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Electronic Supplementary Material

Direct Synthesis of Pyrroles *via* 1,3-Dipolar Cycloaddition of Azomethine Ylides with Ynones

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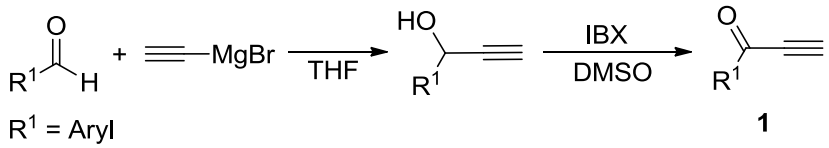
General Information

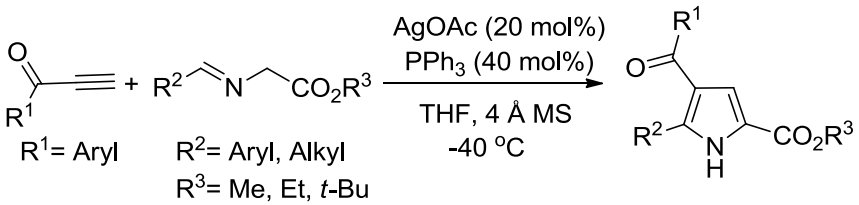
All Chemicals were purchased from commercial sources and they were used without further purification unless otherwise specified. Melting points were obtained on a micro melting apparatus SGW X-4 and uncorrected. HRMS (ESI) spectra were measured on a Waters LCT Premier XE spectrometer. ^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in chloroform-d_3 or DMSO-d_6. ^{13}C NMR spectra were recorded on a Bruker DPX 100 MHz spectrometer in chloroform-d_3 or DMSO-d_6. Chemical shift values are reported in parts per million on the scale (δ_{TMS} = 0). Infrared spectra were recorded on NICOLET 5SXC instrument as thin film; frequencies are given as wavenumbers (cm^{-1}).

General Procedure for the Preparation of Ynones 1.[1,2]



A solution of the aldehyde (10.0 mmol) in dry THF (20 mL) was added to a stirred solution of ethynylmagnesium bromide in THF (0.5 M; 30 mL, 15.0 mmol) at 0 ^{o}C. The mixture was stirred at 0 ^{o}C for 2h, warmed to room temperature and was quenched with aq. sat. NH_4Cl sol (10 mL). The organic layer was separated and the aqueous phase was extracted with EtOAc (2x10 mL). The combined extracts were evaporated to give the propargyl alcohol as yellowish oil. Without purification, this material was added to a solution of IBX (5.6 g, 20.0 mmol) in DMSO and the solution was heated to 35 °C for 6 h. The cooled reaction mixture was diluted with EtOAc (20 mL) and water (30 mL) and stirred vigorously for 10 min. Then it was filtered over celite. The organic layer was separated and the aqueous phase was extracted with ether (3x20 mL). The combined extracts were sequentially washed with aq. sat. $NaHCO_3$ (20 mL) and NaCl (20 mL) solutions, dried (Na_2SO_4) and evaporated in vacuo. The residue was subject to flash chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to afford pure ynone **1**. Spectral data of the products were consistent with the previous report.[2]

General Procedure for AgOAc Catalyzed 1,3-Dipolar Cycloaddition of Azomethine Ylides with Ynones



Under N_2 atmosphere, AgOAc (10 mg, 0.06 mmol), PPh_3 (31.5 mg, 0.12 mmol) and activated 4Å MS were dissolved in 2 mL anhydrous THF and stirred at room temperature for about 1 h. Iminoesters **2** (0.6 mmol) were added and after the reaction mixture was reduced to -40 ^{o}C, ynones **1** (0.3 mmol) were added. Once starting material was consumed (monitored by TLC), the mixture

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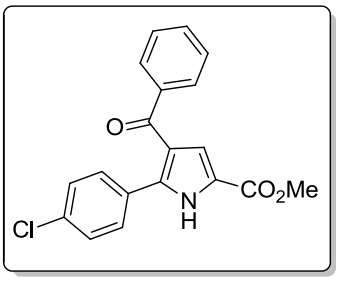
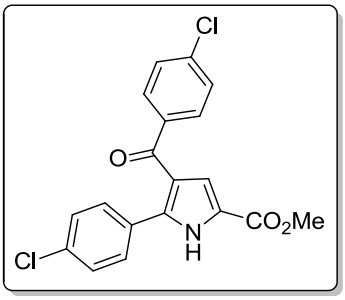
was concentrated to dryness and then the residue was purified by column chromatography to give the corresponding products **3**.



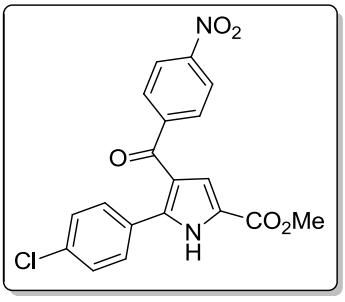
methyl 4-benzoyl-5-(4-chlorophenyl)-1H-pyrrole-2-carboxy late (3aa)

white solid, 69% yield. mp: 200-202 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (brs, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.55-7.46 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 161.7, 139.7, 138.8, 135.2, 132.5, 130.2, 129.7, 129.2, 128.7, 128.4, 122.1, 119.8, 52.1; IR (KBr) ν 3449, 3307, 2922, 1702, 1642, 1598, 1460, 1280, 1200, 1086, 1007, 892, 853, 746, 695, 598, 509 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{13}NO_3Cl$ ($M+H^+$) 338.0584, found 338.0581.



methyl 4-(4-chlorobenzoyl)-5-(4-chlorophenyl)-1H-pyrrole-2-carboxylate (3ba)

white solid, 63% yield. mp: 197-200 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.94 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.51 (dd, *J* = 8.4, 1.9 Hz, 4H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.03 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.5, 160.4, 139.6, 137.3, 137.1, 133.3, 131.2, 131.0, 129.2, 128.4, 127.9, 122.4, 121.0, 118.8, 51.6; IR (KBr) ν 3450, 3298, 2922, 2852, 1694, 1653, 1583, 1557, 1439, 1331, 1280, 1244, 1208, 1156, 1086, 1014, 891, 828, 762, 726, 671, 536 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{14}NO_3Cl_2$ ($M+H^+$) 374.0351, found 374.0348.



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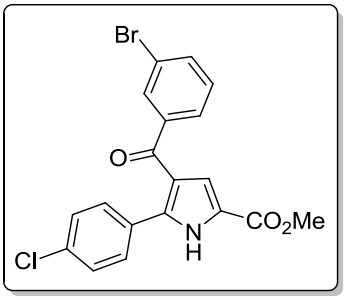
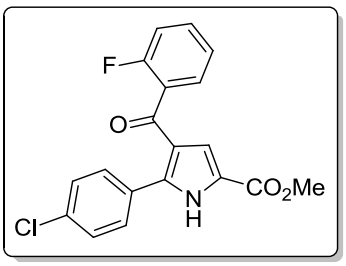
methyl 5-(4-chlorophenyl)-4-(4-nitrobenzoyl)-1H-pyrrole-2-carboxylate (3ca)

yellow solid, 71% yield. mp: 239-241 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.04 (s, 1H), 8.25 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 2.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.1, 160.3, 149.0, 144.2, 140.3, 133.6, 131.5, 130.1, 129.1, 127.9, 123.5, 122.7, 120.6, 119.0, 51.7; IR (KBr) ν 3283, 3104, 2960, 2853, 1705, 1654, 1602, 1558, 1523, 1442, 1412, 1353, 1281, 1251, 1213, 1092, 1005, 902, 848, 764, 745, 713, 510, 484 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{14}N_2O_5Cl$ ($M+H^+$) 385.0591, found 385.0586.



methyl 4-(3-bromobenzoyl)-5-(4-chlorophenyl)-1H-pyrrole-2-carboxylate (3da)

white solid, 69% yield. mp: 234-235 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.96 (s, 1H), 7.79-7.71 (m, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.44-7.36 (m, 3H), 7.04 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.1, 160.4, 140.7, 139.9, 134.7, 133.4, 131.5, 131.3, 130.5, 129.2, 128.1, 127.9, 122.5, 121.6, 120.9, 118.7, 51.6; IR (KBr) ν 3318, 3059, 2950, 1917, 1700, 1643, 1560, 1455, 1414, 1343, 1282, 1244, 1199, 1162, 1087, 1006, 899, 836, 763, 732, 681, 600, 511 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{14}NO_3ClBr$ ($M+H^+$) 417.9846, found 417.9850.



methyl 5-(4-chlorophenyl)-4-(2-fluorobenzoyl)-1H-pyrrole-2-carboxylate (3ea)

white solid, 67% yield. mp: 217-218 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.98 (s, 1H), 7.56-7.45 (m, 4H), 7.40 (d, J = 8.4 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 7.21-7.15 (m, 1H), 6.95 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.0, 160.3, 158.9 (d, J = 247.4 Hz), 140.1, 133.6, 132.8 (d, J = 8.3 Hz), 131.5, 130.0 (d, J = 2.7 Hz), 128.9, 128.4 (d, J = 14.8 Hz), 127.7, 124.4 (d, J = 3.1 Hz), 122.7, 122.1, 118.7, 115.9 (d, J = 21.5 Hz), 51.6; IR (KBr) ν 3447, 3164, 3110, 2946, 1727, 1629, 1611, 1575, 1463, 1337, 1288, 1204, 1169, 1087, 1026, 897, 841, 760, 656, 510 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{14}NO_3ClF$ ($M+H^+$) 358.0646, found 358.0652.

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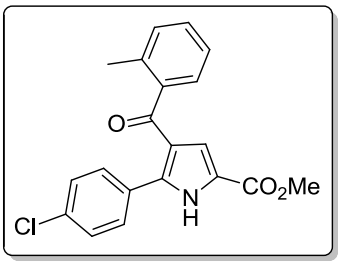
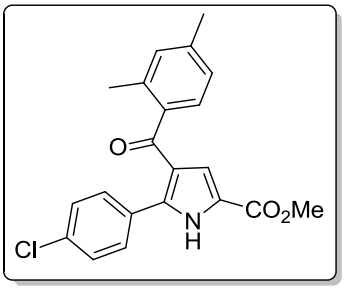


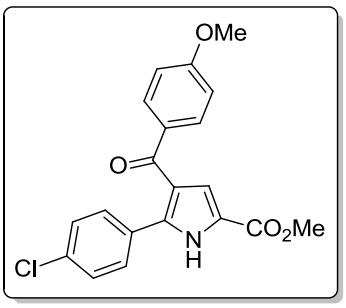
methyl 5-(4-chlorophenyl)-4-(2-methylbenzoyl)-1H-pyrrole-2-carboxylate (3fa)

white solid, 62% yield. mp: 140-141 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.92 (s, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.33 (td, *J* = 7.4, 1.2 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.78 (s, 1H), 3.77 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.5, 160.3, 140.0, 139.8, 135.3, 133.4, 131.4, 130.6, 129.8, 129.2, 127.9, 127.7, 125.2, 122.4, 122.3, 119.2, 51.6, 19.4; IR (KBr) ν 3565, 3472, 3304, 3071, 2956, 2852, 1701, 1638, 1558, 1471, 1443, 1340, 1278, 1254, 1205, 1168, 1092, 1006, 894, 829, 747, 667, 506 cm^{-1}; HRMS(ESI): calcd for $C_{20}H_{17}NO_3Cl$ ($M+H^+$) 354.0897, found 354.0895.



methyl 5-(4-chlorophenyl)-4-(2,4-dimethylbenzoyl)-1H-pyrrole-2-carboxylate (3ga)

white solid, 53 % yield. mp: 195-197 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.88 (s, 1H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.05 (s, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.79 (s, 1H), 3.77 (s, 3H), 2.28 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.4, 160.4, 139.7, 139.6, 137.1, 135.7, 133.3, 131.3, 129.3, 128.5, 127.7, 125.7, 122.6, 122.2, 119.2, 51.6, 20.8, 19.5; IR (KBr) ν 3447, 3296, 2922, 2853, 1701, 1573, 1469, 1380, 1278, 1133, 1007, 871, 831, 720, 506 cm^{-1}; HRMS(ESI): calcd for $C_{20}H_{17}NO_4Cl$ ($M+H^+$) 370.0846, found 370.0849.



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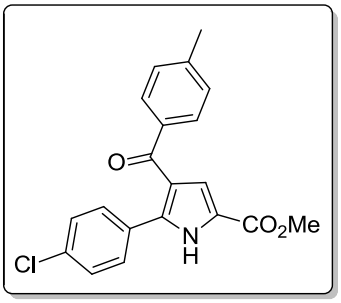
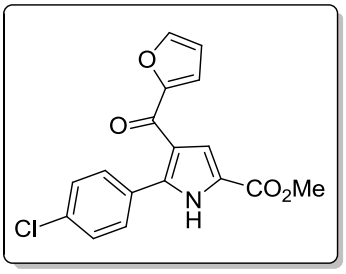
methyl 5-(4-chlorophenyl)-4-(4-methoxybenzoyl)-1H-pyrrole-2-carboxylate (3ha)

white solid, 80 % yield. mp: 189-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 2.5 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 163.3, 161.6, 138.9, 135.0, 132.2, 131.4, 130.0, 129.4, 128.8, 122.6, 122.1, 119.4, 113.6, 55.6, 52.0; IR (KBr) ν 2350, 3291, 3019, 2952, 2852, 1698, 1644, 1611, 1560, 1475, 1450, 1409, 1262, 1204, 1164, 1116, 1037, 1013, 891, 839, 750, 725, 646, 610, 543 cm^{-1}; HRMS(ESI): calcd for $C_{20}H_{17}NO_4Cl$ ($M+H^+$) 370.0846, found 370.0849.



methyl 5-(4-chlorophenyl)-4-(4-methylbenzoyl)-1H-pyrrole-2-carboxylate (3ia)

white solid, 65 % yield. mp: 162-164 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.87 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.4, 160.5, 142.6, 139.1, 135.9, 133.2, 131.1, 129.4, 129.3, 128.9, 127.9, 122.2, 121.5, 118.8, 51.6, 21.1; IR (KBr) ν 3450, 3288, 3269, 2955, 2920, 1692, 1635, 1603, 1556, 1455, 1412, 1339, 1280, 1254, 1204, 1160, 1087, 1002, 896, 836, 762, 673, 552, 511, 465 cm^{-1}; HRMS(ESI): calcd for $C_{20}H_{17}NO_3Cl$ ($M+H^+$) 354.0897, found 354.0893.



methyl 5-(4-chlorophenyl)-4-(furan-2-carbonyl)-1H-pyrrole-2-carboxylate (3ja)

pale yellow solid, 68% yield. mp: 192-194 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.62-7.60 (m, 1H), 7.56-7.52 (m, 3H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 3.1, Hz, 1H), 6.54 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 161.6, 153.4, 146.5, 139.9, 135.2, 130.3, 129.4, 128.7, 122.4, 121.0, 119.2, 118.9, 112.3, 52.1; IR (KBr) ν 3451, 3269, 3126, 2950, 1696, 1624, 1560, 1470, 1436, 1335, 1284, 1259, 1211, 1089, 1018, 938, 845, 759, 598, 560, 513 cm^{-1}; HRMS(ESI): calcd for $C_{17}H_{13}NO_4Cl$ ($M+H^+$) 330.0533, found 330.0530.

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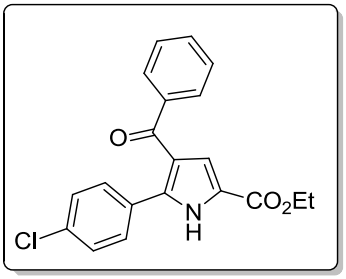
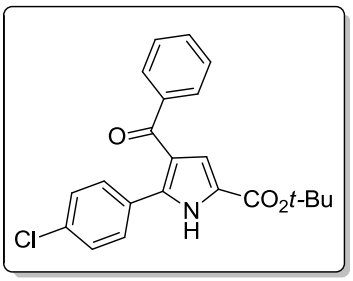


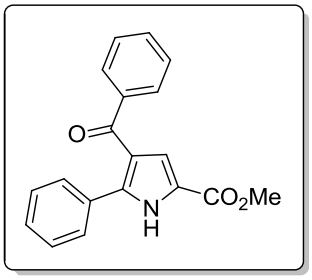
ethyl 4-benzoyl-5-(4-chlorophenyl)-1H-pyrrole-2-carboxylate (3ab)

white solid, 69% yield. mp: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.55-7.46 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 161.4, 139.7, 138.9, 135.1, 132.4, 130.3, 129.7, 129.4, 128.6, 128.3, 122.5, 122.1, 119.6, 61.2, 14.4; IR (KBr) ν 3449, 3280, 2922, 2852, 1683, 1653, 1600, 1455, 1421, 1334, 1280, 1251, 1204, 1164, 1091, 1022, 896, 832, 777, 739, 700, 512 cm^{-1}; HRMS(ESI): calcd for $C_{20}H_{17}NO_3Cl$ ($M+H^+$) 354.0897, found 354.0894.



***tert*-butyl 4-benzoyl-5-(4-chlorophenyl)-1H-pyrrole-2-carboxylate (3ac)**

white solid, 69%. mp: 220-221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (brs, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 2.5 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 160.5, 138.9, 138.9, 135.0, 132.4, 130.1, 129.7, 129.5, 128.8, 128.3, 124.0, 122.0, 118.9, 82.1, 28.3; IR (KBr) ν 3447, 3179, 2924, 2853, 1893, 1707, 1630, 1574, 1456, 1367, 1292, 1152, 1091, 1018, 981, 891, 824, 696, 541, 513 cm^{-1}; HRMS(ESI): calcd for $C_{22}H_{21}NO_3Cl$ ($M+H^+$) 382.1210, found 382.1212.



methyl 4-benzoyl-5-phenyl-1H-pyrrole-2-carboxylate (3ad)

white solid, 82% yield. mp: 157-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (brs, 1H), 7.79 (d, *J* =

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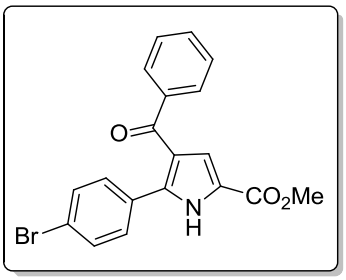
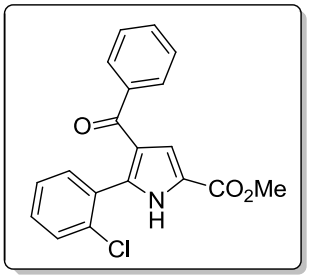
7.1 Hz, 2H), 7.54-7.51 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.34-7.31 (m, 3H), 7.21 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 161.7, 140.9, 138.9, 132.3, 130.8, 129.7, 129.1, 128.9, 128.5, 128.2, 122.0, 122.0, 119.7, 52.1; IR (KBr) ν 3269, 3057, 1692, 1651, 1562, 1460, 1426, 1260, 1210, 1003, 891, 775, 735, 697, 543 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{16}NO_3$ ($M+H^+$) 306.1130, found 306.1126.



methyl 4-benzoyl-5-(4-bromophenyl)-1H-pyrrole-2-carboxylate (3ae)

white solid, 79% yield. mp: 200-202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.48-7.38 (m, 6H), 7.19 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 161.7, 139.7, 138.8, 132.5, 131.7, 130.4, 129.7, 129.7, 128.4, 123.5, 122.2, 122.1, 119.8, 52.1; IR (KBr) ν 3303, 3060, 2950, 1701, 1643, 1464, 1414, 1279, 1250, 1200, 1162, 1069, 1003, 892, 832, 742, 695, 597, 548, 492 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{15}NO_3Br$ ($M+H^+$) 384.0235, found 384.0235.



methyl 4-benzoyl-5-(2-chlorophenyl)-1H-pyrrole-2-carboxylate (3af)

white solid, 89% yield. mp: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (brs, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39-7.32 (m, 4H), 7.30-7.17 (m, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 161.7, 138.7, 137.4, 133.5, 132.2, 132.1, 130.4, 130.3, 129.9, 129.5, 128.1, 126.7, 123.9, 122.3, 118.3, 52.0; IR (KBr) ν 3243, 3022, 2953, 1691, 1655, 1564, 1460, 1345, 1284, 1260, 1213, 1167, 1071, 1002, 894, 852, 768, 735, 699, 557 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{15}NO_3Cl$ ($M+H^+$) 340.0740, found 340.0743.

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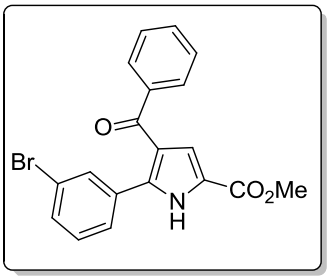
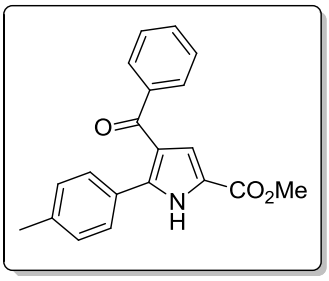


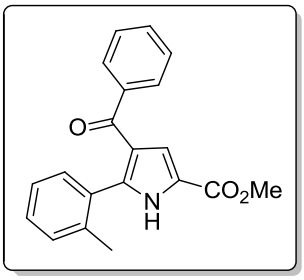
methyl 4-benzoyl-5-(3-bromophenyl)-1H-pyrrole-2-carboxylate (3ag)

white solid, 72% yield. mp: 220-221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.79 (d, *J* = 7.1 Hz, 2H), 7.69-7.67 (m, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.49-7.43 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.23-7.12 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 161.7, 139.1, 138.8, 132.8, 132.4, 132.0, 131.6, 130.0, 129.7, 128.3, 127.8, 122.5, 122.4, 119.7, 52.2; IR (KBr) ν 3445, 3097, 2945, 1726, 1628, 1596, 1573, 1462, 1435, 1335, 1291, 1270, 1200, 1162, 1015, 896, 793, 734, 680, 591, 449 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{15}NO_3Br$ ($M+H^+$) 384.0235, found 384.0235.



methyl 4-benzoyl-5-(*p*-tolyl)-1H-pyrrole-2-carboxylate (3ah)

white solid, 76% yield. mp: 184-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (brs, 1H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.1 Hz), 7.38 (d, *J* = 7.6 Hz), 7.19 (d, *J* = 2.6 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 3.82 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 161.7, 141.1, 139.2, 139.0, 132.2, 129.7, 129.3, 128.6, 128.2, 127.9, 121.7, 121.7, 119.8, 52.0, 21.4; IR (KBr) ν 3407, 3169, 2948, 1715, 1628, 1561, 1478, 1454, 1287, 1204, 1166, 1115, 1012, 892, 739, 701, 608, 538 cm^{-1}; HRMS(ESI): calcd for $C_{20}H_{18}NO_3$ ($M+H^+$) 320.1287, found 320.1286.



methyl 4-benzoyl-5-(*o*-tolyl)-1H-pyrrole-2-carboxylate (3ai)

white solid, 82% yield. mp: 217 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (brs, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.32-7.24 (m, 3H), 7.23-7.15 (m,

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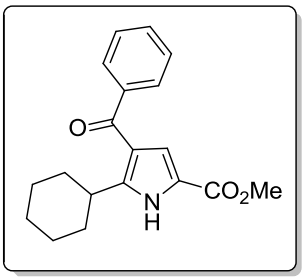
2H), 3.72 (d, *J* = 2.6 Hz, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 161.8, 140.9, 138.9, 137.3, 132.0, 131.2, 130.3, 130.2, 129.4, 129.2, 128.1, 125.7, 123.2, 121.7, 118.5, 52.0, 20.0; IR (KBr) ν 3451, 3249, 2952, 1692, 1651, 1563, 1472, 1430, 1343, 1288, 1264, 1212, 1002, 893, 853, 803, 773, 738, 701, 451 cm^{-1}; HRMS(ESI): calcd for $C_{20}H_{18}NO_3$ ($M+H^+$) 320.1287, found 320.1284.



methyl 4-benzoyl-5-cyclohexyl-1H-pyrrole-2-carboxylate (3aj)

white solid, 31% yield. mp: 168-171 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (brs, 1H), 7.79 (d, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 3.85 (s, 3H), 3.51 (tt, *J* = 11.6, 11.6, 3.1, 3.1 Hz, 1H), 2.07 (d, *J* = 11.0 Hz, 2H), 1.85 (d, *J* = 12.5 Hz, 2H), 1.78 (d, *J* = 13.3 Hz, 1H), 1.54-1.34 (m, 4H), 1.32-1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 161.5, 149.7, 140.1, 131.8, 129.2, 128.3, 120.3, 120.0, 119.3, 51.8, 36.3, 32.4, 26.5, 26.1; IR (KBr) ν 3301, 2921, 2851, 1691, 1639, 1560, 1495, 1456, 1377, 1265, 1203, 1101, 1014, 908, 801, 732, 698, 669, 630, 514 cm^{-1}; HRMS(ESI): calcd for $C_{19}H_{22}NO_3$ ($M+H^+$) 312.1600, found 312.1599.

References

1. V. S. Aulakh and M. A. Ciufolini, *J. Org. Chem.*, 2009, **74**, 5750.
2. Y. Shen, S. Cai, C. He, X. Lin, P. Lu and Y. Wang, *Tetrahedron*, 2011, **67**, 8338.

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X-ray crystal structure of 3aa

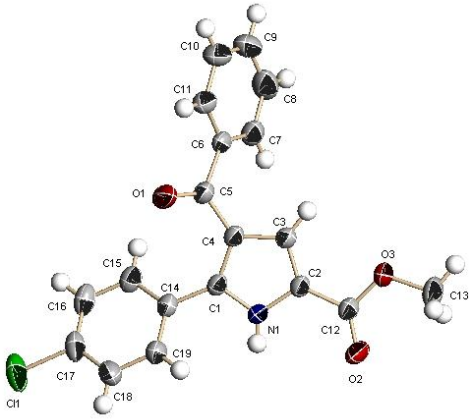

Fig 1. X-ray crystal structure of 3aa (the ORTEP plot is shown at the 30 percent probability level)

Crystal data for 3aa:

(CCDC 918358 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html.)

Empirical formula	$C_{19}H_{14}ClNO_3$
Formula weight	339.76
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2 (1) / c
Unit cell dimensions	a = 12.9597 (11) A alpha = 90 deg.
	b = 9.6741 (8) A beta = 100.796 (2) deg.
	c = 13.3527 (11) A gamma = 90 deg.
Volume	1644.4 (2) A^3
Z, Calculated density	4, 1.372 Mg/m^3
Absorption coefficient	0.249 mm^-1
F(000)	704
Crystal size	0.287 x 0.211 x 0.143 mm
Theta range for data collection	2.62 to 26.00 deg.
Limiting indices	-15<=h<=15, -6<=k<=11, -14<=l<=16
Reflections collected / unique	9581 / 3225 [R (int) = 0.0244]
Completeness to theta = 26.00	100.0 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.72019
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3225 / 0 / 223
Goodness-of-fit on F^2	1.027
Final R indices [I>2 sigma(I)]	R1 = 0.0401, wR2 = 0.1026
R indices (all data)	R1 = 0.0495, wR2 = 0.1103
Largest diff. peak and hole	0.211 and -0.232 e.A^-3

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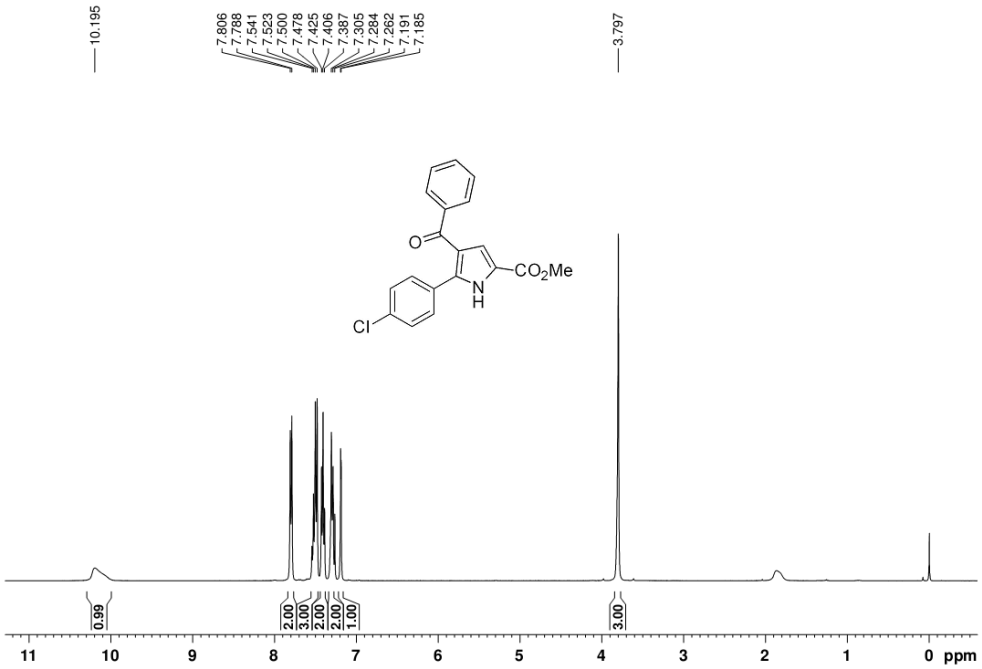
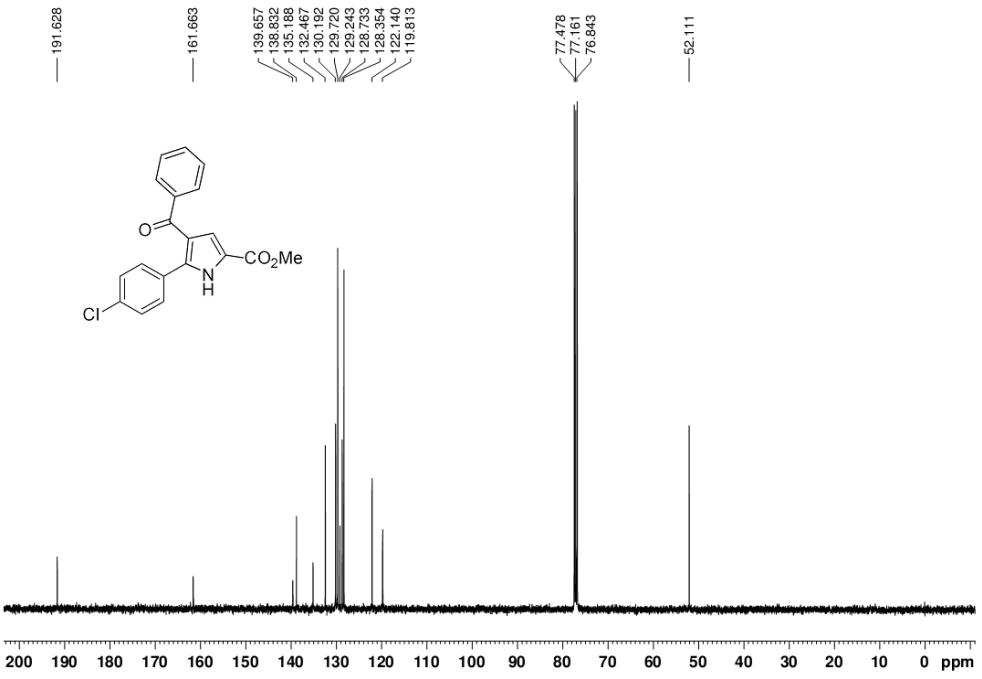
^{1}H NMR and ^{13}C NMR spectra

methyl 4-benzoyl-5-(4-chlorophenyl)-1H-pyrrole-2-carboxy late (3aa)

^{1} H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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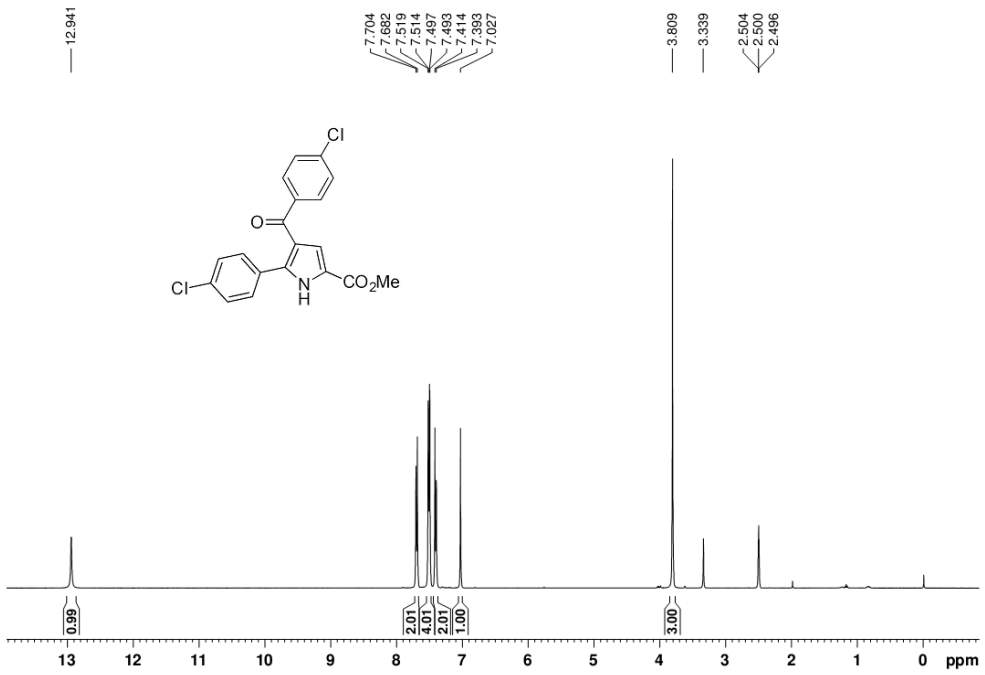
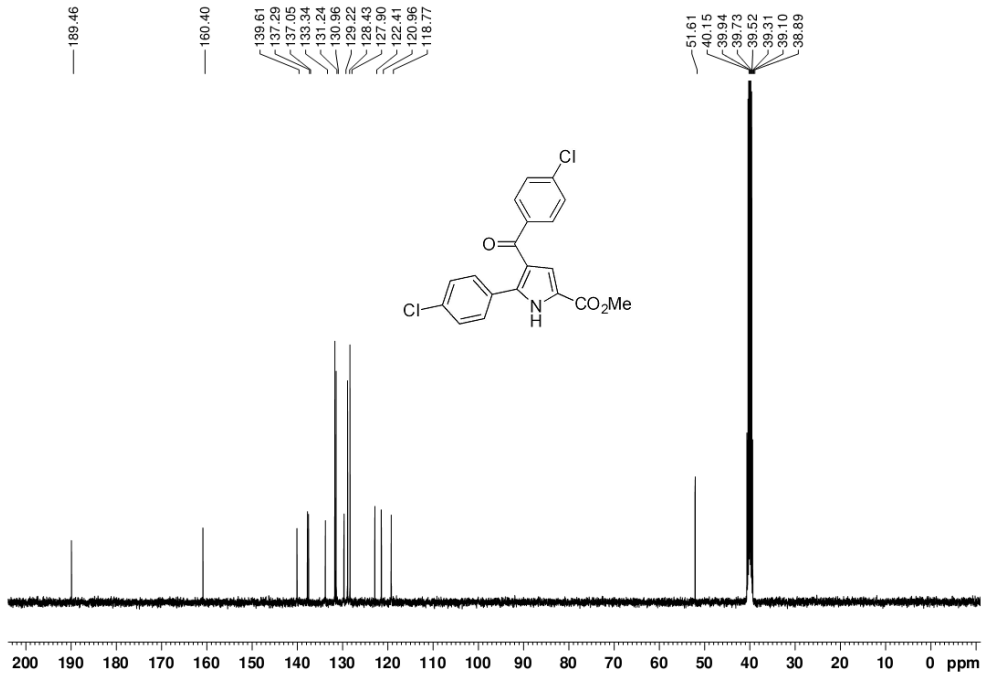
methyl 4-(4-chlorobenzoyl)-5-(4-chlorophenyl)-1H-pyrrole-2-carboxylate (3ba)

^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)



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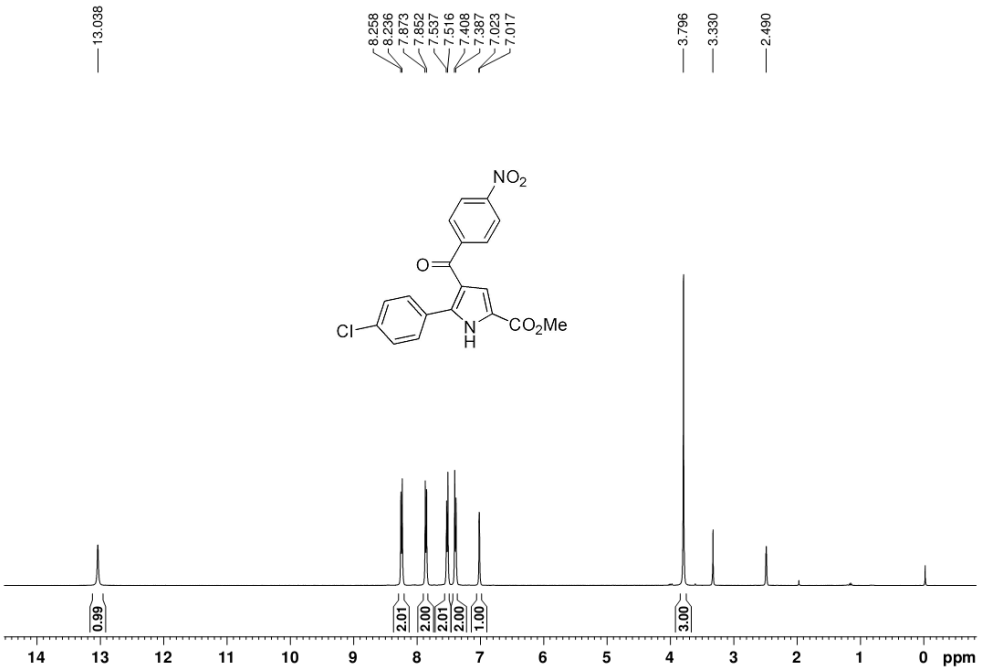
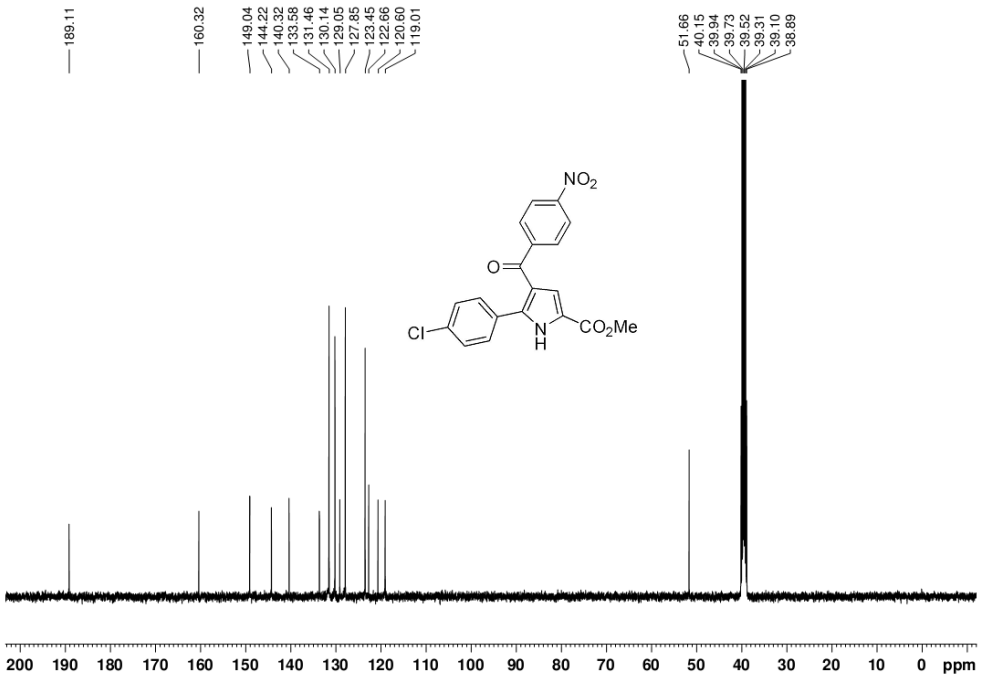
methyl 5-(4-chlorophenyl)-4-(4-nitrobenzoyl)-1H-pyrrole-2-carboxylate (3ca)

^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)



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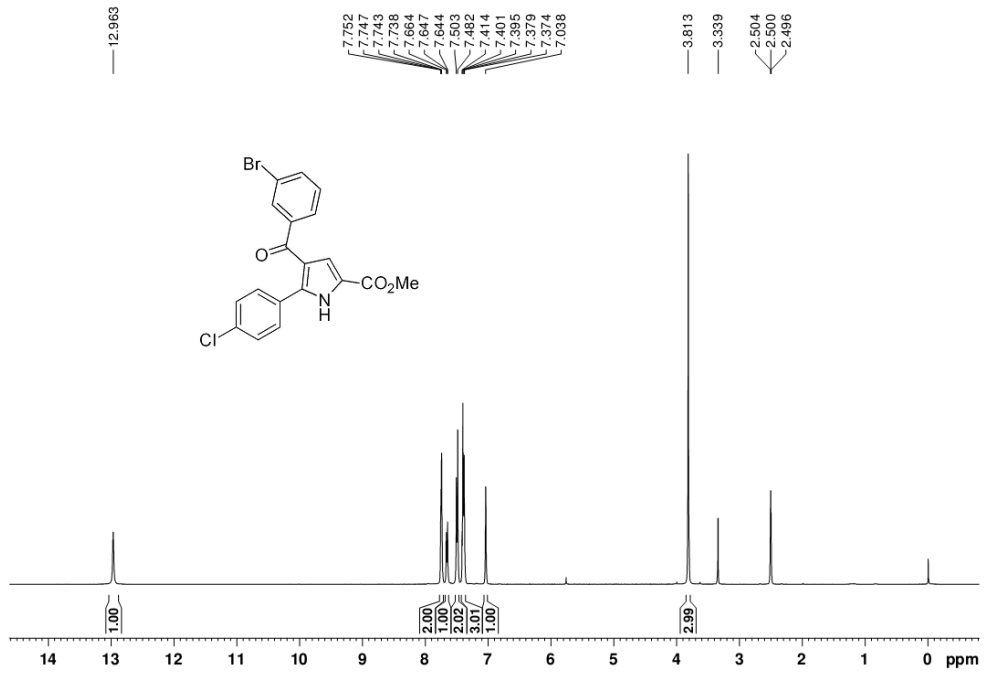
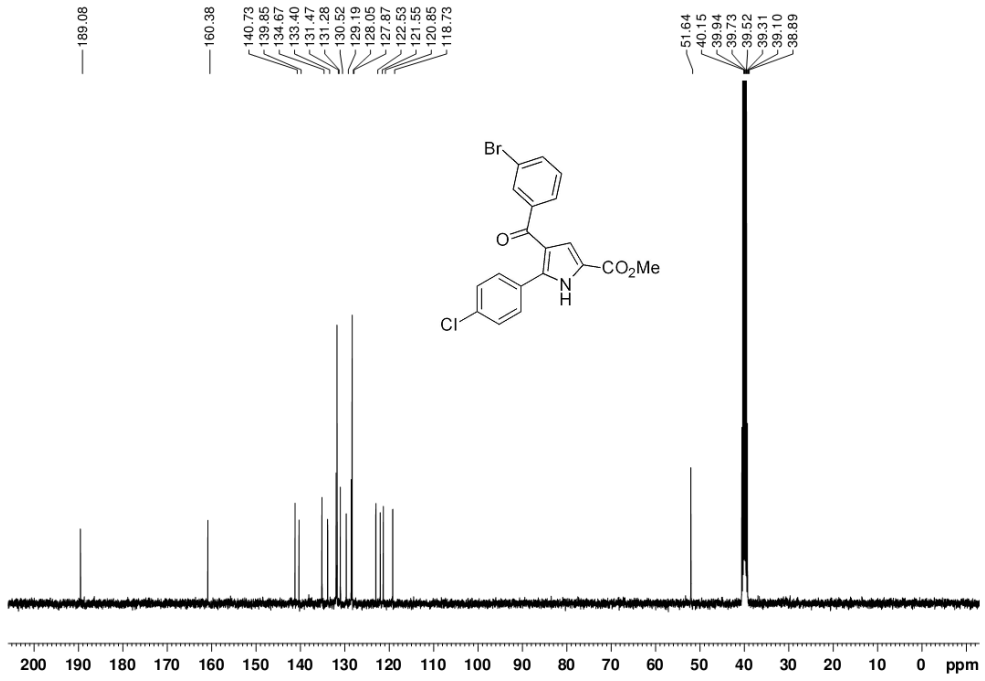
methyl 4-(3-bromobenzoyl)-5-(4-chlorophenyl)-1H-pyrrole-2-carboxylate (3da)

^{1}H NMR (400 MHz, DMSO-*d6*)



^{13}C NMR (100 MHz, DMSO-d_6)



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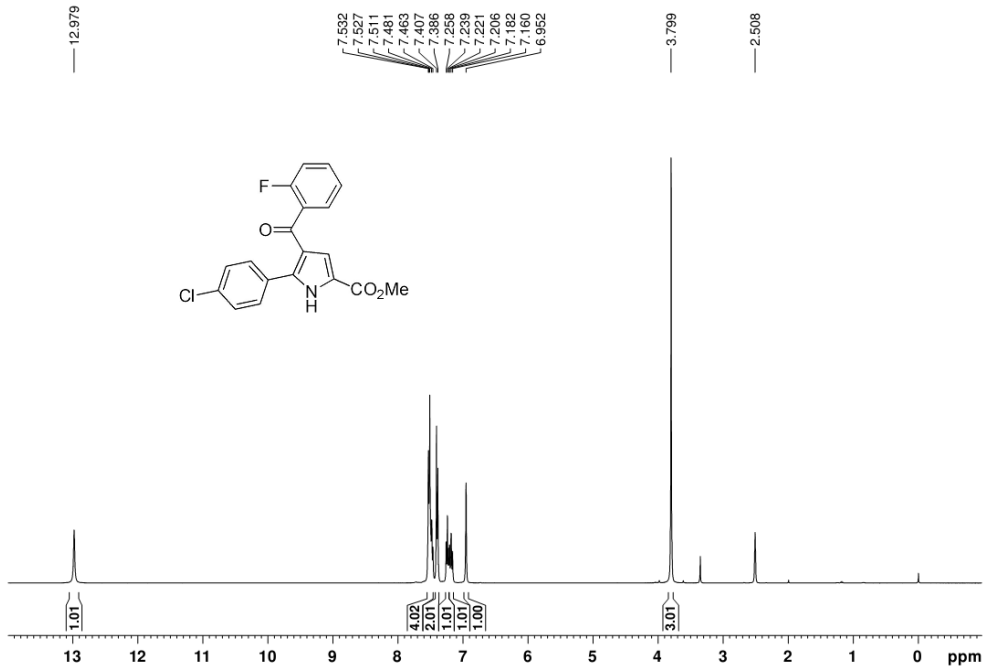
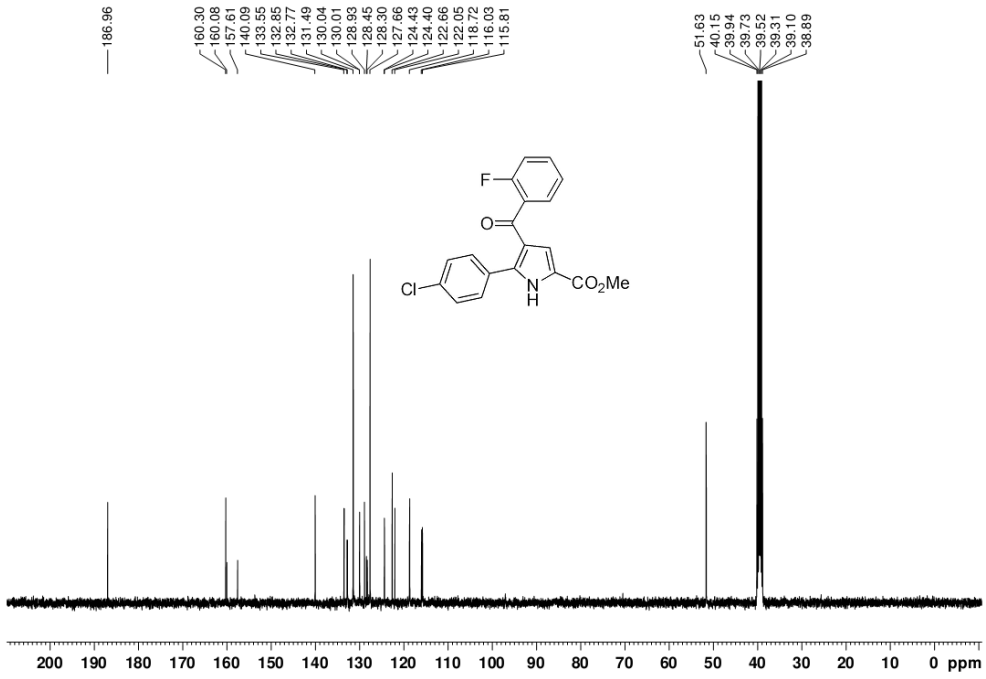
methyl 5-(4-chlorophenyl)-4-(2-fluorobenzoyl)-1H-pyrrole-2-carboxylate (3ea)

^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)



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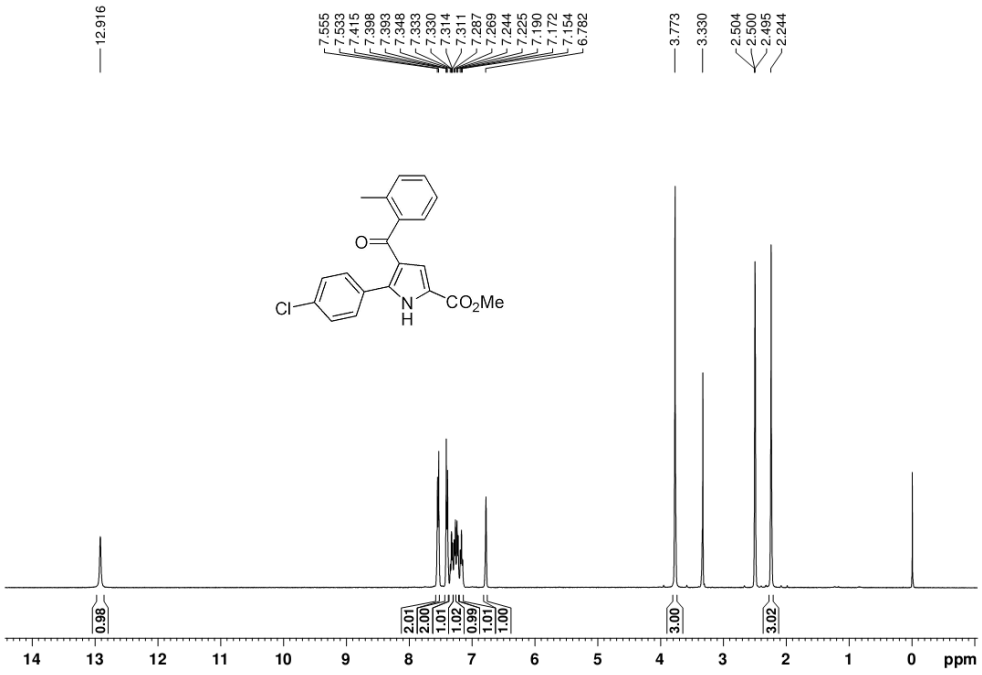
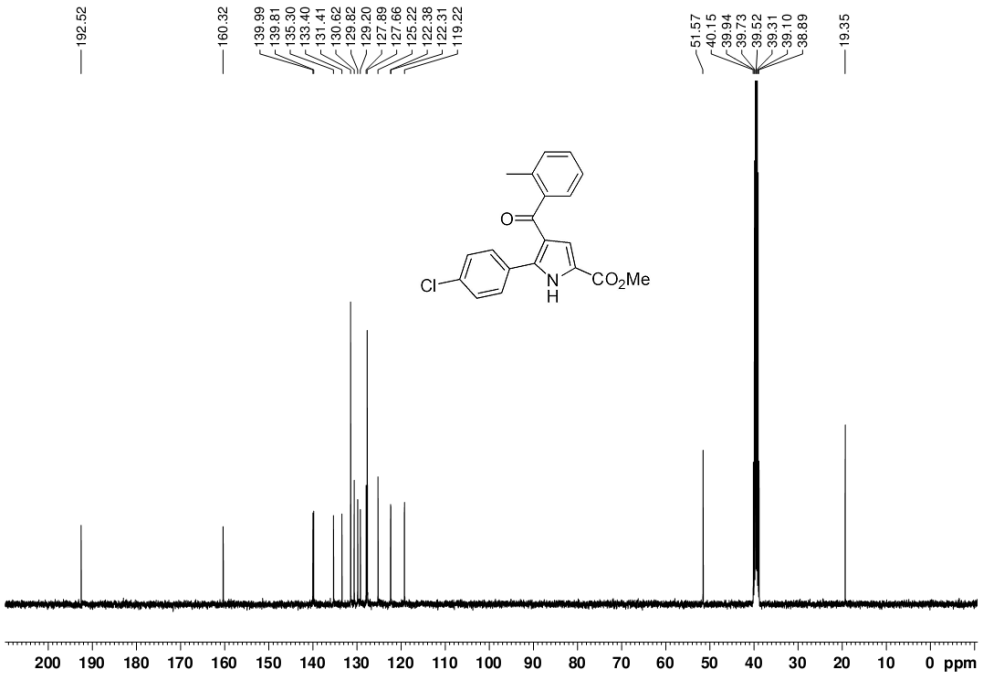
methyl 5-(4-chlorophenyl)-4-(2-methylbenzoyl)-1H-pyrrole-2-carboxylate (3fa)

^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)



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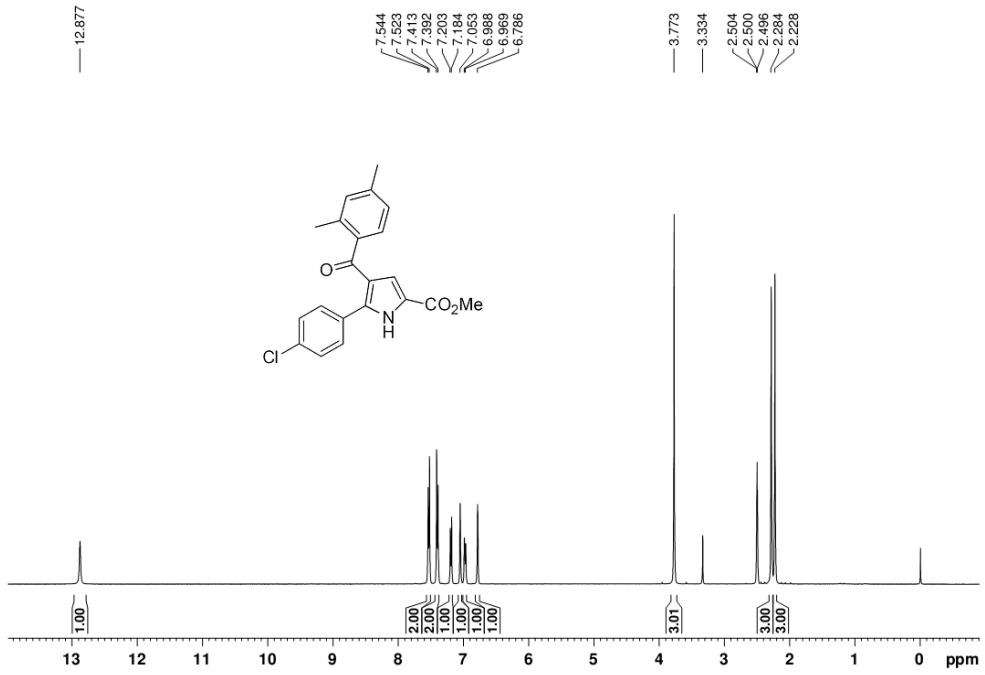
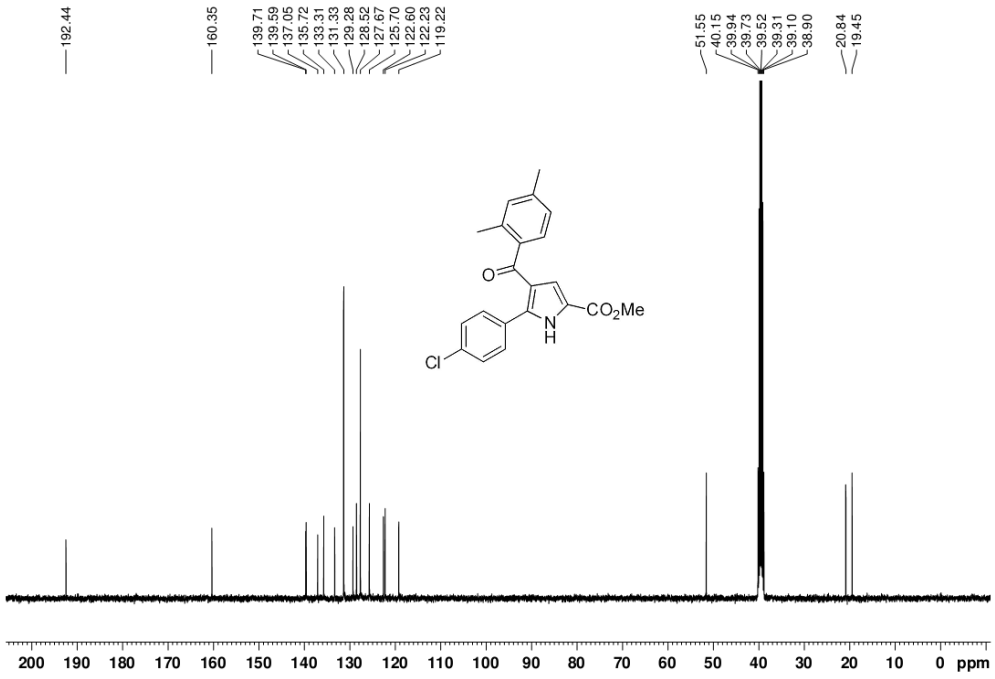
methyl 5-(4-chlorophenyl)-4-(2,4-dimethylbenzoyl)-1H-pyrrole-2-carboxylate (3ga)

^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)



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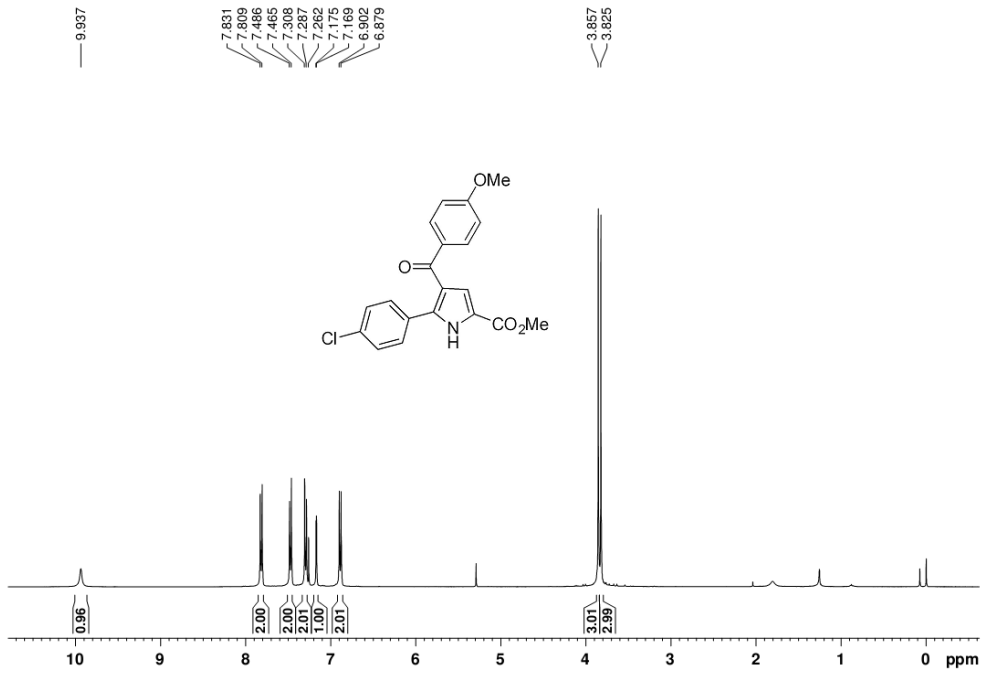
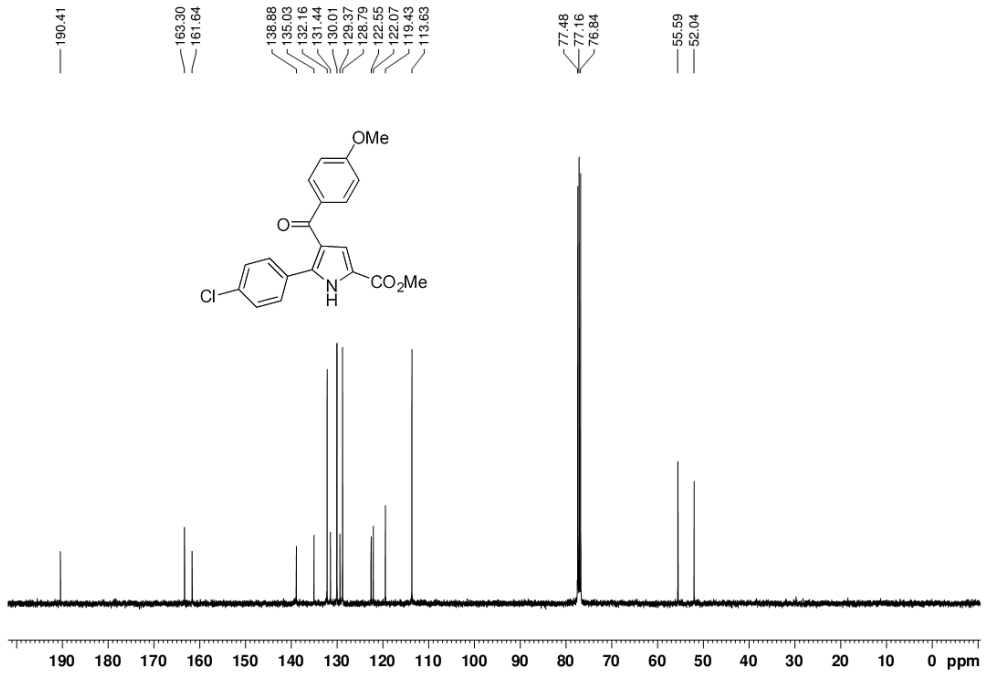
methyl 5-(4-chlorophenyl)-4-(4-methoxybenzoyl)-1H-pyrrole-2-carboxylate (3ha)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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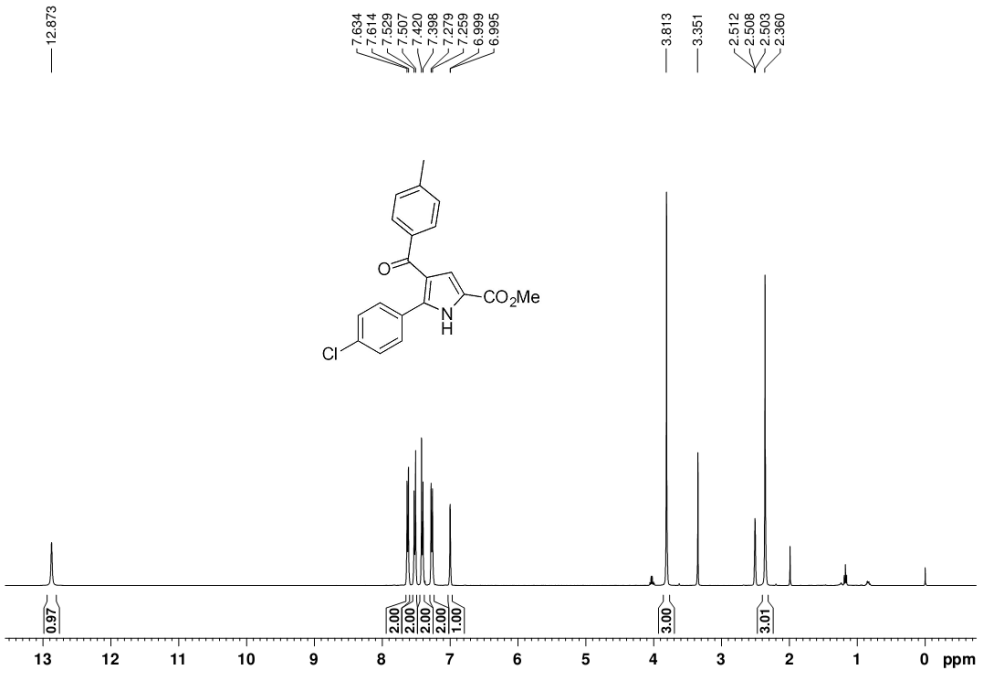
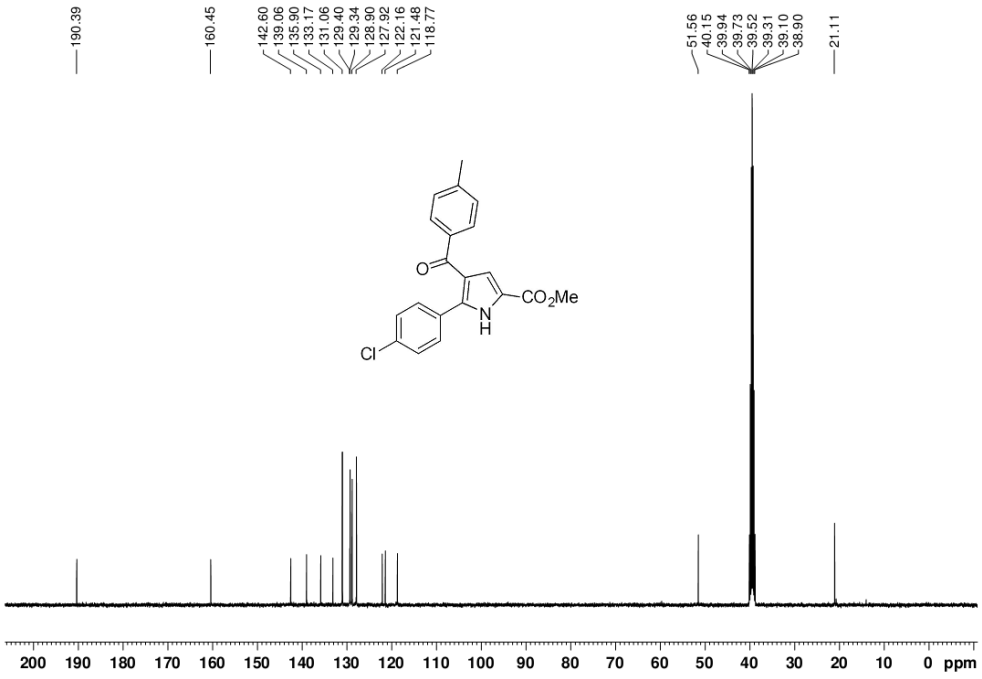
methyl 5-(4-chlorophenyl)-4-(4-methylbenzoyl)-1H-pyrrole-2-carboxylate (3ia)

^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)



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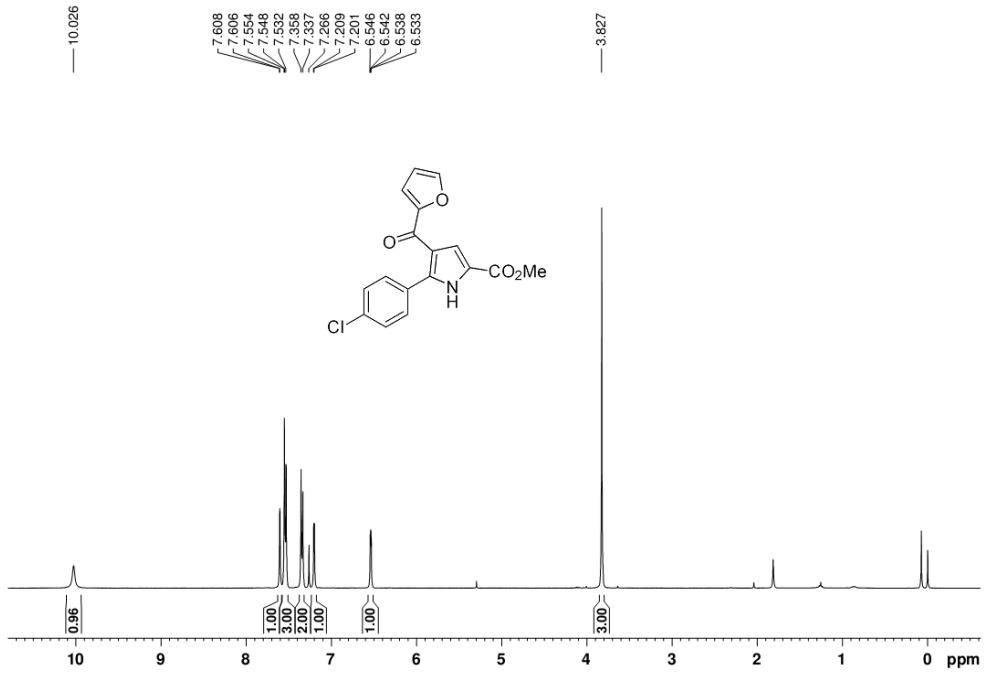
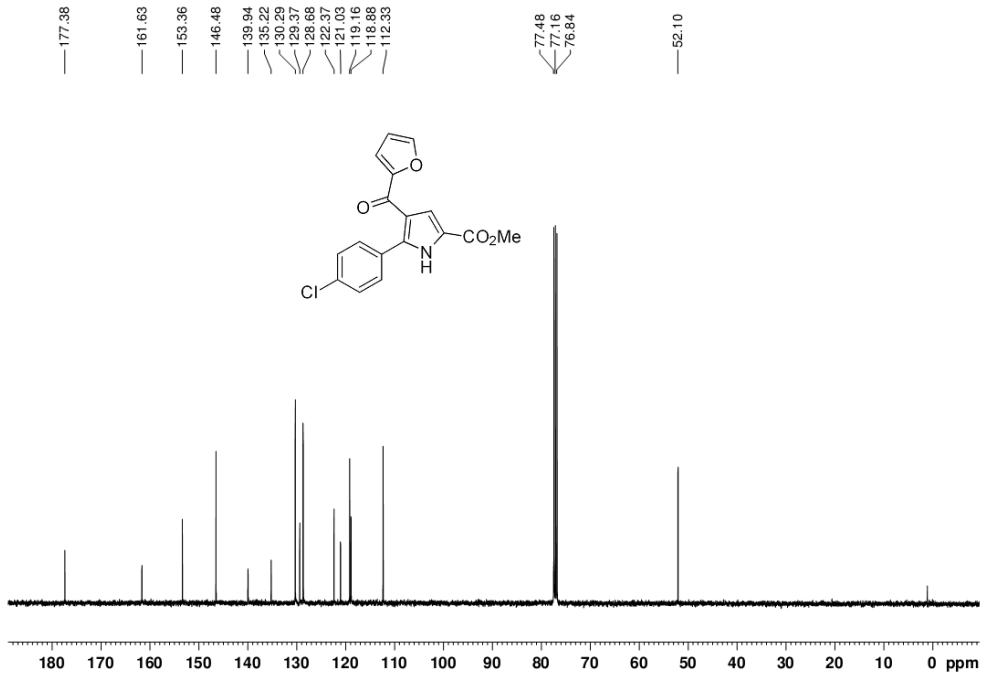
methyl 5-(4-chlorophenyl)-4-(furan-2-carbonyl)-1H-pyrrole-2-carboxylate (3ja)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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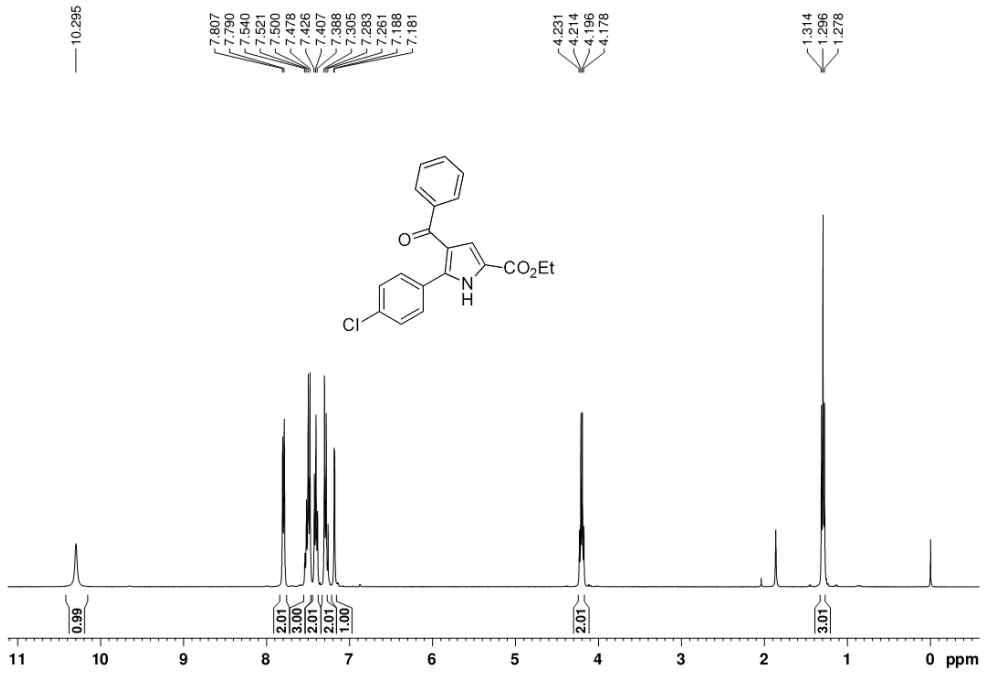
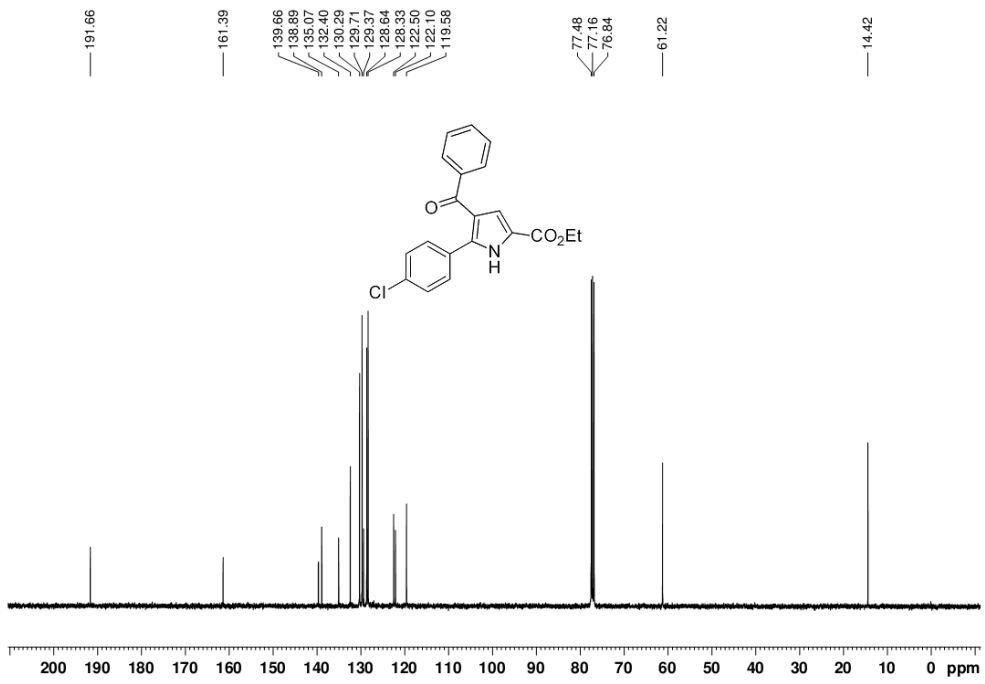
ethyl 4-benzoyl-5-(4-chlorophenyl)-1H-pyrrole-2-carboxylate (3ab)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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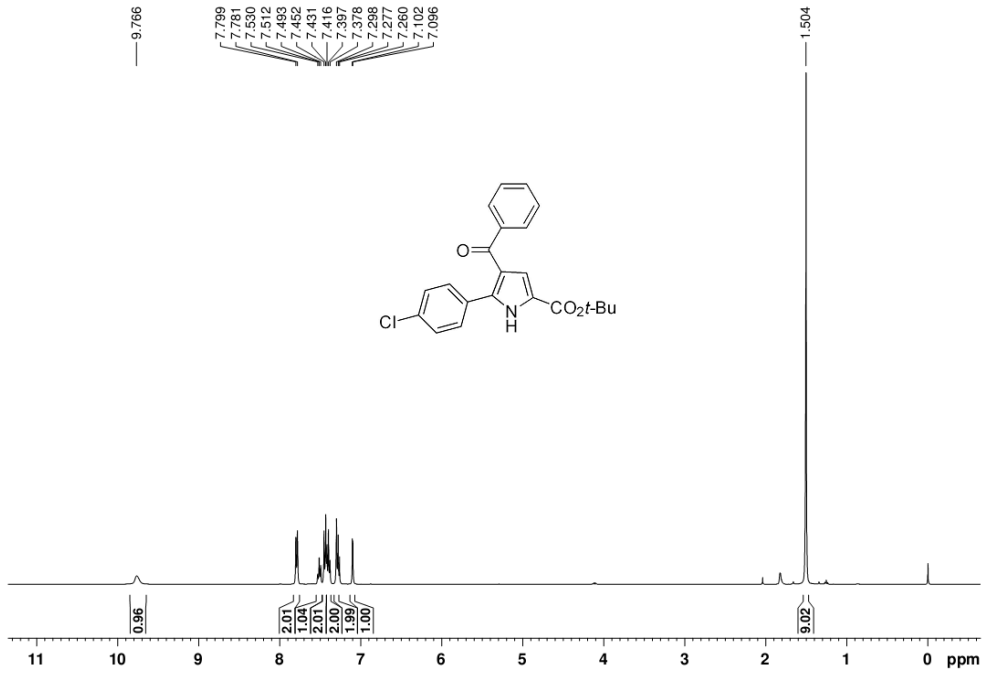
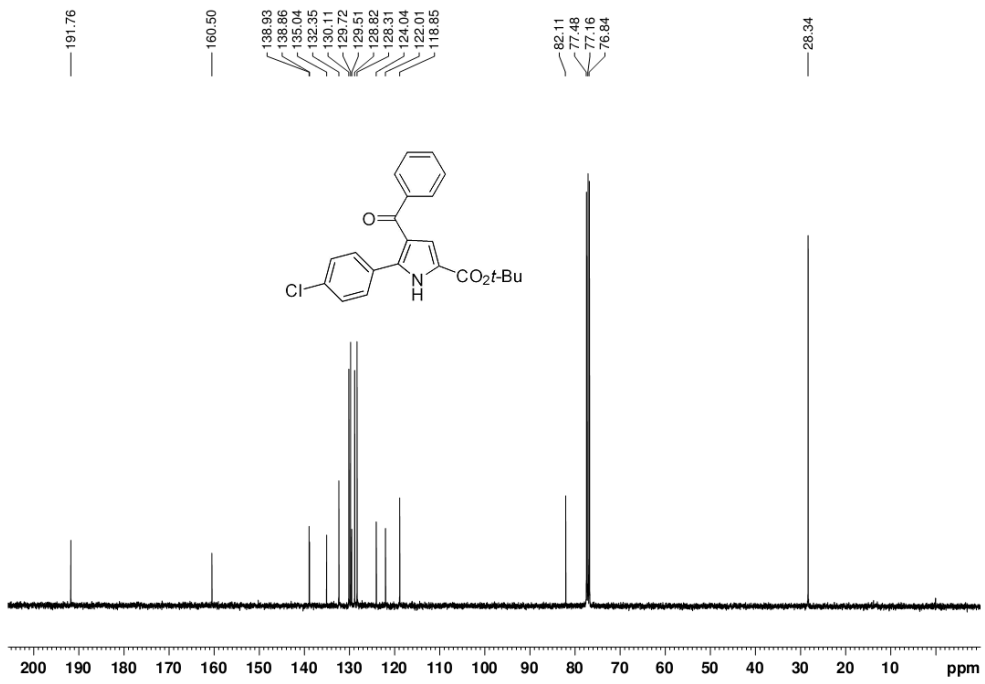
tert-butyl 4-benzoyl-5-(4-chlorophenyl)-1H-pyrrole-2-carboxylate (3ac)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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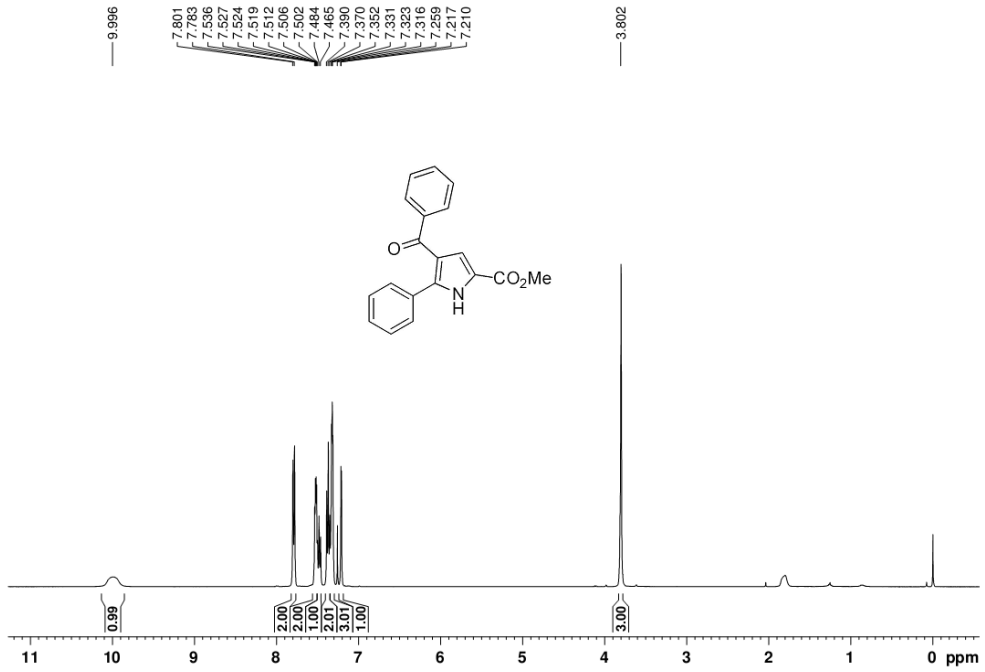
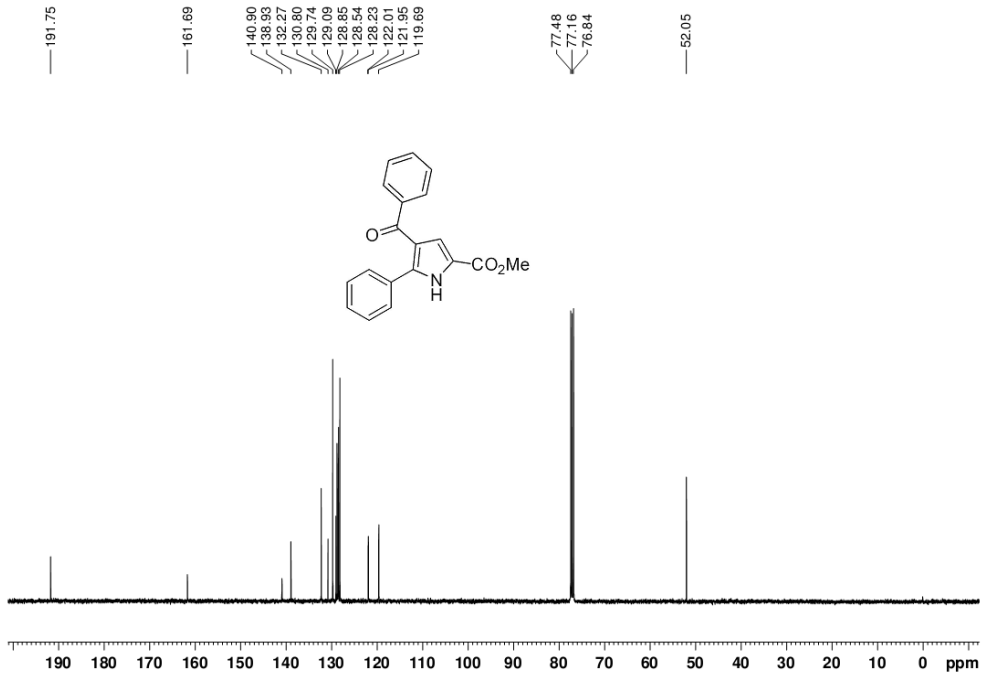
methyl 4-benzoyl-5-phenyl-1H-pyrrole-2-carboxylate (3ad)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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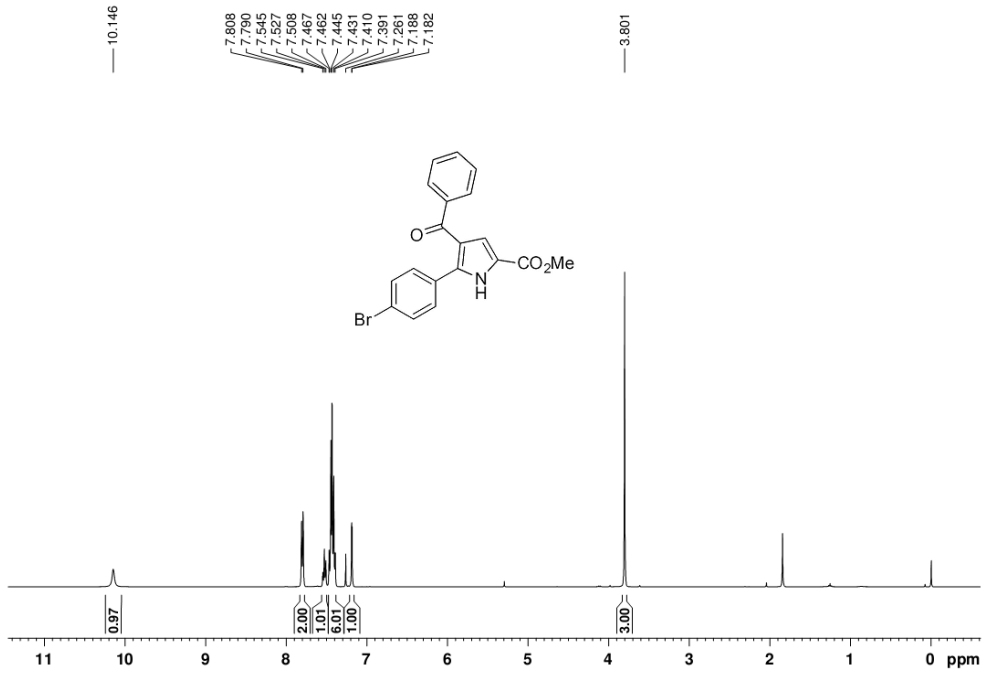
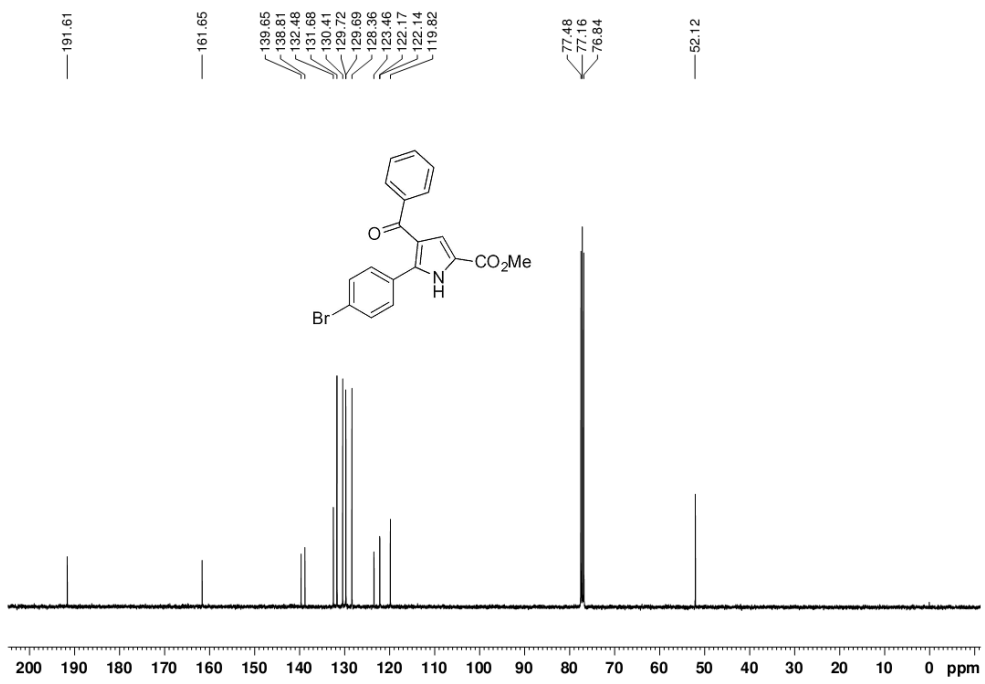
methyl 4-benzoyl-5-(4-bromophenyl)-1H-pyrrole-2-carboxylate (3ae)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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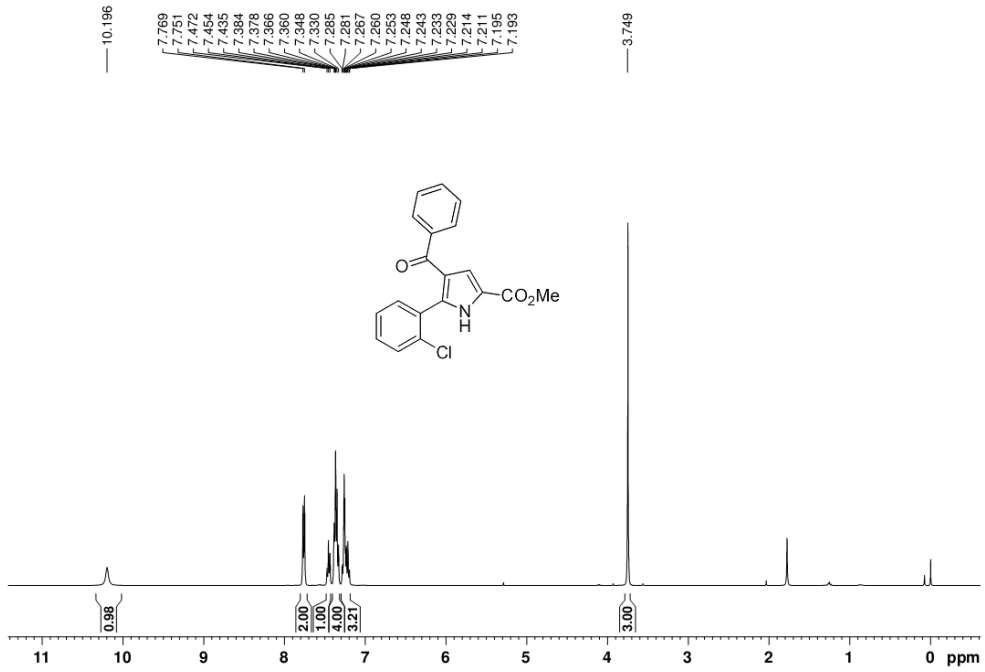
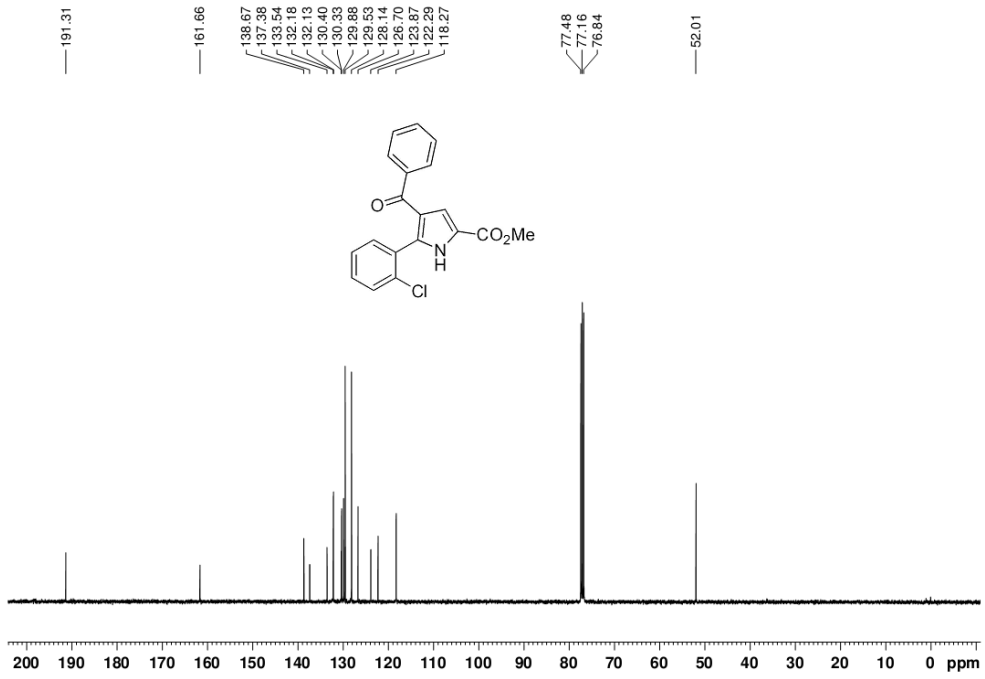
methyl 4-benzoyl-5-(2-chlorophenyl)-1H-pyrrole-2-carboxylate (3af)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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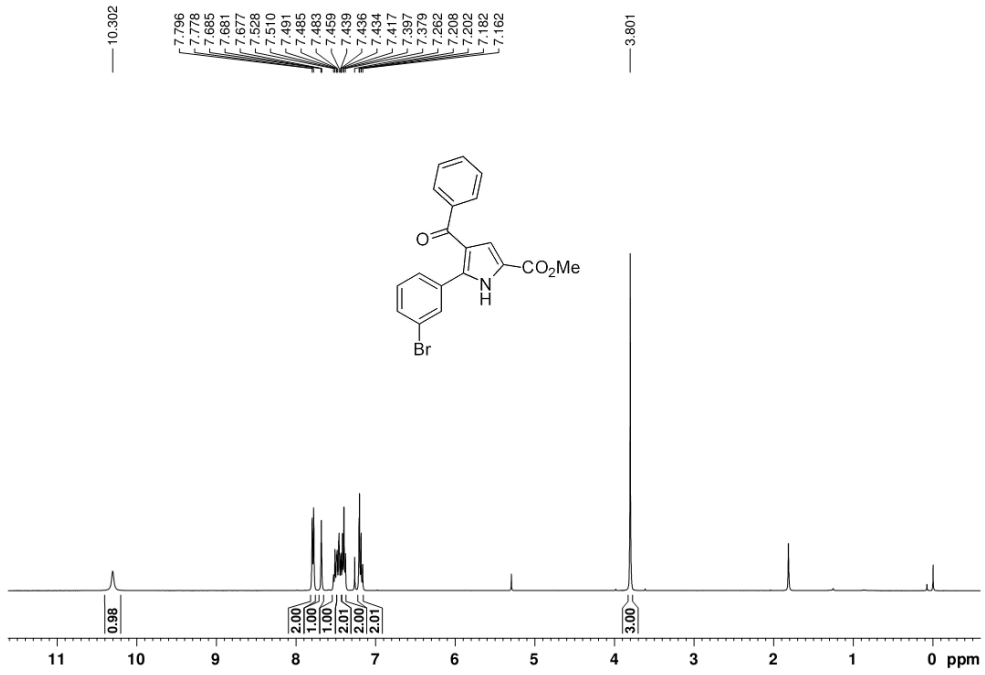
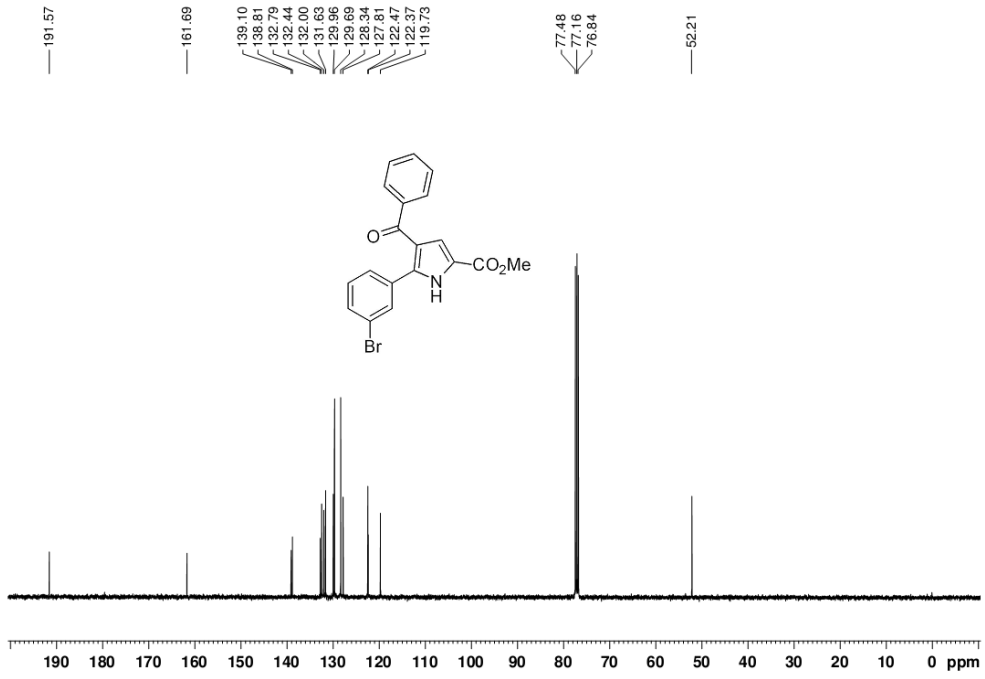
methyl 4-benzoyl-5-(3-bromophenyl)-1H-pyrrole-2-carboxylate (3ag)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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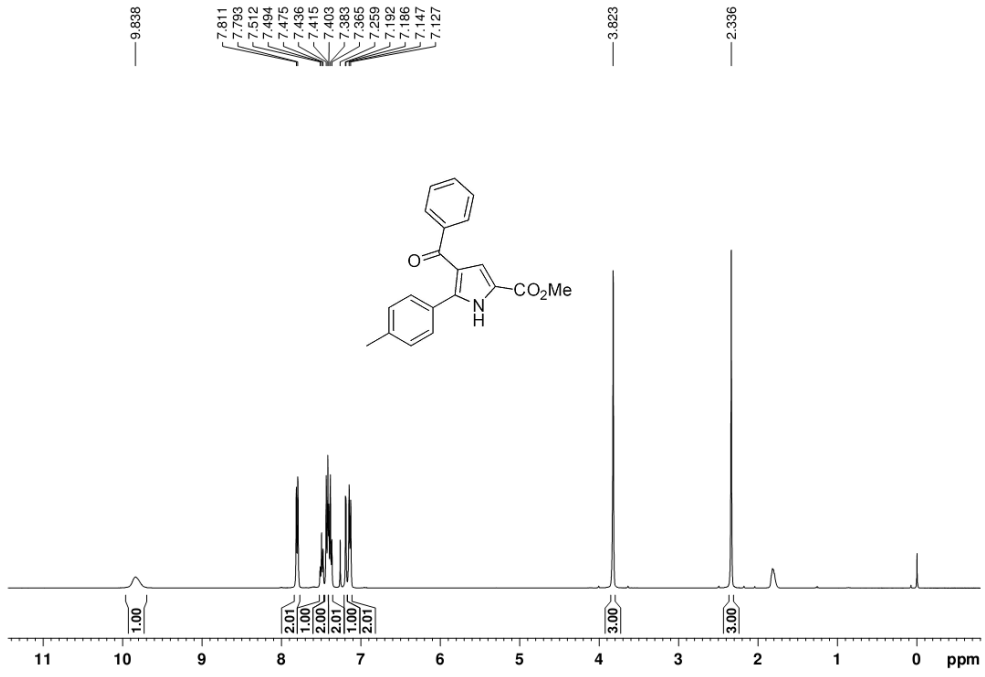
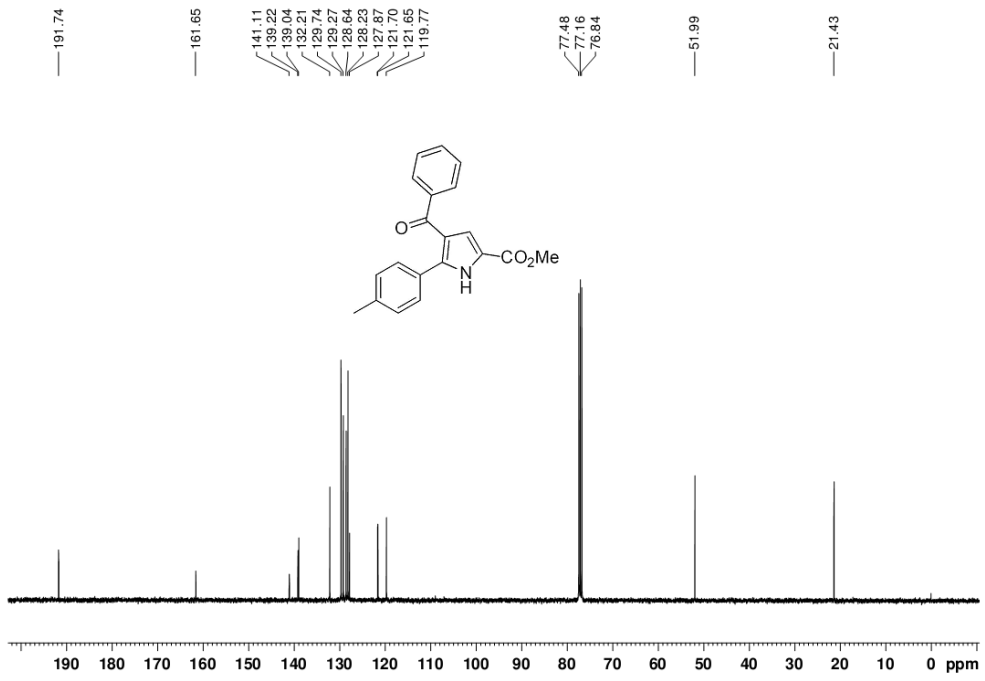
methyl 4-benzoyl-5-(*p*-tolyl)-1H-pyrrole-2-carboxylate (3ah)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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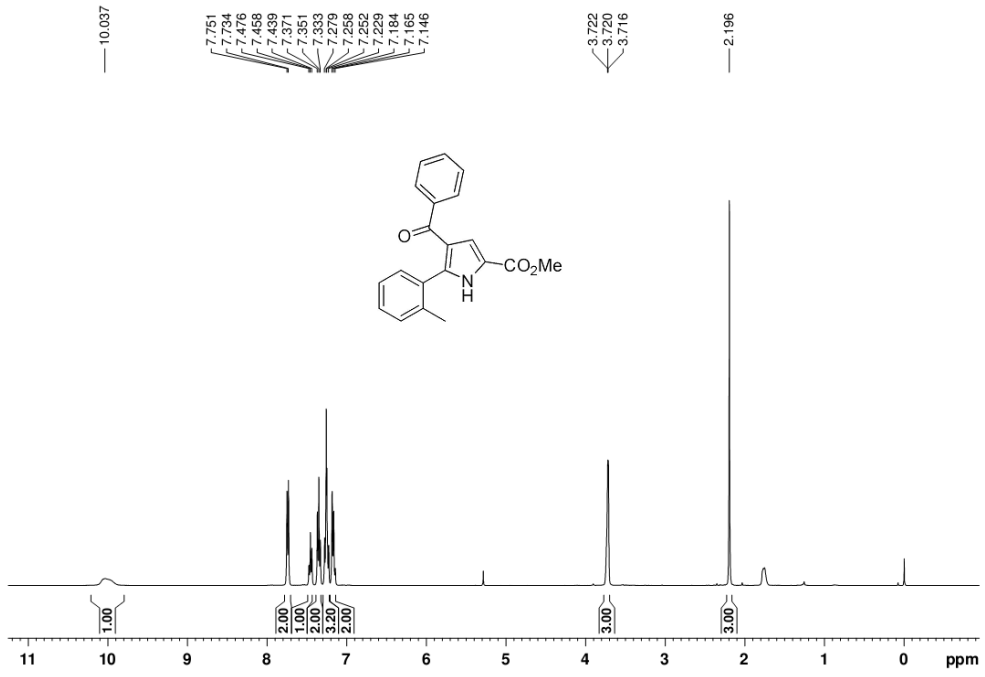
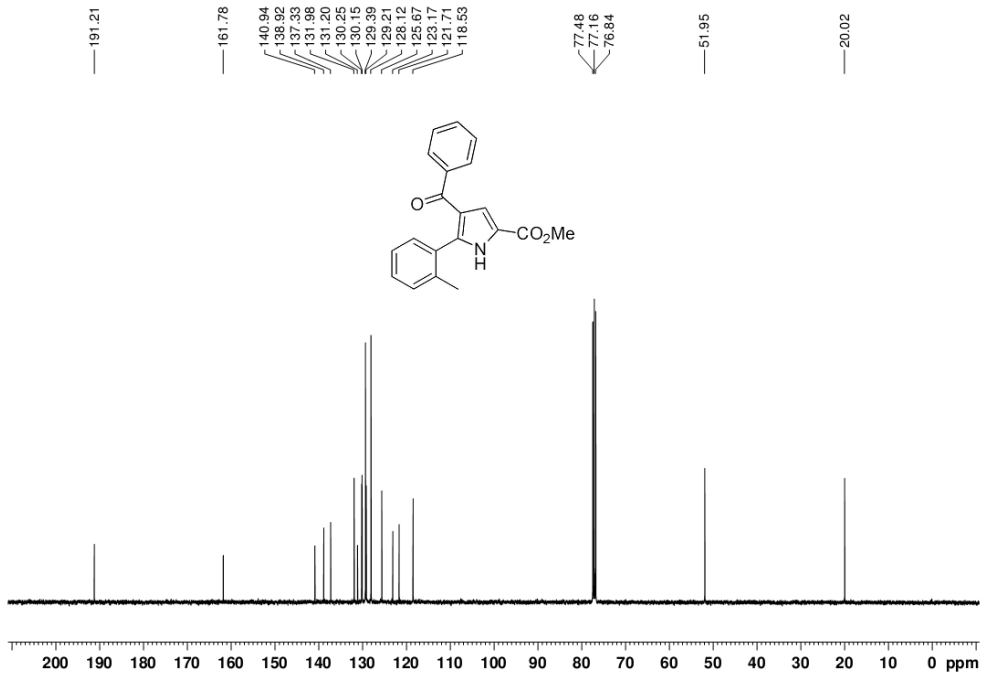
methyl 4-benzoyl-5-(*o*-tolyl)-1H-pyrrole-2-carboxylate (3ai)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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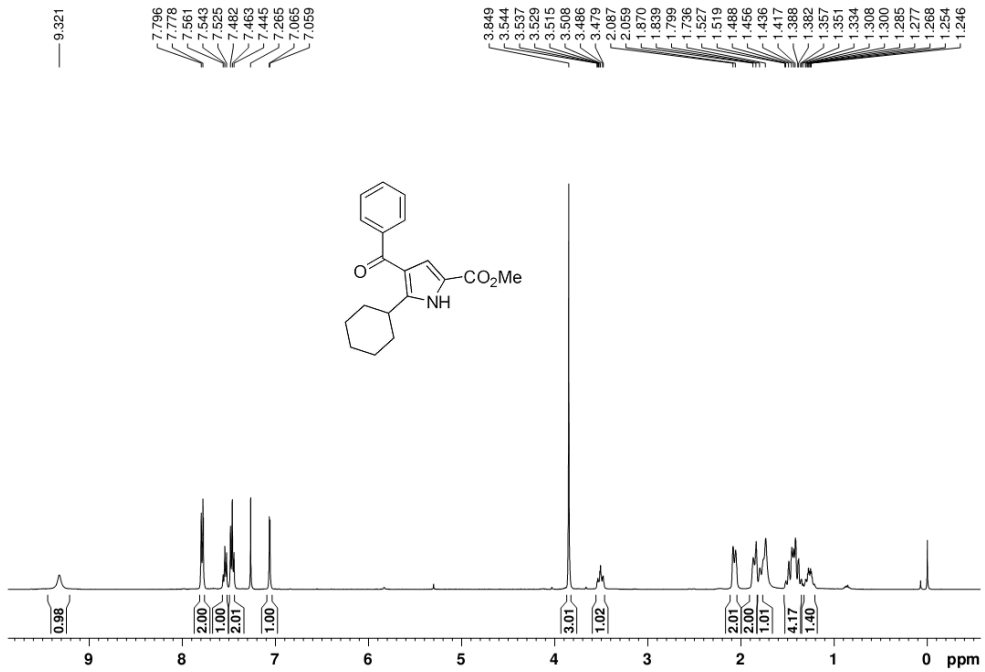
methyl 4-benzoyl-5-cyclohexyl-1H-pyrrole-2-carboxylate (3aj)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)