Supporting Information for

Silver-Catalyzed Cascade Reaction of β-Enaminones and Isocyanoacetates to Construct Functionalized Pyrroles

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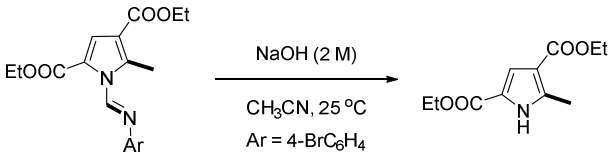
Contents

1. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 25 ºC on a Varian 400 MHz or 500 MHz, and 100 MHz or 125 MHz, or Bruker 600 MHz, 150 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. IR spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer and are reported in terms of wavenumber of absorption (cm^{-1}). High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

2. Additional Experiments

2.1 Deprotection of Pyrrole Derivative 3a to 1*H*-Pyrrole

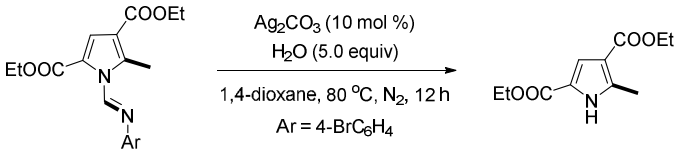


3a **5b**

Treat a sample of **3a** (203 mg, 0.5 mmol) in CH_3CN (15 mL) with 2M aqueous NaOH (15 mL). The resulting biphasic mixture was stirred vigorously at 25 °C. After 3 h, water (60 mL) was added. The mixture was extracted with CH_2Cl_2. The organic extract was washed (saturated aqueous NH_4Cl, water, brine), dried (Na_2SO_4) and concentrated. The product was recrystallized with ethyl acetate/petroleum ether to give **5b** (100 mg) in 90% yield.

Reference see: Ptaszek, M.; McDowell, B. E.; Lindsey, J. S. *J. Org. Chem*. **2006**, *71*, 4328.

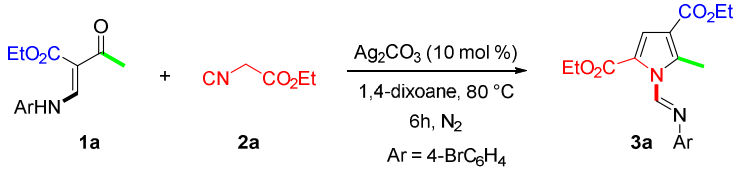
2.2 Ag-Mediated Hydrolysis of Pyrrole Derivative 3a



3a **5b**

The substrate **3a** (203 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of H_2O (90 μL, 5.0 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. No reaction happened after 12 h, and **3a** was recovered with 90% yield.

2.3 1 Mmol Scale Synthesis of Pyrrole Derivative 3a

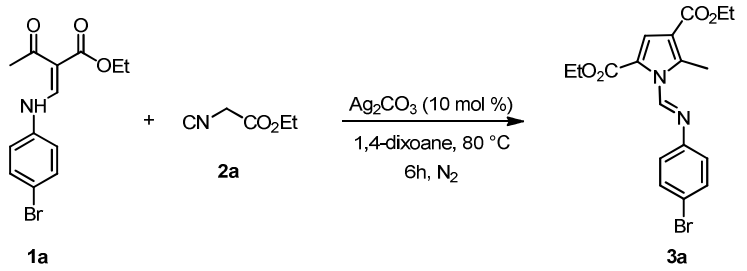


1a **2a** **3a**

The substrate **1a** (311 mg, 1 mmol) and Ag_2CO_3 (27.6 mg, 0.10 mmol) were added in a Schlenk

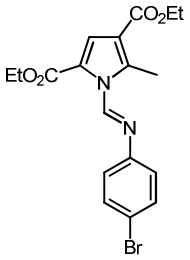
tube. After degassed by nitrogen 3 times, 1,4-dioxane (3 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (176 μL, 1.50 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography to give **3a** (308 mg) in 76% yield.

3. Synthesis and Analytical Data of Pyrrole Derivatives 3a – 3t

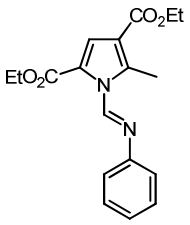


Typical procedure (with **3a** as an example): The substrate **1a**[1] (156 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 40:1) to give **3a** (170 mg) in 83% yield.

[1] The synthesis of starting materials see the following references: a) Ife, R. J.; Brown T. H.; Keeling, D. J.; Leach, C. A.; Meeson, M. L.; Parsons, M. E.; Reavill, D. R.; Theobald, C. J.; Wiggall, K. J. *J. Med. Chem.*, **1992**, *35*, 3413–3422; b) ; Tarabová D, Milata V, Hanusek J. *Acta Chimica Slovaca*, **2013**, *6*, 73–81; c) Cui, S.-F.; Addla, D.; Zhou, C.-H. *J. Med. Chem.*, **2016**, 59, 4488–4510.



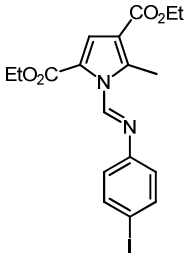
(3a) (*E*)-Diethyl 1-(((4-bromophenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.
White solid, m.p. 121-122ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.47 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.38 – 4.23 (m, 4H), 2.99 (s, 3H), 1.41 – 1.35 (m, 6H).; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.1, 160.6, 147.6, 147.3, 143.7, 132.3, 122.9, 122.6, 121.7, 119.6, 115.7, 60.9, 60.2, 15.0, 14.4, 14.3; **IR** (KBr): 3064, 2987, 1694, 1647, 1562, 1504, 1258, 1230, 1196, 1172, 1128, 1034 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{18}H_{20}BrN_2O_4^+$ $[M+H]^+$: 407.0601, found 409.0586.



(**3b**) (***E*)-Diethyl 5-methyl-1-((phenylimino)methyl)-1*H*-pyrrole-2,4-dicarboxylate**.

The substrate **1b** (117 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 25:1) to give **3b** (135 mg) in 82% yield.

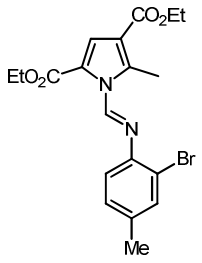
White solid, m.p. 93-94ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.46 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.36 – 4.24 (m, 4H), 3.00 (s, 3H), 1.41 – 1.32 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.1, 160.6, 148.2, 147.1, 143.6, 129.2, 126.1, 122.5, 121.4, 121.2, 115.4, 60.7, 60.1, 14.9, 14.33, 14.26; **IR** (KBr): 2992, 1686, 1669, 1648, 1602, 1578, 1502, 1245, 1197, 1121, 1033 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{18}H_{21}N_2O_4^+$ $[M+H]^+$: 329.1496, found 329.1499.



(**3c**) (***E*)-Diethyl 1-(((4-iodophenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.**

The substrate **1c** (179 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 25:1) to give **3c** (180 mg) in 79% yield.

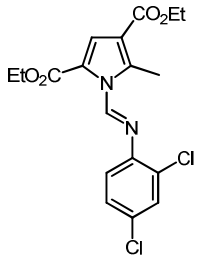
White solid, m.p. 127-128ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.46 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.40 – 4.24 (m, 4H), 2.99 (s, 3H), 1.45 – 1.33 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.0, 160.6, 148.0, 147.6, 143.7, 138.3, 123.3, 122.6, 121.7, 115.7, 90.5, 60.9, 60.2, 15.0, 14.4, 14.3.; **IR** (KBr): 3062, 2985, 1697, 1649, 1601, 1504, 1256, 1233, 1199, 1172, 1118, 1034 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{18}H_{20}IN_2O_4^+$ $[M+H]^+$: 455.0462, found 455.0465.



(3d) (*E*)-Diethyl 1-(((2-bromo-4-methylphenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1d** (163 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 40:1) to give **3d** (184 mg) in 87% yield.

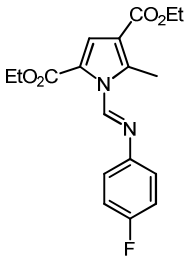
White solid, m.p. 115-116ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.48 (s, 1H), 7.46 (d, J = 1.2 Hz, 1H), 7.12 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 4.36 – 4.28 (m, 4H), 3.12 (s, 3H), 2.34 (s, 3H), 1.41 – 1.35 (m, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.1, 160.6, 147.8, 144.5, 144.1, 137.3, 133.5, 129.1, 122.5, 121.9, 119.7, 118.6, 115.7, 60.8, 60.2, 20.6, 15.3, 14.4, 14.3; **IR** (KBr): 2993, 1699, 1650, 1563, 1505, 1259, 1227, 1200, 1176, 1128, 1034, 552 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{19}H_{22}BrN_2O_4^+$ $[M+H]^+$: 421.0757, found 423.0745.



(3e) (*E*)-Diethyl 1-(((2,4-dichlorophenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1e** (150 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 40:1) to give **3e** (180 mg) in 91% yield.

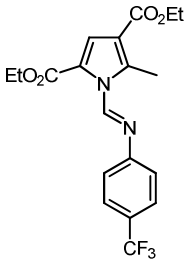
White solid, m.p. 128-129ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.47 (s, 1H), 7.45 (s, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 4.40 – 4.24 (m, 4H), 3.06 (s, 3H), 1.45 – 1.31 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.9, 160.6, 148.6, 144.5, 144.1, 131.6, 129.8, 129.2, 127.8, 122.5, 122.0, 120.9, 115.9, 60.9, 60.2, 15.1, 14.34, 14.27; **IR** (KBr): 3083, 2985, 1701, 1650, 1566, 1504, 1259, 1234, 1204, 1176, 1036, 812, 701 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{18}H_{19}Cl_2N_2O_4^+$ $[M+H]^+$: 397.0716, found 397.0718.



(3f) (*E*)-Diethyl 1-(((4-fluorophenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1f** (126 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 40:1) to give **3f** (140 mg) in 81% yield.

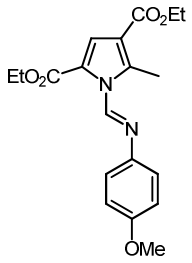
White solid, m.p. 105-106ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.46 (s, 1H), 7.22 – 7.13 (m, 2H), 7.07 (t, *J* = 9.0 Hz, 2H), 4.37 – 4.25 (m, 4H), 2.99 (s, 3H), 1.44 – 1.31 (m, 6H); **^{19}F NMR** (500 MHz, $CDCl_3$) δ -122.5; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.1, 161.2 (d, *J* = 245.0 Hz), 160.6, 147.1 (d, *J* = 1.5 Hz), 144.3 (d, *J* = 3.0 Hz), 143.6, 122.6 (d, *J* = 8.5 Hz), 122.5, 121.5, 116.0 (d, *J* = 22.5 Hz), 115.5, 60.8, 60.1, 14.9, 14.34, 14.26; **IR** (KBr): 2988, 1700, 1650, 1565, 1504, 1260, 1241, 1233, 1204, 1174, 1032 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{18}H_{20}FN_2O_4^+$ $[M+H]^+$: 347.1402, found 347.1409.



(3g) (*E*)-Diethyl 5-methyl-1-(((4-(trifluoromethyl)phenyl)imino)methyl)-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1g** (151 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 40:1) to give **3g** (84 mg) in 42% yield.

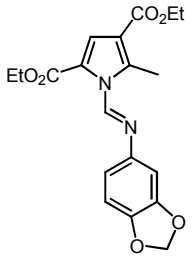
White solid, m.p. 125-126ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.48 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 4.36 – 4.27 (m, 4H), 3.02 (s, 3H), 1.42 – 1.33 (m, 6H); **^{19}F NMR** (500 MHz, $CDCl_3$) δ -64.0; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.0, 160.6, 151.4, 148.4, 143.7, 127.9 (q, *J* = 33.3 Hz), 126.43 (q, *J* = 3.5 Hz), 124.1 (q, *J* = 272.0 Hz), 122.6, 121.8, 121.3, 115.8, 60.9, 60.2, 15.0, 14.3, 14.2; **IR** (KBr): 2983, 1702, 1651, 1566, 1503, 1233, 1202, 1145, 1035 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{19}H_{20}F_3N_2O_4^+$ $[M+H]^+$: 397.1370, found 397.1372.



(3h) (*E*)-Diethyl 1-(((4-methoxyphenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1h** (132 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 30:1) to give **3h** (131 mg) in 73% yield.

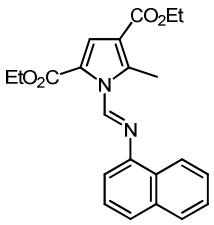
White solid, m.p. 109-110ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.45 (s, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 4.40 – 4.21 (m, 4H), 3.82 (s, 3H), 2.98 (s, 3H), 1.42 – 1.32 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ164.2, 160.6, 158.4, 145.8, 143.5, 141.1, 122.5, 122.4, 121.3, 115.3, 114.5, 60.7, 60.1, 55.5, 14.8, 14.4, 14.3; **IR** (KBr): 3049, 2955, 1699, 1653, 1574, 1510, 1283, 1232, 1200, 1033 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{19}H_{23}N_2O_5^+$ $[M+H]^+$: 359.1601, found 359.1600.



(3i) (*E*)-Diethyl 1-((benzo[d][1,3]dioxol-5-ylimino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1i** (139 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 30:1) to give **3i** (160 mg) in 86% yield.

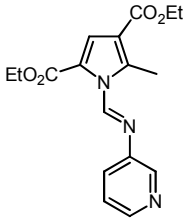
White solid, m.p. 102-103ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.45 (s, 1H), 6.86 – 6.76 (m, 2H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.99 (s, 2H), 4.44 – 4.14 (m, 4H), 2.97 (s, 3H), 1.52 – 1.15 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.2, 160.7, 148.3, 146.3, 146.1, 143.5, 142.6, 122.5, 121.4, 115.4, 114.8, 108.4, 102.4, 101.4, 60.8, 60.1, 14.8, 14.4, 14.3; **IR** (KBr): 3080, 2985, 1700, 1650, 1570, 1506, 1282, 1262, 1232, 1204, 1126, 1033 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{19}H_{21}N_2O_6^+$ $[M+H]^+$: 373.1394, found 373.1398.



(3j) (*E*)-Diethyl 5-methyl-1-((naphthalen-1-ylimino)methyl)-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1j** (142 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 40:1) to give **3j** (135 mg) in 71% yield.

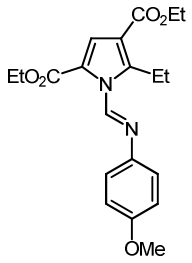
White solid, m.p. 106-107ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.32 – 8.16 (m, 1H), 7.89 – 7.83 (m, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.47 (t, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 4.42 – 4.25 (m, 4H), 3.18 (s, 3H), 1.44 – 1.31 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.2, 160.6, 146.9, 145.4, 143.7, 134.1, 128.8, 127.7, 126.5, 126.3, 126.0, 123.8, 122.78(2), 121.7, 115.7, 113.7, 60.9, 60.2, 15.3, 14.4, 14.3; **IR** (KBr): 3061, 2975, 1695, 1650, 1574, 1511, 1262, 1233, 1205, 1177, 1036, 802 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{22}H_{23}N_2O_4^+$ $[M+H]^+$: 379.1652, found 379.1660.



(3k) (*E*)-Diethyl 5-methyl-1-((pyridin-3-ylimino)methyl)-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1k** (117 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (24 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 8:1) to give **3k** (124 mg) in 75% yield.

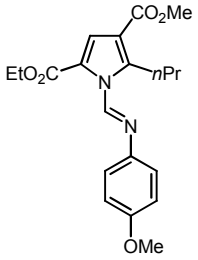
White solid, m.p. 110-111ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.55 – 8.44 (m, 2H), 7.54 – 7.50 (m, 1H), 7.49 (s, 1H), 7.37 – 7.29 (m, 1H), 4.37 – 4.25 (m, 4H), 3.02 (s, 3H), 1.44 – 1.32 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.0, 160.6, 148.5, 147.4, 144.3, 143.8, 143.2, 127.9, 123.8, 122.6, 121.9, 115.9, 60.9, 60.3, 15.1, 14.4, 14.3; **IR** (KBr): 3051, 2990, 1703, 1647, 1565, 1505, 1260, 1232, 1207, 1174, 1128, 1034 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{17}H_{20}N_3O_4^+$ $[M+H]^+$: 330.1448, found 330.1450.



(3l) (*E*)-Diethyl 5-ethyl-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1l** (139 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 25:1) to give **3l** (151 mg) in 81% yield.

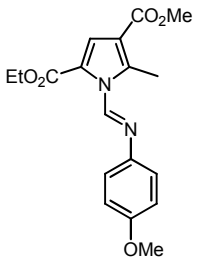
White solid, m.p. 110-112ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.46 (s, 1H), 7.24 – 7.18 (m, 2H), 6.96 – 6.89 (m, 2H), 4.40 – 4.23 (m, 4H), 3.83 (s, 3H), 3.51 (q, *J* = 7.2 Hz, 2H), 1.44 – 1.27 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.9, 160.7, 158.4, 149.2, 145.3, 141.1, 122.49, 122.48, 121.4, 114.7, 114.5, 60.7, 60.1, 55.5, 20.5, 14.4, 14.3, 13.7; **IR** (KBr): 3050, 2963, 1698, 1647, 1562, 1502, 1463, 1277, 1244, 1225, 1199, 1170, 1115, 1032 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{20}H_{25}N_2O_5^+$ $[M+H]^+$: 373.1758, found 373.1762.



(3m) (*E*)-2-Ethyl 4-methyl 1-(((4-methoxyphenyl)imino)methyl)-5-propyl-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1m** (139 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 25:1) to give **3m** (165 mg) in 89% yield.

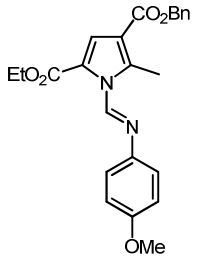
White solid, m.p. 92-95ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.45 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.46 (t, *J* = 7.2, 2H), 1.84 – 1.68 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 160.6, 158.3, 148.0, 145.2, 141.0, 122.5, 122.4, 121.3, 114.6, 114.5, 60.7, 55.4, 51.2, 28.6, 22.7, 14.2, 14.1; **IR** (KBr): 3067, 2962, 1711, 1697, 1645, 1561, 1500, 1463, 1276, 1246, 1223, 1199, 1170, 1032, 1020 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{20}H_{25}N_2O_5^+$ $[M+H]^+$: 373.1758, found 373.1760.



(3n) (*E*)-2-Ethyl 4-methyl 1-(((4-methoxyphenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1n** (125 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 30:1) to give **3n** (115 mg) in 67% yield.

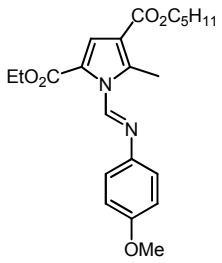
White solid, m.p. 116-118ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.46 (s, 1H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.37 – 4.23 (q, J = 6.8 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.98 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 160.7, 158.4, 145.7, 143.6, 141.1, 122.6, 122.5, 121.3, 115.0, 114.5, 60.8, 55.5, 51.3, 14.8, 14.3; **IR** (KBr): 2983, 1710, 1698, 1648, 1563, 1500, 1462, 1277, 1222, 1199, 1116, 1082 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{18}H_{21}N_2O_5^+$ $[M+H]^+$: 345.1445, found 345.1454.



(3o) (*E*)-4-Benzyl 2-ethyl 1-(((4-methoxyphenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

The substrate **1o** (163 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 20:1) to give **3o** (183 mg) in 87% yield.

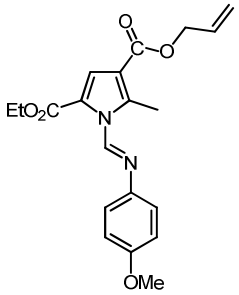
Colorless solid, m.p. 134-135ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.60 – 7.30 (m, 6H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.31 (s, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.99 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ164.0, 160.7, 158.4, 145.7, 143.8, 141.1, 136.3, 128.6, 128.1, 122.6, 122.5, 121.3, 114.9, 114.5, 65.9, 60.8, 55.5, 14.9, 14.3; **IR** (KBr): 2960, 1710, 1698, 1646, 1605, 1578, 1502, 1463, 1285, 1244, 1232, 1197, 1170, 1032 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{24}H_{25}N_2O_5^+$ $[M+H]^+$: 421.1758, found 421.1760.



(**3p**) (***E***)**-2-Ethyl 4-pentyl 1-(((4-methoxyphenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4 -dicarboxylate.**

The substrate **1p** (153 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 20:1) to give **3p** (154 mg) in 77% yield.

White solid, m.p. 123-124ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.45 (s, 1H), 7.20 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 4.25 (t, J = 7.2 Hz, 2H), 3.83 (s, 3H), 2.98 (s, 3H), 1.80 – 1.69 (m, 2H), 1.48 – 1.31 (m, 7H), 0.93 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 160.7, 158.4, 145.8, 143.4, 141.1, 122.49, 122.46, 121.3, 115.4, 114.5, 64.3, 60.7, 55.5, 28.4, 28.2, 22.4, 14.9, 14.3, 14.0; **IR** (KBr): 3042, 2954, 1688, 1574, 1512, 1286, 1232, 1205, 1114, 1083, 1026 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{22}H_{29}N_2O_5^+$ $[M+H]^+$: 401.2071, found 401.2065.

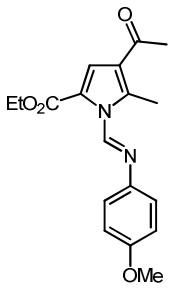


(**3q**) (***E***)**-4-Allyl 2-ethyl 1-(((4-methoxyphenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2,4 -dicarboxylate.**

The substrate **1q** (138 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 20:1) to give **3q** (135 mg) in 73% yield.

Brown solid, m.p. 121-122ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.48 (s, 1H), 7.20 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.11 – 5.95 (m, 1H), 5.45 – 5.35 (m, 1H), 5.32 – 5.25 (m, 1H), 4.77 (dt, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 2.99 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8, 160.6, 158.4, 145.7, 143.7, 141.0, 132.5, 122.5, 122.4, 121.2, 118.0, 114.9, 114.5, 64.8, 60.7, 55.5, 14.8, 14.3; **IR** (KBr): 3049, 2953, 1707, 1689, 1655, 1510, 1283, 1232, 1205, 1116, 1081, 1027, 994, 933 cm^{-1}; **HRMS** (ESI) m/z calculated for

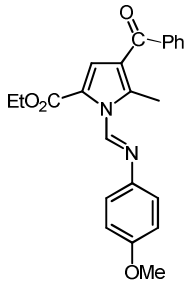
$C_{20}H_{23}N_2O_5^+$ $[M+H]^+$: 371.1601, found 371.1609.



(3r) (*E*)-Ethyl 4-acetyl-1-(((4-methoxyphenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2-carboxylate.

The substrate **1r** (117 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 20:1) to give **3r** (135 mg) in 82% yield.

White solid, m.p. 114-115ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.31 (s, 1H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 3.73 (s, 3H), 2.88 (s, 3H), 2.39 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.6, 160.5, 158.4, 145.4, 142.7, 140.8, 122.7, 122.4, 122.3, 121.0, 114.4, 60.8, 55.4, 29.1, 14.9, 14.3; **IR** (KBr): 3065, 2987, 1696, 1648, 1562, 1504, 1257, 1230, 1196, 1171, 1034 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{18}H_{21}N_2O_4^+$ $[M+H]^+$: 329.1496, found 329.1497.

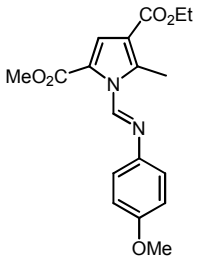


(3s) (*E*)-Ethyl 4-benzoyl-1-(((4-methoxyphenyl)imino)methyl)-5-methyl-1*H*-pyrrole-2-carboxylate.

The substrate **1s** (148 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (24 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 20:1) to give **3s** (156 mg) in 80% yield.

White solid, m.p. 132 -133ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.89 – 7.75 (m, 2H), 7.63 – 7.55 (m, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.25 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.30 (q, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 2.93 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ191.9, 160.7, 158.4, 145.6, 143.4, 141.0, 139.2, 132.1, 129.3, 128.3, 122.6, 122.5, 122.3,

122.2, 114.5, 60.8, 55.5, 15.3, 14.3; **IR** (KBr): 3052, 2978, 1698, 1651, 1637, 1600, 1576, 1508, 1248, 1202, 1173, 1032 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{23}H_{23}N_2O_4^+$ $[M+H]^+$: 391.1652, found 391.1662.

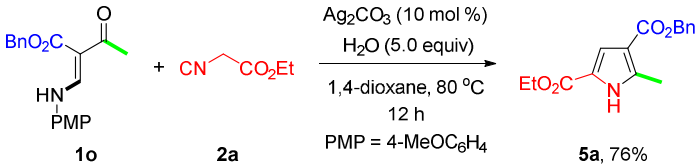


(3t) (*E*)-4-Ethyl 2-methyl 1-(((4-methoxyphenyl)imino)methyl)-5-methyl-1H-pyrrole-2,4-dicarboxylate.

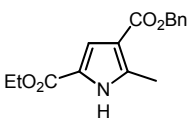
The substrate **1h** (132 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of methyl isocyanoacetate **2b** (68 μL, 0.75 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (6 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 30:1) to give **3t** (124 mg) in 72% yield.

White solid, m.p. 120-121ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.46 (s, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.30 (q, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 3.85 (s, 3H), 2.99 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.7, 160.7, 158.4, 145.7, 143.6, 141.1, 122.6, 122.5, 121.3, 115.0, 114.5, 60.8, 55.5, 51.3, 14.8, 14.3; **IR** (KBr): 3015, 2983, 1706, 1691, 1645, 1576, 1506, 1243, 1195, 1119 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{18}H_{21}N_2O_5^+$ $[M+H]^+$: 345.1445, found 345.1447.

4. Analytical Data of Pyrrole Derivatives 5

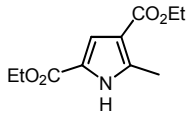


Typical procedure: the substrate **1o** (R = CO_2Bn, 156 mg, 0.5 mmol) and Ag_2CO_3 (13.8 mg, 0.05 mmol) were added in a Schlenk tube. After degassed by nitrogen 3 times, 1,4-dioxane (2 ml) was added into the tube, followed by the addition of ethyl isocyanoacetate **2a** (88 μL, 0.75 mmol) and H_2O (45 μL, 2.5 mmol). The reaction mixture was stirred at 80 °C and indicated by TLC. After completed (12 h), the reaction mixture was cooled down to room temperature and concentrated in *vacuum*. The residue was purified by column chromatography (PE/EA 7:1) to give product **5a** (109 mg) in 76% yield.



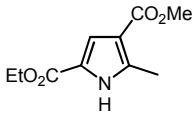
(5a) 4-Benzyl 2-ethyl 5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

White solid, m.p. 147-148ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 5.28 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 161.5, 140.3, 136.5, 128.5, 128.3, 128.0, 120.6, 117.5, 113.6, 65.5, 60.7, 14.3, 13.3; **IR** (KBr): 3256, 3087, 2982, 1709, 1684, 1604, 1574, 1503, 1366, 1283, 1230, 1204, 1119, 1025 cm^{-1}; **HRMS** (ESI) m/z calculated for C16H18NO4+ $[M+H]^+$: 288.1230, found 288.1240.



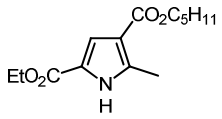
(5b) Diethyl 5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

White solid, m.p. 125-126ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 1.36 (q, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.7, 161.5, 140.0, 120.5, 117.4, 114.0, 60.7, 59.7, 14.4, 14.3, 13.3; **IR** (KBr): 3266, 2983, 2948, 1690, 1664, 1570, 1505, 1366, 1276, 1205 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{11}H_{16}NO_4^+$ $[M+H]^+$: 226.1074, found 226.1080.



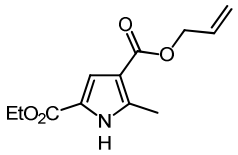
(5c) 2-Ethyl 4-methyl 5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

White solid, m.p. 119-120ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 7.26 (d, *J* = 3.0 Hz, 1H), 4.33 (q, *J* = 7.0, 2H), 3.82 (s, 3H), 2.59 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.1, 161.5, 140.0, 120.6, 117.4, 113.6, 60.7, 51.0, 14.3, 13.2; **IR** (KBr): 3280, 2980, 2954, 1705, 1687, 1574, 1508, 1366, 1275, 1203 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{10}H_{14}NO_4^+$ $[M+H]^+$: 212.0917, found 212.0920.



(5d) 2-Ethyl 4-pentyl 5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

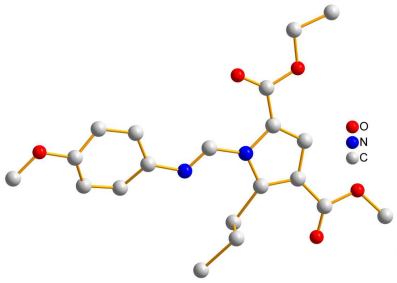
White solid, m.p. 138-139ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.25 (d, *J* = 2.8 Hz, 1H), 4.33 (q, *J* = 6.8 Hz, 2H), 4.22 (t, *J* = 6.8 Hz, 2H), 2.58 (s, 3H), 1.78 – 1.66 (m, 2H), 1.49 – 1.30 (m, 6H), 0.92 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.8, 161.3, 139.6, 120.6, 119.3, 117.3, 115.0, 114.1, 64.0, 60.7, 28.5, 28.2, 22.4, 14.4, 14.0, 13.4; **IR** (KBr): 3278, 2954, 1705, 1688, 1574, 1508, 1378, 1367, 1284, 1233, 1205, 1114 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{14}H_{22}NO_4^+$ $[M+H]^+$: 268.1543, found 268.1550.

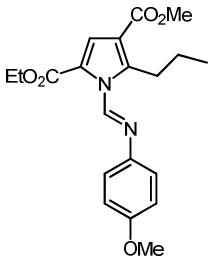


(5e) 4-Allyl 2-ethyl 5-methyl-1*H*-pyrrole-2,4-dicarboxylate.

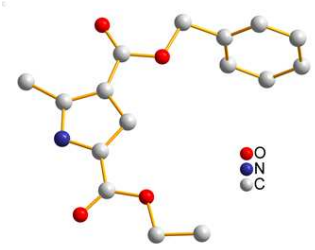
White solid, m.p. 134-135ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.28 (d, *J* = 2.5 Hz, 1H), 6.07 – 5.96 (m, 1H), 5.38 (dq, *J* = 17.0, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.0, 1.5 Hz, 1H), 4.75 (t, *J* = 1.5 Hz, 1H), 4.74 (t, *J* = 1.5 Hz, 1H), 4.33 (q, *J* = 7.0 Hz, 2H), 2.59 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.3, 161.3, 139.9, 132.7, 120.7, 117.7, 117.3, 113.7, 64.4, 60.7, 14.4, 13.4; **IR** (KBr): 3278, 3079, 2985, 2951, 1689, 1645, 1576, 1508, 1378, 1366, 1284, 1232, 1205, 1117, 994, 930 cm^{-1}; **HRMS** (ESI) m/z calculated for $C_{12}H_{16}NO_4^+$ $[M+H]^+$: 238.1074, found 238.1077.

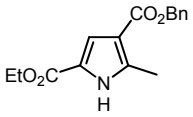
5. Crystallography of product 3m and 5a





CCDC 1528464	
Empirical formula	$C_{20}H_{24}N_2O_5$
Temperature	273(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 10.8506(12) Å b = 6.8604(8) Å c = 13.0790(14) Å alpha = 90 deg. beta = 97.621(2) deg. gamma = 90 deg.
Volume	964.99(19) Å ^{3}
Z	20
Calculated density	1.198 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F(000)	348
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	1.57 to 28.27 deg.
Reflections collected / unique	5856 / 3111 [R(int) = 0.0271]
Data / restraints / parameters	3111 / 4 / 229
Goodness-of-fit on F2	1.949
Final R indices [I>2sigma(I)]	R1 = 0.1683, wR2 = 0.4520
R indices (all data)	R1 = 0.1995, wR2 = 0.5006

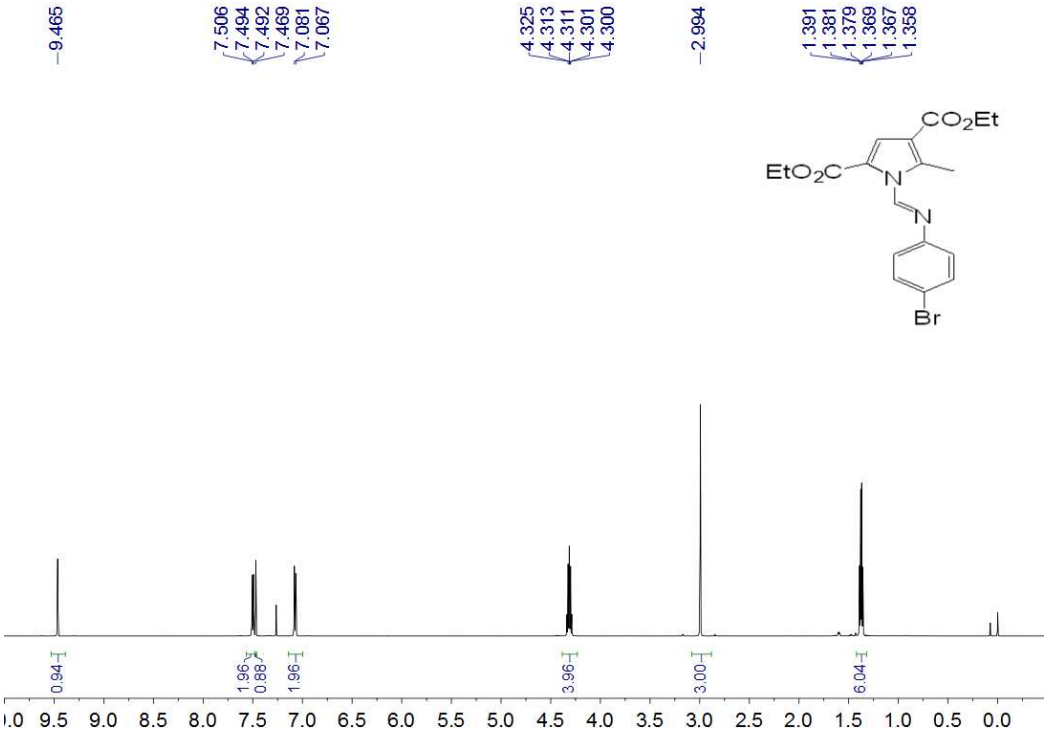


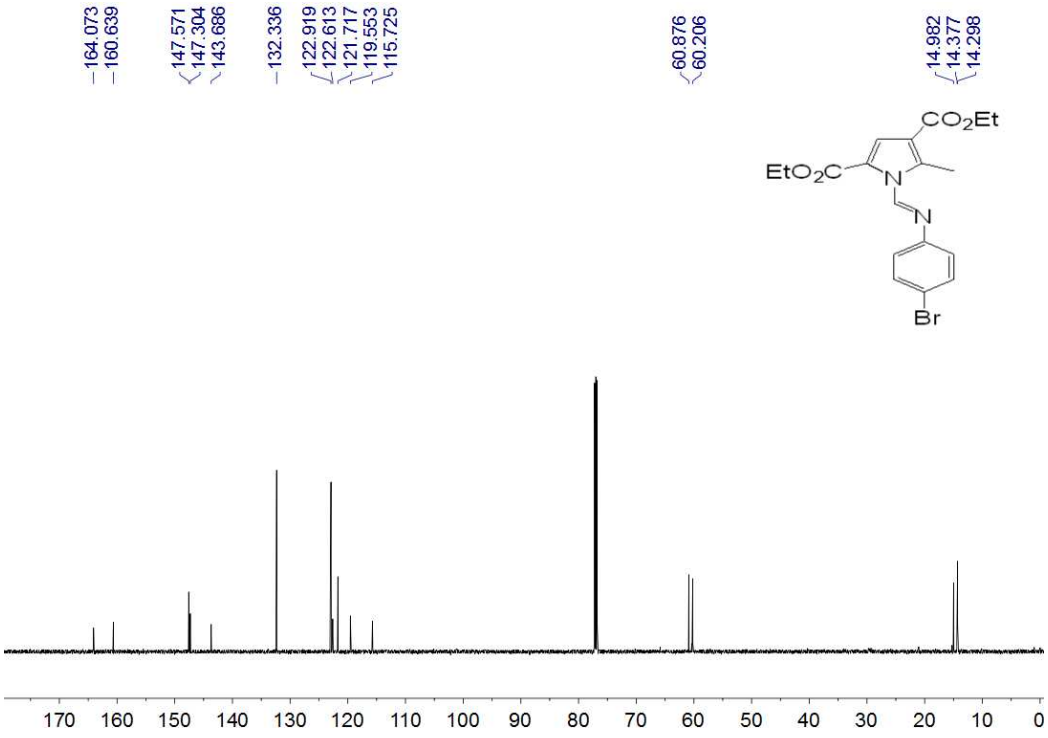


CCDC 1528376	
Empirical formula	$C_{16}H_{17}NO_4$
Temperature	273 K
Wavelength	0.71073 Å
Unit cell dimensions	a = 5.8451(7) Å b = 9.9032(12) Å c = 13.7165(17) Å alpha = 110.081(2) deg. beta = 92.430(2) deg. gamma = 101.712(2) deg.
Volume	724.74(15) $Å^3$
Z	14
Calculated density	1.380 Mg/m^3
Absorption coefficient	0.124 mm^{-1}
F(000)	308.0
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	1.59 to 28.24 deg.
Reflections collected / unique	4401/ 3239 [R(int) = 0.0170]
Data / restraints / parameters	3239 / 0 / 85
Goodness-of-fit on F_2	2.633
Final R indices [I>2sigma(I)]	R1 = 0.1378, wR2 = 0.3668
R indices (all data)	R1 = 0.1567, wR2 = 0.3913

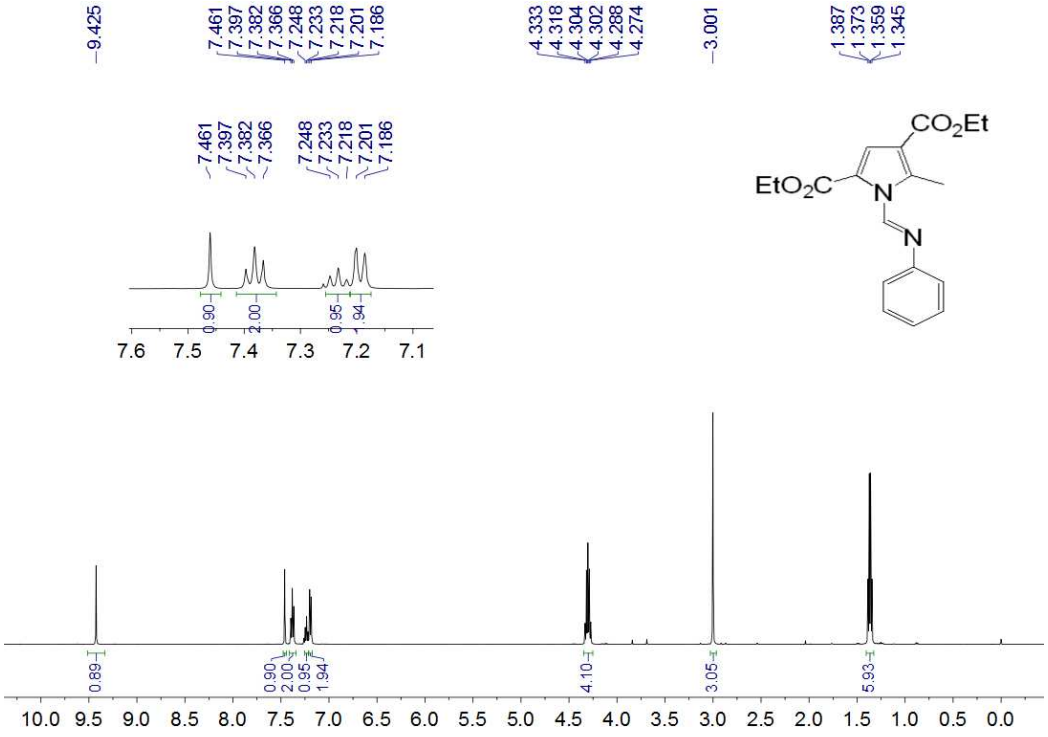
6. NMR spectra copies

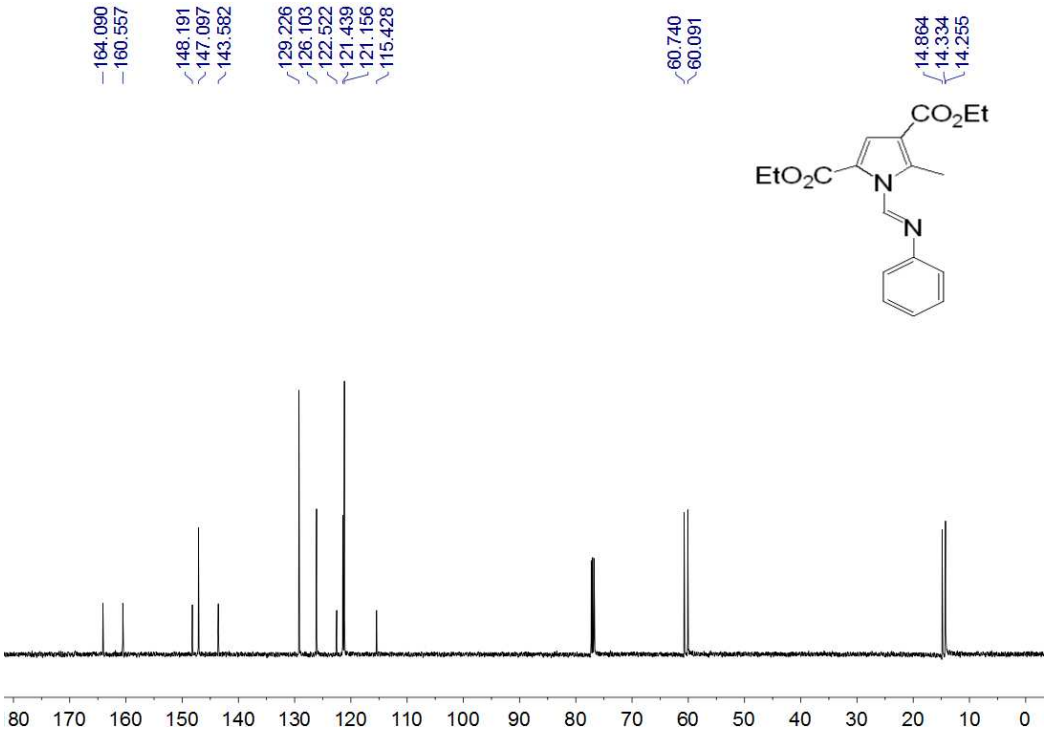
^{1}H and ^{13}C NMR Spectra for Compound 3a



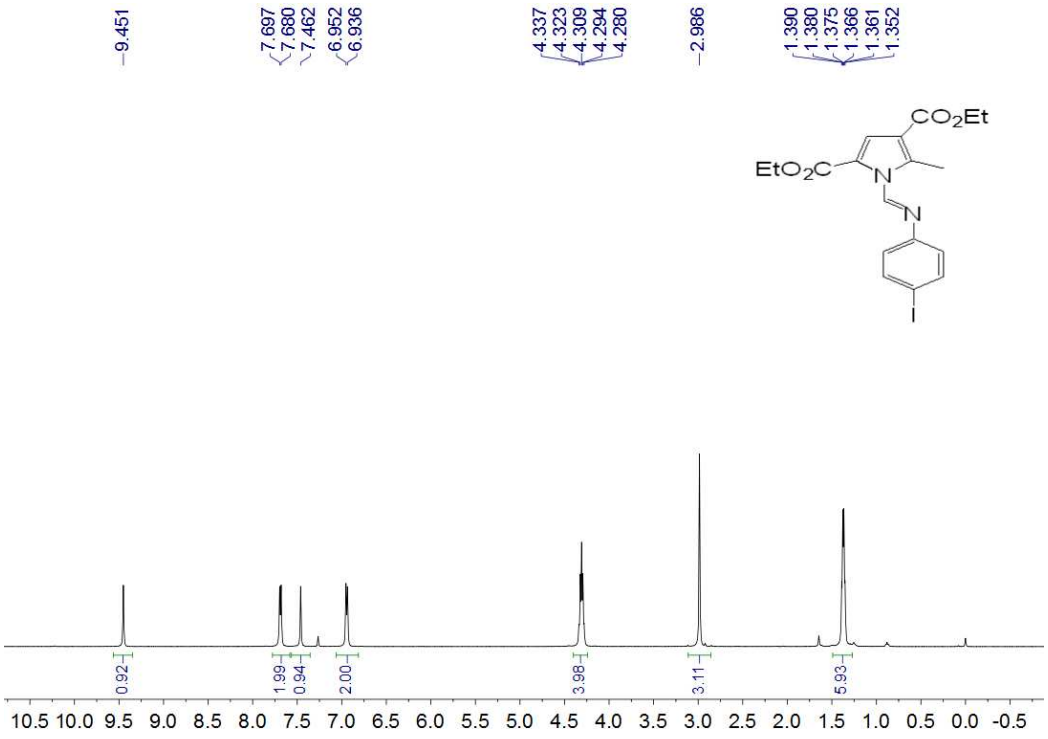


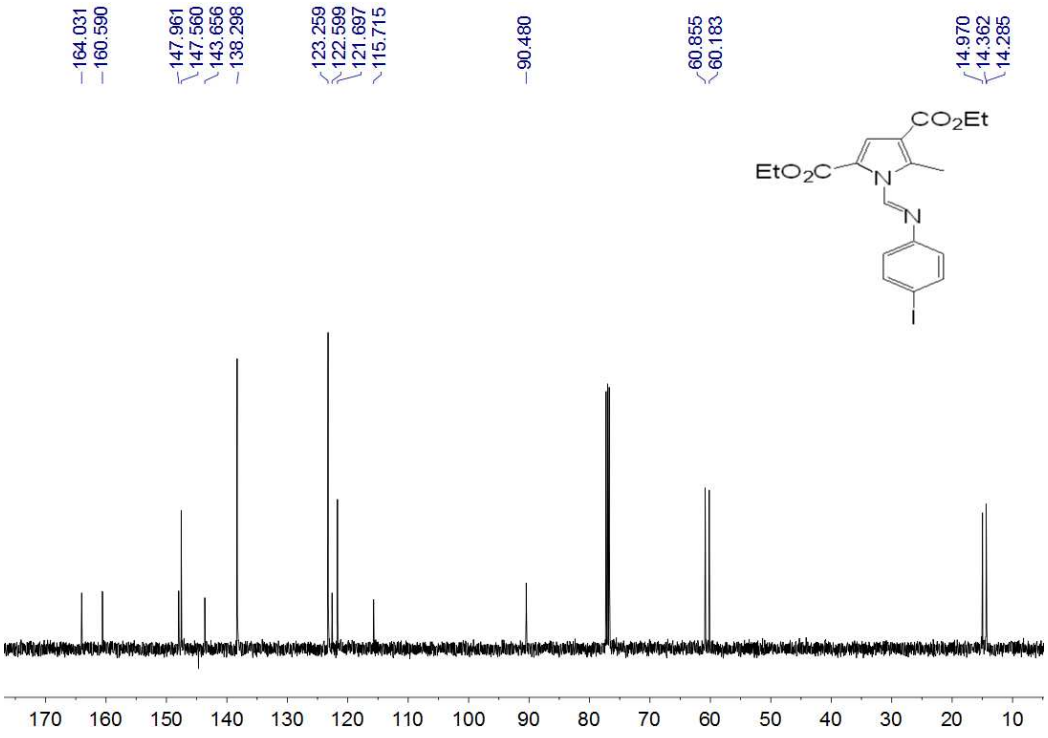
^{1}H and ^{13}C NMR Spectra for Compound 3b



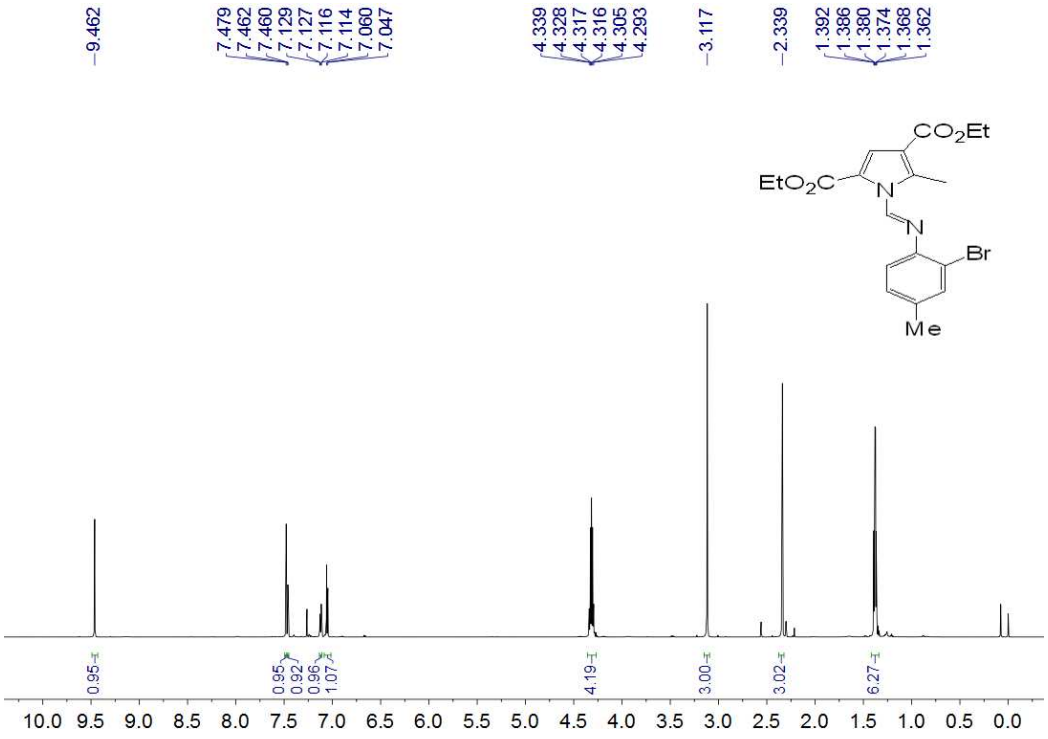


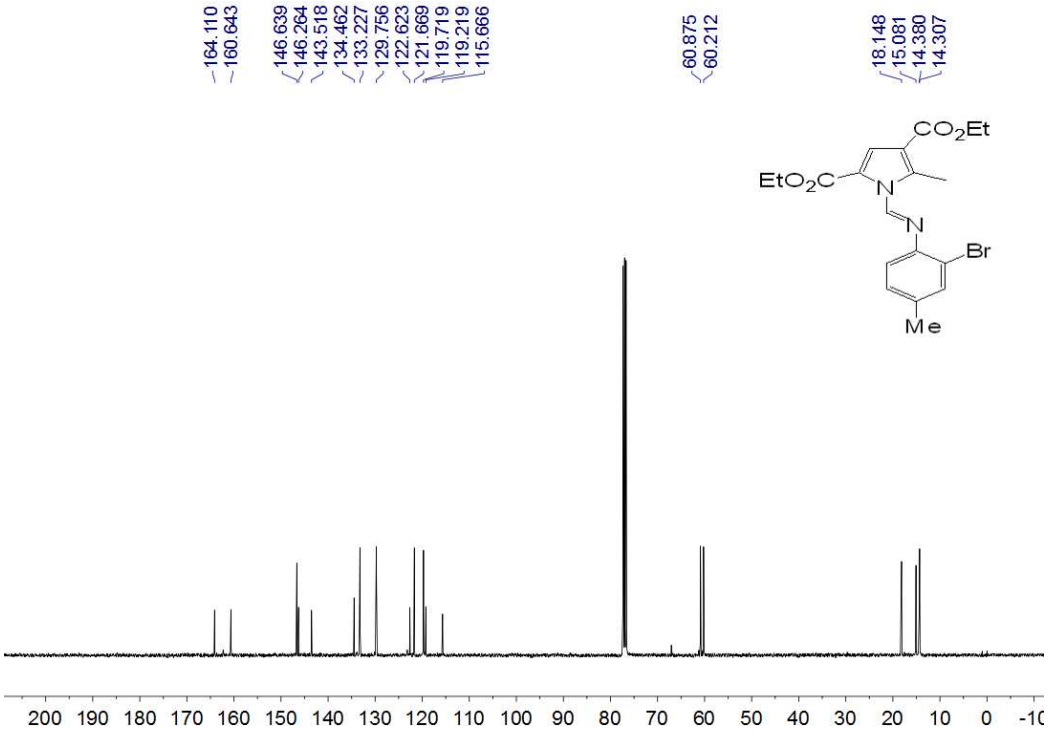
^{1}H and ^{13}C NMR Spectra for Compound 3c



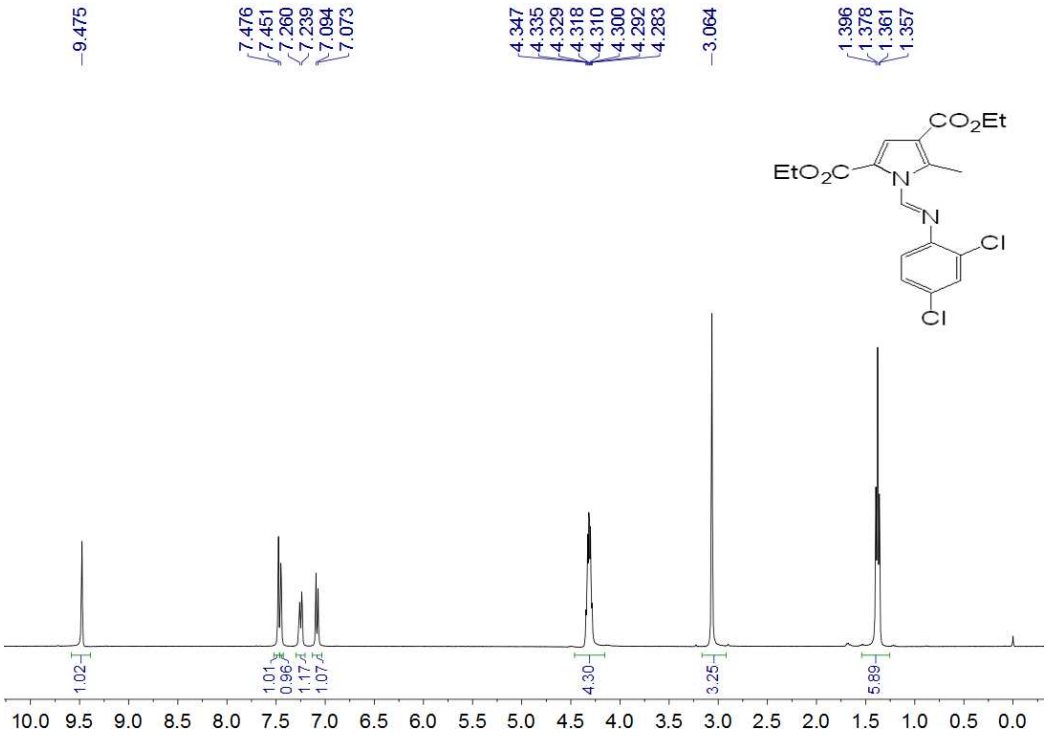


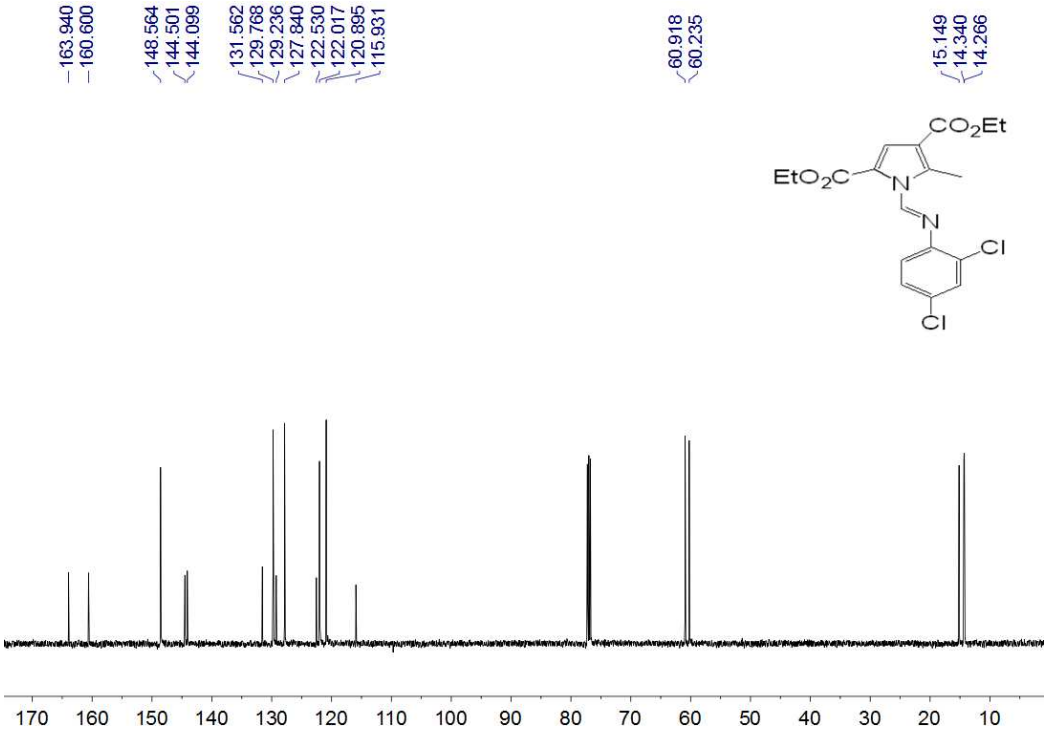
^{1}H and ^{13}C NMR Spectra for Compound 3d



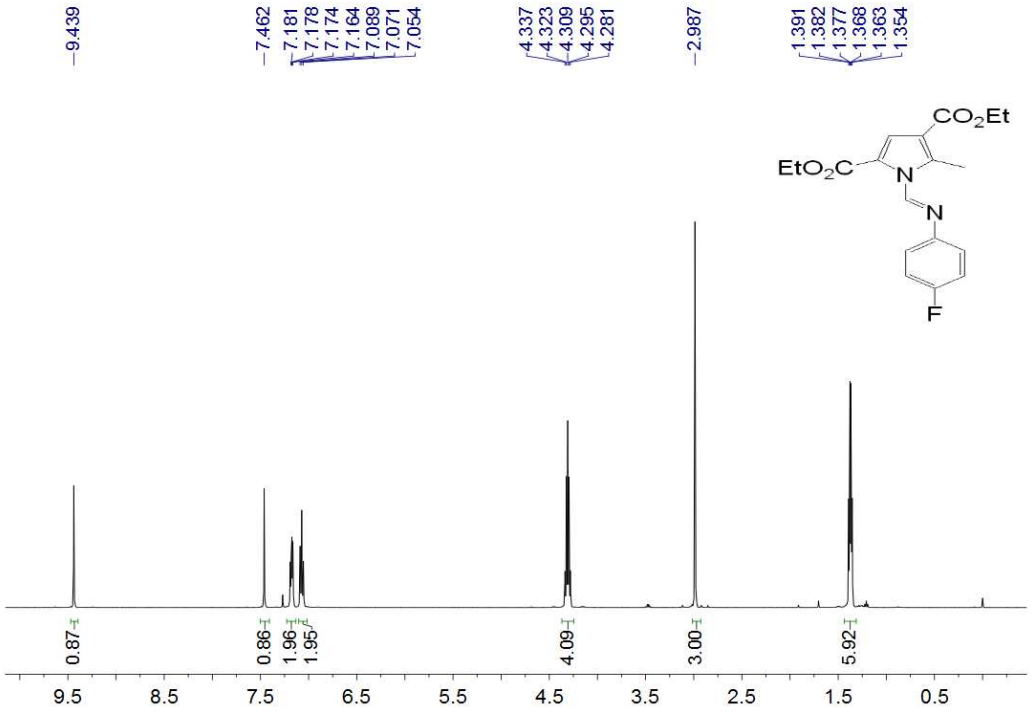


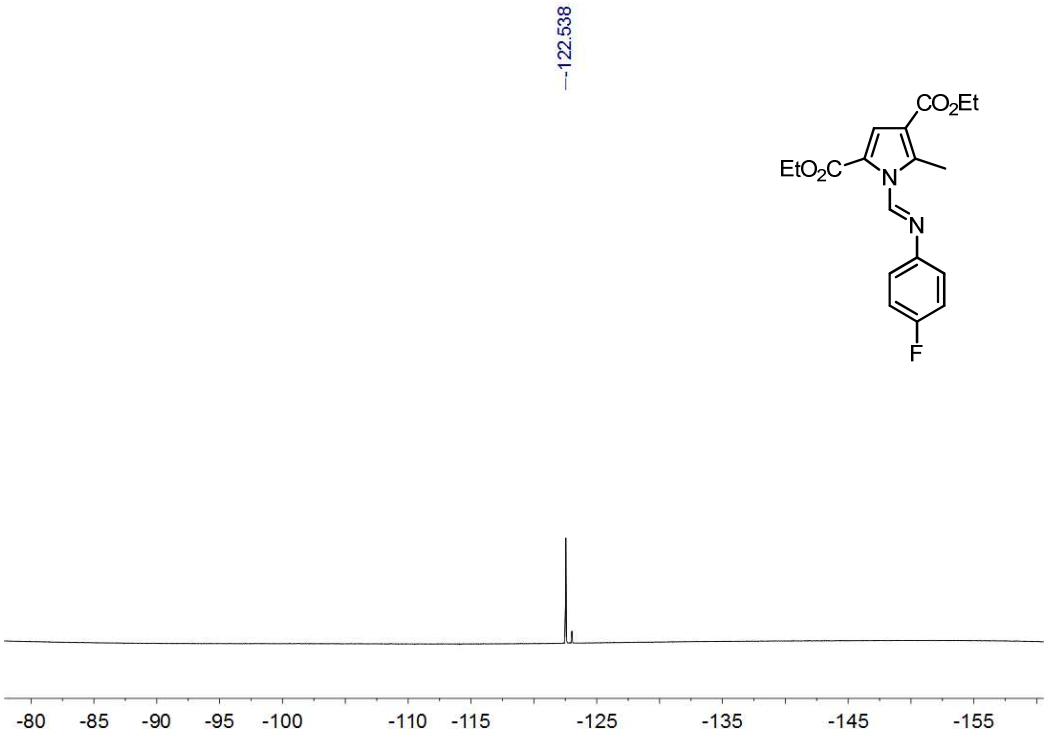
^{1}H and ^{13}C NMR Spectra for Compound 3e

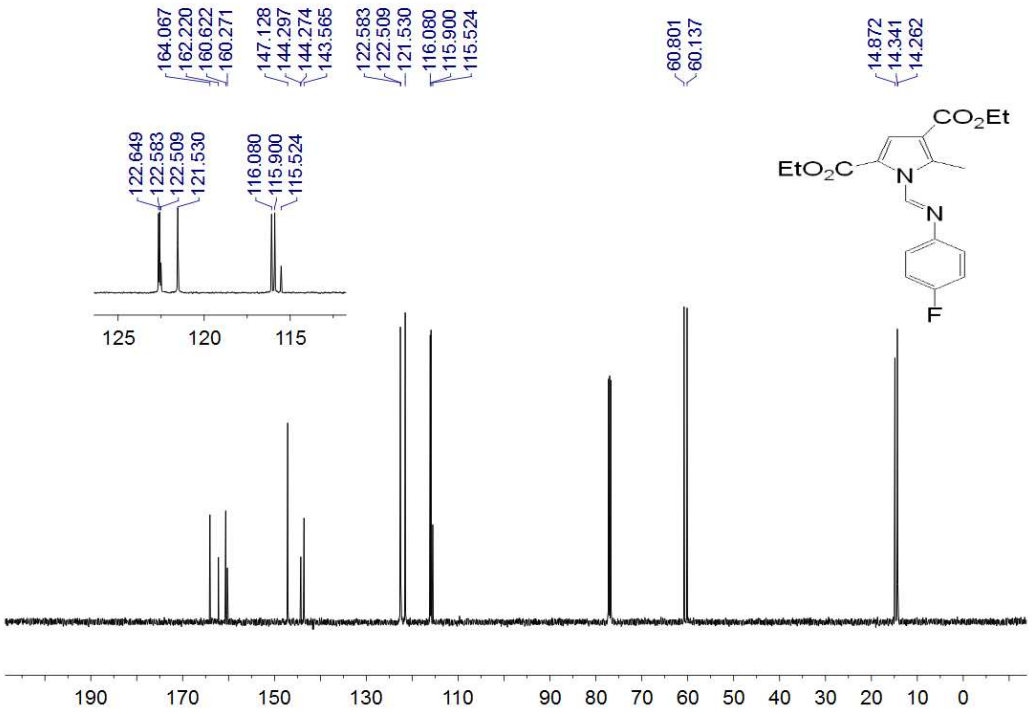




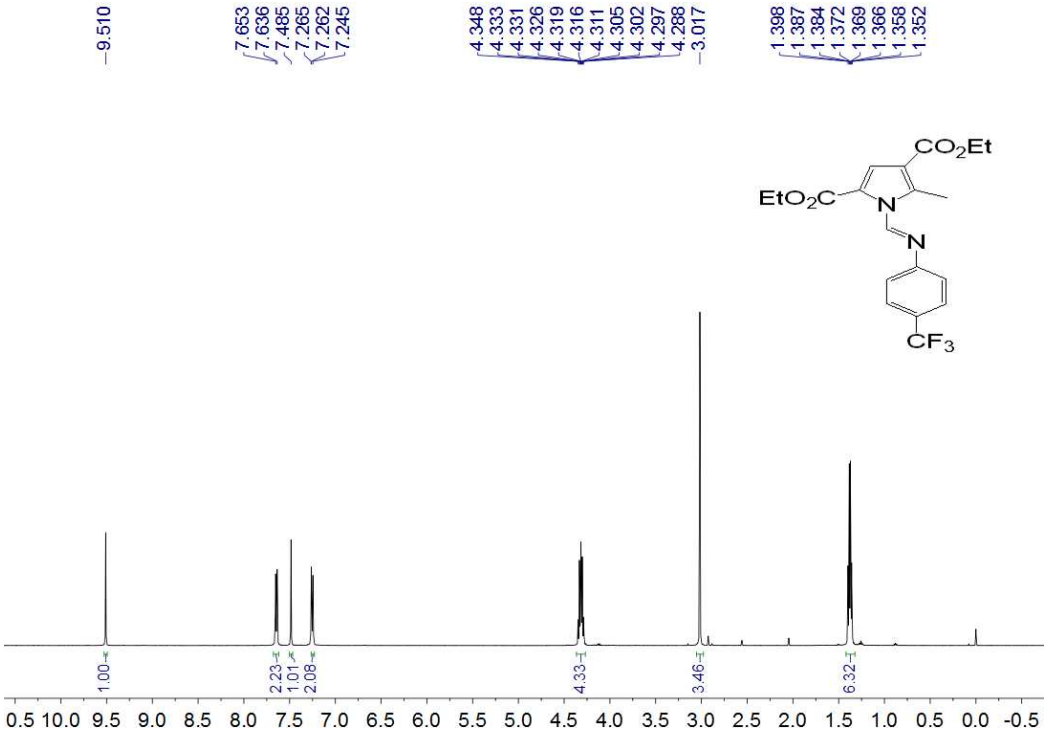
^{1}H, ^{13}C and ^{19}F NMR Spectra for Compound 3f

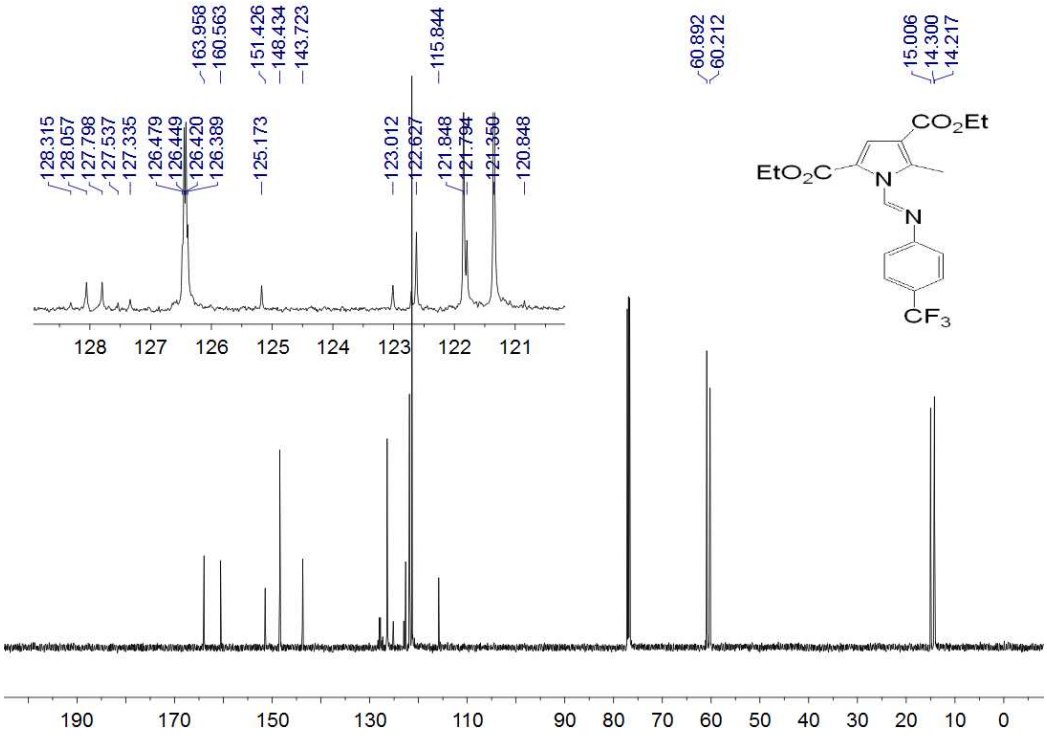






^{1}H, ^{13}C and ^{19}F NMR Spectra for Compound 3g

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148.434
143.723
115.844
60.892
60.212
15.006
14.300
14.217
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128.057
127.798
127.537
127.335
126.479
126.449
126.420
126.389
125.173
123.012
122.627
121.848
121.794
121.350
120.848
CO2Et
EtO2C
N
N
CF3
128
127
126
125
124
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121
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70
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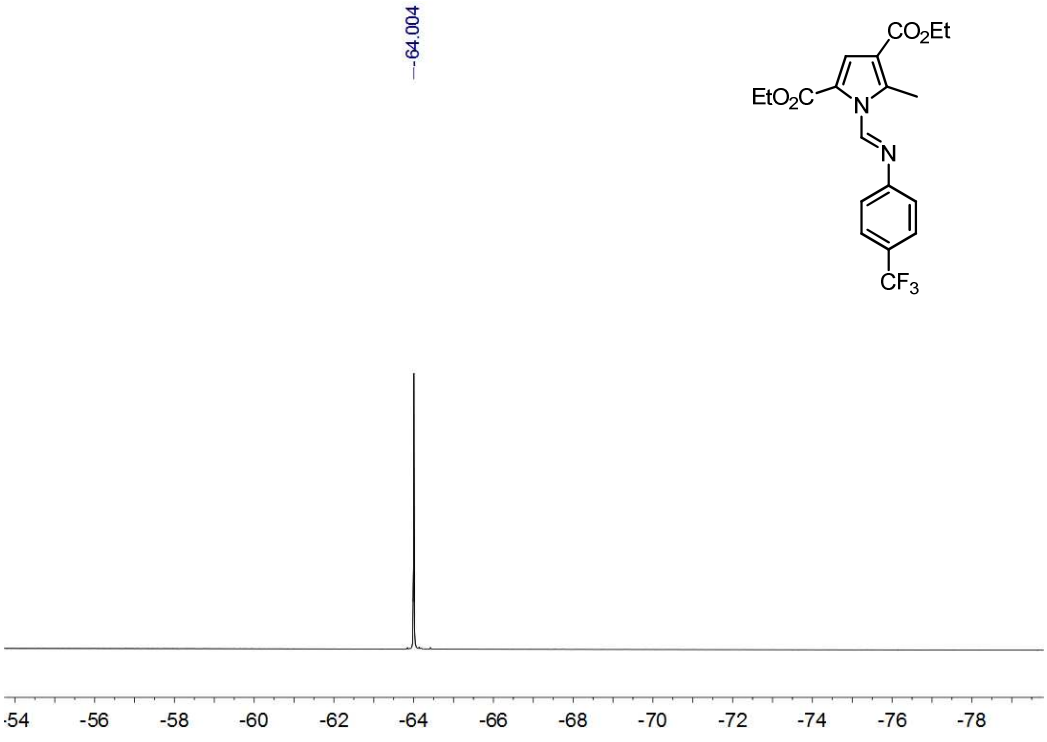
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EtO2C
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N
CF3
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-60
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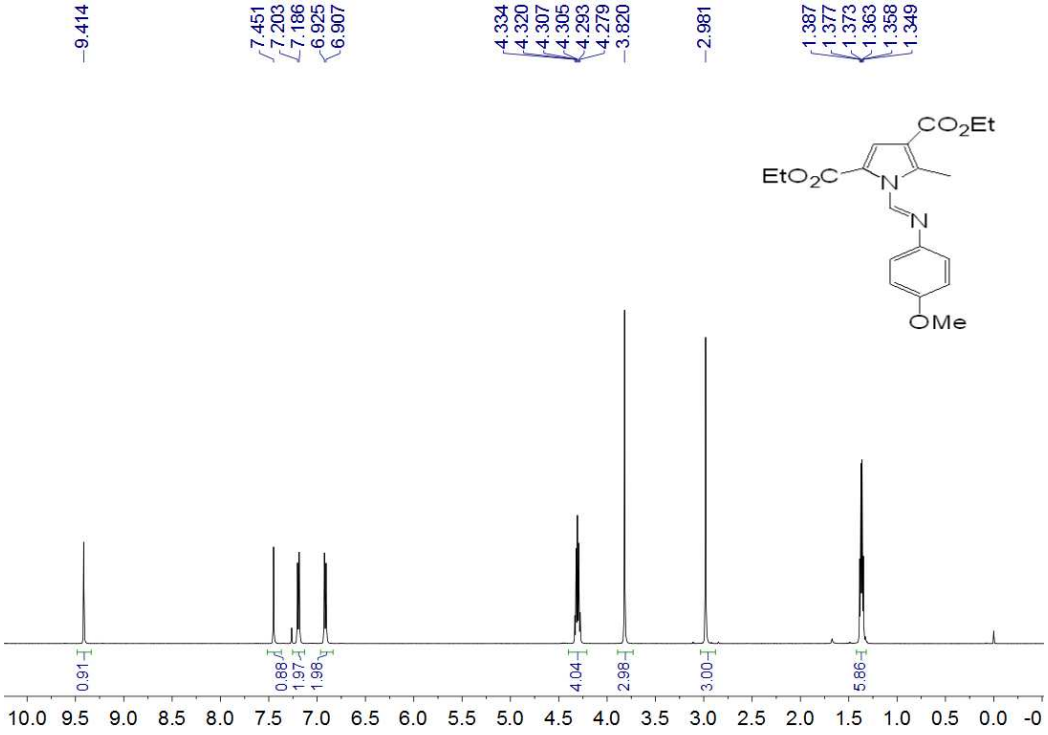
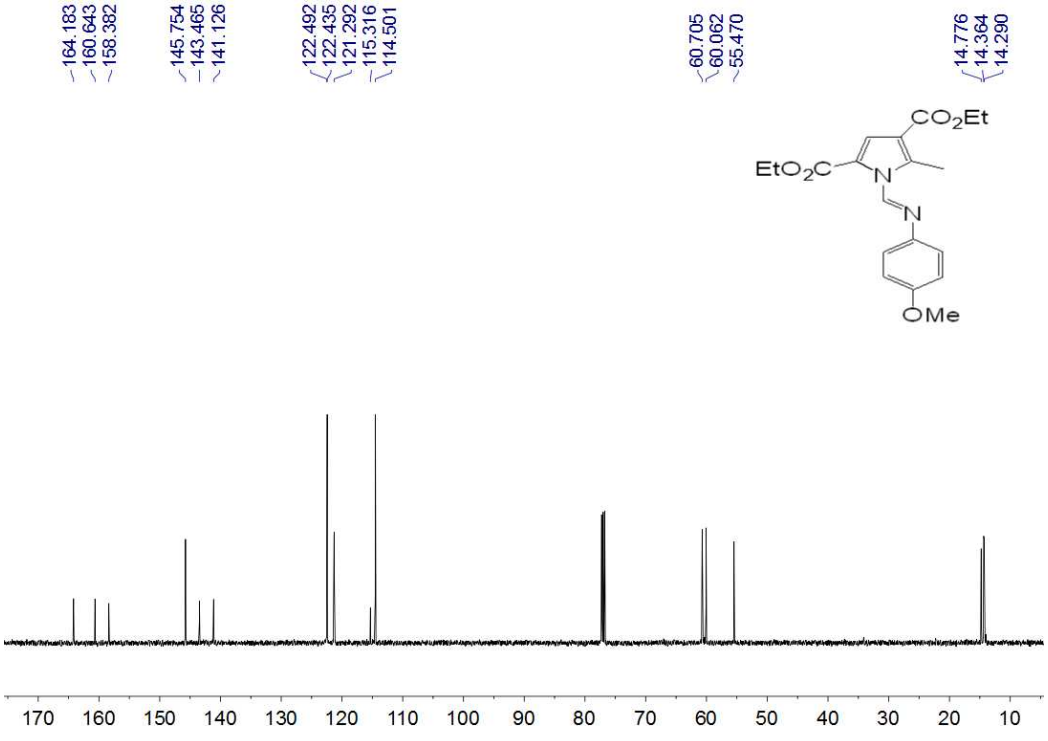
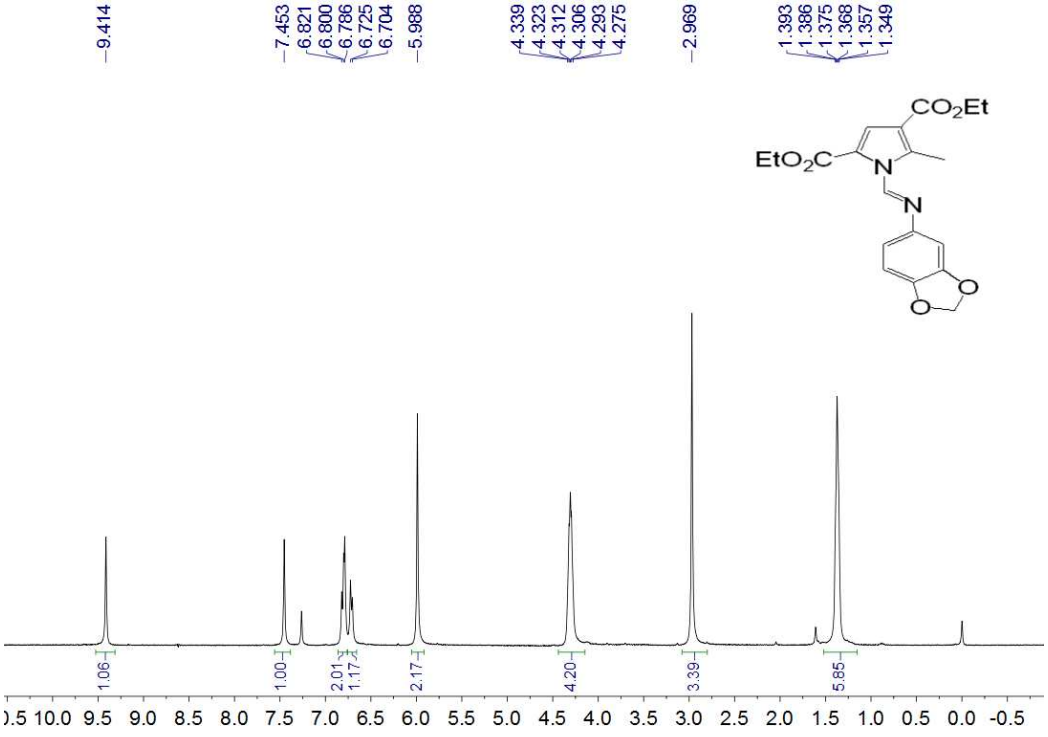
-78

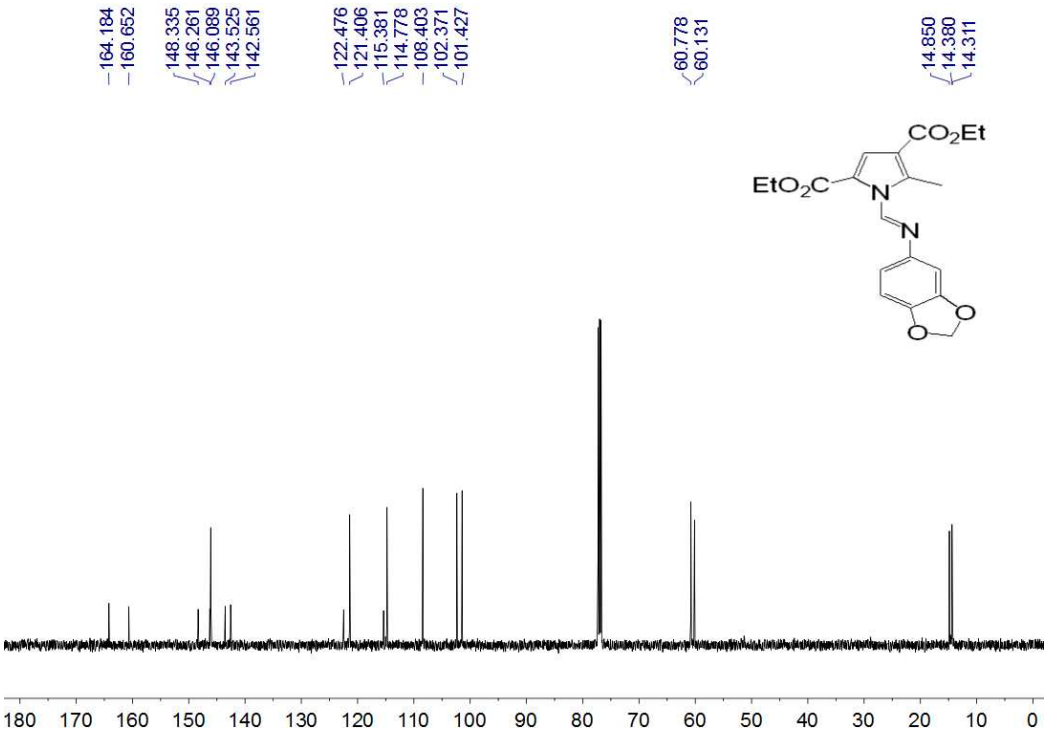
^{1}H and ^{13}C NMR Spectra for Compound 3h



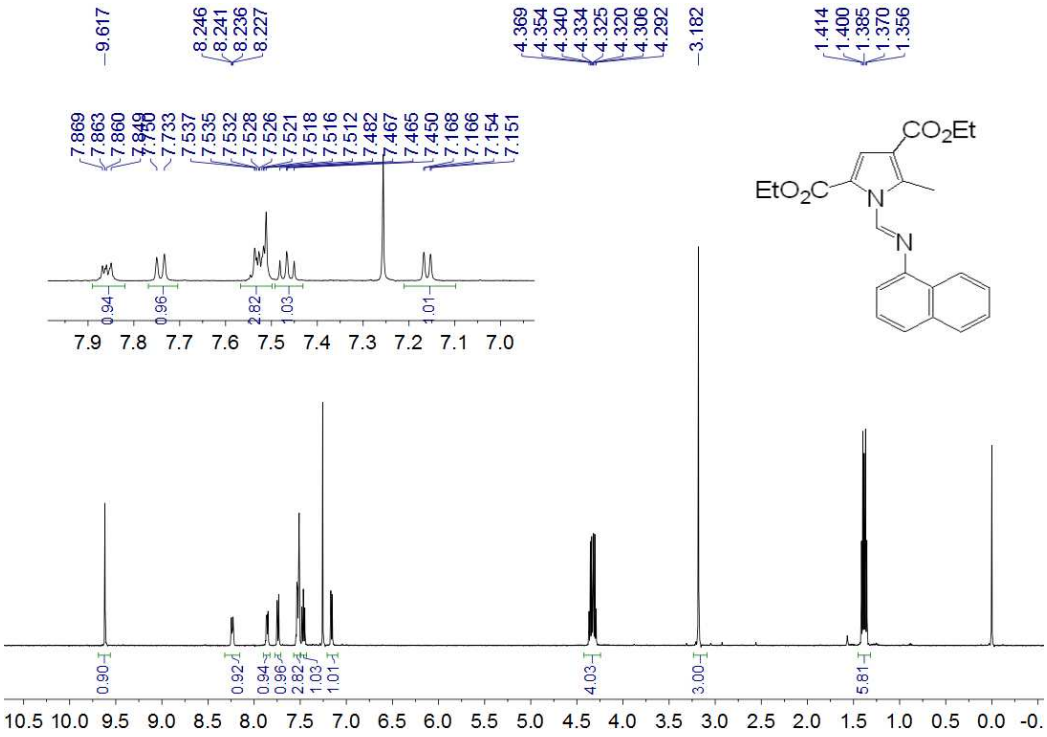


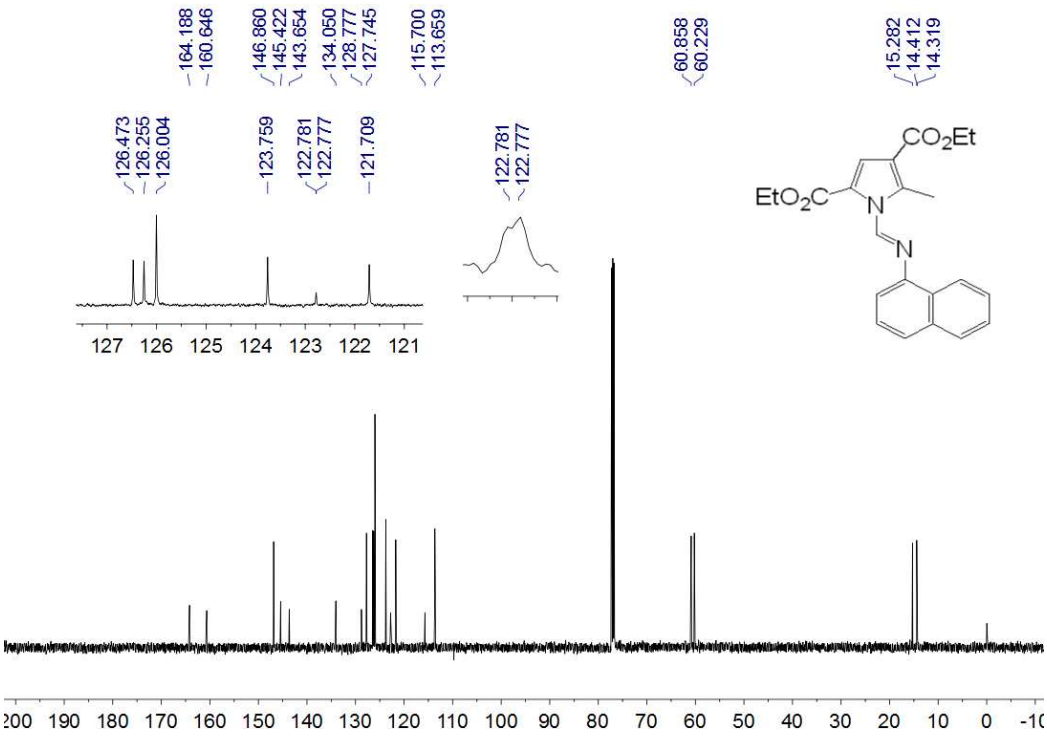
^{1}H and ^{13}C NMR Spectra for Compound 3i



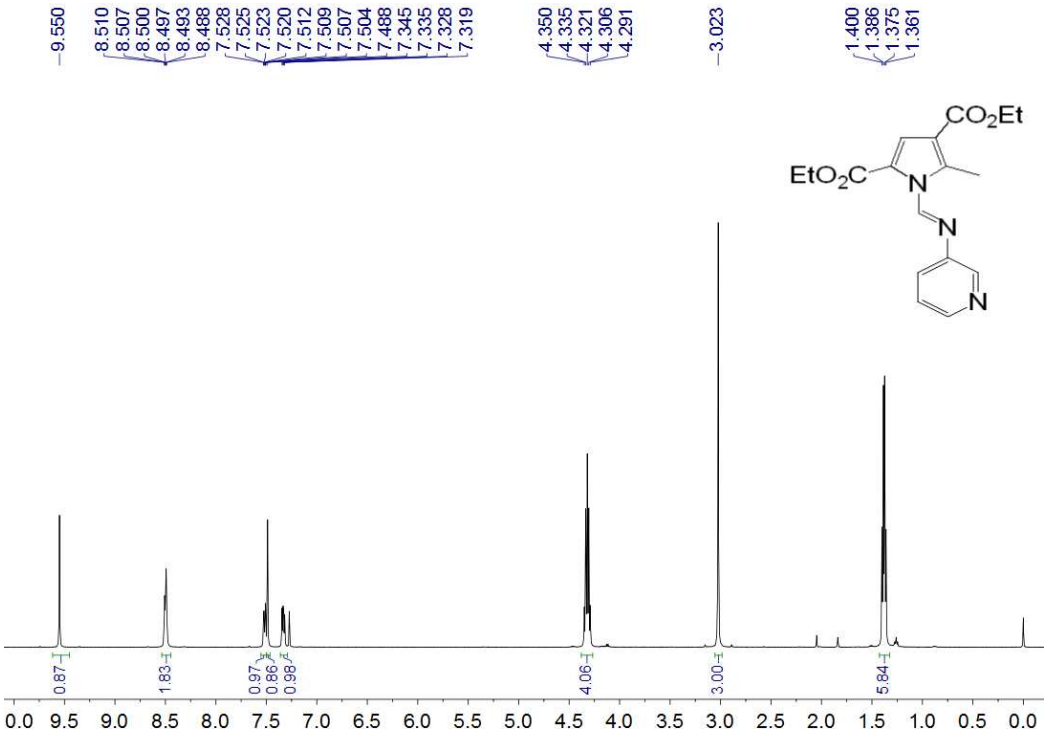


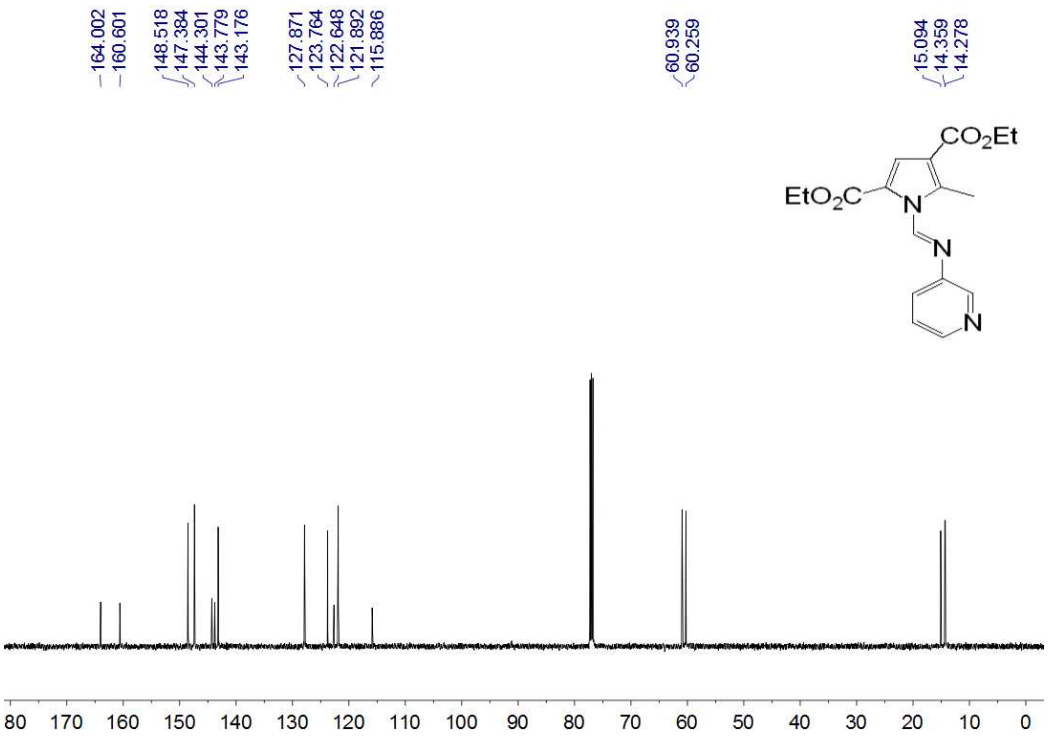
^{1}H and ^{13}C NMR Spectra for Compound 3j



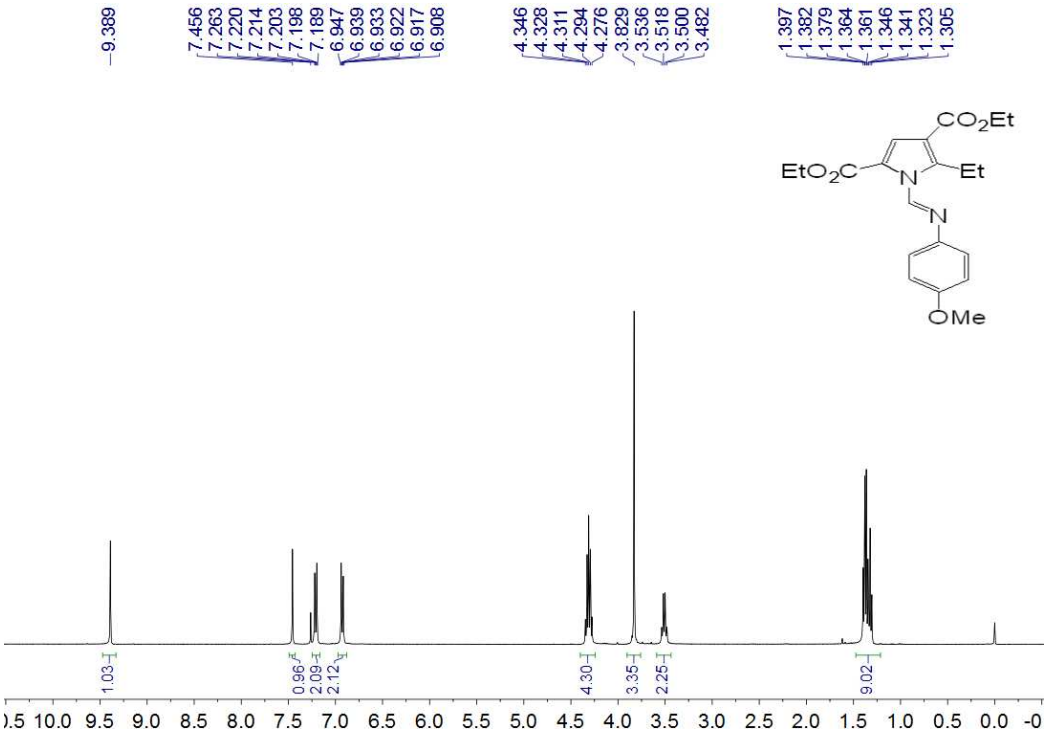


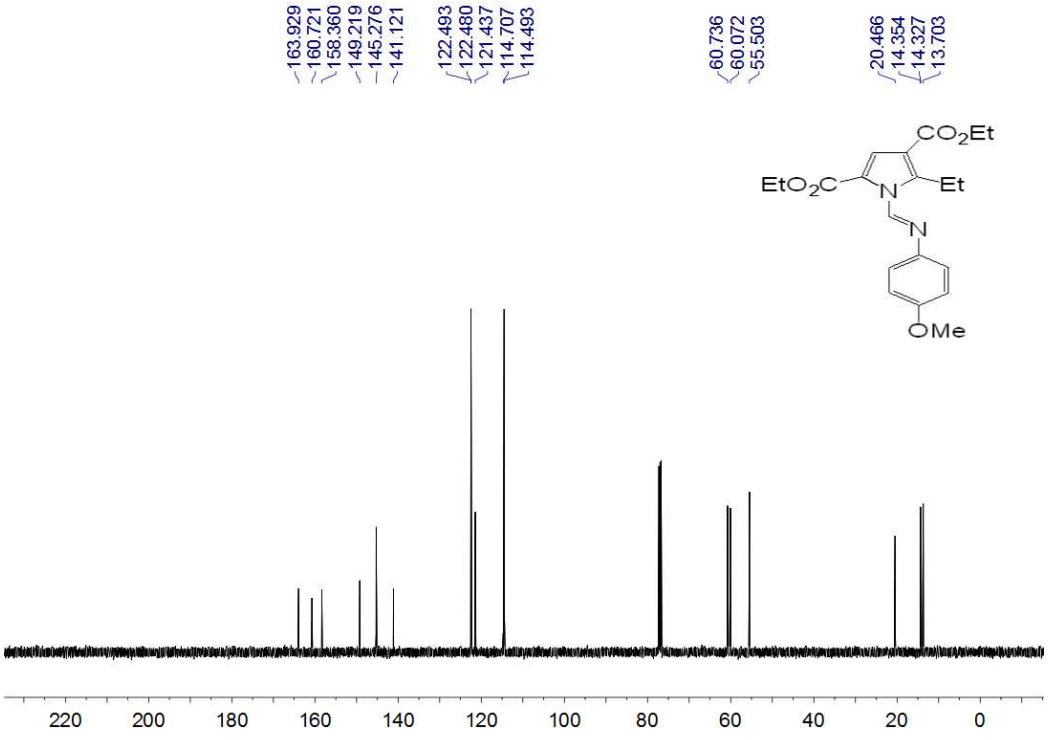
^{1}H and ^{13}C NMR Spectra for Compound 3k



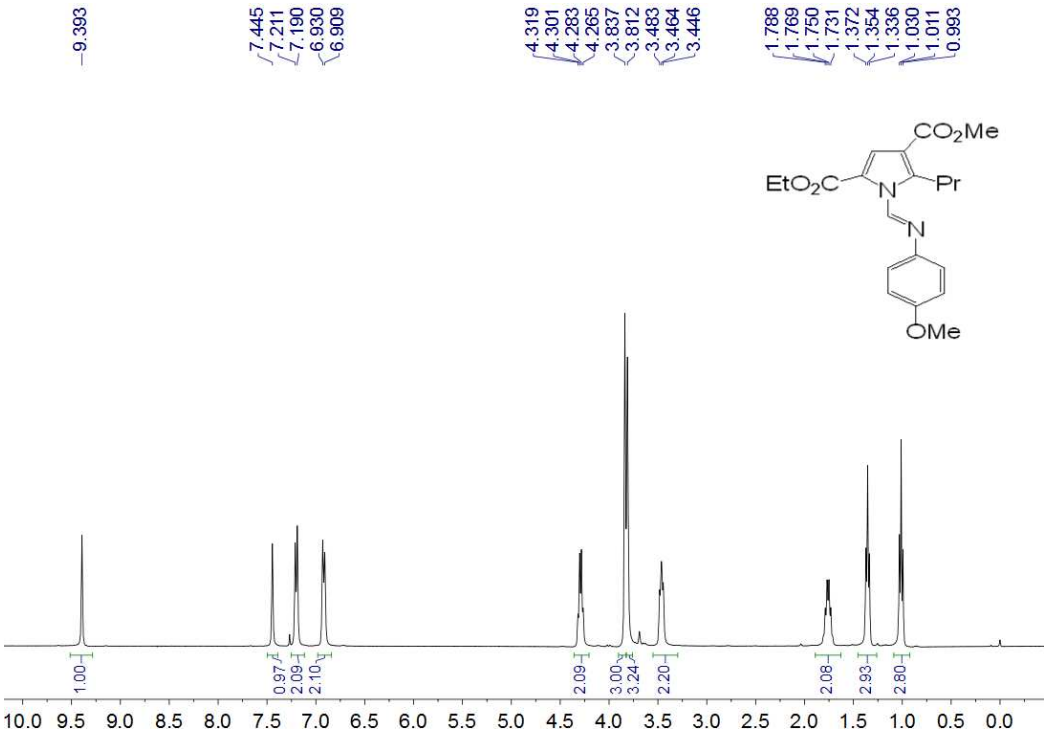


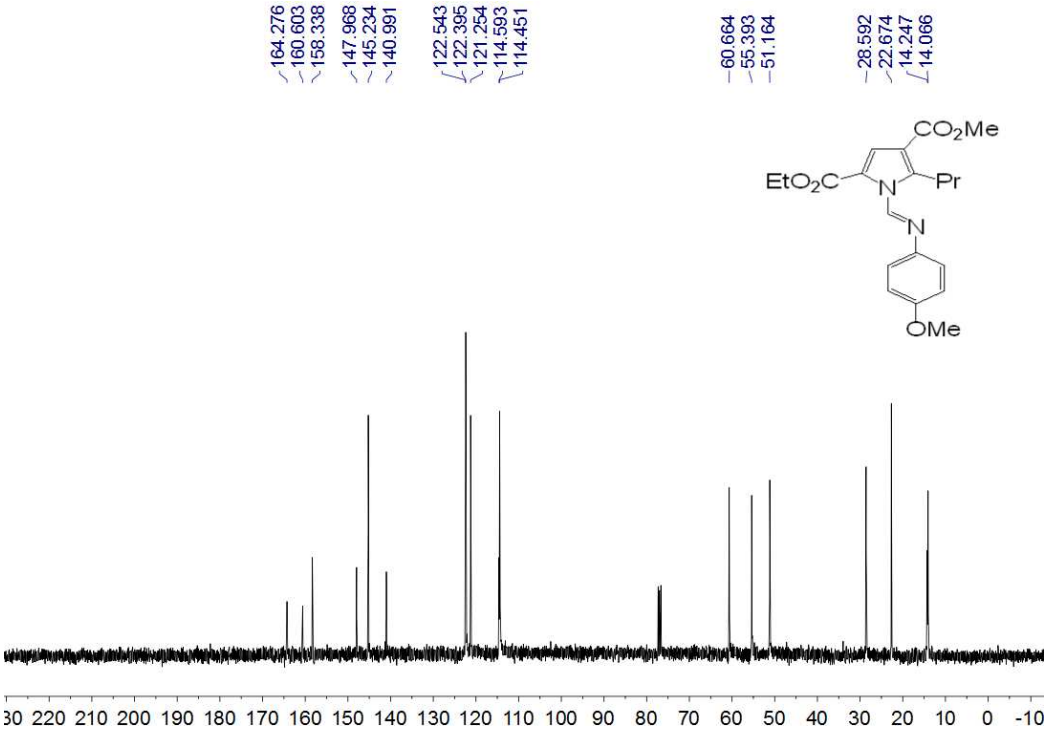
^{1}H and ^{13}C NMR Spectra for Compound 3l



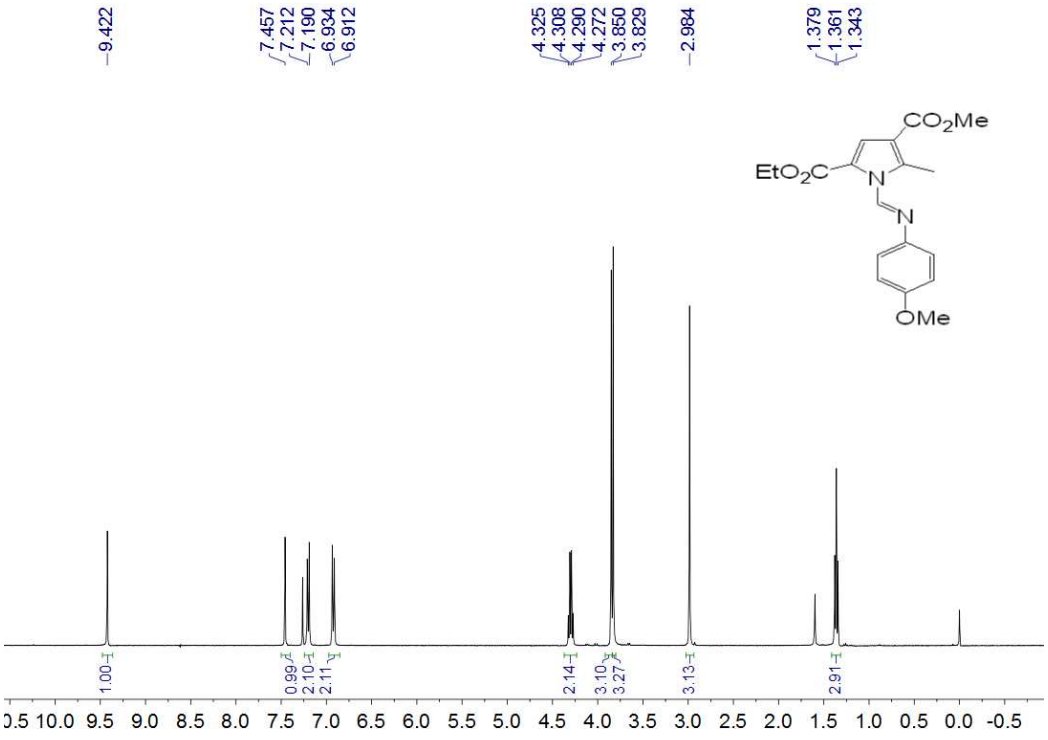


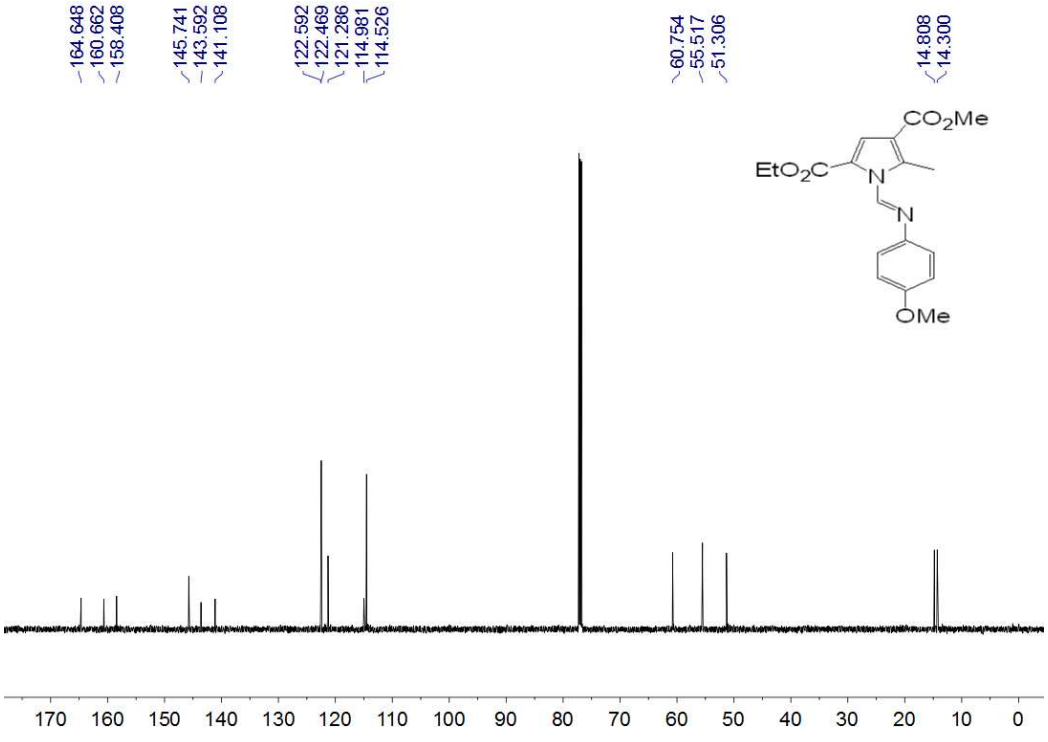
^{1}H and ^{13}C NMR Spectra for Compound 3m



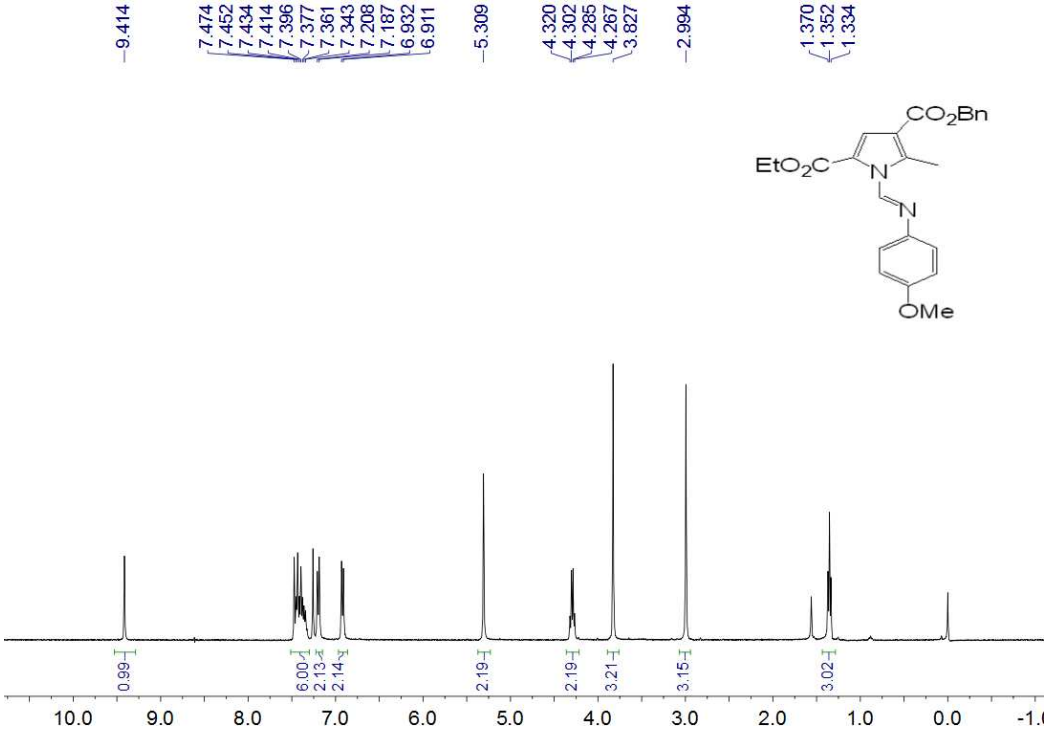


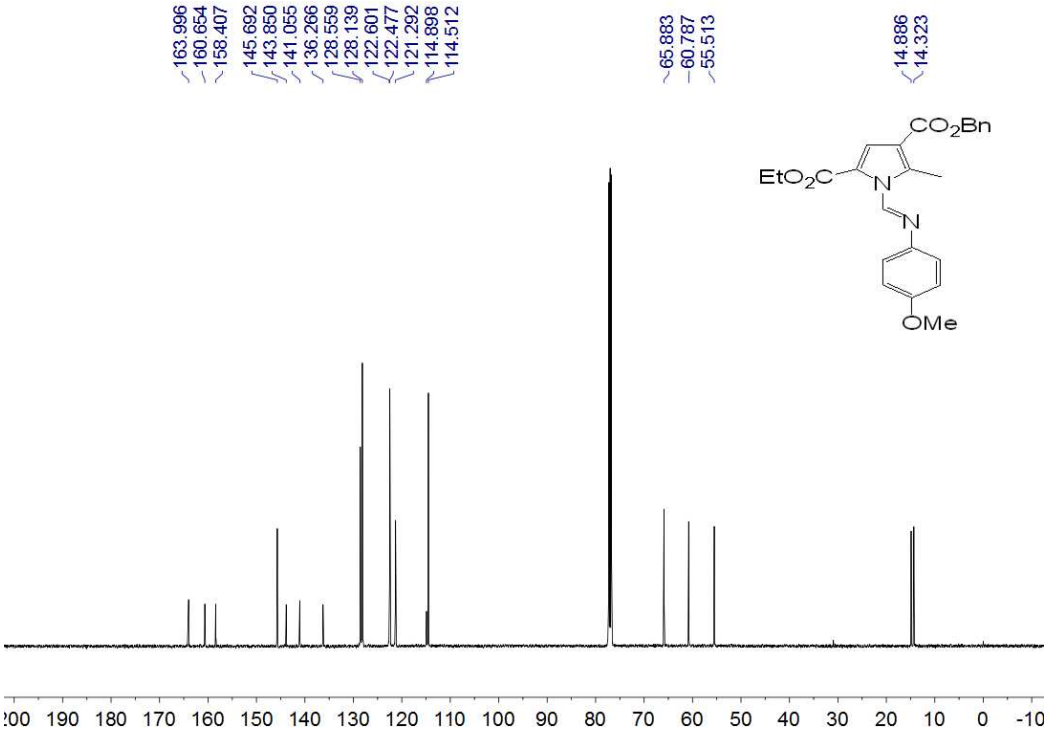
^{1}H and ^{13}C NMR Spectra for Compound 3n



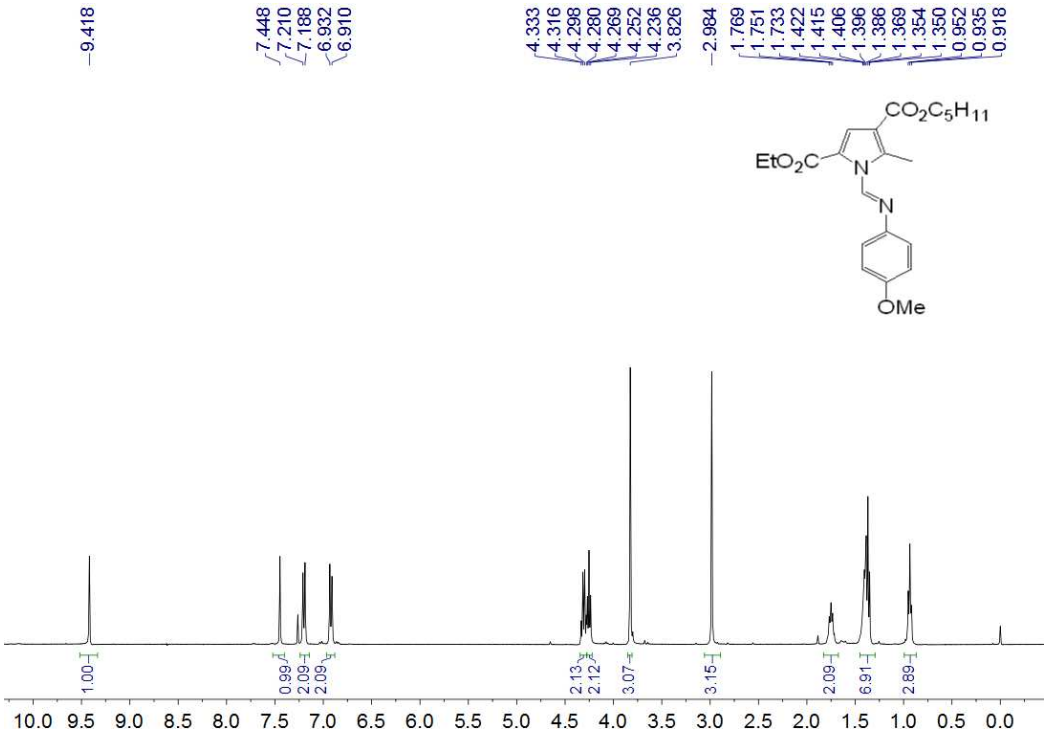


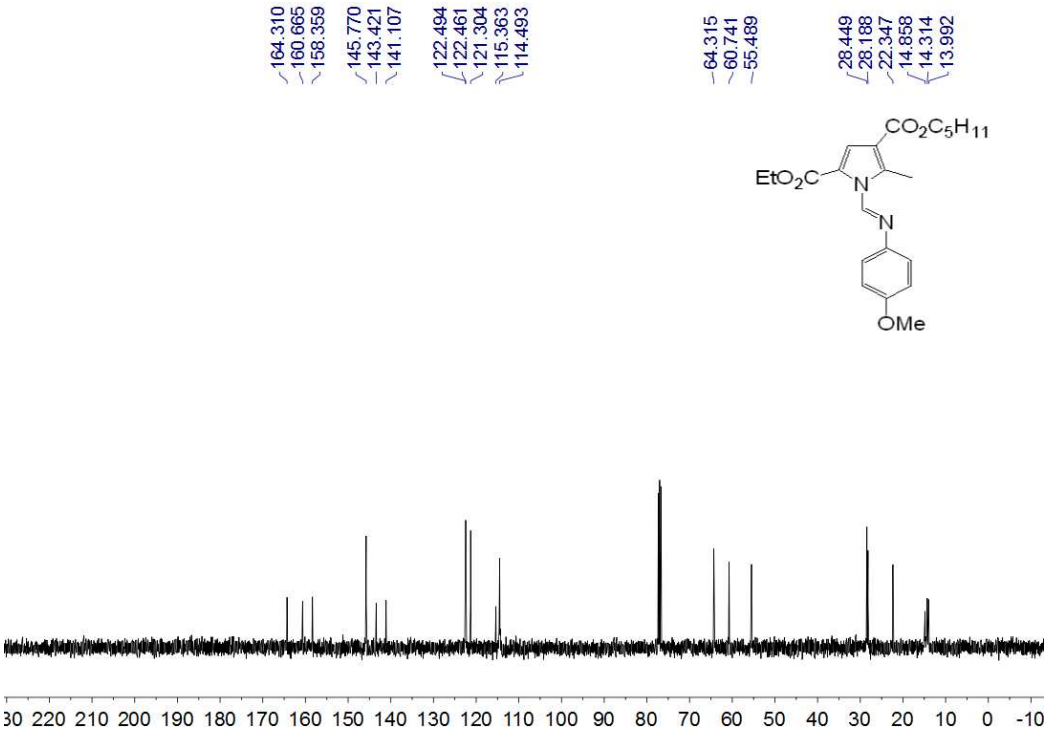
^{1}H and ^{13}C NMR Spectra for Compound 3o



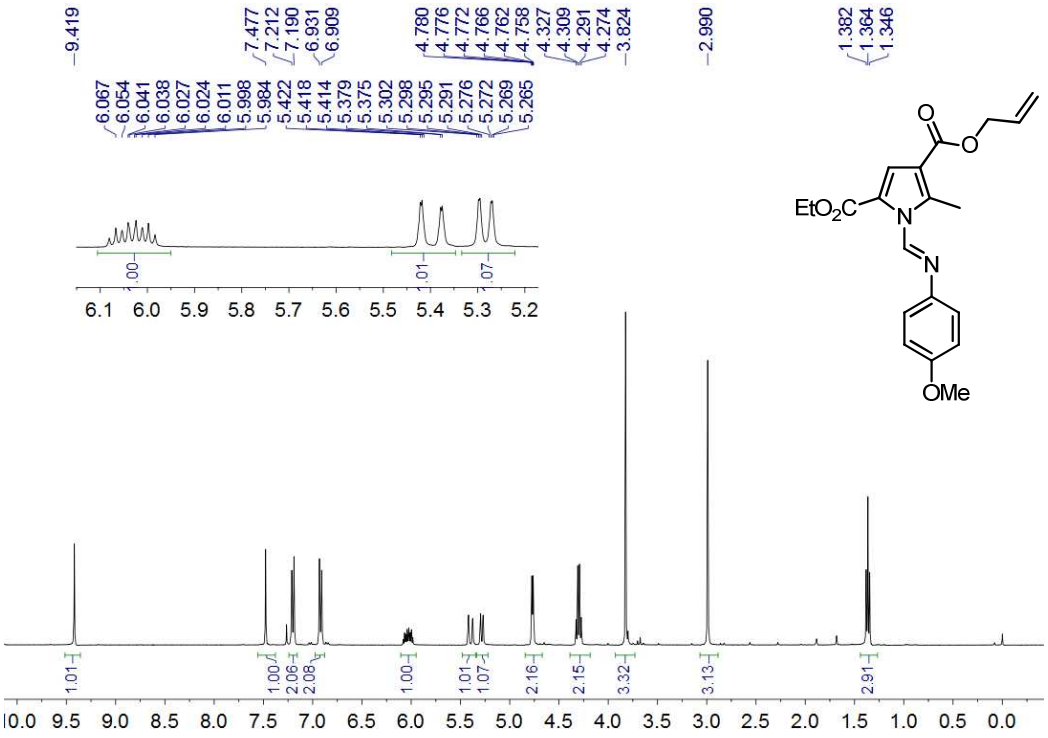


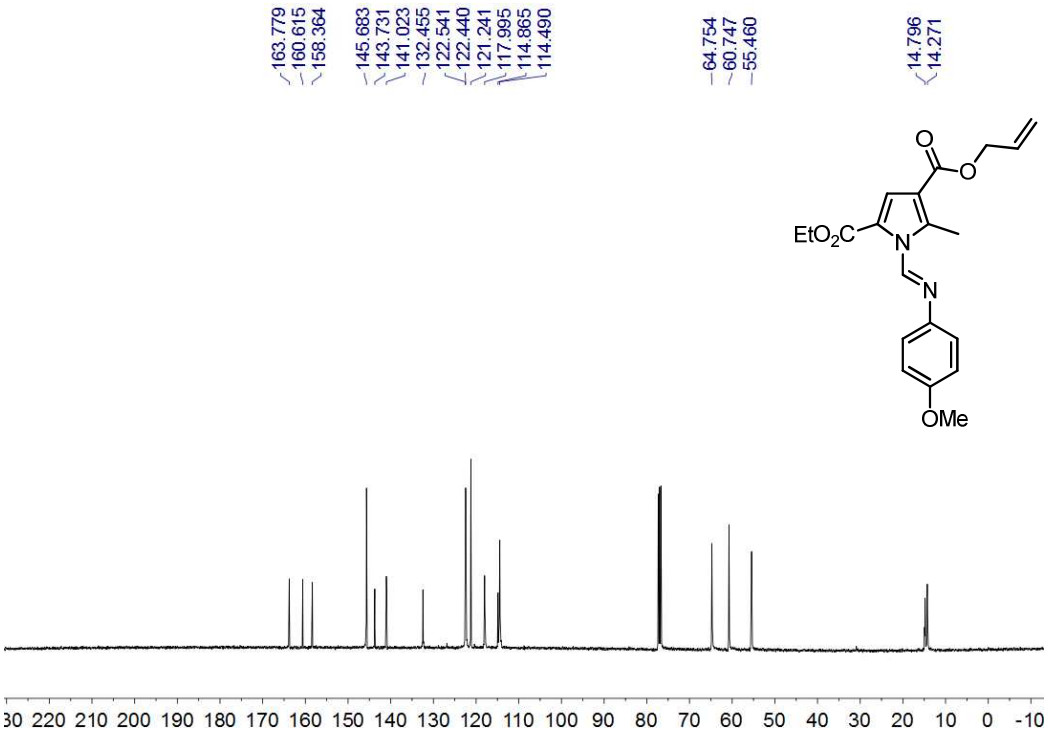
^{1}H and ^{13}C NMR Spectra for Compound 3p



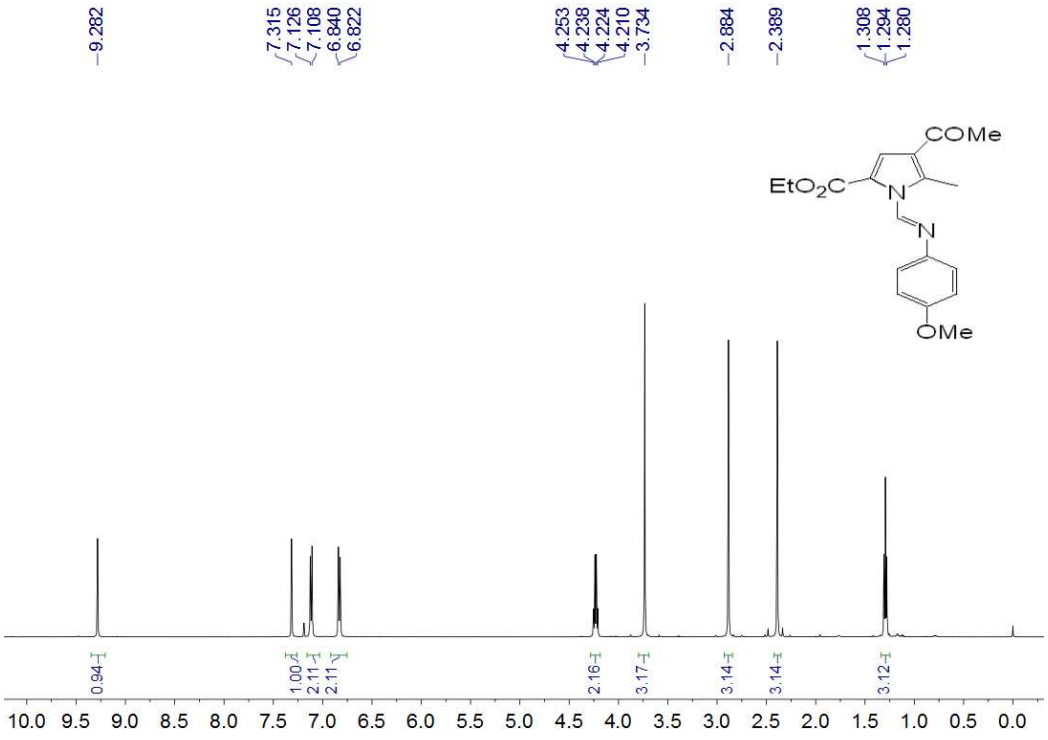


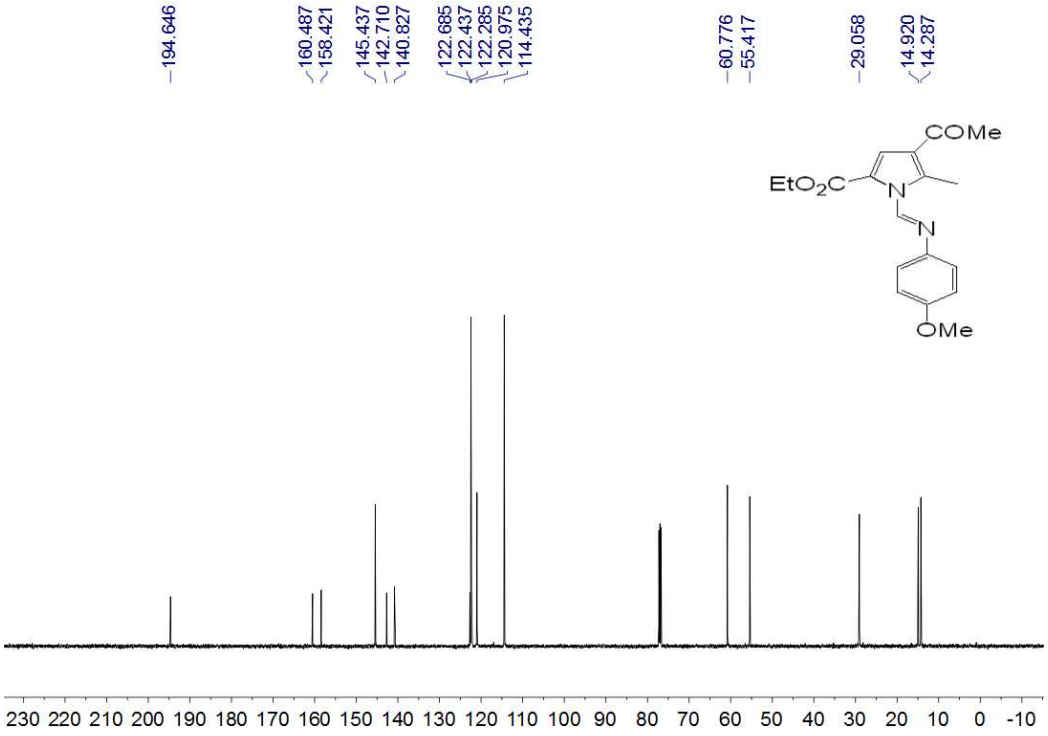
^{1}H and ^{13}C NMR Spectra for Compound 3q



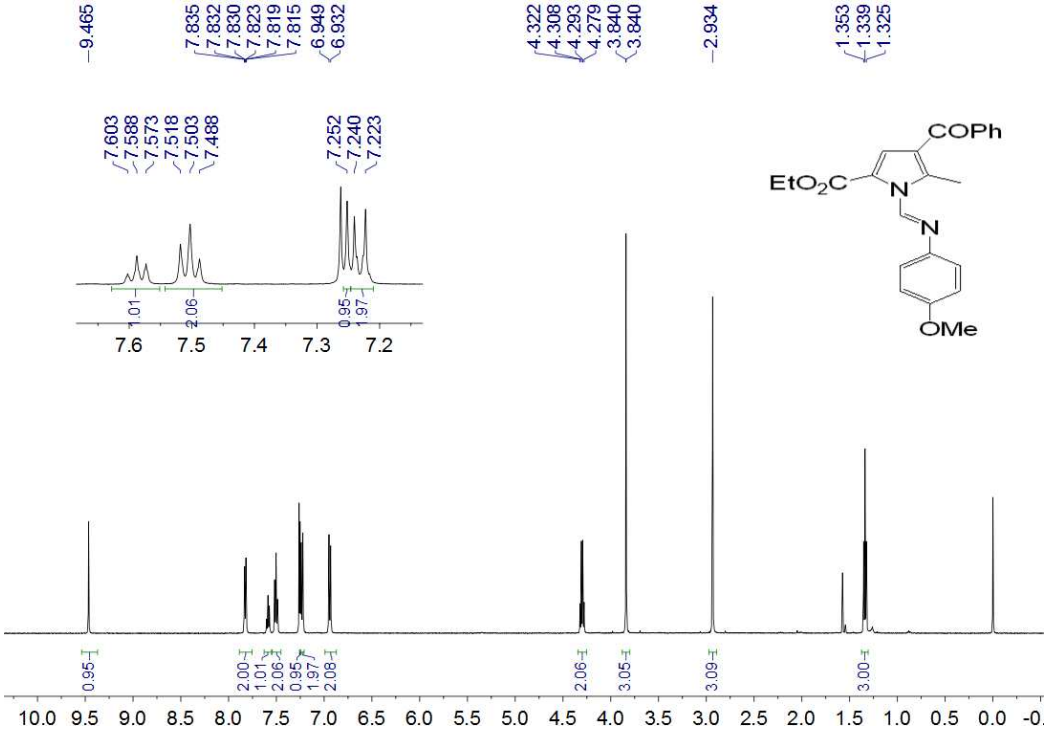


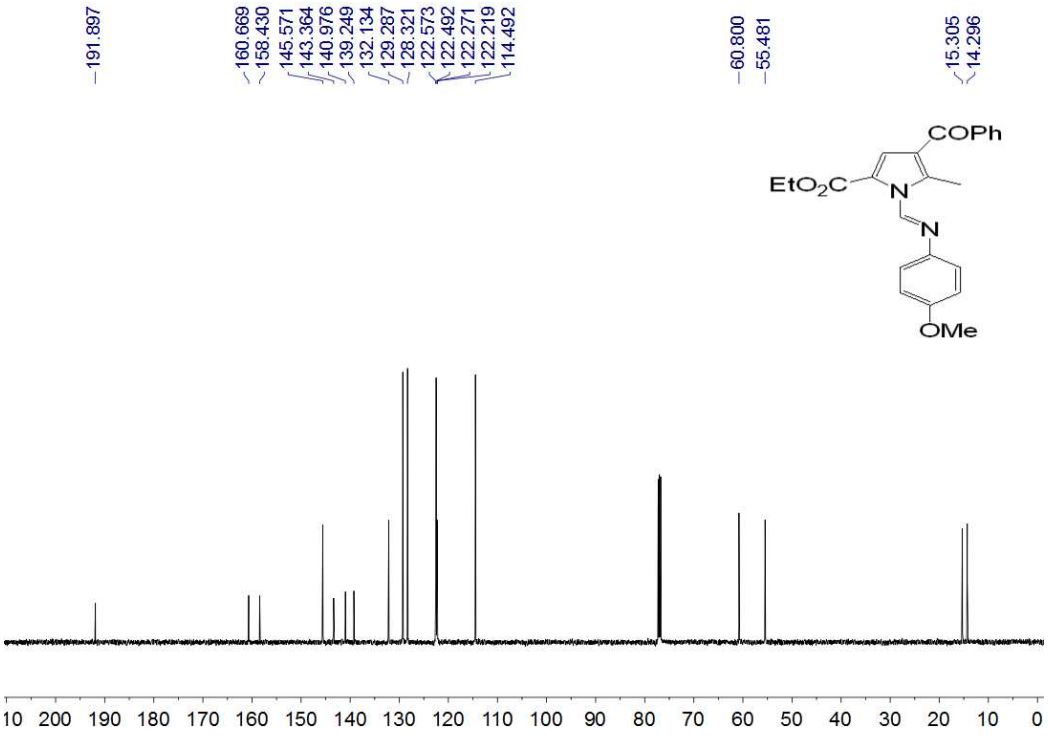
^{1}H and ^{13}C NMR Spectra for Compound 3r



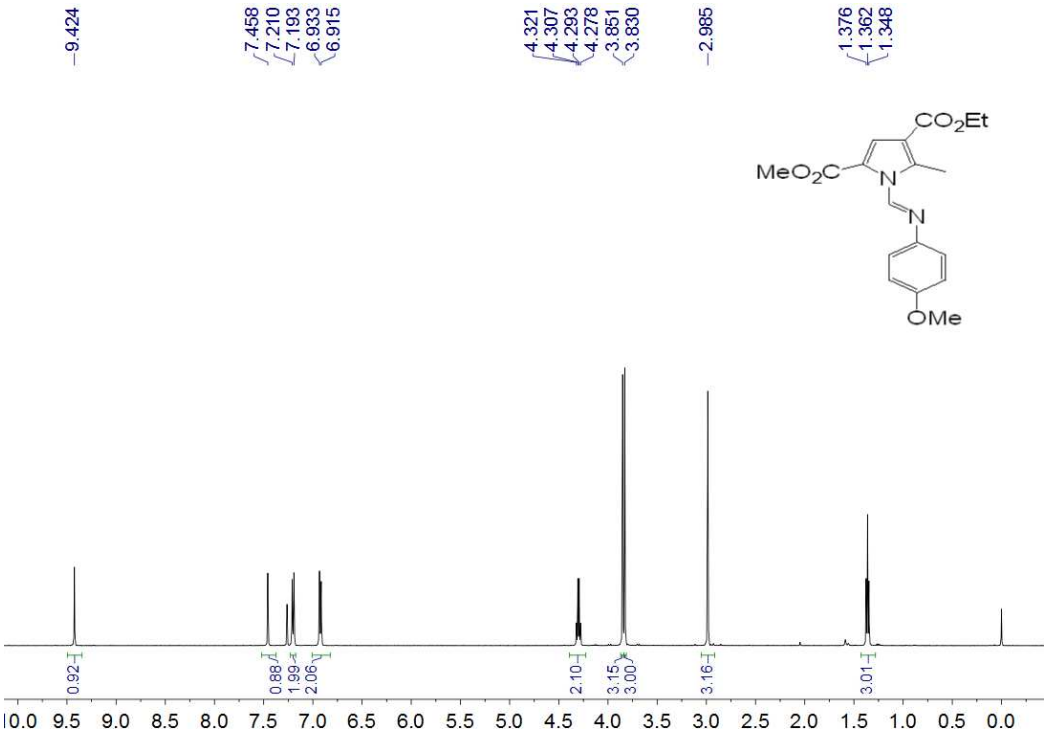


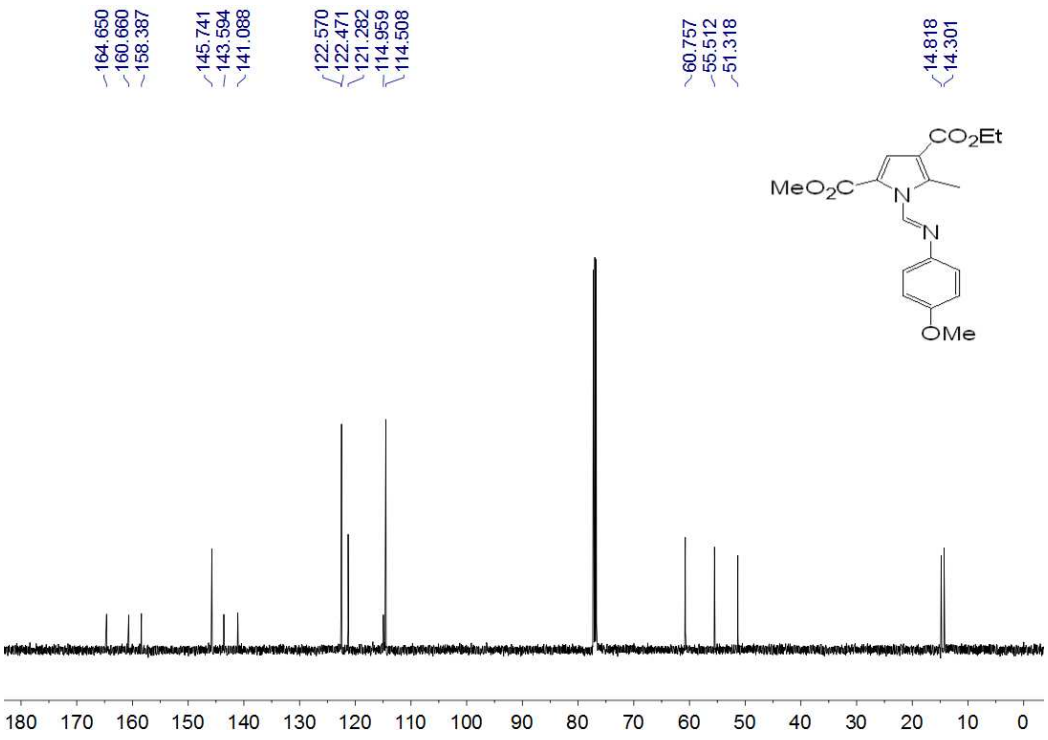
^{1}H and ^{13}C NMR Spectra for Compound 3s



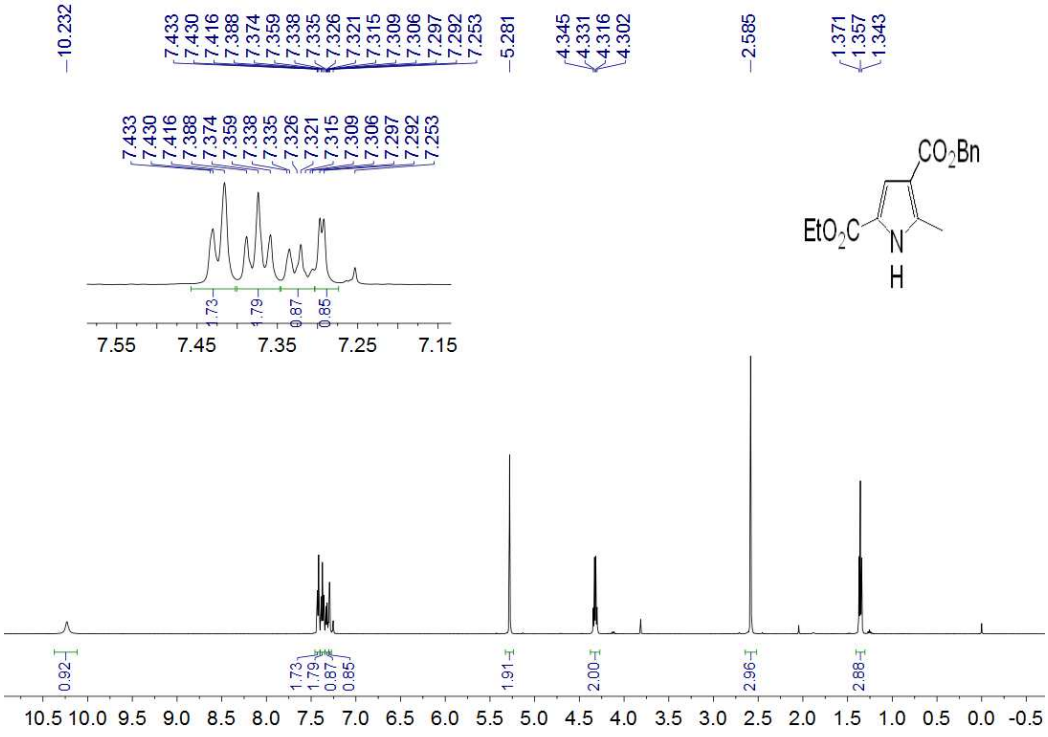


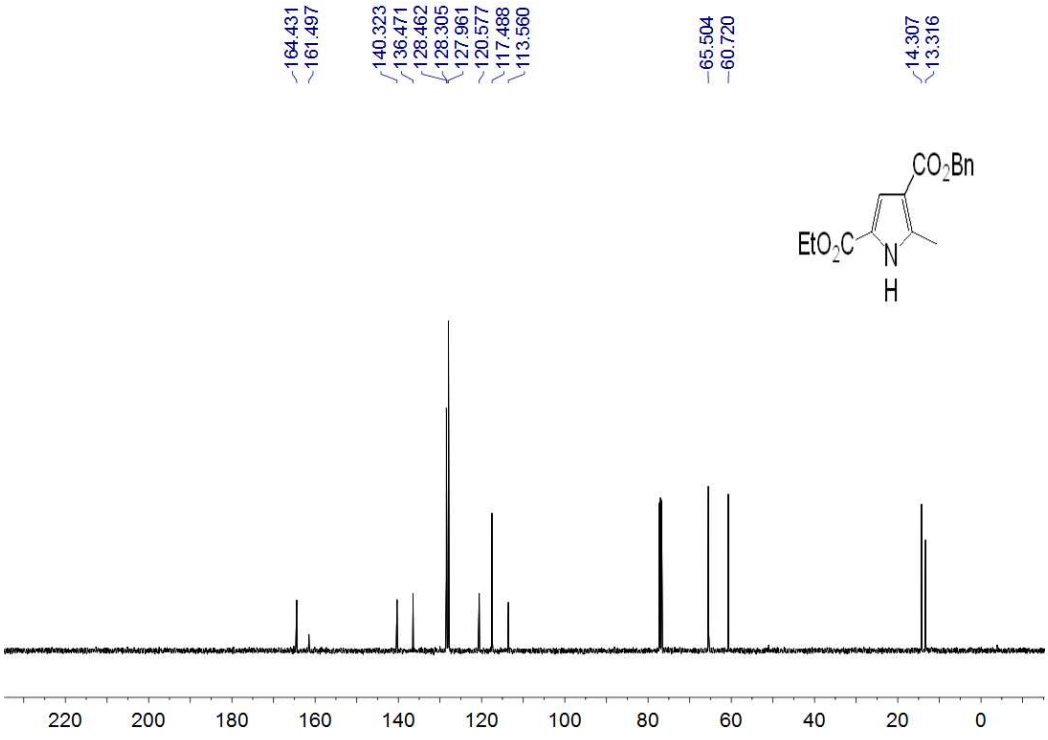
^{1}H and ^{13}C NMR Spectra for Compound 3t



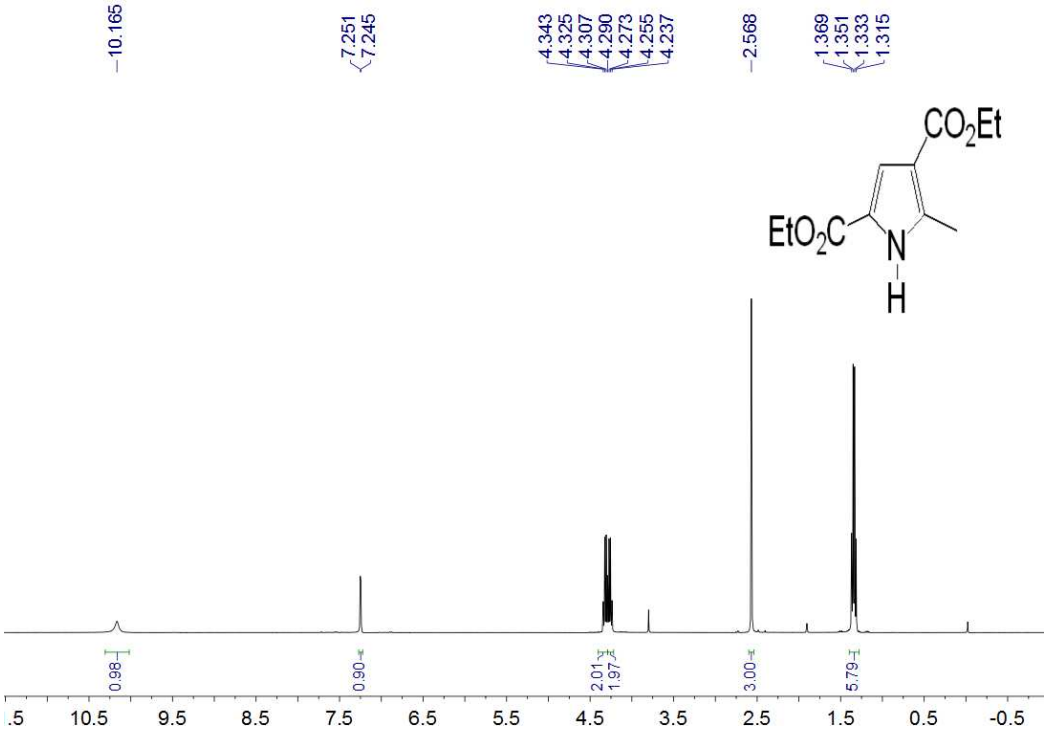


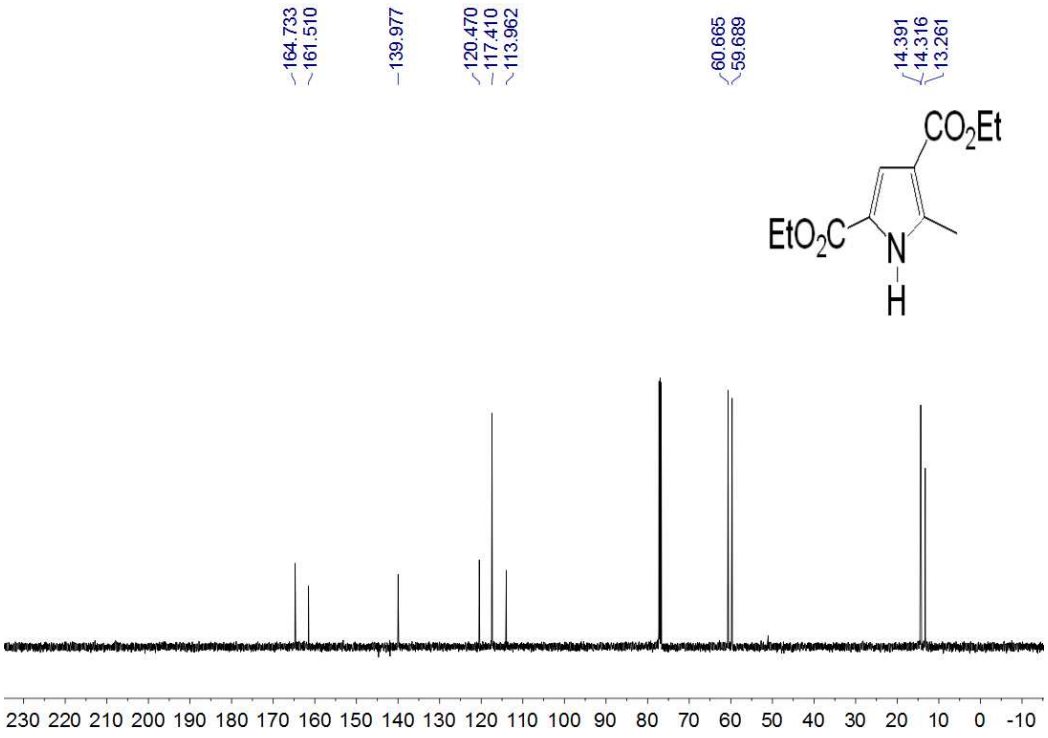
^{1}H and ^{13}C NMR Spectra for Compound 5a



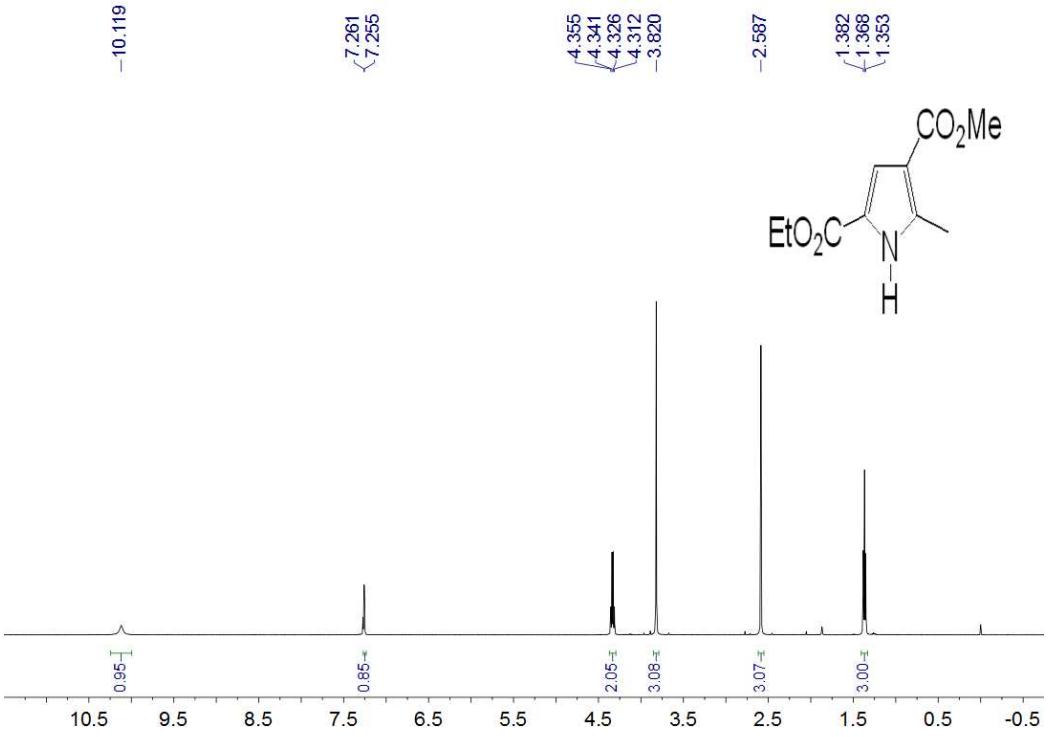


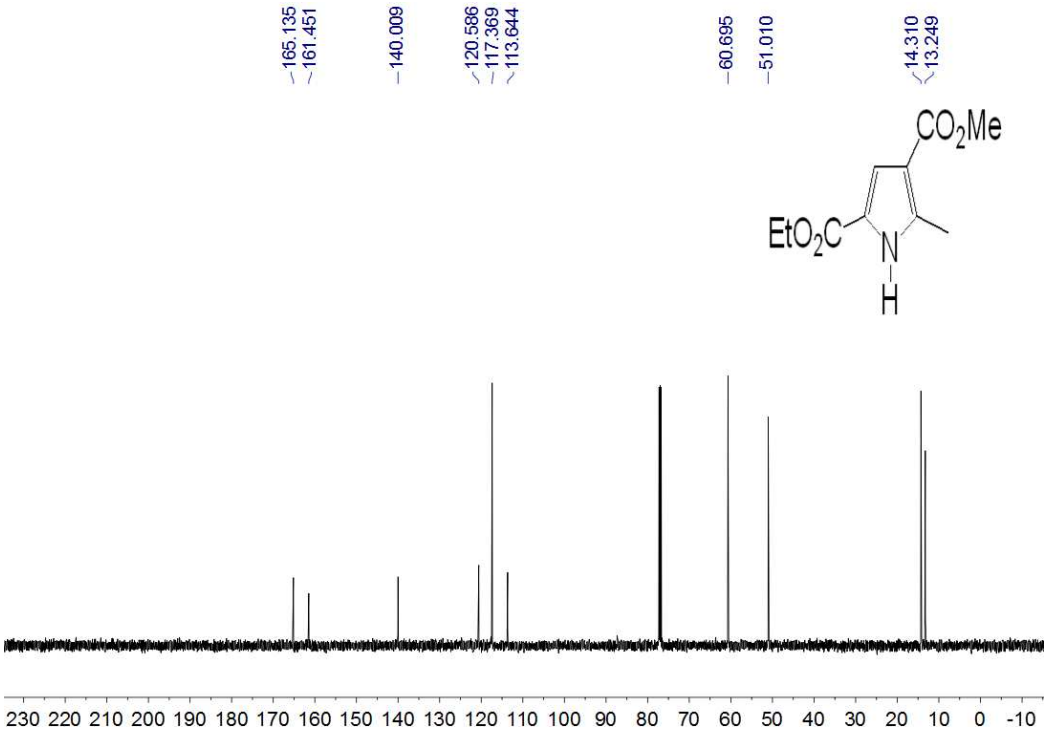
^{1}H and ^{13}C NMR Spectra for Compound 5b



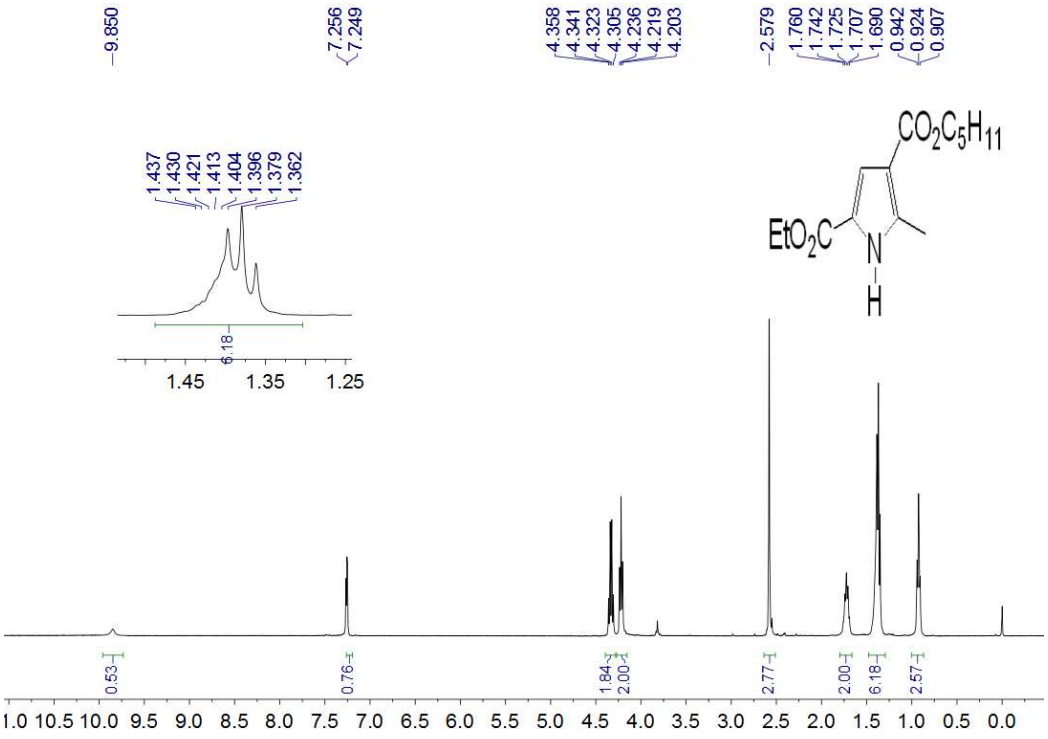


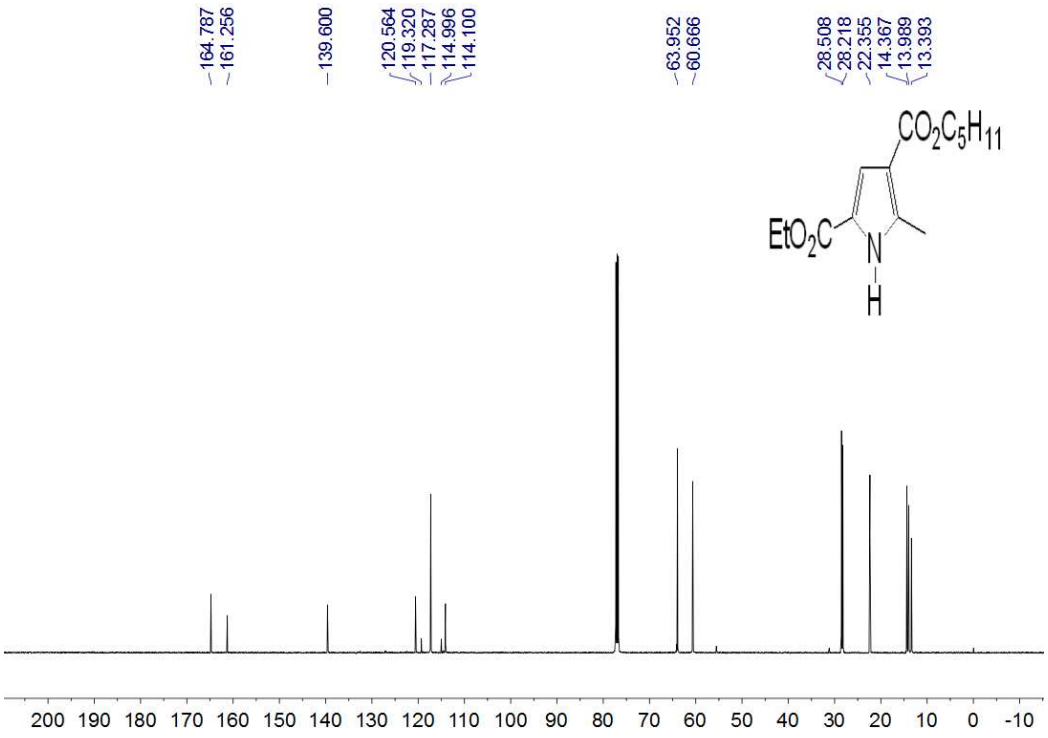
^{1}H and ^{13}C NMR Spectra for Compound 5c





^{1}H and ^{13}C NMR Spectra for Compound 5d





^{1}H and ^{13}C NMR Spectra for Compound 5e