Supporting Information

Highly Efficient One-Pot Synthesis of 2-Pyridones *via* Chemo- and Regioselective Tandem Blaise Reaction of Nitriles with Propiolates

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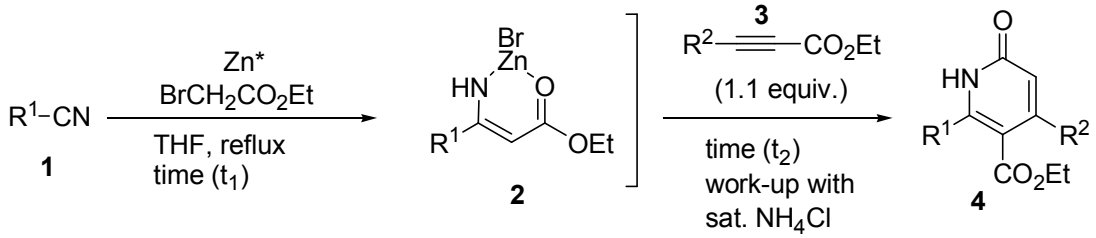
General. All reactions and manipulations were performed in a nitrogen atmosphere using standard Schelenk techniques. The reaction solvents were distilled prior to used (THF was distilled from sodium benzophenone ketyl). All purchased reagents were used without further purification. Anhydrous solvents were transferred by oven-dried syringe. Flasks were flames dried under a stream of nitrogen. The NMR spectra were recorded at 250 MHz (^{1}H) and 62.9 MHz (^{13}C). The chemical shifts were relative to TMS (as an internal reference) for ^{1}H NMR

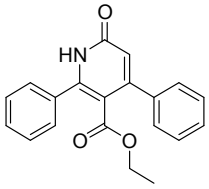
General Procedure for the Tandem Blaise Reaction with ethyl phenylpropiolate.



To a stirred suspension of commercial zinc dust (Aldrich, 10 μm, 1.0 g, 15.3 mmol) was added methanesulfonic acid (3.7 mg) in anhydrous THF (4.0 mL). After 10 min reflux, benzonitrile (0.8 mL, 7.6 mmol) was added all at one. While maintaining reflux temperature, ethyl bromoacetate (1.26 mL, 11.4 mmol) was added over 1h by using syringe pump

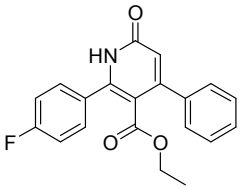
and the reaction mixture was further reflux for 1 h. To this reaction mixture, ethyl-phenylpropiolate (1.4 mL, 8.4 mmol) was added all at once. After stirring for 3h at reflux, the reaction mixture was quenched with saturated aqueous NH_4Cl, at room temperature and, extracted with ethyl acetate (30 mL x 3). The combined organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica chromatography to afford **4a** (98 %, 2.65 g).

1,6-Dihydro-2,4-diphenyl -6-oxo-pyridine-3-carboxylic acid ethyl ester (4a).



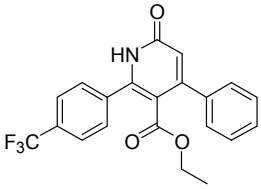
Yield: 98 %; Yellow solid; mp: 208-210 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.75 (t, *J* = 7.1 Hz, 3H), 3.80 (q, *J* = 7.2 Hz, 2H), 6.45 (s, 1H), 7.26 ~ 7.41 (m, 5H), 7.45 ~ 7.52 (m, 5H), 12.21 (brs, 1H) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.2, 61.2, 114.3, 118.5, 127.2, 128.2, 128.4, 128.7, 128.8, 130.3, 132.9, 138.1, 147.2, 154.0, 163.7, 166.7 ppm; IR (KBr pallet) 3441, 2893, 1967, 1651, 1280, 1010, 702; HRMS Cal. for $[M+H]^+$: $C_{20}H_{18}NO_3$: 320.1287. Found: 320.1285.

2-(4-Fluoro-phenyl)-6-oxo-4-phenyl-1,6-dihydro-pyridine-3-carboxylic acid ethyl ester (4b).



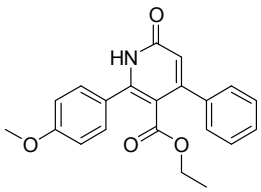
Yield: 97 %; Yellow solid; mp: 192-194 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.79 (t, *J* = 7.1 Hz, 3H), 3.82 (q, *J* = 7.1 Hz, 2H), 6.46 (s, 1H), 7.12 ~ 7.19 (m, 2H), 7.32 ~ 7.41 (m, 5H), 7.51 ~ 7.56 (m, 2H), 12.47 (brs, 1H) ppm; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.1, 61.1, 114.0, 115.5 (d, *J* = 22.1 Hz), 118.3, 127.0, 128.2, 128.6, 128.8, 130.4 (d, *J* = 8.6 Hz), 138.0, 146.3, 153.6, 163.9, 163.5 (d, *J* = 250.8 Hz), 166.6 ppm; IR (KBr pallet) 3433, 2989, 1720, 1658, 1280, 840, 705; HRMS Cal. for $[M+H]^+$: $C_{20}H_{17}FNO_3$: 338.1192. Found: 338.1184.

1,6-Dihydro-2-(4-trifluoromethyl-phenyl)-6-oxo-4-phenyl-pyridine-3-carboxylic acid ethyl ester (4c)



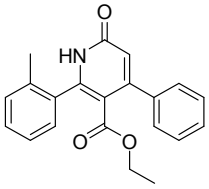
Yield: 95 %; Bright yellow solid; mp: 218-220℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.75 (t, *J* = 7.1 Hz, 3H), 3.81 (q, *J* = 7.2 Hz, 2H), 6.50 (s, 1H), 7.31 ~ 7.36 (m, 2H), 7.40 ~ 7.42 (m, 3H), 7.65-7.76 (m, 4H), 12.90 (brs, 1H) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.2, 61.4, 114.6, 119.2, 125.6 (q, *J* = 3.6/3.8 Hz), 127.2, 128.5, 128.9, 129.0, 131.6(d, *J* = 33.0 Hz), 136.4, 137.9, 145.9, 154.0, 164.0, 166.5 ppm; IR (KBr pallet) 3440, 1674, 1327, 1118, 848, 702; HRMS Cal. for $[M+H]^+$: $C_{21}H_{17}F_3NO_3$: 388.1161. Found: 388.1164.

1,6-Dihydro-2-(4-methoxy-phenyl)-6-oxo-4-phenyl-pyridine-2-carboxylic acid ethyl ester (4d)



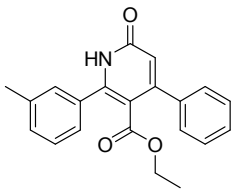
Yield: 95 %; Dark yellow solid; mp: 208-210 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.1 Hz, 3H), 3.83 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H),6.42 (s,1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.31 ~ 7.40 (m, 5H), 7.47 (d, *J* = 8.8 Hz, 2H), 12.25 (brs, 1H) ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.3, 55.3, 61.2, 113.7, 114.2, 118.1, 125.3, 127.2, 128.4, 128.7, 129.7, 138.4, 146.9, 153.9, 161.1, 163.5, 167.0; IR (KBr pallet) 3437, 2935, 1720, 1647, 1249, 1107, 833, 702; HRMS Cal. for $[M+H]^+$: $C_{21}H_{20}NO_4$: 350.1392. Found: 350.1383.

1,6-Dihydro-2-(*o*-tolyl)-6-oxo-4-phenyl-pyridine-3-carboxylic acid ethyl ester (4e)



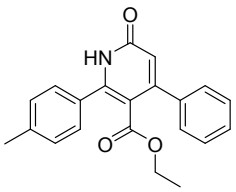
Yield: 56 %; Yellow solid; mp: 182-188 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.65 (t, *J* = 7.1 Hz, 3H), 2.31 (s, 3H), 3.71 (q, *J* = 6.4 Hz, 2H), 6.37 (s, 1H), 7.17 ~ 7.30 (m, 3H), 7.32 ~ 7.40 (m, 6H), 12.08 (brs, 1H) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.1, 19.5, 60.9, 114.1, 118.6, 125.5, 127.2, 128.3, 128.6, 128.7, 129.9, 130.2, 132.8, 136.5, 138.3, 147.8, 153.7, 163.5, 166.1 ppm; IR (KBr pallet) 3430, 2839,1658, 1280, 1411, 1010, 779; HRMS Cal. for $[M+H]^+$: $C_{21}H_{20}NO_3$: 334.1443. Found: 334.1456.

1,6-Dihydro-2-(*m*-tolyl)-6-oxo-4-phenyl-pyridine-3-carboxylic acid ethyl ester (4f)



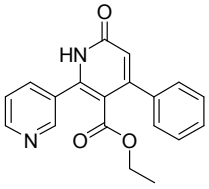
Yield: 81 %; Yellow solid; mp: 210-212 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7.1 Hz, 3H), 2.39 (s, 3H), 3.82 (q, *J* = 7.1 Hz, 2H), 6.45 (s, 1H), 7.30 ~ 7.41 (m, 9H) 11.44 (brs, 1H) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.2, 21.3, 61.1, 113.7, 118.4, 125.3, 127.2, 128.3, 128.4, 128.6, 128.9, 130.9, 132.8, 138.2, 147.5, 153.6, 163.7, 166.9 ppm; IR (KBr pallet) 3417, 2947, 1651, 1280, 864, 702; HRMS Cal. for $[M+H]^+$: $C_{21}H_{20}NO_3$: 334.1443. Found: 334.1456.

1,6-Dihydro-2-(*p*-tolyl)-6-oxo-4-phenyl-pyridine-3-carboxylic acid ethyl ester (4g)



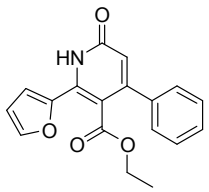
Yield: 87 %; Yellow solid; mp: 218-220 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7.1Hz, 3H), 2.39 (s, 3H), 3.82 (q, *J* = 7.2 Hz, 2H), 6.47 (s, 1H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.28 ~ 7.42 (m, 7H), 11.03 (brs, 1H) ppm; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.3, 21.4, 61.2, 113.8, 118.3, 127.2, 128.1, 128.4, 128.6, 129.4, 130.1, 138.3, 140.4, 147.4, 153.8, 163.7, 167.0 ppm; IR (KBr pallet) 3425, 2908, 1658, 1280, 1110, 825, 779; HRMS Cal. for $[M+H]^+$: $C_{21}H_{20}NO_3$: 334.1443. Found: 334.1456.

1,6-Dihydro-6-oxo-4-phenyl-[2,3′]bipyridinyl-3-carboxylic acid ethyl ester (4h)



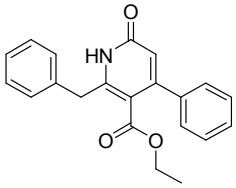
Yield: 83 %; Dark yellow solid; mp: 170-172 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.77 (t, *J* = 7.1Hz, 3H), 3.83 (q, *J* = 7.1Hz, 2H), 6.51 (s, 1H), 7.32 ~ 7.35 (m, 2H), 7.39 ~ 7.43 (m, 3H), 7.43 ~ 7.45 (m, 1H), 7.91-7.96 (m, 1H), 8.71 ~ 8.77 (m, 1H), 8.77 (d, *J* = 1.7 Hz, 1H), 13.37 (brs, 1H) ppm ; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.2, 61.4, 114.7, 119.0, 123.1, 127.1, 128.4, 128.8, 129.2, 136.1, 138.0, 144.5, 148.9, 150.8, 153.8, 164.0, 166.4 ppm; IR (KBr pallet) 3425, 2769, 1651, 1280, 1002, 709; HRMS Cal. for $[M+H]^+$: $C_{19}H_{17}N_2O_3$: 321.1239. Found: 321.1253.

1,6-Dihydro-2-(furan-2-yl)-6-oxo-4-phenyl-pyridine-3-carboxylic acid ethyl ester (4i)



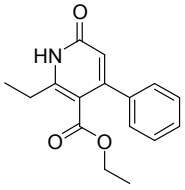
Yield: 90 %; Dark yellow solid; mp: 208-210 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.1 Hz, 3H), 4.03 (q, *J* = 7.1 Hz, 2H), 6.49 (s, 1H), 6.55 ~ 6.57 (m, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.37 ~ 7.43 (m, 5H), 7.54 (d, *J* = 1.2 Hz, 1H), 11.89 (brs, 1H) ppm ; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.6, 61.6, 111.6, 112.6, 113.7, 118.6, 127.4, 128.4, 128.8, 134.7, 137.9, 144.6, 144.9, 153.8, 163.2, 166.8; IR (KBr pallet) 3425, 2900, 1651, 1280, 1018, 771; HRMS Cal. for $[M+H]^+$: $C_{18}H_{16}NO_4$: 310.1079. Found: 310.1075.

2-Benzyl-1,6-dihydro-6-oxo-4-phenyl-pyridine-3-carboxylic acid ethyl ester (4j)



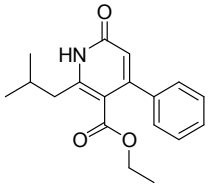
Yield: 92 %; Yellow solid; mp: 160-162 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.75 (t, *J* = 7.1 Hz, 3H), 3.86 (q, *J* = 7.2 Hz, 2H), 4.20 (s, 2H), 6.44 (s, 1H), 7.23 ~ 7.41 (m, 10H), 12.72 (brs, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.3, 37.0, 61.1, 113.1, 117.6, 127.0, 127.1, 128.4, 128.5, 128.7, 129.0, 136.3, 139.1, 149.1, 154.6, 164.3, 167.0 ppm; IR (KBr pallet) 3456, 2777, 1658, 1265, 948, 702; HRMS Cal. for $[M+H]^+$: $C_{21}H_{20}NO_3$: 334.1443. Found: 334.1462.

2-Ethyl-1,6-dihydro-6-oxo-4-phenyl-pyridine-3-carboxylic acid ethyl ester (4k)



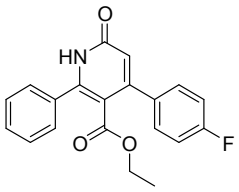
Yield: 92 %; Yellow solid; mp: 136-138 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.1 Hz, 3H), 1.39 (t, *J* = 7.5 Hz, 3H), 2.84 (q, *J* = 7.65Hz, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 6.46 (s, 1H), 7.28 ~ 7.41 (m, 5H), 13.42 (brs, 1H) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.3, 14.3, 25.3, 61.0, 112.5, 116.9, 127.0, 128.3, 128.4, 139.0, 152.6, 154.7, 164.9, 166.9 ppm; IR (KBr pallet) 3433, 2985, 1651, 1265, 1018, 655; HRMS Cal. for $[M+H]^+$: $C_{16}H_{18}NO_3$: 272.1287. Found: 272.1297.

1,6-Dihydro-2-isobutyl-6-oxo-4-phenyl-pyridine-3-carboxylic acid ethyl ester (4l)



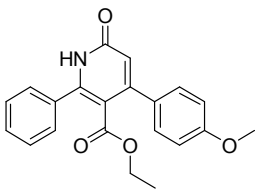
Yield: 88 %; Yellow solid; mp : 138-140 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 6H), 2.05 ~ 2.15 (m, 1H), 2.74 (d, *J* = 7.4 Hz, 2H), 3.92 (q, *J* = 7.2 Hz, 2H), 6.44 (s, 1H), 7.27 ~ 7.42 (m, 5H), 13.08 (s, 1H) ppm; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.4, 22.2, 29.5, 39.9, 61.0, 113.4, 117.1, 127.0, 128.4, 128.5, 139.2, 150.6, 154.5, 164.5, 167.1 ppm; IR (KBr pallet) 3430, 2962, 1651, 1465, 1265, 987, 702; HRMS Cal. for $[M+H]^+$: $C_{18}H_{22}NO_3$: 300.1600. Found: 300.1611.

1,6-Dihydro-4-(4-fluoro-phenyl)-6-oxo-2-phenyl-pyridine-3-carboxylic acid ethyl ester (4m)



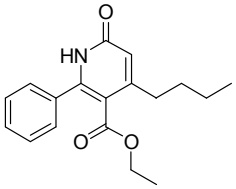
Yield: 92 %; Yellow solid; mp: 205-210 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.1 Hz, 3H), 3.83 (q, *J* = 7.1 Hz, 2H), 6.44 (s, 1H), 7.06 ~ 7.13 (m, 2H), 7.30 ~ 7.36 (m, 2H), 7.49 ~ 7.53 (m, 5H), 11.53 (brs, 1H) ppm; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.4, 61.4, 113.9, 115.5(d, *J* = 21.7 Hz), 118.7, 128.2, 128.7, 129.2 (d, *J* = 8.2 Hz), 130.3, 133.0, 134.2 (d, *J* = 3.4 Hz), 147.5, 152.7, 163.3(d, *J* = 248.6 Hz) 163.7, 166.8 ppm; IR (KBr pallet) 3437, 2900, 1724, 1647, 837; HRMS Cal. for $[M+H]^+$: $C_{20}H_{17}FNO_3$: 338.1192. Found: 338.1180.

1,6-Dihydro-4-(4-methoxy-phenyl)-6-oxo-2-phenyl-pyridine-3-carboxylic acid ethyl ester (4n)



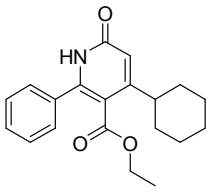
Yield: 94 %; Yellow solid; mp: 228-230 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.1 Hz, 3H), 3.84 (s, 3H), 3.85 (q, *J* = 7.1 Hz, 2H), 6.45 (s, 1H), 6.92 (d, , *J* = 8.8 Hz, 2H), 7.28 (d, , *J* = 8.8 Hz, 2H), 7.45 ~ 7.53 (m, 5H), 11.49 (brs, 1H) ppm; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.4, 55.3, 61.3, 113.9, 114.2, 118.1, 128.3, 128.6, 128.7, 130.2, 130.4, 133.1, 147.1, 153.4, 160.1, 163.9, 167.1 ppm; IR (KBr pallet) 3437, 2900, 1724, 1647, 837; HRMS Cal. for $[M+H]^+$: $C_{21}H_{20}NO_4$: 350.1392. Found: 350.1395.

4-Butyl-1,6-dihydro-6-oxo-2-phenyl-pyridine-3-carboxylic acid ethyl ester (4o)



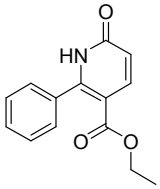
Yield: 90 %; Pale yellow solid; mp: 118-120 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H), 1.34 ~ 1.42 (m, 2H), 1.48 ~ 1.72 (m, 2H), 2.59 (t, *J* = 7.9 Hz, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 6.33 (s, 1H), 7.43 ~ 7.49 (m, 5H), 11.40 (brs, 1H) ppm; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.4, 13.8, 22.3, 31.5, 33.1, 61.1, 113.8, 117.4, 128.0, 128.4, 129.9, 133.6, 147.3, 155.1, 164.1, 167.3 ppm; IR (KBr pallet) 3428, 2958, 1720, 1643, 1276, 698; HRMS Cal. for $[M+H]^+$: $C_{18}H_{22}NO_3$: 300.1600. Found: 300.1613.

4-Cyclohexyl-1,6-dihydro-6-oxo-2-phenyl-pyridine-3-carboxylic acid ethyl ester (4p)



Yield: 91 %; Pale yellow solid; mp: 210-212 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.1 Hz, 3H), 1.15 ~ 1.40 (m, 5H), 1.71 ~ 1.89 (m, 5H), 2.52 ~ 2.71 (m, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 6.39 (s, 1H), 7.44 ~ 7.46 (m, 5H), 11.54 (brs, 1H) ppm; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 13.5, 25.9, 26.5, 33.2, 40.8, 61.2, 114.2, 114.9, 128.2, 128.6, 129.9, 133.7, 146.7, 159.7, 164.7, 167.5 ppm; IR (KBr pallet) 3440, 2927, 1716, 1651, 1265, 702; HRMS Cal. for $[M+H]^+$: $C_{20}H_{24}NO_3$: 326.1756. Found: 326.1753.

1,6-Dihydro-6-oxo-2-phenyl-pyridine-3-carboxylic acid ethyl ester (4q)



Yield: 35 %; Yellow solid; mp: 158-160 ℃; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.1Hz, 3H), 4.06 (q, *J* = 7.2Hz, 2H), 6.45 (d, *J* = 9.6Hz, 1H), 7.37 ~ 7.50 (m, 5H), 7.98 (d, *J* = 9.7 Hz, 1H), 11.13 (s, 1H) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.7, 60.82, 109.2, 118.4, 128.2, 128.3, 130.1, 134.0, 142.1, 151.9, 163.7, 165.0 ppm; IR (KBr pallet); 3448, 1654, 1269, 702; HRMS Cal. for $[M+H]^+$: $C_{14}H_{14}NO_3$: 244.0974. Found: 244.0966.

4-(Amino-phenyl-methylene)-3-phenyl-pent-2-enedionic acid diethyl ester (8)

To a stirred suspension of commercial zinc dust (Aldrich, 10 μm, 1.0 g, 15.3 mmol) was added methanesulfonic acid (3.7 mg) in anhydrous THF (4.0 mL). After 10 min reflux, benzonitrile (0.8 mL, 7.6 mmol) was added all at one. While maintaining reflux temperature, ethyl bromoacetate (1.26 mL, 11.4 mmol) was added over 1h by using syringe pump and the reaction mixture was further reflux for 1h. The reaction mixture was cooled to room temperature and ethyl phenylpropiolate (1.4 mL, 8.4 mmol) was added and stirred at 40 ^{o}C for 24 h. The reaction mixture was quenched with saturated aqueous NH_4Cl, at room temperature and, extracted with ethyl acetate (30 mL x 3). The combined organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica chromatography to afford **8**.

Yield: 45 %; Viscous yellowish liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.84 (brs, 1H), 6.02 (s, 1H), 7.09 ~ 7.22 (m, 10H), 8.86 (brs, 1H) ppm; ^{13}C NMR (62.9MHz, $CDCl_3$) δ 14.0, 14.2, 59.1, 59.5, 96.3, 119.5, 127.2, 127.4, 127.6, 127.7, 128.1, 128.8, 137.8, 142.7, 153.1, 160.3, 166.1, 169.0 ppm.

X-ray Crystallography

The diffraction data for **4k** were collected on a Bruker SMART AXS diffractometer using Mo Kα (λ = 0.71073 Å). The crystallographic data are listed in Table S1. The CIF deposition number: **CCDC 742379**

Table S1. Crystal data and structure refinement for **4k**.

Empirical formula	C16 H17 N O3	
Formula weight	271.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.564(2) Å	□= 90.00°
	b = 16.918(3) Å	□= 109.86(3)°
	c = 15.223(3) Å	□ = 90.00°
Volume	2801.1(10) $Å^3$	
Z	8	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	1152	
Crystal size	0.15 x 0.10 x 0.10 mm^3	
θ range for data collection	1.86 to 26.00 .	
Index ranges	$-13 \leq h \leq 14$, $-19 \leq k \leq 20$, $-18 \leq l \leq 18$	
Reflections collected	15550	
Independent reflections	5490 [R(int) = 0.0551]	
Completeness to theta = 26.00	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5490 / 0 / 373	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1057	
R indices (all data)	R1 = 0.0979, wR2 = 0.1194	
Largest diff. peak and hole	0.167 and -0.199 $e.Å^{-3}$	

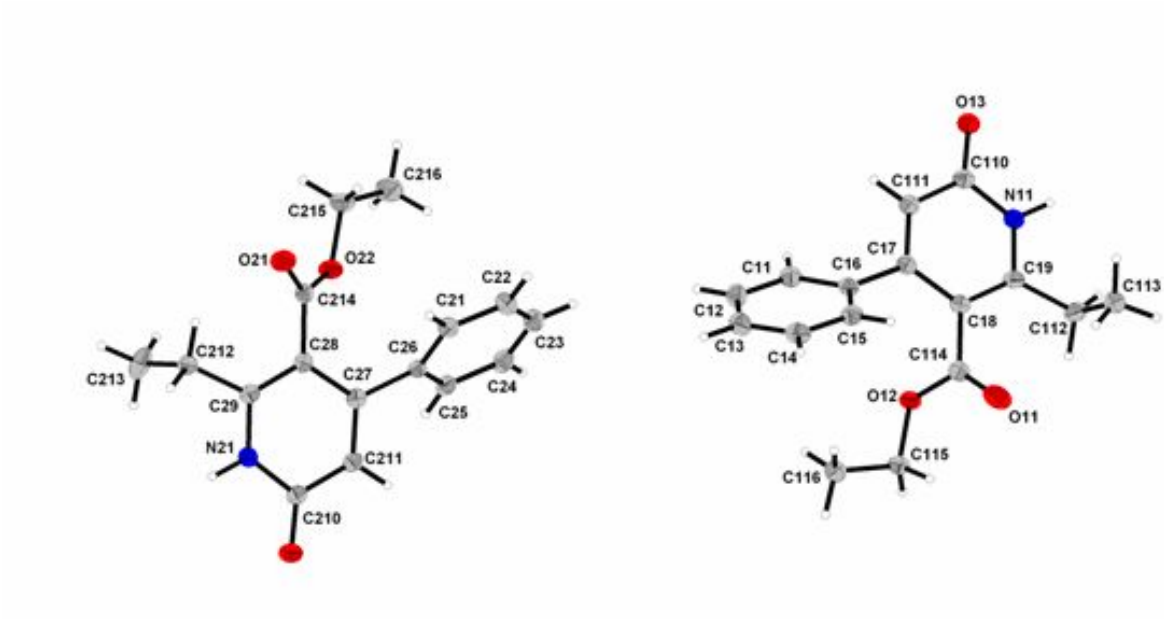
Table S2. Selected Bond lengths [Å] and angles [°] for **4k**.

C(17)-C(111)	1.363(3)
C(18)-C(19)	1.372(3)
C(19)-N(11)	1.365(3)
C(110)-O(13)	1.256(2)
C(110)-N(11)	1.376(3)
C(114)-O(11)	1.202(2)
C(114)-O(12)	1.331(2)
C(115)-O(12)	1.457(3)
C(26)-C(27)	1.498(3)
C(27)-C(211)	1.365(3)
C(28)-C(29)	1.376(3)
C(29)-N(21)	1.356(3)
C(210)-O(23)	1.248(2)
C(210)-N(21)	1.370(3)
C(214)-O(21)	1.210(2)
C(214)-O(22)	1.335(2)
C(215)-O(22)	1.451(3)
C(215)-C(216)	1.496(3)
N(11)-H(11N)	0.89(2)
N(21)-H(21N)	0.88(2)
N(11)-C(19)-C(18)	119.7(2)
N(11)-C(19)-C(112)	114.18(19)
C(18)-C(19)-C(112)	126.1(2)
O(13)-C(110)-N(11)	119.99(19)
O(13)-C(110)-C(111)	124.6(2)
N(11)-C(110)-C(111)	115.4(2)
C(17)-C(111)-C(110)	122.4(2)
O(11)-C(114)-O(12)	123.4(2)
O(11)-C(114)-C(18)	125.5(2)
O(12)-C(114)-C(18)	111.11(19)
O(12)-C(115)-C(116)	109.60(18)
N(21)-C(29)-C(28)	119.35(19)
N(21)-C(29)-C(212)	114.12(18)
C(28)-C(29)-C(212)	126.5(2)
O(23)-C(210)-N(21)	120.25(19)

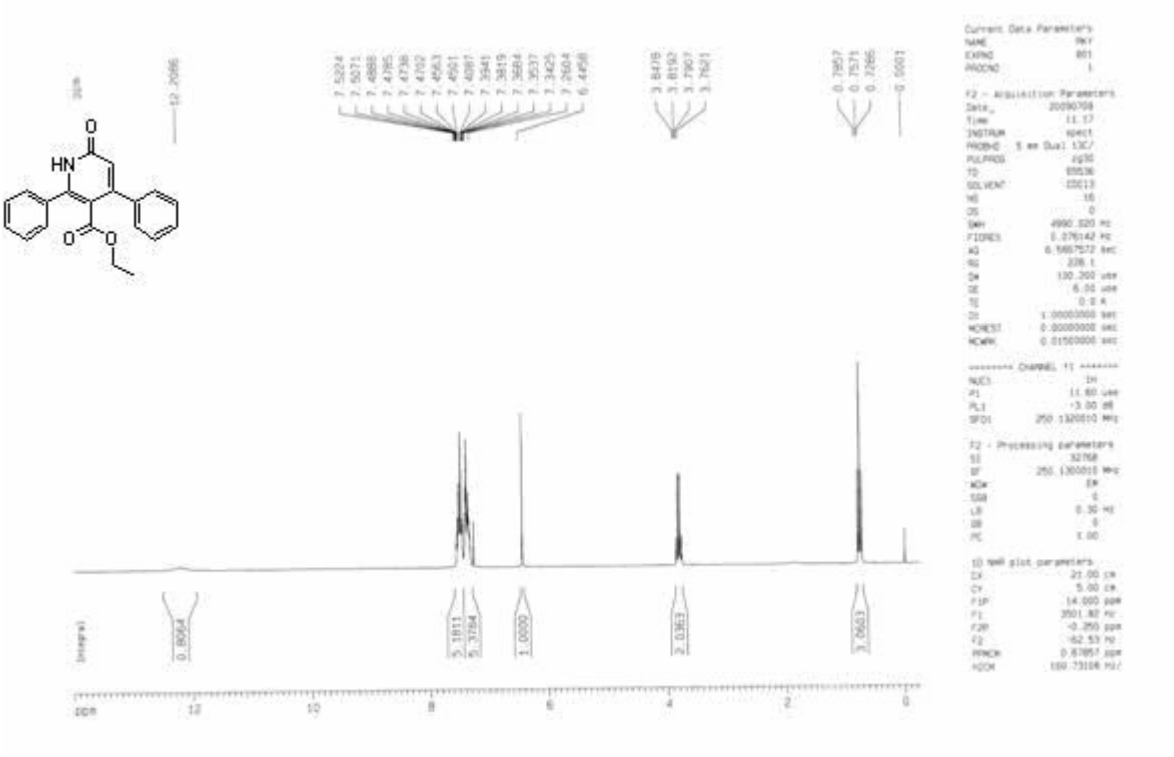
O(23)-C(210)-C(211)	125.30(19)
N(21)-C(210)-C(211)	114.4(2)
C(27)-C(211)-C(210)	122.19(19)
O(21)-C(214)-O(22)	122.6(2)
O(21)-C(214)-C(28)	125.58(19)
O(22)-C(214)-C(28)	111.83(17)
O(22)-C(215)-C(216)	107.56(19)
C(19)-N(11)-C(110)	124.49(19)
C(19)-N(11)-H(11N)	118.7(16)
C(110)-N(11)-H(11N)	116.8(16)
C(29)-N(21)-C(210)	126.01(19)
C(29)-N(21)-H(21N)	118.7(15)
C(210)-N(21)-H(21N)	115.1(15)
C(114)-O(12)-C(115)	118.45(17)
C(214)-O(22)-C(215)	117.09(17)

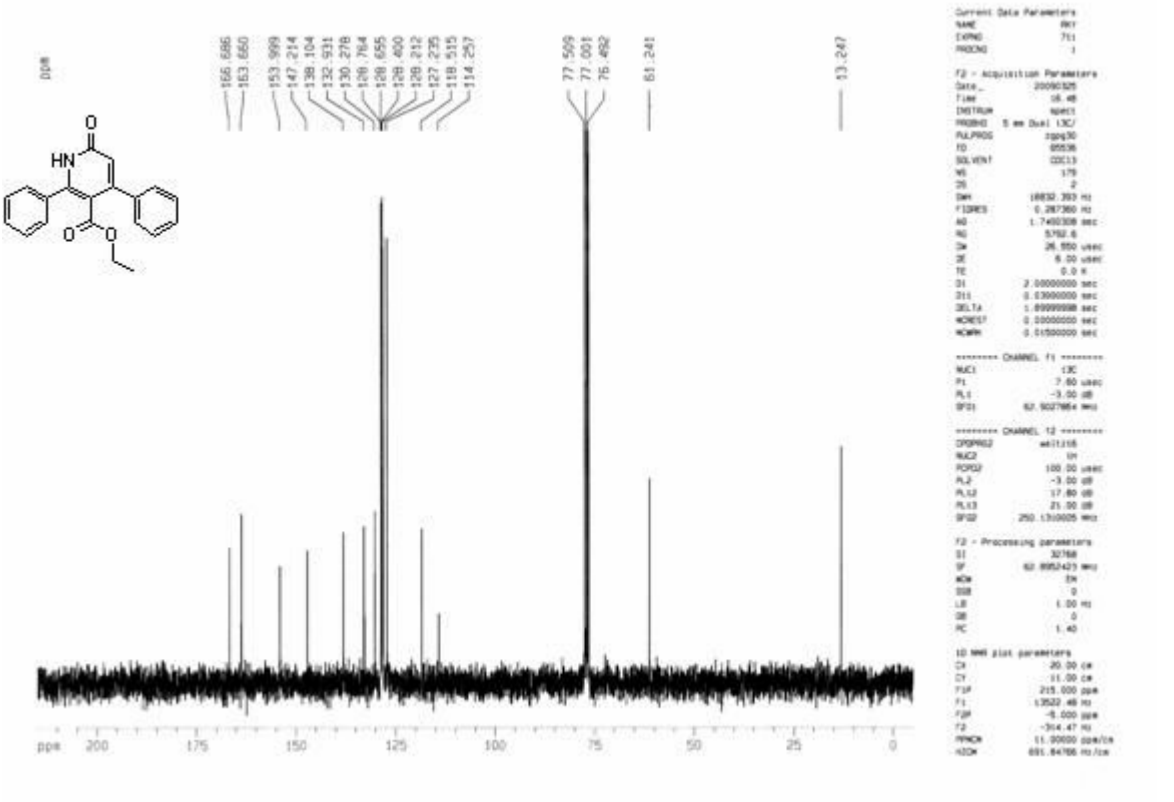
Symmetry transformations used to generate equivalent atoms:

Figure S1. X-Ray crystal structure of **4k**.

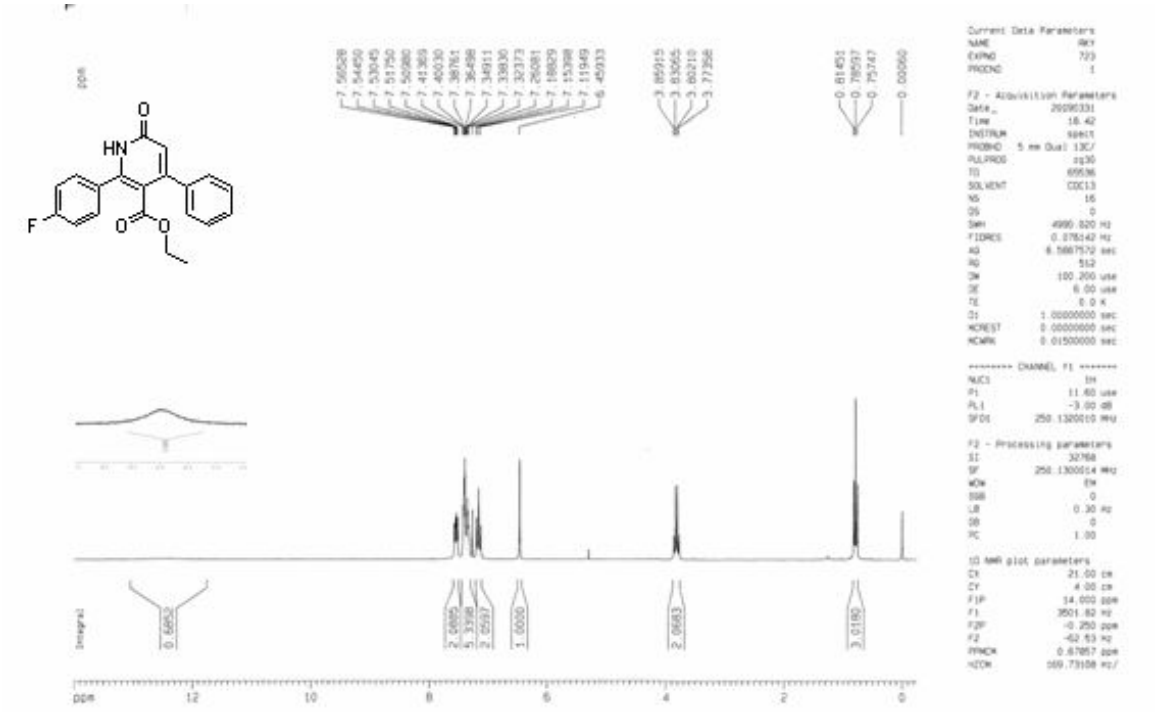


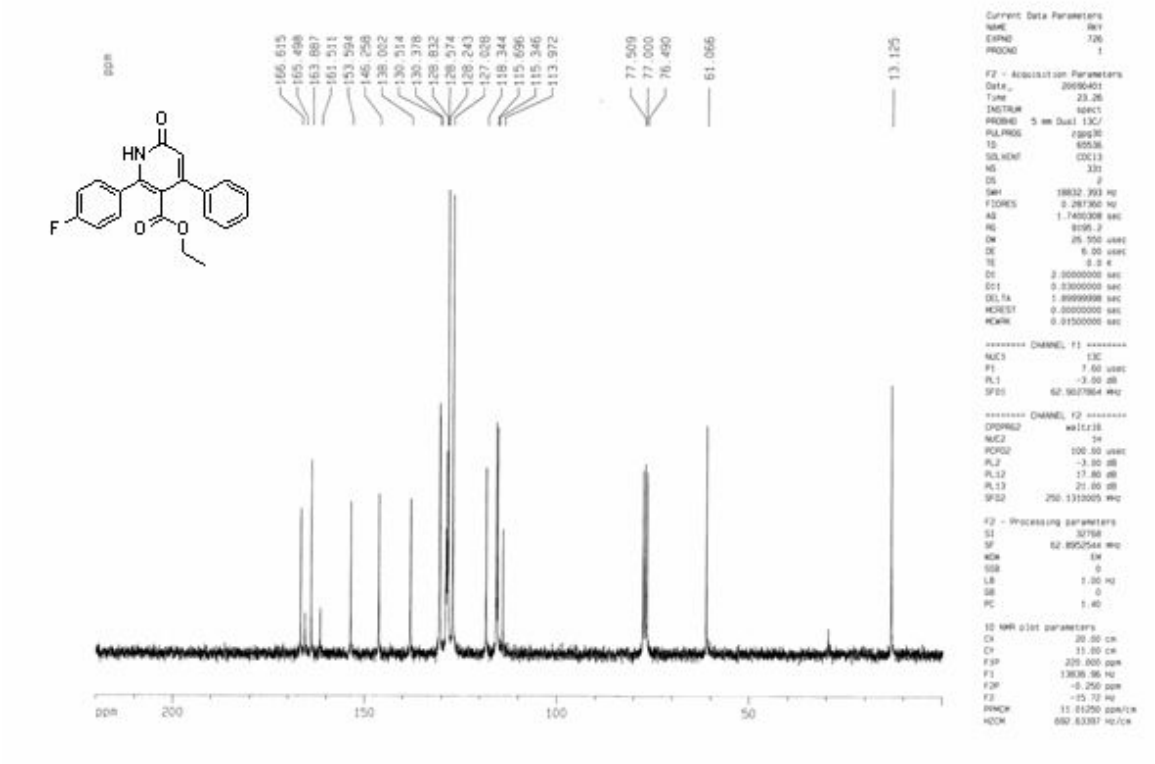
^{1}H and ^{13}C NMR spectra of **4a**



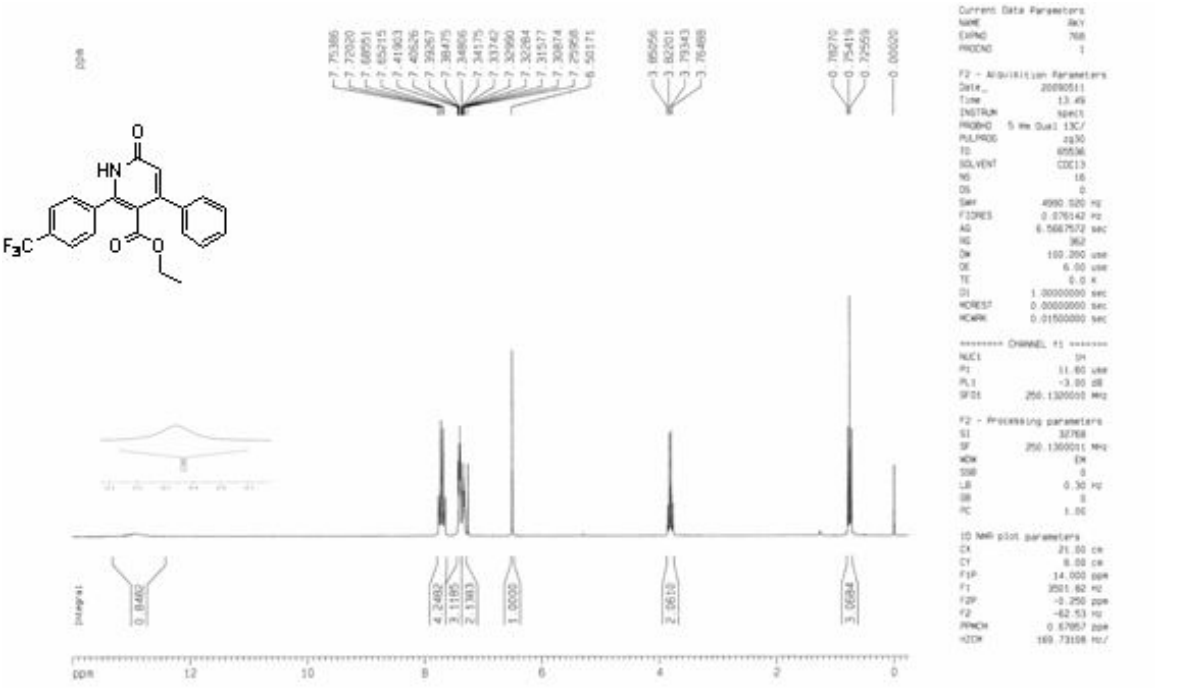


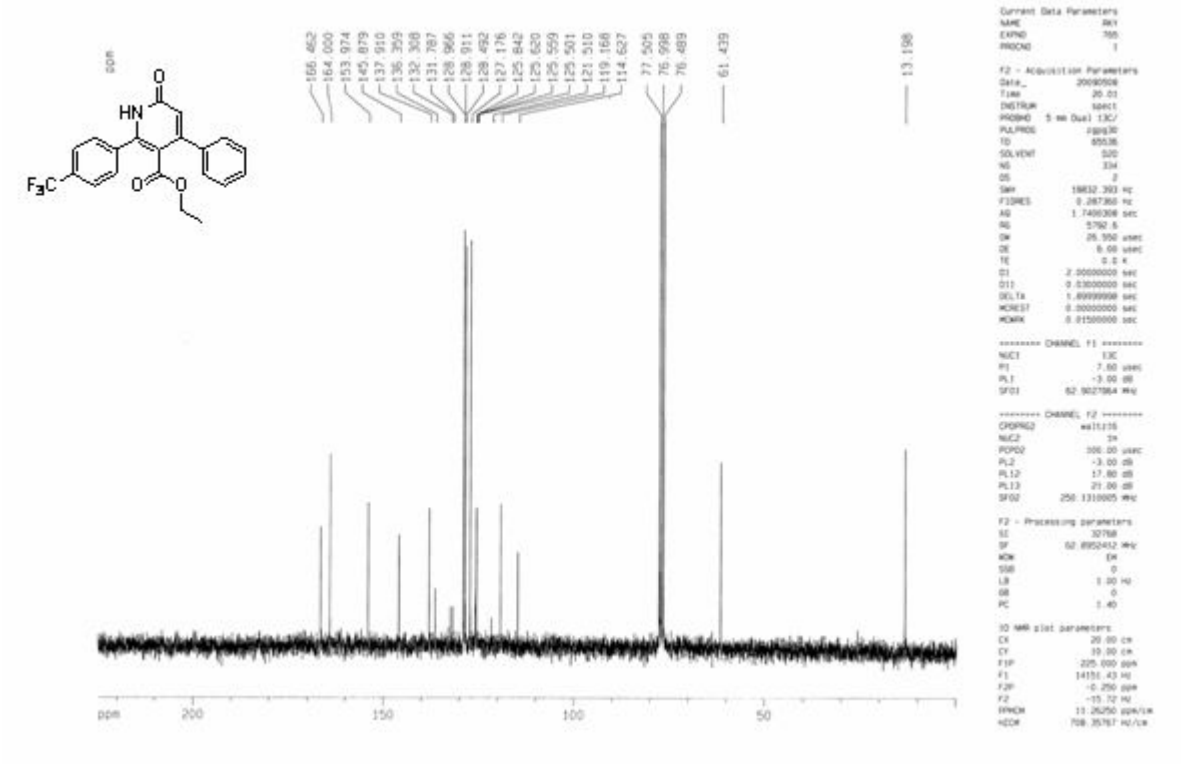
^{1}H and ^{13}C NMR spectra of **4b**



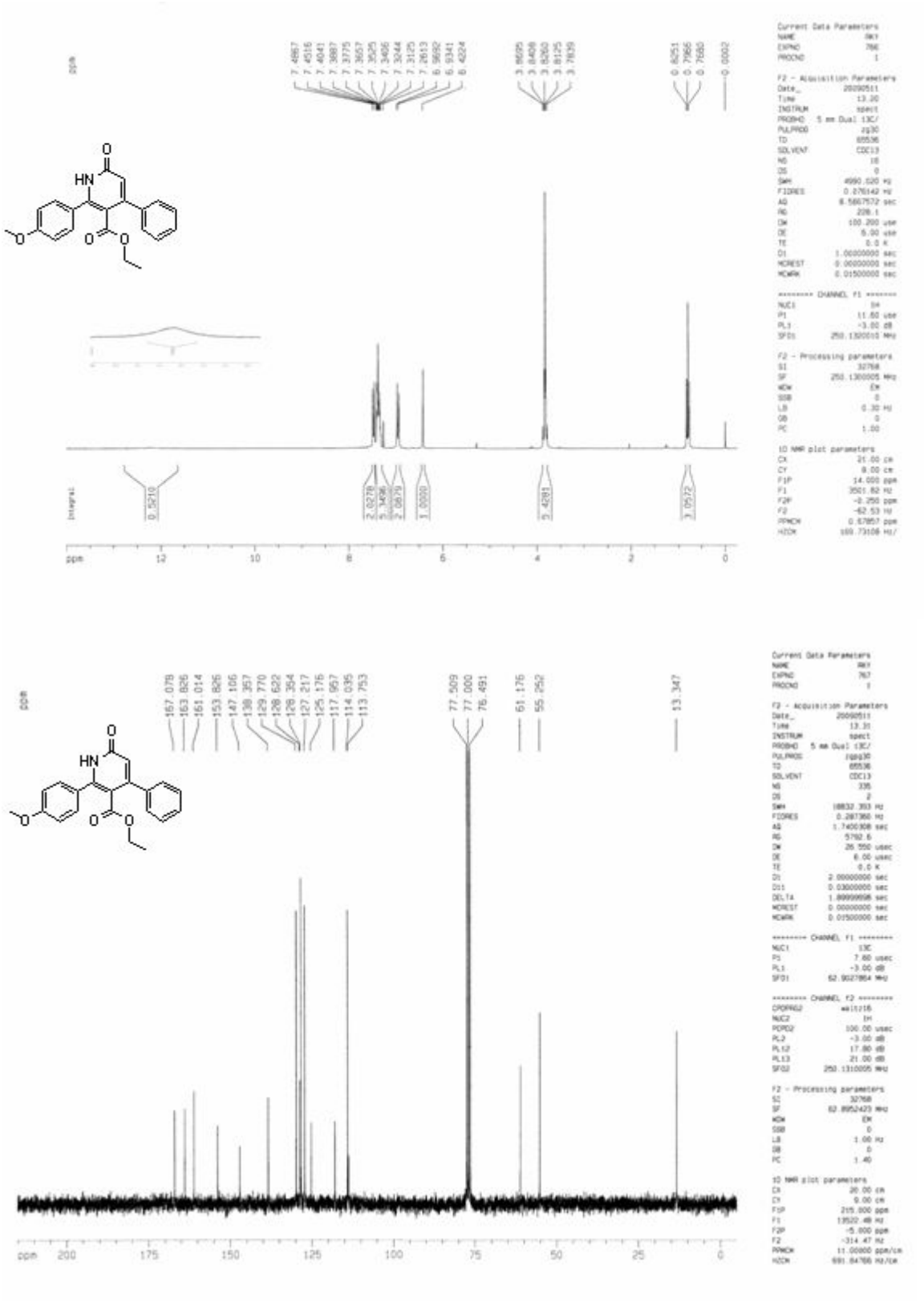


^{1}H and ^{13}C NMR spectra of **4c**

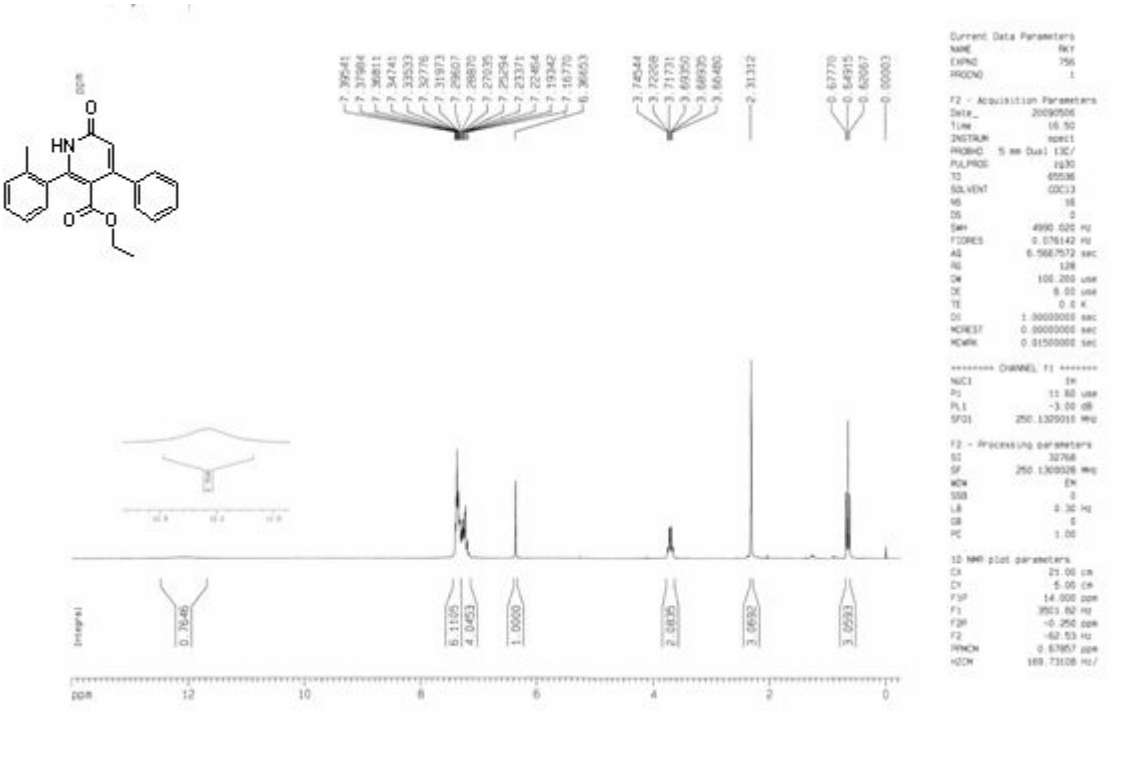


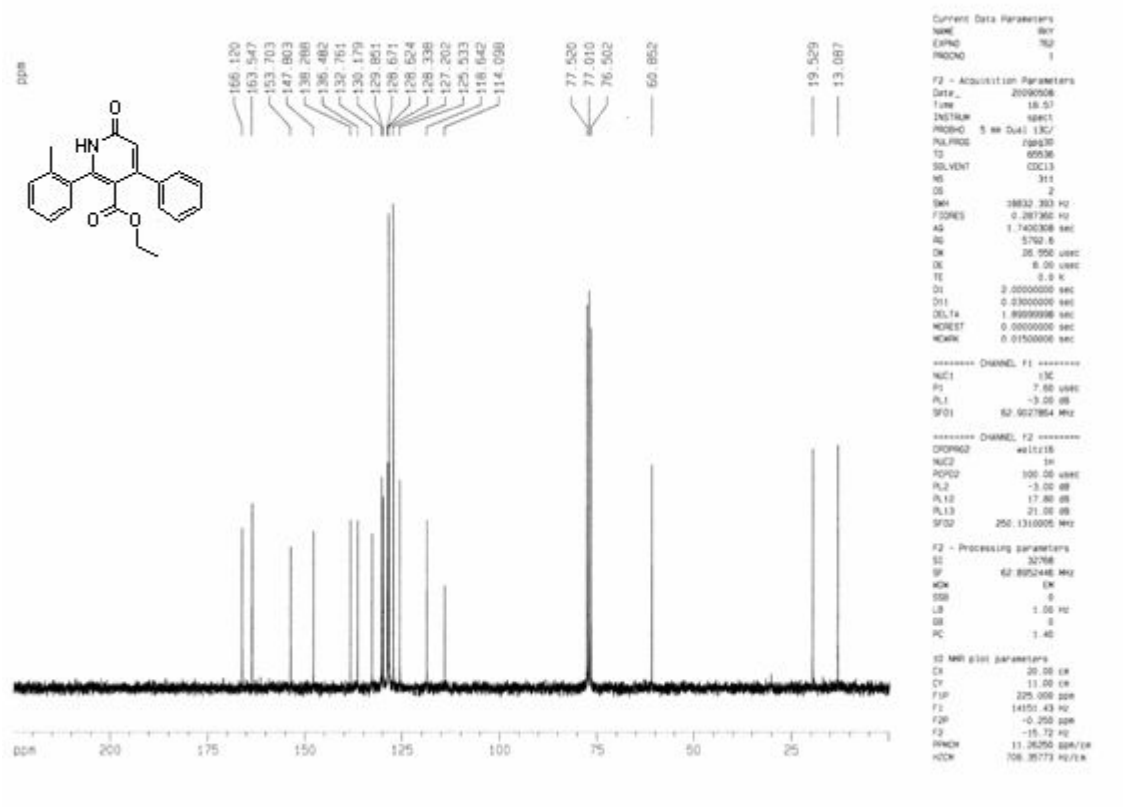


^{1}H and ^{13}C NMR spectra of **4d**

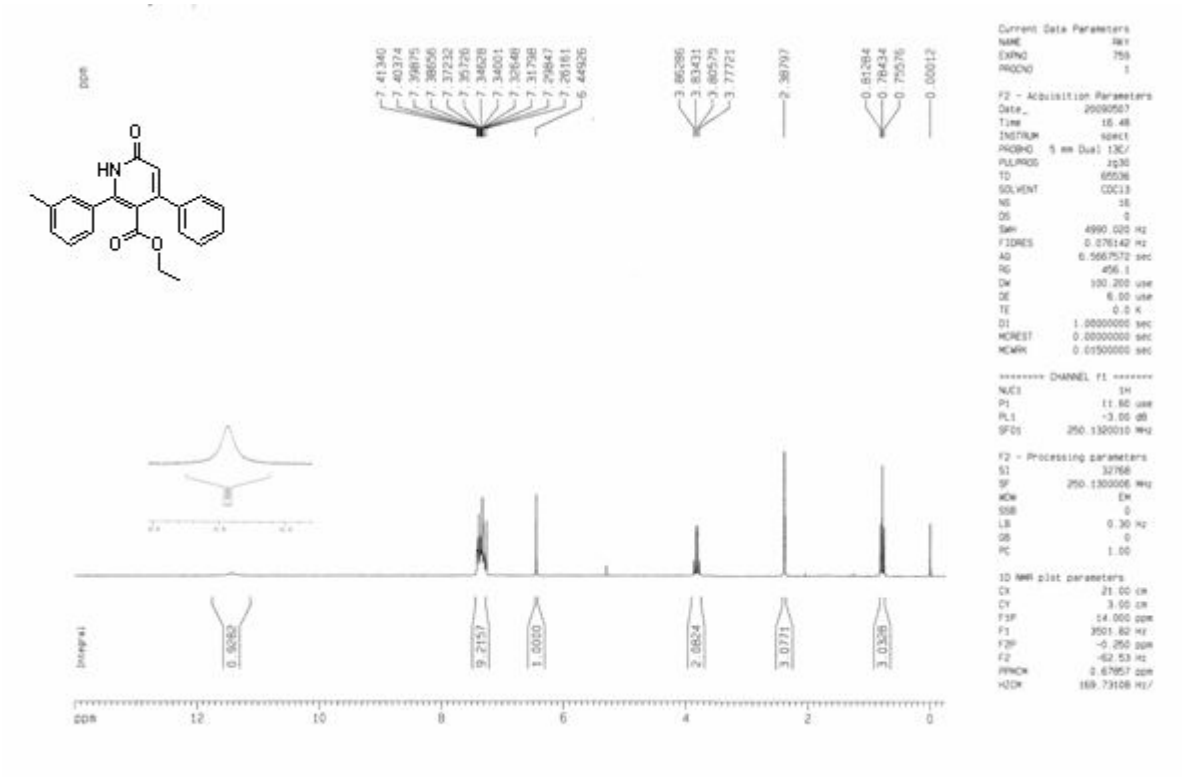


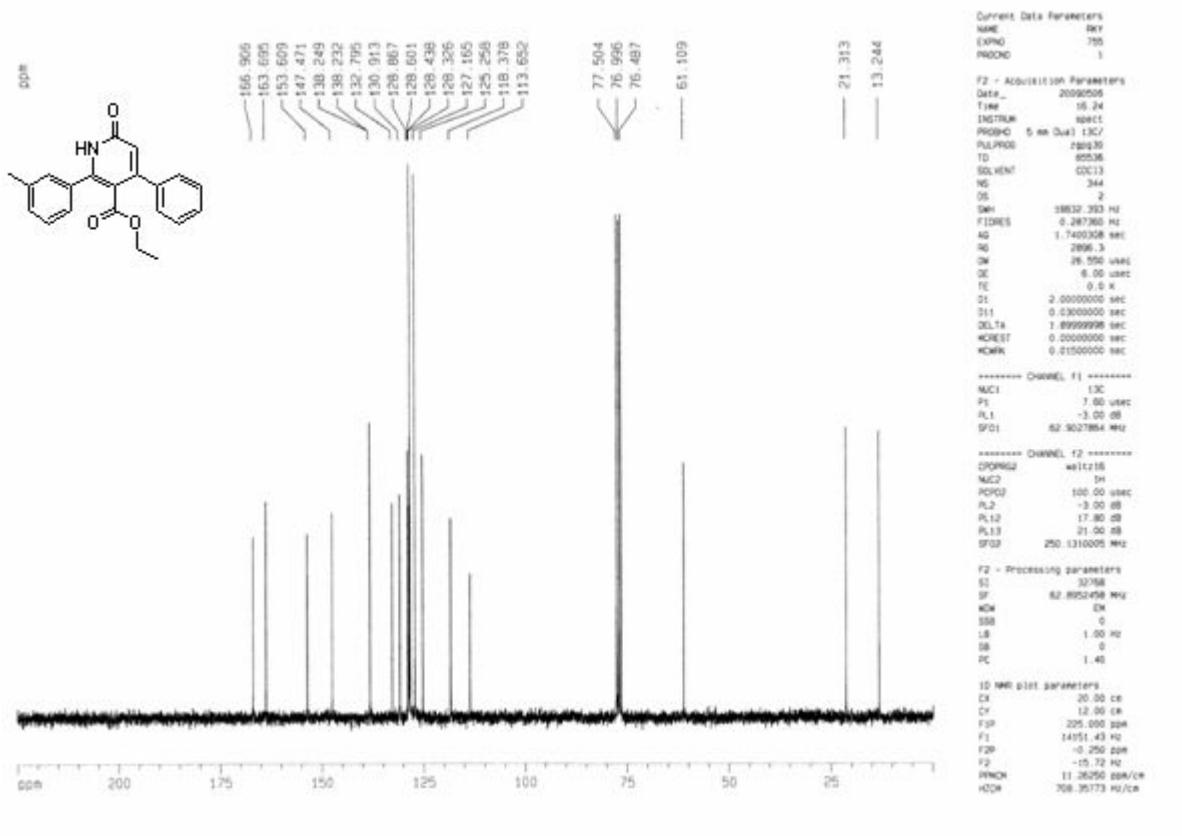
^{1}H and ^{13}C NMR spectra of **4e**



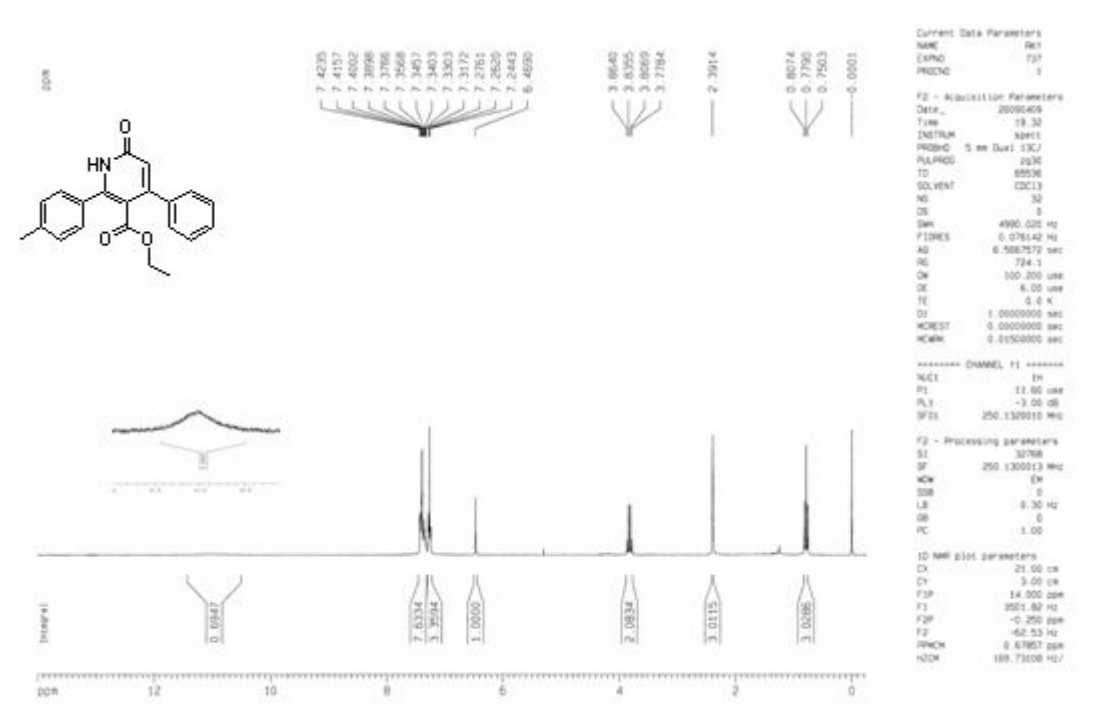


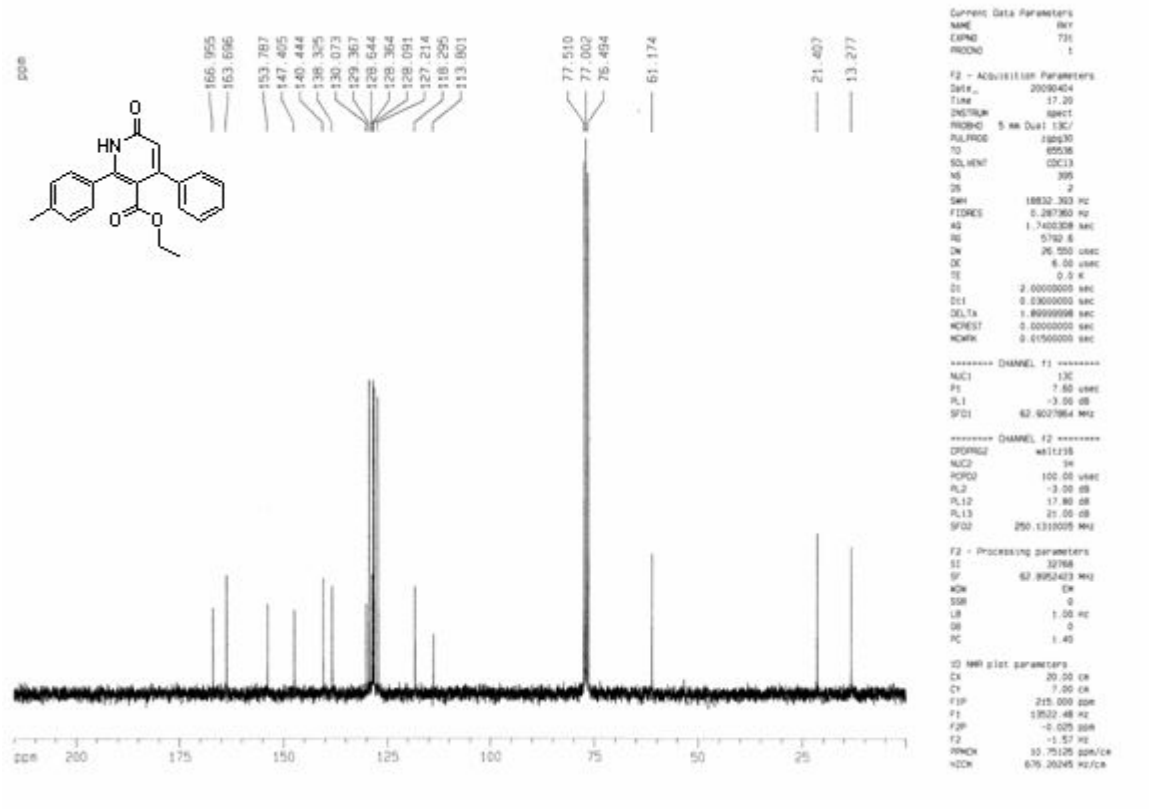
^{1}H and ^{13}C NMR spectra of **4f**



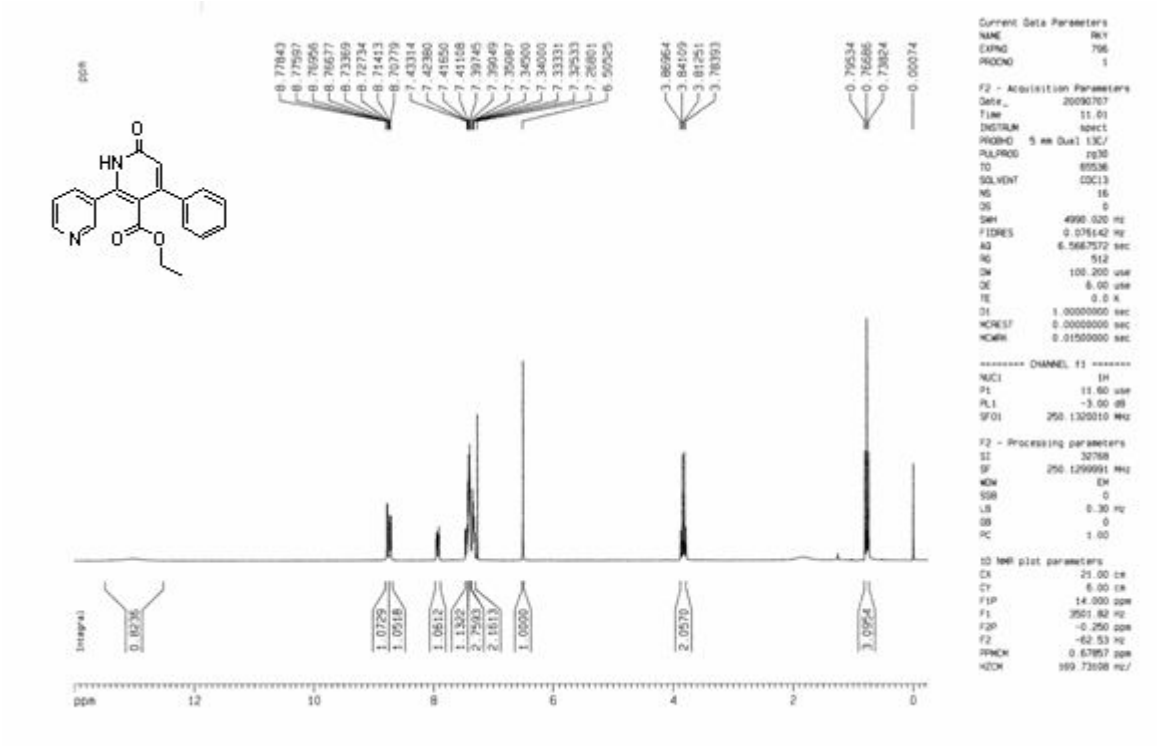


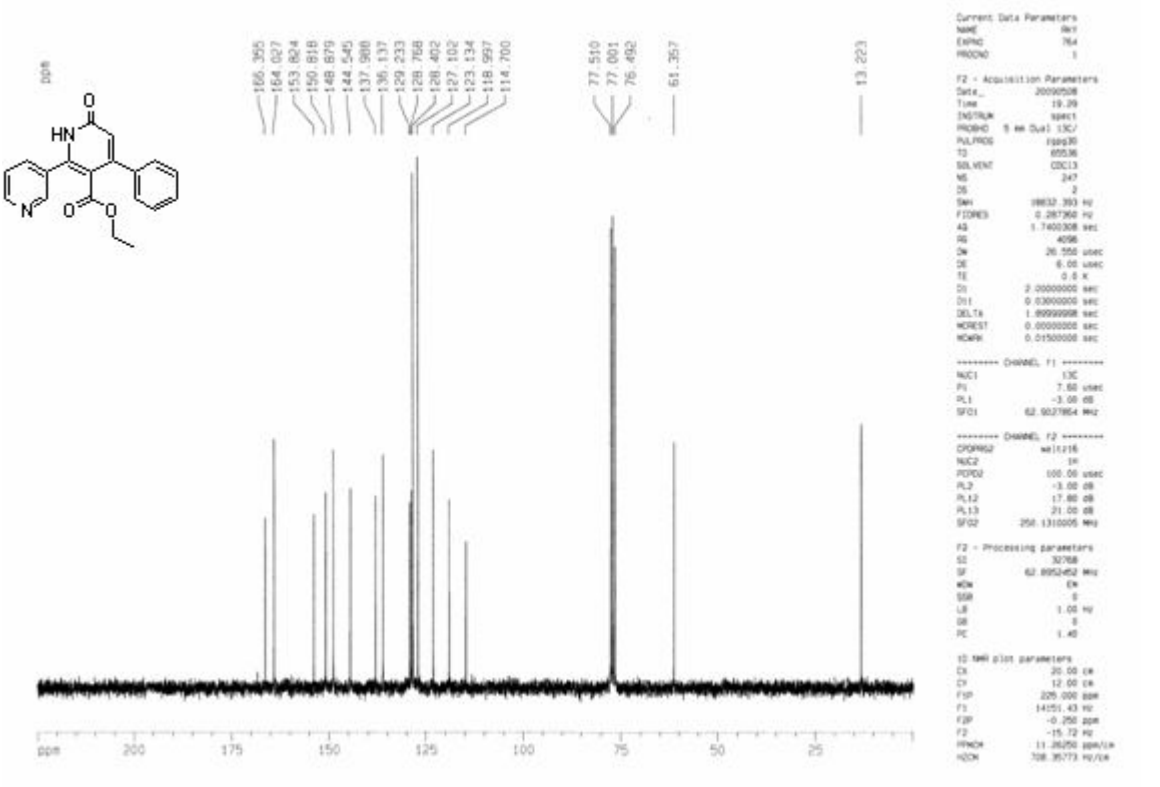
^{1}H and ^{13}C NMR spectra of **4g**



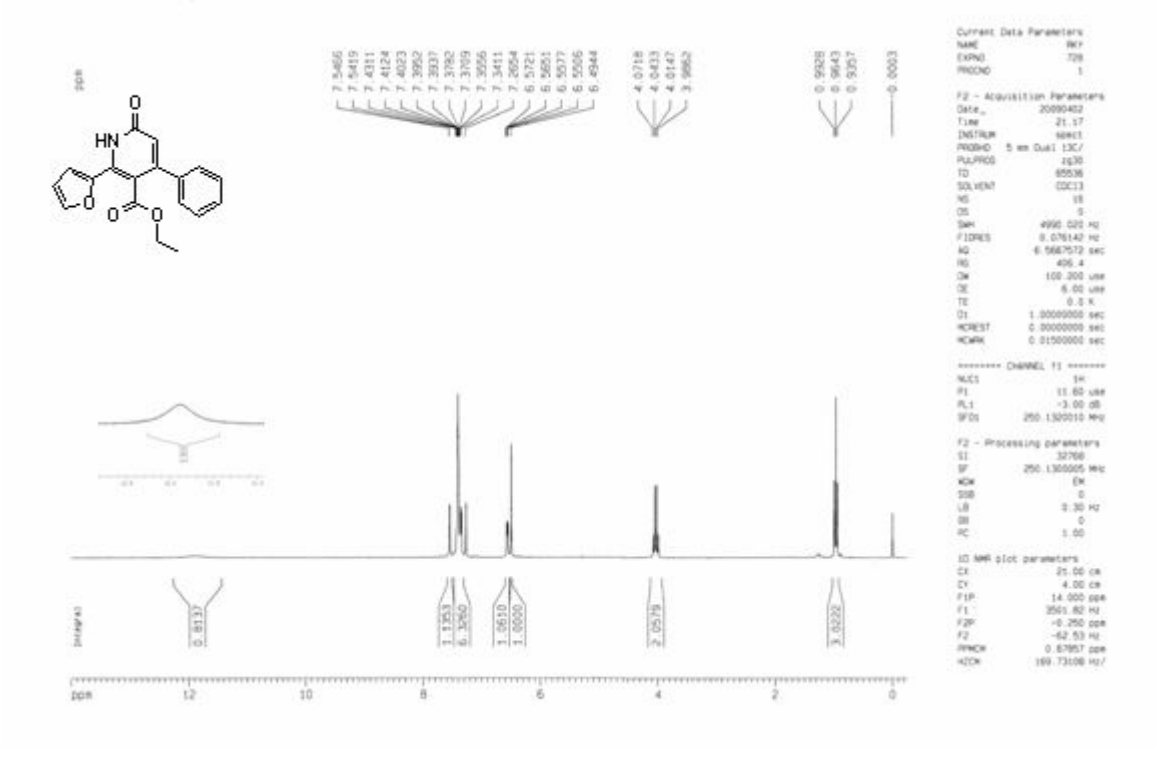


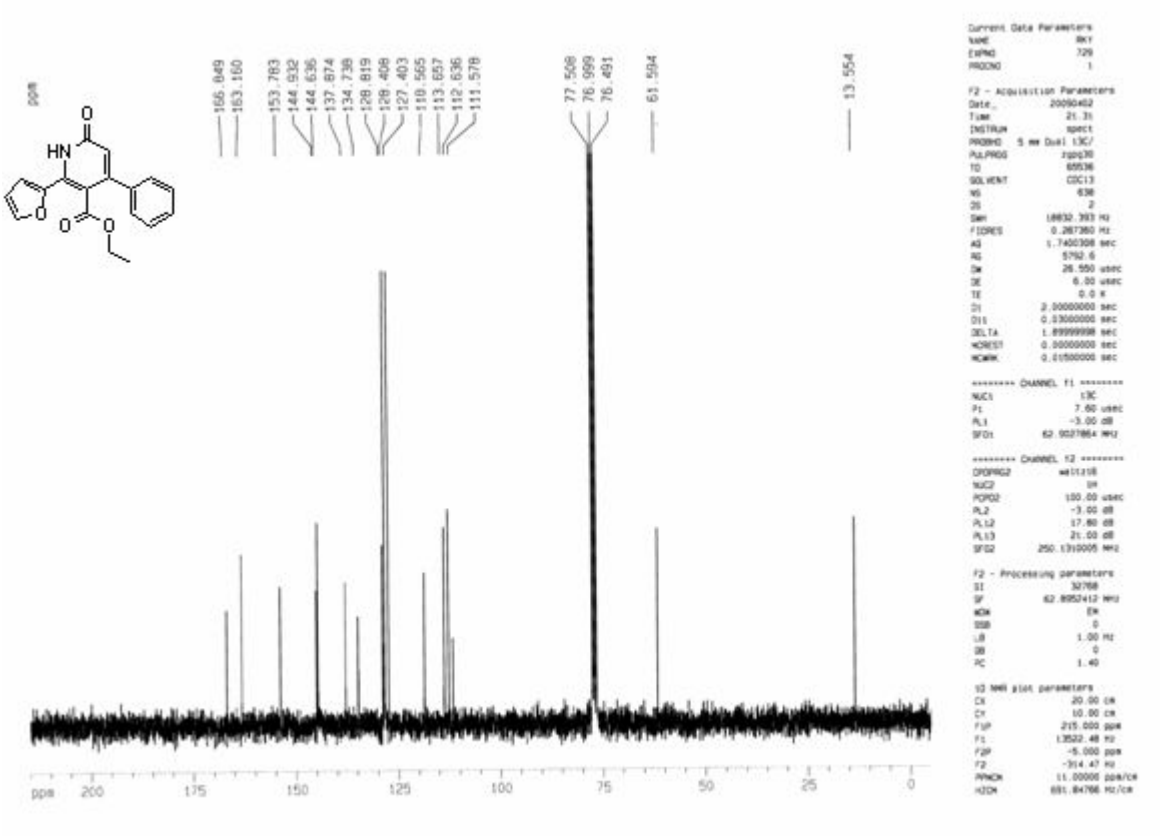
^{1}H and ^{13}C NMR spectra of **4h**



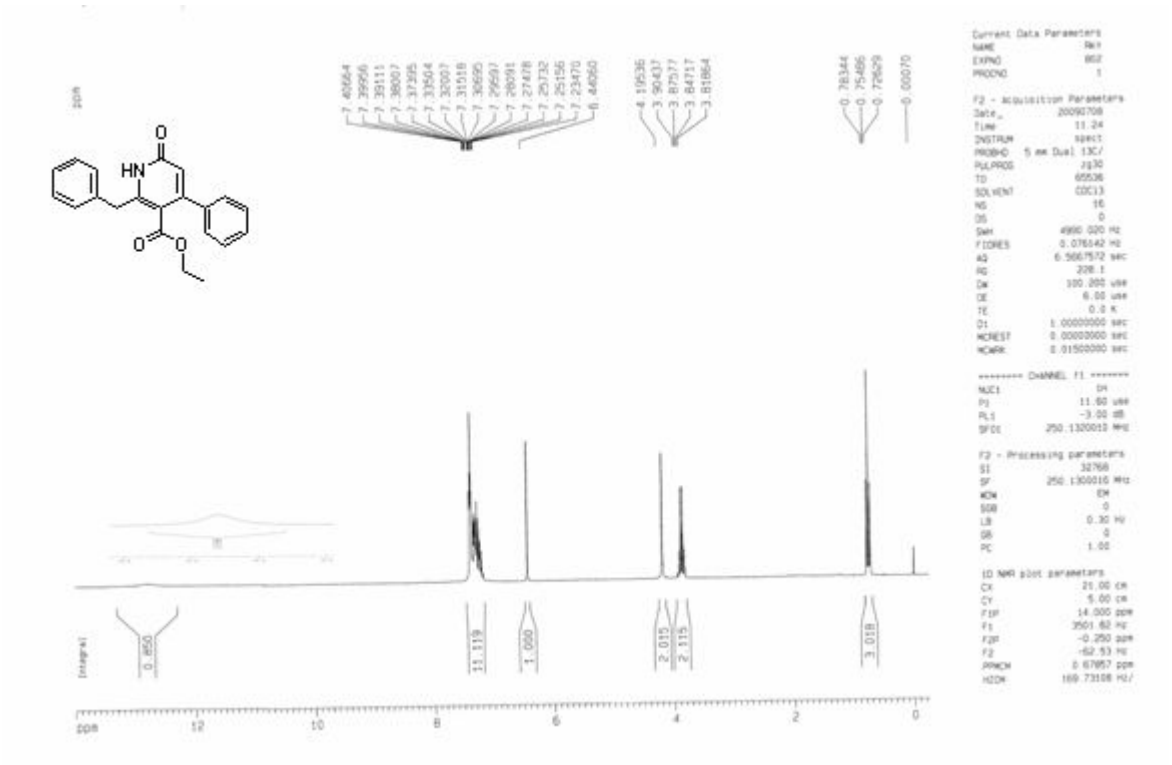


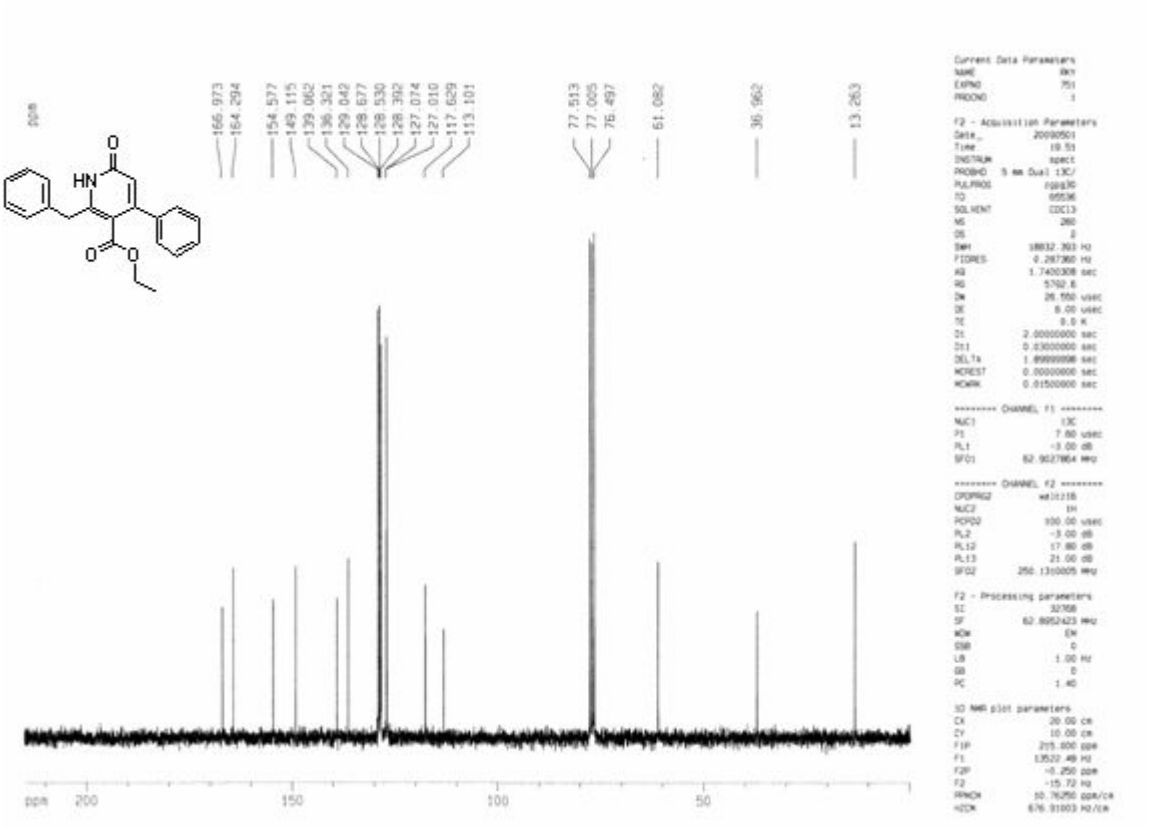
^{1}H and ^{13}C NMR spectra of **4i**



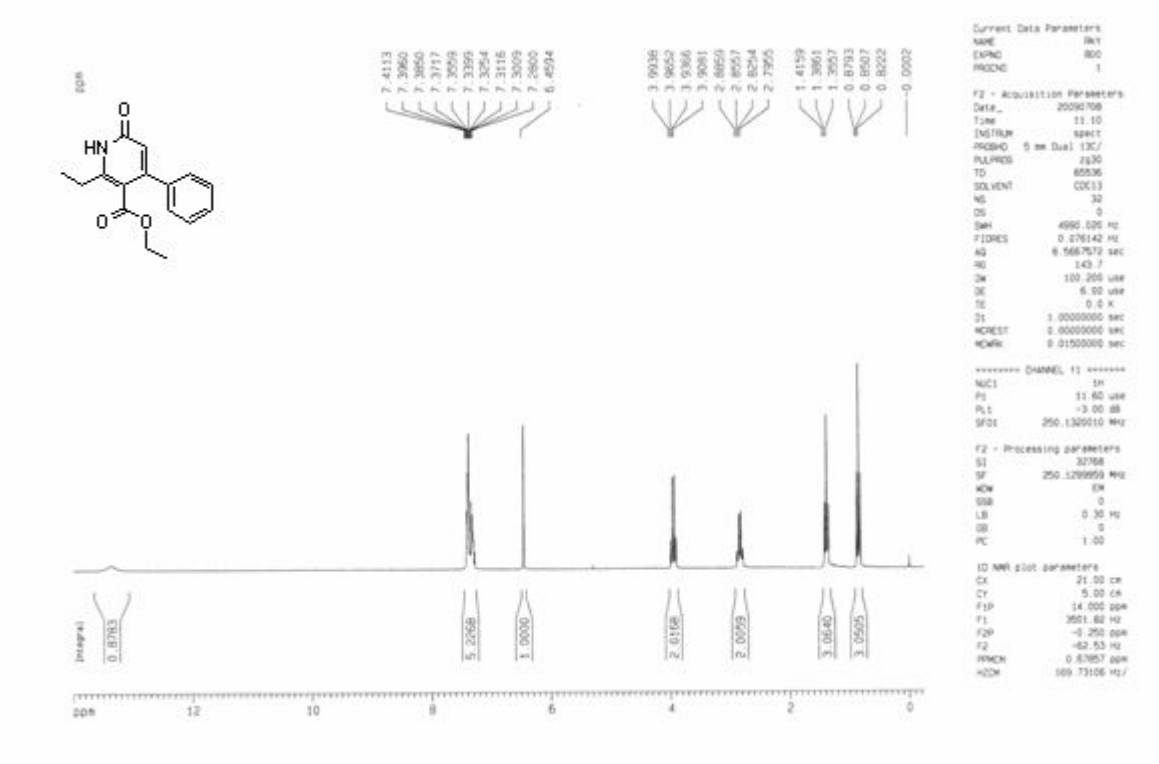


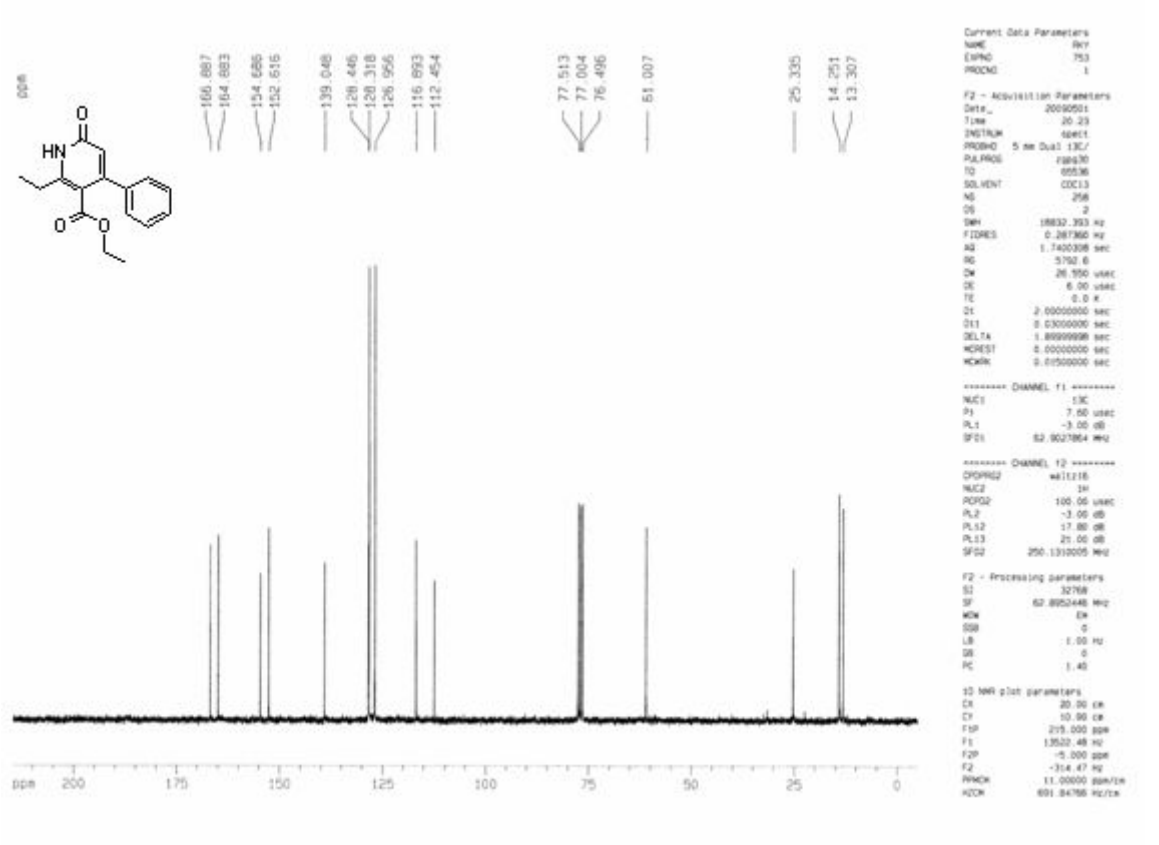
^{1}H and ^{13}C NMR spectra of **4j**



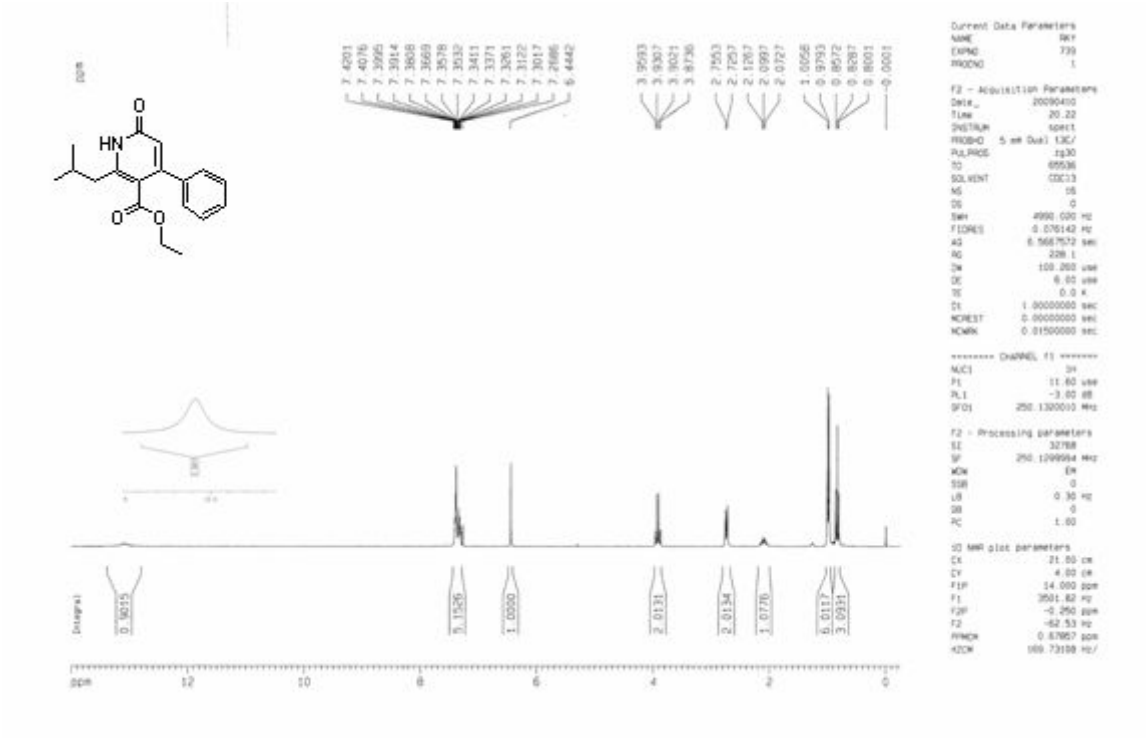


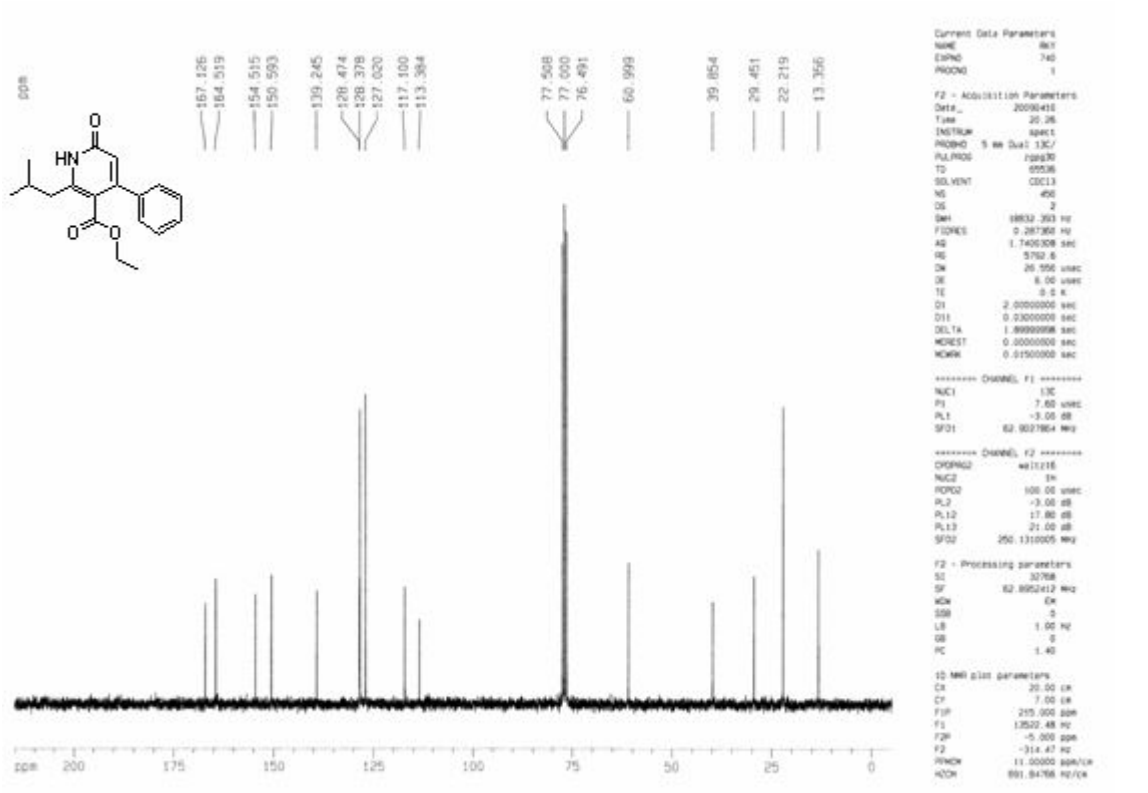
^{1}H and ^{13}C NMR spectra of **4k**



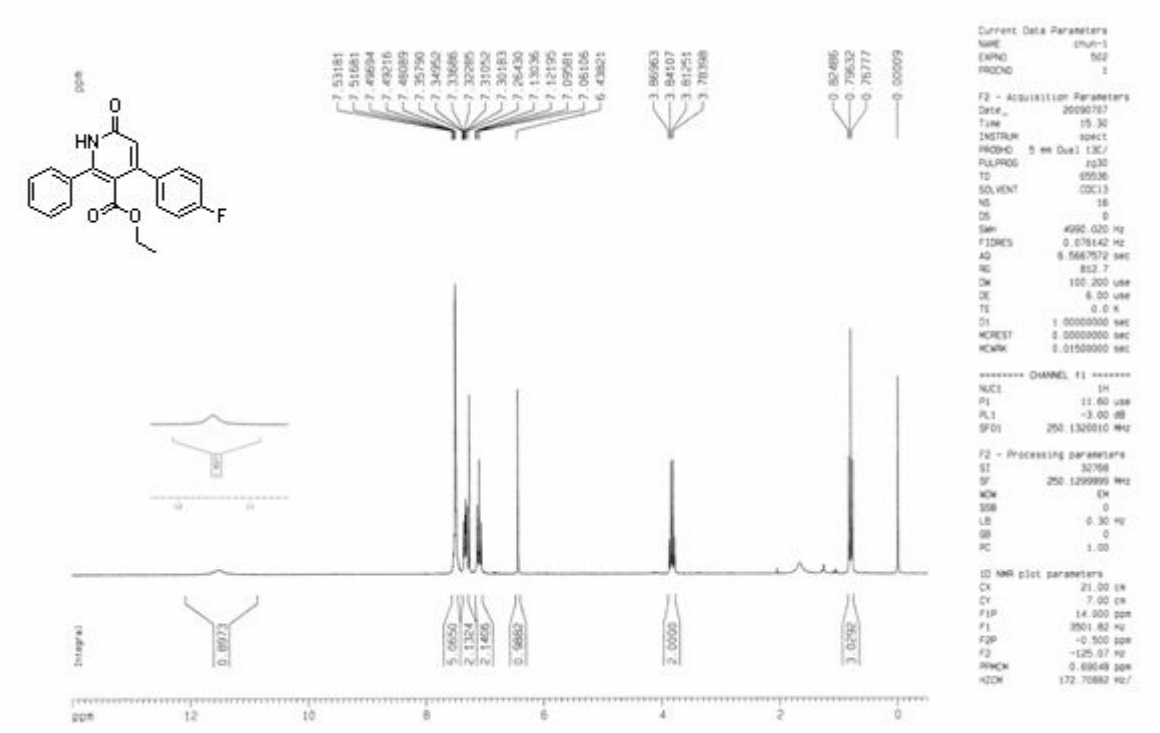


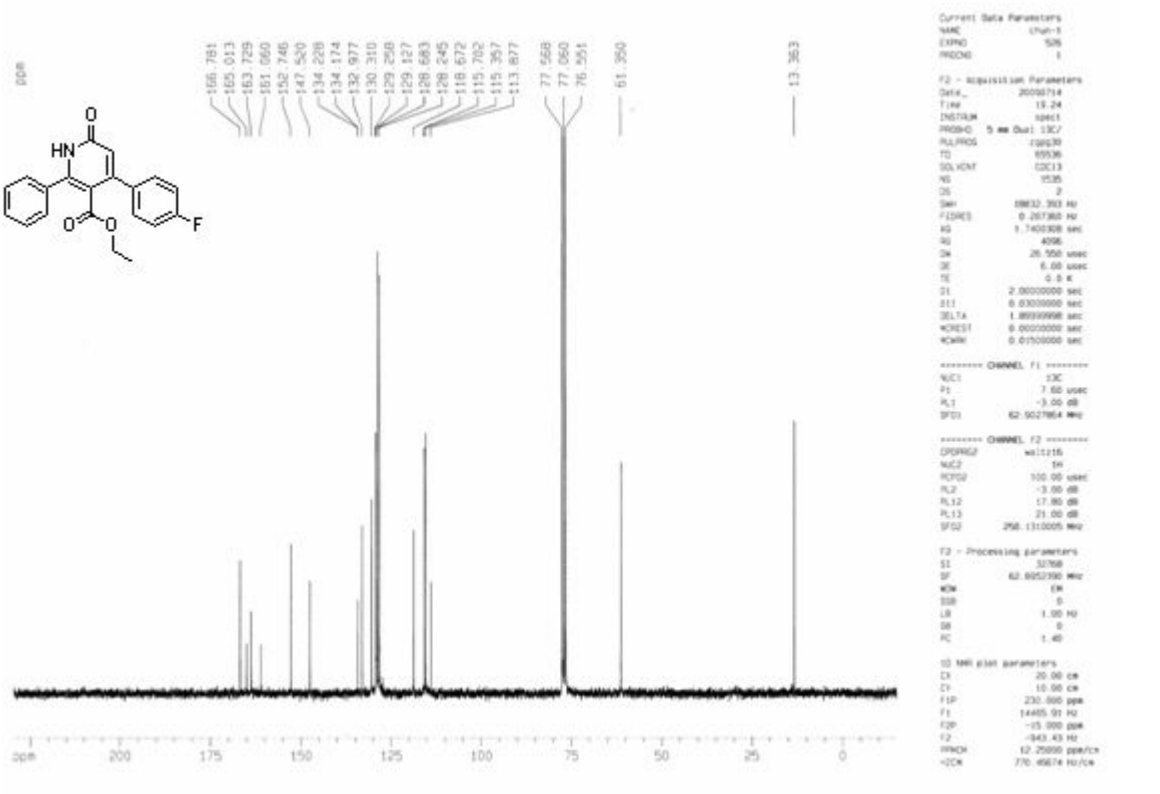
^{1}H and ^{13}C NMR spectra of **4l**



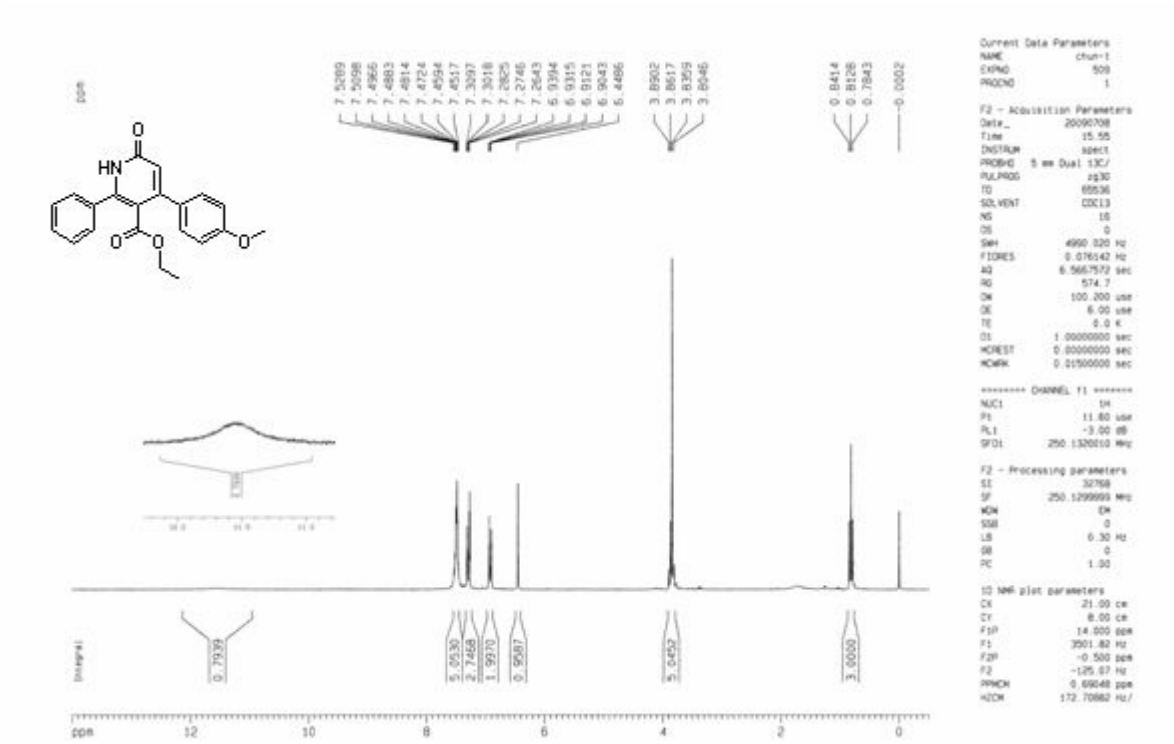


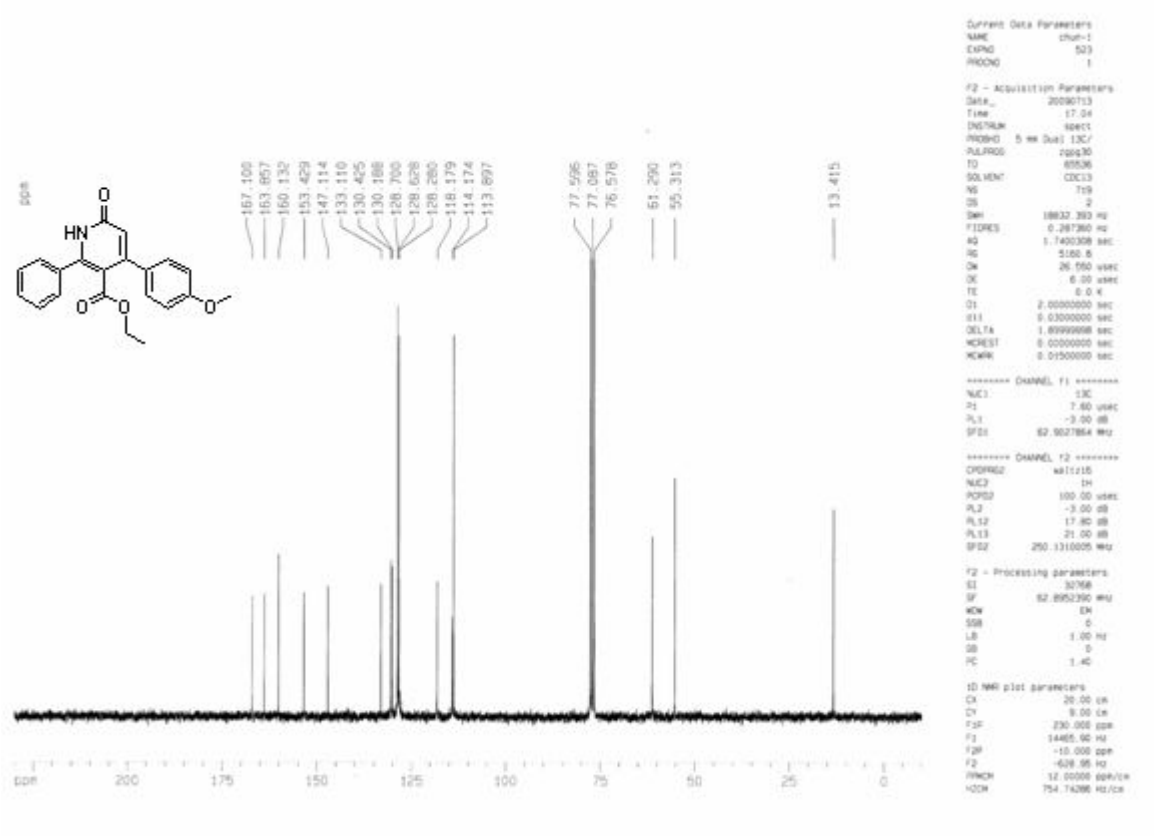
^{1}H and ^{13}C NMR spectra of **4m**



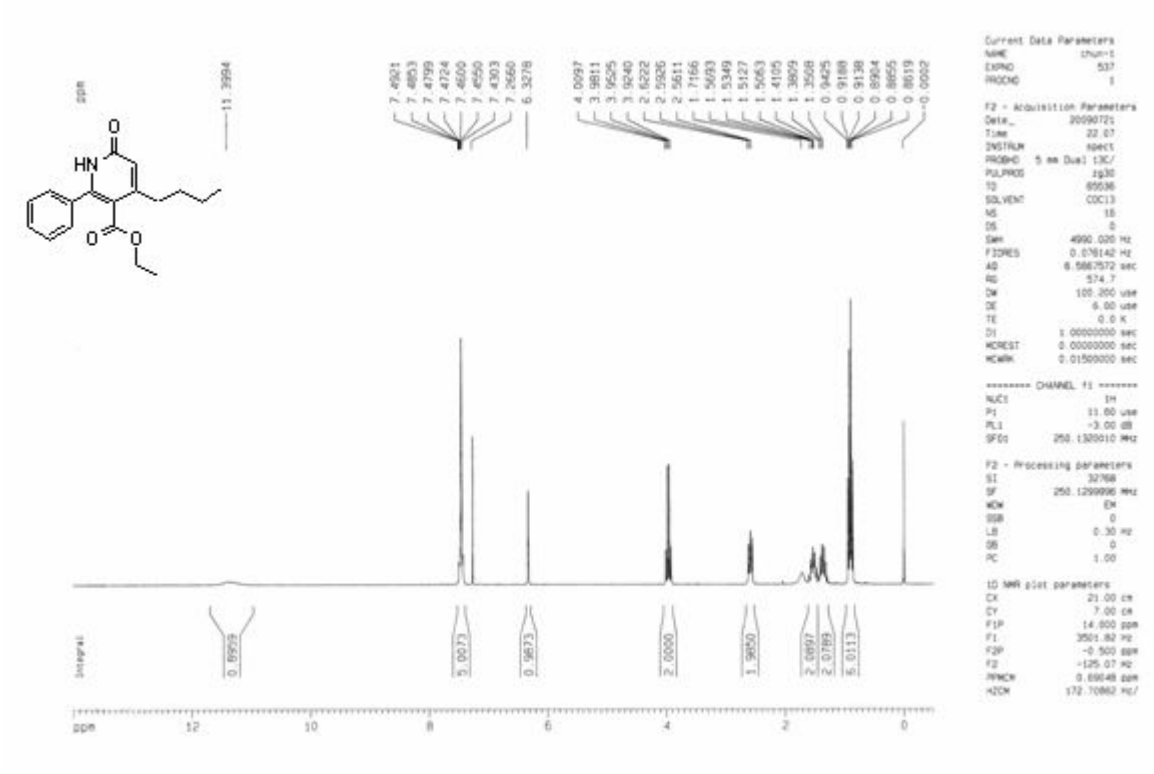


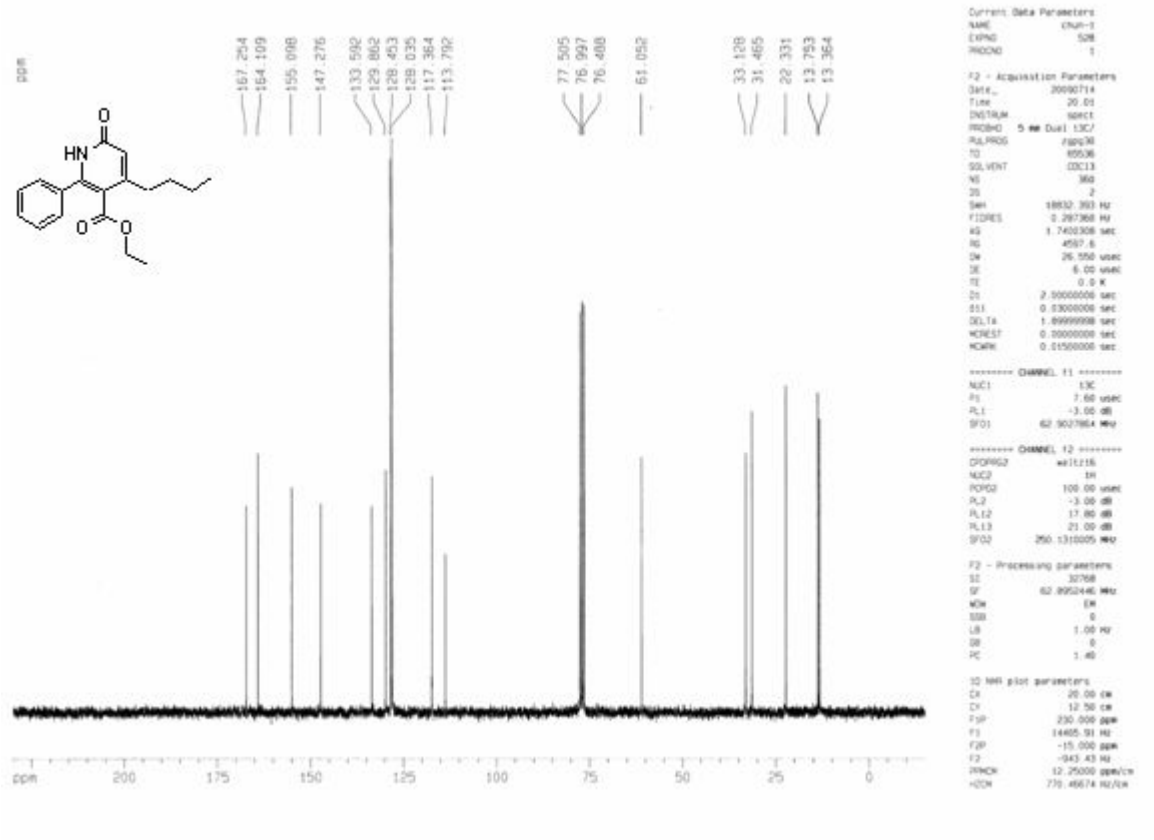
^{1}H and ^{13}C NMR spectra of **4n**



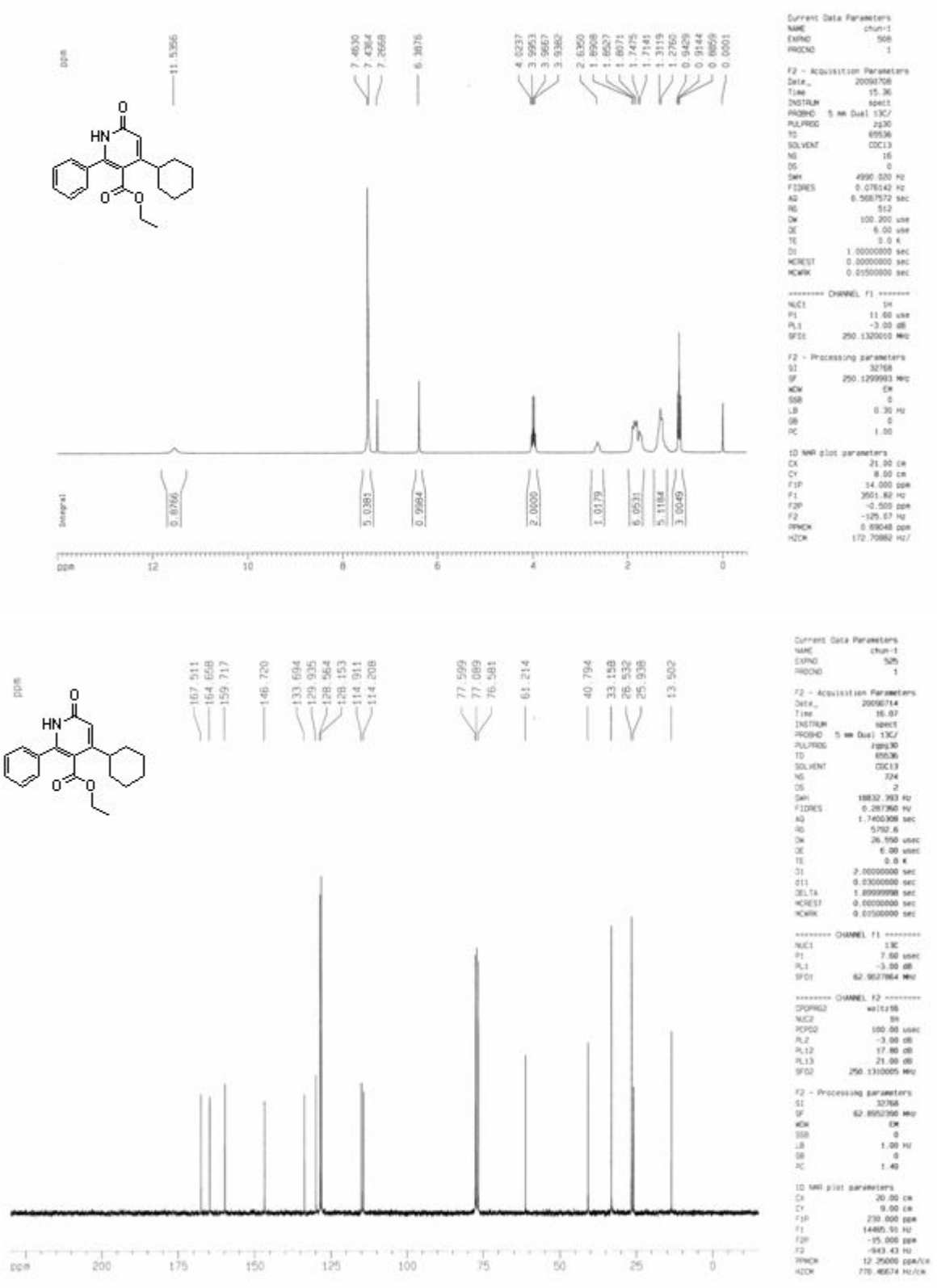


^{1}H and ^{13}C NMR spectra of **4o**

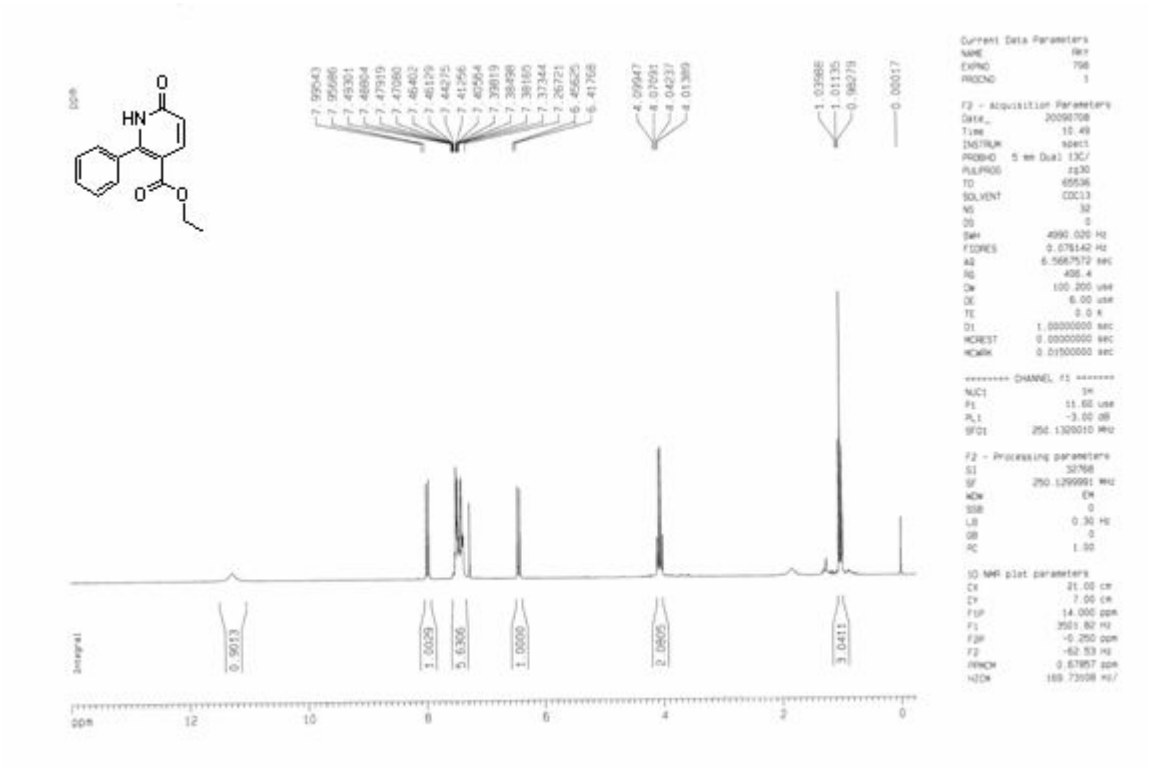


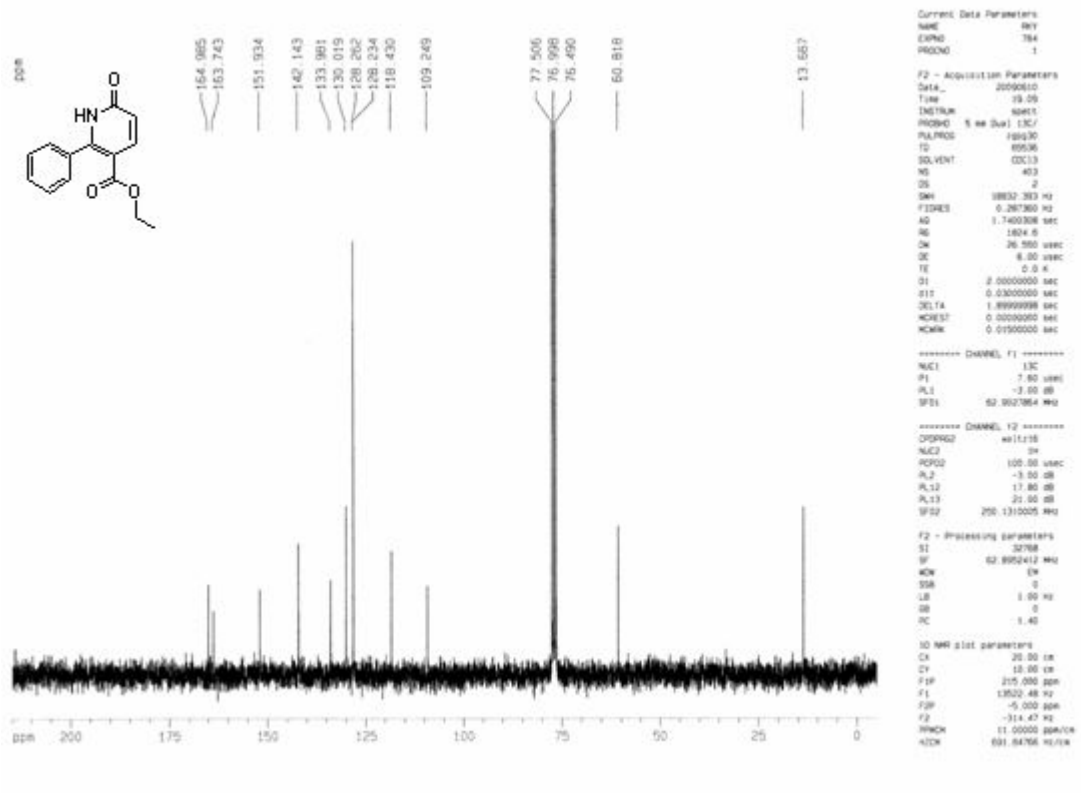


^{1}H and ^{13}C NMR spectra of **4p**



^{1}H and ^{13}C NMR spectra of **4q**





^{1}H and ^{13}C NMR spectra of **8**