Supporting Information

Oxidative Organocatalytic Chemoselective *N*-Acylation of Heterocycles with Aldehydes

Linda Ta and Henrik Sundén

Table of Contents

General Considerations

CH_2Cl_2 were stored over molecular sieves (4 Å). THF was distilled over Na/benzophenone, degassed and stored over molecular sieves (4 Å) before usage. All reagents and other solvents and were purchased from commercial sources and used without further modifications. NHC-catalyst **7**,[1] and **9**[2] were synthesized according to literature procedure. Oxidant **2** was synthesized according to literature procedure.[3]

All reaction were carried out in 4 mL borosilicate glass vials with phenolic cap purchased from Fischer Scientific and no consideration were taken to exclude moisture or oxygen during the reaction unless otherwise noted.

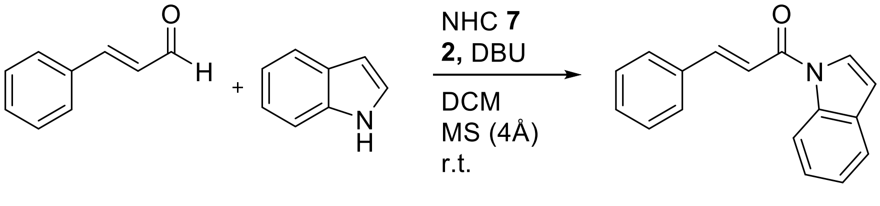
Purification was performed by an automated column chromatography Biotage Isolera™ Spektra One with Biotage SNAP®-10 g KP-sil column together with a 1 g samplet® cartridge unless otherwise noted using petroleum ether (40–60 °C)/ethyl acetate as solvent mixture unless otherwise noted. Silica column chromatography was performed with chromatographic silica media for separation and purifications (40-63 micron). Thin layer chromatography (TLC) was performed on Merck TLC plates pre-coated with silica gel 60 F_{254} (Art 5715, 0.25 mm) and was visualized with UV-light (254 nm).

NMR-spectra, ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) were recorded on Varian 400. The chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) relative to the residual peak from solvent $CDCl_3$ or DMSO-d_6 as the internal standard; ^{1}H NMR at δ 7.26 ppm and ^{13}C NMR at δ 77.2 ppm for $CDCl_3$ and ^{1}H NMR at δ 2.50 ppm and ^{13}C NMR at δ 39.5 ppm for DMSO-d_6. All coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated by s (singlet), d (doublet), dd (doublet of doublet), appd (apparent doublet), appdd (apparent doublet of a doublet), appddd (apparent doublet of doublets of doublets), triplet (t), apt (apparent triplet) and m (multiplet).

FT-ATR-IR spectra were recorded on a Perkin-Elmer Spectrum Frontier infrared spectrometer with pike-GladiATR™ module and reported in wavenumber (cm^{-1}) as follows: s (strong).

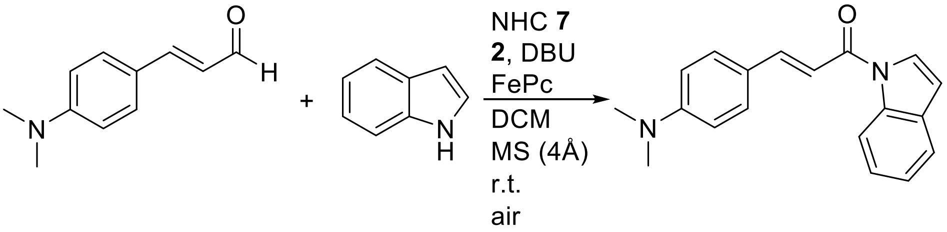
High-resolution mass spectrometry (HRMS) was performed on an Agilent 6520 equipped with an electrospray interface operated in positive ionization mode. Samples were dissolved in acetonitrile (10 µg/mL), and run using flow-through injection. The samples were eluated by using eluation 10% MeOH/water (50:50) and 90% acetonitrile with 0.1% formic acid, with a flow rate of 0.2 mL/min.

General Procedure



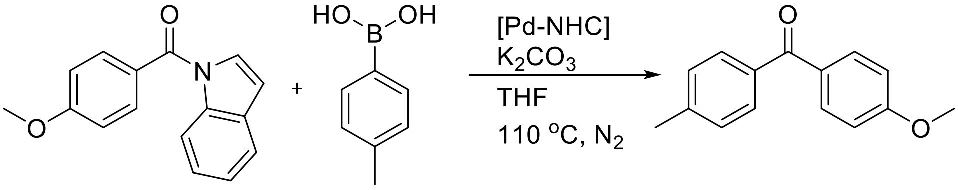
To a 4 mL vial were added NHC **7** (2 mg, 0.008 mmol, 0.05 eq.), **2** (58 mg, 0.14 mmol, 1 eq.), indole (OBS strong odor!) (16.5 mg, 0.14 mmol, 1 eq.), 4 Å molecular sieves (MS) (ca 0.5 g) and a magnetic stir bar followed by CH_2Cl_2 (0.4 ml). Cinnamaldehyde (36 µL, 0.28 mmol, 2 eq.) and DBU (21.3 µL, 0.14 mmol, 1 eq.) were subsequently added to the vial followed by additional CH_2Cl_2 (0.4 ml). The reaction mixture was stirred at room temperature until full conversion (monitored by ^{1}H NMR). The reaction mixture was then loaded onto a samplet® cartridge and let to dry. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 3% → 5% ethyl acetate in petroleum ether) using a SNAP®-10g KP-sil column together with a 1 g samplet® cartridge. The product was obtained as white crystals (24.7 mg, 0.01 mmol, 71%).

Procedure for Oxidation Using Aerobic Oxygen



To a 4 mL vial were added NHC **7** (1.9 mg, 0.0072 mmol, 0.05 eq.), **2** (13.9 mg, 0.034 mmol, 0.25 eq.), FePc (2.6 mg, 0.005 mmol, 0.03 eq.), 4-(dimethylamino)cinnamaldehyde (45 mg, 0.26 mmol, 1.9 eq.), indole (OBS strong odor!) (15.7 mg, 0.134 mmol, 1 eq.), 4 Å molecular sieves (MS) (ca 0.5 g) and a magnetic stir bar followed by CH_2Cl_2 (0.4 ml). DBU (20 µL, 0.13 mmol, 1 eq.) was subsequently added to the vial followed by additional CH_2Cl_2 (0.4 ml). The reaction mixture was stirred at room temperature exposed to the atmosphere for 3 h. The reaction mixture was then loaded onto a samplet® cartridge (1 g) and let to dry. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 3% → 5% ethyl acetate in petroleum ether) using a SNAP®-10g KP-sil column together with the samplet® cartridge. The product was obtained as yellow oil (35.2 mg, 0.012 mmol, 90%).

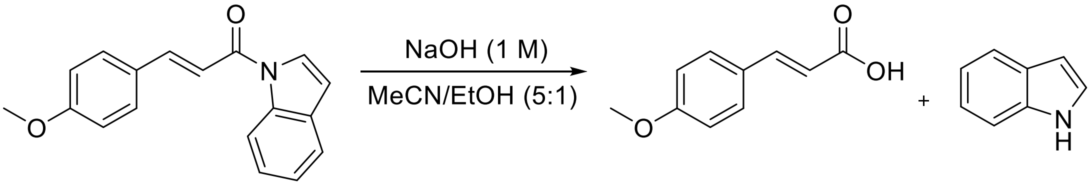
Suzuki-Miyaura Cross-Coupling (Product **34**)



The cross-coupling was carried out according to the procedure of Meng et al.[4]

To an oven dried microwave safe vial was added compound **17** (53.6 mg, 0.21 mmol, 1 eq.) together with 4-tolylboronic acid (65.6 mg, 0.48 mmol, 2.3 eq), [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]chloro[3-phenylallyl]palladium(II) (Neolyst CX 31, CAS 884879-23-6) (8.8 mg, 0.013, 0.06 eq.), K_2CO_3 (107.1 mg, 0.78 mmol, 3.6 eq) and a magnetic stir bar. The vial was capped and subjected to three evacuation/backfilling cycles under vaccum and nitrogen. Dry and degassed THF (0.4 mL) was then added to the vial *via* a syringe. The reaction mixture was stirred vigorously at r.t. and then heated at 110 °C for 23 h. The reaction mixture was diluted with DCM and filtered on a pad of Celite and silica. The volatiles were removed from the filtrate. The product was isolated using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 10% ethyl acetate in petroleum ether) using a SNAP®-10g KP-sil column with 1 g samplet® cartridge. The product was obtained as a white solid with minor impurities from compound **17** (25.5 mg, 0.113 mmol, 53%). The NMR spectra matches literature data.[5] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.84 – 7.78 (m, 2H), 7.71 – 7.65 (m, 2H), 7.30 – 7.25 (m, 2H), 6.99 – 6.94 (m, 2H), 3.88 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 195.5, 163.1, 142.7, 135.6, 132.5, 130.6, 130.1, 129.0, 113.6, 55.6, 21.7.

Hydrolysis of Acylindoles (Product **35** and **4**)

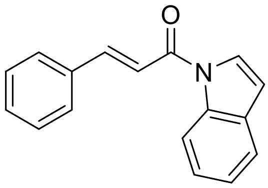


To a 4 ml vial was added compound **11** (15.7 mg, 0.06 mmol, 1 eq.) and a magnetic stir bar, followed by NaOH (1 M, 1 mL, 1 mmol, 17 eq.), ethanol (0.1 mL) and MeCN (0.5 ml). The reaction mixture was stirred for 2 h at r.t. The reaction mixture was then extracted with diethyl ether (3×1 ml). The organic phase was collected and the volatiles were removed *in vacuo*. The product was collected as a white solid yielding indole (6.6 mg, 0.056 mmol, 99%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.68 – 7.62 (m, 1H), 7.43 – 7.38 (m, 1H), 7.23 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 6.58 – 6.54 (m, 1H).

The remaining water phase was treated with HCl (1 M) until pH 6 was reached. A precipitation was observed and filtrated on a frit. Washed with some additional water. The white solids were collected to yield cinnamic acid (10 mg, 0.056 mmol, 99%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.74 (d, J = 15.9 Hz, 1H), 7.55 – 7.45 (m, 2H), 6.96 – 6.87 (m, 2H), 6.32 (d, J = 15.9 Hz, 1H), 3.85 (s, 3H).

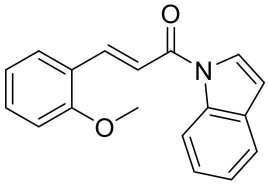
NMR matches authentic samples of cinnamic acid and indole.

Characterization of Compounds



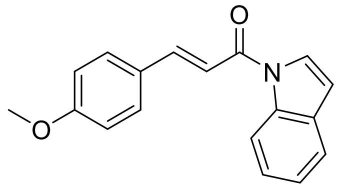
(*E*)-1-(1*H*-indol-1-yl)-3-phenylprop-2-en-1-one (6):

According to the general procedure, cinnamaldehyde (36 µL, 0.286 mmol, 2 eq.) and indole (16.5 mg, 0.141 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 4 h. The product was obtained as white crystals (24.7 mg, 0.01 mmol, 71%). The NMR spectra matches literature data.[6] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.57 (appd, J = 8.3 Hz, 1H), 8.01 (d, J = 15.5 Hz, 1H), 7.68 – 7.59 (m, 4H), 7.48 – 7.43 (m, 3H), 7.43 – 7.37 (m, 1H), 7.32 (m, 1H), 7.25 (d, J = 15.4 Hz, 1H). 6.71 (dd, J = 3.8, 0.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 164.4, 146.7, 136.1, 134.6, 130.91, 130.8, 129.2, 128.5, 125.2, 124.7, 123.9, 121.1, 117.4, 117.0, 109.3.



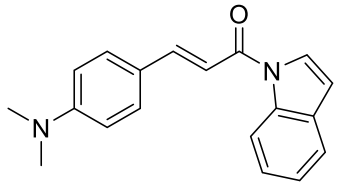
(*E*)-1-(1*H*-indol-1-yl)-3-(2-methoxyphenyl)prop-2-en-1-one (10):

According to the general procedure, 2-methoxycinnamaldehyde (42.7 mg, 0.242 mmol, 1.7 eq.) and indole (17.1 mg, 0.146 mmol, 1 eq.) together with NHC **7** (0.1 eq.), **2** (1.4 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 4 h with exclusion of light (possibility for isomerization). The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (20 ml/min, 100% petroleum ether → 2% → 4% ethyl acetate in petroleum ether). The product was obtained as yellow oil (31.5 mg, 0.114 mmol, 78%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.56 (appd, J = 8.3 Hz, 1H), 8.24 (d, J = 15.6 Hz, 1H), 7.67 (d, J = 3.8 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.47 – 7.35 (m, 3H), 7.32 – 7.27 (m, 1H), 7.06 – 6.95 (m, 3H), 6.69 (d, J = 3.8 Hz, 1H), 3.96 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 165.1, 159.0, 142.5, 136.1, 132.1, 130.8, 130.2, 125.0, 125.0, 123.7, 123.6, 121.0, 121.0, 118.3, 116.9, 111.4, 108.9, 55.7. **FTIR-ATR (cm^{-1})**: 1676 (s). **HRMS (ESI)** calcd for $C_{18}H_{15}NO_2$ $[M+H]^+$: exact mass: 278.1176, found: 278.1168.



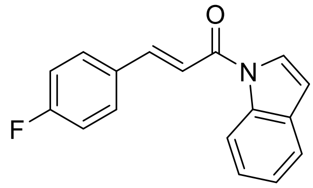
(*E*)-1-(1*H*-indol-1-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (11):

According to the general procedure, 4-methoxycinnamaldehyde (25.2 mg, 0.155 mmol, 1 eq.) and indole (18.7 mg, 0.159 mmol, 1.03 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 4 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 4% → 5% ethyl acetate in petroleum ether). The product was obtained as white solid (30 mg, 0.108 mmol, 70%). The NMR spectra matches literature data.[6] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.55 (appd, J = 8.3 Hz, 1H), 7.97 (d, J = 15.4 Hz, 1H), 7.66 (d, J = 3.8 Hz, 1H), 7.63 – 7.58 (m, 3H), 7.41 – 7.35 (m, 1H), 7.32 – 7.27 (m, 1H), 7.12 (d, J = 15.4 Hz, 1H), 6.96 (appd, J = 8.8 Hz, 2H), 6.70 (d, J = 3.8 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 164.7, 161.9, 146.5, 136.1, 130.7, 130.3, 127.3, 125.1, 124.8, 123.8, 121.0, 116.9, 114.8, 114.6, 109.0, 55.6.



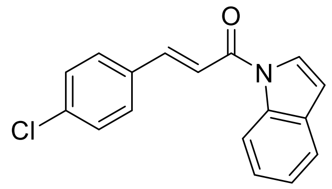
(*E*)-3-(4-(dimethylamino)phenyl)-1-(1*H*-indol-1-yl)prop-2-en-1-one (12):

According to the general procedure, 4-(dimethylamino)cinnamaldehyde (43 mg, 0.245 mmol, 1.9 eq.) and indole (15.2 mg, 0.13 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 3 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 3% → 4% → 5% → 7% → 10% ethyl acetate in petroleum ether). The product was obtained as yellow oil (36.2 mg, 0.125 mmol, 96%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.55 (appd, J = 8.3 Hz, 1H), 7.96 (d, J = 15.2 Hz, 1H), 7.69 (d, J = 3.8 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.40 – 7.34 (m, 1H), 7.30 – 7.26 (m, 1H), 7.03 (d, J = 15.2 Hz, 1H), 6.74 – 6.66 (m, 3H), 3.05 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 165.3, 152.2, 147.5, 136.1, 130.7, 130.4, 125.0, 124.8, 123.5, 122.4, 120.9, 116.9, 112.0, 111.4, 108.5, 40.3. **FTIR-ATR (cm^{-1})**: 1680 (s). **HRMS (ESI)** calcd for $C_{19}H_{18}N_2O$ $[M+H]^+$: exact mass: 291.1497, found: 291.1503.



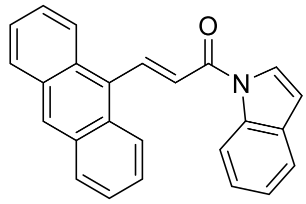
(*E*)-3-(4-fluorophenyl)-1-(1*H*-indol-1-yl)prop-2-en-1-one (13):

According to the general procedure, 4-fluorocinnamaldehyde (37 μL, 0.268 mmol, 2 eq.) and indole (15.6 mg, 0.133 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 23 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 3% → 5% ethyl acetate in petroleum ether). The product was obtained as yellow solid (17.6 mg, 0.066 mmol, 50%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.54 (appd, J = 8.3 Hz, 1H), 7.96 (d, J = 15.4 Hz, 1H), 7.67 – 7.58 (m, 4H), 7.42 – 7.35 (m, 1H), 7.34 – 7.28 (m, 1H), 7.21 – 7.09 (m, 3H), 6.71 (dd, J = 3.8, 0.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 164.3 (d, $^1J_{C\text{-}F}$ = 245Hz), 164.2, 145.4, 136.0, 130.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 130.7, 130.4 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 125.2, 124.6, 124.0, 121.1, 117.1, 116.9, 116.4 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 109.4. **^{19}F NMR (376 MHz $CDCl_3$) δ** −108.63. **FTIR-ATR (cm^{-1})**: 1677 (s). **HRMS (ESI)** calcd for $C_{17}H_{12}FNO$ $[M+H]^+$: exact mass: 266.0976, found: 266.0967.



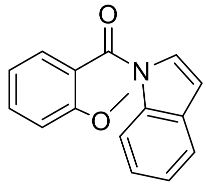
(*E*)-3-(4-chlorophenyl)-1-(1*H*-indol-1-yl)prop-2-en-1-one (14):

According to the general procedure, 4-chlorocinnamaldehyde (40.3 mg, 0.242 mmol, 1.9 eq.) and indole (15.1 mg, 0.129 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 7 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 4% ethyl acetate in petroleum ether). The product was obtained as white crystals (15.1 mg, 0.0536 mmol, 42%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.54 (appd, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 15.4 Hz, 1H), 7.66 – 7.54 (m, 4H), 7.44 – 7.36 (m, 3H), 7.34 – 7.28 (m, 1H), 7.22 (d, *J* = 15.5 Hz, 1H), 6.71 (dd, *J* = 3.8, 0.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 164.1, 145.2, 136.8, 136.0, 133.0, 130.7, 129.7, 129.5, 125.3, 124.61, 124.1, 121.1, 117.9, 117.0, 109.5. **FTIR-ATR (cm^{-1})**: 1676 (s). **HRMS (ESI)** calcd for $C_{17}H_{12}ClNO$ $[M+H]^+$: exact mass: 282.0680, found: 282.0677.



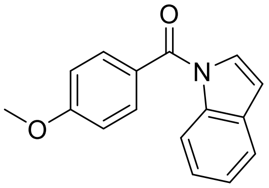
(*E*)-3-(anthracen-9-yl)-1-(1*H*-indol-1-yl)prop-2-en-1-one (15):

According to the general procedure, 3-(9-anthryl)acrolein (57.2 mg, 0.246 mmol, 1.8 eq.) and indole (15.8 mg, 0.135 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 6 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 3% ethyl acetate in petroleum ether). The product was obtained as yellow oil (30.5 mg, 0.0878 mmol, 65%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.95 (d, *J* = 15.7 Hz, 1H), 8.64 (appd, *J* = 8.3 Hz, 1H), 8.47 (s, 1H), 8.33 – 8.26 (m, 2H), 8.05 – 8.00 (m, 2H), 7.61 – 7.57 (m, 1H), 7.55 – 7.47 (m, 5H), 7.44 – 7.38 (m, 1H), 7.34 – 7.29 (m, 1H), 7.23 – 7.22 (m, 1H), 6.66 (d, *J* = 3.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 163.8, 144.1, 136.1, 131.4, 130.8, 129.7, 129.6, 129.1, 128.8, 126.8, 126.6, 125.6, 125.4, 125.2, 124.7, 124.2, 121.1, 117.1, 109.7. **FTIR-ATR (cm^{-1})**: 1680 (s). **HRMS (ESI)** calcd for $C_{25}H_{17}NO$ $[M+H]^+$: exact mass: 348.1383, found: 348.1373.



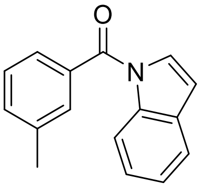
(1*H*-indol-1-yl)(2-methoxyphenyl)methanone (16):

According to the general procedure, 2-methoxybenzaldehyde (30.9 mg, 0.227 mmol, 1.6 eq.) and indole (16.8 mg, 0.143 mmol, 1 eq.) together with NHC **7** (0.1 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 23 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (20 ml/min, 100% petroleum ether → 2% → 5% ethyl acetate in petroleum ether) using a 10 g SNAP-KP sil column with a 1 g samplet® cartridge. The product was obtained as a yellow oil (34.9 mg, 0.139 mmol, 97%). The NMR spectra matches literature data.[7] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.44 (appd, *J* = 8.0 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.51 (appdddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 7.44 (appdd, *J* = 7.5, 1.8 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.30 (apptd, *J* = 7.5, 1.2 Hz, 1H), 7.12 – 7.00 (m, 3H), 6.55 (dd, *J* = 3.8, 0.8 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 167.4, 156.5, 135.7, 132.3, 131.1, 129.2, 127.6, 125.0, 124.0, 120.9, 120.9, 116.7, 111.6, 108.8, 55.8.



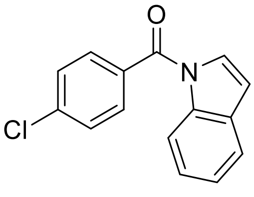
(1*H*-indol-1-yl)(4-methoxyphenyl)methanone (17):

According to the general procedure, 4-methoxybenzaldehyde (73 µL, 0.6 mmol, 1.2 eq.) and indole (57.9 mg, 0.49 mmol, 1 eq.) together with NHC **7** (0.1 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (3.2 mL) were stirred for 23 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (40 ml/min, 100% petroleum ether → 2% → 5% → 10% ethyl acetate in petroleum ether) using a 25 g SNAP-KP sil column with a 3 g samplet® cartridge. The product was obtained as a yellow solid (114.7 mg, 0.456 mmol, 92%). The NMR spectra matches literature data.[8] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.36 (appd, *J* = 8.3 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.62 (appddd, *J* = 7.6, 1.4, 0.7 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.04 – 6.98 (m, 2H), 6.62 (dd, *J* = 3.7, 0.7 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 168.3, 162.8, 136.2, 131.8, 130.8, 127.8, 126.6, 124.8, 123.8, 120.9, 116.3, 114.0, 108.2, 55.6.



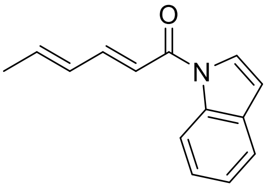
(1*H*-indol-1-yl)(m-tolyl)methanone (18):

According to the general procedure, 3-methylbenzaldehyde (68.9 µL, 0.585 mmol, 1.5 eq.) and indole (44.9 mg, 0.383 mmol, 1 eq.) together with NHC **7** (0.1 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (2.4 mL) were stirred for 23 h. The product was purified using column chromatography with heptane/ethyl acetate (95:5) solvent mixture. The product was obtained as a yellow oil (67.5 mg, 0.287 mmol, 75%). The NMR spectra matches literature data.[7] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.40 (appd, *J* = 8.2 Hz, 1H), 7.63 – 7.49 (m, 3H), 7.44 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 6.61 (dd, *J* = 3.8, 0.8 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 169.1, 138.7, 136.2, 134.7, 132.8, 130.9, 129.8, 128.5, 127.8, 126.4, 125.0, 124.0, 121.0, 116.5, 108.6, 21.5.



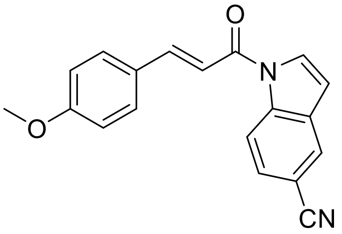
(4-chlorophenyl)(1*H*-indol-1-yl)methanone (19):

According to the general procedure, 4-chlorobenzaldehyde (68.8 mg, 0.489 mmol, 1.3 eq.) and indole (43.4 mg, 0.371 mmol, 1 eq.) together with NHC **7** (0.1 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (2.4 mL) were stirred for 23 h. The product was purified using column chromatography with heptane/ethyl acetate (95:5) solvent mixture. The product was obtained as a white solid (60.1 mg, 0.235 mmol, 63%). The NMR spectra matches literature data.[9] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.37 (appd, *J* = 8.2 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.64 – 7.57 (m, 1H), 7.55 – 7.48 (m, 2H), 7.43 – 7.28 (m, 2H), 7.25 – 7.23 (m, 1H), 6.64 (d, *J* = 3.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 167.7, 138.5, 136.1, 133.1, 130.9, 130.8, 129.1, 127.3, 125.2, 124.3, 121.1, 116.5, 109.1.



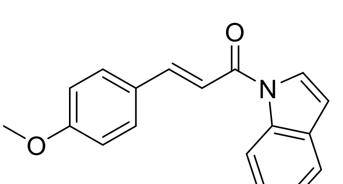
(2*E*,4*E*)-1-(1*H*-indol-1-yl)hexa-2,4-dien-1-one (20):

According to the general procedure, *trans,trans*-2,4-hexadienal (29 µL, 0.25 mmol, 2 eq.) and indole (14.6 mg, 0.125 mmol, 1 eq.) together with NHC **7** (0.1 eq.), **2** (2 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 3 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (35 ml/min, 100% petroleum ether → 1% → 2% → 5% → 10% ethyl acetate in petroleum ether) using a 25 g SNAP-KP sil column with a 3 g samplet® cartridge. The product was obtained as a yellow solid (19.3 mg, 0.092 mmol, 73%). The NMR spectra matches literature data.[8] **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.56 – 8.45 (m, 1H), 7.65 – 7.50 (m, 2H), 7.38 – 7.33 (m, 1H), 7.30 – 7.26 (m, 1H), 6.66 (dd, *J* = 3.8, 0.7 Hz, 1H), 6.61 (d, *J* = 14.8 Hz, 1H), 6.43 – 6.23 (m, 2H), 1.92 (d, *J* = 5.6 Hz, 3H).**^{13}C NMR (101 MHz, CDCl$_3$) δ** 164.8, 147.1, 141.5, 136.0, 130.7, 130.1, 125.0, 124.8, 123.8, 120.9, 118.2, 116.9, 19.0. **FTIR-ATR (cm^{-1})**: 1673 (s). **HRMS (ESI)** calcd for $C_{14}H_{13}NO$ $[M+Na]^+$: exact mass: 234.0889, found: 234.0889.



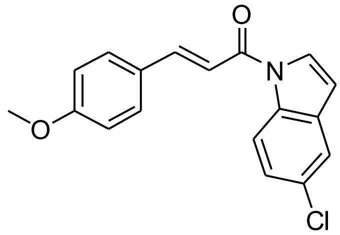
(*E*)-1-(5-chloro-1*H*-indol-1-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (21):

According to the general procedure, 4-methoxycinnamaldehyde (31.5 mg, 0.194 mmol, 1.6 eq.) and 5-cyanoindole (17 mg, 0.12 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 2 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 5% → 10% → 20% ethyl acetate in petroleum ether). The product was obtained as an off-white solid (29.7 mg, 0.098 mmol, 82%). **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.64 (appd, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 15.3 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.78 (d, *J* = 3.9 Hz, 1H), 7.62 (appd, *J* = 8.3 Hz, 3H), 7.07 (d, *J* = 15.3 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.75 (d, *J* = 3.8 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 164.5, 162.2, 147.9, 137.7, 130.5, 130.4, 128.0, 126.8, 125.7, 119.7, 117.6, 114.6, 113.4, 110.0, 108.3, 106.9, 55.5. **FTIR-ATR (cm^{-1})**: 1679 (s). **HRMS (ESI)** calcd for $C_{19}H_{14}N_2O_2$ $[M+H]^+$: exact mass: 303.1128, found: 303,1119.



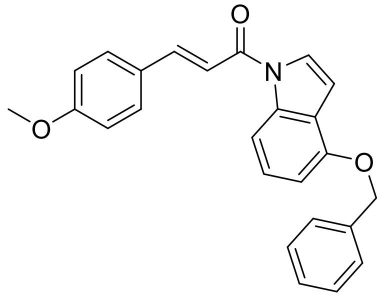
(*E*)-3-(4-methoxyphenyl)-1-(5-methyl-1*H*-indol-1-yl)prop-2-en-1-one (22):

According to the general procedure, 4-methoxycinnamaldehyde (30.5 mg, 0.188 mmol, 1.6 eq.) and 5-methylindole (16.1 mg, 0.122 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 6 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 5% ethyl acetate in petroleum ether). The product was obtained as white solid (26.8 mg, 0.092 mmol, 76%). The NMR spectra matches literature data.[6] **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.41 (appd, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 15.4 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.40 – 7.34 (m, 1H), 7.23 – 7.16 (m, 1H), 7.11 (d, *J* = 15.4 Hz, 1H), 7.01 – 6.91 (m, 2H), 6.62 (d, *J* = 3.7 Hz, 1H), 3.87 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 164.5, 161.9, 146.2, 134.3, 133.4, 131.0, 130.3, 127.4, 126.4, 124.8, 120.9, 116.6, 114.8, 114.6, 108.8, 55.6, 21.6.



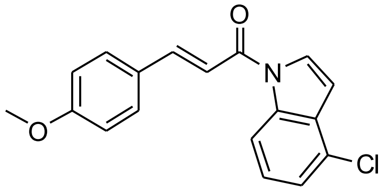
(*E*)-1-(5-chloro-1*H*-indol-1-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (23):

According to the general procedure, 4-methoxycinnamaldehyde (28.8 mg, 0.177 mmol, 1.5 eq.) and 5-chloroindole (18.8 mg, 0.122 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 3 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 5% → 10% → 15% ethyl acetate in petroleum ether). The product was obtained as off-white solid (33.6 mg, 0.108 mmol, 89%). The NMR spectra matches literature data.[6] **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.48 (appd, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 15.3 Hz, 1H), 7.67 (d, *J* = 3.8 Hz, 1H), 7.60 (appd, *J* = 8.7 Hz, 2H), 7.56 (appd, *J* = 2.1 Hz, 1H), 7.32 (appdd, *J* = 8.8, 2.2Hz, 1H), 7.07 (d, *J* = 15.3 Hz, 1H), 6.96 (appd, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 3.8 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 164.5, 162.1, 147.0, 134.4, 131.9, 130.4, 129.31, 127.2, 126.0, 125.2, 120.6, 118.0, 114.7, 114.1, 108.3, 55.6.



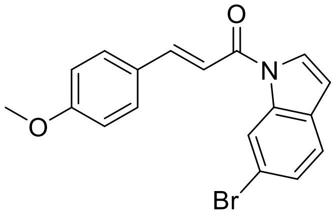
(*E*)-1-(4-(benzyloxy)-1*H*-indol-1-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (24):

According to the general procedure, 4-methoxycinnamaldehyde (21.8 mg, 0.134 mmol, 1 eq.) and 4-benzyloxyindole (31.1 mg, 0.14 mmol, 1.04 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 2 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 5% → 7% → 9% → 10% ethyl acetate in petroleum ether). The product was obtained as white solid (33.3 mg, 0.087 mmol, 65%). **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.15 (appd, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 15.3 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.44 – 7.39 (m, 2H), 7.37 – 7.32 (m, 1H), 7.29 (appt, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 15.4 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.88 (dd, *J* = 3.8, 0.7 Hz, 1H), 6.80 (appd, *J* = 8.0 Hz, 1H), 5.23 (s, 2H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 164.8, 161.9, 152.1, 146.5, 137.4, 137.3, 130.3, 128.7, 128.1, 127.5, 127.3, 126.0, 123.3, 121.3, 114.8, 114.6, 110.3, 106.2, 105.7, 70.2, 55.6. **FTIR-ATR (cm^{-1})**: 1686 (s). **HRMS (ESI)** calcd for $C_{25}H_{21}NO_3$ $[M+H]^+$: exact mass: 384.1594, found: 384.1577.



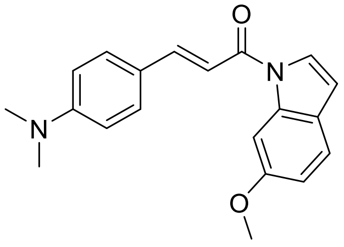
(*E*)-1-(4-chloro-1*H*-indol-1-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (25):

According to the general procedure, 4-methoxycinnamaldehyde (31.4 mg, 0.194 mmol, 1.3 eq.) and 4-chloroindole (18 µL, 0.14 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 2 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 5% ethyl acetate in petroleum ether). The product was obtained as yellow solid (39.4 mg, 0.126 mmol, 85%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.48 – 8.42 (m, 1H), 7.97 (d, *J* = 15.4 Hz, 1H), 7.69 (d, *J* = 3.8 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.32 – 7.26 (m, 2H), 7.08 (d, *J* = 15.3 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.82 (dd, *J* = 3.8, 0.5 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 164.7, 162.1, 147.2, 136.7, 130.4, 129.4, 127.1, 126.2, 125.8, 125.3, 123.5, 115.5, 114.7, 114.2, 107.0, 55.6. **FTIR-ATR (cm^{-1})**: 1677 (s). **HRMS (ESI)** calcd for $C_{18}H_{14}ClNO_2$ $[M+H]^+$: exact mass: 312.0786, found: 312.0783.



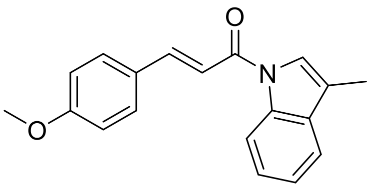
(*E*)-1-(6-bromo-1*H*-indol-1-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (26):

According to the general procedure, 4-methoxycinnamaldehyde (32.1 mg, 0.198 mmol, 1.6 eq.) and 6-bromoindole (25.1 mg, 0.123 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 2 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 5% → 15% ethyl acetate in petroleum ether). The product was obtained as white solid (26.4 mg, 0.0741 mmol, 60%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.80 – 8.74 (m, 1H), 7.96 (d, *J* = 15.2 Hz, 1H), 7.66 – 7.57 (m, 3H), 7.48 – 7.36 (m, 2H), 7.06 (d, *J* = 15.3 Hz, 1H), 7.00 – 6.92 (m, 2H), 6.65 (d, *J* = 3.6 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 164.5, 162.1, 147.2, 136.7, 130.4, 129.4, 127.1, 127.0, 125.2, 122.0, 120.1, 118.8, 114.7, 114.1, 108.7, 55.6. **FTIR-ATR (cm^{-1})**: 1688 (s). **HRMS (ESI)** calcd for $C_{18}H_{14}BrNO_2$ $[M+H]^+$: exact mass: 356.0281, found: 356.0275.



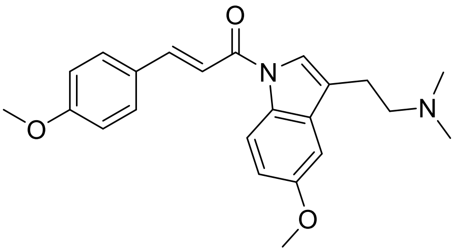
(*E*)-3-(4-(dimethylamino)phenyl)-1-(6-methoxy-1*H*-indol-1-yl)prop-2-en-1-one (27):

According to the general procedure, 4-(dimethylamino)cinnamaldehyde (34.7 mg, 0.198 mmol, 1.6 eq.) and 6-methoxyindole (18.5 mg, 0.123 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 4 h. The product was purified using the Biotage with DCM (100%) (25 ml/min). The product was obtained as a yellow solid (35.5 mg, 0.1108 mmol, 90%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.21 (appd, *J* = 2.3 Hz, 1H), 7.95 (d, *J* = 15.2 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.45 (appd, *J* = 8.6 Hz, 1H), 6.99 (d, *J* = 15.3 Hz, 1H), 6.93 (appdd, *J* = 8.5, 2.4 Hz, 1H), 6.71 – 6.66 (m, 2H), 6.60 (d, *J* = 3.8 Hz, 1H), 3.91 (s, 3H), 3.03 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 165.5, 158.1, 152.2, 147.4, 137.1, 130.4, 124.3, 123.6, 122.3, 121.2, 113.1, 111.9, 111.2, 108.4, 100.8, 55.7, 40.2. **FTIR-ATR (cm^{-1})**: 1679 (s). **HRMS (ESI)** calcd for $C_{20}H_{20}N_2O_2$ $[M+H]^+$: exact mass: 321.1598, found: 321.1613.



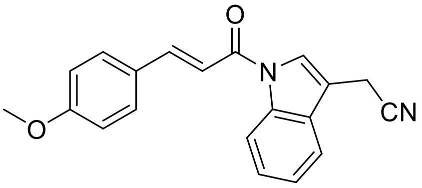
(*E*)-3-(4-methoxyphenyl)-1-(3-methyl-1*H*-indol-1-yl)prop-2-en-1-one (28):

According to the general procedure, 4-methoxycinnamaldehyde (32 mg, 0.197 mmol, 1.6 eq.) and skatole (16.3 mg, 0.124 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 23 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% → 4% → 5% ethyl acetate in petroleum ether). The product was obtained as white crystals (21.1 mg, 0.072 mmol, 58%). **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.53 (appd, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 15.4 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.56 – 7.50 (m, 1H), 7.45 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.11 (d, *J* = 15.4 Hz, 1H), 7.00 – 6.91 (m, 2H), 3.87 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 164.3, 161.8, 145.9, 136.4, 131.7, 130.2, 127.5, 125.1, 123.5, 121.8, 119.0, 118.3, 117.0, 115.1, 114.6, 55.6, 9.9. **FTIR-ATR (cm^{-1})**: 1665 (s). **HRMS (ESI)** calcd for $C_{19}H_{17}NO_2$ $[M+H]^+$: exact mass: 292.1332, found: 292.1339.



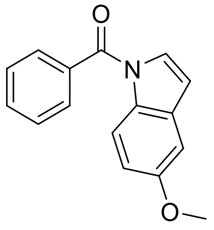
(*E*)-1-(3-(2-(dimethylamino)ethyl)-5-methoxy-1*H*-indol-1-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (29):

4-methoxycinnamaldehyde (33 mg, 0.204 mmol, 1.6 eq.) and 5-methoxygramine (28.1 mg, 0.127 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 21 h. The product was purified using the Biotage with DCM/MeOH solvent mixture (25 ml/min, 100% DCM → 5% → 10% MeOH in DCM). The product was obtained as yellow oil (25.5 mg, 0.0674 mmol, 53%). **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.43 (appd, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 15.3 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.47 (apps, 1H), 7.08 (d, *J* = 15.5 Hz, 1H), 7.03 – 6.90 (m, 4H), 3.88 (s, 3H), 3.86 (s, 3H), 2.96 – 2.87 (m, 2H), 2.77 – 2.68 (m, 2H), 2.40 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 164.0, 161.8, 156.6, 145.9, 131.8, 131.1, 130.2, 127.4, 122.4, 120.2, 118.0, 114.8, 114.6, 113.2, 102.1, 59.2, 55.9, 55.6, 45.4, 23.5. **FTIR-ATR (cm^{-1})**: 1670 (s). **HRMS (ESI)** calcd for $C_{23}H_{26}N_2O_3$ $[M+H]^+$: exact mass: 379.2016, found: 379.2034.



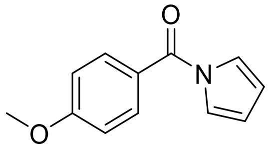
(*E*)-2-(1-(3-(4-methoxyphenyl)acryloyl)-1*H*-indol-3-yl)acetonitrile (30):

According to the general procedure, 4-methoxycinnamaldehyde (30.6 mg, 0.189 mmol, 1.5 eq.) and 3-indoleacetonitrile (19.1 mg, 0.122 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 3 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 4% → 5% → 7% → 9% → 12% → 25% ethyl acetate in petroleum ether). The product was obtained as a yellow solid (29.1 mg, 0.092 mmol, 75%). **^{1}H NMR (400 MHz, CDCl$_3$) δ** 8.56 (appd, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 15.3 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.67 – 7.59 (m, 2H), 7.56 – 7.48 (m, 1H), 7.47 – 7.40 (m, 1H), 7.40 – 7.33 (m, 1H), 7.08 (d, *J* = 15.4 Hz, 1H), 7.00 – 6.93 (m, 2H), 3.88 (s, 3H), 3.84 (s, 2H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 164.4, 162.2, 147.3, 136.5, 130.5, 128.7, 127.1, 126.1, 124.1, 123.1, 118.2, 117.4, 117.2, 114.7, 114.0, 111.3, 55.6, 14.7. **FTIR-ATR (cm^{-1})**: 1668 (s). **HRMS (ESI)** calcd for $C_{20}H_{16}N_2O_2$ $[M+H]^+$: exact mass: 317.1285, found: 317.1294.



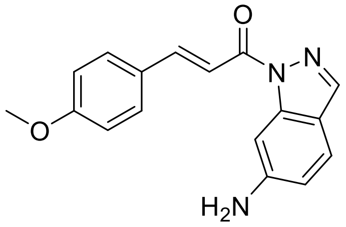
(5-methoxy-1*H*-indol-1-yl)(phenyl)methanone (31):

According to the general procedure, benzaldehyde (28.7 mg, 0.27 mmol, 2.2 eq.) and 5-methoxyindole (18.3 mg, 0.124 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 24 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% ethyl acetate in petroleum ether). The product was obtained as a yellow oil, with a minor unidentified impurity (17.5 mg, 0.0696 mmol, 56%). The NMR spectra matches literature data.[8] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.32 (appd, *J* = 9.0 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.64 – 7.49 (m, 3H), 7.29 – 7.23 (m, 1H), 7.09 – 7.06 (m, 1H), 7.00 (appdd, *J* = 9.0, 2.6 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 168.5, 156.8, 134.7, 131.9, 131.9, 130.8, 129.2, 128.7, 128.4, 117.3, 113.5, 108.7, 103.7, 55.8.



(4-methoxyphenyl)(1*H*-pyrrol-1-yl)methanone (32):

According to the general procedure, 4-methoxybenzaldehyde (16.6 µL, 0.137 mmol, 1 eq.) and pyrrole (14 µL, 0.202 mmol, 1.5 eq.) together with NHC **7** (0.1 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 42 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 2% ethyl acetate in petroleum ether). The product was obtained as a yellow oil (16.4 mg, 0.0815 mmol, 60%). The NMR spectra matches literature data.[10] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.79 – 7.72 (m, 2H), 7.32 – 7.27 (m, 2H), 7.02 – 6.95 (m, 2H), 6.37 – 6.32 (m, 2H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 167.3, 163.1, 132.2, 125.4, 121.6, 113.9, 113.0, 55.6.

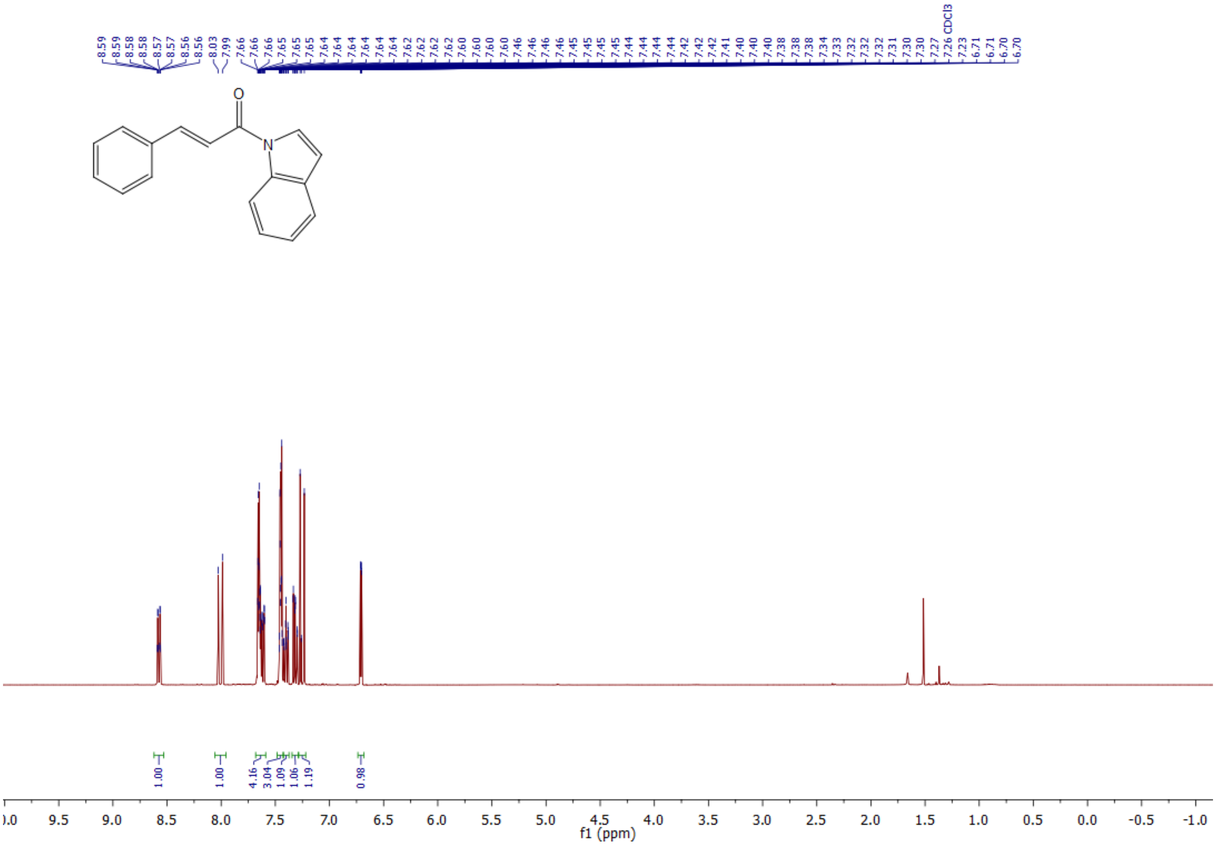


(*E*)-1-(6-amino-1*H*-indazol-1-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (33):

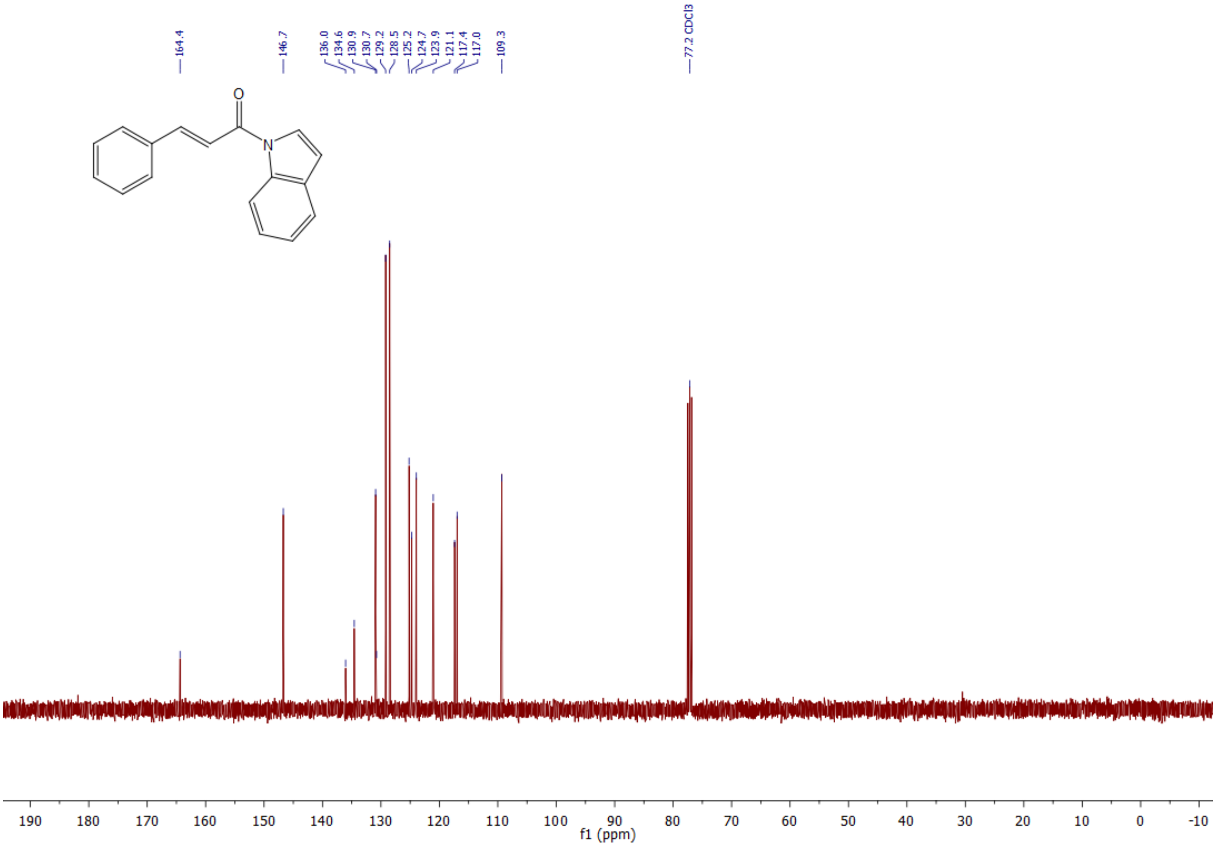
According to the general procedure, 4-methoxycinnamaldehyde (32.9 mg, 0.203 mmol, 1.6 eq.) and 6-aminoindazole (16.5 mg, 0.124 mmol, 1 eq.) together with NHC **7** (0.05 eq.), **2** (1 eq.), DBU (1 eq.), MS (4 Å) in CH_2Cl_2 (0.8 mL) were stirred for 3 h. The product was purified using the Biotage with petroleum ether (40–60 °C)/ethyl acetate solvent mixture (25 ml/min, 100% petroleum ether → 3% → 5% → 20% → 30% ethyl acetate in petroleum ether). The product was obtained as a yellow solid (25 mg, 0.0852 mmol, 69%). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 8.20 – 8.18 (m, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.80 (d, *J* = 16.0 Hz, 1H), 7.77 (appd, *J* = 8.6 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.52 (appd, *J* = 8.4 Hz, 1H), 7.03 (appd, *J* = 8.8 Hz, 2H), 6.72 (appd, *J* = 8.5 Hz, 1H), 3.82 (s, 3H).**^{13}C NMR (101 MHz, DMSO-d_6) δ** 164.8, 161.4, 150.6, 144.7, 141.0, 140.3, 130.5, 127.0, 122.0, 117.3, 114.9, 114.6, 114.3, 97.5, 55.4. **FTIR-ATR (cm^{-1})**: 1681 (s). **HRMS (ESI)** calcd for $C_{17}H_{15}N_3O_2$ $[M+H]^+$: exact mass: 294.1237, found: 294.1232.

NMR Spectra

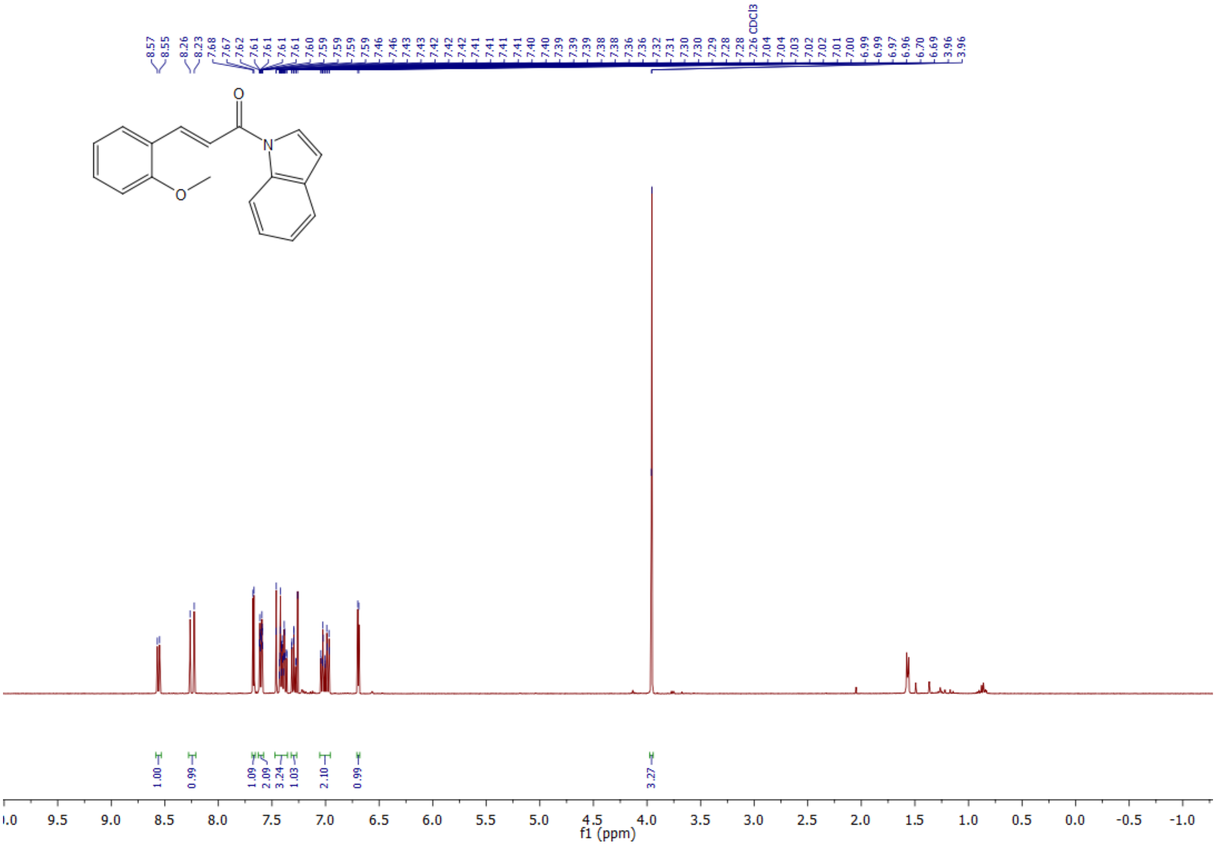
¹H NMR of compound **6** ($CDCl_3$)



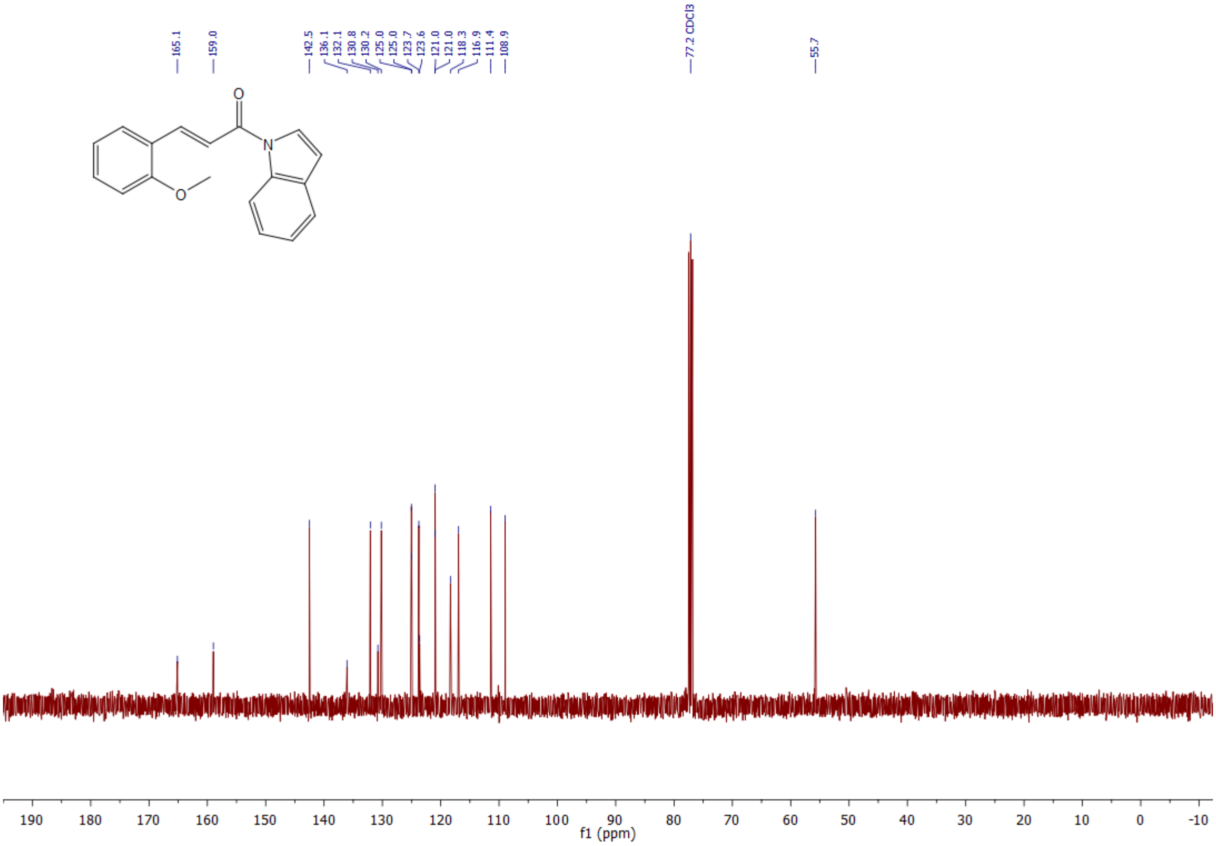
¹³C NMR of compound **6** ($CDCl_3$)



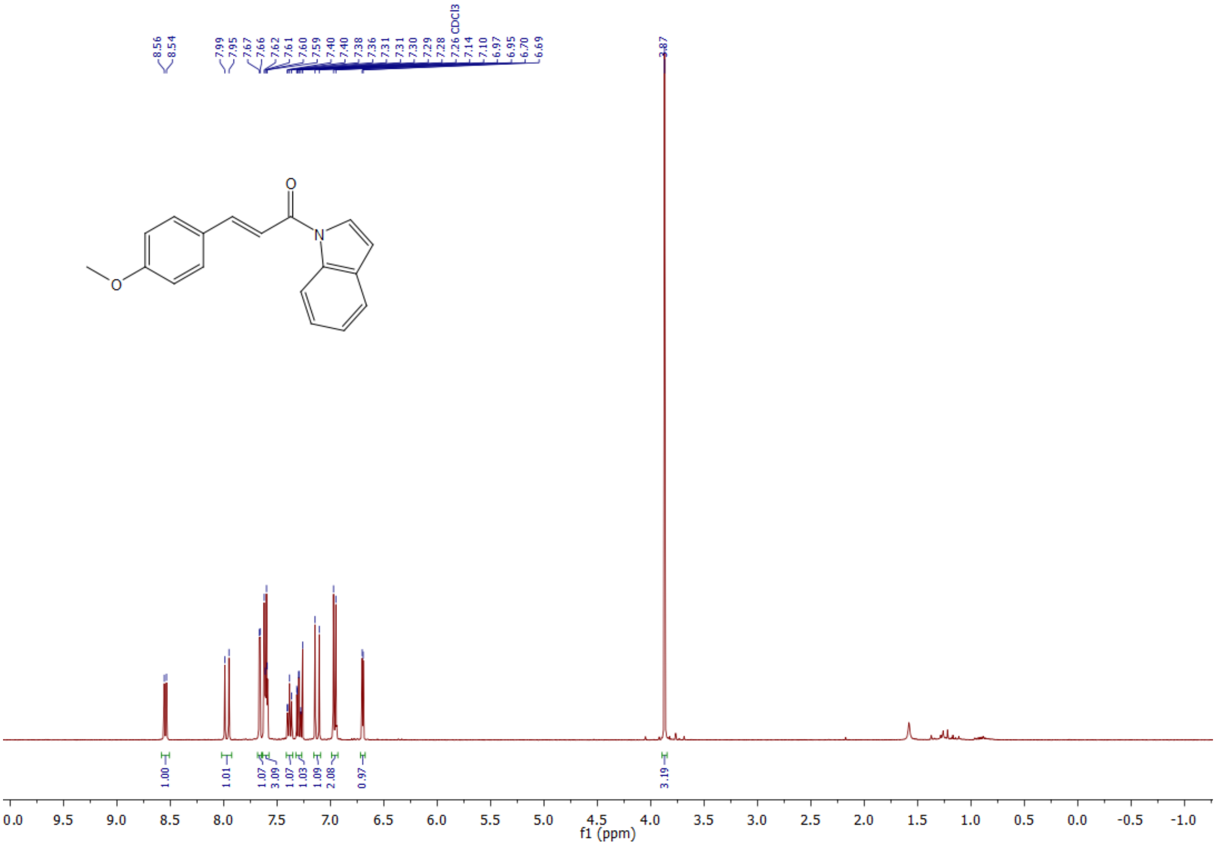
^{1}H NMR of compound **10** ($CDCl_3$)



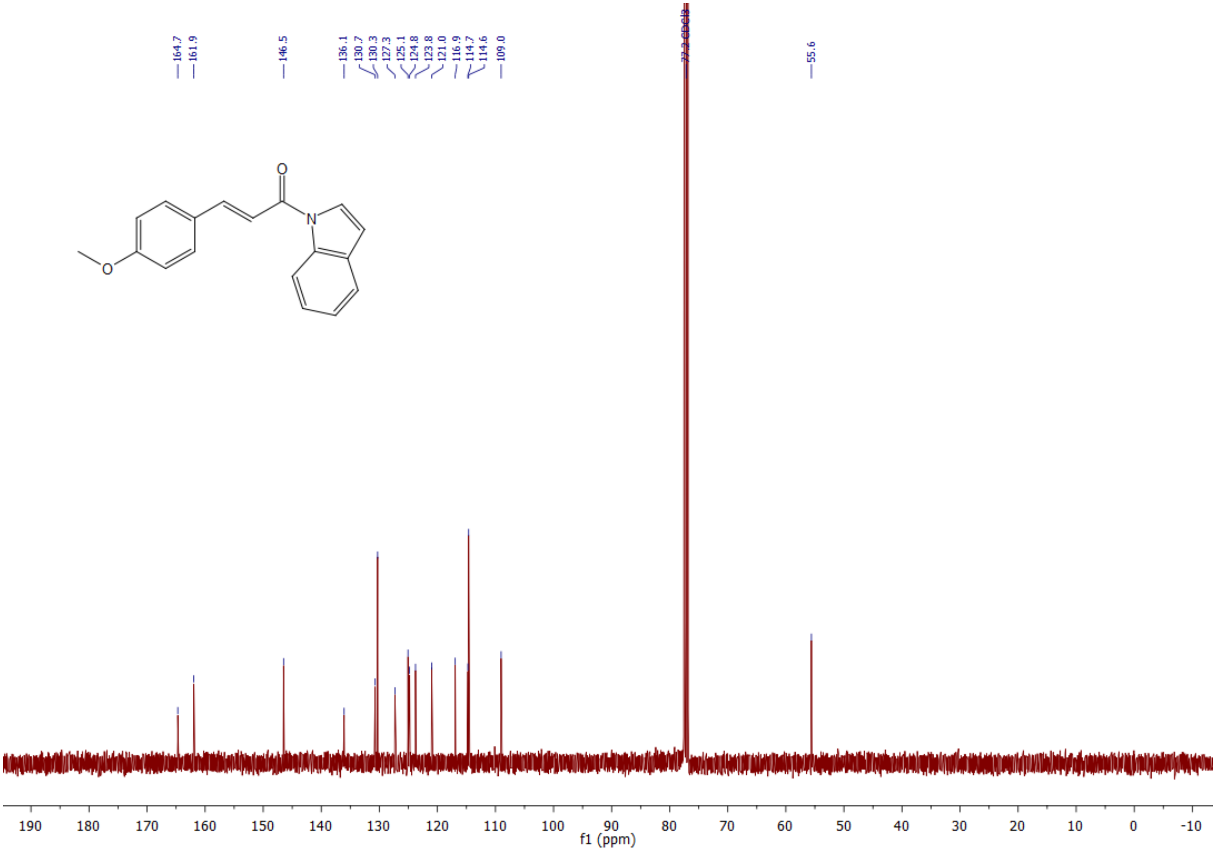
^{13}C NMR of compound **10** ($CDCl_3$)



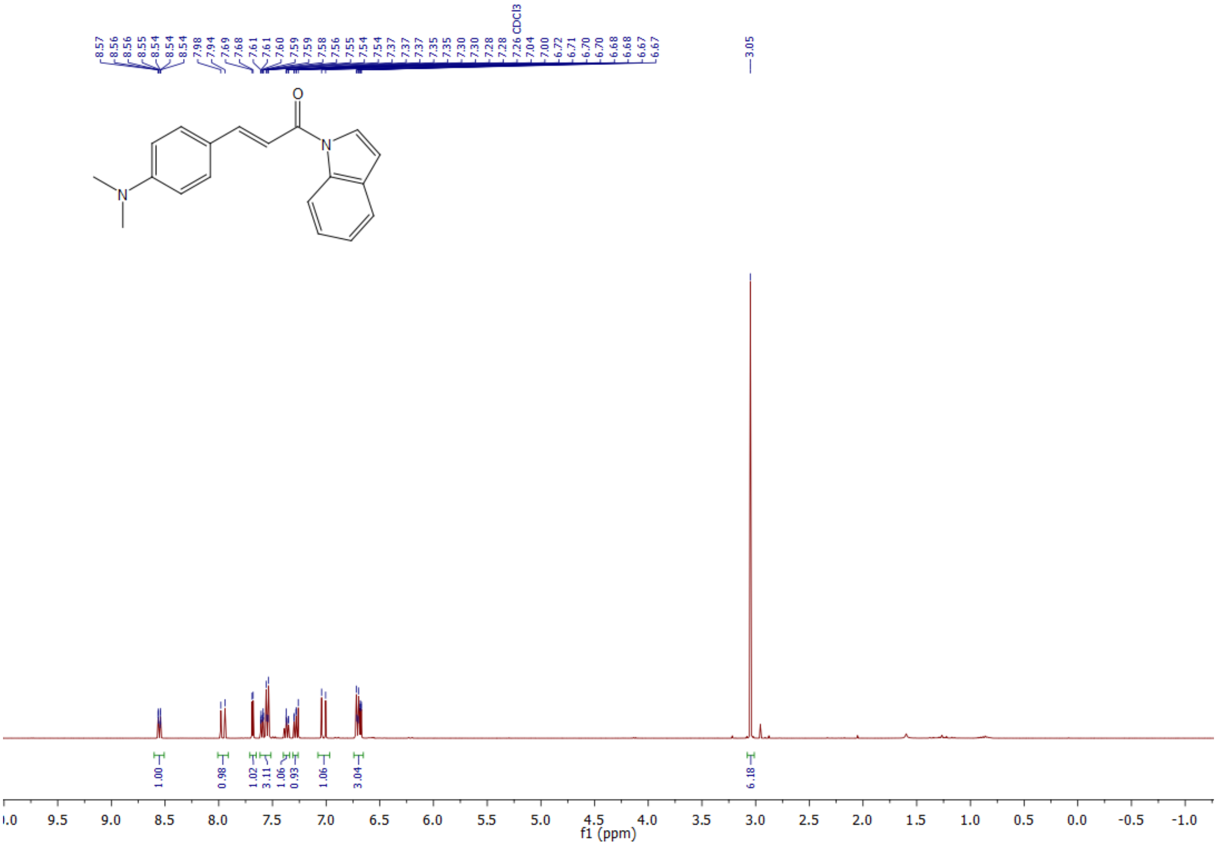
^{1}H NMR of compound **11** ($CDCl_3$)



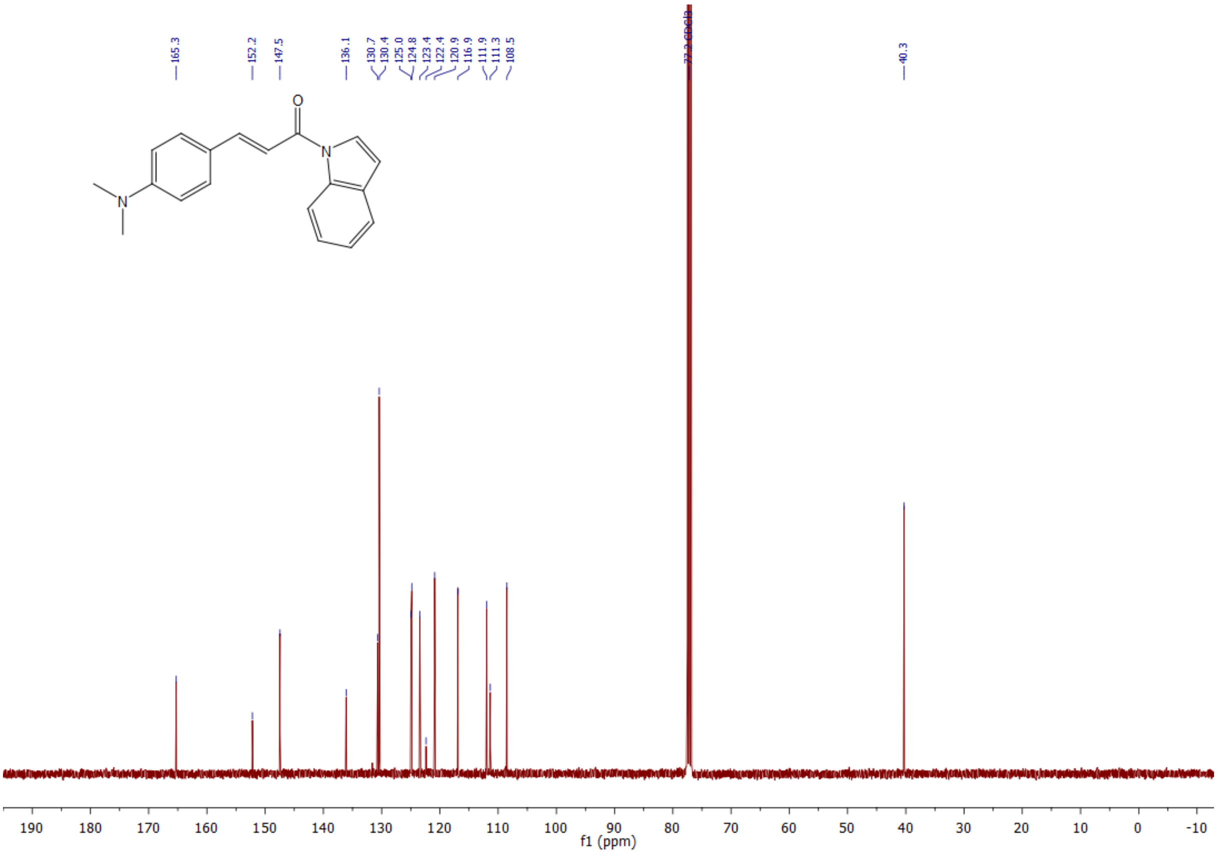
^{13}C NMR of compound **11** ($CDCl_3$)



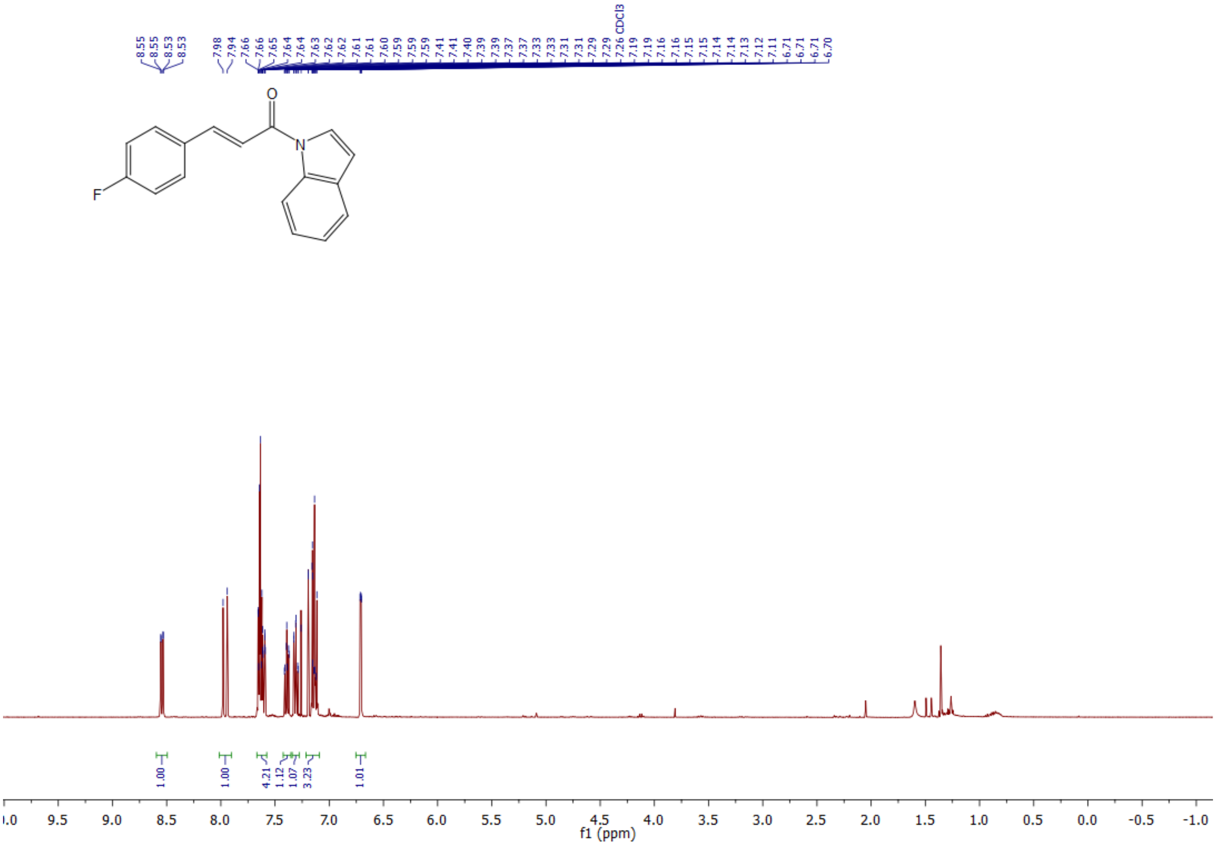
^{1}H NMR of compound **12** (CDCl$_3$)



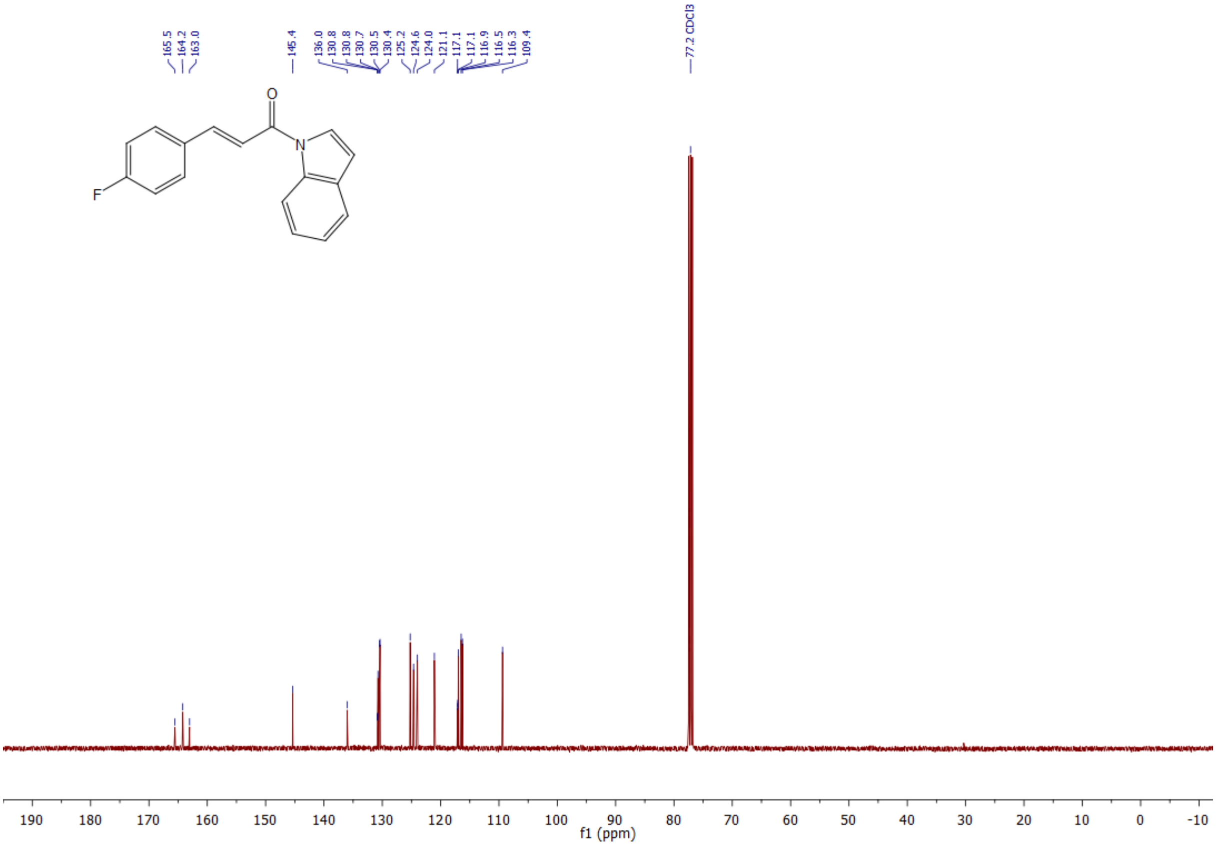
^{13}C NMR of compound **12** (CDCl$_3$)



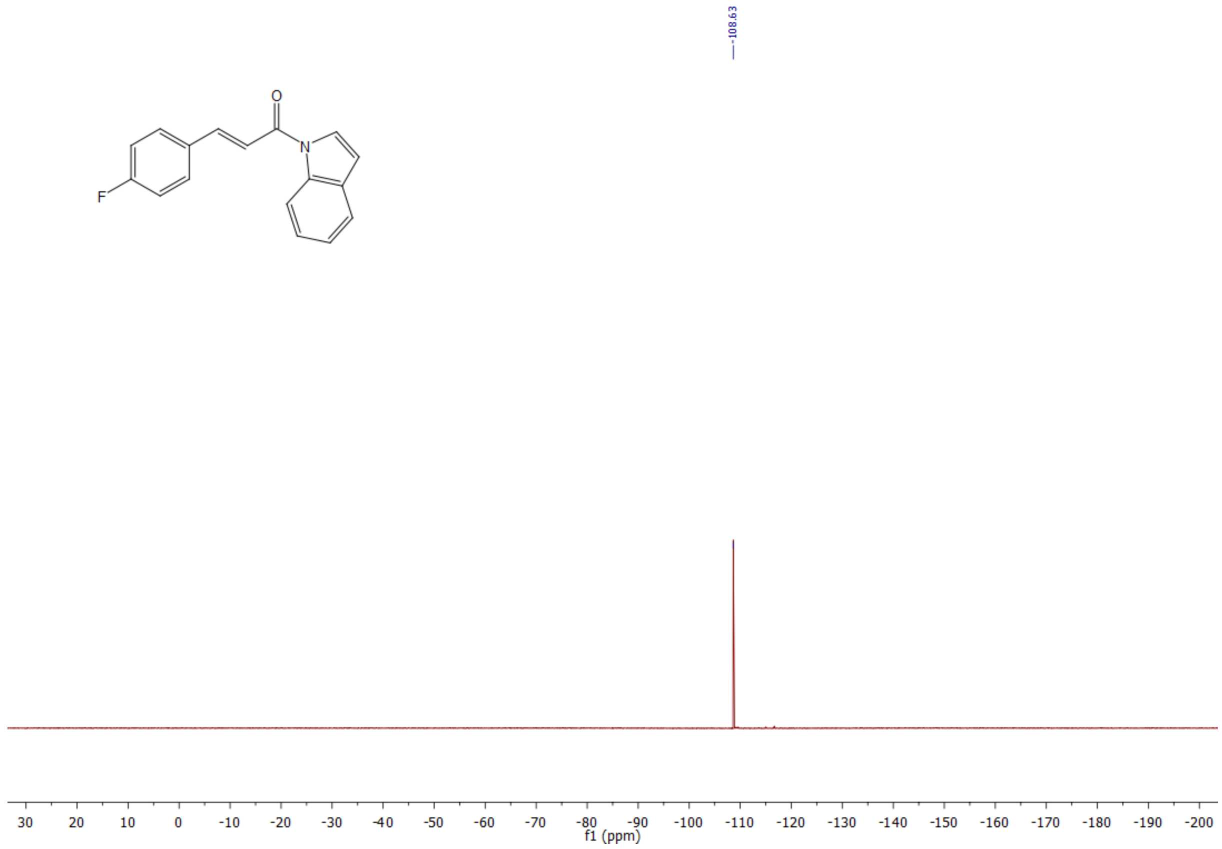
^{1}H NMR of compound **13** ($CDCl_3$)



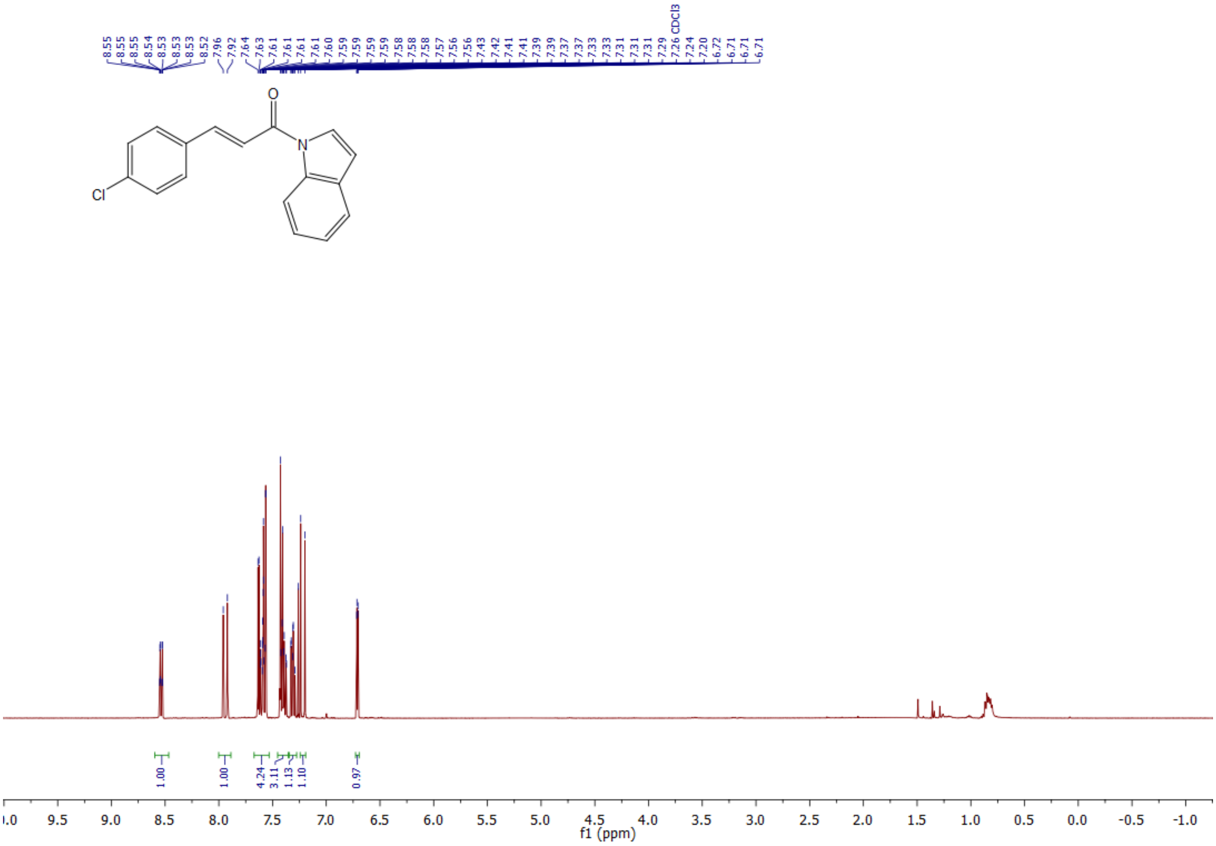
^{13}C NMR of compound **13** ($CDCl_3$)



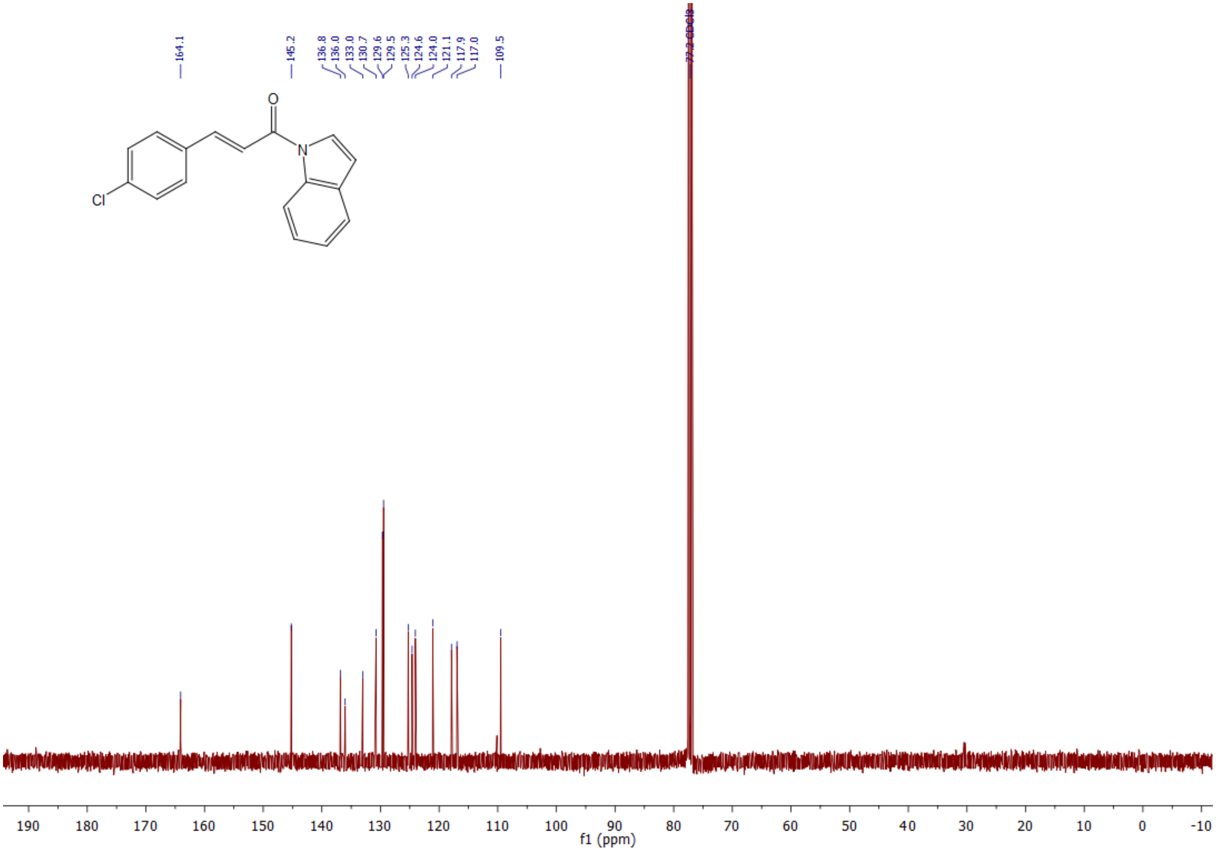
^{19}F NMR of compound **13** ($CDCl_3$)



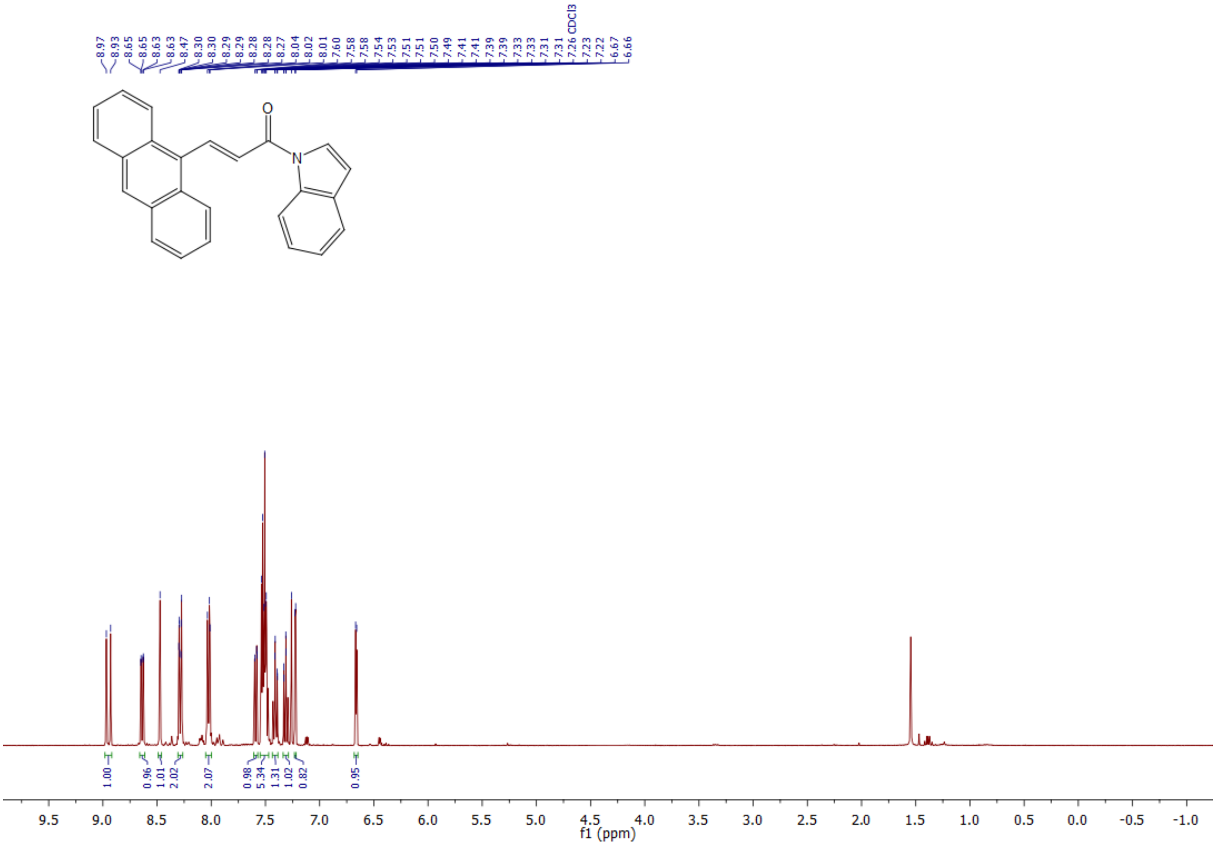
^{1}H NMR of compound **14** ($CDCl_3$)



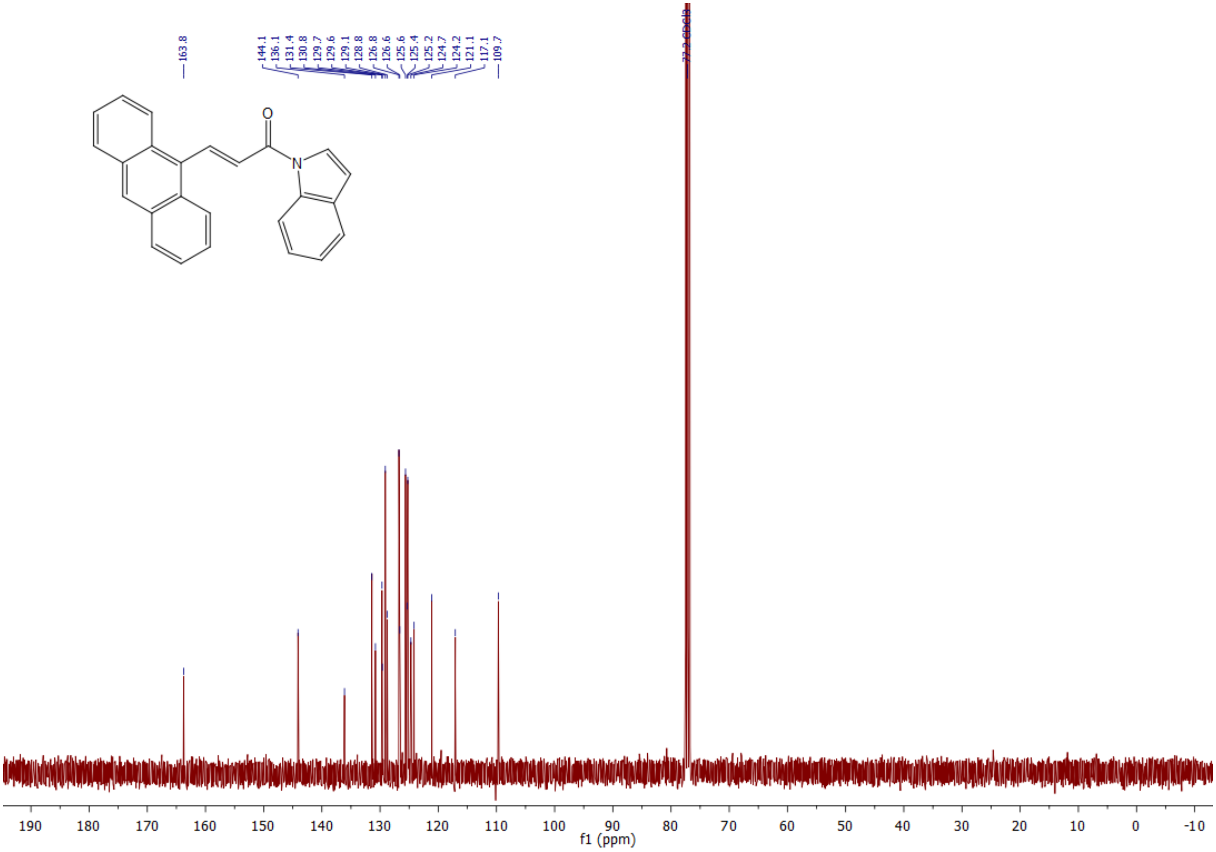
^{13}C NMR of compound **14** ($CDCl_3$)



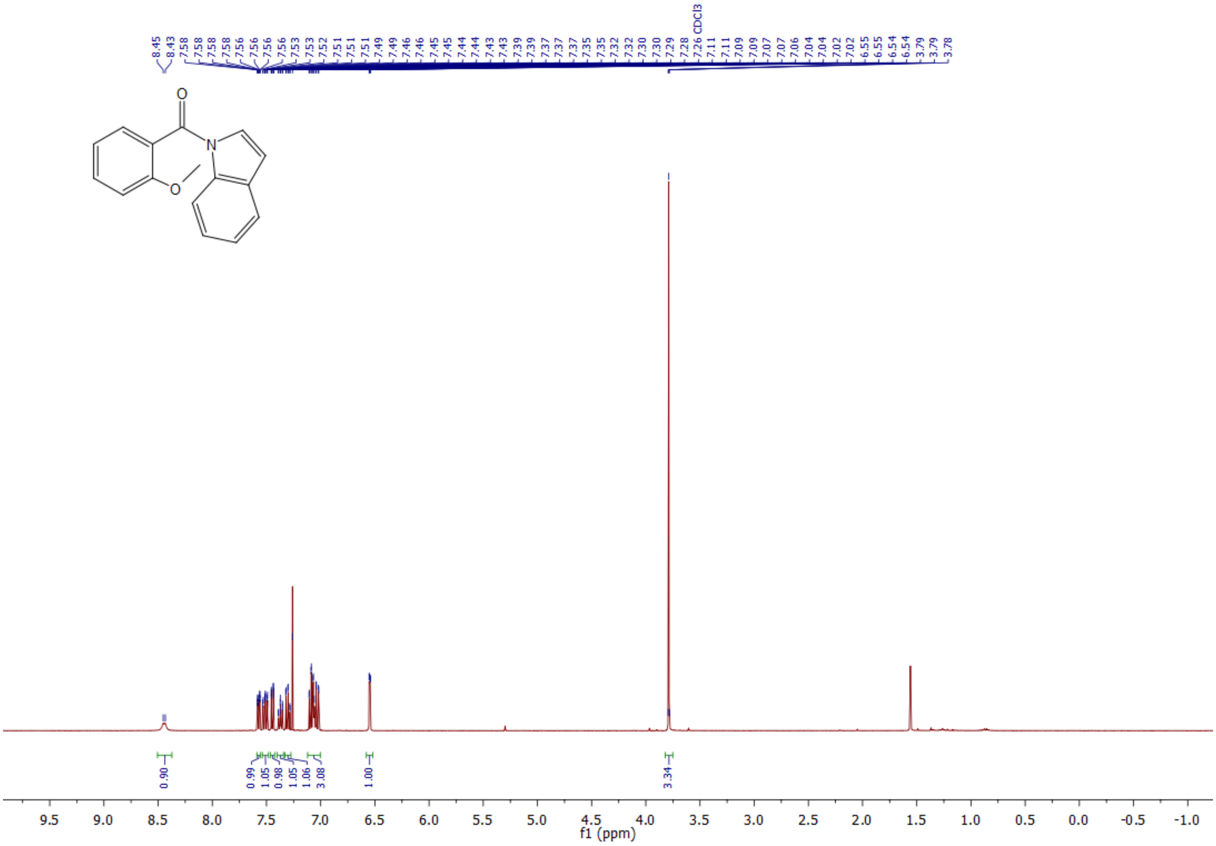
^{1}H NMR of compound **15** ($CDCl_3$)



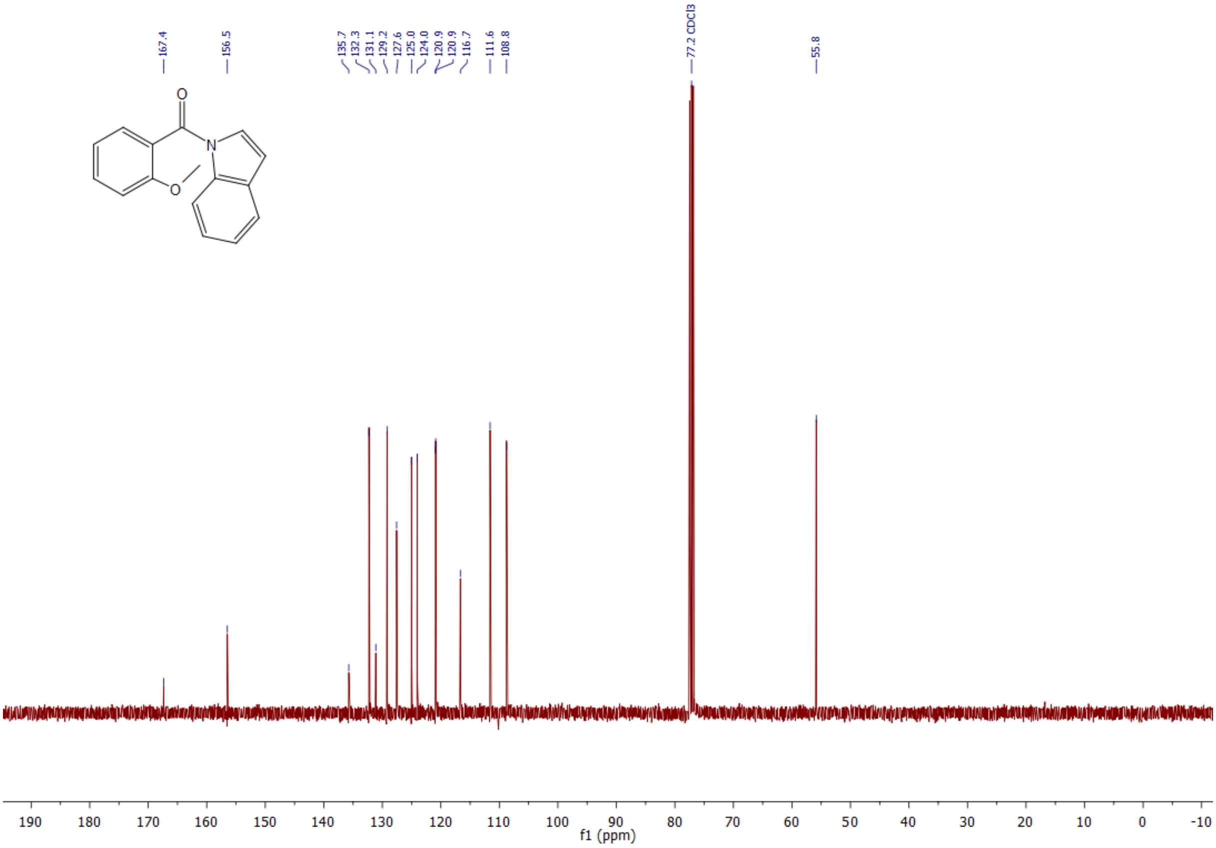
^{13}C NMR of compound **15** ($CDCl_3$)



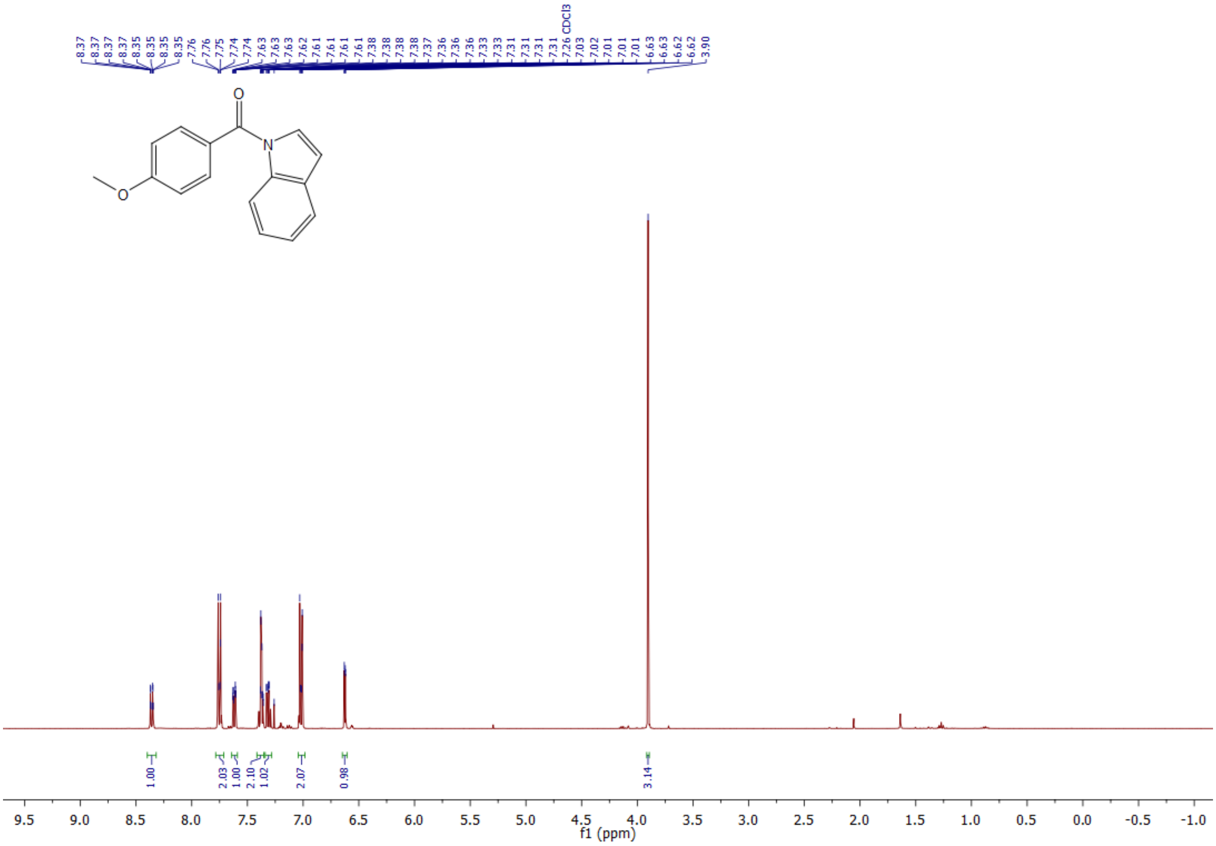
^{1}H NMR of compound **16** ($CDCl_3$)



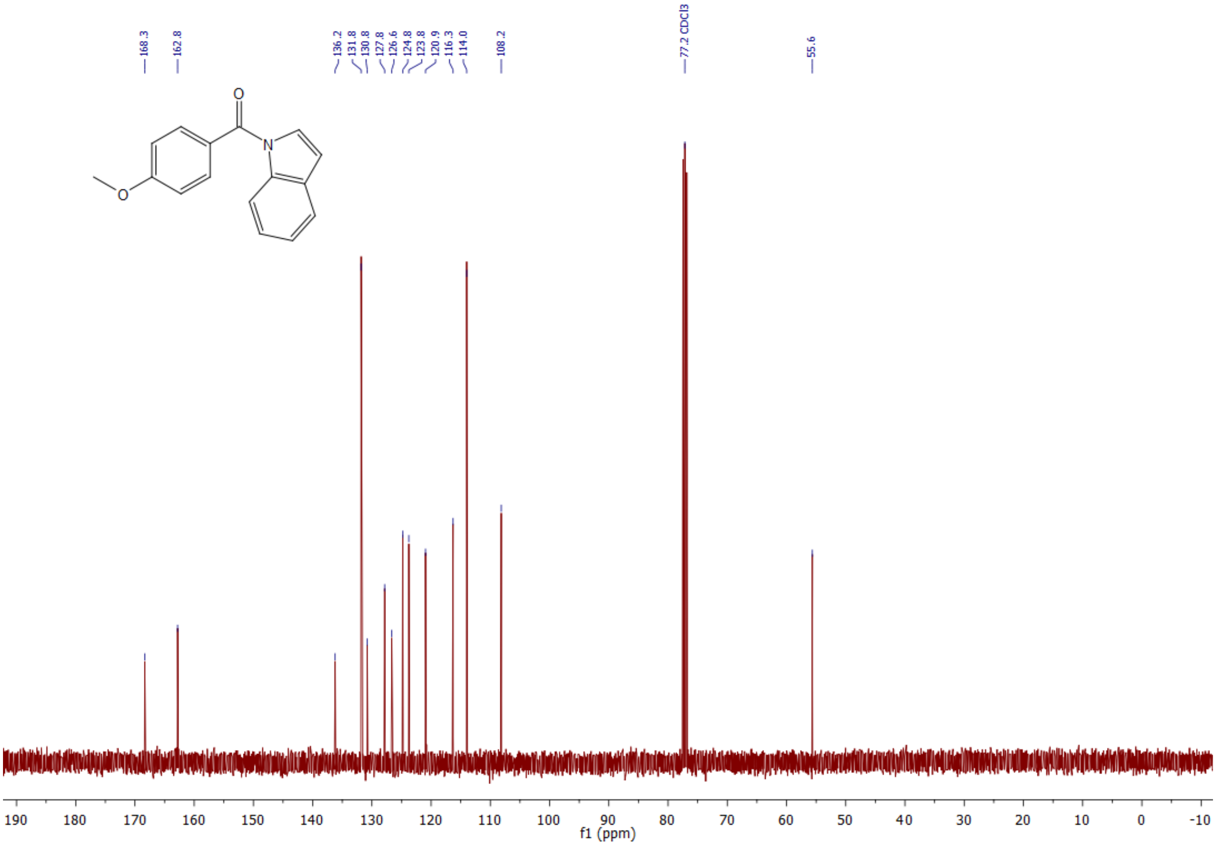
^{13}C NMR of compound **16** ($CDCl_3$)



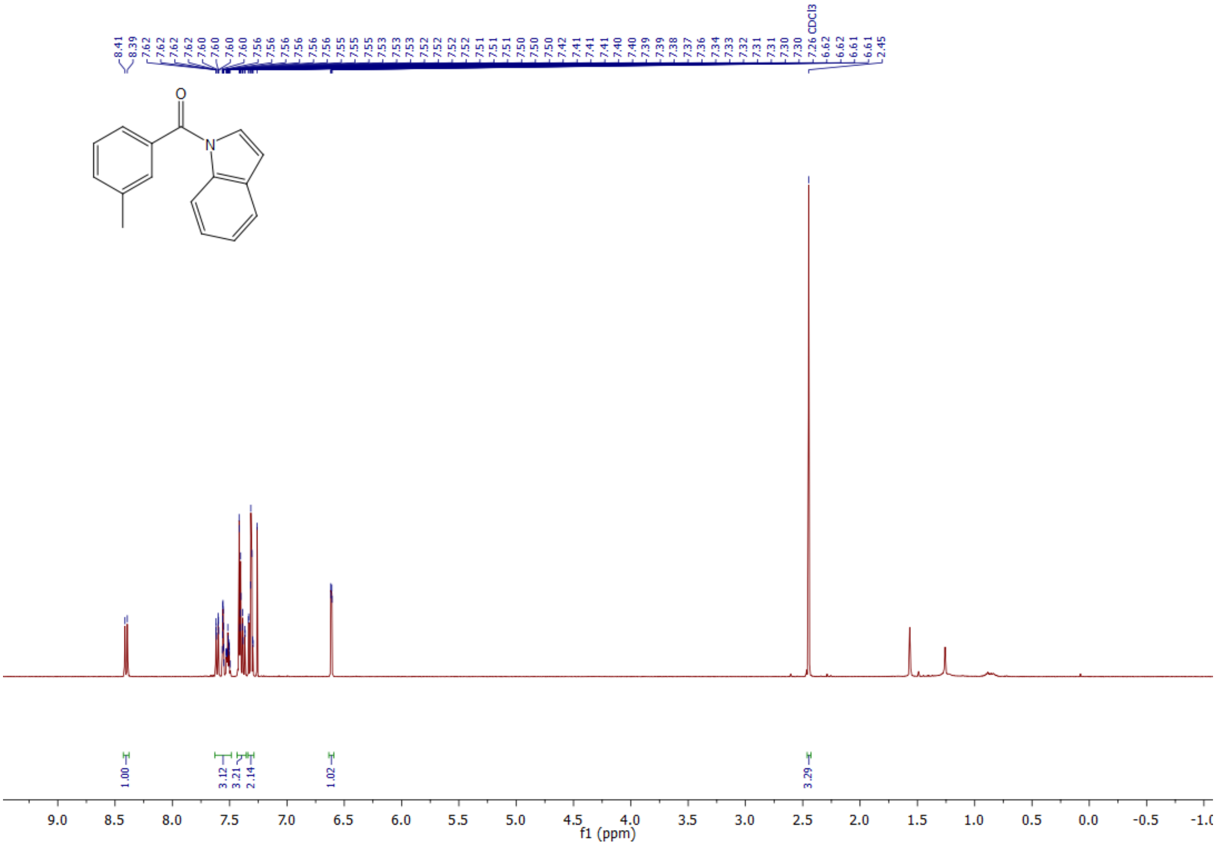
^{1}H NMR of compound **17** ($CDCl_3$)



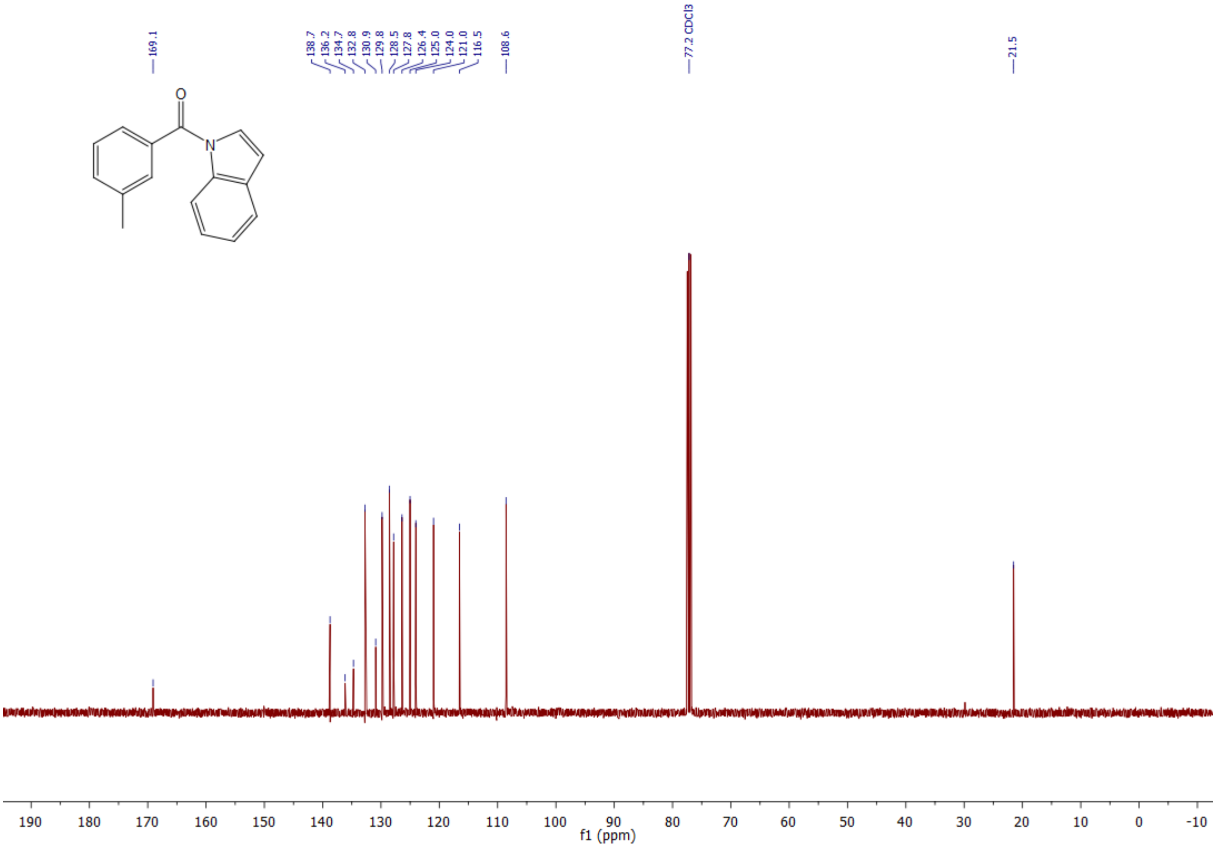
^{13}C NMR of compound **17** ($CDCl_3$)



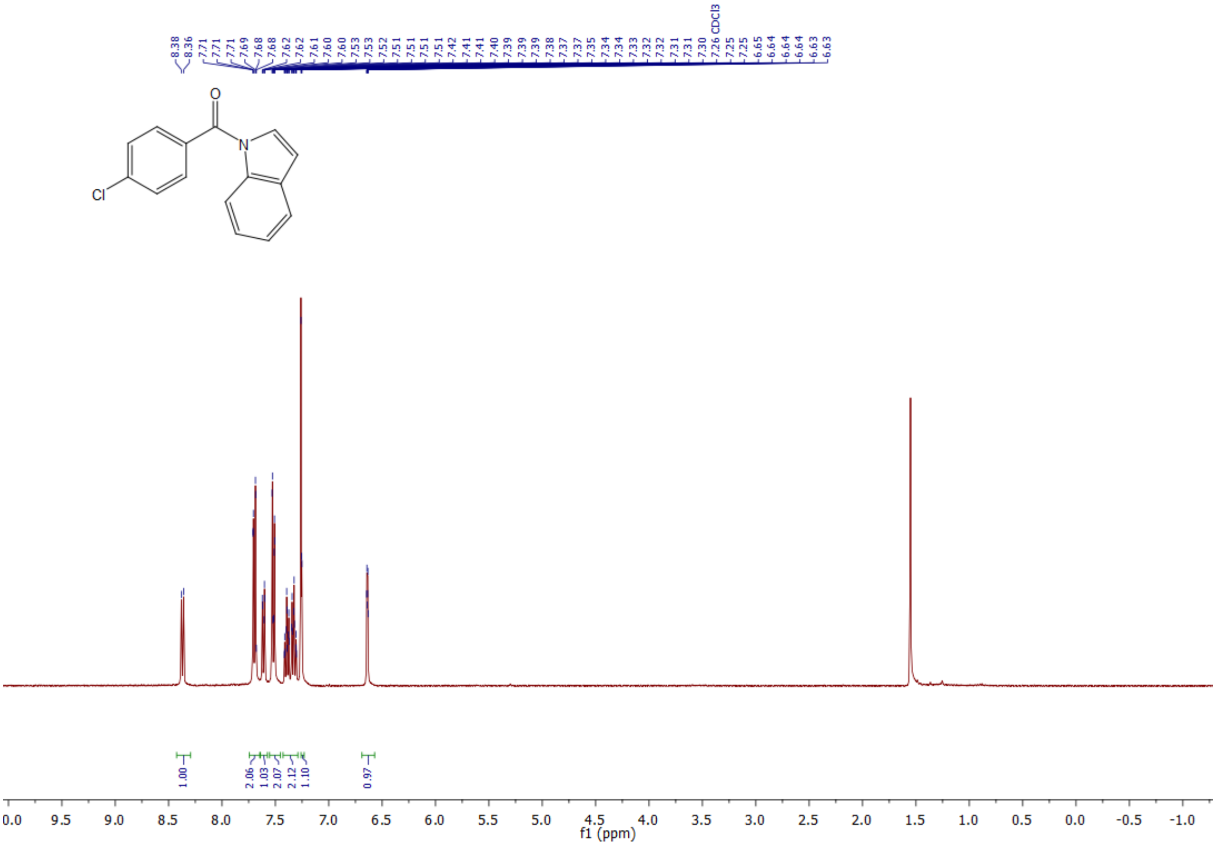
^{1}H NMR of compound **18** ($CDCl_3$)



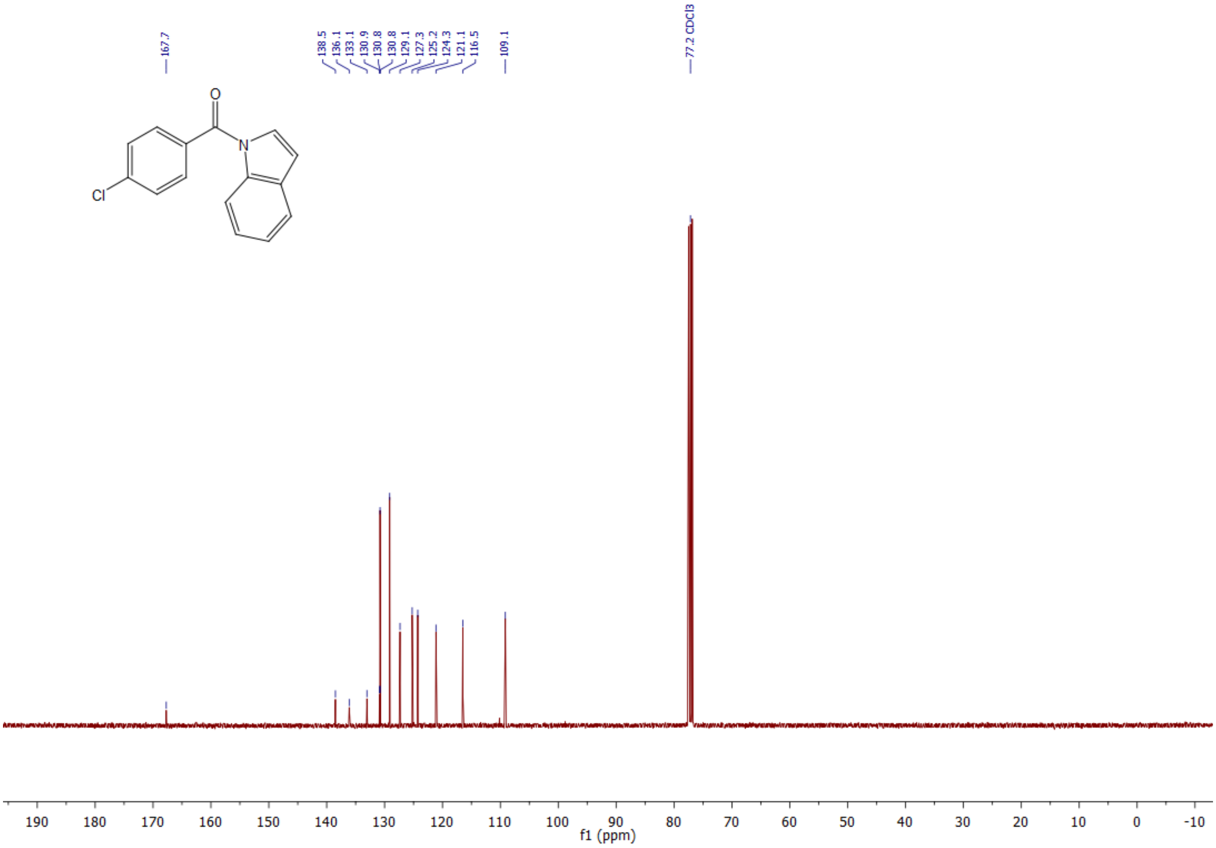
^{13}C NMR of compound **18** ($CDCl_3$)



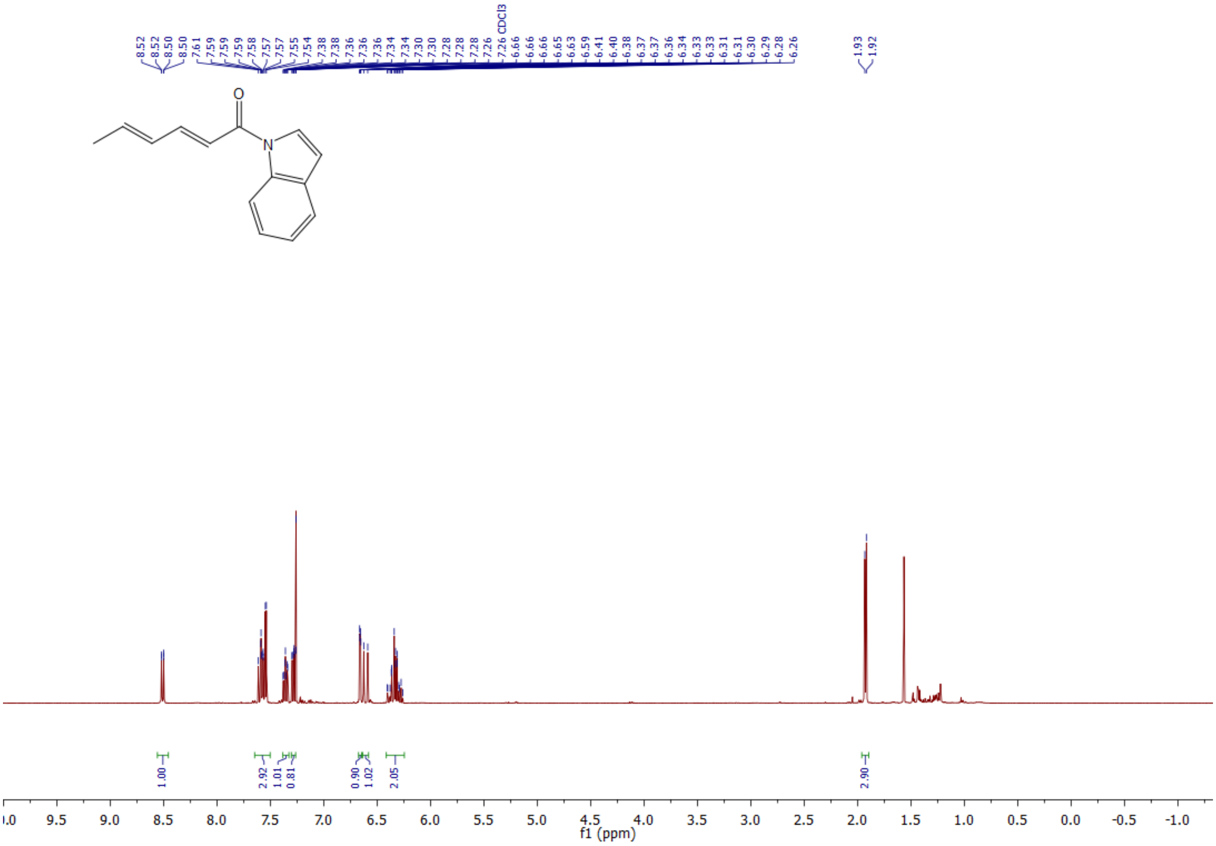
^{1}H NMR of compound **19** ($CDCl_3$)



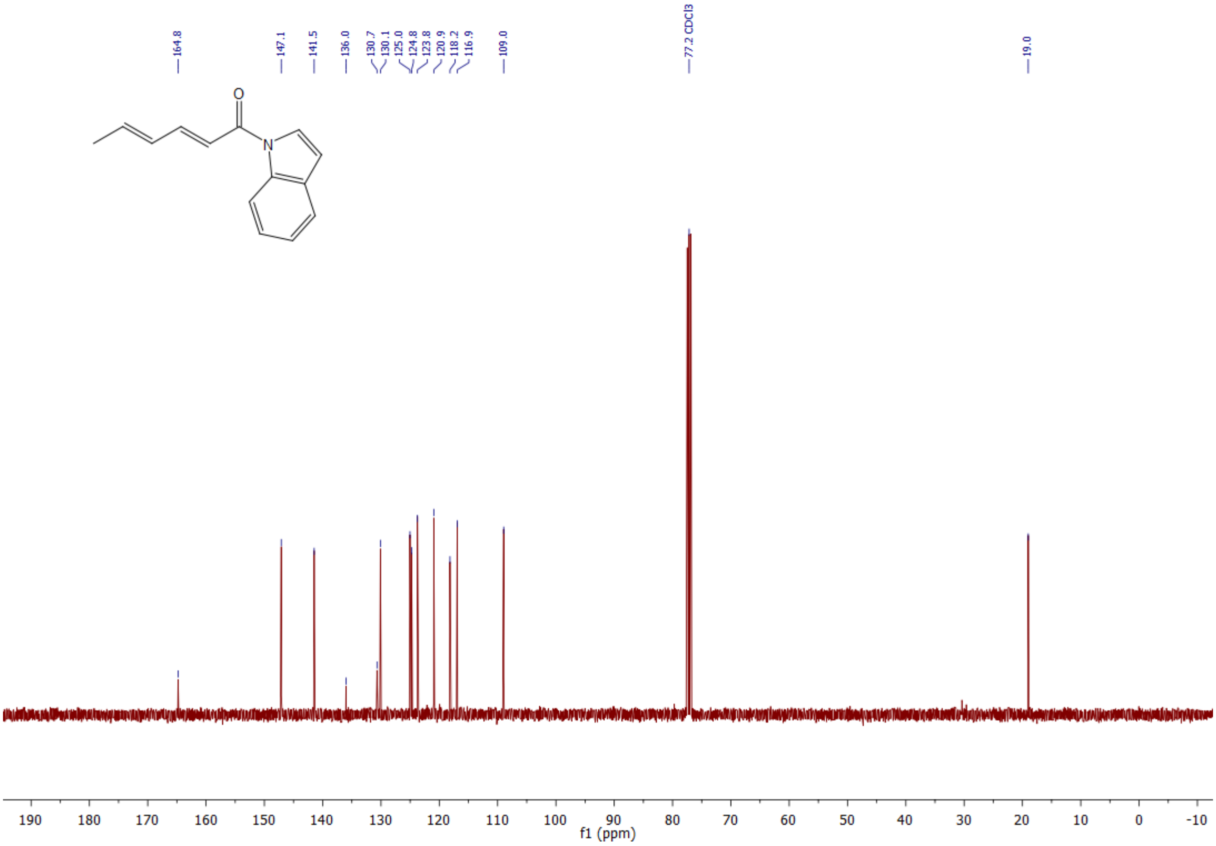
^{13}C NMR of compound **19** ($CDCl_3$)



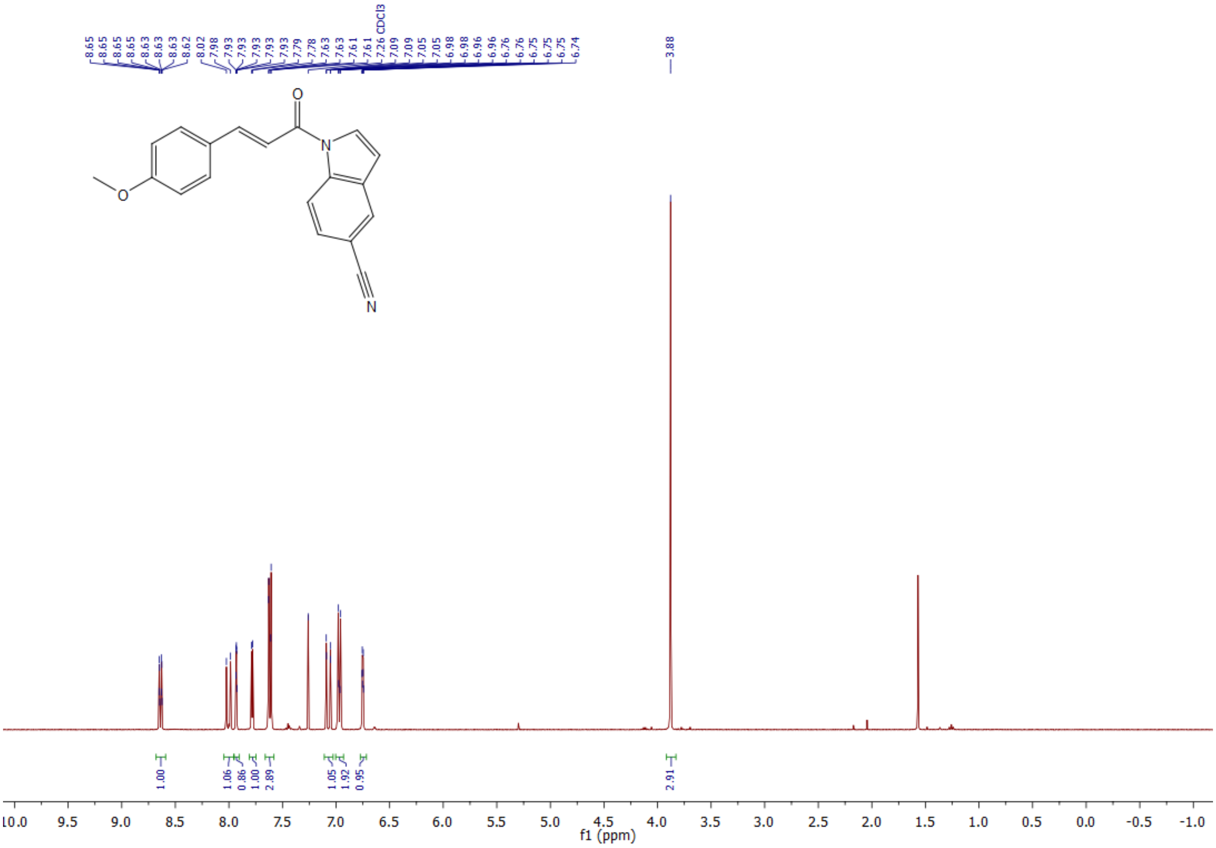
^{1}H NMR of compound **20** ($CDCl_3$)



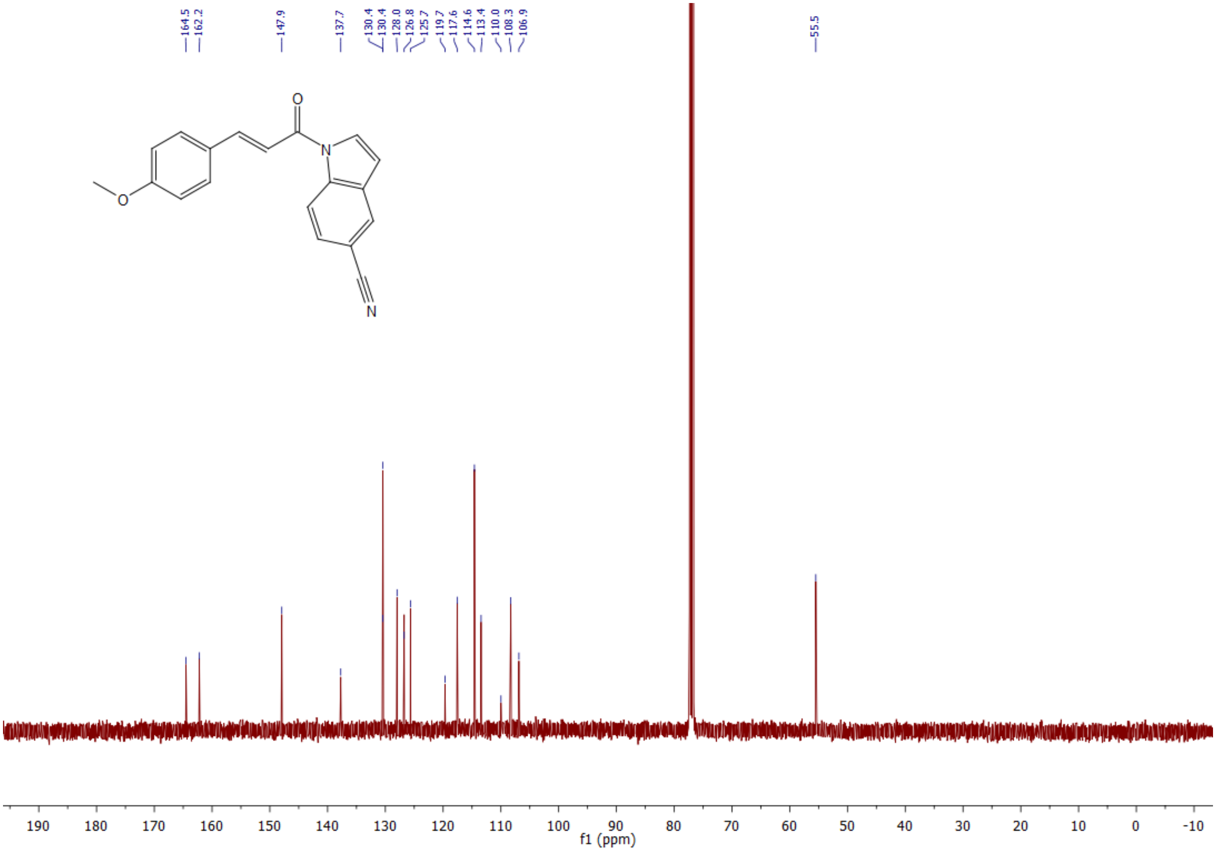
^{13}C NMR of compound **20** ($CDCl_3$)



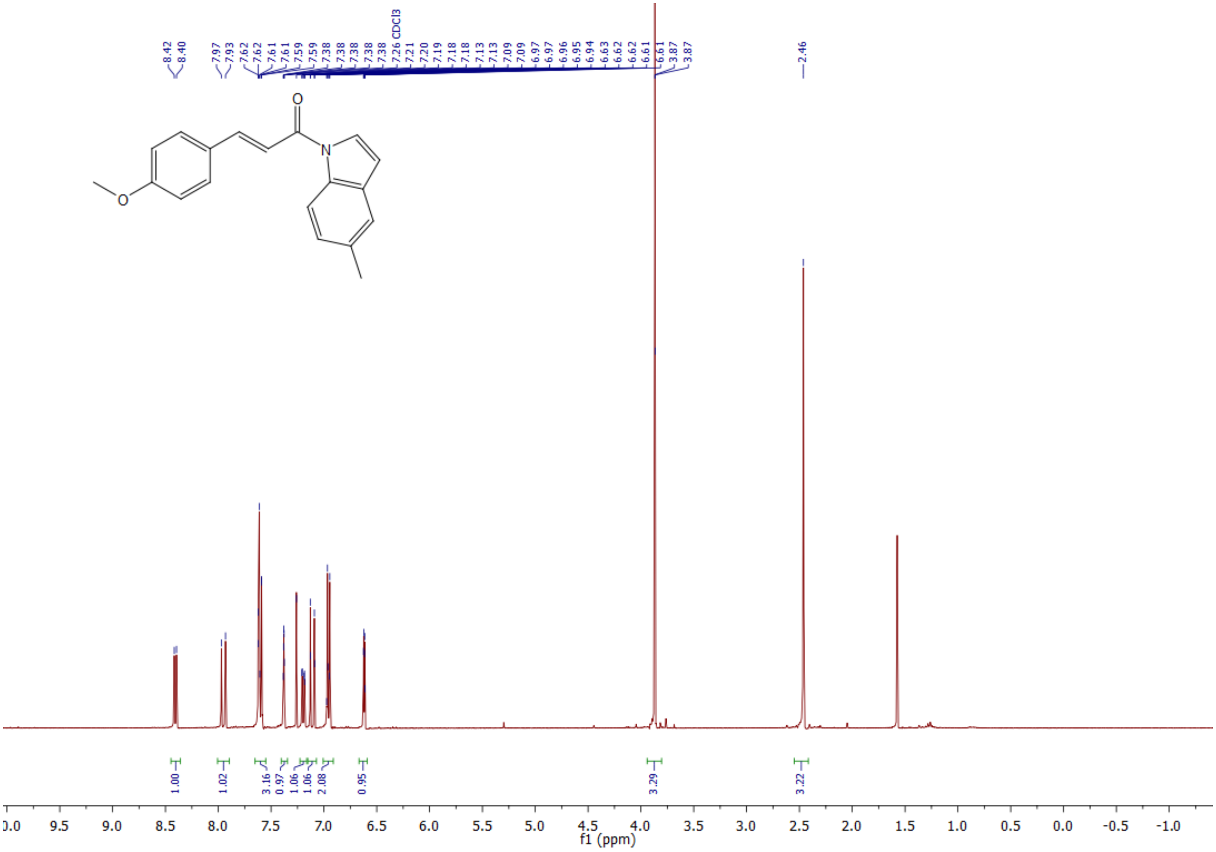
^{1}H NMR of compound **21** (CDCl$_3$)



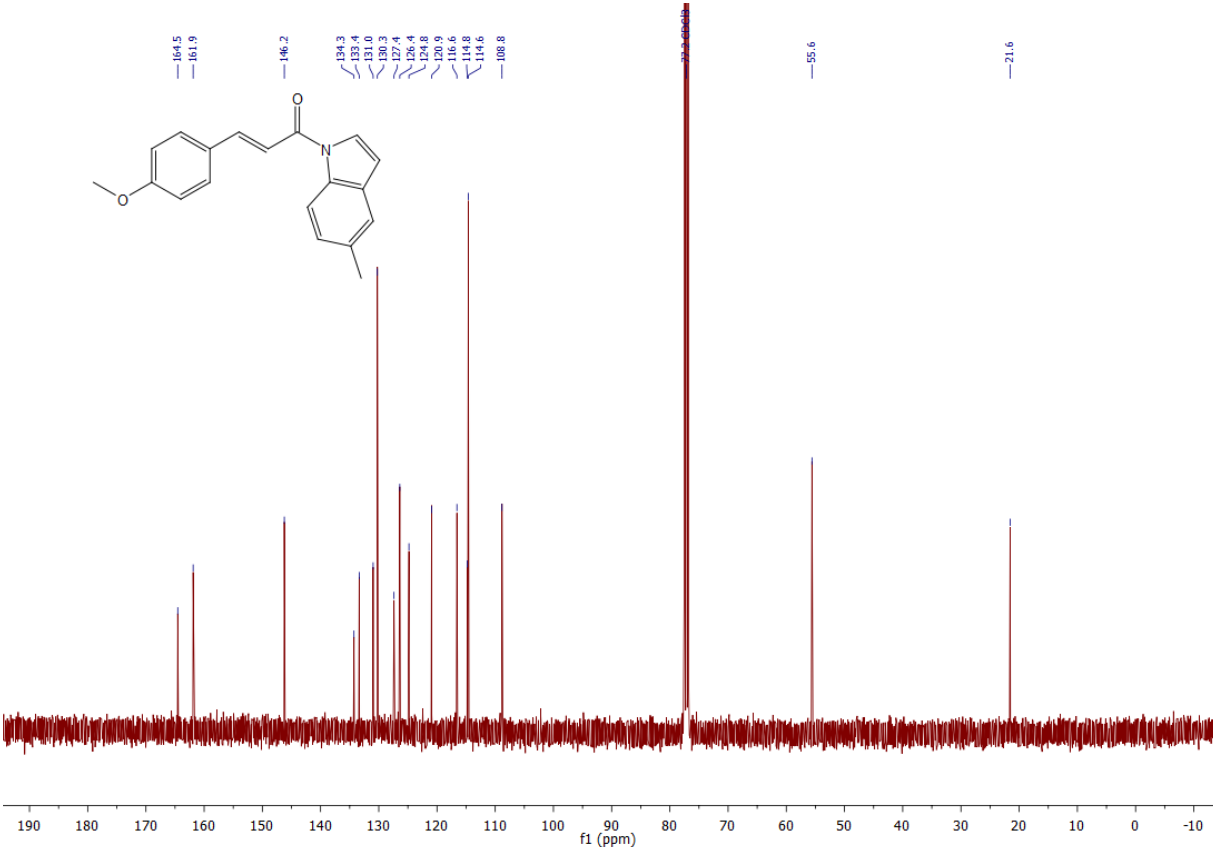
^{13}C NMR of compound **21** (CDCl$_3$)



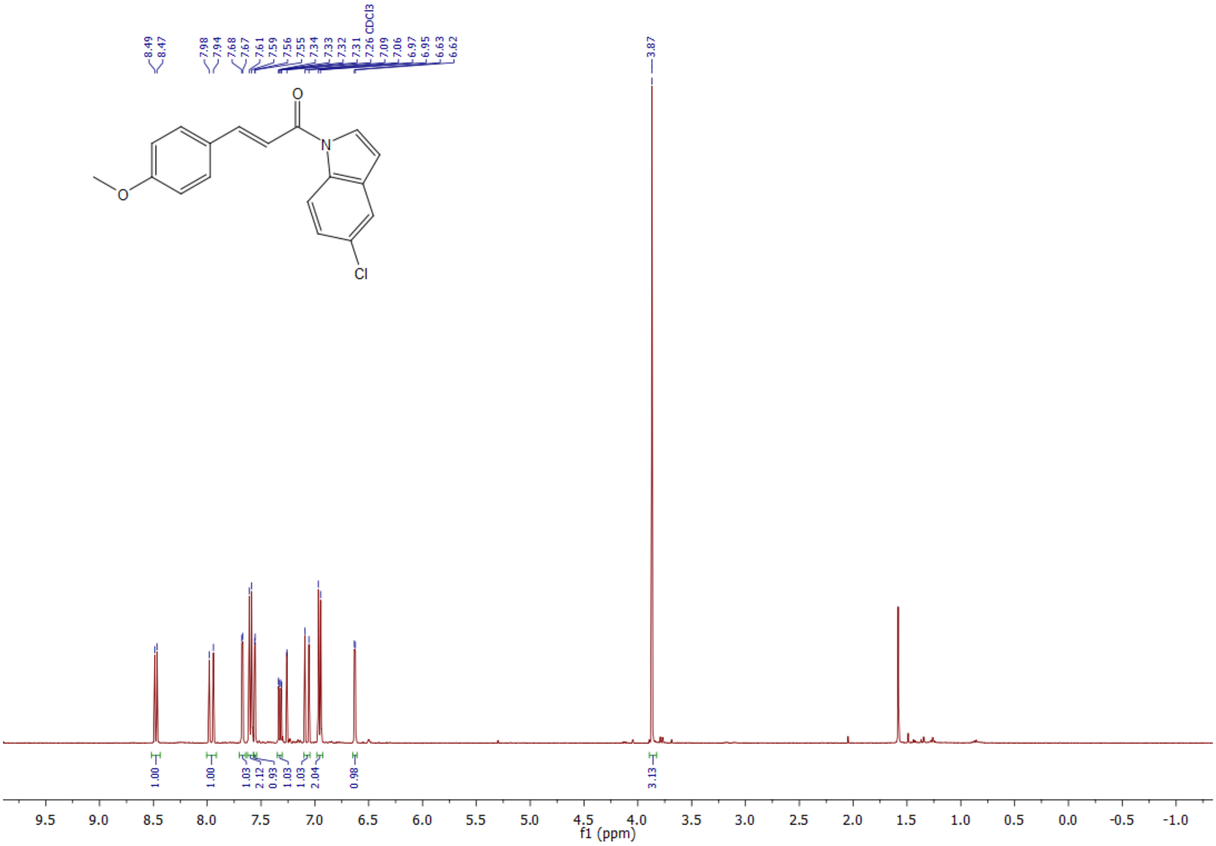
^1H NMR of compound **22** ($CDCl_3$)



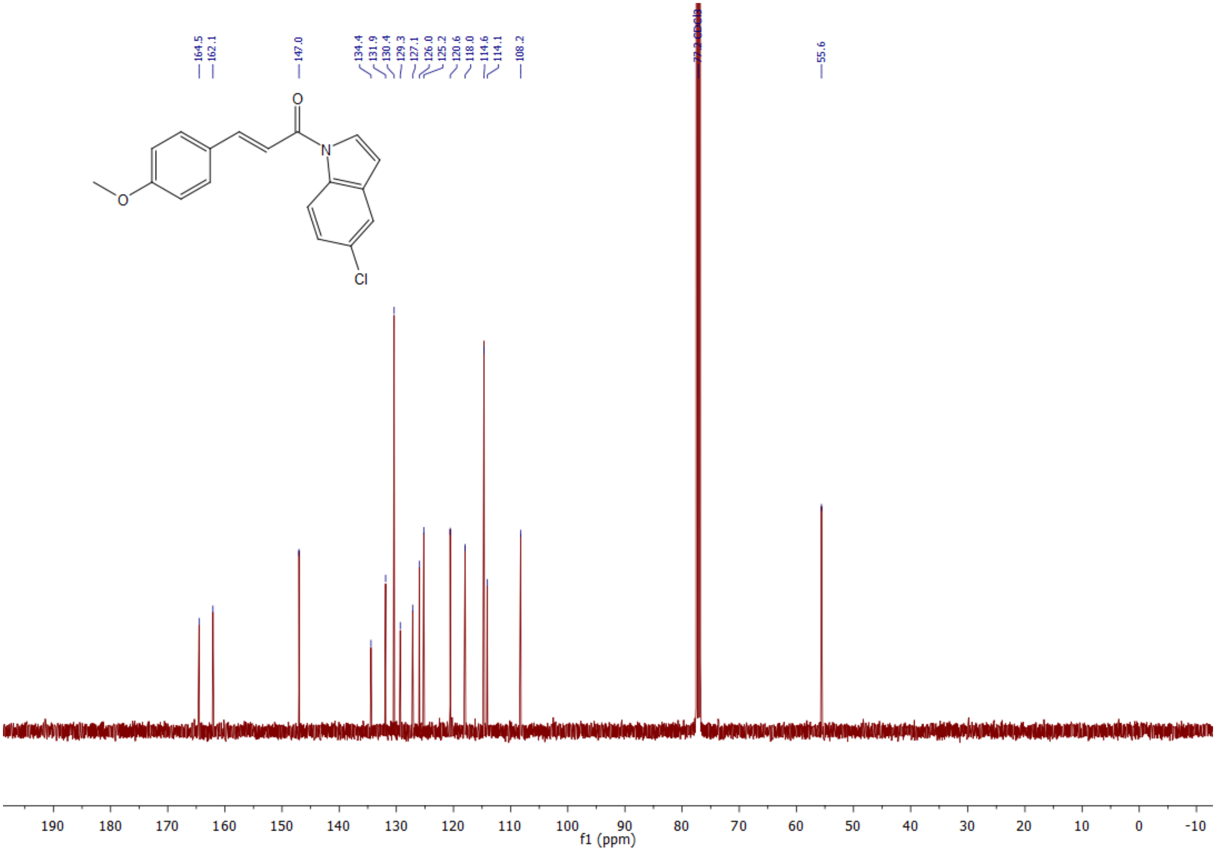
^{13}C NMR of compound **22** ($CDCl_3$)



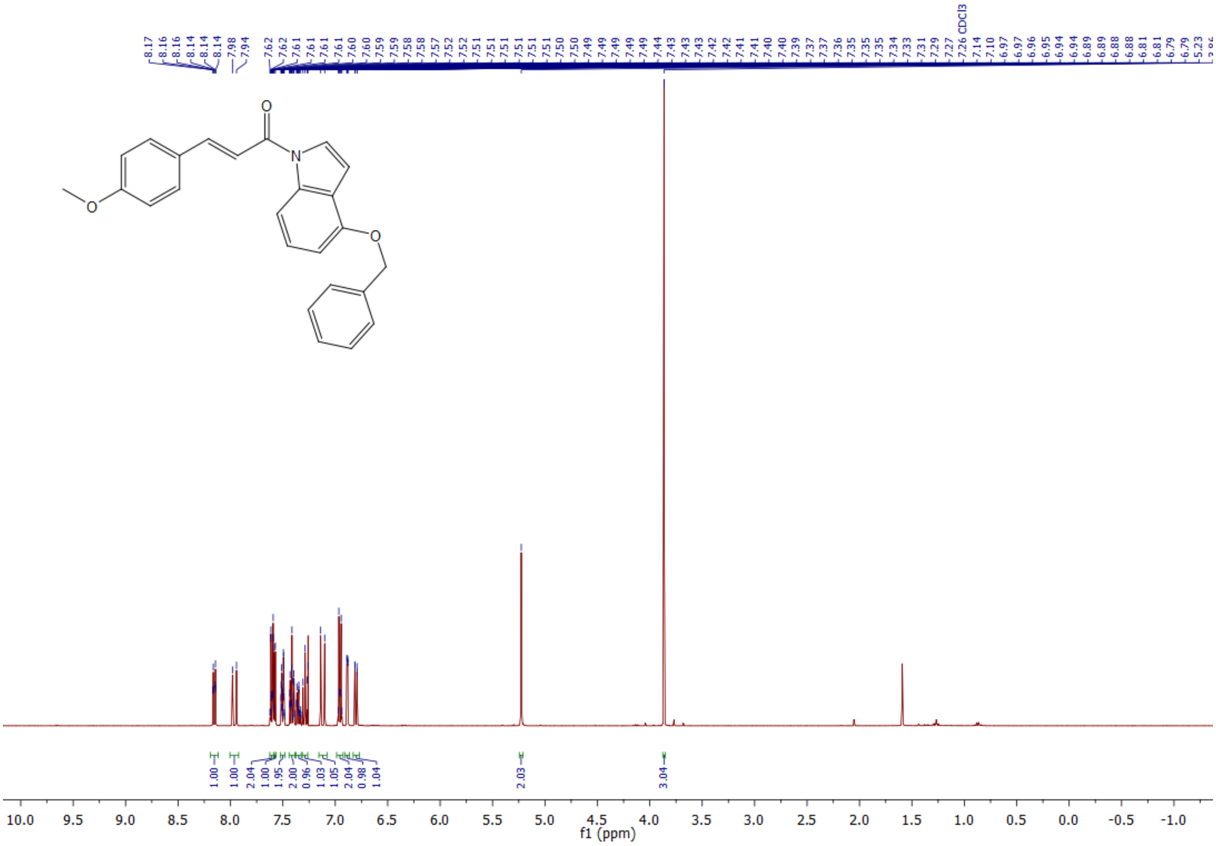
^{1}H NMR of compound **23** ($CDCl_3$)



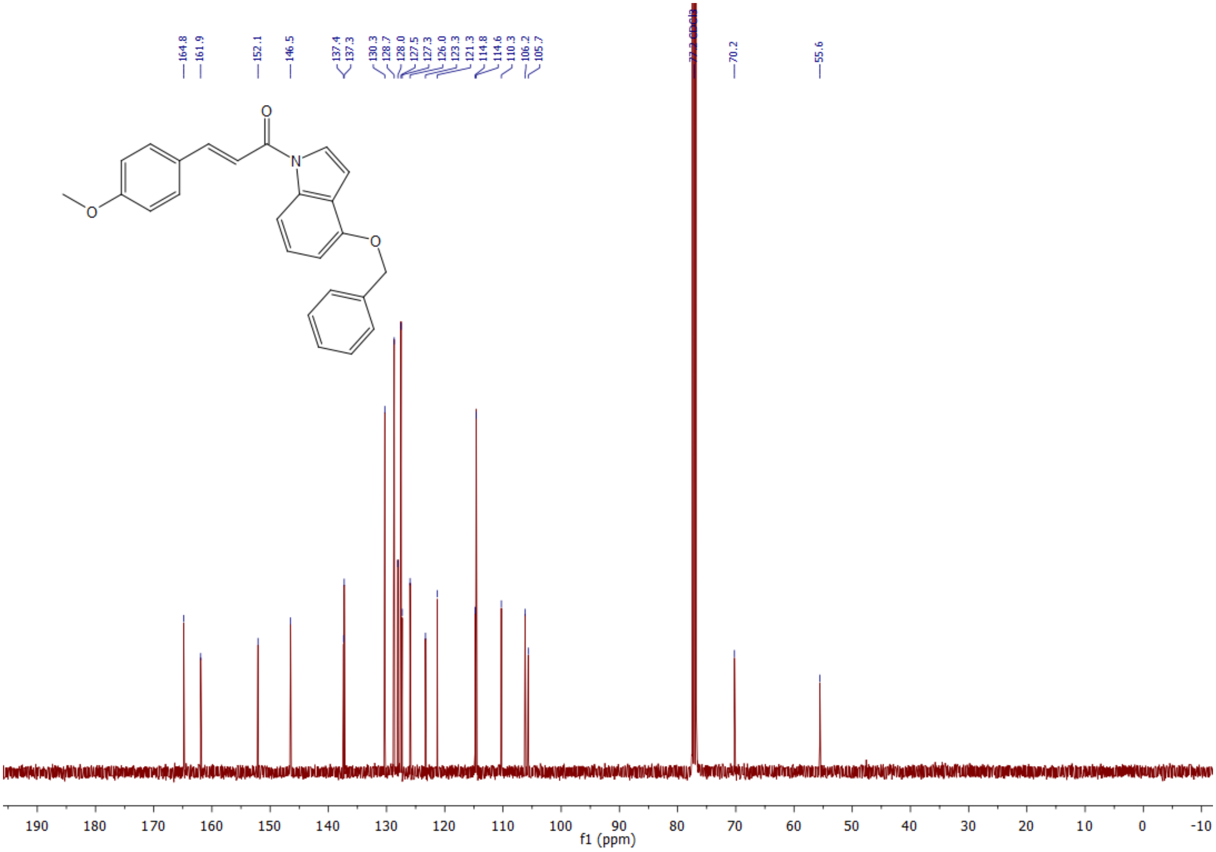
^{13}C NMR of compound **23** ($CDCl_3$)



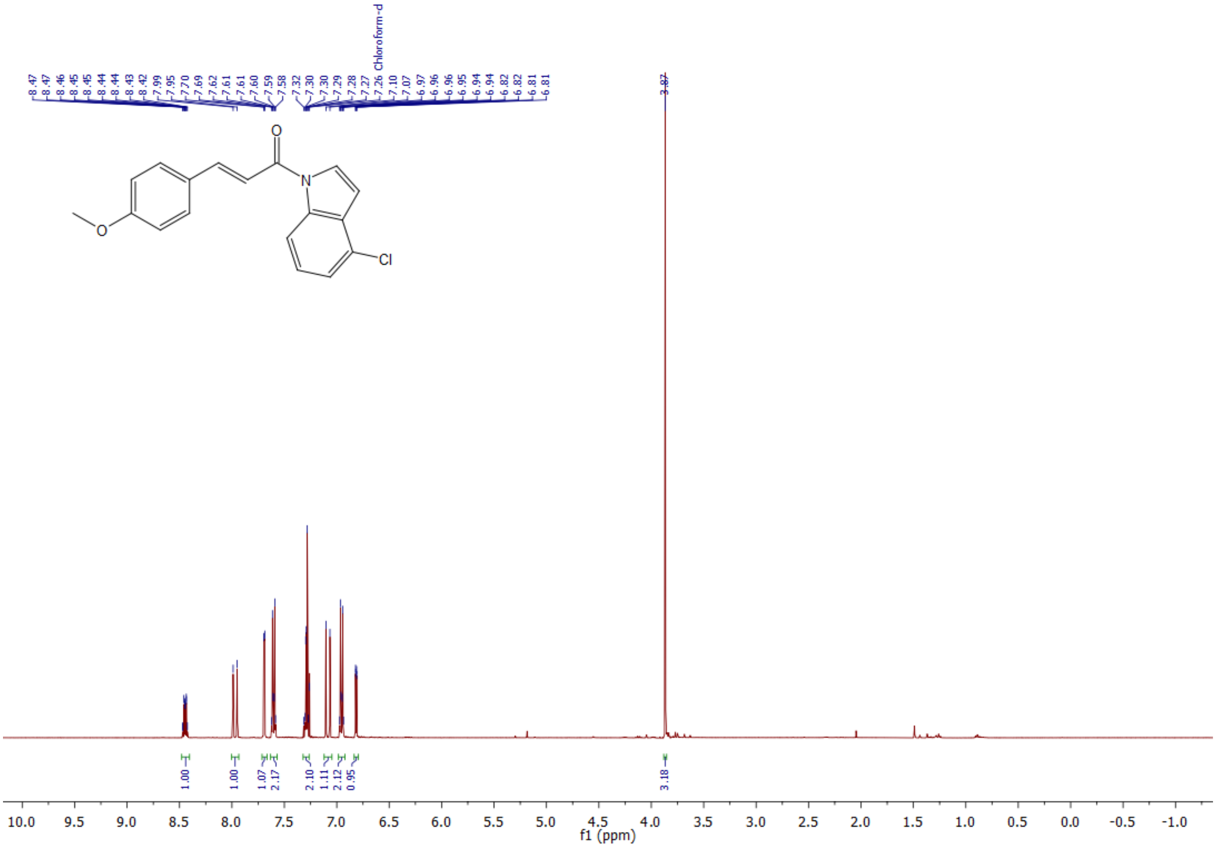
^{1}H NMR of compound **24** (CDCl$_3$)



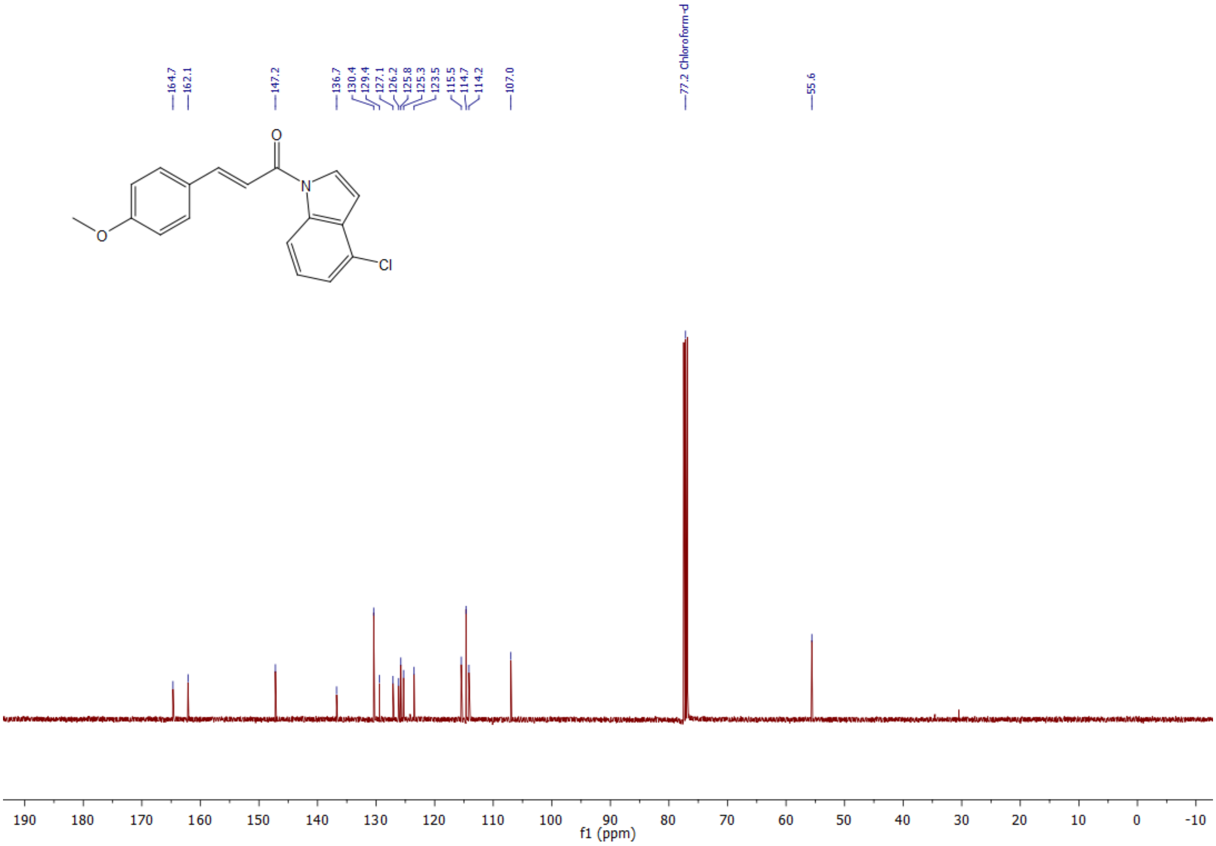
^{13}C NMR of compound **24** (CDCl$_3$)



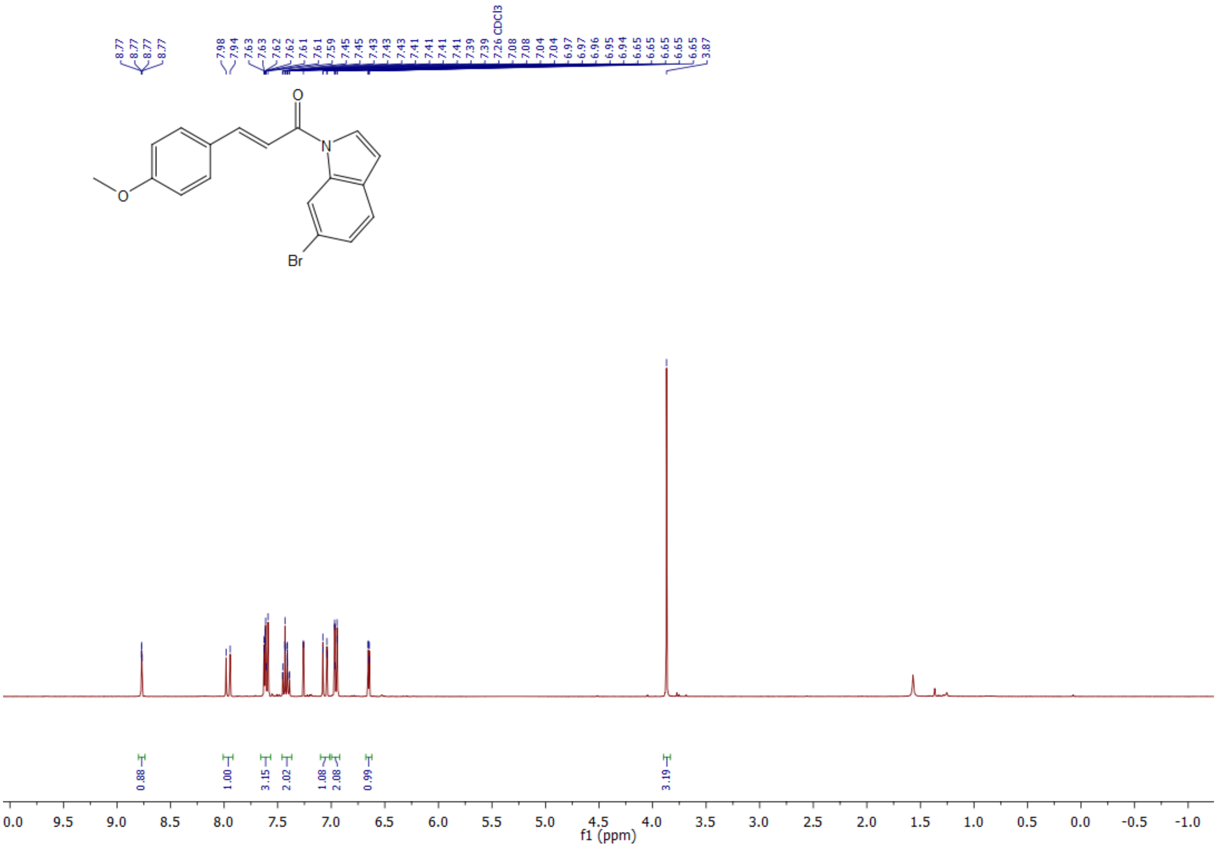
^{1}H NMR of compound **25** ($CDCl_3$)



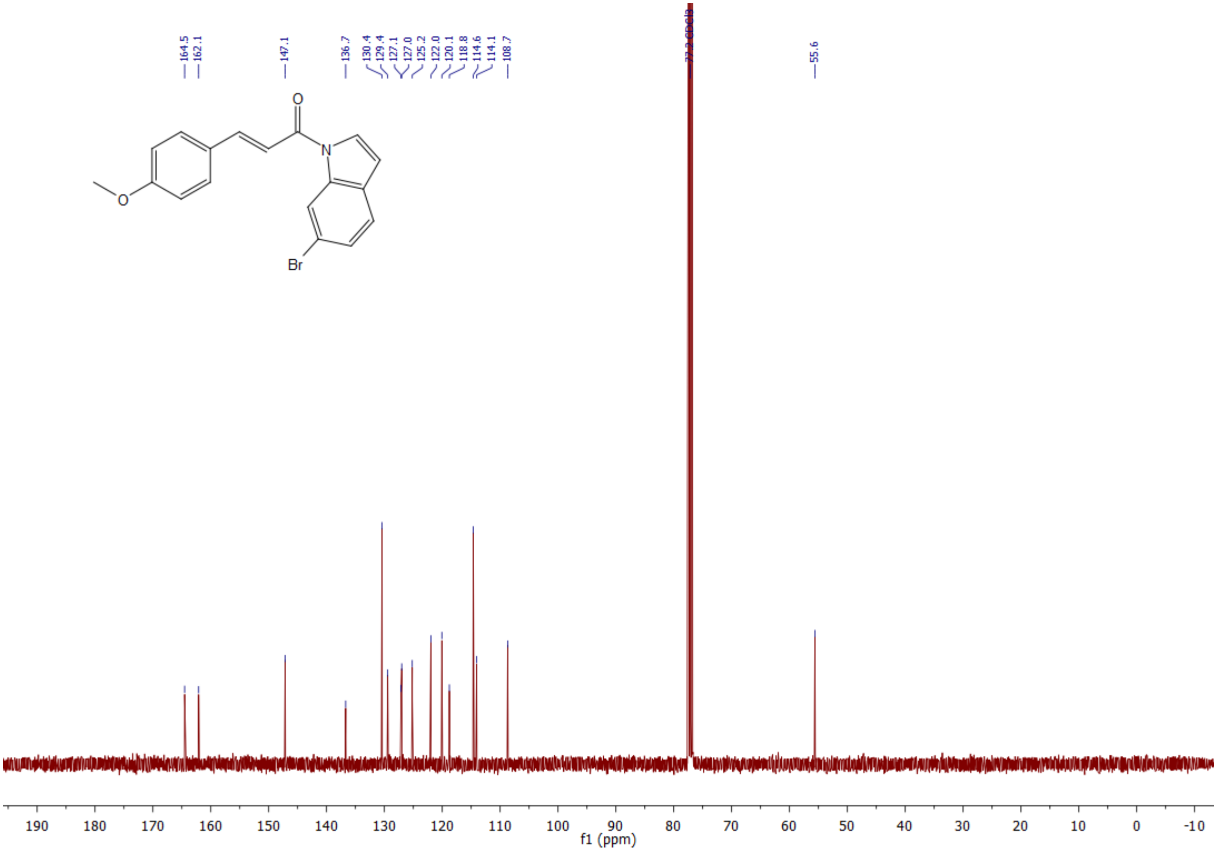
^{13}C NMR of compound **25** ($CDCl_3$)



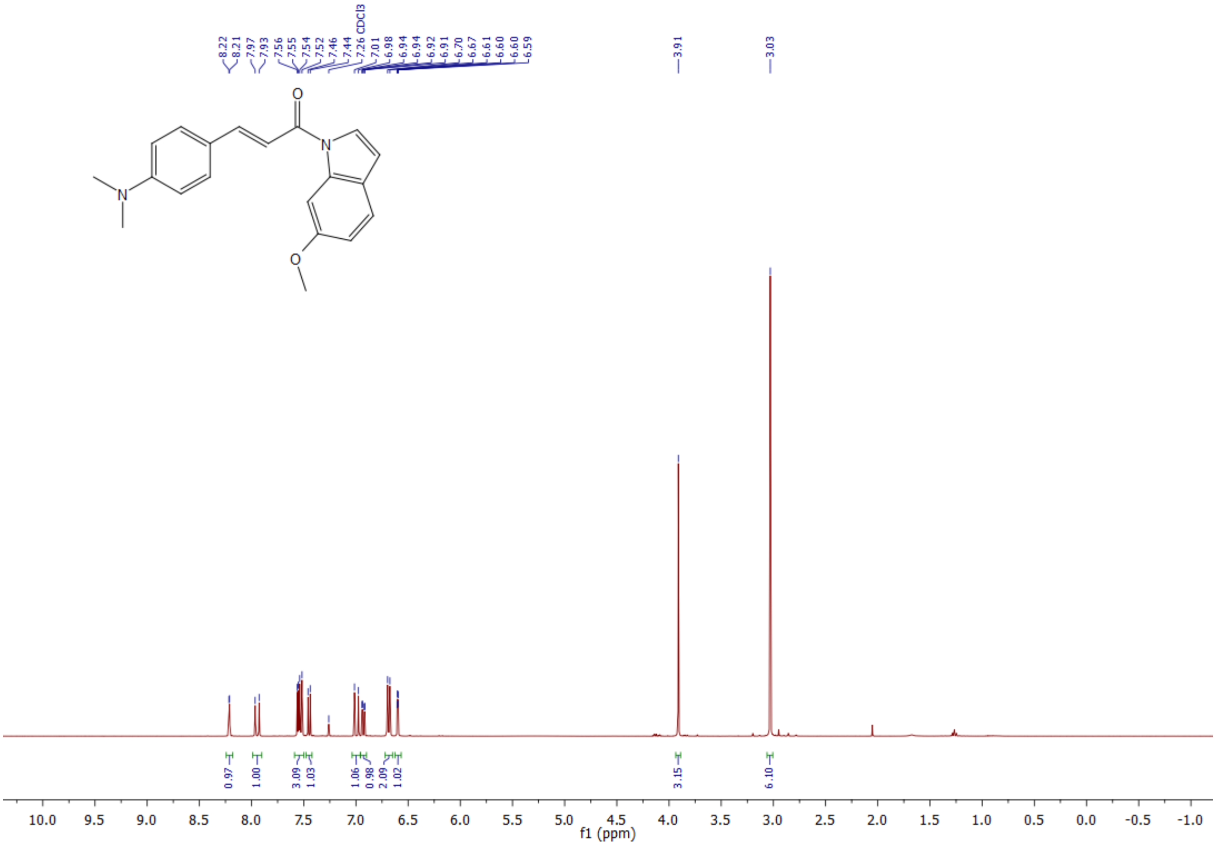
^{1}H NMR of compound **26** ($CDCl_3$)



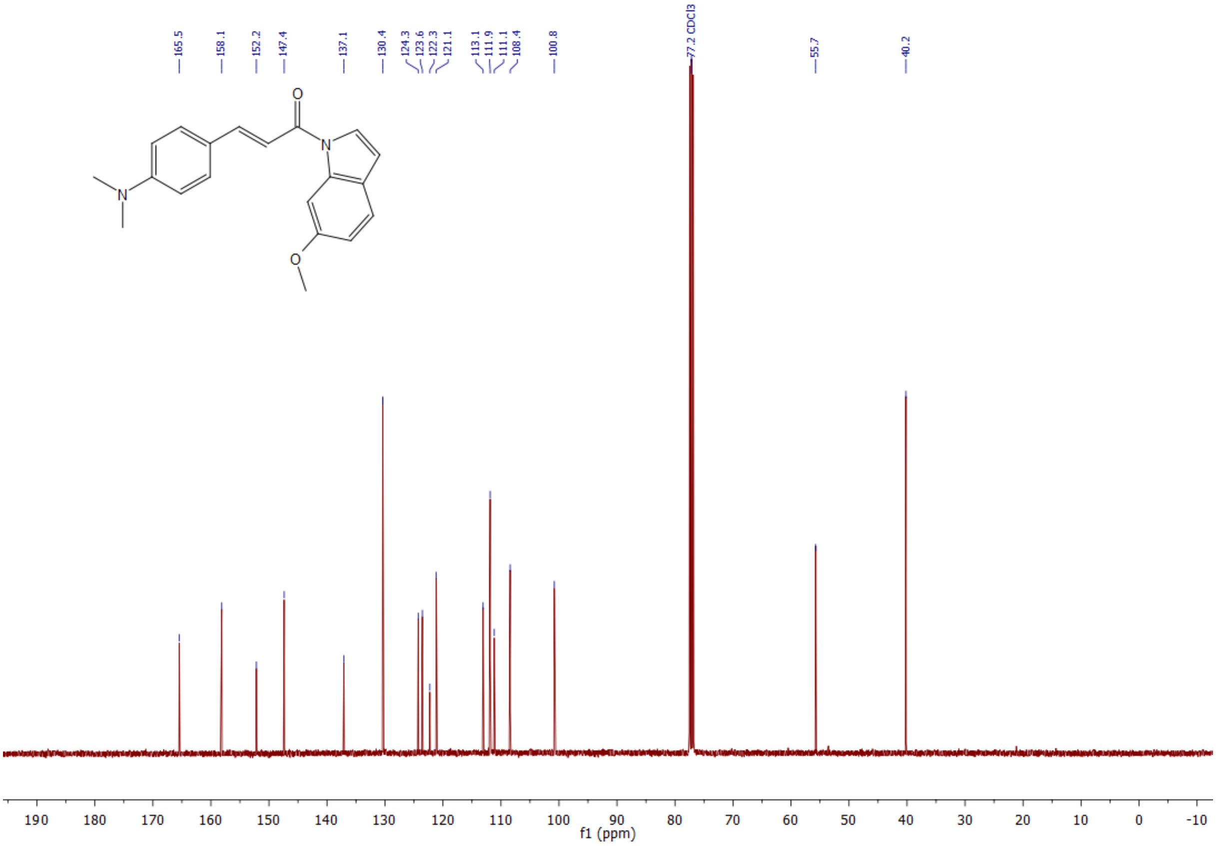
^{13}C NMR of compound **26** ($CDCl_3$)



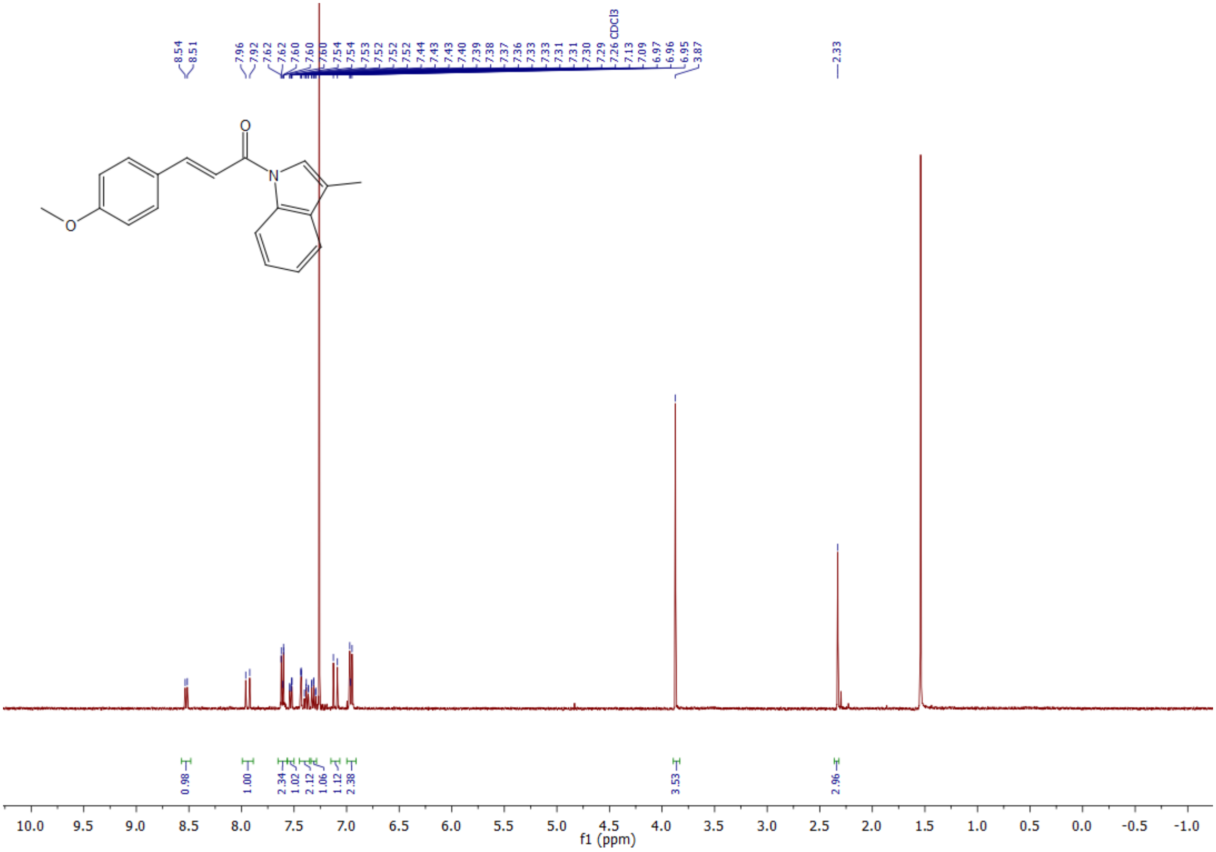
^{1}H NMR of compound **27** (CDCl$_3$)



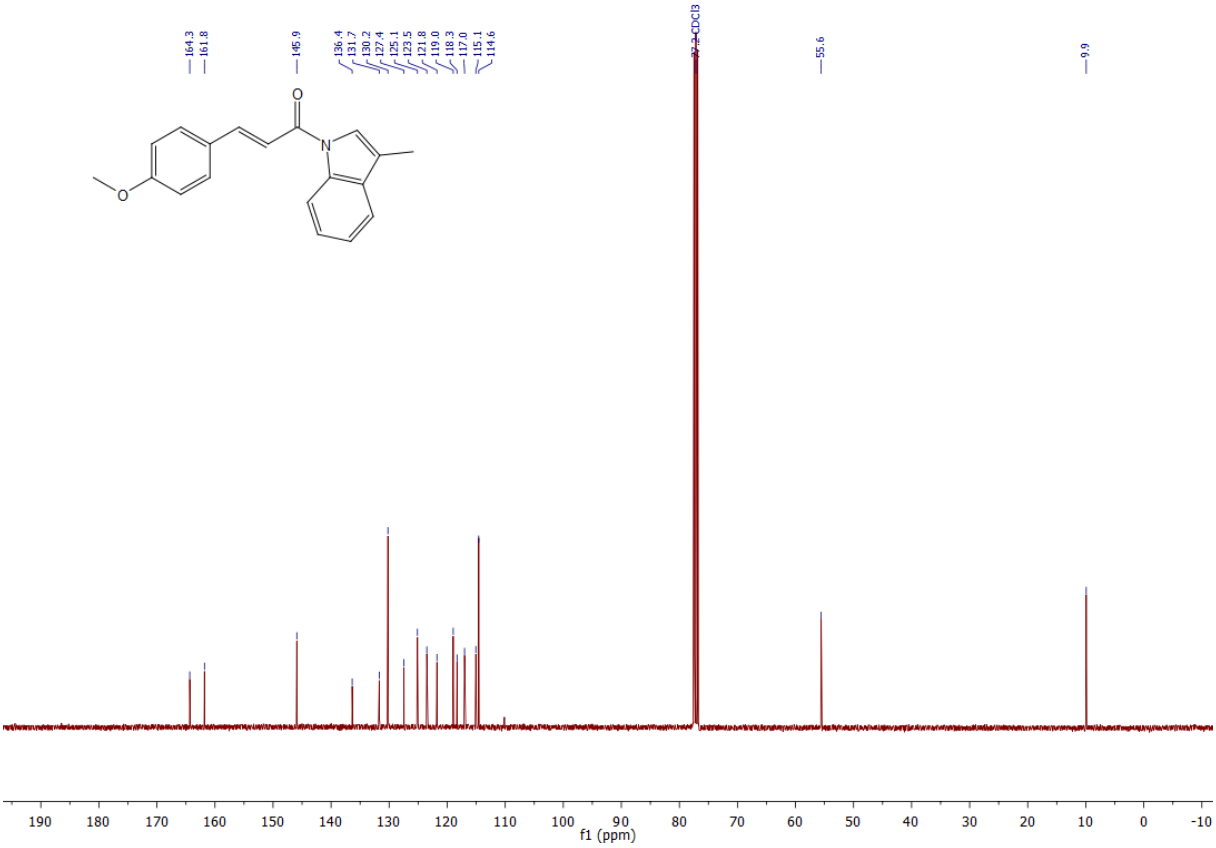
^{13}C NMR of compound **27** (CDCl$_3$)



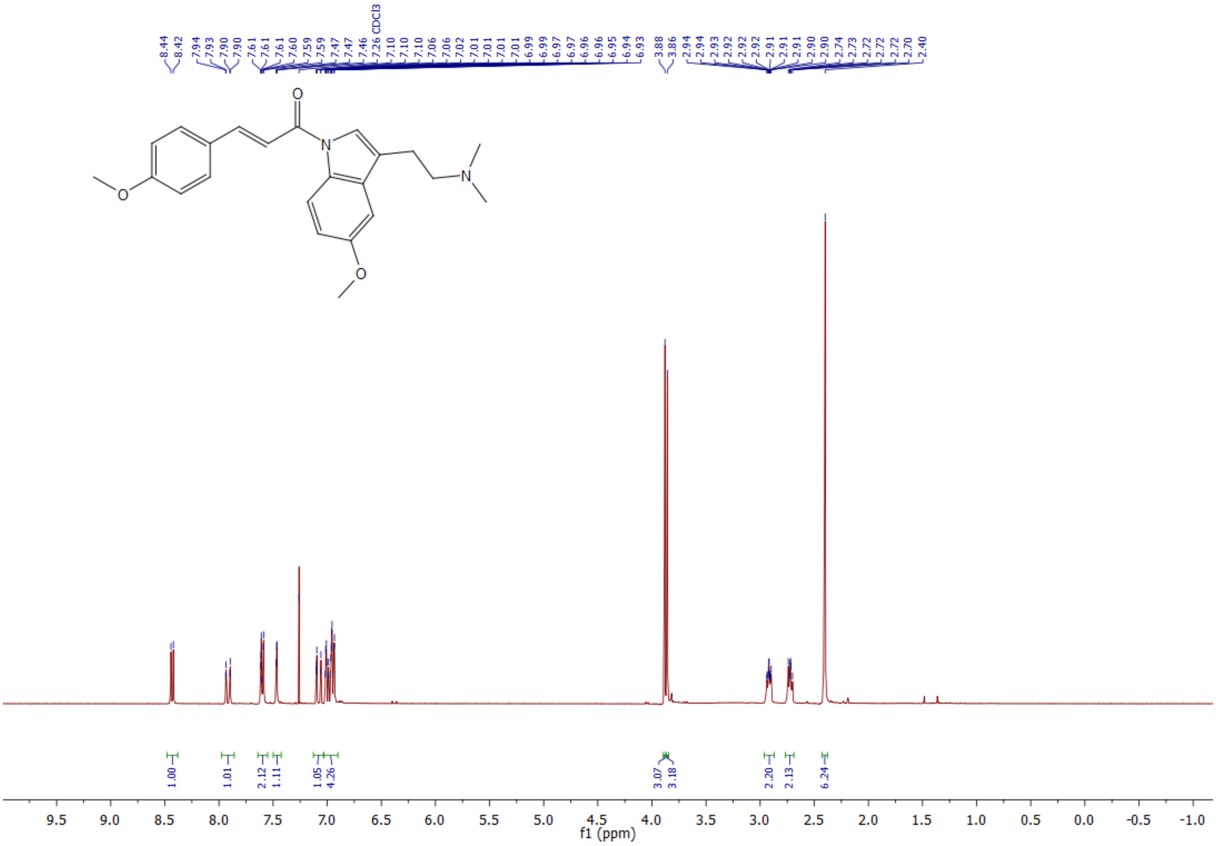
^{1}H NMR of compound **28** ($CDCl_3$)



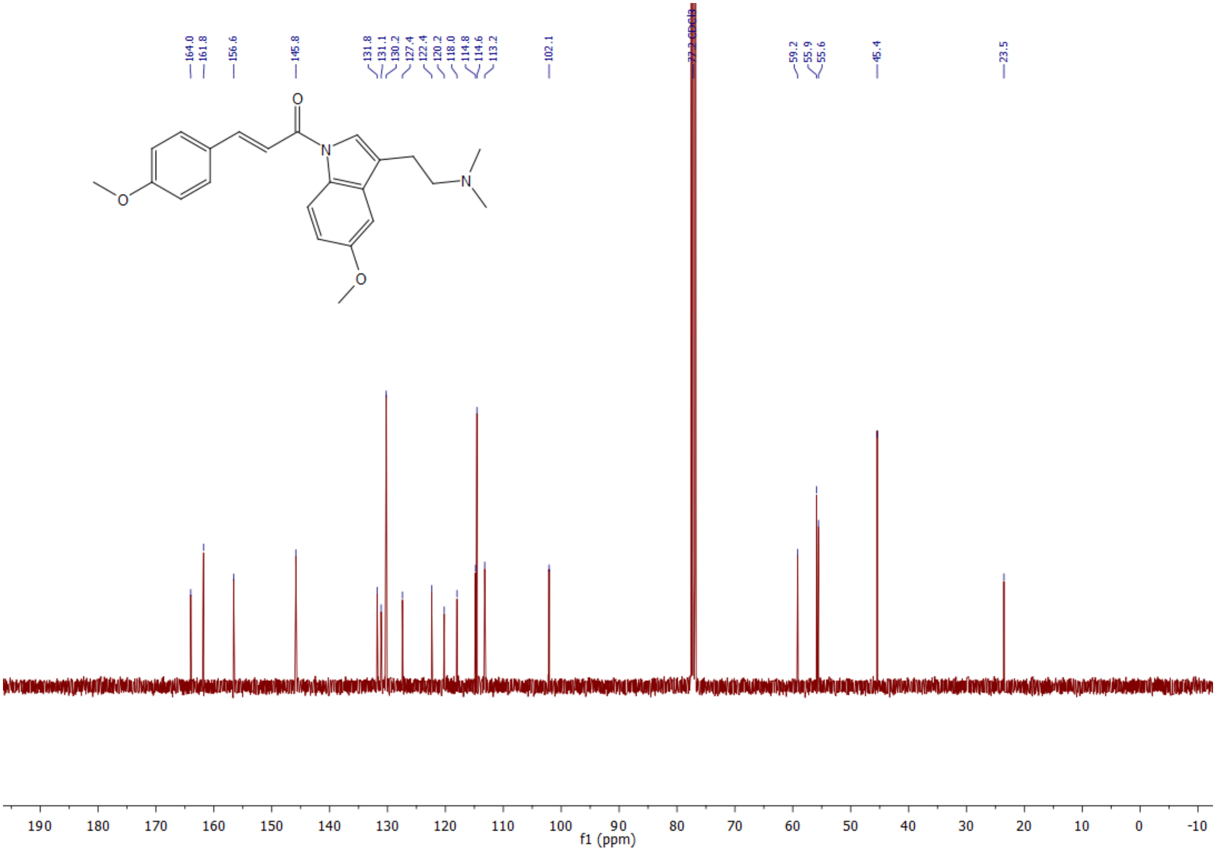
^{13}C NMR of compound **28** ($CDCl_3$)



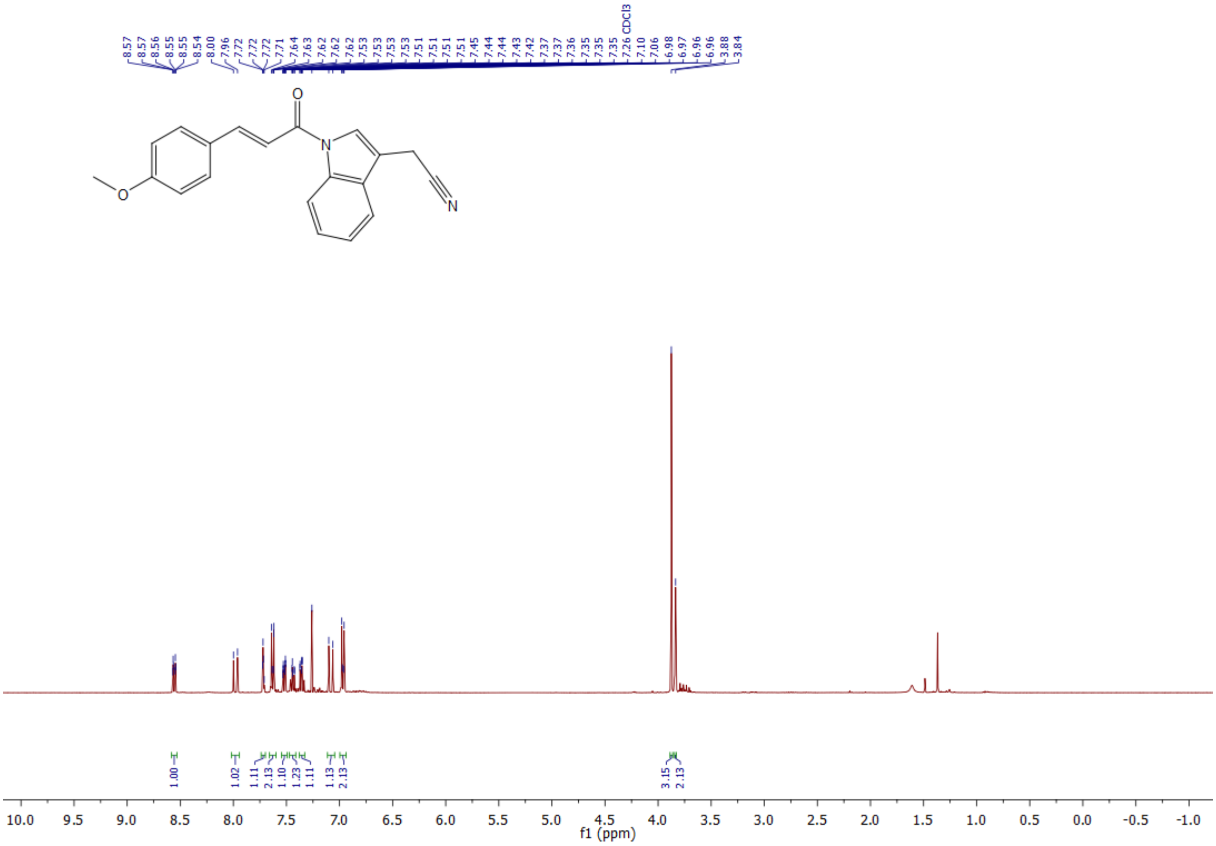
^{1}H NMR of compound **29** (CDCl$_3$)



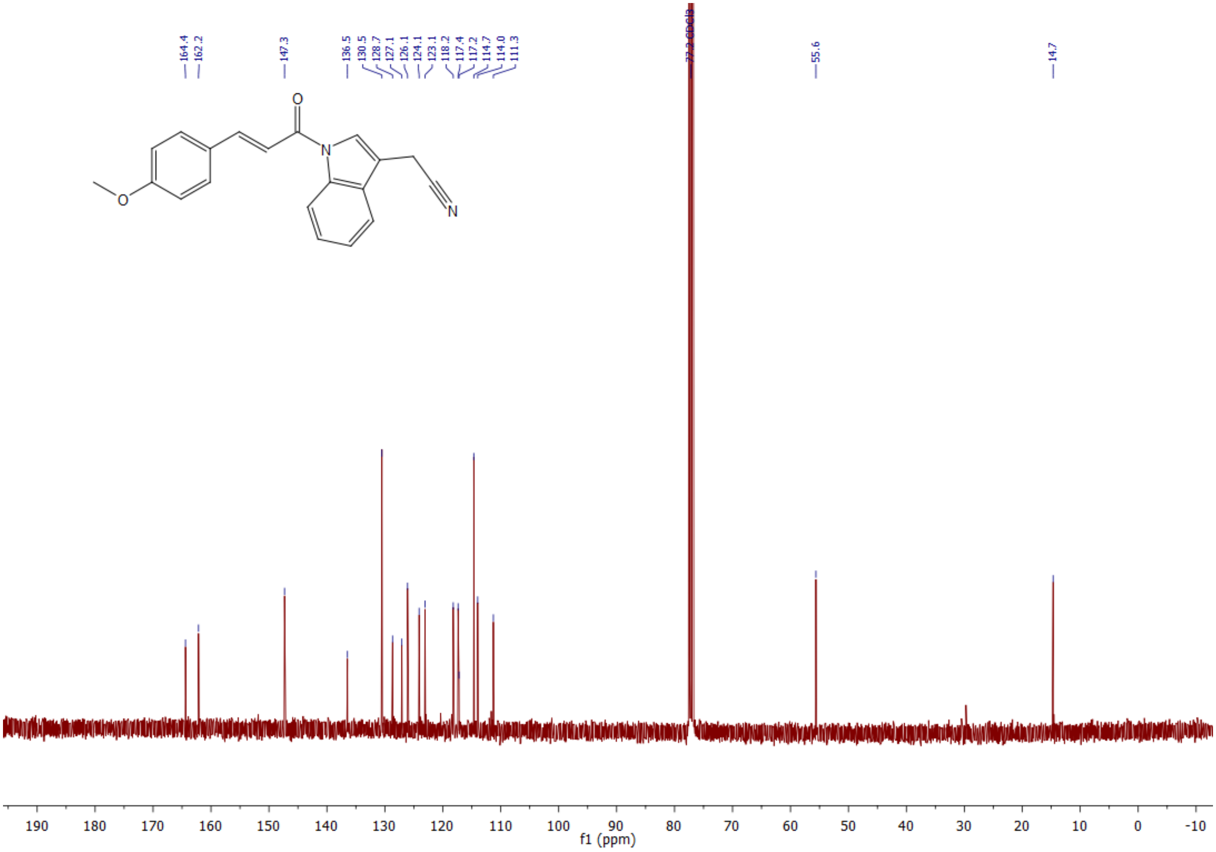
^{13}C NMR of compound **29** (CDCl$_3$)



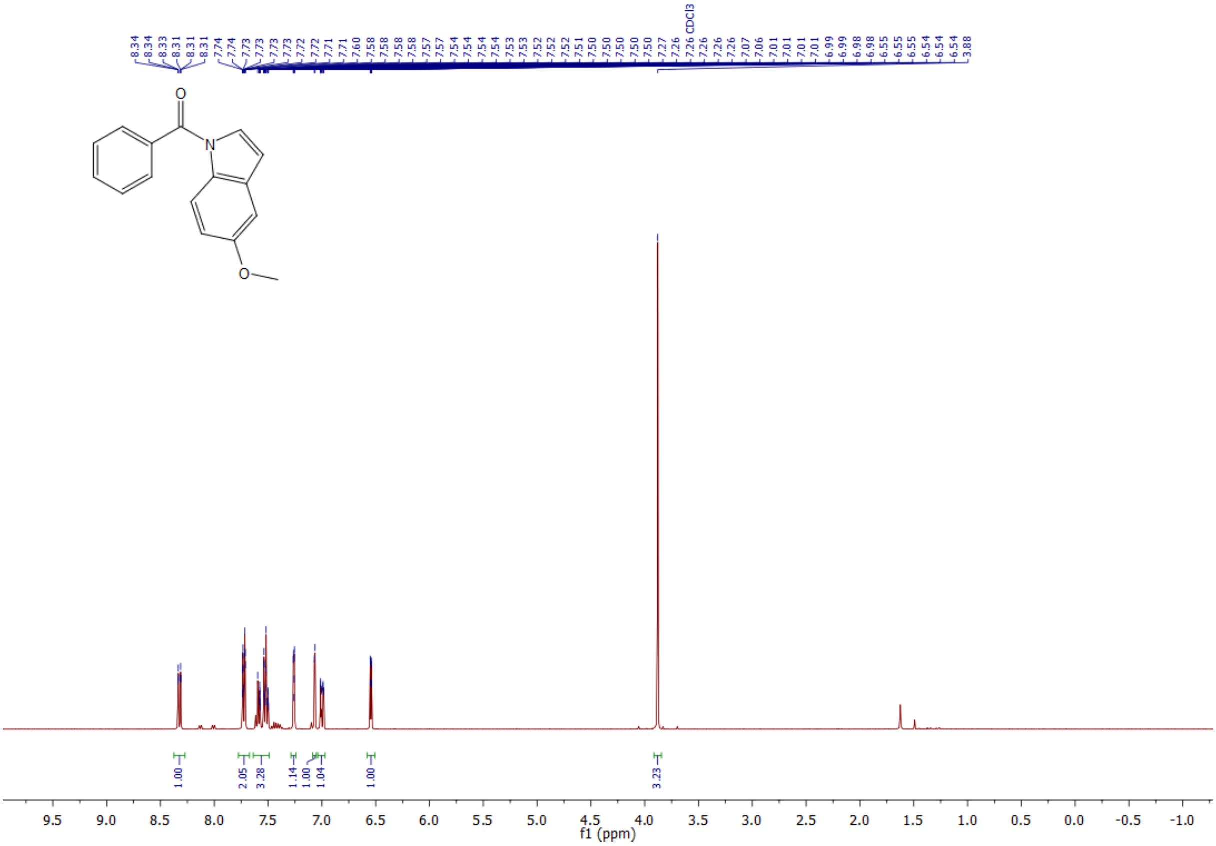
^{1}H NMR of compound **30** ($CDCl_3$)



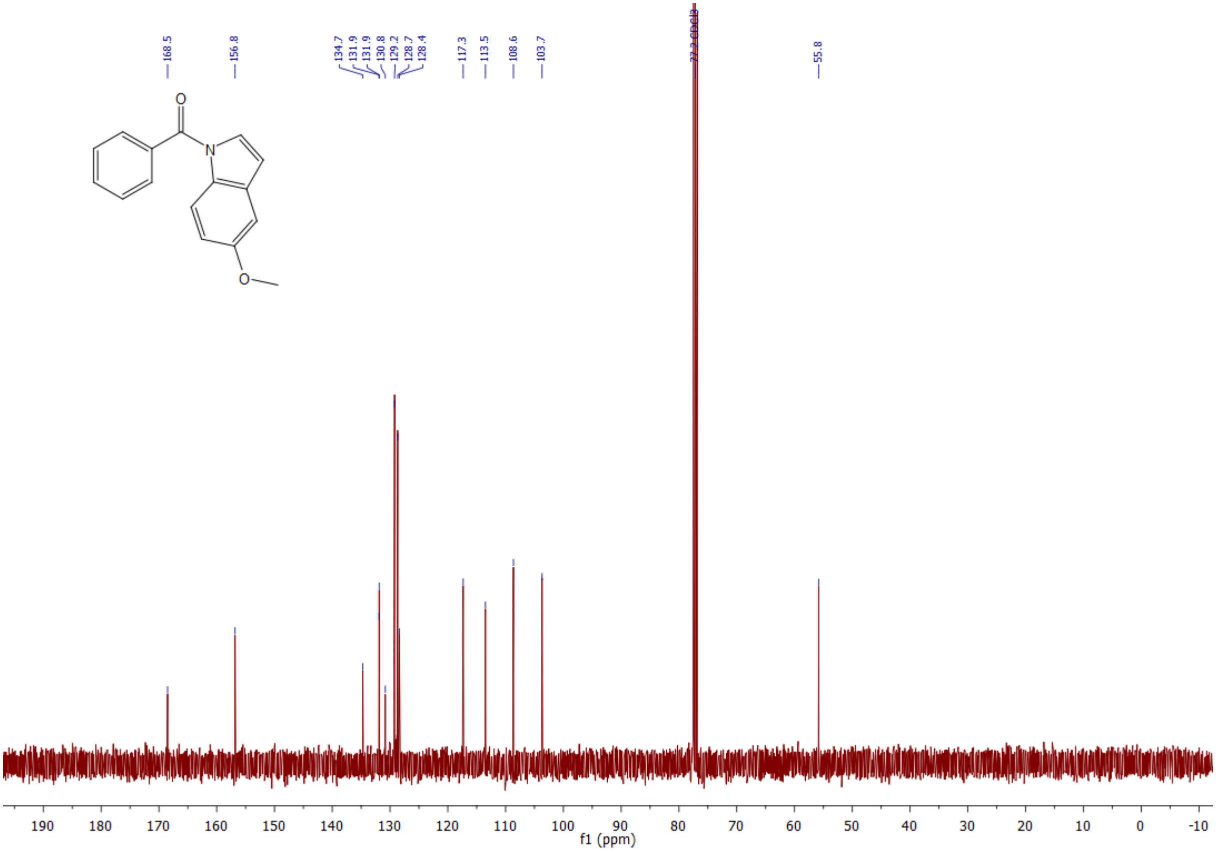
^{13}C NMR of compound **30** ($CDCl_3$)



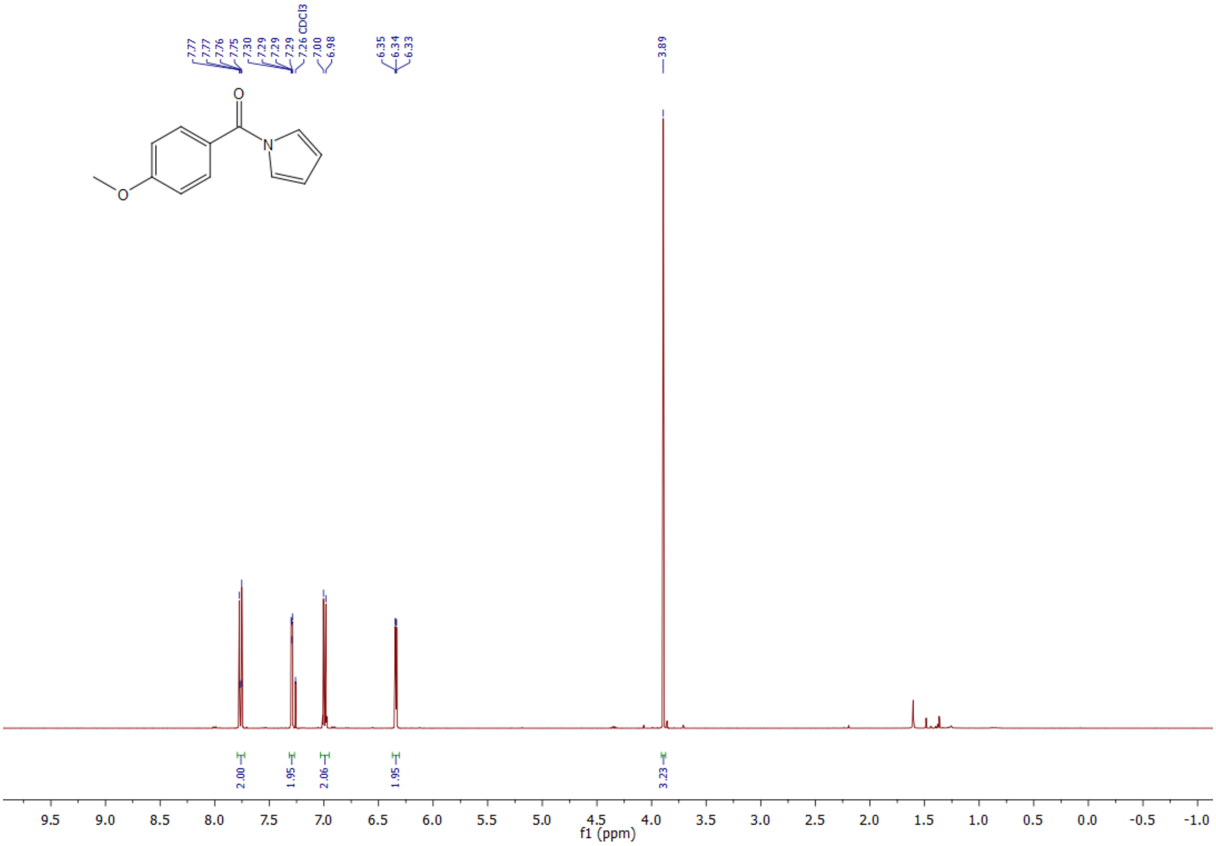
^{1}H NMR of compound **31** ($CDCl_3$)



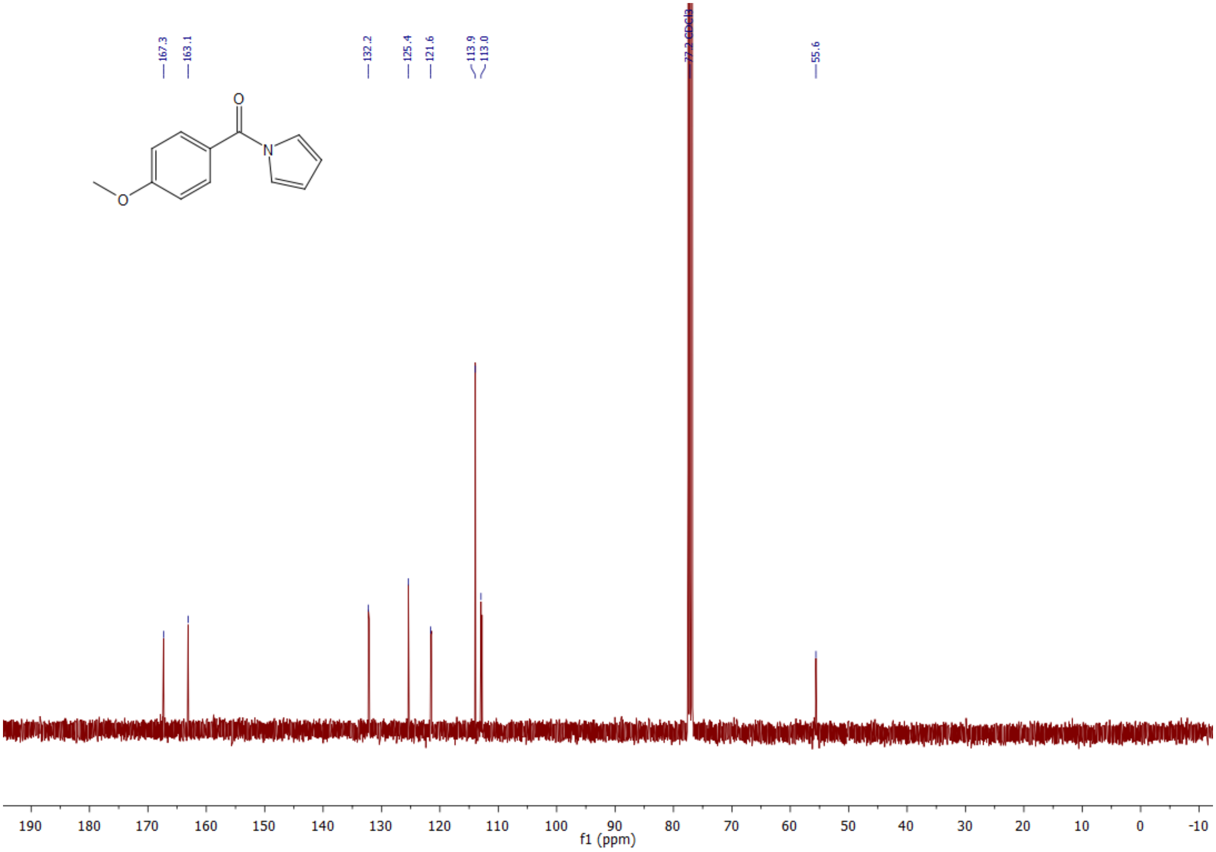
^{13}C NMR of compound **31** ($CDCl_3$)



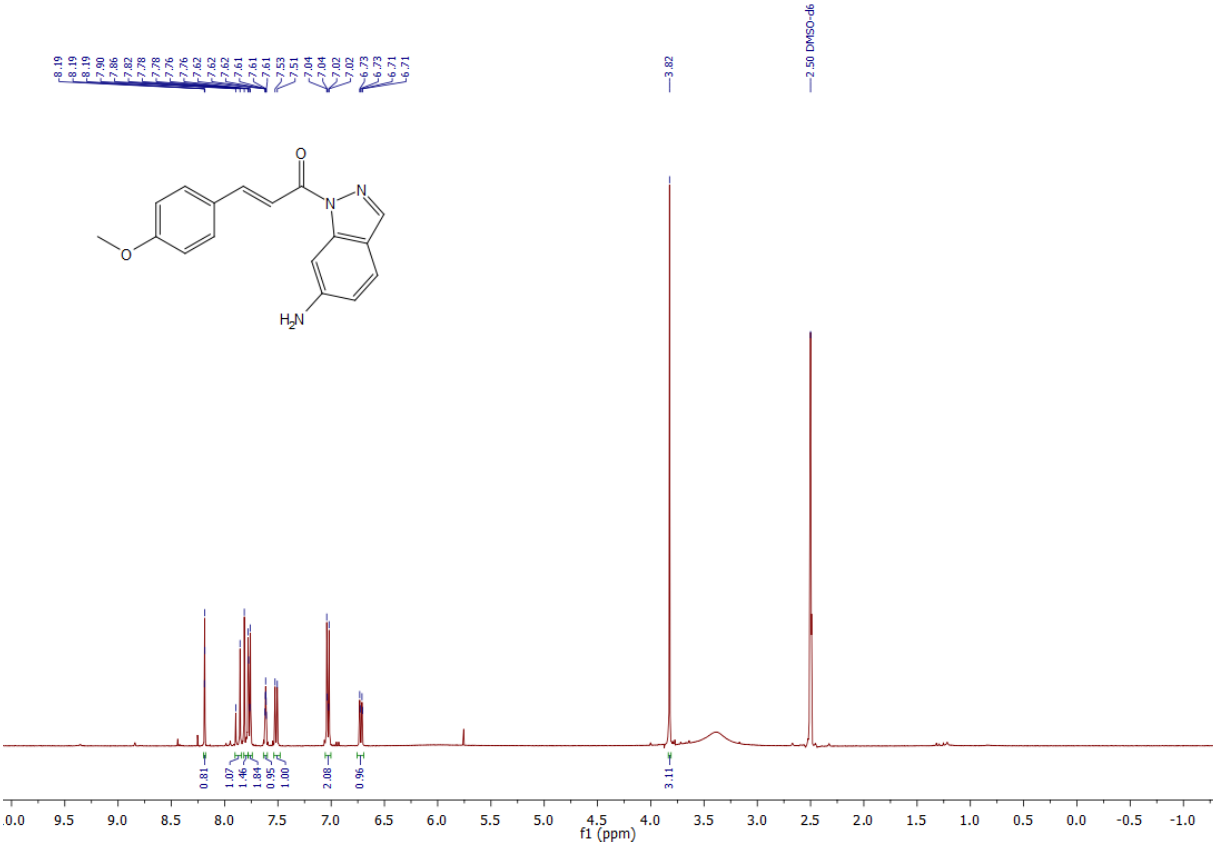
^{1}H NMR of compound **32** ($CDCl_3$)



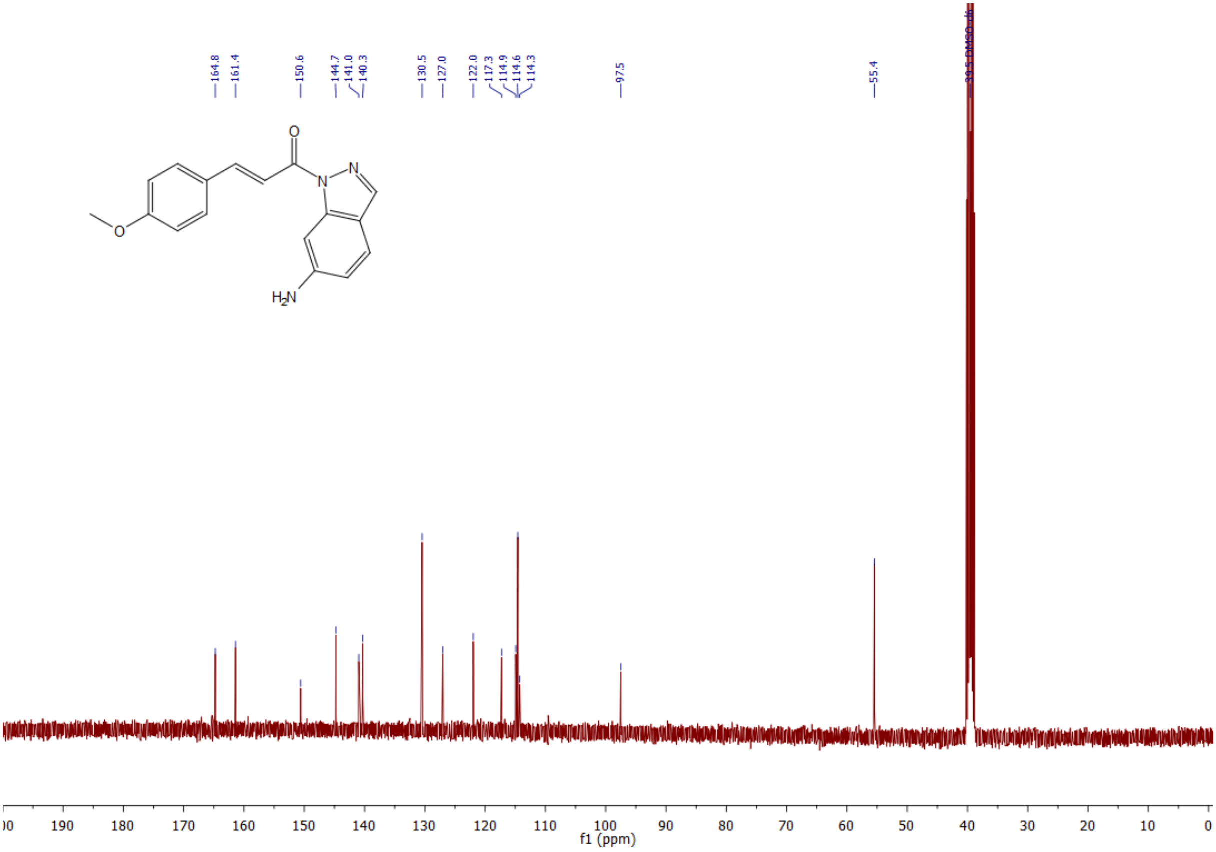
^{13}C NMR of compound **32** ($CDCl_3$)



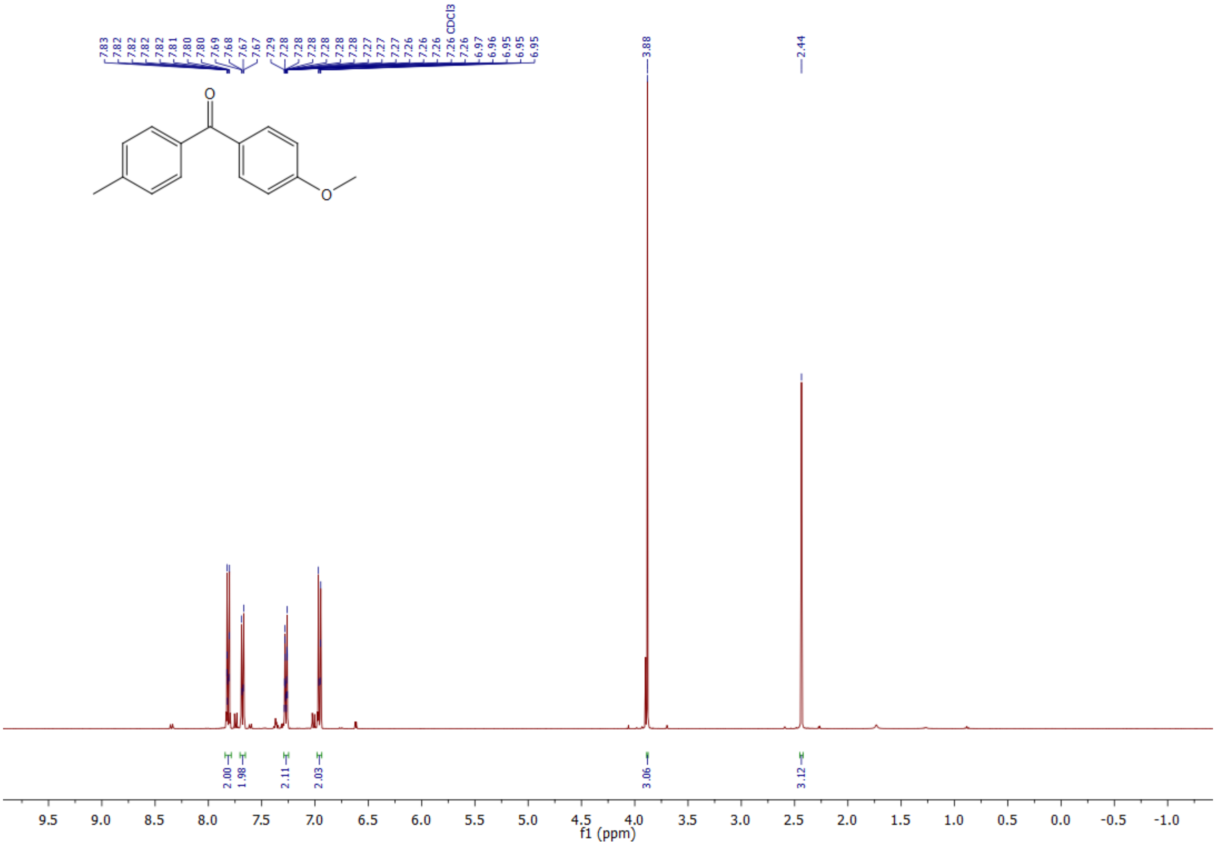
^{1}H NMR of compound **33** (DMSO-d_6)



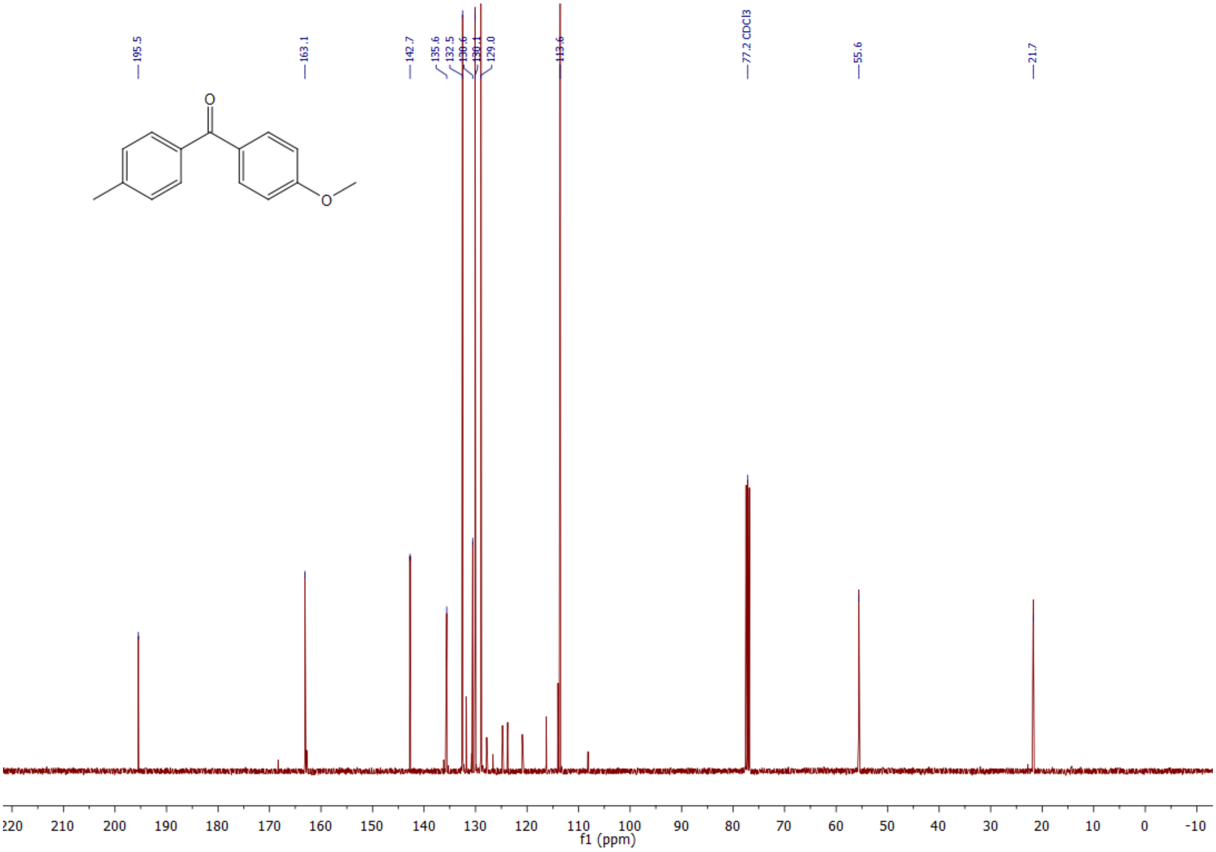
^{13}C NMR of compound **33** (DMSO-d_6)



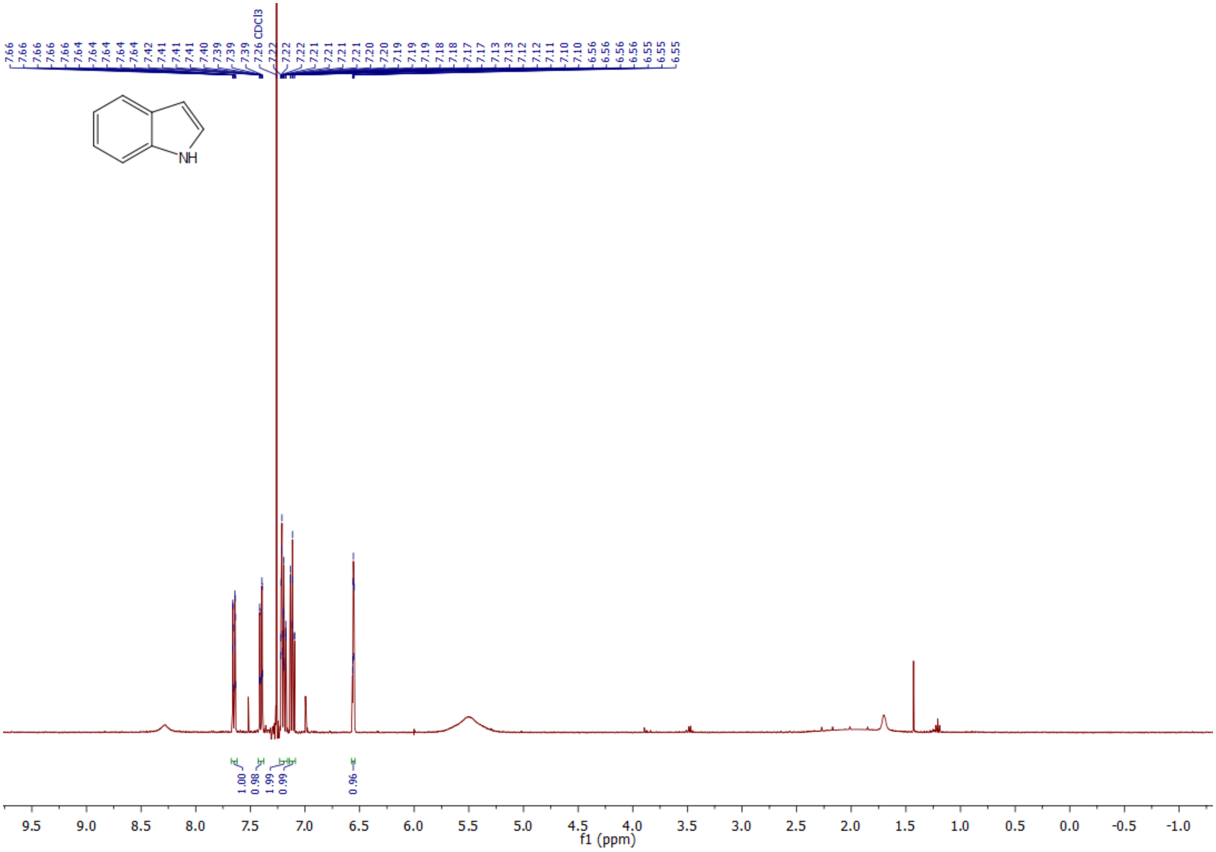
^{1}H NMR of **34** (CDCl3)



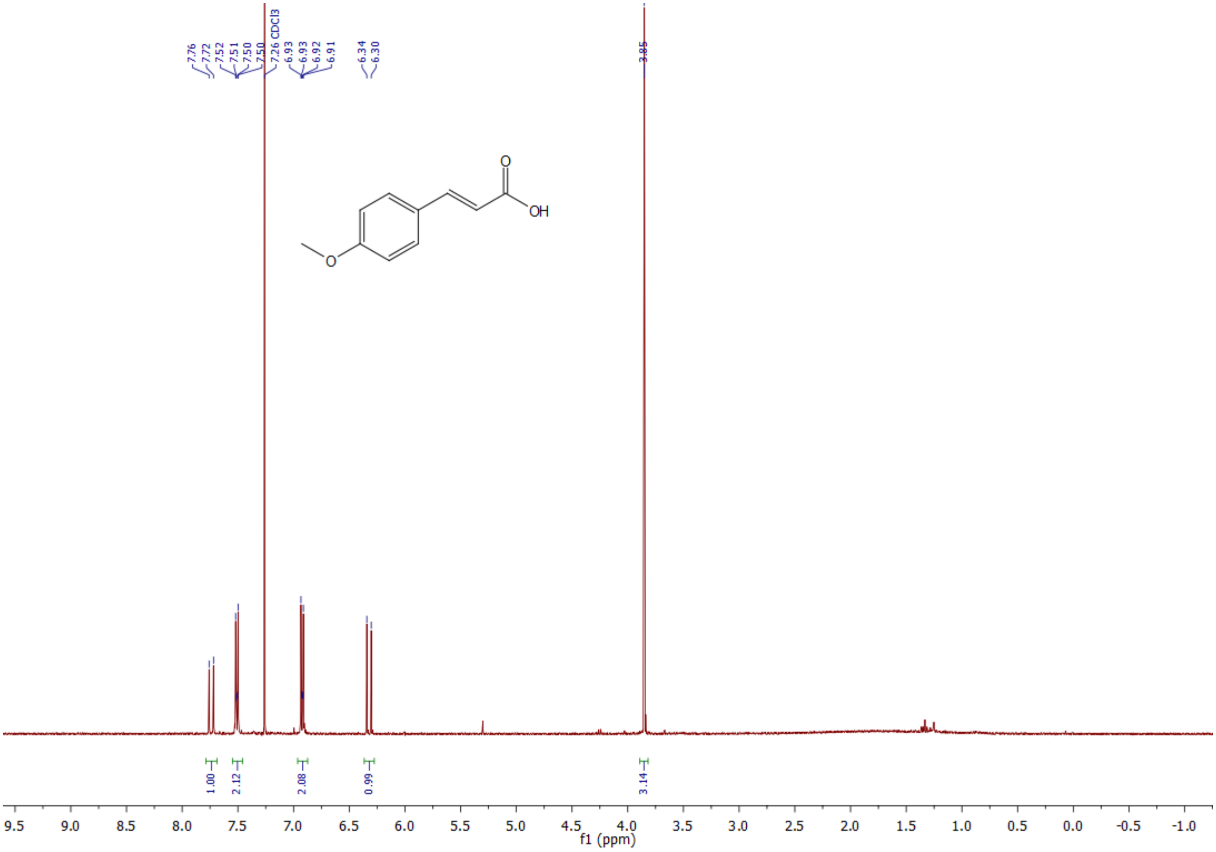
^{13}C NMR of **34** (CDCl$_3$)



^{1}H NMR of indole **4** (CDCl$_3$)



^{1}H NMR of 4-methoxycinnamic acid **35** (CDCl$_3$)



References

[1] F. Romanov-Michailidis, C. Besnard, A. Alexakis, *Org. Lett.* **2012**, *14*, 4906.

[2] S.-H. Ueng, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, *Org. Lett.* **2010**, *12*, 3002.

[3] M. S. Kharasch, B. S. Joshi, *J. Org. Chem.* **1957**, *22*, 1439.

[4] G. Meng, R. Szostak, M. Szostak, *Org. Lett.* **2017**, *19*, 3596.

[5] H. Li, Y. Xu, E. Shi, W. Wei, X. Suo, X. Wan, *Chem. Commun.* **2011**, *47*, 7880.

[6] Y. Yang, X.-H. Duan, J.-Y. Deng, B. Jin, H.-M. Jia, B.-L. Liu, *Bioorg. Med. Chem. Lett.* **2011**, *21*, 5594.

[7] X.-F. Wu, S. Oschatz, M. Sharif, P. Langer, *Synthesis* **2015**, *47*, 2641.

[8] Q. Han, S. Fu, X. Zhang, S. Lin, Q. Huang, *Tetrahedron Lett.* **2016**, *57*, 4165.

[9] A. Cipiciani, C. Ebert, P. Linda, F. Rubessa, G. Savelli, *J. Pharm. Sci.* **1983**, *72*, 1075.

[10] T. Maehara, R. Kanno, S. Yokoshima, T. Fukuyama, *Org. Lett.* **2012**, *14*, 1946.