Electronic Supplementary Material (ESI) for ChemComm.

Tris(trimethylsilyl)silane and Visible-Light Irradiation: A New Metal- and Additive-Free Photochemical Process for the Synthesis of Indoles and Oxindoles**

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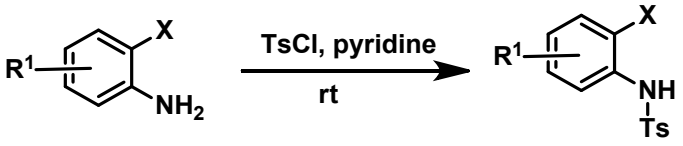
1. General information:

All solvents were dried and distilled prior to use by standard procedures and chemicals were either used as received or purified according to the procedures outlined in *Purification of Common Laboratory Chemicals*[1]. Glassware used was dried in oven or flame dried under vacuum and cooled under inert atmosphere. Reactions were monitored by TLC and visualized by a dual shortwave/longwave UV lamp and stained with an ethanolic solution of potassium permanganate or vanillin. Column flash chromatography was performed using gel 60 (230−400 mesh), and analytical thin-layer chromatography (TLC) was performed using silica gel aluminum sheets. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise noted.
^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz. for ^{1}H and 100 MHz for ^{13}C. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (TMS), and coupling constants (J) are reported in hertz. All signals are reported in ppm with the internal reference of 7.26 ppm or 77.0 ppm for chloroform. Data are presented as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad, dd = doublet of doublet, dt = doublet of triplet), coupling constant (J/Hz) and integration.

[1] Armarengo, W. L. F.; Perrin, D. D. In Purification of Laboratory Chemicals, 4th ed.; Butterworth Heinemann: Oxford, 1996

A. General Procedure for the Preparation of Starting Materials

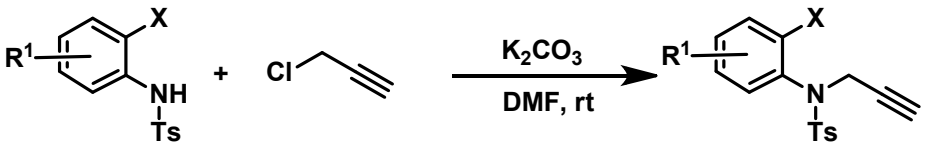
Preparation of the N-tosyl-protected aniline [2]



X= I, Br

In a round bottom flask containing a solution of 2-haloaniline (4.50 mmol, 1 equiv) in pyridine (10 mL), *p*-toluenesulfonyl chloride was added (4.70 mmol, 1.05 equiv). The reaction was stirred at room temperature for 1.5 h, then quenched by addition of water (10 mL). The reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic layers were washed with an aqueous $CuSO_4$ solution (10%, 3 x 20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (hexane/EtOAc) to afford the corresponding tosyl-protected aniline. All spectroscopic data are in accordance with seminal literature.

Preparation of the N-tosyl-propargyl anilines [3]



X= I, Br

To a round bottom flask containing a solution of N-tosyl protected 2-haloaniline (1.0 mmol, 1 equiv) in DMF (5 mL), K_2CO_3 (3.0 mmol, 3 equiv) and propargyl chloride (2.0 mmol, 2 equiv) were added. The reaction was stirred at room temperature for 3 h,

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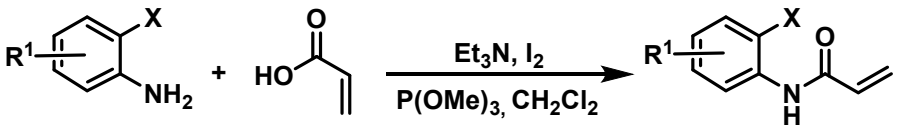
[2] C. Bressy, D. Alberico, M. Lautens, *J. Am. Chem. Soc.* **2005**, *127*, 13148-13149.
[3] Q.L.Luo, L. Lv, Y. Li, P. Tan, W. Nan, Q. Hui, Eur. *J. Org. Chem.* **2011**, *34*, 6916-6922.

and then quenched by addition of water (5 mL). The aqueous layer was extracted with diethyl ether (3 x 10mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by silica gel chromatography (hexane/EtOAc) to afford N-tosyl-propargyl aniline. All spectroscopic data are in accordance with seminal literature.

Preparation of the N-acrylamides [4]

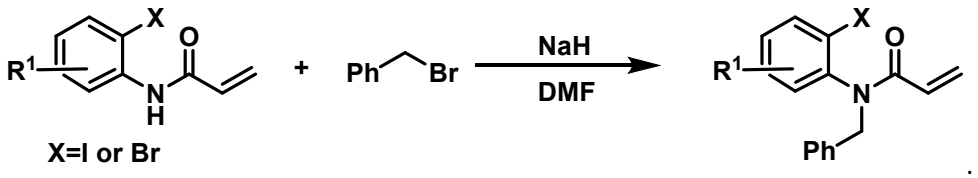


X=I or Br

To a round bottom flask under N_2 atmosphere containing a solution of $P(OMe)_3$ (0.35 mL, 3.0 mmol) in dichloromethane (15 mL), precooled to 10 ^oC, was added I_2 (760 mg, 3.0 mmol). After the solid iodine was completely dissolved, acrylic acid (204.7 µL, 3.0 mmol) and Et_3N (0.70 mL, 5.0 mmol) were added in sequential order, and the solution was stirred for 10 min in a cooling bath. The substituted aniline (2.0 mmol) was then added and the mixture was stirred for 10 min. After removing the cooling bath, the reaction mixture was stirred for additionally 3 h at room temperature (reaction monitored by TLC), then diluted with saturated aqueous $NaHCO_3$ and extracted with dichloromethane (3 x 30 mL). The combined organic layer was sequentially washed with water, 1N HCl and brine (3 x 20mL) dried over anhydrous Na_2SO_4, and then purified by flash chromatography (hexane/EtOAc) to afford substituted *N*-acrylamide. All spectroscopy data are accordance with seminal literature.

[4] X. Liu, X. Ma, Y. Huang, Z. Gu, *Organic Letters* **2013**, 15, 4814-4817.

Preparation of the N-benzyl-acrylamides [5]

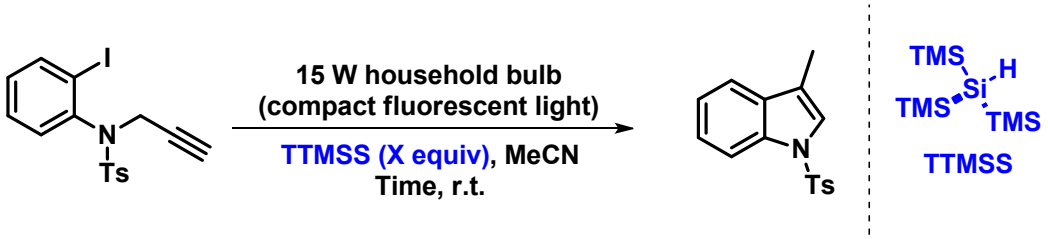


In a round bottom flask, under N_2 atmosphere, NaH (60 mg, 60% in mineral oil, 1.5 mmol, 1.5 equiv) was added in portions to a solution of substituted *N*-(2-halophenyl) acrylamide (1.0 mmol, 1.0 equiv) in DMF (4.0 ml) at 0 °C. After stirring for 20 min, BnBr (70 µl, 0.60 mmol, 1.2 equiv) was added dropwise and the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water and THF was removed by evaporation. The residue was extracted with ethyl acetate twice, and the organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (hexane/EtOAc) to afford the desired product. All spectroscopy data are accordance with seminal literature.

[5] J. D. Nguyen, E. M. D. Amato, J. M. R. Narayaman, C. R. J. Stephenson, *Nature Chemistry* **2012**, *4*, 854-859.

B. Screening and Control Experiments

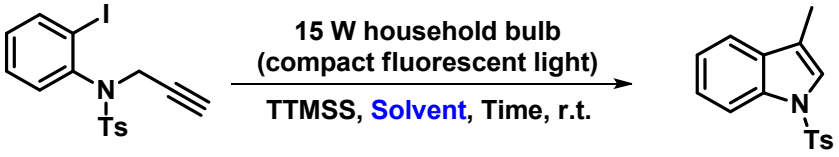
Table S1: Effect of the amount of TTMS [a]



Entry	(X equiv)	Time (h)	Yield[b] (%)
1	1	24	58
2	1.5	24	76
3	**2**	**2**	**99**
4[c]	1	24	nr
5	0	24	nr

[a]Reactions were carried out at 0,1 mmol scale of the aryl halide with varying amounts of TTMSS in 0.4 mL MeCN. [b]Yield determined after column chromatography. [c]Reaction was carry out in the absence of light.

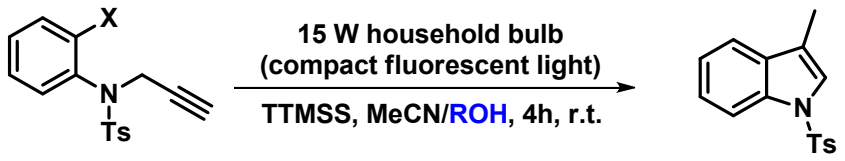
Table S2: Solvent screening



Entry[a]	Solvent	Time (h)	Yield (%)[b]
1	**MeCN**	**2**	**99**
2	DCM	24	57
3	Toluene	24	64
4	THF	24	53
5	DMSO	24	5
6	DMF	24	12
7	AcOEt	24	76
8	EtOH	4	88
9	EtOH	24	90
10	Acetone	6	89
11	H_2O	24	nd

[a] Reactions were carried out at 0,1 mmol scale using 2 equiv of TTMSS. [b] Isolated yield.

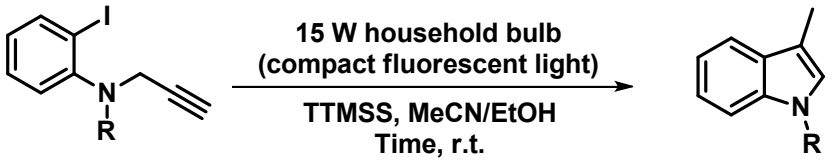
Table S3: Protic Co-solvent Screening



Entry[a]	X	Protic Source	(X Equiv)	Yield[b] (%)
1	I	EtOH	1	82
2	I	EtOH	3,5	80
3	**I**	**EtOH**	**5**	**92**
4	Br	EtOH	5	85
5	I	MeOH	5	75
6	I	*i*PrOH	5	76

[a]Reactions were carried out at 0.1 mmol scale using 1 equiv of TTMSS, 0.4 mL of MeCN. [b]Isolated yield.

Table S4: Effect of N protecting group

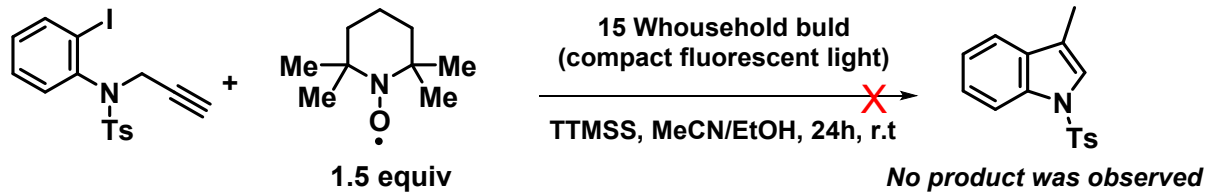


Entry[a]	R	Time (h)	Yield[b] (%)
1	**Tosyl**	**4**	**92**
2	Acetyl	24	13
3	Isobutytyl	24	14

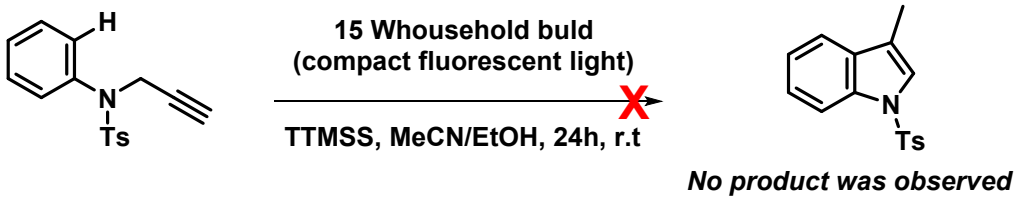
[a] Reactions were carried out at 0,1 mmol scale using 1 equiv of TTMSS, 0,4 mL of MeCN, and 5 equiv of EtOH. [b] Isolated yield.

D. Mechanistic Insights

1. Reaction in the Presence of a Radical Scavenger - 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO)



Comment: *The reaction was completely inhibited when was performed using TEMPO as radical scavenger. This observation indicates that the indole formation is via a radical pathway.*



Comment: *When the substrate used did not displayed a halogen atom attached to the aryl ring, the product formation was not observed. The presence of the halogen atom is crucial for the generation of the aryl radical.*

2. Reaction using Deuterated Methanol

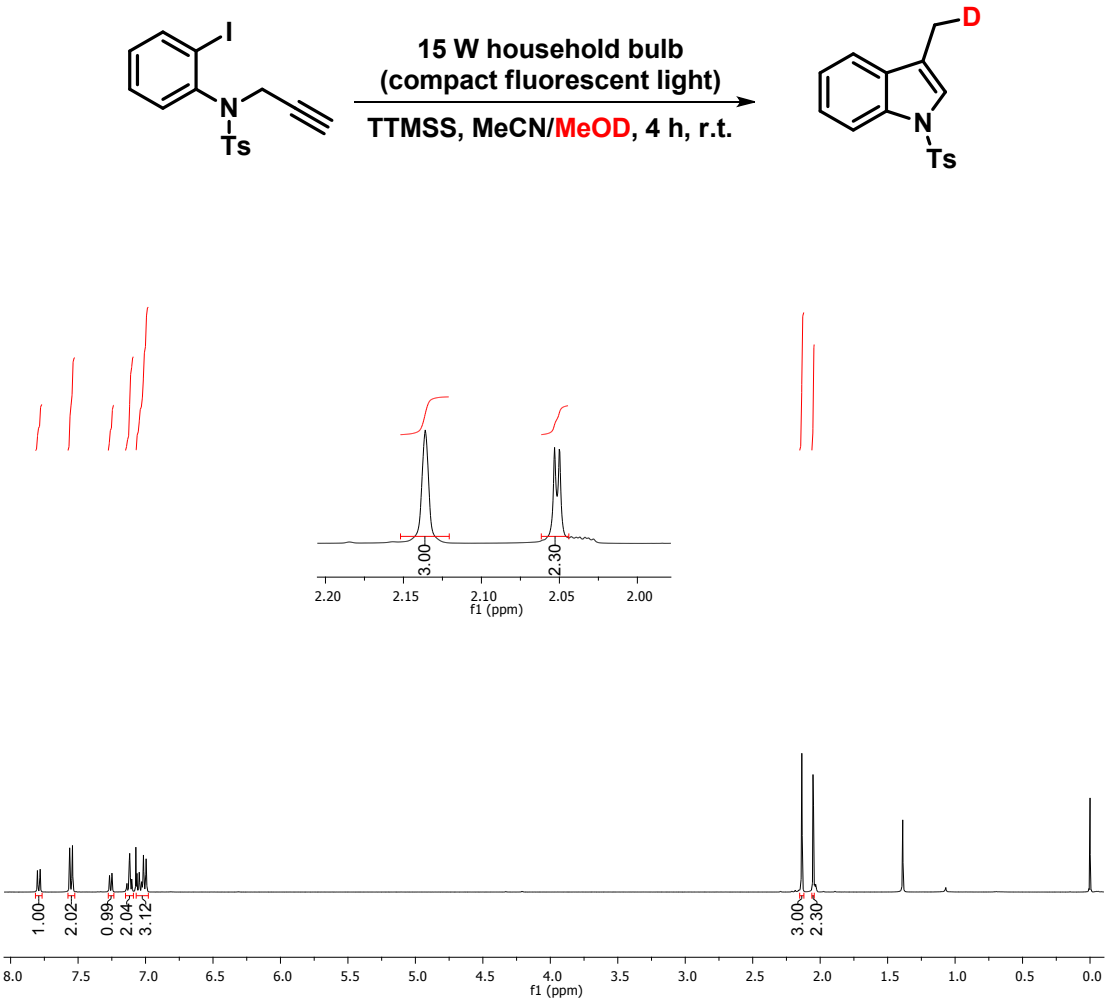


Figure S1: ^{1}H spectra showing the integration of the methyl signal at 2.06 ppm.

Comment: *When the reaction was performed using deuterated methanol as proton source, the insertion of deuterium at the last step on the indole synthesis has been observed. The proportion of deuterium and hydrogen (D/H, 7:3) detected by integration of signal in the ^{1}H NMR experiment.*

3. Kinetic Study using the model reaction

The kinetic study was performed using the GC-MS equipment, giving us the possibility to build the calibration curves and, consequently, the kinetic curves using the kinetic equation. Solutions at different concentration of **1a** and TTMSS (obtained by diluting the original stock solution with MeCN) were prepared.

3.1. Calibration curves of the starting materials

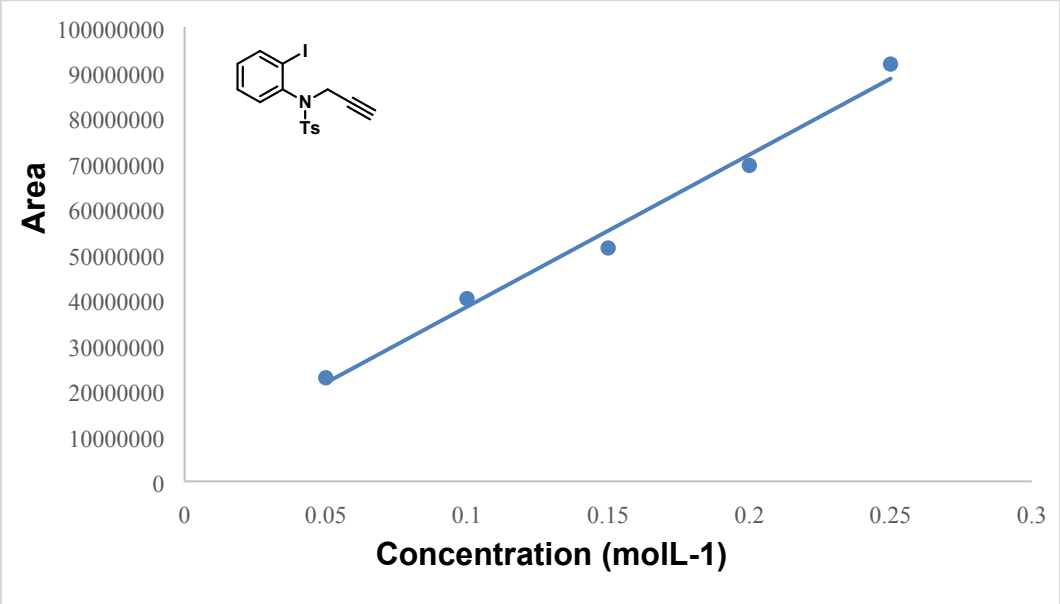


Figure S2: Calibration curve for 2-iodo aniline.

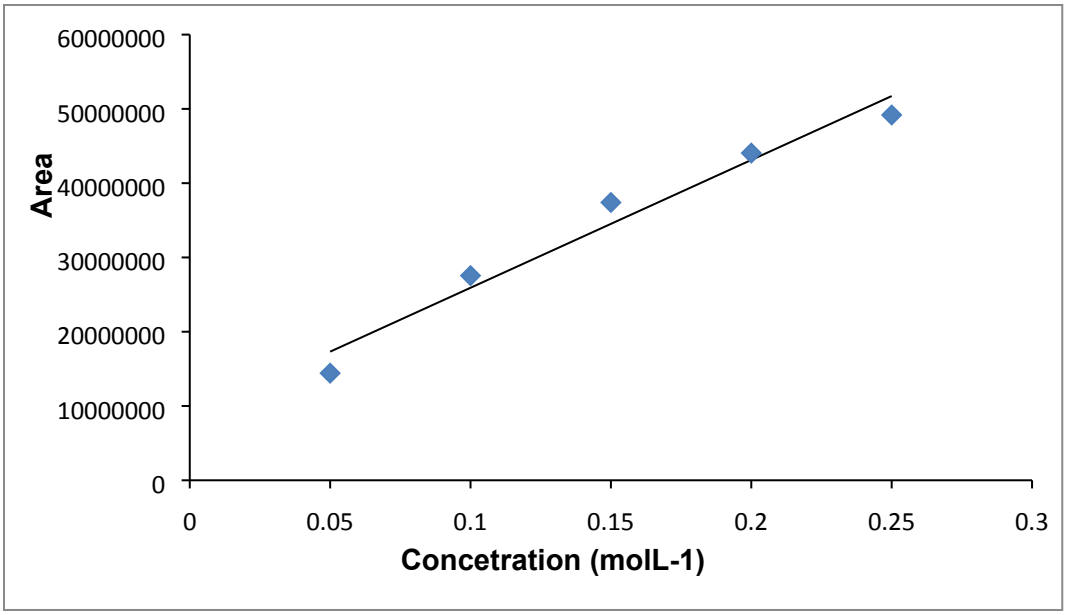


Figure S3: Calibration curve for TTMSS.

3.2. Kinetic equations and curves

Reaction Order	Rate law	Integrated form equation
First to Single reagent – A	***Rate*** **= k[A]**	$\ln\left(\frac{[A]_0}{[A]}\right) = kt$ **or** $[A] = A_0 e^{-kt}$
Second to Single reagent - A	***Rate*** **= k[A]²**	$kt = \left(\frac{1}{A}\right) - \left(\frac{1}{A_0}\right)$
Second to two reagents – A and B	***Rate*** **= k[A][B]**	$kt = \left(\frac{1}{[B]_0 - [A]_0}\right) ln(\frac{[A]_0[B]}{[B]_0[A]})$

Each one of the expressions above provides a graph that can be used to determine the order with respect to the reagents. Graphically, a straight line is necessary to be achieved. Supported by this concept we started our studies to investigate the kinetics of our photo mediated reaction.

First, the expression of first order for both reagents was applied, the following graphs were obtained:

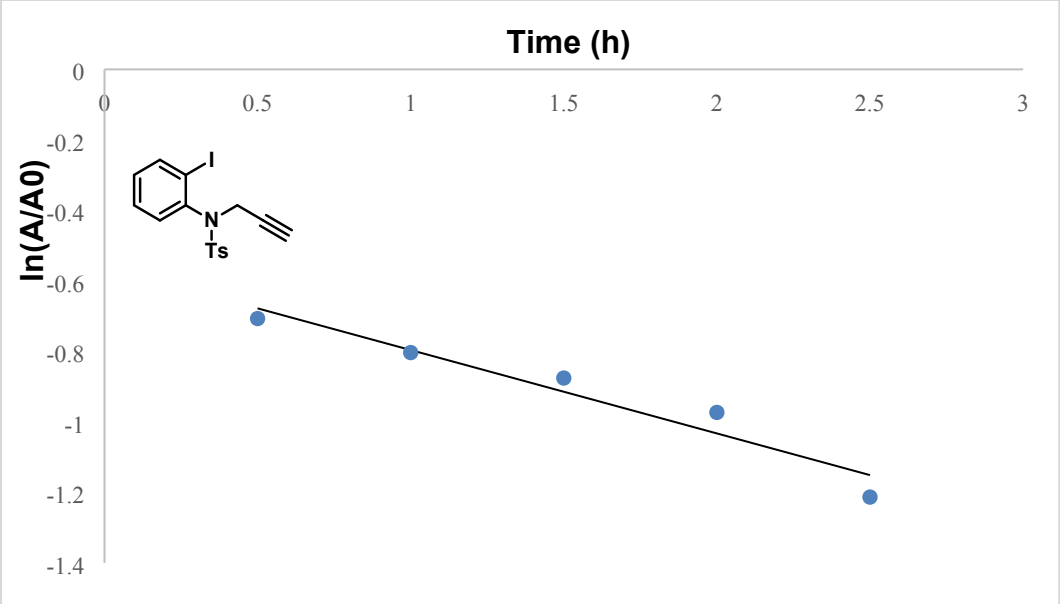


Figure S4: First order applied to 2-iodo aniline.

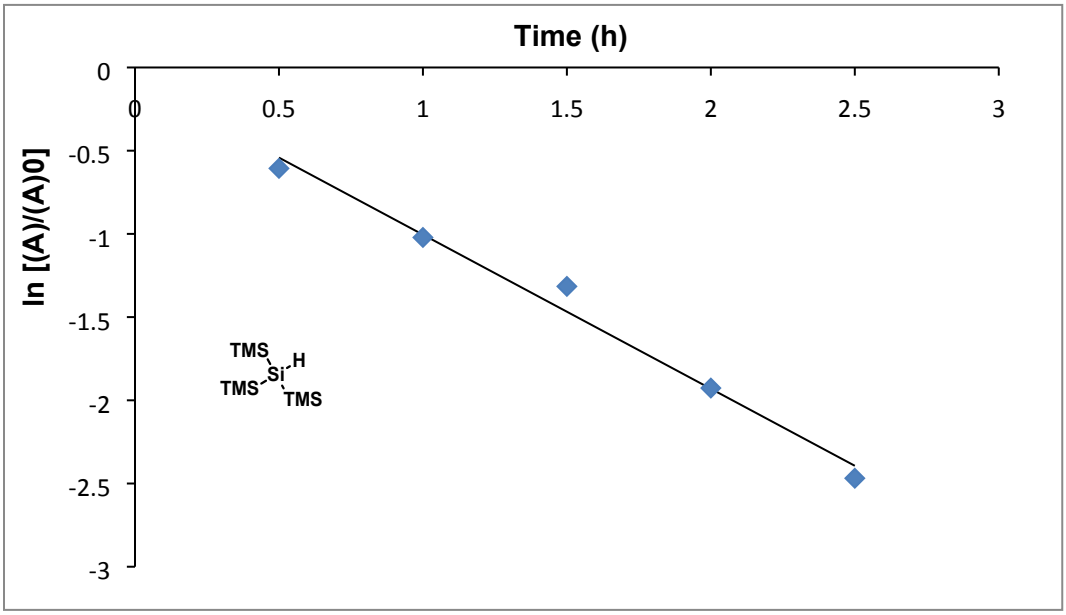


Figure S5: First order applied to TTMSS.

Next, we used the expression of second order for both reagents, and the graphs obtained are given as follows:

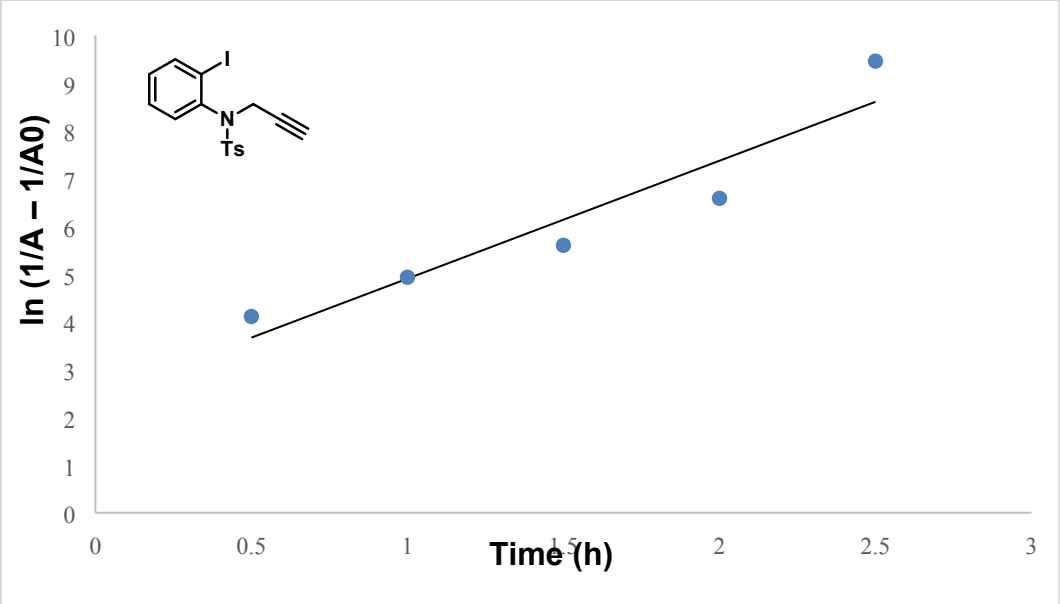


Figure S6: Second order applied to 2-iodo aniline.

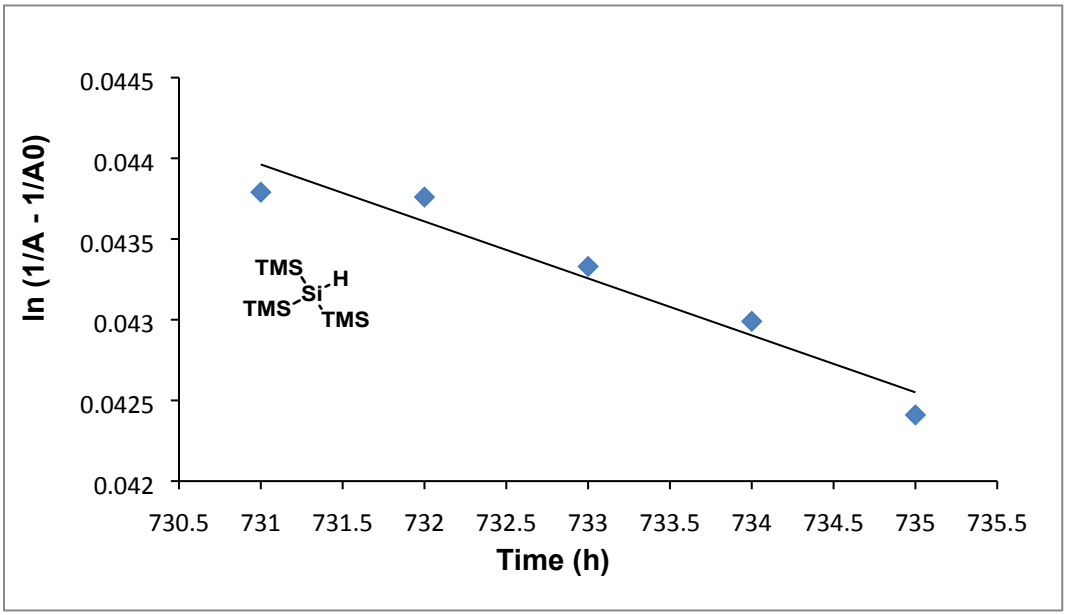


Figure S7: Second order applied to TTMSS.

From there obtained results, it is possible to observed that both reagents following first order kinetics is a better fit. Furthermore, we applied another expression that relates both reagents in a single expression, i.e.:

$$kt = \left(\frac{1}{[B]_0 - [A]_0}\right) ln(\frac{[A]_0[B]}{[B]_0[A]})$$

Using the rate expression and analyzing the graph, we can conclude that this reaction is second order overall, being first order for each reagent.

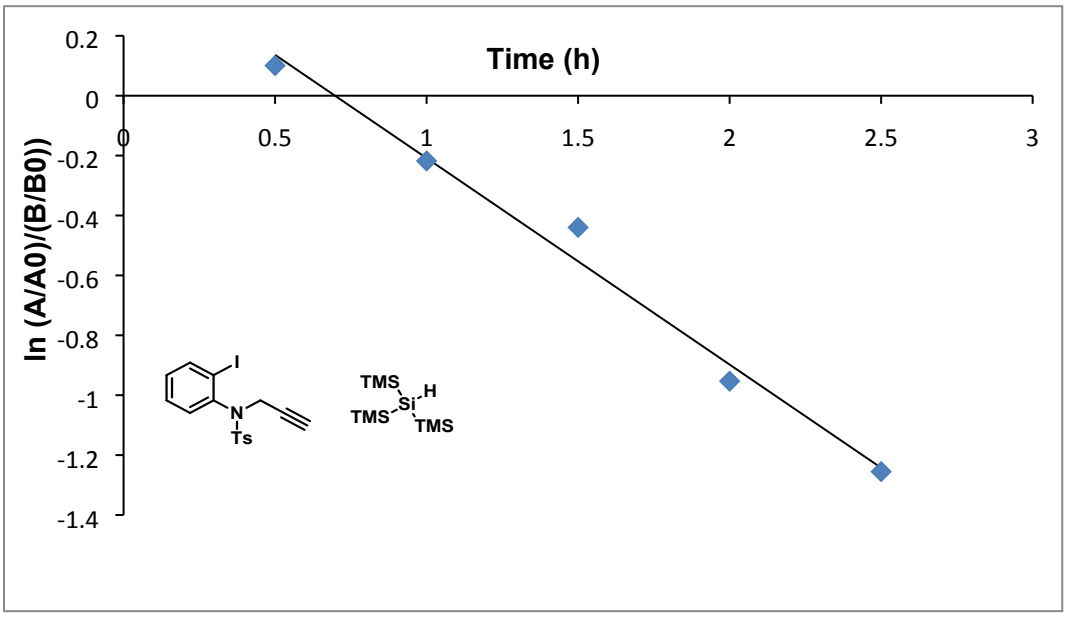


Figure S8: Second order overall – first order with respect to each reagent.

Comment: *The kinetic study provided us a virtuous interpretation of this photo-mediated process. Since the best adjustment of the curve was using the last expression that correlated both reagents by a single expression - the overall reaction order being two, first order in regard to each reagent. Having made this observation, we can conclude that both reagents are involved in the rate determining step.*

4. Ultraviolet-Visible Experiment

We were interested to confirm that a complex between the starting material **1a** and the silicon-based reagent (TTMSS) is responsible for the energy absorption. Thus, all the spectra are recorded in MeCN using the same concentrations as in the reaction conditions.

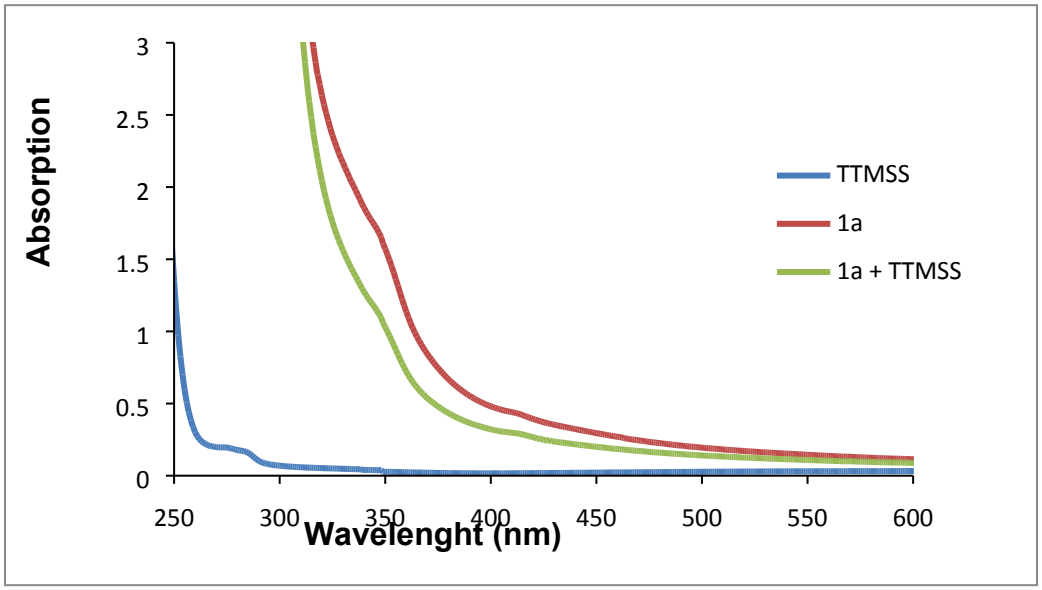


Figure S9: Absorption spectra of the reagents of the model reaction: [TTMSS] = 0,25 $molL^{-1}$, [1a] = 0,25 $molL^{-1}$, and [1a + TTMSS] = 0,25 $molL^{-1}$. The solutions were prepared using 0,5 ml of MeCN and 1 cm cuvettes were used.

Upon mixing **1a** and TTMSS, a new absorption band is observed (green line in **Figure S9**). Additionally, changes in visual color appearance is observed when the reagents are mixed, indicating the formation of a transient interaction between the reagents (EDA Complex).

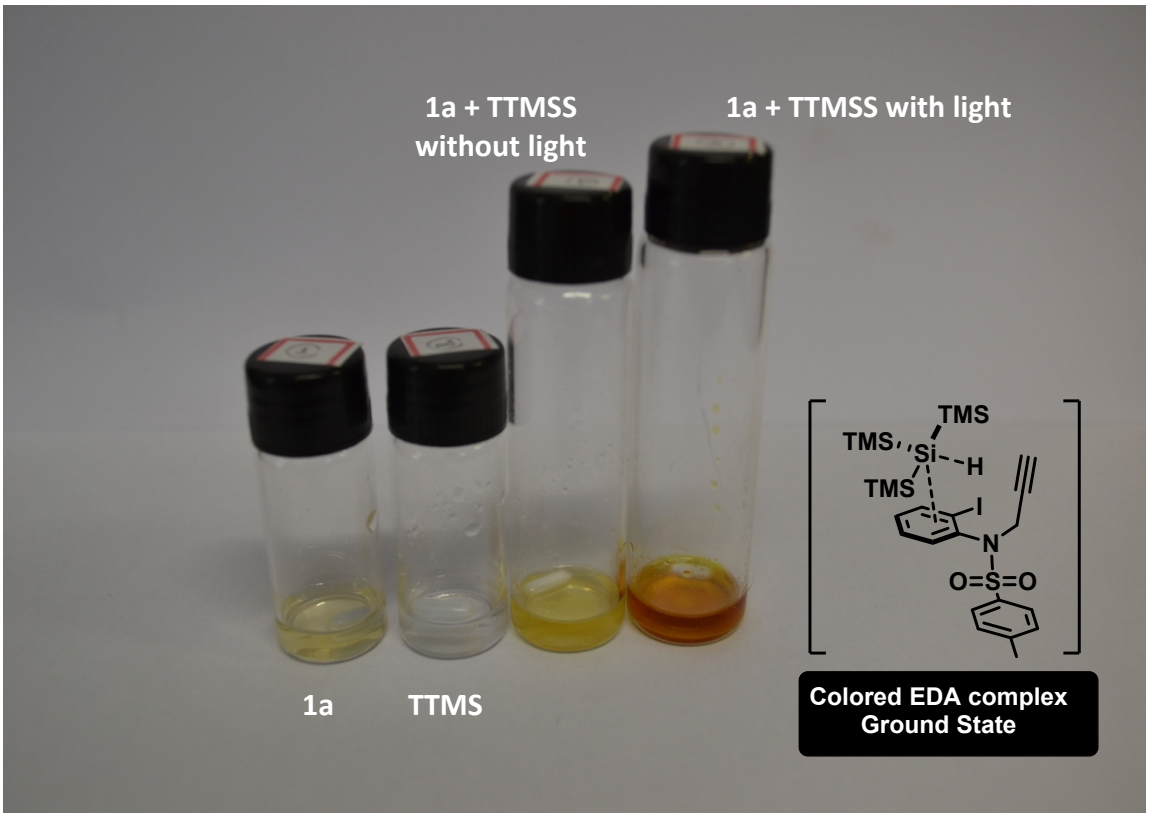


Figure S10: Images showing the colors of the reagents separately and mixed, suggesting the formation of the EDA complex.

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To complete the mechanistic study as well as emphasizing the requirement of visible light irradiation, the reaction was performed using successive interval of irradiation and dark periods for the model reaction. The obtained results are plotted in a graph bellow.

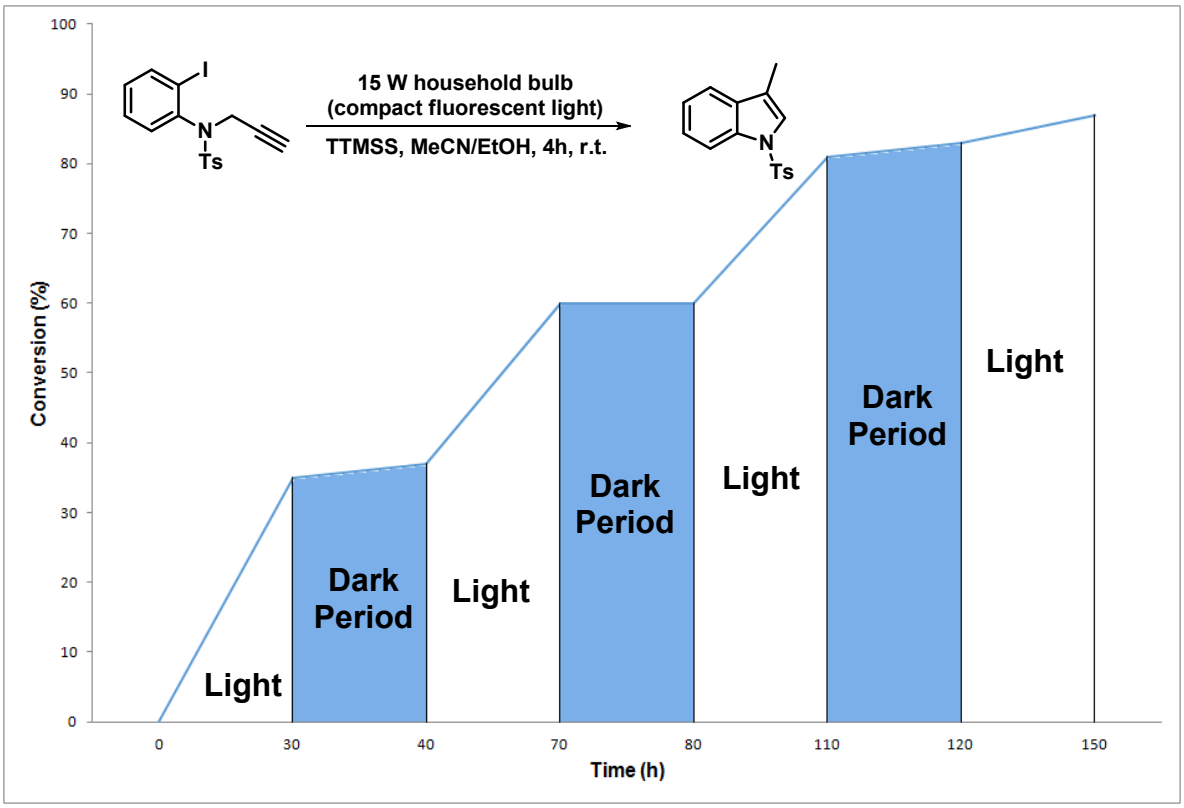
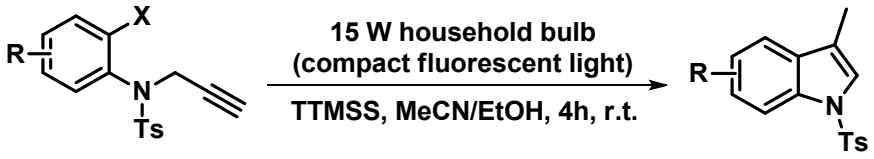


Figure S11: Graph of converstion over time in successive intervals of irradiation and dark periods for the model reaction.

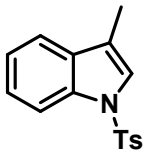
Comment: *These experiments indicate the necessity of irradiation, which presumably promotes the reaction by generating the excited state of the EDA-complex.*

E. General procedure for the photochemical intramolecular cyclization reaction

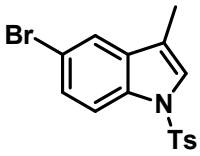
E1. Indole Synthesis



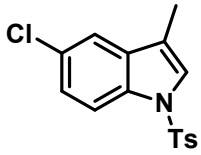
To a 5 mL vial equipped with a Teflon-coated magnetic stirring bar was added the N-tosyl-propargyl aniline (0.1 mmol, 1 equiv.), 0.4 mL acetonitrile (0.25 M), 29.2 µL (5 equiv) ethanol and TTMSS (0.1 mmol, 1 equiv). The reaction mixture was positioned approximately 5 cm away from the light source, and stirred at room temperature. After complete consumption of the starting material (followed by TLC), the reaction was quenched with 2 mL water, then aqueous layer was extracted with DCM (3x10 mL) and the combined organic layers were dried over Na_2SO_4. After vacuum removal of solvents, the crude product was purified by silica gel column chromatography (SiO_2, n-Hexane/EtOAc (9:1).



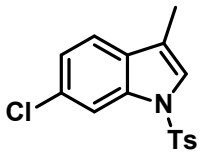
Compound 2a: The title compound was synthesized according to the general procedure in 92% (26.2 mg) isolated yield as a yellow solid (m.p: 102-103 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.00 (m, 5H), 2.19 (s, 3H), 2.11 (d, *J* = 1.2 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.6, 135.4, 135.2, 131.7, 129.7, 126.7, 124.5, 123.0, 122.9, 119.3, 118.5, 113.6, 21.5, 9.6. **HRMS**: calculated for $C_{16}H_{16}NO_2S$ $(M-H)^+$ 286.0902; found 286.0892.



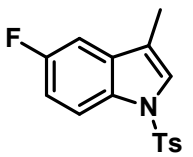
Compound 2d: The title compound was synthesized according to the general procedure in 53% (19.2 mg) isolated yield as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$)) δ 7.72 (d, *J* = 8.8 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.46 – 7.42 (m, 1H), 7.29 – 7.24 (m, 1H), 7.17 (d, *J* = 1.2 Hz, 1H), 7.11 – 7.05 (m, 2H), 2.21 (s, 3H), 2.07 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 135.1, 133.9, 133.5, 129.8, 127.4, 126.7, 124.2, 122.2, 117.9, 116.5, 115.1, 21.5, 9.5. **HRMS**: calculated for $C_{16}H_{15}BrNO_2S$ $(M-H)^+$ 364.0007; found 364.0013.



Compound 2e: The title compound was synthesized according to the general procedure in 62% (19.8 mg) isolated yield as a yellow solid (m.p: 111-113 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.40 (m, 1H), 7.26 (m, 4H), 2.34 (s, 3H), 2.20 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) 144.9, 135.1, 133.6, 133.0, 129.8, 128.9, 126.7, 124.7, 124.4, 119.2, 118.0, 114.7, 21.5, 9.5 ppm. **HRMS**: calculated for $C_{16}H_{15}ClNO_2S$ $(M-H)^+$ 320.0512; found 320.0528.

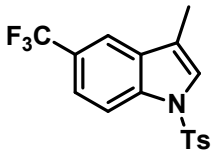


Compound 2f: The title compound was synthesized according to the general procedure in 70% (22.3 mg) isolated yield as yellow solid (m.p: 168-170 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.6 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.11 – 6.98 (m, 4H), 2.16 (s, 3H), 2.02 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 135.5, 135.2, 130.6, 130.2, 129.9, 126.7, 123.6, 123.5, 120.2, 118.3, 113.8, 21.5, 9.6. **HRMS**: calculated for $C_{16}H_{15}ClNO_2S$ $(M-H)^+$ 320.0512; found 320.0523.

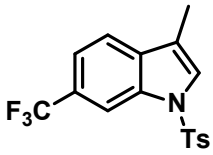


Compound 2g: The title compound was synthesized according to the general procedure in 50% (15.2 mg) isolated yield as a yellow solid (m.p: 98-100 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 1H), 7.56 – 7.49 (m, 2H), 7.17 – 7.12 (m, 1H), 7.05 – 6.99 (m, 2H), 6.93 – 6.80 (m, 2H), 2.15 (s, 3H), 2.01 (d, *J* = 1.3 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.8, 135.1, 129.8, 126.7,

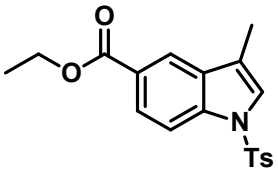
124.7, 118.4, 114.7, 114.6, 112.5, 112.3, 105.2, 104.9, 21.5, 9,6. **HRMS**: calculated for $C_{16}H_{15}FNO_2S$ $(M-H)^+$ 304.0808; found 304.0802.



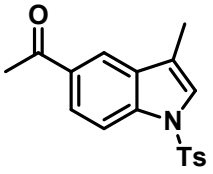
Compound 2h: The title compound was synthesized according to the general procedure in 51% (18.0 mg) isolated yield as a yellow solid (m.p: 117-119 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.36 (d, *J* = 8.7, 1H), 7.23 (d, *J* = 1.2 Hz, 1H), 7.10 – 7.00 (m, 2H), 2.16 (s, 3H), 2.09 (d, *J* = 1.3 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.8, 137.3, 135.7, 132.0, 130.5, 127.3, 125.2, 121.9, 121.9, 119.1, 117.6, 117.6, 114.4, 22.1, 10.1. **HRMS:** calculated for $C_{17}H_{15}F_3NO_2S$ $(M + H)^+$ 354.0776; found 354.0767.



Compound 2i: The title compound was synthesized according to the general procedure in 52% (18.4 mg) isolated yield as a yellow solid (m.p: 131-133 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.41 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 2.26 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.2, 135.0, 134.4, 134.2, 130.0, 126.8, 125.5, 119.9, 119.8, 119.7, 118.2, 111.1, 111.0, 21.6, 9.6. **HRMS:** calculated for $C_{17}H_{15}O_2F_3NS$ $(M + H)^+$ 354.0776; found 354.0766.

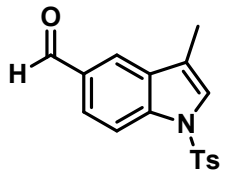


Compound 2j: The title compound was synthesized according to the general procedure in 65% (23.2 mg) isolated yield as an off brown solid (m.p: 115-117 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (t, *J* = 1.2 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.66 (d, 8,6 Hz, 2H), 7.28 (q, *J* = 1.1 Hz, 1H), 7.12 (d, *J* = 8.6, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.24 (s, 3H), 2.19 (d, *J* = 1.3 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 145.1, 137.7, 135.2, 131.6, 129.9, 126.7, 125.8, 125.4, 124.2, 121.7, 119.0, 113.3, 60.9, 21.6, 14.4, 9.6. **HRMS:** calculated for $C_{19}H_{20}O_4NS$ $(M + H)^+$ 358.1113; found 358.1110.

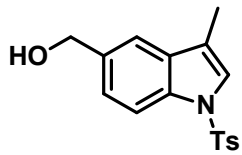


Compound 2k: The title compound was synthesized according to the general procedure in 50% (16.3 mg) isolated yield as a yellow solid (m.p: 143-145 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 1.7, 0.6 Hz, 1H), 7.86 (dd, *J* = 8.7, 0.6 Hz, 1H), 7.77 (dd, *J* = 8.7, 1.7 Hz, 1H),

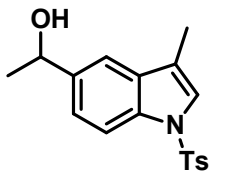
7.59 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 1.3 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 2.49 (s, 3H), 2.18 (s, 3H), 2.13 (d, *J* = 1.3 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 145.2, 137.8, 135.1, 132.5, 131.7, 129.9, 126.8, 124.9, 124.4, 120.5, 119.2, 113.4, 26.8, 21.6, 9.6. **HRMS:** calculated for $C_{18}H_{18}O_3NS$. $(M + H)^+$ 328.1007, found 328.0996.



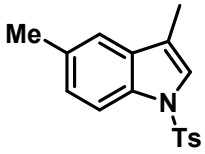
Compound 2l: The title compound was synthesized according to the general procedure in 45% (14.1 mg) isolated yield as a yellow solid (m.p: 138-140 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 1.0 Hz, 1H), 7.77 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.69 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.34 (d, *J* = 1.2 Hz, 1H), 7.18 ((d, *J* = 8.5 Hz, 2H) 2.28 (s, 3H), 2.23 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.9, 145.3, 138.6, 135.1, 131.9, 130.0, 127.0, 126.8, 125.7, 124.7, 122.4, 119.0, 113.9, 21.6, 9.6. **HRMS:** calculated for $C_{17}H_{16}O_3NS$ $(M + H)^+$ 314.0851; found 314.0857.



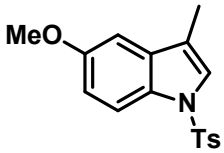
Compound 2m: The title compound was synthesized according to the general procedure in 82% (25.8 mg) isolated yield as a yellow solid (m.p: 60-62 °C). **^{1}H NMR** (400 MHz, $CDCl_3$ δ 7.87 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.6, 2H), 7.38 – 7,37 (m, 1H), 7.25 – 7.20 (m, 2H), 7.11 (d, *J* = 8.6, 2H), 4.67 (s, 2H), 2.24 (s, 3H), 2.15 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 135.8, 135.3, 134.8, 132.0, 129.8, 126.7, 123.9, 123.6, 118.6, 118.0, 113.8, 65.5, 21.5, 9.7. **HRMS:** calculated for $C_{17}H_{18}NO_3S$ $(M+H)^+$ 316.1007; found 316.1002.



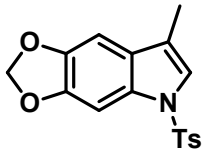
Compound 2n: The title compound was synthesized according to the general procedure in 52% (17.1 mg) isolated yield as a yellow solid (m.p: 81-83 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 - 7.72 (m, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (s, 1H), 7.18 (d, *J* = 8.6, 2H), 7.05 – 7.00 (m, 1H), 6.81 (d, *J* = 8.6, 2H) ,4.95 (q, *J* = 6.5 Hz), 2.34 (s, 3H), 2.18 (d, *J* = 1.3 Hz, 3H), 1.49 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 145.0, 144.1, 131.9, 131.4, 128.9, 128.8, 128.4, 127.2, 126.4, 124.6, 122.4, 69.8, 25.5, 21.7, 21.4. **HRMS:** calculated for $C_{18}H_{20}NO_3S$ $(M+H)^+$ 330.1164; found 330.1128.



Compound 2o: The title compound was synthesized according to the general procedure in 85% (25.4 mg) isolated yield as a yellow solid (m.p: 64-66 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.93 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.22 (s, 3H), 2.12 (s, 3H), 2.01 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.1, 136.0, 134.1, 133.2, 132.6, 130.3, 127.3, 126.5, 123.8, 119.9, 119.1, 113.9, 22.1, 21.9, 10.2. **HRMS:** calculated for $C_{17}H_{18}NO_2S$ $(M+H)^+$ 300.1058; found 300.1028.

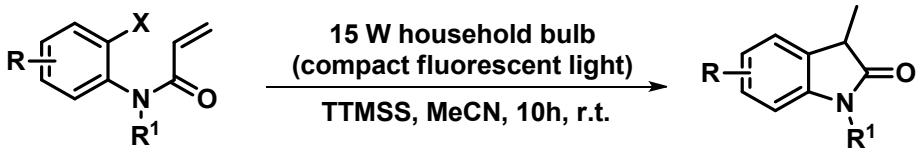


Compound 2p: The title compound was synthesized according to the general procedure in 85% (26.8 mg) isolated yield as a white solid (m.p: 111-113 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.17 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.74 (m, 2H), 3.75 (s, 3H), 2.25 (s, 3H), 2.12 (d, *J* = 1.1 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 144.5, 135.4, 132.8, 129.9, 129.7, 126.7, 123.9, 118.7, 114.6, 113.4, 101.9, 55.7, 21.5, 9.8. **HRMS:** calculated for $C_{17}H_{18}NO_3S$ $(M+H)^+$ 316.1007; found 316.0995.

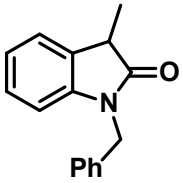


Compound 2q: The title compound was synthesized according to the general procedure in 82% (27.0 mg) isolated yield as a white viscous oil.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.49 (m, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.18 (m, 1H), 6.81 – 6.75 (m, 1H), 5.96 (s, 2H), 2.34 (s, 3H), 2.15 (d, *J* = 1.2 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 144.9, 144.6, 135.3, 130.0, 129.8, 126.7, 126.1, 122.08, 118.8, 101.3, 98.3, 95.5, 21.6, 9.8. **HRMS:** calculated for $C_{17}H_{16}NO_4S$ $(M+H)^+$ 330.0800; found 330.0791.

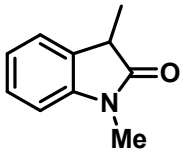
E2. Oxindole Synthesis



To a 5 mL vial equipped with a Teflon-coated magnetic stirring bar was added the N-benzyl-acrylamides (0.1 mmol, 1 equiv.), 0.4 ml acetonitrile (0.25 M) and TTMSS (0.2 mmol, 2 equiv). The reaction mixture was positioned approximately 5 cm away from the light source, and stirred at room temperature. After complete consumption of the starting material (followed by TLC), the reaction was quenched with 2 mL water, then aqueous layer was extracted with DCM (3x10 mL) and the combined organic layers were dried over Na_2SO4. After vacuum removal of solvents, the crude product was purified by silica gel chromatography (SiO_2, n-Hexane/EtOAc (9:1).

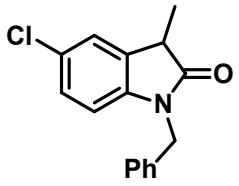


Compound 4a: The title compound was synthesized according to the general procedure in 80% (19.0 mg) isolated yield as viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 6H), 7.35 – 7.30 (m, 1H), 7.21 – 7.16 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.08 (s, 2H), 3.71 (q, *J* = 7.6 Hz, 1H), 1.71 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8, 143.1, 135.9, 130.6, 128.7, 127.8, 127.6, 127.3, 123.6, 122.4, 108.9, 43.7, 40.6, 15.6. **HRMS:** calculated for $C_{16}H_{16}NO$ $(M+H)^+$ 238.1232; found 238.1223.

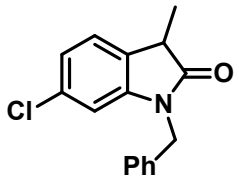


Compound 4b: The title compound was synthesized according to the general procedure in 54% (8.7 mg) isolated yield as yellow oil.[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 2H), 6.94 – 6.89 (m, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 3.29 (q, *J* = 7.6 Hz, 1H), 3.06 (s, 3H), 1.33 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.7, 127.9, 123.5, 123.2, 122.4, 108.5, 107.9, 40.6, 26.2, 15.3. **HRMS:** calculated for $C_{10}H_{12}NO$ $(M+H)^+$ 162.0919; found 162.0863.

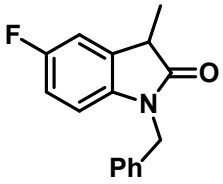
[6] B. Li, Y. Park, S. Chang, *J. Am. Chem. Soc*. **2014**, 136, 1125−1131



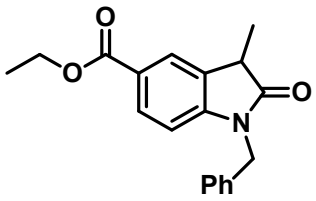
Compound 4c: The title compound was synthesized according to the general procedure in 65% (17.6 mg) isolated yield as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.07 (m, 6H), 7.03 – 6.94 (m, 1H), 6.48 (d, *J* = 8.3 Hz, 1H), 4.76 (s, 2H), 3.41 (q, *J* = 7.6 Hz, 1H), 1.40 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.2, 142.8, 141.6, 135.5, 132.3, 128.8, 127.9, 127.7, 127.2, 124.2, 109.9, 43.8, 40.6, 15.5. **HRMS:** calculated for $C_{16}H_{15}ClNO$ $(M+H)^+$ 272.0842; found 272.0867.



Compund 4d: The title compound was synthesized according to the general procedure in 45% (12.2 mg) isolated yield as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 5H), 7.02 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.87 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.58 (d, *J* = 1.8 Hz, 1H), 4.75 (s, 2H), 3.38 (q, *J* = 7.6 Hz, 1H), 1.40 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$ δ 178.6, 144.2, 135.4, 133.5, 128.9, 128.5, 127.8, 127.2, 124.4, 122.3, 109.5, 43.7, 40.1, 15.5. **HRMS:** calculated for $C_{16}H_{15}ClNO$ $(M+H)^+$ 272.0842; found 272.0823.

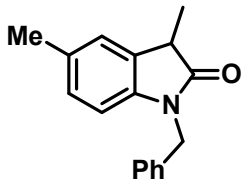


Compund 4e: The title compound was synthesized according to the general procedure in 56% (14.3 mg) isolated yield as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 5H), 7.16 – 7.08 (m, 1H), 7.04 – 6.91 (m, 1H), 6.74 (dd, *J* = 8.5, 4.2 Hz, 1H), 5.01 (s, 2H), 3.67 (q, *J* = 7.7 Hz, 1H), 1.73 (s, 3H), 1.67 (d, *J* = 7.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.4, 158.0, 135.7, 128.8, 127.7, 127.2, 114.1, 113.8, 111.9, 111.6, 109.4, 43.8, 40.9, 15.5. **HRMS:** calculated for $C_{16}H_{15}FNO$ $(M+H)^+$ 256.1138; found 256.1107.

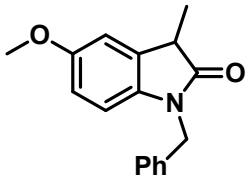


Compund 4f: The title compound was synthesized according to the general procedure in 51% (15.6 mg) isolated yield as oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.3 – 7.2 (m, 5H), 6.7 (d, *J* = 8.7 Hz, 1H), 4.8 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.5 (q, *J* = 7.6 Hz, 1H), 1.5 (d, *J* = 7.6 Hz, 3H), 1.3 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.9, 166.4, 147.1, 135.4, 130.5, 130.5, 128.9, 128.9, 127.8,

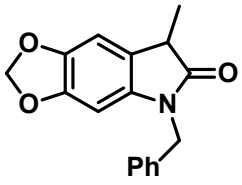
127.2, 124.8, 108.4, 60.8, 43.8, 40.3, 15.5, 14.4. **HRMS:** calculated for $C_{19}H_{20}NO_3$ $(M+H)^+$ 310.1453; found 310.1447.



Compound 4g: The title compound was synthesized according to the general procedure in 70% (17.8 mg) isolated yield as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 5H), 7.22 (m, 1H), 7.13 – 7.06 (m, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.05 (s, 2H), 3.66 (q, *J* = 7.6 Hz, 1H), 2.46 (s, 3H), 1.68 (d, *J* = 7.6 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8, 140.6, 136.1, 131.9, 130.7, 128.7, 127.9, 127.5, 127.2, 124.5, 108.7, 43.7, 40.6, 21.0, 15.7. **HRMS:** calculated for $C_{17}H_{18}NO$ $(M+H)^+$ 252.1388; found 252.1369.

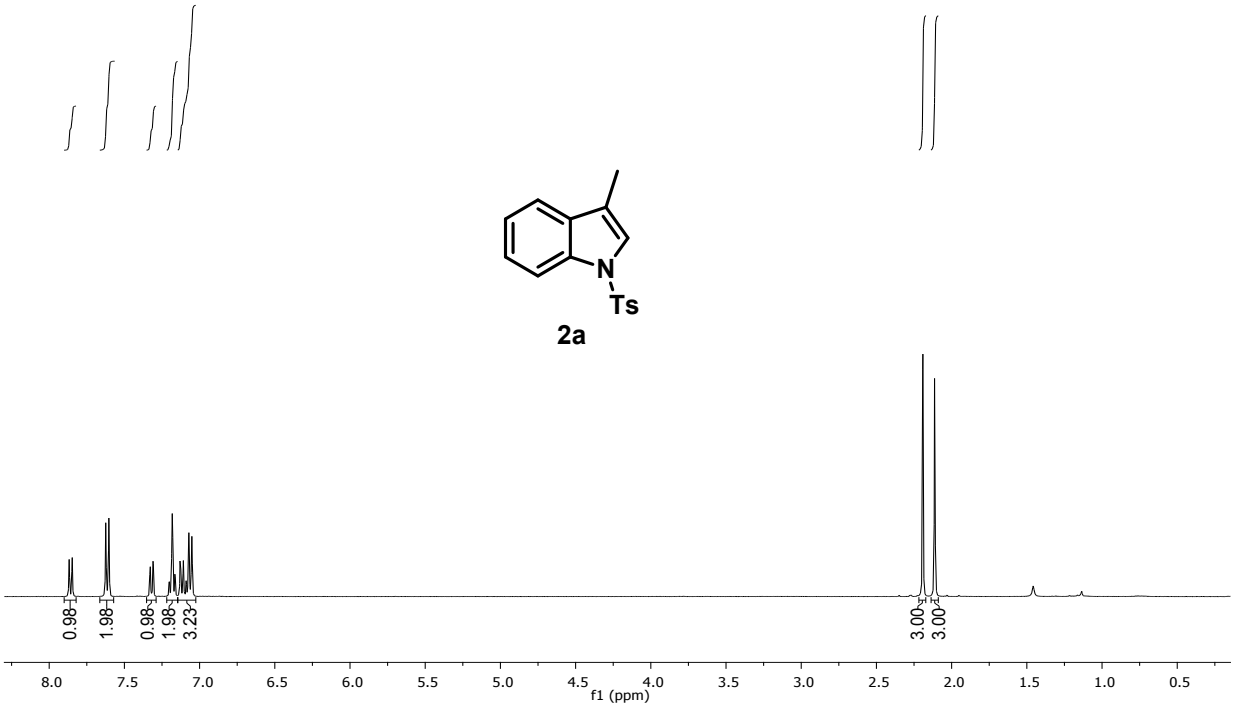


Compound 4h: The title compound was synthesized according to the general procedure in 72% (19.2 mg) isolated yield as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 5H), 6.82 – 6.77 (m, 1H), 6.61 - 6.59 (m, 1H), 6.52 (d, *J* = 8.5 Hz, 1H), 4.81 (s, 2H), 3.68 (s, 3H), 3.45 (q, *J* = 7.6 Hz, 1H), 1.45 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.4, 155.9, 136.5, 136.0, 132.0, 128.8, 127.5, 127.3, 111.9, 111.2, 109.3, 55.8, 43.7, 40.9, 15.7. **HRMS:** calculated for $C_{17}H_{18}NO_2$ $(M+H)^+$ 268.1338; found 268.1356.



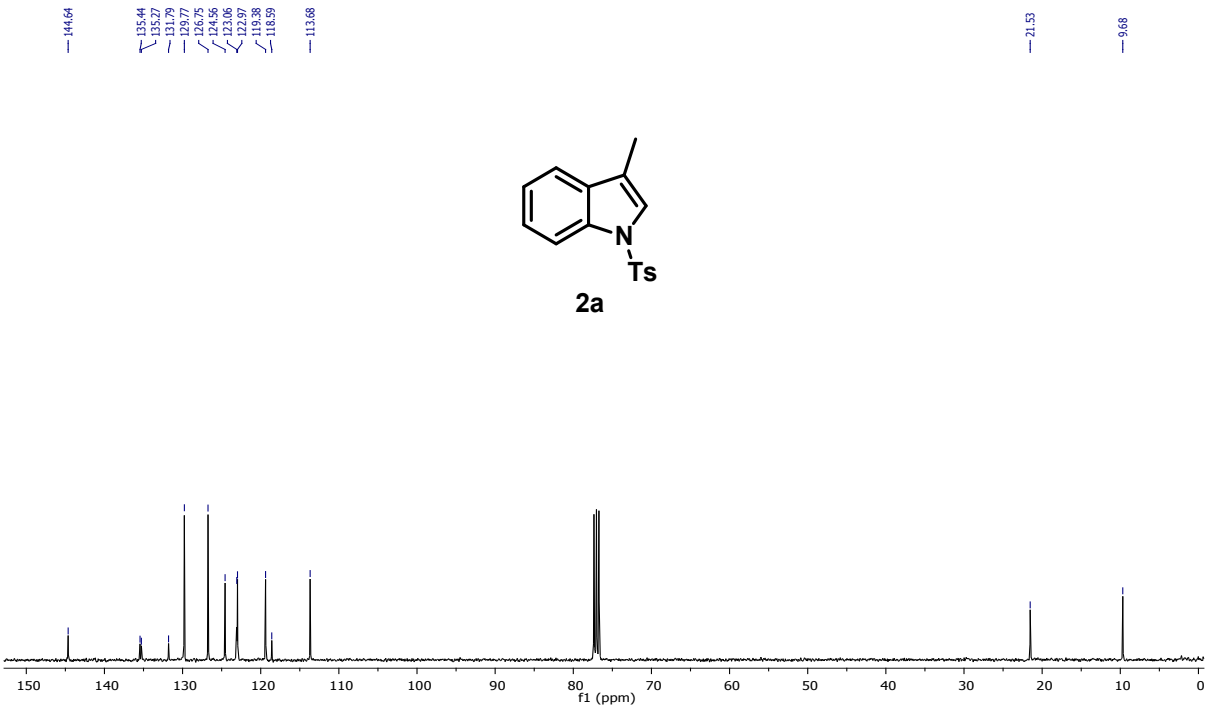
Compound 4h: The title compound was synthesized according to the general procedure in 45% (12.6 mg) isolated yield as oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ) δ 7.30 – 7.12 (m, 5H), 6.68 (s, 1H), 6.22 (s, 1H), 5.82 (s, 2H), 4.79 (s, 2H), 3.39 (q, *J* = 7.5 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.0, 146.9, 143.2, 137.1, 135.8, 128.8, 127.6, 127.2, 122.5, 105.3, 100.9, 93.0, 43.8, 40.8, 15.9. **HRMS:** calculated for $C_{17}H_{16}NO_3$ $(M+H)^+$ 282.1130; found 282.1138.

F. NMR Spectra



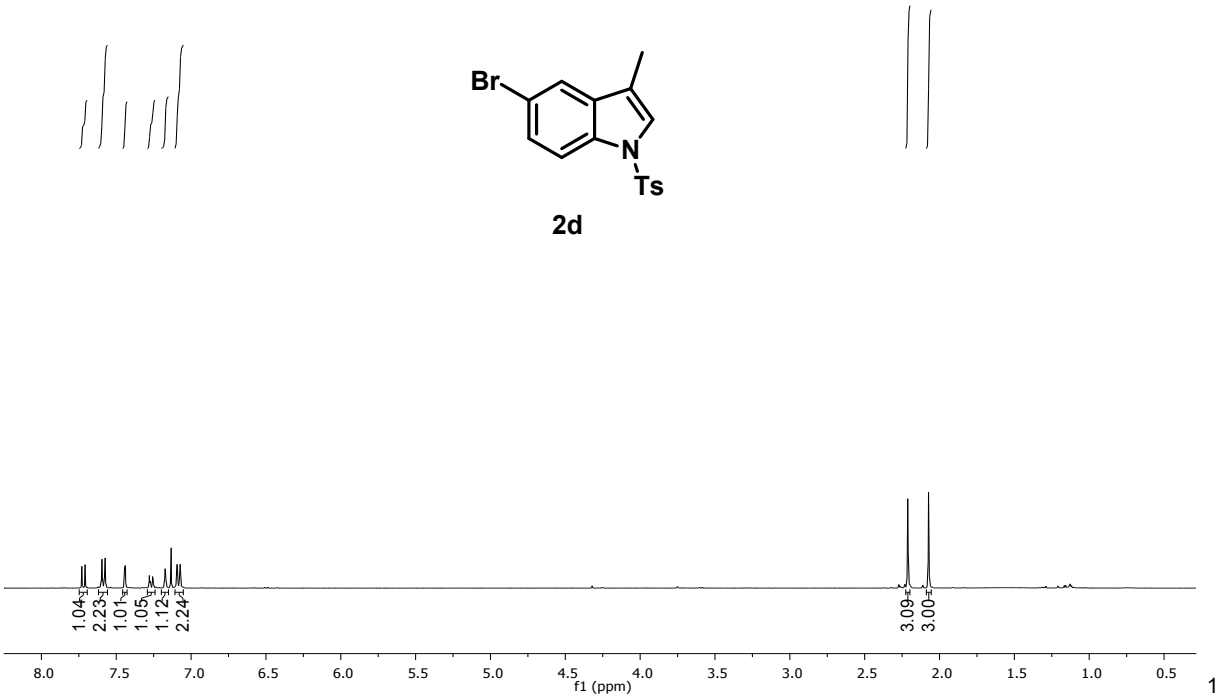
2a

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



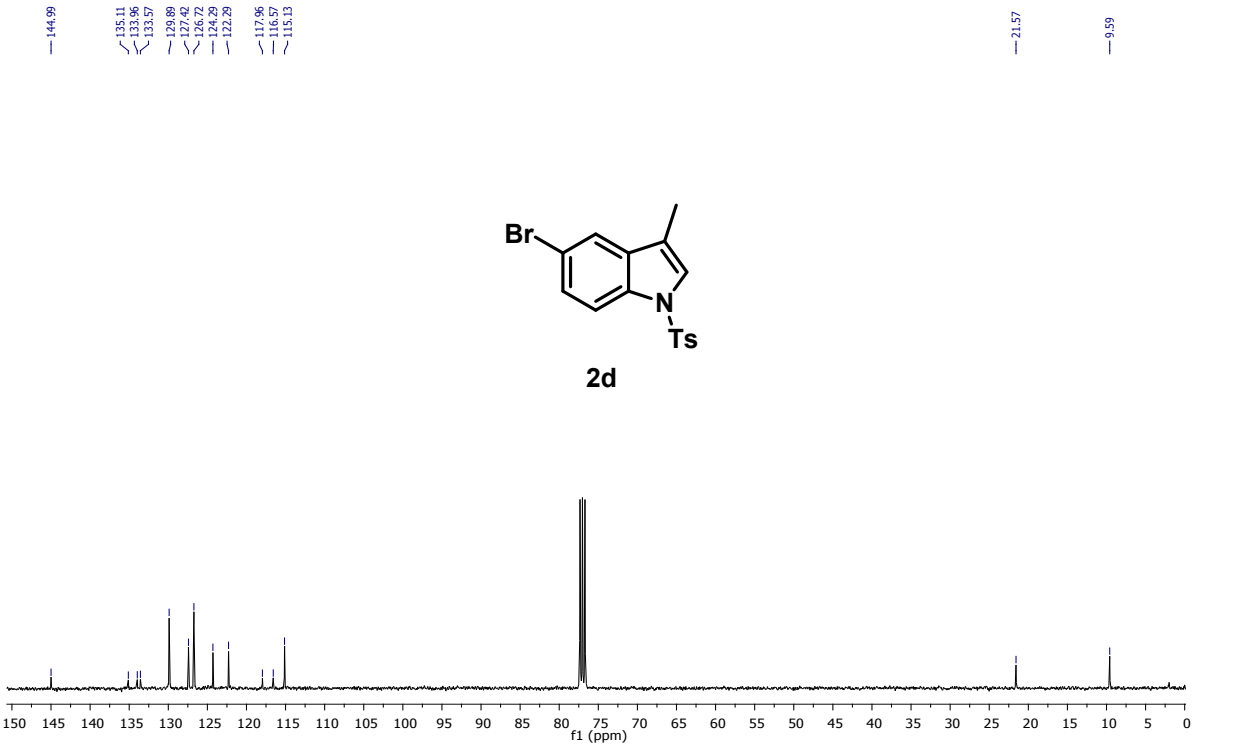
2a

^{13}C NMR of compound **2a** (100 MHz, $CDCl_3$)



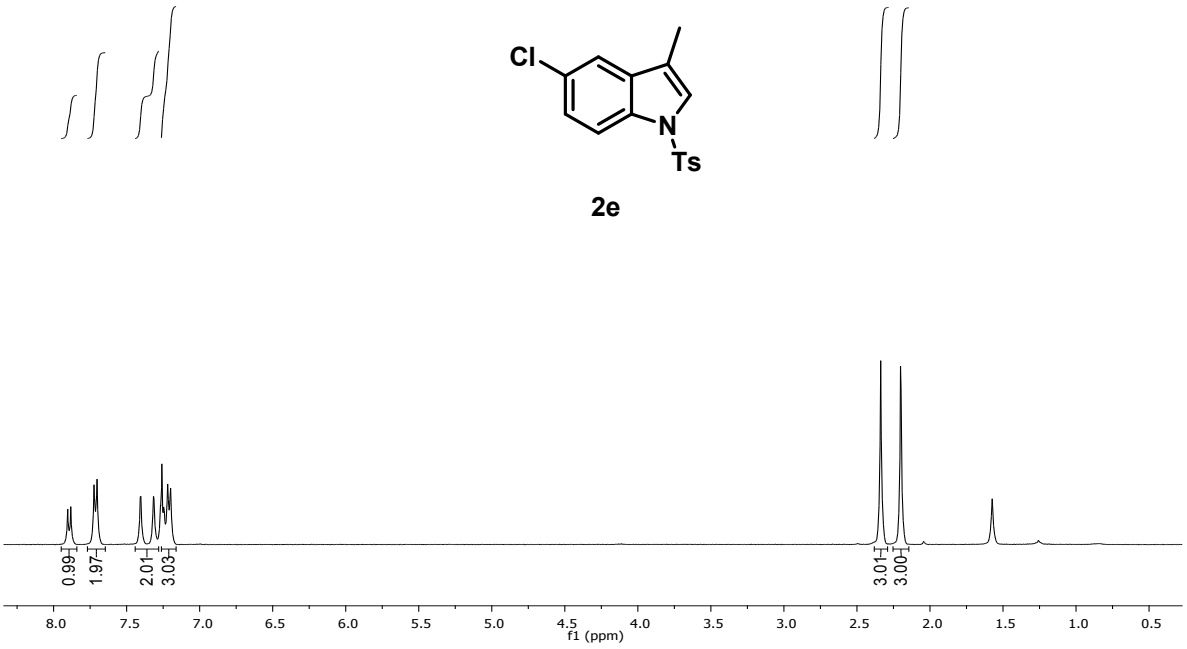
2d

H NMR of compound **2d** (400 MHz, $CDCl_3$)



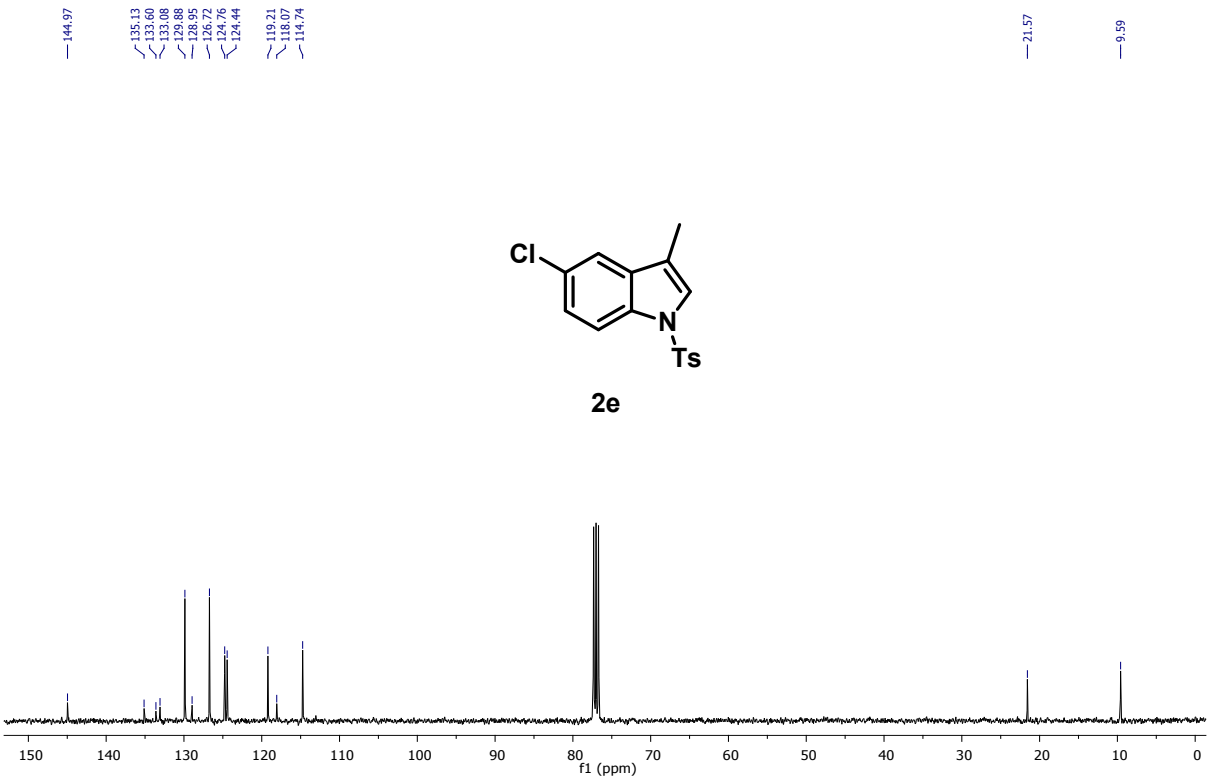
2d

^{13}C NMR of compound **2d** (100 MHz, $CDCl_3$)



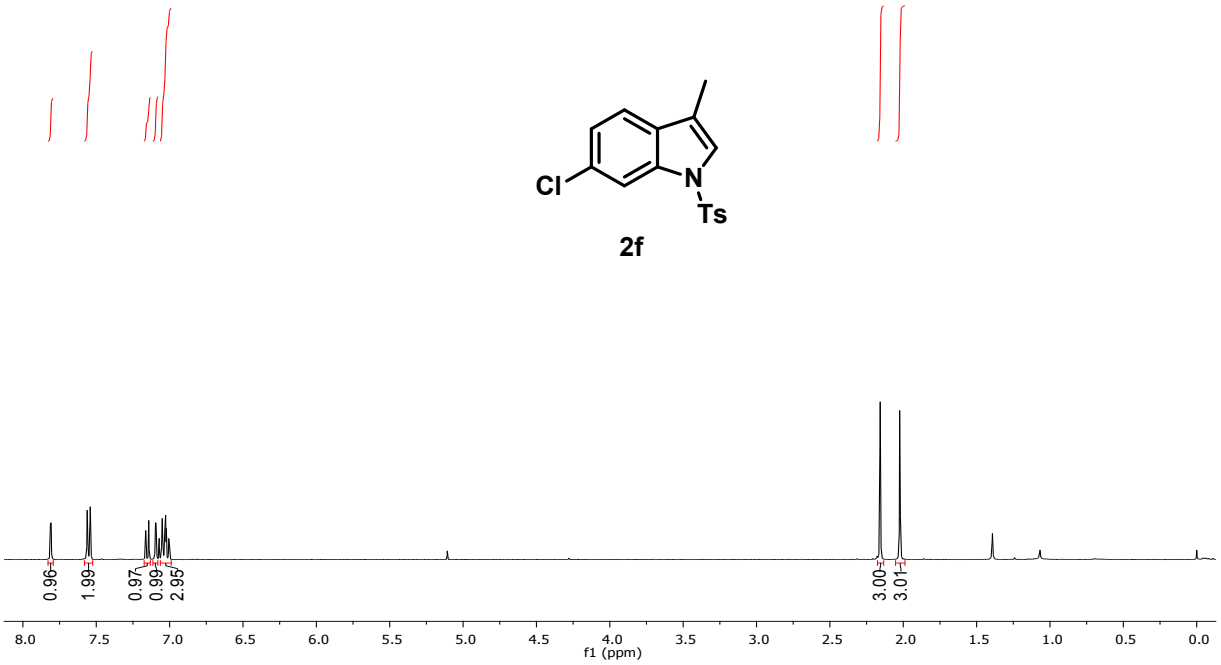
2e

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

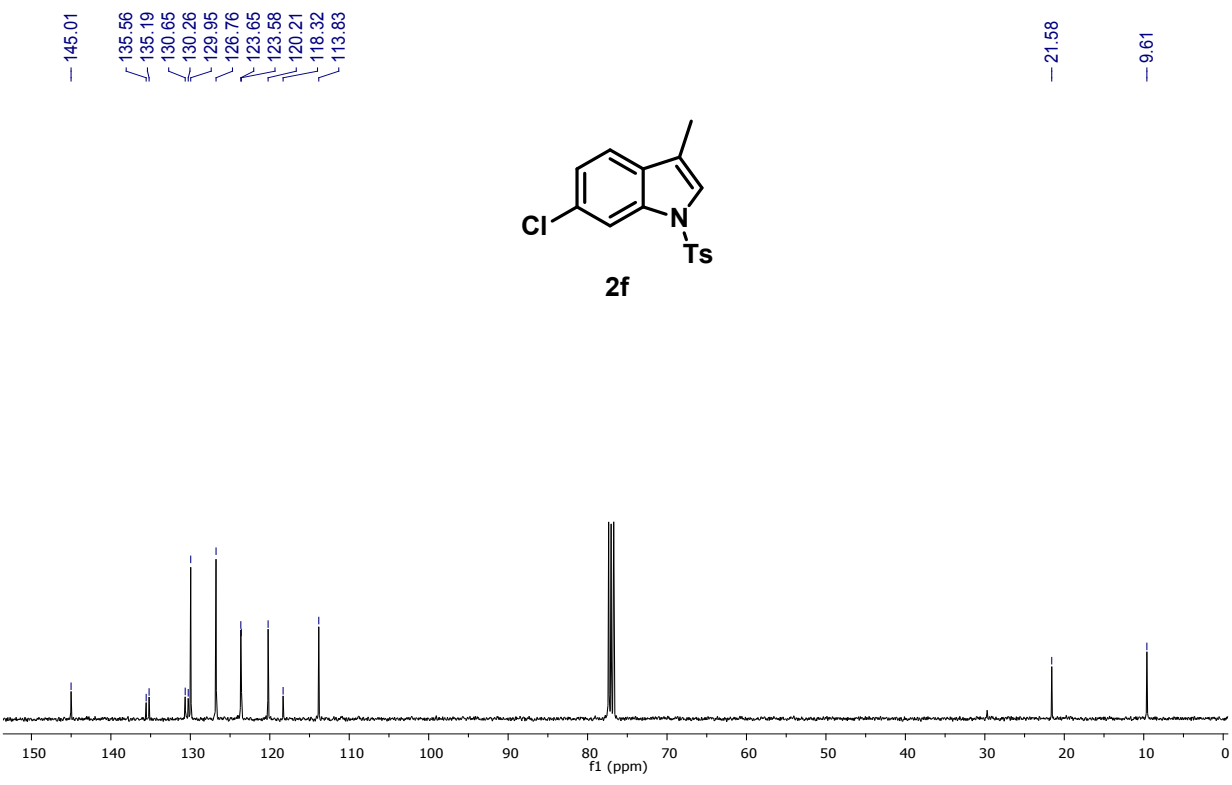


2e

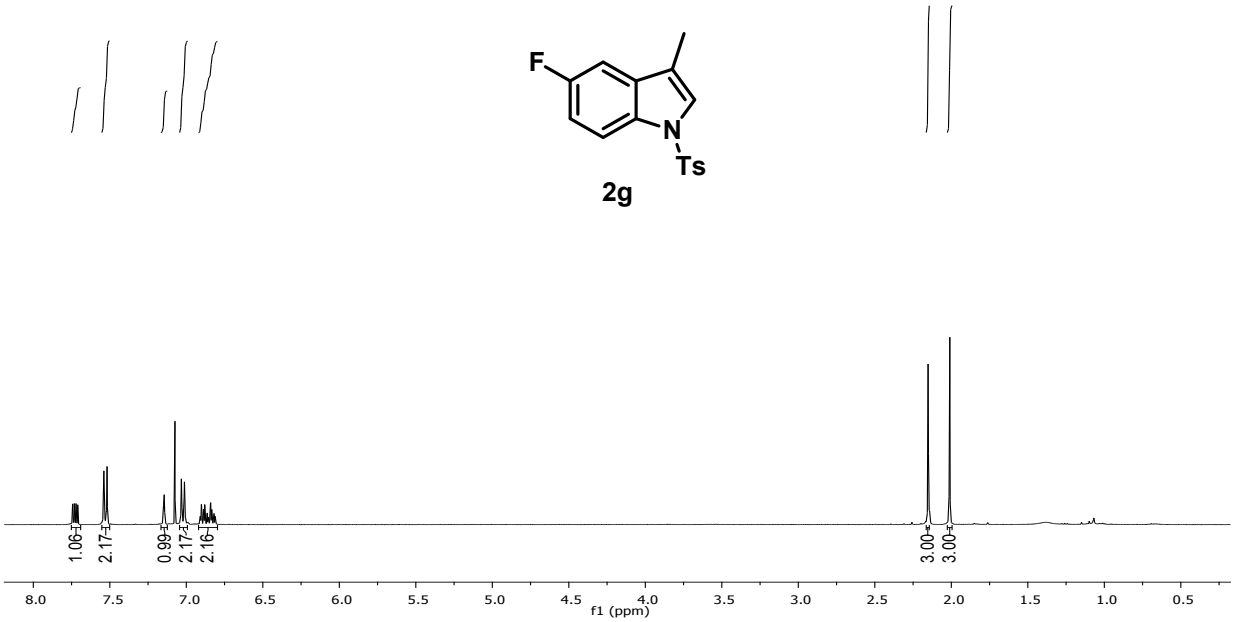
^{13}C NMR of compound **2e** (100 MHz, $CDCl_3$)



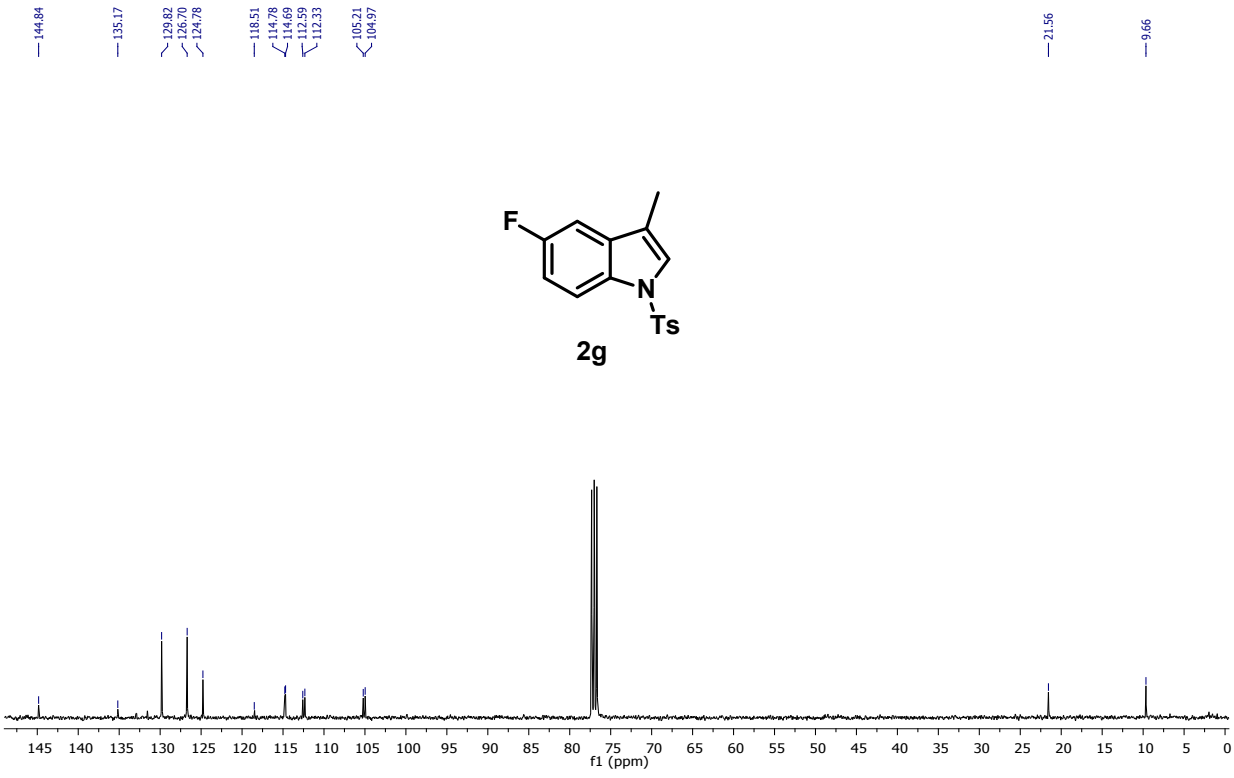
^{1}H NMR of compound **2f** (400 MHz, $CDCl_3$)



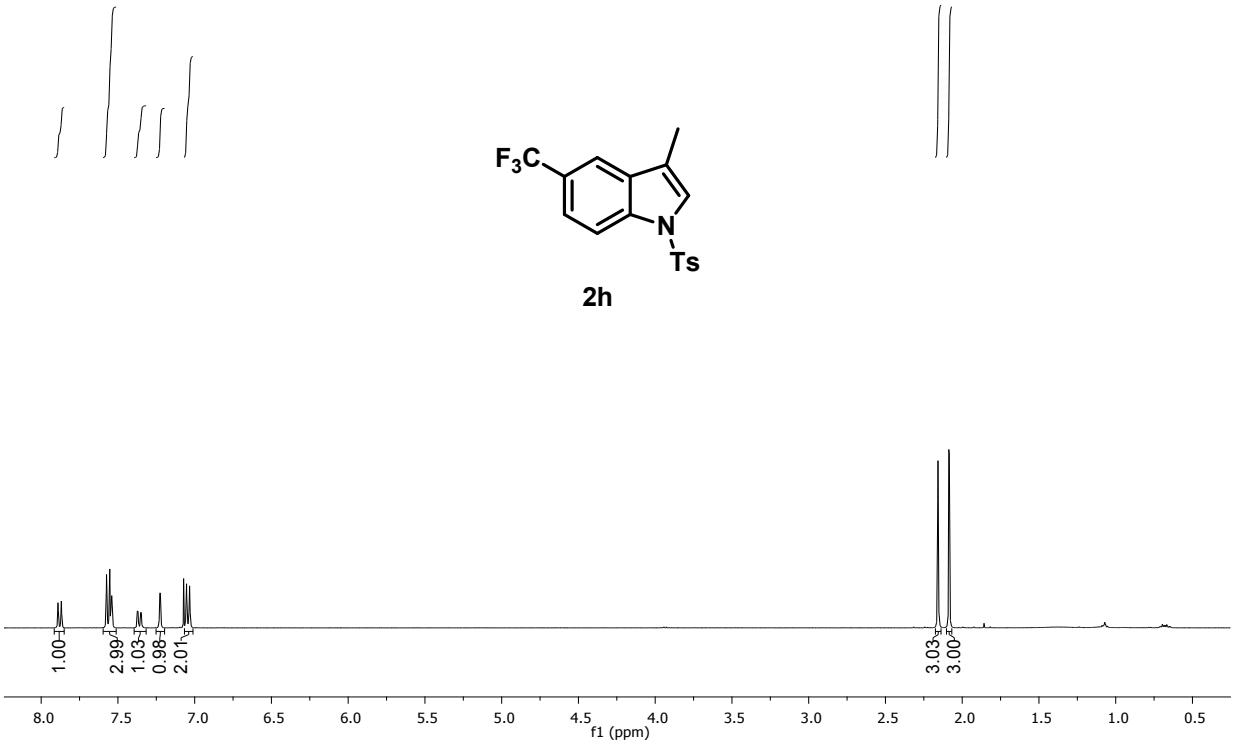
^{13}C NMR of compound **2f** (100 MHz, $CDCl_3$)



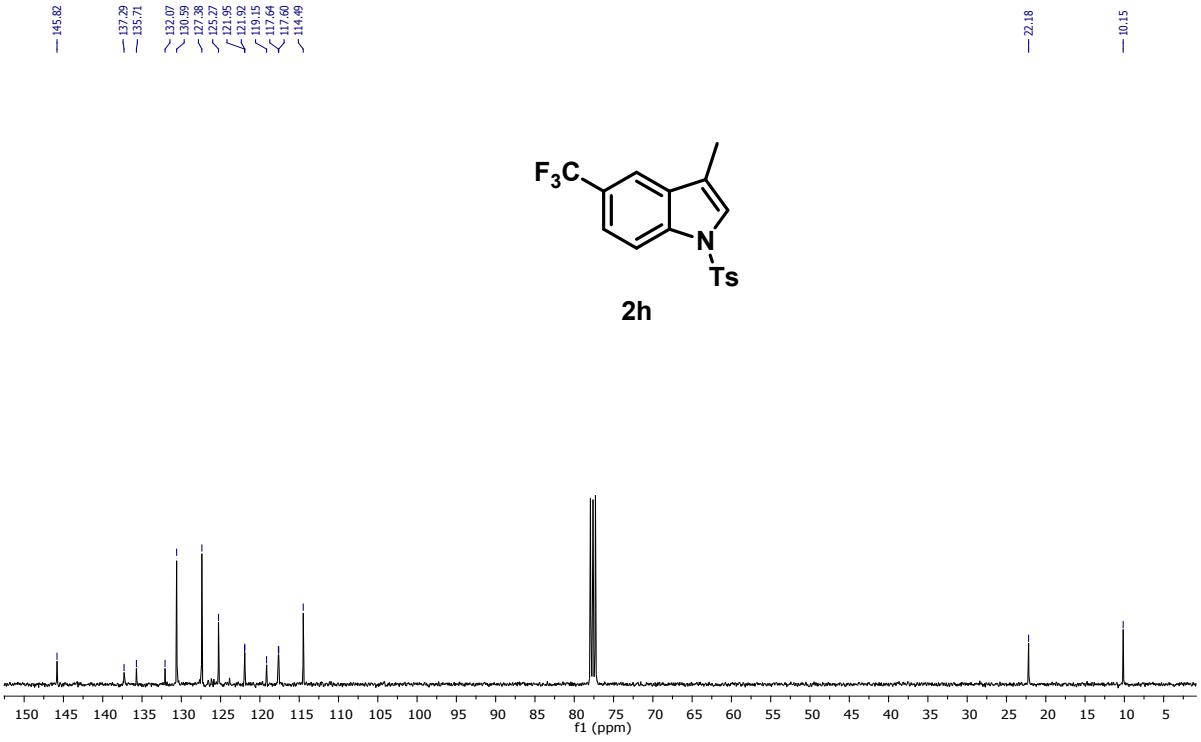
^{1}H NMR of compound **2g** (400 MHz, $CDCl_3$)



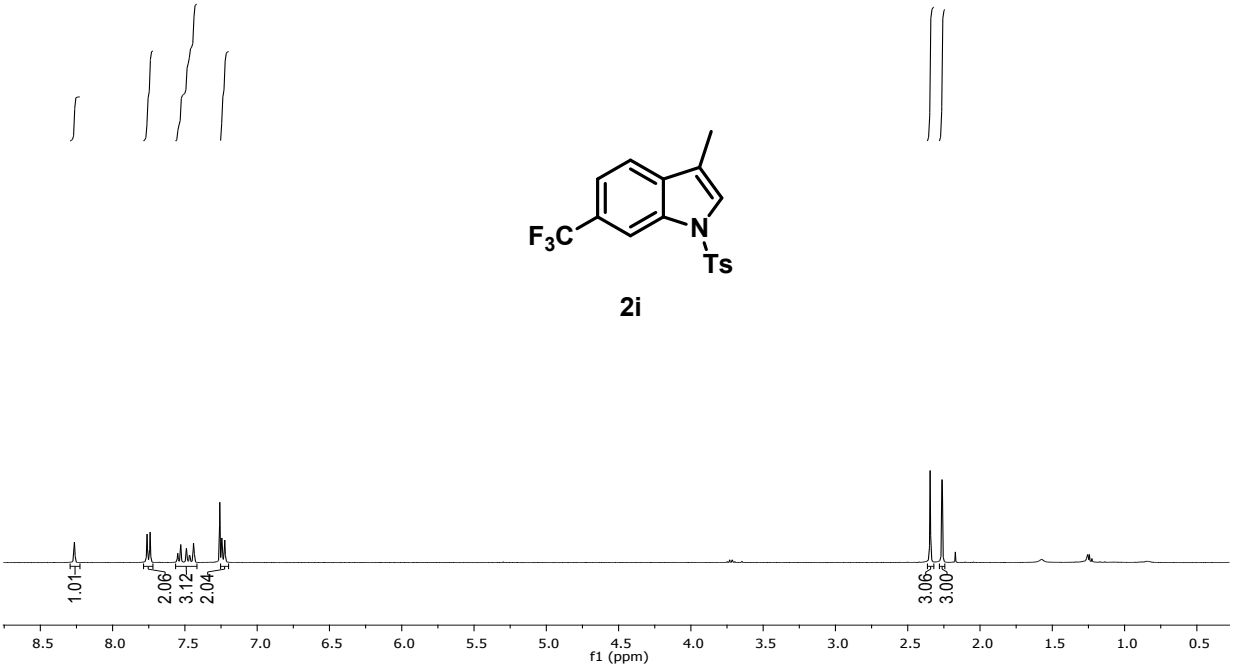
^{13}C NMR of compound **2g** (100 MHz, $CDCl_3$)



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

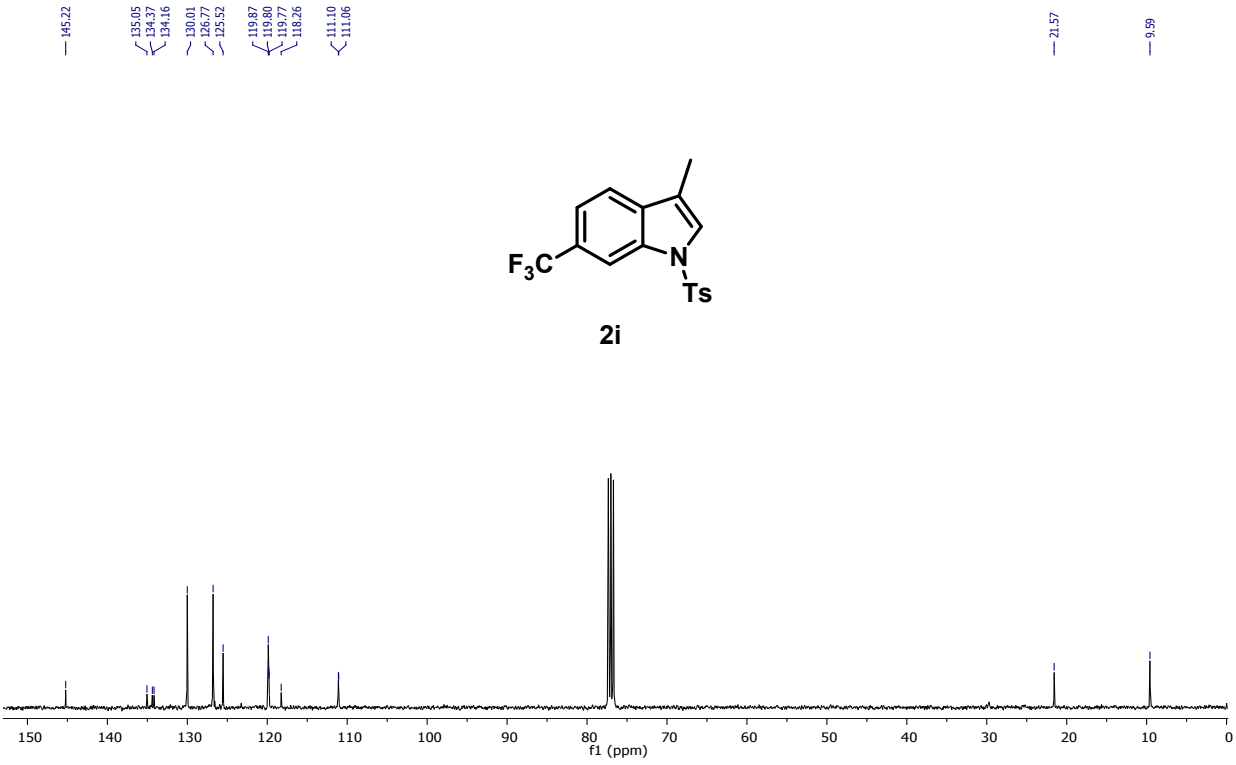


^{13}C NMR of compound **2h** (100 MHz, $CDCl_3$)



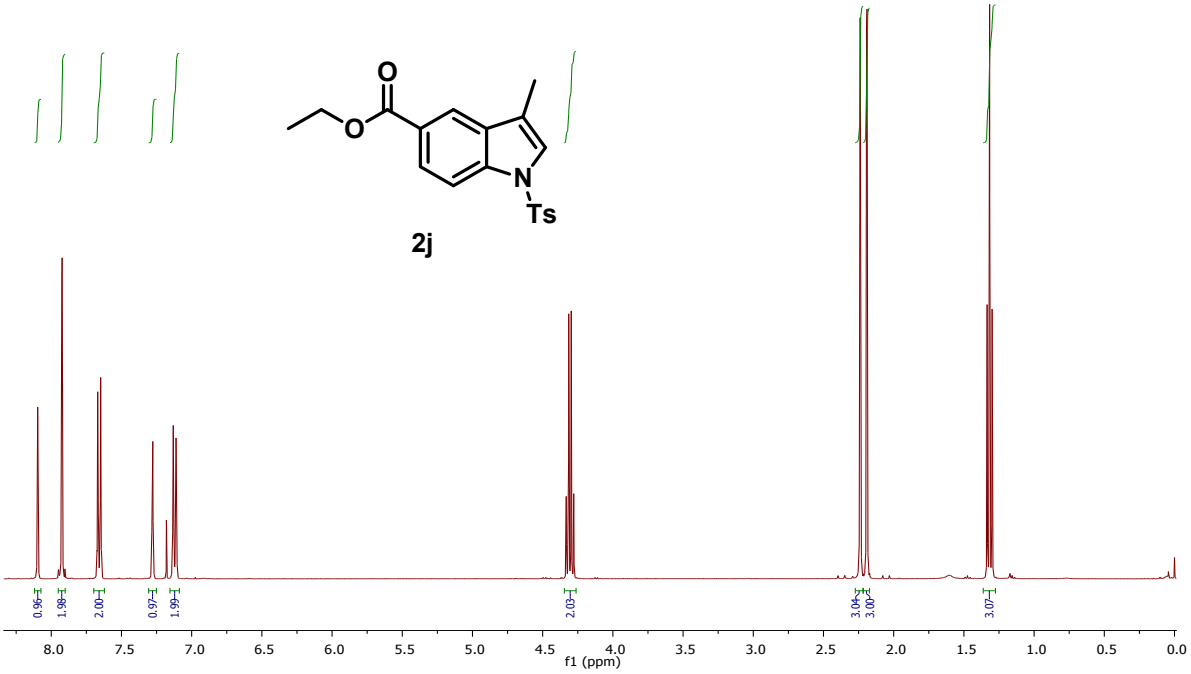
2i

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

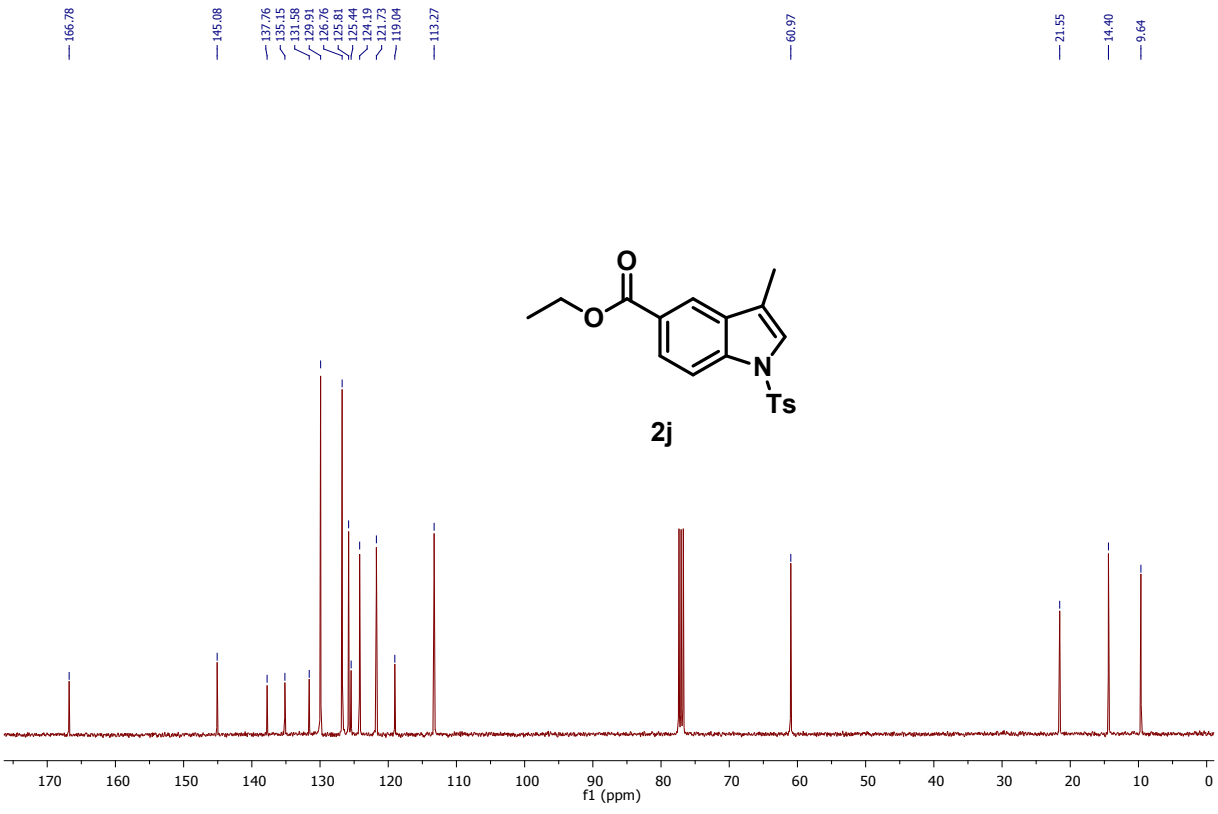


2i

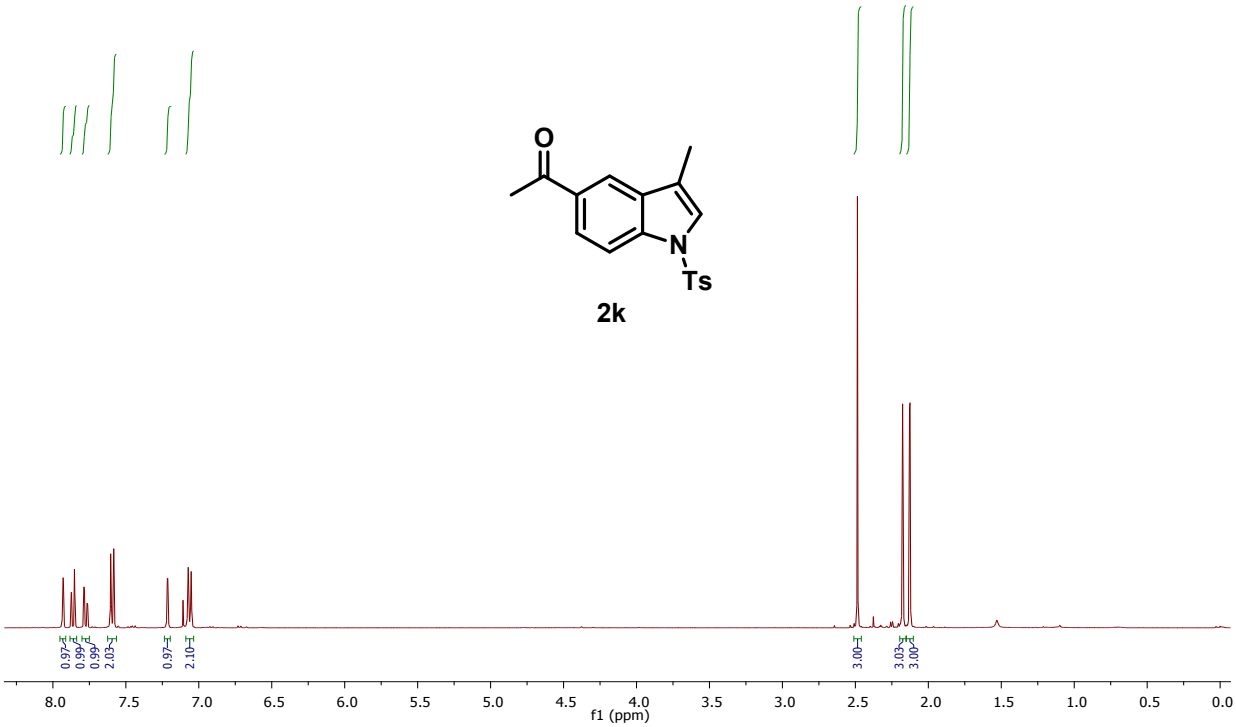
^{13}C NMR of compound **2i** (100 MHz, $CDCl_3$)



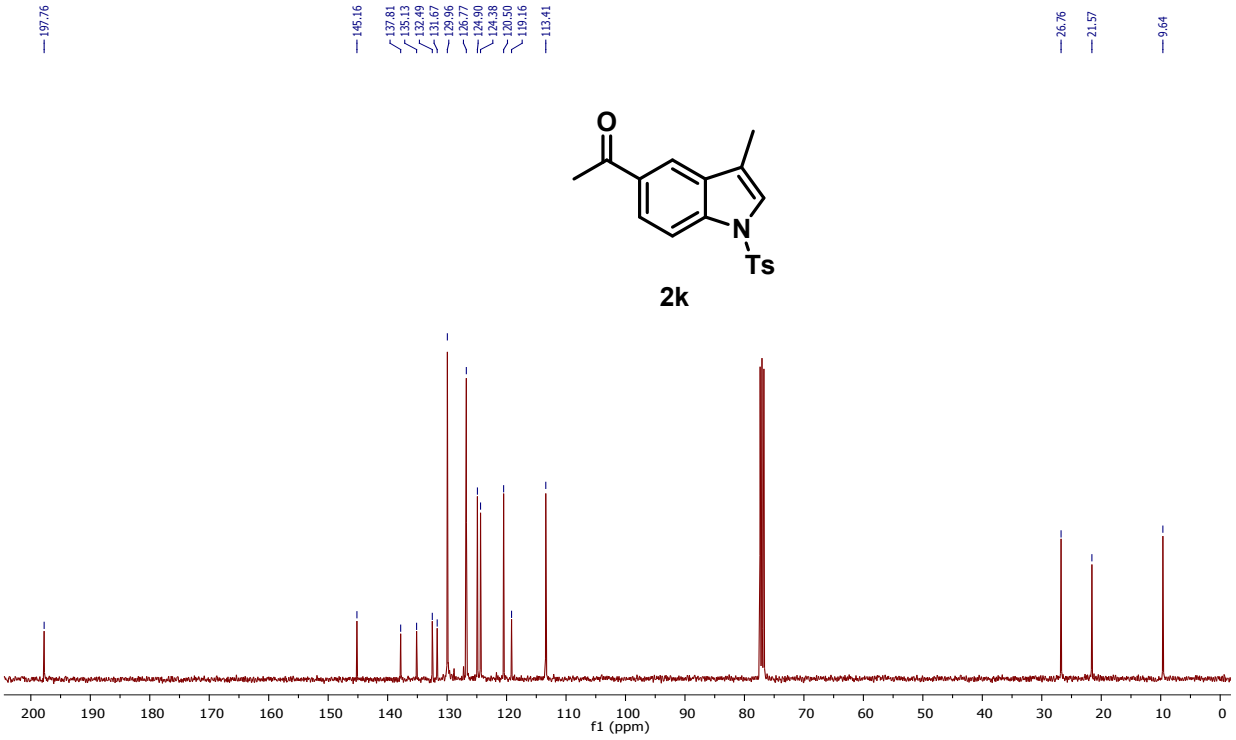
^{1}H NMR of compound **2j** (400 MHz, $CDCl_3$)



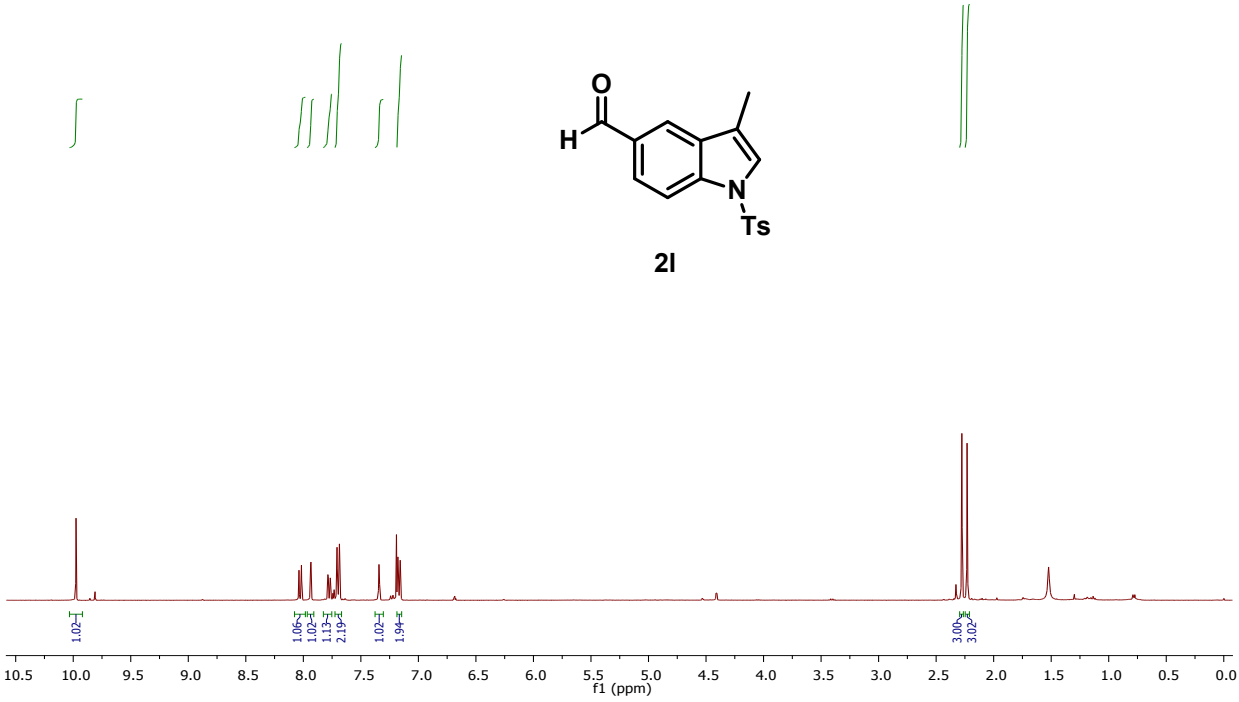
^{13}C NMR of compound **2j** (100 MHz, $CDCl_3$)



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

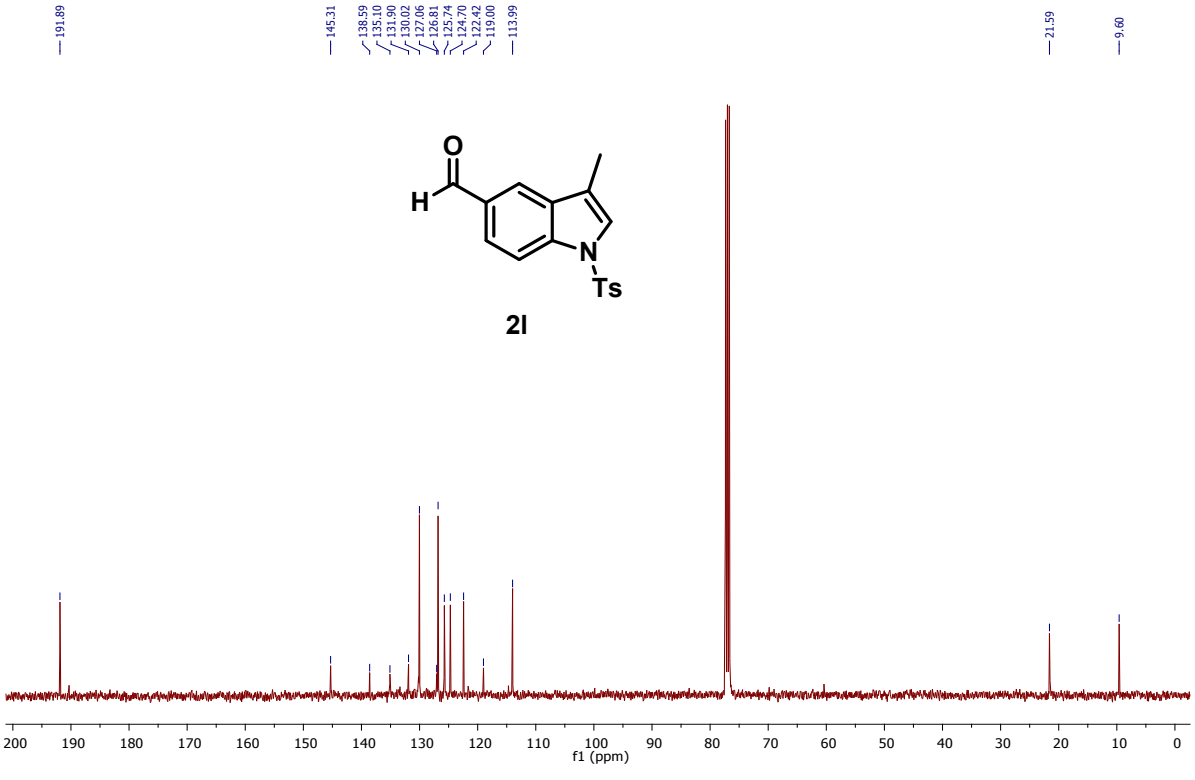


^{13}C NMR of compound **2k** (100 MHz, $CDCl_3$)



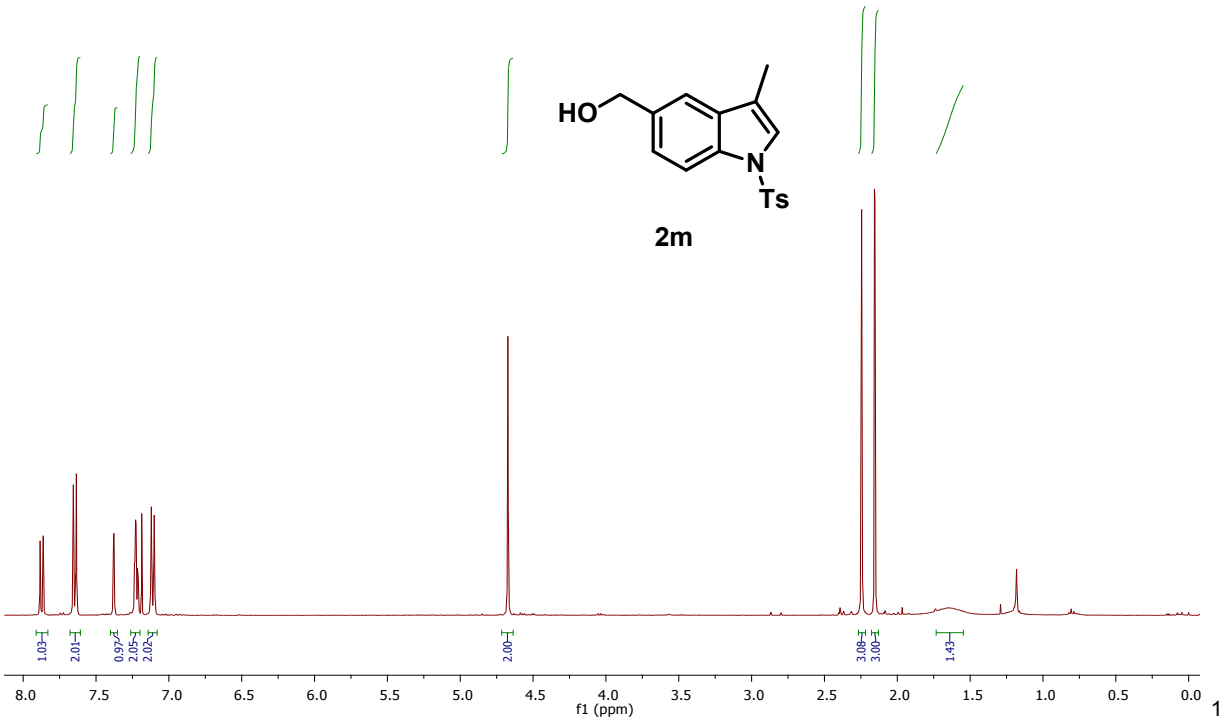
2l

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

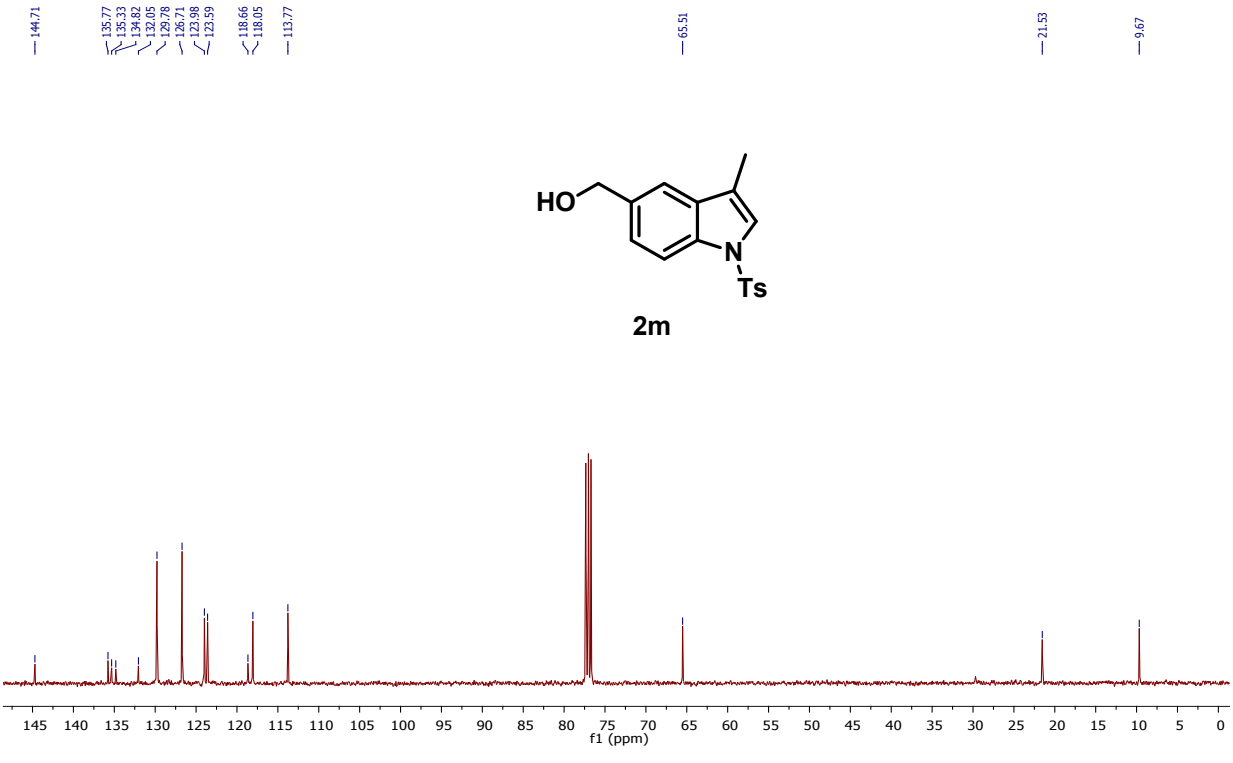


2l

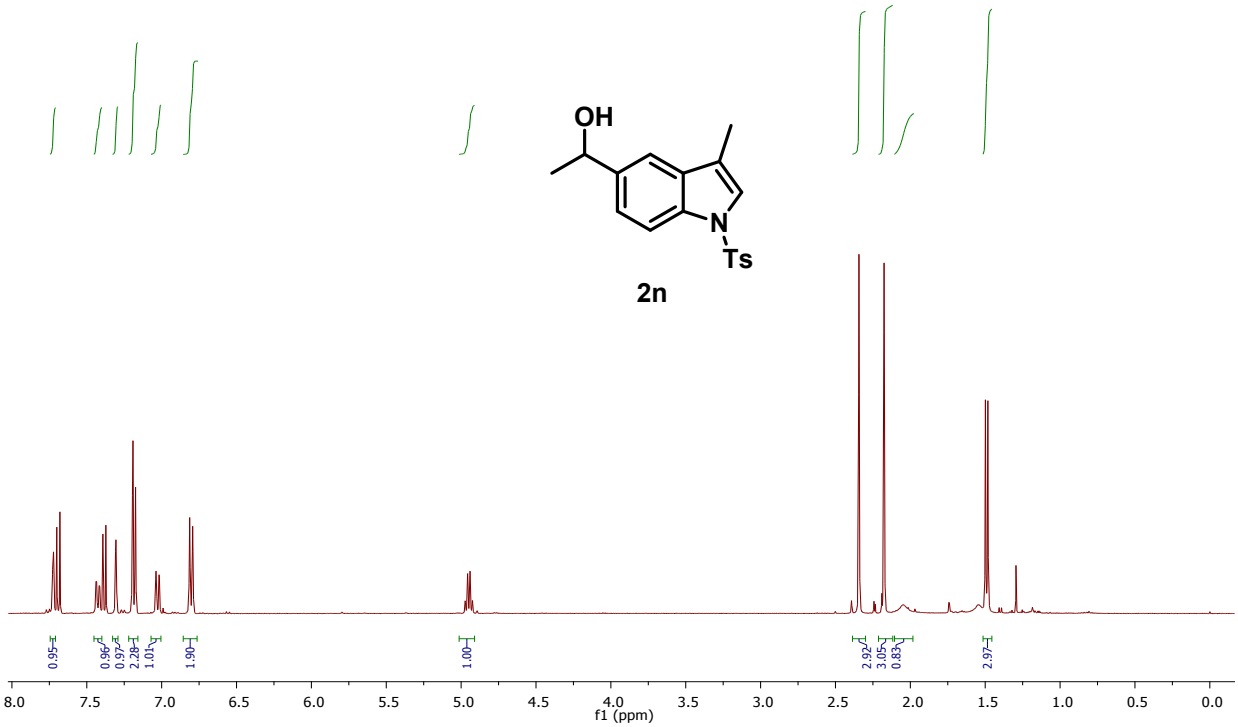
^{13}C NMR of compound **2l** (100 MHz, $CDCl_3$)



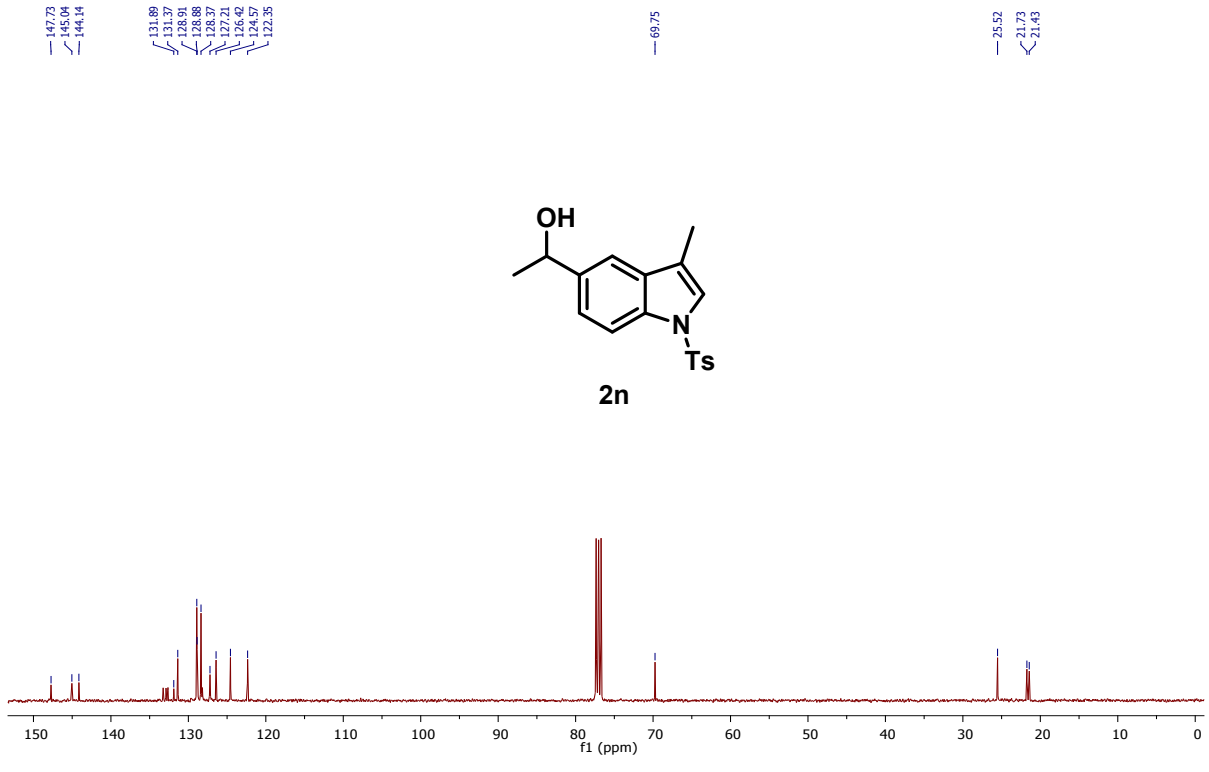
H NMR of compound **2m** (400 MHz, $CDCl_3$)



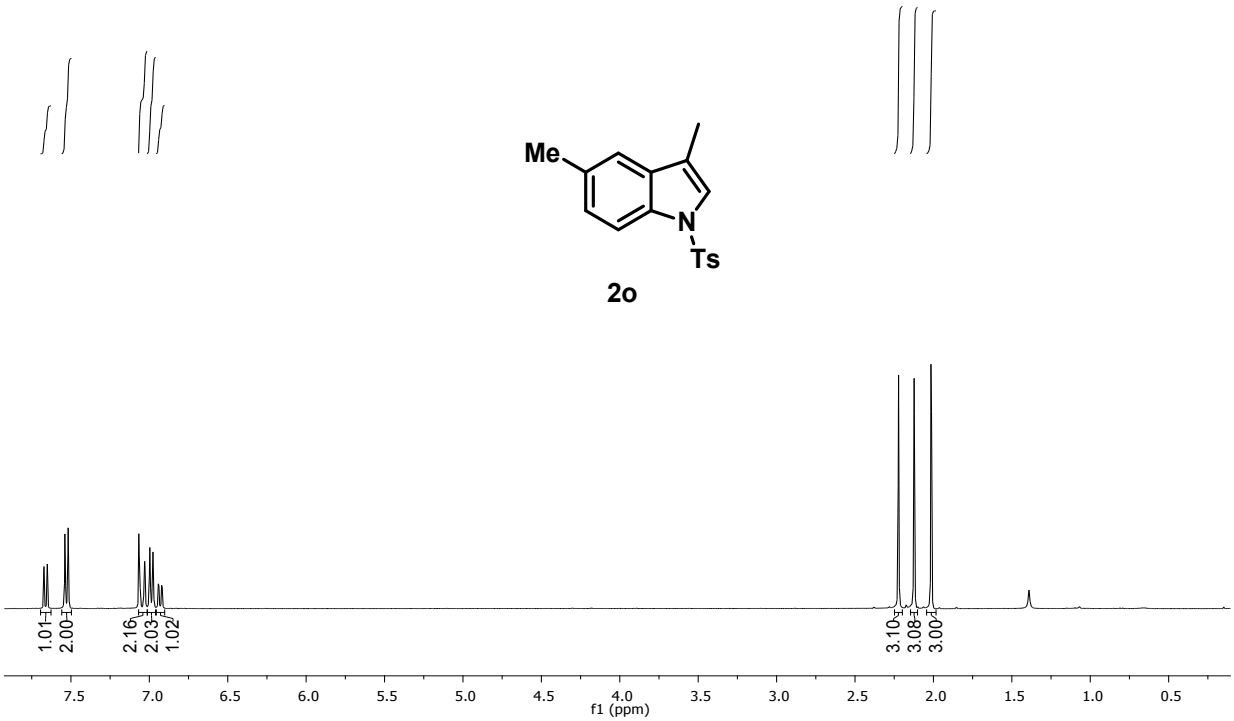
^{13}C NMR of compound **2m** (100 MHz, $CDCl_3$)



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

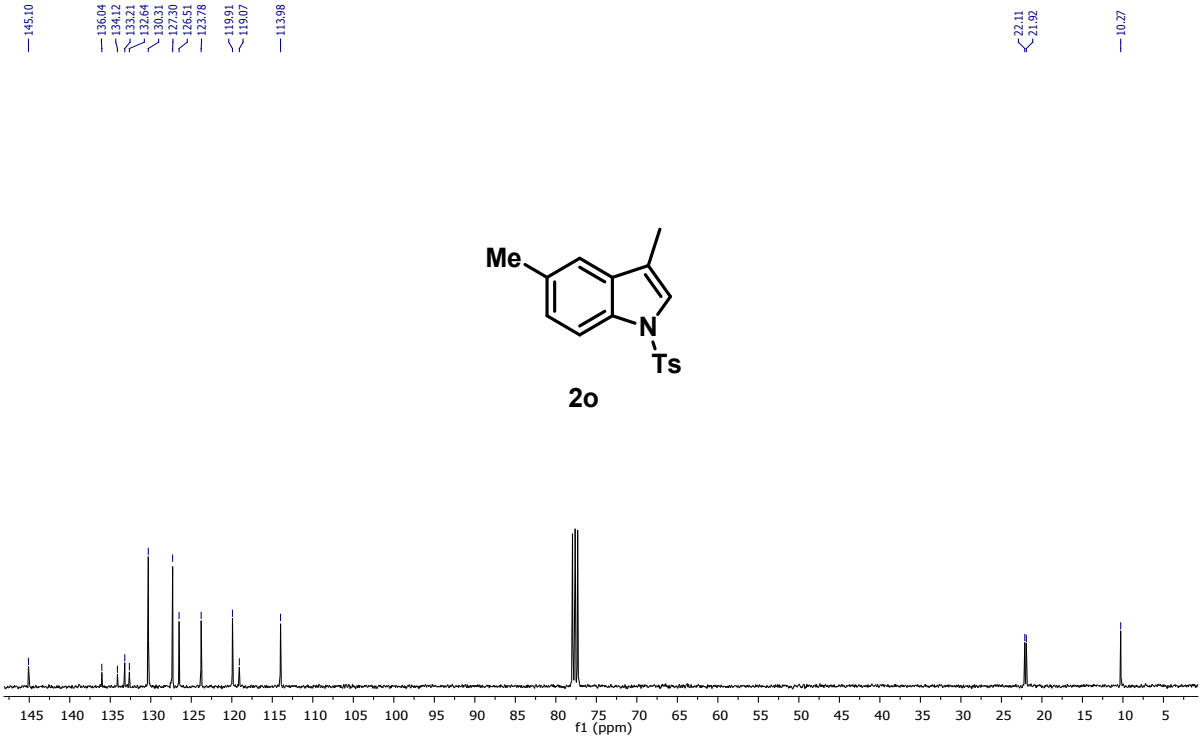


^{13}C NMR of compound **2n** (100 MHz, $CDCl_3$)



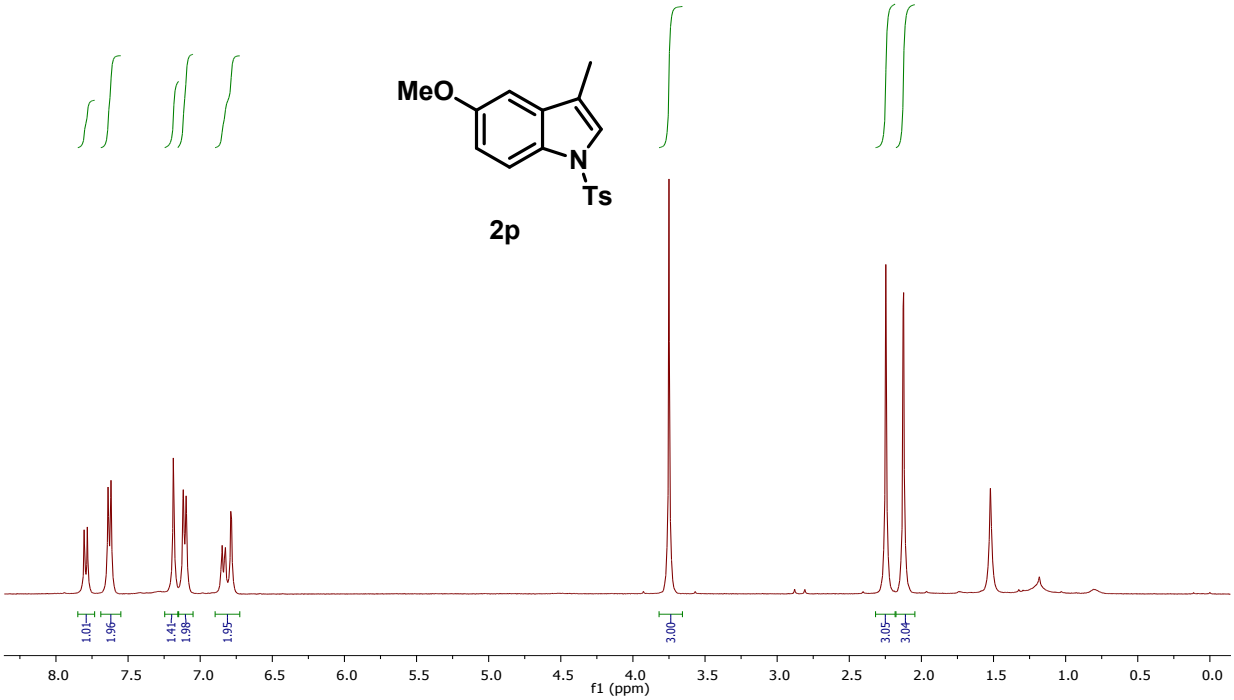
2o

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

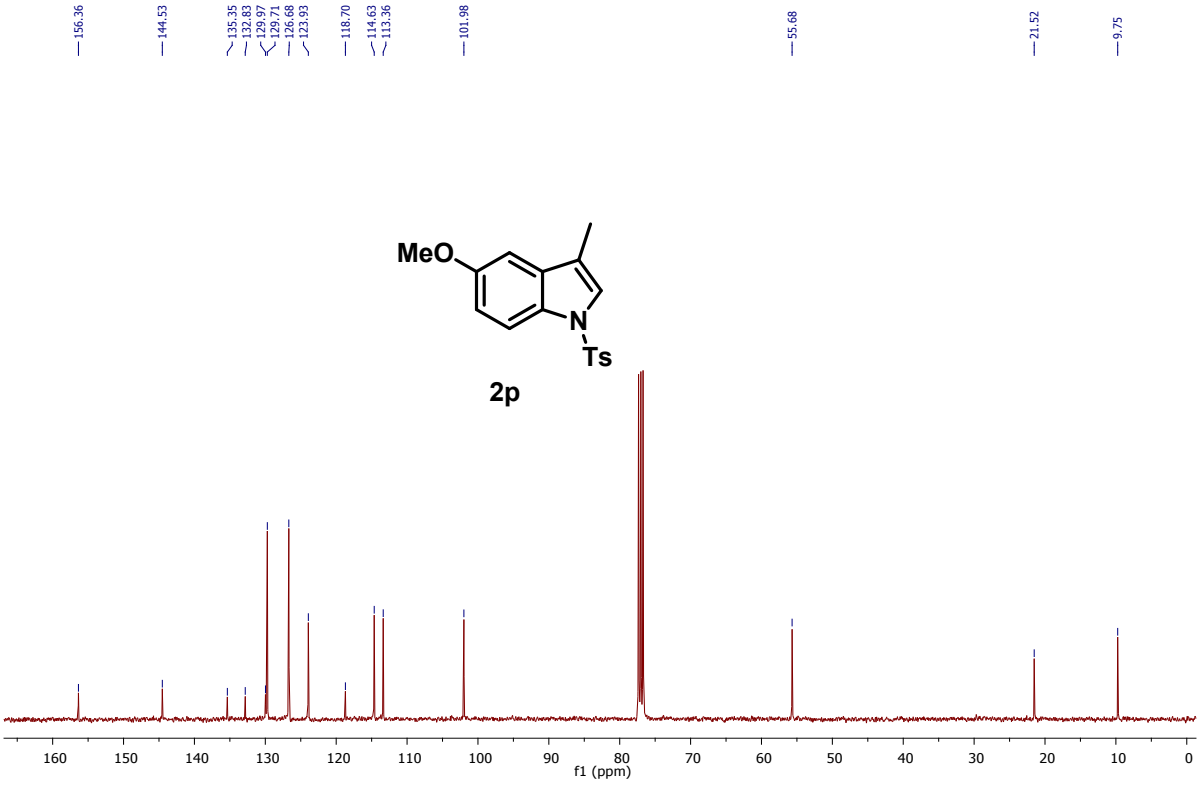


2o

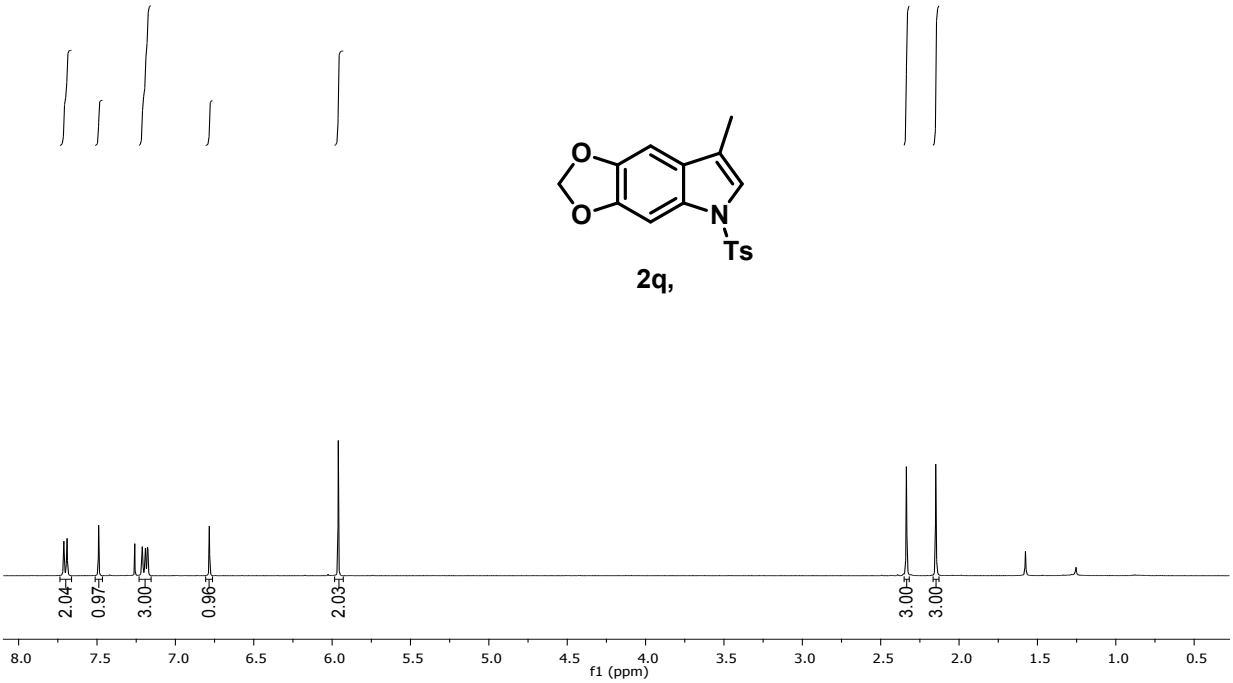
^{13}C NMR of compound **2o** (100 MHz, $CDCl_3$)



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

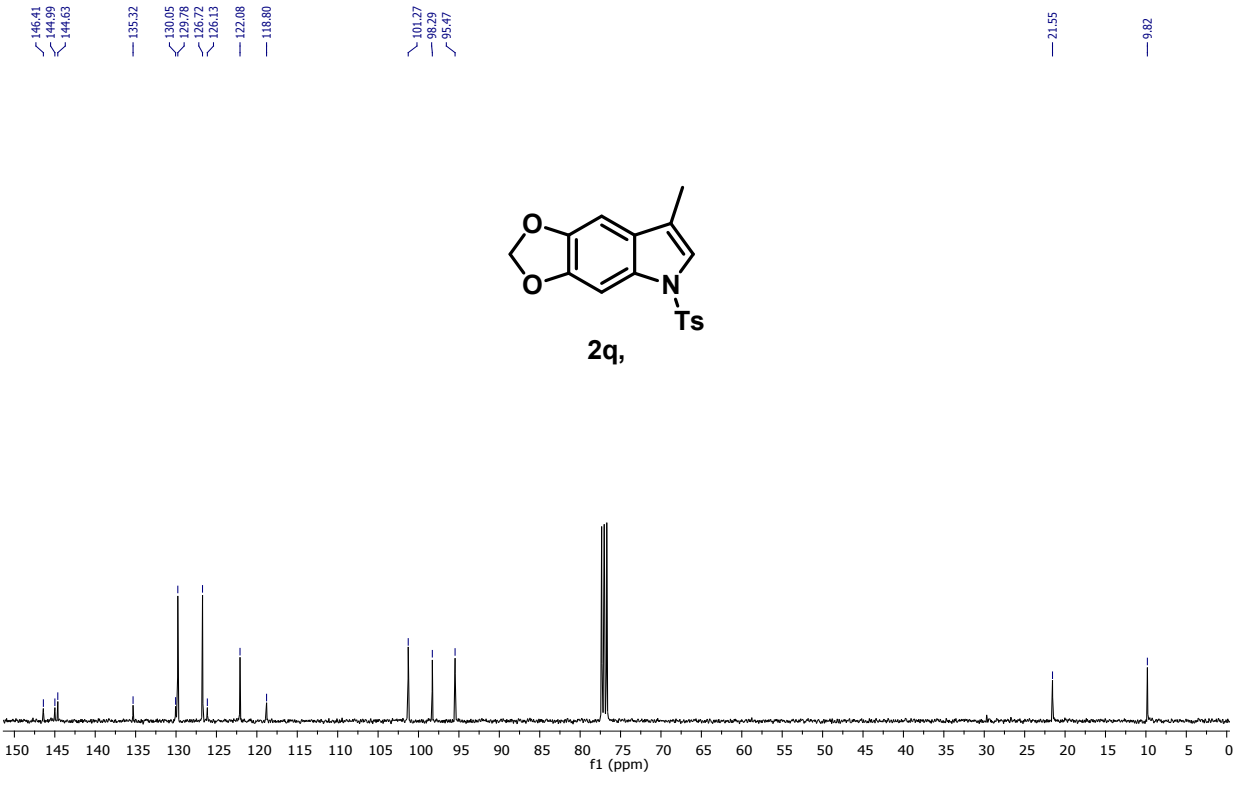


^{13}C NMR of compound **2p** (100 MHz, $CDCl_3$)



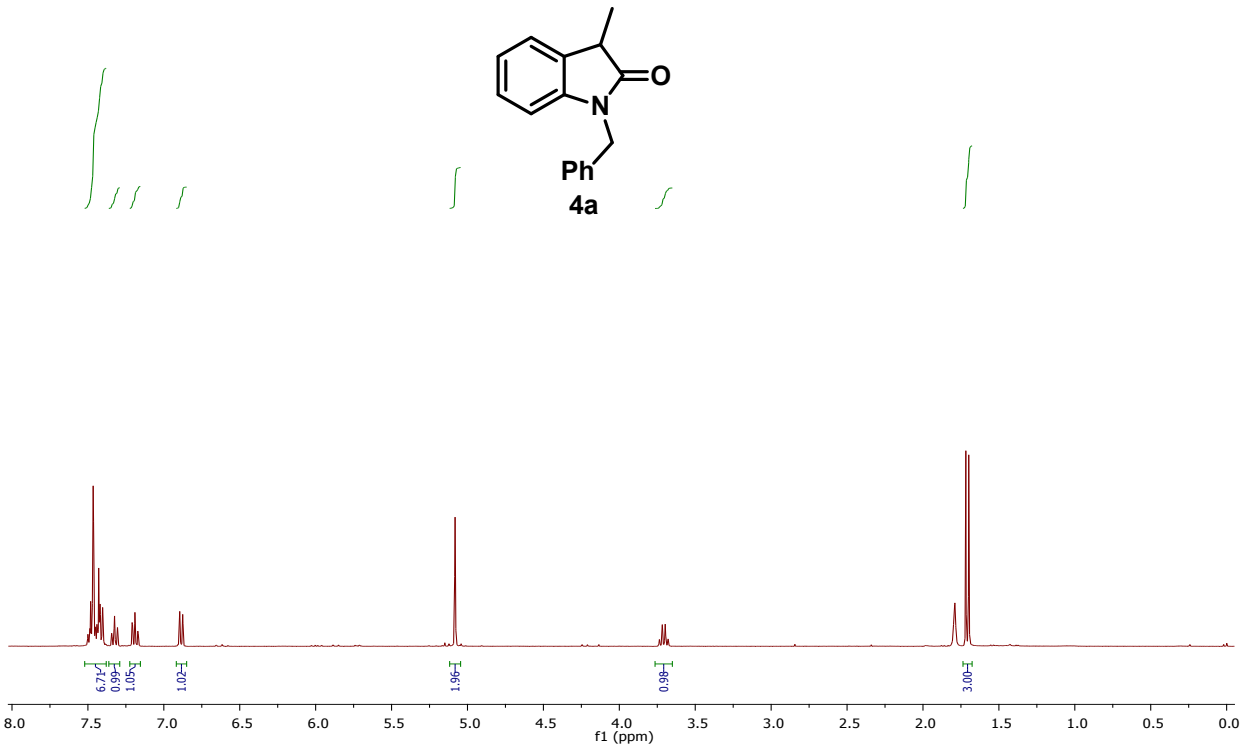
2q,

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

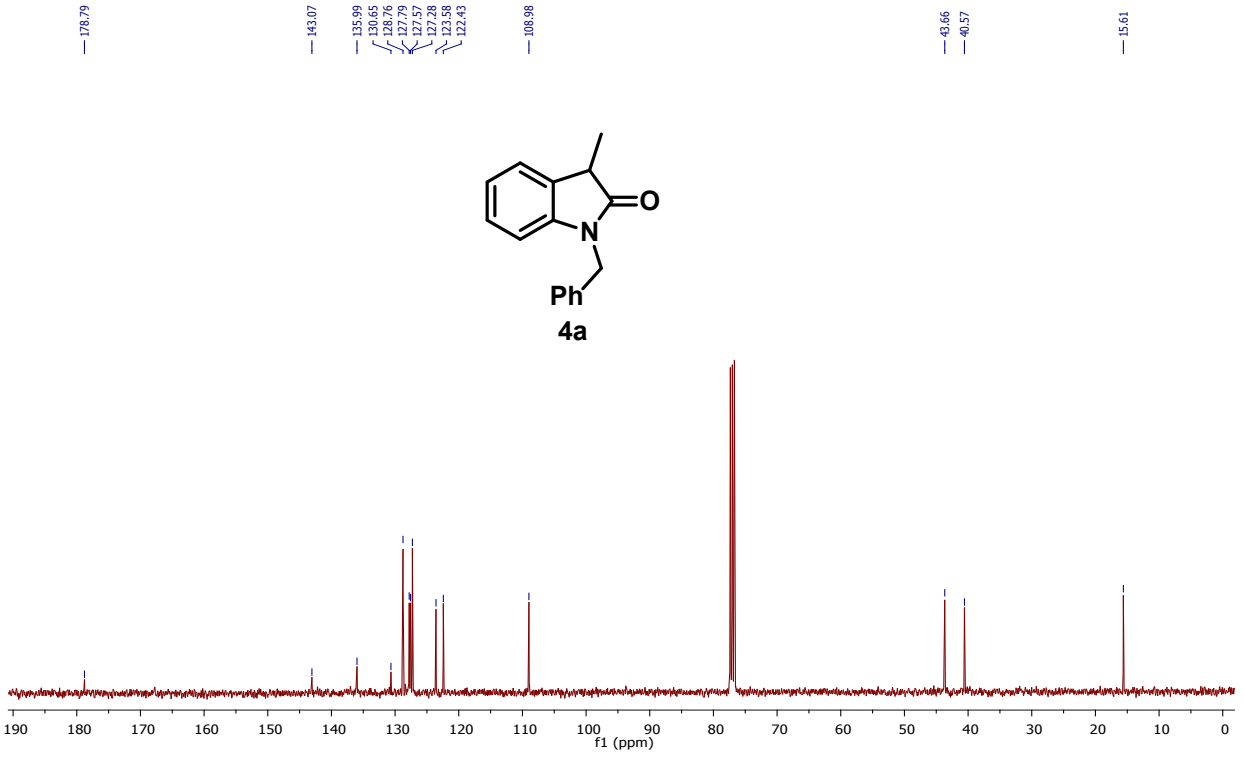


2q,

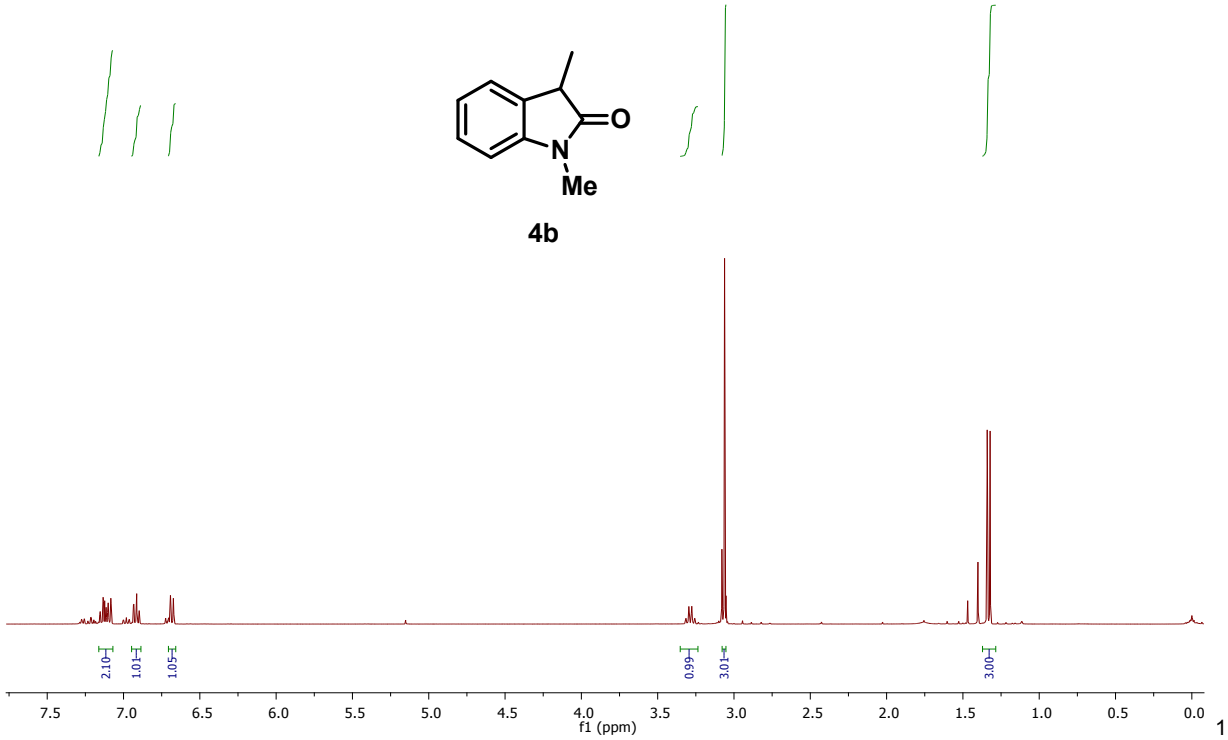
^{13}C NMR of compound **2q** (100 MHz, $CDCl_3$)



^{1}H NMR of compound **4a** (400 MHz, $CDCl_3$)

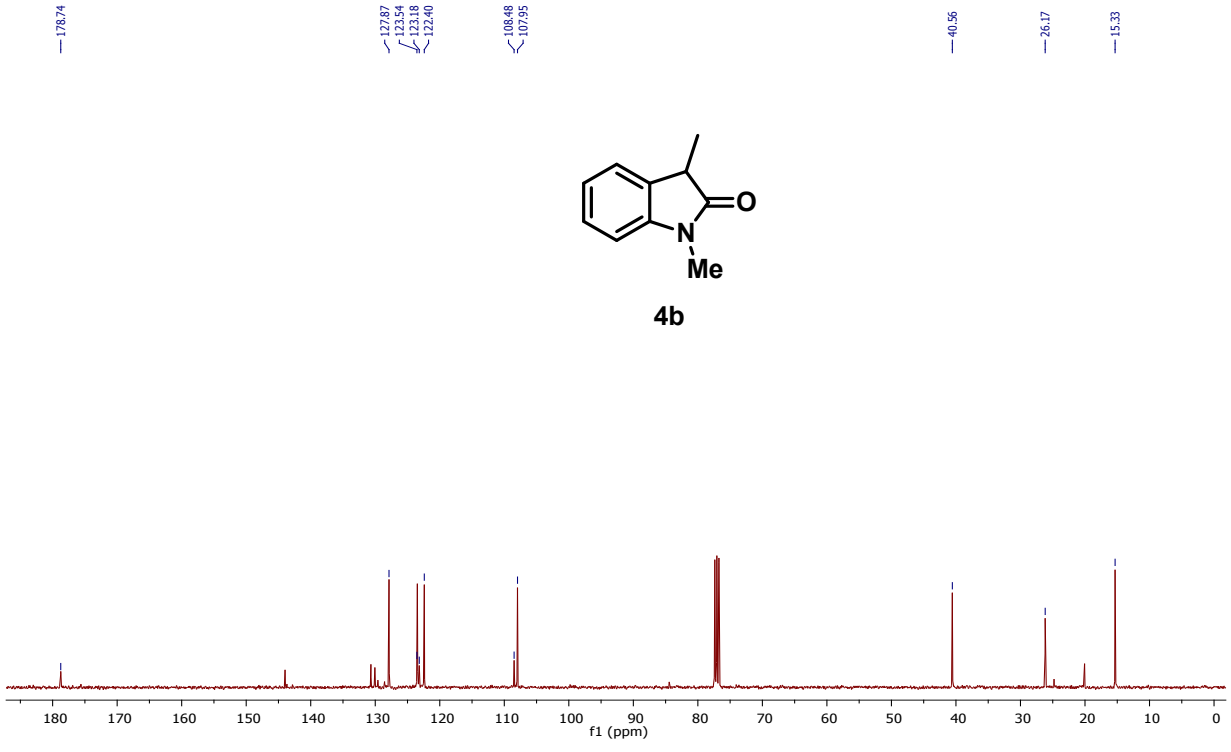


^{13}C NMR of compound **4a** (100 MHz, $CDCl_3$)



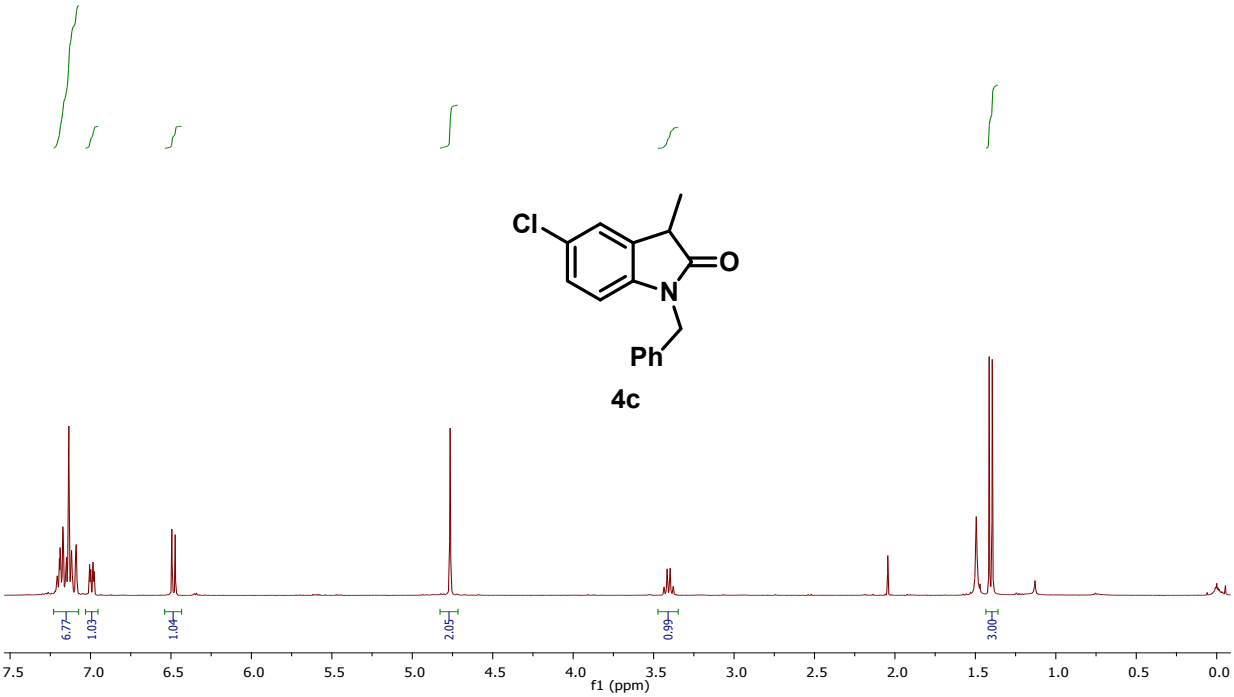
4b

H NMR of compound **4b** (400 MHz, $CDCl_3$)

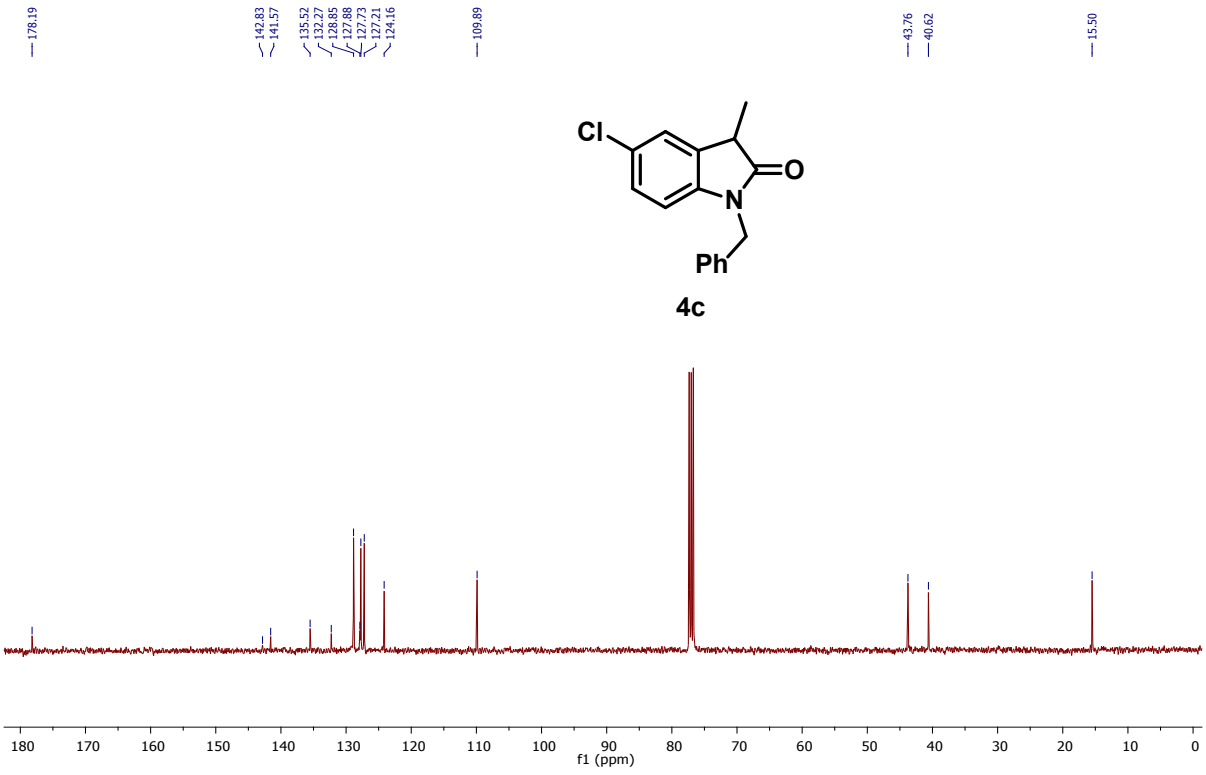


4b

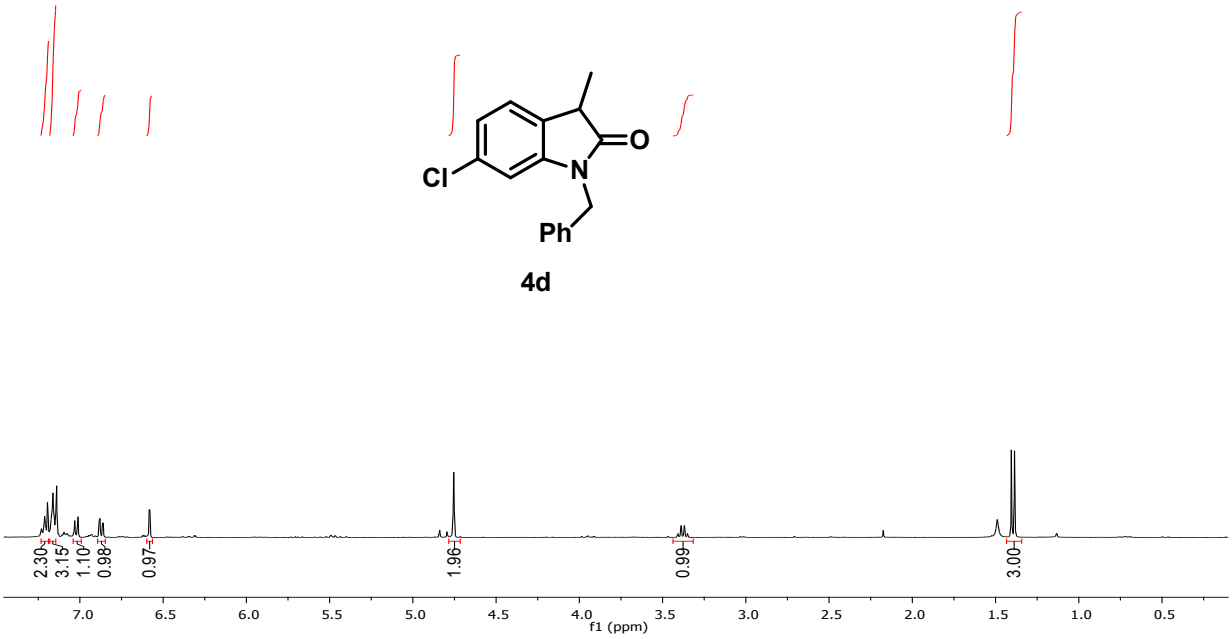
^{13}C NMR of compound **4b** (100 MHz, $CDCl_3$)



^{1}H NMR of compound **4c** (400 MHz, $CDCl_3$)

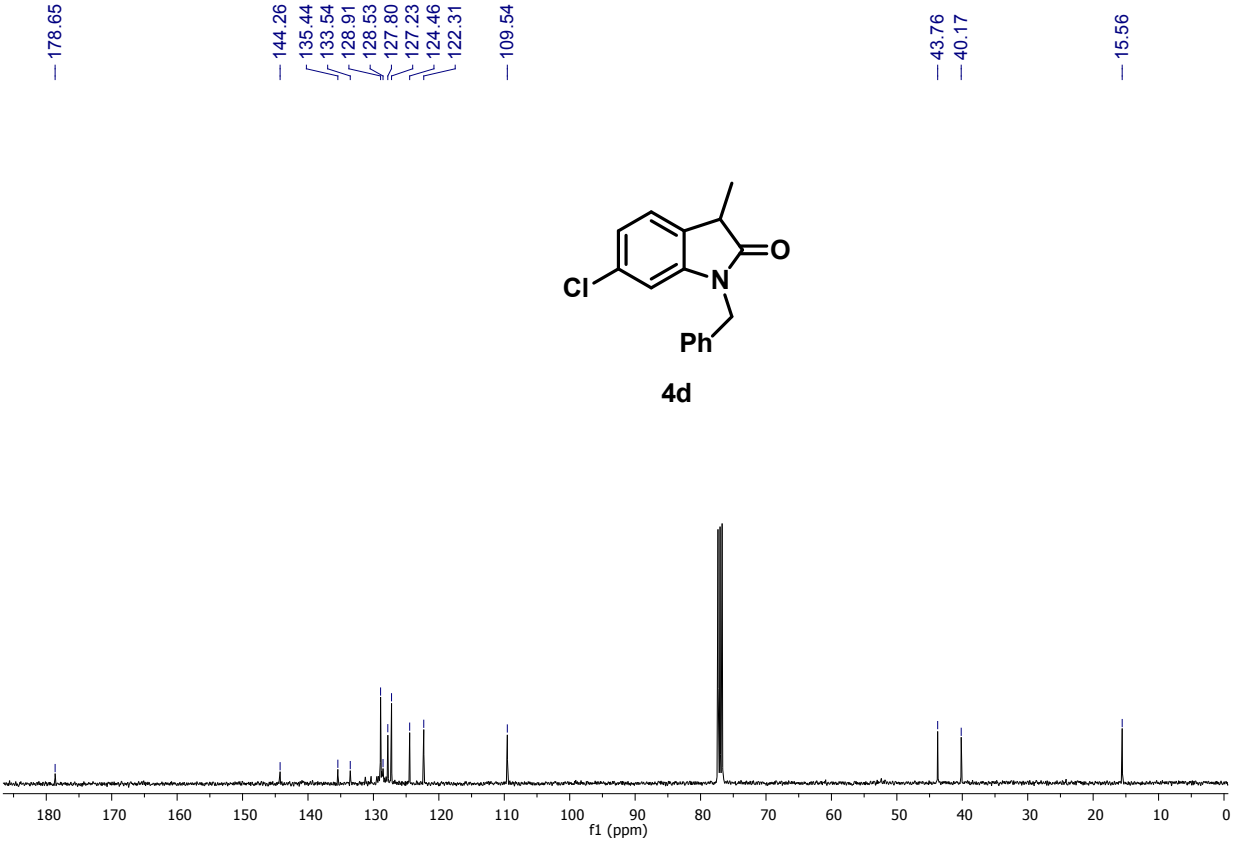


^{13}C NMR of compound **4c**(100 MHz, $CDCl_3$)



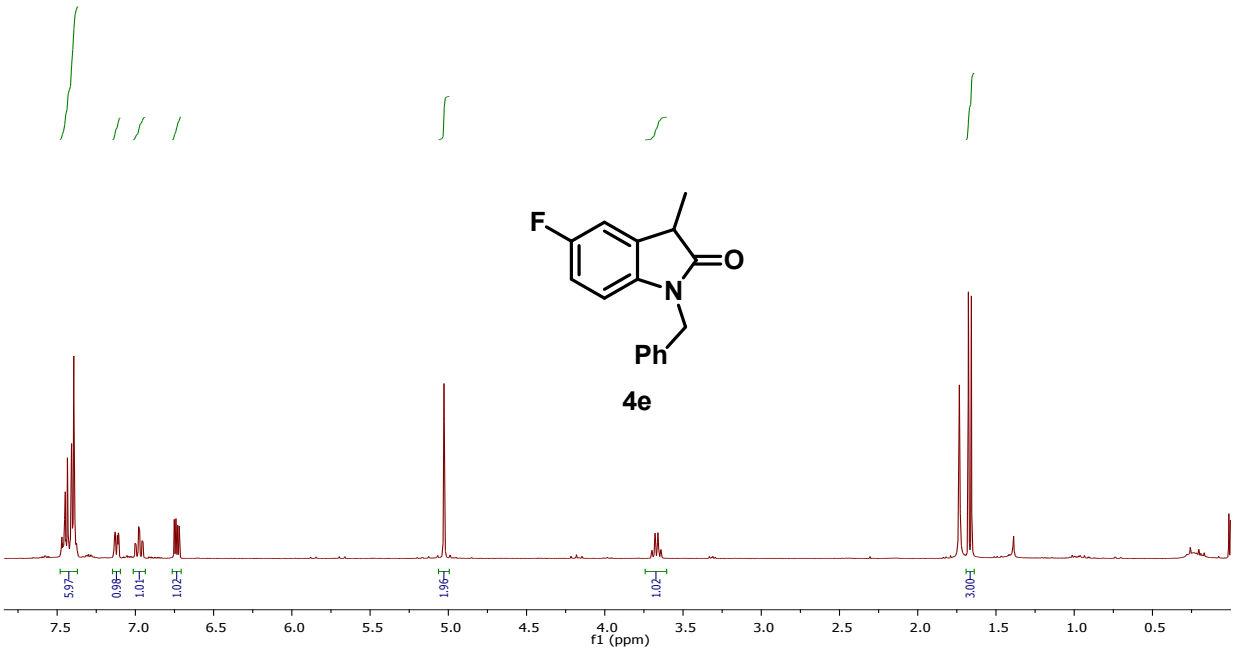
4d

^{1}H NMR of compound **4d** (400 MHz, $CDCl_3$)

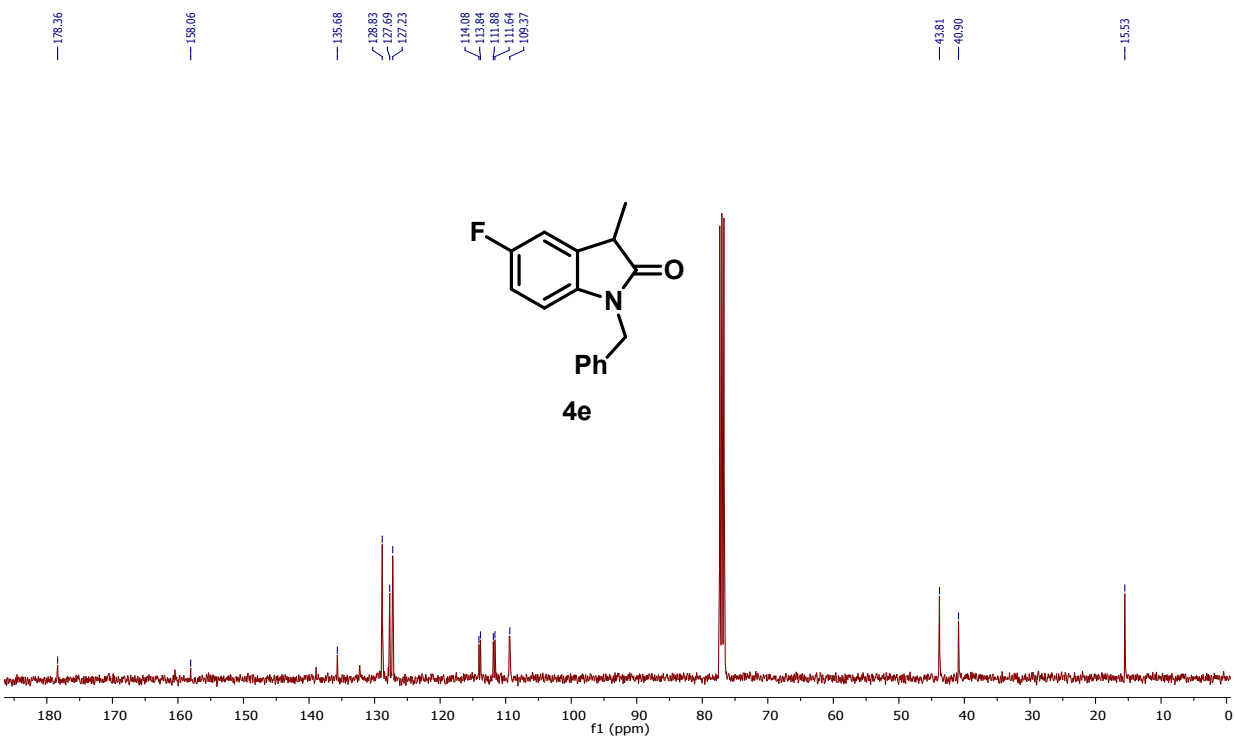


4d

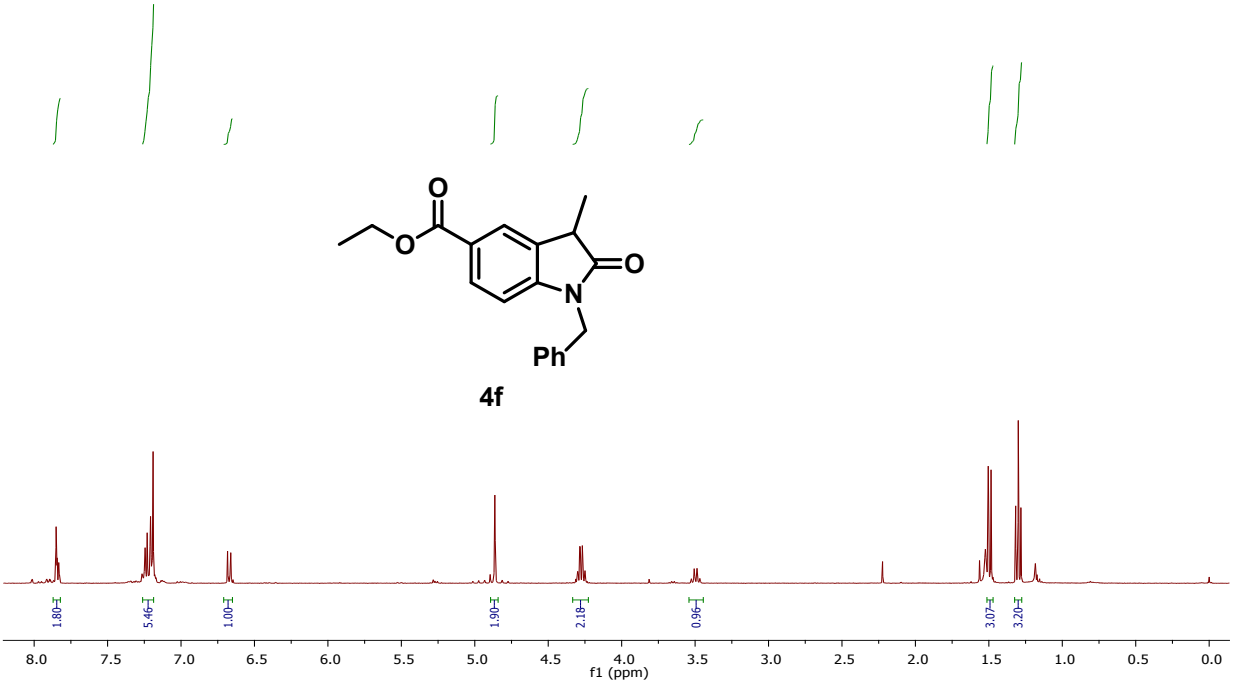
^{13}C NMR of compound **4d** (100 MHz, $CDCl_3$)



^{1}H NMR of compound **4e** (400 MHz, $CDCl_3$)

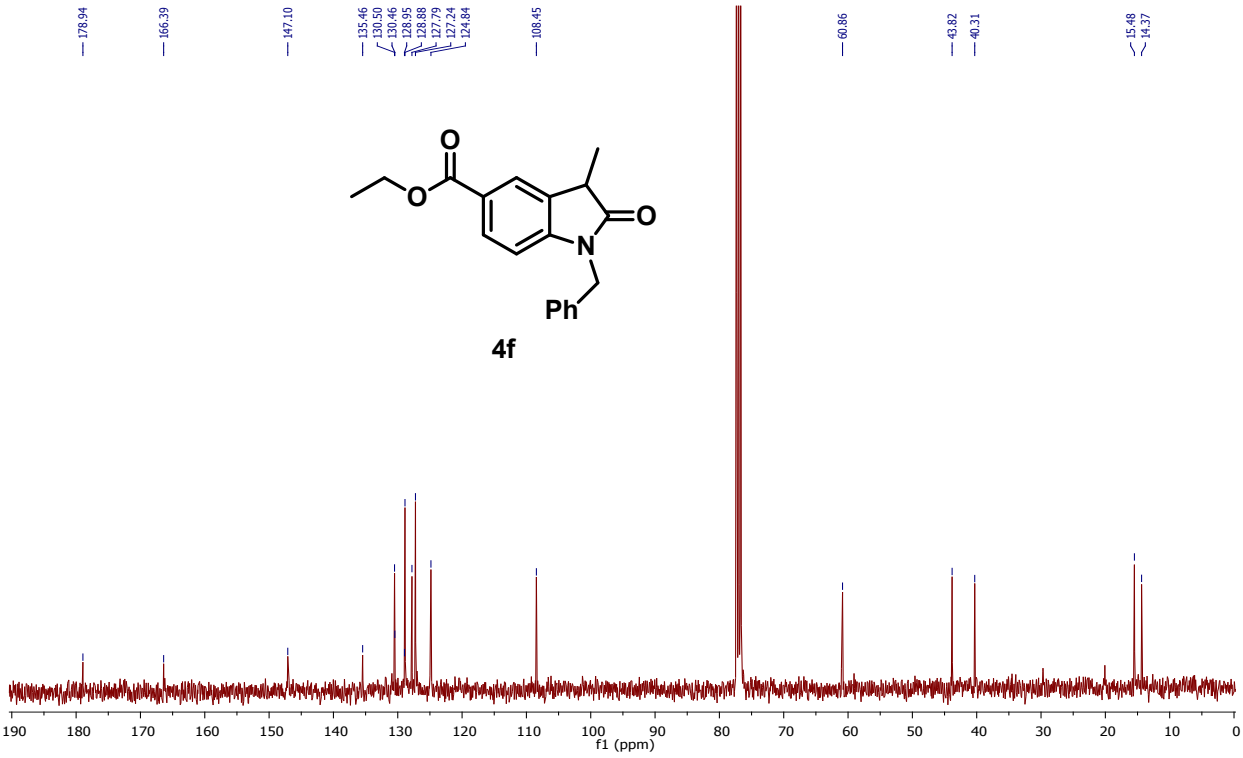


^{13}C NMR of compound **4e** (100 MHz, $CDCl_3$)



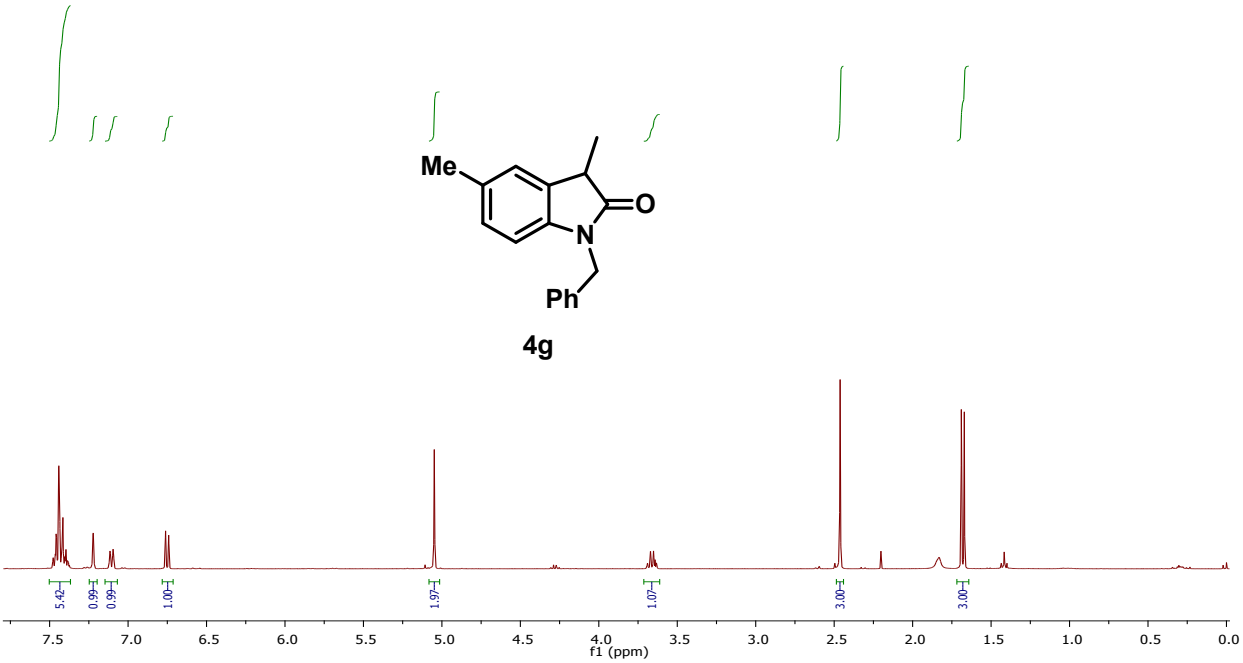
4f

^{1}H NMR of compound **4f** (400 MHz, $CDCl_3$)



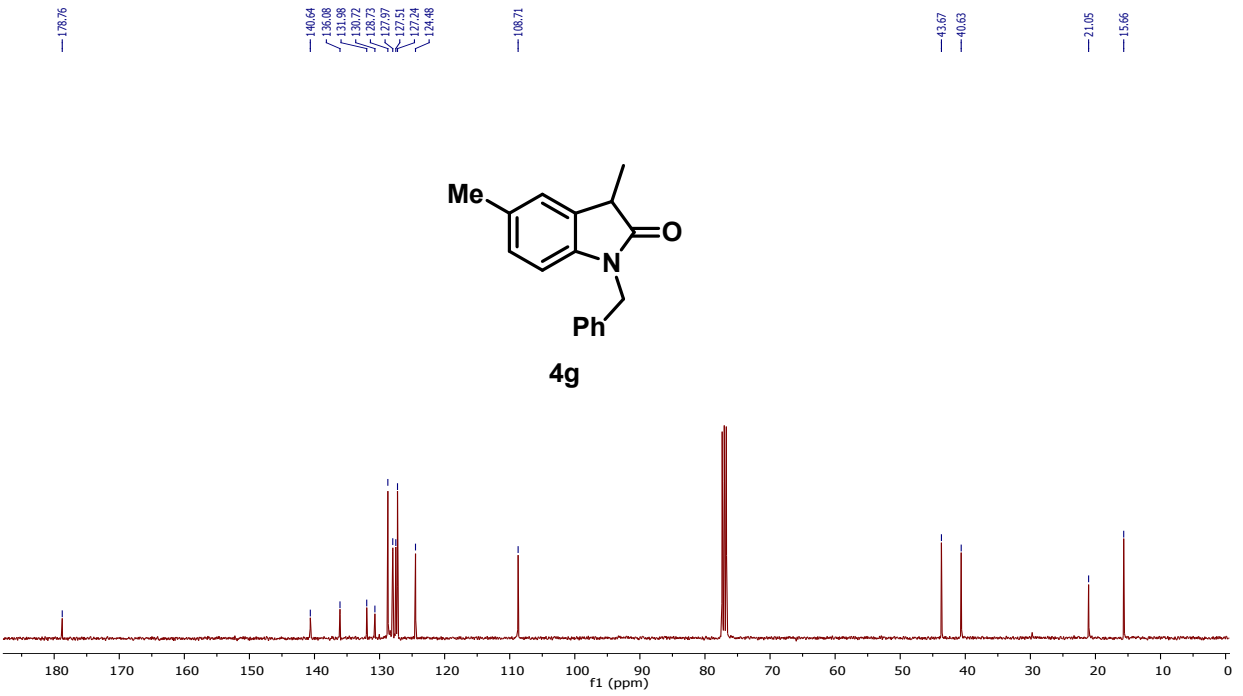
4f

^{13}C NMR of compound **4f** (100 MHz, $CDCl_3$)



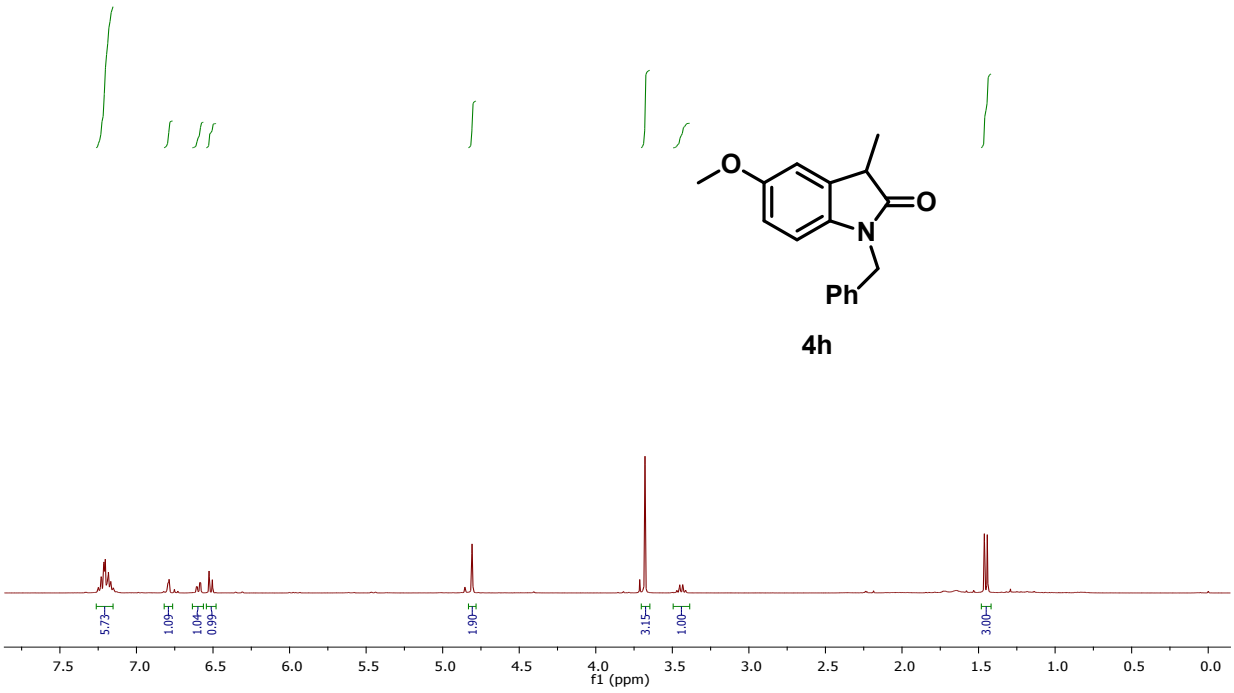
4g

^{1}H NMR of compound **4g** (400 MHz, $CDCl_3$)



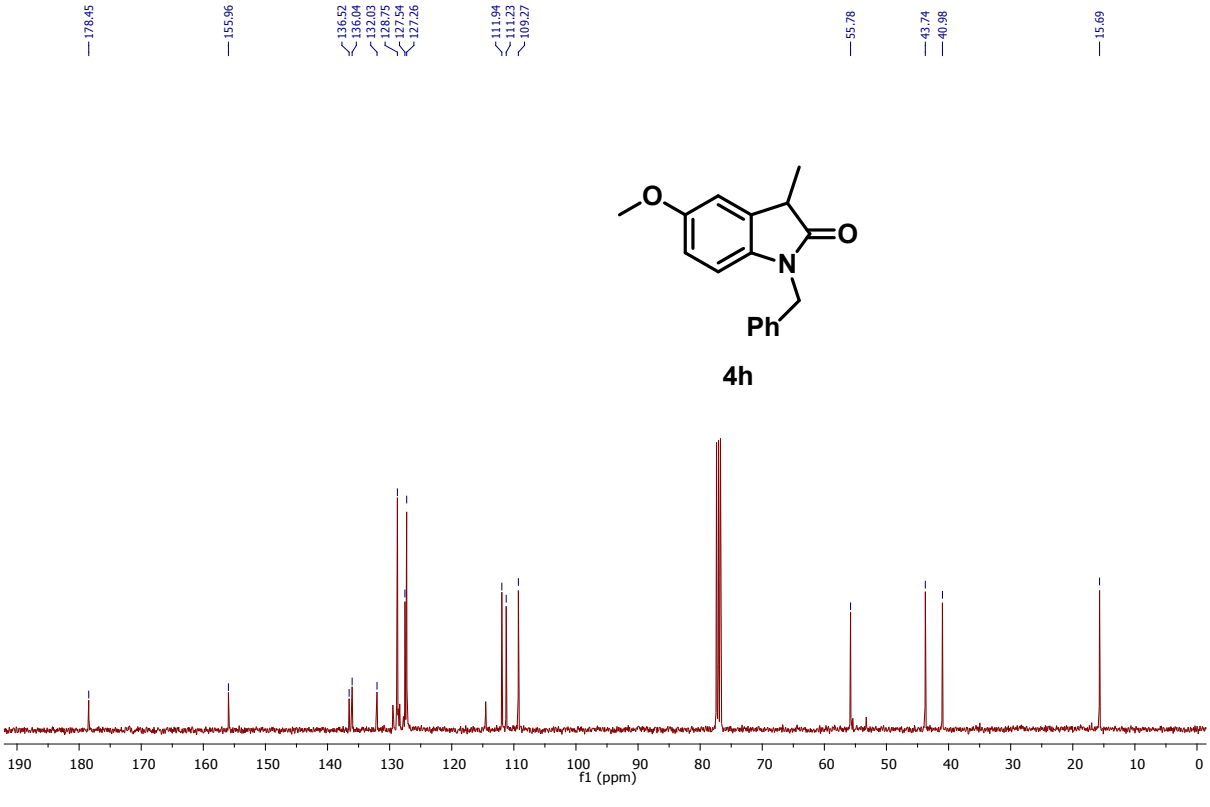
4g

^{13}C NMR of compound **4g** (100 MHz, $CDCl_3$)



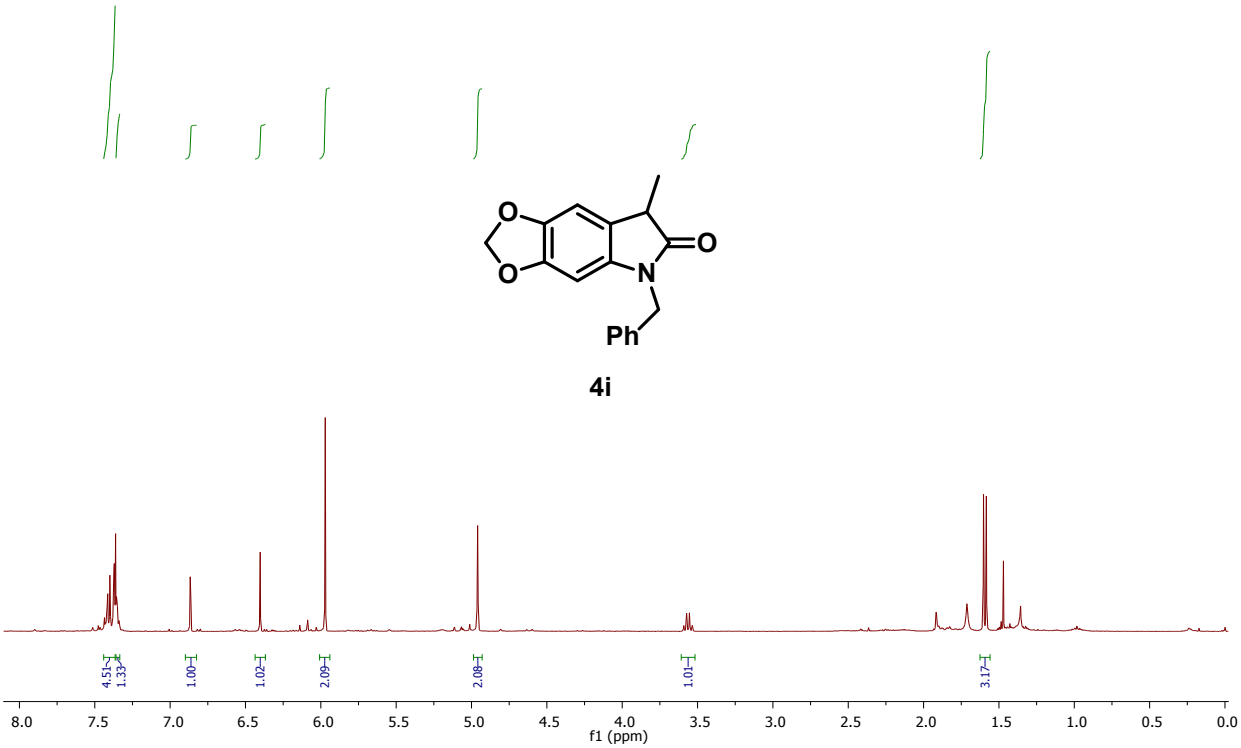
4h

^{1}H NMR of compound **4h** (400 MHz, $CDCl_3$)



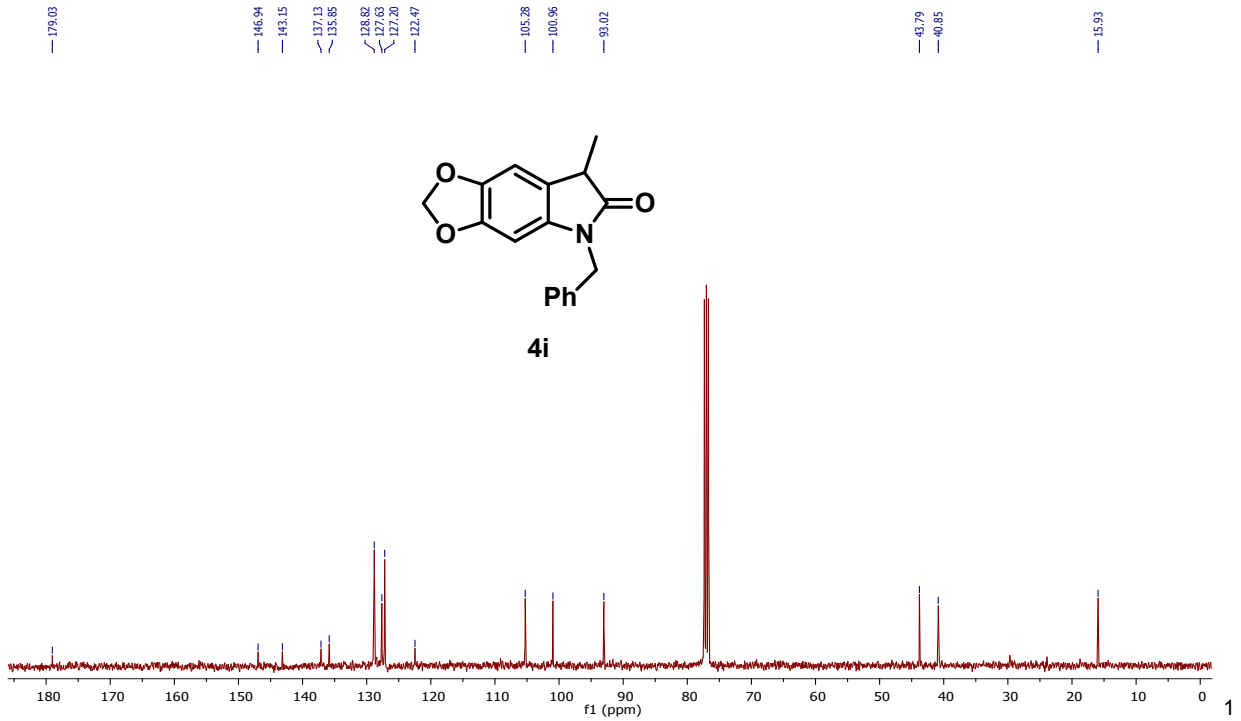
4h

C NMR of compound **4h** (100 MHz, $CDCl_3$)



4i

^{1}H NMR of compound **4i** (400 MHz, $CDCl_3$)



4i

^{3}C NMR of compound **4i** (100 MHz, $CDCl_3$)