Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cp*Co(III)-Catalyzed Vinylic C–H Bond Activation under Mild Conditions: Expedient Pyrrole Synthesis via (3+2) Annulation of Enamides and Alkynes

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1. General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (100–200 mesh) using a proper eluent system. NMR spectra were recorded in chloroform-d at 300 or 400 MHz for ^{1}H NMR spectra and 75 MHz or 100 MHz for ^{13}C NMR spectra. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, dd = doublet of doublet, td = triplet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). For ^{13}C NMR chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-*d*. Cp*Co(CO)I_2 was synthesized according to the literature.[1] The enamide **1aa** was prepared according to literature procedure.[2]

2. General Procedure for Co-Catalyzed Synthesis of *N*-Acetyl Pyrroles

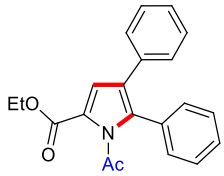
To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added enamide **1a** (31.4 mg, 0.20 mmol), alkyne (**2**, 0.24 mmol, 1.2 equiv), Cp*Co(CO)I_2 (4.8 mg, 5 mol %), $AgSbF_6$ (6.9 mg, 20 mol %), $Cu(OAc)_2.H_2O$ (40.0 mg, 1.0 equiv), and TFE (1.2 mL). The reaction mixture was stirred at room temperature (or 50 °C) for 14 h, poured into water (20 mL), diluted with 30% aqueous NH_3 solution (20 mL) and then washed with EtOAc (25 mL × 2). The organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to give the desired products.

3. General Procedure for Co-Catalyzed Synthesis of *N*-H Pyrroles

To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added enamide **1a** (31.4 mg, 0.20 mmol), alkyne (**2**, 0.24 mmol, 1.2 equiv), Cp*Co(CO)I_2 (4.8 mg, 5 mol %), $AgSbF_6$ (6.9 mg, 20 mol %), $Cu(OAc)_2.H_2O$ (40.0 mg, 1.0 equiv), and TFE (1.2 mL). The reaction mixture was stirred at 120 °C for 14 h, cooled to room temperature, poured into water (20 mL), diluted with 30% aqueous NH_3 solution (20 mL) and then washed with EtOAc (25 mL × 2). The organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to give the desired products.

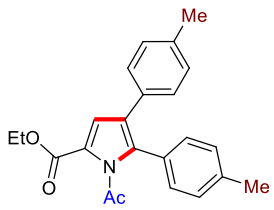
4. Spectroscopic Data of Compounds Obtained in this Study

Ethyl 1-acetyl-4,5-diphenyl-1*H*-pyrrole-2-carboxylate (3aa).[3]



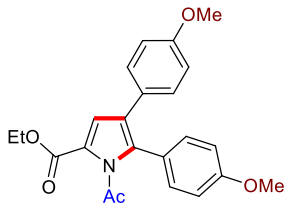
White solid (58.6 mg, 88%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 3H), 7.25 – 7.21 (m, 2H), 7.15 – 7.03 (m, 6H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.24 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 160.7, 134.4, 134.0, 130.7, 128.9, 128.6, 128.3, 128.0, 126.4, 124.8, 123.4, 118.3, 60.9, 28.9, 14.3.

Ethyl 1-acetyl-4,5-di-p-tolyl-1*H*-pyrrole-2-carboxylate (3ab).[3]



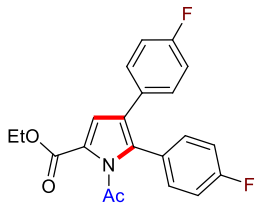
Light yellow solid (62.0 mg, 86%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 – 7.03 (m, 5H), 7.00 – 6.89 (m, 4H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.22 (s, 3H), 2.20 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 160.7, 138.7, 136.0, 134.4, 131.2, 130.5, 129.3, 128.9, 127.8, 124.6, 123.1, 118.3, 60.8, 28.9, 21.3, 21.0, 14.3 (One carbon is missing due to overlap).

Ethyl 1-acetyl-4,5-bis(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate (3ac).[3]



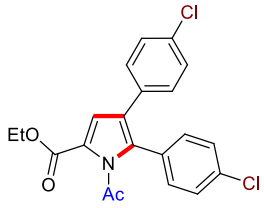
Gummy solid (62.3 mg, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.7 Hz, 2H), 7.05 (s, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 3.69 (s, 3H), 2.23 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 160.8, 159.9, 158.2, 134.0, 132.1, 129.1, 126.7, 124.4, 123.0, 122.9, 118.2, 114.0, 113.7, 60.8, 55.20, 55.15, 28.9, 14.3.

Ethyl 1-acetyl-4,5-bis(4-fluorophenyl)-1H-pyrrole-2-carboxylate (3ad).



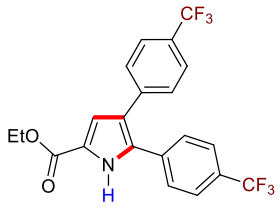
Light yellow solid (57.6 mg, 78%); m.p. 100– 102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.15 (m, 2H), 7.05 (s, 1H), 7.03 – 6.92 (m, 4H), 6.88 – 6.78 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 162.9 (d, $J_{C\text{-}F}$ = 248.2 Hz), 161.6 (d, $J_{C\text{-}F}$ = 244.5 Hz), 160.6, 133.3, 132.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 129.6 (d, $J_{C\text{-}F}$ = 7.9 Hz), 126.4 (d, $J_{C\text{-}F}$ = 2.6 Hz), 124.2, 123.5, 118.2, 115.8 (d, $J_{C\text{-}F}$ = 21.6 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 61.0, 29.0, 14.3; HRMS (ESI) m/z calcd. for $C_{21}H_{18}NO_3F_2$ $[M+H]^+$: 370.1256, found: 370.1249.

Ethyl 1-acetyl-4,5-bis(4-chlorophenyl)-1*H*-pyrrole-2-carboxylate (**3ae**).[3]



White solid (65.0 mg, 81%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2H), 7.17 – 7.08 (m, 4H), 7.06 (s, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 160.5, 135.3, 133.2, 132.6, 132.3, 132.1, 129.3, 129.0, 128.8, 128.6, 124.1, 123.7, 118.1, 61.1, 29.0, 14.3.

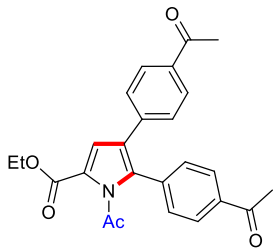
Ethyl 4,5-bis[4-(trifluoromethyl)phenyl]-1*H*-pyrrole-2-carboxylate (**4af**).



White solid (72.6 mg, 85%); m.p. 206– 208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 2.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 138.6, 135.0, 132.1 (q, $J_{C\text{-}F}$ = 32.4 Hz), 128.9, 128.6, 128.5, 128.4,

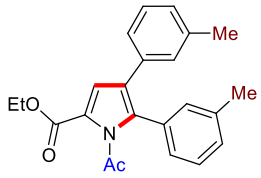
126.1, 125.8 (q, J_{C-F} = 3.8 Hz), 125.5 (q, J_{C-F} = 3.8 Hz), 125.7, 123.6 (d, J_{C-F} = 5.5 Hz), 122.2 (d, J_{C-F} = 23.9 Hz), 116.7, 60.9, 14.3; HRMS (ESI) m/z calcd. for $C_{21}H_{14}NO_2F_6$ $[M-H]^-$: 426.0931, found: 426.0923.

Ethyl 1-acetyl-4,5-bis(4-acetylphenyl)-1*H*-pyrrole-2-carboxylate (**3ag**).



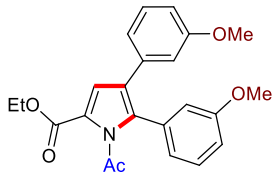
White solid (58.4 mg, 70%); m.p. 124– 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.83 – 7.77 (m, 2H), 7.42 – 7.37 (m, 2H), 7.26 (s, 1H), 7.21 – 7.16 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 3H), 2.55 (s, 3H), 2.38 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 197.3, 173.4, 160.5, 138.6, 137.2, 135.3, 135.1, 133.8, 131.0, 128.6, 128.1, 124.4, 124.3, 118.2, 61.3, 29.1, 26.6, 26.5, 14.3 (One carbon is missing due to overlap); HRMS (ESI) m/z calcd. for $C_{25}H_{24}NO_5$ $[M+H]^+$: 418.1647, found: 418.1649.

Ethyl 1-acetyl-4,5-di-*m*-tolyl pyrrole-2-carboxylate (3ah).



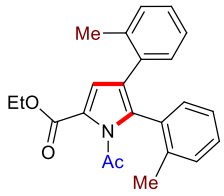
White solid (62.0 mg, 86%); m.p. 58– 60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.15 (m, 3H), 7.13 – 7.00 (m, 4H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 160.7, 138.2, 137.7, 134.6, 133.9, 131.2, 130.8, 129.6, 128.7, 128.4, 128.0, 127.8, 127.1, 125.0, 124.6, 123.2, 118.2, 60.8, 28.9, 21.4, 21.3, 14.3; HRMS (ESI) m/z calcd. for $C_{23}H_{24}NO_3$ $[M+H]^+$: 362.1754, found: 362.1750.

Ethyl 1-acetyl-4,5-bis(3-methoxyphenyl)-1*H*-pyrrole-2-carboxylate (**3ai**).



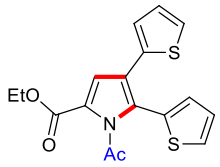
Pale yellow oil (63.5 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.9 Hz, 1H), 7.10 (s, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.87 – 6.80 (m, 2H), 6.79 – 6.75 (m, 1H), 6.70 (dt, *J* = 7.8, 1.2 Hz, 1H),, 6.67 – 6.59 (m, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 3.54 (s, 3H), 2.25 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 160.7, 159.5, 159.4, 135.3, 134.2, 132.2, 129.7, 129.2, 124.5, 123.3, 123.1, 120.4, 118.0, 116.1, 114.8, 113.1, 112.5, 60.9, 55.3, 54.9, 28.9, 14.3; HRMS (ESI) m/z calcd. for $C_{23}H_{24}NO_5$ $[M+H]^+$: 394.1654, found: 394.1649.

Ethyl 1-acetyl-4,5-di-*o*-tolyl-1*H*-pyrrole-2-carboxylate (**3aj**).



Yellow oil (61.3 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.11 (m, 2H), 7.09 – 7.00 (m, 4H), 6.96 (s, 1H), 6.89 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.18 (s, 3H), 2.15 (s, 3H), 1.92 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 161.0, 138.4, 136.4, 135.0, 133.6, 131.3, 130.44, 130.41, 130.1, 130.0, 129.1, 127.1, 125.4, 125.3, 125.1, 123.4, 120.3, 60.9, 28.1, 20.5, 19.8, 14.3; HRMS (ESI) m/z calcd. for $C_{23}H_{24}NO_3$ $[M+H]^+$: 362.1756, found: 362.1750.

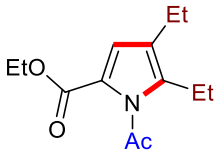
Ethyl 1-acetyl-4,5-di(thiophen-2-yl)-1*H*-pyrrole-2-carboxylate (**3ak**).[3]



White solid (47.0 mg, 68%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.09 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.08 (s, 1H), 7.05 – 7.02 (m, 2H), 6.83 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.81 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H);

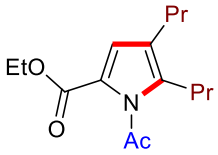
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 160.4, 135.6, 131.8, 129.7, 129.1, 127.4, 127.0, 125.6, 124.5, 124.4, 121.3, 117.0, 61.2, 28.4, 14.3 (One carbon is missing due to overlap).

Ethyl 1-acetyl-4,5-diethyl-1*H*-pyrrole-2-carboxylate (3al).[3]



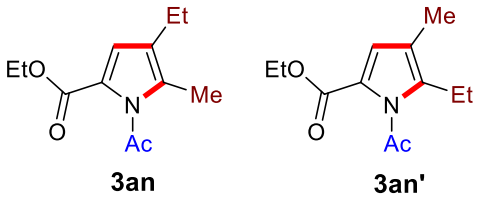
Pale yellow oil (38.8 mg, 82%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 2.32 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.5 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 160.7, 139.3, 124.3, 121.9, 120.8, 60.5, 28.5, 18.5, 18.4, 15.0, 14.8, 14.3.

Ethyl 1-acetyl-4,5-dipropyl-1*H*-pyrrole-2-carboxylate (3am).[3]



Yellow oil (42.4 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.54 – 1.40 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.90 – 0.82 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 160.7, 138.2, 123.3, 121.9, 121.2, 60.5, 28.6, 27.4, 27.0, 23.61, 23.58, 14.3, 13.9 (One carbon is missing due to overlap).

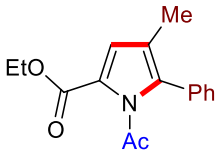
Ethyl 1-acetyl-4-ethyl-5-methyl-1*H*-pyrrole-2-carboxylate & Ethyl 1-acetyl-5-ethyl-4-methyl-1*H*-pyrrole-2-carboxylate (3an & 3an').



Yellow oil (46.0 mg, 65%); ^{1}H NMR (300 MHz, $CDCl_3$) Major: δ 6.77 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 2.30 (q, *J* = 7.5 Hz, 2H), 2.15 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) Major + Minor: δ 173.9, 160.7, 140.0, 133.2,

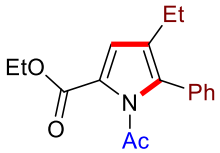
124.9, 122.5, 122.1, 121.6, 121.1, 117.5, 60.5, 60.5, 28.5, 28.4, 18.7, 14.8, 14.4, 14.3, 11.3, 10.5. HRMS (ESI) m/z calcd. for $C_{12}H_{17}NO_3$ $[M+H]^+$: 224.1281, found: 224.1294.

Ethyl 1-acetyl-4-methyl-5-phenyl-1*H*-pyrrole-2-carboxylate (**3ao**).[3]



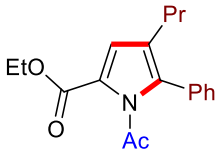
Colourless solid (47.0 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 3H), 7.24 – 7.19 (m, 2H), 6.79 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.19 (s, 3H), 1.91 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 160.8, 135.5, 131.1, 129.9, 128.42, 128.37, 123.0, 120.3, 119.5, 60.7, 28.5, 14.3, 11.1.

Ethyl 1-acetyl-4-ethyl-5-phenyl-1*H*-pyrrole-2-carboxylate (**3ap**).[2]



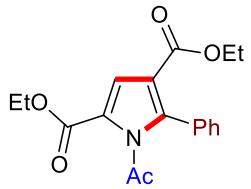
Colourless oil (45.6 mg, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 3H), 7.25 – 7.17 (m, 2H), 6.85 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.27 (q, *J* = 7.6 Hz, 2H), 2.19 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 160.8, 134.9, 131.2, 130.0, 128.5, 128.4, 126.4, 123.2, 118.7, 60.7, 28.5, 18.7, 15.1, 14.3.

Ethyl 1-acetyl-5-phenyl-4-propyl-1*H*-pyrrole-2-carboxylate (**3aq**).[3]



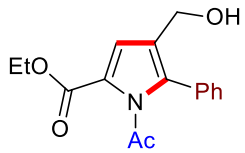
Colourless oil (43.0 mg, 72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 3H), 7.22 – 7.17 (m, 2H), 6.82 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.25 – 2.19 (m, 2H), 2.18 (s, 3H), 1.43 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 160.8, 135.4, 131.2, 130.1, 128.43, 128.37, 124.8, 123.2, 119.2, 60.7, 28.5, 27.4, 23.8, 14.3, 13.8.

Diethyl 1-acetyl-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (**3ar**).



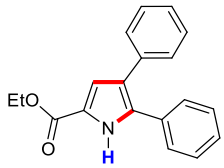
White solid (47.4 mg, 68%); m.p. 70– 73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 6H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.18 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 163.3, 160.3, 140.7, 130.3, 129.7, 129.4, 128.0, 123.3, 119.0, 115.3, 60.2, 60.1, 28.8, 14.2, 14.0; HRMS (ESI) m/z calcd. for $C_{18}H_{19}NNaO_5$ $[M+Na]^+$: 352.1159, found: 352.1155.

Ethyl 1-acetyl-4-(hydroxymethyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (**3as**).



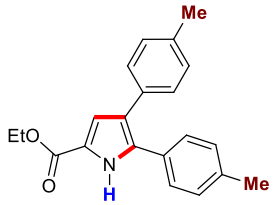
Colourless solid (34.4 mg, 60%); m.p. 116– 118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.31 – 7.26 (m, 2H), 7.02 (s, 1H), 4.33 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 160.6, 136.2, 129.9, 128.9, 128.5, 123.6, 123.5, 118.7, 60.9, 56.9, 28.6, 14.2 (One carbon is missing due to overlap); HRMS (ESI) m/z calcd. for $C_{16}H_{17}NNaO_4$ $[M+Na]^+$: 310.1049, found: 310.1049.

Ethyl 4,5-diphenyl-1*H*-pyrrole-2-carboxylate (4aa).[2]



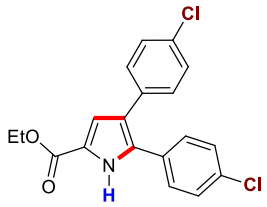
White solid (50.6 mg, 87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (brs, 1H), 7.32 – 7.29 (m, 2H), 7.27 – 7.16 (m, 7H), 7.15 – 7.11 (m, 1H), 6.99 (d, *J* = 2.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 135.4, 133.2, 131.9, 128.7, 128.5, 128.4, 128.0, 127.9, 126.3, 124.0, 122.5, 116.7, 60.5, 14.5.

Ethyl 4,5-di-p-tolyl-1*H*-pyrrole-2-carboxylate (**4ab**).



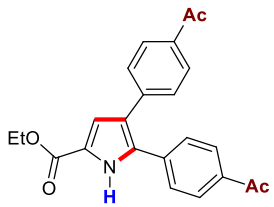
White solid (51.6 mg, 81%); m.p. 159– 161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (brs, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 2.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 137.8, 135.9, 133.2, 132.6, 129.4, 129.2, 129.1, 128.3, 127.8, 123.8, 122.1, 116.7, 60.5, 21.3, 21.2, 14.5; HRMS (ESI) m/z calcd. for $C_{21}H_{22}NO_2$ $[M+H]^+$: 320.1655, found: 320.1645.

Ethyl 4,5-bis(4-chlorophenyl)-1*H*-pyrrole-2-carboxylate (**4ae**).



White solid (57.6 mg, 80%); m.p. 182– 184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.22 (brs, 4H), 7.19 – 7.09 (m, 4H), 6.93 (d, *J* = 2.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 134.05, 133.6, 132.3, 132.2, 130.1, 129.7, 129.4, 129.0, 128.7, 123.1, 122.9, 116.5, 60.7, 14.4; HRMS (ESI) calcd. for $C_{19}H_{14}NO_2Cl_2$ $[M-H]^-$: 358.0413, found: 365.0396.

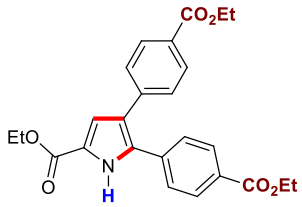
Ethyl 4,5-bis(4-acetylphenyl)-1*H*-pyrrole-2-carboxylate (**4ag**).



Light yellow solid (60.0 mg, 84%); m.p. 164– 166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (brs, 1H), 7.83 (m, 4H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 2.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.53 (s, 3H), 2.52 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 197.2, 161.1, 140.1, 136.3, 136.0, 135.2, 132.5, 128.8, 128.7, 128.4,

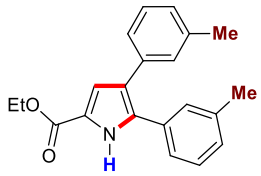
128.1, 124.1, 123.8, 116.7, 60.8, 26.6, 26.5, 14.4; HRMS (ESI) calcd. for $C_{23}H_{22}NO_4$ $[M+H]^+$: 376.1549, found: 376.1543.

Diethyl 4,4'-(5-(ethoxycarbonyl)-1*H*-pyrrole-2,3-diyl)dibenzoate (**4at**).



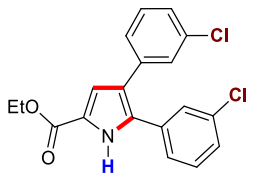
Colourless solid (61.8 mg, 71%); m.p. 163– 165 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (brs, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 2.6 Hz, 1H), 4.34 – 4.27 (m, 4H), 4.24 (d, *J* = 7.1 Hz, 2H), 1.34 – 1.26 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 166.0, 161.1, 139.7, 135.8, 132.6, 130.0, 129.9, 129.8, 128.5, 128.3, 127.8, 124.1, 123.6, 116.7, 61.1, 60.9, 60.8, 14.4, 14.32, 14.30; HRMS (ESI) m/z calcd. for $C_{25}H_{26}NO_6$ $[M+H]^+$: 436.1760, found: 436.1754.

Ethyl 4,5-di-m-tolyl-1*H*-pyrrole-2-carboxylate (**4ah**).



White solid (39.5 mg, 62%); m.p. 120– 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (brs, 1H), 7.16 – 7.12 (m, *J* = 2.0 Hz, 1H), 7.11 – 6.91 (m, 8H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 2.21 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 138.3, 137.8, 135.3, 133.4, 131.9, 129.1, 128.6, 128.44, 128.37, 128.1, 127.0, 125.5, 125.2, 124.0, 122.2, 116.7, 60.4, 21.4, 21.3, 14.4; ; HRMS (ESI) m/z calcd. for $C_{21}H_{22}NO_2$ $[M+H]^+$: 320.1649, found: 320.1645.

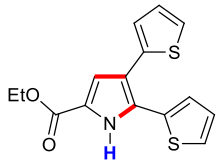
Ethyl 4,5-bis(3-chlorophenyl)-1*H*-pyrrole-2-carboxylate (**4au**).



White solid (57.6 mg, 80%); m.p. 106– 108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (brs, 1H), 7.31 (t, *J* = 1.6 Hz, 1H), 7.24 – 7.08 (m, 6H), 7.04 – 7.00 (m, 1H), 6.94 (d, *J* = 2.7 Hz, 1H),

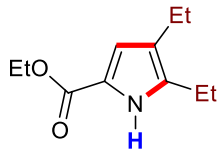
4.20 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 136.9, 134.7, 134.3, 133.3, 131.9, 130.0, 129.7, 128.3, 128.2, 127.8, 126.6, 126.4, 123.2, 123.1, 116.6, 60.8, 14.4 (One carbon is missing due to overlap); HRMS (ESI) m/z calcd. for $C_{19}H_{14}NO_2Cl_2$ $[M-H]^-$: 358.0413, found: 358.0396.

Ethyl 1-acetyl-4,5-di(thiophen-2-yl)-1*H*-pyrrole-2-carboxylate (**4ak**).



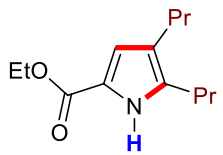
White solid (47.2 mg, 78%); m.p. 96– 98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ δ 9.51 (brs, 1H), 7.23 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.00 – 6.86 (m, 4H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 136.5, 132.5, 127.4, 127.3, 127.1, 127.0, 126.4, 125.5, 124.6, 122.4, 118.0, 116.7, 60.7, 14.4; HRMS (ESI) m/z calcd. for $C_{15}H_{12}NO_2S_2$ $[M-H]^-$: 302.0314, found: 302.0304.

Ethyl 1-acetyl-4,5-diethyl-1H-pyrrole-2-carboxylate (4al).



White solid (28.1 mg, 72%); m.p. 57– 59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (brs, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.33 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.09 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 135.9, 123.6, 119.7, 115.1, 59.9, 19.1, 18.7, 15.3, 14.5, 13.8; HRMS (ESI) m/z calcd. for $C_{11}H_{18}NO_2$ $[M+H]^+$: 196.1334, found: 196.1332.

Ethyl 1-acetyl-4,5-dipropyl-1*H*-pyrrole-2-carboxylate (**4am**).



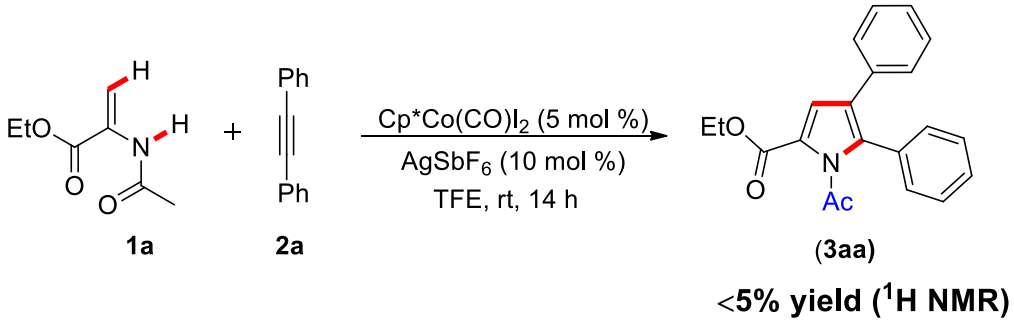
White solid (33.8 mg, 76%); m.p. 48– 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.28 (t, *J* = 7.6 Hz,

2H), 1.61 – 1.43 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.90 – 0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 134.9, 122.5, 119.8, 115.6, 59.9, 27.9, 27.7, 24.1, 22.9, 14.5, 13.9, 13.8; HRMS (ESI) m/z calcd. for $C_{13}H_{22}NO_2$ $[M+H]^+$: 224.1648, found: 224.1645.

5. Reaction with and without oxidant (Scheme 3a)

a. Reaction without oxidant

To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added enamide **1a** (15.7 mg, 0.10 mmol), diphenylacetylne (**2a**, 0.24 mmol, 1.2 equiv**),** Cp*Co(CO)I_2 (2.4 mg, 5 mol %), $AgSbF_6$ (3.4 mg, 20 mol %), The reaction mixture was stirred at room temperature for 14 h, poured into water (20 mL), then washed with EtOAc (10 mL × 2). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The conversions of **3aa** was determined by ^{1}H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as a internal standard.



1a **2a** **(3aa)**

<5% yield (^{1}H NMR)

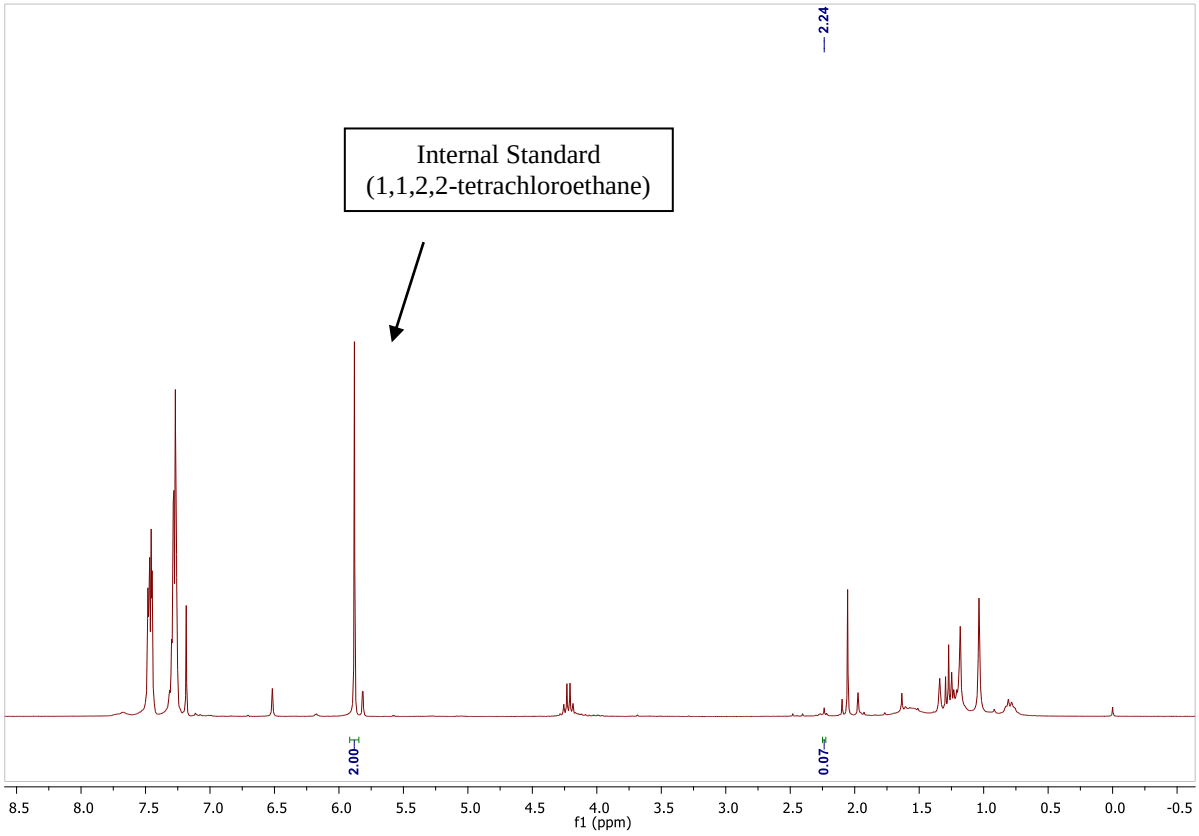
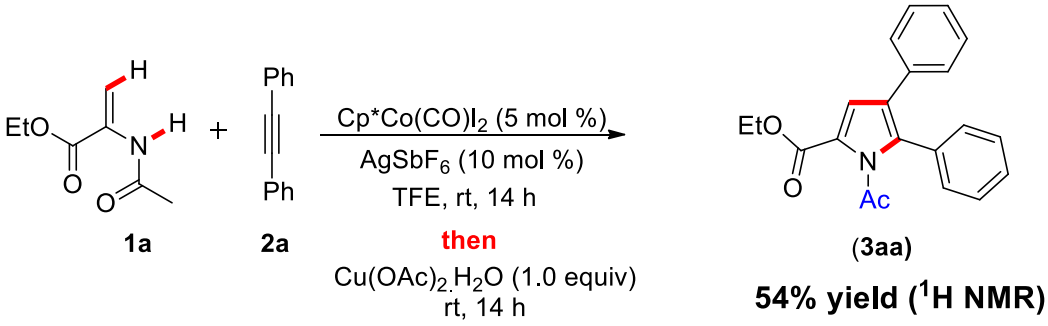


Figure S2. Crude ^{1}H NMR for reaction without oxidant.

b. Reaction with oxidant

To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added enamide **1a** (15.7 mg, 0.10 mmol), diphenylacetylne (**2a**, 0.24 mmol, 1.2 equiv**),** Cp*Co(CO)I_2 (2.4 mg, 5 mol %), $AgSbF_6$ (3.4 mg, 20 mol %), The reaction mixture was stirred at room temperature for 14 h. Afterwards $Cu(OAc)_2.H_2O$ (20 mg, 1.0 equiv) was added to the reaction under air. The reaction mixture was continued to stir at room temperature for another 14 h. Then it was poured into water (20 mL), washed with EtOAc (10 mL × 2). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The conversions of **3aa** was determined by ^{1}H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as a internal standard.



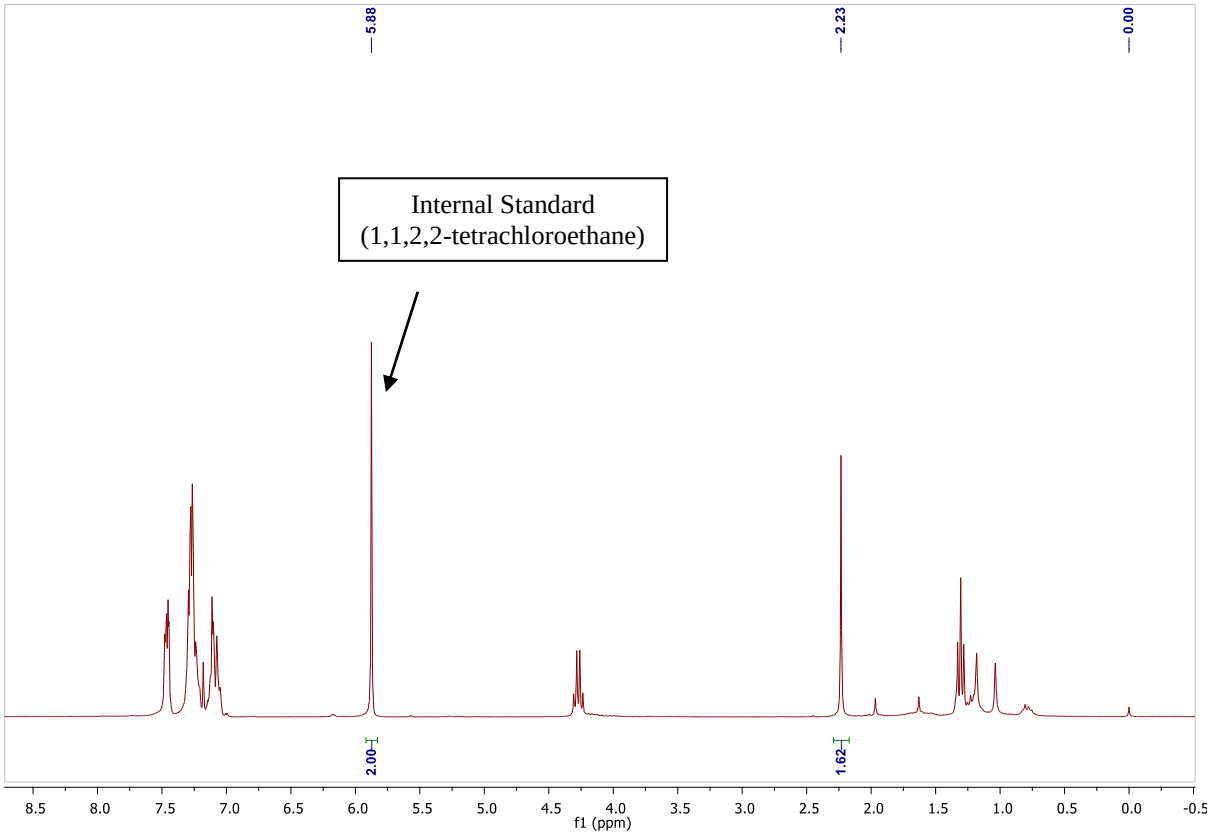
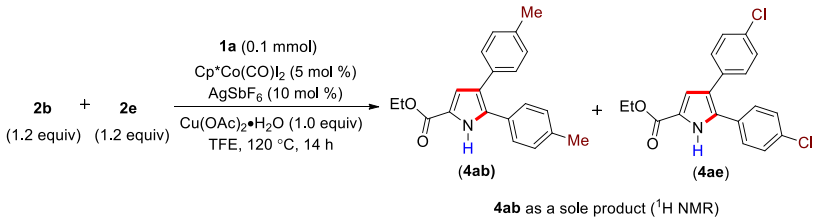


Figure S3. Crude ^{1}H NMR for reaction with oxidant.

6. Intermolecular competitive experiment (Scheme 3b)



To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added enamide **1a** (15.7 mg, 0.10 mmol), diphenylacetylne (**2a**, 0.24 mmol, 1.2 equiv**),** Cp*Co(CO)I_2 (2.4 mg, 5 mol %), $AgSbF_6$ (3.4 mg, 20 mol %), The reaction mixture was stirred at 120 °C for 14 h, cooled to room temerature poured into water (20 mL), then washed with EtOAc (10 mL × 2). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The conversions of **4ab** and **4ae** were determined by ^{1}H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as a internal standard.

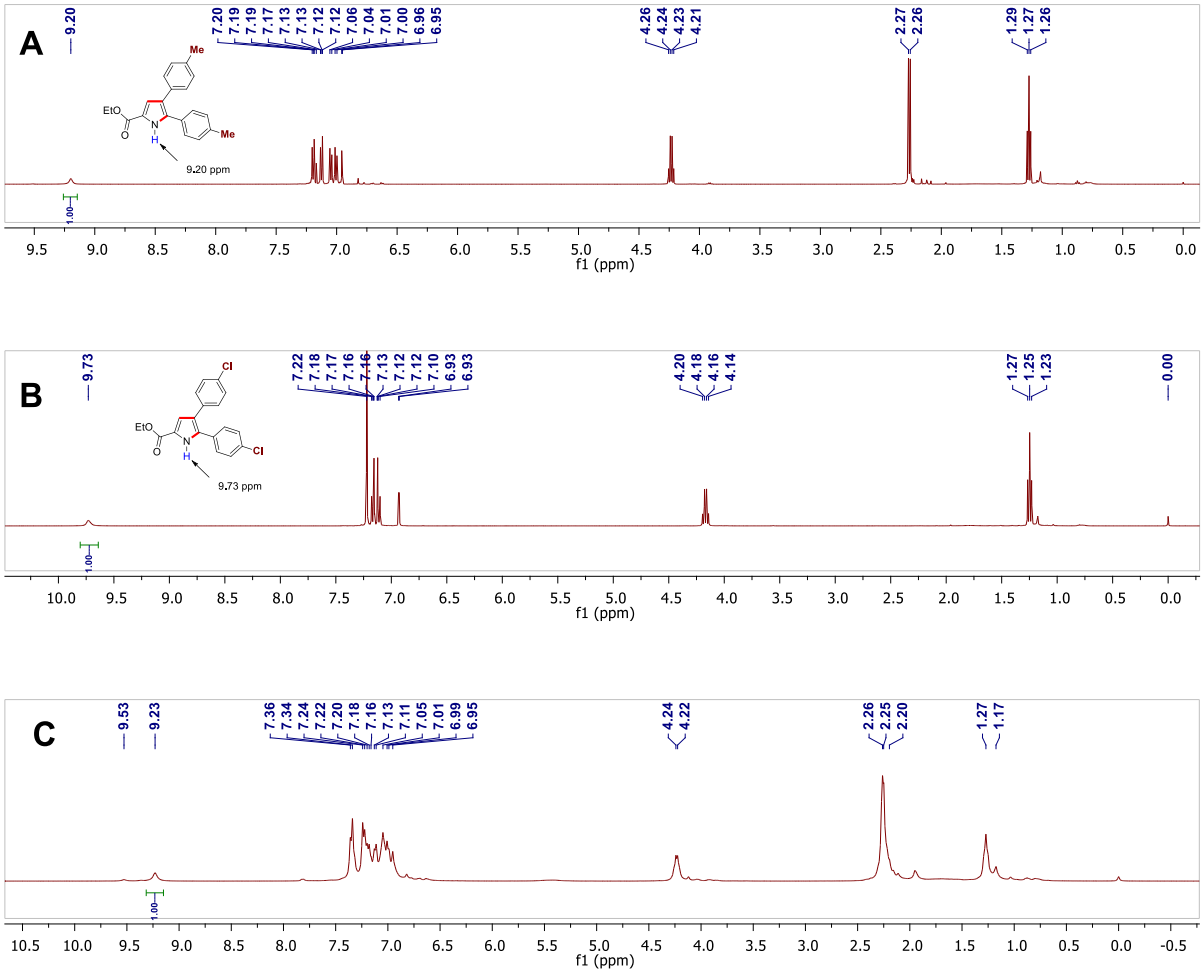


Figure S4. (A) ^{1}H NMR of **4ab** (B) ^{1}H NMR of **4ae** (C) Crude ^{1}H NMR for intermolecular competitive experiment between **2b** and **2e**.

7. References

1. B. Sun, T. Yoshino, S. Matsunaga and M. Kanai, *Adv. Synth. Catal.* 2014, **356**, 1491.

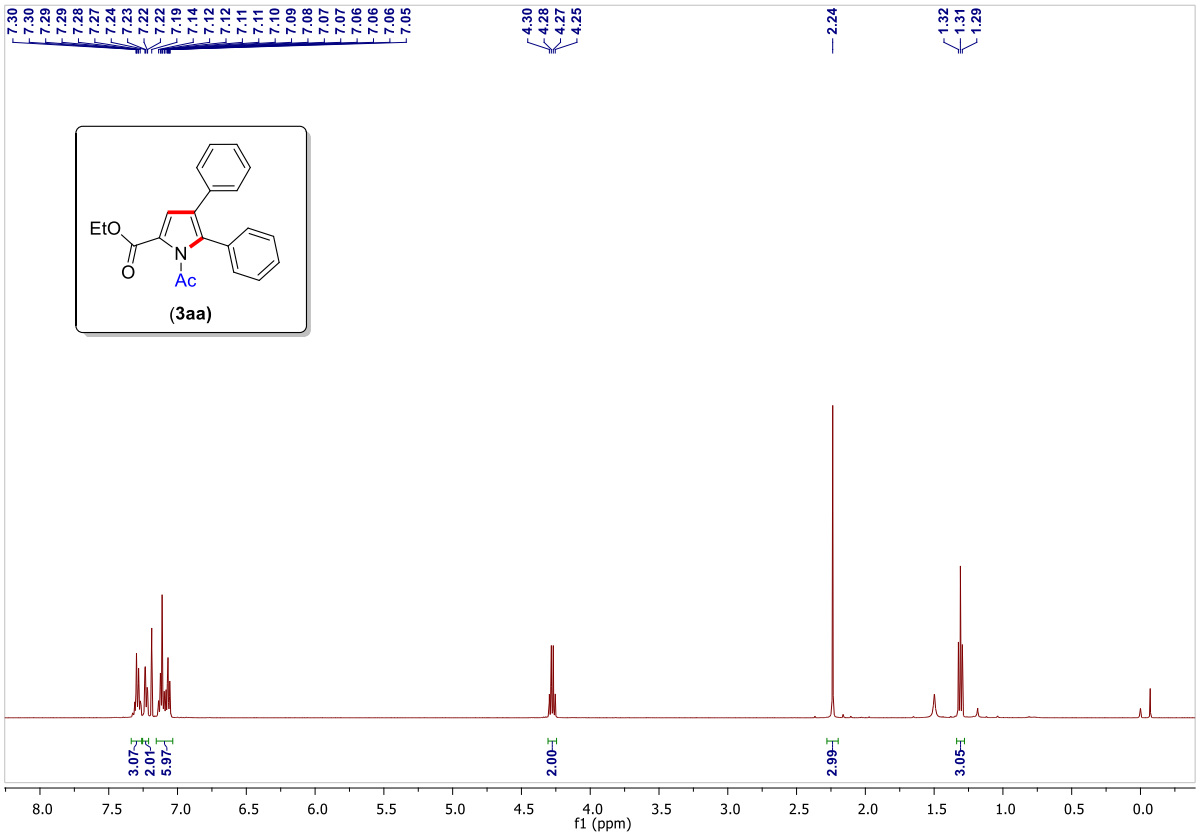
2. B. Li, N. Wang, Y. Liang, S. Xu and B. Wang, *Org. Lett*. 2013, **15**, 136.

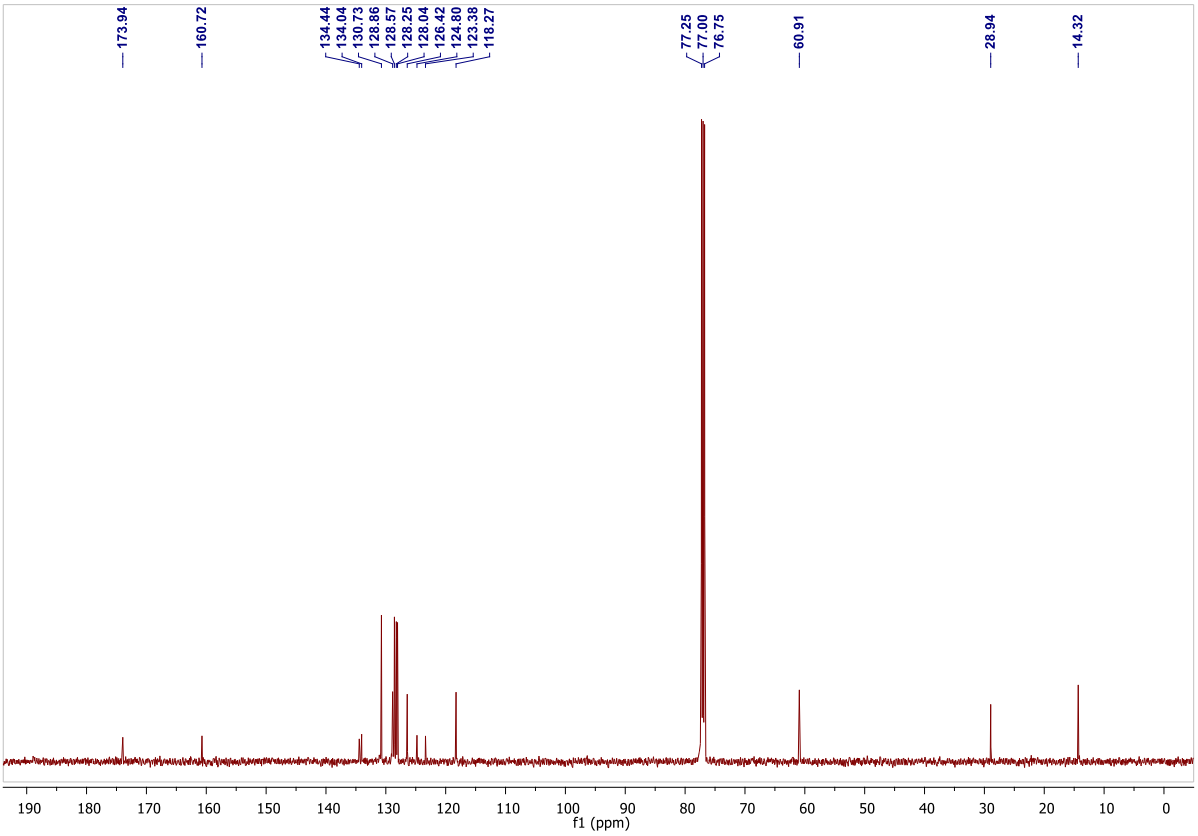
3. K. Murugan and S. T. Liu, *Tetrahedron Lett*, 2013, **54**, 2608.

Appendix I

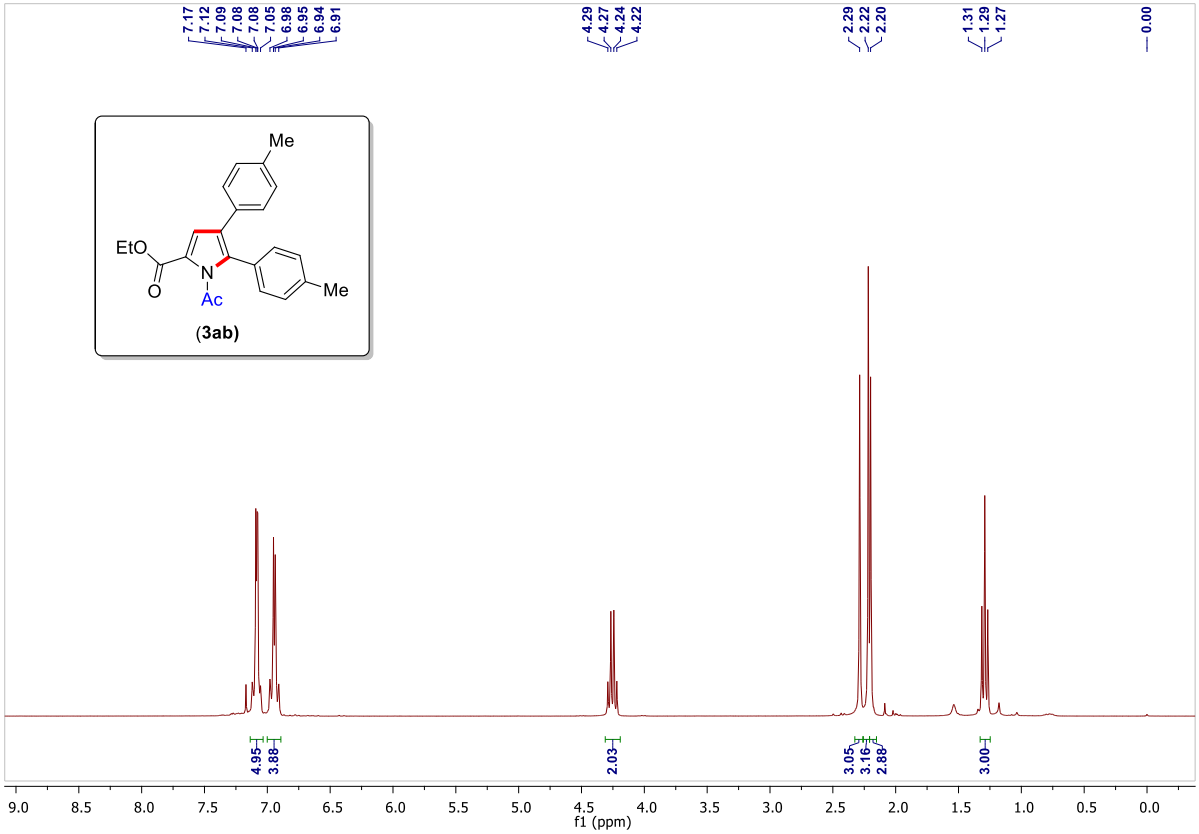
Spectral Copies of ^{1}H and ^{13}C NMR of Compounds Obtained in this study

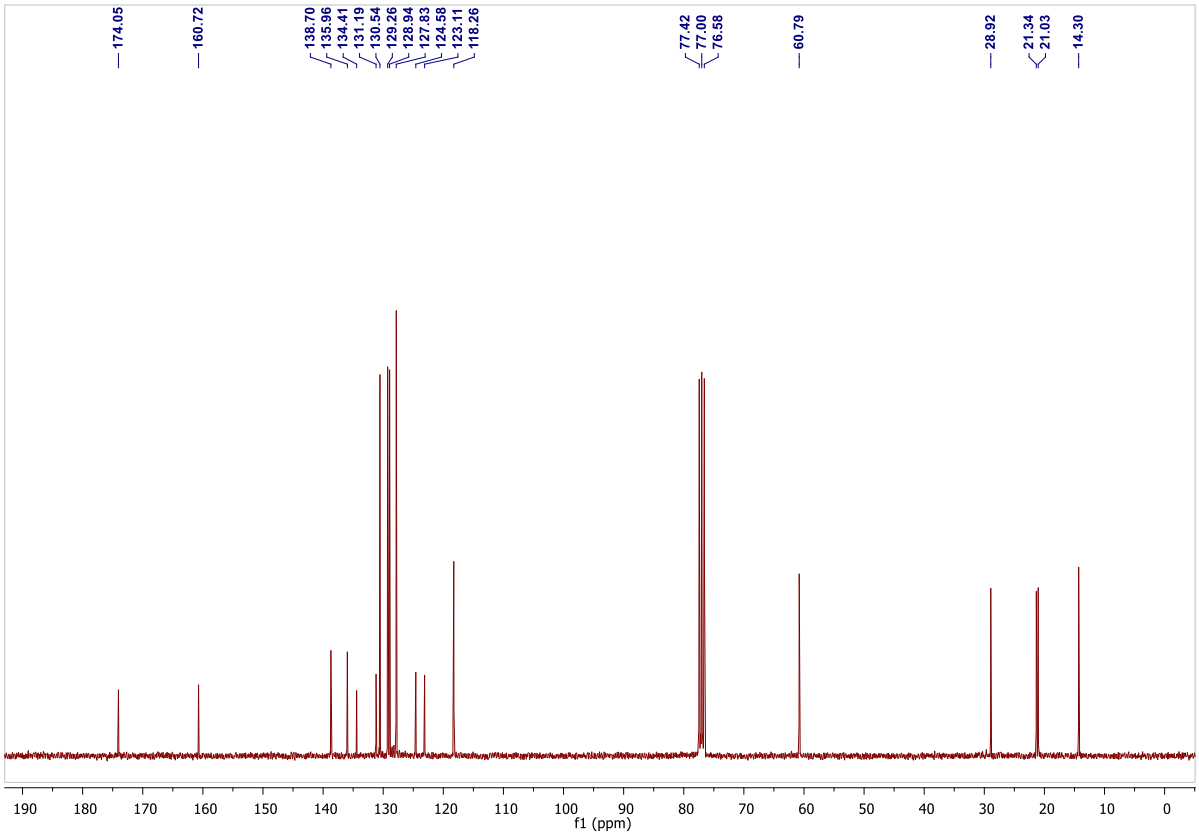
Ethyl 1-acetyl-4,5-diphenyl-1*H*-pyrrole-2-carboxylate (Table 2, **3aa**)



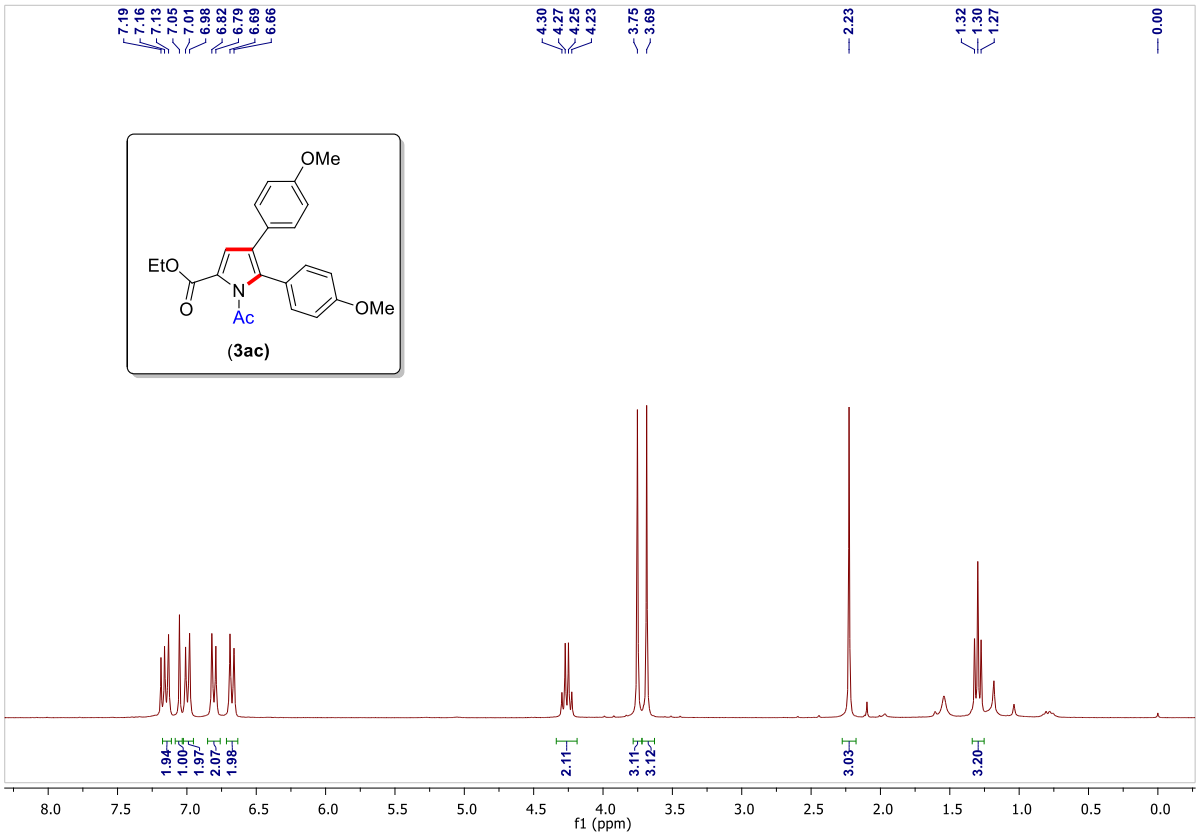


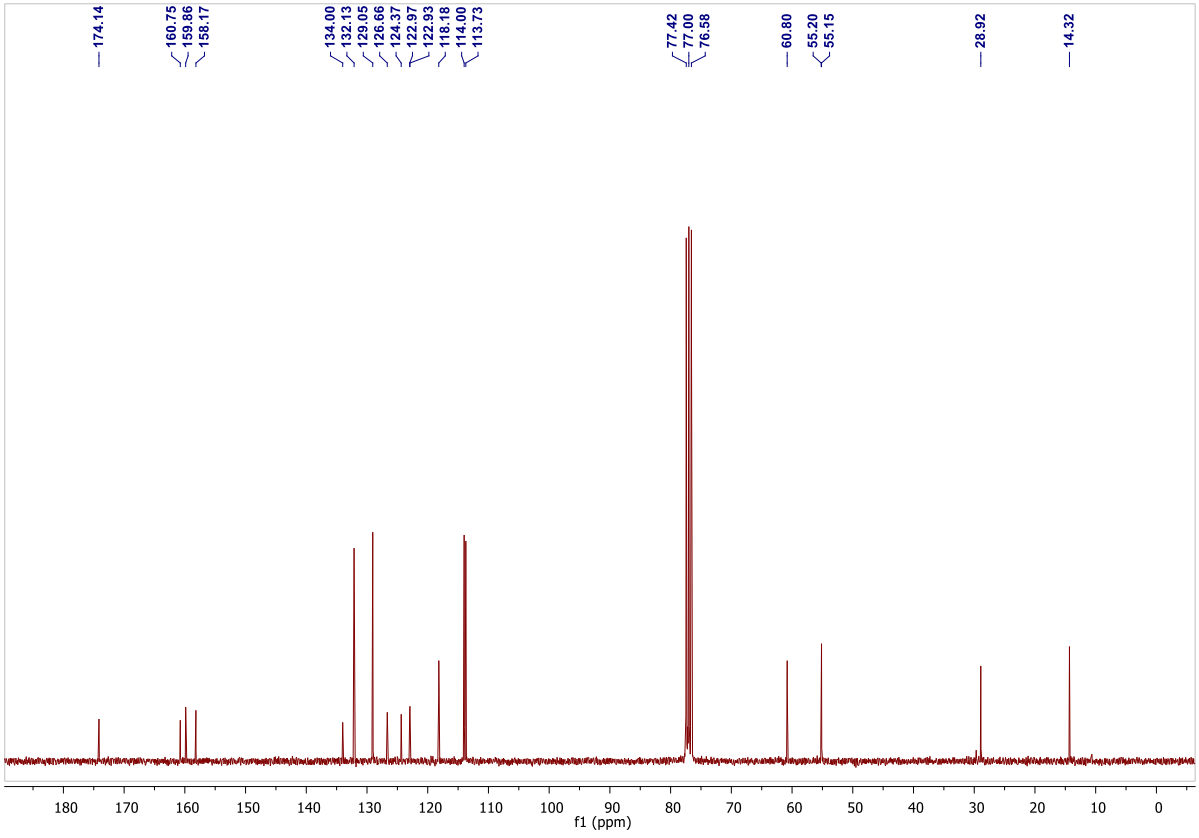
Ethyl 1-acetyl-4,5-di-*p*-tolyl-1*H*-pyrrole-2-carboxylate (Table 2, **3ab**)



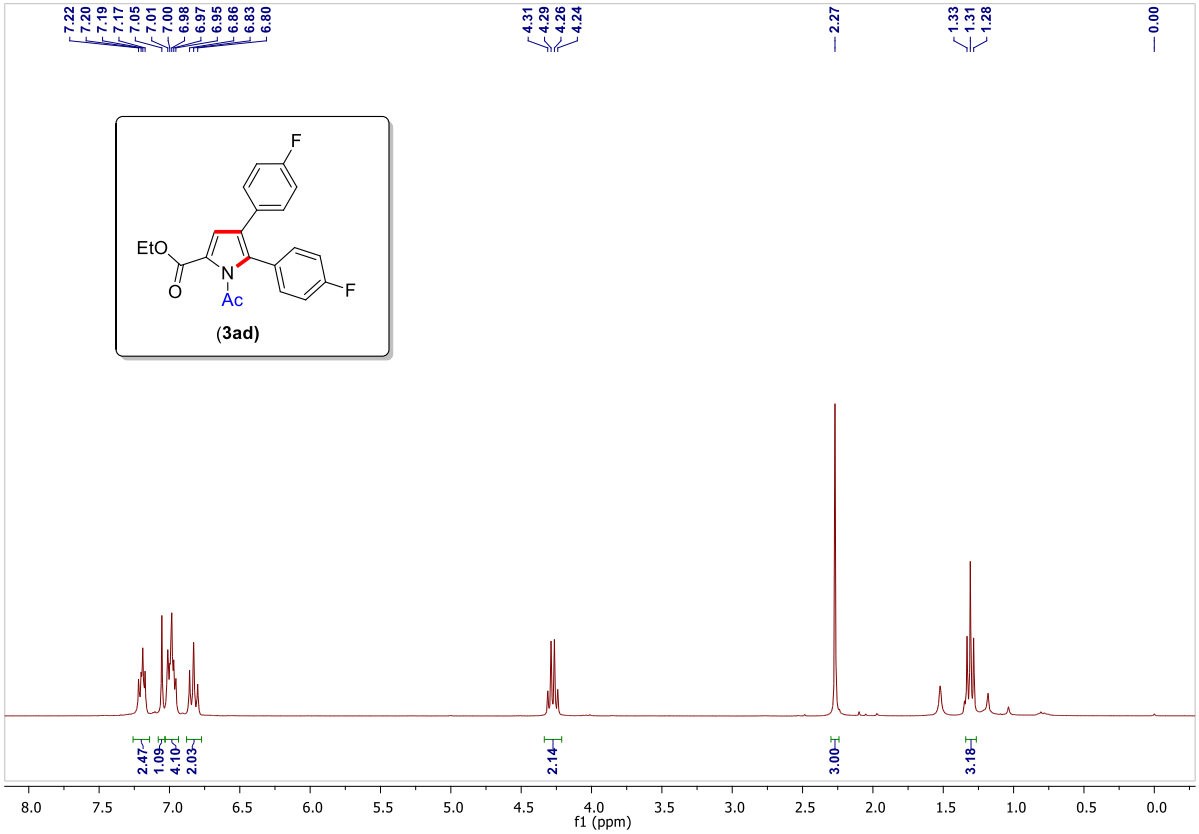


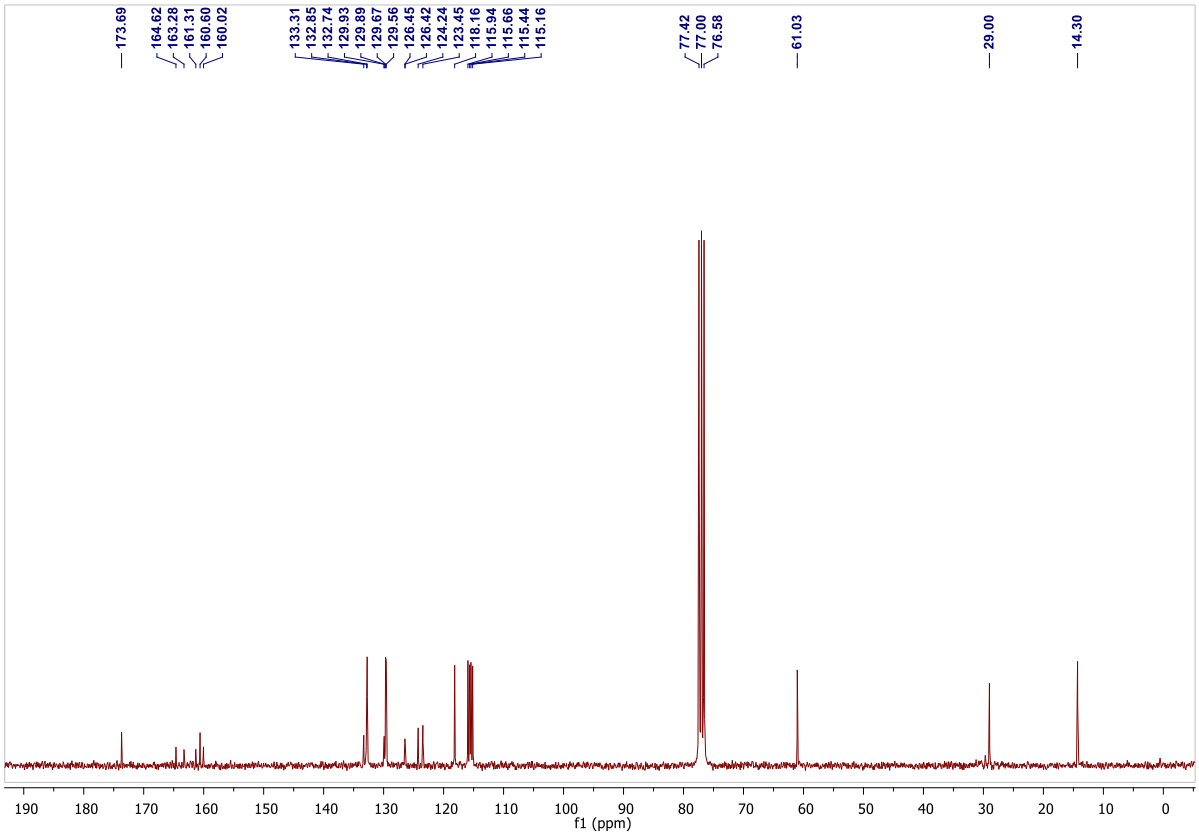
Ethyl 1-acetyl-4,5-bis(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (Table 2, **3ac**)



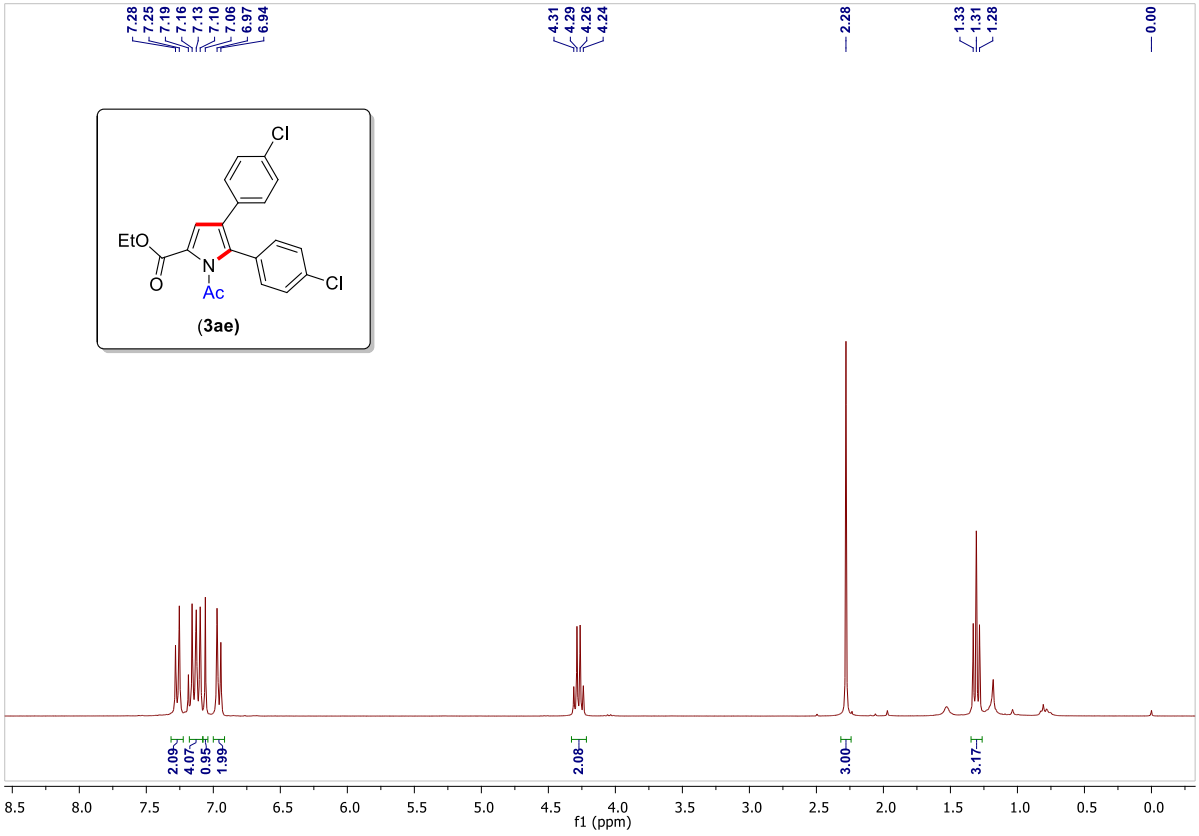


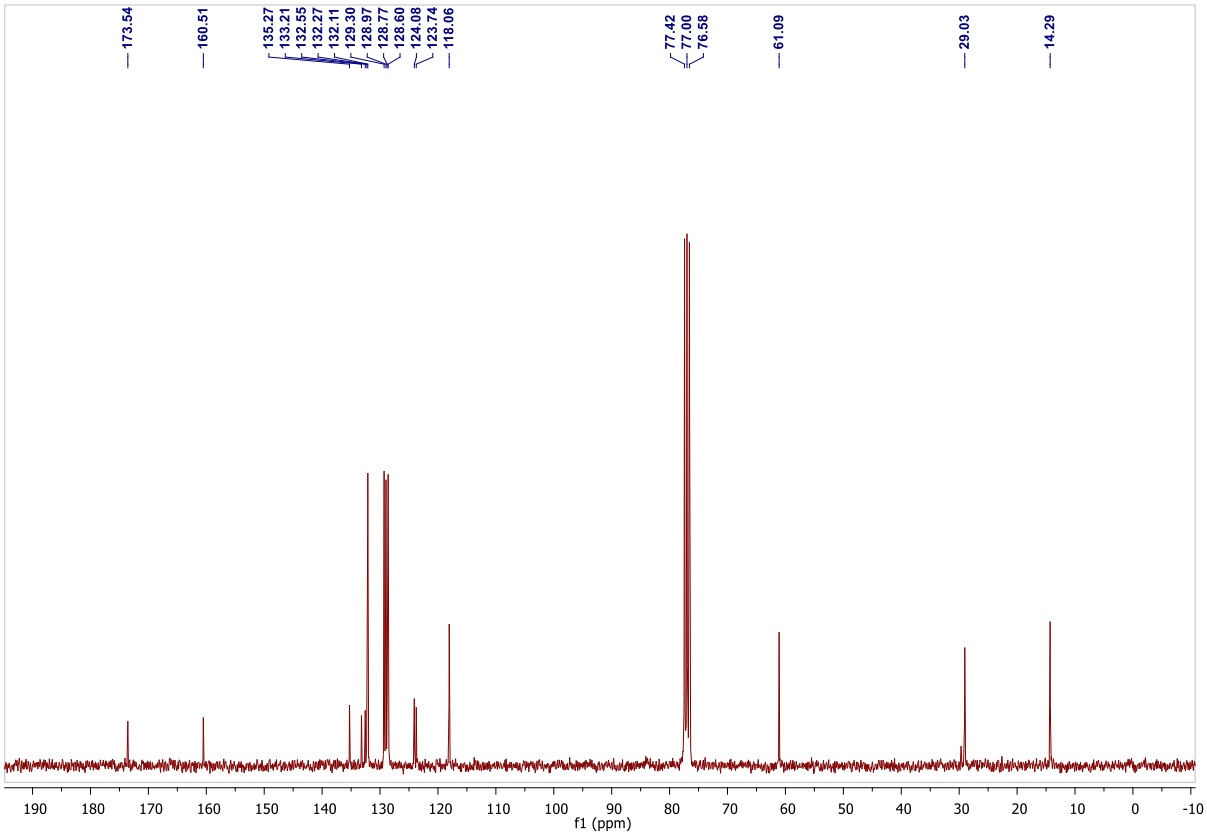
Ethyl 1-acetyl-4,5-bis(4-fluorophenyl)-1H-pyrrole-2-carboxylate (Table 2, **3ad**)



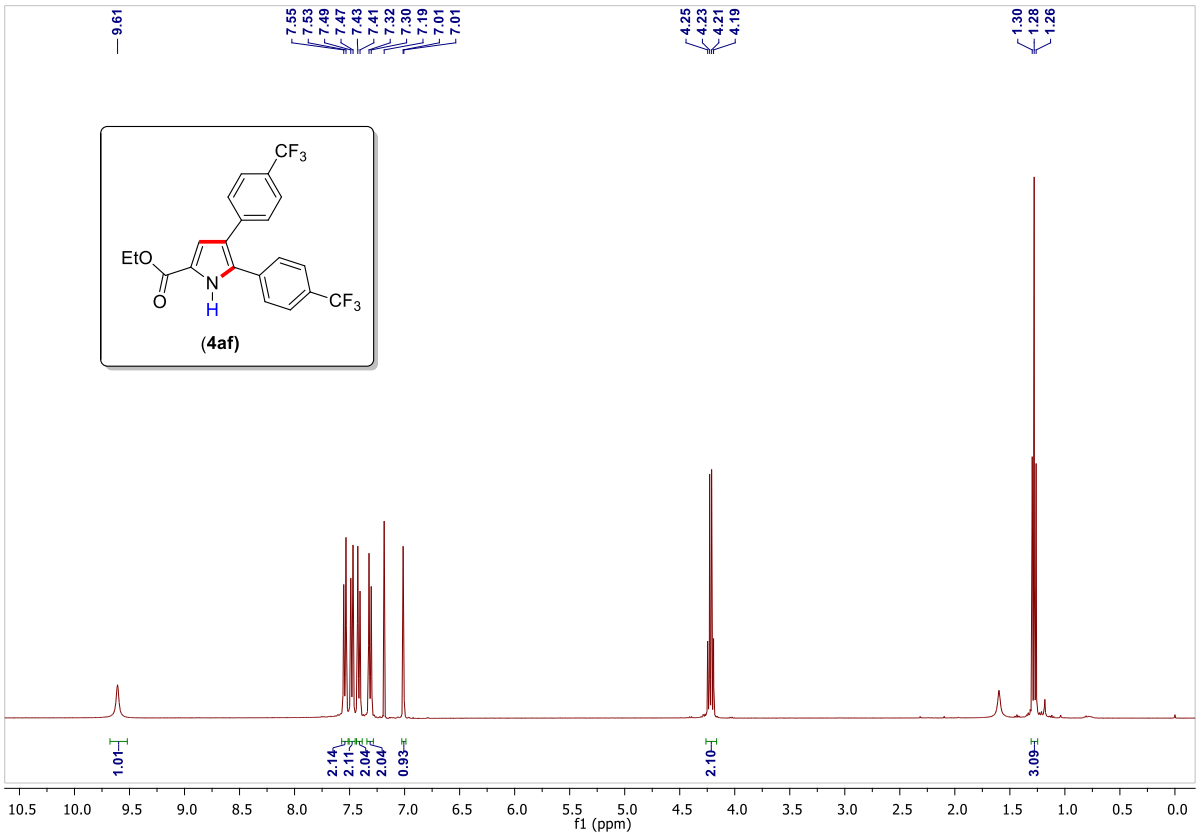


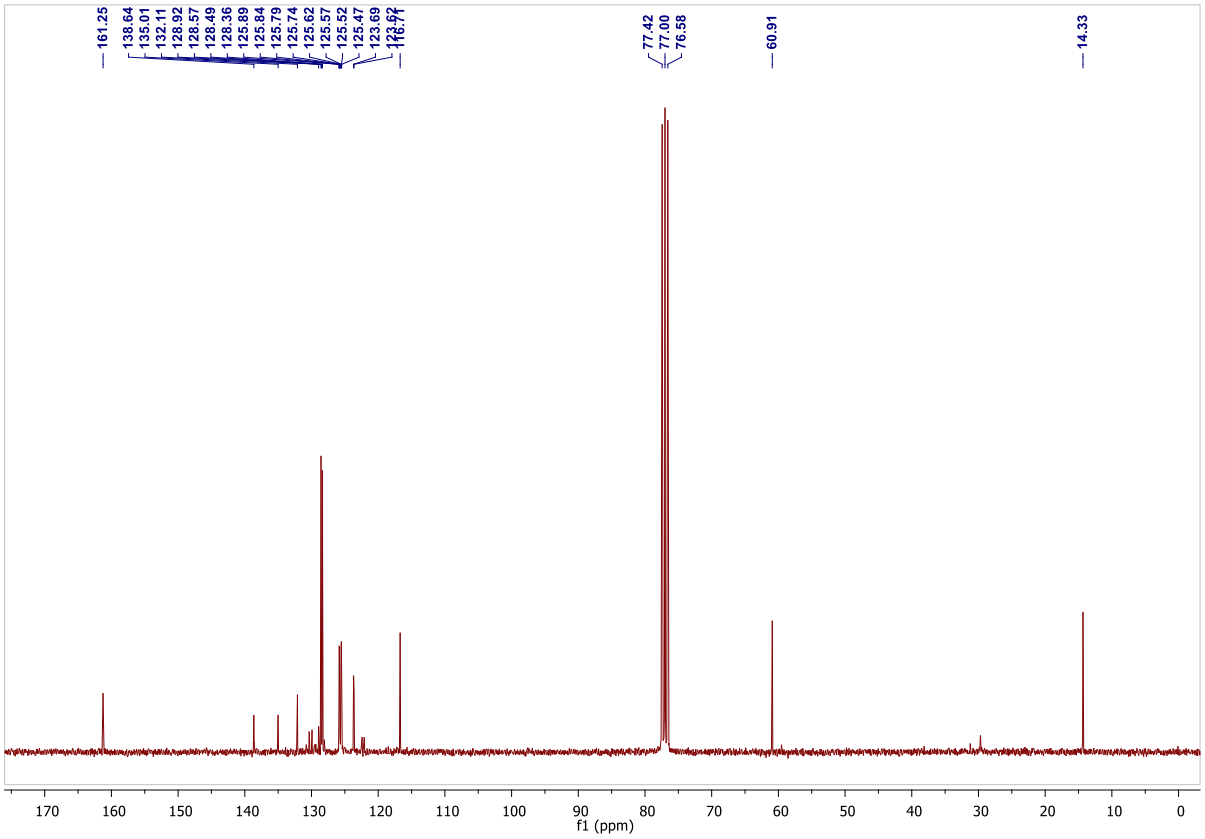
Ethyl 1-acetyl-4,5-bis(4-chlorophenyl)-1H-pyrrole-2-carboxylate (Table 2, **3ae**)



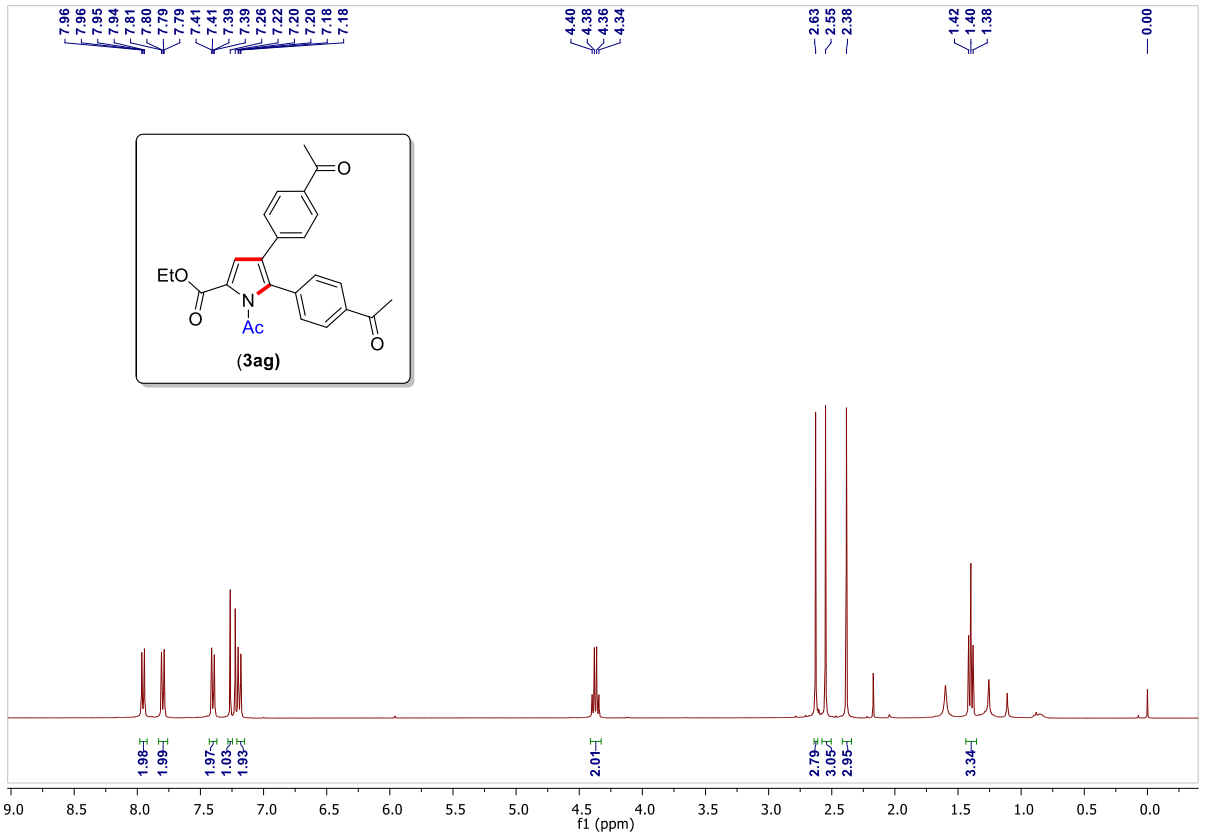


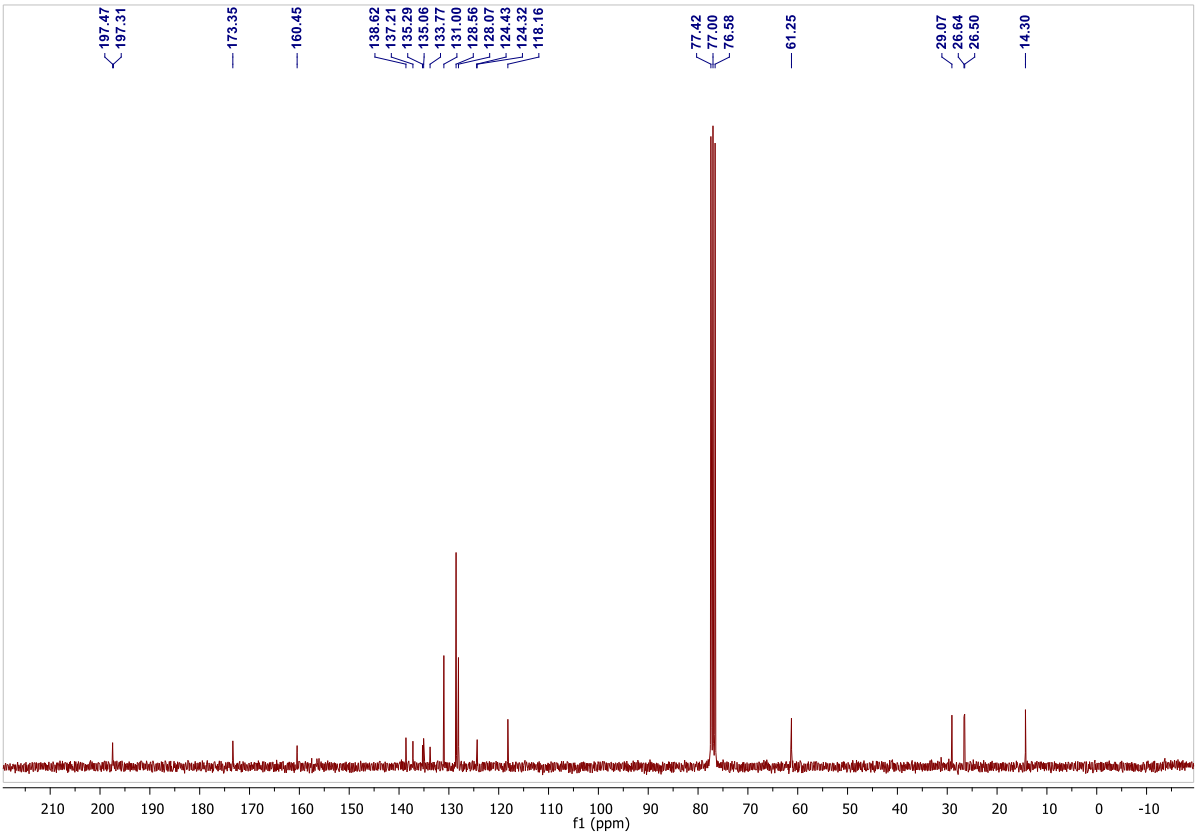
Ethyl 4,5-bis(4-(trifluoromethyl)phenyl)-1H-pyrrole-2-carboxylate (Table 2, **4af**)



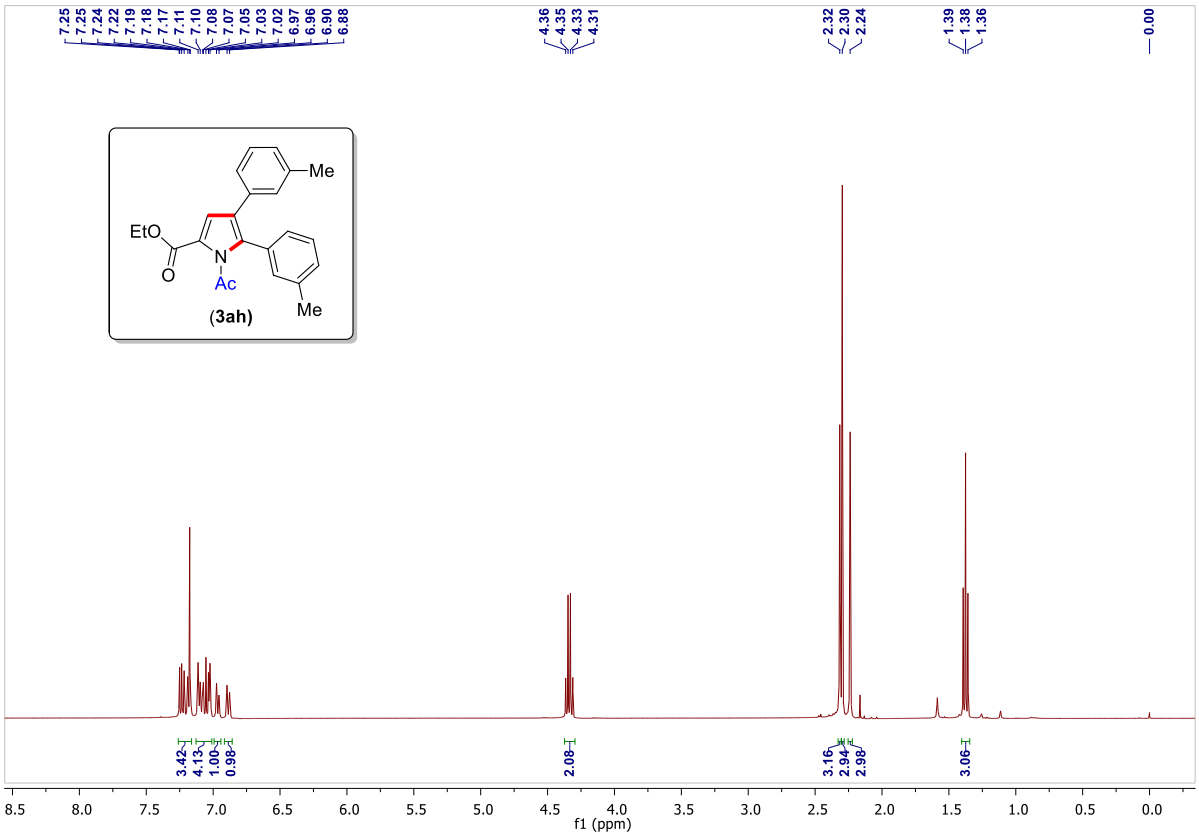


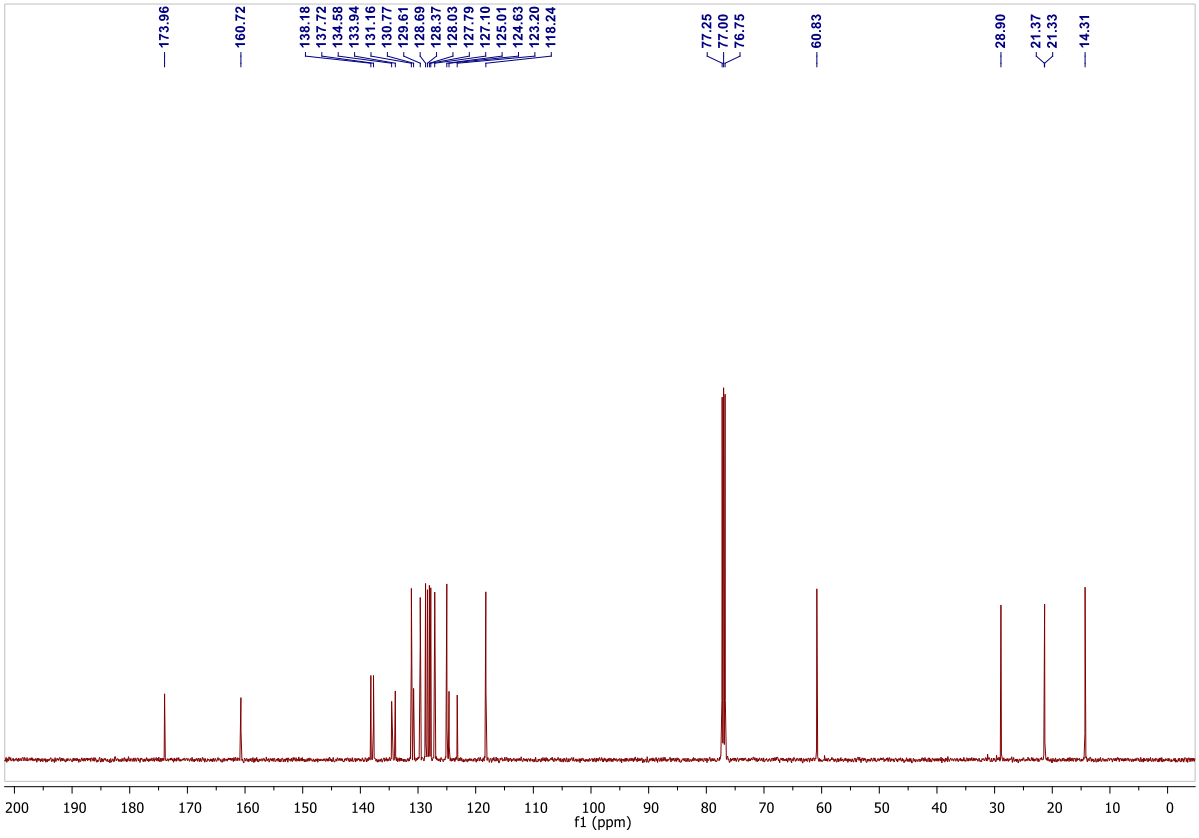
Ethyl 1-acetyl-4,5-bis(4-acetylphenyl)-1H-pyrrole-2-carboxylate (Table 2, **3ag**)



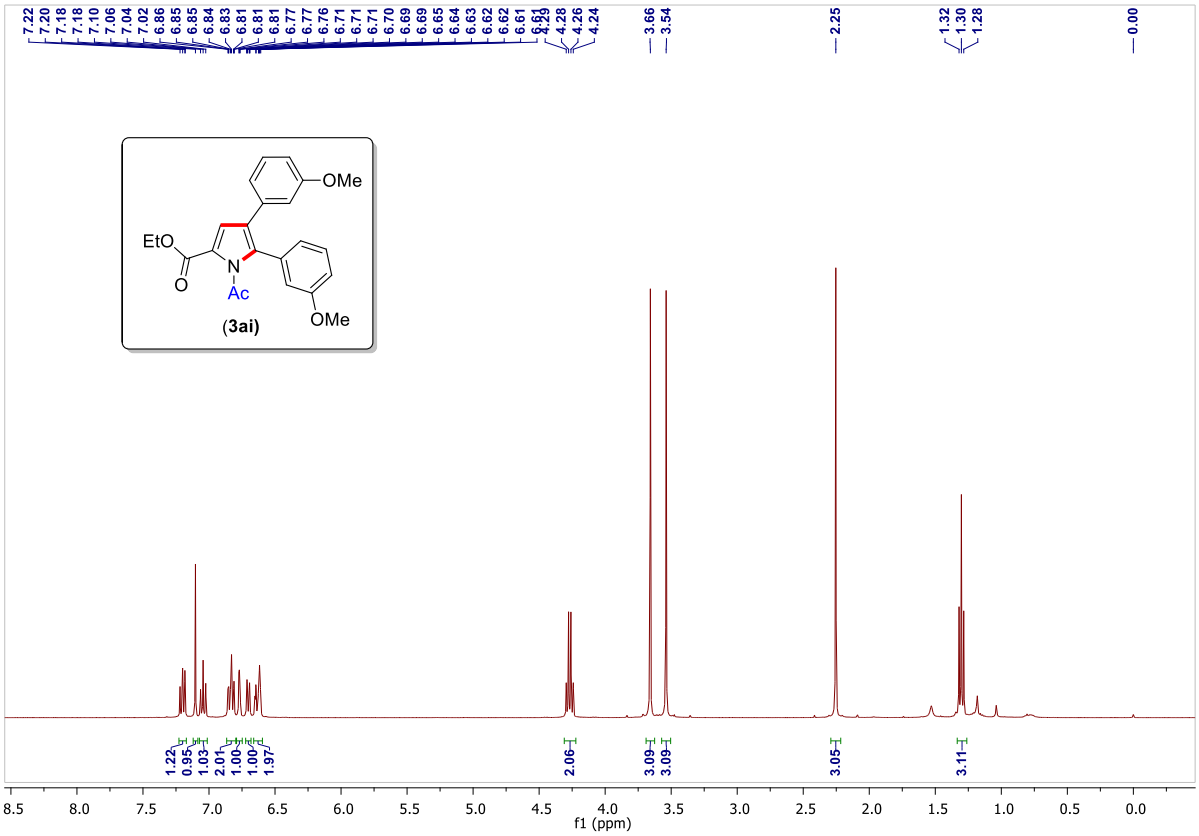


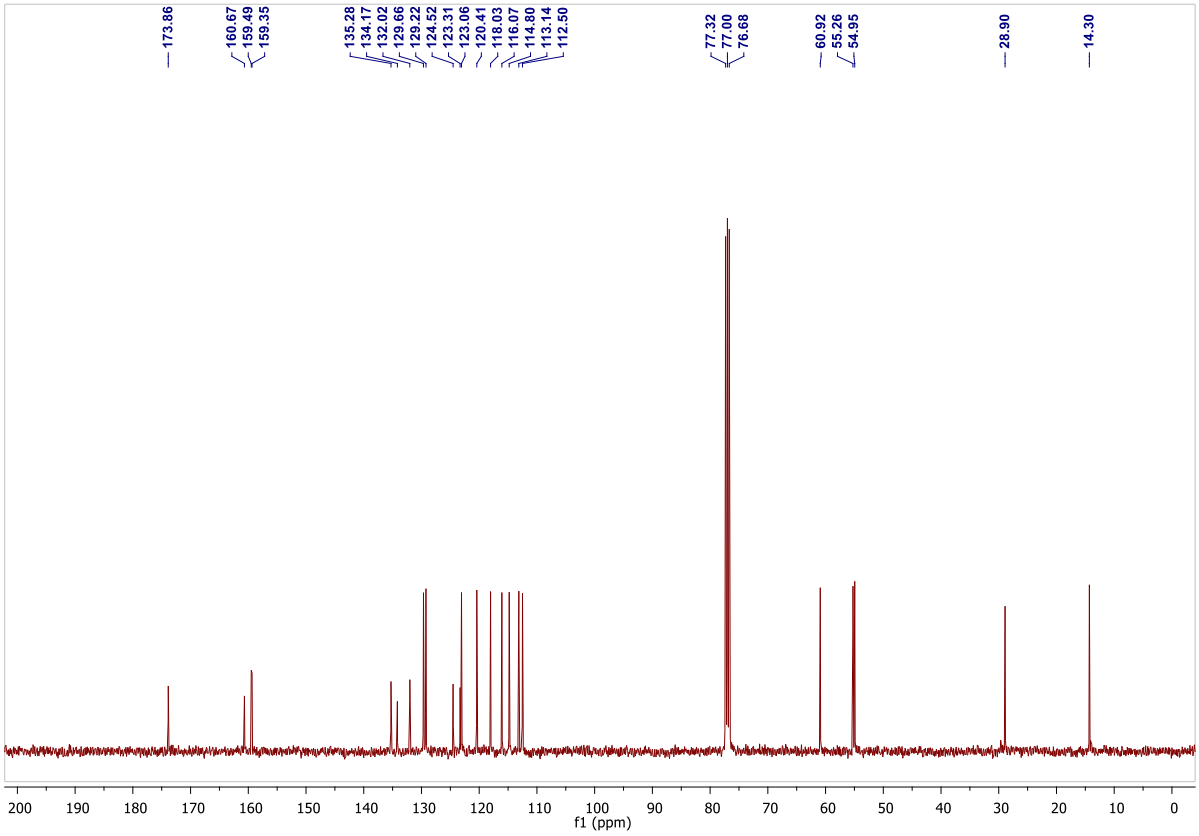
Ethyl 1-acetyl-4,5-di-m-tolyl-1H-pyrrole-2-carboxylate (Table 2, **3ah**)



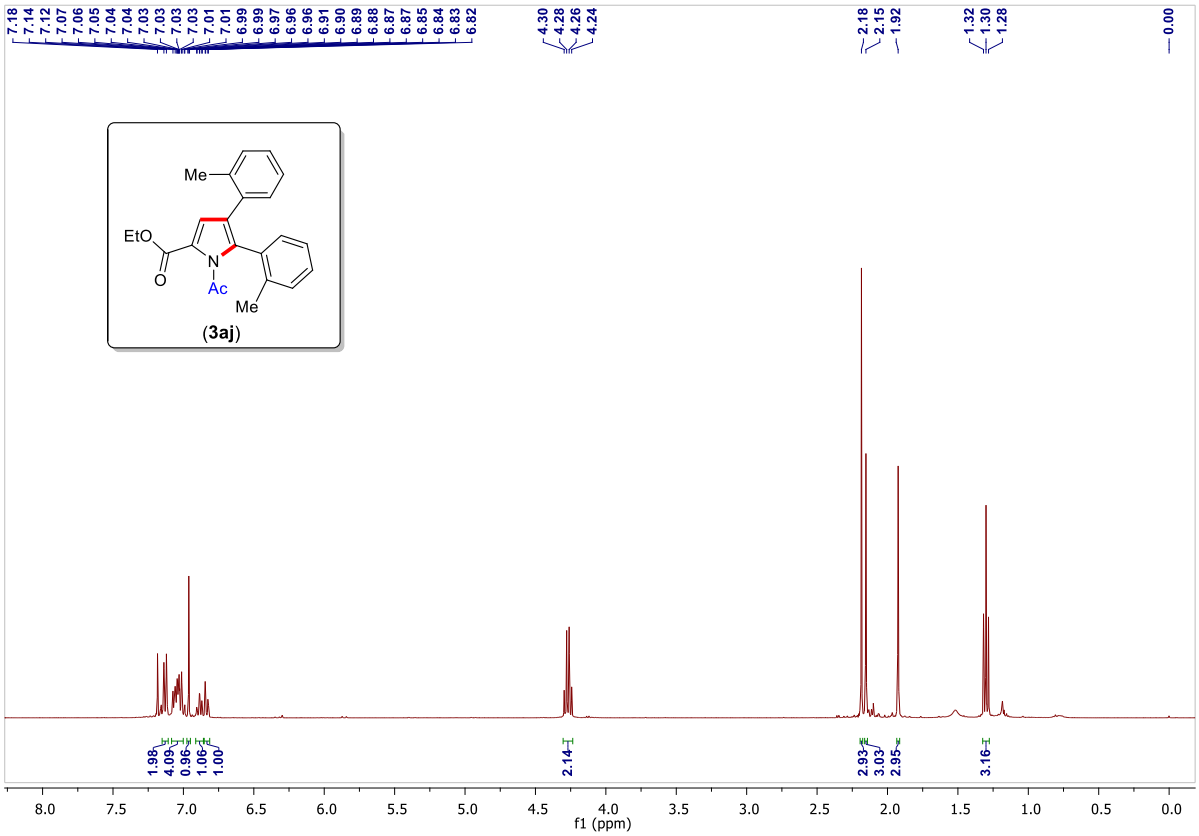


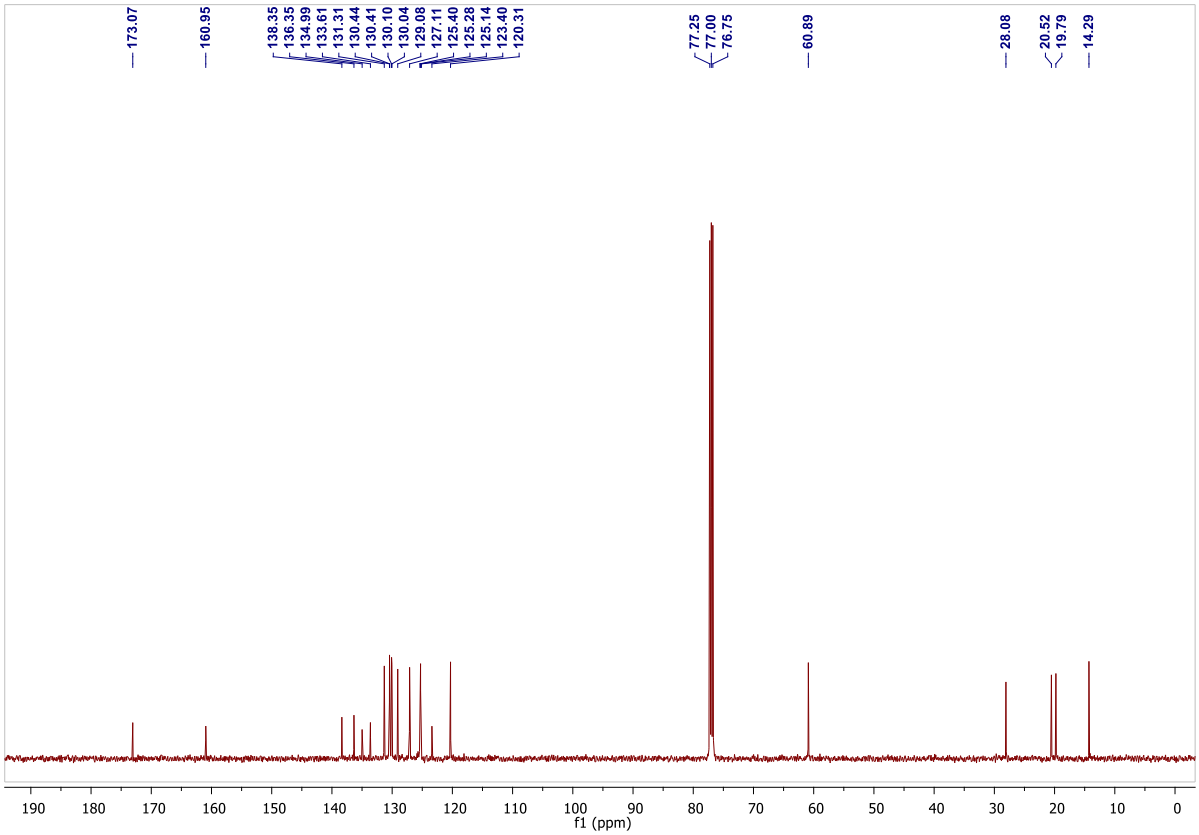
Ethyl 1-acetyl-4,5-bis(3-methoxyphenyl)-1H-pyrrole-2-carboxylate (Table 2, **3ai**)



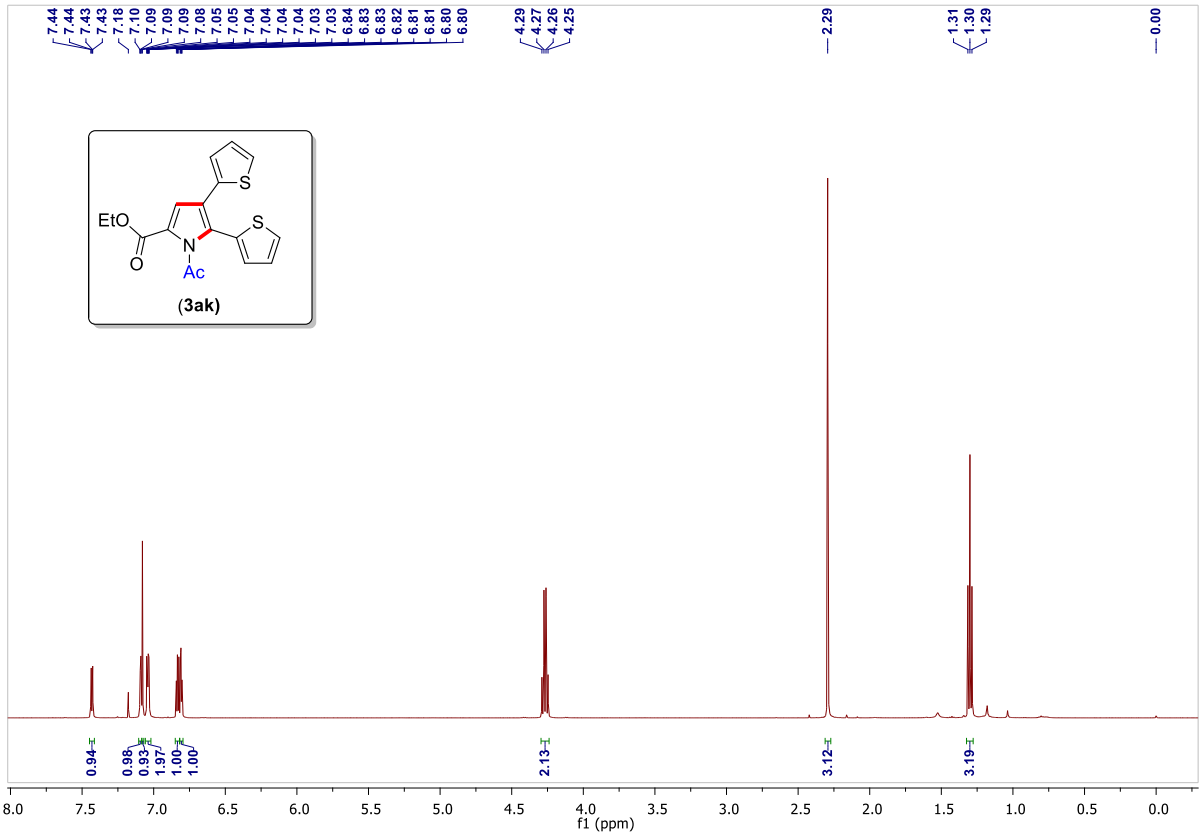


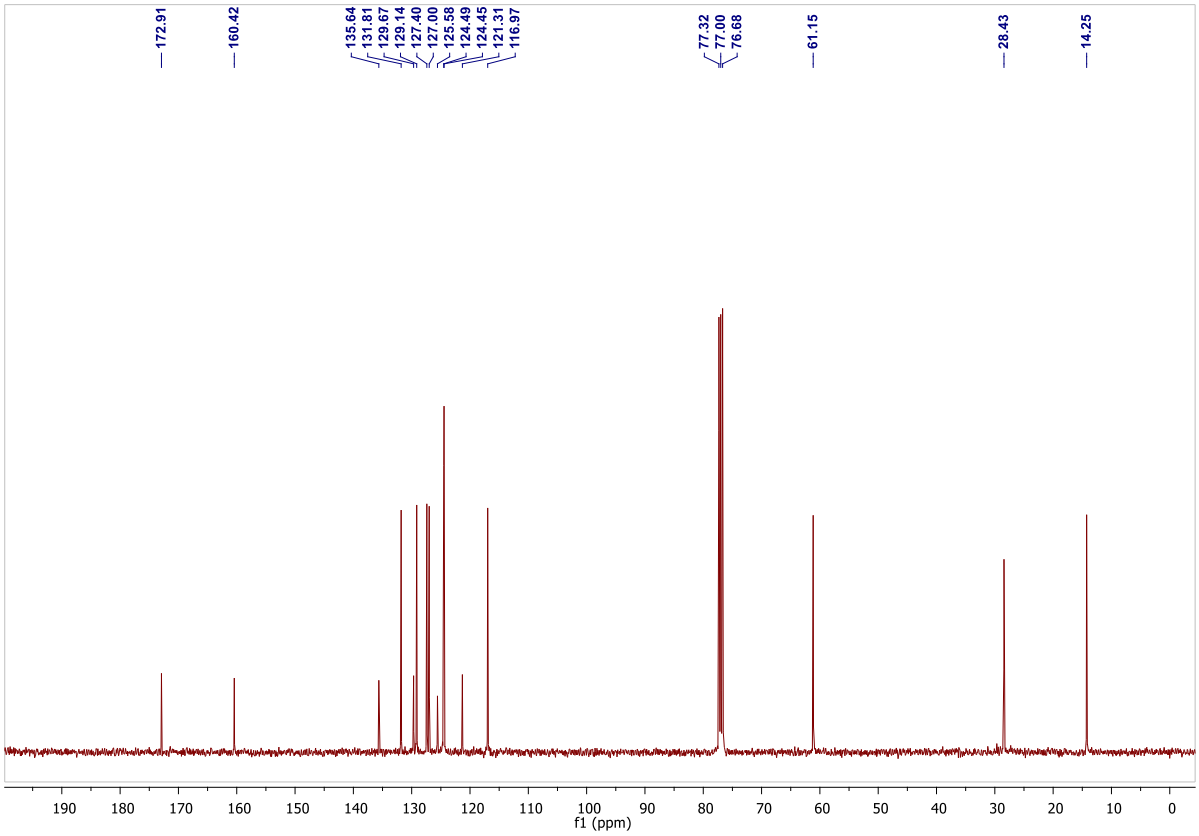
Ethyl 1-acetyl-4,5-di-*o*-tolyl-1H-pyrrole-2-carboxylate (Table 2, **3aj**)



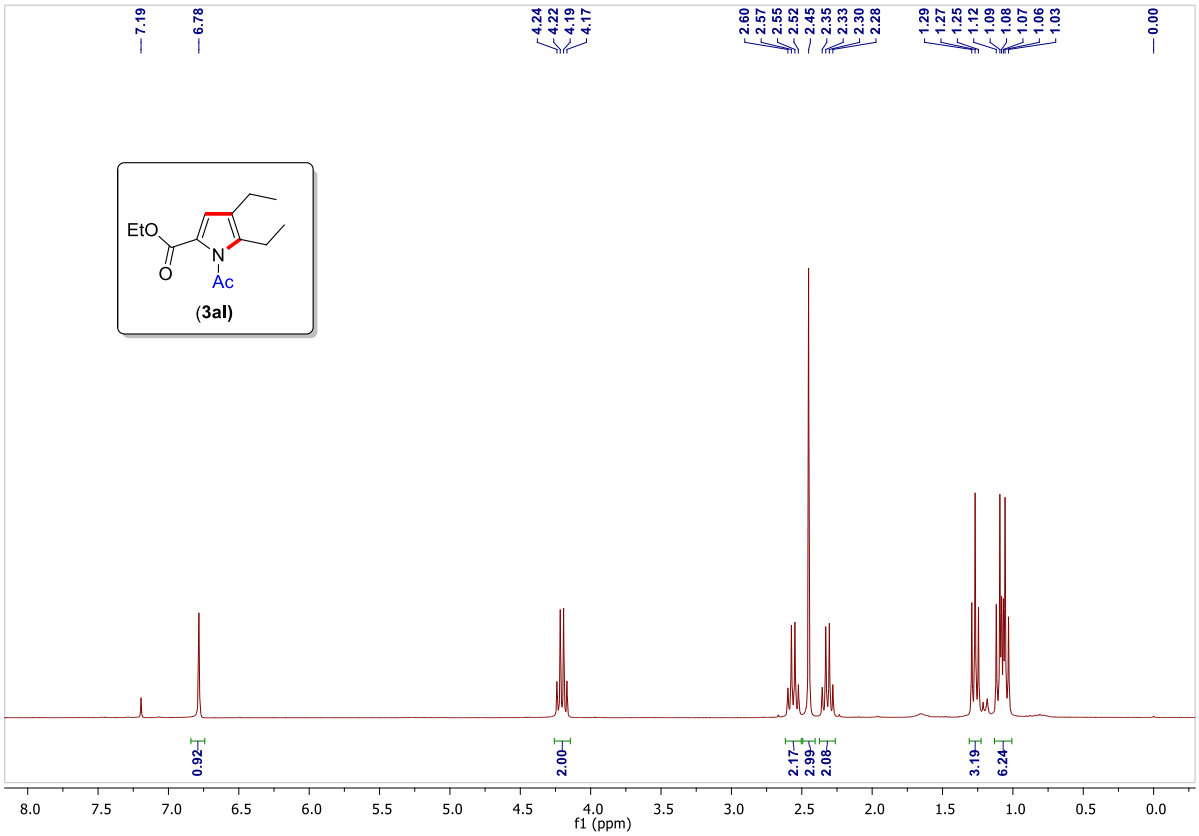


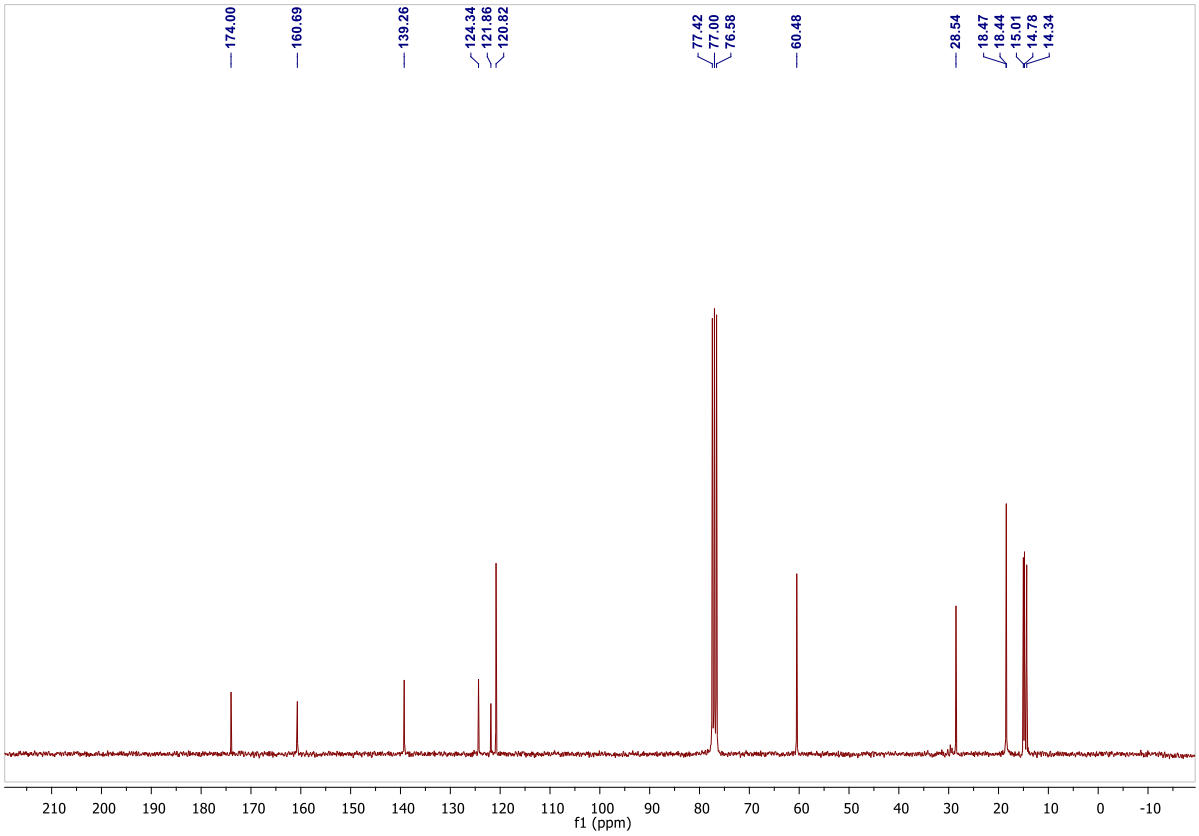
Ethyl 1-acetyl-4,5-di(thiophen-2-yl)-1H-pyrrole-2-carboxylate (Table 2, **3ak**)



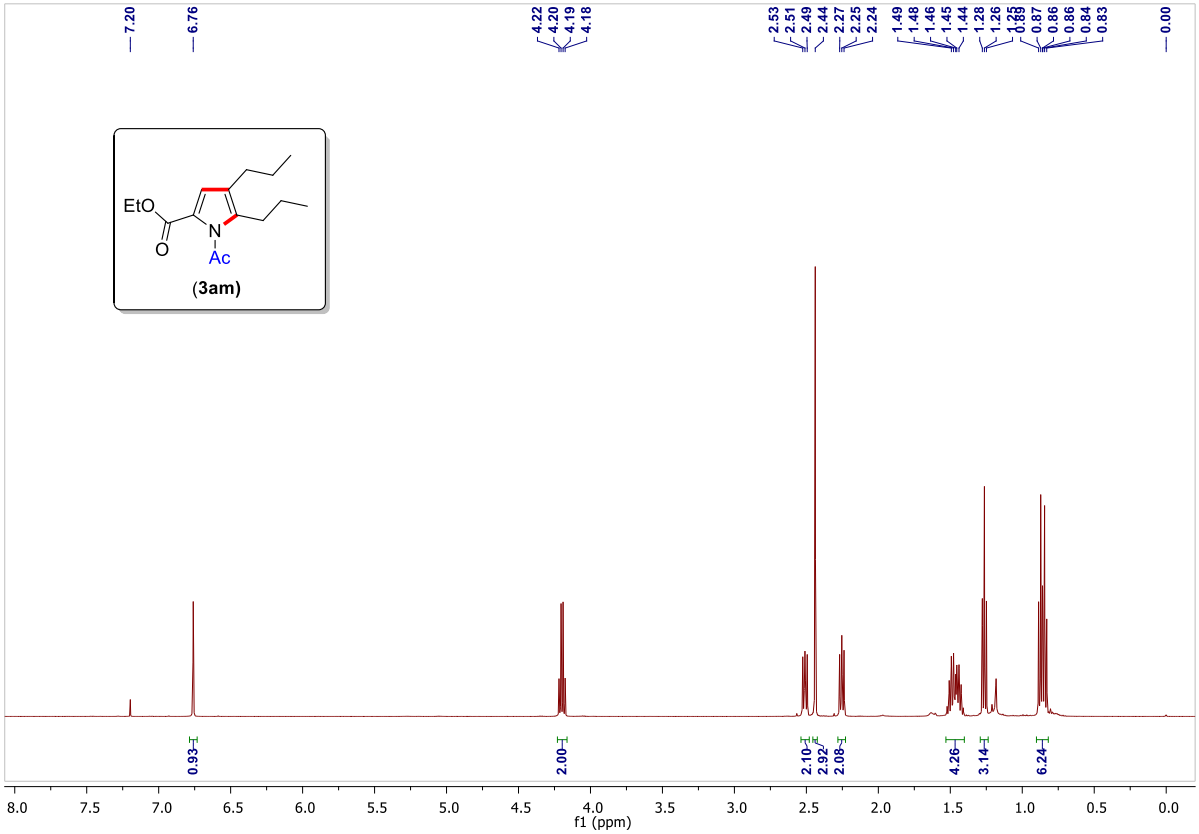


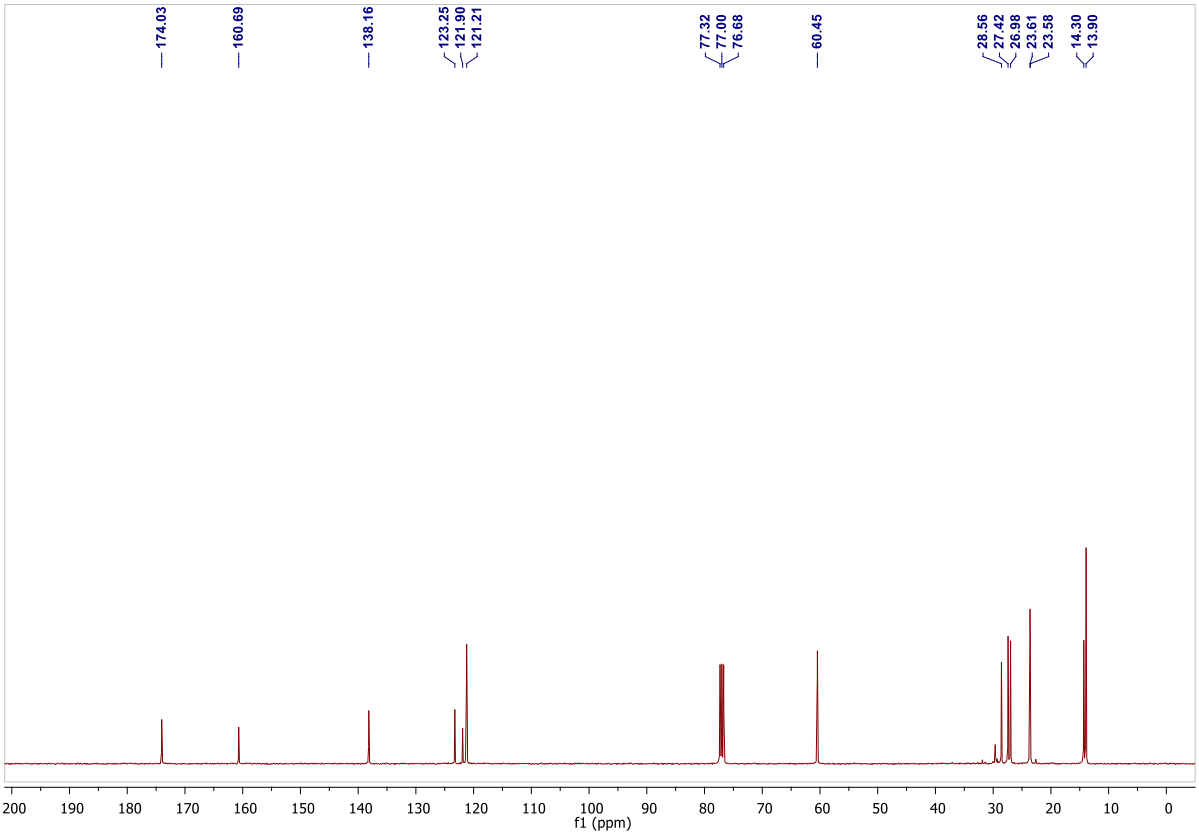
Ethyl 1-acetyl-4,5-diethyl-1H-pyrrole-2-carboxylate (Table 2, **3al**)



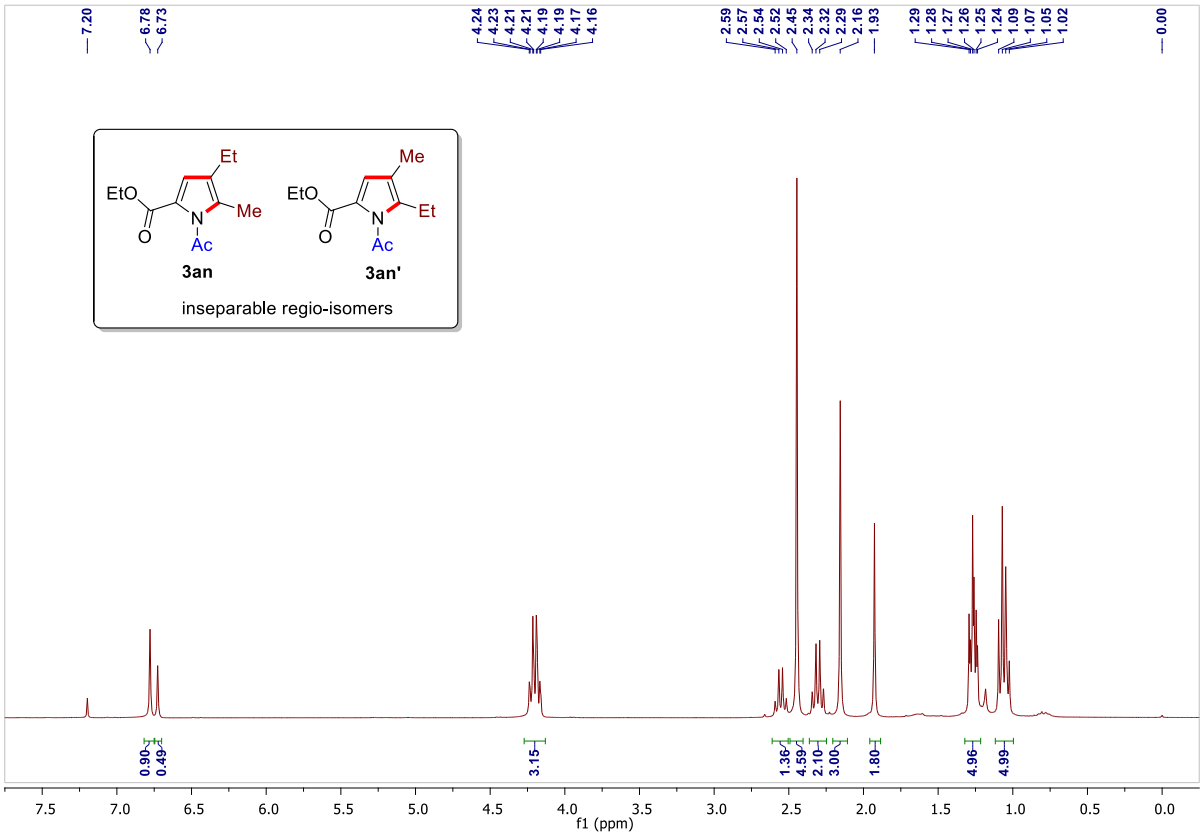


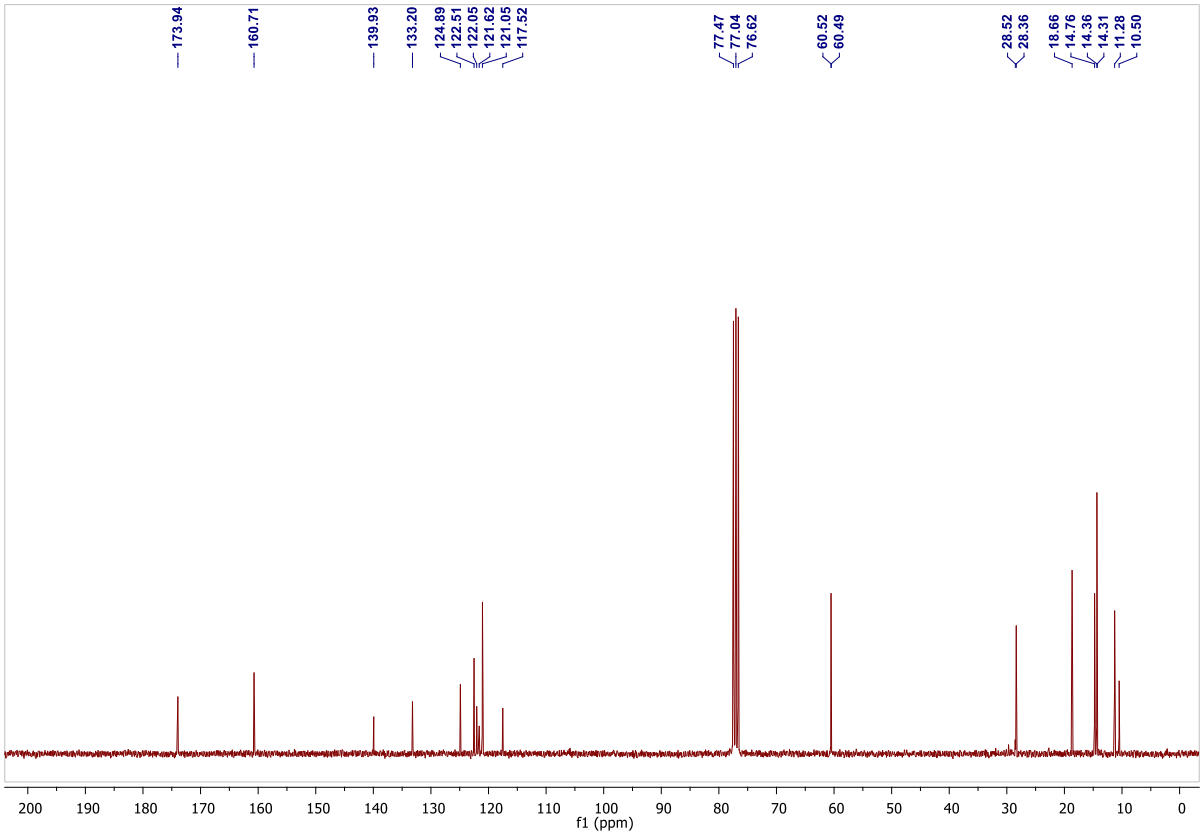
Ethyl 1-acetyl-4,5-dipropyl-1H-pyrrole-2-carboxylate (Table 2, **3am**)



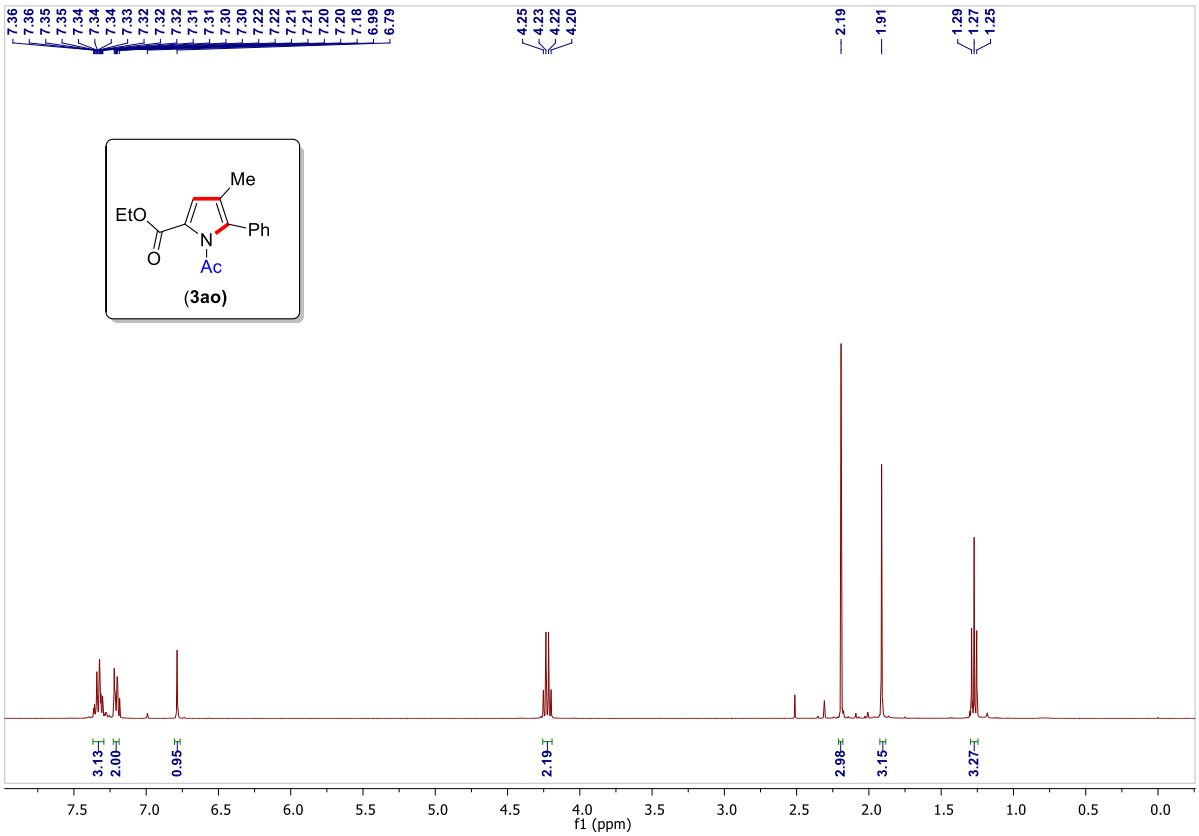


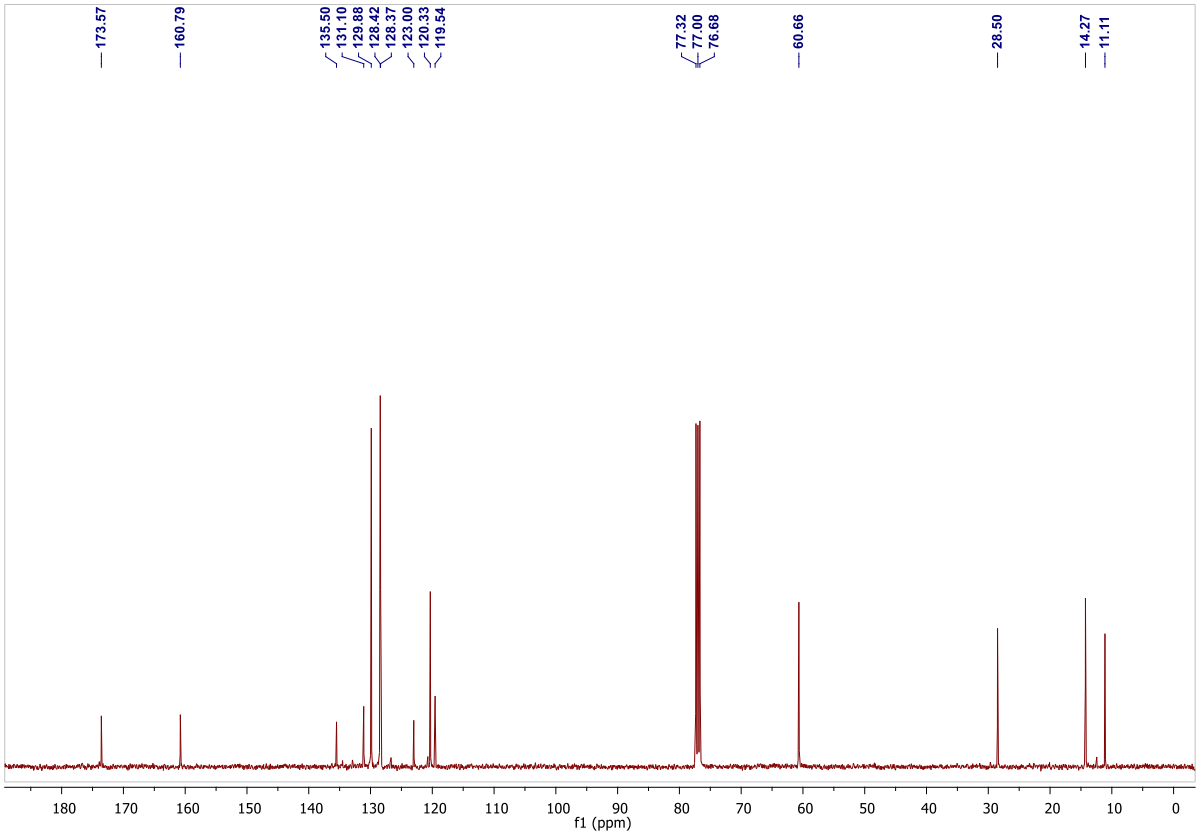
Ethyl 1-acetyl-4-ethyl-5-methyl-1*H*-pyrrole-2-carboxylate & Ethyl 1-acetyl-5-ethyl-4-methyl-1*H*-pyrrole-2-carboxylate (Table 2, **3an & 3an'**)



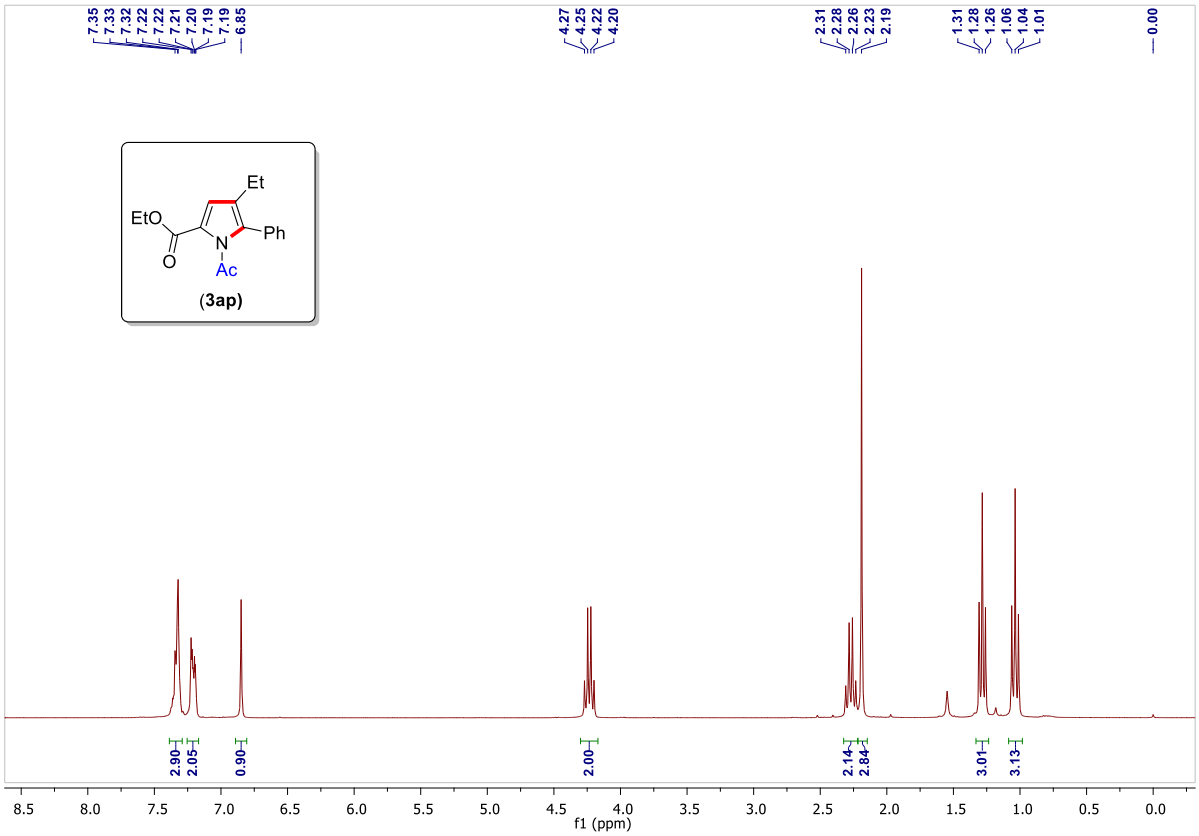


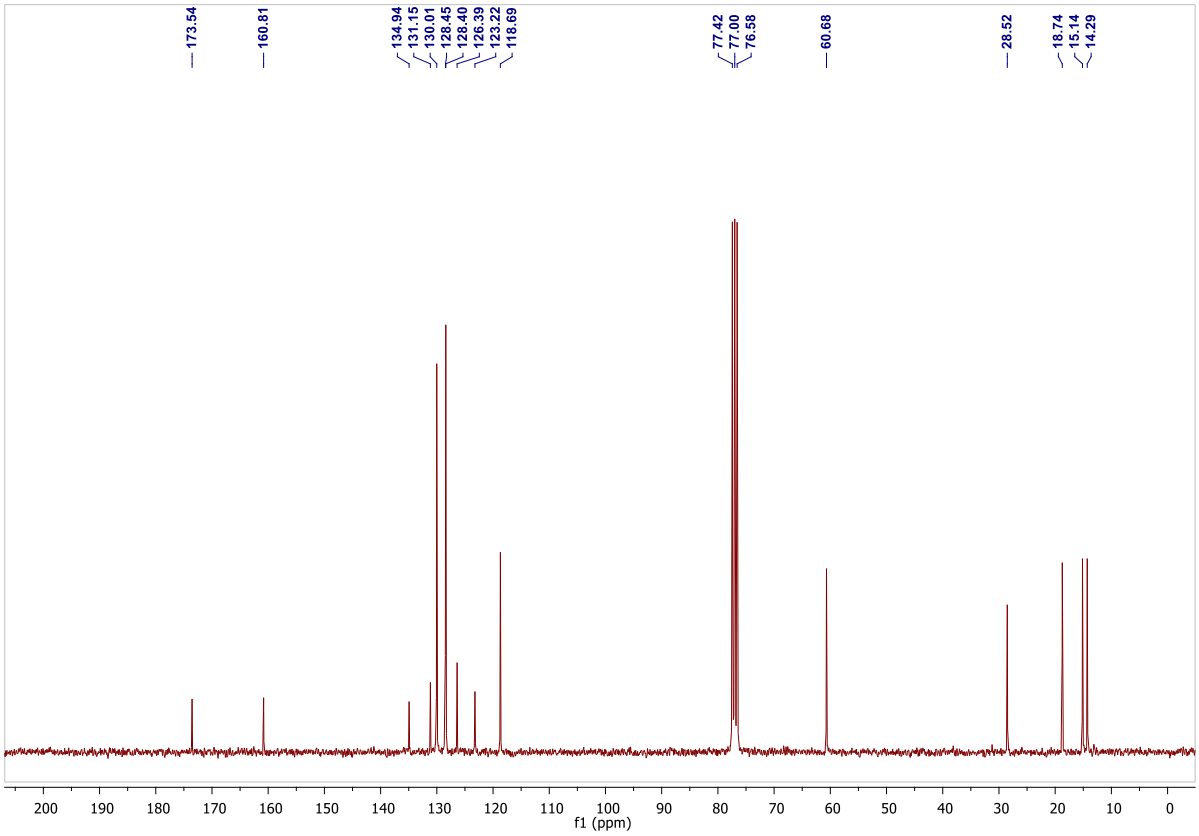
Ethyl 1-acetyl-4-methyl-5-phenyl-1H-pyrrole-2-carboxylate (Table 2, **3ao**)



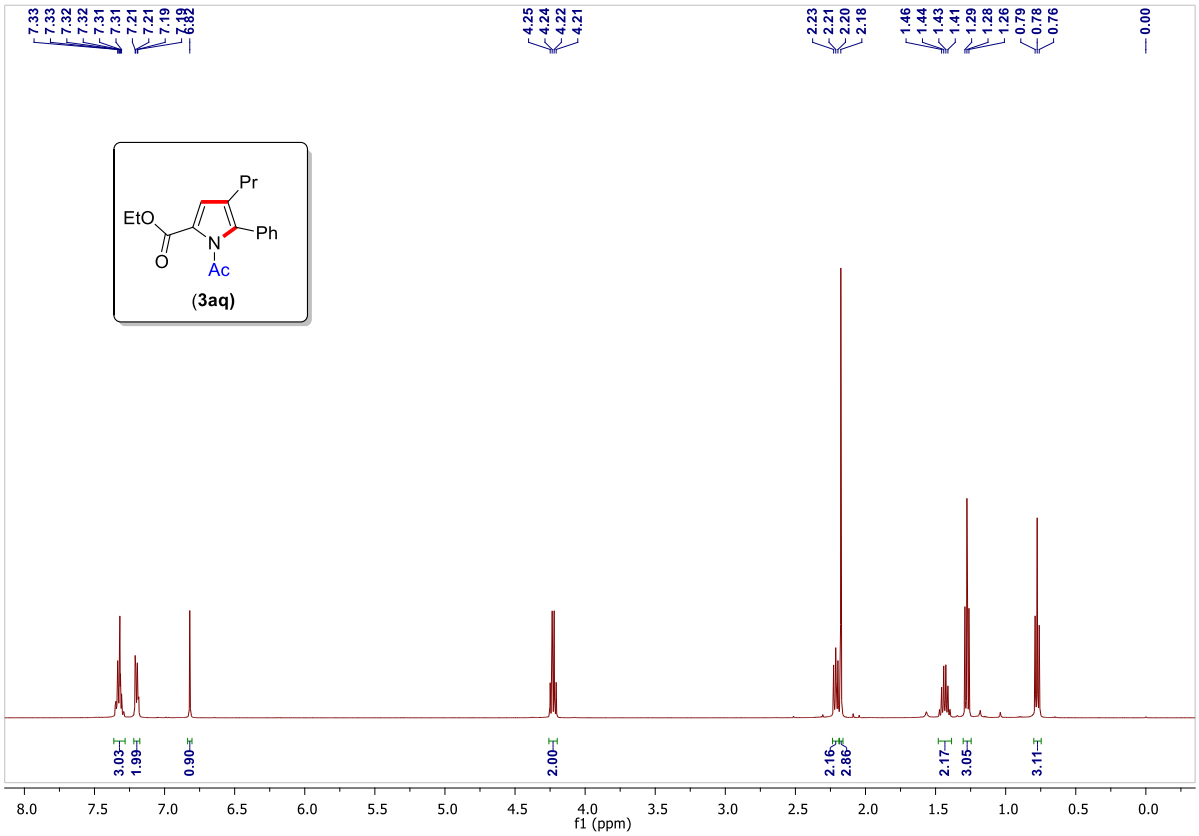


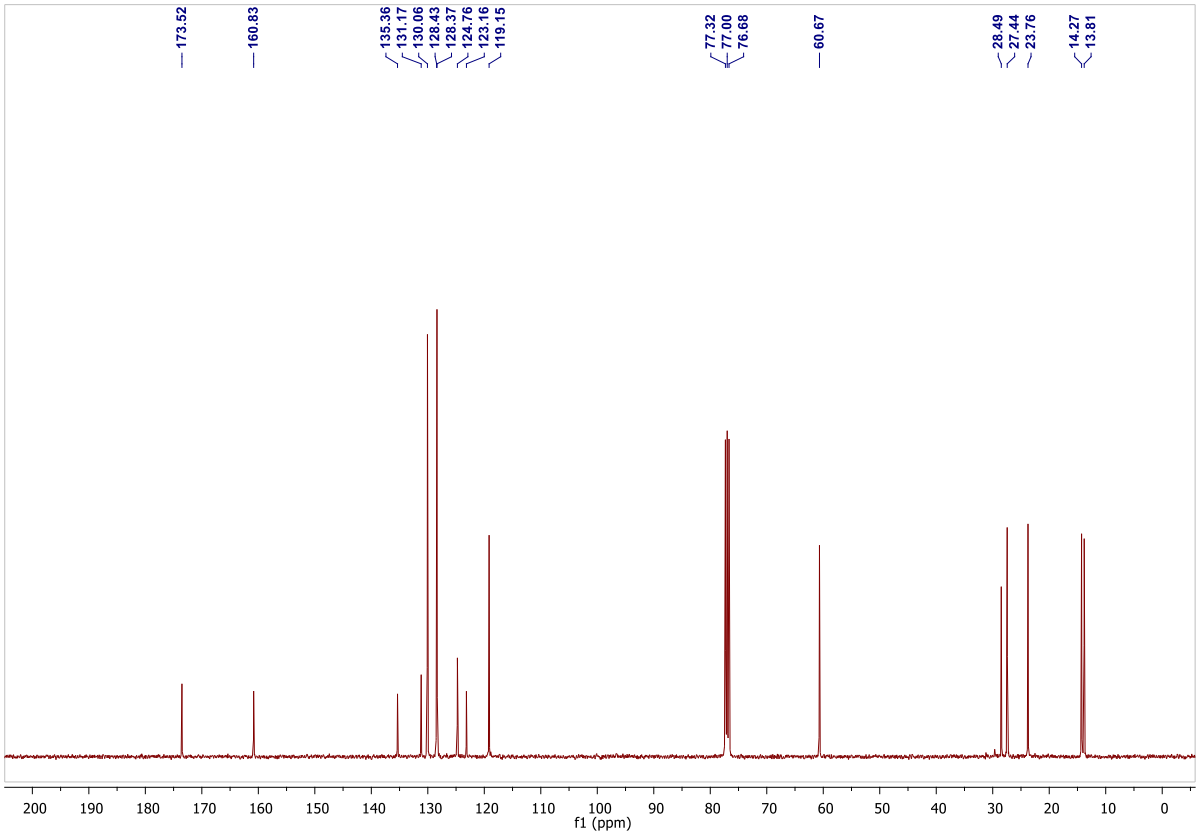
Ethyl 1-acetyl-4-ethyl-5-phenyl-1H-pyrrole-2-carboxylate (Table 2, **3ap**)



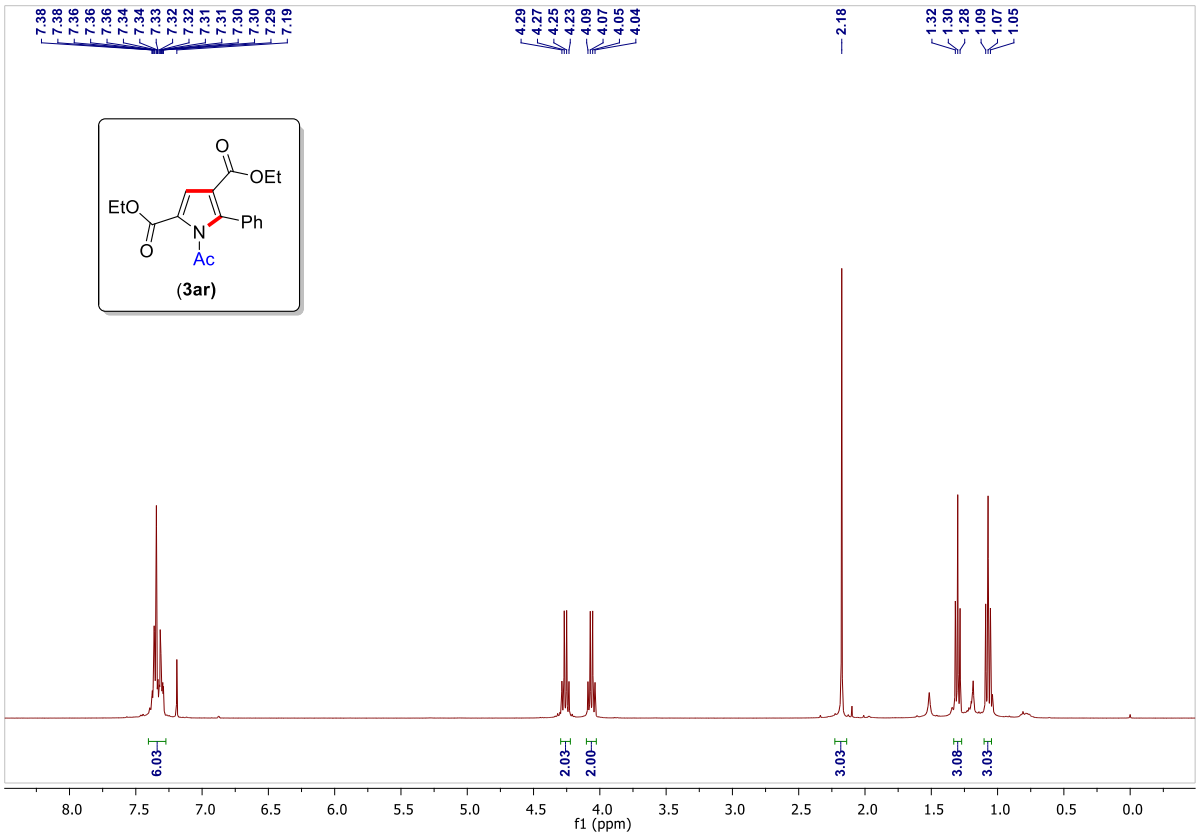


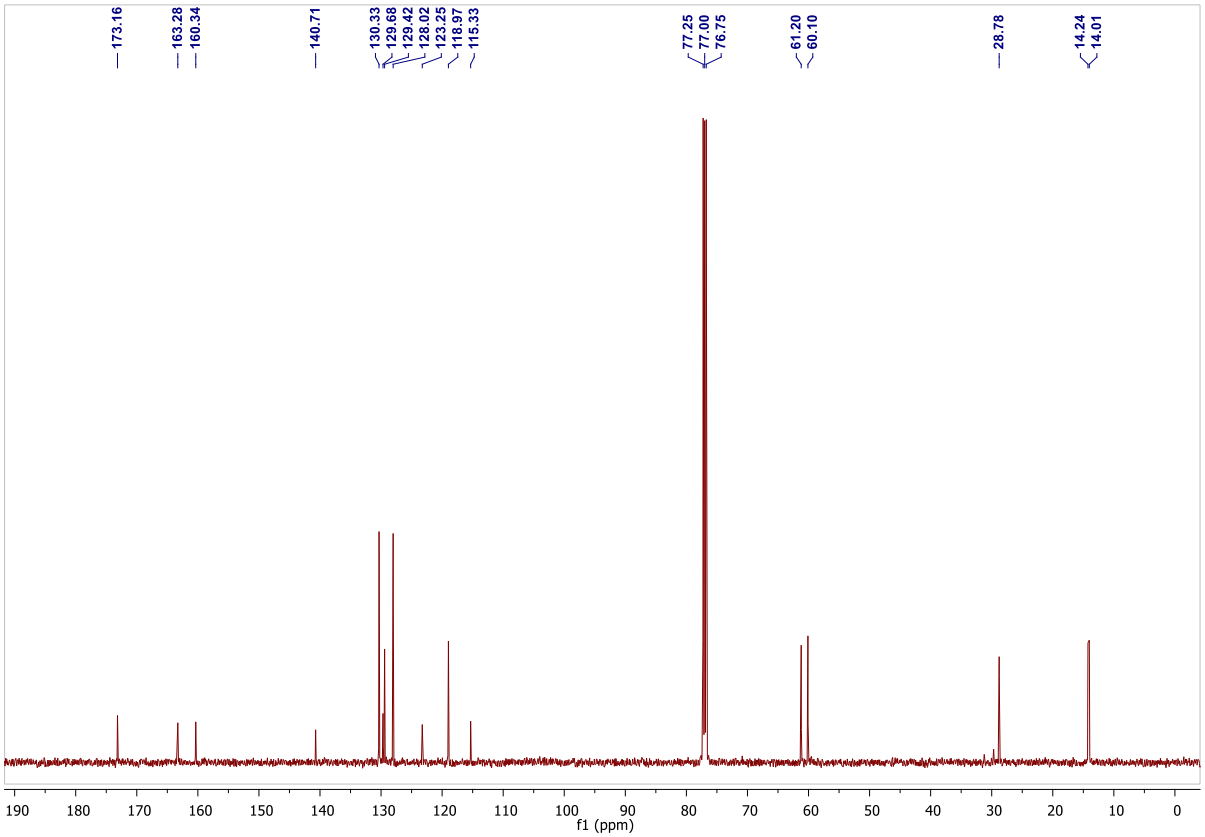
Ethyl 1-acetyl-5-phenyl-4-propyl-1H-pyrrole-2-carboxylate (Table 2, **3aq**)



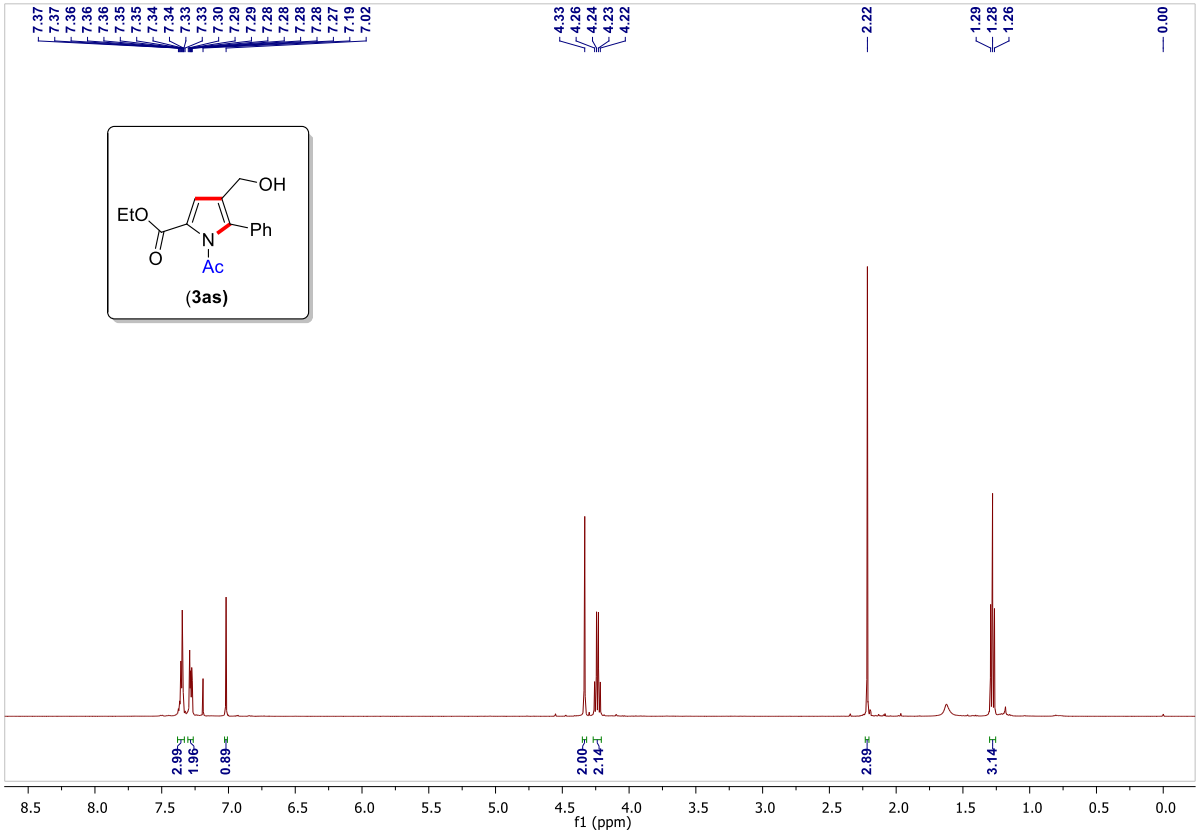


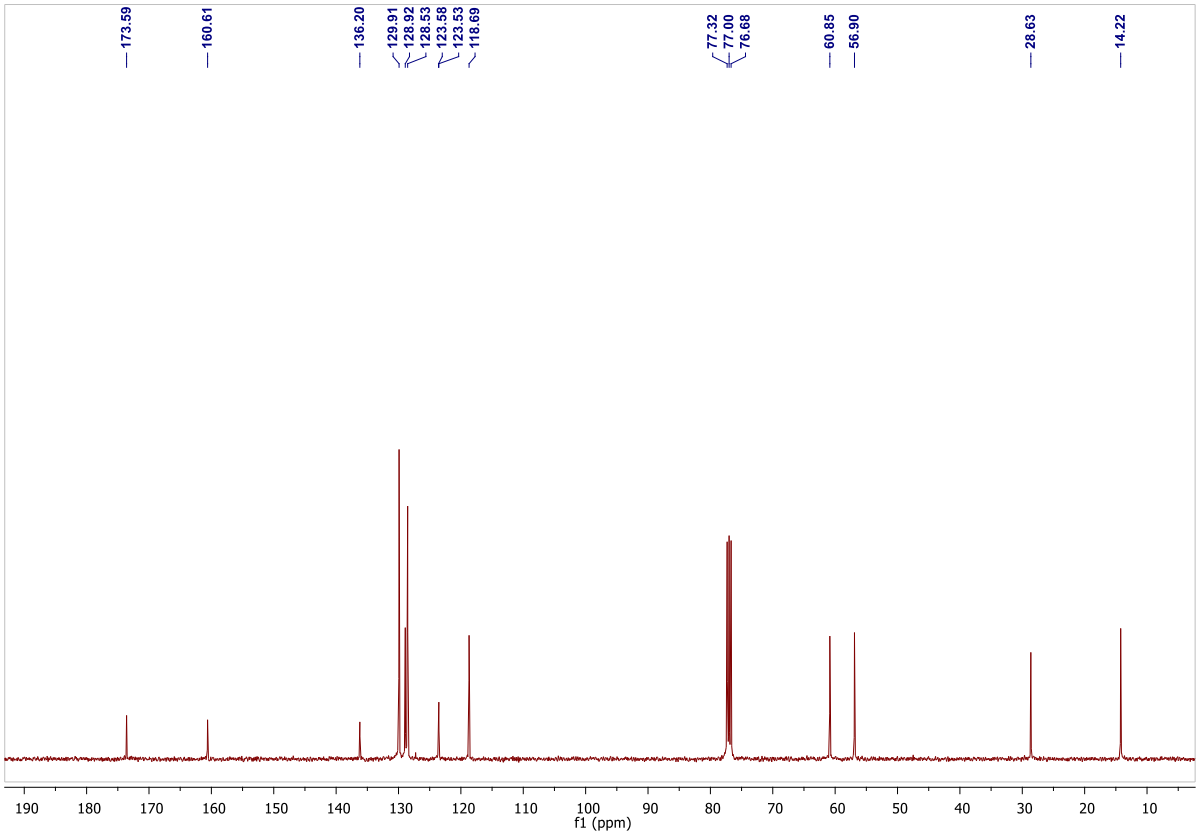
Diethyl 1-acetyl-5-phenyl-1H-pyrrole-2,4-dicarboxylate (Table 2, **3ar**)



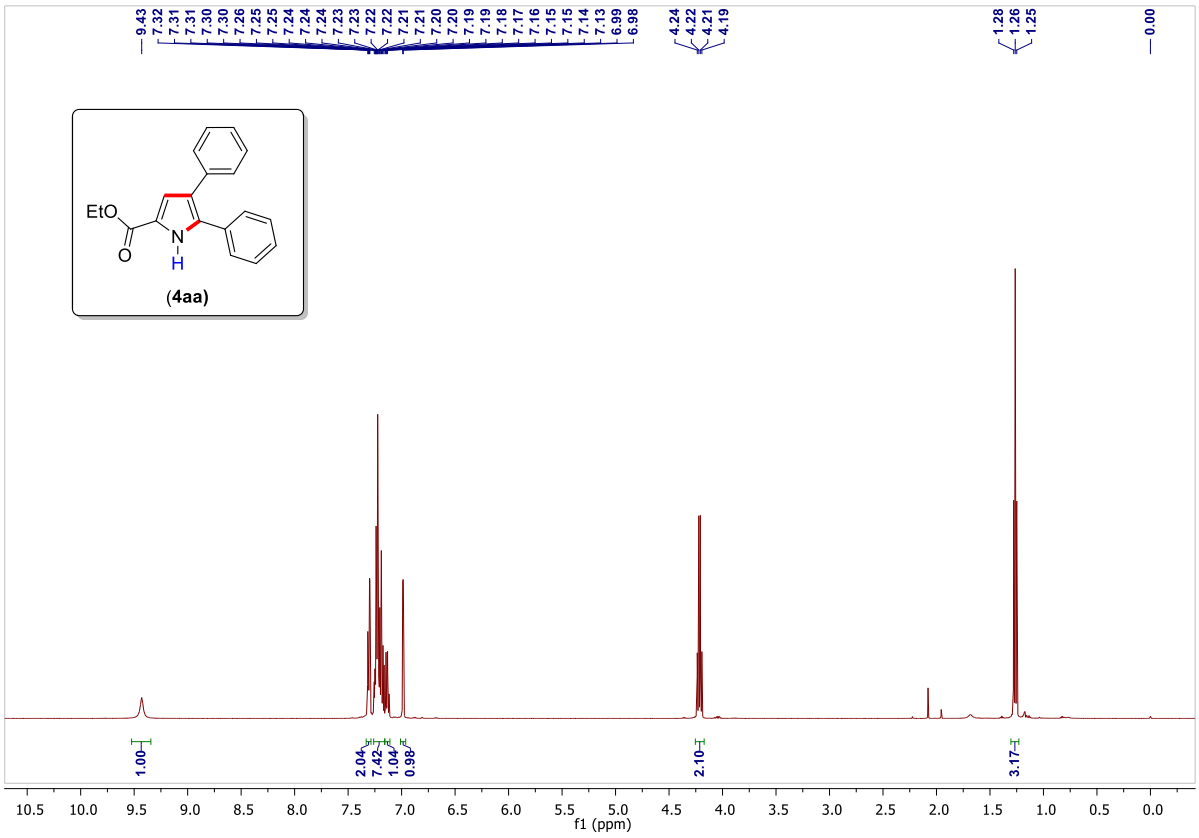


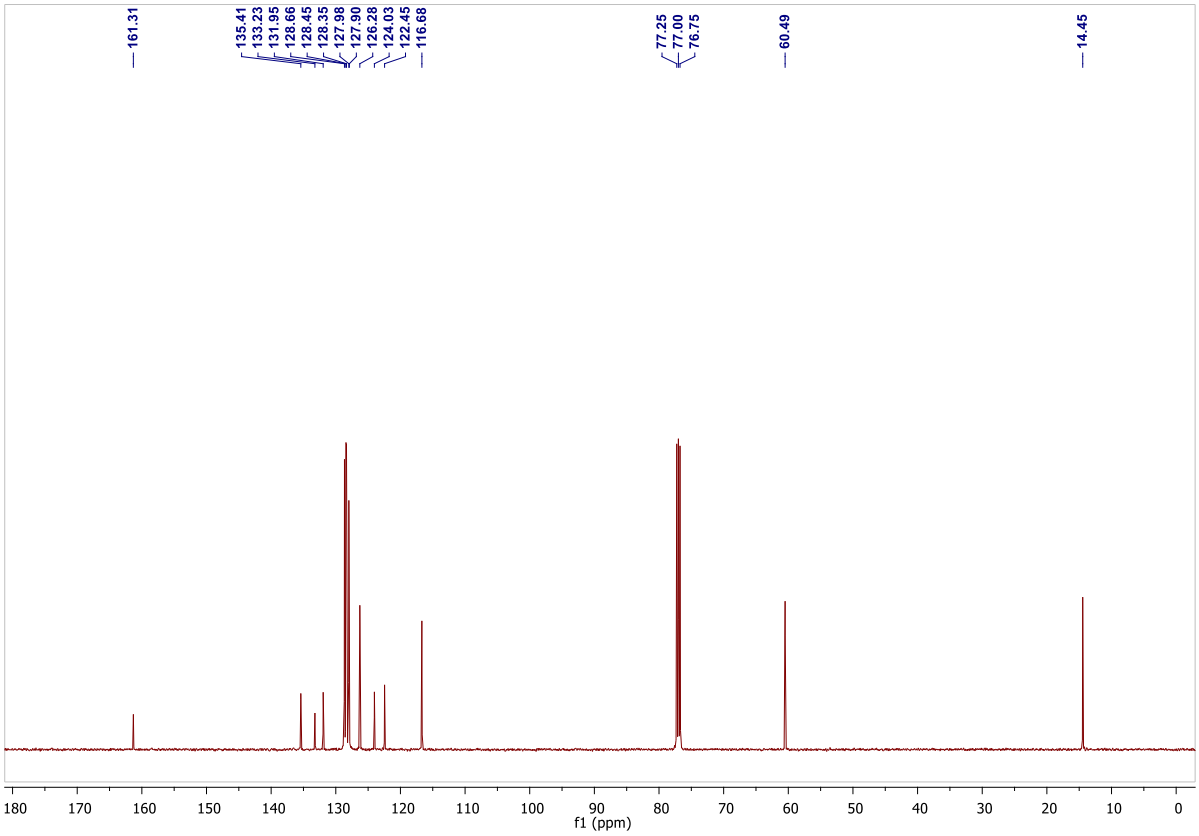
Ethyl 1-acetyl-4-(hydroxymethyl)-5-phenyl-1H-pyrrole-2-carboxylate (Table 2, **3as**)



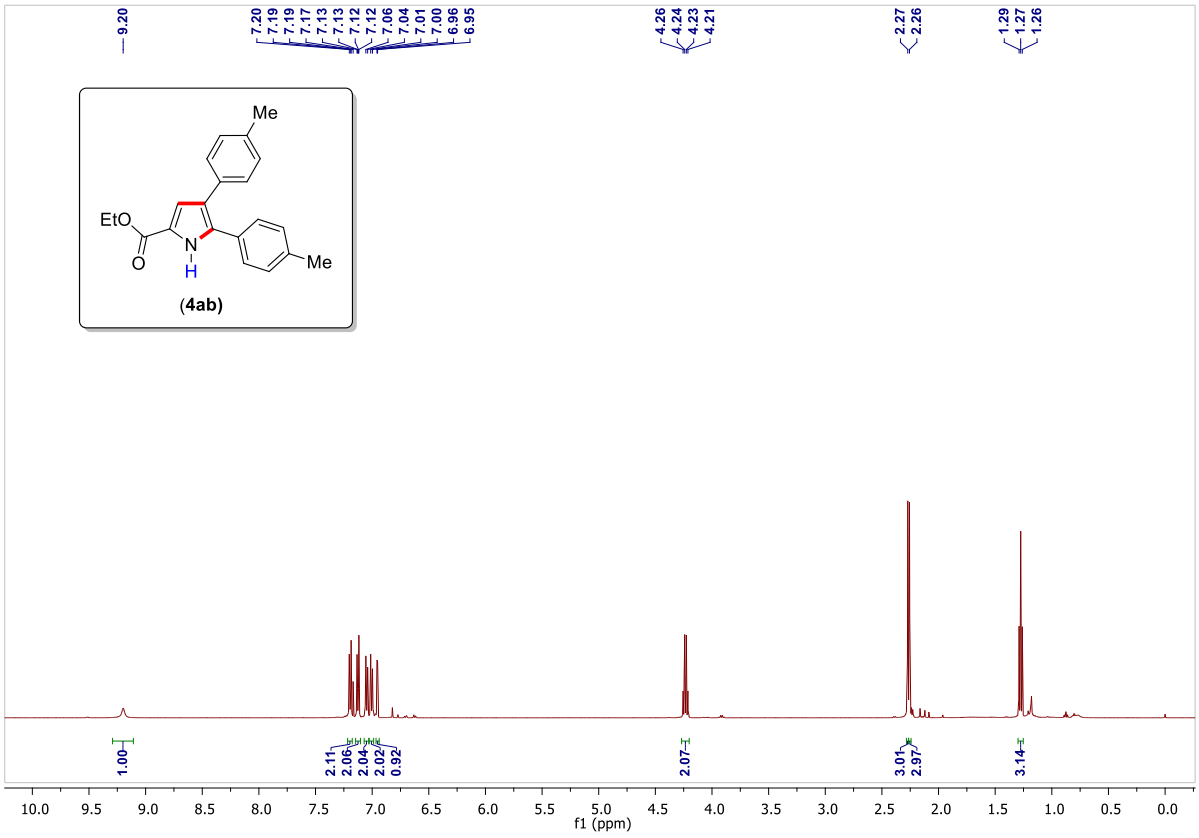


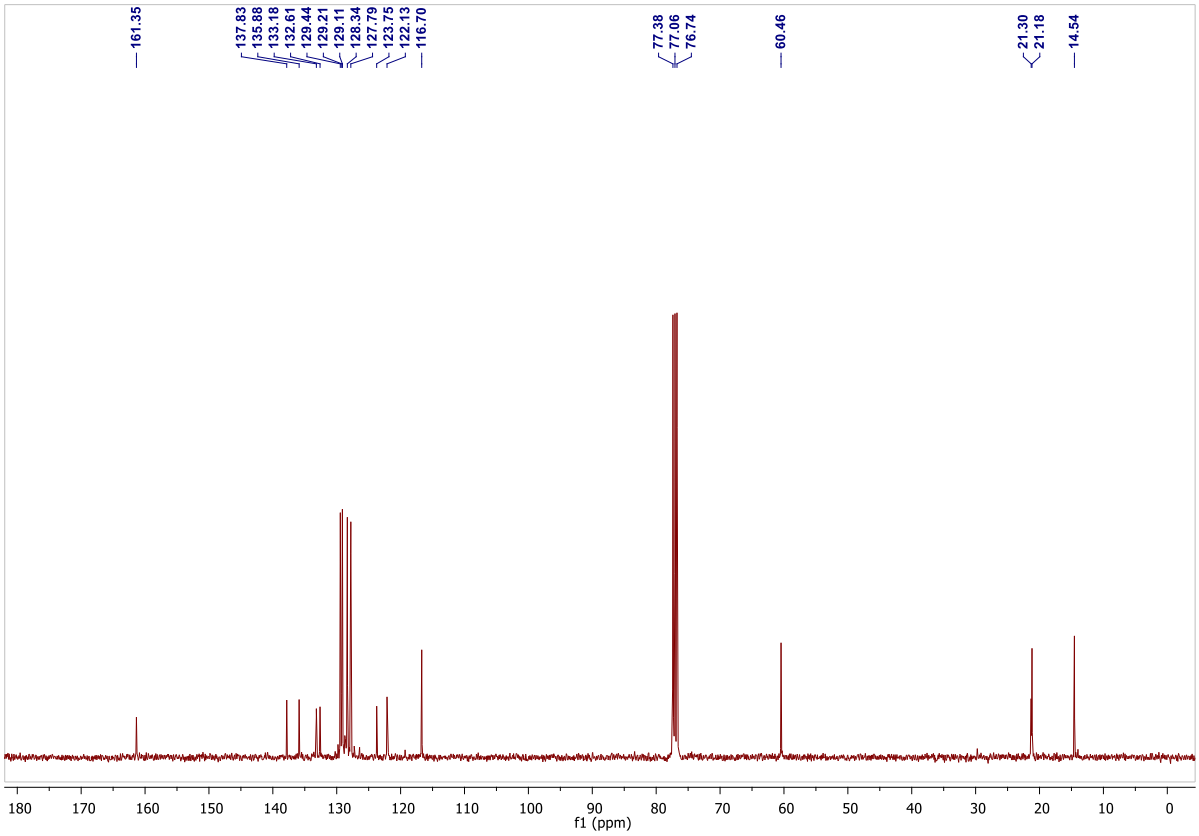
Ethyl 4,5-diphenyl-1H-pyrrole-2-carboxylate (Table 3, **4aa**)



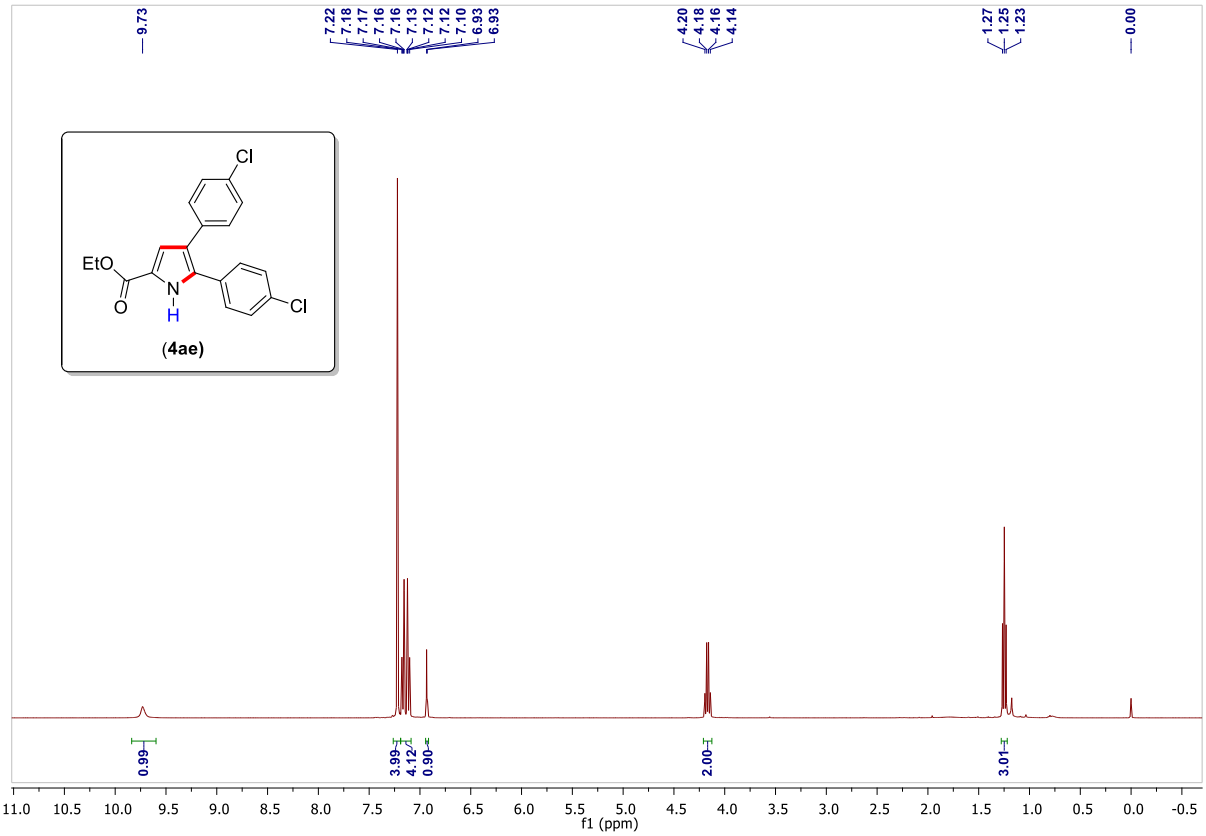


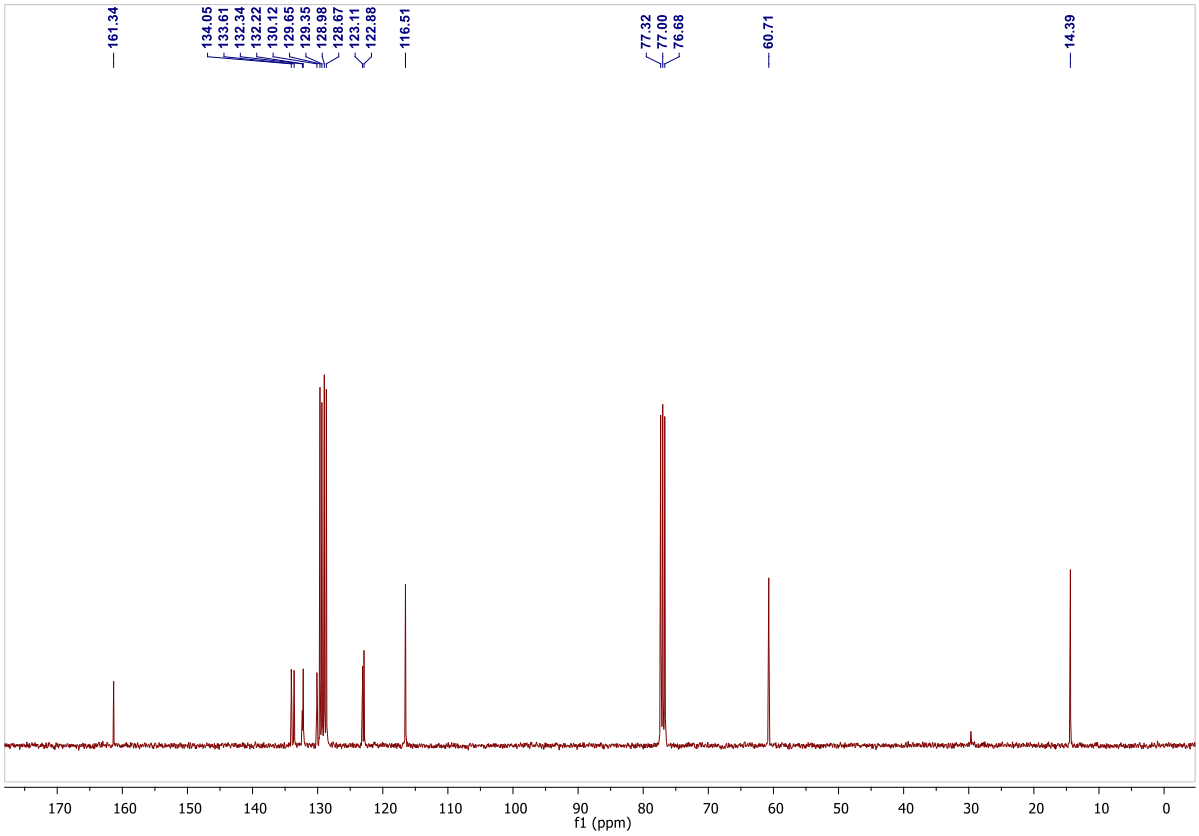
Ethyl 4,5-di-*p*-tolyl-1H-pyrrole-2-carboxylate (Table 3, **4ab**)



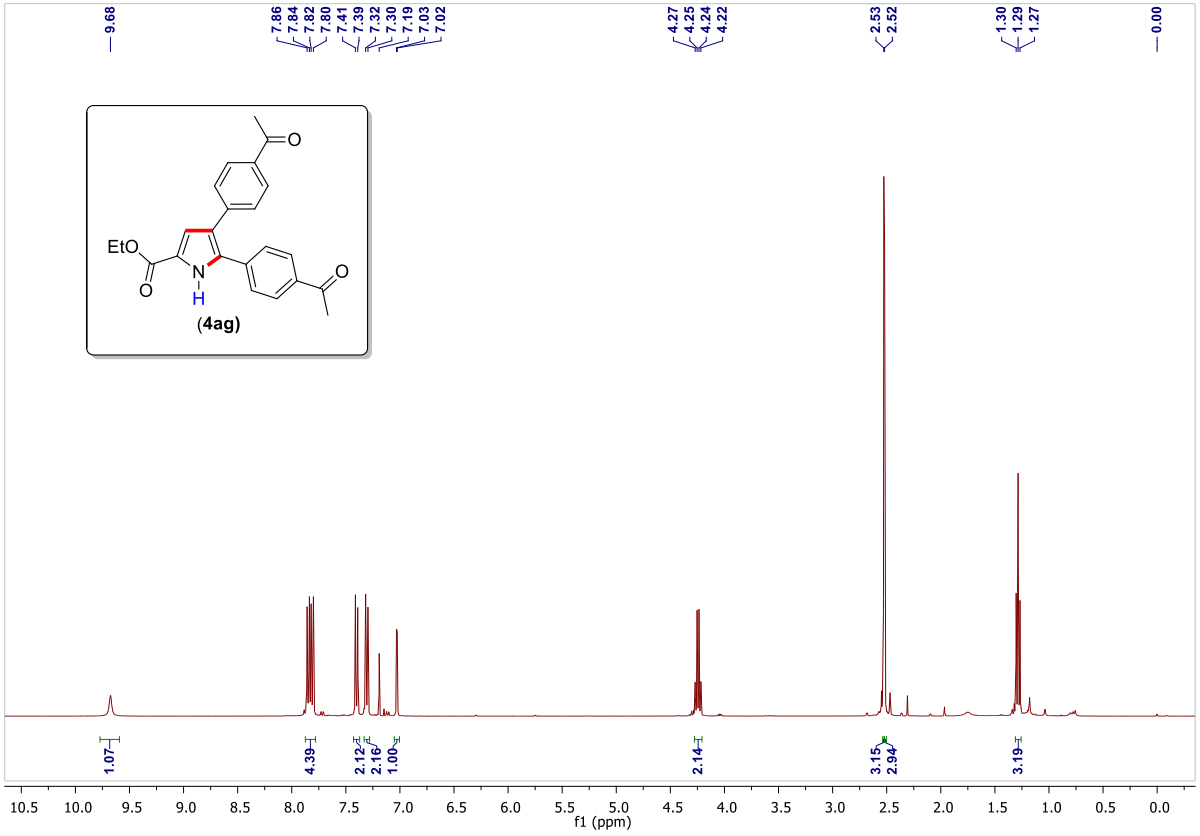


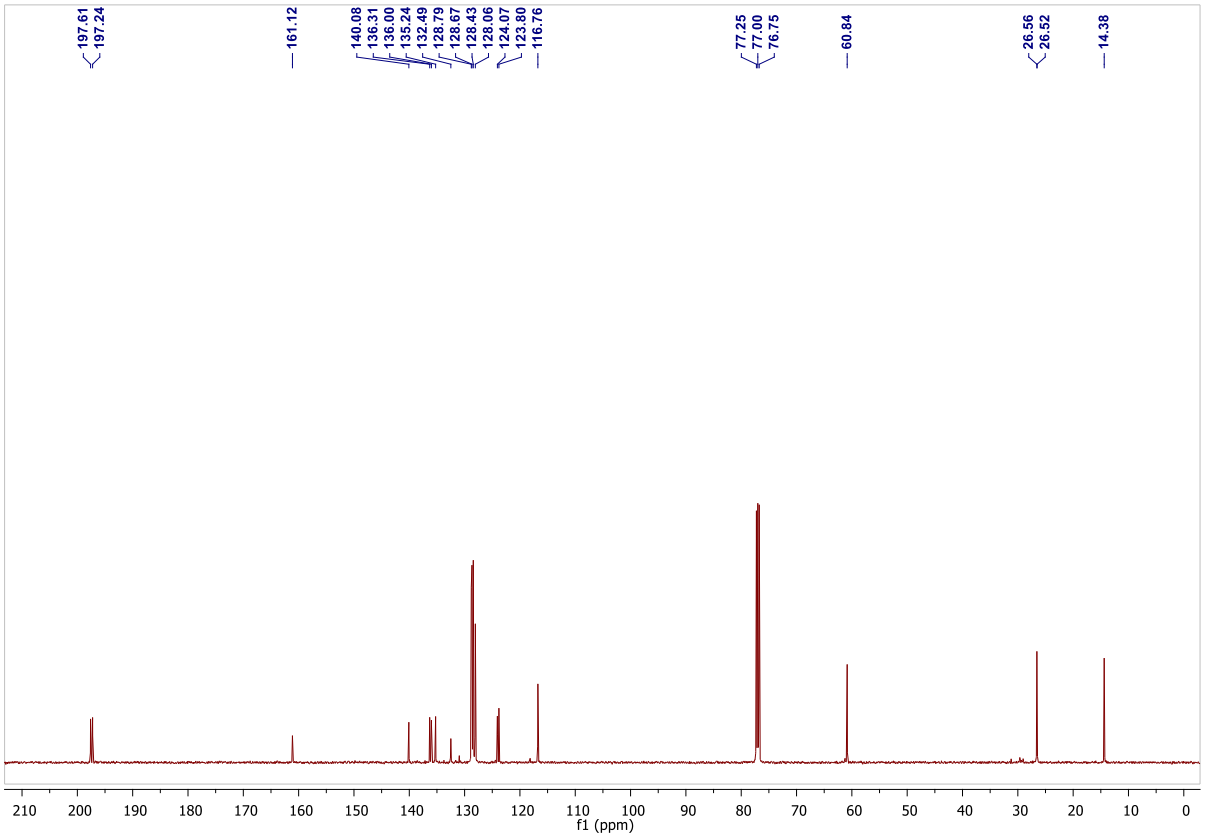
Ethyl 4,5-bis(4-chlorophenyl)-1H-pyrrole-2-carboxylate (Table 3, **4ae**)



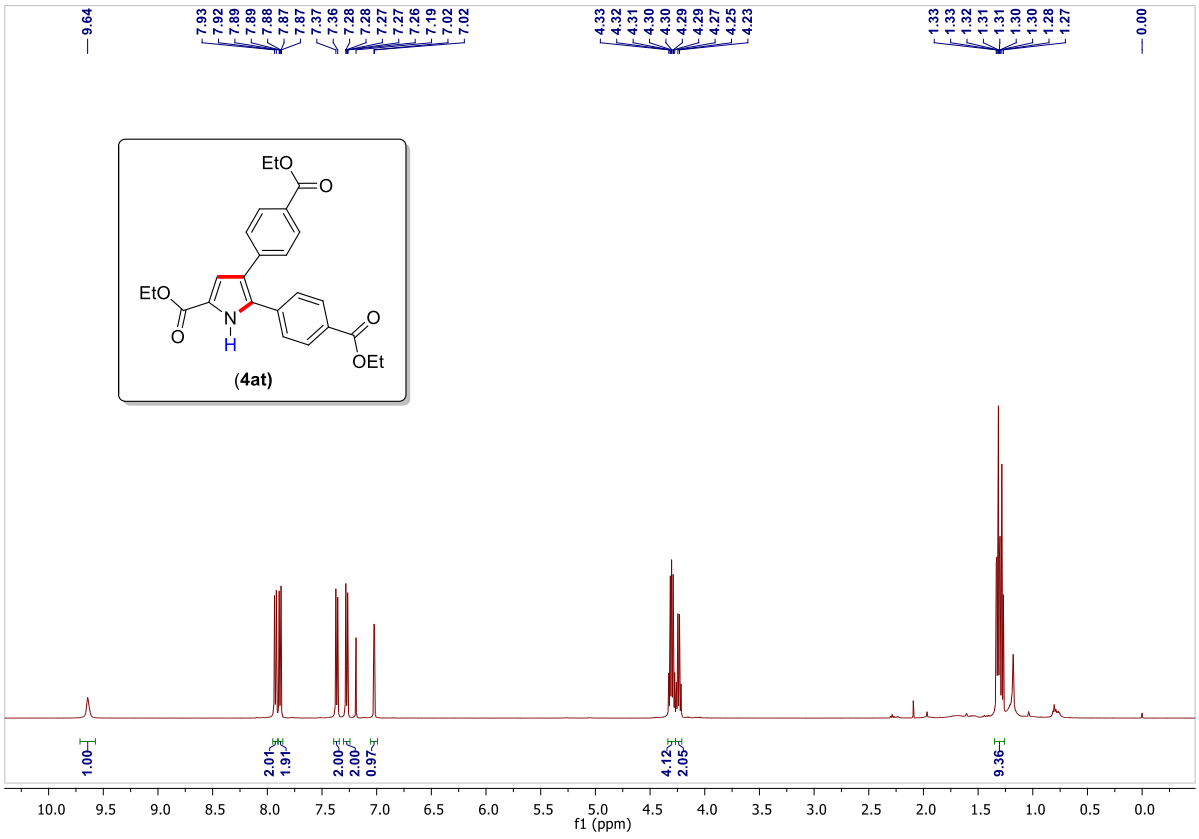


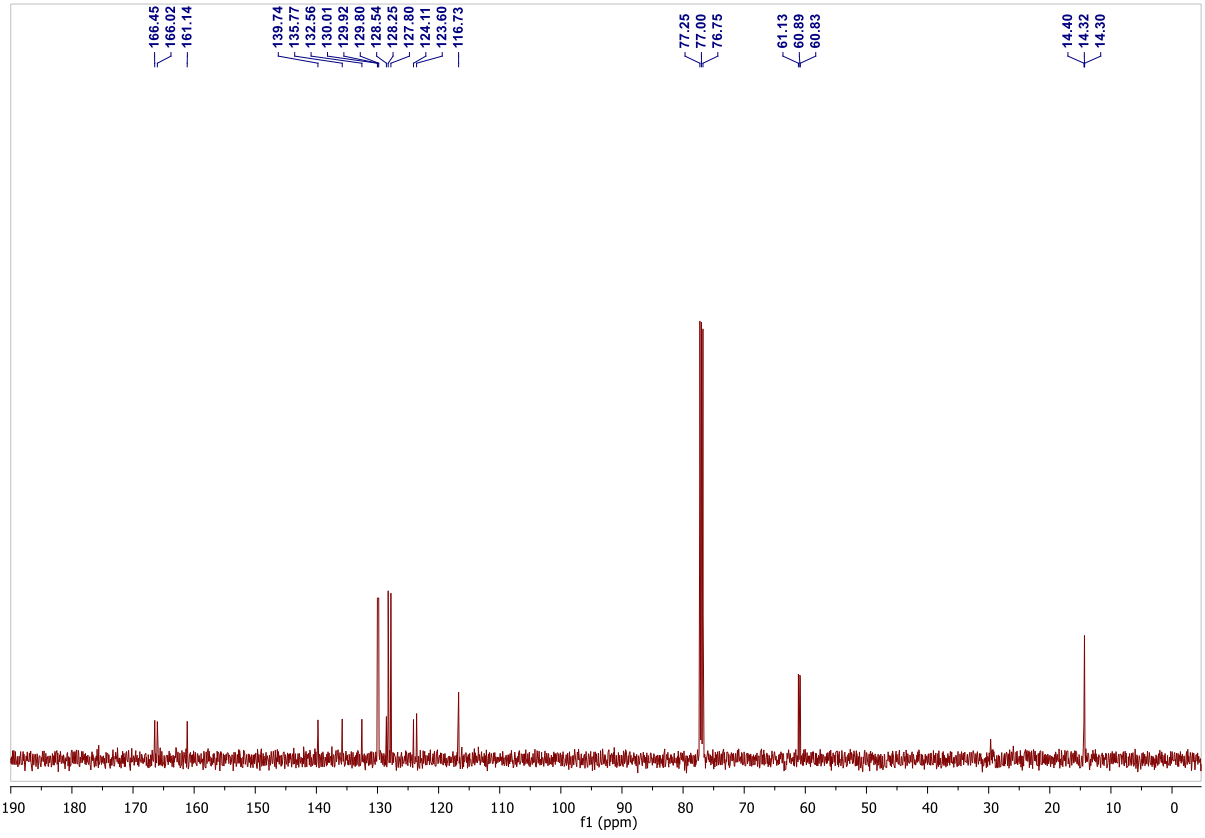
Ethyl 4,5-bis(4-acetylphenyl)-1H-pyrrole-2-carboxylate (Table 3, **4ag**)



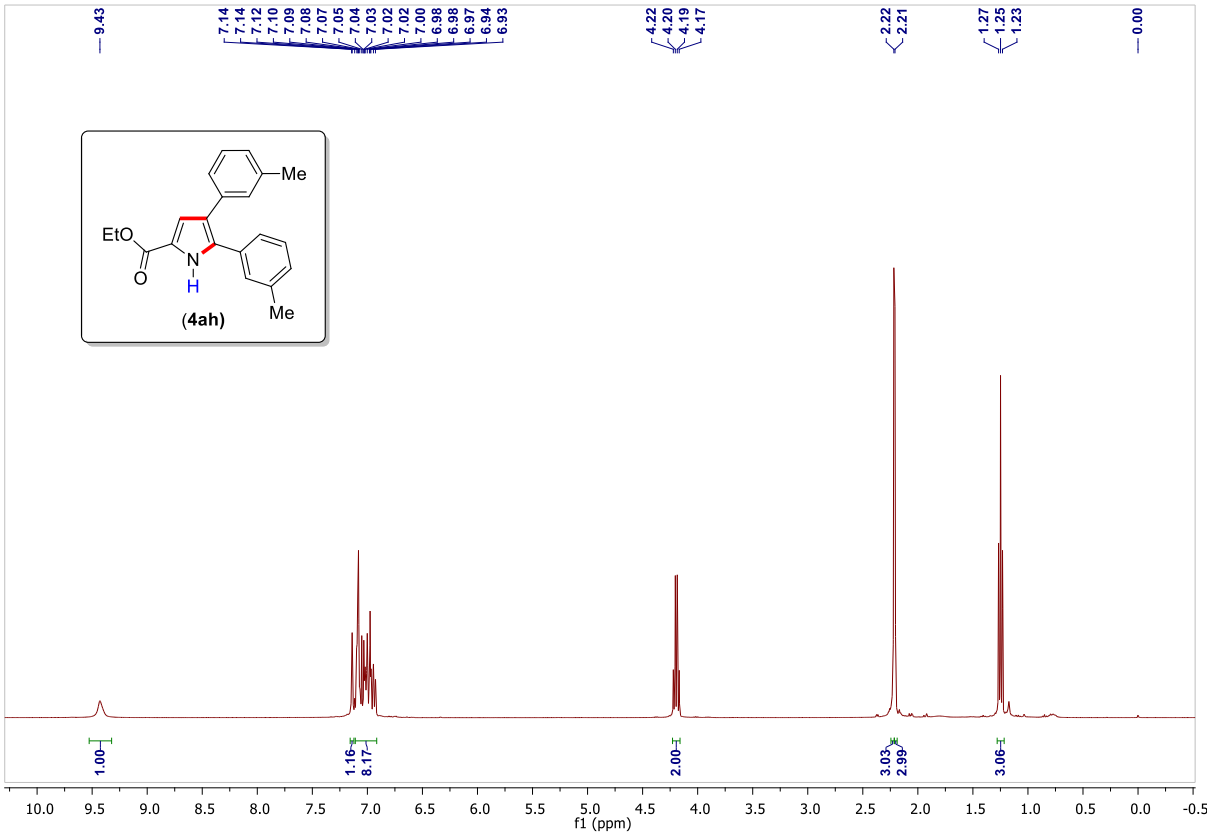


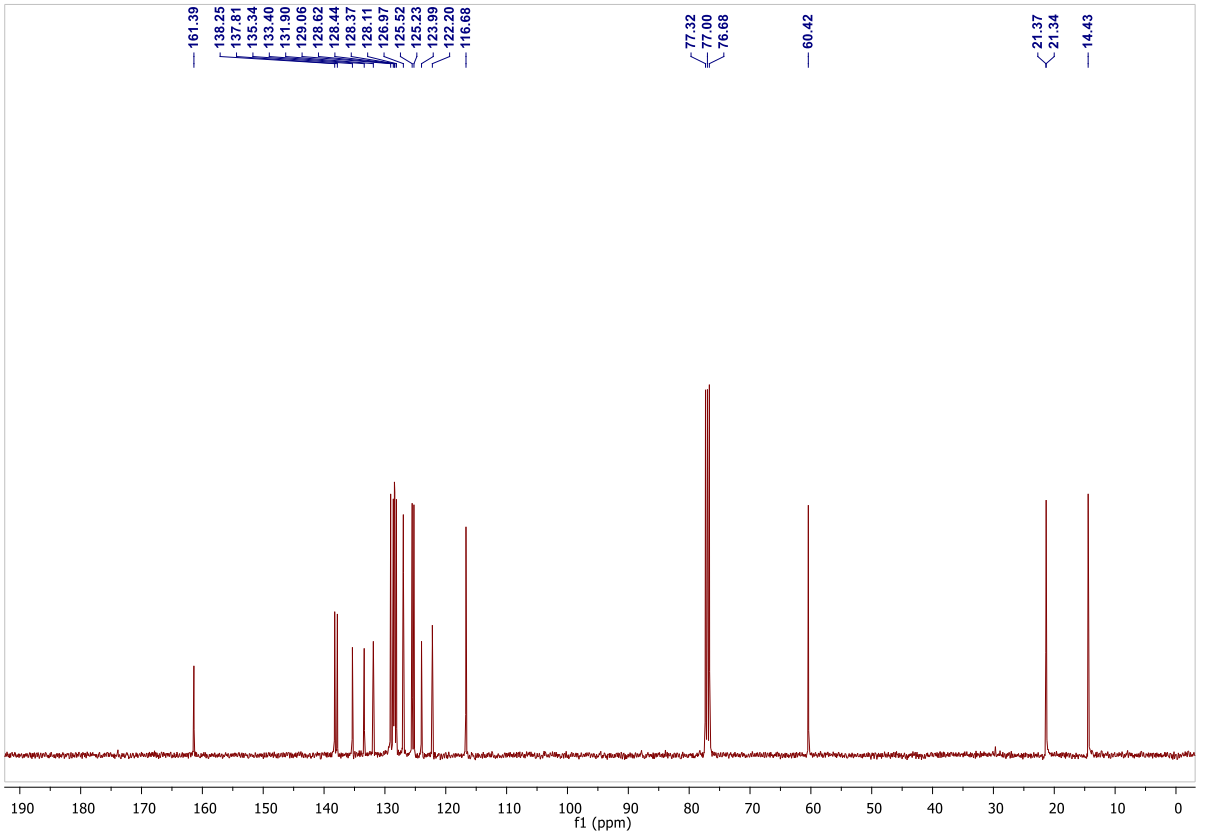
Diethyl 4,4'-(5-(ethoxycarbonyl)-1H-pyrrole-2,3-diyl)dibenzoate (Table 3, **4at**)



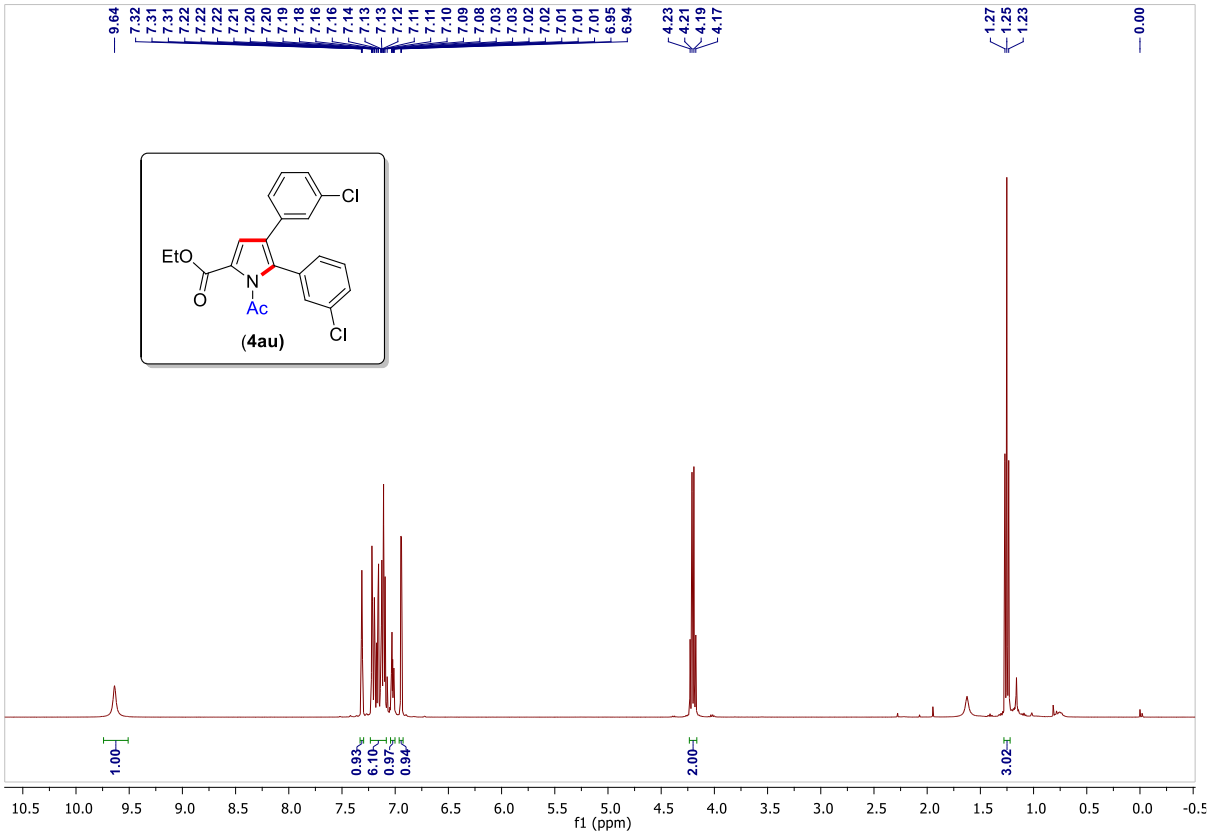


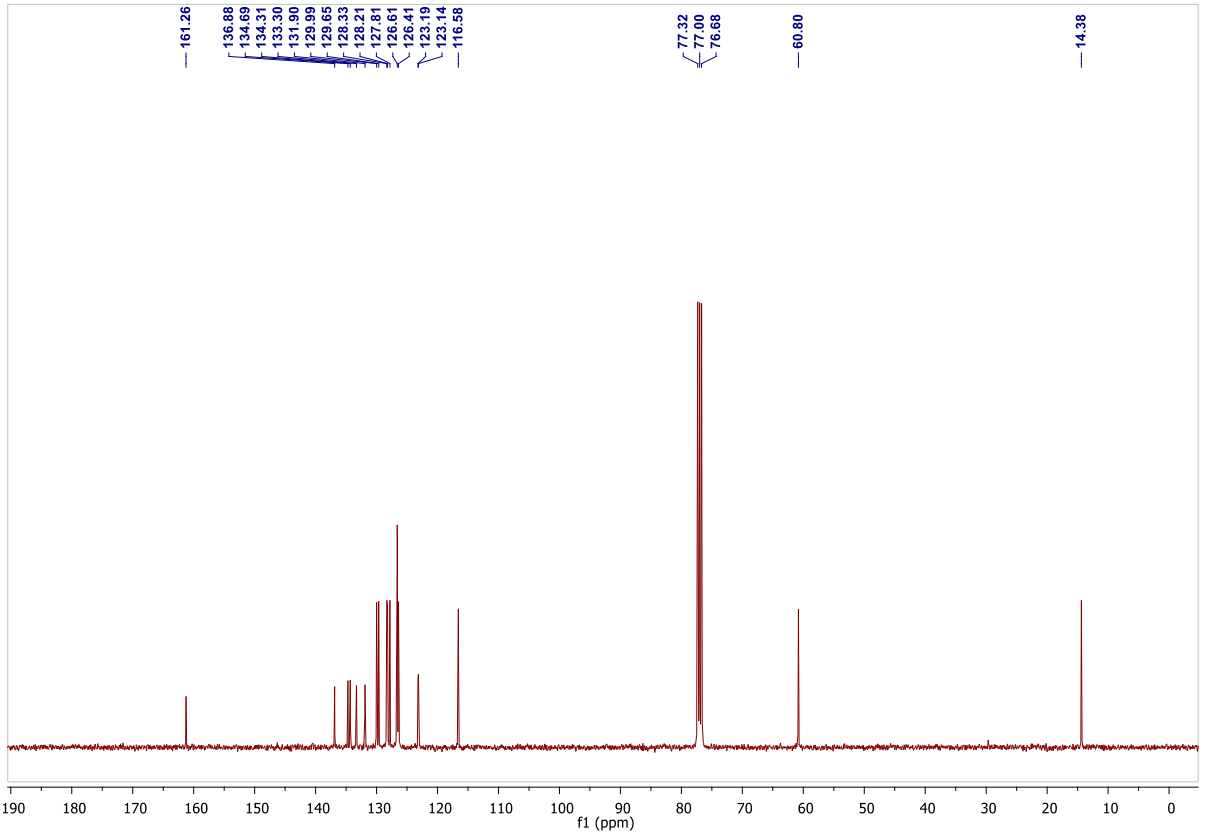
Ethyl 4,5-di-m-tolyl-1H-pyrrole-2-carboxylate (Table 3, **4ah**)



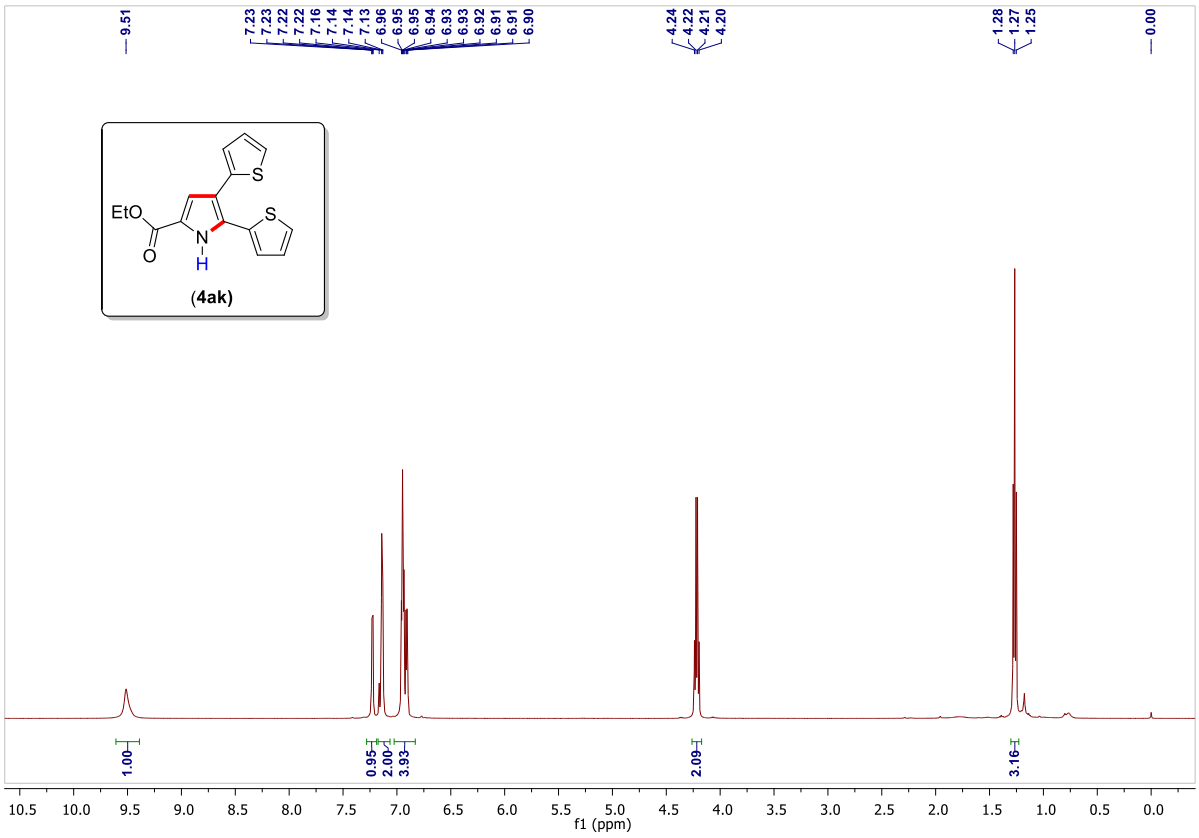


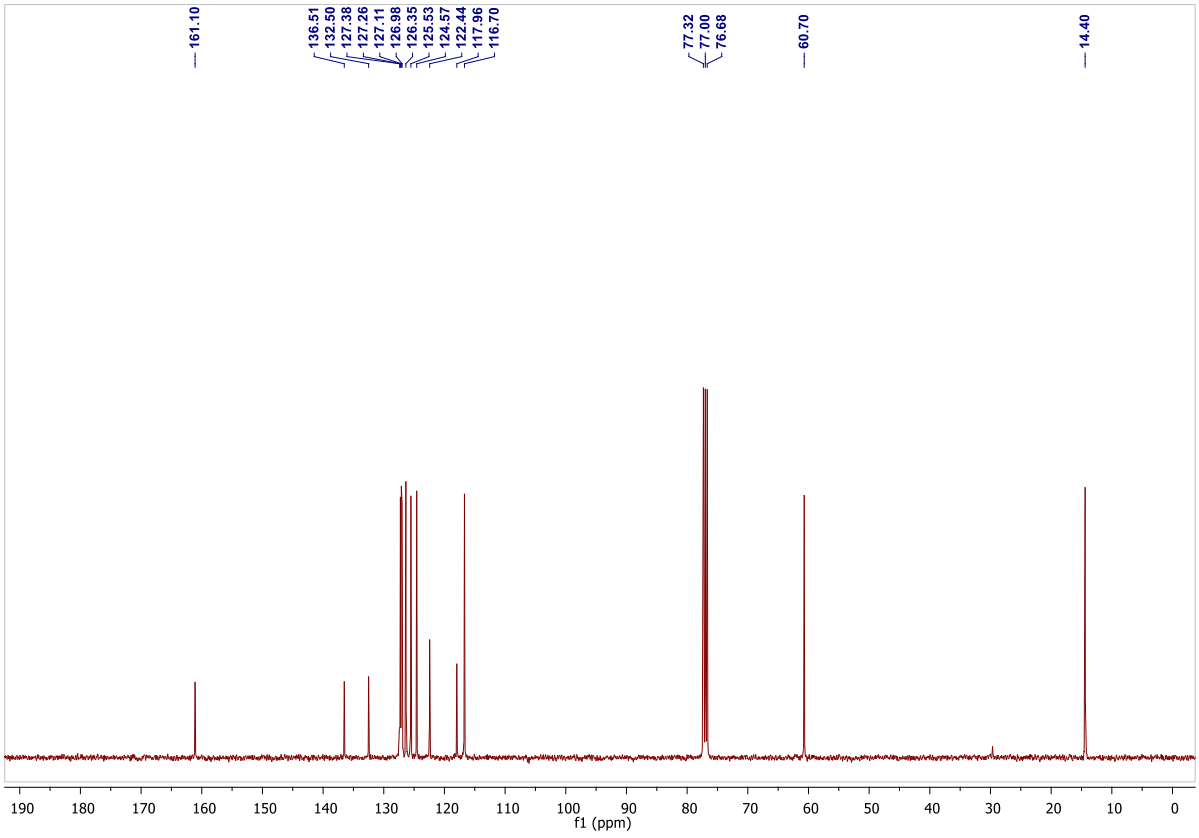
Ethyl 4,5-bis(3-chlorophenyl)-1H-pyrrole-2-carboxylate (Table 3, **4au**)



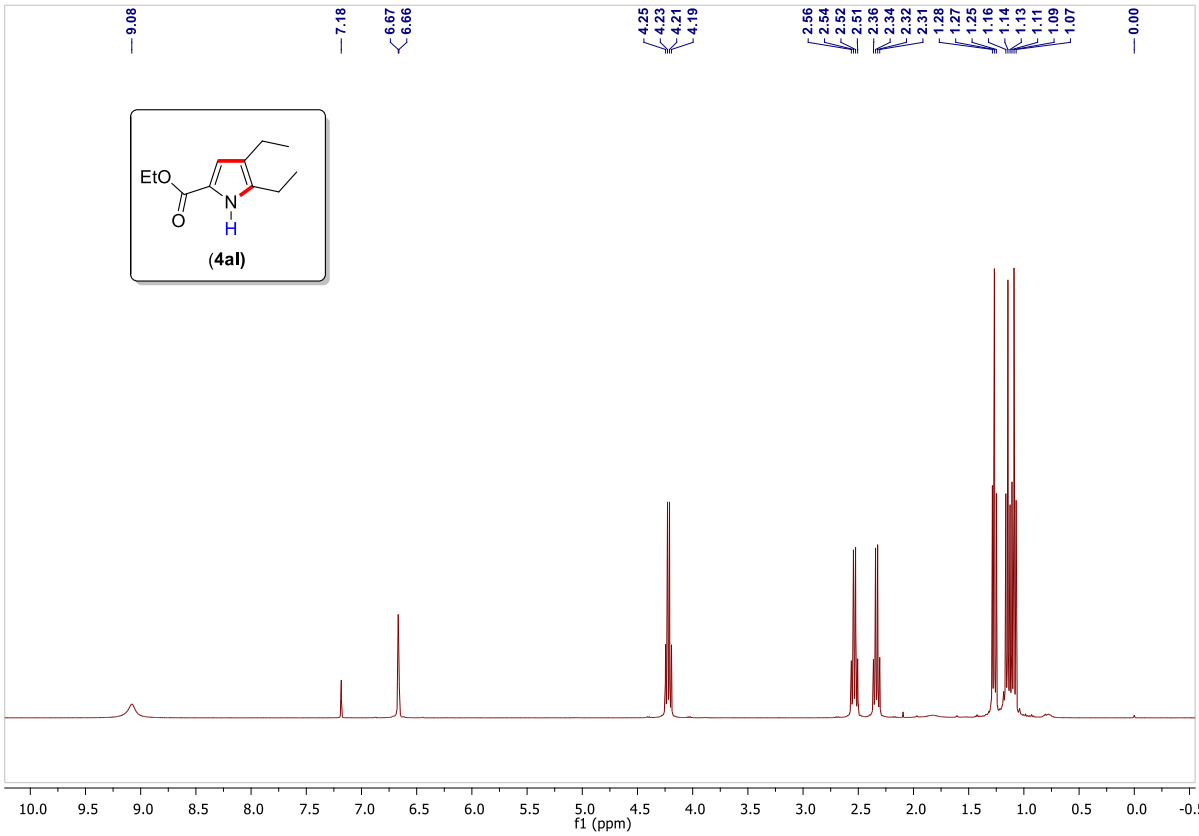


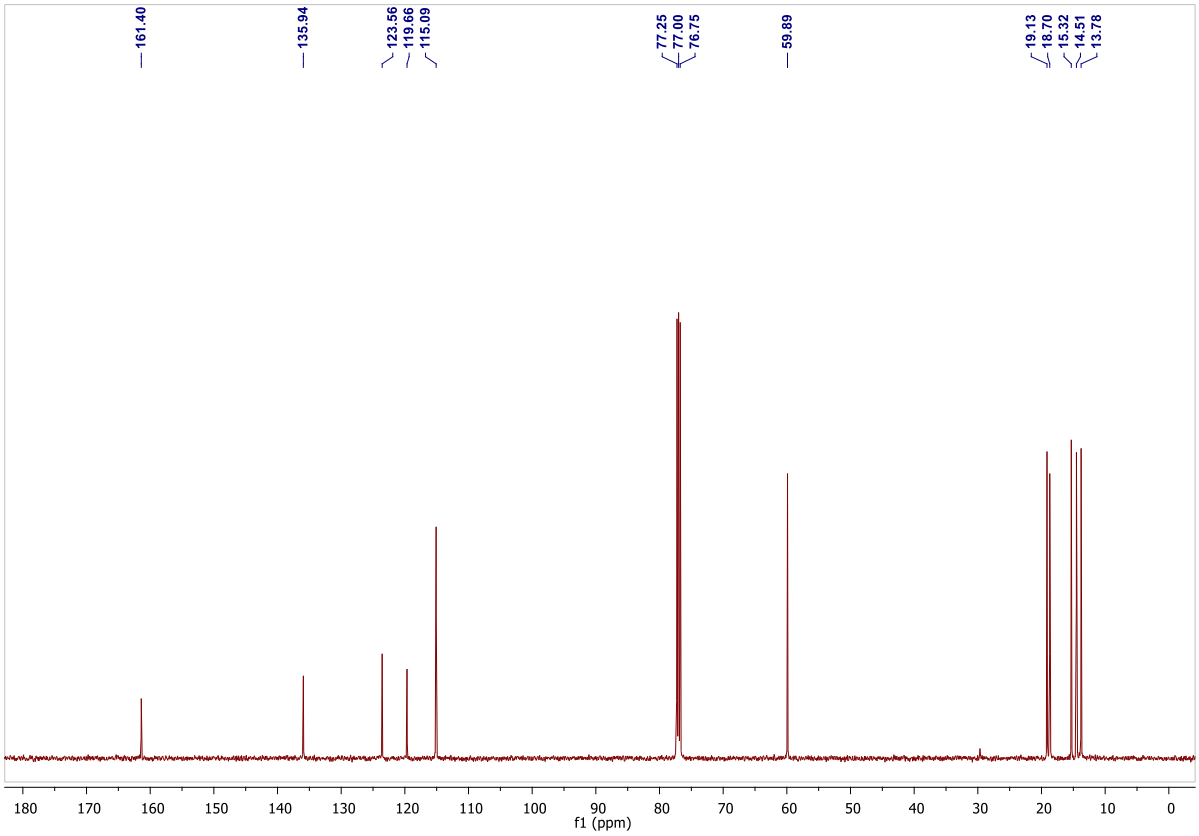
Ethyl 1-acetyl-4,5-di(thiophen-2-yl)-1H-pyrrole-2-carboxylate (Table 3, **4ak**)



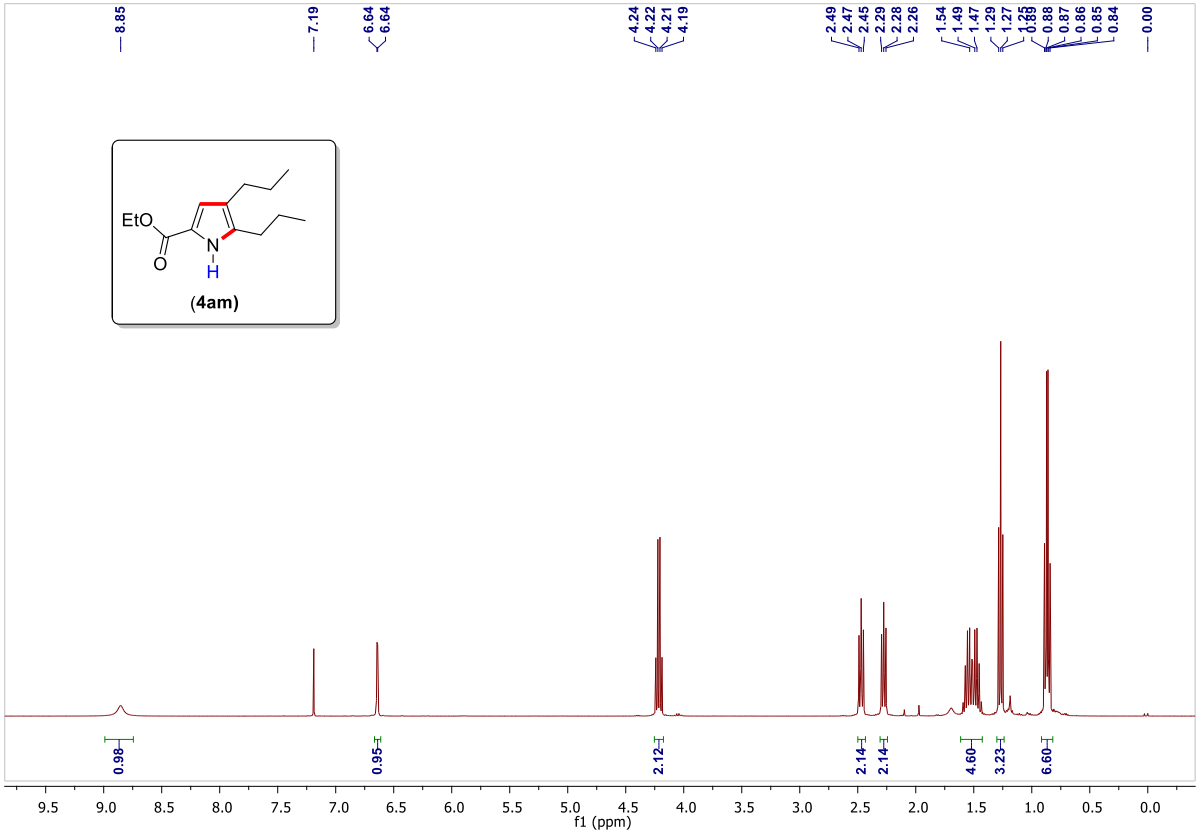


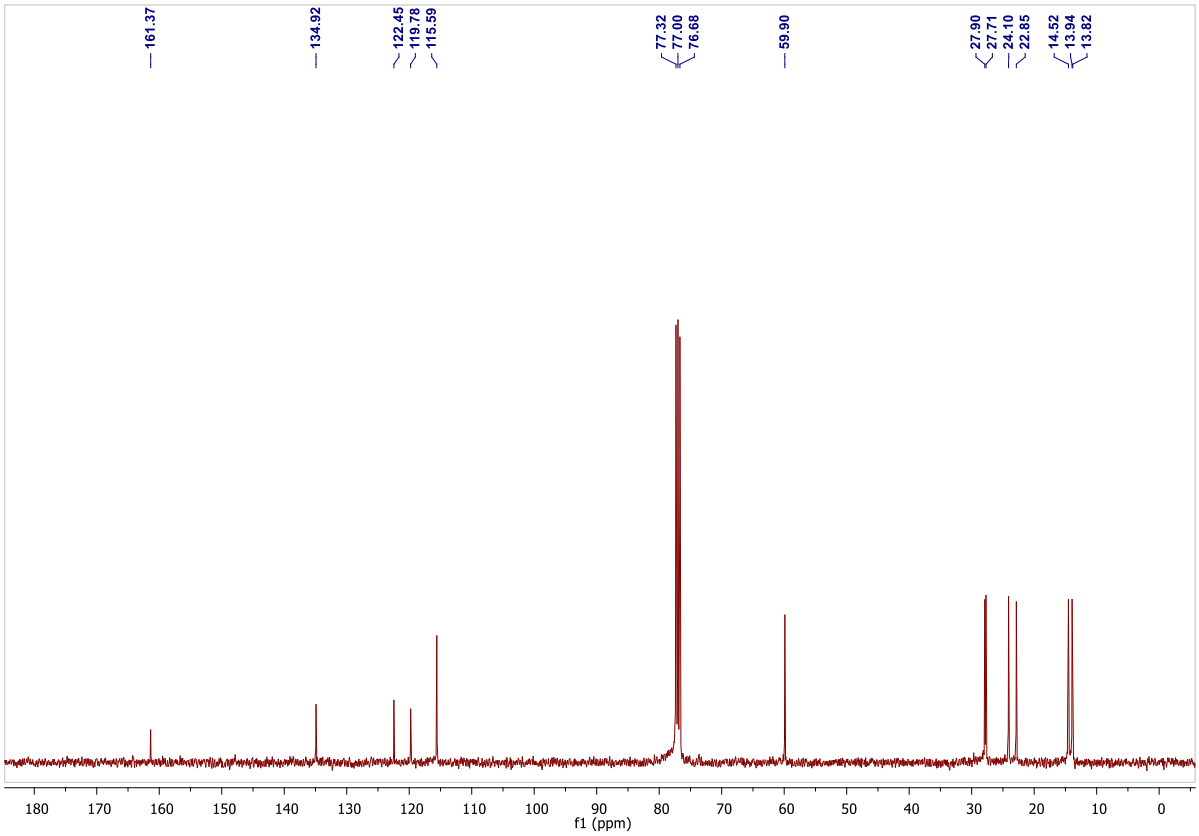
Ethyl 1-acetyl-4,5-diethyl-1H-pyrrole-2-carboxylate (Table 3, **4al**)





Ethyl 1-acetyl-4,5-dipropyl-1H-pyrrole-2-carboxylate (Table 3, **4am**)





NOE spectra for 3an &3an'