

A straightforward one-pot multicomponent synthesis of polysubstituted pyrroles

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Supporting Information

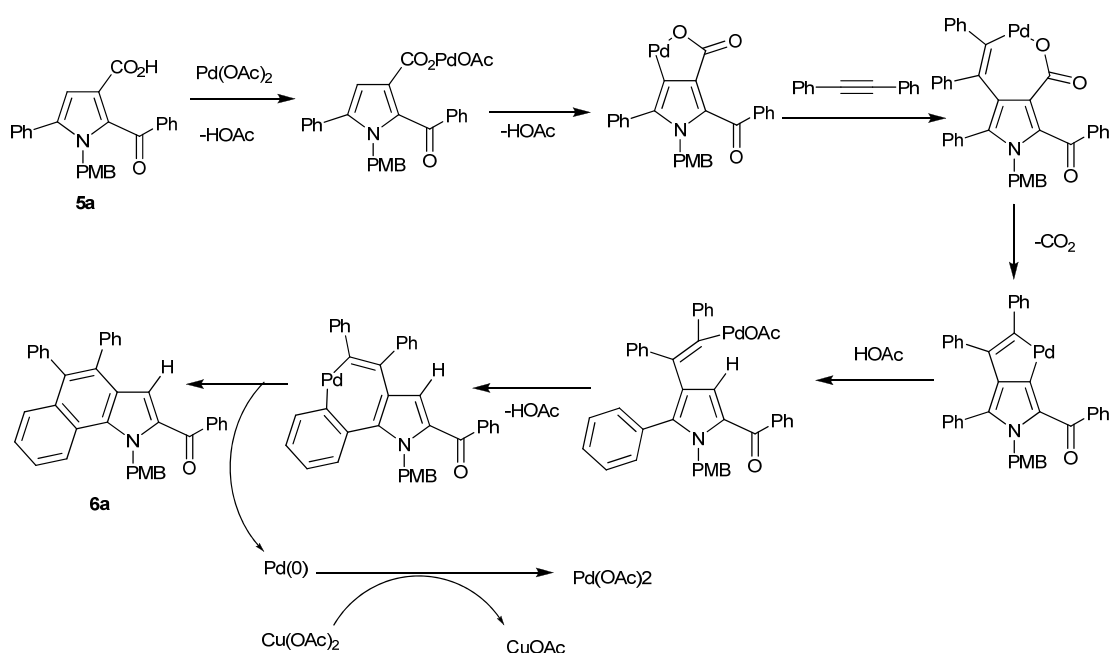
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General Considerations

IR spectra were recorded on a ATR spectrometer (neat) and reported in reciprocal centimeters (cm^{-1}). NMR spectra were recorded for ^1H NMR at 400 MHz and for ^{13}C NMR at 100 MHz. For ^1H NMR, tetramethylsilane (TMS) served as internal standard ($\delta = 0$) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constant in Hz. For ^{13}C NMR, CDCl_3 ($\delta = 77.00$) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS data were obtained using ESI ionization. HRMS data were obtained using EI ionization. Mp data were measured with micro melting point apparatus. Elemental Analyses were recorded on an automatic analyzer.

A proposed mechanism scheme for 6a



General procedure for the synthesis of **4**

A mixture of ethyl glyoxylate (1 mmol), primary amine (1 mmol) in CH₃CN (5 mL) was stirred at room temperature for 1 h. Subsequently, phenacyl bromide (2.2 mmol) and pyridine (5.0 mmol) were added to this mixture and refluxed for 12 h. After removal of the solvent in vacuum, the residue was then diluted with CH₂Cl₂ (50 mL), and washed with brine, dried over anhydrous Na₂SO₄, and evaporated in vacuum. The residue was subject to a flash chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford the corresponding product **4**.

Procedure for the synthesis of **5a**

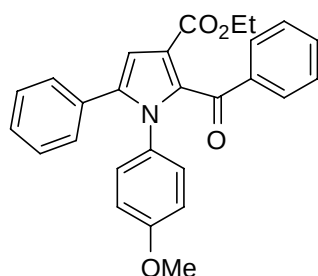
A 25-mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar is charged with 425 mg (1 mmol) of **4a** and 200 mg (5 mmol, 5 equiv) of sodium hydroxide, 5 mL methanol and 5 mL water. The mixture was refluxed for 2 h. After cooling to room temperature, the pH was then carefully adjusted to 2 using 2 M HCl, and the mixture is extracted with EtOAc (3 × 10 mL). The combined organic phases are washed with brine, then dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure on a rotary evaporator and drying under reduced pressure affords 390 mg (0.98 mmol, 98%) of **5a**, which can be directly used without further purification.

Procedure for the synthesis of **6a**

To a 10 mL two-necked flask were added **5a** (0.5 mmol, 198 mg), diphenylacetylene (0.6 mmol, 107 mg), Pd(OAc)₂ (0.025 mmol, 5.6 mg), Cu(OAc)₂ · H₂O (1.0 mmol, 200 mg), LiOAc (2.0 mmol, 132 mg) and 4Å MS (400 mg), and DMAc (3 mL) were added. The resulting mixture was stirred under N₂ at 120 °C for 12 h. After cooling, the reaction mixture was extracted with EtOAc (3 × 10 mL). Then, the organic layer was washed with brine (2 × 10 mL) and dried over Na₂SO₄. Product **6a** was isolated by column chromatography on silica gel using hexane-ethyl acetate.

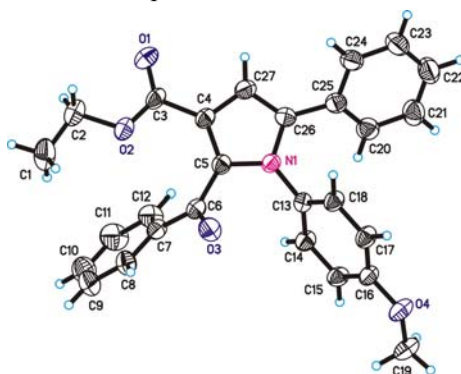
Characterization Data

Ethyl 2-benzoyl-1-(4-methoxyphenyl)-5-phenyl-1H-pyrrole-3-carboxylate (4a)

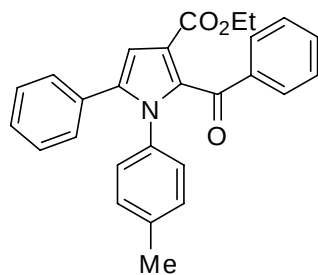


White solid, m.p.136–137 °C; IR (neat) ν 1689, 1649, 1507, 1470, 1235, 1082, 1030, 929, 833, 738, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, J = 7.6 Hz, 2 H), 7.53(t, J = 7.2 Hz, 1 H), 7.41 (t, J = 7.6 Hz, 2 H), 7.22 – 7.20 (m, 3 H), 7.15 – 7.13 (m, 2 H), 7.05 (d, J = 8.4 Hz, 2 H), 6.90 (s, 1 H), 6.72 (d, J = 8.0 Hz, 2 H), 3.95 (q, J = 7.2 Hz, 2 H), 3.73 (s, 3 H), 0.88 (t, J = 7.2 Hz, 3 H) ppm ; ^{13}C NMR (100 MHz, CDCl_3) δ 189.51, 163.84, 159.13, 138.62, 137.20, 135.69, 133.18, 131.19, 129.32, 129.09, 128.55, 128.37, 128.16, 127.35, 117.91 , 113.93, 110.18, 60.11, 55.23, 13.55 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 448; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{23}\text{NO}_4$): 425.1627; found: 425.1626.

The single-crystal X-ray Structure of compound **4a** is below.



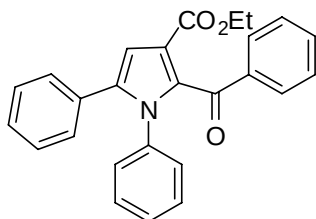
Ethyl 2-benzoyl-5-phenyl-1-p-tolyl-1H-pyrrole-3-carboxylate (4b)



White solid, m.p.125–126 °C; IR (neat) ν 1707, 1667, 1547, 1512, 1381, 1078, 1022, 927, 821, 757, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 7.2 Hz, 2 H), 7.47 – 7.45 (m, 1 H), 7.33

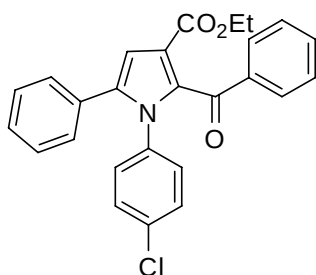
(t, $J = 7.6$ Hz, 2 H), 7.14 – 7.11 (m, 3 H), 7.07–7.04 (m, 2 H), 6.93 (s, 4 H), 6.83 (s, 1 H), 3.86 (q, $J = 7.2$ Hz, 2 H), 2.18 (s, 3 H), 0.79 (t, $J = 7.2$ Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 189.47, 163.85, 138.65, 138.31, 137.08, 134.85, 133.16, 131.20, 129.49, 128.55, 128.12, 127.66, 127.35, 118.06, 110.34, 60.12, 21.09, 13.54 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 432; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{23}\text{NO}_3$): 409.1678; found: 409.1685.

Ethyl 2-benzoyl-1,5-diphenyl-1H-pyrrole-3-carboxylate (4c)



White solid, m.p. 163–164 °C; IR (neat) ν 1700, 1661, 1496, 1471, 1227, 1074, 1021, 925, 761, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 7.6$ Hz, 2 H), 7.54 (t, $J = 7.2$ Hz, 1 H), 7.42 (t, $J = 7.2$ Hz, 2 H), 7.24 – 7.21 (m, 6 H), 7.14 – 7.02 (m, 4 H), 6.93 (s, 1 H), 3.96 (q, $J = 7.2$ Hz, 2 H), 0.89 (t, $J = 7.2$ Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 189.39, 163.83, 138.62, 137.49, 137.10, 135.46, 133.21, 131.12, 129.34, 128.87, 128.60, 128.41, 128.39, 128.16, 128.01, 127.44, 118.25, 110.50, 60.18, 13.58 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 418; HRMS (EI): m/z calcd for ($\text{C}_{26}\text{H}_{21}\text{NO}_3$): 395.1521; found: 395.1522.

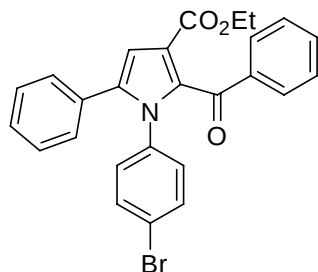
Ethyl 2-benzoyl-1-(4-chlorophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (4d)



Light yellow solid, m.p. 132–133 °C; IR (neat) ν 1708, 1656, 1491, 1464, 1224, 1070, 1016, 927, 830, 767, 679 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 7.6$ Hz, 2 H), 7.55 (t, $J = 7.6$ Hz, 1 H), 7.44 (t, $J = 8.0$ Hz, 2 H), 7.27 – 7.20 (m, 5 H), 7.14 – 7.07 (m, 4 H), 6.92 (s, 1 H), 3.95 (q, $J = 7.2$ Hz, 2 H), 0.88 (t, $J = 7.2$ Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 189.16, 163.71, 138.54, 137.59, 136.02, 135.25, 134.34, 133.40, 130.77, 129.31, 129.27, 129.15, 128.68, 128.51, 128.34, 127.71, 118.76, 110.74, 60.29, 13.54 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 452; HRMS (EI):

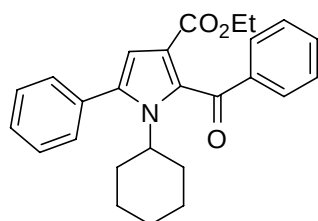
m/z calcd for ($C_{26}H_{20}ClNO_3$): 429.1132; found: 429.1137.

Ethyl 2-benzoyl-1-(4-bromophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (4e)



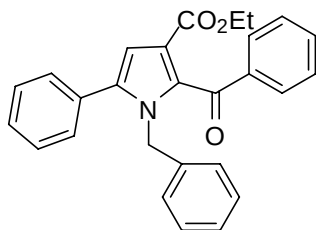
Light yellow solid, m.p.155–156 °C; IR (neat) ν 1690, 1647, 1470, 1239, 1066, 1011, 929, 830, 763, 724, 695 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.6 Hz, 2 H), 7.57 (t, J = 7.6 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 2 H), 7.27 – 7.24 (m, 3 H), 7.13 – 7.11 (m, 2 H), 7.02 (d, J = 8.4 Hz, 2 H), 6.92 (s, 1 H), 3.95 (q, J = 7.2 Hz, 2 H), 0.88 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.39, 163.83, 138.62, 137.49, 135.46, 133.21, 129.34, 128.87, 128.60, 128.41, 128.39, 128.15, 128.01, 127.44, 118.25, 110.50, 60.18, 13.58 ppm; MS (ESI): m/z ($[M+Na]^+$): 496; HRMS (EI): m/z calcd for ($C_{26}H_{20}BrNO_3$): 473.0627; found: 473.0636.

Ethyl 2-benzoyl-1-cyclohexyl-5-phenyl-1H-pyrrole-3-carboxylate (4f)



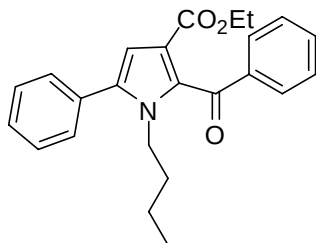
White solid, m.p.108–109 °C; IR (neat) ν 2924, 2850, 1695, 1660, 1450, 1365, 1249, 1219, 1176, 1072, 1032, 926, 758, 714, 692 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2 H), 7.56 (t, J = 7.2 Hz, 1 H), 7.47 – 7.42 (m, 7 H), 6.60 (s, 1 H), 4.05 – 3.97 (m, 1 H), 3.87 (q, J = 7.2 Hz, 2 H), 1.87 – 1.85 (m, 4 H), 1.68 – 1.62 (m, 2 H), 1.49 – 1.47 (m, 1 H), 1.08 – 0.96 (m, 3 H), 0.86 (t, J = 7.2 Hz, 3 H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.53, 163.90, 139.15, 137.06, 133.36, 133.13, 132.68, 129.93, 129.39, 128.43, 128.28, 118.05, 110.36, 59.90, 59.27, 33.67, 26.18, 24.81, 13.60 ppm; MS (ESI) : m/z ($[M+Na]^+$): 424; HRMS (EI): m/z calcd for ($C_{26}H_{27}NO_3$): 401.1991; found: 401.1977.

Ethyl 2-benzoyl-1-cyclohexyl-5-phenyl-1H-pyrrole-3-carboxylate (4g)



Light yellow liquid; IR (neat) ν 2980, 1707, 1644, 1452, 1248, 1210, 1175, 1075, 1029, 922, 761, 725, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, J = 8.0 Hz, 2 H), 7.37 – 7.31 (m, 6 H), 7.23 – 7.17 (m, 2 H), 6.93 – 6.98 (m, 3 H), 6.71 – 6.69 (m, 2 H), 6.65 (s, 1 H), 5.29 (s, 2 H), 3.68 (q, J = 7.2 Hz, 2 H), 0.70 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 189.34, 164.14, 139.10, 137.50, 132.99, 132.55, 131.32, 129.60, 129.11, 128.67, 128.51, 128.30, 127.99, 127.35, 126.52, 120.89, 110.85, 60.21, 48.96, 13.44 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 432; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{23}\text{NO}_3$): 409.1678; found: 409.1674.

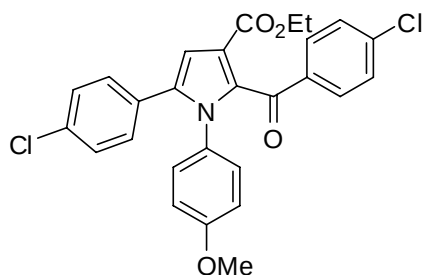
Ethyl 2-benzoyl-1-butyl-5-phenyl-1H-pyrrole-3-carboxylate (4h)



Light yellow liquid; IR (neat) ν 2960, 2931, 1708, 1644, 1464, 1421, 1238, 1208, 1180, 1064, 1031, 921, 763, 724, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 7.2 Hz, 2 H), 7.49 – 7.48 (m, 1 H), 7.40 – 7.33 (m, 7 H), 6.56 (s, 1 H), 4.05 (t, J = 7.2 Hz, 2 H), 3.72 (q, J = 7.2 Hz, 2 H), 1.32 – 1.29 (m, 2 H), 0.94 – 0.89 (m, 2 H), 0.74 (t, J = 7.2 Hz, 3 H), 0.54 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 189.57, 164.22, 139.38, 132.96, 132.46, 131.80, 129.59, 129.26, 128.61, 128.42, 128.35, 120.06, 110.74, 60.13, 45.25, 35.55, 19.37, 13.51, 13.28 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 330; HRMS (EI): m/z calcd for ($\text{C}_{24}\text{H}_{25}\text{NO}_3$): 329.1627; found: 329.1635.

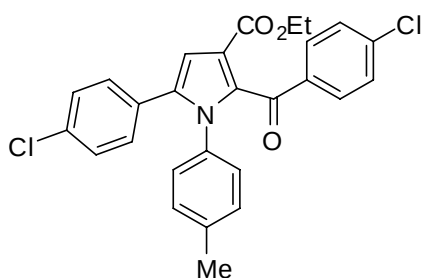
Ethyl

2-(4-chlorobenzoyl)-5-(4-chlorophenyl)-1-(4-methoxyphenyl)-1H-pyrrole-3-carboxylate (4i)



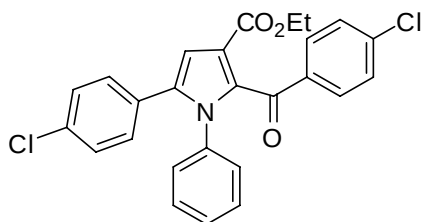
Light yellow solid, m.p.170–171 °C; IR(neat) ν 1706, 1662, 1583, 1471, 1425, 1396, 1224, 1080, 1011, 923, 834, 778, 758, 738, 688 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.0Hz, 2), 7.40 (d, J = 8.0Hz, 2), 7.20 (d, J = 8.0Hz, 2H), 7.05 (dd, J = 11.2, 8.4 Hz, 4 H), 6.90 (s, 1 H), 6.75 (d, J = 8.4 Hz, 2 H), 4.02 (q, J = 7.2 Hz, 2 H), 3.76 (s, 3 H), 0.97 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 188.20, 163.54, 159.40, 139.48, 136.85, 136.12, 135.57, 133.53, 130.65, 129.70, 129.56, 129.03, 128.80, 128.50, 117.97, 114.17, 110.41, 60.31, 55.31, 13.73 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 516; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{21}\text{Cl}_2\text{NO}_4$): 493.0848; found: 493.0847.

Ethyl 2-(4-chlorobenzoyl)-5-(4-chlorophenyl)-1-p-tolyl-1H-pyrrole-3-carboxylate (4j)



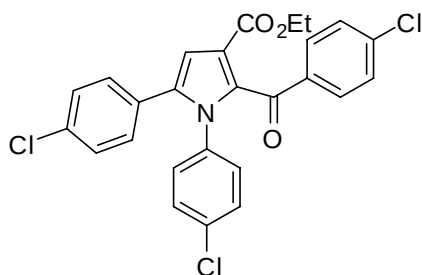
Light yellow solid, m.p.158–159 °C; IR (neat) ν 1715, 1677, 1543, 1513, 1468, 1437, 1215, 1084, 1012, 922, 828, 771, 734, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.07 – 7.04 (m, 4 H), 6.97 (d, J = 8.4 Hz, 2 H), 6.91 (s, 1 H), 4.02 (q, J = 7.2 Hz, 2 H), 2.30 (s, 3 H), 0.97(t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 188.12, 163.52, 139.74, 138.76, 136.87, 135.97, 134.46, 133.50, 130.64, 129.73, 129.70, 128.76, 128.46, 127.58, 118.10, 110.57, 60.30, 21.11, 13.71 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 500 ; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{21}\text{Cl}_2\text{NO}_3$): 477.0898; found: 477.0891.

Ethyl 2-(4-chlorobenzoyl)-5-(4-chlorophenyl)-1-phenyl-1H-pyrrole-3-carboxylate (4k)



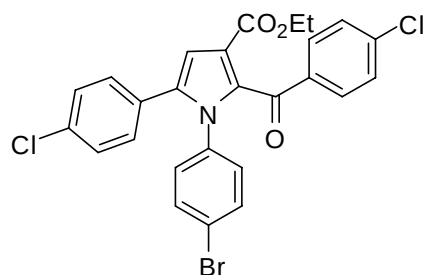
Light yellow solid, m.p.132–133 °C; IR (neat) ν 1711, 1669, 1587, 1463, 1375, 1139, 1209, 1087, 1011, 927, 828, 775, 753, 691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.6 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H), 7.27 – 7.22 (m, 3 H), 7.16 (d, J = 8.8 Hz, 2 H), 7.08 (d, J = 7.6 Hz, 2 H), 7.01 (d, J = 8.0 Hz, 2 H), 6.90 (s, 1 H), 4.00 (q, J = 7.2 Hz, 2 H), 0.95 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 188.05, 163.50, 139.80, 137.07, 136.80, 135.97, 135.31, 133.59, 130.63, 129.71, 129.44, 129.12, 128.80, 128.75, 128.49, 127.87, 118.27, 110.71, 60.37, 13.72 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 464; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{21}\text{Cl}_2\text{NO}_3$): 463.0742; found: 463.0750.

Ethyl 2-(4-chlorobenzoyl)-1,5-bis(4-chlorophenyl)-1H-pyrrole-3-carboxylate (4l)



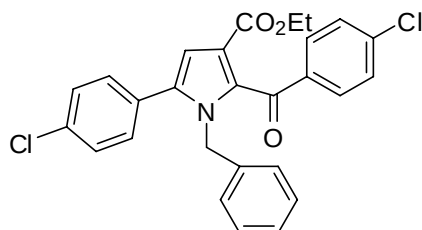
Light yellow solid, m.p.151–152 °C; IR (neat) ν 1714, 1674, 1584, 1490, 1469, 1377, 1216, 1087, 1012, 922, 832, 773, 741, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 7.22 (dd, J = 15.6, 8.0 Hz, 4 H), 7.04 – 7.01 (m, 4 H), 6.88 (s, 1 H), 3.99 (q, J = 6.8 Hz, 2 H), 0.94 (t, J = 6.8 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 187.80, 163.36, 140.02, 136.77, 136.19, 135.62, 135.15, 134.76, 133.93, 130.61, 129.81, 129.18, 129.12, 128.68, 118.79, 110.96, 60.47, 13.70 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 520; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{18}\text{Cl}_3\text{NO}_3$): 497.0352; found: 497.0349.

Ethyl 1-(4-bromophenyl)-2-(4-chlorobenzoyl)-5-(4-chlorophenyl)-1H-pyrrole-3-carboxylate (4m)



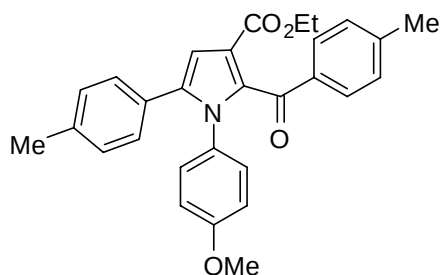
Light yellow solid, m.p.156–157 °C; IR (neat) ν 1715, 1675, 1584, 1488, 1468, 1214, 1084, 1011, 922, 830, 772, 735, 689 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.8 Hz, 2 H), 7.39 (dd, J = 8.4, 7.2 Hz, 4 H), 7.21 (d, J = 7.2 Hz, 2 H), 7.02 (d, J = 7.6 Hz, 2 H), 6.97 (d, J = 8.4 Hz, 2 H), 6.89 (s, 1 H), 3.99 (q, J = 6.8 Hz, 2 H), 0.94 (t, J = 6.8 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 187.75, 163.35, 140.04, 136.81, 136.18, 135.14, 133.98, 132.38, 130.62, 129.83, 129.49, 129.14, 128.91, 128.71, 122.86, 118.87, 111.02, 60.47, 13.71 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 542; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{18}\text{BrCl}_2\text{NO}_3$): 540.9847; found: 540.9854.

Ethyl 1-benzyl-2-(4-chlorobenzoyl)-5-(4-chlorophenyl)-1H-pyrrole-3-carboxylate (4n)



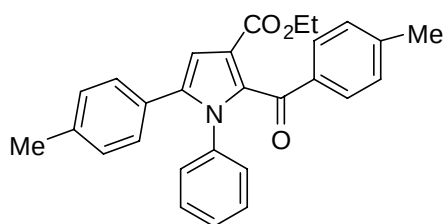
Light yellow solid, m.p.133–134 °C; IR (neat) ν 2975, 1701, 1646, 1584, 1450, 1382, 1255, 1215, 1166, 1087, 921, 835, 777, 753, 723, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.56 (d, J = 8.0, 2 H), 7.37 (dd, J = 20.8, 8.4, 4 H), 7.27 (d, J = 8.4, 2 H), 7.07 – 7.05 (m, 3 H), 6.76 (d, J = 7.2, 2 H), 6.72 (s, 1 H), 5.30 (s, 2 H), 3.85 (q, J = 7.2, 2 H), 0.87 (t, J = 7.2, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 188.09, 163.68, 139.06, 137.86, 137.18, 137.16, 134.81, 133.00, 130.82, 130.42, 129.62, 129.02, 128.47, 128.33, 127.63, 126.48, 120.89, 111.12, 60.36, 48.99, 13.60 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 478; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{21}\text{Cl}_2\text{NO}_3$): 477.0898; found: 477.0896.

Ethyl 1-(4-methoxyphenyl)-2-(4-methylbenzoyl)-5-p-tolyl-1H-pyrrole-3-carboxylate (4o)



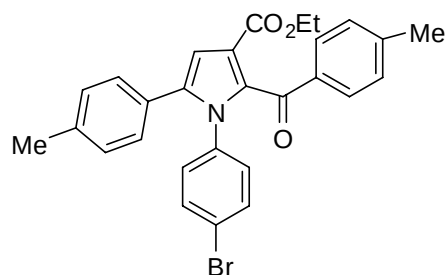
Yellow solid, m.p. 124–125 °C; IR (neat) ν 1707, 1661, 1604, 1510, 1214, 1077, 1024, 923, 831, 758, 722 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, J = 8.0 Hz, 2 H), 7.21 (d, J = 7.6 Hz, 2 H), 7.07 – 7.03 (m, 6 H), 6.86 (s, 1 H), 6.72 (d, J = 8.4 Hz, 2 H), 3.98 (q, J = 7.6 Hz, 2 H), 3.73 (s, 3 H), 2.40 (s, 3 H), 2.29 (s, 3 H), 0.91 (t, J = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 189.33, 163.96, 159.07, 144.09, 137.12, 137.09, 136.23, 135.88, 130.38, 129.52, 129.11, 129.09, 128.90, 128.43, 117.50, 113.91, 109.71, 60.06, 55.24, 21.71, 21.12, 13.64 ppm; MS (ESI): m/z ($[\text{M}+\text{Na}]^+$): 476; HRMS (ESI): m/z calcd for ($\text{C}_{29}\text{H}_{27}\text{NO}_4$): 453.1940; found: 453.1939.

Ethyl 2-(4-methylbenzoyl)-1-phenyl-5-p-tolyl-1H-pyrrole-3-carboxylate (4p)



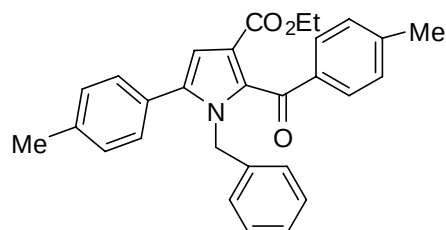
Light yellow solid, m.p. 129–130 °C; IR (neat) ν 1704, 1663, 1602, 1383, 1228, 1208, 1080, 1019, 928, 812, 772, 753, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, J = 8.0 Hz, 2 H), 7.25 – 7.20 (m, 5 H), 7.14 – 7.11 (m, 2 H), 7.03 – 6.99 (m, 4 H), 6.88 (s, 1 H), 3.98 (q, J = 6.8 Hz, 2 H), 2.40 (s, 3 H), 2.29 (s, 3 H), 0.92 (t, J = 6.8 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 189.20, 163.95, 144.13, 137.63, 137.24, 136.97, 136.22, 135.66, 129.53, 129.11, 128.89, 128.83, 128.46, 128.30, 128.03, 117.83, 110.02, 60.12, 21.72, 21.13, 13.65 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 424; HRMS (EI): m/z calcd for ($\text{C}_{28}\text{H}_{25}\text{NO}_3$): 423.1834; found: 423.1849.

Ethyl 1-(4-bromophenyl)-2-(4-methylbenzoyl)-5-p-tolyl-1H-pyrrole-3-carboxylate (4q)



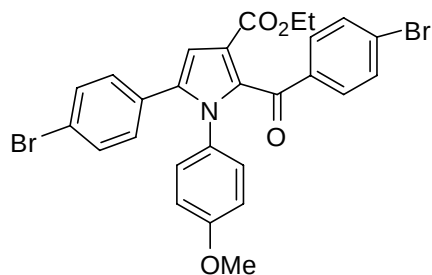
Light yellow solid, m.p. 129–130 °C; IR (neat) ν 1706, 1605, 1487, 1266, 1228, 1176, 1073, 1012, 924, 823, 733 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.04 – 6.97 (m, 6 H), 6.85 (s, 1 H), 3.95 (q, J = 7.2 Hz, 2 H), 2.39 (s, 3 H), 2.29 (s, 3 H), 0.89 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 188.93, 163.79, 144.37, 137.56, 137.11, 136.70, 136.15, 135.41, 132.06, 129.58, 129.50, 129.21, 129.06, 128.55, 127.94, 122.32, 118.34, 110.29, 60.20, 21.73, 21.13, 13.60 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 502; HRMS (EI): m/z calcd for ($\text{C}_{28}\text{H}_{24}\text{BrNO}_3$): 501.0940; found: 501.0932.

Ethyl 1-benzyl-2-(4-methylbenzoyl)-5-p-tolyl-1H-pyrrole-3-carboxylate (4r)



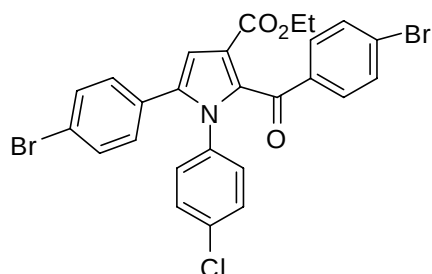
Light yellow liquid; IR (neat) ν 1706, 1645, 1604, 1455, 1378, 1249, 1209, 1177, 1080, 1030, 922, 819, 775, 750, 727, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 7.21 (d, J = 7.6 Hz, 2 H), 7.15 – 7.04 (m, 5 H), 6.78 (d, J = 7.2 Hz, 2 H), 6.70 (s, 1 H), 5.35 (s, 2 H), 3.80 (q, J = 7.2 Hz, 2 H), 2.38 (s, 3 H), 2.34 (s, 3 H), 0.82 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 189.06, 164.25, 143.32, 138.93, 138.41, 137.62, 136.54, 133.13, 129.48, 129.33, 129.30, 128.69, 128.44, 128.25, 127.23, 126.45, 120.51, 110.53, 60.12, 48.84, 21.57, 21.20, 13.47 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 438; HRMS (EI): m/z calcd for ($\text{C}_{29}\text{H}_{27}\text{NO}_3$): 437.1991; found: 437.2000.

Ethyl (4-bromobenzoyl)-5-(4-bromophenyl)-1-(4-methoxyphenyl)-1H-pyrrole-3-carboxylate (4s)



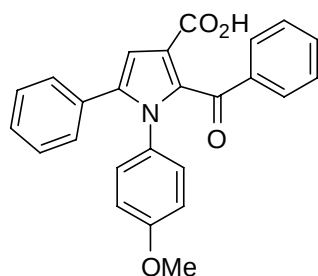
Light yellow solid, m.p. 172–173 °C; IR (neat) ν 1716, 1678, 1583, 1511, 1438, 1252, 1213, 1079, 1008, 921, 829, 769, 727, 685 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.33 (d, J = 8.8 Hz, 2 H), 6.99 (dd, J = 13.2, 8.8 Hz, 4 H), 6.88 (s, 1 H), 6.73 (d, J = 8.4 Hz, 2 H), 4.00 (q, J = 7.2 Hz, 2 H), 3.73 (s, 3 H), 0.95 (t, J = 7.2 Hz, 3 H).ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 188.37, 163.50, 159.39, 137.22, 136.12, 135.54, 131.78, 131.44, 130.73, 130.00, 129.95, 129.70, 129.01, 128.60, 121.74, 118.02, 114.18, 110.41, 60.33, 55.32, 13.73 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 582; HRMS (EI): m/z calcd for ($\text{C}_{27}\text{H}_{21}\text{Br}_2\text{NO}_4$): 580.9837; found: 580.9840.

Ethyl 2-(4-bromobenzoyl)-5-(4-bromophenyl)-1-(4-chlorophenyl)-1H-pyrrole-3-carboxylate (4t)



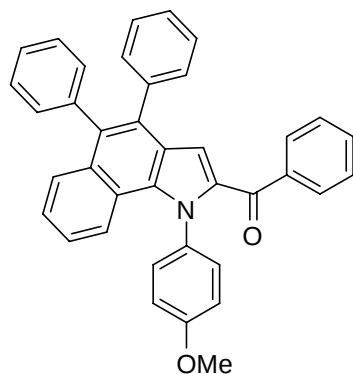
Light yellow solid, m.p. 153–154 °C; IR (neat) ν 1708, 1664, 1549, 1491, 1468, 1266, 1224, 1078, 1009, 924, 830, 776, 732, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 8.8 Hz, 2 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.23 (d, J = 8.4 Hz, 2 H), 7.04 (d, J = 8.4 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 6.90 (s, 1 H), 4.00 (q, J = 7.2 Hz, 2 H), 0.95 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 187.97, 163.32, 137.16, 136.21, 135.59, 135.14, 134.79, 131.89, 131.63, 130.69, 130.05, 129.57, 129.41, 129.16, 128.83, 122.14, 118.85, 110.98, 60.48, 13.70 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 586; HRMS (EI): m/z calcd for ($\text{C}_{26}\text{H}_{18}\text{Br}_2\text{ClNO}_3$): 584.9342; found: 584.9344.

2-Benzoyl-1-(4-methoxyphenyl)-5-phenyl-1H-pyrrole-3-carboxylic acid (5a)



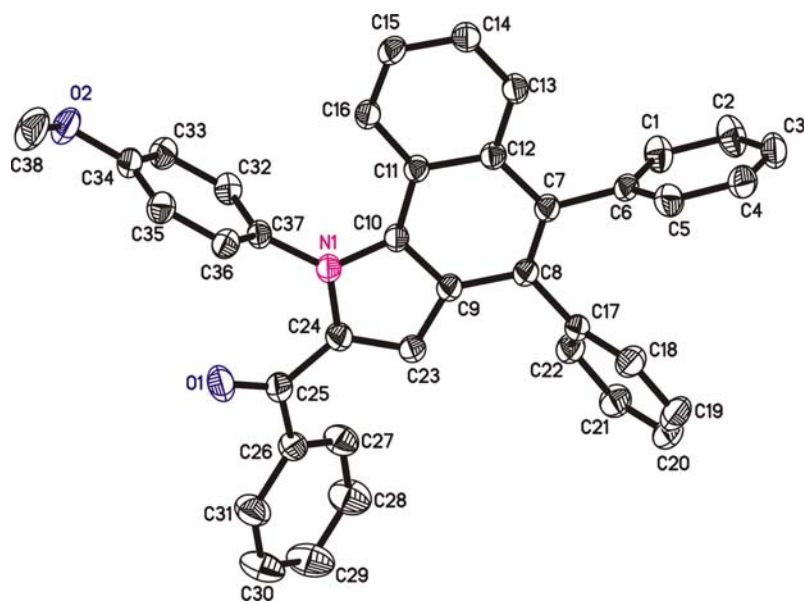
White solid; m.p. 205–206 °C; IR (neat) ν 1676, 1596, 1509, 1475, 1283, 1249, 1172, 1030, 914, 760, 732, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, J = 8.0 Hz, 2 H), 7.46 (t, J = 7.5 Hz, 1 H), 7.33 (t, J = 8.0 Hz, 2 H), 7.20 – 7.18 (m, 3 H), 7.11 – 7.09 (m, 2 H), 6.97 (d, J = 8.0 Hz, 2 H), 6.89 (s, 1 H), 6.85 (d, J = 9.0 Hz, 2 H), 3.68 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 190.17, 168.30, 159.16, 137.88, 137.11, 136.83, 133.32, 130.99, 129.92, 129.34, 129.05, 128.56, 128.27, 128.19, 127.48, 116.91, 113.96, 110.92, 55.26 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 398; HRMS (EI): m/z calcd for ($\text{C}_{25}\text{H}_{19}\text{NO}_4$): 397.1314; found: 397.1323.

(1-(4-Methoxyphenyl)-4,5-diphenyl-1H-benzo[*g*]indol-2-yl)(phenyl)methanone (6a)

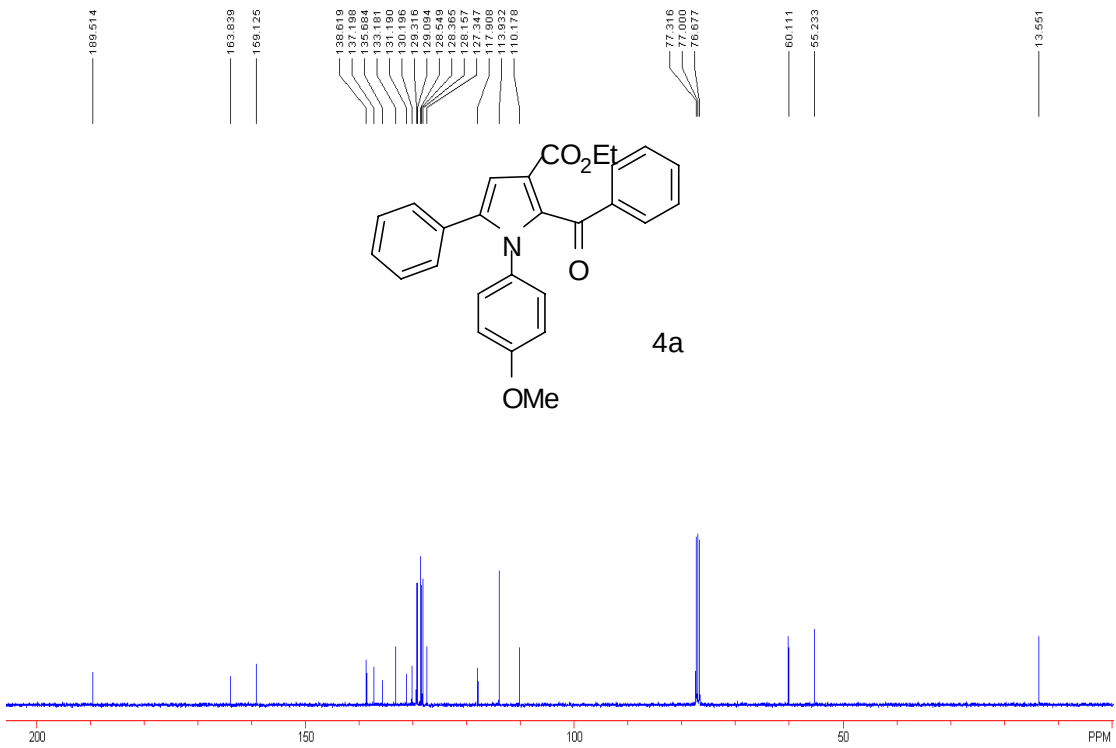
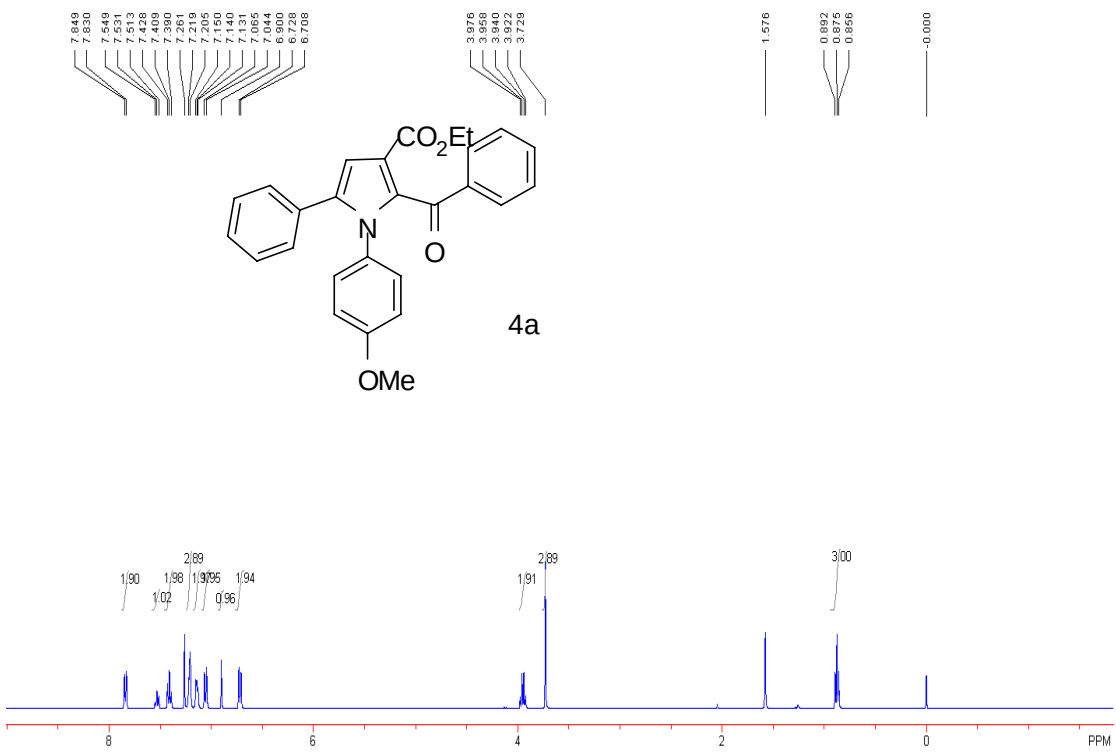


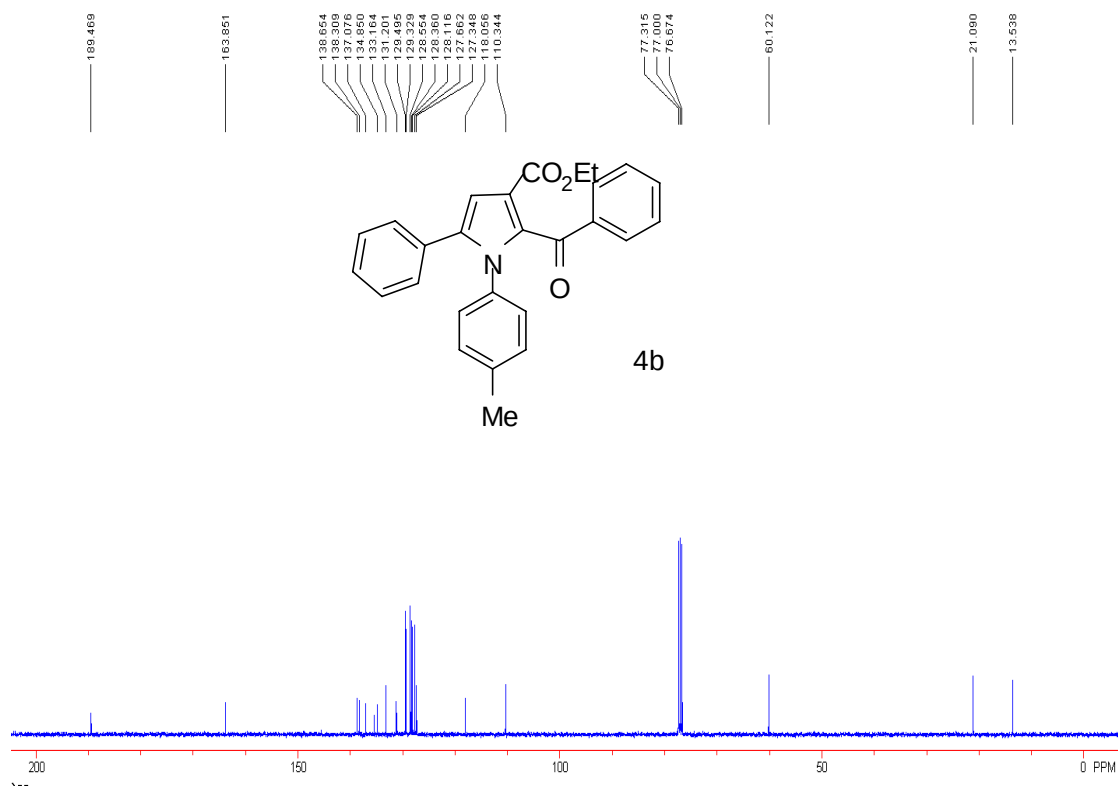
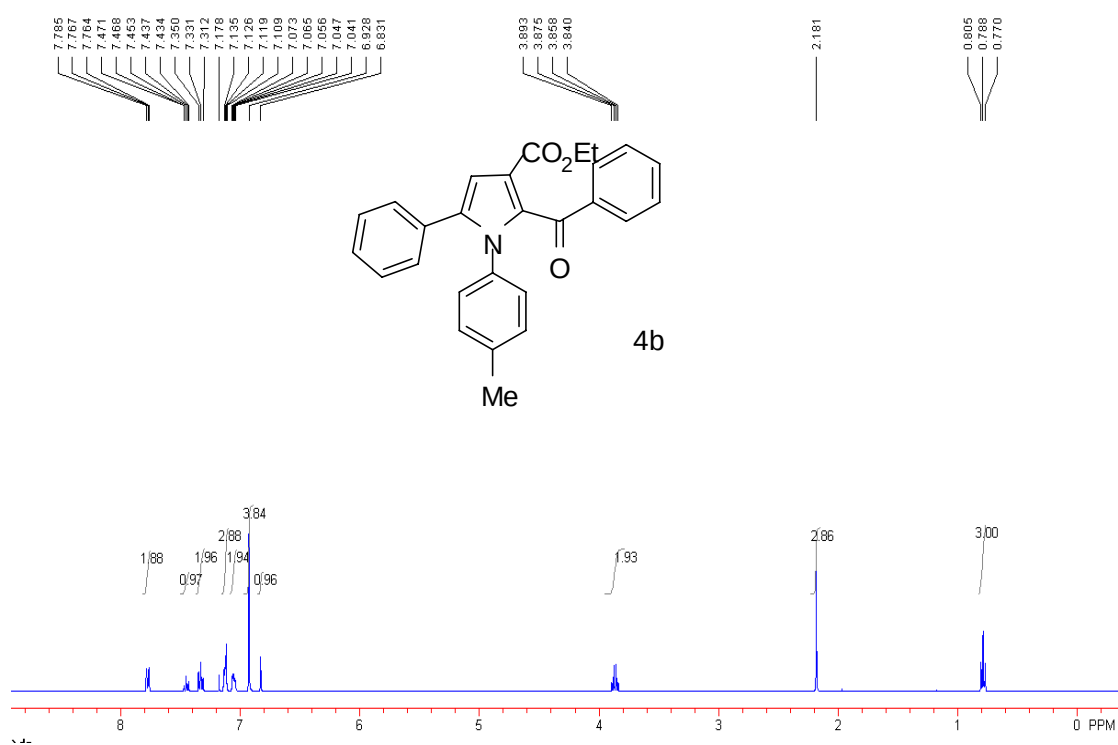
Off-white solid; m.p. 245–246 °C; IR (neat) ν 1641, 1598, 1578, 1512, 1248, 1217, 1176, 1036, 911, 828, 760, 733, 699 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.86 – 7.84 (m, 2 H), 7.38 (d, J = 8.5 Hz, 1 H), 7.52 – 7.48 (m, 3 H), 7.41 – 7.36 (m, 3 H), 7.29 – 7.27 (m, 1 H), 7.26 – 7.18 (m, 10 H), 7.15 – 7.09 (m, 3 H), 6.96 (s, 1 H), 3.93 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 186.54, 159.73, 139.39, 139.03, 138.98, 135.55, 134.82, 133.53, 133.27, 132.58, 132.18, 131.73, 130.42, 129.80, 129.79, 128.34, 128.13, 127.65, 127.59, 126.48, 125.48, 125.23, 123.80, 122.28, 121.90, 115.93, 114.55, 55.49 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 530; HRMS (EI): m/z calcd for ($\text{C}_{38}\text{H}_{27}\text{NO}_2$): 529.2042; found: 529.2045.

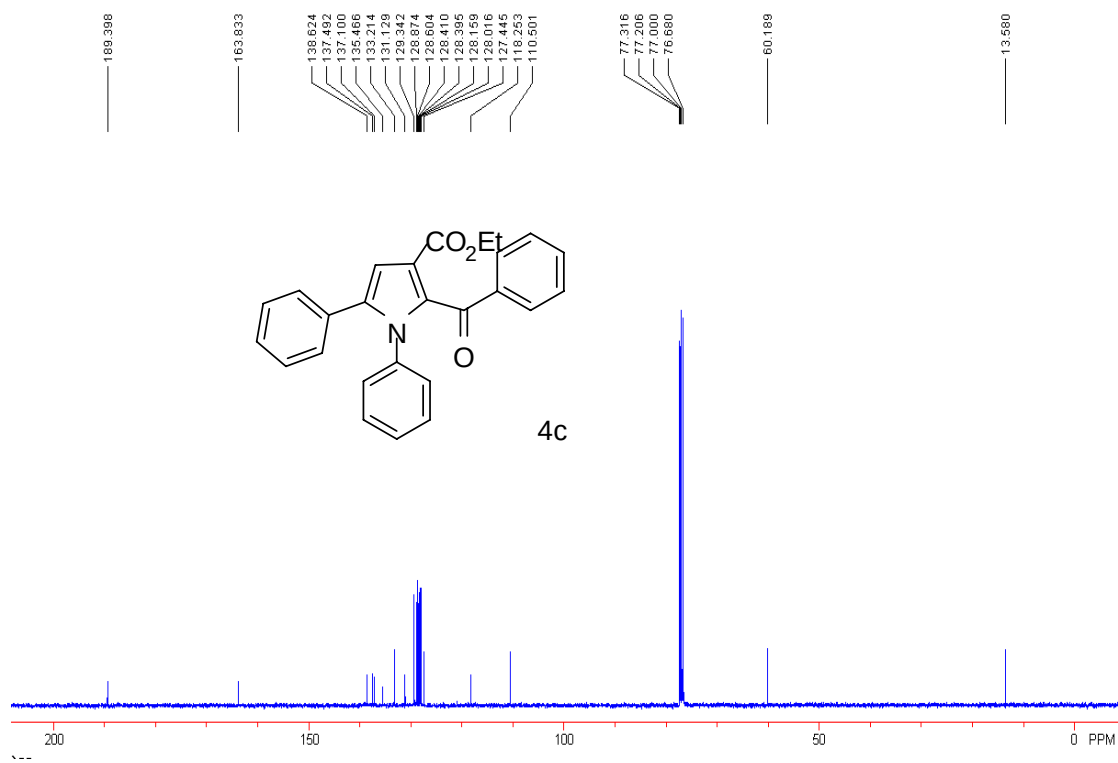
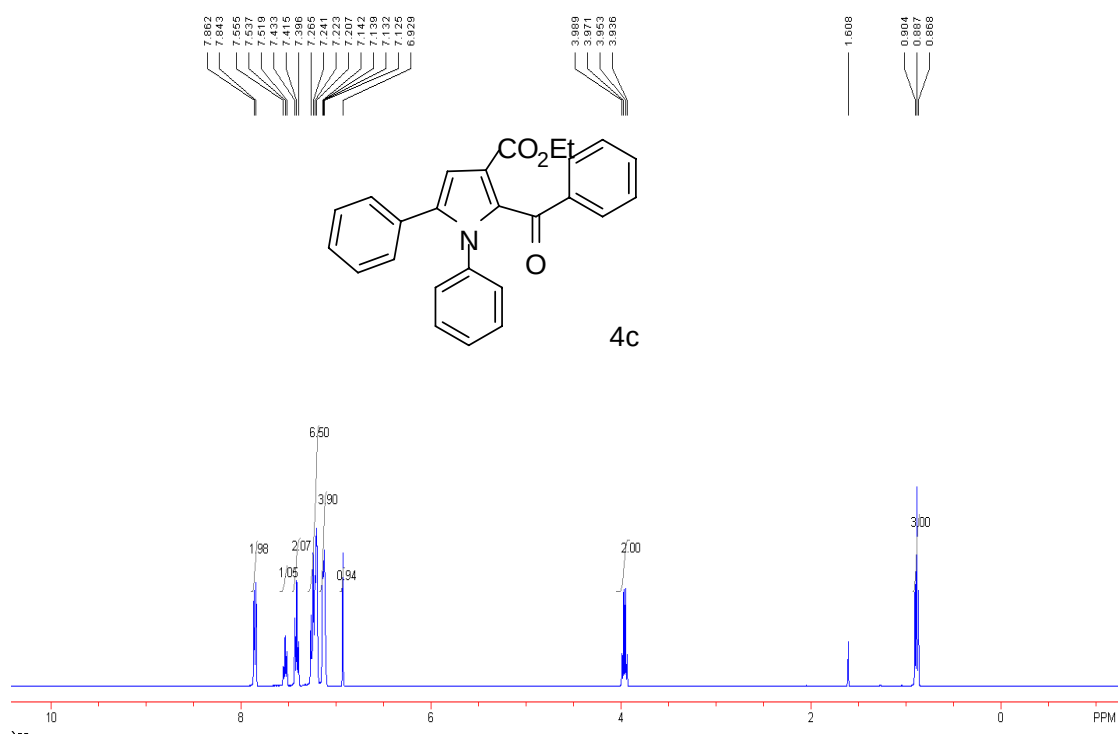
The single-crystal X-ray Structure of compound **6a** is below.

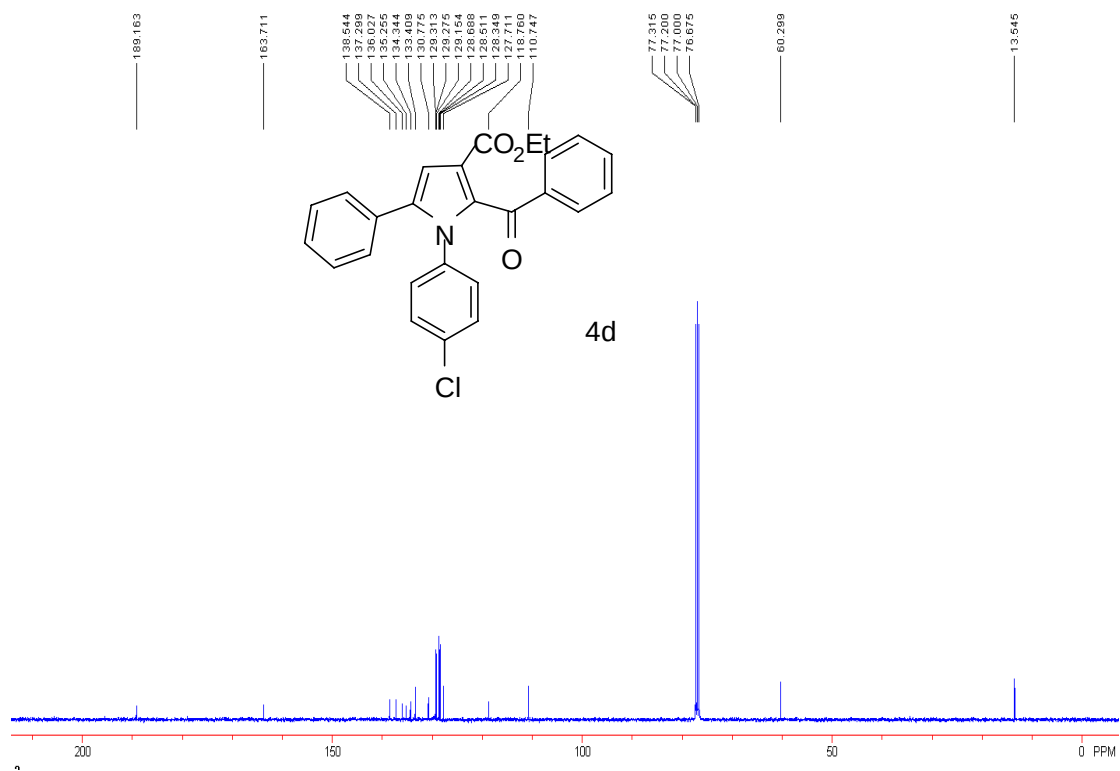
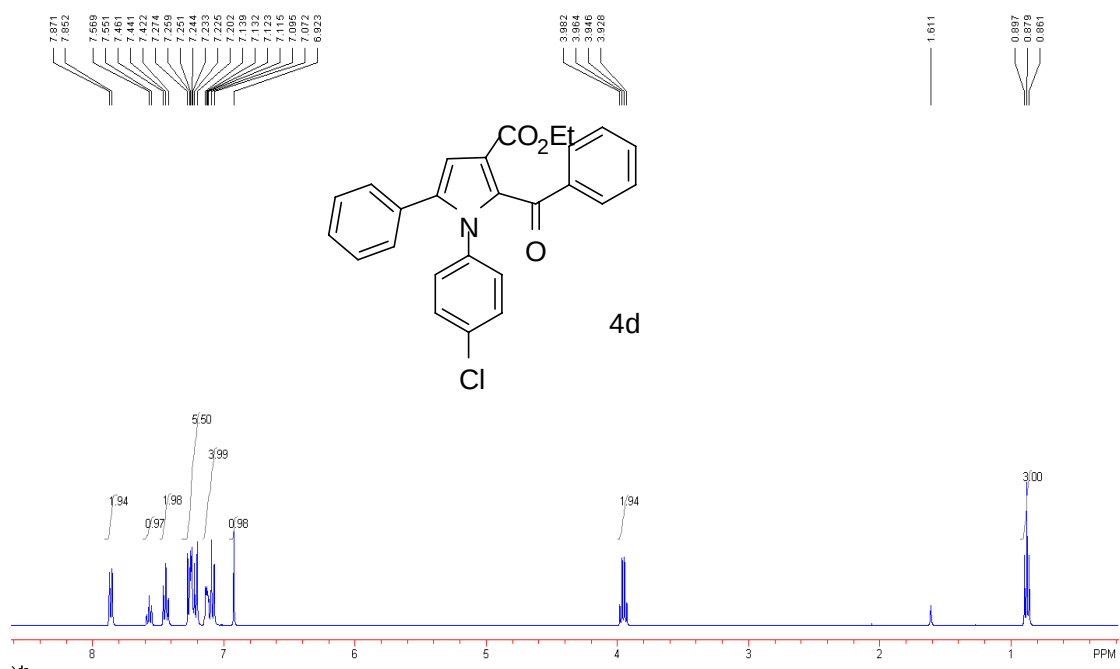


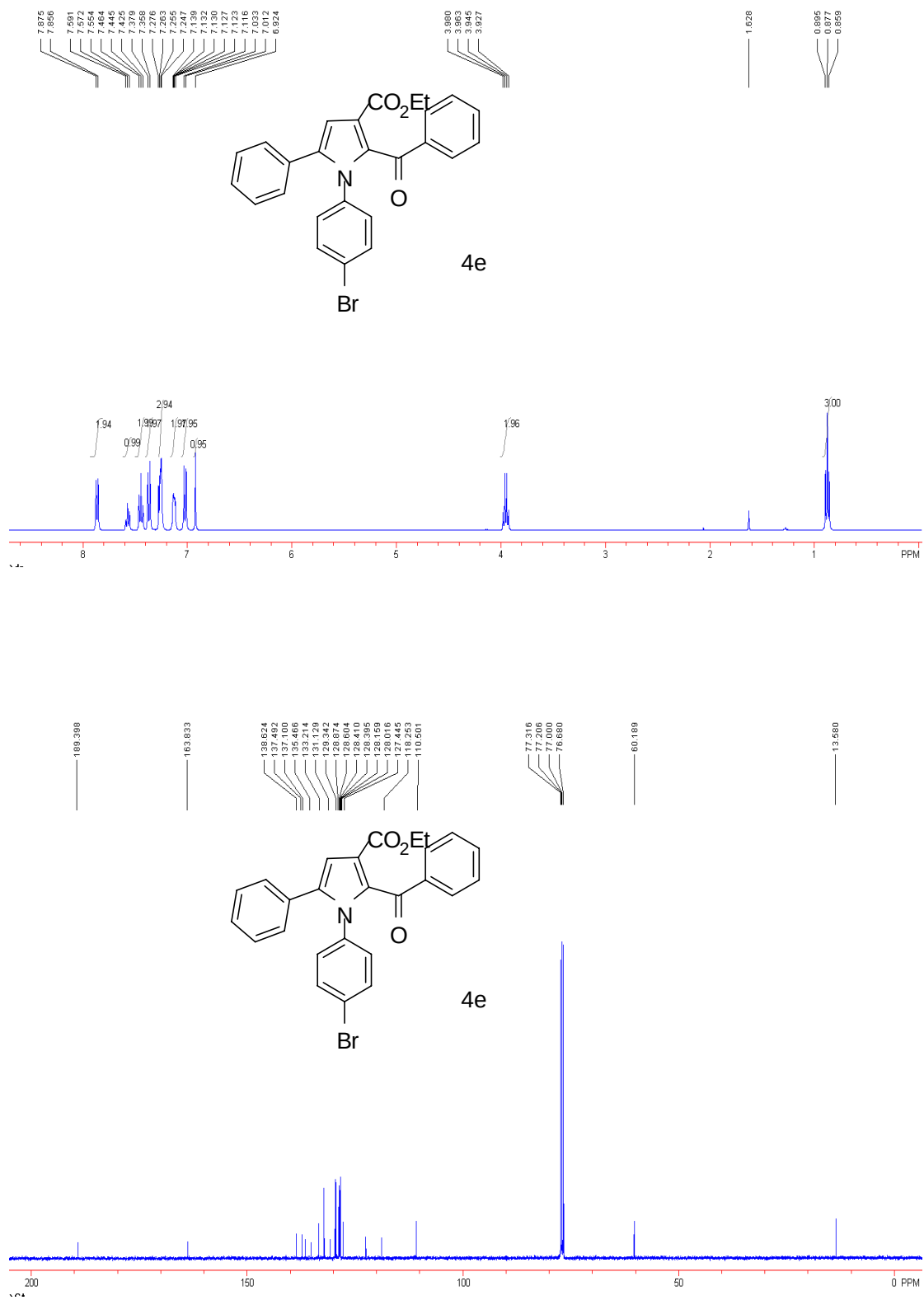
Copies of ¹H NMR and ¹³C NMR

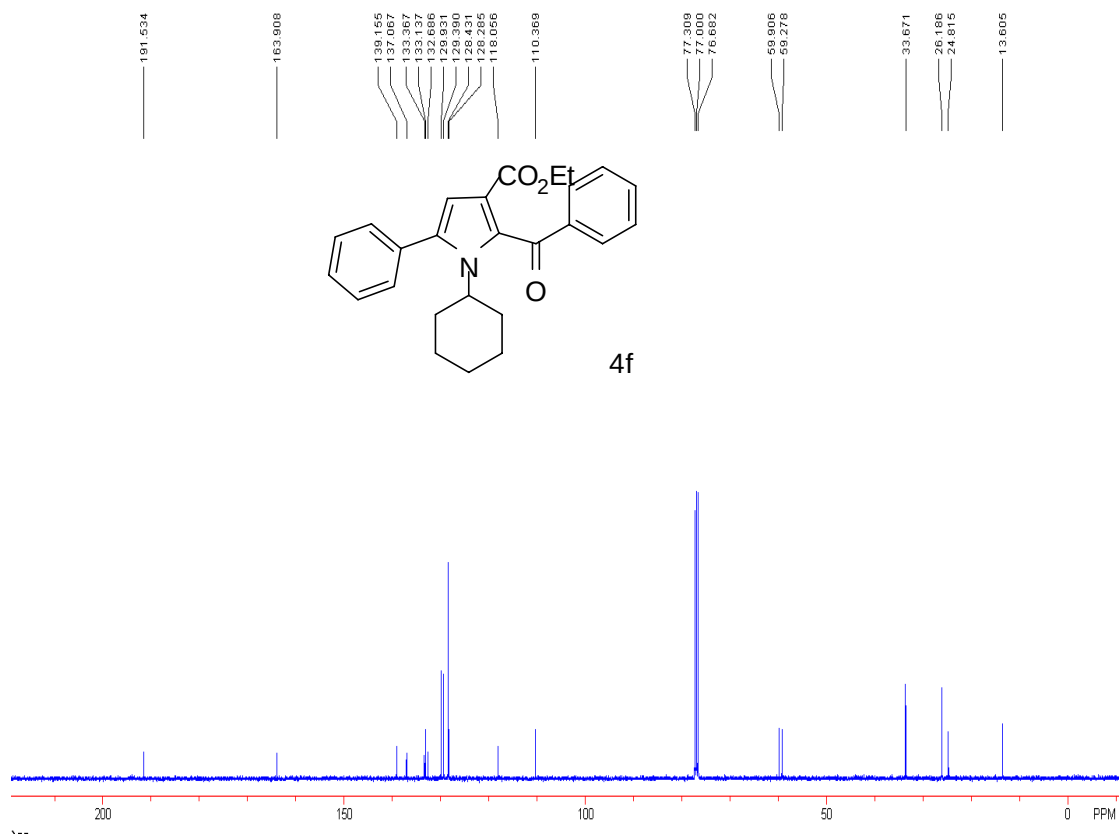
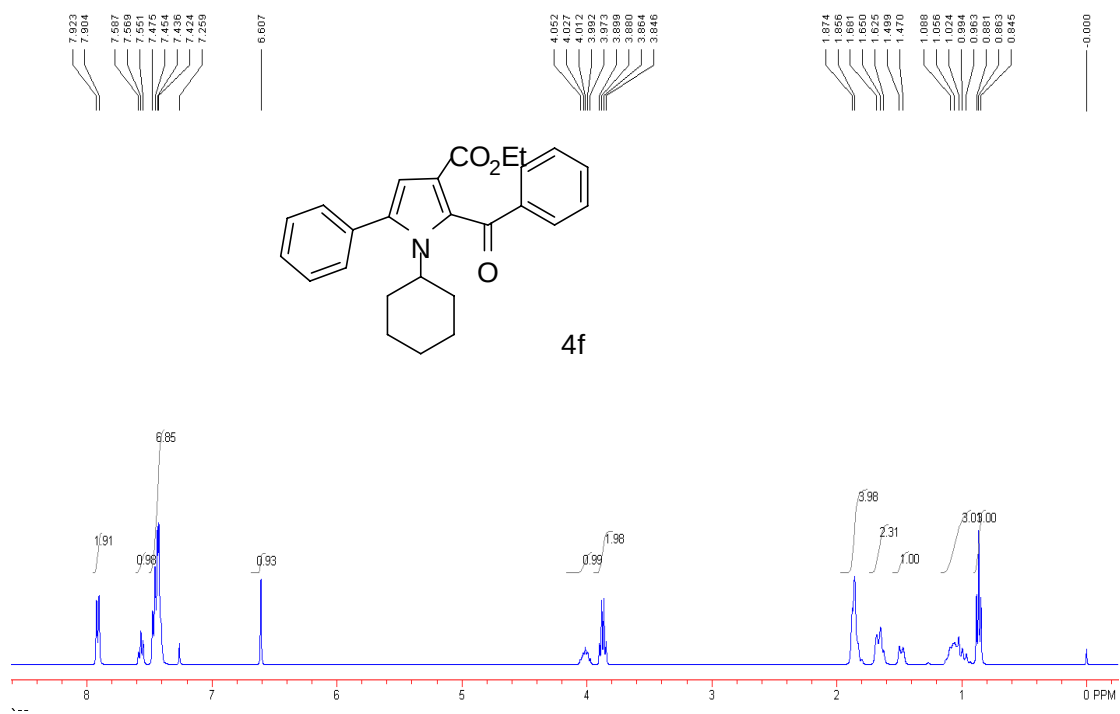


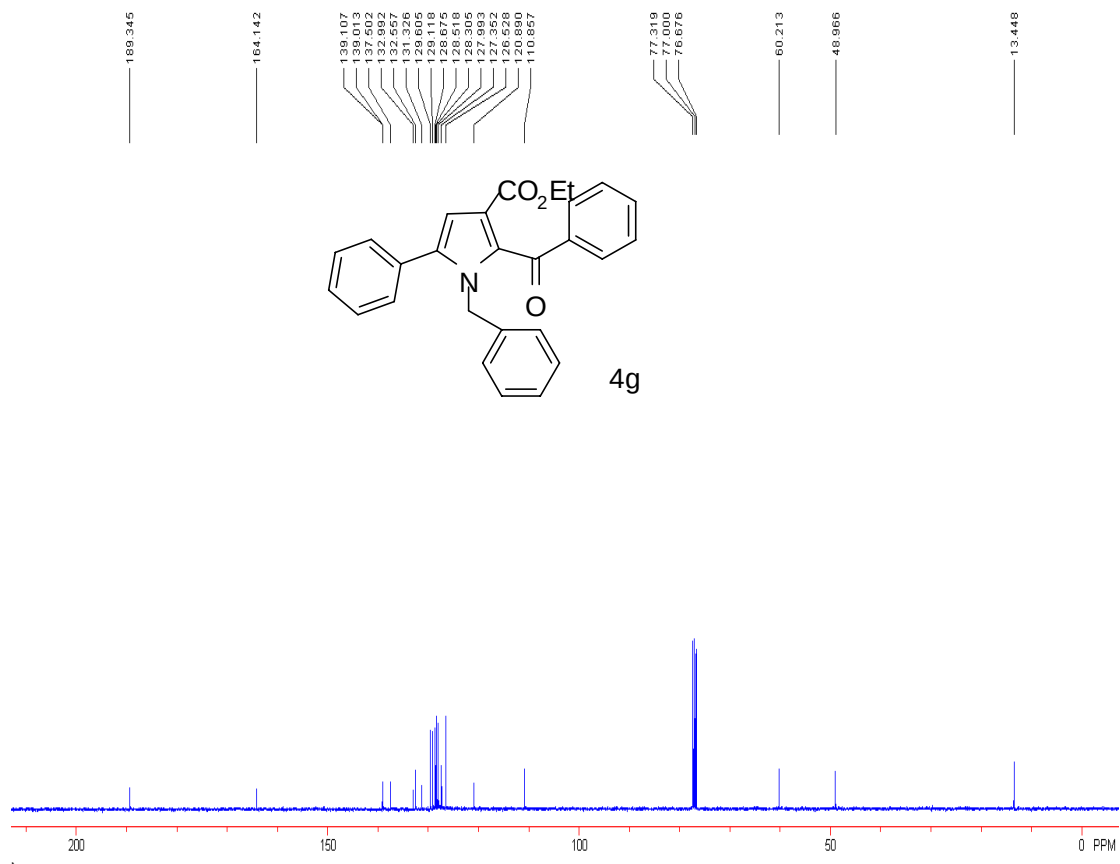
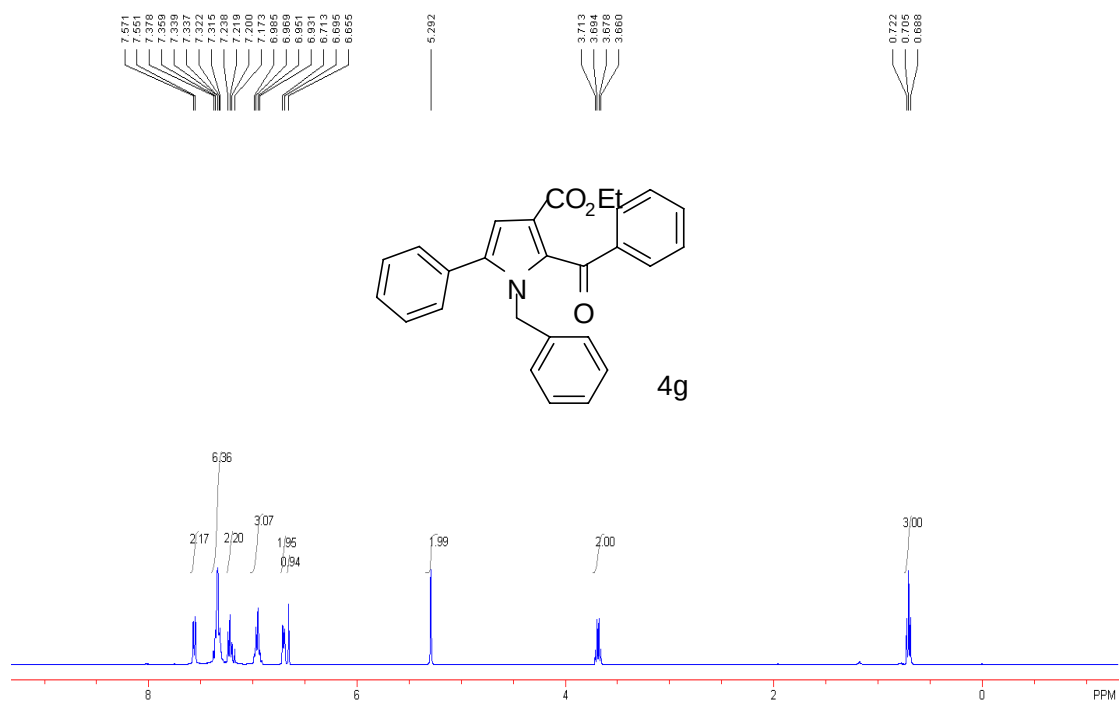


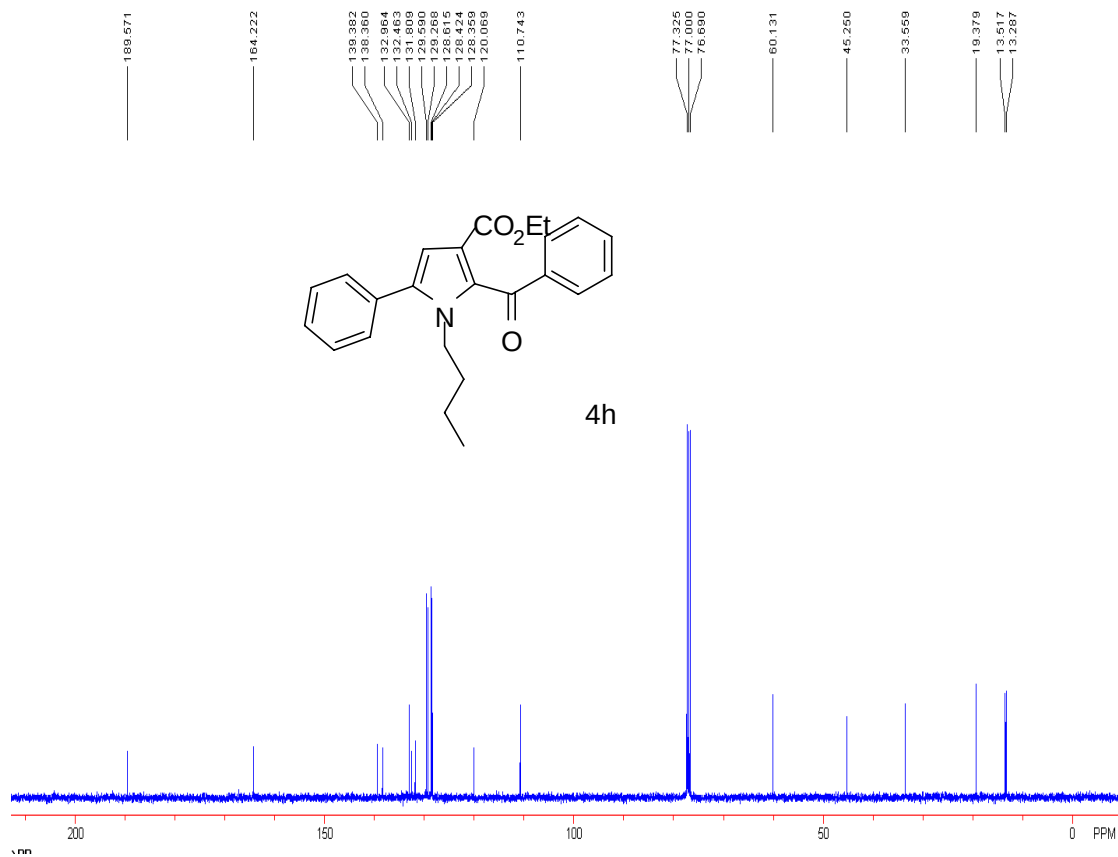
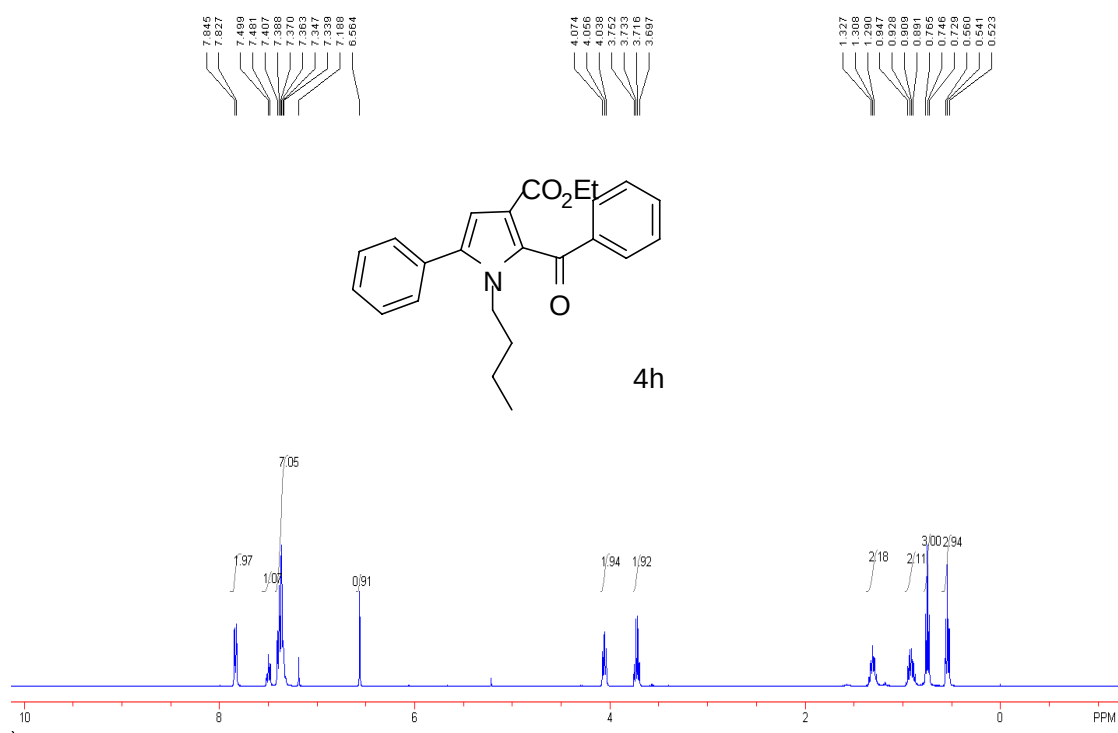


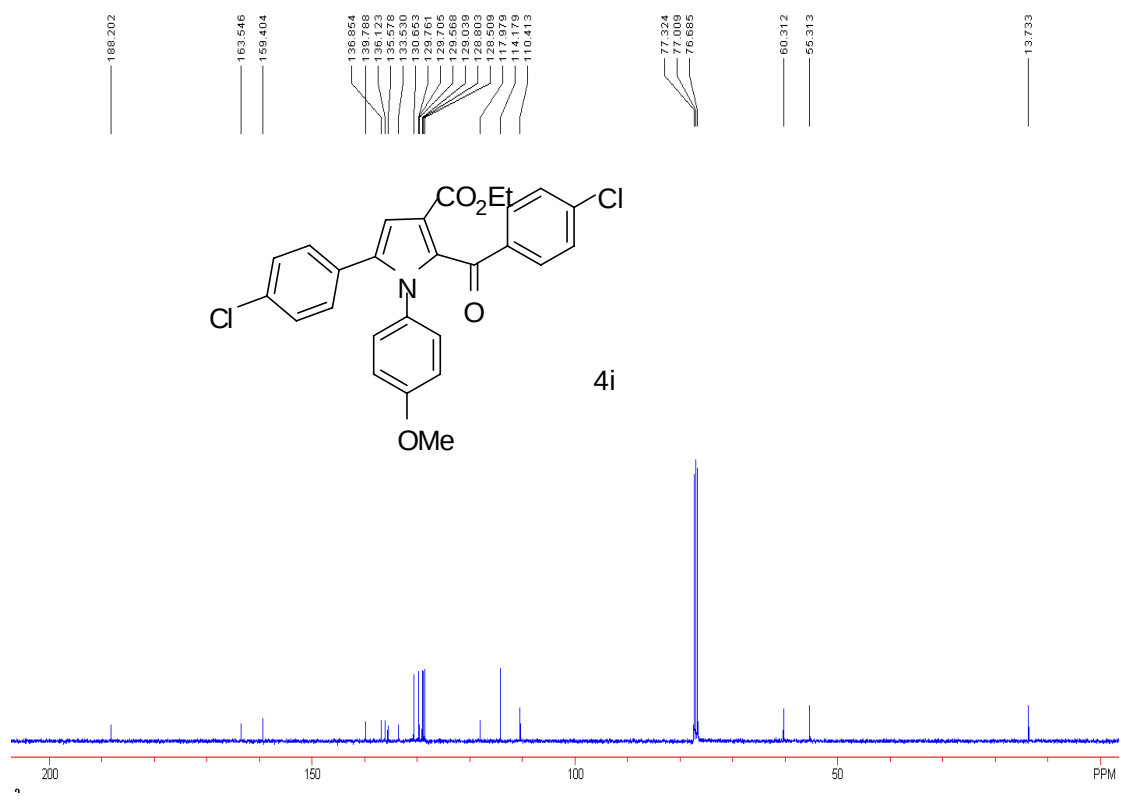
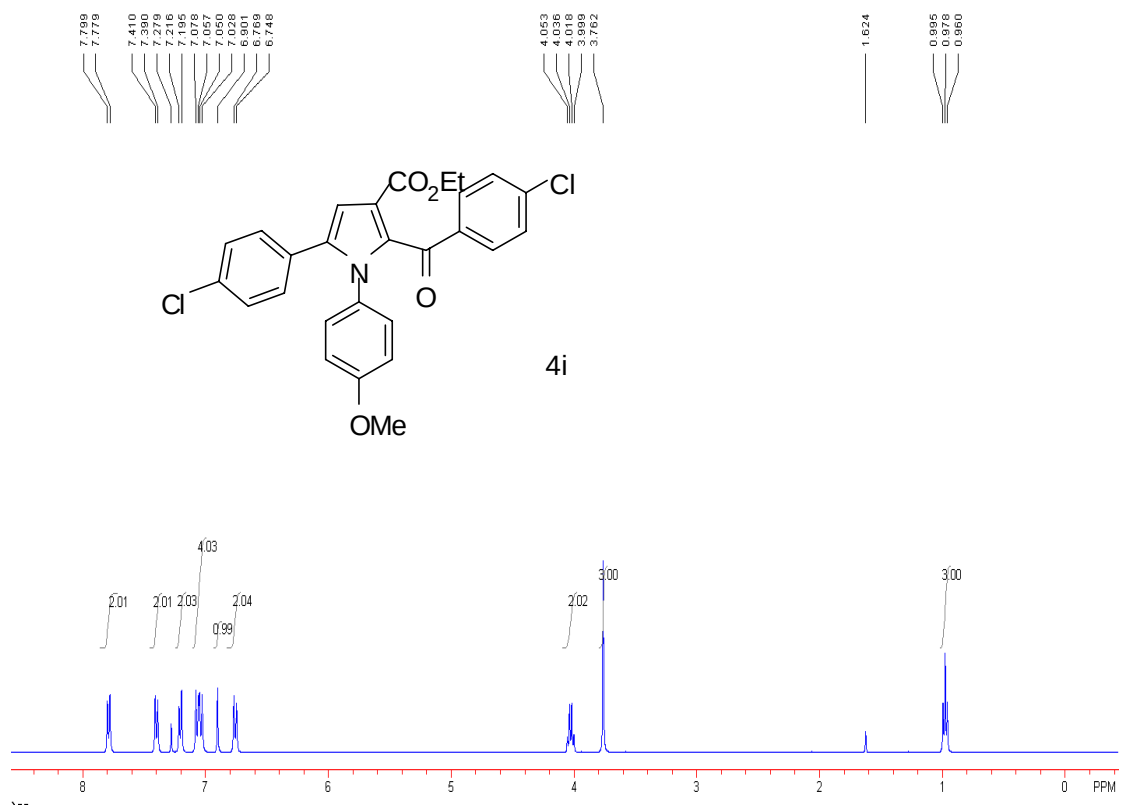


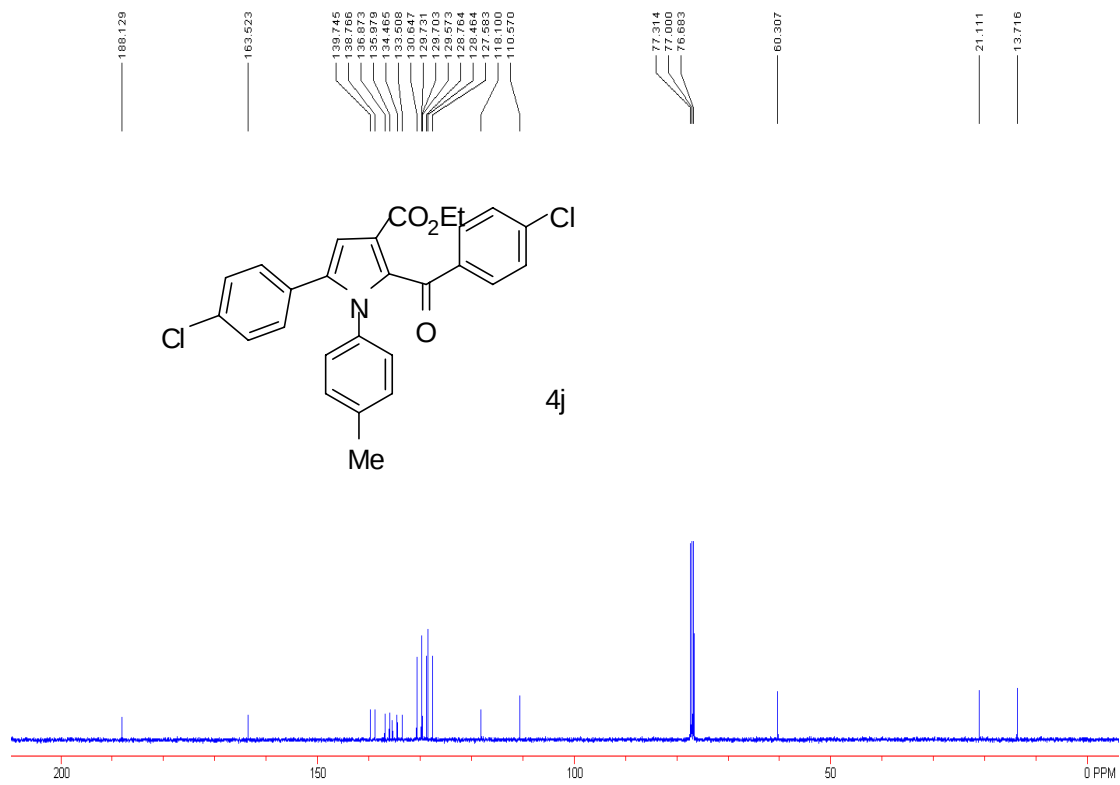
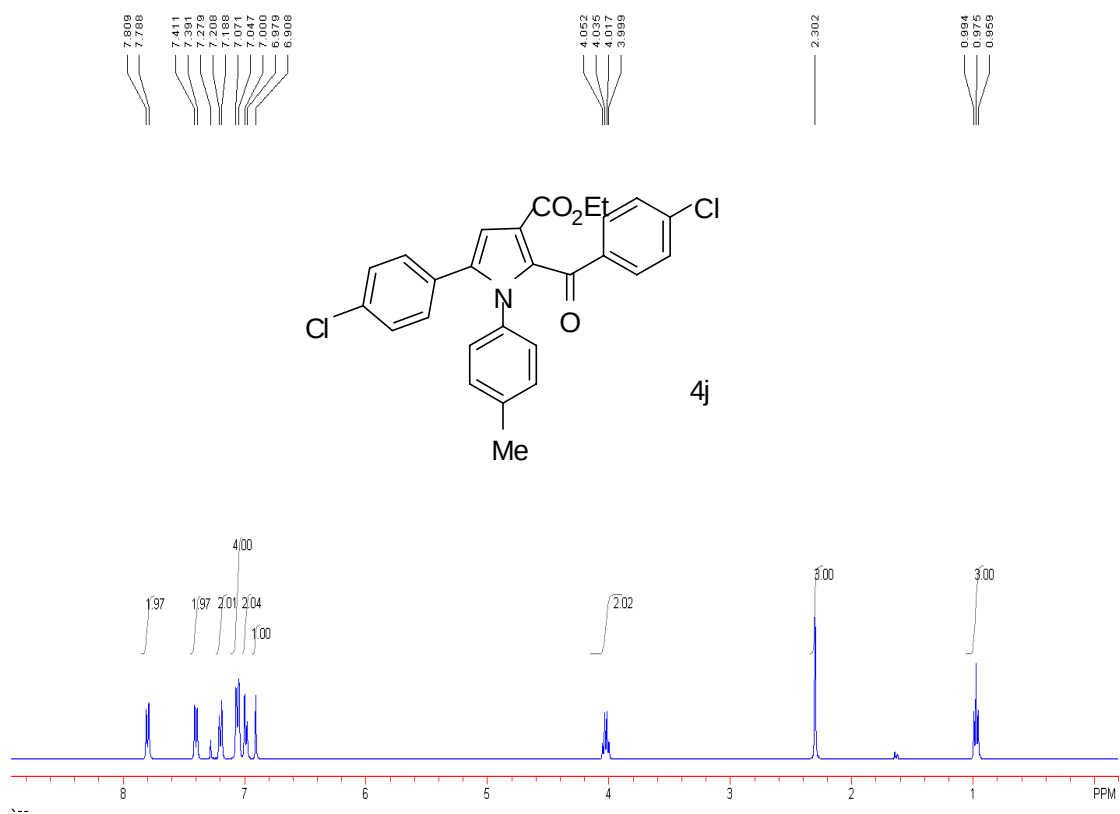


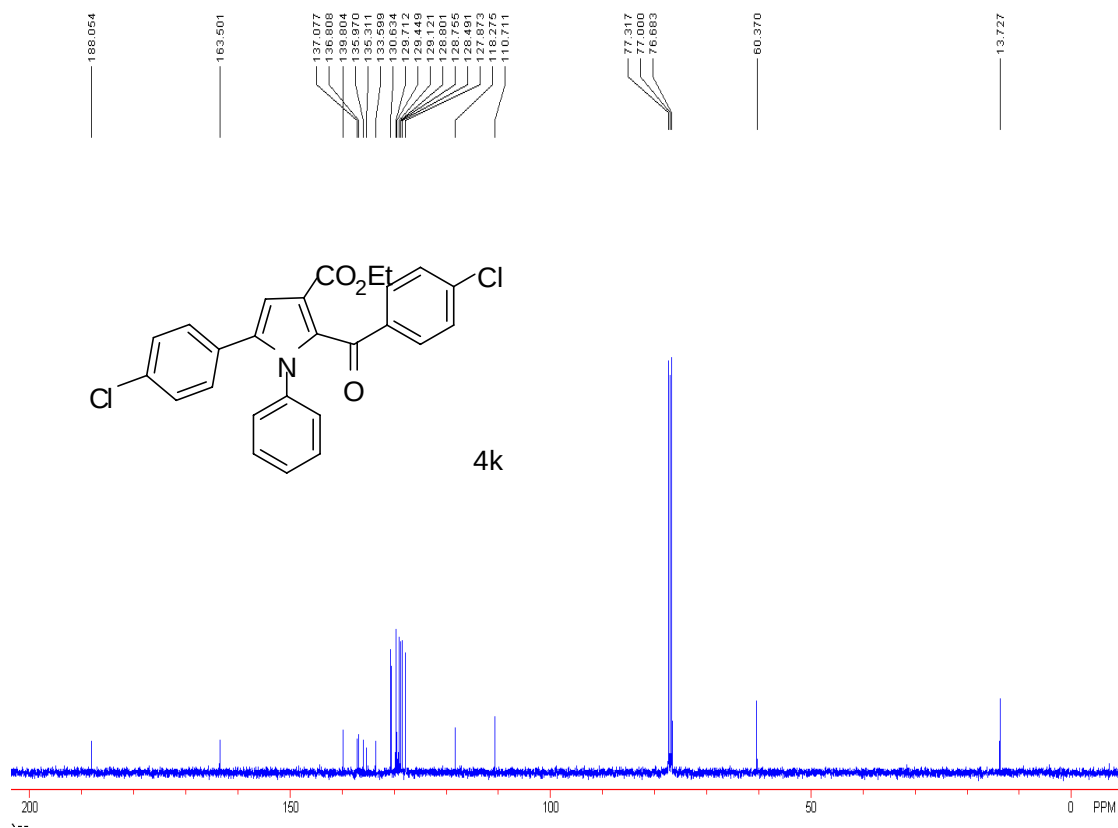
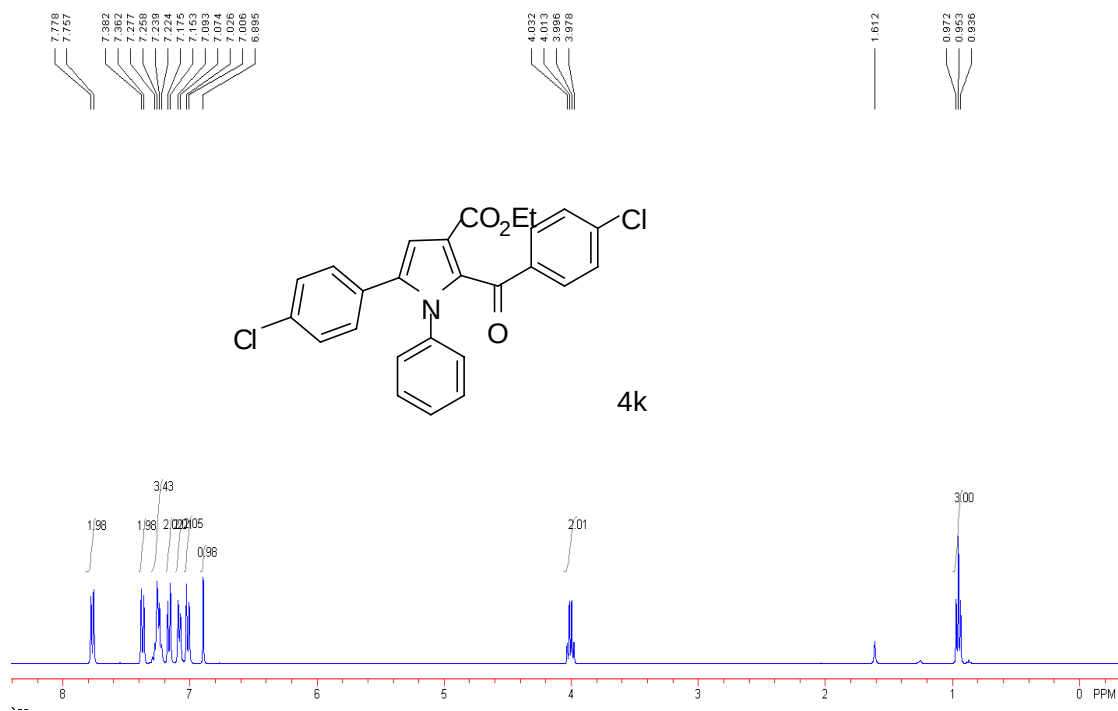


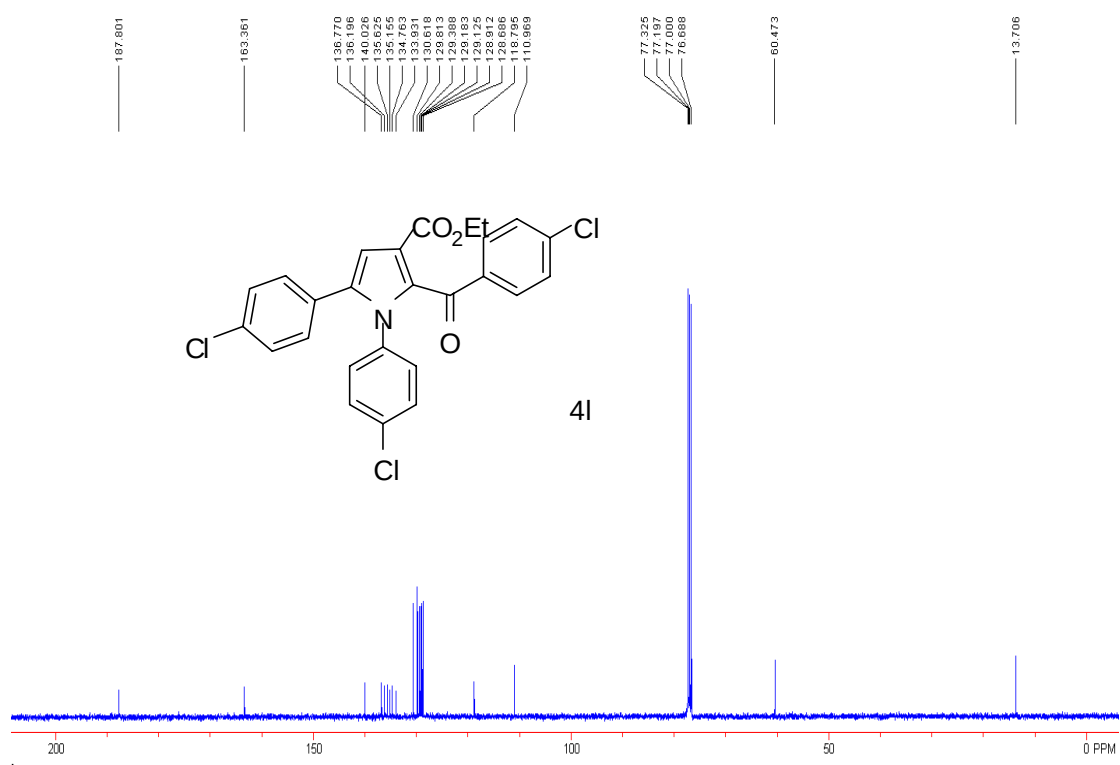
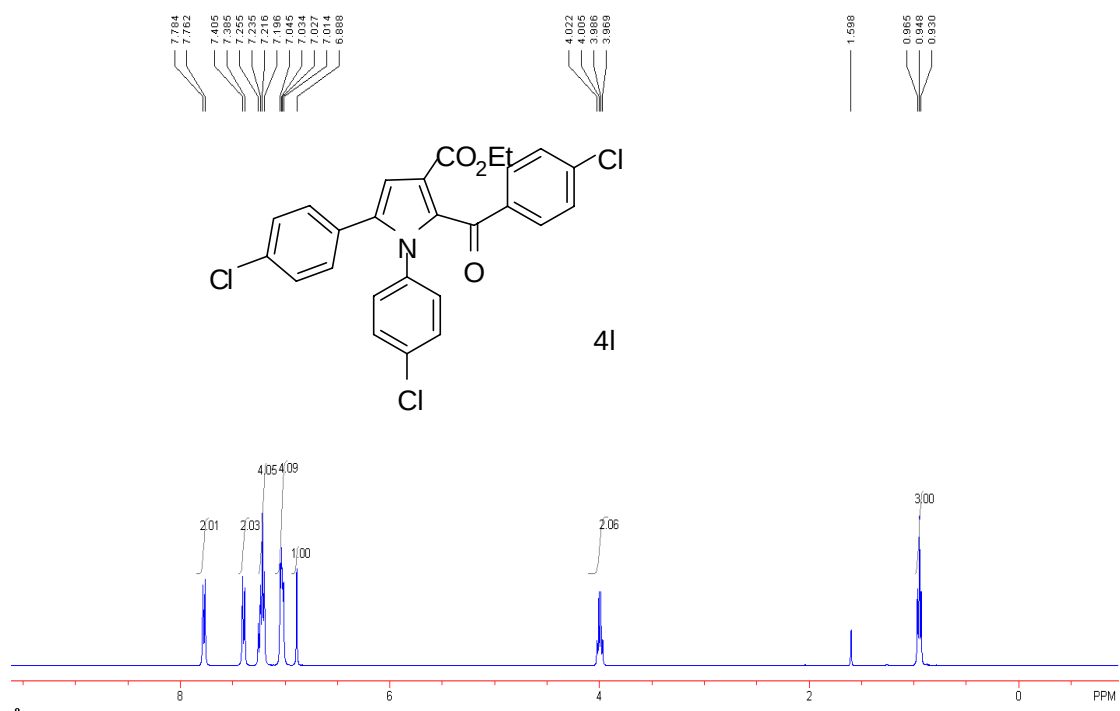


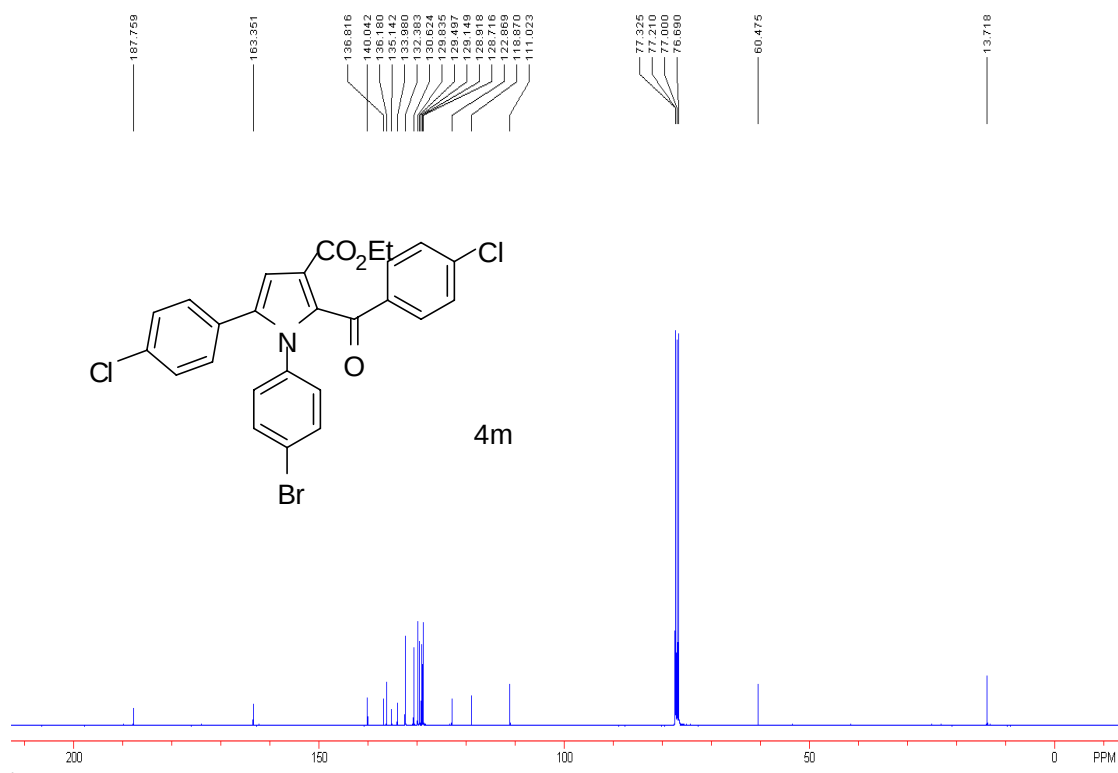
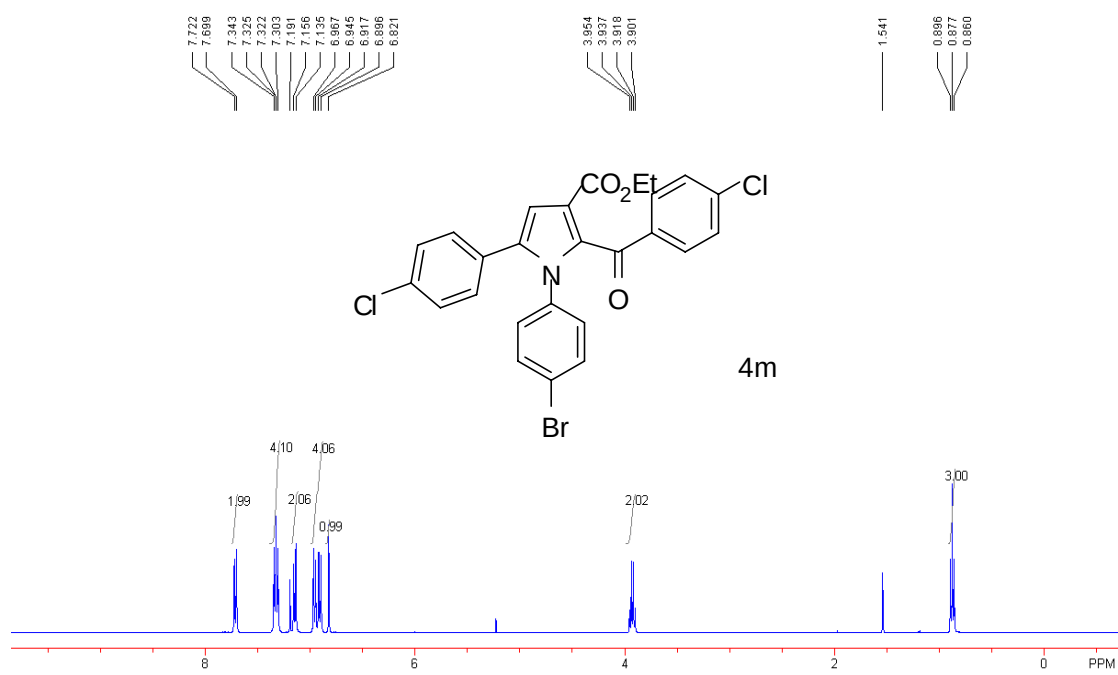


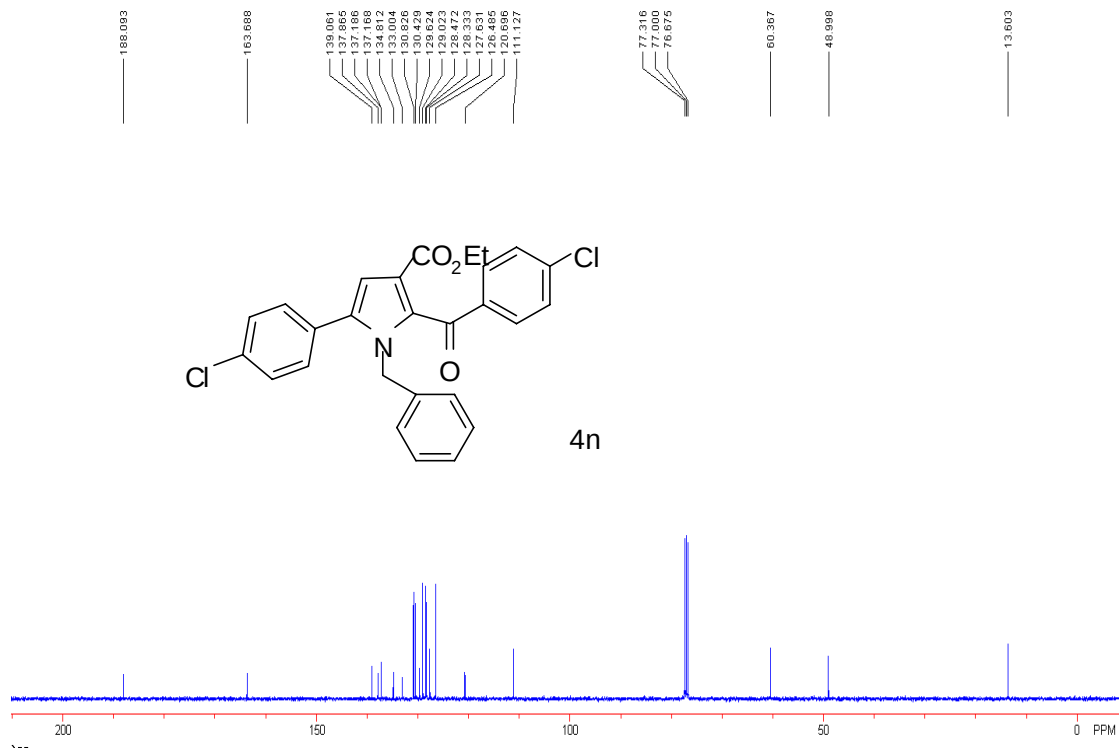
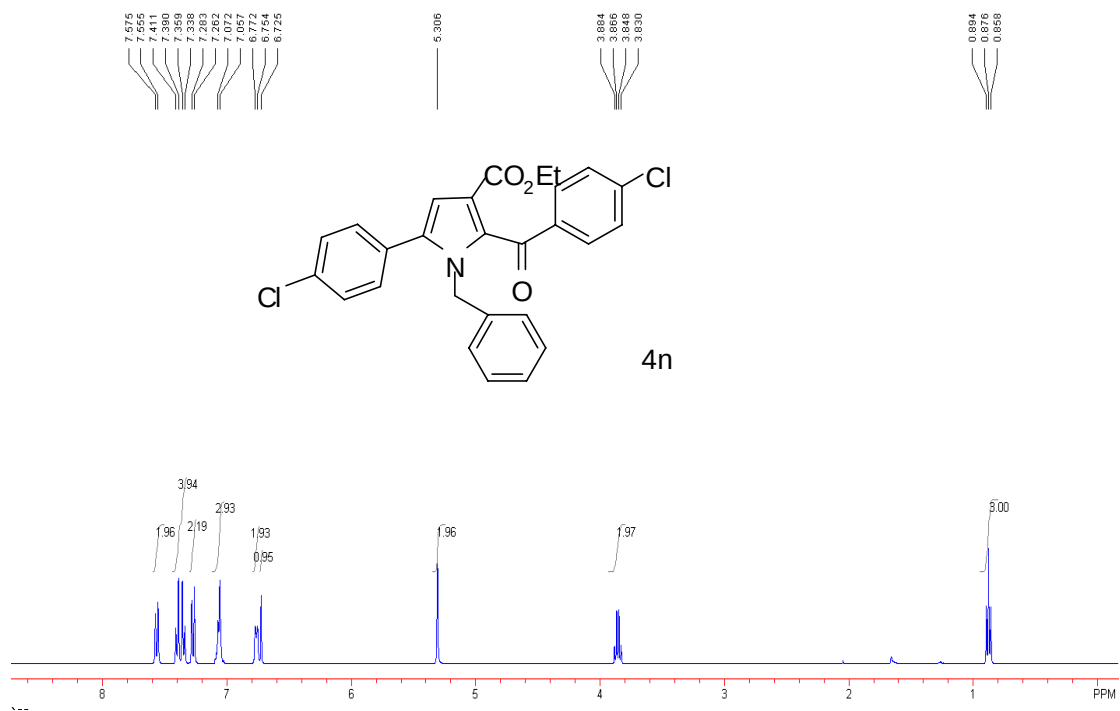


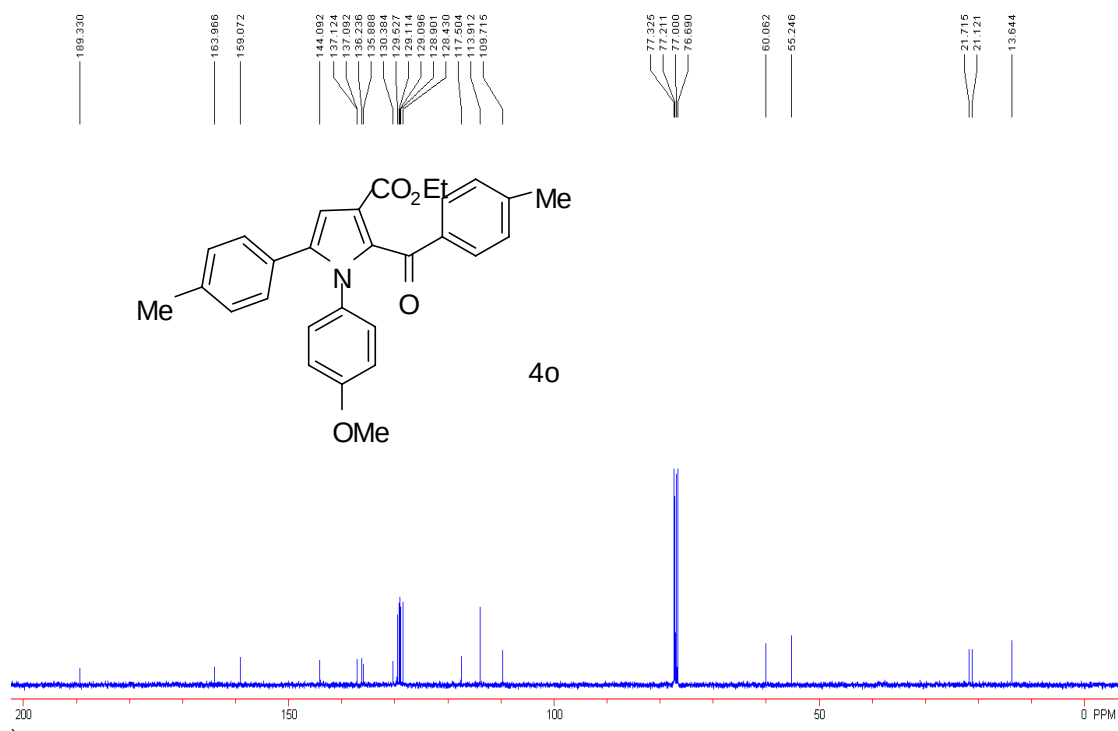
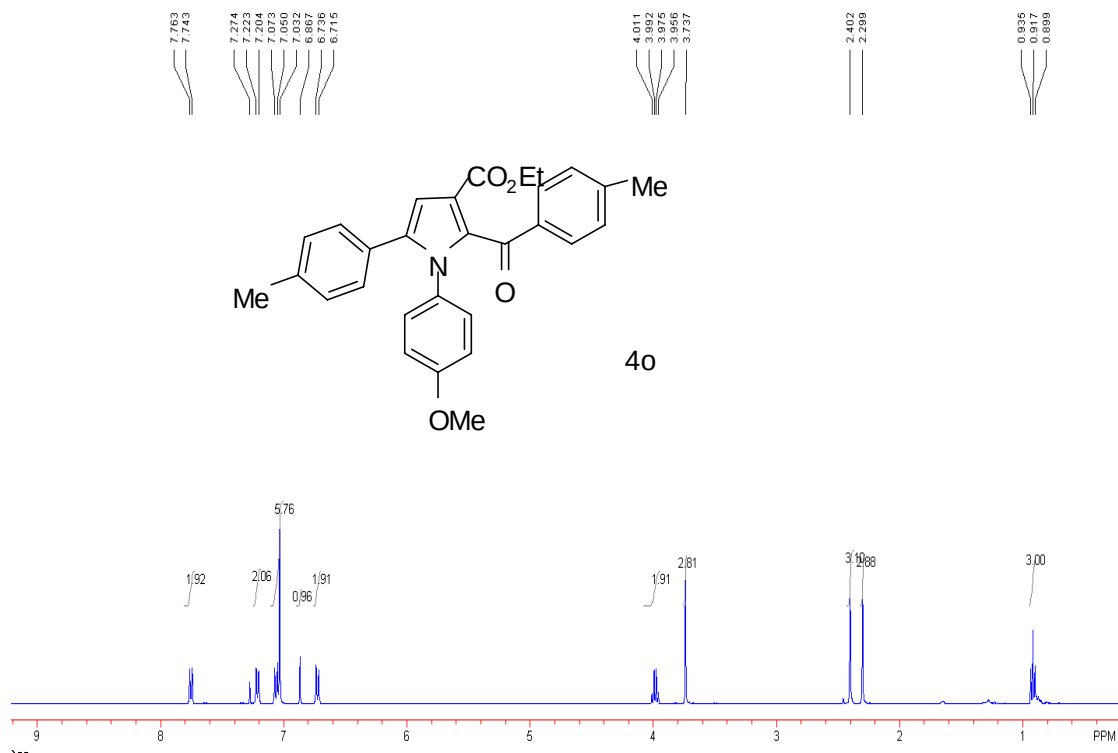


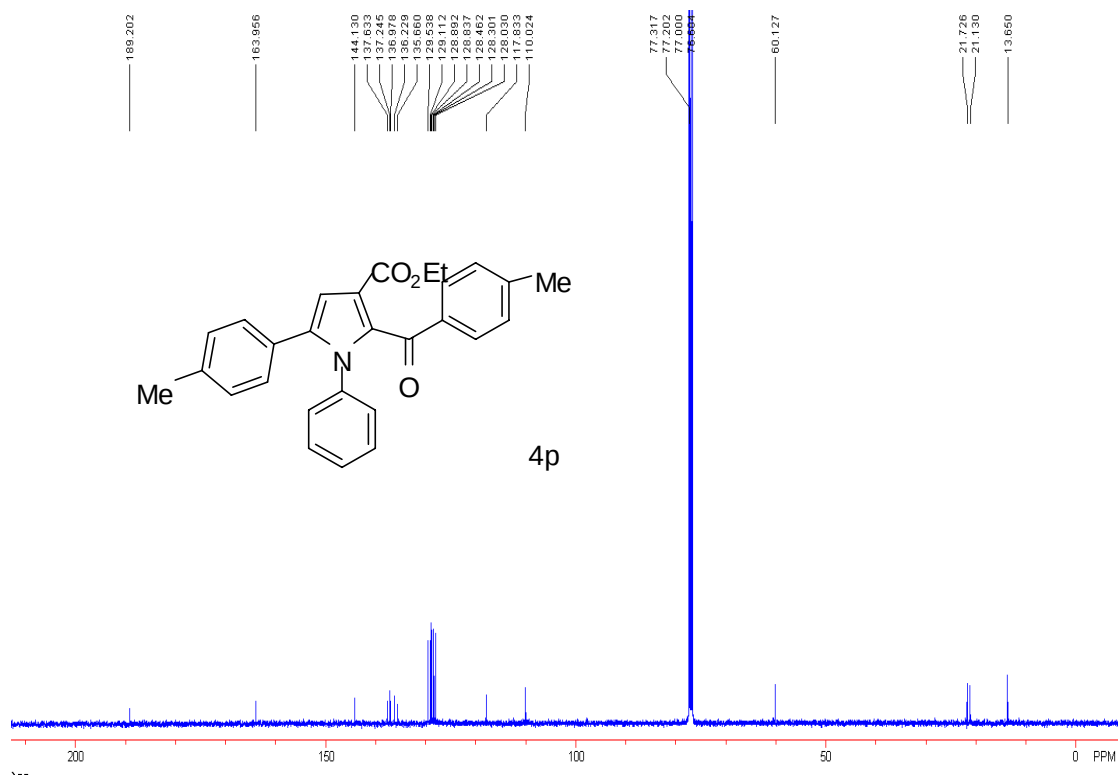
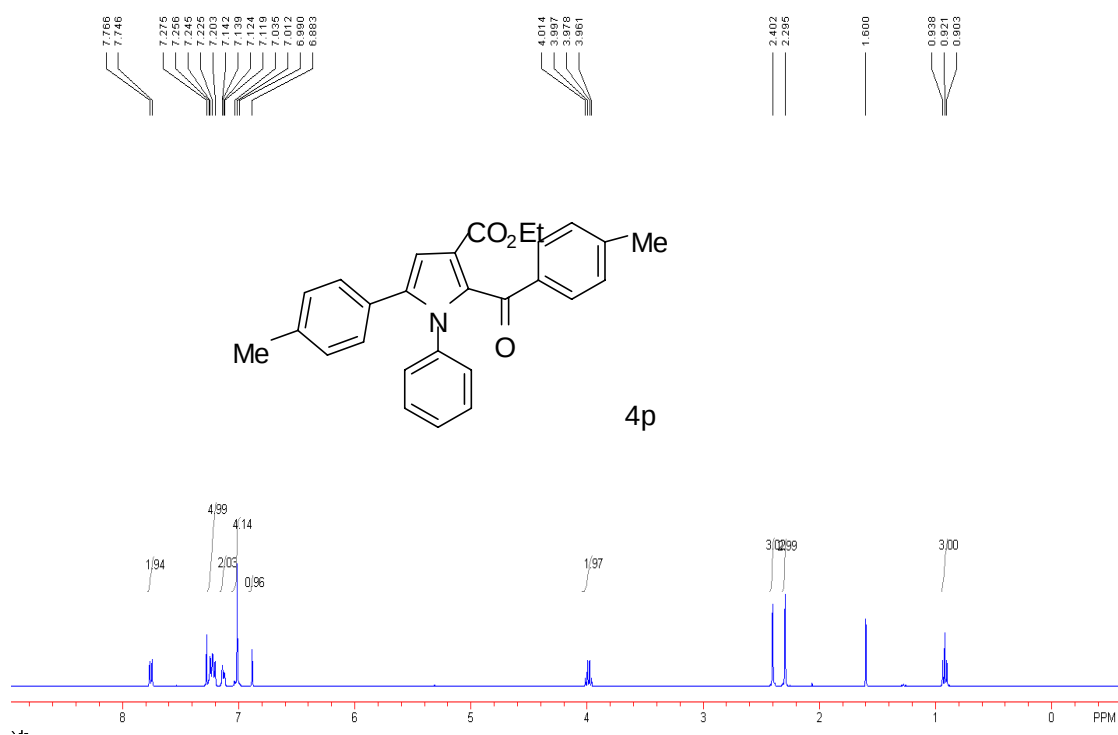


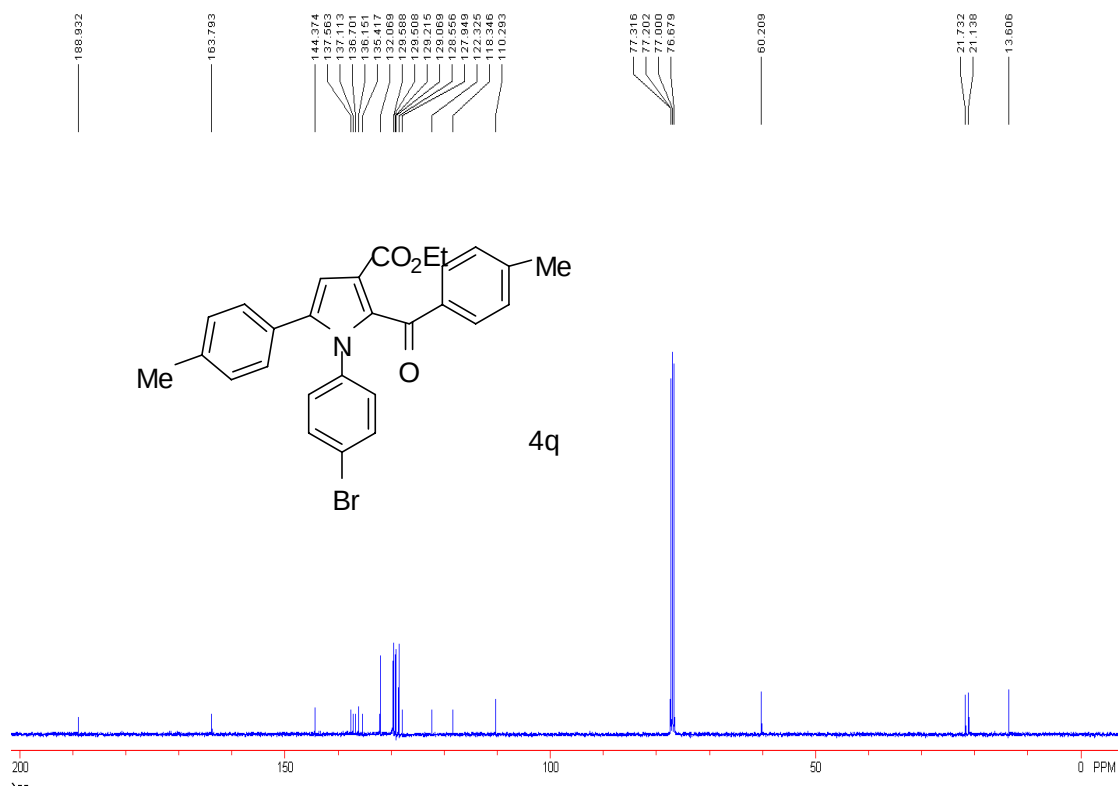
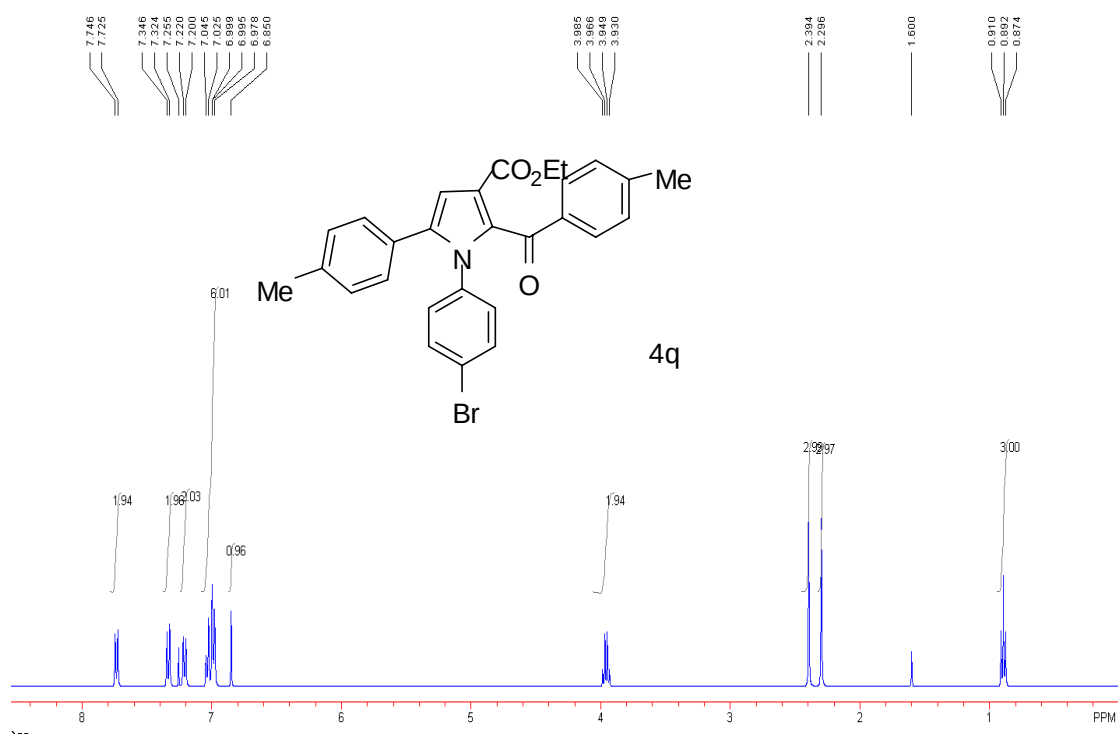


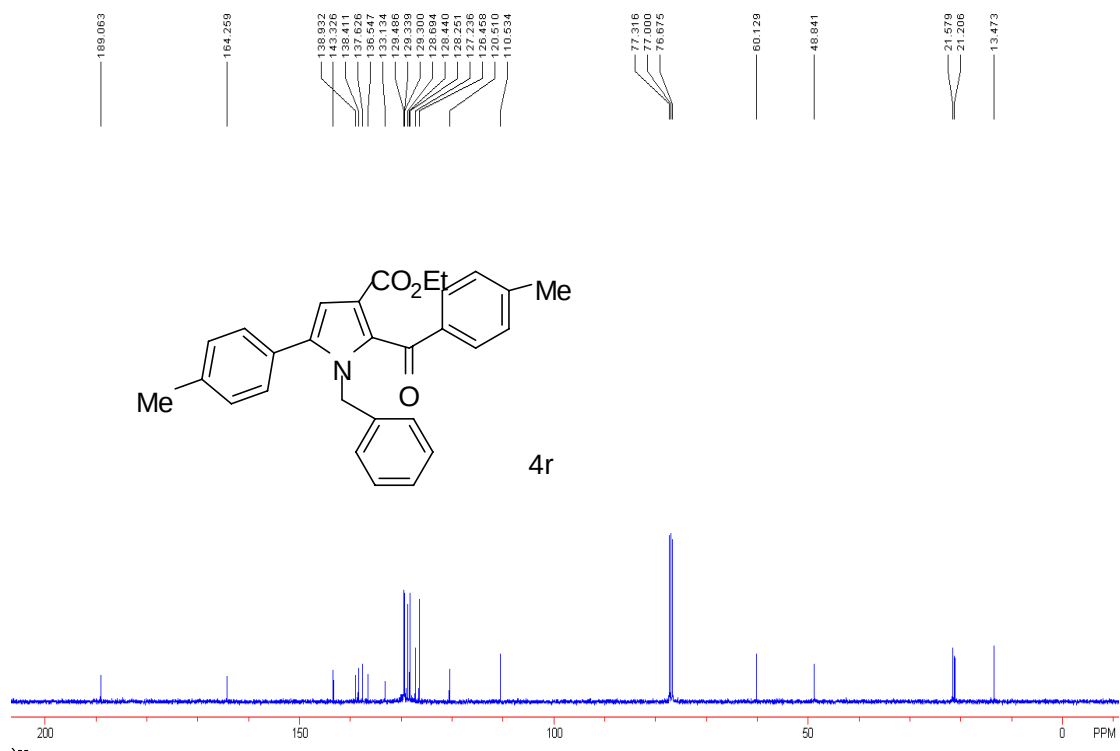
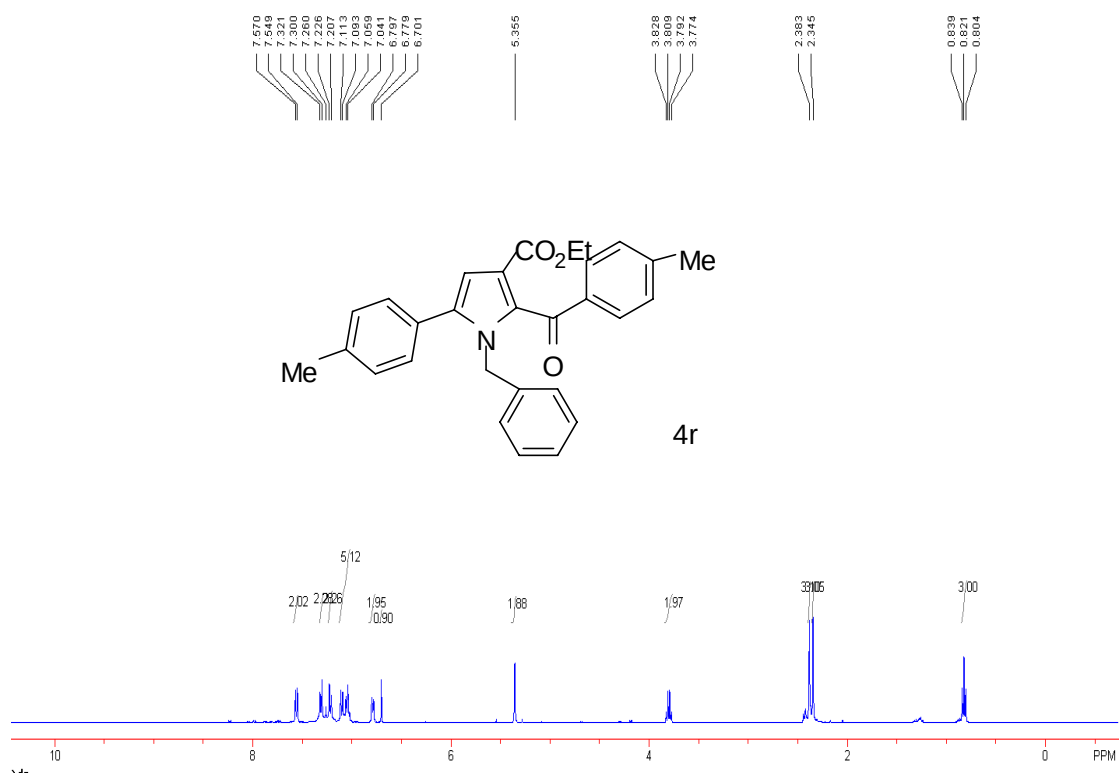


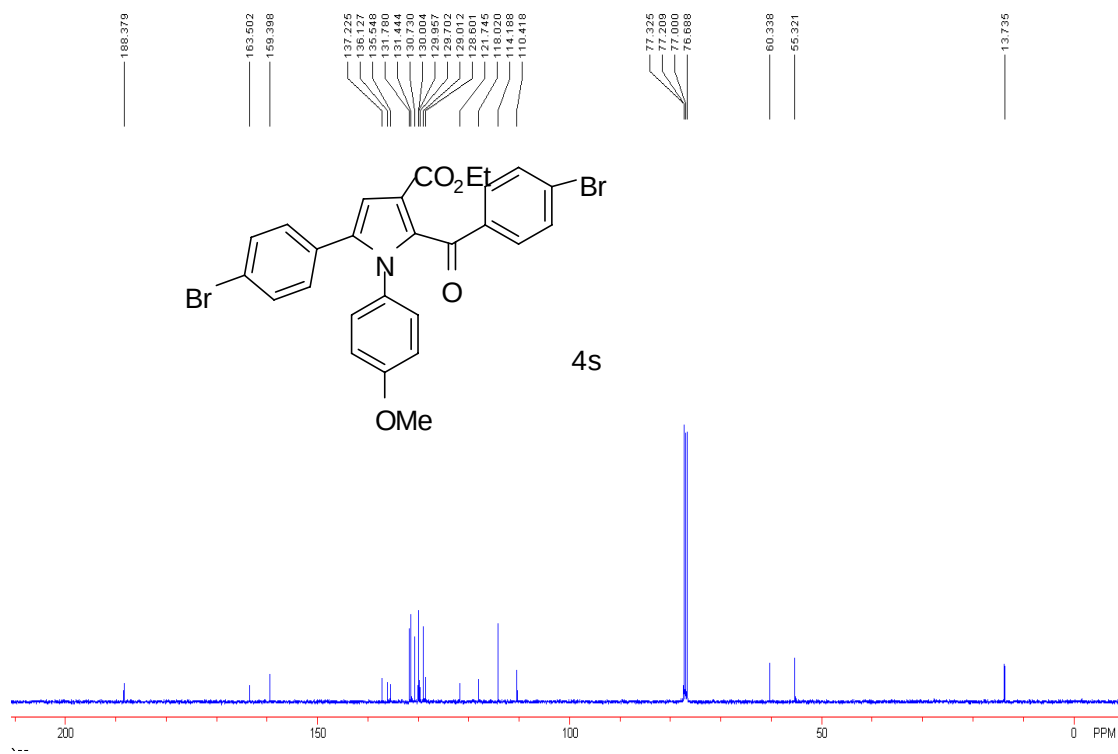
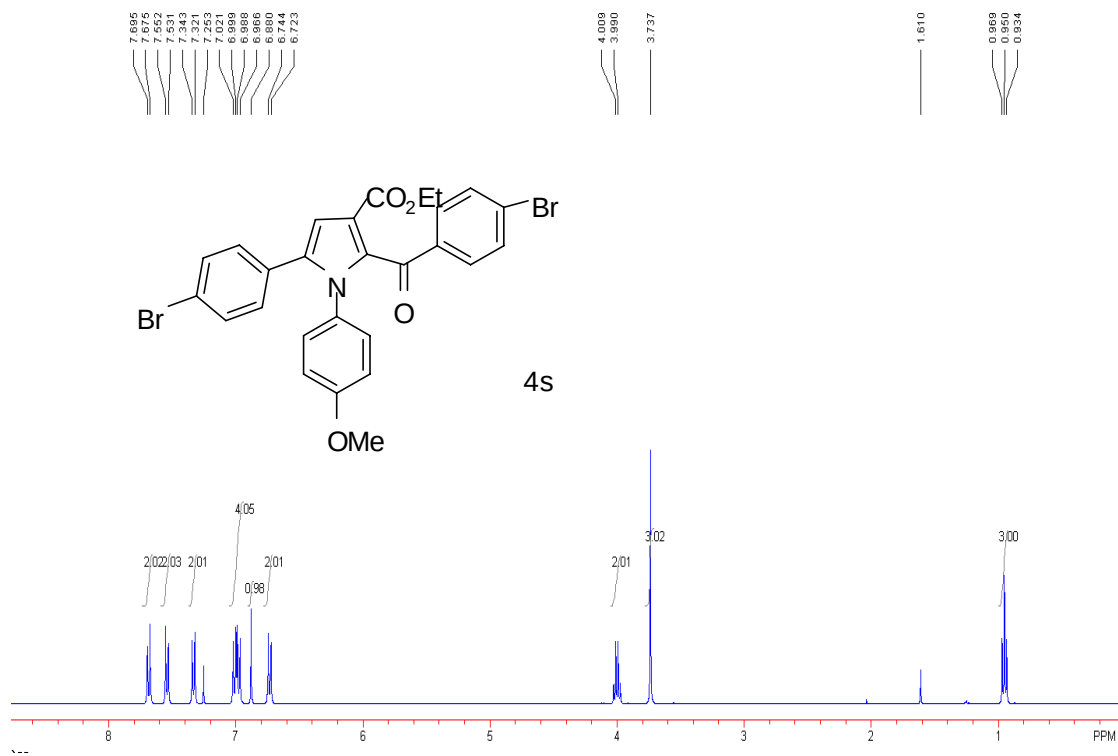


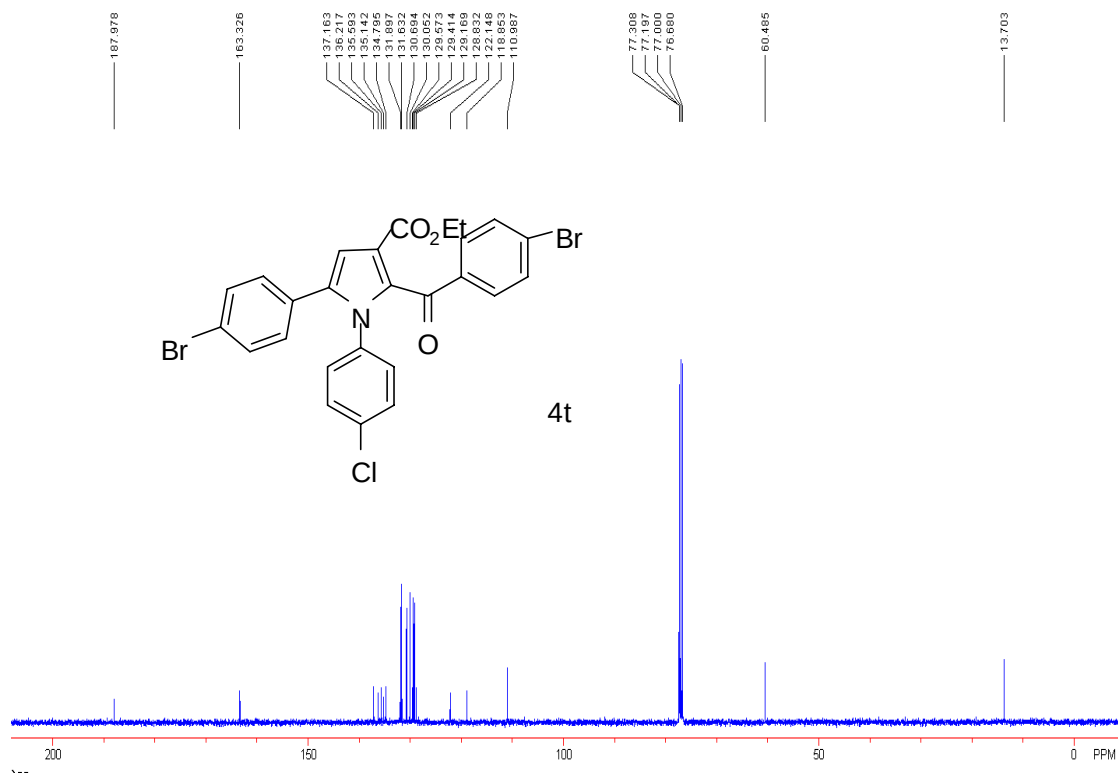
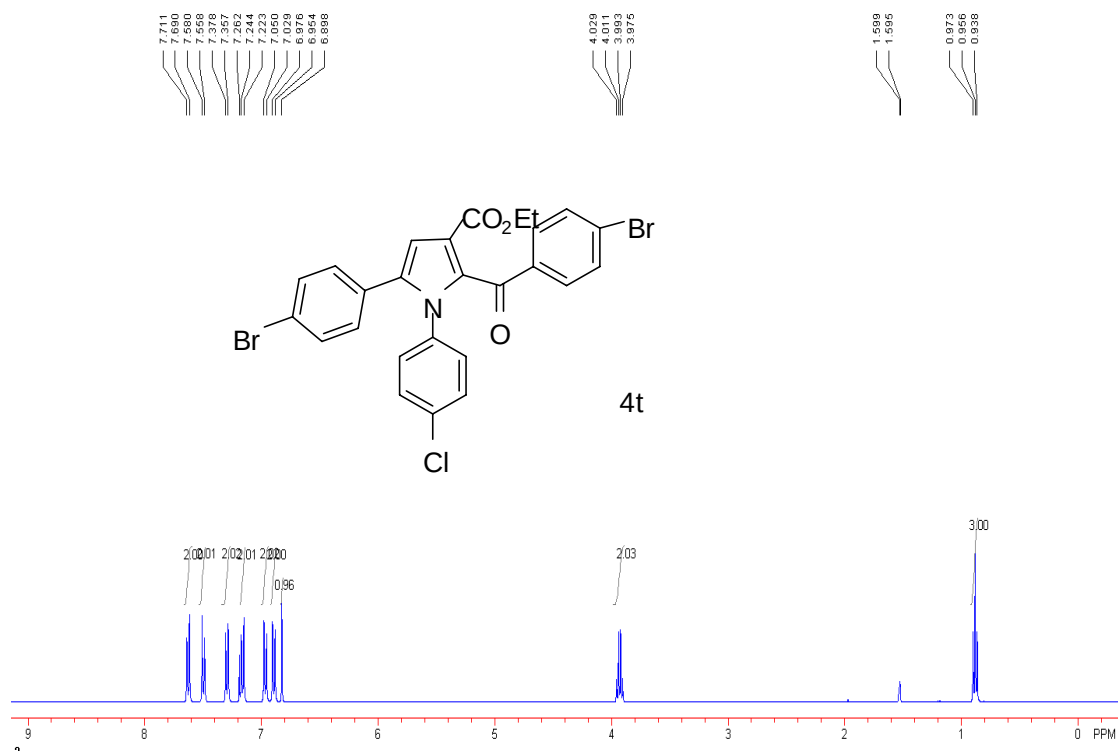


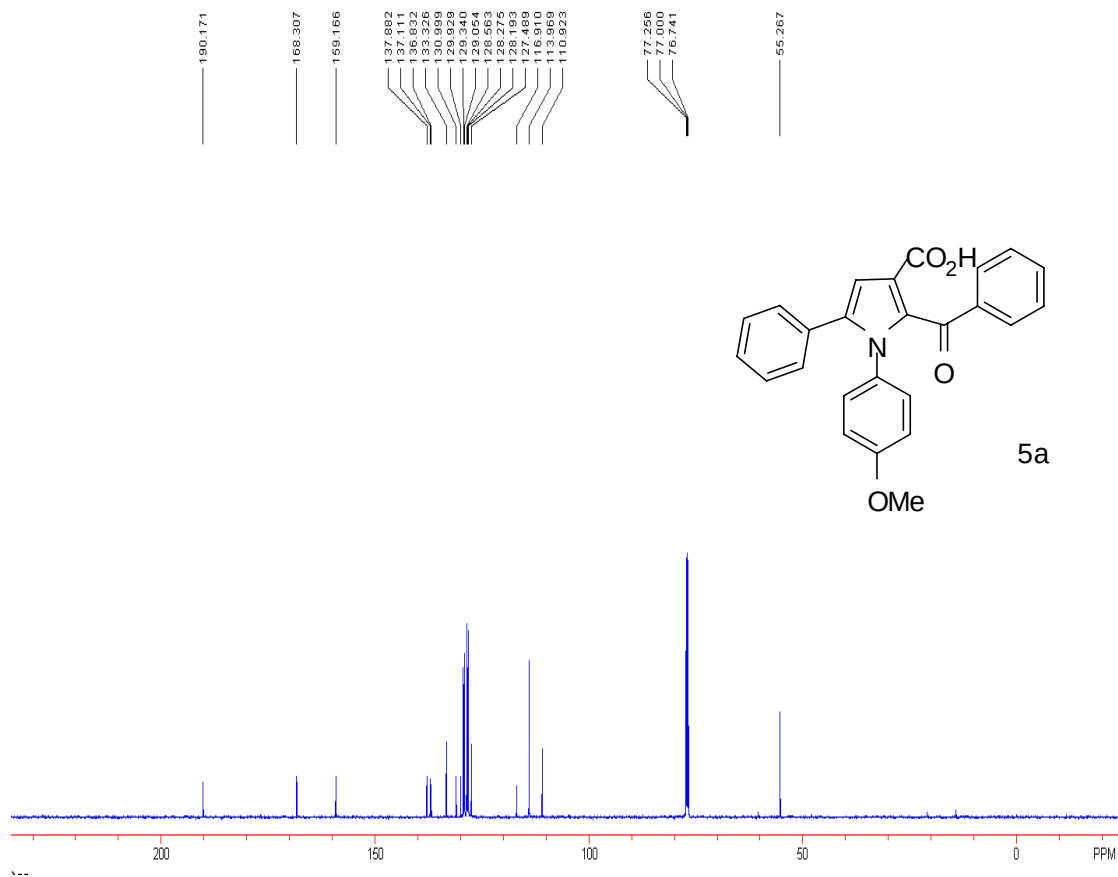
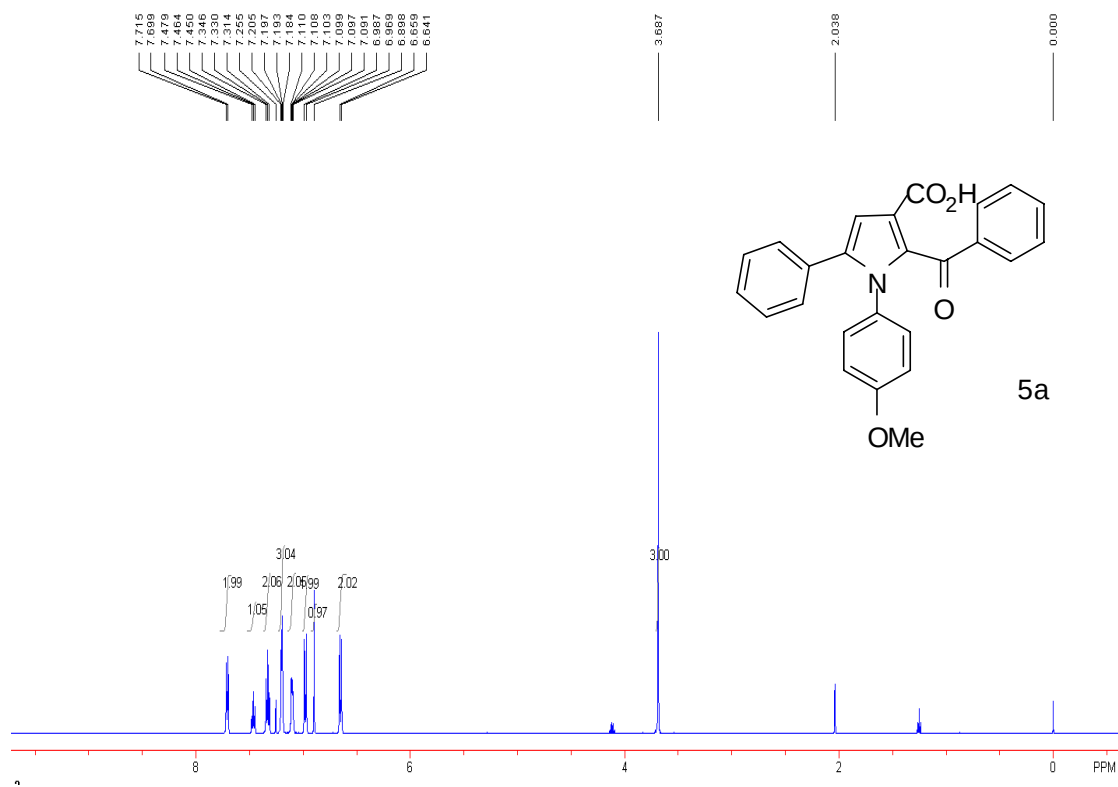


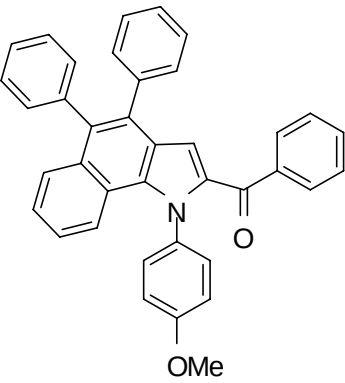




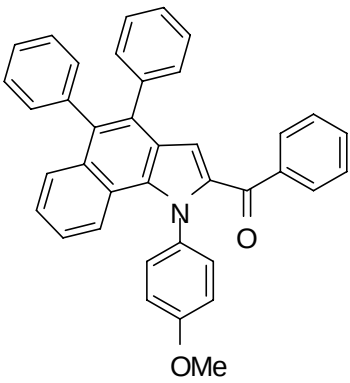








6a



6a