Supporting Information

TBADT Enabled Photo-Induced Radical Cyclization Pathway: A Concise Access to Functionalized Oxindoles

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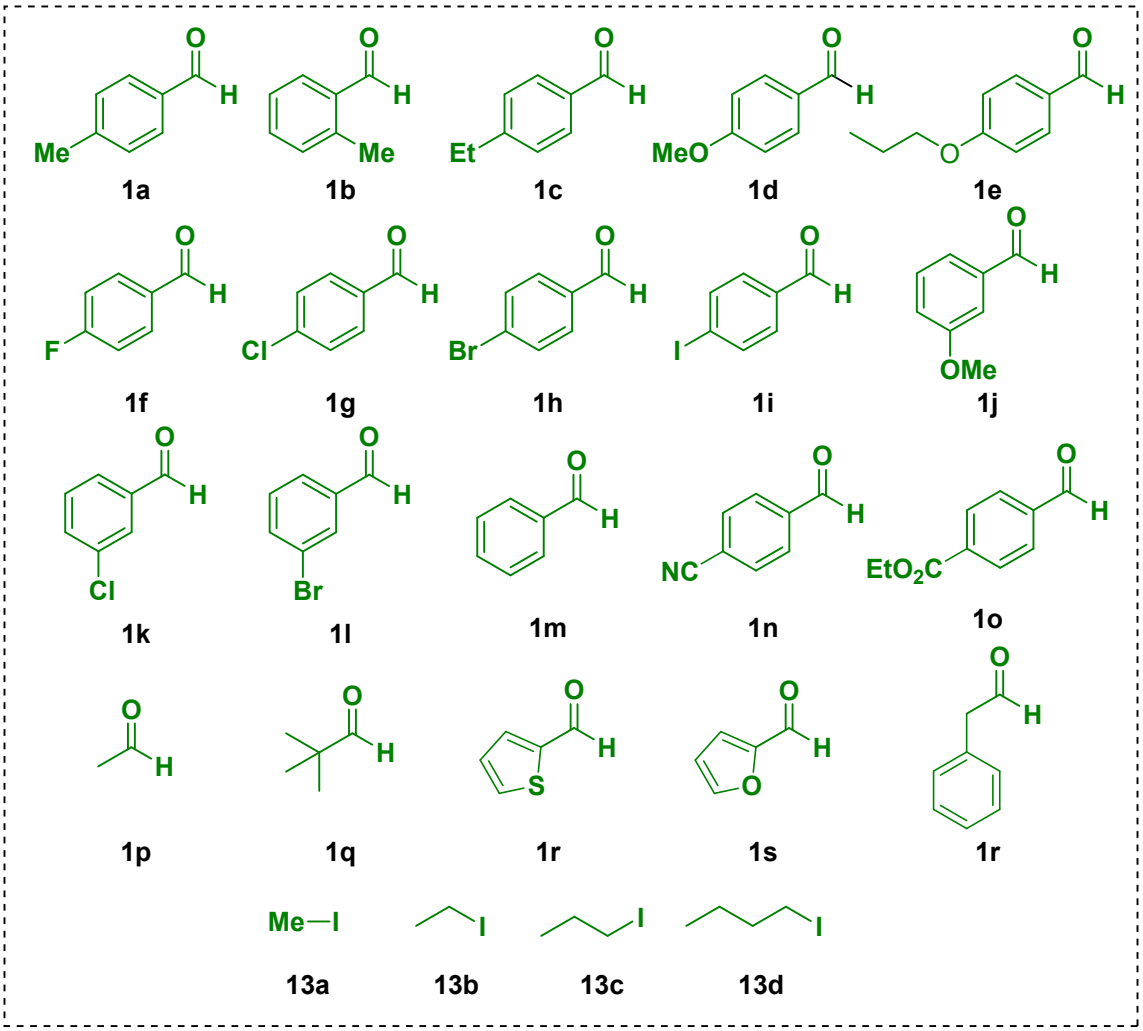
Experimental:

General methods:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Advance 400 (400 MHz) and 600 (600 MHz) spectrometers at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CDCl_3$ (δH = 7.26 ppm). $^{13}C\{1H\}$ NMR spectra were recorded on Bruker Advance 400 (101 MHz) and 600 (151 MHz) spectrometers at RT in $CDCl_3$. Chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δ = 77.16 ppm (central line of the triplet)]. In the $^{13}C\{^{1}H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, $^{13}C\{^{1}H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HRMS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. A single crystal of **3ag** was selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using direct methods and refined with the olex2. refinement package using Gauss−Newton minimization. Reactions were conducted using Kessil PR160-390 nm LED Package supply purchased from Bandi technology. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether the boiling range of 60-80 °C was used. Cyclic voltammetry (CV) analysis was performed on autolab 302N potentiostat, using a flourine-doped tin oxide (FTO) as working electrode, a platinum electrode as counter electrode and Ag/AgCl electrode as a reference electrode. Cyclic voltammogram was recorded at 100 mV/s scan rate. Alkynes, aliphatic and aromatic aldehydes, and CH_3CN were purchased from Sigma-Aldrich/Avra/BLD/TCI/local sources and used as received, the solvent MeCN was dried and used with purification. Tetrabutylammonium decatungstate (TBADT) was prepared according to the literature procedure.[1] Acme's silica gel (60-120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

Table-S1. Starting material **1/13.**



General Procedure – 1 (GP-1)

Step one: An oven-dried round bottom flask was charged with aniline **10** (0.5 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, mmol, 1.3 equiv). The reaction mixture was stirred at 0 °C. Then, The resultant reaction mixture was stirred at 25 °C for 12 h; The resulting solution was diluted with sat. aq. NH_4Cl (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were separated and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure.

Step two: The ynamide **12** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI (12.37 mmol, 1.3 equiv) was added dropwise at the same temperature. The reaction mixture was allowed to reach

rt and stirred for 6 h. The resulting solution was diluted with sat. aq. NH_4Cl (50 mL) and extracted with EtOAc (50 mL X 2). The combined organic layer was dried over anhydrous (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to give the product **2** (66 to 81%) as a yellow or white oil. The synthesis of the substituted 2-alkynyl aryl ethers **2a-2k** was carried out following a procedure established in the literature reports).[2]

General Procedure – 1 (GP-1) for the Preparation of phenyl propiolamide (2):

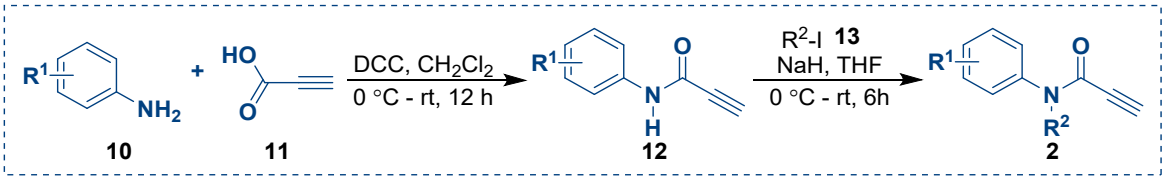
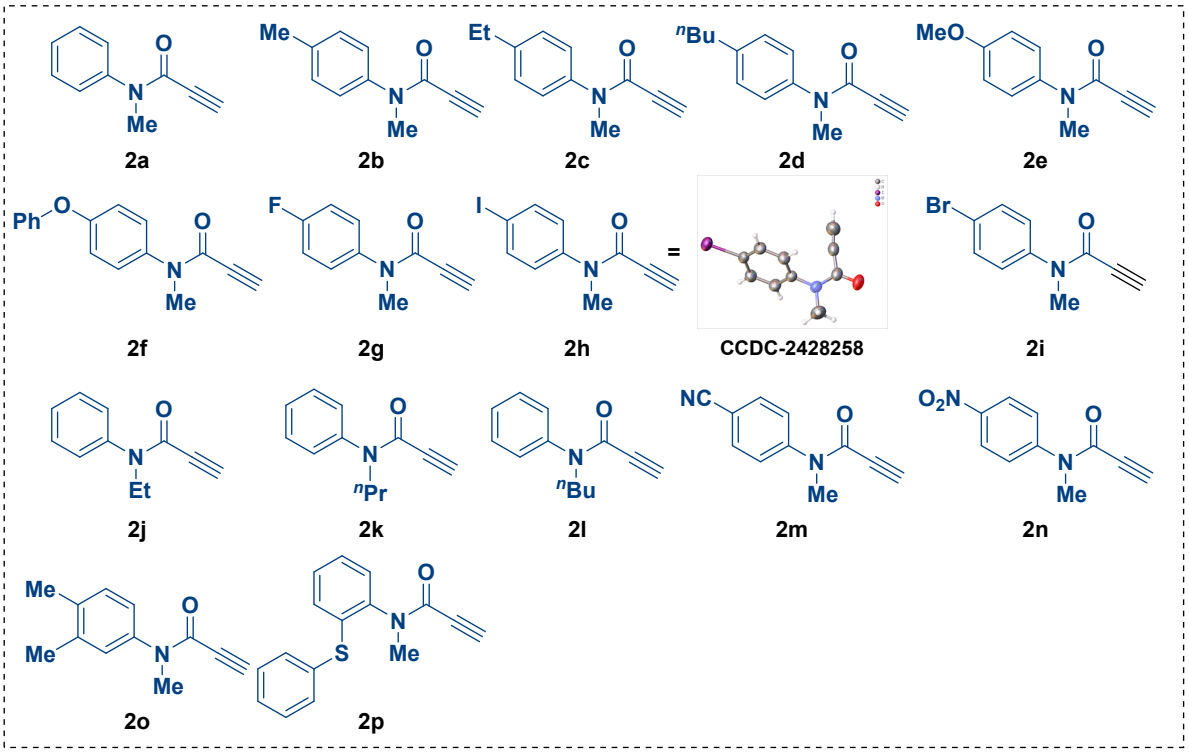
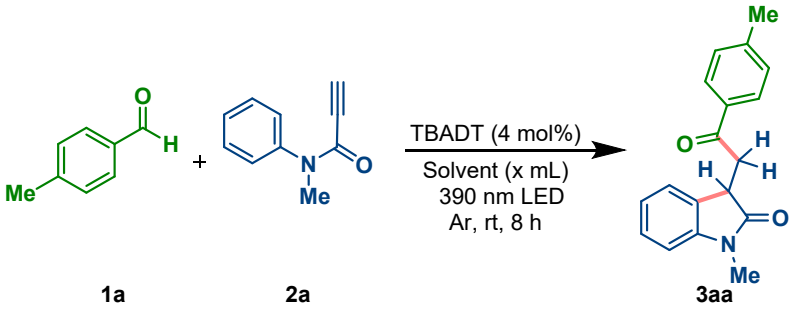


Table-S2. Starting material **2.**



Optimization of reaction condition:

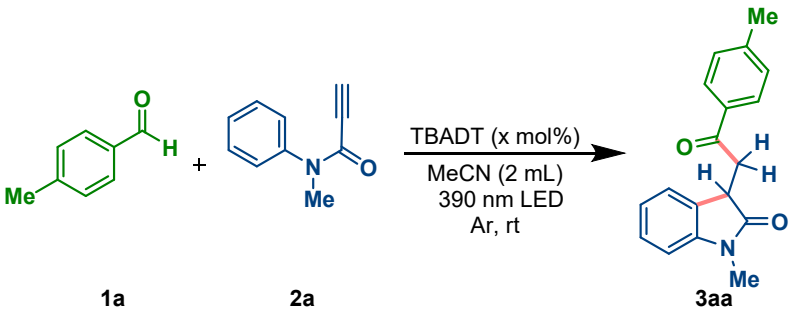
Table 1: Screening study with solvent.[a]



Entry	condition	Yield of 3aa (%)[a]
1	**MeCN [2 mL]**	**86**
2	MeCN [3 mL]	78[c]
3	Acetone [2 mL]	trace
4	DMF [2 mL]	0
5	MeCN : DCM (5 : 1) [2 mL]	52
6	MeCN : H_2O (3 : 2) [2 mL]	trace
7	EtOAC [2 mL]	0
8	MeCN : DCM (5 : 1) [2 mL]	46

[a]Yields of the isolated product **3aa** after column chromatography. [c]Time 12 h.

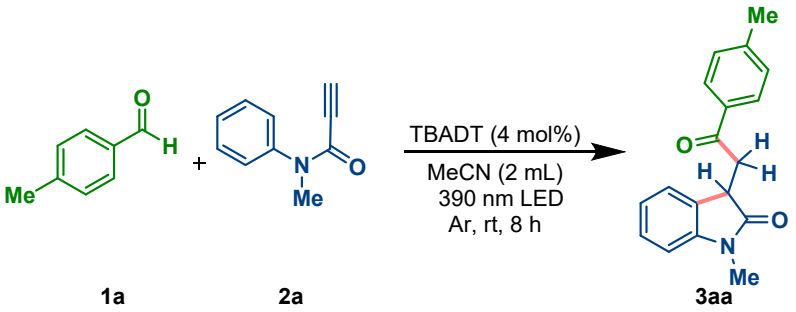
Table 2: Screening study with photo-catalyst (PC) loading.



Entry	PC loading	Yield[a] of 3aa (%)	Time in hours (h)
1	**4 mol%**	**86**	**8 h**
2	3.5 mol%	80	10 h
3	3 mol%	77	12 h
4	2 mol%	73	11 h
5	1 mol%	68	12 h
6	5 mol%	84	8 h

[a]Yield of the isolated product **3aa** after column chromatography.

Table 3: Variations from the optimized reaction conditions.[a,b]

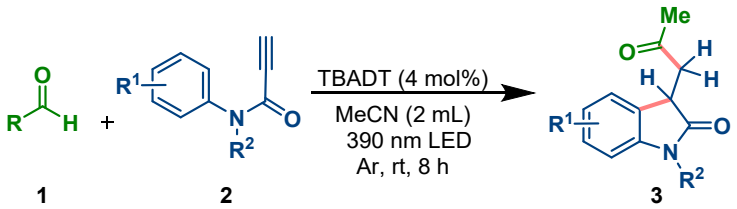


1a 2a 3aa

Entry	Variation from the optimal conditions	Yield of 3aa (%)[b]
1	**None**	**86**
2	Without TBADT	0
3	Without light	0
4	Sunlight	trace
5	427 nm	0
6	1 equiv of **2a**	64
7	1.5 equiv of **2a**	76
8	1.75 equiv of **2a**	80
9	2.5 equiv of **2a**	86
10	1 equiv of TBAB	trace
11	1 equiv of CuI	trace

[a]Unless otherwise specified, reactions were carried out using 4-methylbenzaldehyde **1a** (0.41 mmol), phenyl propiolamide **2a** (0.82 mmol), TBADT (4 mol%), MeCN (2 mL), irradiated by a KESSIL - 390 nm, at room temperature for 8 h, under Ar. [b]Yield of the isolated product **3aa** after column chromatography.

General Procedure - 2 (GP-2) for the Preparation of oxindoles (3):



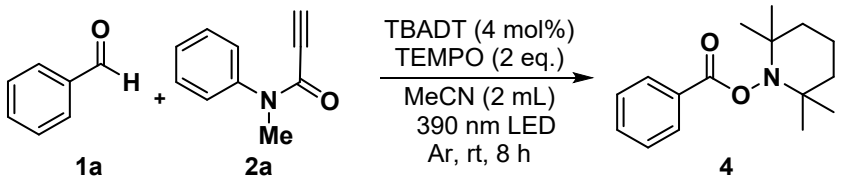
1 2 3

To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added aldehydes **1** (0.41 mmol), phenyl propiolamides **2** (0.82 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and backfilled with Argon (purged three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (i.e., the reaction vial is approximately 5 cm away from the light

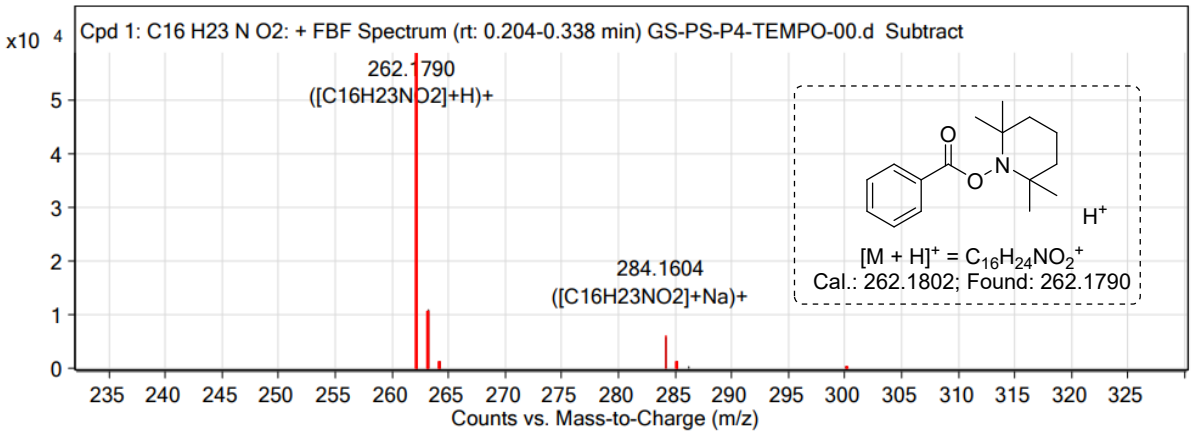
source) with 390 nm LED under vigorous stirring at room temperature for 8-12 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence. The solvent was then removed under a rotary evaporator, and purification of the crude product was done by using column chromatography (petroleum ether to 17% ethyl acetate/petroleum ether), furnished oxindoles **3** (56 to 81%), as yellow liquid or yellow (or white) solids.

Scheme S1: Control experiments.

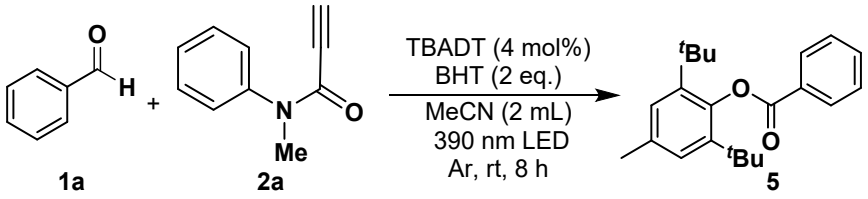
a) TEMPO



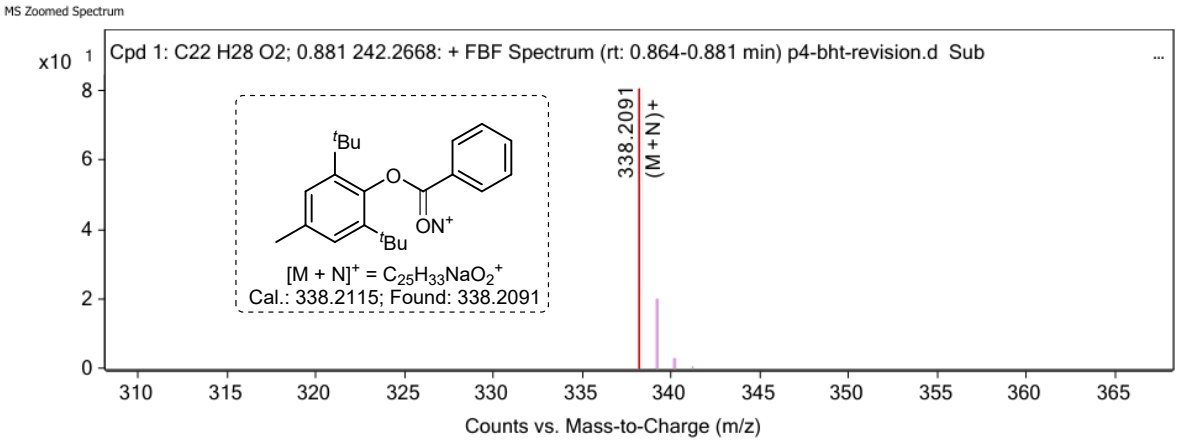
To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added with benzaldehyde **1a** (50 mg, 0.47 mmol) phenylpropiolamide **2a** (149 mg, 0.94 mmol), TBADT (4 mol%), CH_3CN (2 mL), and TEMPO (147 mg, 0.94 mmol) were added and backfilled with Argon (purged three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (i.e., reaction vial is approximately 5 cm away from the light source) with 390 nm LED under vigorous stirring at room temperature for 8 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence. No desired product **3aa** was observed, indicating that the reaction was completely inhibited. Meanwhile, a trapping product **4** was observed through the HRMS analysis from the reaction solution.



b) BHT



To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added benzaldehyde **1a** (50 mg, 0.47 mmol) phenylpropiolamide **2a** (149 mg, 0.94 mmol), TBADT (4 mol%), CH_3CN (2 mL), and BHT (207 mg, 0.94 mmol) were added and backfilled with Argon (purged three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (i.e., reaction vial is approximately 5 cm away from the light source) with 390 nm LED under vigorous stirring at room temperature for 4 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence. No desired product **3aa** was observed or detected by HRMS, indicating that the reaction was completely inhibited. Meanwhile, a trapping product **5** was observed through the HRMS analysis from the reaction solution.



Cyclic Voltammograms:

The cyclic voltammetry (CV) studies were carried out to further investigate the reaction mechanism, and Figure S1 shows the cyclic voltammetry (CV) curves with 0.01 M $^{n}Bu_4NPF_6$ solution in CH_3CN as a background. The voltammogram was obtained at a scan rate of 100 mV/s with Pt electrode as a counter electrode, Ag/AgCl as a reference electrode, and (FTO) Flourine-doped tin oxide electrode as a working electrode. Within the scanning window (-1.0 to 2.5 V), the CV of benzaldehyde **1a** displayed an oxidation peak at 1.83 V vs Ag/AgCl (curve 1). When testing *N*-methyl-*N*-phenylpropiolamide **2a**, an oxidation peak was seen at 1.84 V vs Ag/AgCl in (curve 2), signifying that the reduction of propiolamide required a strong oxidation potential. The mixture of benzaldehyde **1a** and *N*-methyl-*N*-phenylpropiolamide **2a** showed an oxidation peak at 1.86 V vs Ag/AgCl in the reaction (curve 3). Based on the above results, we hypothesized that

benzaldehyde might produce acyl radicals by anodic oxidation in the presence of a TBADT catalyst and further activates alkynes in the reaction process.

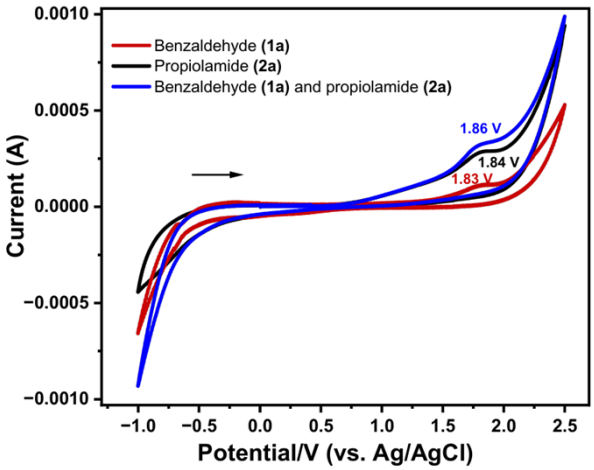
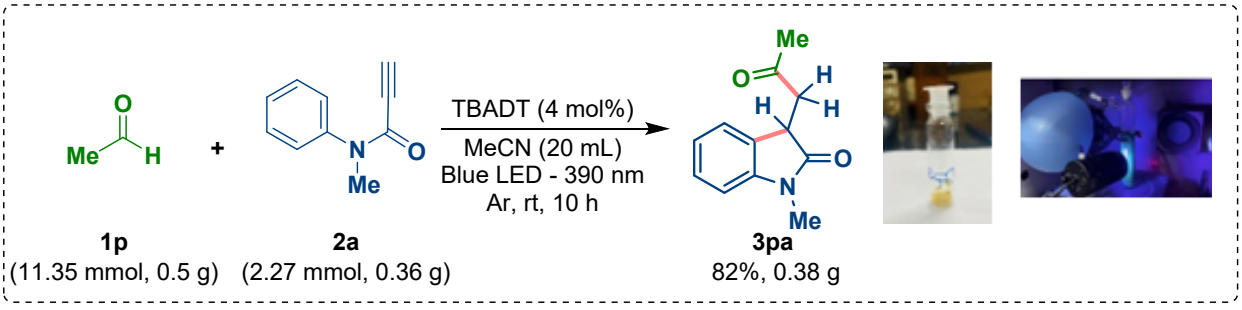


Figure S1: Cyclic voltammograms of reactants and their mixtures in 0.01 M $^{n}Bu_4NPF_6$ solution in CH_3CN at room temperature:1) benzaldehyde **1a** (0.01 M); 2) *N*-methyl-*N*-phenylpropiolamide **2a** (0.01 M); 3) benzaldehyde **1a** (0.01 M) + *N*-methyl-*N*-phenylpropiolamide **2a** (0.01 M); The voltammogram was obtained at a scan rate of 100 mV/s with Pt electrode as a counter electrode, Ag/AgCl as a reference electrode, and Flourine-doped tin oxide (FTO) electrode as a working electrode.

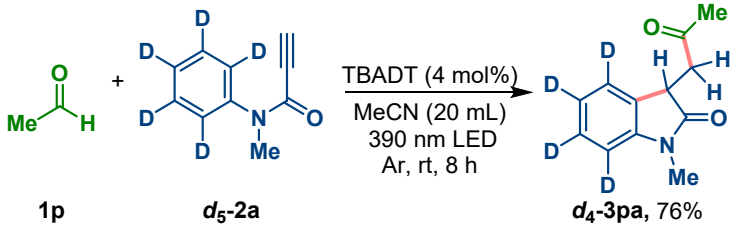
Scheme S2: Scale-up reaction of **1p** with phenylpropiolamide **2a**.



To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added acetaldehyde **1p** (0.5 g, 11.35 mmol) phenylpropiolamide **2a** (0.36 g, 2.27 mmol), TBADT (4 mol%), and CH_3CN (20 mL) and backfilled with Argon (purged three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (i.e., the reaction vial is approximately 5 cm away from the light source) with 30 W blue LEDs under vigorous stirring at room temperature for 10 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence. The solvent was then removed under a rotary evaporator and purification of the crude product using was column chromatography (petroleum

ether to 15 % ethyl acetate/petroleum ether), furnished oxindole **3pa** (0.38 g, 82 %), as a yellow solid.

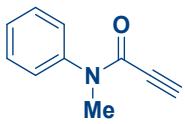
Scheme S3: Reaction of **1p** with *N*-methyl-*N*-(phenyl-d_5)propiolamide **6**.



1p **d_5-2a** **d_4-3pa,** 76%

To an oven-dried Schlenk tube equipped with a magnetic stir bar, were added acetaldehyde **1p** (37 mg, 0.41 mmol) *N*-methyl-*N*-(phenyl-d_5)propiolamide ***d_5*-2a** (32 mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and backfilled with Argon (purged three times). The Schlenk tube was sealed with Teflon, and the reaction mixture was irradiated (i.e., the reaction vial is approximately 5 cm away from the light source) with 30 W blue LEDs under vigorous stirring at room temperature for 10 h under Argon conditions. The progress of the reaction was monitored by TLC until the completion of the reaction with visualization under UV fluorescence. The solvent was then removed under a rotary evaporator and purification of the crude product using was column chromatography (petroleum ether to 15% ethyl acetate/petroleum ether), furnished oxindole ***d_4*-3pa** (13 mg, 76%), as a yellow oil.

Characterization of compounds:



N-Methyl-N-phenylpropiolamide (2a):

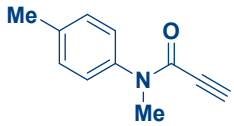
GP 1 was carried out with aniline **10a** (0.5 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.98 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12a** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2a** (81% overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3218, 2931, 2103, 1632, 1492, 1373, 1124, 766, 696 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.44 - 7.29 (m, 3H), 7.29 (d, J = 7.7 Hz, 2H), 3.33 (s, 3H), 2.83 (s, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.1, 142.6, 129.4 (2 × Ar–CH), 128.2, 127.3 (2 × Ar–CH), 79.7, 76.3, 36.6 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{10}H_{10}NO^+$ for 160.0757; found 160.0753.



N-Methyl-N-(p-tolyl)propiolamide (2b):

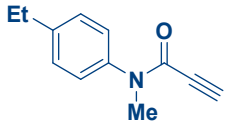
GP 1 was carried out with *p*-toluidine **10b** (0.573 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.98 mmol, 1.3 equiv). 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12b** were charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2b** (75 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3202, 2929, 2101, 1632, 1511, 1378, 1125, 756, 733 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.21 – 7.20 (m, 2H), 7.17 – 7.15 (m, 2H), 3.30 (s, 3H), 2.81 (s, 1H), 2.39 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.2, 140.2, 138.3, 130.0 (2 × Ar–CH), 127.1 (2 × Ar–CH), 79.6, 76.5, 36.7, 21.3 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{11}H_{12}NO^+$ for 174.0913; found 174.0905.



N-(4-Ethylphenyl)-N-methylpropiolamide (2c):

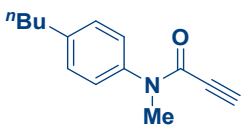
GP 1 was carried out with 4-ethylaniline **10c** (0.649 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.9 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12c** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2c** (75 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2965, 2930, 2104, 1634, 1368, 1290, 1120, 913, 836 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.22 – 7.14 (m, 4H), 3.27 – 326 (m, 3H), 2.79 (s, 1H), 2.68 – 2.62 (m, 2H), 1.25 – 1.21 (m, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.1, 144.4, 140.1, 128.7 (2 × Ar–CH), 127.0 (2 × Ar–CH), 79.6, 76.4, 36.6, 28.4, 15.3 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{12}H_{14}NO^+$ for 188.1070; found 188.1076.



N-(4-Butylphenyl)-N-methylpropiolamide (2d):

GP 1 was carried out with 4-butylaniline **10d** (0.724 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.9 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12d** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C

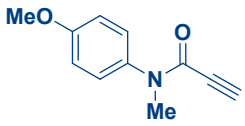
and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2d** (71 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2929, 2104, 1733, 1639, 1370, 1237, 1045, 682, 599 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.17 – 7.12 (m, 4H), 3.25 – 3.22 (m, 3H), 2.78 (d, J = 0.9 Hz, 1H), 2.59 (t, J = 7.7 Hz, 2H), 1.59 – 1.53 (m, 2H), 1.33 – 1.32 (m, 2H), 0.91 – 0.87 (m, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.8, 142.8, 139.9, 129.0 (2 × Ar–CH), 126.7 (2 × Ar–CH), 79.4, 76.1, 36.3, 35.0, 33.2, 22.1, 13.7 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ calculated $C_{14}H_{17}NNaO^+$ for 238.1202; found 238.1210.



N-(4-Methoxyphenyl)-N-methylpropiolamide (2e):

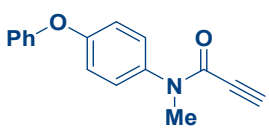
GP 1 was carried out with 4-methoxyaniline **10e** (0.659 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.98 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12e** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2e** (78 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3218, 2931, 2104, 1632, 1508, 1373, 1246, 1027 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.14 – 7.10 (m, 2H), 6.86 – 6.82 (m, 2H), 3.75 (s, 3H), 3.20 (s, 3H), 2.81 (s, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.1, 153.1, 135.3, 128.3 (2 × Ar–CH), 114.3 (2 × Ar–CH), 79.6, 76.3, 55.3, 36.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{11}H_{12}NO_2^+$ for 190.0863; found 190.0859.



N-Methyl-N-(4-phenoxyphenyl)propiolamide (2f):

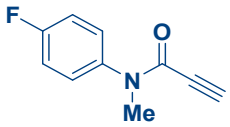
GP 1 was carried out with 4-phenoxyaniline **10f** (0.992 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.9 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12f** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2f** (67 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 2857, 1637, 1492, 1232, 1120, 750, 691 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 2H), 7.16 – 7.12 (m, 2H), 7.09 – 7.03 (m, 1H), 6.96 – 6.90 (m, 4H), 3.21 (s, 3H), 2.78 (s, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.2, 156.3, 153.1, 137.4, 129.9 (2 × Ar–CH), 128.7 (2 × Ar–CH), 124.0, 119.4 (2 × Ar–CH), 118.8 (2 × Ar–CH), 79.8, 76.3, 36.6 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{16}H_{14}NO_2^+$ for 252.1019 found 252.1027.



N-(4-Fluorophenyl)-N-methylpropiolamide (2g):

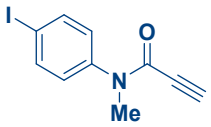
GP 1 was carried out with 4-fluoroaniline **10g** (0.595 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.9 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12g** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2g** (66 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3193, 2099, 1628, 1502, 1381, 1225, 1122, 834, 754 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28 - 7.26 (m, 2H), 7.12 - 7.09 (m, 2H), 3.30 (s, 3H), 2.86 (s, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 162.1 (d, $J_{C\text{-}F}$ = 248.4 Hz), 153.1, 138.7 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.2 (d, $J_{C\text{-}F}$ = 8.8 Hz), 116.35 (d, $J_{C\text{-}F}$ = 22.8 Hz) 80.0, 76.1, 36.6 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{10}H_9FNO^+$for 178.0663; found 178.0663.



N-(4-Iodophenyl)-N-methylpropiolamide (2h):

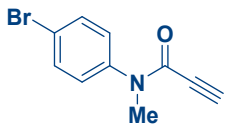
GP 1 was carried out with 4-iodoaniline **10h** (1.168 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.9 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12h** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2h** (72 % overall yield) as a light-yellow white oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2927, 1635, 1635, 1478, 1452, 1271, 1118, 814 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.73 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 3.29 (s, 3H), 2.86 (s, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.66, 142.30, 138.50 (2 × Ar–CH), 129.12 (2 × Ar–CH), 93.39, 80.13, 76.05, 36.41 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{10}H_9INO^+$ for 285.9723 found 285.9726.



N-(4-Bromophenyl)-N-methylpropiolamide (2i):

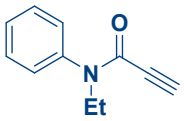
GP 1 was carried out with 4-bromoaniline **10i** (0.916 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.98 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12i** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was allowed to reach rt and stirred for 6 h. The residue was purified by column chromatography to give the product **2i** (68 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3228, 2104, 1632, 1482, 1363, 1173, 830, 736 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.53 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 3.28 (s, 3H), 2.85 (s, 1H). ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.8, 141.7, 132.6 (2 × Ar–CH), 128.9 (2 × Ar–CH), 122.0, 80.1, 76.1, 36.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{10}H_9Br^{79}NO^+$ for 237.9863; found 237.9869, $C_{10}H_9Br^{81}NO^+$ for 239.9842; found 239.9849.



N-Ethyl-N-phenylpropiolamide(2j):

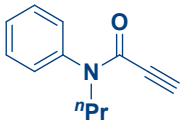
GP 1 was carried out with aniline **10a** (0.5 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.98 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12j** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, EtI **13b** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The residue was purified by column chromatography to give the product **2j** (79 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3219, 2979, 2103, 1636, 1449, 1281, 703, 702 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.44 – 7.38 (m, 3H), 7.25 (d, J = 7.6 Hz, 2H), 3.81 (q, J = 7.1 Hz, 2H), 2.78 (s, 1H), 1.14 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.7, 141.0, 129.3 (2 × Ar–CH), 128.5 (2 × Ar–CH), 128.4, 79.4, 76.5, 43.7, 12.7 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{11}H_{12}NO^+$ for 174.0913; found 174.0922.



N-Phenyl-N-propylpropiolamide (2k):

GP 1 was carried out with aniline **10a** (0.5 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.98 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12k** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and

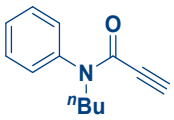
continued stirring for 30 min. Then, PrI **13c** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The residue was purified by column chromatography to give the product **2k** (75 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2975, 2103, 1734, 1639, 1379, 1234, 1043, 696, 617 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.42 – 7.34 (m, 3H), 7.24 – 7.18 (m, 2H), 3.71- 3.68 (m, 2H), 2.78 (s, 1H), 1.55 – 1.48 (m, 2H), 0.90 – 0.83 (m, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.8, 141.2, 129.2 (2 × Ar–CH), 128.3 (2 × Ar–CH), 128.2, 126.9, 79.6, 76.4, 50.2, 20.6, 11.08 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{12}H_{14}NO^+$ for 188.1070; found 188.1065.



N-Butyl-N-phenylpropiolamide (2l):

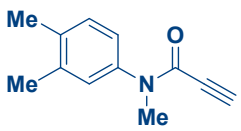
GP 1 was carried out with **10a** (0.5 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.98 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12l** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, BuI **13d** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The residue was purified by column chromatography to give the product **2l** (72 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 1698, 1609, 1421, 1350, 1212, 1094, 748, 693 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.38 – 7.31 (m, 3H), 7.20 (dd, J = 8.1, 1.1 Hz, 2H), 3.70 (t, J = 7.6 Hz, 2H), 2.76 (s, 1H), 1.48 – 1.41 (m, 2H), 1.29 – 1.23 (m, 2H), 0.85 – 0.80 (m, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.7, 141.1, 129.1 (2 × Ar–CH), 128.2 (2 × Ar–CH), 126.8, 79.5, 76.3, 48.3, 29.3, 19.7, 13.6 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{16}NO^+$ for 202.1226; found 202.1230.



N-(3,4-Dimethylphenyl)-N-methylpropiolamide (2m):

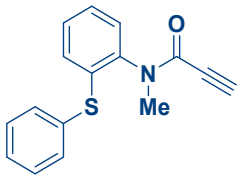
GP 1 was carried out with 3,4-dimethylaniline **10m** (0.648 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.9 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12m** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The residue was purified by column chromatography to give the product **2m** (68 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2927, 2104, 1635, 1419, 1197, 1112, 889, 815 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.15 (d, J = 7.9 Hz, 1H), 7.03 (s, 1H), 7.00 (dd, J = 8.0, 1.8 Hz, 1H), 3.28 (s, 3H), 2.80 (s, 1H), 2.28 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.2, 140.4, 137.9, 136.9, 130.4, 128.1, 124.5, 79.5, 76.5, 36.7, 19.9, 19.5 ppm.

HRMS (ESI) m/z: $[M+K]^+$ calculated $C_{12}H_{17}KN_2O^+$ for 226.0629 found 226.0639.



N-Methyl-N-(2-(phenylthio)phenyl)propiolamide (2n):

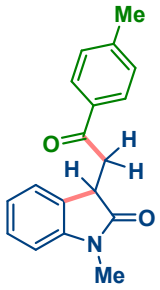
GP 1 was carried out with 2-(phenylthio)aniline **10n** (1.077 g, 5.36 mmol, 1.0 equiv) in DCM (5 mL), propiolic acid **11** (0.48 g, 6.9 mmol, 1.3 equiv), dicyclohexyl carbodiimide (DCC, 6.9 mmol, 1.3 equiv) at 0 °C. The resultant reaction mixture was stirred at 25 °C for 12 h; ***step two***: the ynamide **12n** was charged with NaH (60% in mineral oil, 9.52 mmol, 1.0 equiv) in THF (5.0 mL), at 0 °C and continued stirring for 30 min. Then, MeI **13a** (1.3 equiv) was added dropwise to the reaction mixture at the same temperature. The residue was purified by column chromatography to give the product **2n** (66 % overall yield) as a yellow oil.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3217, 3061, 2104, 1634, 1469, 1298, 1127, 738 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.34 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 7.17 – 7.16 (m, 3H), 7.08 – 7.03 (m, 1H), 3.15 (s, 3H), 2.67 (s, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.4, 140.9, 137.3, 132.9 (2 × Ar–CH), 131.0, 129.5 (2 × Ar–CH), 129.4, 129.3 (2 × Ar–CH), 128.2, 127.5, 78.6, 76.3, 35.3 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{16}H_{14}NOS^+$ for 268.0791 found 268.0780.



1-Methyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3aa):

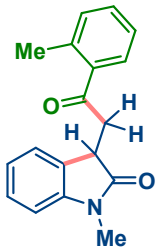
GP – 2 was carried out with 4-methylbenzaldehyde **1a** (50 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3aa** (102 mg, 89%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (65 mg) of **2a** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 2854, 1708, 1608, 1305, 1096, 694, 617 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.23 (m, 4H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 4.08 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.80 (dd, *J* = 18.1, 2.9 Hz, 1H), 3.37 (dd, *J* = 18.1, 9.3 Hz, 1H), 3.27 (s, 3H), 2.40 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 196.7, 177.9, 144.4, 144.3, 133.9, 129.5 (2 × Ar–CH), 129.3, 128.4 (2 × Ar–CH), 128.1, 124.5, 122.6, 108.1, 41.3, 40.0, 26.5, 21.8 ppm.

HRMS (ESI) m/z: $[M+K]^+$ calculated $C_{18}H_{17}KNO_2^+$ for 318.0891 found 318.0925.



1-Methyl-3-(2-oxo-2-(o-tolyl)ethyl)indolin-2-one (3ba):

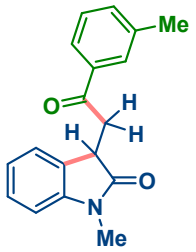
GP – 2 was carried out with 2-methylbenzaldehyde **1b** (50 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ba** (90 mg, 78%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection]. (60 mg) of **2a** were recovered. This compound is reported.[3]

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 1683, 1572, 1466, 1346, 1218, 1088, 749 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 – 7.55 (m, 1H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.26 – 7.08 (m, 5H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 4.01 (dd, *J* = 9.0, 3.1 Hz, 1H), 3.65 (dd, *J* = 18.0, 3.4 Hz, 1H), 3.23 (dd, *J* = 18.0, 9.0 Hz, 1H), 3.17 (s, 3H), 2.43 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 200.9, 177.9, 144.4, 138.5, 137.2, 132.2, 131.81, 129.2, 128.8, 128.2, 125.9, 124.4, 122.7, 108.2, 42.8, 41.6, 26.5, 21.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{18}NO_2^+$ 280.1332; found 280.1316.



3-(2-(3-Methoxyphenyl)-2-oxoethyl)-1-methylindolin-2-one (3ca):

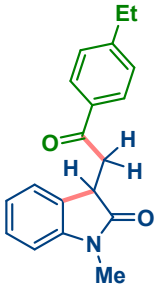
GP – 2 was carried out with 3-methoxybenzaldehyde **1c** (55 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ca** (91 mg, 76%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (60 mg) of **2a** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2921, 1681, 1417, 1351, 1246, 1169, 1091, 745, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.72 (m, 2H), 7.40 – 7.34 (m, 2H), 7.27 – 7.24 (m, 2H), 6.99 (td, *J* = 7.6, 0.9 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.08 (dd, *J* = 9.4, 2.6 Hz, 1H), 3.82 (dd, *J* = 18.2, 3.0 Hz, 1H), 3.38 (dd, *J* = 18.2, 9.3 Hz, 1H), 3.27 (s, 3H), 2.40 (s, 3H).

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.3, 177.9, 144.3, 138.6, 136.4, 134.3, 129.2, 128.8, 128.6, 128.1, 125.4, 124.5, 122.6, 108.1, 41.3, 40.2, 26.5, 21.4 ppm.

HRMS (ESI) m/z: $[M+N]^+$ calculated $C_{18}H_{17}N_2O_2^+$ for 293.1285; found 293.1263.



3-(2-(4-Ethylphenyl)-2-oxoethyl)-1-methylindolin-2-one (3da):

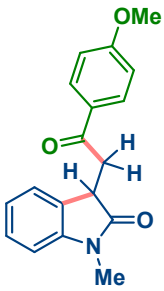
GP – 2 was carried out with 4-ethylbenzaldehyde **1d** (54 mg, 0.41 mmol), *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3da** (105 mg, 87%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection]. (65 mg) of **2a** were recovered

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2963, 2924, 1707, 1608, 1466, 1349, 1225, 1113, 1091, 699 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 – 7.81 (m, 2H), 7.21 – 7.18 (m, 4H), 6.90 (td, *J* = 7.6, 0.6 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 4.00 (dd, *J* = 9.2, 2.7 Hz, 1H), 3.73 (dd, *J* = 18.1, 3.0 Hz, 1H), 3.29 (dd, *J* = 18.1, 9.3 Hz, 1H), 3.18 (s, 3H), 2.61 (q, 2H), 1.18 (t, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 196.8, 178.0, 150.6, 144.4, 134.2, 129.3, 128.5 (2 × Ar–CH), 128.3 (2 × Ar–CH), 128.2, 124.6, 122.6, 108.1, 41.4, 40.1, 29.1, 26.5, 15.3 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ calculated $C_{19}H_{19}NNaO_2^+$ for 316.1308; found 316.1301.



3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methylindolin-2-one (3ea):

GP – 2 was carried out with 4-methoxybenzaldehyde **1e** (56 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ea** (91 mg,

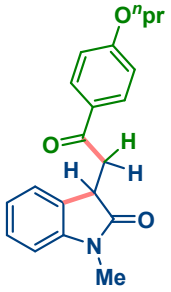
76%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (62 mg) of **2a** were recovered. This compound is reported.[3]

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2924, 2852, 1707, 1676, 1598, 1420, 1024, 838, cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 – 7.94 (m, 2H), 7.28 – 7.24 (m, 2H), 6.99 (td, *J* = 7.6, 0.7 Hz, 1H), 6.95 – 6.91 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 4.07 (dd, *J* = 9.3, 2.8 Hz, 1H), 3.86 (s, 3H), 3.78 (dd, *J* = 17.9, 3.0 Hz, 1H), 3.34 (dd, *J* = 17.9, 9.3 Hz, 1H), 3.27 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 195.4, 177.8, 163.7, 144.2, 130.4 (2 × Ar–CH), 129.4, 129.2, 128.0, 124.4, 122.4, 113.8 (2 × Ar–CH), 107.9, 55.4, 41.2, 39.6, 26.4 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{18}NO_3^+$ 296.1281; found 296.1287.



1-Methyl-3-(2-oxo-2-(4-propoxyphenyl)ethyl)indolin-2-one (3fa):

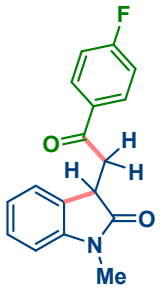
GP – 2 was carried out with 4-propoxybenzaldehyde **1f** (67 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3fa** (94 mg, 71%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection]. (65 mg) of **2a** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2924, 2878, 1707, 1674, 1572, 1311, 1122, 970 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 – 7.91 (m, 2H), 7.29 – 7.23 (m, 2H), 7.01 – 6.96 (m, 1H), 6.93 – 6.89 (m, 2H), 6.85 (d, *J* = 7.7 Hz, 1H), 4.07 (dd, *J* = 9.3, 2.8 Hz, 1H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.77 (dd, *J* = 18.0, 2.9 Hz, 1H), 3.33 (dd, *J* = 18.0, 9.3 Hz, 1H), 3.26 (s, 3H), 1.87 – 1.78 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 195.5, 178.1, 163.5, 144.4 (2 × Ar–CH), 130.5, 129.4, 129.3, 128.1, 124.6, 122.6, 114.4 (2 × Ar–CH), 108.1, 69.9, 41.4, 39.8, 26.5, 22.5, 10.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{22}NO_3^+$ 324.1594; found 324.1593.



3-(2-(4-Fluorophenyl)-2-oxoethyl)-1-methylindolin-2-one (3ga):

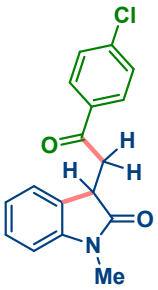
GP – 2 was carried out with 4-fluorobenzaldehyde **1g** (51 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ga** (81 mg, 69%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (65 mg) of **2a** were recovered

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2922, 2853, 1707, 1685, 1595, 1310, 1020, 698 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.03 – 7.99 (m, 2H), 7.30 – 7.23 (m, 2H), 7.16 – 7.10 (m, 2H), 7.00 (td, *J* = 7.6, 0.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.07 (dd, *J* = 9.1, 2.9 Hz, 1H), 3.80 (dd, *J* = 18.2, 3.1 Hz, 1H), 3.37 (dd, *J* = 18.2, 9.1 Hz, 1H), 3.27 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 195.5, 177.7, 166.0 (d, $J_{C\text{-}F}$ = 255.5 Hz), 144.4, 132.9 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.9 (d, $J_{C\text{-}F}$ = 9.6 Hz), 129.1, 128.2, 124.4, 122.6, 115.9 (d, $J_{C\text{-}F}$ = 22.0 Hz), 108.2, 41.2, 40.0, 26.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{17}H_{15}FNO_2^+$ for 284.1081; found 284.1070.



3-(2-(4-Chlorophenyl)-2-oxoethyl)-1-methylindolin-2-one (3ha):

GP – 2 was carried out with 4-chlorobenzaldehyde **1h** (57 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ha** (85 mg,

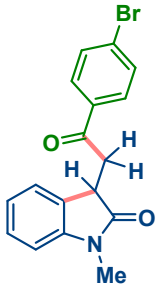
70%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (65 mg) of **2a** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2927, 1637, 1452, 1358, 1271, 1192, 1058, 814 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.21 (m, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.05 (dd, *J* = 9.0, 2.8 Hz, 1H), 3.79 (dd, *J* = 18.2, 3.1 Hz, 1H), 3.36 (dd, *J* = 18.2, 9.0 Hz, 1H), 3.26 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 195.7, 177.5, 144.2, 139.8, 134.5, 129.5 (2 × Ar–CH), 128.9 (2 × Ar–CH), 128.8, 128.1, 124.2, 122.5, 108.0, 41.0, 39.9, 26.3 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{17}H_{15}ClNO_2^+$ 300.0786; for found 300.0777.



3-(2-(4-Bromophenyl)-2-oxoethyl)-1-methylindolin-2-one (3ia):

GP – 2 was carried out with 4-bromobenzaldehyde **1i** (75 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ia** (102 mg, 72%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (65 mg) of **2a** were recovered.

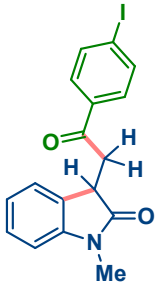
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2924, 1685, 1490, 1313, 1175, 1091, 932, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 – 7.81 (m, 2H), 7.65 – 7.58 (m, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.00 (td, *J* = 7.6, 0.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.05 (dd, *J* = 9.1, 3.0 Hz, 1H), 3.78 (dd, *J* = 18.2, 3.1 Hz, 1H), 3.35 (dd, *J* = 18.2, 9.1 Hz, 1H), 3.26 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 196.0, 177.6, 144.3, 135.0 (2 × Ar–CH), 132.1 (2 × Ar–CH), 129.7, 129.0, 128.8, 128.3, 124.4, 122.7, 108.2, 41.2, 40.1, 26.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{15}Br^{79}NO_2^+$ 344.0281; found 344.0263.

$[M+H]^+$ calculated for $C_{17}H_{15}Br^{81}NO_2^+$ 346.0261; found 346.0283.



3-(2-(4-Iodophenyl)-2-oxoethyl)-1-methylindolin-2-one (3ja):

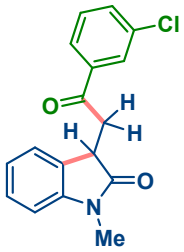
GP – 2 was carried out with 4-iodobenzaldehyde **1j** (95 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ja** (112 mg, 72%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (65 mg) of **2a** were recovered. This compound is reported.[3]

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2921, 2852, 1685, 1580, 1467, 1309, 1179, 750 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 – 7.80 (m, 2H), 7.70 – 7.62 (m, 2H), 7.30 – 7.21 (m, 2H), 7.00 (td, *J* = 7.6, 0.8 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.05 (dd, *J* = 9.0, 2.9 Hz, 1H), 3.78 (dd, *J* = 18.2, 3.1 Hz, 1H), 3.40 – 3.30 (m, 1H), 3.27 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 196.5, 177.7, 144.4, 138.2 (2 × Ar–CH), 135.7, 129.6 (2 × Ar–CH), 129.3, 129.0, 128.3, 124.5, 122.7, 108.2, 41.2, 40.0, 26.5 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}INNaO_2^+$ 413.9961; found 413.9959.



3-(2-(3-Chlorophenyl)-2-oxoethyl)-1-methylindolin-2-one (3ka):

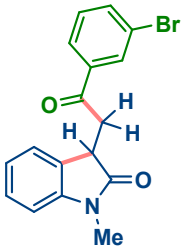
GP – 2 was carried out with 3-chlorobenzaldehyde **1k** (57 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ka** (90 mg, 74%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (65 mg) of **2a** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2922, 1690, 1571, 1468, 1207, 749, 679 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.94 (t, *J* = 7.94 Hz, 1H), 7.83 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.53 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 6.99 (dd, *J* = 10.9, 4.1 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.06 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.81 (dd, *J* = 18.3, 3.1 Hz, 1H), 3.38 (dd, *J* = 18.3, 9.0 Hz, 1H), 3.27 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 195.9, 177.8, 144.3, 137.9, 135.2, 133.5, 130.1, 128.9, 128.4, 128.3, 126.3, 124.4, 122.7, 108.3, 41.2, 40.1, 26.6 ppm.

HRMS (ESI) m/z: $[M+K]^+$ calculated for $C_{17}H_{14}ClKNO_2^+$ 338.0345; found 338.0350.



3-(2-(3-Bromophenyl)-2-oxoethyl)-1-methylindolin-2-one (3la):

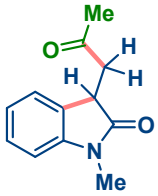
GP – 2 was carried out with 3-bromobenzaldehyde **1l** (75 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (132 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3la** (105 mg, 73%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (65 mg) of **2a** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 1690, 1566, 1419, 1302, 1204, 1024, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.20 (ddd, *J* = 31.6, 16.0, 7.5 Hz, 3H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 3.97 (d, *J* = 8.0 Hz, 1H), 3.72 (d, *J* = 18.2 Hz, 1H), 3.29 (dd, *J* = 18.3, 8.9 Hz, 1H), 3.18 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 195.6, 177.5, 144.1, 137.8, 136.2, 131.1, 130.2, 128.7, 128.1, 126.5, 124.2, 122.9, 122.5, 108.1, 40.9, 39.9, 26.4 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{15}Br^{79}NO_2^+$ 344.0281; found 344.0255.
$[M+H]^+$ calculated for $C_{17}H_{15}Br^{81}NO_2^+$ 346.0261; found 346.0258.



1-Methyl-3-(2-oxopropyl)indolin-2-one (3pa):

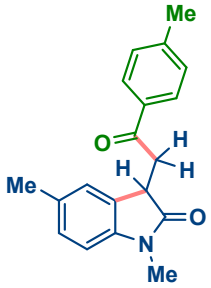
GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added *N*-methyl-*N*-phenylpropiolamide **2a** (32 mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3pa** (14 mg, 83%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2931, 1701, 1609, 1492, 1347, 1019, 752 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ =7.26 (dd, *J* = 9.7, 5.8 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.86 (dd, *J* = 9.0, 3.2 Hz, 1H), 3.24 (dd, *J* = 18.4, 3.4 Hz, 1H), 3.21 (s, 3H), 2.82 (dd, *J* = 18.4, 9.0 Hz, 1H), 2.21 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 205.6, 177.5, 144.3, 129.0, 128.2, 124.3, 122.6, 108.1, 77.2, 44.5, 41.1, 30.1, 26.4 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{12}H_{14}NO_2^+$ for 204.1019; found 204.1019.



1,5-Dimethyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3ab):

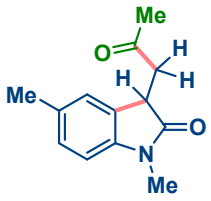
GP – 2 was carried out with 4-methylbenzaldehyde **1a** (50 mg, 0.41 mmol), added *N*-methyl-*N*-(*p*-tolyl)propiolamide **2a** (143 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ab** (105 mg, 88%), as a yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (70 mg) of **2a** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2920, 1704, 1573, 1348, 1258, 1094, 809, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.2 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.06 (d, J = 5.8 Hz, 2H), 6.79 – 6.68 (m, 1H), 4.05 (dd, J = 9.3, 2.4 Hz, 1H), 3.80 (dd, J = 18.2, 2.9 Hz, 1H), 3.35 (dd, J = 18.2, 9.4 Hz, 1H), 3.25 (s, 3H), 2.41 (s, 3H), 2.27 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 196.6, 177.8, 144.3, 141.8, 133.9, 132.0, 129.3 (2 × Ar–CH), 129.2, 128.2 (2 × Ar–CH), 128.2, 125.3, 107.6, 41.2, 40.0, 26.4, 21.6, 21.0 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{20}NO_2^+$ 294.1489 found 294.1495.



1,5-Dimethyl-3-(2-oxopropyl)indolin-2-one (3pb):

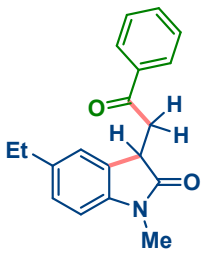
GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added 4 *N*-methyl-*N*-(*p*-tolyl)propiolamide **2b** (14 mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 8 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 82:18) furnished the product **3pb** (15 mg, 87%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2921, 1701, 1496, 1420, 1298, 1037, 756, 577 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.06 (d, J = 7.9 Hz, 1H), 7.02 (s, 1H), 6.71 (d, J = 7.9 Hz, 1H), 3.83 (dd, J = 9.1, 2.9 Hz, 1H), 3.24 (dd, J = 18.4, 3.2 Hz, 1H), 3.19 (s, 3H), 2.80 (dd, J = 18.4, 9.2 Hz, 1H), 2.30 (s, 3H), 2.22 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 205.6, 177.3, 141.7, 131.9, 128.9, 128.2, 124.9, 107.6, 44.4, 40.9, 29.9, 26.3, 20.9 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{16}NO_2^+$ 218.1176; found 218.1161.



5-Ethyl-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3mc):

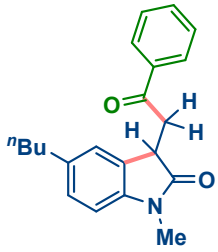
GP – 2 was carried out with benzaldehyde **1m** (43 mg, 0.41 mmol), added *N*-(4-ethylphenyl)-*N*-methylpropiolamide **2c** (155 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3mc** (105 mg, 88%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (75 mg) of **2c** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2963, 2925, 1685, 1602, 1496, 1351, 1263, 732, 695 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.01 – 7.97 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 7.10 (d, *J* = 6.8 Hz, 2H), 6.79 – 6.71 (m, 1H), 4.08 (dd, *J* = 9.4, 2.8 Hz, 1H), 3.83 (dd, *J* = 18.2, 2.9 Hz, 1H), 3.38 (dd, *J* = 18.2, 9.4 Hz, 1H), 3.25 (s, 3H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.1, 177.7, 142.0, 138.8, 136.3, 133.4, 129.2, 128.7 (2 × Ar–CH), 128.1 (2 × Ar–CH), 127.1, 124.3, 107.8, 41.2, 40.2, 28.5, 26.4, 16.0 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{20}NO_2^+$ 294.1489; found 294.1478.



5-Butyl-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3md):

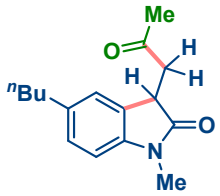
GP – 2 was carried out with benzaldehyde **1m** (43 mg, 0.41 mmol), added *N*-(4-butylphenyl)-*N*-methylpropiolamide **2d** (178 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3md** (105 mg, 80%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (86 mg) of **2d** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2954, 2926, 1706, 1495, 1349, 1179, 1022, 689, 616 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 – 7.97 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 – 7.44 (m, 2H), 7.10 – 7.05 (m, 2H), 6.79 – 6.74 (m, 1H), 4.07 (dd, *J* = 9.3, 2.8 Hz, 1H), 3.82 (dd, *J* = 18.2, 3.0 Hz, 1H), 3.38 (dd, *J* = 18.2, 9.3 Hz, 1H), 3.25 (s, 3H), 2.60 – 2.45 (m, 2H), 1.56 – 1.46 (m, 2H), 1.30 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 197.1, 177.6, 142.0, 137.3, 136.3, 133.3, 129.0, 128.6 (2 × Ar–CH), 128.1 (2 × Ar–CH), 127.6, 124.6, 107.6, 41.2, 40.1, 35.3, 34.0, 26.3, 22.2, 13.8 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{23}NNaO_2^+$ 344.1621; found 344.1599.



5-Butyl-1-methyl-3-(2-oxopropyl)indolin-2-one (3pd):

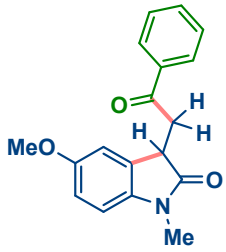
GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added *N*-(4-butylphenyl)-*N*-methylpropiolamide **2d** (17 mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3pd** (16 mg, 79%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2926, 2105, 1640, 1469, 1431, 1364, 1128, 815, 737 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.05 (d, *J* = 7.9 Hz, 1H), 7.01 (s, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 3.83 (dd, *J* = 9.1, 3.2 Hz, 1H), 3.22 (dd, *J* = 18.3, 3.4 Hz, 1H), 3.18 (s, 3H), 2.78 (dd, *J* = 18.3, 9.1 Hz, 1H), 2.57 – 2.48 (m, 2H), 2.21 (s, 3H), 1.53 (ddd, *J* = 15.3, 10.0, 4.2 Hz, 2H), 1.31 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 205.83, 177.57, 142.13, 137.58, 129.09, 127.88, 124.62, 107.86, 44.72, 41.23, 35.50, 34.23, 30.15, 26.51, 22.47, 14.07 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{22}NO_2^+$ 260.1645; found 260.1648.



5-Methoxy-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3me):

GP – 2 was carried out with benzaldehyde **1m** (43 mg, 0.41 mmol), added *N*-(4-methoxyphenyl)-*N*-methylpropiolamide **2e** (156 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel

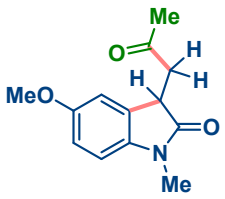
column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3me** (94mg, 78%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (75 mg) of **2e** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 2852, 1683, 1495, 1358, 1031, 766, 730 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 – 7.95 (m, 2H), 7.5 (td, *J* = 7.1, 3.4 Hz, 1H), 7.48 – 7.45 (m, 2H), 6.81 – 6.74 (m, 1H), 6.78 (dt, *J* = 17.7, 5.4 Hz, 2H), 4.06 (dd, *J* = 9.3, 2.7 Hz, 1H), 3.83 (dd, *J* = 18.3, 2.9 Hz, 1H), 3.73 (s, 3H), 3.38 (dd, *J* = 18.4, 9.3 Hz, 1H), 3.24 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.1, 177.5, 156.1, 137.9, 136.4, 133.6, 130.6, 128.8 (2 × Ar–CH), 128.3 (2 × Ar–CH), 112.5, 112.2, 108.4, 55.9, 41.7, 40.3, 26.6 ppm.

HRMS (ESI) m/z: $[M+K]^+$ calculated for $C_{18}H_{17}KNO_3^+$ 334.0840; found 334.0817.



5-Methoxy-1-methyl-3-(2-oxopropyl)indolin-2-one (3pe):

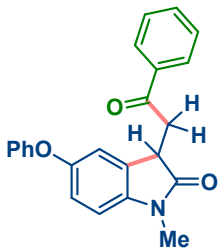
GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added *N*-(4-methoxyphenyl)-*N*-methylpropiolamide **2e** (15 mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3pe** (15 mg, 83%) as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 1699, 1489, 1358, 1235, 1150, 1031, 809 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 6.77 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 3.81 (dd, J = 9.0, 3.1 Hz, 1H), 3.74 (s, 3H), 3.22 (dd, *J* = 18.5, 3.2 Hz, 1H), 3.17 (s, 3H), 2.79 (dd, *J* = 18.4, 9.1 Hz, 1H), 2.19 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 205.6, 177.0, 156.0, 137.8, 130.3, 112.3, 111.9, 108.3, 55.9, 44.6, 41.4, 30.0, 26.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{16}NO_3^+$ 234.1125; found 234.1106.



1-Methyl-3-(2-oxo-2-phenylethyl)-5-phenoxyindolin-2-one (3mf):

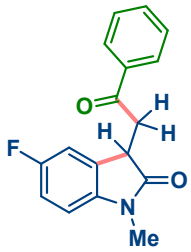
GP – 2 was carried out with benzaldehyde **1m** (43 mg, 0.41 mmol), added *N*-methyl-*N*-(4-phenoxyphenyl)propiolamide **2f** (208 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3mf** (118 mg, 81%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (101 mg) of **2f** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2922, 1707, 1486, 1448, 1220, 1095, 753, 690 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.94 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.61 – 7.54 (m, 1H), 7.45 (dd, *J* = 10.7, 4.9 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.05 – 7.00 (m, 2H), 6.95 (ddd, *J* = 8.4, 2.4, 0.6 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.07 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.83 (dd, *J* = 18.2, 3.1 Hz, 1H), 3.42 (dd, *J* = 18.2, 8.9 Hz, 1H), 3.28 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 196.8, 177.6, 158.3, 152.4, 140.5, 136.3, 133.6, 130.7, 129.7 (2 × Ar–CH), 128.8 (2 × Ar–CH), 128.2 (2 × Ar–CH), 122.7, 119.2, 117.7 (2 × Ar–CH), 117.3, 108.6, 41.6, 40.0, 26.7 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{20}NO_3^+$ 358.1438; found 358.1425.



5-Fluoro-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3mg):

GP – 2 was carried out with benzaldehyde **1m** (43 mg, 0.41 mmol), added *N*-(4-fluorophenyl)-*N*-methylpropiolamide **2g** (146 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3mg** (79 mg,

68%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (71 mg) of **2g** were recovered.

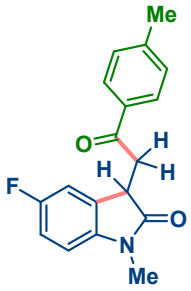
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 1683, 1492, 1466, 1351, 1219, 1021, 627 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H), 7.04 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 7.01 – 6.90 (m, 1H), 6.77 (dd, *J* = 8.5, 4.2 Hz, 1H), 4.06 (dd, *J* = 9.2, 1.9 Hz, 1H), 3.85 (dd, *J* = 18.3, 2.9 Hz, 1H), 3.39 (dd, *J* = 18.3, 9.3 Hz, 1H), 3.26 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 196.8, 177.5, 159.3 (d, *J* = 240.2 Hz), 140.4, 136.2, 133.7, 130.7 (d, *J* = 8.3 Hz), 128.8 (2 × Ar–CH), 128.2 (2 × Ar–CH), 114.3 (d, *J* = 23.6 Hz), 112.9 (d, *J* = 25.2 Hz), 108.4 (d, *J* = 8.1 Hz), 41.6, 40.1, 26.7 ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ = -120.66 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}FNNaO_2^+$ 306.0901; found 306.0901.



5-Fluoro-1-methyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3ag):

GP – 2 was carried out with 4-methylbenzaldehyde **1a** (50 mg, 0.41 mmol), added *N*-(4-fluorophenyl)-*N*-methylpropiolamide **2g** (146 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ag** (84 mg, 69%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (75 mg) of **2g** were recovered.

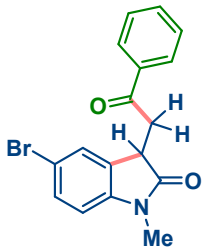
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2956, 2929, 1695, 1606, 1465, 1034, 810, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.03 (ddd, *J* = 8.3, 2.4, 0.8 Hz, 1H), 6.96 (dt, *J* = 8.9, 4.3 Hz, 1H), 6.76 (dd, *J* = 8.5, 4.2 Hz, 1H), 4.04 (dd, *J* = 9.2, 1.9 Hz, 1H), 3.82 (dd, *J* = 18.3, 2.9 Hz, 1H), 3.36 (dd, *J* = 18.2, 9.4 Hz, 1H), 3.25 (s, 3H), 2.41 (s, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 196.48, 177.59, 159.3 (d, $J_{C\text{-}F}$ = 240.6 Hz), 144.6, 140.3, 133.8, 130.8 (d, $J_{C\text{-}F}$ = 8.5 Hz), 129.5 (2 × Ar–CH), 128.3 (2 × Ar–CH), 114.2 (d, J = 23.2 Hz), 112.9 (d, $J_{C\text{-}F}$ = 25.2 Hz), 108.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 41.6, 39.9, 26.6, 21.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -120.72 ppm. 311.1190.

HRMS (ESI) m/z: $[M+N]^+$ calculated for $C_{18}H_{16}FN_2O_2^+$ 311.1190; found 311.1182.



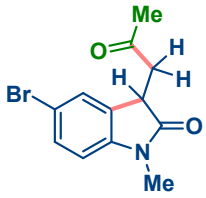
5-Bromo-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3mh):

GP – 2 was carried out with benzaldehyde **1m** (43 mg, 0.41 mmol), added *N*-(4-bromophenyl)-*N*-methylpropiolamide **2h** (236 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3mh** (113 mg, 70%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (115 mg) of **2h** were recovered. This compound is reported.[3]

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2924, 1709, 1487, 1343, 1219, 1098, 810, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.95 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.45 (m, 2H), 7.39-7.38 (m, 2H), 6.73 (d, J = 8.2 Hz, 1H), 4.04 (dd, J = 9.0, 2.7 Hz, 1H), 3.85 (dd, J = 18.4, 2.9 Hz, 1H), 3.42 (dd, J = 18.4, 9.0 Hz, 1H), 3.25 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 196.7, 177.3, 143.5, 136.2, 133.8, 131.2, 131.1, 128.9 (2 × Ar–CH), 128.3 (2 × Ar–CH), 127.7, 115.3, 109.5, 41.3, 40.0, 26.6 ppm.



5-Bromo-1-methyl-3-(2-oxopropyl)indolin-2-one (3ph):

GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added *N*-(4-bromophenyl)-*N*-methylpropiolamide **2h** (mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column

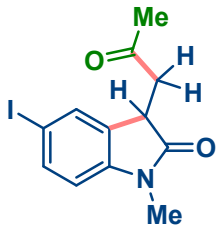
chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ph** (15 mg, 74%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2926, 1703, 1605, 1479, 1348, 1262, 1096, 805, 547 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.41 – 7.34 (m, 1H), 7.31 (s, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 3.80 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.25 (dd, *J* = 18.7, 3.0 Hz, 1H), 3.19 (s, 3H), 2.84 (dd, *J* = 18.6, 8.8 Hz, 1H), 2.21 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 205.27, 176.91, 143.41, 131.01, 130.96, 127.47, 115.26, 109.50, 44.28, 41.02, 29.93, 26.55 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{12}H_{13}Br^{79}NO_2^+$ 282.0125; found 282.0123. $[M+H]^+$ calculated for $C_{12}H_{13}Br^{81}NO_2^+$ 284.0104; found 284.0106.



5-Iodo-1-methyl-3-(2-oxopropyl)indolin-2-one (3pi):

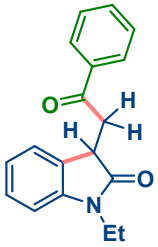
GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added *N*-(4-iodophenyl)-*N*-methylpropiolamide **2i** (58 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3pi** (99 mg, 73%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 1706, 1607, 1464, 1343, 1098, 756, 628 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 8.1 Hz, 1H), 7.48 (s, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 3.80 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.24 (dd, *J* = 18.7, 3.1 Hz, 1H), 3.19 (s, 3H), 2.84 (dd, *J* = 18.6, 8.8 Hz, 1H), 2.21 (s, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 205.2, 176.7, 144.1, 137.0, 133.0, 131.3, 110.1, 85.1, 44.3, 40.8, 29.9, 26.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{12}H_{13}INO_2^+$ 329.9986; found 329.9979.



1-Ethyl-3-(2-oxo-2-phenylethyl)indolin-2-one one (3mj):

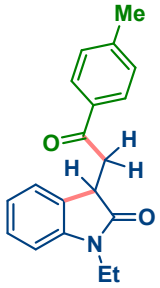
GP – 2 was carried out with benzaldehyde **1m** (43 mg, 0.41 mmol), added *N*-ethyl-*N*-phenylpropiolamide **2j** (143 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3mj** (92 mg, 81%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (70 mg) of **2j** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2924, 2854, 1686, 1610, 1371, 1219, 811, 712, 691 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 – 7.97 (m, 2H), 7.63 – 7.56 (m, 1H), 7.49 – 7.44 (m, 2H), 7.30 – 7.23 (m, 2H), 7.05 – 6.95 (m, 1H), 6.92 – 6.79 (m, 1H), 4.08 (dd, *J* = 9.1, 2.9 Hz, 1H), 3.91 – 3.77 (m, 3H), 3.41 (dd, *J* = 18.2, 9.1 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.1, 177.5, 143.4, 133.5, 130.2, 128.8 (2 × Ar–CH), 128.5, 128.2 (2 × Ar–CH), 128.1, 124.7, 122.4, 108.3, 41.3, 40.1, 35.0, 12.7 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{18}NO_2^+$ 280.1332 found 280.1329.



1-Ethyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3aj):

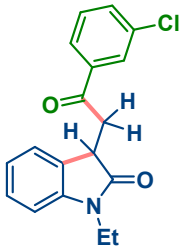
GP – 2 was carried out with 4-methylbenzaldehyde **1a** (50 mg, 0.41 mmol), added *N*-ethyl-*N*-phenylpropiolamide **2j** (143 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3aj** (101 mg, 84%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (70 mg) of **2j** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2923, 2853, 1681, 1608, 1404, 1356, 1227, 751 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, J = 8.2 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.01 – 6.94 (m, 1H), 6.87 (d, J = 7.7 Hz, 1H), 4.06 (dd, J = 9.3, 2.8 Hz, 1H), 3.81 (m, 3H), 3.36 (dd, J = 18.1, 9.3 Hz, 1H), 2.41 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 196.5, 177.4, 144.2, 143.3, 133.9, 129.4, 129.3 (2 × Ar–CH), 128.2 (2 × Ar–CH), 127.9, 124.6, 122.2, 108.1, 41.2, 39.9, 34.8, 21.6, 12.6 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{20}NO_2^+$ 294.1489 found 294.1475.



3-(2-(3-Chlorophenyl)-2-oxoethyl)-1-ethylindolin-2-one (3kj):

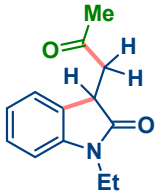
GP – 2 was carried out with 4-chlorobenzaldehyde **1k** (57 mg, 0.41 mmol), added *N*-ethyl-*N*-phenylpropiolamide **2j** (143 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3kj** (88 mg, 69%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (70 mg) of **2j** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2926, 1695, 1607, 1413, 1360, 1276, 1092, 893, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (t, J = 1.8 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.54 (ddd, J = 8.0, 2.1, 1.0 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 7.26 (ddd, J = 10.7, 8.7, 4.1 Hz, 2H), 6.98 (td, J = 7.6, 0.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 4.04 (dd, J = 9.0, 3.0 Hz, 1H), 3.80 (tt, J = 5.3, 4.7 Hz, 3H), 3.38 (dd, J = 18.3, 9.0 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 195.8, 177.2, 143.5, 137.9, 135.1, 133.4, 130.1, 129.1, 128.3, 128.2, 126.3, 124.5, 122.4, 108.3, 41.2, 40.2, 35.0, 12.7 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{17}ClNO_2^+$ 314.0942; found 314.0948.



1-Ethyl-3-(2-oxopropyl)indolin-2-one (3pj):

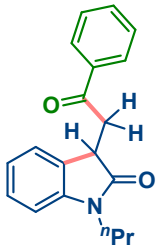
GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added *N*-ethyl-*N*-phenylpropiolamide **2j** (14 mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3pj** (14 mg, 78%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2980, 1701, 1610, 1464, 1359, 1162, 1020, 699 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.26 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.83 (dd, *J* = 8.7, 3.3 Hz, 1H), 3.81 – 3.74 (m, 2H), 3.25 (dd, *J* = 18.4, 3.4 Hz, 1H), 2.85 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.20 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 205.4, 176.9, 143.2, 129.0, 127.9, 124.2, 122.2, 108.1, 44.3, 40.9, 34.7, 29.9, 12.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{16}NO_2^+$ 218.1176; found 218.1170.



3-(2-Oxo-2-phenylethyl)-1-propylindolin-2-one (3mk):

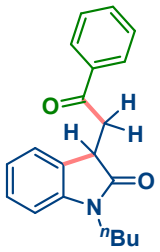
GP – 2 was carried out with 4-methylbenzaldehyde **1m** (50 mg, 0.41 mmol), added *N*-phenyl-*N*-propylpropiolamide **2k** (155 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3mk** (100 mg, 83%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (75 mg) of **2k** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2963, 2925, 1683, 1609, 1359, 1218, 750, 691 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.48 – 7.45 (m, 2H), 7.27 – 7.24 (m, 2H), 6.98 (td, *J* = 7.6, 0.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.08 (dd, *J* = 9.2, 2.9 Hz, 1H), 3.84 (dd, *J* = 18.2, 3.0 Hz, 1H), 3.73 (td, *J* = 7.2, 3.0 Hz, 2H), 3.40 (dd, *J* = 18.2, 9.2 Hz, 1H), 1.76 (h, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 197.1, 177.8, 143.9, 136.5, 133.6, 129.4, 128.8 (2 × Ar–CH), 128.3 (2 × Ar–CH), 128.1, 124.7, 122.4, 108.4, 41.9, 41.3, 40.3, 20.9, 11.6 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{20}NO_2^+$ 294.1489 found 294.1457.



1-Butyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3ml):

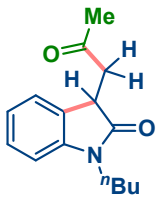
GP – 2 was carried out with benzaldehyde **1m** (43 mg, 0.41 mmol), added *N*-butyl-*N*-phenylpropiolamide **2l** (166 mg, 0.83 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ml** (106 mg, 84%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection], (81 mg) of **2j** were recovered.

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2957, 1686, 1611, 1489, 1465, 1360, 1215, 751, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 – 7.95 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.25 (dd, *J* = 10.6, 3.8 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 4.08 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.83 (dd, *J* = 18.2, 3.0 Hz, 1H), 3.76 (td, *J* = 7.1, 1.3 Hz, 2H), 3.39 (dd, *J* = 18.2, 9.2 Hz, 1H), 1.71 (dt, *J* = 20.4, 7.4 Hz, 2H), 1.43 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 196.9, 177.6, 143.7, 136.3, 133.4, 129.3, 128.6 (2 × Ar–CH), 128.1 (2 × Ar–CH), 127.9, 124.5, 122.2, 108.3, 41.1, 40.1, 39.9, 29.5, 20.2, 13.8 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{22}NO_2^+$ 308.1645 found 308.1631.



1-Butyl-3-(2-oxopropyl)indolin-2-one(3pl):

GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added *N*-butyl-*N*-phenylpropiolamide **2l** (16 mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel

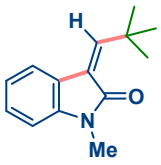
column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3pl** (16 mg, 78%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2958, 2927, 1704, 1609, 1359, 1198, 1094, 811, 547 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.22 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 6.98 (td, *J* = 7.6, 0.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.84 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.70 (t, *J* = 7.4 Hz, 2H), 3.24 (dd, *J* = 18.3, 3.4 Hz, 1H), 2.83 (dd, *J* = 18.3, 8.9 Hz, 1H), 2.20 (s, 3H), 1.73 – 1.59 (m, 2H), 1.48 – 1.32 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 205.4, 177.3, 143.6, 129.0, 127.9, 124.2, 122.2, 108.3, 44.4, 40.9, 39.8, 29.9, 29.3, 20.1, 13.7 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{15}H_{20}NO_2^+$ 246.1489 found 246.1493.



(Z)-3-(2,2-Dimethylpropylidene)-1-methylindolin-2-one (3qa):

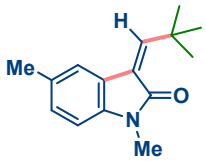
GP – 2 was carried out with pivalaldehyde **1q** (70 mg, 0.82 mmol), added 4-ethyl-2-ethynyl-1-isopropoxybenzene **2a** (26 mg, 0.16 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3qa** (21 mg, 61%), as a dark yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2922, 1699, 1615, 1477, 1269, 1107, 869, 800, 668 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (dd, *J* = 7.5, 0.4 Hz, 1H), 7.23 (td, *J* = 7.7, 1.1 Hz, 1H), 7.00 (td, *J* = 7.6, 0.9 Hz, 1H), 6.95 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 1.42 (s, 9H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 165.7, 152.7, 142.3, 128.5, 126.9, 124.2, 121.8, 118.6, 107.8, 33.8, 29.4 (3C), 25.9 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated $C_{14}H_{18}NO^+$ for 216.1383; found 216.1388.



(Z)-3-(2,2-Dimethylpropylidene)-1,5-dimethylindolin-2-one (3qb):

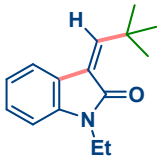
GP – 2 was carried out with pivalaldehyde **1q** (86 mg, 0.82 mmol), added 4-ethyl-2-ethynyl-1-isopropoxybenzene **2b** (28 mg, 0.16 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3qb** (23 mg, 63%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2953, 1696, 1494, 1462, 1204, 944, 875, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.91 (s, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 3.20 (s, 3H), 2.33 (s, 3H), 1.42 (s, 9H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 165.6, 152.0, 139.9, 130.9, 128.6, 126.9, 124.0, 119.2, 107.3, 33.5, 29.3 (3C), 25.8, 21.1 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{15}H_{20}NO^+$ 230.1539; found 230.1530.



(Z)-3-(2,2-Dimethylpropylidene)-1-ethylindolin-2-one (3qj):

GP – 2 was carried out with pivalaldehyde **1q** (86 mg, 0.82 mmol), added N-methyl-N-phenylpropiolamide **2j** (28 mg, 0.16 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3qj** (23 mg, 63%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2955, 1695, 1470, 1360, 1264, 1095, 788, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 7.4 Hz, 1H), 7.22 (td, *J* = 7.8, 1.0 Hz, 1H), 6.98 (td, *J* = 7.6, 0.7 Hz, 1H), 6.94 (s, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 2H), 1.42 (s, 9H), 1.25 (d, *J* = 7.3 Hz, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 165.0, 152.4, 141.2, 128.3, 126.9, 124.2, 121.3, 118.6, 107.7, 34.3, 33.6, 29.3 (3C), 12.7 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{15}H_{20}NO^+$ 230.1540: found 230.1526.

(Z)-3-(2,2-Dimethylpropylidene)-1-isopropylindolin-2-one (3qk):

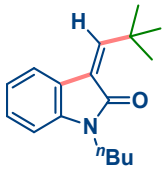
GP – 2 was carried out with pivalaldehyde **1q** (86 mg, 0.82 mmol), added 4-ethyl-2-ethynyl-1-isopropoxybenzene **2k** (30 mg, 0.16 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3qk** (26 mg, 66%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2956, 2931, 1697, 1606, 1465, 1359, 1179, 1095, 947 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, J = 7.5 Hz, 1H), 7.21 (td, J = 7.8, 0.8 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.94 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 3.73 – 3.64 (m, 2H), 1.78 – 1.65 (m, 2H), 1.42 (s, 9H), 0.97 (t, J = 7.4 Hz, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 165.4, 152.5, 141.7, 128.3, 126.8, 124.2, 121.3, 118.5, 107.9, 41.3, 33.6, 29.3 (3C), 20.9, 11.5 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{22}NO^+$ 244.1696 found 244.1678.



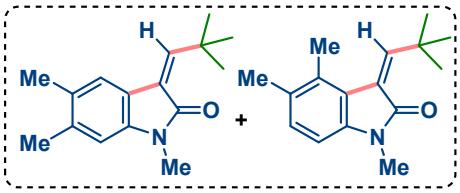
(Z)-1-Butyl-3-(3,3-dimethyl-2-oxobutylidene)indolin-2-one (3ql):

GP – 2 was carried out with pivalaldehyde **1q** (86 mg, 0.82 mmol), added 4-ethyl-2-ethynyl-1-isopropoxybenzene **2l** (32 mg, 0.16 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3ql** (28 mg, 67%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3217, 2105, 1634, 1438, 1300, 1069, 691, 583 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (dd, J = 7.5, 0.5 Hz, 1H), 7.22 (td, J = 7.7, 1.1 Hz, 1H), 6.98 (td, J = 7.6, 0.8 Hz, 1H), 6.94 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 3.76 – 3.68 (m, 2H), 1.72 – 1.60 (m, 2H), 1.46 – 1.35 (m, 11H), 0.96 (t, J = 7.4 Hz, 3H) ppm.

^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 165.3, 152.4, 141.6, 128.2, 126.8, 124.2, 121.3, 118.5, 107.9, 39.5, 33.6, 29.6, 29.3 (3C), 20.3, 13.0 ppm.



(Z)-3-(3,3-Dimethyl-2-oxobutylidene)-1-ethylindolin-2-one(3qo):

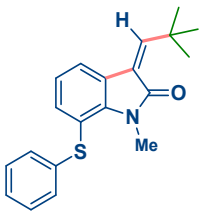
GP – 2 was carried out with pivalaldehyde **1q** (86 mg, 0.82 mmol), added 4-ethyl-2-ethynyl-1-isopropoxybenzene **2o** (30 mg, 0.16 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product {**(3qo+3qo′)** (28 mg, 71%) (r.r = 3.3:1)}, as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2925, 1692, 1647, 1611, 1356, 1248, 1013, 746, cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.12 (s, 1H), 7.10 (s, 1H), 7.04 (d, J = 7.9 Hz, 1H), 6.85 (s, 1H), 6.55 (s, 1H), 6.53 (s, 1H), 3.19 (d, J = 1.8 Hz, 6H), 2.39 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 1.44 (s, 12H), 1.41 (s, 12H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 165.8, 165.7, 156.1, 156.0, 150.9, 140.9, 140.7, 140.3, 136.9, 131.9, 130.6, 129.4, 129.4, 129.1, 126.9, 121.6, 121.4, 119.8, 109.1, 104.9, 34.0, 33.5 29.5 (3C), 29.4 (3C), 25.8, 25.7, 20.4, 20.2, 19.5, 16.7 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{22}NO^+$ 244.1696; found 244.1696.



(Z)-3-(2,2-Dimethylpropylidene)-1-methyl-7-(phenylthio)indolin-2-one (3qp):

GP – 2 was carried out with pivalaldehyde **1q** (86 mg, 0.82 mmol), added 4-ethyl-2-ethynyl-1-isopropoxybenzene **2p** (43 mg, 0.16 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the

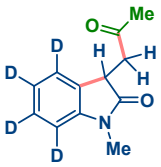
resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **3qp** (29 mg, 56%), as pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2956, 2926, 1687, 1654, 1437, 1345, 736, 693 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.42 – 7.40 (m, 2H), 7.36 – 7.32 (m, 3H), 7.18 – 7.15 (m, 2H), 7.10 (s, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 2.73 (d, *J* = 4.9 Hz, 3H), 0.95 (s, 9H) ppm.

^{13}C{H} NMR (151 MHz, $CDCl_3$) δ = 167.4, 150.9, 139.3, 135.4, 133.8 (2 × Ar–CH), 133.3, 131.5, 129.9, 129.5 (2 × Ar–CH), 128.9, 128.7, 128.4, 125.7, 34.3, 29.9 (3C), 26.9 ppm.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{22}NOS^+$ 324.1417; found 324.1409.



(R)-1-methyl-3-(2-oxopropyl)indolin-2-one-4,5,6,7-d_4:

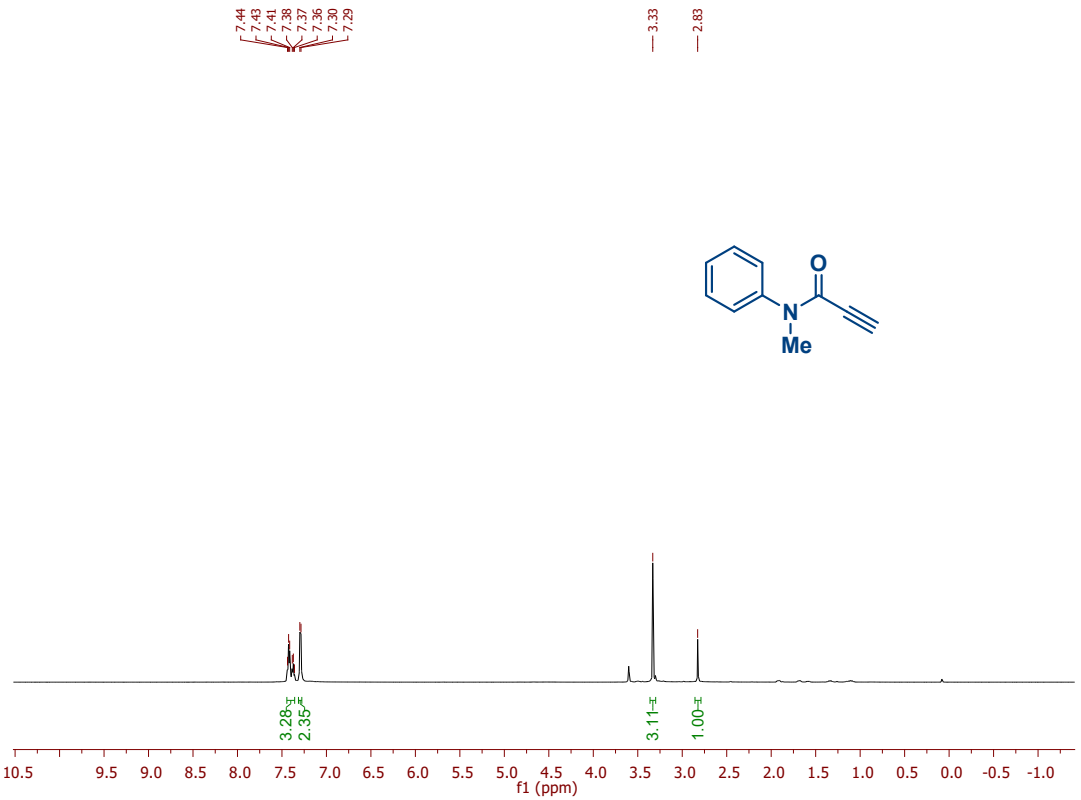
GP – 2 was carried out with acetaldehyde **1p** (37 mg, 0.41 mmol), added *N*-methyl-*N*-(phenyl-d_5)propiolamide **6** (32 mg, 0.08 mmol), TBADT (4 mol%), and CH_3CN (2 mL) and the resultant reaction mixture was irradiated for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15) furnished the product **7p** (13 mg, 76%), as a pale yellow oil. [TLC control (petroleum ether/ethyl acetate, 85:15) *Rf* = 0.20, UV detection].

^{1}H NMR (600 MHz, $CDCl_3$) δ = 3.82 (dd, *J* = 8.9, 3.3 Hz, 1H), 3.24 – 3.18 (m, 4H), 2.80 (dd, *J* = 18.4, 9.0 Hz, 1H), 2.18 (s, 3H) ppm.

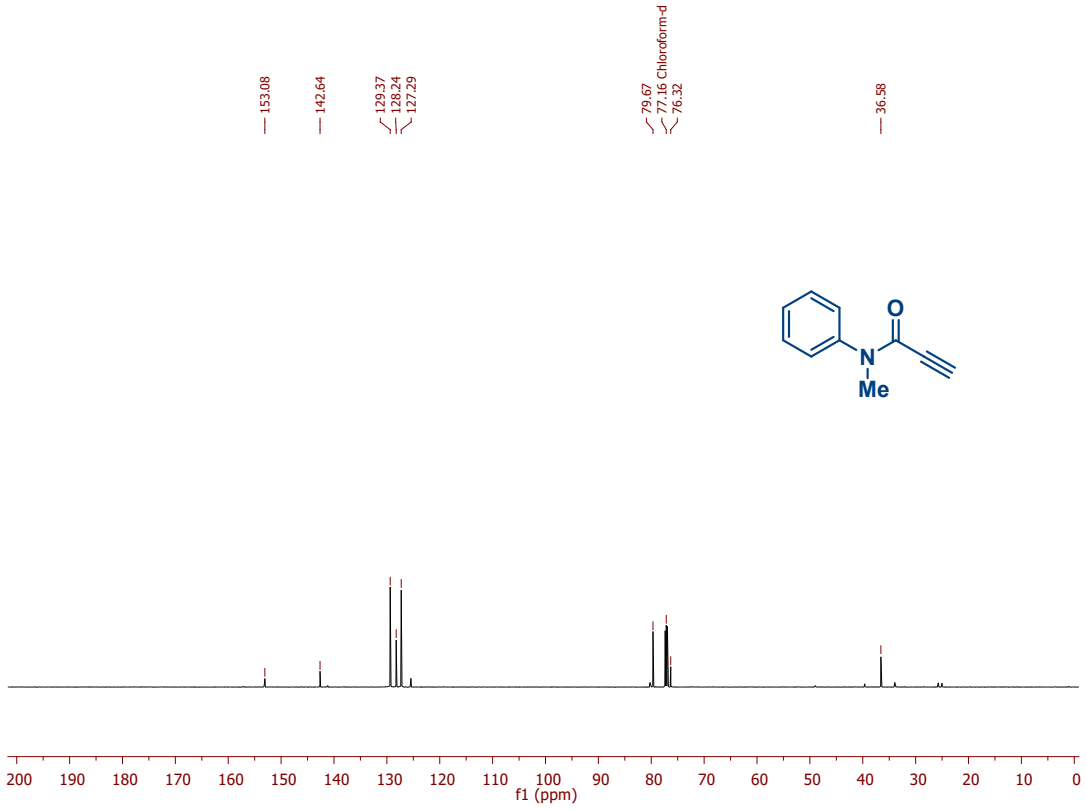
HRMS (ESI) m/z: $[M + K]^+$ calculated $C_{12}H_7D_4NO_2^+$ for 246.0829; found 204.0839.

NMR spectra for the products:

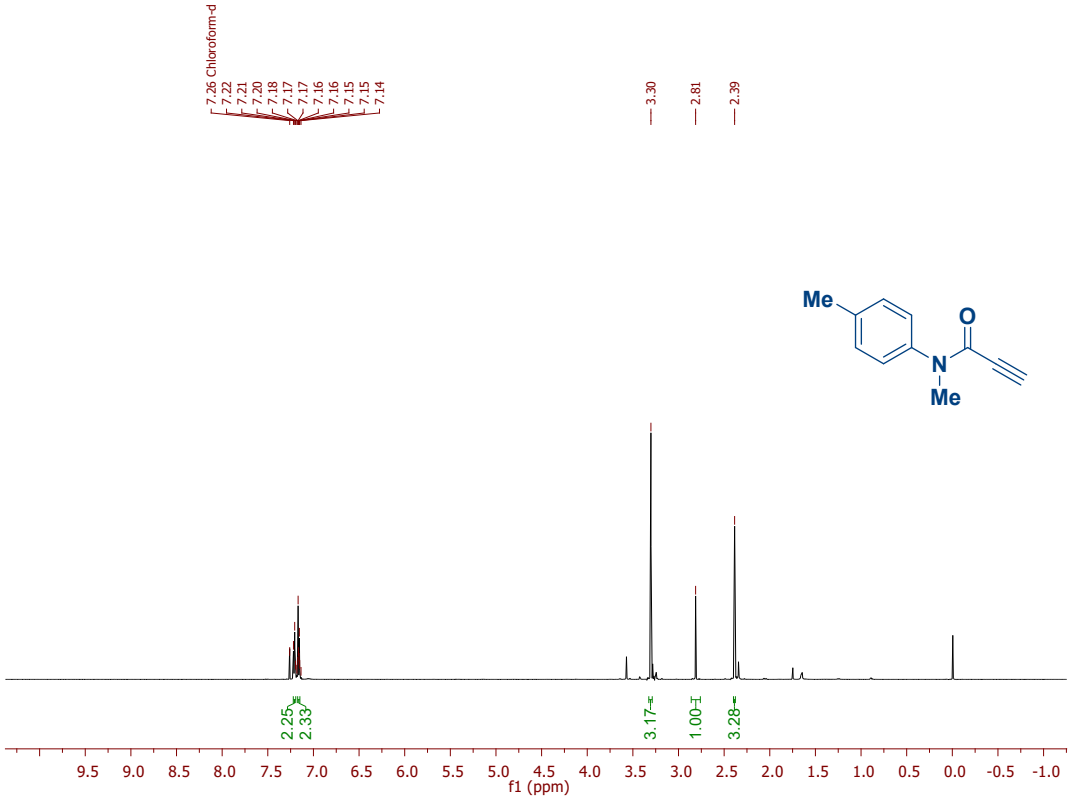
^{1}H NMR (101 MHz) spectrum of **2a** in $CDCl_3$



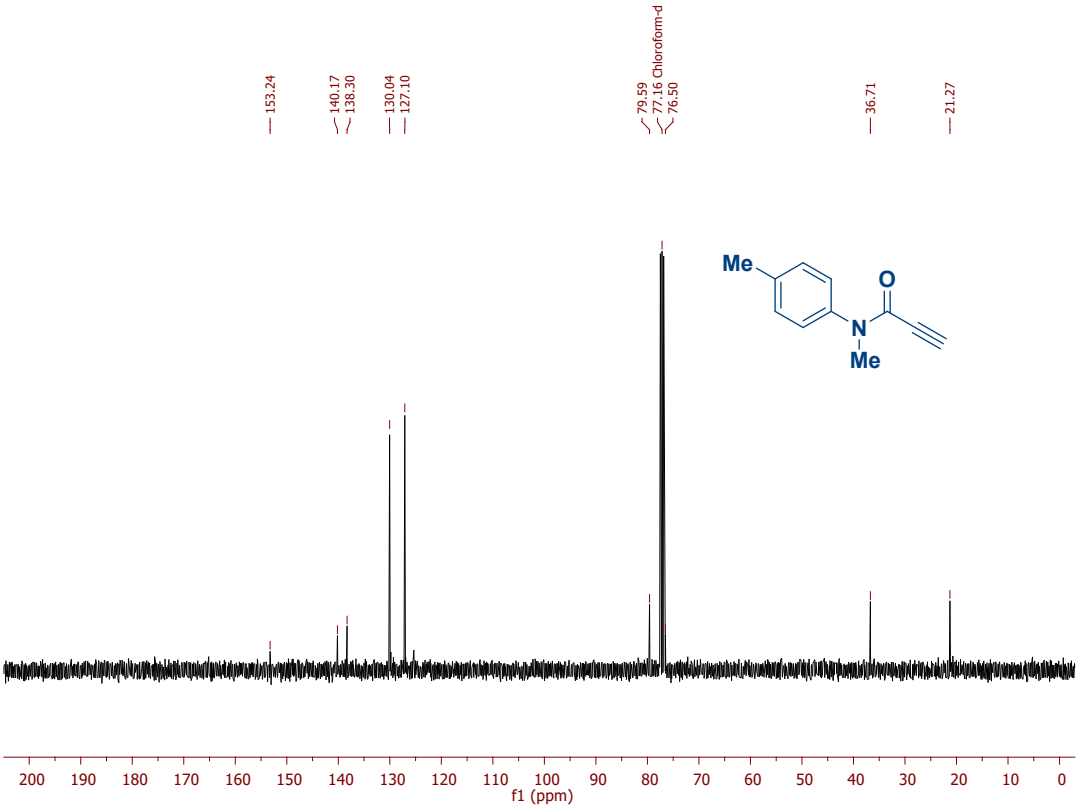
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **2a** in $CDCl_3$



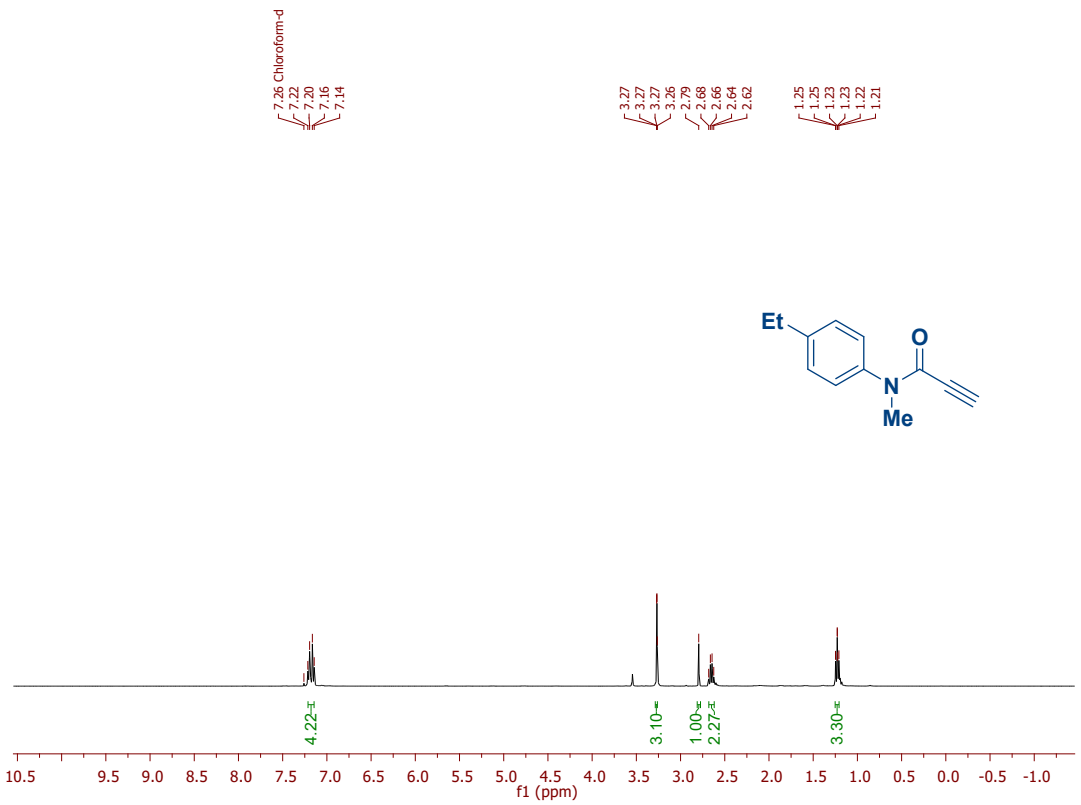
^{1}H NMR (101 MHz) spectrum of **2b** in $CDCl_3$



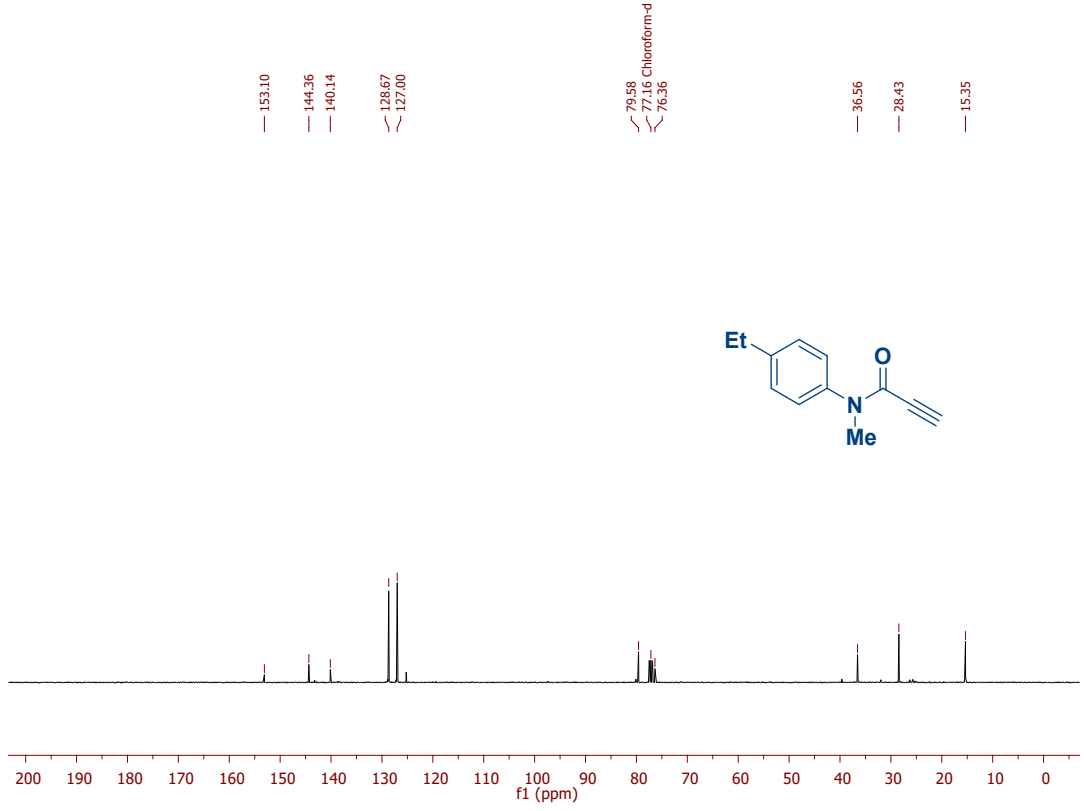
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **2b** in $CDCl_3$



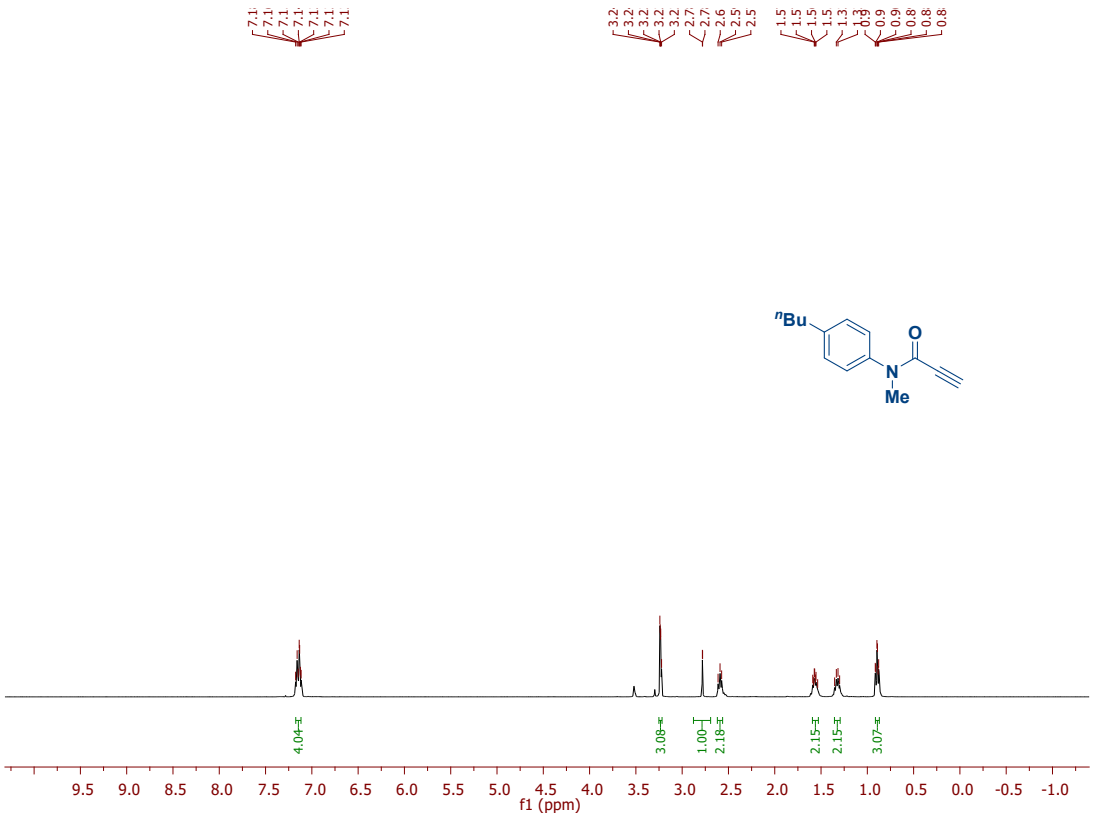
^{1}H NMR (101 MHz) spectrum of **2c** in $CDCl_3$



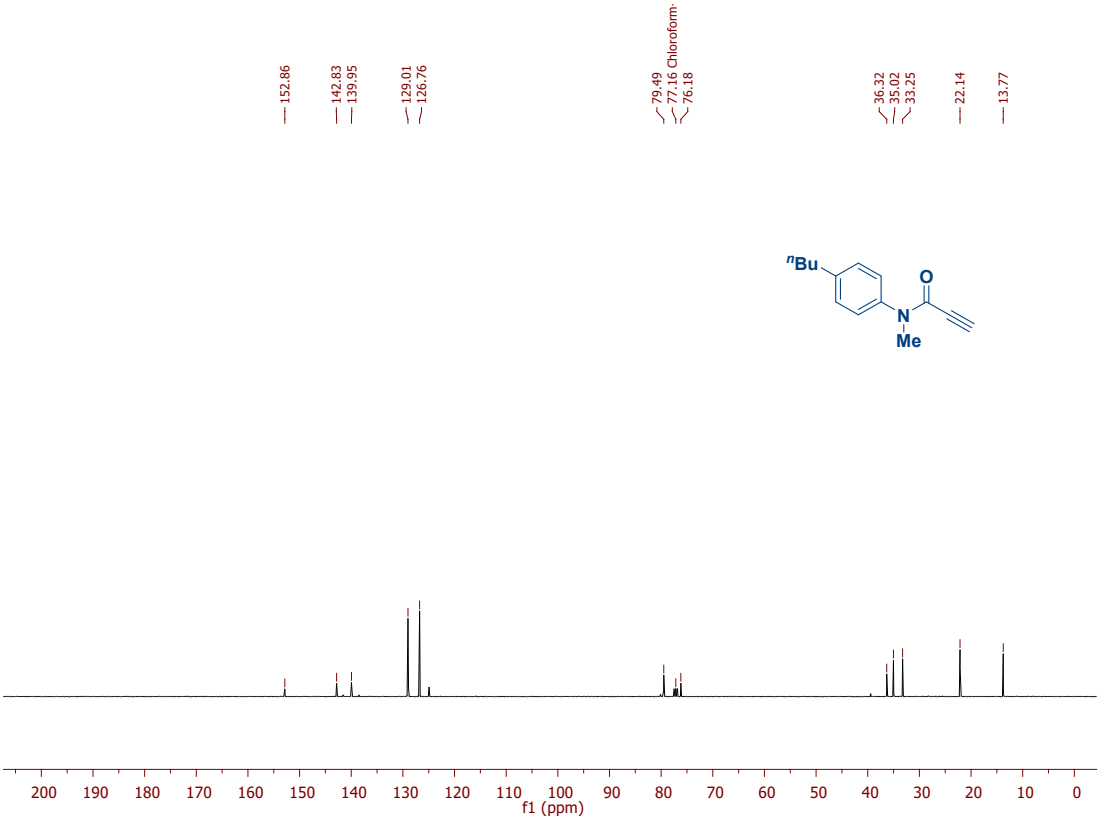
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **2c** in $CDCl_3$



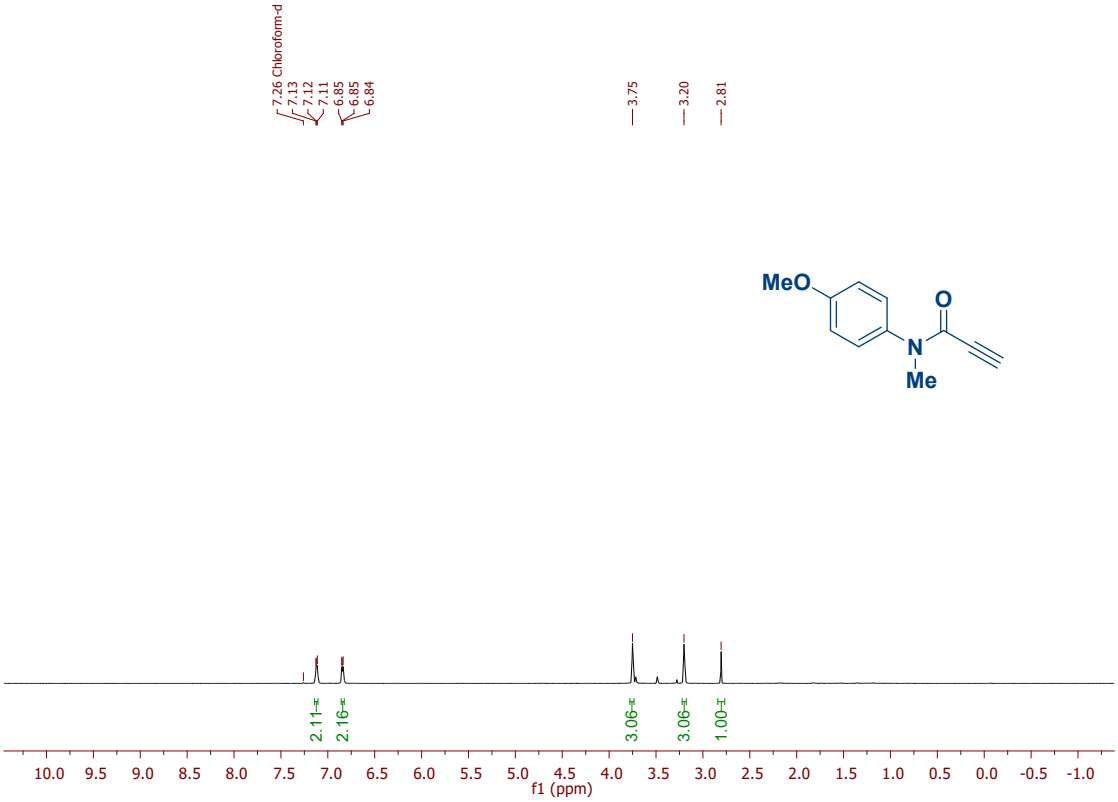
^{1}H NMR (101 MHz) spectrum of **2d** in $CDCl_3$



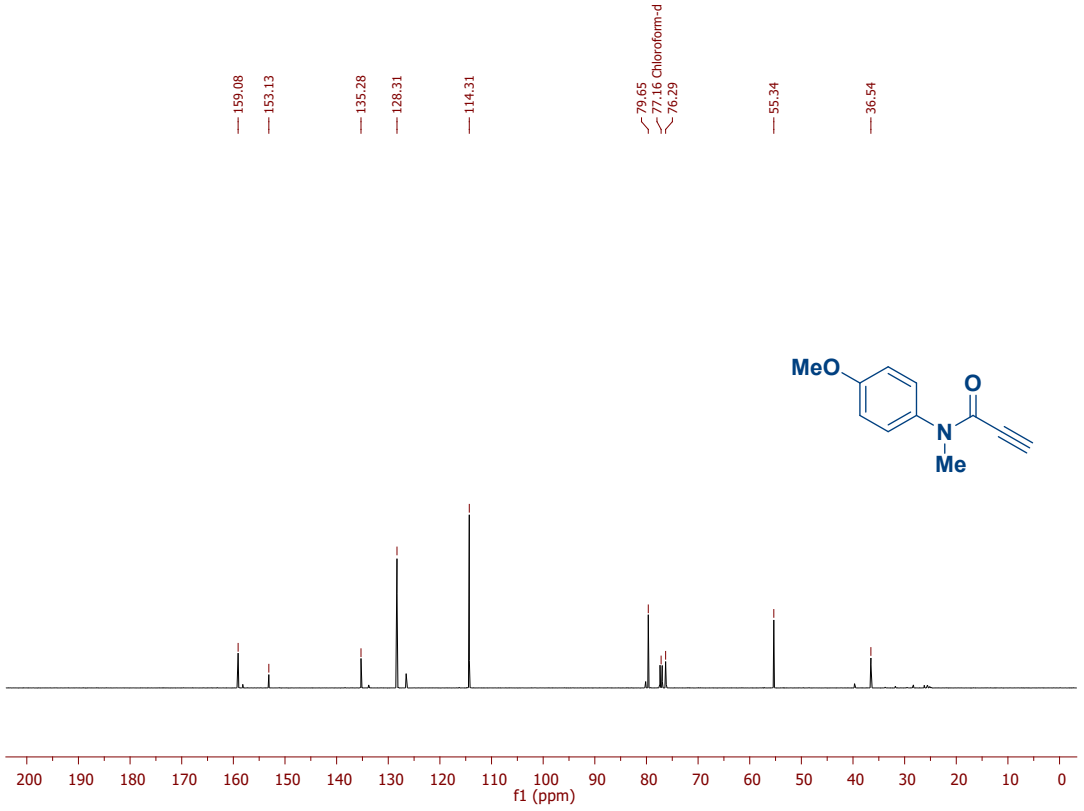
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **2d** in $CDCl_3$



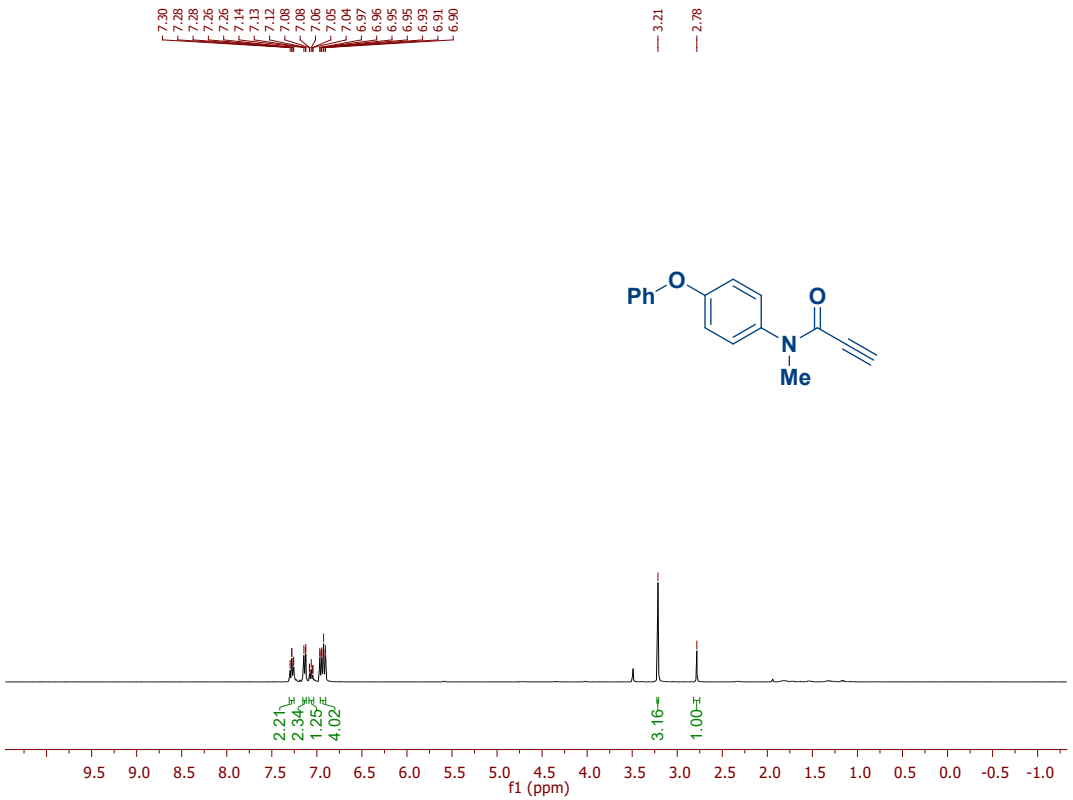
^{1}H NMR (101 MHz) spectrum of **2e** in $CDCl_3$



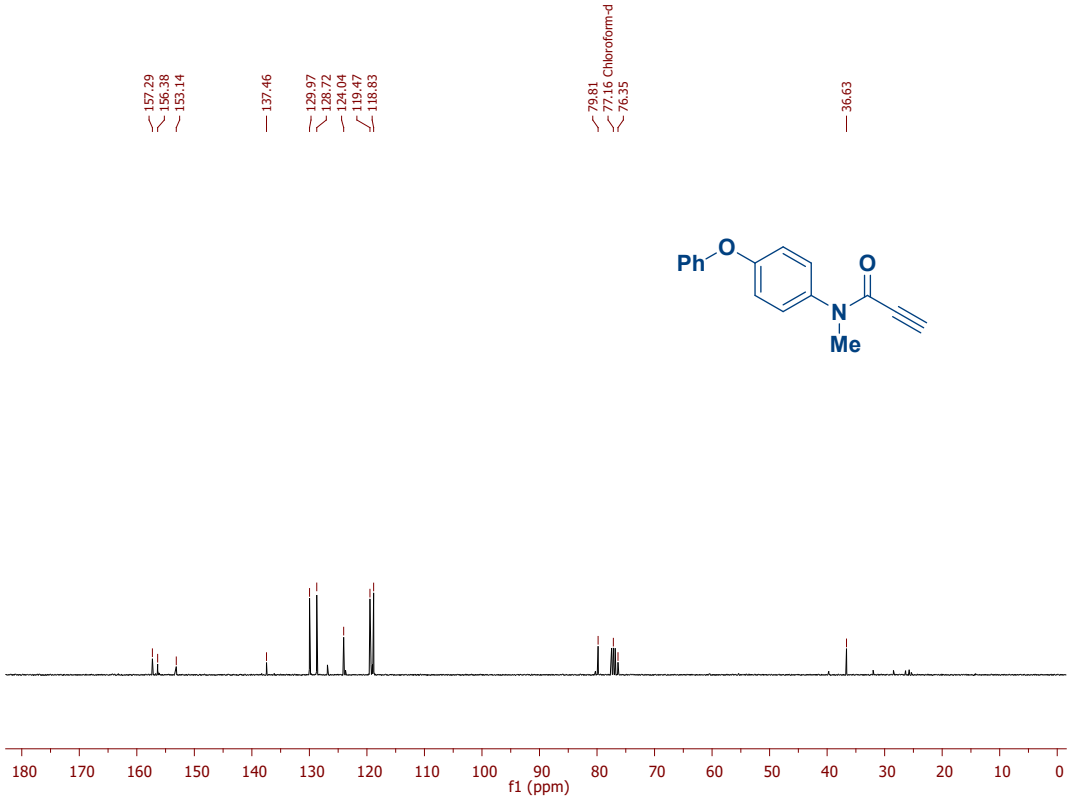
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **2e** in $CDCl_3$



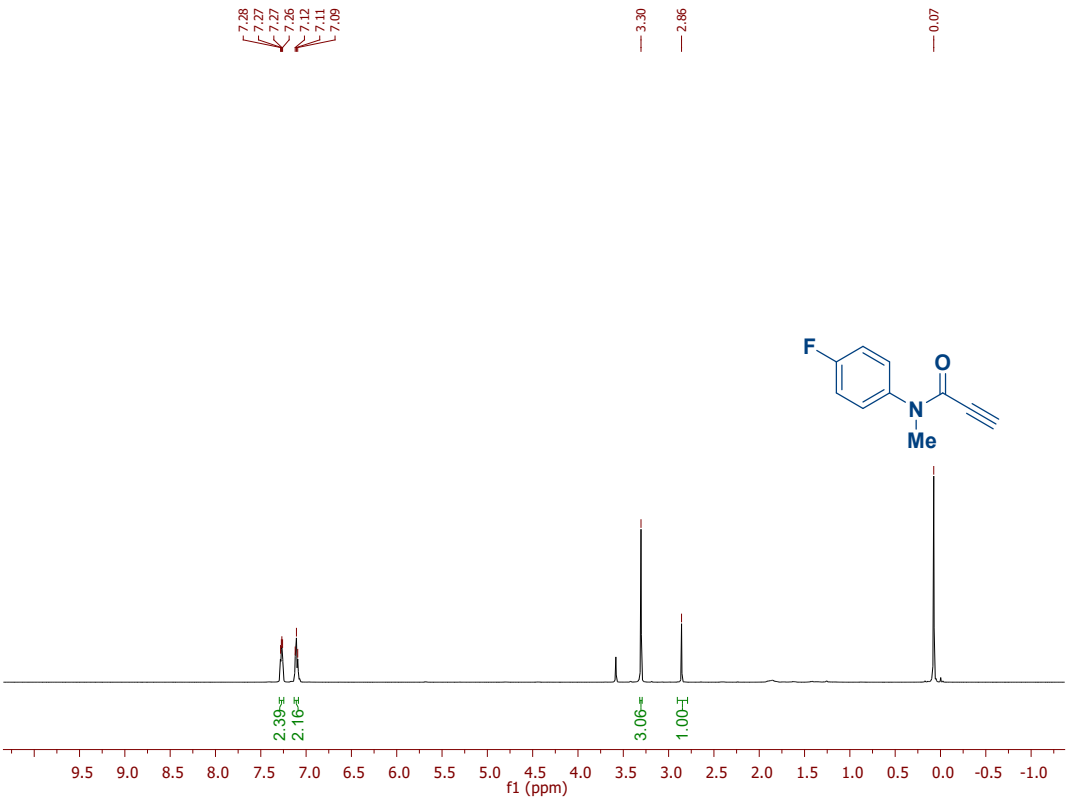
^{1}H NMR (101 MHz) spectrum of **2f** in $CDCl_3$



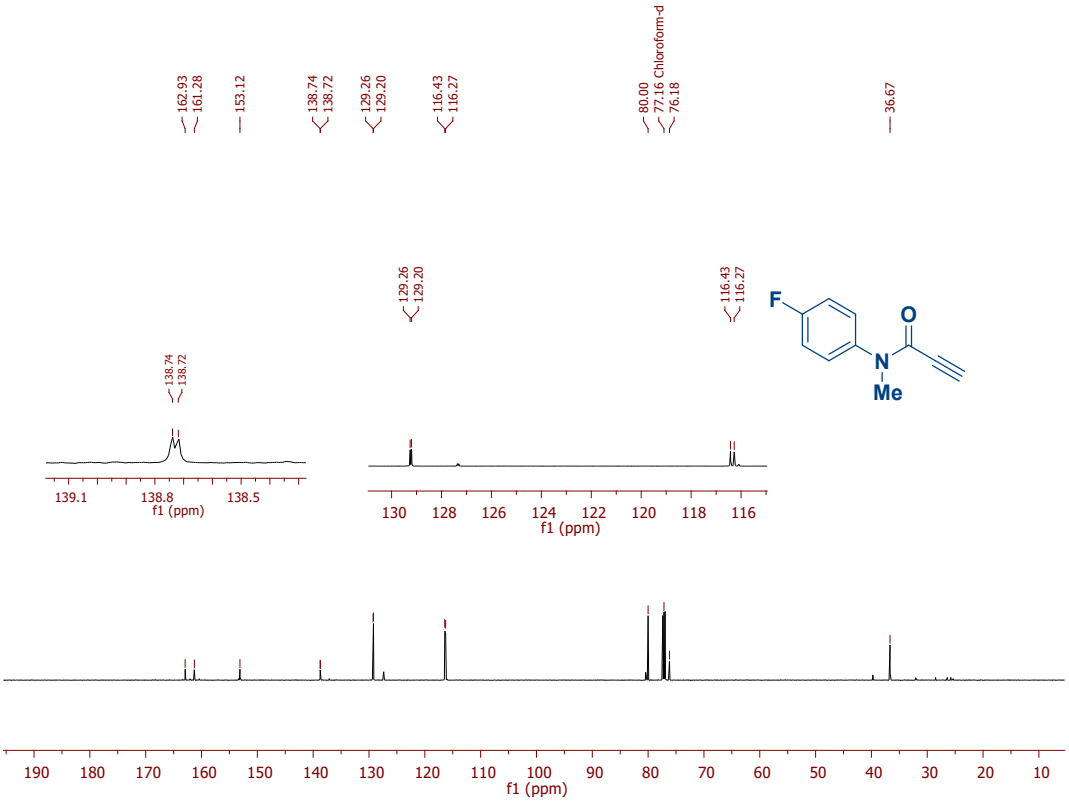
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **2f** in $CDCl_3$



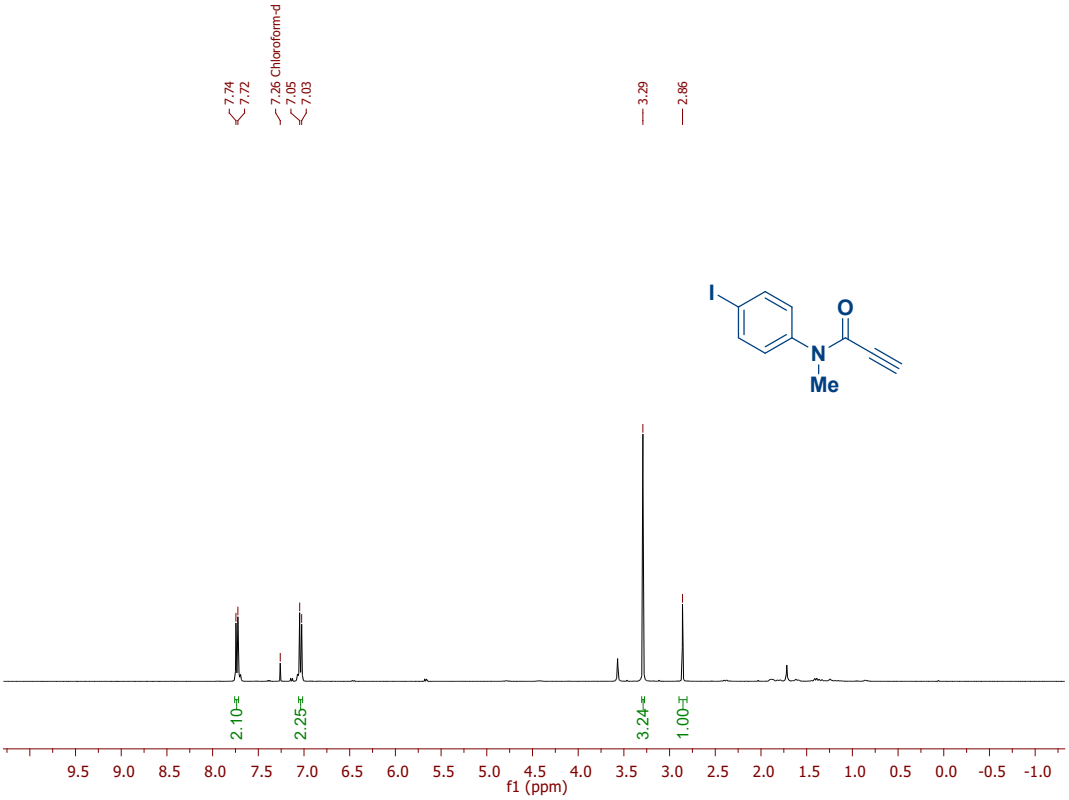
^{1}H NMR (101 MHz) spectrum of **2g** in $CDCl_3$



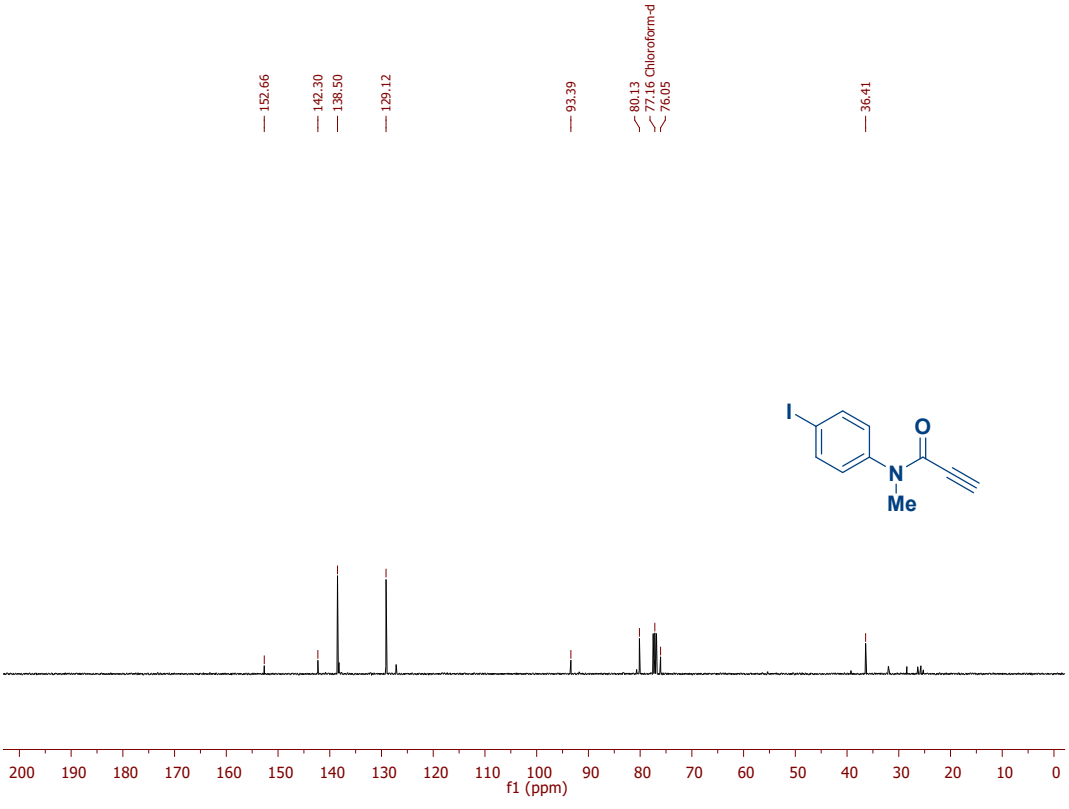
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **2g** in $CDCl_3$



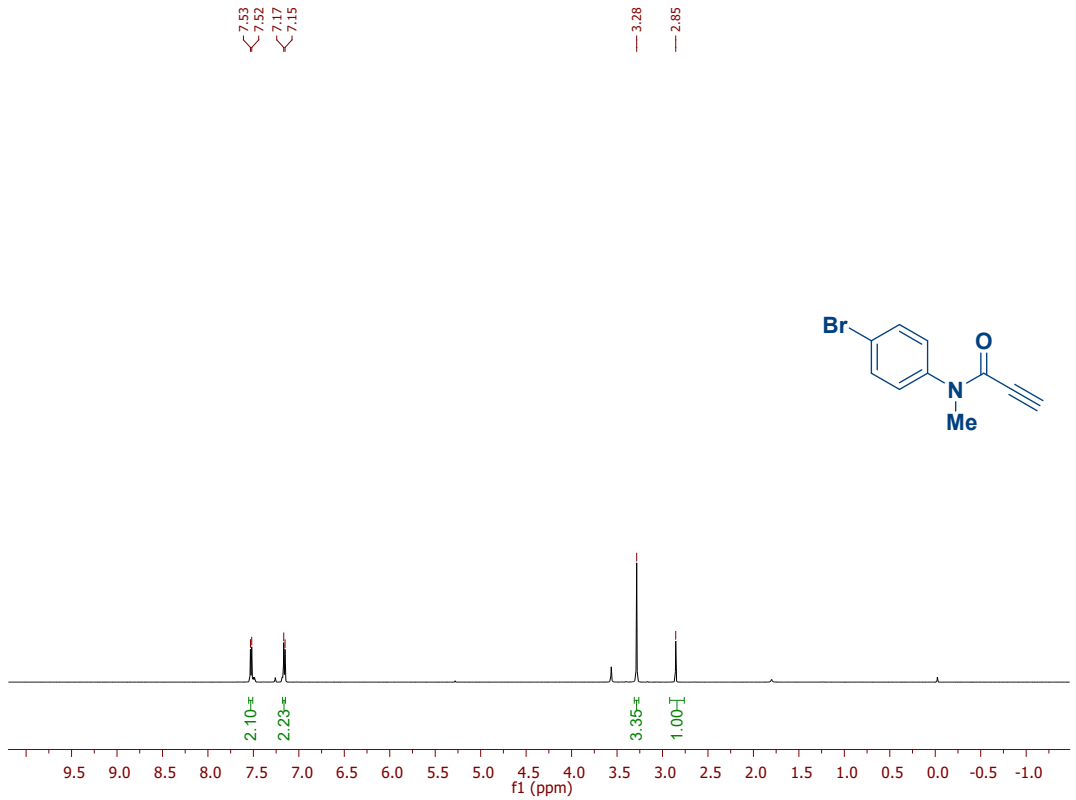
^{1}H NMR (101 MHz) spectrum of **2h** in $CDCl_3$



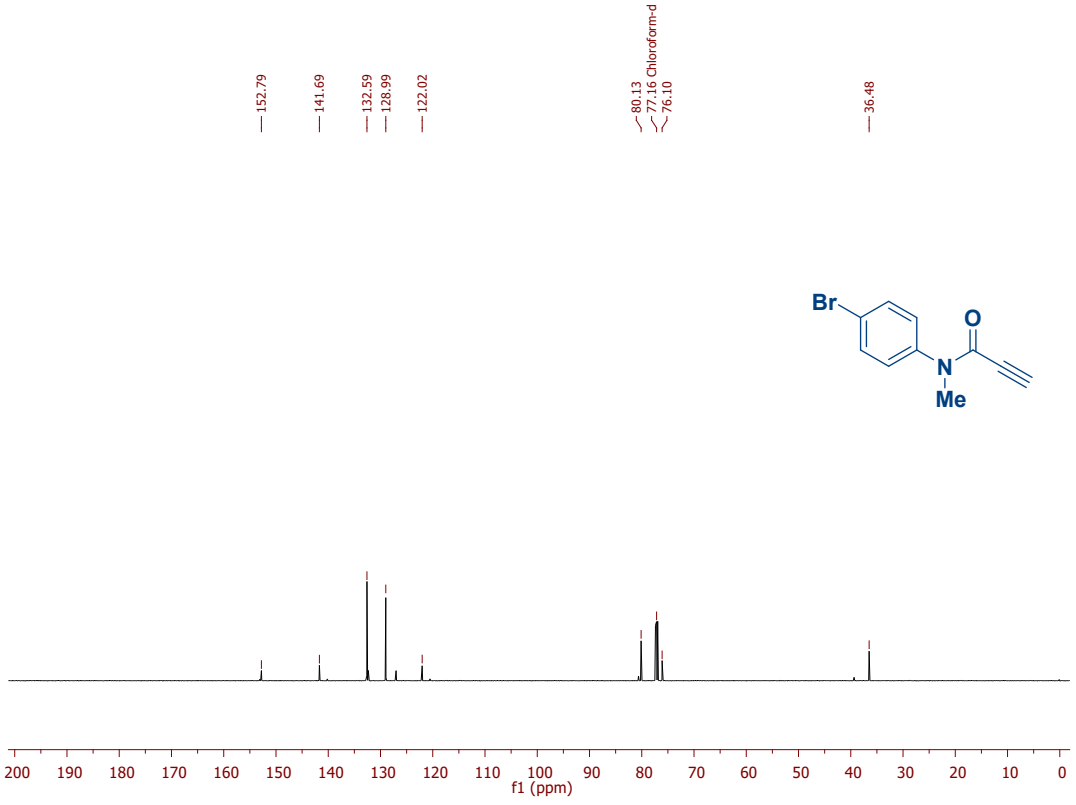
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **2h** in $CDCl_3$



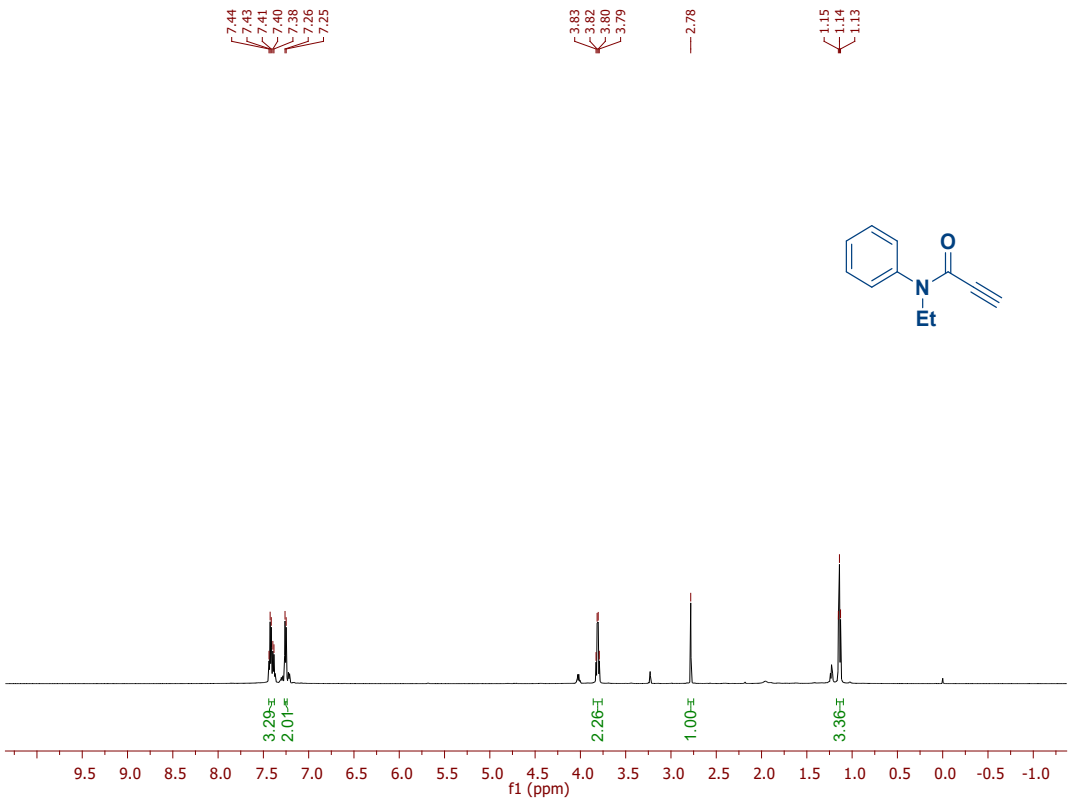
^{1}H NMR (101 MHz) spectrum of **2i** in $CDCl_3$



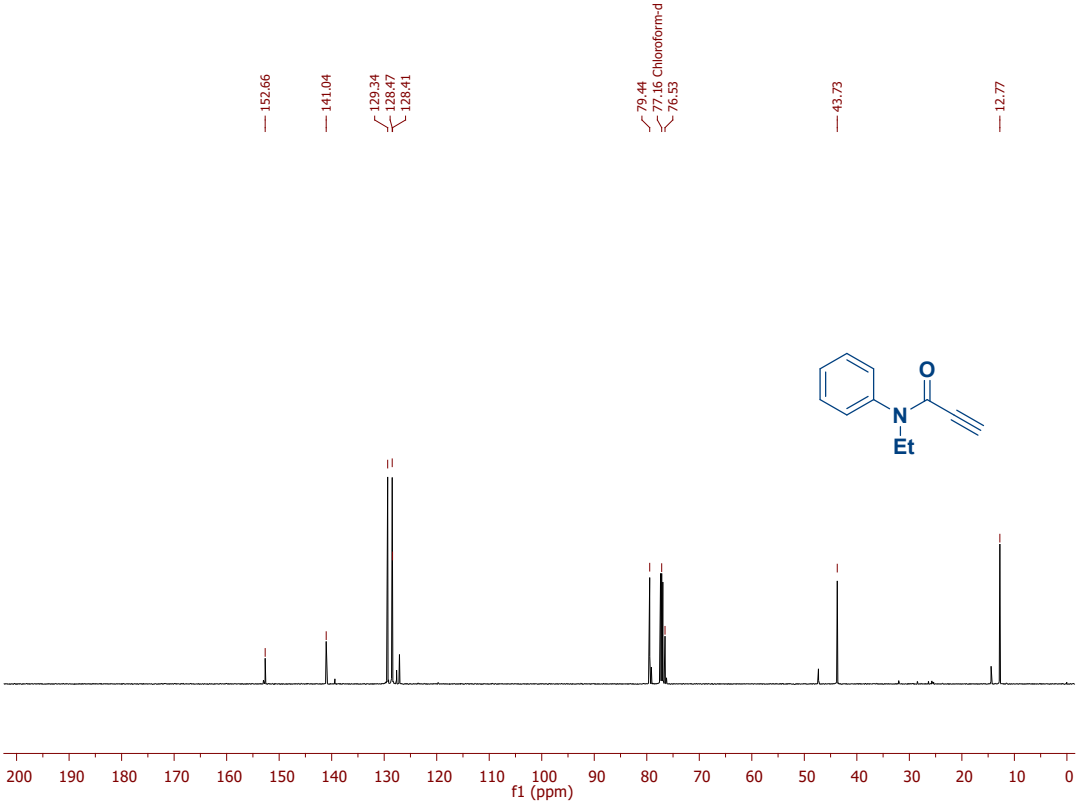
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **2i** in $CDCl_3$



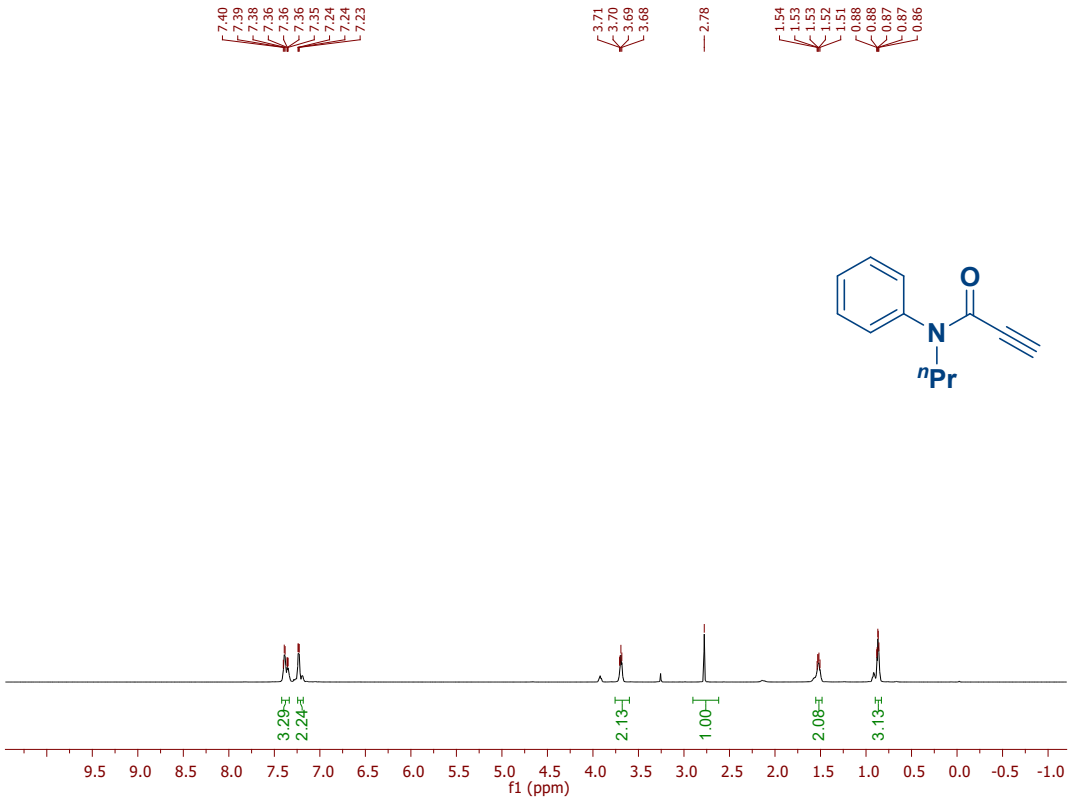
^{1}H NMR (101 MHz) spectrum of **2j** in $CDCl_3$



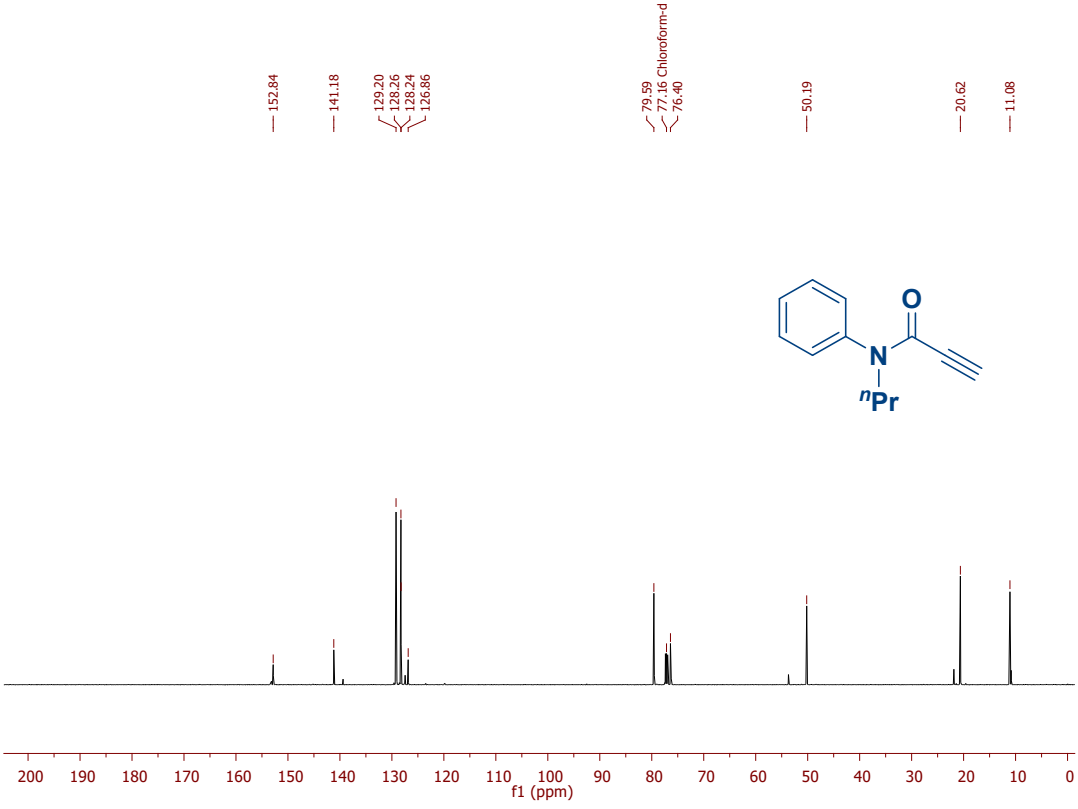
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **2j** in $CDCl_3$



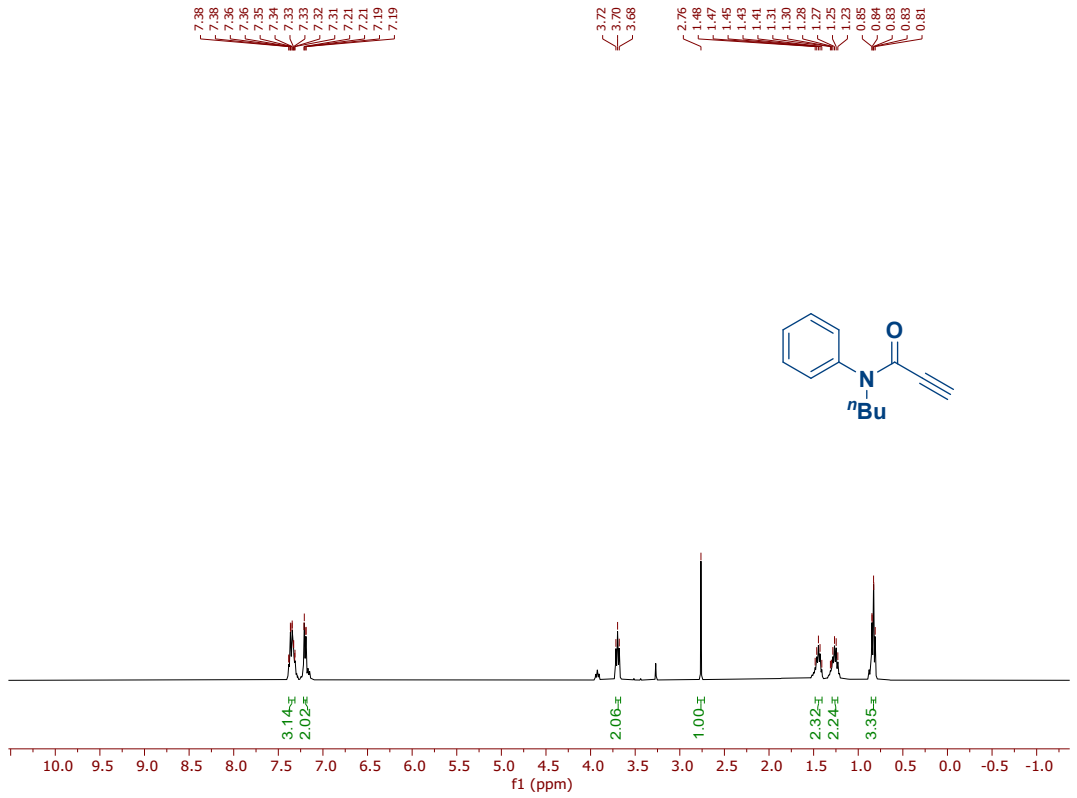
^{1}H NMR (101 MHz) spectrum of **2k** in $CDCl_3$



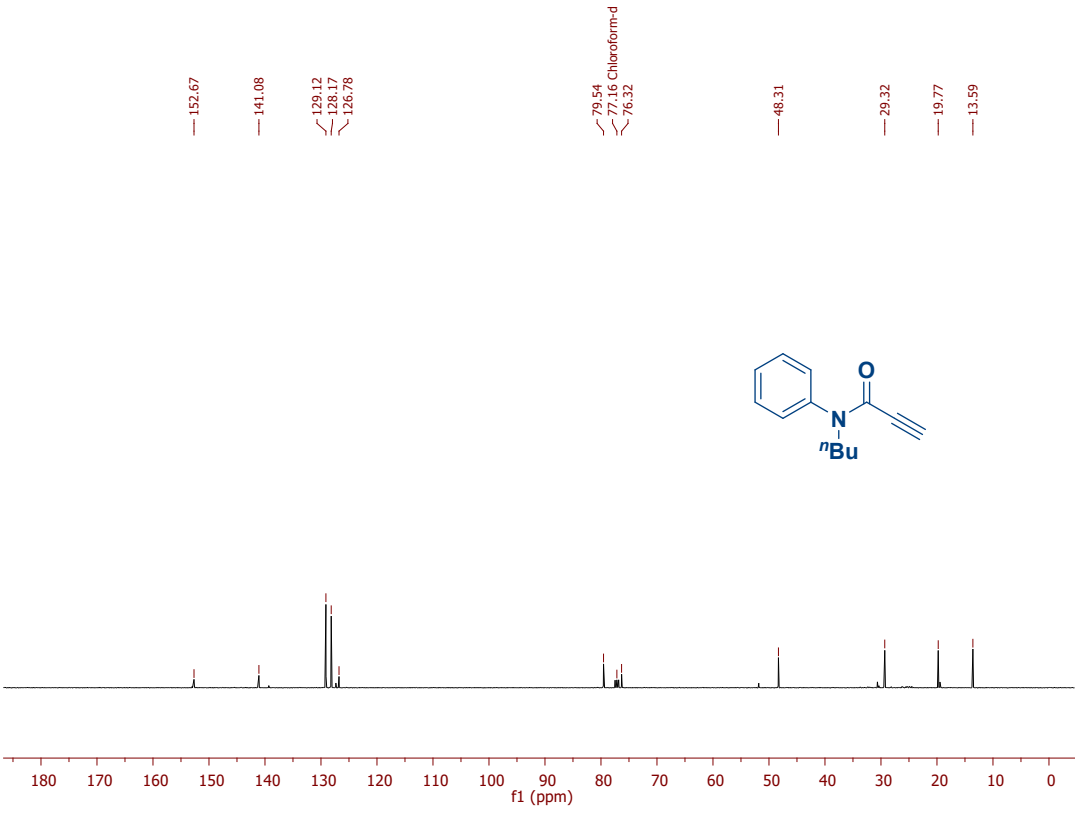
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **2k** in $CDCl_3$



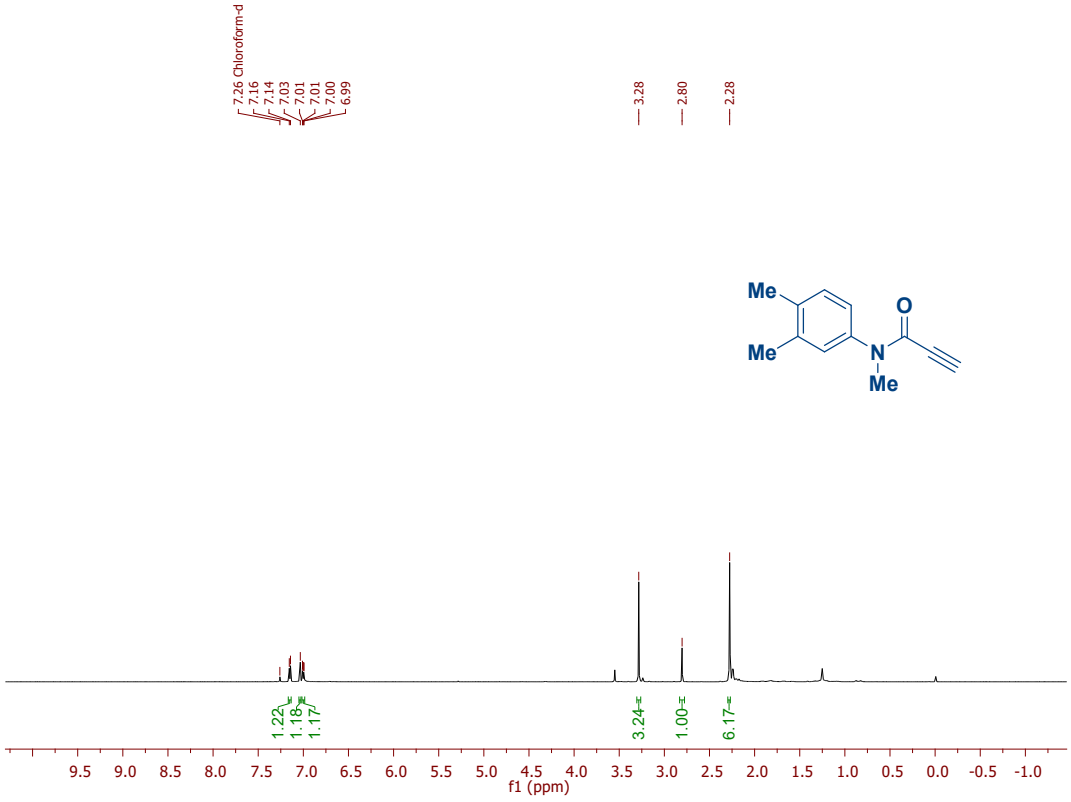
^{1}H NMR (101 MHz) spectrum of **2l** in $CDCl_3$



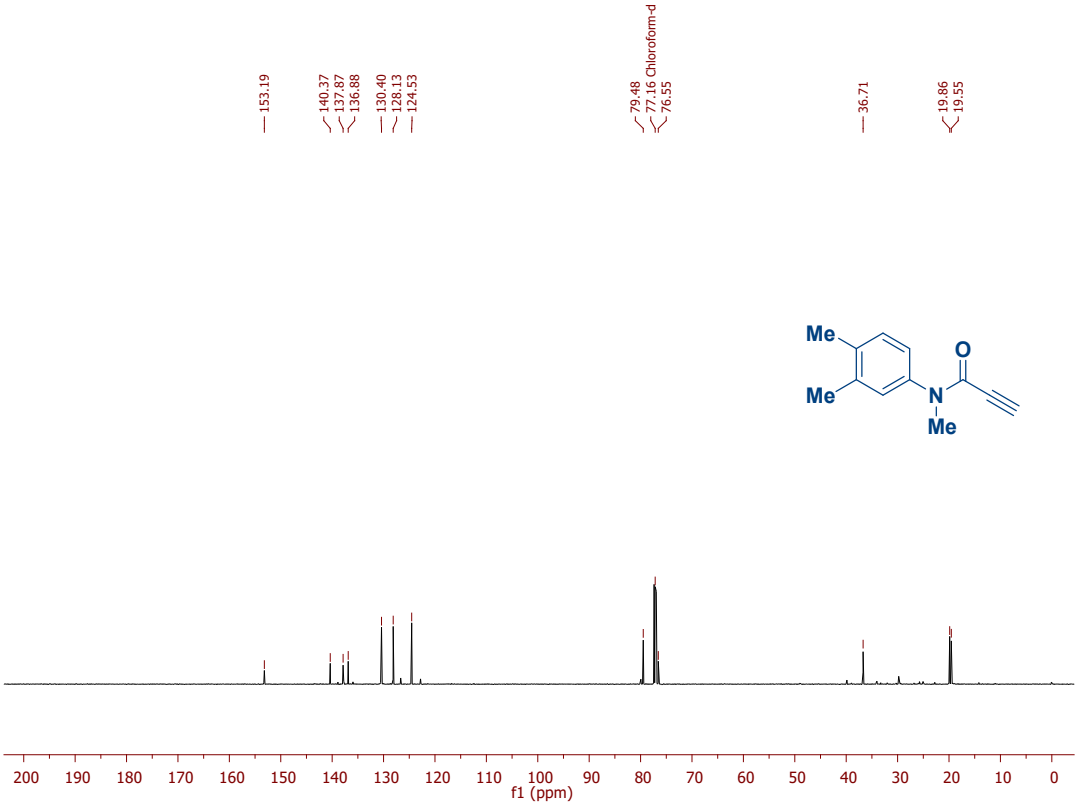
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **2l** in $CDCl_3$



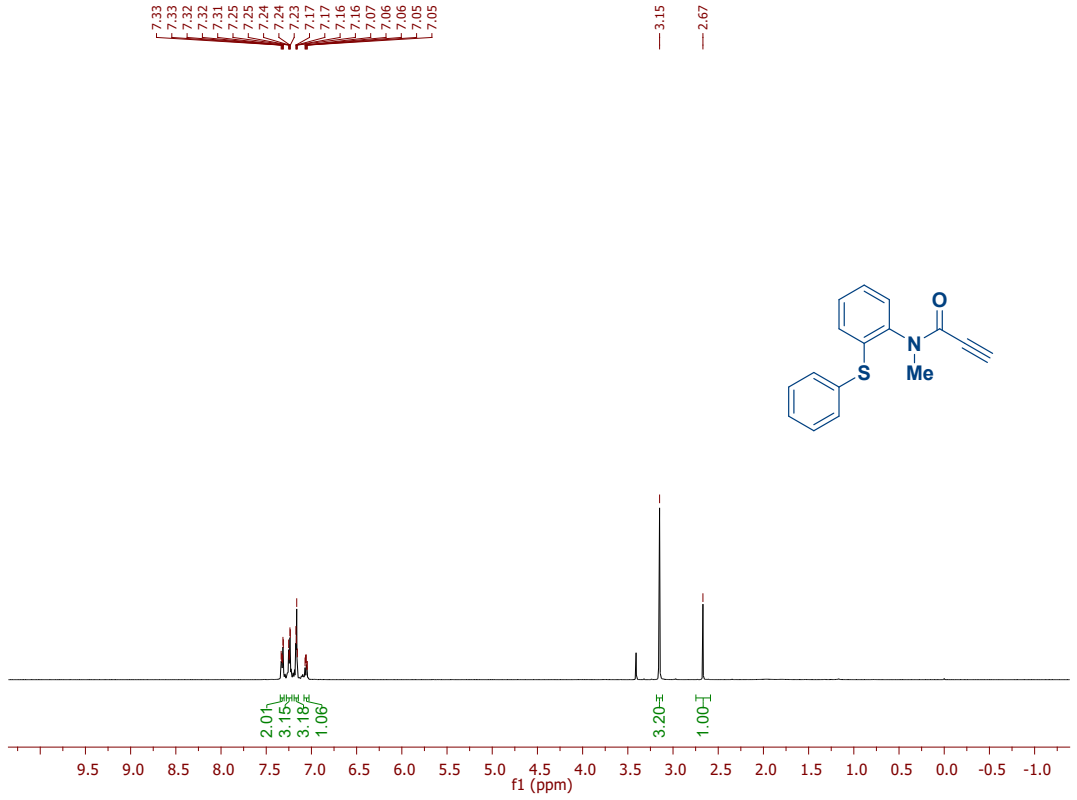
^{1}H NMR (101 MHz) spectrum of **2m** in $CDCl_3$



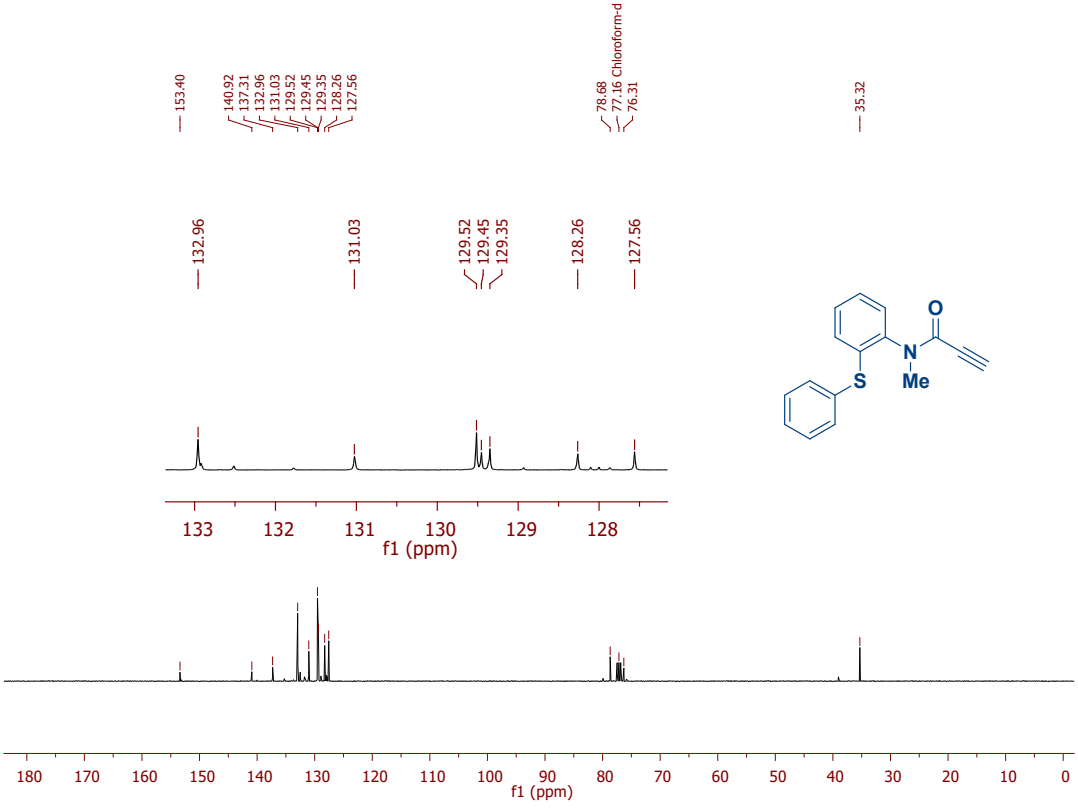
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **2m** in $CDCl_3$



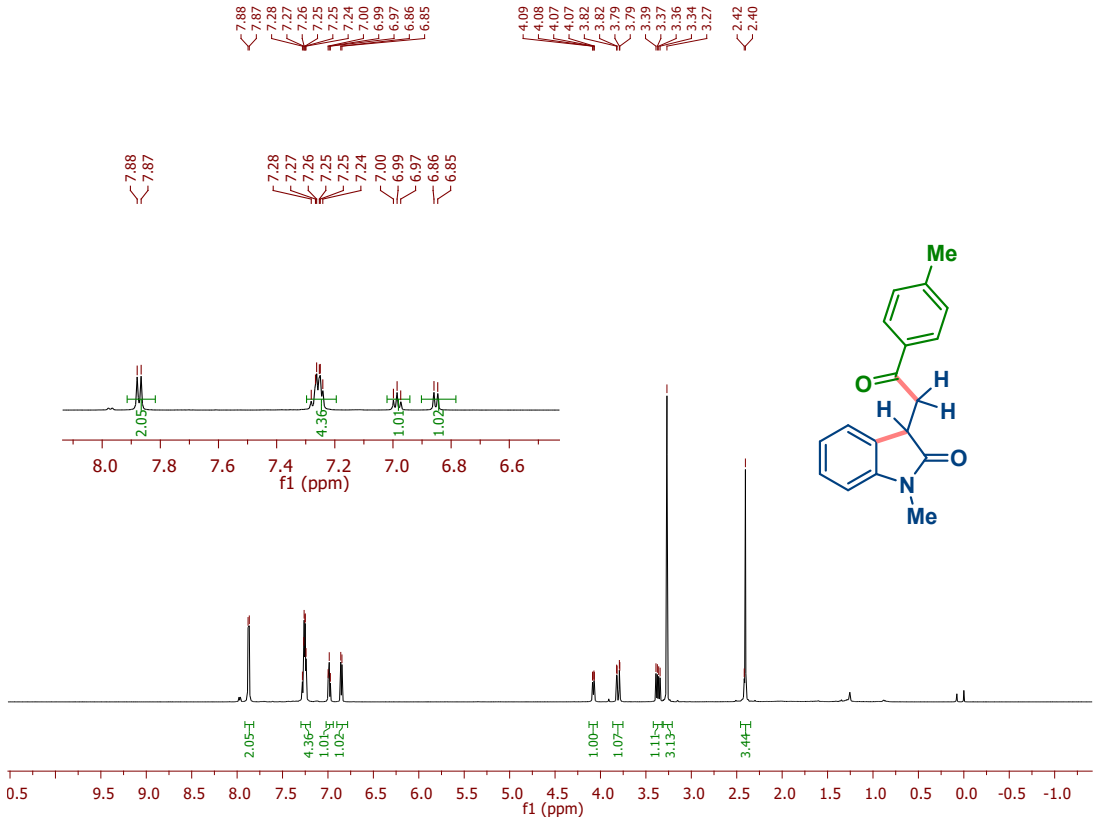
^{1}H NMR (101 MHz) spectrum of **2n** in $CDCl_3$



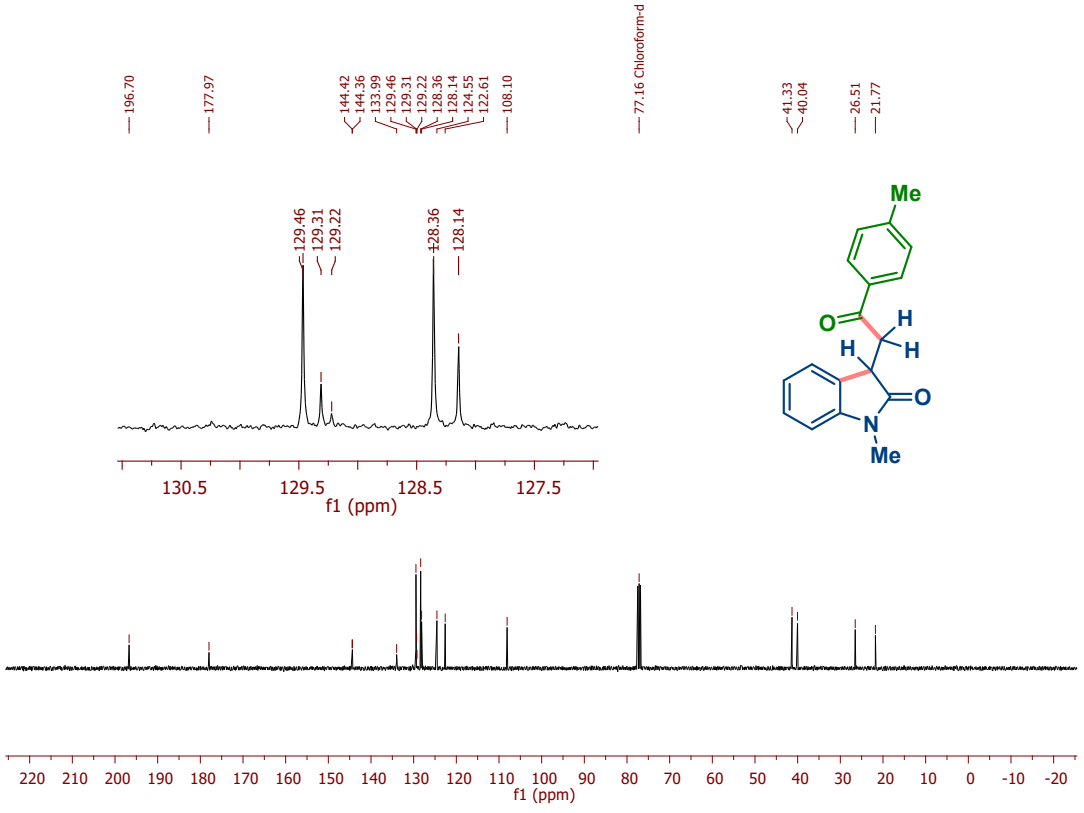
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **2n** in $CDCl_3$



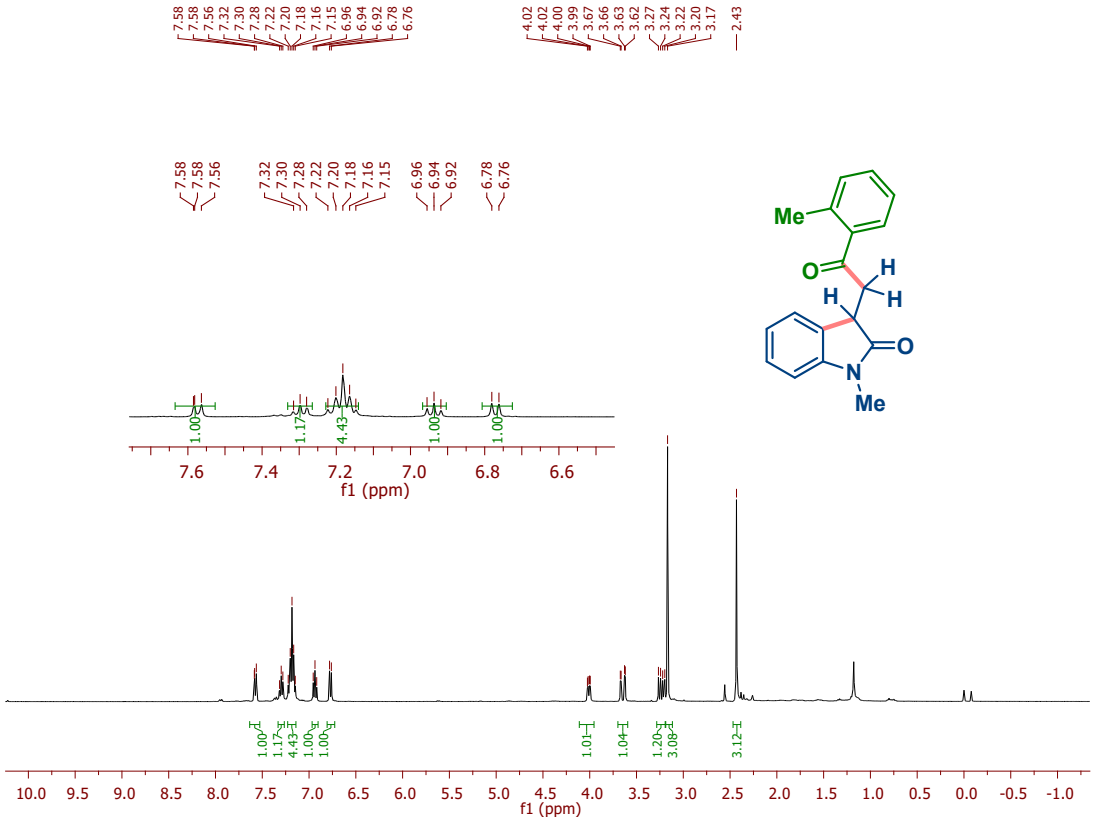
^{1}H NMR (600 MHz) spectrum of **3aa** in $CDCl_3$



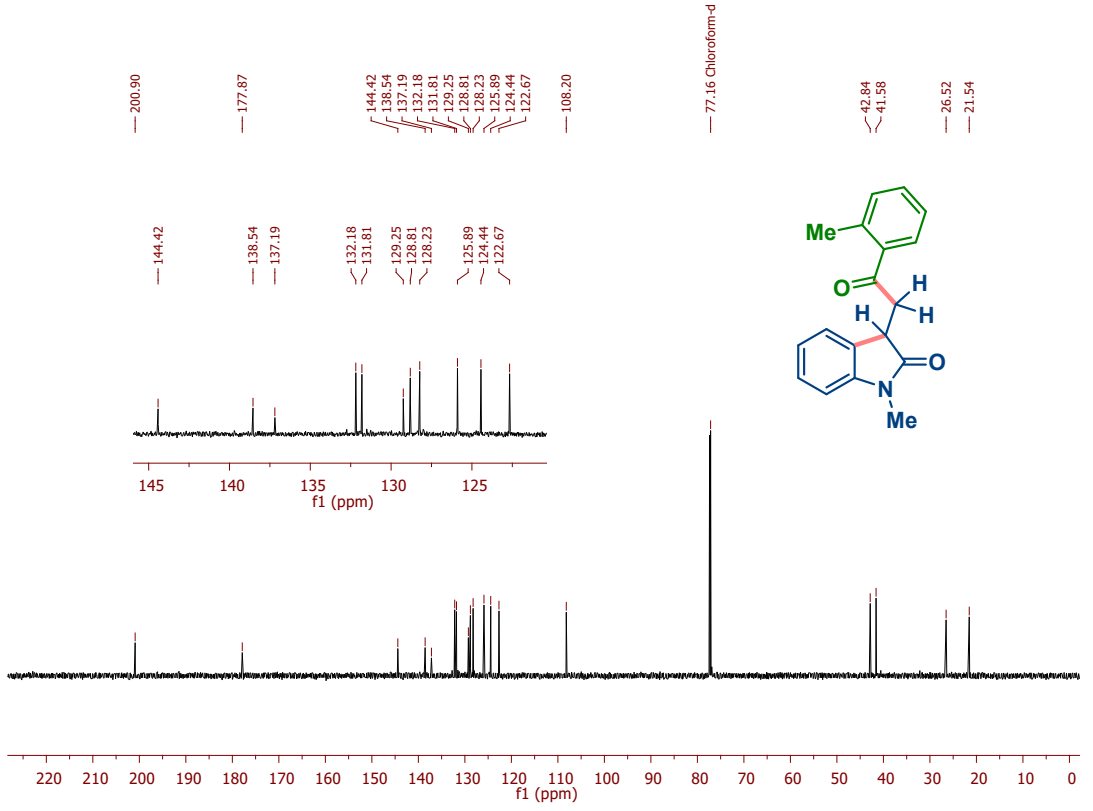
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3aa** in $CDCl_3$



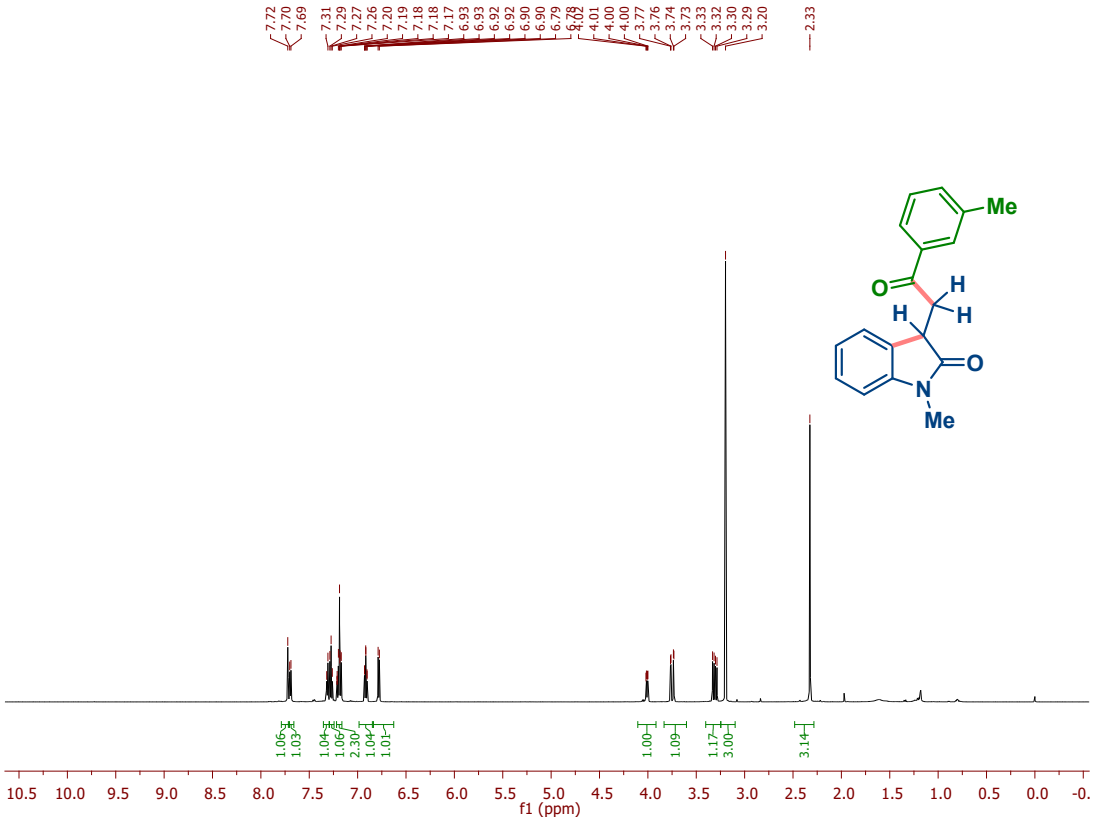
^{1}H NMR (400 MHz) spectrum of **3ba** in $CDCl_3$



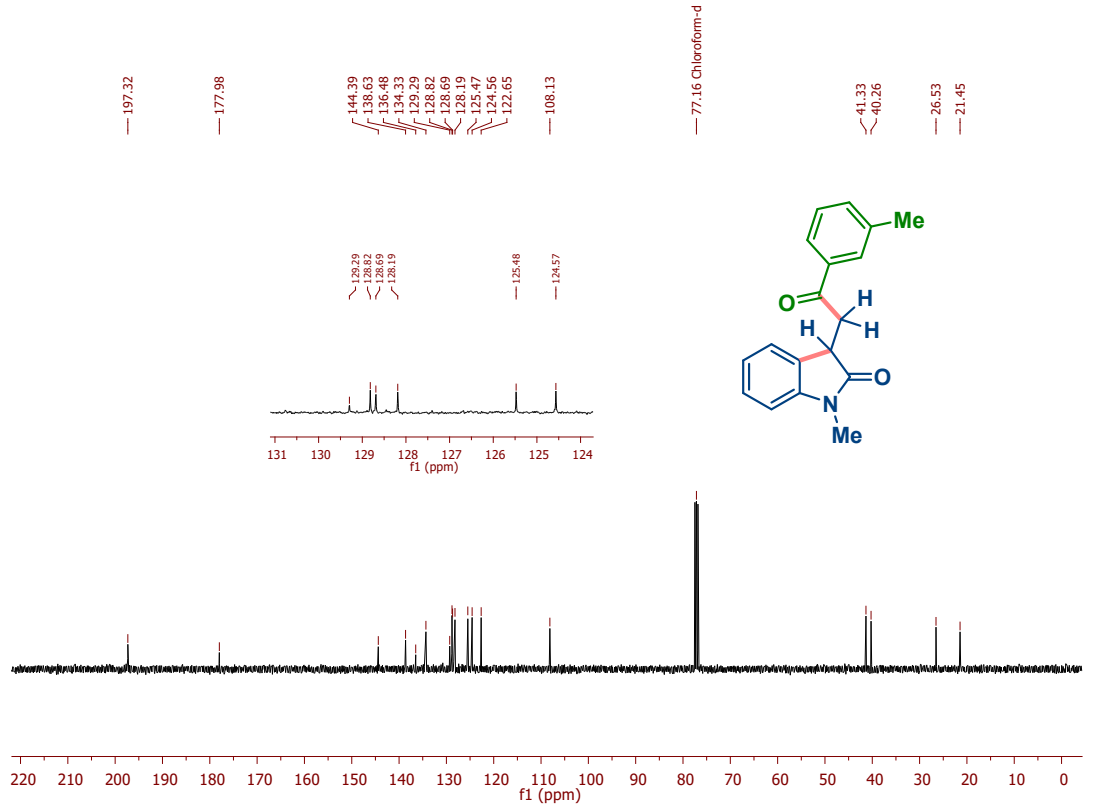
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ba** in $CDCl_3$



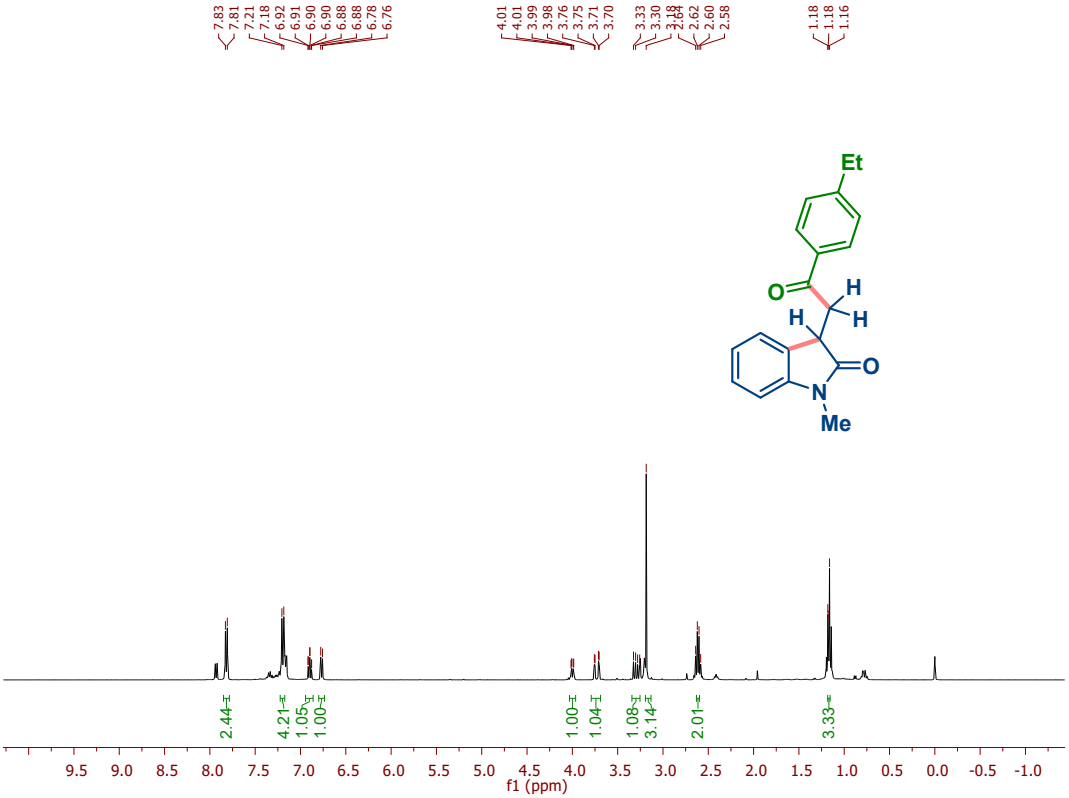
^{1}H NMR (600 MHz) spectrum of **3ca** in $CDCl_3$



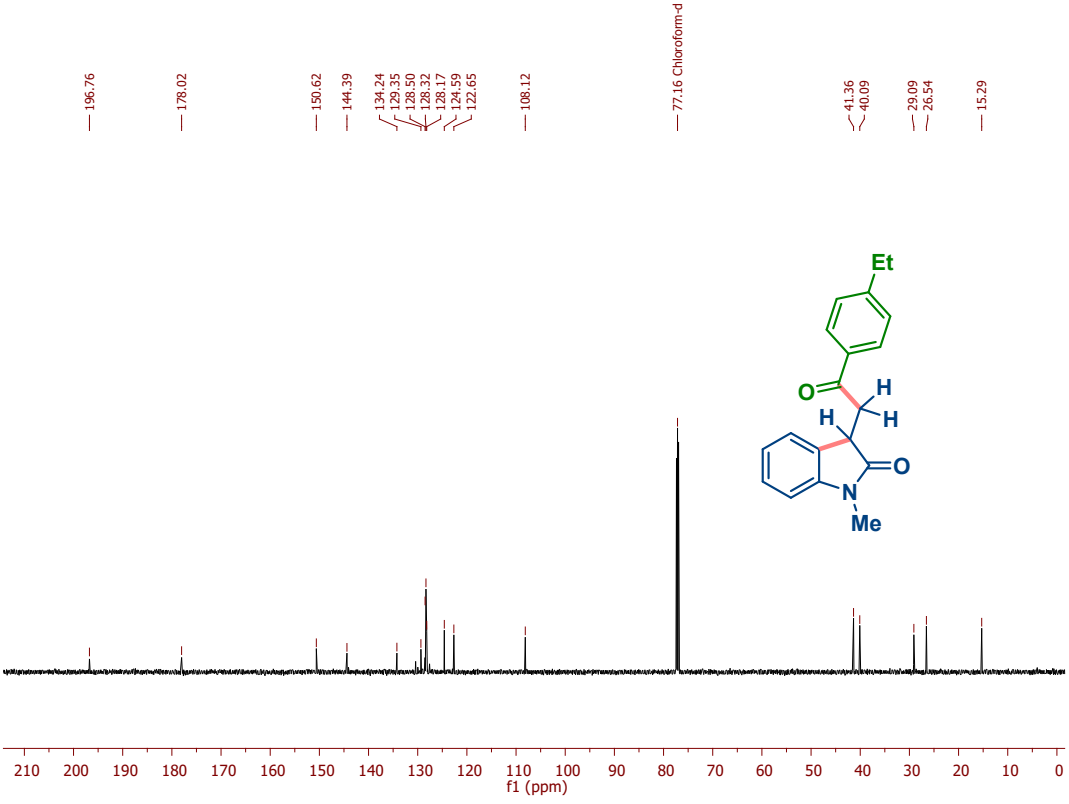
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ca** in $CDCl_3$



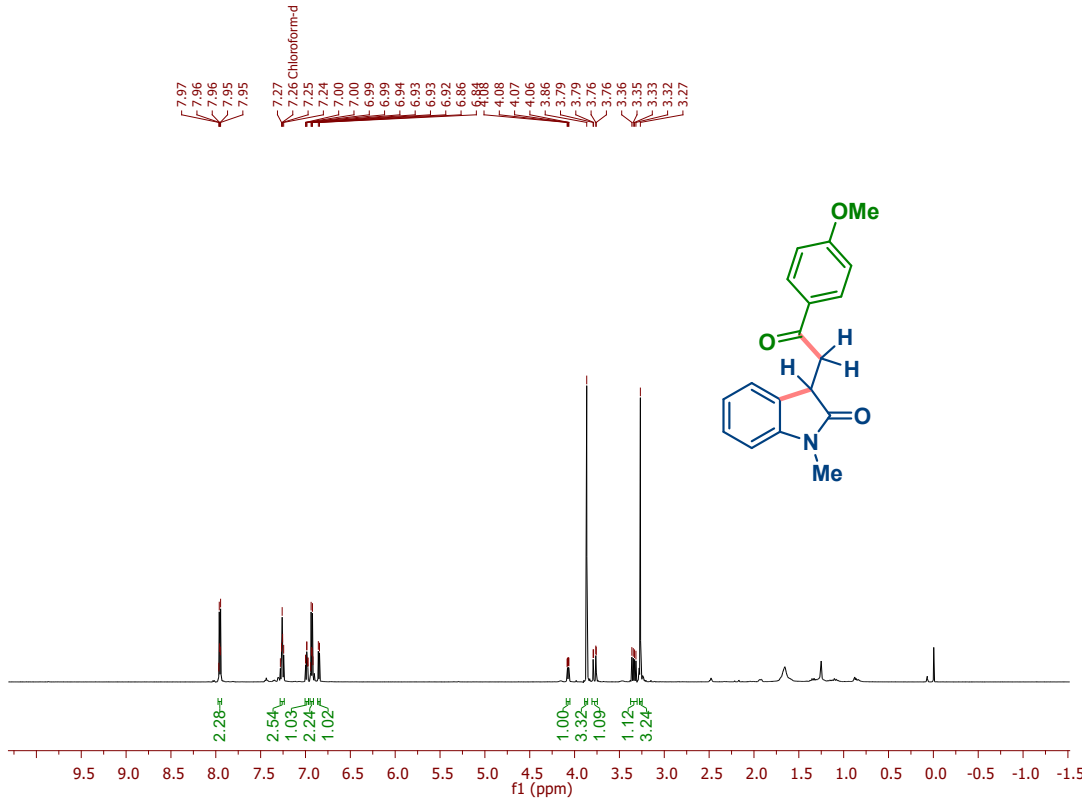
^{1}H NMR (600 MHz) spectrum of **3da** in $CDCl_3$



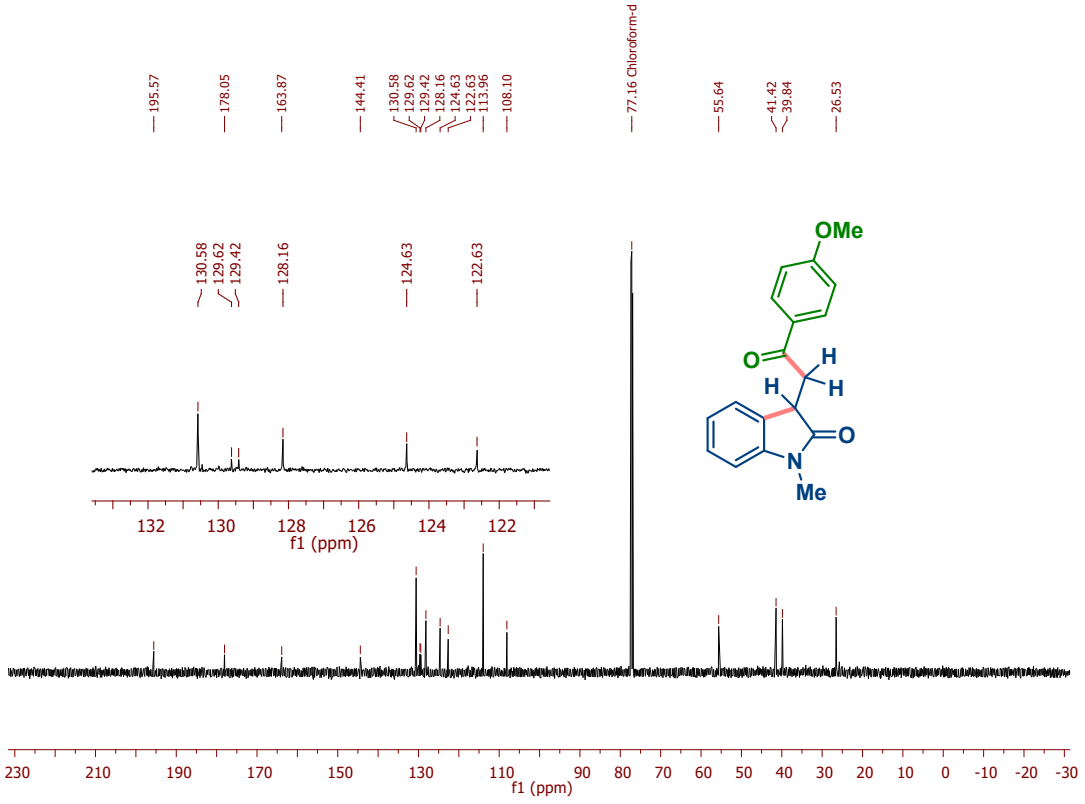
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3da** in $CDCl_3$



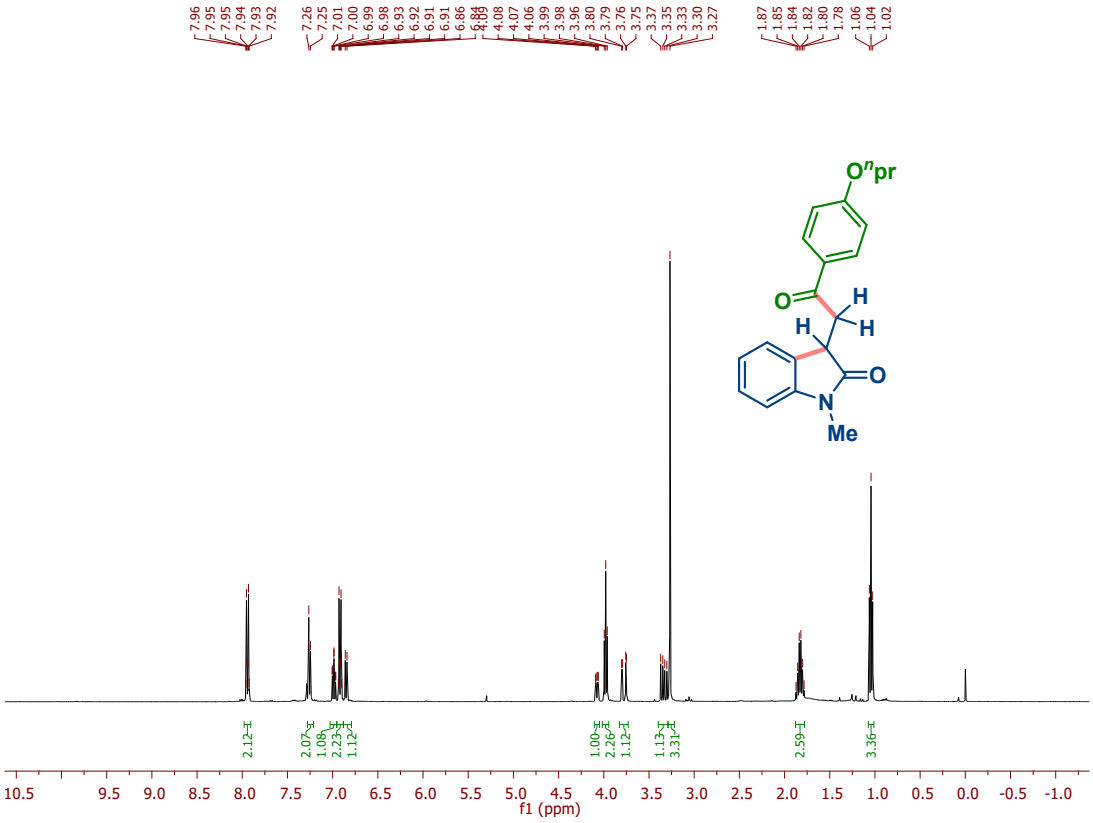
^{1}H NMR (600 MHz) spectrum of **3ea** in $CDCl_3$



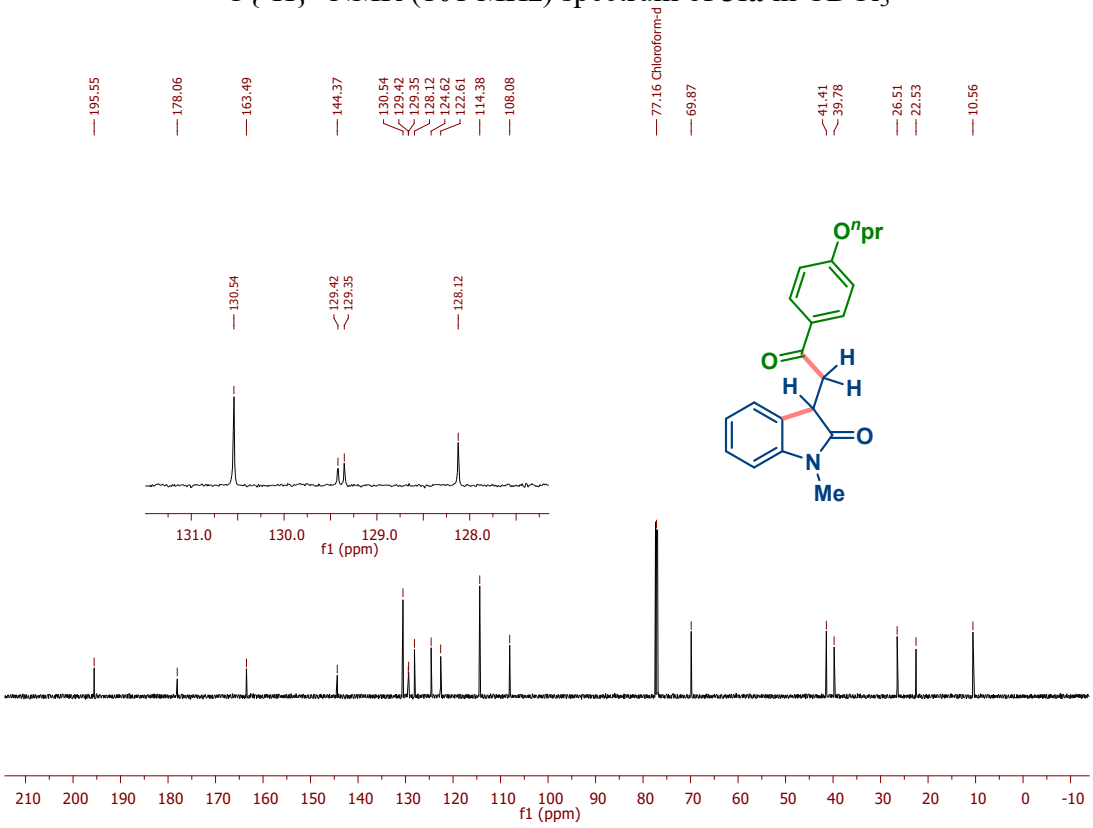
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3ea** in $CDCl_3$



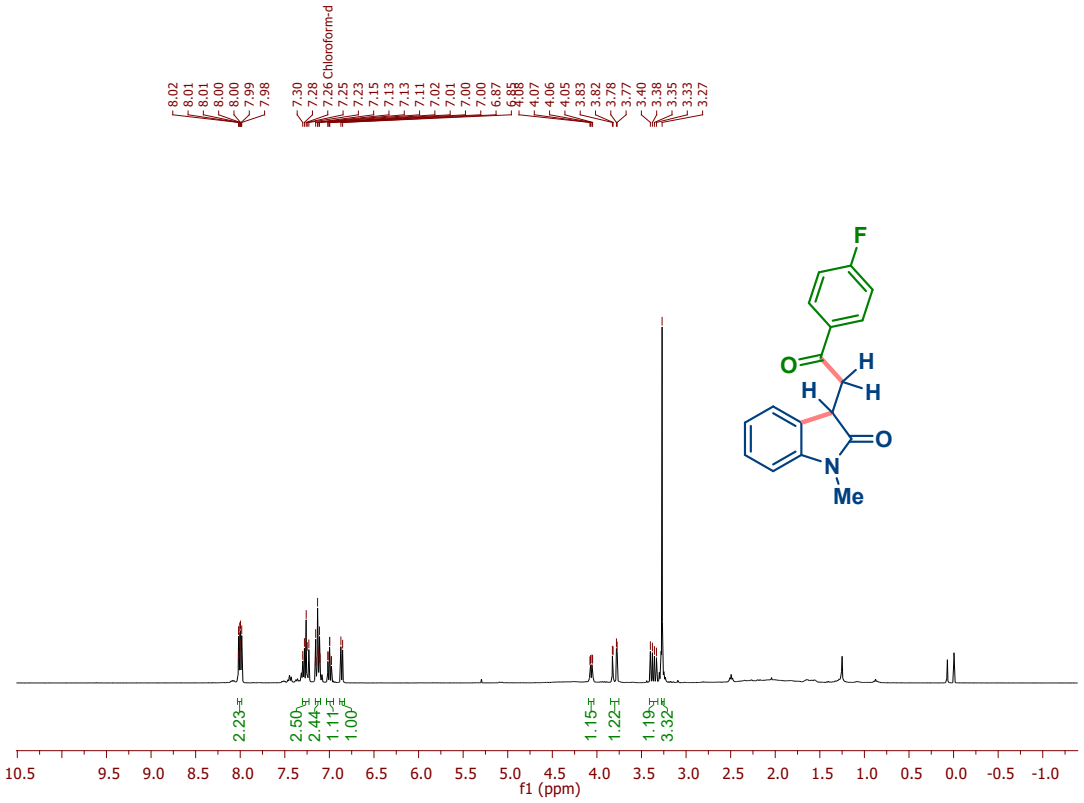
^{1}H NMR (400 MHz) spectrum of **3fa** in $CDCl_3$



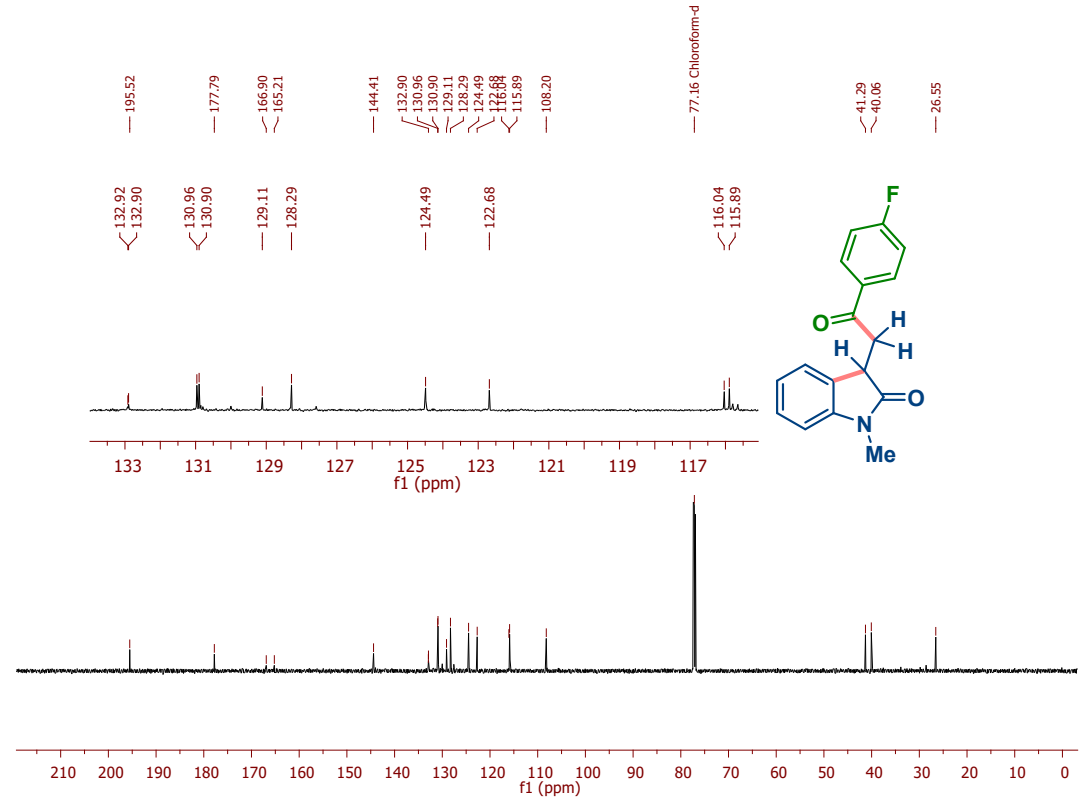
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3fa** in $CDCl_3$



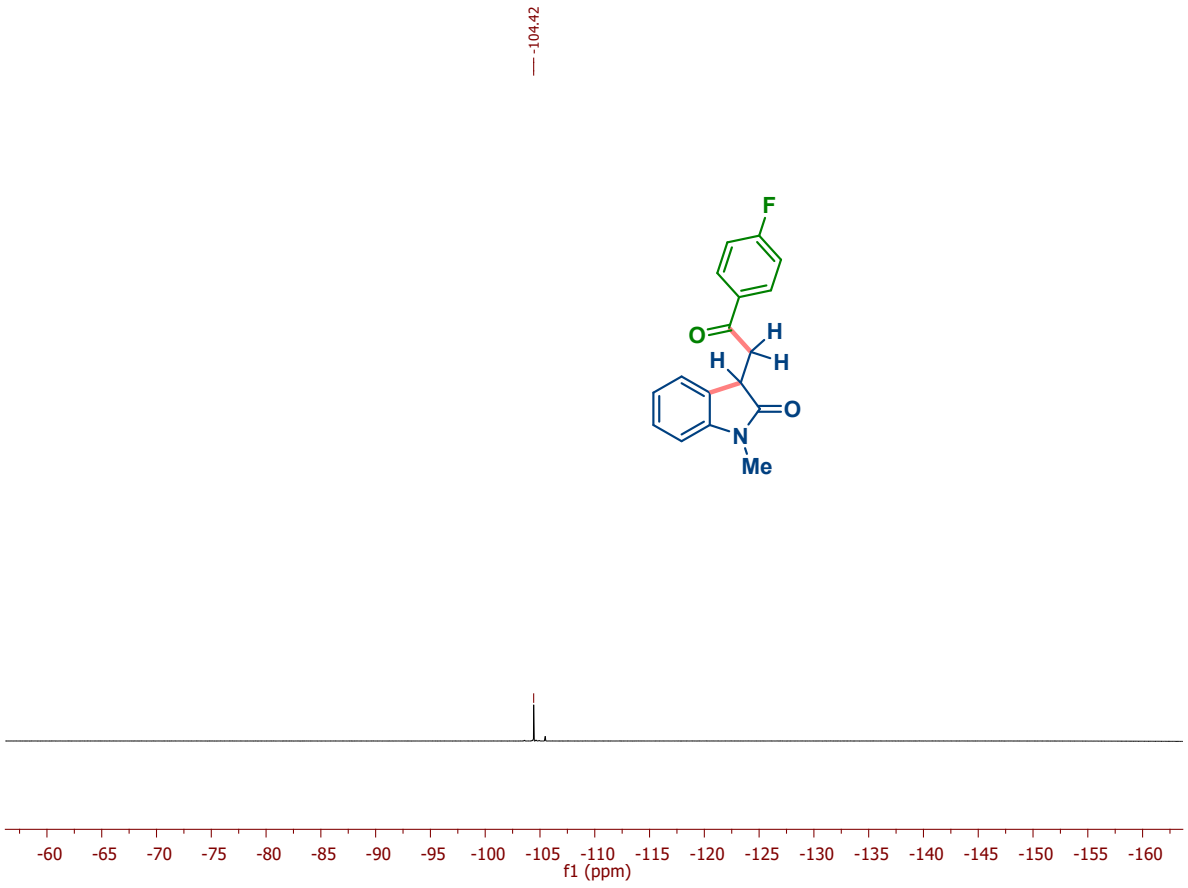
^{1}H NMR (600 MHz) spectrum of **3ga** in $CDCl_3$



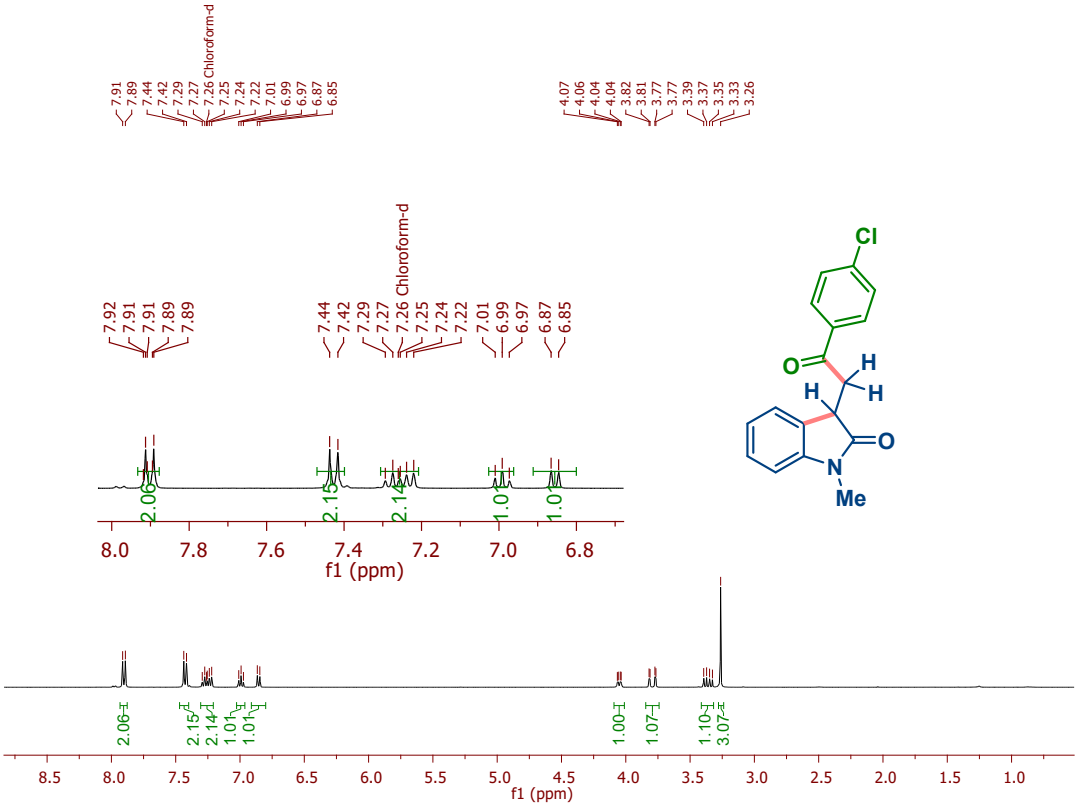
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3ga** in $CDCl_3$



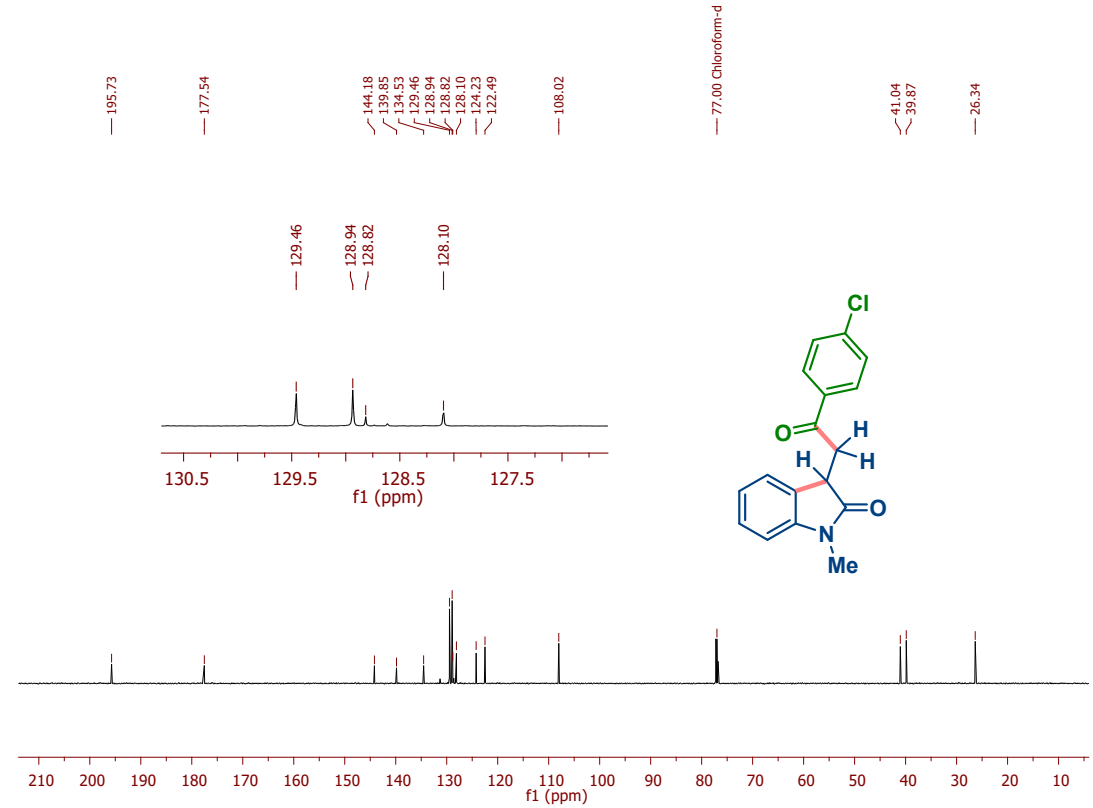
^{19}F-NMR (376 MHz) spectrum of **3ga** in $CDCl_3$



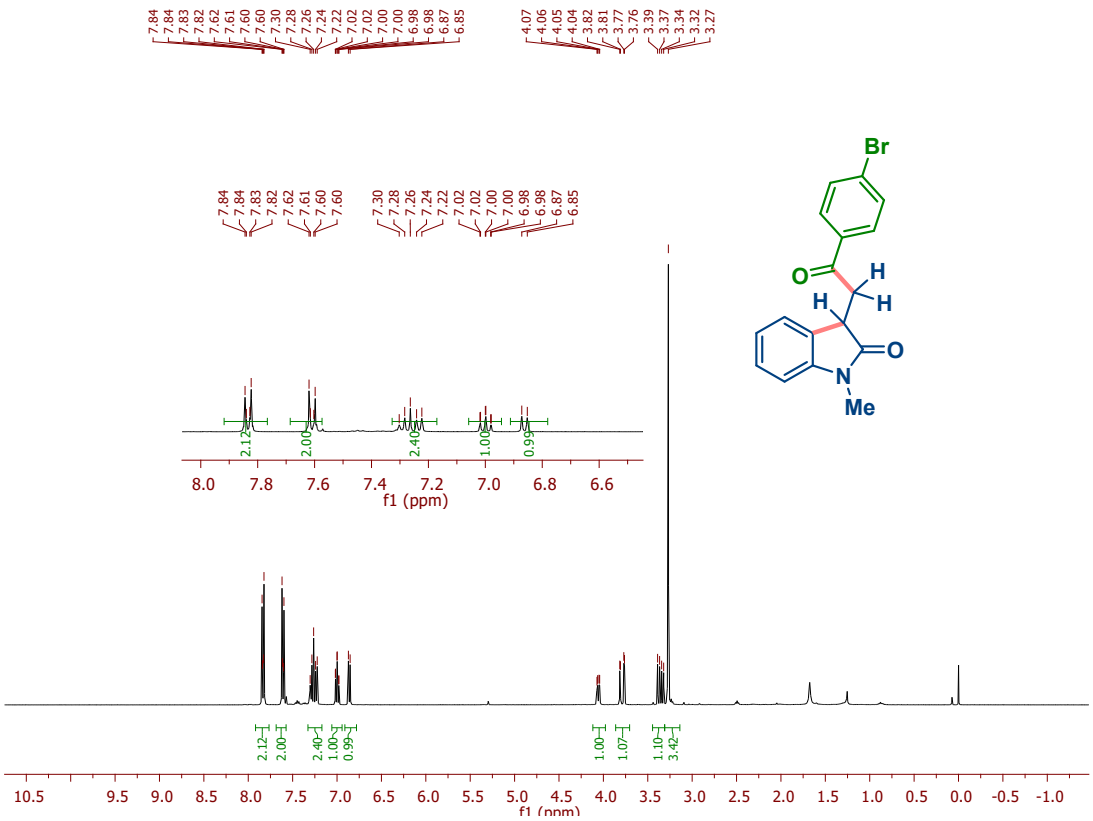
^{1}H NMR (400 MHz) spectrum of **3ha** in $CDCl_3$



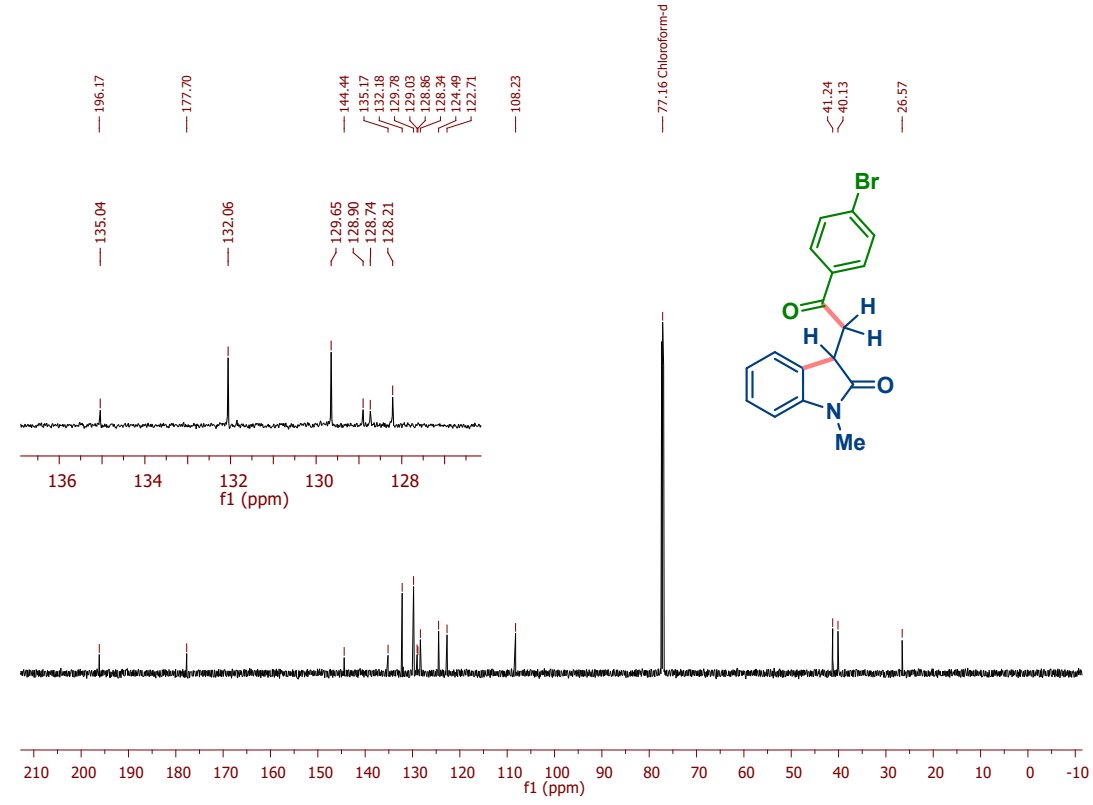
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3ha** in $CDCl_3$



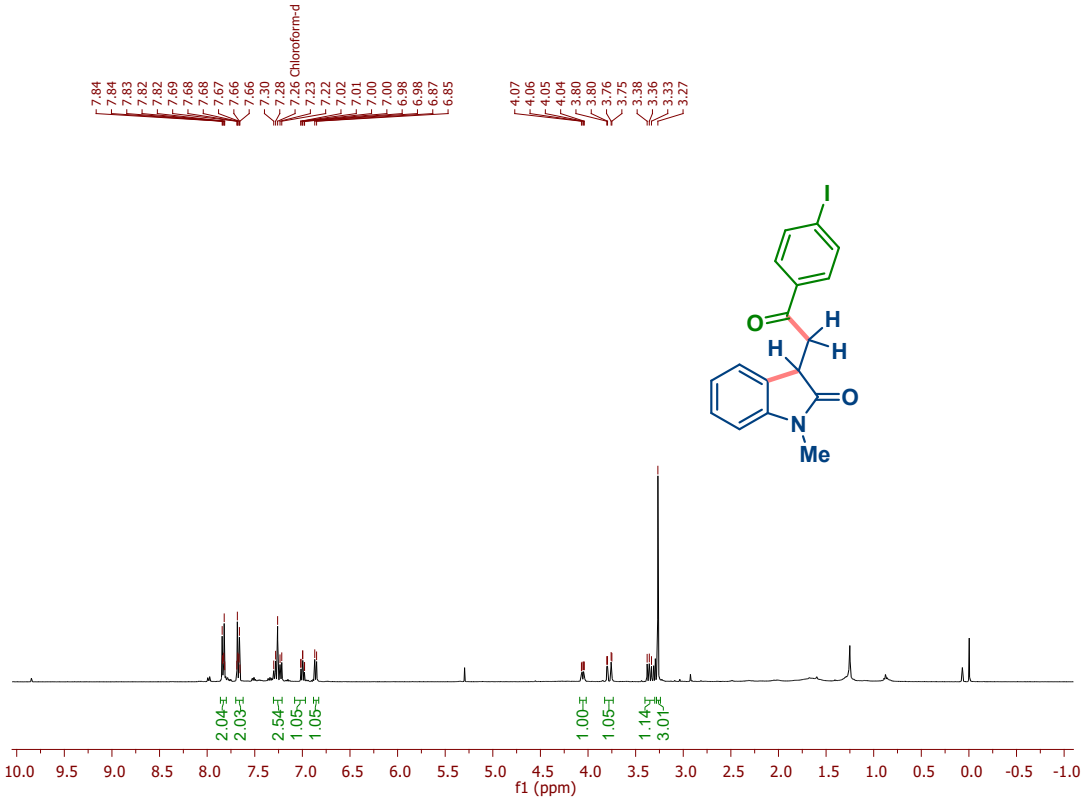
^{1}H NMR (400 MHz) spectrum of **3ia** in $CDCl_3$



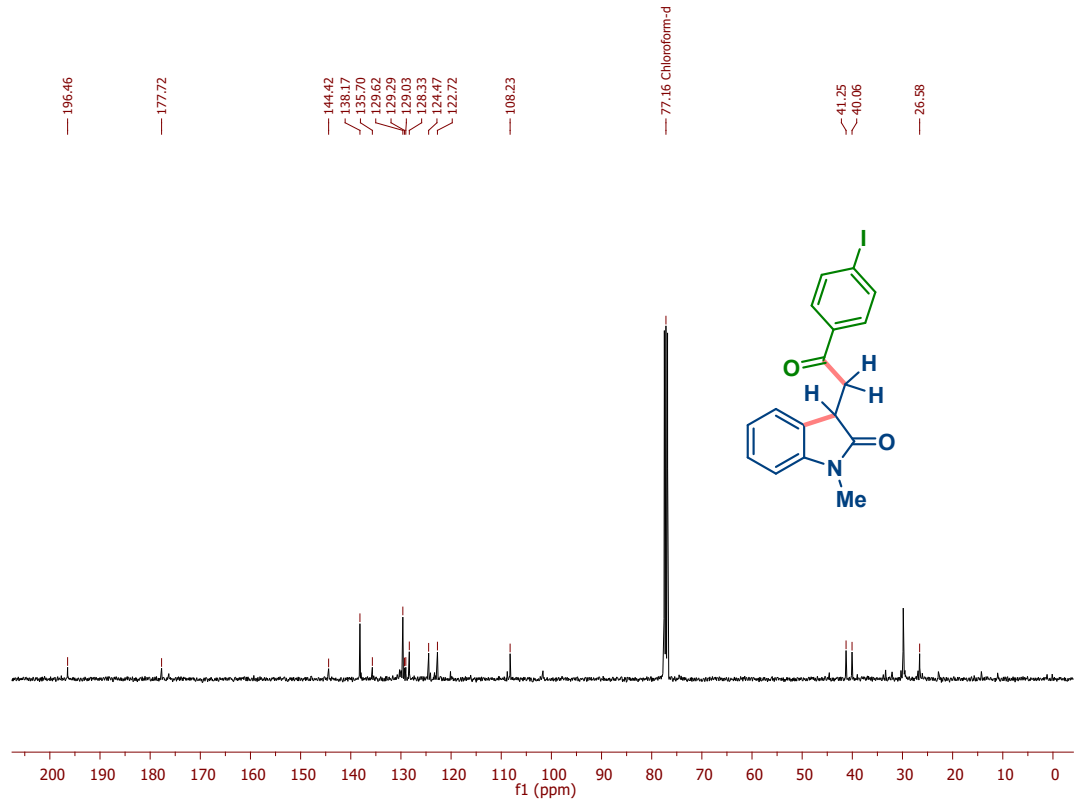
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3ia** in $CDCl_3$



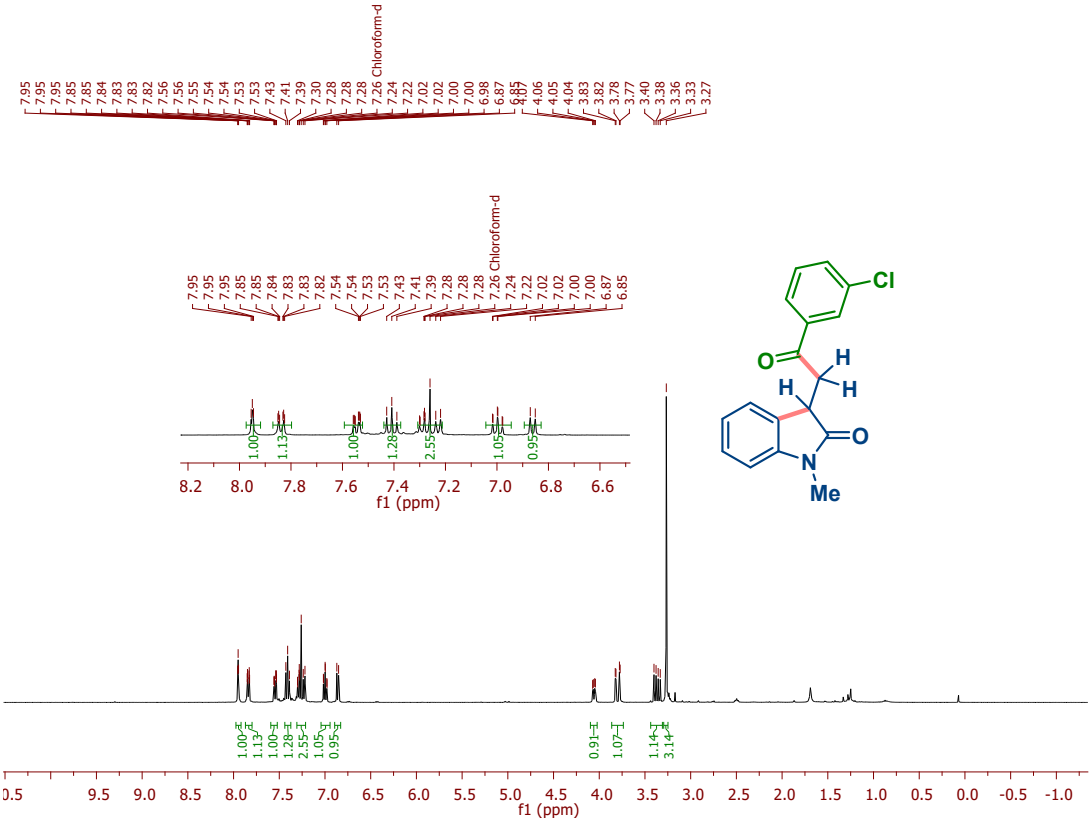
^{1}H NMR (600 MHz) spectrum of **3ja** in $CDCl_3$



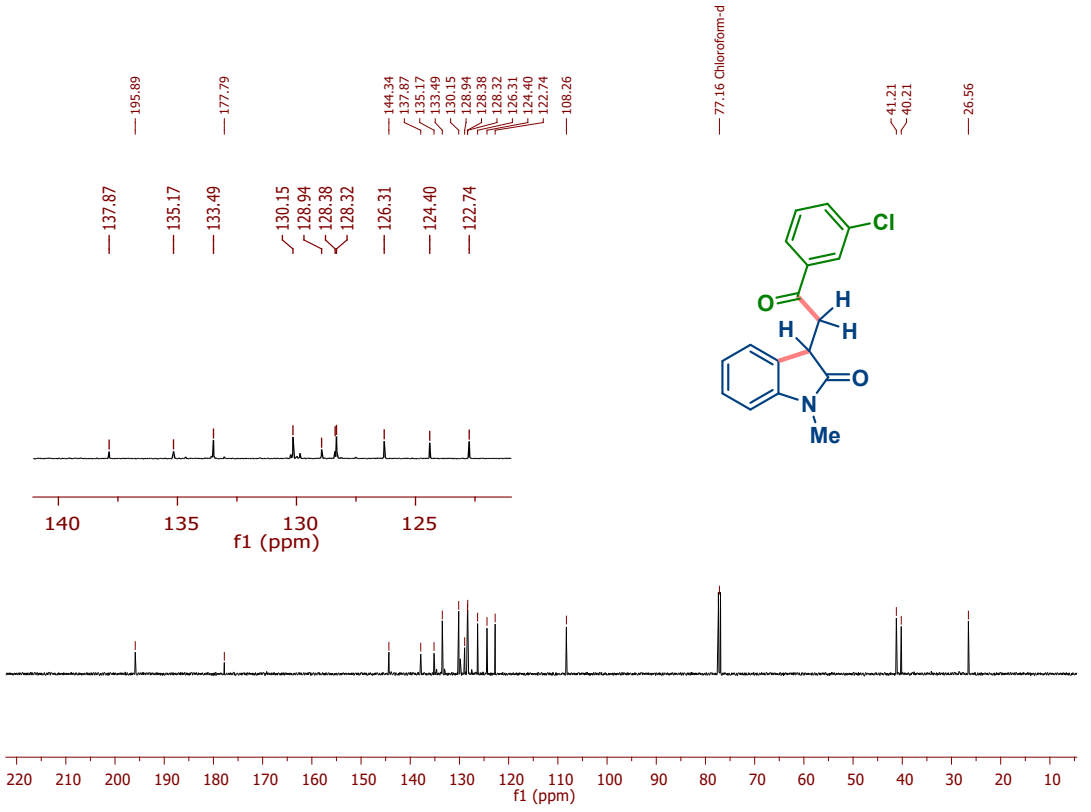
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ja** in $CDCl_3$



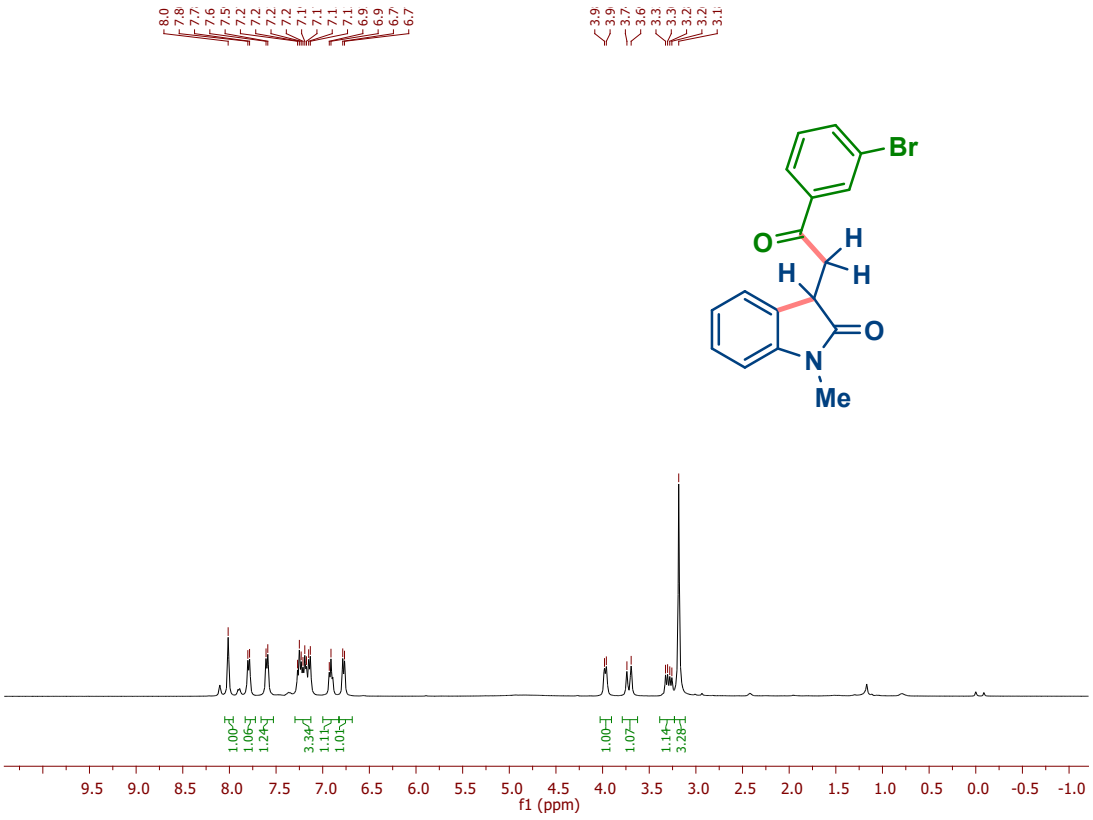
^{1}H NMR (600 MHz) spectrum of **3ka** in $CDCl_3$



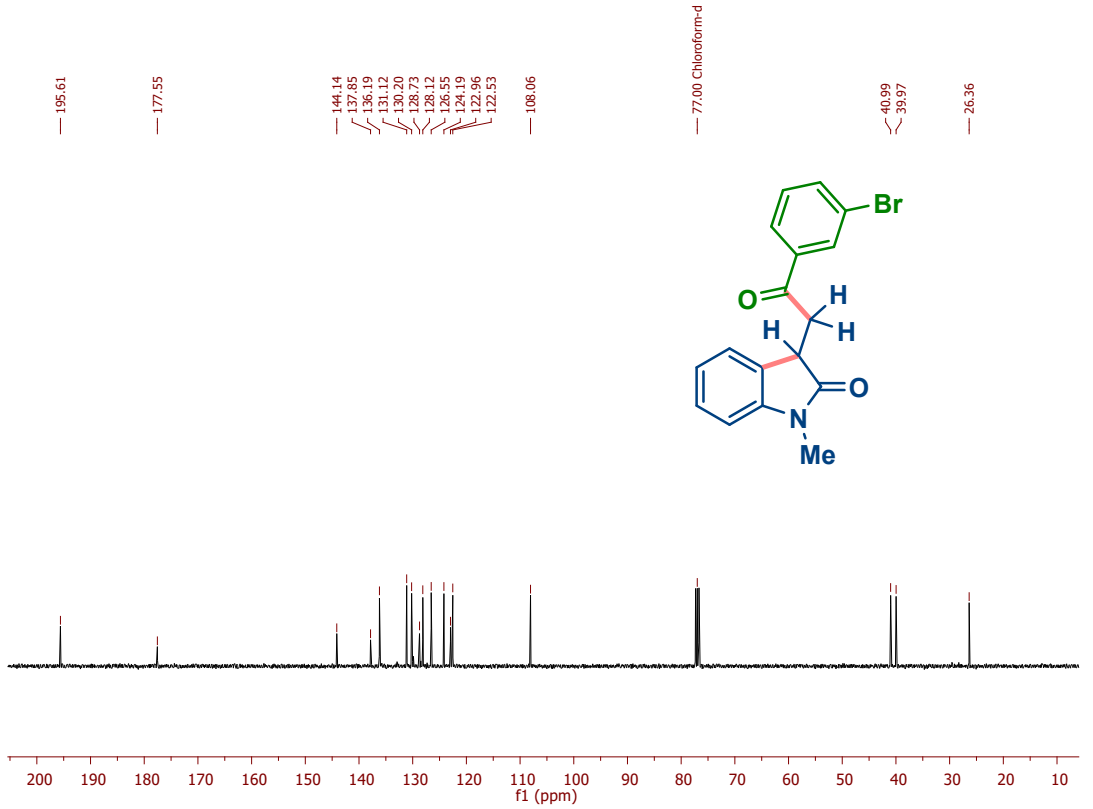
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3ka** in $CDCl_3$



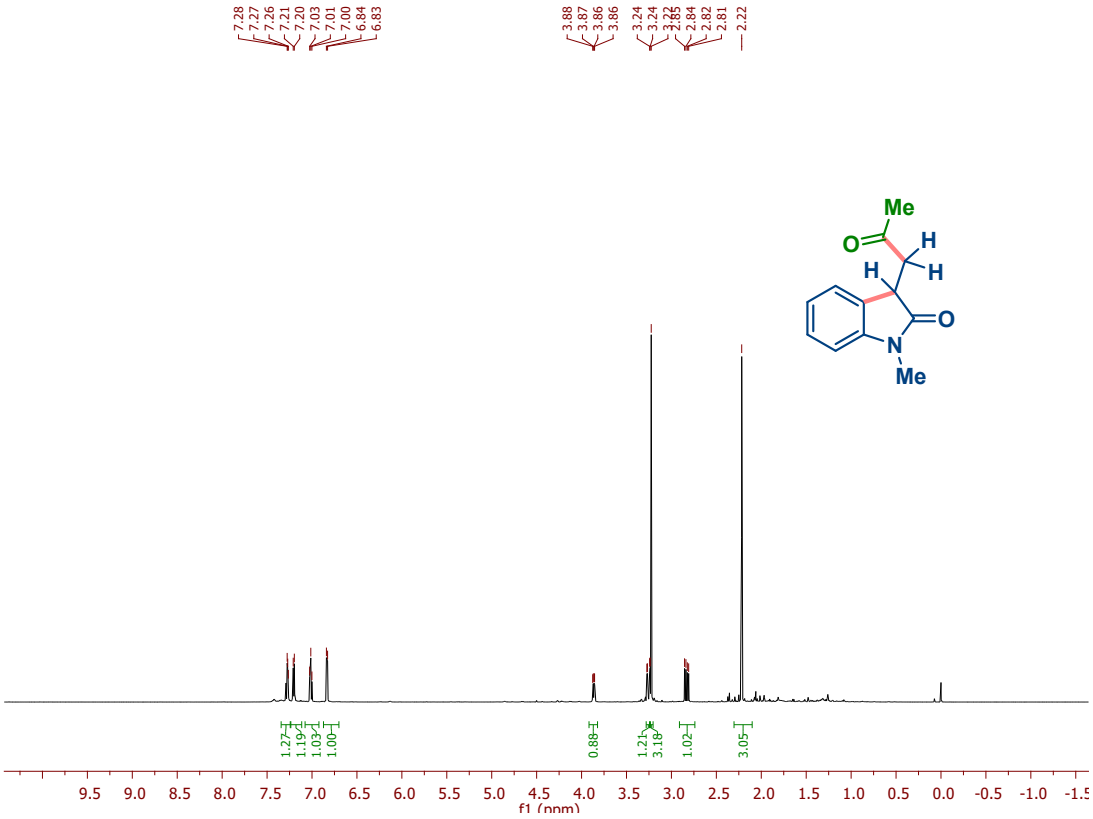
^{1}H NMR (400 MHz) spectrum of **3la** in $CDCl_3$



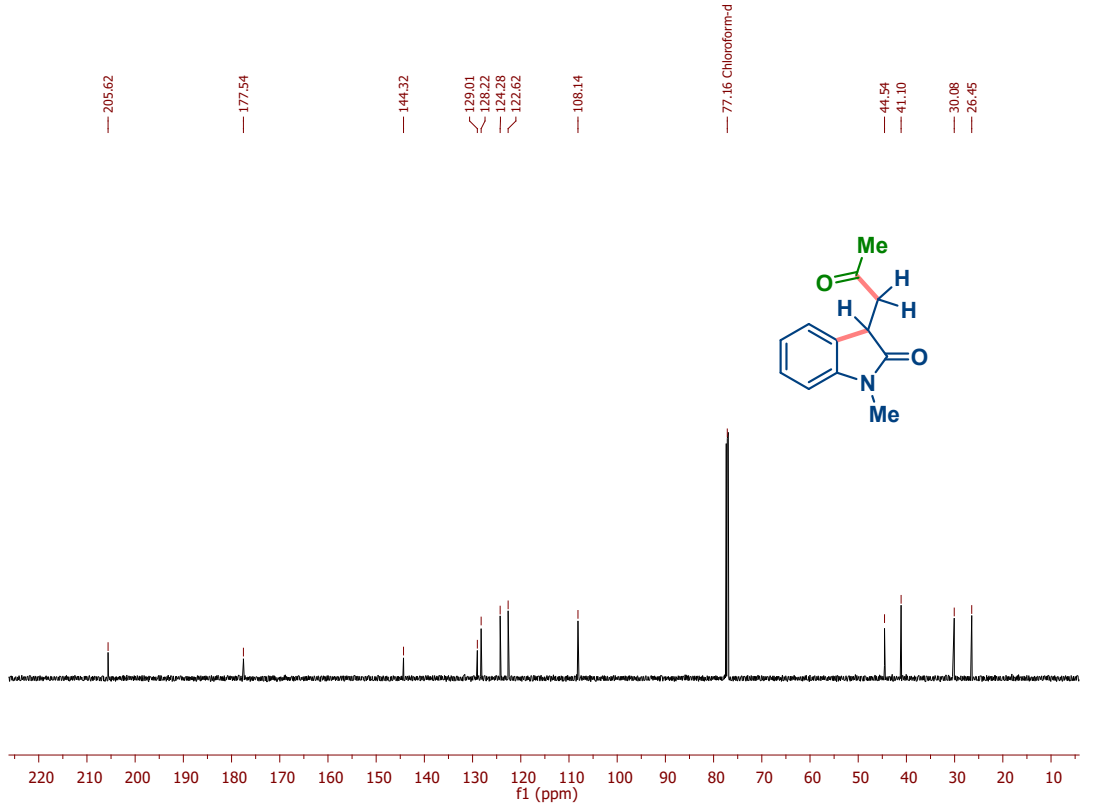
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3la** in $CDCl_3$



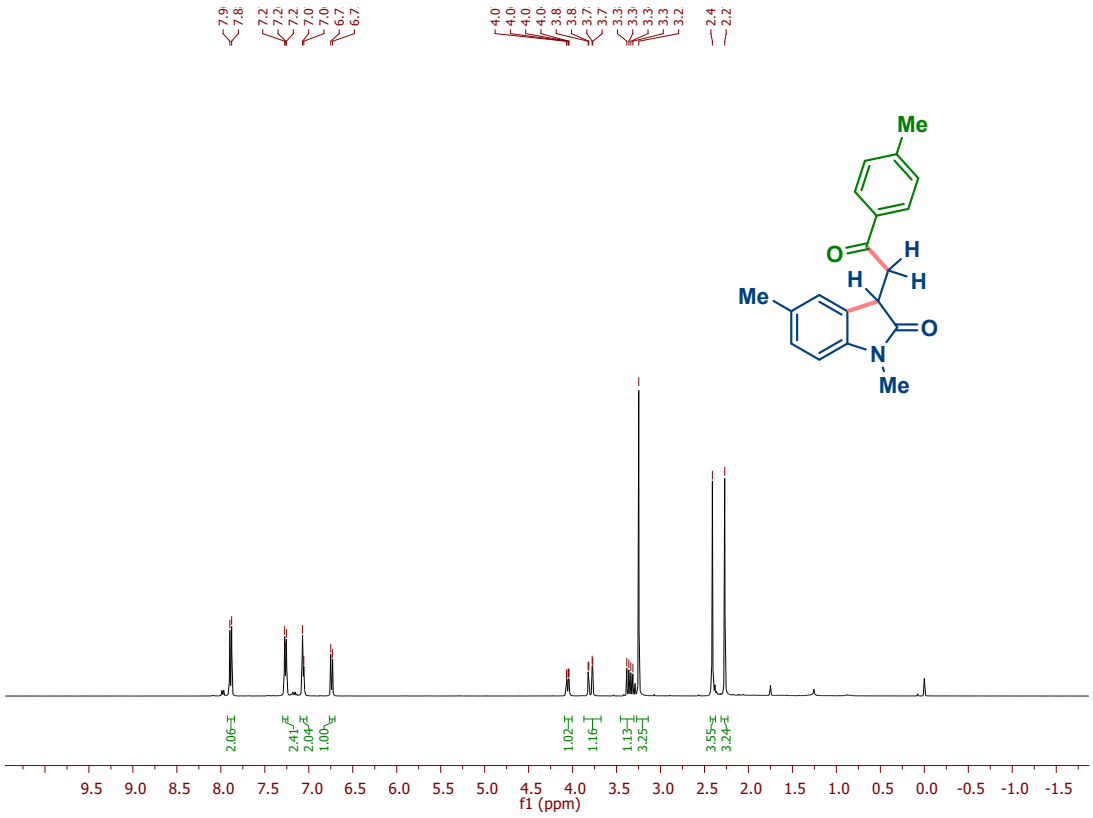
^{1}H NMR (600 MHz) spectrum of **3pa** in $CDCl_3$



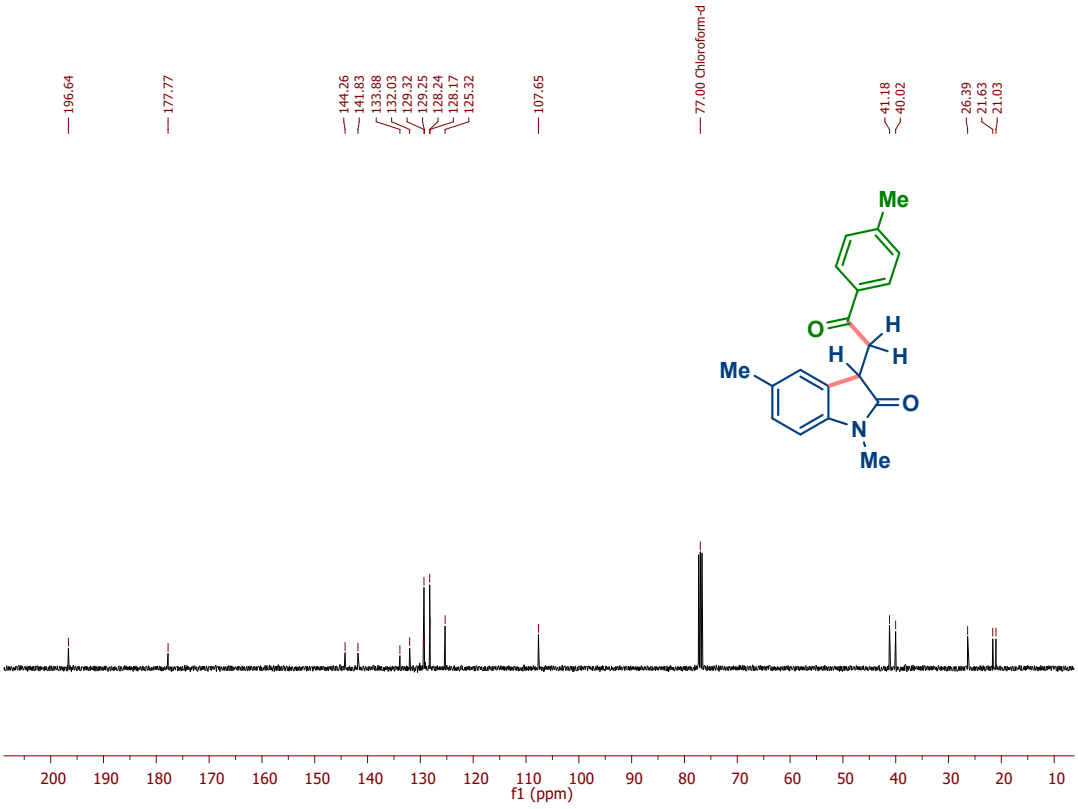
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3pa** in $CDCl_3$



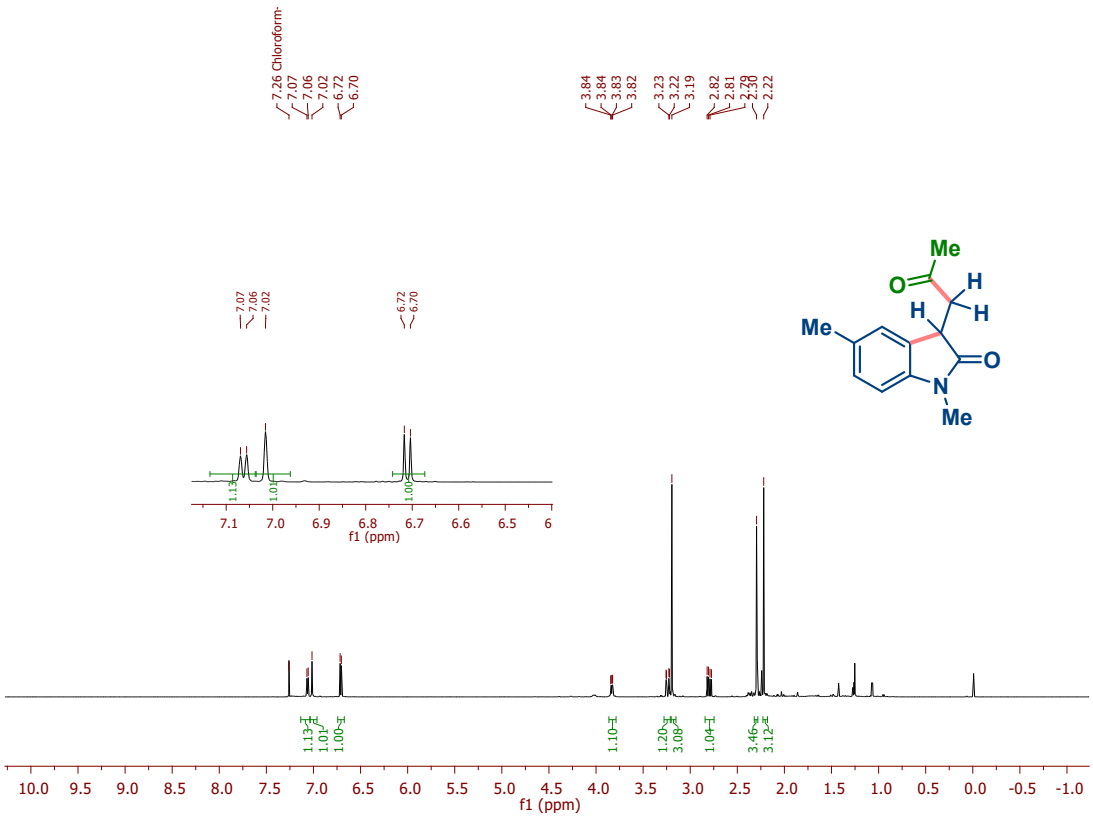
^{1}H NMR (400 MHz) spectrum of **3ab** in $CDCl_3$



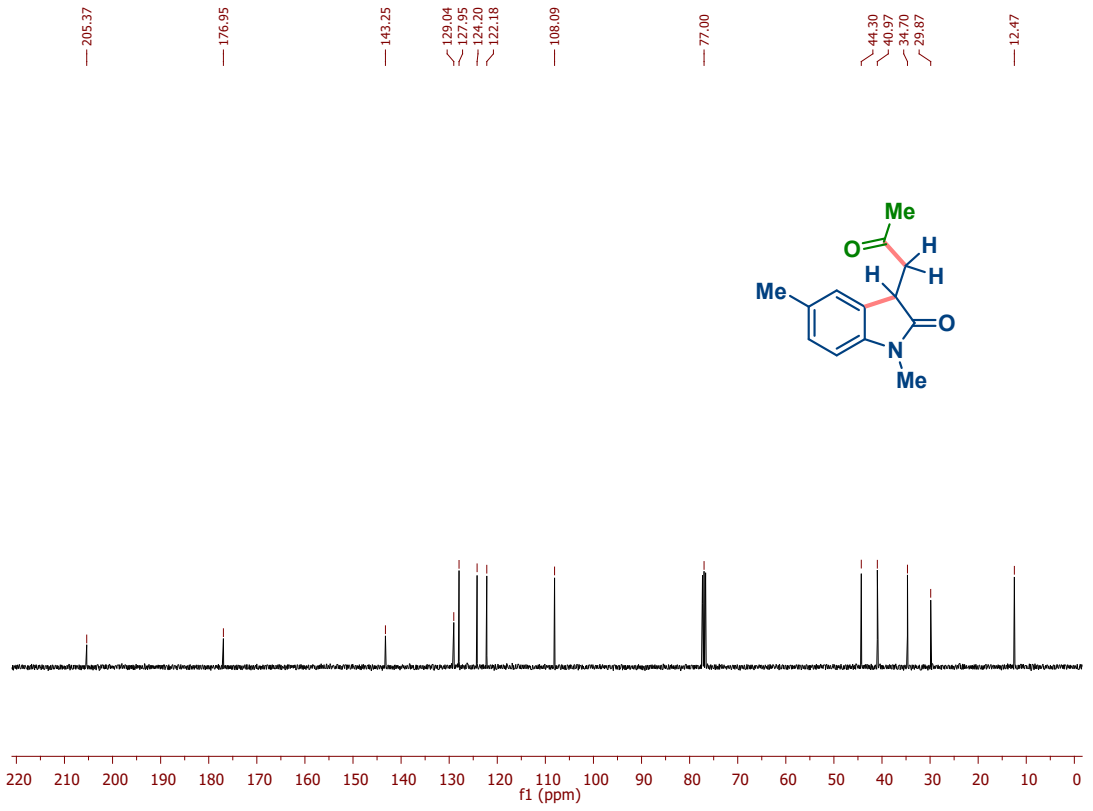
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3ab** in $CDCl_3$



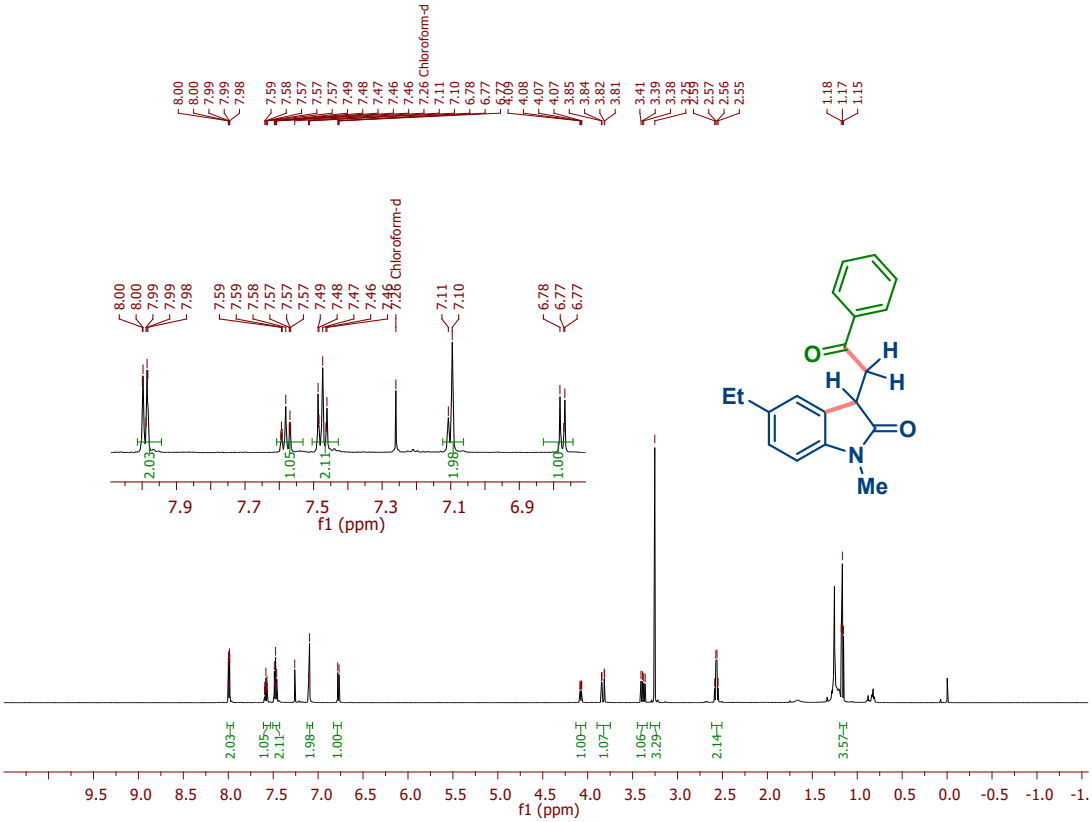
^{1}H NMR (600 MHz) spectrum of **3pb** in $CDCl_3$



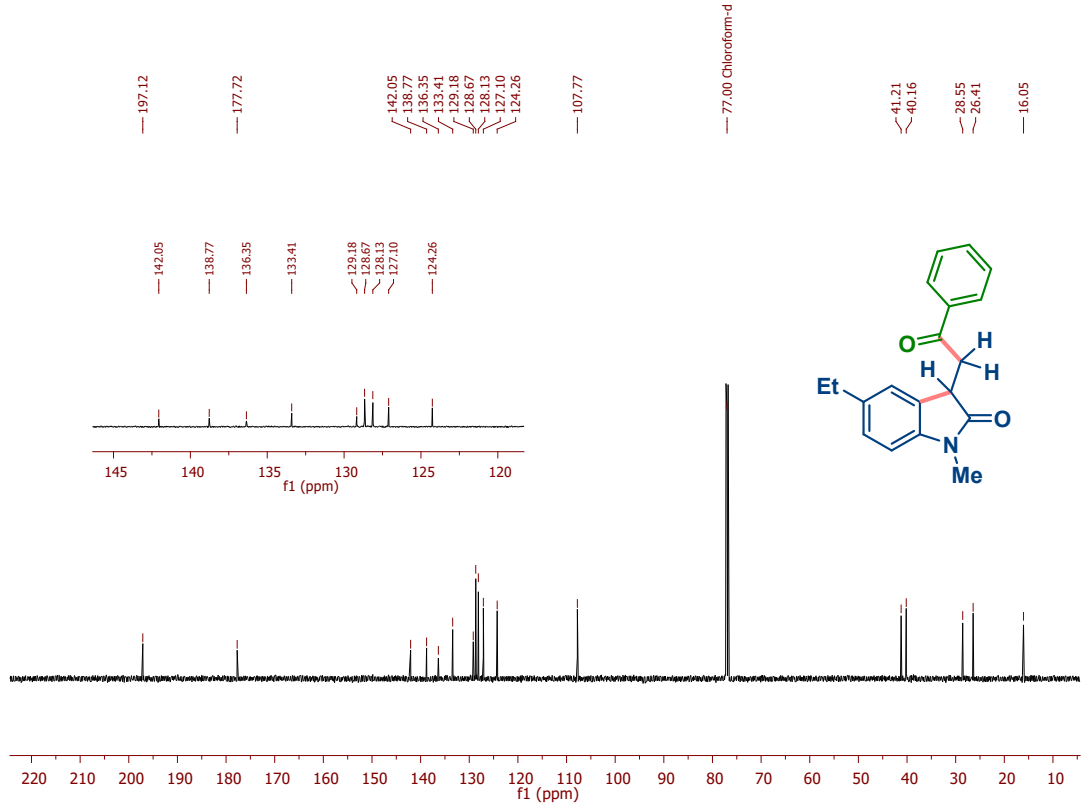
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3pb** in $CDCl_3$



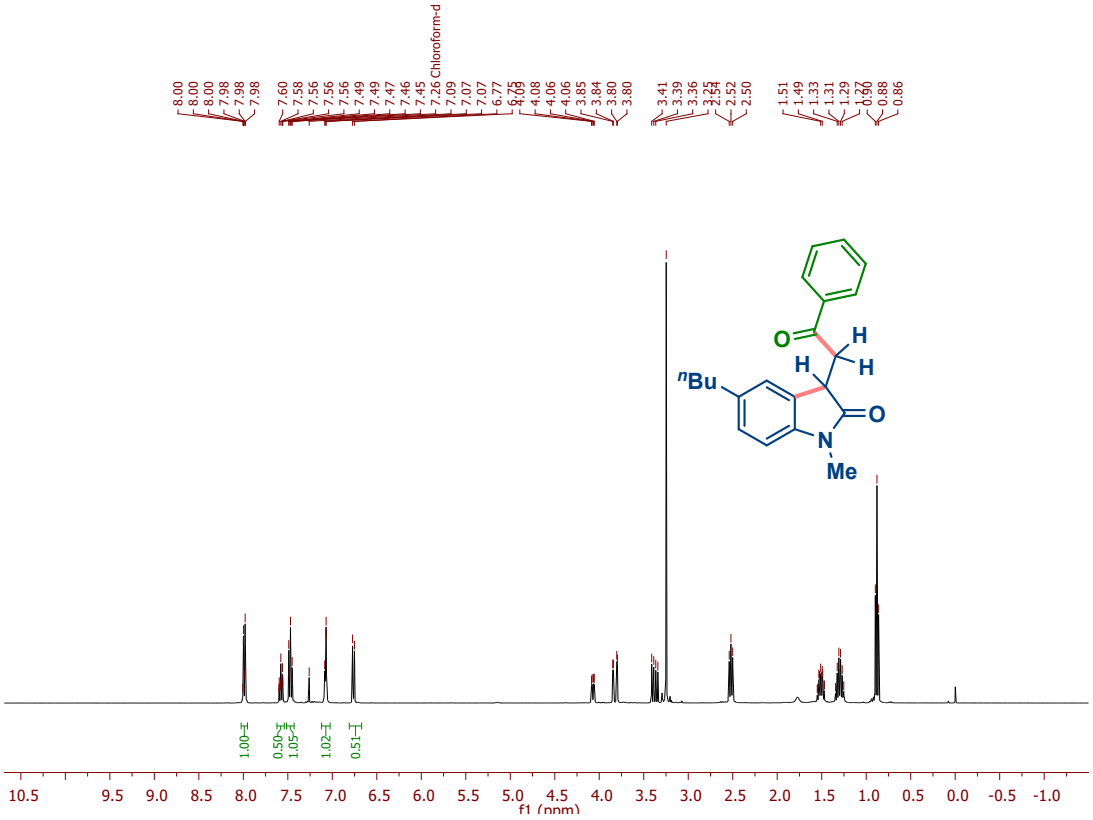
^{1}H NMR (600 MHz) spectrum of **3mc** in $CDCl_3$



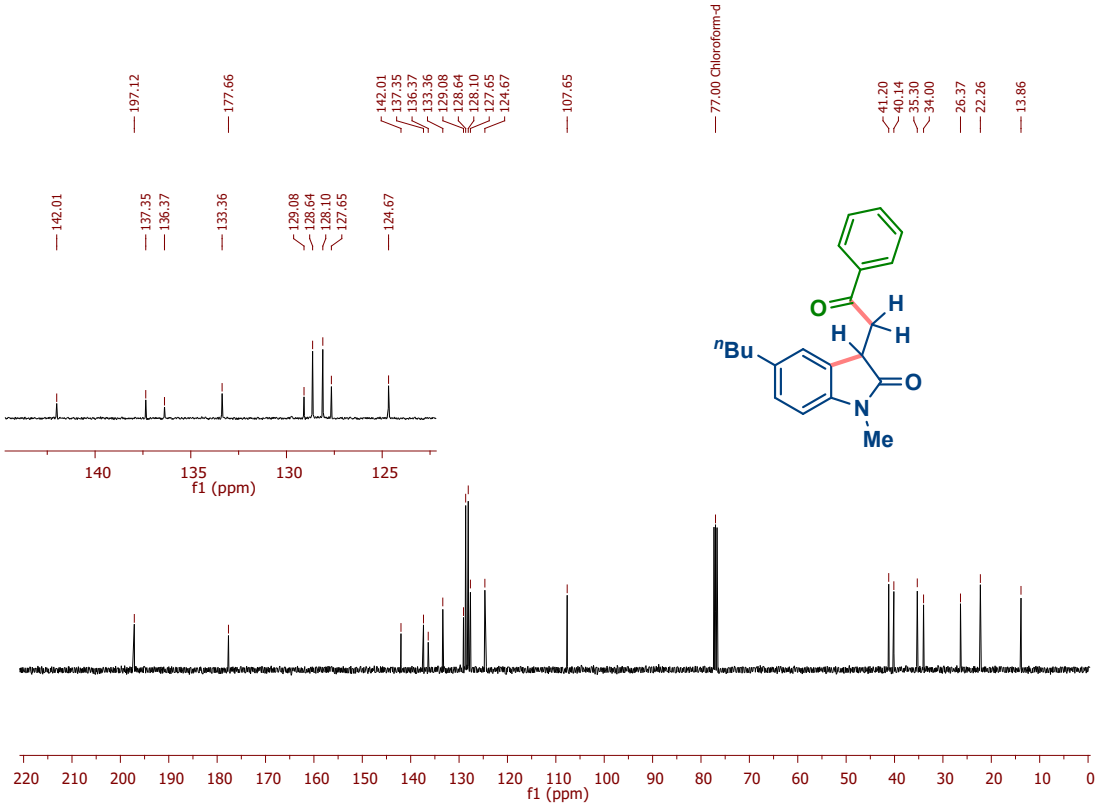
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3mc** in $CDCl_3$



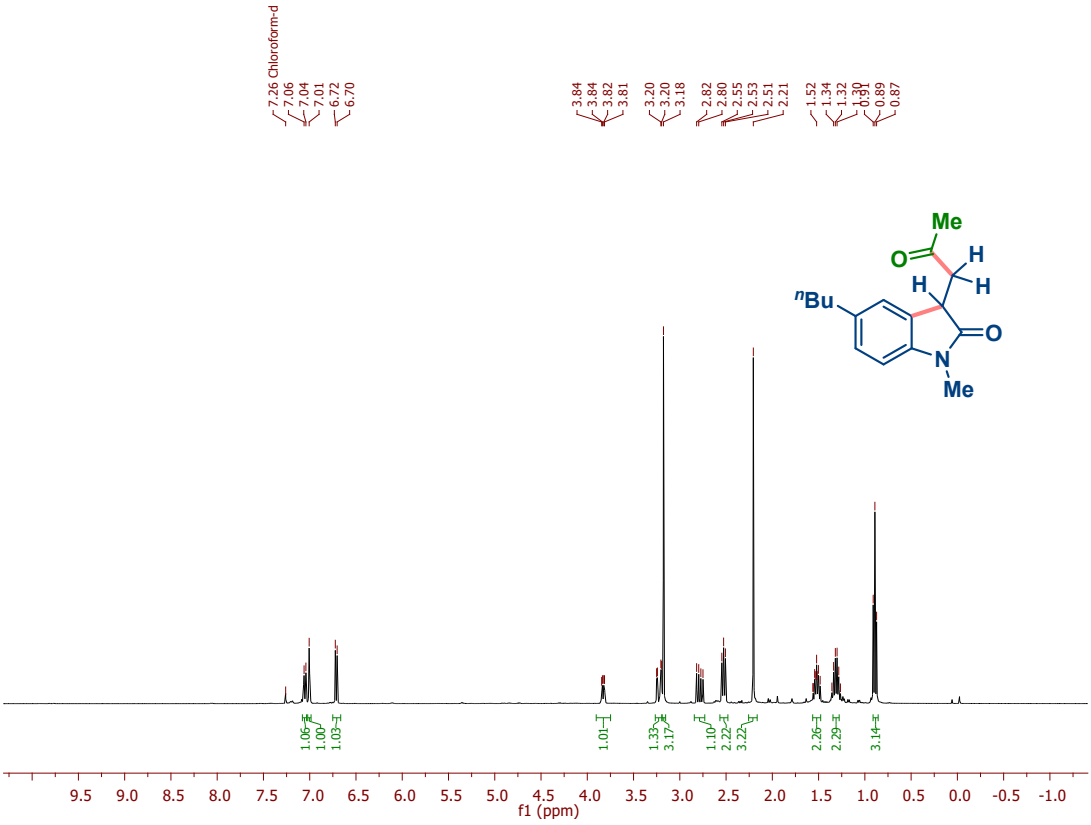
^{1}H NMR (400 MHz) spectrum of **3md** in $CDCl_3$



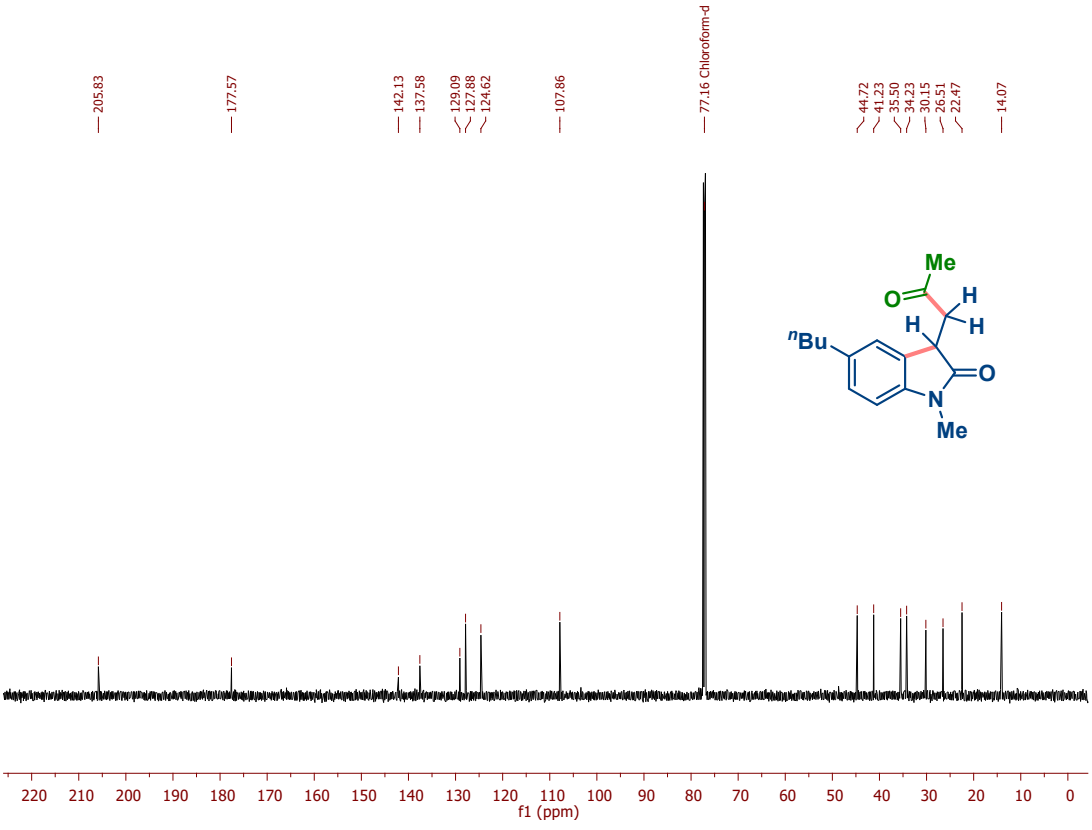
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3md** in $CDCl_3$



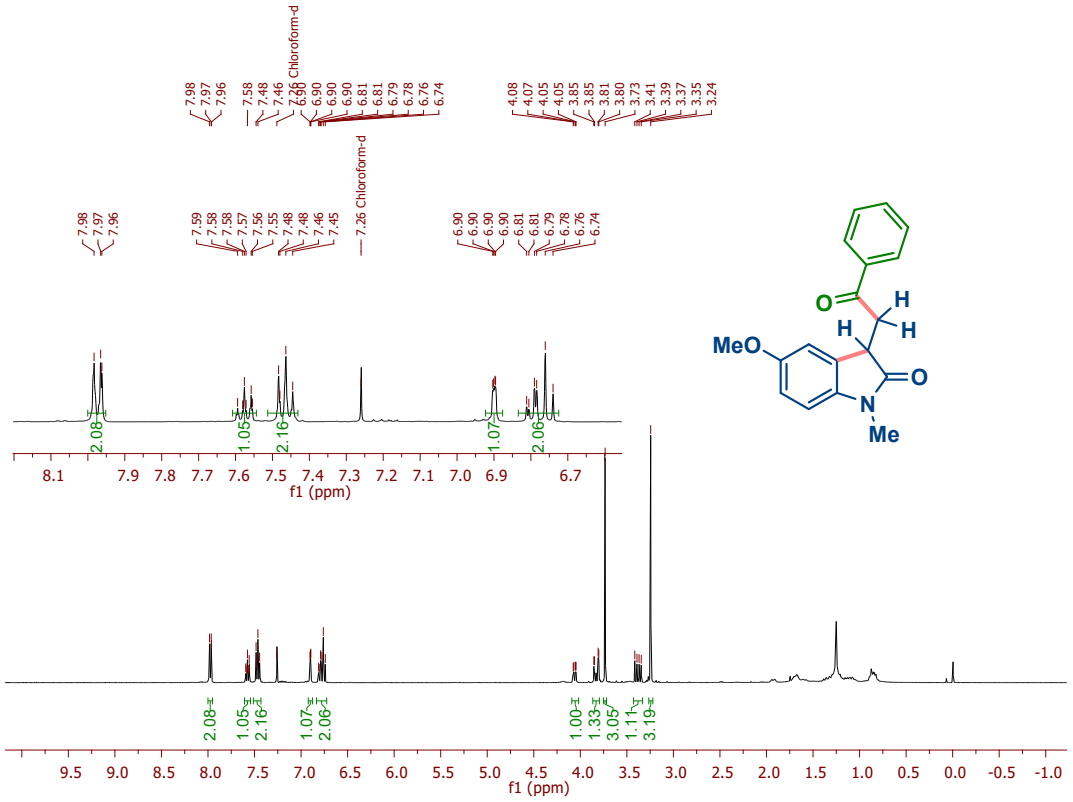
^{1}H NMR (400 MHz) spectrum of **3pd** in $CDCl_3$



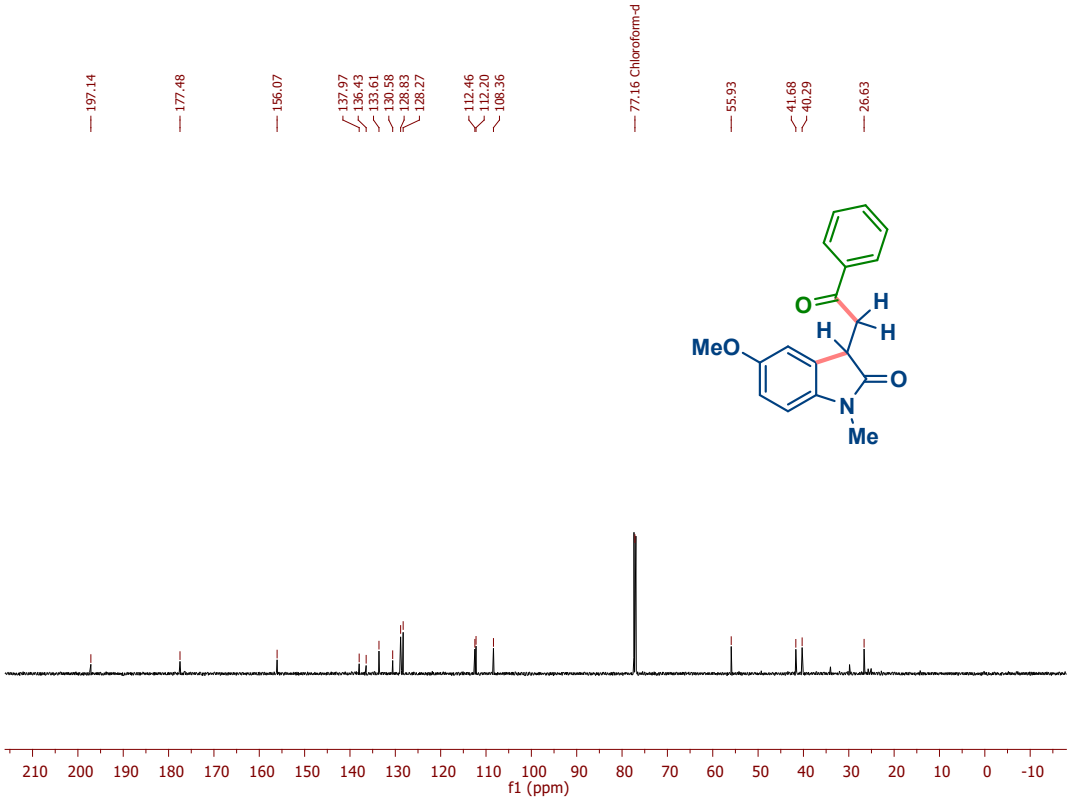
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3pd** in $CDCl_3$



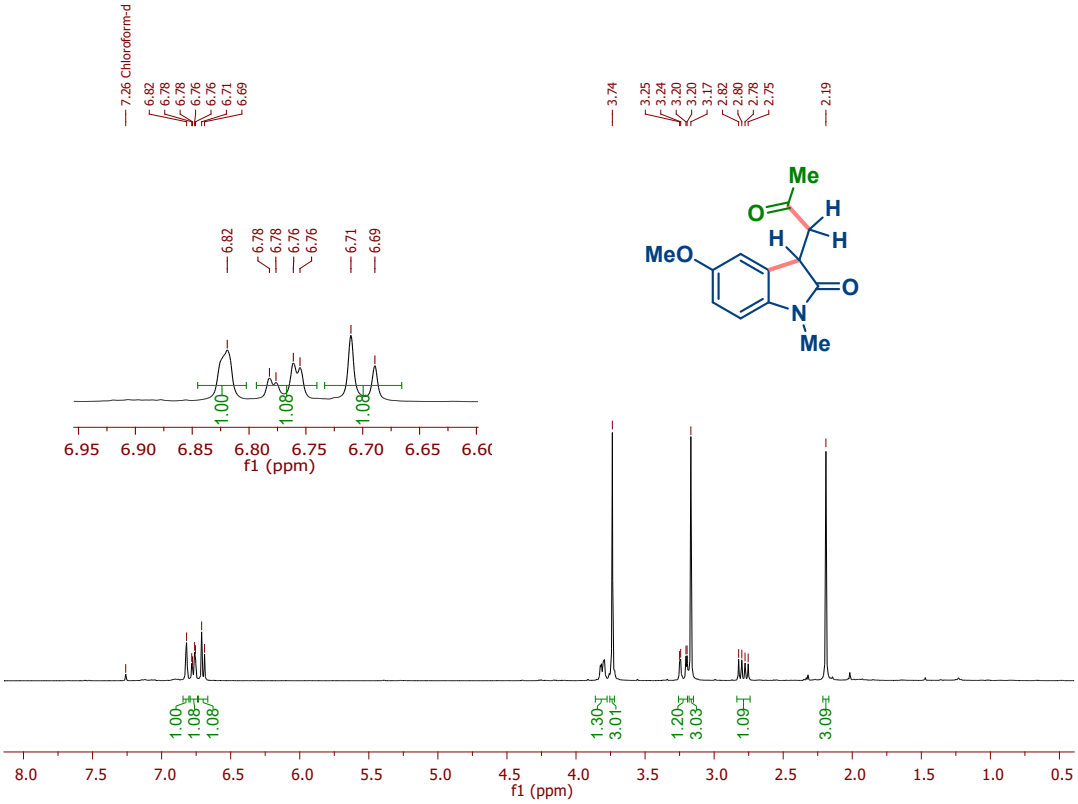
^{1}H NMR (600 MHz) spectrum of **3me** in $CDCl_3$



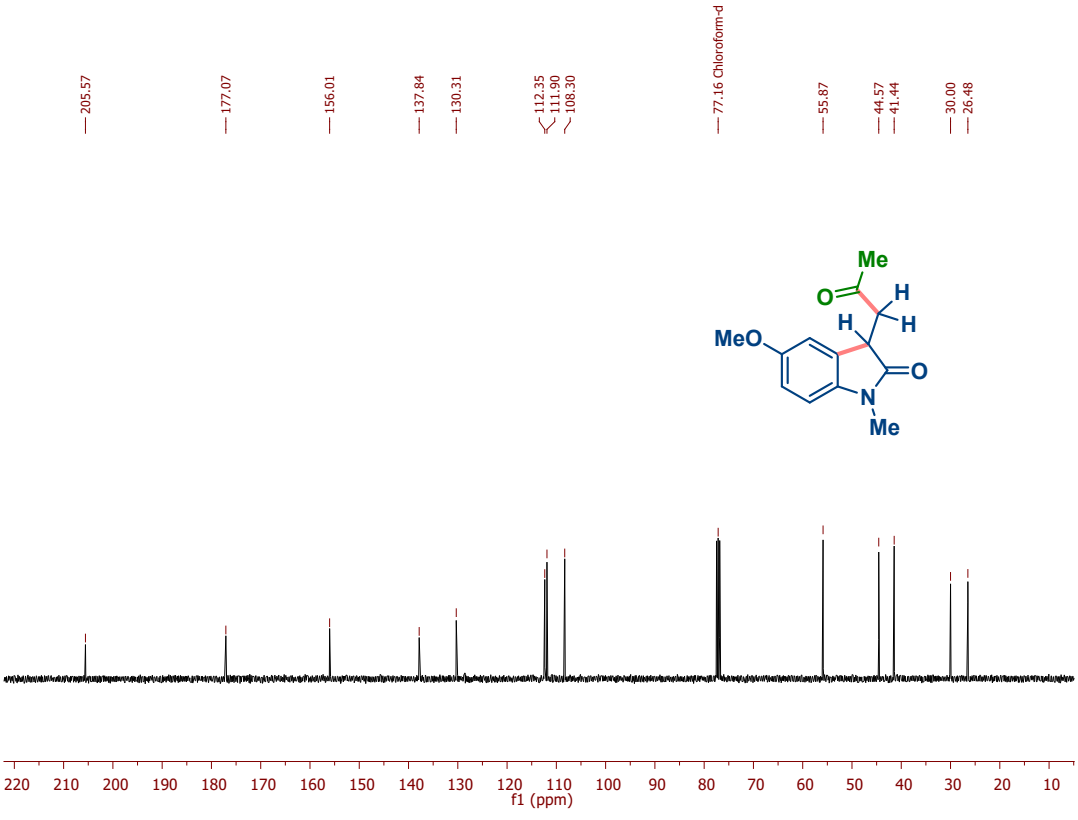
^{13}C{^{1}H}- NMR (151 MHz) spectrum of **3me** in $CDCl_3$



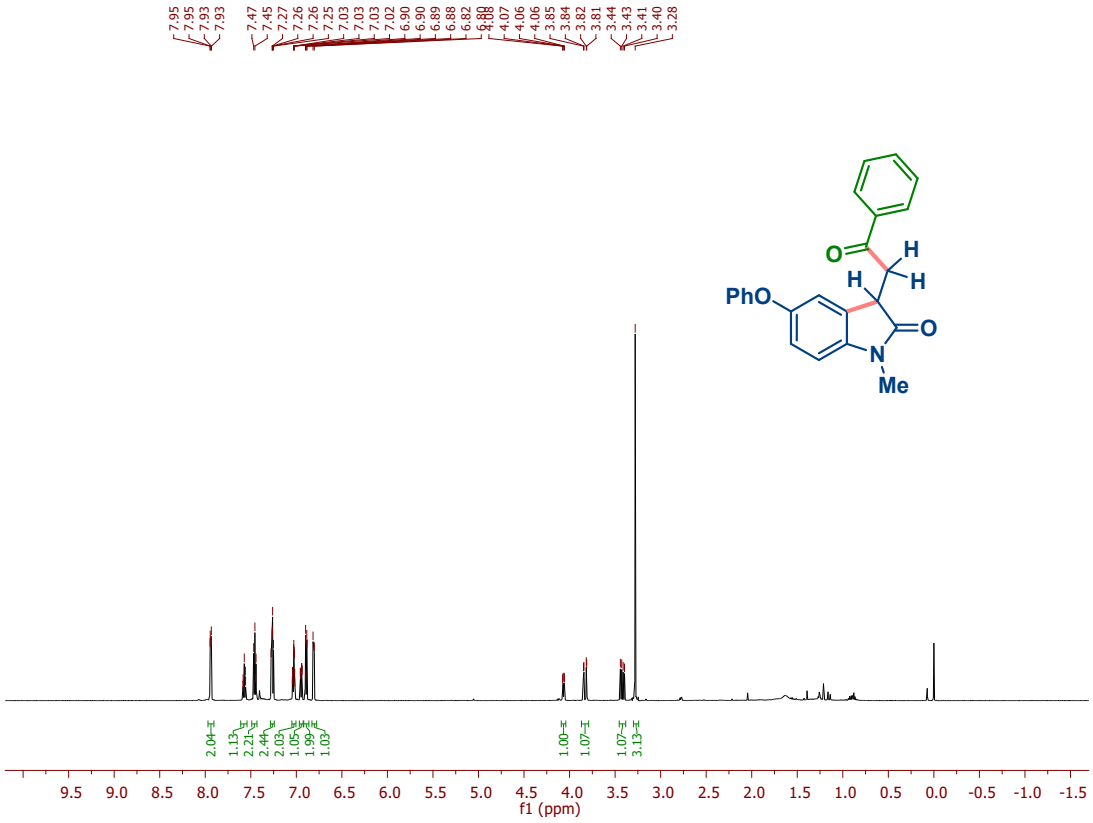
^{1}H NMR (400 MHz) spectrum of **3pe** in $CDCl_3$



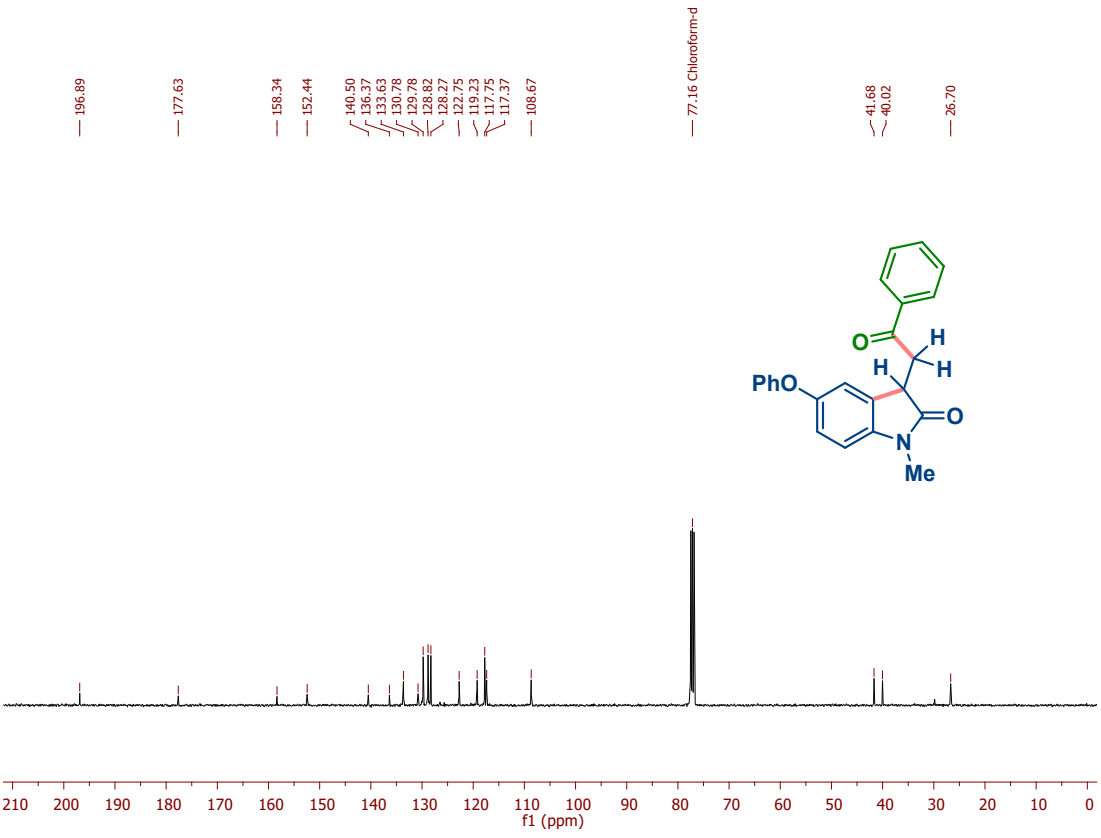
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3pe** in $CDCl_3$



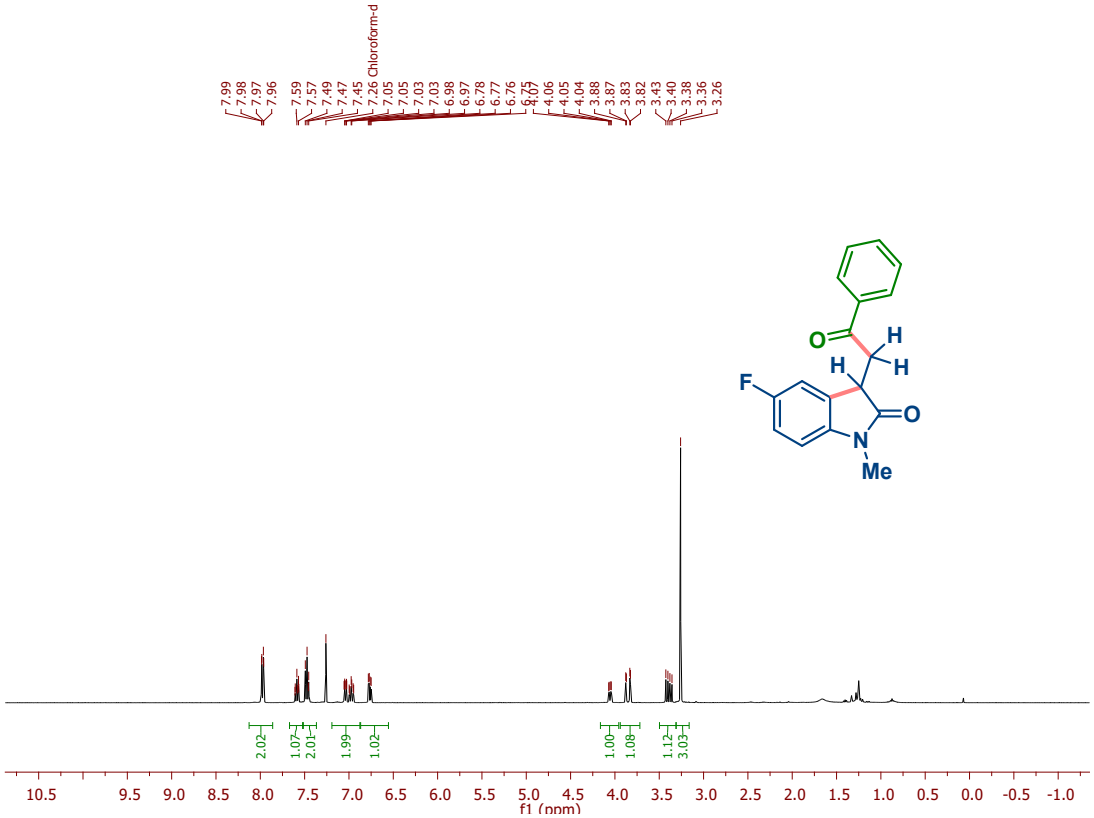
^{1}H NMR (400 MHz) spectrum of **3mf** in $CDCl_3$



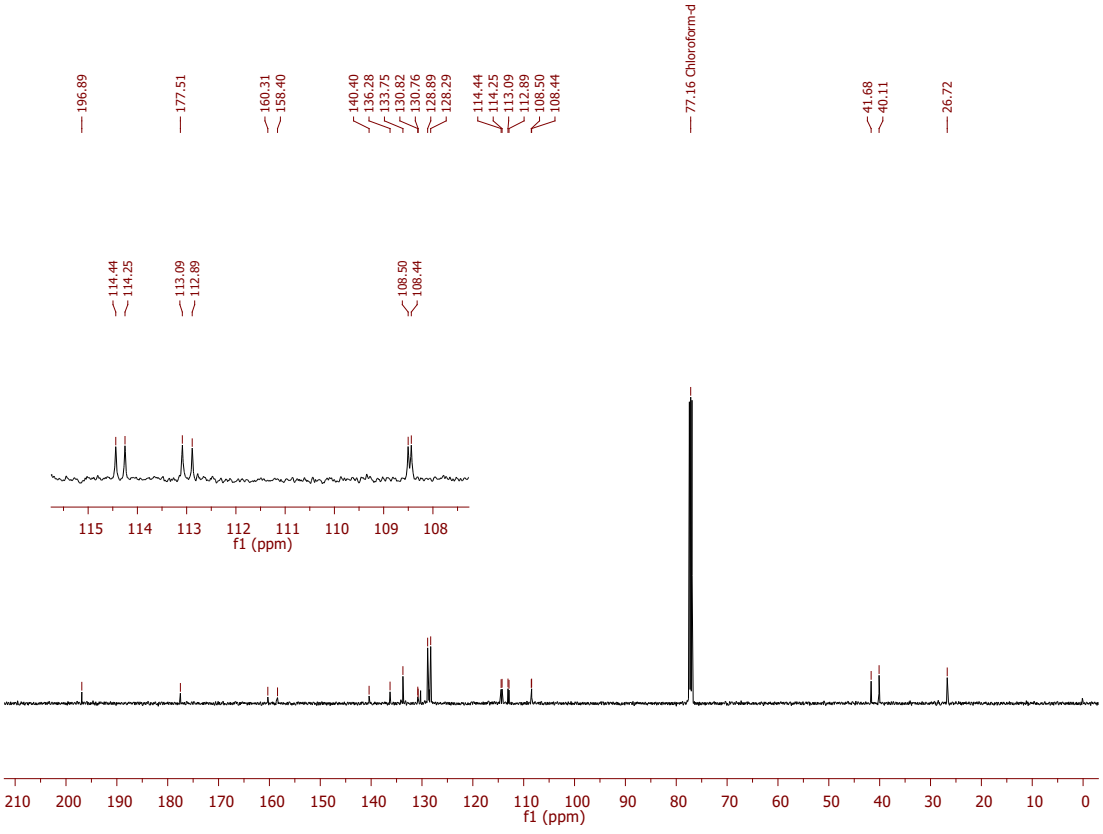
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3mf** in $CDCl_3$



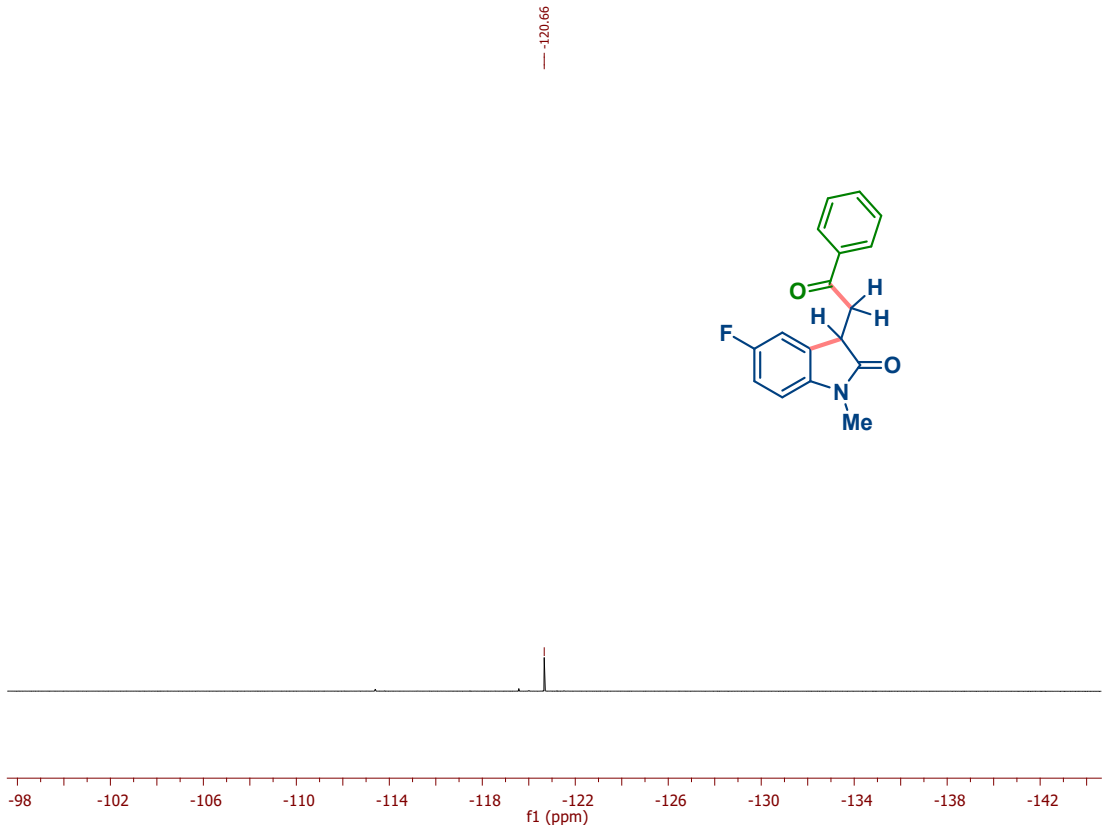
^{1}H NMR (400 MHz) spectrum of **3mg** in $CDCl_3$



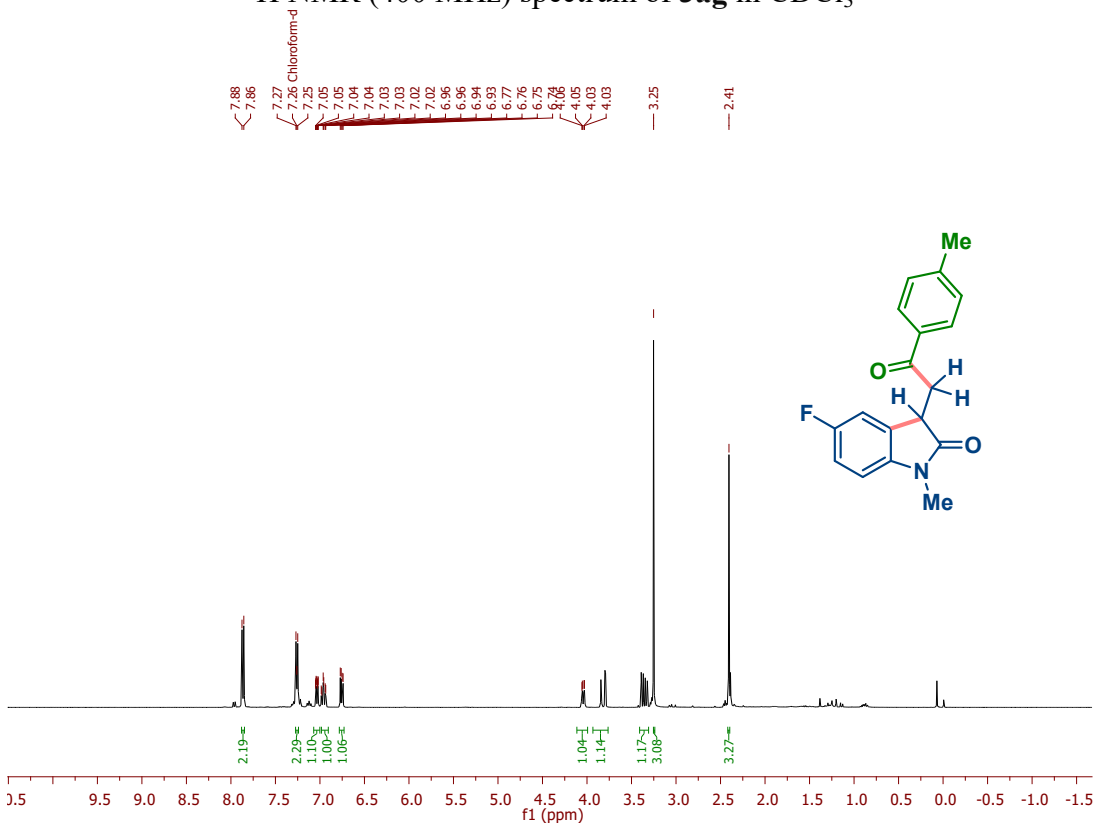
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3mg** in $CDCl_3$



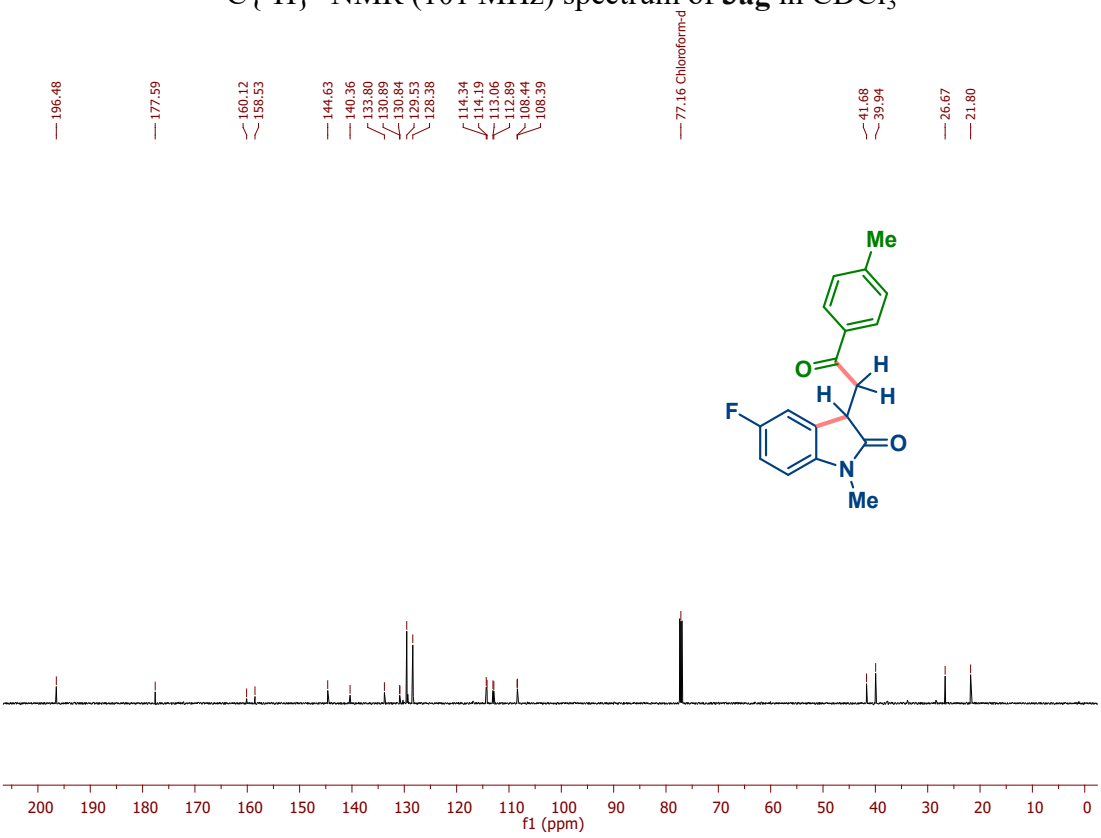
^{19}F-NMR (376 MHz) spectrum of **3mg** in $CDCl_3$



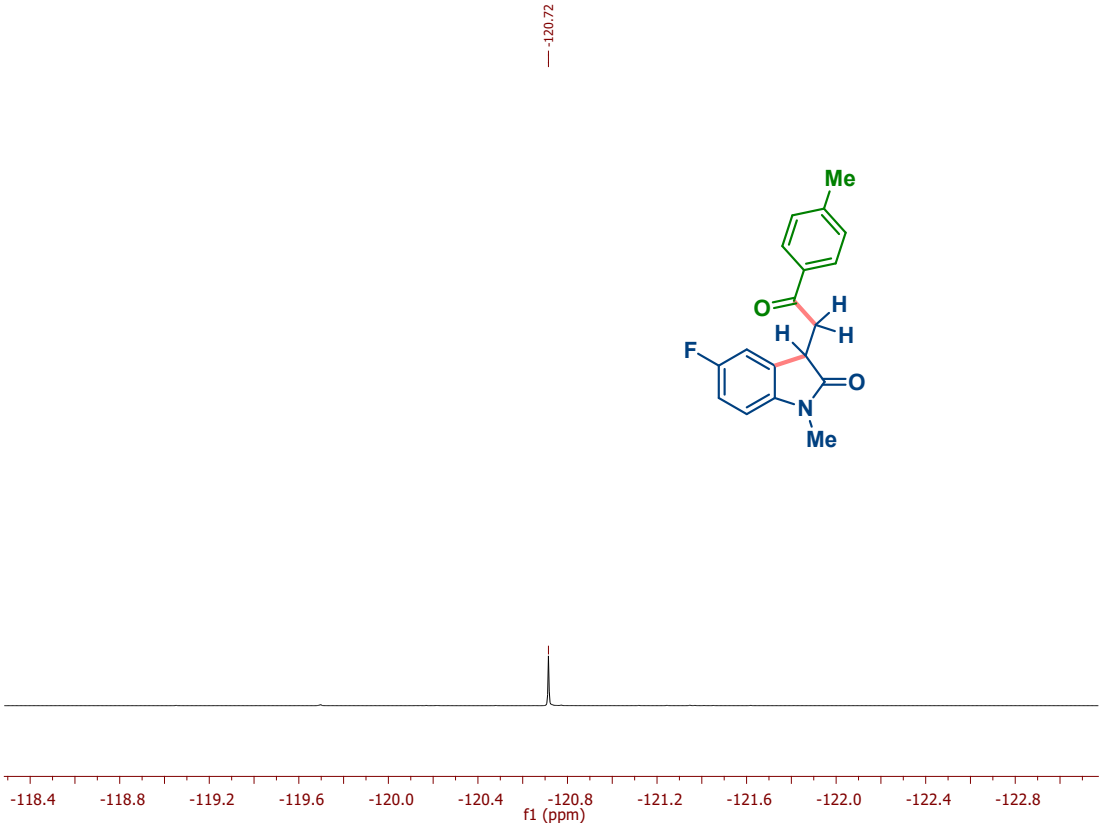
^{1}H NMR (400 MHz) spectrum of **3ag** in $CDCl_3$



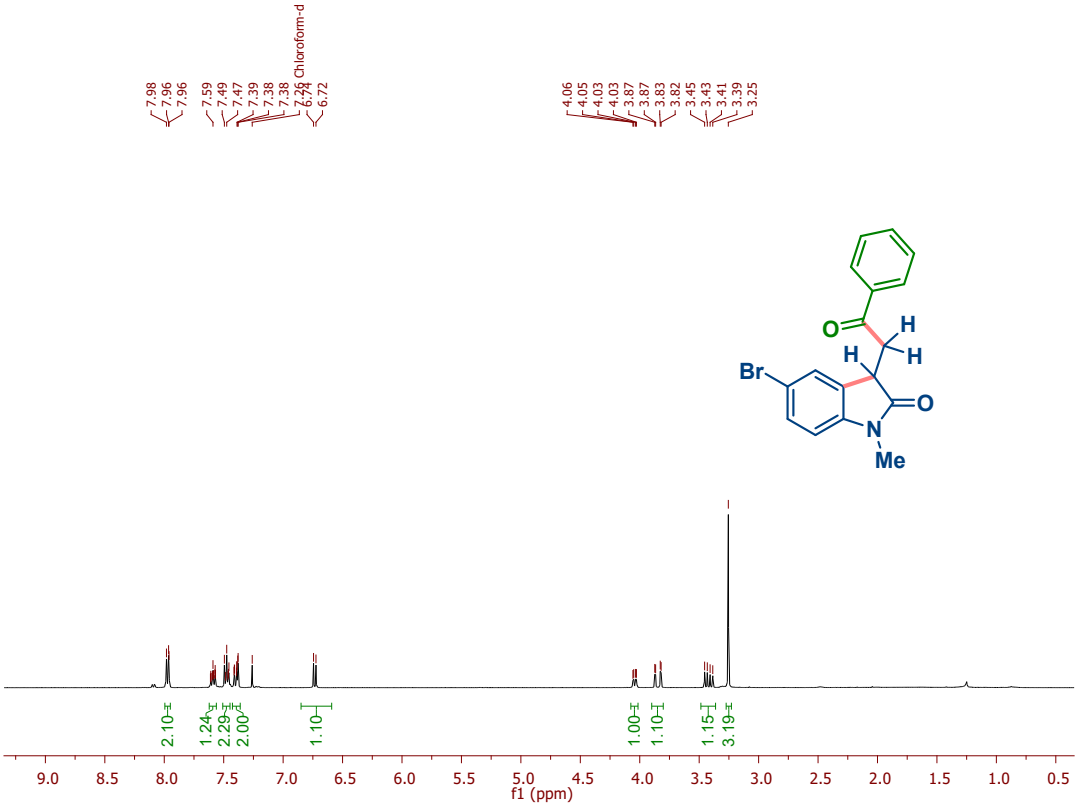
^{13}C{^{1}H}- NMR (101 MHz) spectrum of **3ag** in $CDCl_3$



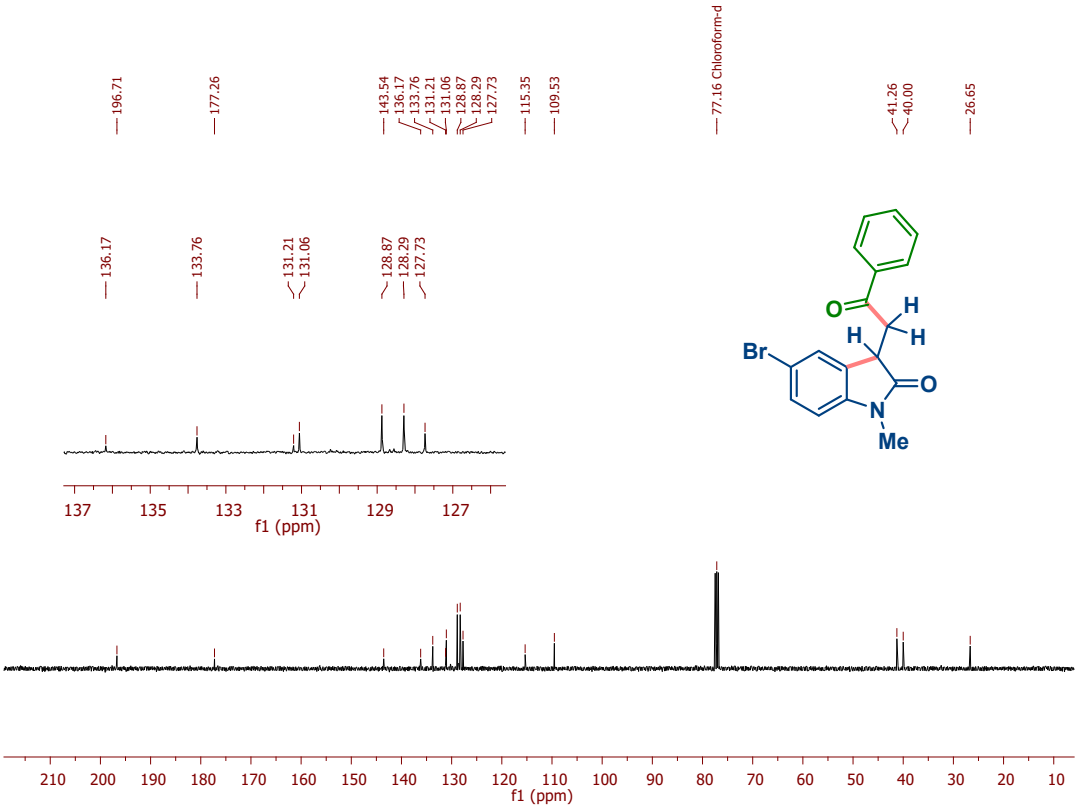
^{19}F-NMR (376 MHz) spectrum of **3ag** in $CDCl_3$



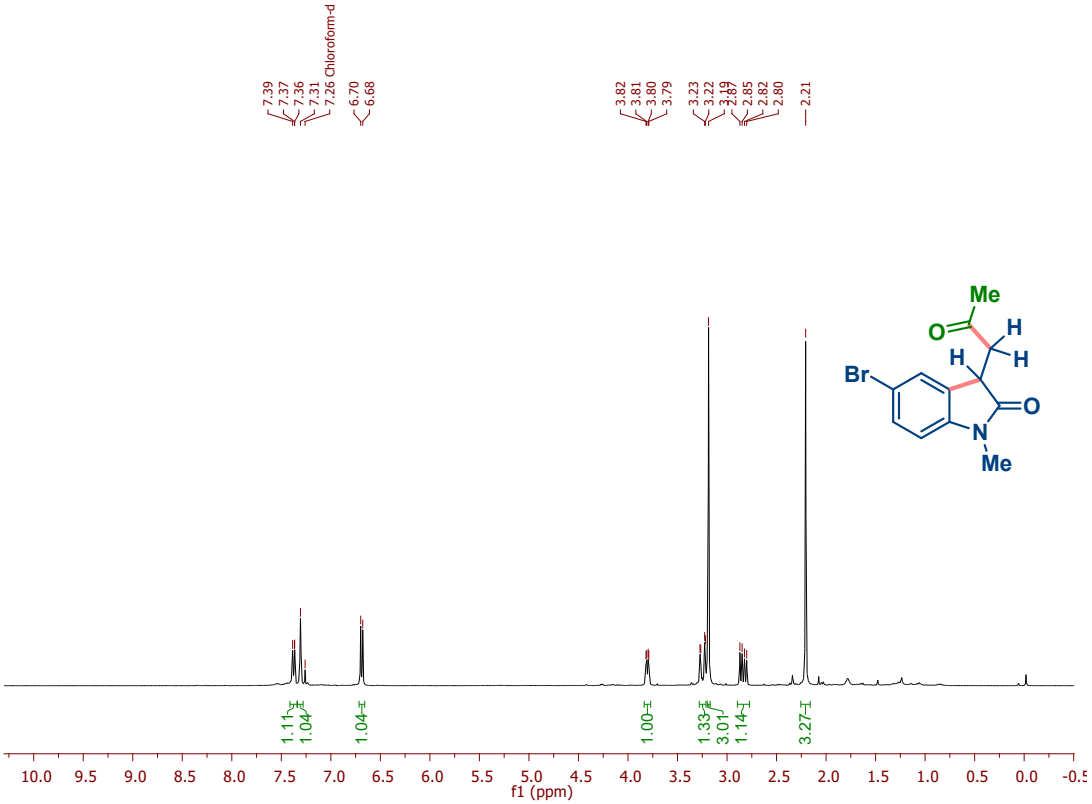
^{1}H NMR (400 MHz) spectrum of **3mh** in $CDCl_3$



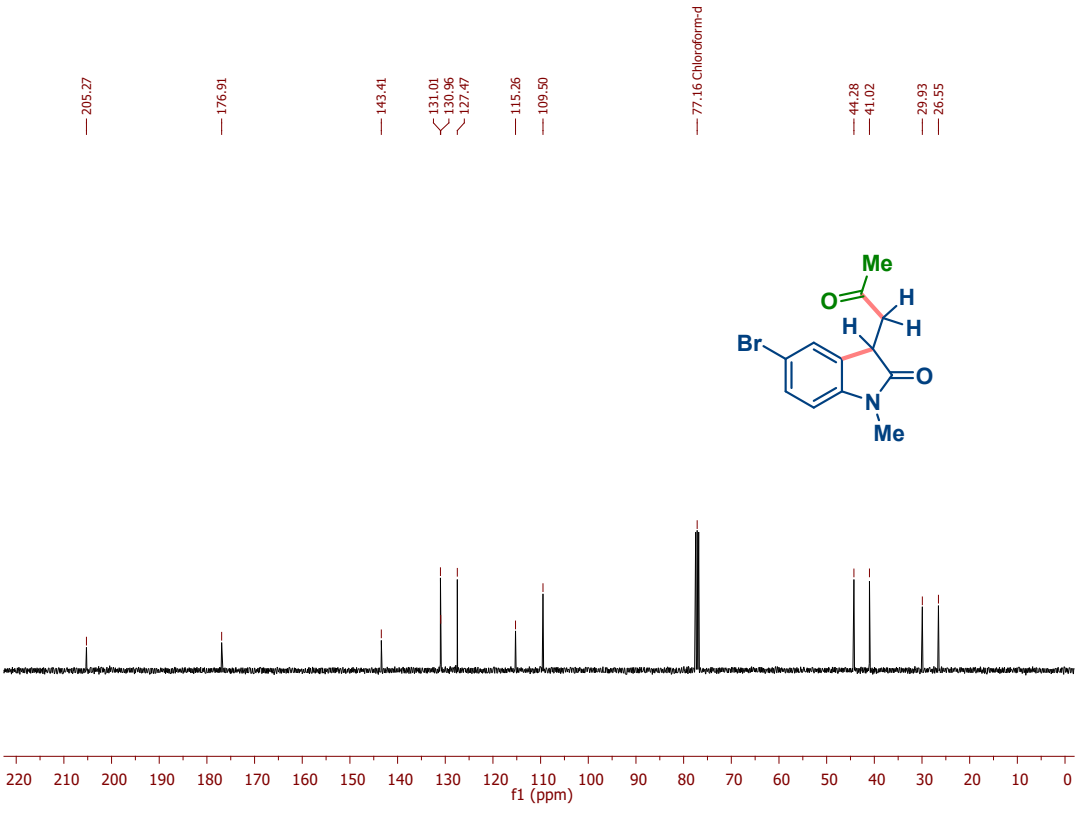
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3mh** in $CDCl_3$



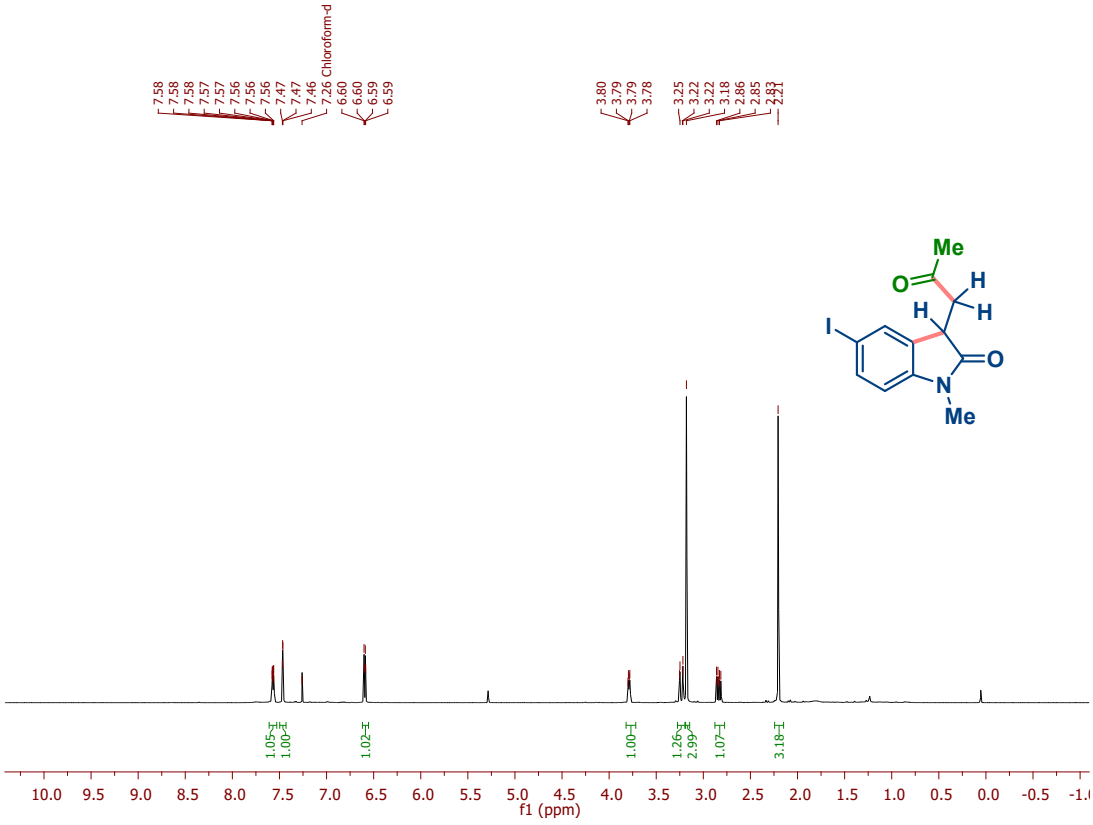
^{1}H NMR (600 MHz) spectrum of **3ph** in $CDCl_3$



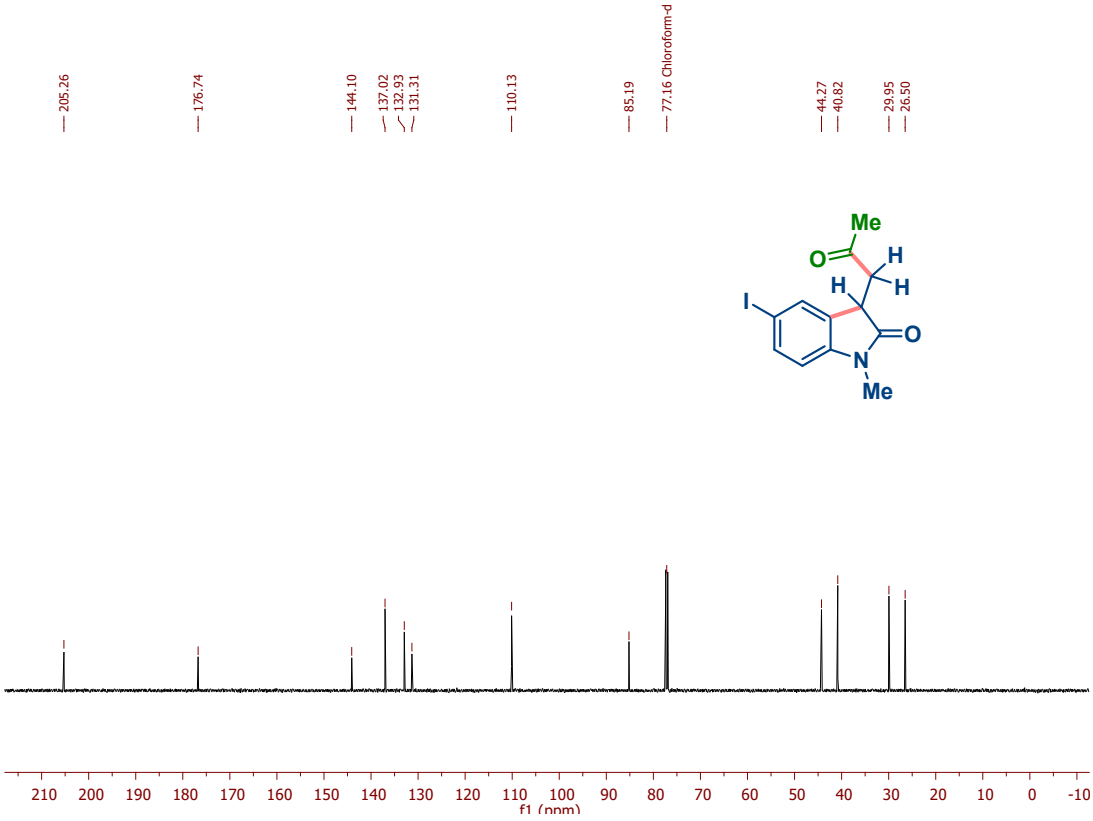
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ph** in $CDCl_3$



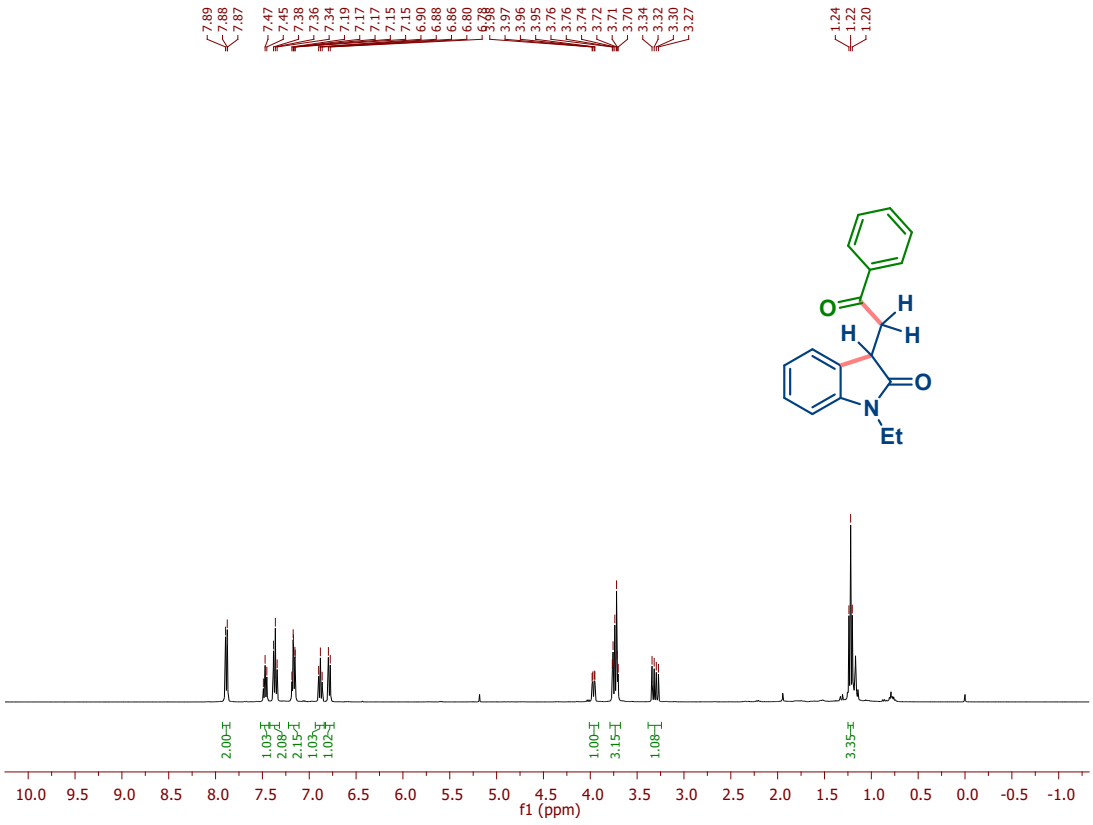
^{1}H NMR (400 MHz) spectrum of **3pi** in $CDCl_3$



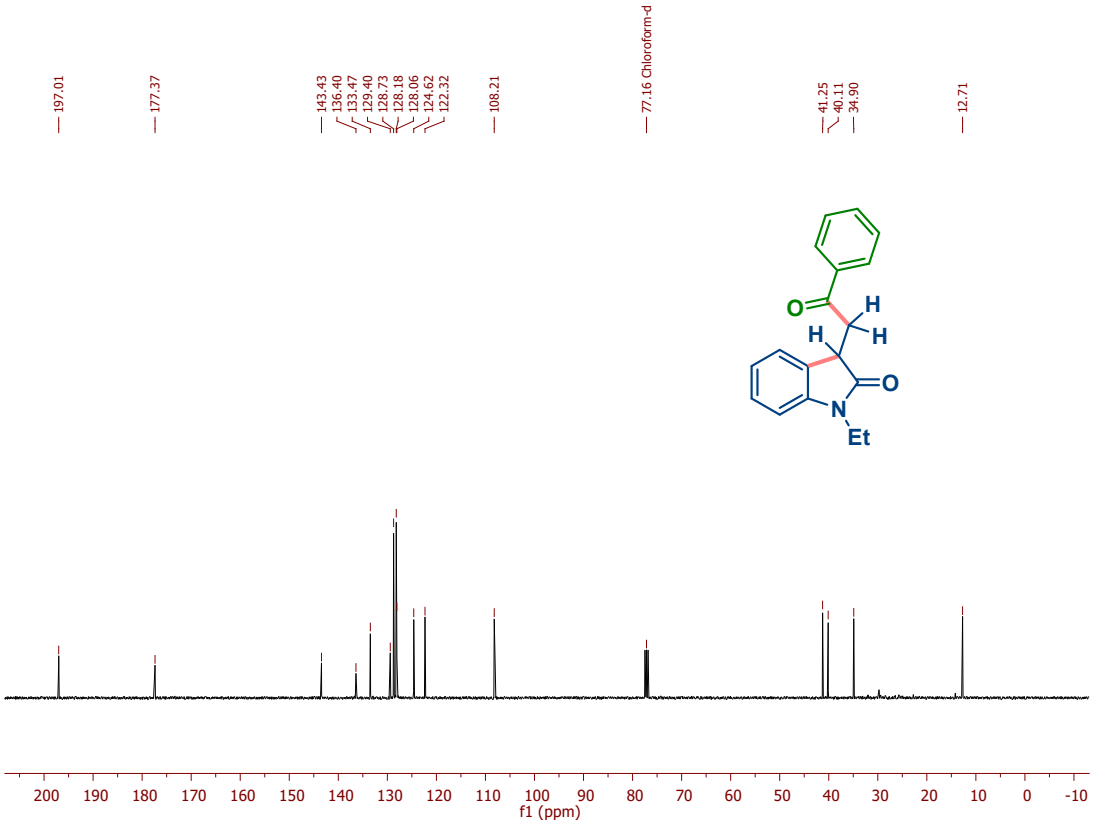
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3pi** in $CDCl_3$



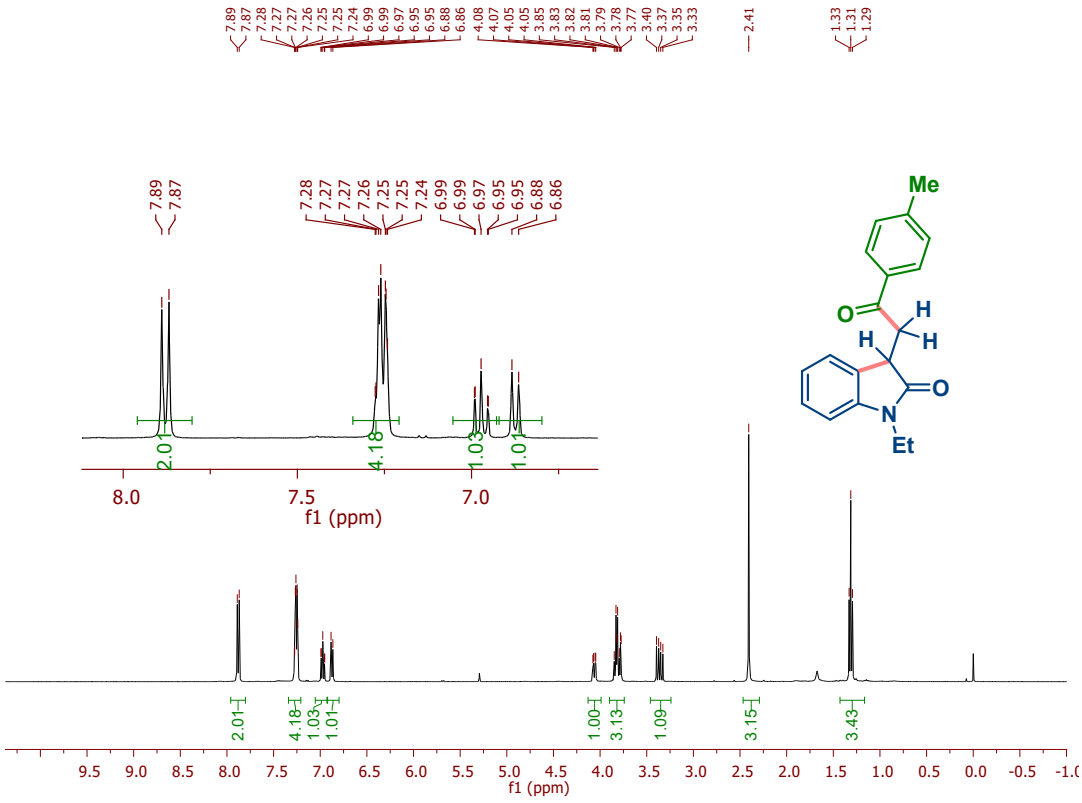
^{1}H NMR (400 MHz) spectrum of **3mj** in $CDCl_3$



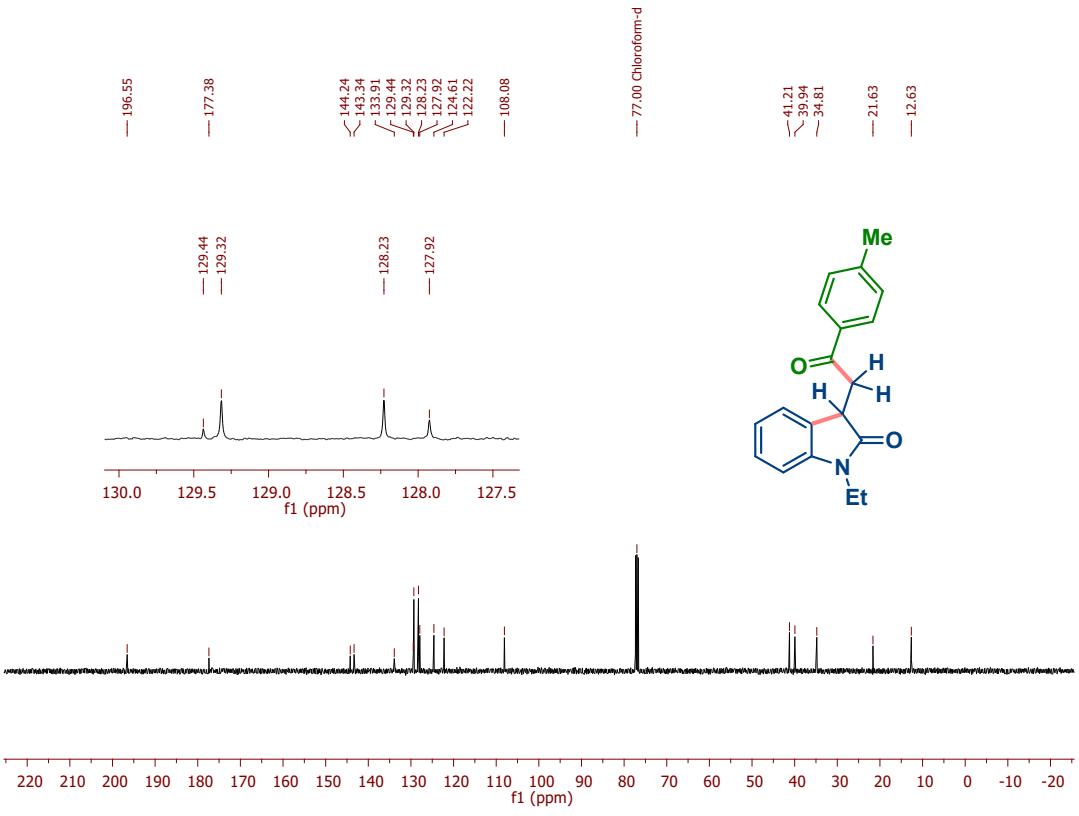
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3mj** in $CDCl_3$



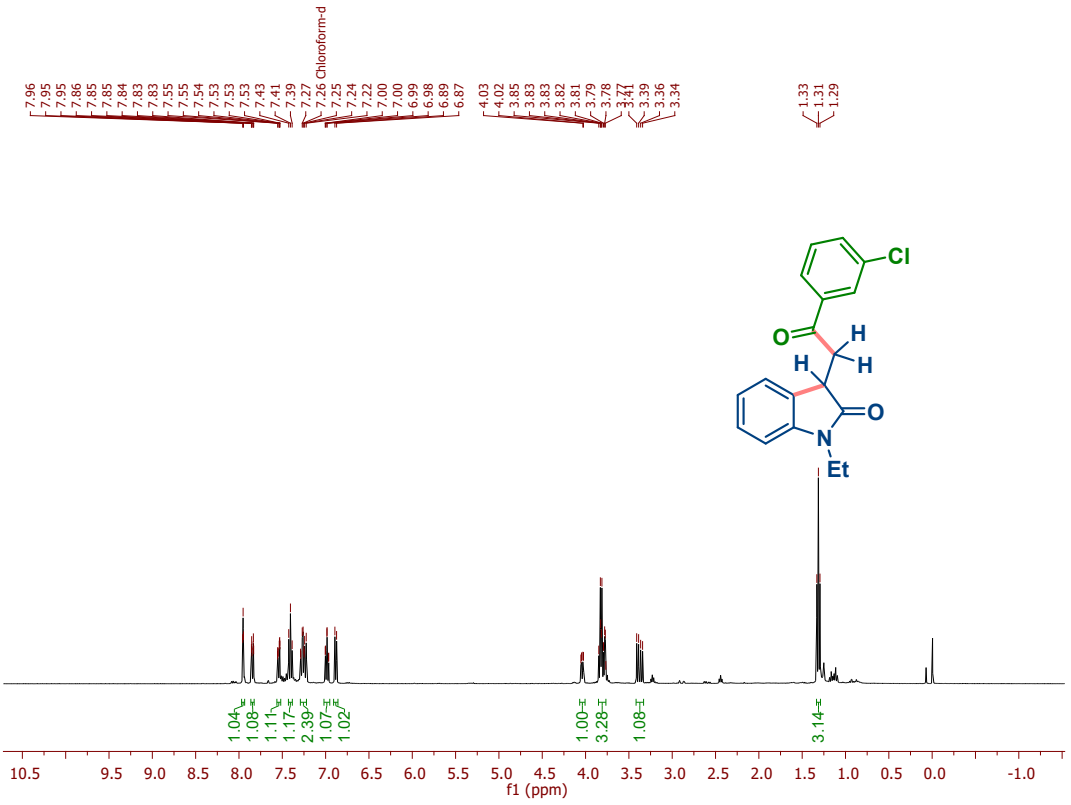
^{1}H NMR (600 MHz) spectrum of **3aj** in $CDCl_3$



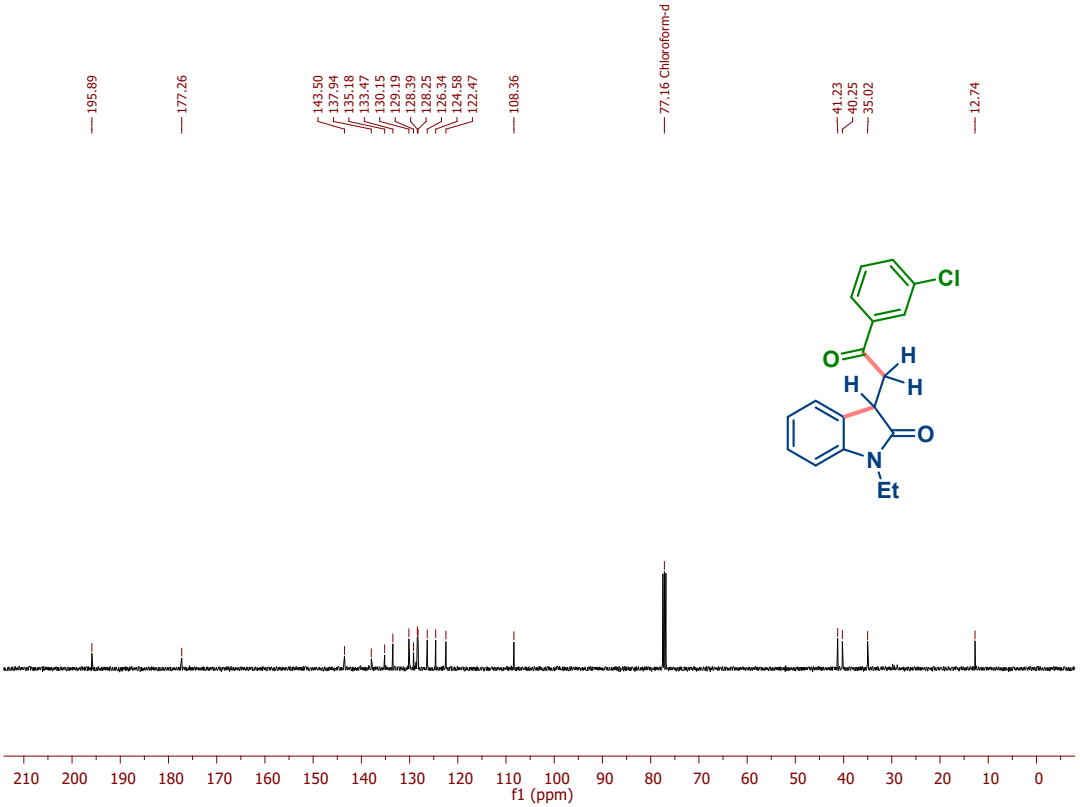
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3aj** in $CDCl_3$



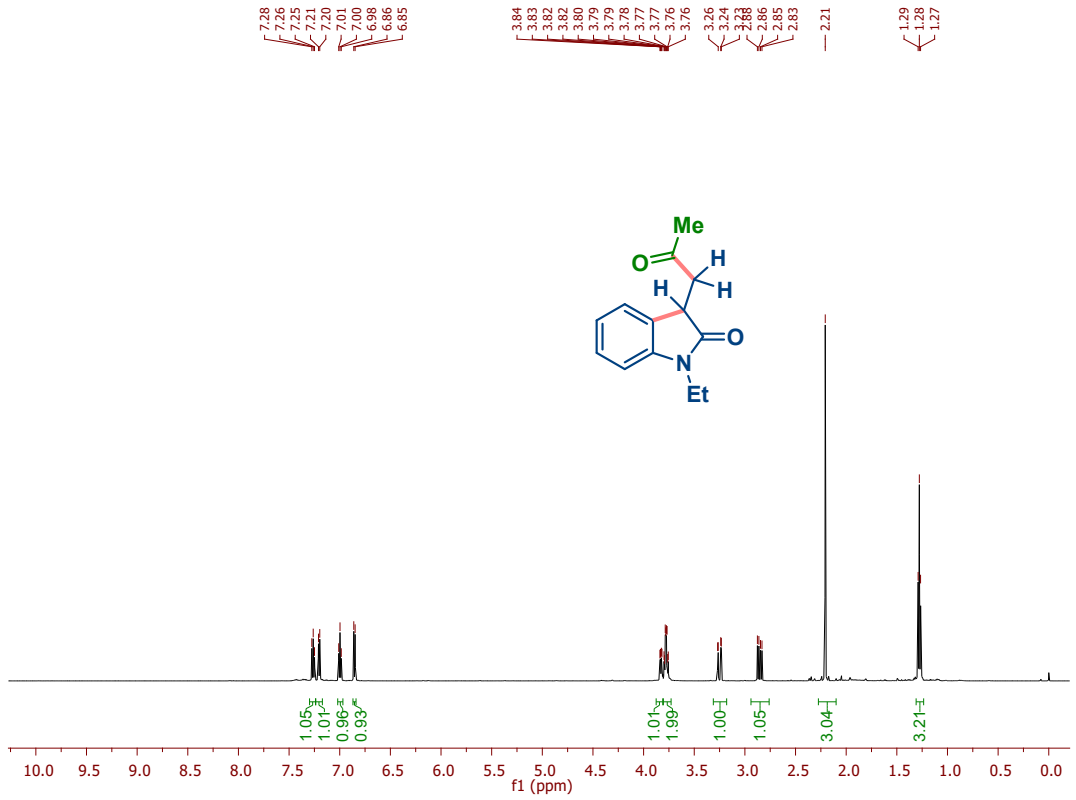
^{1}H NMR (400 MHz) spectrum of **3kj** in $CDCl_3$



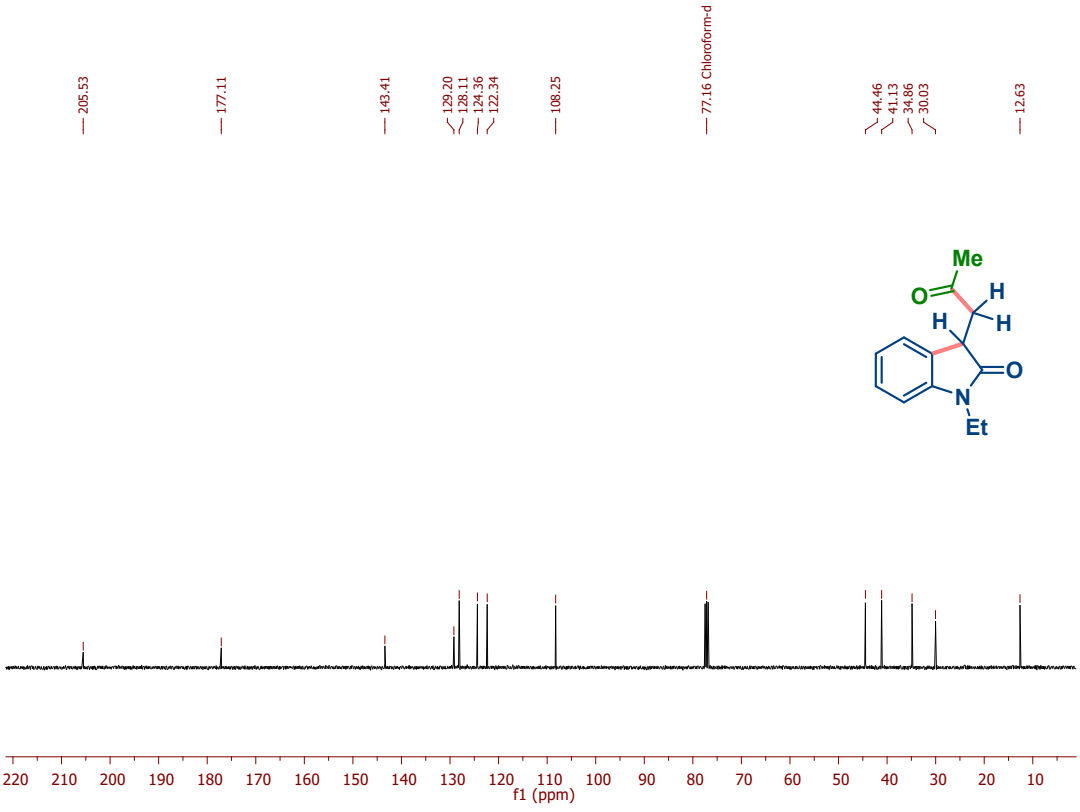
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3kj** in $CDCl_3$



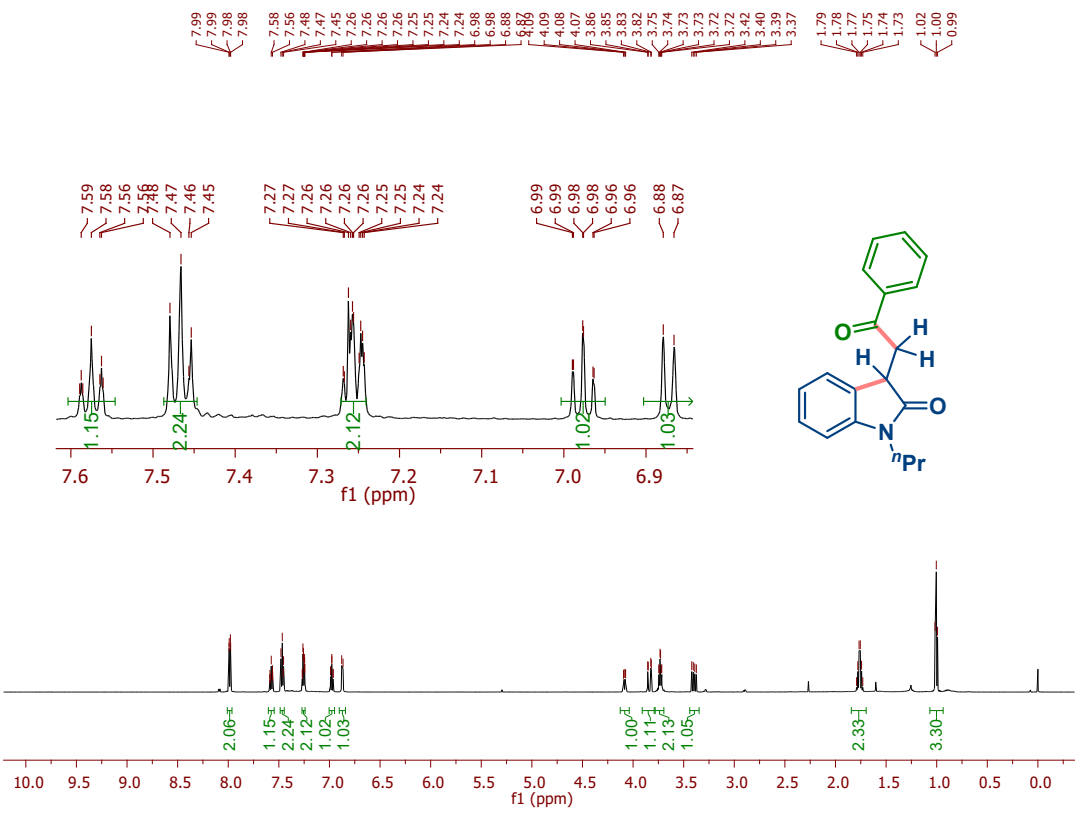
^{1}H NMR (400 MHz) spectrum of **3pj** in $CDCl_3$



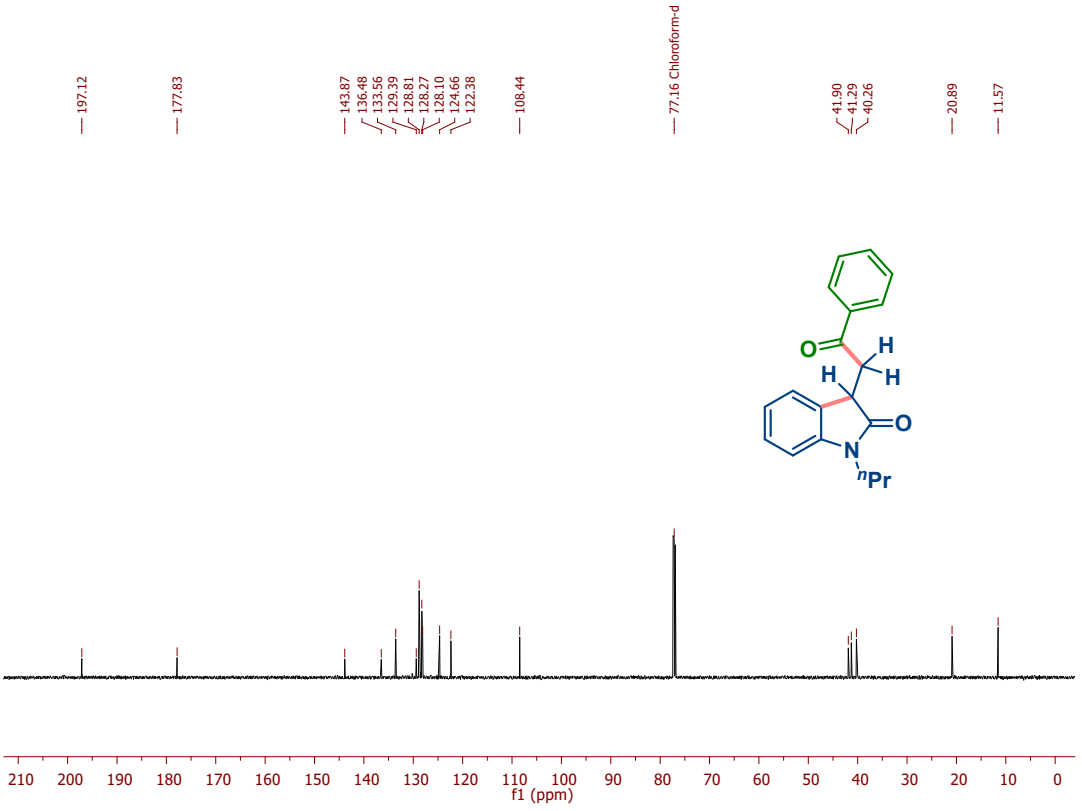
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3pj** in $CDCl_3$



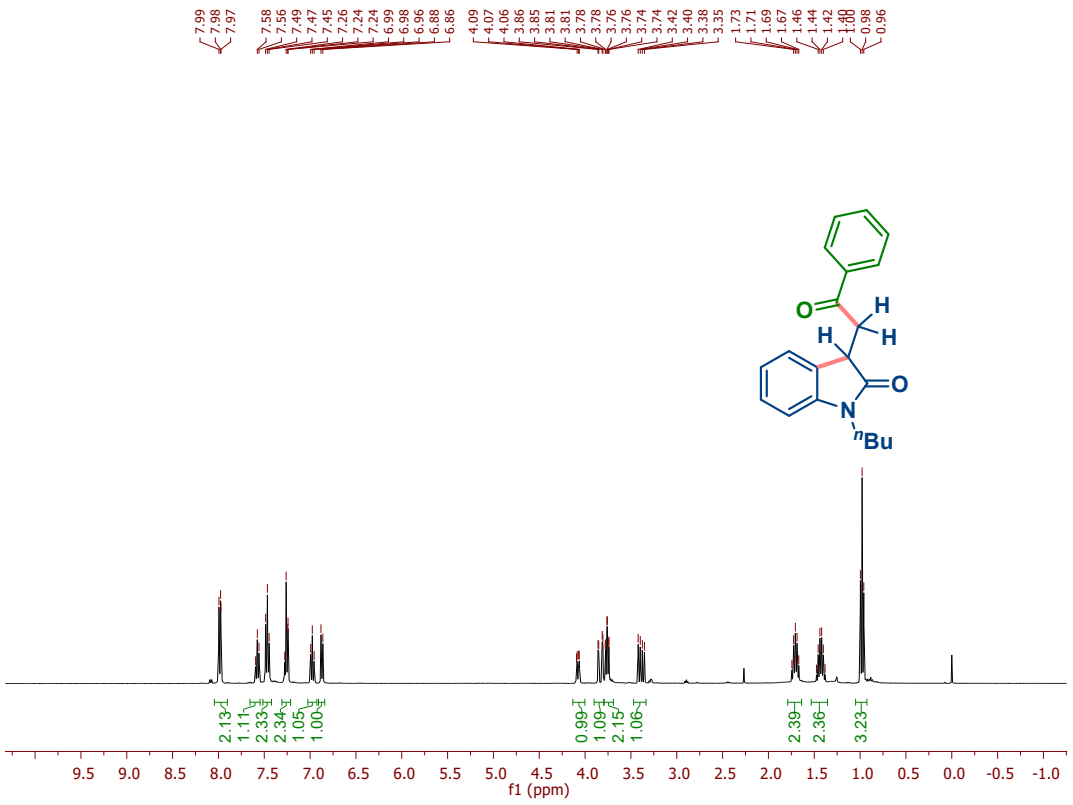
^{1}H NMR (600 MHz) spectrum of **3mk** in $CDCl_3$



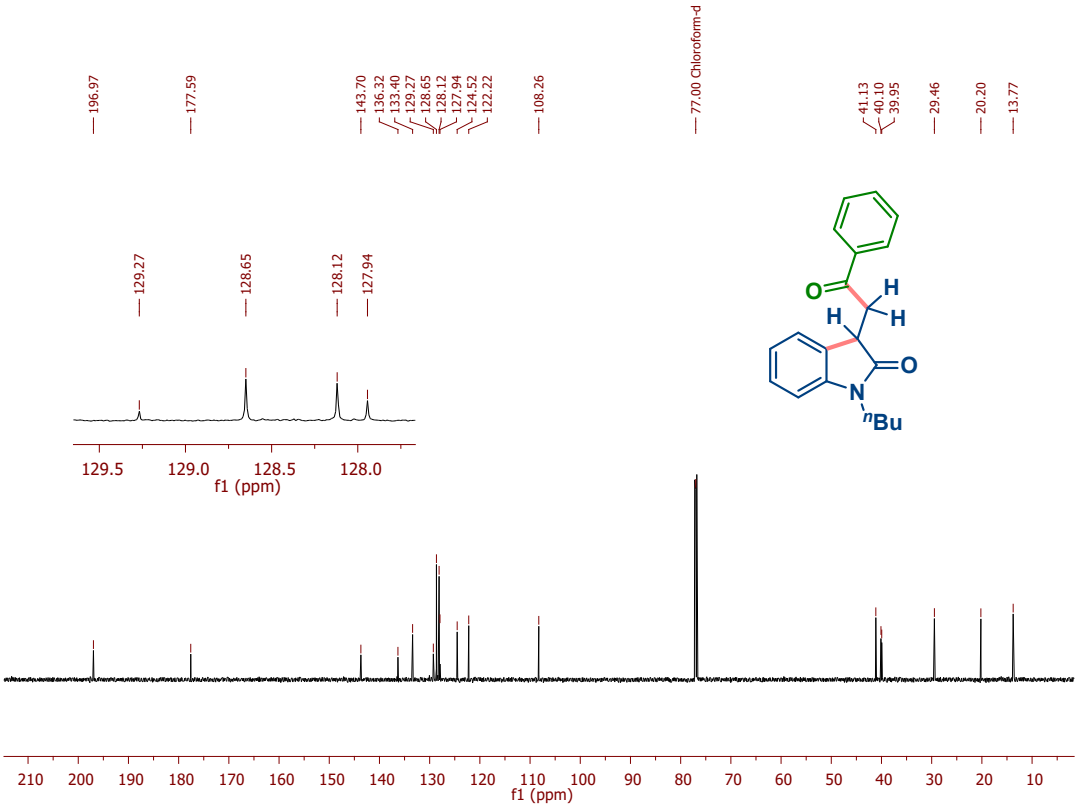
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3mk** in $CDCl_3$



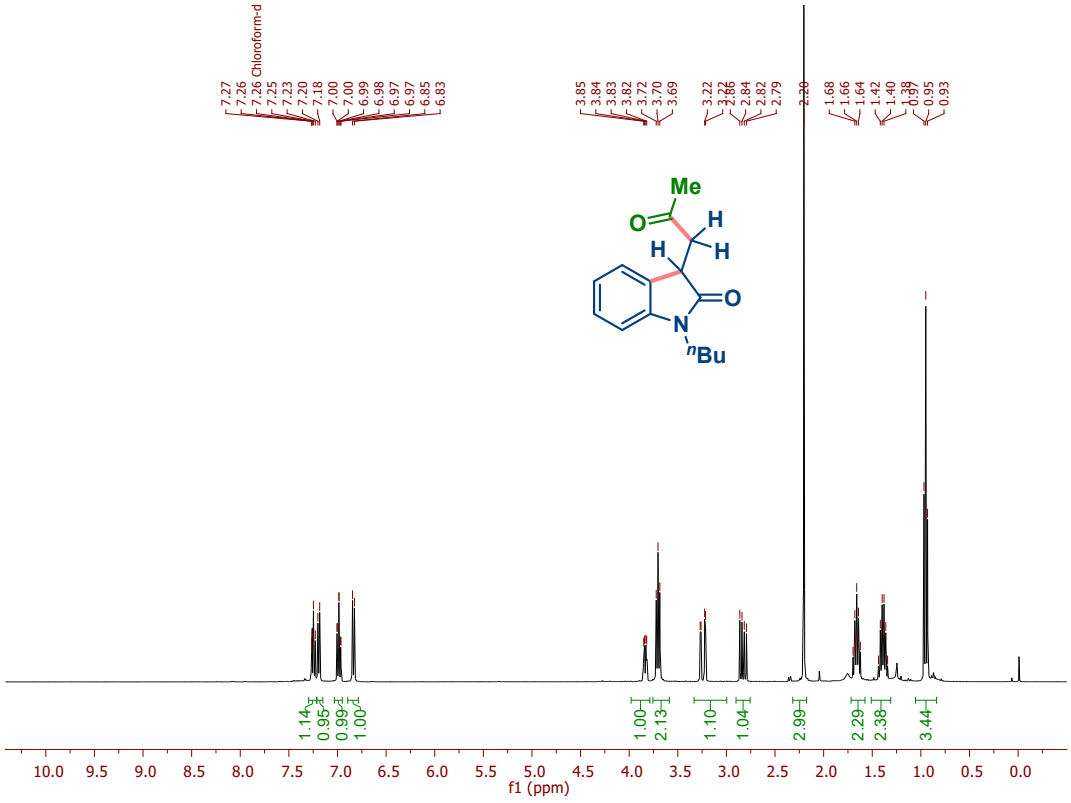
^{1}H NMR (400 MHz) spectrum of **3ml** in $CDCl_3$



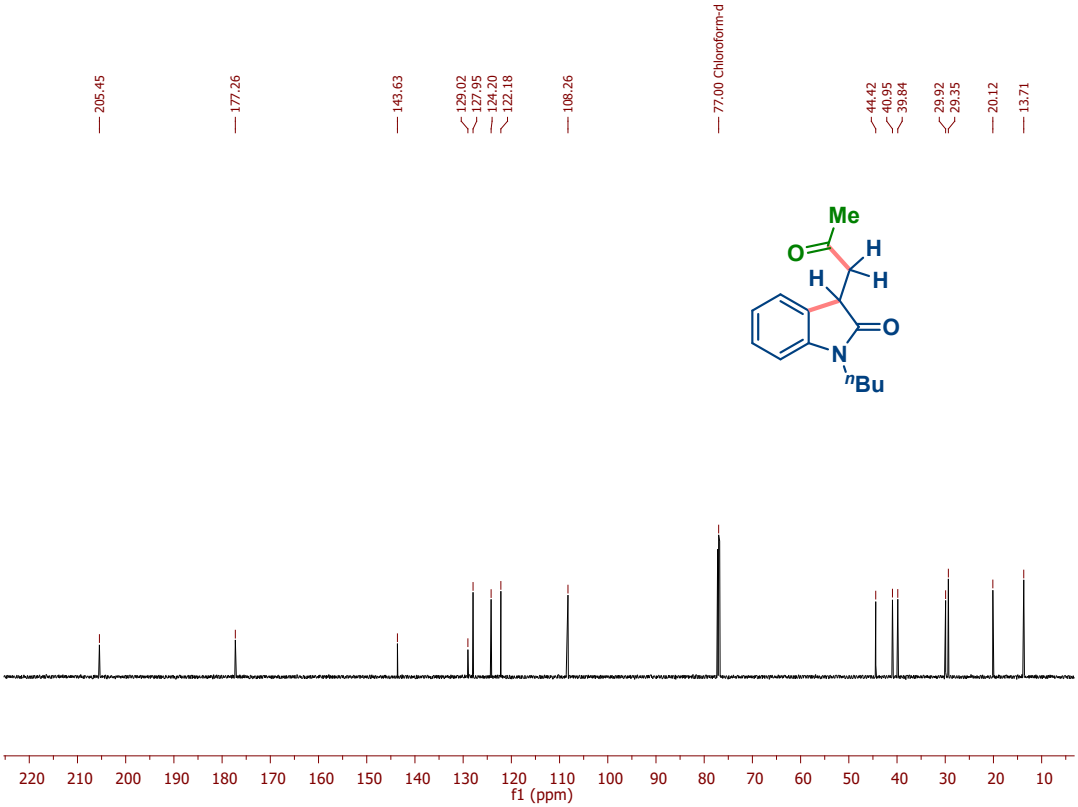
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3ml** in $CDCl_3$



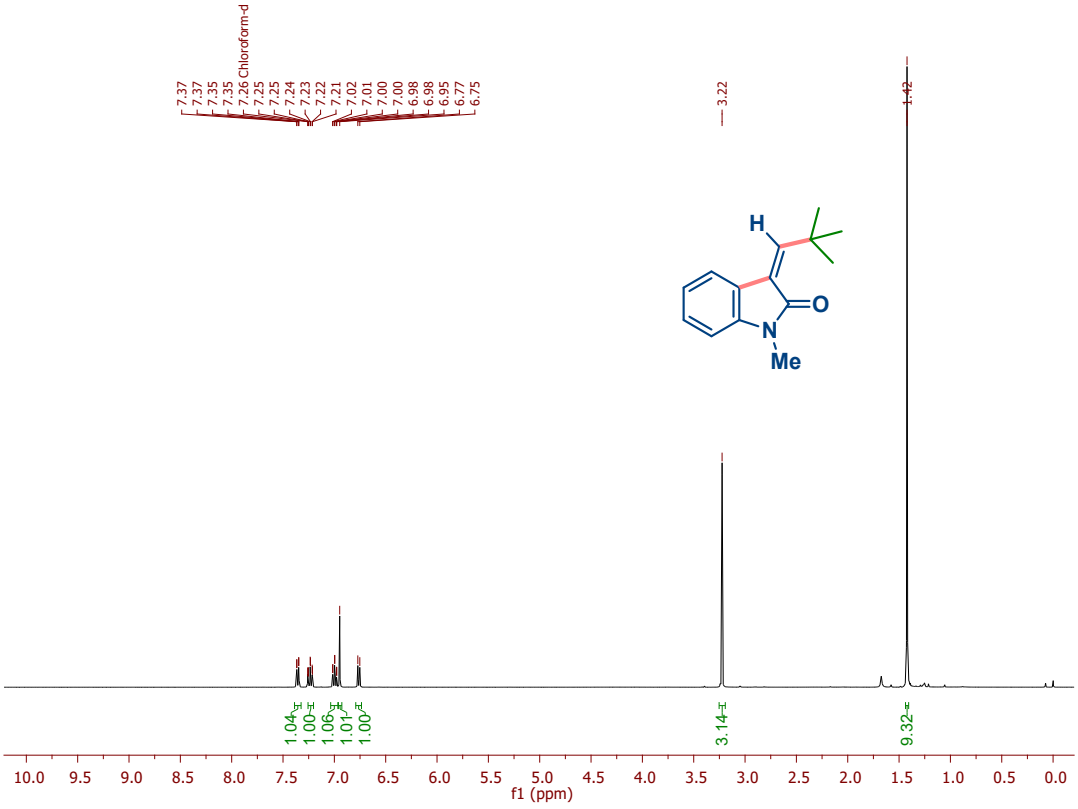
^{1}H NMR (400 MHz) spectrum of **3pl** in $CDCl_3$



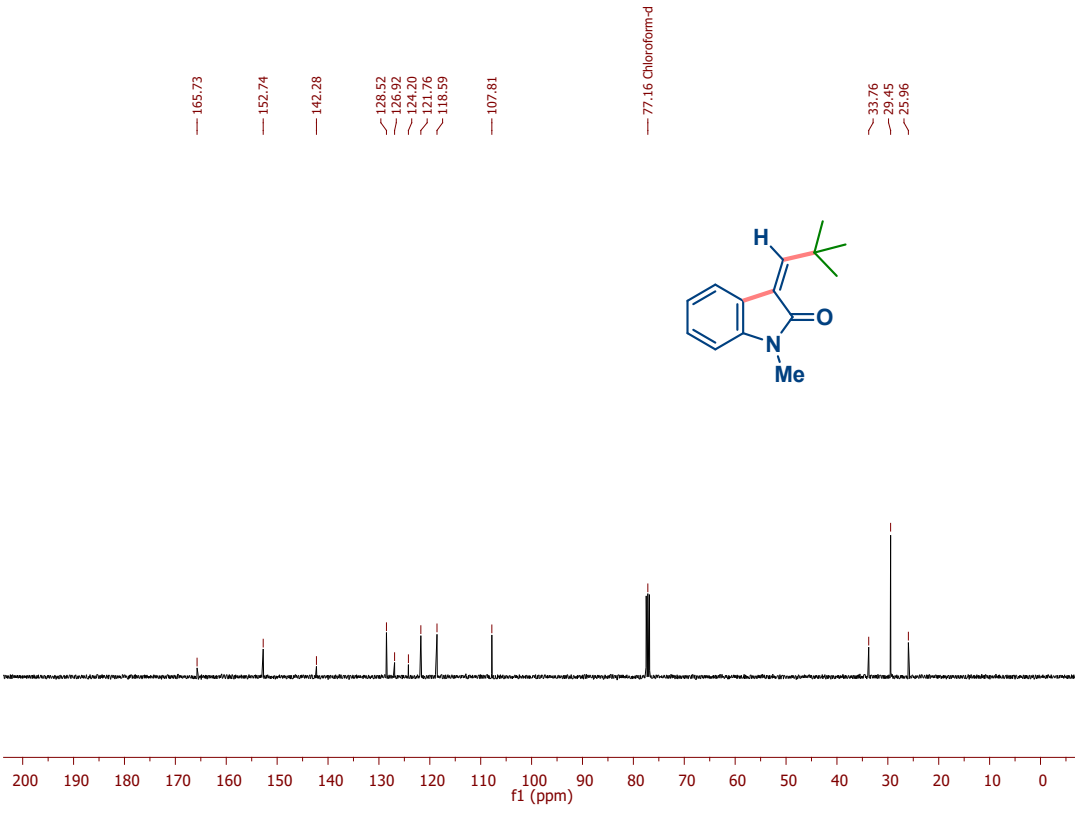
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3pl** in $CDCl_3$



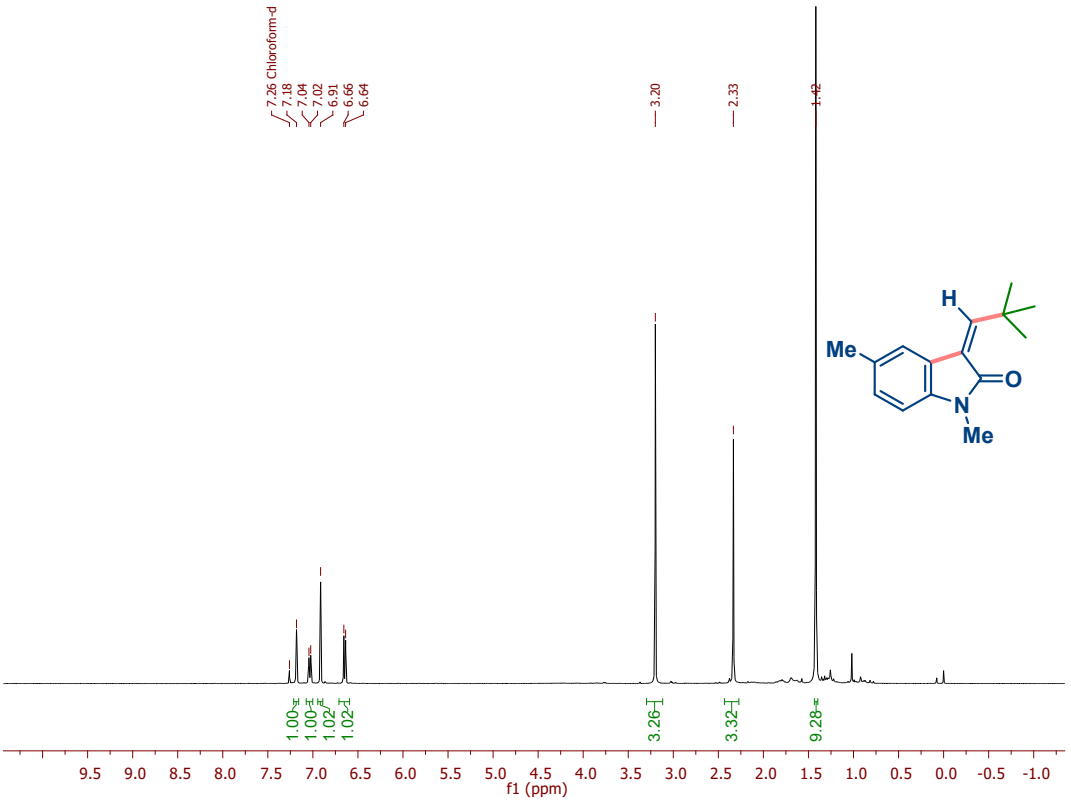
^{1}H NMR (400 MHz) spectrum of **3qa** in $CDCl_3$



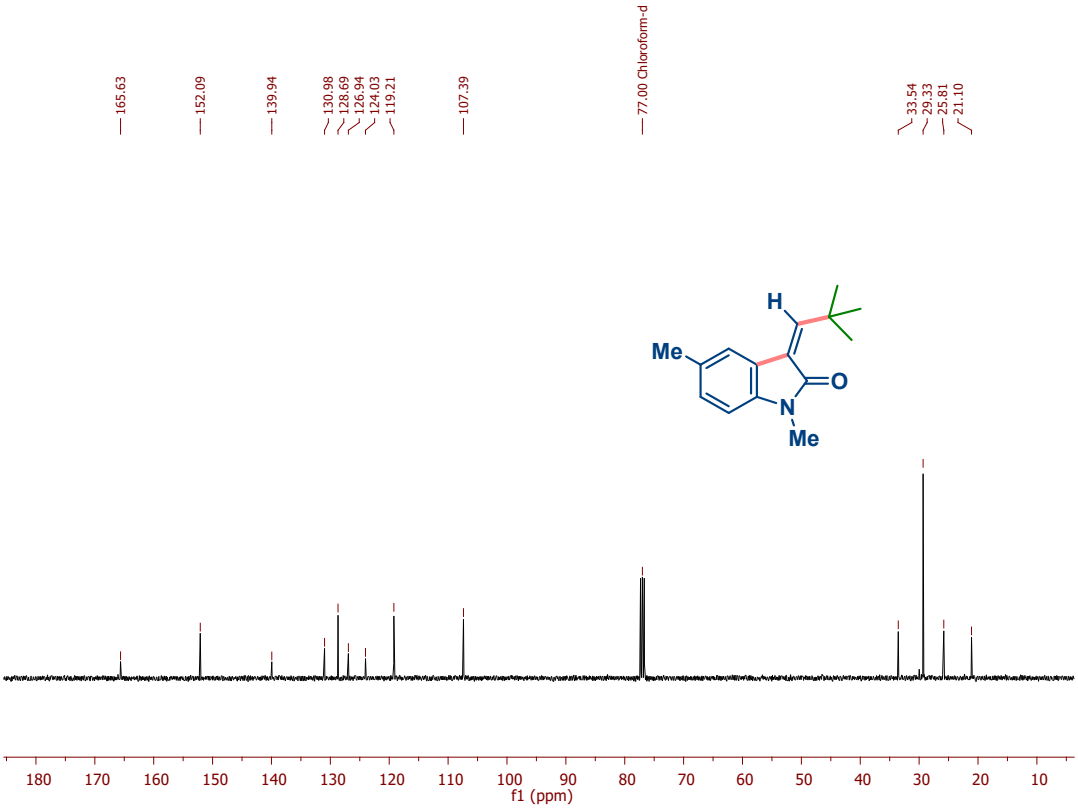
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3qa** in $CDCl_3$



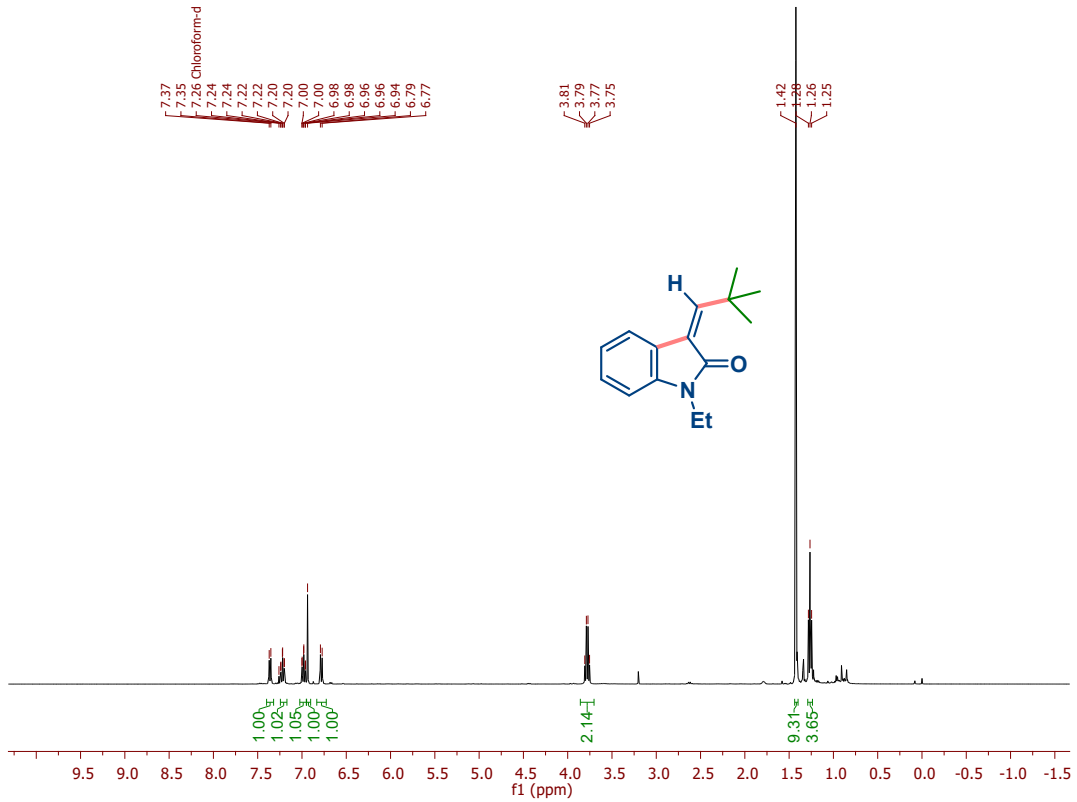
^{1}H NMR (400 MHz) spectrum of **3qb** in $CDCl_3$



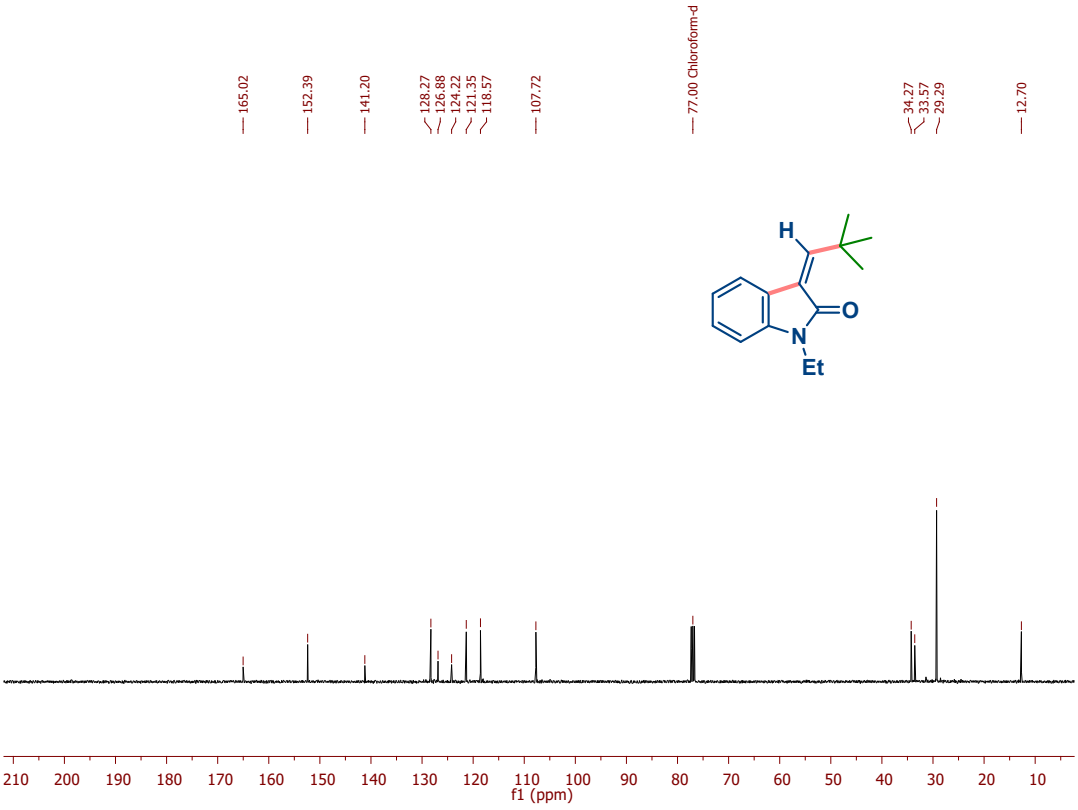
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3qb** in $CDCl_3$



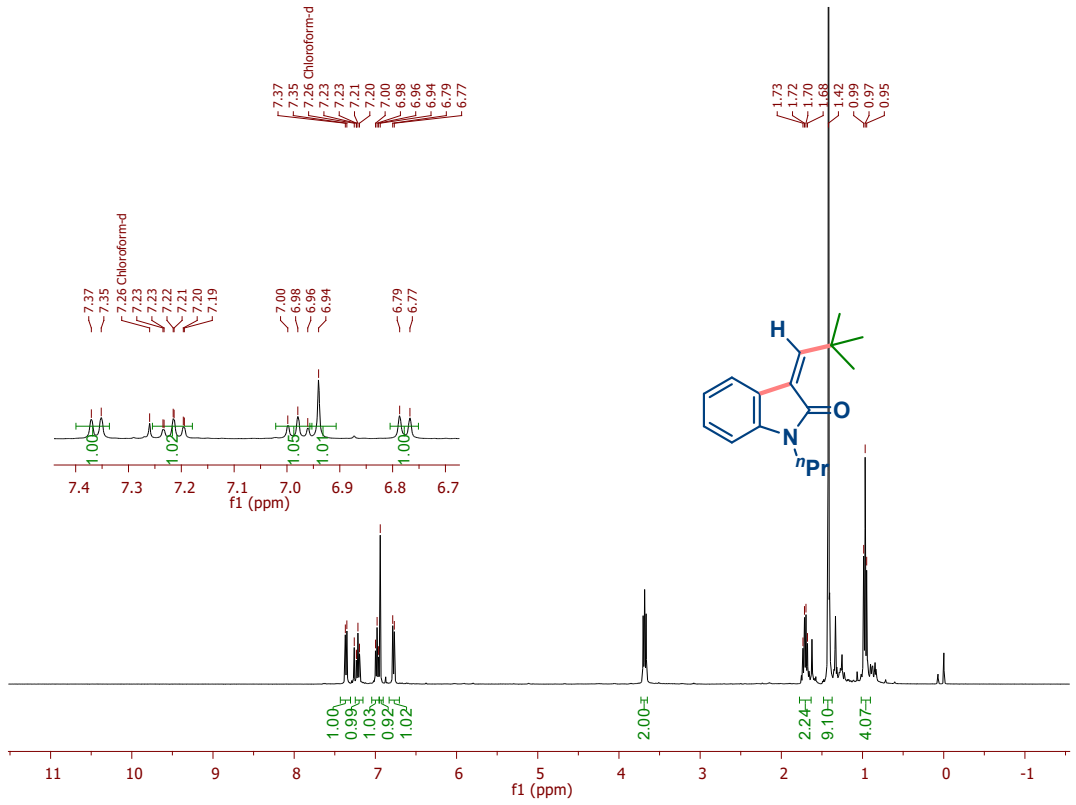
^{1}H NMR (400 MHz) spectrum of **3qj** in $CDCl_3$



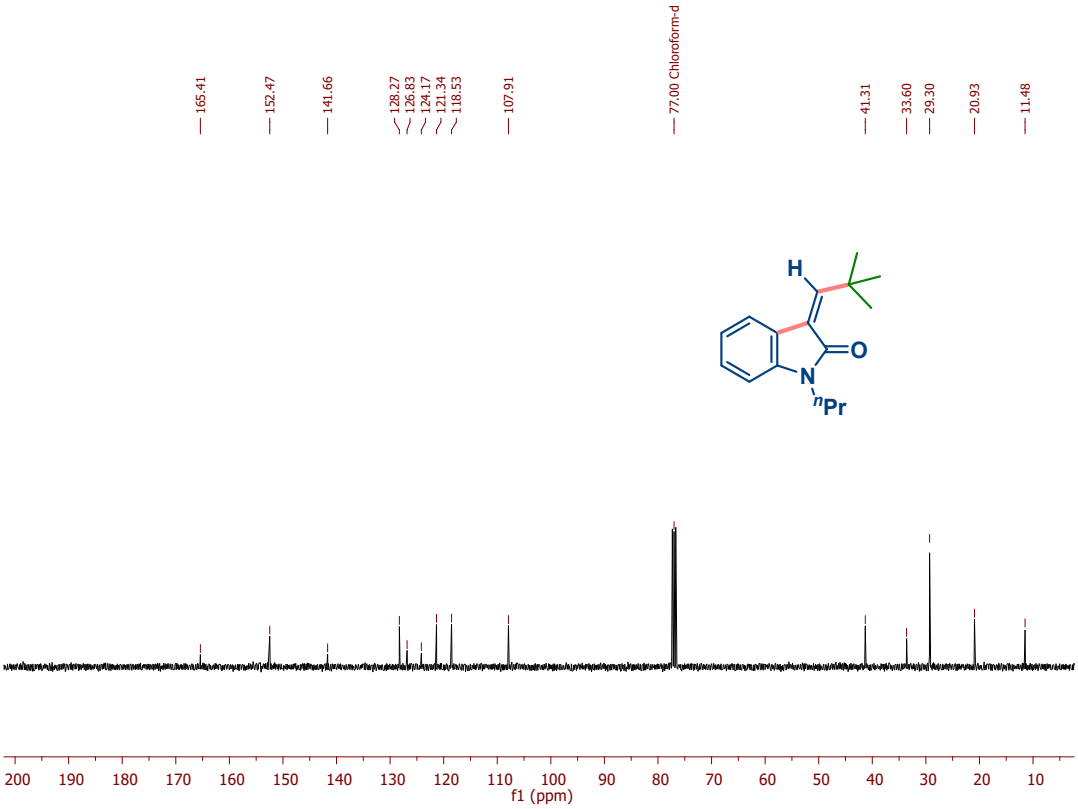
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3qj** in $CDCl_3$



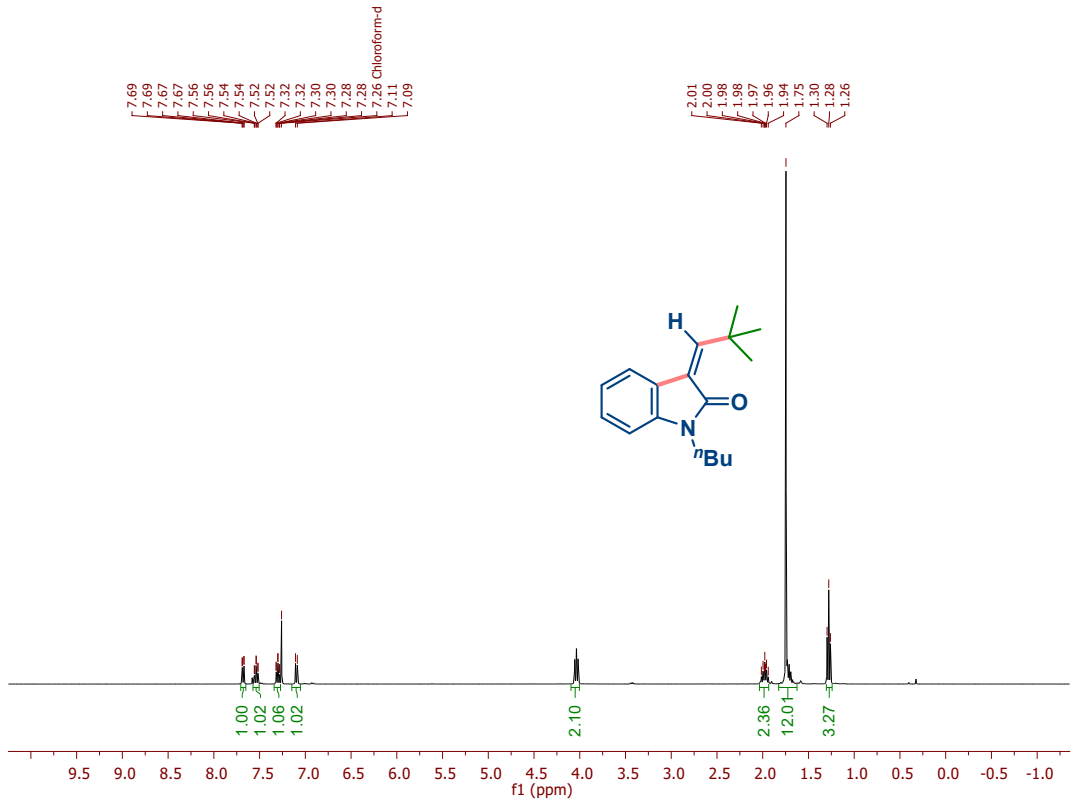
^{1}H NMR (400 MHz) spectrum of **3qk** in $CDCl_3$



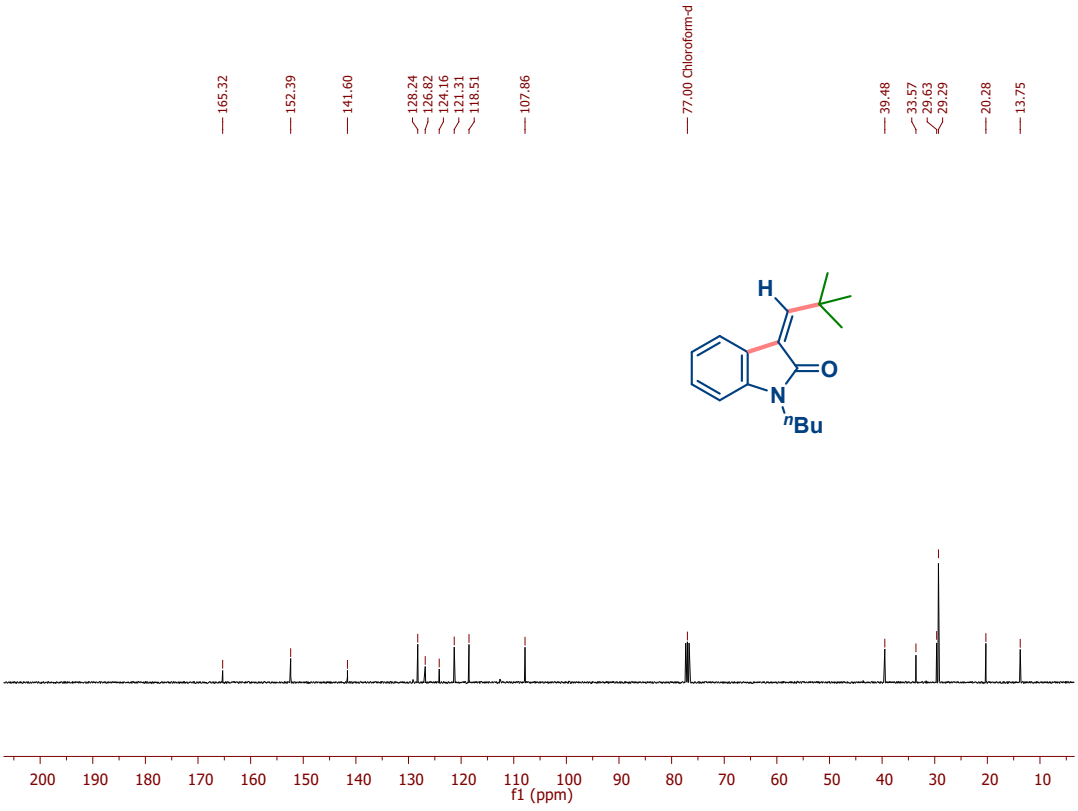
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3qk** in $CDCl_3$



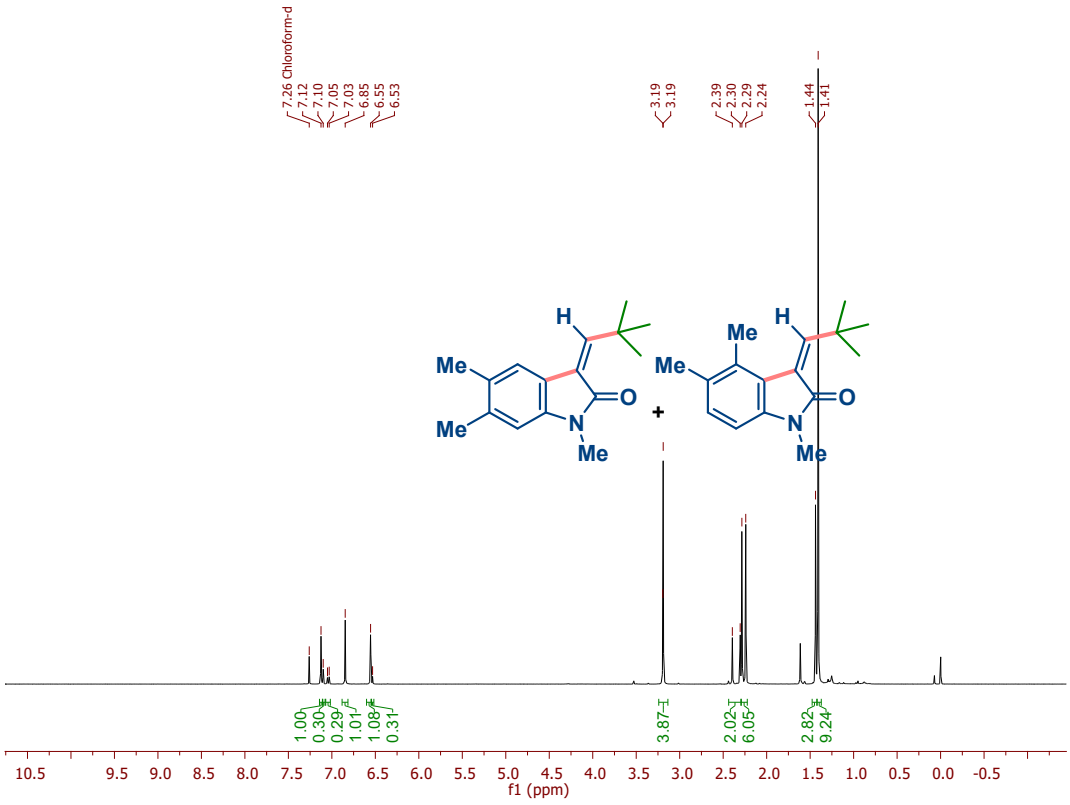
^{1}H NMR (400 MHz) spectrum of **3ql** in $CDCl_3$



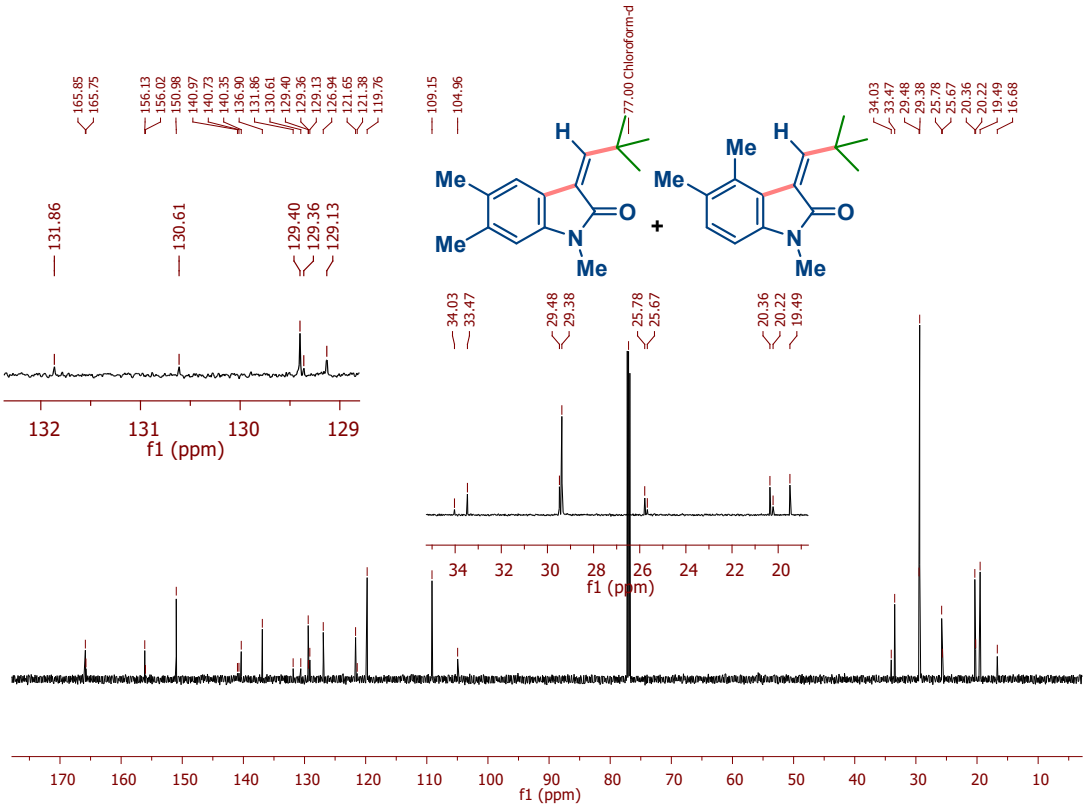
$^{13}C\{^{1}H\}$- NMR (101 MHz) spectrum of **3ql** in $CDCl_3$



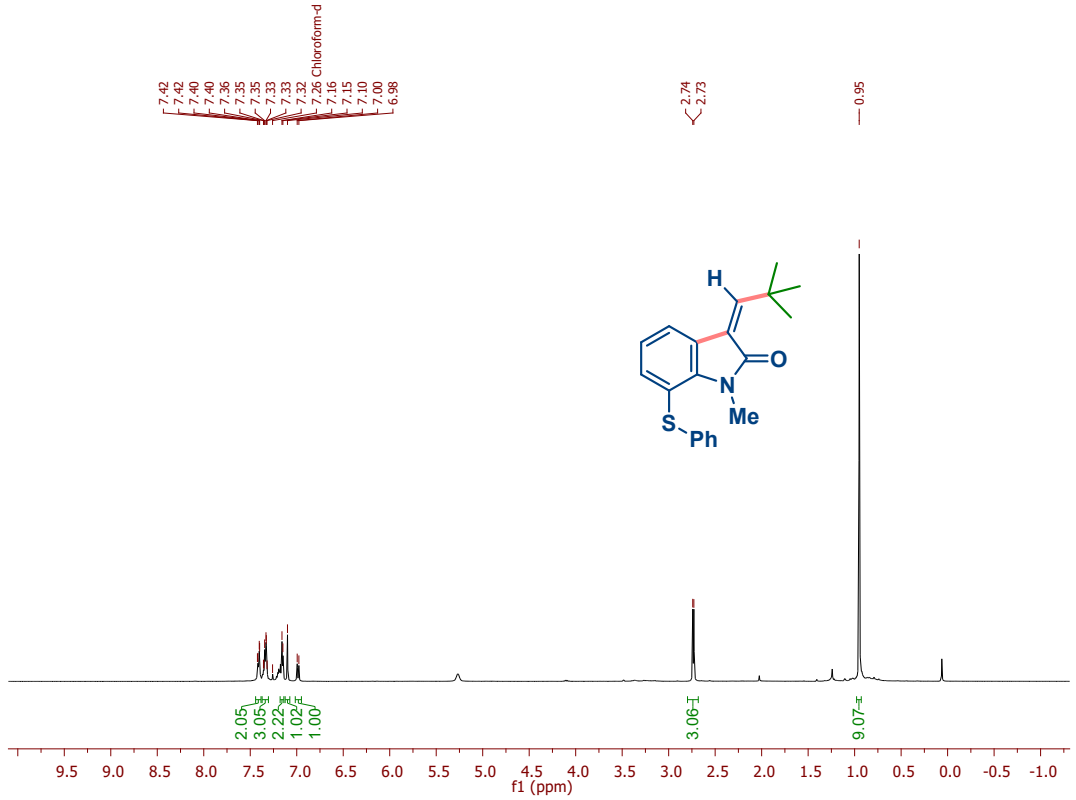
^{1}H NMR (400 MHz) spectrum of (**3qo+3qo′**) in $CDCl_3$



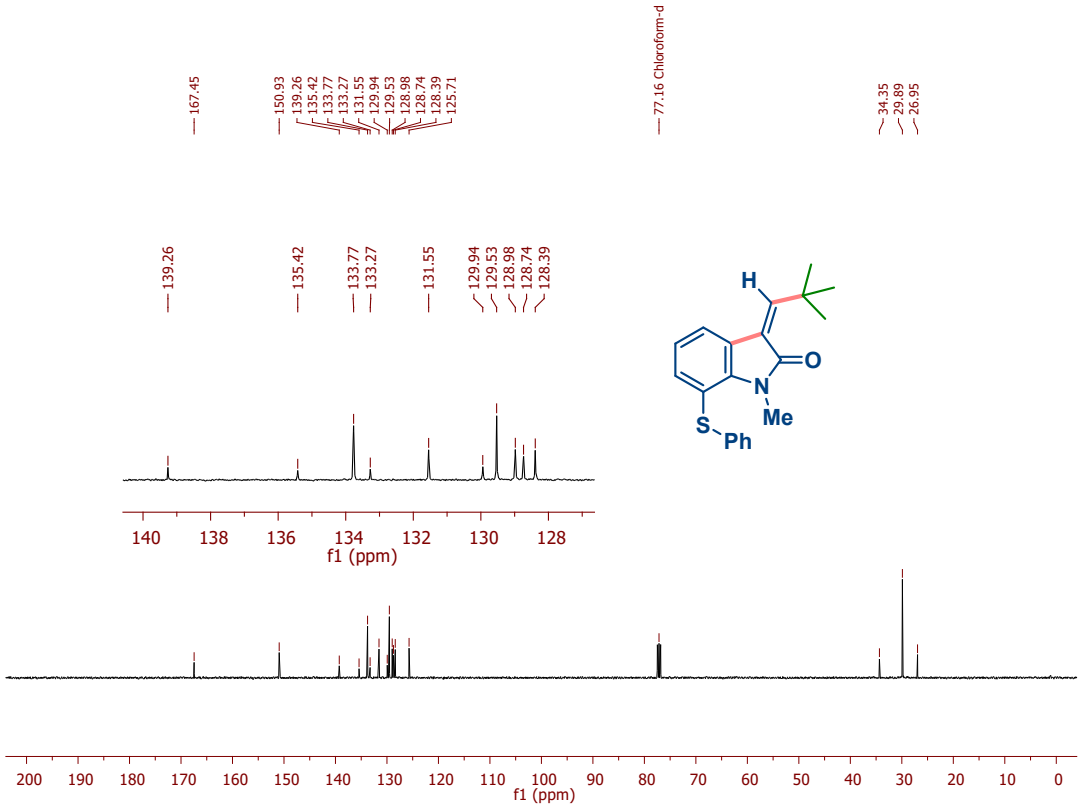
$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of (**3qo+3qo′)** in $CDCl_3$



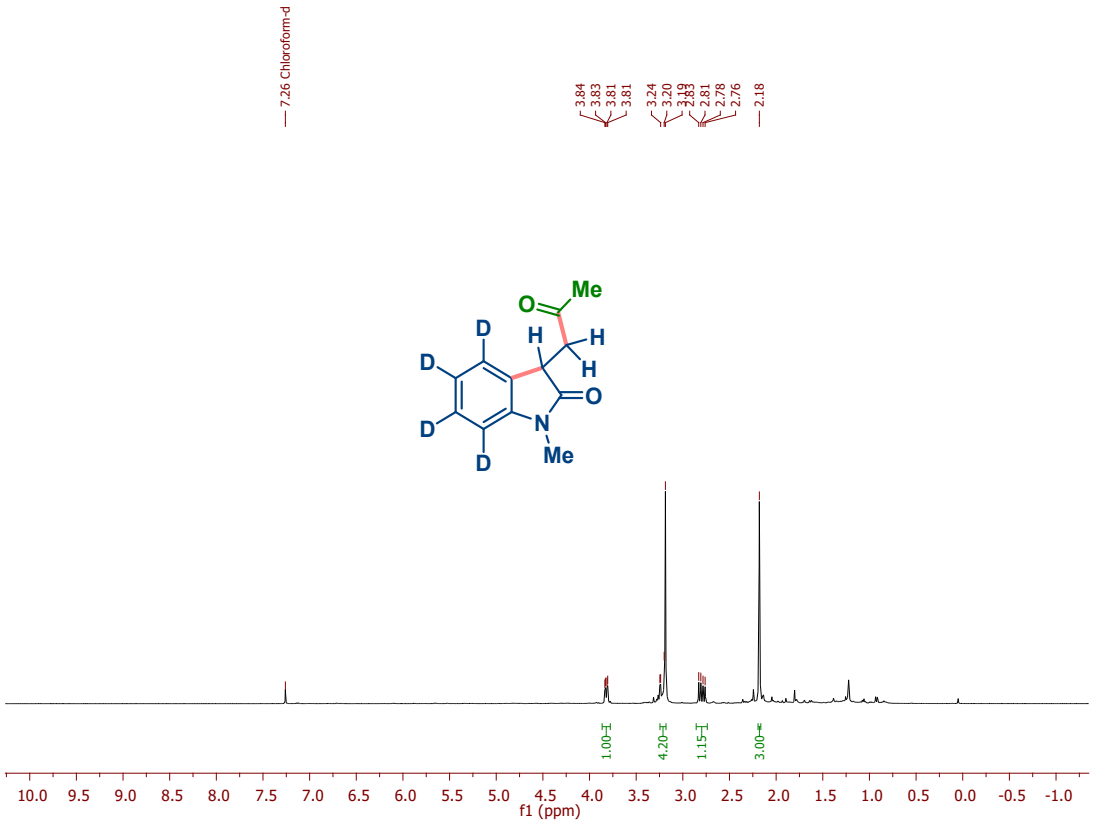
^{1}H NMR (600 MHz) spectrum of **3qp** in $CDCl_3$



$^{13}C\{^{1}H\}$- NMR (151 MHz) spectrum of **3qp** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of ***d*$_4$-2pa** in $CDCl_3$



Crystal structure data:

X-Ray crystal structure of compound **2h**:

The crystal of compound **2h** was obtained by dissolving the product in CH_2Cl_2/ACN and allowing the solvent to slowly evaporate at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC No. 2428258 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk

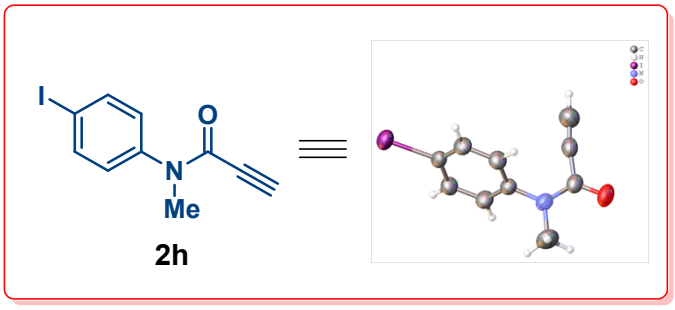


Figure S2: ORTEP diagram of compound **2h** with ellipsoid shown at the 50% contour percent probability level (**CCDC**-2428258).

Table 3S: Crystal data and structure refinement for **2h** (**CCDC**-2428258).

Crystal data and structure refinement for mo_GS_PS_142_1.	
Identification code	mo_GS_PS_142_1
Empirical formula	$C_{10}H_8INO$
Formula weight	285.07
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.9735(16)
b/Å	11.629(2)
c/Å	8.9604(16)
α/°	90
β/°	98.377(6)
γ/°	90
Volume/Å^3	1028.1(3)
Z	4
ρ_{calc}g/cm^3	1.842
μ/mm^{-1}	3.074
F(000)	544.0
Crystal size/mm^3	0.42 × 0.32 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.414 to 54.266
Index ranges	-11 ≤ h ≤ 12, -14 ≤ k ≤ 14, -11 ≤ l ≤ 11
Reflections collected	14723
Independent reflections	2247 [R_{int} = 0.0483, R_{sigma} = 0.0301]

Data/restraints/parameters	2247/0/120
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0775
Final R indexes [all data]	R_1 = 0.0377, wR_2 = 0.0813
Largest diff. peak/hole / e $Å^{-3}$	1.03/-0.98

X-ray crystal structure of compound **3pe**:

The crystal of compound **3pe** was obtained by dissolving the product in CH_2Cl_2/ACN and allowing the solvent to slowly evaporate at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC No. 2402041 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk

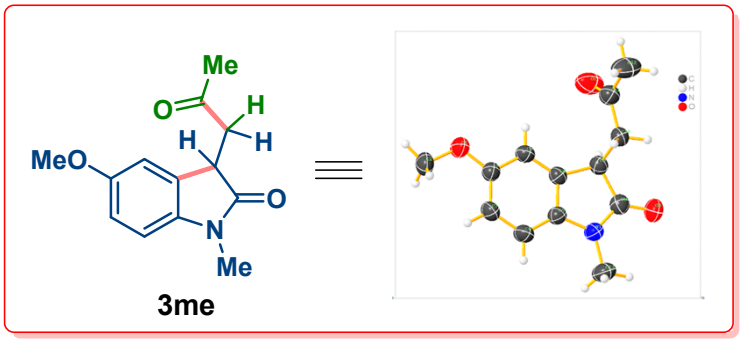


Figure S2: ORTEP diagram of compound **3pe** with ellipsoid shown at the 50% contour percent probability level (**CCDC**-2402041).

Table 3S: Crystal data and structure refinement for **3pe** (**CCDC**-2402041).

Crystal data and structure refinement for mo_GS_PS_P4Me_2.	
Identification code	mo_GS_PS_P4Me_2
Empirical formula	$C_{13}H_{15}NO_3$
Formula weight	233.26
Temperature/K	298.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.1369(3)

b/Å	9.3444(5)
c/Å	25.1733(16)
α/°	90
β/°	92.300(2)
γ/°	90
Volume/Å^3	1207.38(12)
Z	4
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	0.091
F(000)	496.0
Crystal size/mm^3	0.25 × 0.23 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.65 to 54.284
Index ranges	-6 ≤ h ≤ 5, -11 ≤ k ≤ 11, -32 ≤ l ≤ 31
Reflections collected	16379
Independent reflections	2675 [R_{int} = 0.0640, R_{sigma} = 0.0440]
Data/restraints/parameters	2675/0/157
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0536, wR_2 = 0.1301
Final R indexes [all data]	R_1 = 0.0845, wR_2 = 0.1483
Largest diff. peak/hole / e Å^{-3}	0.22/-0.18

X-Ray crystal structure of compound **3qo**:

The crystal of compound **3qo** was obtained by dissolving the product in CH_2Cl_2/ACN and allowing the solvent to slowly evaporate at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC No. 2402030 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk

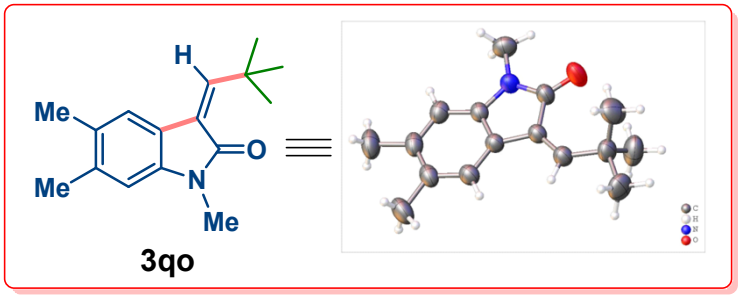


Figure S3: ORTEP diagram of compound **3qo** with ellipsoid shown at the 50% contour percent probability level (**CCDC**-2402030).

Table 4S: Crystal data and structure refinement for **3qo** (**CCDC**-2402030).

Crystal data and structure refinement for mo_GS_PS_P4_141.	
Identification code	mo_GS_PS_P4_141
Empirical formula	$C_{16}H_{21}NO$
Formula weight	243.34
Temperature/K	298
Crystal system	monoclinic
Space group	C2/m
a/Å	19.461(3)
b/Å	7.0742(11)
c/Å	10.8476(15)
α/°	90
β/°	103.577(10)
γ/°	90
Volume/Å^3	1451.7(4)
Z	4
ρ_{calc}g/cm^3	1.113
μ/mm^{-1}	0.069
F(000)	528.0
Crystal size/mm^3	0.23 × 0.19 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.066 to 54.178
Index ranges	-24 ≤ h ≤ 24, -9 ≤ k ≤ 9, -12 ≤ l ≤ 13

Reflections collected	16148
Independent reflections	1720 [R_{int} = 0.0993, R_{sigma} = 0.0546]
Data/restraints/parameters	1720/0/118
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1305
Final R indexes [all data]	R_1 = 0.1009, wR_2 = 0.1525
Largest diff. peak/hole / e $Å^{-3}$	0.17/-0.13

References:

1. I. B. Perry, T. F. Brewer, P. J. Sarver, D. M. Schultz, D. A. DiRocco, D. W. C. MacMillanm, *Nature*., 2018, **560** (7716), 70–75.
2. S. Park, K. J. Shin and J. H. Seo, *Synlett.*, 2015, **26**, 2296–2300.
3. H. Hua, Li. Xin, Su. Jianke, S. Qiuling, *Chin. J. Org. Chem*., 2023, **43**, 1146–1156.