Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rh(III)-Catalyzed Regioselective Versatile Indole Derivatization:

Delivering Potential of Rare β-(1*H*-Indol-2-yl)-β-Amino Acids in One Pot

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Table of Contents

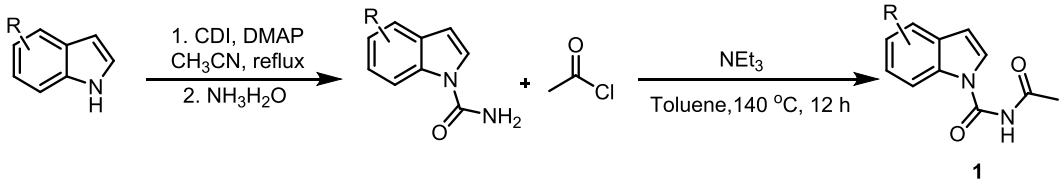
1. General Information

Catalytic reactions were carried out in Schlenk tubes using pre-dried glassware. Acrylates (2) were synthesized according to previously described procedures[1]. Commercially available reagents were purchased from Energy Chemical, Bidepharm, Sigma Aldrich, Alfa Aesar, Acros or TCI, and used without purification unless otherwise noted. Column chromatography purification was performed using 200–300 mesh silica gel. NMR spectra were mostly recorded for ^{1}H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. $CDCl_3$ and DMSO-d_6 were used as solvents. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$: ^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm; DMSO-d_6: ^{1}H NMR: δ 2.50 ppm, ^{13}C NMR: δ 39.52 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). HRMS was performed on Agilent Technologies 6224 TOF LC/MS apparatus (ESI).

2. Experimental Section

2.1 Substrates Preparation

2.1.1 Preparation of *N*-acetyl-1*H*-indole-1-carboxamide derivatives (Method A)

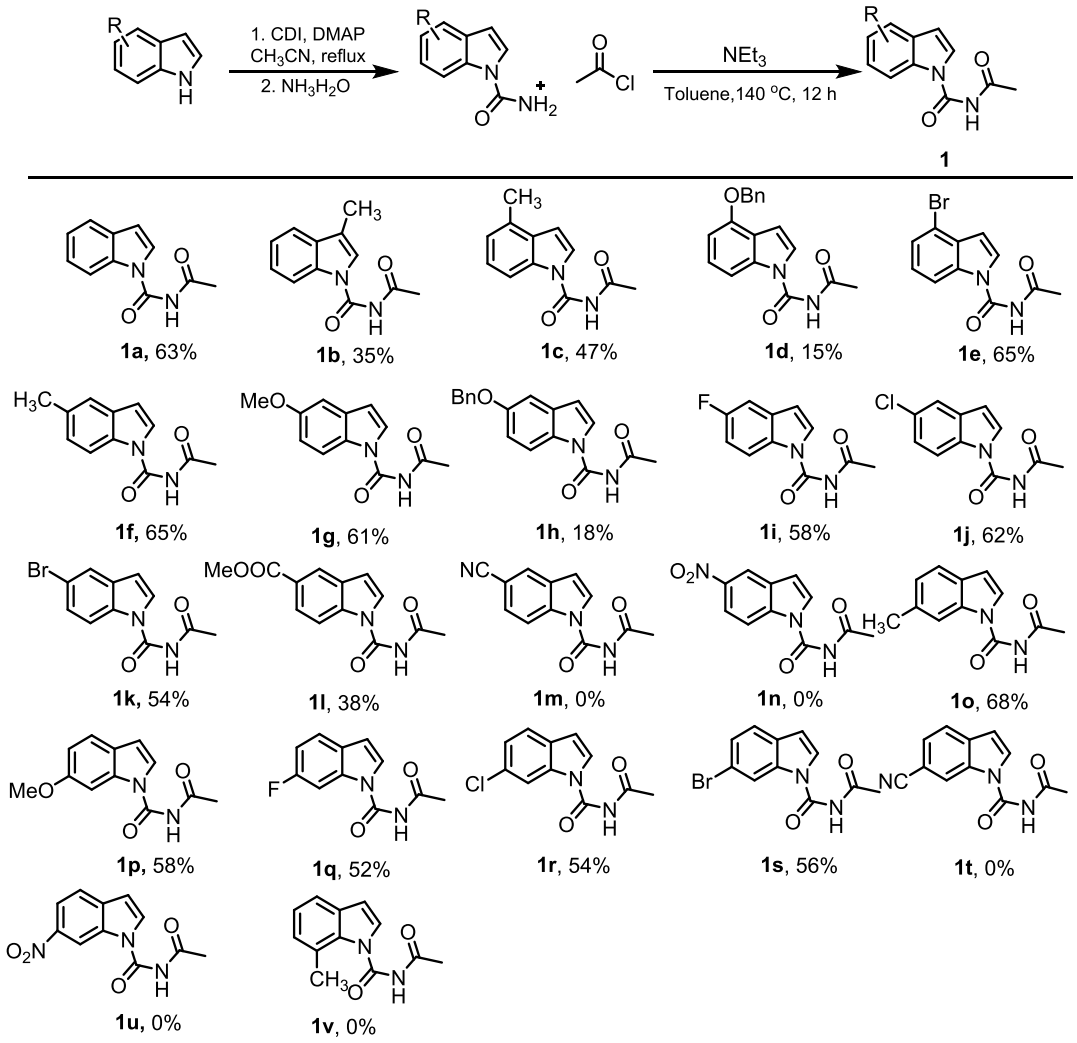


1

Step 1: A reaction tube (100 mL) with magnetic stir bar was charged with indole (5.0 mmol, 1.0 equiv.), 1,1'-carbonyldiimidazole (CDI, 7.5 mmol, 1.5 equiv.) and 4-dimethylaminepyridine (DMAP, 5.0 mol%). Then 25 mL anhydrous acetonitrile was added to the reaction tube. The reaction system was stirred at 85 °C oil bath for 10 h. After cooling to room temperature, ammonium hydroxide (15.0 mmol) was added and then the reaction was stirred at 60 °C oil bath for another 6 h until most of indole was consumed by TLC detection. Then the reaction was cooled to room temperature and the reaction mixture was poured in 70 mL water and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine and dried over sodium sulphate. The solvent was removed under reduced pressure, and the solid obtained

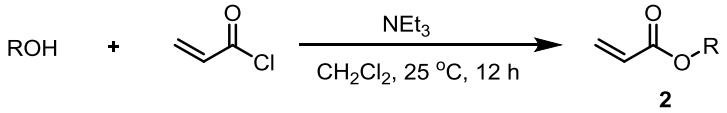
was washed with ether to remove excess complexes to afford white 1*H*-indole-1-carboxamide.

Step 2: A reaction tube (100 mL) with magnetic stir bar was charged with 1*H*-indole-1-carboxamide (5.0 mmol, 1.0 equiv.), NEt_3 (15.0 mmol, 3.0 equiv.) and acetyl chloride (10.0 mmol, 2.0 equiv.). Then 20 mL anhydrous toluene was added to the reaction tube. The reaction system was stirred at 140 ^{o}C oil bath for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to afford **1**.



Scheme S1 Preparation of substrates **1**.

2.1.2 Preparation of acrylate derivatives (Method B)[1]



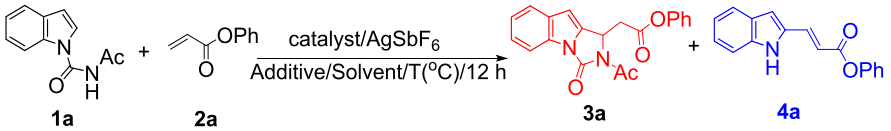
Alcohol or phenol derivative (3.0 mmol) was mixed with Et_3N (4.5 mmol) in dry CH_2Cl_2 (10 mL) and cooled to 0 °C in an ice-water bath. Then acryloyl chloride (3.6 mmol) was added dropwise. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PET: EtOAc = 30:1) to get the desired product (80–96% yield).

2.2 Preliminary Optimization of Reaction Conditions

Our initial studies began with *N*-acetyl-1*H*-indole-1-carboxamide (**1a**) and phenyl acrylate (**2a**) by screening a wide range of reaction parameters, including catalysts, solvents, additives, and temperature (Table S1). Treating **1a** with **2a** in the presence of 5 mol% of $[Cp^*RhCl_2]_2$, 30 mol% of $AgSbF_6$, and 1.5 equiv of NaOAc in MeOH at 45 ℃ for 12 h provided the desired C(sp^2)–H alkenylation–annulation product **3a** and alkenylation–elimination product **4a** with the yields of 21% and 28%, respectively (Table S1, entry 1). Changing the catalysts to $Cp^*Co(CO)I_2$ could also drive this alkenylation–annulation transformation with 8% yield (entry 2). Other catalyst such as $[Cp^*IrCl_2]_2$, $[Cp^*RuCl_2]_2$, and $Pd(OAc)_2$ failed to afforded **3a** and **4a** (entry 3–5). Next, we also screened the solvent and found that dichloroethane(DCE) could also drive this reaction with slightly lower yield (entry 6). Notably, replacing MeOH with 2,2,2-trifluoroethanol(TFE) boosted the yield of **3a** to 37%, while the yield of **4a** decreased to 7%, which identified TFE as the best solvent for **3a** formation (entry 7). Further screening of $AgSbF_6$ showed that 20 mol% of $AgSbF_6$ resulted in the similar yield of **3a** than 30 mol% of $AgSbF_6$ (entry 7–10). Entry 11 showed that absence of NaOAc also resulted in a decrease in the production of **3a**. Since $KHSO_4$ has been reported to benefit similar cyclizations[2], we replaced NaOAc with NaOAc/$KHSO_4$ and the yield of **3a** increased to 68% (entry 12). However, substituting $KHSO_4$ with $K_2S_2O_8$ resulted in a slight decrease in the production of **3a** (entry 13)**.** Further temperature screening showed that the yield of **3a** increased to 85% at 60 ℃ (entry 14), and a slight decrease was observed when the temperature continuously increased to 80 ℃ (entry 15). Interestingly, simple substitution of NaOAc (entry 1)

with CsOAc (entry 16) in MeOH resulted in a slightly decreased yield of **3a** and a significantly increased yield of **4a** to 57%. Next, we also tested the reaction temperature for **4a** formation, which indicated that 80 ℃ was the best choice for alkenylation–elimination of **1a** (entries 17 and 18).

Table S1. Optimization of Reaction Conditions of 3a and 4a[a]



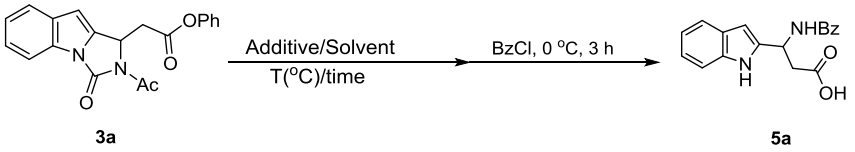
1a **2a** **3a** **4a**

entry	catalyst(mol%)	solvent	additive	T (°C)	yield (%)[b]	
					3a	4a
1	$[Cp^*RhCl_2]_2$	MeOH	$AgSbF_6$/NaOAc	45	21	28
2	$Cp^*Co(CO)I_2$	MeOH	$AgSbF_6$/NaOAc	45	8	<5
3	$[Cp^*IrCl_2]_2$	MeOH	$AgSbF_6$/NaOAc	45	<5	<5
4	$[Cp^*RuCl_2]_2$	MeOH	$AgSbF_6$/NaOAc	45	<5	<5
5	$Pd(OAc)_2$	MeOH	NaOAc	45	<5	<5
6	$[Cp^*RhCl_2]_2$	DCE	$AgSbF_6$/NaOAc	45	19	20
7	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$/NaOAc	45	37	7
8[c]	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$/NaOAc	45	36	<5
9[d]	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$/NaOAc	45	25	<5
10	$[Cp^*RhCl_2]_2$	TFE	NaOAc	45	<5	<5
11	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$	45	8	<5
12	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$/NaOAc/$KHSO_4$	45	68	<5
13	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$/NaOAc/$K_2S_2O_8$	45	57	10
14	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$/NaOAc/$KHSO_4$	60	85	<5
15	$[Cp^*RhCl_2]_2$	TFE	$AgSbF_6$/NaOAc/$KHSO_4$	80	72	12
16	$[Cp^*RhCl_2]_2$	MeOH	$AgSbF_6$/CsOAc	45	18	57
17	$[Cp^*RhCl_2]_2$	MeOH	$AgSbF_6$/CsOAc	60	13	68
18	$[Cp^*RhCl_2]_2$	MeOH	$AgSbF_6$/CsOAc	80	8	76

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $AgSbF_6$ (0.06 mmol), additive (0.3 mmol), and solvent (1 mL). [b]Isolated yield. [c] $AgSbF_6$ (0.04 mmol). [d] $AgSbF_6$ (0.02 mmol).

Our studies began with **3a** by screening a wide range of reaction parameters, including solvents, additives, temperature and reaction time (Table S2). The results showed that treating **3a** with KOH in THF/H_2O at 130 °C for 6 h are the most favorable condition for **5a** production.

Table S2. Optimization of Reaction Conditions of 5a[a]



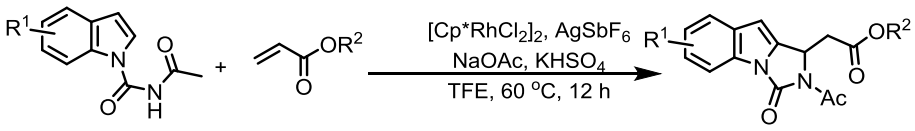
3a 5a

entry	solvent	additive	T (°C)	time	yield (%)[b]
1	THF/H_2O	K_2CO_3	110	3 h	<5
2	THF/H_2O	NaOH	110	3 h	12
3	THF/H_2O	KOH	110	3 h	18
4	MeOH/H_2O	KOH	110	3 h	8
5	MeCN/H_2O	KOH	110	3 h	<5
6	THF/H_2O	KOH	90	3 h	<5
7	THF/H_2O	KOH	130	3 h	46
8	THF/H_2O	KOH	130	6 h	67
9	THF/H_2O	KOH	130	12 h	68

[a]Reaction conditions: **3a** (0.2 mmol), KOH (0.6 mmol), H_2O (1.0 mL), and other solvent; then BzCl (0.50 mmol) was added and reacted at 0 °C for 3 h. [b]Isolated yield.

2.3 General Procedures

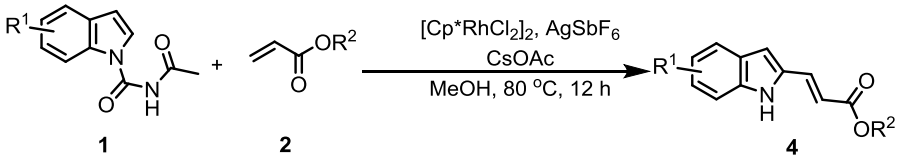
2.3.1 Preparation of alkenylation–annulation products 3 (GP1)



1 2 3

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-acetyl amide substituted indole **1** (0.20 mmol), acrylate **2** (0.60 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 0.010 mmol), $AgSbF_6$ (21 mg, 0.060 mmol), NaOAc (25 mg, 0.30 mmol), $KHSO_4$ (41 mg, 0.30 mmol) and TFE (1.0 mL). The reaction was allowed to stir at 60 °C oil bath for 12 h. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired products **3**.

2.3.2 Preparation of alkenylation–elimination products 4 (GP2)



1 2 4

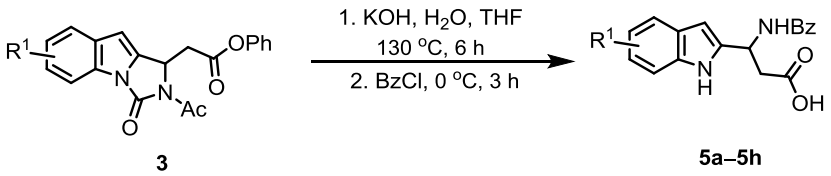
A reaction tube (10 mL) with magnetic stir bar was charged with *N*-acetyl amide substituted indole **1** (0.20 mmol), acrylate **2** (0.60 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 0.010 mmol), $AgSbF_6$ (21 mg, 0.060 mmol), CsOAc (57 mg, 0.30 mmol) and MeOH (1.0 mL). The reaction was allowed to stir at 80 °C oil bath for 12 h. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired products **4**.

2.3.3 Preparation of 3-benzamido-3-(1*H*-indol-2-yl)propanoic acid products 5a–5h (GP3)

1 2 5a–5h

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-acetyl amide substituted indole **1** (0.20 mmol), acrylate **2a** (89 mg, 0.60 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 0.010 mmol), $AgSbF_6$ (21 mg, 0.060 mmol) , NaOAc (25 mg, 0.30 mmol), $KHSO_4$ (41 mg, 0.30 mmol) and TFE (1.0 mL). The reaction was allowed to stir at 60 °C oil bath for 12 h. After cooling to room temperature, KOH (56 mg, 1.0 mmol), H_2O (1.0 mL), and THF (2.0 mL) was added and the reaction was stirred at 130 °C oil bath for another 3 h. After cooling to room temperature, BzCl (71 mg, 0.50 mmol) was added and then the reaction was stirred at 0 °C for another 3 h. Then the reaction was poured in 20 mL 0.5 M HCl and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, and collected organic layers were dried over sodium sulphate. The solvent was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (CH_2Cl_2/MeOH) to afford the desired products **5a–5d**, **5g**, **5h**. However, substrates **1** with electron-withdrawing fluorine and chlorine groups couldn't afford the corresponding **5e** and **5f**.

2.3.4 Preparation of products 5a–5h from 3 (GP4)



3 **5a–5h**

A reaction tube (10 mL) with magnetic stir bar was charged with 3 (0.20 mmol) KOH (56 mg, 1.0 mmol), H_2O (1.0 mL), and THF (2.0 mL) was added and the reaction was stirred at 130 °C oil bath for another 6 h. After cooling to room temperature, BzCl (71 mg, 0.50 mmol) was added and then the reaction was stirred at 0 °C for another 3 h. Then the reaction was poured in 10 mL 0.5 M HCl and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, and collected organic layers were dried over sodium sulphate. The solvent was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (CH_2Cl_2/MeOH) to afford the desired products **5a–5h**. However, **3y** and **3z** with electron-withdrawing fluorine and chlorine groups couldn't afford the corresponding **5e** and **5f**.

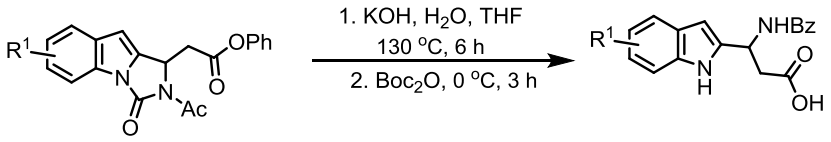
2.3.5 Preparation of 3-Boc-3-(1*H*-indol-2-yl)propanoic acid products 5i–5k (GP5)

1 **2** **5i–5k**

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-acetyl amide substituted indole **1** (0.20 mmol), acrylate **2a** (89 mg, 0.60 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 0.010 mmol), $AgSbF_6$ (21 mg, 0.060 mmol), NaOAc (25 mg, 0.30 mmol), $KHSO_4$ (41 mg, 0.30 mmol) and TFE (1.0 mL). The reaction was allowed to stir at 60 °C oil bath for 12 h. After cooling to room temperature, KOH (56 mg, 1.0 mmol), H_2O (1.0 mL), and THF (2.0 mL) was added and the reaction was stirred at 130 °C oil bath for another 3 h. After cooling to room temperature, Boc_2O (109 mg, 0.50 mmol) was added and then the reaction was stirred at 0 °C for another 3 h. Then the reaction was poured in 30 mL 0.3 M HCl and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, and collected organic layers were dried over sodium sulphate.

The solvent was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (CH_2Cl_2/MeOH) to afford the desired products **5i** and **5j**. However, substrate **1** with electron-withdrawing fluorine group couldn't afford the corresponding **5k**.

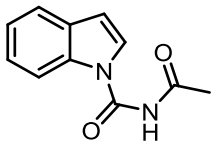
2.3.6 Preparation of products 5i–5k from 3 (GP6)



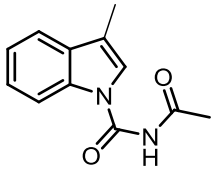
3 **5i–5k**

A reaction tube (10 mL) with magnetic stir bar was charged with 3 (0.20 mmol) KOH (56 mg, 1.0 mmol), H_2O (1.0 mL), and THF (2.0 mL) was added and the reaction was stirred at 130 °C oil bath for another 6 h. After cooling to room temperature, Boc_2O (109 mg, 0.50 mmol) was added and then the reaction was stirred at 0 °C for another 3 h. Then the reaction was poured in 30 mL 0.3 M HCl and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, and collected organic layers were dried over sodium sulphate. The solvent was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (CH_2Cl_2/MeOH) to afford the desired products **5i** and **5j**. However, **3y** with electron-withdrawing fluorine group couldn't afford the corresponding **5k**.

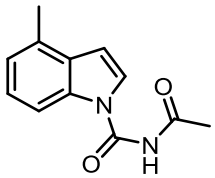
3. Characterization Data



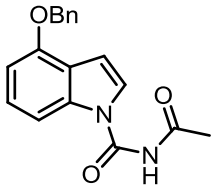
***N*-Acetyl-1*H*-indole-1-carboxamide (1a):** The title compound was obtained as a white soild (636 mg) in 63% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.99 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 3.5 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.32 (td, J = 7.5, 1.5 Hz, 1H), 7.27−7.24 (m, 1H), 6.73 (dd, J = 3.5, 0.5 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.7, 148.7, 135.3, 130.2, 126.0, 124.2, 123.1, 120.9, 115.2, 107.4, 24.9; HRMS (ESI) m/z calcd. for $C_{11}H_{11}N_2O_2$ $[M+H]^+$ 203.0815, found 203.0819.



***N*-Acetyl-3-methyl-1*H*-indole-1-carboxamide (1b):** The title compound was obtained as a white soild (378 mg) in 35% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.83 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 1.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.34−7.31 (m, 1H), 7.27 (dt, J = 7.5, 1.0 Hz, 1H), 2.32 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.5, 148.5, 135.5, 131.0, 124.4, 122.9, 122.8, 119.1, 116.0, 115.2, 24.8, 9.3; HRMS (ESI) m/z calcd. for $C_{12}H_{13}N_2O_2$ $[M+H]^+$ 217.0952, found 217.0953.

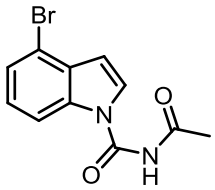


***N*-Acetyl-4-methyl-1*H*-indole-1-carboxamide (1c):** The title compound was obtained as a white soild (508 mg) in 47% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.97 (s, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 3.5 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.78 (d, J = 4.0 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.7, 148.7, 135.1, 123.0, 129.8, 125.4, 124.3, 123.4, 112.8, 106.0 , 24.9, 18.1; HRMS (ESI) m/z calcd. for $C_{12}H_{13}N_2O_2$ $[M+H]^+$ 217.0952, found 217.0958.

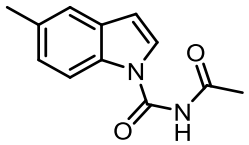


***N*-Acetyl-4-(benzyloxy)-1*H*-indole-1-carboxamide (1d):** The title compound was obtained as a white soild (231 mg) in 15% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.48 (d, J = 7.0 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.36−7.32 (m, 2H), 7.29 (t, J = 7.5 Hz, 1H), 6.90 (dd, J = 4.0, 1.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 5.22 (s, 2H), 2.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.7, 152.6, 137.6, 136.8, 128.8, 128.2, 127.5, 126.5, 125.4, 122.0, 108.2, 107.2, 105.6, 70.3, 25.0; HRMS (ESI) m/z calcd. for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ 309.1234,

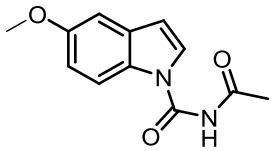
found 309.1238.



***N*-Acetyl-4-bromo-1*H*-indole-1-carboxamide (1e):** The title compound was obtained as a white soild (586 mg) in 65% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.10 (s, 1H), 8.21 (dt, *J* = 8.5, 1.0 Hz, 1H), 8.02 (d, *J* = 4.0 Hz, 1H), 7.48 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 6.69 (dd, *J* = 8.5, 1.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 148.6, 135.7, 130.4, 127.3, 125.8, 125.6, 114.7, 113.7, 106.4, 24.9; HRMS (ESI) m/z calcd. for $C_{11}H_{10}BrN_2O_2$ $[M+H]^+$ 280.9920, found 280.9923.

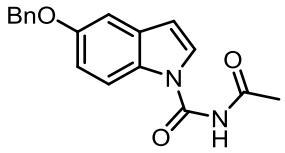


***N*-Acetyl-5-methyl-1*H*-indole-1-carboxamide (1f):** The title compound was obtained as a white soild (702 mg) in 65% yield according to the **Method A**.^{1}H NMR (500 MHz, DMSO-d_6): δ 10.93 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.39 (d, *J* = 1.5 Hz, 1H), 7.14 (dd, *J* = 3.5, 1.5 Hz, 1H), 6.65 (d, *J* = 4.0 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 148.6, 133.5, 132.0, 130.4, 126.6, 125.5, 120.7, 114.9, 107.2, 24.9, 20.9; HRMS (ESI) m/z calcd. for $C_{12}H_{13}N_2O_2$ $[M+H]^+$ 217.0952, found 217.0948.

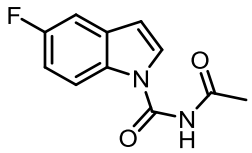


***N*-Acetyl-5-methoxy-1*H*-indole-1-carboxamide (1g):** The title compound was obtained as a white soild (707 mg) in 61% yield according to the **Method A**.^{1}H NMR (500 MHz, DMSO-d_6): δ 10.92 (s, 1H), 8.08 (d, *J* = 9.5 Hz, 1H), 7.88 (d, *J* = 3.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.65 (d, *J* = 4.0 Hz, 1H), 3.79 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 155.7, 148.5, 131.1, 129.9, 126.4, 115.9, 112.9, 107.5, 103.5, 55.3, 24.9; HRMS (ESI) m/z calcd.

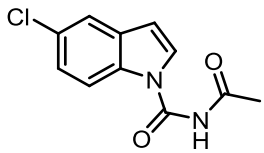
for $C_{12}H_{13}N_2O_3$ $[M+H]^+$ 233.0921, found 233.0918.



***N*-Acetyl-5-(benzyloxy)-1*H*-indole-1-carboxamide (1h):** The title compound was obtained as a white soild (277 mg) in 18% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.93 (s, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 4.0 Hz, 1H), 7.46 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 3.0 Hz, 2H), 7.33 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 2.5 Hz, 1H), 7.01 (dd, J = 9.0, 2.5 Hz, 1H), 6.65 (d, J = 3.5 Hz, 1H), 5.14 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 154.7, 137.2, 131.1, 130.0, 128.3, 127.7, 127.6, 126.5, 125.7, 116.0, 113.6, 107.4, 104.8, 69.6, 24.9; HRMS (ESI) m/z calcd. for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ 309.1234, found 309.1231.

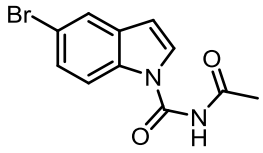


***N*-Acetyl-5-fluoro-1*H*-indole-1-carboxamide (1i):** The title compound was obtained as a white soild (638 mg) in 58% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.02 (s, 1H), 8.21−8.18 (m, 1H), 7.99 (d, J = 3.5 Hz, 1H), 7.43 (dd, J = 9.0, 2.5 Hz, 1H), 7.19−7.15 (m, 1H), 6.72 (d, J = 4.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 158.6 (d, J = 236 Hz), 148.6, 131.8, 131.2 (d, J = 10 Hz), 127.8, 116.4 (d, J = 10 Hz), 111.8 (d, J = 25 Hz), 107.2 (d, J = 5 Hz), 106.3 (d, J = 24 Hz), 24.89; HRMS (ESI) m/z calcd. for $C_{11}H_{10}FN_2O_2$ $[M+H]^+$ 221.0721, found 221.0729.

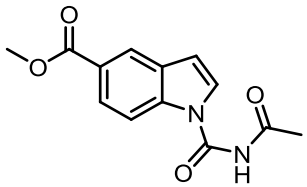


***N*-Acetyl-5-chloro-1*H*-indole-1-carboxamide (1j):** The title compound was obtained as a white soild (732 mg) in 62% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.04 (s, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 3.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.34 (dd, J = 9.0, 2.0 Hz, 1H), 6.71 (d, J = 3.5 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 148.5, 133.8,

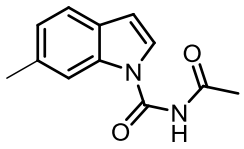
131.6, 127.6, 127.4, 124.1, 120.3, 116.6, 106.7, 24.9; HRMS (ESI) *m/z* calcd. for $C_{11}H_{10}ClN_2O_2$ $[M+H]^+$ 237.0425, found 237.0421.



***N*-Acetyl-5-bromo-1*H*-indole-1-carboxamide (1k):** The title compound was obtained as a white soild (732 mg) in 54% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.04 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 4.0 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.71 (d, *J* = 2.35 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 148.5, 134.1, 132.1, 127.4, 126.7, 123.4, 117.0, 115.5, 106.6, 24.9; HRMS (ESI) *m/z* calcd. for $C_{11}H_{10}BrN_2O_2$ $[M+H]^+$ 280.9920, found 280.9924.

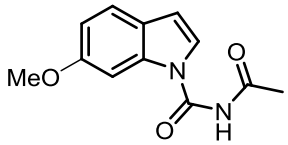


Methyl-1-(acetylcarbamoyl)-1*H*-indole-5-carboxylate (1l): The title compound was obtained as a white soild (494 mg) in 38% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.10 (s, 1H), 8.29–8.27 (m, 2H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.93 (dd, *J* = 9.0, 1.0 Hz, 1H), 6.87 (d, *J* = 1.5 Hz, 1H), 3.87 (s, 3H), 2.36 (s, 3H) ; ^{13}C NMR (125 MHz, DMSO-d_6): δ 200.1,176.4, 166.4, 153.0, 143.6, 127.7, 125.0, 124.4, 122.8, 115.2, 107.8, 52.0, 25.0; HRMS (ESI) m/z calcd. for $C_{13}H_{13}N_2O_4$ $[M+H]^+$ 261.0870, found 261.0878.

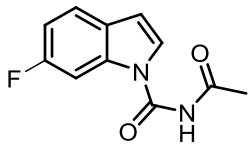


***N*-Acetyl-6-methyl-1*H*-indole-1-carboxamide (1o):** The title compound was obtained as a white soild (734 mg) in 68% yield according to the **Method A**.^{1}H NMR (500 MHz, DMSO-d_6): δ 10.94 (s, 1H), 8.04 (s, 1H), 7.81 (d, *J* = 4.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 4.0 Hz, 1H), 2.43 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.7, 148.8, 135.7,

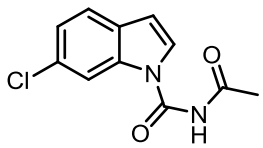
133.6, 127.9, 125.3, 124.5, 120.5, 115.4, 107.4, 24.9, 21.5; HRMS (ESI) m/z calcd. for $C_{12}H_{13}N_2O_2$ $[M+H]^+$ 217.0952, found 217.0944.



***N*-Acetyl-6-methoxy-1*H*-indole-1-carboxamide (1p):** The title compound was obtained as a white soild (672 mg) in 58% yield according to the **Method A**.^{1}H NMR (500 MHz, DMSO-d_6): δ 11.94 (s, 1H), 7.80−7.78 (m, 2H), 7.49 (d, J = 8.5 Hz, 1H), 6.90 (dd, J = 8.5, 2.5 Hz, 1H), 6.64 (d, J = 4.5 Hz, 1H), 3.80 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.7, 157.2, 148.9, 136.3, 124.6, 123.8, 121.4, 112.0, 107.4, 99.6, 55.3, 24.9; HRMS (ESI) m/z calcd. for $C_{12}H_{13}N_2O_3$ $[M+H]^+$ 233.0921, found 233.0928.

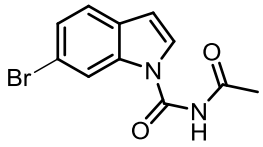


***N*-Acetyl-5-fluoro-1*H*-indole-1-carboxamide (1q):** The title compound was obtained as a white soild (572 mg) in 52% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.02 (s, 1H), 7.96−7.93 (m, 2H), 7.64 (dd, J = 8.5, 5.5 Hz, 1H), 7.16−7.12 (m, 1H), 6.74 (d, J = 4.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.7, 159.9 (d, J = 236 Hz), 148.8, 135.4 (d, J = 13 Hz) , 126.7, 126.5 (d, J = 4 Hz), 122.0 (d, J = 10 Hz), 111.1 (d, J = 24 Hz), 107.2, 102.2 (d, J = 28 Hz), 25.0; HRMS (ESI) m/z calcd. for $C_{11}H_{10}FN_2O_2$ $[M+H]^+$ 221.0721, found 221.0729.

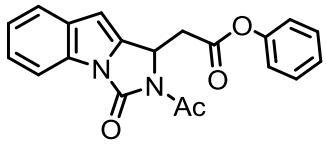


***N*-Acetyl-6-chloro-1*H*-indole-1-carboxamide (1r):** The title compound was obtained as a white soild (614 mg) in 52% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.05 (s, 1H), 8.22 (d, J = 2.0 Hz, 1H), 7.95 (d, J = 4.0 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.30 (dd, J = 8.0, 2.0 Hz, 1H), 6.76 (dd, J = 4.0, 1.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.7, 148.6,

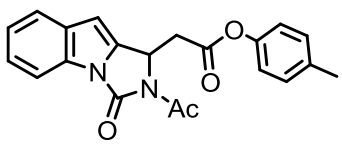
135.7, 129.0, 128.8, 127.0, 123.3, 122.3, 115.1, 107.2, 25.0; HRMS (ESI) *m/z* calcd. for $C_{11}H_{10}ClN_2O_2$ $[M+H]^+$ 237.0425, found 237.0428.



***N*-Acetyl-5-bromo-1*H*-indole-1-carboxamide (1s):** The title compound was obtained as a white soild (725 mg) in 52% yield according to the **Method A**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.05 (s, 1H), 8.21 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 4.0 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.31 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.76 (d, *J* = 3.50 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.7, 148.6, 135.6, 129.0, 128.8, 126.9, 123.3, 122.3, 115.1, 107.2, 25.0; HRMS (ESI) *m/z* calcd. for $C_{11}H_{10}BrN_2O_2$ $[M+H]^+$ 280.9920, found 280.9928.

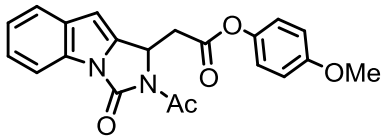


Phenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3a): The title compound was obtained as a white soild (59 mg) in 85% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.39−7.34 (m, 3H), 7.31 (td, *J* = 7.5, 1.0 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.51 (s, 1H), 5.68−5.65 (m, 1H), 3.69−3.65 (m, 1H), 3.12−3.06 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.4, 150.3, 148.4, 135.8, 133.9, 130.9, 129.7, 126.3, 124.4, 124.3, 121.7, 121.5, 113.2, 100.6, 51.9, 38.1, 24.6; HRMS (ESI) m/z calcd. for $C_{20}H_{17}N_2O_4$ $[M+H]^+$ 349.1183, found 349.1189.

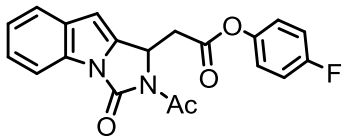


***p*-Tolyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3b):** The title compound was obtained as a white soild (62 mg) in 86% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.37−7.31 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.49 (s, 1H), 5.65−5.62 (m, 1H), 3.67−3.63 (m, 1H), 3.08−3.03 (m,

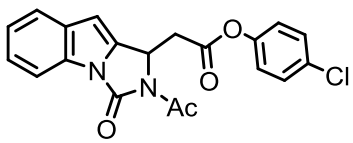
1H), 2.70 (s, 3H)，2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.6, 148.4, 148.0, 136.0, 135.8, 133.9, 130.8, 130.1, 124.3, 124.2, 121.7, 121.1, 113.1, 100.5, 51.8, 38.0, 24.6, 21.0; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ 363.1339, found 363.1334.



4-Methoxyphenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3c): The title compound was obtained as a white soild (68 mg) in 90% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.37−7.29 (m, 2H), 6.95 (dt, J = 8.5, 3.0 Hz, 2H), 6.87 (d, J = 8.5, 3.0 Hz, 2H), 6.49 (s, 1H), 5.67−5.63 (m, 1H), 3.79 (s, 3H), 3.67−3.62 (m, 1H), 3.09−3.04 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.8, 157.6, 148.4, 143.8, 135.9, 133.9, 130.8, 124.4, 124.3, 122.3, 121.7, 114.7, 113.2, 100.5, 55.7, 51.9, 38.1, 24.6; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_5$ $[M+H]^+$ 379.1288, found 379.1281.

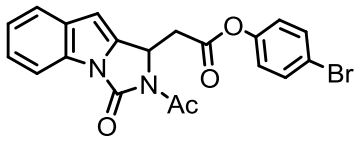


4-Fluorophenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3d): The title compound was obtained as a white soild (26 mg) in 36% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.38−7.30 (m, 2H), 7.07−6.99 (m, 4H), 6.49 (s, 1H), 5.67−5.64 (m, 1H), 3.66−3.62 (m, 1H), 3.12−3.06 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 168.5, 160.5 (d, J = 243 Hz), 148.4, 146.1 (d, J = 3 Hz), 135.7, 133.9, 130.9, 124.4 (d, J = 18 Hz), 130.0 (d, J = 8 Hz), 121.7, 116.5, 116.3, 113.2, 100.5, 51.8, 38.2, 24.6; HRMS (ESI) m/z calcd. for $C_{20}H_{16}FN_2O_4$ $[M+H]^+$ 367.1089, found 367.1092.

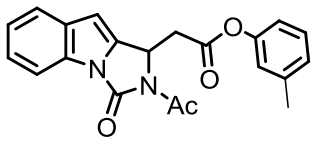


4-Chlorophenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3e): The title compound was obtained as a white soild (40 mg) in 53% yield according to the **GP1**. ^{1}H NMR

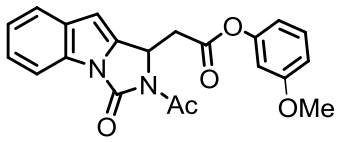
(500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.38−7.30 (m, 4H), 6.99 (dt, J = 8.5, 2.0 Hz, 2H), 6.49 (s, 1H), 5.67−5.64 (m, 1H), 3.66−3.62 (m, 1H), 3.12−3.07 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 168.2, 148.7, 148.4, 135.7, 133.8, 131.8, 130.8, 129.7, 124.5, 124.3, 122.9, 121.7, 113.2, 100.5, 51.8, 38.2, 24.6; HRMS (ESI) m/z calcd. for $C_{20}H_{16}ClN_2O_4$ $[M+H]^+$ 383.0793, found 383.0790.



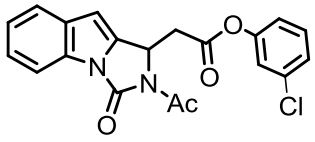
4-Bromophenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3f): The title compound was obtained as a white soild (55 mg) in 65% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.47 (dt, J = 9.0, 2.5 Hz, 2H), 7.38−7.30 (m, 2H), 6.95 (dt, J = 9.0, 2.5 Hz, 2H), 6.48 (s, 1H), 5.66−5.63 (m, 1H), 3.65−3.61 (m, 1H), 3.12−3.07 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 168.1, 149.3, 148.3, 135.7, 133.8, 132.7, 130.8, 124.5, 124.3, 123.3, 121.7, 119.5, 113.2, 100.5, 51.8, 38.2, 24.6; HRMS (ESI) m/z calcd. for $C_{20}H_{16}BrN_2O_4$ $[M+H]^+$ 427.0288, found 427.0282.



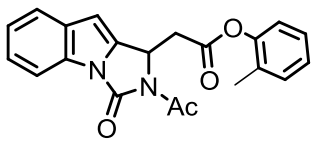
***m*-Tolyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3i):** The title compound was obtained as a white soild (59 mg) in 82% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.36−7.28 (m, 2H), 7.23 (d, J = 7.5 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.82 (d, J = 10.0 Hz, 1H), 6.79 (s, 1H), 6.49 (s, 1H), 5.65−5.62 (m, 1H), 3.66−3.61 (m, 1H), 3.10−3.05 (m, 1H), 2.69 (s, 3H)，2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.5, 150.2, 148.4, 139.9, 135.8, 133.9, 130.8, 129.3, 127.1, 124.4, 124.2, 122.0, 121.7, 118.4, 113.2, 100.5, 51.8, 38.0, 24.6, 21.4; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ 363.1339, found 363.1331.



3-Methoxyphenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3j): The title compound was obtained as a white soild (64 mg) in 84% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.37−7.30 (m, 2H), 7.26 (d, *J* = 8.5 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.64 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.54 (t, *J* = 7.0 Hz, 1H), 6.51 (s, 1H), 5.68−5.65 (m, 1H), 3.74 (s, 3H), 3.67−3.63 (m, 1H), 3.13−3.08 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 168.3, 160.7, 151.2, 148.4, 135.8, 133.9, 130.9, 130.1, 124.4, 124.3, 121.8, 113.7, 113.2, 112.2, 107.5, 100.6, 55.5, 51.9, 38.1, 24.7; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_5$ $[M+H]^+$ 379.1288, found 379.1284.

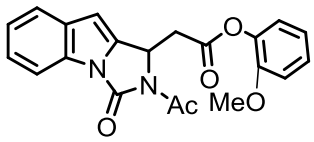


3-Chlorophenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3k): The title compound was obtained as a white soild (44 mg) in 58% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.38−7.28 (m, 3H), 7.24−7.21 (m, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 6.97−6.95 (m, 1H), 6.49 (t, *J* = 0.5 Hz, 1H), 5.66−5.63 (m, 1H), 3.66−3.62 (m, 1H), 3.12−3.07 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 168.0, 150.7, 148.3, 135.6, 134.9, 133.8, 130.8, 130.4, 126.6, 124.5, 124.3, 122.2, 121.8, 119.9, 113.2, 100.5, 51.8, 38.2, 24.6; HRMS (ESI) m/z calcd. for $C_{20}H_{16}ClN_2O_4$ $[M+H]^+$ 383.0793, found 383.0795.

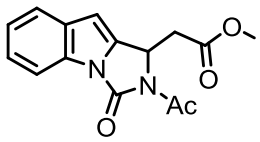


***o*-Tolyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3l):** The title compound was obtained as a white soild (55 mg) in 76% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.37−7.29 (m, 2H), 7.23−7.18 (m, 2H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 6.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.49 (d, *J* = 0.5 Hz, 1H), 5.64−5.61

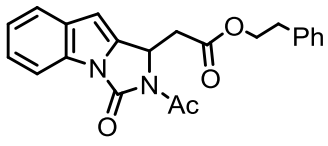
(m, 1H), 3.71−3.67 (m, 1H), 3.17−3.12 (m, 1H), 2.70 (s, 3H)，2.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.2, 149.0, 148.3, 135.9, 133.8, 131.3, 130.8, 130.0, 127.1, 126.5, 124.3, 124.2, 121.8, 121.6, 113.1, 100.4, 51.8, 37.5, 24.6, 16.2; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ 363.1339, found 363.1333.



2-Methoxyphenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3m): The title compound was obtained as a white soild (61 mg) in 81% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.37−7.29 (m, 2H), 7.22−7.19 (m, 1H), 7.26 (dd, J = 8.0, 1.5 Hz, 1H), 6.96−6.91 (m, 2H), 6.54 (s, 1H), 5.69−5.66 (m, 1H), 3.74 (s, 3H), 3.727−3.68 (m, 1H), 3.16−3.11 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 167.9, 156.0, 148.5, 139.4, 135.9, 134.0, 130.9, 127.4, 124.3, 124.2, 122.7, 121.6, 120.9, 113.2, 112.5, 100.6, 55.8, 51.9, 37.5, 24.7; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_5$ $[M+H]^+$ 379.1288, found 379.1281.

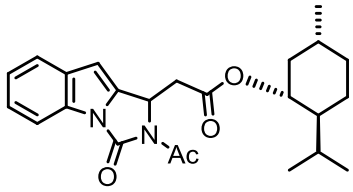


Methyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3n): The title compound was obtained as a white soild (59 mg) in 72% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.36−7.28 (m, 2H), 6.43−6.42 (m, 1H), 5.58−5.55 (m, 1H), 3.72 (s, 3H), 3.46−3.41 (m, 1H), 2.83−2.78 (m, 1H), 2.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 170.2, 148.5, 136.1, 133.9, 130.8, 124.3, 124.2, 121.7, 113.2, 100.3, 52.1, 51.9, 37.7, 24.6; HRMS (ESI) m/z calcd. for $C_{15}H_{15}N_2O_4$ $[M+H]^+$ 287.1026, found 287.1021.

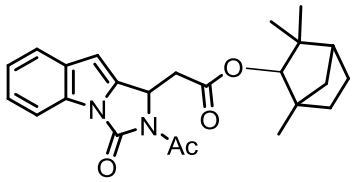


Phenethyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3o): The title

compound was obtained as a white soild (42 mg) in 56% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.36−7.27 (m, 4H), 7.22 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.5 Hz, 2H), 6.27 (d, *J* = 1.0 Hz, 1H), 5.54−5.51 (m, 1H), 4.35−4.32 (m, 2H), 3.44−3.39 (m, 1H), 2.90 (t, *J* = 7.0 Hz, 2H), 2.80−2.75 (m, 1H), 2.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.6, 148.5, 137.5, 136.0, 133.9, 130.7, 128.9, 128.7, 126.8, 124.2, 124.1, 121.6, 113.1, 100.2, 65.5, 51.8, 37.9, 35.1, 24.6; HRMS (ESI) m/z calcd. for $C_{22}H_{21}N_2O_4$ $[M+H]^+$ 377.1496, found 377.1491.

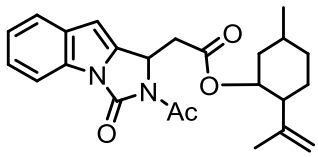


(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*] indol-1-yl)acetat*e* (3p): The title compound was obtained as a white soild (48 mg) in 58% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 6.42 (s, 1H), 5.55−5.52 (m, 1H), 4.63−4.58 (m, 1H), 3.26−3.22 (m, 1H), 3.10−3.06 (m, 1H), 2.67 (s, 3H), 1.69−1.57 (m, 4H), 1.36−1.28 (m, 2H), 1.00−0.82 (m, 2H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.72 (d, *J* = 7.0 Hz, 3H), 0.62 (d, *J* = 8.0 Hz, 3H), 0.53 (q, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 169.1, 148.7, 136.0, 134.0, 130.9, 124.2, 124.1, 121.7, 113.2, 99.9, 75.1, 52.0, 46.9, 40.6, 37.6, 34.2, 31.3, 26.3, 24.6, 23.4, 21.9, 20.8, 16.2; HRMS (ESI) m/z calcd. for $C_{24}H_{31}N_2O_4$ $[M+H]^+$ 411.2278, found 411.2269.

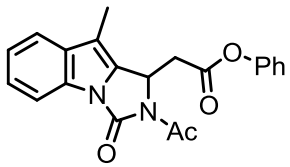


1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*] indol-1-yl)acetate (3q): The title compound was obtained as a white soild (48 mg) in 59% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.33 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.29 (tt, *J* = 7.5, 1.5 Hz, 1H), 6.42 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.58−5.55 (m, 1H), 4.40 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.50−3.44 (m, 1H), 2.90−2.83 (m, 1H), 2.66 (d, J = 1.5 Hz,

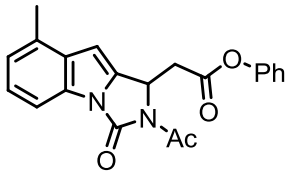
3H), 1.70−1.68 (m, 1H), 1.66−1.53 (m, 3H), 1.45−1.38 (m, 1H), 1.18−1.15 (m, 1H), 1.08 (d, J = 20.0 Hz, 3H), 1.04−0.93 (m, 4H), 0.69 (d, J = 35.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 170.2, 148.5, 136.2, 133.9, 130.8, 124.2, 121.6, 113.1, 100.2, 87.2, 52.1, 48.3, 41.4, 39.5, 37.7, 29.8, 26.6, 25.9, 24.6, 20.2, 19.3; HRMS (ESI) m/z calcd. for $C_{24}H_{29}N_2O_4$ $[M+H]^+$ 409.2122, found 409.2129.



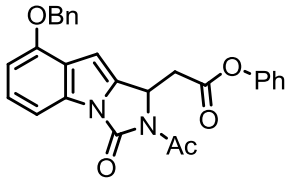
5-Methyl-2-(prop-1-en-2-yl)cyclohexyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*] indol-1-yl)acetate (3r): The title compound was obtained as a white soild (30 mg) in 35% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.33 (td, *J* = 7.0, 1.0 Hz, 1H), 7.29 (td, *J* = 7.5, 1.0 Hz, 1H), 6.38 (d, *J* = 1.0 Hz, 1H), 5.53−5.50 (m, 1H), 4.88−4.83 (m, 1H), 4.58 (d, *J* = 1.0 Hz, 2H), 3.36−3.32 (m, 1H), 2.78−2.73 (m, 1H), 2.65 (s, 3H), 2.01−1.95 (m, 1H), 1.91−1.87 (m, 1H), 1.69−1.63 (m, 2H), 1.60 (s, 3H), 1.53−1.29 (m, 2H), 0.99−0.85 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 169.1, 148.5, 145.8, 136.3, 134.0, 130.7, 124.1, 121.5, 113.1, 112.1, 100.2, 77.4, 74.4, 51.9, 50.7, 40.4, 37.8, 34.1, 31.5, 30.3, 24.6, 22.1, 19.6; HRMS (ESI) m/z calcd. for $C_{24}H_{29}N_2O_4$ $[M+H]^+$ 409.2127, found 409.2121.



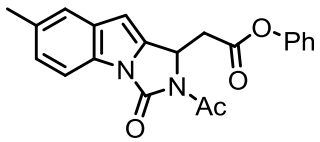
Phenyl-2-(2-acetyl-9-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3s): The title compound was obtained as a white soild (26 mg) in 36% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.38−7.31 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 2H), 5.69−5.67 (m, 1H), 3.52−3.48 (m, 1H), 3.33−3.29 (m, 1H), 2.69 (s, 3H)， 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 168.1, 150.3, 148.4, 134.9, 130.8, 130.6, 129.6, 126.2, 124.5, 123.9, 121.4, 119.6, 113.2, 108.9, 51.6, 37.2, 24.6, 8.6; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ 363.1339, found 363.1330.



Phenyl-2-(2-acetyl-8-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3t): The title compound was obtained as a white soild (53 mg) in 73% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.26−7.23 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.52 (s, 1H), 5.65−5.62 (m, 1H), 3.69−3.65 (m, 1H), 3.08−3.03 (m, 1H), 2.69 (s, 3H)，2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.5, 150.3, 148.5, 135.2, 133.5, 131.3, 130.5, 129.7, 126.3, 124.7, 124.5, 121.5, 110.6, 99.1, 51.8, 38.2, 24.6, 18.8; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ 363.1339, found 363.1334.

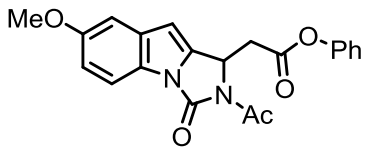


Phenyl-2-(2-acetyl-8-(benzyloxy)-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3u): The title compound was obtained as a white soild (53 mg) in 58% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.41−7.33 (m, 5H), 7.28−7.22 (m, 2H), 7.05 (d, *J* = 9.5 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 5.66−5.64 (m, 1H), 5.21 (s, 2H), 3.65−3.61 (m, 1H), 3.14−3.09 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.4, 152.5, 150.3, 148.6, 137.0, 134.2, 132.1, 129.7, 128.7, 128.1, 127.5, 126.3, 125.5, 124.3, 121.6, 106.5, 106.1, 98.0, 70.3, 51.9, 38.1, 24.7; HRMS (ESI) m/z calcd. for $C_{27}H_{23}N_2O_5$ $[M+H]^+$ 455.1601, found 455.1065.

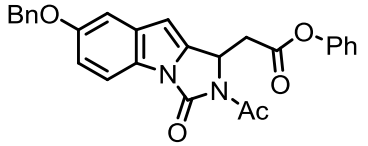


Phenyl-2-(2-acetyl-7-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3v): The title compound was obtained as a white soild (64 mg) in 88% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 1.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.39−7.35 (m, 2H), 7.24 (tt, *J* =

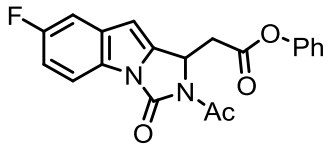
7.5, 1.0 Hz, 1H), 7.13 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.06−7.035 (m, 2H), 6.44 (s, 1H), 5.65−5.62 (m, 1H), 3.68−3.64 (m, 1H), 3.10−3.05 (m, 1H), 2.70 (s, 3H)，2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 170.7, 168.4, 150.3, 148.5, 135.1, 134.7, 131.6, 131.2, 129.7, 126.3, 125.8, 121.5, 121.3, 113.4, 100.4, 51.9, 38.2, 24.6, 21.8; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ 363.1339, found 363.1333.



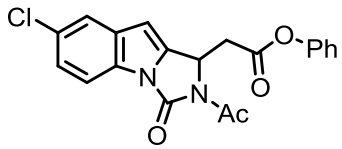
Phenyl-2-(2-acetyl-7-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3w): The title compound was obtained as a white soild (69 mg) in 91% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.86 (d, *J* = 9.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 8.5, 1.0 Hz, 3H), 6.96 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.43 (s, 1H), 5.65−5.62 (m, 1H), 3.86 (s, 3H), 3.69−3.65 (m, 1H), 3.10−3.05 (m, 1H), 2.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 170.6, 168.4, 157.1, 150.3, 148.2, 136.6, 134.9, 129.7, 126.3, 125.5, 121.5, 113.8, 113.3, 104.4, 100.5, 55.9, 51.8, 38.1, 24.6; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_5$ $[M+H]^+$ 379.1288, found 379.1287.



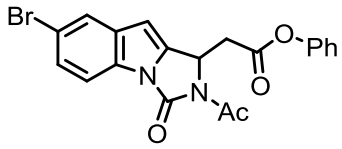
Phenyl-2-(2-acetyl-7-(benzyloxy)-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3x): The title compound was obtained as a white soild (69 mg) in 61% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.88 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.42−7.32 (m, 5H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.06−7.02 (m, 3H), 6.42 (d, *J* = 1.0 Hz, 1H), 5.65−5.62 (m, 1H), 5.11 (s, 2H), 3.69−3.64 (m, 1H), 3.09−3.04 (m, 1H), 2.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 170.6, 168.4, 156.3, 150.3, 148.2, 137.1, 136.7, 134.9, 129.7, 128.7, 128.1, 127.6, 126.3, 125.6, 121.5, 114.1, 113.8, 105.8, 100.5, 70.8, 51.8, 38.1, 24.6; HRMS (ESI) m/z calcd. for $C_{27}H_{23}N_2O_5$ $[M+H]^+$ 455.1601, found 455.1068.



Phenyl-2-(2-acetyl-7-fluoro-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3y): The title compound was obtained as a white soild (31 mg) in 43% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95−7.92 (m, 1H), 7.40−7.36 (m, 2H), 7.26−7.23 (m, 2H), 7.08 (td, *J* = 8.0, 2.5 Hz, 1H), 7.05−7.03 (m, 2H), 6.48 (d, J = 1.0 Hz, 1H), 5.67−5.64 (m, 1H), 3.69−3.65 (m, 1H), 3.14−3.09 (m, 1H), 2.70 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$): δ170.6, 168.4, 161.1 (d, *J* = 240 Hz), 150.3, 148.2, 137.6, 134.8 (d, *J* = 10 Hz), 129.7, 127.3, 126.5, 121.5, 114.0 (d, *J* = 10 Hz), 112.5 (d, *J* = 26 Hz), 107.5 (d, *J* = 24 Hz), 100.45 (d, *J* = 4 Hz), 51.9, 37.9, 24.6;; HRMS (ESI) m/z calcd. for $C_{20}H_{16}FN_2O_4$ $[M+H]^+$ 367.1089, found 367.1082.

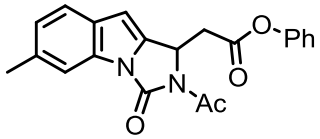


Phenyl-2-(2-acetyl-7-chloro-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3z): The title compound was obtained as a white soild (30 mg) in 39% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.46 (s, 1H), 5.67−5.64 (m, 1H), 3.69−3.65 (m, 1H), 3.15−3.10 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 168.3, 150.2, 148.2, 137.3, 135.0, 130.0, 129.7, 129.2, 126.4, 124.7, 121.5, 121.4, 114.0, 100.0, 51.9, 37.9, 24.6; HRMS (ESI) m/z calcd. for $C_{20}H_{16}ClN_2O_4$ $[M+H]^+$ 383.0793, found 383.0791.

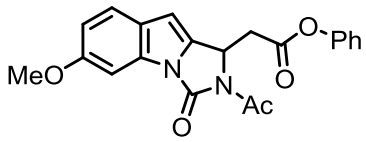


Phenyl-2-(2-acetyl-7-bromo-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3aa): The title compound was obtained as a white soild (47 mg) in 55% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 1.5 Hz, 1H), 7.45 (dd, *J* = 78.0, 2.0 Hz, 1H), 7.40−7.36 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.03 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.45 (d, *J* = 1.0 Hz, 1H), 5.67−5.64 (m, 1H), 3.69−3.65 (m, 1H), 3.15−3.10 (m, 1H), 2.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$):

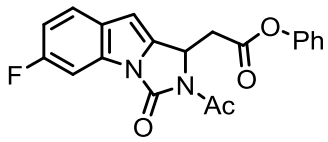
δ 170.5, 168.3, 150.2, 148.2, 137.1, 135.5, 129.7, 129.5, 127.4, 126.4, 124.5, 121.5, 117.6, 114.4, 99.8, 51.9, 37.9, 24.6; HRMS (ESI) m/z calcd. for $C_{20}H_{16}BrN_2O_4$ $[M+H]^+$ 427.0288, found 427.0287.



Phenyl-2-(2-acetyl-6-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ab): The title compound was obtained as a white soild (61 mg) in 84% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.0 Hz, 1H), 7.37−7.34 (m, 3H), 7.24−7.21 (m, 1H), 7.14 (d, J = 8.5 Hz, 1H), 7.03 (d, J = 7.5 Hz, 2H), 6.39 (s, 1H), 5.60−5.57 (m, 1H), 3.65−3.61 (m, 1H), 3.06−3.01 (m, 1H), 2.67 (s, 3H)，2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.4, 150.3, 148.3, 135.9, 134.1, 133.9, 129.6, 128.9, 126.3, 125.7, 121.6, 121.5, 112.7, 100.2, 51.8, 38.1, 24.6, 21.7; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ 363.1339, found 363.1334.

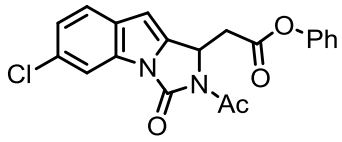


Phenyl-2-(2-acetyl-6-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ac): The title compound was obtained as a white soild (65 mg) in 86% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 2.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.39−7.35 (m, 2H), 7.24 (t, J = 7.5 Hz, 1H), 7.05−7.03 (m, 2H), 6.93 (dd, J = 8.5, 2.0 Hz, 1H), 6.41 (d, J = 1.0 Hz, 1H), 5.63−5.60 (m, 1H), 3.88 (s, 3H), 3.66−3.62 (m, 1H), 3.10−3.05 (m, 1H), 2.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.4, 157.8, 150.3, 148.5, 134.2, 131.6, 129.6, 127.4, 126.3, 122.2, 121.5, 113.9, 100.3, 96.9, 55.9, 51.9, 38.2, 24.6; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2O_5$ $[M+H]^+$ 379.1288, found 379.1281.

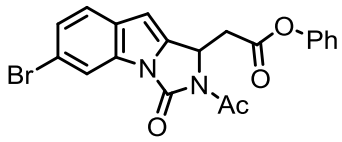


Phenyl-2-(2-acetyl-6-fluoro-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ad): The title compound was obtained as a white soild (30 mg) in 41% yield according to the **GP1**. ^{1}H NMR

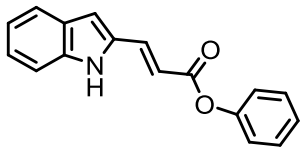
(500 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.52−7.49 (m, 1H), 7.39−7.35 (m, 2H), 7.24 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.09−7.03 (m, 3H), 6.48 (d, *J* = 1.0 Hz, 1H), 5.67−5.64 (m, 1H), 3.68−3.64 (m, 1H), 3.13−3.08 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 168.4, 160.6 (d, *J* = 241 Hz), 150.3, 148.3, 136.1 (d, *J* = 4 Hz), 130.8 (d, *J* = 13 Hz), 130.1, 129.7, 126.4, 122.5 (d, *J* = 9.5 Hz), 121.5, 112.7 (d, *J* = 24 Hz), 100.5 (d, *J* = 28 Hz), 100.3, 51.9, 38.0, 24.7; HRMS (ESI) m/z calcd. for $C_{20}H_{16}FN_2O_4$ $[M+H]^+$ 367.1089, found 367.1081.



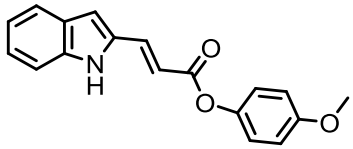
Phenyl-2-(2-acetyl-6-chloro-3-oxo-2,3-dihydro-1H-imidazo[1,5-a]indol-1-yl)acetate (3ae): The title compound was obtained as a white soild (28 mg) in 37% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.46−7.41 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.48 (s, 1H), 5.67−5.64 (m, 1H), 3.69−3.65 (m, 1H), 3.14−3.10 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 170.6, 148.2, 136.3, 132.7, 131.4, 129.7, 127.6, 126.4, 122.9, 121.5, 117.9, 116.4, 111.1, 100.4, 52.0, 37.9, 24.7; HRMS (ESI) m/z calcd. for $C_{20}H_{16}ClN_2O_4$ $[M+H]^+$ 383.0793, found 383.0799.



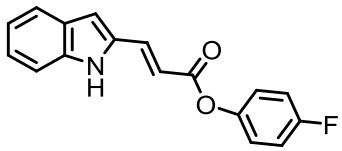
Phenyl-2-(2-acetyl-6-bromo-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3af): The title compound was obtained as a white soild (45 mg) in 53% yield according to the **GP1**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.45−7.41 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 5.66−5.63 (m, 1H), 3.69−3.65 (m, 1H), 3.14−3.09 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 168.3, 150.3, 148.2, 136.3, 132.7, 131.4, 129.7, 127.6, 126.4, 122.8, 121.5, 117.9, 116.4, 100.4, 51.9, 37.9, 24.7; HRMS (ESI) m/z calcd. for $C_{20}H_{16}BrN_2O_4$ $[M+H]^+$ 427.0288, found 427.0282.



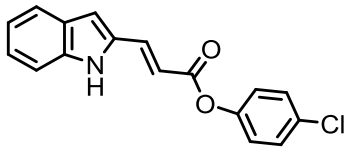
Phenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4a): The title compound was obtained as a yellow soild (40 mg) in 76% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.71 (s, 1H), 7.85 (d, J = 16.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.47−7.41 (m, 3H), 7.29 (t, J = 7.5 Hz, 1H), 7.25−7.22 (m, 3H), 7.04 (t, J = 8.0 Hz, 1H), 7.01 (s, 1H), 6.75 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.0, 150.6, 138.3, 136.6, 133.6, 129.5, 127.8, 125.8, 124.4, 121.9, 121.4, 119.9, 114.3, 111.6, 109.5; HRMS (ESI) m/z calcd. for $C_{17}H_{14}NO_2$ $[M+H]^+$ 264.1019, found 264.1011.



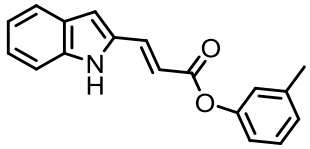
4-Methoxyphenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4b): The title compound was obtained as a yellow soild (33 mg) in 56% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.69 (s, 1H), 7.82 (d, J = 15.5 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 9.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.13 (dt, J = 9.0, 3.0 Hz, 2H), 7.04 (t, J = 7.0 Hz, 1H), 7.00−6.96 (m, 3H), 6.72 (d, J = 16.0 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.3, 156.8, 143.9, 138.3, 136.4, 133.6, 127.8, 124.3, 122.6, 121.3, 119.9, 114.39, 114.38, 111.6, 109.3, 55.4; HRMS (ESI) m/z calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1125, found 294.1127.



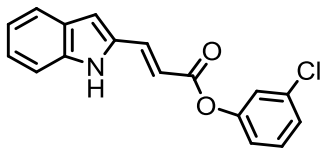
4-Fluorophenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4c): The title compound was obtained as a yellow soild (50 mg) in 89% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.71 (s, 1H), 7.85 (d, J = 16.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 7.0 Hz, 4H), 7.23 (t, J = 7.0 Hz, 1H), 7.05 (t, J = 8.0 Hz, 1H), 7.01 (s, 1H), 6.75 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.1, 159.6 (d, J = 240 Hz), 146.7 (d, J = 2 Hz), 138.3, 136.8, 133.6, 127.8, 124.4, 123.6 (d, J = 8 Hz), 121.3, 119.9, 116.0 (d, J = 23 Hz), 114.0, 111.6, 109.5; HRMS (ESI) m/z calcd. for $C_{17}H_{13}FNO_2$ $[M+H]^+$ 282.0925, found 282.0928.



4-Chlorophenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4d): The title compound was obtained as a yellow soild (50 mg) in 84% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.72 (s, 1H), 7.86 (d, *J* = 15.5 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.51 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.41 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.27 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.23 (td, *J* = 7.0, 1.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.75 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.9, 149.4, 138.4, 137.1, 133.5, 129.9, 129.4, 127.8, 124.4, 123.9, 121.4, 120.0, 113.9, 111.6, 109.7; HRMS (ESI) m/z calcd. for $C_{17}H_{13}ClNO_2$ $[M+H]^+$ 298.0629, found 298.0627.

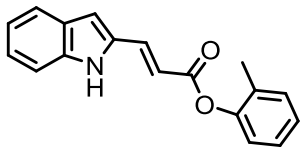


***m*-Tolyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4g):** The title compound was obtained as a yellow soild (34 mg) in 62% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.69 (s, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.25−7.21 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.06−7.00 (m, 4H), 6.73 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.0, 150.5, 139.2, 138.3, 136.5, 133.6, 129.2, 127.8, 126.4, 124.3, 122.3, 121.3, 119.9, 118.8, 114.3, 111.6, 109.4, 20.8; HRMS (ESI) m/z calcd. for $C_{18}H_{16}NO_2$ $[M+H]^+$ 278.1176, found 278.1172.

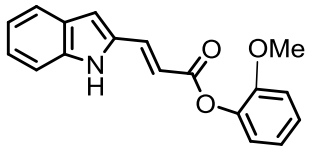


3-Chlorophenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4h): The title compound was obtained as a yellow soild (52 mg) in 87% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.72 (s, 1H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.43−7.41 (m, 2H), 7.38−7.36 (m, 1H), 7.25−7.22 (m, 2H), 7.06−7.02 (m, 2H), 6.74 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.7, 151.3, 138.3, 137.0, 133.5, 133.3, 130.9, 127.8, 125.9, 124.4, 122.3,

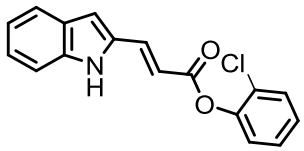
121.4, 120.9, 119.9, 113.8, 111.6, 109.7; HRMS (ESI) m/z calcd. for $C_{17}H_{13}ClNO_2$ $[M+H]^+$ 298.0629, found 298.0622.



***o*-Tolyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4i):** The title compound was obtained as a yellow soild (33 mg) in 59% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.69 (s, 1H), 7.82 (d, J = 16.0 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.40 (dd, J = 8.0, 1.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.24−7.21 (m, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.06−6.99 (m, 4H), 6.73 (d, J = 16.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.9, 150.4, 139.0, 138.1, 136.4, 133.4, 129.0, 127.7, 126.2, 124.1, 122.1, 121.2, 119.7, 118.7, 114.1, 111.4, 109.2, 20.6; HRMS (ESI) m/z calcd. for $C_{18}H_{16}NO_2$ $[M+H]^+$ 278.1176, found 278.1173.

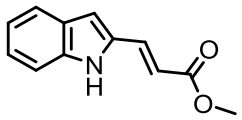


2-Methoxyphenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4j): The title compound was obtained as a yellow soild (28 mg) in 48% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.70 (s, 1H), 7.83 (d, J = 16.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.42 (dd, J = 8.0, 1.0 Hz, 1H), 7.27−7.22 (m, 2H), 7.17 (dd, J = 7.5, 1.5 Hz, 1H), 7.14 (dd, J = 8.0, 1.5 Hz, 1H), 7.07−7.04 (m, 1H), 7.01−6.97 (m, 2H), 6.76 (d, J = 16.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.5, 151.0, 139.4, 138.3, 136.6, 133.6, 127.9, 126.9, 124.3, 123.0, 121.3, 120.6, 119.9, 114.1, 112.8, 111.6, 109.4, 55.7; HRMS (ESI) m/z calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1125, found 294.1121.

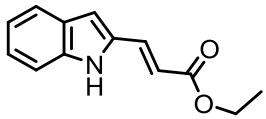


2-Chlorophenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4k): The title compound was obtained as a yellow soild (52 mg) in 86% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.74 (s, 1H), 7.90 (d, J = 16.0 Hz, 1H), 7.63−7.60 (m, 2H), 7.46−7.40 (m, 3H), 7.36−7.32 (m, 1H), 7.26−7.22 (m,

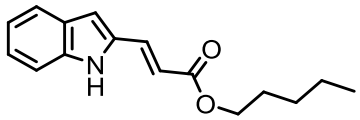
1H), 7.07−7.04 (m, 2H), 6.79 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.1, 146.7, 138.4, 137.5, 133.4, 130.1, 128.5, 127.8, 127.5, 126.0, 124.5, 124.4, 121.4, 112.0, 113.2, 111.6, 109.9; HRMS (ESI) m/z calcd. for $C_{17}H_{13}ClNO_2$ $[M+H]^+$ 298.0629, found 298.0622.



Methyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4l): The title compound was obtained as a yellow soild (30 mg) in 75% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.59 (s, 1H), 7.64 (d, *J* = 15.5 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 6.55 (d, *J* = 15.5 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.8, 138.1, 134.9, 133.7, 127.8, 124.0, 121.2, 119.8, 115.1, 111.5, 108.6, 51.5; HRMS (ESI) m/z calcd. for $C_{12}H_{12}NO_2$ $[M+H]^+$ 202.0863, found 202.0863.

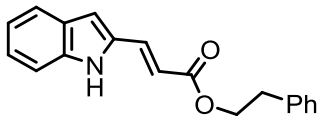


Ethyl-*(E)*-3-(1*H*-indol-2-yl)acrylate (4m): The title compound was obtained as a yellow soild (27 mg) in 63% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.57 (s, 1H), 7.64 (d, *J* = 16.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.21−7.18 (m, 1H), 7.02 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.90 (s, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 4.19 (q, *J* = 76.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.3, 138.0, 134.7, 133.7, 127.8, 123.9, 121.1, 119.8, 115.6, 111.5, 108.4, 59.9, 14.2; HRMS (ESI) m/z calcd. for $C_{13}H_{14}NO_2$ $[M+H]^+$ 216.1019, found 216.1012.

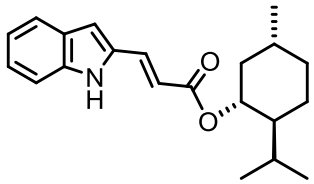


Pentyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4n): The title compound was obtained as a yellow soild (37 mg) in 72% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.57 (s, 1H), 7.62 (d, *J* = 16.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.21−7.17 (m, 1H), 7.03−7.00 (m, 1H), 6.91 (s, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 4.14 (t, *J* = 7.0 Hz, 2H), 1.66−1.63 (m, 2H), 1.35−1.32 (m, 4H), 0.90−0.88 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.4, 138.0, 134.7, 133.7,

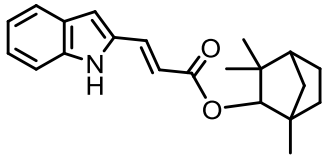
127.8, 123.9, 121.1, 119.8, 115.5, 111.5, 108.4, 63.9, 28.0, 27.7, 21.8, 13.9; HRMS (ESI) m/z calcd. for $C_{16}H_{20}NO_2$ $[M+H]^+$ 258.1489, found 258.1485.



Phenethyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4o): The title compound was obtained as a yellow soild (40 mg) in 68% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.59 (s, 1H), 7.62 (d, J = 16.0 Hz, 1H), 7.56 (d, J = 80 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.34−7.29 (m, 4H), 7.25−7.18 (m, 2H), 7.02 (t, J = 8.0 Hz, 1H), 6.90 (s, 1H), 6.53 (d, J = 16.0 Hz, 1H), 4.37 (t, J = 7.0 Hz, 2H), 2.97 (t, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.3, 138.1, 138.1, 134.9, 133.6, 128.8, 128.4, 127.8, 126.4, 124.0, 121.1, 119.8, 115.3, 111.5, 108.6, 64.5 34.5; HRMS (ESI) m/z calcd. for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1332, found 292.1336.

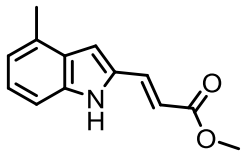


(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4p): The title compound was obtained as a yellow soild (53 mg) in 55% yield according to the **GP2**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (s, 1H), 7.69 (d, J = 16.0 Hz, 1H), 7.59 (dd, J = 8.0, 1.0 Hz, 1H), 7.34 (dd, J = 8.0, 1.0 Hz, 1H), 7.23 (td, J = 7.0, 1.0 Hz, 1H), 7.11−7.07 (m, 1H), 6.79 (d, J = 2.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 4.88−4.83 (m, 1H), 2.08−2.05 (m, 1H), 1.96−1.93 (m, 1H), 1.71−1.67 (m, 2H), 1.49−1.44 (m, 2H), 1.11−1.00 (m, 2H), 0.92−0.86 (m, 6H), 0.80−0.79 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 138.1, 134.6, 133.7, 128.5, 124.5, 121.5, 120.5, 116.2, 111.4 108.7, 74.6, 47.3, 41.2, 34.4, 31.5, 26.5, 23.7, 22.1, 20.9, 16.6; HRMS (ESI) m/z calcd. for $C_{21}H_{28}NO_2$ $[M+H]^+$ 326.2115, found 326.2118.

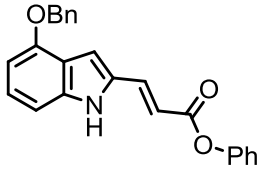


1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4q): The title compound

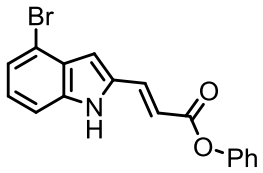
was obtained as a yellow soild (33 mg) in 51% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.60 (s, 1H), 7.65 (d, J = 16.0 Hz, 1H), 7.56 (dd, J = 8.0, 1.0 Hz, 1H), 7.37 (dd, J = 8.0, 1.0 Hz, 1H), 7.21−7.17 (m, 1H), 7.03−7.00 (m, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 4.41 (d, J = 1.5 Hz, 1H), 1.73−1.63 (m, 4H), 1.48−1.47 (m, 1H), 1.22−1.12 (m, 2H), 1.11 (s, 3H), 1.06 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.8, 138.1, 134.7, 133.7, 127.8, 123.9, 121.1, 119.7, 115.6, 111.5, 108.4, 85.3, 47.9, 47.8, 40.8, 29.5, 26.3, 25.5, 20.0, 19.2; HRMS (ESI) m/z calcd. for $C_{21}H_{26}NO_2$ $[M+H]^+$ 324.1958, found 324.1963.



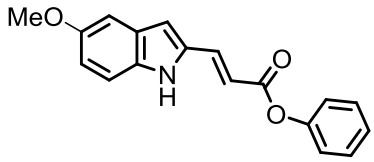
Methyl-(*E*)-3-(4-methyl-1*H*-indol-2-yl)acrylate (4r): The title compound was obtained as a yellow soild (31 mg) in 72% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.57 (s, 1H), 7.64 (d, J = 16.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 7.0 Hz, 1H), 6.93 (s, 1H), 6.81 (d, J = 7.0 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 3.73 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.8, 137.9, 134.9, 133.1, 130.2, 128.0, 124.2, 119.7, 114.8, 109.1, 107.3, 51.4, 18.4; HRMS (ESI) m/z calcd. for $C_{13}H_{14}NO_2$ $[M+H]^+$ 216.1019, found 216.1018.



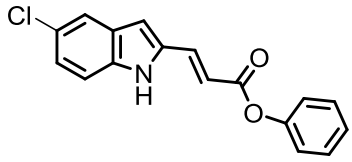
Phenyl-(*E*)-3-(4-(benzyloxy)-1*H*-indol-2-yl)acrylate (4s): The title compound was obtained as a yellow soild (32 mg) in 43% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.71 (s, 1H), 7.82 (d, J = 16.0 Hz, 1H), 7.51 (d, J = 7.50 Hz, 2H), 7.47−7.40 (m, 4H), 7.34 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 7.50 Hz, 1H), 7.22−7.21 (m, 2H), 7.14 (t, J = 8.0 Hz, 1H), 7.07 (d, J = 7.0 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 6.72 (d, J = 16.0 Hz, 1H), 6.62 (d, J = 7.5 Hz, 1H), 5.24 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.1, 152.4, 150.6, 139.7, 137.3, 136.6, 132.4, 129.5, 128.4, 127.8, 127.5, 125.7, 125.5, 121.9, 119.3, 113.6, 107.1, 104.8, 101.0, 69.1; HRMS (ESI) m/z calcd. for $C_{24}H_{20}NO_3$ $[M+H]^+$ 370.1438, found 370.1432.



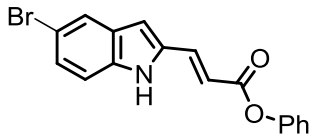
Phenyl-(*E*)-3-(4-bromo-1*H*-indol-2-yl)acrylate (4t): The title compound was obtained as a yellow soild (49 mg) in 72% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.08 (s, 1H), 7.89 (d, J = 16.0 Hz, 1H), 7.46−7.43 (m, 3H), 7.30−7.28 (m, 2H), 7.24−7.23 (m, 2H), 7.15 (t, J = 8.0 Hz, 1H), 6.99 (s, 1H), 6.85 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.8, 150.6, 138.4, 136.0, 134.3, 129.5, 128.4, 125.8, 125.2, 122.6, 121.8, 115.8, 114.3, 111.2, 108.4; HRMS (ESI) m/z calcd. for $C_{17}H_{13}BrNO_2$ $[M+H]^+$ 342.0124, found 342.0127.



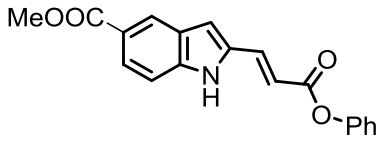
Phenyl-(*E*)-3-(5-methoxy-1*H*-indol-2-yl)acrylate (4u): The title compound was obtained as a yellow soild (38 mg) in 64% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.57 (s, 1H), 7.80 (d, J = 16.0 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.32−7.27 (m, 2H), 7.21 (dt, J = 7.5, 1.0 Hz, 2H), 7.07 (d, J = 2.5 Hz, 1H), 6.93 (d, J = 1.5 Hz, 1H), 6.88 (d, J =8.0, 2.5 Hz, 1H), 6.70 (d, J = 16.0 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.5, 154.2, 151.0, 137.1, 134.3, 134.0, 129.9, 128.6, 126.2, 122.3, 115.9, 114.2, 112.9, 109.4, 102.3, 55.7; HRMS (ESI) m/z calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1125, found 294.1120.



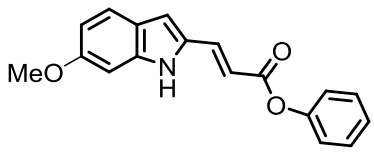
Phenyl-(*E*)-3-(5-chloro-1*H*-indol-2-yl)acrylate (4v): The title compound was obtained as a yellow soild (51 mg) in 86% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.90 (s, 1H), 7.83 (d, J = 16.0 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H), 7.47−7.42 (m, 3H), 7.29 (t, J = 7.5 Hz, 1H), 7.23−7.21 (m, 3H), 7.15 (d, J = 1.5 Hz, 1H), 6.78 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.8, 150.5, 136.6, 136.2, 135.0, 129.5, 128.9, 125.8, 124.4, 124.2, 121.8, 120.3, 115.5, 113.2, 108.5; HRMS (ESI) m/z calcd. for $C_{17}H_{13}ClNO_2$ $[M+H]^+$ 298.0629, found 298.0627.



Phenyl-(*E*)-3-(5-bromo-1*H*-indol-2-yl)acrylate (4w): The title compound was obtained as a yellow soild (56 mg) in 83% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.91 (s, 1H), 7.86−7.81 (m, 2H), 7.52 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 8.5 Hz, 1H), 7.32 (dd, J = 8.5, 2.0 Hz, 1H), 7.28 (t, J = 7.0 Hz, 1H), 7.22 (d, J = 7.5 Hz, 2H), 6.99 (s, 1H), 6.79 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.8, 150.5, 136.8, 136.1, 134.9, 129.6, 129.5, 126.7, 125.8, 123.4, 121.8, 115.5, 113.6, 112.3, 108.4; HRMS (ESI) m/z calcd. for $C_{17}H_{13}BrNO_2$ $[M+H]^+$ 342.0124, found 342.0121.

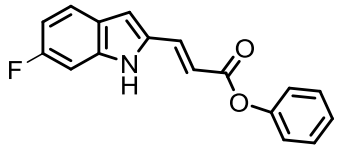


Methyl-(*E*)-2-(3-oxo-3-phenoxyprop-1-en-1-yl)-1*H*-indole-5-carboxylate (4x): The title compound was obtained as a yellow soild (50 mg) in 78% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.08 (s, 1H), 8.30 (s, 1H), 7.88−7.83 (m, 2H), 7.50 (d, J = 8.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 7.5 Hz, 1H), 7.22 (dd, J = 8.5, 1.0 Hz, 2H), 7.15 (s, 1H), 6.82 (d, J = 16.0 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.9, 164.8, 150.5, 140.6, 136.1, 135.3, 129.5, 127.4, 125.8, 124.8, 124.0, 121.8, 121.4, 115.7, 111.6, 110.3, 51.8; HRMS (ESI) m/z calcd. for $C_{19}H_{16}NO_4$ $[M+H]^+$ 322.1074, found 322.1071.

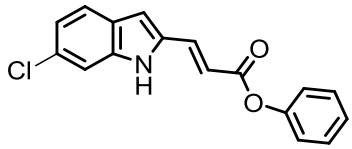


Phenyl-(*E*)-3-(6-methoxy-1*H*-indol-2-yl)acrylate (4y): The title compound was obtained as a yellow soild (32 mg) in 54% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.57 (s, 1H), 7.80 (d, J = 16.0 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.32−7.27 (m, 2H), 7.22 (dd, J = 8.5, 1.0 Hz, 2H), 7.07 (d, J = 2.5 Hz, 1H), 6.93 (d, J = 1.5 Hz, 1H), 6.87 (dd, J = 9.0, 2.5 Hz, 1H), 6.70 (d, J = 16.0 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.1, 153.8, 150.6, 136.7, 133.9, 133.6,

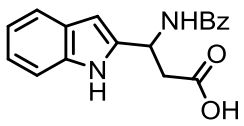
129.5, 128.2, 125.7, 121.9, 115.4, 113.7, 112.4, 109.0, 101.9, 55.3; HRMS (ESI) m/z calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1125, found 294.1127.



Phenyl-(*E*)-3-(6-fluoro-1*H*-indol-2-yl)acrylate (4z): The title compound was obtained as a yellow soild (48 mg) in 86% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.84 (s, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.64−7.62 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.0 Hz, 2H), 7.19 (dd, *J* = 10.0, 2.0 Hz, 1H), 7.03 (d, *J* = 1.5 Hz, 1H), 6.95−6.91 (m, 1H), 6.75 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.0, 160.5 (d, *J* = 238 Hz), 150.6, 138.4 (d, *J* = 13 Hz), 136.3, 134.4 (d, *J* = 4 Hz), 129.5, 125.8, 124.7, 122.8 (d, *J* = 10 Hz), 121.9, 114.3, 109.6, 108.9 (d, *J* = 25 Hz), 97.4 (d, *J* = 26 Hz); HRMS (ESI) m/z calcd. for $C_{17}H_{13}FNO_2$ $[M+H]^+$ 282.0925, found 282.0924.

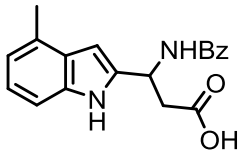


Phenyl-(*E*)-3-(6-chloro-1*H*-indol-2-yl)acrylate (4aa): The title compound was obtained as a yellow soild (53 mg) in 88% yield according to the **GP2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.86 (s, 1H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.59−7.56 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.03 (s, 1H), 6.78 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.9, 150.5, 138.9, 136.2, 134.5, 129.5, 126.8, 125.8, 123.1, 123.0, 121.8, 117.0, 115.2, 114.0, 109.2,; HRMS (ESI) m/z calcd. for $C_{17}H_{13}ClNO_2$ $[M+H]^+$ 298.0629, found 298.0621.

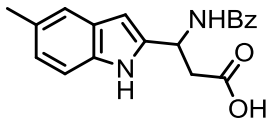


3-Benzamido-3-(1*H*-indol-2-yl)propanoic acid (5a): The title compound was obtained as a white soild (32 mg) in 53% yield according to the **GP3** and (41 mg) in 67% yield according to the **GP4**. ^{1}H

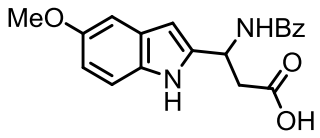
NMR (500 MHz, DMSO-d_6): δ 12.36 (s, 1H), 10.96 (s, 1H), 8.84 (d, J = 8.0 Hz, 1H), 7.90−7.89 (m, 2H), 7.54 (t, J = 7.0 Hz, 1H), 7.49−7.44 (m, 3H), 7.33 (d, J = 8.5 Hz, 1H), 7.04−7.01 (m, 1H), 6.96−6.93 (m, 1H), 6.21 (s, 1H), 5.72−5.67 (m, 1H), 3.02−2.92 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.8, 165.7, 139.9, 136.0, 134.3, 131.2, 128.2, 127.6, 127.4, 120.7, 119.6, 118.8, 111.2, 98.1, 44.5; HRMS (ESI) m/z calcd. for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ 309.1234, found 309.1238.



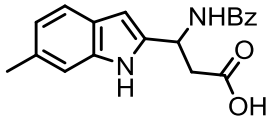
3-Benzamido-3-(4-methyl-1*H*-indol-2-yl)propanoic acid (5b): The title compound was obtained as a white soild (30 mg) in 48% yield according to the **GP3** and (41 mg) in 63% yield according to the **GP4**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.35 (s, 1H), 10.95 (s, 1H), 8.83 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.0 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.15 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 7.0 Hz, 1H), 6.74 (d, J = 7.0 Hz, 1H), 6.33 (d, J = 2.0 Hz, 1H), 5.72−5.67 (m, 1H), 3.03−2.92 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.8, 165.7, 139.2, 135.7, 134.3, 131.3, 128.3, 128.2, 127.5, 127.4, 120.9, 118.9, 108.9, 96.6, 44.5, 18.6; HRMS (ESI) m/z calcd. for $C_{19}H_{19}N_2O_3$ $[M+H]^+$ 323.1390, found 323.1392.



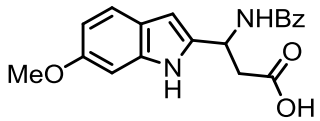
3-Benzamido-3-(5-methyl-1*H*-indol-2-yl)propanoic acid (5c): The title compound was obtained as a white soild (32 mg) in 50% yield according to the **GP3** and (42 mg) in 65% yield according to the **GP4**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.34 (s, 1H), 10.82 (s, 1H), 8.83 (d, J = 8.0 Hz, 1H), 7.90−7.89 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.85 (dd, J = 8.5, 1.0 Hz, 1H), 6.22 (s, 1H), 5.70−5.66 (m, 1H), 3.01−2.91 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.9, 165.7, 139.9, 134.4, 134.3, 131.3, 128.2, 127.9, 127.5, 127.2, 122.3, 119.3, 110.9, 97.6, 44.5, 21.2; HRMS (ESI) m/z calcd. for $C_{19}H_{19}N_2O_3$ $[M+H]^+$ 323.1390, found 323.1396.



3-Benzamido-3-(5-methoxy-1*H*-indol-2-yl)propanoic acid (5d): The title compound was obtained as a white soild (38 mg) in 56% yield according to the **GP3** and (49 mg) in 73% yield according to the **GP4**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.34 (s, 1H), 10.78 (s, 1H), 8.83 (d, J = 8.5 Hz, 1H), 7.90−7.88 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.67 (dd, J = 8.5, 2.5 Hz, 1H), 6.23 (d, J = 2.0 Hz, 1H), 5.68−5.64 (m, 1H), 3.71 (s, 3H), 3.00−2.90 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.8, 165.7, 153.3, 140.5, 134.3, 131.3, 131.1, 128.2, 128.0, 127.4, 111.8, 110.7, 101.6, 99.5, 98.0, 55.3, 44.5; HRMS (ESI) m/z calcd. for $C_{19}H_{19}N_2O_4$ $[M+H]^+$ 339.1339, found 339.1345.

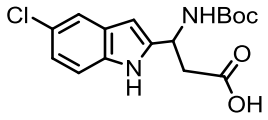


3-Benzamido-3-(6-methyl-1*H*-indol-2-yl)propanoic acid (5g): The title compound was obtained as a white soild (29 mg) in 46% yield according to the **GP3** and (44 mg) in 68% yield according to the **GP4**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.33 (s, 1H), 10.80 (s, 1H), 9.16 (s, 1H), 8.82 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 6.24 (s, 1H), 5.70−5.65 (m, 1H), 3.01−2.90 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.8, 165.7, 139.2, 136.5, 134.3, 131.3, 129.7, 128.2, 127.5, 125.5, 120.6, 119.4, 111.1, 97.9, 44.5, 21.5; HRMS (ESI) m/z calcd. for $C_{19}H_{19}N_2O_3$ $[M+H]^+$ 323.1390, found 323.1391.

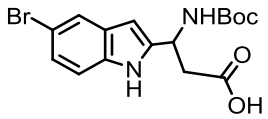


3-Benzamido-3-(6-methoxy-1*H*-indol-2-yl)propanoic acid (5h): The title compound was obtained as a white soild (39 mg) in 58% yield according to the **GP3 and** (51 mg) in 76% yield according to the **GP4**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.51 (s, 0.7H), 10.81 (s, 1H), 8.96 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.0 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.30 (d, J = 9.0 Hz, 1H), 6.85 (d, J = 1.5 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 6.20 (s, 1H), 5.67−5.63 (m, 1H), 3.72 (s, 3H),

3.04−2.79 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.9, 165.7, 155.3, 138.6, 136.8, 134.4, 131.3, 128.2, 127.5, 121.8, 120.2, 108.9, 98.0, 94.6, 55.2, 44.5; HRMS (ESI) m/z calcd. for $C_{19}H_{19}N_2O_4$ $[M+H]^+$ 339.1339, found 339.1345.



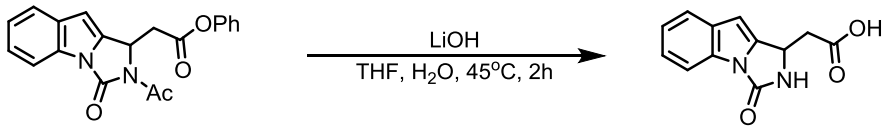
3-((Tert-butoxycarbonyl)amino)-3-(5-chloro-1*H*-indol-2-yl)propanoic acid (5i): The title compound was obtained as a white soild (18 mg) in 27% yield according to the **GP5 and** (32 mg) in 48% yield according to the **GP6**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.33 (s, 1H), 11.12 (s, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.01 (dd, J = 8.0, 2.0 Hz, 1H), 6.22 (d, J = 2.0 Hz, 1H), 5.12−5.07 (m, 1H), 2.82−2.70 (m, 2H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 154.9, 142.5, 134.4, 128.9, 123.3, 120.6, 118.8, 112.6, 97.7, 78.1, 45.6, 28.2; HRMS (ESI) m/z calcd. for $C_{16}H_{20}ClN_2O_4$ $[M+H]^+$ 339.1106, found 339.1109.



3-((Tert-butoxycarbonyl)amino)-3-(5-bromo-1*H*-indol-2-yl)propanoic acid (5j): The title compound was obtained as a white soild (32 mg) in 43% yield according to the **GP4 and** (41 mg) in 54% yield according to the **GP3**. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.27 (s, 1H), 11.13 (s, 1H), 7.64 (d, J = 1.5 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 8.5 Hz, 1H), 7.14 (d, J = 7.0, Hz, 1H), 6.22 (d, J = 2.0 Hz, 1H), 5.11−5.07 (m, 1H), 2.82−2.69 (m, 2H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 154.9, 142.3, 134.6, 129.6, 123.1, 121.9, 113.2, 111.3, 97.6, 78.1, 45.5, 28.2; HRMS (ESI) m/z calcd. for $C_{16}H_{20}BrN_2O_4$ $[M+H]^+$ 383.0601, found 383.0612.

4. Synthetic Applications

4.1 Hydrolysis of 3a

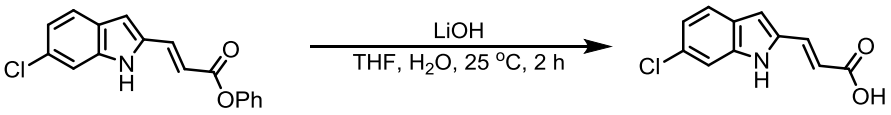


3a **6**, 78%

A reaction tube (10 mL) with magnetic stir bar was charged with phenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate **3a** (35 mg, 0.10 mmol), LiOH (6 mg, 0.25 mmol), H_2O (1.0 mL), and THF (1.0 mL). The reaction was allowed to stir at 45°C oil bath for 2h. After cooling to room temperature, the reaction was poured in 10 mL 0.5 M HCl and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine and dried over sodium sulphate. The solvent was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (CH_2Cl_2/MeOH) to afford the desired products **6** as white solide (18 mg) in 78 % yield.

2-(3-Oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetic acid (6): ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.99 (s, 1H), 8.44 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.23 (t, J = 7.0 Hz, 1H), 7.18 (t, J = 7.0 Hz, 1H), 6.42 (s, 1H), 5.00 (t, J = 6.0 Hz, 1H), 2.73 (d, J = 5.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.2, 152.3, 141.8, 133.1, 129.5, 122.4, 122.0, 121.1, 111.5, 96.9, 75.1, 49.2; HRMS (ESI) m/z calcd. for $C_{12}H_{11}N_2O_3$ $[M+H]^+$ 231.0764, found 231.0769.

4.2 Hydrolysis of 4aa



4aa **7**, 85%

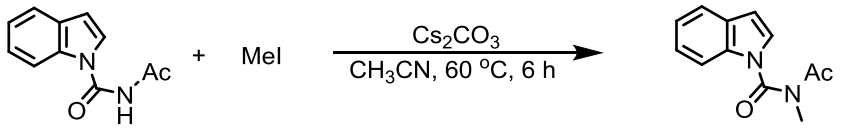
A reaction tube (10 mL) with magnetic stir bar was charged with phenyl-(*E*)-3-(6-chloro-1*H*-indol-2-yl)acrylate (**4aa**) (30 mg, 0.10 mmol), LiOH (6 mg, 0.25 mmol), H_2O (1.0 mL), and THF (1.0 mL). The reaction was allowed to stir at 25 °C oil bath for 2 h. After cooling to room temperature, the reaction was poured in 10 mL 0.5 M HCl and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine and dried over sodium sulphate. The solvent was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (CH_2Cl_2/MeOH) to afford the desired products **7** as yellow solide (19 mg) in 85 % yield.

(*E*)-3-(6-Chloro-1*H*-indol-2-yl)acrylic acid (7): ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.83 (s, 1H), 7.54−7.46 (m, 3H), 7.13 (s, 1H), 6.80 (s, 1H), 6.53 (d, J = 14.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.4, 138.6, 135.5, 132.0, 127.0, 122.5, 122.4, 120.8, 115.9, 113.9, 106.5; HRMS (ESI) m/z calcd. for $C_{11}H_9ClNO_2$ $[M+H]^+$ 222.0316, found 222.0317.

5. Mechanism Study

5.1 Effect of NH on C-H Bond Activation

5.1.1 Preparation of 8

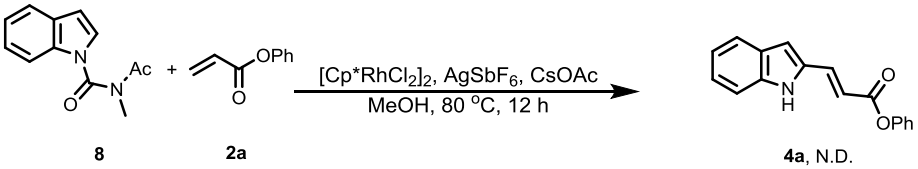


1a **8**, 62%

A reaction tube (20 mL) with magnetic stir bar was charged with *N*-acetyl-1*H*-indole-1-carboxamide **1a** (101 mg, 0.50 mmol), MeI (212 mg, 1.5 mmol), Cs_2CO_3 (326 mg, 1.0 mmol) and CH_3CN (8.0 mL). The reaction was allowed to stir at 60 °C oil bath for 6 h. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired products **8** as white solid (67 mg) in 62 % yield.

***N*-Acetyl-*N*-methyl-1*H*-indole-1-carboxamide (8)**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.01 (dd, J = 8.0, 0.5 Hz, 1H), 7.65−7.64 (m, 2H), 7.36 (td, J = 7.5, 1.0 Hz, 1H), 7.29 (td, J = 7.5, 1.0 Hz, 1H), 6.76 (dd, J = 3.5, 0.5 Hz, 1H), 3.21 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.6, 153.7, 134.9, 130.5, 127.4, 124.6, 123.6, 121.2, 114.6, 108.6, 34.1, 23.2;HRMS (ESI) m/z calcd. for $C_{12}H_{13}N_2O_2$ $[M+H]^+$ 217.0972, found 217.0968.

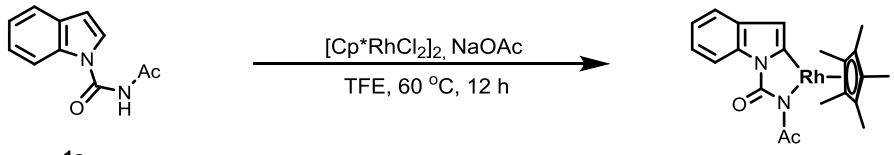
5.1.2 Effect of NH on C-H bond activation



8 **2a** **4a**, N.D.

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-acetyl-*N*-methyl-1*H*-indole-1-carboxamide **12** (44 mg, 0.20 mmol), phenyl acrylate **2a** (89 mg, 0.60 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 0.010 mmol), $AgSbF_6$ (21 mg, 0.060 mmol) , CsOAc (57 mg, 0.30 mmol) and MeOH (1.0 mL). The reaction was allowed to stir at 80 °C oil bath for 12 h. However, no **4a** was detected.

5.2 Preparation of Rhodacycle 9



1a **9**, 85%

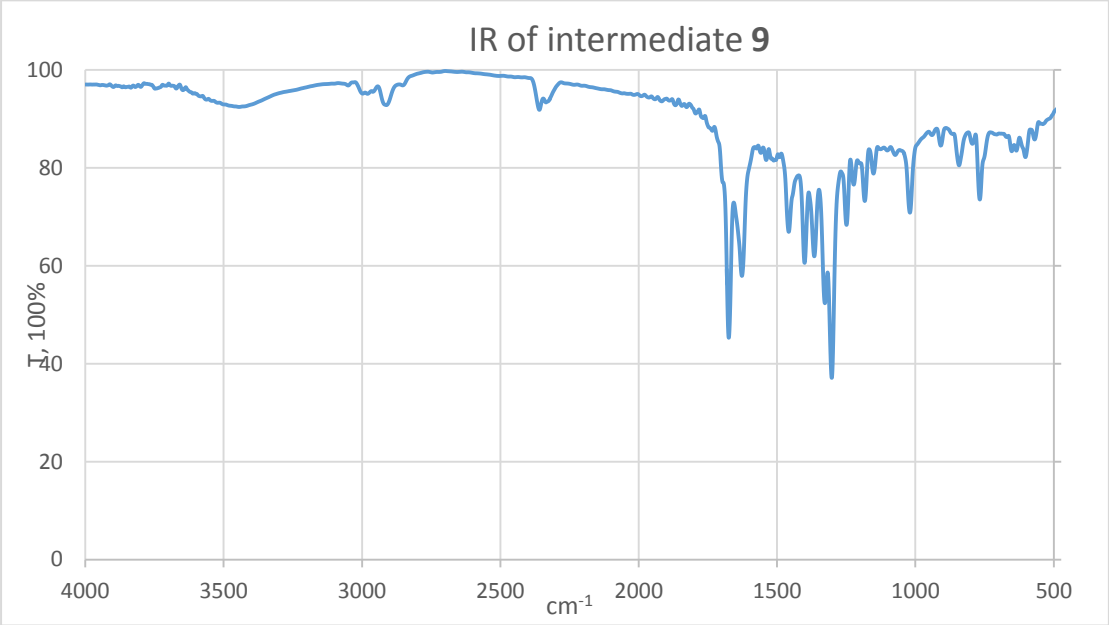
A reaction tube (10 mL) with magnetic stir bar was charged with *N*-acetyl-1*H*-indole-1-carboxamide **1a** (30 mg, 0.15 mmol), $[Cp^*RhCl_2]_2$ (30 mg, 0.050 mmol), , NaOAc (25 mg, 0.30 mmol) and TFE (5.0 mL). The reaction was allowed to stir at 60 °C oil bath for 12 h. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and dissolved in dichloromethane (15 mL). Then the mixture was filtered and evaporated to dryness. The solid obtained was washed with ether to remove excess **1a**. The solvent was then removed under vacuum. Analytically pure **9** (37 mg, 85% yield) was obtained by recrystallization using dichloromethane and ethyl acetate.

5-Membered rhodacycle 9: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.20 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.0 Hz, 1H), 7.26 (td, J = 7.5, 1.5 Hz, 1H), 7.21 (td, J = 8.0, 1.5 Hz, 1H), 6.35 (s, 1H), 2.84 (s, 3H), 0.90 (s, 15H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.0, 161.3, 140.8, 134.6, 124.0, 122.6, 121.4, 113.5, 99.6, 82.6, 28.7, 8.5; HRMS (ESI) m/z calcd. for $C_{21}H_{24}N_2O_2Rh$ $[M+H]^+$ 439.0887, found 439.0885.

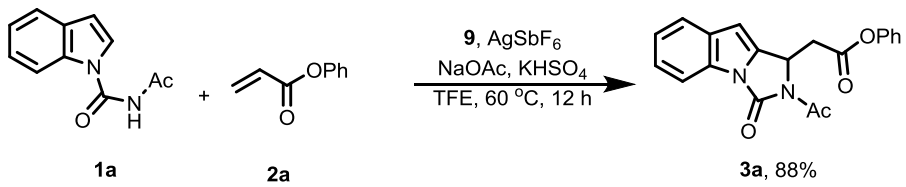
The infrared spectroscopy of intermediate **9** was undertaken and the result was as following figure S1. The N–H stretching signals of amide are unfound, which indicated that the hydrogen was substituted. The C–H stretching signals can be assigned primarily to CH_3– (2907 and 2849 cm^{-1}). A central region contains peaks at 1673 and 1623 cm^{-1} which is assigned to the C=O

stretch.

Figure S1 infrared spectroscopy of intermediate **9**

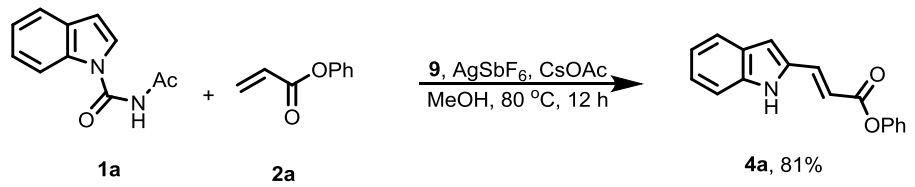


5.3 9 Leading to Products 3a and 4a



1a **2a** **3a**, 88%

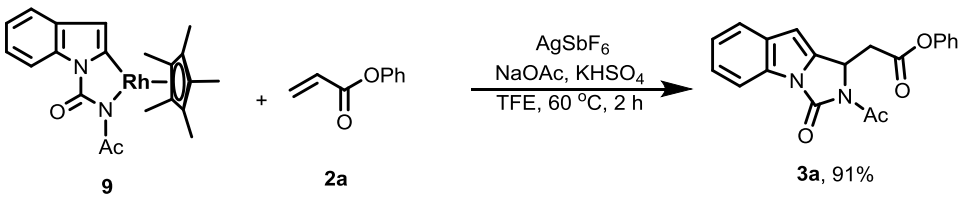
A reaction tube (10 mL) with magnetic stir bar was charged with *N*-acetyl-1*H*-indole-1-carboxamide **1a** (40 mg, 0.20 mmol), phenyl acrylate **2a** (89 mg, 0.60 mmol), **9** (9 mg, 0.020 mmol), $AgSbF_6$ (21 mg, 0.060 mmol) , NaOAc (25 mg, 0.30 mmol), $KHSO_4$ (41 mg, 0.30 mmol) and TFE (1.0 mL). The reaction was allowed to stir at 60 °C oil bath for 12 h. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired products **3a** in 88% yied.



1a **2a** **4a**, 81%

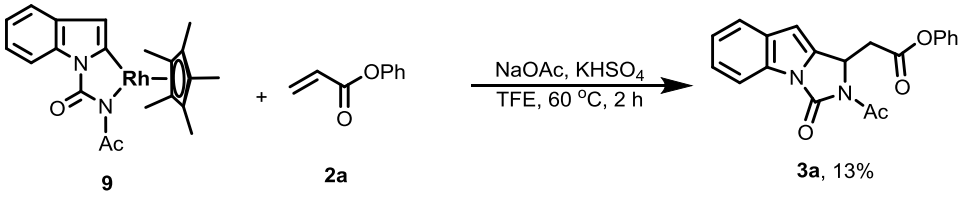
A reaction tube (10 mL) with magnetic stir bar was charged with *N*-acetyl-1*H*-indole-1-carboxamide **1a** (40 mg, 0.20 mmol), phenyl acrylate **2a** (89 mg, 0.60 mmol), **9** (9 mg, 0.020 mmol), $AgSbF_6$ (21 mg, 0.060 mmol) , CsOAc (57 mg, 0.30 mmol) and MeOH (1.0 mL). The reaction was allowed to stir at 80 °C oil bath for 12 h. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired products **4a** in 81% yield.

5.4 Effect of $AgSbF_6$ on C-H Bond Activation



9 **2a** **3a**, 91%

A reaction tube (10 mL) with magnetic stir bar was charged with **9** (9 mg, 0.020 mmol), phenyl acrylate **2a** (9 mg, 0.060 mmol), $AgSbF_6$ (21 mg, 0.060 mmol), NaOAc (5 mg, 0.060 mmol), $KHSO_4$ (8 mg, 0.060 mmol) and TFE (0.50 mL). The reaction was allowed to stir at 60 °C oil bath for 2 h. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired products **3a** in 91% yied.



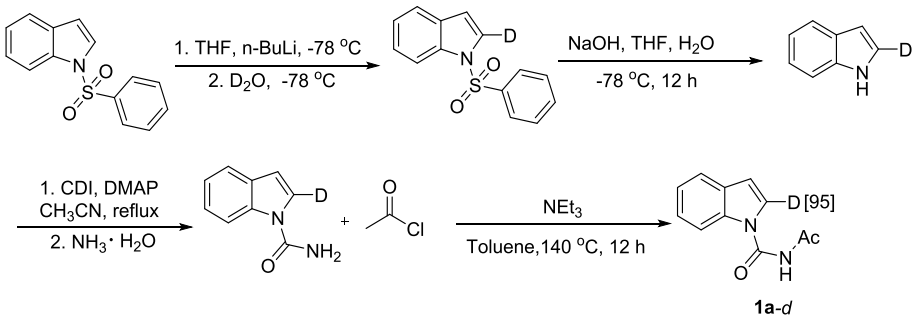
9 **2a** **3a**, 13%

A reaction tube (10 mL) with magnetic stir bar was charged with **9** (9 mg, 0.020 mmol), phenyl acrylate **2a** (9 mg, 0.060 mmol), NaOAc (5 mg, 0.060 mmol), $KHSO_4$ (8 mg, 0.060 mmol) and TFE (0.50 mL). The reaction was allowed to stir at 60 °C oil bath for 2 h. After cooling to room

temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired products **3a** in 13% yied.

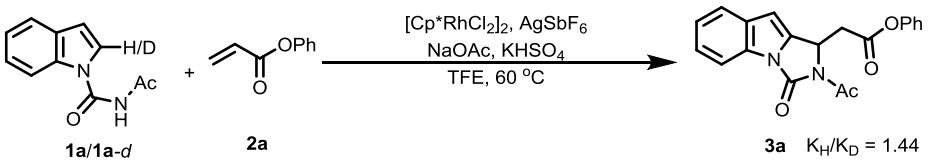
5.5 KIE Experiments

5.5.1 Reaction procedure for the preparation of deuterium labeled compounds[3]



2-Deutero-*N*-acetyl-1*H*-indole-1-carboxamide (**1a**-*d*): a white solid. 55% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.00 (s, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 4.0 Hz, 0.05H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1H), 7.25 (td, *J* = 7.5, 1.5 Hz, 1H), 6.73 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.8, 148.8, 135.3, 130.2, 126.0 (t, *J* = 28.1 Hz), 124.2, 123.1, 121.0, 115.3, 107.3, 25.0; HRMS (ESI) m/z calcd. for $C_{11}H_{10}DN_2O_2$ $[M+H]^+$ 204.0878, found 204.0875.

5.5.2 kinetic isotope effect experiment



A reaction tube (10 mL) with magnetic stir bar was charged with **1a** or **1a**-*d* (40 mg, 0.20 mmol), phenyl acrylate **2a** (89 mg, 0.60 mmol), $[Cp^*RhCl_2]_2$ (3 mg, 0.005 mmol), $AgSbF_6$ (21 mg, 0.060 mmol), NaOAc (25 mg, 0.30 mmol), $KHSO_4$ (41 mg, 0.30 mmol) and TFE (2.0 mL). The mixture was then stirred at room temperature for 10mins before heating to 60 °C. Base on the above procedure, the reaction was heated to 60 °C for 5 min, 15 min, 30 min, 40 min, 50 min, 60 min

separately. The aliquots was got from the reaction and diluted with solvent. The sample was then analyzed by Analytical high performance liquid chromatography (HPLC). HPLC was performed on Agilent 1200 compact chromatograph equipped with Eclipse Plus C18 column (Agilent, 5 μm, 4.6 × 150 mm).

Table S3. Yield of **3a** using **1a** or **1a**-*d* as starting material[a].

Entry	Time (min)	Amount of **3a** (mmol)	
		3a[b]	**3a**[c]
1	5	0.01005	0.01092
2	15	0.03218	0.02561
3	30	0.04739	0.03633
4	40	0.06952	0.04670
5	50	0.07868	0.05362
6	60	0.09182	0.07177

[a] HPLC yield. [b] **1a** using as starting material. [c] **1a**-*d* using as starting material.

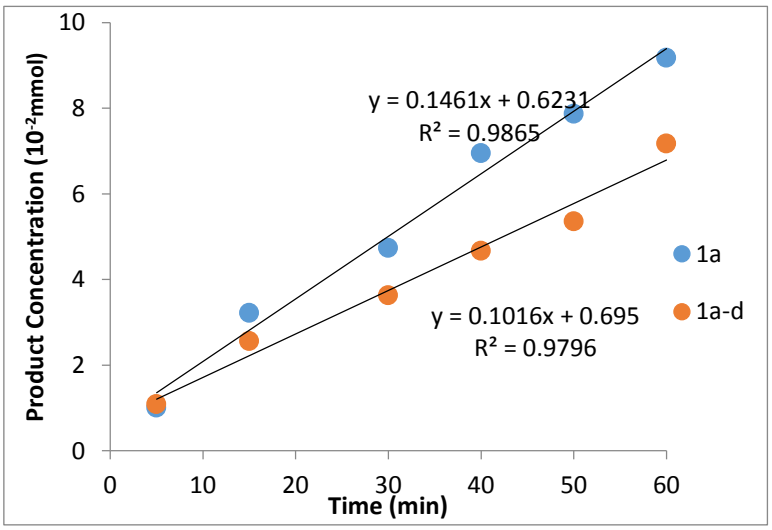
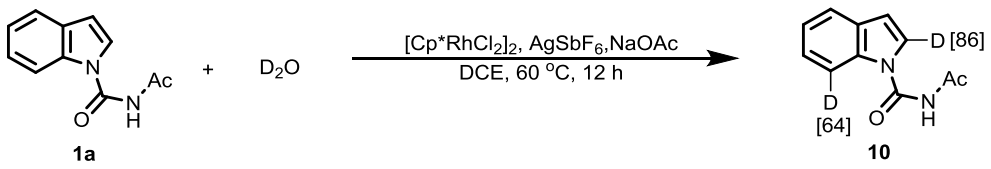


Figure S2. Rate profile at initial stage within 60 min.

$KIE = K_H/K_D = 1.44$

5.6 Deuterium Labeling Experiment



1a **10**

A reaction tube (10 mL) with magnetic stir bar was charged with **1a** (40 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 0.010 mmol), $AgSbF_6$ (21 mg, 0.060 mmol), NaOAc (25 mg, 0.30 mmol), D_2O (0.50 mL) and DCE (2.0 mL). The reaction was allowed to stir at 60 °C oil bath for 12 h. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired products **10**.

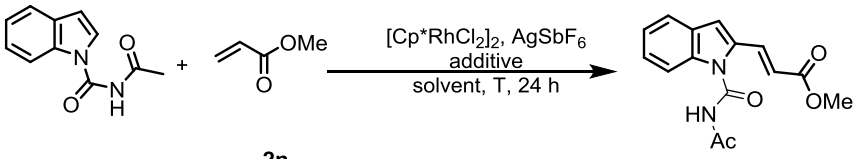
2,7-Dideutero-*N*-acetyl-1*H*-indole-1-carboxamide (**10**): a white solid. 85% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.99 (s, 1H), 8.20 (d, J = 8.0 Hz, 0.36 H), 7.90 (d, J = 3.5 Hz, 0.14 H), 7.61 (dd, J = 8.0, 1.5 Hz, 1H), 7.34−7.30 (m, 1H), 7.25 (t, J = 7.5 Hz, 1H), 6.73 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.8, 148.8, 135.2 (t, J = 8.8 Hz), 130.2, 125.9 (t, J = 26.2 Hz), 124.2 (d, J = 14.0 Hz), 123.1, 121.0, 115.0 (t, J = 27.0 Hz), 107.3 (d, J = 22.5 Hz), 25.0; HRMS (ESI) m/z calcd. for $C_{11}H_9D_2N_2O_2$ $[M+H]^+$ 205.0941, found 205.0938.

5.7 The Synthesis of Ortho Alkenylated Complex E

The following three ways were tried and all failed to afford the ortho alkenylated complex **E**. We suppose that the ortho alkenylated complex **E** is unstabitily and unavailable.

Firstly, we tried to change the reaction conditions to obtain the complex **E**. Based on the previous research reports,[4] we attempt the following conditions and failed to obtain the ortho alkenylated complex **E**.

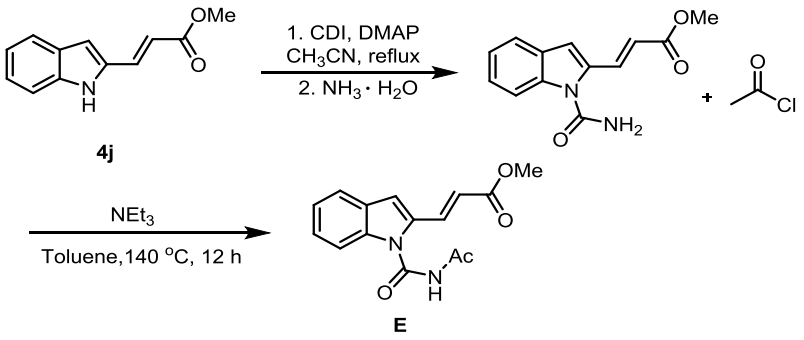
Table S4. Optimization of Reaction Conditions of E[a]



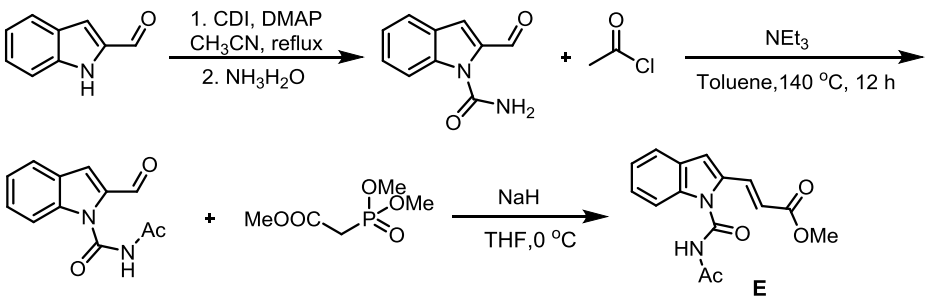
1a **2n** **E**

entry	solvent	additive	T (°C)	yield (%)[b]
1	TFE	$AgSbF_6$/NaOAc	45	<5
2	TFE	$AgSbF_6$/NaOAc	25	<5
3	DCE	$AgSbF_6$/NaOAc	45	<5
4	MeOH	$AgSbF_6$/NaOAc	45	<5
5	MeCN	$AgSbF_6$/NaOAc	45	<5
6	THF	$AgSbF_6$/NaOAc	45	<5

[a]Reaction conditions: **1a** (0.2 mmol), **2n** (0.6 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $AgSbF_6$ (0.06 mmol), NaOAc (0.3 mmol), and solvent (1 mL). [b]Isolated yield.



A reaction tube (10 mL) with magnetic stir bar was charged with indole **4j** (1.0 mmol, 1.0 equiv.), 1,1'-carbonyldiimidazole (CDI, 1.5 mmol, 1.5 equiv.) and 4-dimethylaminepyridine (DMAP, 5.0 mol %). Then 5 mL anhydrous acetonitrile was added to the reaction tube. The reaction system was stirred at 120 °C oil bath for 10 h. After cooling to room temperature, ammonium hydroxide (1.5 mmol) was added and then the reaction was stirred at 60°C oil bath for another 6 h. However, no product **E** was detected.



A reaction tube (10 mL) with magnetic stir bar was charged with 1*H*-indol-2-ylcarboxaldehyde (1.0 mmol, 1.0 equiv.), 1,1'-carbonyldiimidazole (CDI, 1.5 mmol, 1.5 equiv.) and 4-dimethylaminepyridine (DMAP, 5.0 mol %). Then 5 mL anhydrous acetonitrile was added to the reaction tube. The reaction system was stirred at 120 °C oil bath for 10 h. After cooling to room temperature, ammonium hydroxide (1.5 mmol) was added and then the reaction was stirred at 60°C oil bath for another 6h. However, no product **E** was detected.

6. References

(1) Q. Xiao, Q. He, J. Li and J. Wang, *Org. Lett.*, 2015, **17**, 6090.

(2) (a) K. N. Parida and J. N. Moorthy, *J. Org. Chem.*, 2015, **80**, 8354; (b) P. Zhou, B. Hu, J. Yang, L. Li, K. Rao, D. Zhu and F. Yu, *Eur. J. Org. Chem.*, 2017, **2017**, 7256.

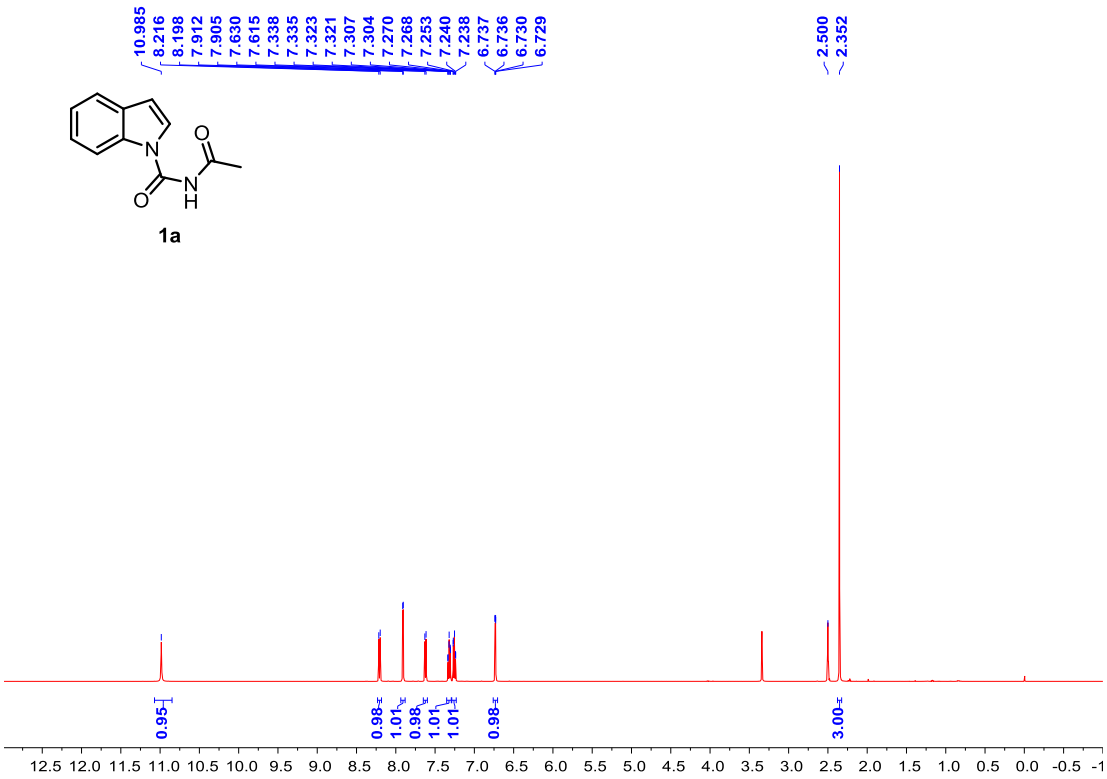
(3) (a) J. J. Maresh, L. Giddings, A. Friedrich, E. A. Loris, S. Panjikar, B. L. Trout, J. Stöckigt, B. Peters and S. E. O'Connor, *J. Am. Chem. Soc.* 2008, **130**, 710; (b) W. Kong, X. Chen, M. Wang, H.-X. Dai and J. Yu, *Org. Lett.*, 2017, **20**, 284.

(4) J. Zhang, H. Xie, H. Zhu, S. Zhang, M. Reddy Lonka and H. Zou, *ACS Catal*., 2019, **9**, 10233.

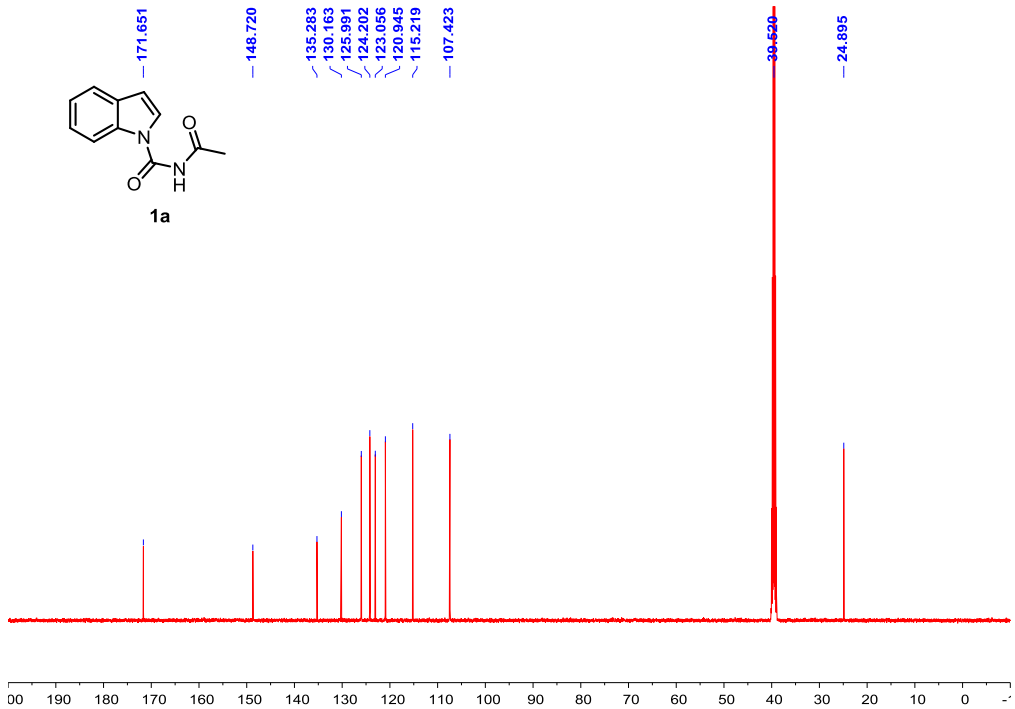
7. NMR Spectra

N-Acetyl-1*H*-indole-1-carboxamide (1a)

^{1}H NMR, 500 MHz, DMSO-d_6

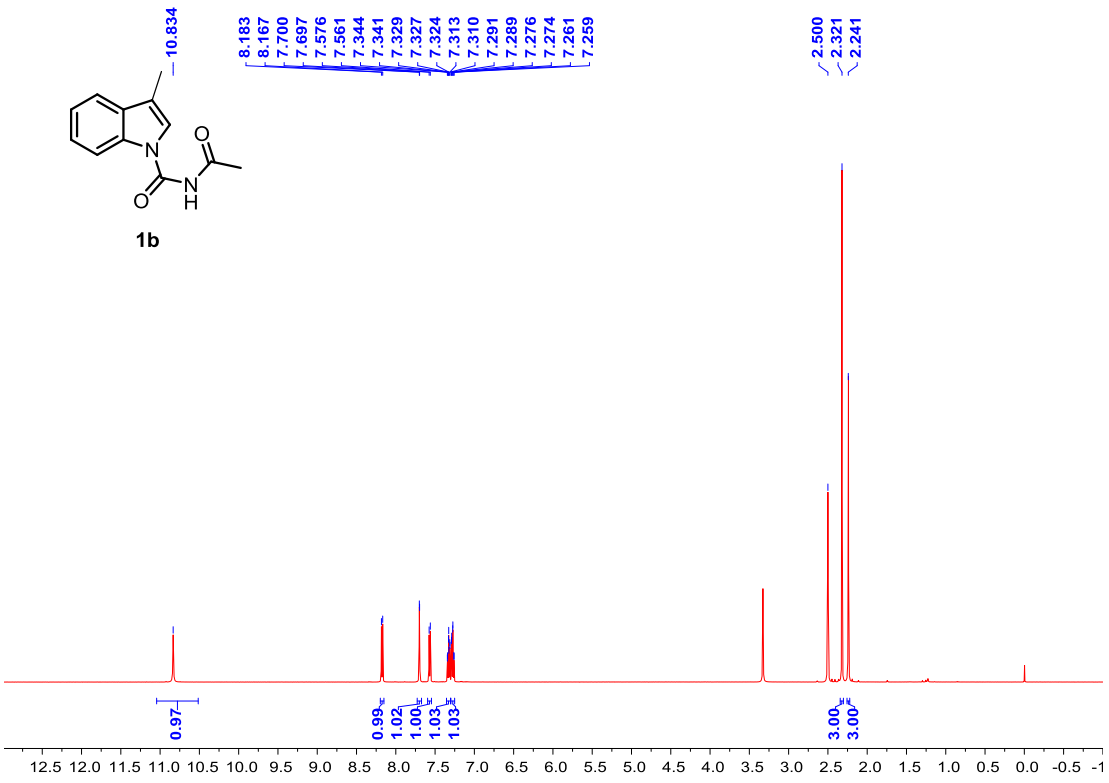


^{13}C NMR, 125 MHz, DMSO-d_6

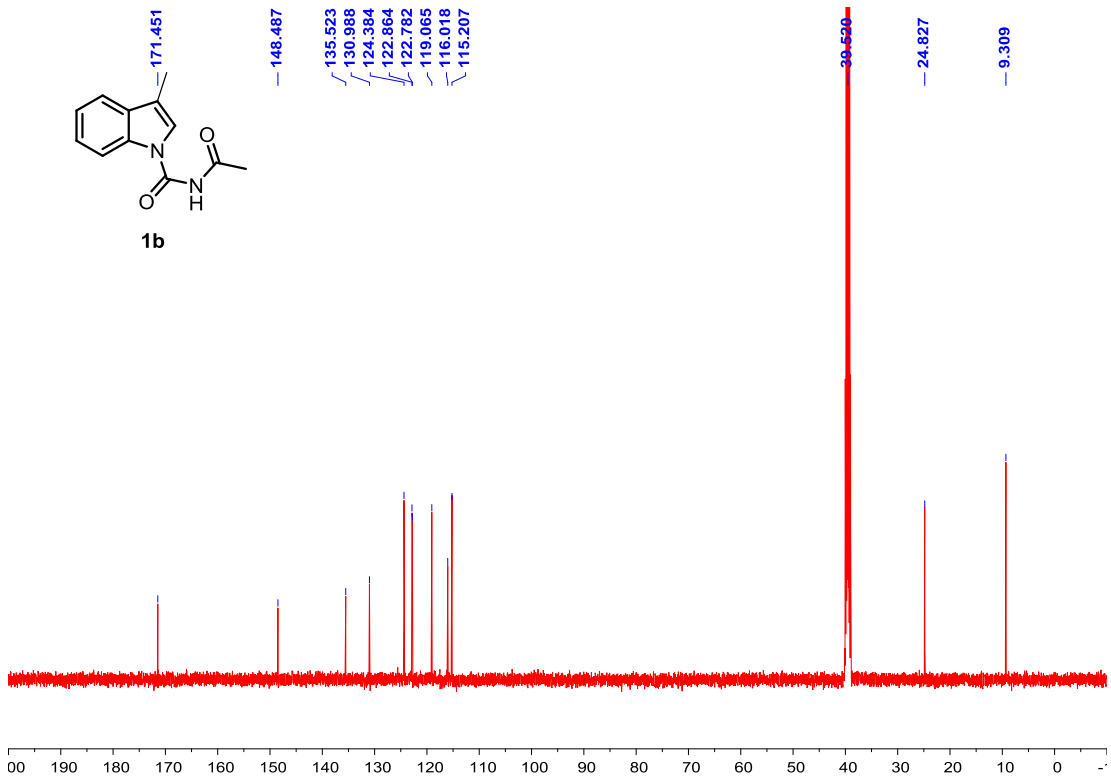


_N_-Acetyl-4-methyl-1_H_-indole-1-carboxamide (1b)

^{1}H NMR, 500 MHz, DMSO-d_6

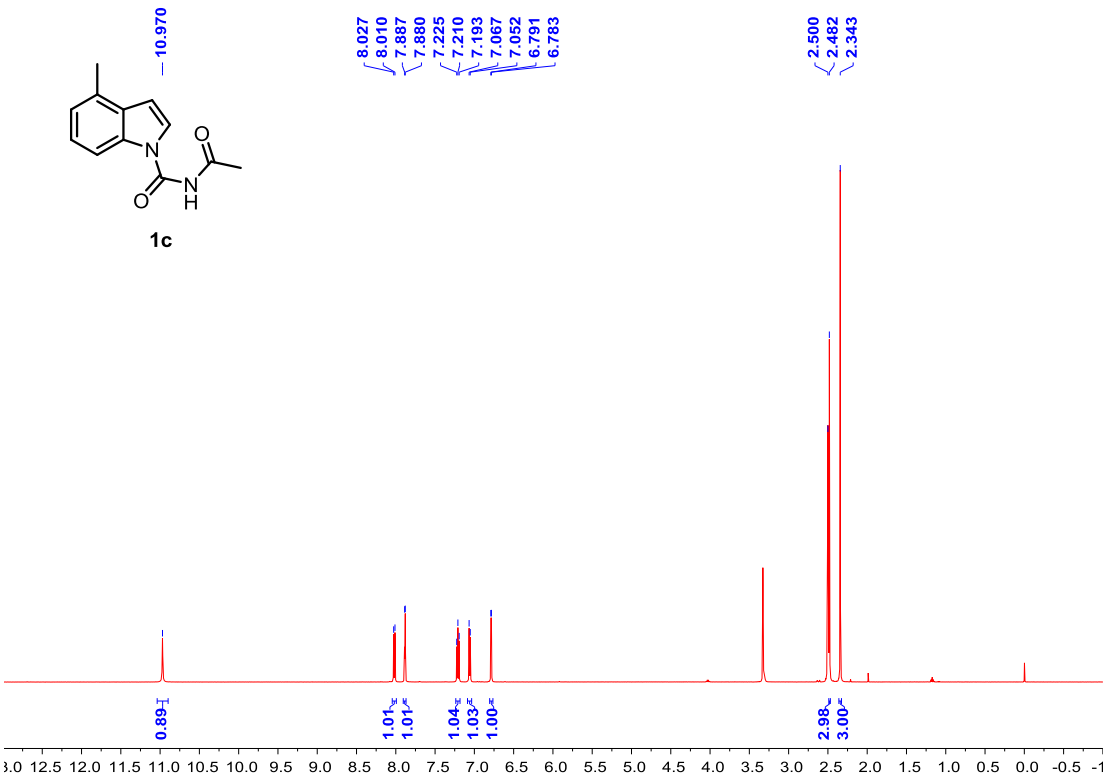


^{13}C NMR, 125 MHz, DMSO-d_6

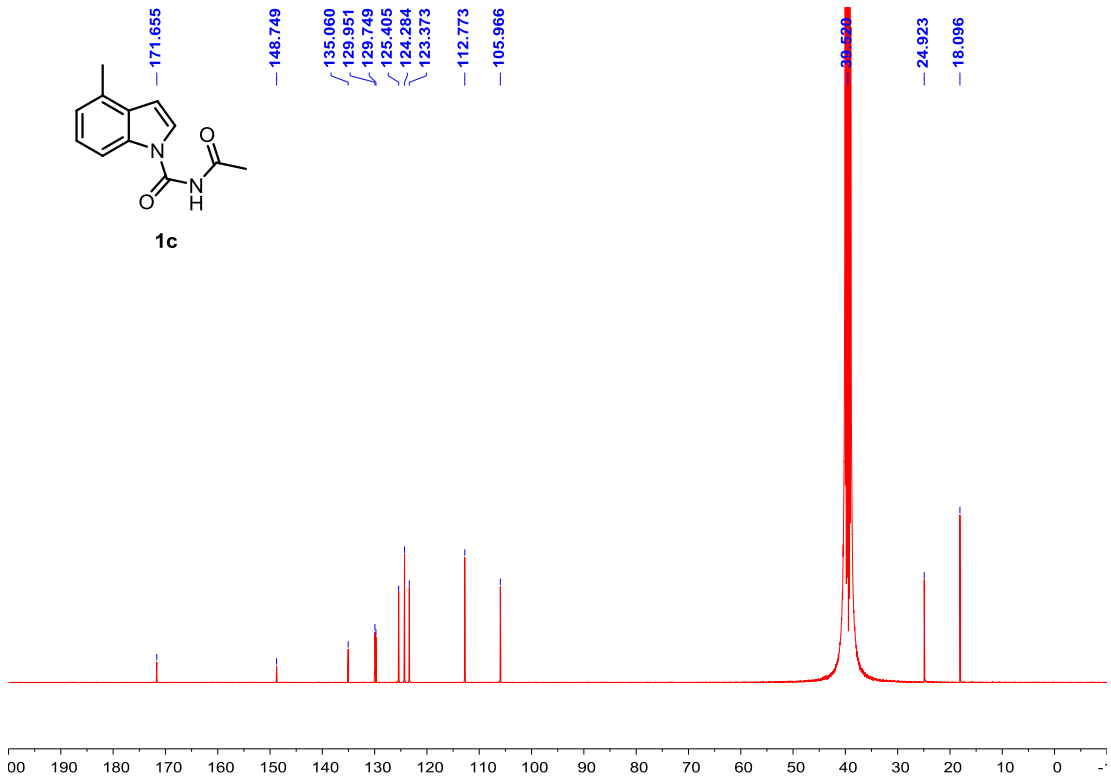


_N_-Acetyl-4-methyl-1_H_-indole-1-carboxamide (1c)

^{1}H NMR, 500 MHz, DMSO-d_6

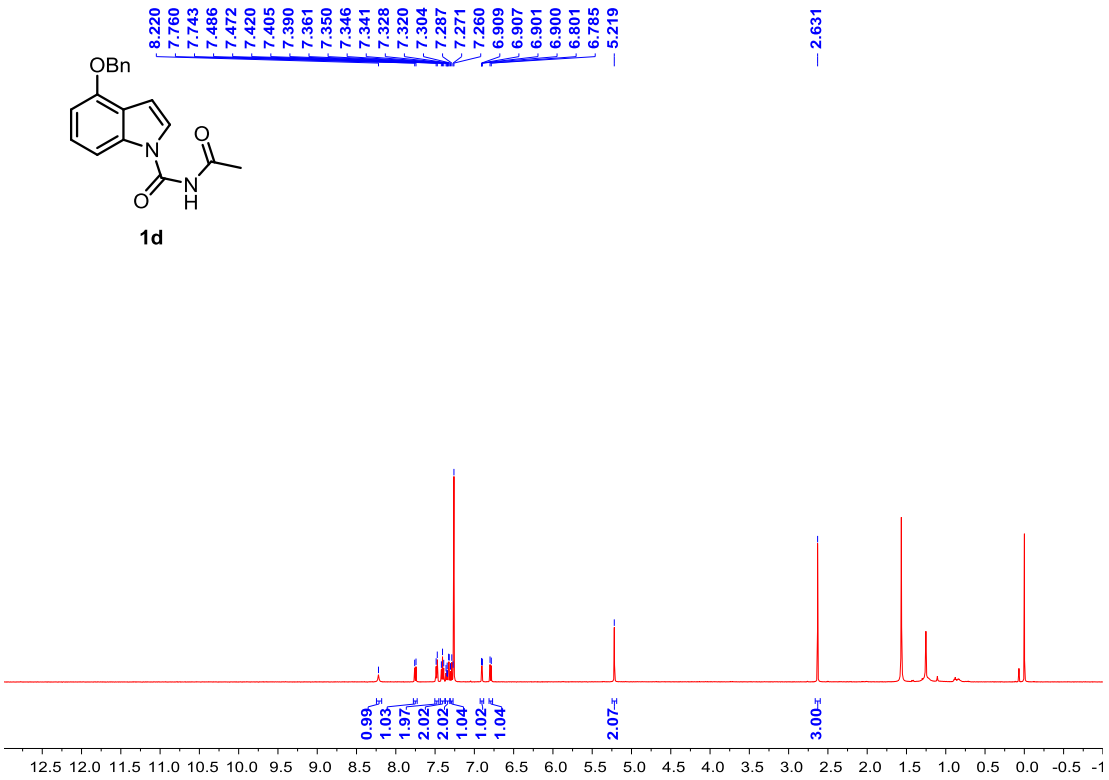


^{13}C NMR, 125 MHz, DMSO-d_6

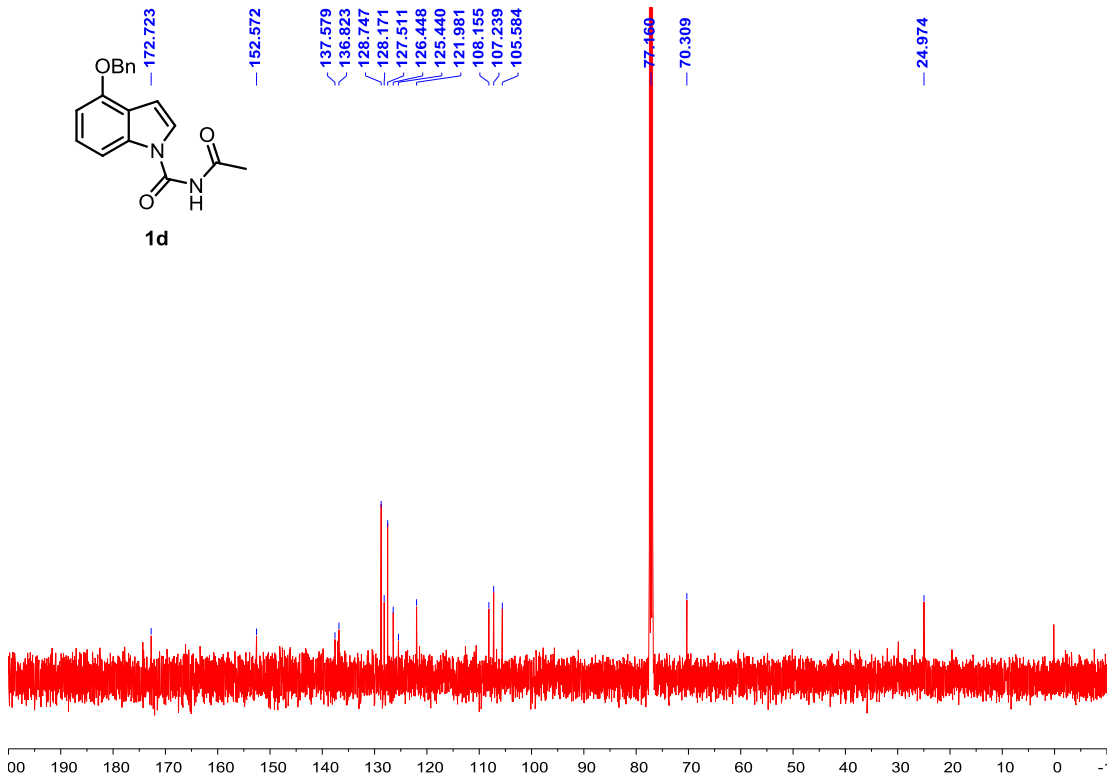


_N_-Acetyl-4-(benzyloxy)-1_H_-indole-1-carboxamide (1d)

^{1}H NMR, 500 MHz, $CDCl_3$

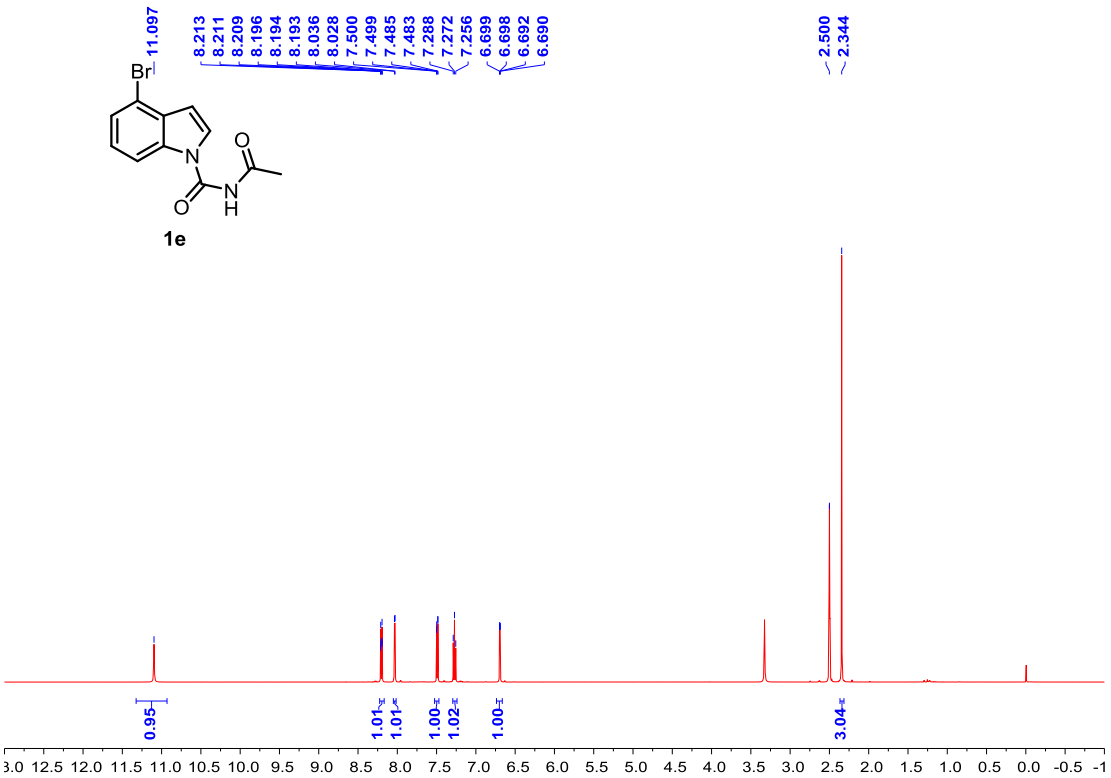


^{13}C NMR, 125 MHz, $CDCl_3$

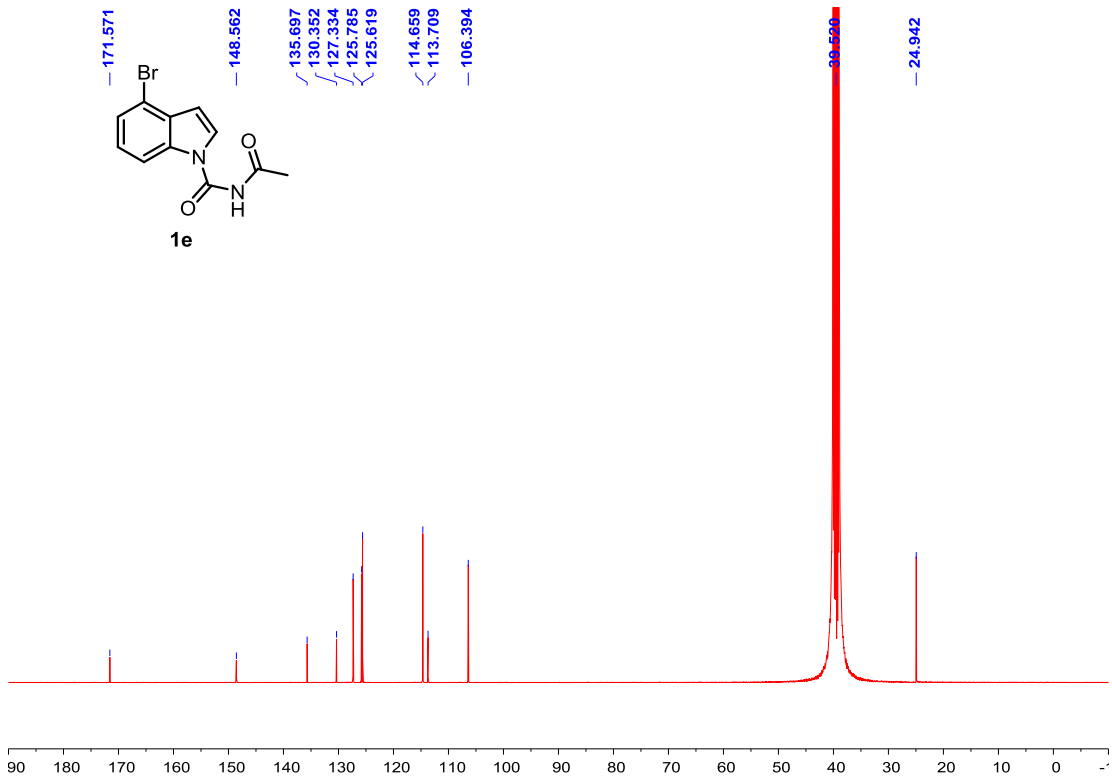


_N_-Acetyl-4-bromo-1_H_-indole-1-carboxamide (1e)

^{1}H NMR, 500 MHz, DMSO-d_6

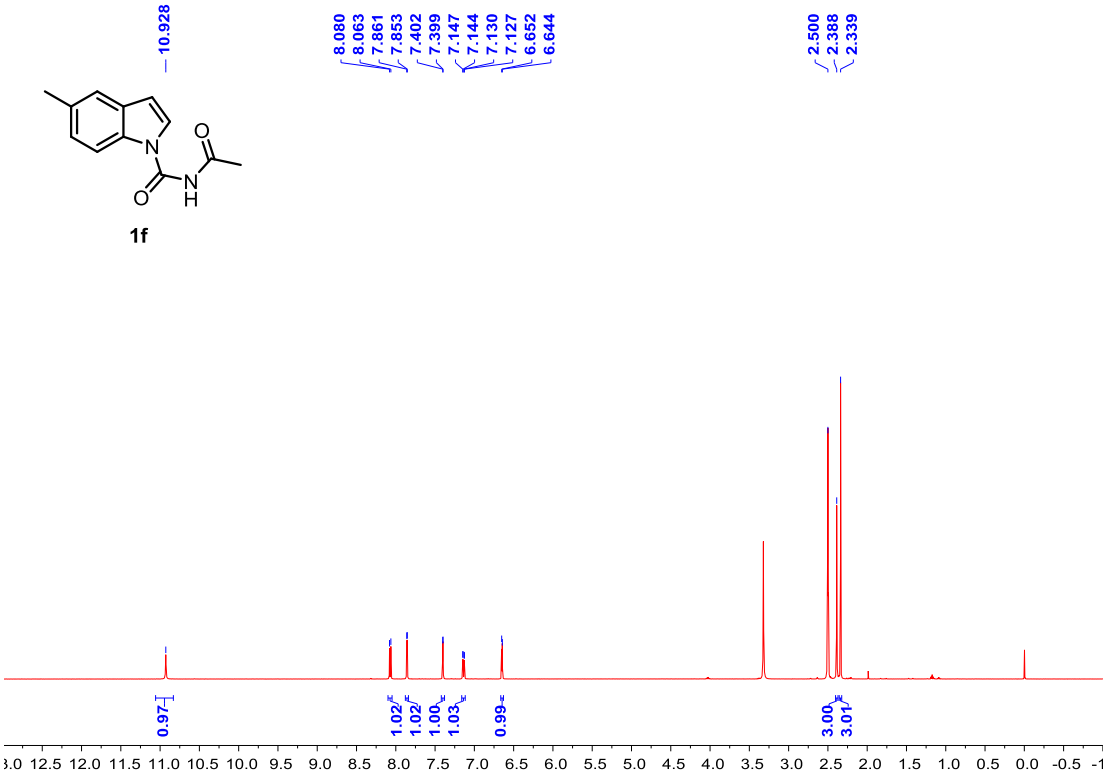


^{13}C NMR, 125 MHz, DMSO-d_6

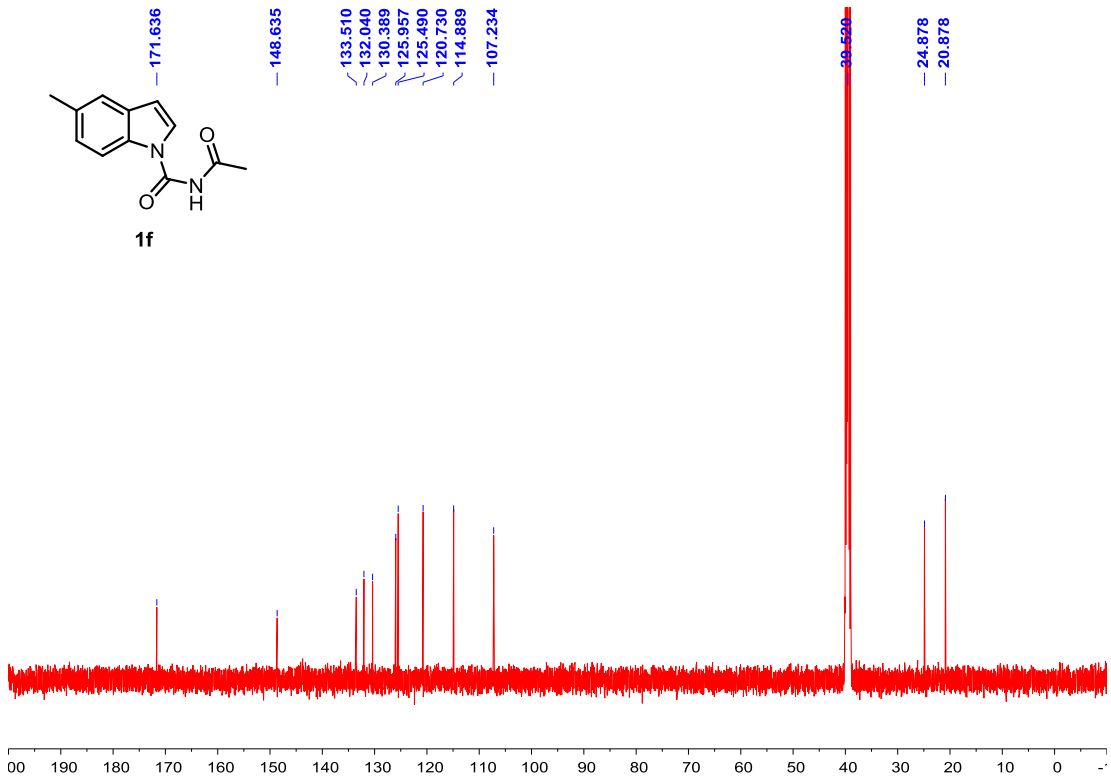


_N_-Acetyl-5-methyl-1_H_-indole-1-carboxamide (1f)

^{1}H NMR, 500 MHz, DMSO-d_6

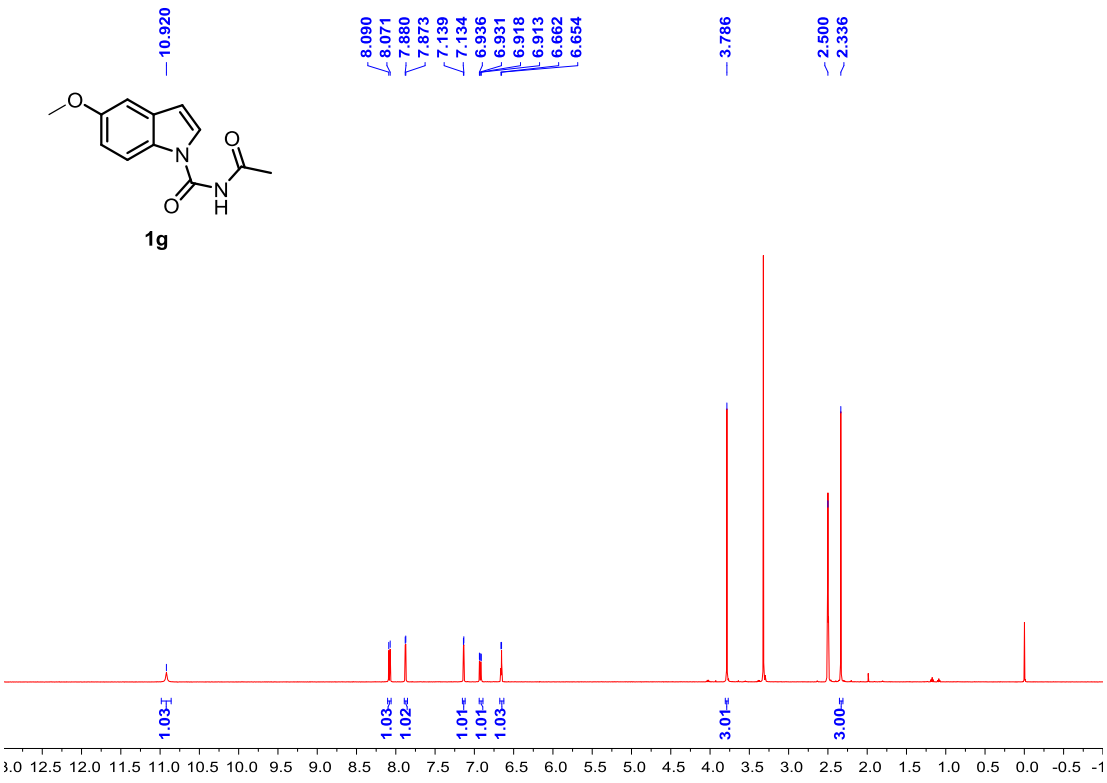


^{13}C NMR, 125 MHz, DMSO-d_6

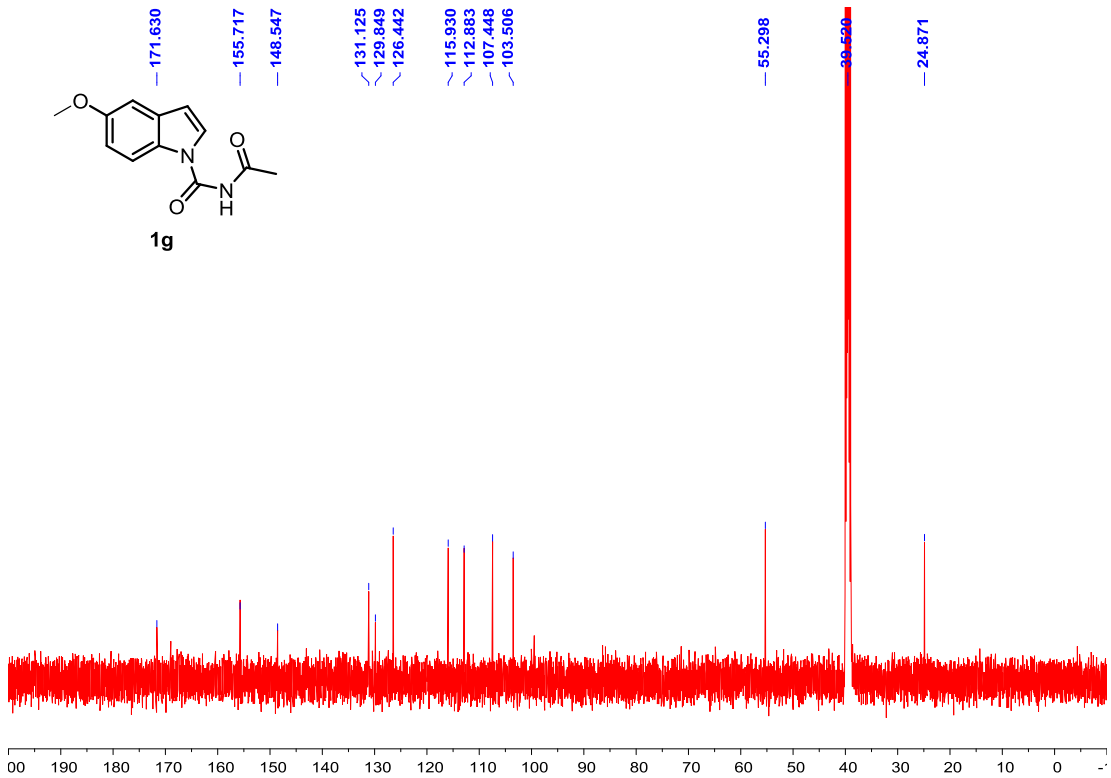


_N_-Acetyl-5-methoxy-1_H_-indole-1-carboxamide (1g)

^{1}H NMR, 500 MHz, DMSO-d_6

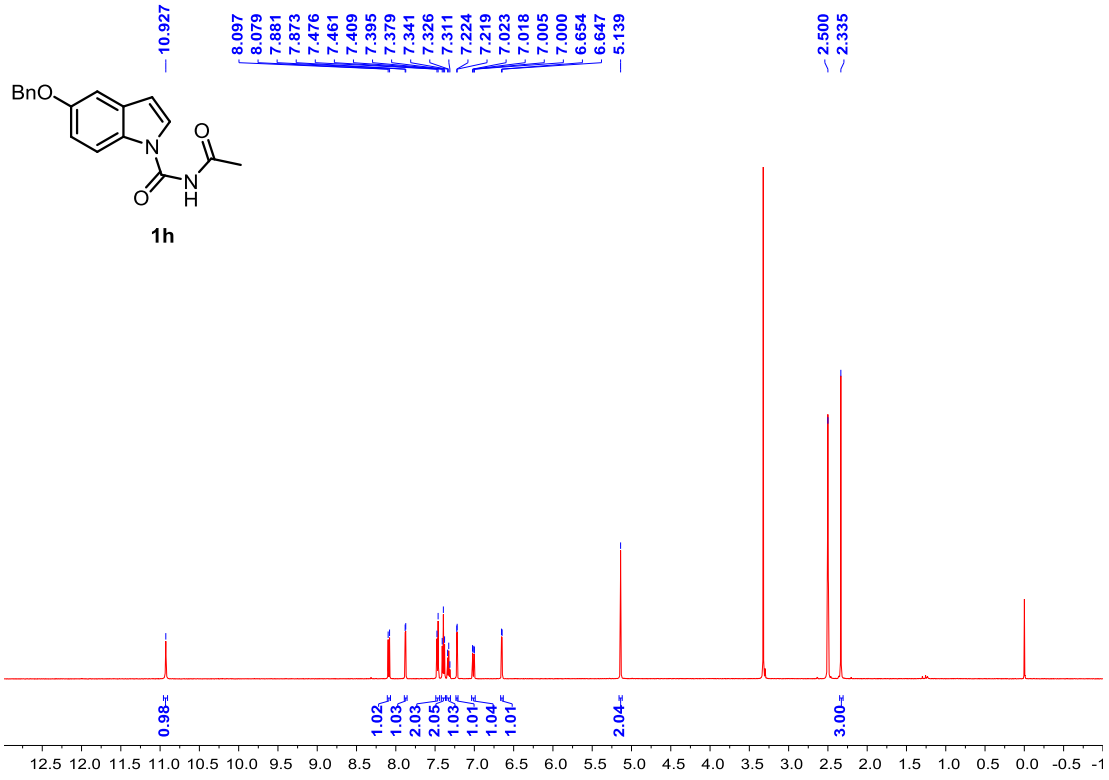


^{13}C NMR, 125 MHz, DMSO-d_6

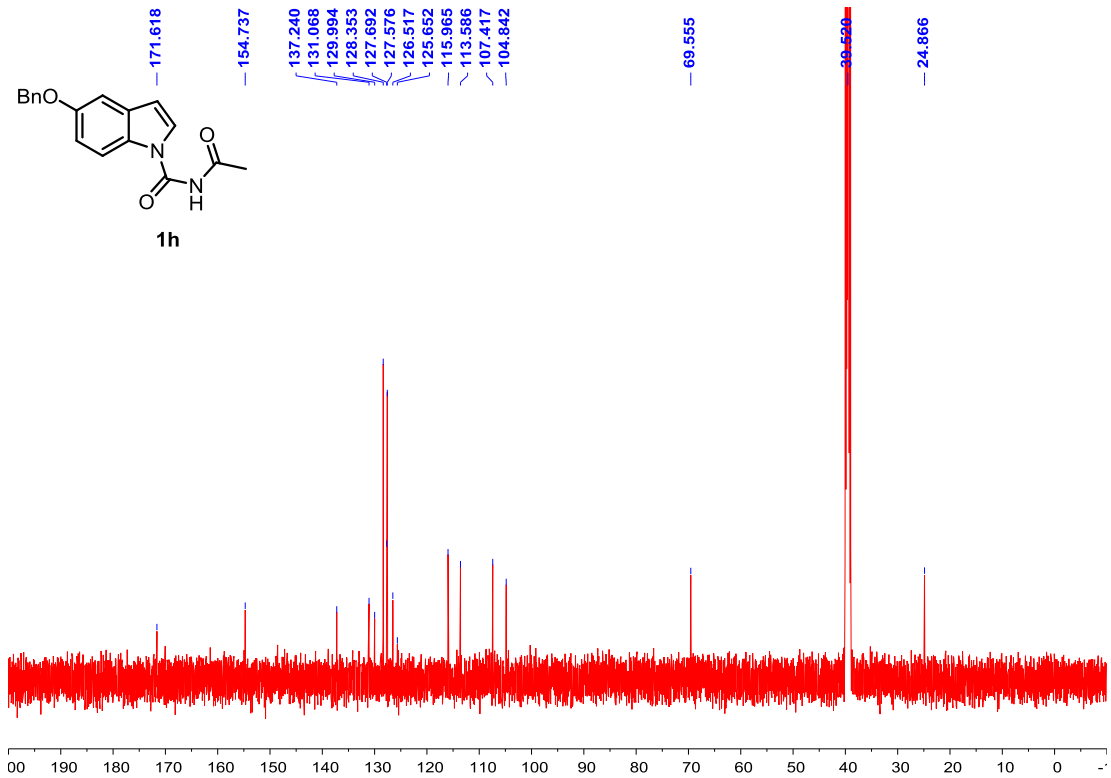


_N_-Acetyl-5-(benzyloxy)-1_H_-indole-1-carboxamide (1h)

^{1}H NMR, 500 MHz, DMSO-d_6

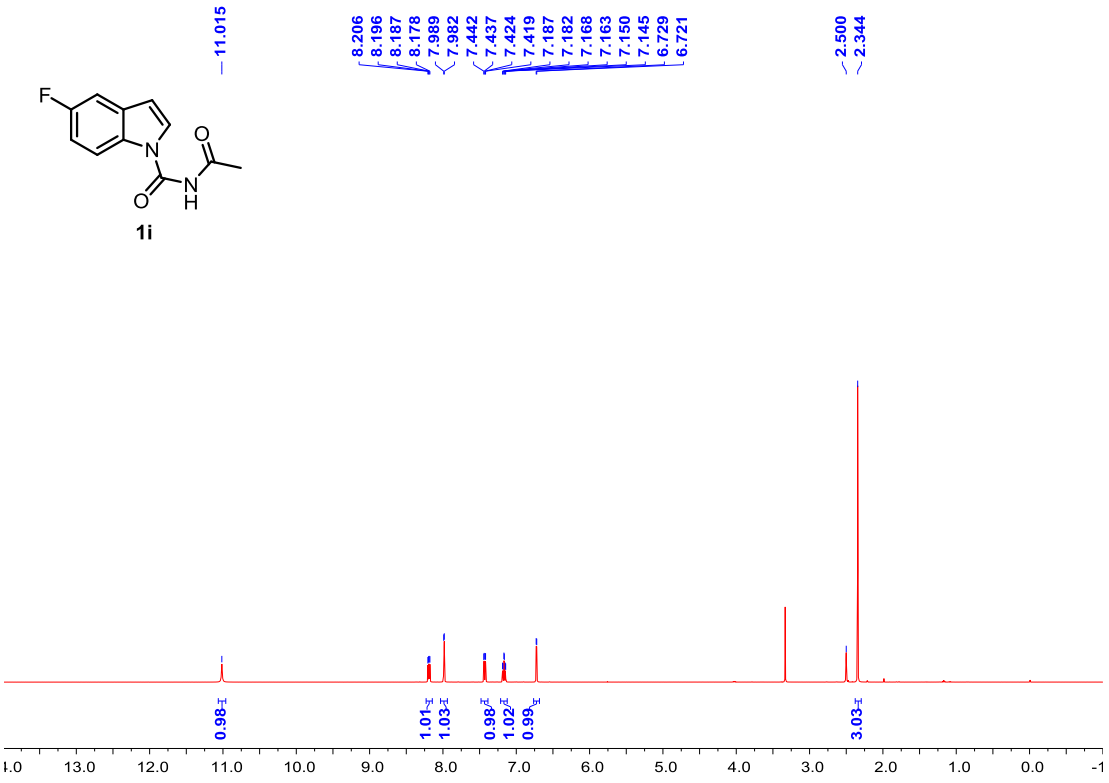


^{13}C NMR, 125 MHz, DMSO-d_6

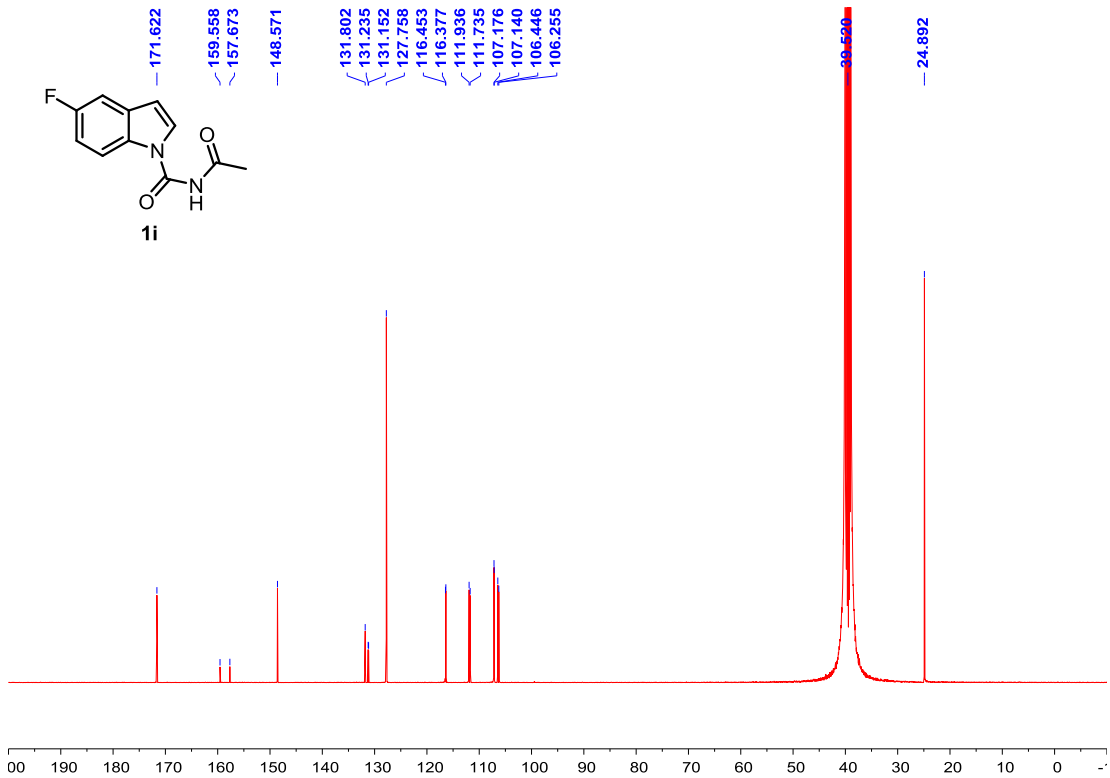


_N_-Acetyl-5-fluoro-1_H_-indole-1-carboxamide (1i)

^{1}H NMR, 500 MHz, DMSO-d_6

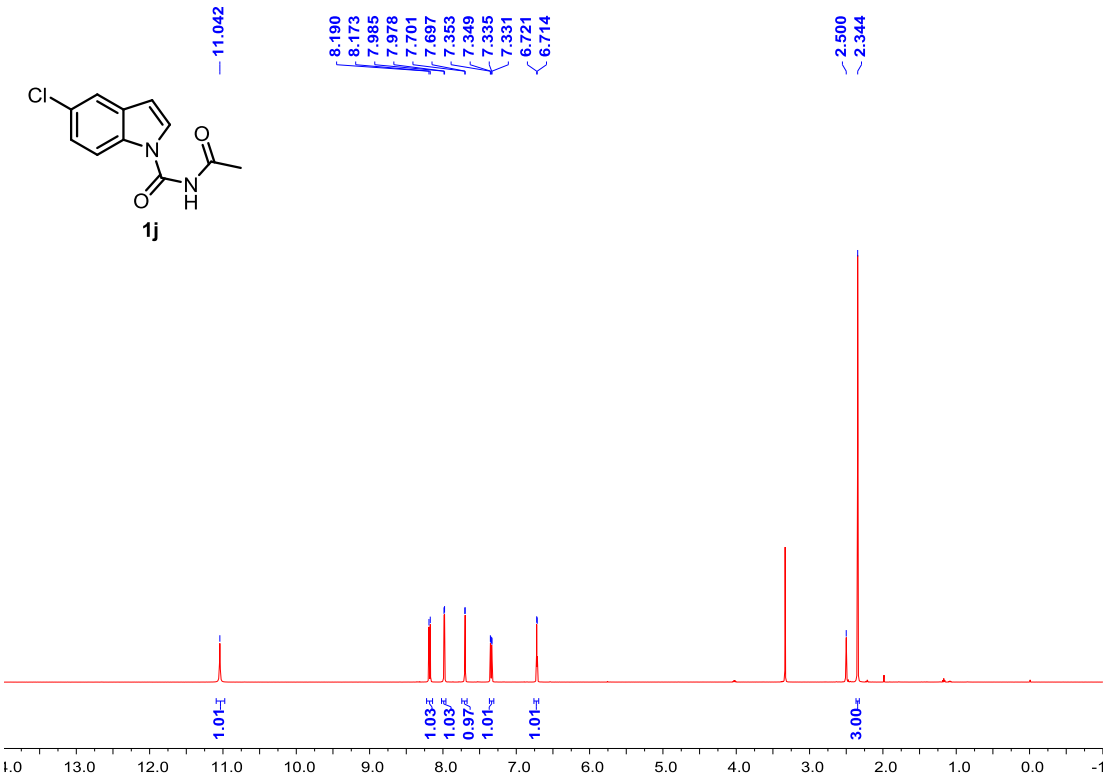


^{13}C NMR, 125 MHz, DMSO-d_6

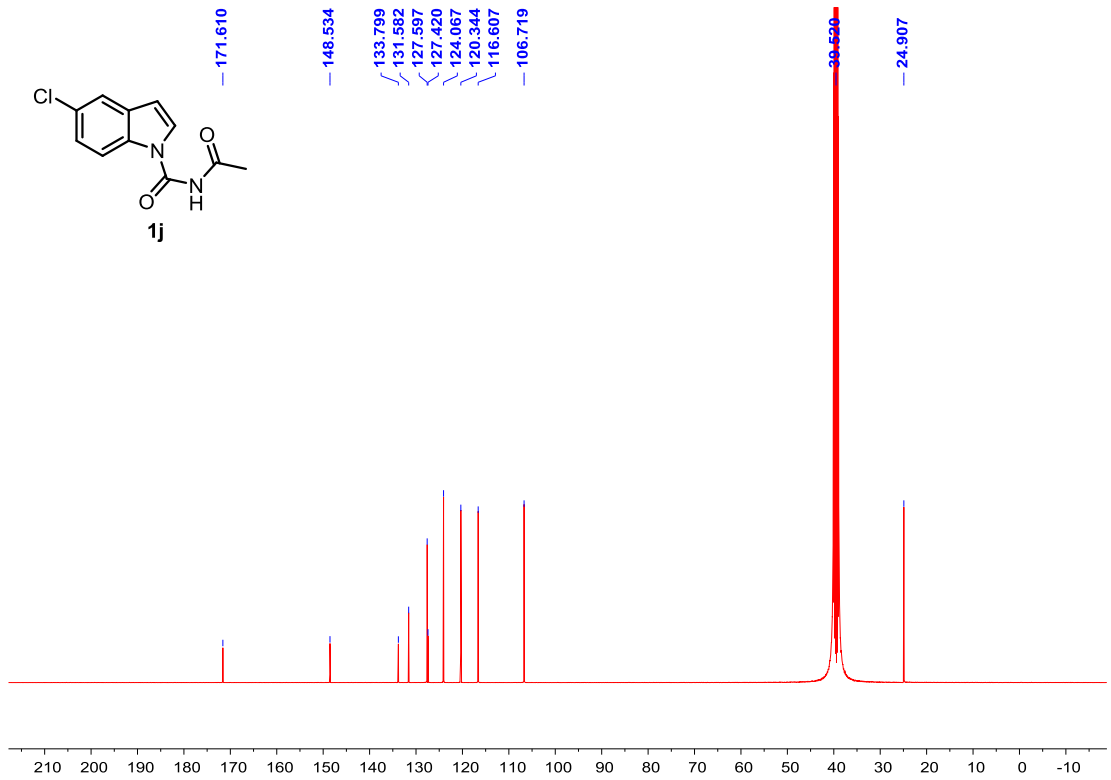


_N_-Acetyl-5-chloro-1_H_-indole-1-carboxamide (1j)

^{1}H NMR, 500 MHz, DMSO-d_6

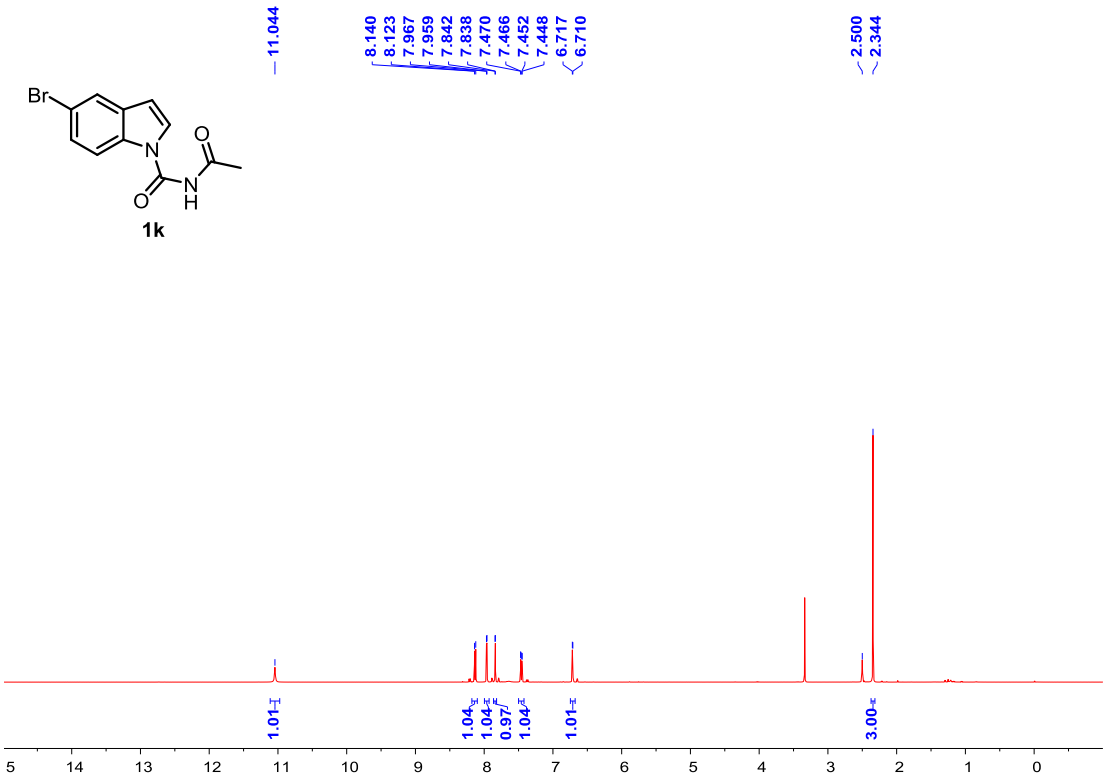


^{13}C NMR, 125 MHz, DMSO-d_6

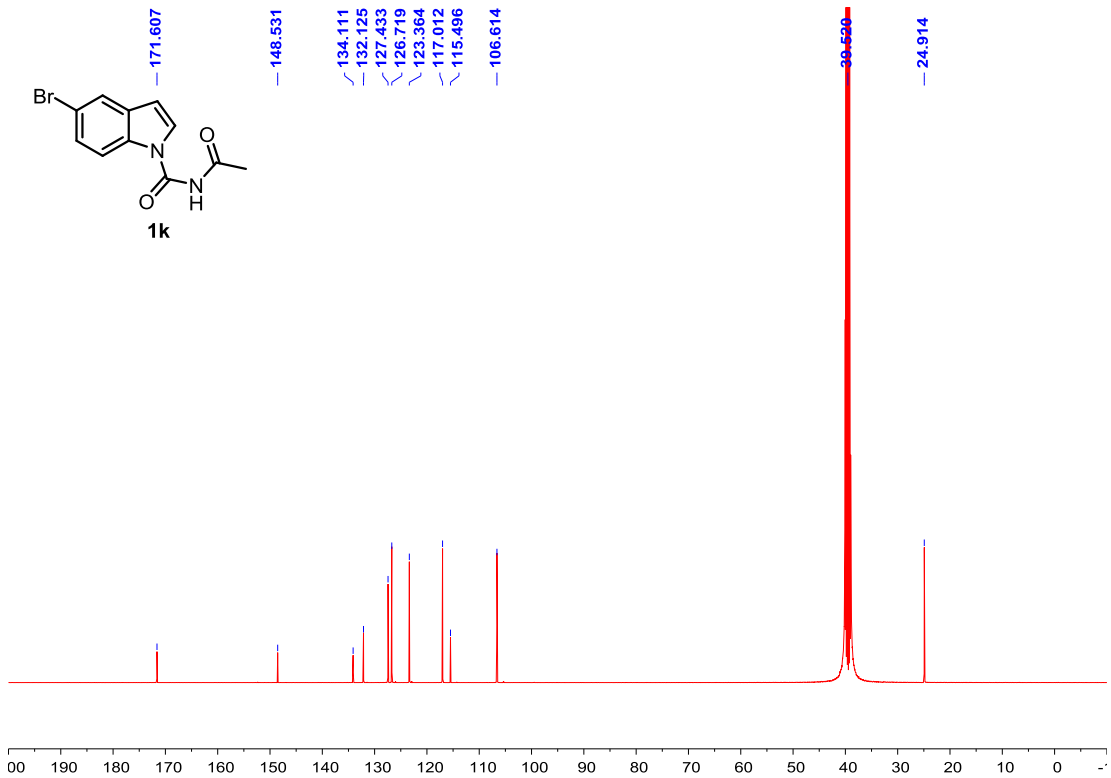


_N_-Acetyl-5-bromo-1_H_-indole-1-carboxamide (1k)

^{1}H NMR, 500 MHz, DMSO-d_6

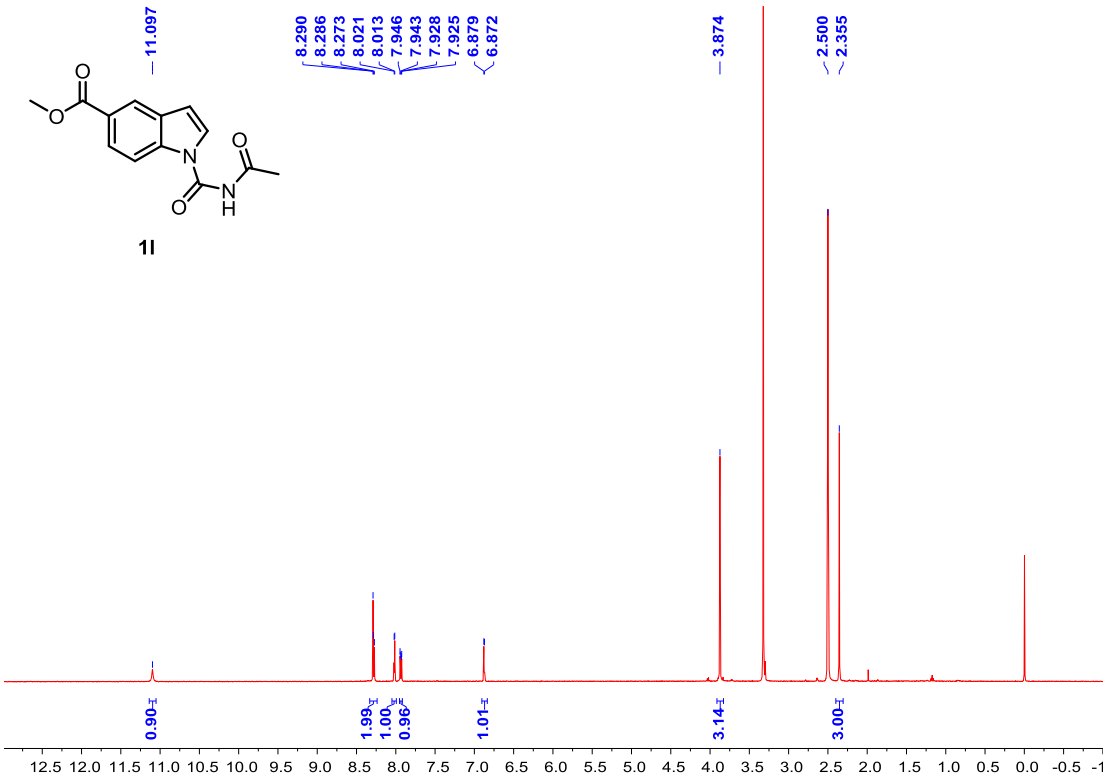


^{13}C NMR, 125 MHz, DMSO-d_6

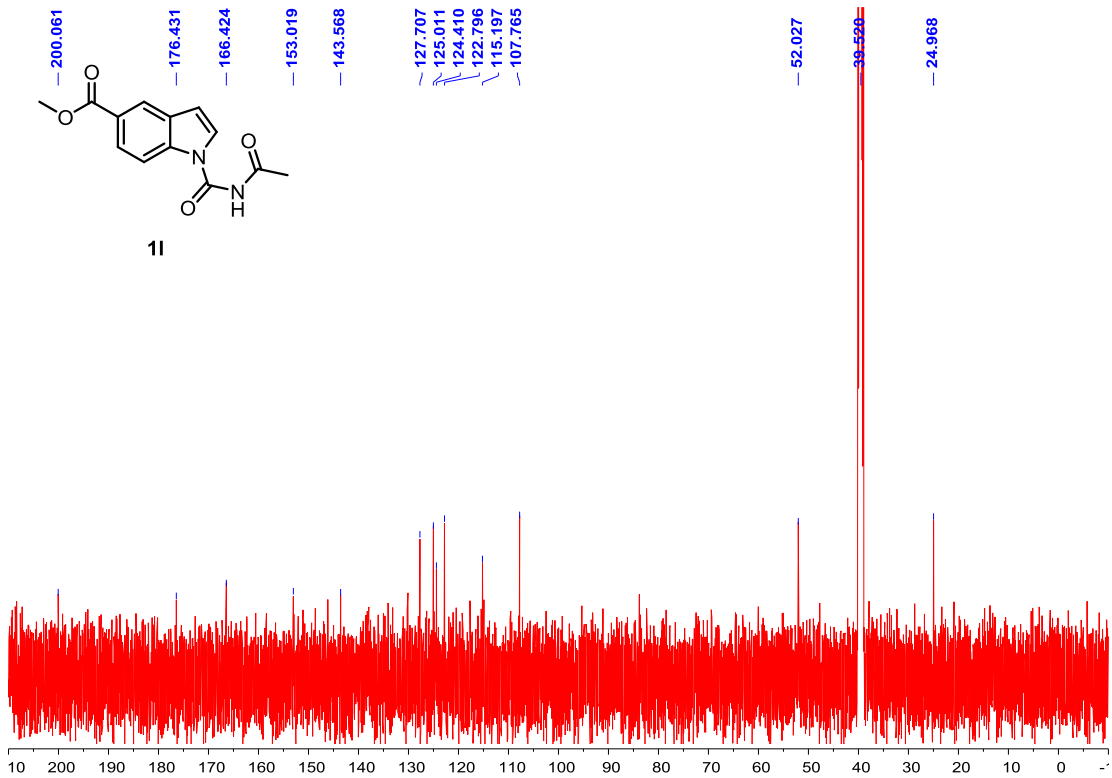


Methyl-1-(acetylcarbamoyl)-1*H*-indole-5-carboxylate (1l)

^{1}H NMR, 500 MHz, DMSO-d_6

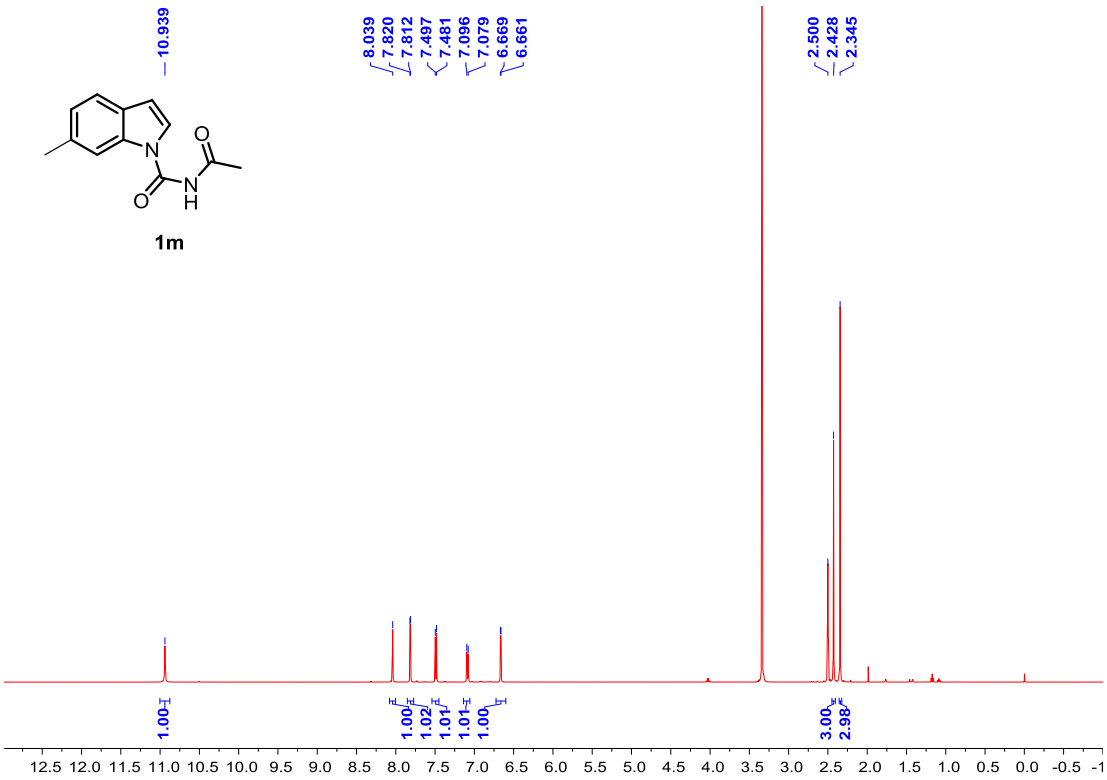


^{13}C NMR, 125 MHz, DMSO-d_6

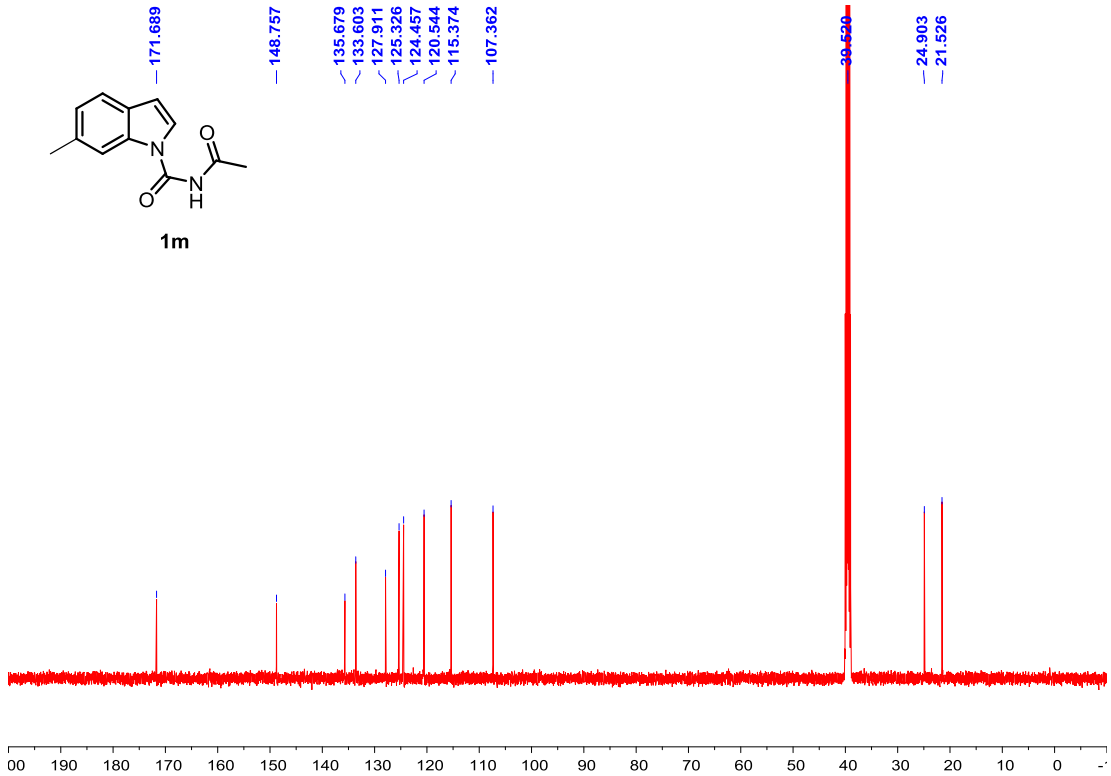


_N_-Acetyl-6-methyl-1_H_-indole-1-carboxamide (1o)

^{1}H NMR, 500 MHz, DMSO-d_6

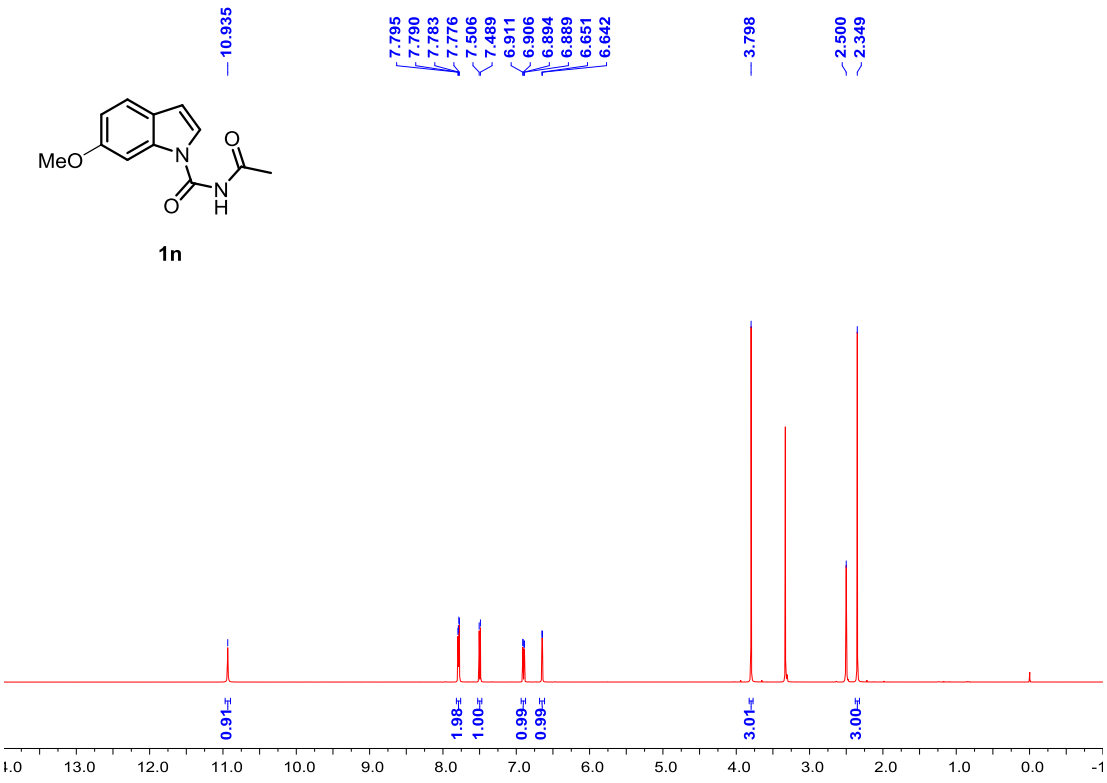


^{13}C NMR, 125 MHz, DMSO-d_6

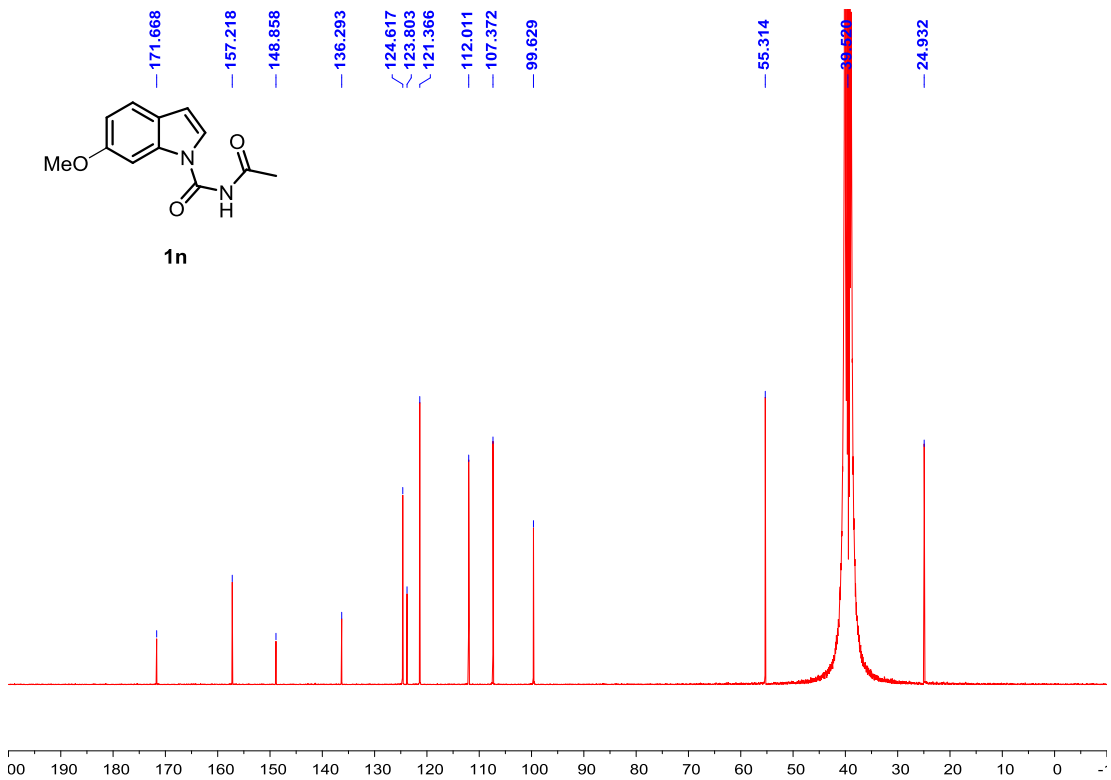


_N_-Acetyl-6-methoxy-1_H_-indole-1-carboxamide (1p)

^{1}H NMR, 500 MHz, DMSO-d_6

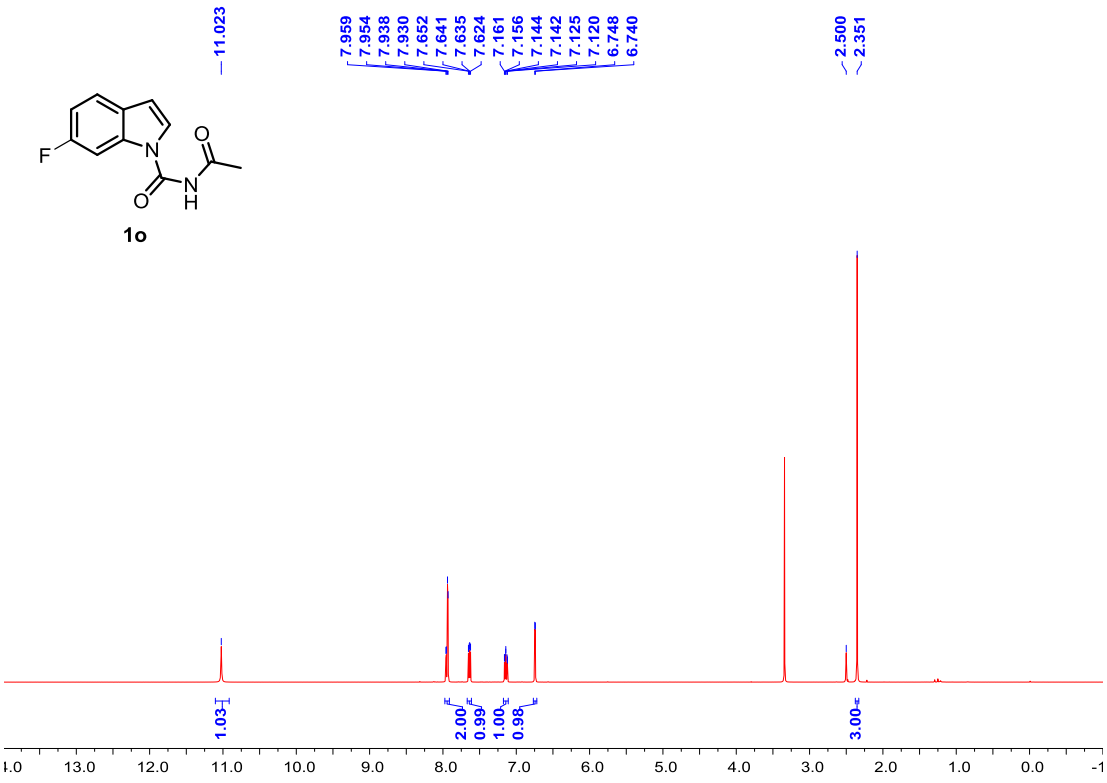


^{13}C NMR, 125 MHz, DMSO-d_6

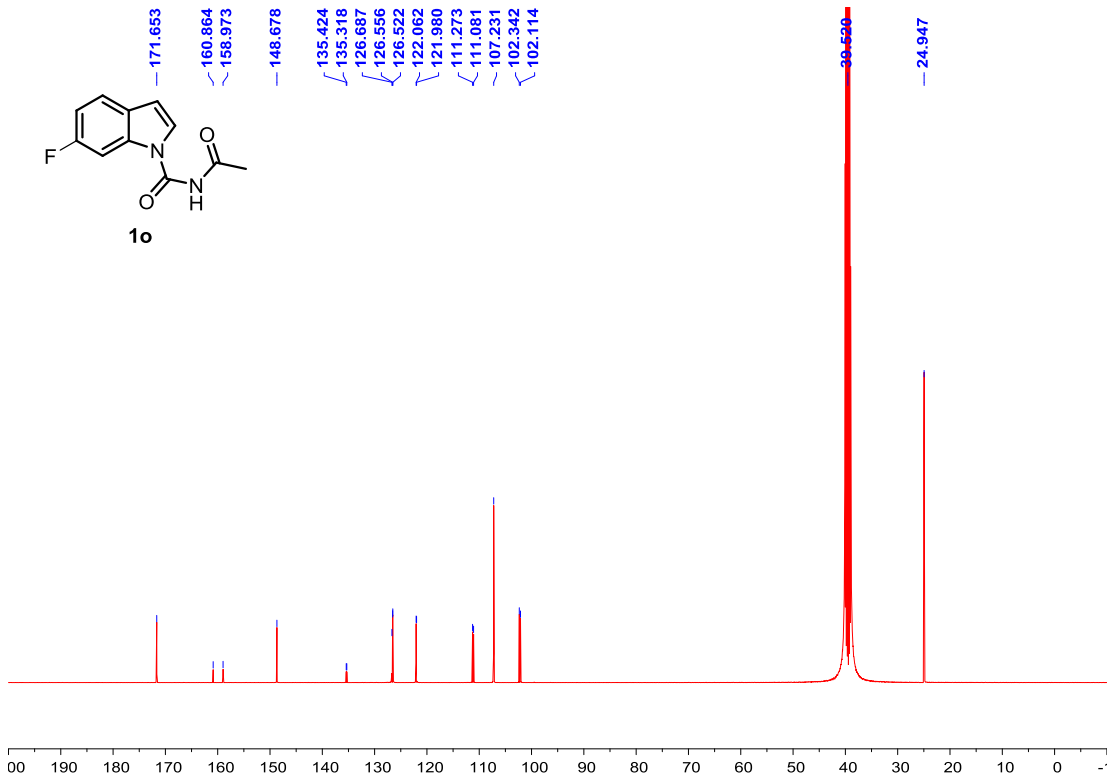


_N_-Acetyl-5-fluoro-1_H_-indole-1-carboxamide (1q)

^{1}H NMR, 500 MHz, DMSO-d_6

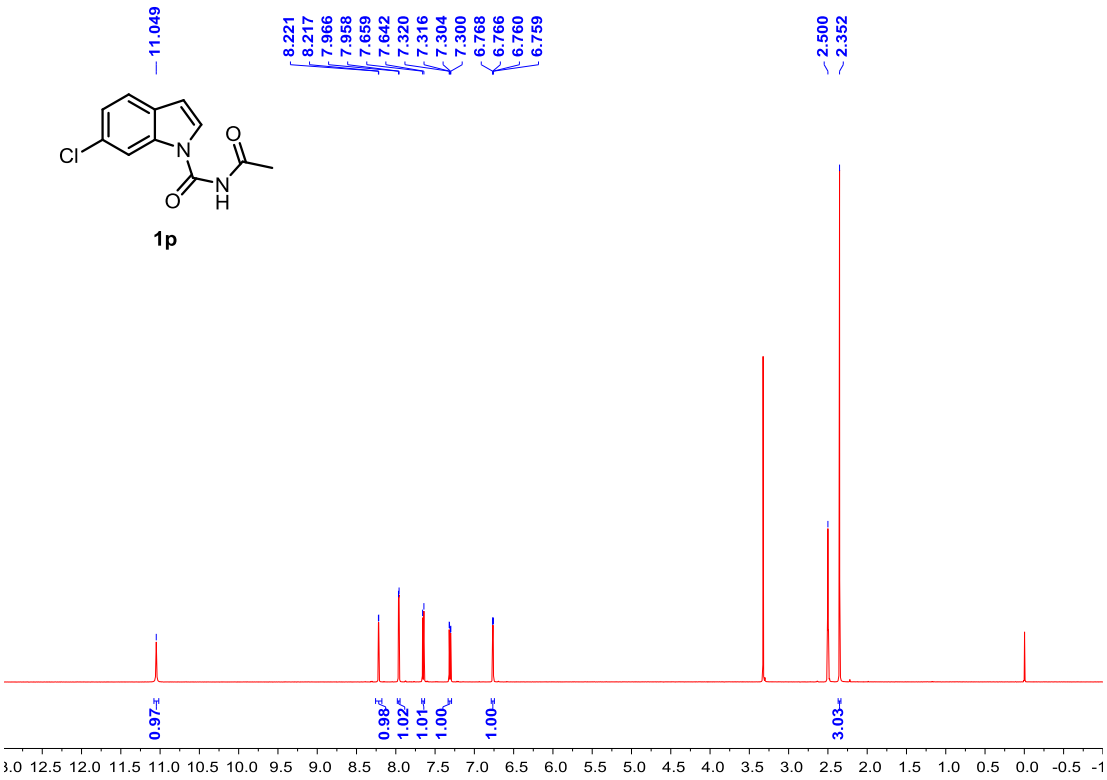


^{13}C NMR, 125 MHz, DMSO-d_6

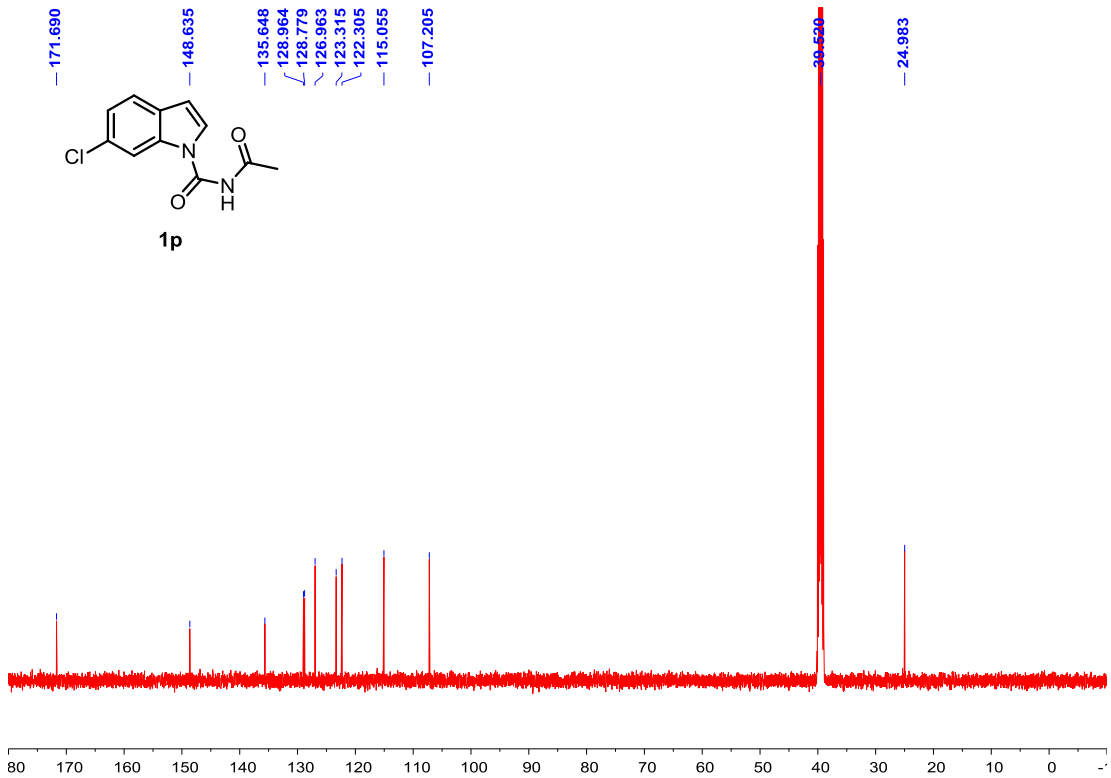


_N_-Acetyl-6-chloro-1_H_-indole-1-carboxamide (1r)

^{1}H NMR, 500 MHz, DMSO-d_6

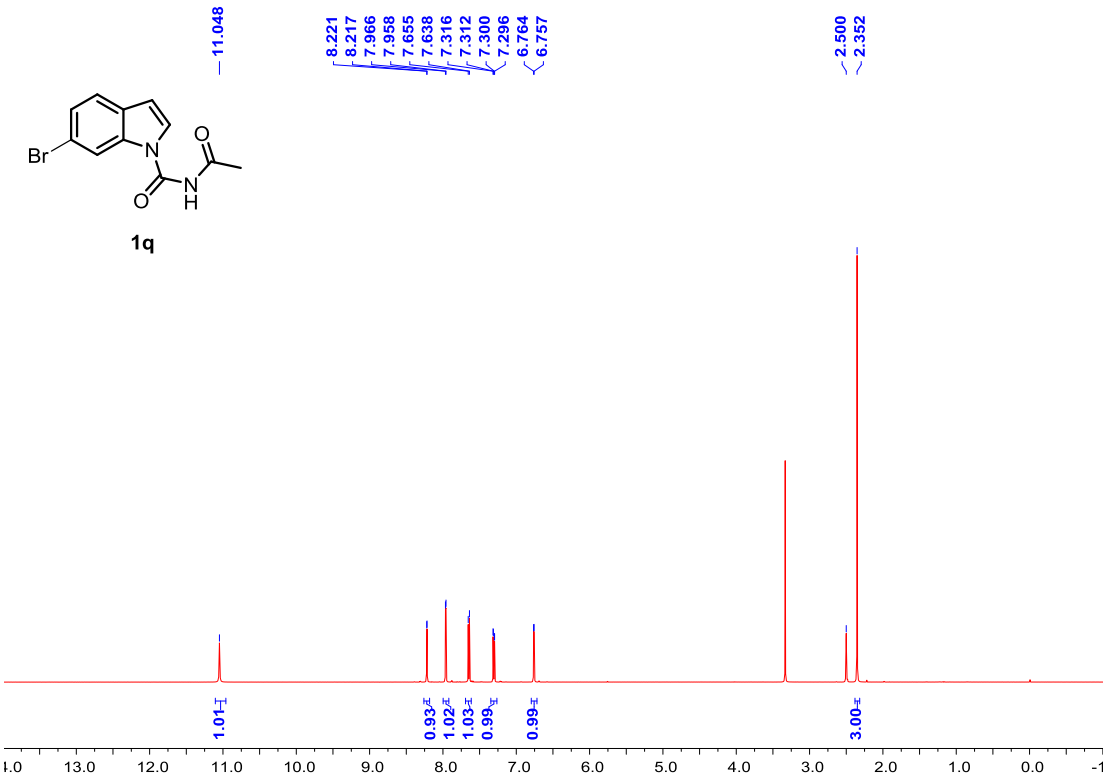


^{13}C NMR, 125 MHz, DMSO-d_6

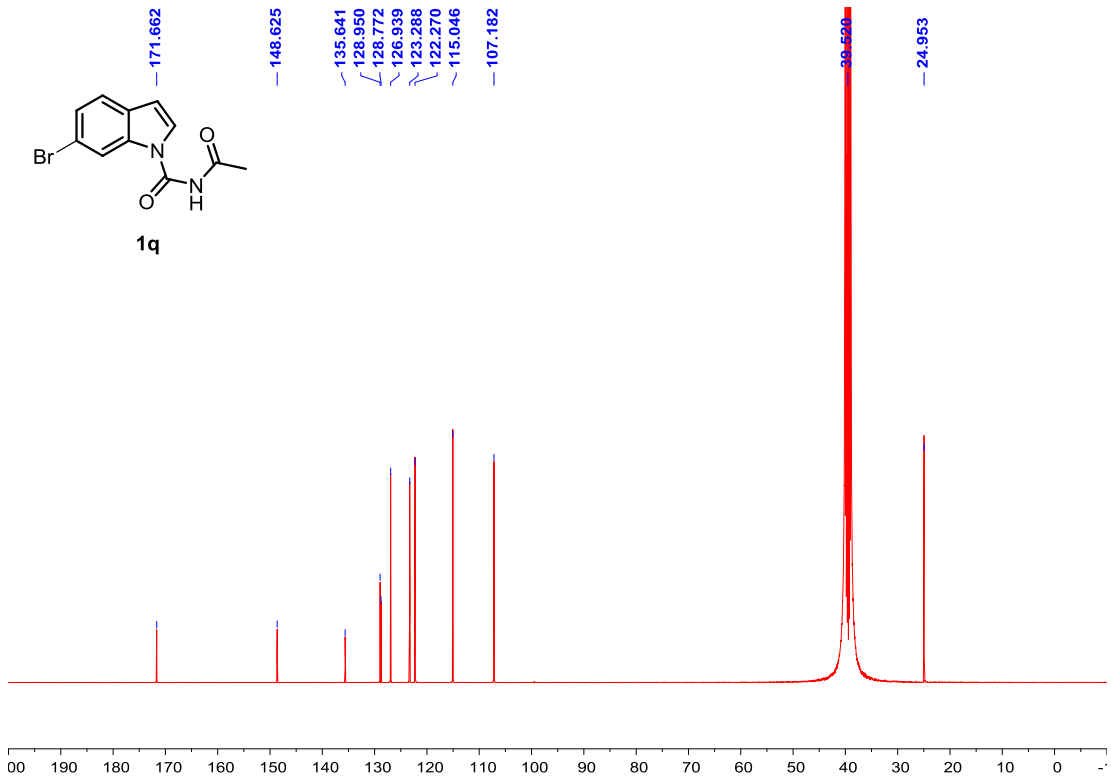


_N_-Acetyl-5-bromo-1_H_-indole-1-carboxamide (1s)

^{1}H NMR, 500 MHz, DMSO-d_6

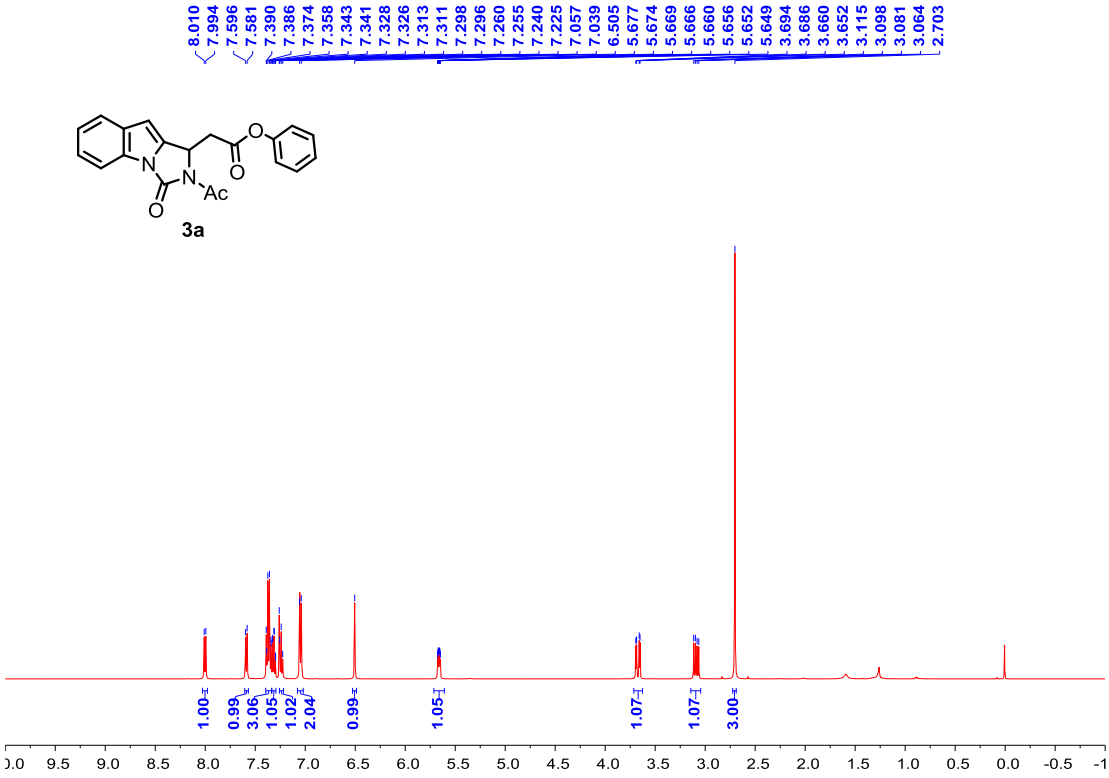


^{13}C NMR, 125 MHz, DMSO-d_6

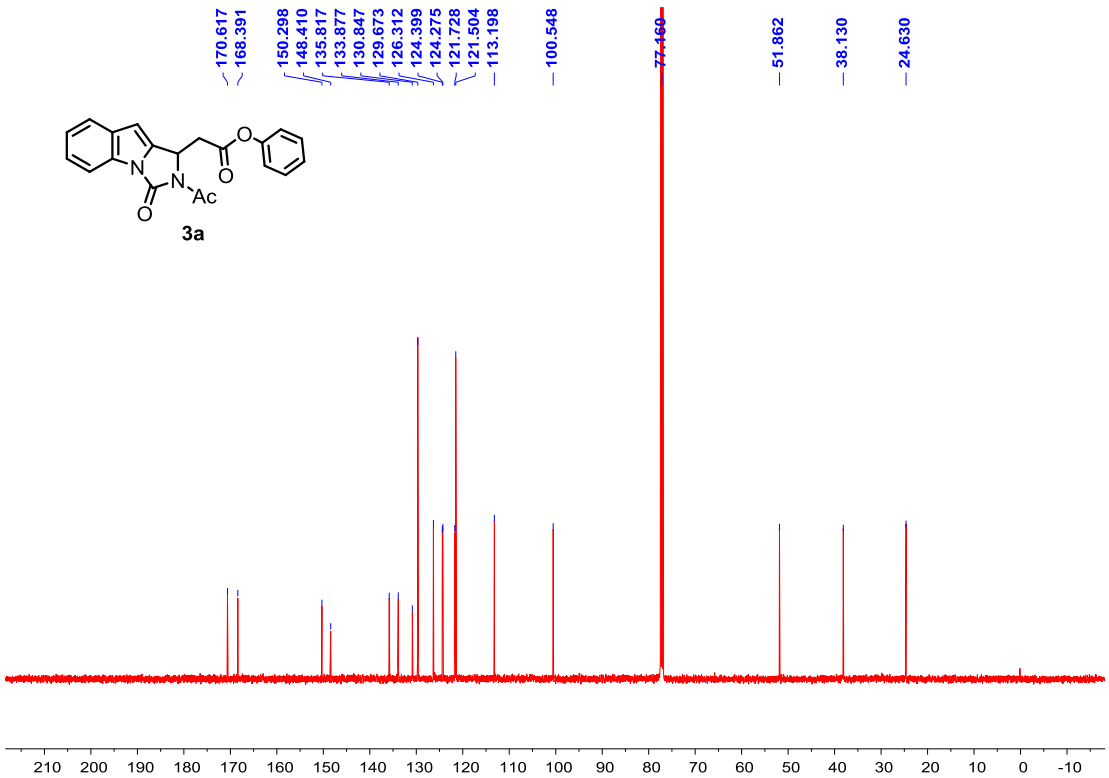


Phenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3a)

^{1}H NMR, 500 MHz, $CDCl_3$

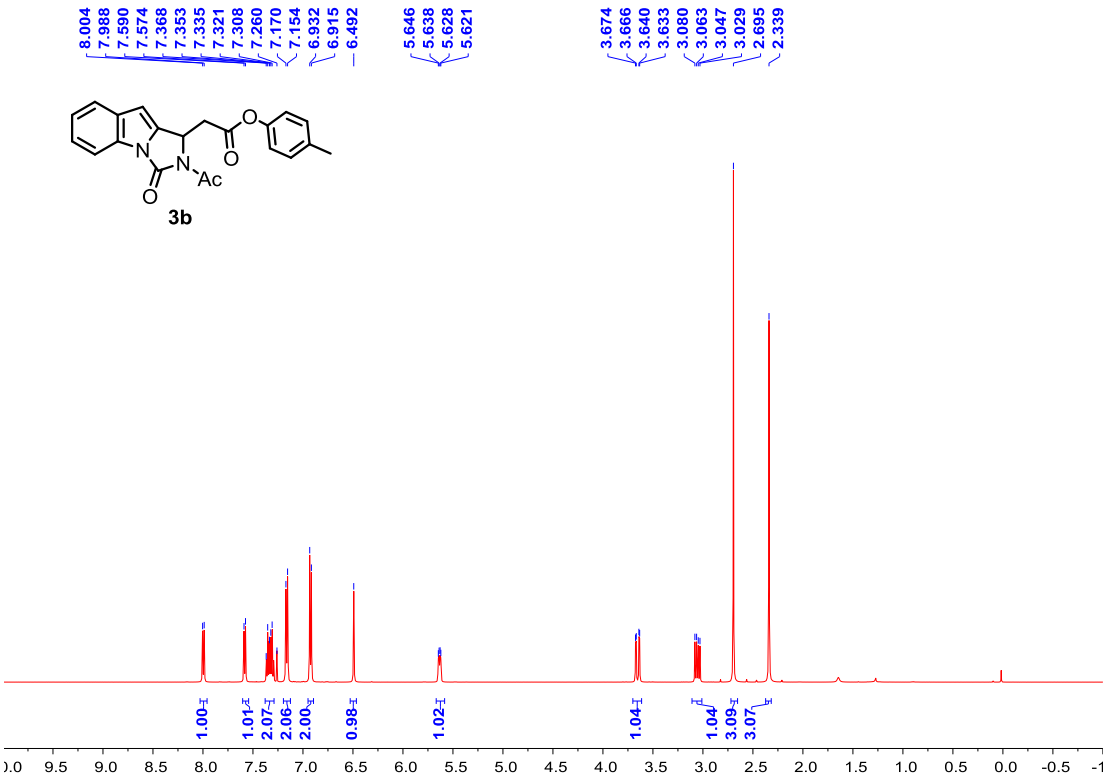


^{13}C NMR, 125 MHz, $CDCl_3$

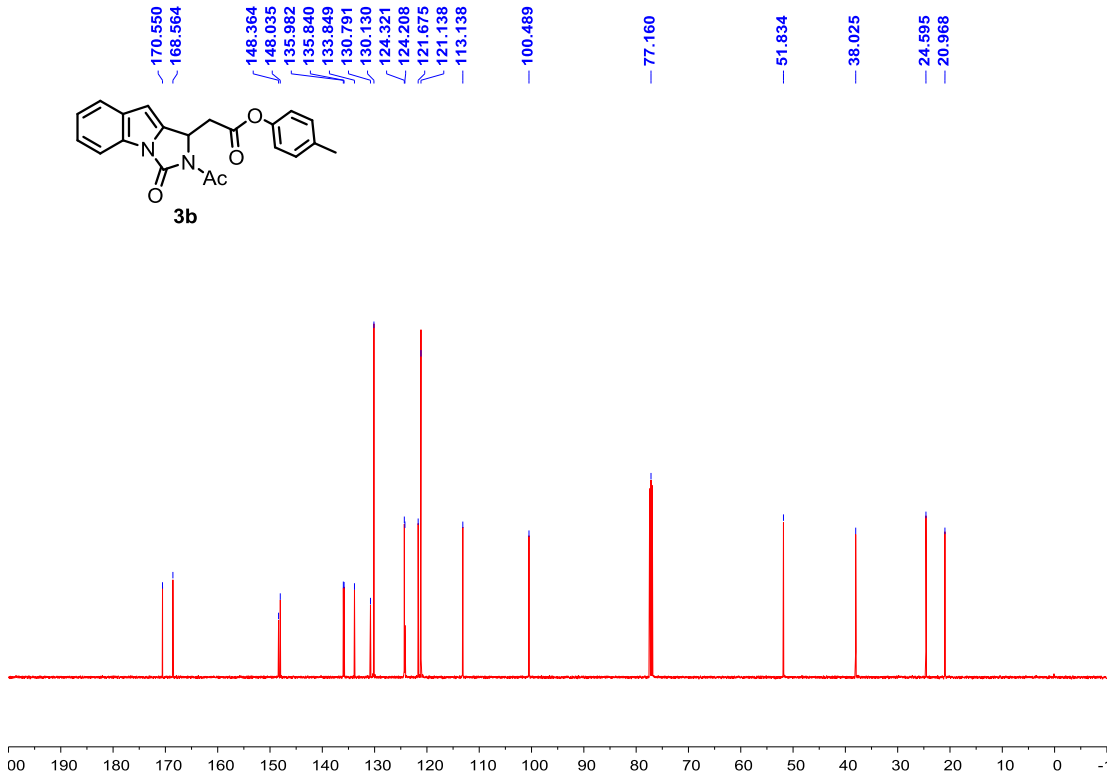


p-Tolyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3b)

^{1}H NMR, 500 MHz, $CDCl_3$

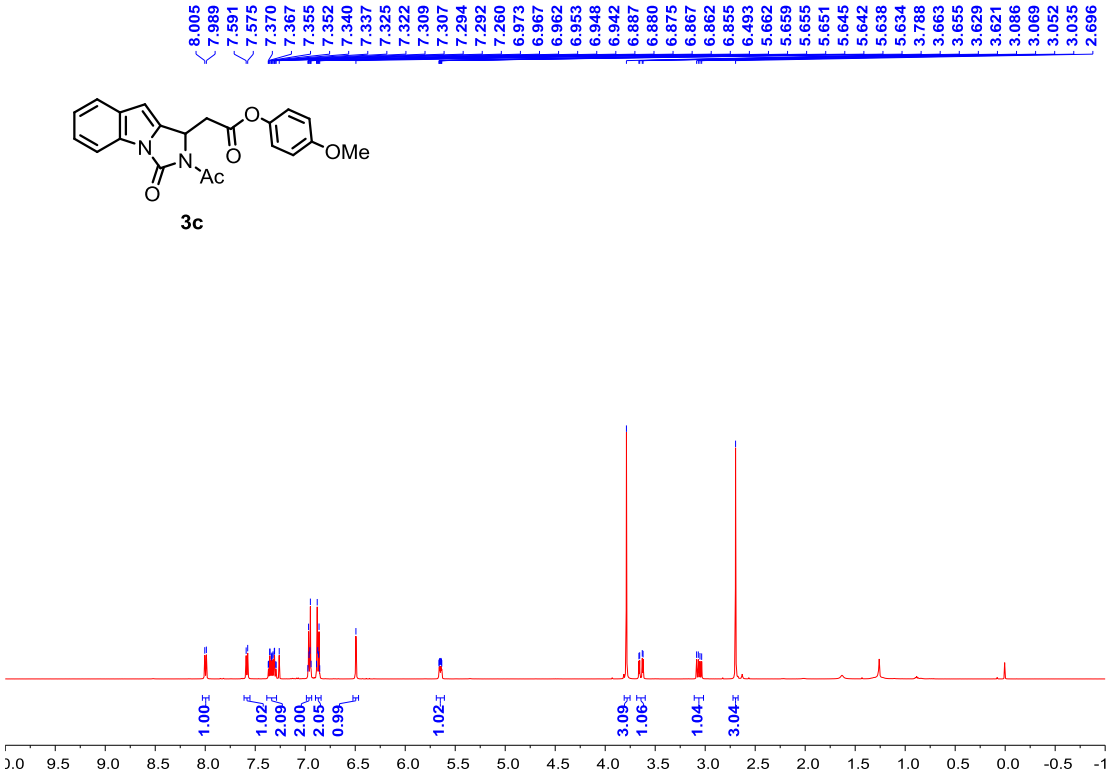


^{13}C NMR, 125 MHz, $CDCl_3$



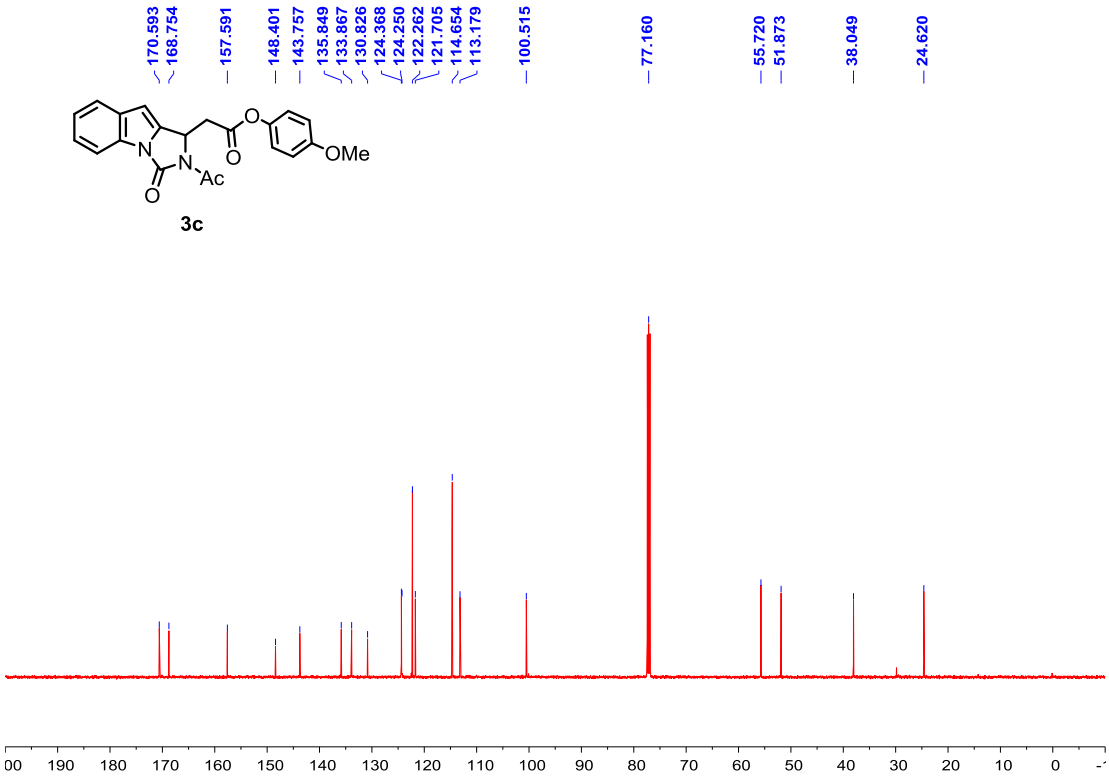
4-Methoxyphenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3c)

^{1}H NMR, 500 MHz, $CDCl_3$



3c

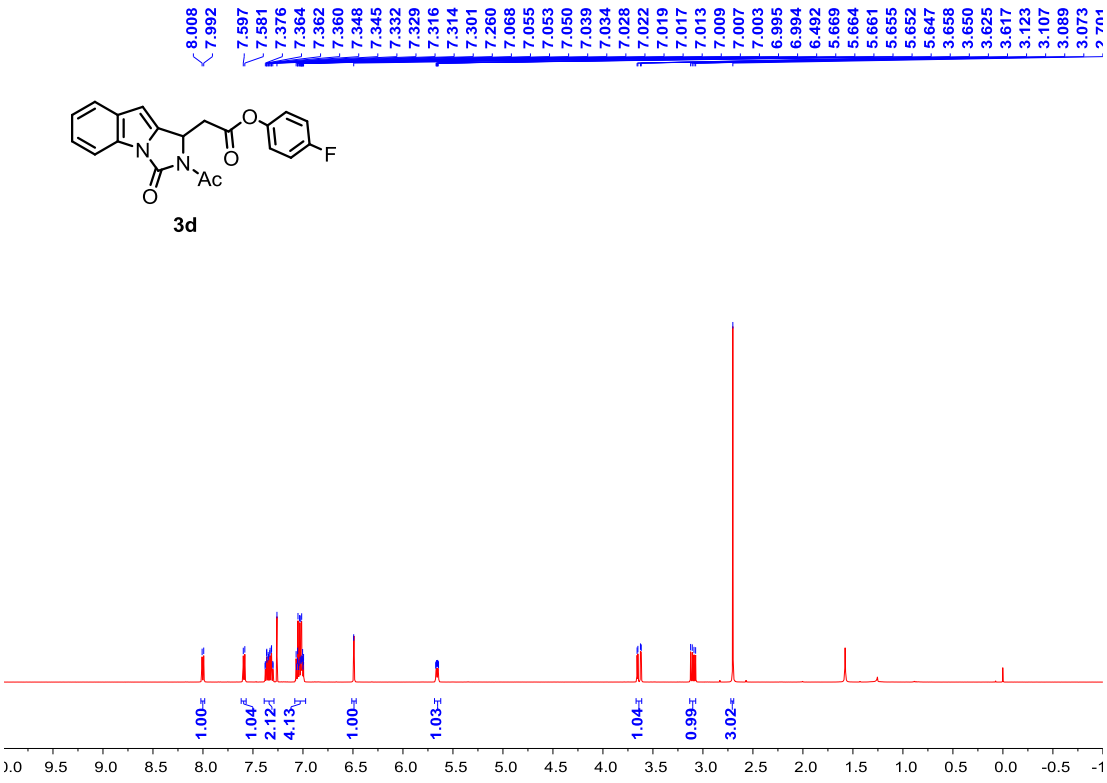
^{13}C NMR, 125 MHz, $CDCl_3$



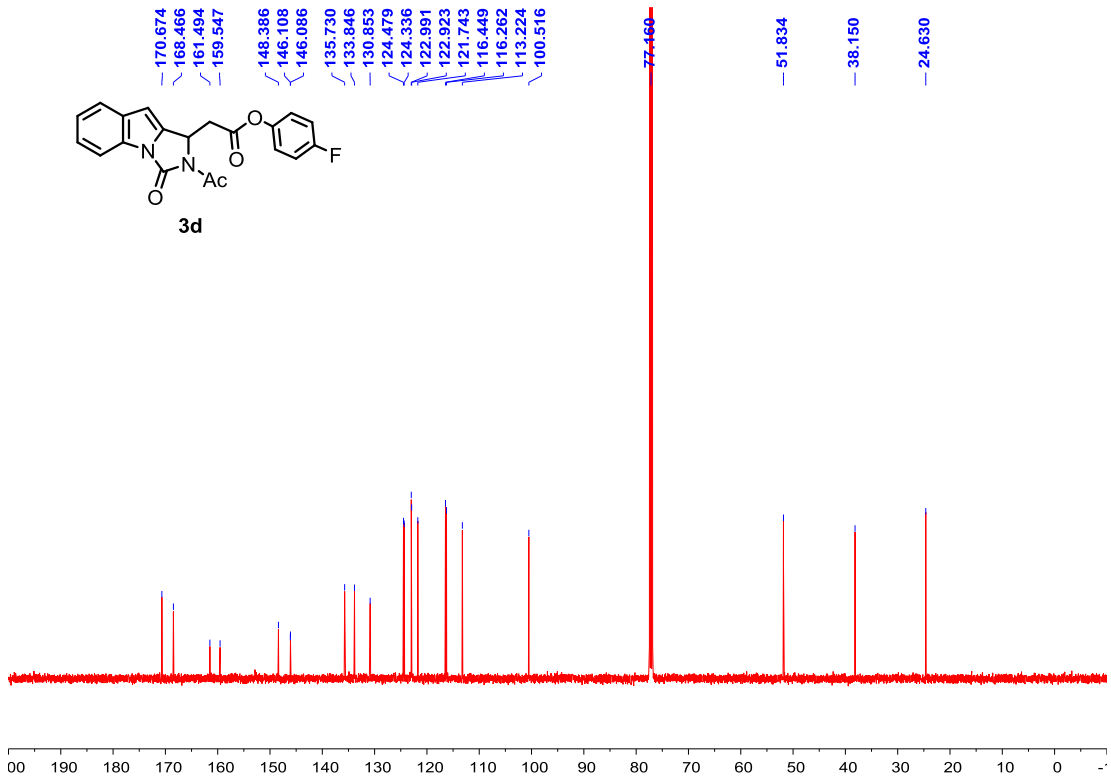
3c

4-Fluorophenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3d)

^{1}H NMR, 500 MHz, $CDCl_3$

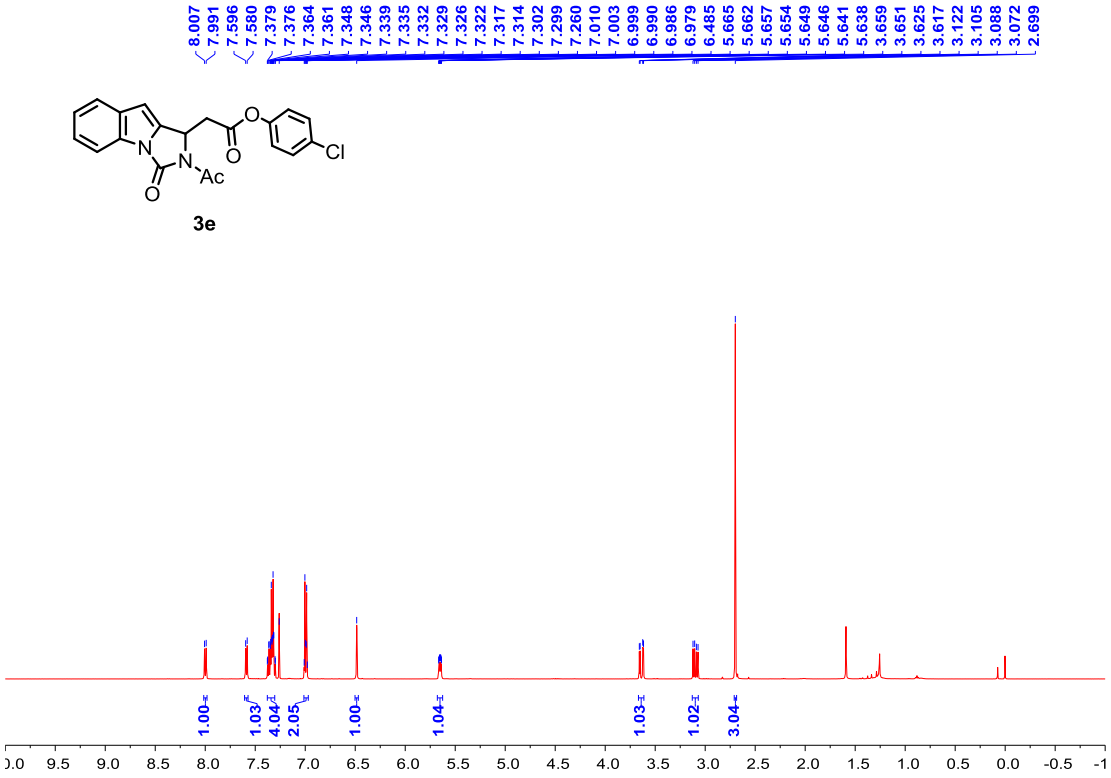


^{13}C NMR, 125 MHz, $CDCl_3$

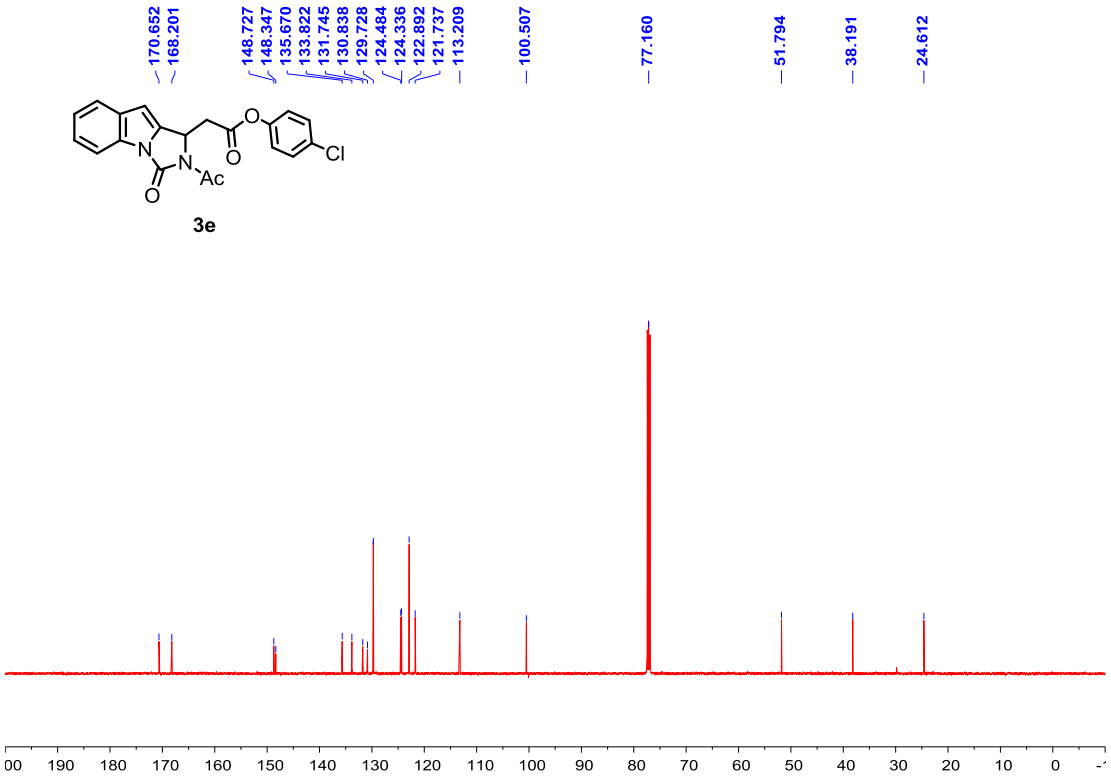


4-Chlorophenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3e)

^{1}H NMR, 500 MHz, $CDCl_3$

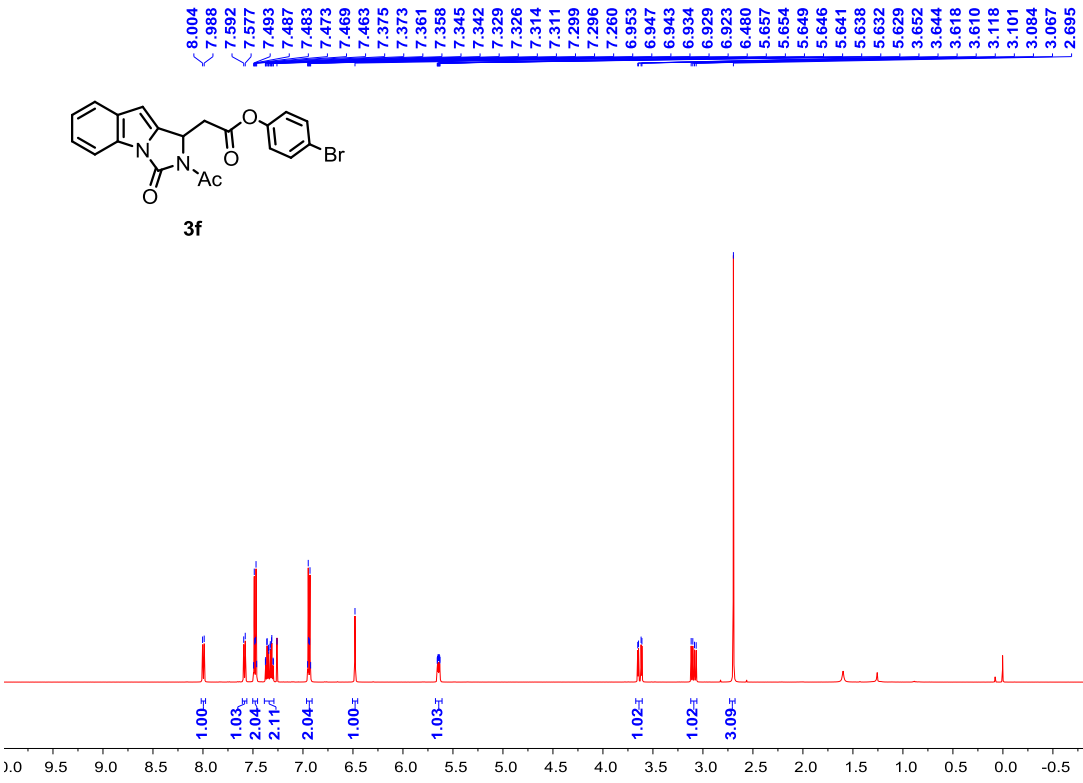


^{13}C NMR, 125 MHz, $CDCl_3$

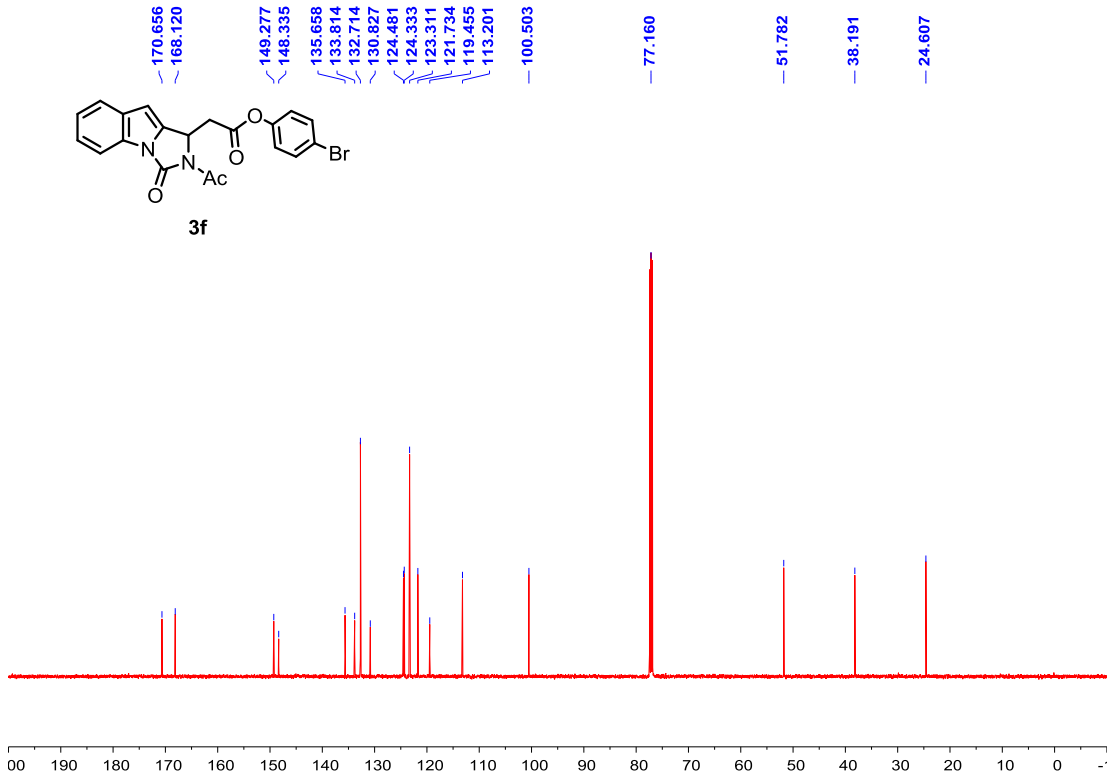


4-Bromophenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3f)

^{1}H NMR, 500 MHz, $CDCl_3$

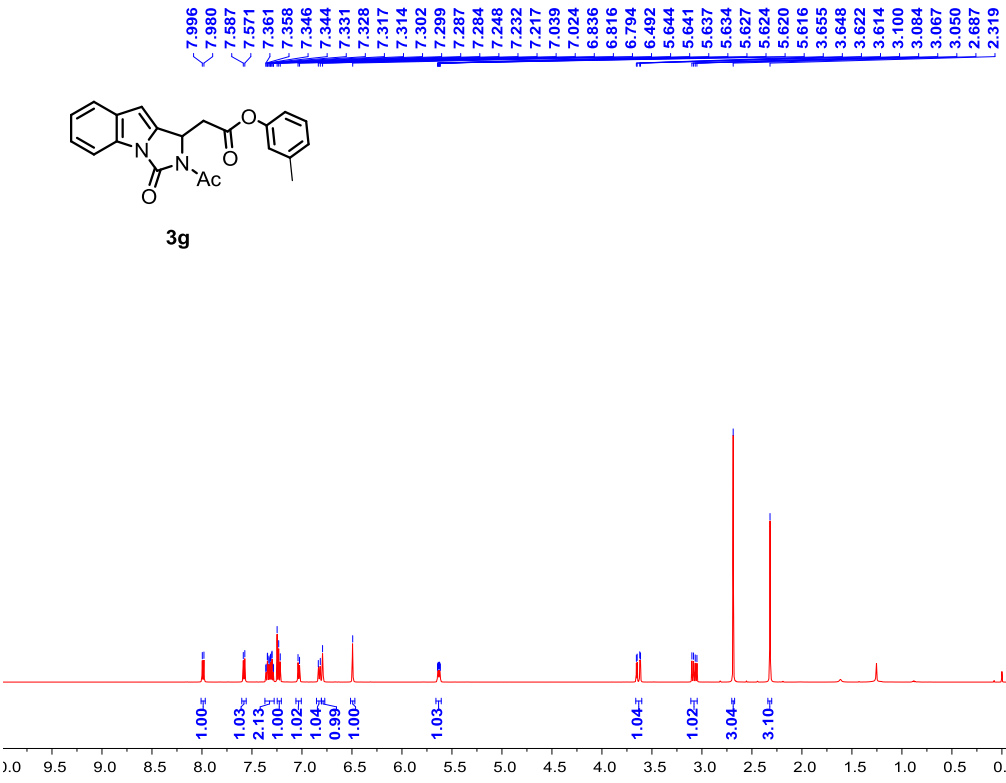


^{13}C NMR, 125 MHz, $CDCl_3$



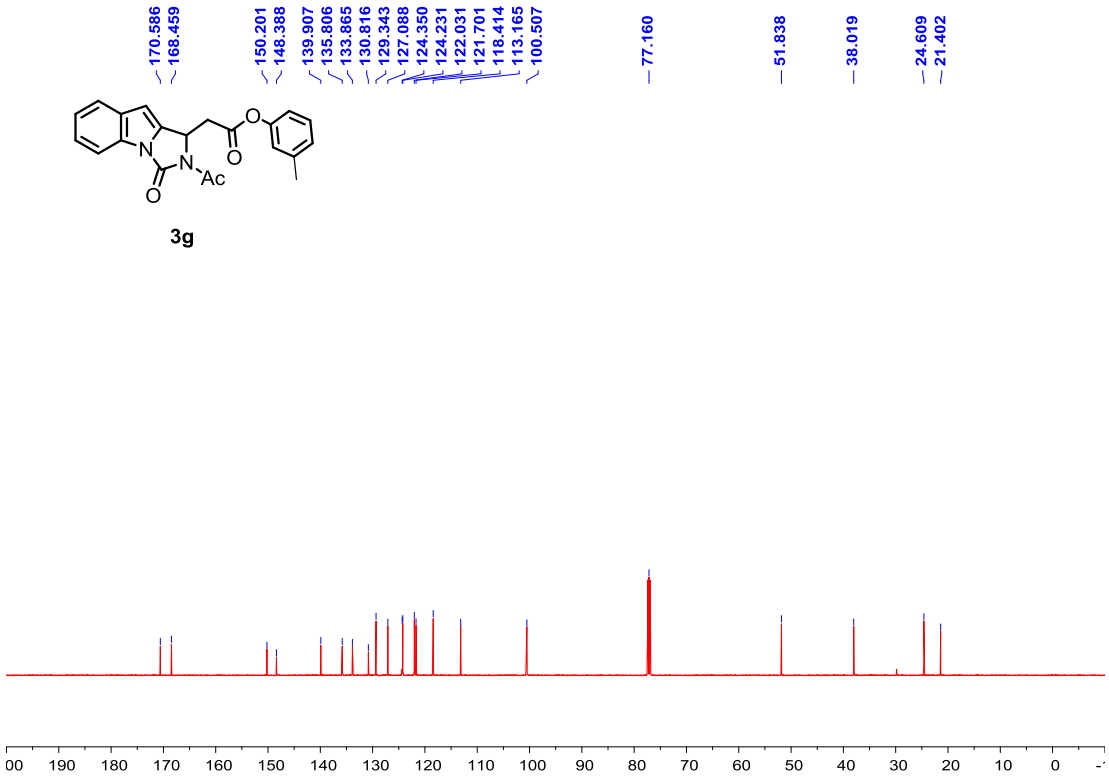
m-Tolyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3i)

^{1}H NMR, 500 MHz, $CDCl_3$



3g

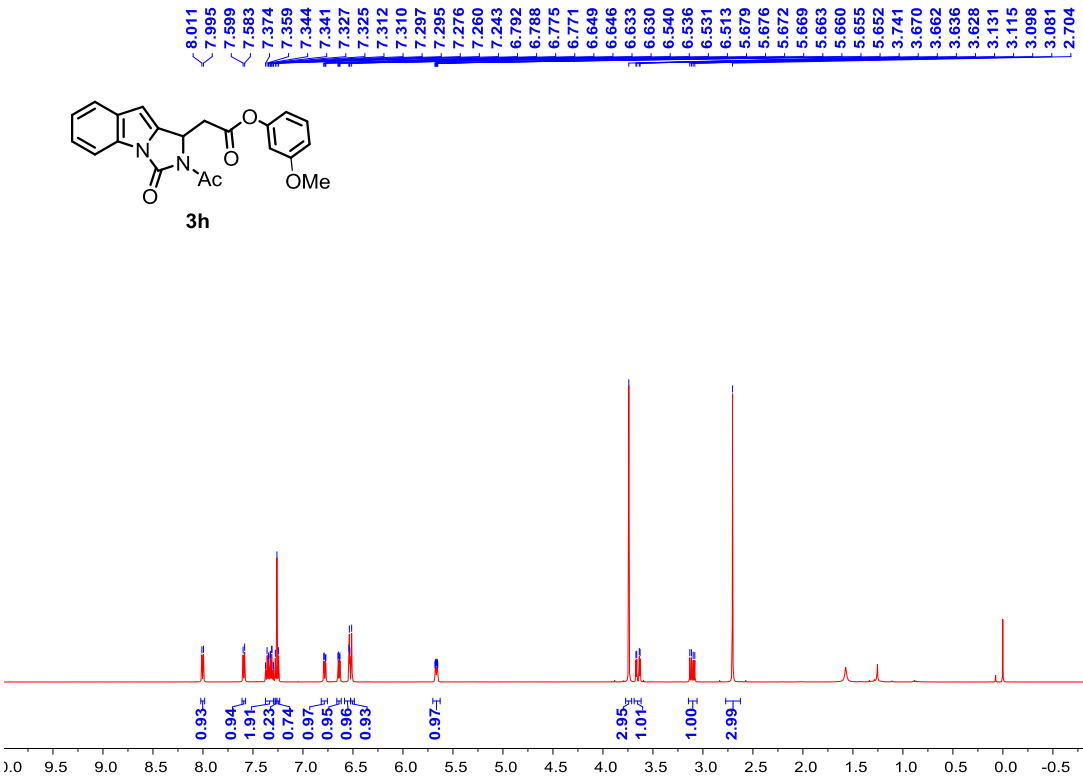
^{13}C NMR, 125 MHz, $CDCl_3$



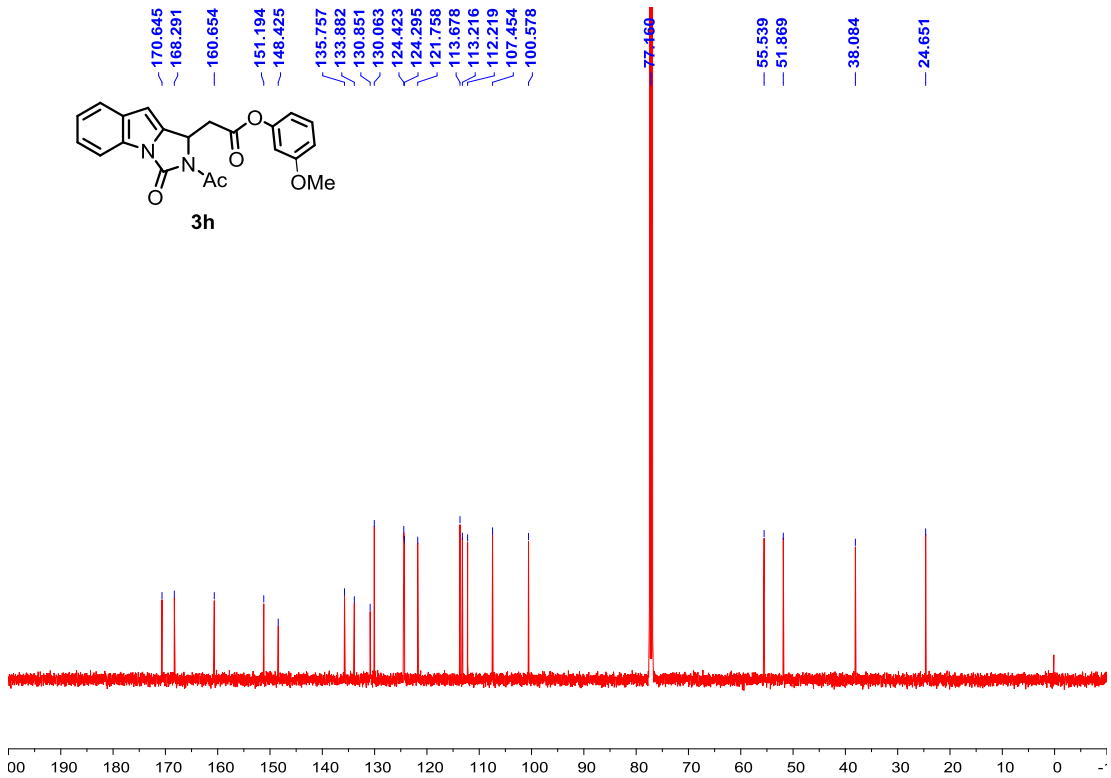
3g

3-Methoxyphenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3j)

^{1}H NMR, 500 MHz, $CDCl_3$

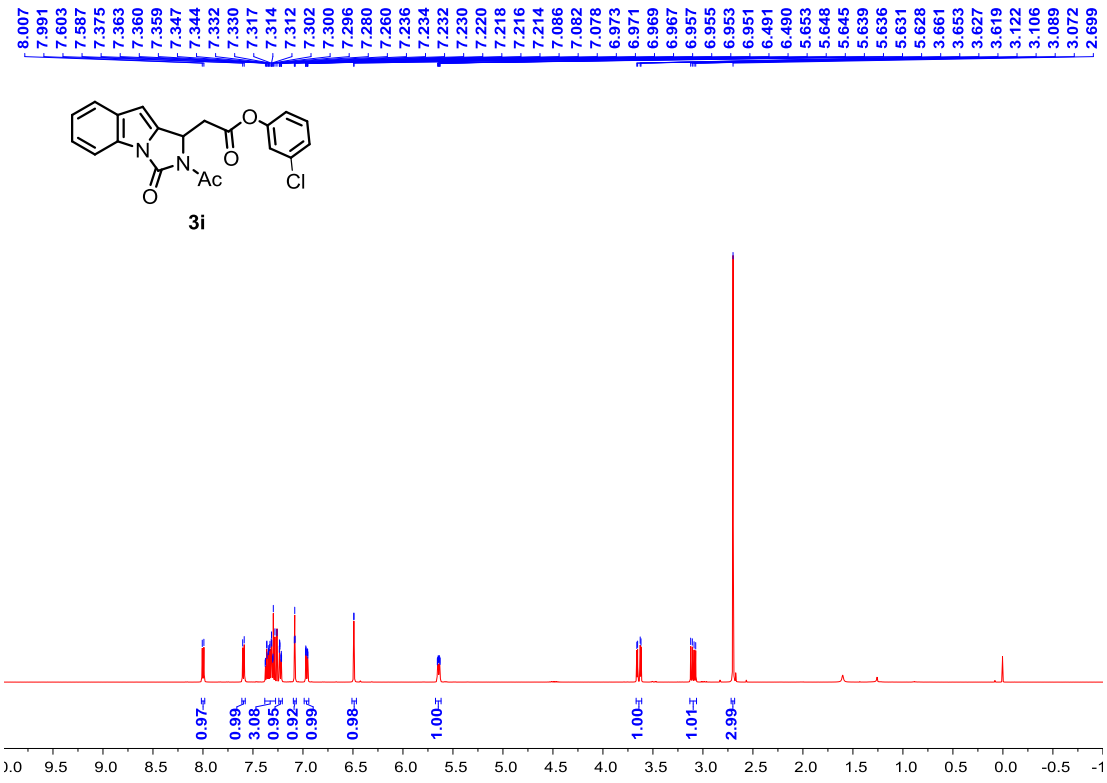


^{13}C NMR, 125 MHz, $CDCl_3$

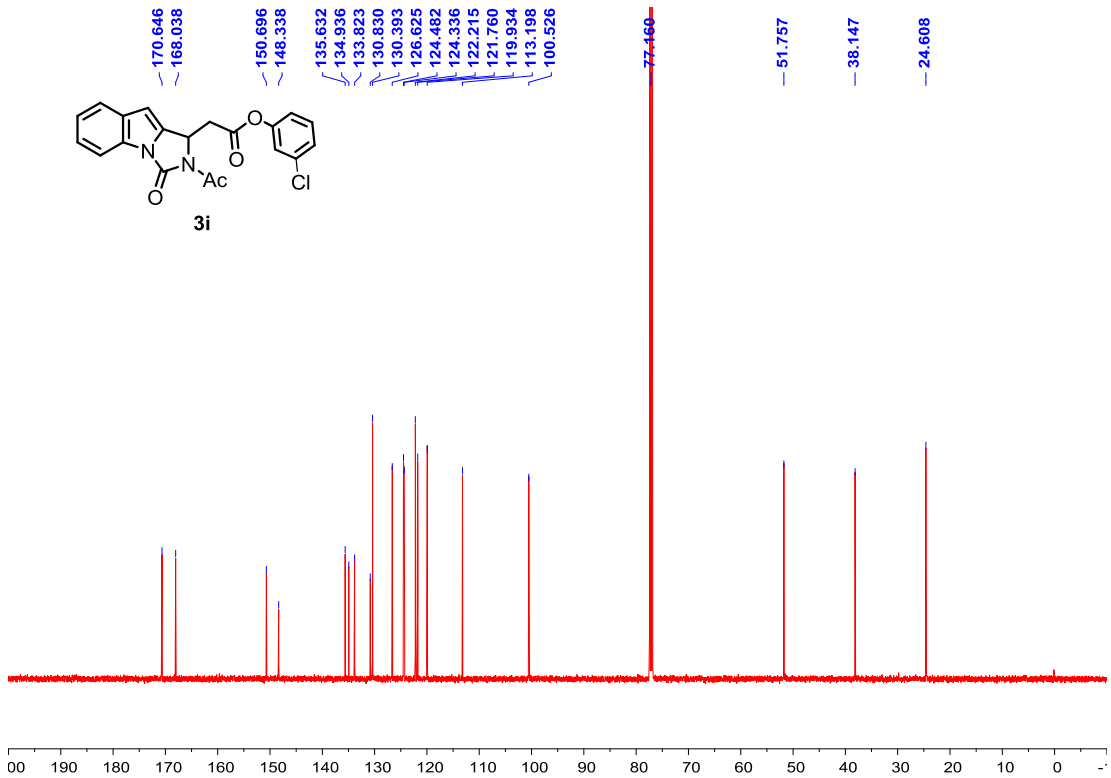


3-Chlorophenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3k)

^{1}H NMR, 500 MHz, $CDCl_3$

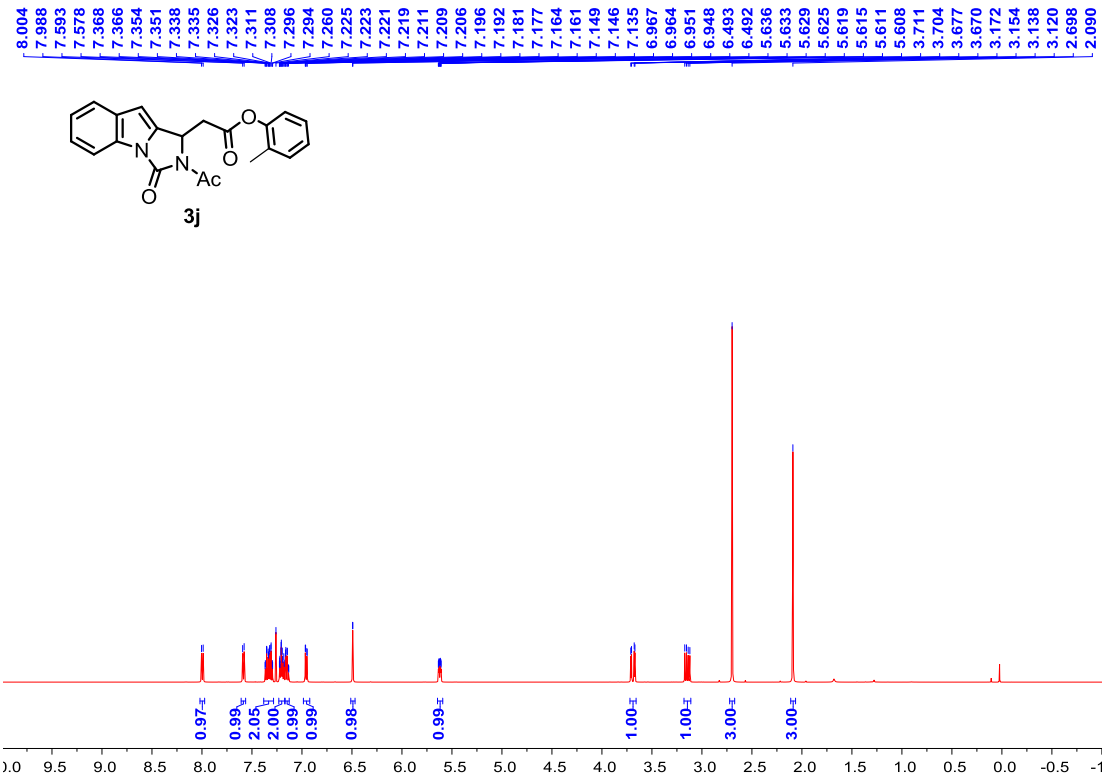


^{13}C NMR, 125 MHz, $CDCl_3$

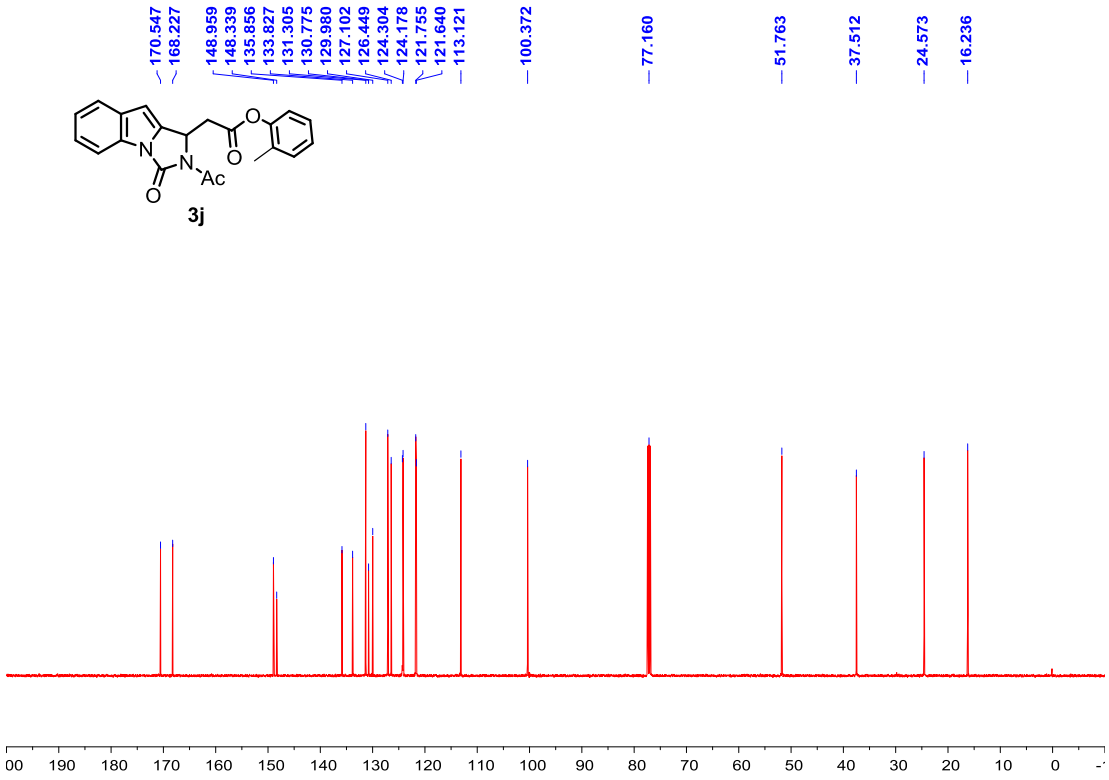


o-Tolyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3l)

^{1}H NMR, 500 MHz, $CDCl_3$

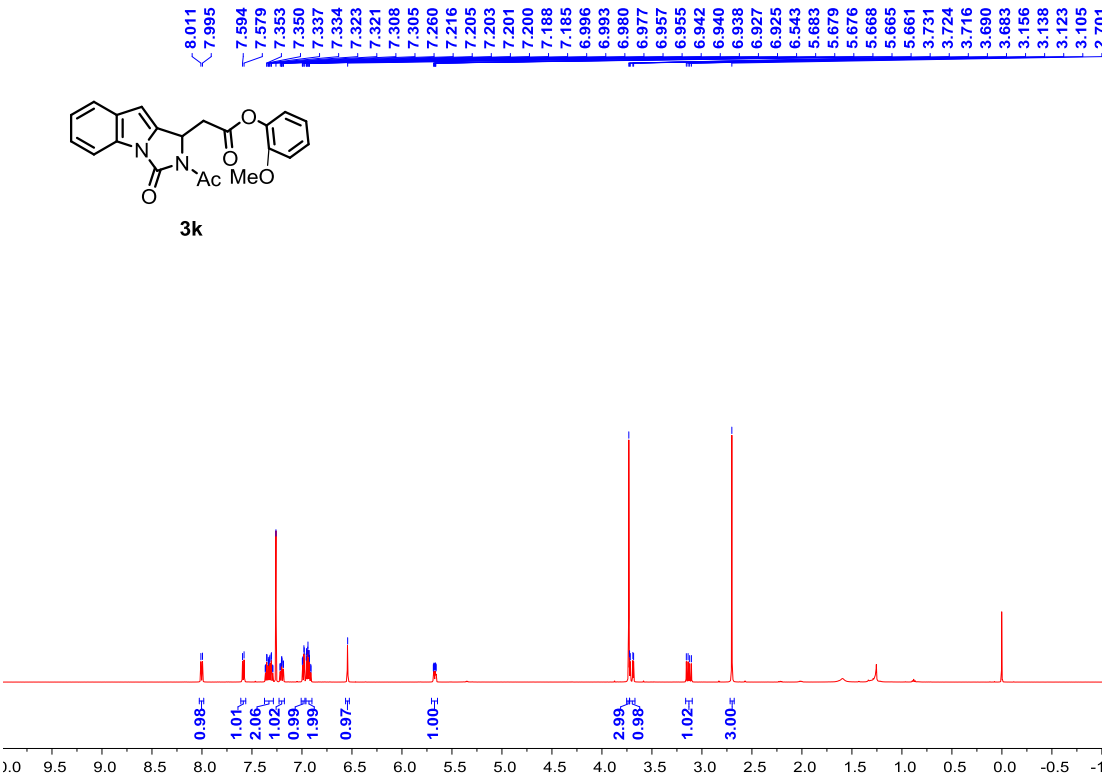


^{13}C NMR, 125 MHz, $CDCl_3$

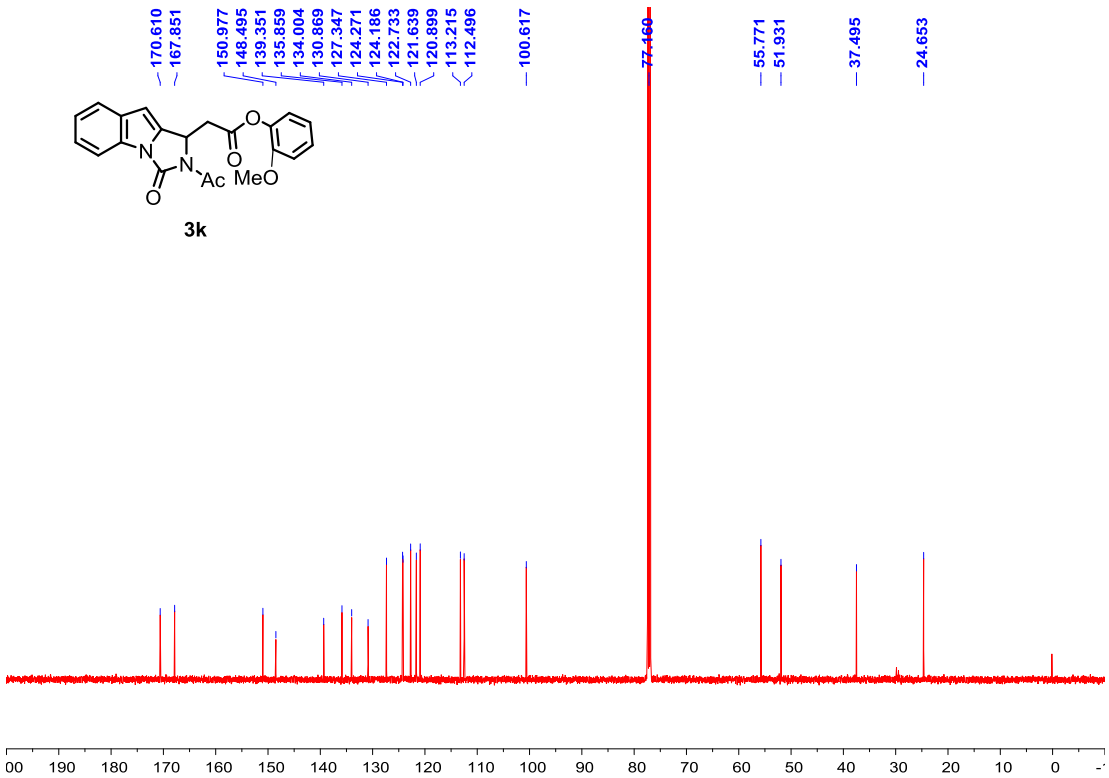


2-Methoxyphenyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3m)

^{1}H NMR, 500 MHz, $CDCl_3$

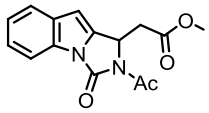


^{13}C NMR, 125 MHz, $CDCl_3$

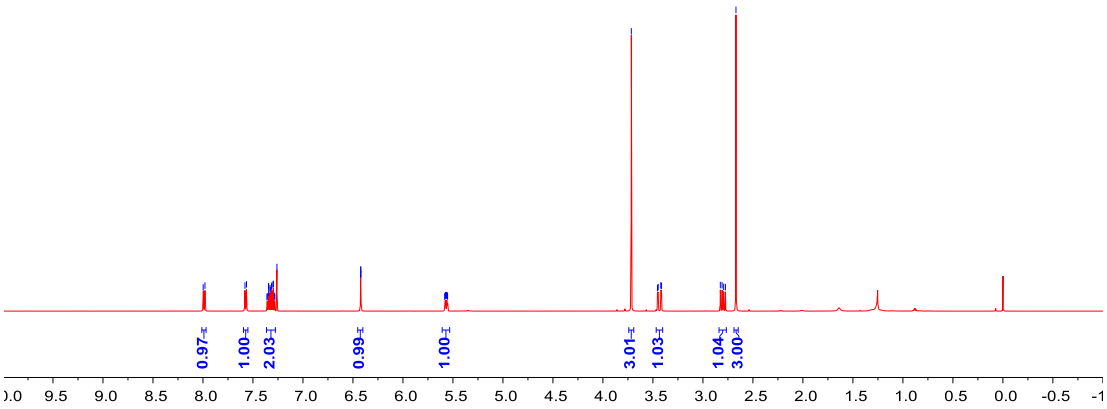


Methyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3n)

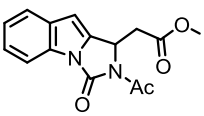
^{1}H NMR, 500 MHz, $CDCl_3$



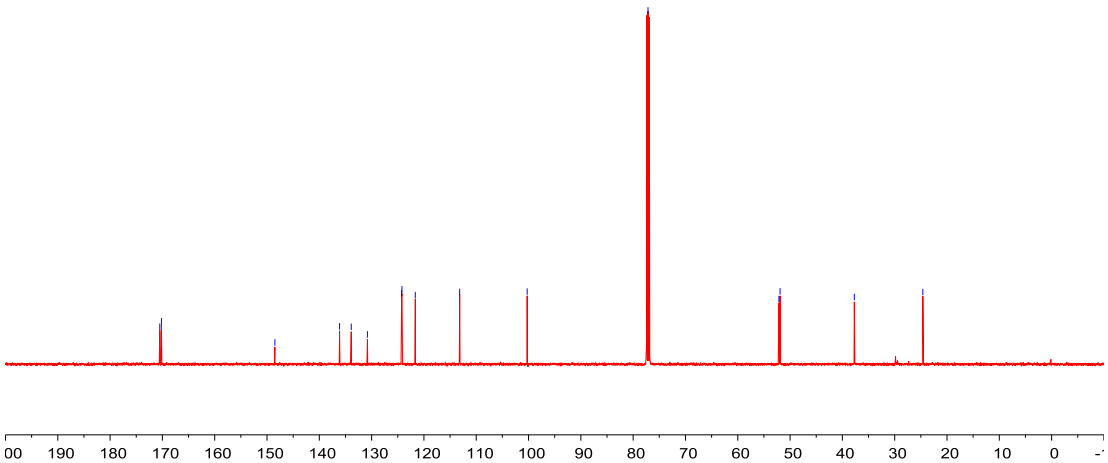
3l



^{13}C NMR, 125 MHz, $CDCl_3$

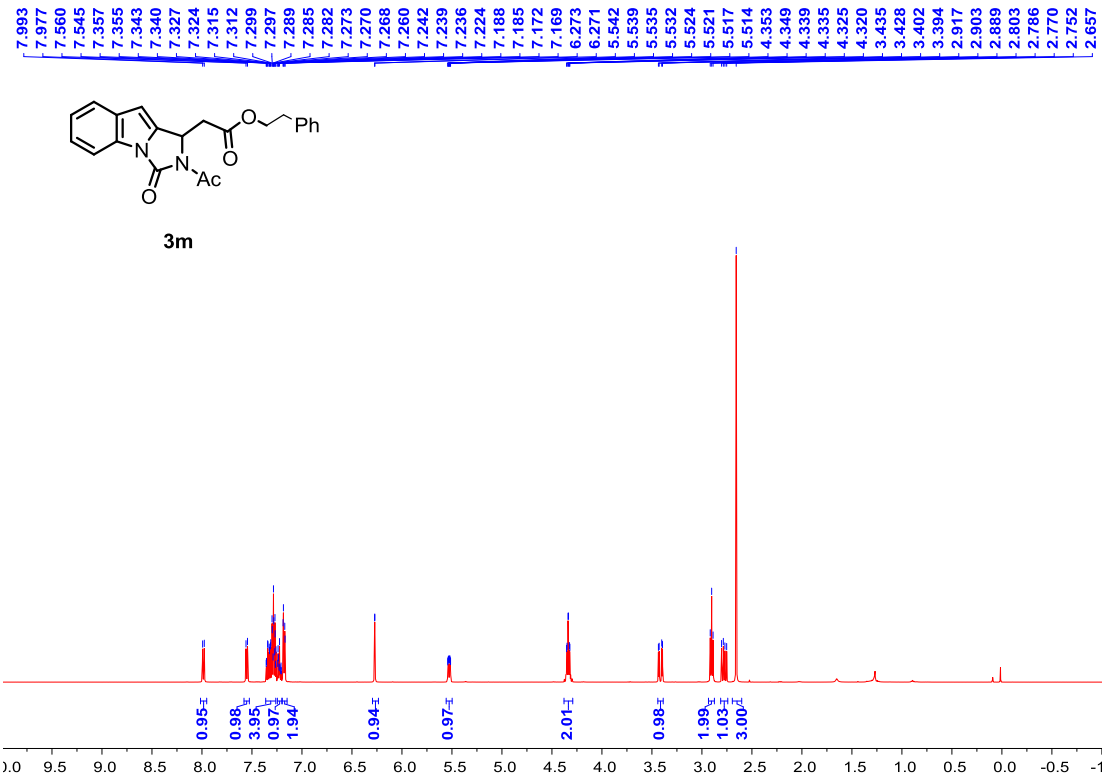


3l

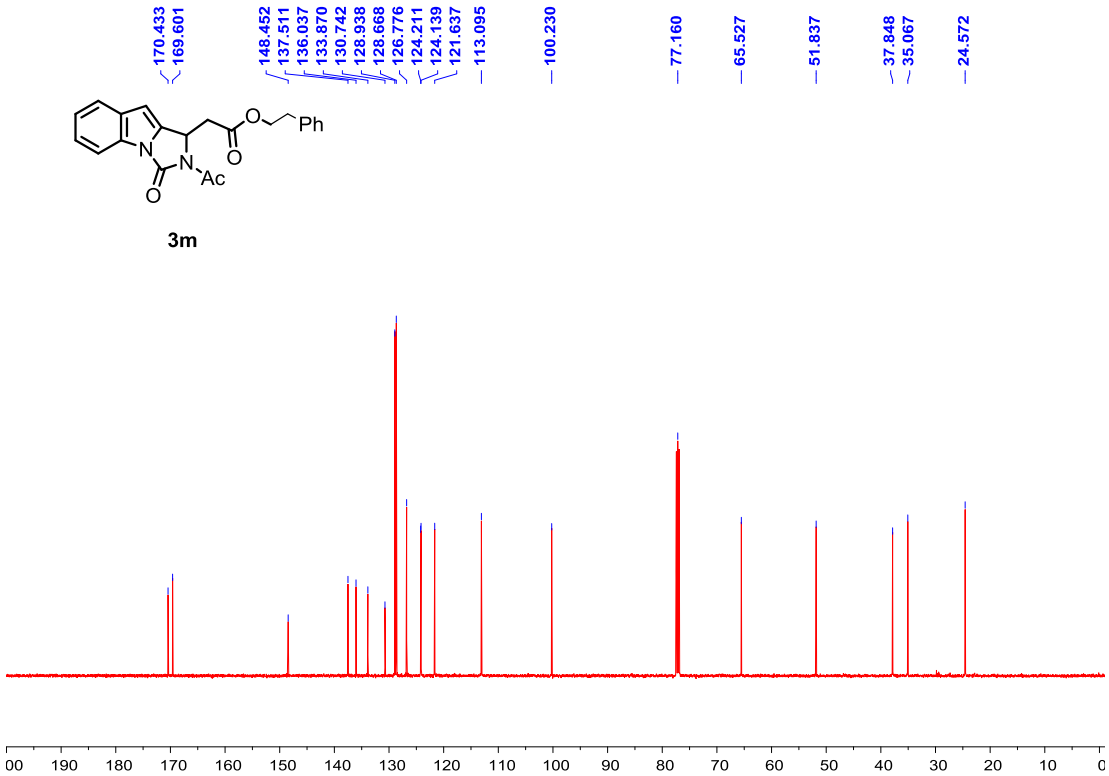


Phenethyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3o)

^{1}H NMR, 500 MHz, $CDCl_3$

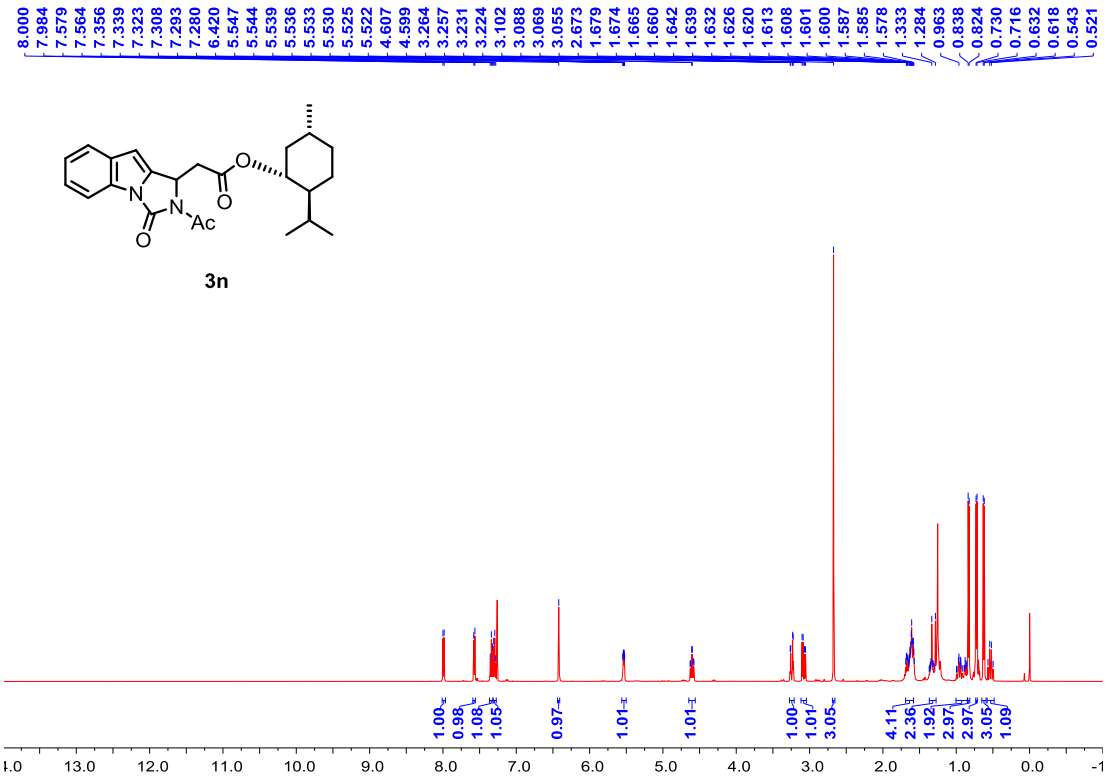


^{13}C NMR, 125 MHz, $CDCl_3$



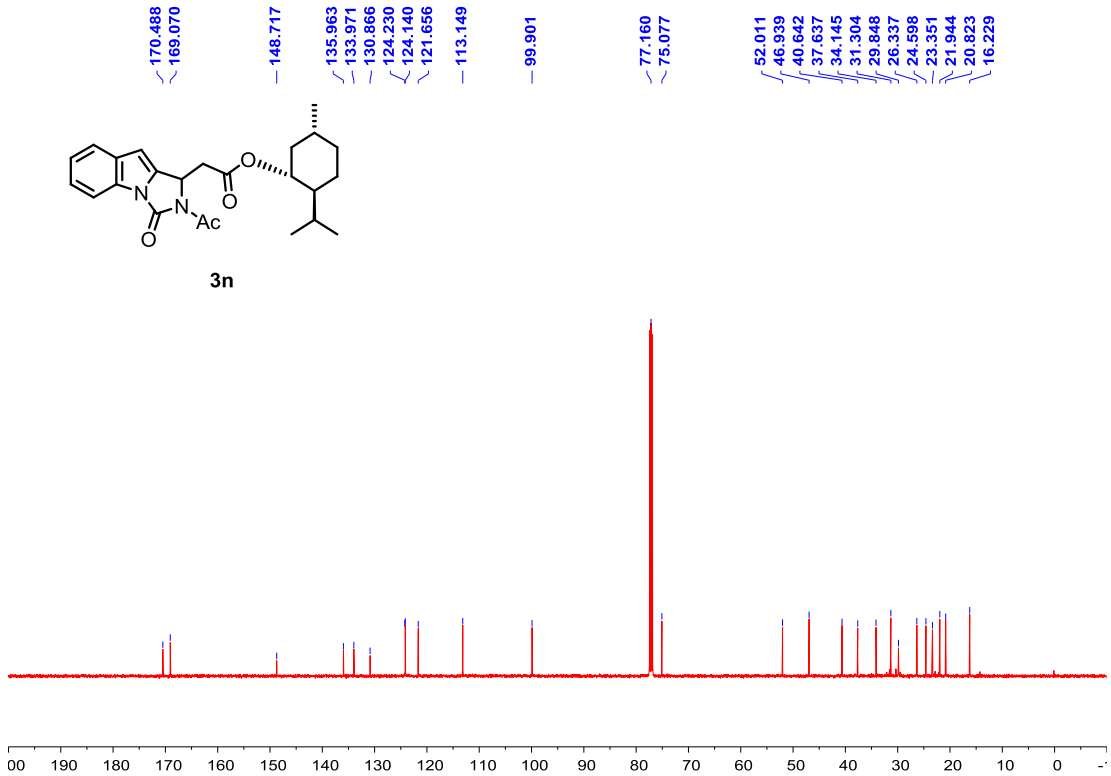
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol -1-yl)acetat*e* (3p)

^{1}H NMR, 500 MHz, $CDCl_3$



3n

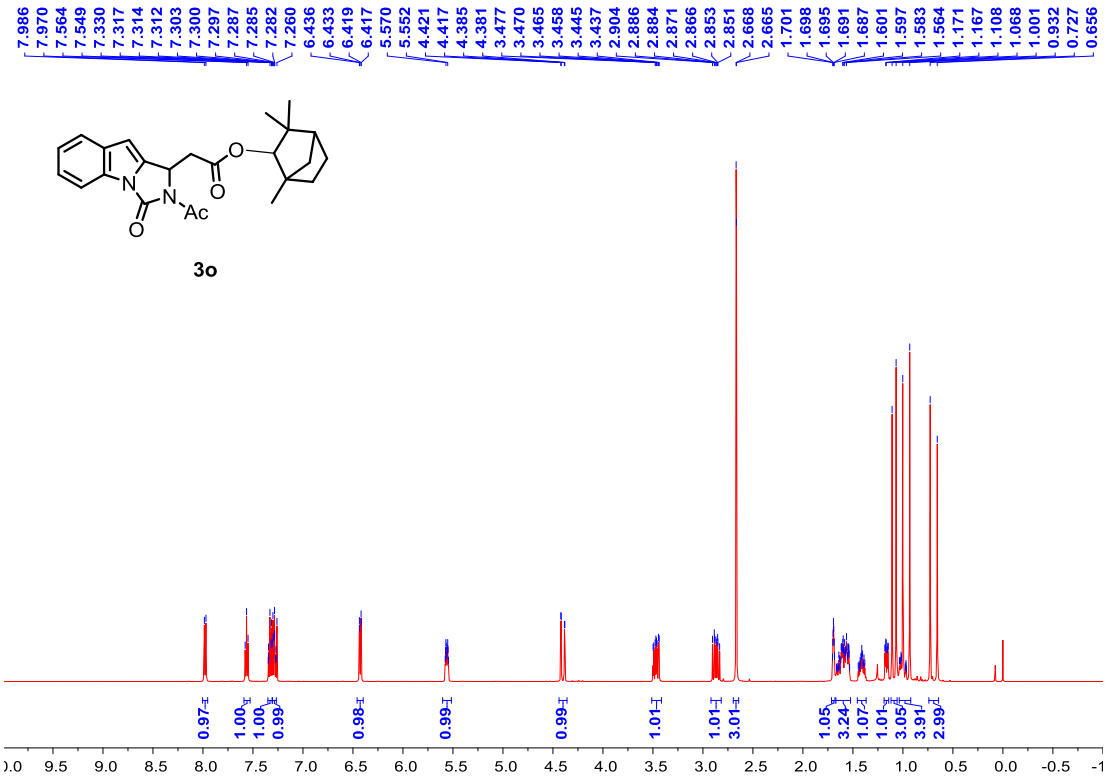
^{13}C NMR, 125 MHz, $CDCl_3$



3n

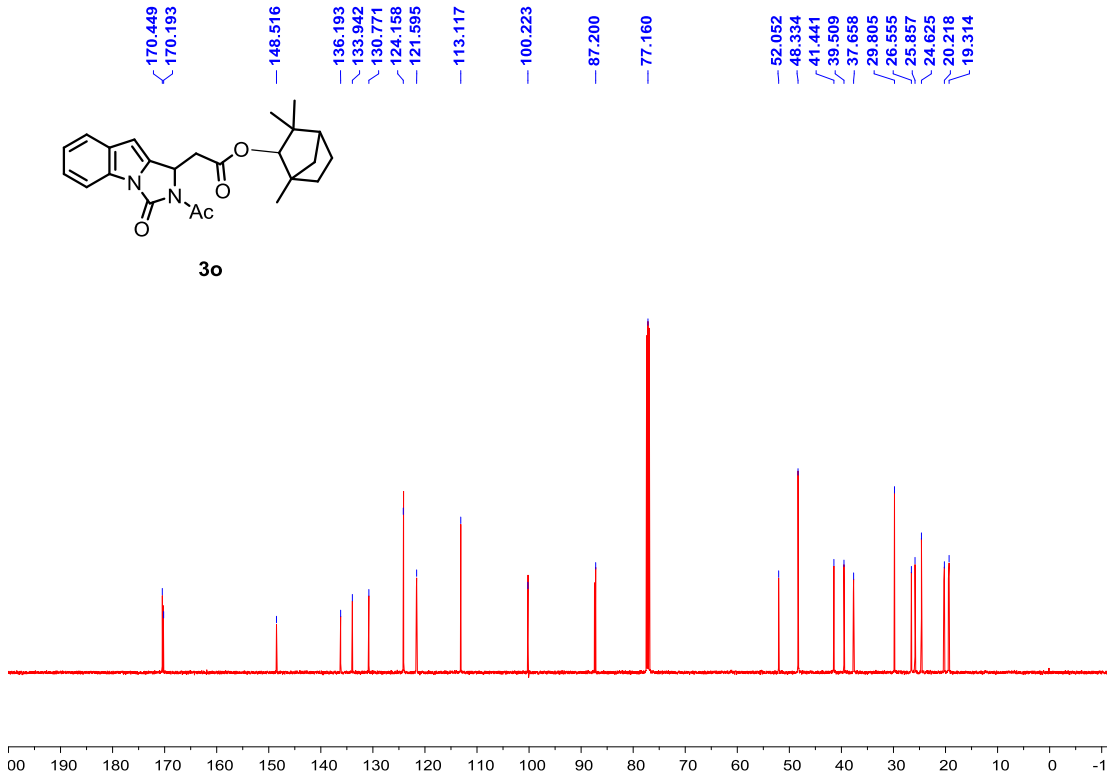
1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*] indol-1-yl)acetate (3q)

^{1}H NMR, 500 MHz, $CDCl_3$



3o

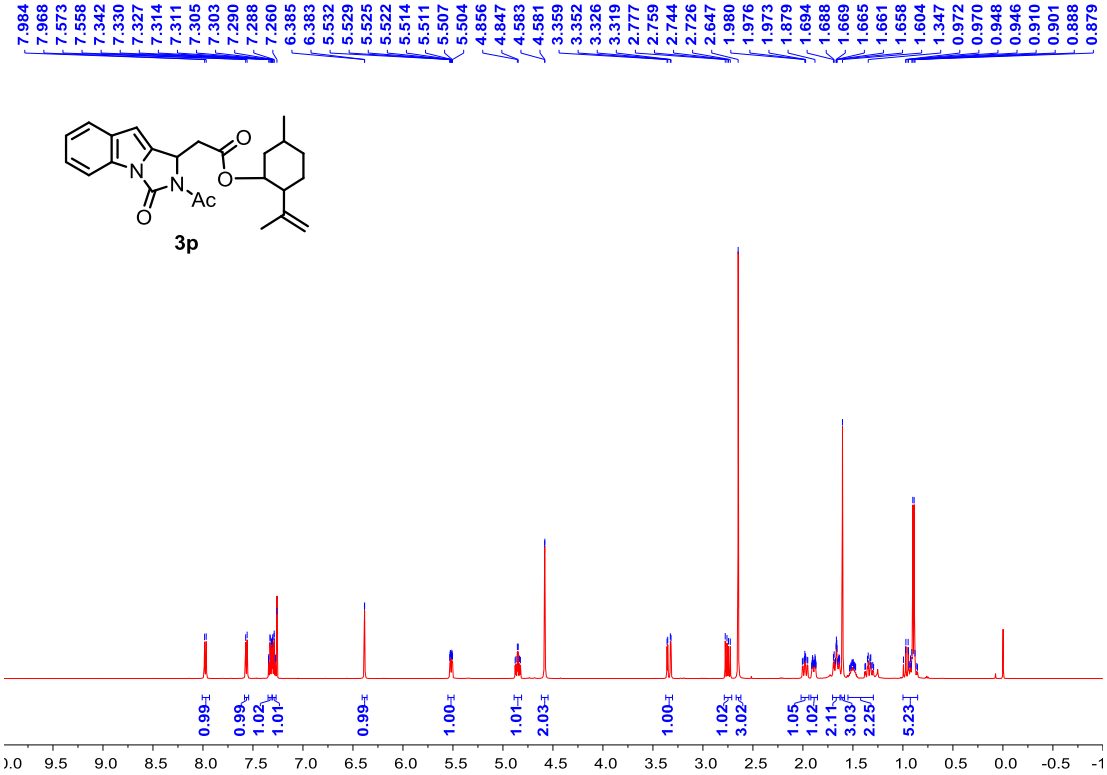
^{13}C NMR, 125 MHz, $CDCl_3$



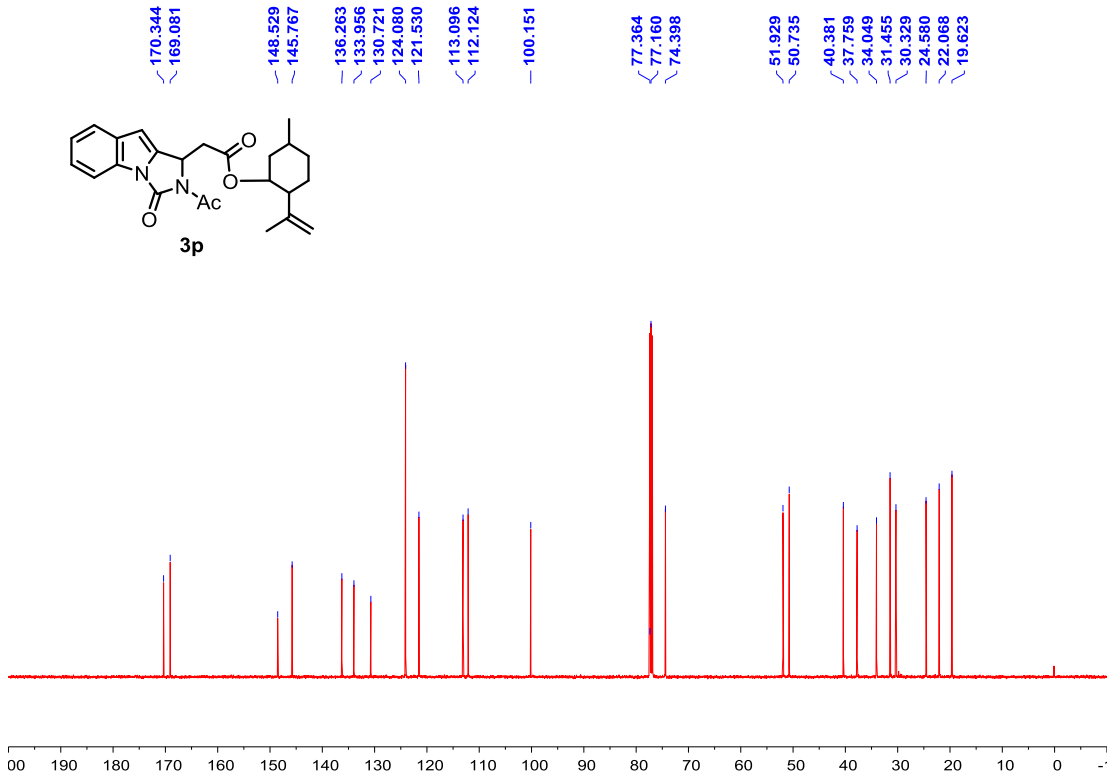
3o

5-Methyl-2-(prop-1-en-2-yl)cyclohexyl-2-(2-acetyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3r)

^{1}H NMR, 500 MHz, $CDCl_3$

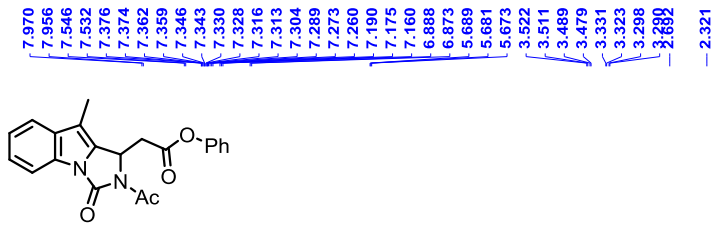


^{13}C NMR, 125 MHz, $CDCl_3$

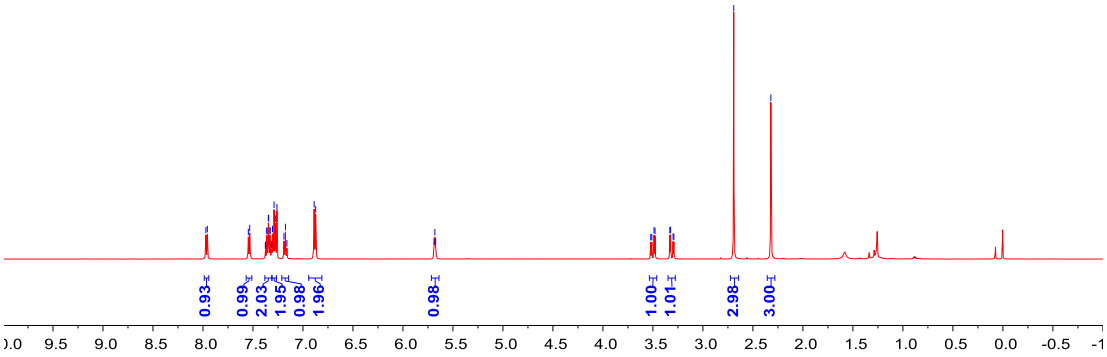


Phenyl-2-(2-acetyl-9-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3s)

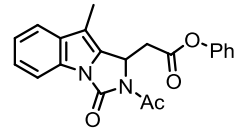
^{1}H NMR, 500 MHz, $CDCl_3$



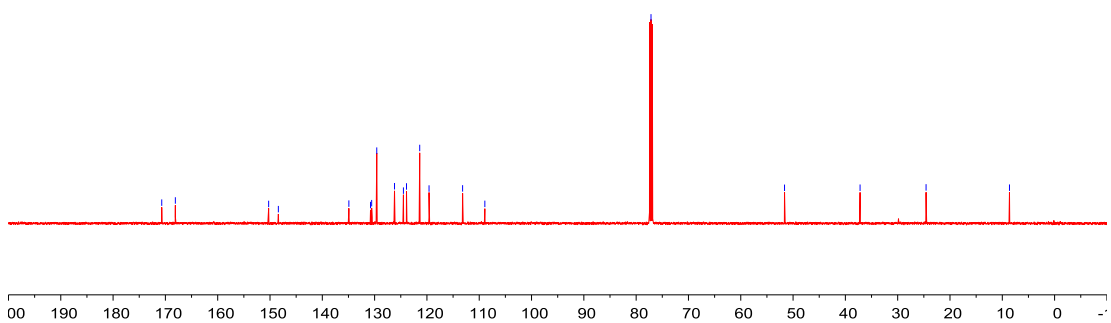
3q



^{13}C NMR, 125 MHz, $CDCl_3$

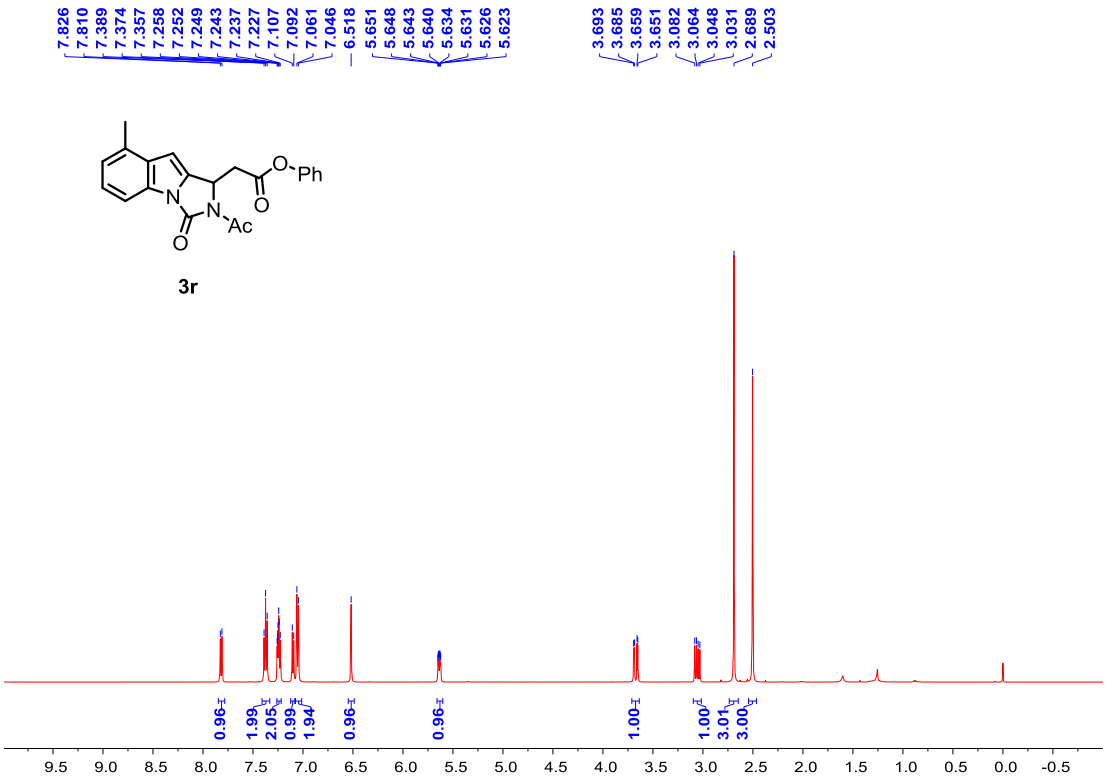


3q

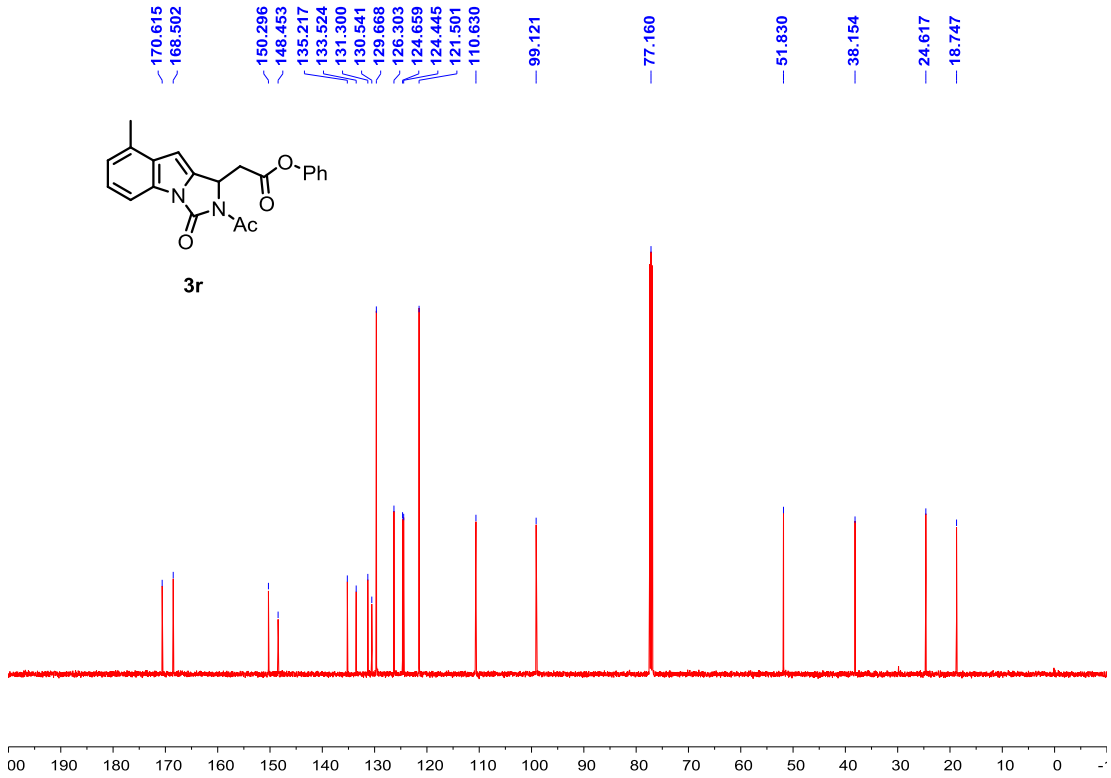


Phenyl-2-(2-acetyl-8-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3t)

^{1}H NMR, 500 MHz, $CDCl_3$

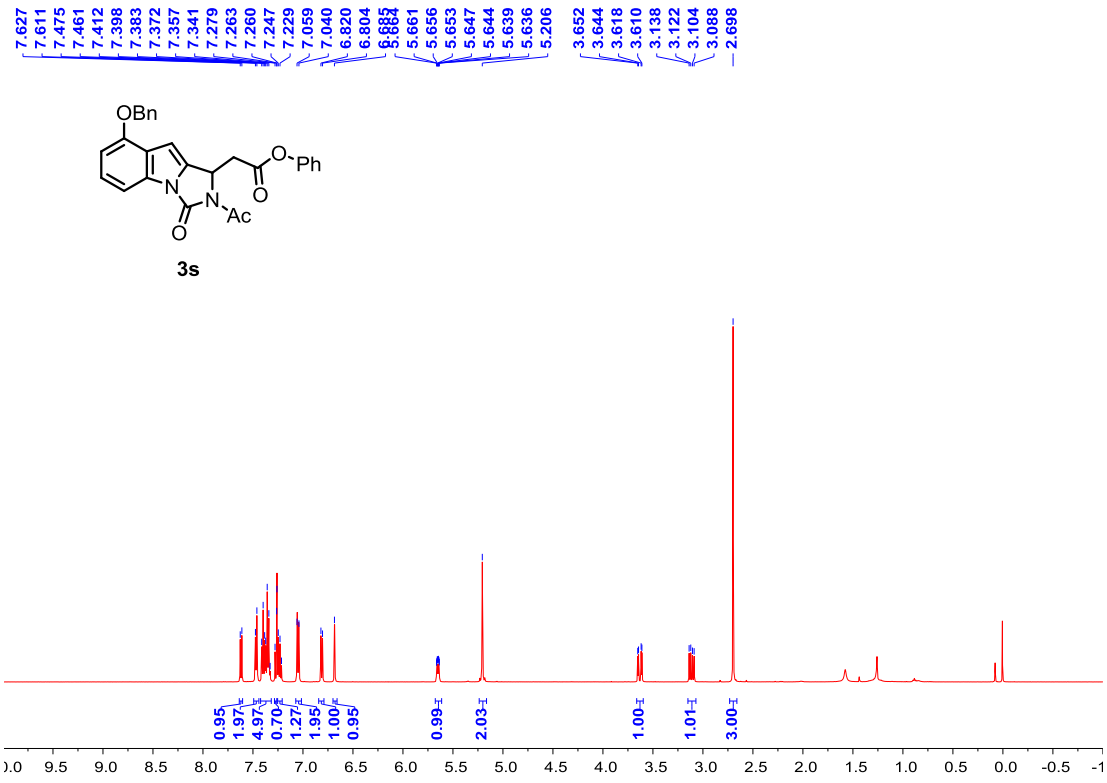


^{13}C NMR, 125 MHz, $CDCl_3$

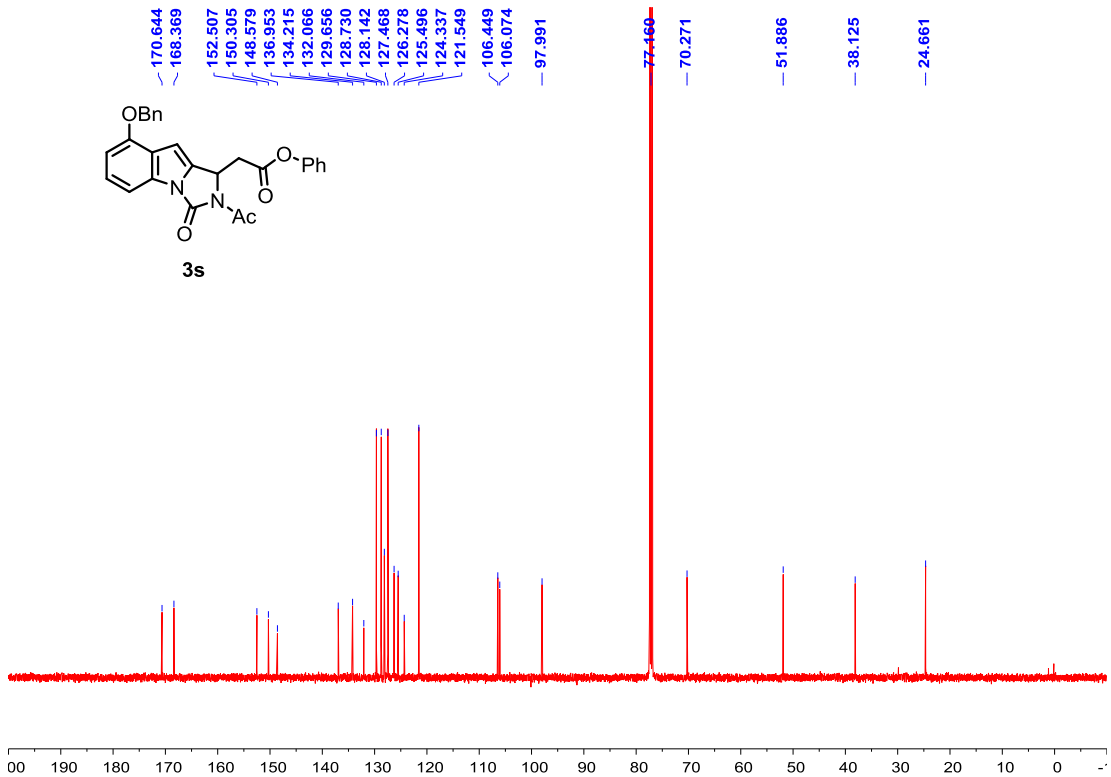


Phenyl-2-(2-acetyl-8-(benzyloxy)-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3u)

^{1}H NMR, 500 MHz, $CDCl_3$

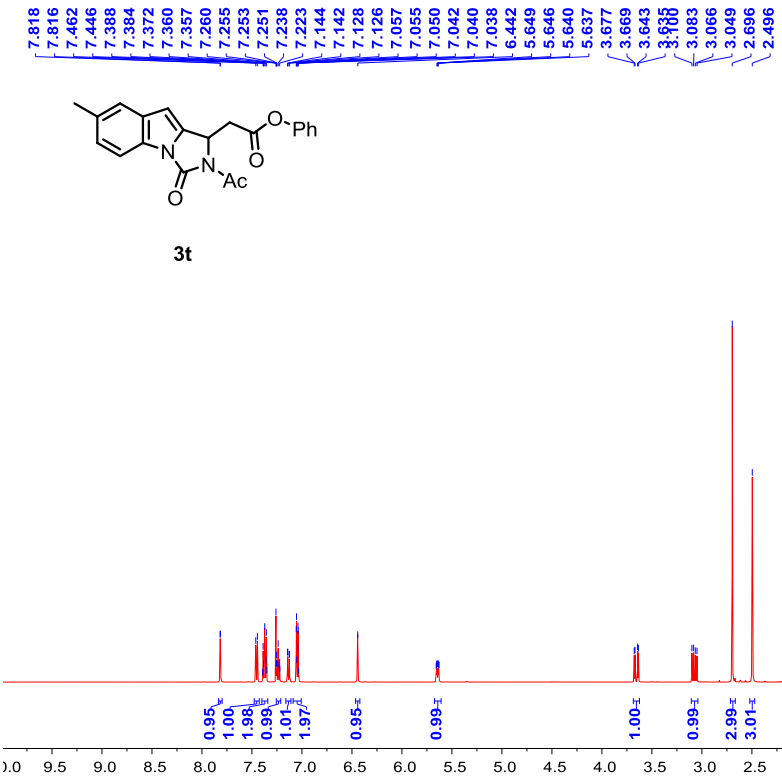


^{13}C NMR, 125 MHz, $CDCl_3$



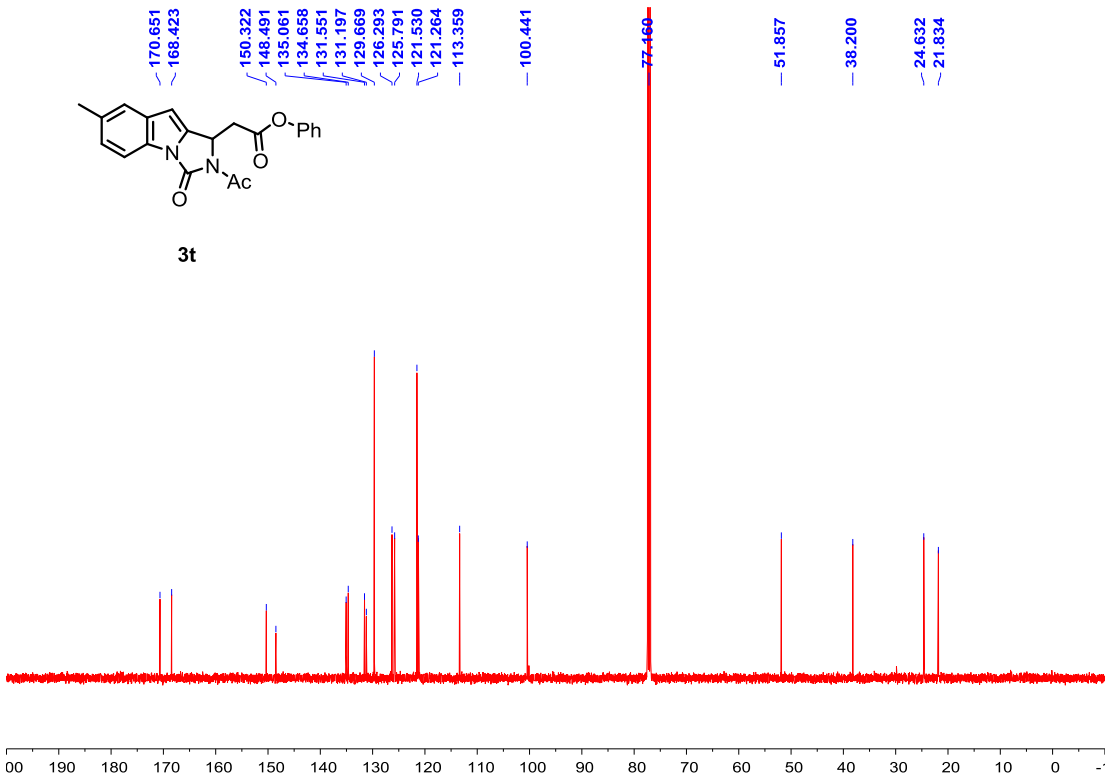
Phenyl-2-(2-acetyl-7-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3v)

^{1}H NMR, 500 MHz, $CDCl_3$



3t

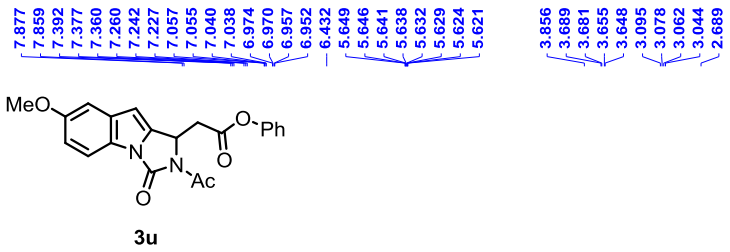
^{13}C NMR, 125 MHz, $CDCl_3$



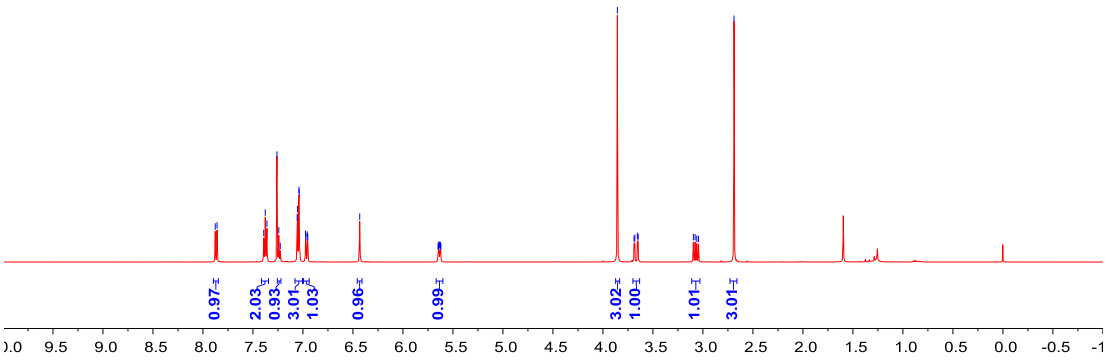
3t

Phenyl-2-(2-acetyl-7-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3w)

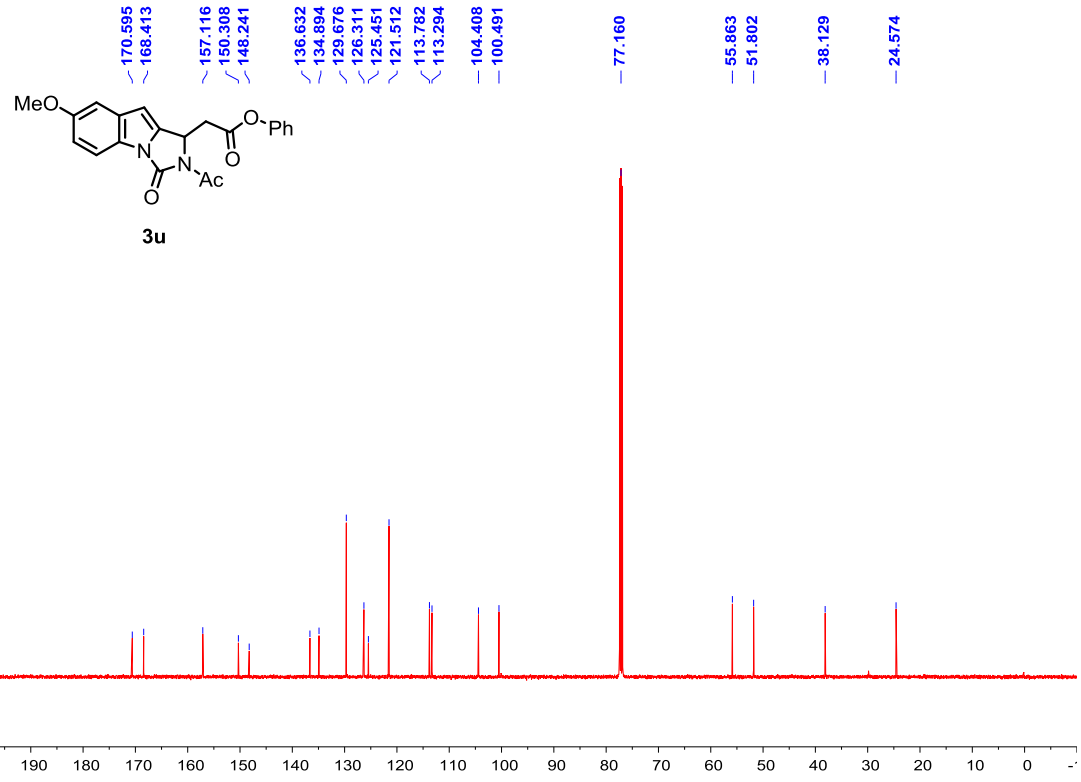
^{1}H NMR, 500 MHz, $CDCl_3$



3u



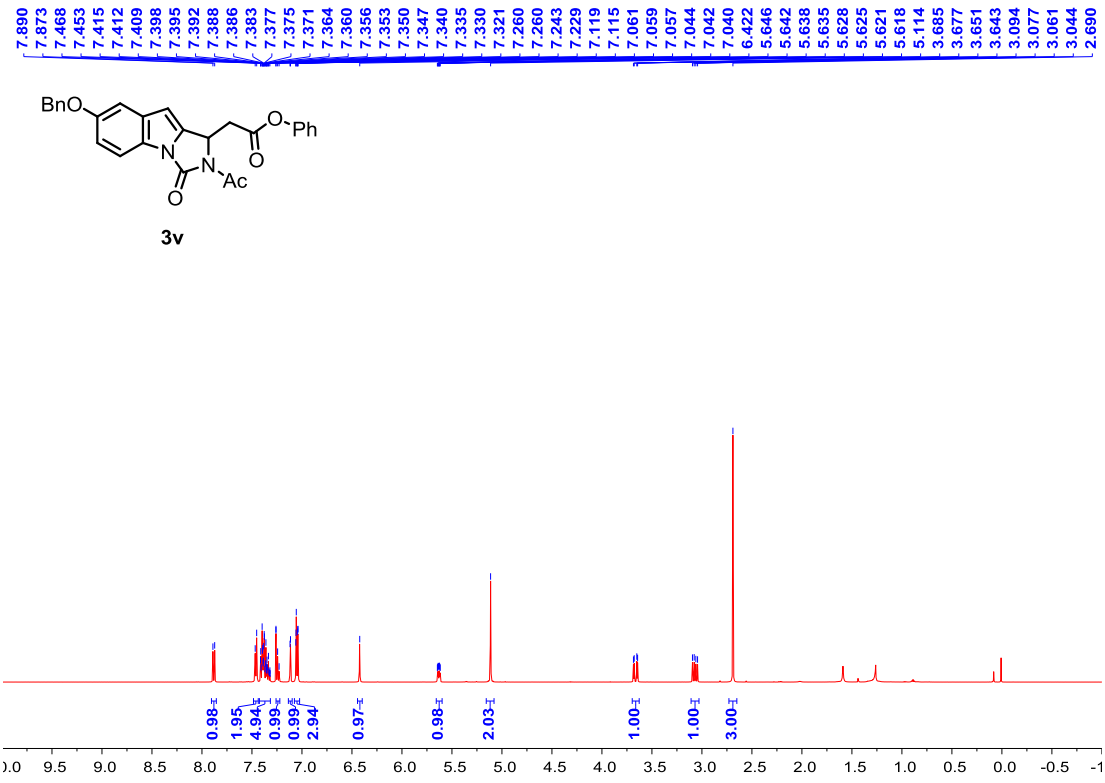
^{13}C NMR, 125 MHz, $CDCl_3$



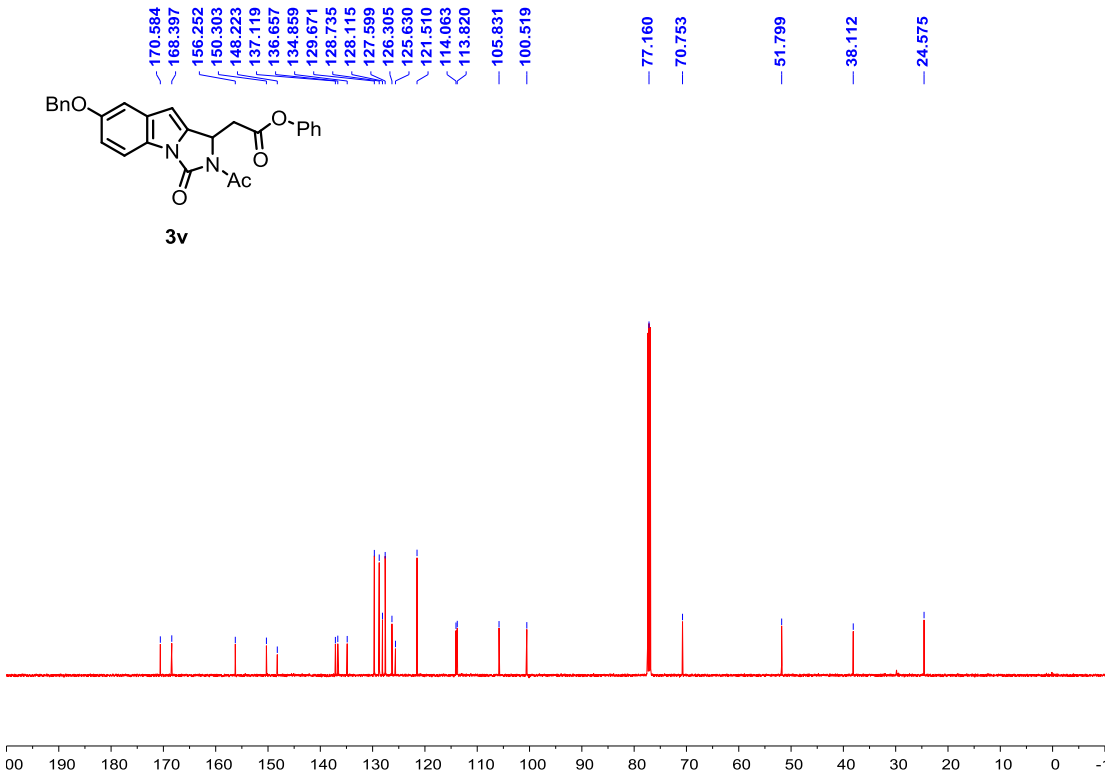
3u

Phenyl-2-(2-acetyl-7-(benzyloxy)-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3x)

^{1}H NMR, 500 MHz, $CDCl_3$

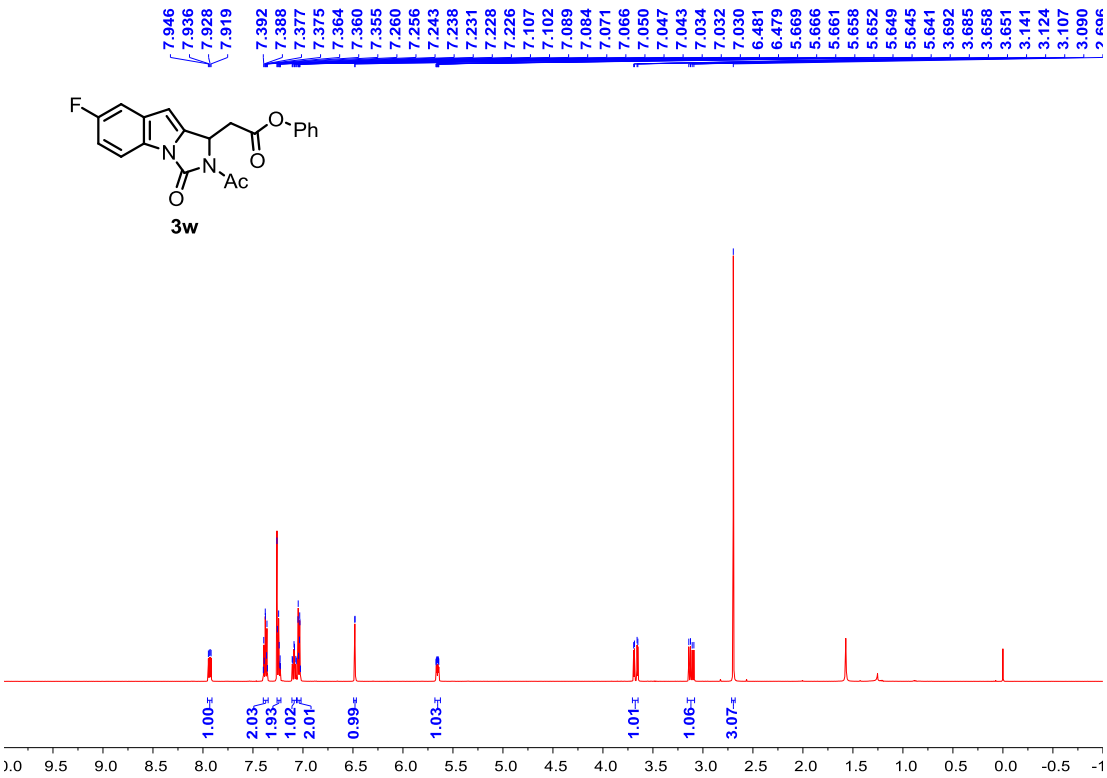


^{13}C NMR, 125 MHz, $CDCl_3$

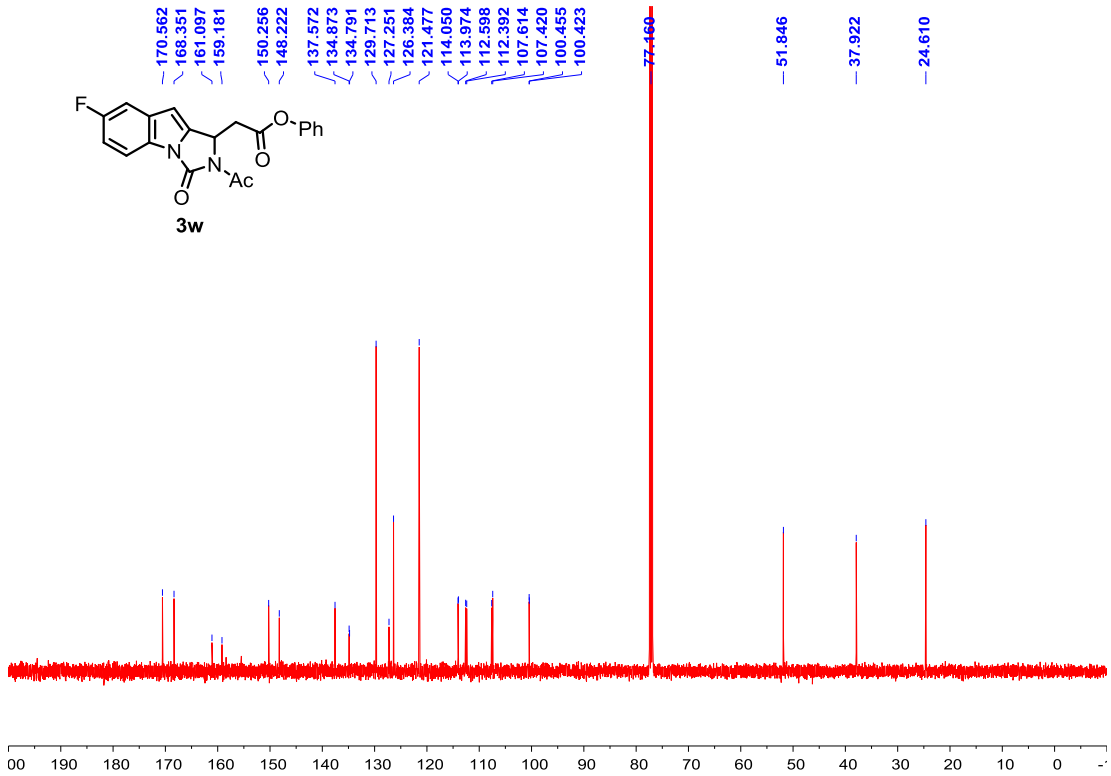


Phenyl-2-(2-acetyl-7-fluoro-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3y)

^{1}H NMR, 500 MHz, $CDCl_3$

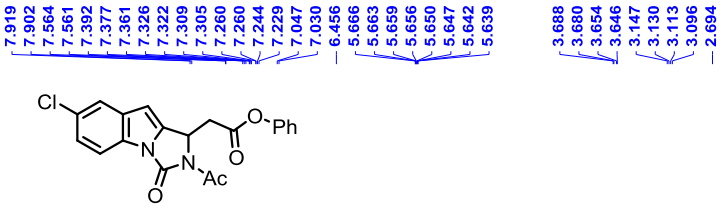


^{13}C NMR, 125 MHz, $CDCl_3$

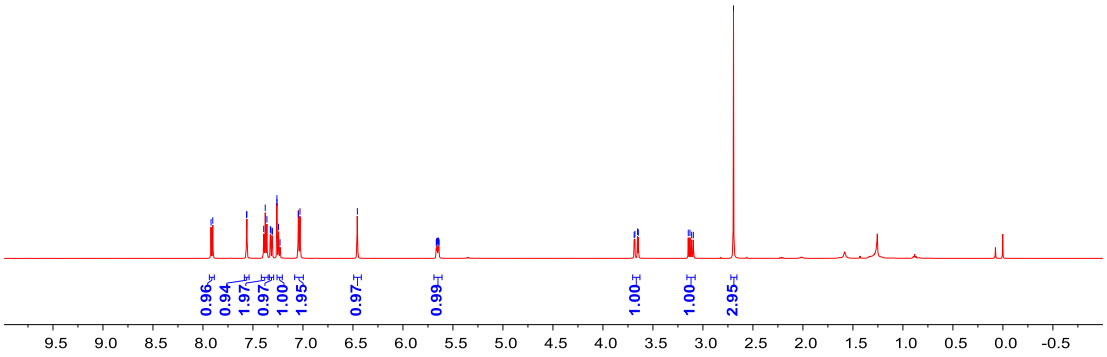


Phenyl-2-(2-acetyl-7-chloro-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3z)

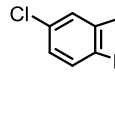
^{1}H NMR, 500 MHz, $CDCl_3$



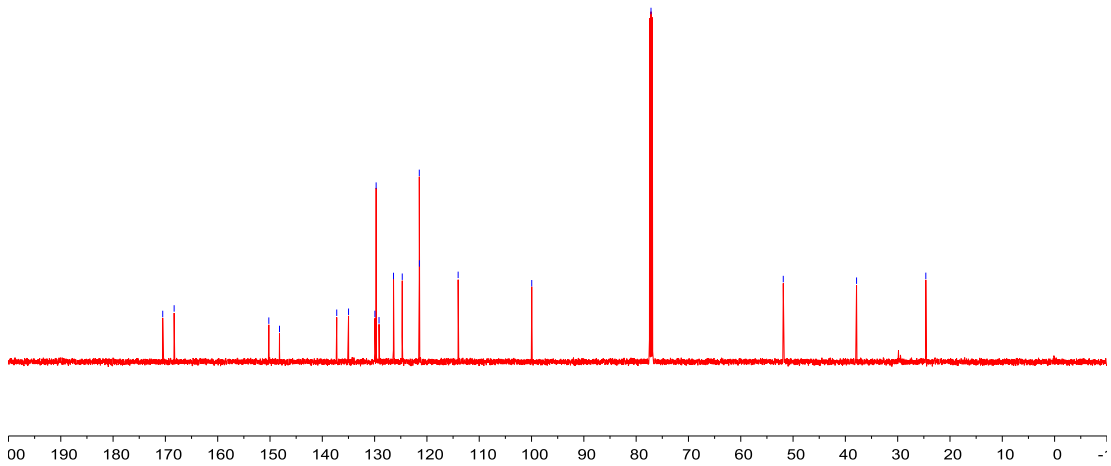
3x



^{13}C NMR, 125 MHz, $CDCl_3$

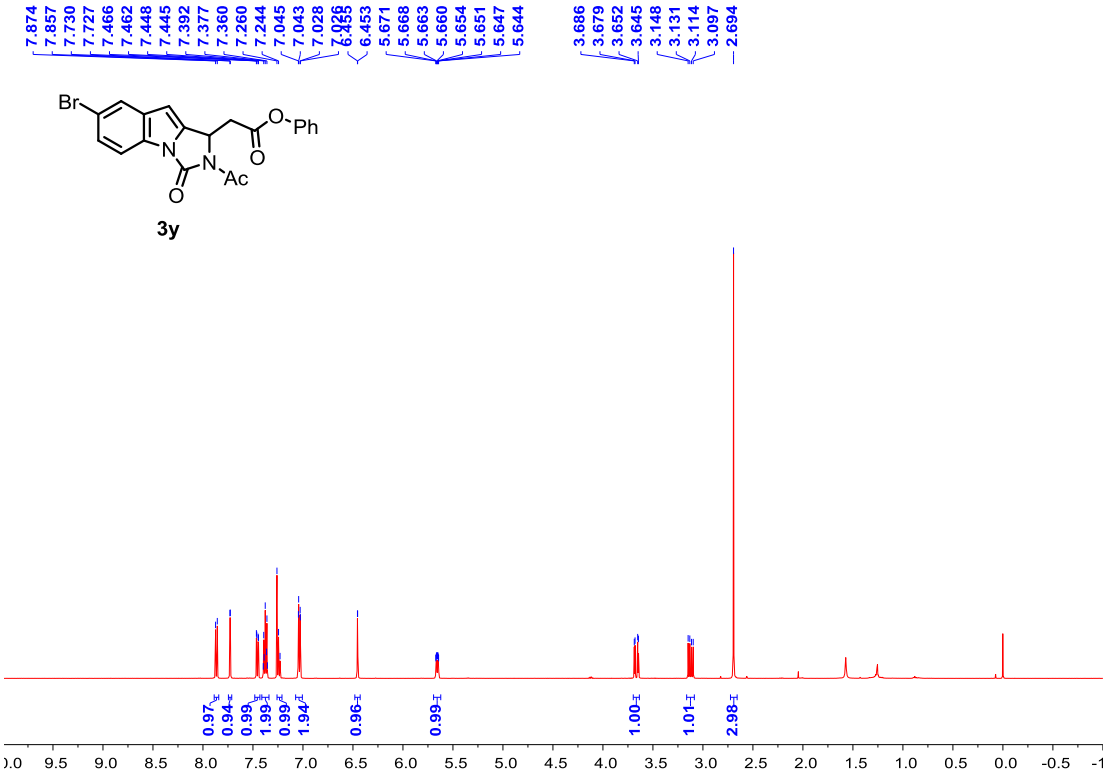


3x

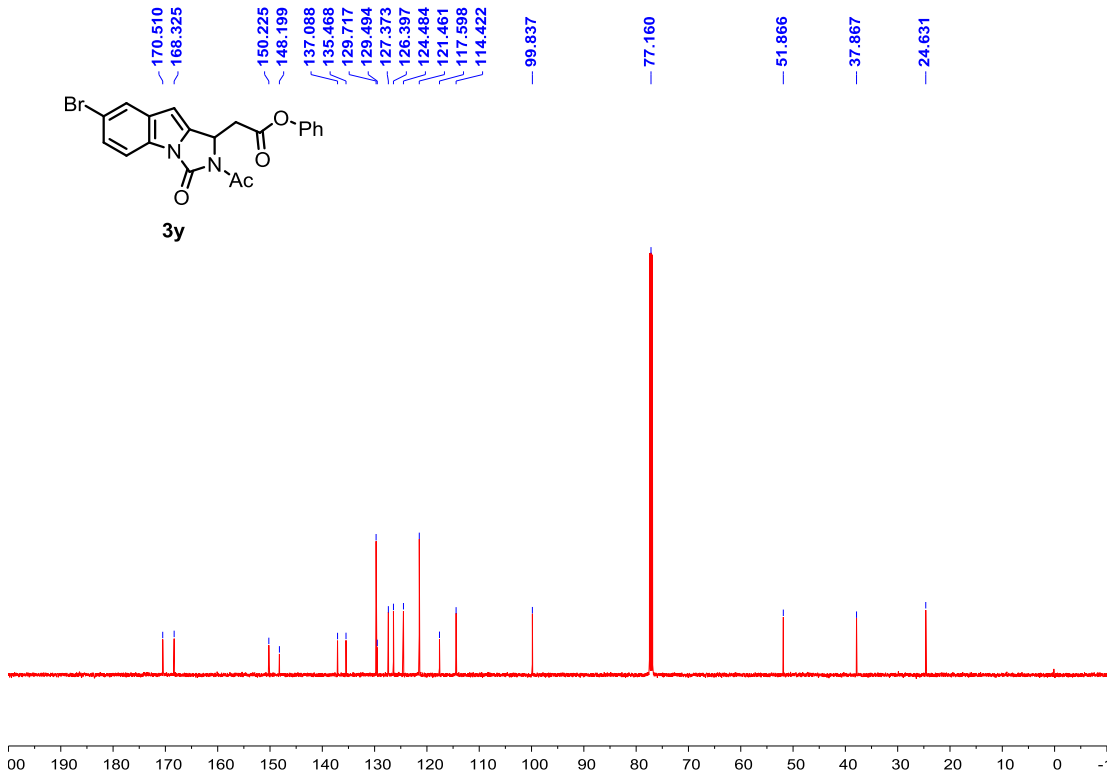


Phenyl-2-(2-acetyl-7-bromo-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3aa)

^{1}H NMR, 500 MHz, $CDCl_3$

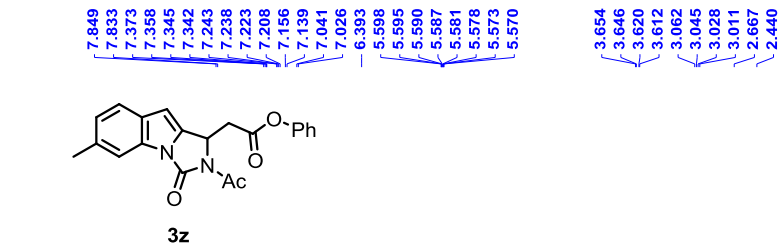


^{13}C NMR, 125 MHz, $CDCl_3$

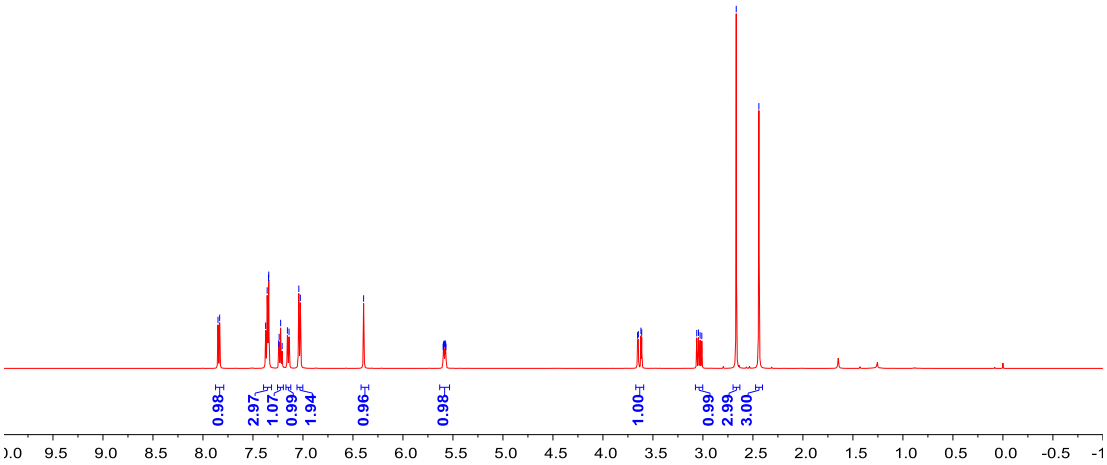


Phenyl-2-(2-acetyl-6-methyl-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ab)

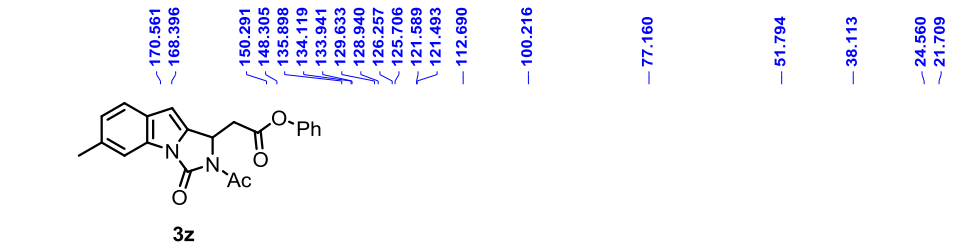
^{1}H NMR, 500 MHz, $CDCl_3$



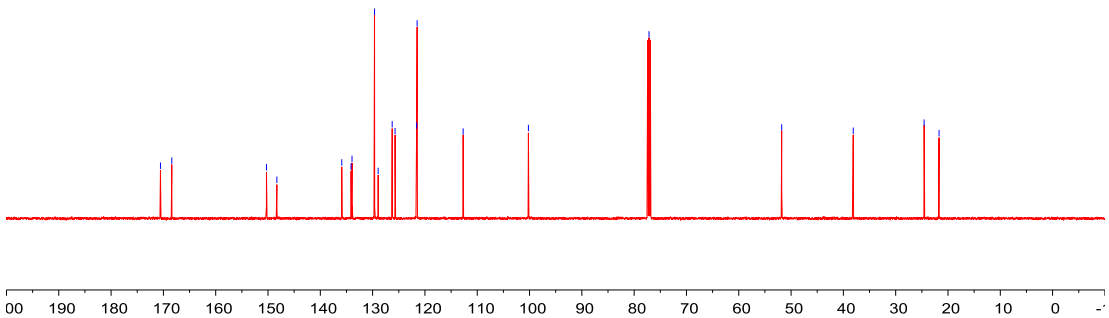
3z



^{13}C NMR, 125 MHz, $CDCl_3$

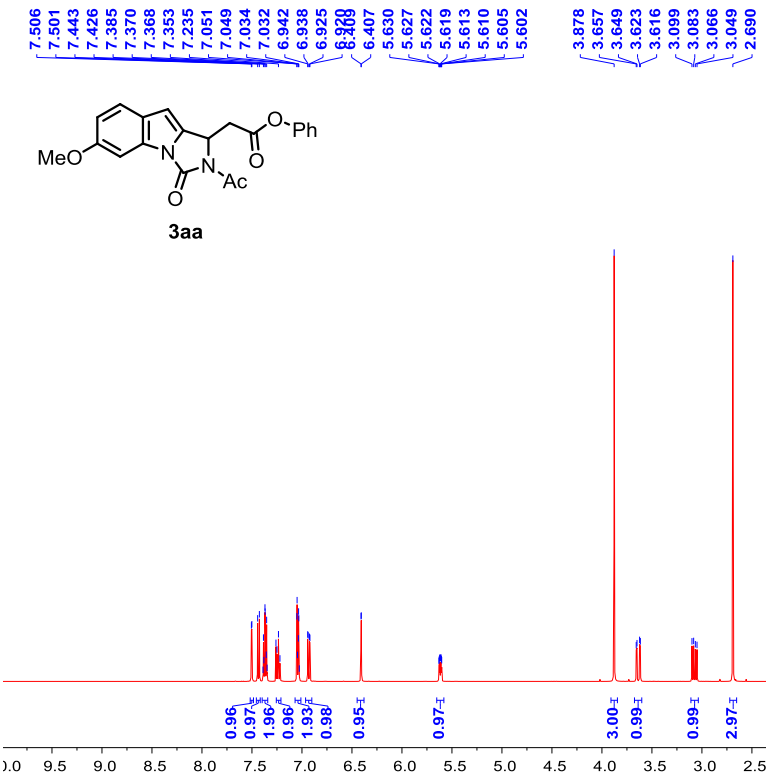


3z

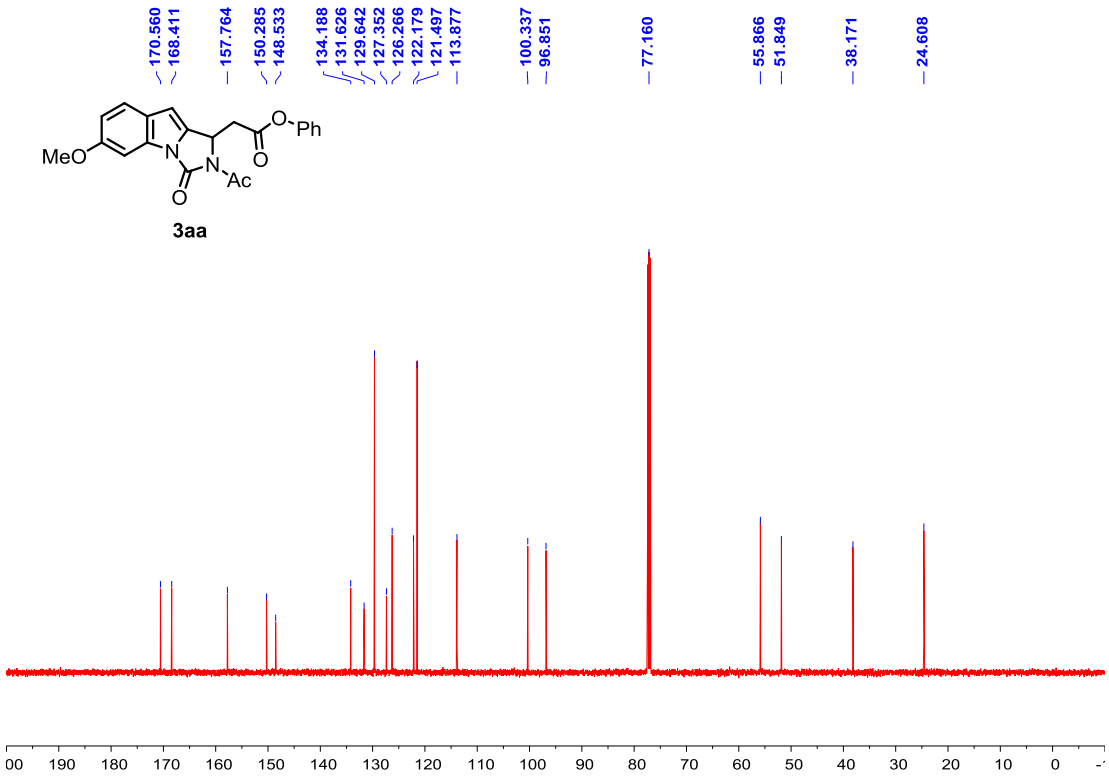


Phenyl-2-(2-acetyl-6-methoxy-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ac)

^{1}H NMR, 500 MHz, $CDCl_3$

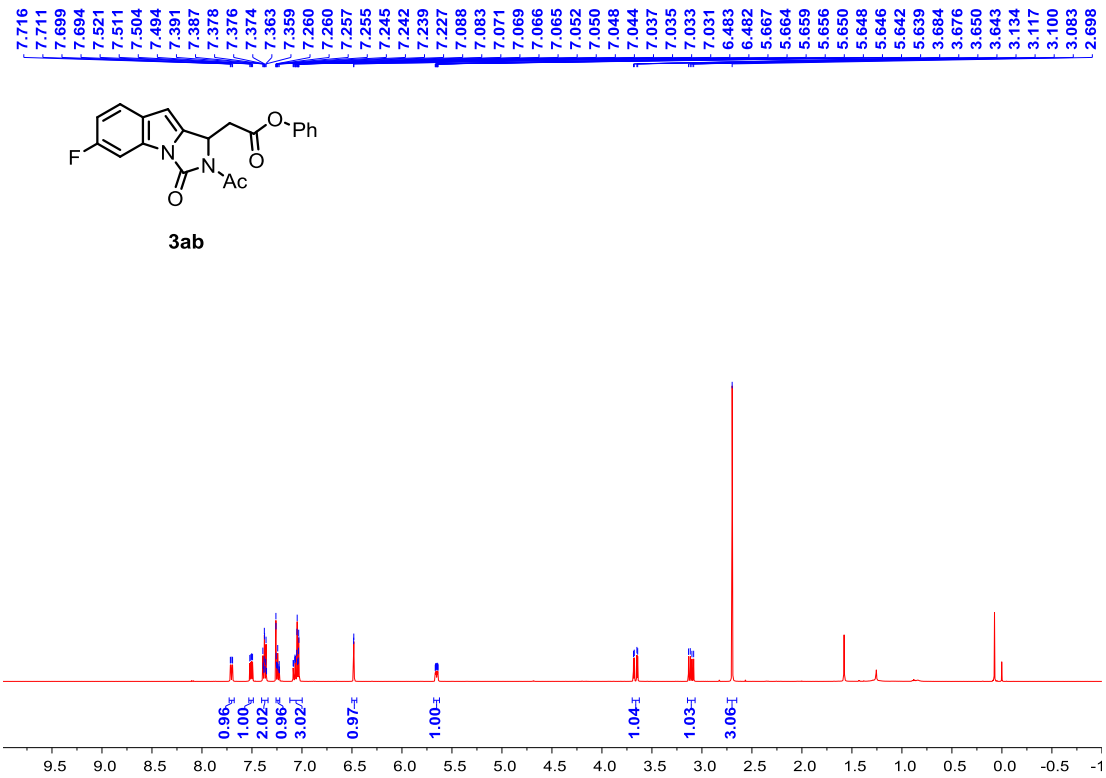


^{13}C NMR, 125 MHz, $CDCl_3$

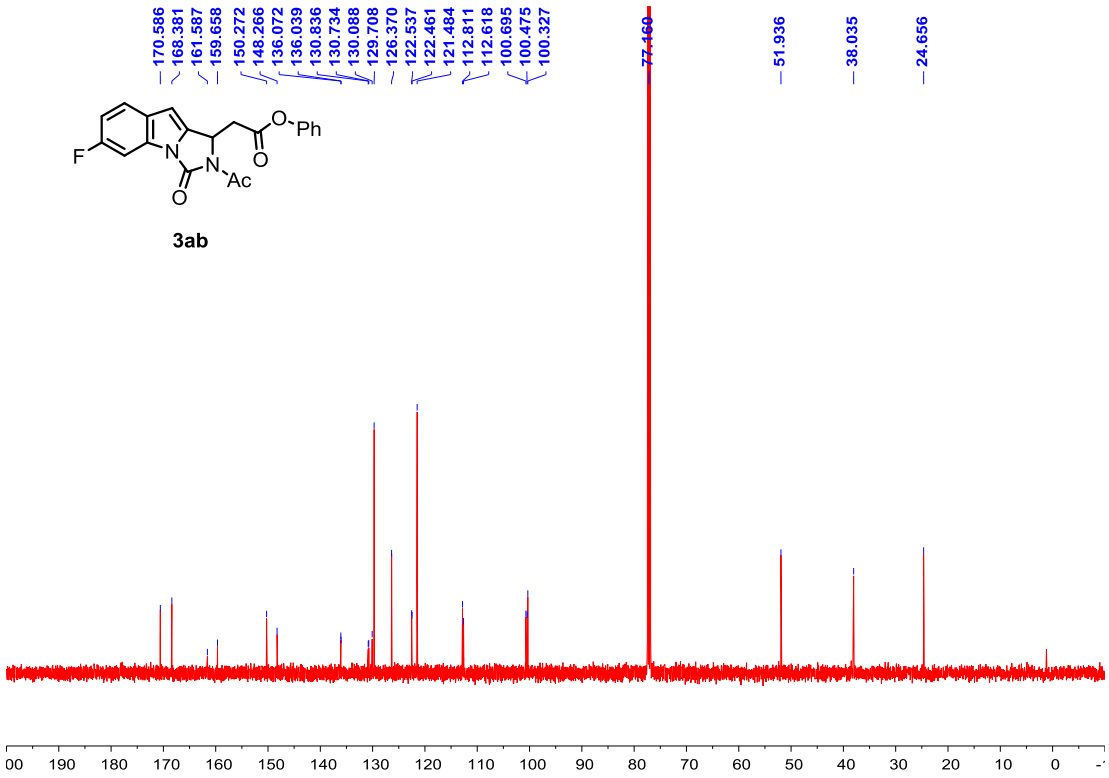


Phenyl-2-(2-acetyl-6-fluoro-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3ad)

^{1}H NMR, 500 MHz, $CDCl_3$

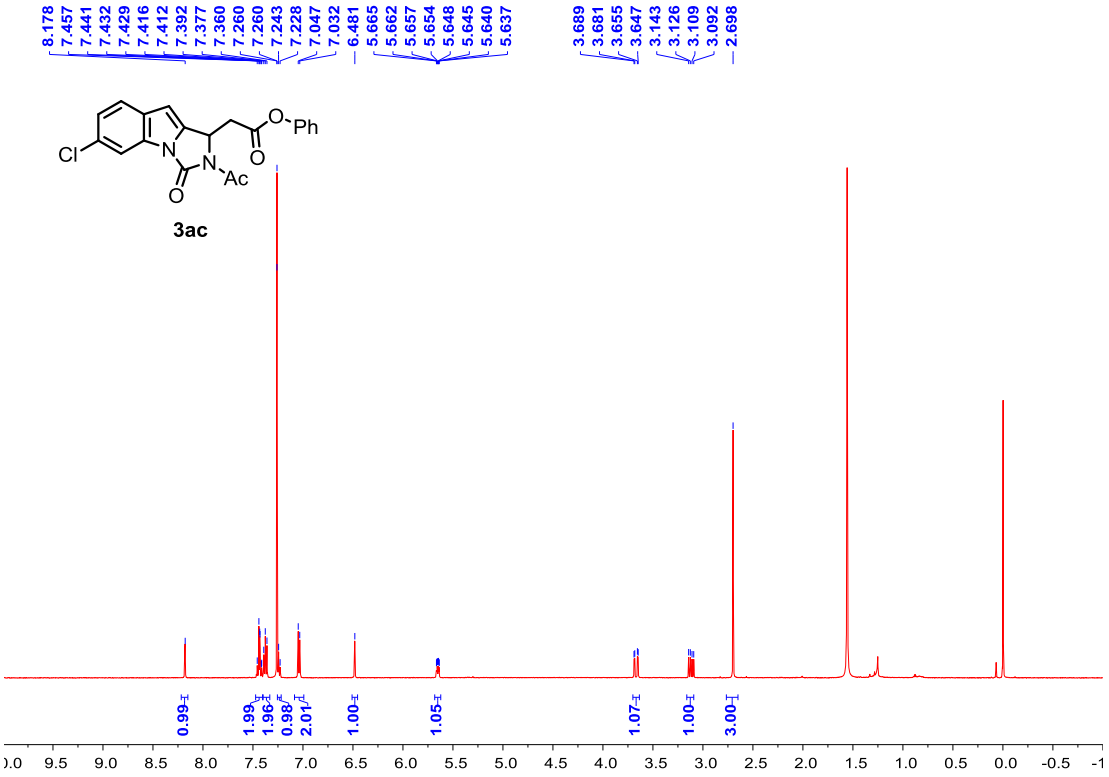


^{13}C NMR, 125 MHz, $CDCl_3$

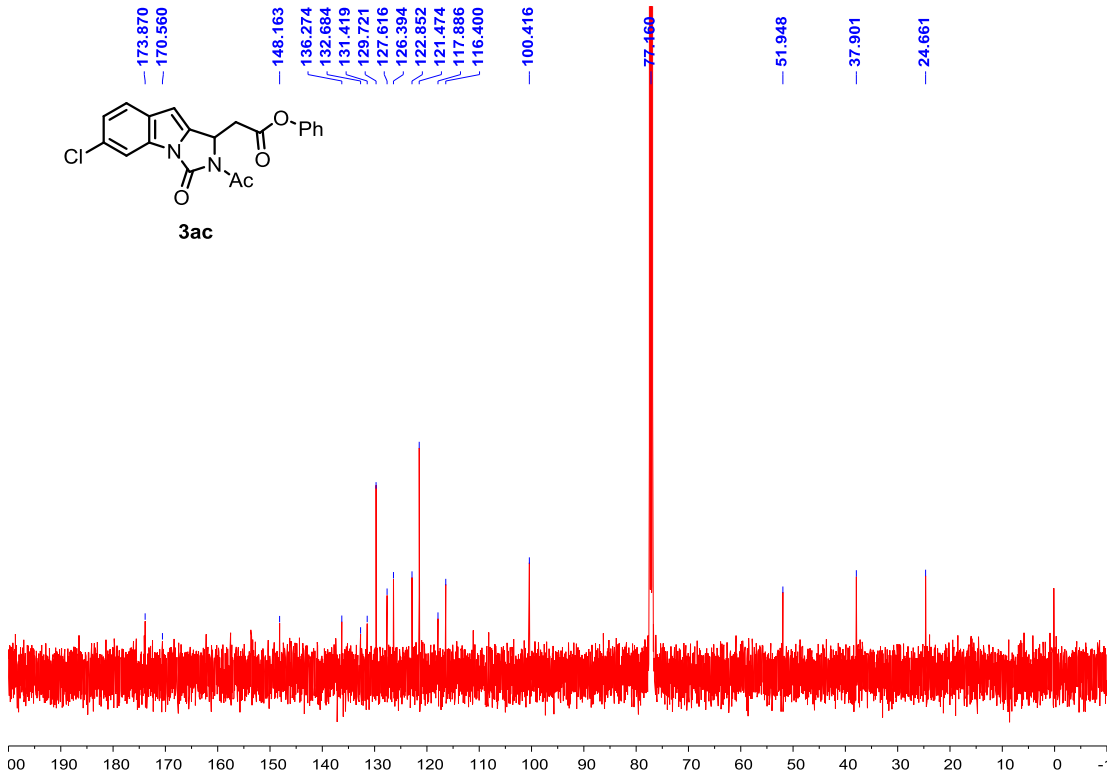


Phenyl-2-(2-acetyl-6-chloro-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-a]indol-1-yl)acetate (3ae)

^{1}H NMR, 500 MHz, $CDCl_3$

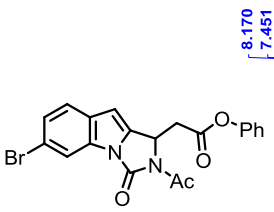


^{13}C NMR, 125 MHz, $CDCl_3$



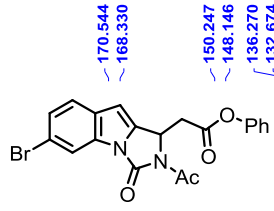
Phenyl-2-(2-acetyl-6-bromo-3-oxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-yl)acetate (3af)

^{1}H NMR, 500 MHz, $CDCl_3$



3ad

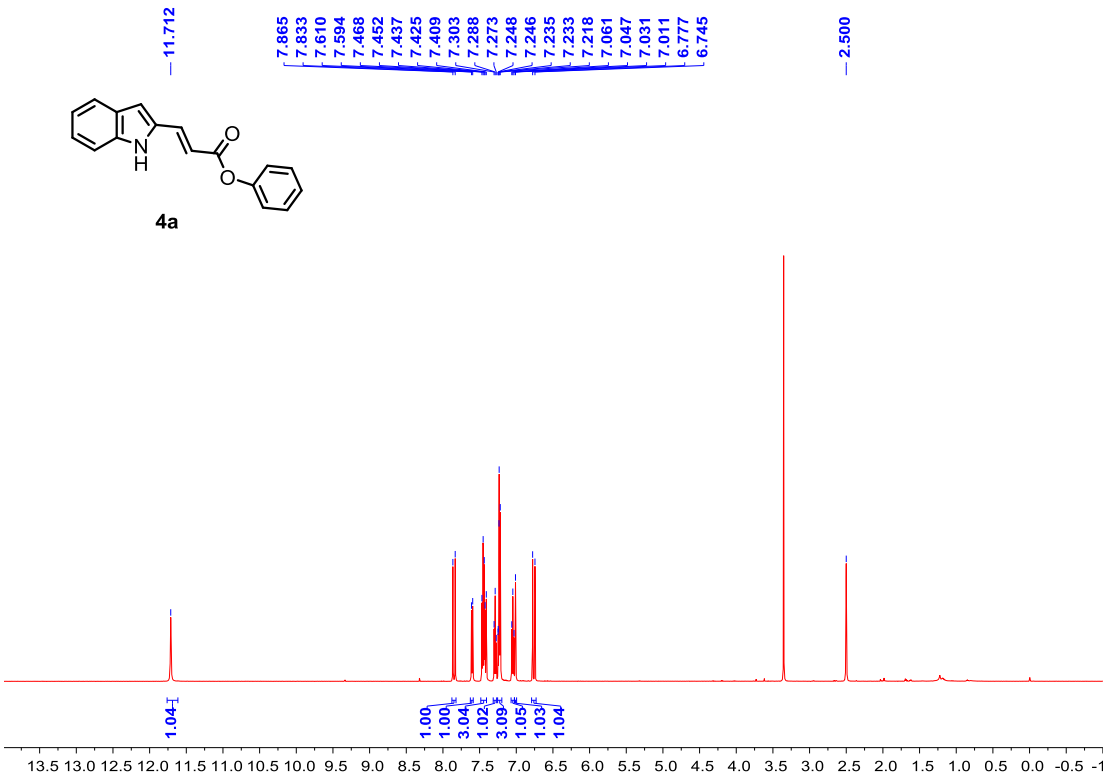
^{13}C NMR, 125 MHz, $CDCl_3$



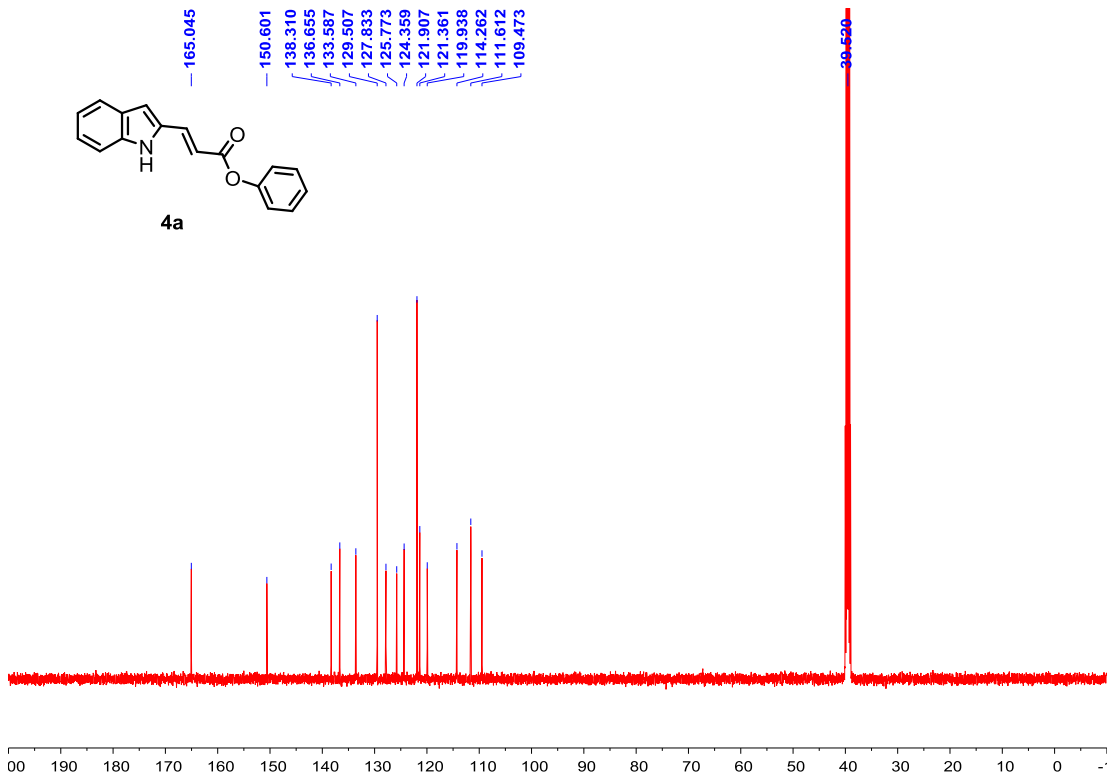
3ad

Phenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4a)

^{1}H NMR, 500 MHz, DMSO-d_6

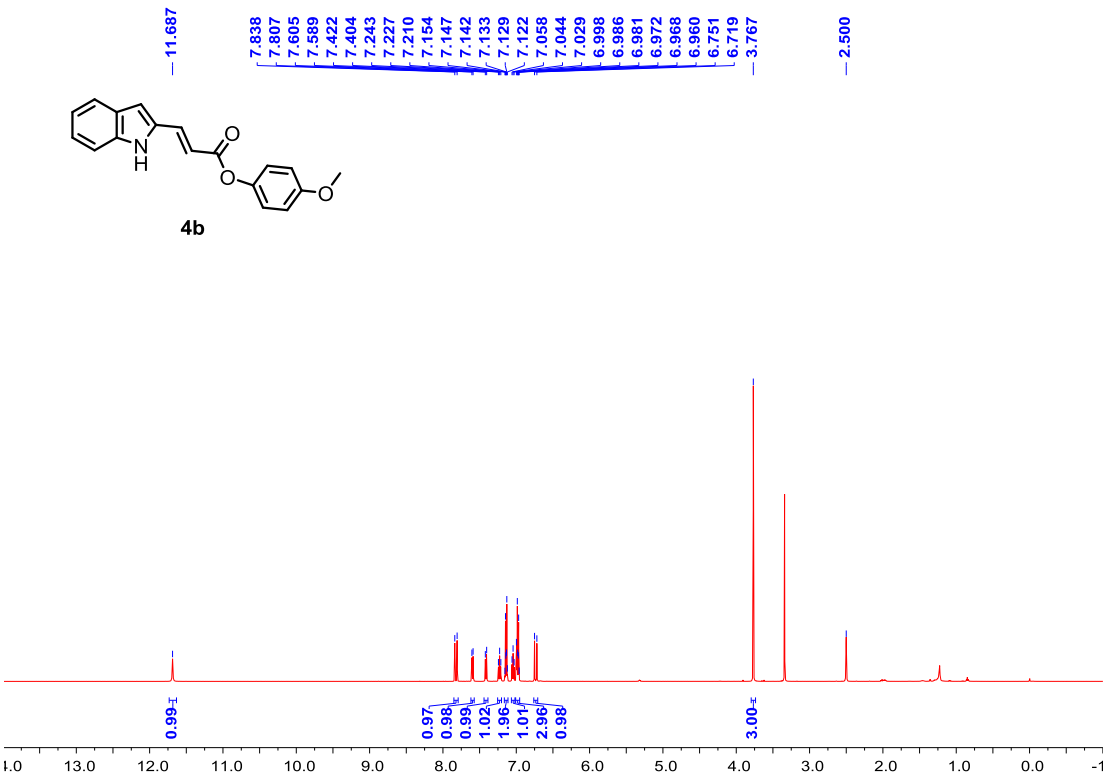


^{13}C NMR, 125 MHz, DMSO-d_6

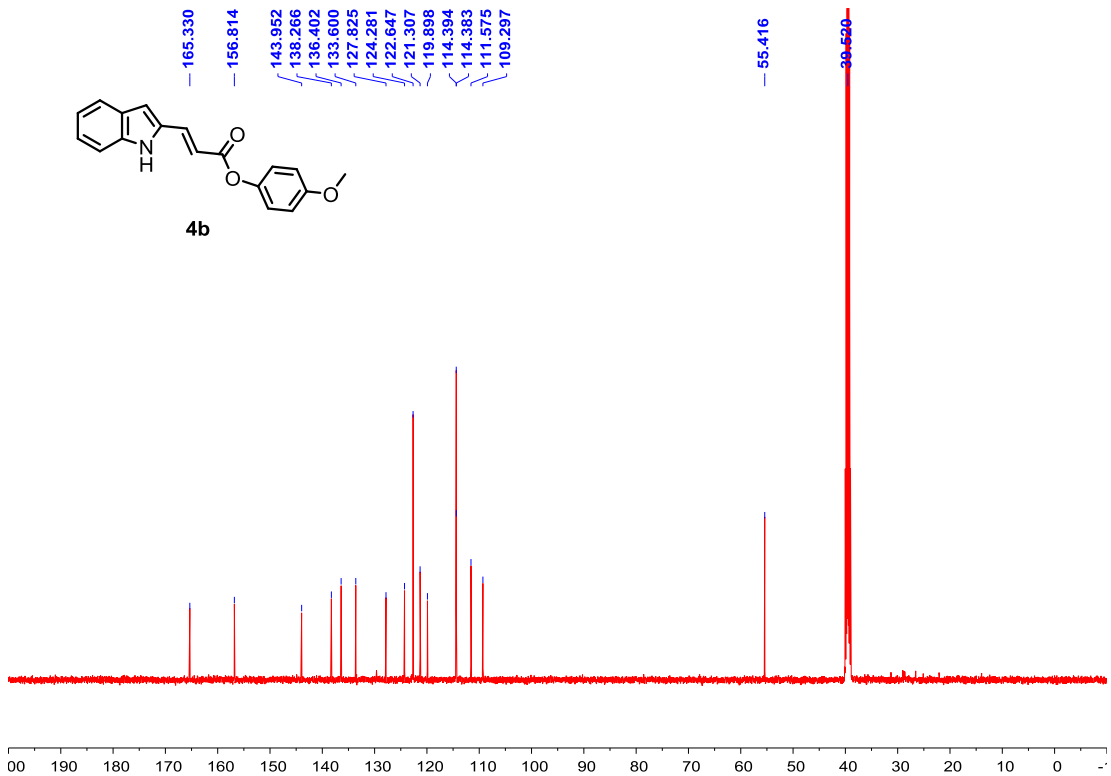


4-Methoxyphenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4b)

^{1}H NMR, 500 MHz, DMSO-d_6

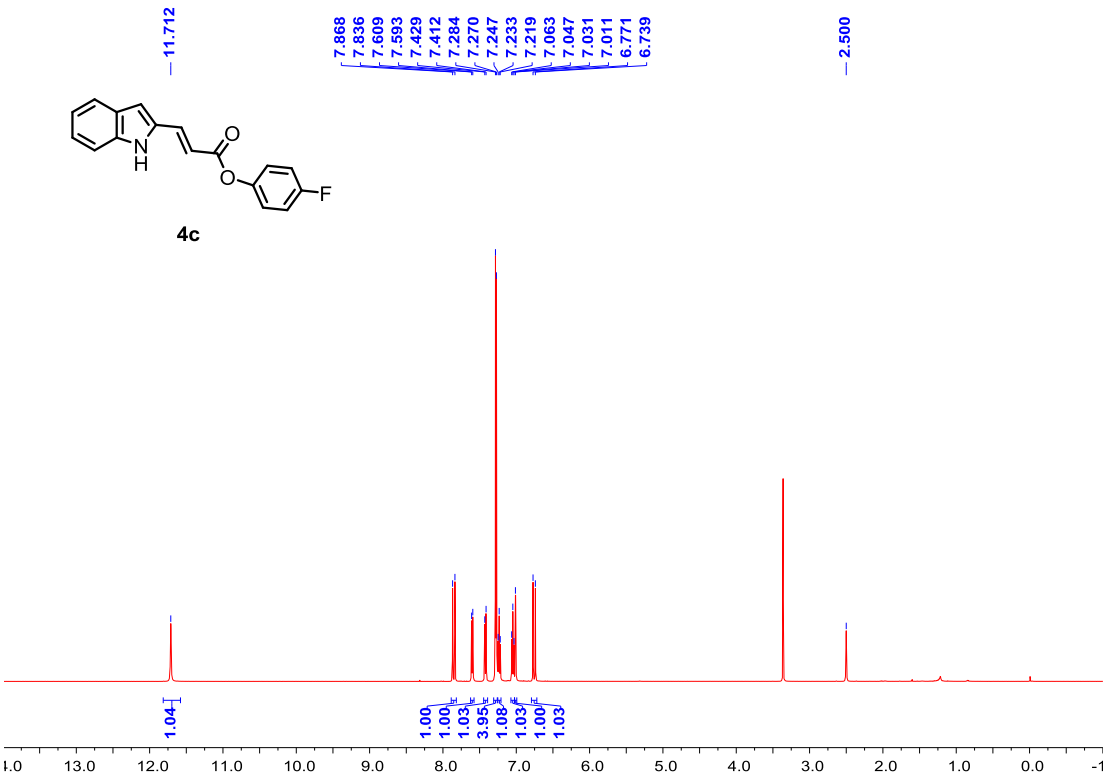


^{13}C NMR, 125 MHz, DMSO-d_6

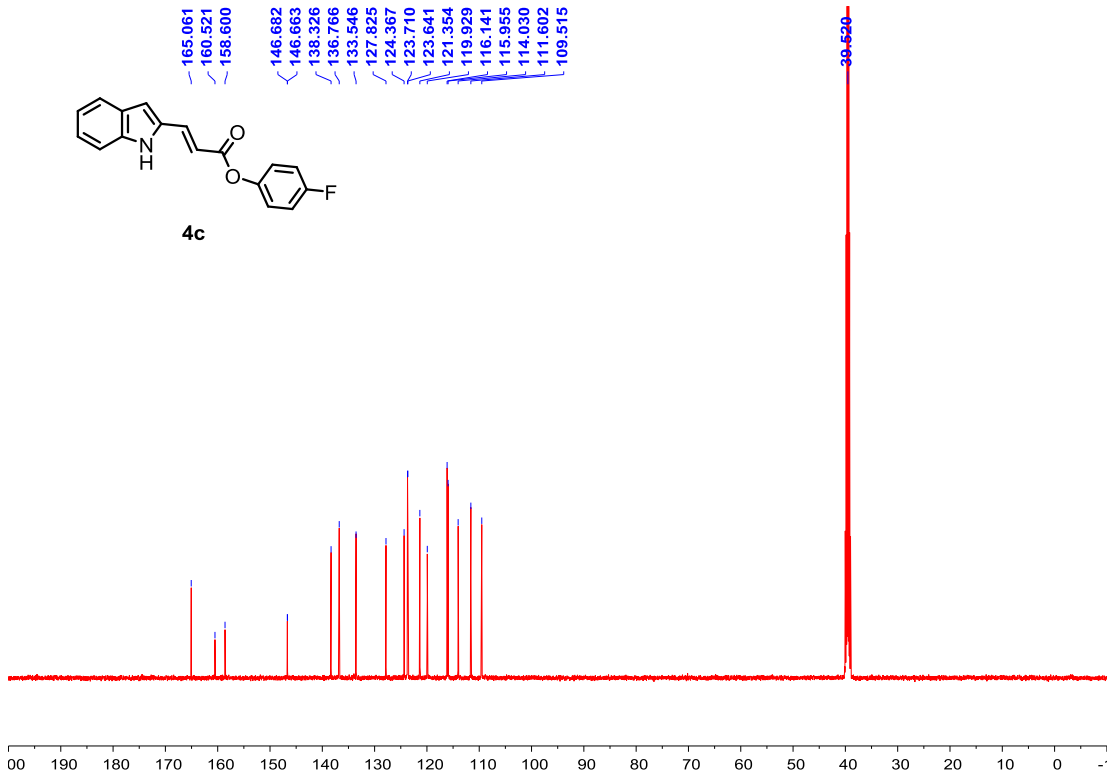


4-Fluorophenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4c)

^{1}H NMR, 500 MHz, DMSO-d_6

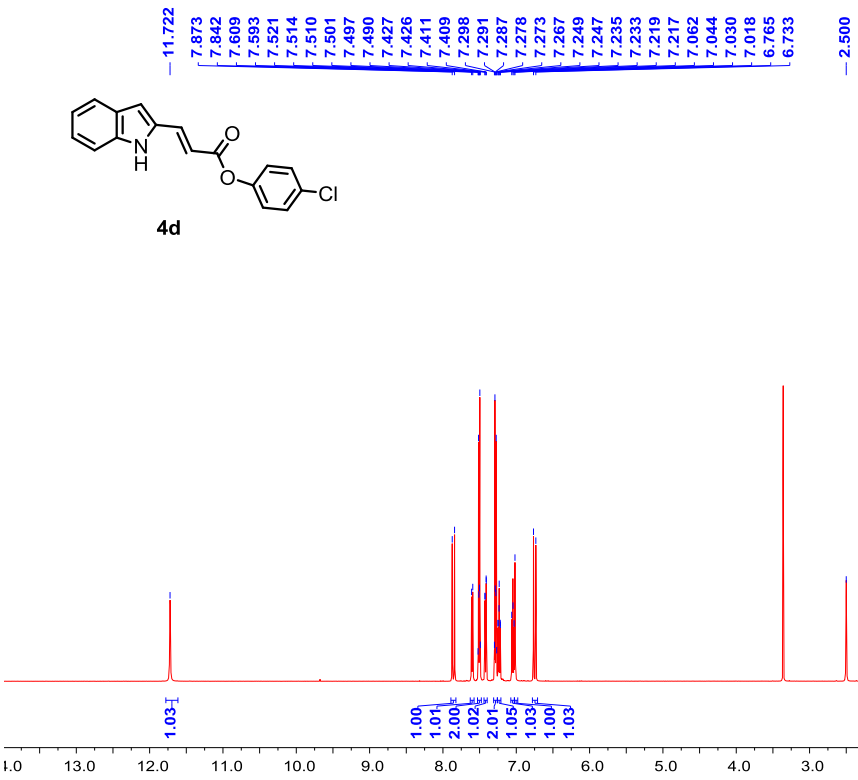


^{13}C NMR, 125 MHz, DMSO-d_6

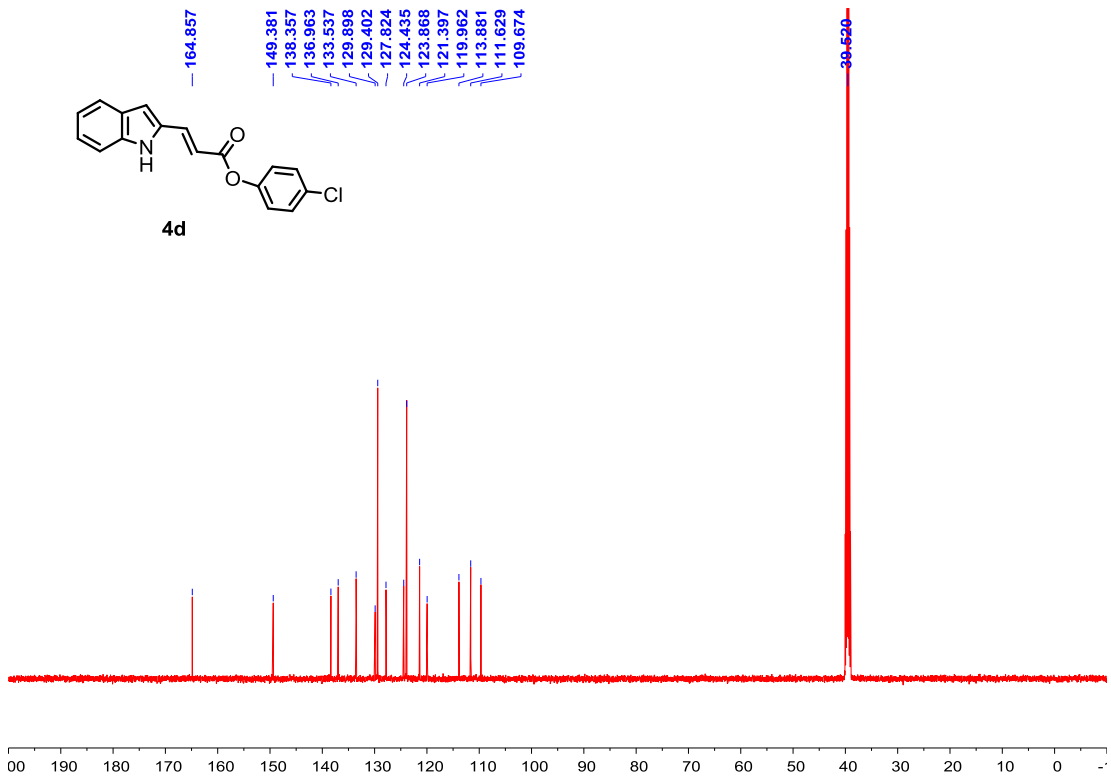


4-Chlorophenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4d))

^{1}H NMR, 500 MHz, DMSO-d_6

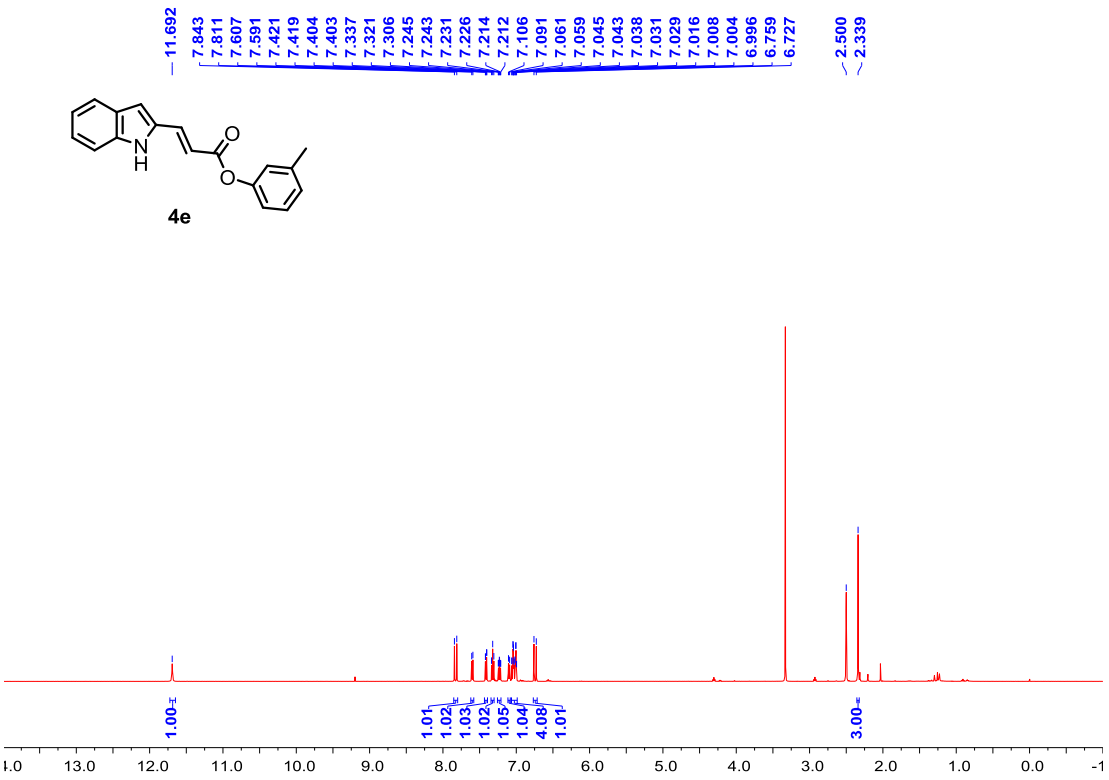


^{13}C NMR, 125 MHz, DMSO-d_6

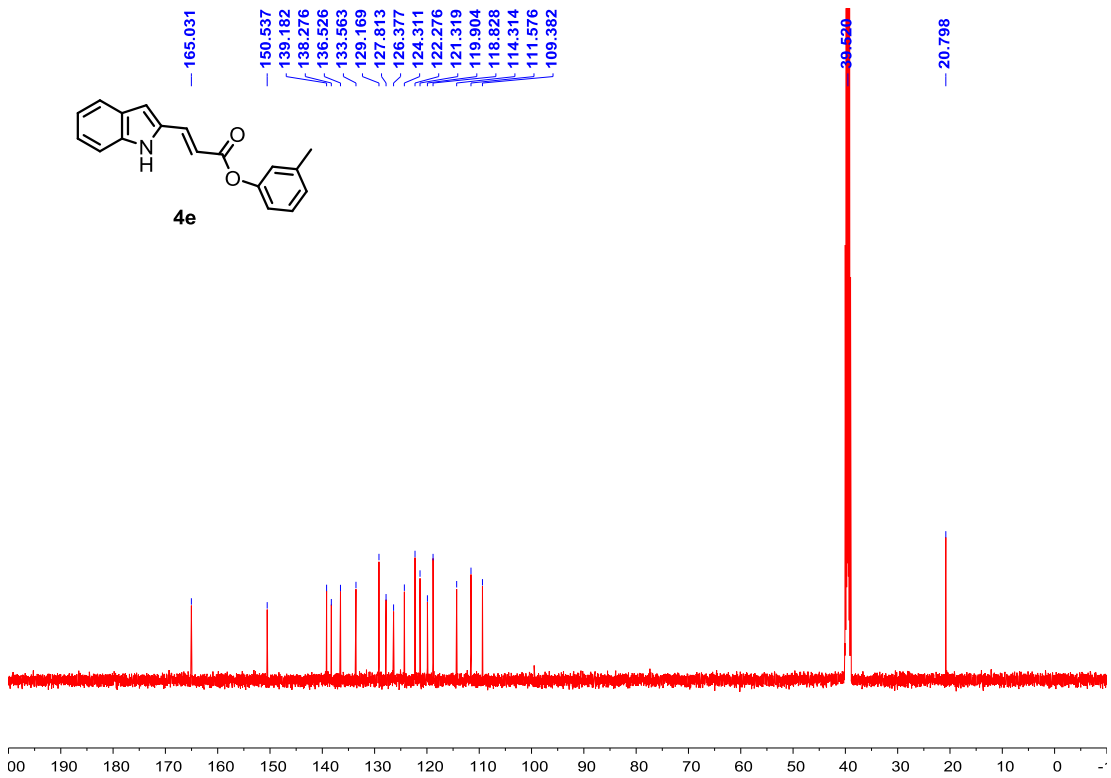


_m_-Tolyl (_E_)-3-(1_H_-indol-2-yl)acrylate (4g)

^{1}H NMR, 500 MHz, DMSO-d_6

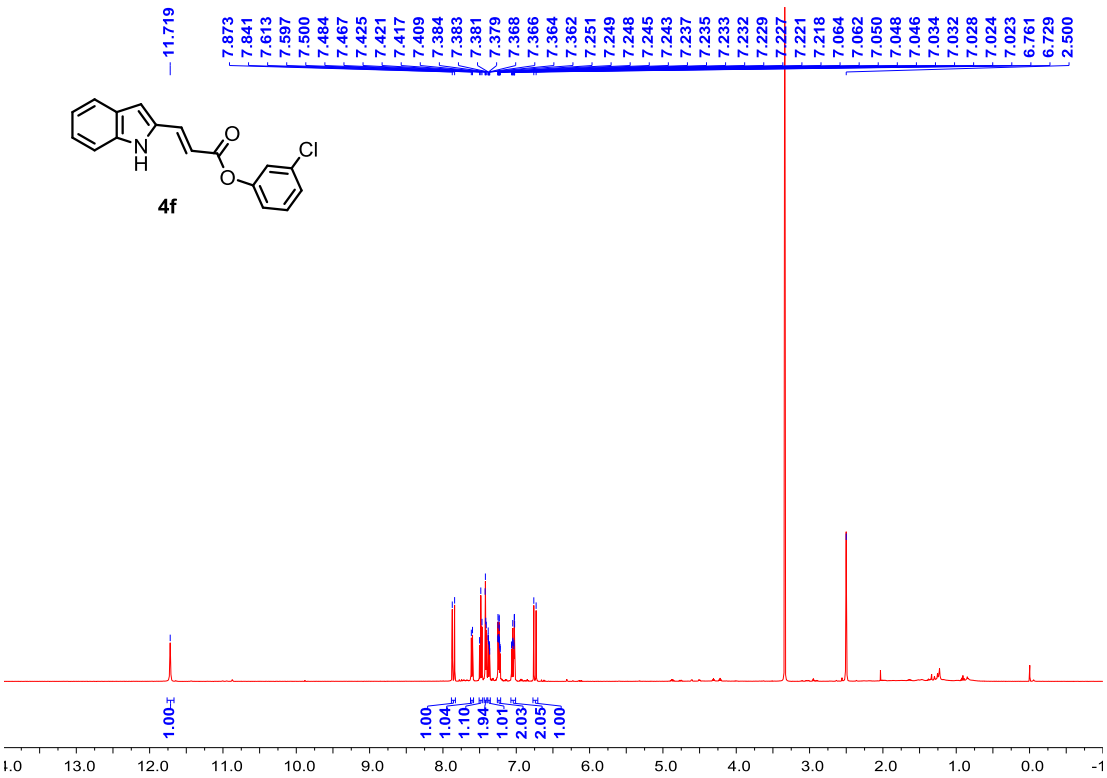


^{13}C NMR, 125 MHz, DMSO-d_6

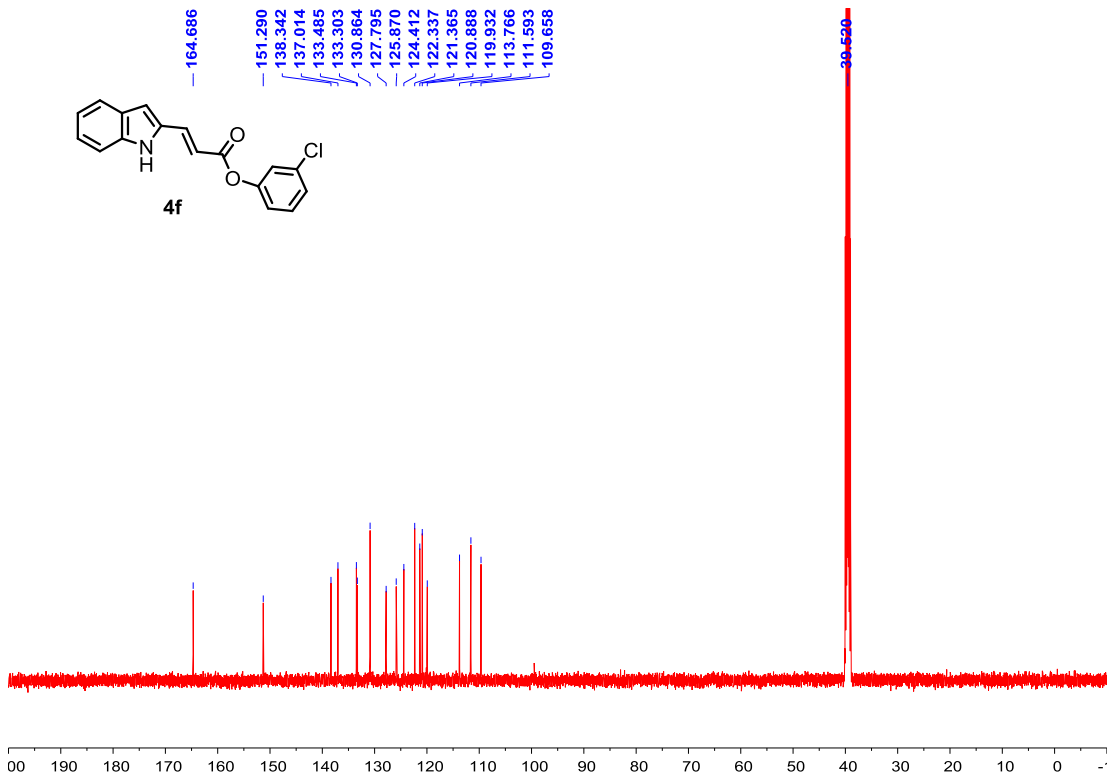


3-Chlorophenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4h)

^{1}H NMR, 500 MHz, DMSO-d_6

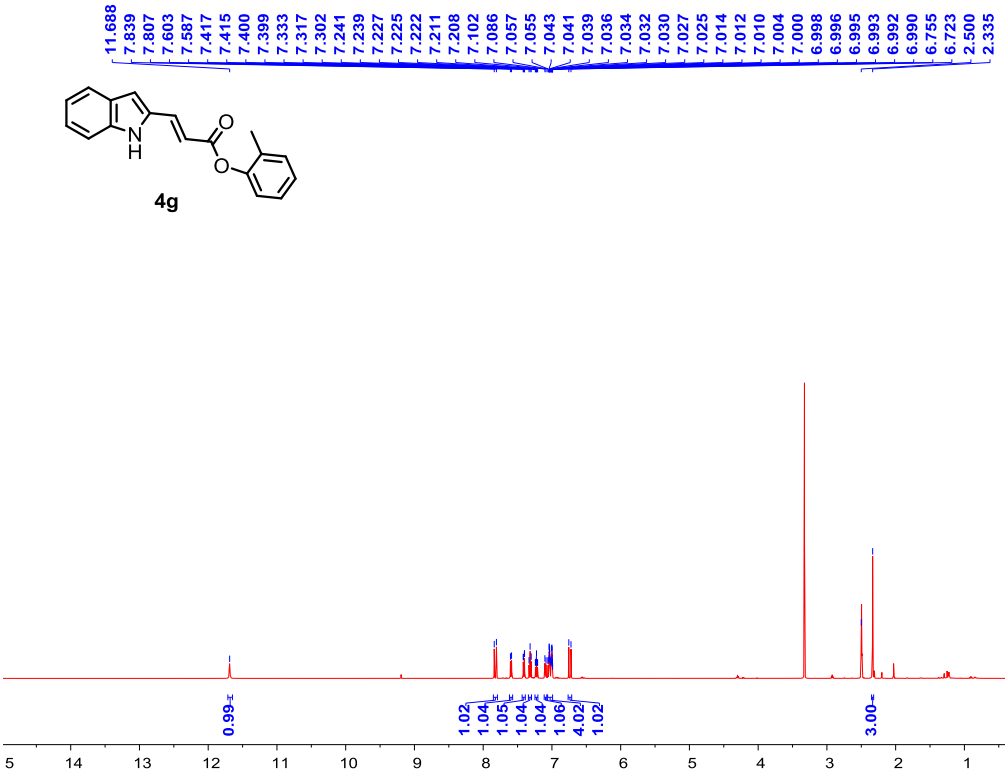


^{13}C NMR, 125 MHz, DMSO-d_6

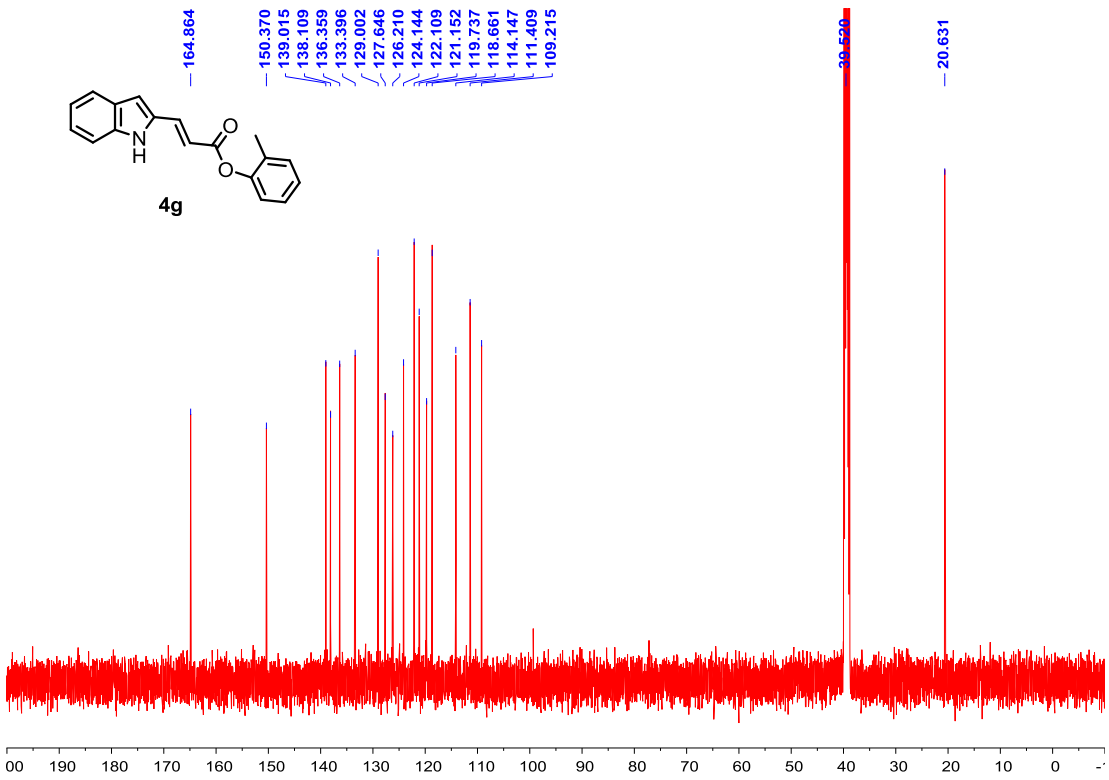


o-Tolyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4i)

^{1}H NMR, 500 MHz, DMSO-d_6

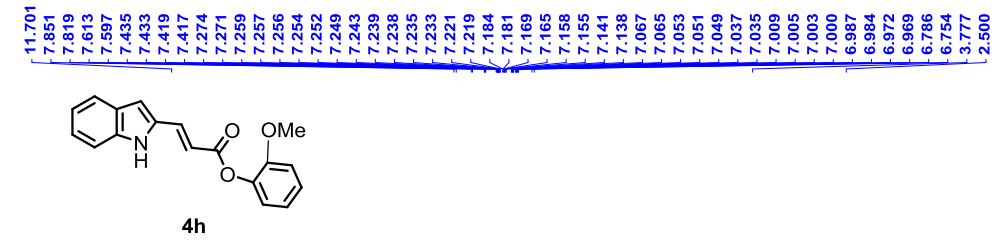


^{13}C NMR, 125 MHz, DMSO-d_6

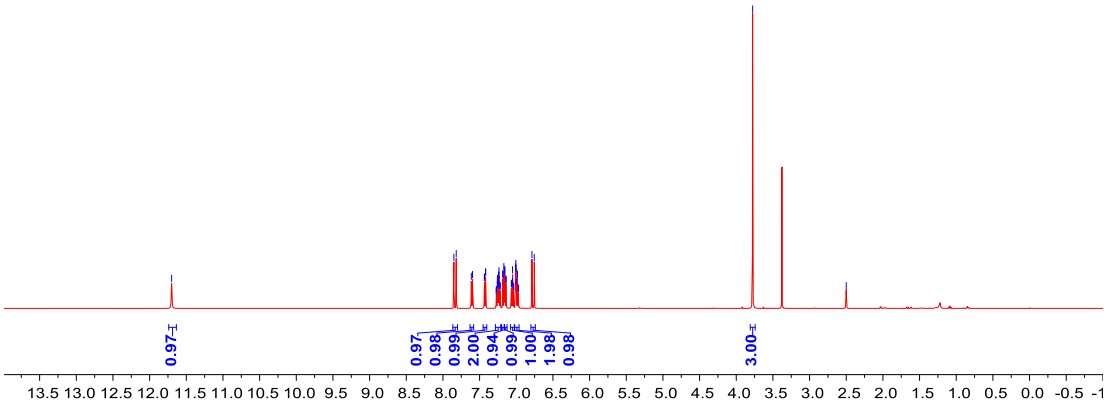


2-Methoxyphenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4j)

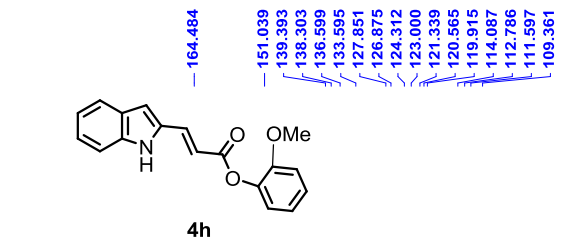
^{1}H NMR, 500 MHz, DMSO-d_6



4h



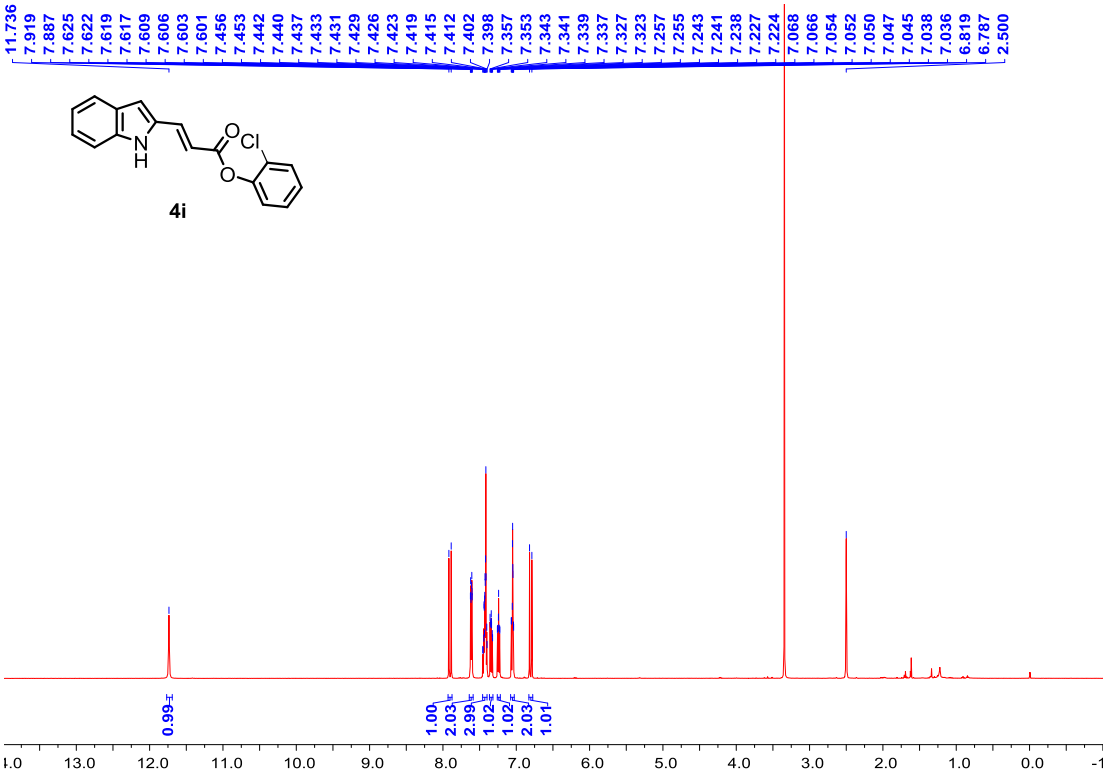
^{13}C NMR, 125 MHz, DMSO-d_6



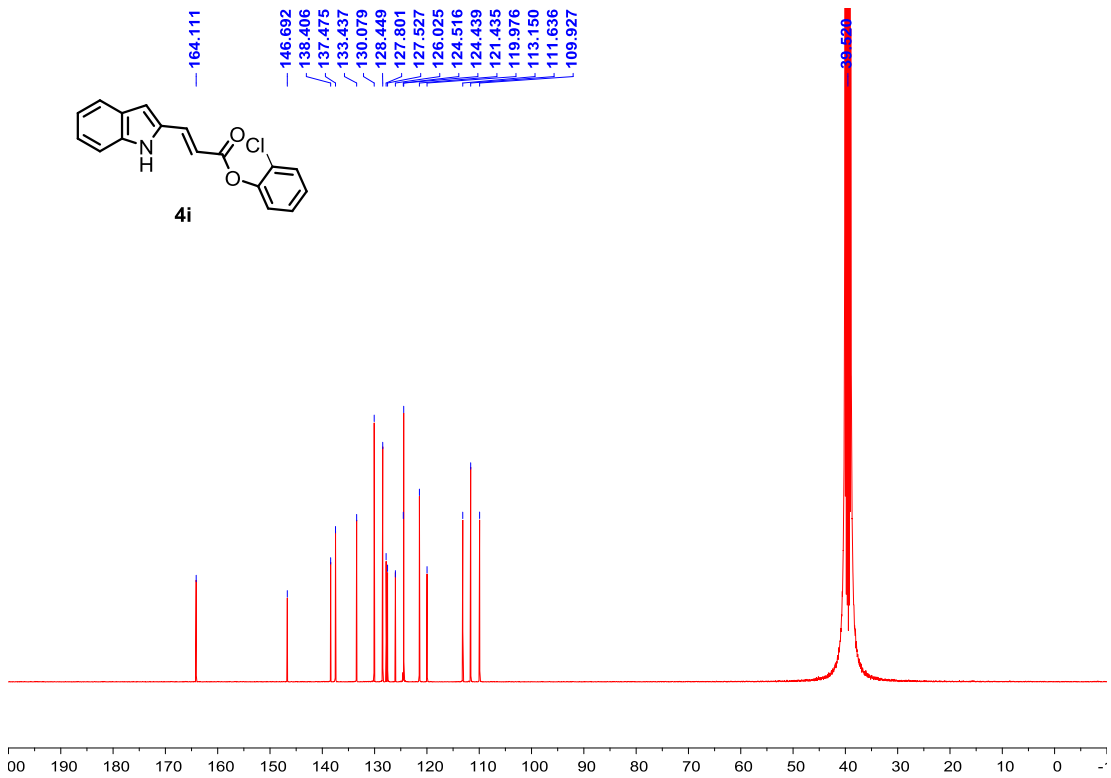
4h

2-Chlorophenyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4k)

^{1}H NMR, 500 MHz, DMSO-d_6

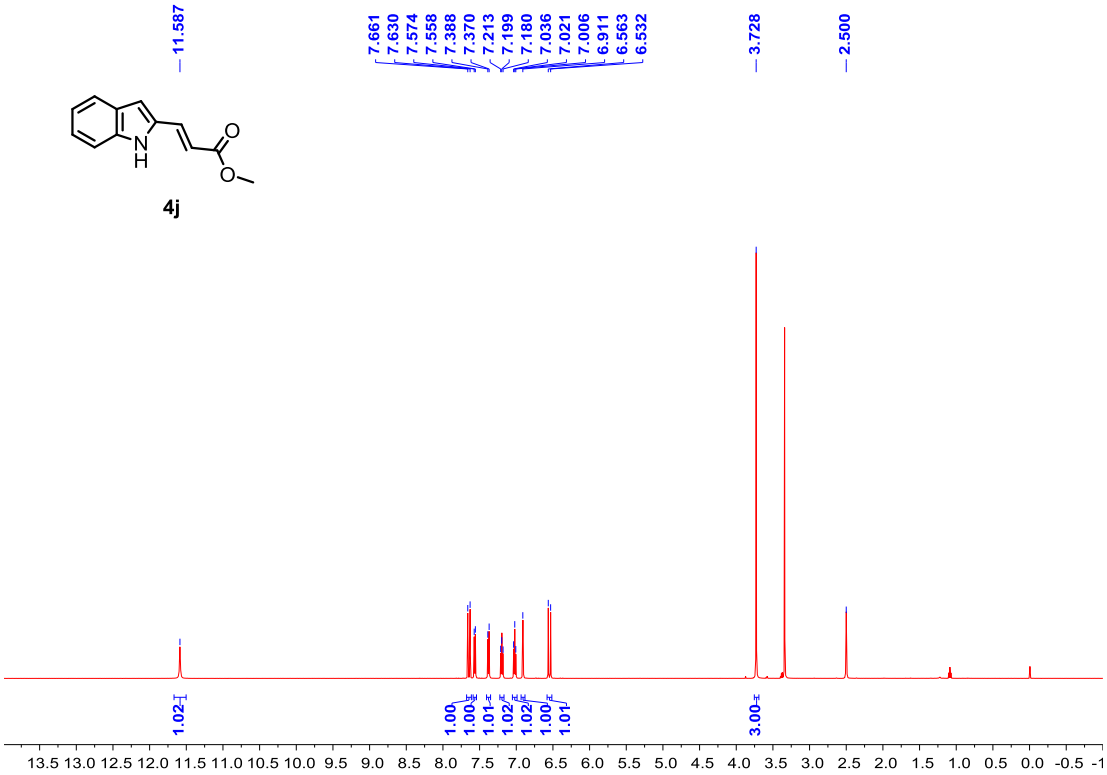


^{13}C NMR, 125 MHz, DMSO-d_6

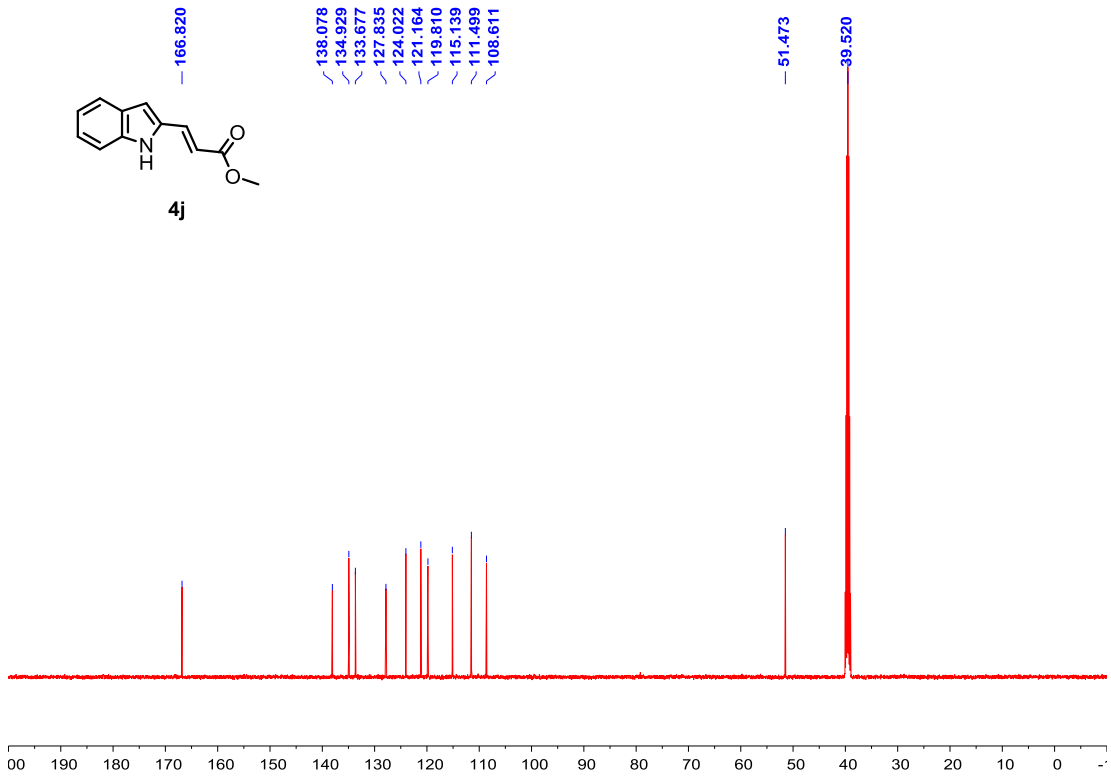


Methyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4l)

^{1}H NMR, 500 MHz, DMSO-d_6

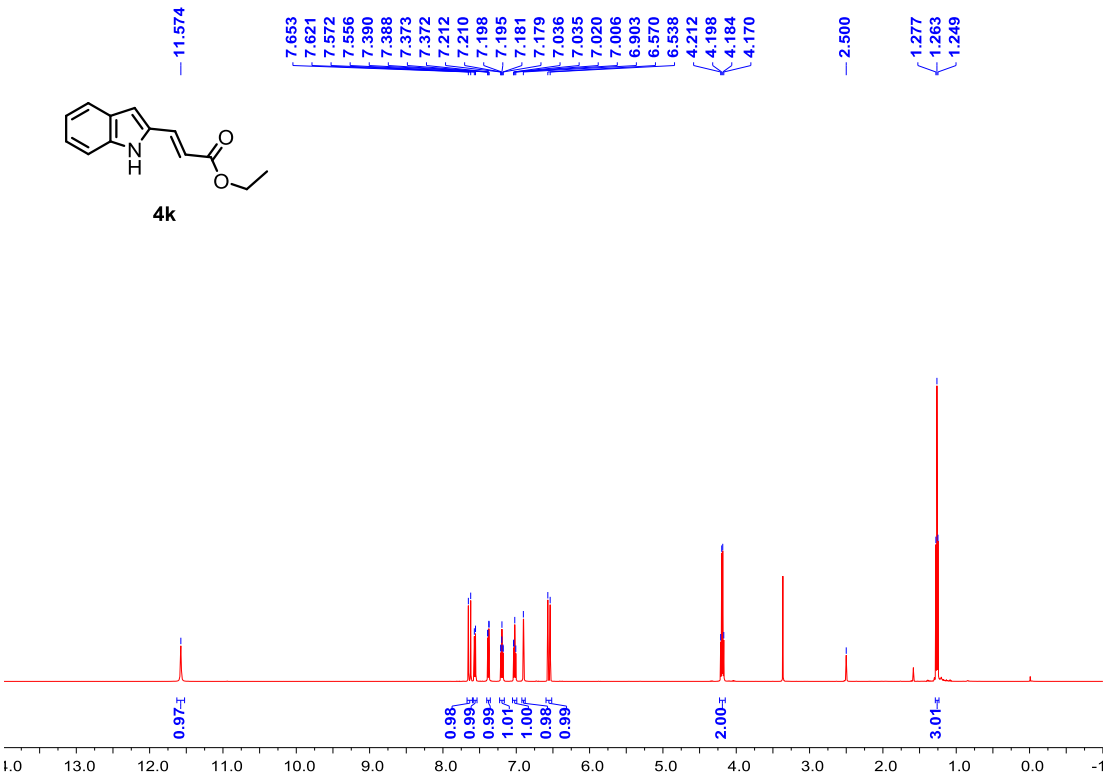


^{13}C NMR, 125 MHz, DMSO-d_6

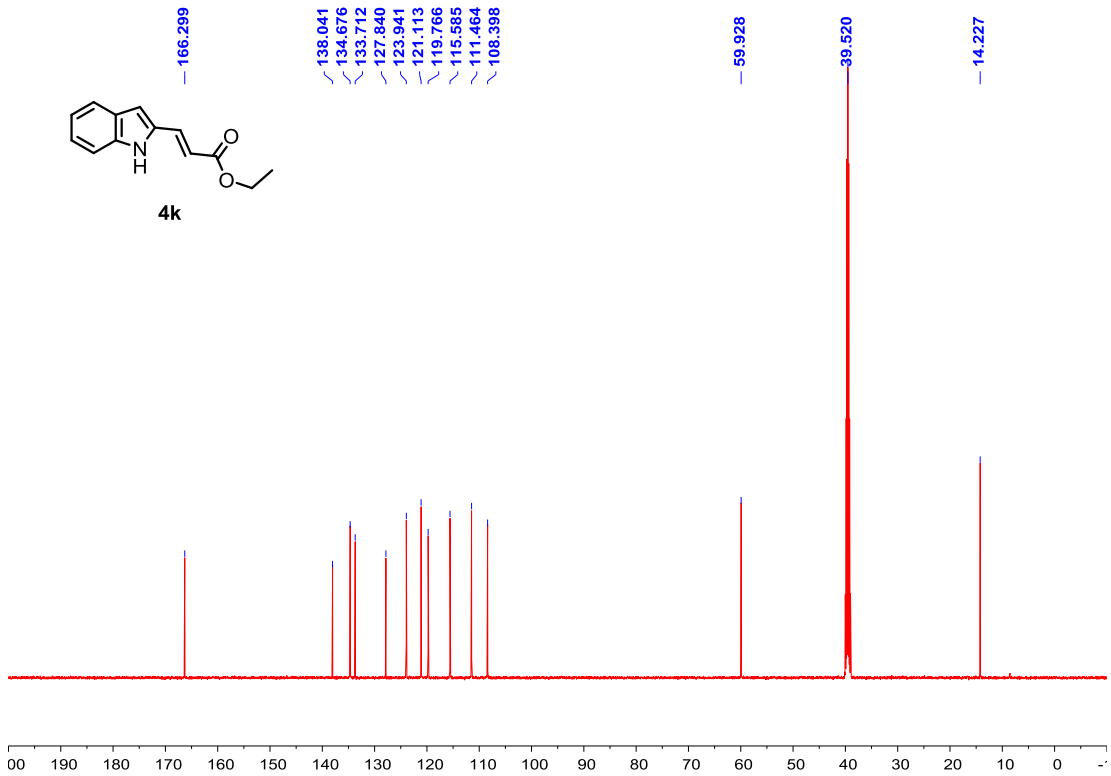


Ethyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4m):

^{1}H NMR, 500 MHz, DMSO-d_6

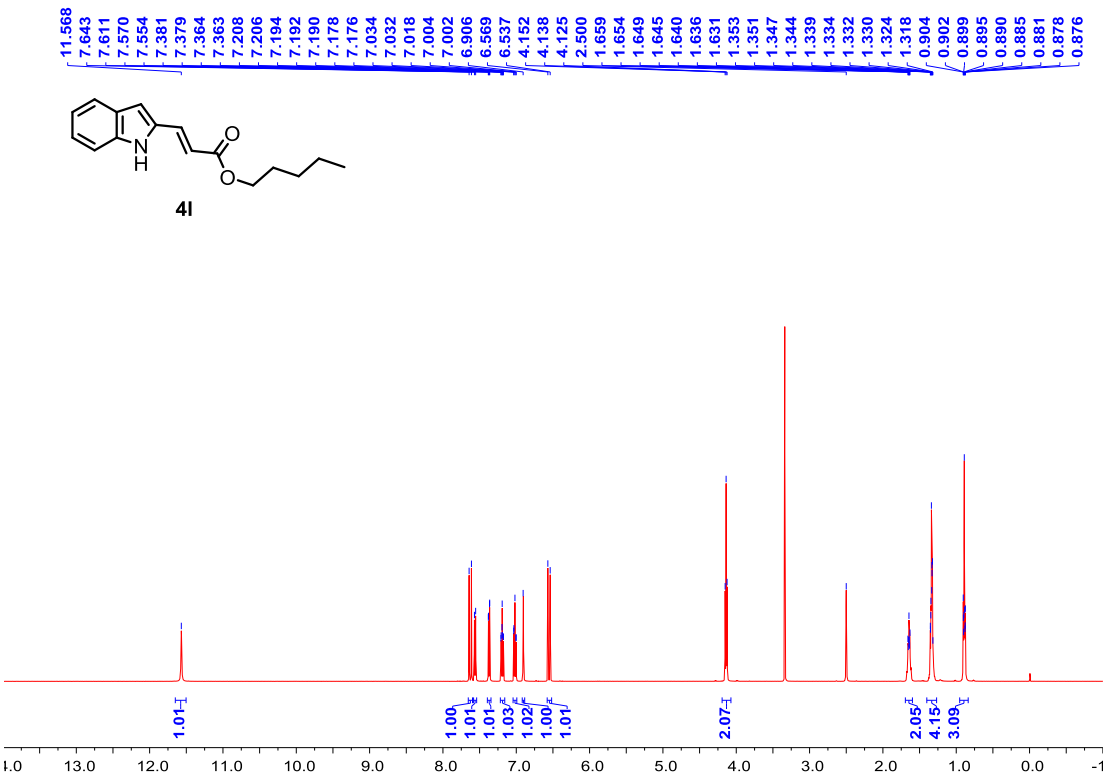


^{13}C NMR, 125 MHz, DMSO-d_6

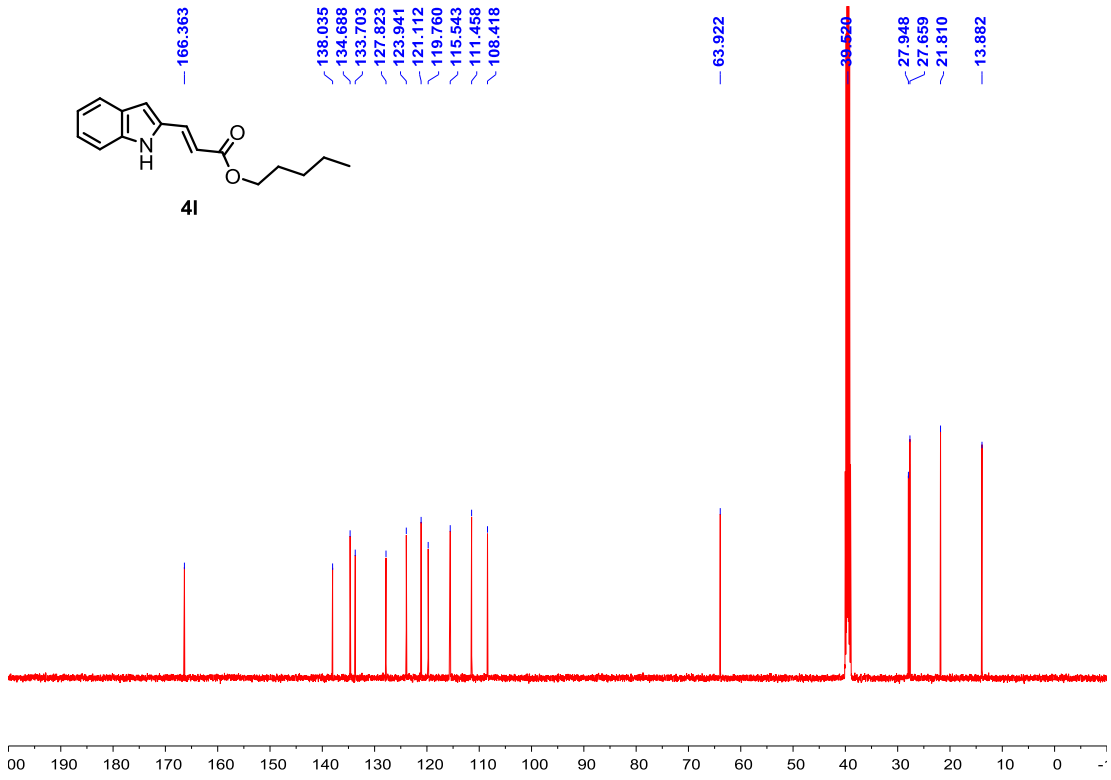


Pentyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4n)

^{1}H NMR, 500 MHz, DMSO-d_6

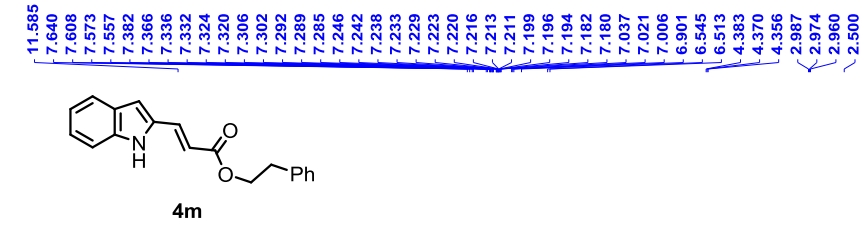


^{13}C NMR, 125 MHz, DMSO-d_6

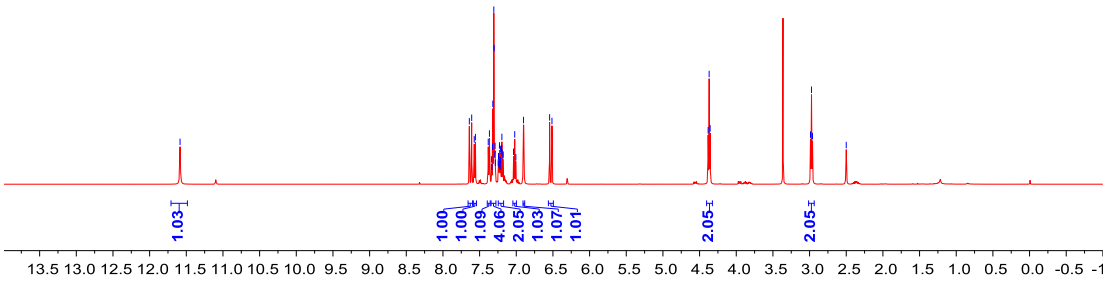


Phenethyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4o)

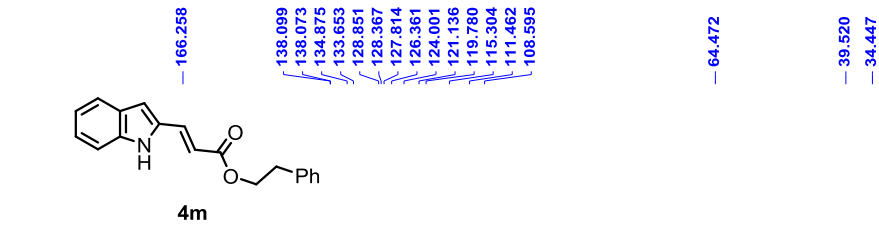
^{1}H NMR, 500 MHz, DMSO-d_6



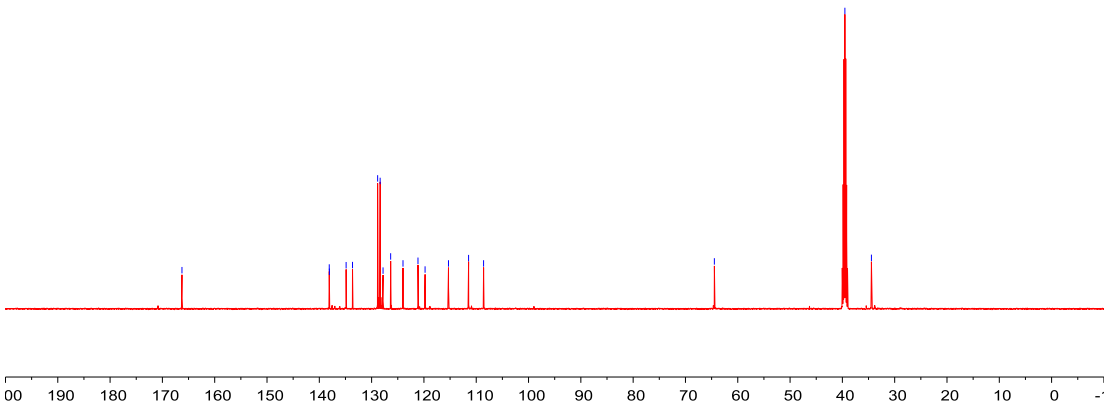
4m



^{13}C NMR, 125 MHz, DMSO-d_6

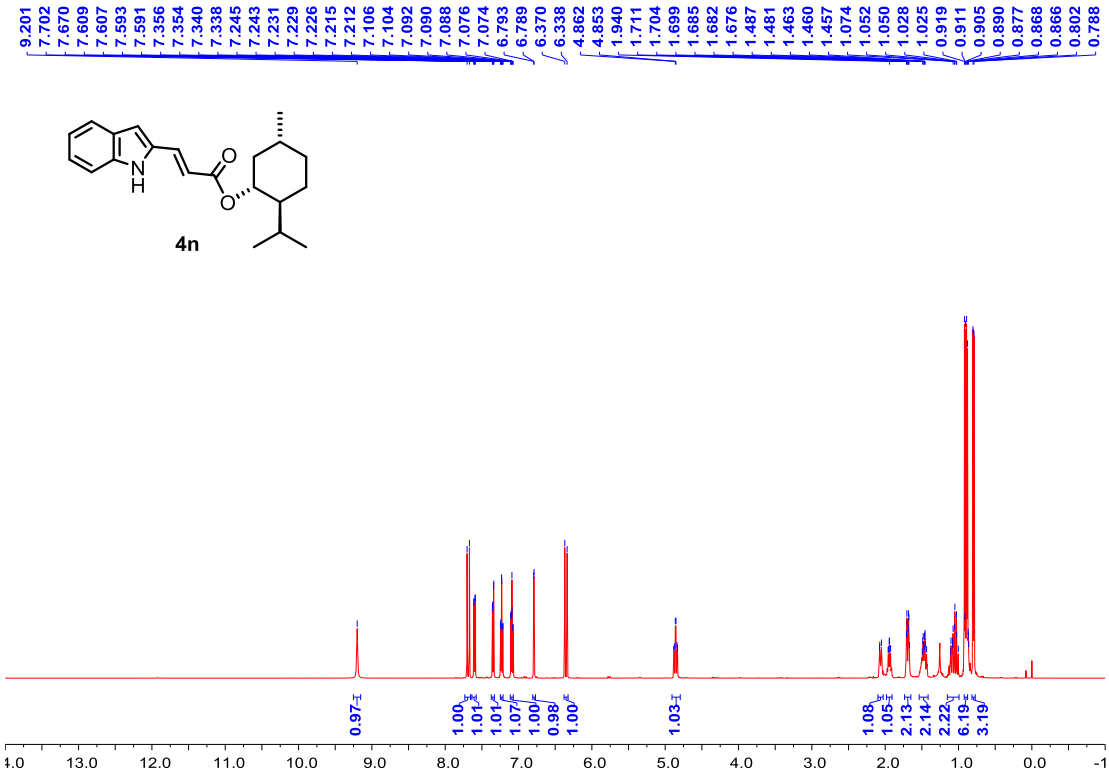


4m

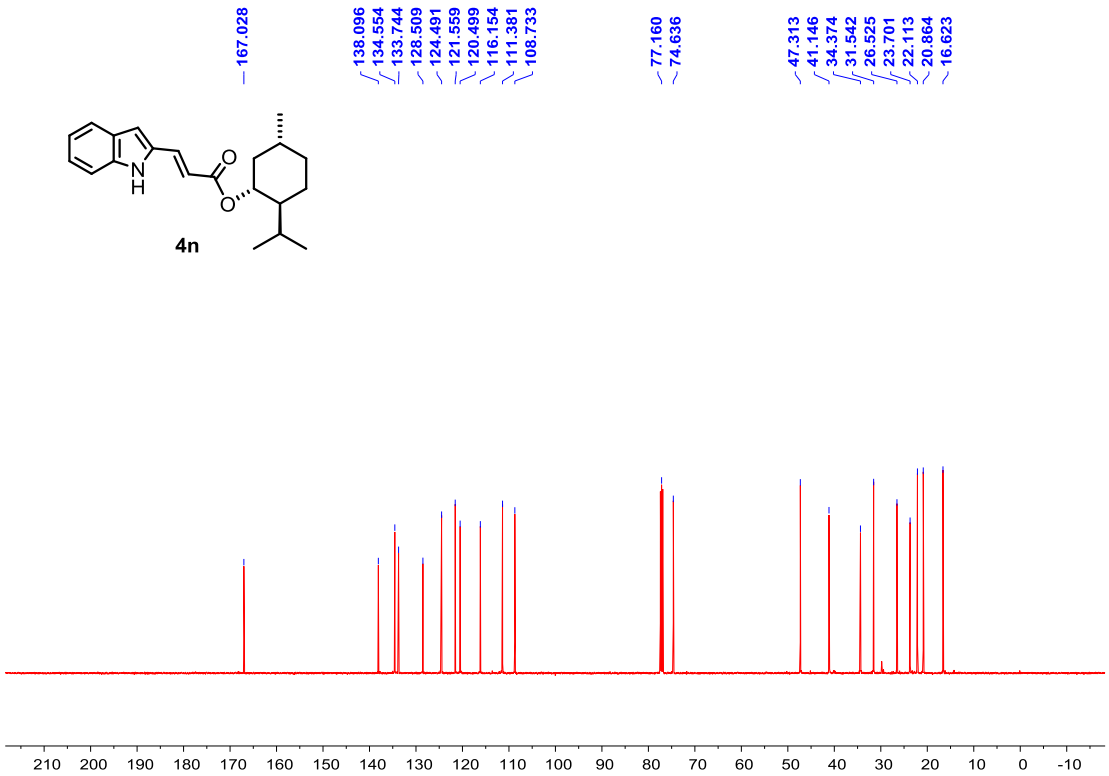


(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4p)

^{1}H NMR, 500 MHz, $CDCl_3$

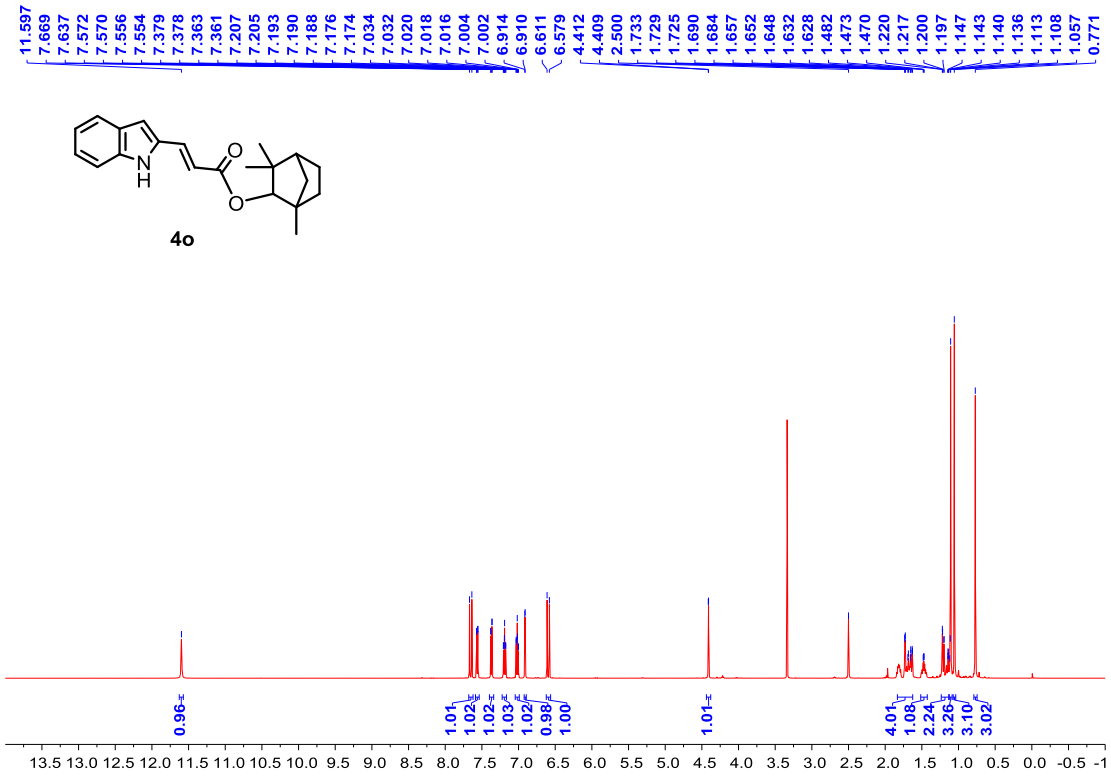


^{13}C NMR, 125 MHz, $CDCl_3$

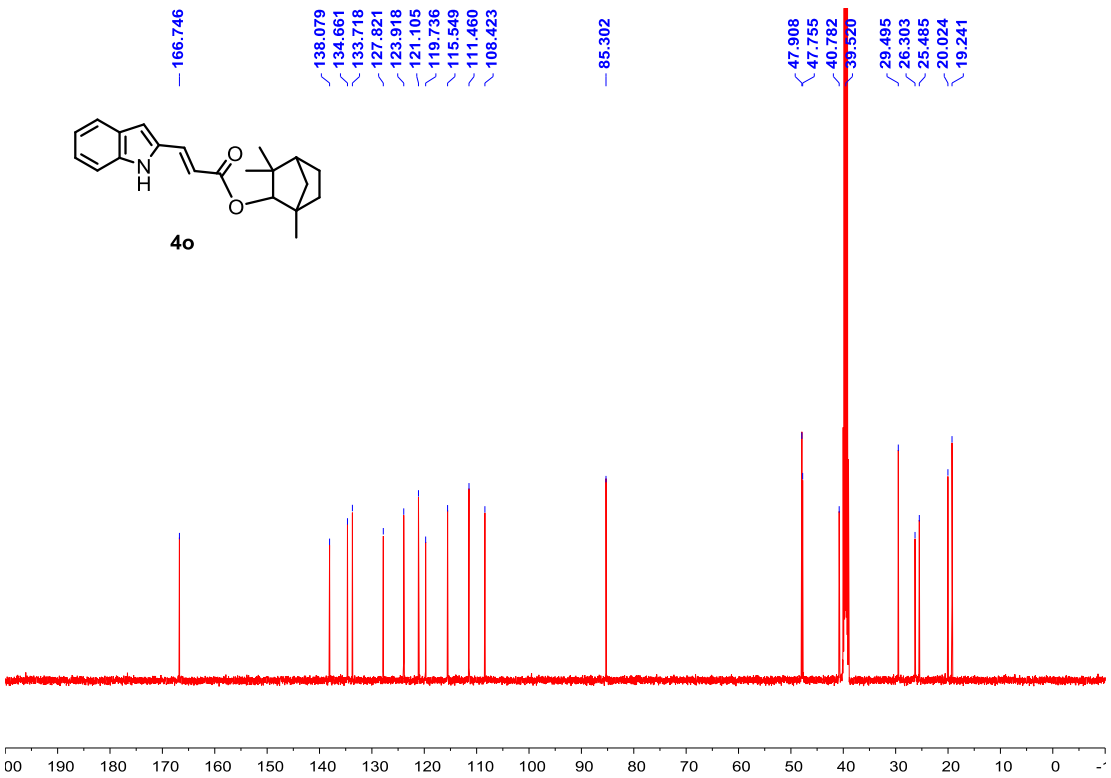


1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl-(*E*)-3-(1*H*-indol-2-yl)acrylate (4q)

^{1}H NMR, 500 MHz, DMSO-d_6

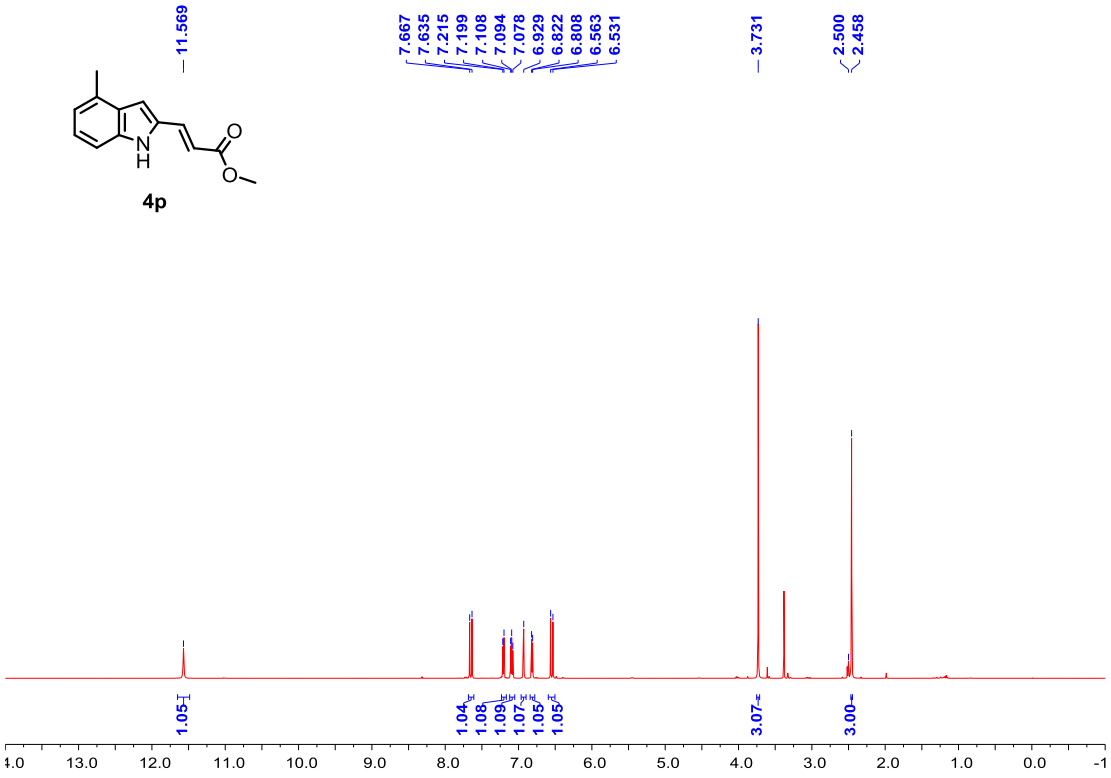


^{13}C NMR, 125 MHz, DMSO-d_6

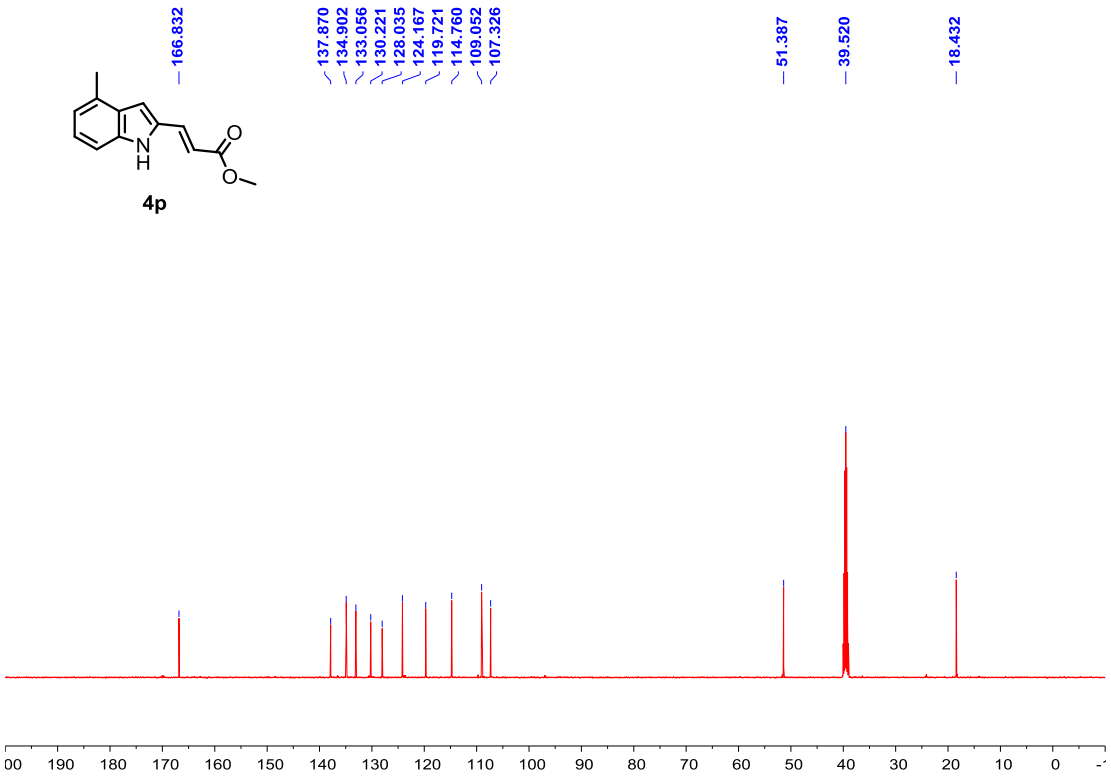


Methyl-(*E*)-3-(4-methyl-1H-indol-2-yl)acrylate (4r)

^{1}H NMR, 500 MHz, DMSO-d_6

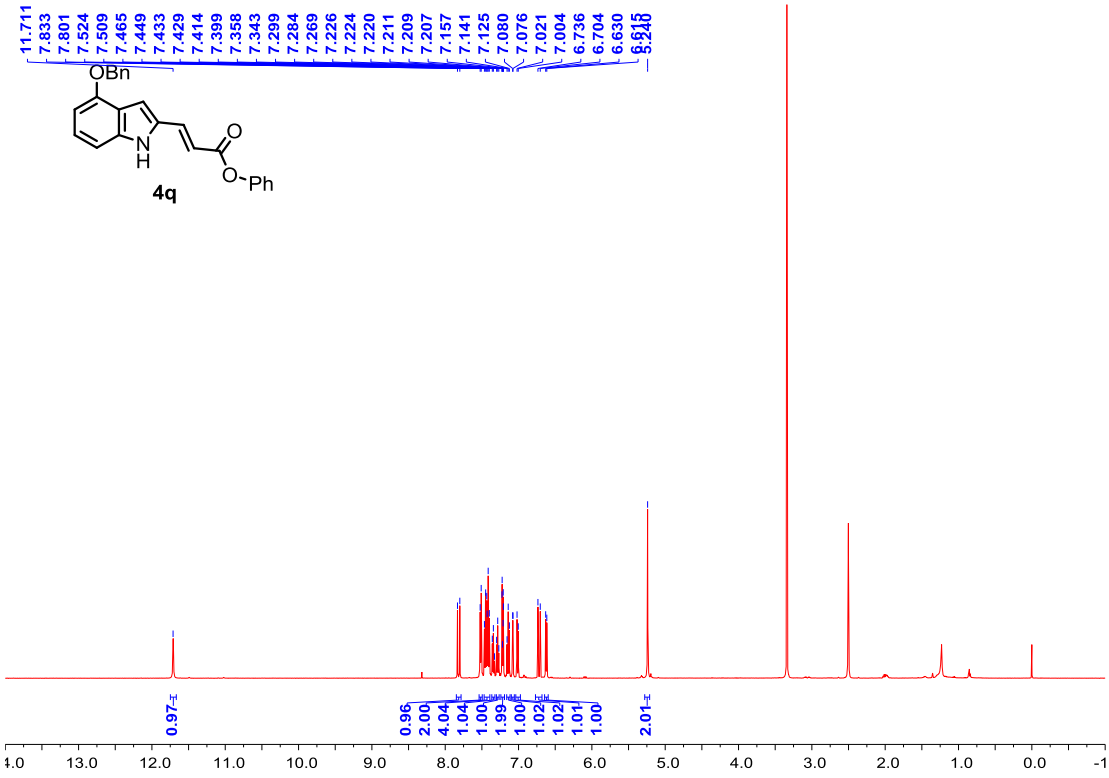


^{13}C NMR, 125 MHz, DMSO-d_6

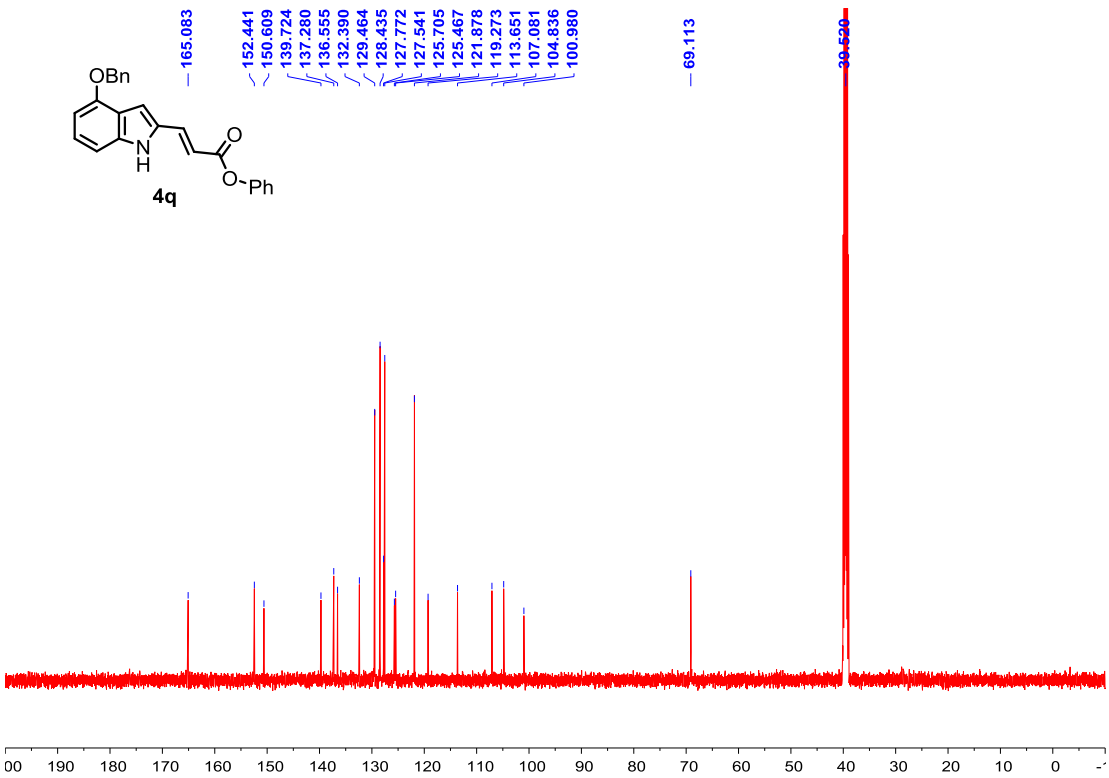


Phenyl-(*E*)-3-(4-(benzyloxy)-1*H*-indol-2-yl)acrylate (4s)

^{1}H NMR, 500 MHz, DMSO-d_6

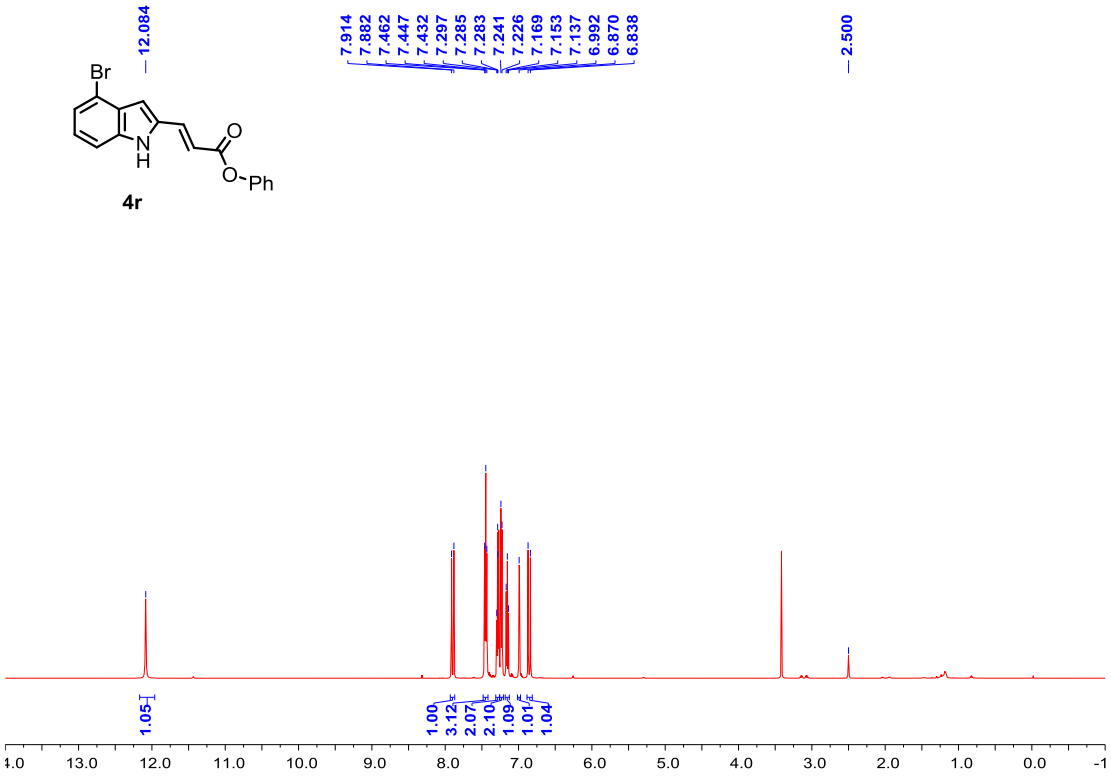


^{13}C NMR, 125 MHz, DMSO-d_6

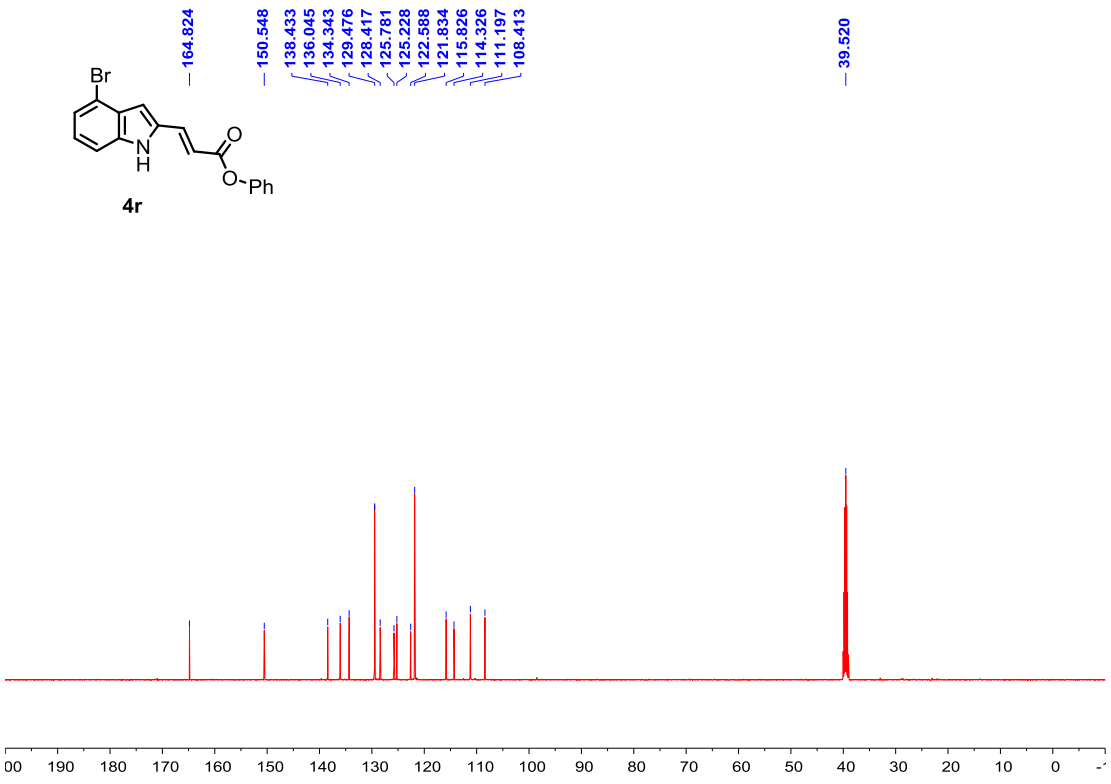


Phenyl-(*E*)-3-(4-bromo-1*H*-indol-2-yl)acrylate (4t)

^{1}H NMR, 500 MHz, DMSO-d_6

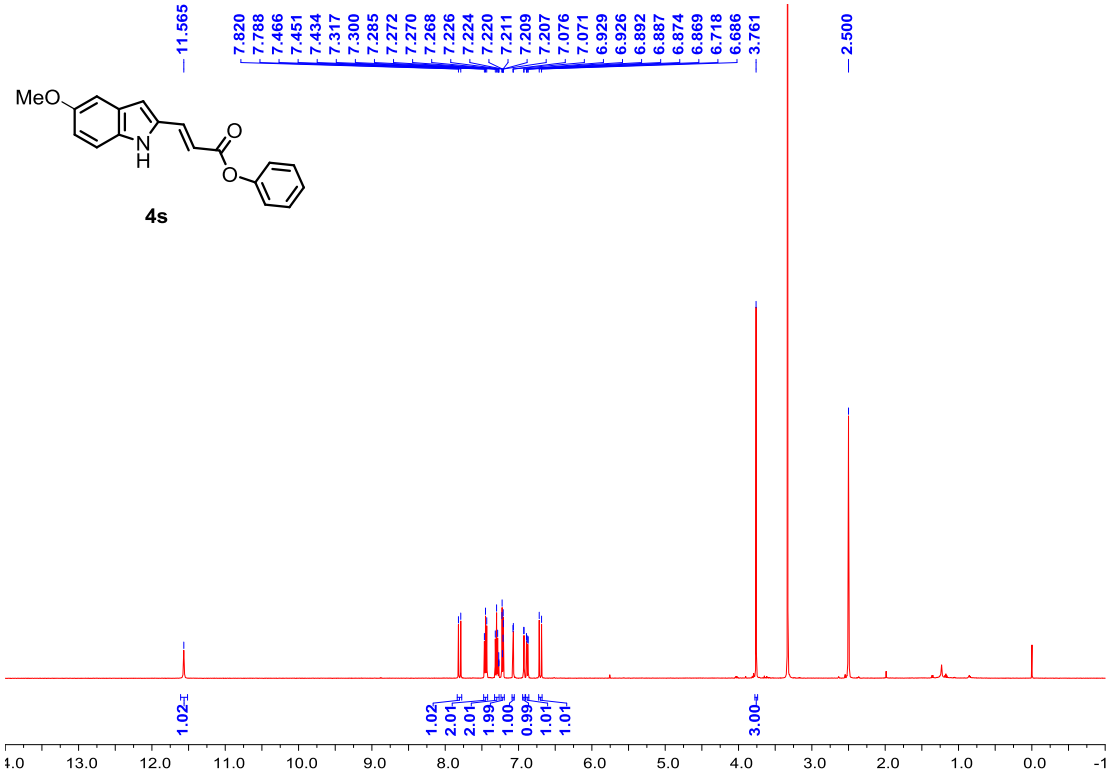


^{13}C NMR, 125 MHz, DMSO-d_6

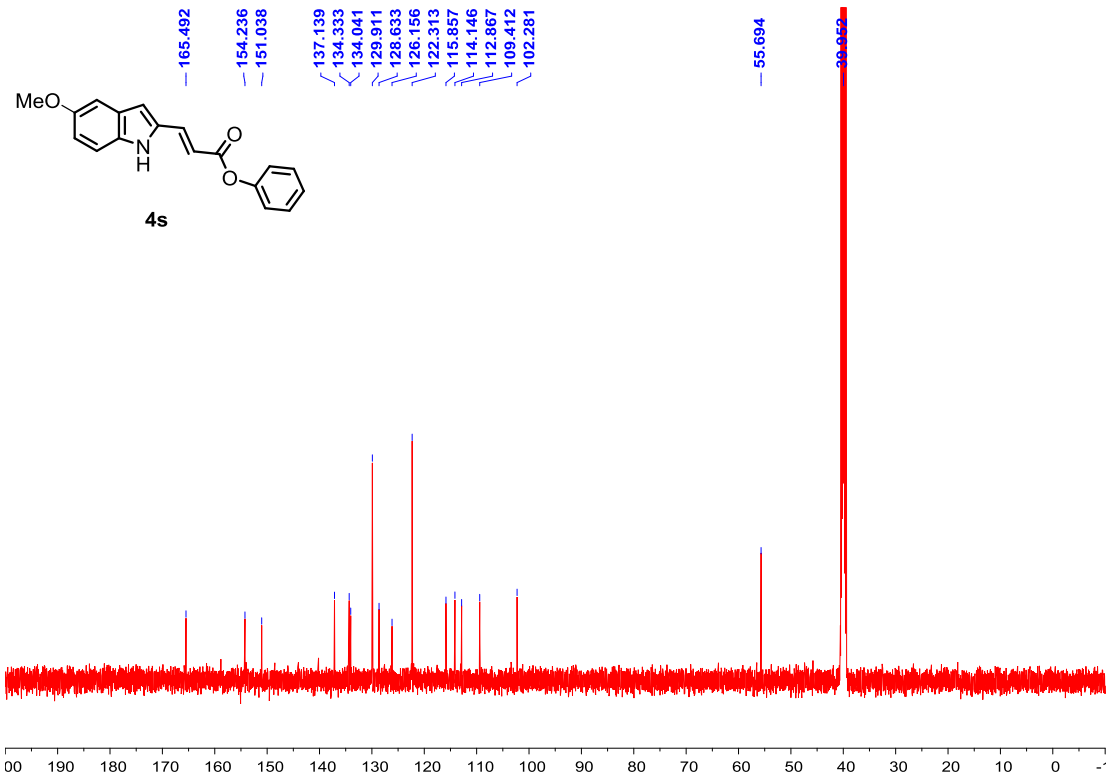


Phenyl-(*E*)-3-(5-methoxy-1*H*-indol-2-yl)acrylate (4u)

^{1}H NMR, 500 MHz, DMSO-d_6

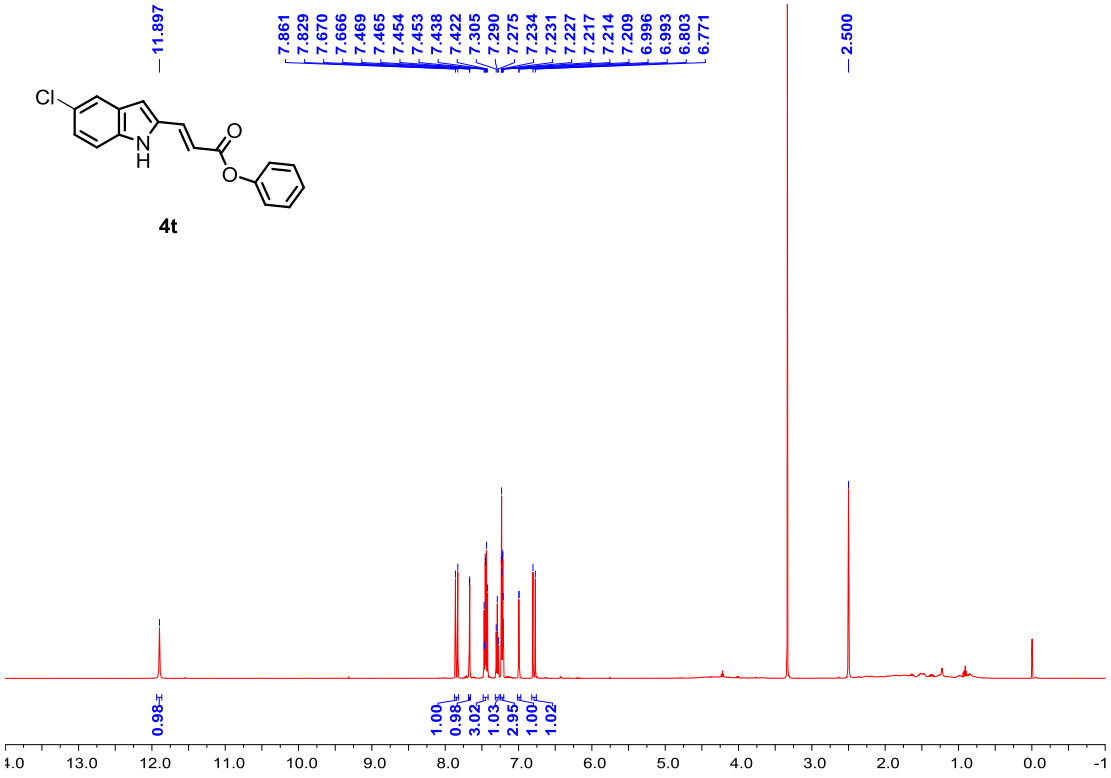


^{13}C NMR, 125 MHz, DMSO-d_6

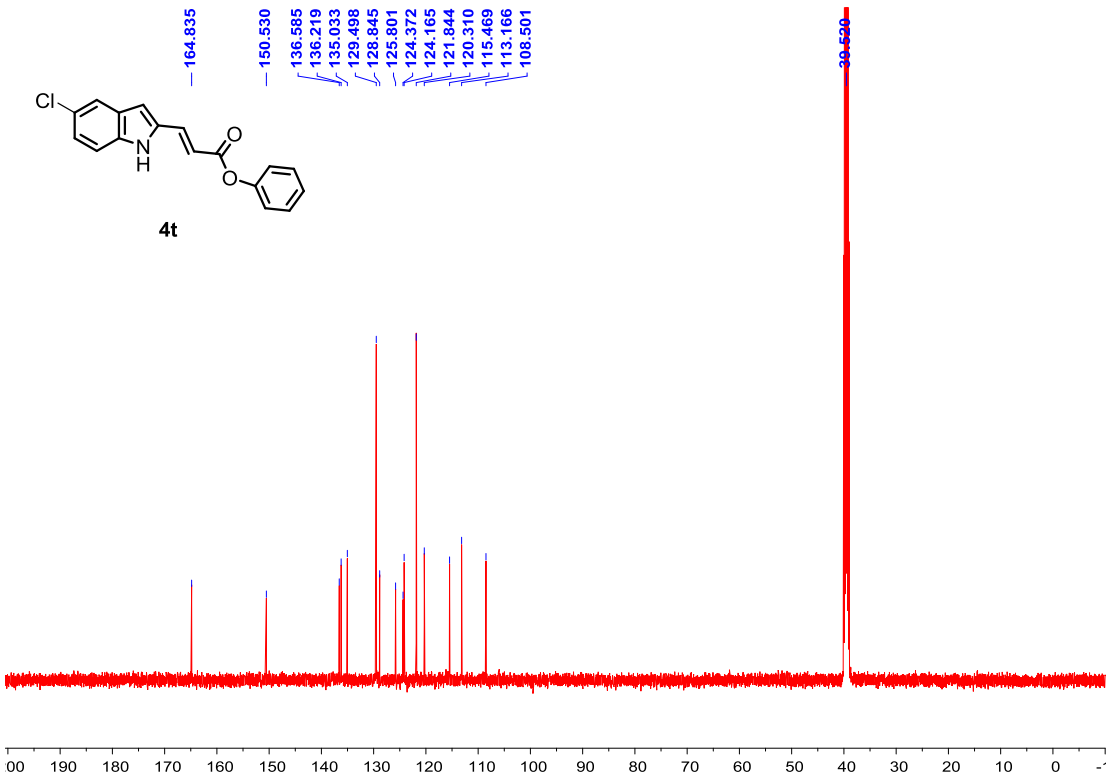


Phenyl-(*E*)-3-(5-chloro-1*H*-indol-2-yl)acrylate (4v)

^{1}H NMR, 500 MHz, DMSO-d_6

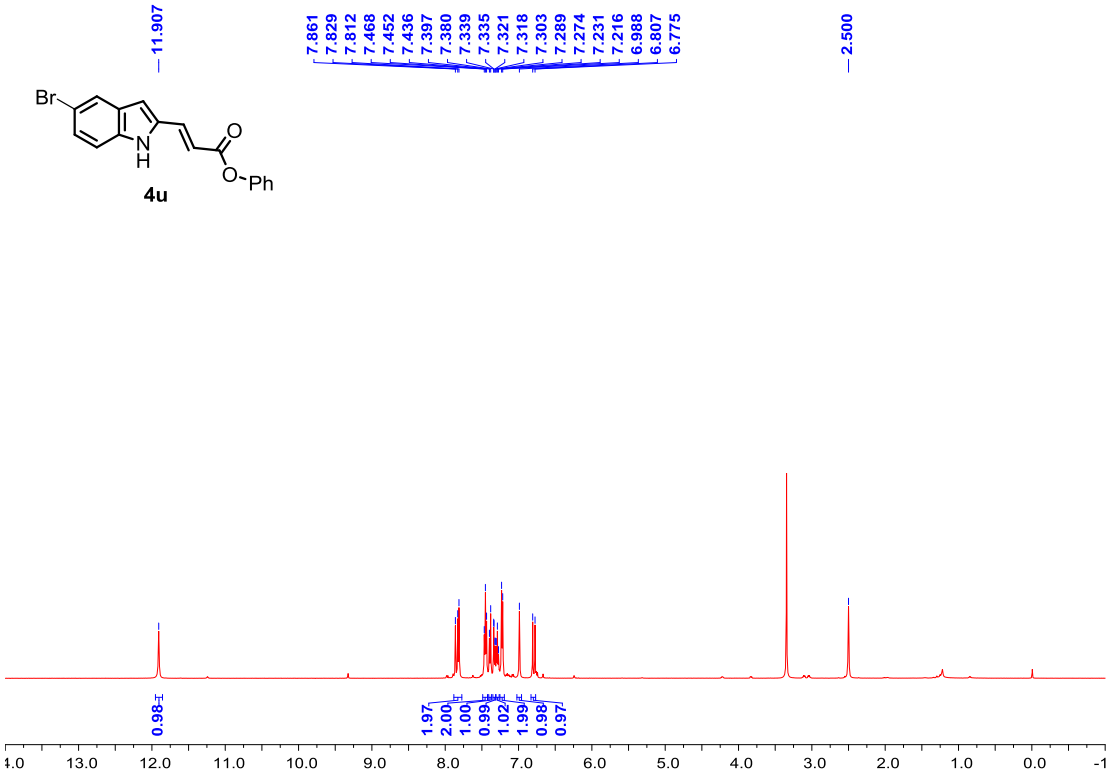


^{13}C NMR, 125 MHz, DMSO-d_6

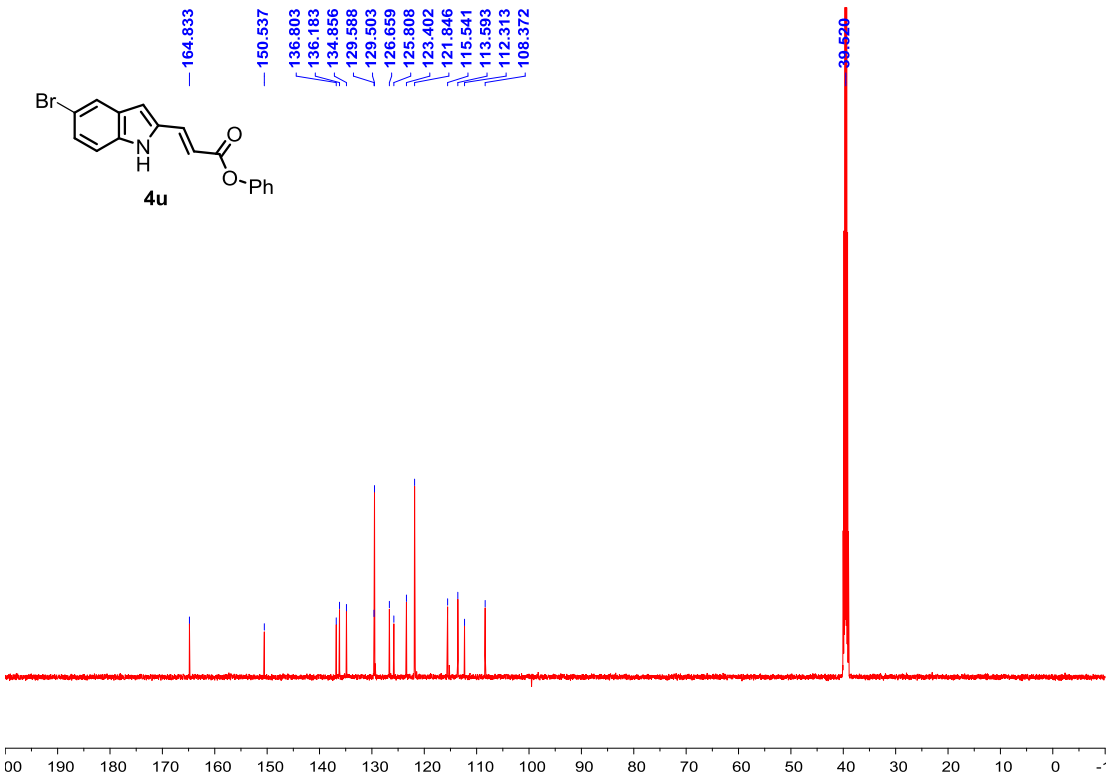


Phenyl-(*E*)-3-(5-bromo-1*H*-indol-2-yl)acrylate (4w)

^{1}H NMR, 500 MHz, DMSO-d_6

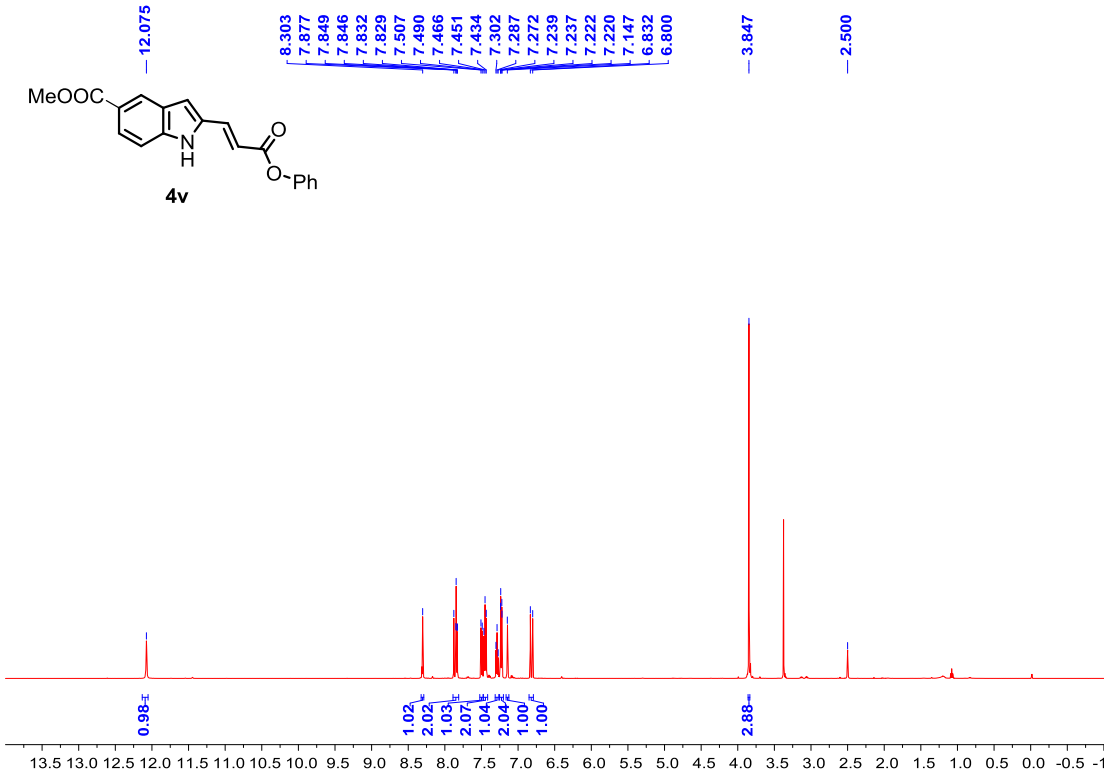


^{13}C NMR, 125 MHz, DMSO-d_6

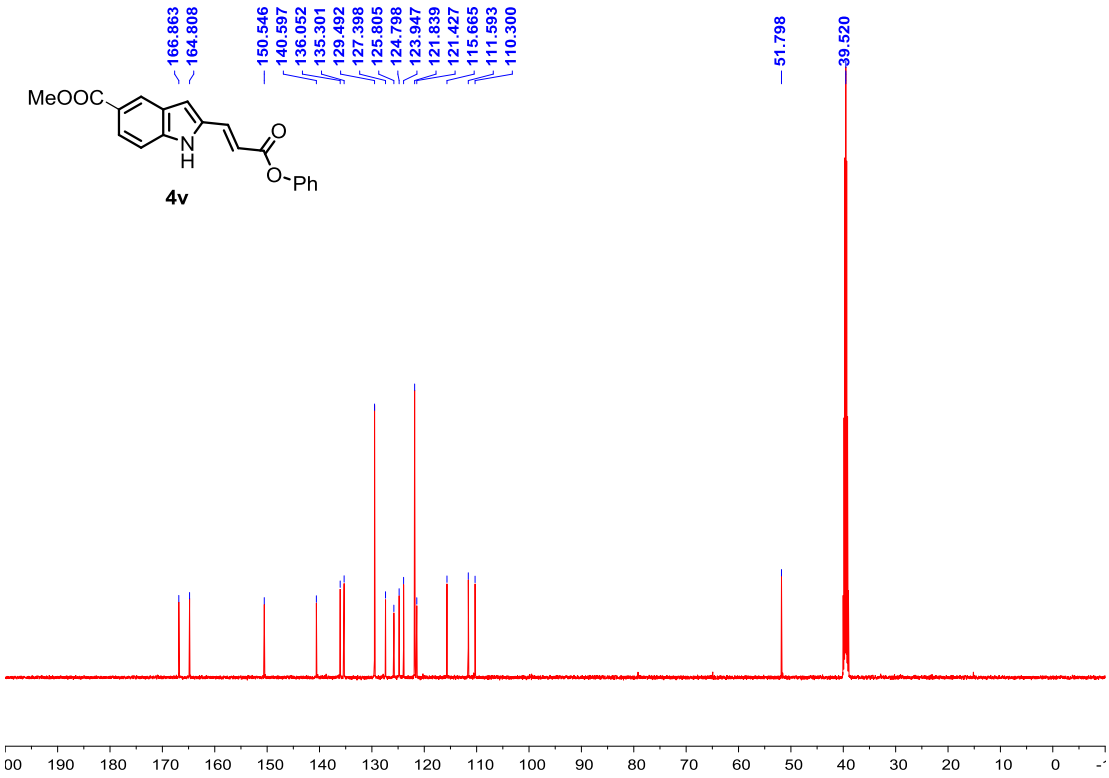


Methyl-(*E*)-2-(3-oxo-3-phenoxyprop-1-en-1-yl)-1*H*-indole-5-carboxylate (4x)

^{1}H NMR, 500 MHz, DMSO-d_6

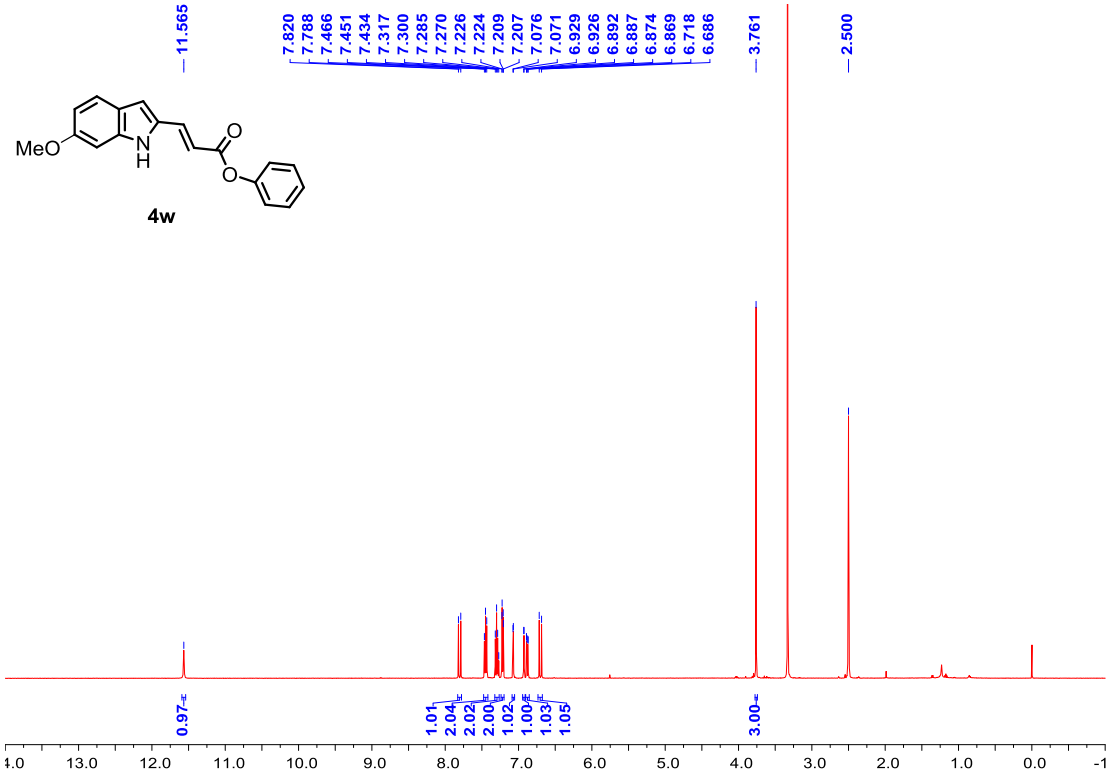


^{13}C NMR, 125 MHz, DMSO-d_6

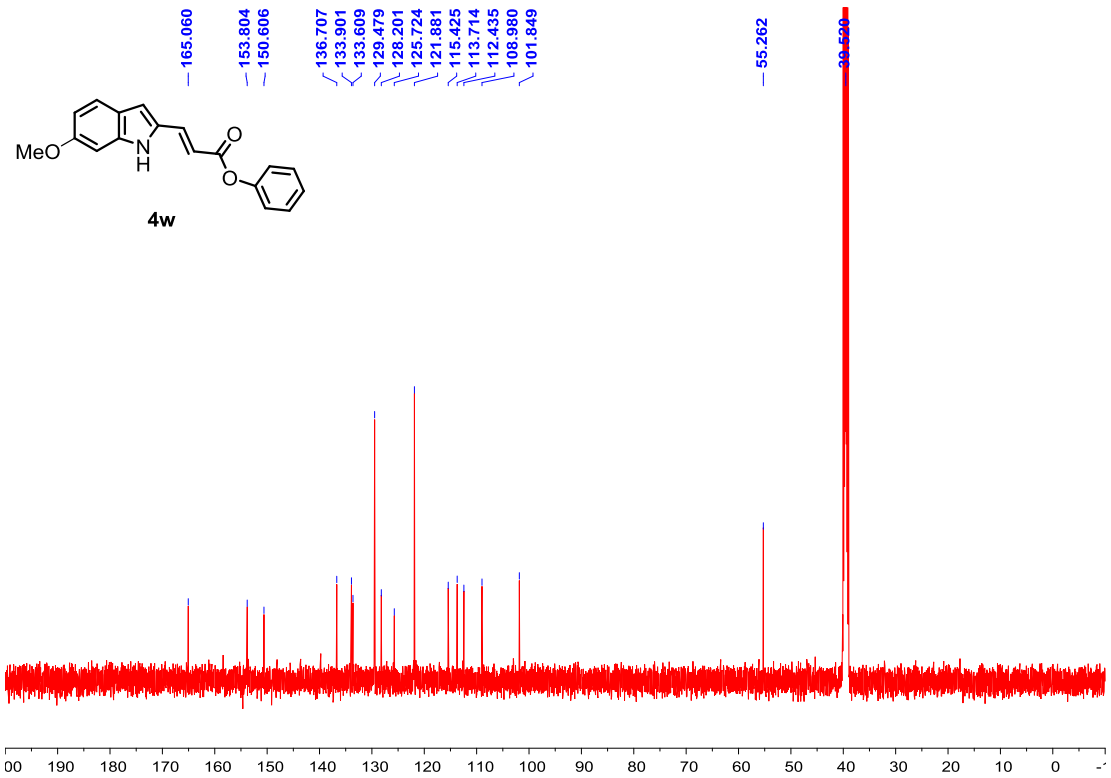


Phenyl-(*E*)-3-(6-methoxy-1*H*-indol-2-yl)acrylate (4y)

^{1}H NMR, 500 MHz, DMSO-d_6

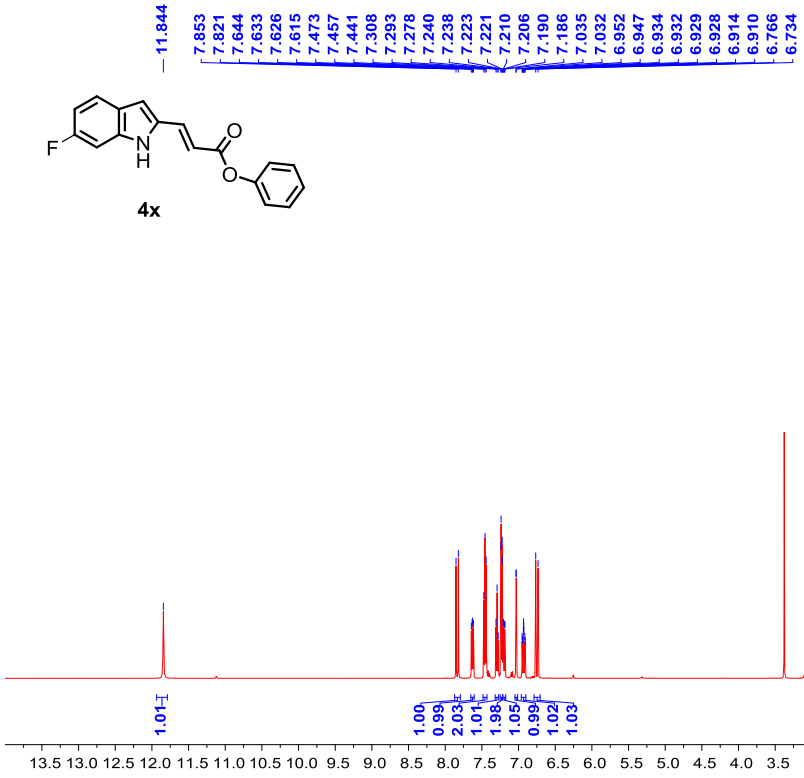


^{13}C NMR, 125 MHz, DMSO-d_6

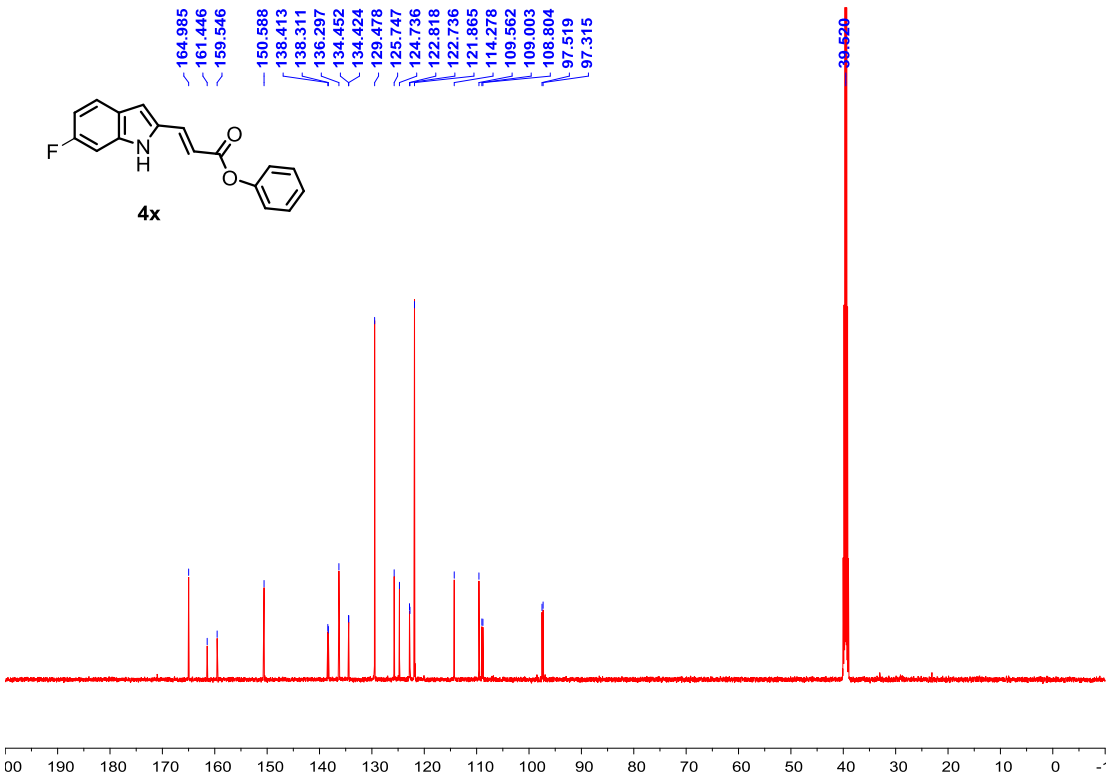


Phenyl-(*E*)-3-(6-fluoro-1*H*-indol-2-yl)acrylate (4z)

^{1}H NMR, 500 MHz, DMSO-d_6

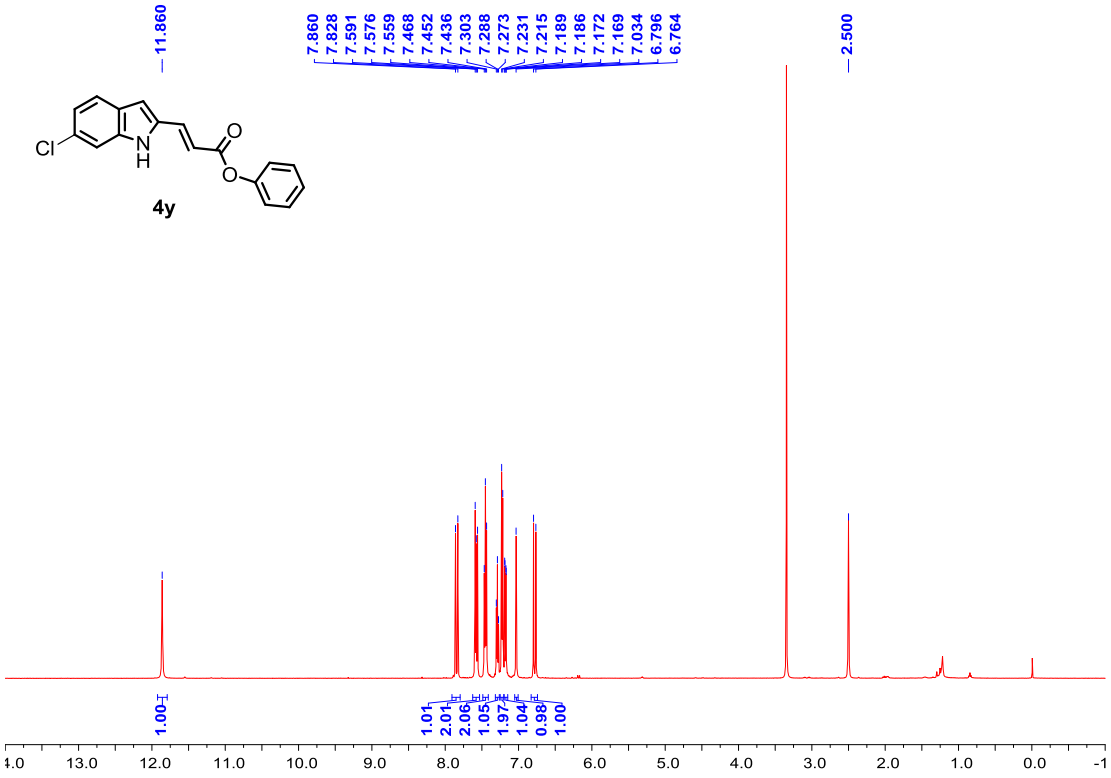


^{13}C NMR, 125 MHz, DMSO-d_6

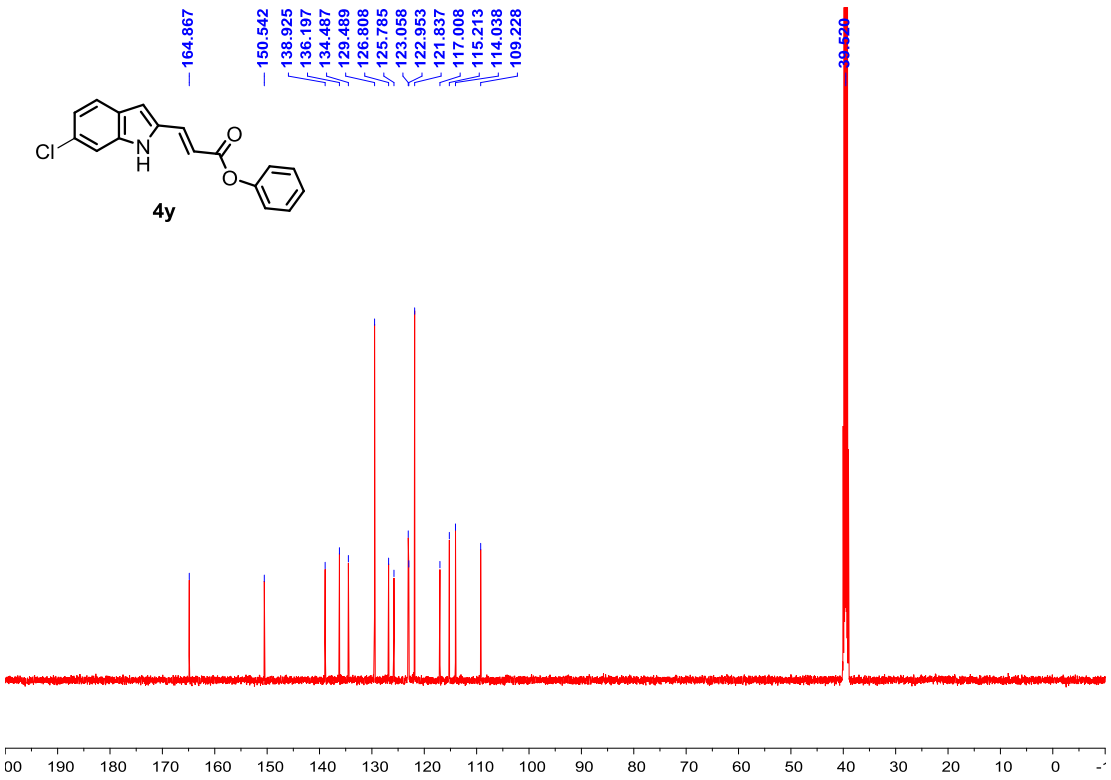


Phenyl-(*E*)-3-(6-chloro-1*H*-indol-2-yl)acrylate (4aa)

^{1}H NMR, 500 MHz, DMSO-d_6

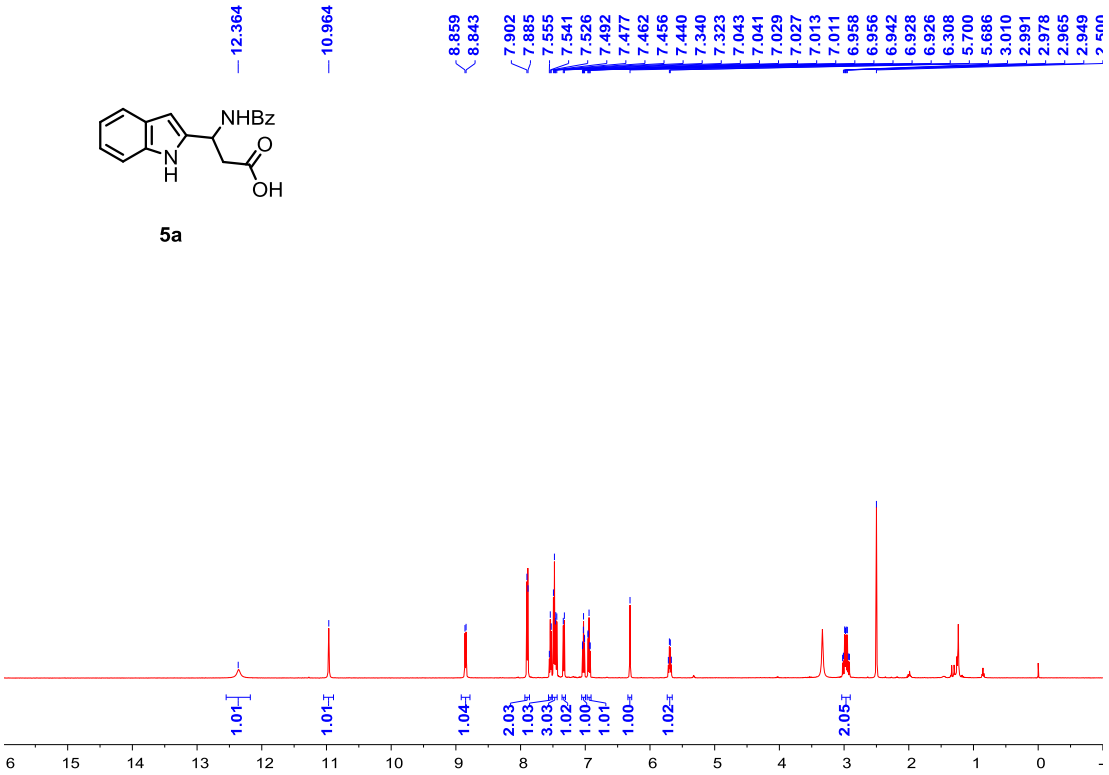


^{13}C NMR, 125 MHz, DMSO-d_6



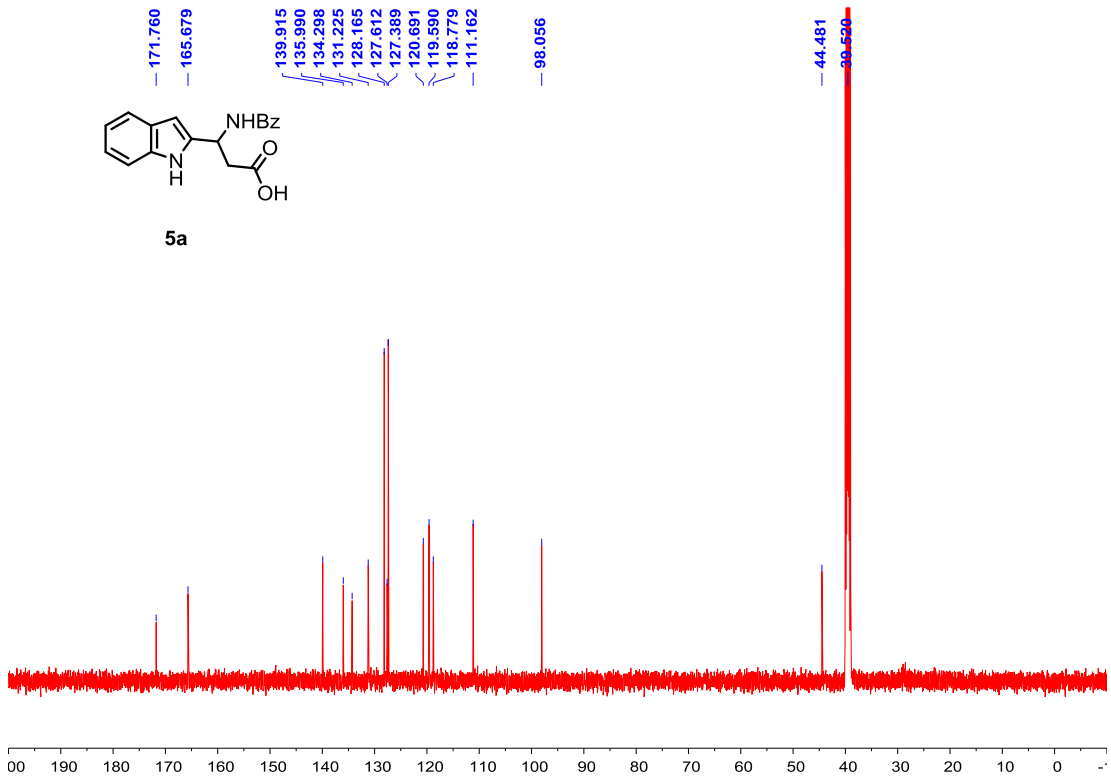
3-Benzamido-3-(1*H*-indol-2-yl)propanoic acid (5a)

^{1}H NMR, 500 MHz, DMSO-d_6



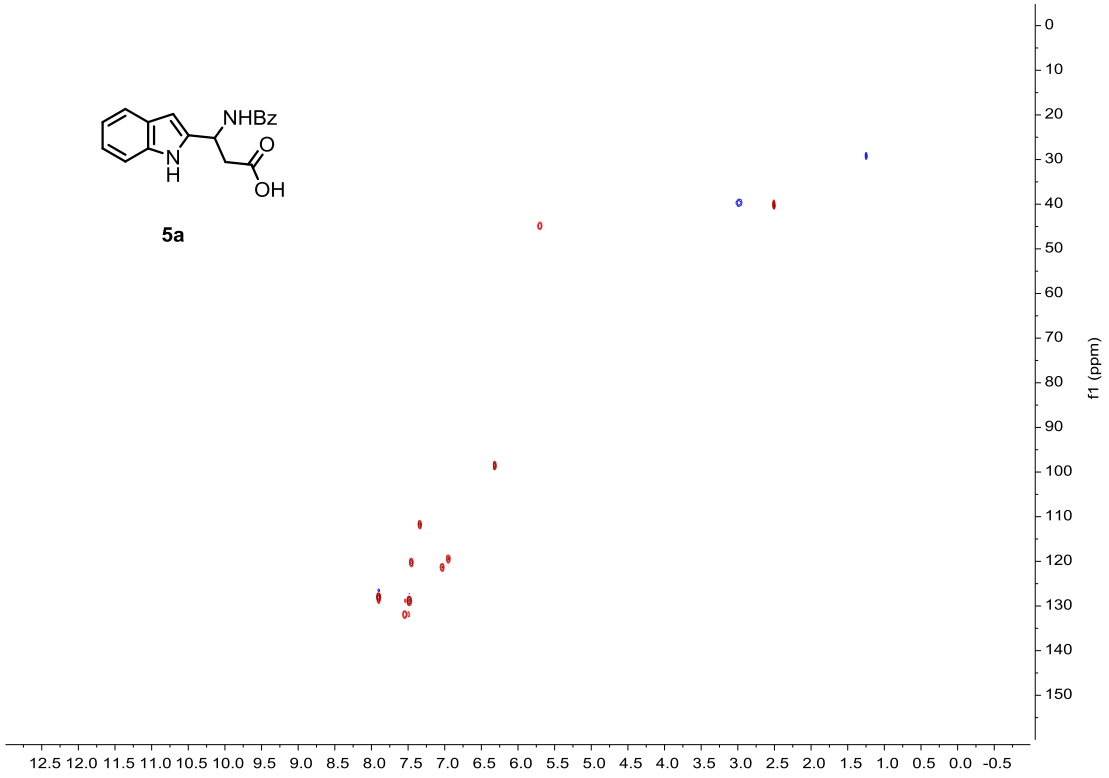
5a

^{13}C NMR, 125 MHz, DMSO-d_6

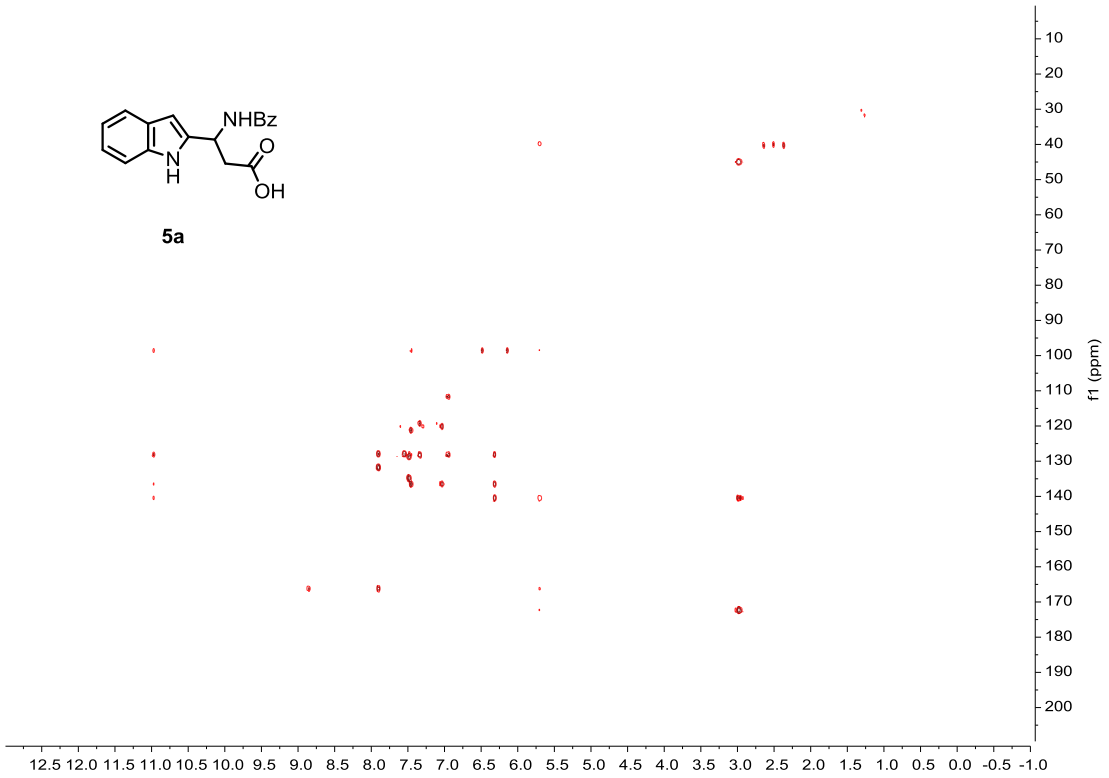


5a

HSQC, DMSO-d_6

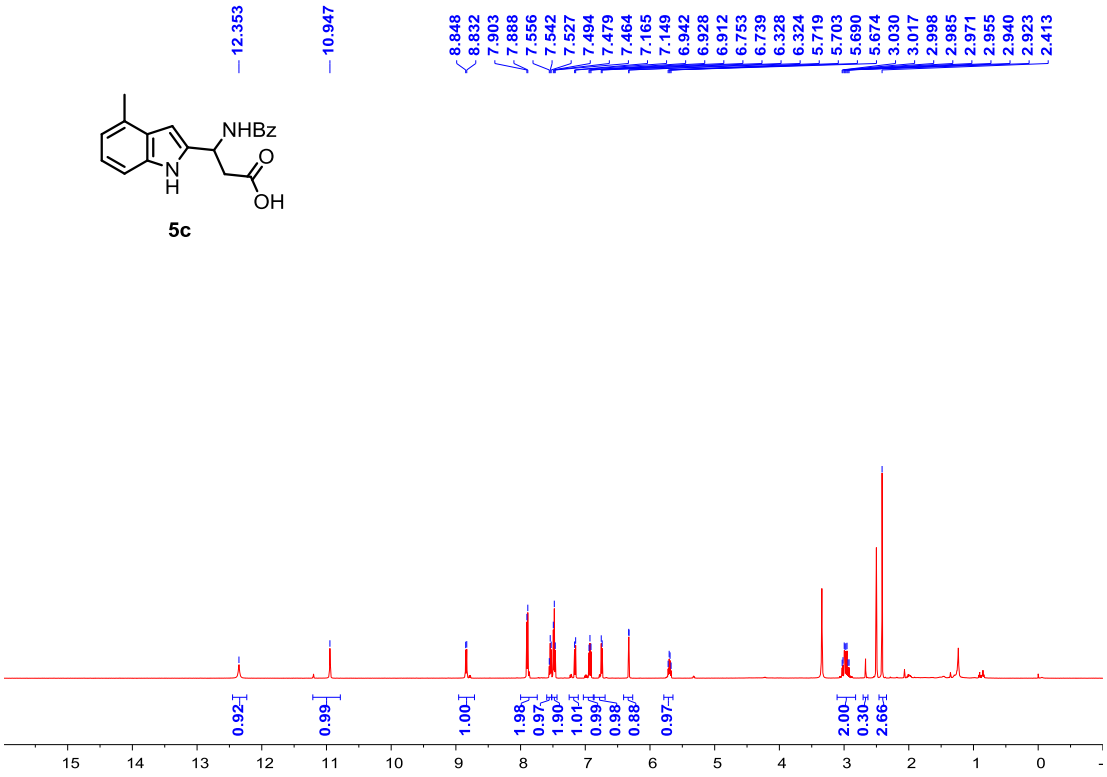


HMBC, DMSO-d_6

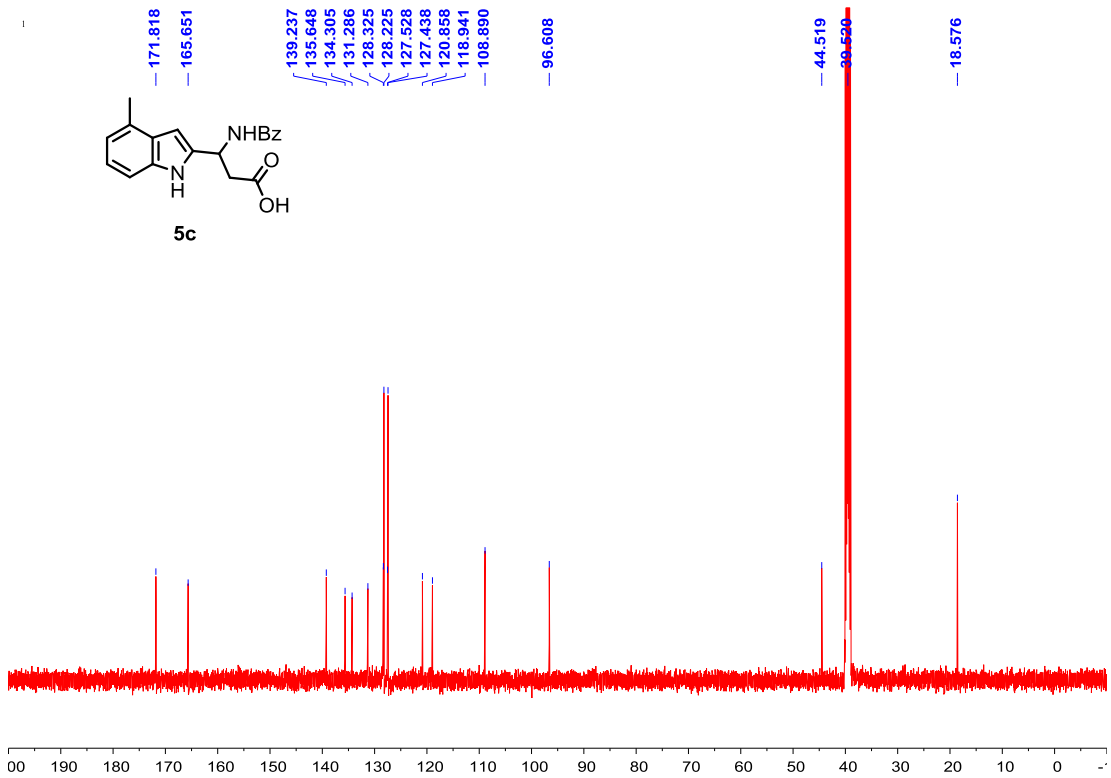


3-Benzamido-3-(4-methyl-1*H*-indol-2-yl)propanoic acid (5b)

^{1}H NMR, 500 MHz, DMSO-d_6

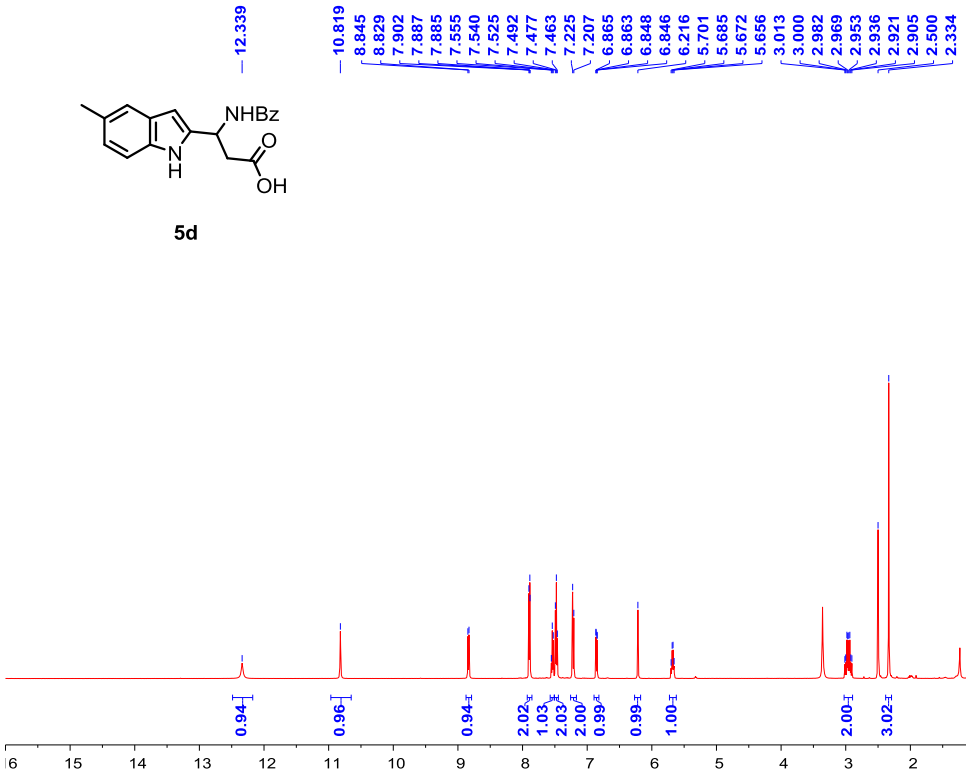


^{13}C NMR, 125 MHz, DMSO-d_6



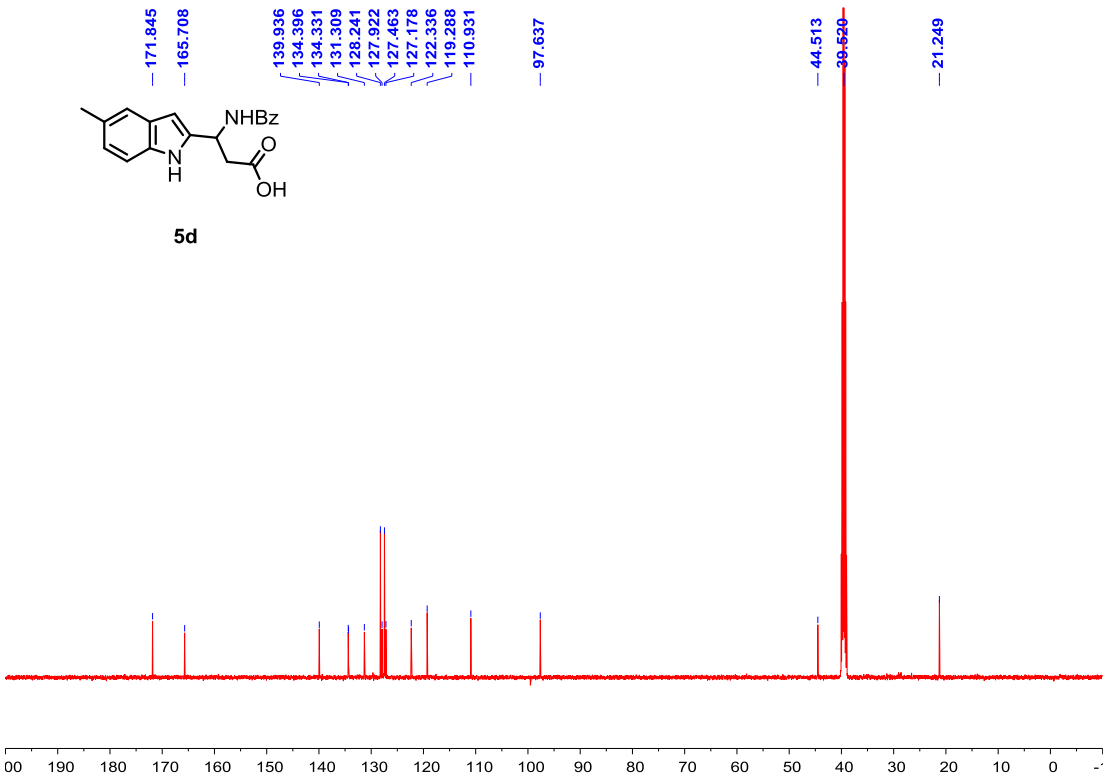
3-Benzamido-3-(5-methyl-1*H*-indol-2-yl)propanoic acid (5c)

^{1}H NMR, 500 MHz, DMSO-d_6



5d

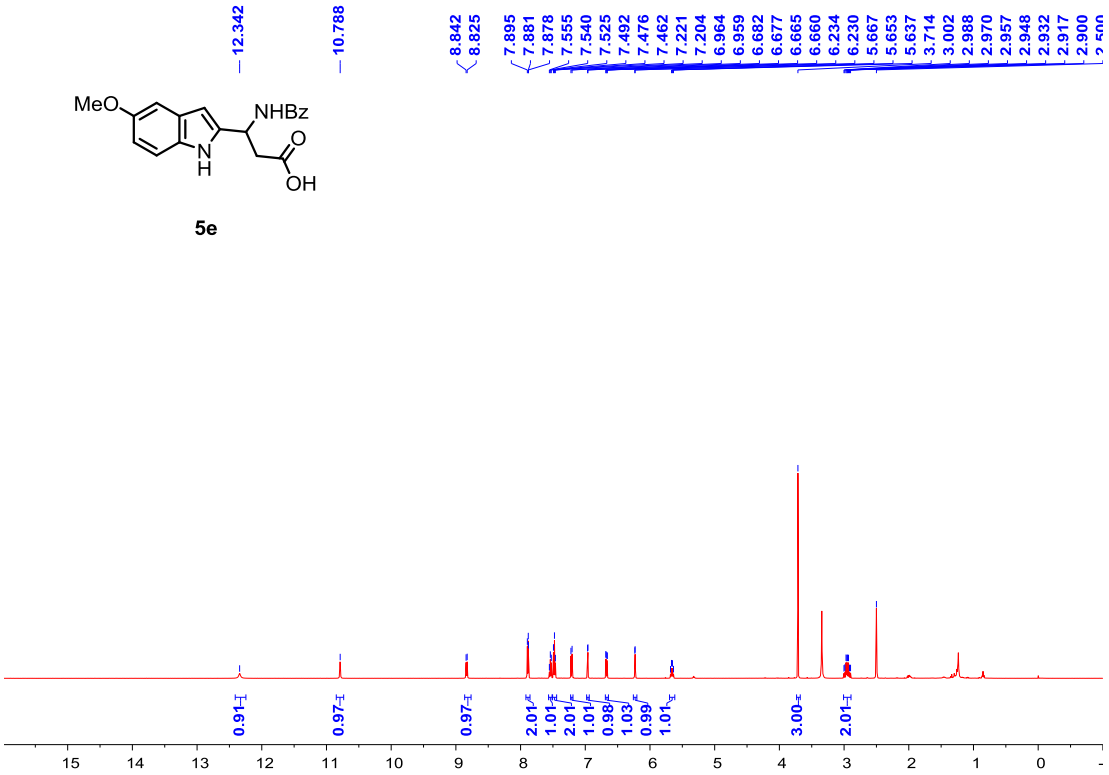
^{13}C NMR, 125 MHz, DMSO-d_6



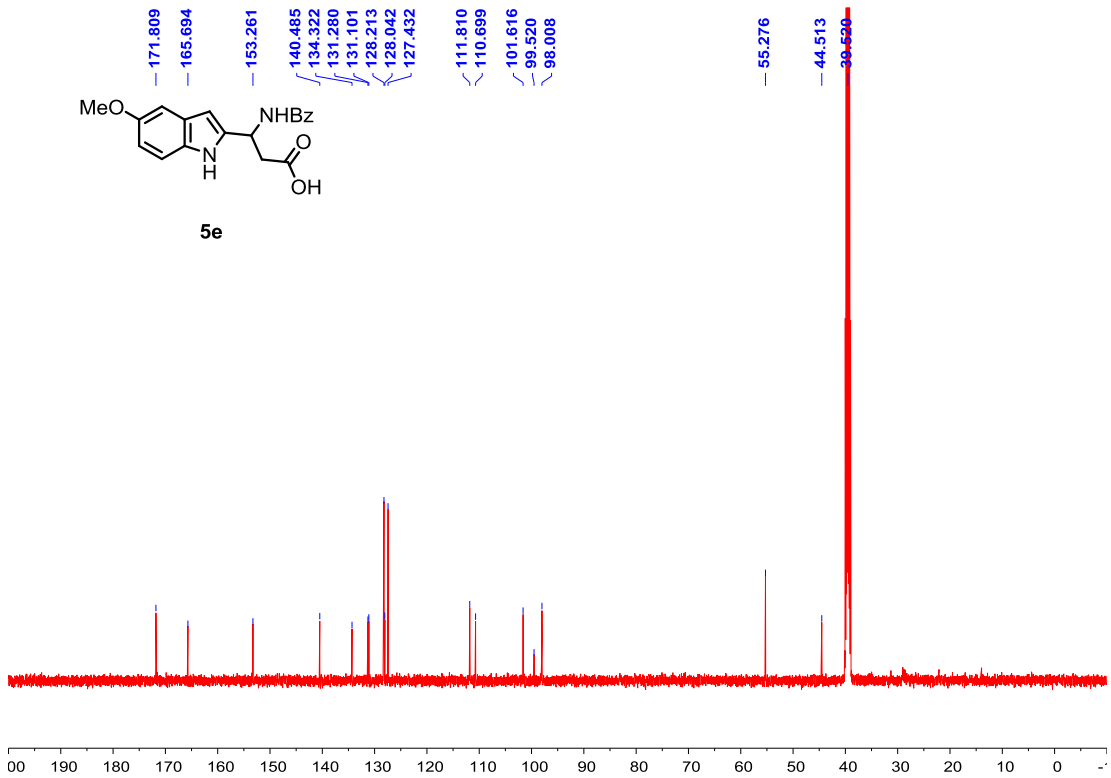
5d

3-Benzamido-3-(5-methoxy-1*H*-indol-2-yl)propanoic acid (5d)

^{1}H NMR, 500 MHz, DMSO-d_6

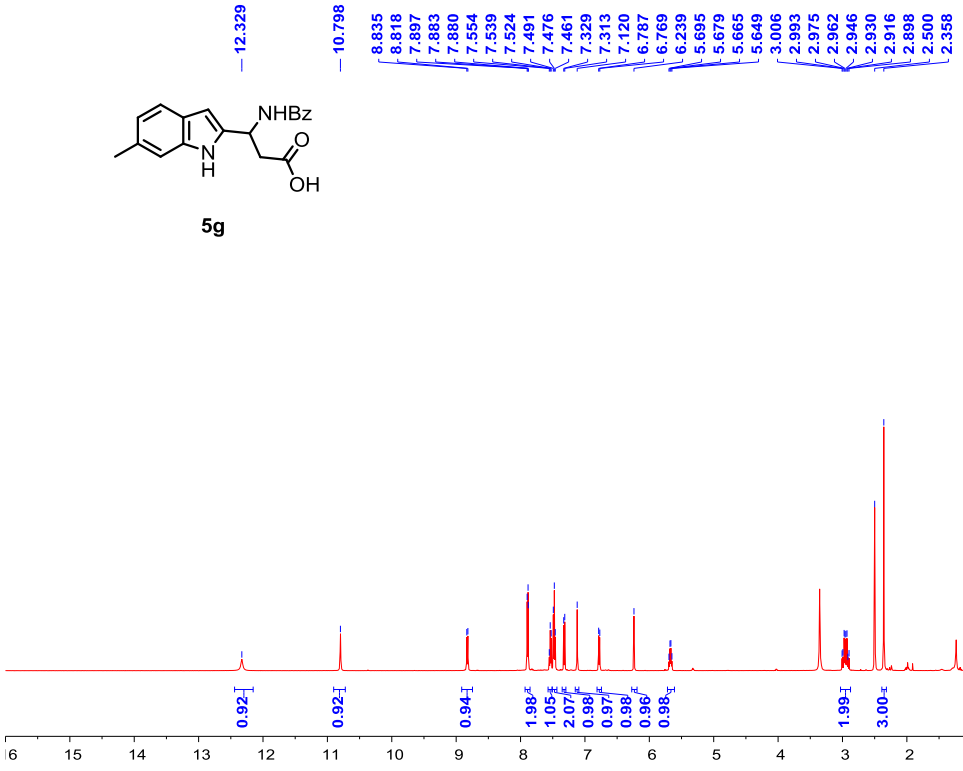


^{13}C NMR, 125 MHz, DMSO-d_6



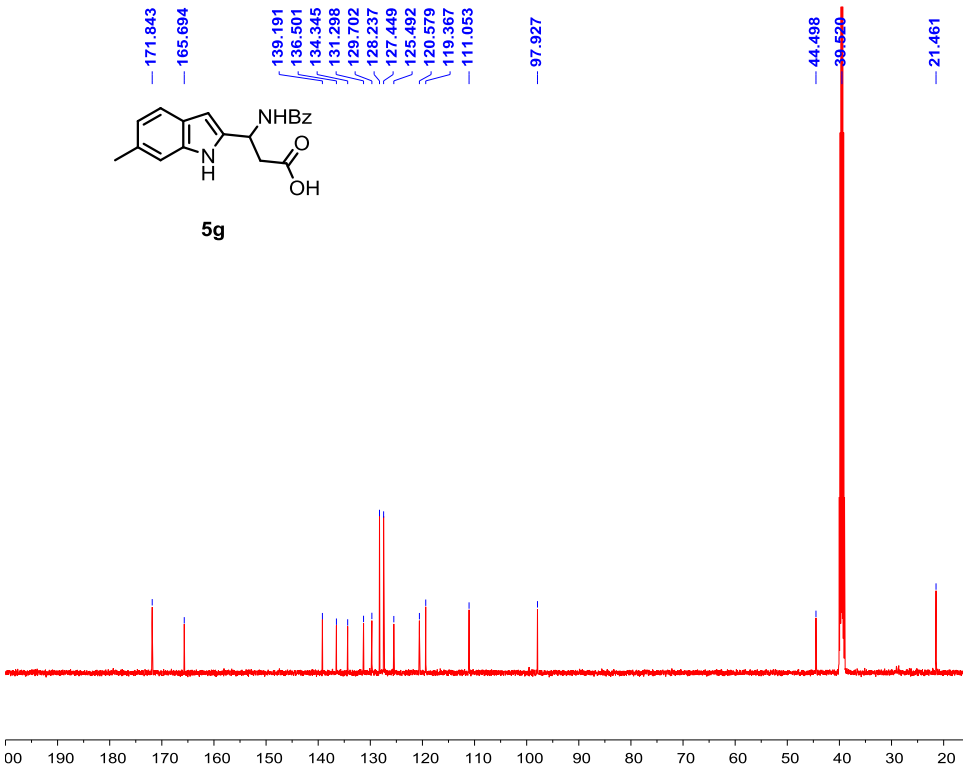
3-Benzamido-3-(6-methyl-1*H*-indol-2-yl)propanoic acid (5g)

^{1}H NMR, 500 MHz, DMSO-d_6



5g

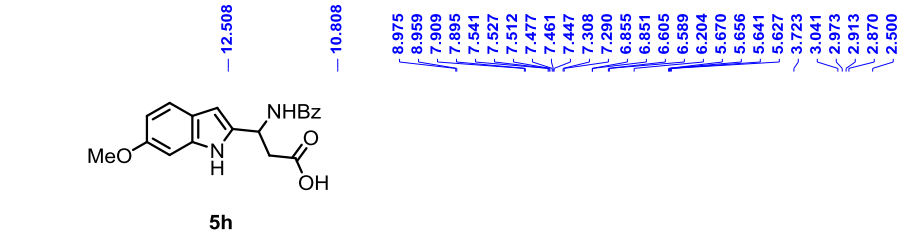
^{13}C NMR, 125 MHz, DMSO-d_6



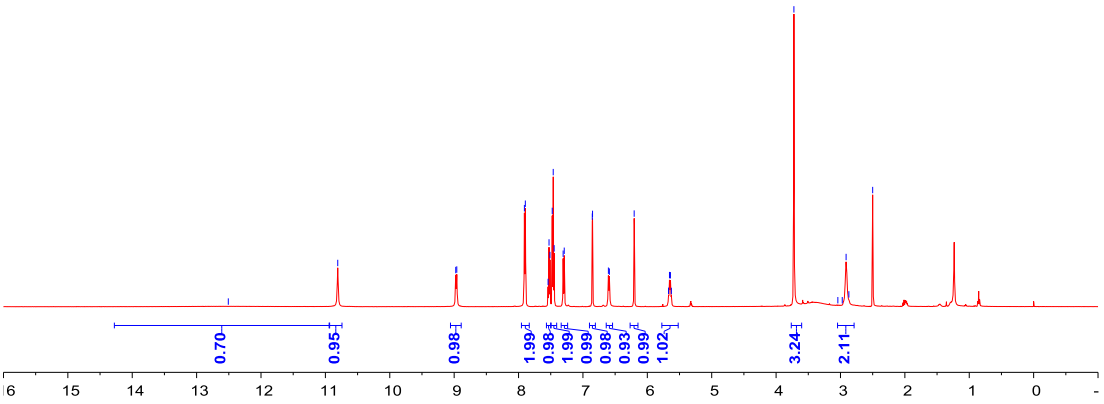
5g

3-Benzamido-3-(6-methoxy-1*H*-indol-2-yl)propanoic acid (5h)

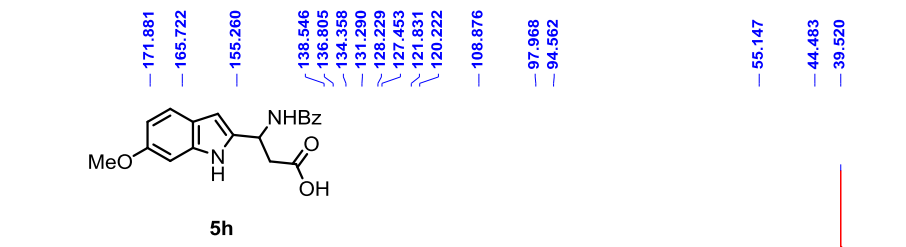
^{1}H NMR, 500 MHz, DMSO-d_6



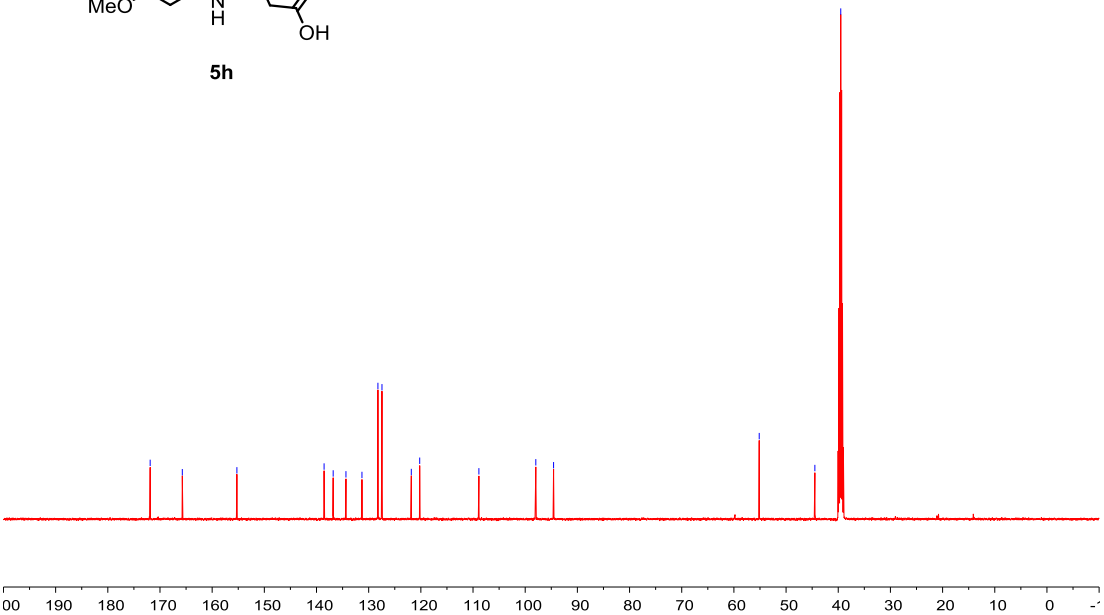
5h



^{13}C NMR, 125 MHz, DMSO-d_6

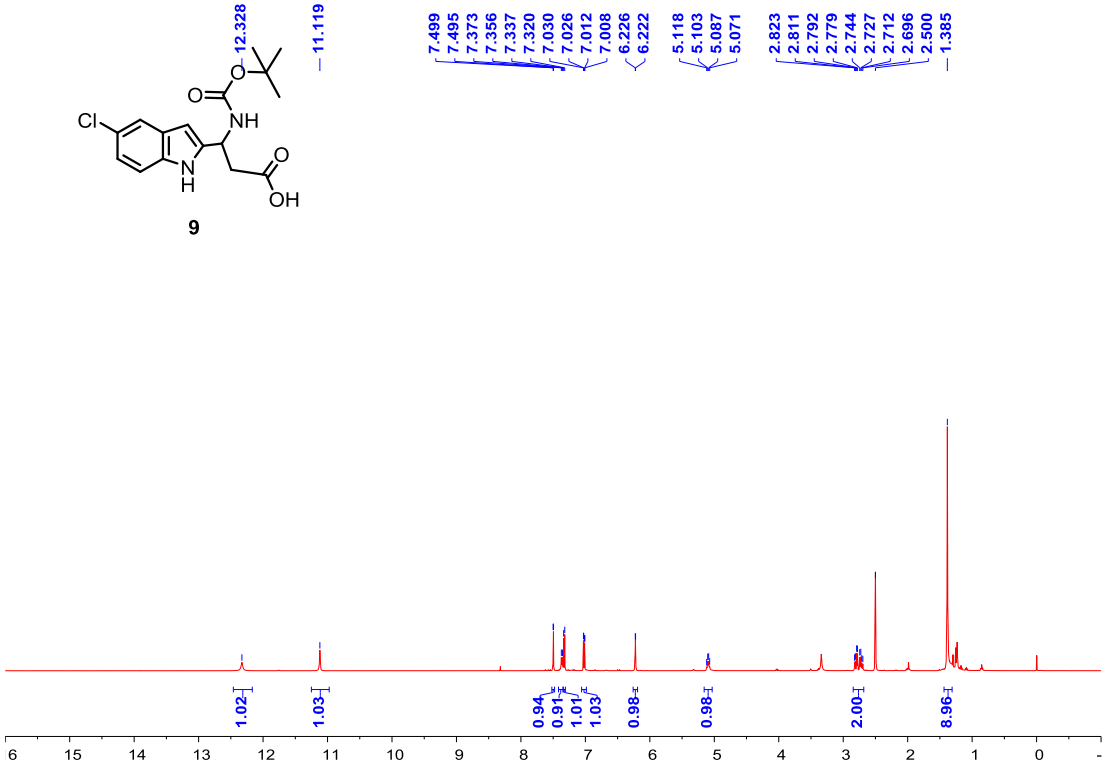


5h

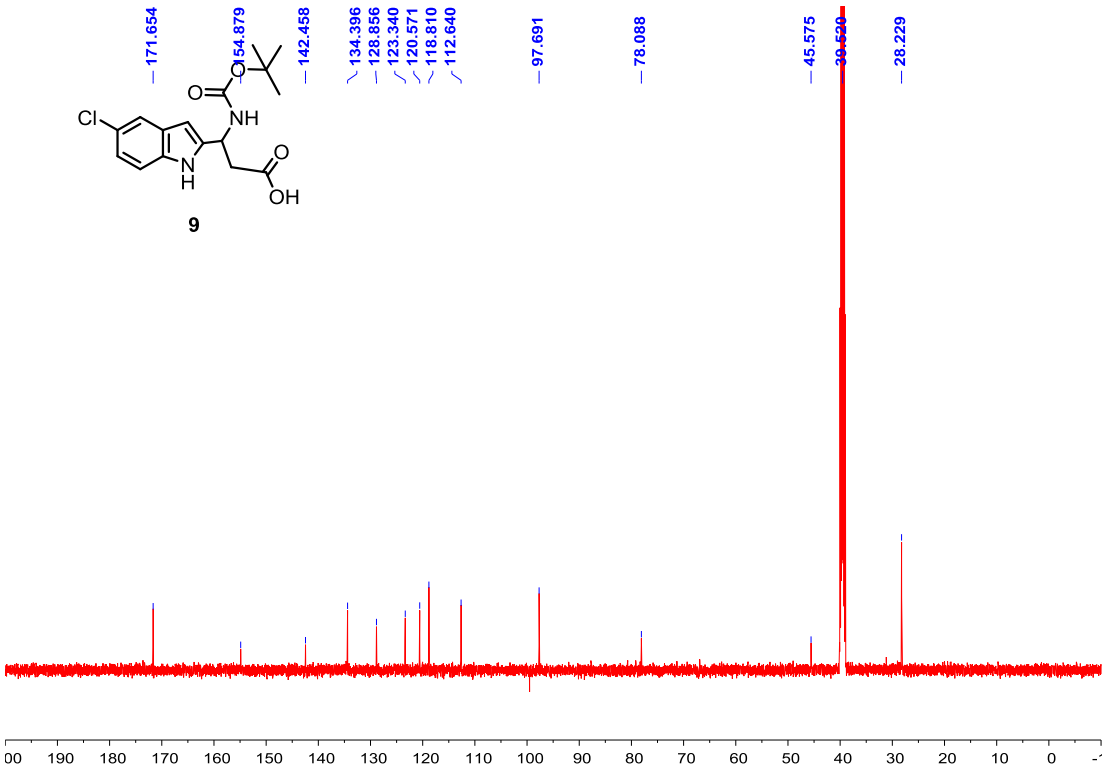


3-((Tert-butoxycarbonyl)amino)-3-(5-chloro-1*H*-indol-2-yl)propanoic acid (5i)

^{1}H NMR, 500 MHz, DMSO-d_6

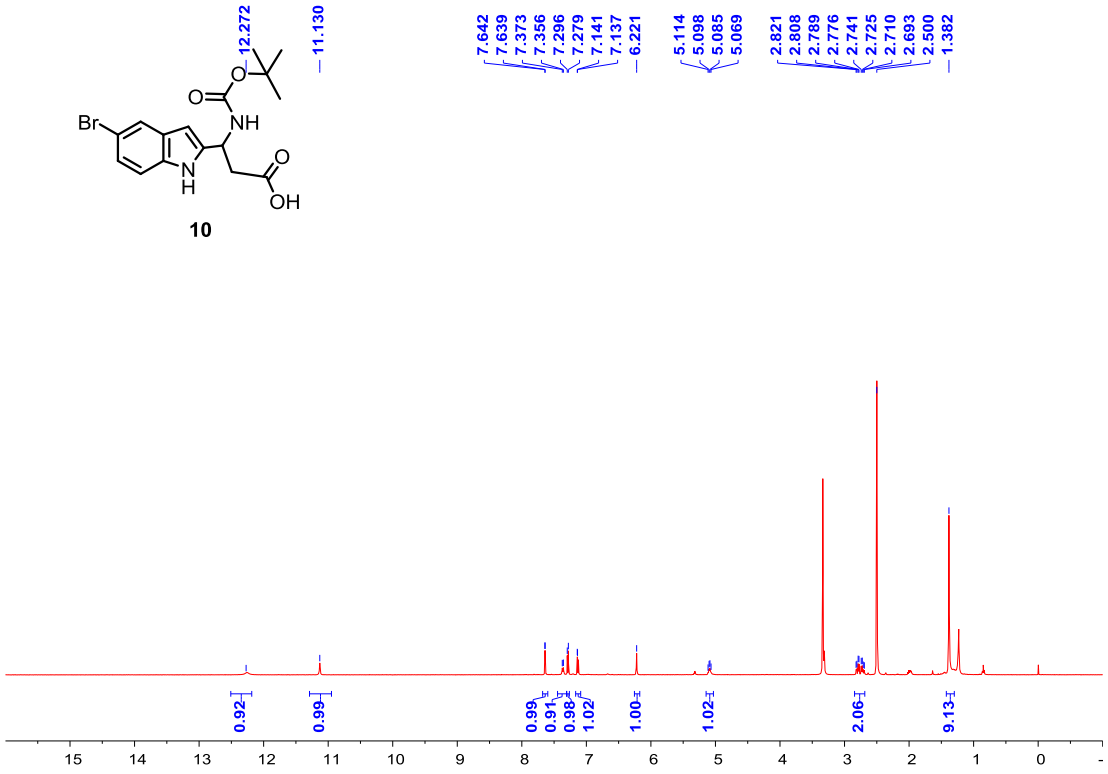


^{13}C NMR, 125 MHz, DMSO-d_6

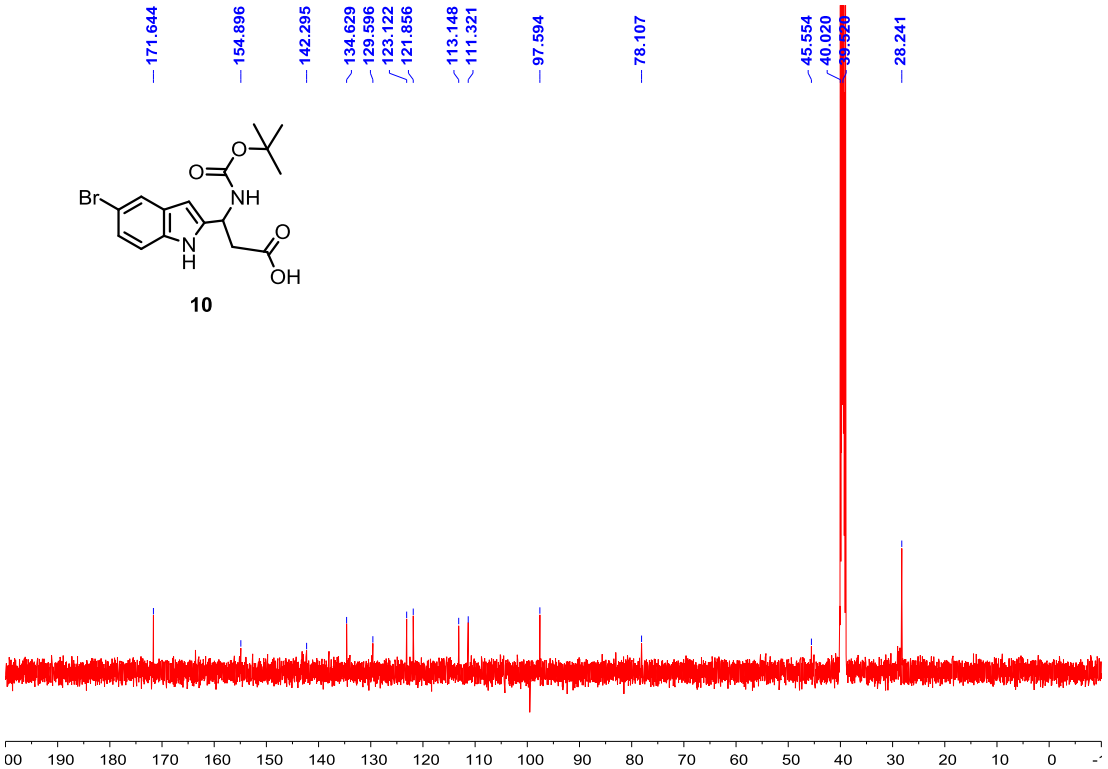


3-((Tert-butoxycarbonyl)amino)-3-(5-bromo-1*H*-indol-2-yl)propanoic acid (5j)

^{1}H NMR, 500 MHz, DMSO-d_6

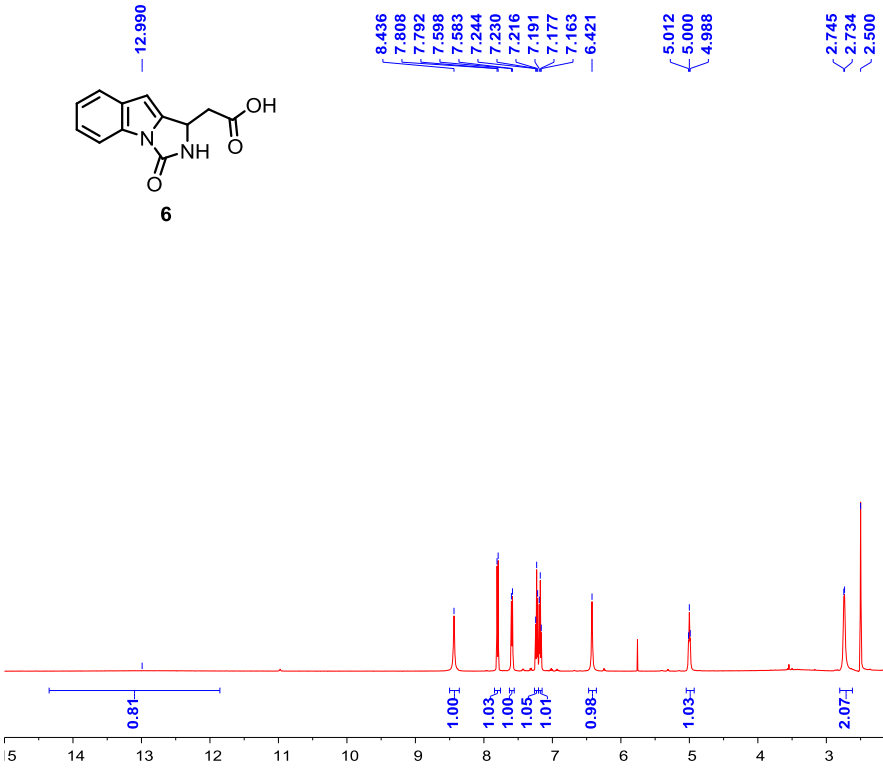


^{13}C NMR, 125 MHz, DMSO-d_6

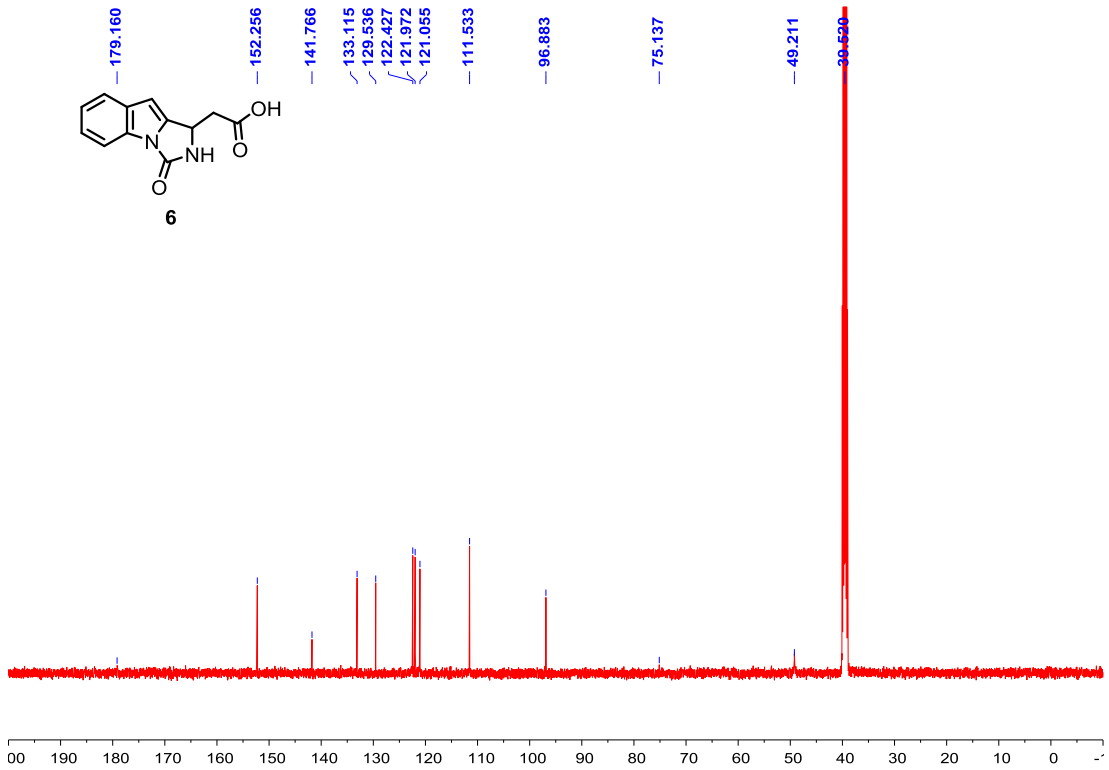


_N_-(4-Hydroxy-2-methylbutan-2-yl)benzamide (6)

^{1}H NMR, 500 MHz, DMSO-d_6

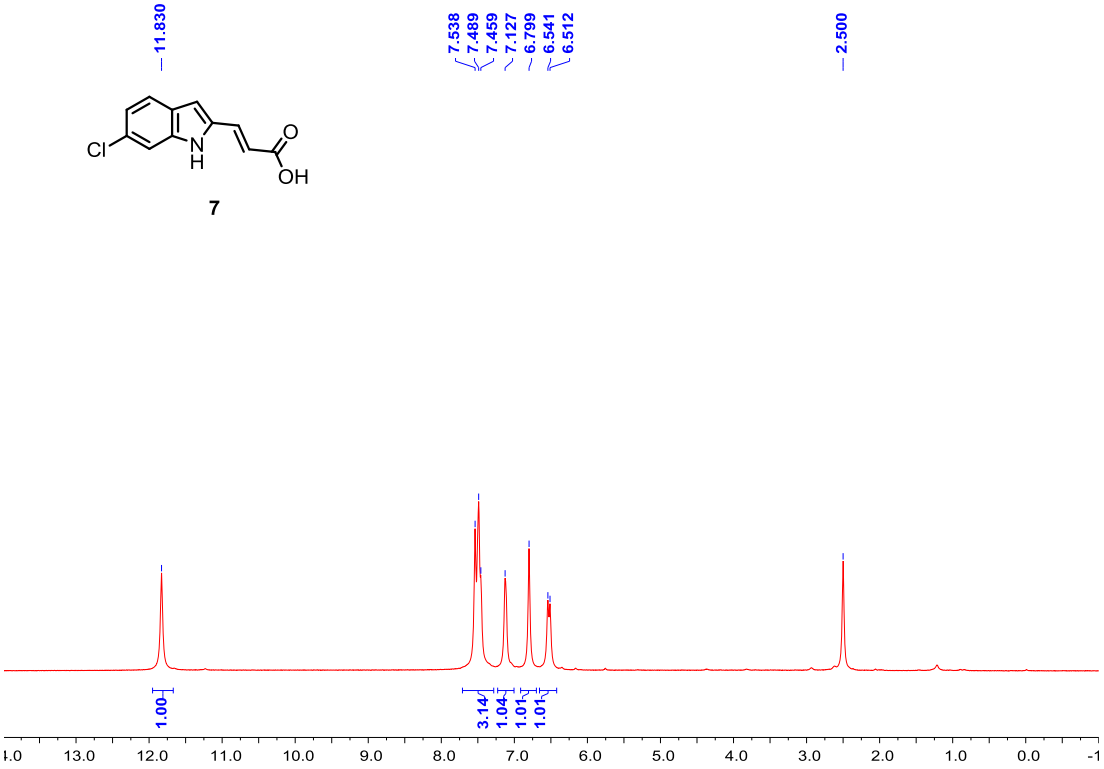


^{13}C NMR, 125 MHz, DMSO-d_6

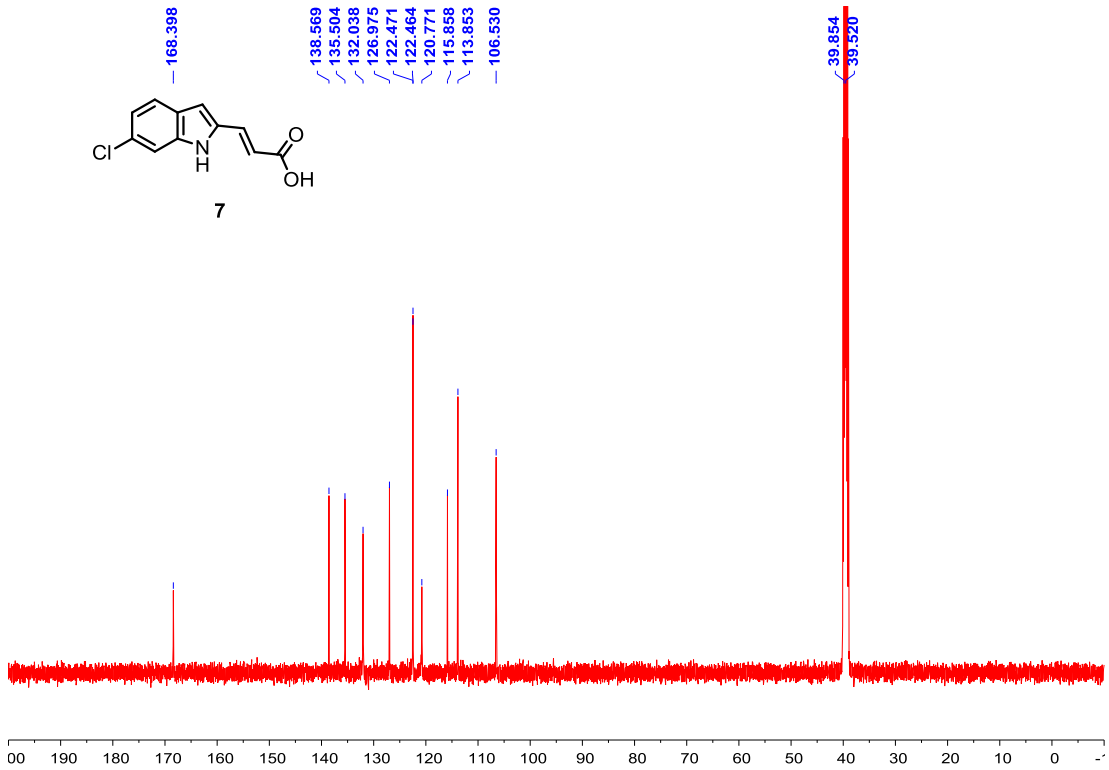


(*E*)-3-(6-Chloro-1*H*-indol-2-yl)acrylic acid (7)

^{1}H NMR, 500 MHz, DMSO-d_6

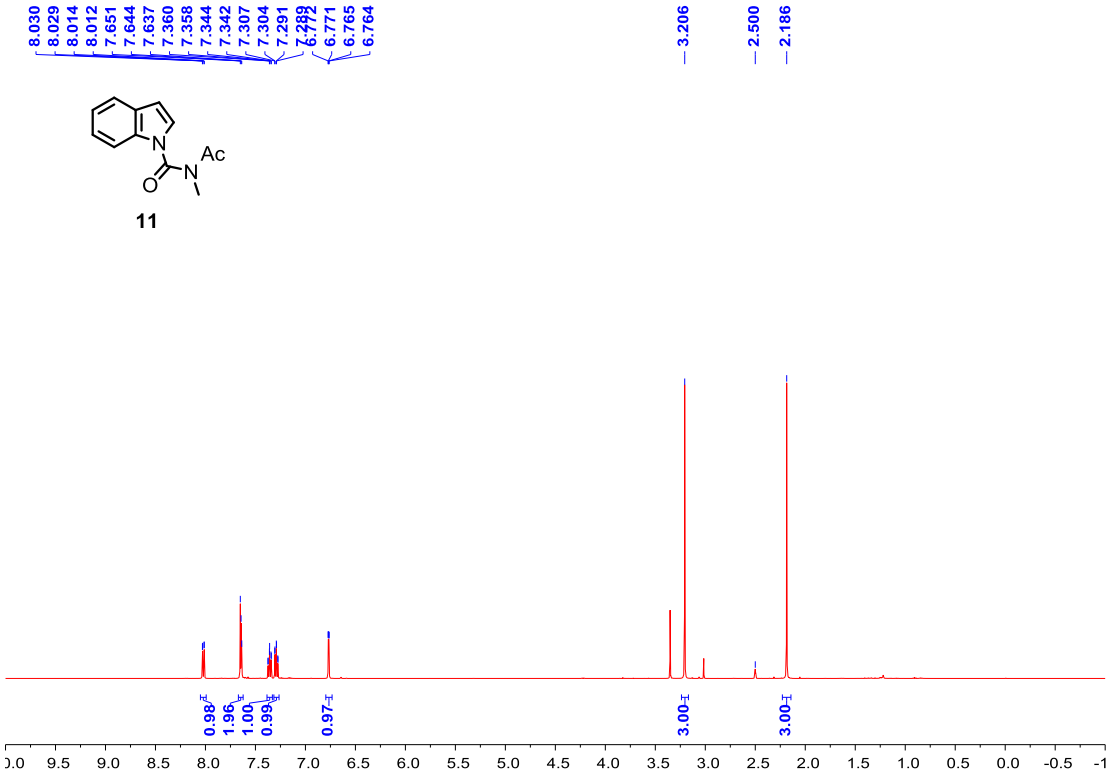


^{13}C NMR, 125 MHz, DMSO-d_6



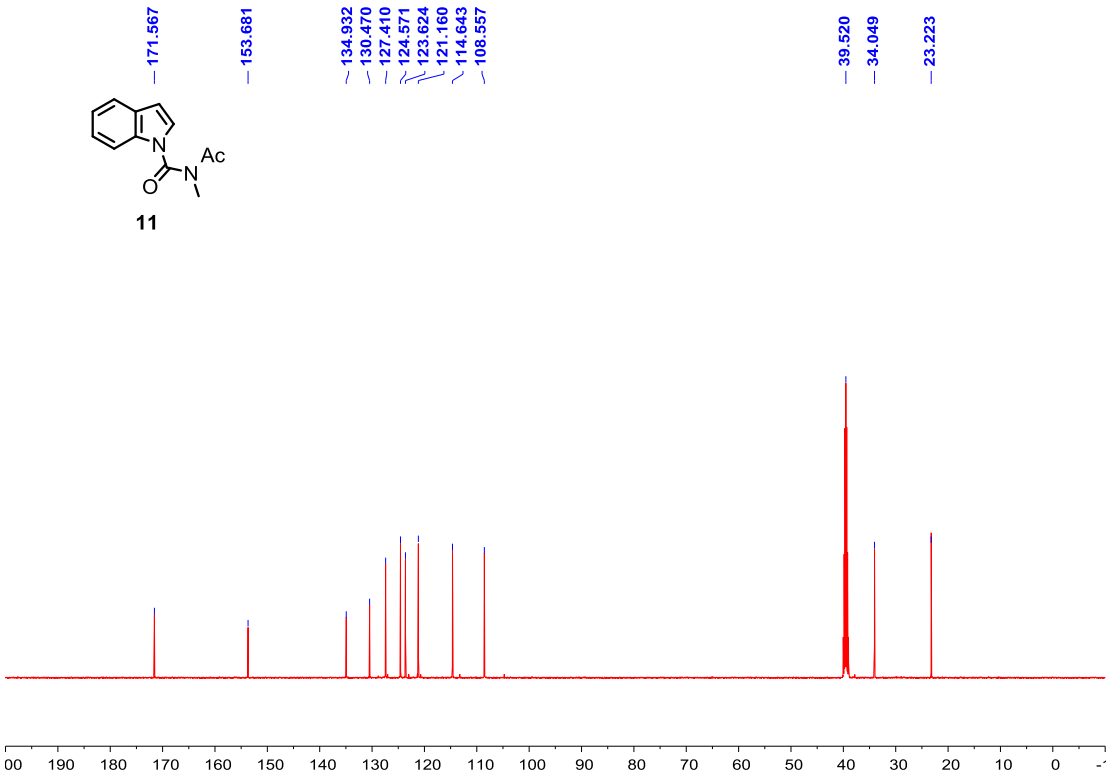
_N_-Acetyl-_N_-methyl-1H-indole-1-carboxamide (8)

^{1}H NMR, 500 MHz, DMSO-d_6



11

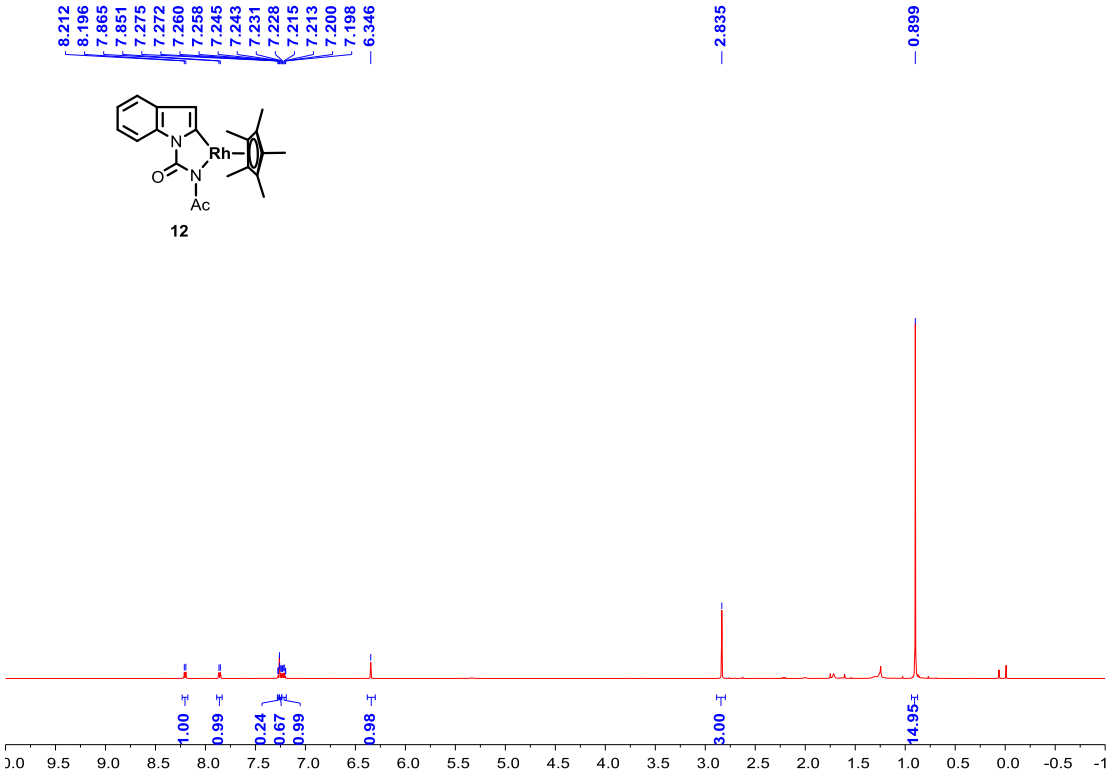
^{13}C NMR, 125 MHz, DMSO-d_6



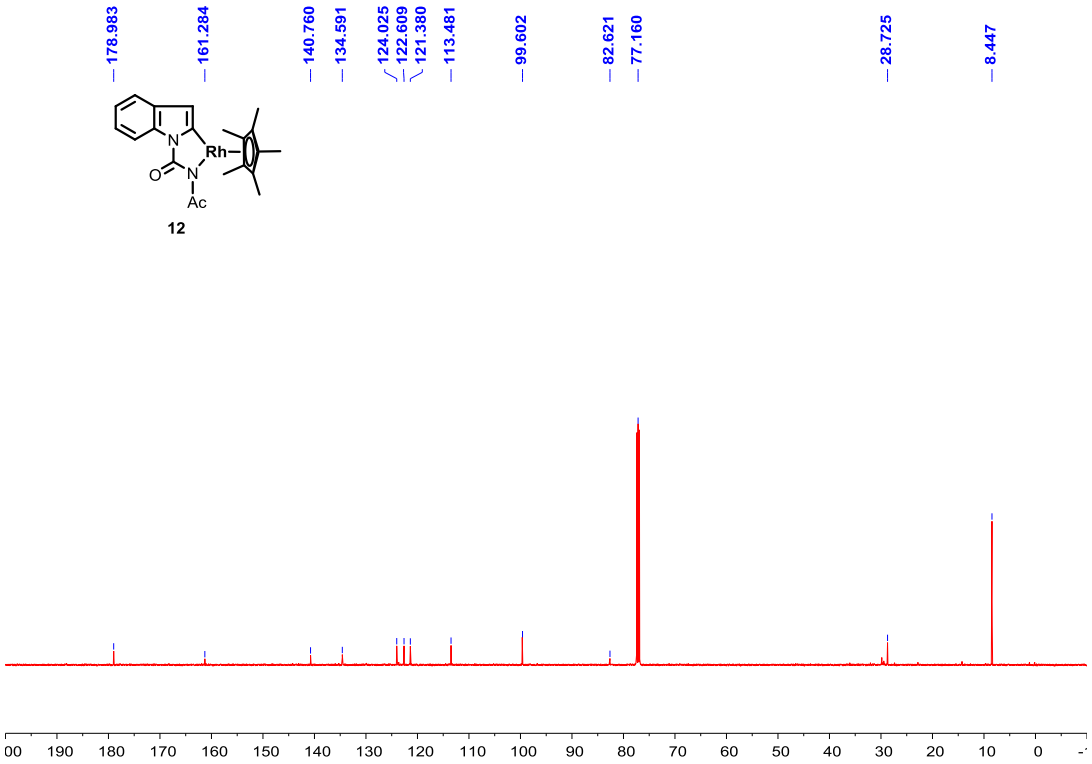
11

5-Membered rhodacycle 9

^{1}H NMR, 500 MHz, $CDCl_3$

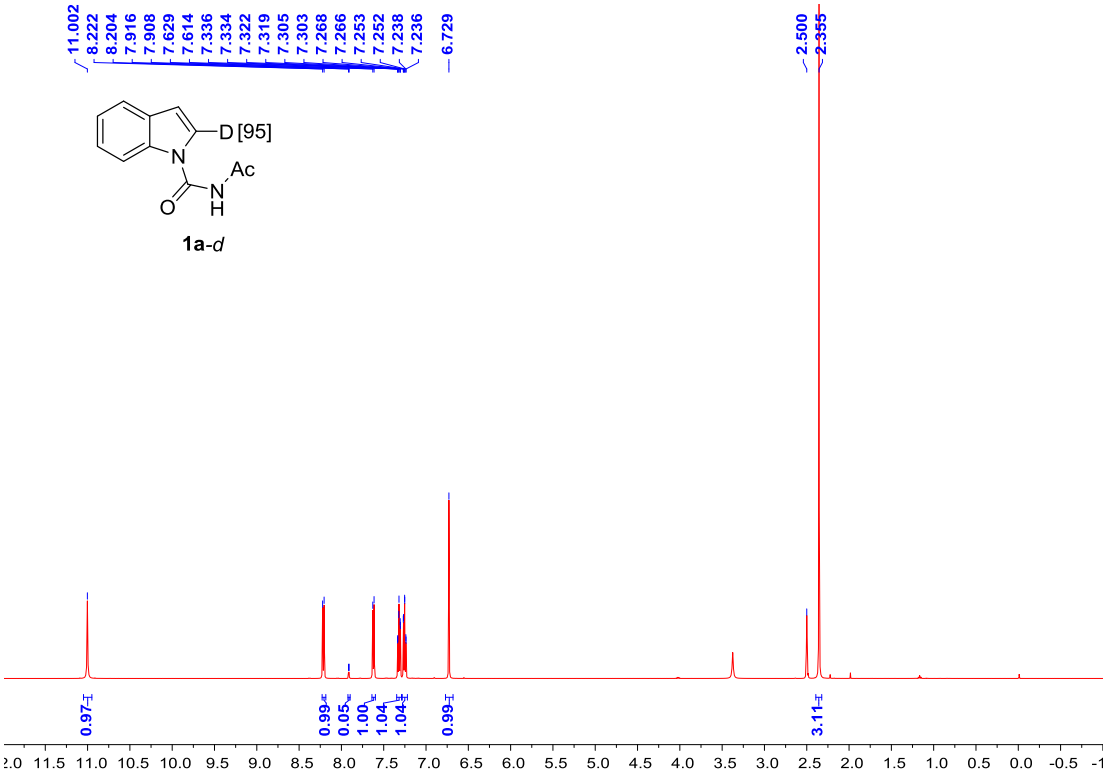


^{13}C NMR, 125 MHz, $CDCl_3$

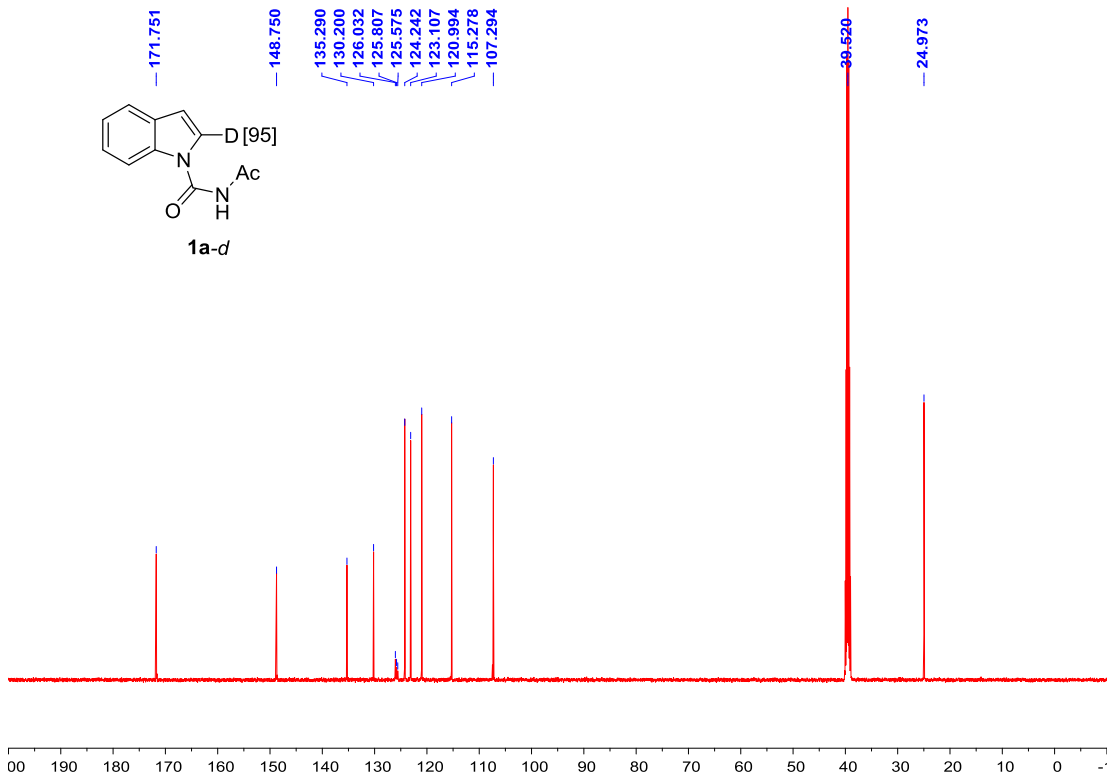


2-Deutero-*N*-acetyl-1*H*-indole-1-carboxamide (**1a**-*d*)

^{1}H NMR, 500 MHz, DMSO-d_6

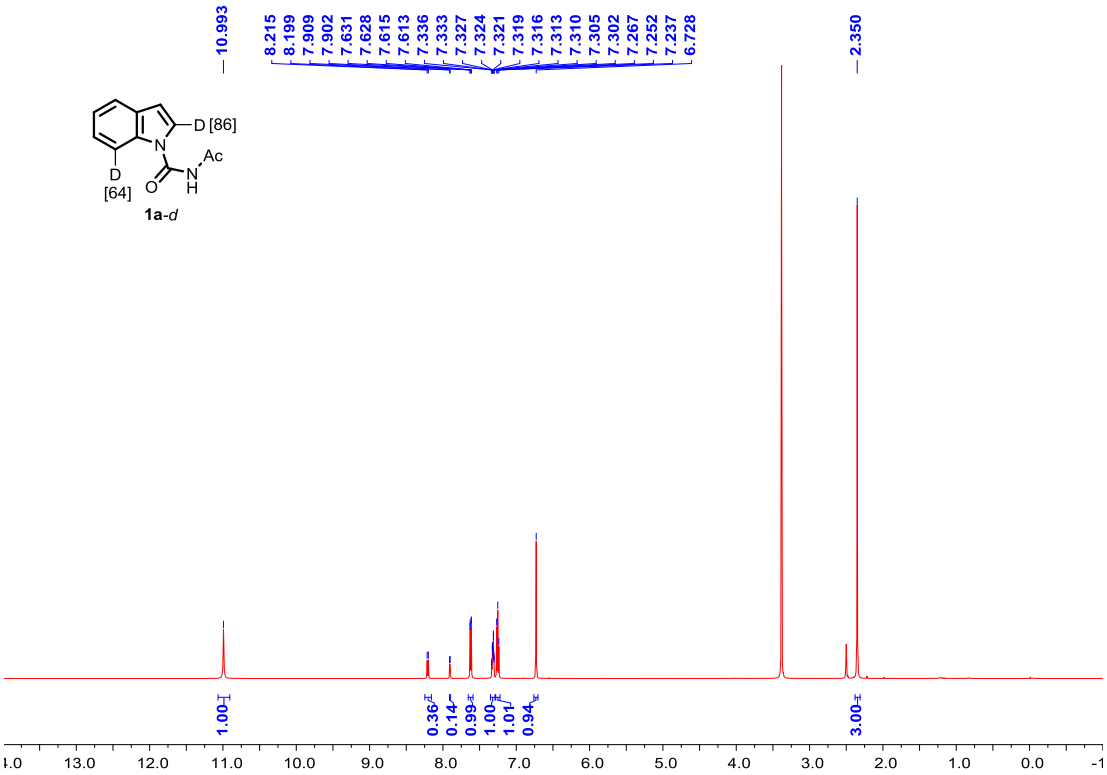


^{13}C NMR, 125 MHz, DMSO-d_6



2,7-Dideutero-*N*-acetyl-1*H*-indole-1-carboxamide (10)

^{1}H NMR, 500 MHz, DMSO-d_6



^{13}C NMR, 125 MHz, DMSO-d_6