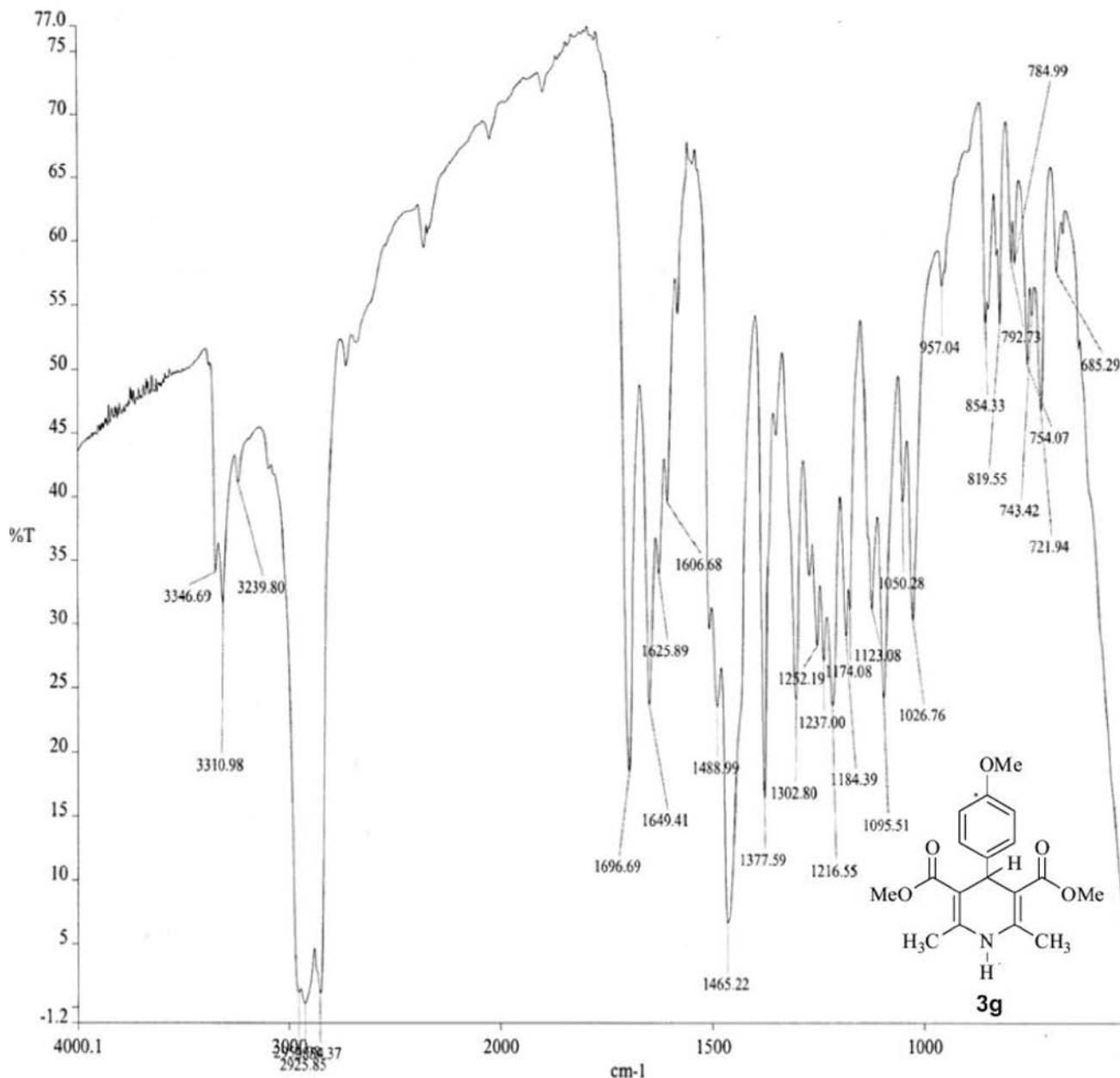
**Figure S16.** IR spectrum of 2,6-dimethyl-4-(4-bromophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



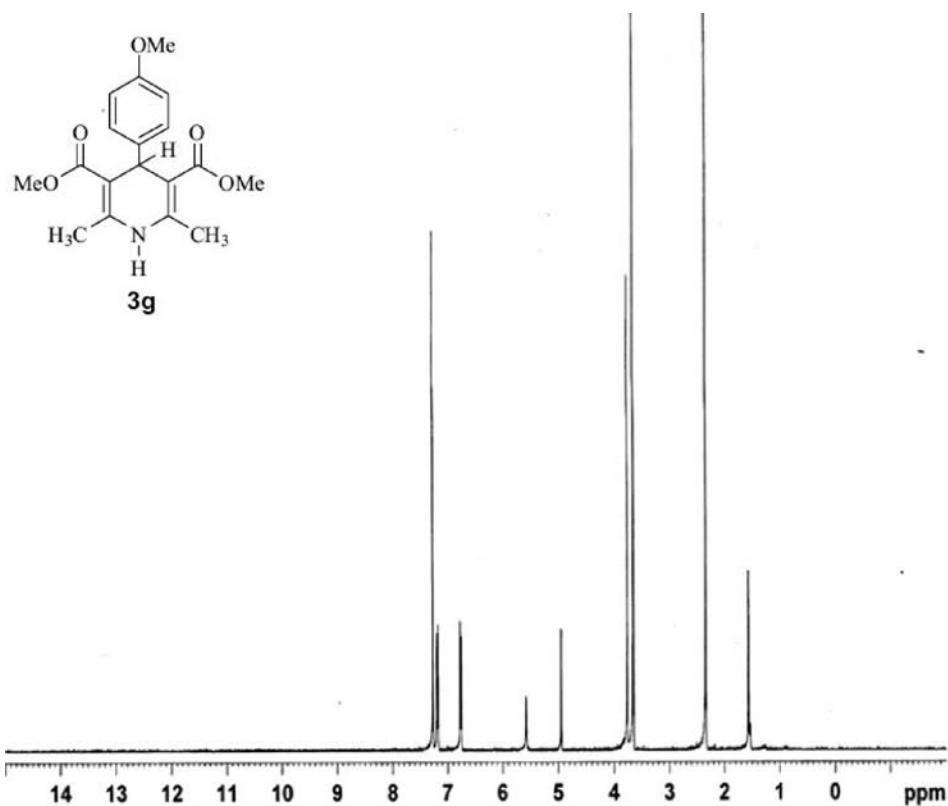
**Figure S17.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-bromophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



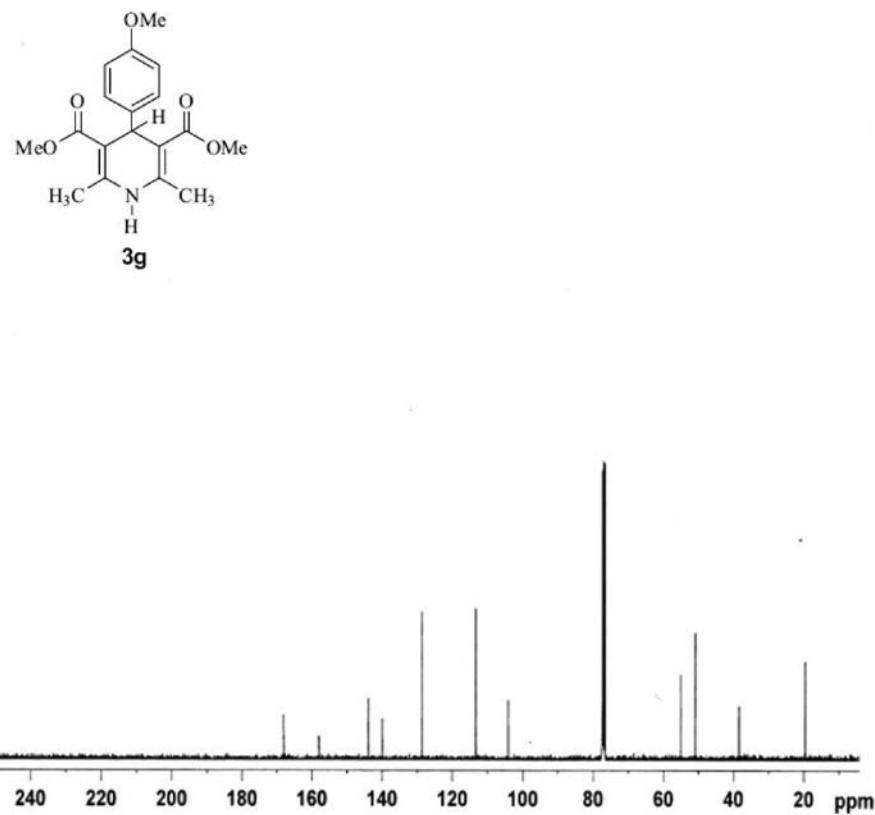
**Figure S18.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-bromophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



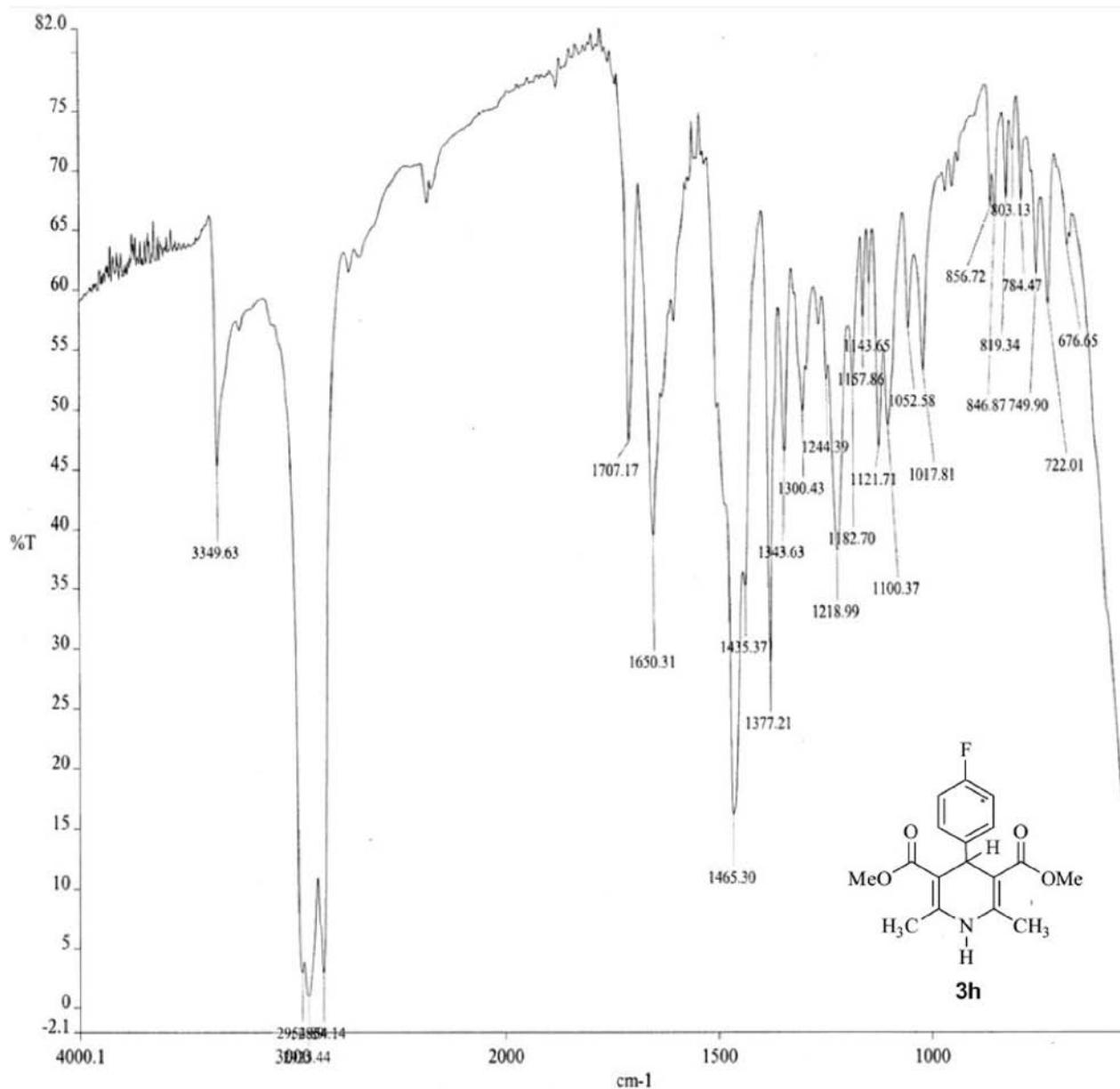
**Figure S19.** IR spectrum of 2,6-dimethyl-4-(4-methoxyphenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



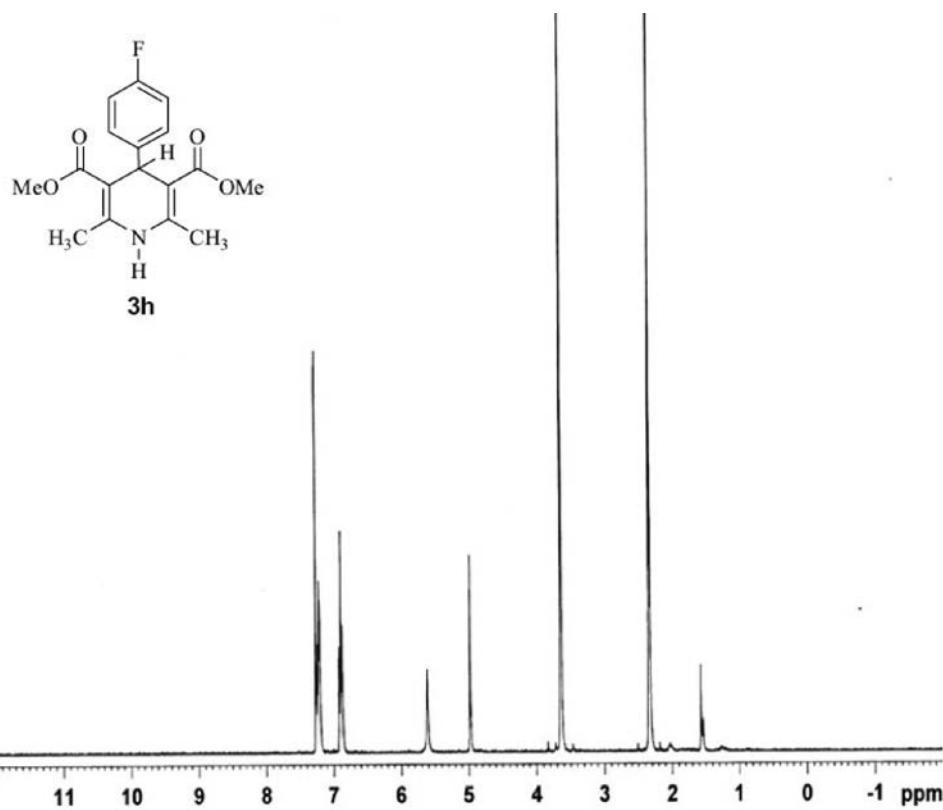
**Figure S20.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-methoxyphenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



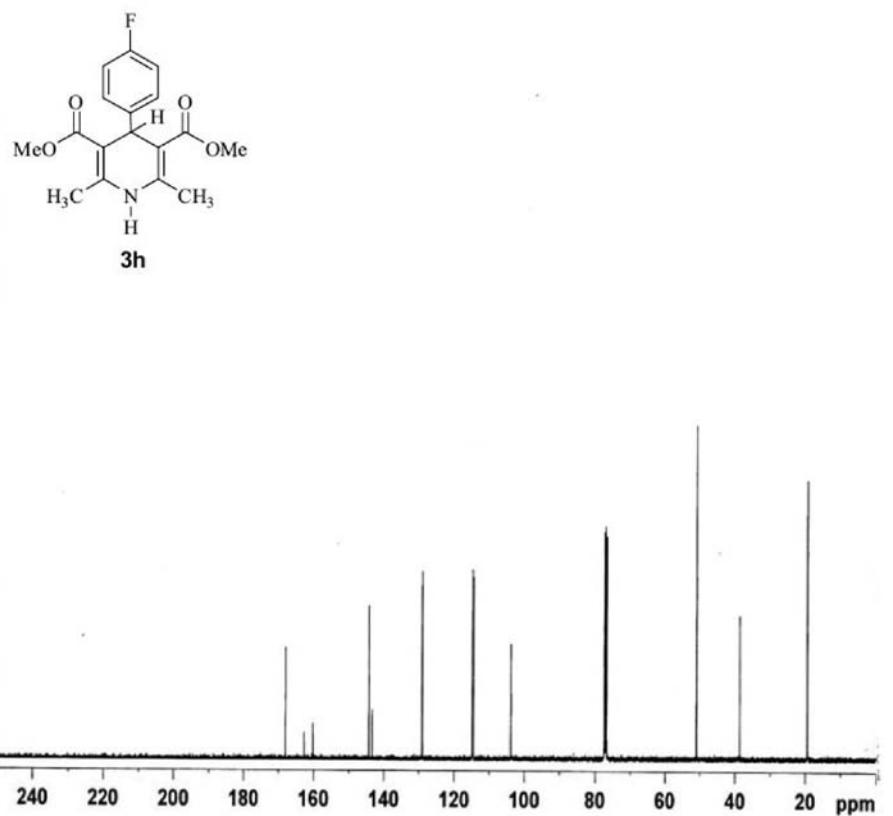
**Figure S21.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-methoxyphenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



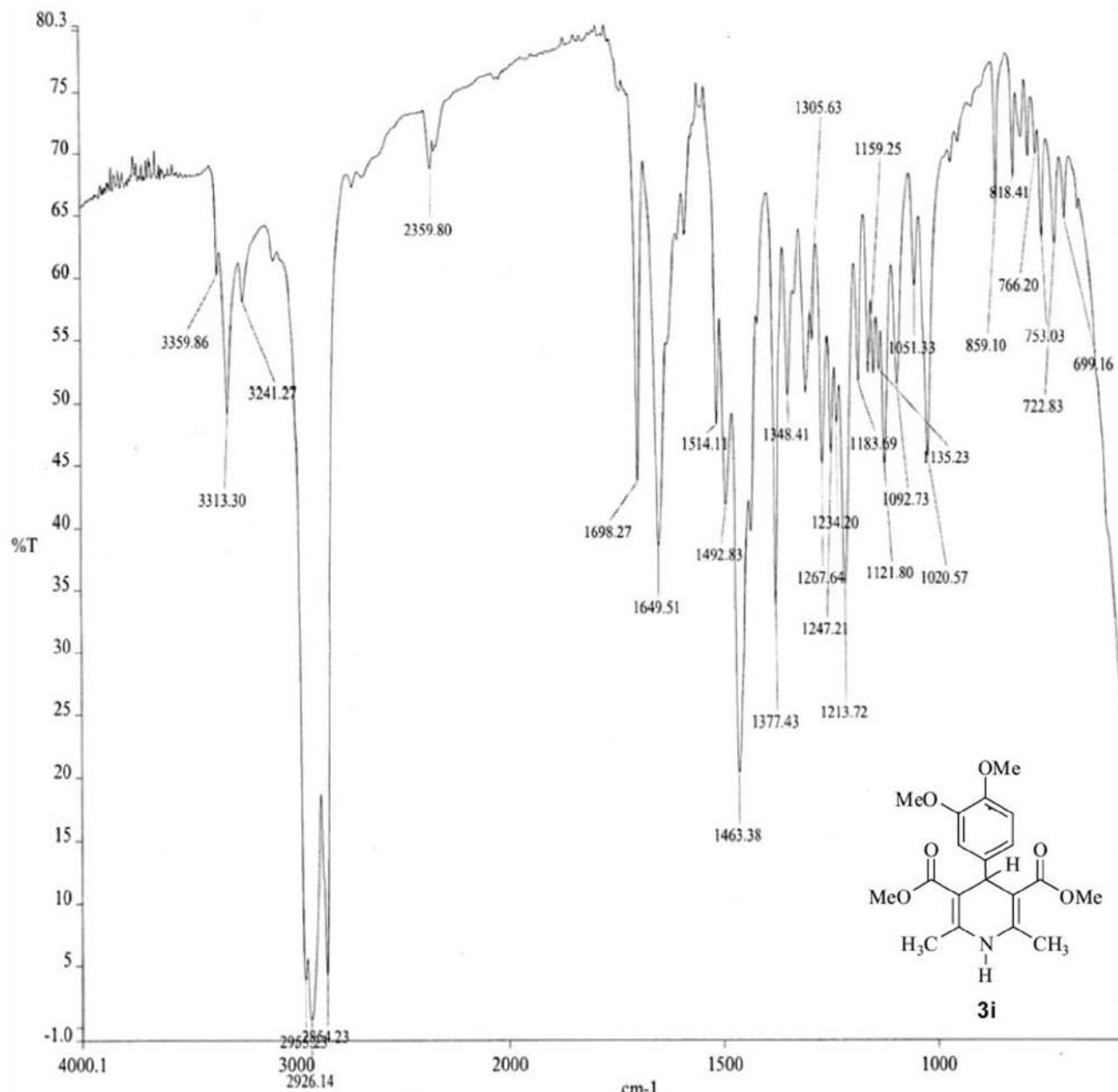
**Figure S22.** IR spectrum of 2,6-dimethyl-4-(4-fluorophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



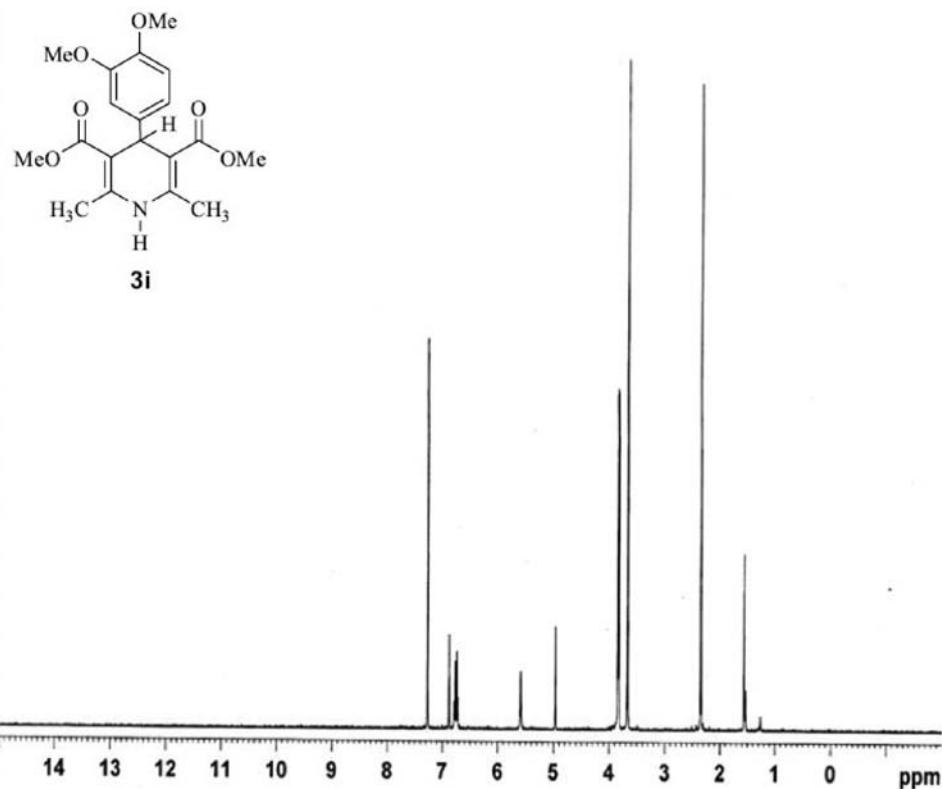
**Figure S23.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-fluorophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



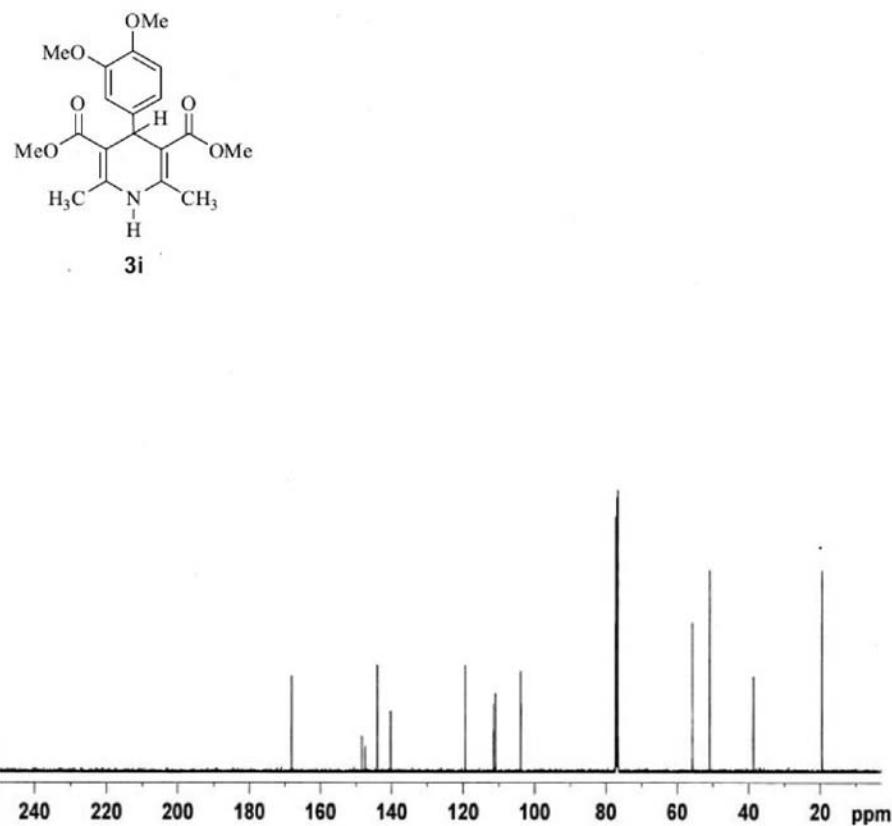
**Figure S24.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-fluorophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



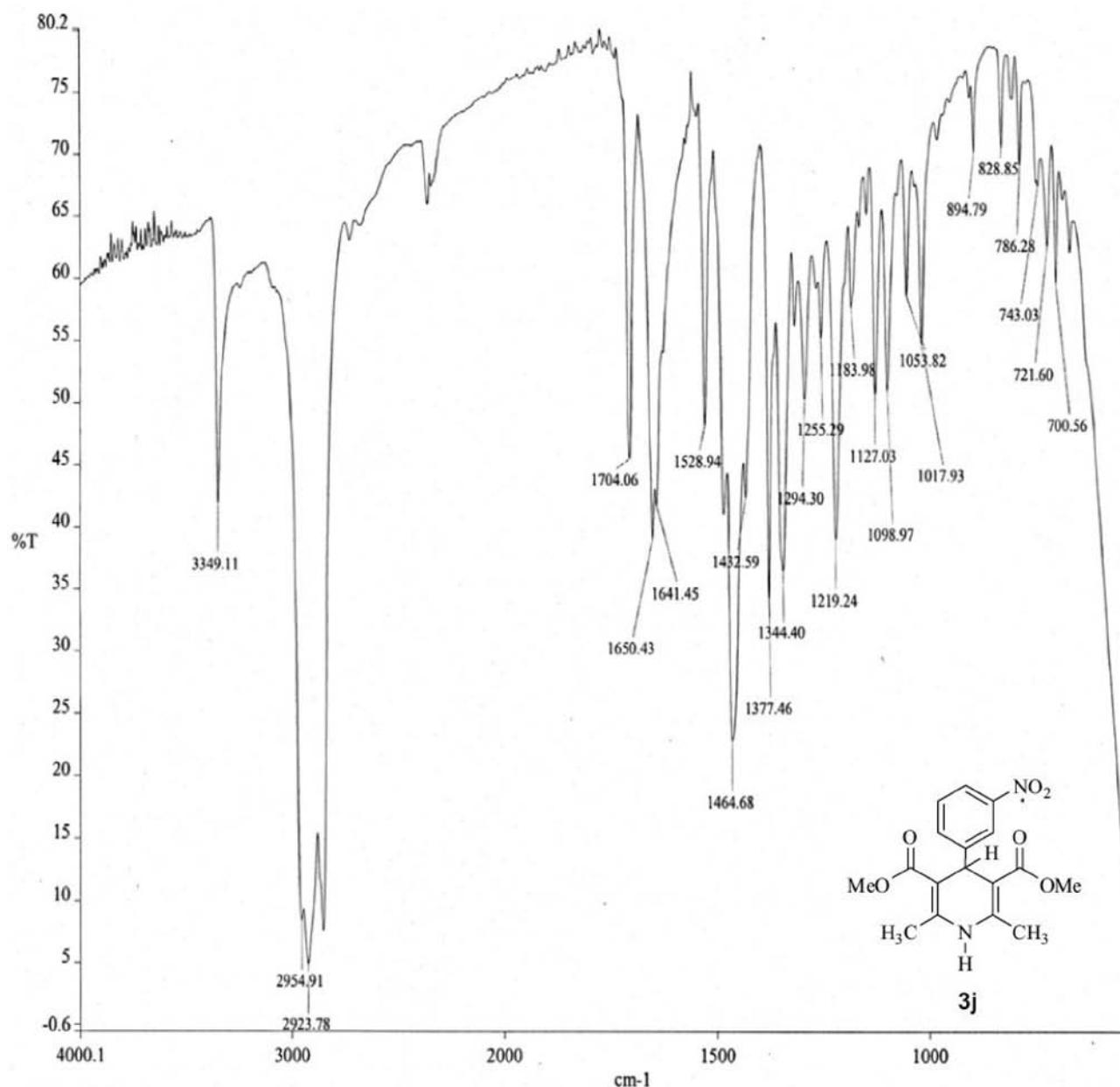
**Figure S25.** IR spectrum of 2,6-dimethyl-4-(3,4-dimethoxyphenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



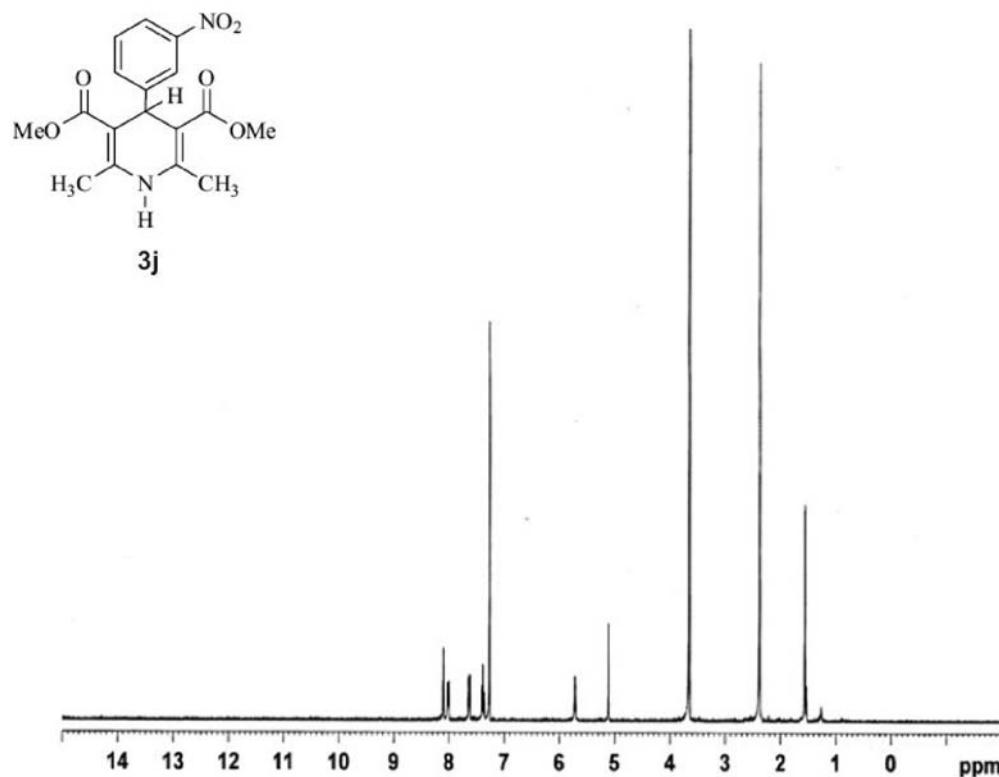
**Figure S26.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(3,4-dimethoxyphenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



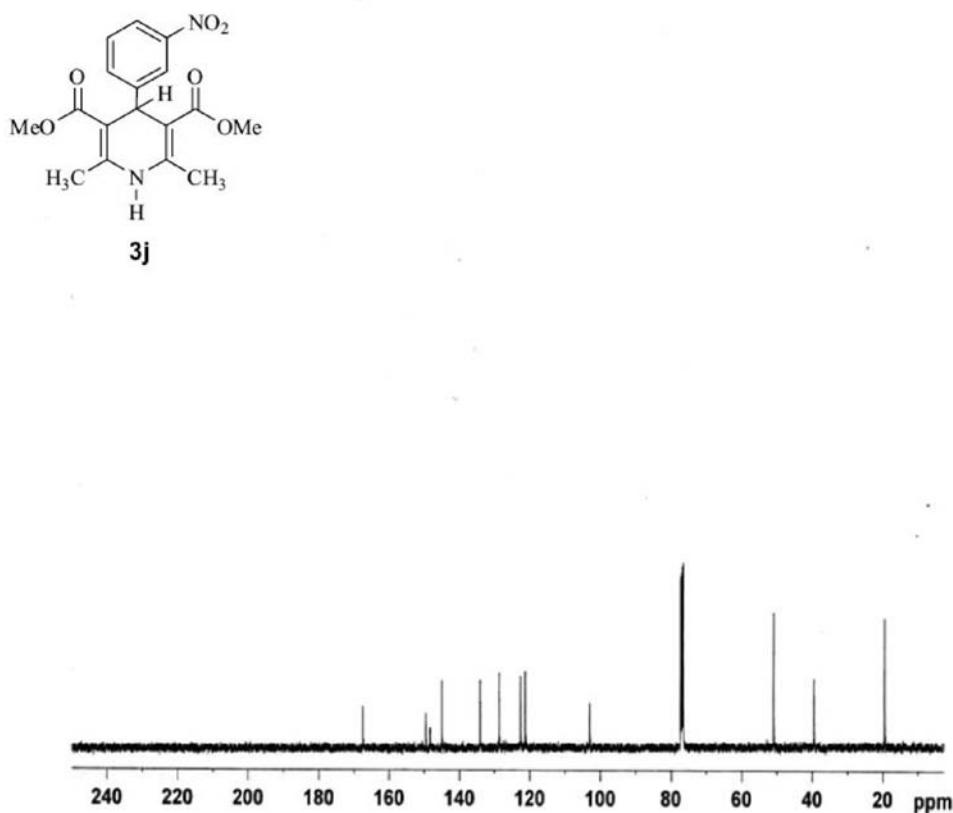
**Figure S27.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(3,4-dimethoxyphenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



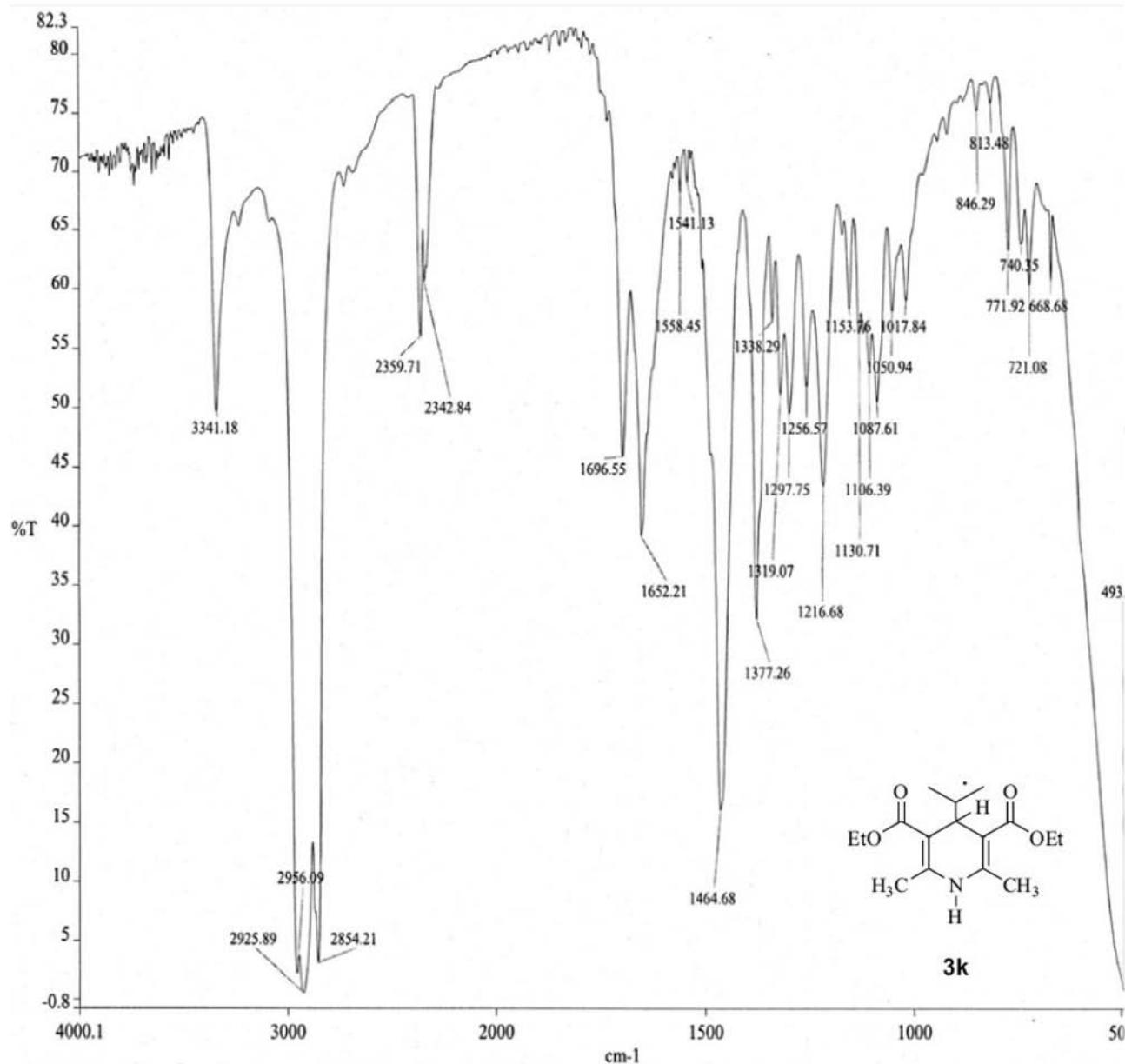
**Figure S28.** IR spectrum of 2,6-dimethyl-4-(3-nitrophenyl)-3,5-dicarbomethoxy-1,4-dihydropyridine.



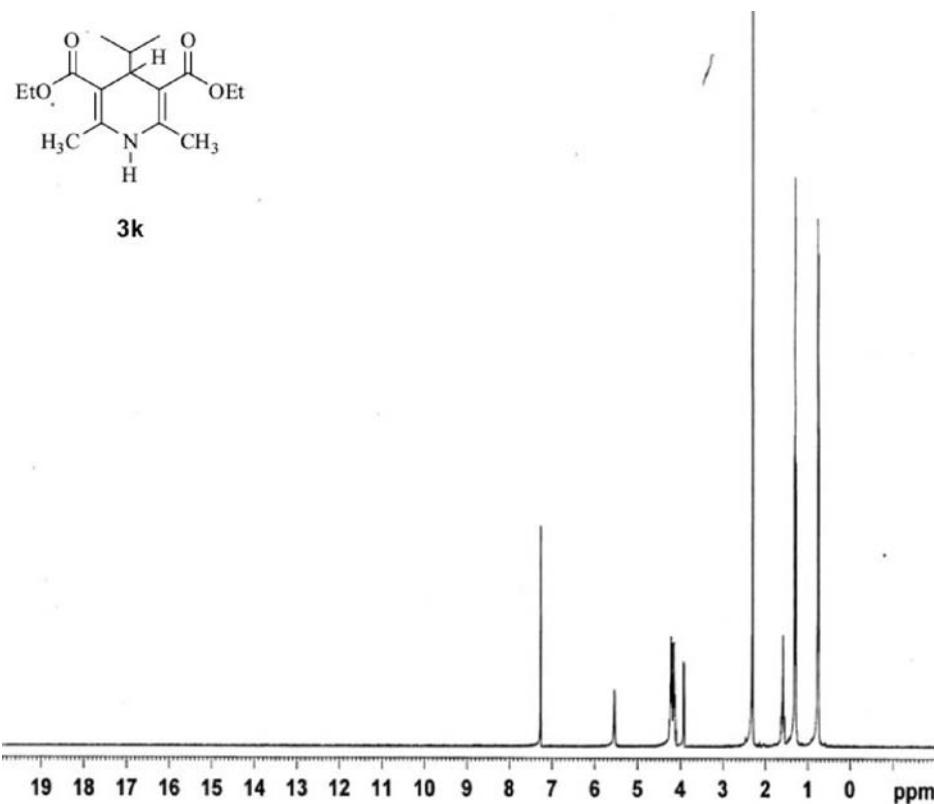
**Figure S29.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(3-nitrophenyl)-3,5-dicarbomethoxy-1,4- dihydropyridine.



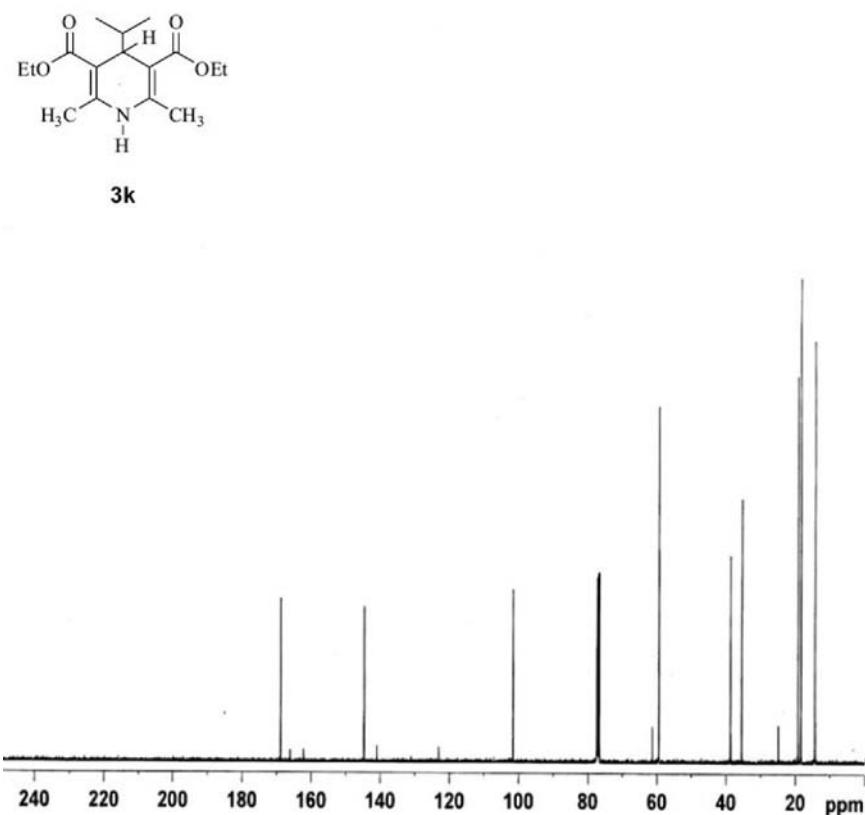
**Figure S30.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(3-nitrophenyl)-3,5-dicarbomethoxy-1,4- dihydropyridine.



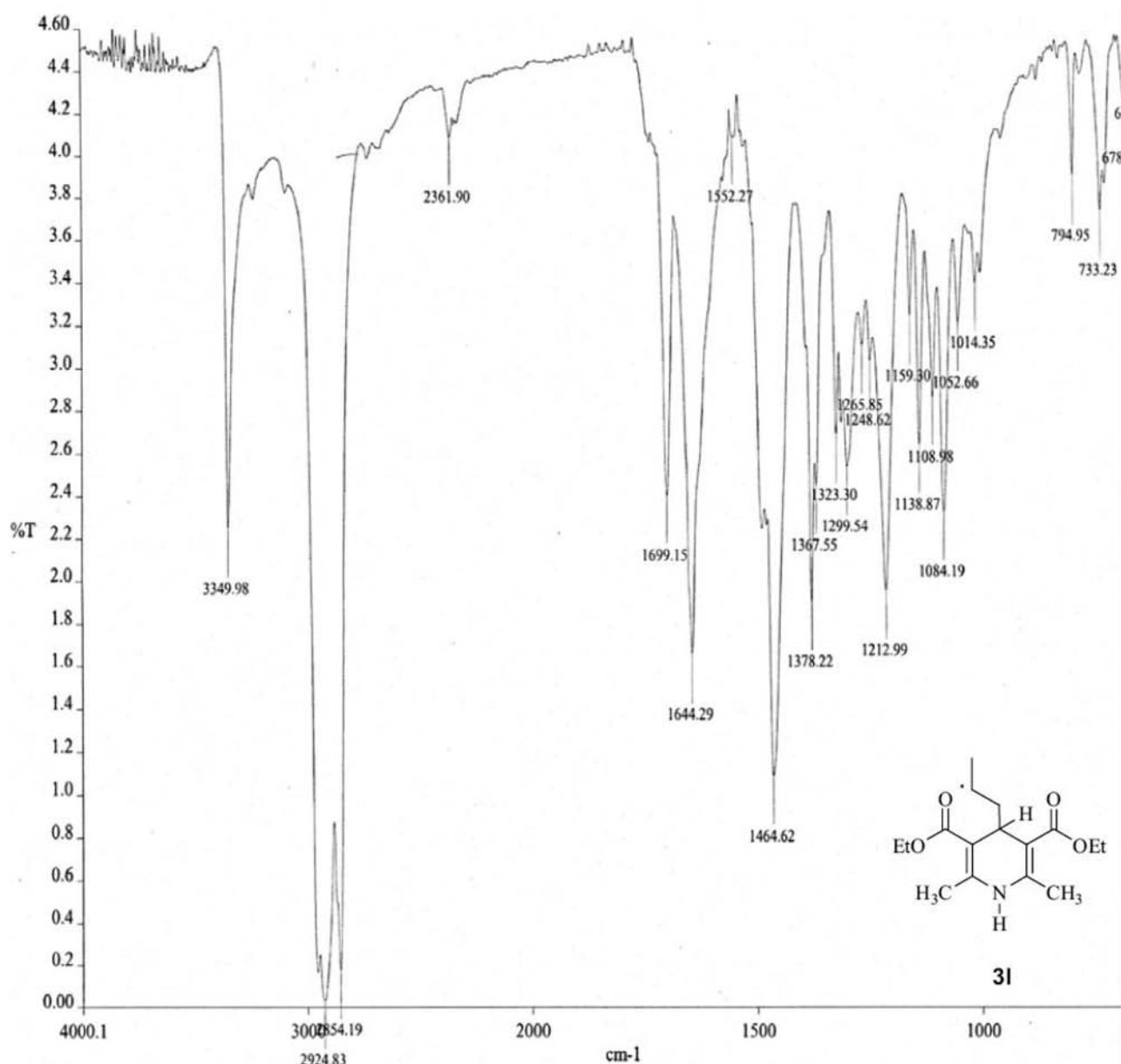
**Figure S31.** IR spectrum of 2,6-dimethyl-4-(iso-propyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



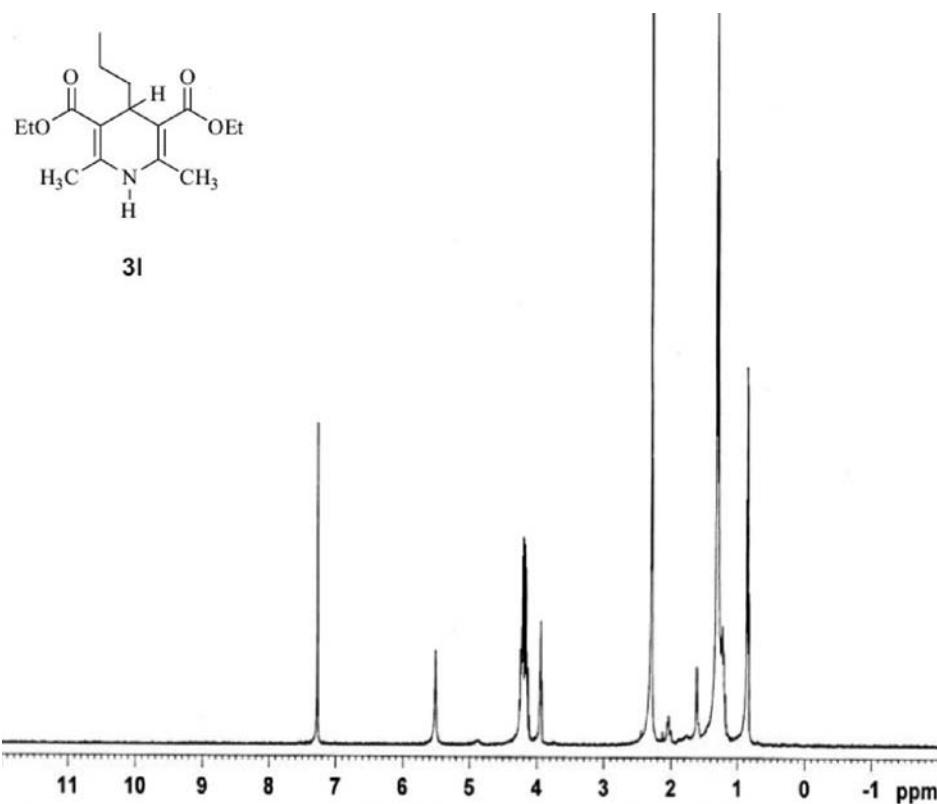
**Figure S32.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(iso-propyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



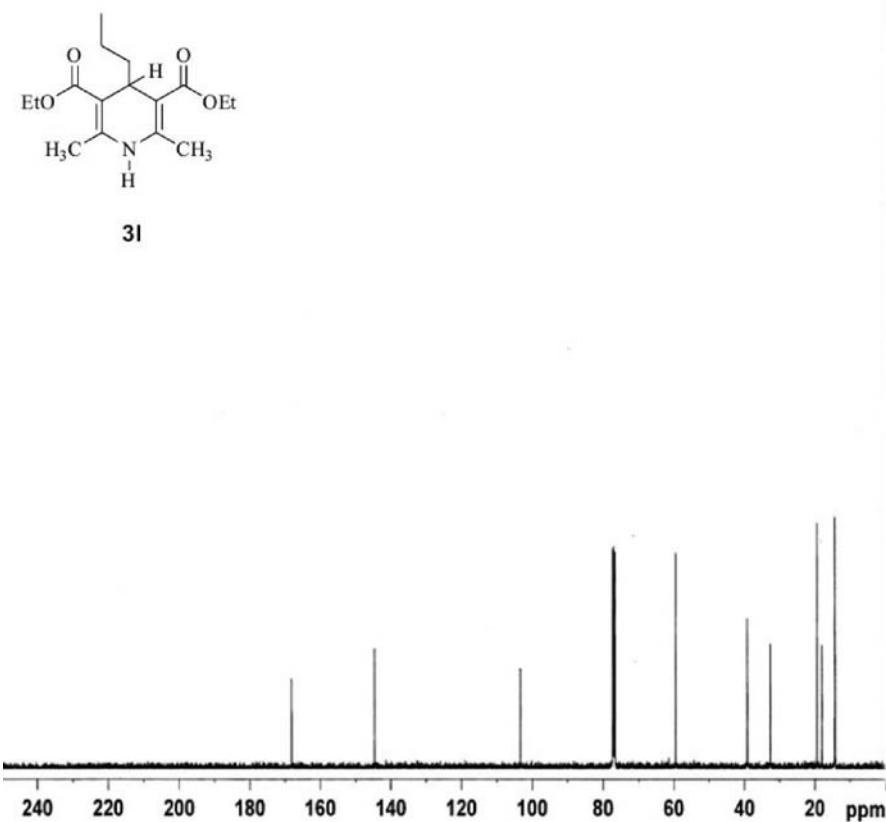
**Figure S33.**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(iso-propyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



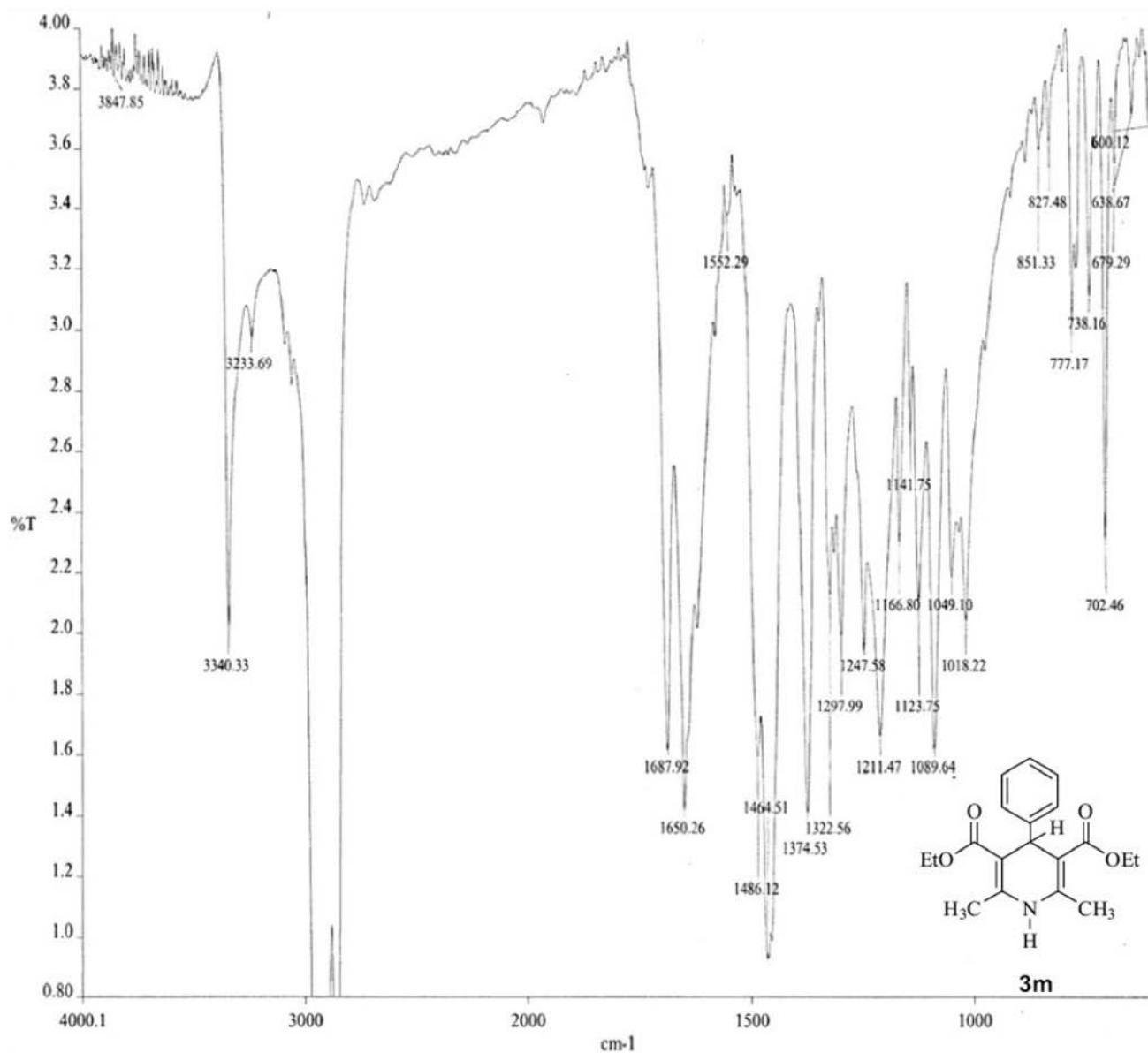
**Figure S34.** IR spectrum of 2,6-dimethyl-4-(n-propyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



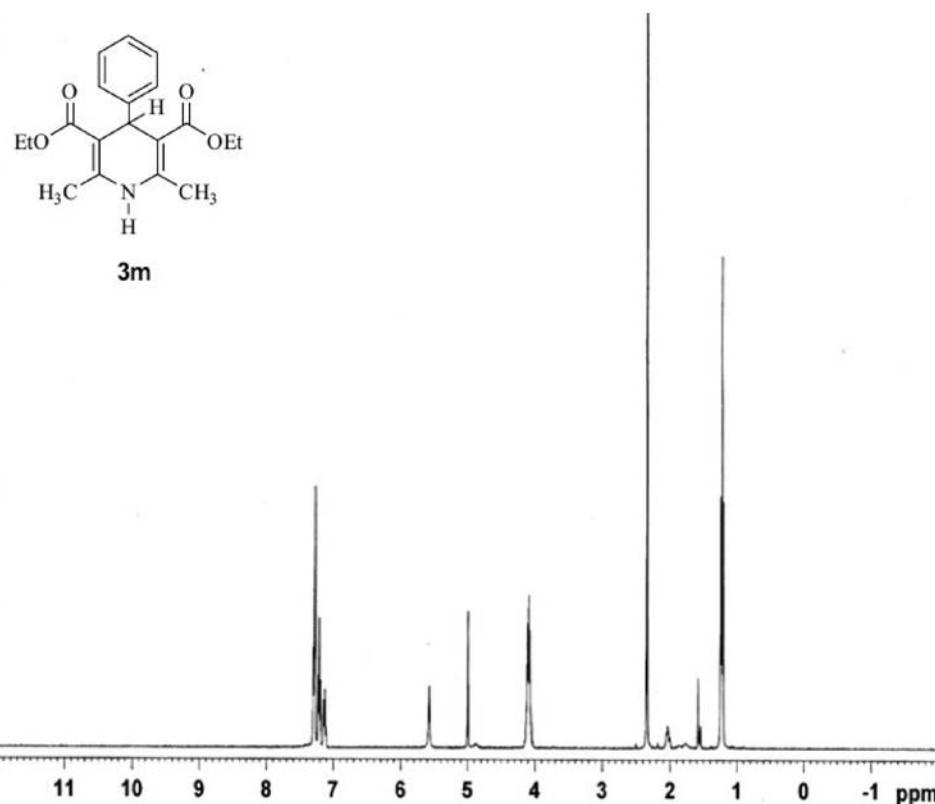
**Figure S35.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(n-propyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



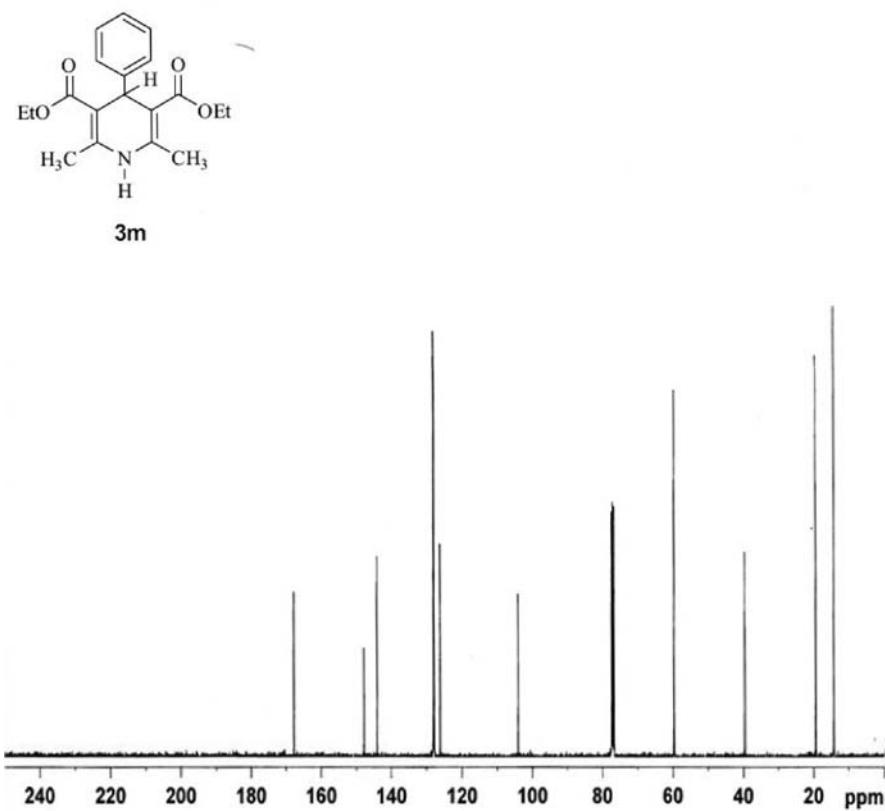
**Figure S36.**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(n-propyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



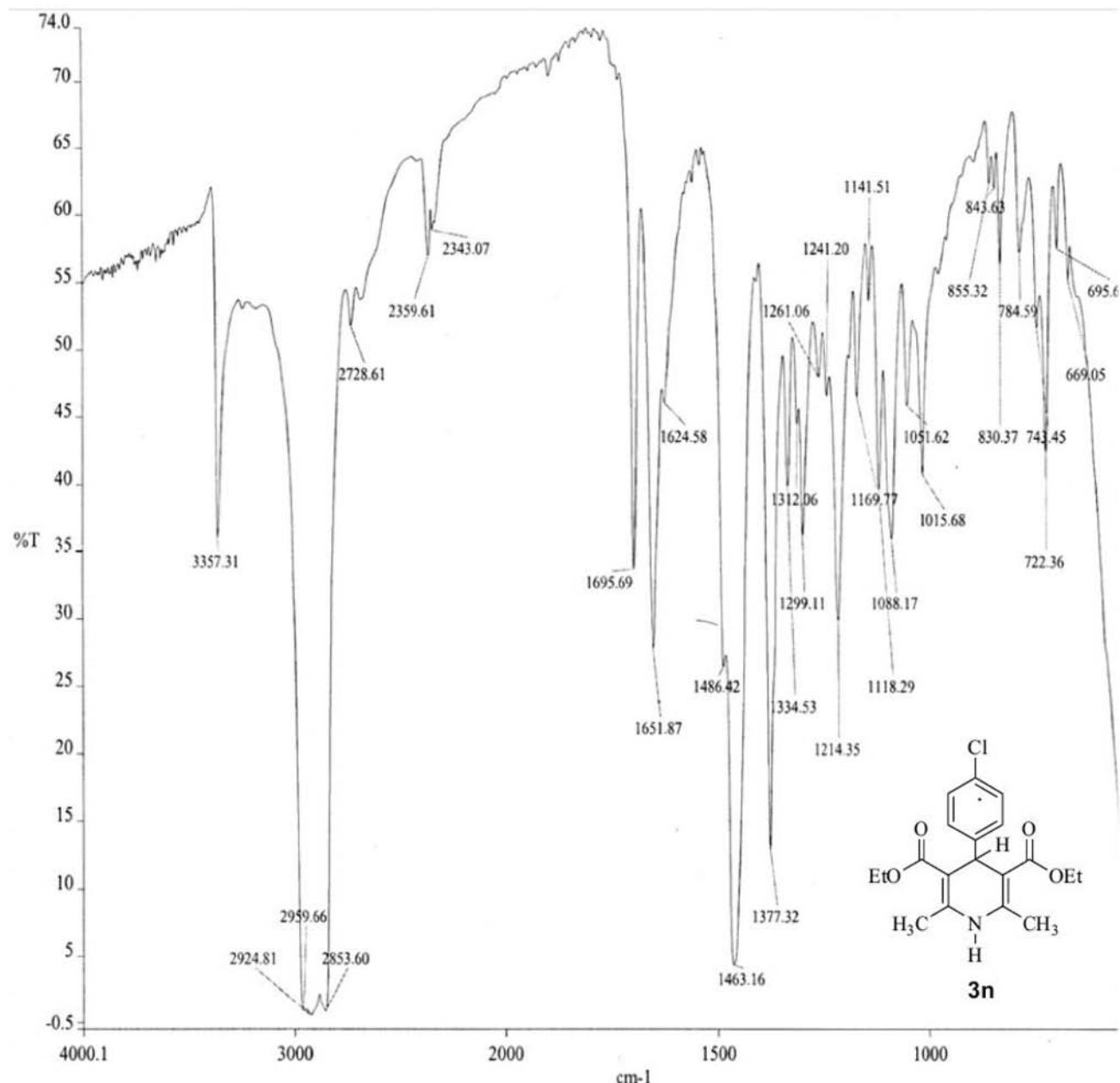
**Figure S37.** IR spectrum of 2,6-dimethyl-4-(phenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



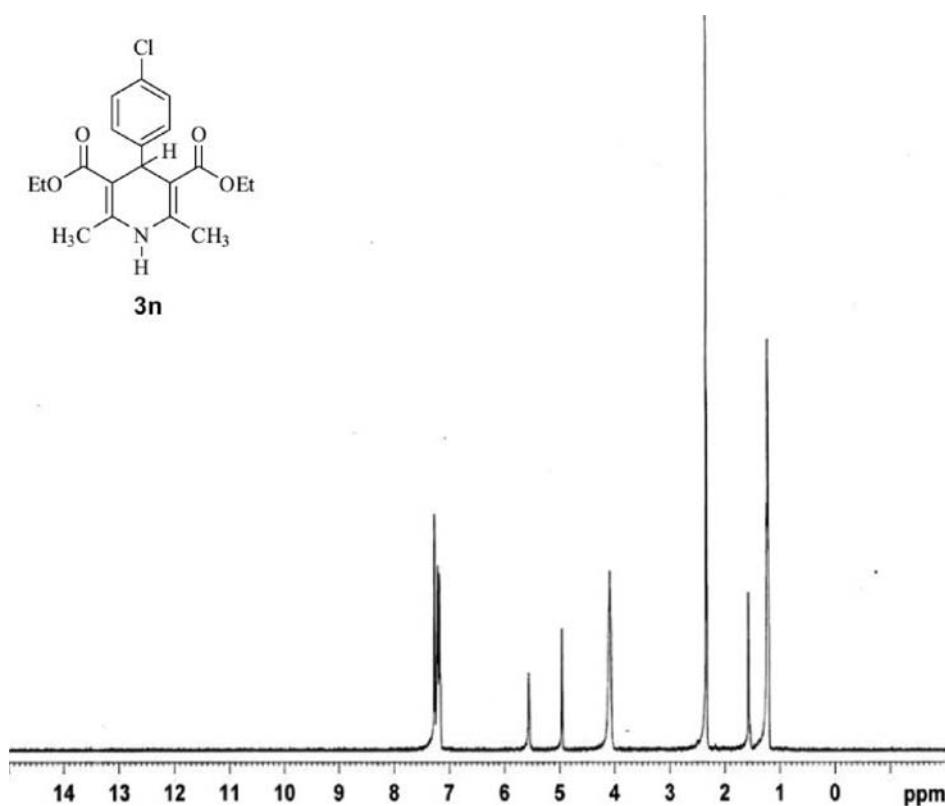
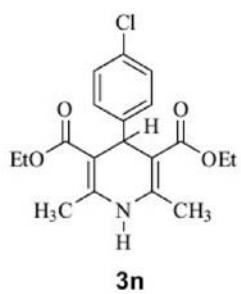
**Figure S38.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(phenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



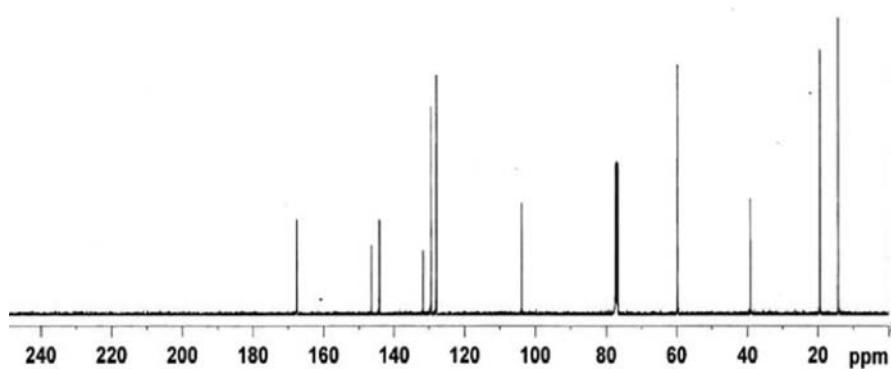
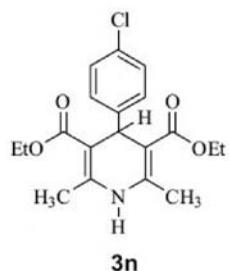
**Figure S39.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(phenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



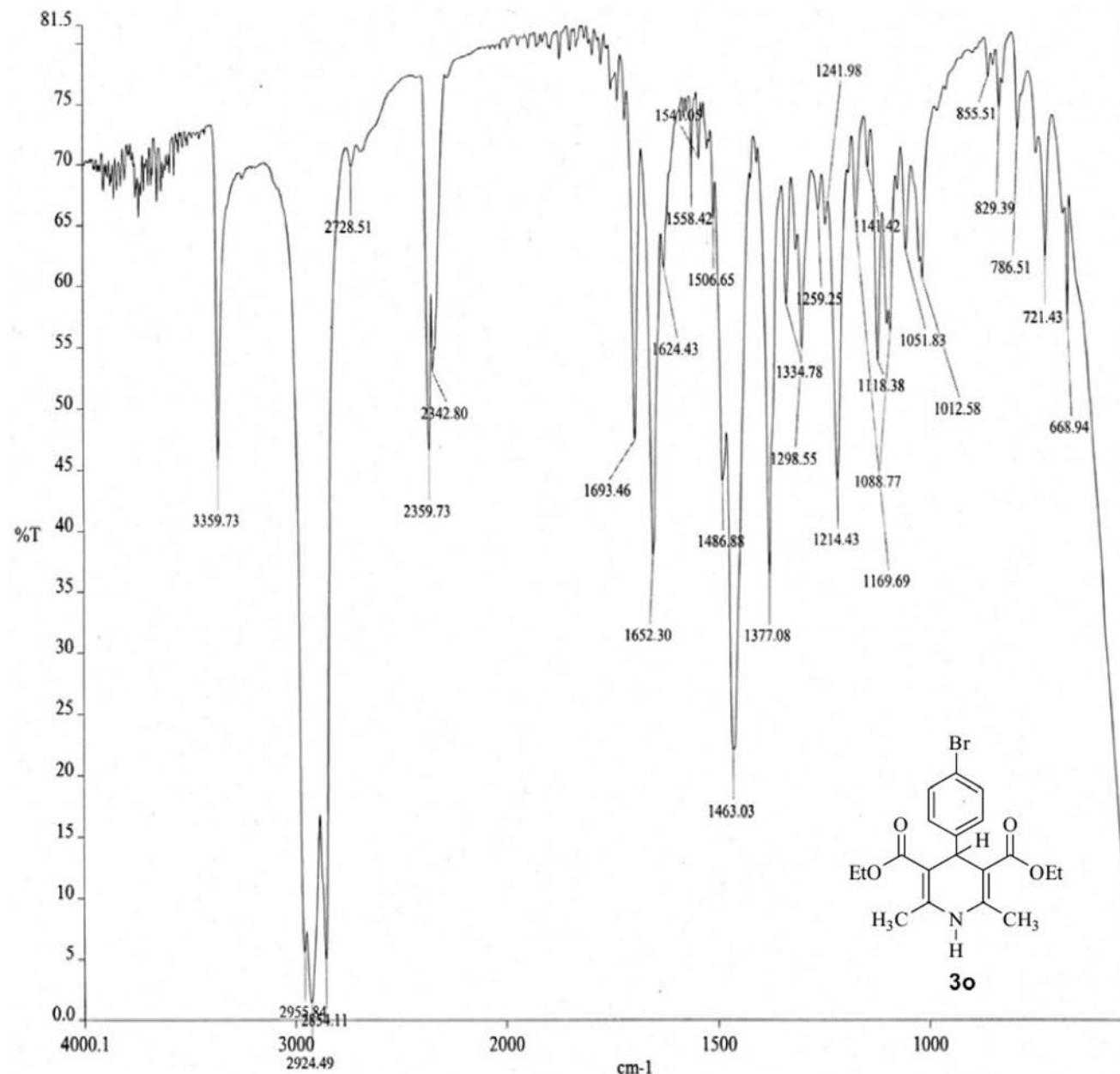
**Figure S40.** IR spectrum of 2,6-dimethyl-4-(4-chlorophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



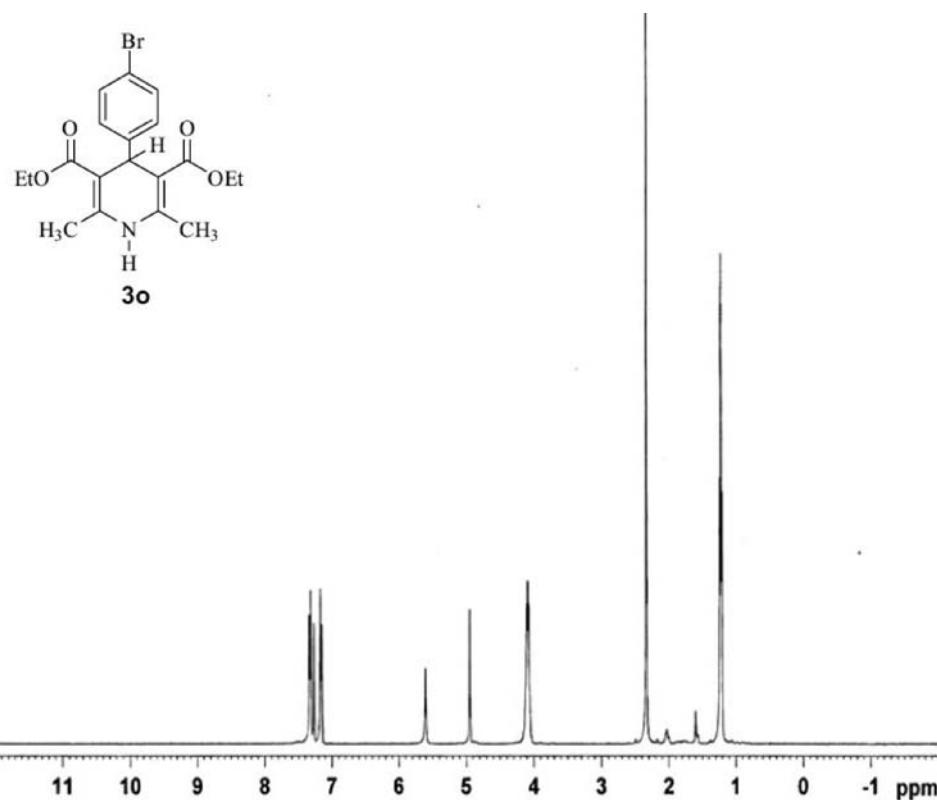
**Figure S41.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(4-chlorophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



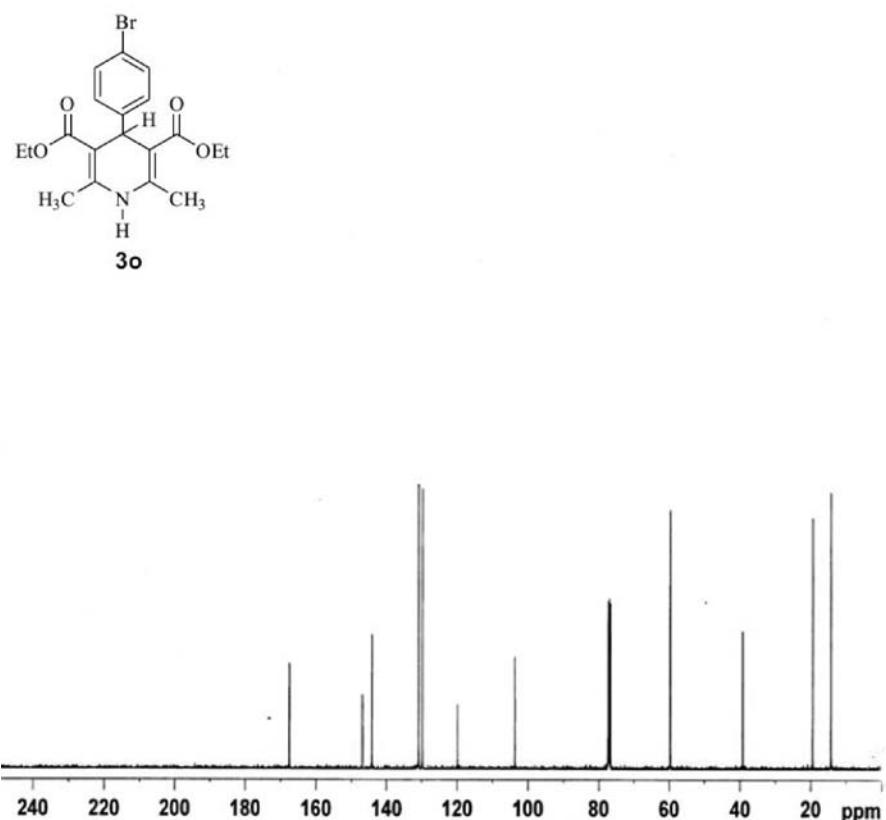
**Figure S42.**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(4-chlorophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



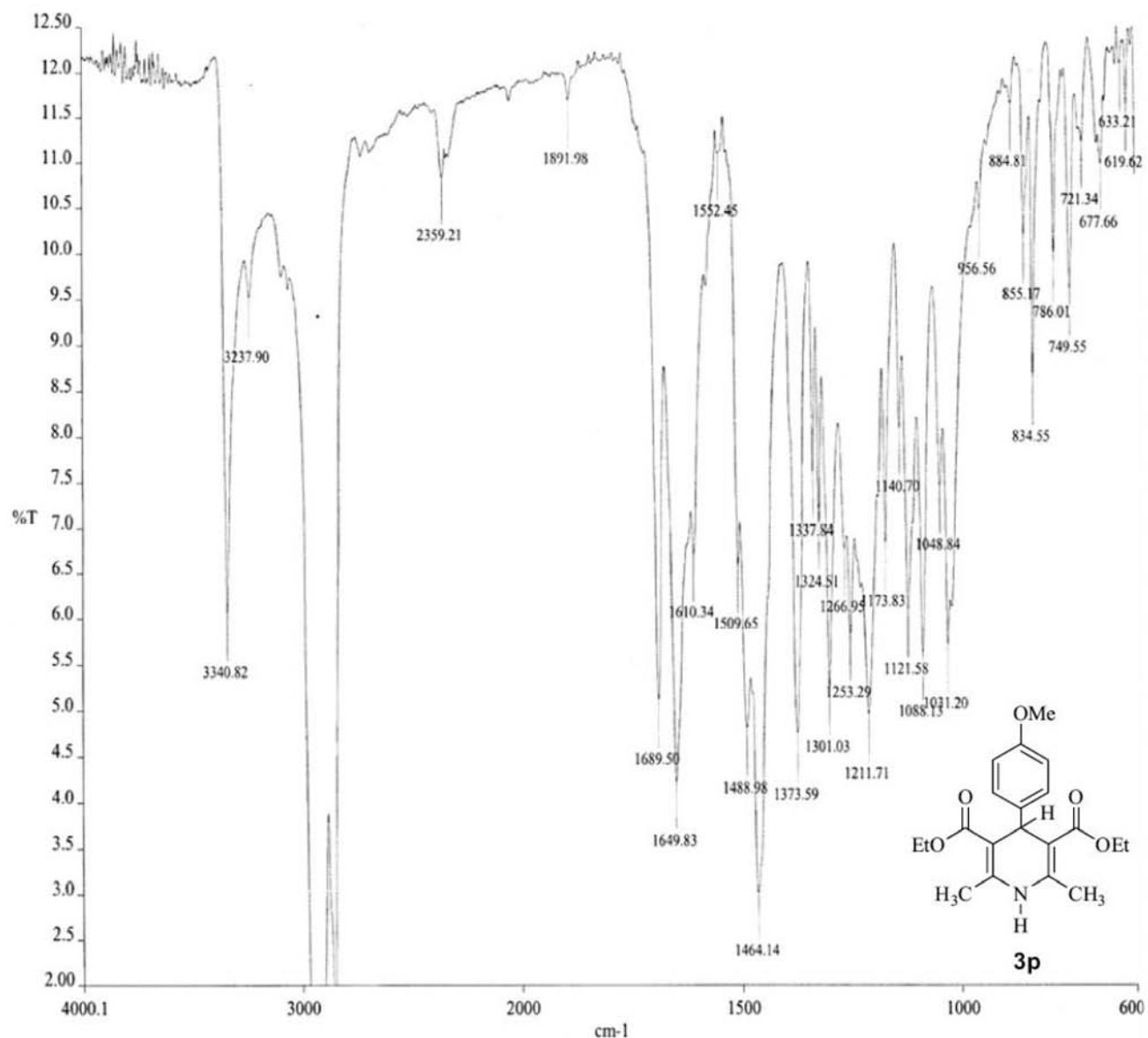
**Figure S43.** IR spectrum of 2,6-dimethyl-4-(4-bromophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



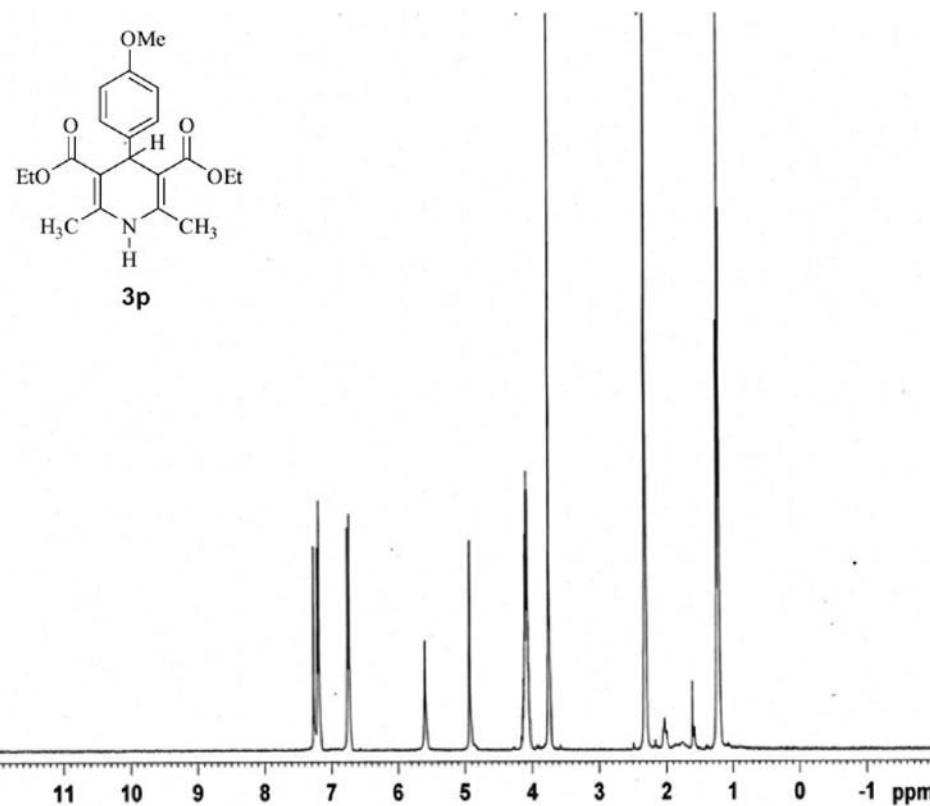
**Figure S44.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-bromophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



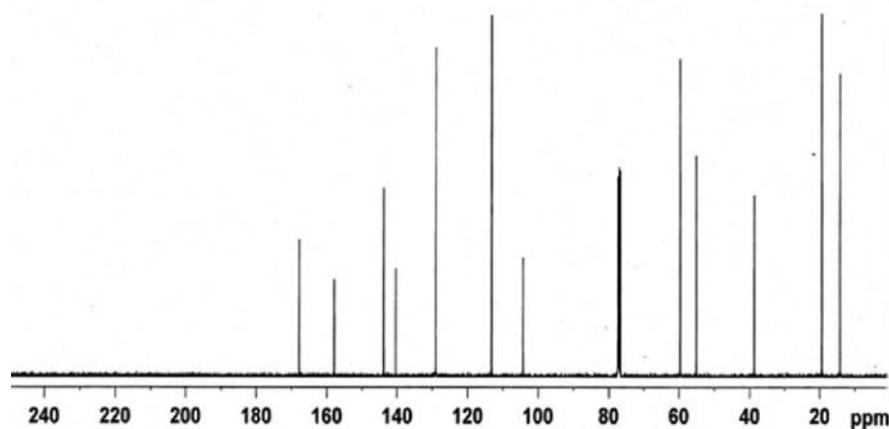
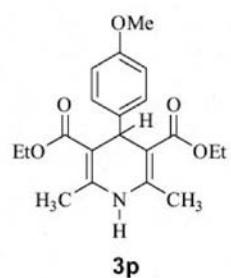
**Figure S45.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(4-bromophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



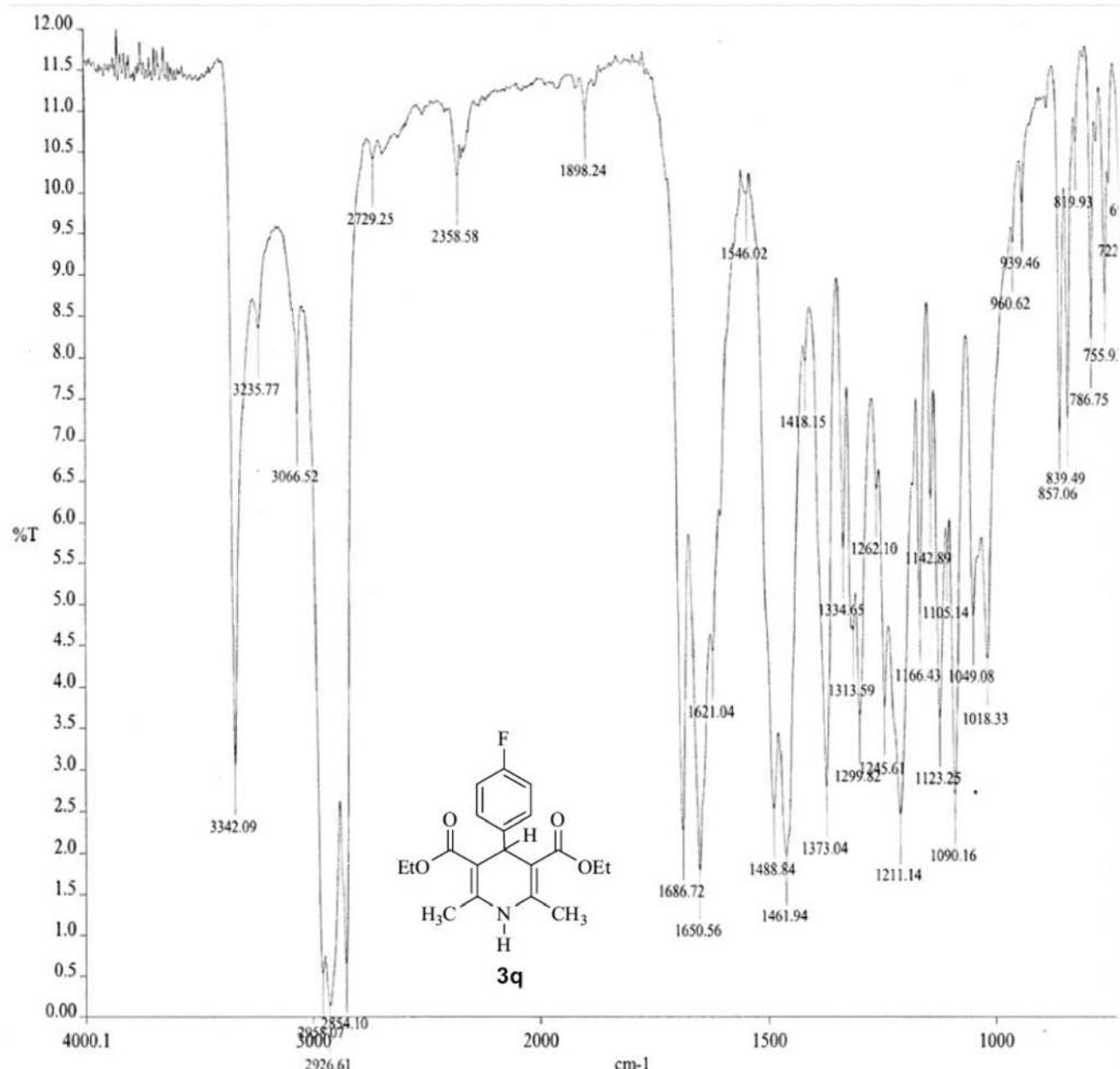
**Figure S46.** IR spectrum of 2,6-dimethyl-4-(4-methoxyphenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



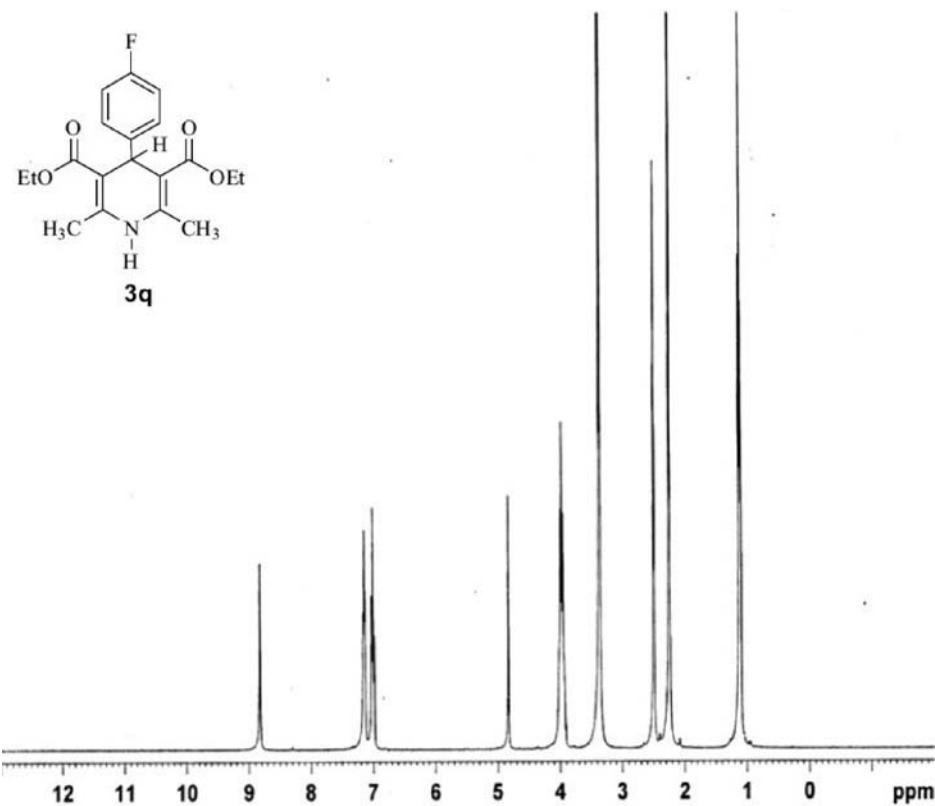
**Figure S47.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(4-methoxyphenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



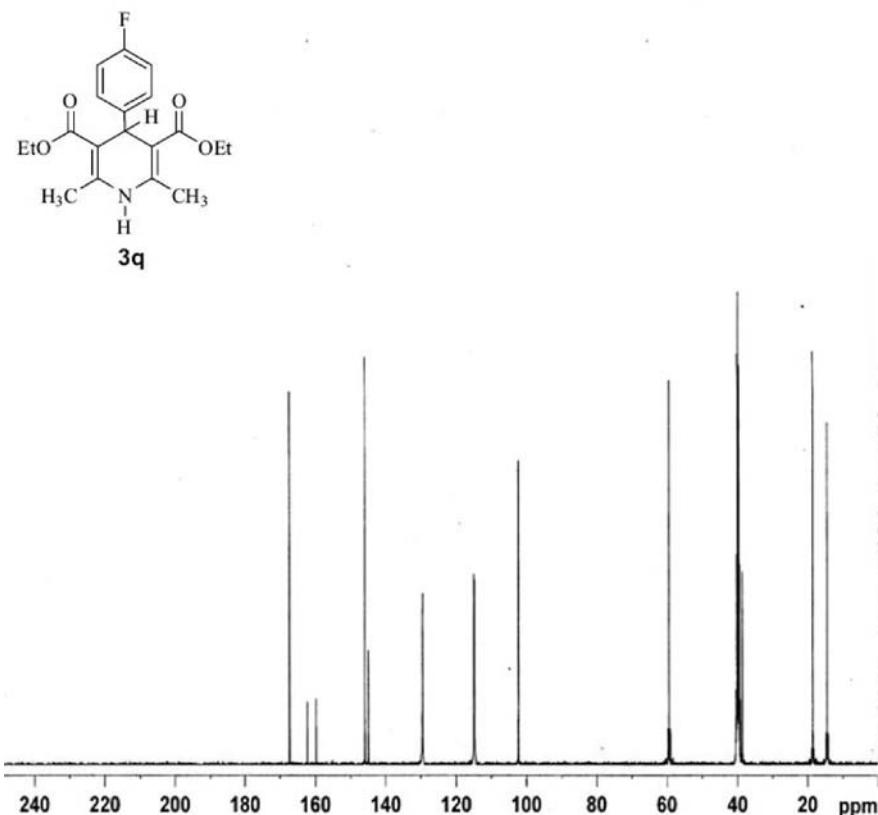
**Figure S48.**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ ) of 2,6-dimethyl-4-(4-methoxyphenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



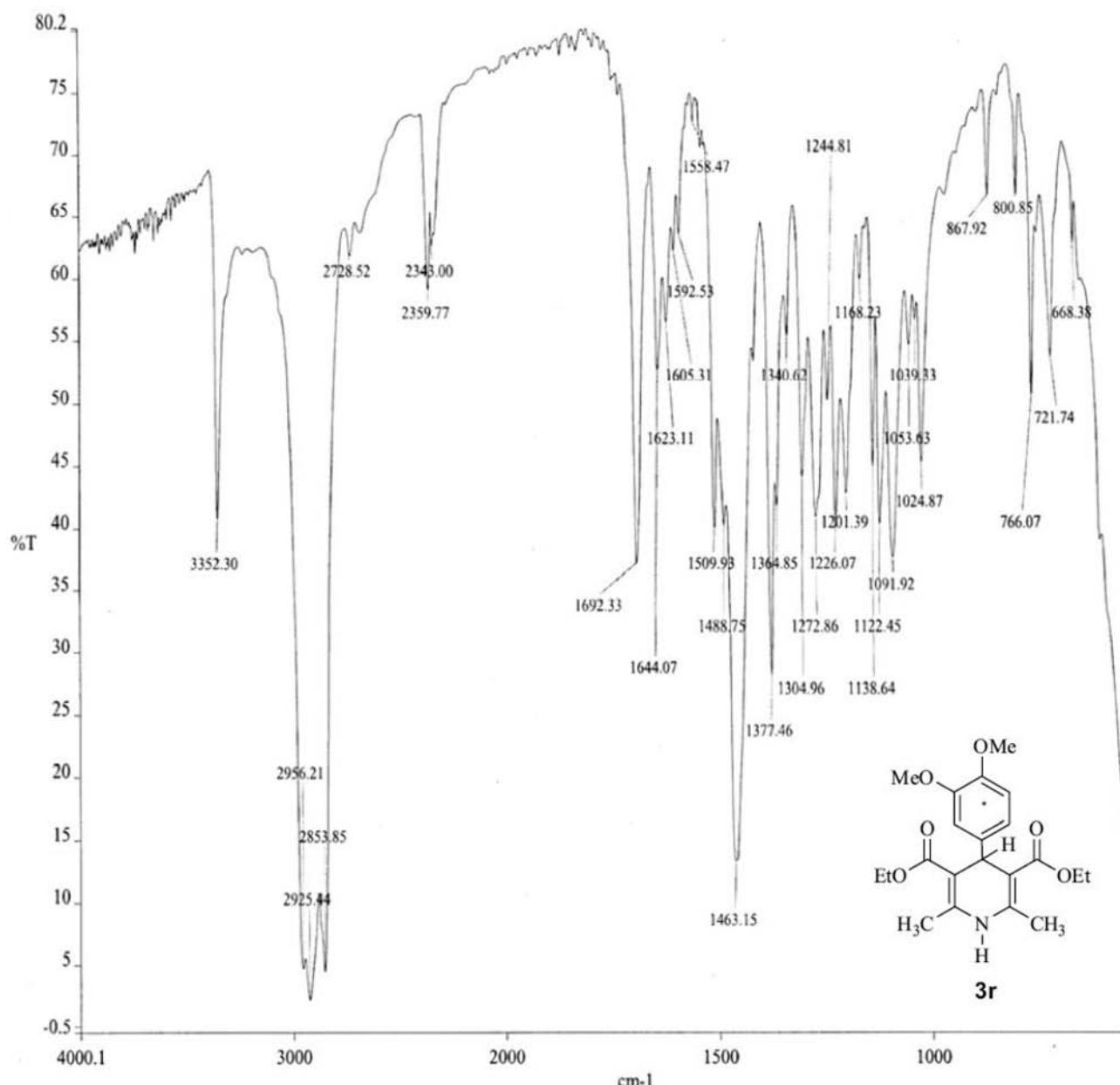
**Figure S49.** IR spectrum of 2,6-dimethyl-4-(4-fluorophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



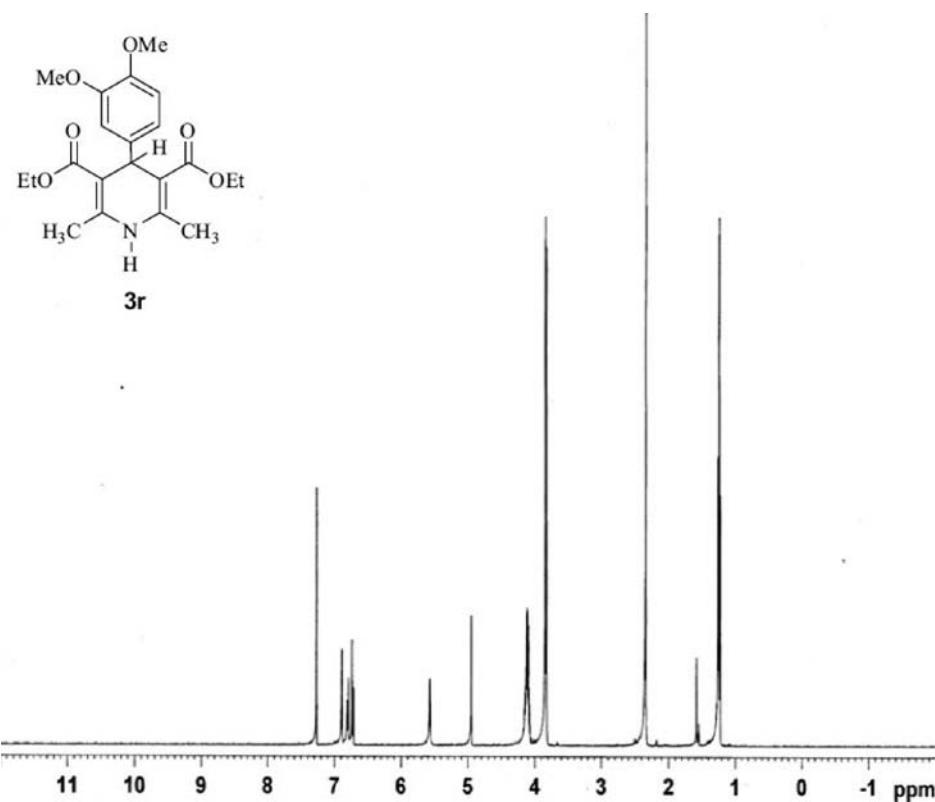
**Figure S50.** <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of 2,6-dimethyl-4-(4-fluorophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



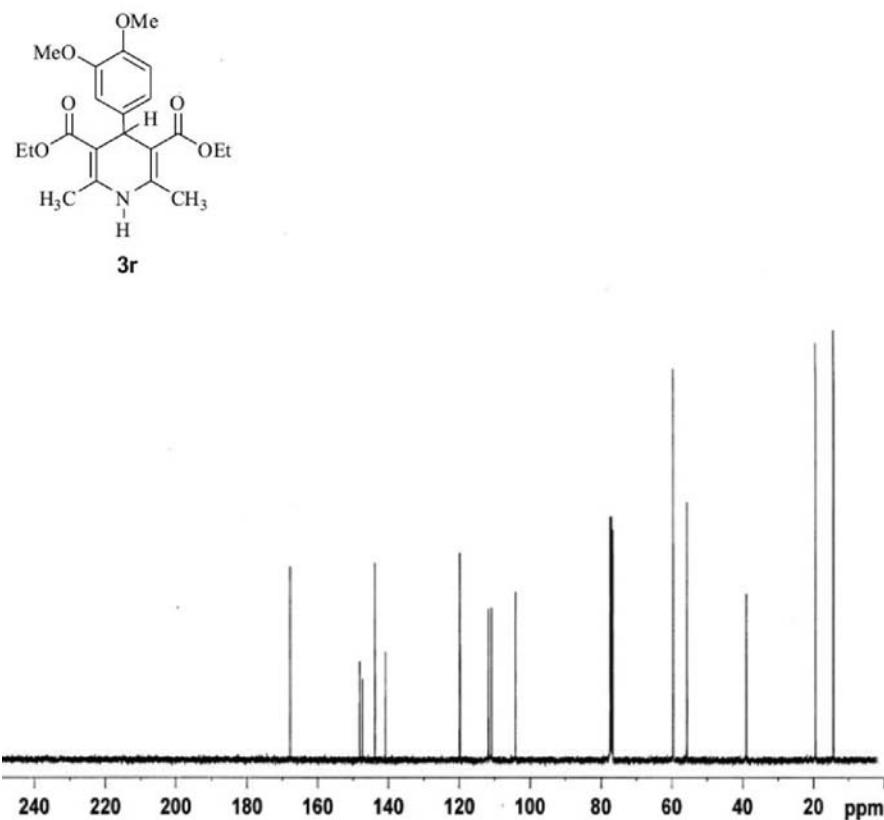
**Figure S51.** <sup>13</sup>C NMR spectrum (100 MHz, DMSO-*d*<sub>6</sub>) of 2,6-dimethyl-4-(4-fluorophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



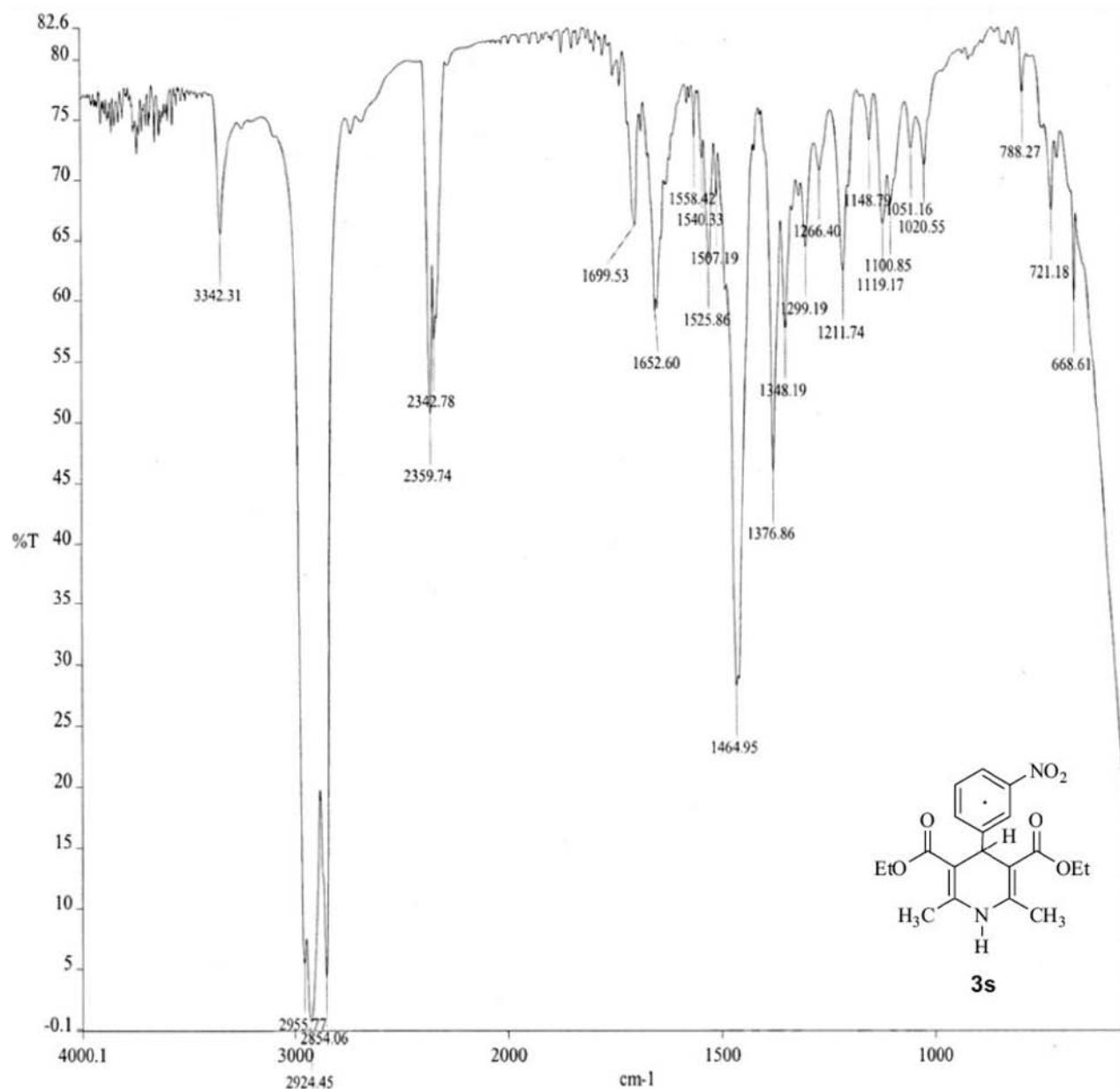
**Figure S52.** IR spectrum of 2,6-dimethyl-4-(3,4-dimethoxyphenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



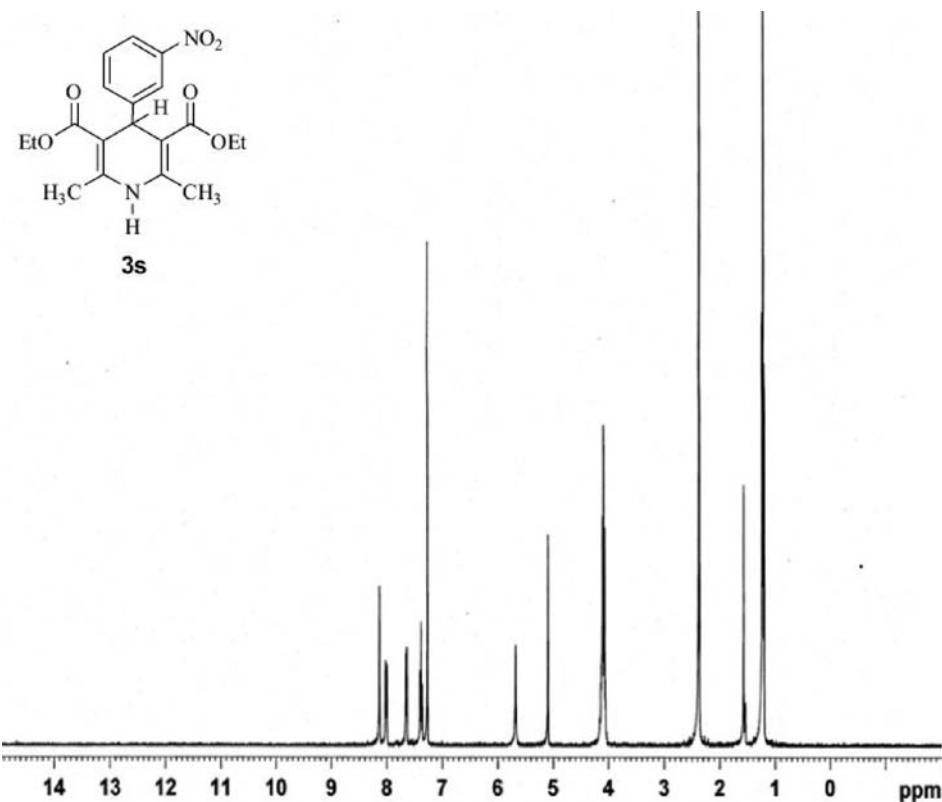
**Figure S53.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(3,4-dimethoxyphenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



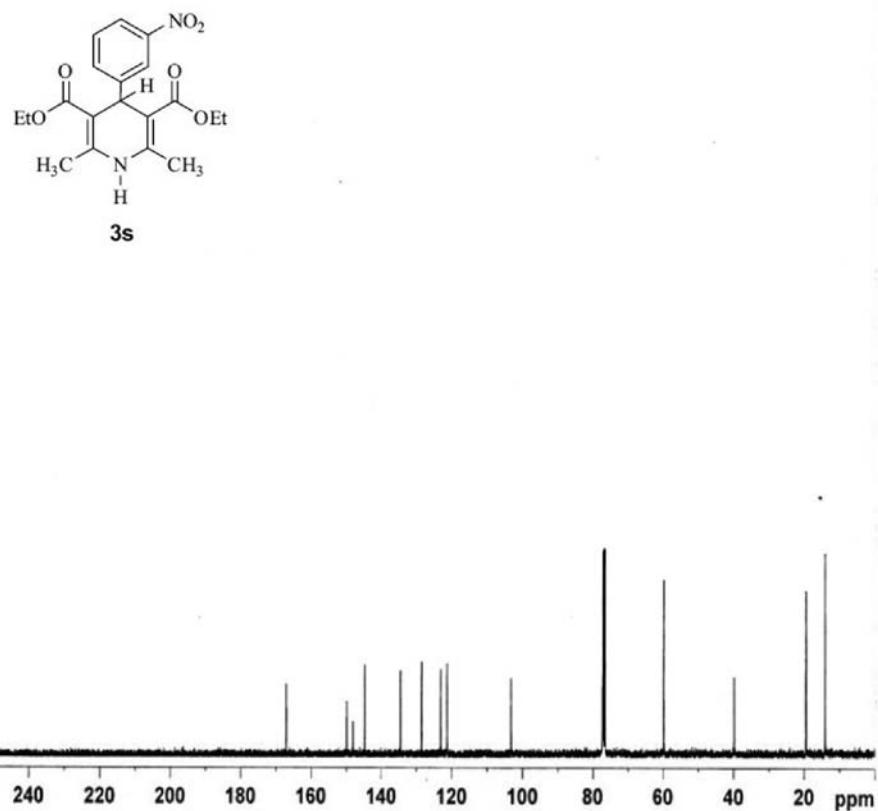
**Figure S54.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(3,4-dimethoxyphenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



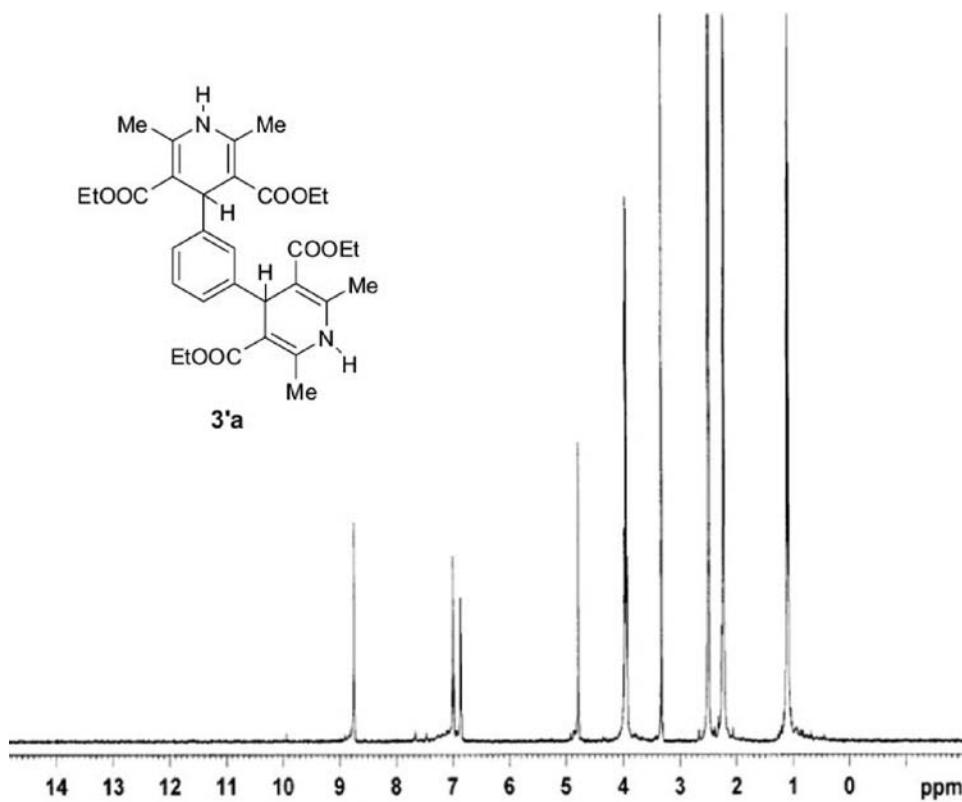
**Figure S55.** IR spectrum of 2,6-dimethyl-4-(3-nitrophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



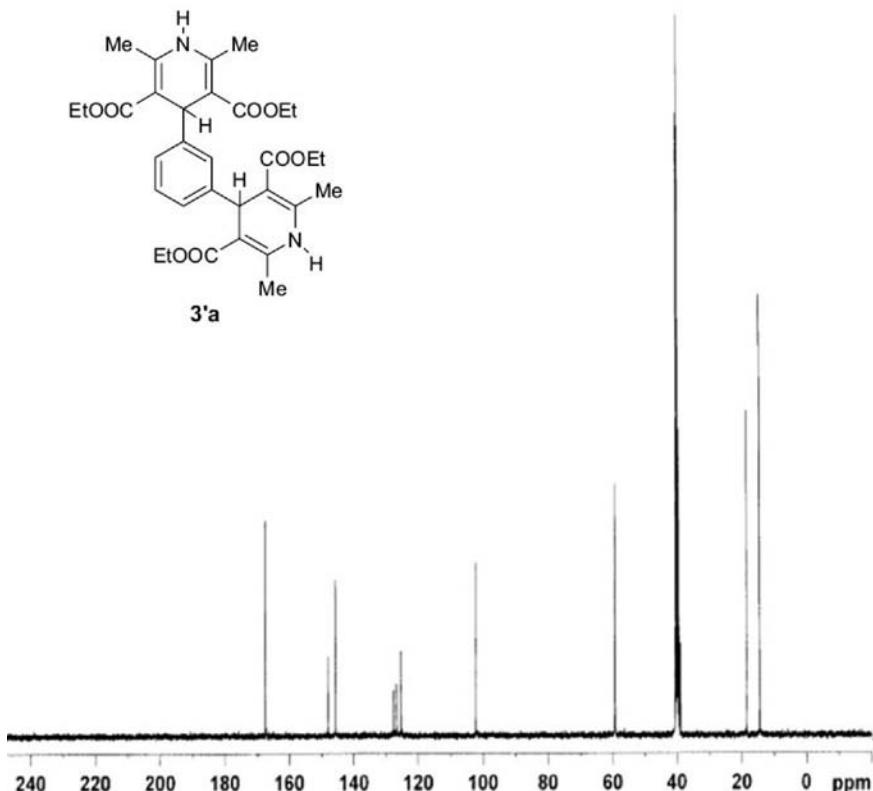
**Figure S56.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(3-nitrophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



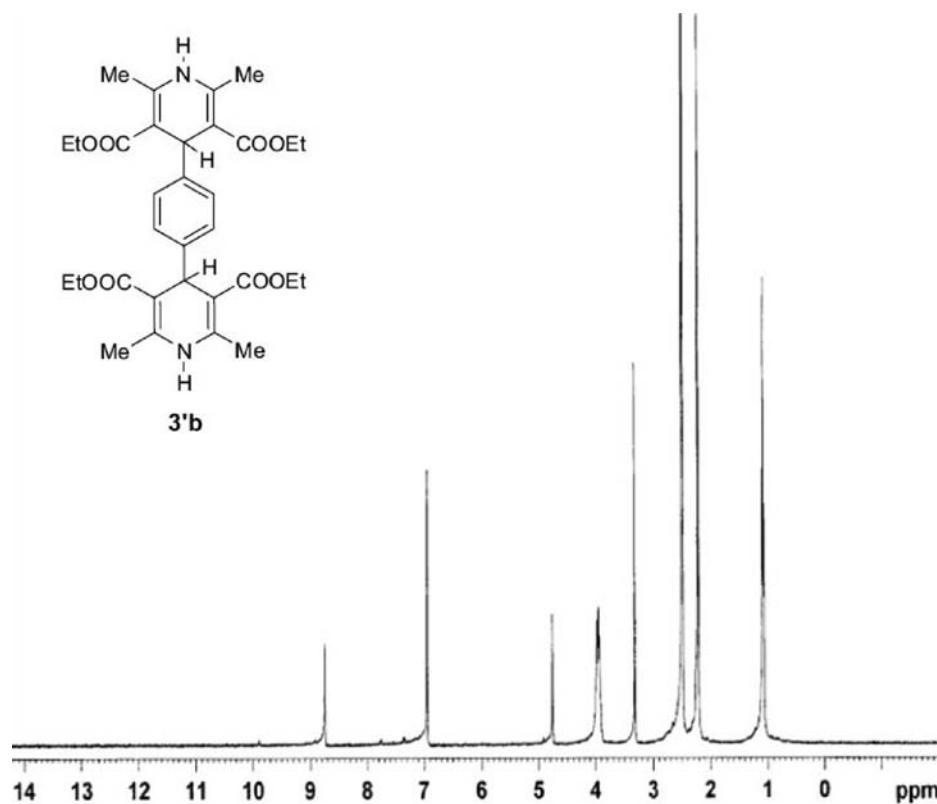
**Figure S57.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 2,6-dimethyl-4-(3-nitrophenyl)-3,5-dicarboethoxy-1,4-dihydropyridine.



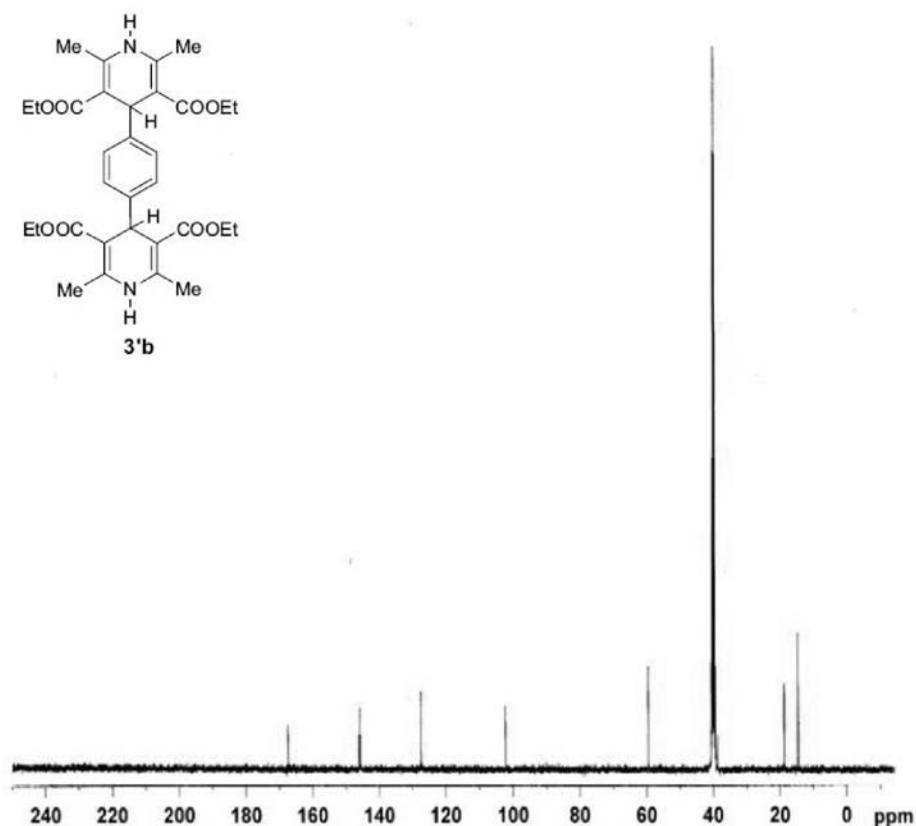
**Figure S58.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 1,3-bis-(2,6-diethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene.



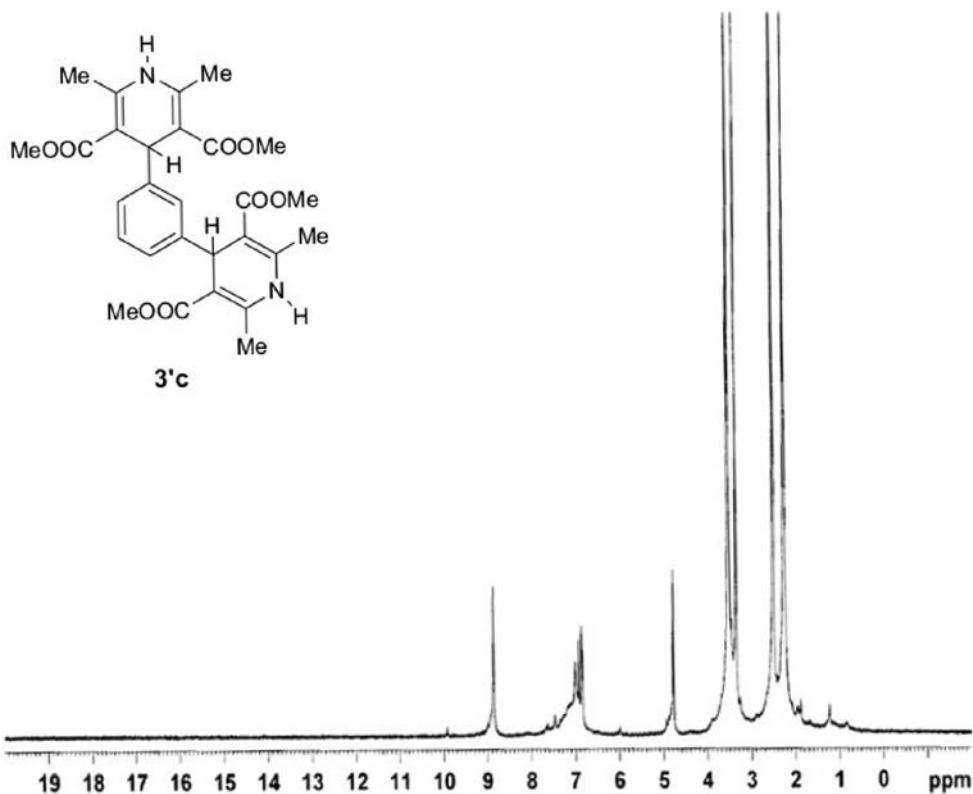
**Figure S59.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 1,3-bis-(2,6-diethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene.



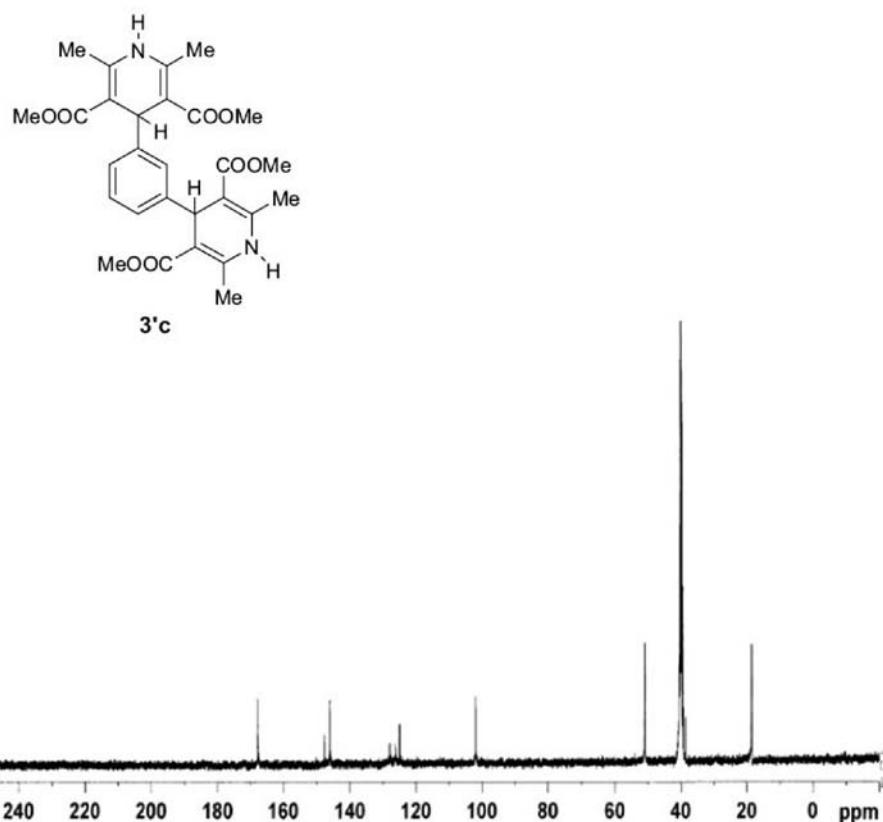
**Figure S60.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 1,4-bis-(2,6-diethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene.



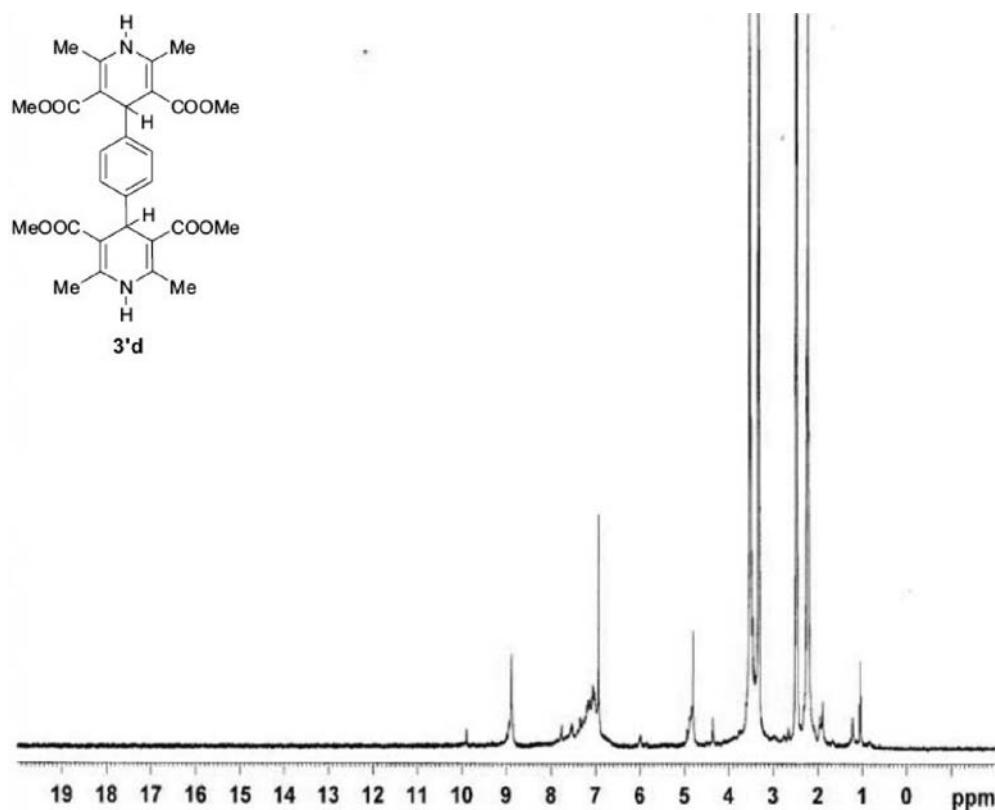
**Figure S61.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 1,4-bis-(2,6-diethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene.



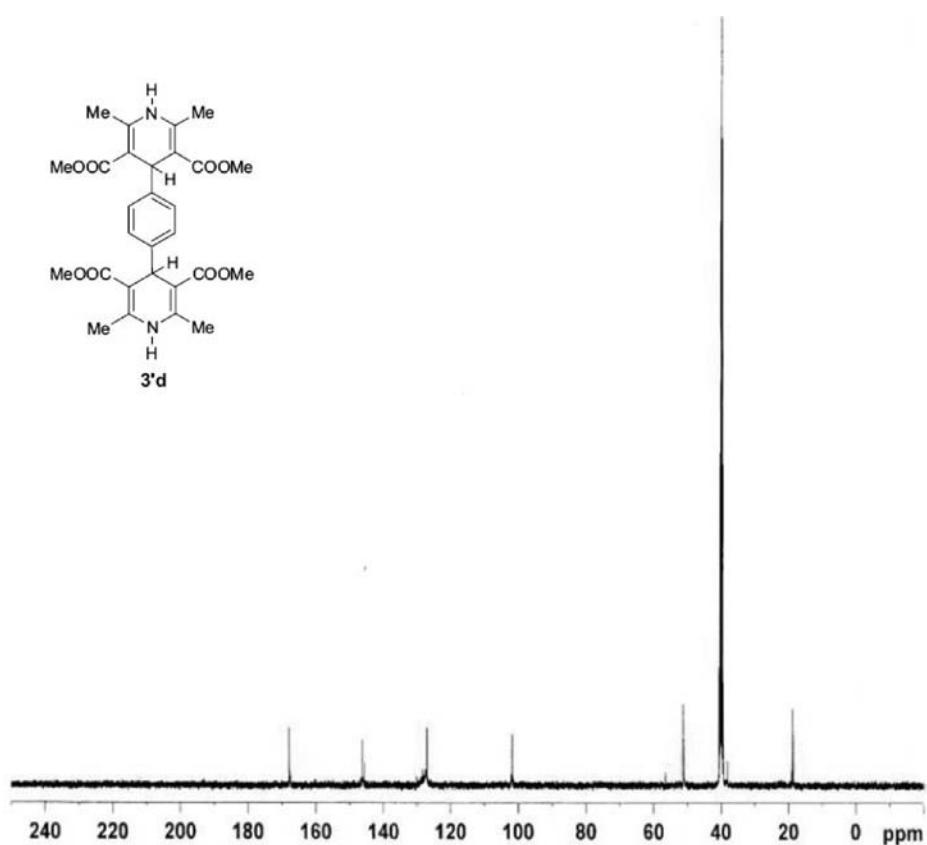
**Figure S62.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 1,3-bis-(2,6-dimethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene.



**Figure S63.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 1,3-bis-(2,6-dimethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene.



**Figure S64.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 1,4-bis-(2,6-dimethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene.



**Figure S65.** <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 1,4-bis-(2,6-dimethyl-3,5-dicarboethoxy-1,4-dihydropyridine) benzene.