Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Regiodivergent cascade cyclization/alkoxylation of allenamides via N-protecting group driven rearrangement to access indole and indoline derivatives

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General Information

Unless otherwise noted, all the reactions were performed using oven-dried Schlenk tubes under nitrogen. The reactions were monitored by Merck silica gel 60 F_{254} precoated plates (0.25 mm) visualizing under UV light (254 nm) or I_2 staining. The temperature mentioned for any reaction is corresponding to the oil bath temperature. Column chromatography was performed using silica gel 60-120 Å or 100-200 Å mesh of Merck Company.

All the commercial reagents and anhydrous solvents were purchased from Sigma-Aldrich, Alfa Aesar, Merck, Spectrochem, Avra Synthesis Pvt. Ltd. and directly used as received without any further purification.

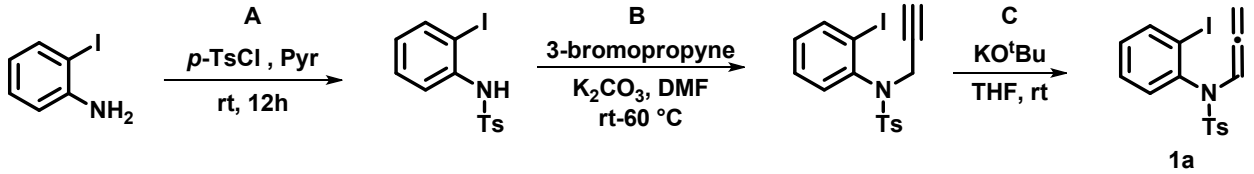
Analytical Methods

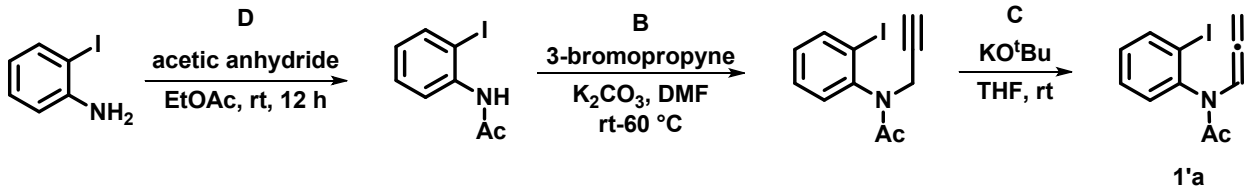
^1H, ^{13}C and ^{19}F nuclear magnetic resonance spectra were recorded on Bruker Advance III 400 MHz spectrometer at 25 °C. NMRs of the products were measured in $CDCl_3$. The chemical shifts in ^1H NMR and $^{13}C\{^1H\}$ NMR spectra are reported in parts per million (ppm) and are referenced to the residual solvent signal as the internal standard; ^1H NMR spectra ($CDCl_3$ δ 7.26 ppm) ,^{13}C ($CDCl_3$ δ 77.16), ^1H (D_4-methanol δ 3.31 ppm), ^{13}C (D_4-methanol δ 49.00) and ^1H (D_6-acetone δ 2.05 ppm), ^{13}C (D_4-methanol δ 29.84, 206.26). The coupling constant (J) was reported in Hertz (Hz). Splitting patterns are denoted as "s" for singlet; "d" for doublet; "t" for triplet; "q" for quartet; "sext" for sextet; "sept" for septet; "m" for multiplet, "br" for broad; "dt" for doublet of triplets; "td" for triplet of doublets. ESI-HRMS were recorded on AGILENT 6520 Q-TOF spectrometer. IR spectra were recorded with Agilent Cary 630 FTIR Spectrometer.

2. Experimental procedures

The starting materials **1a-1x**[1,2,3,4,5,6,7] and **1'a**[5], **7a-7b**[8] were prepared according to the previously reported methods.

2.1 Preparation of Allenamides:





General procedure A for tosylation:

To a solution of *o*-iodoaniline (1.0 equiv.) in pyridine was added *p*-TsCl (1.05 equiv.) at 0 °C. The reaction was stirred at rt over night before being quenched with H_2O. The quenched mixture was extracted three times with DCM. The combined organic layers were first washed with 1M HCl to remove excess pyridine, and then with saturated aq. $NaHCO_3$, H_2O, followed by saturated aq. NaCl, and dried over anhyd. Na_2SO_4. The filtrate was concentrated under reduced pressure and purified using silica gel flash column chromatography to give the desired product tosylamine.

General procedure B for propargylamides:

To a solution of the crude carbamate/tosylamine product (1.00 equiv.) in DMF, K_2CO_3 (1.5 equiv.) and 3-bromopropyne (1.5 equiv.) was added. The mixture was stirred in an oil bath at 60 °C for overnight. After the reaction was complete, the mixture was filtered through Celite. The filtrate was concentrated under reduced pressure and purified by flash column chromatography to give the propargylamide.

General procedure C for allenation reaction:

To a solution of propargylamide (1.0 equiv) in THF was added *t*-BuOK (0.5 equiv.) at 0 °C. The reaction was stirred at room temperature for 1 h before being concentrated under reduced pressure. Subsequently, the residue was suspended in DCM and then filtered through Celite. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash column chromatography to give the allenamide**.**

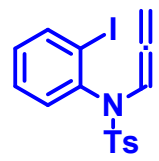
General procedure D for acetylation:[11, 12]

In a 25 mL round bottom flask, 2-iodoaniline (1.0 equiv) was dissolved in EtOAc, and acetic anhydride (1.4 equiv.) was added, and the reaction mixture was stirred at room temperature overnight. The solution was filtered and concentrate under reduced pressure to give the crude carbamate that was used in the next step without further purification.

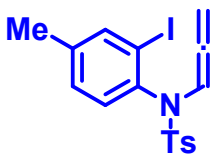
General procedure D' for Benzoylation:[13]

To a solution of corresponding 2-iodo aniline (1.0 equiv.) in dicholoromethane was added benzoyl chloride (1.2 mmol) followed by triethylamine (1.5 equiv.) at room temperature. After complete addition, the reaction was allowed to stir continuously until all the starting material was consumed completely (monitored by TLC, approx. 8-10 h after completion), the reaction mixture was quenched with water and extracted with dichloromethane. The combined organic layer was washed with brine solution, dried over Na_2SO_4, evaporated and washed with hexane to give pure benzamide product in quantitative yields.

Table S1. Substrates employed in the reaction:



1a



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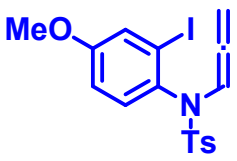

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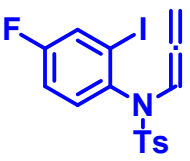

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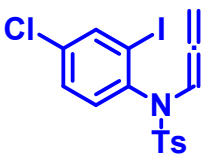

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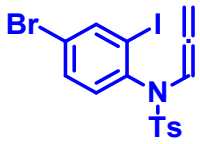

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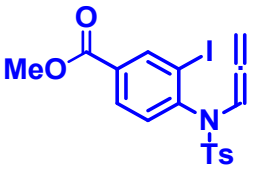

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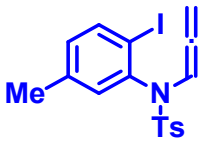

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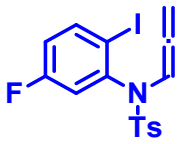

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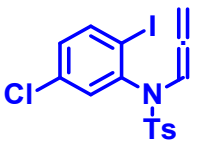

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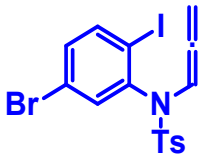

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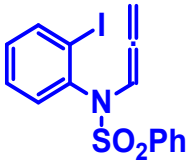

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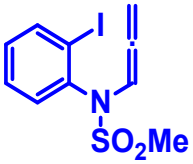

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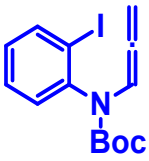

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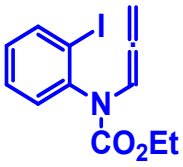

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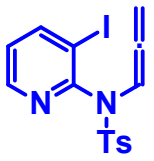

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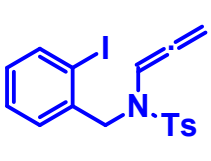

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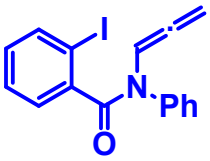

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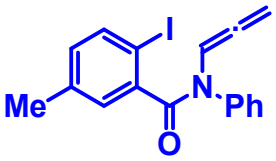
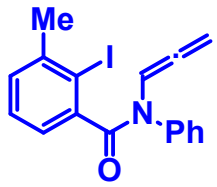


1s

1t



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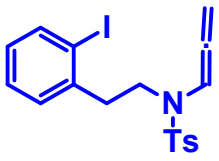

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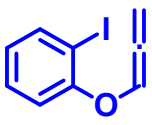

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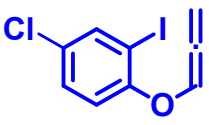
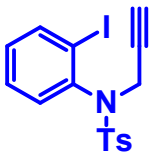
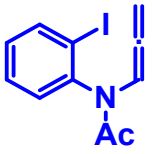


1x

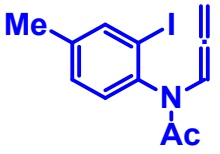


1a'

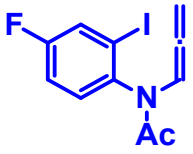
Table S2. Substrates employed in the reaction:



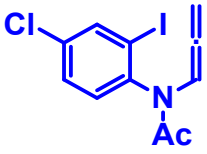
1'a



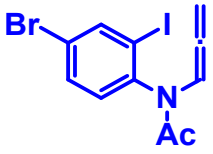
1' b



1'c



1'd



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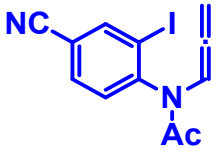
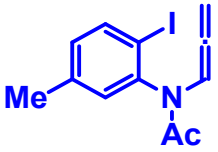
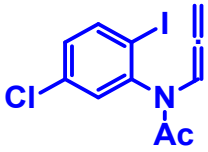


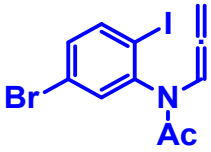
1'f



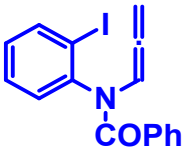
1'g



1'h



1'i



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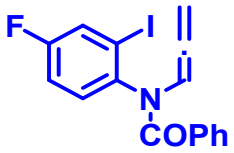
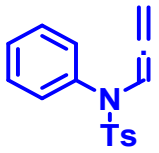
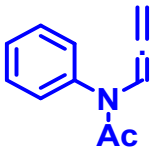


1'k



7a



7b

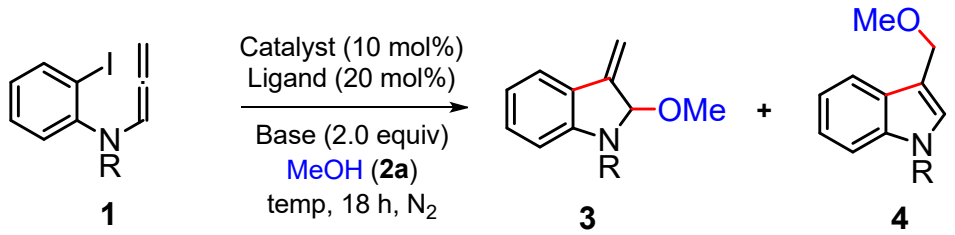
2.2 General Procedure E for the synthesis of 3a-4i:

To an oven dried Schlenk tube was charged with allenamide (1 equiv.), palladium chloride (10 mol%), tri(2-furyl)phosphine (20 mol%), and K_2CO_3 (2 equiv.), and the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). Then, the solvent methanol/ethanol (**2a)** 3mL was added to the reaction mixture. The reaction was stirred at rt for (18-20 h), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc) to yield the corresponding product.

2.3 General Procedure F for the Synthesis of 4ad:

To an oven dried Schlenk tube was charged with allenamide **1a** (1 equiv.), and piperidine (1.2 equiv.), palladium chloride (10 mol%), tri(2-furyl)phosphine(20 mol%), and Cs_2CO_3 (2 equiv.), and the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). DCE (3mL) was added to the reaction mixture. The reaction was stirred at 80 °C for (18-20 h), the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (acetone in hexane) to afford the desired product **4ad**.

2.4 Optimization of the reaction conditions:[a,b]



1 **3** **4**

1a, R = Ts; entries 1-25
1'a, R = Ac; entry 26

3a, R = Ts
3'a, R = Ac

4a, R = H
4a', R = Ts
4'a, R = Ac

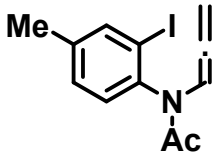
Entry	Catalyst	Ligand	Base	Temp °C	**3a** (%)	**4a** (%)
1	$Pd(OAc)_2$	XPhos	Cs_2CO_3	80	17	20
2	″	DPPP	″	″	n.d.	37
3	″	PPh_3	″	″	**(50)**	**(46)**
4	″	1,10 Phen	″	″	trace	nd
5	″	2,2 bipyridyl	″	″	nd	nd
6	″	Tri(2-furyl)phosphine (TFP)	″	″	62	9
7	$Pd(acac)_2$	″	″	″	67	15
8	$Pd(PPh_3)_2Cl_2$	″	″	″	44	n.d.
9	$Pd(Ph_3)_4$	″	″	″	n.d.	n.d.
10	$Pd_2(dba)_3$	″	″	″	n.d.	n.d.
11	**$PdCl_2$**	″	″	″	**78**	**11**
12	″	PPh_3	Cs_2CO_3	″	11	56
13	″	PCy_3	Cs_2CO_3	″	n.d.	n.d.
14	″	$P(OPh)_3$	Cs_2CO_3	″	21	13
15	″	JohnPhos	Cs_2CO_3	″	n.d.	n.d.
16	″	$P(o\text{-}tol)_3$	Cs_2CO_3	″	n.d.	n.d.
17	$PdCl_2$	TFP	K_2CO_3	″	(78)	n.d.
18	″	″	K_3PO_4	″	73	8
19	″	″	Na_2CO_3	″	70	n.d
20	″	″	NaO^tBu	″	61	40
21	**$PdCl_2$**	**TFP**	**K_2CO_3**	**r.t.**	**(88)**	**trace**
22	$PdCl_2$ (5 mol%)	TFP (10 mol%)	K_2CO_3	r.t.	(78)	trace

23	$PdCl_2$ (2 mol%)	TFP (4 mol%)	K_2CO_3	r.t.	(70)	~5
24	$PdCl_2$ (10 mol%)	TFP (10 mol%)	K_2CO_3	r.t.	(65)	~5
25	$PdCl_2$	TFP	Ag_2CO_3	r.t.	5	trace
26	None	TFP	K_2CO_3	r.t.	n.d.	n.d.
27	$PdCl_2$	None	K_2CO_3	r.t.	10	n.d.
28	$PdCl_2$	TFP	None	r.t.	n.d.	n.d.
29[c]	**$PdCl_2$**	**TFP**	**K_2CO_3**	**r.t.**	**(7)**	**(79)**

[a]Reaction conditions: **1a/1'a** (1.0 equiv.), catalyst (10 mol%), ligand (20 mol%), base (2.0 equiv.), MeOH (1 mL) at 80 °C/rt for 18 h under N_2. [1]HNMR yield using 1,3,5-trimethoxybenzene as internal standard. n.d. = not detected. [b]Isolated yields on parantheses. [c]R = Ac in **1**.

3. Characterization Data of Starting Materials:

N-(2-iodo-4-methylphenyl)-N-(propa-1,2-dien-1-yl)acetamide (1'b):



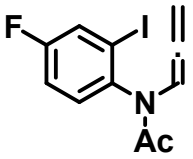
The representative general procedure **C** was followed, using propargylamide (470 mg, 1.5 mmol), in THF was added *t*-BuOK (0.5 equiv.) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 6% EtOAc in hexane) furnished **1'b** (320 mg, 68% yield) as a pale yellow solid. R_f 0.72 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.59 (td, J = 6.3, 1.2 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 5.05-4.94 (m, 2H), 2.34 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.4, 168.2, 140.6, 140.4, 140.0, 130.4, 129.2, 99.8, 99.6, 86.6, 23.0, 20.6.

HRMS (ESI) Calcd. for $C_{12}H_{12}INO$: $[M+H]^+$, 314.0042. Found: m/z 314.0033.

N-(4-fluoro-2-iodophenyl)-N-(propa-1,2-dien-1-yl)acetamide (1'c):



The representative general procedure **C** was followed, using propargylamide (350 mg, 1.1 mmol), in THF was added *t*-BuOK (0.5 equiv) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 6% EtOAc in hexane) furnished **1'c** (195 mg, 56% yield) as a pale yellow solid. R_f 0.71 (20% EtOAc in hexane).

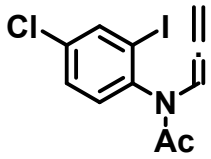
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (dd, J = 7.6, 2.8 Hz, 1H), 7.59 (t, J = 6.4, Hz, 1H), 7.23 (dd, J = 8.7, 5.3 Hz, 1H), 7.16-7.12 (m, 1H), 5.07-4.97 (m, 2H), 1.86 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 202.3, 167.9, 161.4 (d, J = 254.3 Hz), 139.0, 130.5 (d, J = 8.9 Hz), 127.0 (d, J = 24.6 Hz), 116.7 (d, J = 22.5 Hz), 99.9 (d, J = 8.8 Hz), 99.8, 86.9, 22.9.

^{19}F NMR (376 MHz): δ –110.5.

HRMS (ESI) Calcd. for $C_{11}H_9FINO$: $[M+H]^+$, 317.9791. Found: m/z 317.9785.

N-(4-chloro-2-iodophenyl)-N-(propa-1,2-dien-1-yl)acetamide (1'd):



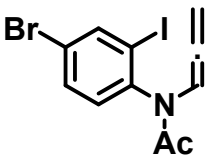
The representative general procedure **C** was followed, using propargylamide (500 mg, 1.5 mmol), in THF was added *t*-BuOK (0.5 equiv) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 7% EtOAc in hexane) furnished **1'd** (300 mg, 60% yield) as a pale yellow solid. R_f 0.71 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 2.3 Hz, 1H), 7.59 (t, J = 6.4 Hz, 1H), 7.41 (dd, J = 8.4, 2.3 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 5.09-4.98 (m, 2H), 1.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 202.1, 167.6, 141.4, 139.5, 135.1, 130.4, 129.9, 100.4, 99.6, 87.1, 23.0.

HRMS (ESI) Calcd. for $C_{11}H_9ClINO$: $[M+H]^+$, 333.9496. Found: m/z 333.9488.

N-(4-bromo-2-iodophenyl)-N-(propa-1,2-dien-1-yl)acetamide (1'e):



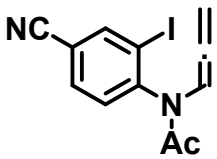
The representative general procedure **C** was followed, using propargylamide (565 mg, 1.5 mmol), in THF was added *t*-BuOK (0.5 equiv) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **1'e** (342 mg, 60% yield) as a pale yellow solid. R_f 0.72 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 1.8 Hz, 1H), 7.59-7.54 (m, 2H), 7.12 (d, J = 8.3 Hz, 1H), 5.08-4.99 (m, 2H), 1.86 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 202.1, 167.6, 142.2, 141.9, 132.9, 130.8, 123.1, 100.8, 99.6, 87.1, 23.0.

HRMS (ESI) Calcd. for $C_{11}H_9BrINO$: $[M+H]^+$, 377.8990. Found: m/z 377.8980.

N-(4-cyano-2-iodophenyl)-N-(propa-1,2-dien-1-yl)acetamide (1'f):



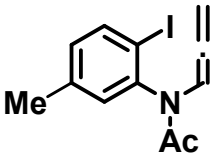
The representative general procedure **C** was followed, using propargylamide (324 mg, 1.1 mmol), in THF was added *t*-BuOK (0.5 equiv) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **1'f** (220 mg, 62% yield) as a pale yellow solid. R_f 0.65 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 1.2 Hz, 1H), 7.73 (dd, J = 8.0, 1.3 Hz, 1H), 7.59 (t, J = 6.3 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 5.08-4.98 (m, 2H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 166.8, 146.9, 143.4, 133.2, 130.6, 116.1, 114.3, 100.6, 99.4, 87.5, 23.1.

HRMS (ESI) Calcd. for $C_{12}H_9IN_2O$: $[M+H]^+$, 324.9838. Found: m/z 324.9828.

N-(2-iodo-5-methylphenyl)-N-(propa-1,2-dien-1-yl)acetamide (1'g):



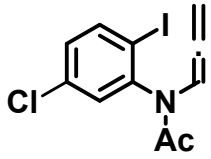
The representative general procedure **C** was followed, using propargylamide (532 mg, 1.7 mmol), in THF was added *t*-BuOK (0.5 equiv) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 7% EtOAc in hexane) furnished **1'g** (350 mg, 66% yield) as a pale yellow solid. R_f 0.72 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 1H), 7.59 (t, J = 6.4 Hz, 1H), 7.06 (s, 1H), 6.90 (d, J = 8.1 Hz, 1H), 5.05-4.95 (m, 2H), 2.34 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 202.4, 168.0, 142.4, 140.0, 139.6, 131.2, 130.4, 99.7, 95.6, 86.6, 23.0, 20.9.

HRMS (ESI) Calcd. For $C_{12}H_{12}INO$: $[M+H]^+$, 314.0042. Found: m/z 314.0011.

N-(5-chloro-2-iodophenyl)-N-(propa-1,2-dien-1-yl)acetamide (1'h):



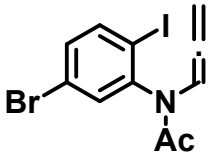
The representative general procedure **C** was followed, using propargylamide (433 mg, 1.3 mmol), in THF was added *t*-BuOK (0.5 equiv) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 7% EtOAc in hexane) furnished **1'h** (250 mg, 58% yield) as a pale yellow solid. R_f 0.71 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.5 Hz, 1H), 7.57 (t, J = 6.3 Hz, 1H), 7.25 (s, 1H), 7.09 (dd, J = 8.4, 2.1 Hz, 1H), 5.08-5.00 (m, 2H), 1.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 202.1, 167.5, 143.8, 140.8, 135.3, 130.5, 130.0, 99.5, 97.5, 87.2, 23.1.

HRMS (ESI) Calcd. for $C_{11}H_9ClINO$: $[M+H]^+$, 333.9496. Found: m/z 333.9487.

N-(5-bromo-2-iodophenyl)-N-(propa-1,2-dien-1-yl)acetamide (1'i):



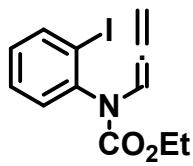
The representative general procedure **C** was followed, using propargylamide (565 mg, 1.5 mmol), in THF was added *t*-BuOK (0.5 equiv) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 7% EtOAc in hexane) furnished **1'i** (350 mg, 62% yield) as a pale yellow solid. R_f 0.71 (20% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 1H), 7.58 (t, J = 6.4 Hz, 1H), 7.41 (d, J = 2.2 Hz, 1H), 7.23 (dd, J = 8.4, 2.2 Hz, 1H), 5.08-5.01 (m, 2H), 1.88 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 202.1, 167.5, 143.9, 141.1, 133.4, 132.9, 122.8, 99.6, 98.4, 87.2, 23.1.

HRMS (ESI) Calcd. for $C_{11}H_9BrINO$: $[M+H]^+$, 377.8990. Found: m/z 377.8988.

ethyl (2-iodophenyl(propa-1,2-dien-1-yl)carbamate (1o):



2-Iodoaniline (1.0 equiv), ethyl chloroformate (4.0 equiv.) and K_2CO_3 (6.0 equiv) were stirred in 40 mL of acetone at room temperature for 3 h. The reaction was monitored by TLC to establish completion. Then the reaction mixture was diluted with water. The organic phase was separated, and the aqueous phase was extracted with ether. Organic fractions were combined, washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using 8:1 hexanes/ethyl acetate to give the ethyl (2-iodophenyl)carbamate as off-white solid.

To a solution of the ethyl (2-iodophenyl)carbamate (1.0 equiv.) in DMF, potassium carbonate (1.5 equiv.) and 3-bromopropyne (1.5 equiv.) was added. The mixture stirred in an oil bath at 60 °C for overnight. After the reaction was complete, the mixture was filtered through Celite. The filtrate was concentrated under reduced pressure and purified by flash column chromatography to give the ethyl (2-iodophenyl)(prop-2-yn-1-yl)carbamate.

To a solution ethyl (2-iodophenyl)(prop-2-yn-1-yl)carbamate (324 mg, 1.1 mmol), in THF was added *t*-BuOK (0.5 equiv.) at 0 °C. The reaction was stirred at room temperature for 1 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **1o** (220 mg, 62% yield) as a sticky yellow solid. R_f 0.65 (20% EtOAc in hexane).

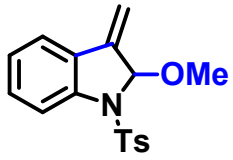
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.38 -7.19 (m, 3H), 7.02 (t, J = 7.6 Hz, 1H), 5.06-4.97 (m, 2H), 4.26-4.10 (m, 2H), 1.18 (t, J = 6.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 201.6, 152.6, 141.4, 139.5, 129.6, 129.5, 128.9, 101.4, 99.6, 87.2, 62.6, 14.6.

HRMS (ESI) Calcd. for $C_{12}H_{12}INO_2$: $[M+Na]^+$, 351.9810. Found: m/z 351.9808.

4. Characterization Data of Isolated Products

2-methoxy-3-methylene-1-tosylindoline (3a):



The representative general procedure **E** was followed, using **1a** (82 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3a** (55 mg, 88% yield) as a brown solid. R_f 0.71 (20% EtOAc in hexane).

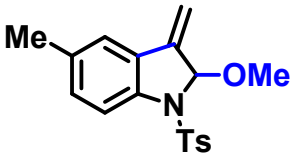
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.29-7.24 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.04 (td, J = 7.5, 0.9 Hz, 1H), 5.89 (t, J = 1.6 Hz, 1H), 5.68 (d, J = 1.7 Hz, 1H), 5.35 (d, J = 1.3 Hz, 1H), 3.31 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 142.7, 141.2, 135.4, 130.2, 129.6, 128.1, 127.2, 124.2, 120.9, 115.8, 109.3, 92.9, 52.2, 21.5.

Melting point: 125-127 °C.

HRMS (ESI) Calcd. for $C_{17}H_{17}NO_3S$: $[M\text{-}OCH_3]^+$, 284.0740. Found: m/z 284.0751.

2-methoxy-5-methyl-3-methylene-1-tosylindoline (3b):



The representative general procedure **E** was followed, using **1b** (85 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3b** (56 mg, 85% yield) as a white solid. R_f 0.71 (20 % EtOAc in hexane).

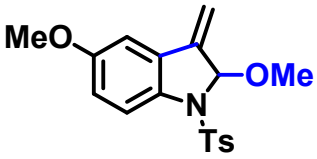
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.14 (s, 1H), 7.08 (d, J = 8.3 Hz, 1H), 5.85 (t, J = 1.5 Hz, 1H), 5.63 (d, J = 1.7 Hz, 1H), 5.30 (d, J = 1.3 Hz, 1H), 3.32 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 141.4, 140.5, 135.3, 134.1, 131.0, 129.6, 128.2, 127.2, 121.3, 115.8, 108.9, 93.1, 52.3, 21.5, 20.9.

Melting point: 103-105 °C.

HRMS (ESI) Calcd. for $C_{18}H_{19}NO_3S$: $[M\text{-}OCH_3]^+$, 298.0896. Found: m/z 298.0898.

2,5-dimethoxy-3-methylene-1-tosylindoline (3c):



The representative general procedure **E** was followed, using **1c** (88 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3c** (55 mg, 80% yield) as a brown solid. R_f 0.71 (20 % EtOAc in hexane).

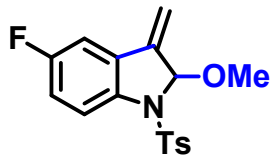
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 3H), 7.16 (d, J = 7.9 Hz, 2H), 6.86-6.82 (m, 2H), 5.77 (t, J = 1.5 Hz, 1H), 5.60 (d, J = 1.5 Hz, 1H), 5.31 (d, J = 1.0 Hz, 1H), 3.77 (s, 3H), 3.38 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 144.1, 141.7, 136.4, 134.9, 129.7, 129.6, 127.2, 117.6, 116.6, 109.5, 105.5, 93.5, 55.7, 52.8, 21.5.

Melting point: 98-100 °C.

HRMS (ESI) Calcd. for $C_{18}H_{19}NO_4S$: $[M\text{-}OCH_3]^+$, 314.0845. Found: m/z 314.0843.

5-fluoro-2-methoxy-3-methylene-1-tosylindoline (3d):



The representative general procedure **E** was followed, using **1d** (86 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 10% EtOAc in hexane) furnished **3d** (49 mg, 74% yield) as a sticky brown solid. R_f 0.71 (20 % EtOAc in hexane).

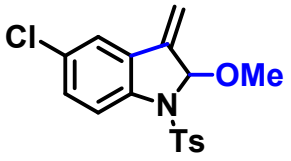
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.57 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.01-6.94 (m, 2H), 5.84 (t, J = 1.6 Hz, 1H), 5.64 (d, J = 1.5 Hz, 1H), 5.39 (s, 1H), 3.37 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (d, J = 243.5 Hz), 144.4, 140.9 (d, J = 2.8 Hz), 138.7, 134.9, 130.1 (d, J = 8.7 Hz), 129.7, 127.2, 117.6 (d, J = 8.5 Hz), 117.0 (d, J = 24.1 Hz), 110.8, 107.8 (d, J = 24.4 Hz), 93.5, 52.9, 21.5.

^{19}F NMR (376 MHz): δ –118.2.

HRMS (ESI) Calcd. for $C_{17}H_{16}FNO_3S$: $[M\text{-}OCH_3]^+$, 302.0646. Found: m/z 302.0652.

5-chloro-2-methoxy-3-methylene-1-tosylindoline (3e):



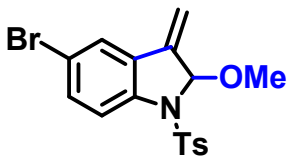
The representative general procedure **E** was followed, using **1e** (89 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3e** (44 mg, 63% yield) as a sticky yellow. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.6 Hz, 1H), 7.29 (d, J = 2.1 Hz, 1H), 7.24-7.18 (m, 3H), 5.88 (t, J = 1.6 Hz, 1H), 5.68 (d, J = 1.2 Hz, 1H), 5.39 (s, 1H), 3.31 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 141.2, 140.2, 135.1, 130.1, 129.9, 129.8, 127.2, 121.1, 116.9, 110.8, 93.2, 52.4, 21.6.

HRMS (ESI) Calcd. for $C_{17}H_{16}ClNO_3S$: $[M\text{-}OCH_3]^+$, 318.0350. Found: m/z 318.0392.

5-bromo-2-methoxy-3-methylene-1-tosylindoline (3f):



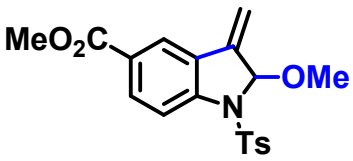
The representative general procedure **E** was followed, using **1f** (98 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3f** (62 mg, 79% yield) as a sticky yellow. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.6 Hz, 1H), 7.44 (d, J = 1.9 Hz, 1H), 7.36 (dd, J = 8.6, 2.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 5.88 (t, J = 1.6 Hz, 1H), 5.68 (d, J = 1.2 Hz, 1H), 5.39 (s, 3H), 3.29 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 141.7, 140.1, 135.1, 132.9, 130.1, 129.8, 127.2, 124.1, 117.3, 117.2, 110.8, 93.0, 52.4, 21.5.

HRMS (ESI) Calcd. for $C_{17}H_{16}BrNO_3S$: $[M\text{-}OCH_3]^+$, 361.9845. Found: m/z 361.9841.

methyl 2-methoxy-3-methylene-1-tosylindoline-5-carboxylate (3g):



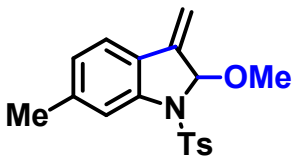
The representative general procedure **E** was followed, using **1g** (94 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 10% EtOAc in hexane) furnished **3g** (49 mg, 65% yield) as a sticky yellow. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 1.6 Hz, 1H), 7.96 (dd, J = 8.6, 1.7 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H), 6.02 (t, J = 1.5 Hz, 1H), 5.82 (d, J = 1.6 Hz, 1H), 5.44 (s, 1H), 3.89 (s, 3H), 3.23 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 146.2, 144.6, 139.9, 135.4, 132.0, 129.8, 127.9, 127.2, 125.9, 122.6, 114.5, 110.7, 93.2, 52.2, 51.9, 21.5.

HRMS (ESI) Calcd. for $C_{19}H_{19}NO_5S$: $[M\text{-}OCH_3]^+$, 342.0795. Found: m/z 342.0797.

2-methoxy-6-methyl-3-methylene-1-tosylindoline (3h):



The representative general procedure **E** was followed, using **1h** (85 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3h** (55 mg, 83% yield) as a brown solid. R_f 0.71 (20 % EtOAc in hexane).

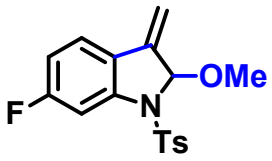
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 8.3 Hz, 2H), 7.45 (s, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 7.8 Hz, 1H), 5.88 (s, 1H), 5.59 (d, J = 1.5 Hz, 1H), 5.27 (s, 1H), 3.28 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 142.9, 141.0, 140.8, 135.5, 129.6, 127.2, 125.5, 125.2, 120.7, 116.3, 108.0, 93.2, 52.0, 22.0, 21.5.

Melting point: 83-85 °C.

HRMS (ESI) Calcd. for $C_{18}H_{19}NO_3S$: $[M\text{-}OCH_3]^+$, 298.0896. Found: m/z 298.0903.

6-fluoro-2-methoxy-3-methylene-1-tosylindoline (3i):



The representative general procedure **E** was followed, using **1i** (86 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 10% EtOAc in hexane) furnished **3i** (55 mg, 82% yield) as a brown solid. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.3 Hz, 2H), 7.29-7.15 (m, 4H), 6.66 (td, J = 8.6, 2.3 Hz, 1H), 5.86 (t, J = 1.6 Hz, 1H), 5.54 (d, J = 1.4 Hz, 1H), 5.24 (s, 1H), 3.19 (s, 3H), 2.29 (s, 3H).

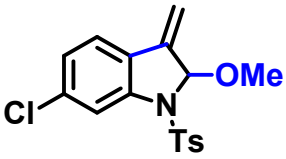
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1 (d, J = 248.4 Hz), 144.5, 144.0 (d, J = 11.9 Hz), 140.0, 135.3, 129.8, 127.2, 123.9 (d, J = 2.5 Hz), 122.1 (d, J = 10.1 Hz), 111.3 (d, J = 23.5 Hz), 108.7 (d, J = 2.7 Hz), 103.6 (d, J = 28.4 Hz), 93.4, 52.1, 21.6.

^{19}F NMR (376 MHz): δ –108.6.

Melting point: 88-90 °C.

HRMS (ESI) Calcd. for $C_{17}H_{16}FNO_3S$: $[M\text{-}OCH_3]^+$, 302.0646. Found: m/z 302.0646.

6-chloro-2-methoxy-3-methylene-1-tosylindoline (3j):



The representative general procedure **E** was followed, using **1j** (89 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3j** (51 mg, 73% yield) as a brown solid. R_f 0.71 (20 % EtOAc in hexane).

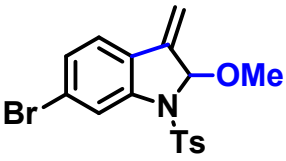
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 1.8 Hz, 1H), 7.26-7.21 (m, 3H), 6.99 (dd, J = 8.2, 1.8 Hz, 1H), 5.92 (t, J = 1.6 Hz, 1H), 5.67 (d, J = 1.3 Hz, 1H), 5.36 (d, J = 0.9 Hz, 1H), 3.25 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 143.6, 140.1, 135.9, 135.2, 129.8, 127.2, 126.5, 124.4, 121.7, 115.8, 109.8, 93.2, 52.1, 21.6.

Melting point: 80-82 °C.

HRMS (ESI) Calcd. for $C_{17}H_{16}ClNO_3S$: $[M\text{-}OCH_3]^+$, 318.0350. Found: m/z 318.0386.

6-bromo-2-methoxy-3-methylene-1-tosylindoline (3k):



The representative general procedure **E** was followed, using **1k** (98 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3k** (67 mg, 85% yield) as a brown solid. R_f 0.71 (20 % EtOAc in hexane).

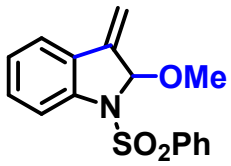
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 1.5 Hz, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.26-7.14 (m, 4H), 5.92 (t, J = 1.6 Hz, 1H), 5.69 (d, J = 1.7 Hz, 1H), 5.38 (d, J = 0.9 Hz, 1H), 3.25 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 143.7, 140.2, 135.2, 129.8, 127.3, 127.2, 126.9, 123.9, 122.0, 118.7, 110.0, 93.1, 52.1, 21.6.

Melting point: 98-100 °C.

HRMS (ESI) Calcd. for $C_{17}H_{16}BrNO_3S$: $[M\text{-}OCH_3]^+$, 361.9845. Found: m/z 361.9844.

2-methoxy-3-methylene-1-(phenylsulfonyl)indoline (3l):



The representative general procedure **E** was followed, using **1l** (79 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3l** (49 mg, 82% yield) as a yellow solid. R_f 0.71 (20 % EtOAc in hexane).

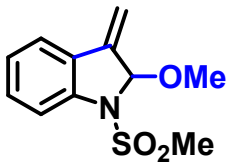
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.39-7.35 (m, 2H), 7.31 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 7.1 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 5.88 (s, 1H), 5.65 (d, J = 1.3 Hz, 1H), 5.32 (s, 1H), 3.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6, 141.1, 138.4, 133.3, 130.2, 129.0, 128.1, 127.2, 124.4, 121.0, 115.7, 109.4, 92.9, 52.3.

Melting point: 60-62°C.

HRMS (ESI) Calcd. for $C_{16}H_{15}NO_3S$: $[M\text{-}OCH_3]^+$, 270.0583. Found: m/z 270.0583.

2-methoxy-3-methylene-1-(methylsulfonyl)indoline (3m):



The representative general procedure **E** was followed, using **1m** (67 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 15% EtOAc in hexane) furnished **3m** (40 mg, 84% yield) as a brown solid. R_f 0.51 (20 % EtOAc in hexane).

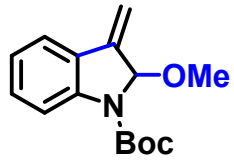
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.45 (m, 2H), 7.32-7.28 (m, 1H), 7.10 (td, J = 7.5, 0.9 Hz, 1H), 5.85 (t, J = 1.5 Hz, 1H), 5.82 (d, J = 1.6 Hz, 1H), 5.46 (d, J = 1.1 Hz, 1H), 3.39 (s, 3H), 2.96 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6, 141.0, 130.5, 127.5, 124.2, 121.4, 114.5, 109.6, 93.0, 52.8, 39.0.

Melting point: 78-80 °C.

HRMS (ESI) Calcd. for $C_{11}H_{13}NO_3S$: $[M\text{-}OCH_3]^+$, 208.0427. Found: m/z 208.0425.

tert-butyl 2-methoxy-3-methyleneindoline-1-carboxylate (3n):



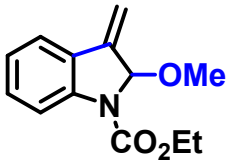
The representative general procedure **E** was followed, using **1n** (72 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3n** (44 mg, 83% yield) as a sticky yellow solid. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (br, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 5.86 (s, 1H), 5.67 (d, J = 1.2 Hz, 1H), 5.32 (s, 1H), 3.20 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0, 143.6, 141.8, 130.0, 127.0, 122.8, 120.3, 115.5, 108.0, 90.1, 81.8, 52.0, 28.4.

HRMS (ESI) Calcd. for $C_{15}H_{19}NO_3$: $[M+Na]^+$, 284.1263. Found: m/z 284.1259.

ethyl 2-methoxy-3-methyleneindoline-1-carboxylate (3o):



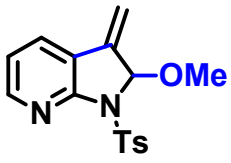
The representative general procedure **E** was followed, using **1o** (66 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3o** (36 mg, 77% yield) as a sticky yellow. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (br, 1H), 7.45 (dd, J = 7.6, 0.6 Hz, 1H), 7.30-7.25 (m, 1H), 7.03 (td, J = 7.5, 0.9 Hz, 1H), 6.02 (t, J = 1.5 Hz, 1H), 5.78 (d, J = 1.8 Hz, 1H), 5.42 (d, J = 1.4 Hz, 1H), 4.39-4.31 (m, 2H), 3.26 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 141.5, 130.2, 127.0, 123.2, 123.1, 120.5, 115.5, 108.5, 108.4, 89.9, 53.0, 62.1, 14.6.

HRMS (ESI) Calcd. for $C_{13}H_{15}NO_3$: $[M+Na]^+$, 256.0950. Found: m/z 256.0941.

2-methoxy-3-methylene-1-tosyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (3p):



The representative general procedure **E** was followed, using **1p** (82 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3p** (52 mg, 82% yield) as a yellow solid. R_f 0.71 (20 % EtOAc in hexane).

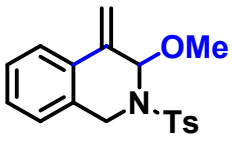
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 5.1, 1.6 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.54 (dd, J = 7.5, 1.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.83 (dd, J = 7.5, 5.1 Hz, 1H), 6.13 (t, J = 1.6 Hz, 1H), 5.75 (d, J = 1.5 Hz, 1H), 5.47 (s, 1H), 3.10 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 149.2, 144.2, 138.5, 136.8, 129.3, 128.7, 128.1, 120.7, 118.6, 111.9, 91.0, 51.8, 21.6.

Melting point: 95-96 °C.

HRMS (ESI) Calcd. for $C_{16}H_{16}N_2O_3S$: $[M+H]^+$, 317.0960. Found: m/z 317.0958.

3-methoxy-4-methylene-2-tosyl-1,2,3,4-tetrahydroisoquinoline (3q)[9]:



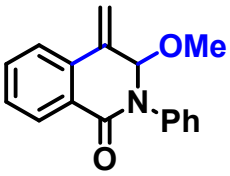
The representative general procedure **E** was followed, using **1q** (75 mg, 0.2 mmol), for 18 h. Purification by column chromatography (eluted with 7% EtOAc in hexane) furnished **3q** (58mg, 88% yield) as a yellow liquid. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.9 Hz, 2H), 7.52 (d, J = 6.1 Hz, 1H), 7.19 (d, J = 7.5 Hz, 4H), 7.02 (d, J = 6.0 Hz, 1H), 5.65 (d, J = 8.1 Hz, 2H), 5.25 (s, 1H), 4.56 (d, J = 16.1 Hz, 1H), 4.37 (d, J = 16.1 Hz, 1H), 3.36 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.5, 137.8, 136.2, 130.8, 129.8, 129.4, 128.4, 127.4, 127.2, 125.9, 124.8, 112.5, 87.3, 54.9, 43.2, 21.5.

HRMS (ESI) Calcd. for $C_{18}H_{19}NO_3S$: $[M+Na]^+$, 352.0983. Found: m/z 352.0974.

3-methoxy-4-methylene-2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3r)[9]:



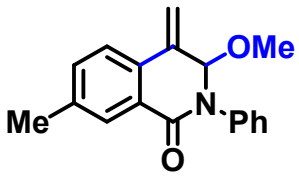
The representative general procedure **E** was followed, using **1r** (72 mg, 0.2 mmol), for 18 h. Purification by column chromatography (eluted with 10% EtOAc in hexane) furnished **3r** (44 mg, 84% yield) as a sticky red. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, J = 7.8, 0.9 Hz, 1H), 7.65-7.62 (m, 1H), 7.58 (td, J = 7.3, 1.4 Hz, 1H), 7.50-7.41 (m, 5H), 7.35-7.30 (m, 1H), 5.87 (s, 1H), 5.42 (s, 1H), 5.18 (s, 1H), 3.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 141.8, 136.5, 133.8, 132.7, 129.1, 129.0, 128.8, 127.2, 126.8, 123.9, 115.9, 93.4, 54.1.

HRMS (ESI) Calcd. for $C_{17}H_{15}NO_2$: $[M+H]^+$, 266.1181. Found: m/z 266.1179.

3-methoxy-7-methyl-4-methylene-2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3s):



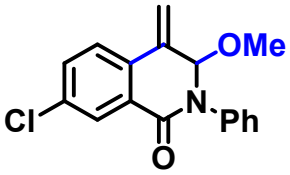
The representative general procedure **E** was followed, using **1s** (75 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3s** (49 mg, 88% yield) as a sticky yellow. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.49-7.37 (m, 5H), 7.34-7.30 (m, 1H), 5.82 (s, 1H), 5.36 (s, 1H), 5.16 (s, 1H), 3.22 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 141.9, 139.3, 136.4, 134.7, 133.6, 131.1, 129.0, 127.1, 126.9, 126.8, 123.9, 114.9, 93.4, 54.1, 21.3.

HRMS (ESI) Calcd. for $C_{18}H_{17}NO_2$: $[M+H]^+$, 280.1338. Found: m/z 280.1341.

7-chloro-3-methoxy-4-methylene-2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3t):



The representative general procedure **E** was followed, using **1t** (79 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3t** (50 mg, 83% yield) as a pale yellow solid. R_f 0.71 (20 % EtOAc in hexane).

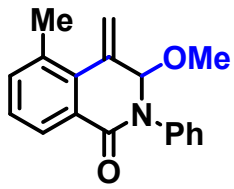
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 1.8 Hz, 1H), 7.45-7.41 (m, 5H), 7.36-7.31 (m, 1H), 5.87 (s, 1H), 5.46 (s, 1H), 5.16 (s, 1H), 3.22 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5, 141.5, 138.9, 135.6, 135.3, 130.6, 129.3, 129.1, 127.4, 126.8, 125.7, 124.1, 116.9, 93.3, 54.3.

Melting point: 118-120 °C.

HRMS (ESI) Calcd. for $C_{17}H_{14}ClNO_2$: $[M+H]^+$, 300.0791. Found: m/z 300.0788.

3-methoxy-5-methyl-4-methylene-2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3u):



The representative general procedure **E** was followed, using **1u** (75 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3u** (42 mg, 75% yield) as a yellow solid. R_f 0.72 (20 % EtOAc in hexane).

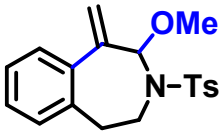
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, J = 7.7, 0.8 Hz, 1H), 7.49-7.41 (m, 5H), 7.38-7.29 (m, 2H), 5.71 (s, 1H), 5.66 (s, 1H), 5.07(s, 1H), 3.22 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 141.8, 136.6, 135.4, 135.1, 132.4, 129.0, 128.7, 128.1, 127.1, 126.9, 126.6, 120.0, 95.1, 54.5, 21.2.

Melting point: 123-125 °C.

HRMS (ESI) Calcd. for $C_{18}H_{17}NO_2$: $[M+H]^+$, 280.1338. Found: m/z 280.1326.

2-methoxy-1-methylene-3-tosyl-2,3,4,5-tetrahydro-1H-benzo[d]azepine (3v):



The representative general procedure **E** was followed, using **1v** (88 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 7%

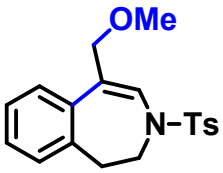
EtOAc in hexane) furnished **3v** (15 mg, 22% yield) as a yellow liquid. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H), 7.21-7.13 (m, 5H), 6.96-6.94 (m, 1H), 5.79 (s, 1H), 5.41 (s, 1H), 5.26 (d, J = 0.9 Hz, 1H), 3.65-3.59 (m, 1H), 3.48-3.40 (m, 1H), 3.29 (s, 3H), 2.89-2.74 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 140.1, 135.3, 134.7, 129.9, 129.4, 128.7, 127.3, 127.1, 126.8, 126.5, 114.7, 77.8, 57.0, 49.4, 35.4, 21.5.

HRMS (ESI) Calcd. for $C_{19}H_{21}NO_3S$: $[M\text{-}OCH_3]^+$, 312.1053. Found: m/z 312.1050.

5-(methoxymethyl)-3-tosyl-2,3-dihydro-1H-benzo[d]azepine (4v):



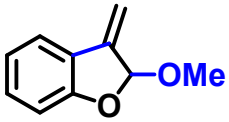
The representative general procedure **E** was followed, using **1v** (88 mg, 0.2 mmol) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **4v** (21 mg, 31% yield) as a yellow liquid. R_f 0.58 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.3 Hz, 2H), 7.51 (dd, J = 8.0, 0.7 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.23-7.19 (m, 2H), 7.09 (td, J = 7.4, 1.1 Hz, 1H), 6.97 (dd, J = 7.4, 0.8 Hz, 1H), 4.31 (s, 2H), 3.78-3.76 (m, 2H), 3.34 (s, 3H), 2.80-2.78 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 140.1, 135.3, 134.7, 129.9, 129.4, 128.7, 127.3, 127.1, 126.8, 126.5, 114.7, 77.8, 57.0, 49.4, 35.4, 21.5.

HRMS (ESI) Calcd. for $C_{19}H_{21}NO_3S$: $[M\text{-}OCH_3]^+$, 312.1053. Found: m/z 312.1057.

2-methoxy-3-methylene-2,3-dihydrobenzofuran (3w):



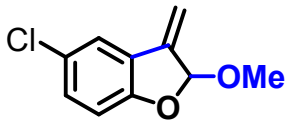
The representative general procedure **E** was followed, using **1w** (77 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 2% EtOAc in hexane) furnished **3w** (32 mg, 66% yield) as a yellow liquid. R_f 0.51 (5 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, J = 7.5, 0.8 Hz, 1H), 7.25-7.20 (m, 1H), 6.92 (td, J = 7.5, 0.9 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 5.98 (t, J = 1.9 Hz, 1H), 5.70 (d, J = 2.1 Hz, 1H), 5.34 (d, J = 1.7 Hz, 1H) 3.52 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9, 143.2, 130.7, 124.3, 121.1, 121.0, 110.5, 107.1, 106.9, 54.5.

HRMS (ESI) Calcd. for $C_{10}H_{10}O_2$: $[M\text{-}2H]^+$, 161.0597. Found: m/z 161.0599.

5-chloro-2-methoxy-3-methylene-2,3-dihydrobenzofuran (3x):



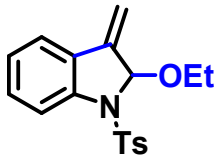
The representative general procedure **E** was followed, using **1x** (88 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 2% EtOAc in hexane) furnished **3x** (31 mg, 53% yield) as a yellow liquid. R_f 0.53 (5% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 2.2 Hz, 1H), 7.17 (dd, J = 8.6, 2.3 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 5.98 (t, J = 1.9 Hz, 1H), 5.70 (d, J = 2.0 Hz, 1H), 5.38 (d, J = 1.7 Hz, 1H) 3.51 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 142.2, 130.5, 126.2, 125.9, 121.1, 111.5, 108.5, 107.7, 54.7.

HRMS (ESI) Calcd. for $C_{10}H_9ClO_2$: $[M-2H]^+$, 195.0207. Found: m/z 195.0202.

2-ethoxy-3-methylene-1-tosylindoline (3aa):



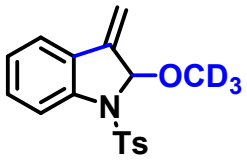
The representative general procedure **E** was followed, using **1a** (82 mg, 0.2 mmol), and **Ethanol** (3ml) at 50°C for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3aa** (35 mg, 53% yield) as a yellow liquid. R_f 0.71 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.1 Hz, 1H), 7.33 (dd, J = 7.6, 0.6 Hz, 1H), 7.27-7.23 (m, 1H), 7.18 (d, J = 7.9 Hz, 2H), 7.03 (td, J = 7.5, 0.9 Hz, 1H), 5.92 (t, J = 1.6 Hz, 1H), 5.64 (d, J = 1.6 Hz, 1H), 5.34 (d, J = 1.3 Hz, 1H), 3.77-3.69 (m, 1H), 3.61-3.54 (m, 1H), 2.34 (s, 3H), 1.19 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 142.7, 141.9, 135.5, 130.1, 129.6, 128.2, 127.2, 124.3, 121.0, 116.0, 109.1, 92.3, 61.2, 21.5, 15.0.

HRMS (ESI) Calcd. for $C_{18}H_{19}NO_3S$: $[M+Na]^+$, 352.0983. Found: m/z 352.0982.

2-(methoxy-d_3)-3-methylene-1-tosylindoline (3a-D):



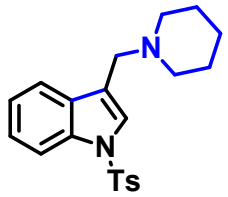
The representative general procedure **E** was followed, using **1a** (82 mg, 0.2 mmol), and **CD_3OD** (3mL) for 18 h. Purification by column chromatography (eluted with 8% EtOAc in hexane) furnished **3a-D** (31 mg, 49% yield) as a brown solid. R_f 0.71 (% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.28-7.24 (m, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.04 (td, J = 7.5, 0.8 Hz, 1H), 5.89 (t, J = 1.5 Hz, 1H), 5.68 (d, J = 1.5 Hz, 1H), 5.35 (s, 1H), 2.34 (s, 3H).

Melting point: 86-88 °C.

HRMS (ESI) Calcd. for $C_{17}H_{14}D_3NO_3S$: $[M+Na]^+$, 341.1015. Found: m/z 341.1001.

3-(piperidin-1-ylmethyl)-1-tosyl-1H-indole (4ad):



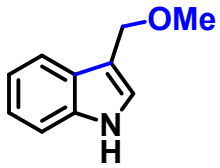
The representative general procedure **F** was followed, using **1a** (123 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 20% acetone in hexane) furnished **4ad** (62 mg, 56% yield) as a sticky yellow. R_f 0.52 (30 % acetone in hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.49 (s, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 7.19 (d, J = 8.3 Hz, 2H), 3.61 (s, 2H), 2.41 (br, 4H), 2.32 (s, 3H), 1.59-1.54 (m, 4H), 1.41 (br, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8, 135.4, 135.3, 131.2, 129.8, 126.8, 125.0, 124.6, 123.1, 120.4, 119.3, 113.6, 54.3, 53.6, 25.8, 24.2, 21.5.

HRMS (ESI) Calcd. for $C_{21}H_{24}N_2O_2S$: $[M+H]^+$, 369.1637. Found: m/z 369.1629.

3-(methoxymethyl)-1H-indole (4a):[10]



The representative general procedure **E** was followed, using **1'a** (90 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4a** (38 mg, 79% yield) as a yellow solid. R_f 0.51 (20 % EtOAc in hexane).

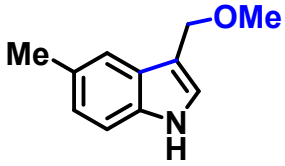
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (brs, 1H), 7.73-7.71 (m, 1H), 7.37-7.34 (m, 1H), 7.23-7.19 (m, 1H), 7.18-7.13 (m, 2H), 4.68 (d, J = 0.6 Hz, 2H), 3.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 126.1, 122.7, 121.3, 118.8, 118.1, 112.2, 110.1, 65.5, 56.5.

Melting point: 98-99 °C.

HRMS (ESI) Calcd. for $C_{10}H_{11}NO$: $[M-OCH_3]^+$, 130.0651. Found: m/z 130.0650.

3-(methoxymethyl)-5-methyl-1H-indole (4b):[10]



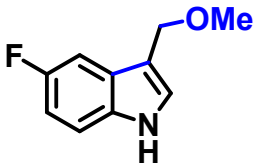
The representative general procedure **E** was followed, using **1'b** (94 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4b** (41 mg, 77% yield) as a sticky brown. R_f 0.51 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, D_6-acetone): δ 9.99 (brs, 1H), 7.44 (d, J = 0.7 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 7.24 (d, J = 2.3 Hz, 1H), 6.96 (dd, J = 8.3, 1.4 Hz, 1H), 4.60 (s, 2H), 3.29 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, D_6-acetone): δ 136.2, 128.8, 128.6, 125.4, 123.9, 119.5, 112.9, 111.9, 67.0, 57.1, 21.6.

HRMS (ESI) Calcd. for $C_{11}H_{13}NO$: $[M\text{-}OCH_3]^+$,144.0808. Found: m/z 144.0803.

5-fluoro-3-(methoxymethyl)-1H-indole (4c):[10]



The representative general procedure **E** was followed, using **1'c** (95 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4c** (37 mg, 68% yield) as a sticky brown. R_f 0.51 (20 % EtOAc in hexane).

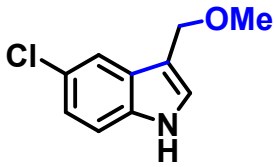
^{1}H NMR (400 MHz, D_6-acetone): δ 10.26 (brs, 1H), 7.41-7.37 (m, 2H), 7.31 (dd, J = 9.9, 2.5 Hz, 1H), 6.91 (td, J = 9.2, 2.5 Hz, 1H), 4.59 (s, 2H), 3.28 (s, 3H).

^{13}C NMR (100 MHz, D_6-acetone): δ 158.5 (d, J = 232.1 Hz), 134.4, 128.7 (d, J = 9.9 Hz), 127.3, 113.8 (d, J = 4.7 Hz), 113.1 (d, J = 9.6 Hz), 110.4 (d, J = 26.4 Hz), 104.4 (d, J = 23.4 Hz), 66.8, 57.2.

^{19}F NMR (376 MHz, D_6-acetone): δ –126.7.

HRMS (ESI) Calcd. for $C_{10}H_{10}FNO$: $[M\text{-}OCH_3]^+$, 148.0557. Found: m/z 148.0551.

5-chloro-3-(methoxymethyl)-1H-indole (4d):[10]



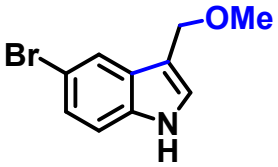
The representative general procedure **E** was followed, using **1'd** (100 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4d** (41 mg, 70% yield) as a sticky yellow. R_f 0.51 (20 % EtOAc in hexane).

^{1}H NMR (500 MHz, D_6-acetone): δ 10.35 (brs, 1H), 7.64 (d, J = 1.9 Hz, 1H), 7.41 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 2.1 Hz, 1H), 7.11(dd, J = 8.6, 1.7 Hz, 1H), 4.60 (s, 2H), 3.29 (s, 3H).

^{13}C NMR (125 MHz, D_6-acetone): δ 136.2, 129.5, 126.9, 125.2, 122.4, 119.2, 113.6, 113.4, 66.8, 57.3.

HRMS (ESI) Calcd. for $C_{10}H_{10}ClNO$: $[M\text{-}OCH_3]^+$, 164.0262. Found: m/z 164.0251.

5-bromo-3-(methoxymethyl)-1H-indole (4e):[10]



The representative general procedure **E** was followed, using **1**'**e** (113 mg, 0.3 mmol), for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4e** (49 mg, 68% yield) as a pale yellow solid. R_f 0.51 (20 % EtOAc in hexane).

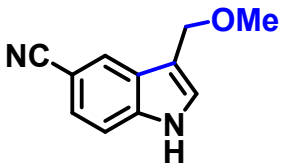
^{1}H NMR (400 MHz, D$_4$-methanol): δ 7.73 (d, J = 1.5 Hz, 1H), 7.28-7.26 (m, 2H), 7.20 (dd, J = 8.6, 1.9 Hz, 1H), 4.60 (s, 2H), 3.33 (s, 3H).

^{13}C NMR (100 MHz, D$_4$-methanol): δ 136.9, 130.2, 127.2, 125.4, 122.3, 113.9, 113.3, 112.7, 67.3, 57.4.

Melting point: 94-96 °C.

HRMS (ESI) Calcd. for $C_{10}H_{10}BrNO$: $[M\text{-}OCH_3]^+$, 207.9756. Found: m/z 207.9757.

3-(methoxymethyl)-1H-indole-5-carbonitrile (4f):



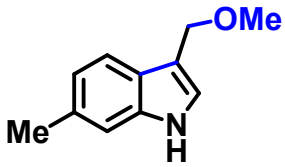
The representative general procedure **E** was followed, using **1**'**f** (97 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4f** (36 mg, 65% yield) as a sticky brown. R_f 0.51 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, D$_4$-methanol): δ 8.02 (d, J = 0.8 Hz, 1H), 7.48 (dd, J = 8.4, 0.6 Hz, 1H), 7.41 (s, 1H), 7.38 (dd, J = 8.5, 1.5 Hz, 1H), 4.65 (s, 2H), 3.35 (s, 3H).

^{13}C NMR (100 MHz, D$_4$-methanol): δ 140.0, 128.3, 128.2, 125.7, 125.4, 121.8, 114.3, 113.6, 102.8, 67.0, 57.7.

HRMS (ESI) Calcd. for $C_{11}H_{10}N_2O$: $[M+Na]^+$, 209.0691 Found: m/z 209.0688.

3-(methoxymethyl)-6-methyl-1H-indole (4g):



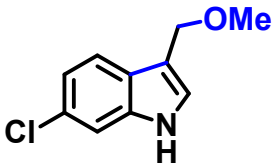
The representative general procedure **E** was followed, using **1**'**g** (94 mg, 0.3 mmol) for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4g** (40 mg, 76% yield) as a sticky brown. R_f 0.51 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, D$_6$-acetone): δ 9.95 (brs, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.19 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 8.1 Hz, 1H), 4.60 (s, 2H), 3.28 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, D$_6$-acetone): δ 138.3, 131.7, 126.3, 124.6, 121.6, 119.5, 113.3, 112.1, 67.1, 57.1, 21.8.

HRMS (ESI) Calcd. for $C_{11}H_{13}NO$: $[M\text{-}OCH_3]^+$,144.0808. Found: m/z 144.0800.

6-chloro-3-(methoxymethyl)-1H-indole (4h):[10]



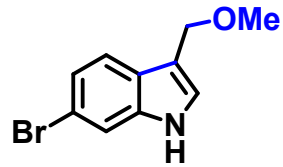
The representative general procedure **E** was followed, using **1'h** (100 mg, 0.3 mmol), for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4h** (42 mg, 72% yield) as a sticky brown. R_f 0.51 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, D_6-acetone): δ 10.30 (brs, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 7.04 (dd, J = 8.4, 1.9 Hz, 1H), 4.60 (s, 2H), 3.28 (s, 3H).

^{13}C NMR (100 MHz, D_6-acetone): δ 138.2, 127.8, 127.1, 126.3, 121.1, 120.3, 113.8, 112.0, 66.8, 57.3.

HRMS (ESI) Calcd. for $C_{10}H_{10}ClNO$: $[M\text{-}OCH_3]^+$, 164.0262. Found: m/z 164.0260.

6-bromo-3-(methoxymethyl)-1H-indole (4i):[10]



The representative general procedure **E** was followed, using **1'i** (113 mg, 0.3 mmol), for 18 h. Purification by column chromatography (eluted with 12% EtOAc in hexane) furnished **4i** (46 mg, 64% yield) as a dark yellow solid. R_f 0.51 (20 % EtOAc in hexane).

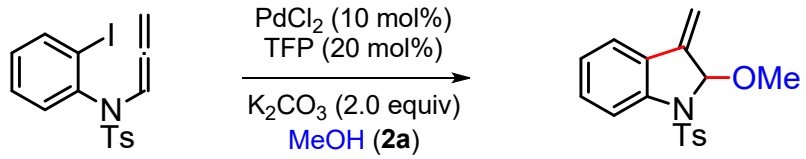
^{1}H NMR (400 MHz, D_4-methanol): δ 7.52 (d, J = 1.7 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.22 (s, 1H), 7.14 (dd, J = 8.4, 1.7 Hz, 1H), 4.61 (s, 2H), 3.33 (s, 3H).

^{13}C NMR (100 MHz, D_4-methanol): δ 139.0, 127.4, 126.6, 123.3, 121.2, 116.1, 115.2, 113.2, 67.2, 57.5.

Melting point: 78-80 °C.

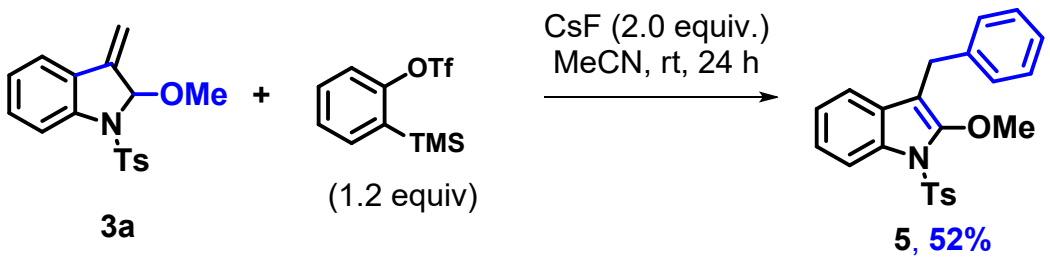
HRMS (ESI) Calcd. for $C_{10}H_{10}BrNO$: $[M\text{-}OCH_3]^+$, 207.9756. Found: m/z 207.9770.

5. Gram scale synthesis of 3a:



To an oven dried Schlenk tube was charged with allenamide **1a** (1g, 2.43 mmol), palladium chloride (43 mg, 10 mol%), tri(2-furyl)phosphine (118 mg, 20 mol%), and K_2CO_3 (671 mg, 2 equiv.), and the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). Methanol (**2a**) 20 mL was added to the reaction mixture. The reaction was stirred at rt for 18 h, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **3a** as a brown solid (550 mg, 72% yield).

Synthesis of 3-benzyl-2-methoxy-1-tosyl-1H-indole (5):



To an oven dried Schlenk tube was charged with **3a** (95 mg, 0.3 mmol, 1 equiv.), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1.2 equiv.) and CsF (2 equiv.) in MeCN (3 mL) was added to the reaction mixture. The reaction was stirred at rt for 24 h, and the solvent was evaporated under reduced pressure. Purification by column chromatography (eluted with 5% EtOAc in hexane) furnished **5** (61 mg, 52% yield) as a white solid. R_f 0.72 (20 % EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.25-7.22 (m, 1H), 7.18-7.11 (m, 7H), 7.02-6.99 (m, 2H), 4.01 (s, 3H), 3.89 (s, 2H), 2.35 (s, 3H).

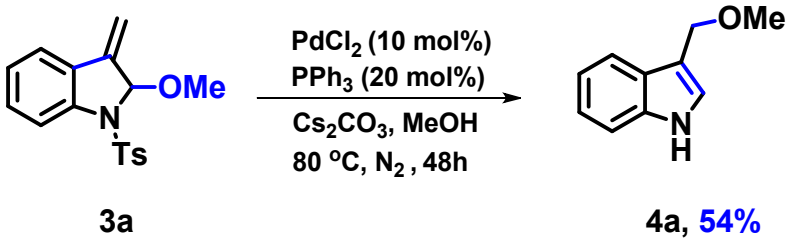
^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 144.7, 139.3, 135.2, 132.6, 129.5, 129.4, 128.3, 128.1, 126.9, 126.1, 123.9, 123.8, 118.9, 115.2, 105.8, 64.9, 28.4, 21.6.

Melting point: 120-122 °C.

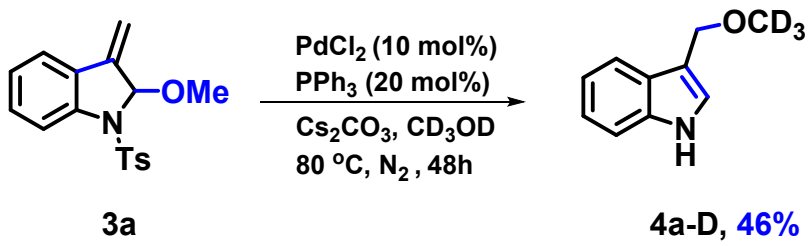
HRMS (ESI) Calcd. for $C_{23}H_{21}NO_3S$: $[M-H]^+$, 392.1320. Found: m/z 392.1312.

6. Mechanistic experiments:

a.



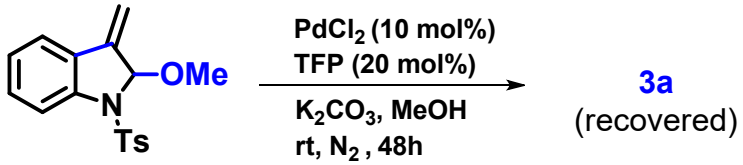
To an oven dried Schlenk tube was charged with **3a** (0.28 mmol, 1 equiv.), palladium chloride (10 mol%), triphenylphosphine (20 mol%), and Cs_2CO_3 (2 equiv.), and the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). Then, the methanol (3 mL) was added to the reaction mixture. The reaction was stirred at rt for 48 h, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **4a** as a yellow solid (25 mg, 54% yield).



3a **4a-D, 46%**

To an oven dried Schlenk tube was charged with **3a** (0.318 mmol, 1 equiv.), palladium chloride (10 mol%), triphenylphosphine (20 mol%), and Cs_2CO_3 (2 equiv.), and the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). Then, the CD_3OD (3 mL) was added to the reaction mixture. The reaction was stirred at rt for 48 h, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **4a-D** as a yellow solid (24 mg, 46% yield).

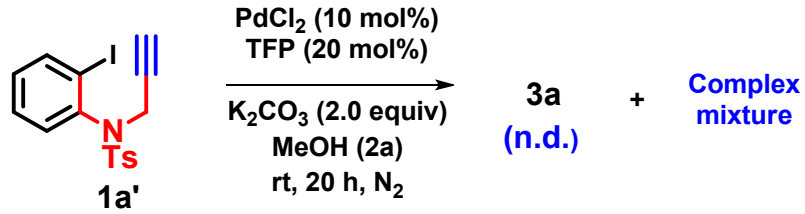
^{1}H NMR (400 MHz, D_6-acetone): δ 10.14 (brs, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 2.2 Hz, 1H), 7.13-7.09 (m, 1H), 7.05-7.01 (m, 1H), 4.61 (s, 2H).



3a

To an oven dried Schlenk tube was charged with **3a** (0.28 mmol, 1 equiv.), palladium chloride (10 mol%), tri(2-furyl)phosphine (20 mol%), and K_2CO_3 (2 equiv.), and the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). Methanol (**2a)** 3 mL was added to the reaction mixture. The reaction was stirred at rt for 18 h. No reaction was observed and **3a** was recovered.

b.

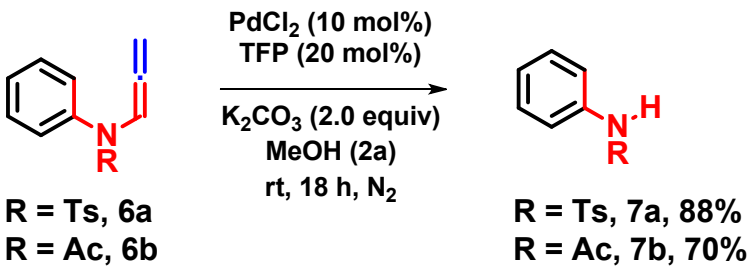


1a'

To an oven dried Schlenk tube, was charged with allenamide **1a'** (1 equiv.), palladium chloride (10 mol%), tri(2-furyl)phosphine (20 mol%), and K_2CO_3 (2 equiv.), and the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). Methanol (**2a)** 3

mL was added to the reaction mixture. The reaction was stirred at rt for 20 h. **3a** was not detected in this reaction, however, we observed a complex reaction mixture.

c.



To an oven dried Schlenk tube was charged with allenamide **6** (1 equiv.), palladium chloride (10 mol%), tri(2-furyl)phosphine (20 mol%), and K_2CO_3 (2 equiv.), the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). Methanol (**2a)** 3 mL was added to the reaction mixture. The reaction was stirred at rt for 18 h, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc).

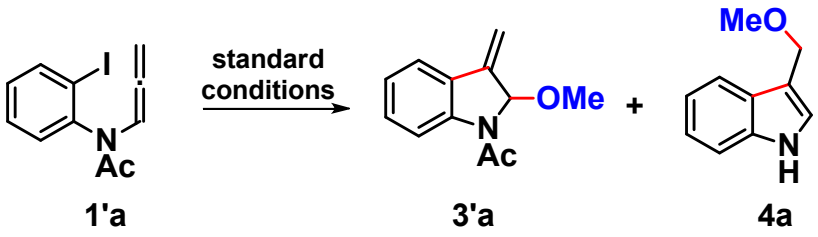
4-methyl-N-phenylbenzenesulfonamide (7a):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 7.8 Hz, 2H), 7.24-7.20 (m, 4H), 7.11-7.04 (m, 4H), 2.36 (s, 3H).

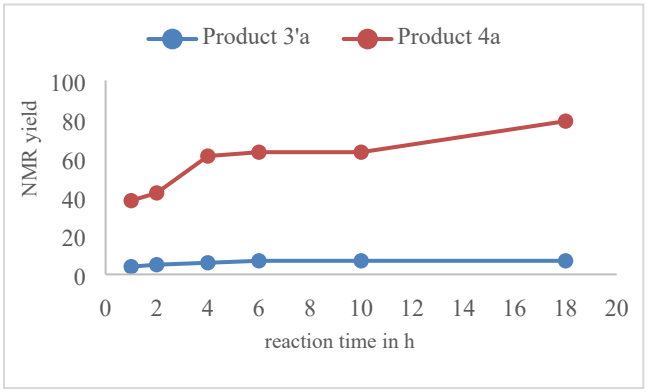
N-phenylacetamide (7b):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.9 Hz, 2H), 7.23 (t, J = 7.8 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 2.08 (s, 3H).

d. Formation of 3'a and 4a versus time

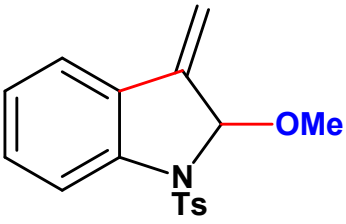


To an oven dried Schlenk tube was charged with allenamide **1'a** (0.034 mmol, 1 equiv.), palladium chloride (10 mol%), tri(2-furyl)phosphine (20 mol%), and K_2CO_3 (2 equiv.), the vial was sealed with a septum and put under vacuum, followed by flushing with N_2 gas (3X). methanol (2a) 1 mL was added to the reaction mixture. The reaction was stirred at rt. The same reaction was run for different time intervals (1-10h) and the ^{1}H NMR yield was calculated using 1,3,5-trimethoxybenzene as an internal standard.

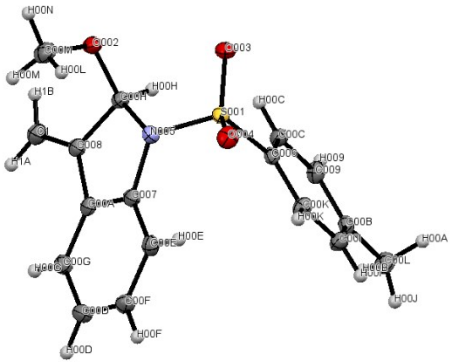


Entry	Time	**3'a** (NMR Yield %)	**4a** (NMR Yield %)
1.	1h	4	38
2.	2h	5	42
3.	4h	6	61
4.	6h	7	63
5.	10h	7	63
6.	18h	7	79

7. Crystal Structure



3a
CCDC 2168612



Compound	**3a**		
CCDC	2168612	Formula	$C_{17}H_{17}NO_3S$
M_w	315.38		
crystal system	Monoclinic		
space group	$P2_1/c$		

T [K]	296		
a [Å]	9.6139(10)	α [°]	90
b [Å]	14.7059(13)	β [°]	100.759(3)
c [Å]	10.8929(10)	γ [°]	90
Z	4	V [Å^3]	1513.0(2)
D_{calc} [g cm^{-3}]	1.385	μ [mm^{-1}]	0.226
total reflns	3797	unique reflns	3789
observed reflns	3241		
$R_1[I > 2\sigma(I)]$	0.0362		
wR_2 [all]	0.0927		
GOF	0.994		
Diffractometer	Bruker APEX-II CCD		

8. References

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14. Deposition number 2168612 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre.

9.NMR Spectra

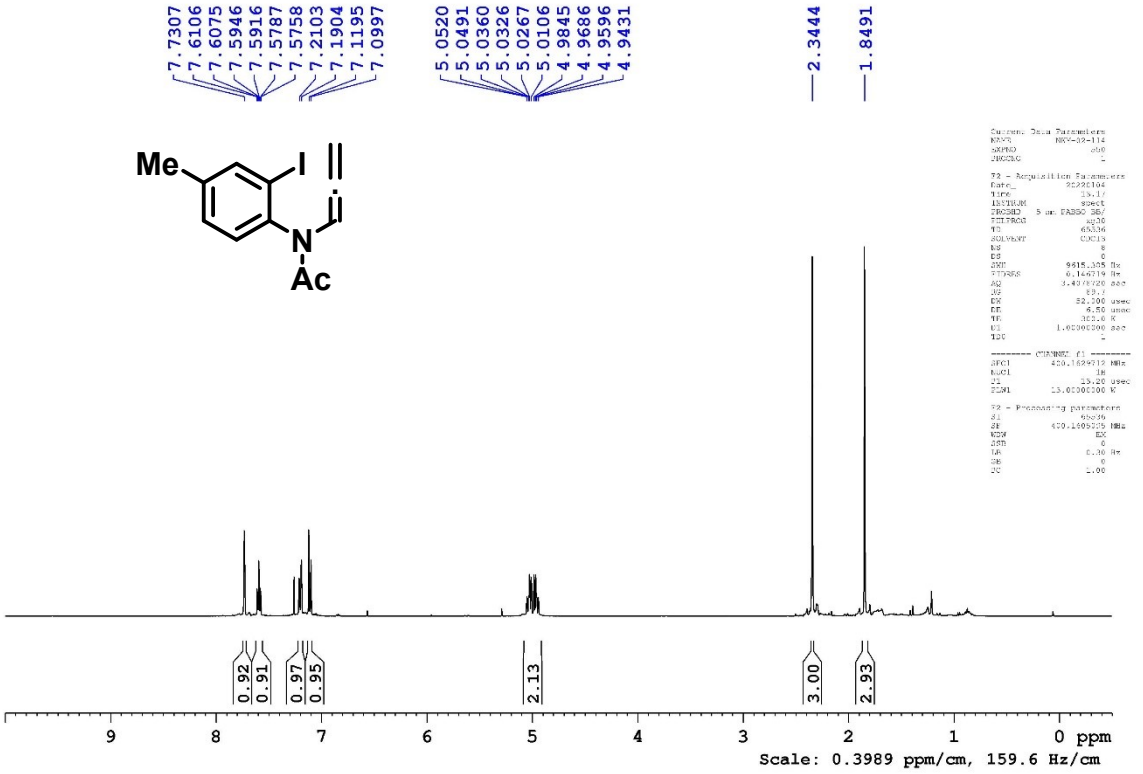

Figure S-1: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1'b**

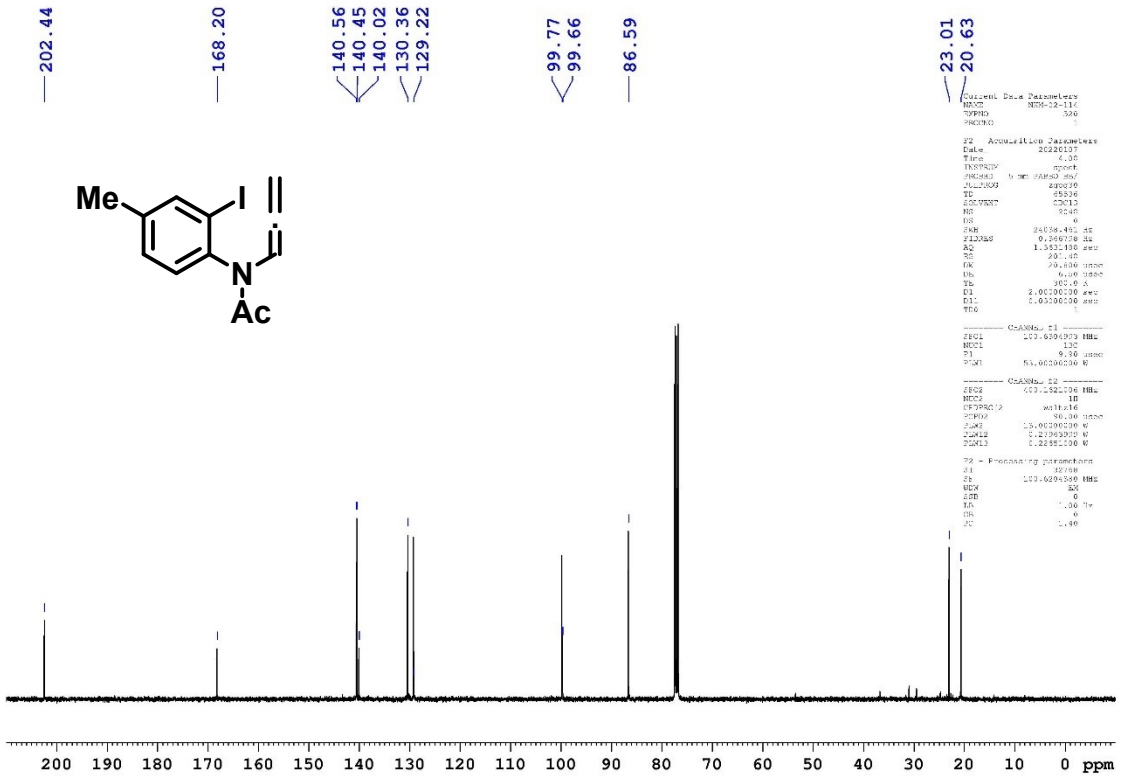

Figure S-2: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1'b**

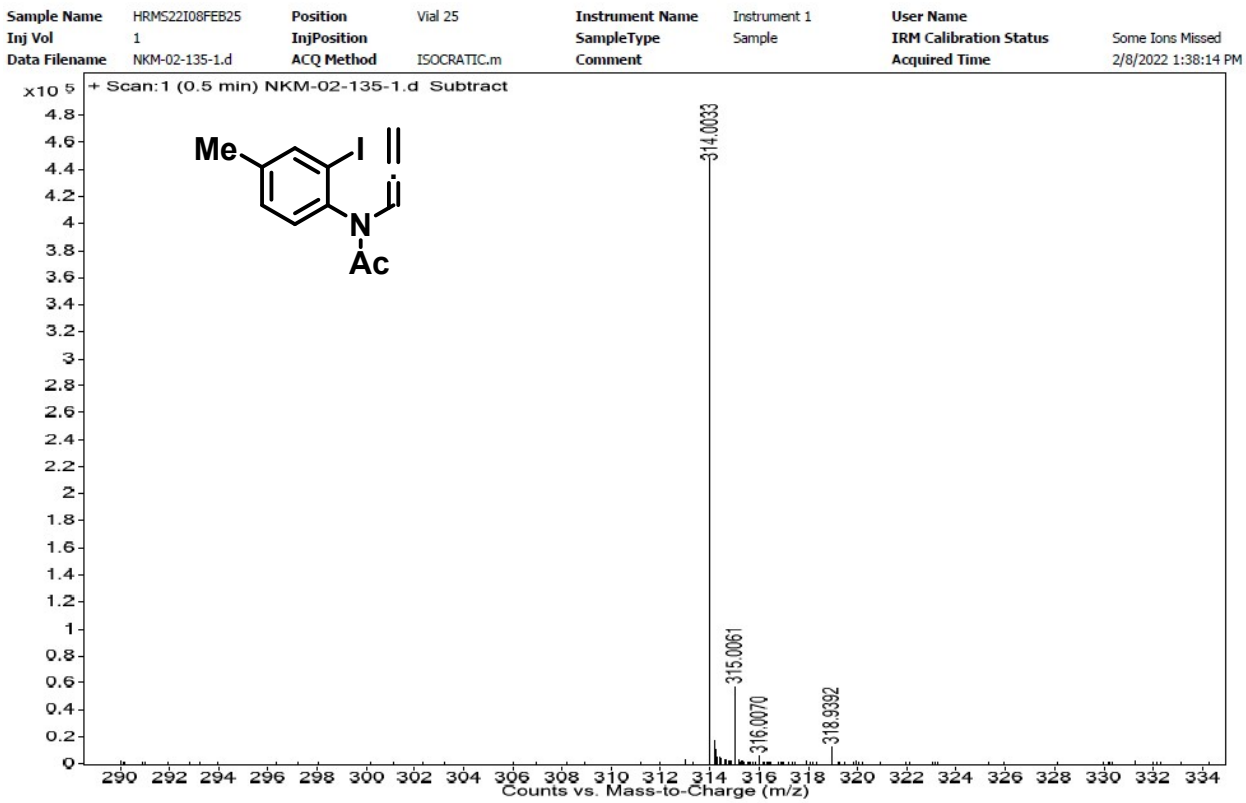

Figure S-3: HRMS spectrum of compound **1'b**

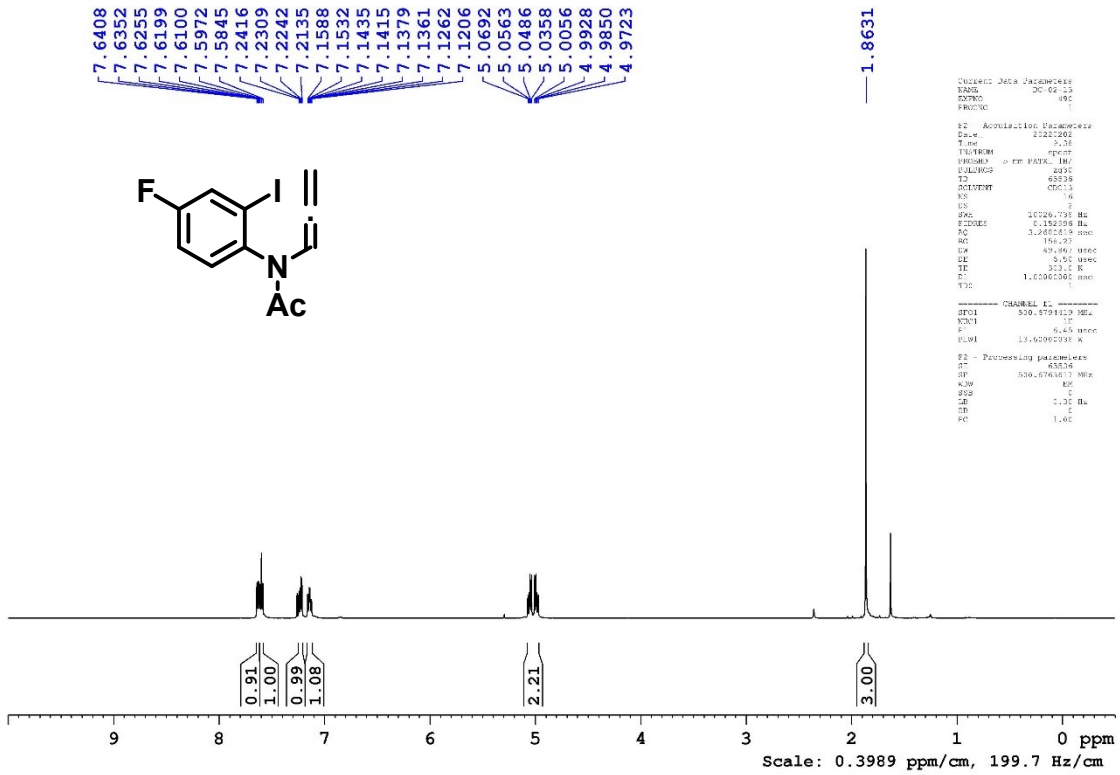

Figure S-4: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1'c**

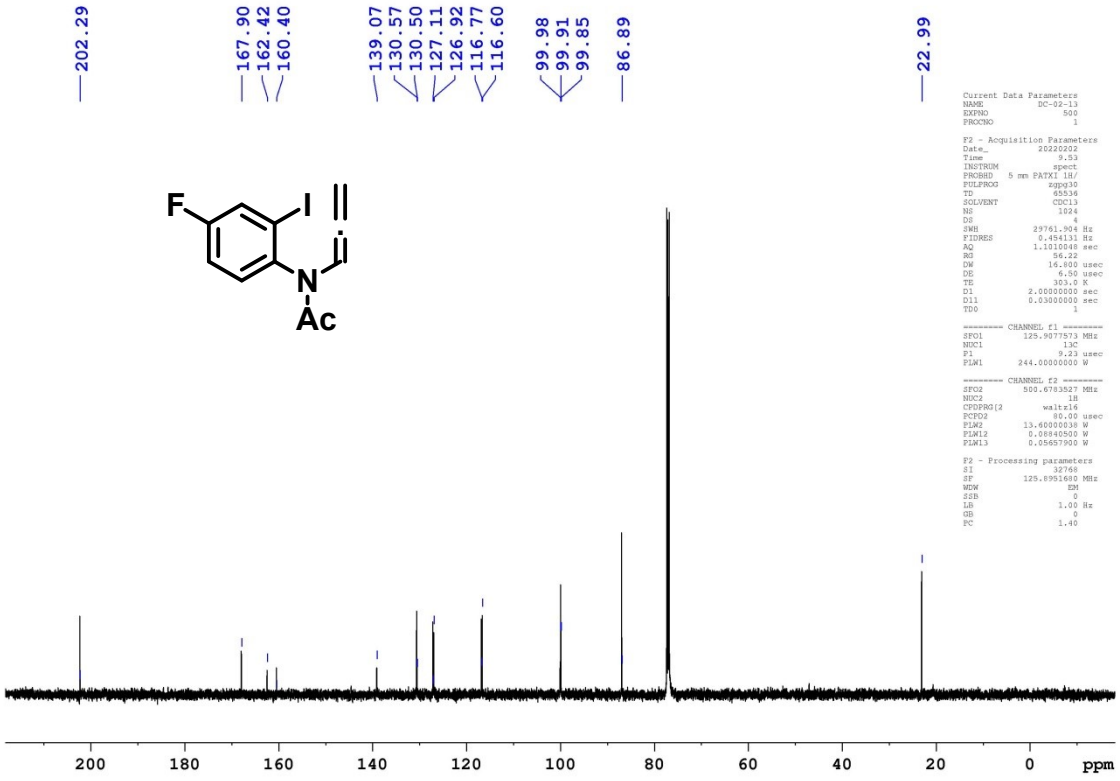

Figure S-5: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1'c**

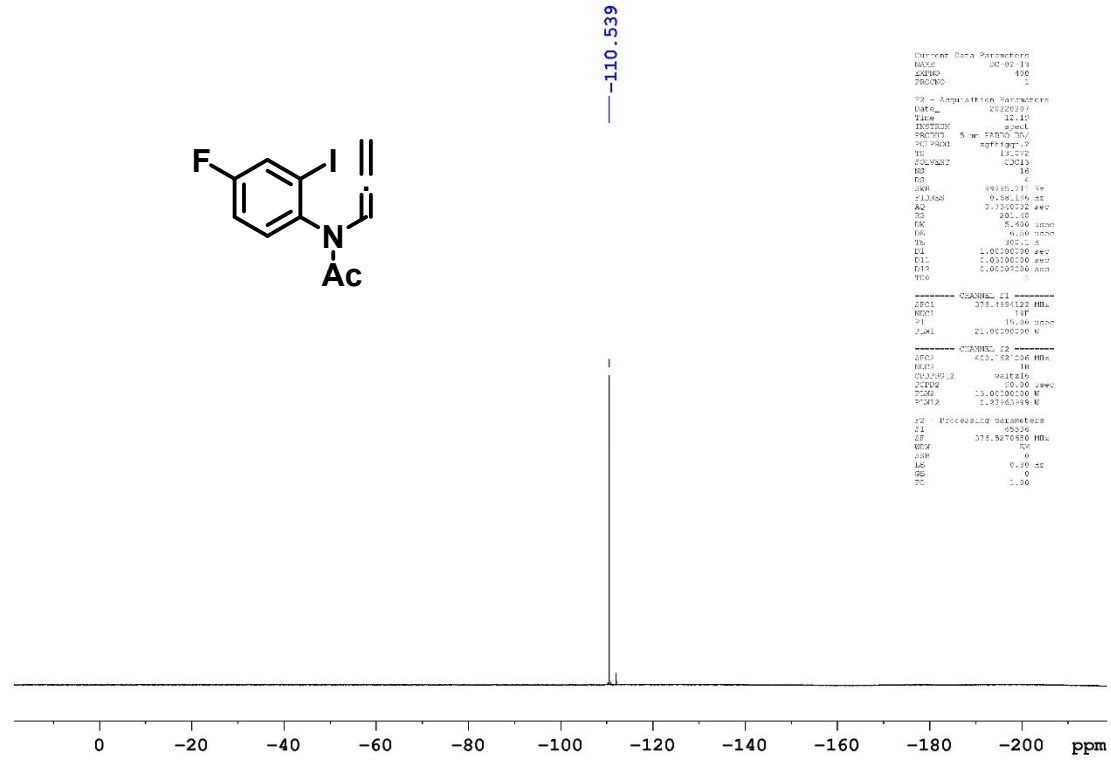

Figure S-6: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **1'c**

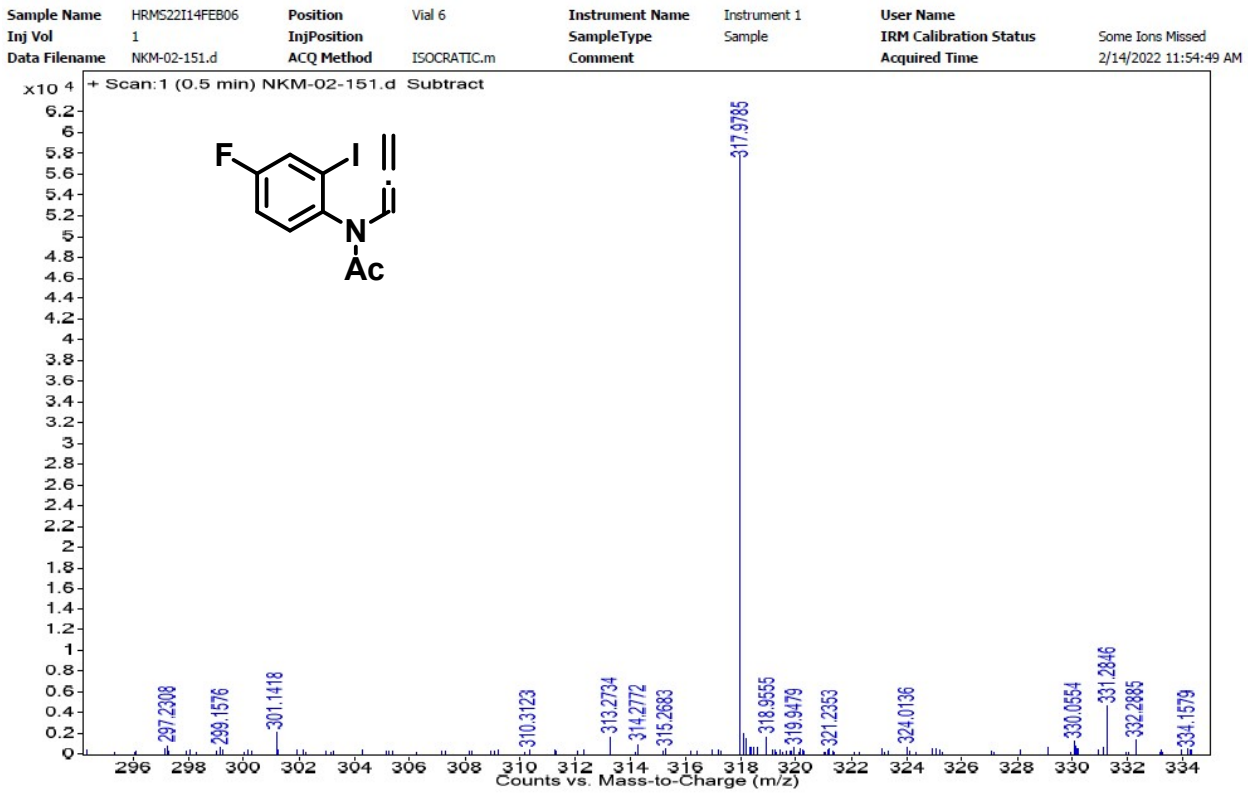

Figure S-7: HRMS spectrum of compound **1'**c

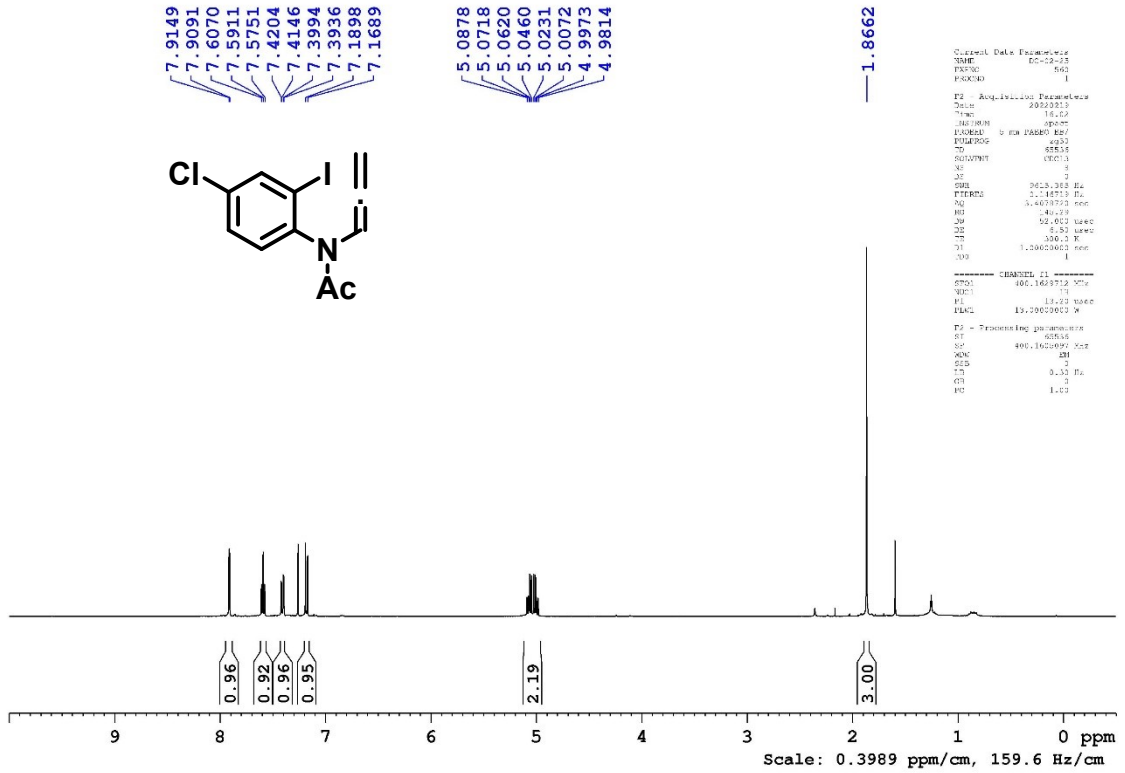

Figure S-8: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1'd**

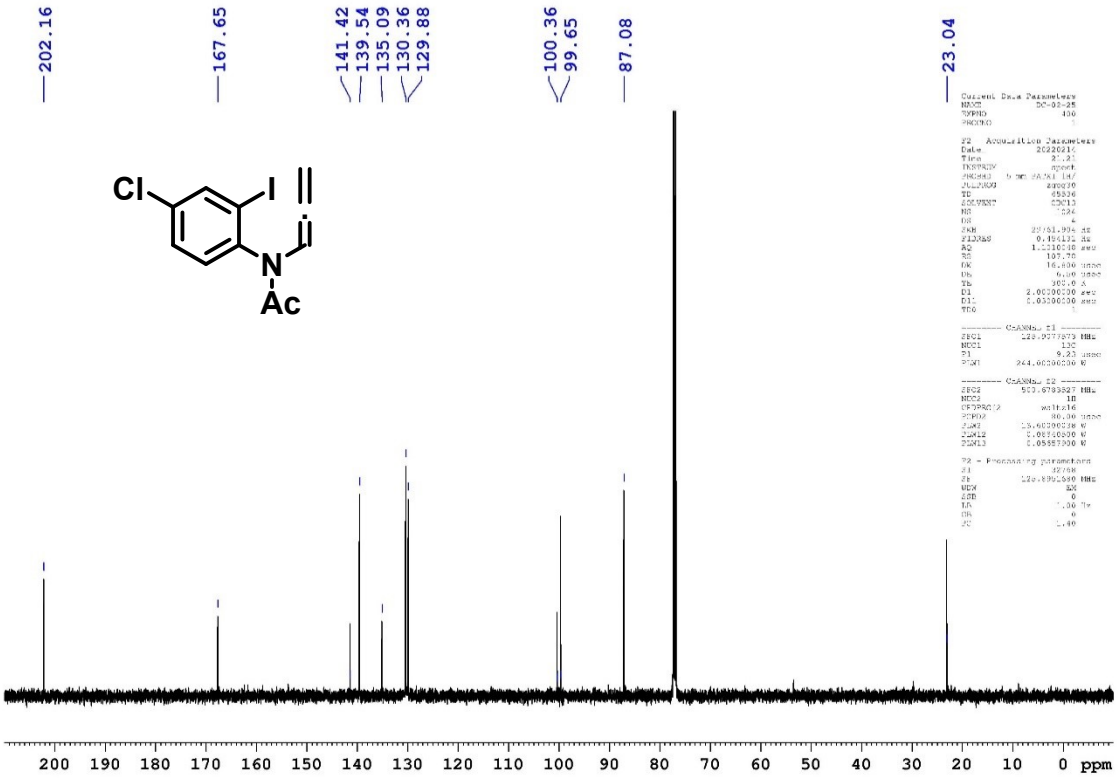

Figure S-9: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1'd**

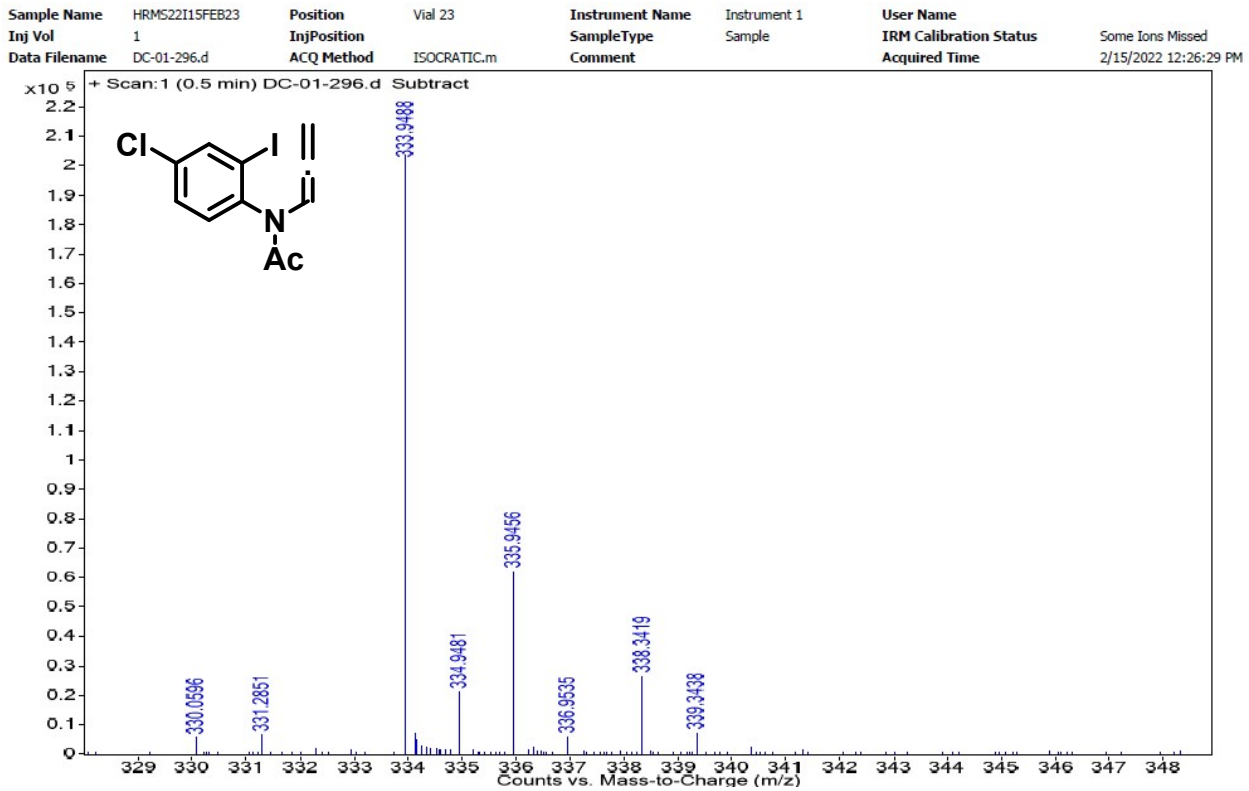

Figure S-10: HRMS spectrum of compound **1'd**

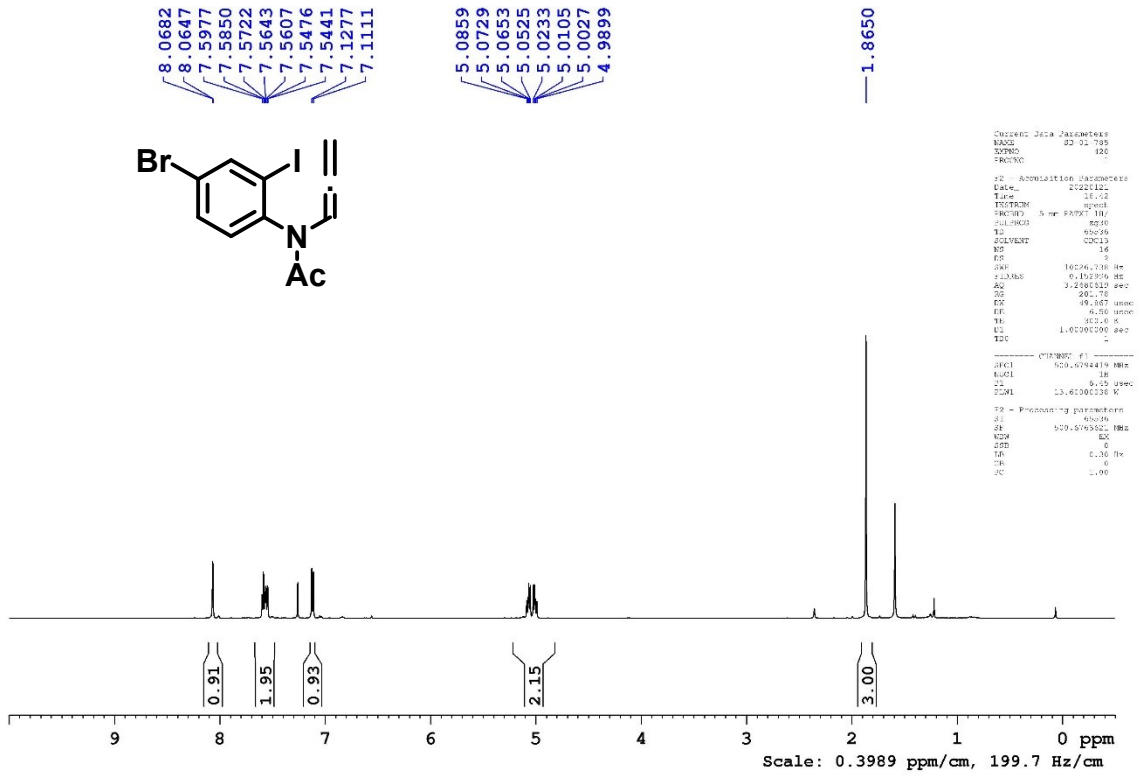

Figure S-11: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1'e**

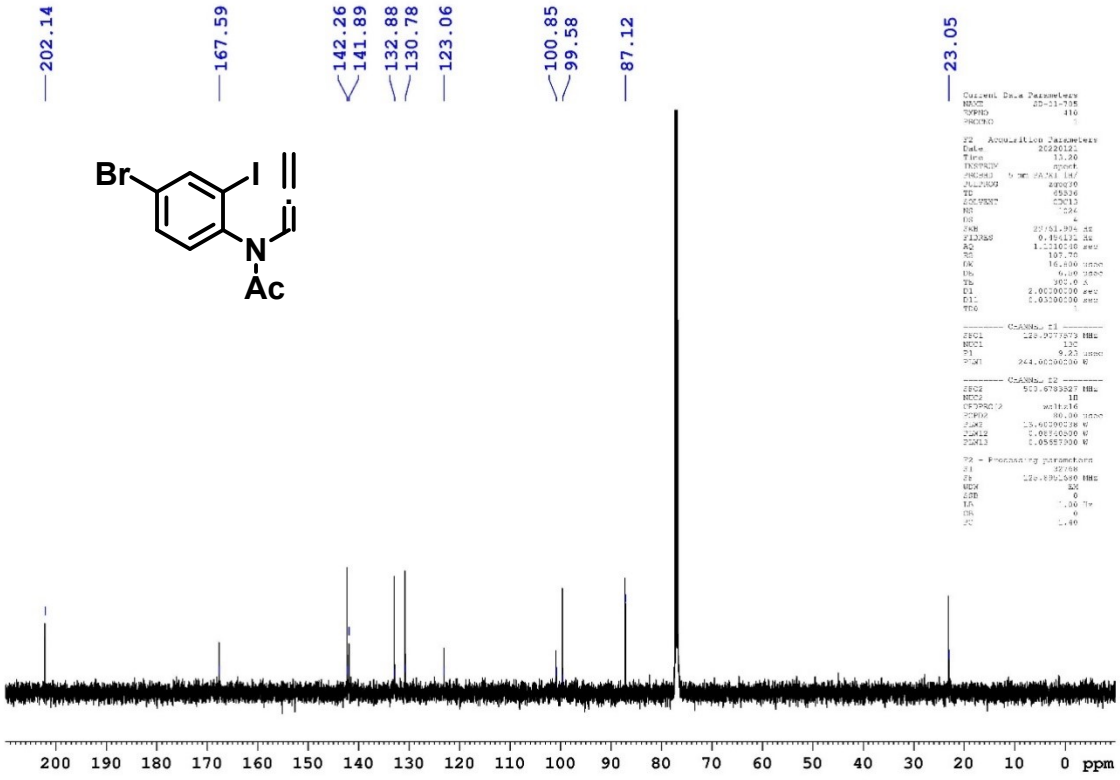

Figure S-12: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1'e**

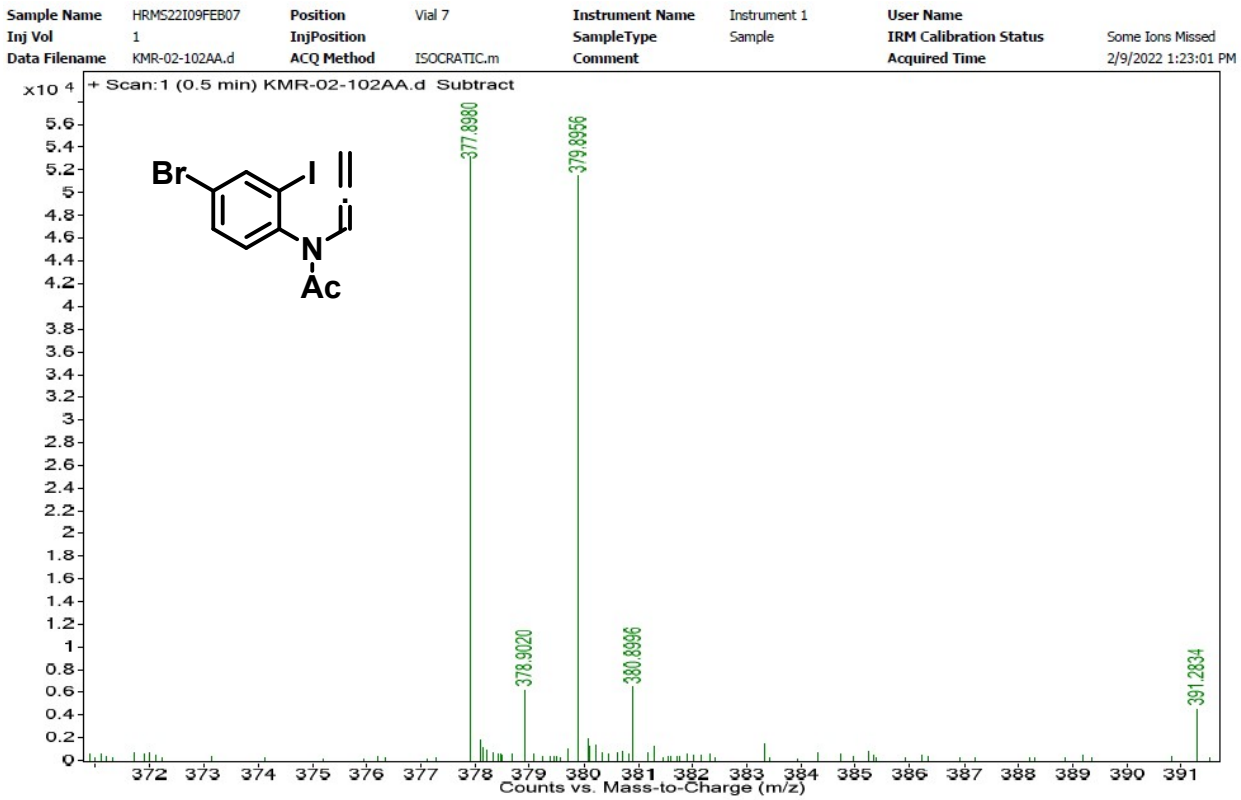

Figure S-13: HRMS spectrum of compound **1'e**

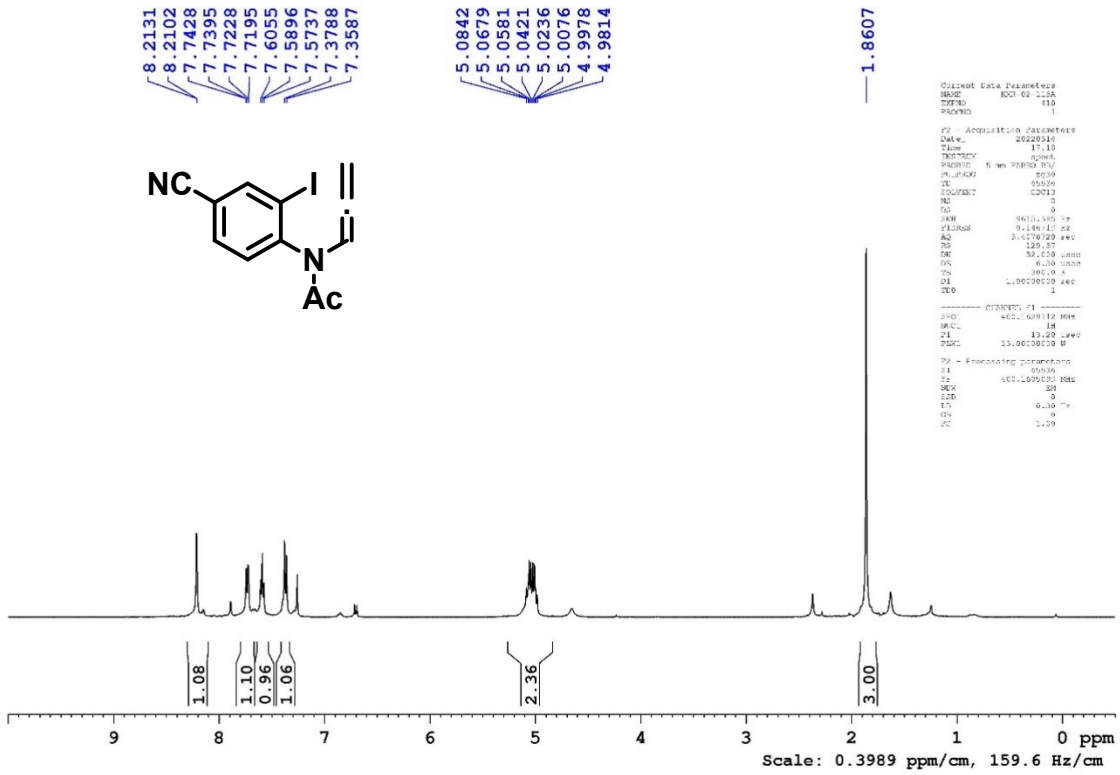

Figure S-14: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1'f**

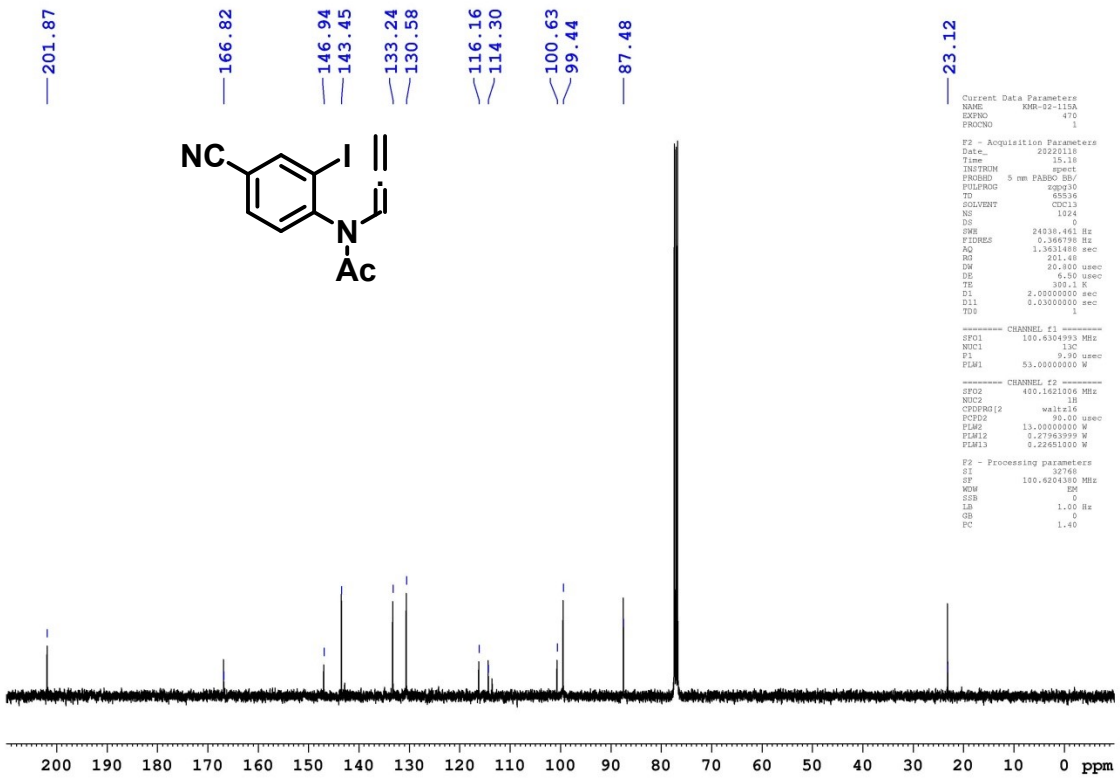

Figure S-15: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1'f**

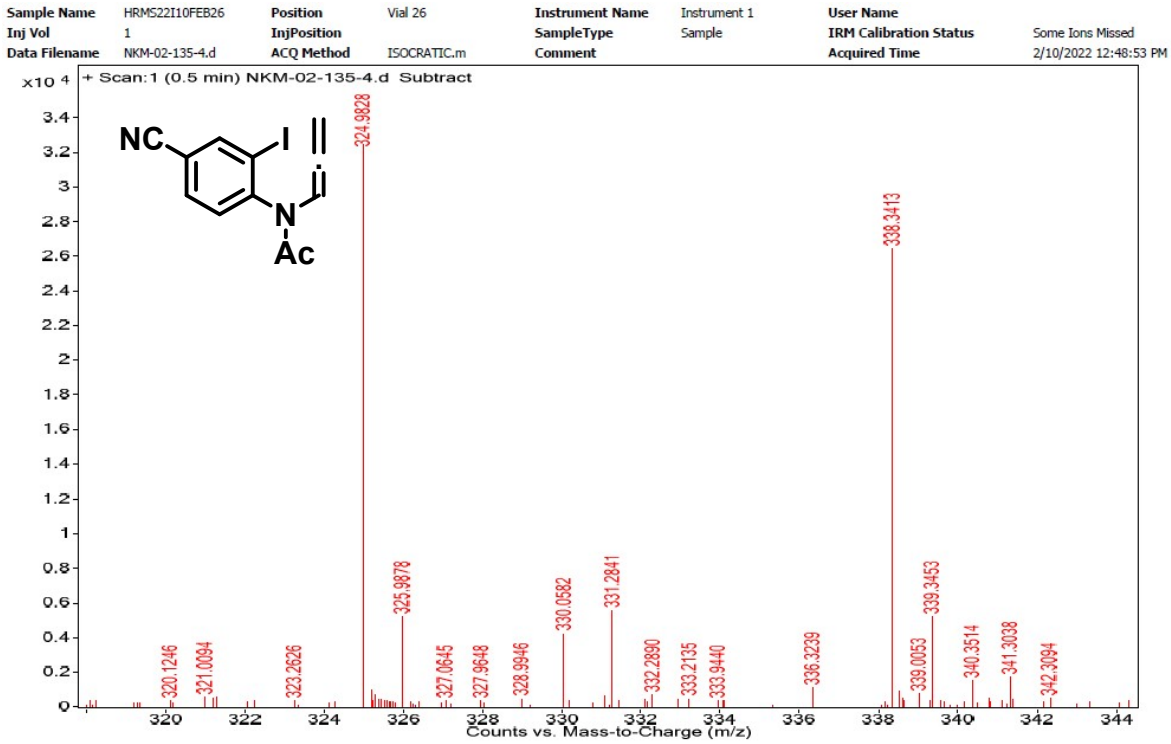

Figure S-16: HRMS spectrum of compound **1'f**

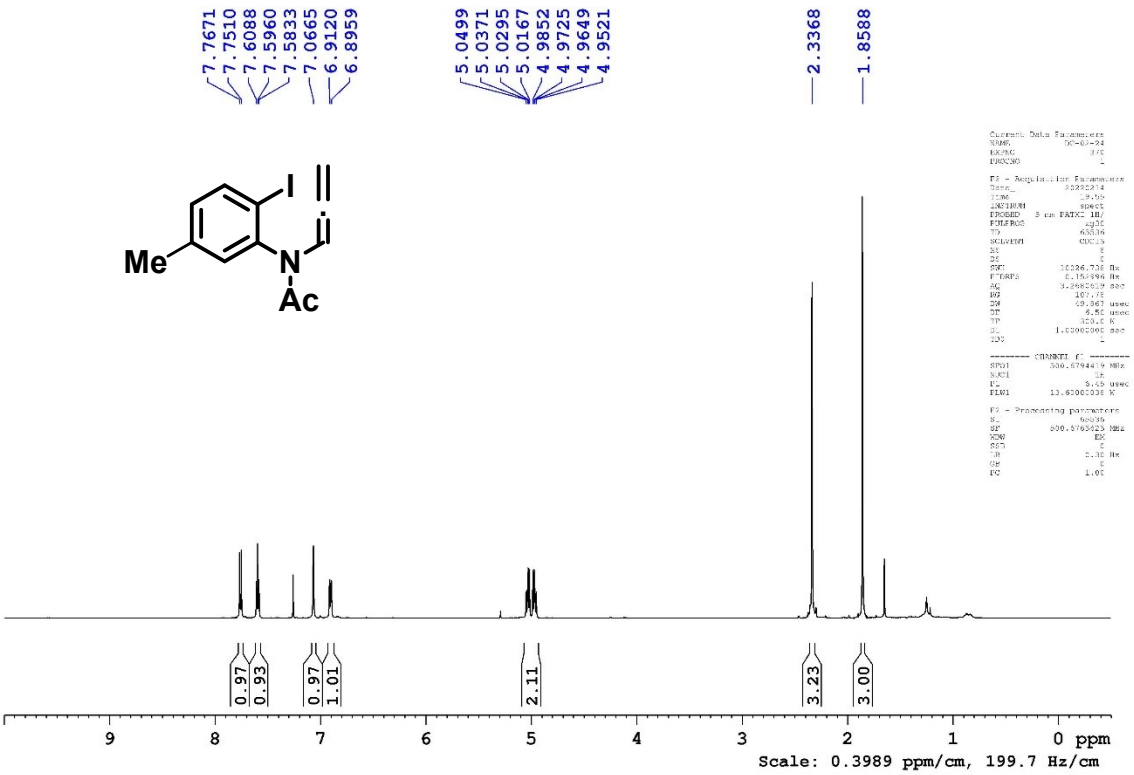

Figure S-17: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1'g**

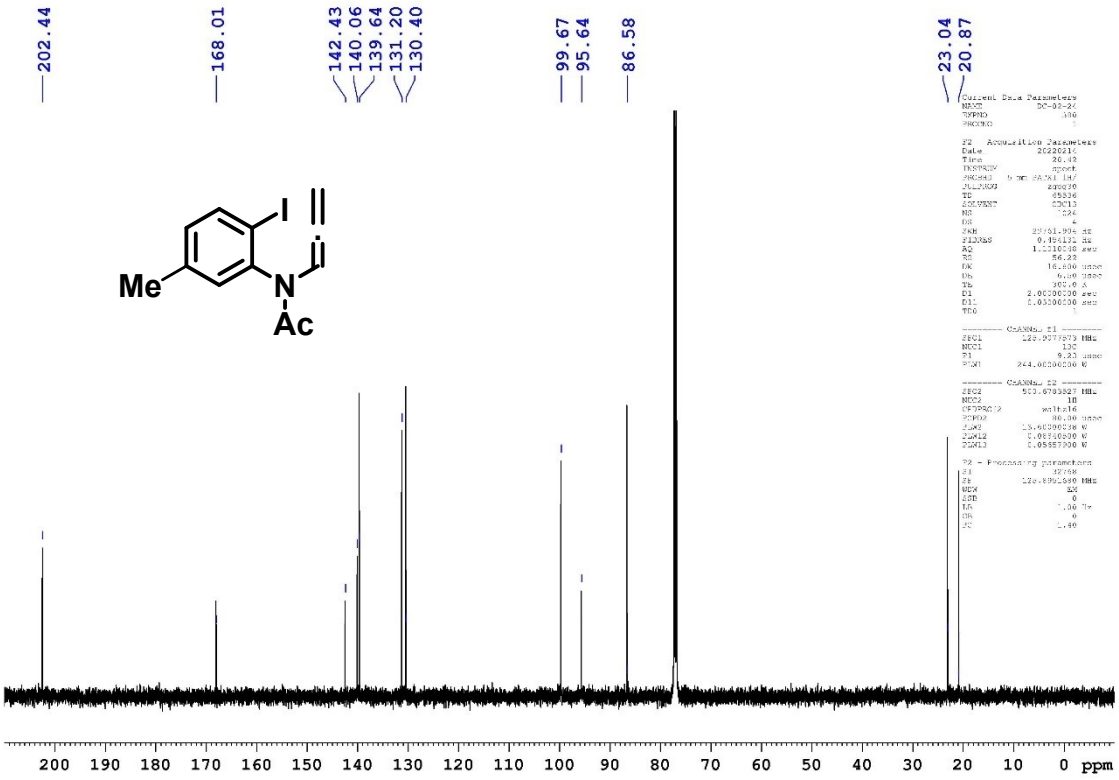

Figure S-18: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1'g**

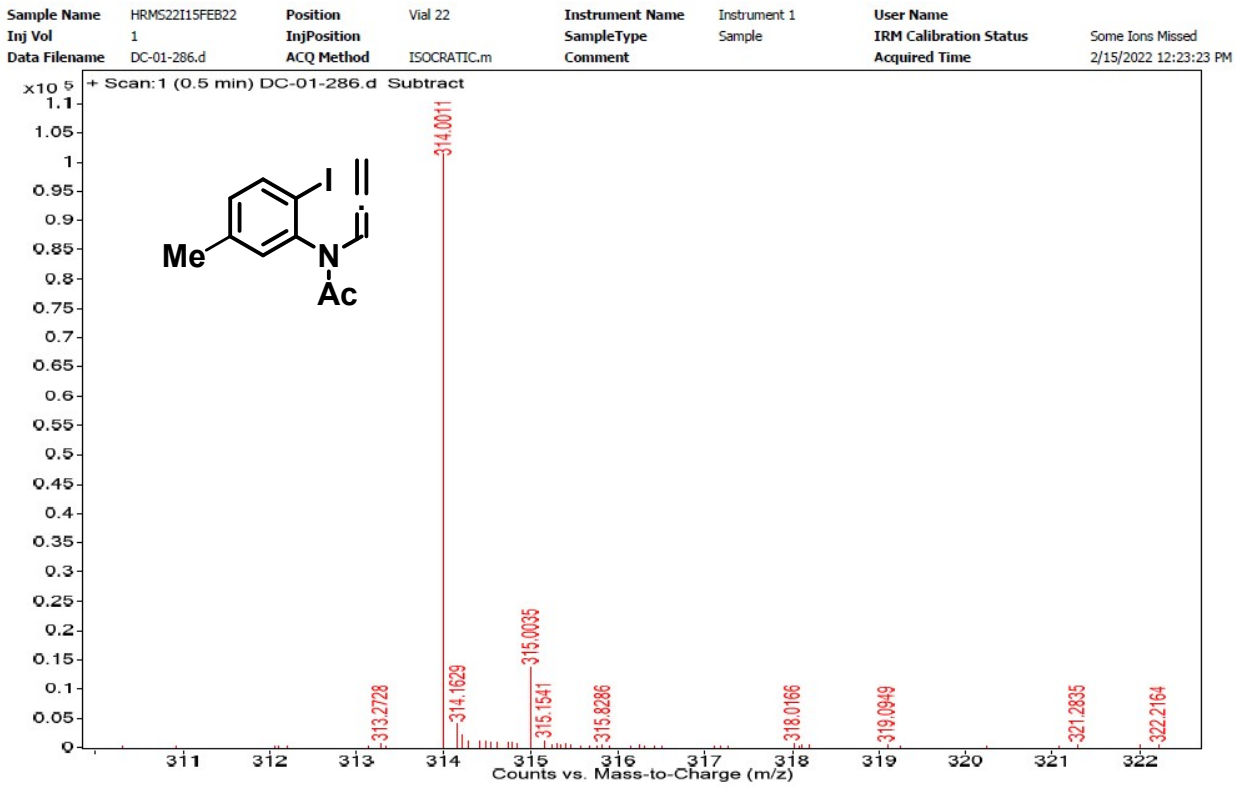

Figure S-19: HRMS spectrum of compound **1'g**

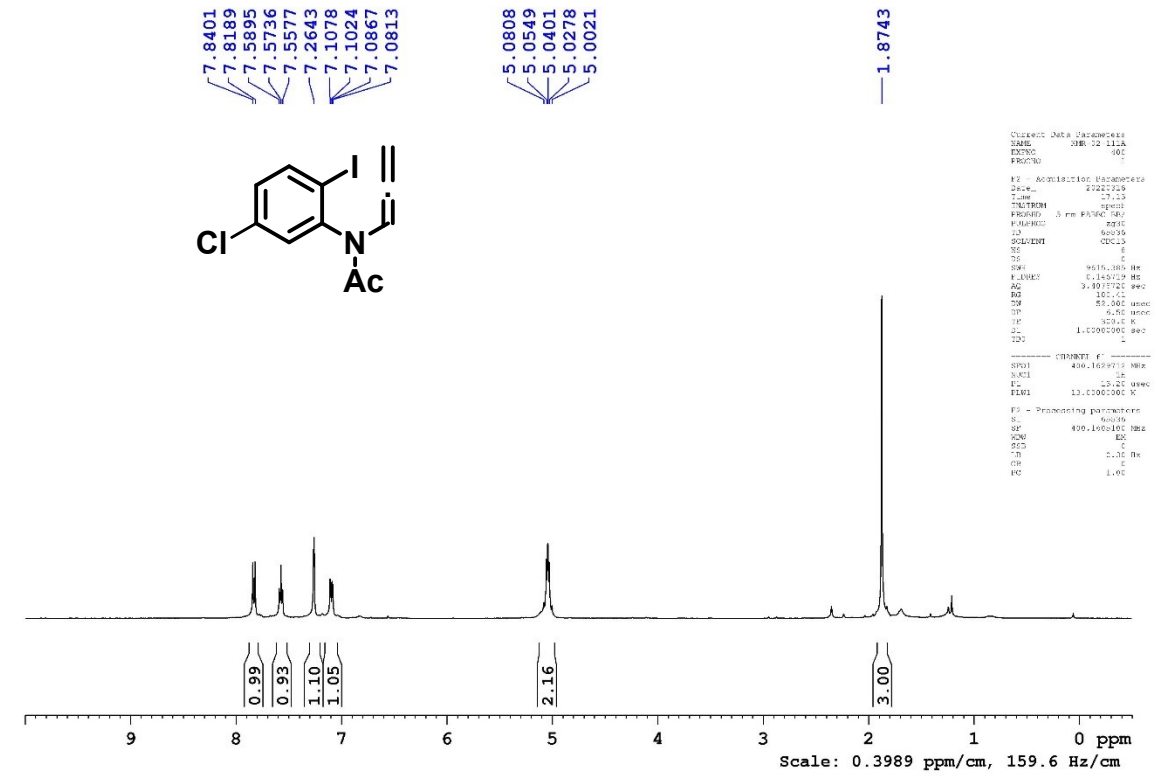

Figure S-20: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1'h**

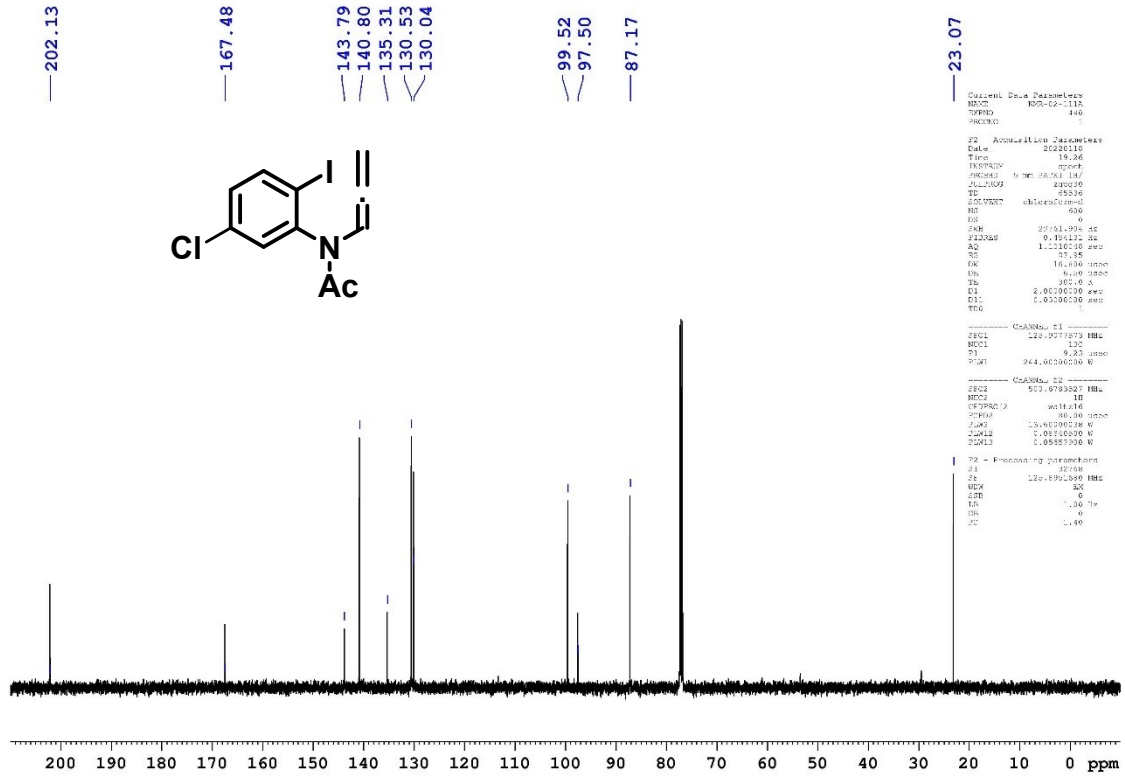

Figure S-21: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1'h**

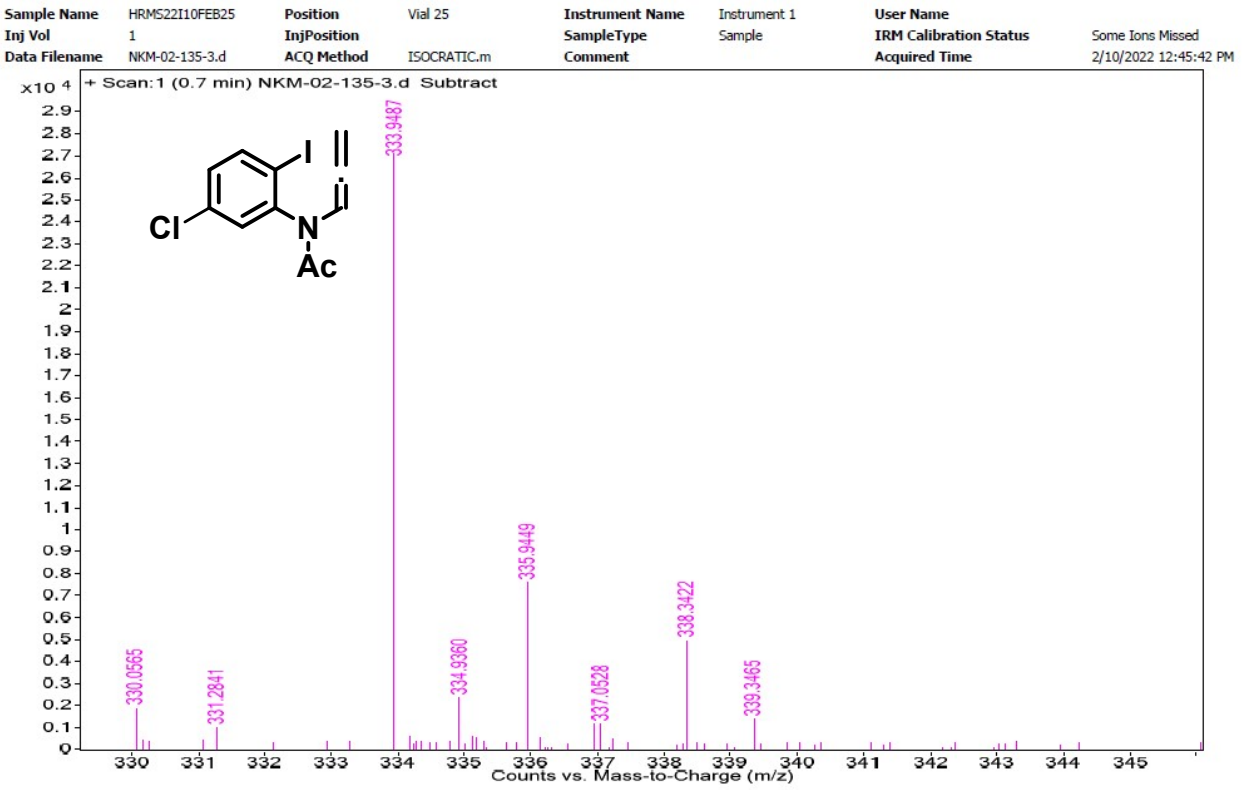

Figure S-22: HRMS spectrum of compound **1'h**

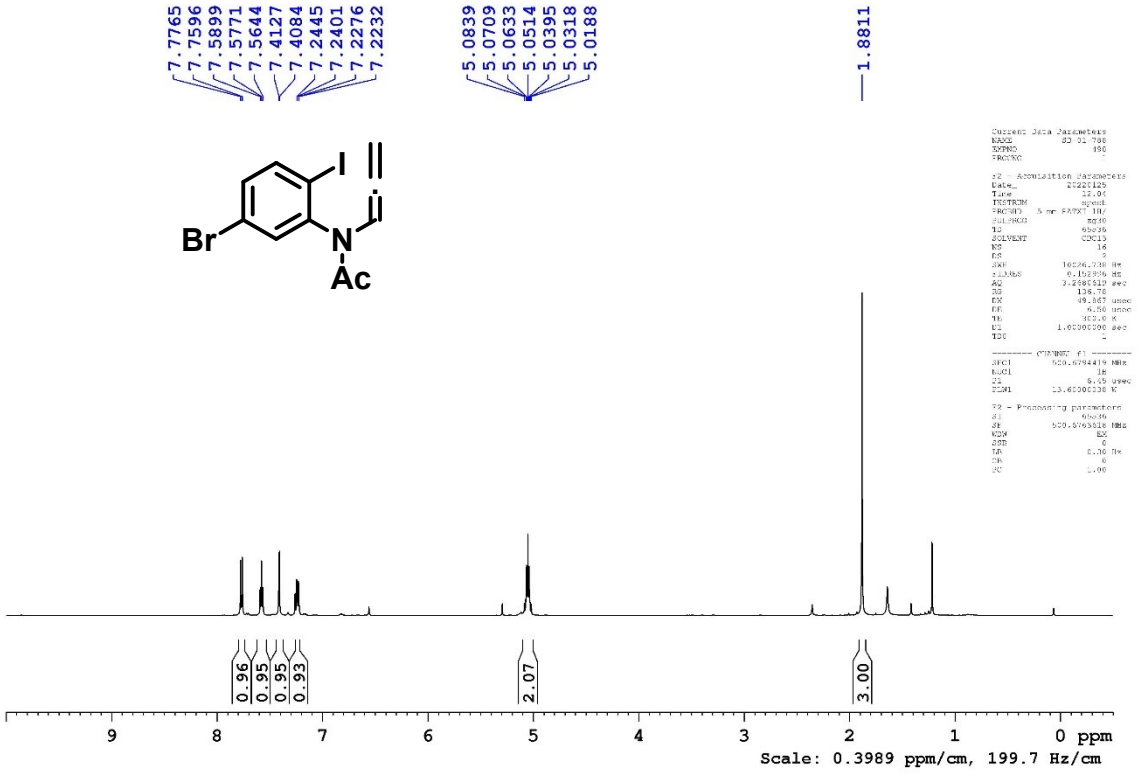

Figure S-23: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1'i**

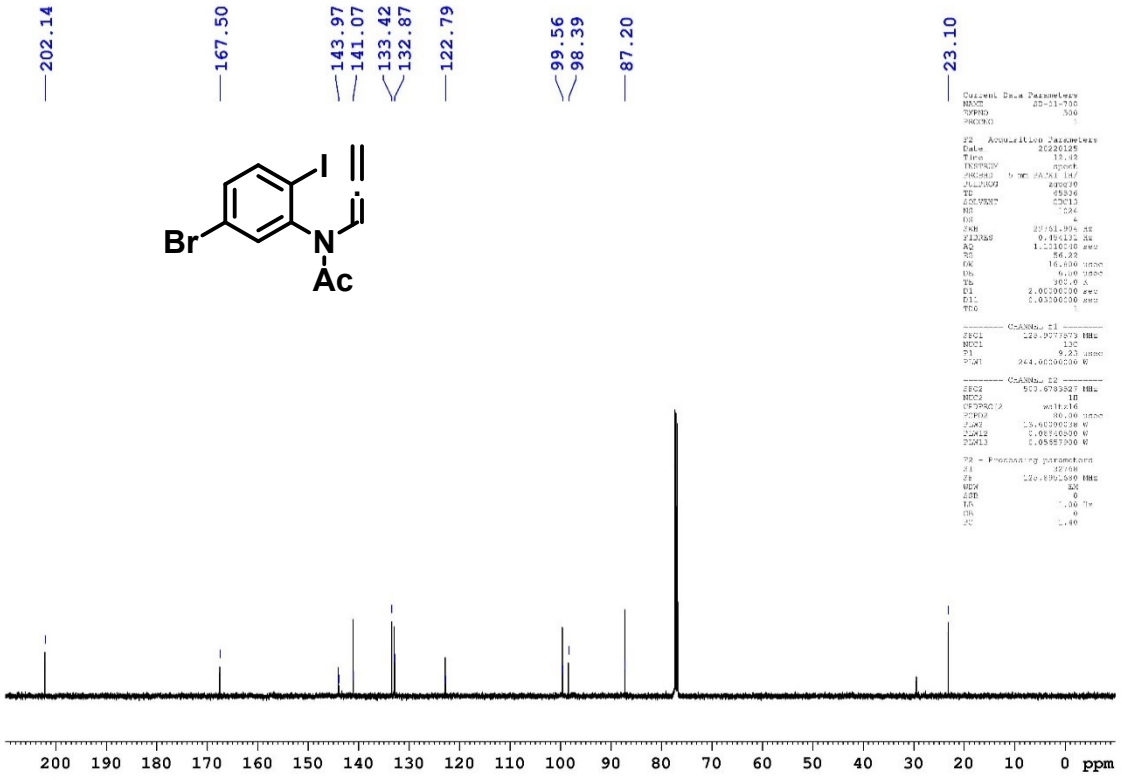

Figure S-24: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1'i**

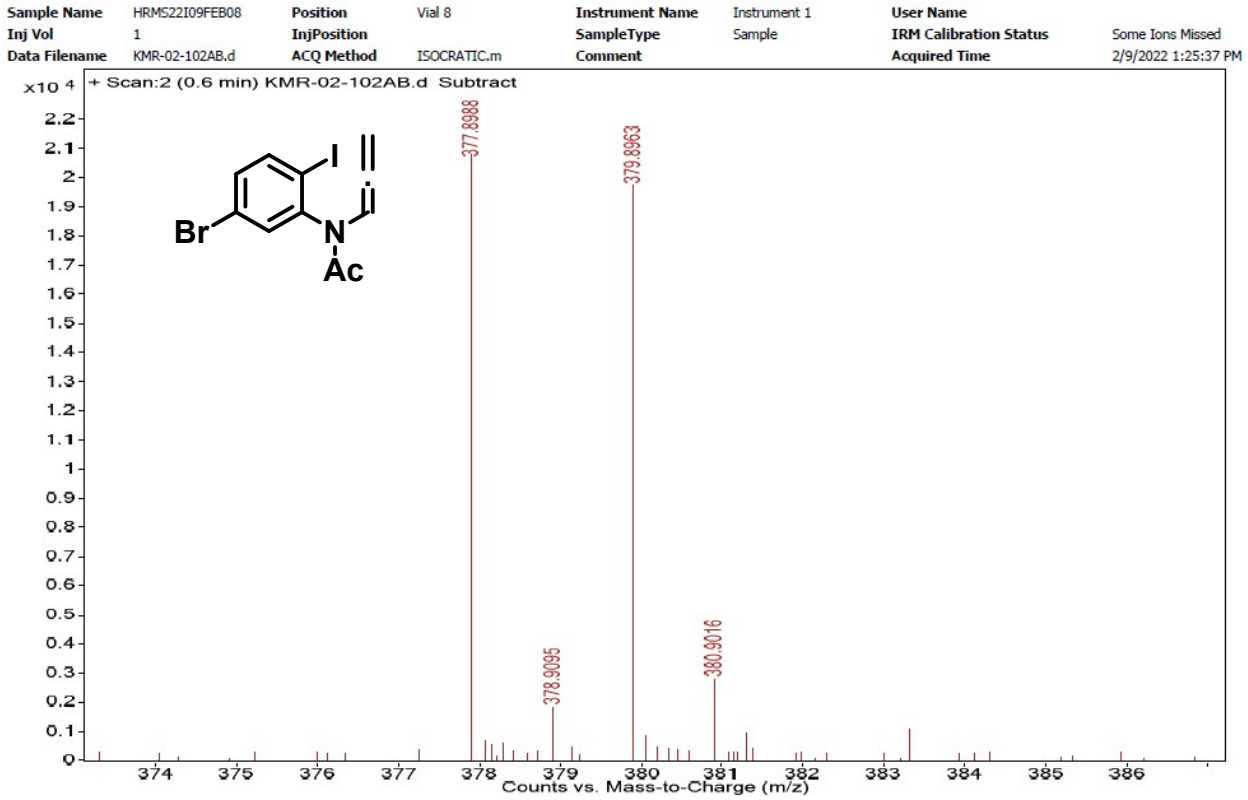

Figure S-25: HRMS spectrum of compound **1'i**

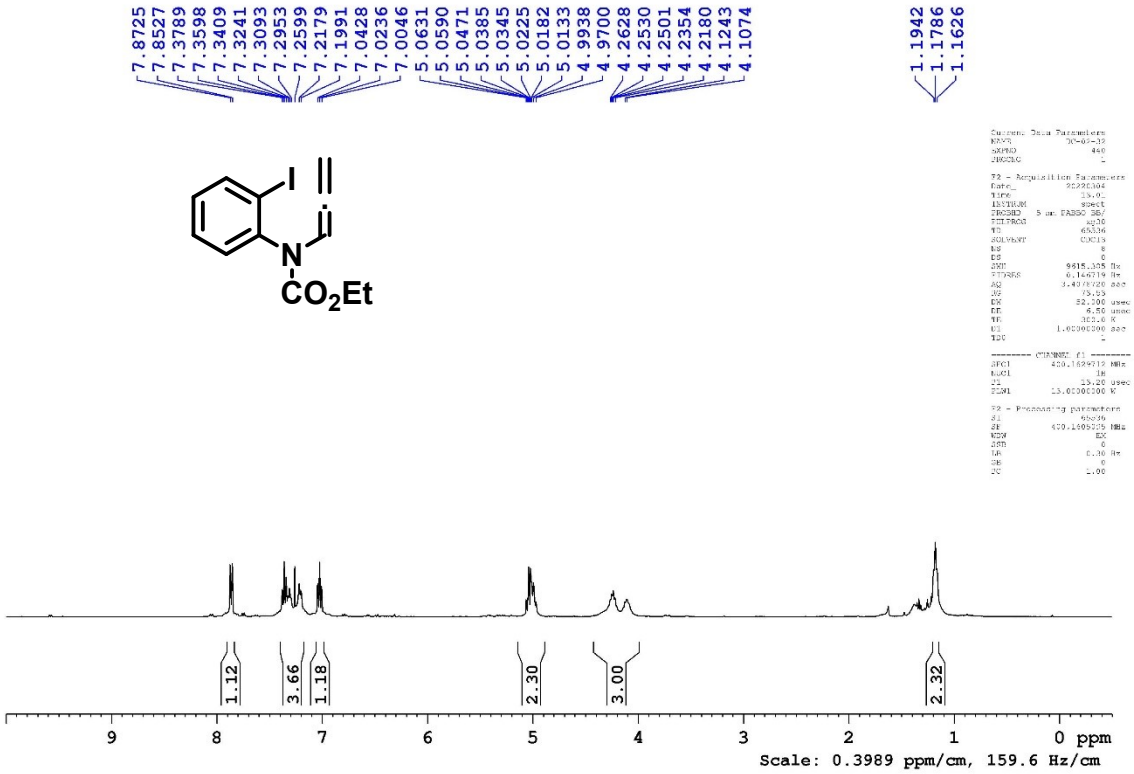

Figure S-26: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1o**

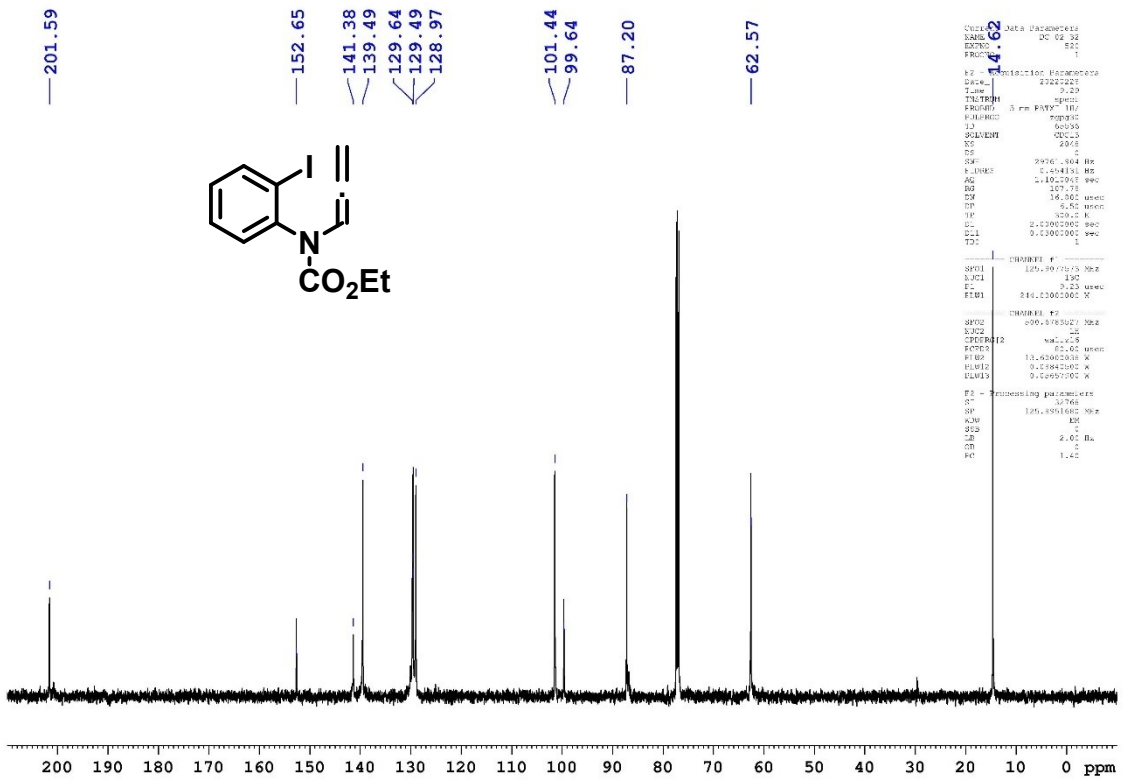

Figure S-27: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1o**

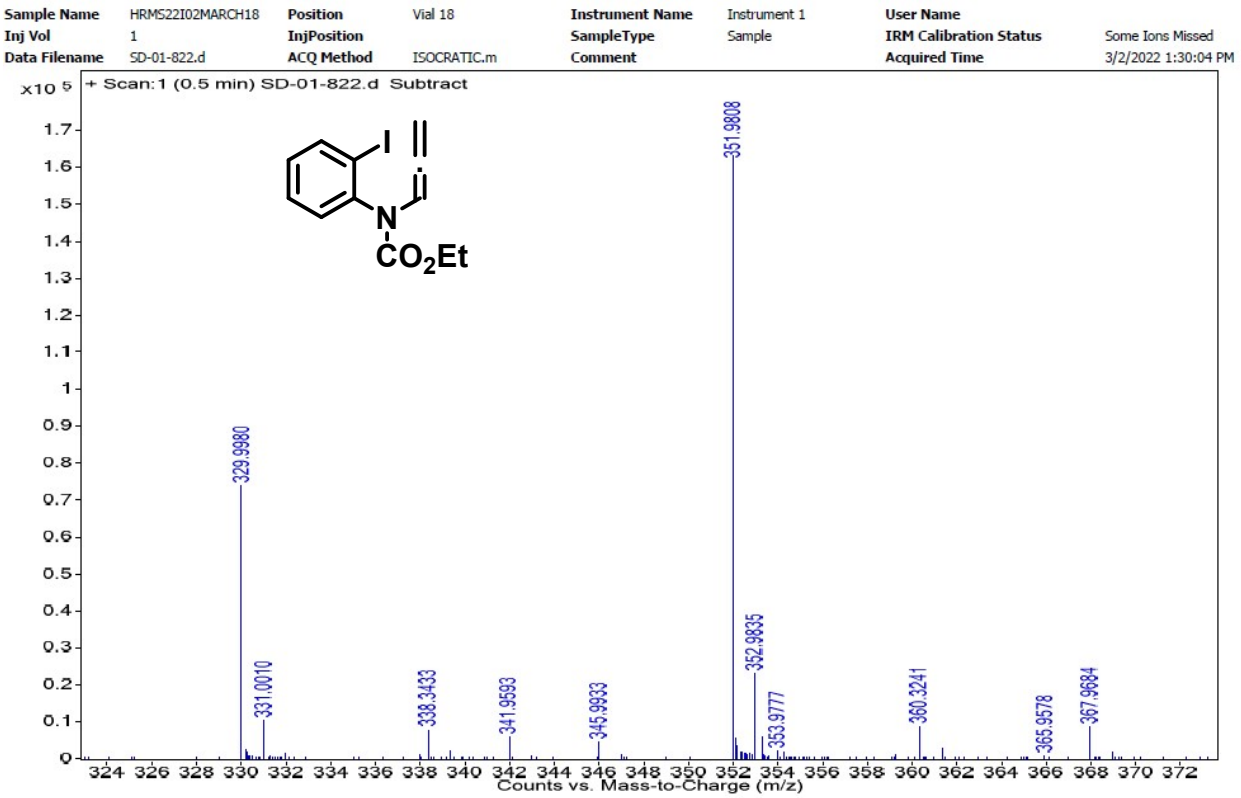

Figure S-28: HRMS spectrum of compound **1o**

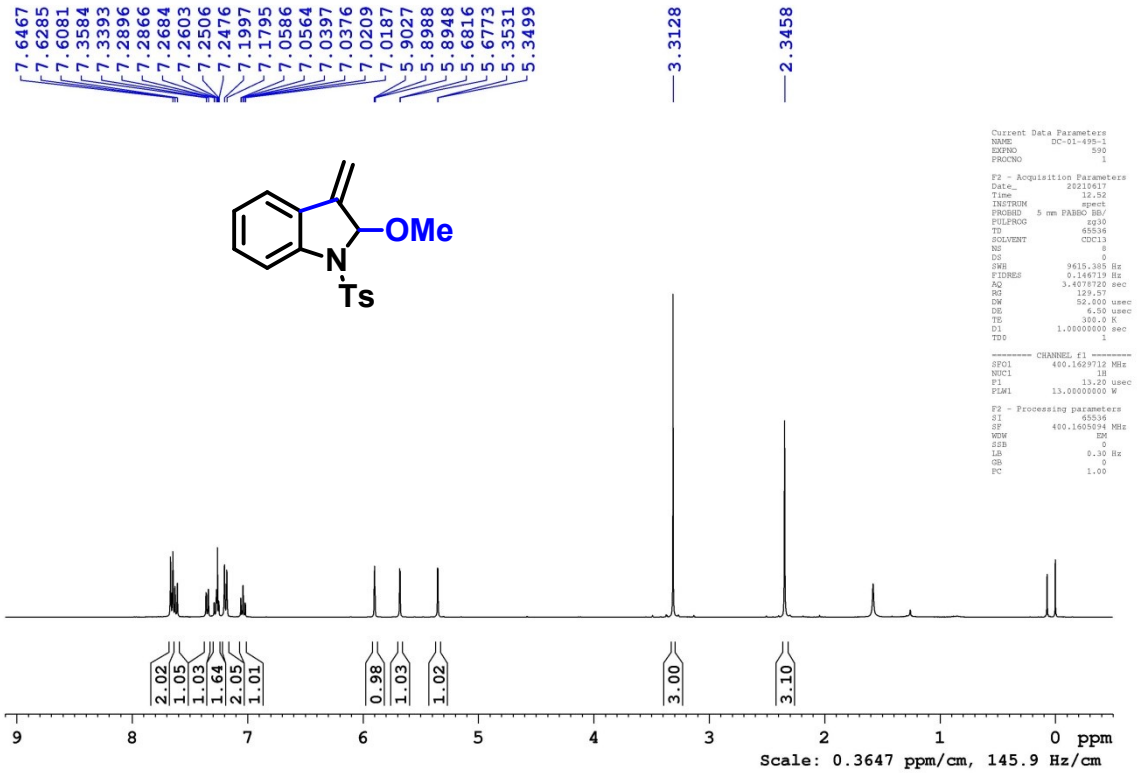

Figure S-29: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**

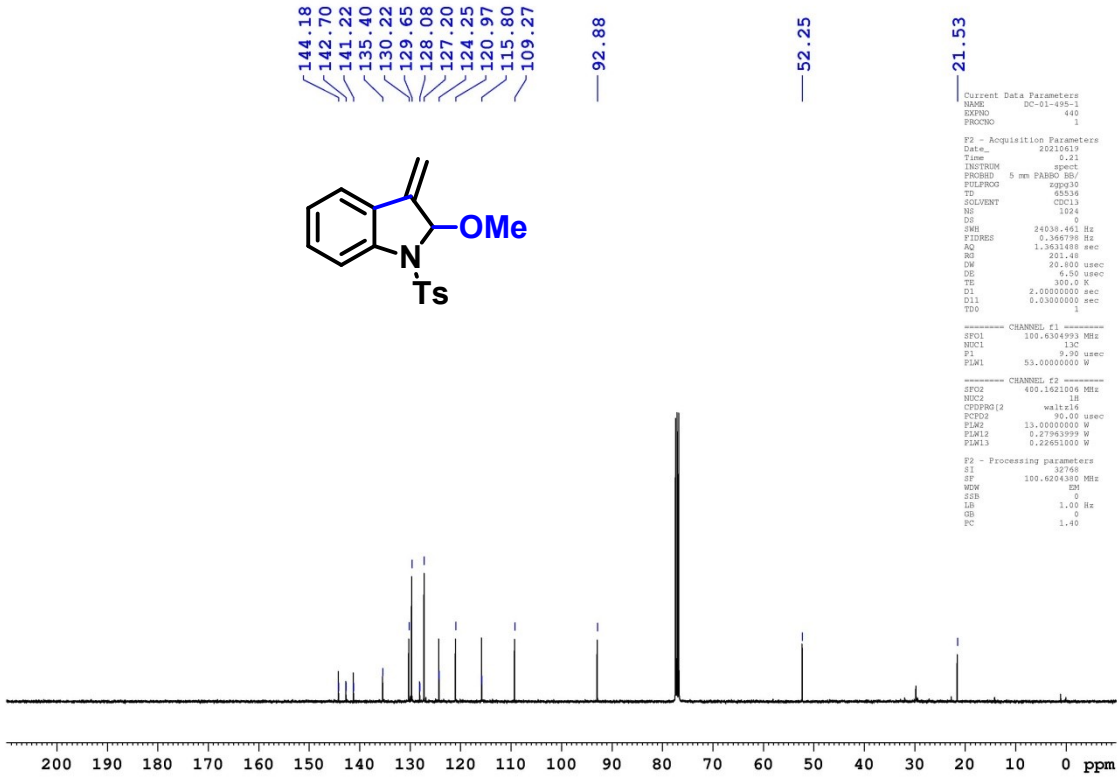

Figure S-30: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**

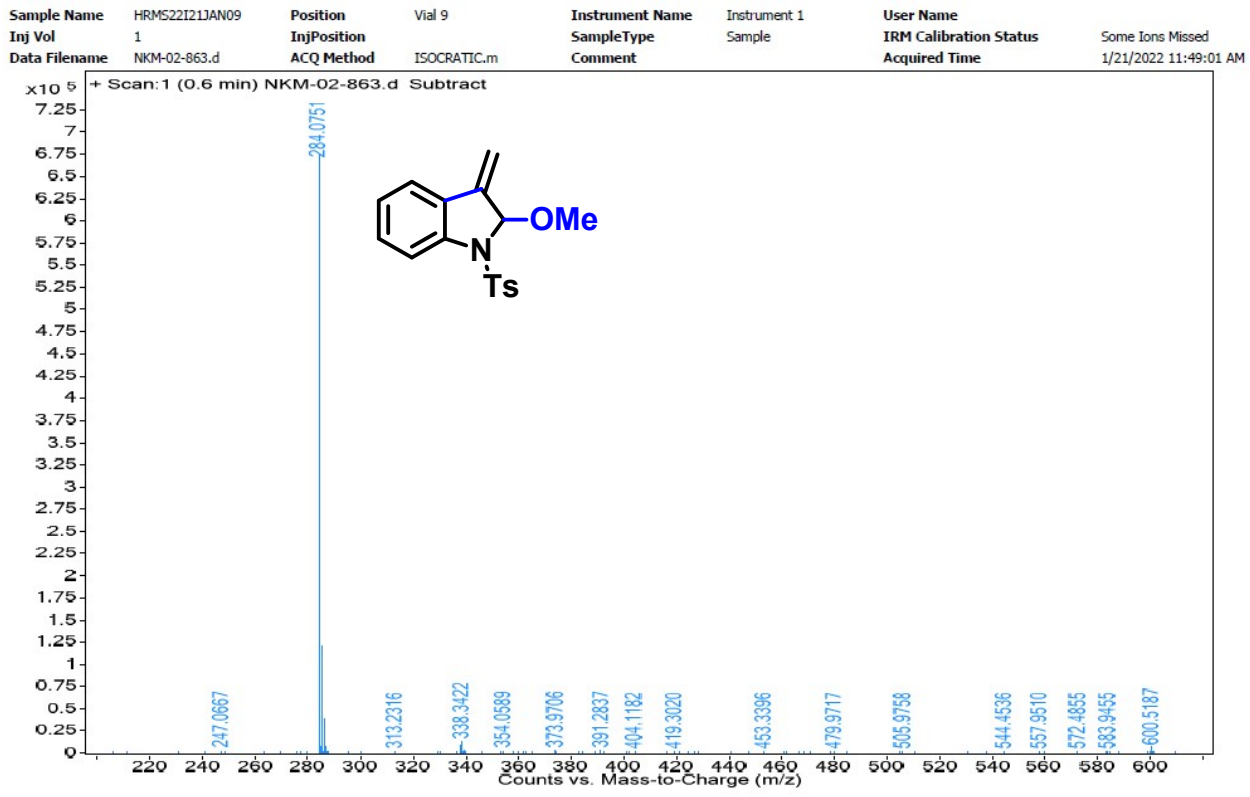

Figure S-31: HRMS spectrum of compound **3a**

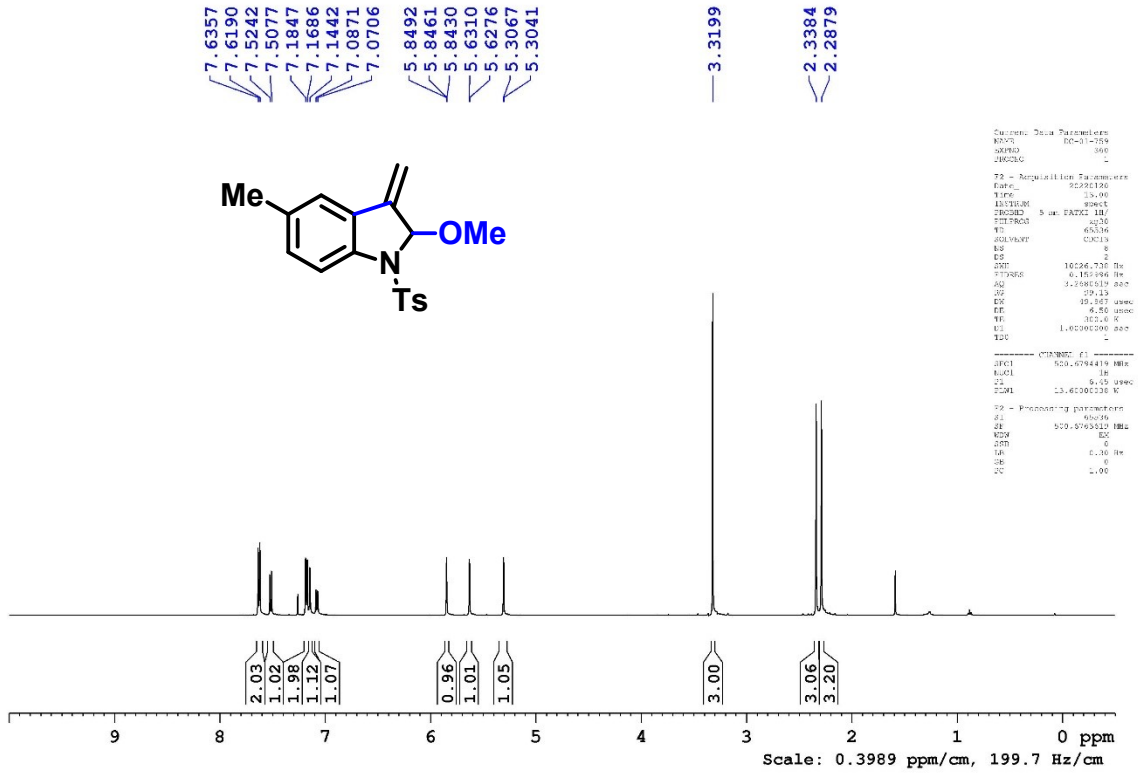

Figure S-32: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3b**

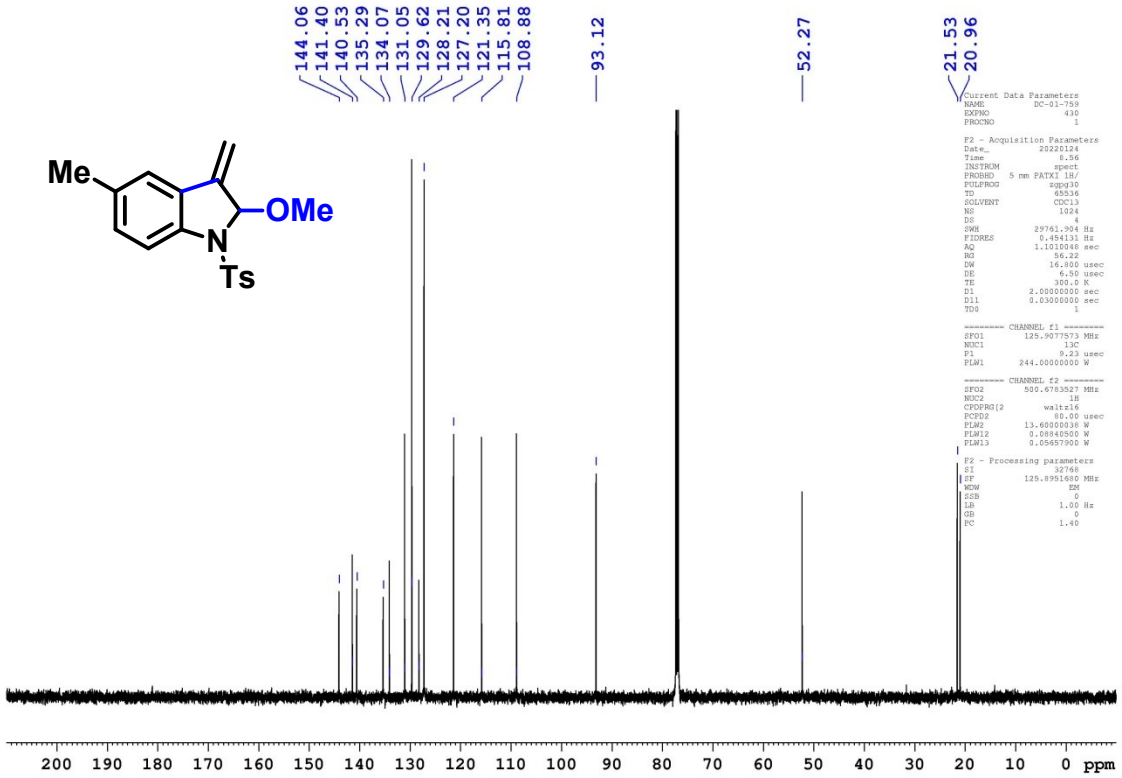

Figure S-33: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3b**

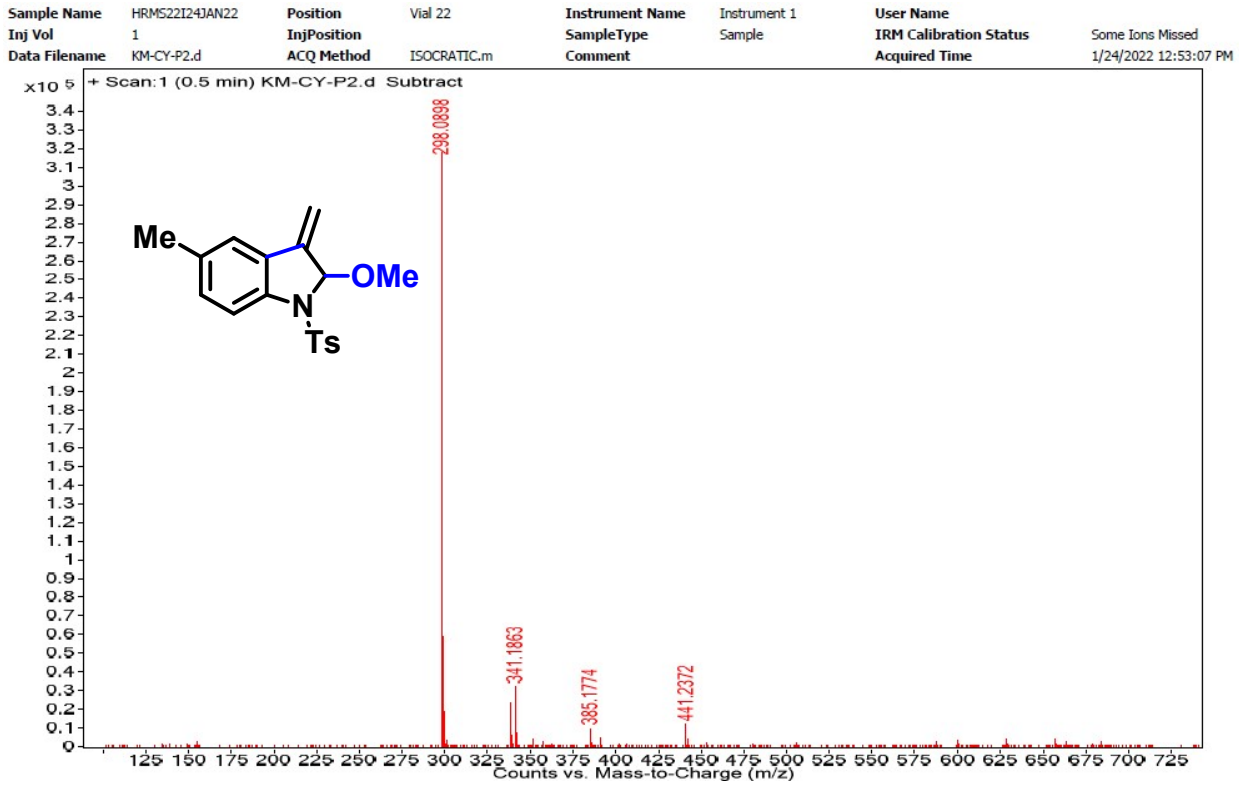

Figure S-34: HRMS spectrum of compound **3b**

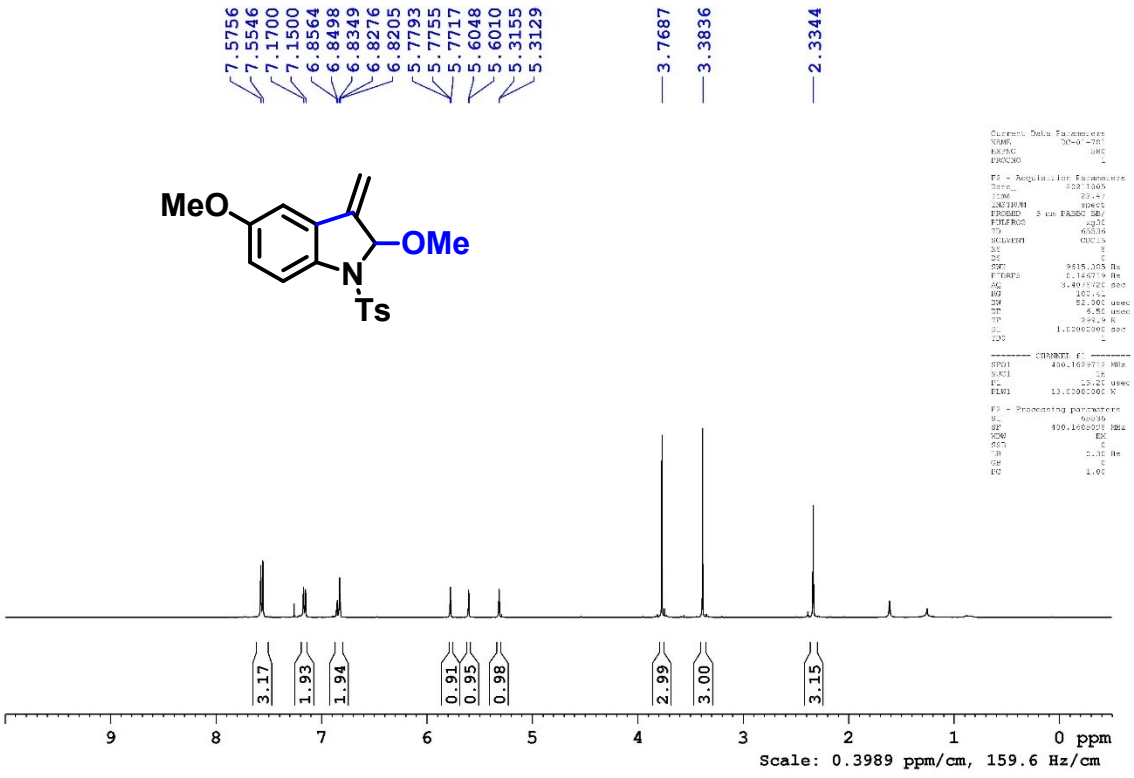

Figure S-35: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**

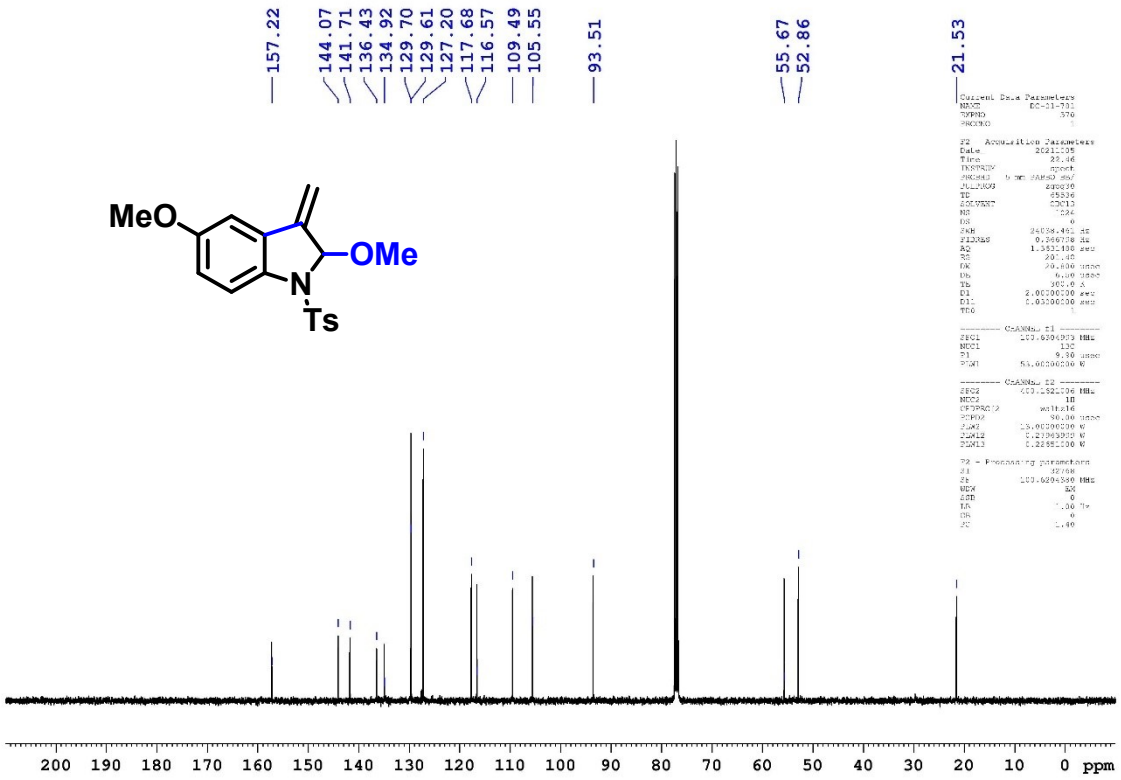

Figure S-36: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3c**

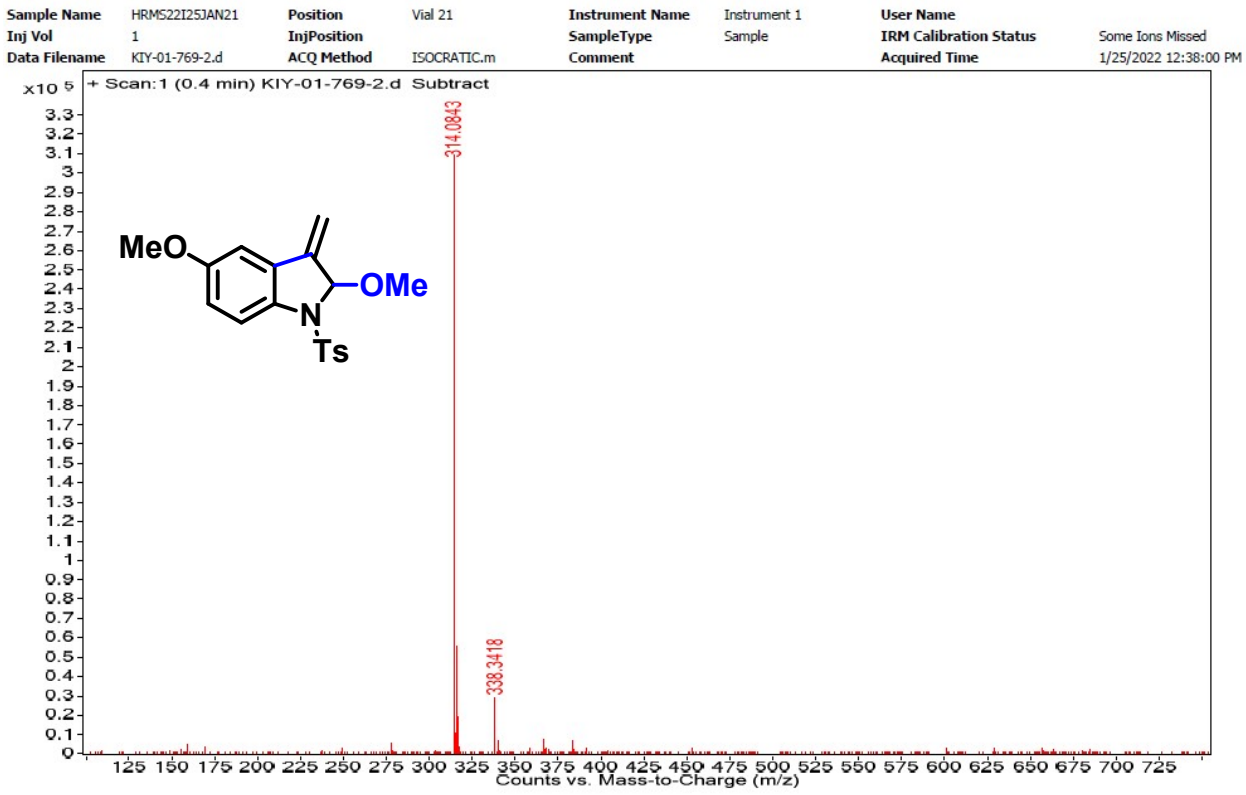

Figure S-37: HRMS spectrum of compound **3c**

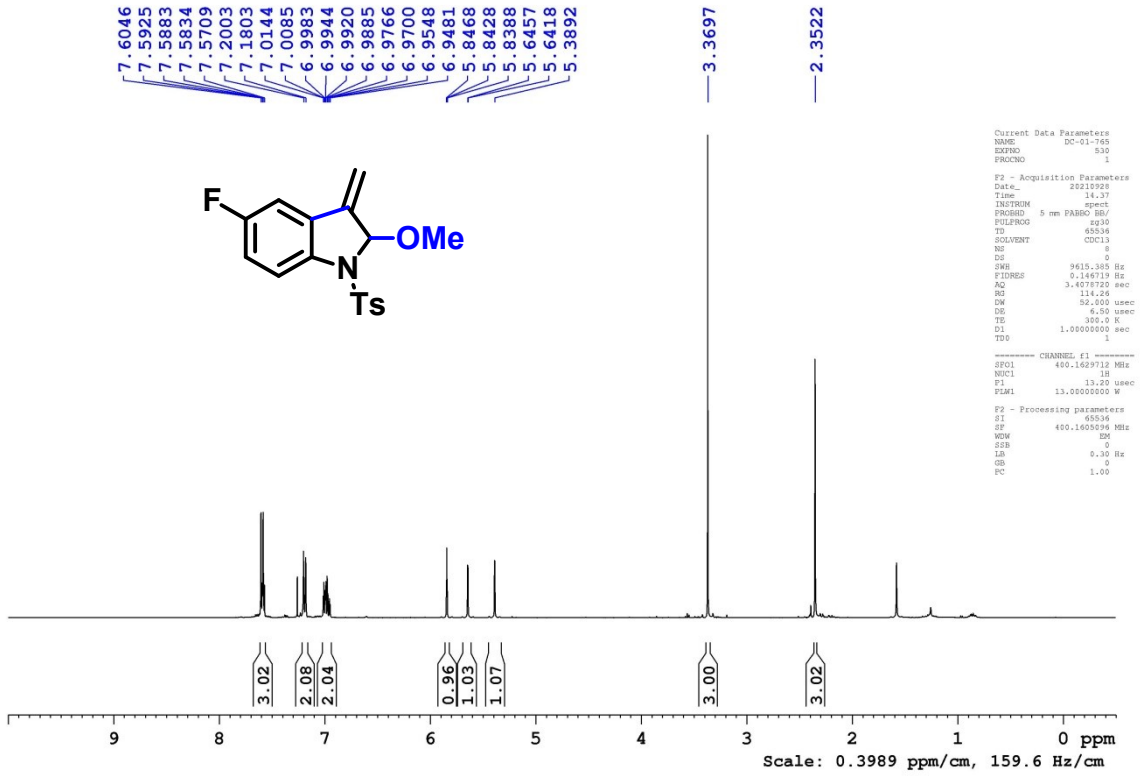

Figure S-38: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**

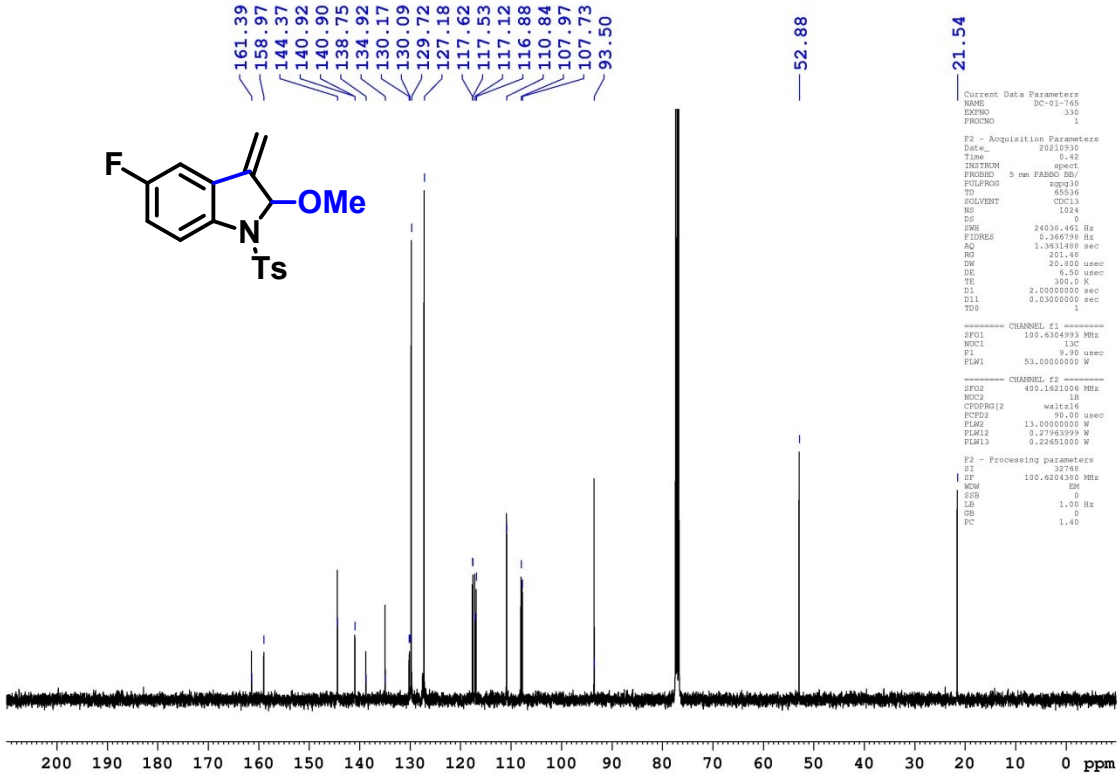

Figure S-39: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**

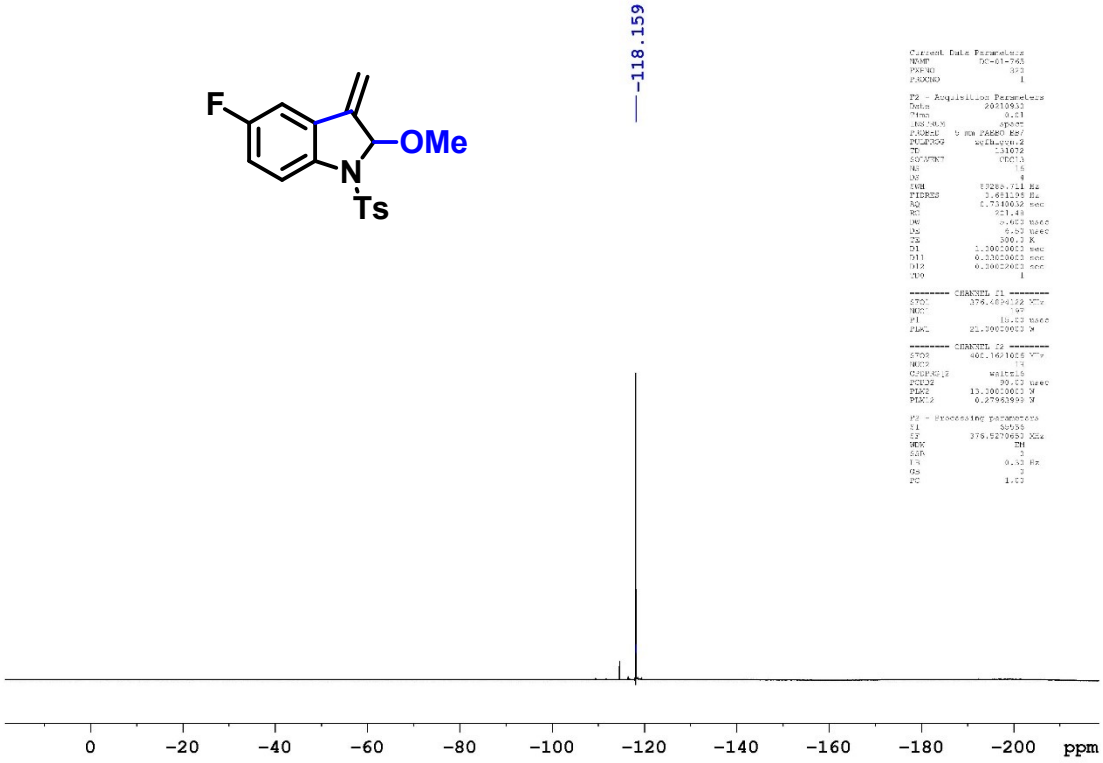

Figure S-40: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3d**

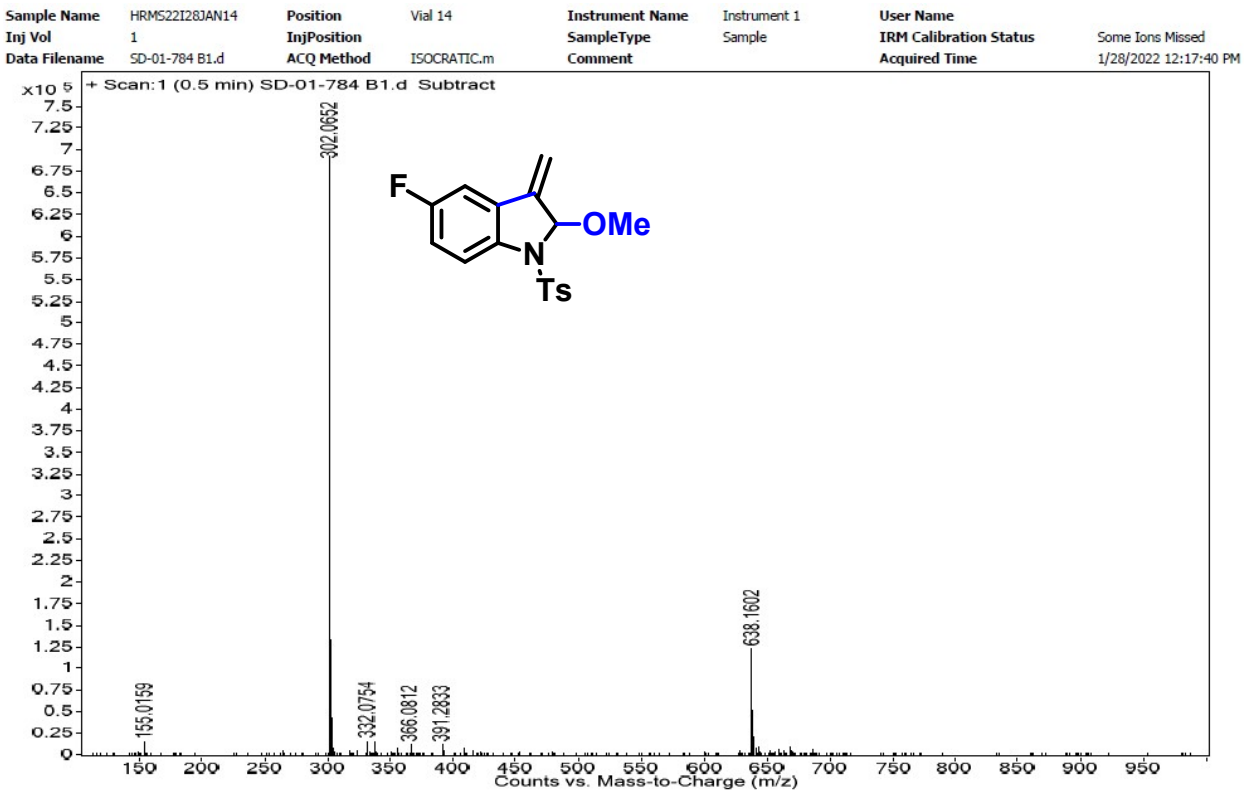

Figure S-41: HRMS spectrum of compound **3d**

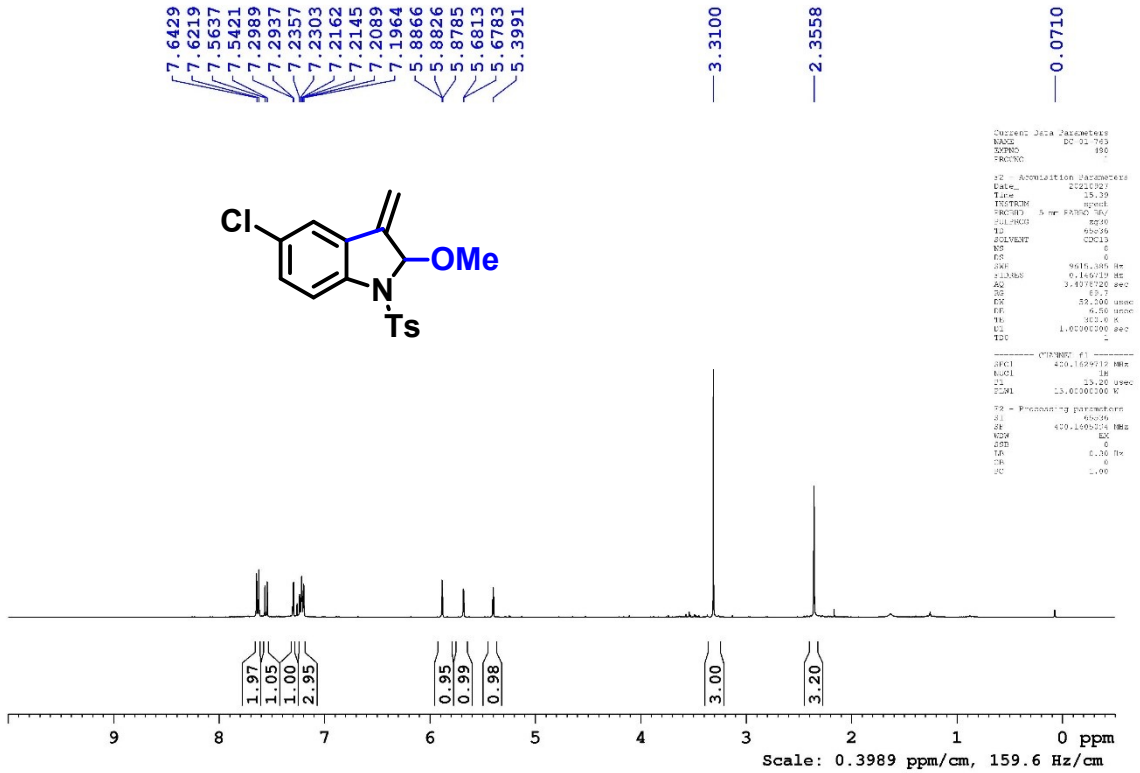

Figure S-42: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**

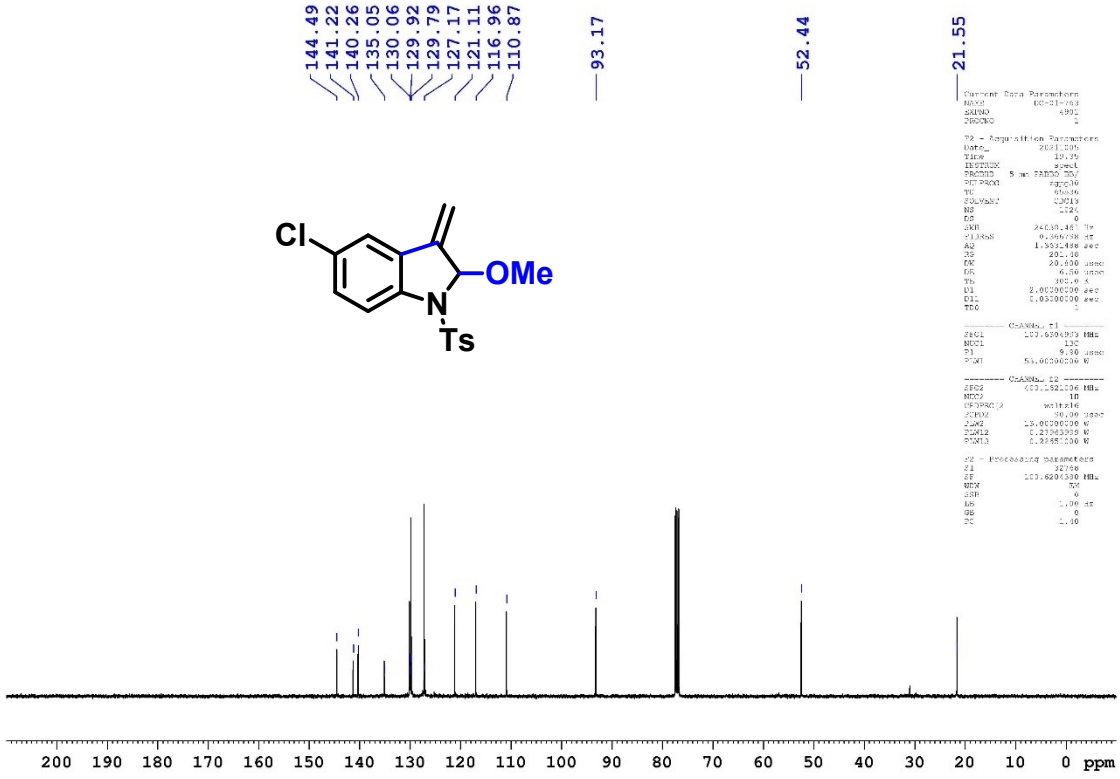

Figure S-43: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**

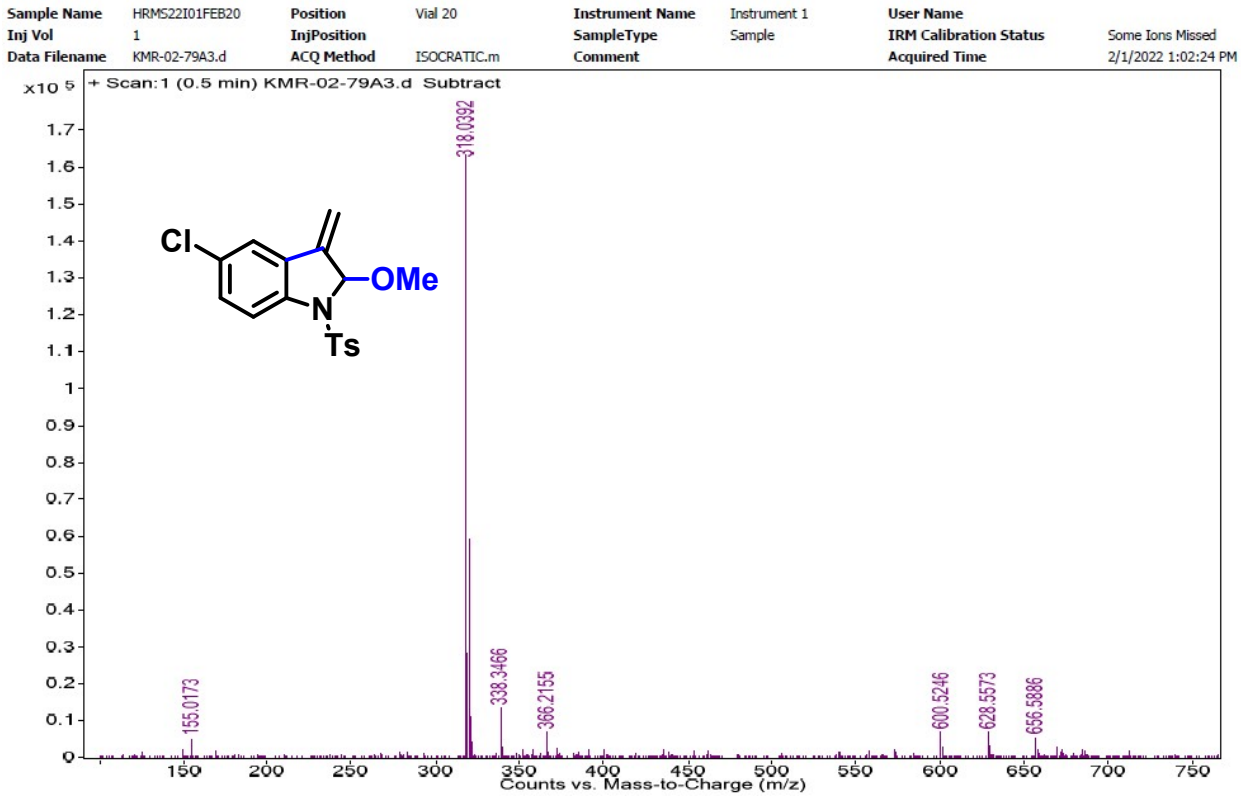

Figure S-44: HRMS spectrum of compound **3e**

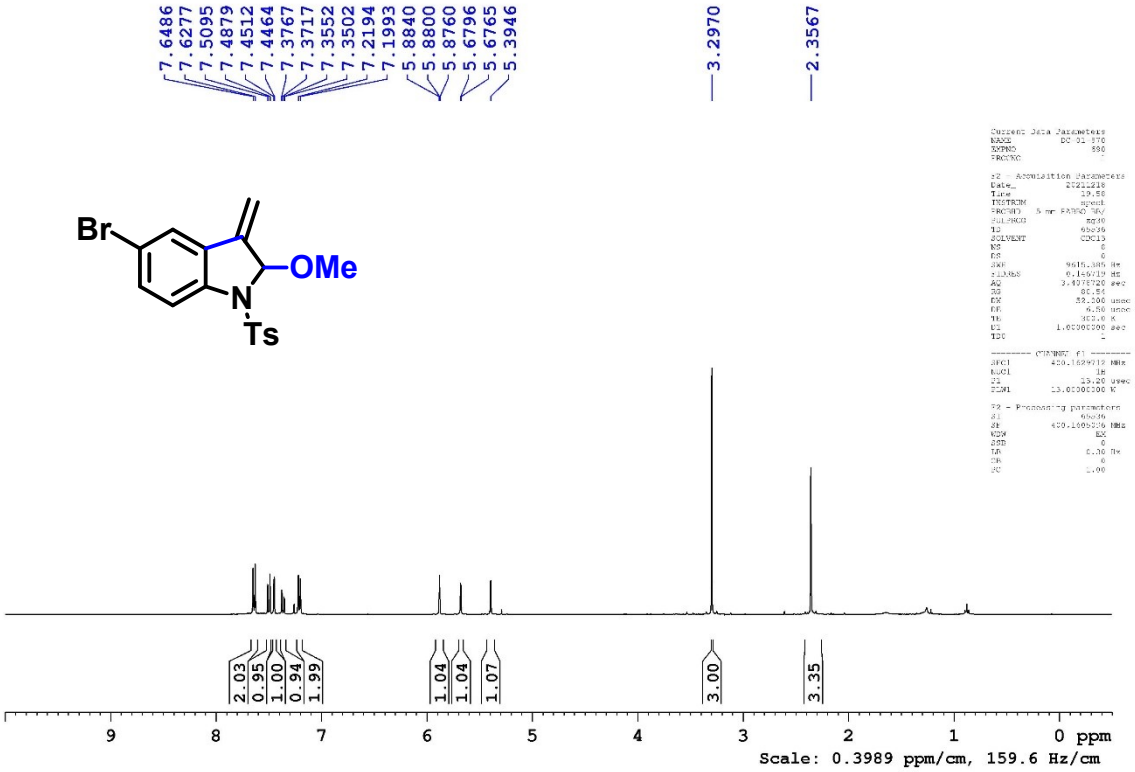

Figure S-45: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**

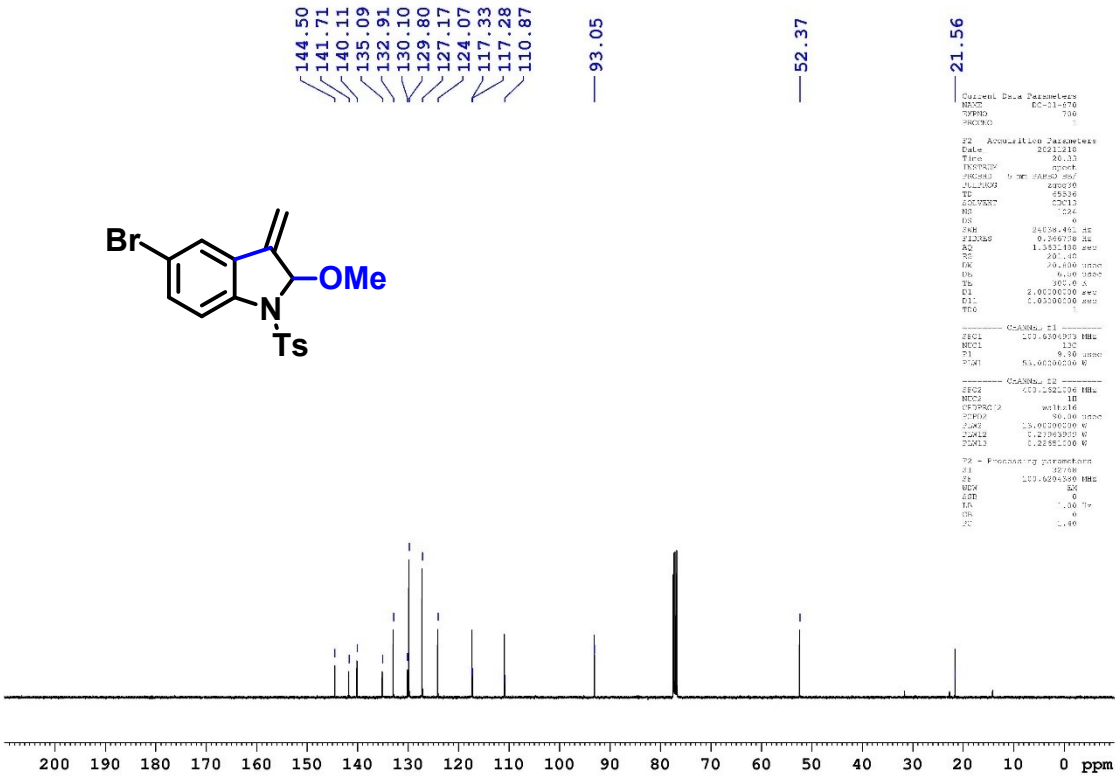

Figure S-46: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3f**

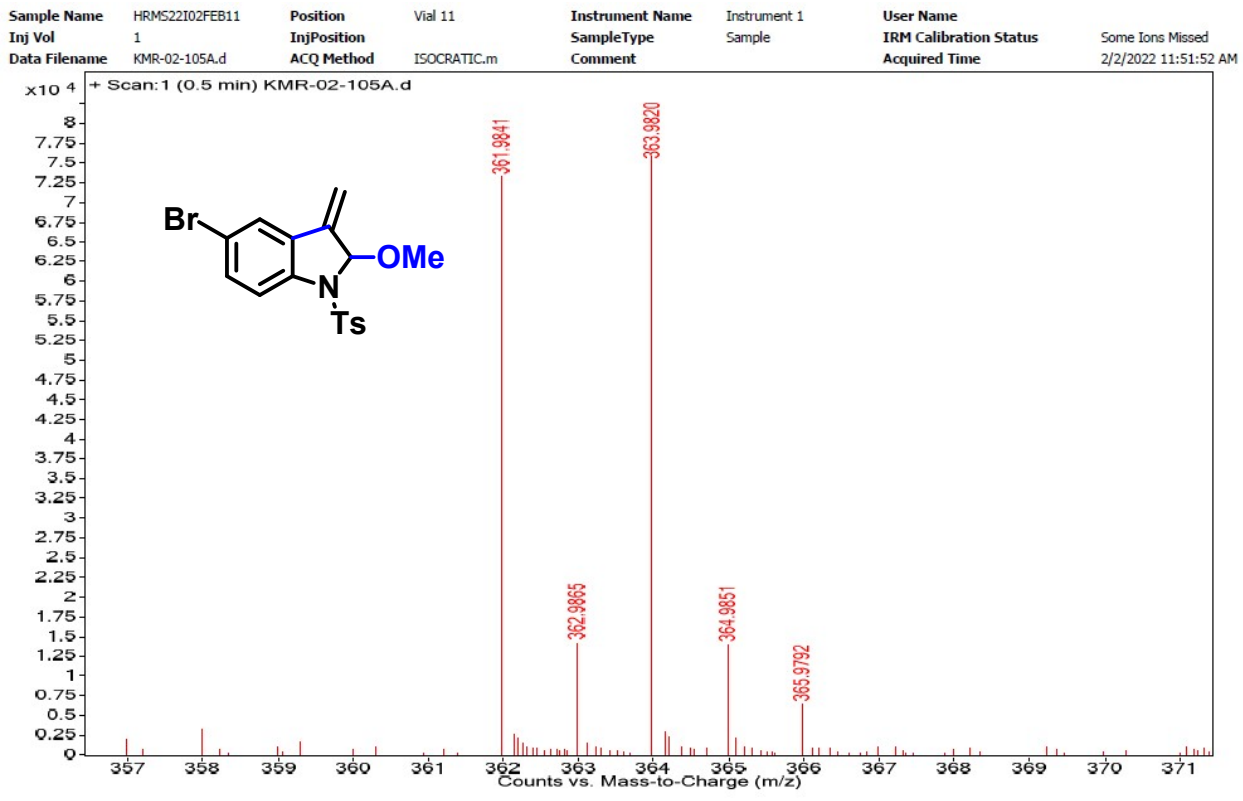

Figure S-47: HRMS spectrum of compound **3f**

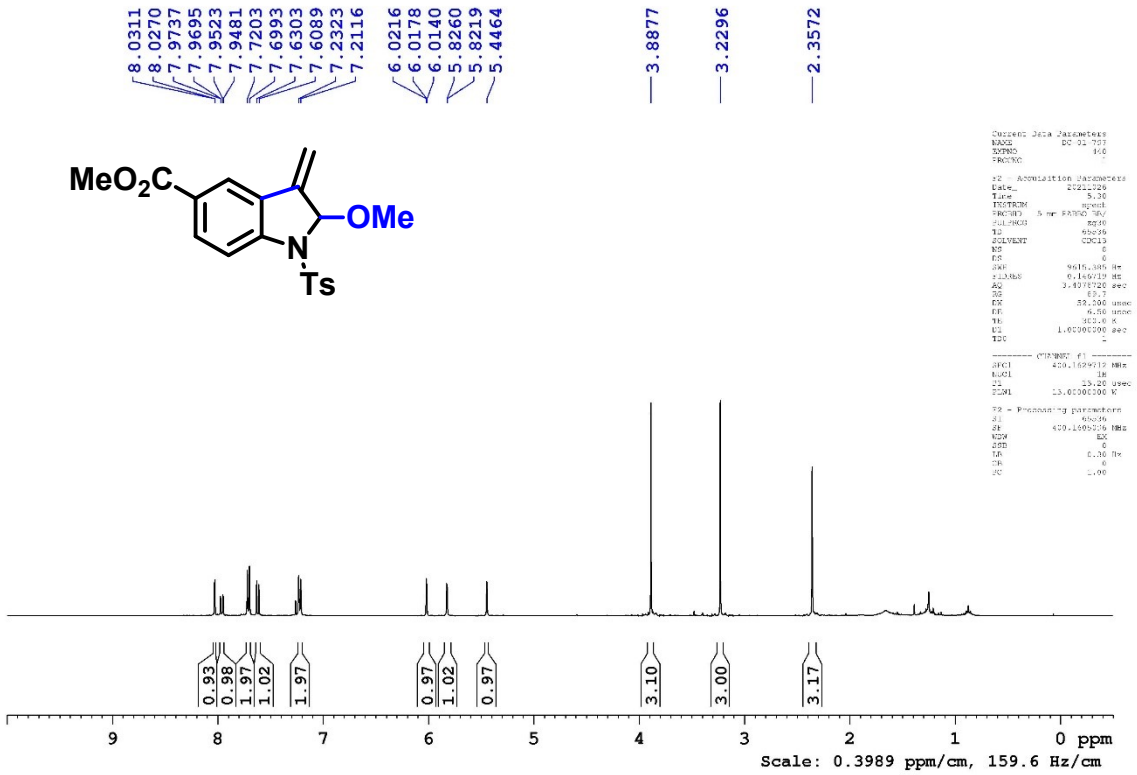

Figure S-48: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**

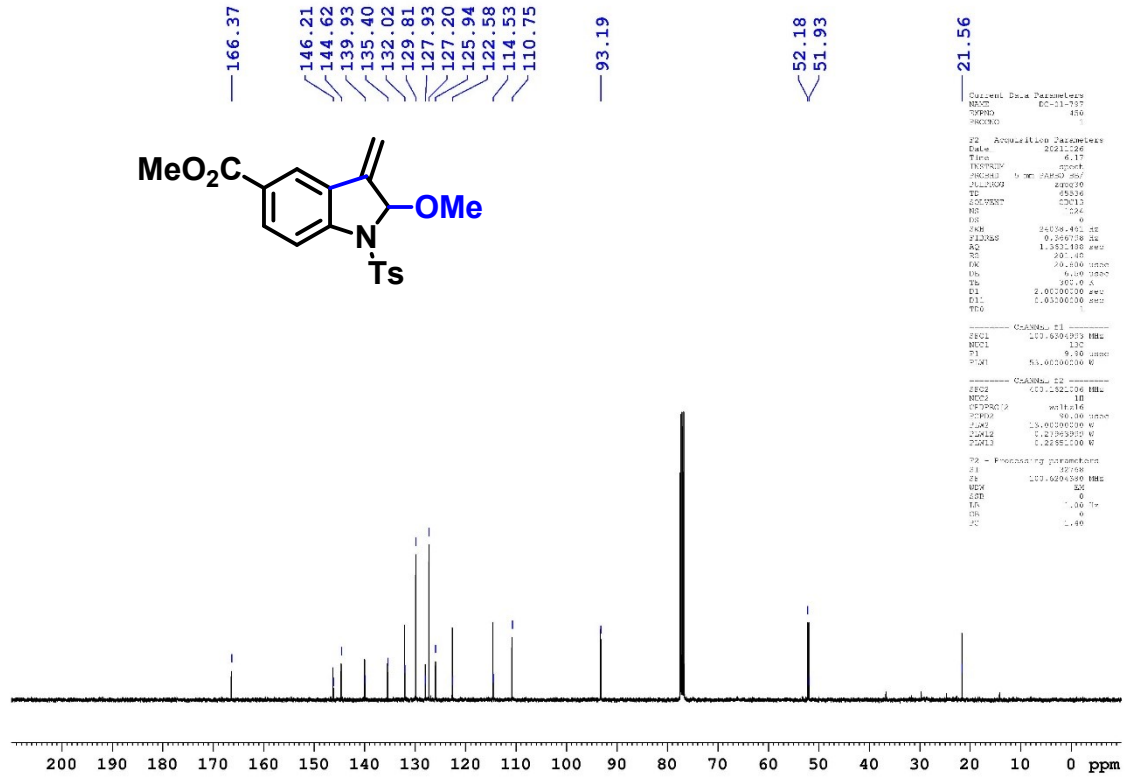

Figure S-49: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3g**

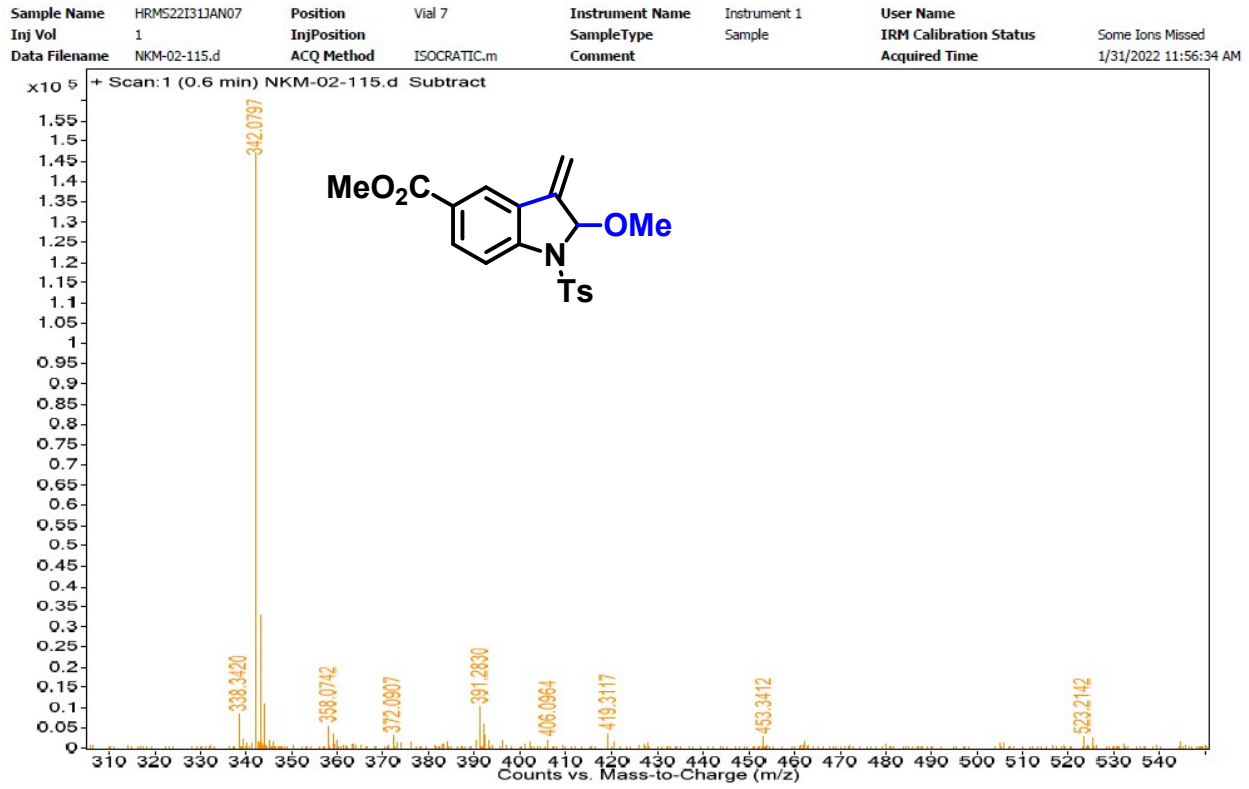

Figure S-50: HRMS spectrum of compound **3g**

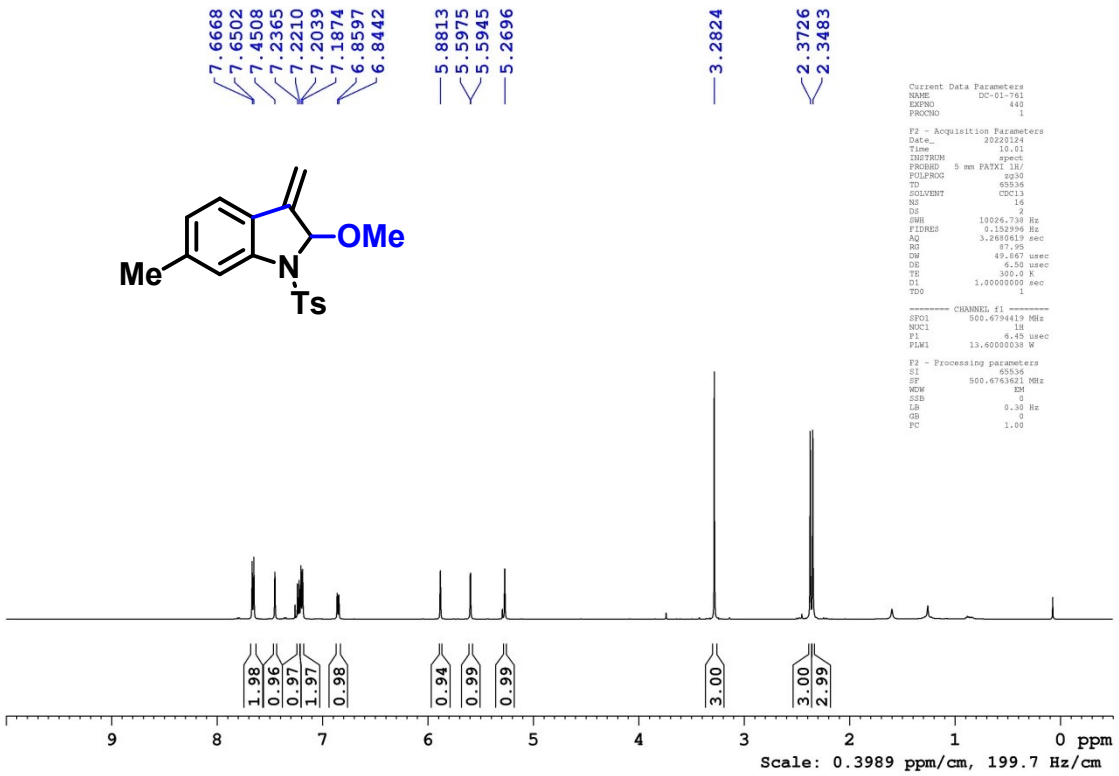

Figure S-51: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3h**

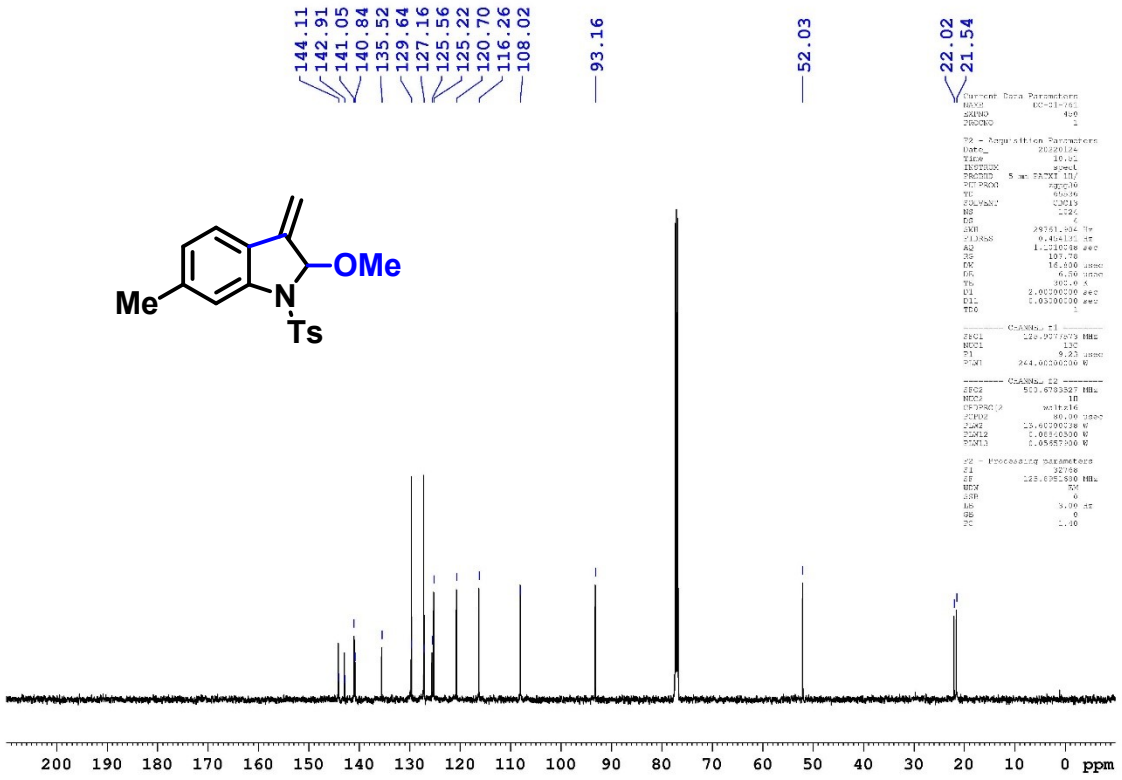

Figure S-52: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3h**

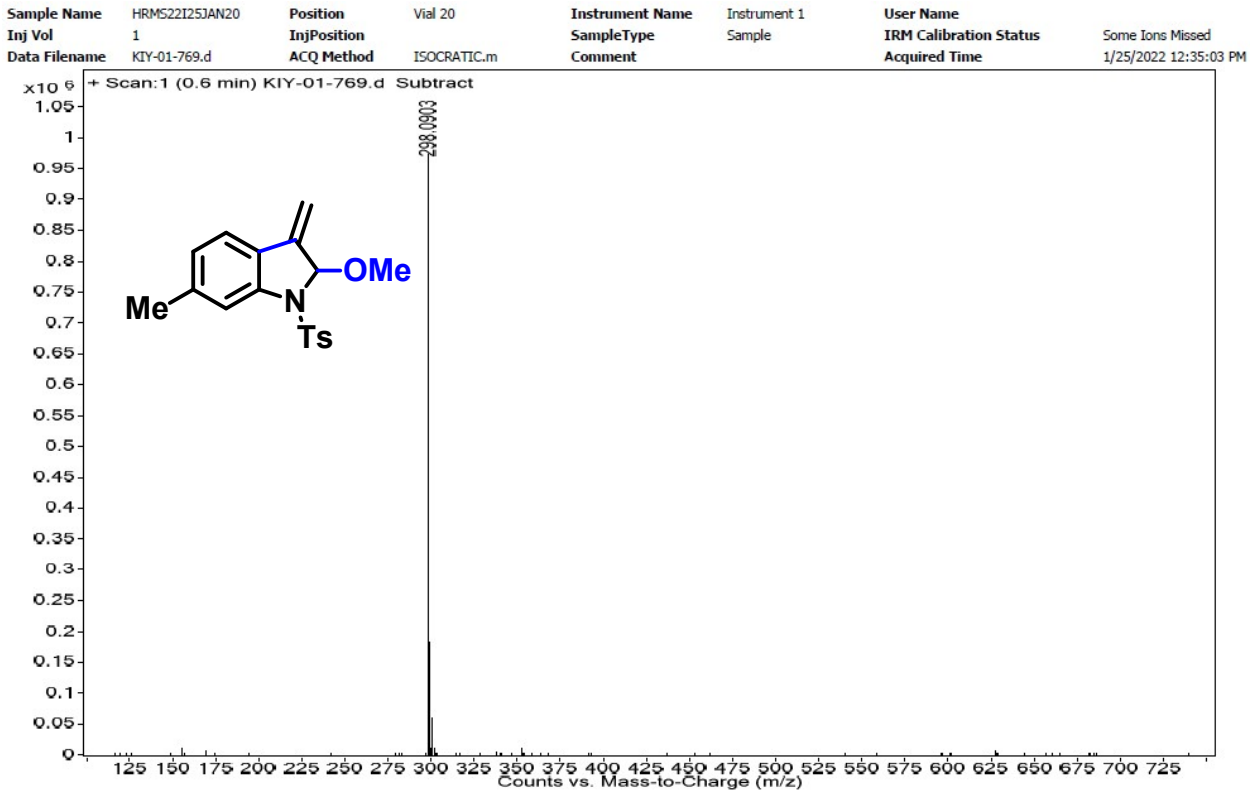

Figure S-53: HRMS spectrum of compound **3h**

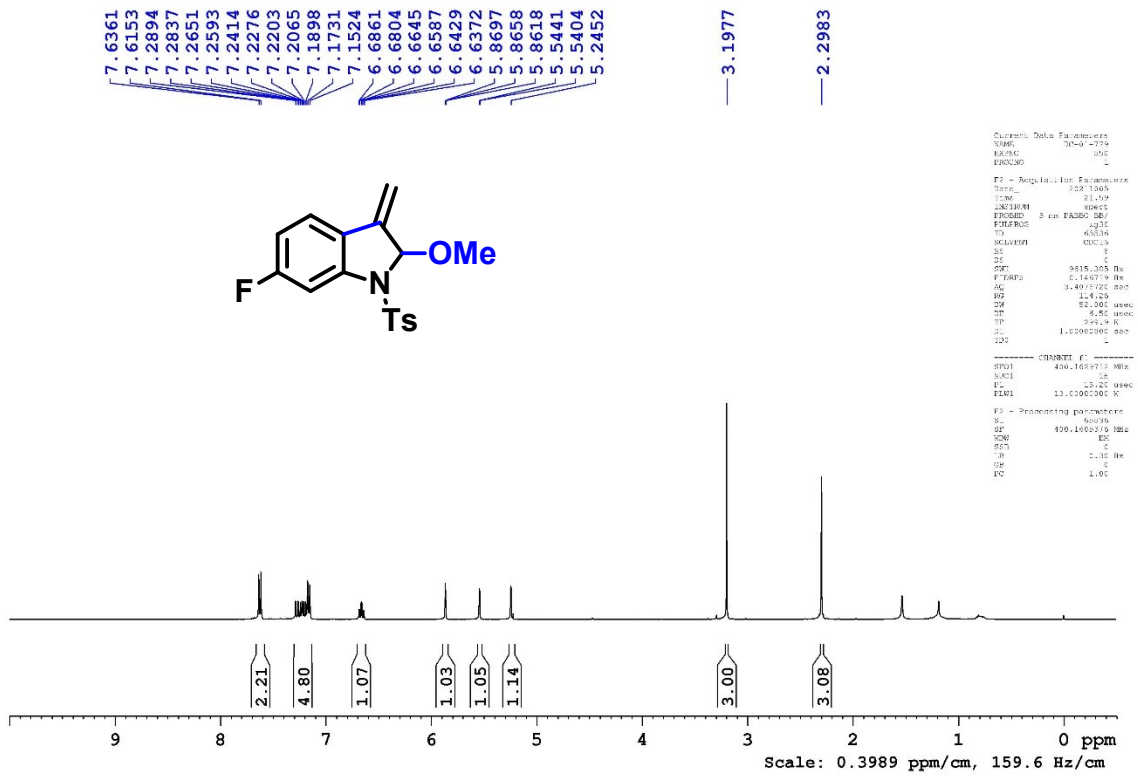

Figure S-54: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**

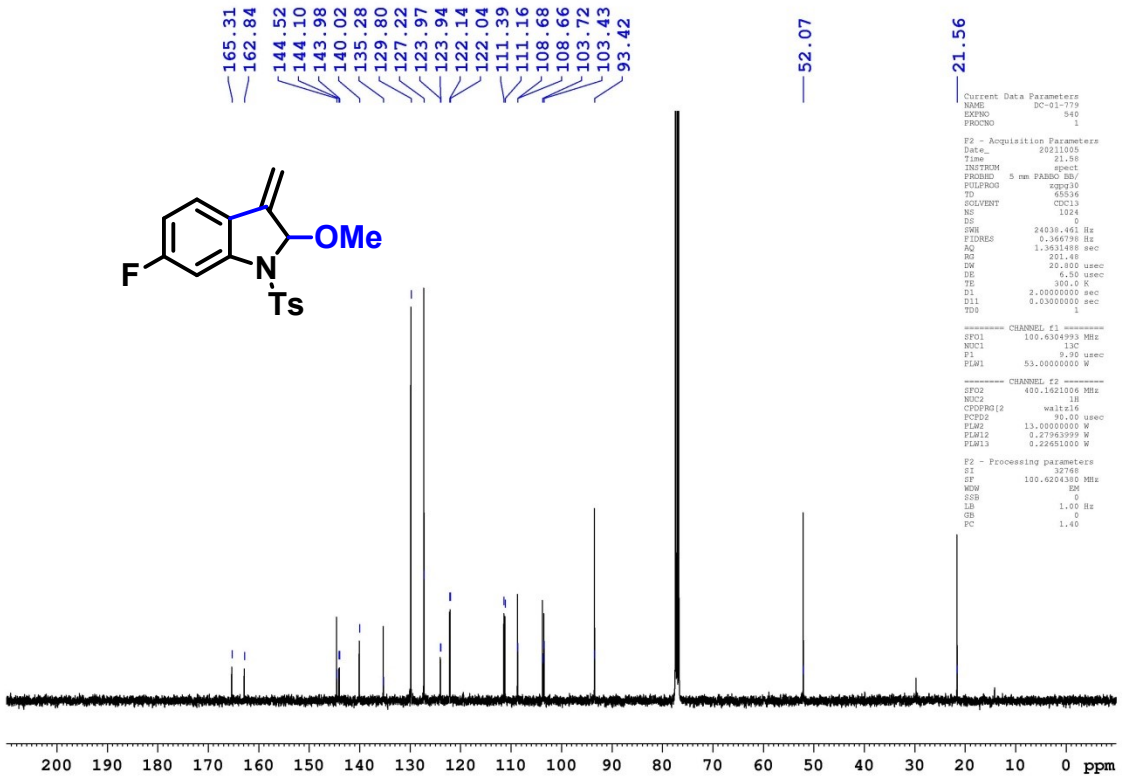

Figure S-55: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**

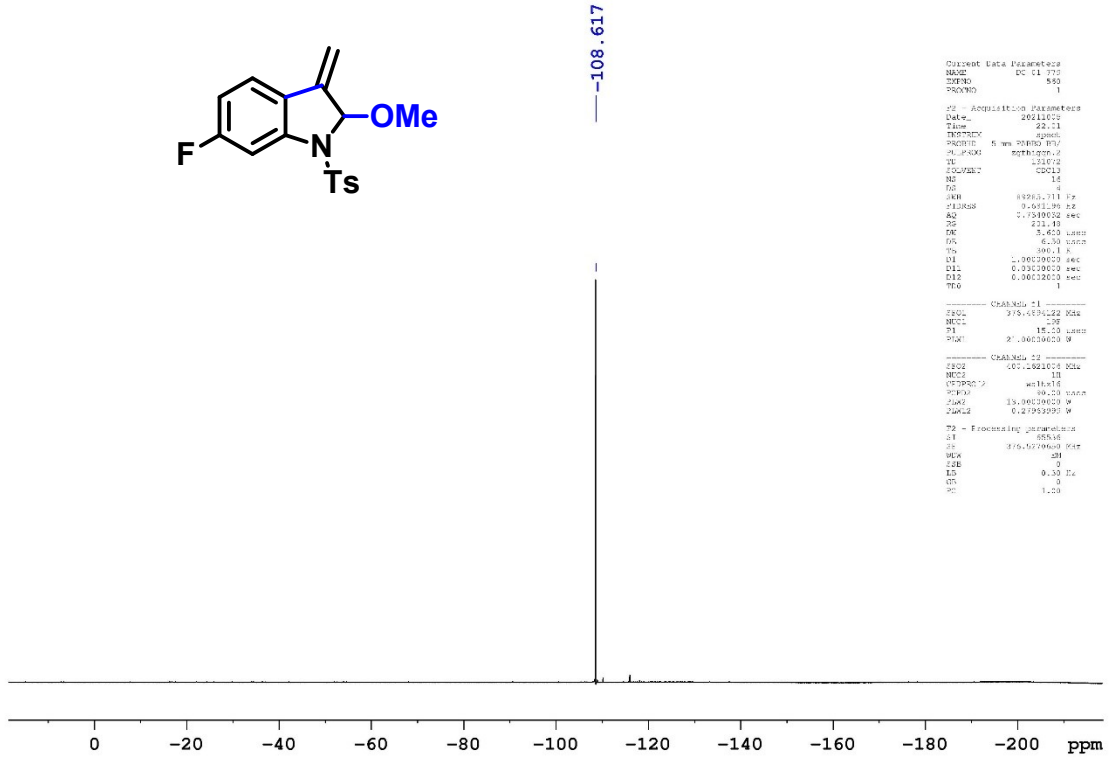

Figure S-56: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3i**

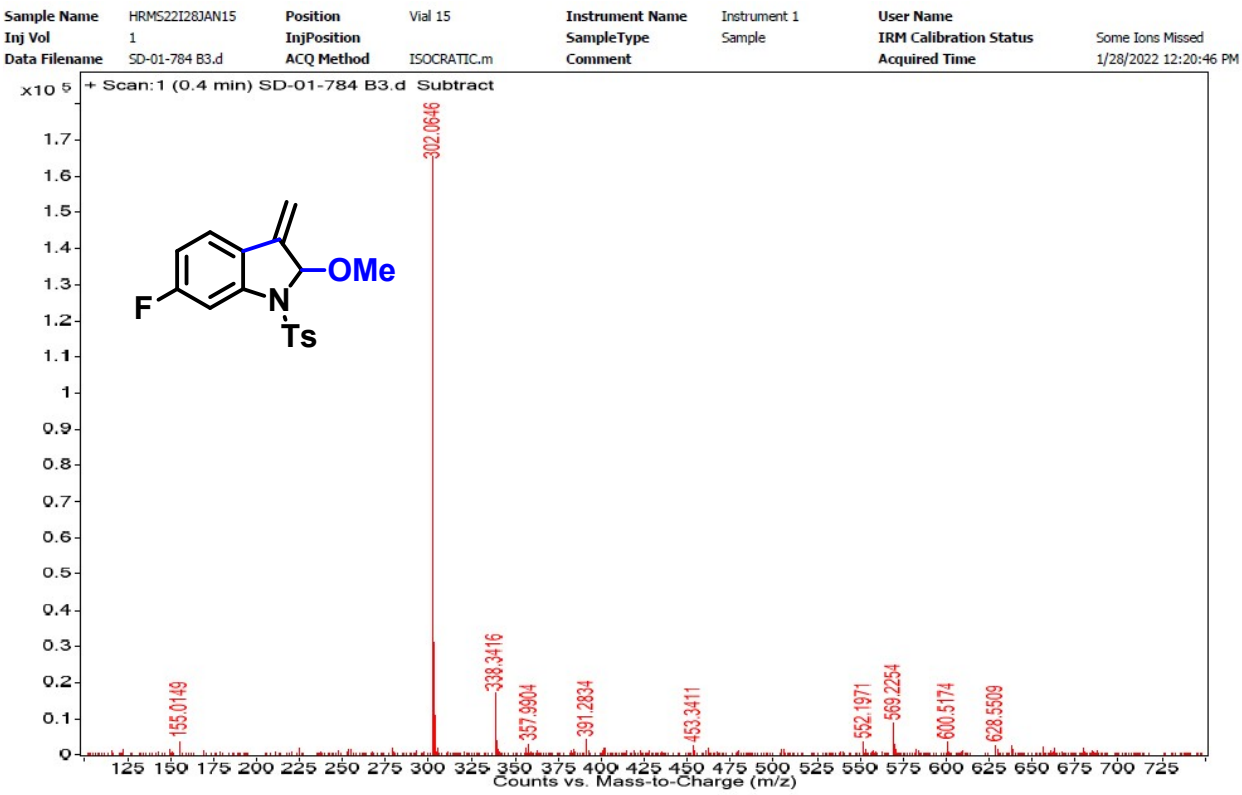

Figure S-57: HRMS spectrum of compound **3i**

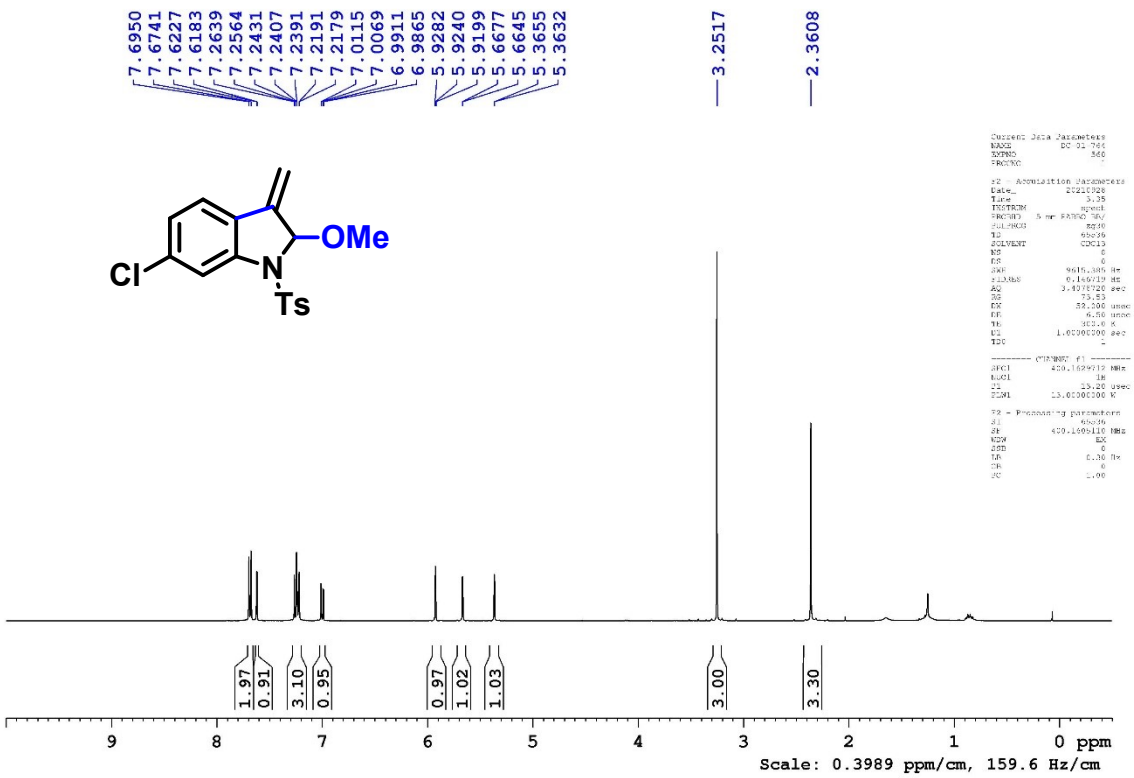

Figure S-58: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**

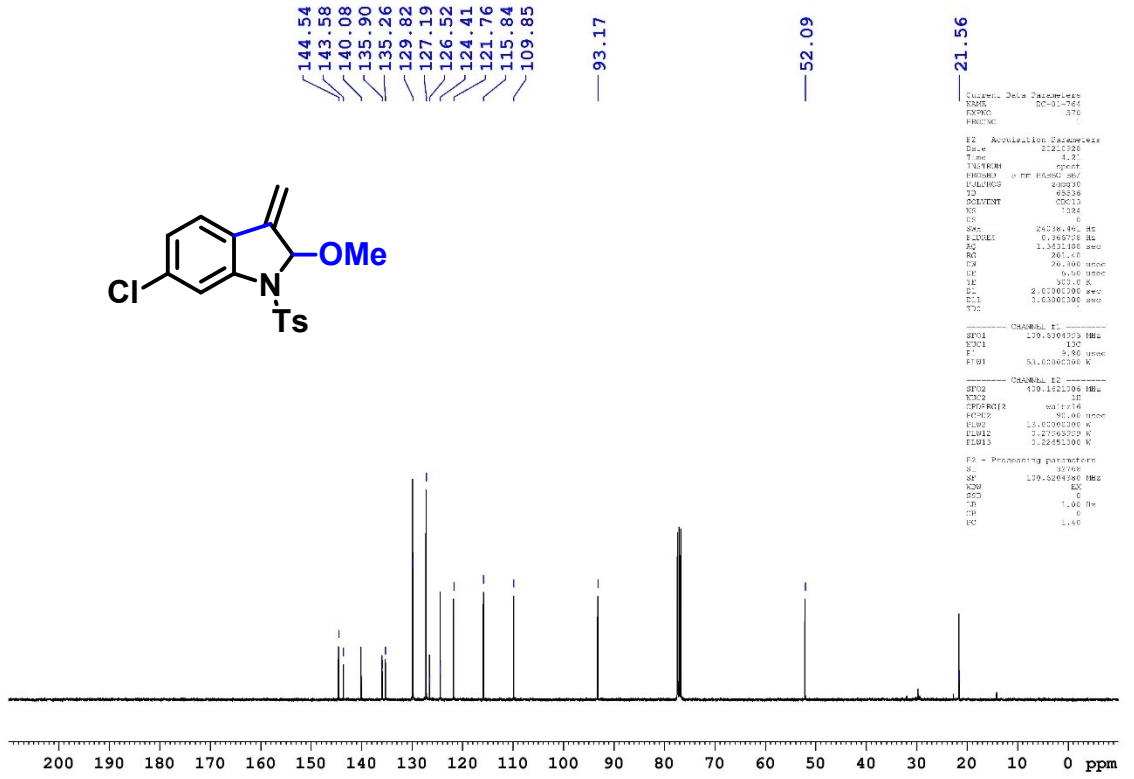

Figure S-59: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**

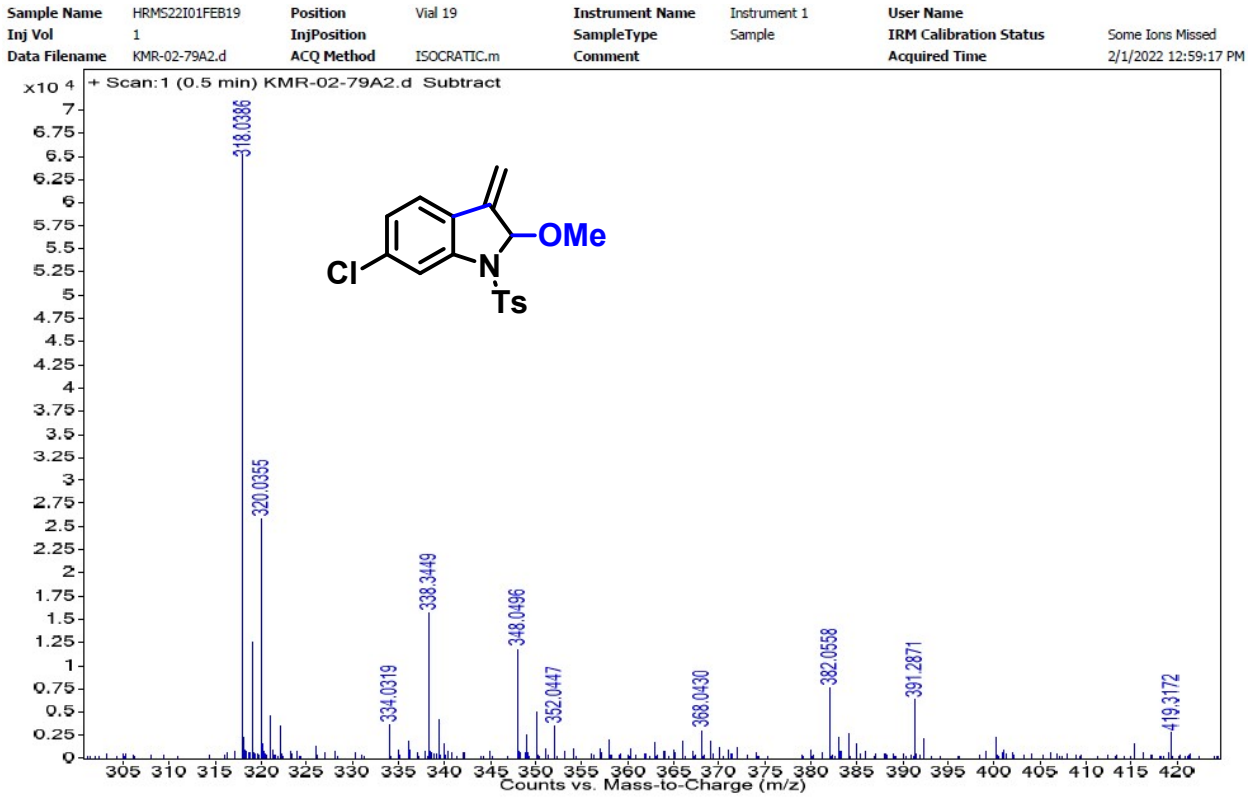

Figure S-60: HRMS spectrum of compound **3j**

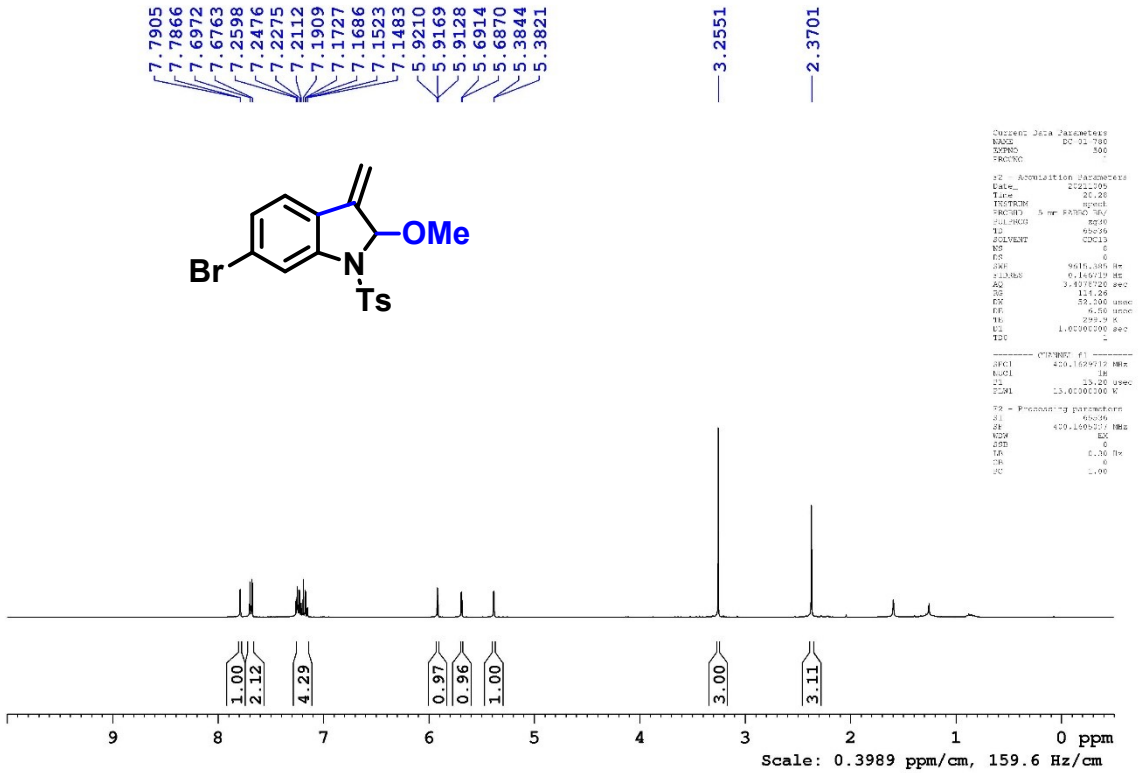

Figure S-61: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**

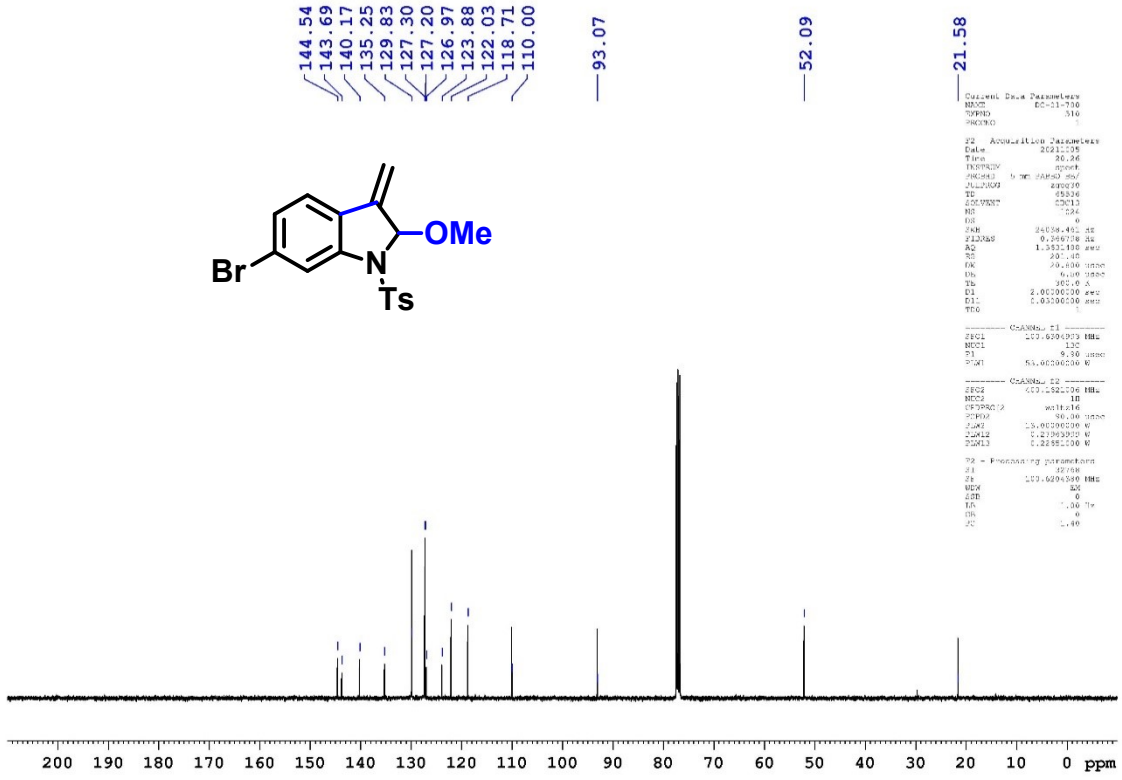

Figure S-62: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3k**

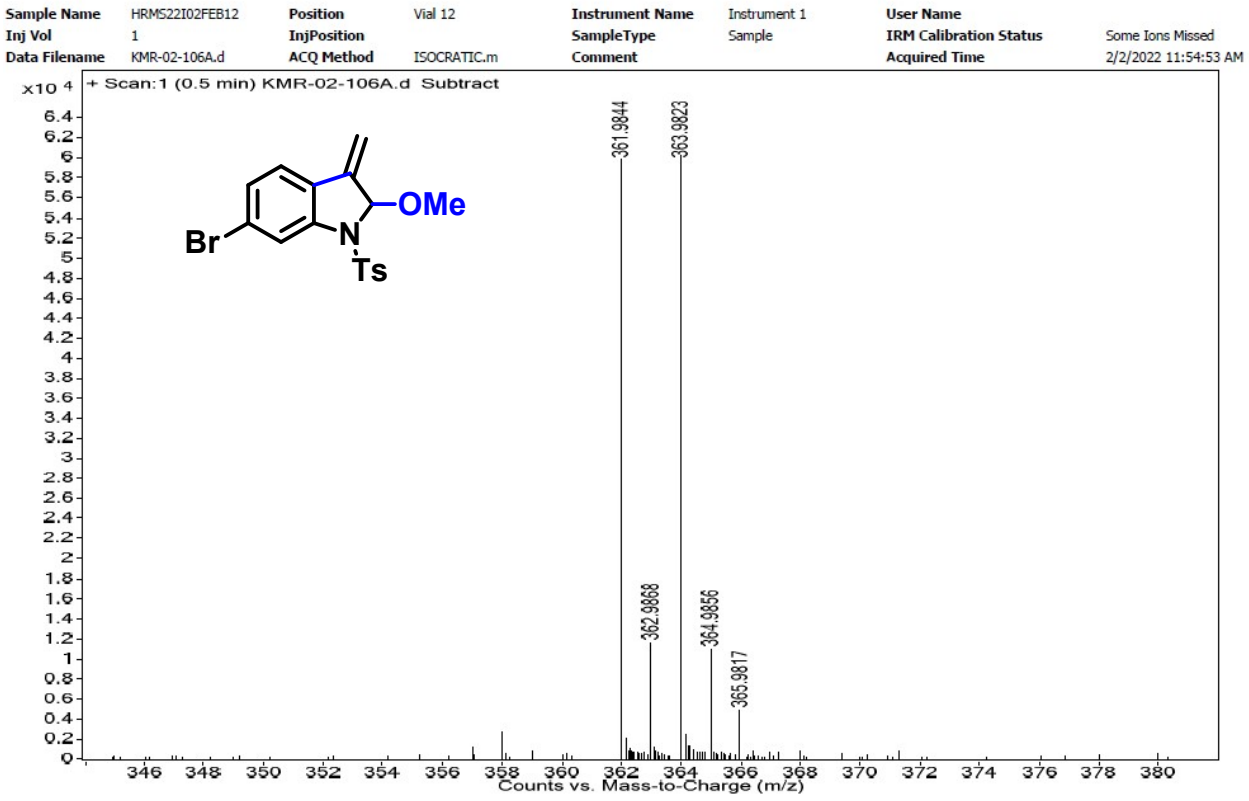

Figure S-63: HRMS spectrum of compound **3k**

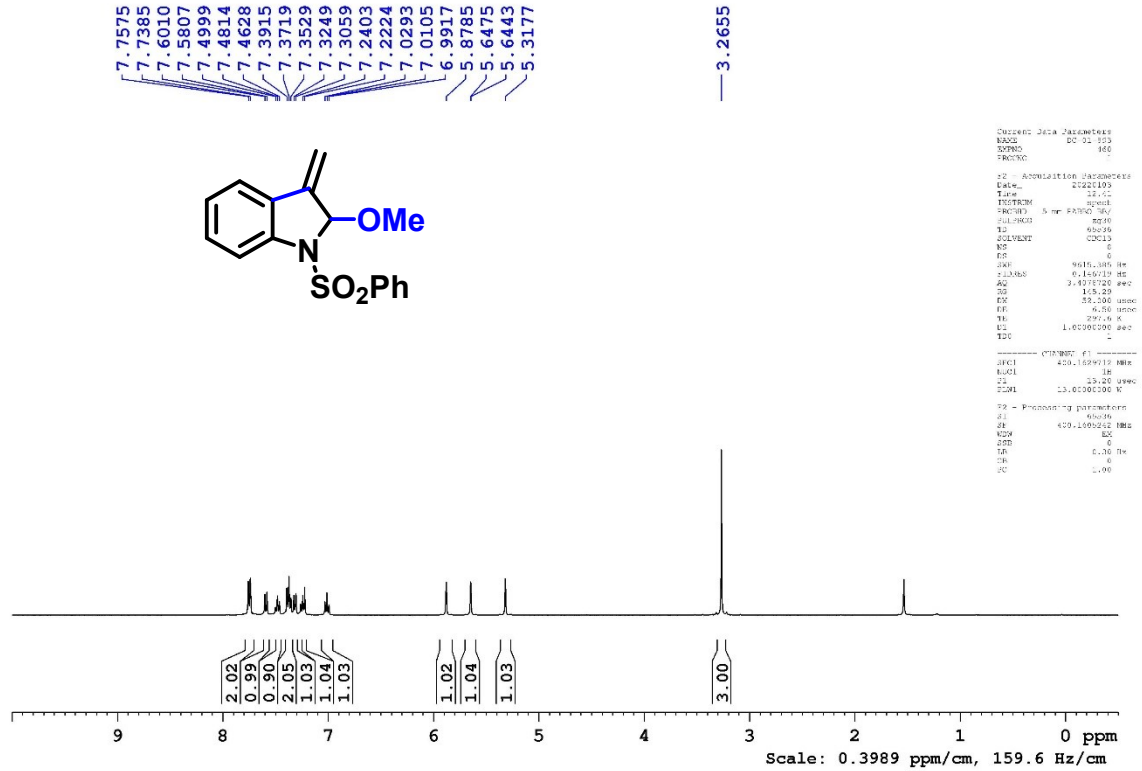

Figure S-64: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**

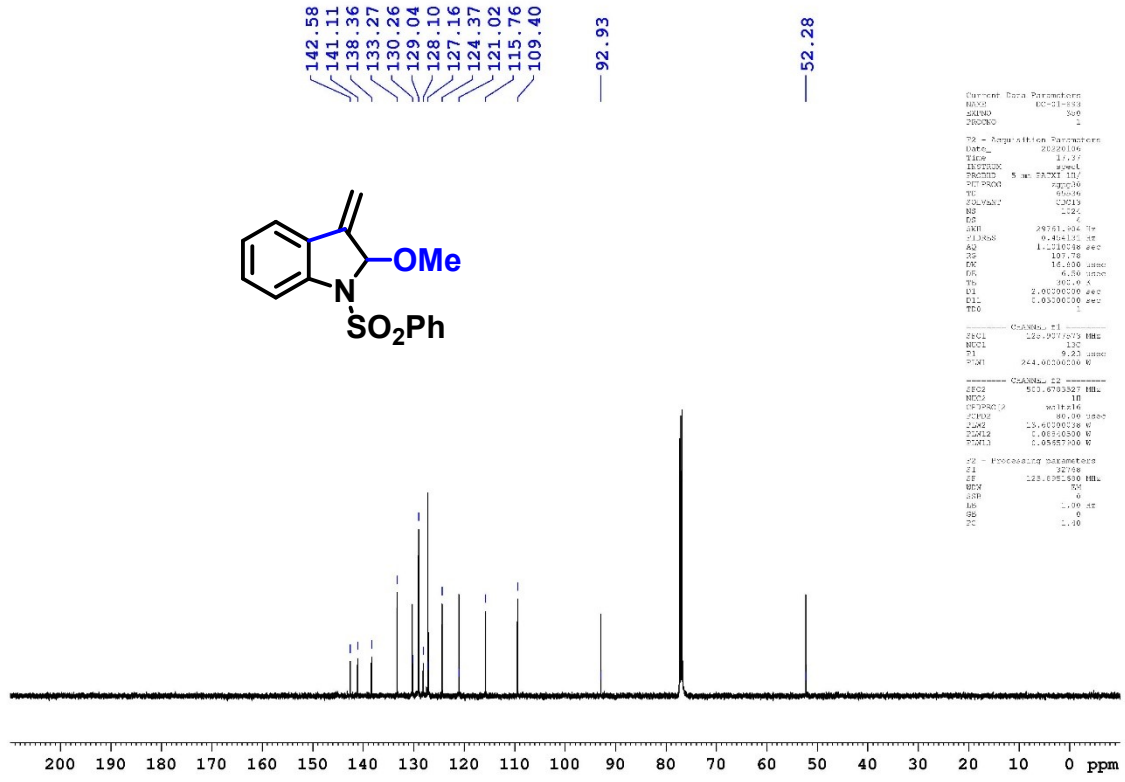

Figure S-65: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3l**

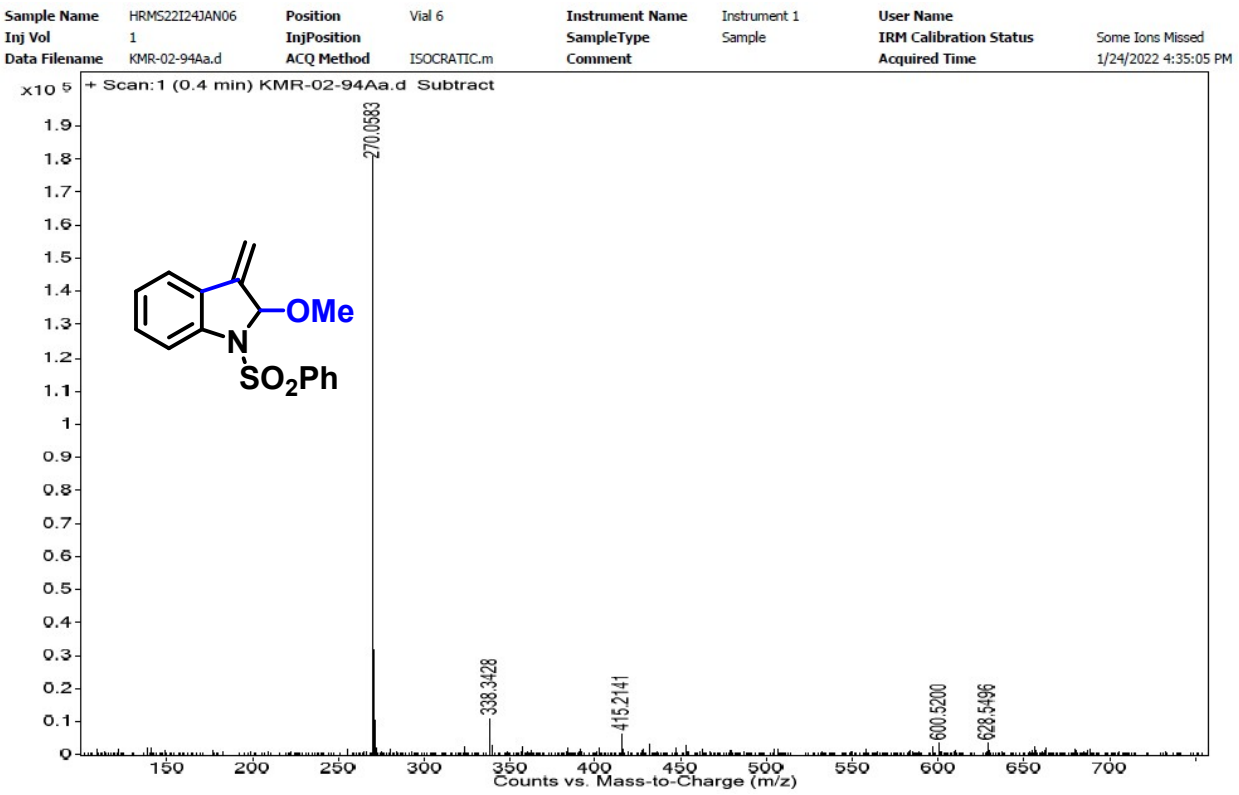

Figure S-66: HRMS spectrum of compound **3l**

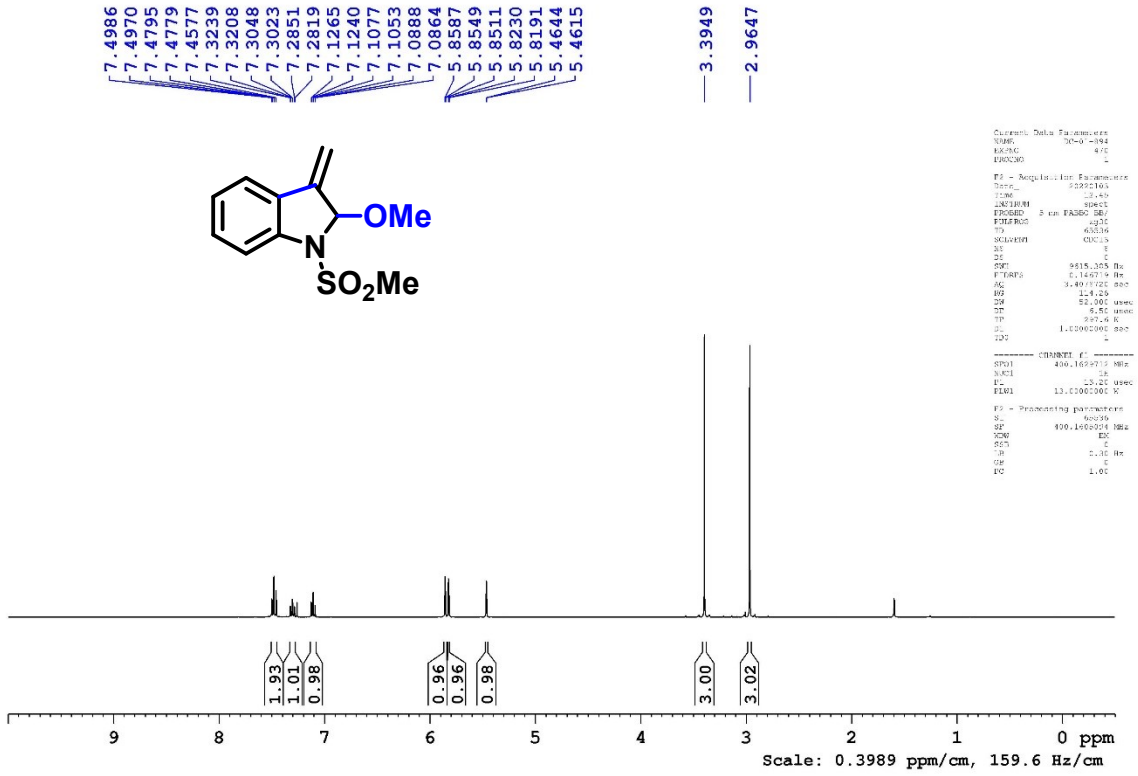

Figure S-67: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**

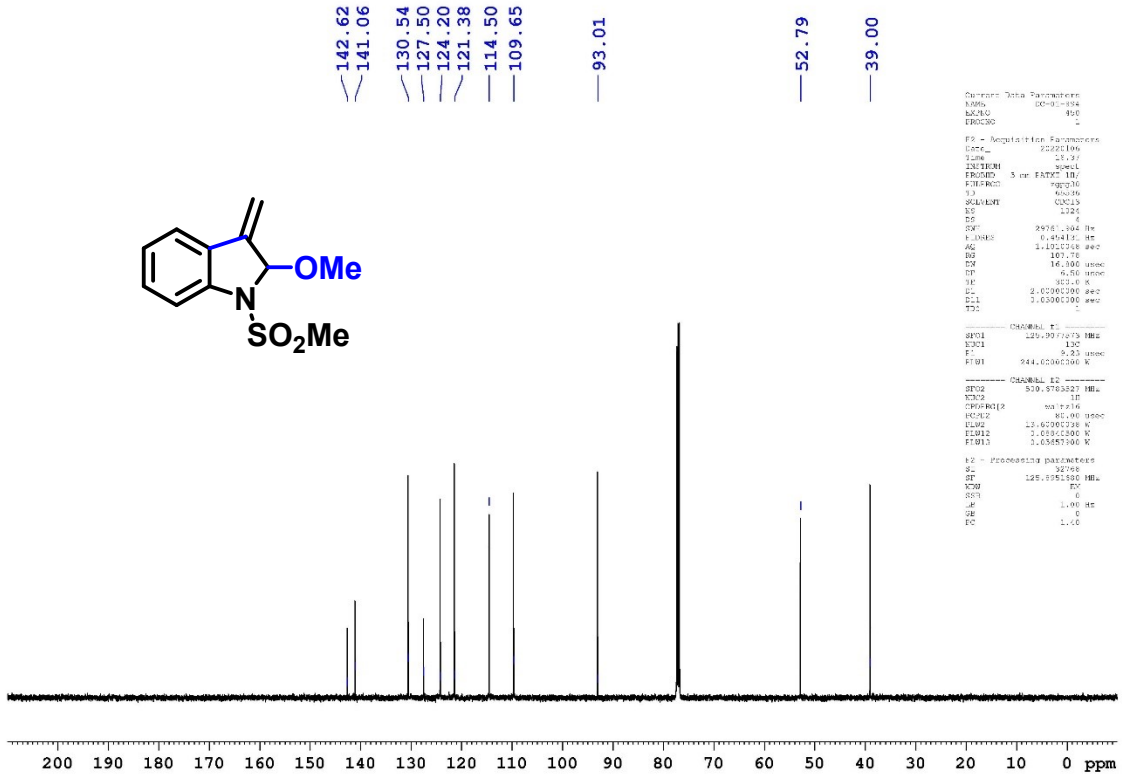

Figure S-68: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3m**

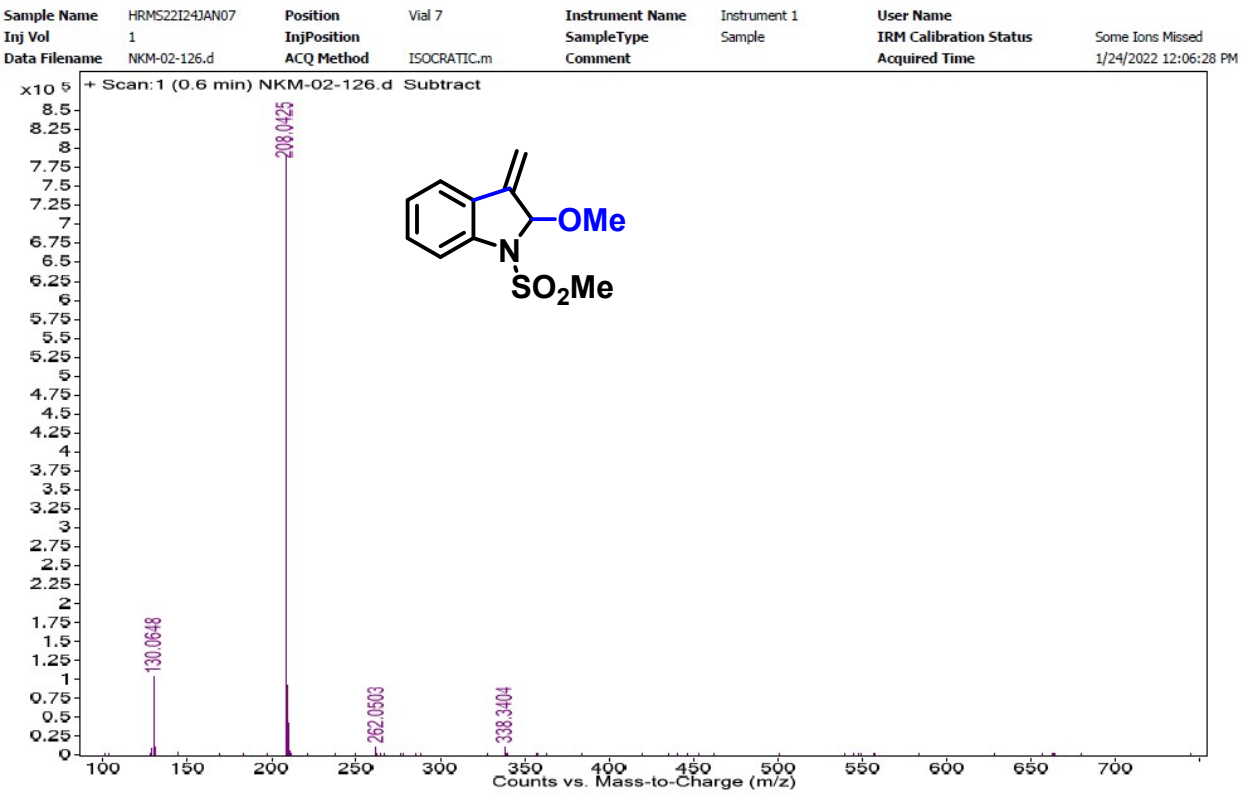

Figure S-69: HRMS spectrum of compound **3m**

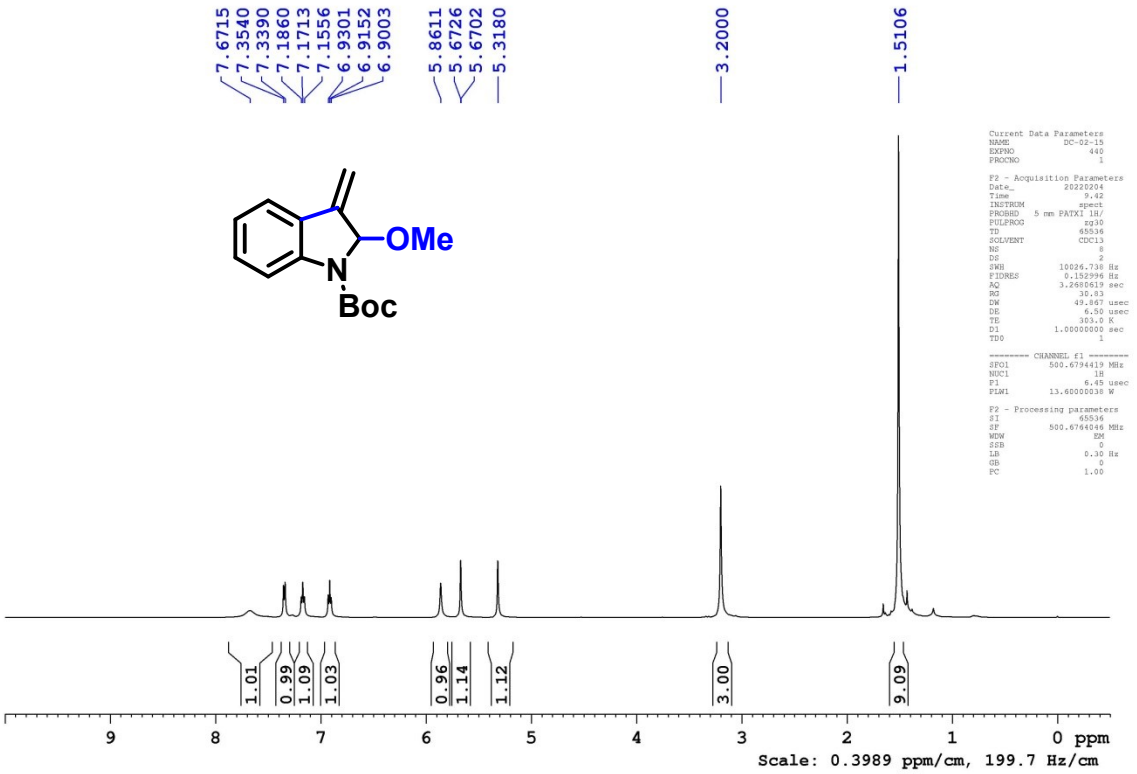

Figure S-70: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3n**

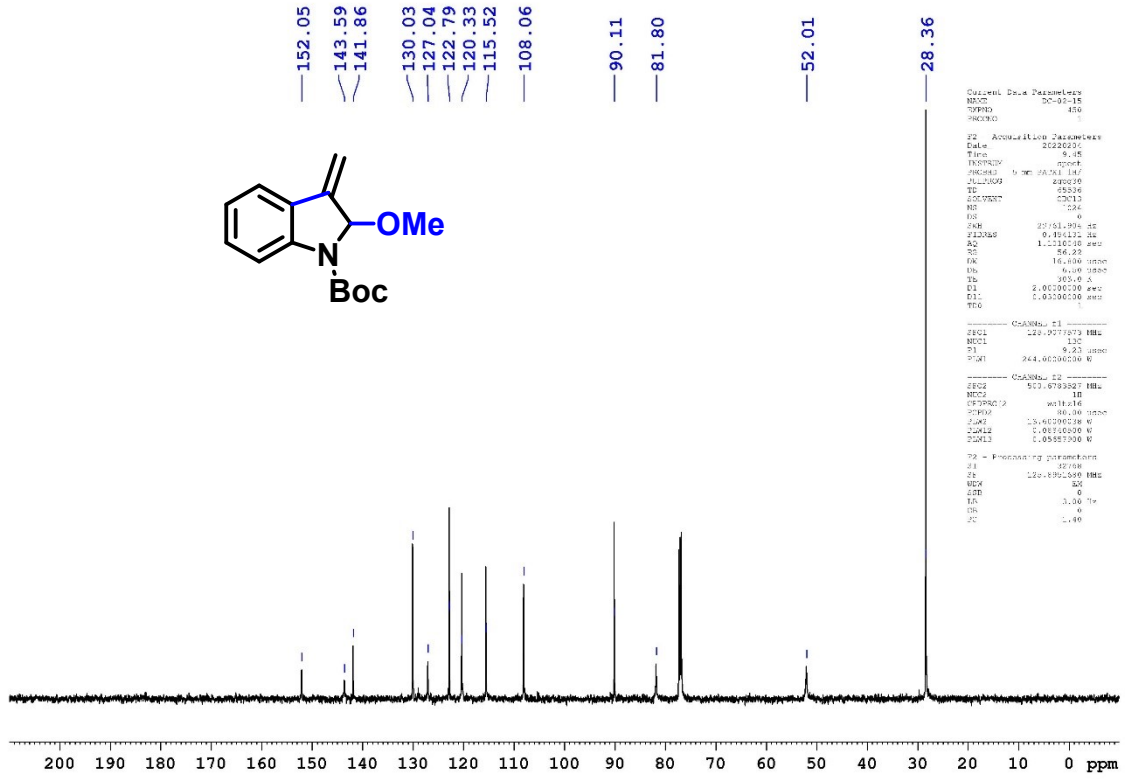

Figure S-71: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3n**

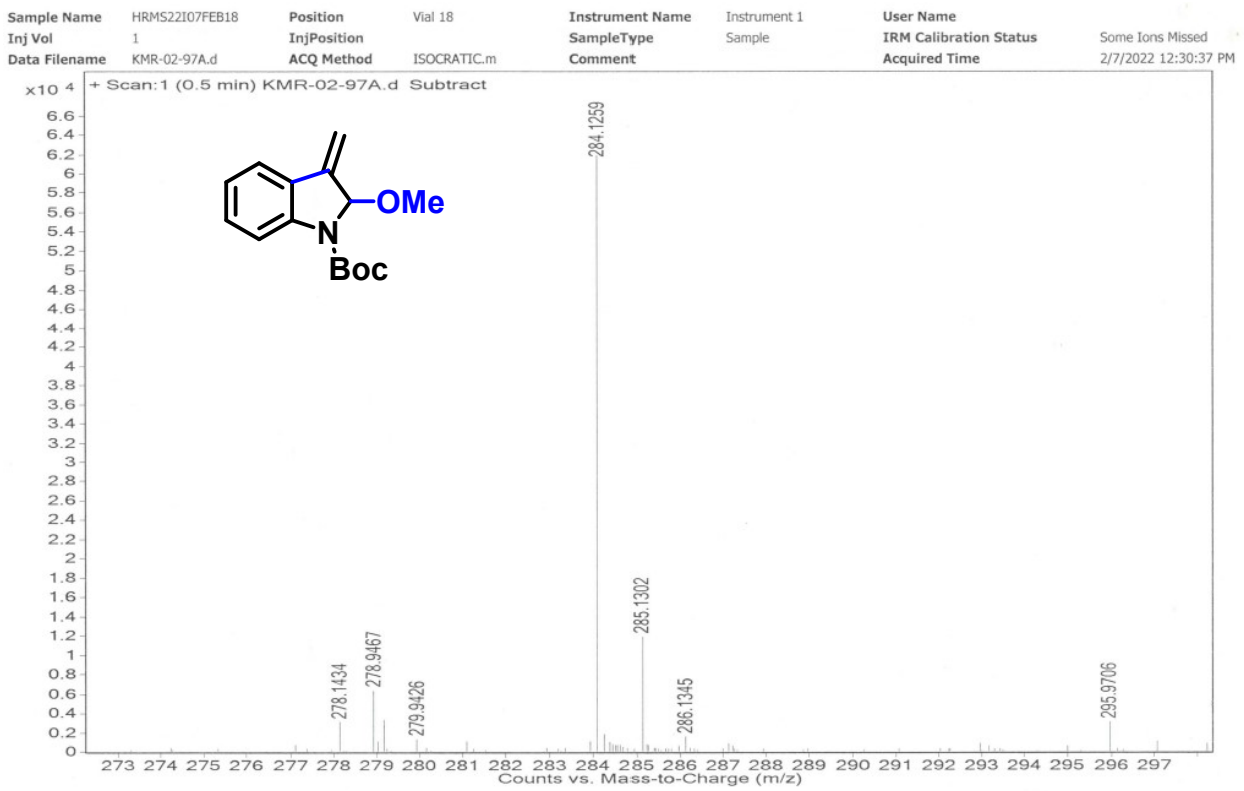

Figure S-72: HRMS spectrum of compound **3n**

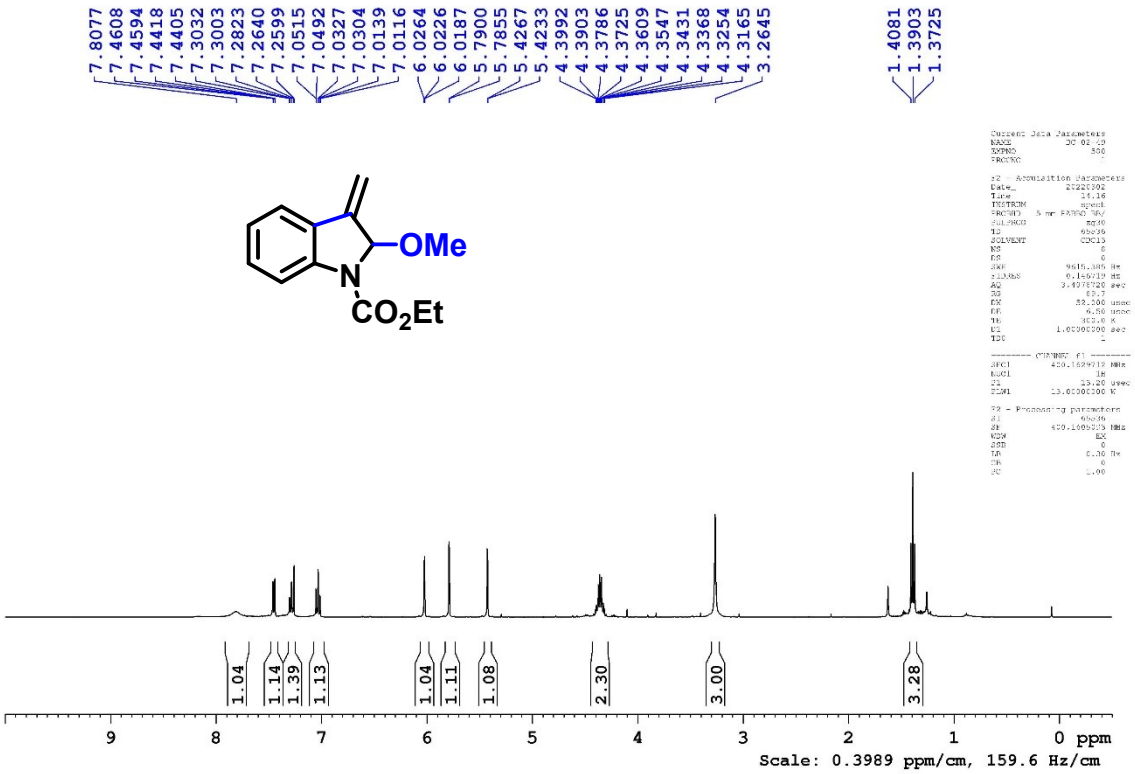

Figure S-73: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**

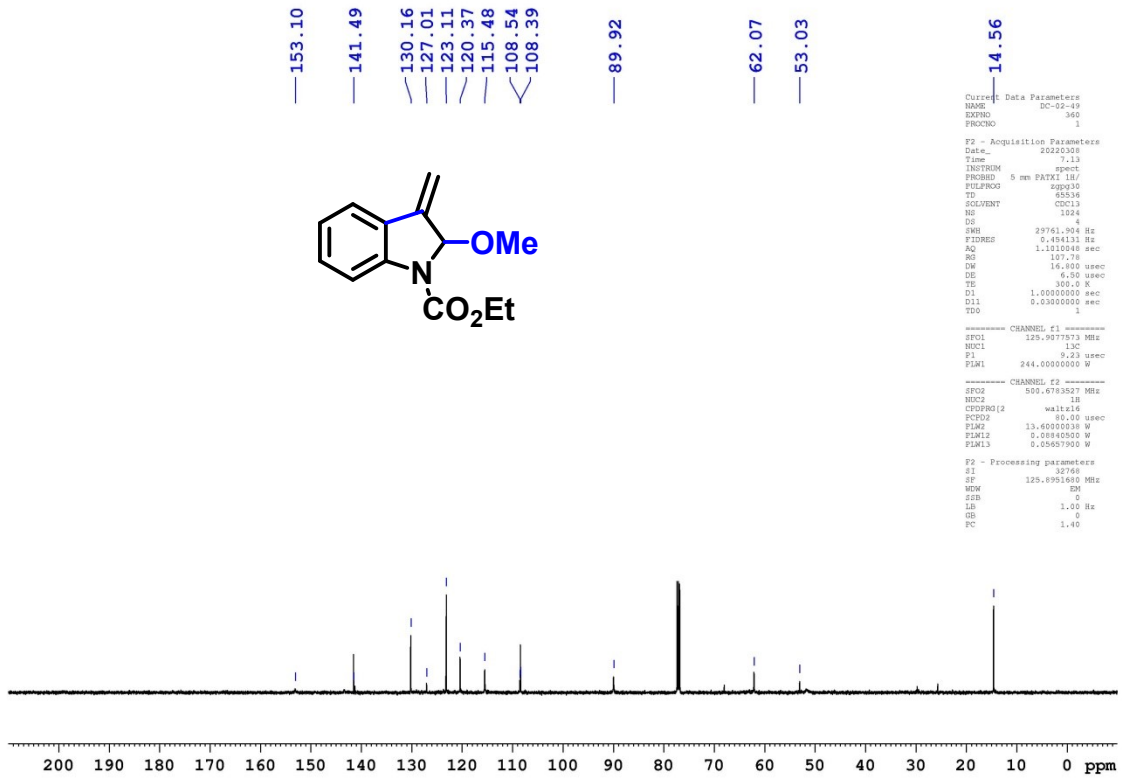

Figure S-74: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3o**

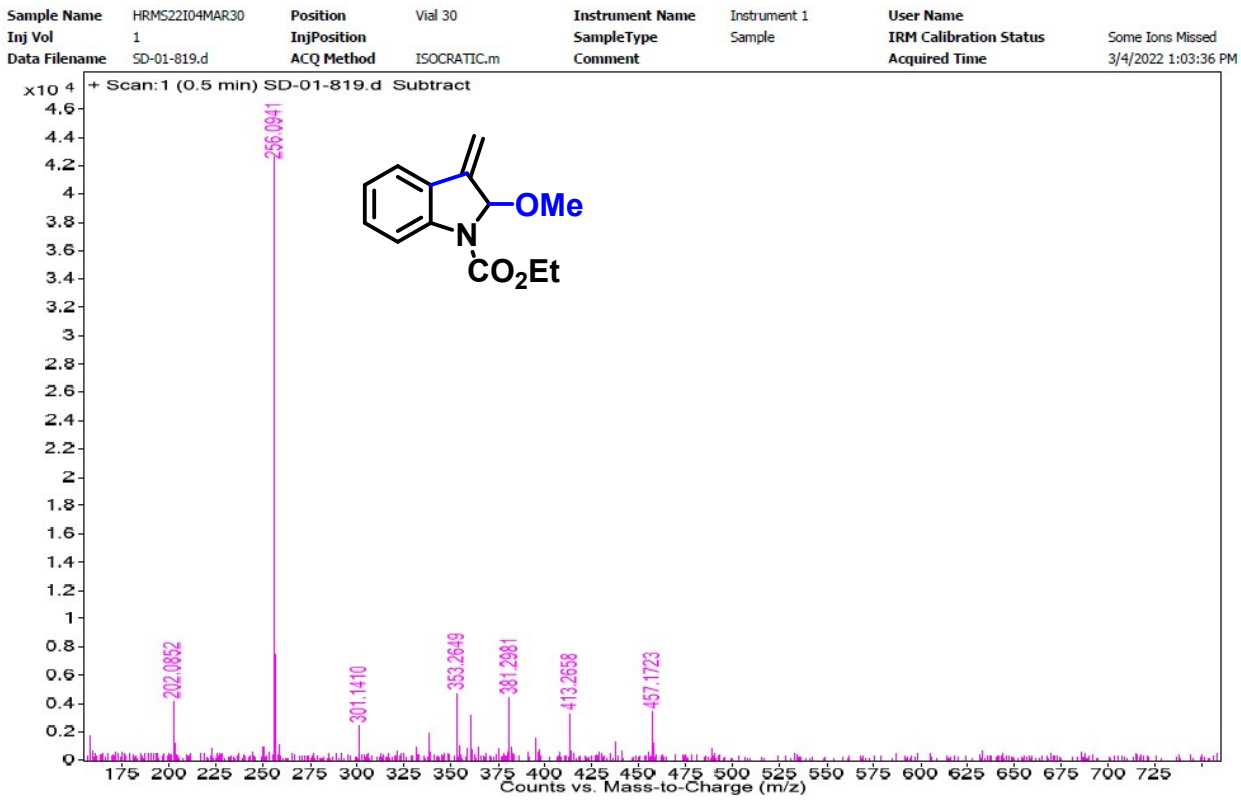

Figure S-75: HRMS spectrum of compound **3o**

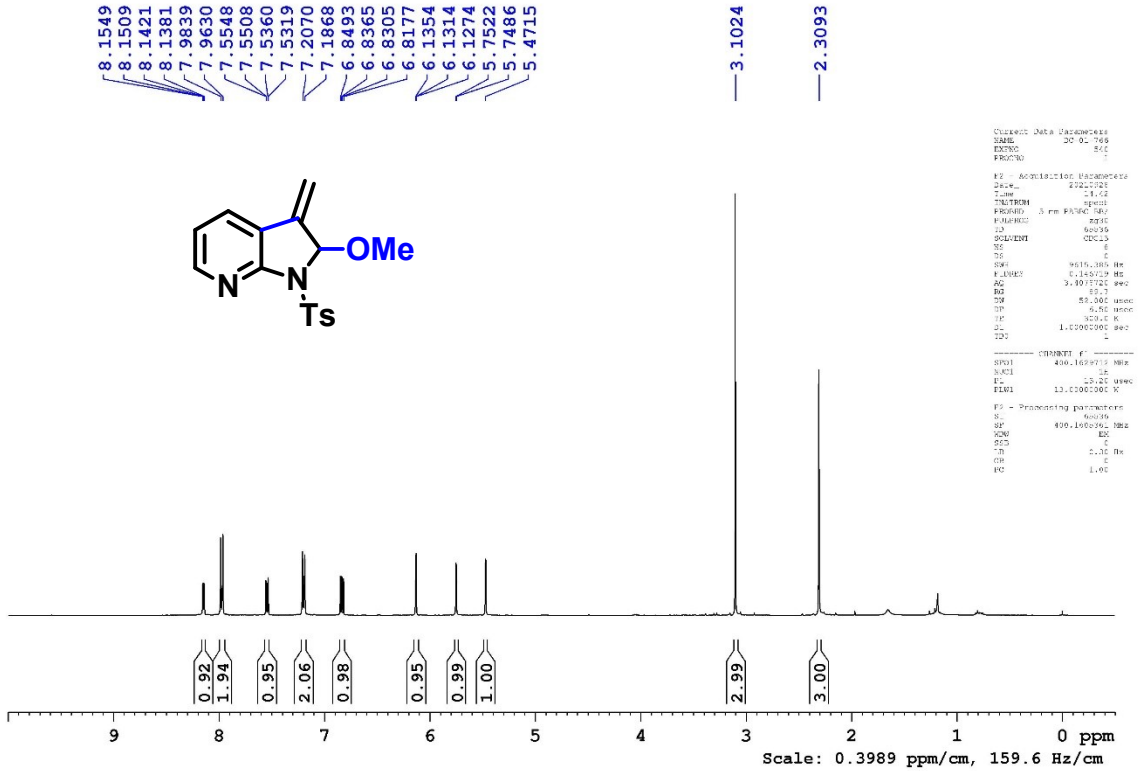

Figure S-76: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**

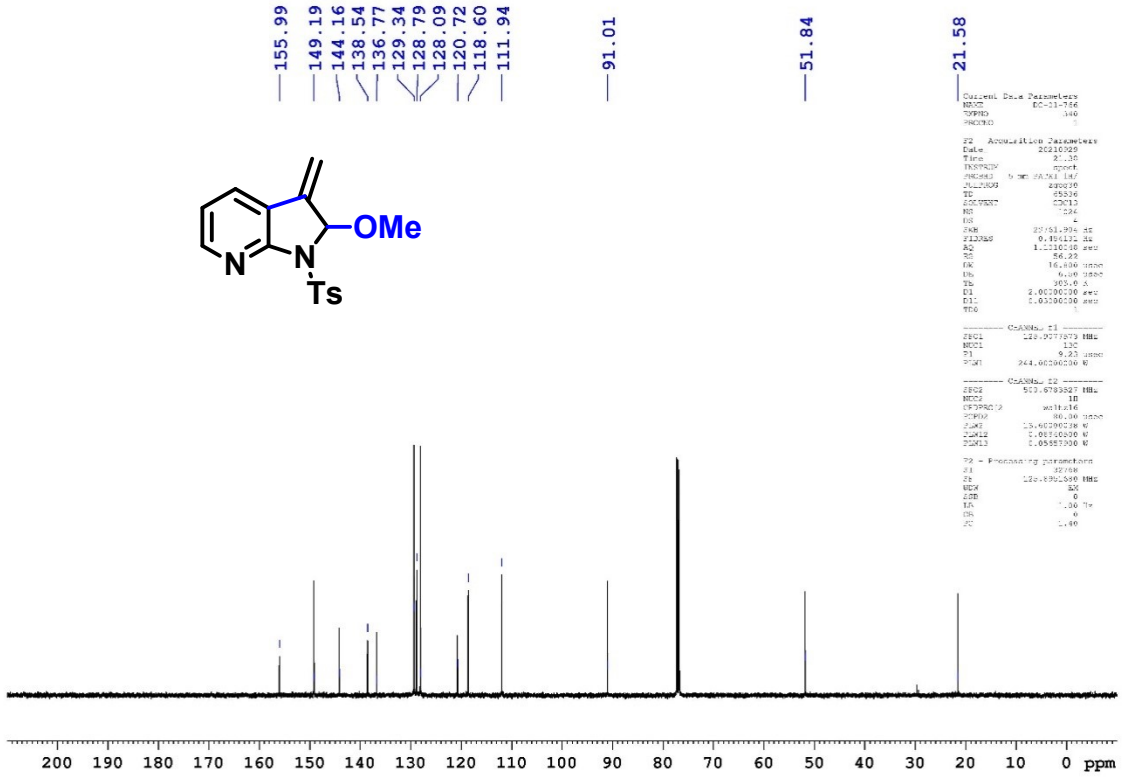

Figure S-77: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3p**

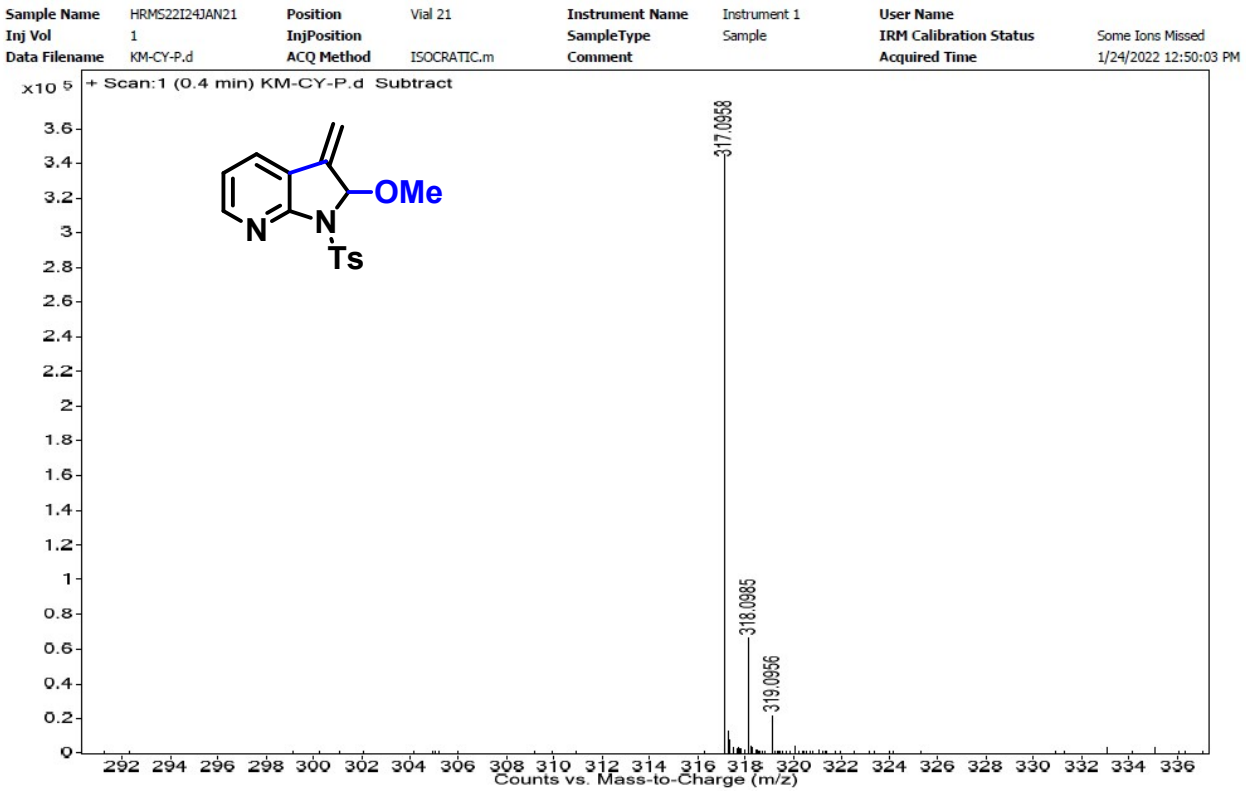

Figure S-78: HRMS spectrum of compound **3p**

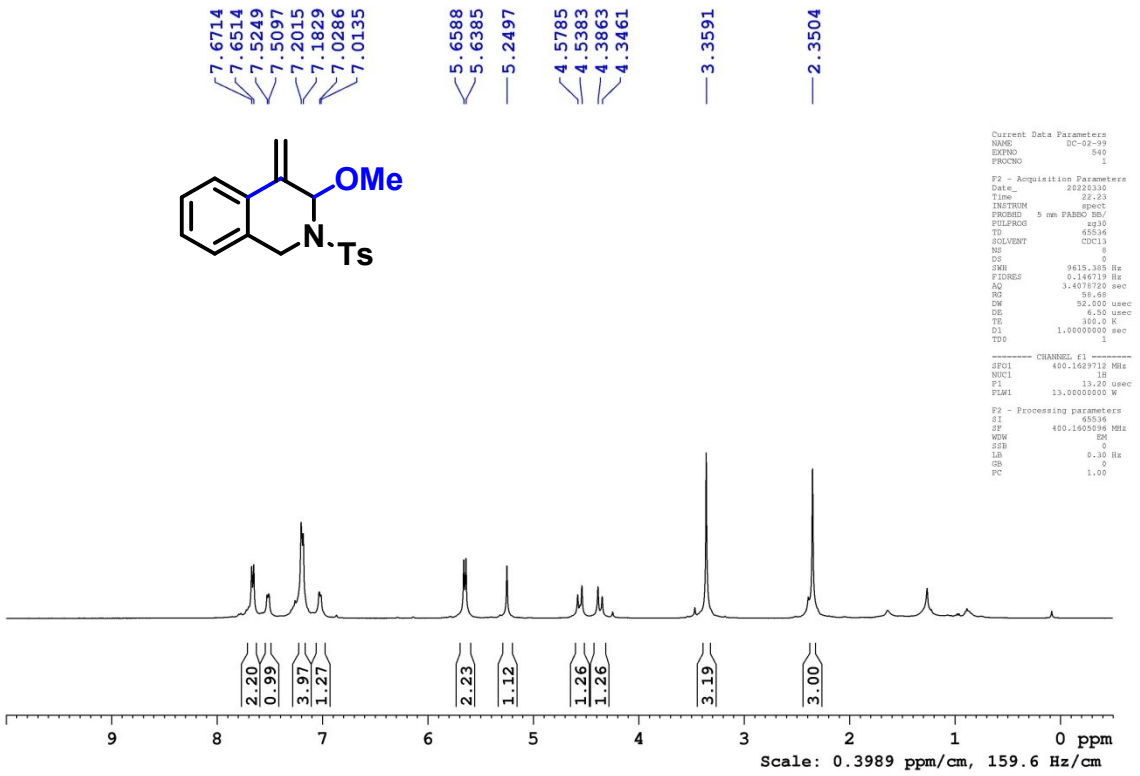

Figure S-79: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3q**

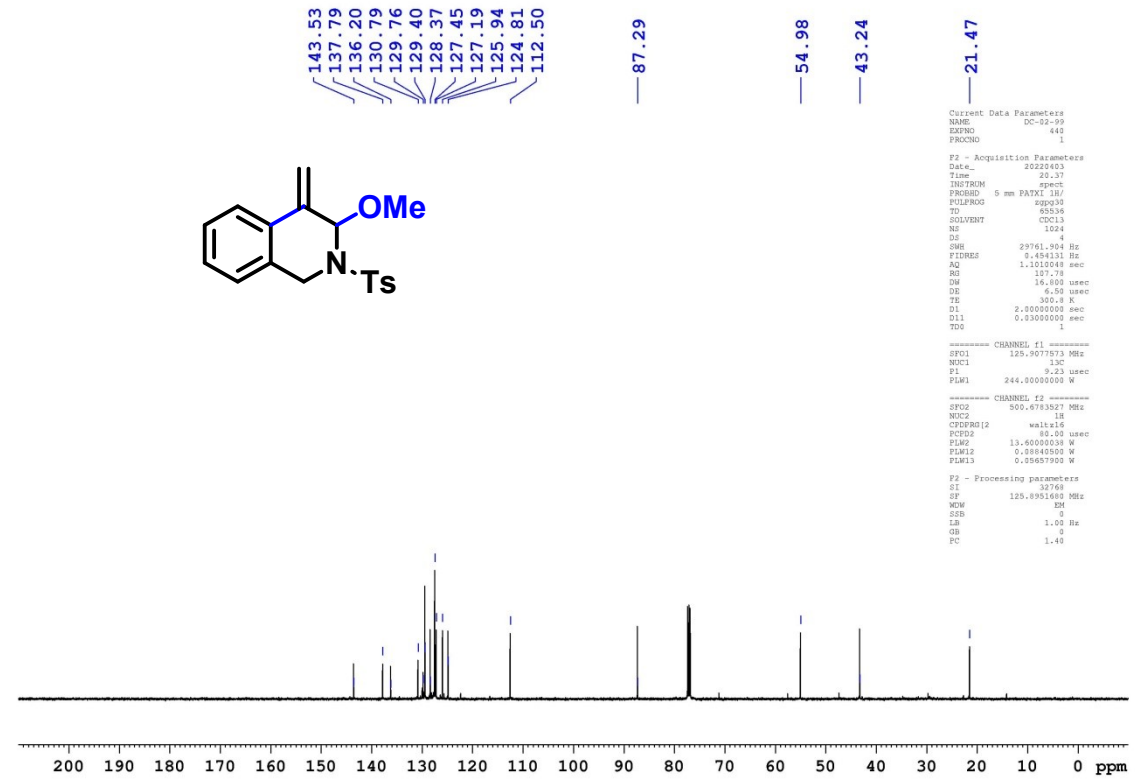

Figure S-80: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3q**

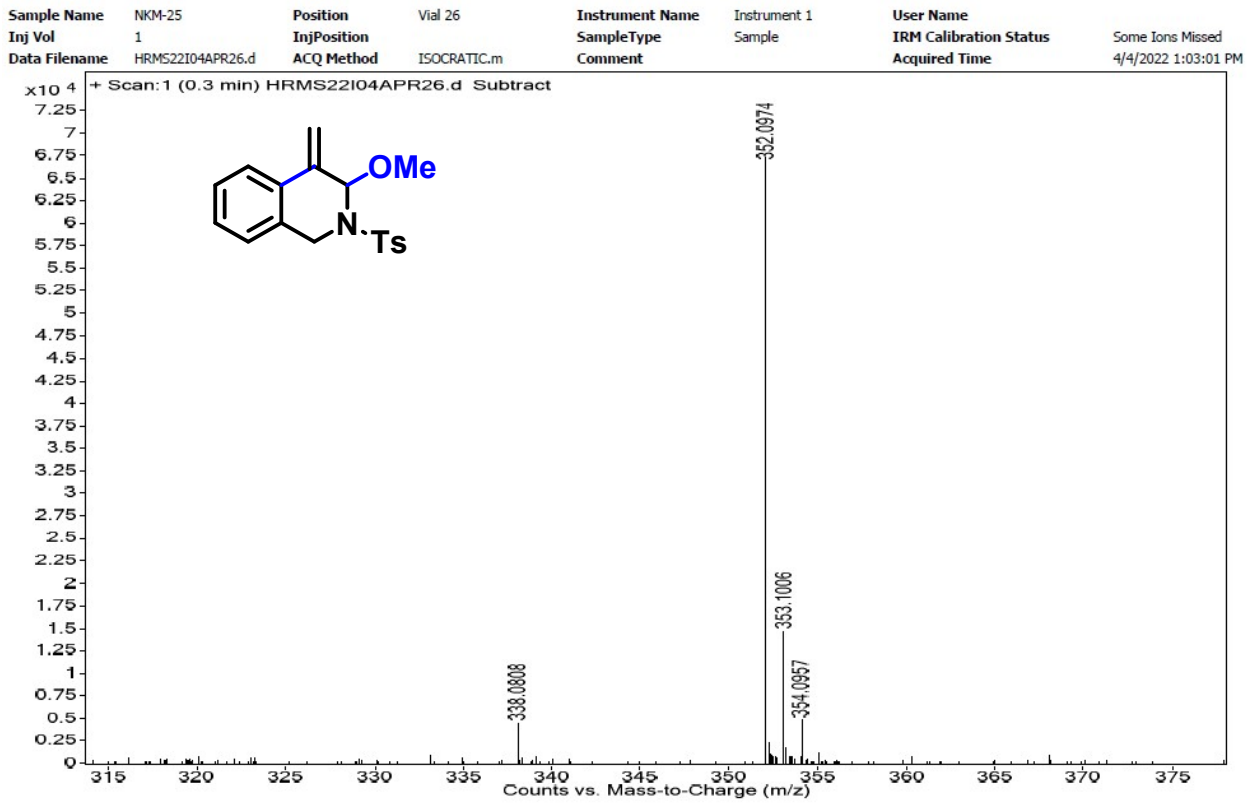

Figure S-81: HRMS spectrum of compound **3q**

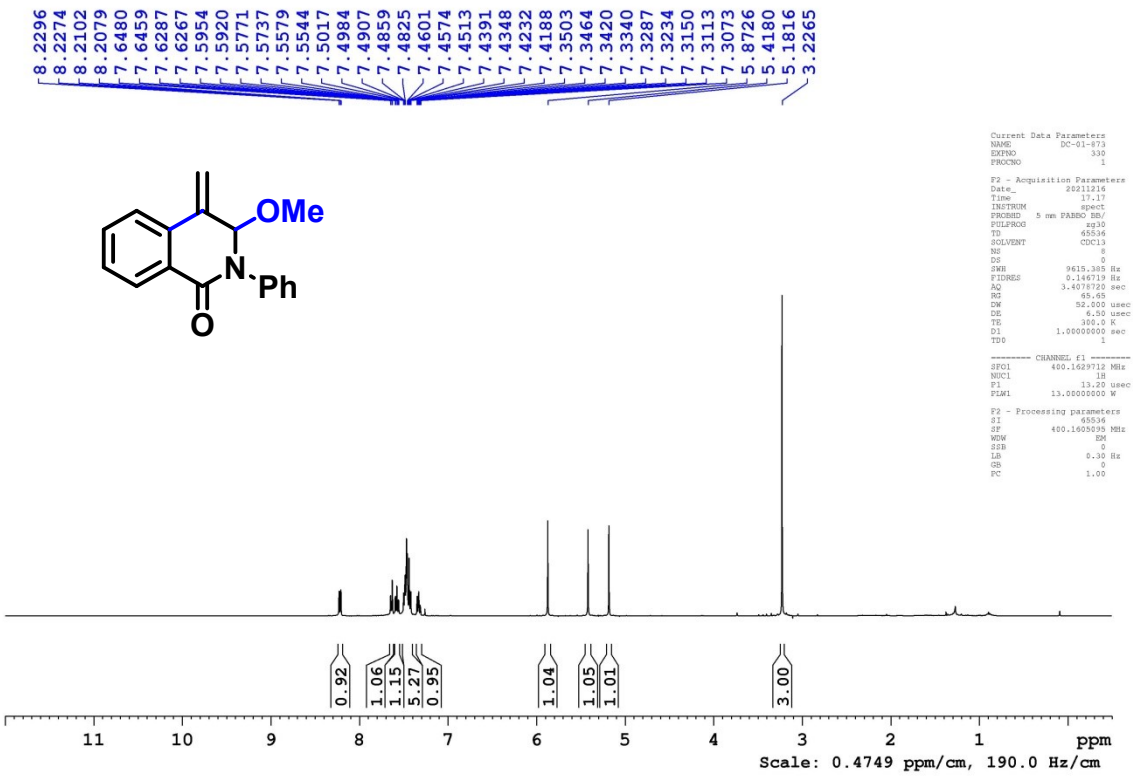

Figure S-82: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**

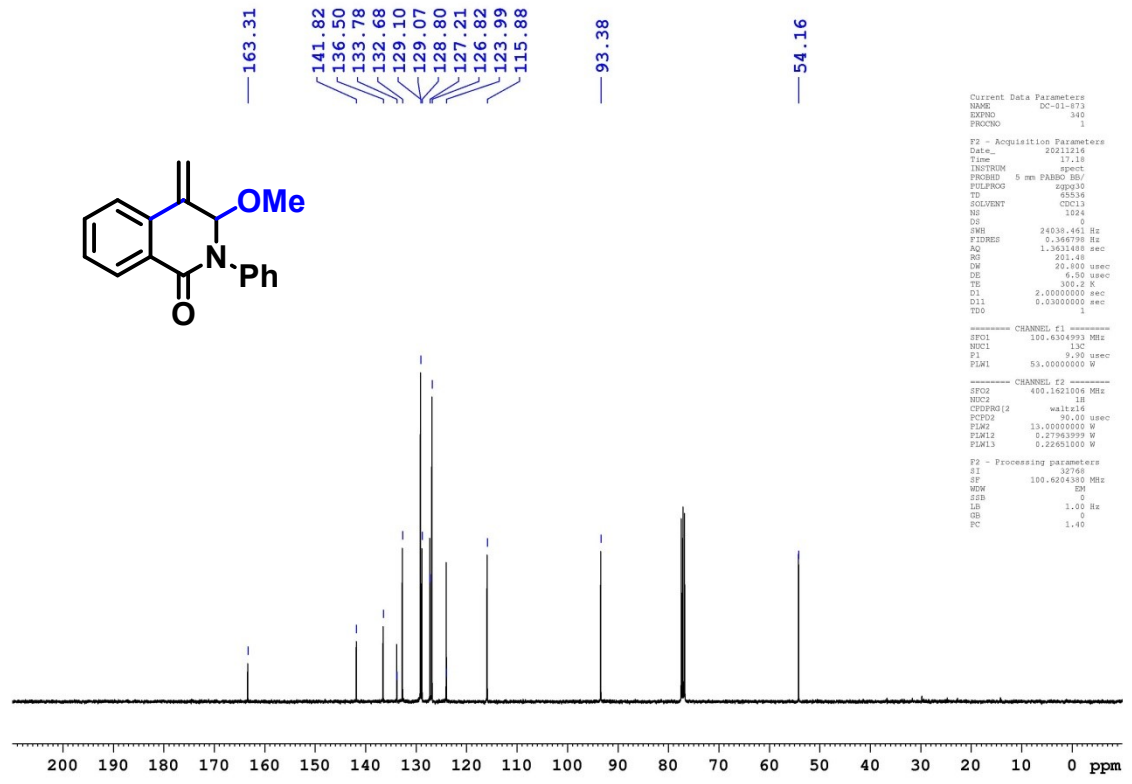

Figure S-83: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3r**

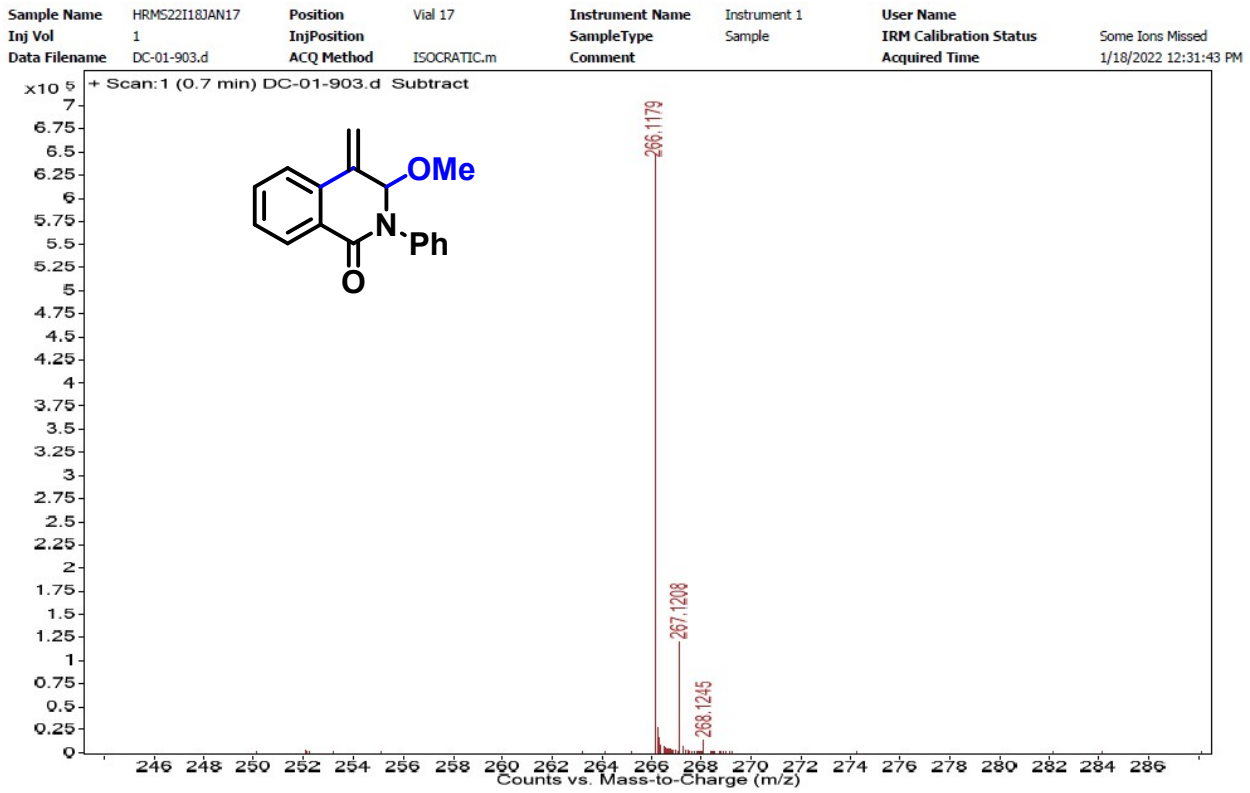

Figure S-84: HRMS spectrum of compound **3r**

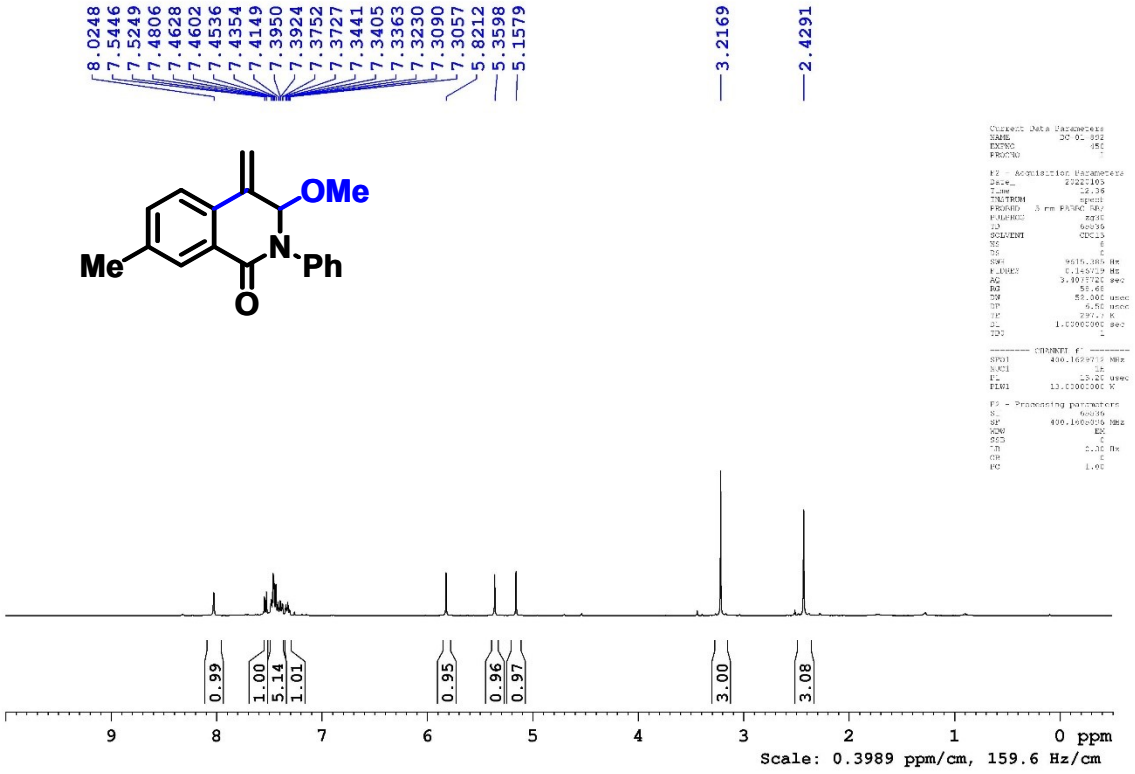

Figure S-85: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3s**

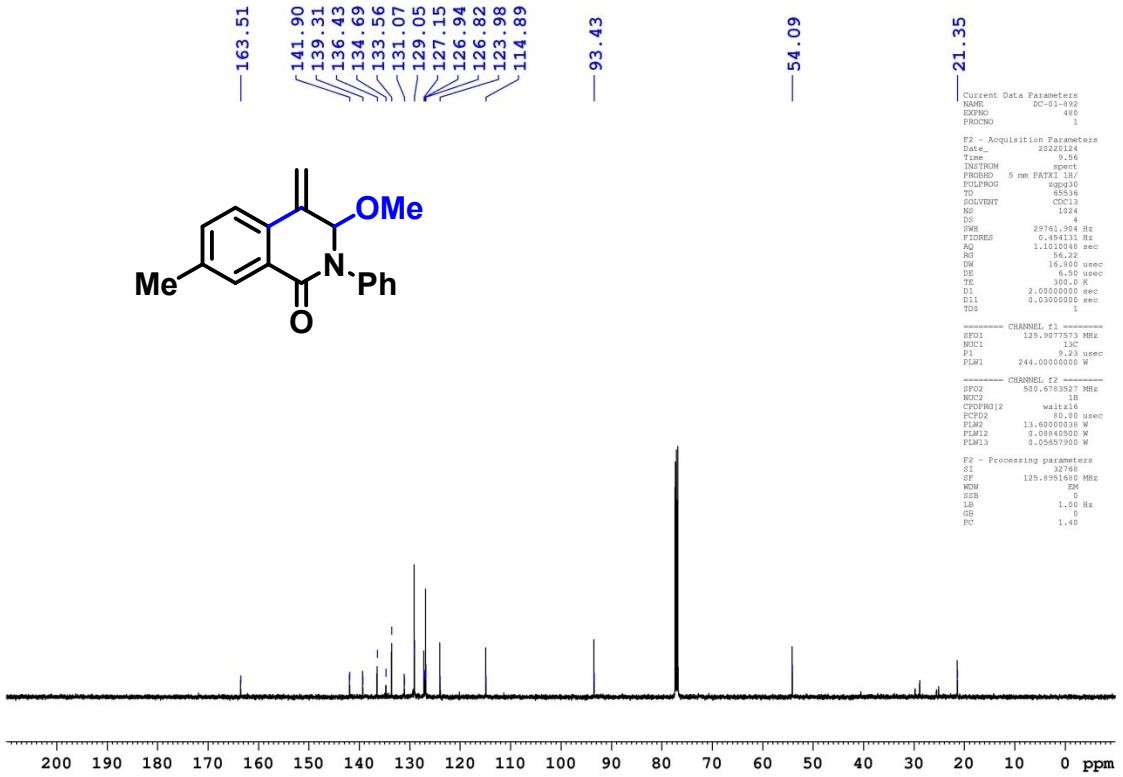

Figure S-86: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3s**

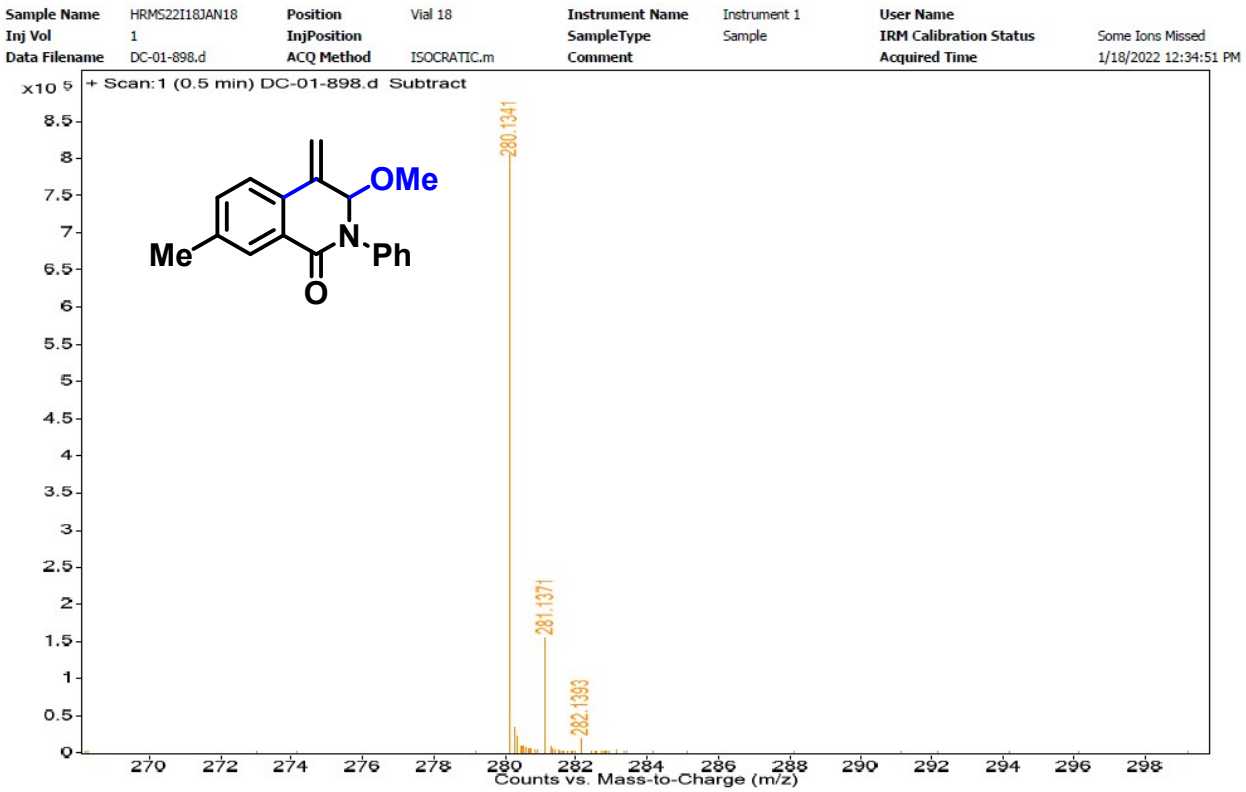

Figure S-87: HRMS spectrum of compound **3s**

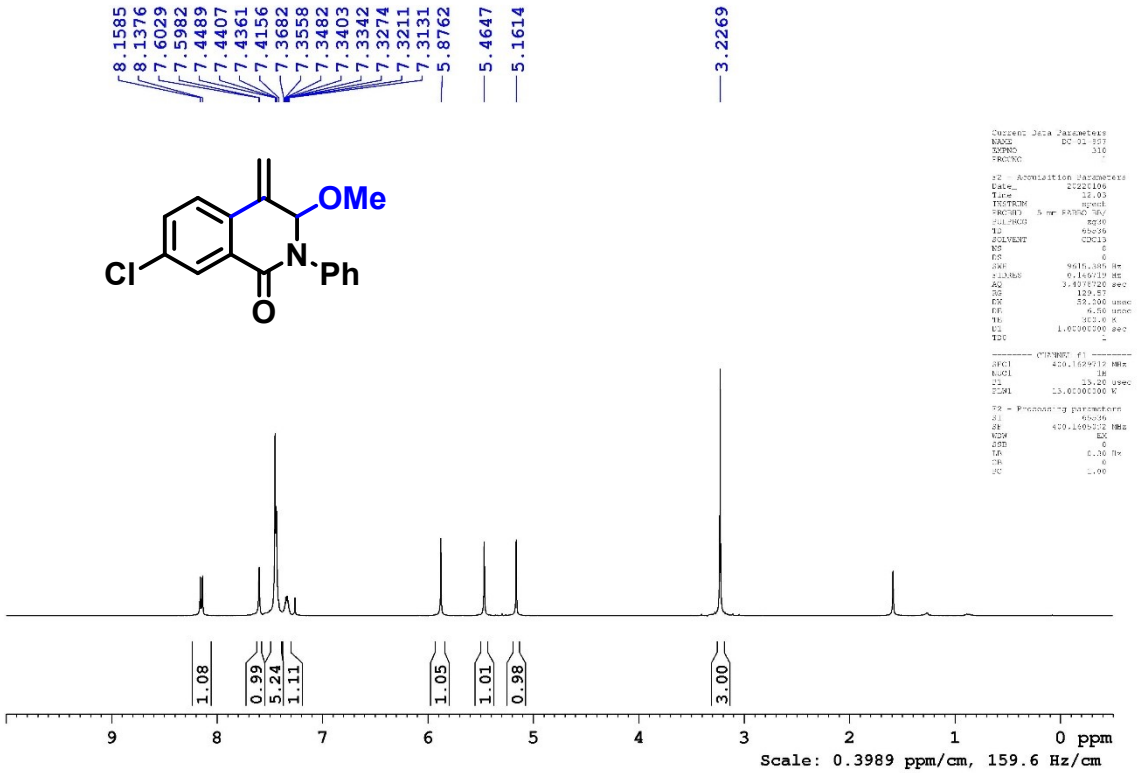

Figure S-88: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3t**

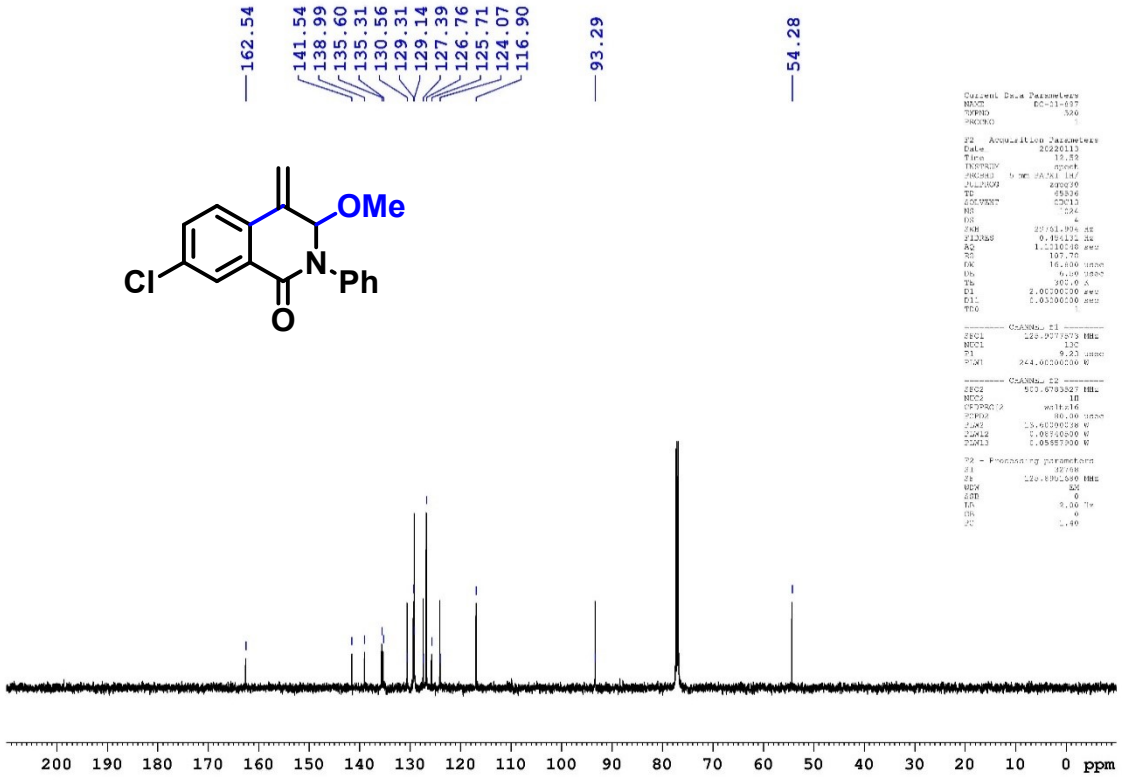

Figure S-89: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3t**

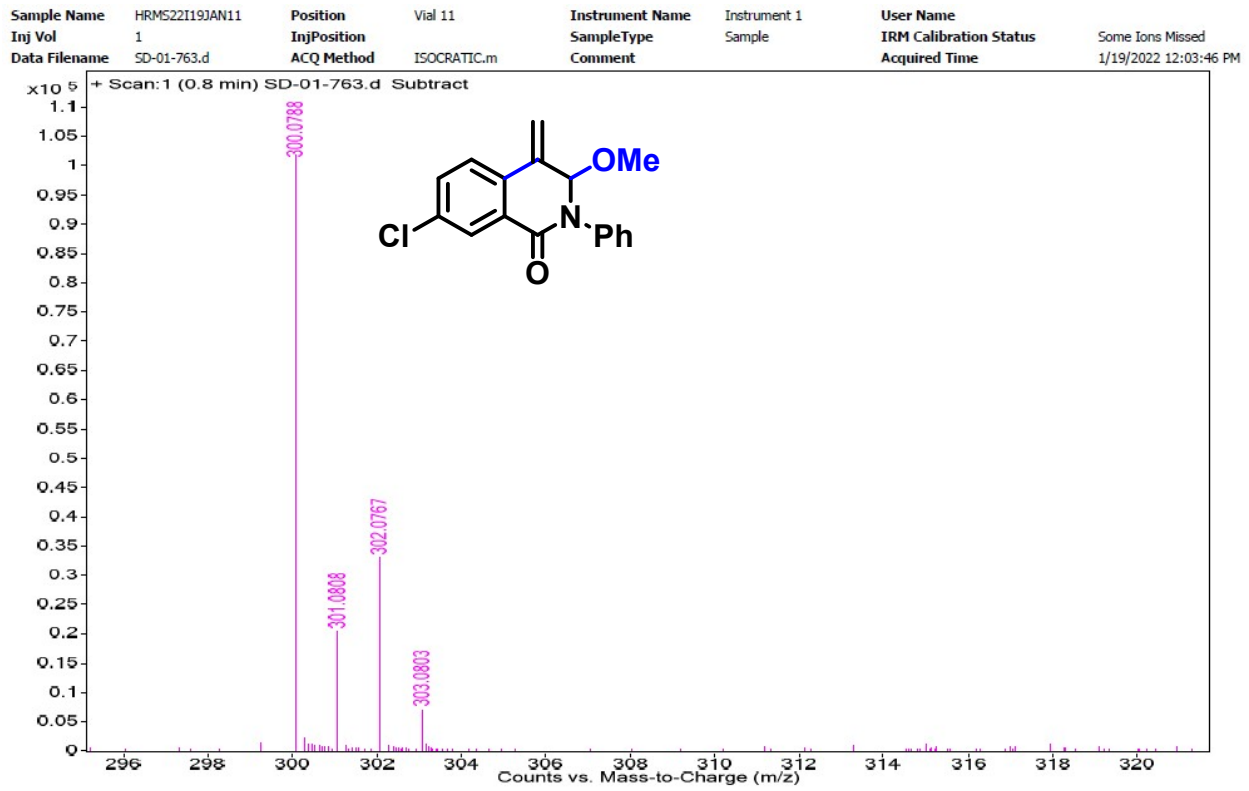

Figure S-90: HRMS spectrum of compound **3t**

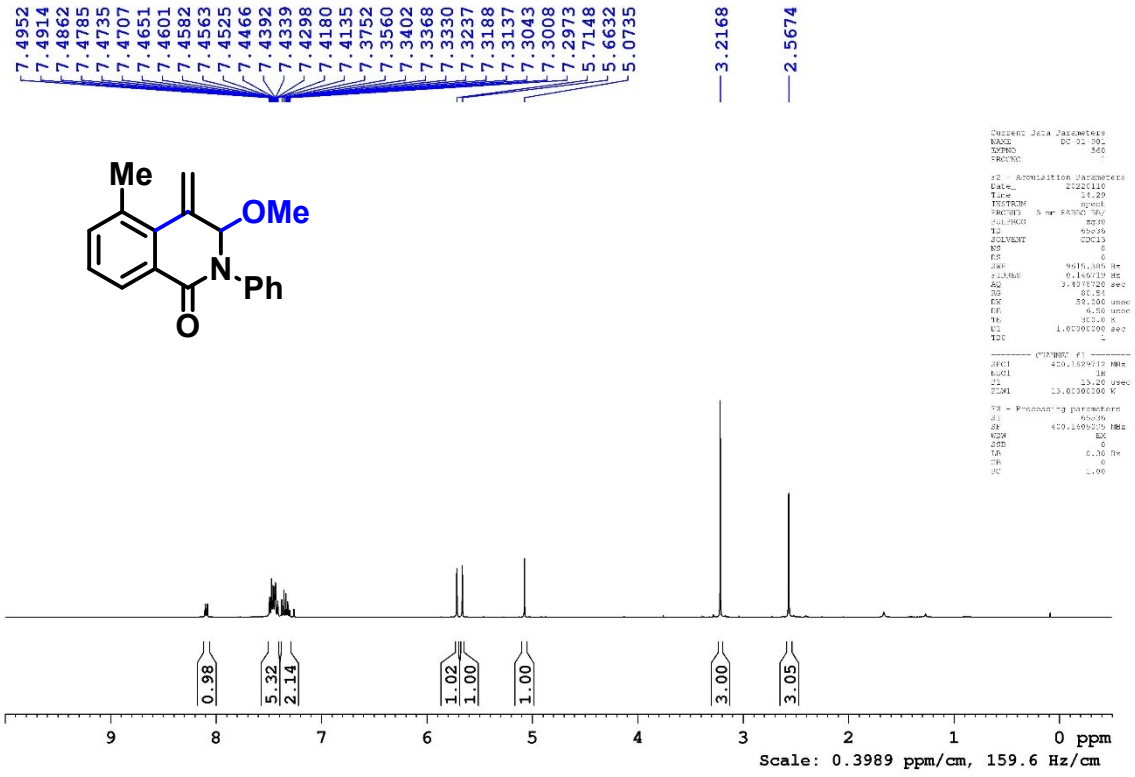

Figure S-91: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3u**

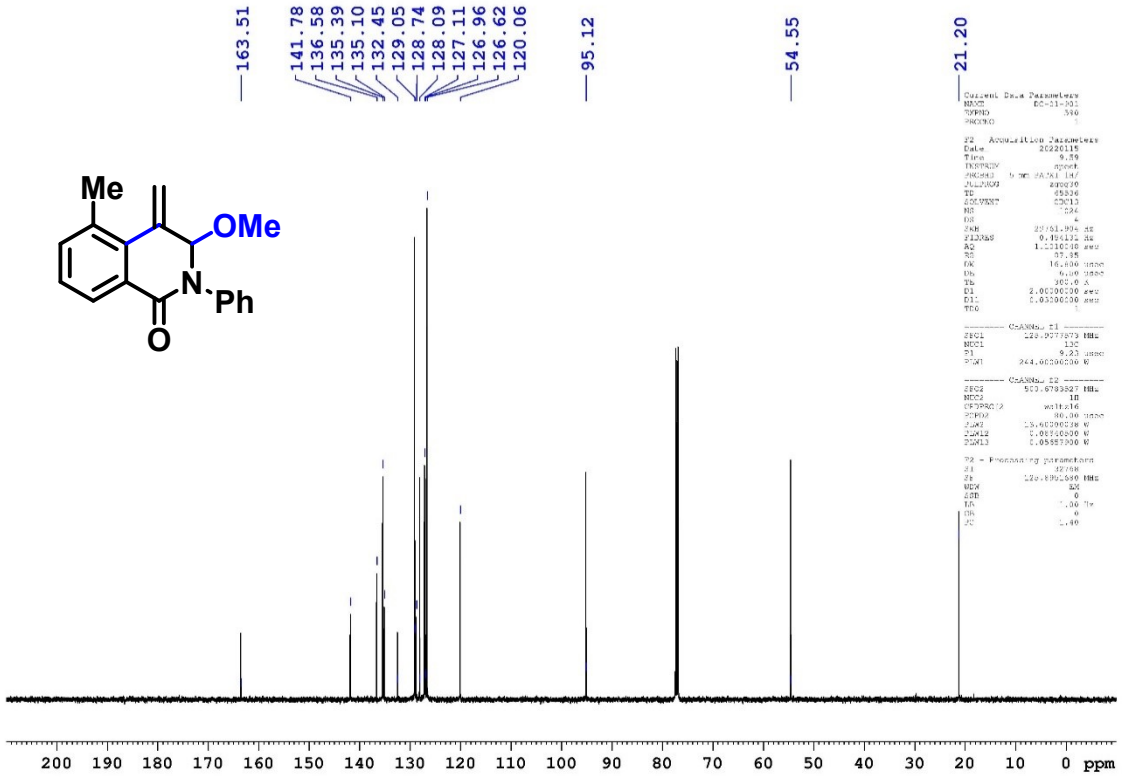

Figure S-92: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3u**

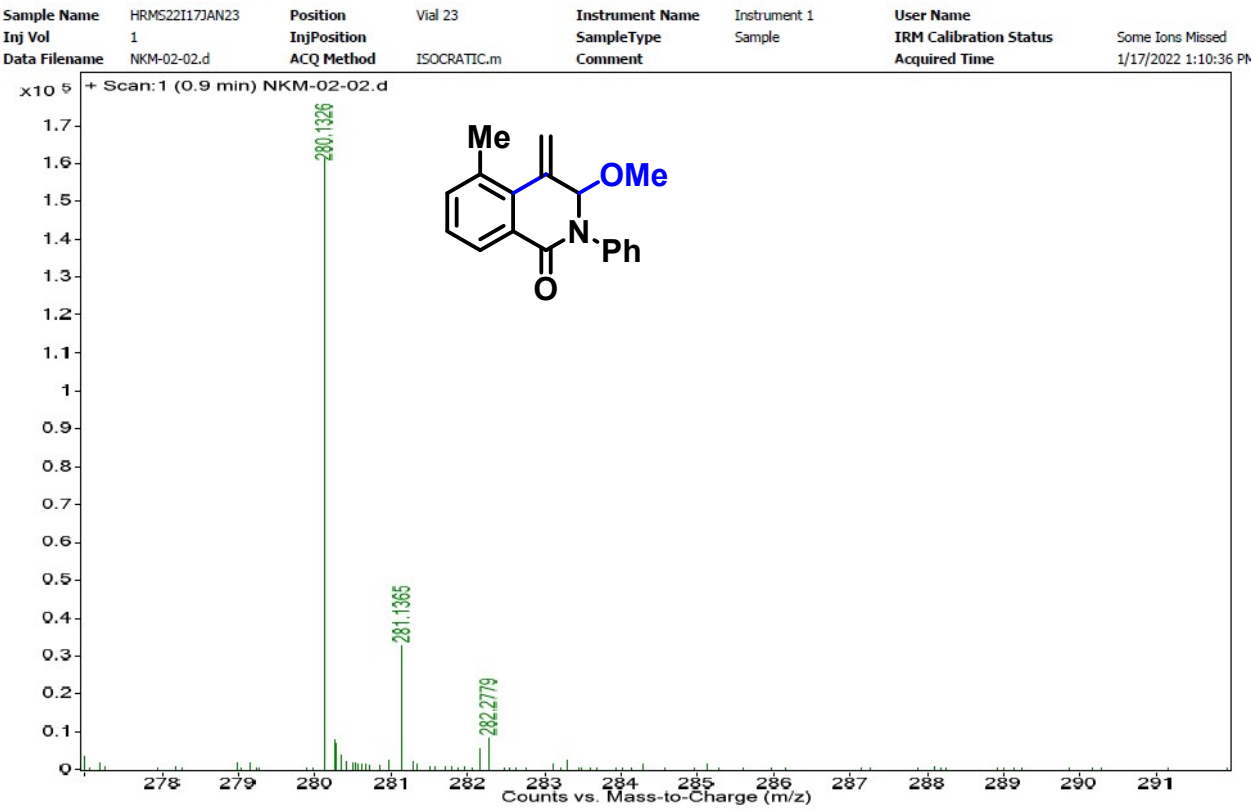

Figure S-93: HRMS spectrum of compound **3u**

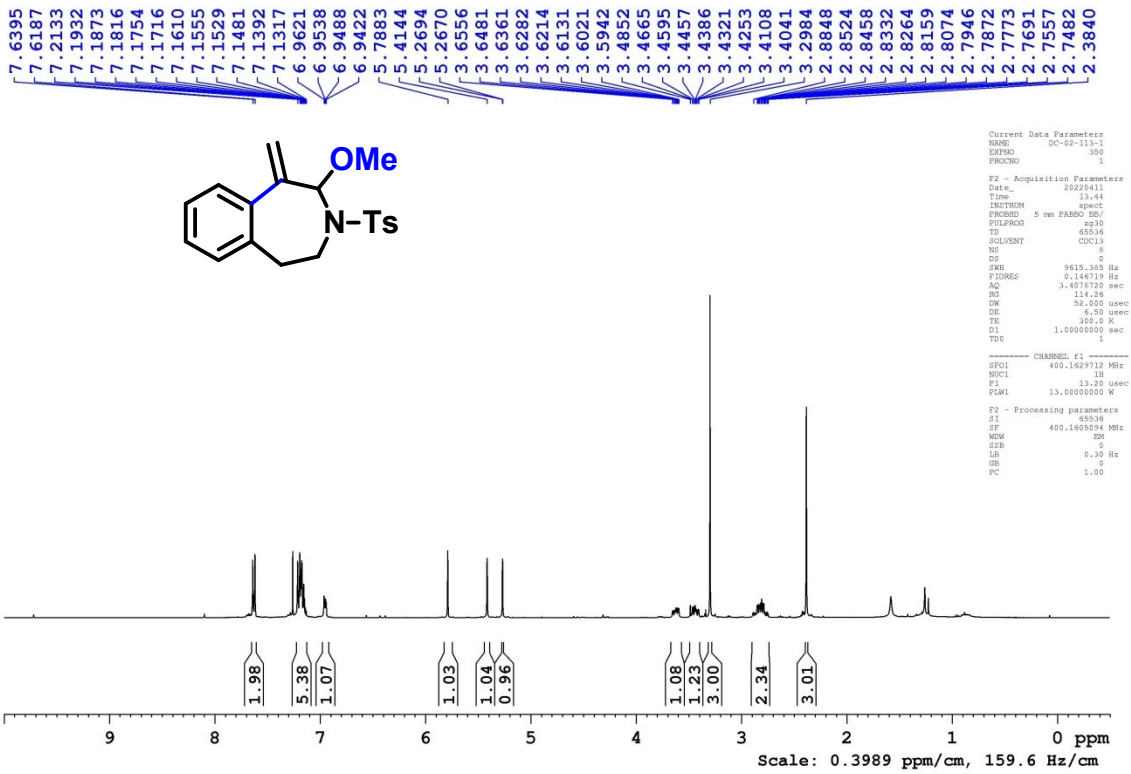

Figure S-94: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3v**

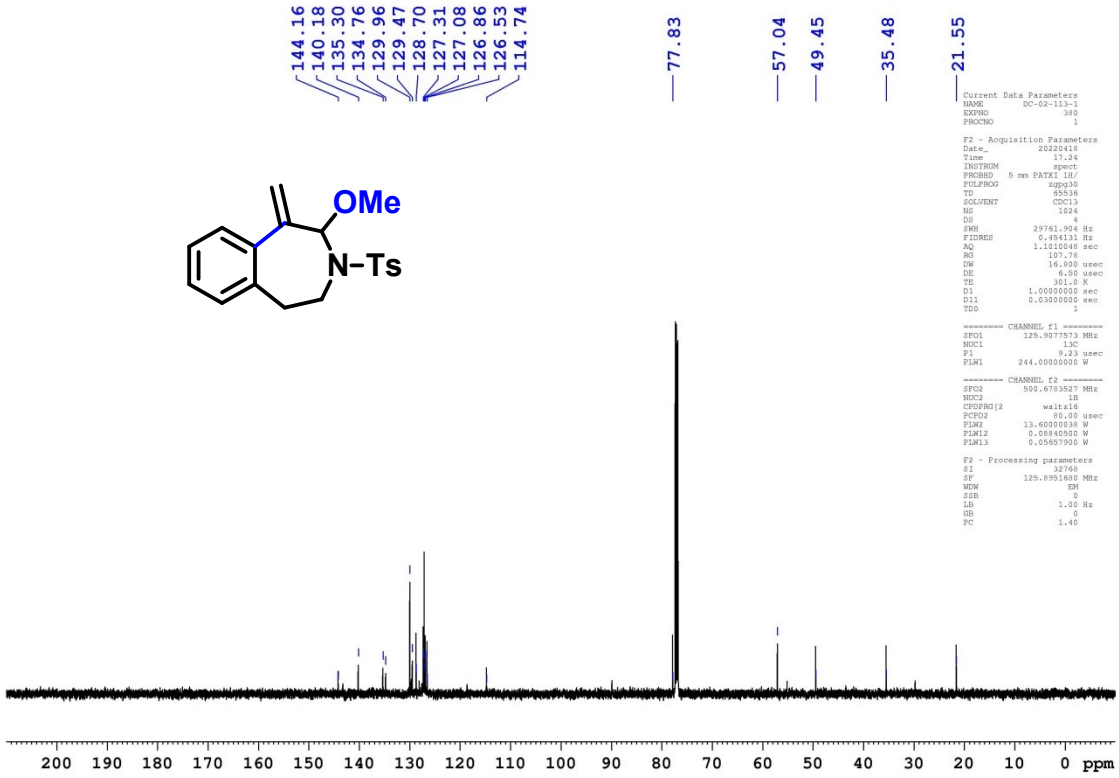

Figure S-95: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3V**

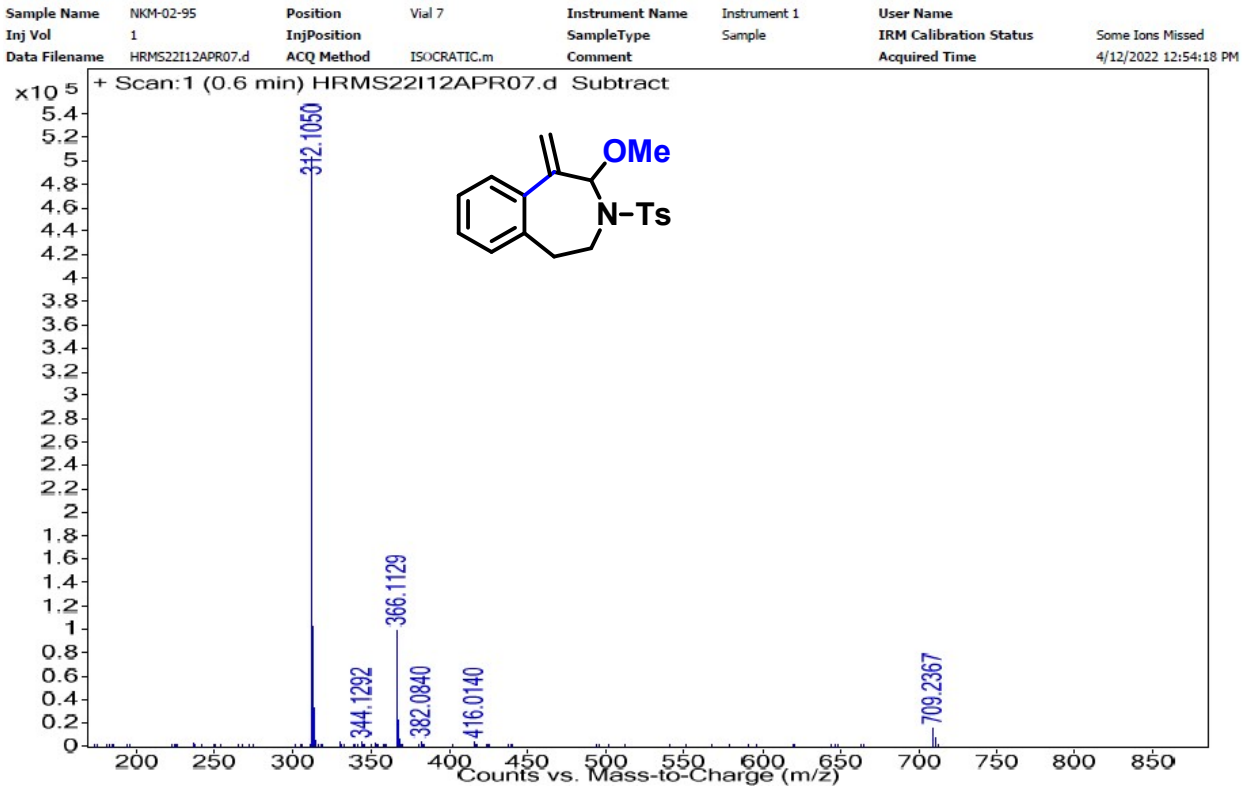

Figure S-96: HRMS spectrum of compound **3v**

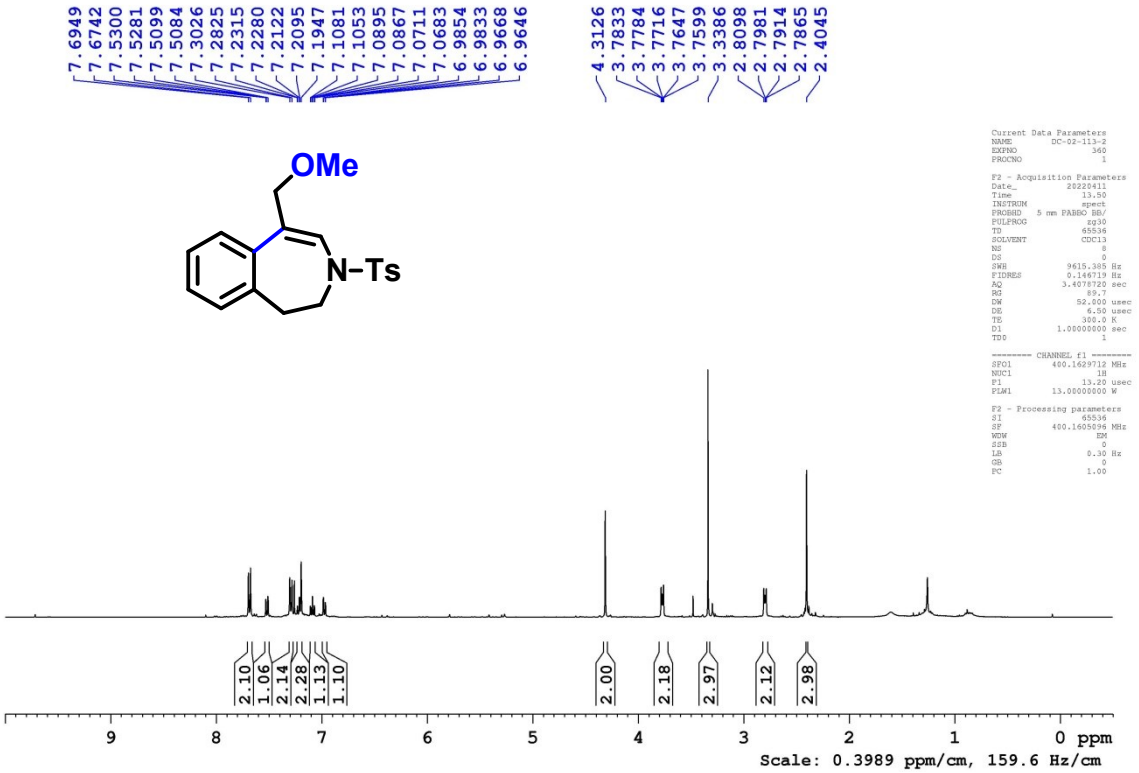

Figure S-97: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4v**

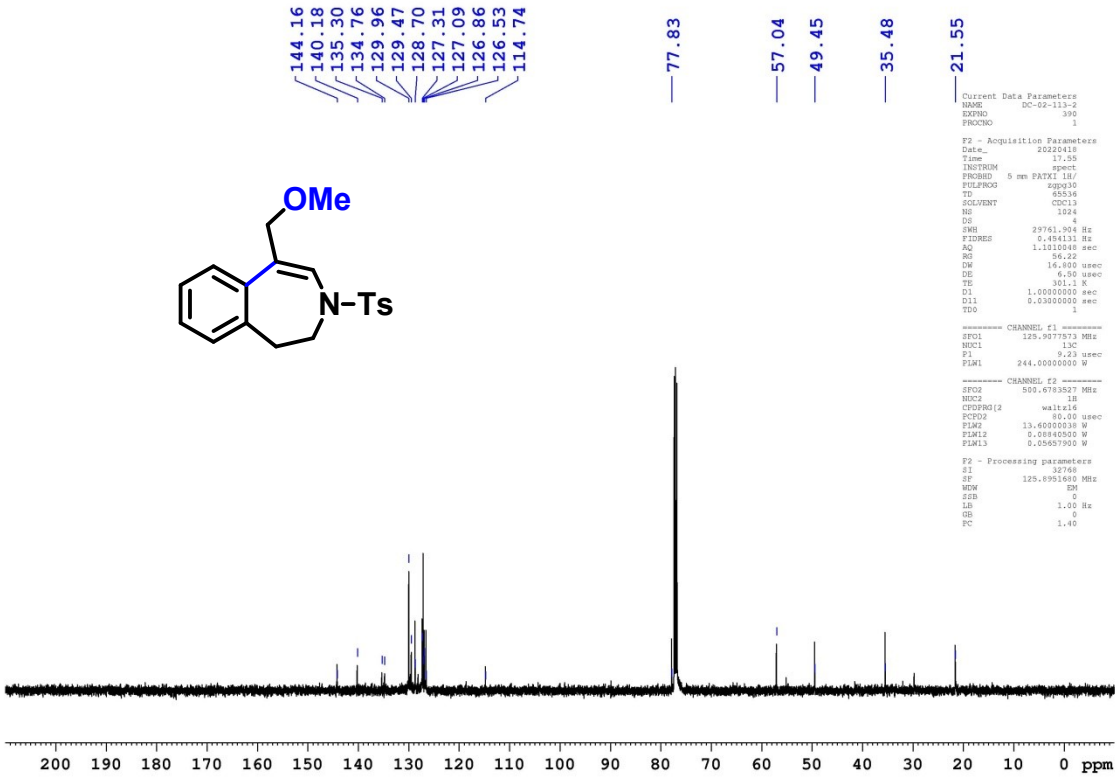

Figure S-98: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4v**

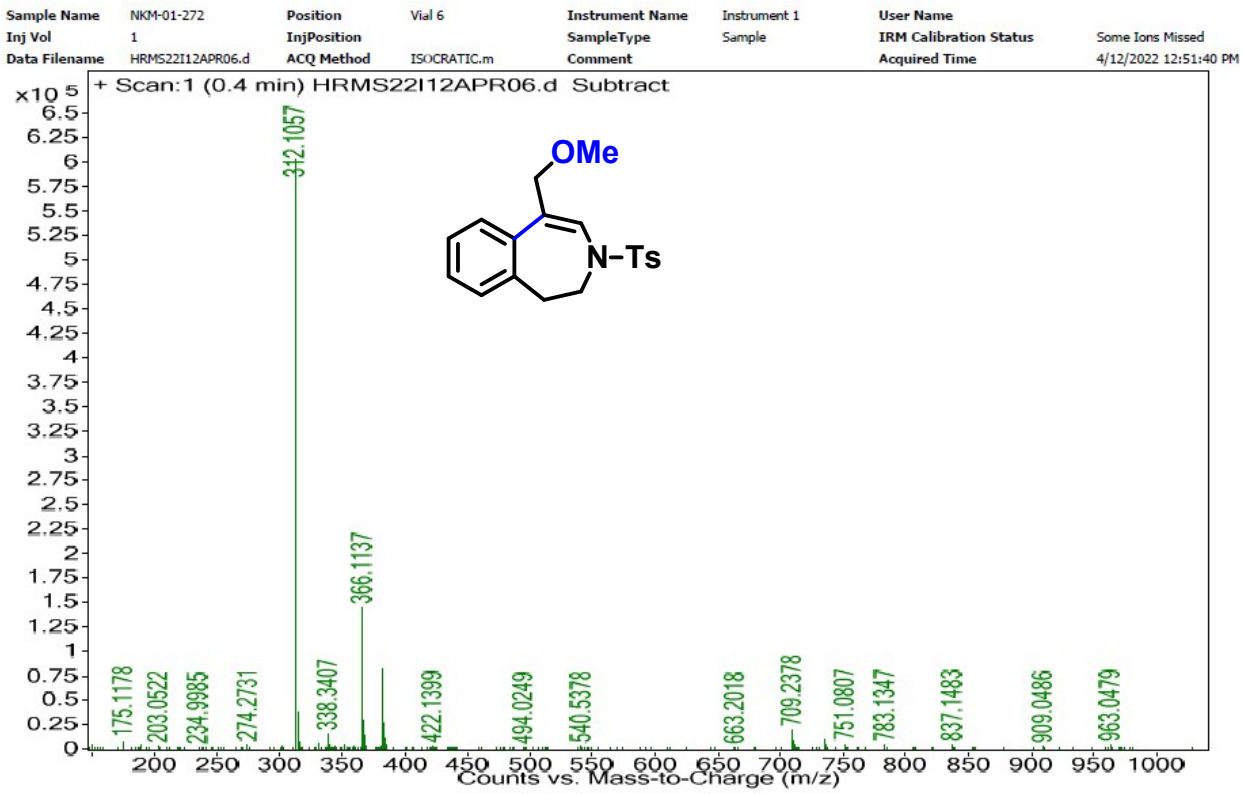

Figure S-99: HRMS spectrum of compound **4v**

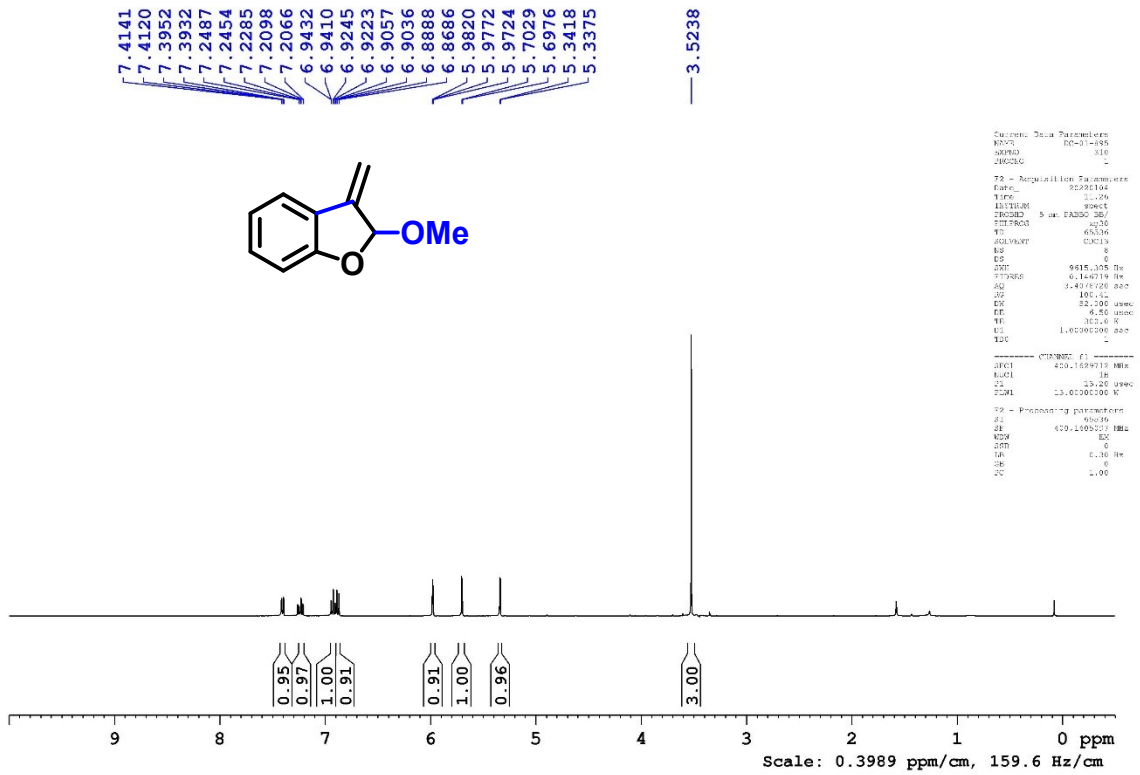

Figure S-100: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3w**

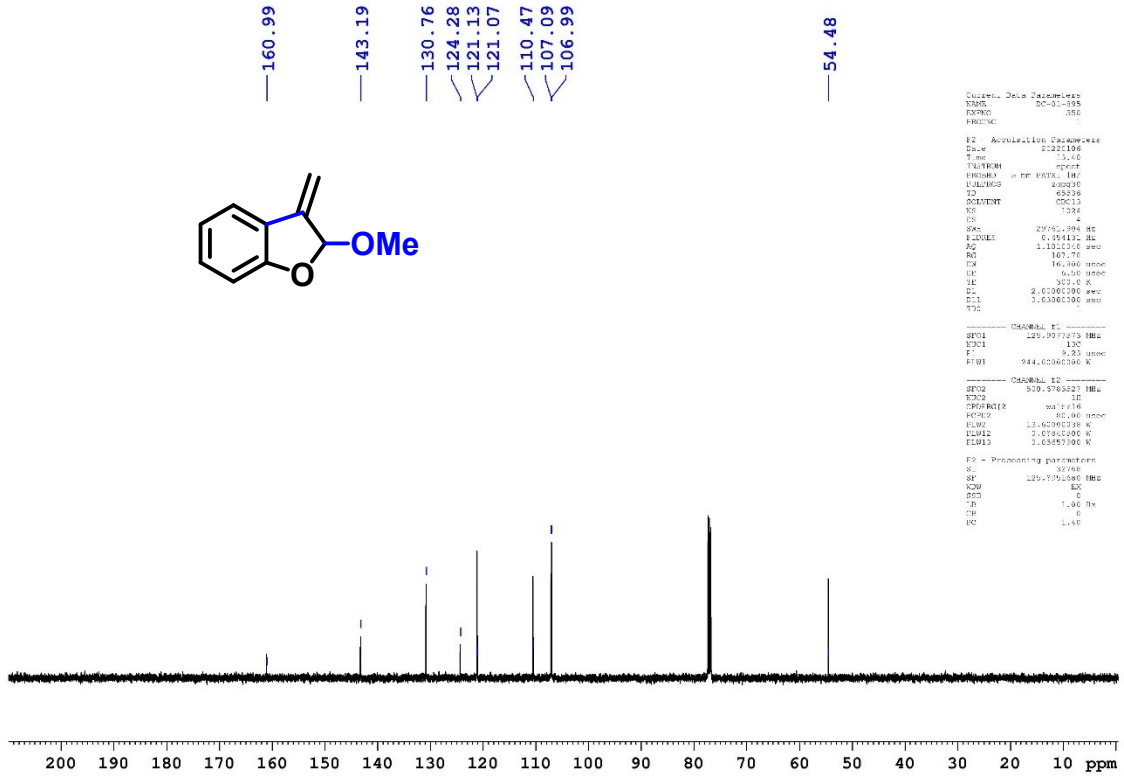

Figure S-101: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3w**

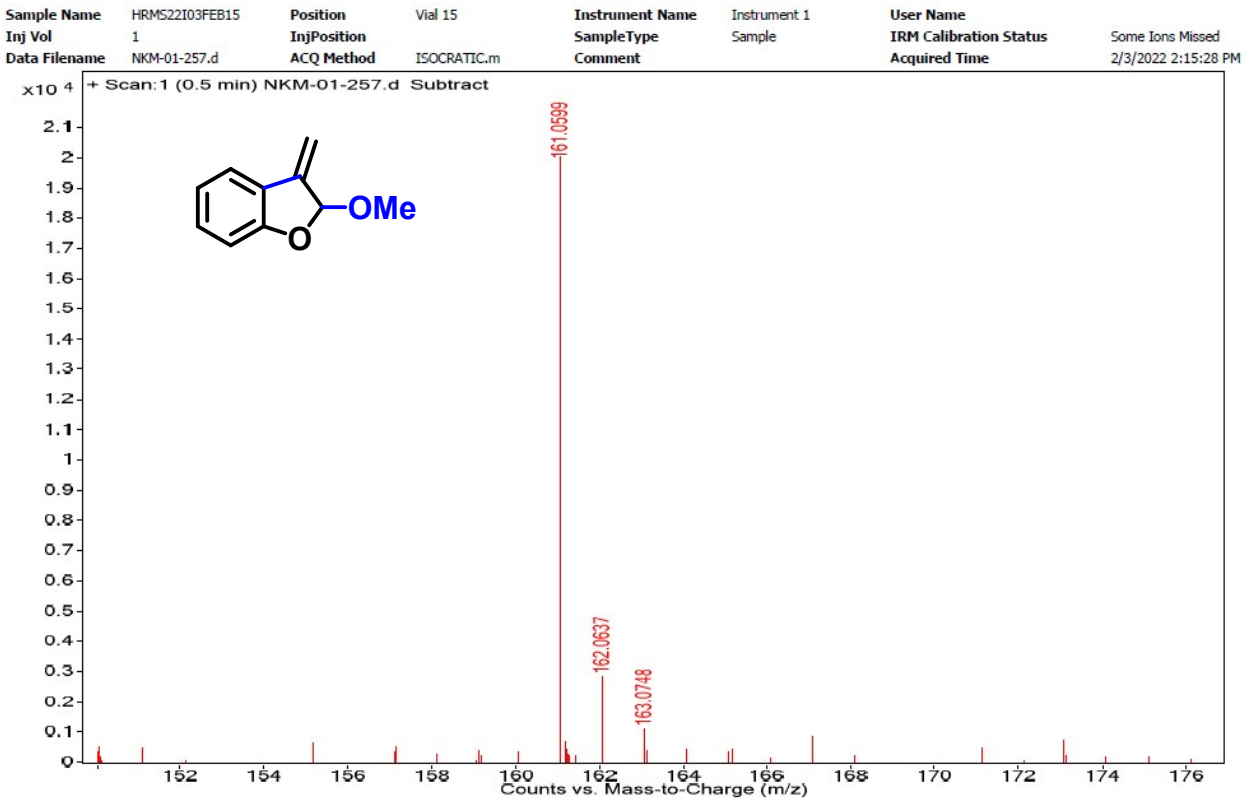

Figure S-102: HRMS spectrum of compound **3w**

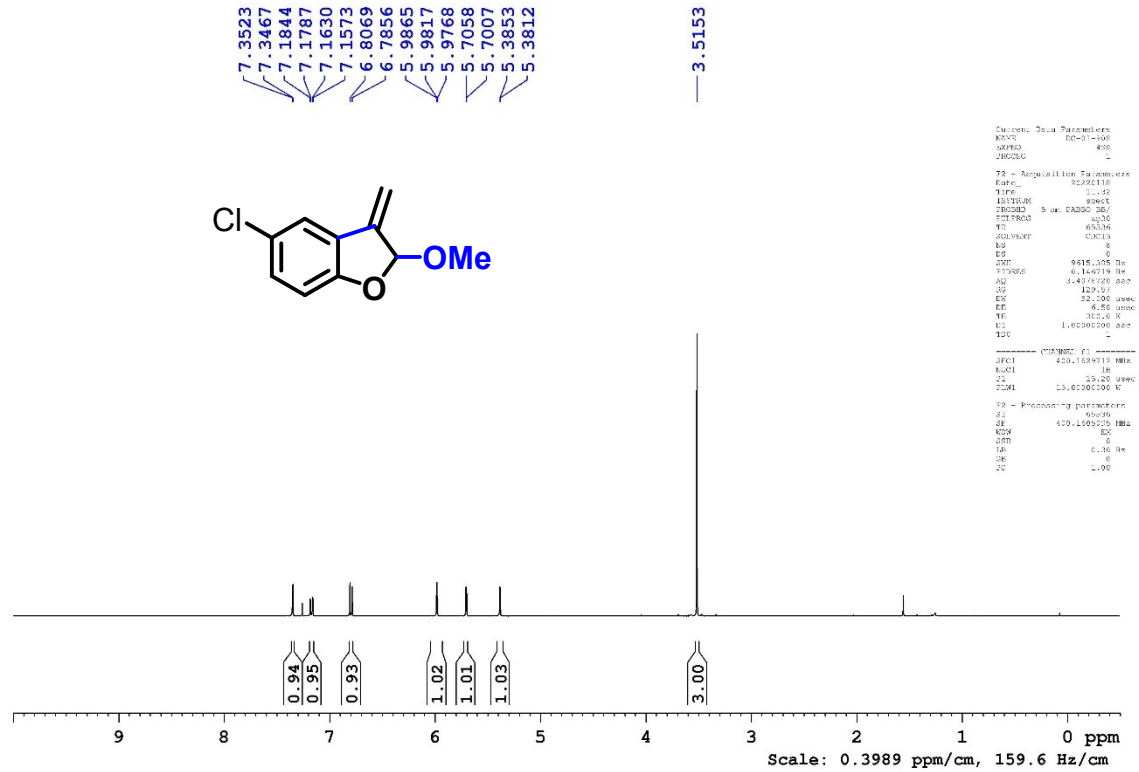

Figure S-103: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3x**

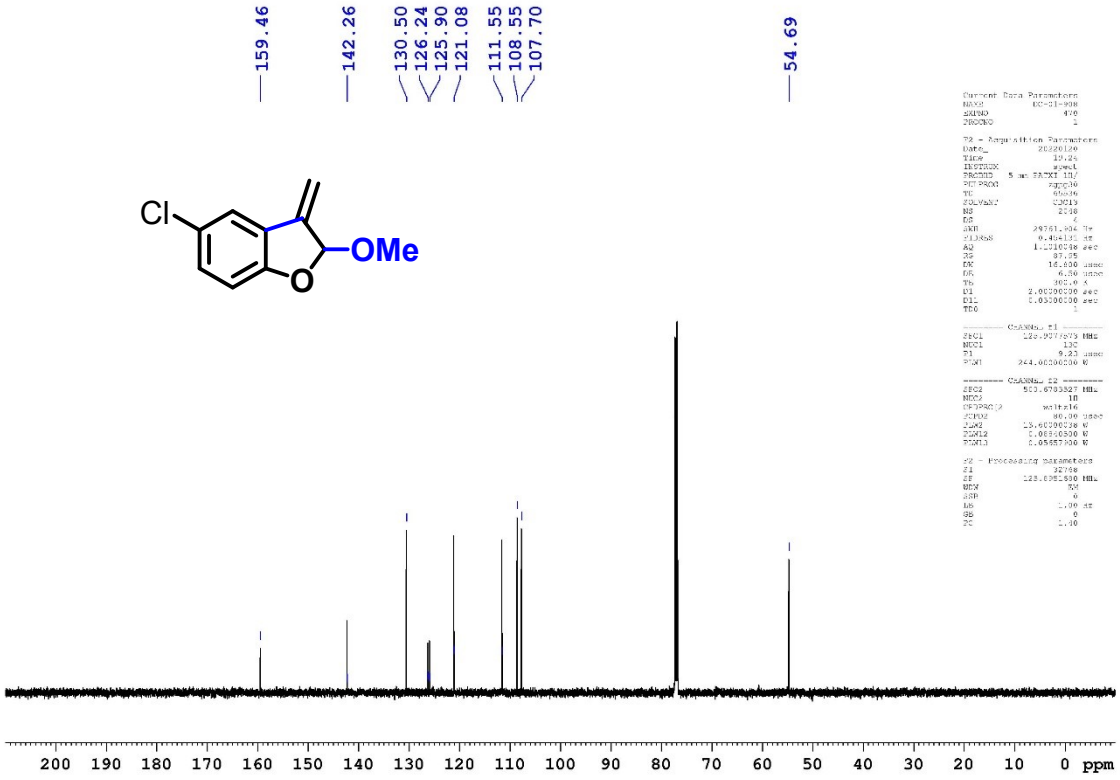

Figure S-104: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3x**

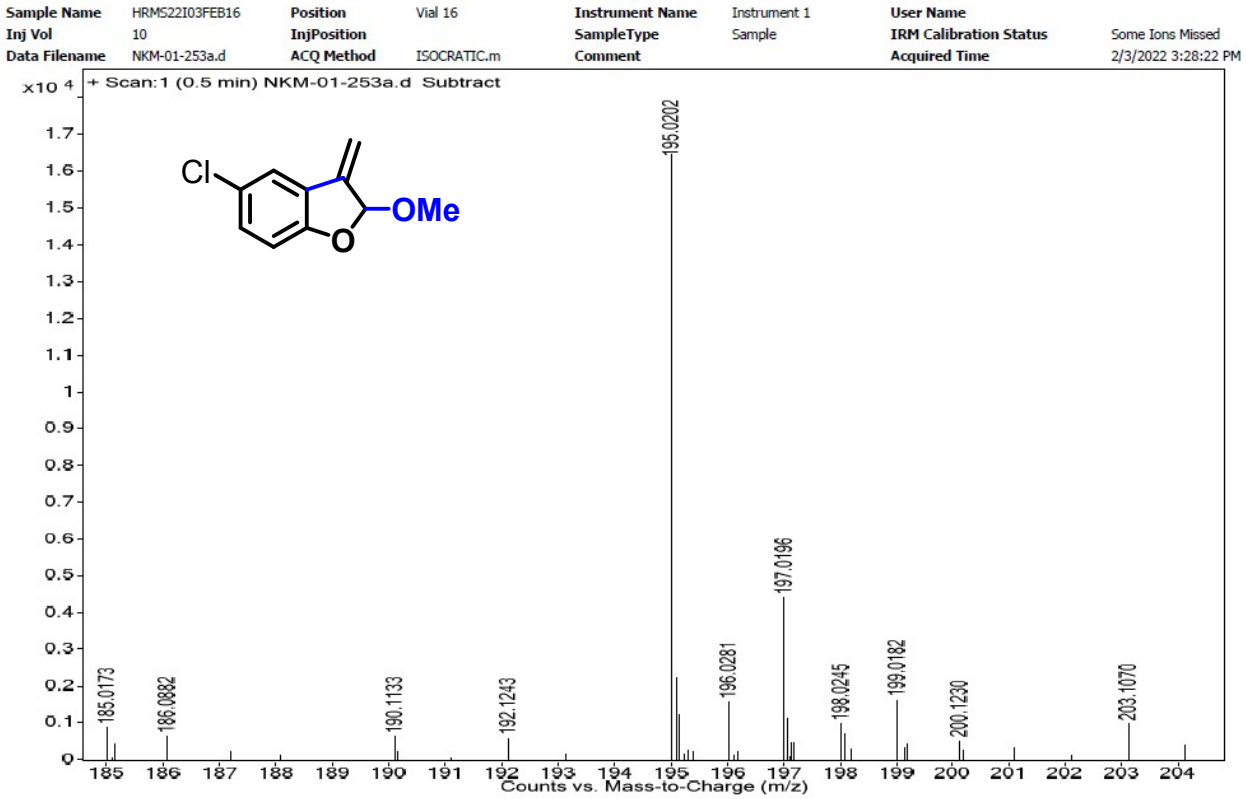

Figure S-105: HRMS spectrum of compound **3x**

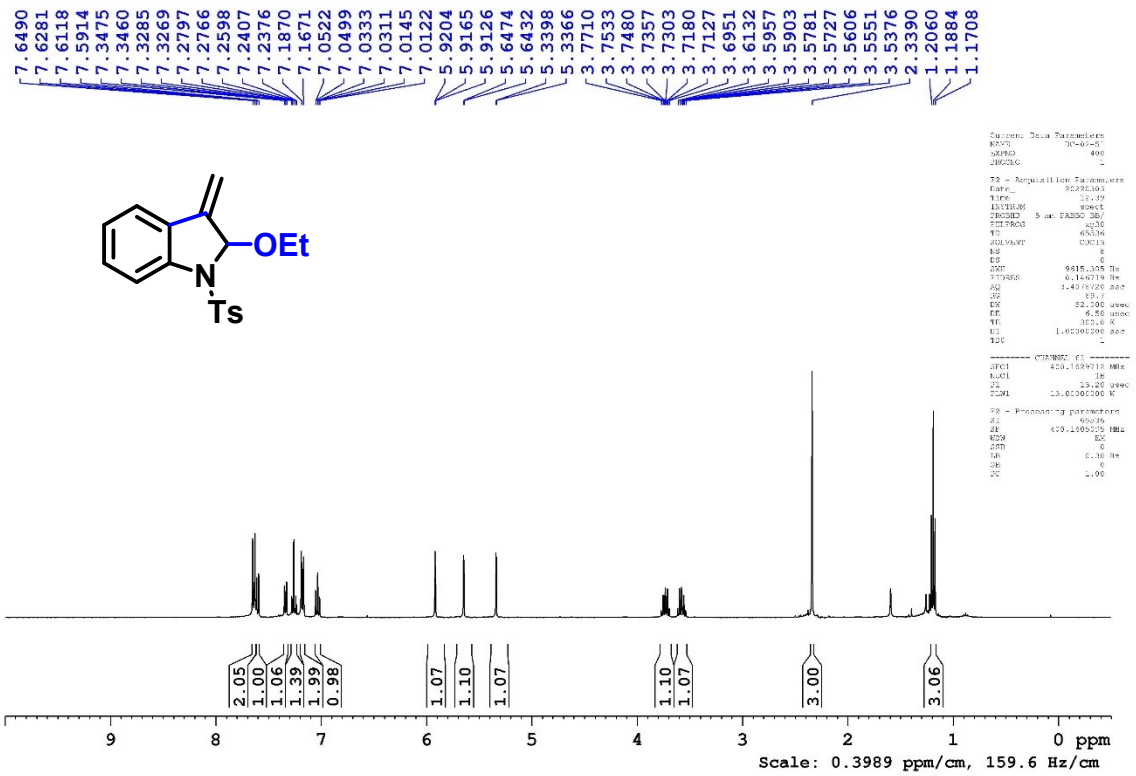

Figure S-106: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aa**

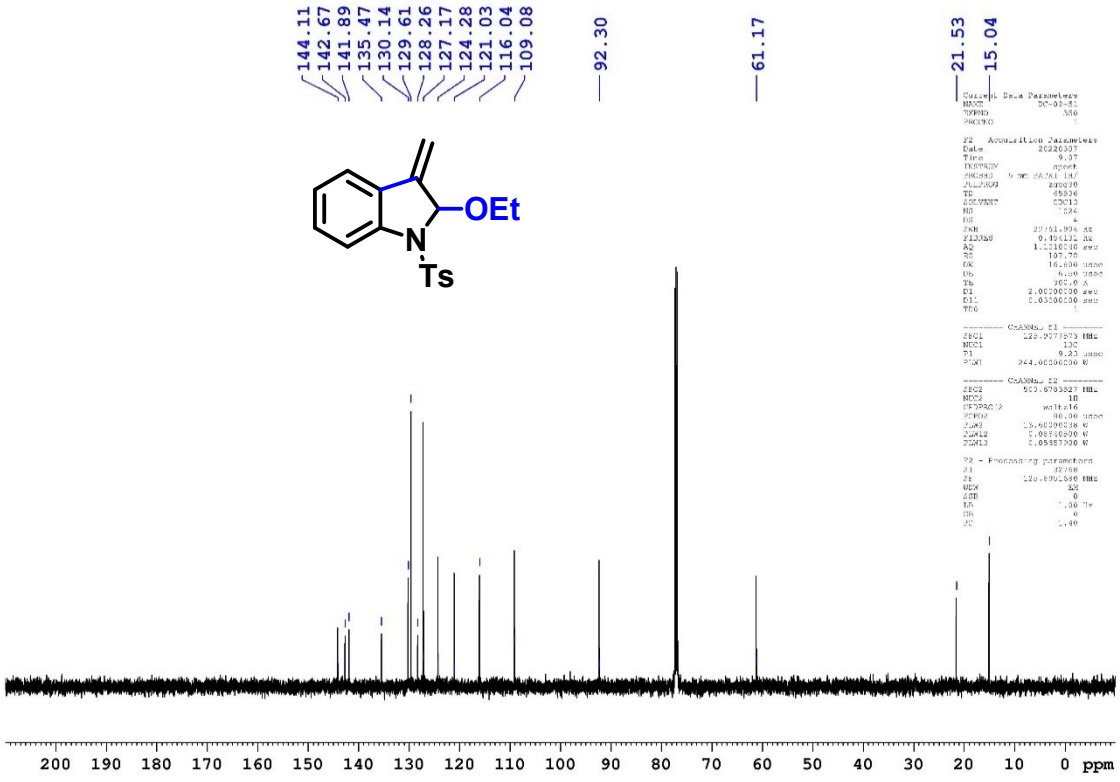

Figure S-107: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3aa**

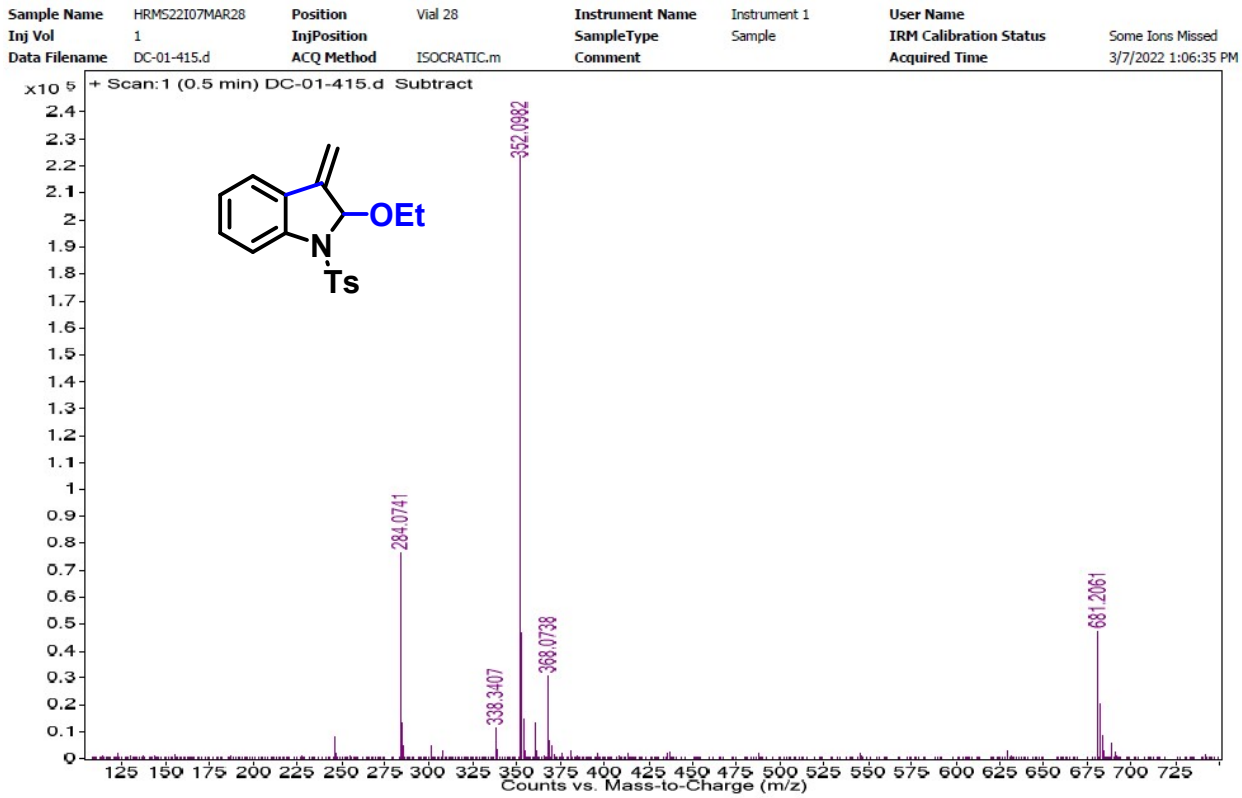

Figure S-108: HRMS spectrum of comound **3aa**

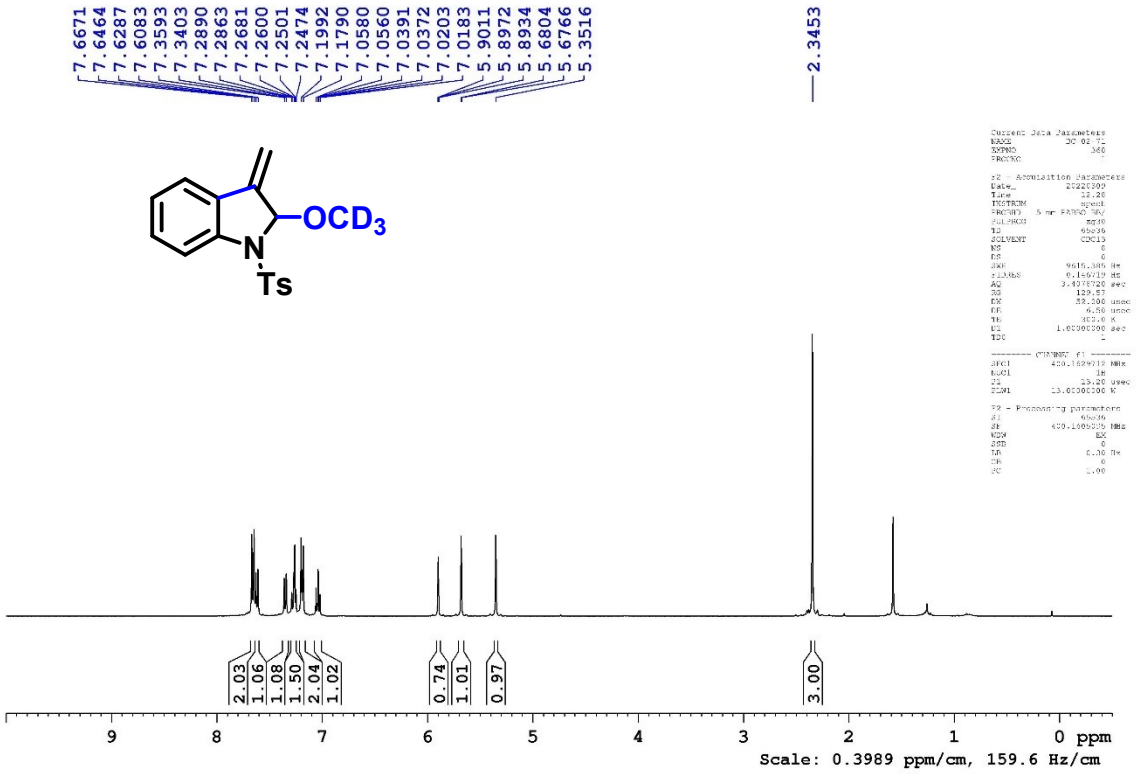

Figure S-109: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a-D**

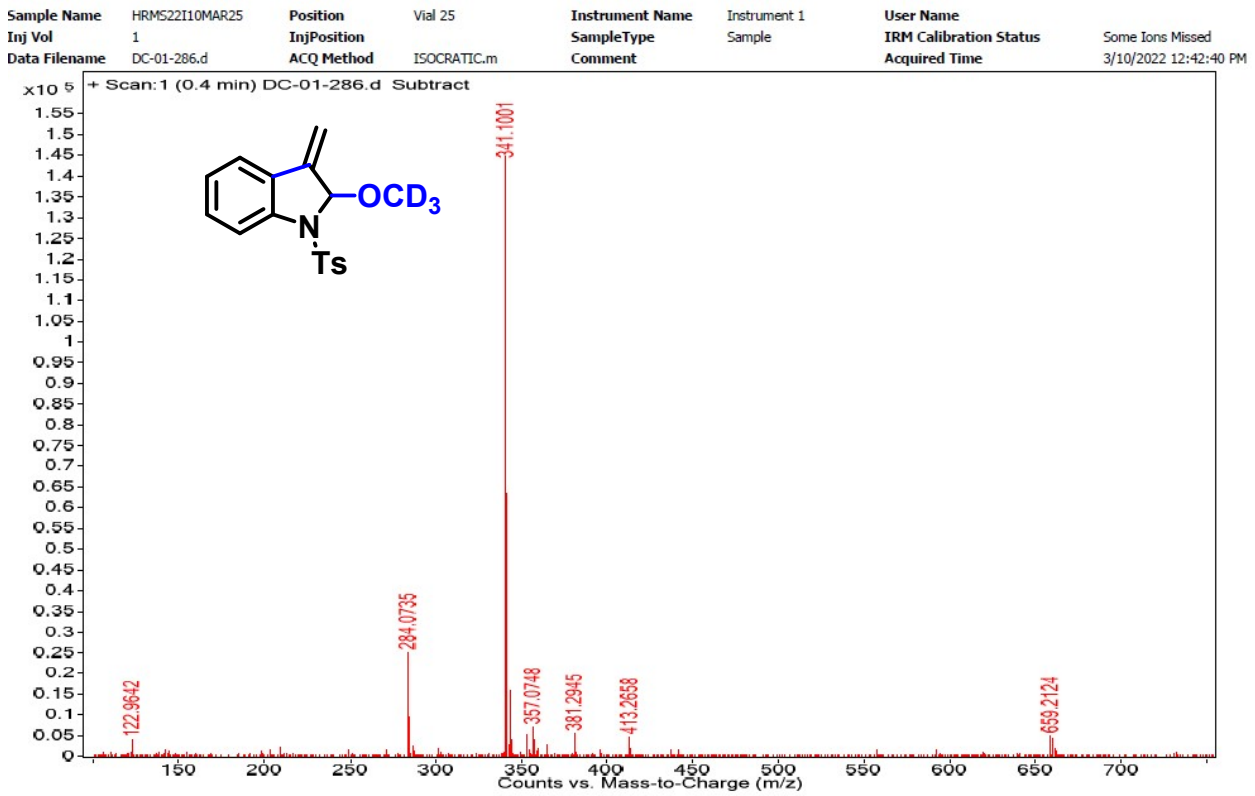

Figure S-110: HRMS spectrum of compound **3a-D**

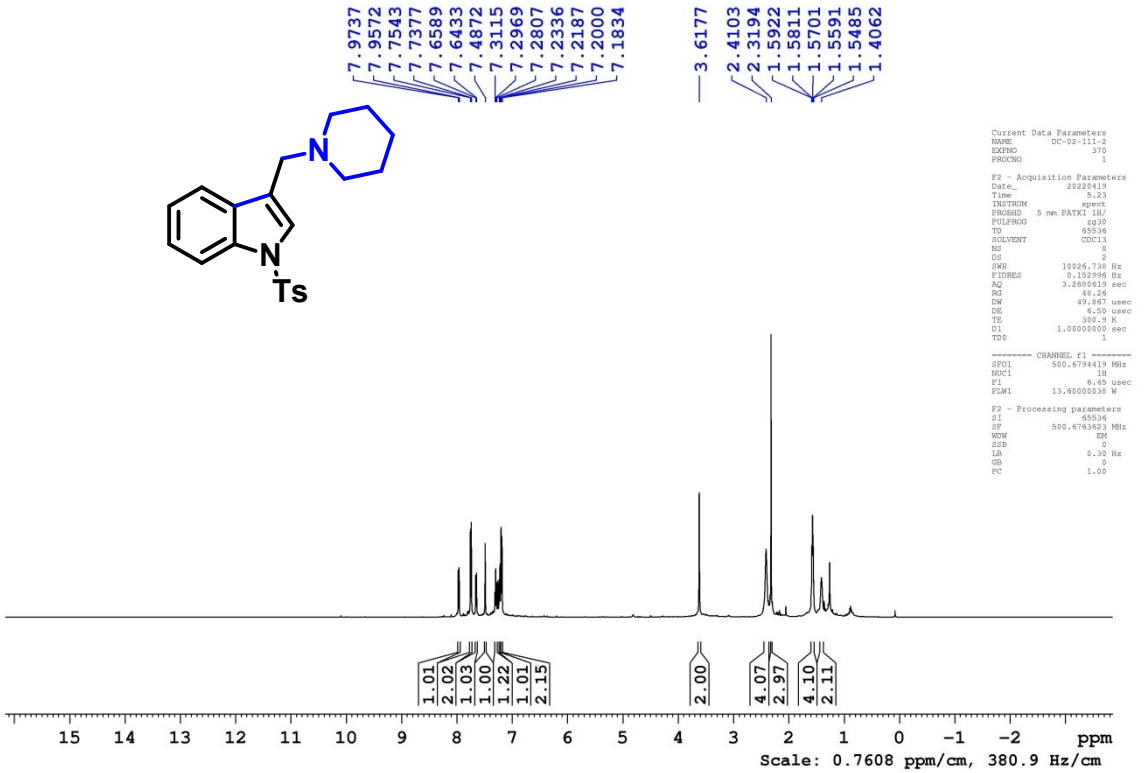

Figure S-111: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4ad**

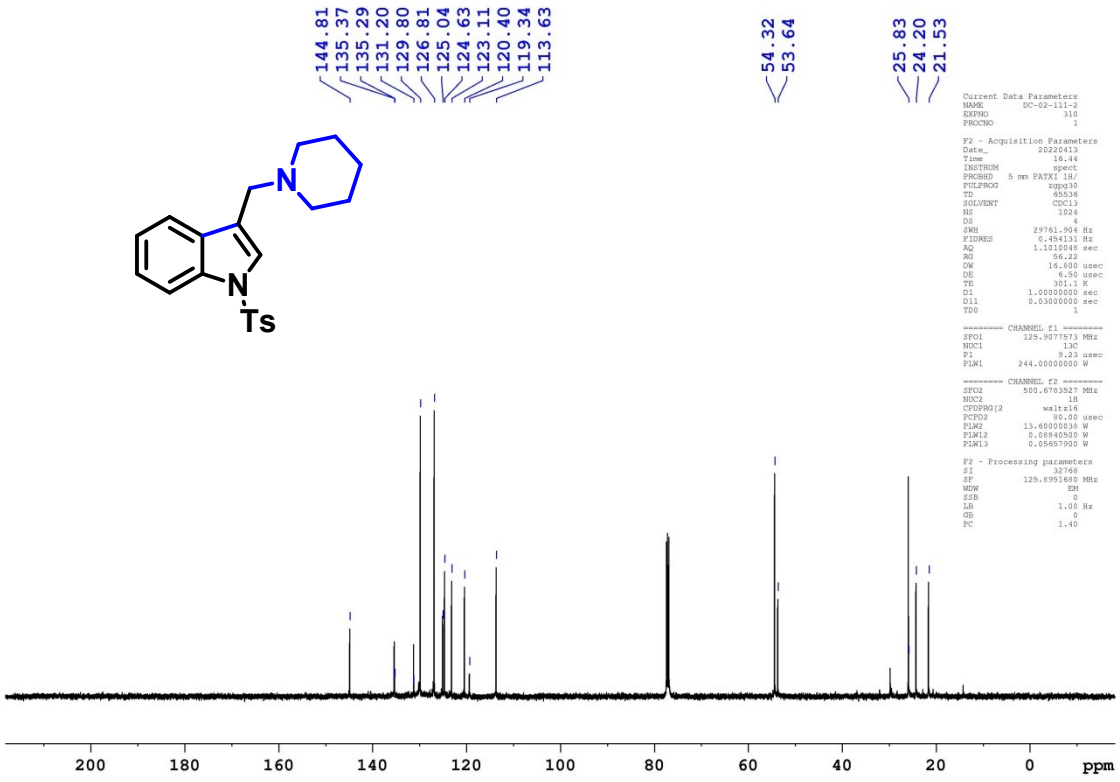

Figure S-112: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4ad**

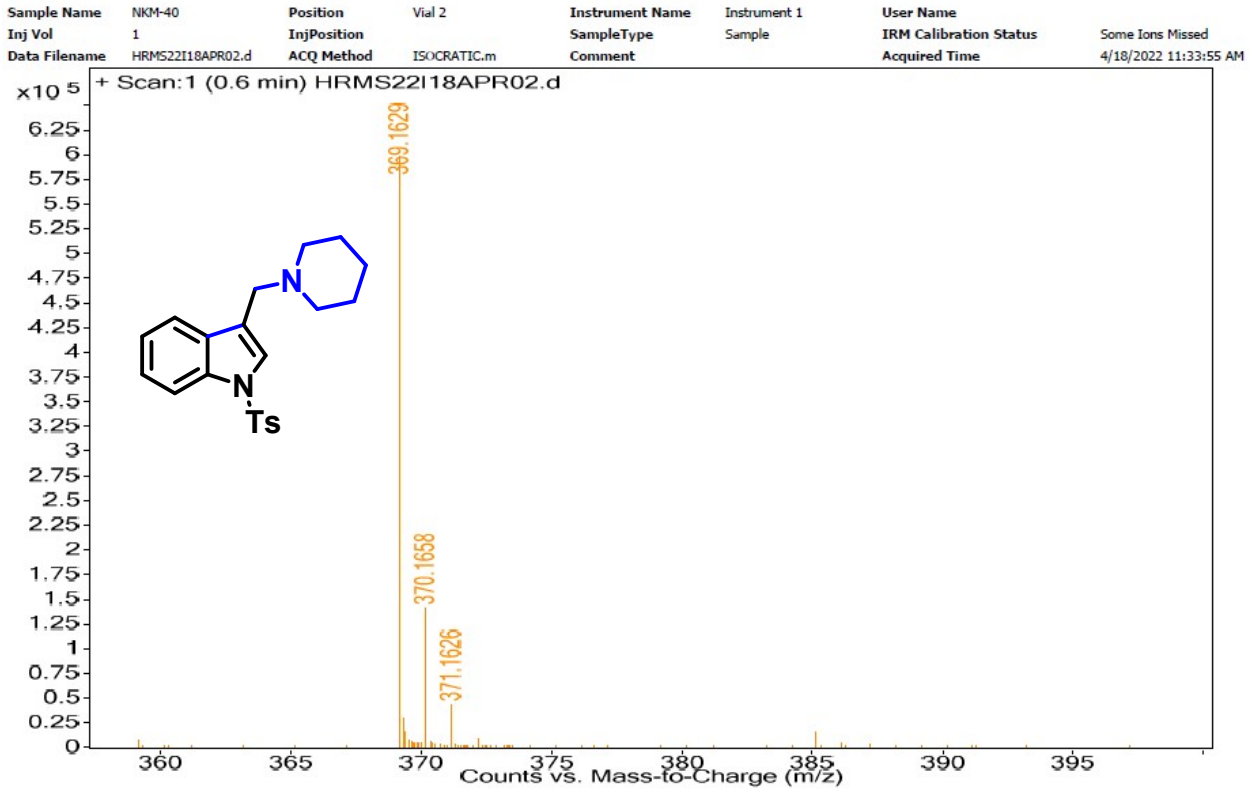

Figure S-113: HRMS spectrum of compound **4ad**

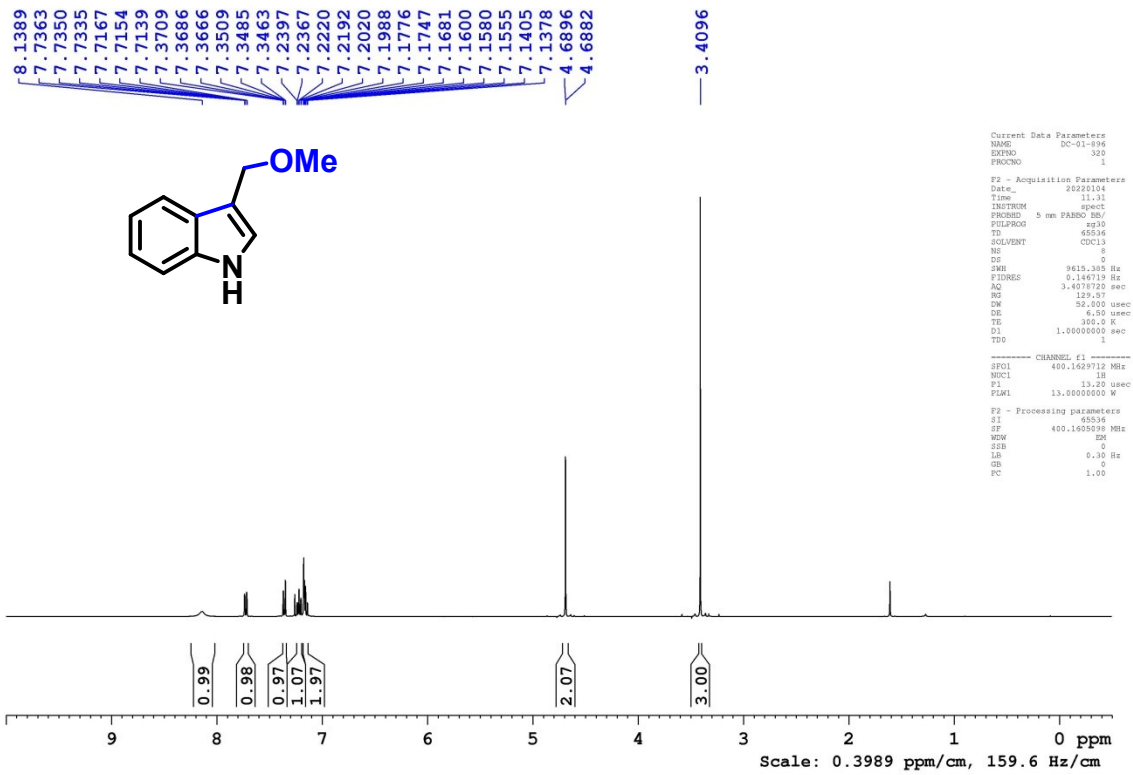

Figure S-114: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4a**

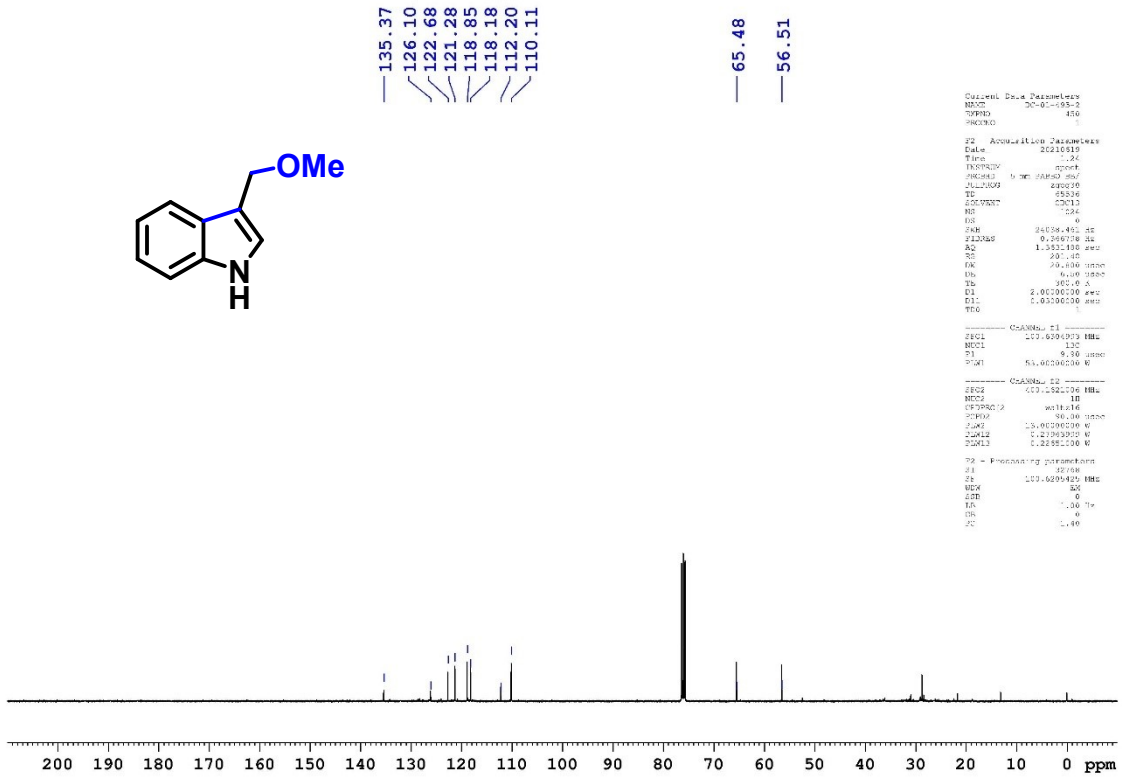

Figure S-115: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4a**

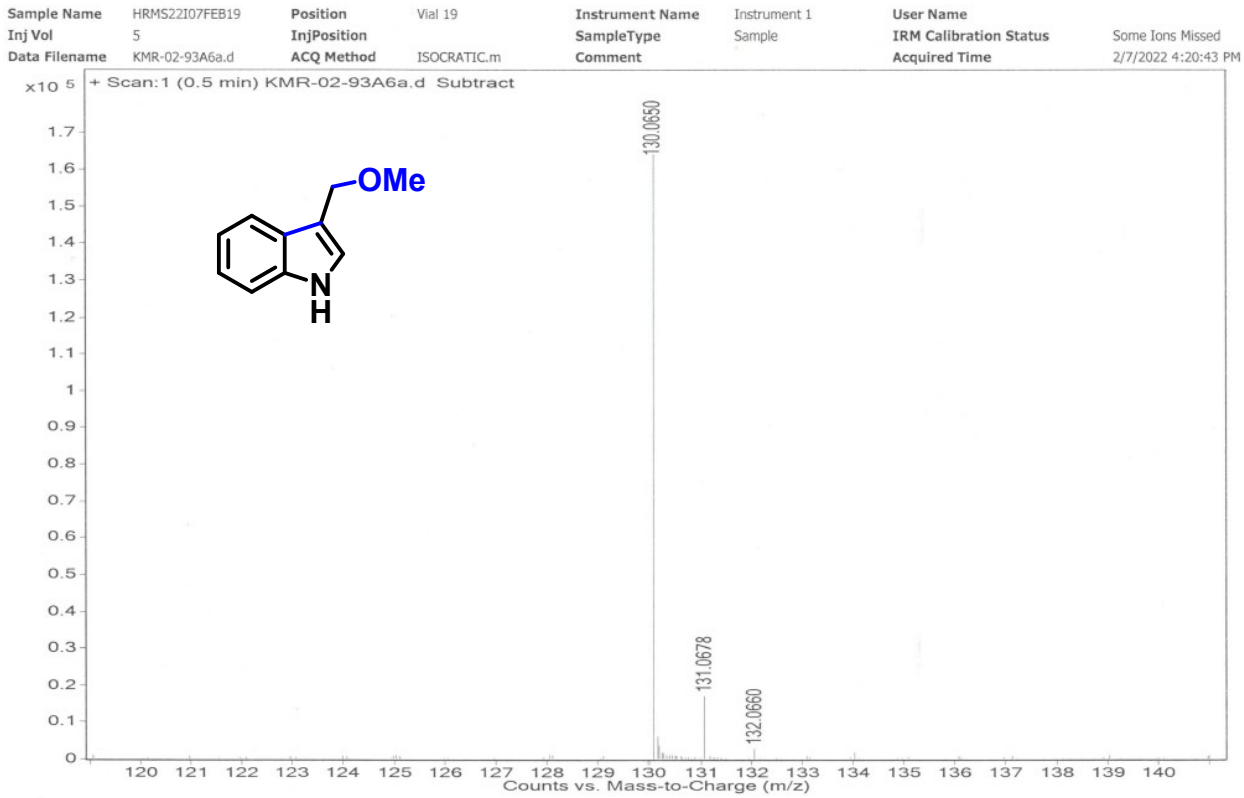

Figure S-116: HRMS spectrum of compound **4a**

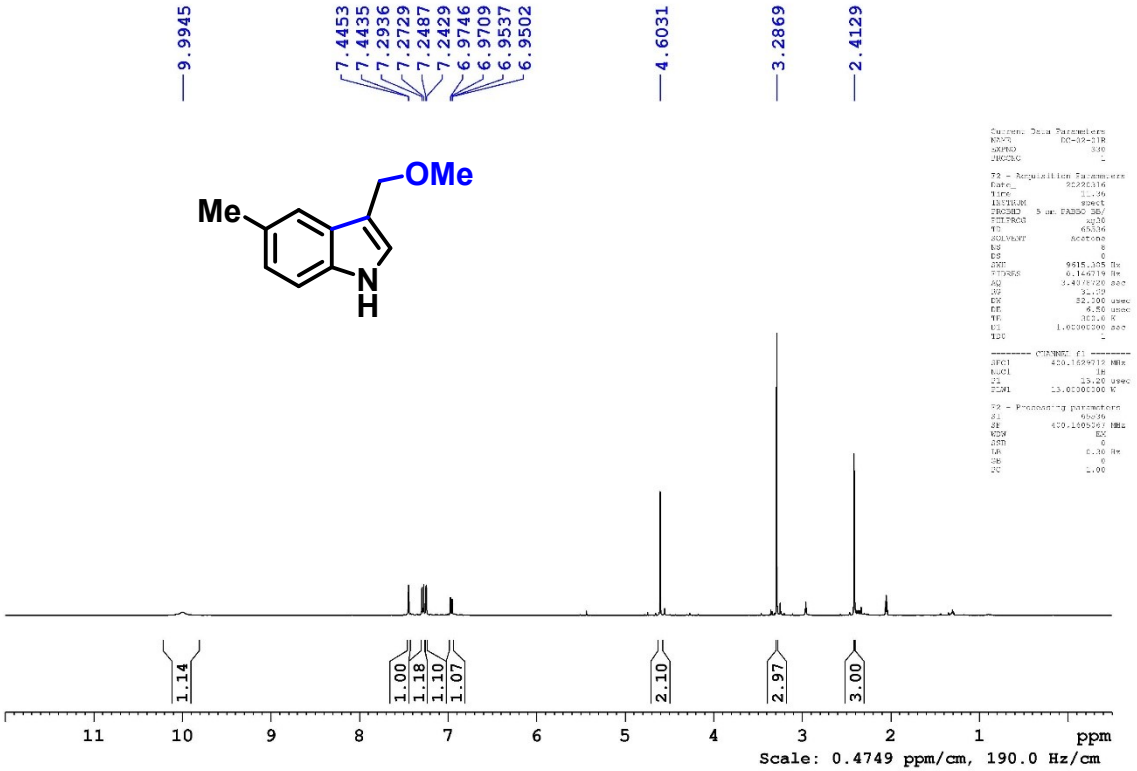

Figure S-117: ^{1}H NMR (400 MHz, D_6-acetone) spectrum of compound **4b**

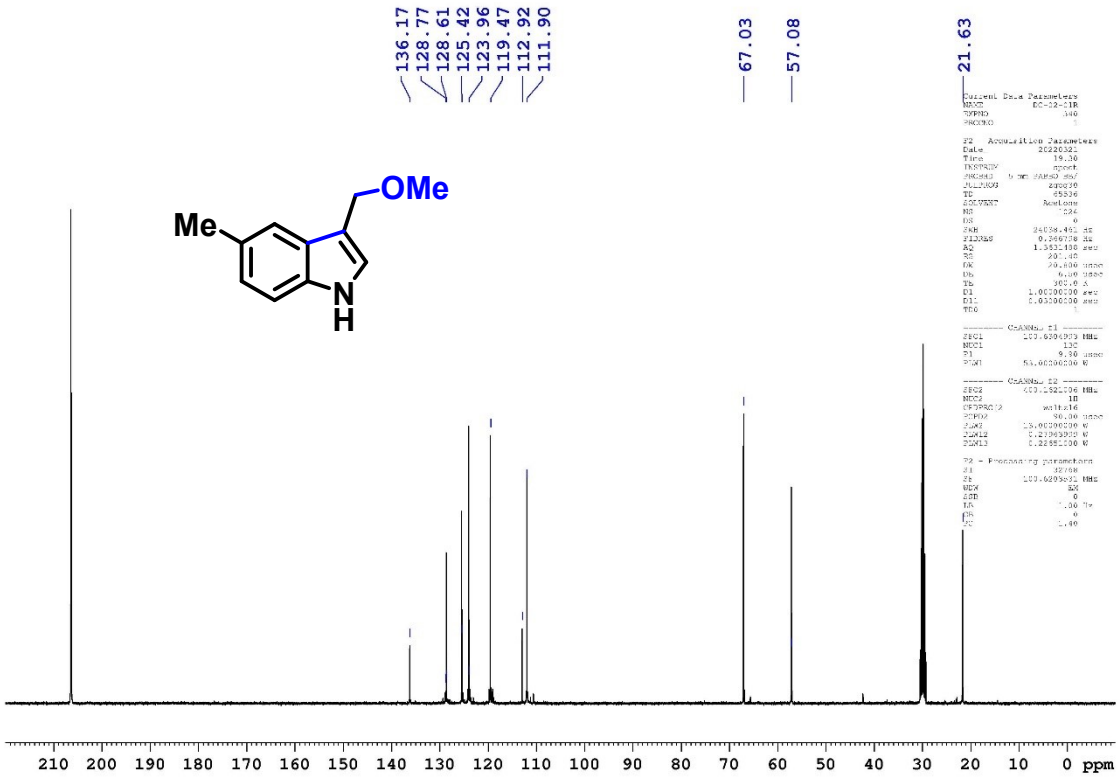

Figure S-118: ^{13}C NMR (100 MHz, D_6-acetone) spectrum of compound **4b**

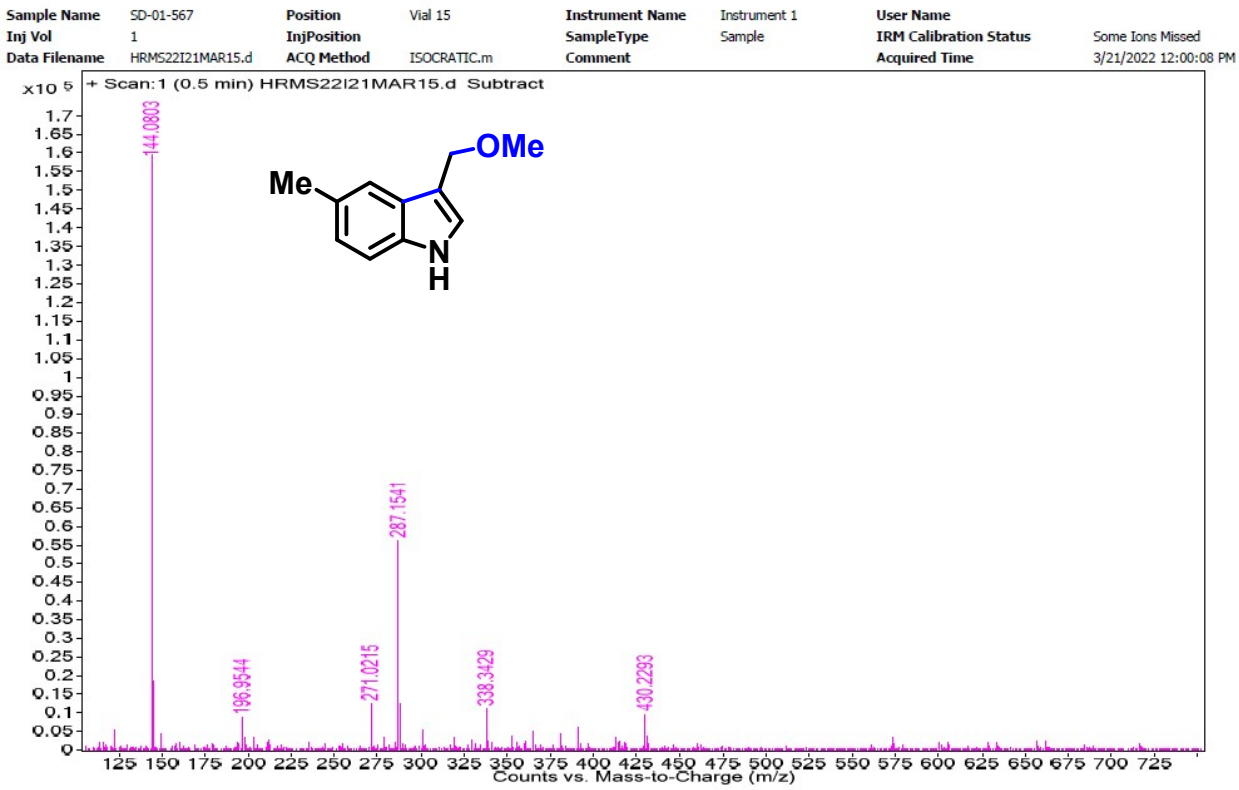

Figure S-119: HRMS spectrum of compound **4b**

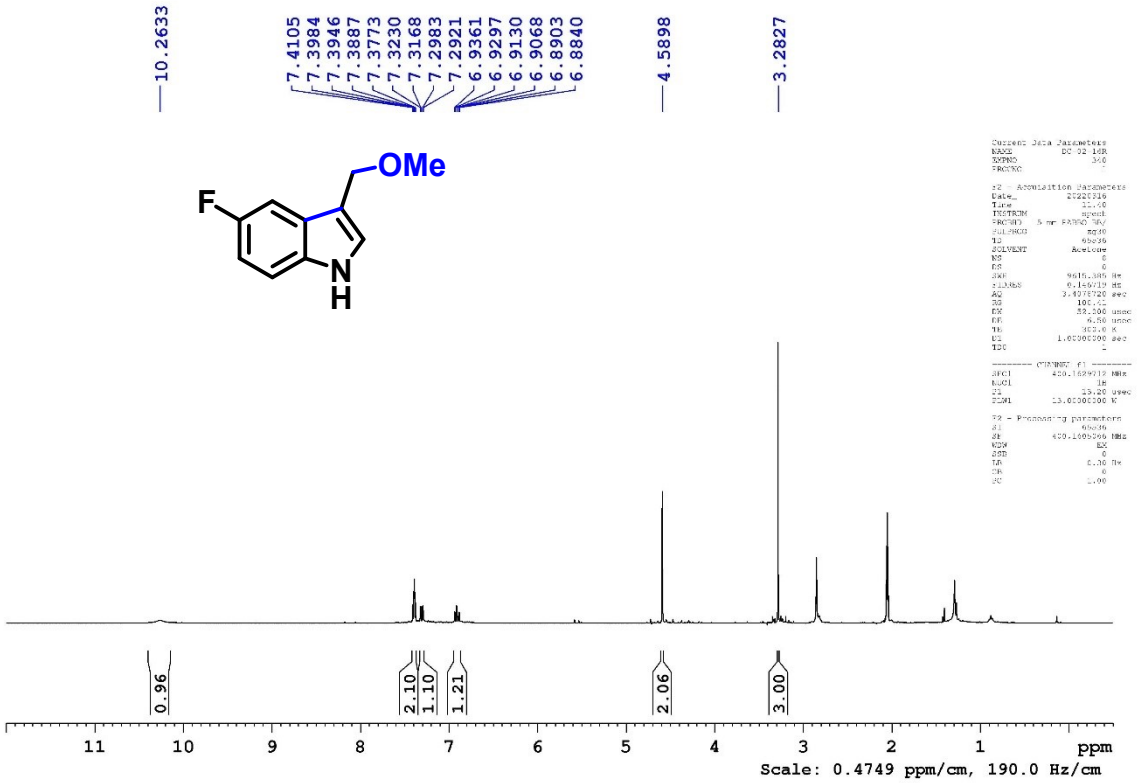

Figure S-120: ^{1}H NMR (400 MHz, D_6-acetone) spectrum of compound **4c**

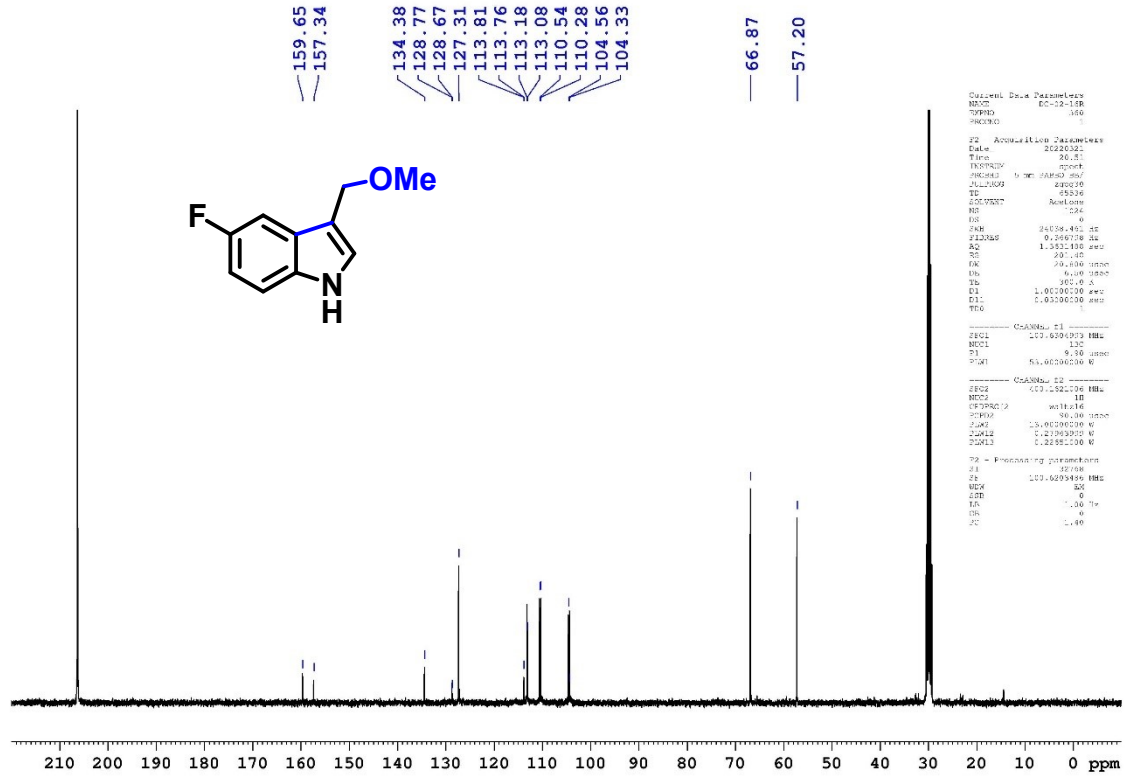

Figure S-121: ^{13}C NMR (100 MHz, D_6-acetone) spectrum of compound **4c**

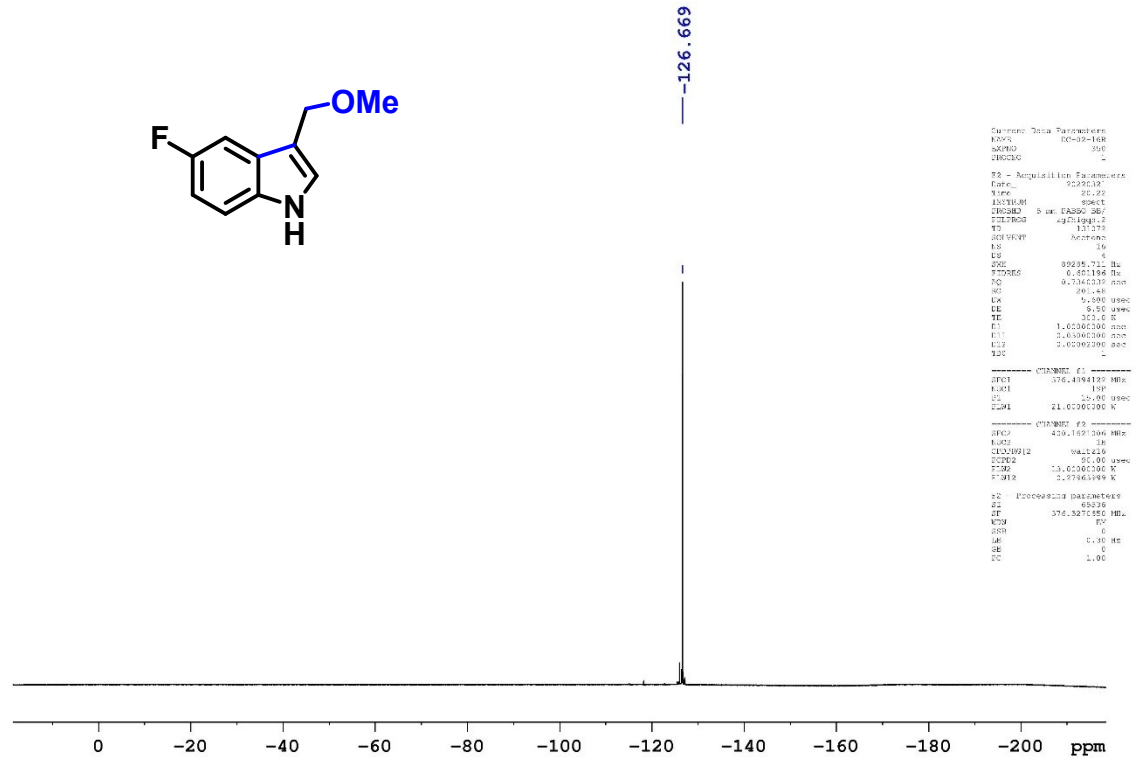

Figure S-122: ^{19}F NMR (376 MHz, D_6-acetone) spectrum of compound **4c**

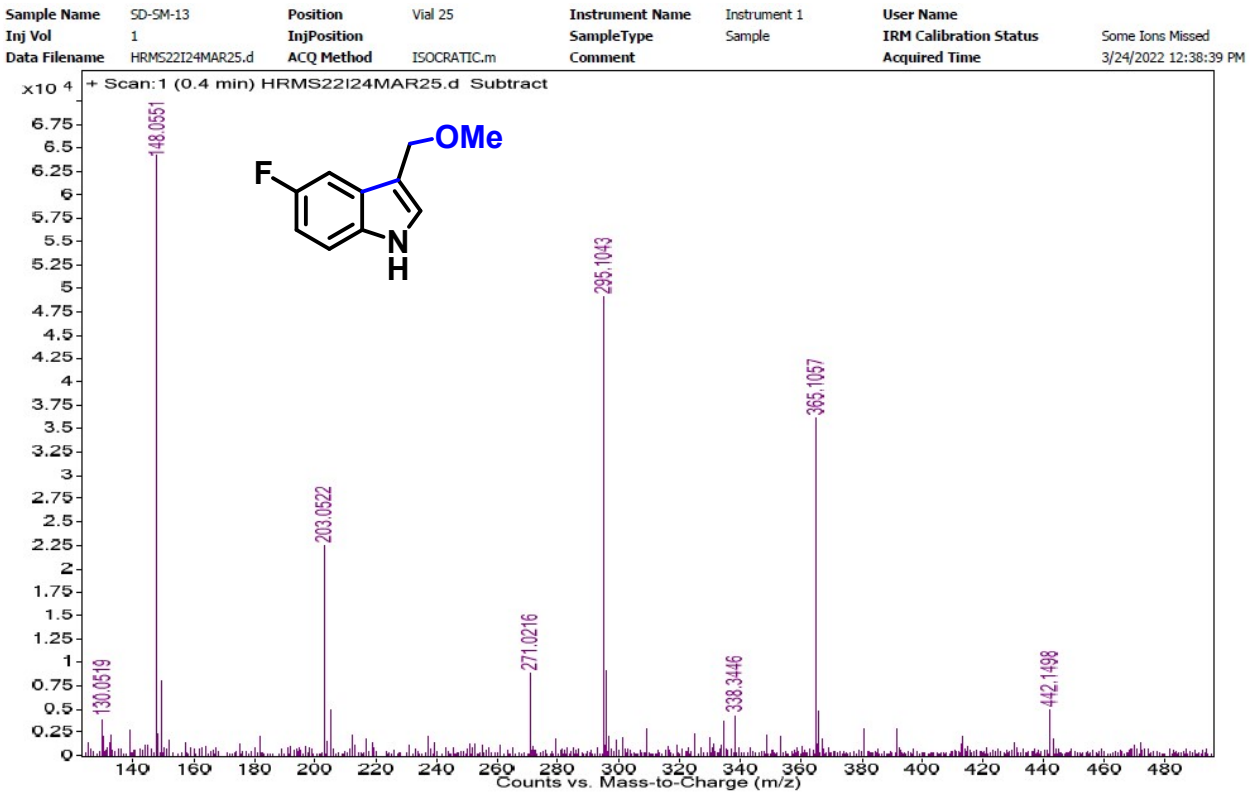

Figure S-123: HRMS spectrum of compound **4c**

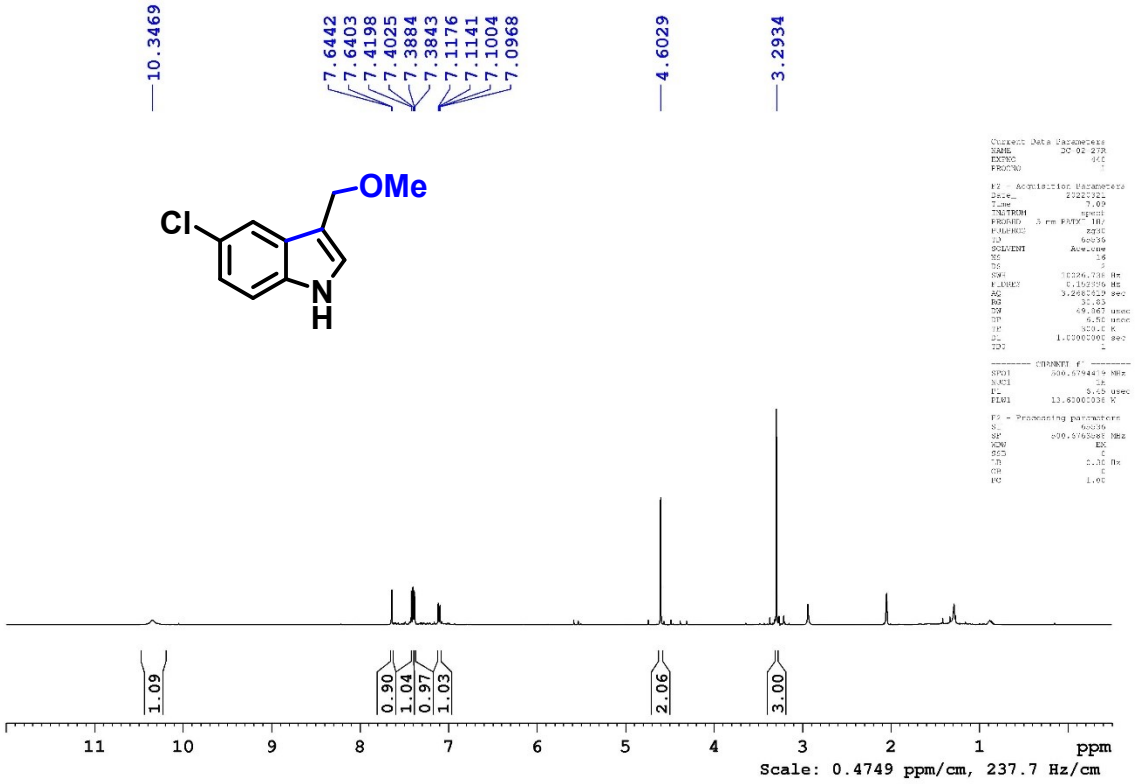

Figure S-124: ^{1}H NMR (500 MHz, D_6-acetone) spectrum of compound **4d**

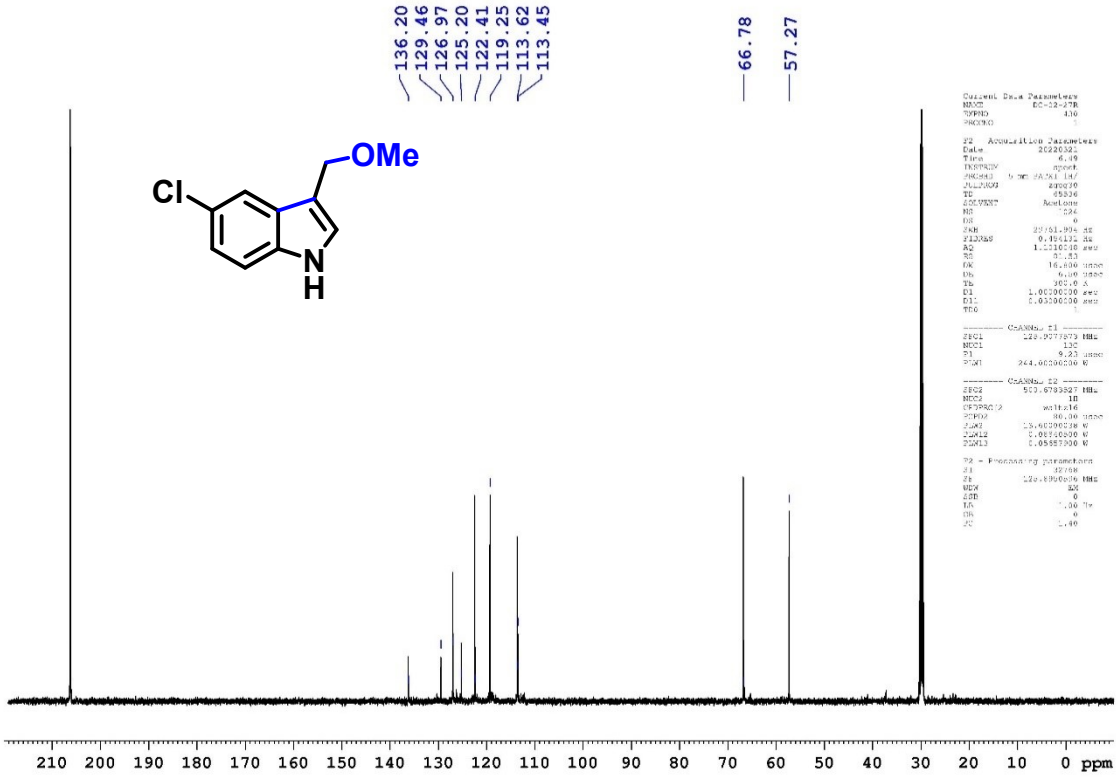

Figure S-125: ^{13}C NMR (125 MHz, D_6-acetone) spectrum of compound **4d**

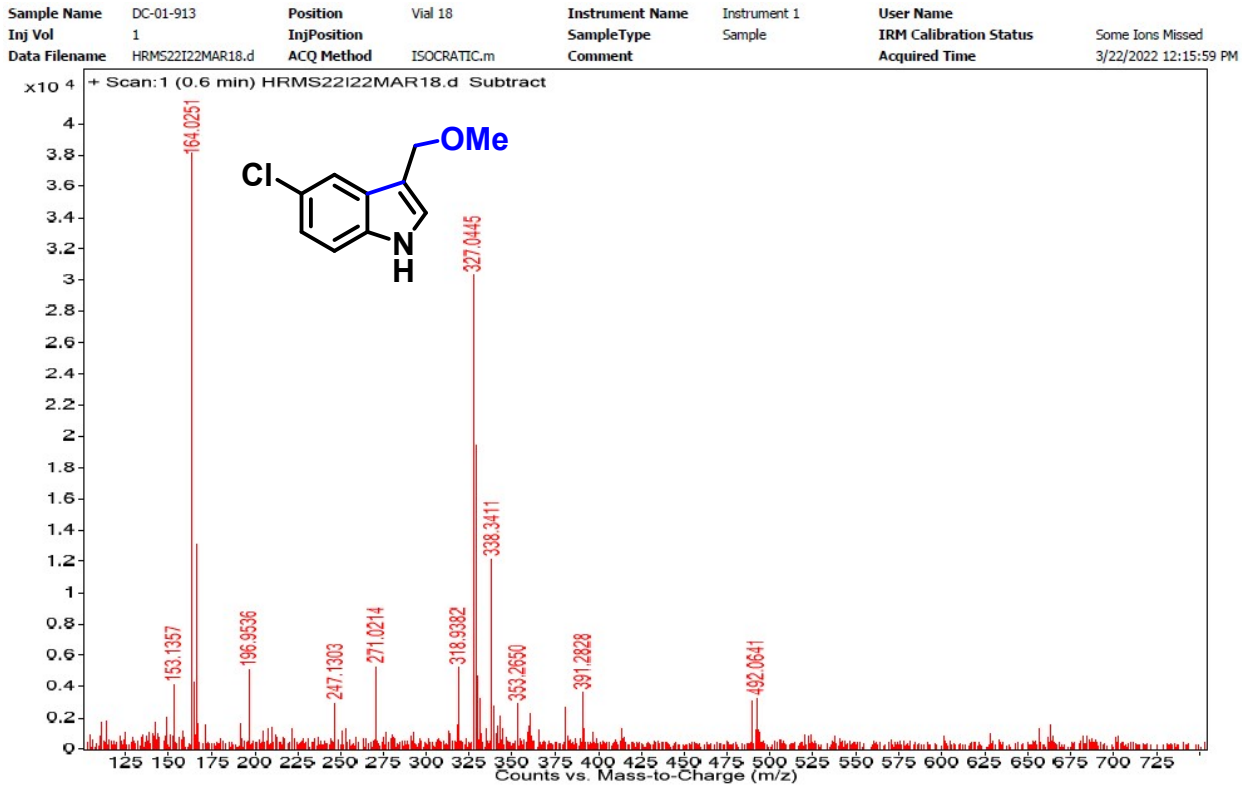

Figure S-126: HRMS spectrum of compound **4d**

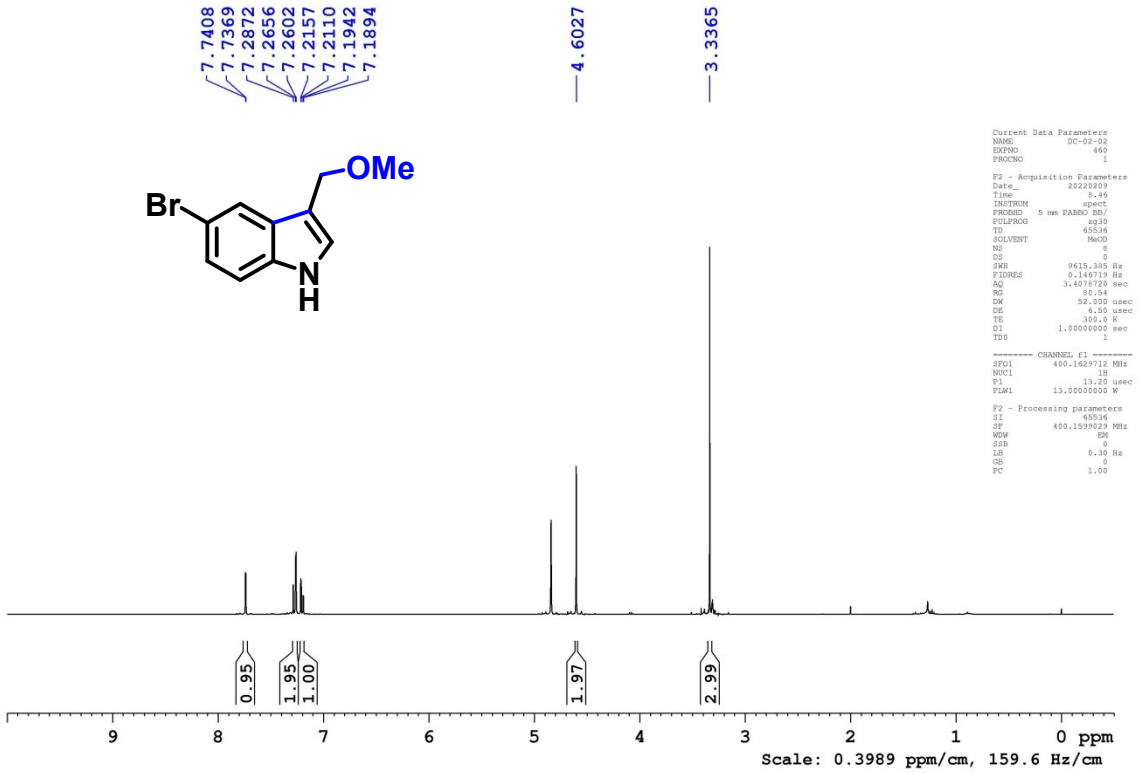

Figure S-127: ^{1}H NMR (400 MHz, D_4-methanol) spectrum of compound **4e**

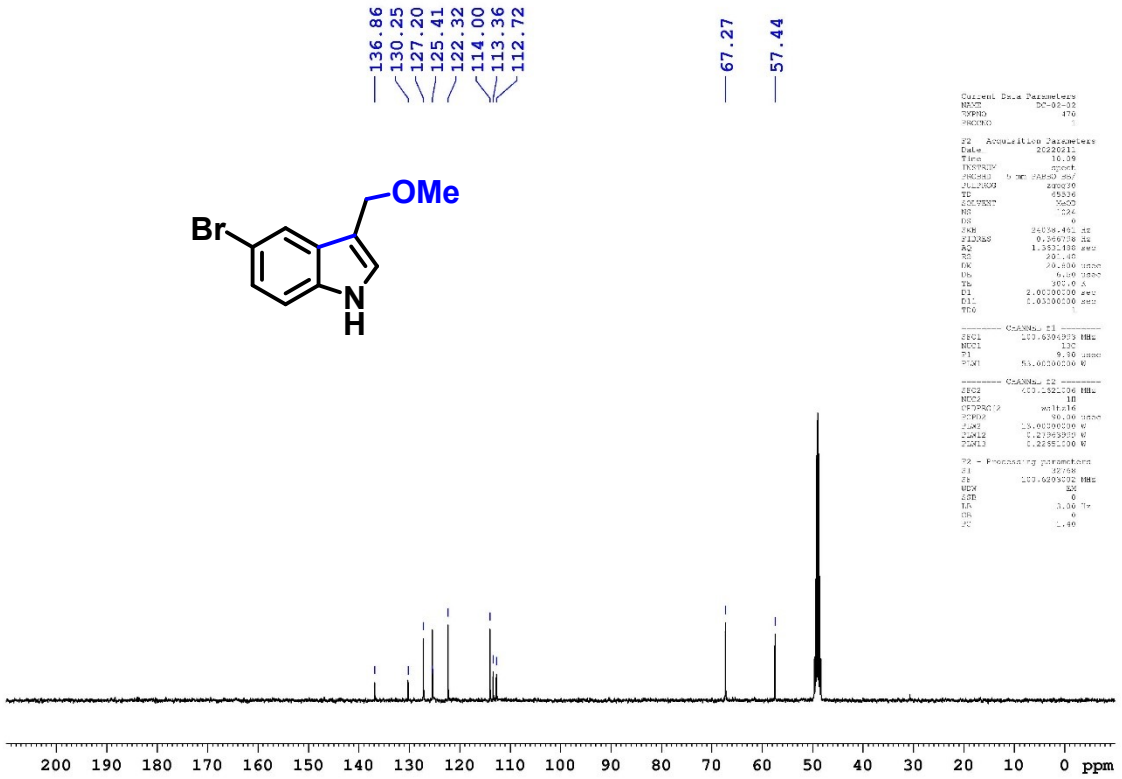

Figure S-128: ^{13}C NMR (100 MHz, D_4-methanol) spectrum of compound **4e**

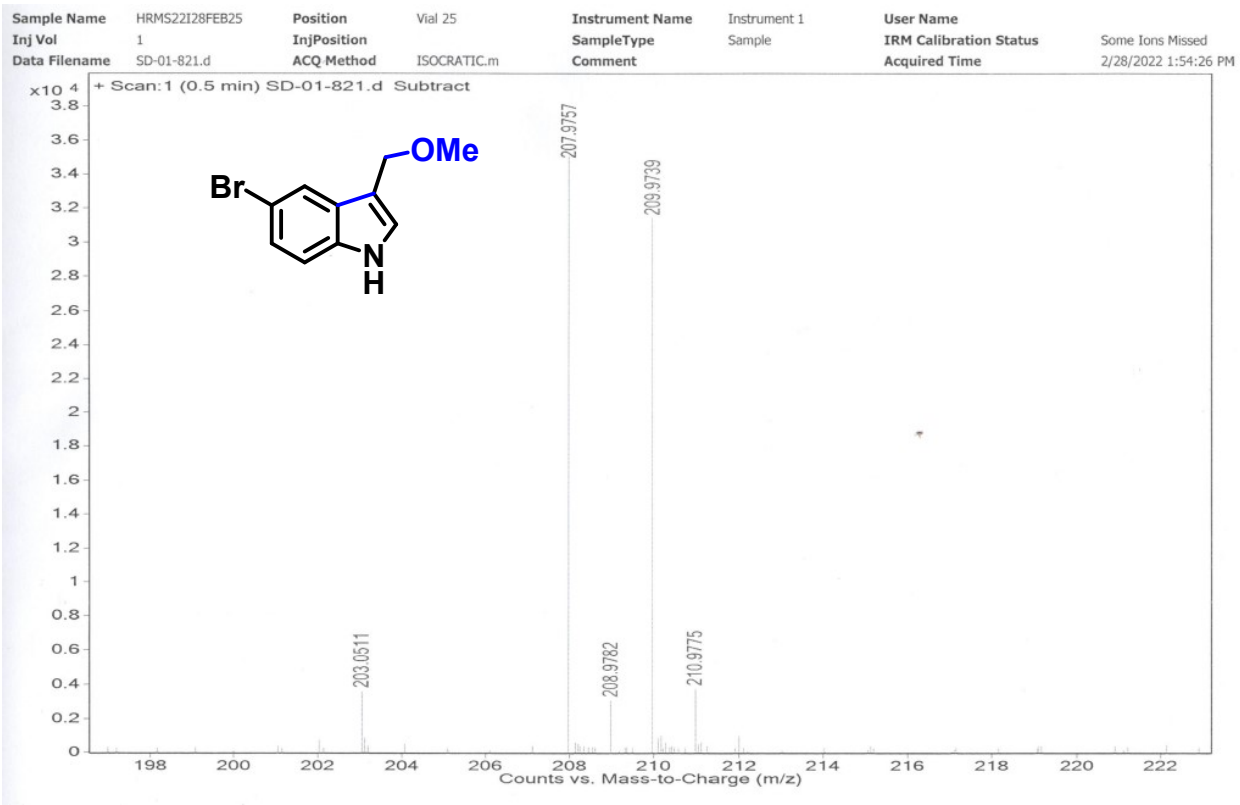

Figure S-129: HRMS spectrum of compound **4e**

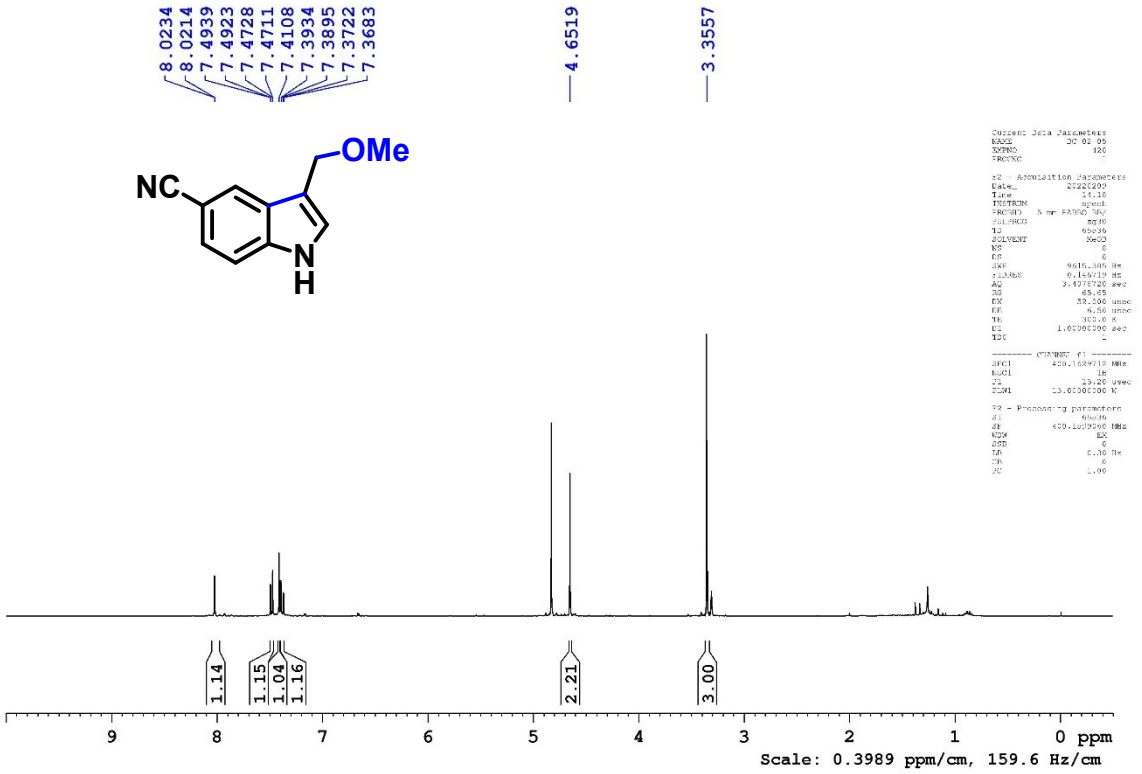

Figure S-130: ^{1}H NMR (400 MHz, D_4-methanol) spectrum of compound **4f**

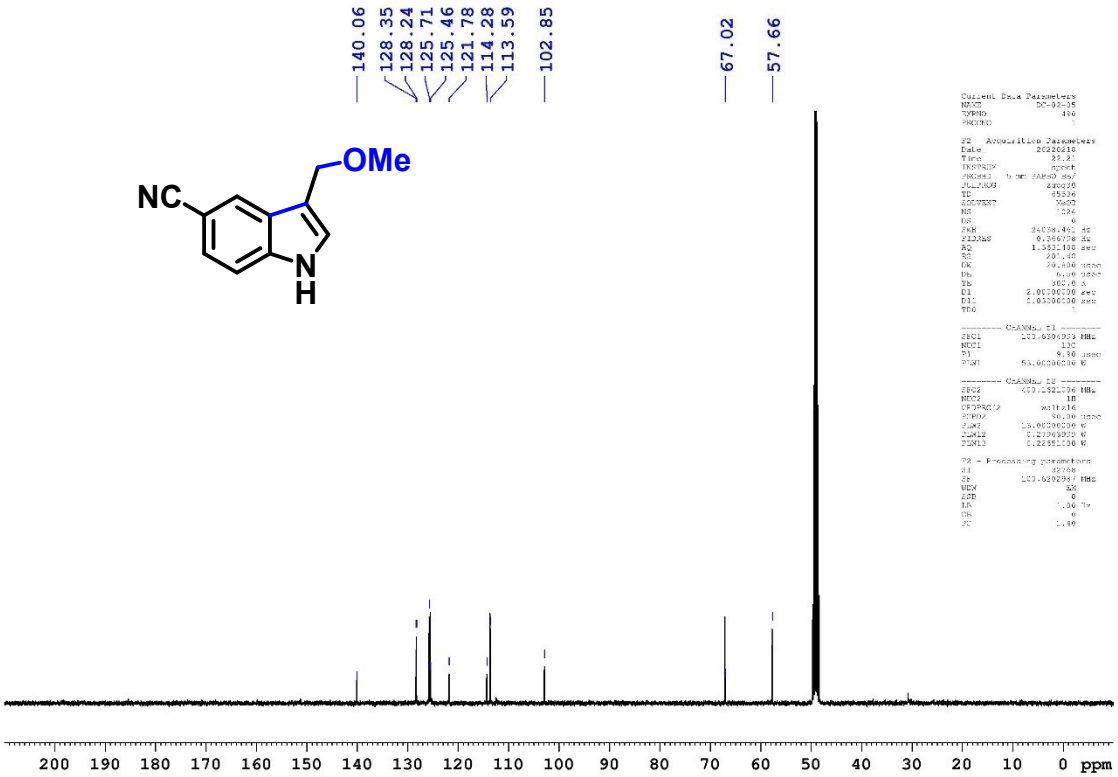

Figure S-131: ^{13}C NMR (100 MHz, D_4-methanol) spectrum of compound **4f**

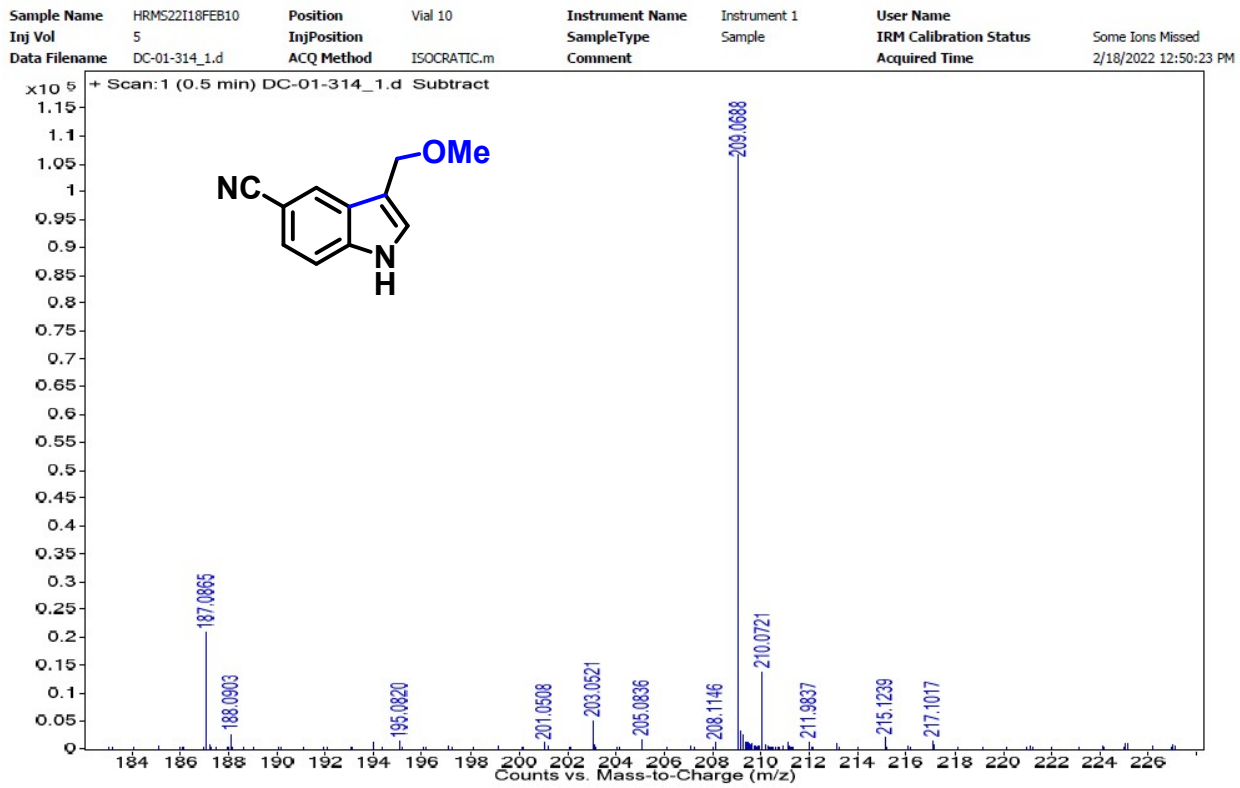

Figure S-132: HRMS spectrum of compound **4f**

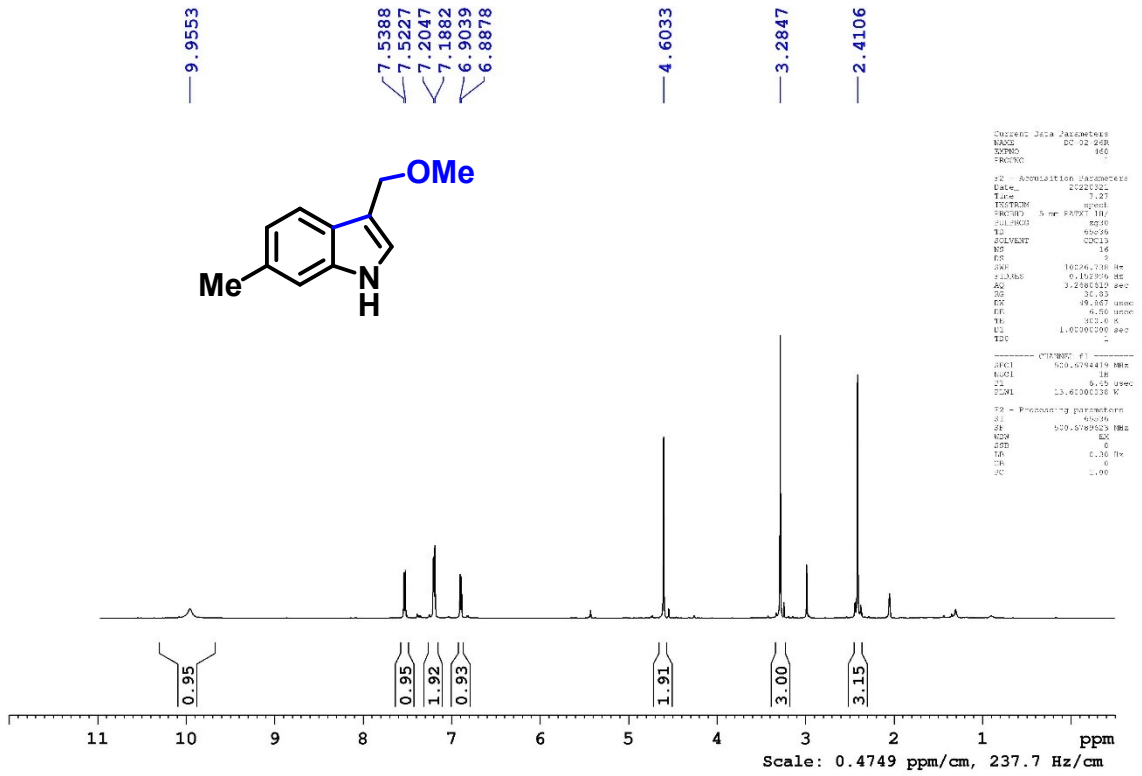

Figure S-133: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4g**

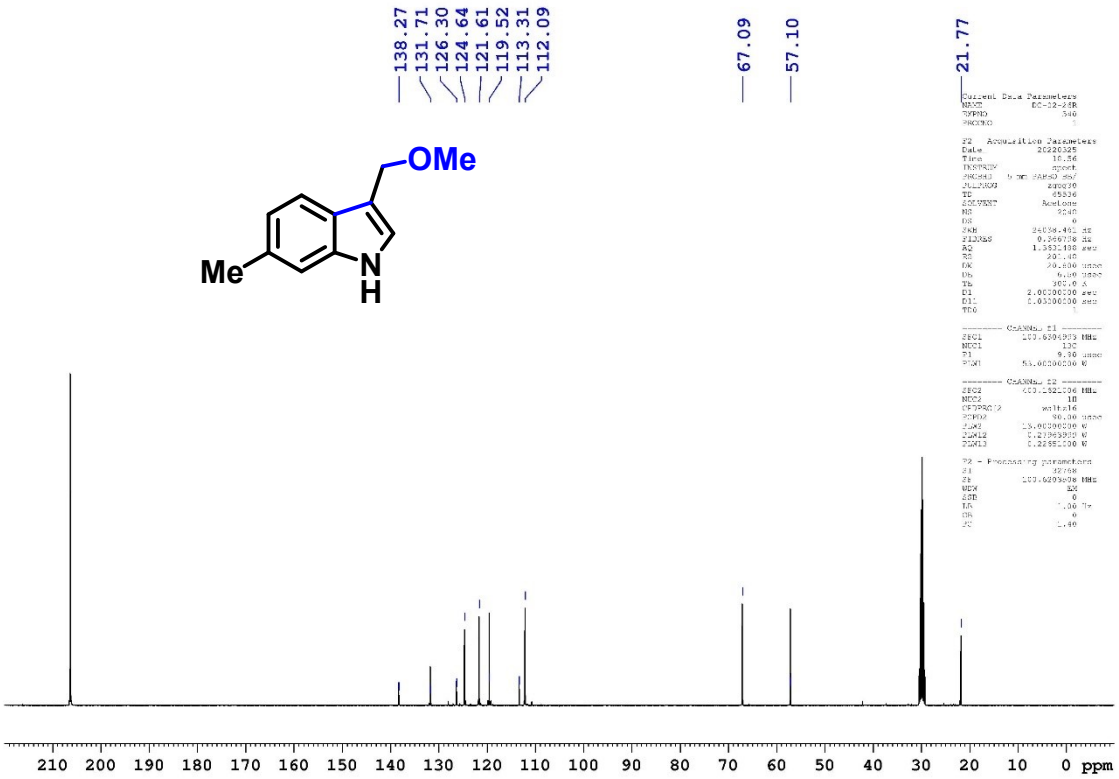

Figure S-134: ^{13}C NMR (100 MHz, D_6-acetone) spectrum of compound **4g**

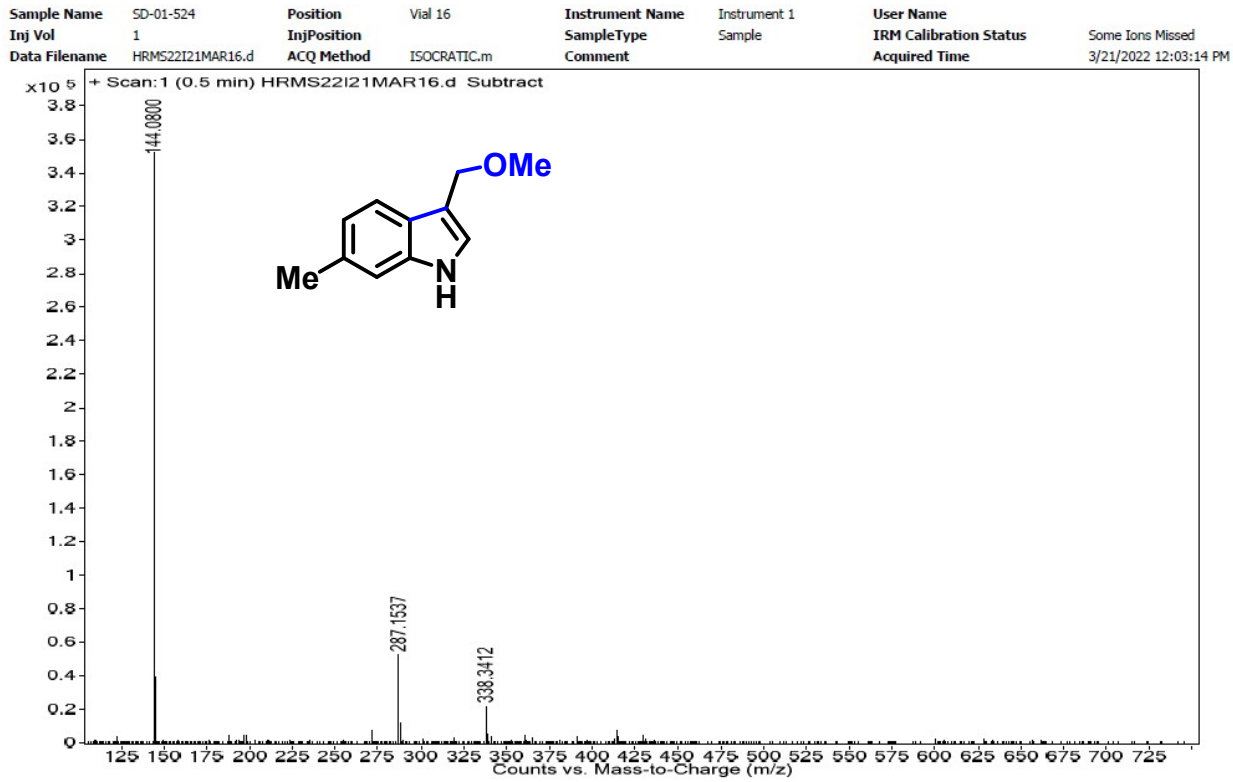

Figure S-135: HRMS spectrum of compound **4g**

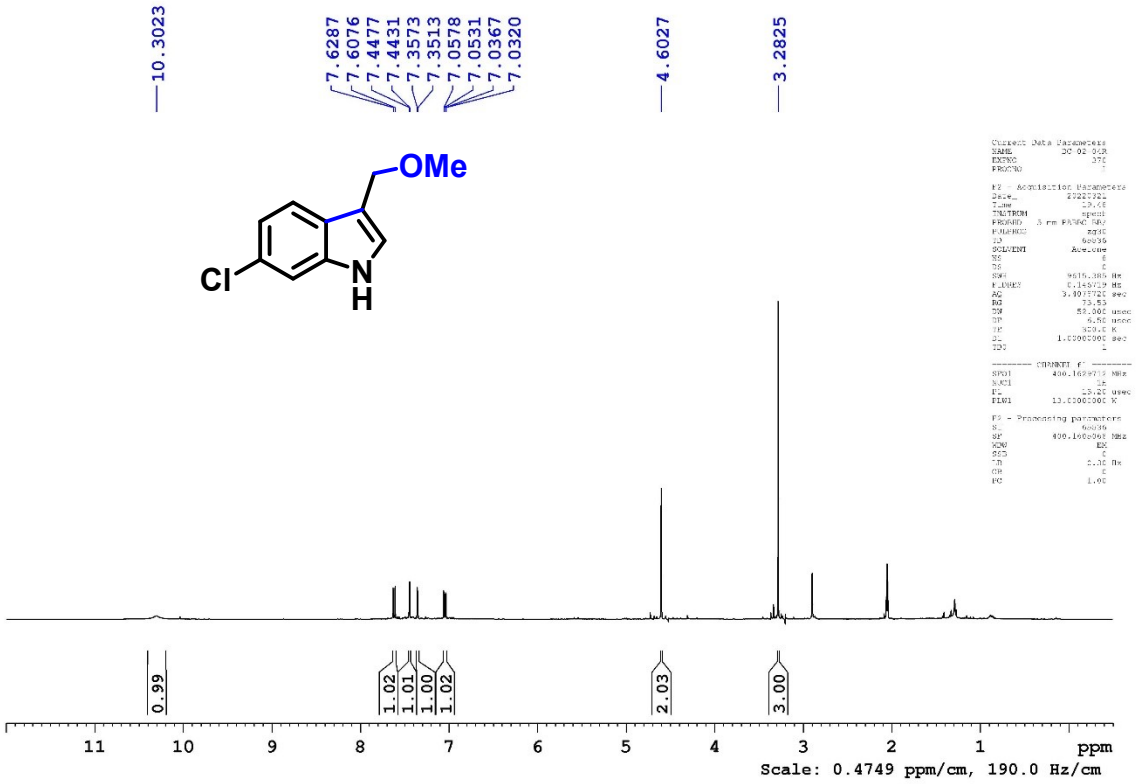

Figure S-136: ^{1}H NMR (400 MHz, D_6-acetone) spectrum of compound **4h**

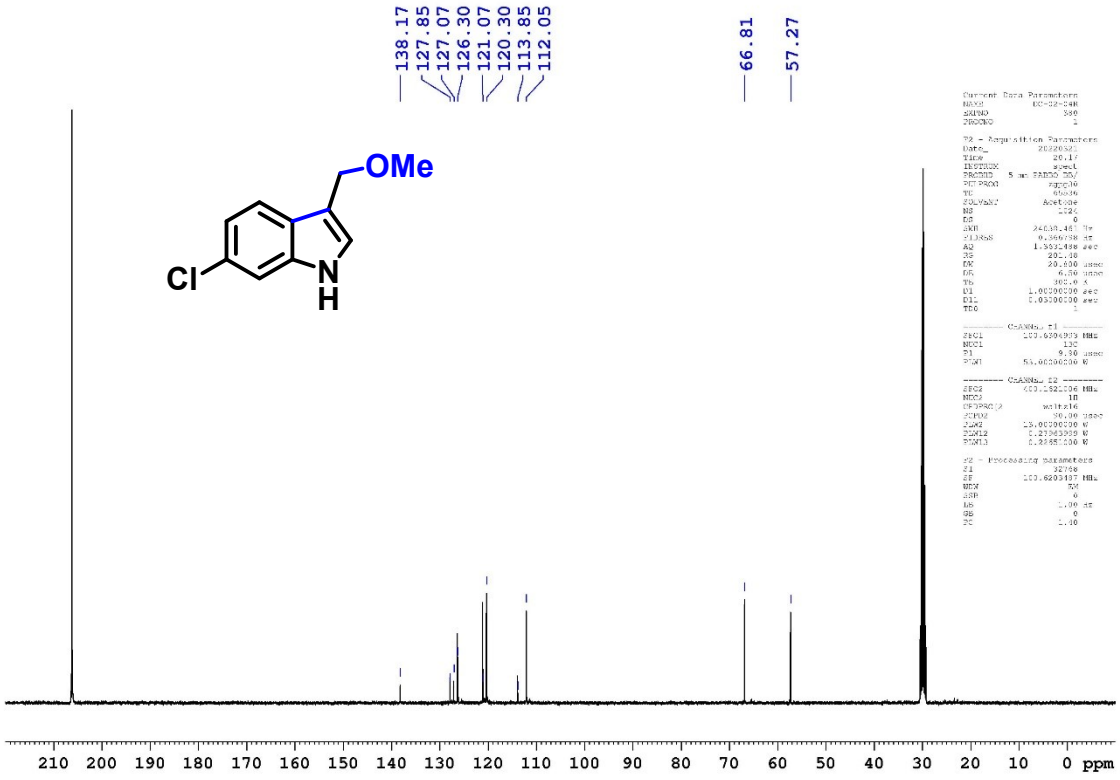

Figure S-137: ^{13}C NMR (100 MHz, D_6-acetone) spectrum of compound **4h**

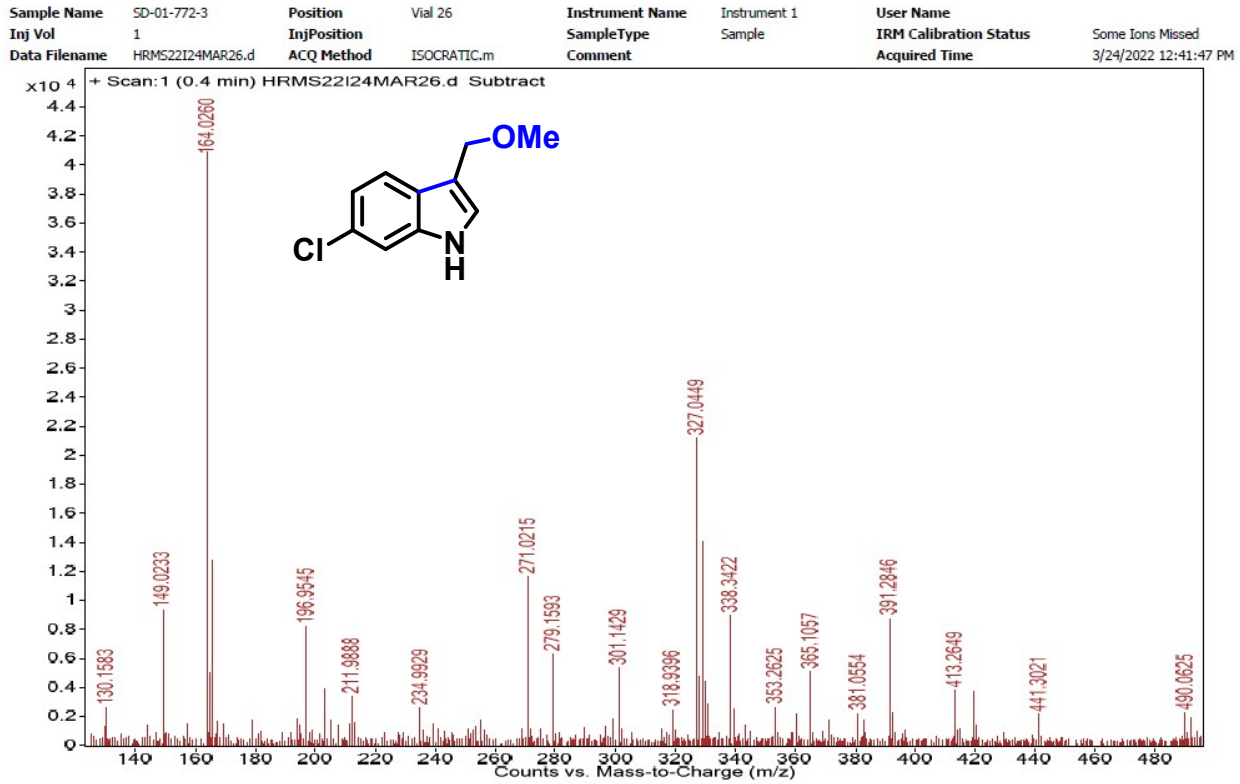

Figure S-138: HRMS spectrum of compound **4h**

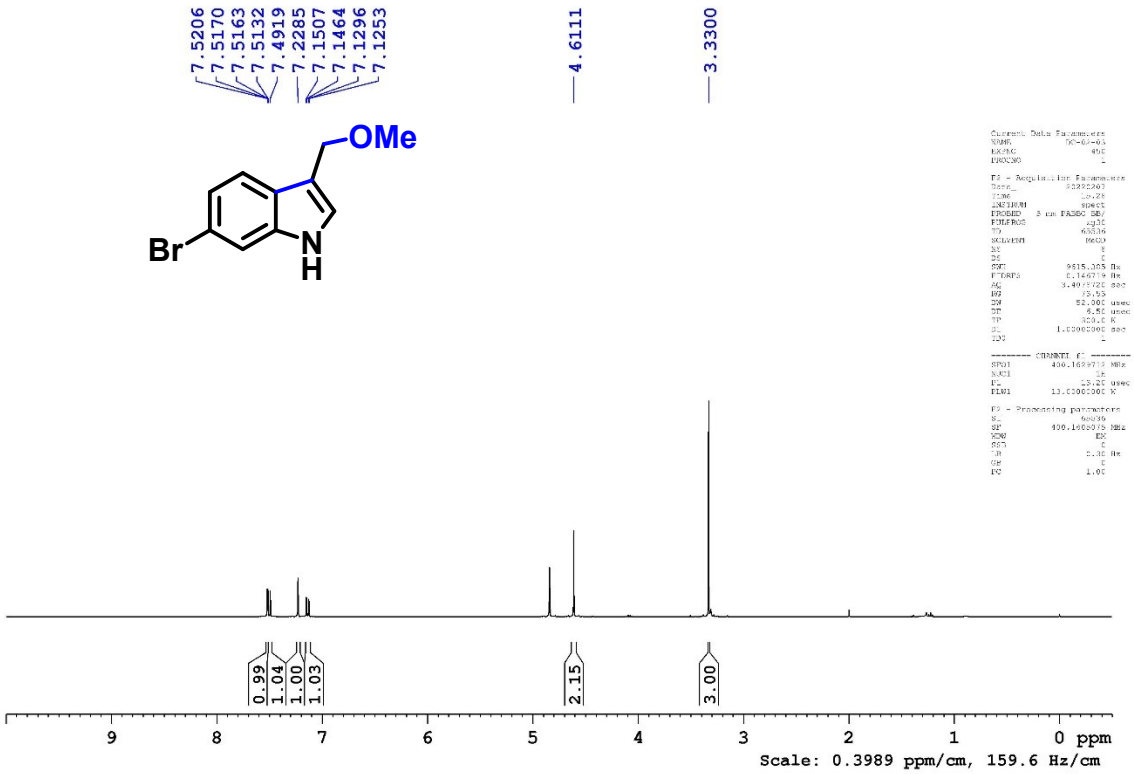

Figure S-139: ^{1}H NMR (400 MHz, D_4-methanol) spectrum of compound **4i**

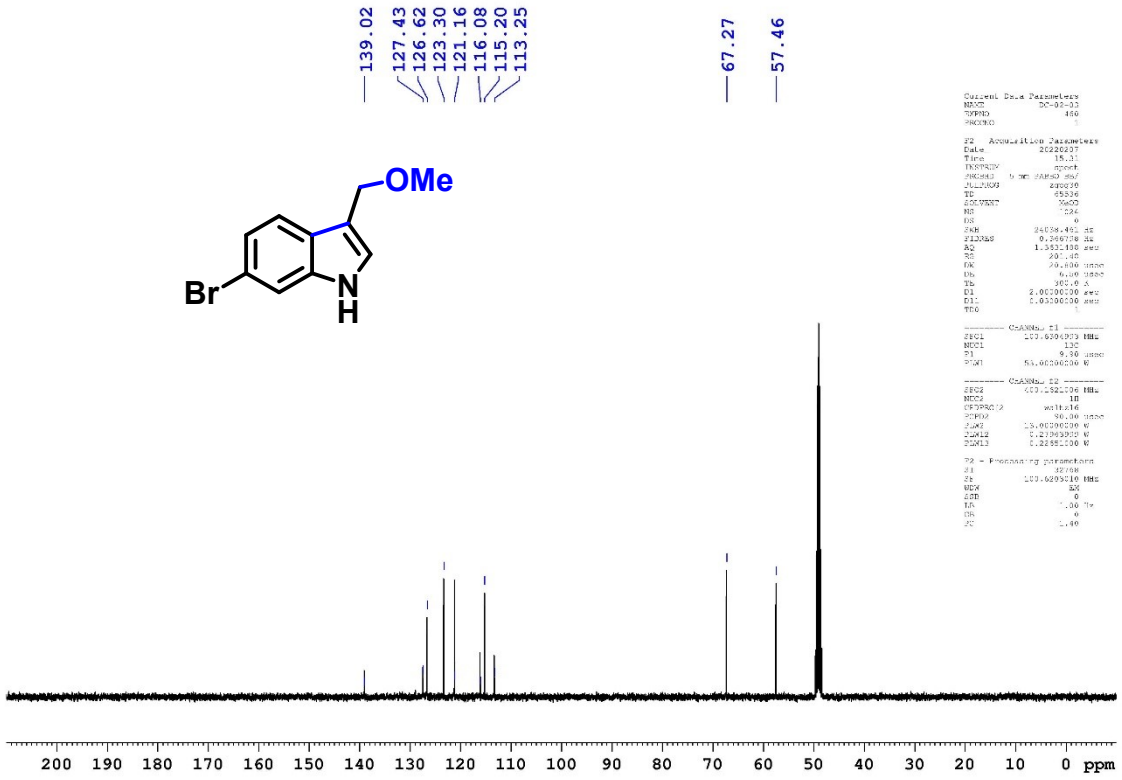

Figure S-140: ^{13}C NMR (100 MHz, D_4-methanol) spectrum of compound **4i**

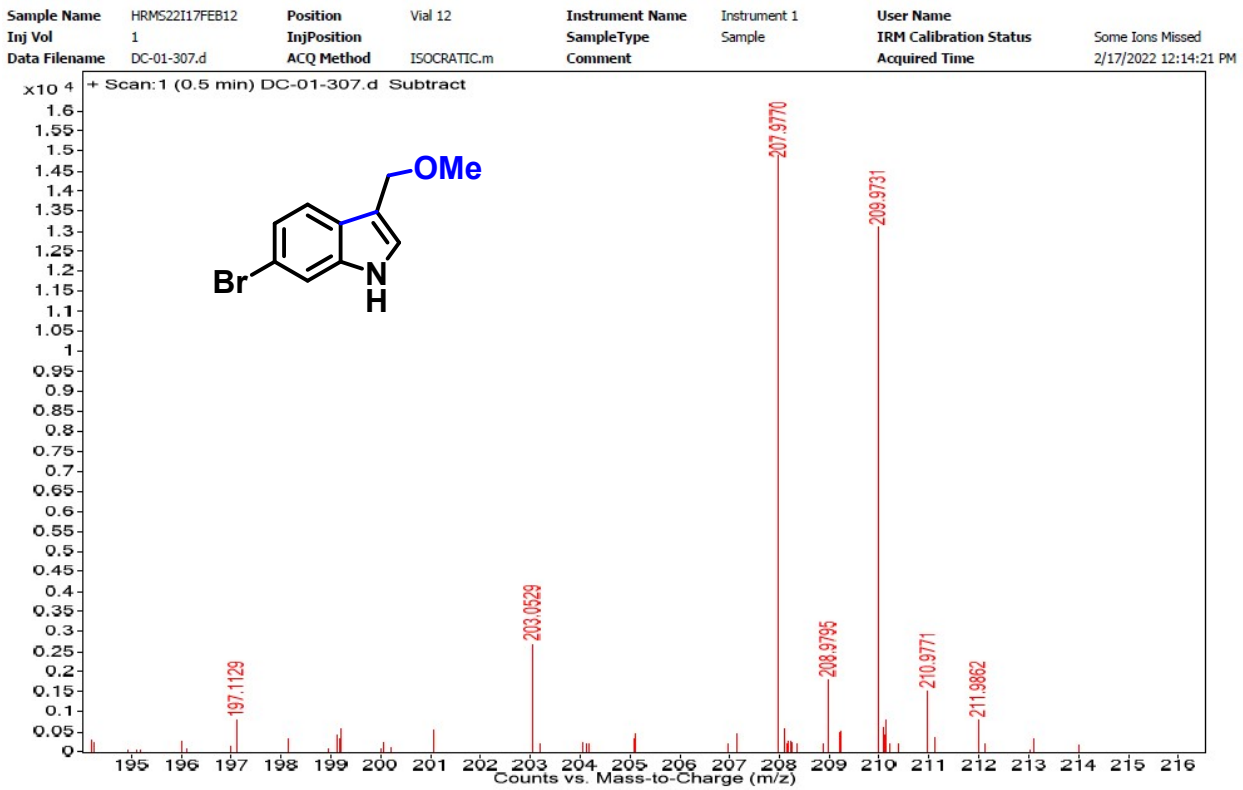

Figure S-141: HRMS spectrum of compound **4i**

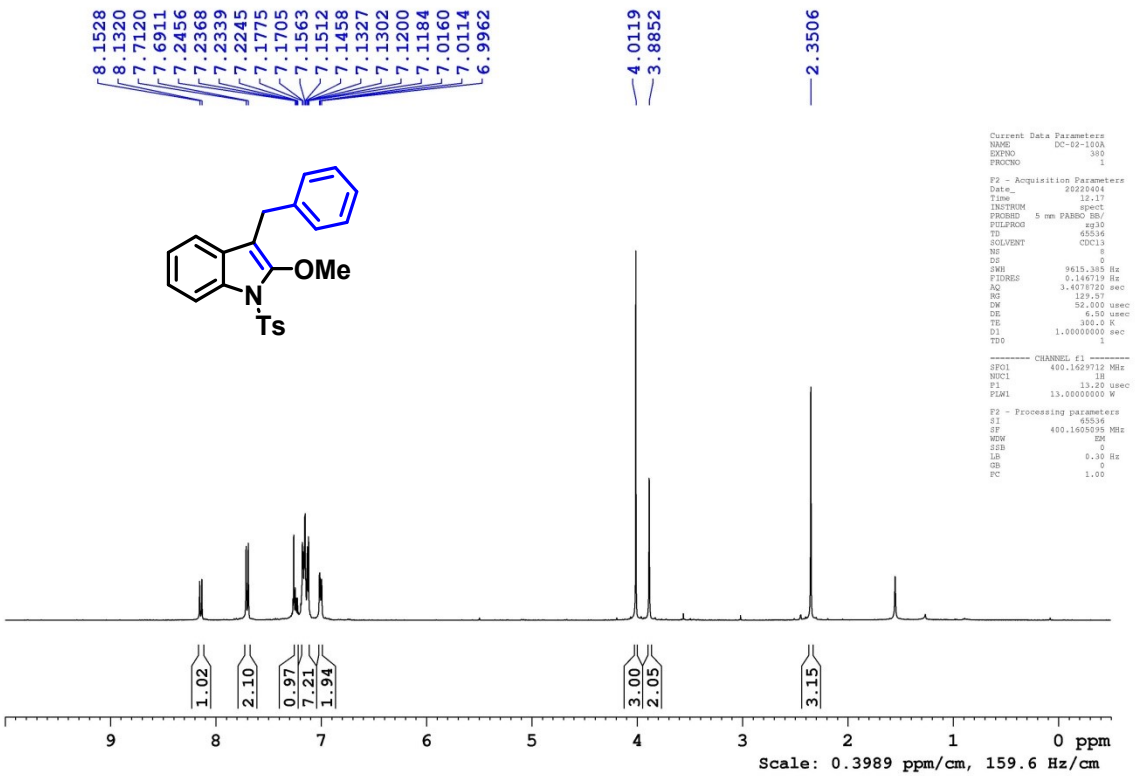

Figure S-142: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**

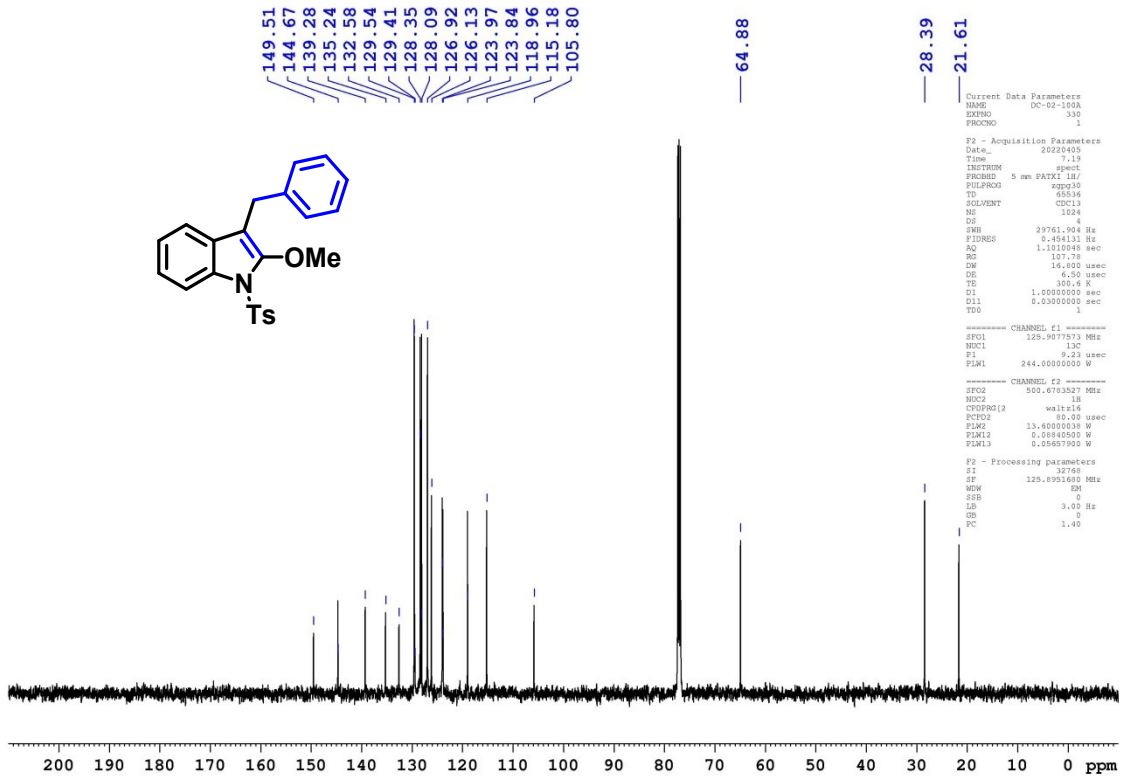

Figure S-143: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **5**

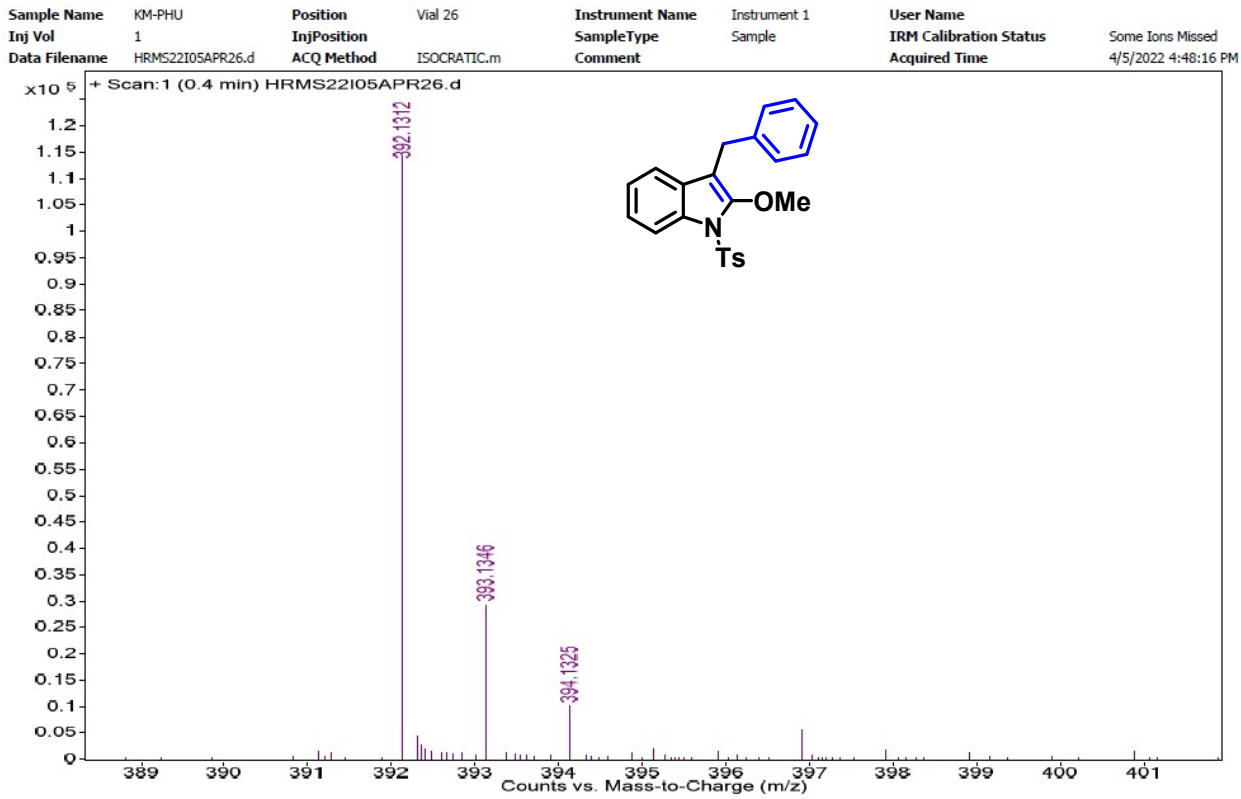

Figure S-144: HRMS spectrum of compound **5**

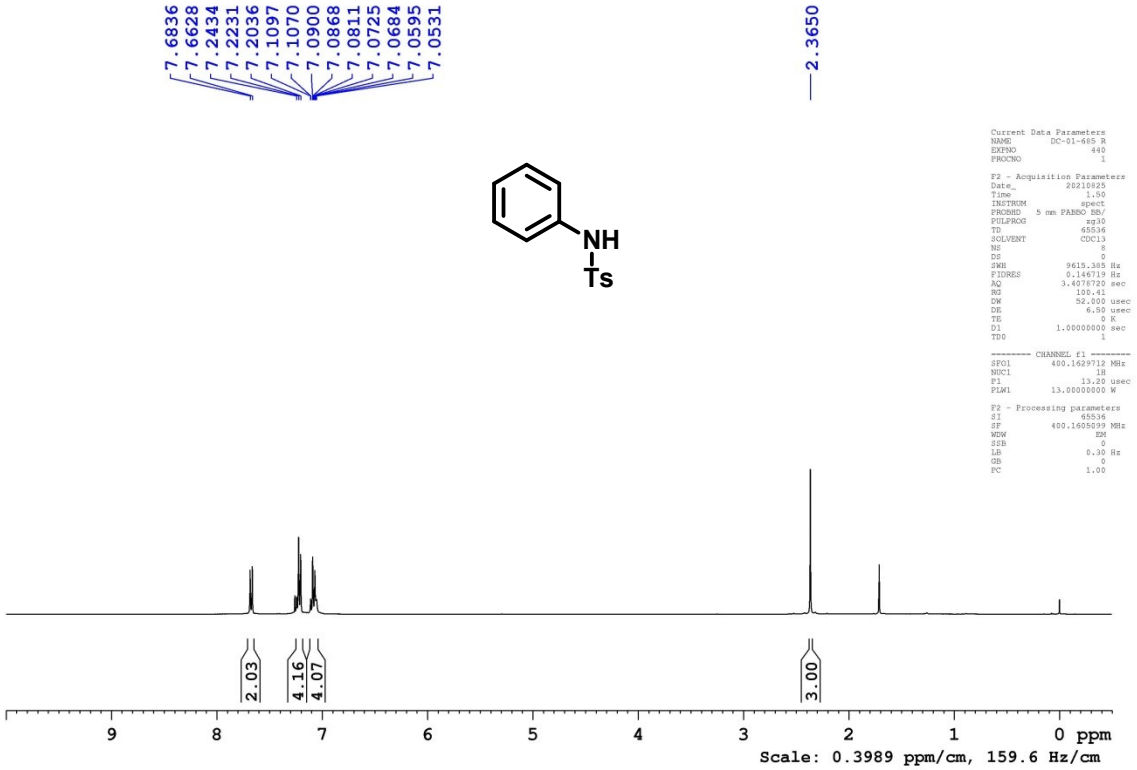

Figure S-145: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7a**

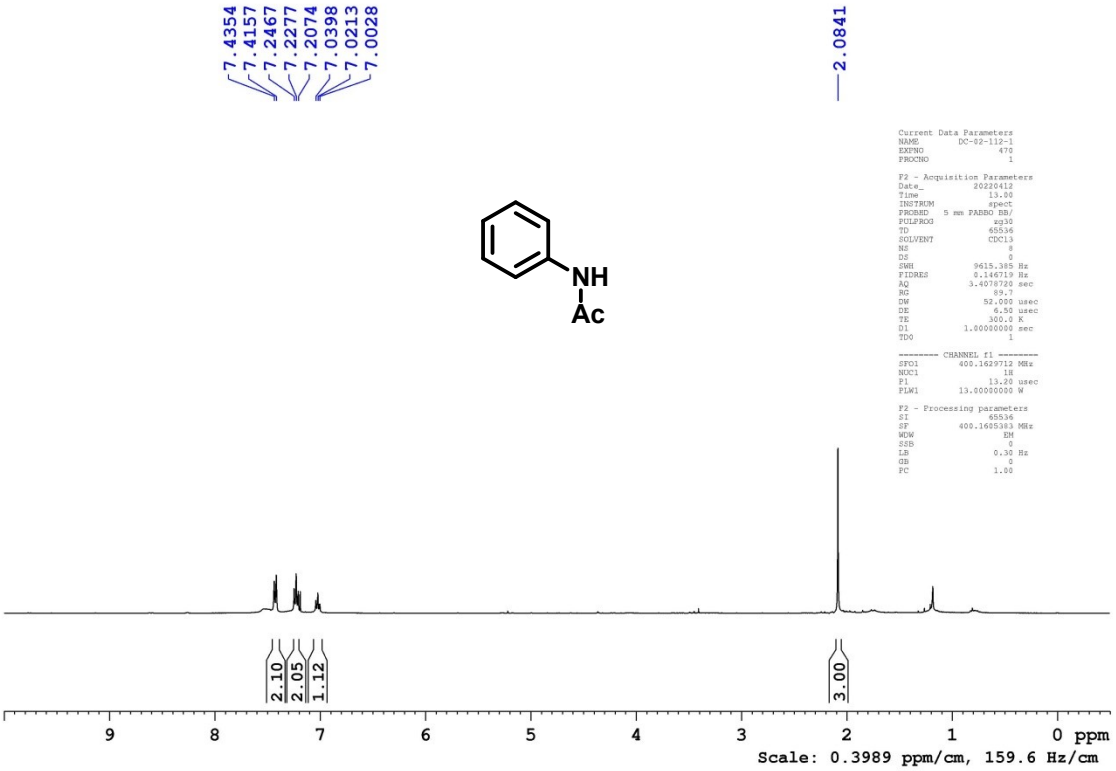

Figure S-146: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7b**

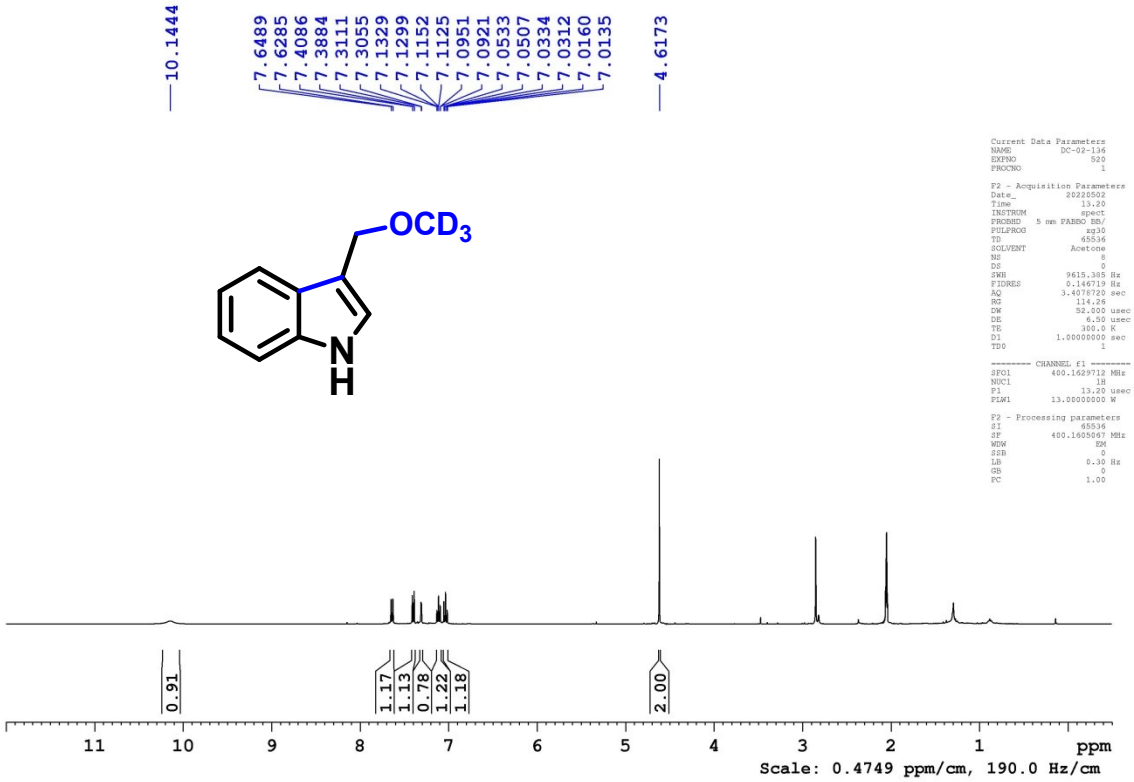

Figure S-147: ^{1}H NMR (400 MHz, D_6-acetone) spectrum of compound **4a-D**