Supporting Information

Synthesis of tricyclic oxazinoindolones via Pd-catalyzed intramolecular addition of carboxylic acids to alkynes

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Table of Contents

1 General Information:

The spectra for ^{1}H and ^{13}C were obtained using a Bruker AVANCE NEO Ascend 400 MHz FT-NMR. Proton magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz. Carbon magnetic resonance (^{13}C NMR) spectra were recorded at 101 MHz. The ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ and DMSO at 297 K, and the chemical shifts (δ) are depicted in parts per million (ppm). Data for 1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, ddd= doublet of doublet of doublets, qd = quartet of doublets). Splitting patterns that could not be interpreted are designated as multiplet (m). Coupling constant (J) are measured in Hertz (Hz). Data for ^{13}C NMR spectra were reported in a similar pattern, as singlet peaks in the ^{13}C NMR spectra were reported only with their chemical shifts. For ^{1}H NMR, the chemical shifts were calibrated in reference to tetramethylsilane (0 ppm), or the residual undeuterated solvents ($CDCl_3$, 7.26 ppm or DMSO, 2.50 ppm). Data of the ^{13}C NMR spectra were calibrated in reference to the deuterated solvents ($CDCl_3$, 77.1 ppm or DMSO, 39.5 ppm). High resolution mass spectra (HRMS) were measured on a Xevo G2-XS QTOF Quadrupole Time of Flight Mass Spectrometer Waters instrument with an ESI ion source. X-ray crystallography was performed on a Rigaku XtaLab Supernova instrument. Unless otherwise specified, all commercial chemicals were used in their received form. Solvents were either dried and kept over molecular sieves (4 Å) after being distilled using CaH2 or dried solvents were purchased commercially and used as such. Reactions above room temperature were carried out in aluminium metal block. Using TLC Silica gel 60 F254 from Merck, thin layer chromatography (TLC) was carried out, and the results were observed using UV light and PMA stain. Silica gel with a mesh size of 100–200 was used for the silica gel column chromatography (Merck).

2 Structures of the ligands used during optimization study (Table 1, in manuscript)

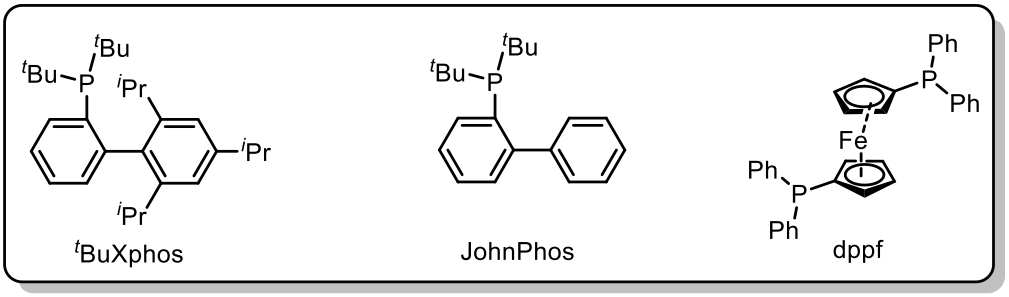
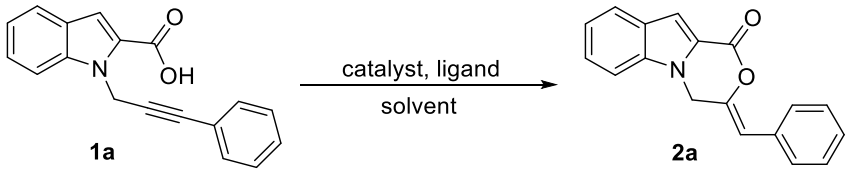


Figure S1. Structures of the ligands used during optimization study

3 Optimization of the reaction conditions for the synthesis of 2a

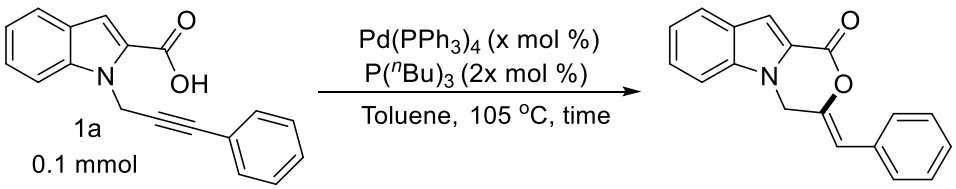
Table S1: Optimization of the catalysts in different solvents



Entry	Catalyst	Ligand	Solvent	Temp(°C)	Yield (%)[a]
1	$Pd(PPh_3)_4$	$P(^nBu)_3$	Acetonitrile	80	10
2	$Pd(PPh_3)_4$	$P(^nBu)_3$	Tetrahydrofuran	70	0
3	$Pd(PPh_3)_4$	$P(^nBu)_3$	1,4 dioxane	100	0
4	$Pd(PPh_3)_4$	$P(^nBu)_3$	**Toluene**	**105**	**85**
5	$Pd(PPh_3)_4$	$P(^nBu)_3$	Chlorobenzene	130	0
6[b]	$[Pd(allyl)Cl]_2$	$P(^nBu)_3$	Toluene	105	61
7[c]	AgOTf	-	DCE	80	10
8[d]	$Cu(OTf)_2$	-	DCE	80	<5
9[df]	TfOH	-	Chlorobenzene	120	0
10[ef]	K_2CO_3	-	DMF	90	0
11[g]	$Pd(PPh_3)_4$	$P(^nBu)_3$	Toluene	105	33

Reaction conditions: 1a (0.1 mmol), catalyst (5 mol %), ligand (10 mol %) and solvent (300 µL) were heated in a schlenk tube for 9 h under Ar atmosphere. [a]Isolated yield. [b]20 mol % ligand [c]10 mol % catalyst. [d]2 eq. of TfOH were used. [e]3 eq. of K_2CO_3 were used. [f]48 h. [g]O_2 atmosphere

Table S2: Optimization of the catalyst loading

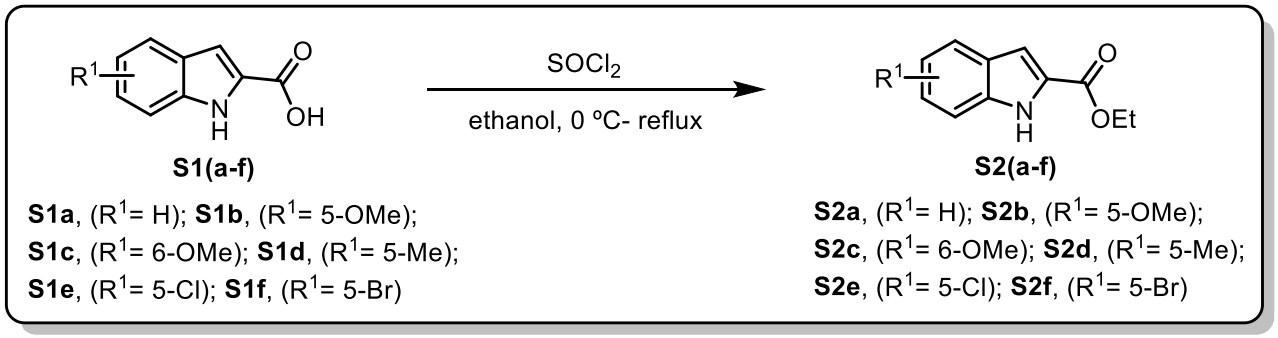


Entry	$Pd(PPh_3)_4$	$P(^nBu)_3$	Time(h)	Yield(%)[a]
1	1 %	2 %	24	45
2	2.5 %	5 %	11	61
3	4 %	8 %	11	73
5	**5 %**	**10 %**	**9**	**85**

Reaction conditions: **1a** (0.1 mmol), $Pd(PPh_3)_4$, $P(^nBu)_3$ and toluene (300 µL) were heated at 105 °C in a schlenk tube under Ar atmosphere. [a]Isolated yield.

4 General procedures of intermediate substrate synthesis:

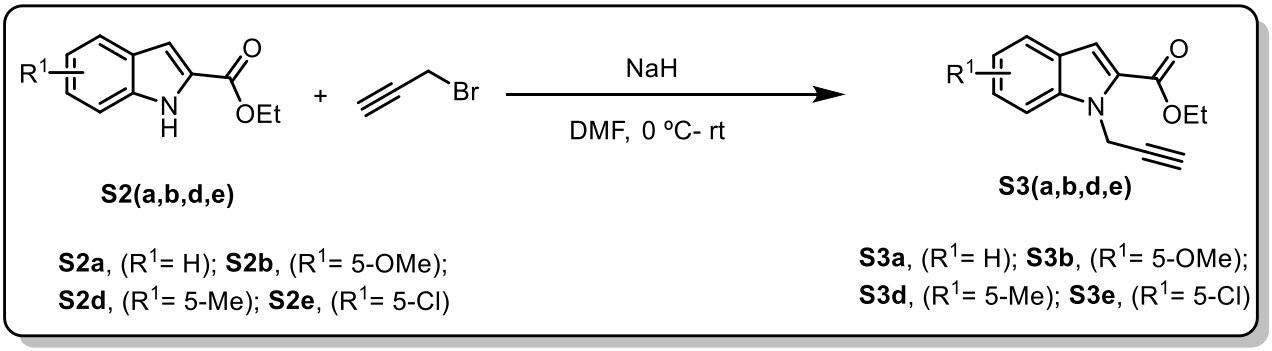
4.1 General Procedure A: Esterification of 1H-indole-2-carboxylic acid



Scheme S1

According to literature procedure[1], substrate **S2** was prepared from 1H-indole-2-carboxylic acid.

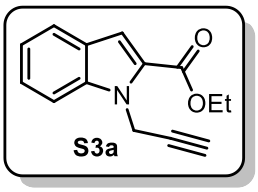
3.2 General Procedure B: N-alkylation of ethyl 1H-indole-2-carboxylate



Scheme S2

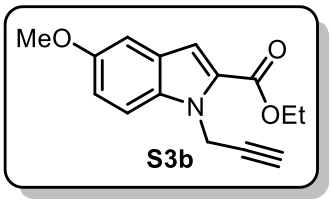
A 50 ml round bottom flask was charged with a solution of **S2** (1 eq) in dry DMF (1ml/ mmol) and NaH (1.5 eq) under constant stirring at 0 ºC. After 30 mins, propargyl bromide (1.1 eq) diluted in 1:3 ratio with dry DMF was added to the stirring solution over a 15 min period. After completion of reaction as indicated by TLC, the reaction mixture was quenched with distilled water and the residue was extracted with EtOAc (2×30 mL). The combined organic layers were washed with brine solution, dried over sodium sulphate and then concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (5% Ethyl acetate in Hexane) to afford **S3(a, b, d, e)** as solids.

3.2.1 Preparation of S3a: *ethyl 1-(prop-2-yn-1-yl)-1H-indole-2-carboxylate*



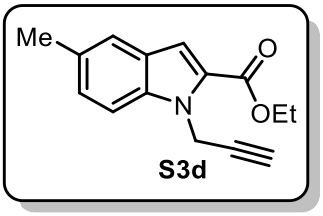
The compound was synthesized by general procedure B, **S3a**, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* =8.4 Hz, 1H), 7.31 (dd, *J* = 8.4, 7.0 Hz 1H), 7.26 (d, *J* = 0.7 Hz, 1H), 7.10 (dd, *J* = 8.0, 7.0 Hz, 1H), 5.35 (d, *J* = 2.5 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.17 (t, *J* = 2.5 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 162.0, 139.0, 127.0, 126.3, 125.5,122.8, 121.2, 111.4, 110.5, 78.8, 72.0, 60.8, 33.9, 14.3. The physical and spectral data are well in agreement with the literature data[2].

3.2.2 Preparation of S3b: *ethyl 5-methoxy-1-(prop-2-yn-1-yl)-1H-indole-2-carboxylate*



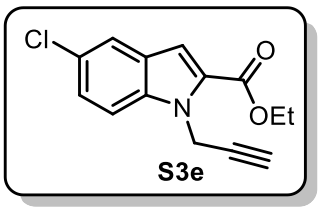
The compound was synthesized by general procedure B, **S3b**, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37 (dd, *J* = 9.8, 0.9 Hz, 1H), 7.23 (d, *J* = 0.9 Hz, 1H), 7.05 (dq, *J* = 5.3, 2.5 Hz, 2H), 5.38 (d, *J* = 2.5 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.25 (t, *J* = 2.5 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 161.9, 155.0, 134.4, 127.1, 126.5, 116.8, 111.4, 110.8, 102.8, 78.8, 71.9, 60.7, 55.6, 33.9, 14.3. The physical and spectral data are well in agreement with the literature data[3].

3.2.3 Preparation of S3d: *ethyl 5-methyl-1-(prop-2-yn-1-yl)-1H-indole-2-carboxylate*



The compound was synthesized by general procedure B, **S3d**, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 (dt, *J* = 1.6, 0.9 Hz, 1H), 7.38 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.26 (d, *J* = 0.9 Hz, 1H), 7.24 – 7.20 (m, 1H), 5.41 (d, *J* = 2.5 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.46 (d, *J* = 0.9 Hz, 3H), 2.24 (t, *J* = 2.5 Hz, 1H), 1.42 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ = 162.0, 137.4, 130.4, 127.3, 126.8, 126.4, 122.0, 110.9, 110.2, 78.8, 71.8, 60.7, 33.8, 21.3, 14.3. The physical and spectral data are well in agreement with the literature data[3].

3.2.4 Preparation of S3e: *ethyl 5-chloro-1-(prop-2-yn-1-yl)-1H-indole-2-carboxylate*

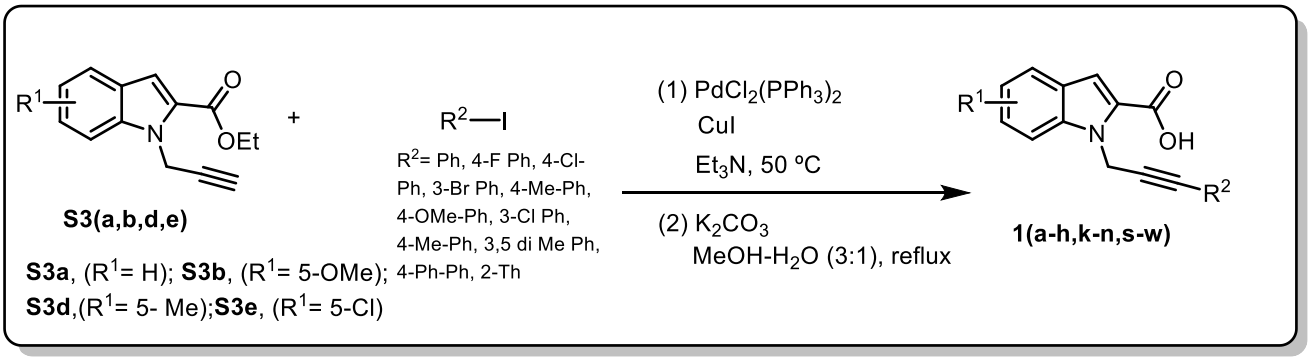


The compound was synthesized by general procedure B, **S3e**, white solid, **MP**: 130-134ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.30 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.22 (s, 1H), 5.39 (d, *J* = 2.4 Hz, 2H), 4.38 (q, *J* = 6.8 Hz, 2H), 2.25 (t, *J* =

2.4 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ 161.6, 137.1, 128.0, 127.1, 126.8, 125.8, 121.8, 111.7, 110.6, 78.3, 72.4, 61.0, 34.0, 14.3. **HRMS** (ESI) calculated for $[M+H]^+$ ($C_{14}H_{13}NO_2Cl$) *m/z* 262.0630, found 262.0619

5 General procedure C: Synthesis of final substrate molecule (1a-1z)

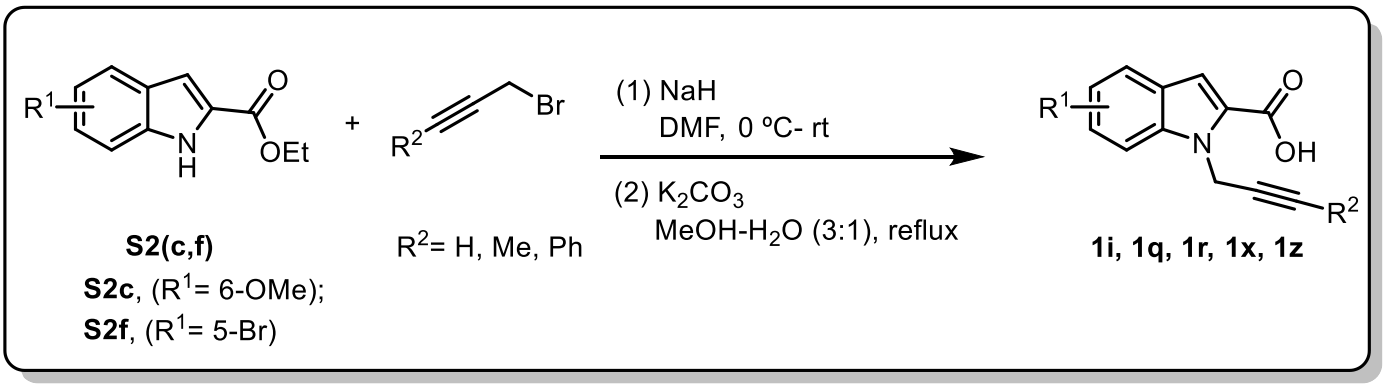
4.1 General Procedure C 1(a-h, k-n, s-w) :



Scheme S3

An oven-dried round bottom flask with a magnetic stir bar was charged with **S3(a, b, d, e)** (1.0 eq), degassed (for 30 min) triethylamine (3 ml/mmol), bis(triphenylphosphine)palladium dichloride (0.01 eq), copper iodide (0.02 eq) and aryl iodide (1.1 eq). The reaction mixture was stirred at 50 ºC for 12 h. After completion of reaction as indicated by TLC, the reaction mixture was filtered with celite pad and concentrated under reduced pressure. Then the crude mixture was passed through flash column chromatography (Hexane/Ethyl acetate, 20/1). Following solvent evaporation under reduced pressure, the compound was redissolved in a mixture of MeOH-H_2O (MeOH: H_2O=3:1) (3ml/mmol). Then it was refluxed under constant stirring for 24 h after the addition of K_2CO_3 (3 eq) into it. After checking TLC, solvent was evaporated under reduced pressure. The reaction medium was made acidic by adding 1N HCl solution and extracted with EtOAc (3 × 30 mL). The collected organic layers were dried with anhydrous Na_2SO_4 after washing with brine solution. Then the crude residue was purified by silica gel column chromatography (2-5% DCM in methanol) to afford **1(a-h, k-n, s-w)** as solids.

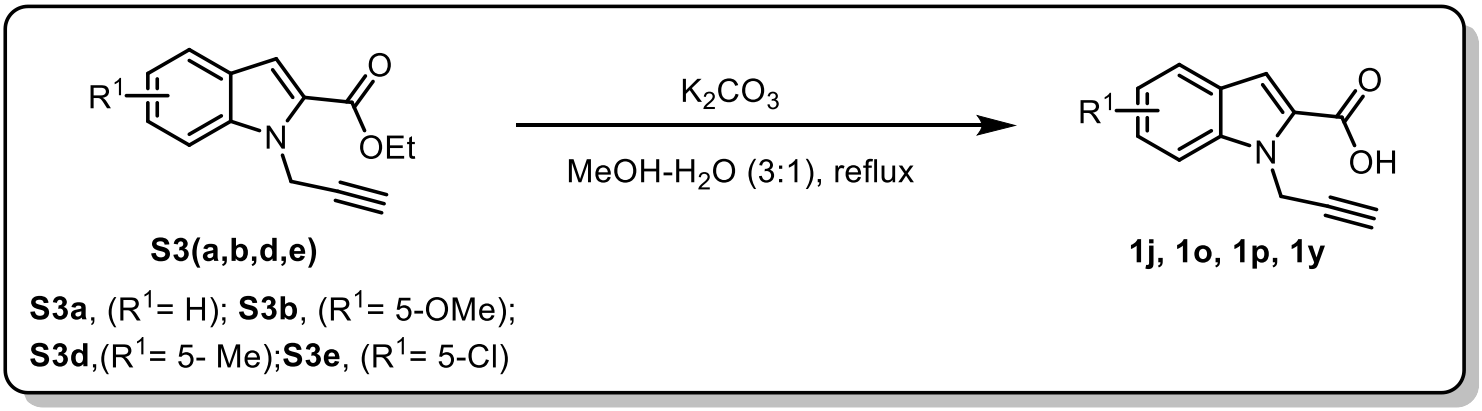
4.2 General Procedure C 1(i, q, r, x, z) :



Scheme S4

A 50 mL round bottom flask was charged with a solution of **S2(c,f)** (1 eq) in dry DMF(1ml/ mmol) and NaH (1.5 eq) under constant stirring at 0 ºC . After 30 mins, substituted propargyl bromide (1.1 eq) diluted in 1:3 ratio with dry DMF was added to the stirring solution over a 15 min period. After completion of reaction as indicated by TLC, the reaction mixture was quenched with distilled water and the residue was extracted with EtOAc (2×30 mL). The combined organic layers were washed with brine solution, dried over sodium sulphate, and then concentrated under reduced pressure. The crude residue was passed through silica gel flash column chromatography (Hexane/Ethyl acetate, 20/1). Following solvent evaporation, the compound was redissolved in a mixture of MeOH-H_2O (MeOH: H_2O=3:1) (3ml/mmol). Then it was refluxed under constant stirring for 24 h after the addition of K_2CO_3 (3 eq) into it. After checking TLC, solvent was evaporated under reduced pressure. The reaction medium was made acidic by adding 1N HCl solution and extracted with EtOAc (3 × 30 mL). The collected organic layers were dried with anhydrous Na_2SO_4 after washing with brine solution. Then the crude residue was purified by silica gel column chromatography (2-5% DCM in methanol) to afford **1(i, q, r, x, z)** as solids.

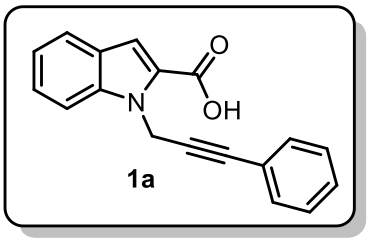
4.3 General Procedure C 1(j, o, p, y) :



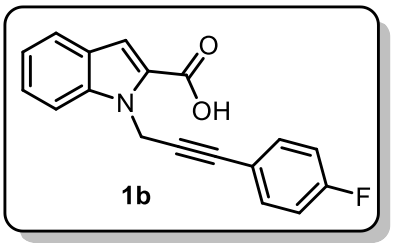
Scheme S5

A 100 mL round bottom flask was charged with a solution of **S3(a, b, d, e)** (1 eq) in MeOH-H_2O (MeOH: H_2O=3:1) (3 ml/ mmol) and 3 eq of K_2CO_3. Then it was refluxed for 24 h under constant stirring. After completion of reaction as indicated by TLC, solvent was evaporated under reduced pressure. The reaction medium was made acidic by adding 1N HCl solution and extracted with EtOAc (3 × 30 mL). The collected organic layers were dried with anhydrous Na_2SO_4 after washing with brine solution. Then the crude residue was purified by silica gel column chromatography (2-5% DCM in methanol) to afford **1(j, o, p, y)** as solids.

6 Spectral data of final substrates:

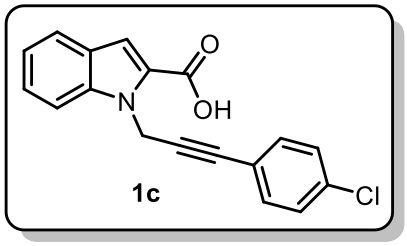


*1-(3-phenylprop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1a**):* White solid, 210 mg, 76%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 176-178ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.13 (s, 1H), 7.72 (dd, *J* = 8.5, 4.8 Hz, 2H), 7.40 (dd, *J* = 7.8, 7.5 Hz, 1H), 7.35-7.31 (m, 5H), 7.30 (s, 1H), 7.18 (dd, *J* = 7.7, 7.2 Hz, 1H), 5.74 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 162.8, 138.6, 131.4, 128.7, 128.6, 127.5, 125.7, 125.1, 122.4, 121.7, 120.9, 111.1, 110.7, 85.5, 82.8, 34.1.; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{14}NO_2$) m/z 276.1020, found 276.1037.



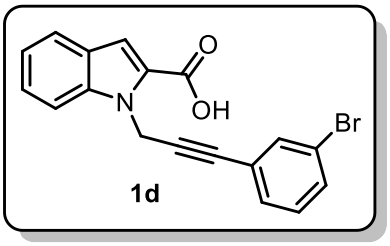
1b

*1-(3-(4-fluorophenyl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1b**):* White solid, 250 mg, 85%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 189-191ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.16 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.42- 7.36 (m, 3H), 7.32 (s, 1H), 7.20-7.13 (m, 3H), 5.75 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 162.8, 162.3 (d, *J* = 248.4 Hz), 138.6, 133.8 (d, *J* = 8.1 Hz), 127.6, 125.7, 125.1, 122.4, 120.9, 118.2 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 21.2 Hz), 111.1, 110.7, 85.3, 81.8, 34.1; ^{19}F NMR (376 MHz, DMSO): δ -110.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2F$) m/z 294.0926, found 294.0926.



1c

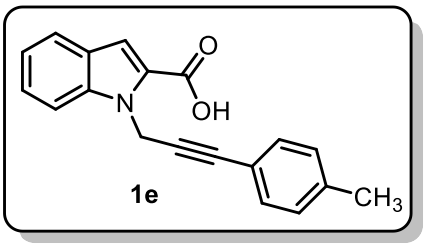
*1-(3-(4-chlorophenyl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1c**):* White solid, 227 mg, 73%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 192-194ºC; ^{1}H NMR (400 MHz, DMSO): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.34 (m, 5H), 7.31 (s, 1H), 7.19 (dd, *J* = 7.7, 7.4 Hz, 1H), 5.75 (s, 2H) ; ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.2, 139.0, 133.9, 133.6, 129.3, 128.0, 126.1, 125.6, 122.9, 121.4, 121.1, 111.6, 111.2, 87.2, 82.1, 34.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NClO_2$) m/z 310.0630, found 310.0625.



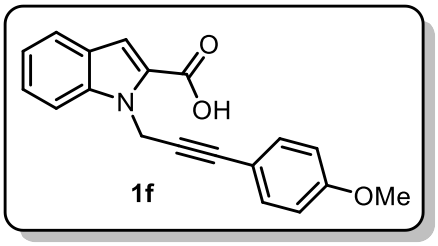
1d

*1-(3-(3-bromophenyl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1d**):* White solid, 240 mg, 68%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 194-196ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.16 (s, 1H), 7.73 (d, *J* = 8.0 Hz,

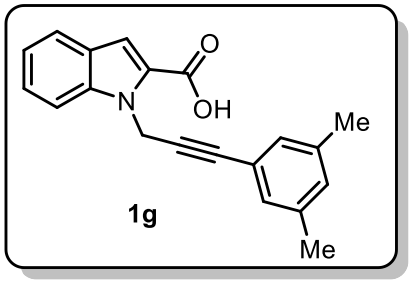
2H), 7.60 – 7.50 (m, 2H), 7.41 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.37-7.26 (m, 3H), 7.19 (dd, *J* = 7.3, 7.3 Hz, 1H), 5.77 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO): δ 163.9, 139.8, 134.8, 132.9, 131.9, 131.6, 128.7, 126.9, 126.3, 125.1, 123.6, 122.7, 122.1, 112.3, 112.0, 88.3, 82.4, 35.3. HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2Br$) m/z 354.0125, found 354.0139.



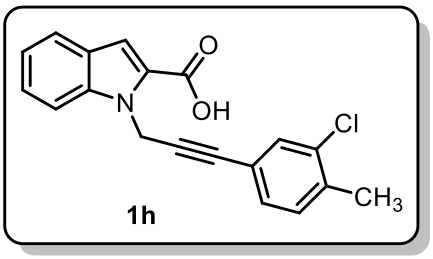
*1-(3-(p-tolyl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1e**):* White solid, 210 mg, 73%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 171-174ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.53 (s, 1H), 7.44 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.27-7.20 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 2H), 2.30 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 166.3, 139.7, 138.5, 131.7, 128.9, 126.2, 126.0, 125.7, 123.0, 121.2, 119.4, 113.5, 111.0, 84.0, 83.2, 34.8, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_2$) m/z 290.1176, found 290.1195.



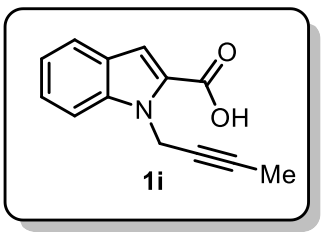
*1-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1f**):* White solid, 195 mg, 64%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 170-172ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 7.44 (dd, *J* = 7.9, 7.5 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.22 (dd, *J* = 7.6, 7.5 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.66 (s, 2H), 3.76 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 166.2, 159.6, 139.7, 133.3, 126.1, 126.0, 125.7, 123.0, 121.2, 114.6, 113.8, 113.5, 111.0, 83.8, 82.5, 55.2, 34.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_3$) m/z 306.1125, found 306.1158.



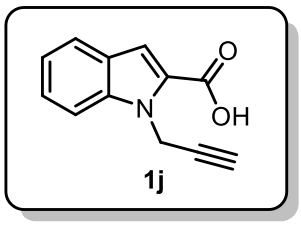
*1-(3-(3,5-dimethylphenyl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1g**):* White solid, 210 mg, 70% purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 217-219ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.10 (s, 1H), δ 7.71 (dd, *J* = 8.4, 3.2 Hz, 2H), 7.40 (ddd, *J* = 8.0, 8.0, 1.2 Hz, 1H), 7.30 (d, *J* = 0.8 Hz, 1H), 7.18 (dt, *J* = 8.0, 8.0, 0.8 Hz, 1H), 6.97 (s, 1H), 6.95 (s, 2H), 5.72 (s, 2H), 2.19 (s, 6H) ; ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.2, 139.0, 138.3, 130.8, 129.4, 128.0, 126.1, 125.5, 122.9, 121.9, 121.3, 111.6, 111.2, 85.3, 83.4, 34.5, 20.9; HRMS (ESI) calculated for $[M+H]^+$ ($C_{20}H_{18}NO_2$) m/z 304.1332 , found 304.1350.



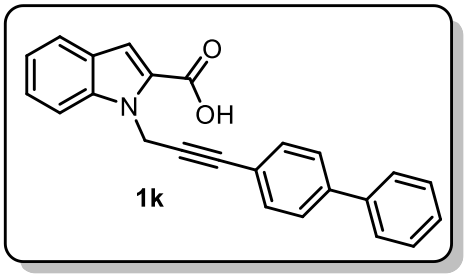
*1-(3-(3-chloro-4-methylphenyl) prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1h**):* White solid, 230 mg, 71%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 185-187ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.53 (s, 1H), 7.45 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.35 (s, 1H), 7.23 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 5.67 (s, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.1, 139.6, 136.7, 134.0, 132.0, 130.6, 129.9, 126.2, 125.6, 123.1, 121.4, 121.3, 113.6, 110.8, 84.4, 82.6, 34.7, 20.0; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{15}NO_2Cl$) m/z 324.0786, found 324.0814.



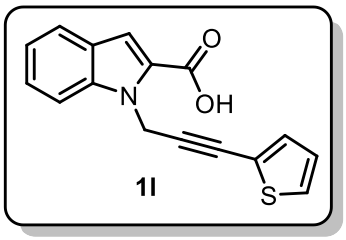
*1-(but-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1i**):* White solid, 130 mg, 61%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 167-169ºC; ^{1}H NMR (400 MHz, DMSO): δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.36 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.26 (s, 1H), 7.16 (dd, *J* = 7.5, 7.5 Hz, 1H), 5.43 (s, 2H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 162.8, 138.5, 127.5, 125.6, 124.9, 122.4, 120.8, 111.1, 110.5, 79.3, 75.2, 33.6, 3.0; HRMS (ESI) calculated for $[M+H]^+$ ($C_{13}H_{12}NO_2$) m/z 214.0864, found 214.0859.



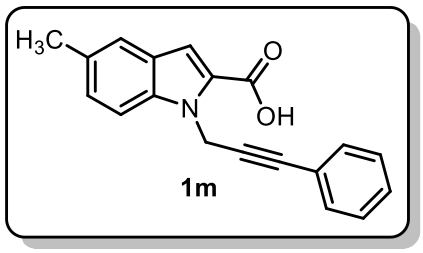
*1-(prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1j**):* White solid, 168 mg, 84%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 190-192ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.08 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.37 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.28 (s, 1H), 7.16 (dd, *J* = 7.7, 7.3 Hz, 1H), 5.48 (d, *J* = 2.4 Hz, 2H), 3.28 (t, *J* = 4.5 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.2, 139.0, 127.9, 126.1, 125.5, 122.8, 121.3, 111.5, 111.2, 80.2, 74.8, 33.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{12}H_{10}NO_2$) m/z 200.0708, found 200.0726.



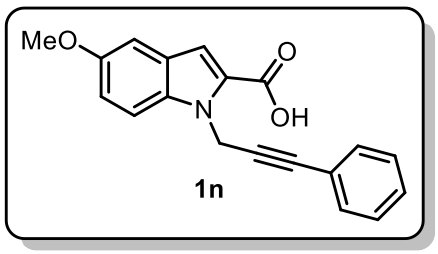
*1-(3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1k**):* White solid, 306 mg, 87%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 249-251ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.16 (s, 1H), 7.74 (dd, *J* = 8.9, 8.4 Hz, 2H), 7.66-7.61 (m, 4H), 7.48-7.41 (m, 5H), 7.40-7.36 (m, 1H), 7.33 (s, 1H), 7.19 (dd, *J* = 7.5, 7.4 Hz, 1H), 5.78 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.3, 140.7, 139.5, 139.1, 132.5, 129.5, 128.3, 128.0, 127.3, 127.2, 127.0, 126.2, 125.6, 122.9, 121.4, 121.2, 111.6, 111.2, 86.8, 83.1, 34.7; HRMS (ESI) calculated for $[M+H]^+$ ($C_{24}H_{18}NO_2$) m/z 352.1332, found 352.1349.



*1-(3-(thiophen-2-yl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1l**):* Greyish-white solid, 205 mg, 73%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 209-211ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.12 (s, 1H), 7.71 (dd, *J* = 4.9, 3.0 Hz, 2H), 7.56 (d, *J* = 5.1 Hz, 1H), 7.39 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.31 (s, 1H), 7.24 (d, *J* = 3.5 Hz, 1H), 7.17 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.02 (dd, *J* = 5.2, 3.8 Hz, 1H), 5.76 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.2, 139.0, 133.2, 129.1, 128.02, 126.1, 125.6, 122.9, 121.7, 121.4, 111.5, 111.3, 90.0, 76.5, 34.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{16}H_{12}NO_2S$) m/z 282.0584, found 282.0597.

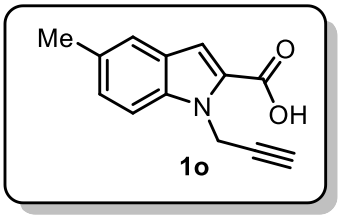


*5-methyl-1-(3-phenylprop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1m**):* White solid, 219 mg, 75%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 233-235ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.07 (s, 1H), δ 7.61 (d, *J* = 8.8 Hz, 1H), 7.48 (s, 1H), 7.35-7.31 (m, 5H), 7.23 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.20 (s, 1H), 5.71 (s, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.3, 137.6, 131.8, 130.2, 129.2, 129.1, 127.9, 127.4, 126.4, 122.2, 122.1, 111.3, 110.7, 86.1, 83.2, 34.6, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_2$) m/z 290.1176, found 290.1209.



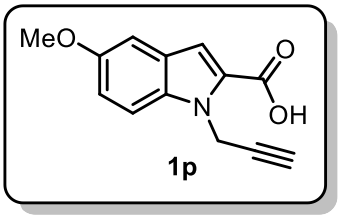
*5-methoxy-1-(3-phenylprop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1n**):* White solid, 240 mg, 79%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 200-202ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.06 (s, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.35-7.32 (m, 5H), 7.20 (s, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.05 (dd, *J* = 9.2, 2.4 Hz, 1H),

5.71 (s, 2H), 3.78 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO): δ 163.2, 154.9, 134.5, 131.8, 129.2, 129.1, 128.2, 126.5, 122.2, 116.8, 112.6, 110.8, 103.1, 86.1, 83.2, 55.8, 34.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_3$) m/z 306.1125, found 306.1151.



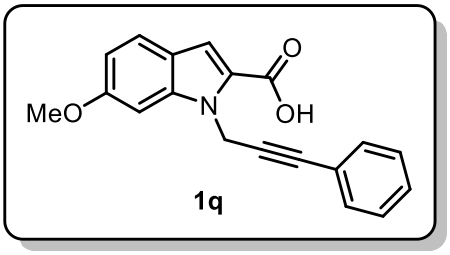
1o

*5-methyl-1-(prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1o**):* White solid, 167 mg, 78%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 208-211ºC; ^{1}H NMR (400 MHz, DMSO): δ 7.52 (d, *J* = 8.8 Hz, 1H), 7.47 (s, 1H), 7.24-7.11 (m, 2H), 5.45 (s, 2H), 3.20 (s, 1H), 2.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO): δ 163.2, 137.6, 130.1, 127.9, 127.3, 126.3, 122.0, 111.2, 110.7, 80.2, 74.7, 33.8, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{13}H_{12}NO_2$) m/z 214.0864, found 214.0859.



1p

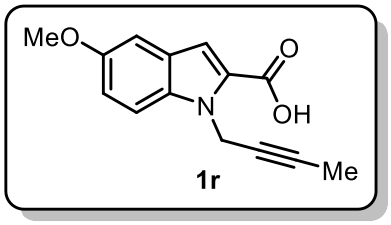
*5-methoxy-1-(prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1p**):* White solid, 195 mg, 85%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 213-215ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.02 (s, 1H), δ 7.54 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 9.2 Hz, 1H), 5.45 (s, 2H), 3.78 (s, 3H), 3.21 (s, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO): δ 163.1, 154.9, 134.4, 128.1, 126.5, 116.7, 112.5, 110.8, 103.1, 80.3, 74.7, 55.8, 33.9; HRMS (ESI) calculated for $[M+H]^+$ ($C_{13}H_{12}NO_3$) m/z 230.0813, found 230.0810.



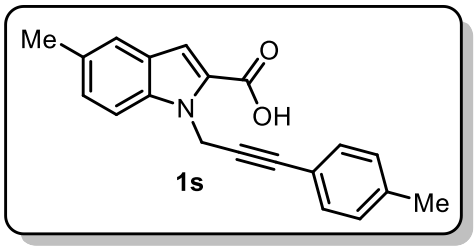
1q

*6-methoxy-1-(3-phenylprop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1q**):* White solid, 205 mg, 67%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1

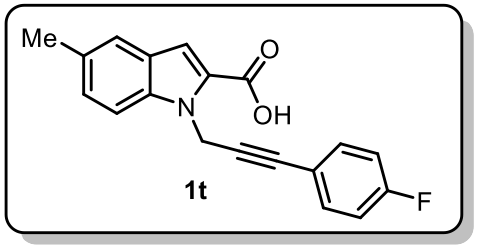
to 20:1); MP: 178-180ºC; ^{1}H NMR (400 MHz, DMSO): δ 12.87 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.37-7.33 (m, 5H), 7.24 (s, 1H), 7.23 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 5.72 (s, 2H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.2, 158.8, 140.3, 131.9, 129.1, 126.8, 123.7, 122.3, 120.2, 112.6, 111.8, 93.8, 86.1, 83.2, 55.9, 34.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_3$) m/z 306.1125, found 306.1145.



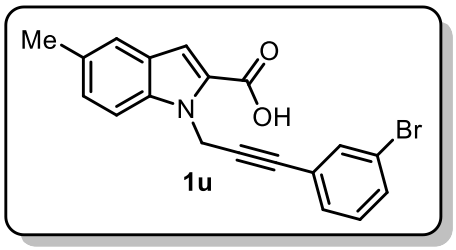
*1-(but-2-yn-1-yl)-5-methoxy-1H-indole-2-carboxylic acid (**1r**):* White solid, 144 mg, 59%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 207-210ºC; ^{1}H NMR (400 MHz, DMSO): δ 12.97 (s, 1H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.15-7.12 (m, 2H), 7.00 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.39 (s, 2H), 3.78 (s, 3H), 1.70 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.2, 154.8, 134.4, 128.1, 126.4, 116.6, 112.5, 110.5, 103.0, 79.6, 75.7, 55.8, 34.1, 3.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{14}H_{14}NO_3$) m/z 244.0969, found 244.0981.



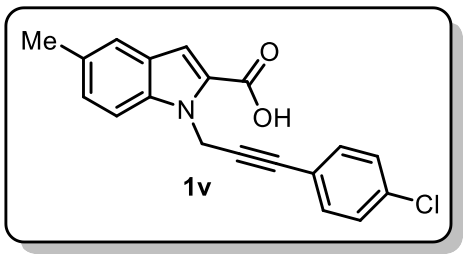
*5-methyl-1-(3-(p-tolyl)prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1s**):* White solid, 235 mg, 77%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 215-218ºC; ^{1}H NMR (400 MHz, DMSO): δ 12.99 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.48 (s, 1H), 7.24-7.19 (m, 4H), 7.14 (s, 1H), 7.12 (s, 1H), 5.69 (s, 2H), 2.40 (s, 3H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.3, 138.9, 131.7, 130.1, 129.7, 127.9, 127.4, 126.6, 126.3, 122.1, 119.2, 111.3, 110.7, 85.4, 83.3, 34.6, 21.4, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{20}H_{18}NO_2$) m/z 304.1332, found 304.1338.



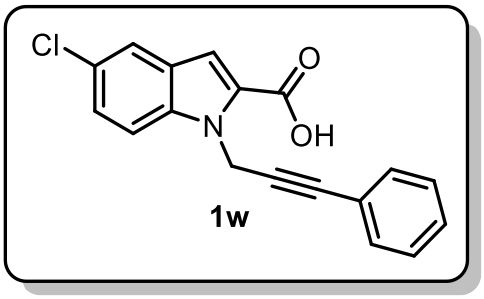
*1-(3-(4-fluorophenyl)prop-2-yn-1-yl)-5-methyl-1H-indole-2-carboxylic acid (**1t**):* White solid, 258 mg, 84%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 212-214ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.06 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.48 (s, 1H), 7.42-7.37 (m, 2H), 7.25 – 7.14 (m, 4H), 5.70 (s, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.3, 162.4 (d, *J* = 248.5 Hz), 137.6, 134.2 (d, *J* = 8.5 Hz), 130.2, 127.9, 127.4, 126.4, 122.1, 118.7 (d, *J* = 3.5 Hz), 116.3 (d, *J* = 22.3 Hz), 111.3, 110.7, 85.8, 82.2, 34.5, 21.4; ^{19}F NMR (376 MHz, DMSO): δ -110.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{15}NO_2F$) m/z 308.1082, found 308.1115.



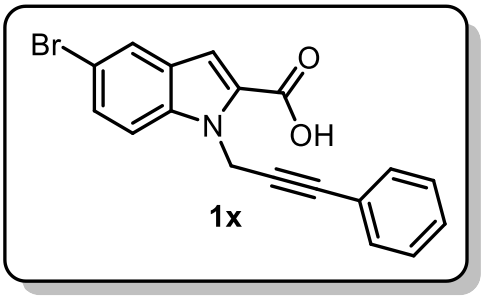
*1-(3-(3-bromophenyl)prop-2-yn-1-yl)-5-methyl-1H-indole-2-carboxylic acid (**1u**):* White solid, 283 mg, 77%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 210-212ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.06 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.53 (s, 1H), 7.49 (s, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.25-7.20 (m, 2H), 5.72 (s, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.3, 137.6, 134.0, 132.2, 131.2, 130.9, 130.2, 127.9, 127.4, 126.4, 124.4, 122.1, 122.0, 111.3, 110.8, 87.7, 81.6, 34.5, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{15}NO_2Br$) m/z 368.0281, found 368.0273.



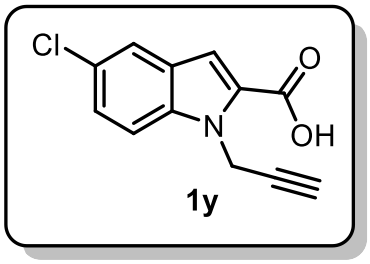
*1-(3-(4-chlorophenyl)prop-2-yn-1-yl)-5-methyl-1H-indole-2-carboxylic acid (**1v**):* White solid, 233 mg, 72%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 201-203ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.10 (s, 1H), δ 7.61 (d, *J* = 8.4 Hz, 1H), 7.48 (s, 1H), 7.41-7.33 (m, 4H), 7.24-7.19 (m, 2H), 5.71 (s, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.3, 137.6, 133.9, 133.6, 130.2, 129.2, 127.9, 127.4, 126.4, 122.1, 121.1, 111.3, 110.7, 87.3, 82.0, 34.6, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{15}NO_2Cl$) m/z 324.0786, found 324.0793.



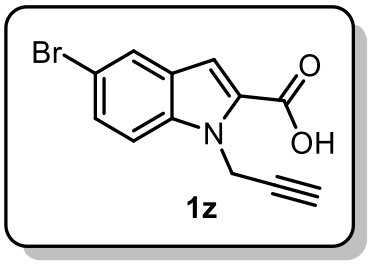
*5-chloro-1-(3-phenylprop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1w**):* White solid, 214 mg, 69%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 228-230ºC; ^{1}H NMR (400 MHz, DMSO): δ 7.87 – 7.83 (m, 2H), 7.47 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.42-7.38 (m, 5H), 7.34 (s, 1H), 5.81 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 162.9, 137.4, 131.9, 129.5, 129.2, 129.1, 127.1, 125.9, 125.6, 122.1, 121.9, 113.4, 110.6, 85.7, 83.5, 34.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2Cl$) m/z 310.0630, found 310.0652.



*5-bromo-1-(3-phenylprop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1x**):* White solid, 198 mg, 56%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 229-231ºC; ^{1}H NMR (400 MHz, DMSO): δ 13.28 (s, 1H), 7.95 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.36-7.32 (m, 5H), 7.28 (s, 1H), 5.75 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 162.9, 137.6, 131.9, 129.3, 129.2, 129.1, 128.0, 127.9, 125.0, 122.1, 113.8, 110.5, 85.6, 83.5, 34.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2Br$) m/z 354.0125, found 354.0146.

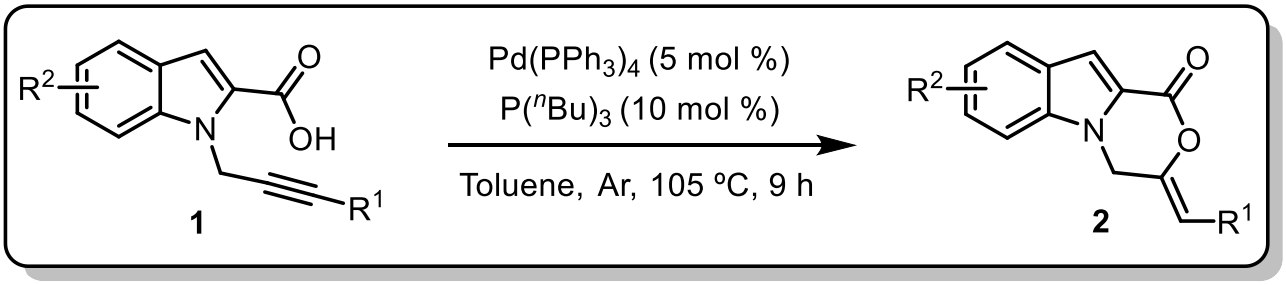


*5-chloro-1-(prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1y**):* White solid, 171 mg, 73%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 199-200ºC; ^{1}H NMR (400 MHz, DMSO): δ 7.77 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.22 (s, 1H), 5.52 (s, 2H), 3.25 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 163.1, 137.2, 130.3, 127.2, 125.8, 125.2, 121.8, 113.3, 110.1, 80.0, 75.0, 34.0; HRMS (ESI) calculated for $[M+H]^+$ ($C_{12}H_9NO_2Cl$) m/z 234.0318, found 234.0342.



*5-bromo-1-(prop-2-yn-1-yl)-1H-indole-2-carboxylic acid (**1z**):* White solid, 171 mg, 73%; purified by column chromatography (silica gel 100-200 mesh, DCM/MeOH = 50:1 to 20:1); MP: 232-234ºC; ^{1}H NMR (400 MHz, DMSO): δ 7.91 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.24 (s, 1H), 5.48 (s, 2H), 3.25 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ 162.9, 137.6, 129.3, 127.9, 127.8, 125.0, 113.8, 113.7, 110.4, 79.9, 75.1, 34.1; HRMS (ESI) calculated for $[M+H]^+$ ($C_{12}H_9NO_2Br$) m/z 277.9813, found 277.9841.

7 General procedure for the Palladium catalysed intramolecular cyclization of N-alkylated indole 2- carboxylic acid:



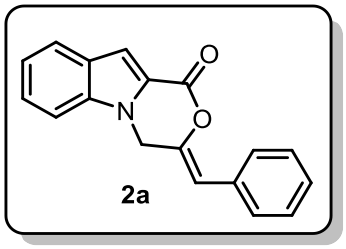
Scheme S6

An oven dried 10 mL schlenk tube was charged with N-alkylated indole-2-carboxylic acid **1** (0.1 mmol), $Pd(PPh_3)_4$ (0.005 mmol), $P(^nBu)_3$ (0.01 mmol) and toluene (300 µL) under Ar atmosphere. Then the schlenk tube was sealed with septum, and it was left to stir for 9 h at 105 ºC. After 9 h of stirring, the reaction mixture was allowed to cool to room temperature before diluting with ethyl acetate and transferred to a round bottom flask. Then it was concentrated under reduced pressure and the crude mixture was purified by flash chromatography (silica gel, Hexane/EtOAc = 20:3 to 20:4) to give pure solid product **2**.

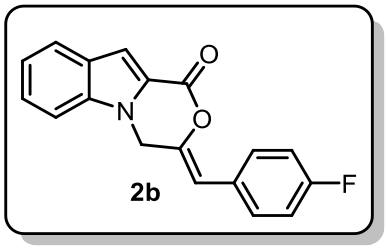
8 Procedure for the Large-Scale Reaction:

An oven dried 10 mL schlenk tube was charged with N-alkylated indole-2-carboxylic acid **1a** (1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), $P(^nBu)_3$ (0.1 mmol) and toluene (1 mL) under Ar atmosphere. Then the schlenk tube was sealed with septum, and it was left to stir for 9 h at 105 ºC. After 9 h of stirring, the reaction mixture was allowed to cool to room temperature before diluting with ethyl acetate and transferred to a round bottom flask. Then it was concentrated under reduced pressure and the crude mixture was purified by flash chromatography (silica gel, Hexane/EtOAc = 20:3 to 20:4) to give pure solid product **2a** (180 mg, 65%) as a white solid.

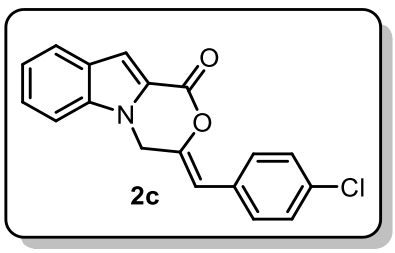
9 Characterisation data of final compounds:



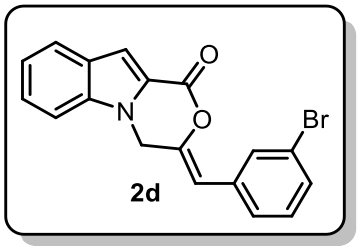
*(Z)-3-benzylidene-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2a**).* White solid, 23 mg, 85%; MP: 168-170 ºC; column chromatography (Hexane/EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.75 (m, 3H), 7.54 (s, 1H), 7.46 (d, *J* = 7.2 Hz,1H), 7.44 – 7.38 (m, 3H), 7.34-7.29 (m, 1H), 7.26 (dd, *J* = 8, 6.7 Hz, 1H), 5.9 (s, 1H), 4.98 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.9, 141.1, 136.6, 133.7, 132.7, 130.2, 129.5, 128.1, 126.5, 123.4, 122.1, 121.8, 113.2, 111.0, 110.0, 43.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{14}NO_2$) m/z 276.1020, found 276.1021.



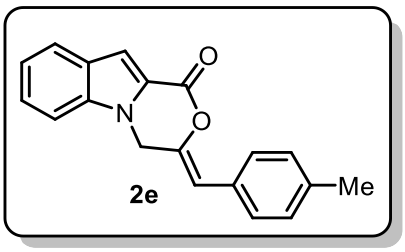
*(Z)-3-(4-fluorobenzylidene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2b**).* White solid, 26 mg, 88%; MP: 169-171ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.70 (m, 3H), 7.52 (s, 1H), 7.45 (dd, *J* = 7.6 Hz, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.25-7.21 (m, 1H), 7.07 (dd, *J* = 8.7, 8.7 Hz, 2H), 5.94 (s, 1H), 4.98 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.3 (d, *J* = 249.5 Hz), 155.7, 140.7, 136.0, 131.2 (d, *J* = 8.2 Hz), 128.8 (d, *J* = 3.5 Hz), 127.1, 126.5, 123.5, 122.0, 121.8, 115.6 (d, *J* = 21.6 Hz), 112.0, 111.1, 110.0, 43.7; ^{19}F NMR (376 MHz, DMSO): δ -112.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2F$) m/z 294.0926, found 294.0936.



(Z)-3-(4-chlorobenzylidene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2c)****.* White solid, 27 mg, 83%; MP: 205-208ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 0.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H), 7.41-7.33 (m, 3H), 7.25-7.21(m, 1H), 5.93 (s, 1H), 4.99 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.6, 141.6, 136.6, 133.8, 131.1, 130.7, 128.8, 127.2, 126.6, 123.5, 121.9, 111.9, 111.2, 110.0, 43.7; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2Cl$) m/z 310.0630, found 310.0617.

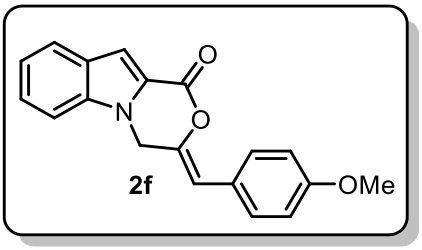


(Z)-3-(3-bromobenzylidene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2d)****.* White solid, 29 mg, 81%; MP: 180-182ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.75 (m, 3H), 7.54 (s, 1H), 7.48-7.37 (m, 3H), 7.29-7.27 (m, 1H), 7.25-7.22 (m, 1H), 5.89 (s, 1H), 4.99 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.3, 142.3, 136.6, 134.7, 132.2, 130.9, 130.1, 127.9, 127.2, 126.6, 123.5, 122.5, 121.9, 111.6, 111.3, 110.0, 43.7; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2Br$) m/z 354.0125, found 354.0156.

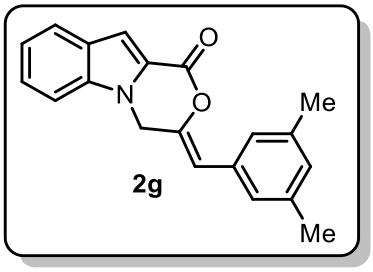


(Z)-3-(4-methylbenzylidene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2e)****.* White solid, 18.5 mg, 64%; MP: 173-175ºC: column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.52 (s, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.41-7.37 (m, 1H), 7.24 – 7.17 (m, 3H), 5.95 (s, 1H), 4.98 (s, 2H), 2.36 (s, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.0, 140.3, 138.1, 136.5, 129.8,

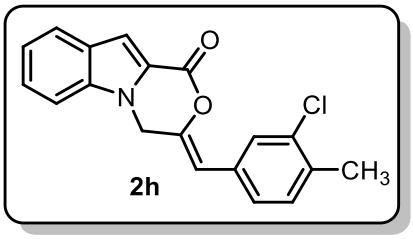
129.4, 129.3, 127.1, 126.4, 123.4, 122.2, 121.7, 113.2, 110.9, 110.0, 43.8, 21.3; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_2$) m/z 290.1176, found 290.1185.



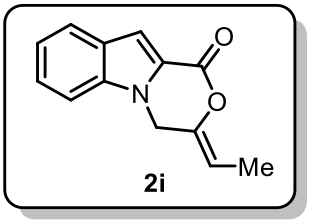
(Z)-3-(4-methoxybenzylidene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2f)***. White solid, 19.5 mg, 64%; MP: 158-160ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.51 (s, 1H), 7.47 – 7.41 (m, 1H), 7.41-7.36 (m, 1H), 7.23 (dd, *J* = 7.1, 7.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.92 (s, 1H), 4.97 (s, 2H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.3, 156.1, 139.4, 136.5, 130.9, 127.1, 126.4, 125.4, 123.4, 122.3, 121.7, 114.0, 112.8, 110.8, 110.0, 55.3, 43.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_3$) m/z 306.1125, found 306.1143.



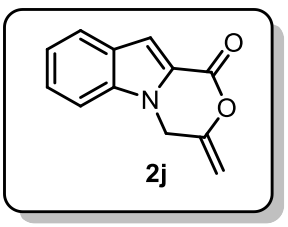
(Z)-3-(3,5-dimethylbenzylidene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2g)***. White solid, 17.5 mg, 58%; MP: 187-189ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80- 7.73 (m, 1H), 7.52 (s, 1H), 7.48 – 7.34 (m, 4H), 7.25 – 7.21 (m, 1H), 6.95 (s, 1H), 5.91 (s, 1H), 4.98 (s, 2H), 2.35 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.9, 140.7, 138.0, 136.5, 132.5, 129.9, 127.3, 127.2, 126.4, 123.4, 122.2, 121.7, 113.5, 110.8, 110.0, 43.9, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{20}H_{18}NO_2$) m/z 304.1332, found 304.1327.



(Z)-3-(3-chloro-4-methylbenzylidene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2h)****.* White solid, 24 mg, 74%; MP: 178-180ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.53 (s, 1H), 7.45 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.41-7.37 (m 1H), 7.26 – 7.22 (m, 2H), 5.88 (s, 1H), 4.98 (s, 2H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.5, 141.5, 136.6, 135.9, 134.4, 131.8, 131.1, 129.7, 127.6, 127.2, 126.5, 123.4, 121.9, 121.8, 111.8, 111.1, 110.0, 43.7, 19.9; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{15}NO_2Cl$) m/z 324.0786, found 324.0803.

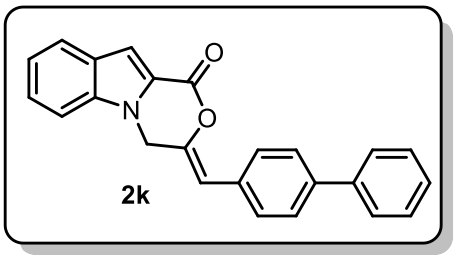


(Z)-3-ethylidene-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2i)****.*White solid, 12 mg, 55%; MP: 142-144ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.47 (s, 1H), 7.44-7.39 (m, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.21 (dd, *J* = 7.5, 7.4 Hz, 1H), 5.20 (q, *J* = 6.8 Hz, 1H), 4.81 (s, 2H), 1.82 (d, *J* = 5.6 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.8, 141.8, 136.4, 127.1, 126.2, 123.3, 122.7, 121.6, 110.4, 110.0, 109.7, 43.1, 9.9.; HRMS (ESI) calculated for $[M+H]^+$ ($C_{13}H_{12}NO_2$) m/z 214.0864, found 214.0882. The NMR data matched with the literature.[5]

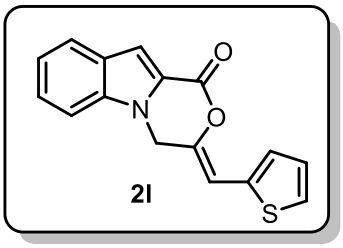


3-methylene-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2j)****.* White solid, 16 mg, 82%; MP: 170-173ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.46-7.40 (m, 1H), 7.38-7.33 (m, 1H), 7.23 (dd, *J* = 7.7,7.6 Hz, 1H), 5.10 (s, 1H), 4.89 (s, 2H), 4.82 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz,

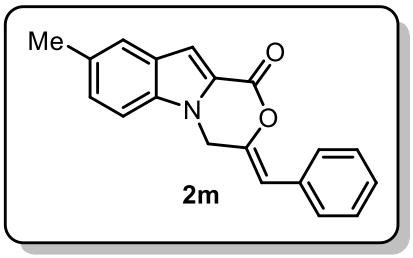
$CDCl_3$): δ 156.2, 148.6, 136.6, 127.2, 126.4, 123.4, 122.0, 121.8, 110.8, 110.0, 98.8, 42.5; HRMS (ESI) calculated for $[M+H]^+$ ($C_{12}H_{10}NO_2$) m/z 200.0708, found 200.0699.



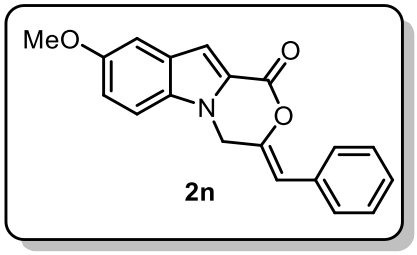
*(Z)-3-([1,1'-biphenyl]-4-ylmethylene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2k**).* White solid, 24 mg, 70%; MP: 248-251ºC; column chromatography (Hexane/EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.60 (m, 4H), 7.54 (s, 1H), 7.48 – 7. 43(m, 3H), 7.41 (s, 1H), 7.39 – 7.35 (m, 1H), 7.25(dd, *J* = 7.1,7.0 Hz, 1H), 6.01 (s, 1H), 5.01 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.8, 141.2, 140.7, 140.5, 136.6, 131.7, 129.9, 128.8, 127.5, 127.2, 127.0, 126.5, 123.5, 122.1, 121.8, 112.8, 111.0, 110.0, 43.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{24}H_{18}NO_2$) m/z 352.1332, found 352.1355.



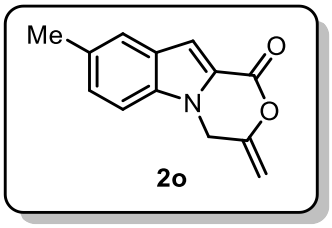
*(Z)-3-(thiophen-2-ylmethylene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2l**).* White solid, 22 mg, 78%; MP: 228-230ºC; column chromatography (Hexane/EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 1H), 7.40 (s, 1H), 7.34 – 7.28 (m, 1H), 7.27-7.22 (m, 2H), 7.15-7.09 (m, 2 H), 6.91 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.16 (s, 1H), 4.85 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.5, 139.0, 136.5, 134.9, 128.3, 127.6, 127.2, 126.7, 126.5, 123.5, 122.1, 121.8, 111.1, 110.0, 107.4, 43.1; HRMS (ESI) calculated for $[M+H]^+$ ($C_{16}H_{12}NO_2S$) m/z 282.0584, found 282.0601.



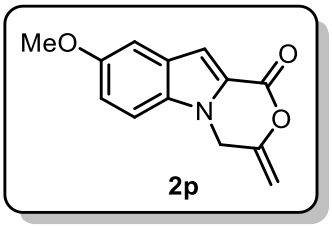
(Z)-3-benzylidene-8-methyl-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (***2m***). White solid, 24 mg, 84%; MP: 148-150ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.51 (s, 1H), 7.41 (s, 1H), 7.37 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.30-7.26 (m, 2H), 7.25-7.23 (m, 1H), 5.94 (s, 1H), 4.93 (s, 2H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.0, 141.3, 135.3, 132.8, 131.4, 129.6, 128.7, 128.7, 128.1, 127.5, 122.7, 122.1, 113.1, 110.5, 109.8, 43.9, 21.5; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_2$) m/z 290.1176, found 290.1179.



(Z)-3-benzylidene-8-methoxy-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (***2n***). White solid, 27.5 mg, 90%; MP: 139-141ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.42 (s, 1H), 7.39 (dd, *J* = 7.7,7.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.14-7.10 (m, 2H), 5.96 (s, 1H), 4.96 (s, 2H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.80, 155.40, 141.14, 132.72, 132.18, 129.50, 128.63, 128.05, 127.61, 122.29, 118.71, 113.08, 110.99, 110.28, 102.74, 55.69, 43.93; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_3$) m/z 306.1125, found 306.1118.

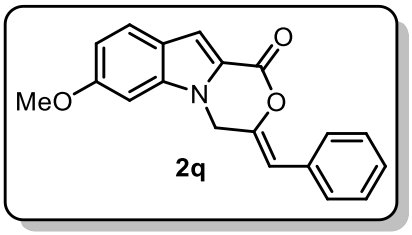


*8-methyl-3-methylene-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2o**).* White solid, 18 mg, 84%; MP: 160-162ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.31 (s, 1H), 7.19 - 7.16 (m, 2H), 5.00 (s, 1H), 4.77 (s, 2H), 4.72 (s, 1H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.2, 148.7, 135.2, 131.2, 128.5, 127.4, 122.5, 122.0, 110.2, 109.6, 98.6, 42.5, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{13}H_{12}NO_2$) m/z 214.0864, found 214.0886.



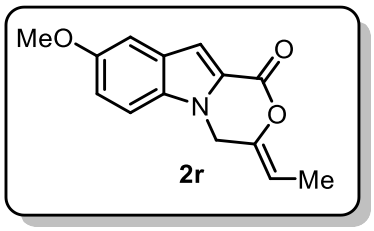
2p

*8-methoxy-3-methylene-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2p**).* White solid, 19.5 mg, 86%; MP: 151-153ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 1H), 7.17 (d, *J* = 9.6 Hz, 1H), 7.04 - 7.00 (m, 2H), 5.01 (s, 1H), 4.77 (s, 2H), 4.72 (s, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.1, 155.4, 148.7, 132.2, 127.6, 122.2, 118.6, 110.9, 110.1, 102.7, 98.6, 55.7, 42.5; HRMS (ESI) calculated for $[M+H]^+$ ($C_{13}H_{12}NO_3$) m/z 230.0813, found 230.0822.

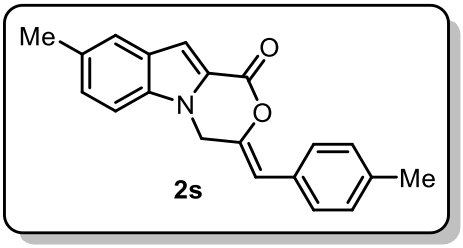


2q

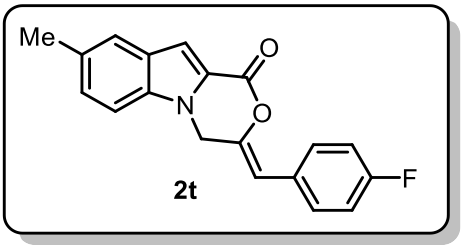
*(Z)-3-benzylidene-7-methoxy-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2q**).* White solid, 23 mg, 76%; MP: 137-139ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.46 (s, 1H), 7.38 (dd, *J* = 7.6, 7.5 Hz, 2H), 7.29 (dd, *J* = 7.4, 7.2 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.73 (s, 1H), 5.95 (s, 1H), 4.92 (s, 2H), 3.92 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.8, 155.7, 141.2, 137.7, 132.7, 129.4, 128.6, 128.0, 124.3, 121.6, 120.9, 113.6, 112.9, 111.6, 91.5, 55.6, 43.8; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{16}NO_3$) m/z 306.1125, found 306.1136.



(Z)-3-ethylidene-8-methoxy-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2r)****.* White solid, 16 mg, 67%; MP: 126-129ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.12 – 7.06 (m, 2H), 5.17 (q, *J* = 6.8 Hz, 1H), 4.77 (s, 2H), 3.86 (s, 3H), 1.82 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.8, 155.4, 141.9, 132.1, 127.6, 123.0, 118.5, 111.0, 109.8, 109.7, 102.8, 55.8, 43.3, 10.0; HRMS (ESI) calculated for $[M+H]^+$ ($C_{14}H_{14}NO_3$) m/z 244.0969, found 244.0981.

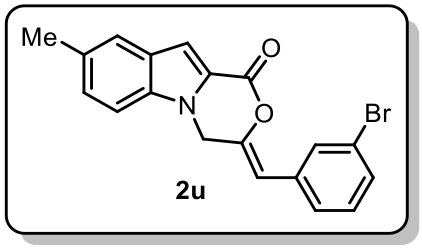


(Z)-8-methyl-3-(4-methylbenzylidene)-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2s)****.* White solid, 22.5 mg, 74%; MP: 155-157ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 1H), 7.34 (s, 1H), 7.20-7.18 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.84 (s, 1H), 4.85 (s, 2H), 2.38 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.1, 140.5, 138.0, 135.1, 131.2, 129.9, 129.4, 129.3, 128.5, 127.4, 122.5, 122.1, 113.0, 110.3, 109.7, 43.8, 21.4, 21.3; HRMS (ESI) calculated for $[M+H]^+$ ($C_{20}H_{18}NO_2$) m/z 304.1332, found 304.1329.

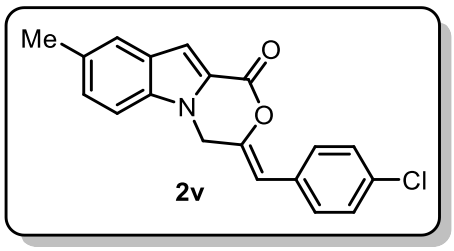


(Z)-3-(4-fluorobenzylidene)-8-methyl-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2t)****.* White solid, 29 mg, 93%; MP: 157-159ºC; column chromatography (Hexane /EtOAc = 20:3

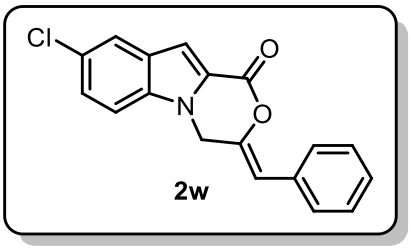
to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 5.9, 5.7 Hz, 2H), 7.53 (s, 1H), 7.43 (s, 1H), 7.28-7.26 (m, 2H), 7.07 (dd, *J* = 8.6, 8.6 Hz, 2H), 5.91 (s, 1H), 4.94 (s, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.2 (d, *J* = 249.5 Hz), 155.8, 140.9, 135.1, 131.3, 131.2 (d, *J* = 8.1 Hz), 128.9 (d, *J* = 3.4 Hz), 128.6, 127.4, 122.6, 121.9, 115.6 (d, *J* = 21.5 Hz), 111.8, 110.5, 109.7, 43.7, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.7; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{15}NO_2F$) m/z 308.1082, found 308.1106.



*(Z)-3-(3-bromobenzylidene)-8-methyl-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2u**).* White solid, 27 mg, 74%; MP: 171-173ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.74 (m, 2H), 7.52 (s, 1H), 7.42 (s, 1H), 7.40 (d, *J*= 8.3 Hz, 1H), 7.27-7.25 (m, 2H), 7.25-7.21 (m, 1H), 5.85 (s, 1H), 4.94 (s, 2H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.4, 142.4, 135.2, 134.8, 132.2, 132.0, 131.4, 130.9, 130.2, 128.7, 127.9, 127.5, 122.6, 121.7, 111.4, 110.7, 109.7, 43.7, 21.4; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{15}NO_2Br$) m/z 368.0281, found 368.0300.

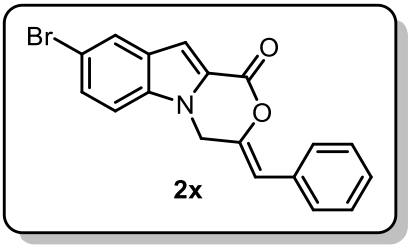


*(Z)-3-(4-chlorobenzylidene)-8-methyl-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2v**).* White solid, 28.5 mg, 88%; MP: 189-191ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.45 (s, 1H), 7.35 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.20-7.17 (m, 2H), 5.82 (s, 1H), 4.86 (s, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.7, 141.8, 135.3, 133.8, 131.5, 131.3, 130.8, 128.9, 128.8, 127.5, 122.7, 121.9, 111.8, 110.7, 109.8, 43.8, 21.5; HRMS (ESI) calculated for $[M+H]^+$ ($C_{19}H_{15}NO_2Cl$) m/z 324.0786, found 324.0804.



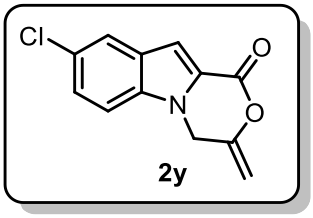
2w

(Z)-3-benzylidene-8-chloro-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2w)****.* White solid, 19 mg, 61%; MP: 146-148ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.71 (m, 3H), 7.44 (s, 1H), 7.42-7.36 (m, 3H), 7.34 – 7.29 (m, 2H), 5.98 (s, 1H), 4.98 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.4, 140.5, 134.8, 132.4, 129.5, 128.6, 128.2, 127.9, 127.5, 127.0, 123.2, 122.5, 113.6, 111.2, 110.1, 43.9; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2Cl$) m/z 310.0630, found 310.0647.



2x

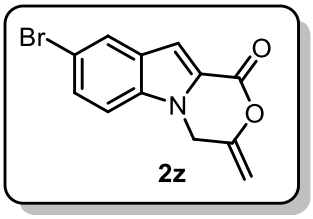
(Z)-3-benzylidene-8-bromo-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2x)****.* White solid, 27 mg, 79%; MP: 180-182ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.45 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.36 (s, 1H), 7.31 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.25-7.21 (m, 1H), 7.20 7.17 (m, 1H), 5.98 (s, 1H), 4.97 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.4, 140.5, 135.0, 132.4, 129.5, 129.5, 128.7, 128.5, 128.2, 125.7, 123.1, 115.0, 113.7, 111.5, 110.0, 43.9; HRMS (ESI) calculated for $[M+H]^+$ ($C_{18}H_{13}NO_2Br$) m/z 354.0125, found 354.0160.



2y

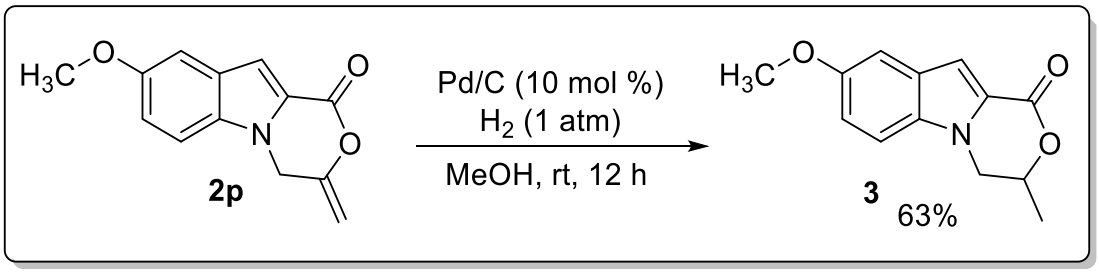
8-chloro-3-methylene-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one ***(2y)****.* White solid, 12 mg, 55%; MP: 153-156ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.37-7.31 (m, 2H), 7.23 (d, *J* =8.8 1H), 5.08 (s, 1H), 4.84 (s, 2H), 4.80 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.8, 148.2, 134.8, 127.9, 127.6,

127.0, 122.5, 111.1, 110.0, 99.2, 77.3, 42.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{12}H_9NO_2Cl$) m/z 234.0318, found 234.0307.



*8-bromo-3-methylene-3,4-dihydro-1H-1,4]oxazino[4,3-a]indol-1-one(**2z**).* White solid, 20.5 mg, 77%; MP: 162-164ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.31 (s, 1H), 7.16 (d, *J* = 8.8 Hz, 1 H), 5.04 (s, 1H), 4.79 (s, 2H), 4.76 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.7, 148.2, 135.0, 129.4, 128.6, 125.7, 123.0, 115.0, 111.5, 109.8, 99.3, 42.6; HRMS (ESI) calculated for $[M+H]^+$ ($C_{12}H_9NO_2Br$) m/z 277.9813, found 277.9832.

10 Procedure for the Synthetic Transformation Reaction of 2p:



Scheme S7

An oven dried 10 mL round bottom flask was charged with 8-methoxy-3-methylene-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**2p**) (0.1 mmol), Pd/C (0.01 mmol) and MeOH (1 mL) under Ar atmosphere . Subsequently, the flask was subjected to three cycles of backfilling with hydrogen gas (H_2). The reaction was stirred at room temperature under H_2 atmosphere for 12 h. After completion of reaction as indicated by TLC , solvent was evaporated under reduced pressure and the crude mixture was purified by flash chromatography (silica gel, Hexane/EtOAc = 20:3 to 20:4) to give pure solid product 3 (14.5 mg, 63 %) as a white solid.

*8-methoxy-3-methyl-3,4-dihydro-1H-[1,4]oxazino[4,3-a]indol-1-one (**3**)*. White solid, 14.5 mg, 63%; MP: 169-171ºC; column chromatography (Hexane /EtOAc = 20:3 to 20:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.22 (d, *J* = 9.2 Hz, 1H), 7.12 – 7.05 (m, 2H), 4.96-4.87 (m, 1H), 4.31 (dd, *J* = 12.7, 3.2 Hz, 1H), 3.95 (dd, *J* = 12.7, 10.4 Hz, 1H), 3.86 (s, 3H), 1.60 (d, *J*

= 6.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 159.8, 155.2, 132.1, 127.4, 123.4, 118.1, 110.8, 109.3, 102.7, 74.3, 55.7, 45.7, 18.4.; HRMS (ESI) calculated for $[M+H]^+$ ($C_{13}H_{14}NO_3$) m/z 232.0969; found 232.0952.

11 Mechanistic insights

Detection of intermediate using HRMS: An oven dried 10 mL schlenk tube was charged with N-alkylated indole-2-carboxylic acid **1** (0.05 mmol), $Pd(PPh_3)_4$ (0.05 mmol), $P(^nBu)_3$ (0.1 mmol) and toluene (150 µL) under Ar atmosphere. Then the schlenk tube was sealed with septum, and it was left to stir for 1 h at 105 ºC. After 1 h of stirring, the crude reaction mixture was injected in the HRMS instrument. HRMS (ESI) calculated for $[M+H]^+$ ($C_{42}H_{68}NO_2P_2Pd$) m/z 786.3740; found 786.3751.

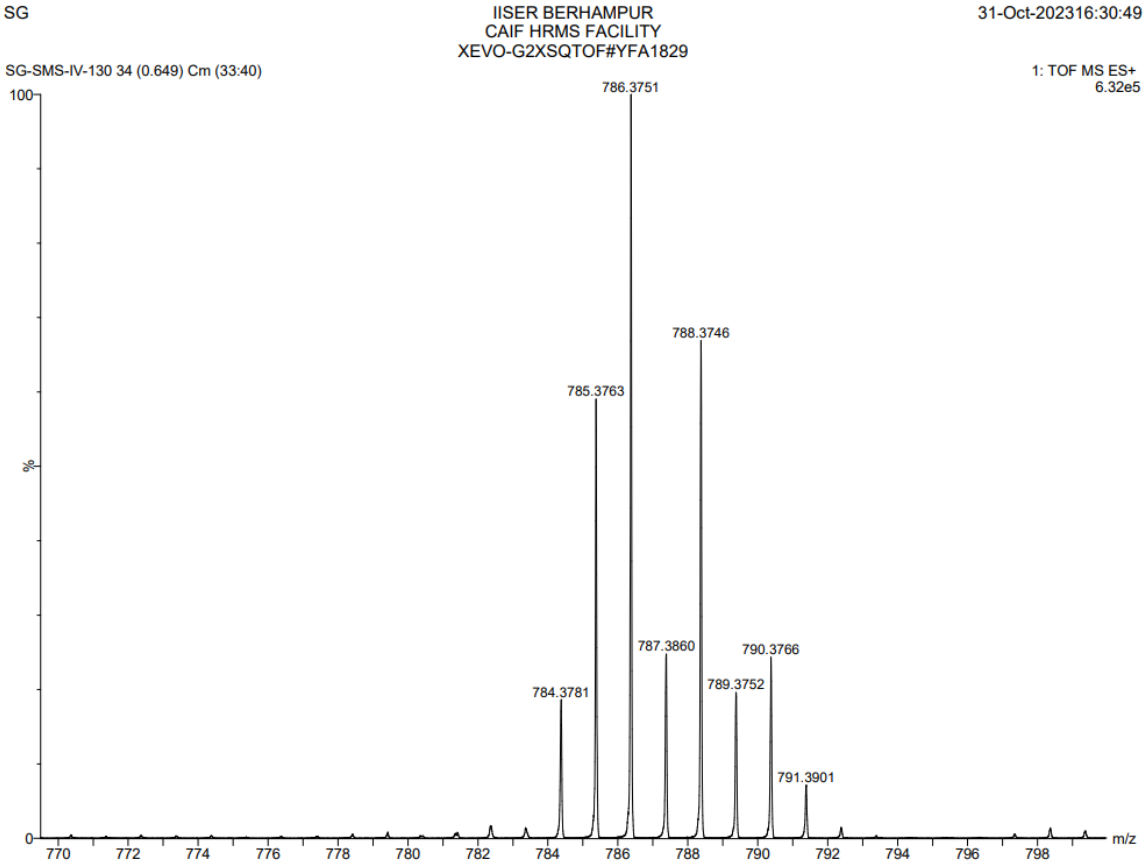


Figure S2. HRMS data for intermediate

12 X-ray Crystallographic information of the product 2a

Crystal (**2a**) suitable for X-ray crystallography was obtained from recrystallization of the solid in DCM and hexane combination using vapour phase diffusion method at room temperature.

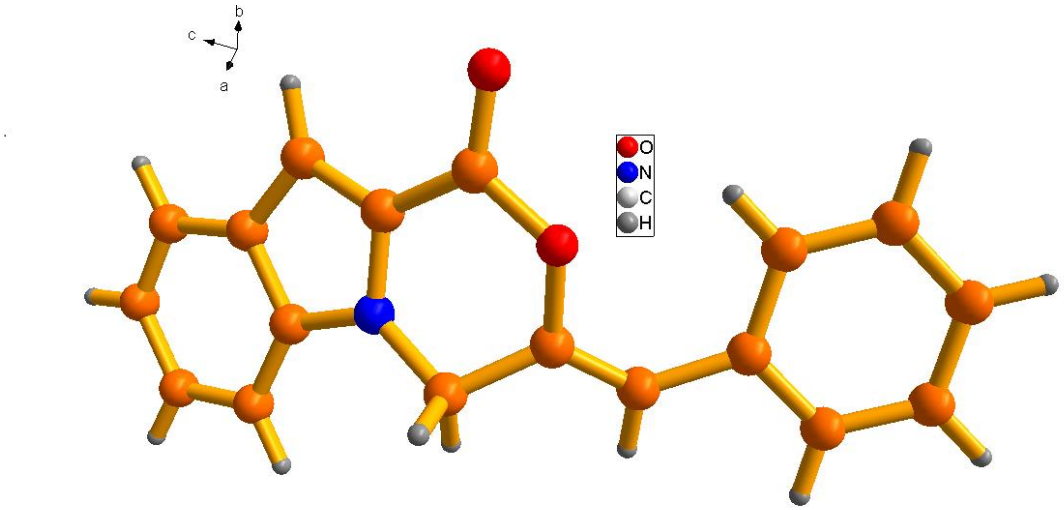


Figure S3. Crystal structure of product **2a**

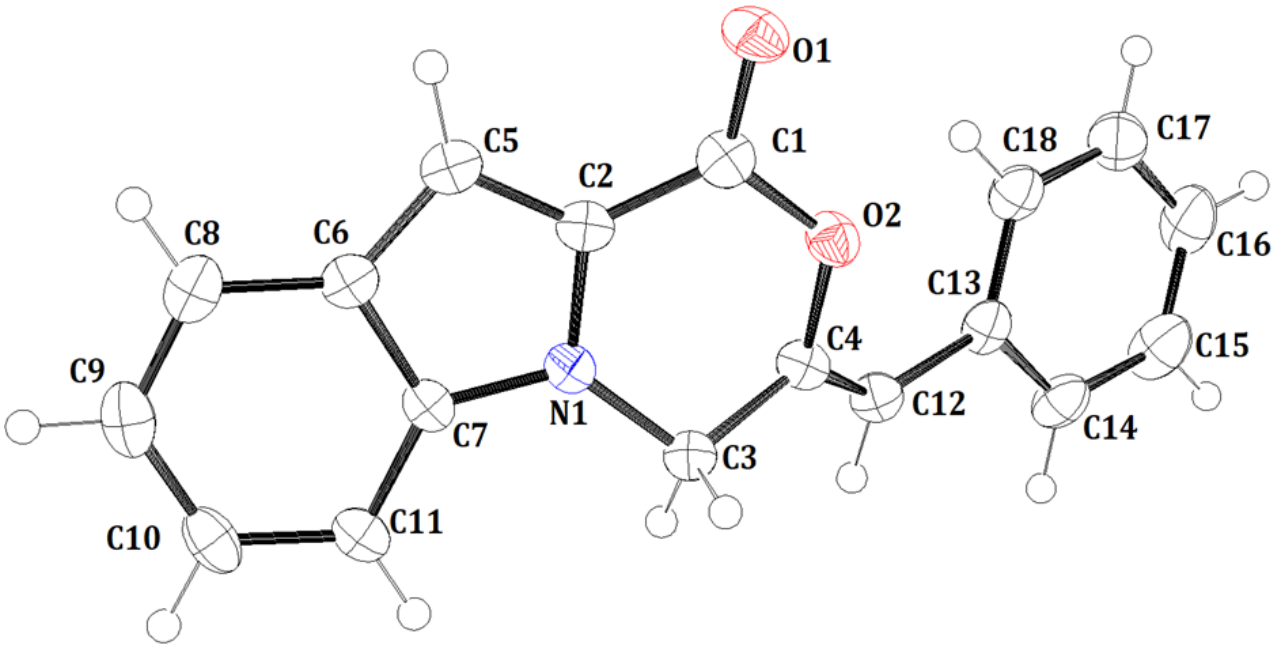


Figure S4. ORTEP view of **2a** with thermal ellipsoids drawn at 50% probability level.

13 Crystal Data of 2a:

Table S3 Crystal data and structure refinement for s*J*p-smc-pm_auto.

Identification code	s*J*p-smc-pm_auto
Empirical formula	$C_{18}H_{13}NO_2$
Formula weight	275.309
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.4846(2)
b/Å	6.6085(2)
c/Å	27.8900(8)
α/°	90
β/°	96.294(2)
γ/°	90
Volume/Å^3	1371.18(7)
Z	4
ρ_{calc}g/cm^3	1.334
μ/mm^{-1}	0.702
F(000)	577.9
Crystal size/mm^3	0.32 × 0.29 × 0.16
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	11.98 to 158.54
Index ranges	$-9 \le h \le 9$, $-8 \le k \le 7$, $-35 \le l \le 35$
Reflections collected	11916
Independent reflections	2932 [R_{int} = 0.0467, R_{sigma} = 0.0410]
Data/restraints/parameters	2932/0/190
Goodness-of-fit on F^2	1.149
Final R indexes [I>=2σ (I)]	R_1 = 0.0648, wR_2 = 0.1493
Final R indexes [all data]	R_1 = 0.0698, wR_2 = 0.1518
Largest diff. peak/hole / e Å^{-3}	0.44/-0.31

Table S4 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for s*J*p-smc-pm_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	6964(2)	7433(3)	3769.6(6)	27.5(4)
O1	6200(2)	10108(3)	4179.3(7)	32.4(4)
N1	7554(2)	5155(3)	4603.9(7)	21.8(4)
C1	6647(3)	8330(4)	4192.7(9)	26.2(5)
C9	7497(3)	3436(4)	6016.5(9)	32.9(6)
C3	8197(3)	4343(4)	4171.2(8)	24.0(5)
C14	5853(3)	3968(5)	2464.6(9)	34.2(6)
C6	6993(3)	5799(4)	5364.0(8)	23.1(5)
C8	6898(3)	5302(4)	5855.3(9)	29.4(5)
C11	8298(3)	2450(4)	5227.1(9)	25.1(5)
C17	4090(4)	7657(5)	2363.9(10)	40.1(7)
C2	6876(3)	7086(4)	4623.5(8)	23.4(5)
C16	4207(4)	6437(6)	1962.5(10)	46.3(8)
C12	6657(3)	4384(4)	3329.8(9)	26.5(5)
C15	5087(4)	4605(6)	2014.1(10)	44.3(8)
C13	5775(3)	5192(4)	2869.8(8)	27.3(5)
C10	8195(3)	2032(4)	5708.7(9)	31.0(6)
C7	7673(3)	4344(3)	5057.8(8)	20.7(5)
C18	4880(3)	7048(4)	2813.7(9)	31.8(6)
C4	7206(3)	5333(4)	3738.3(9)	23.7(5)
C5	6503(3)	7529(4)	5083.8(9)	25.6(5)

Table S5 Anisotropic Displacement Parameters ($Å^2×10^3$) for s*J*p-smc-pm_auto. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O2	33.0(9)	22.2(8)	26.8(8)	-2.8(7)	1.4(7)	0.3(7)
O1	39.7(10)	17.7(8)	38.8(10)	-2.6(7)	0.6(8)	-1.8(7)
N1	19.0(9)	21.9(10)	23.7(9)	-2.0(7)	-0.7(7)	0.3(8)
C1	25.6(11)	23.0(12)	29.3(12)	-7.2(9)	-0.2(9)	-4.8(10)
C9	26.1(12)	45.6(16)	25.6(12)	-12.8(11)	-3.2(9)	5.0(11)
C3	23.4(11)	22.8(11)	25.6(11)	-0.7(9)	1.3(9)	-1.8(9)
C14	25.6(12)	45.7(16)	31.0(13)	2.8(11)	1.9(10)	-8.0(12)
C6	15.0(9)	26.9(12)	26.6(11)	-4.0(9)	-1.7(8)	-4.9(9)
C8	20.1(11)	40.9(15)	26.7(12)	-8.4(10)	1.2(9)	-6.8(11)
C11	20.0(10)	24.1(12)	29.6(12)	-3.5(9)	-4.2(9)	1.9(9)
C17	28.3(13)	51.4(18)	40.0(15)	6.6(13)	1.0(11)	7.7(13)
C2	20.0(10)	20.2(11)	29.4(12)	-3.5(9)	-0.8(9)	-2.8(9)
C16	32.8(14)	79(2)	25.7(13)	6.7(15)	-3.1(11)	4.8(14)
C12	22.6(11)	28.1(12)	28.4(12)	-0.5(9)	0.8(9)	-2.1(10)
C15	32.9(14)	71(2)	27.6(13)	3.0(14)	-3.1(11)	-12.8(14)
C13	18.3(10)	38.9(14)	24.3(11)	-2.3(10)	0.7(8)	-2.1(10)
C10	28.2(12)	31.1(13)	31.3(13)	-7.7(10)	-7.8(10)	9.1(11)
C7	15.4(9)	21.9(11)	23.5(11)	-5.3(8)	-3.2(8)	0.9(9)
C18	23.7(11)	42.0(15)	29.4(13)	1.1(11)	2.0(10)	-2.2(11)
C4	20.1(10)	21.5(11)	29.0(12)	-3.3(9)	-0.2(9)	-0.0(9)
C5	19.9(10)	26.1(12)	30.0(12)	-2.7(9)	-0.4(9)	-6.6(10)

Table S6 Bond Lengths for s*J*p-smc-pm_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C1	1.364(3)	C6	C8	1.419(3)
O2	C4	1.404(3)	C6	C7	1.417(3)
O1	C1	1.221(3)	C6	C5	1.410(3)
N1	C3	1.450(3)	C11	C10	1.382(3)
N1	C2	1.377(3)	C11	C7	1.400(3)
N1	C7	1.369(3)	C17	C16	1.390(4)
C1	C2	1.450(3)	C17	C18	1.387(4)
C9	C8	1.371(4)	C2	C5	1.375(3)
C9	C10	1.403(4)	C16	C15	1.378(5)
C3	C4	1.496(3)	C12	C13	1.477(3)
C14	C15	1.388(4)	C12	C4	1.326(3)
C14	C13	1.396(4)	C13	C18	1.398(4)

Table S7 Bond Angles for s*J*p-smc-pm_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	O2	C1	121.25(19)	C5	C2	N1	110.4(2)
C2	N1	C3	122.23(19)	C5	C2	C1	129.4(2)
C7	N1	C3	129.1(2)	C15	C16	C17	119.8(3)
C7	N1	C2	108.24(19)	C4	C12	C13	130.0(2)
O1	C1	O2	117.7(2)	C16	C15	C14	120.4(3)
C2	C1	O2	117.0(2)	C12	C13	C14	116.1(2)
C2	C1	O1	125.3(2)	C18	C13	C14	118.7(2)
C10	C9	C8	121.6(2)	C18	C13	C12	125.3(2)
C4	C3	N1	109.25(19)	C11	C10	C9	121.8(2)
C13	C14	C15	120.5(3)	C6	C7	N1	107.5(2)
C7	C6	C8	119.0(2)	C11	C7	N1	130.3(2)
C5	C6	C8	133.3(2)	C11	C7	C6	122.2(2)
C5	C6	C7	107.7(2)	C13	C18	C17	120.5(3)
C6	C8	C9	118.4(2)	C3	C4	O2	116.0(2)
C7	C11	C10	117.0(2)	C12	C4	O2	119.4(2)
C18	C17	C16	120.2(3)	C12	C4	C3	124.5(2)
C1	C2	N1	120.2(2)	C2	C5	C6	106.1(2)

Table S8 Torsion Angles for s*J*p-smc-pm_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C1	C2	N1	6.2(2)	C1	C2	C5	C6	-179.4(3)
O2	C1	C2	C5	−173.73(19)	C9	C8	C6	C7	1.0(2)
O2	C4	C3	N1	43.2(2)	C9	C8	C6	C5	179.7(2)
O2	C4	C12	C13	-0.1(3)	C9	C10	C11	C7	0.0(3)
O1	C1	C2	N1	-173.6(2)	C3	C4	C12	C13	-175.8(2)
O1	C1	C2	C5	6.5(3)	C14	C15	C16	C17	0.2(4)
N1	C3	C4	C12	−140.90(19)	C14	C13	C12	C4	161.0(2)
N1	C2	C5	C6	0.7(2)	C14	C13	C18	C17	-0.1(3)
N1	C7	C6	C8	177.54(17)	C6	C7	C11	C10	1.1(2)
N1	C7	C6	C5	-1.47(19)	C17	C18	C13	C12	-179.7(2)
N1	C7	C11	C10	-177.9(2)					

Table S9 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for s*J*p-smc-pm_auto.

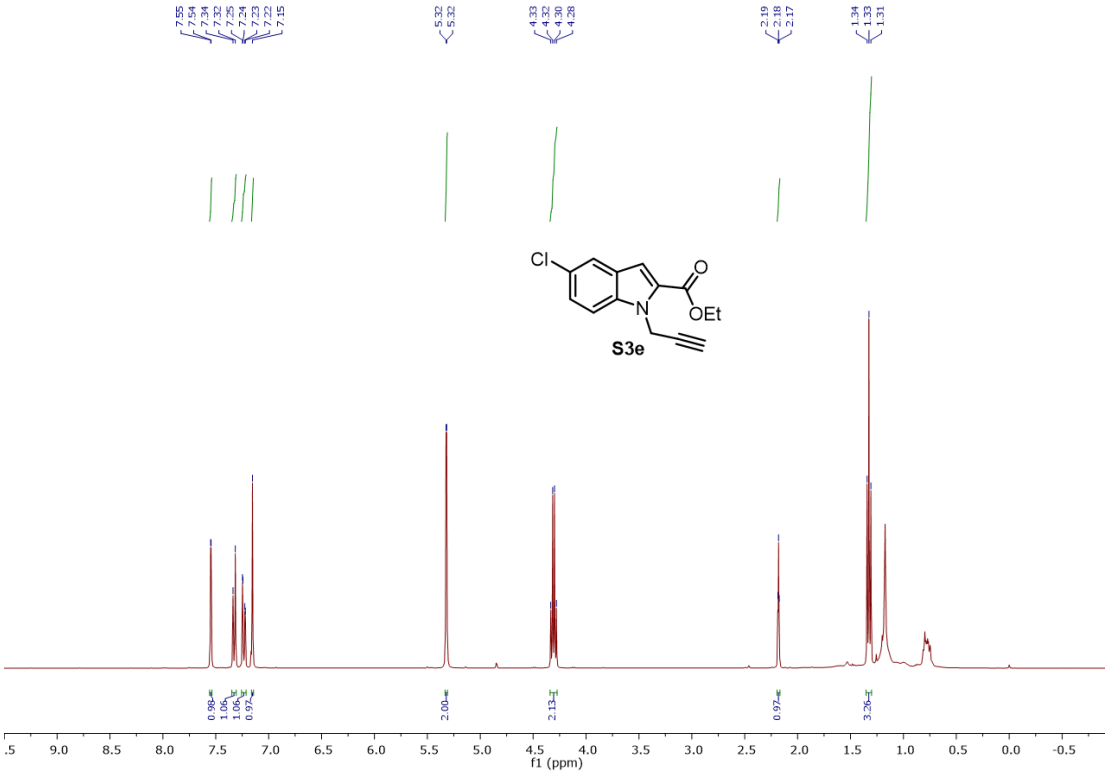
Atom	*x*	*y*	*z*	U(eq)
H9	7439(3)	3085(4)	6344.7(9)	39.5(7)
H3a	9502(3)	4601(4)	4177.1(8)	28.9(6)
H3b	7999(3)	2863(4)	4156.2(8)	28.9(6)
H14	6434(3)	2690(5)	2497.4(9)	41.0(7)
H8	6431(3)	6240(4)	6067.7(9)	35.2(7)
H11	8772(3)	1494(4)	5020.0(9)	30.1(6)
H17	3468(4)	8910(5)	2330.0(10)	48.1(8)
H16	3682(4)	6865(6)	1653.6(10)	55.6(10)
H12	6864(3)	2965(4)	3333.6(9)	31.8(6)
H15	5170(4)	3773(6)	1739.6(10)	53.1(9)
H10	8608(3)	759(4)	5834.9(9)	37.2(7)
H18	4812(3)	7899(4)	3085.8(9)	38.1(7)
H5	6015(3)	8754(4)	5191.4(9)	30.7(6)

14 References:

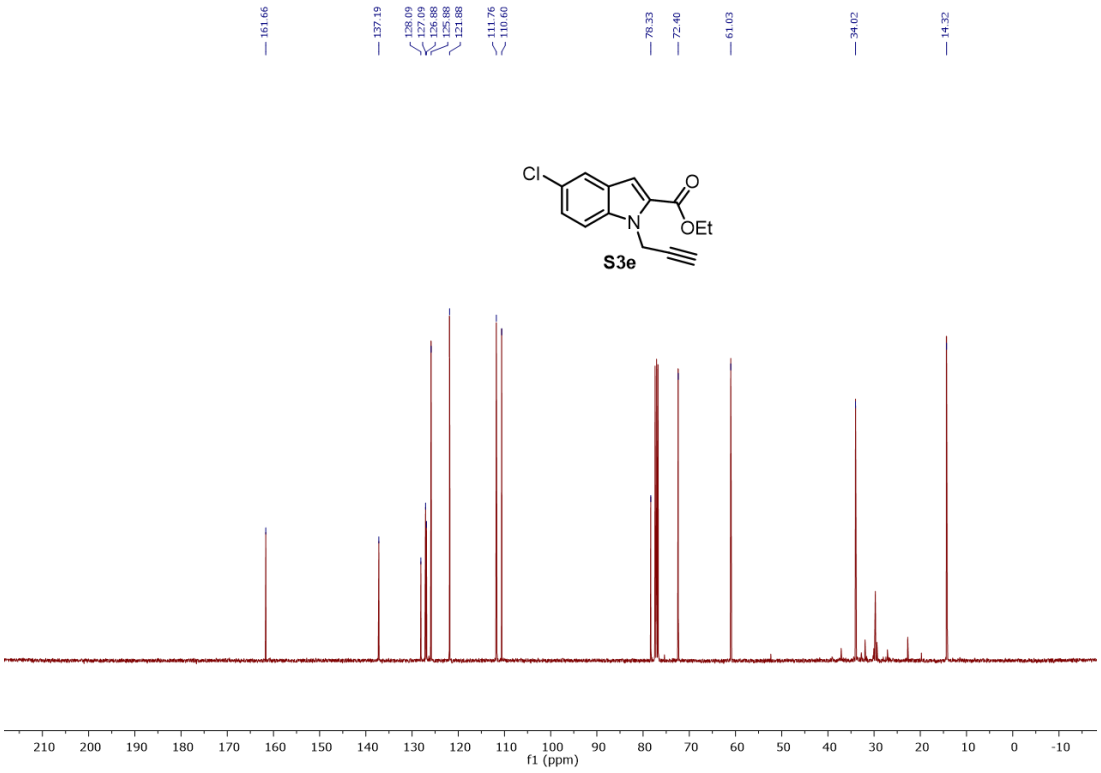
(1) A. J. Fugard, B. K. Thompson, A. M. Z. Slawin, J. E. Taylor and A. D. Smith, *Org. Lett.*, 2015, **17**, 5824–5827.
(2) S. Basceken, S. Kaya and M. Balci, *J. Org. Chem.*, 2015, **80**, 12552–12561.
(3) R. Pedrazzani, E. Pinosa, G. Bertuzzi, M. Monari, S. Lauzon, T. Ollevier and M. Bandini, Chem. Commun., 2022, **58**, 8698–8701
(4) S. Hammoud, E. Anselmi, K. Cherry, J.-C. Kizirian and J. Thibonnet, *European J. Org. Chem.*, 2018, **2018**, 6314–6327.
(5) S. Taskaya, N. Menges and M. Balci, Beilstein *J. Org. Chem.*, 2015, **11**, 897–905

15 NMR spectral data of starting materials:

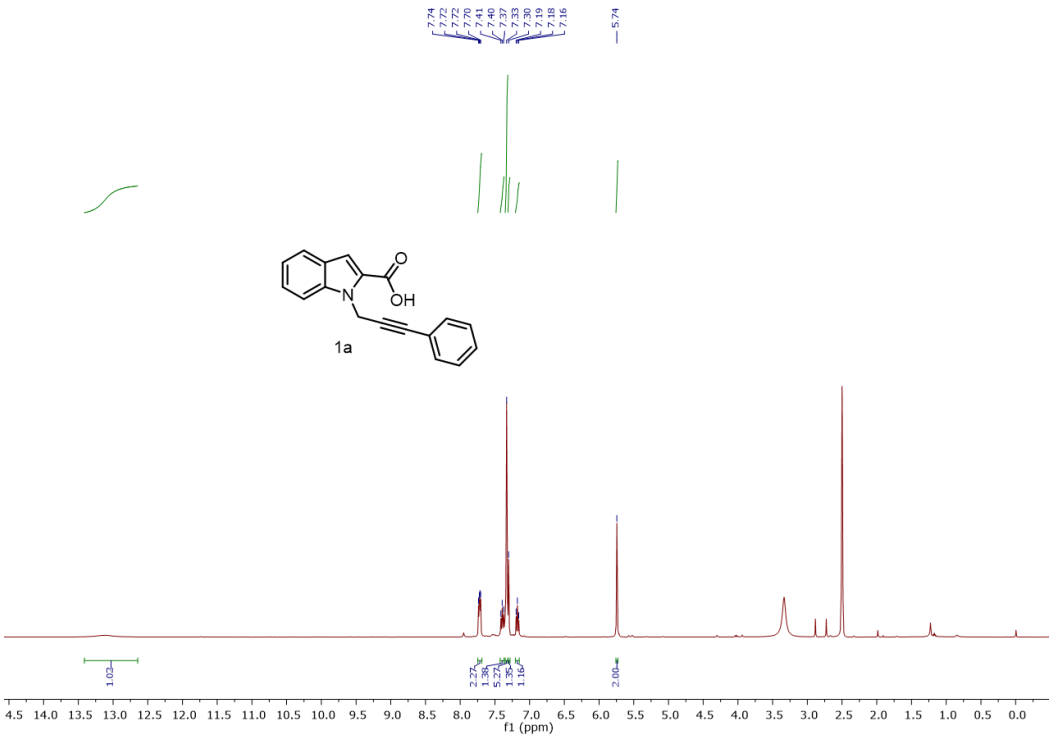
^{1}H NMR of **S3e** (400 MHz, $CDCl_3$)



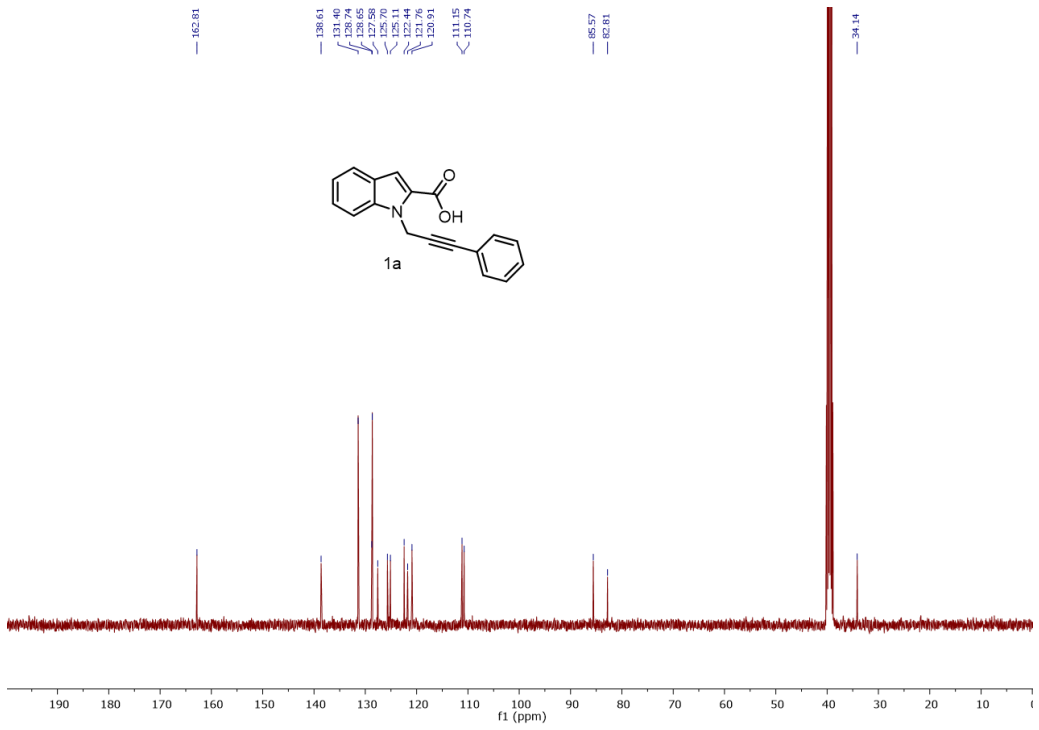
^{13}C{1H} NMR of **S3e** (101 MHz, $CDCl_3$)



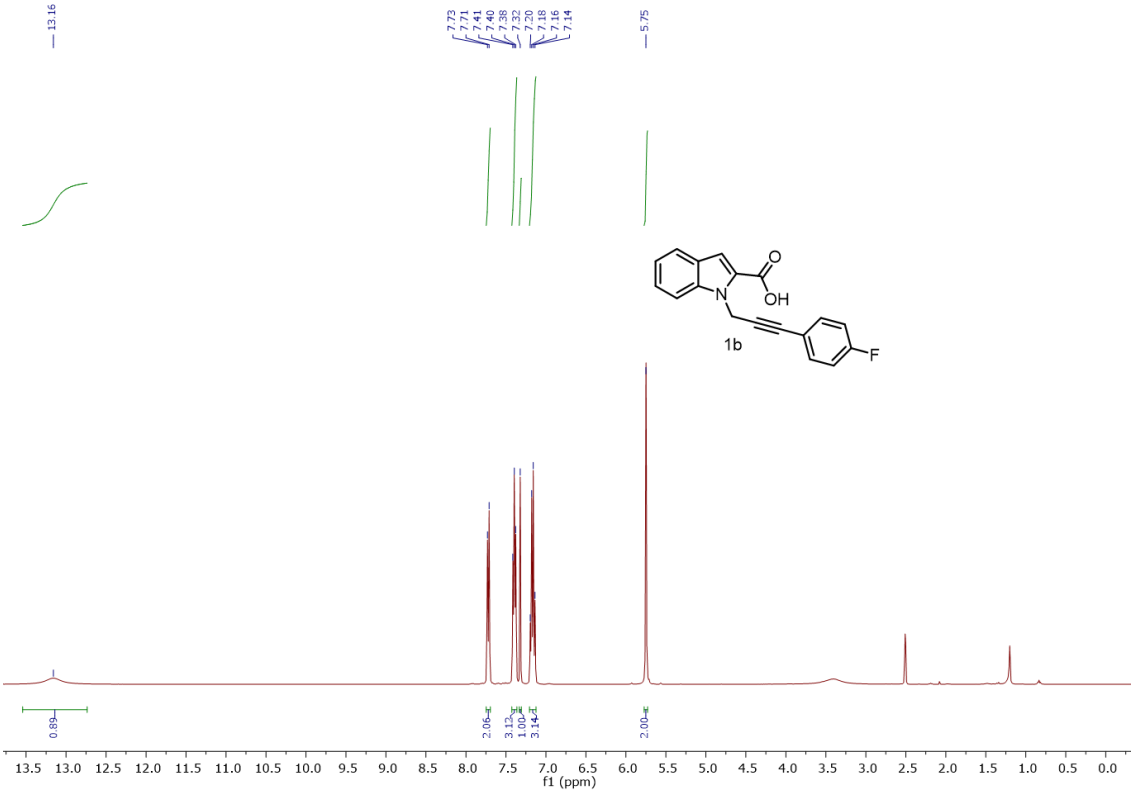
^{1}H NMR of **1a** (400 MHz, DMSO)



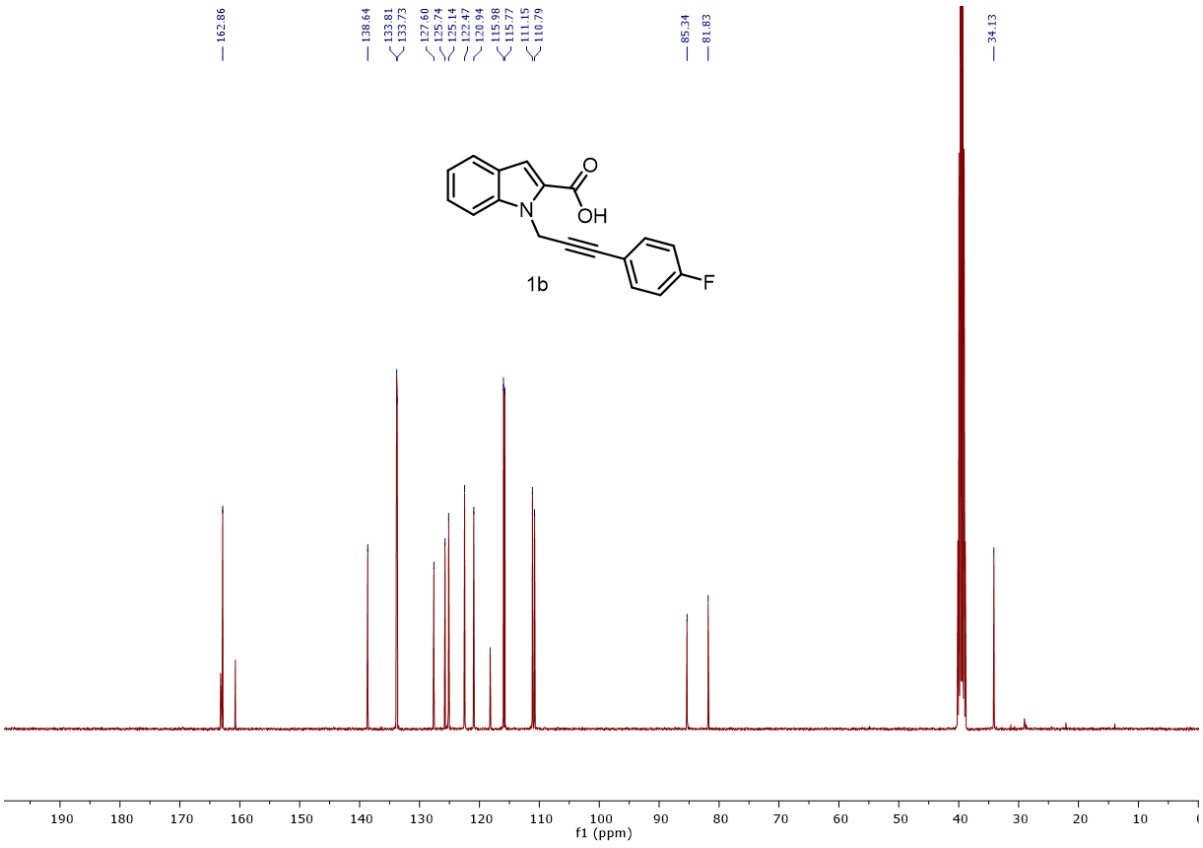
^{13}C{1H} NMR of **1a** (101 MHz, DMSO)



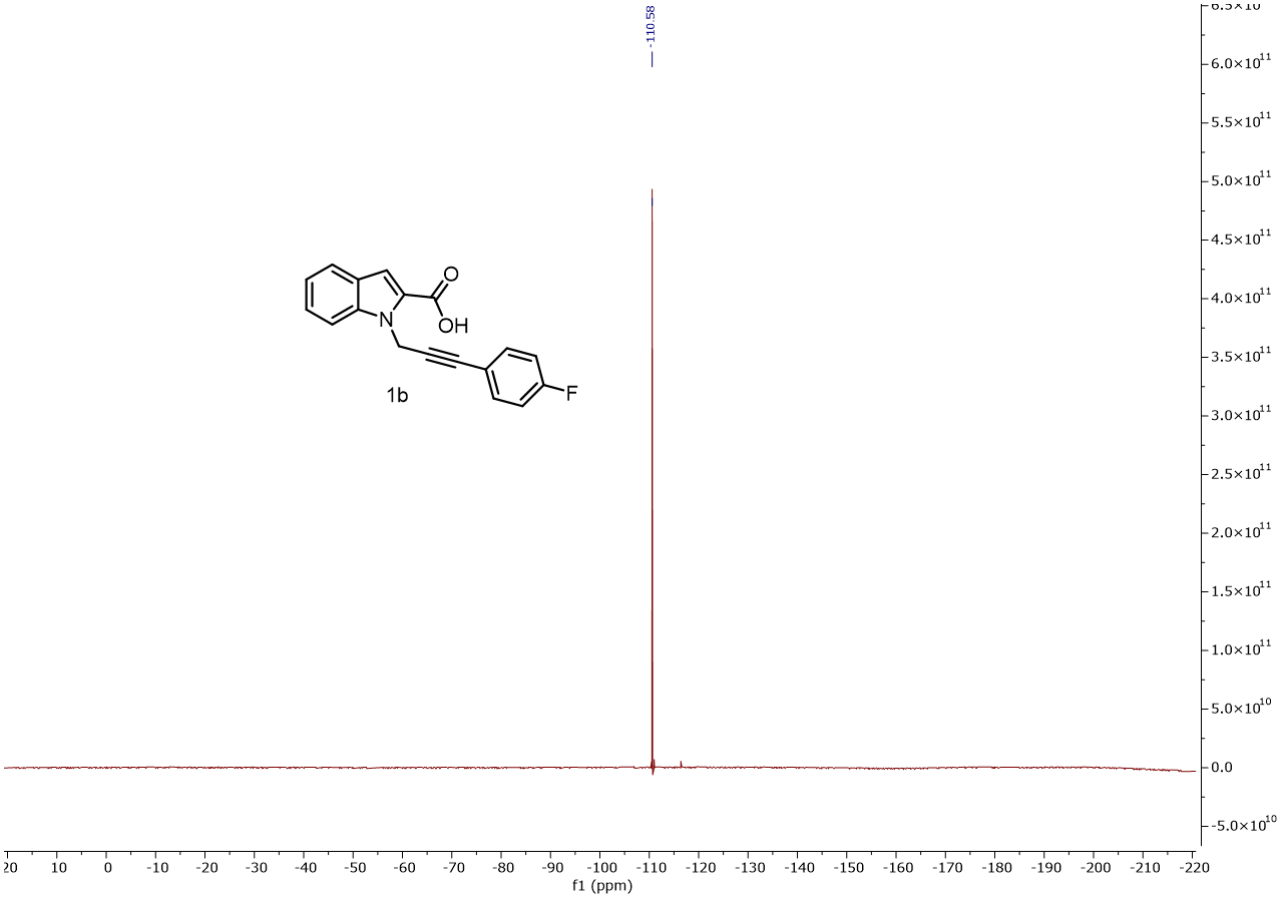
^{1}H NMR of **1b** (400 MHz, DMSO)



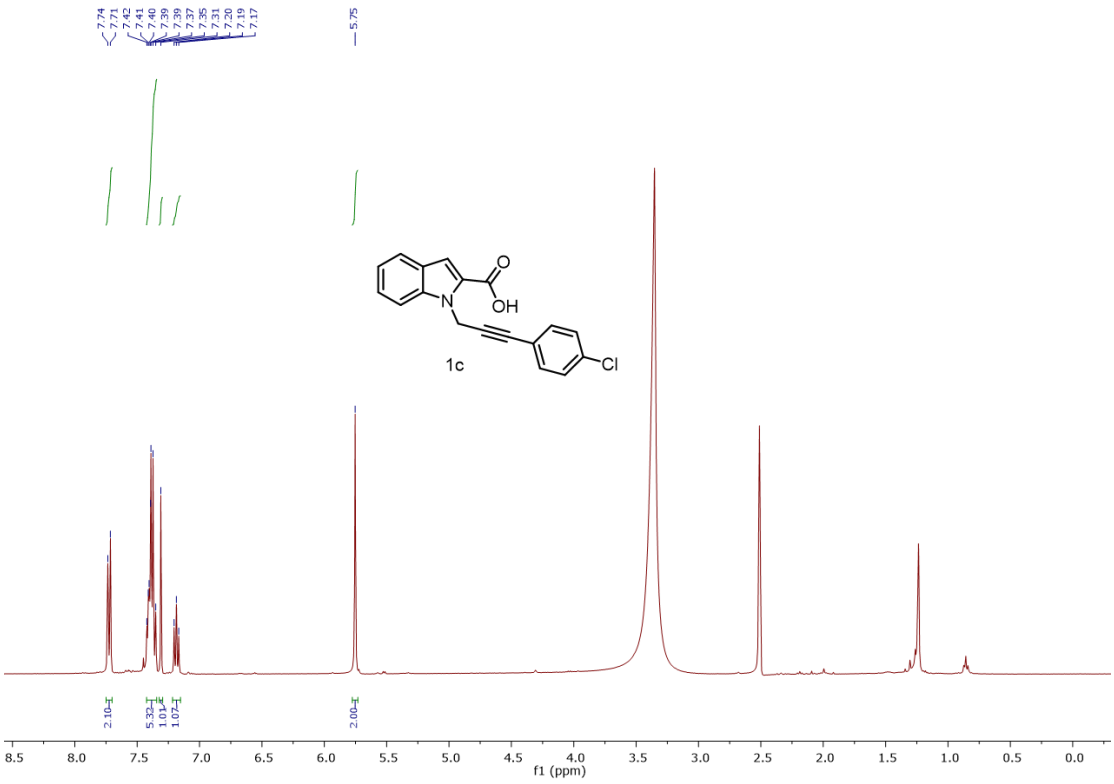
^{13}C{1H} NMR of **1b** (101 MHz, DMSO)



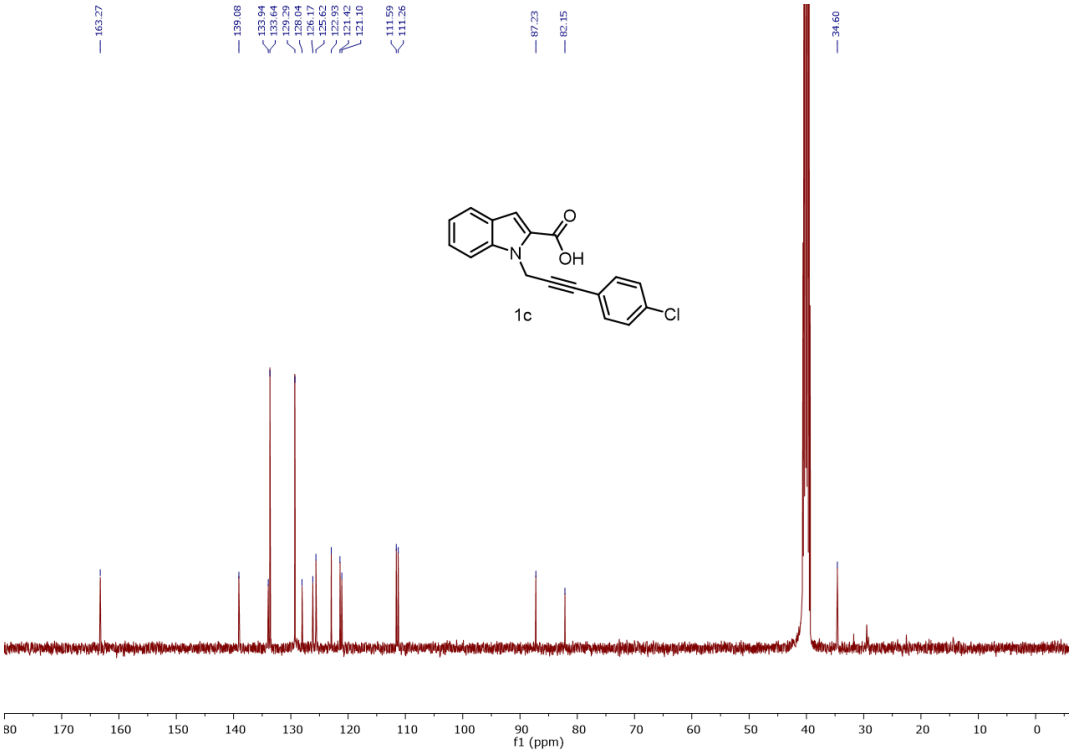
^{19}F NMR of **1b** (376 MHz, DMSO)



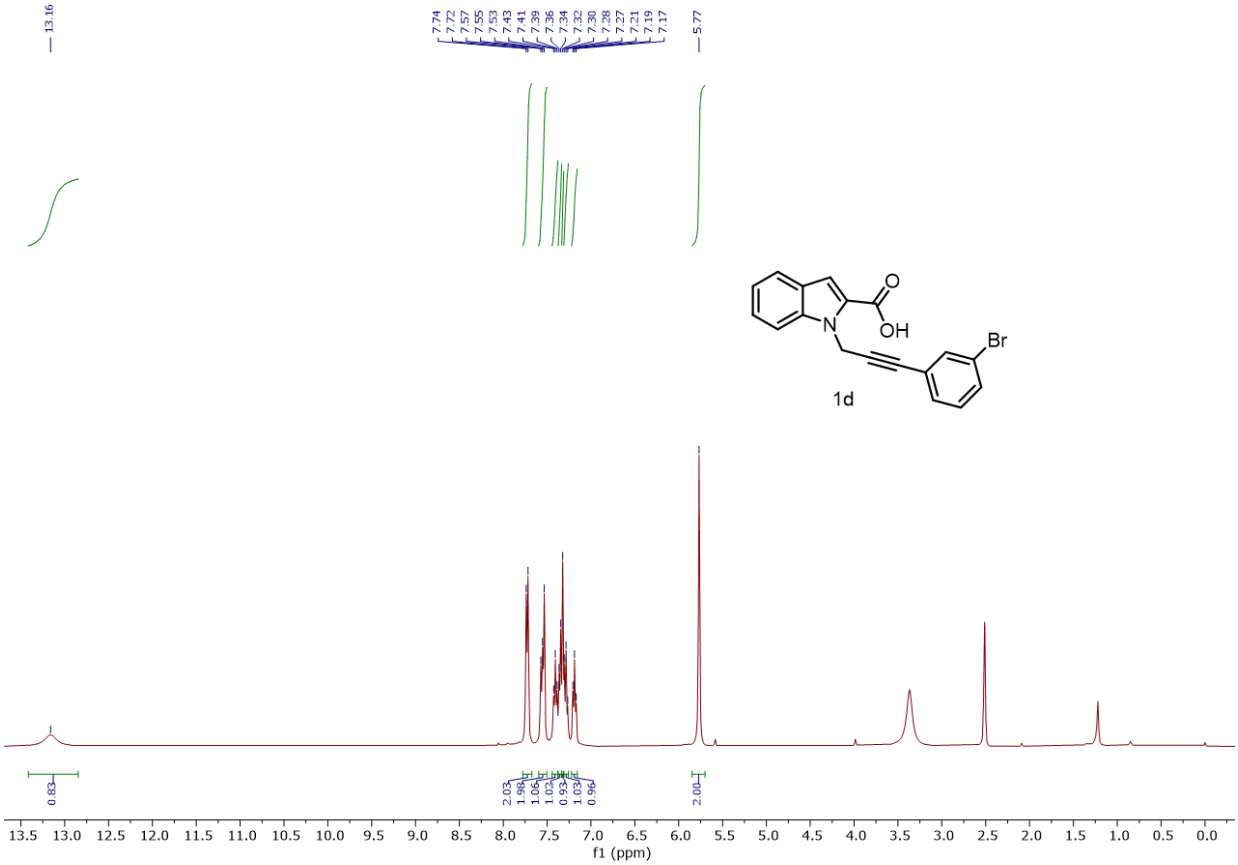
^{1}H NMR of **1c** (400 MHz, DMSO)



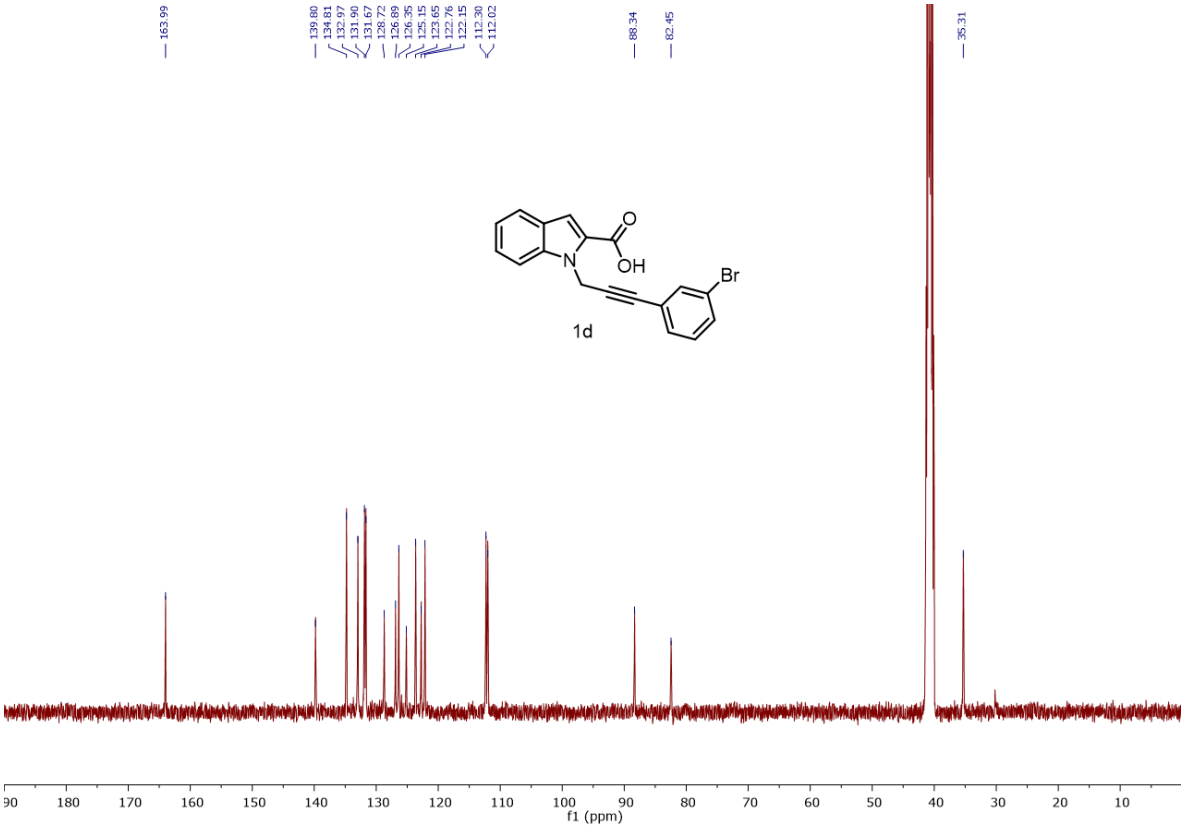
^{13}C{1H} NMR of **1c** (101 MHz, DMSO)



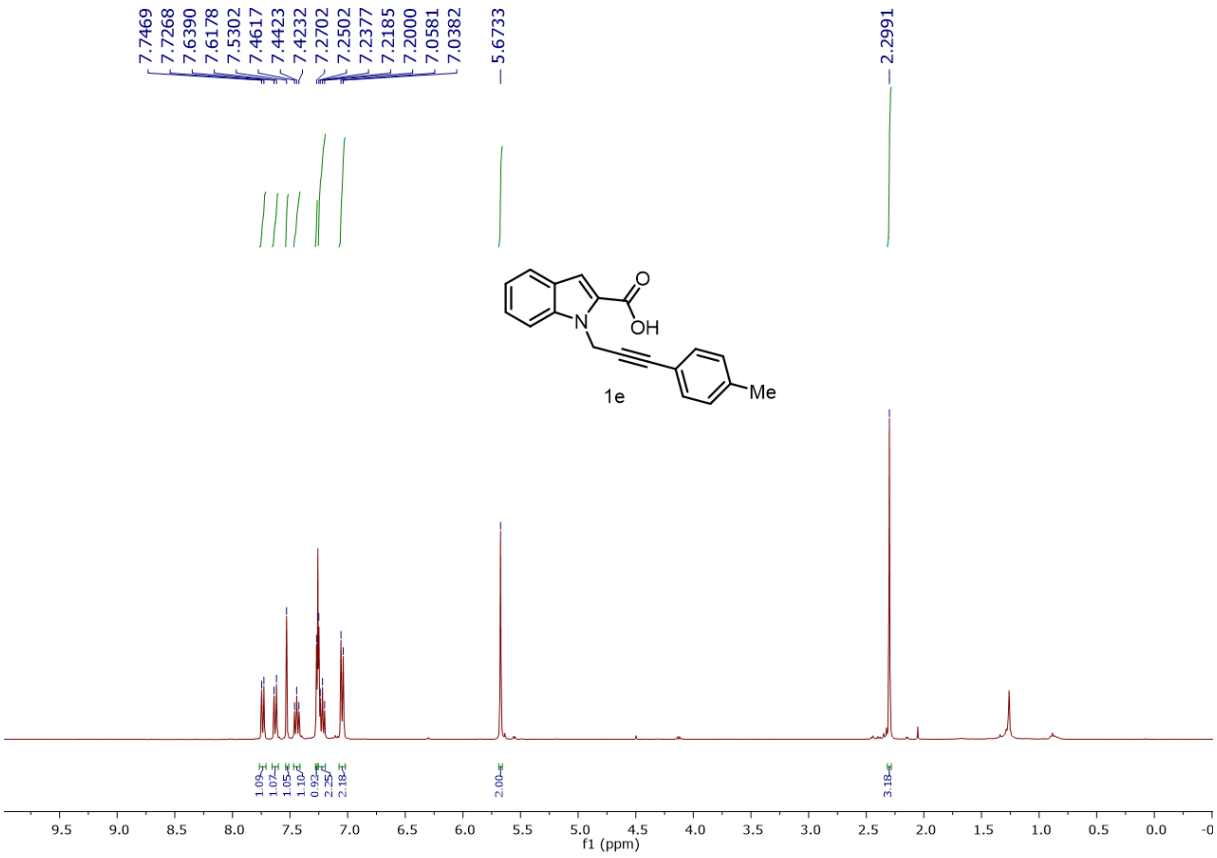
^{1}H NMR of **1d** (400 MHz, DMSO)



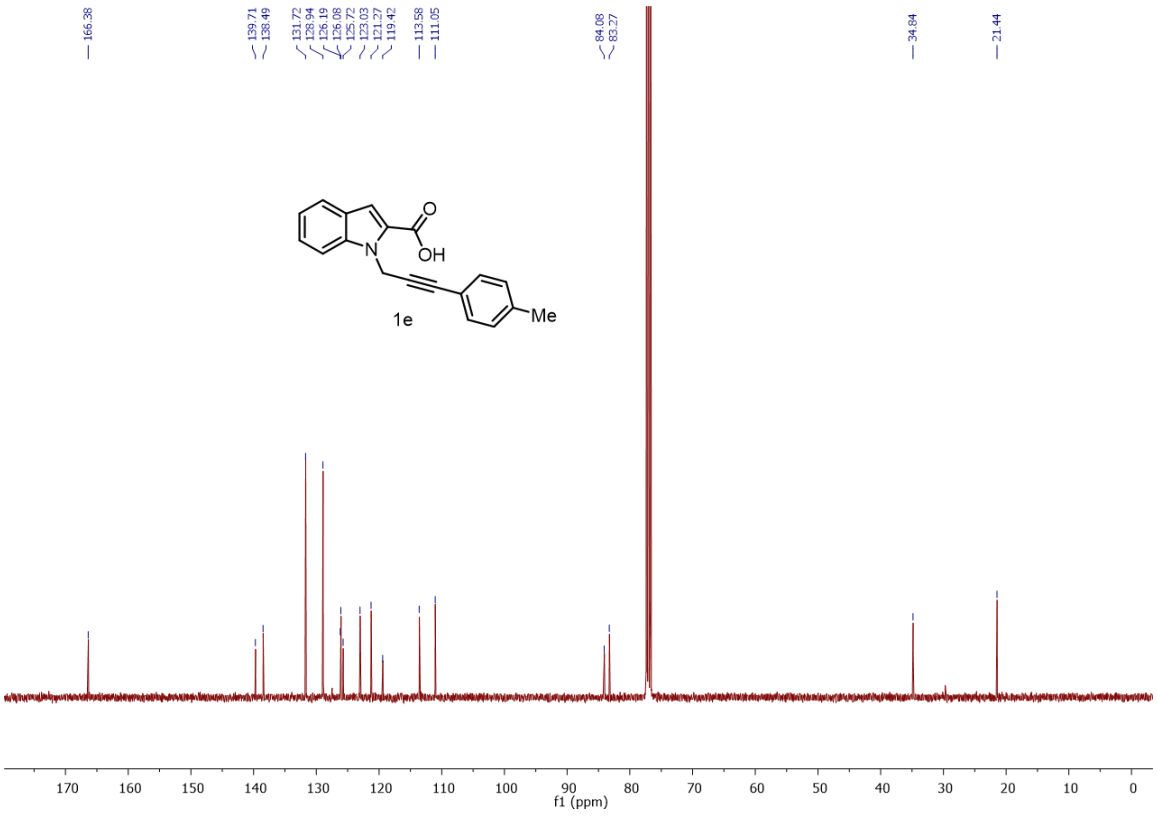
$^{13}C\{1H\}$ NMR of **1d** (101 MHz, DMSO)



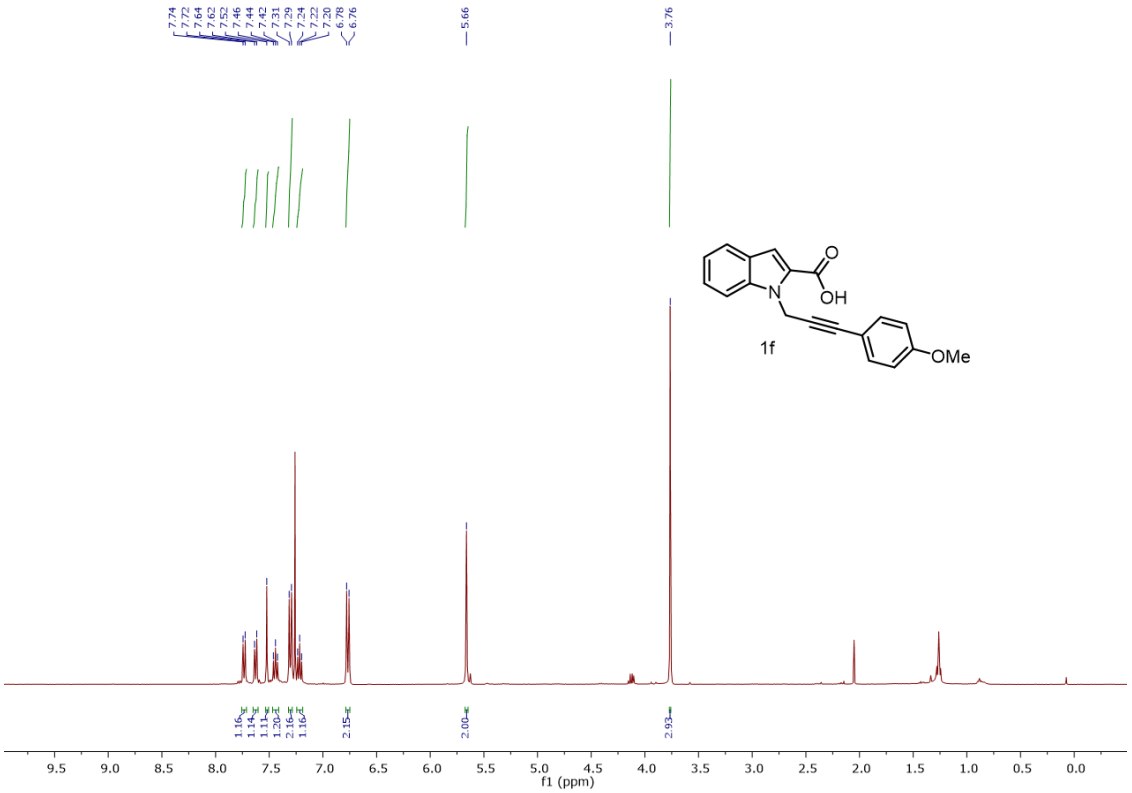
^{1}H NMR of **1e** (400 MHz, $CDCl_3$)



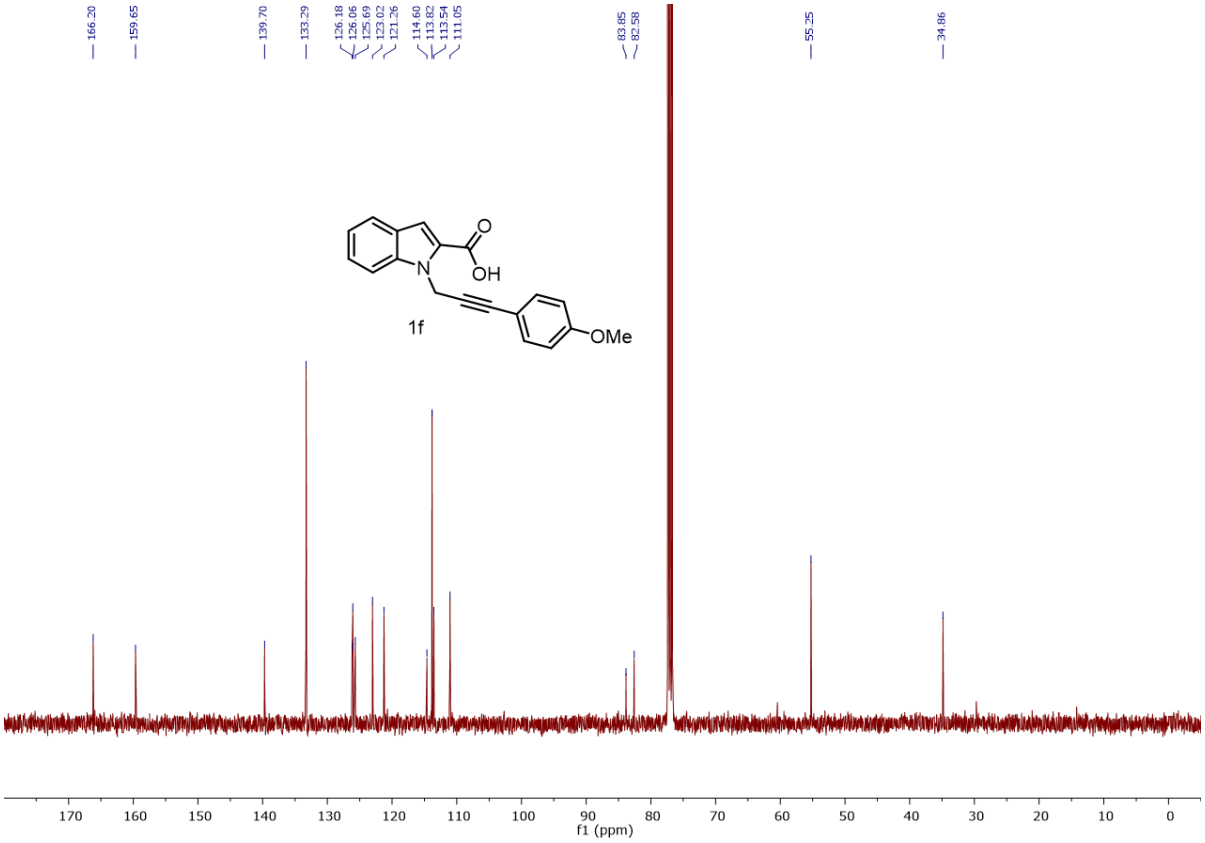
$^{13}C\{1H\}$ NMR of **1e** (101 MHz, $CDCl_3$)



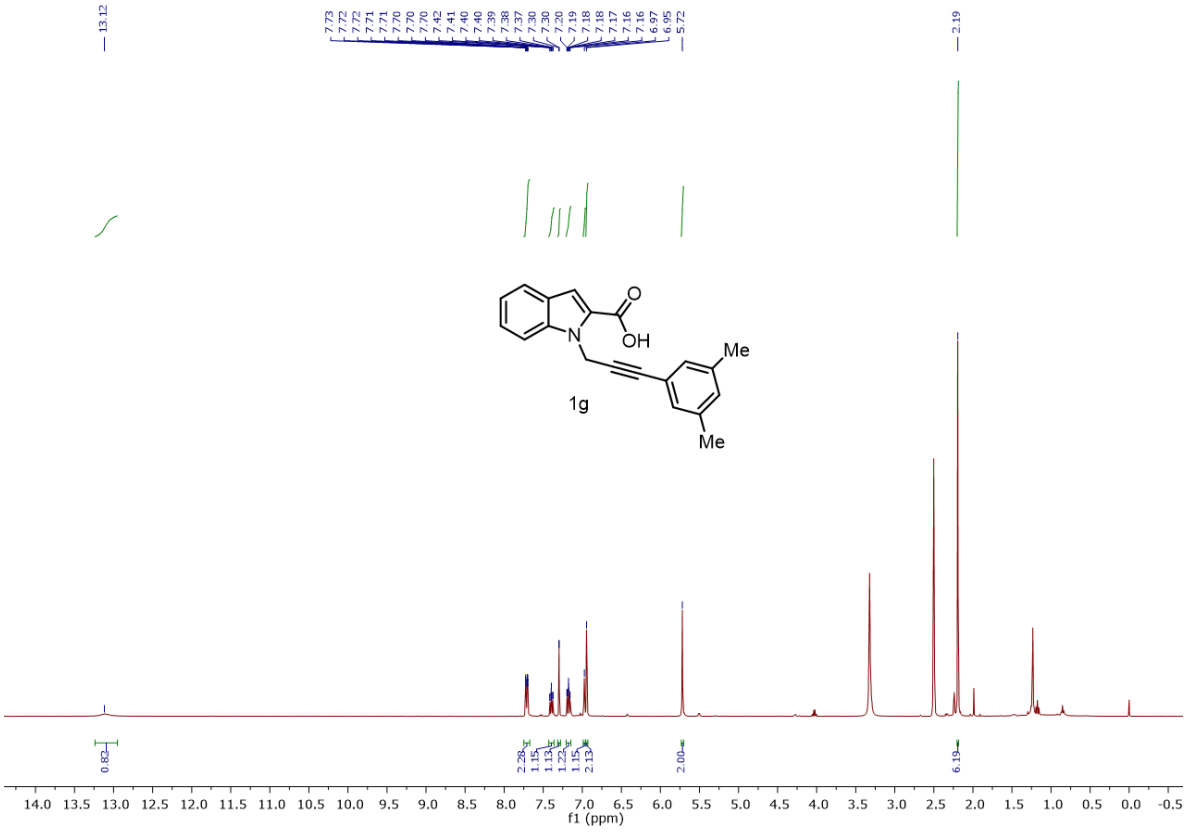
^{1}H NMR of **1f** (400 MHz, DMSO)



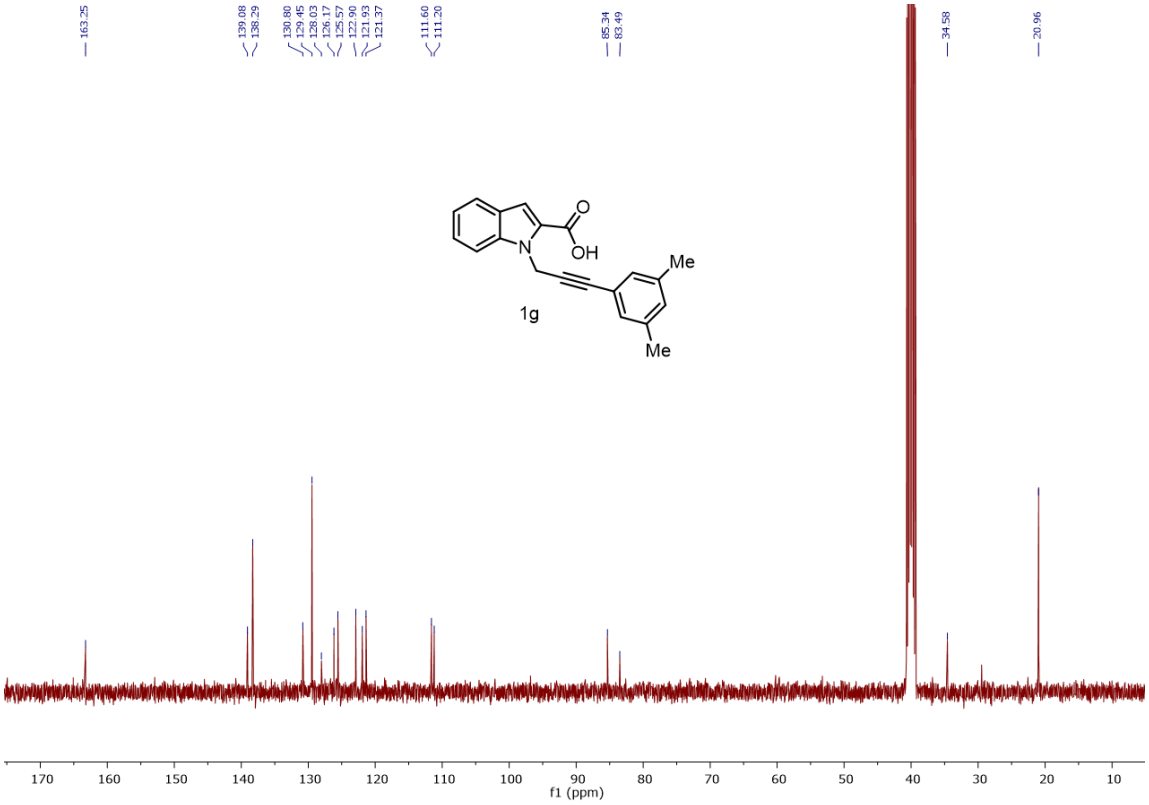
$^{13}C\{1H\}$ NMR of **1f** (101 MHz, DMSO)



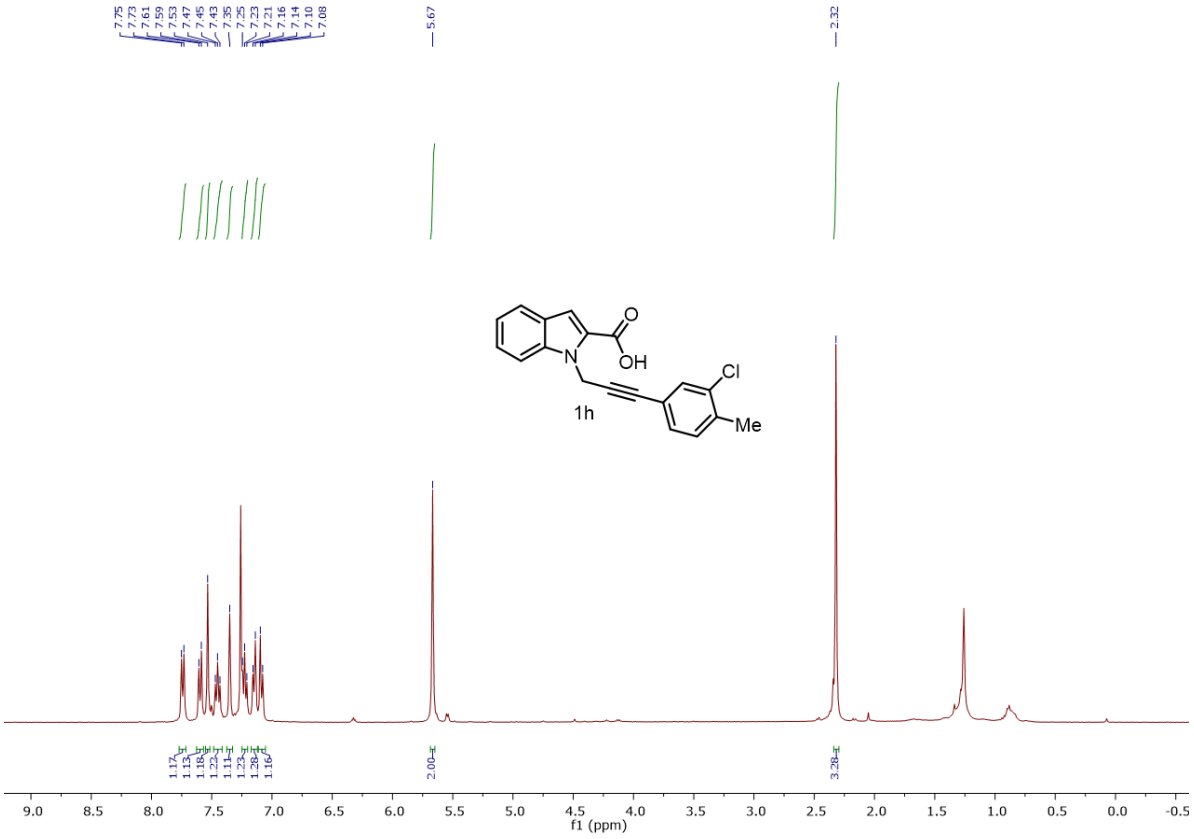
^{1}H NMR of **1g** (400 MHz, DMSO)



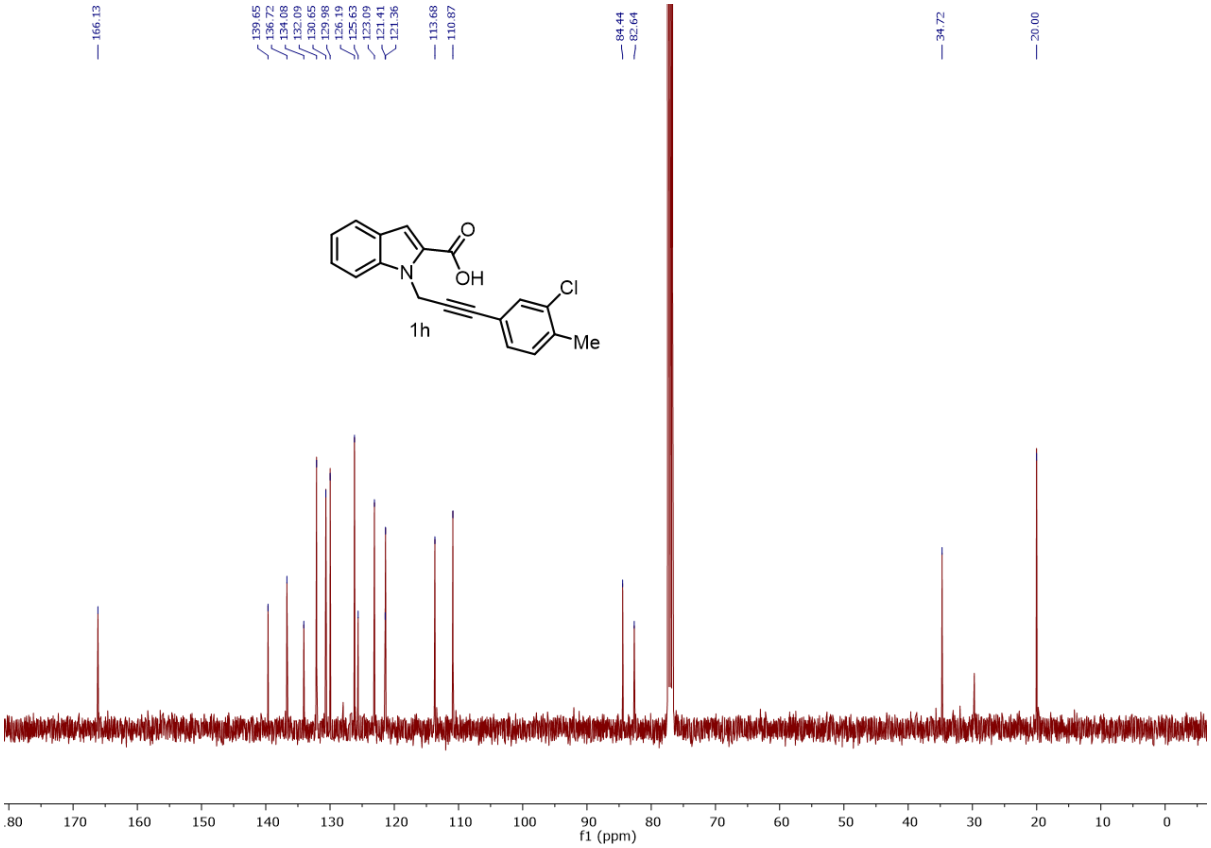
$^{13}C\{1H\}$ NMR of **1g** (101 MHz, DMSO)



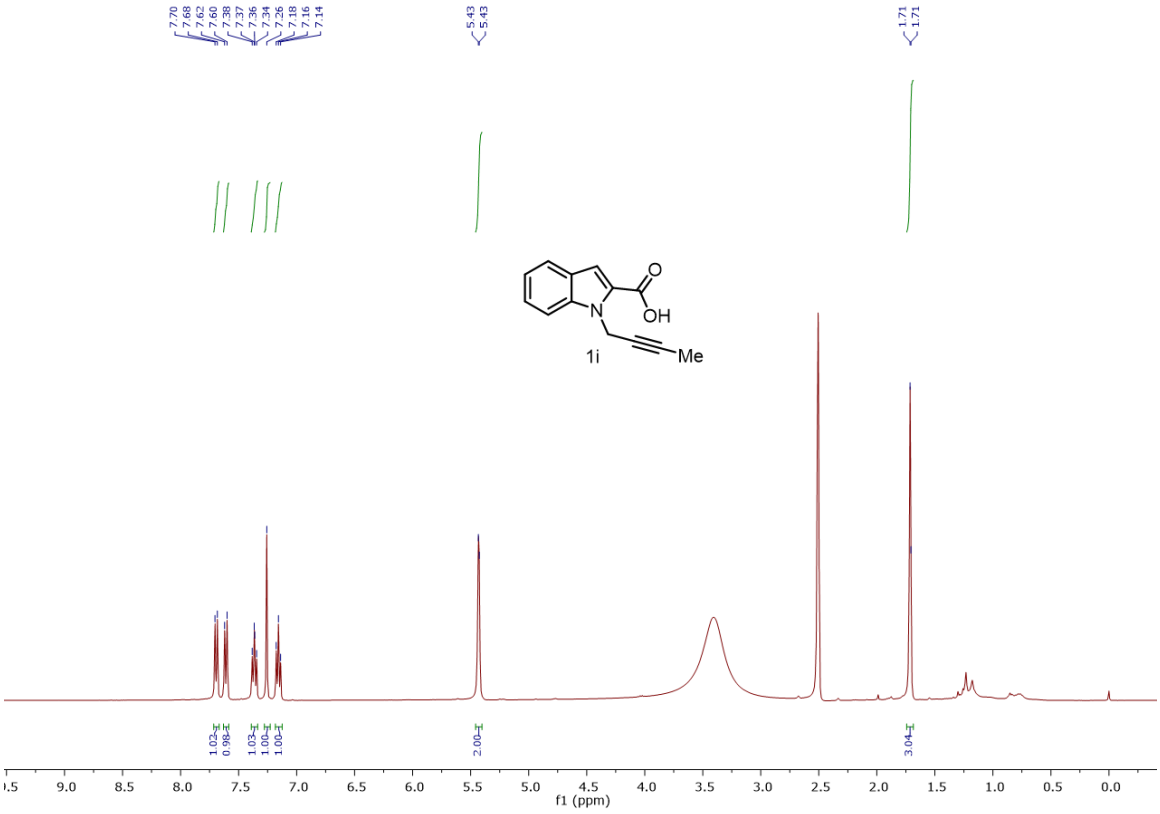
^{1}H NMR of **1h** (400 MHz, $CDCl_3$)



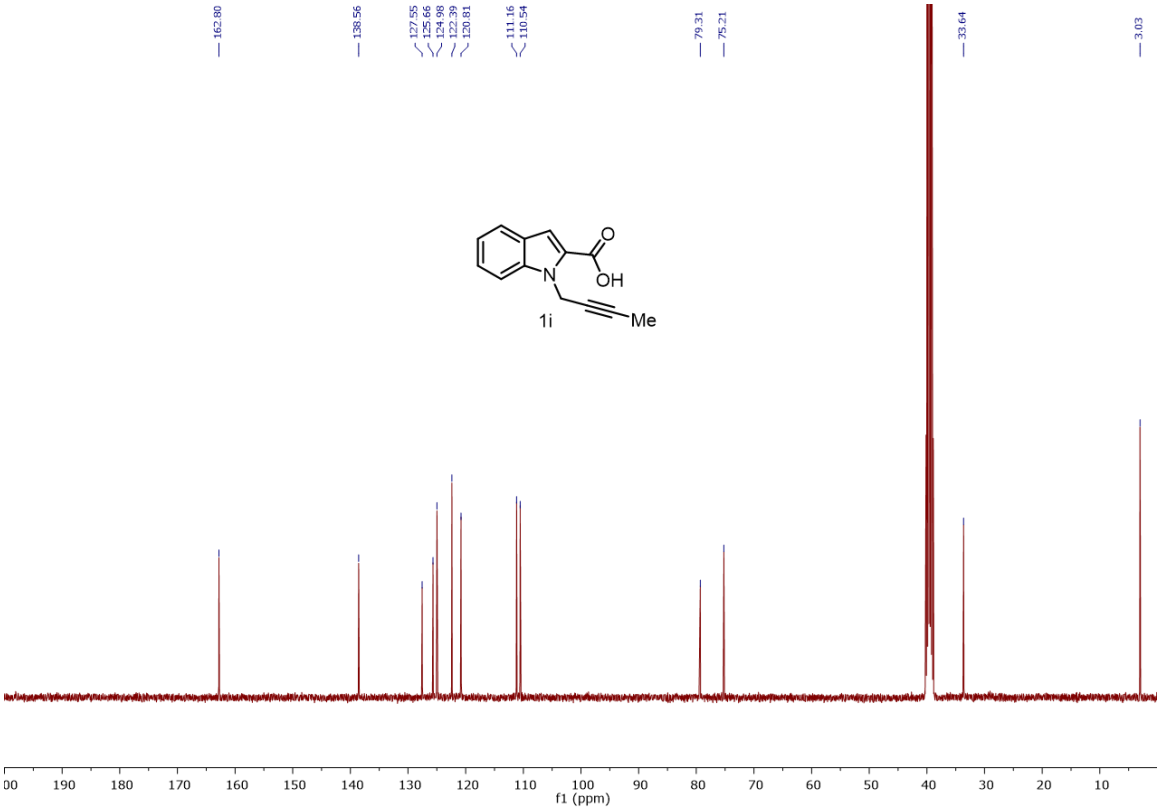
$^{13}C\{1H\}$ NMR of **1h** (101 MHz, $CDCl_3$)



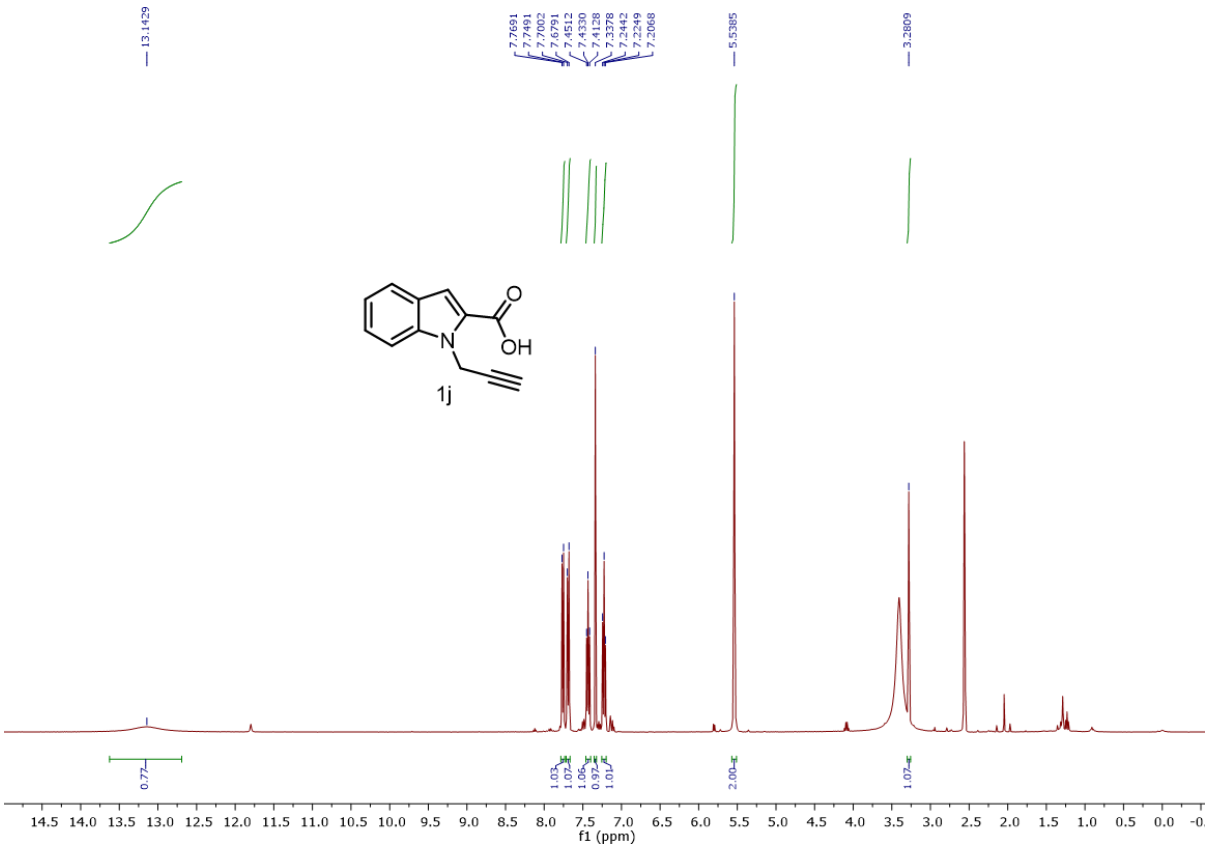
^{1}H NMR of **1i** (400 MHz, DMSO)



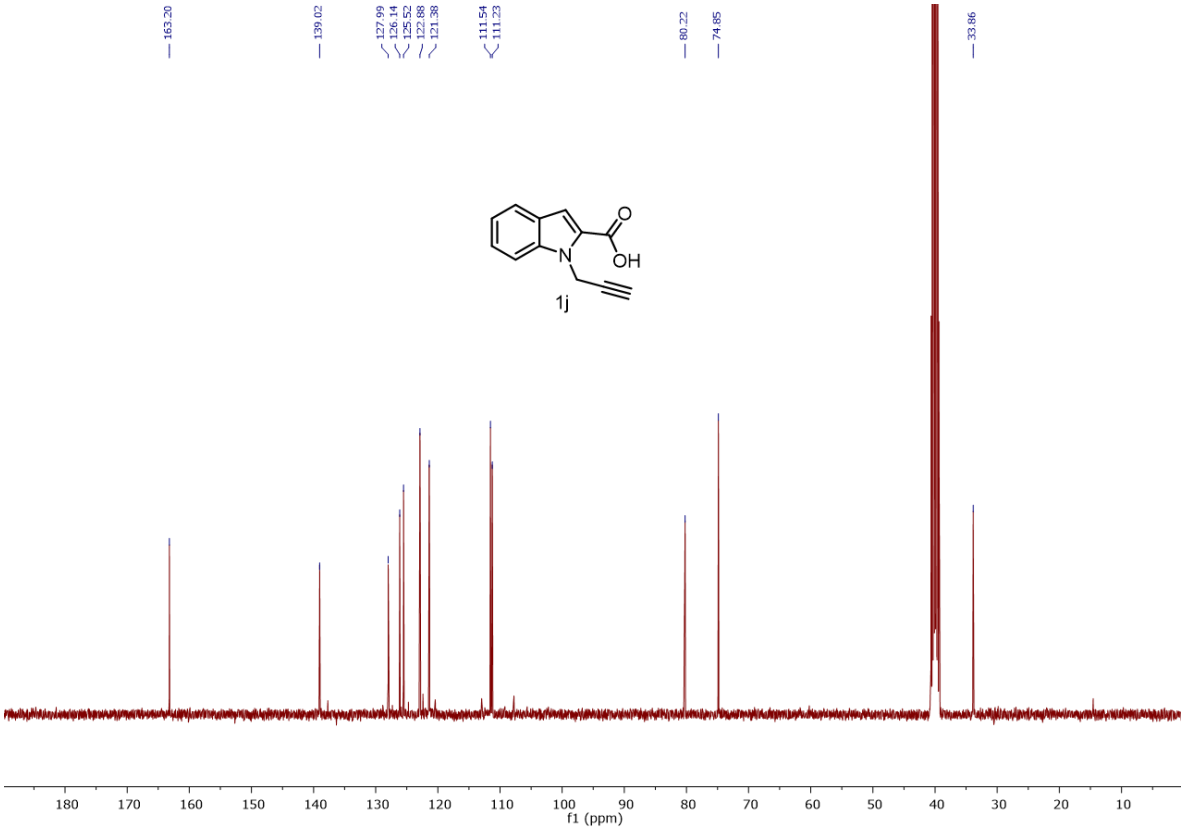
^{13}C{1H} NMR of **1i** (101 MHz, DMSO)



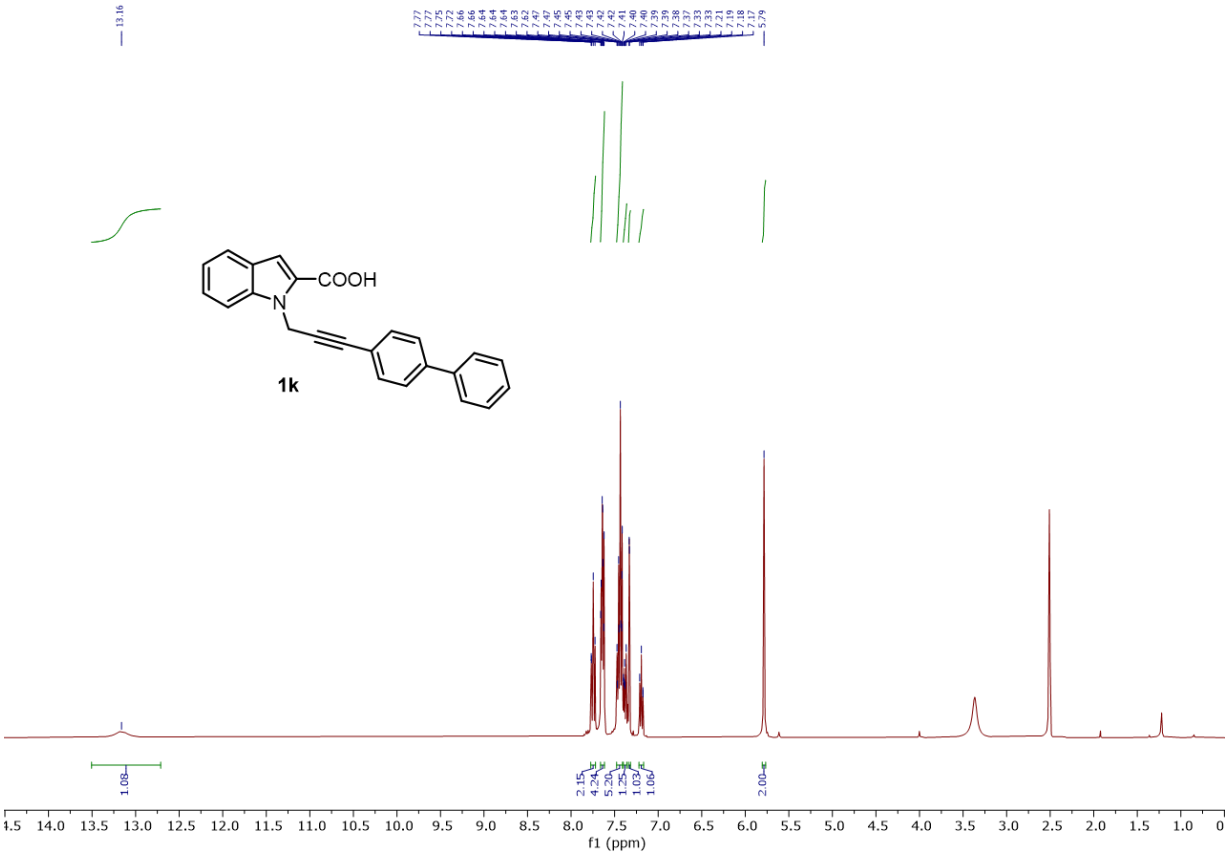
^{1}H NMR of **1j** (400 MHz, DMSO)



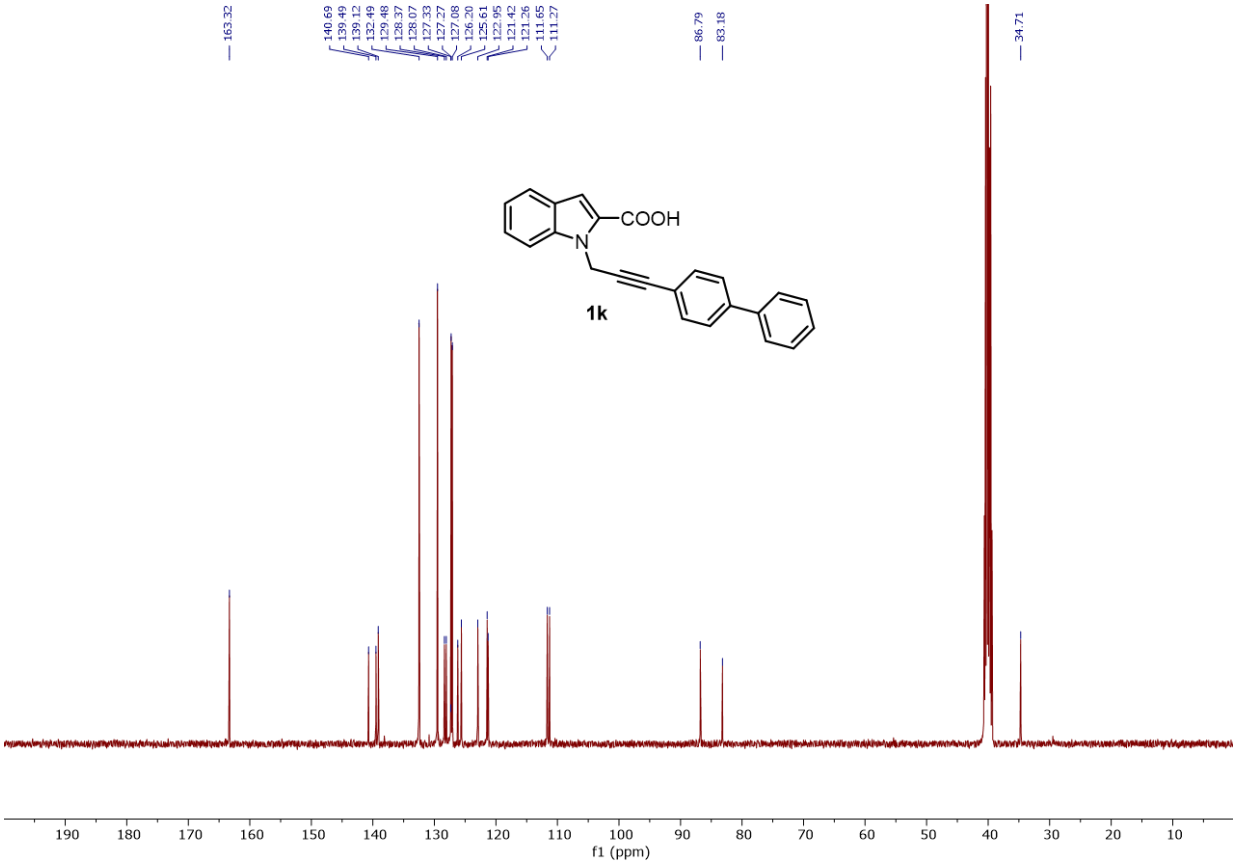
$^{13}C\{1H\}$ NMR of **1j** (101 MHz, DMSO)



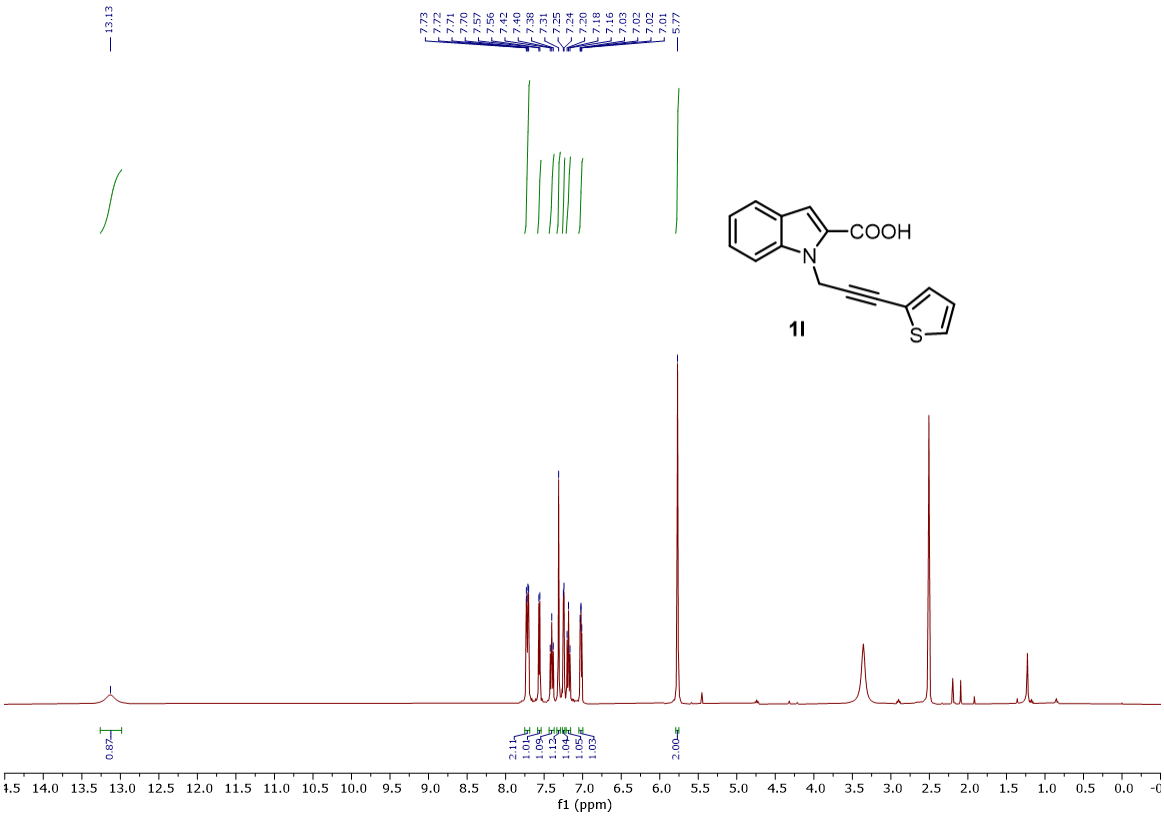
^{1}H NMR of **1k** (400 MHz, DMSO)



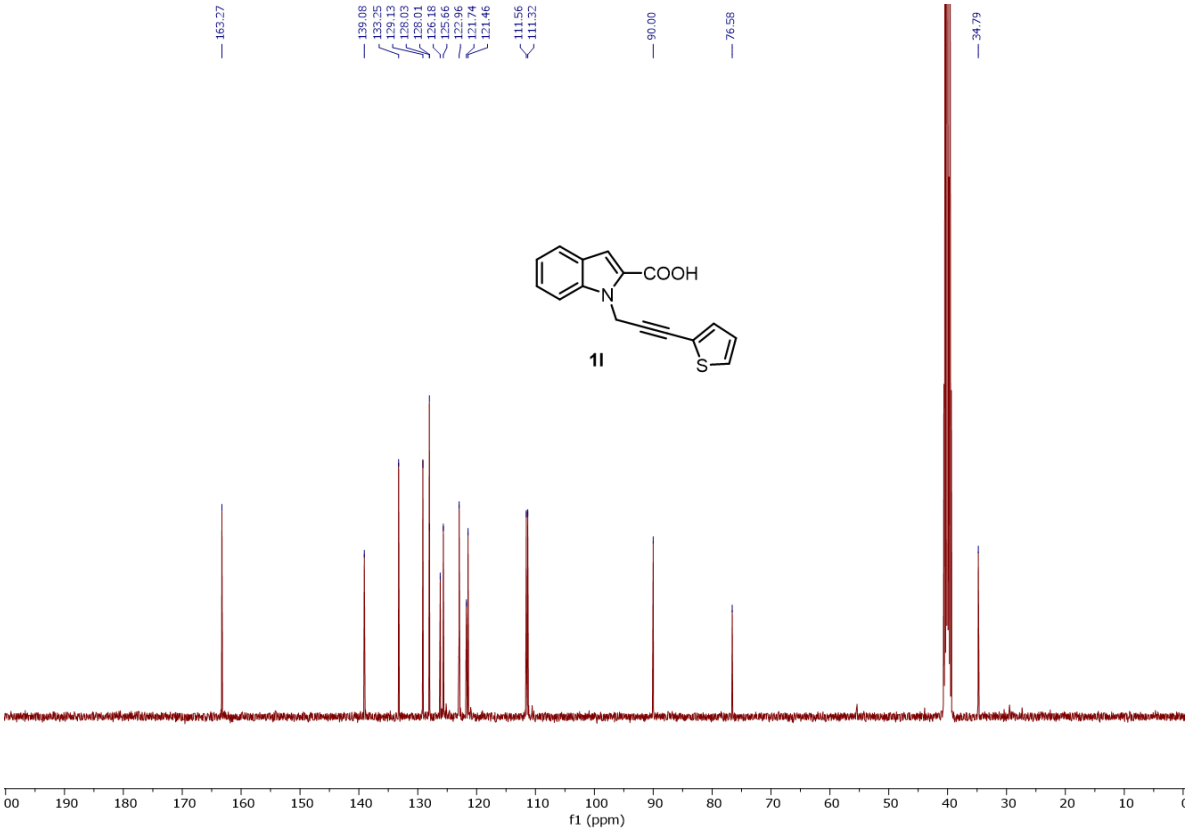
^{13}C{1H} NMR of **1k** (101 MHz, DMSO)



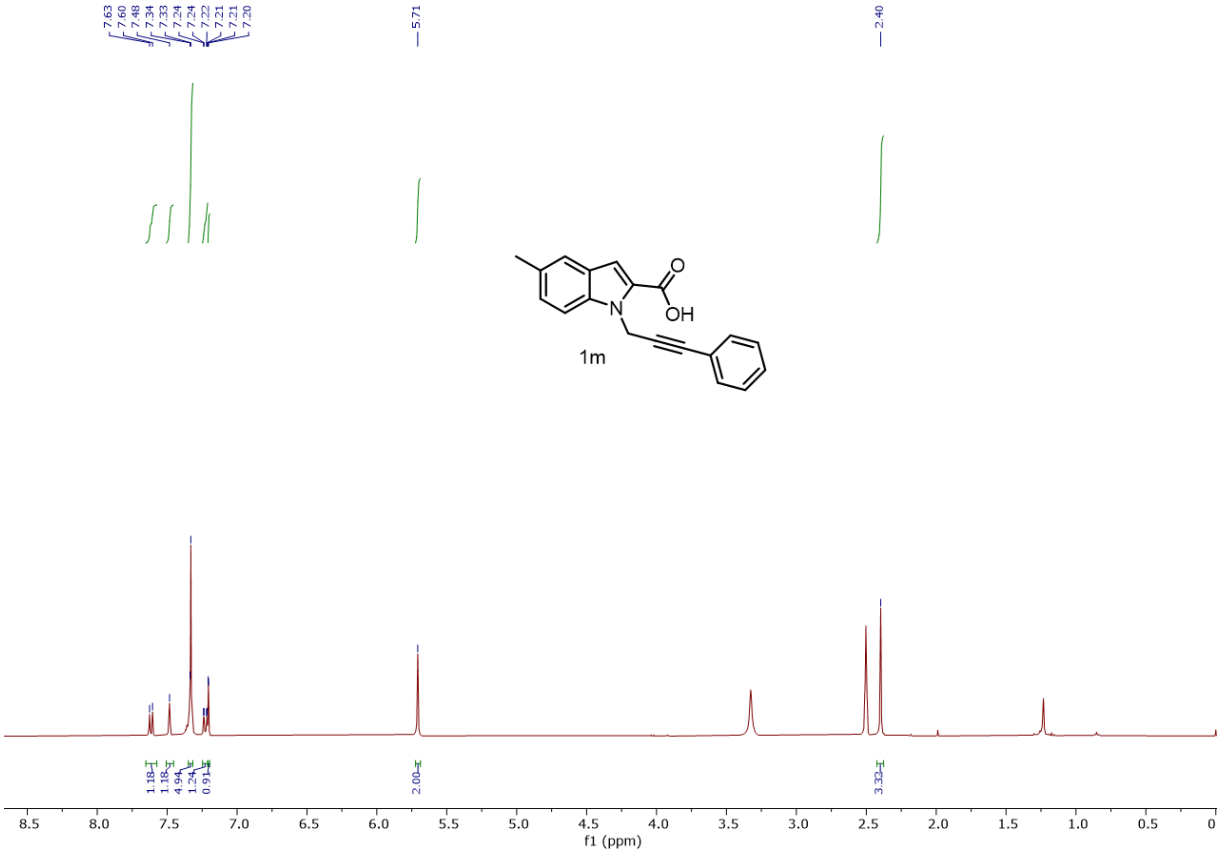
^{1}H NMR of **1l** (400 MHz, DMSO)



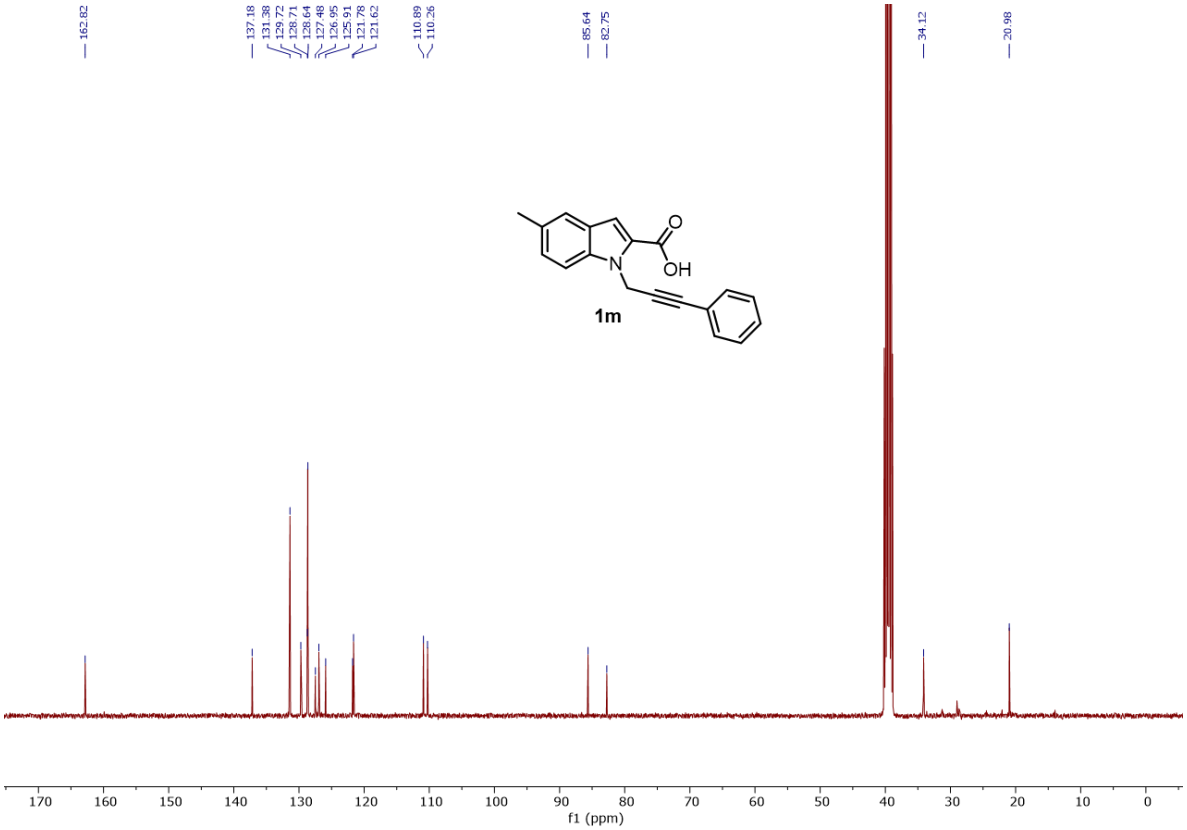
$^{13}C\{1H\}$ NMR of **1l** (101 MHz, DMSO)



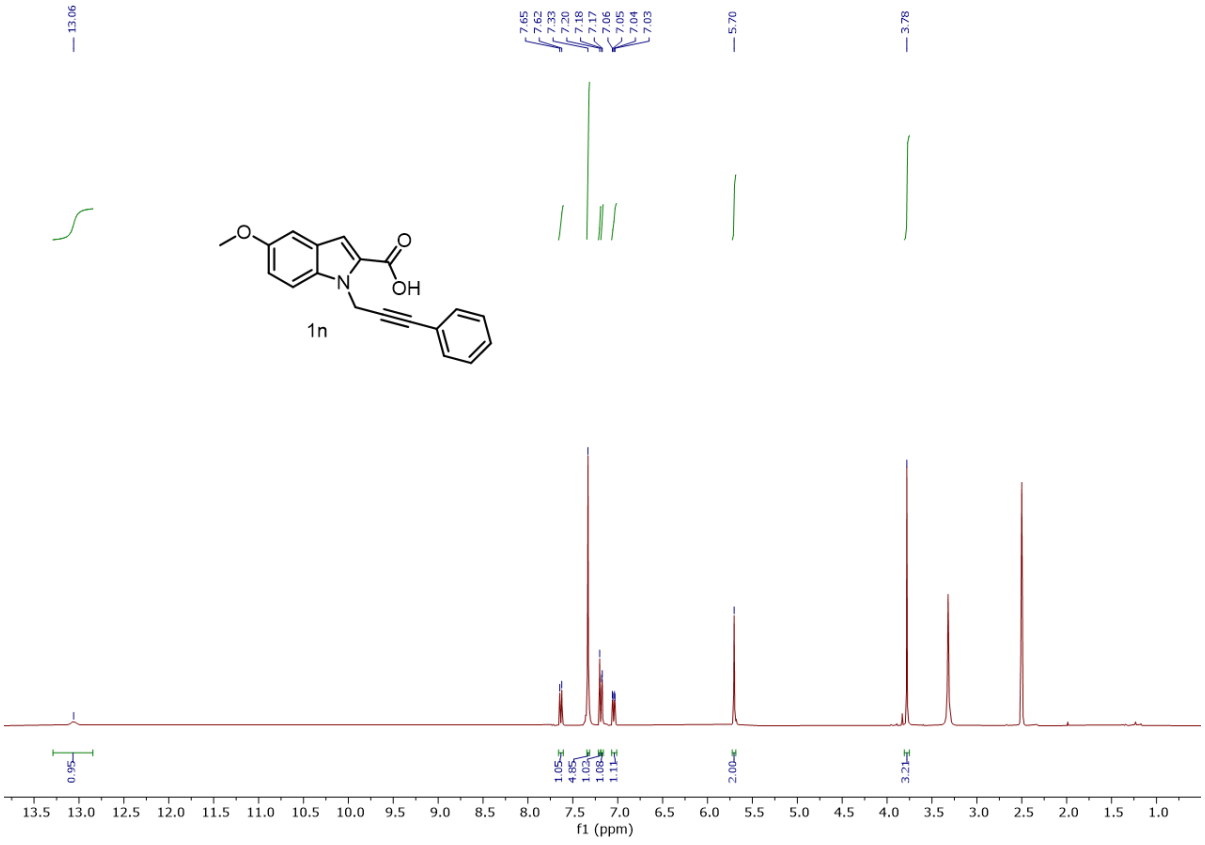
^{1}H NMR of **1m** (400 MHz, DMSO)



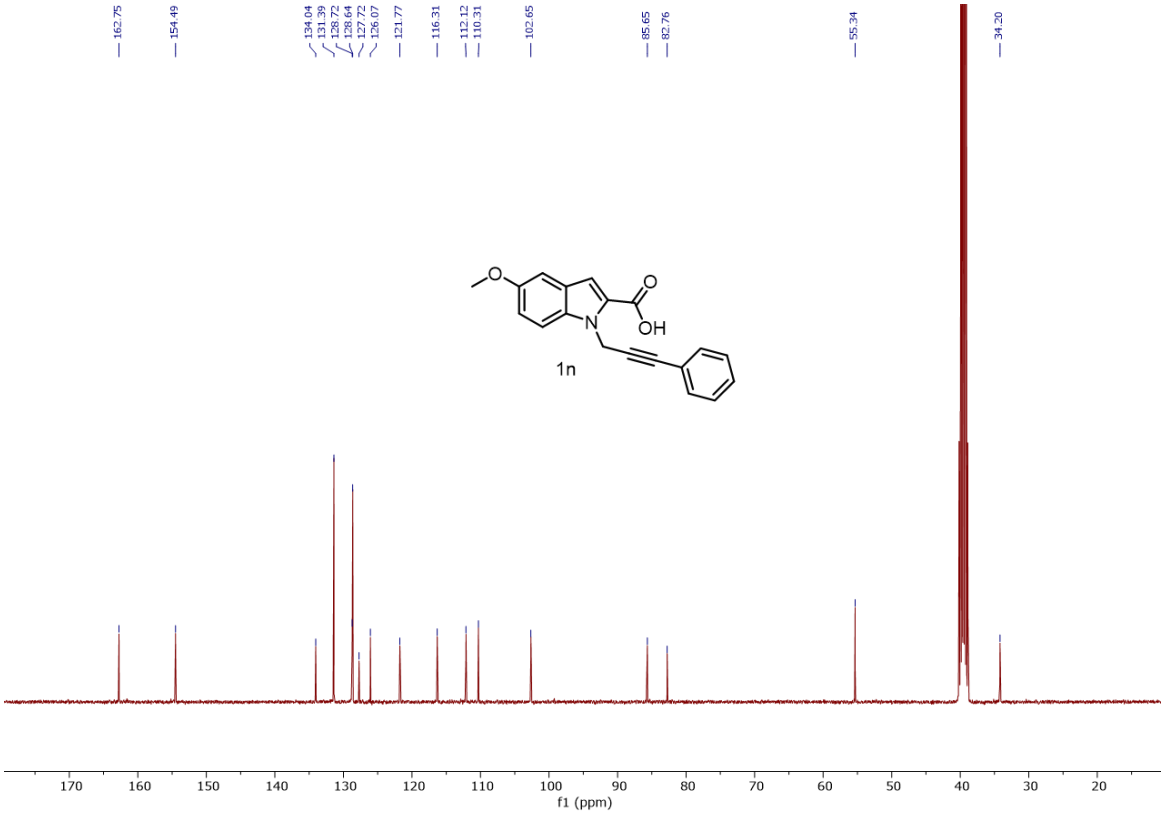
^{13}C{1H} NMR of **1m** (101 MHz, DMSO)



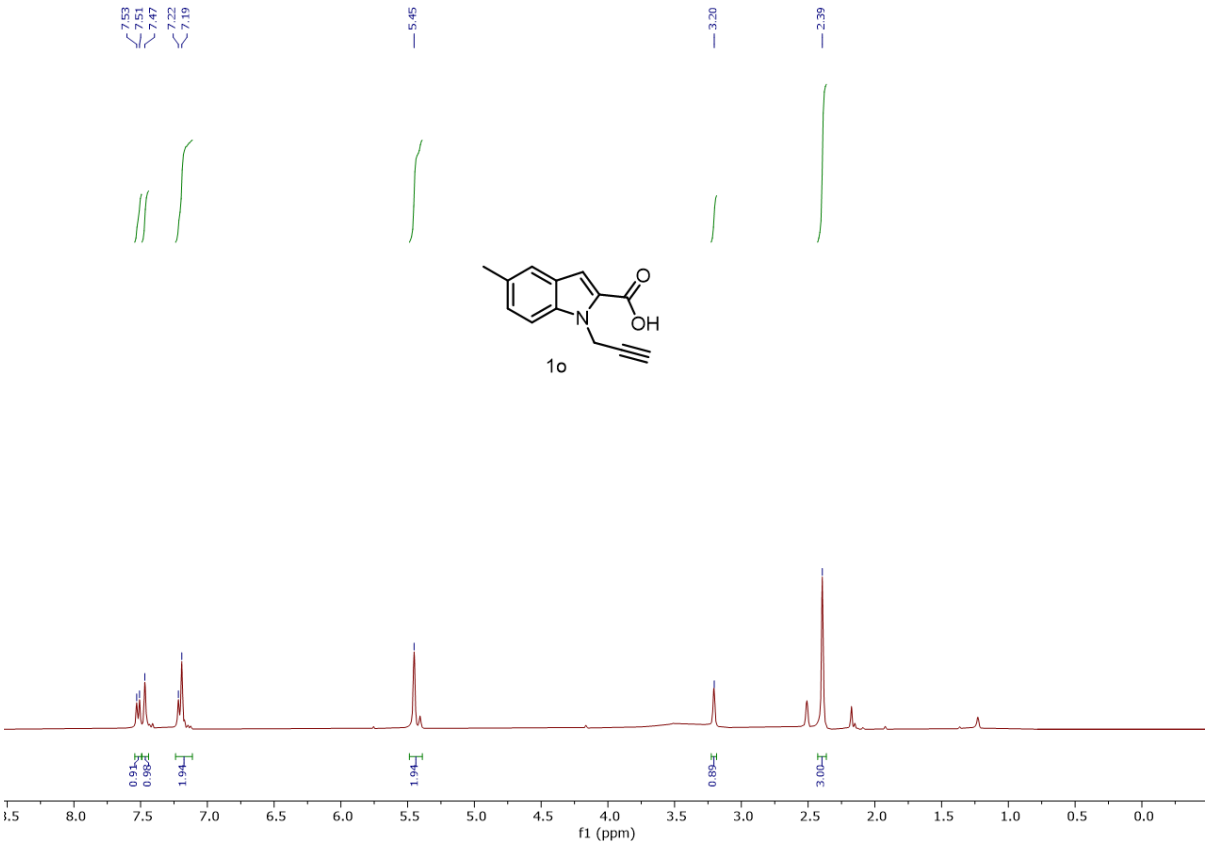
^{1}H NMR of **1n** (400 MHz, DMSO)



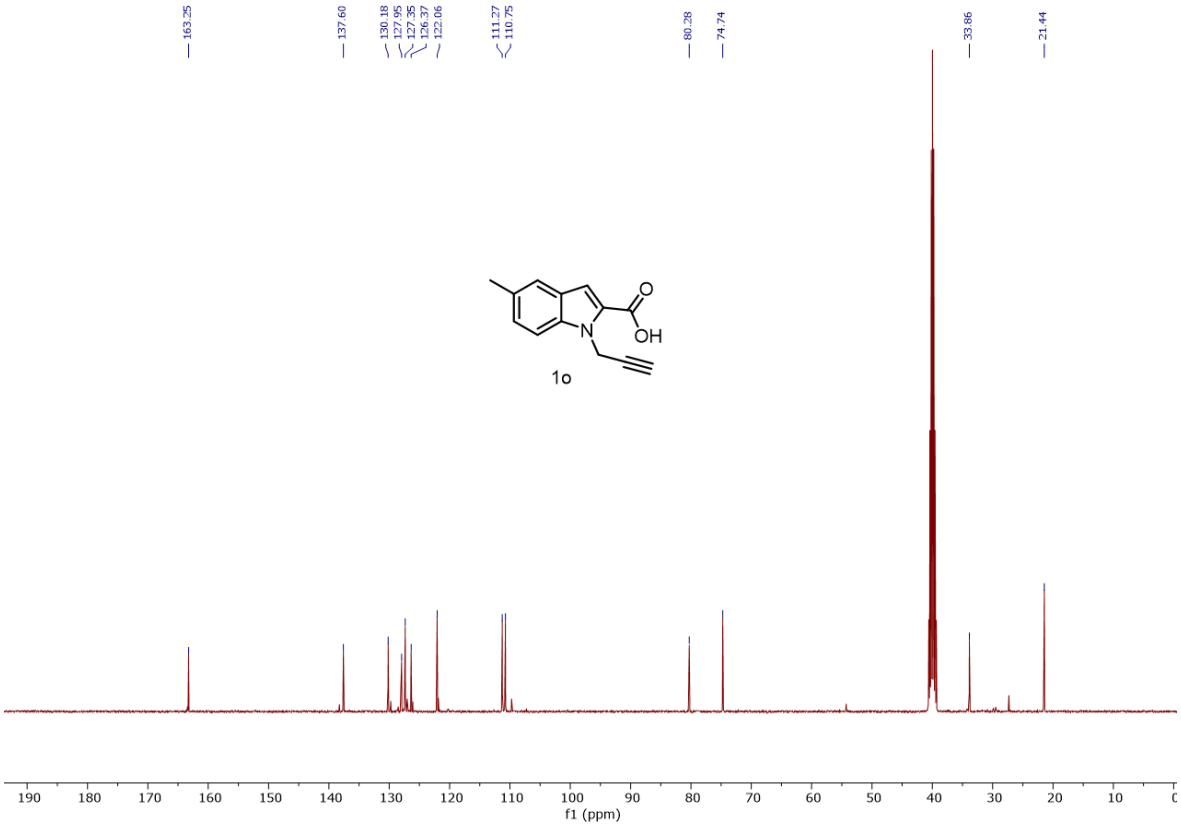
^{13}C{1H} NMR of **1n** (101 MHz, DMSO)



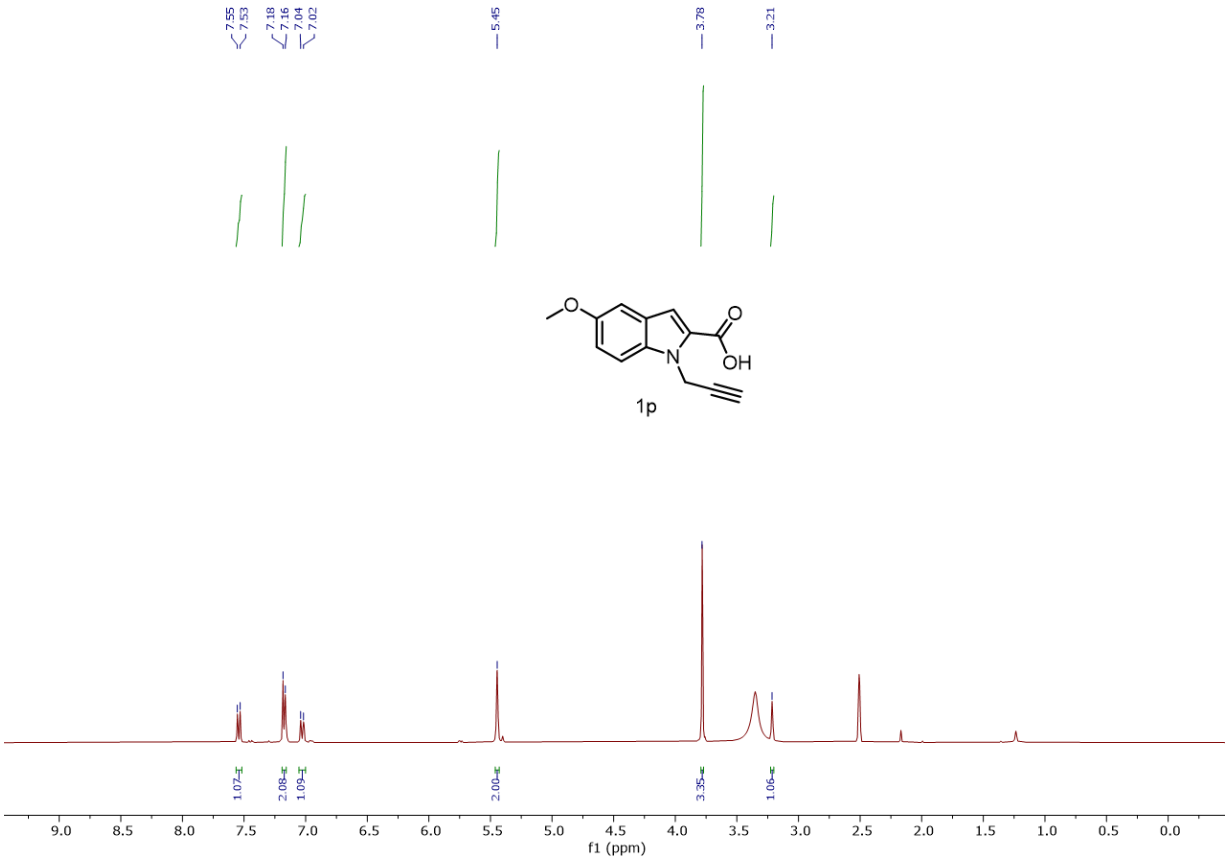
^{1}H NMR of **1o** (400 MHz, DMSO)



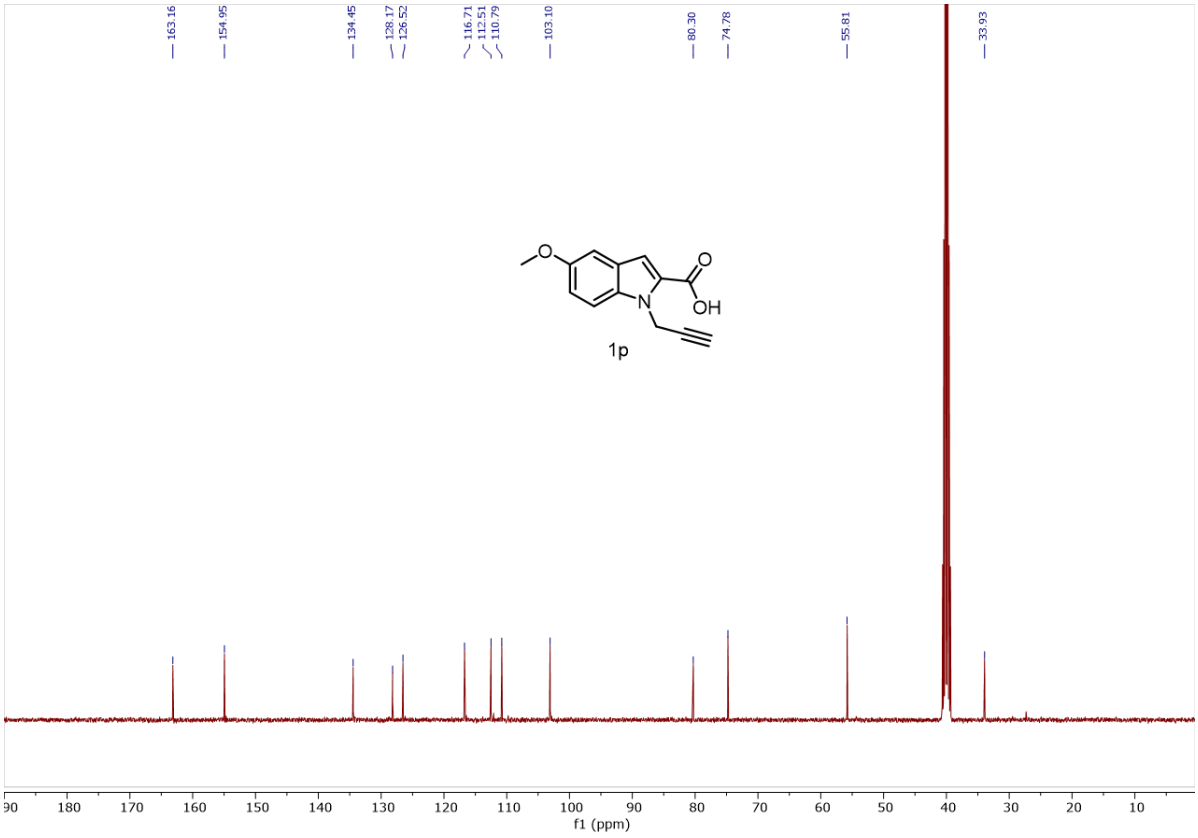
$^{13}C\{1H\}$ NMR of **1o** (101 MHz, DMSO)



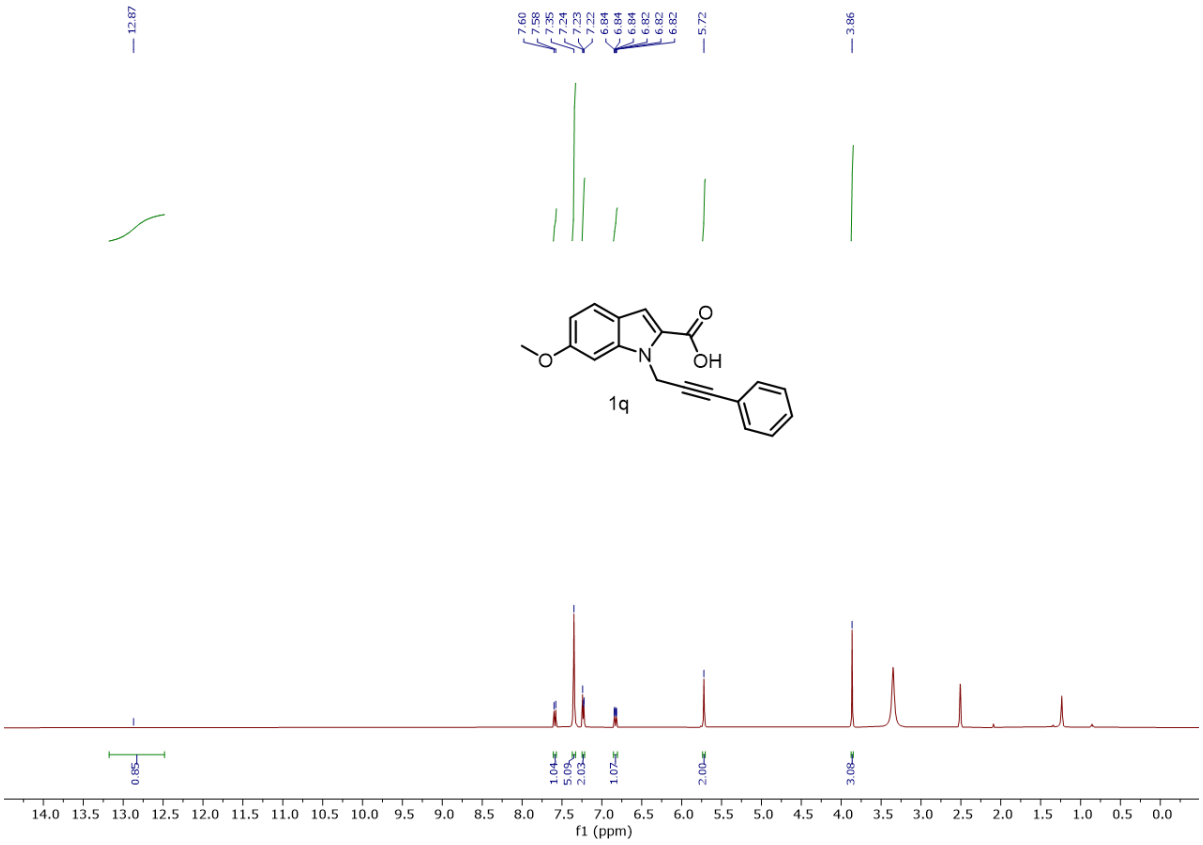
^{1}H NMR of **1p** (400 MHz, DMSO)



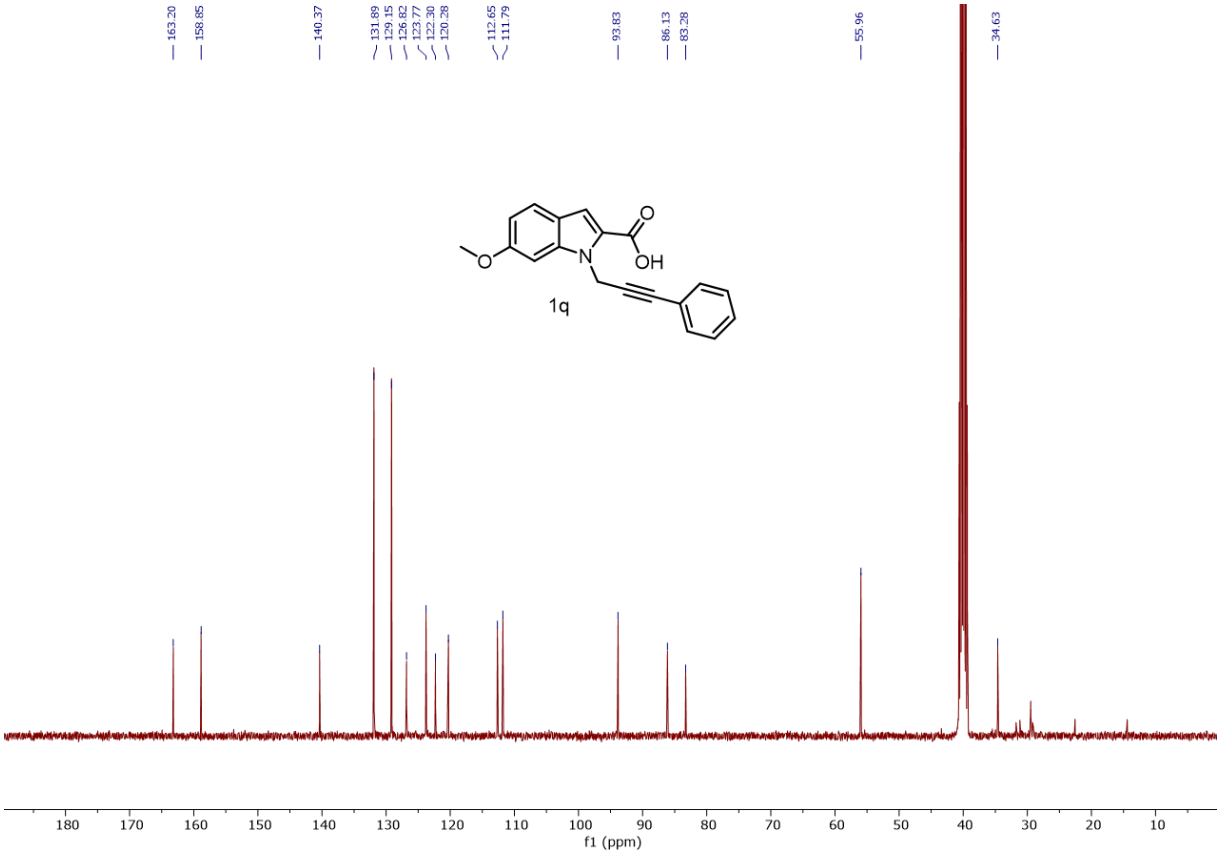
^{13}C{1H} NMR of **1p** (101 MHz, DMSO)



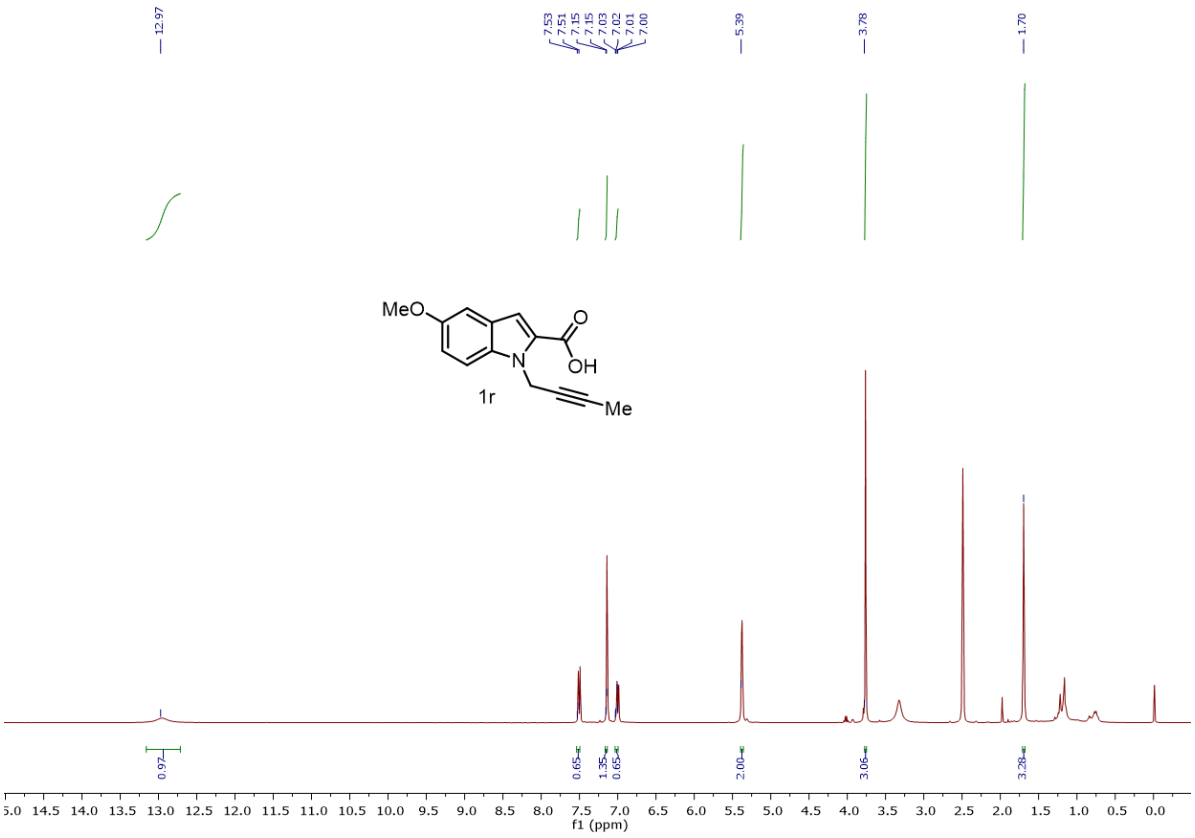
^{1}H NMR of **1q** (400 MHz, DMSO)



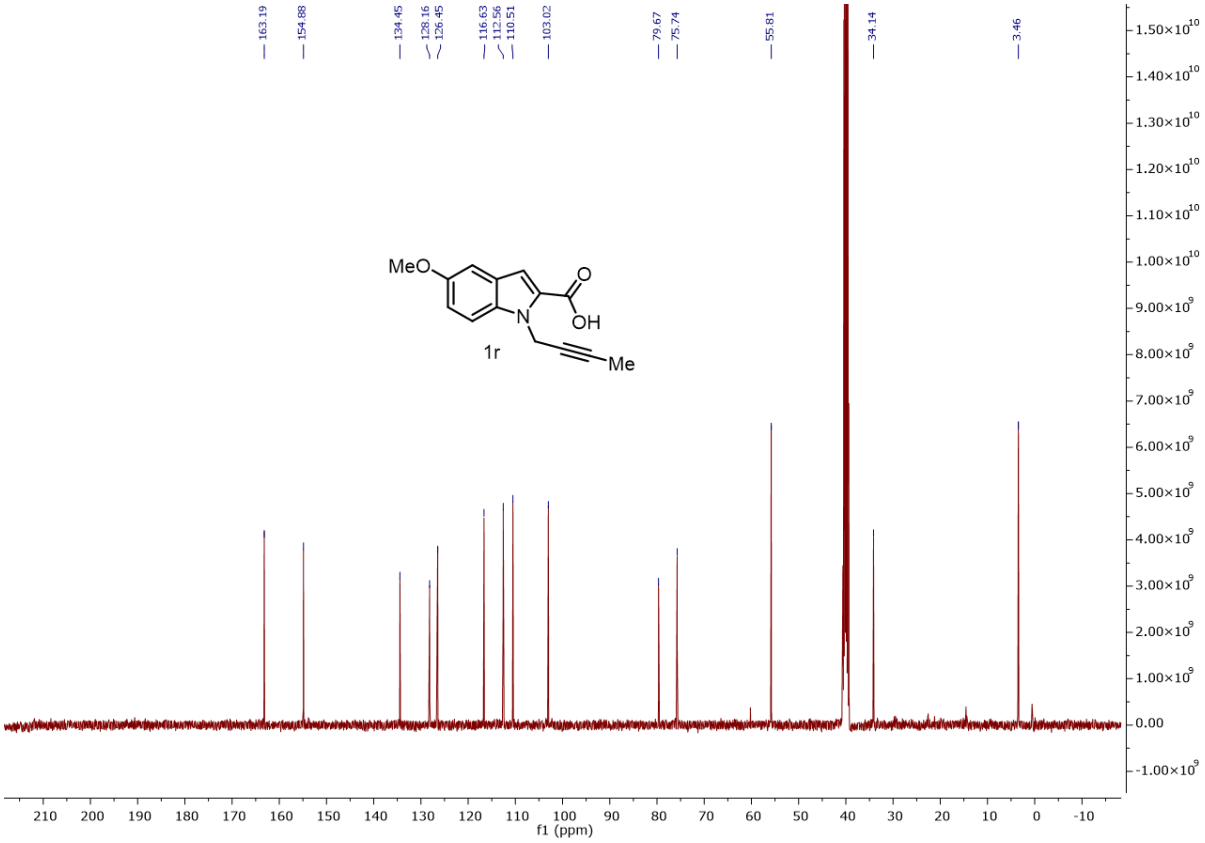
^{13}C{1H} NMR of **1q** (101 MHz, DMSO)



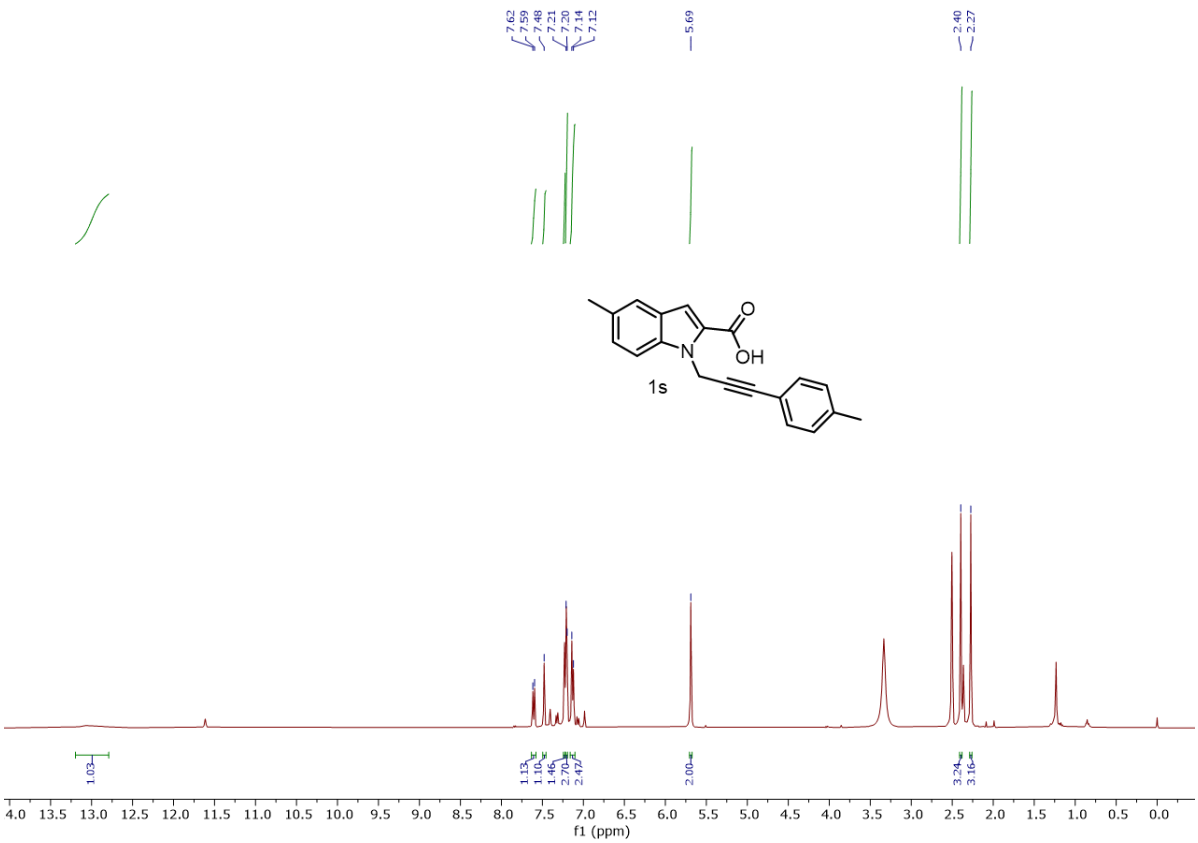
^{1}H NMR of **1r** (400 MHz, DMSO)



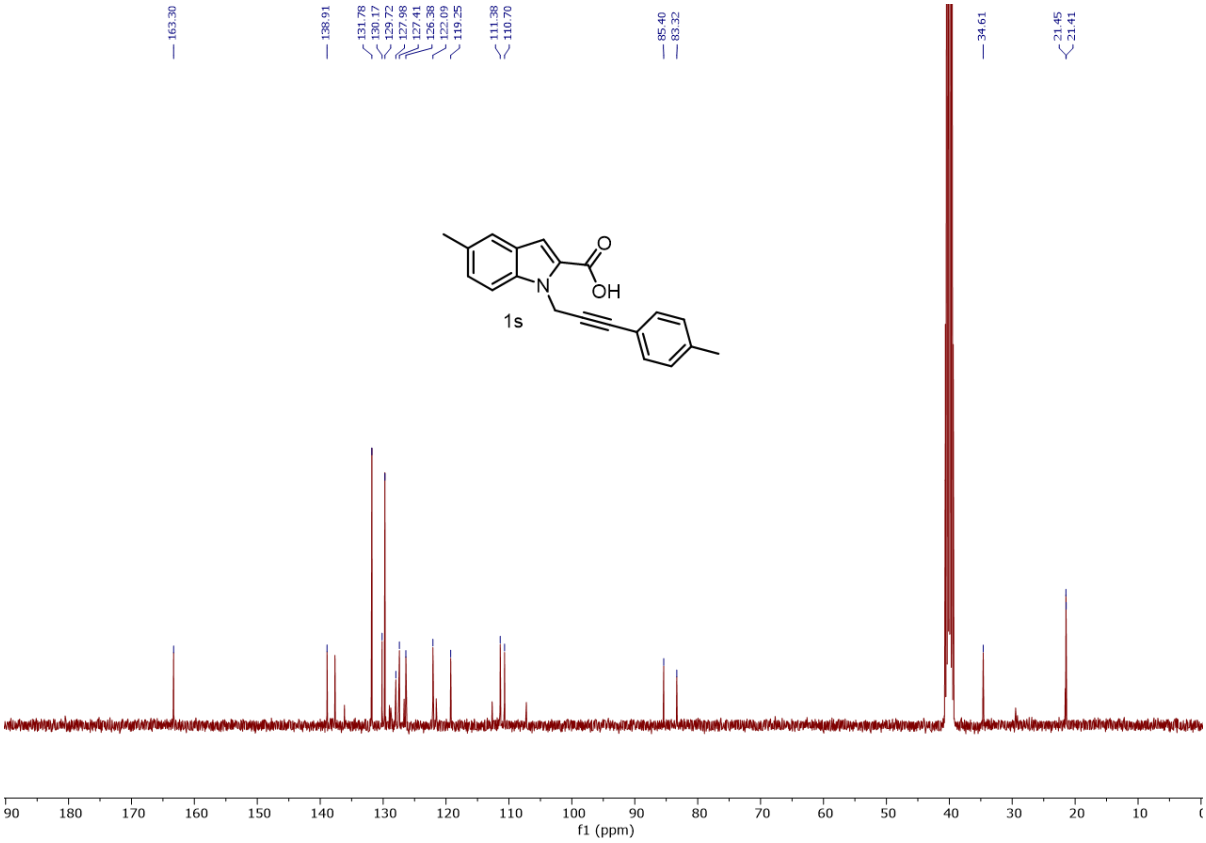
^{13}C{1H} NMR of **1r** (101 MHz, DMSO)



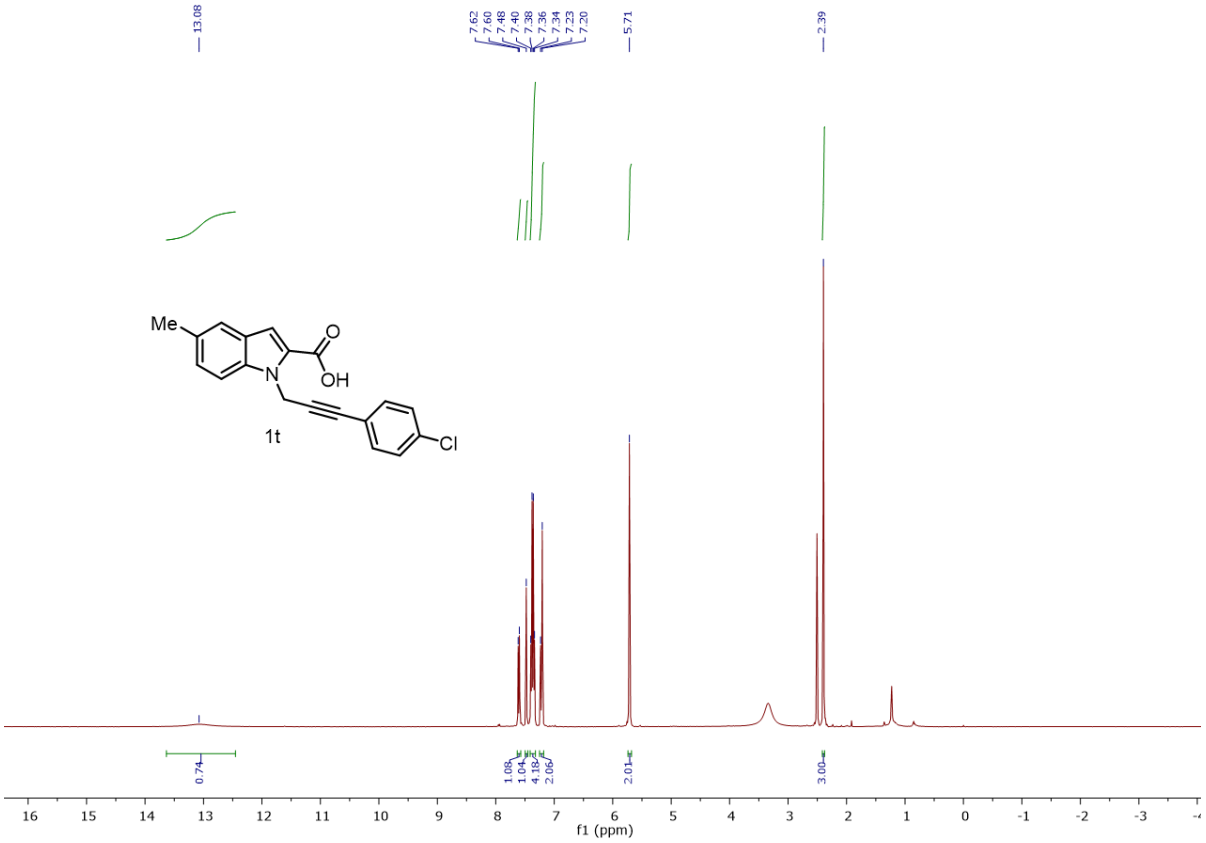
^{1}H NMR of **1s** (400 MHz, DMSO)



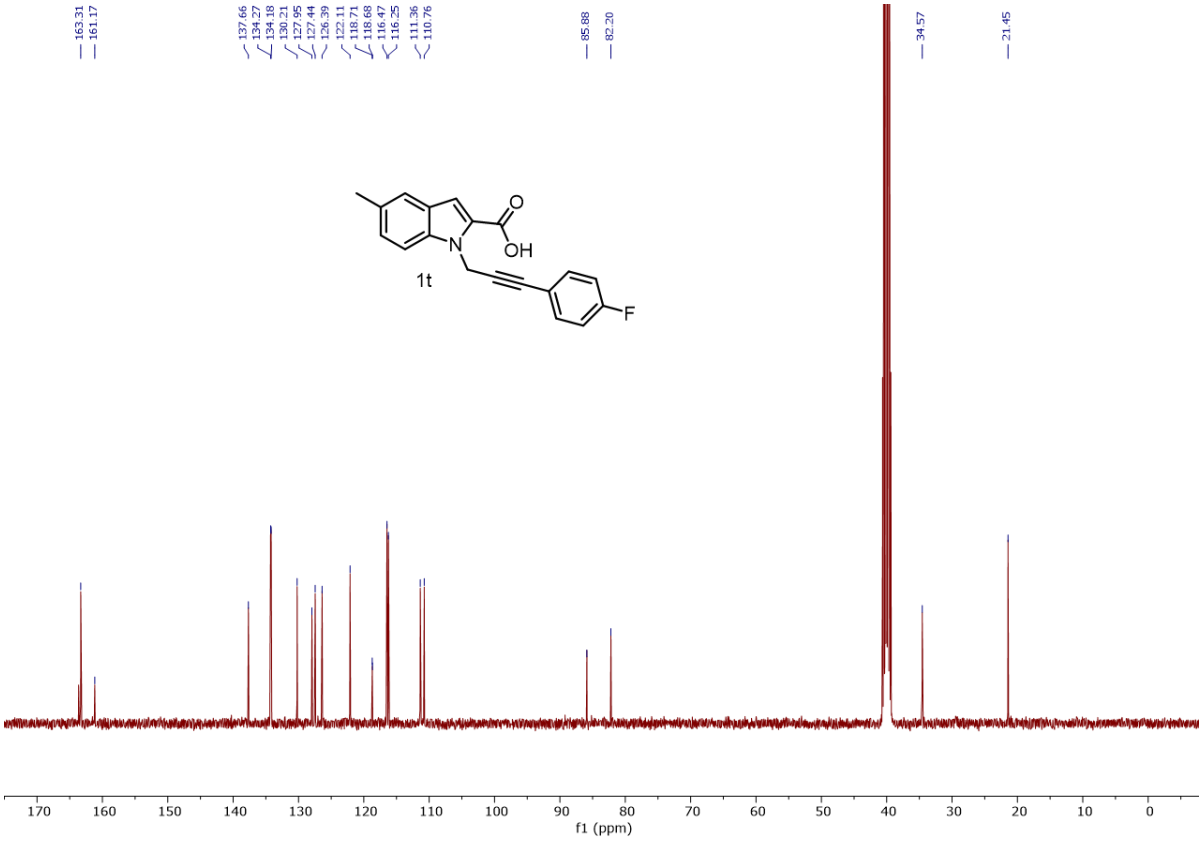
$^{13}C\{1H\}$ NMR of **1s** (101 MHz, DMSO)



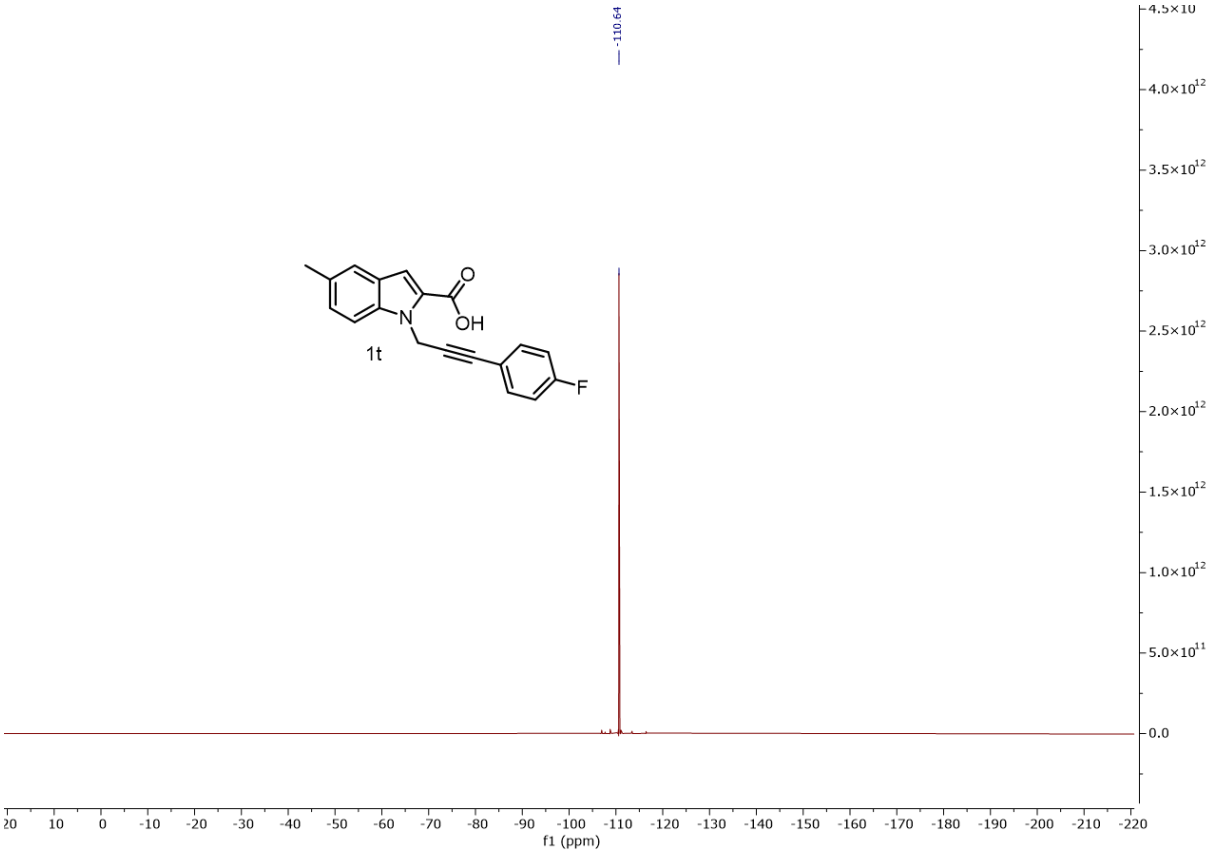
^{1}H NMR of **1t** (400 MHz, DMSO)



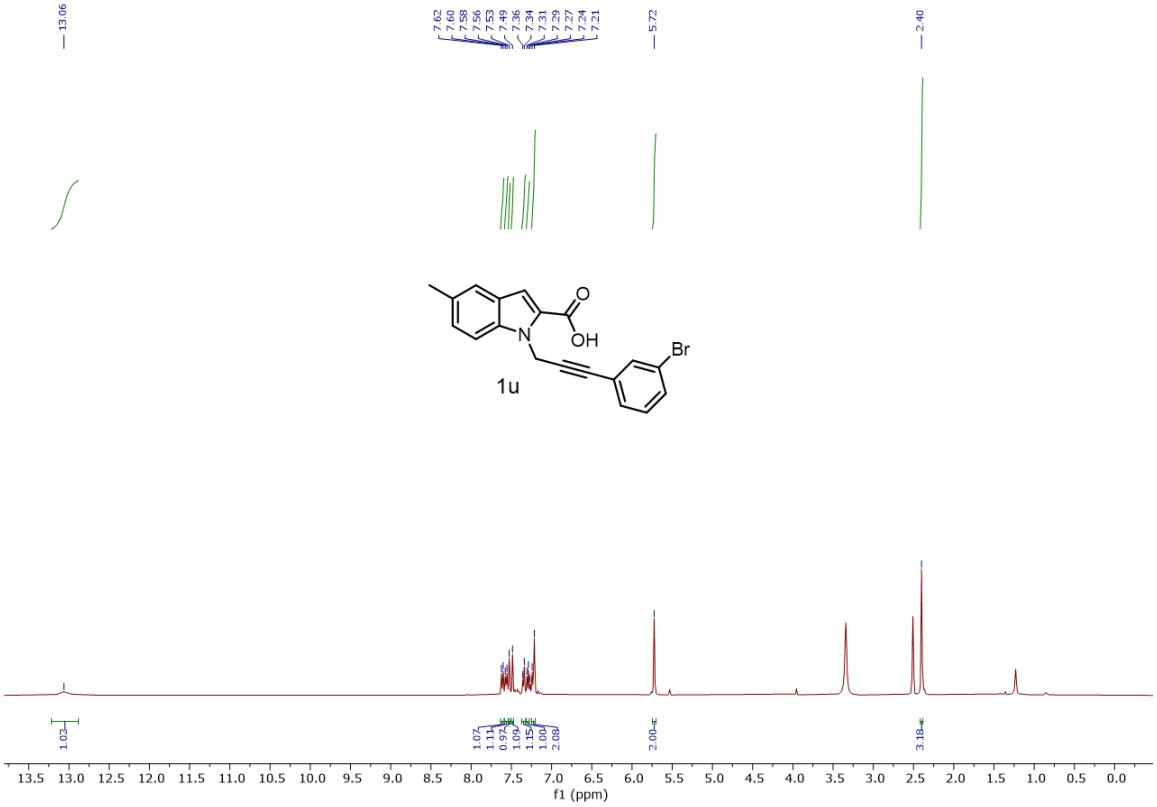
^{13}C{1H} NMR of **1t** (101 MHz, DMSO)



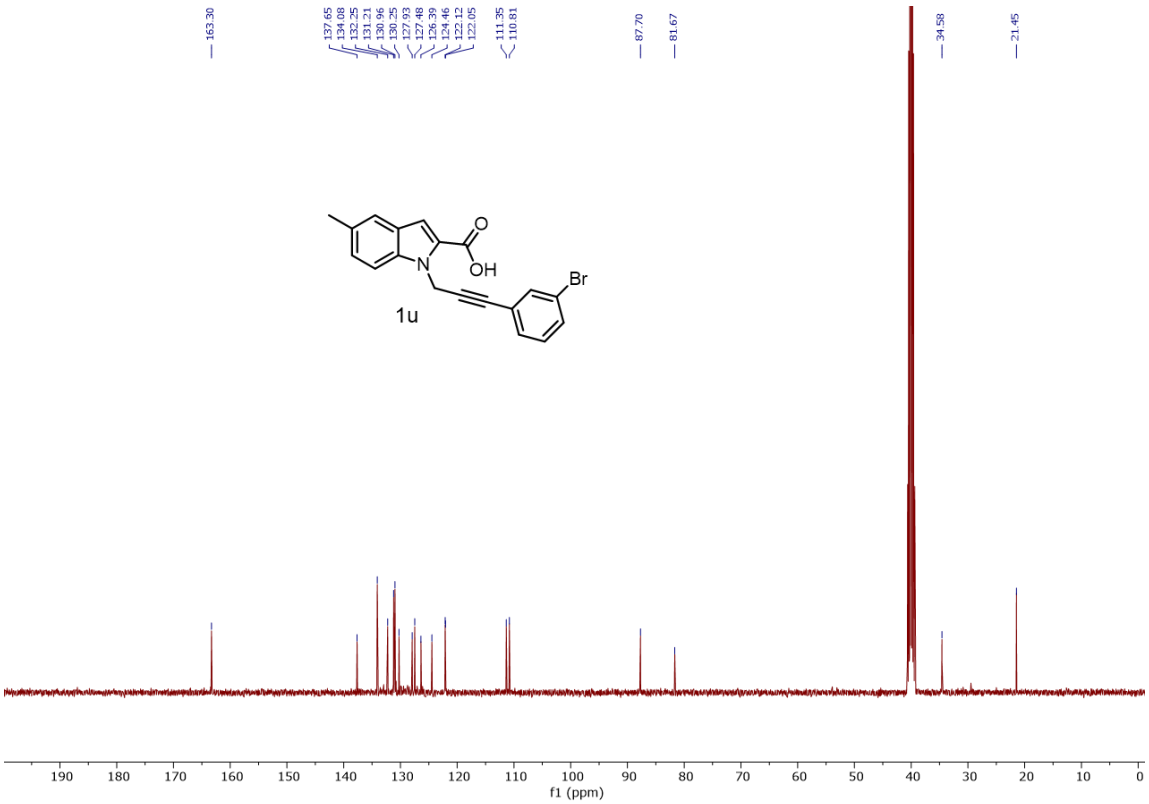
^{19}F NMR of **1t** (376 MHz, DMSO)



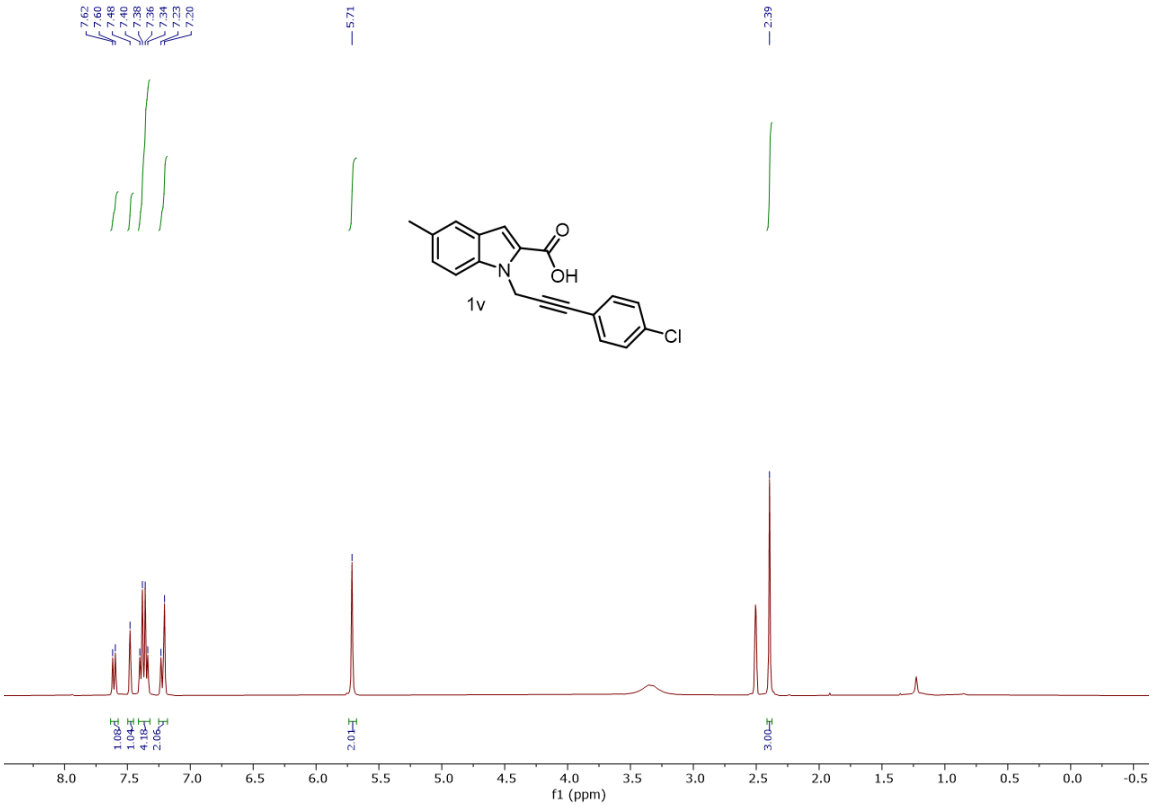
^{1}H NMR of **1u** (400 MHz, DMSO)



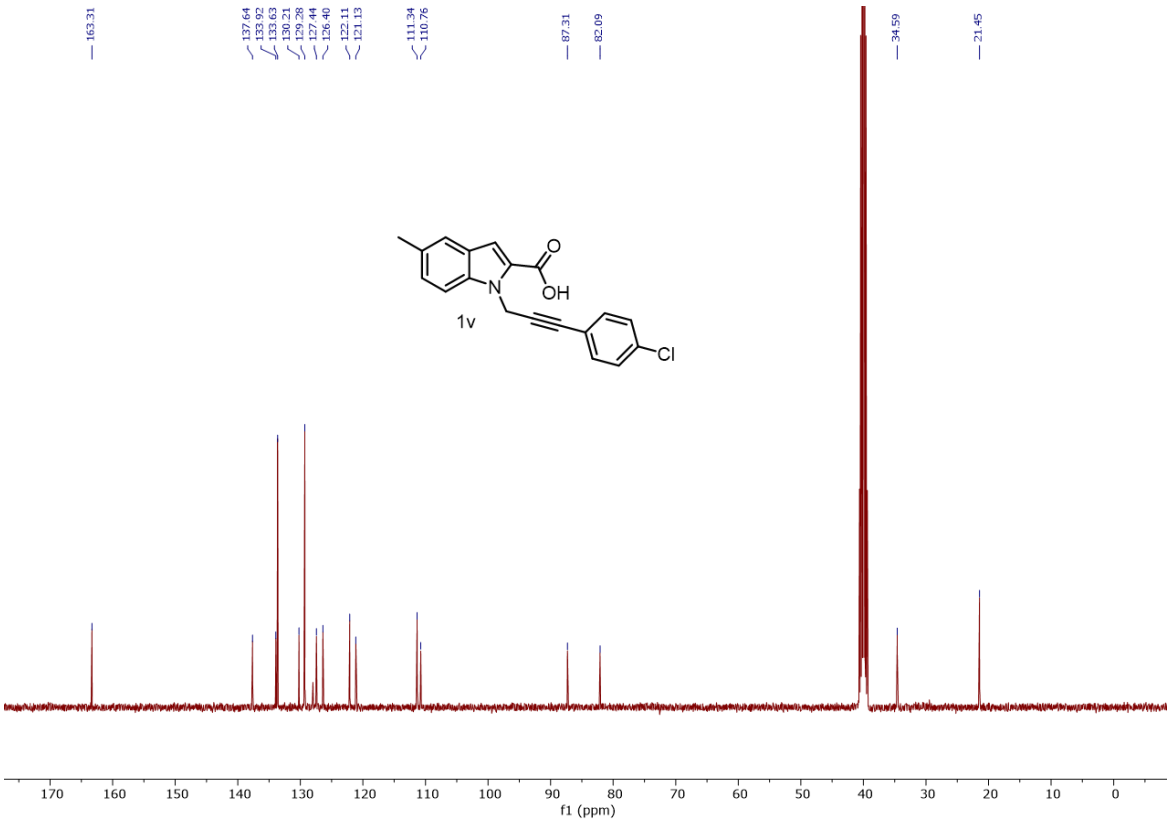
^{13}C{1H} NMR of **1u** (101 MHz, DMSO)



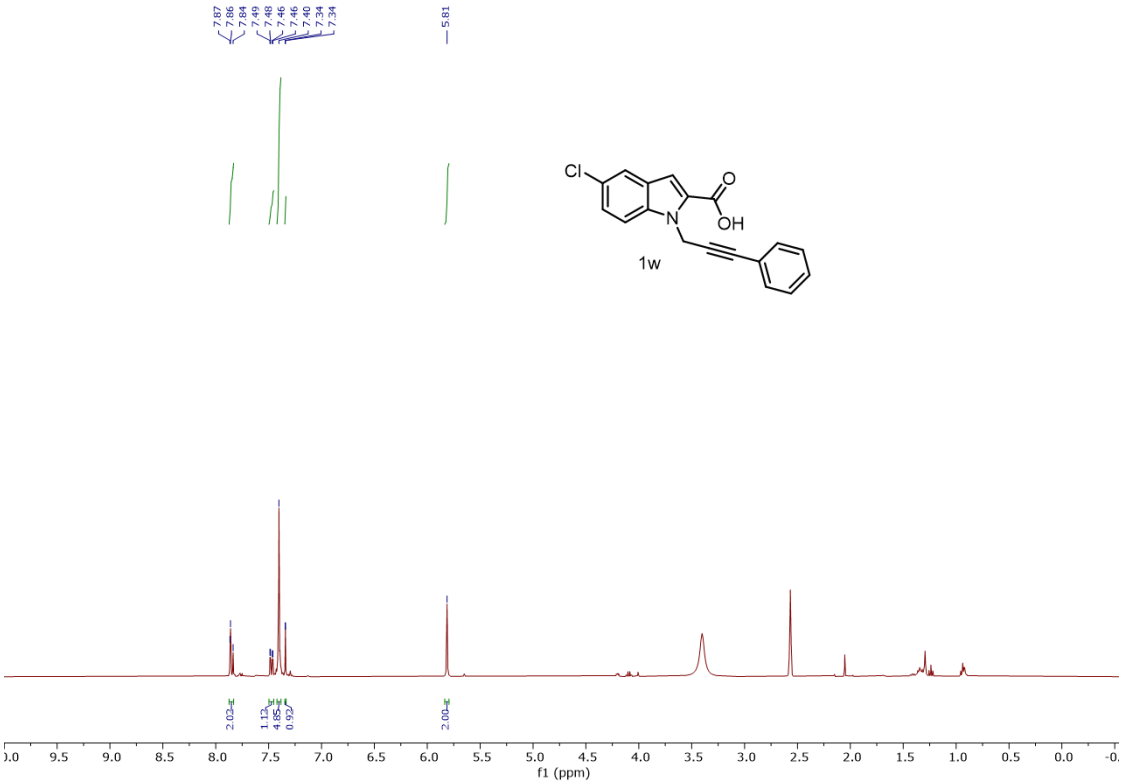
^{1}H NMR of **1v** (400 MHz, DMSO)



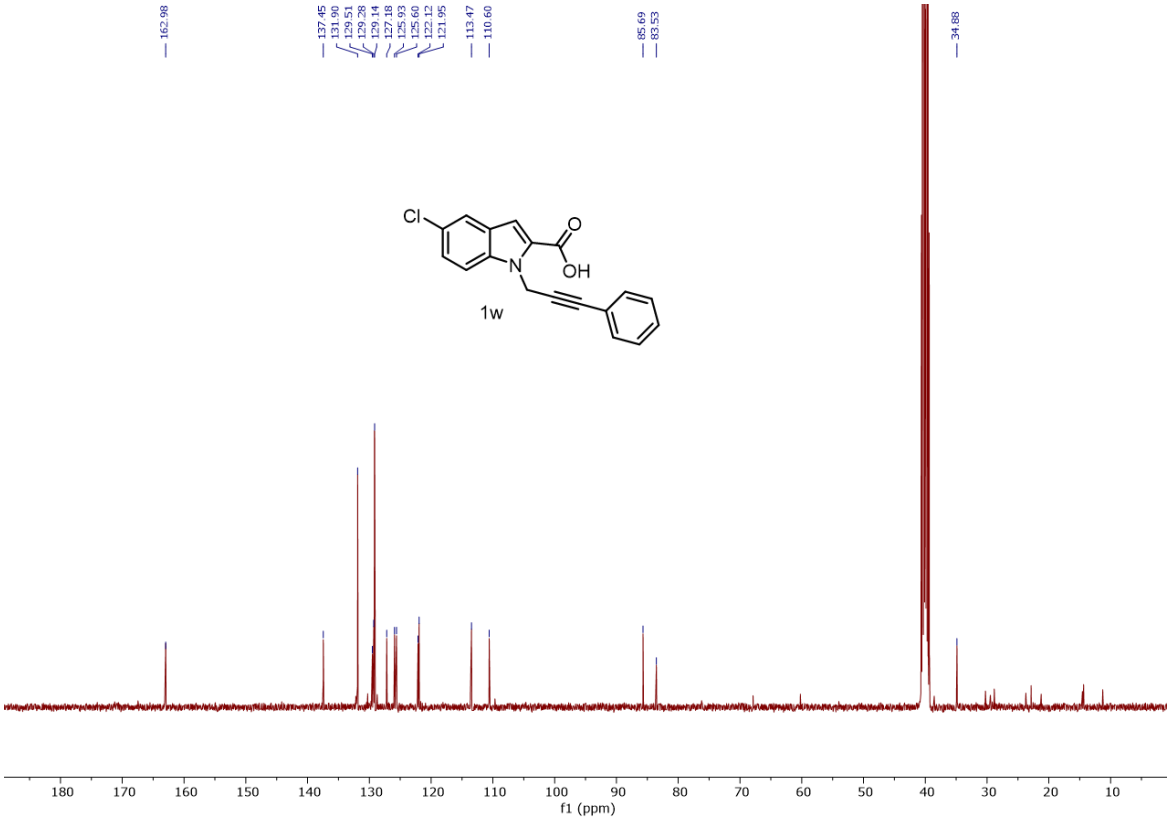
^{13}C{1H} NMR of **1v** (400 MHz, DMSO)



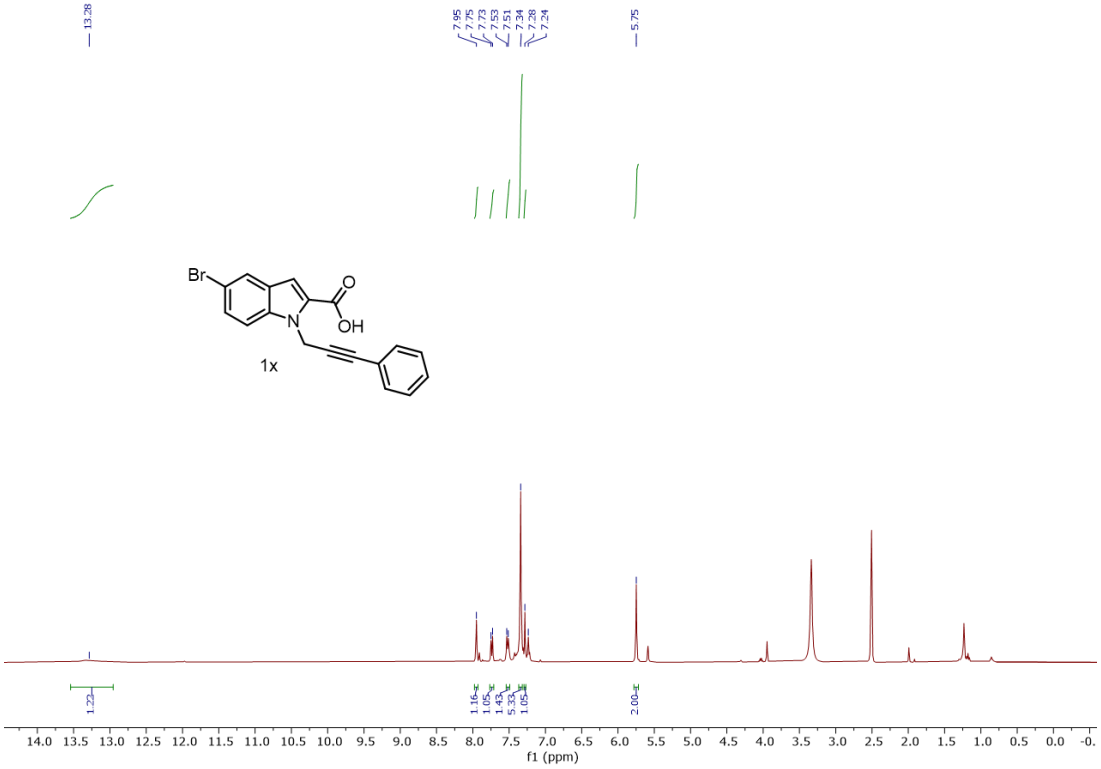
^{1}H NMR of **1w** (101 MHz, DMSO)



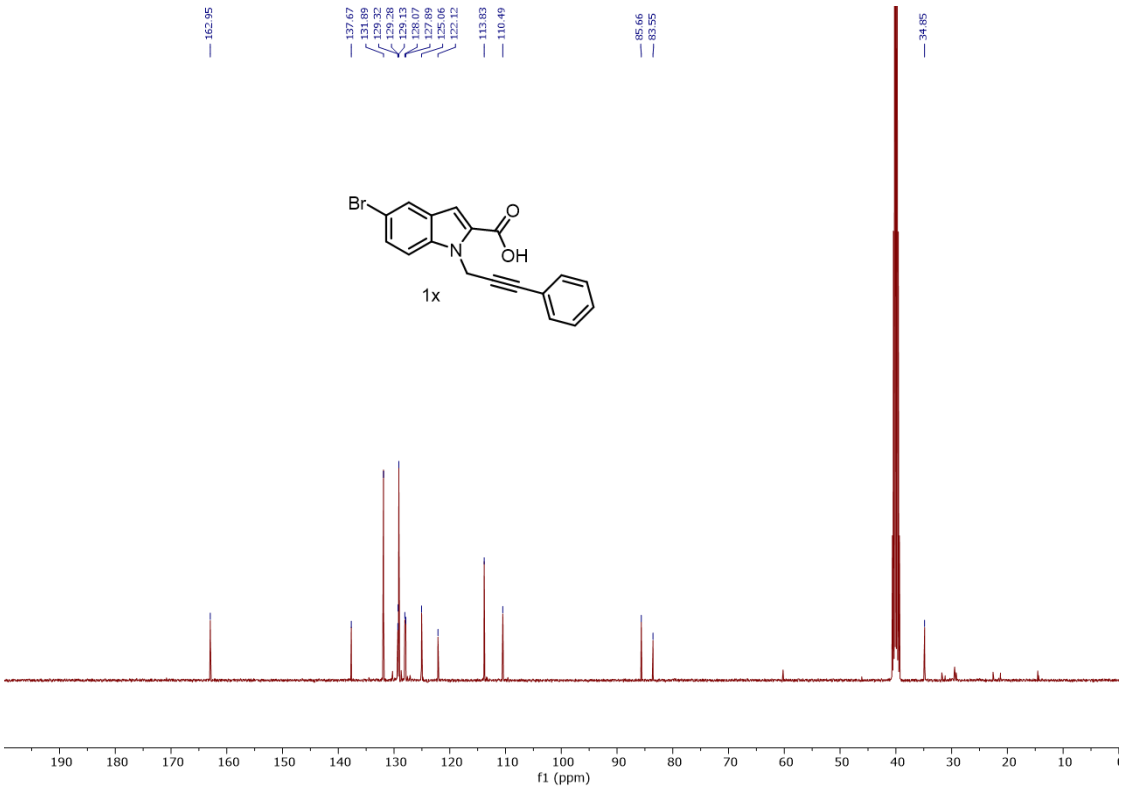
^{13}C{1H} NMR of **1w** (101 MHz, DMSO)



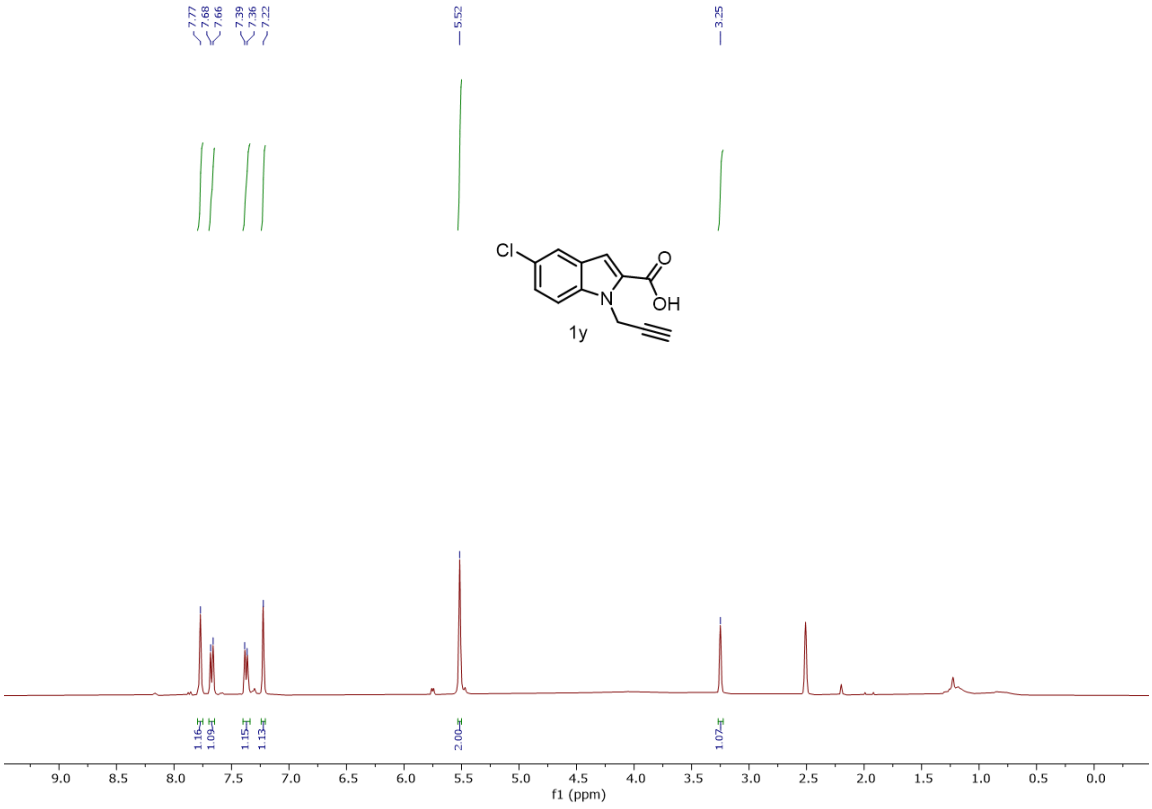
^{1}H NMR of **1x** (400 MHz, DMSO)



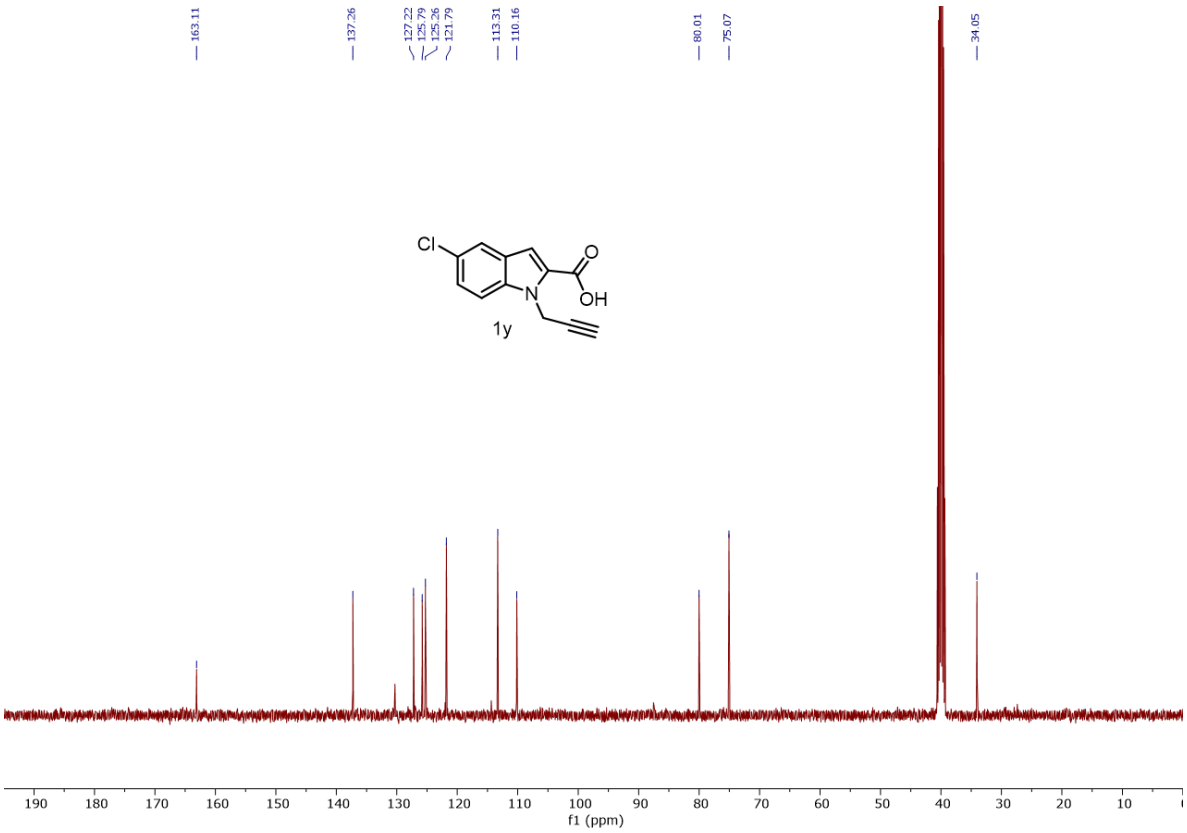
^{13}C{1H} NMR of **1x** (101 MHz, DMSO)



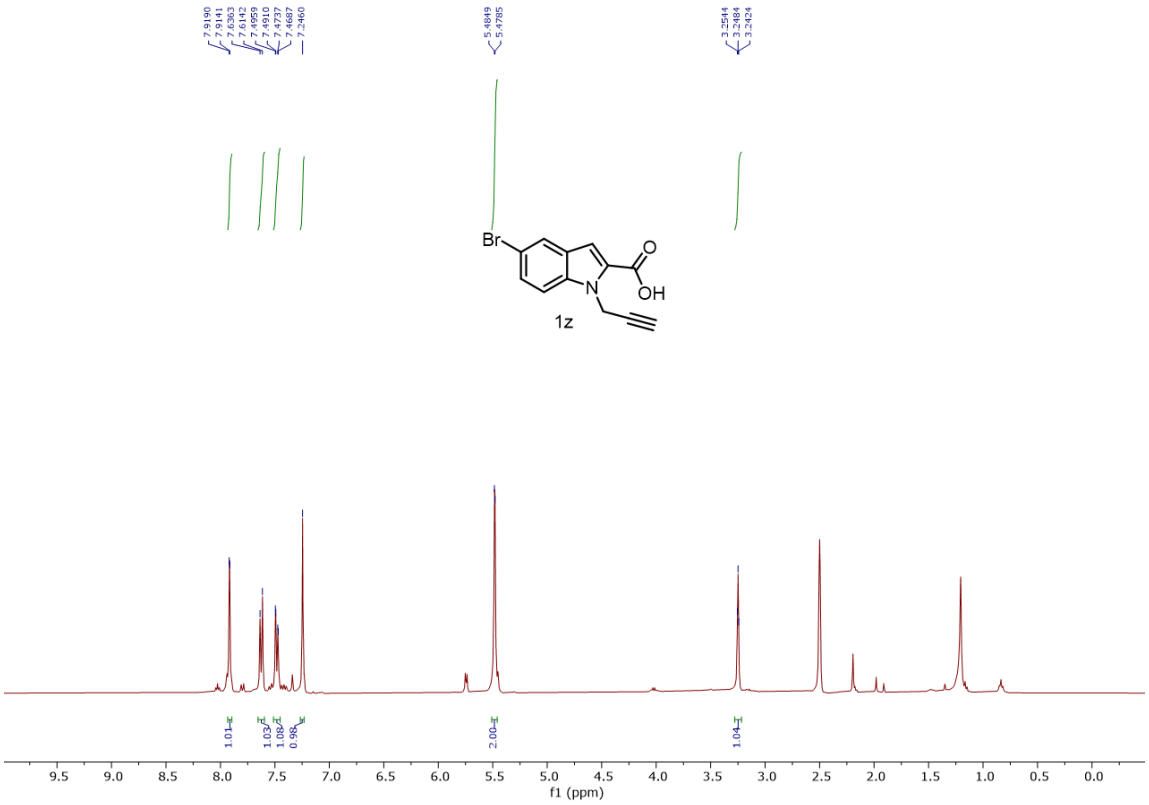
^{1}H NMR of **1y** (400 MHz, DMSO)



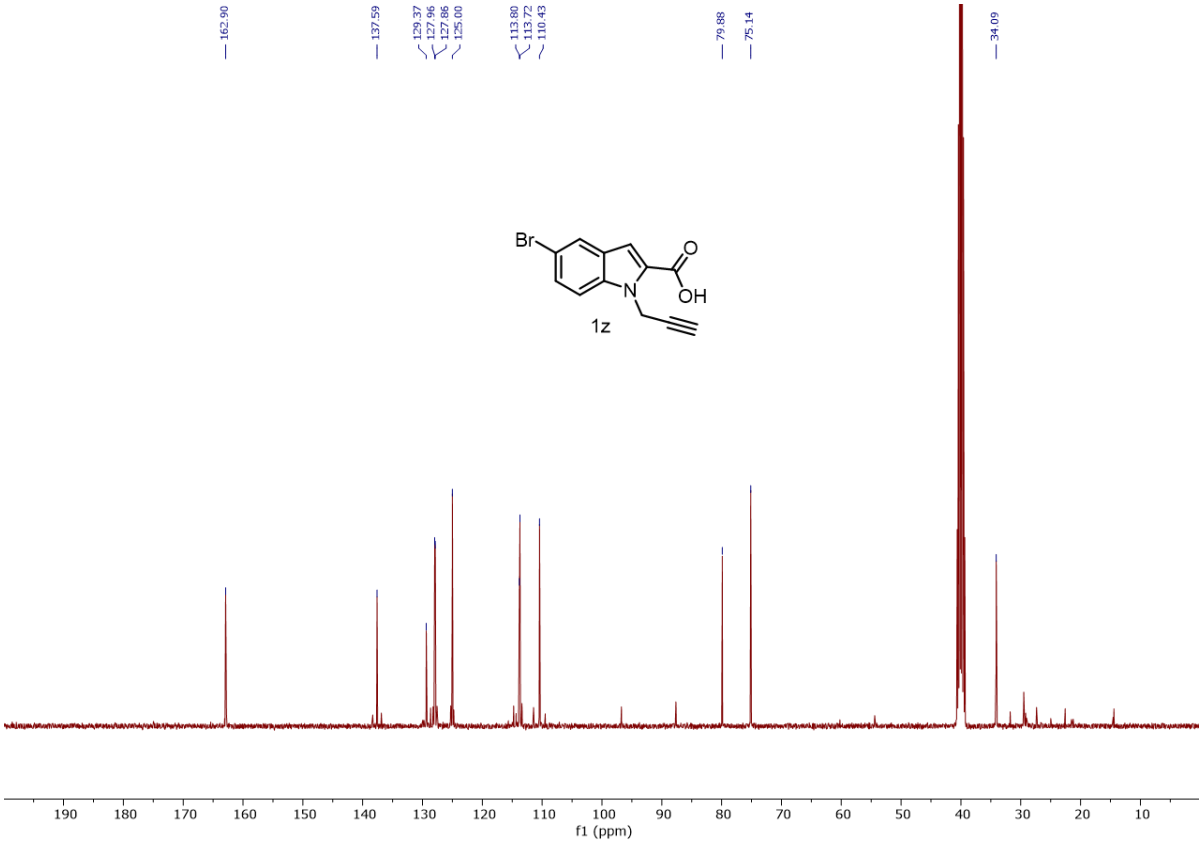
^{13}C{1H} NMR of **1y** (101 MHz, DMSO)



^{1}H NMR of **1z** (400 MHz, DMSO)

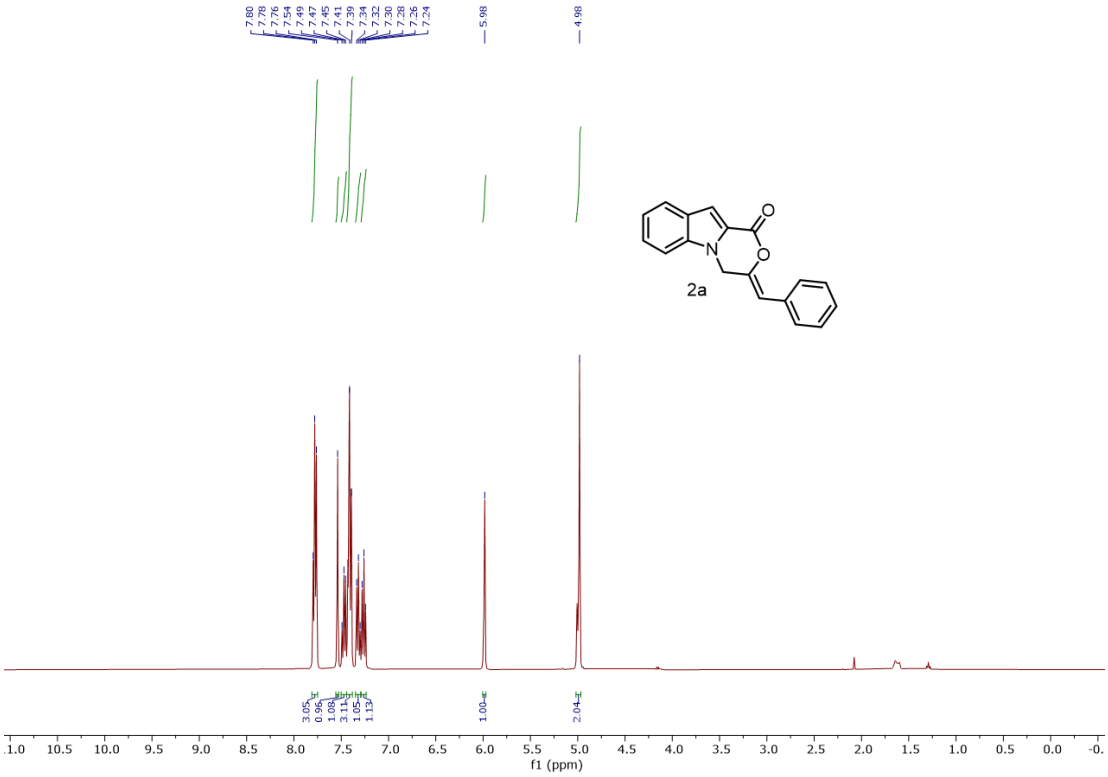


^{13}C{1H} NMR of **1z** (101 MHz, DMSO)

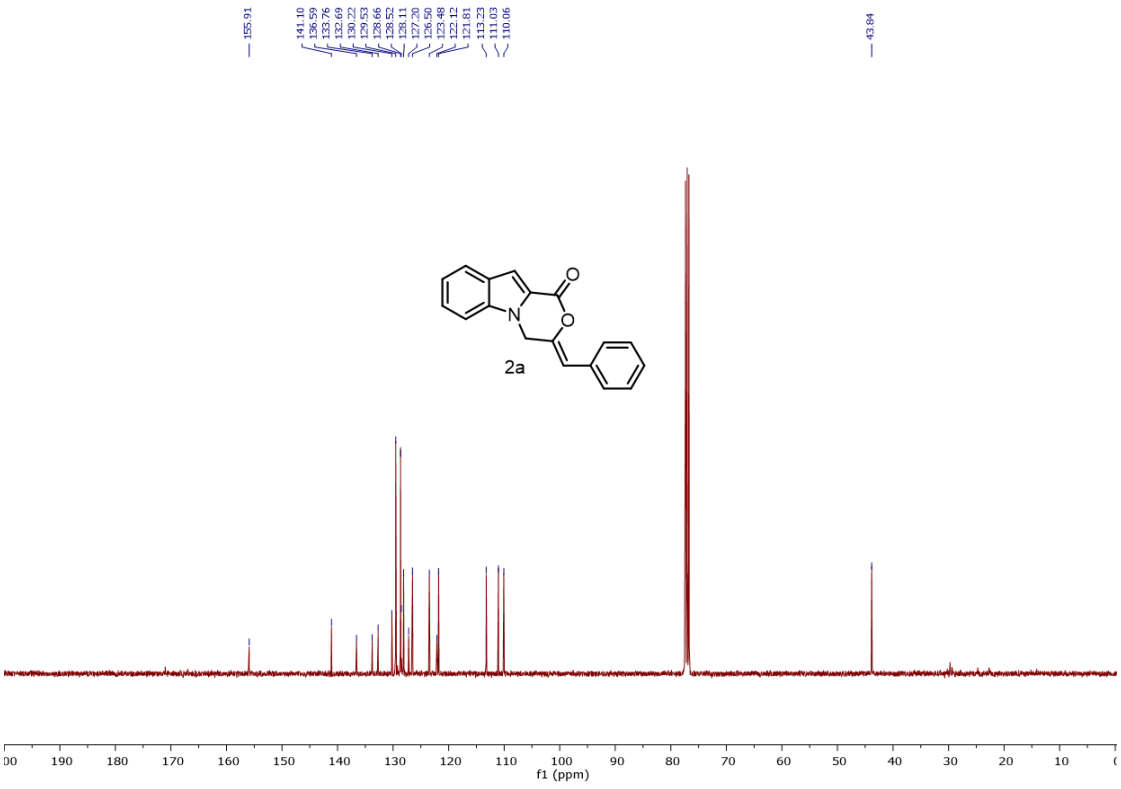


16 NMR spectral data of final products:

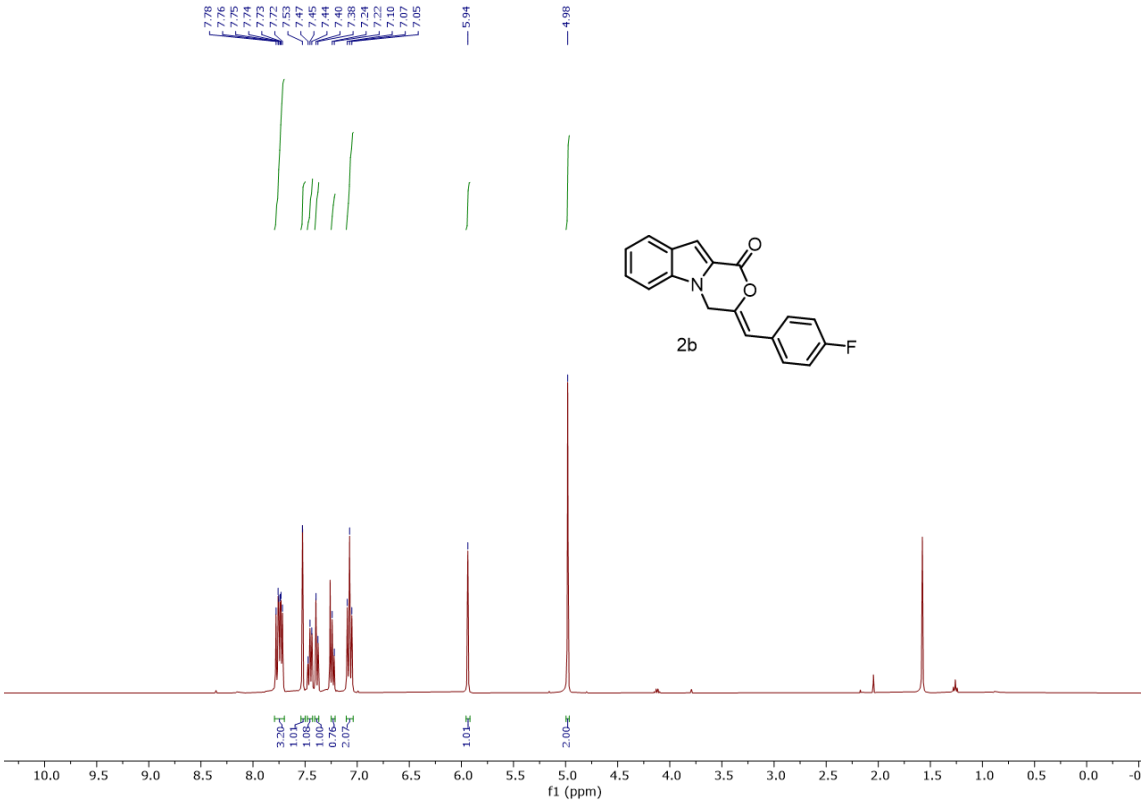
^{1}H NMR of **2a** (400 MHz, $CDCl_3$)



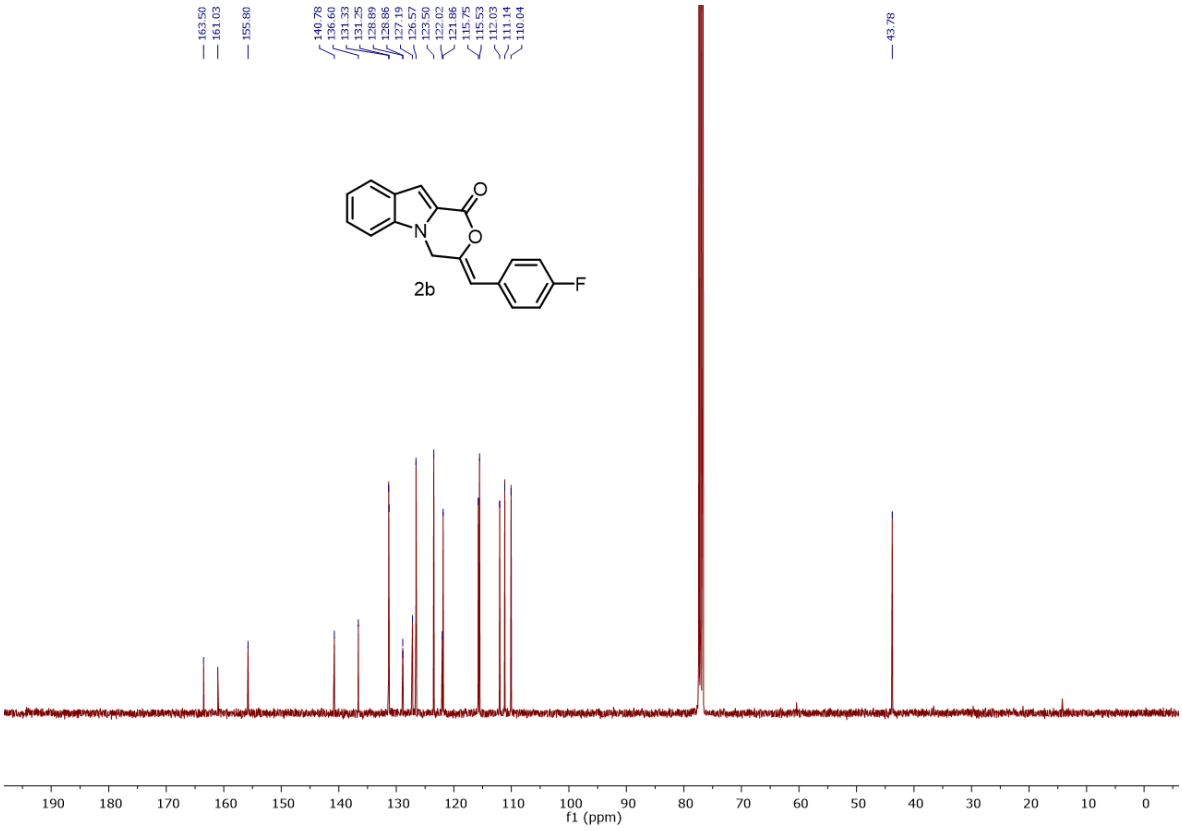
^{13}C{1H} NMR of **2a** (101 MHz, $CDCl_3$)



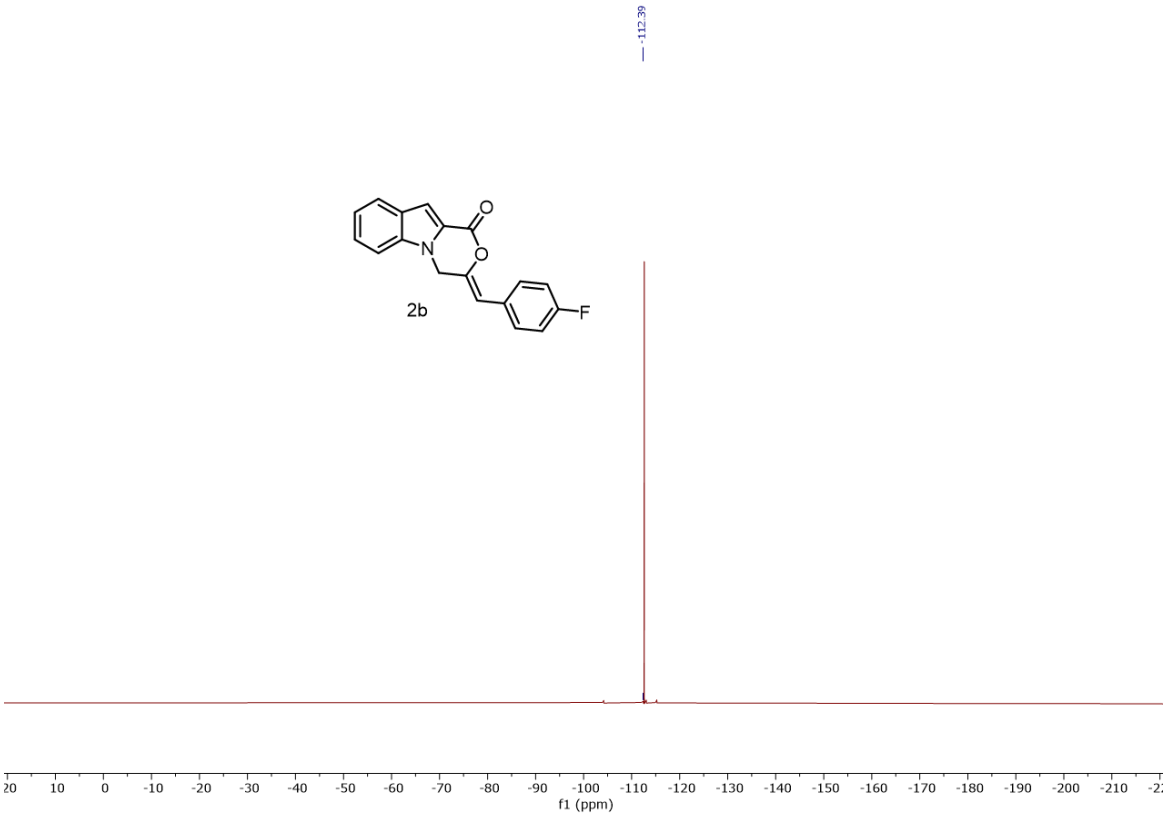
^{1}H NMR of **2b** (400 MHz, $CDCl_3$)



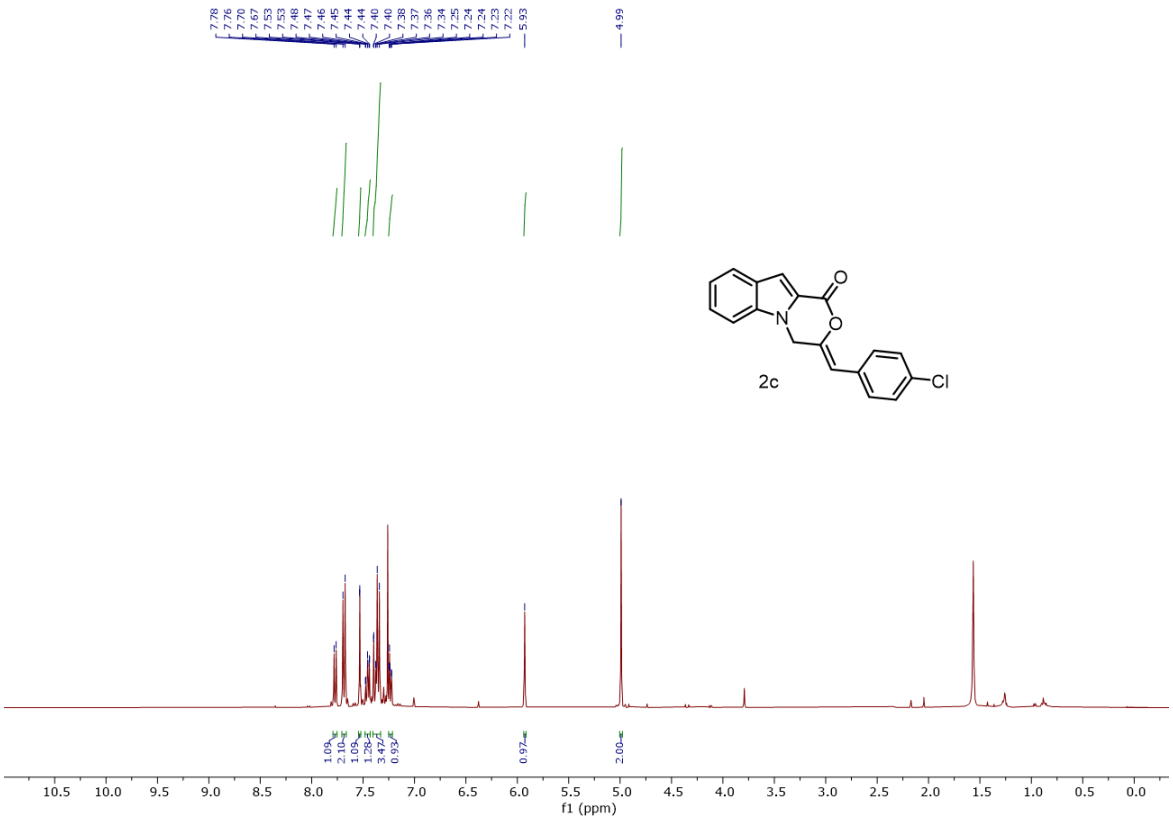
^{13}C{1H} NMR of **2b** (101 MHz, $CDCl_3$)



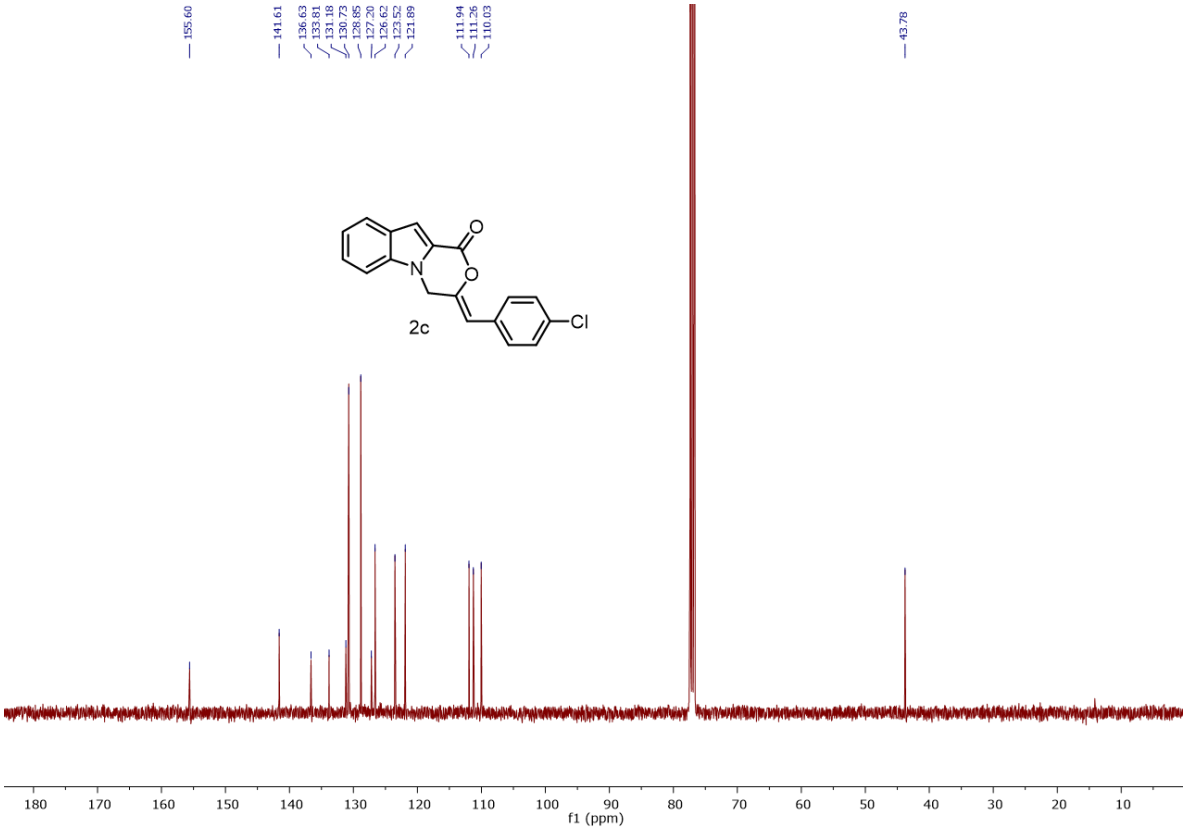
^{19}F NMR of **2b** ($CDCl_3$)



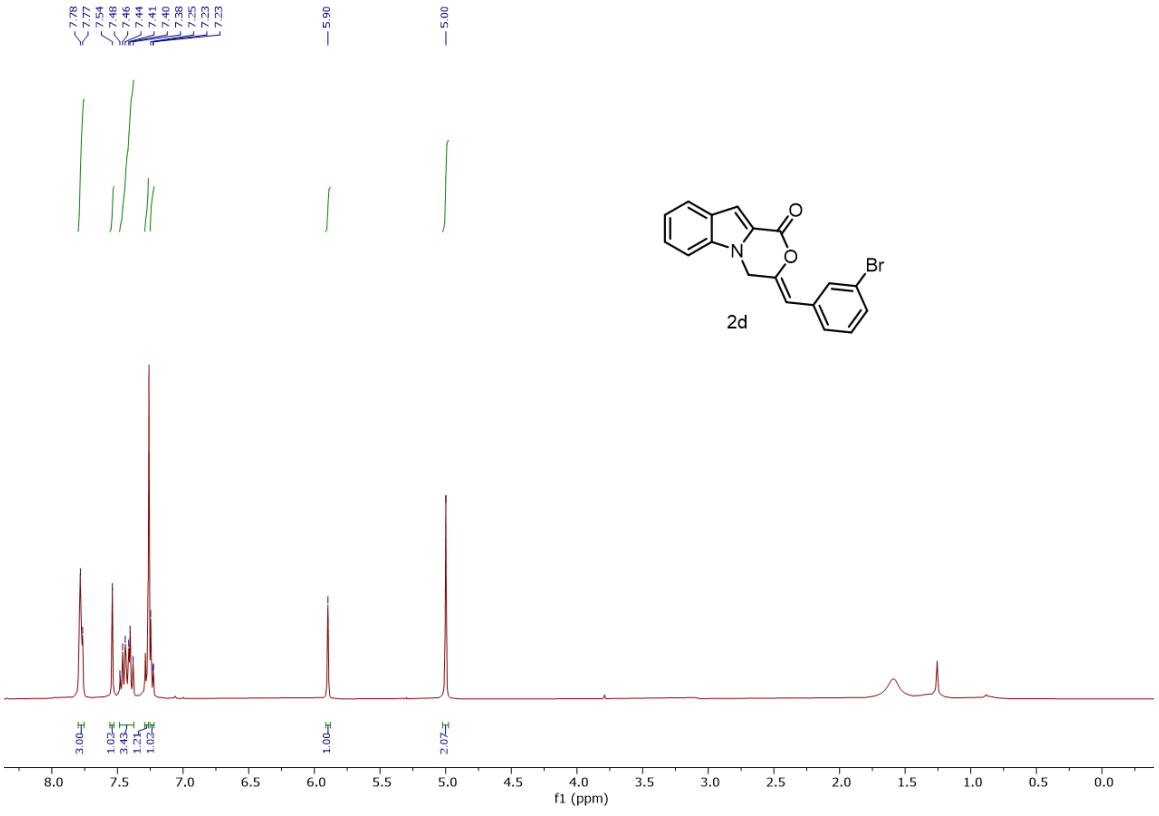
^{1}H NMR of **2c** ($CDCl_3$)



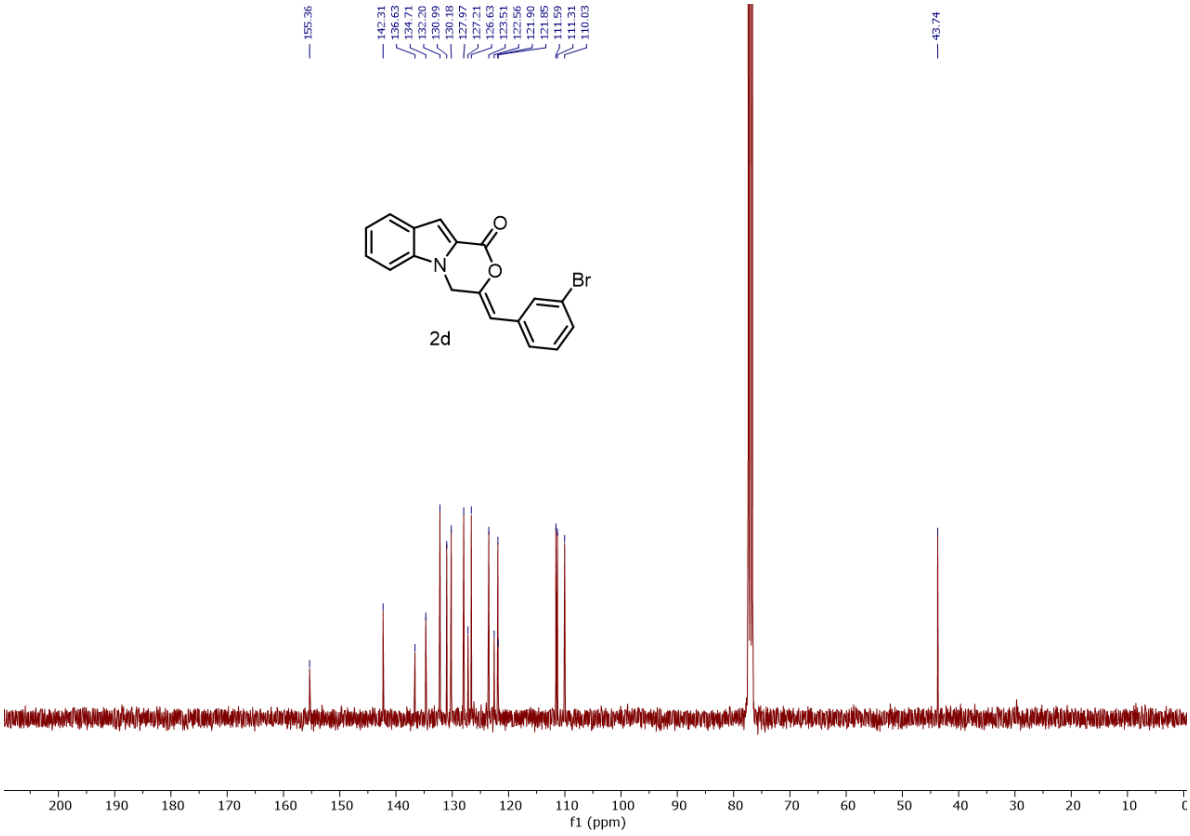
$^{13}C\{1H\}$ NMR of **2c** (101 MHz, $CDCl_3$)



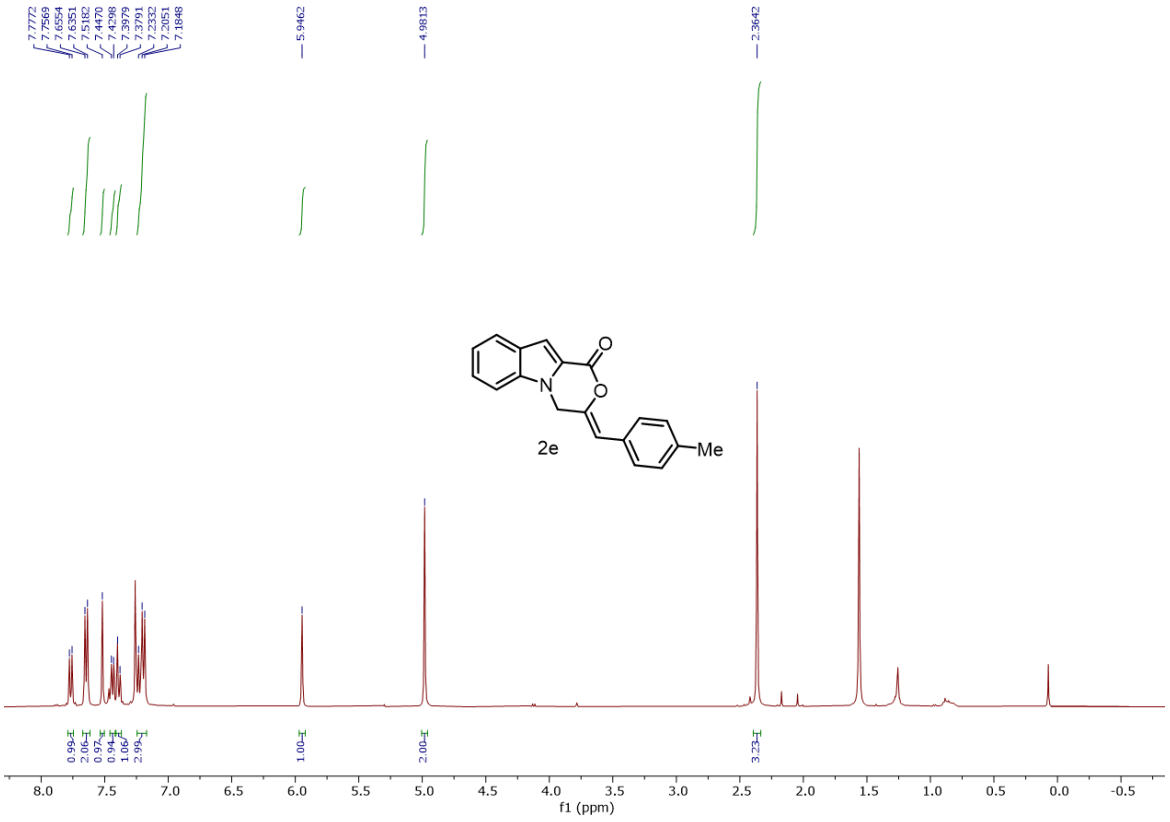
^{1}H NMR of **2d** (400 MHz, $CDCl_3$)



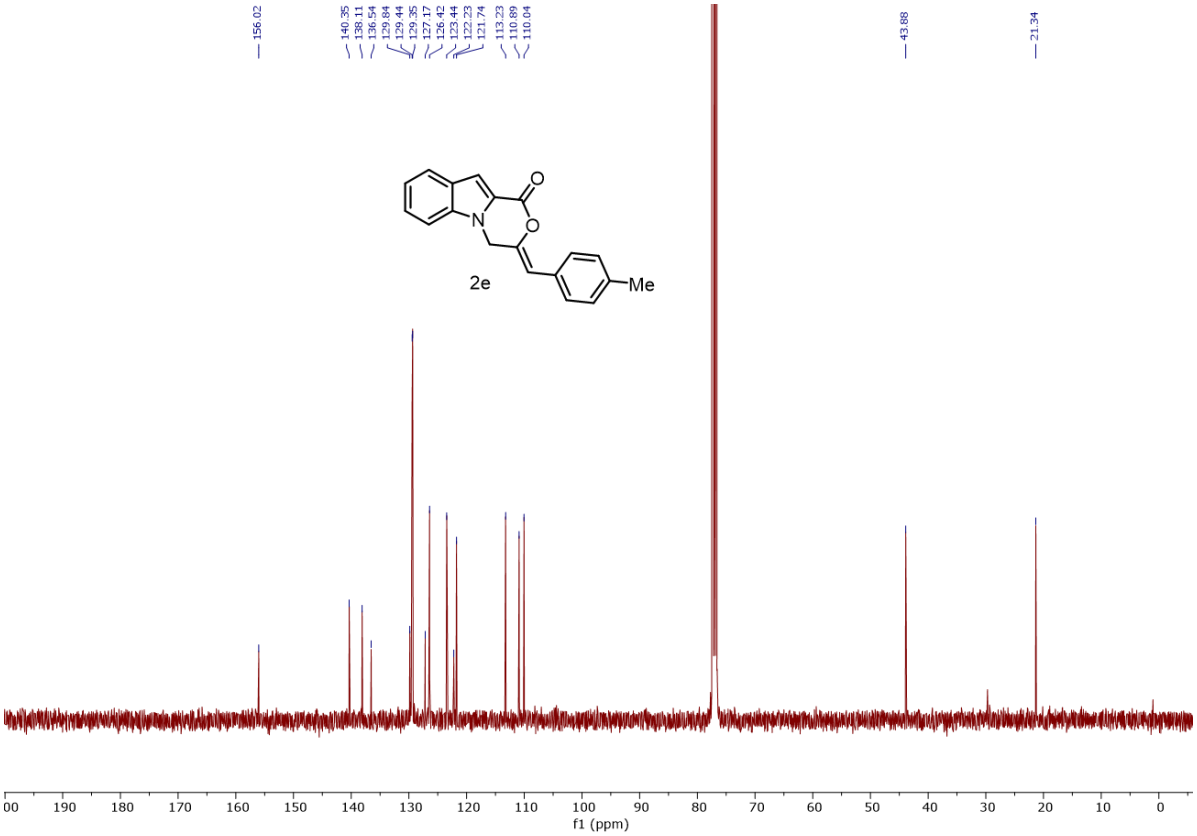
$^{13}C\{1H\}$ NMR of **2d** (101 MHz, $CDCl_3$)



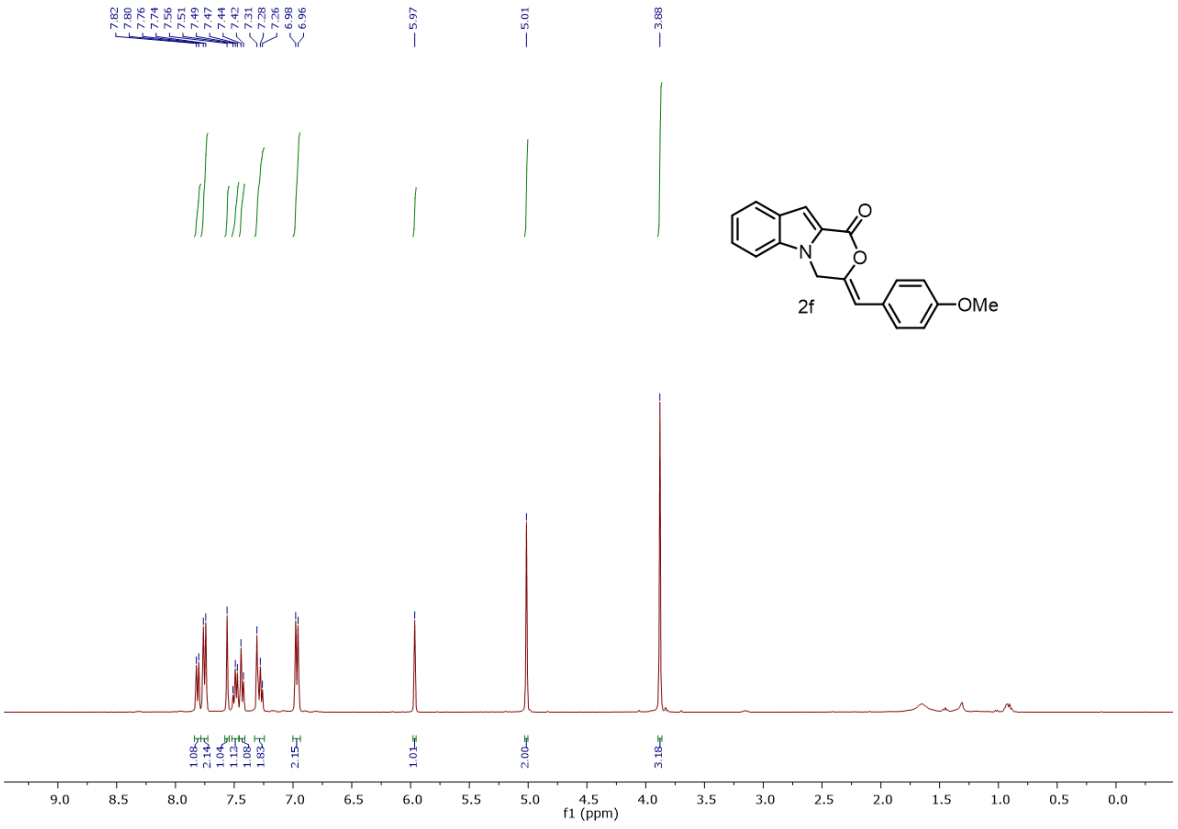
^{1}H NMR of **2e** (400 MHz, $CDCl_3$)



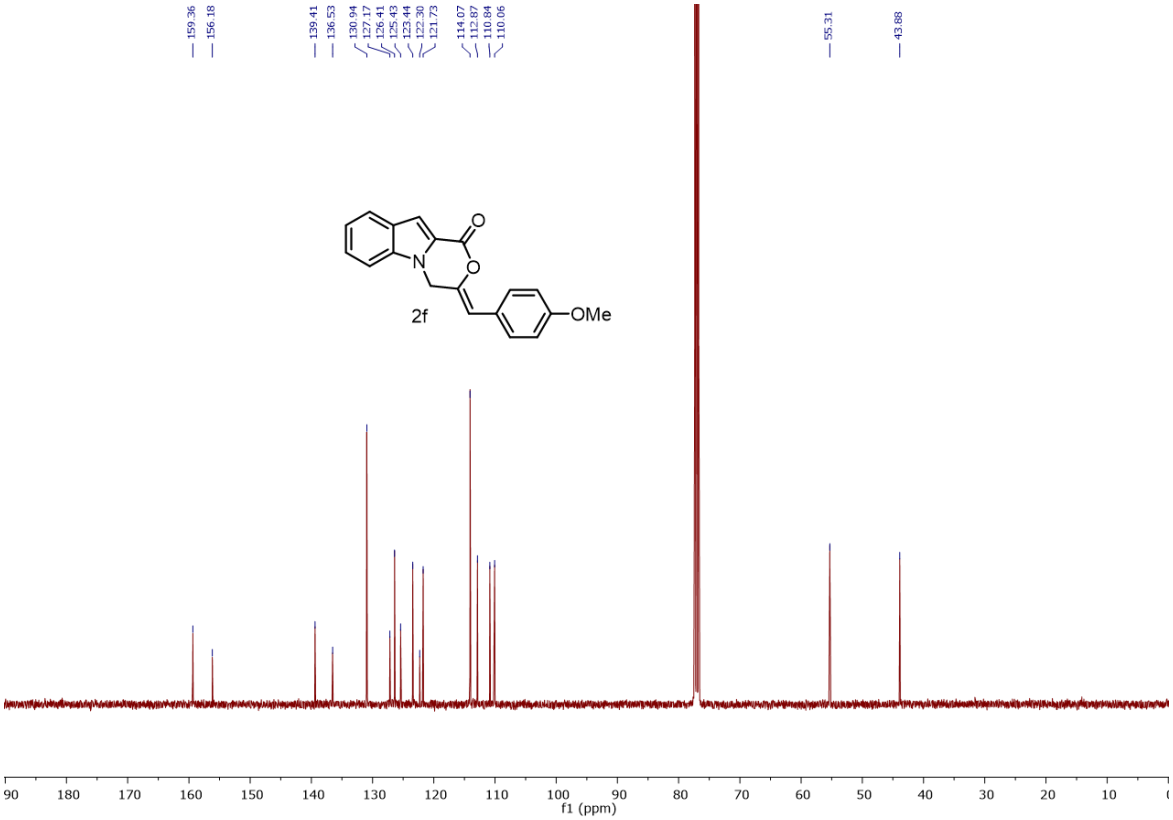
$^{13}C\{1H\}$ NMR of **2e** (101 MHz, $CDCl_3$)



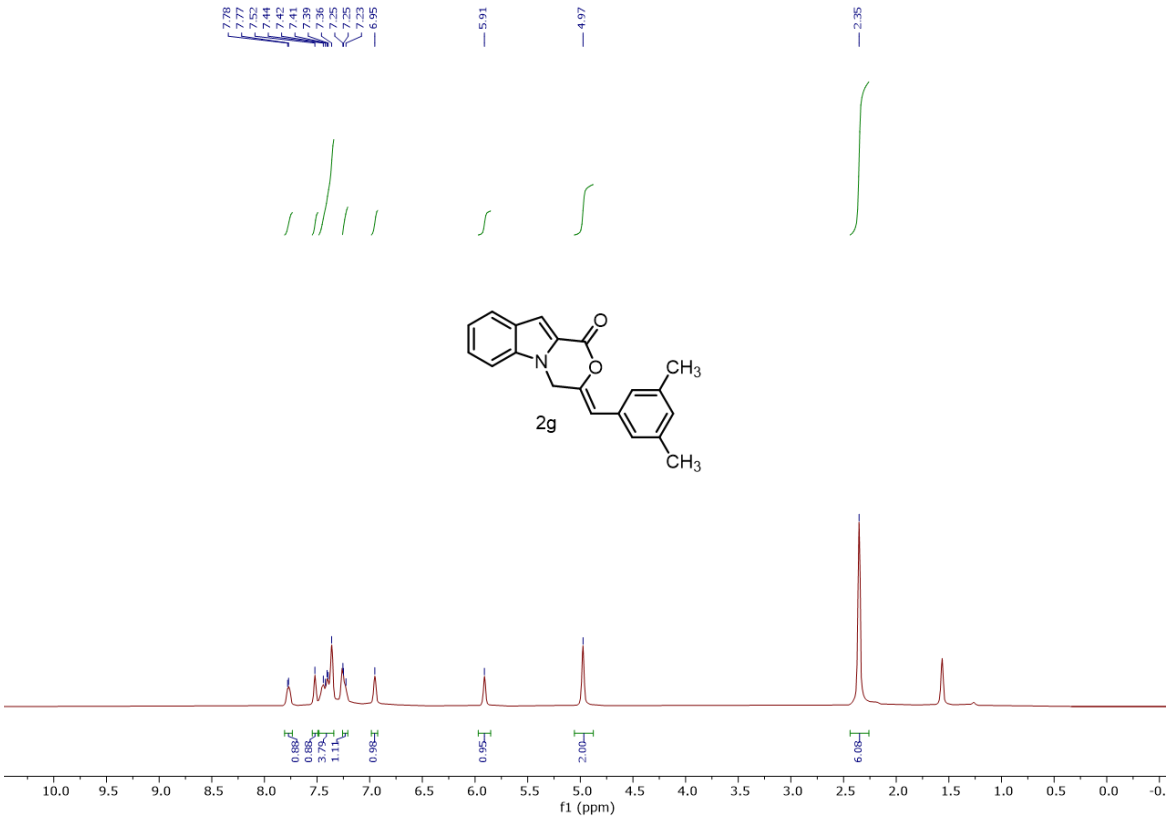
^{1}H NMR of **2f** (400 MHz, $CDCl_3$)



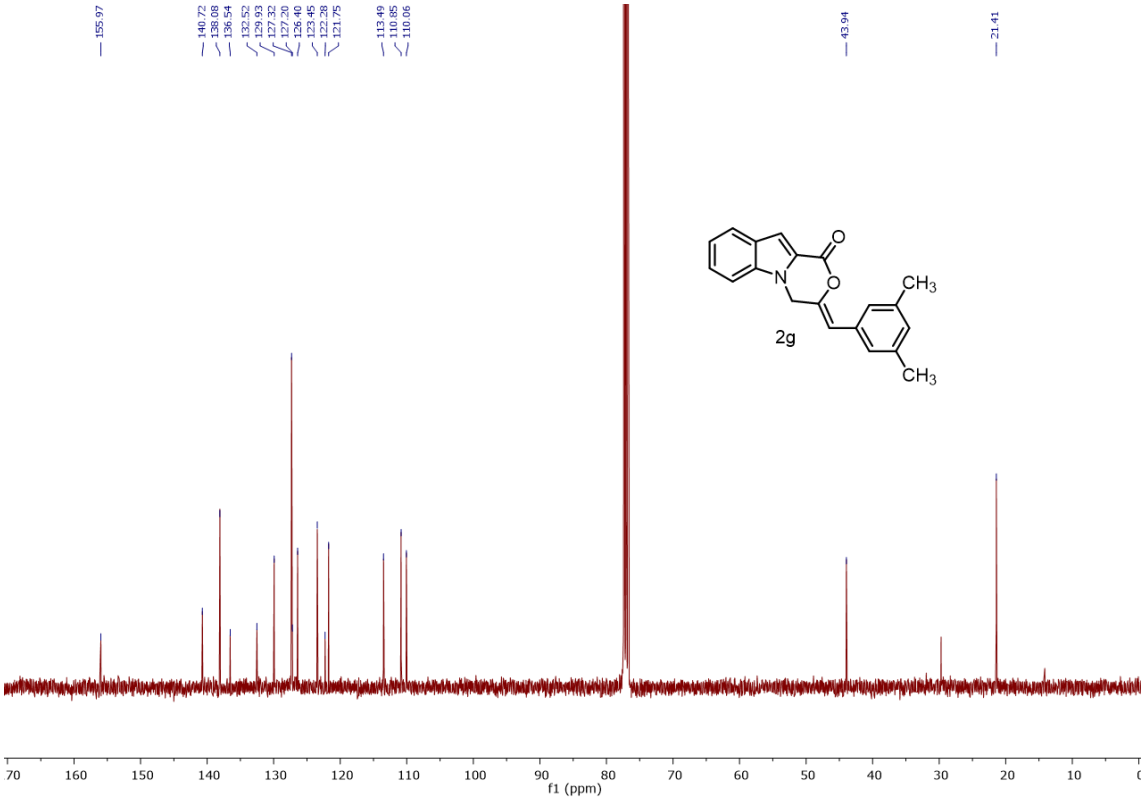
$^{13}C\{1H\}$ NMR of **2f** (101 MHz, $CDCl_3$)



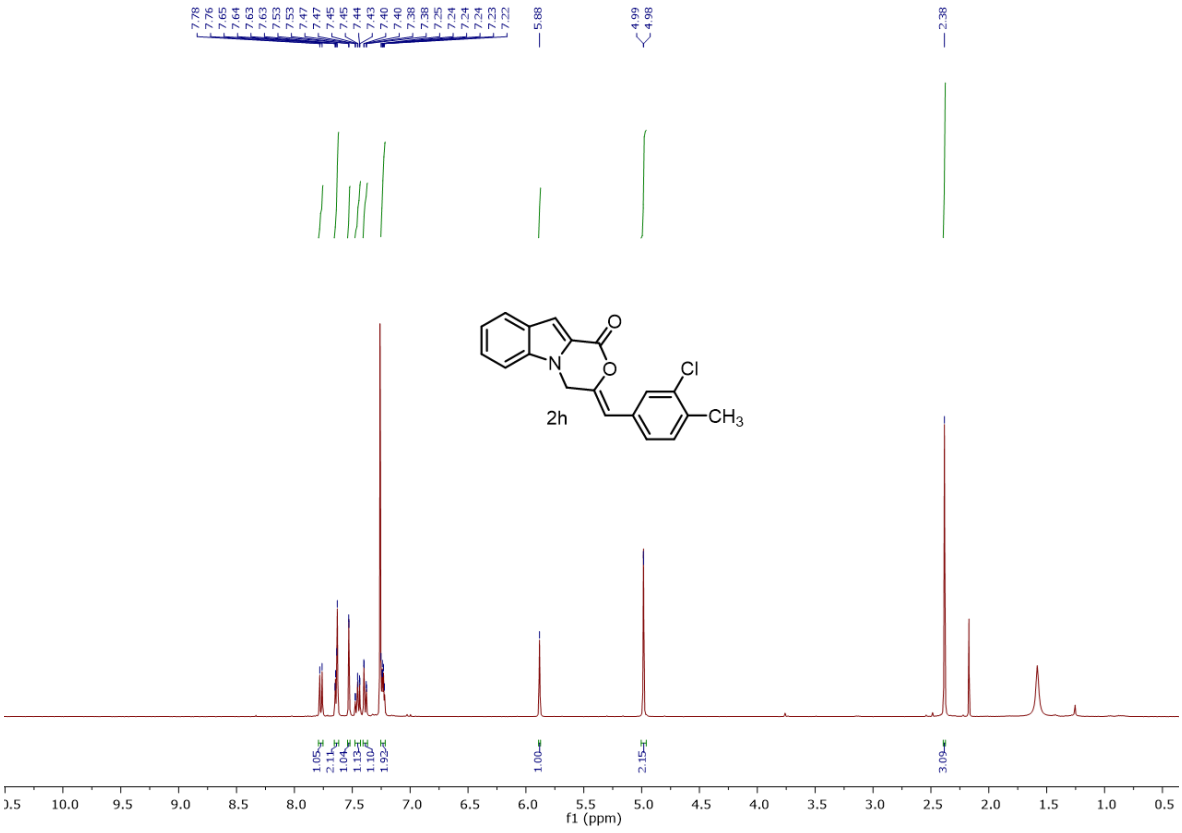
^{1}H NMR of **2g** (400 MHz, $CDCl_3$)



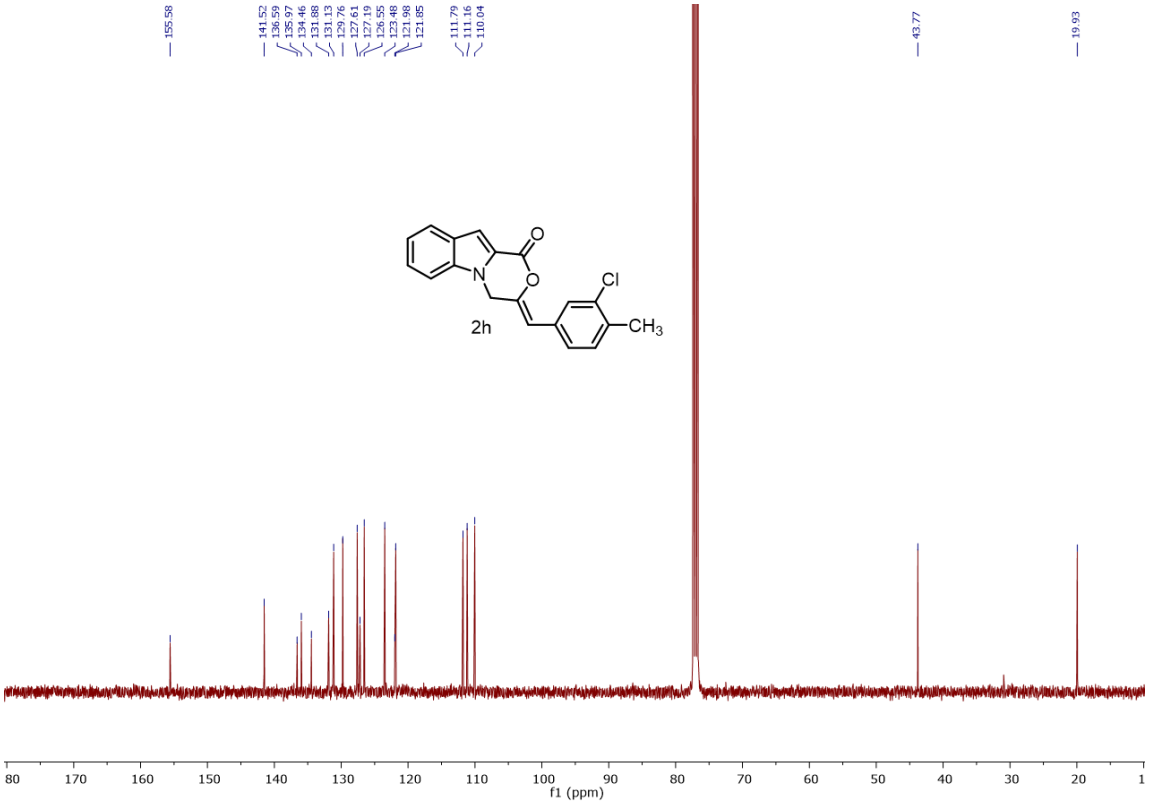
$^{13}C\{1H\}$ NMR of **2g** (101 MHz, $CDCl_3$)



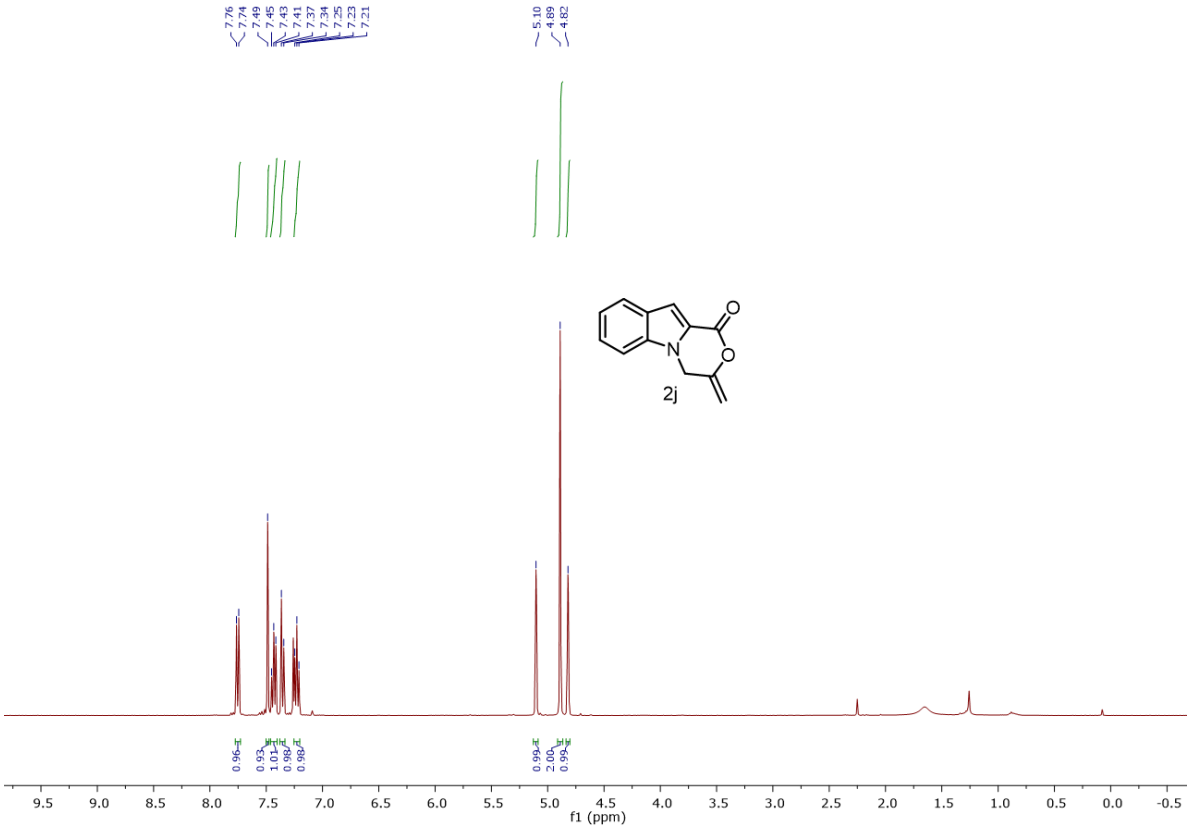
^{1}H NMR of **2h** (400 MHz, $CDCl_3$)



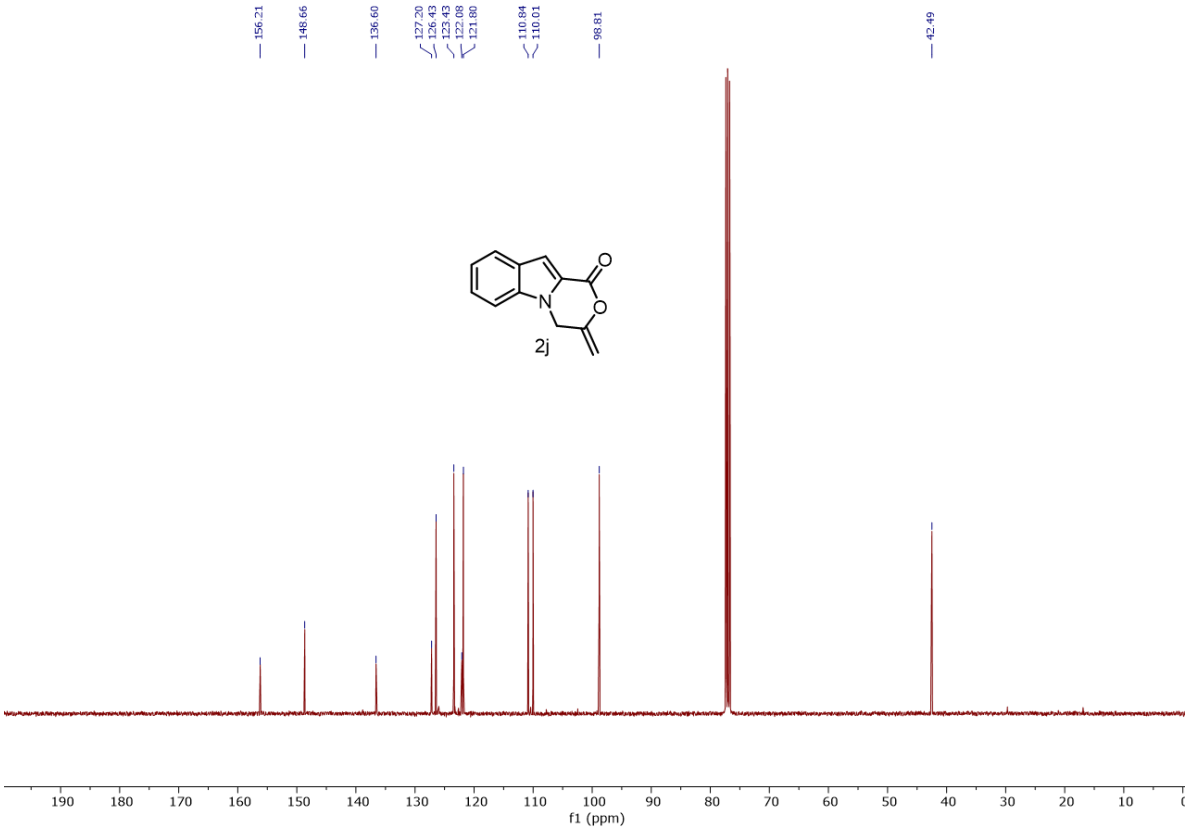
$^{13}C\{1H\}$ NMR of **2h** ($CDCl_3$)



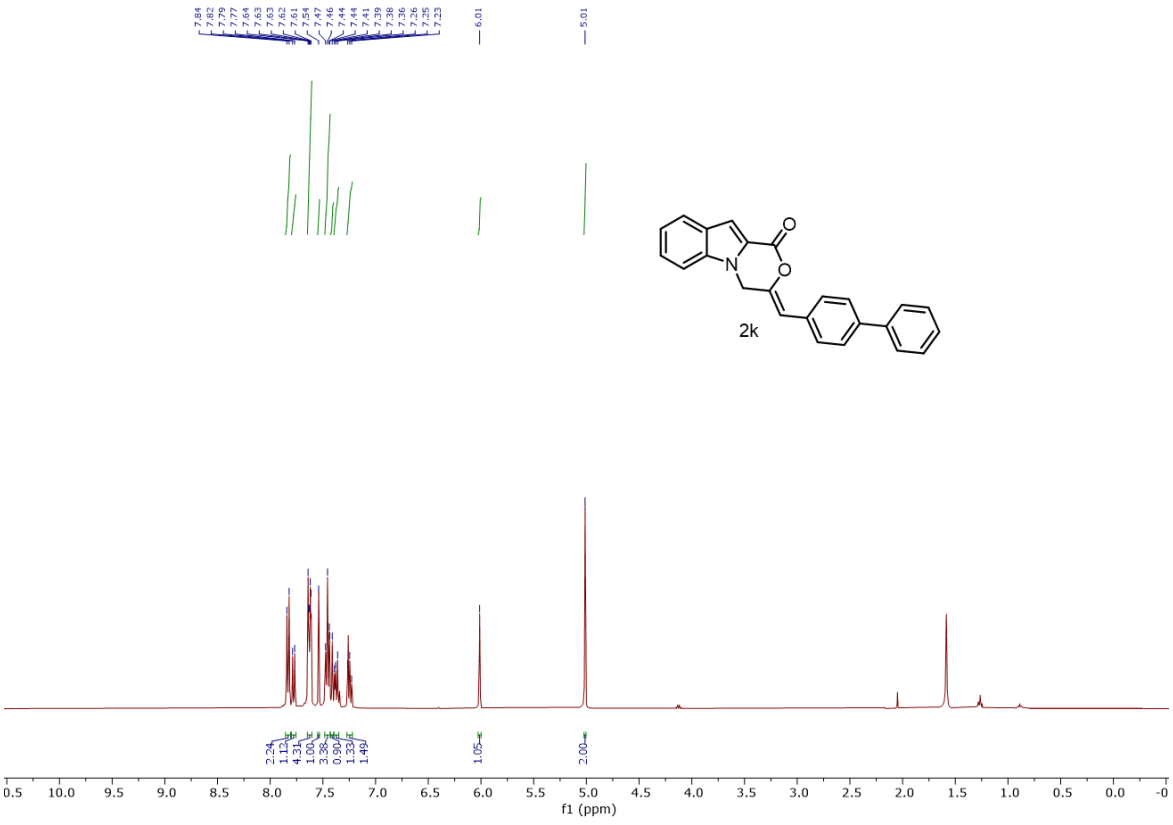
^{1}H NMR of **2j** ($CDCl_3$)



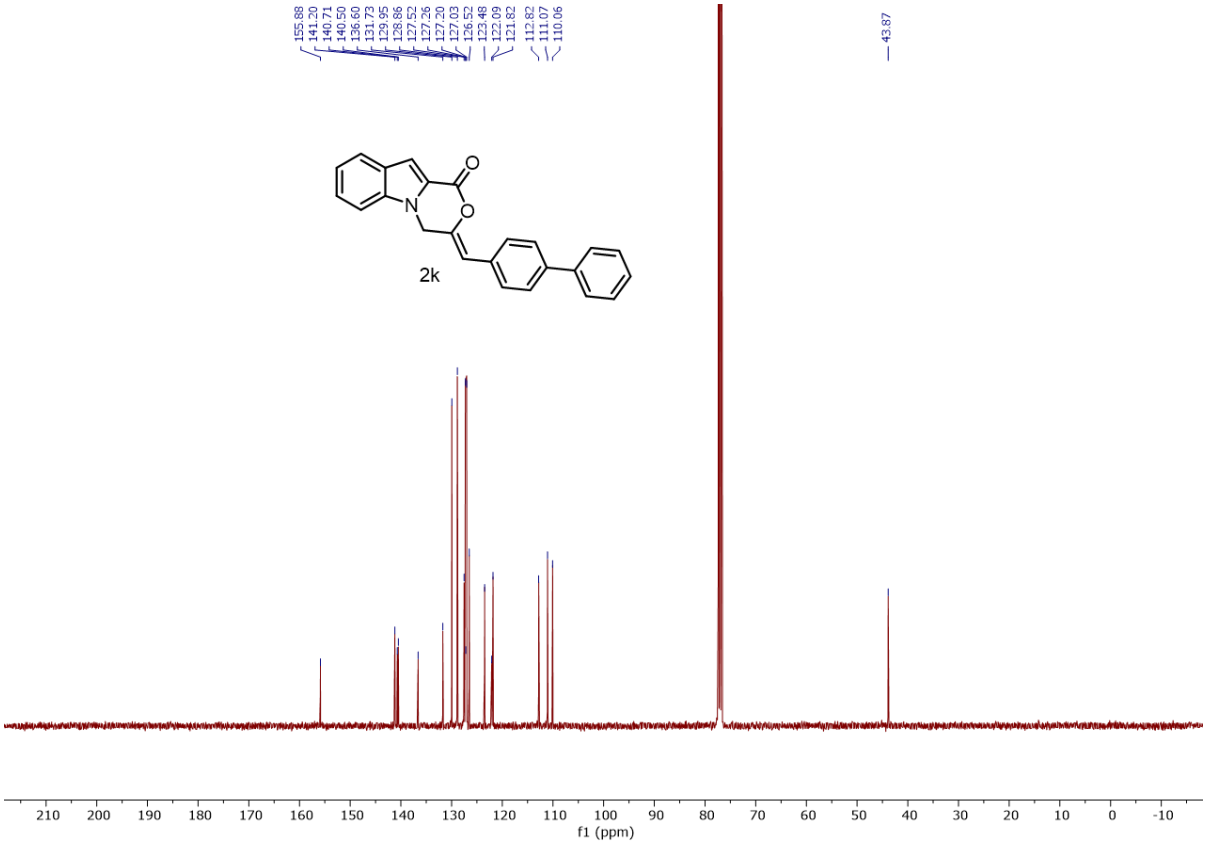
$^{13}C\{1H\}$ NMR of **2j** (101 MHz, $CDCl_3$)



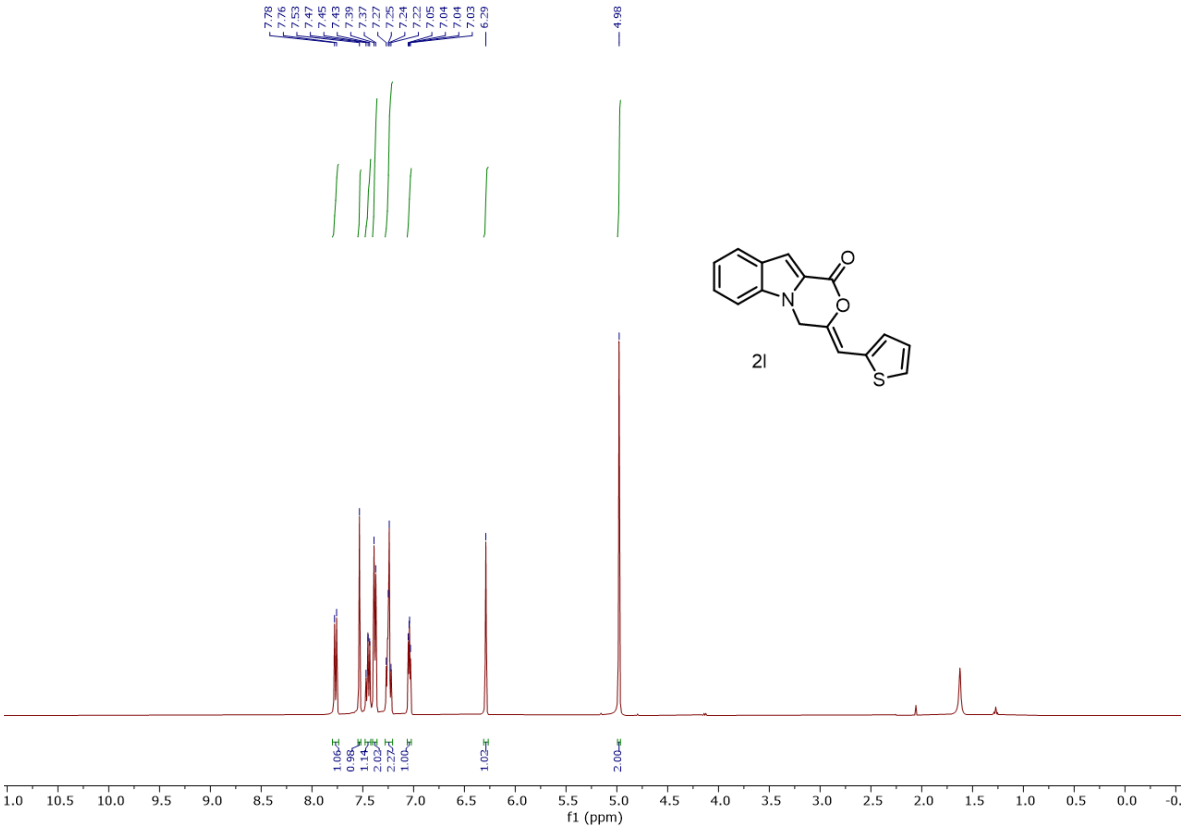
^{1}H NMR of **2k** (400 MHz, $CDCl_3$)



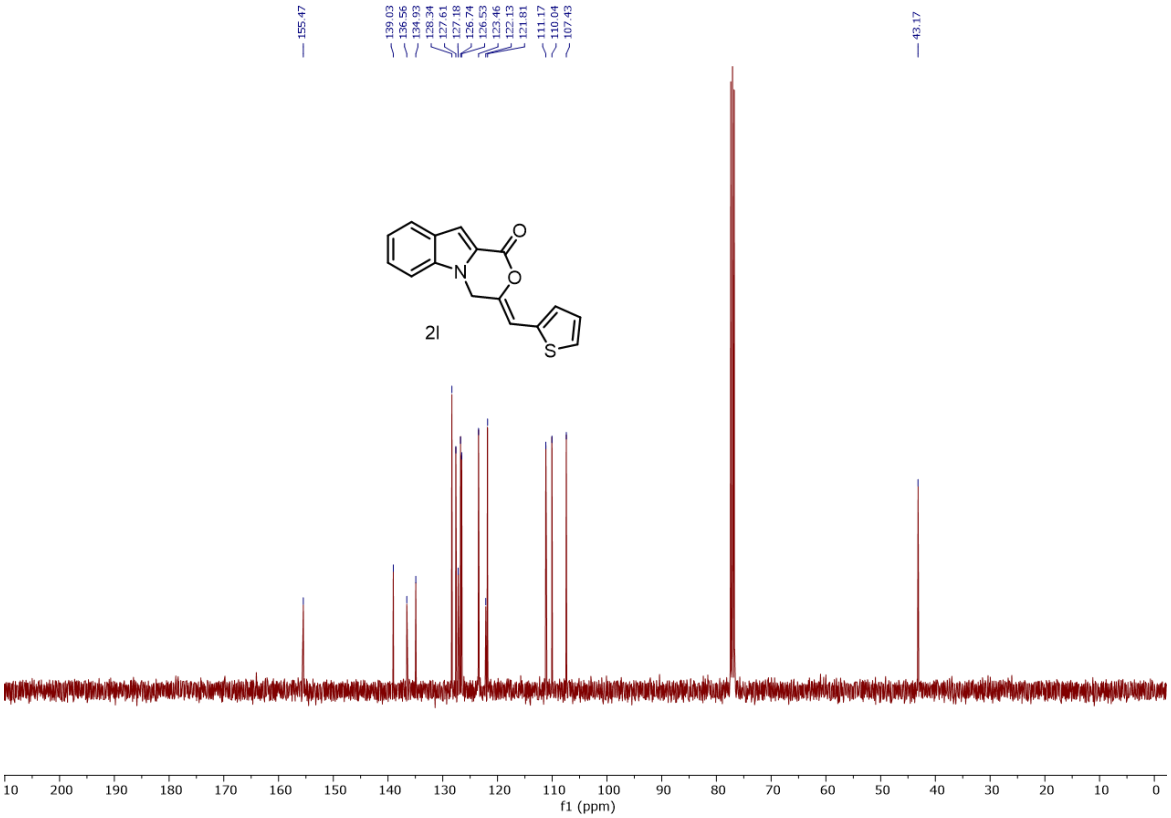
$^{13}C\{1H\}$ NMR of **2k** (101 MHz, $CDCl_3$)



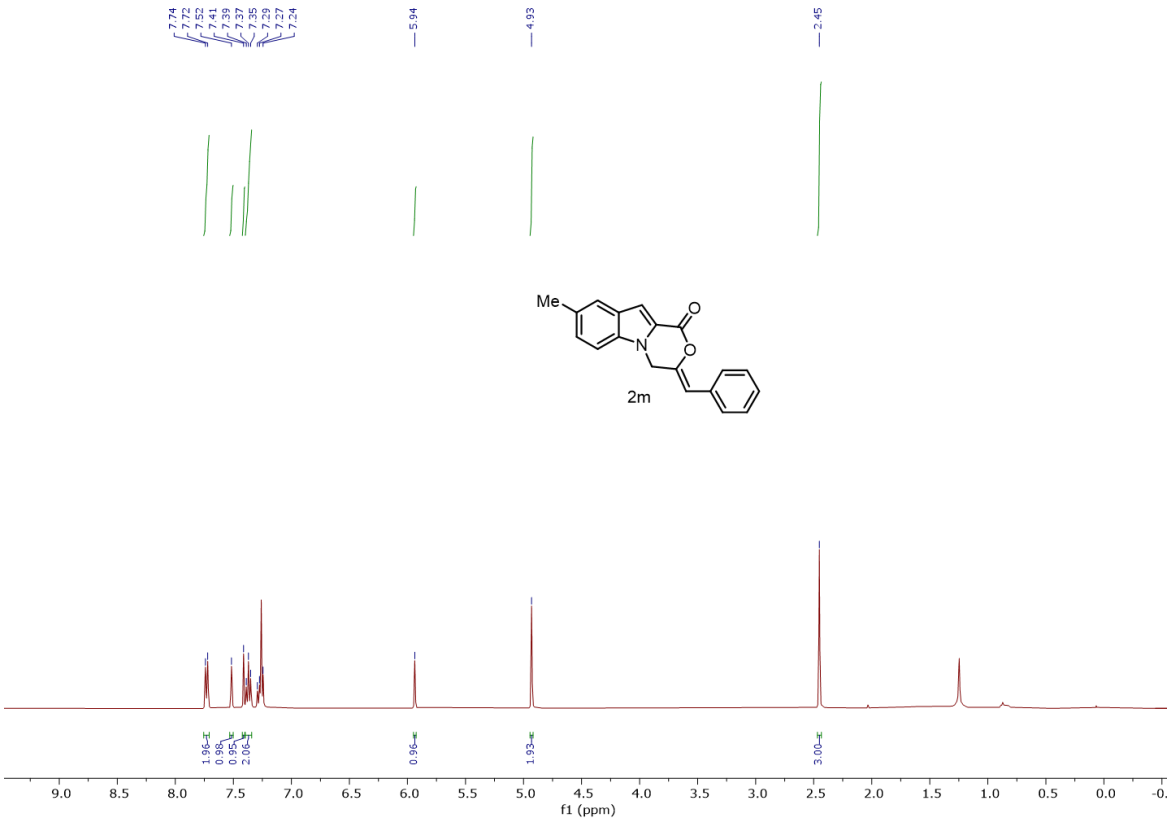
^{1}H NMR of **2l** (400 MHz, $CDCl_3$)



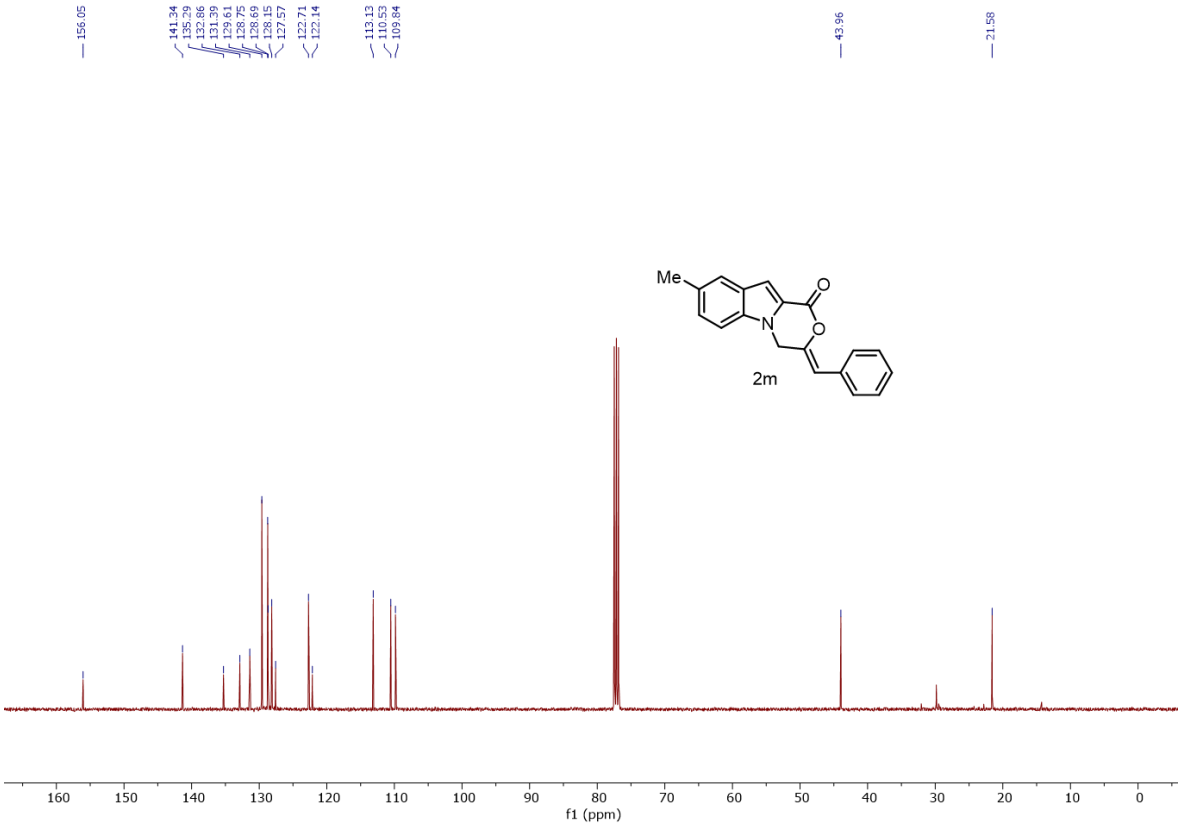
$^{13}C\{1H\}$ NMR of **2l** (101 MHz, $CDCl_3$)



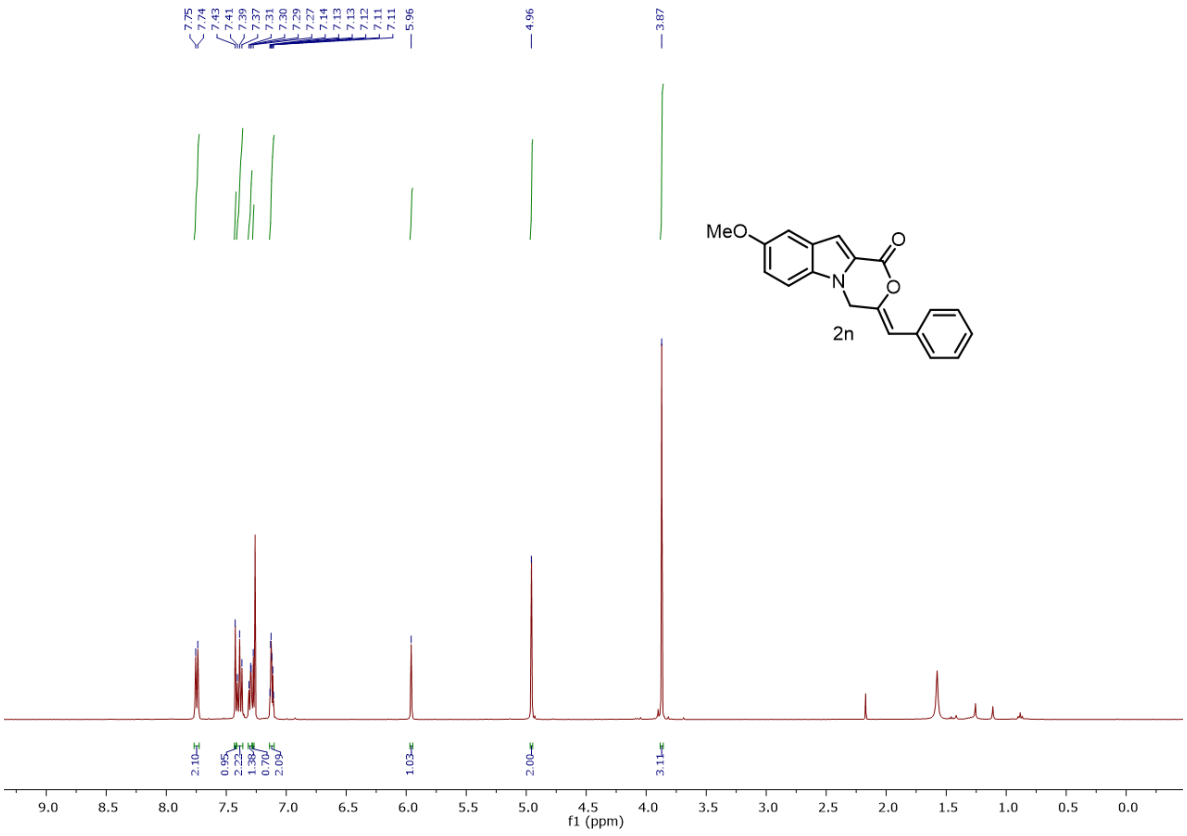
^{1}H NMR of **2m** (400 MHz, $CDCl_3$)



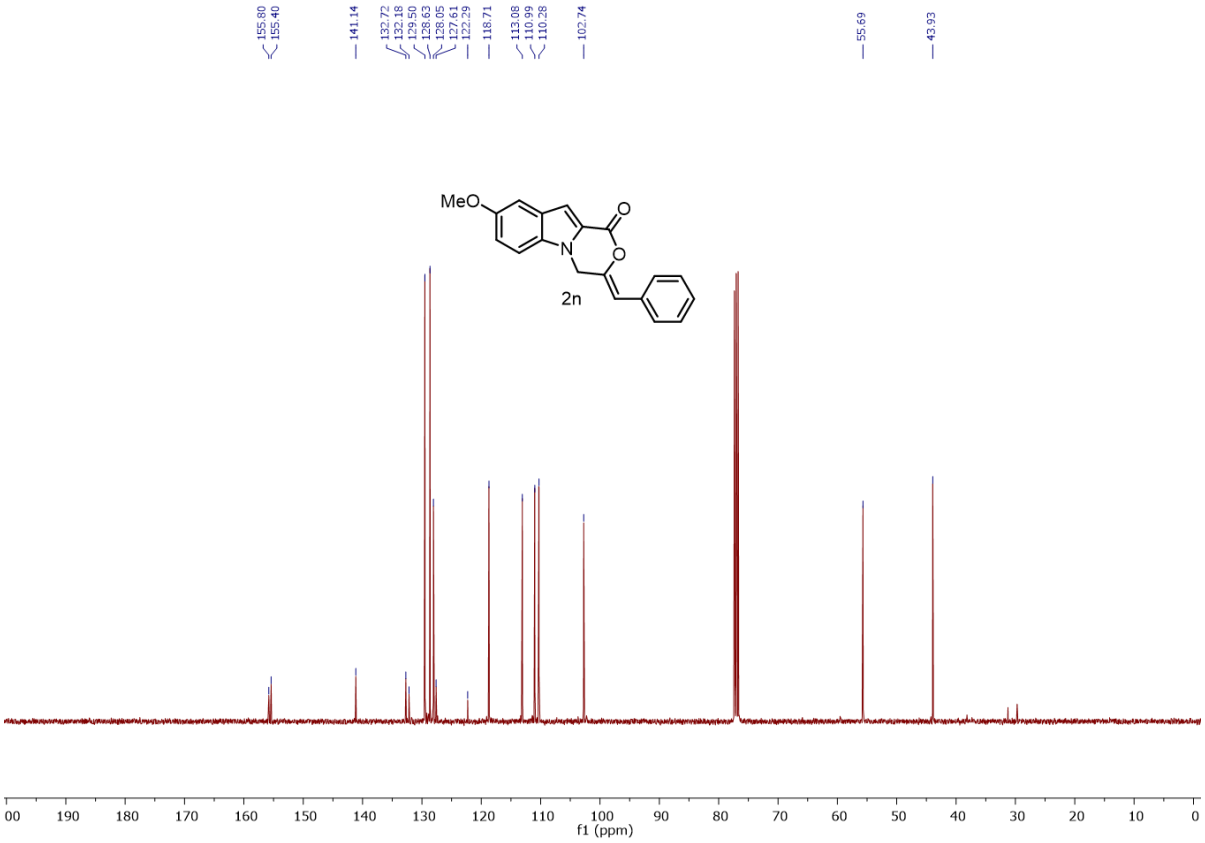
$^{13}C\{1H\}$ NMR of **2m** (101 MHz, $CDCl_3$)



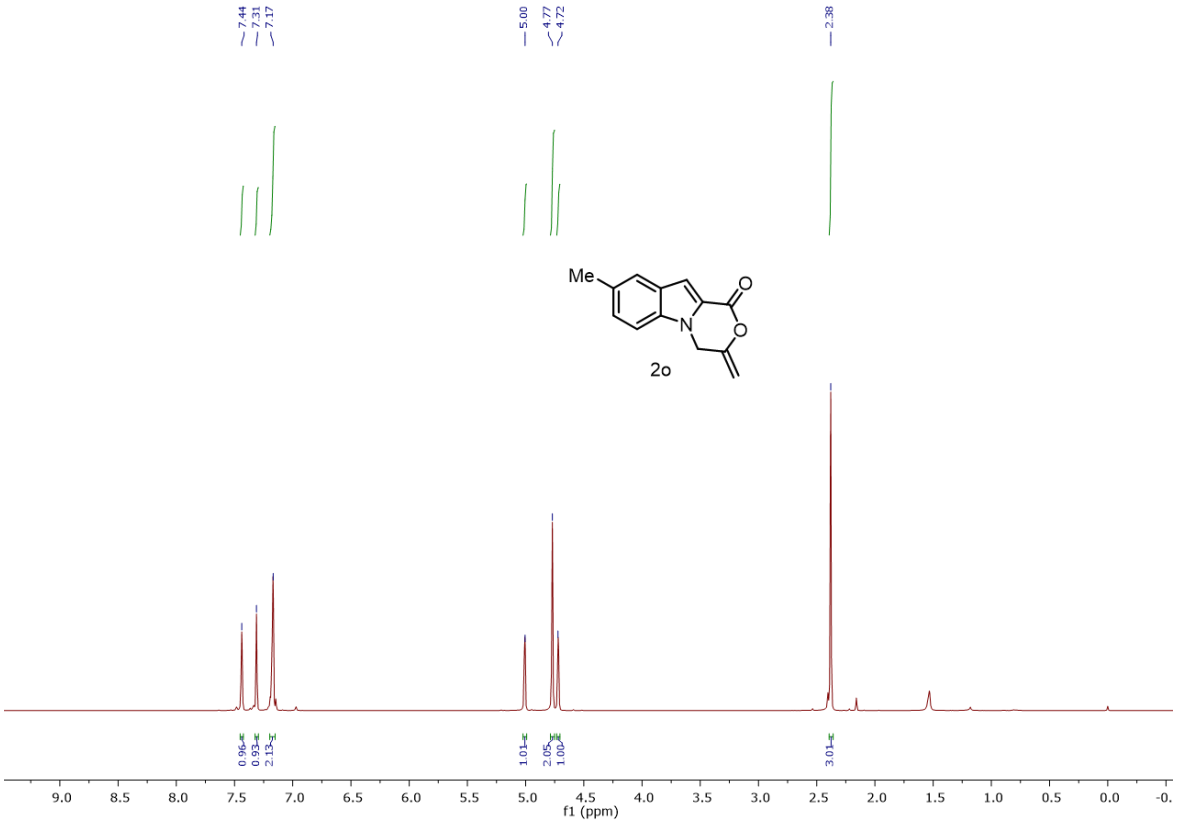
^{1}H NMR of **2n** (400 MHz, $CDCl_3$)



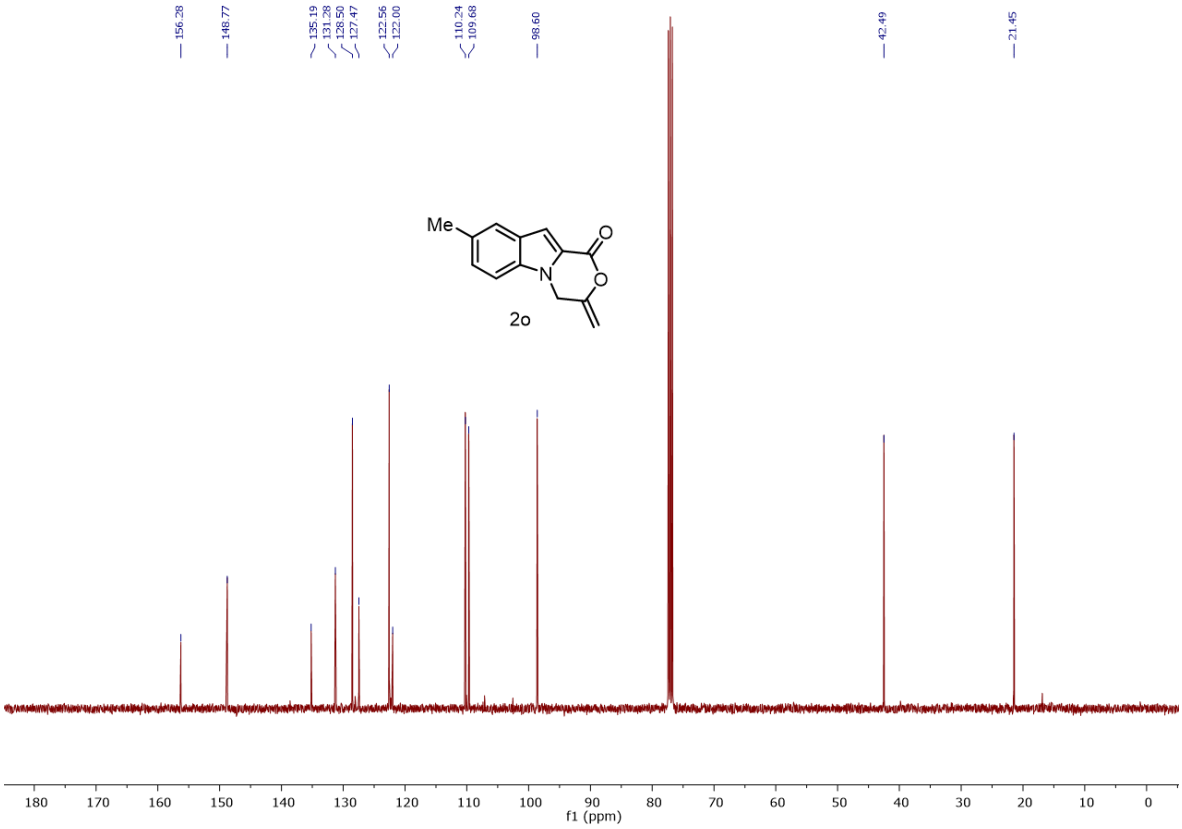
$^{13}C\{1H\}$ NMR of **2n** (101 MHz, $CDCl_3$)



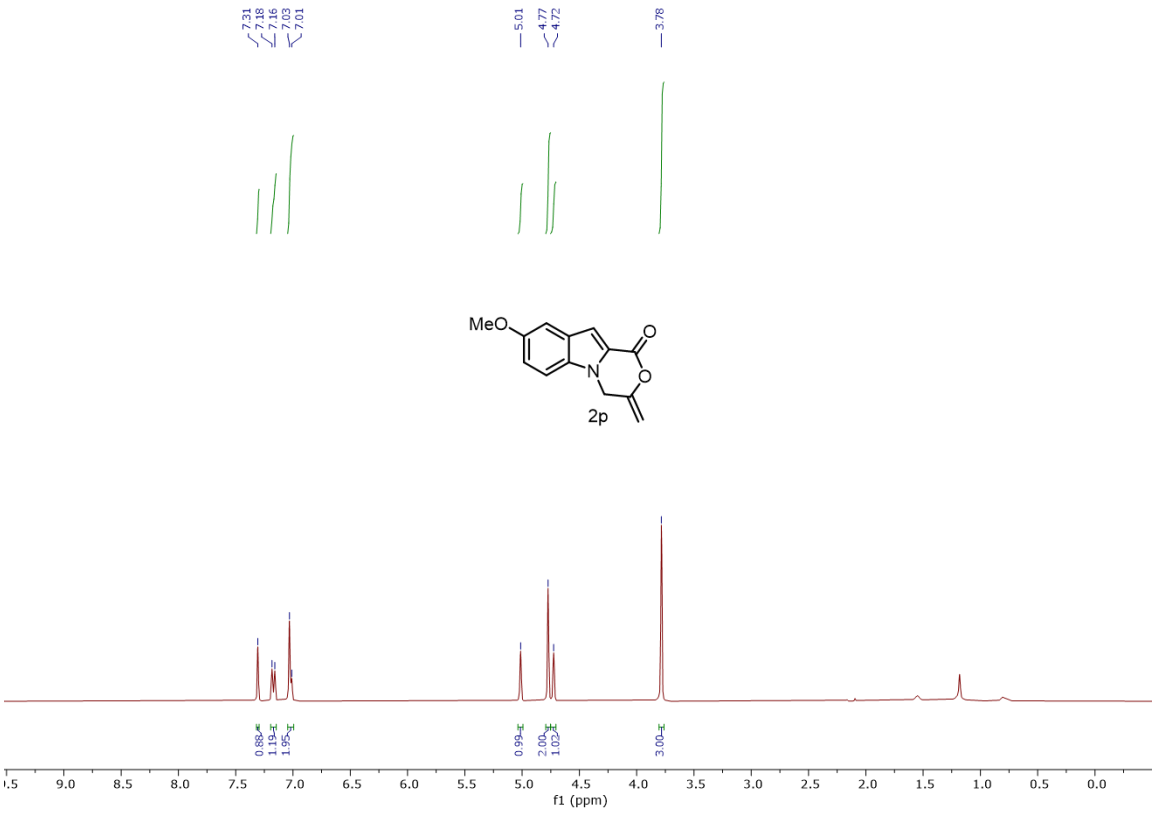
^{1}H NMR of **2o** (400 MHz, $CDCl_3$)



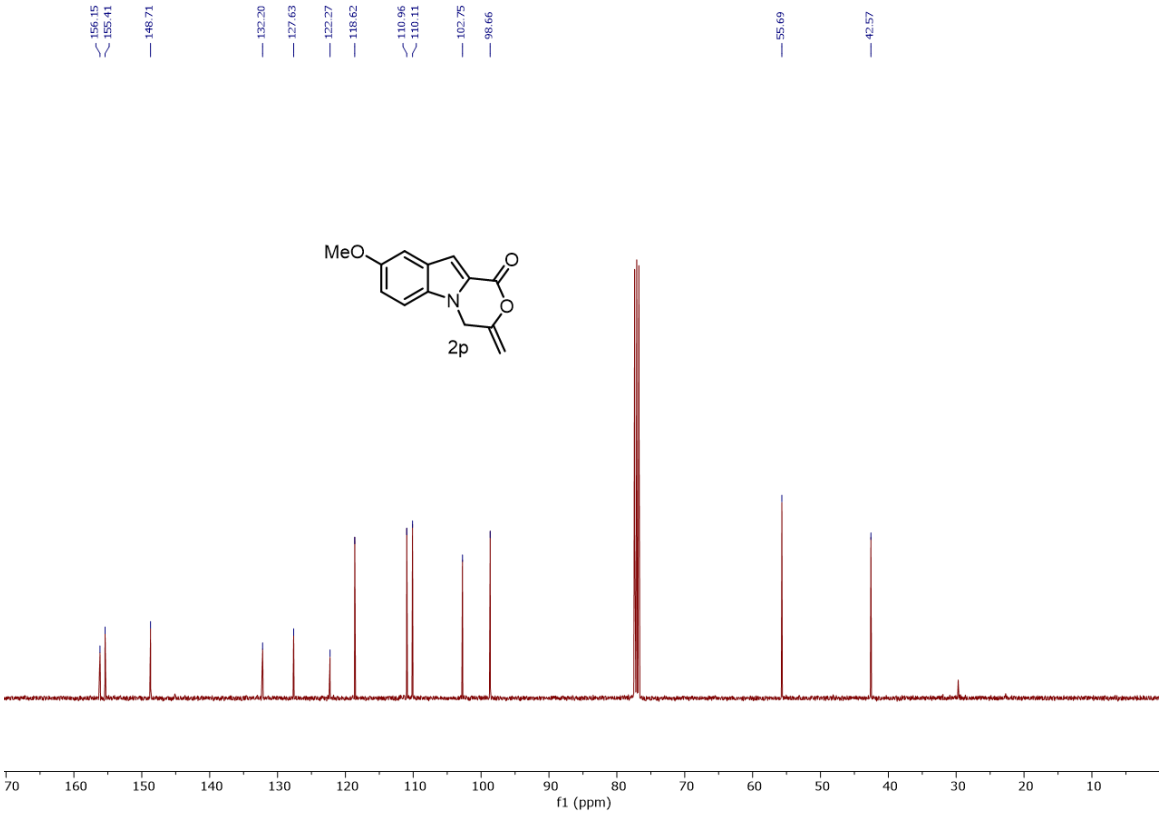
$^{13}C\{1H\}$ NMR of **2o** (101 MHz, $CDCl_3$)



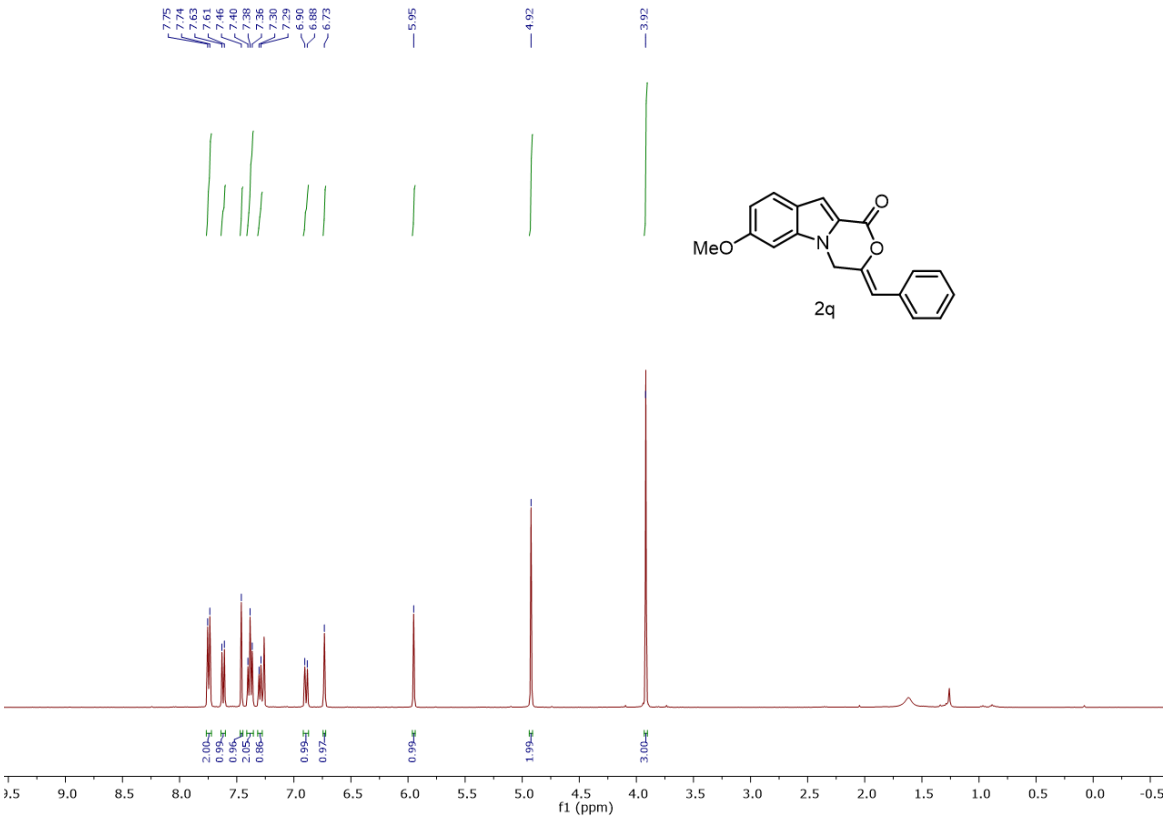
^{1}H NMR of **2p** (400 MHz, $CDCl_3$)



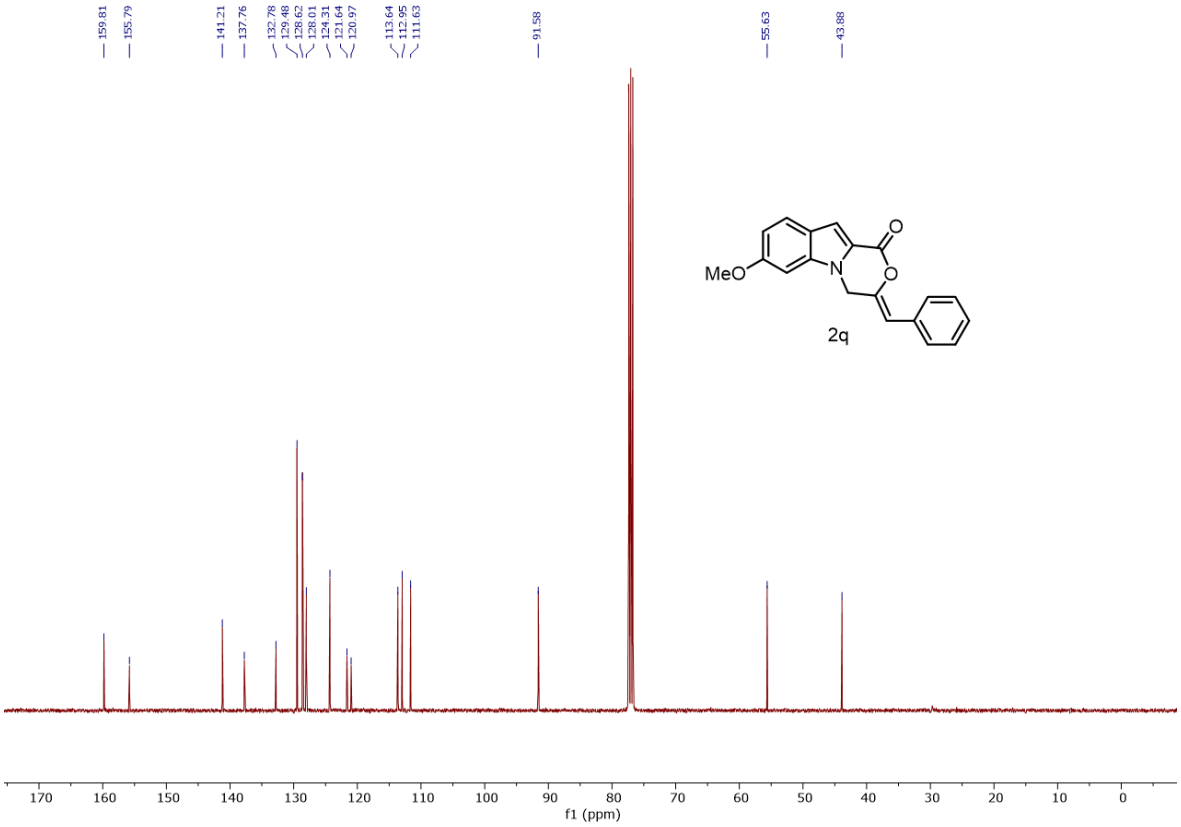
$^{13}C\{1H\}$ NMR of **2p** (101 MHz, $CDCl_3$)



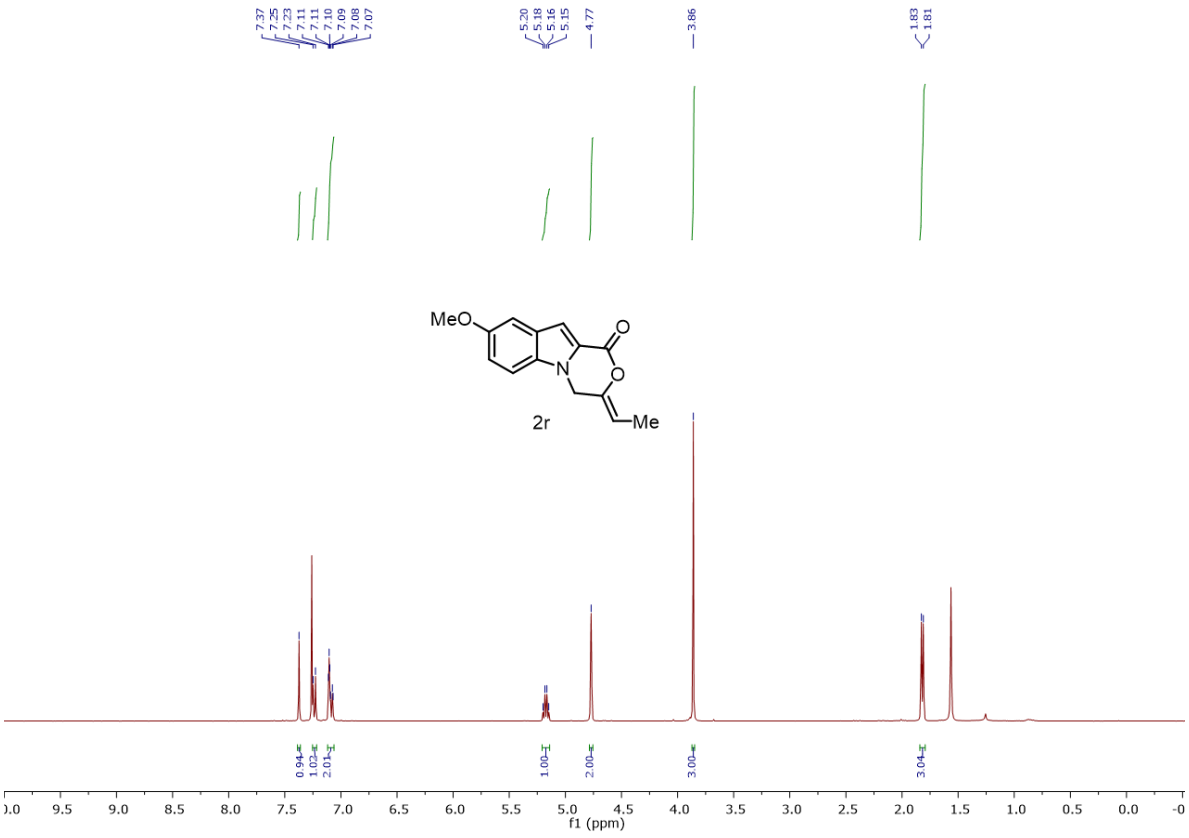
^{1}H NMR of **2q** (400 MHz, $CDCl_3$)



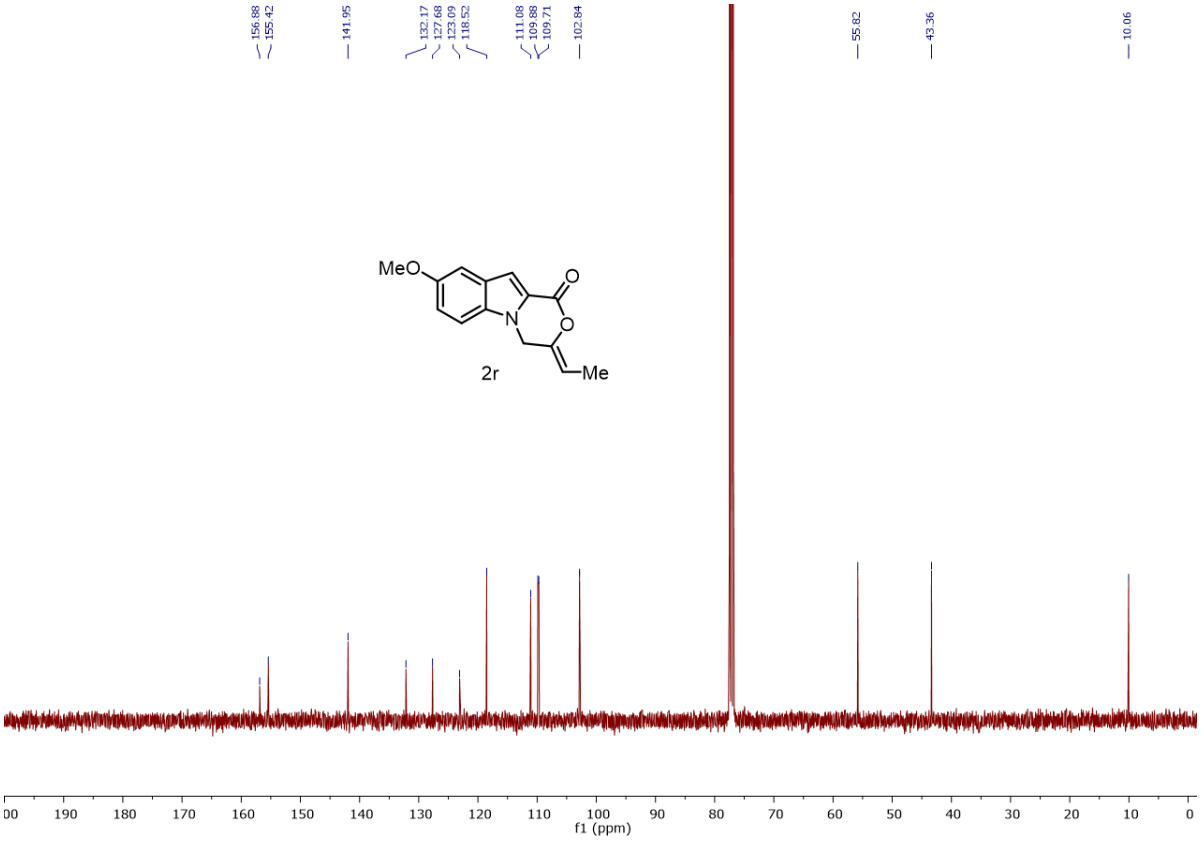
$^{13}C\{1H\}$ NMR of **2q** (101 MHz, $CDCl_3$)



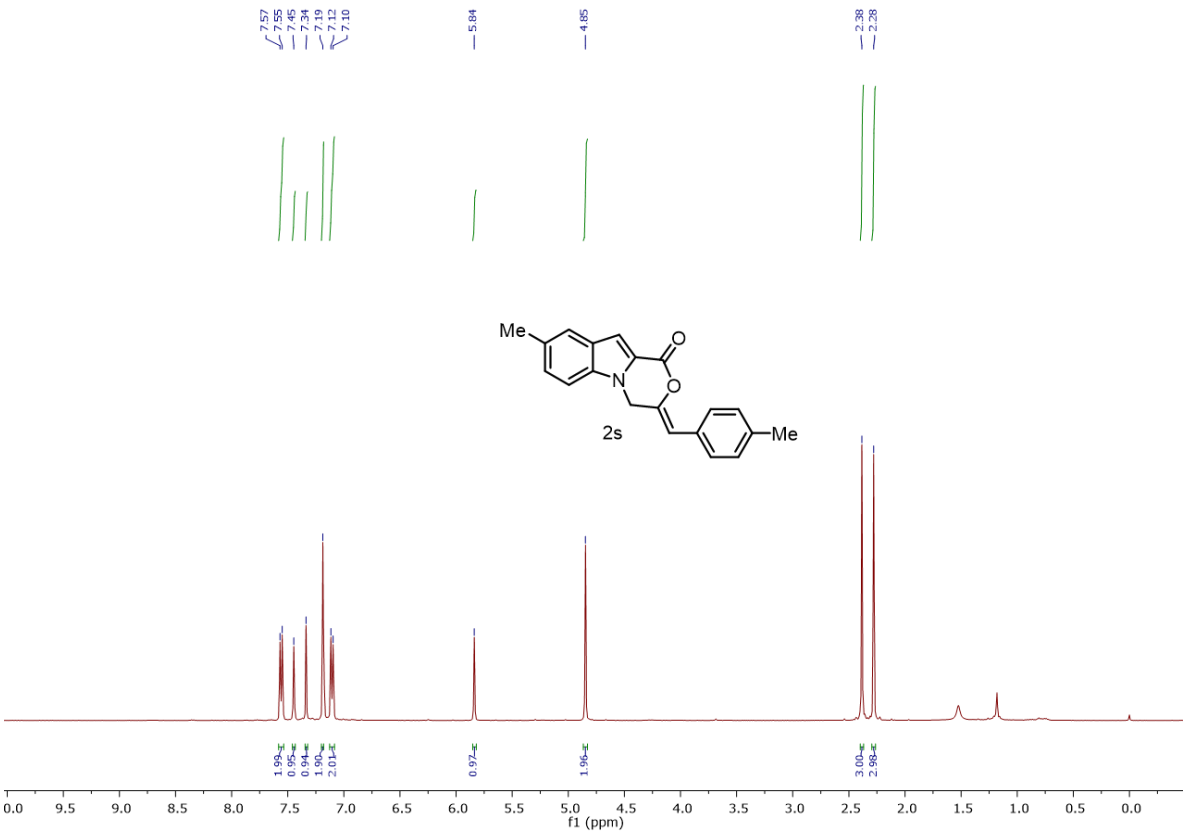
^{1}H NMR of **2r** (400 MHz, $CDCl_3$)



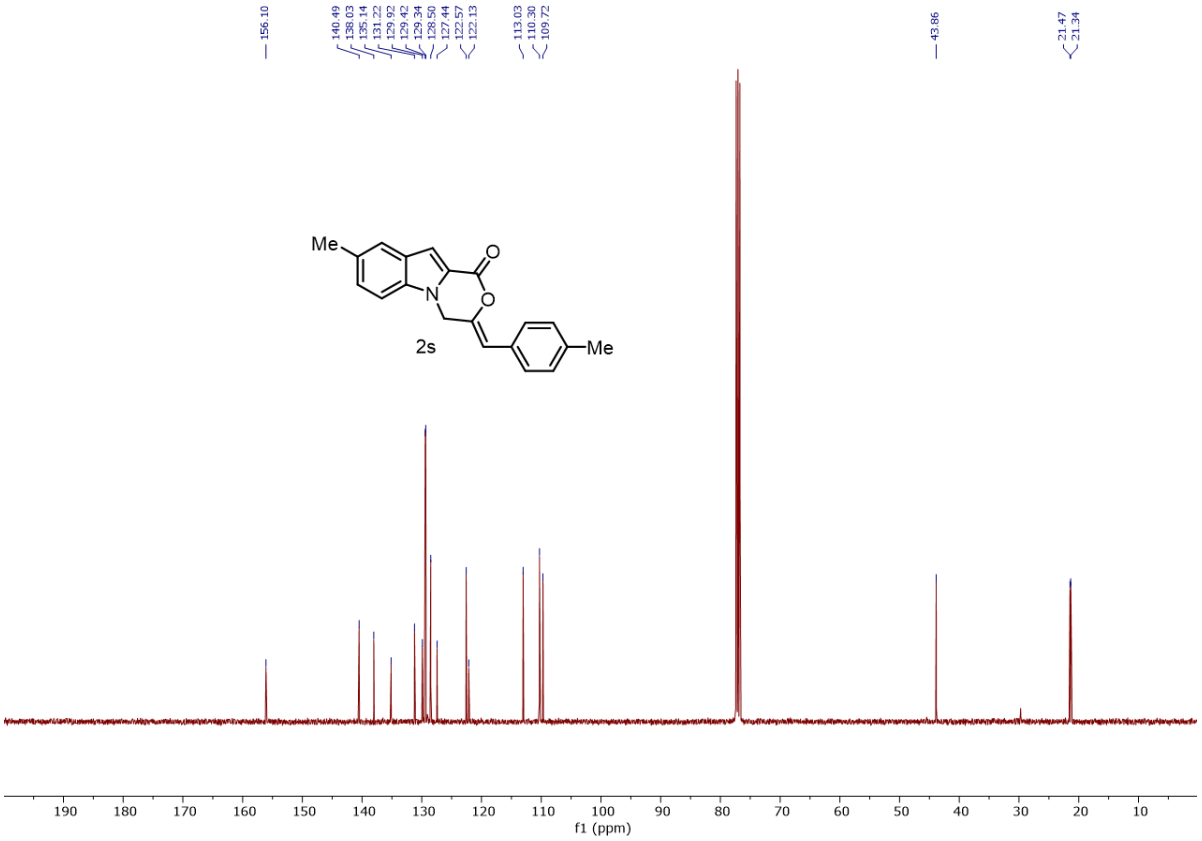
$^{13}C\{1H\}$ NMR of **2r** (101 MHz, $CDCl_3$)



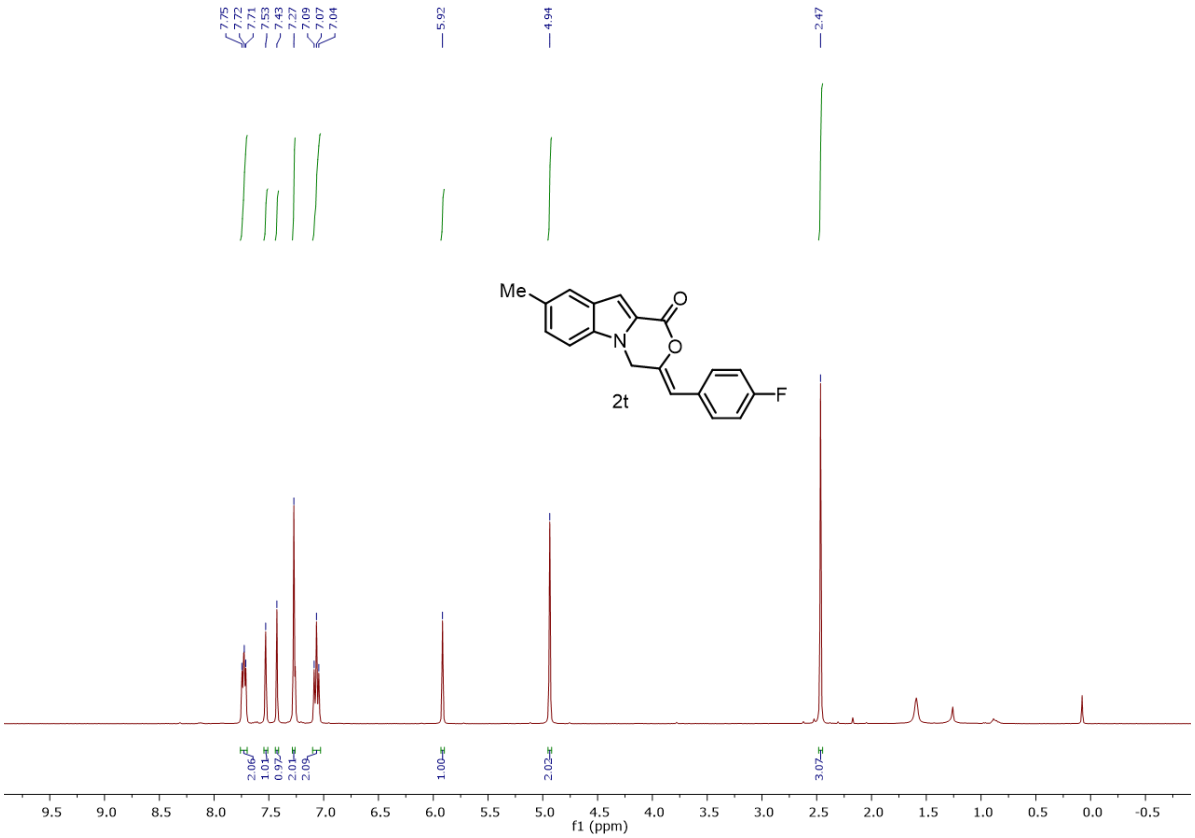
^{1}H NMR of **2s** (400 MHz, $CDCl_3$)



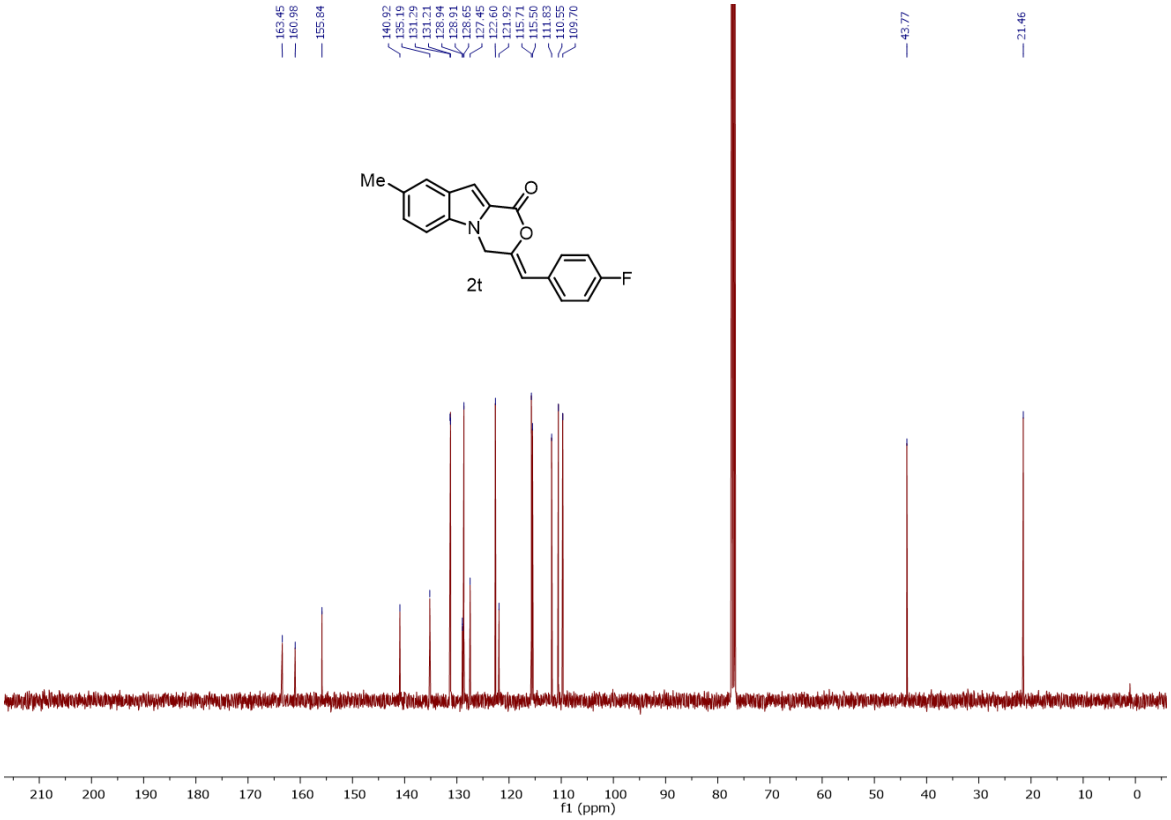
$^{13}C\{1H\}$ NMR of **2s** (101 MHz, $CDCl_3$)



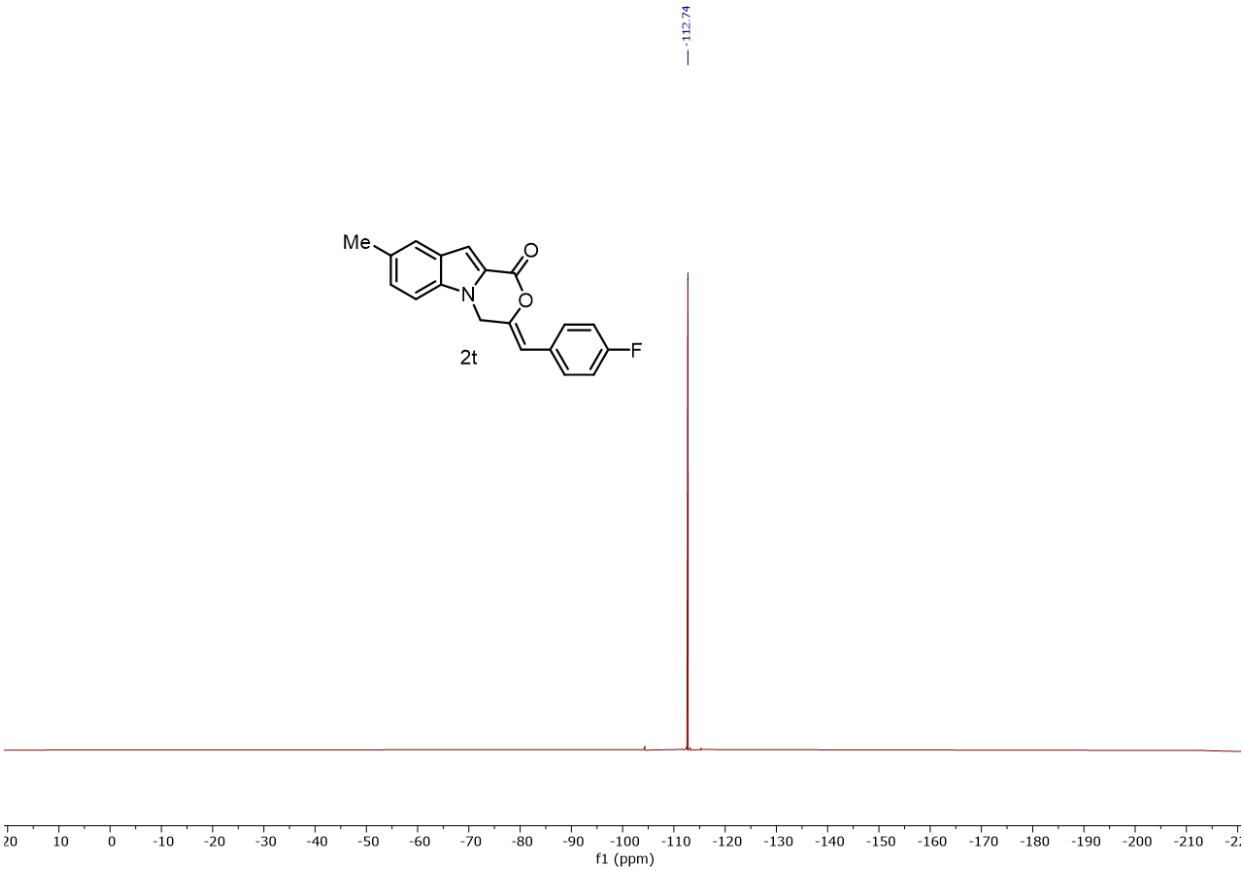
^{1}H NMR of **2t** (400 MHz, $CDCl_3$)



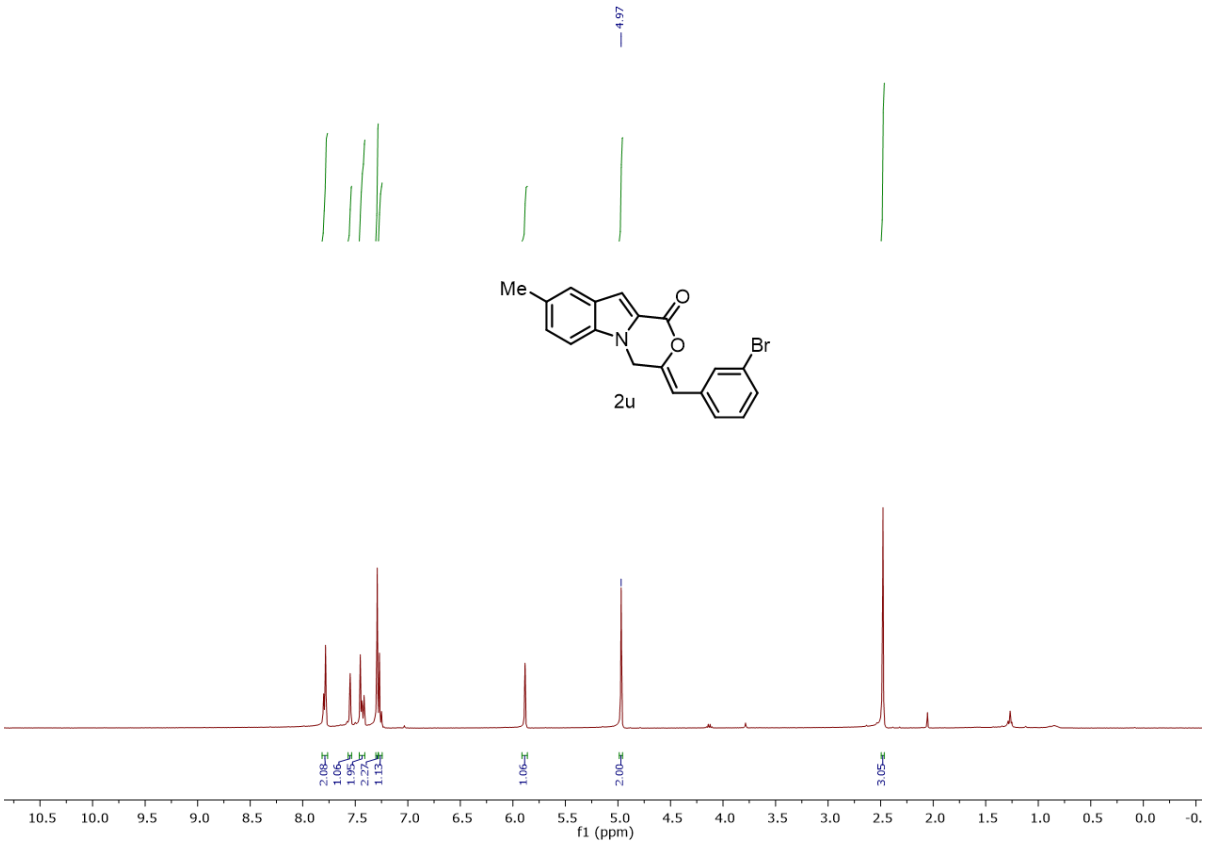
$^{13}C\{1H\}$ NMR of **2t** (101 MHz, $CDCl_3$)



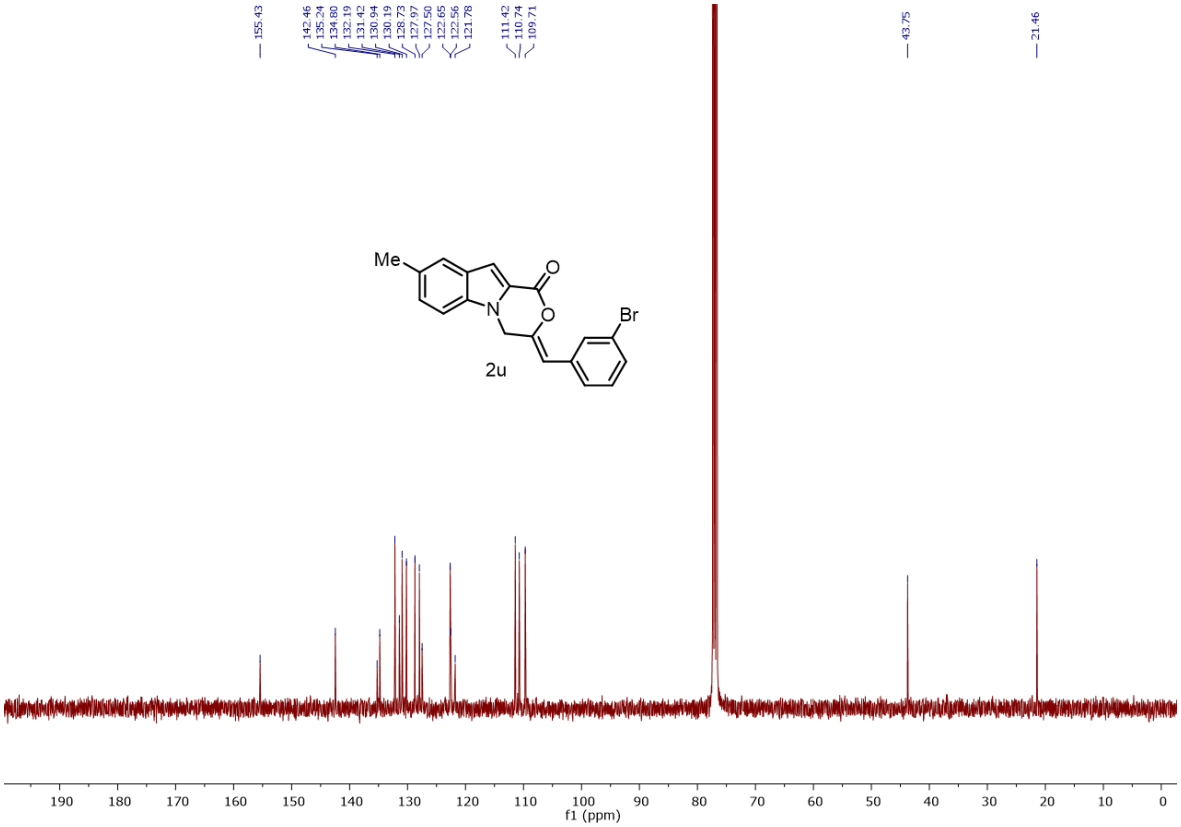
^{19}F NMR of **2t** (376 MHz, $CDCl_3$)



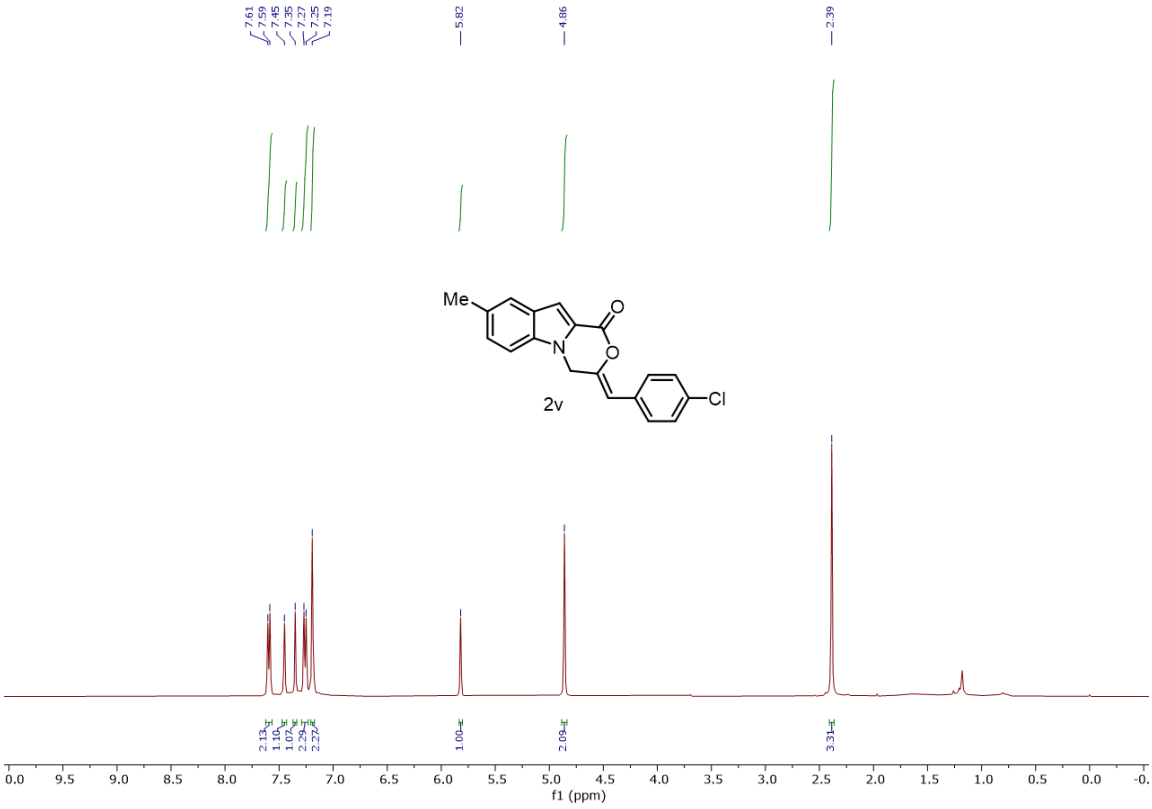
^{1}H NMR of **2u** (400 MHz, $CDCl_3$)



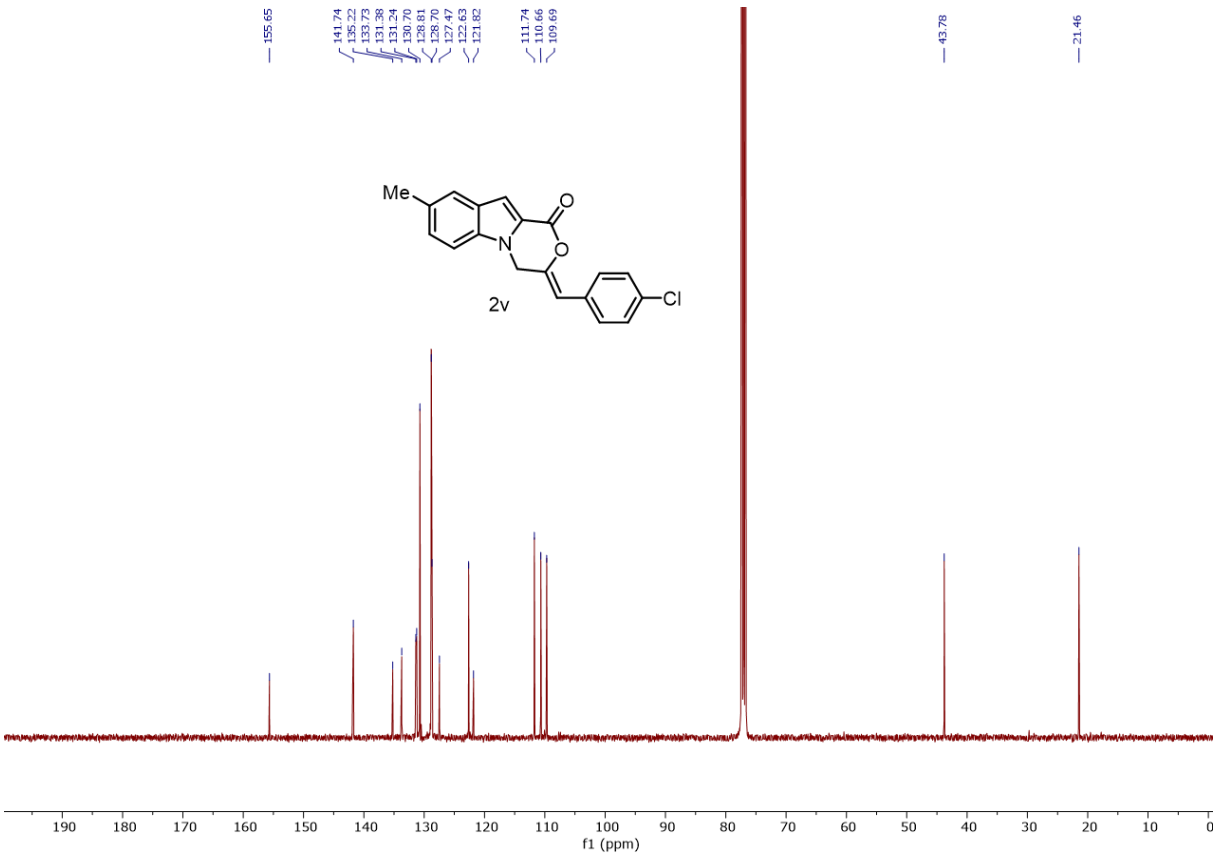
^{13}C{1H} NMR of **2u** (101 MHz, $CDCl_3$)



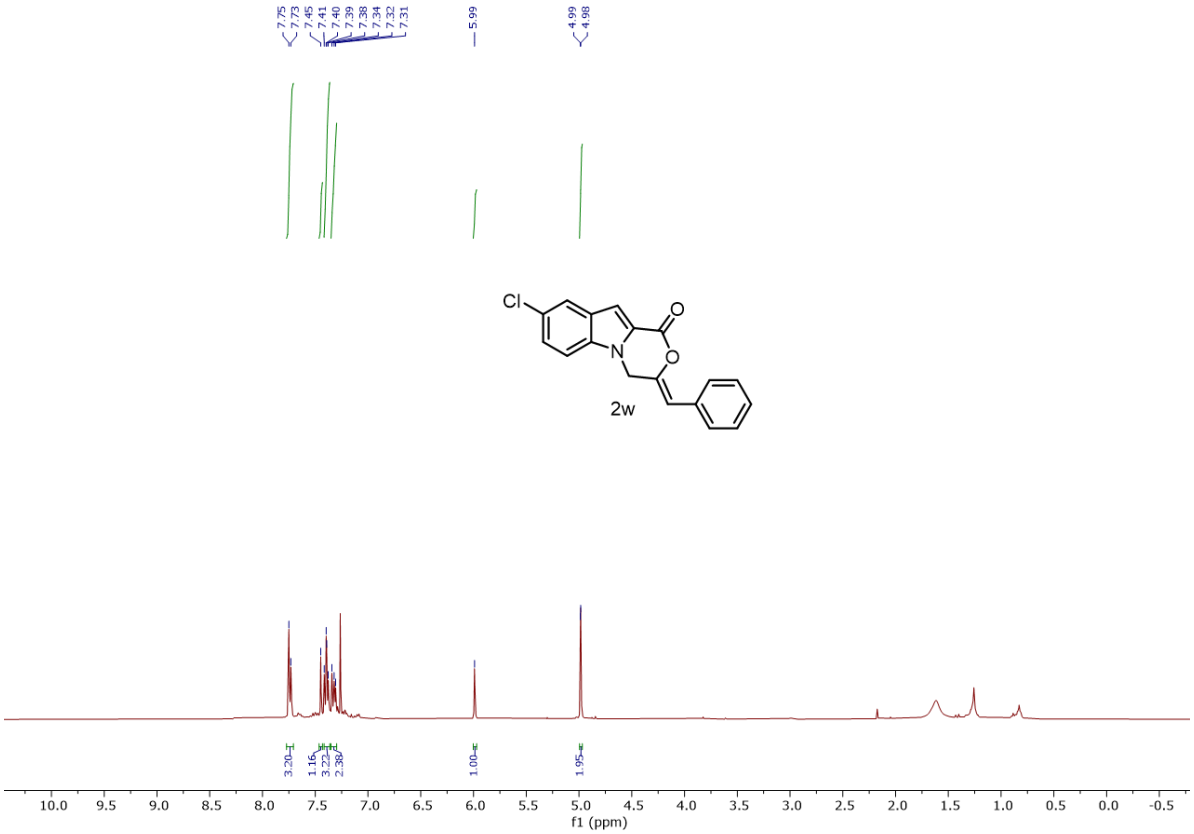
^{1}H NMR of **2v** (400 MHz, $CDCl_3$)



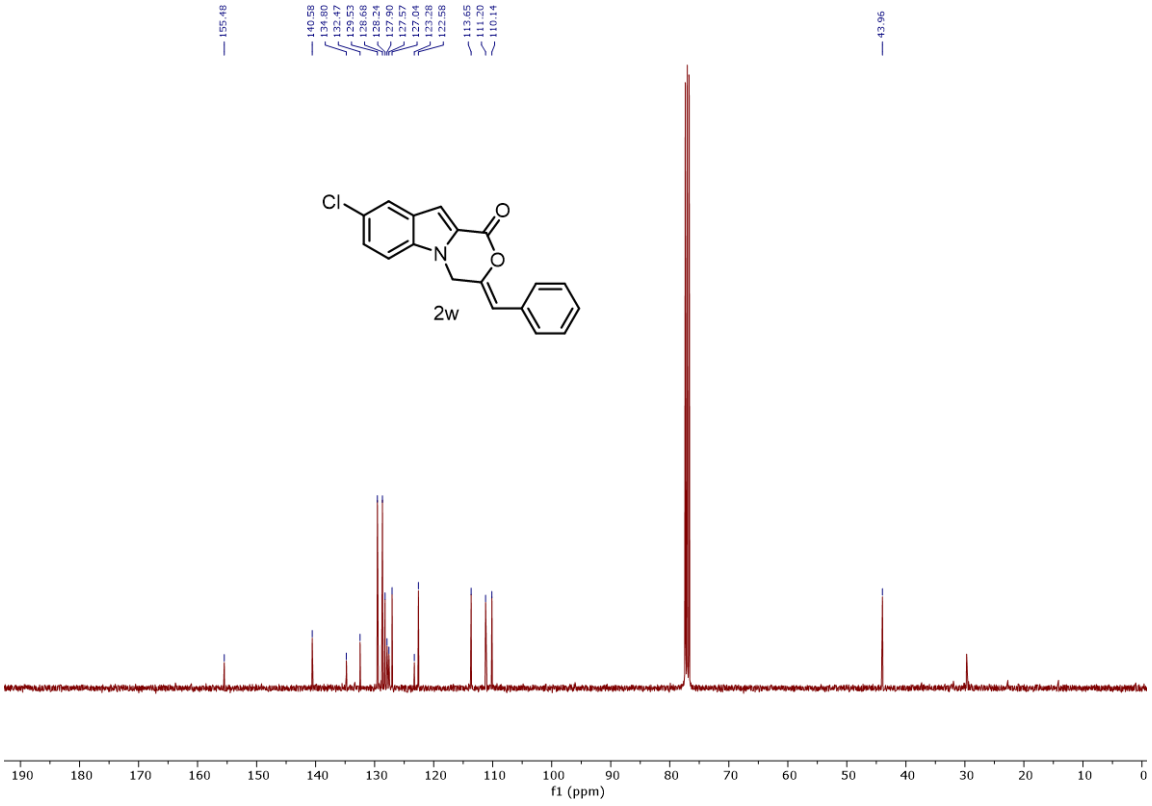
^{13}C{1H} NMR of **2v** (101 MHz, $CDCl_3$)



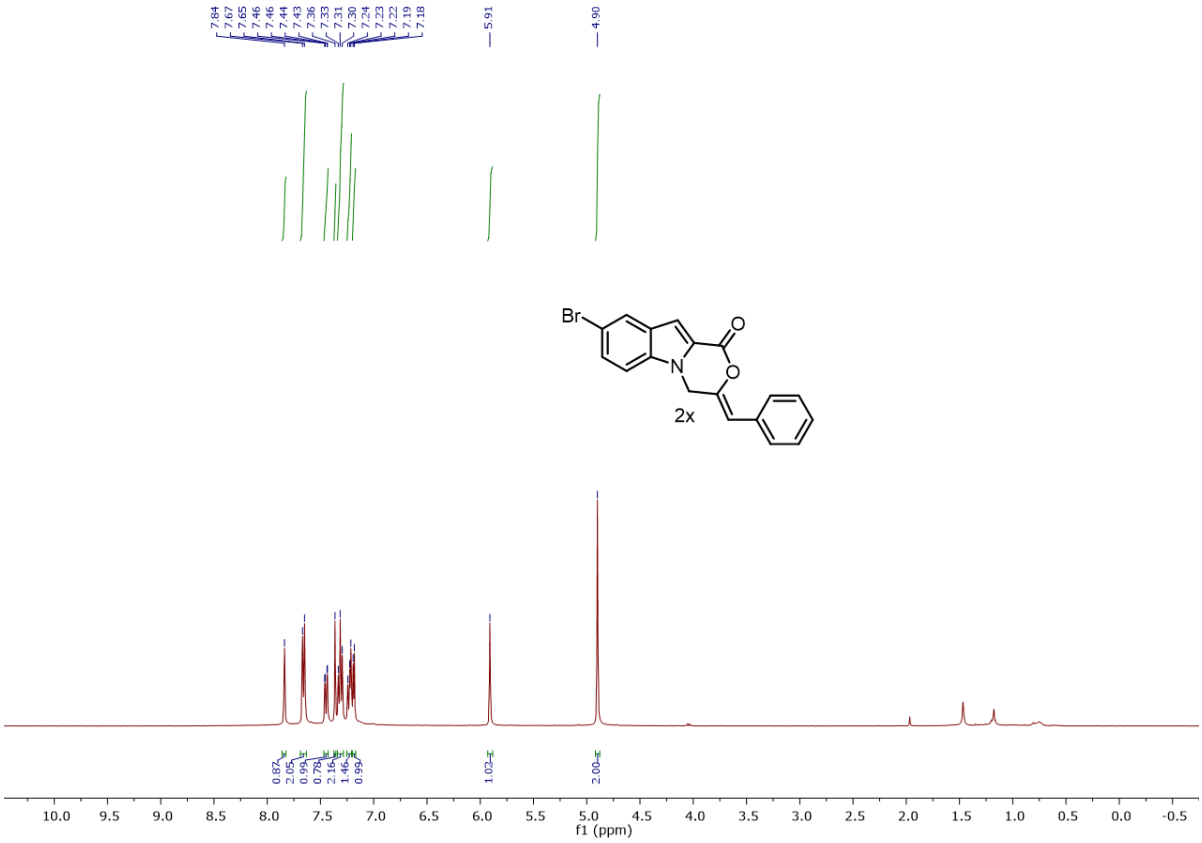
^{1}H NMR of **2w** (400 MHz, $CDCl_3$)



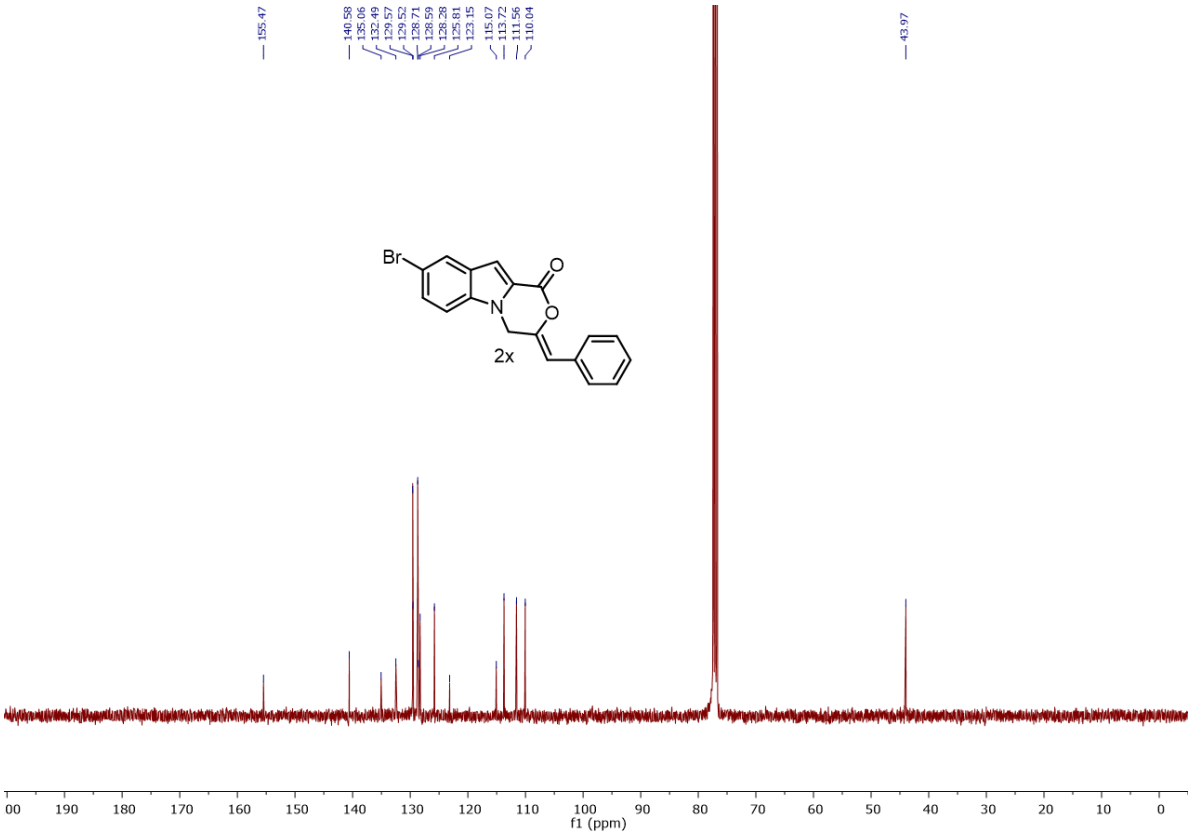
^{13}C{1H} NMR of **2w** (101 MHz, $CDCl_3$)



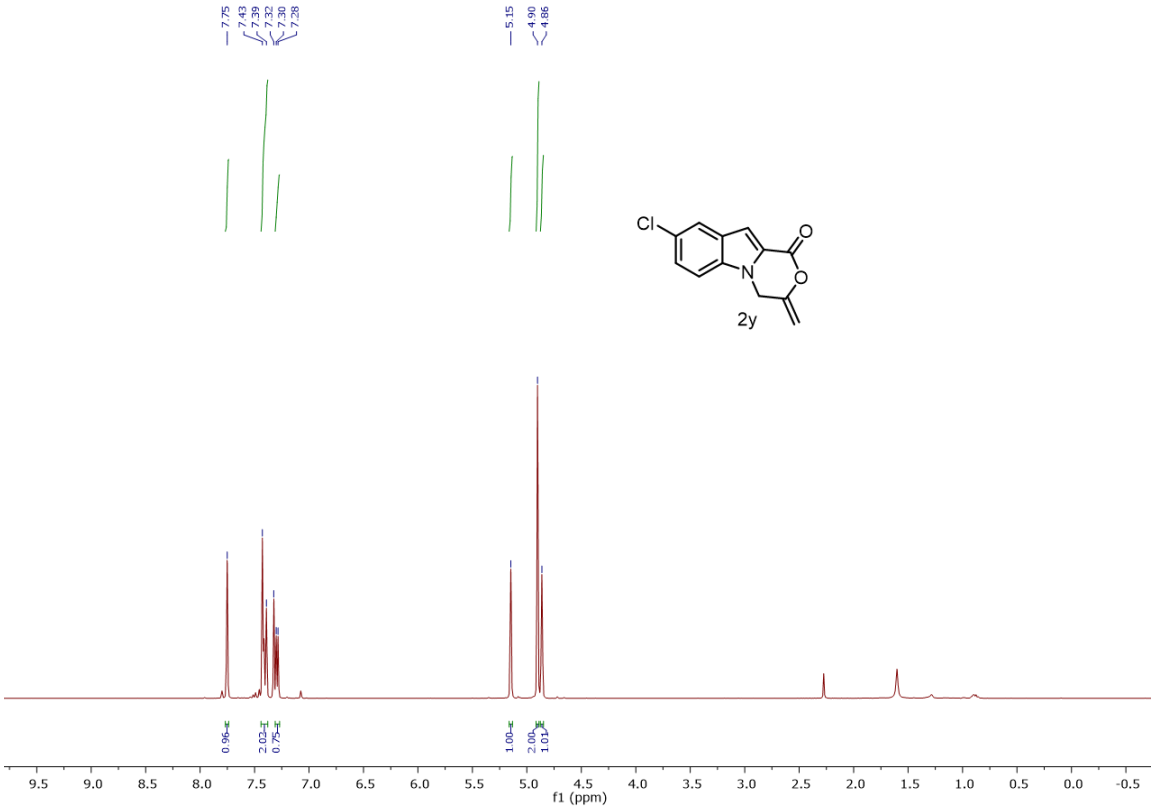
^{1}H NMR of **2x** (400 MHz, $CDCl_3$)



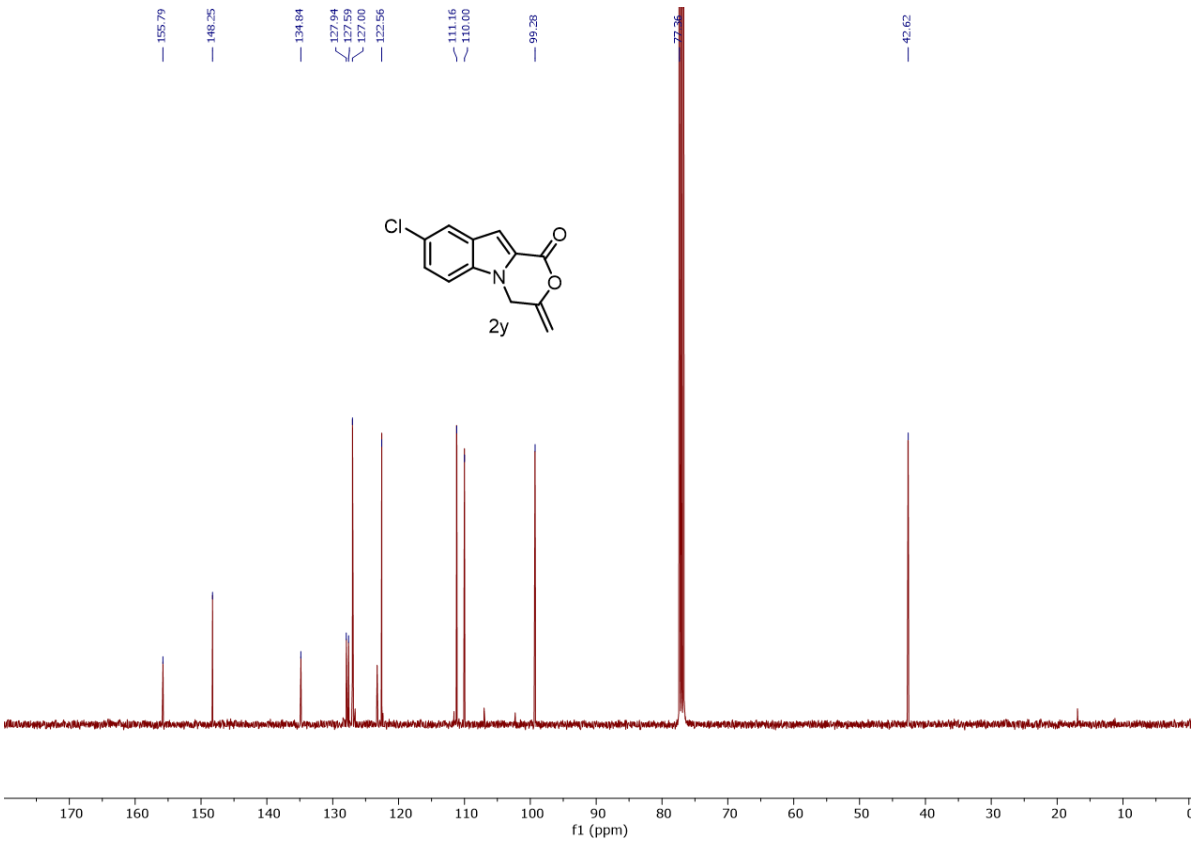
^{13}C{1H} NMR of **2x** (101 MHz, $CDCl_3$)



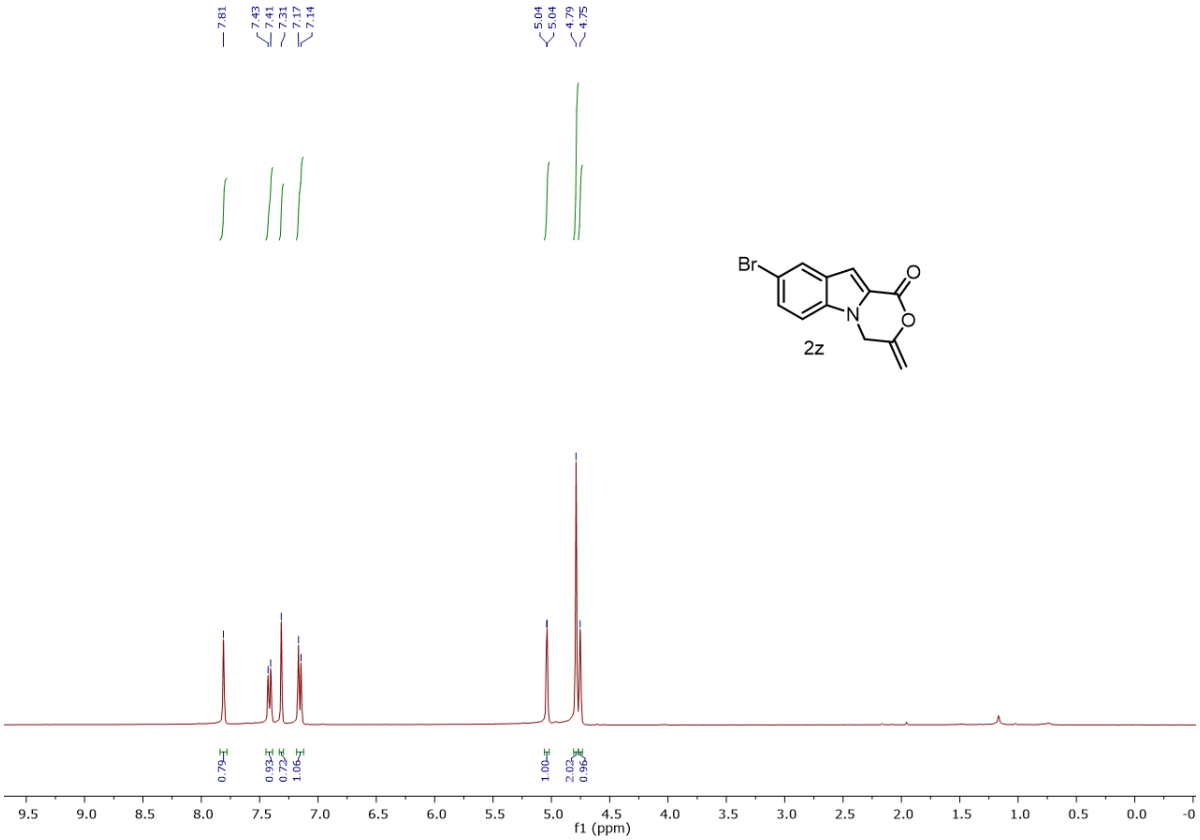
^{1}H NMR of **2y** (400 MHz, $CDCl_3$)



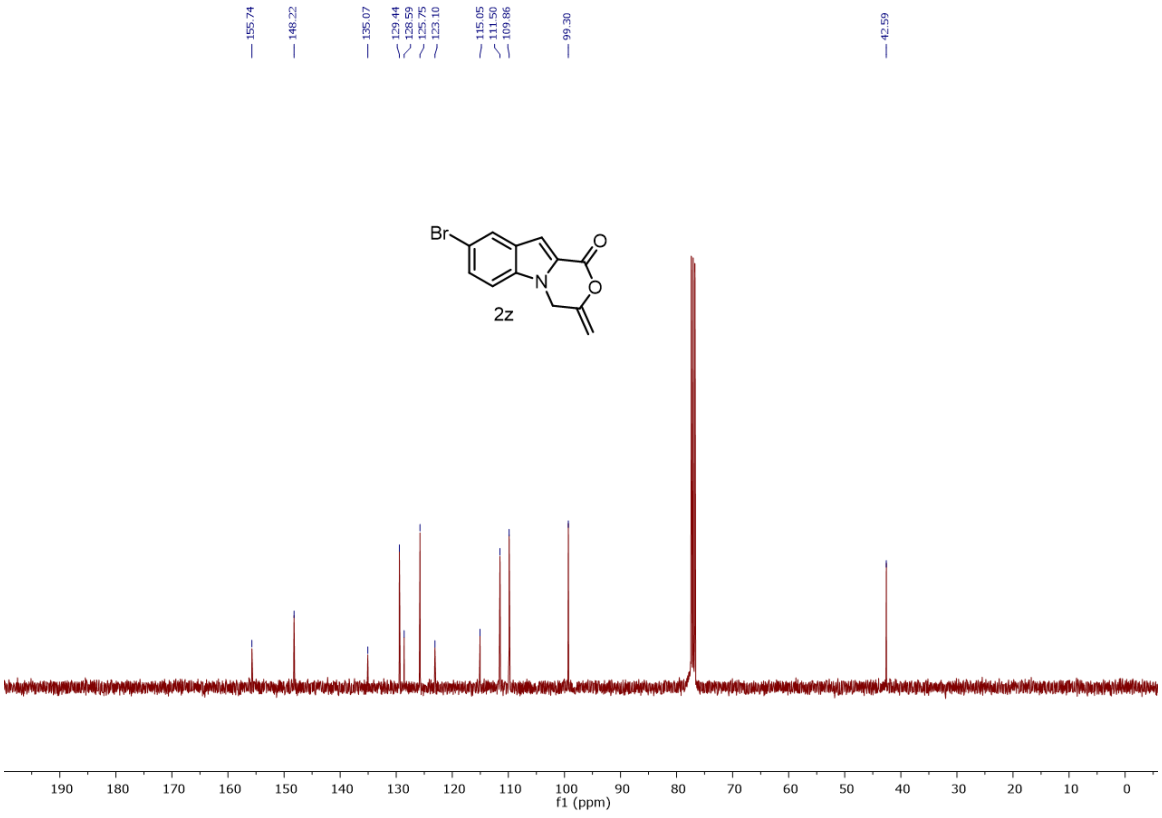
^{13}C{1H} NMR of **2y** (101 MHz, $CDCl_3$)



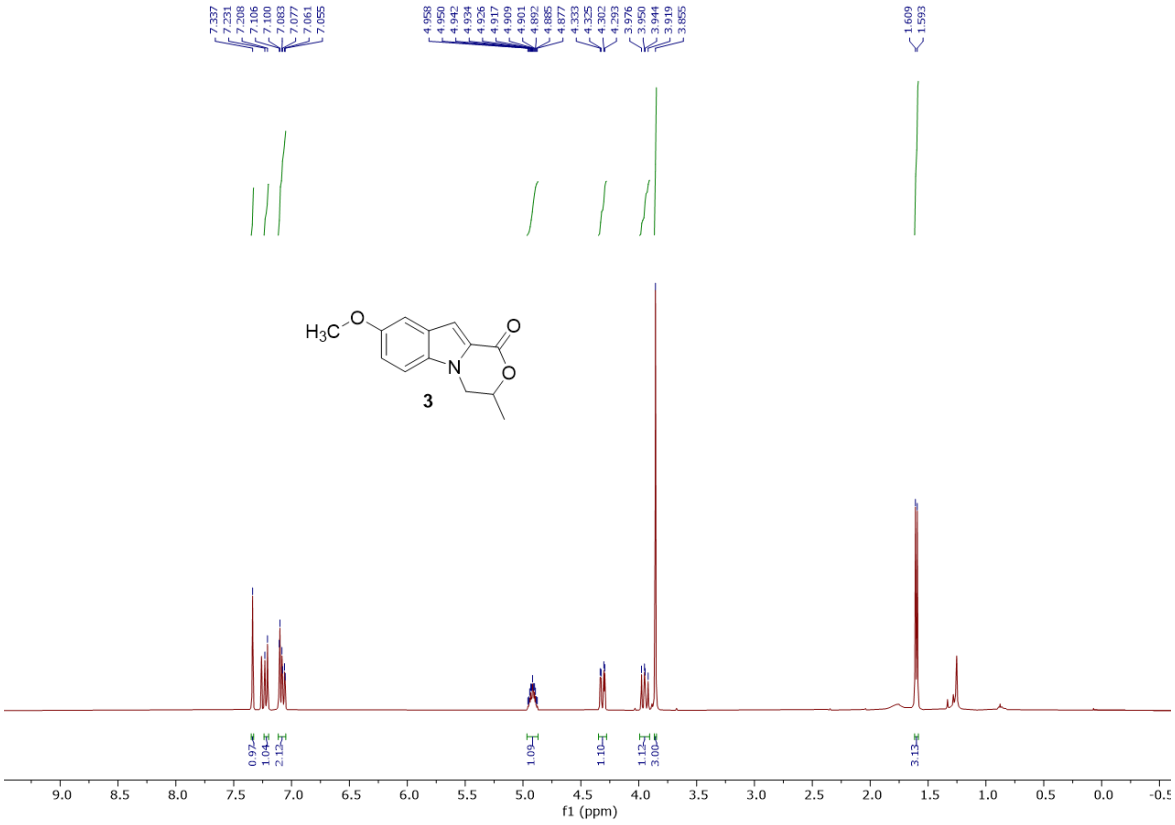
^{1}H NMR of **2z** (400 MHz, $CDCl_3$)



^{13}C{1H} NMR of **2z** (101 MHz, $CDCl_3$)



^{1}H NMR of **3** (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of **3** (101 MHz, $CDCl_3$)