Supporting Information

Catalyst-Controlled Divergent Transformations of *N*-Sulfonyl-1,2,3-triazoles into Isoquinolin-3-ones and 2-Aminoindanones

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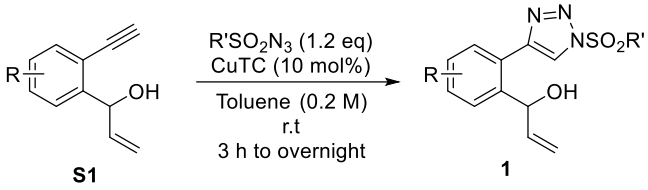
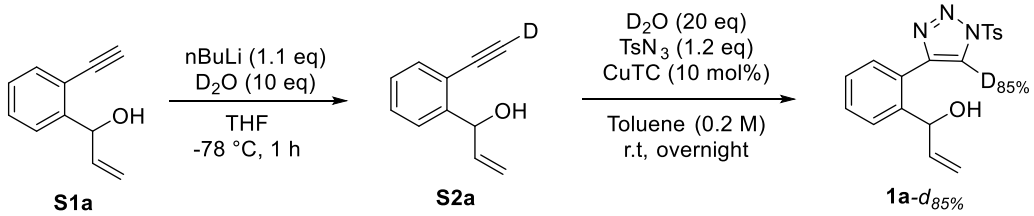
1. General Information.

All reactions were performed under an argon atmosphere using standard Schelenk techniques. Reaction flasks were flame-dried under vacuum. All purchased reagents were used without further purification. Dry toluene was distilled prior to be used. Anhydrous solvent was transferred by an oven dried syringe of a cannula. All reactions were monitored by TLC with silica gel coated plates. Visualization on TLC was achieved by use of UV light (254 nm) or by staining with Cerium Ammonium Molybdate (CAM). NMR spectra were recorded on a Bruker 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 282 MHz for ^{19}F. The melting points were measured on a Fisher-Johns apparatus and uncorrected. HRMS, high resolution mass spectra were obtained by electron ionization (EI), fast atom bombardment (FAB) with a magnetic sector-electronic sector double focusing mass analyzer at the Daegu Center of the Korea Basic Science Institute.

2. General Procedure of Substrate 1 and 1a-*d*.



The compound **S1** was prepared according to the literature procedures.[1] The substrate **1** was prepared according to the general *N*-sulfonyl-1,2,3-triazole synthesis.[2] ***(Note.*** The compound **1** should be stored at low temperatures, otherwise it would decompose as it turns green. Also, the catalytic reactivity of the starting material **1** decreases over time, therefore it must be used within a week after synthesis.)



Under a nitrogen atmosphere, to a solution of dry THF (0.2 M) in a flame-dried round bottom flask was added acetylene **S1a** (1 equiv.) and stirred at -78 ℃ then added nBuLi (1.6 M in hexane, 1.1 equiv.) dropwise. The reaction mixture was stirred for an hour, then diluted with Et_2O and quenched with D_2O (10 equiv.). The resulting suspension was dried over $MgSO_4$ and filtered. The residue was concentrated under reduced pressure to afford compound **S2**.

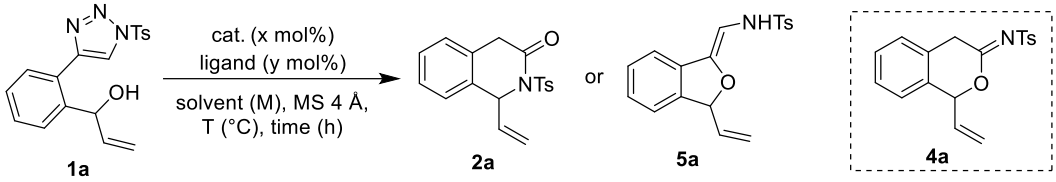
1a-*d* was prepared from **S2a** according to the ref. (2) with additional D_2O (20 equiv.).

Reference

(1) M. Rosillo, G. Domínguez, L. Casarrubios, U. Amador and J. Pérez-Castells, Tandem Enyne Methathesis-Diels-Alder Reaction for Construction of Natural Product Frameworks. *J. Org. Chem.* 2004, **69**, 2084-2093.

(2) J. Raushel and V. V. Fokin, Efficient Synthesis of 1-Sulfonyl-1,2,3-Triazoles. *Org. Lett*. 2010, **12**, 4952-4955.

3. Table S1. Optimization for the Synthesis of 5a and 2a via Rh(II)- and Pd(0)-Catalysis.

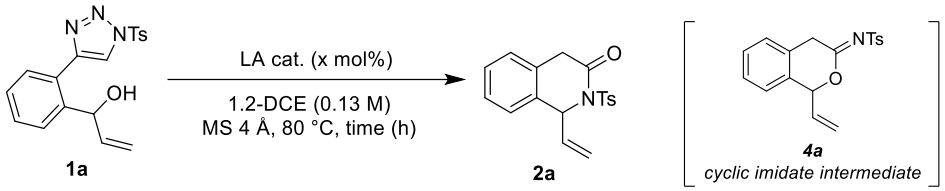


In a glovebox, a flame-dried vial equipped with a stirrer bar was charged with triazole **1a** (0.2 mmol), catalyst, 4 Å molecular sieves and sealed under an argon atmosphere. A solvent was added to the mixture and the solution was heated until all triazole was consumed (determined by TLC analysis). After being cooled to room temperature, the solvent was evaporated, dried under vacuum, and determined the product ratio from crude ^{1}H NMR spectrum. The product was purified by silica-gel column chromatography. (***Note.*** ^{1}H NMR analysis should be conducted immediately after completion of the reaction, since compound **5a** was readily decomposed in one day even at -20 ℃.)

Entry	Rh Catalyst (mol%)	Pd Catalyst (mol%)	Ligand (mol%)	Solvent (M)	T (°C) /time (h)[b]	Yield (%)[c]	**2a** : 5**a** ratio[d]
1	$Rh_2(TMA)_4$ (2)	$Pd(PPh_3)_4$ (2)	-	Toluene (0.2)	90 / 21	31	99>1
2	$Rh_2(TMA)_4$ (3)	$Pd_2(dba)_3$ (1)	Dppp (2)	Toluene (0.2)	120 / 1	53	1.63:1
3	$Rh_2(TMA)_4$ (2)	-	-	Toluene (0.2)	90 / 2	75	1:9
4	$Rh_2(TMA)_4$ (2)	-	-	Toluene (0.2)	<80	N.R.	-
5	$Rh_2(TMA)_4$ (2)	-	-	1,2-DCE (0.2)	90 / 2	64	1:10
6	$Rh_2(TMA)_4$ (2)	-	-	PhCl (0.2)	90 / 3	69	1:5
7	$Rh_2(TMA)_4$ (2)	-	-	MeCN (0.2)	90 / 7	13	3.7:1
8	$Rh_2(TMA)_4$ (2)	-	-	Toluene (0.2)	120 / 0.5	89	1<99
9	$Rh_2(TMA)_4$ (4)	-	-	Toluene (0.2)	70 / 2.5	72	1<99
10	$Rh_2(oct)_4$ (4)	-	-	Toluene (0.2)	70 / 21	30	1:2.3
11	$Rh_2(OAc)_4$ (4)	-	-	Toluene (0.2)	70 / 21	43[e]	1.87:1
12	$Rh_2(esp)_2$ (4)	-	-	Toluene (0.2)	70 / 4	68	1<99
13	Rh_2(*S*-DOSP)$_4$ (4)	-	-	Toluene (0.2)	70 / 5	80	1:9
14	$Rh_2(TMA)_4$ (4)	-	-	Toluene (0.2)	80 / 1	76	1<99
15	$Rh_2(TMA)_4$ (4)	-	-	Toluene (0.2)	90 / 1	80	1<99
16	$Rh_2(TMA)_4$ (4)	-	-	Toluene (0.2)	100 / 1	83	1:32
17	-	$Pd(PPh_3)_4$ (4)	-	1,2-DCE (0.13)	80 / 6	61	99>1
18	-	$Pd_2(dba)_3$ (2)	P(4-MeOPh)$_3$ (8)	1,2-DCE (0.13)	80 / 5	76	99>1
19	-	$Pd_2(dba)_3$ (2)	P(4-MeOPh)$_3$ (8)	MeCN (0.13)	80 / 3	70	99>1
20	-	$Pd_2(dba)_3$ (2)	P(4-MeOPh)$_3$ (8)	Toluene (0.13)	80 / 7	35	99>1
21	-	$Pd_2(dba)_3$ (2)	P(4-MeOPh)$_3$ (8)	1,4-dioxane (0.13)	80 / 7	31	99>1
22	-	$Pd_2(dba)_3$ (2)	Dppf (4)	1,2-DCE (0.13)	80 / 6	30	99>1
23	-	$Pd_2(dba)_3$ (2)	PPh_3 (8)	1,2-DCE (0.13)	80 / 6	41	99>1
24	-	$Pd_2(dba)_3$ (2)	Xantphos (4)	1,2-DCE (0.13)	80 / 5	15	99>1
25	-	$Pd_2(dba)_3$ (2)	*rac*-BINAP (4)	1,2-DCE (0.13)	80 / 5	N.D[f]	99>1
26	-	$Pd_2(dba)_3$ (2)	Segphos (4)	1,2-DCE (0.13)	80 / 5	N.D[f]	99>1
27	-	$Pd_2(dba)_3$ (2)	P(*o*-tolylPh)$_3$ (8)	1,2-DCE (0.13)	80 / 5	72	99>1
28	-	$Pd_2(dba)_3$ (2)	P(4-MeOPh)$_3$ (8)	1,2-DCE (0.13)	90 / 3	80	99>1

[a]Reaction conditions: **1a** (0.2 mmol), catalyst, and MS 4 Å in solvent at designated temperature. [b]Time for complete conversion of **1a** determined by TLC. [c]Isolated yield. N.R.: No reaction occured at all. [d]**2a:5a** ratio were determined by ^{1}H NMR analysis. [e]Starting material was recovered in 46% yield. [f]Only cyclic imidate intermediate **4a** was detected.

4. Table S2. Optimization for the Synthesis of 2a Using Lewis Acid Catalyst.[a]

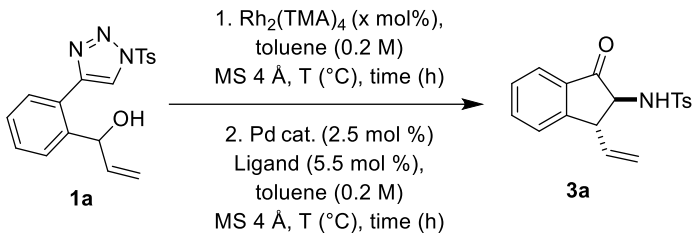


In a glovebox, a flame-dried vial equipped with a stirrer bar was charged with triazole **1a** (0.2 mmol), catalyst, 4 Å molecular sieves and sealed under an argon atmosphere. A solvent was added to the mixture and the solution was heated until all triazole was consumed (determined by TLC analysis). After being cooled to room temperature, the solvent was evaporated, dried under vacuum, and determined the product from crude ^{1}H NMR spectrum.

Entry	Lewis acid Catalyst (mol%)	time (h)[b]	Yield (%)
1	$PdCl_2(PhCN)_2$ (4)	12	N.D[c]
2	$PdCl_2(MeCN)_2$ (4)	12	N.D[c]
3	PPh_3 (2)	12	No reaction
4	$Sc(OTf)_3$ (2)	12	Decomposed
5	$Cu(OTf)_2$ (2)	12	Decomposed
6	$Zn(OTf)_2$ (2)	6	N.D[c]

[a]Reaction conditions: **1a** (0.2 mmol) Lewis acid cat. and MS 4 Å in 1,2-DCE (1.5 ml) at 80 °C. [b]Time for complete conversion of **1a** determined by TLC. [c]Only cyclic imidate intermediate was detected.

5. Table S3. Optimization for the Synthesis of 3a via Tandem One-Pot Rh(II)/Pd(0) Catalysis.[a]



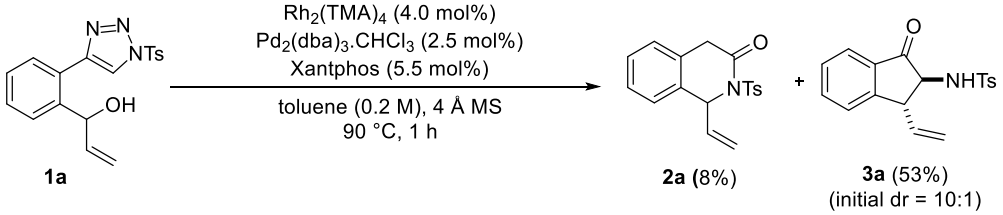
To a flame-dried vial equipped with a stirrer bar was added $Rh_2(TMA)_4$, MS 4 Å, triazole **1a** (0.2 mmol), and toluene (1 mL, 0.2 M) then the vial was sealed by the cap in a glove box. The solution was stirred and heated for 0.5 h to 1 h. After completion of the reaction, the mixture was cooled to room temperature, and charged with Pd cat. and ligand in a glovebox. The solution was stirred and heated until the reaction was completed (determined by TLC). The crude mixture was purified by column chromatography to afford the corresponding 2-aminoindanone **3a**.

Note. Initial configuration of the product **3a** was exclusively *trans* which was determined by ^{1}H NMR analysis of the crude reaction mixture. However, the configuration of **3a** was changed to *trans*/*cis* mixture after column chromatography due to highly enolizable α-proton to the carbonyl.

Entry	Rh catalyst (mol%)	T (°C) /time (h)[b]	Pd Catalyst	Ligand	T (°C) /time (h)	Yield (%)[b]
1	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd(PPh_3)_4$	-	60 / 12	trace
2	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd(PPh_3)_4$	-	120 / 1	decomposed
3	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd_2(dba)_3{\cdot}CHCl_3$	*rac*-BINAP	60 / 2	50
4	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd_2(dba)_3{\cdot}CHCl_3$	(*R*)-Segphos	60 / 12	12
5	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd_2(dba)_3{\cdot}CHCl_3$	dppp	60 / 12	12
6	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd_2(dba)_3{\cdot}CHCl_3$	dppb	60 / 12	30
7	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd_2(dba)_3{\cdot}CHCl_3$	dppf	60 / 12	20
8	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd_2(dba)_3{\cdot}CHCl_3$	xantphos	60 / 2	72
9	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd_2(dba)_3$	xantphos	60 / 2.5	15
10	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd(OAc)_2$	xantphos	60 / 1	74
11	$Rh_2(TMA)_4$ (2)	120 / 0.5	$Pd_2(dba)_3{\cdot}CHCl_3$	xantphos	80 / 1	61
12[c]	$Rh_2(TMA)_4$ (4)	90 / 1	$Pd_2(dba)_3{\cdot}CHCl_3$	xantphos	60 / 2	72

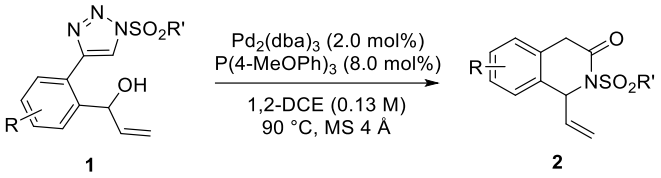
[a]Reaction conditions: **1a** (0.2 mmol) $Rh_2(TMA)_4$ (4.0×10^{-3} mmol) and MS 4 Å in toluene (1.0 ml) at designated temperature. [b]Isolated yield of the *cis* and *trans* mixture. [c]The reaction conditions with 4 mol% $Rh_2(TMA)_4$ at 90 °C were more suitable for other substrates than with 2 mol% $Rh_2(TMA)_4$ at 120 °C.

6. All in One-Pot Rh(II)/Pd(0) Catalysis of 1a for the Synthesis of 3a.



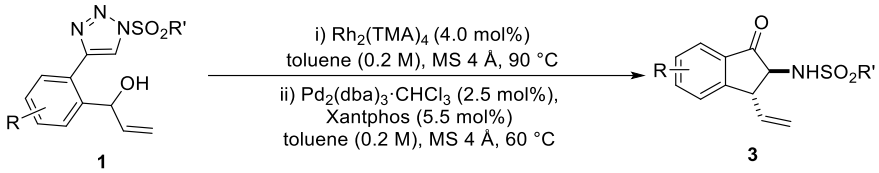
To a flame-dried vial equipped with a stirrer bar was added $Rh_2(TMA)_4$ (4.9 mg, 8.0×10^{-3} mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (5.5 mg, 5.0×10^{-3} mmol), Xantphos (6.4 mg, 1.1×10^{-2} mmol), MS 4 Å, triazole **1a** (0.2 mmol), and toluene (1 mL, 0.2 M) then the vial was sealed by the cap in a glove box. The solution was stirred and heated to 120 °C for 1 h. The diastereomeric ratio of **3a** was determined by ^{1}H NMR of crude mixture (*trans*:*cis*=10:1). The reaction mixture was purified by column chromatography to afford the products **2a** (8%) and **3a** (53%).

7. General Procedure for the Synthesis of 2.



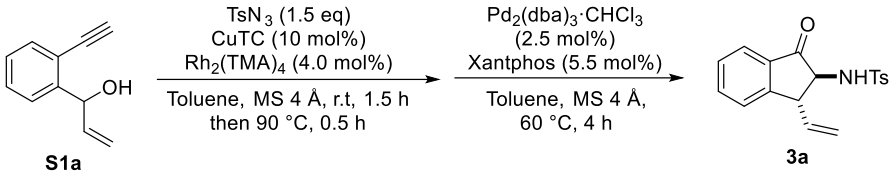
In a glovebox, a flame-dried vial equipped with a stir bar was charged with $Pd_2(dba)_3$ (3.7 mg, 4.0 x 10^{-3} mmol), $P(4\text{-MeOPh})_3$ (5.6 mg, 1.6 x 10^{-2} mmol), MS 4 Å and triazole **1** (0.2 mmol), then sealed by the pressure tube cap. To that mixture, 1,2-DCE (1.5 ml, 0.13 M) was added. The solution was heated at 90 °C until all triazole **1** was consumed (determined by TLC analysis). After being cooled to room temperature, the crude mixture was concentrated under reduced pressure. The residue was purified by column chromatography to afford the corresponding 1,4-dihydro-isoquinolin-3(2*H*)-one **2**.

8. General Procedure for Synthesis of 3.



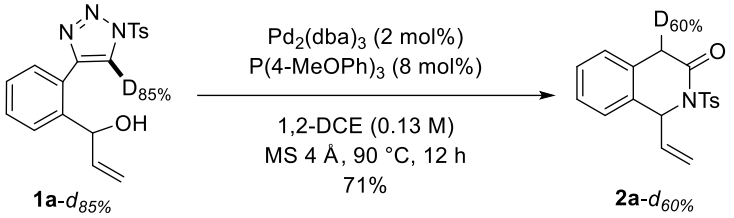
In a glovebox, a flame-dried vial equipped with a stirrer bar was charged with $Rh_2(TMA)_4$ (4.9 mg, 8.0 x 10^{-3} mmol), MS 4 Å, triazole (0.2 mmol) and toluene (1.0 mL, 0.2 M), then the vial was sealed by the cap. The solution was stirred and heated until all triazole **1** was consumed (determined by TLC). After cooled to room temperature, the reaction mixture was moved to a glovebox and charged with $Pd_2(dba)_3{\cdot}CHCl_3$ (5.5 mg, 5.0 x 10^{-3} mmol), and Xantphos (6.4 mg, 1.1 x 10^{-2} mmol). The solution was stirred at 60 ℃ until the reaction was completed. The crude mixture was purified by column chromatography to afford the corresponding 2-aminoindanone **3**.

9. General Procedure for Tandem Synthesis of 3a.



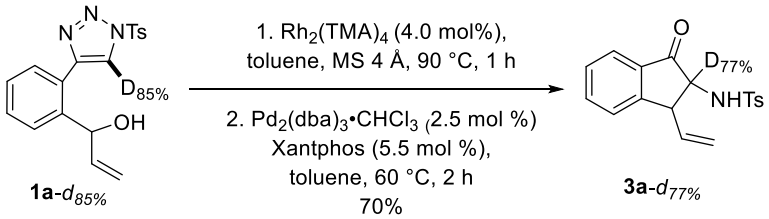
A solution of **S1a** (47 mg, 0.3 mmol, 1.0 equiv), tosyl azide (71 mg, 0.36 mmol, 1.2 equiv), CuTC (2.9 mg, TC= thiophene-2-carboxylate), $Rh_2(TMA)_4$ (7.3 mg, 1.2 x 10^{-2} mmol), and MS 4 Å in toluene (1.5 mL, 0.2 M) was stirred for 1.5 h at room temperature. Then, the mixture was heated to 90 °C for 0.5 h. After cooled to room temperature, the reaction mixture was moved to a glovebox and charged with $Pd_2dba_3{\cdot}CHCl_3$ (7.8 mg, 7.5 x 10^{-3} mmol), and Xantphos (9.5 mg, 1.65 x 10^{-2} mmol). The solution was stirred at 60 °C for 4 h, then the crude mixture was purified by column chromatography to afford the corresponding **3a** in 45 % overall yield.

10. Deuterium Labeling Experiment.



1a-$d_{85\%}$ **2a**-$d_{60\%}$

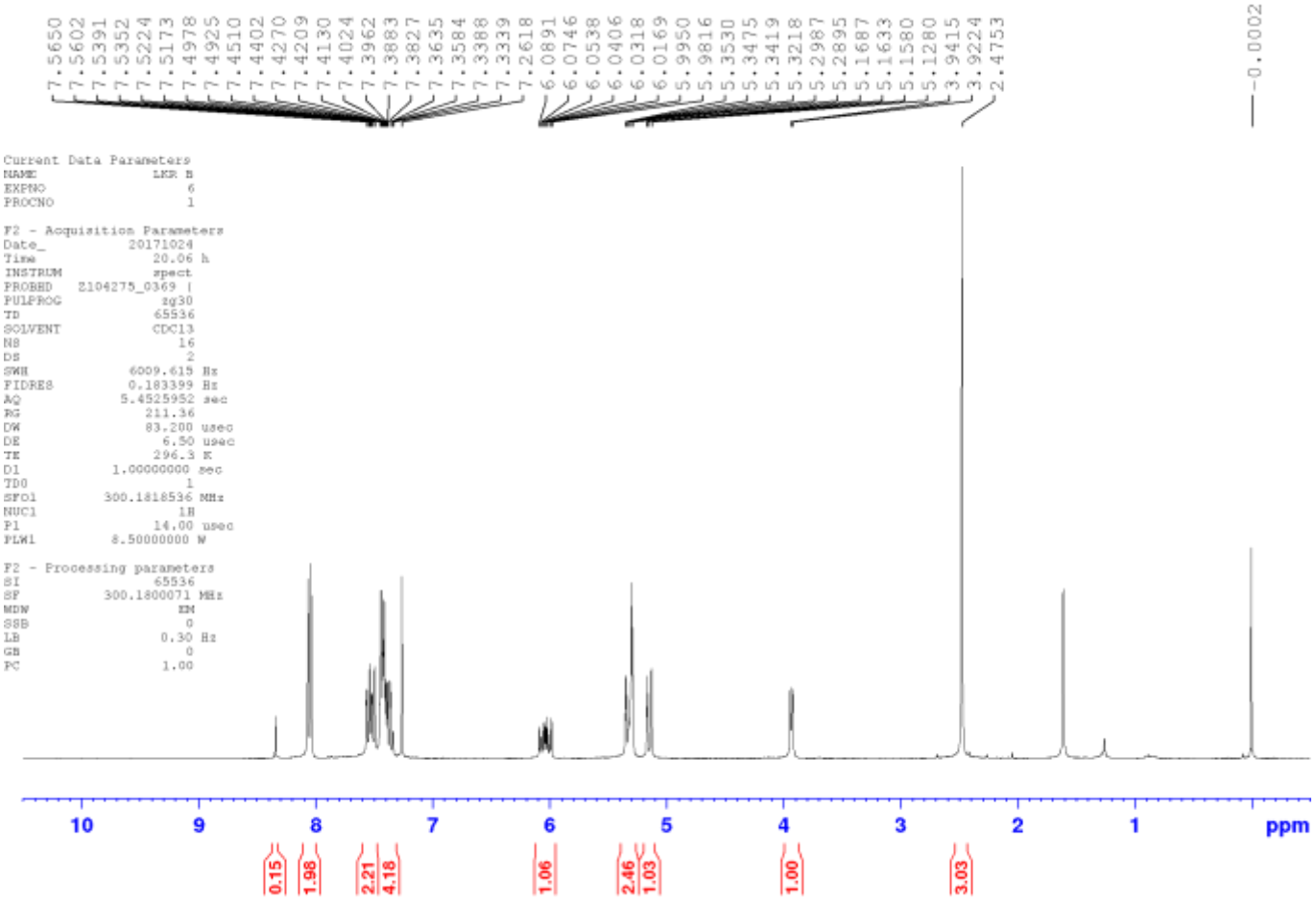
Deuterium labelled **2a**-$d_{60\%}$ was produced from **1a**-$d_{85\%}$ according to the general procedure.



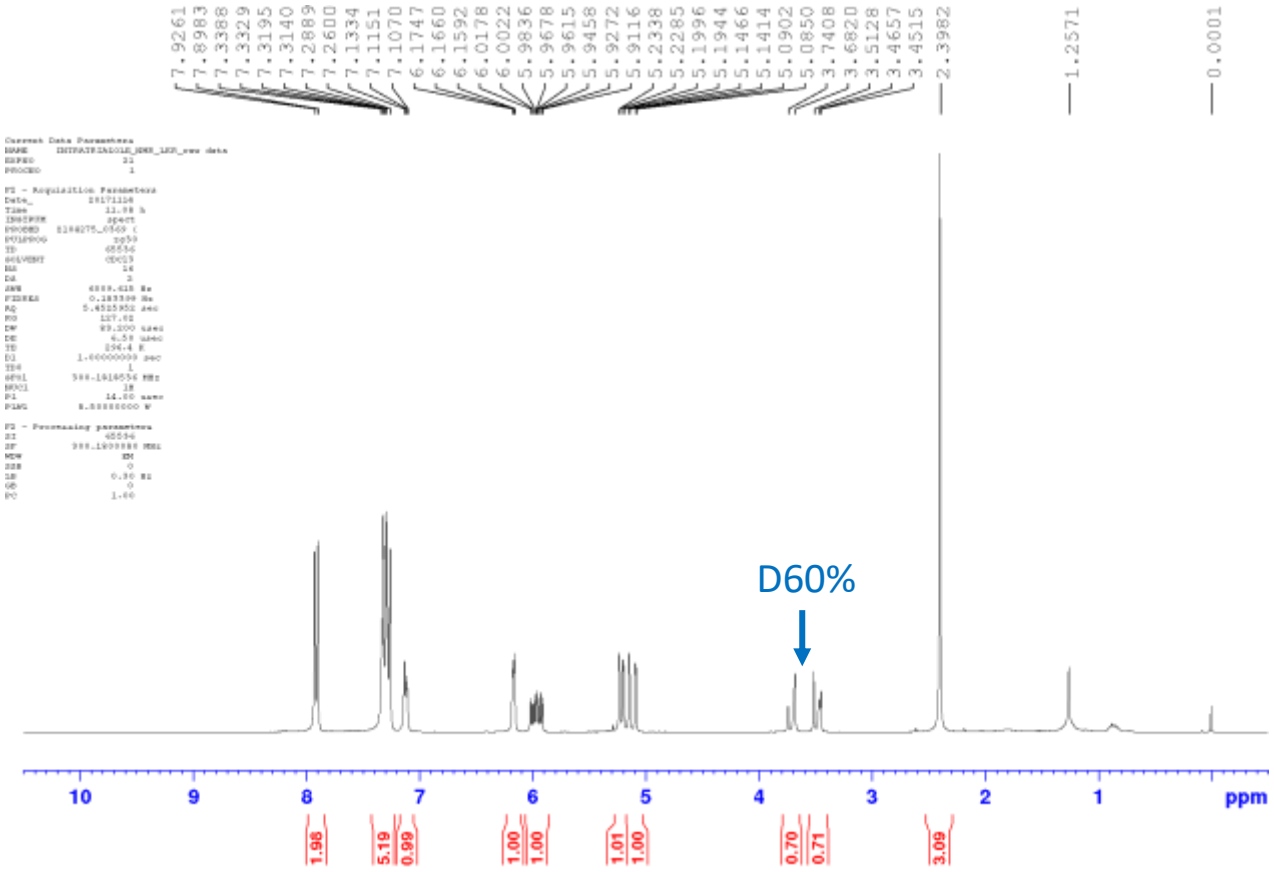
1a-$d_{85\%}$ **3a**-$d_{77\%}$

Deuterium labelled **3a**-$d_{77\%}$ was produced from **1a**-$d_{85\%}$ according to the general procedure. The deuterium incorporation was observed by only in ^{1}H NMR of the crude mixture since proton exchange occured while conducting column chromatography.

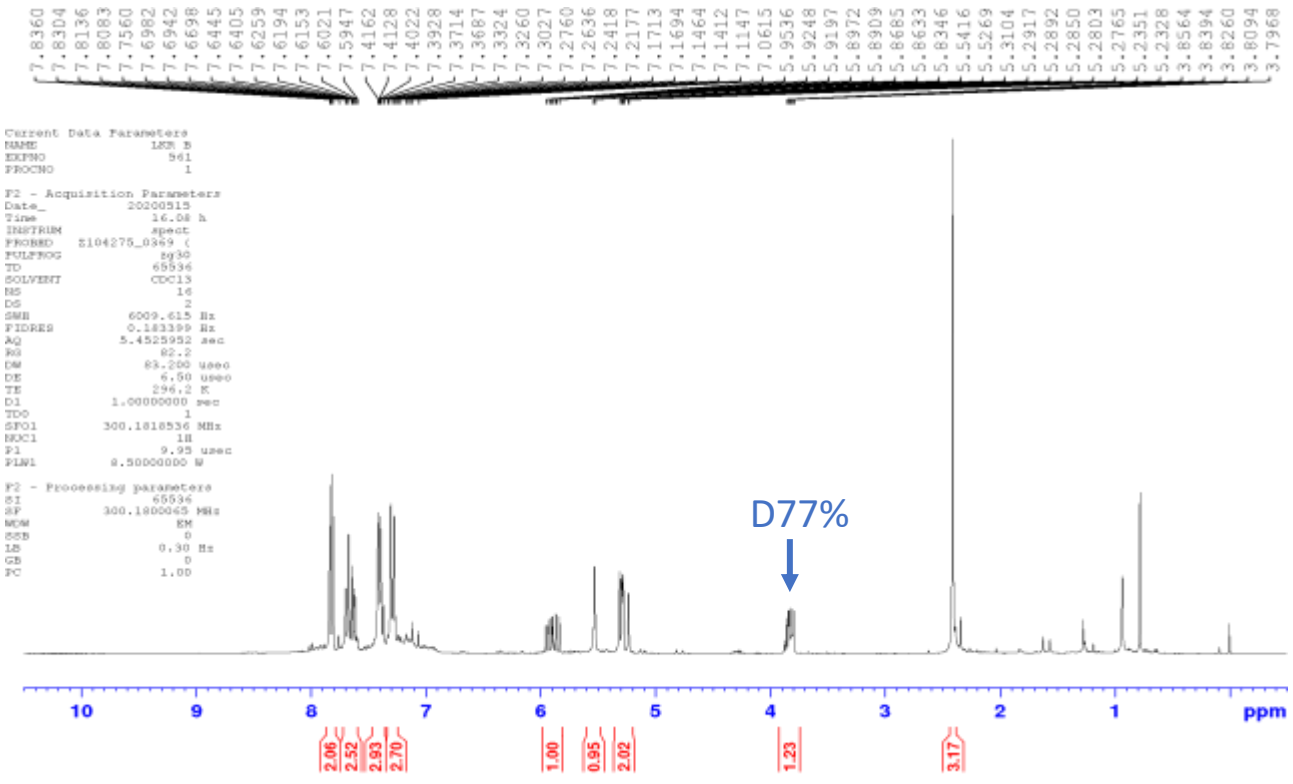
Copies of ^{1}H spectra of compound **1a**-$d_{85\%}$



Copies of ^{1}H spectra of compound **2a**-$d_{60\%}$

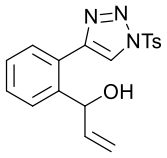


Copies of ^{1}H spectra of crude mixture of compound **3a**-$d_{77\%}$



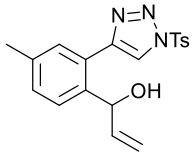
11. Characterization Data

1-{2-[1-(4-Methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl}prop-2-en-1-ol (1a).



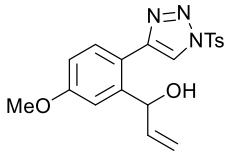
Yield: 75%; Eluent: *n*-hexane/ethyl acetate = 4/1; White solid; mp: 100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 1H), 3.94 (brs, O–H), 5.09–5.20 (m, 1H), 5.26–5.39 (m, 2H), 5.96–6.12 (m, 1H), 7.32–7.47 (m, 4H), 7.47–7.60 (m, 2H), 8.00–8.09 (m, 2H), 8.34 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.0, 71.8, 115.2, 121.6, 127.9, 128.3, 128.7, 129.0, 129.8, 130.0, 130.7, 132.9, 138.7, 141.1, 147.0, 147.8 ppm; HRMS (EI) Calcd *m/z* for $C_{18}H_{17}N_3O_3S$ $[M]^+$: 355.0991. Found: 355.0989.

1-{4-Methyl-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl}prop-2-en-1-ol (1b).



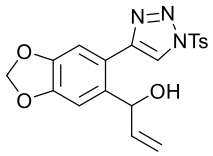
Yield: 70%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 98–100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.47 (s, 3H), 3.89 (brs, O–H), 5.08–5.16 (m, 1H), 5.22–5.35 (m, 2H), 5.94–6.10 (m, 1H), 7.21 (dd, *J* = 7.9 Hz, *J* = 1.2 Hz, 1H), 7.30–7.37 (m, 1H), 7.38–7.46 (m, 3H), 8.00–8.10 (m, 2H), 8.35 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.1, 22.0, 71.6, 115.0, 121.5, 127.7, 128.7, 128.9, 130.4, 130.6, 130.7, 133.0, 138.1, 138.2, 138.9, 147.0, 147.7 ppm; HRMS (EI) Calcd *m/z* for $C_{19}H_{19}N_3O_3S$ $[M]^+$: 369.1147. Found: 369.1144.

1-{5-Methoxy-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl}prop-2-en-1-ol (1c).



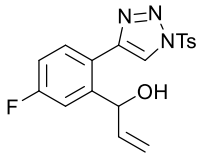
Yield: 50%; Eluent: *n*-hexane/ethyl acetate = 2/1; Yellow sticky solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.83 (s, 3H), 4.00–4.13 (m, 1H), 5.07-5.21 (m, 1H), 5.21–5.39 (m, 2H), 5.91–6.11 (m, 1H), 6.89 (dd, *J* = 8.6 Hz, *J* = 2.7 Hz, 1H), 7.07 (d, *J* = 2.7 Hz, 1H), 7.38–7.47 (m, 3H), 8.00–8.09 (m, 2H), 8.26 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.0, 55.5, 71.8, 113.7, 114.0, 115.3, 120.2, 120.9, 128.9, 130.7, 131.3, 133.0, 138.5, 142.8, 146.9, 147.7, 160.6 ppm; HRMS (EI) Calcd *m/z* for $C_{19}H_{19}N_3O_4S$ $[M]^+$: 385.1096. Found: 385.1093.

1-{6-[1-(4-Methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]-2H-1,3-benzodioxol-5-yl}prop-2-en-1-ol (1d).



Yield: 35%; Eluent: *n*-hexane/ethyl acetate = 2/1; Yellow solid; mp: 101–103 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.53–3.70 (m, O–H), 5.09–5.26 (m, 2H), 5.26–5.45 (m, 1H), 5.92–6.07 (m, 3H), 6.98 (d, *J* = 19.7, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.96–8.15 (m, 2H), 8.27 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.0, 71.0, 101.8, 108.7, 109.6, 115.2, 121.2, 129.0, 130.7, 133.0, 135.8, 138.7, 146.6, 147.5, 147.8, 148.8 ppm; HRMS (FAB) Calcd *m/z* for $C_{19}H_{18}N_3O_5S$ $[M+H]^+$: 400.0967. Found: 400.0965.

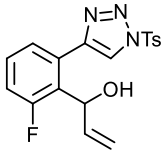
1-{5-Fluoro-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl}prop-2-en-1-ol (1e).



Yield: 69%; Eluent: *n*-hexane/ethyl acetate = 4/1; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.98 (brs, O–H), 5.12–5.22 (m, 1H), 5.25–5.35 (m, 2H), 5.88–6.09 (m, 1H), 6.98–7.07 (m, 1H), 7.22–7.29 (m, 1H), 7.41–7.45 (d, *J* = 8.1 Hz, 2H), 7.48 (dd, *J* = 8.5 Hz, *J* = 5.6 Hz, 1H), 7.99–8.08 (m, 2H), 8.33 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.0, 71.1 (d, *J* = 1.0 Hz), 115.2 (d, *J* = 22.0 Hz), 115.5 (d, *J* = 22.6 Hz), 115.8, 121.5, 123.8 (d, *J* = 3.3 Hz), 128.9, 130.7, 131.8 (d, *J* =

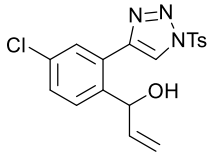
8.4 Hz), 132.8, 138.0, 143.8 (d, *J* = 6.9 Hz), 146.0, 147.9, 163.3 (d, *J* = 249.8 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.10 – -111.02 (m) ppm; HRMS (EI) Calcd *m/z* for $C_{18}H_{16}FN_3O_3S$ $[M]^+$: 373.0896. Found: 373.0894.

1-(2-Fluoro-6-(1-tosyl-1H-1,2,3-triazol-4-yl)phenyl)prop-2-en-1-ol (1f).



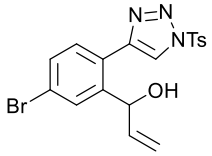
Yield: 50%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H), 4.76–4.89 (m, 1H), 4.96–5.11 (m, 1H), 5.59–5.72 (m, 1H), 5.81–5.99 (m, 1H), 7.09–7.21 (m, 1H), 7.22–7.28 (m, 1H), 7.29–7.38 (m, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 8.00–8.10 (m, 2H), 8.28 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.0, 67.7 (d, *J* = 6.4 Hz), 114.8, 117.1 (d, *J* = 24.3 Hz), 122.1, 126.3 (d, *J* = 3.3 Hz), 128.9(6) (d, *J* = 13.8 Hz), 128.9(7), 129.5 (d, *J* = 9.8 Hz), 129.8 (d, *J* = 4.2 Hz), 130.7, 132.8, 138.6 (d, *J* = 1.7 Hz), 146.4 (d, *J* = 3.3 Hz), 147.9, 161.4 (d, *J* = 247.0 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.60 – -114.54 (m) ppm; HRMS (FAB) Calcd *m/z* for $C_{18}H_{17}FN_3O_3S$ $[M+H]^+$: 374.0975. Found: 374.0978.

1-{4-Chloro-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl}prop-2-en-1-ol (1g).



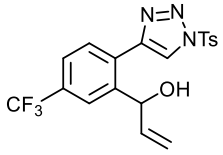
Yield: 72%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 110–115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.78 (brs, O–H), 5.12–5.22 (m, 1H), 5.24–5.39 (m, 2H), 5.93–6.08 (m, 1H), 7.34–7.40 (m, 1H), 7.42 (s, 1H), 7.45 (s, 1H), 7.47–7.54 (m, 2H), 8.00–8.11 (m, 2H), 8.37 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.0, 71.1, 115.6, 122.0, 129.0, 129.5, 129.6, 130.2, 130.8, 132.8, 133.9, 138.3, 139.5, 145.6, 148.0 ppm; HRMS (EI) Calcd *m/z* for $C_{18}H_{16}{}^{35}ClN_3O_3S$ $[M]^+$: 389.0601. Found: 389.0604.

1-{5-Bromo-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl}prop-2-en-1-ol (1h).



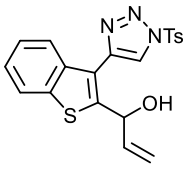
Yield: 76%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 108–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.83 (d, *J* = 5.4 Hz, O-H), 5.15–5.26 (m, 1H), 5.25–5.31 (m, 1H), 5.31–5.41 (m, 1H), 5.91–6.11 (m, 1H), 7.36–7.40 (m, 1H), 7.42 (s, 1H), 7.44 (s, 1H), 7.50 (dd, *J* = 8.3 Hz, *J* = 2.1 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 8.00–8.11 (m, 2H) 8.35 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.1, 71.2, 116.0, 121.6, 124.1, 126.8, 129.0, 130.8, 131.3, 131.4, 131.8, 132.8, 137.9, 143.1, 146.0, 148.0 ppm; HRMS (EI) Calcd *m/z* for $C_{18}H_{16}{}^{79}BrN_3O_3S$ $[M]^+$: 433.0096. Found: 433.0097.

1-(2-(1-Tosyl-1H-1,2,3-triazol-4-yl)-5-(trifluoromethyl)phenyl)prop-2-en-1-ol (1i).



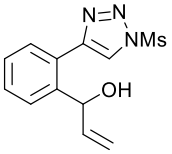
Yield: 72%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 119–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.77 (d, *J* = 5.3 Hz, 1H), 5.18–5.30 (m, 1H), 5.32–5.46 (m, 2H), 5.92–6.14 (m, 1H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.51–7.69 (m, 2H), 7.83 (s, 1H), 8.00–8.18 (m, 2H), 8.42 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 22.1, 71.2, 116.2, 122.1, 122.3, 125.0–125.1 (m), 125.6–125.7 (m), 129.1, 130.3, 130.8, 131.4, 130.3–131.8 (m), 132.7, 137.8, 141.9, 145.6, 148.1 δ ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.77 ppm; HRMS (EI) Calcd *m/z* for $C_{19}H_{16}F_3N_3O_3S$ $[M]^+$: 424.0943. Found: 424.0946.

1-(3-(1-tosyl-1H-1,2,3-triazol-4-yl)benzo[b]thiophen-2-yl)prop-2-en-1-ol (1j).



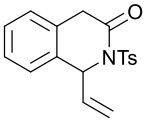
Yield: 70%; Eluent: *n*-hexane/ethyl acetate = 4/1; Brown solid; mp: 148–156 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (s, 1H), 5.17–5.29 (m, 1H), 5.32–5.42 (m, 2H), 7.36–7.50 (m, 2H), 7.53–7.62 (m, 2H), 8.36 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.7, 71.6, 115.2, 121.5, 127.5, 128.3, 128.6, 129.8, 129.9, 138.6, 140.8, 146.8 ppm; HRMS (FAB) Calcd *m/z* for $C_{20}H_{18}N_3O_3S_2$ $[M+H]^+$: 412.0790. Found: 412.0787.

1-{2-(1-(Methylsulfonyl)-1H-1,2,3-triazol-4-yl)phenyl}prop-2-en-1-ol (1k).



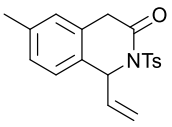
Yield: 45%; Eluent: *n*-hexane/ethyl acetate = 4/1; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (s, 3H), 5.20–5.26 (m, 1H), 5.33–5.42 (m, 2H), 6.03–6.16 (m, 1H), 7.36–7.50 (m, 2H), 7.53–7.62 (m, 2H), 8.36 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.7, 71.6, 115.2, 121.5, 127.5, 128.3, 128.6, 129.8, 129.9, 138.6, 140.9, 146.8 ppm; HRMS (FAB) Calcd *m/z* for $C_{12}H_{14}N_3O_3S$ $[M+H]^+$: 280.0756. Found: 280.0758.

2-(Toluene-4-sulfonyl)-1-vinyl-1,4-dihydro-2H-isoquinolin-3-one (2a).



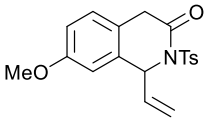
Yield: 80%; Eluent: *n*-hexane/ethyl acetate = 6/1; Light yellow solid; mp: 145–146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.48 (d, *J* = 18.5 Hz, 1H), 3.71 (dd, *J* = 18.4 Hz, *J* = 1.1 Hz, 1H), 5.12 (dd, *J* = 17.0 Hz, *J* = 1.4 Hz, 1H), 5.17–5.28 (m, 1H), 5.97 (ddd, *J* = 16.9 Hz, *J* = 10.3 Hz, *J* = 4.7 Hz, 1H), 6.13–6.20 (m, 1H), 7.04–7.19 (m, 1H), 7.22–7.40 (m, 5H), 7.84–8.00 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 39.5, 62.5, 116.7, 126.3, 127.6, 127.7, 128.6, 129.2, 129.4, 130.9, 133.6, 135.1, 136.0, 145.1, 169.0 ppm; HRMS (FAB) *m/z* Calcd for $[M+H]^+$: $C_{18}H_{18}NO_3S$: 328.1007. Found: 328.1009.

1-Ethenyl-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2b).



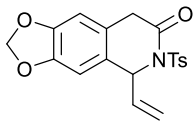
Yield: 88%; Eluent: *n*-hexane/ethyl acetate = 4/1 to 2/1; White solid; mp: 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 1H), 2.39 (s, 1H), 3.42 (d, *J* = 18.4 Hz, 1H), 3.68 (d, *J* = 18.4 Hz, 1H), 5.11 (dd, *J* = 16.9 Hz, *J* = 1.6 Hz, 1H), 5.19 (dd, *J* = 10.2 Hz, *J* = 1.6 Hz, 1H), 5.88–6.03 (m, 1H), 6.09–6.17 (m, 1H), 6.93 (s, 1H), 7.07–7.15 (m, 1H), 7.18–7.24 (m, 1H), 7.25 (m, 1H), 7.28 (m, 1H), 7.85–7.95 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.2, 21.7, 39.5, 62.4, 116.4, 126.2, 128.2(6), 128.2(9), 129.1, 129.3, 130.6, 130.8, 135.4, 136.0, 138.6, 145.0, 169.2 ppm; HRMS (EI) *m/z* Calcd for $C_{19}H_{19}NO_3S$ $[M]^+$: 341.1086. Found: 341.1083.

1-Ethenyl-7-methoxy-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2c).



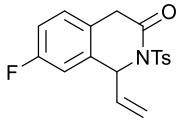
Reaction temperature: 100 °C; Yield: 50%; Eluent: *n*-hexane/ethyl acetate = 4/1; Light yellow solid; mp: 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 1H), 3.43 (d, *J* = 18.4 Hz, 1H), 3.63 (d, *J* = 18.4 Hz, 1H), 3.83 (s, 1H), 5.14 (dd, *J* = 16.9 Hz, *J* = 1.6 Hz, 1H), 5.22 (dd, *J* = 10.2 Hz, *J* = 1.6 Hz, 1H), 5.95 (ddd, *J* = 16.9 Hz, *J* = 10.3 Hz, *J* = 4.7 Hz, 1H), 6.06–6.15 (m, 1H), 6.78–6.90 (m, 2H), 6.99–7.07 (m, 1H), 7.23–7.33 (m, 2H), 7.85–7.95 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 38.8, 55.6, 62.6, 111.9, 114.2, 116.8, 122.7, 128.8, 129.2, 129.4, 134.7, 135.0, 136.1, 145.1, 159.1, 169.3 ppm; HRMS (EI) *m/z* Calcd for $C_{19}H_{19}NO_4S$ $[M]^+$: 357.1035. Found: 357.1032.

5-Ethenyl-6-[(4-methylphenyl)sulfonyl]-5,8-dihydro[1,3]dioxolo[4,5-g]isoquinolin-7(6H)-one (2d).



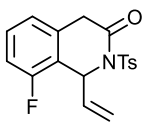
Yield: 50%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow green solid; mp: 176–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 1H), 3.36 (d, *J* = 18.5 Hz, 1H), 3.61 (d, *J* = 18.4 Hz, 1H), 5.06–5.17 (m, 1H), 5.17–5.25 (m, 1H), 5.85–5.96 (m, 1H), 5.96–6.00 (m, 2H), 6.00–6.07 (m, 1H), 6.57 (s, 1H), 6.79 (s, 1H), 7.20–7.38 (m, 2H), 7.80–8.01 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 39.4, 62.3, 101.6, 106.9, 108.0, 116.5, 124.3, 126.9, 129.1, 129.4, 135.0, 136.0, 145.1, 147.2, 148.0, 168.9 ppm; HRMS (EI) *m/z* Calcd for $C_{19}H_{17}NO_5S$ $[M]^+$: 371.0827. Found: 371.0825.

1-Ethenyl-7-fluoro-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2e).



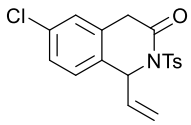
Yield: 64%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 138–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 1H), 3.47 (d, *J* = 18.4 Hz, 1H), 3.65 (d, *J* = 18.5 Hz, 1H), 5.13 (dd, *J* = 16.9 Hz, *J* = 1.7 Hz, 1H), 5.25 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 5.87–6.01 (m, 1H), 6.06–6.20 (m, 1H), 6.91–7.13 (m, 3H), 7.25–7.33 (m, 2H), 7.83–8.01 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 38.9, 62.1, 113.5 (d, *J* = 22.8 Hz), 115.7 (d, *J* = 21.6 Hz), 117.2, 126.7 (d, *J* = 3.2 Hz), 129.2, 129.3, 129.4 134.5, 135.5 (d, *J* = 7.6 Hz), 135.8, 145.3, 162.0 (d, *J* = 247.4 Hz), 168.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.21 – -114.13 (m) ppm; HRMS (EI) *m/z* Calcd for $C_{18}H_{16}FNO_3S$ $[M]^+$: 345.0835. Found: 345.0837.

1-Ethenyl-8-fluoro-2-[-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2f).



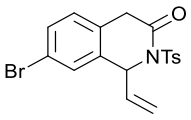
Yield: 30%; Eluent: *n*-hexane/ethyl acetate = 6/1; Orange solid; mp: 138–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 1H), 3.52 (d, *J* = 18.5 Hz, 1H), 3.70 (d, *J* = 18.5 Hz, 1H), 5.18 (dd, *J* = 17.0 Hz, *J* = 1.6 Hz, 1H), 5.26 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 5.95 (ddd, *J* = 16.9 Hz, *J* = 10.3 Hz, *J* = 4.8 Hz, 1H), 6.46 – 6.59 (m, 1H), 6.87 – 6.97 (m, 1H), 6.99 – 7.11 (m, 1H), 7.23 – 7.33 (m, 3H), 7.89 – 7.99 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 39.2, 56.0 (d, *J* = 3.3 Hz), 114.4 (d, *J* = 21.0 Hz), 117.0, 121.2 (d, *J* = 16.4 Hz), 123.2 (d, *J* = 3.5 Hz), 129.3 (d, *J* = 8.1 Hz), 130.2 (d, *J* = 8.3 Hz), 133.5(8), 133.6(1), 135.8, 145.3, 158.4 (d, *J* = 249.1 Hz), 168.5 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -119.74 – -119.69 (m) ppm; HRMS (FAB) Calcd *m/z* for $C_{18}H_{17}FN_3O_3S$ $[M]^+$: 346.0913. Found: 346.0910.

6-Chloro-1-ethenyl-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2g).



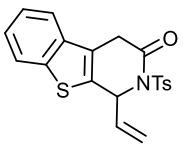
Reaction temperature: 100 °C; Yield: 41%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 132–134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 1H), 3.45 (d, *J* = 18.5 Hz, 1H), 3.69 (d, *J* = 18.5 Hz, 1H), 5.11 (dd, *J* = 17.0 Hz, *J* = 1.7 Hz, 1H), 5.24 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 5.87–6.02 (m, 1H), 6.08–6.20 (m, 1H), 7.13 (brs, 1H), 7.25–7.33 (m, 4H), 7.82–7.99 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 39.2, 61.9, 117.0, 127.7, 127.7(8), 127.8(3), 129.2, 129.4, 132.1, 132.9, 134.5, 134.7, 135.8, 145.3, 168.2 ppm; HRMS (FAB) *m/z* Calcd for $C_{18}H_{17}{}^{35}ClNO_3S$ $[M]^+$: 362.0618. Found: 362.0621; $C_{18}H_{17}{}^{37}ClNO_3S$ $[M+2]^+$: 364.0593. Found: 364.0612.

7-bromo-1-ethenyl-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2h).



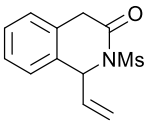
Reaction temperature: 100 ℃; Yield: 76%; Eluent: *n*-hexane/ethyl acetate = 4/1; White solid; mp: 177–179 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 1H), 3.45 (d, *J* = 18.5 Hz, 1H), 3.63 (d, *J* = 18.3 Hz, 1H), 5.14 (dd, *J* = 16.9 Hz, *J* = 1.7 Hz, 1H), 5.25 (dd, *J* = 10.3 Hz, *J* = 1.7 Hz, 1H), 5.94 (ddd, *J* = 16.9 Hz, *J* = 10.3 Hz, *J* = 4.7 Hz, 1H), 6.07–6.16 (m, 1H), 6.97–7.04 (m, 1H), 7.26–7.34 (m, 2H), 7.40–7.46 (m, 1H), 7.46–7.53 (m, 1H), 7.84–7.99 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 39.1, 61.9, 117.3, 121.3, 129.2, 129.3, 129.3(7), 129.4(4), 130.0, 131.7, 134.5, 135.6, 135.8, 145.3, 168.3 ppm; HRMS (FAB) *m/z* Calcd for $C_{18}H_{17}{}^{79}BrNO_3S$ $[M]^+$: 406.0113. Found: 406.0114; $C_{18}H_{17}{}^{81}BrNO_3S$ $[M]^+$: 408.0093. Found: 408.0134.

2-Tosyl-1-vinyl-1,4-dihydrobenzo[4,5]thieno[2,3-c]pyridin-3(2H)-one (2j).



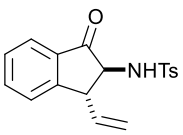
Yield: 24%; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 198–200 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 1H), 3.63 (dd, *J* = 20.4 Hz, *J* = 1.4 Hz, 1H), 3.84 (d, *J* = 20.4 Hz, 1H), 5.28–5.36 (m, 1H), 5.36–5.48 (m 1H), 5.91–6.11 (m, 1H), 6.23–6.37 (m, 1H), 7.29–7.34 (m, 2H), 7.34–7.43 (m, 2H), 7.50–7.59 (m, 1H), 7.79–7.90 (m, 1H), 7.91–8.01 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 33.7, 59.4, 117.9, 121.1,123.0, 124.9, 125.4, 125.7, 129.3, 129.4, 132.6, , 135.8, 135.9, 137.0, 140.2, 145.2, 167.8 ppm; HRMS (FAB) Calcd *m/z* for $C_{20}H_{18}NO_3S_2$ $[M+H]^+$: 384.0728. Found: 384.0729.

1-Ethenyl-2-(methylsulfonyl)-1,4-dihydroisoquinolin-3(2H)-one (2k).



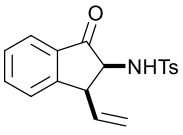
Yield: 64%; Eluent: *n*-hexane/ethyl acetate = 4/1 ; Light yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.39 (s, 3H), 3.67 (d, *J* = 18.6 Hz, 1H), 3.83 (d, *J* = 18.6 Hz, 1H), 5.07–5.31 (m, 2H), 5.82–6.03 (m, 2H), 7.14–7.25 (m, 1H), 7.25–7.40 (m, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 39.4, 42.6, 61.9, 116.8, 126.5, 127.7, 127.8, 128.8, 130.8, 133.2, 134.8, 170.5 ppm; HRMS (EI) *m/z* Calcd for $C_{12}H_{13}NO_3S$ $[M]^+$: 251.0616. Found: 251.0614.

***N*-[1-Ethenyl-3-oxo-2,3-dihydro-1H-inden-2-yl]-4-methylbenzene-1-sulfonamide (3a)**.



trans-**3a**

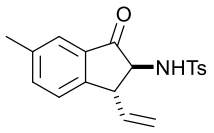
Yield: 72%; d.r > 99:1; Eluent: *n*-hexane/ethyl acetate = 4/1; White solid; mp: 135–138 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.78–3.90 (m, 2H), 5.22–5.39 (m, 3H), 5.84–6.01 (m, 1H), 7.31 (d, *J* = 8.1Hz, 2H), 7.38–7.48 (m, 2H), 7.62–7.76 (m, 2H), 7.83 (d, *J* = 8.3, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 51.4, 65.2, 119.2, 124.3, 126.6, 127.8, 128.7, 129.8, 133.2, 136.2(0), 136.2(4), 136.6, 144.0, 152.9, 200.5 ppm. HRMS (EI) Calcd *m/z* for $C_{18}H_{17}NO_3S$ $[M]^+$: 327.0929. Found: 327.0930.



cis-**3a**

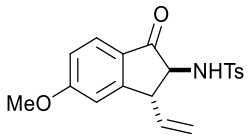
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 4.22–4.26 (m, 1H), 4.32–4.37 (m, 1H), 4.80 (dt, *J* = 17.1 Hz, *J* = 1.2 Hz, 1H), 5.08–5.21 (m, 2H), 5.70–5.83 (m, 1H), 7.28–7.36 (m, 2H), 7.39–7.49 (m, 2H), 7.62–7.76 (m, 2H), 7.80–7.88 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 48.0, 62.9, 118.6, 124.4, 127.5(5), 127.5(7), 128.8, 129.9, 133.2, 136.1, 136.5, 136.6, 144.0, 152.8, 200.4 ppm. HRMS (EI) Calcd *m/z* for $C_{18}H_{17}NO_3S$ $[M]^+$: 327.0929. Found: 327.0930.

***N*-[1-Ethenyl-5-methyl-3-oxo-2,3-dihydro-1H-inden-2-yl]-4-methylbenzene-1-sulfonamide (3b)**.



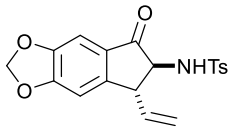
Yield: 71%; d.r > 99:1; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 127–129 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.42 (s, 3H), 3.72–3.86 (m, 2H), 5.29–5.33 (m, 2H), 5.39 (d, *J* = 4.5 Hz, 1H), 5.80–5.97 (m, 1H), 7.25–7.36 (m, 3H), 7.43–7.53 (m, 2H), 7.77–7.88 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.2, 21.7, 51.0, 65.4, 118.8, 124.1, 126.2, 127.7, 129.7, 133.3, 136.4, 136.7, 137.4, 138.8, 143.8, 150.3, 200.5 ppm. HRMS (EI) Calcd *m/z* for $C_{19}H_{19}NO_3S$ $[M]^+$: 341.1086. Found: 341.1083.

***N*-(3-Ethenyl-5-methoxy-1-oxo-2,3-dihydro-1H-inden-2-yl)-4-methylbenzene-1-sulfonamide (3c)**.



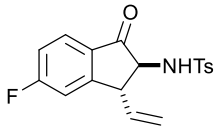
6.0 mol% of $Rh_2(TMA)_4$ was used at 60 ℃; Yield: 65%; d.r > 99:1; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 90–92 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.71–3.84 (m, 2H), 3.88 (s, 3H), 5.24–5.39 (m, 2H), 5.81–5.99 (m, 1H), 6.77– 6.87 (m, 1H), 6.89–6.97 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.78–7.87 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 51.5, 55.8, 64.9, 109.6, 116.9, 119.2, 126.1(8), 126.1(9), 127.8, 129.8, 136.3, 136.4, 143.9, 156.4, 166.6, 198.3 ppm; HRMS (EI) Calcd *m/z* for $C_{19}H_{19}NO_4S$ $[M]^+$: 357.1035. Found: 357.1033.

***N*-(5-Ethenyl-7-oxo-6,7-dihydro-2H,5H-indeno[5,6-d][1,3]dioxol-6-yl)-4-methylbenzene-1-sulfonamide (3d)**.



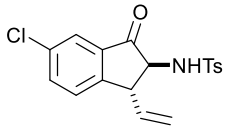
6.0 mol% of $Rh_2(TMA)_4$ was used at 60 ℃; Yield: 51%, d.r = 91:9; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 170–172 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.65–3.82 (m, 2H), 5.18–5.40 (m, 3H), 5.79–5.94 (m, 1H), 6.08 (s, 2H), 6.77 (s, 1H), 7.03 (s, 1H), 7.28–7.36 (m, 2H), 7.78–7.86 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 51.3, 65.1, 102.6, 102.7, 105.9, 119.1, 127.7, 127.8, 129.8, 136.3(6), 136.4(2), 144.0, 149.2, 151.3, 155.6, 198.1 ppm; HRMS (EI) Calcd *m/z* for $C_{19}H_{17}NO_5S$ $[M]^+$: 371.0827. Found: 371.0827.

***N*-(3-Ethenyl-5-fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)-4-methylbenzene-1-sulfonamide (3e)**.



Yield: 78%; d.r > 99:1; Eluent: *n*-hexane/ethyl acetate = 4/1; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.77–3.90 (m, 2H), 5.22–5.42 (m, 3H), 5.82–5.99 (m, 1H), 7.05–7.17 (m, 2H), 7.32(d, *J* = 8.0 Hz, 2H), 7.68–7.79 (m, 1H), 7.79–7.87 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 51.3 (d, *J* = 7.5 Hz), 65.2, 113.5 (d, *J* = 22.6 Hz), 117.2 (d, *J* = 24.0 Hz), 119.8, 126.8, 126.9 (d, *J* = 10.4 Hz), 127.8, 129.6 (d, *J* = 2.0 Hz), 129.8, 135.6, 136.5, 144.1, 156.2 (d, *J* = 9.9 Hz), 168.1 (d, *J* = 259 Hz), 198.6 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.19 – -99.11 (m) ppm; HRMS (EI) Calcd *m/z* for $C_{18}H_{16}FNO_3S$ $[M]^+$: 345.0835. Found: 345.0833.

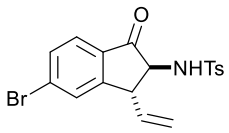
***N*-(5-Chloro-1-ethenyl-3-oxo-2,3-dihydro-1H-inden-2-yl)-4-methylbenzene-1-sulfonamide (3g)**.



Yield: 61%; d.r = 91:9; Eluent: *n*-hexane/ethyl acetate = 4/1; Yellow solid; mp: 145–148 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.74–3.92 (m, 2H), 5.22–5.39 (m, 3H), 5.88 (ddd, *J* = 17.0 Hz, *J* = 8.4 Hz, *J* = 10.2 Hz, 1H), 7.28–7.41 (m, 3H), 7.56–7.69 (m, 2H), 7.78–7.86 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 50.9, 65.5, 119.6, 123.9, 127.7, 127.9, 129.8, 134.6, 135.2, 135.7,

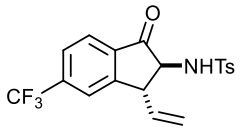
136.2, 136.6, 144.1, 150.9, 199.3 ppm; HRMS (EI) Calcd *m/z* for $C_{18}H_{16}{}^{35}ClNO_3S$ $[M]^+$: 361.0539. Found: 361.0541; $C_{18}H_{16}{}^{37}ClNO_3S$ $[M+2]^+$: 363.0515. Found: 363.0523.

***N*-(5-Bromo-1-oxo-3-vinyl-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzenesulfonamide (3h)**.



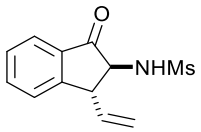
20 mol% of TFA was added in Pd catalysis step; Yield: 62%; d.r = 91:9; Eluent: *n*-hexane/ethyl acetate = 4/1; White solid; mp: 138–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.72–3.93 (m, 2H), 5.22-5.45 (m, 3H), 5.78–5.99 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.53–7.63 (m, 3H), 7.77–7.87 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 51.2, 65.2, 119.9, 125.5, 127.8, 129.9, 130.0, 131.9, 132.0, 132.5, 135.5, 136.5, 144.1, 154.5, 199.3 ppm; HRMS (EI) Calcd *m/z* for $C_{18}H_{16}{}^{79}BrNO_3S$ $[M]^+$: 405.0034. Found: 405.0037; $C_{18}H_{16}{}^{81}BrNO_3S$ $[M]^+$: 407.0015. Found: 407.0006.

4-Methyl-N-(1-oxo-5-(trifluoromethyl)-3-vinyl-2,3-dihydro-1H-inden-2-yl)benzenesulfonamide (3i).



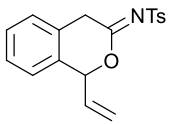
Yield: 68%; d.r = 95:5; Eluent: *n*-hexane/ethyl acetate = 4/1; White solid; mp: 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.83–4.02 (m, 2H), 5.27–5.49 (m, 3H), 5.81–6.01 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.64–7.77 (m, 2H), 7.84 (d, *J* = 8.3 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 51.3, 65.6, 118.0–128.9 (m), 120.3, 123.7–123.8 (m), 124.9, 125.8–125.9 (m), 127.7, 129.8, 135.2, 135.8, 136.7, 136.7–138.1 (m), 144.1, 153.0, 199.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.04 ppm; HRMS (EI) Calcd *m/z* for $C_{19}H_{16}F_3NO_3S$ $[M]^+$: 395.0803. Found: 395.0802.

N-(1-Ethenyl-3-oxo-2,3-dihydro-1H-inden-2-yl)methanesulfonamide (3h).



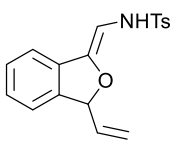
Yield: 50%; d.r = 91:9; Eluent: *n*-hexane/ethyl acetate = 4/1; Colorless oil; Major product ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.21 (s, 3H), 3.73–3.84 (m, 1H), 4.20 (dd, *J* = 7.2 Hz, *J* = 6.1 Hz, 1H), 5.20–5.33 (m, 1H), 5.38–5.58 (m, 2H), 5.90–6.10 (m, 1H), 7.41–7.52 (m, 2H), 7.64–7.83 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 43.2, 51.6, 65.8, 120.1, 124.3, 126.3, 128.9, 133.2, 135.9, 136.3, 152.1, 201.0 ppm; HRMS (EI) Calcd *m/z* for $C_{12}H_{13}NO_3S$ $[M]^+$: 251.0616. Found: 251.0615.

(*Z*)-4-Methyl-*N*-(1-vinylisochroman-3-ylidene)benzenesulfonamide (4a).



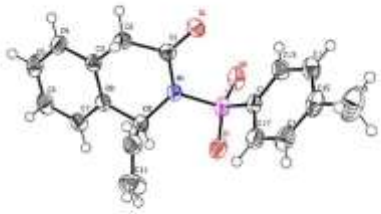
Yield: 66%; Eluent: *n*-hexane/ethyl acetate = 3/1; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (s, 3H), 3.58–3.84 (m, 1.67H), 4.16–4.73 (brs, 0.26H), 5.26 (d, *J* = 16.7 Hz, 1H) 5.42 (d, *J* = 10.0 Hz, 1H), 5.76–6.09 (m, 2H), 7.12–7.44 (m, 6H), 7.81–7.94 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 35.4, 83.5, 120.5, 125.1, 127.5, 127.8, 129.0, 129.3, 129.4, 129.7, 132.2, 132.5, 138.5, 143.4, 168.1 ppm; HRMS (FAB) Calcd *m/z* for $C_{18}H_{18}NO_3S$ [M+H]: 328.1007. Found: 328.1010.

(*Z*)-4-Methyl-N-((3-vinylisobenzofuran-1(3H)-ylidene)methyl)benzenesulfonamide (5a).



Yield: 80%; Eluent: *n*-hexane/ethyl acetate = 6/1; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.12–5.27 (m, 1H), 5.27–5.42 (m, 1H), 5.60–5.81 (m, 2H), 6.03 (d, *J* = 10.3 Hz, 1H) 6.37 (d, *J* = 10.3 Hz, 1H), 7.03–7.18 (m, 1H), 7.21–7.34 (m, 5H), 7.78 (d, *J* = 8.31, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5, 86.6, 95.0, 117.9, 118.8, 122.0, 127.0, 128.5, 128.6, 129.7, 131.8, 135.4, 137.0, 140.7, 143.5, 145.1 ppm; HRMS (EI) Calcd *m/z* for $C_{18}H_{17}NO_3S$ $[M]^+$: 327.0929. Found: 327.0928.

12. X-ray Crystal Structure and Data of 2a



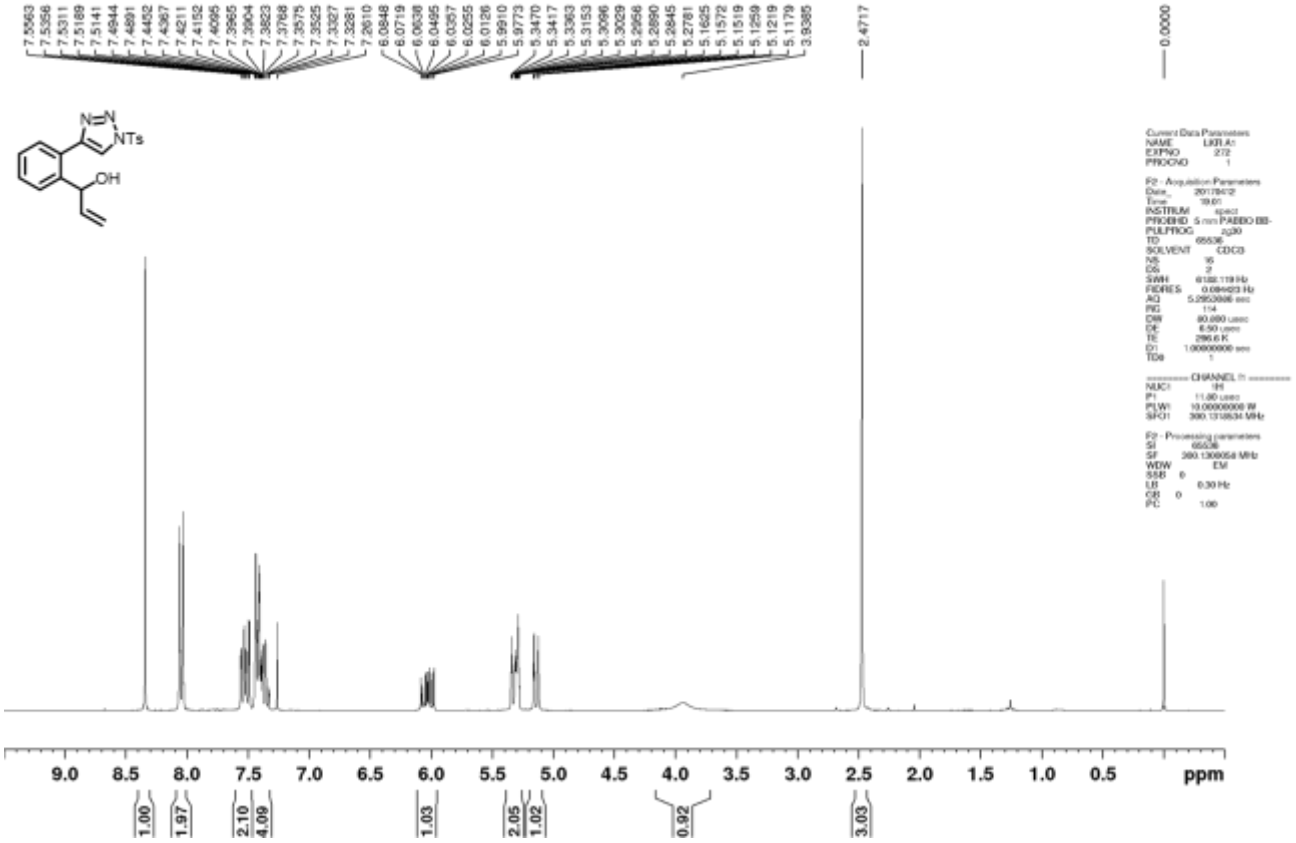
Empirical formula	$C_{18}H_{17}NO_3S$	
Formula weight	327.39	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.3301(5) Å	α= 106.868(2)°.
	b = 10.1313(5) Å	β= 106.256(2)°.
	c = 10.5314(6) Å	γ = 99.042(2)°.
Volume	788.58(8) $Å^3$	
Z	2	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	0.220 mm^{-1}	
F(000)	344	
Crystal size	0.19 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.15 to 28.34°.	
Index ranges	-11<=h<=11, -13<=k<=13, -14<=l<=14	
Reflections collected	33101	
Independent reflections	3937 [R(int) = 0.0268]	
Completeness to theta = 28.34°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9784 and 0.9594	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3937 / 0 / 209	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1055	
R indices (all data)	R1 = 0.0458, wR2 = 0.1112	
Largest diff. peak and hole	0.394 and -0.227 $e.Å^{-3}$	

13. X-ray Crystal Structure and Data of 3a

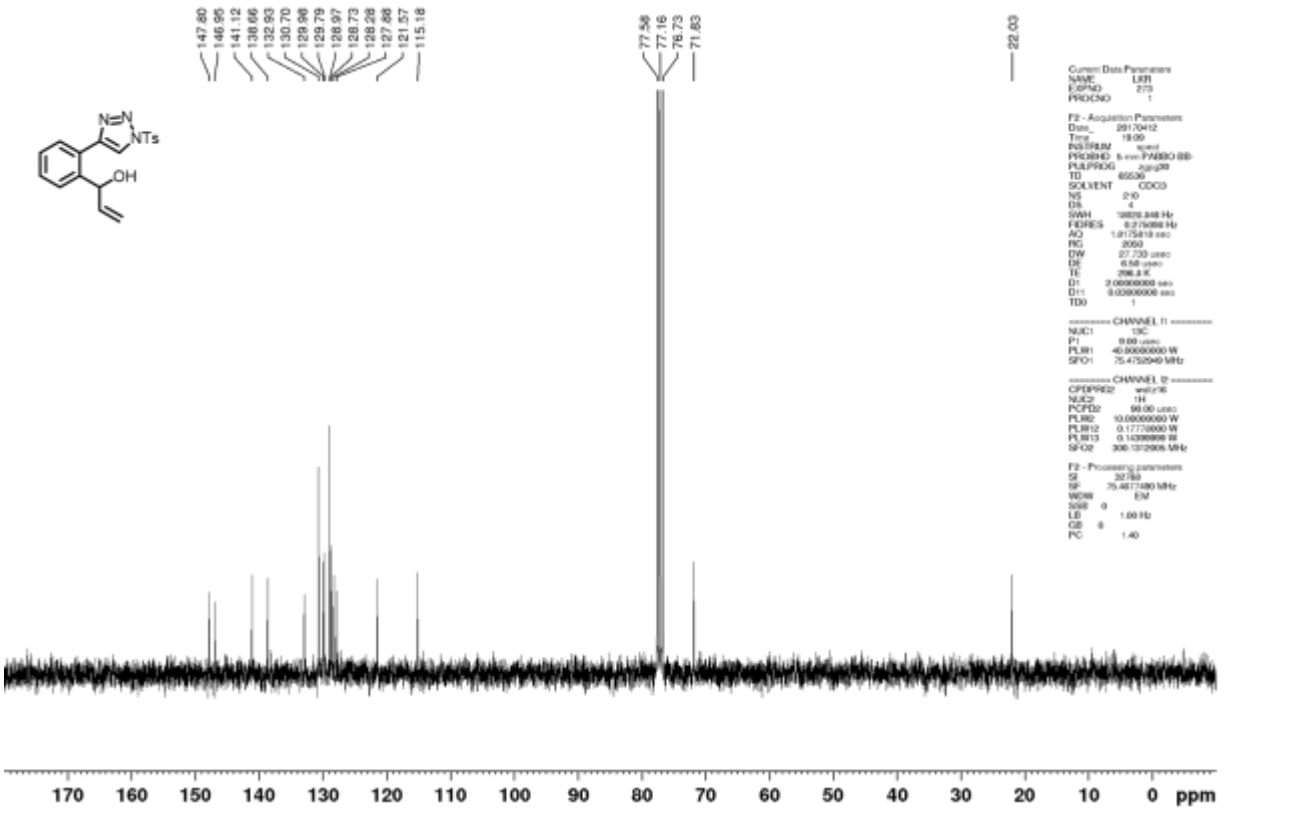
Chemical formula	$C_{18}H_{17}NO_3S$
Formula weight	327.38
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal size	0.100 x 0.200 x 0.280 mm
Crystal habit	colorless plate
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 9.4401(2) Å α = 64.5184(10)°
	b = 9.7860(2) Å β = 74.1018(11)°
	c = 10.7338(2) Å γ = 69.7646(10)°
Volume	830.67(3) $Å^3$
Z	2
Density (calculated)	1.309 g/cm^3
Absorption coefficient	0.209 mm^{-1}
F(000)	344
Theta range for data collection	2.13 to 28.54°
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14
Reflections collected	29279
Independent reflections	4207 [R(int) = 0.0338]
Coverage of independent reflections	99.3%
Absorption correction	multi-scan
Max. and min. transmission	0.9790 and 0.9440
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4207 / 0 / 209
Goodness-of-fit on F2	1.028
Final R indices	3102 data; I>2σ(I) R1 = 0.0451, wR2 = 0.1092
	all data R1 = 0.0685, wR2 = 0.1243
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0569P)^2+0.2196P]$
	where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.330 and -0.285 $eÅ^{-3}$
R.M.S. deviation from mean	0.043 $eÅ^{-3}$

14. Copies of ^{1}H and ^{13}C NMR Spectra

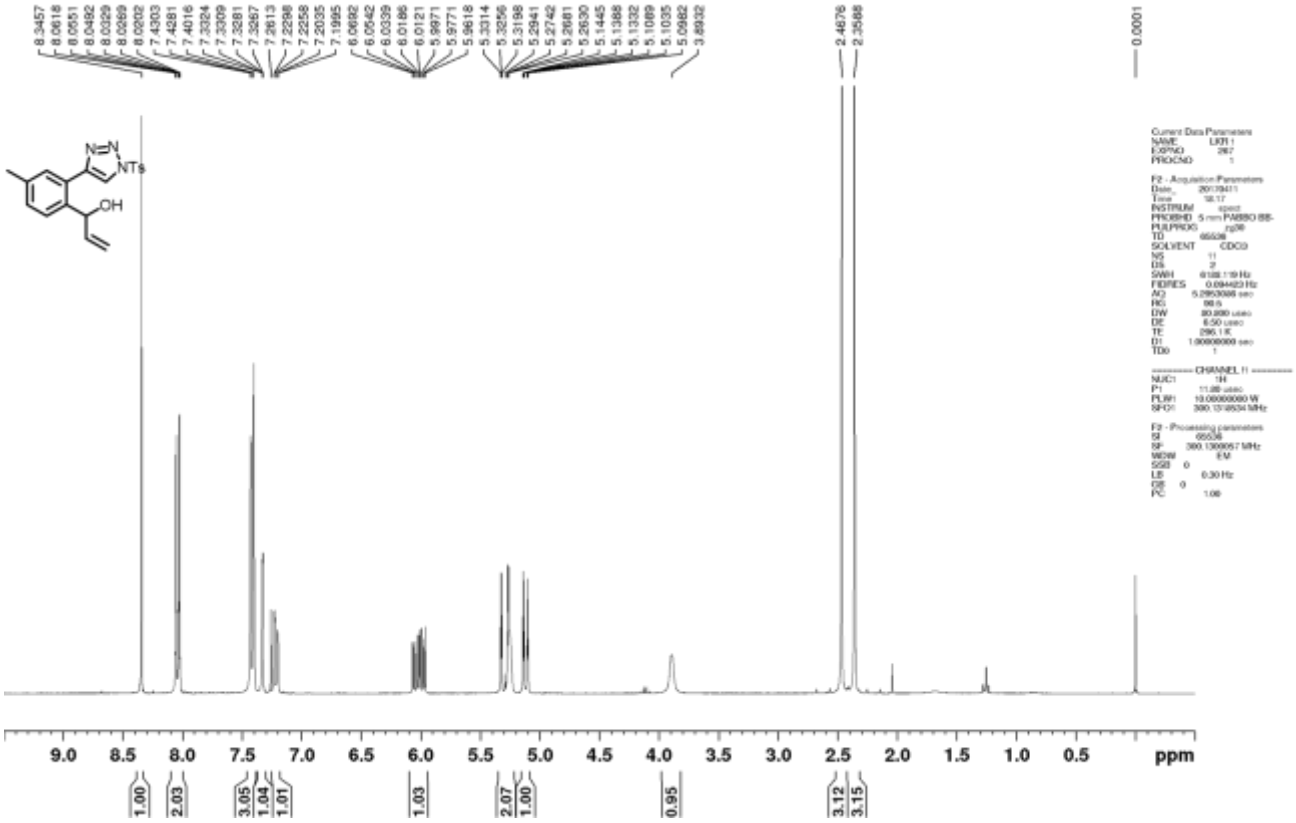
^{1}H spectra of compound **1a**



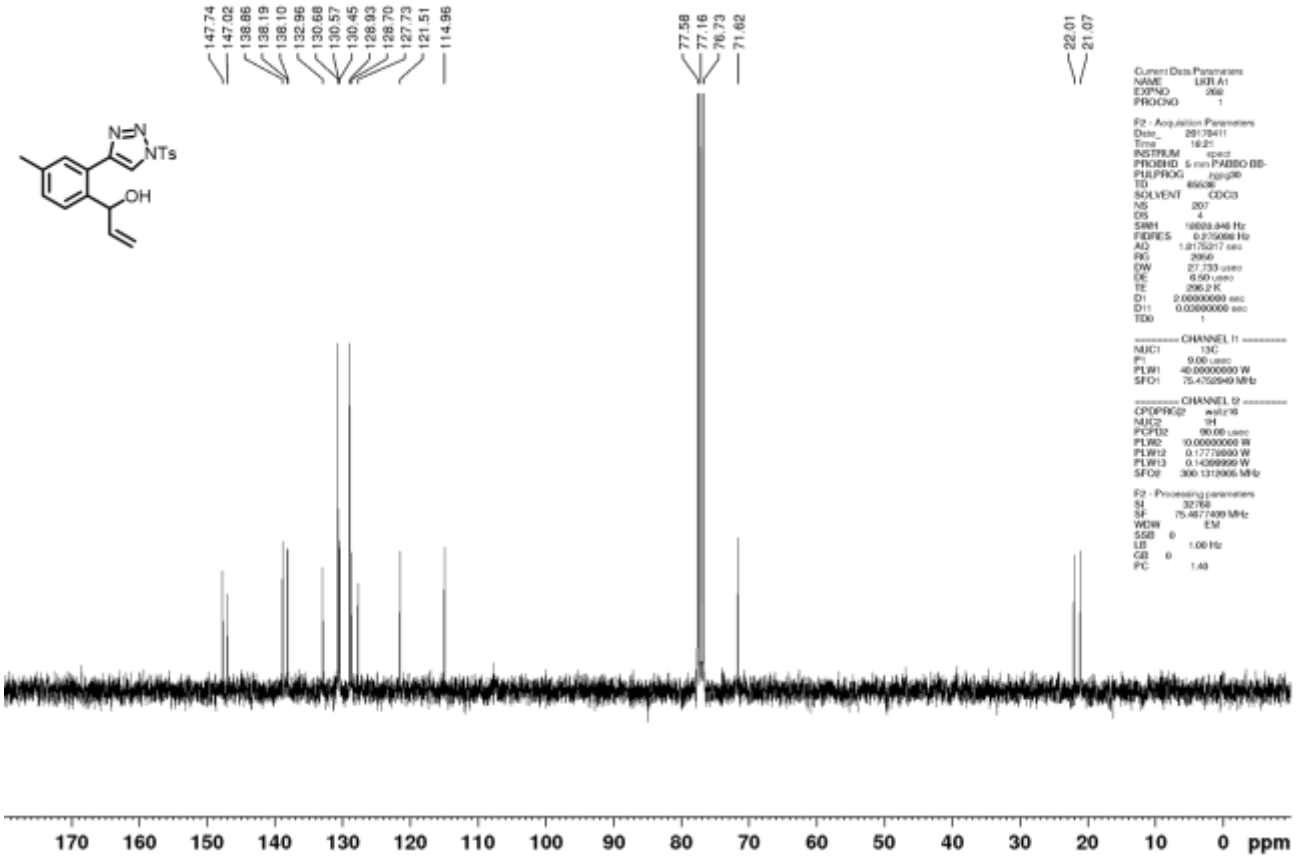
^{13}C spectra of compound **1a**



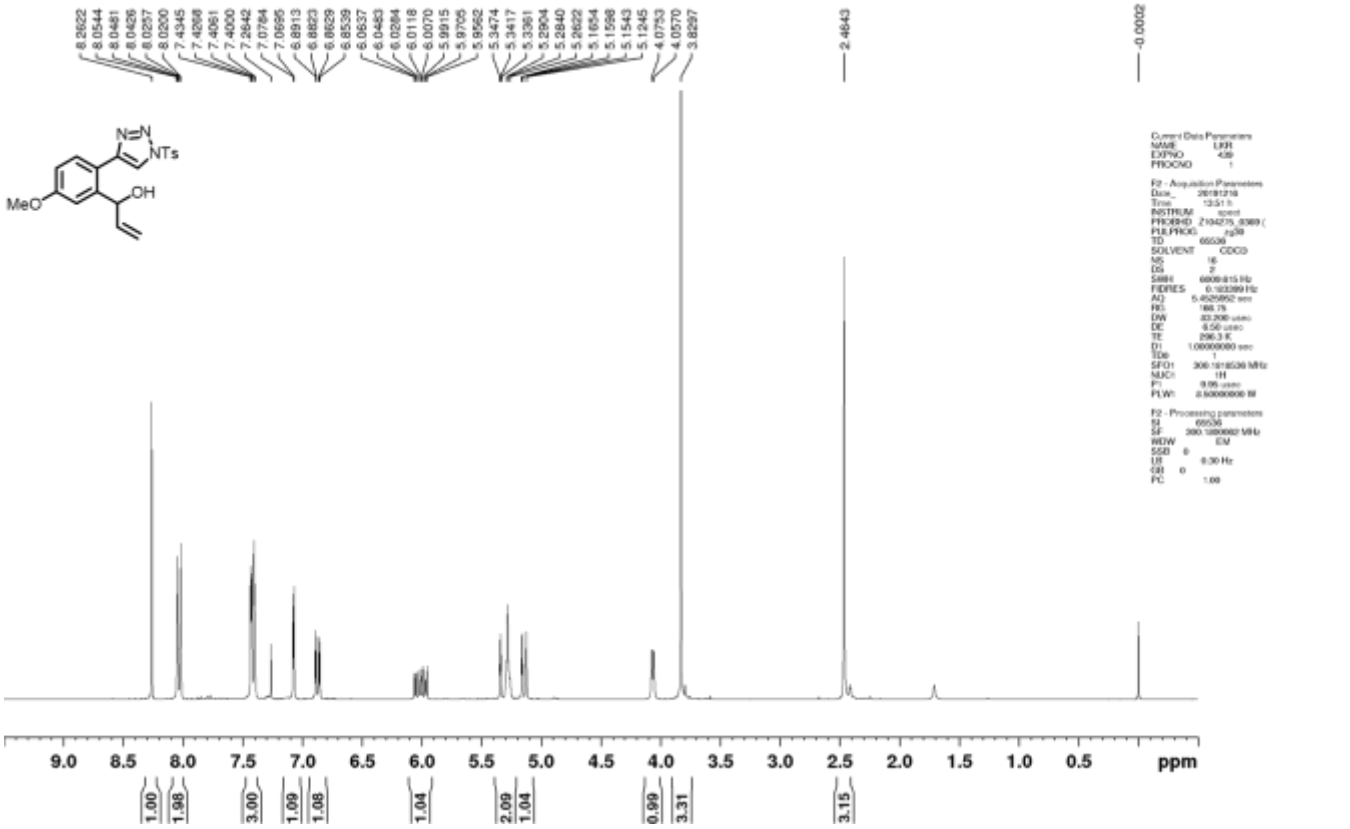
^{1}H spectra of compound **1b**



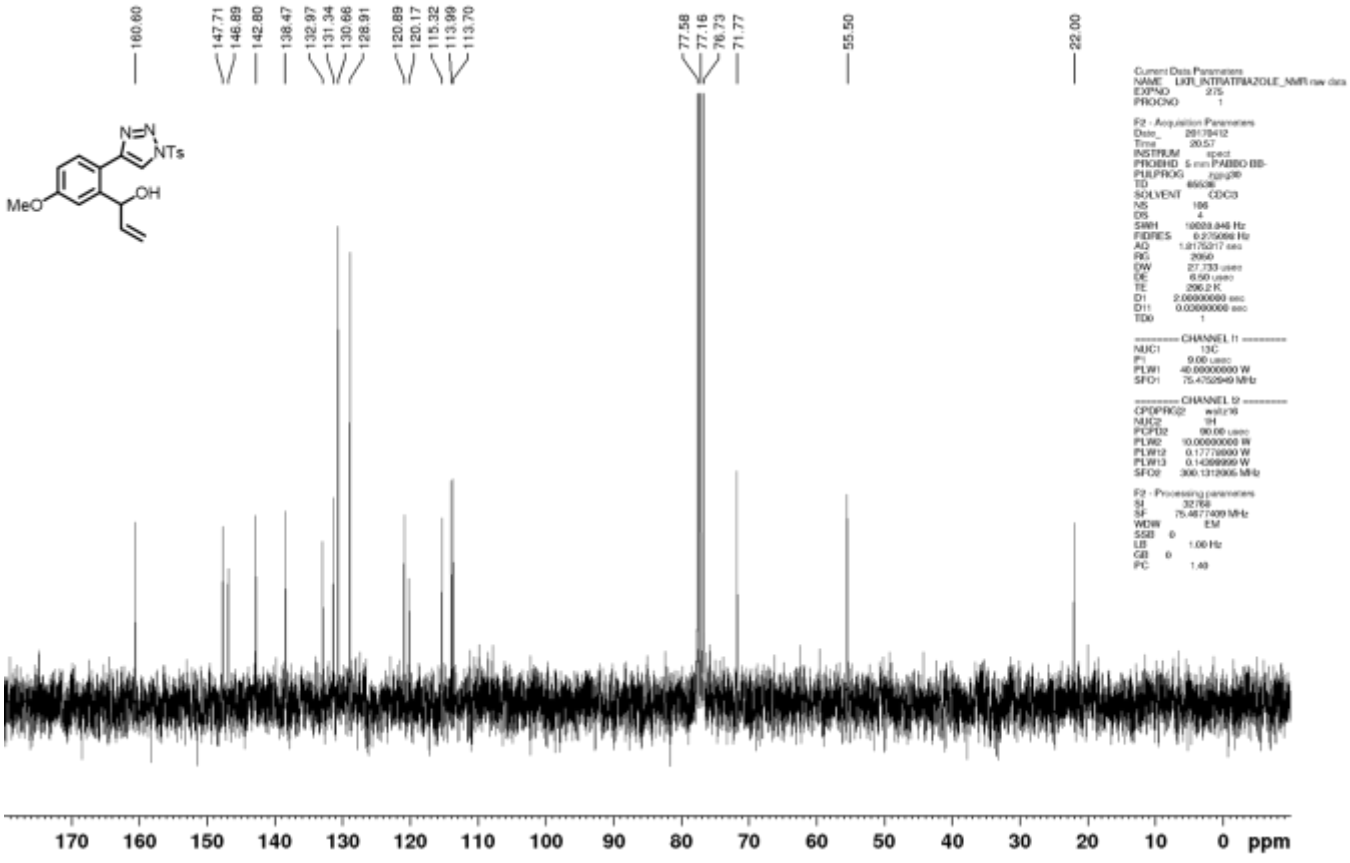
^{13}C spectra of compound **1b**



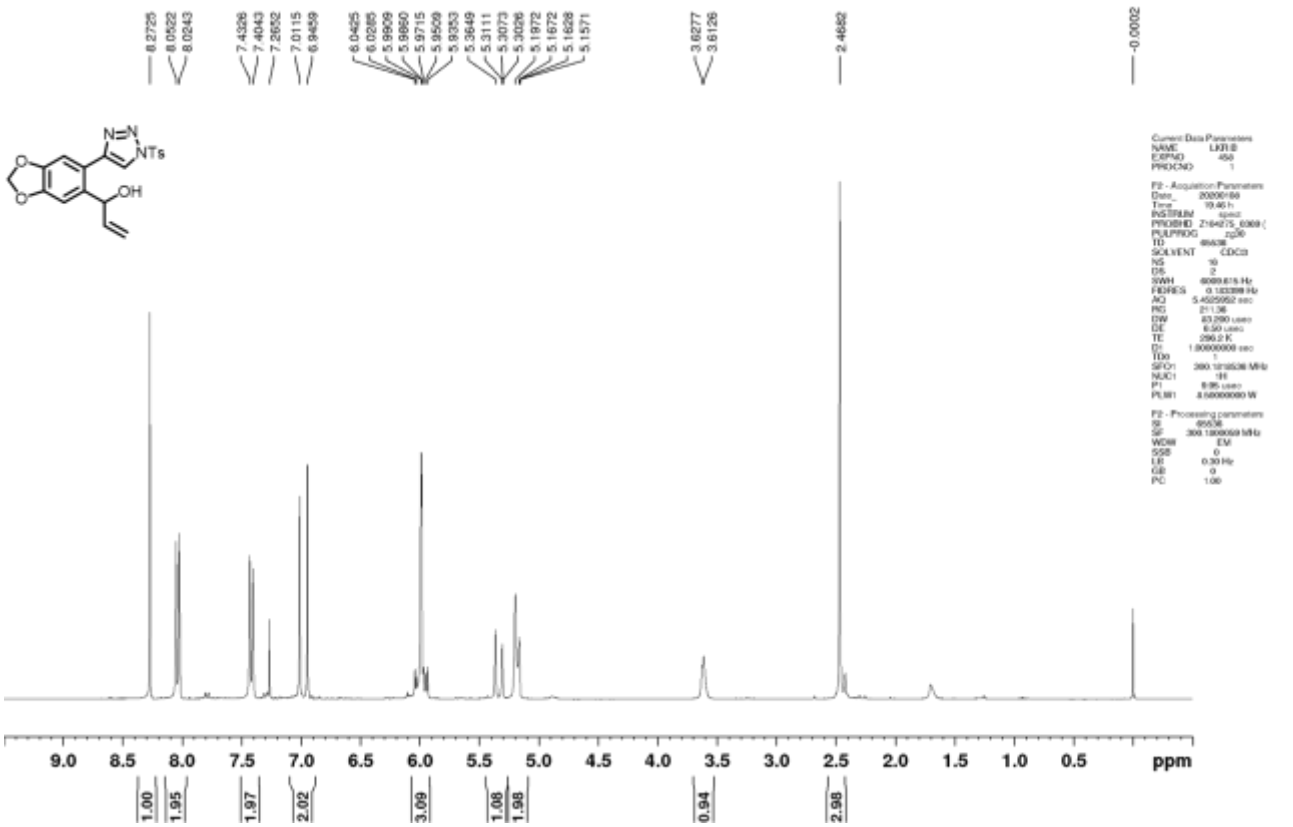
^{1}H spectra of compound **1c**



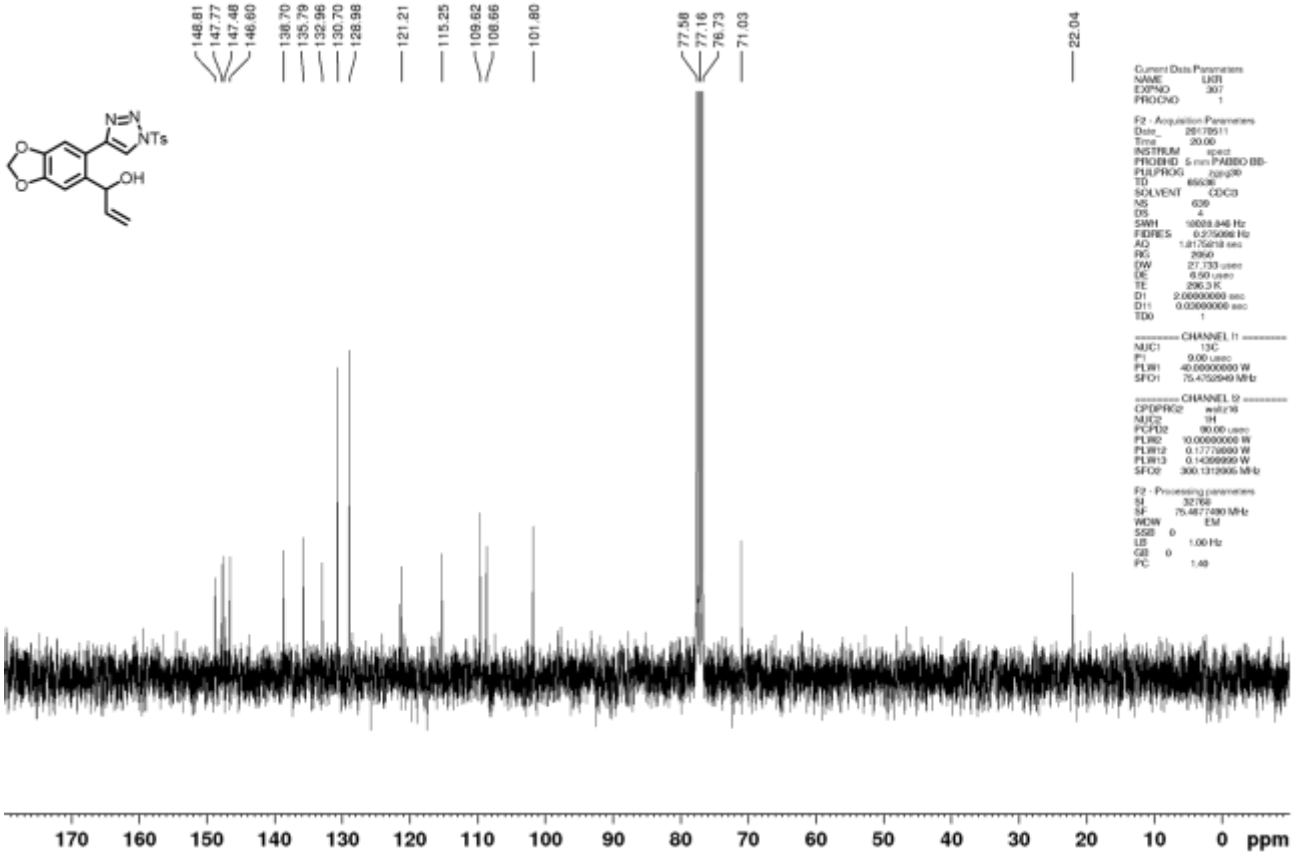
^{13}C spectra of compound **1c**



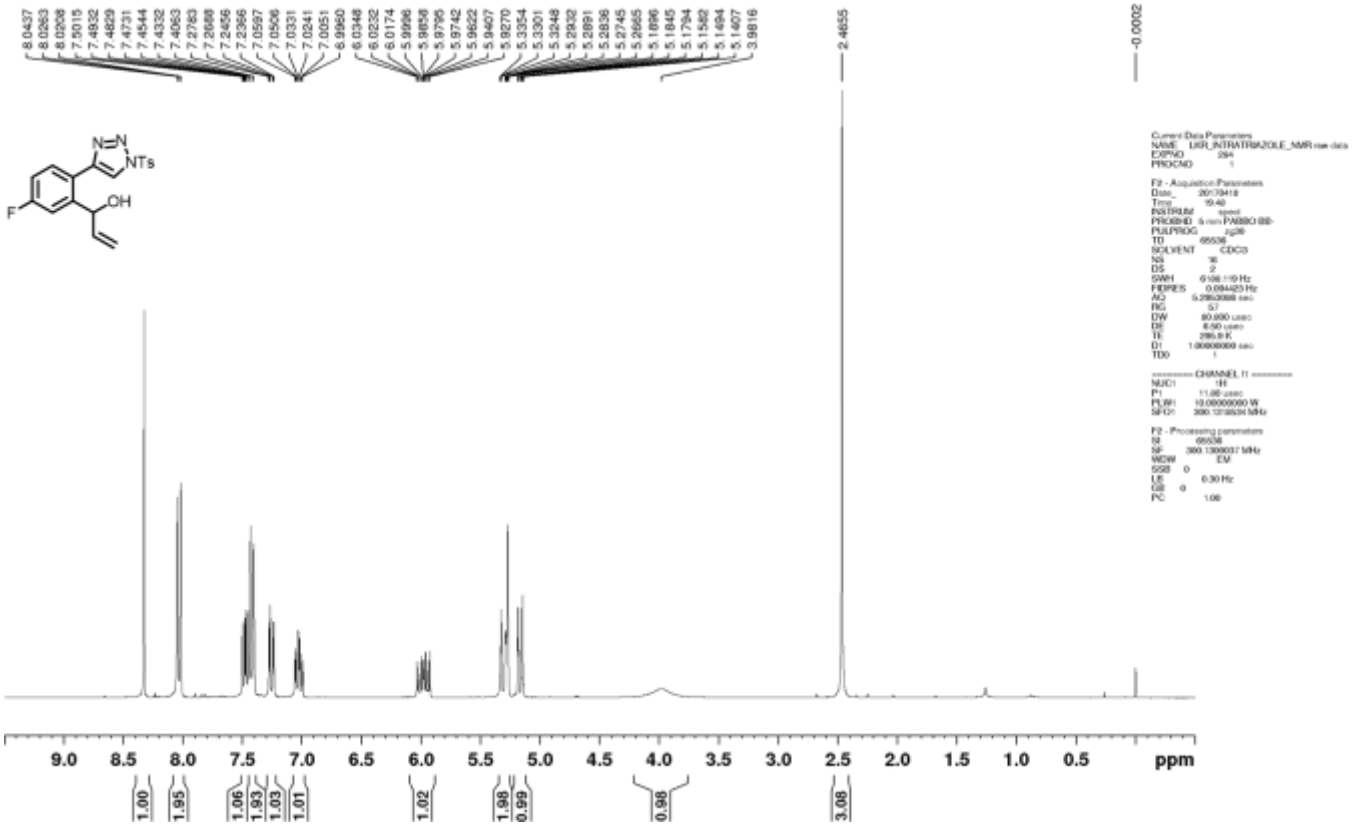
^{1}H spectra of compound **1d**



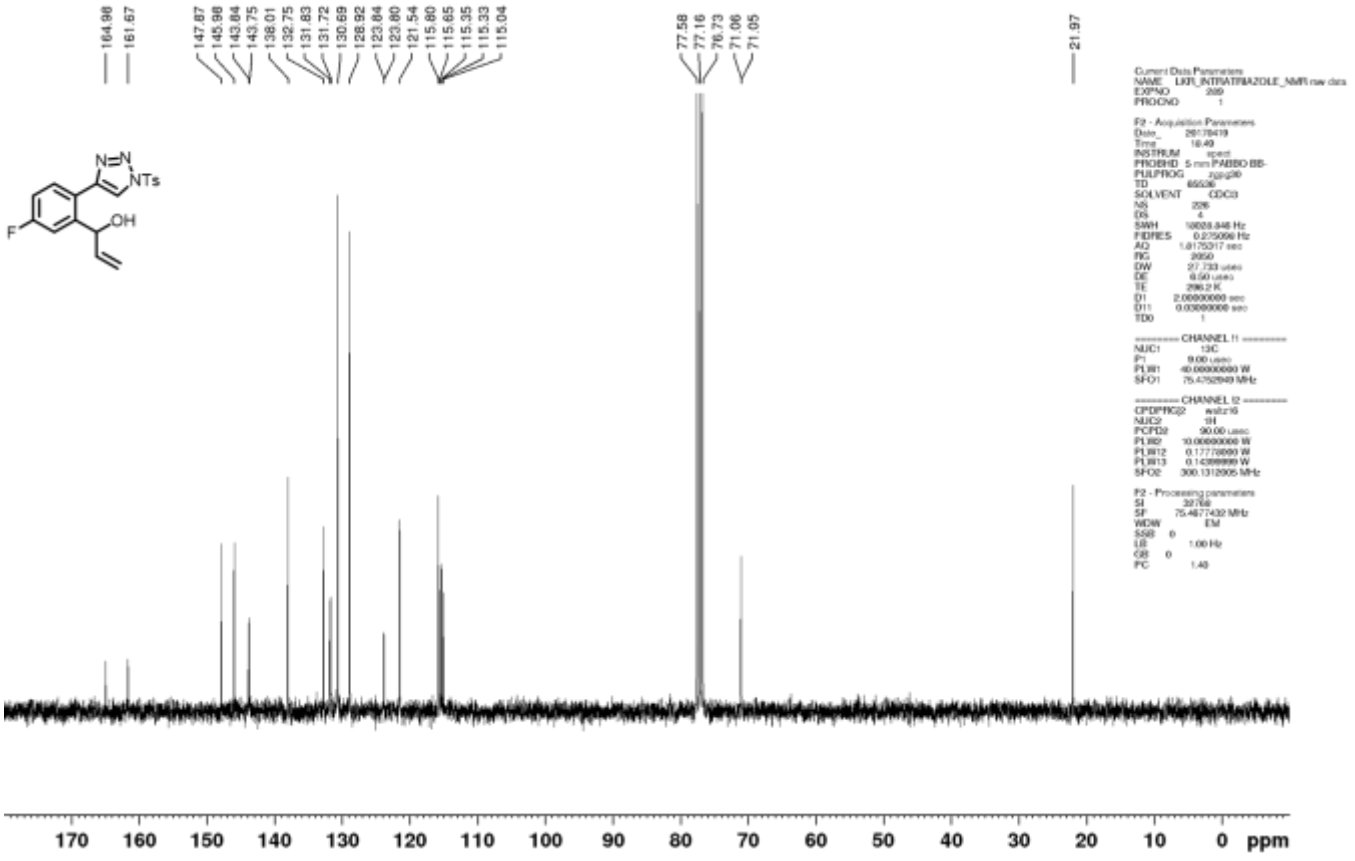
^{13}C spectra of compound **1d**



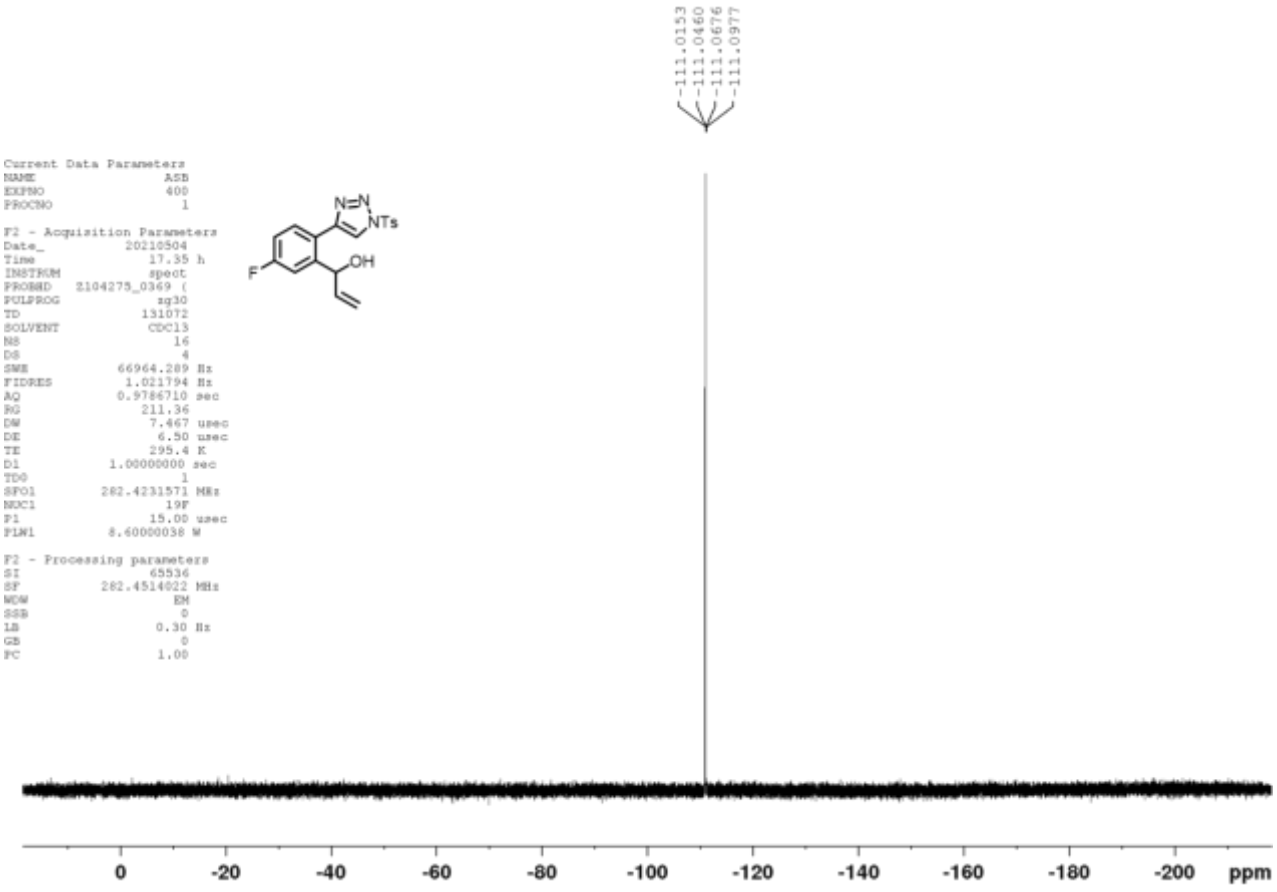
^{1}H spectra of compound **1e**



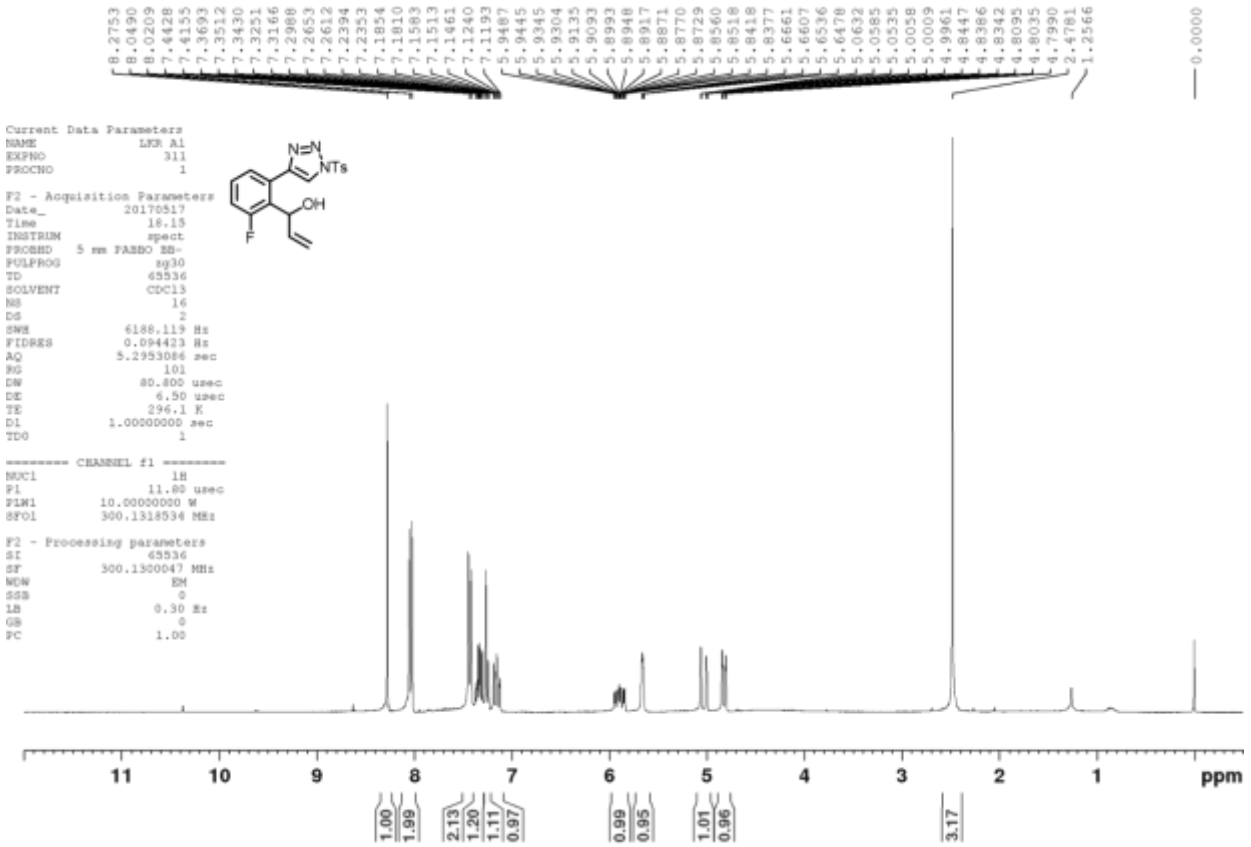
^{13}C spectra of compound **1e**



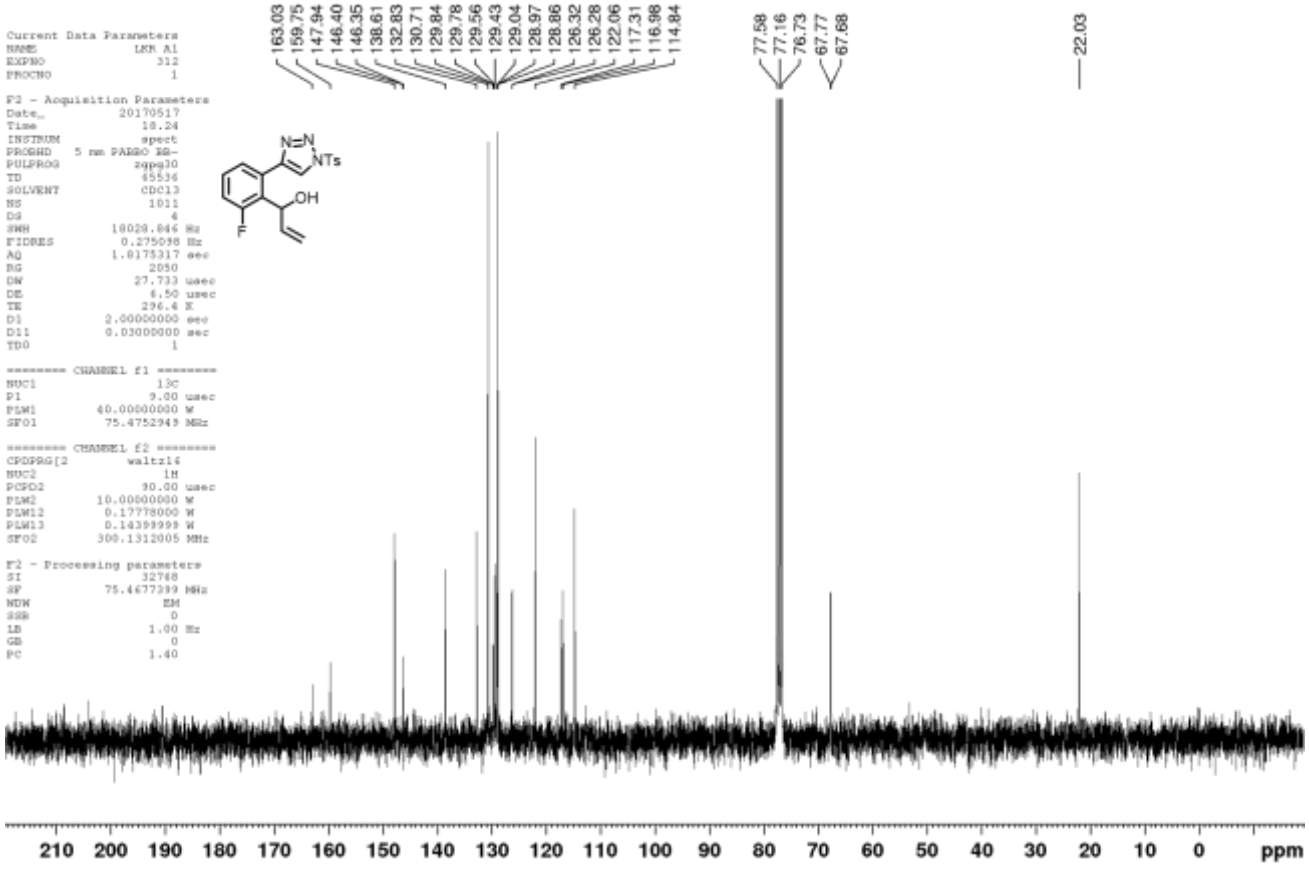
^{19}F spectra of compound **1e**



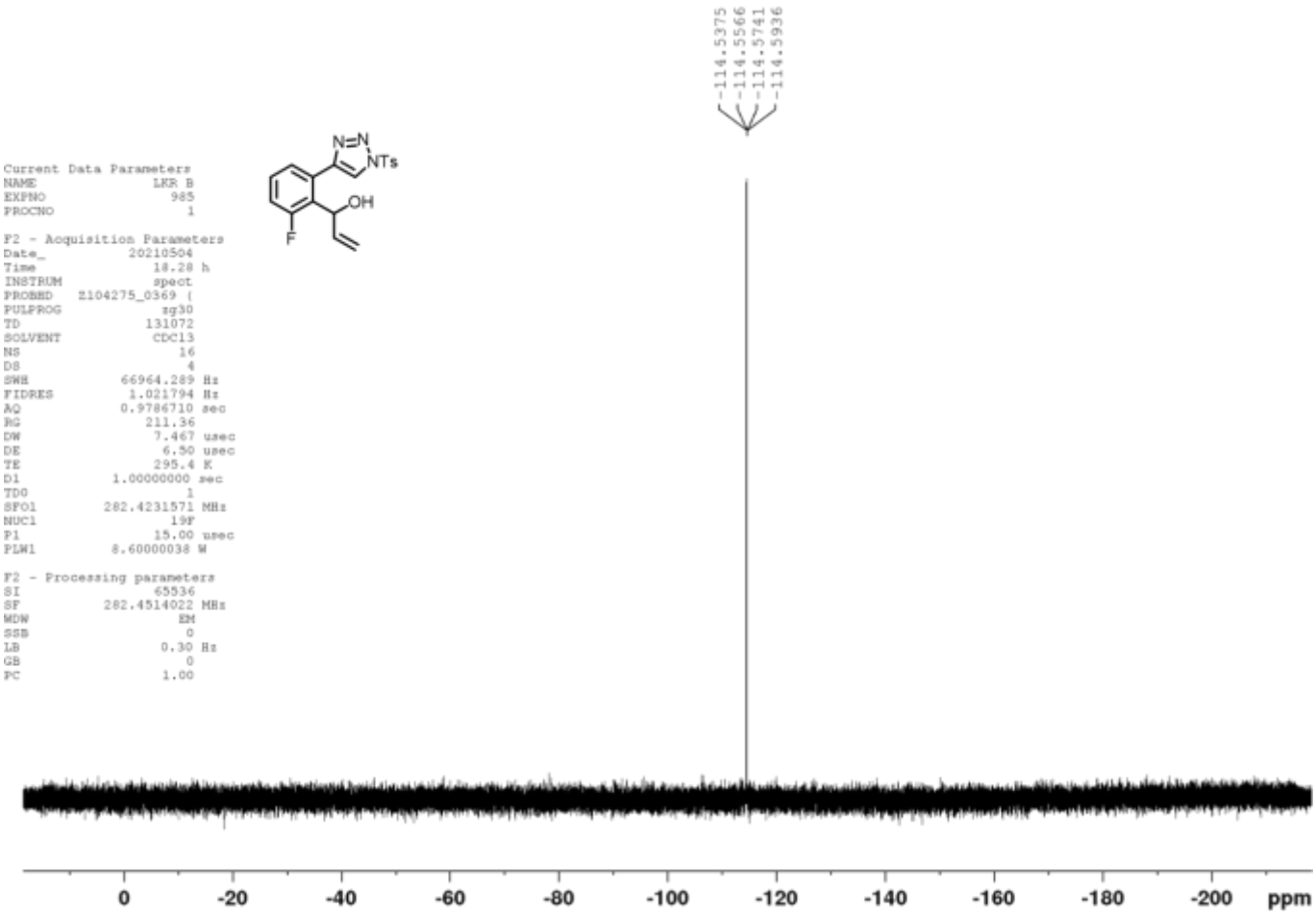
^{1}H spectra of compound **1f**



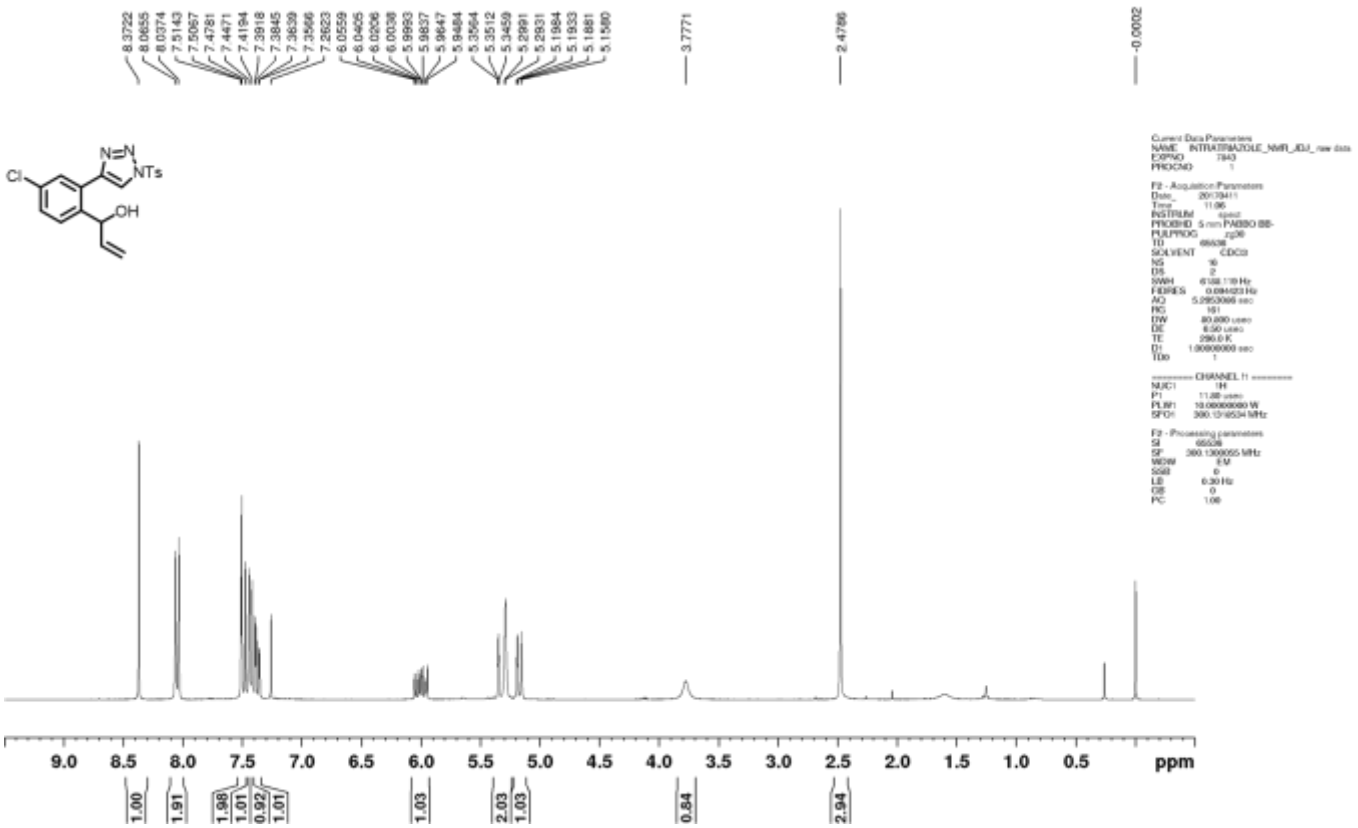
^{13}C spectra of compound **1f**



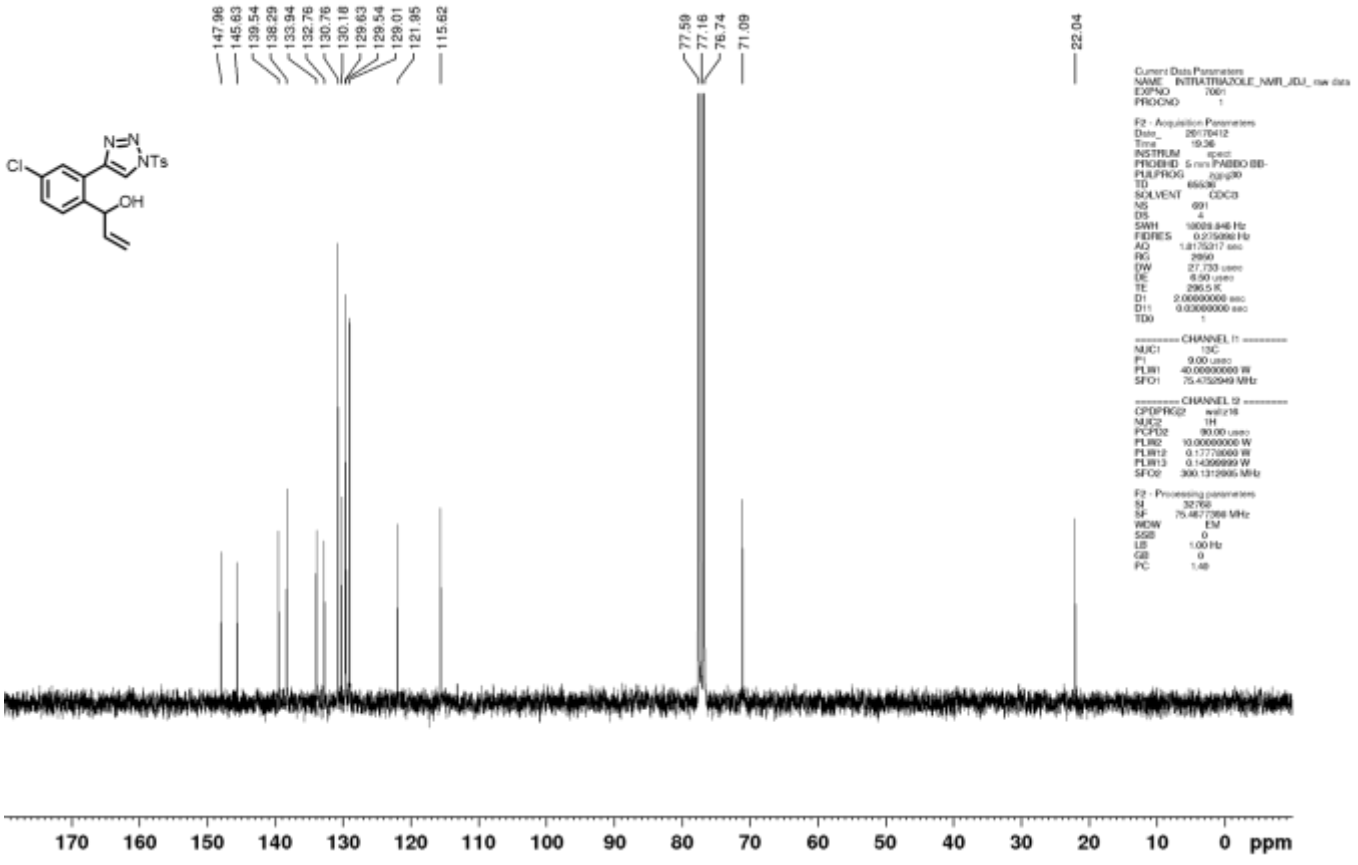
^{19}F spectra of compound **1f**



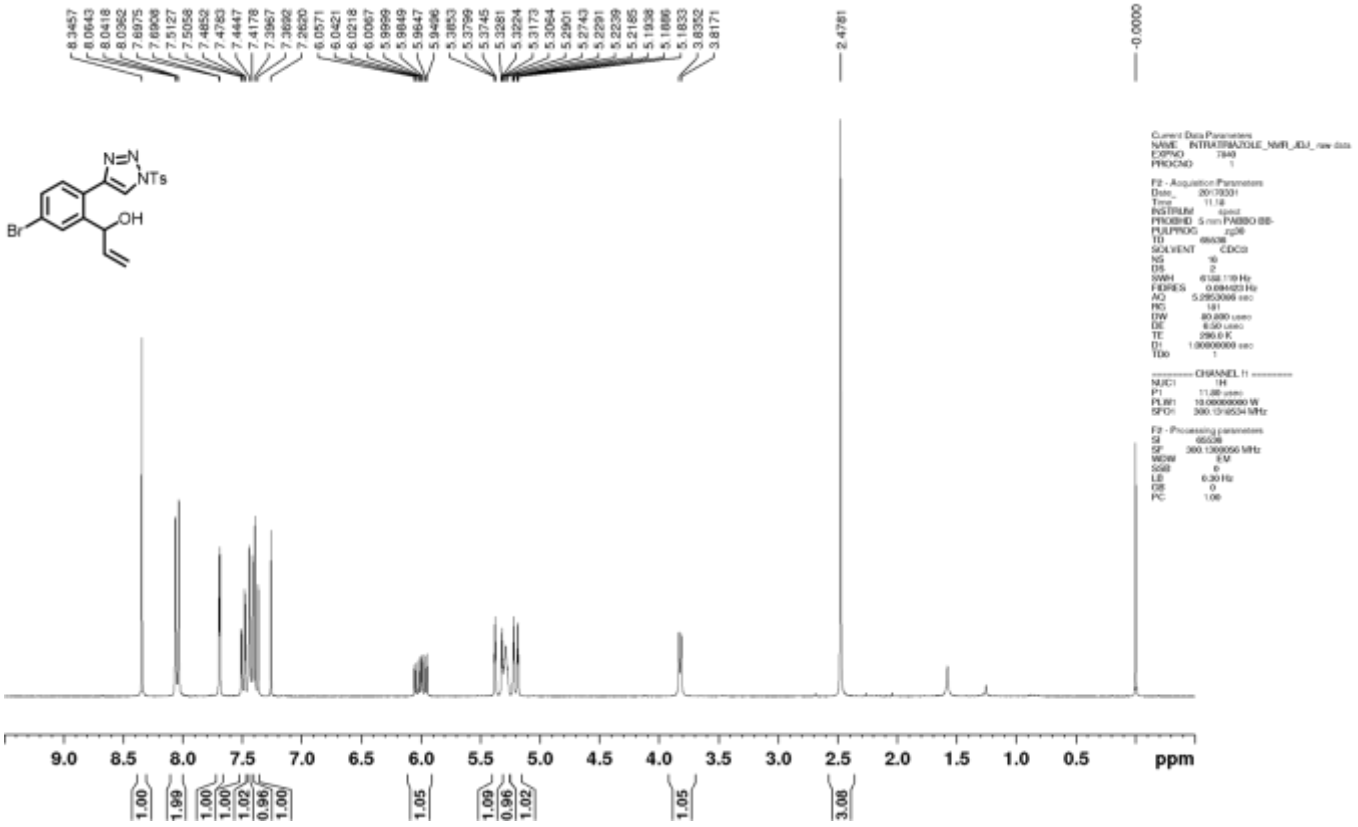
^{1}H spectra of compound **1g**



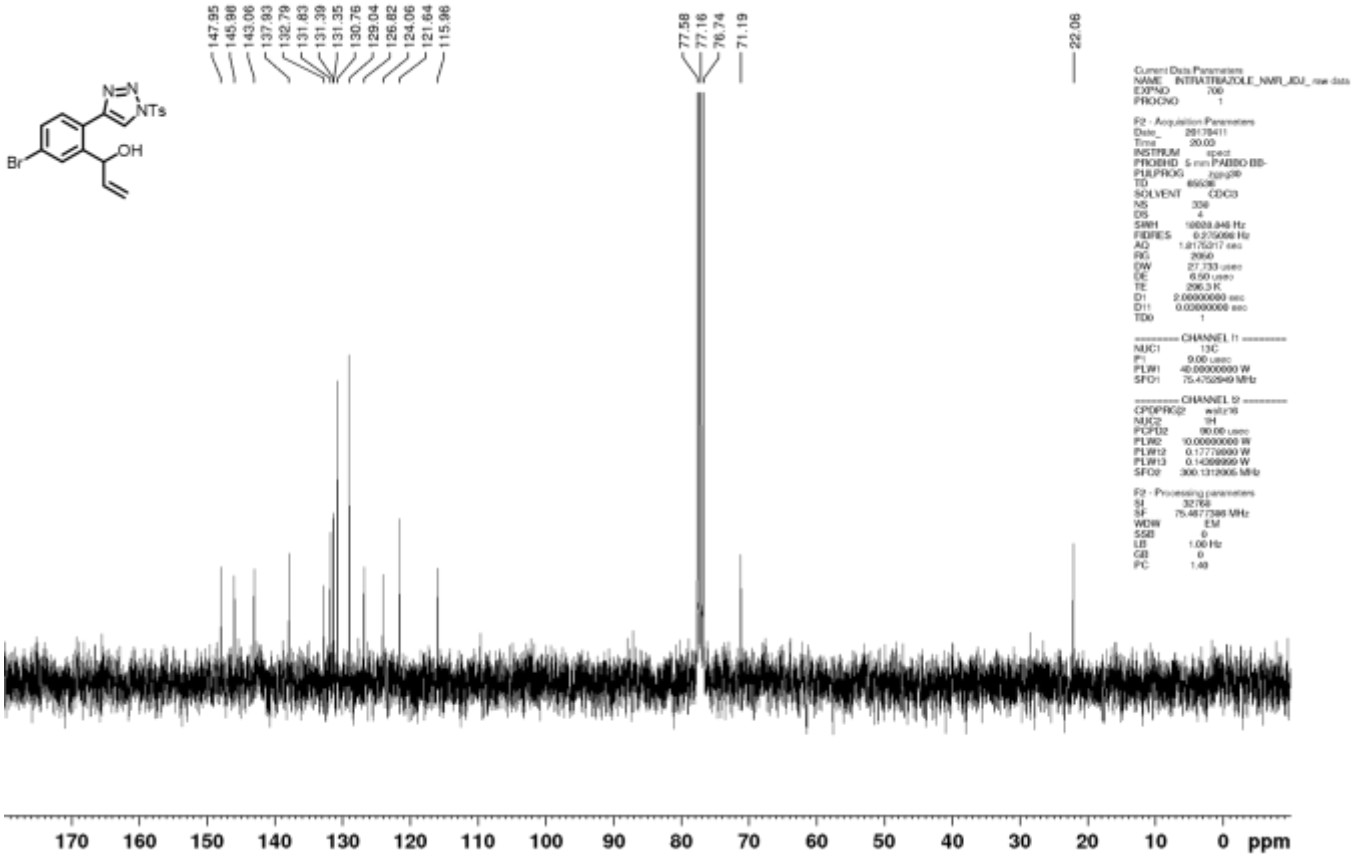
^{13}C spectra of compound **1g**



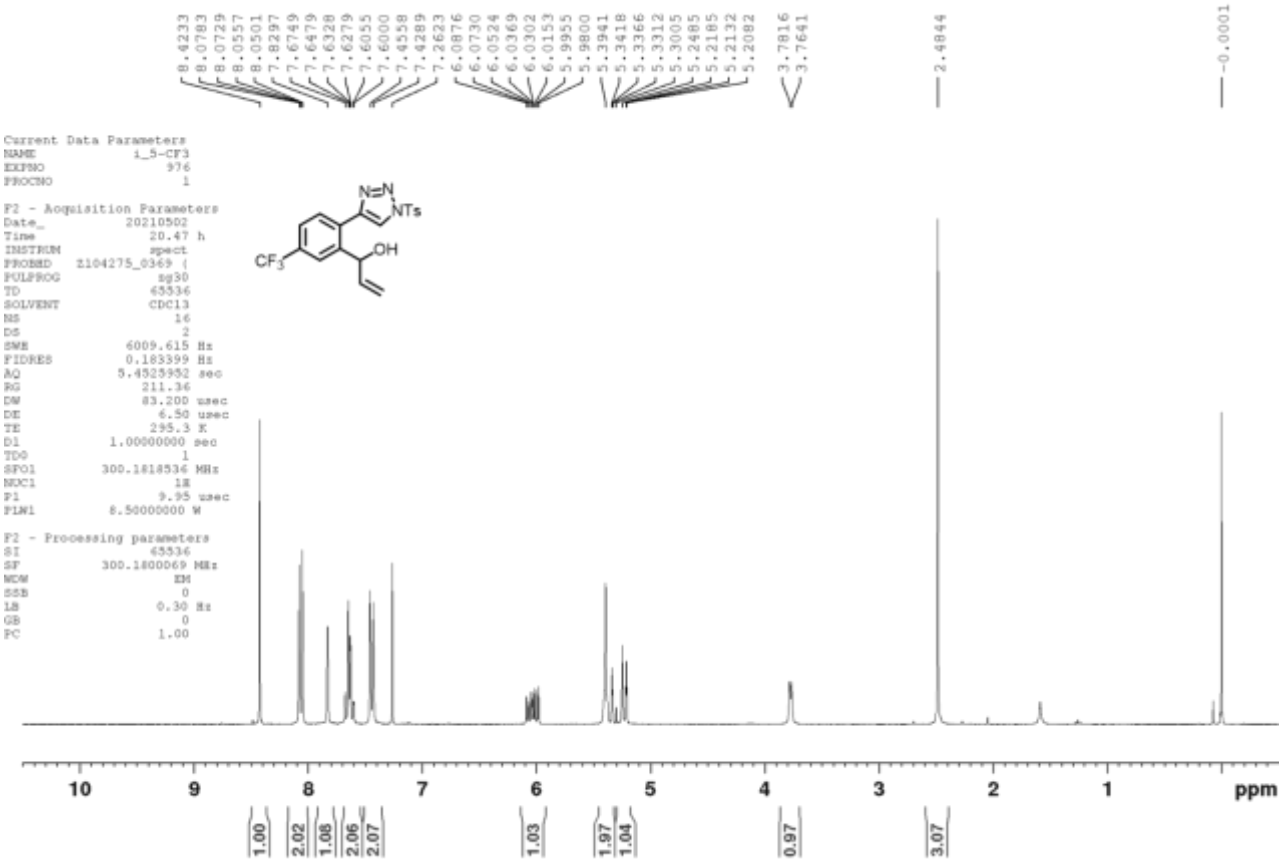
^{1}H spectra of compound **1g**



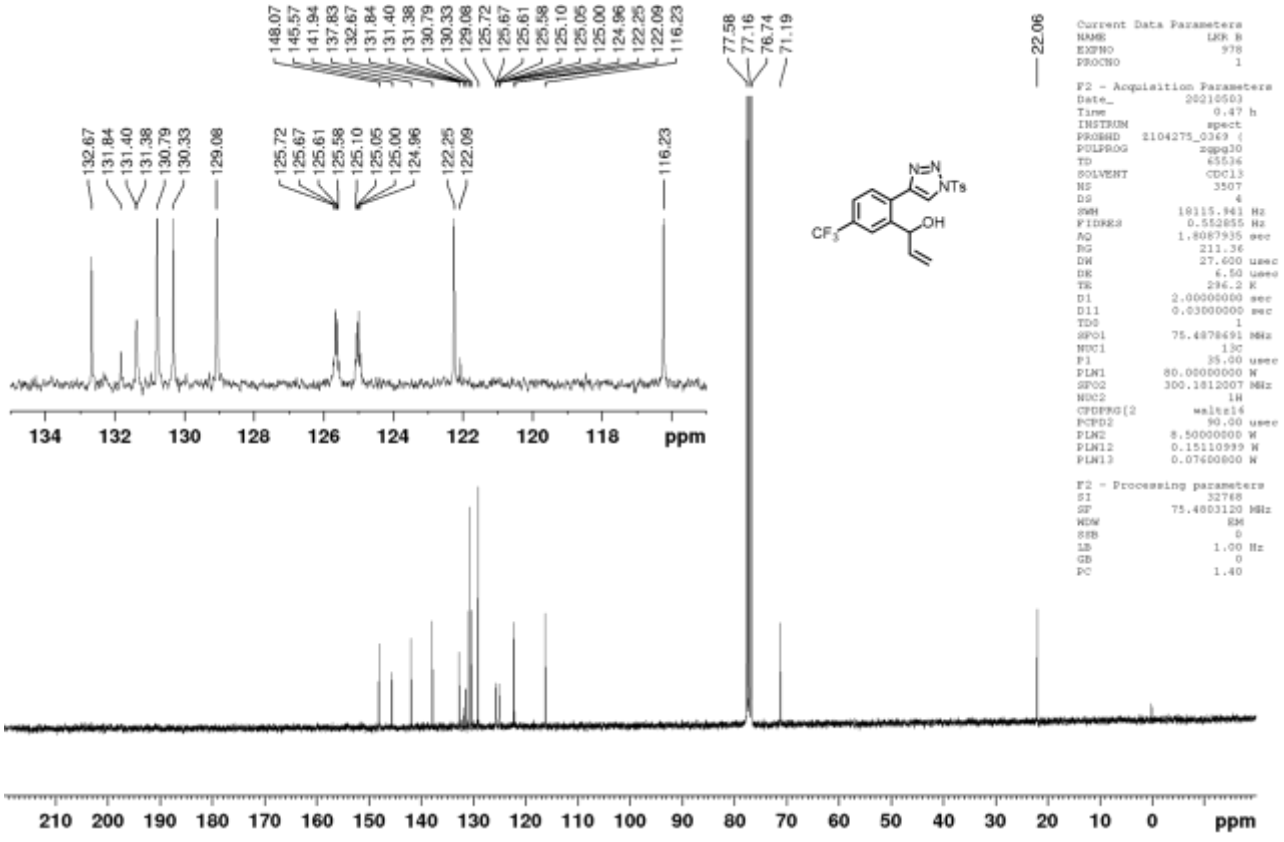
^{13}C spectra of compound **1g**



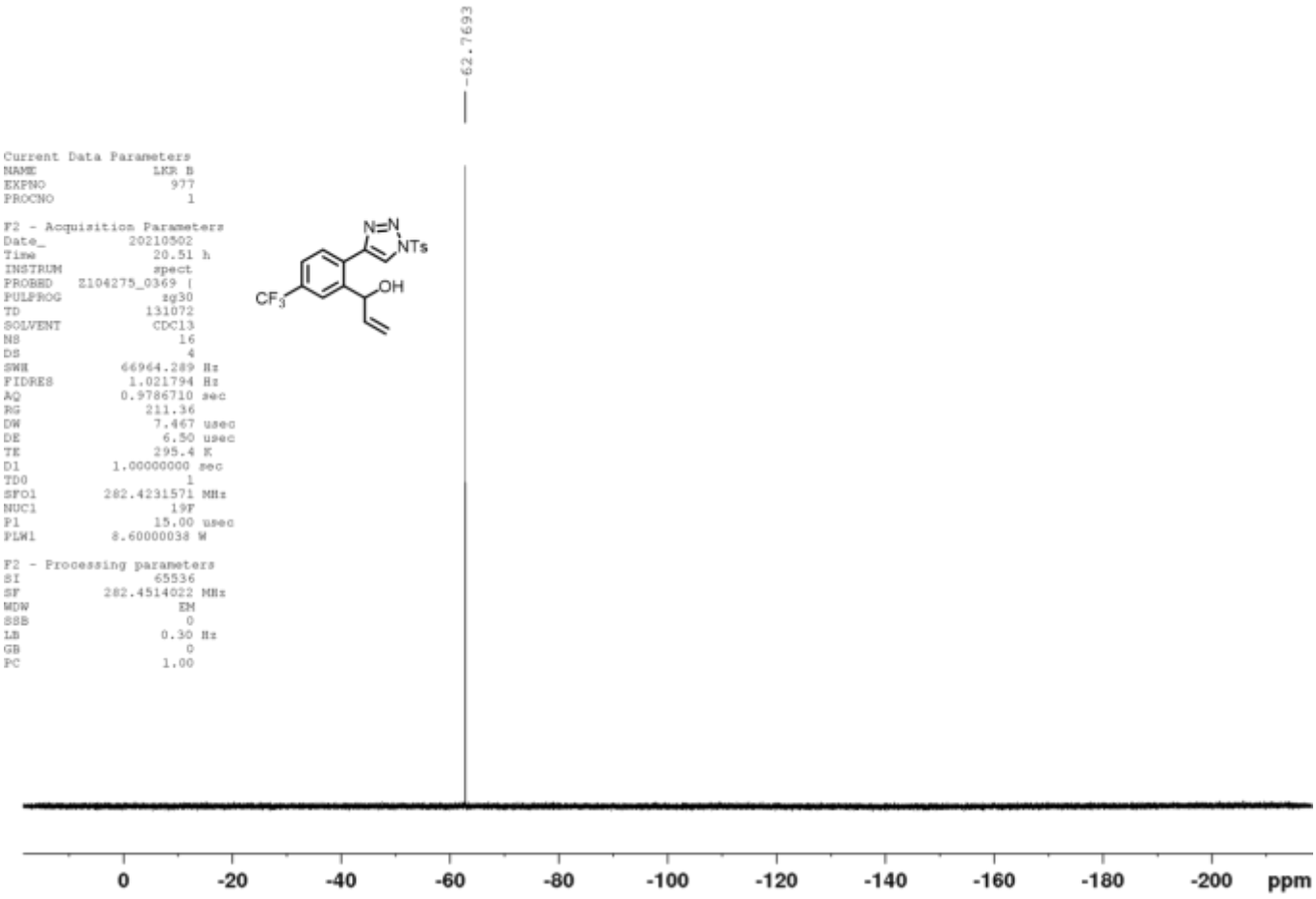
^{1}H spectra of compound **1i**



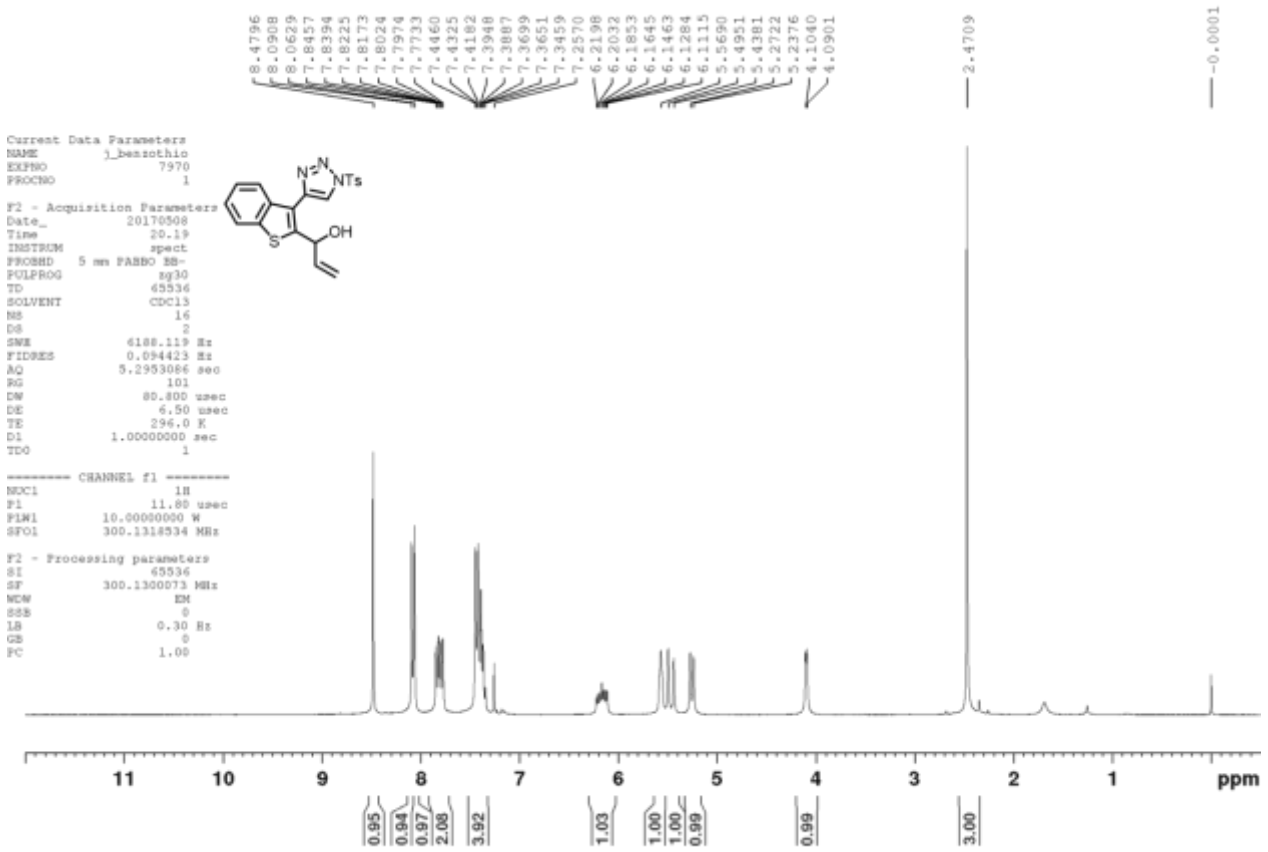
^{13}C spectra of compound **1i**



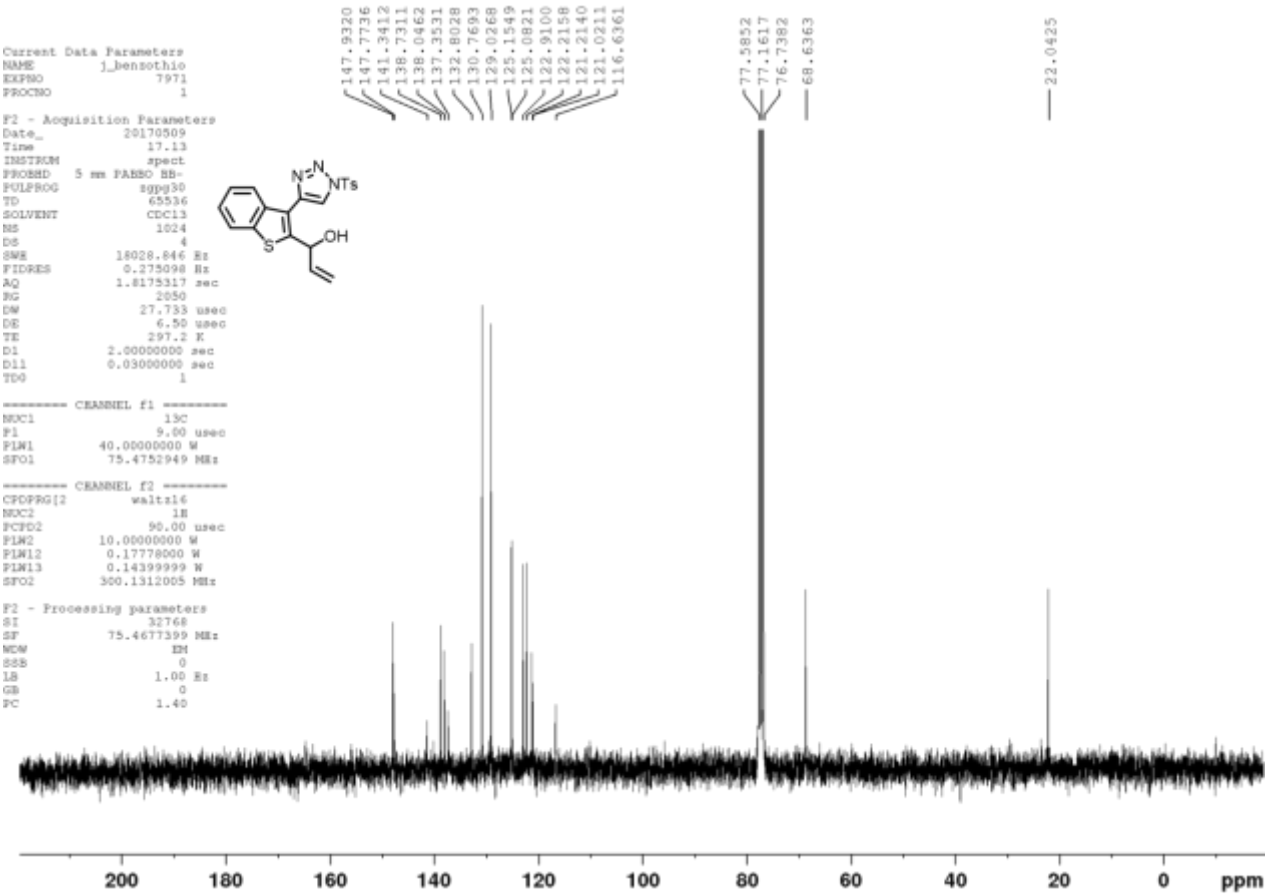
^{19}F spectra of compound **1i**



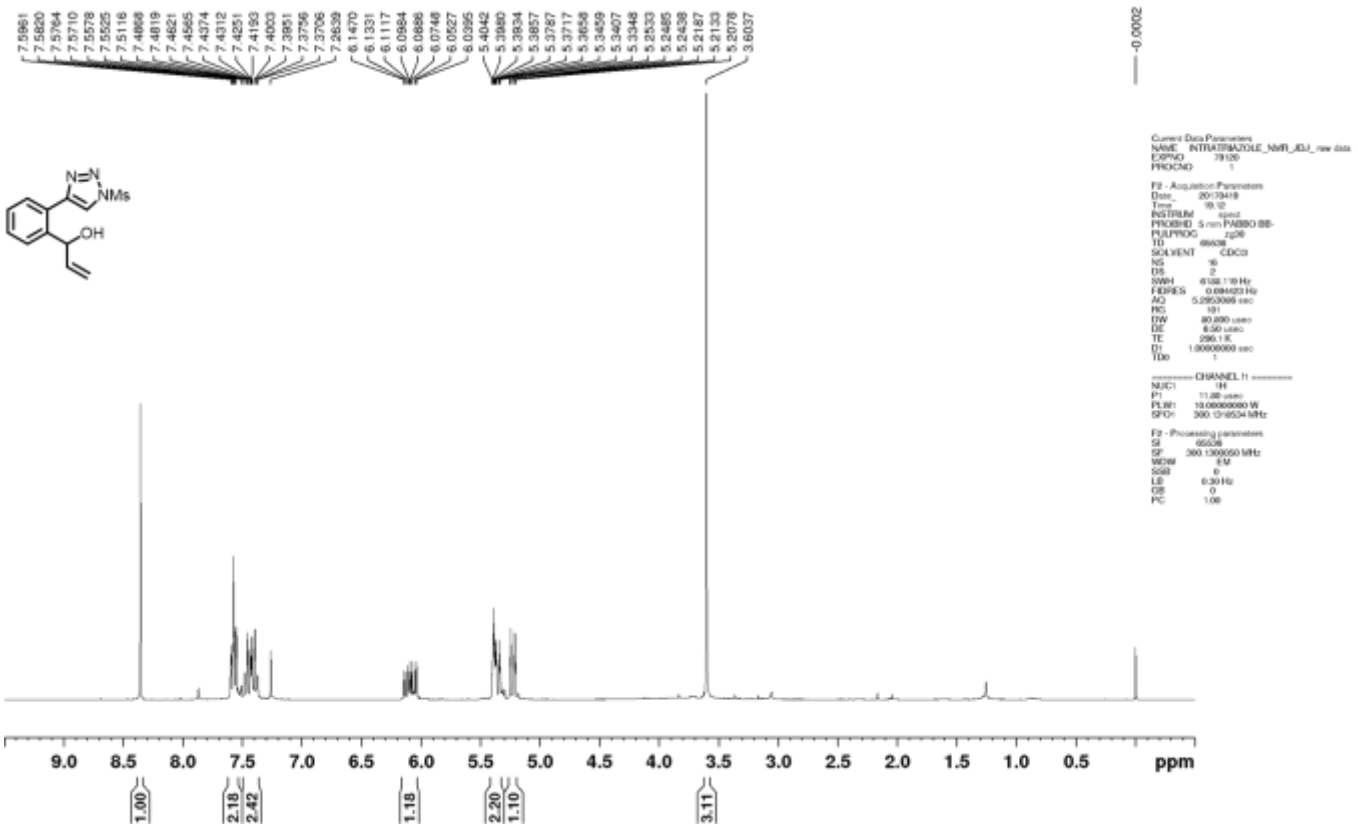
^{1}H spectra of compound **1j**



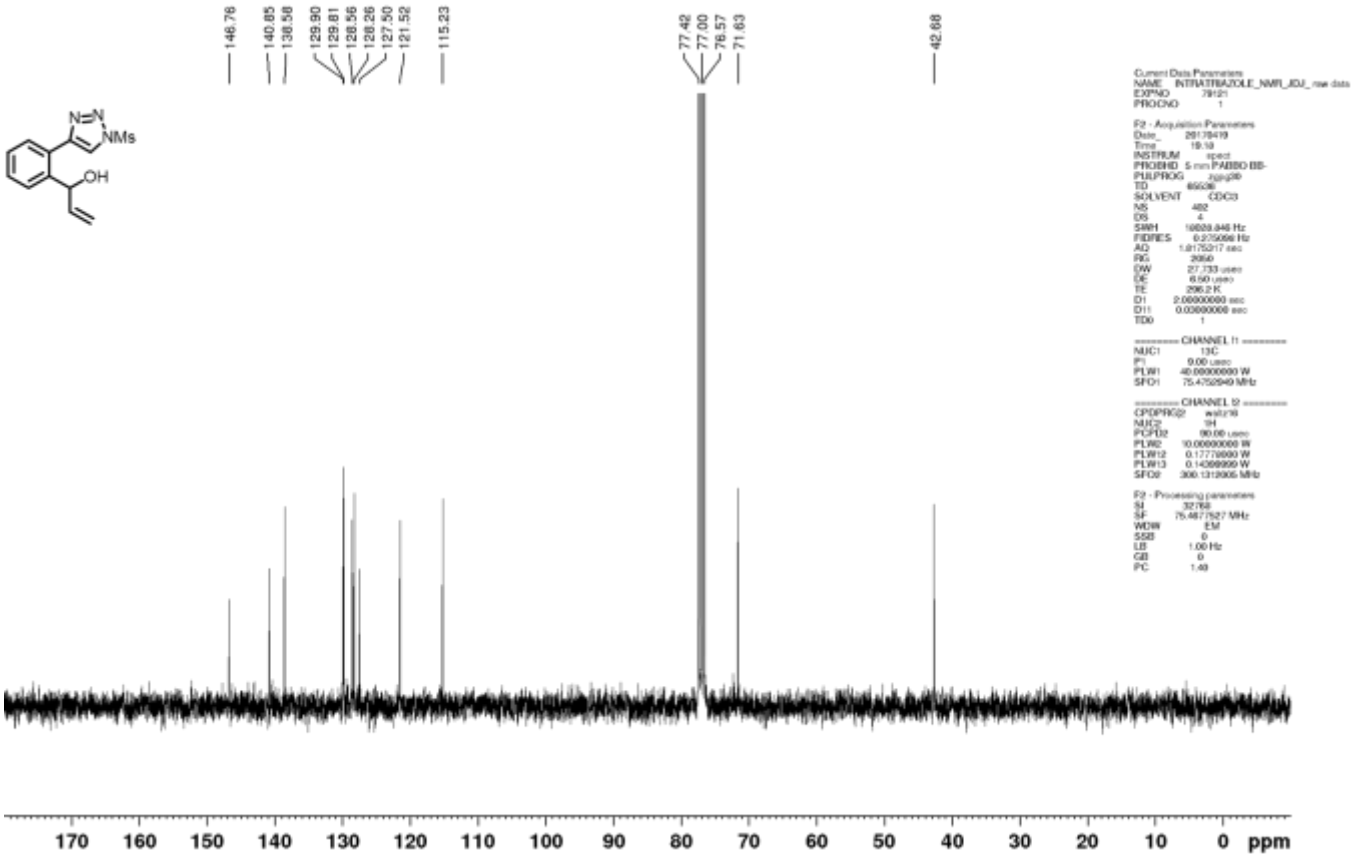
^{13}C spectra of compound **1j**



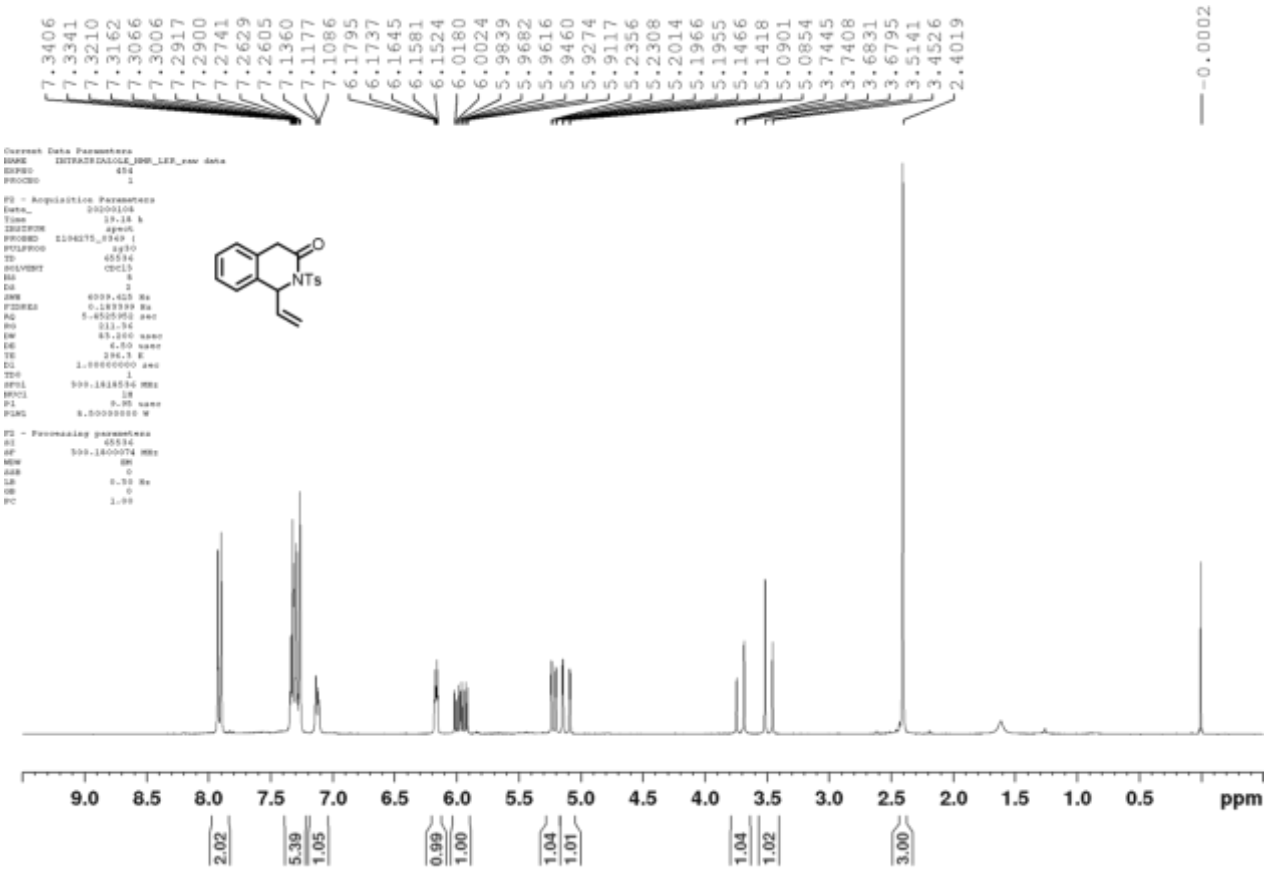
^{1}H spectra of compound **1k**



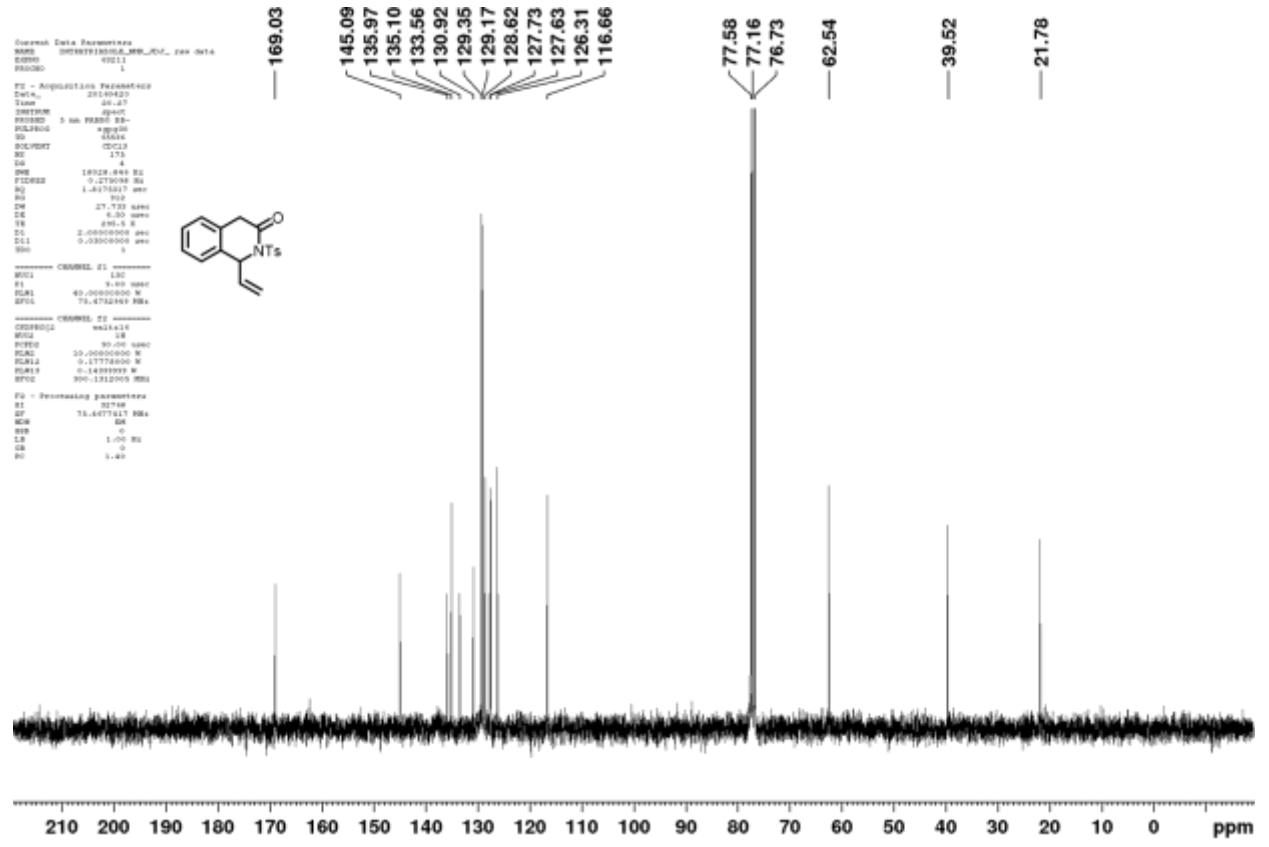
^{13}C spectra of compound **1k**



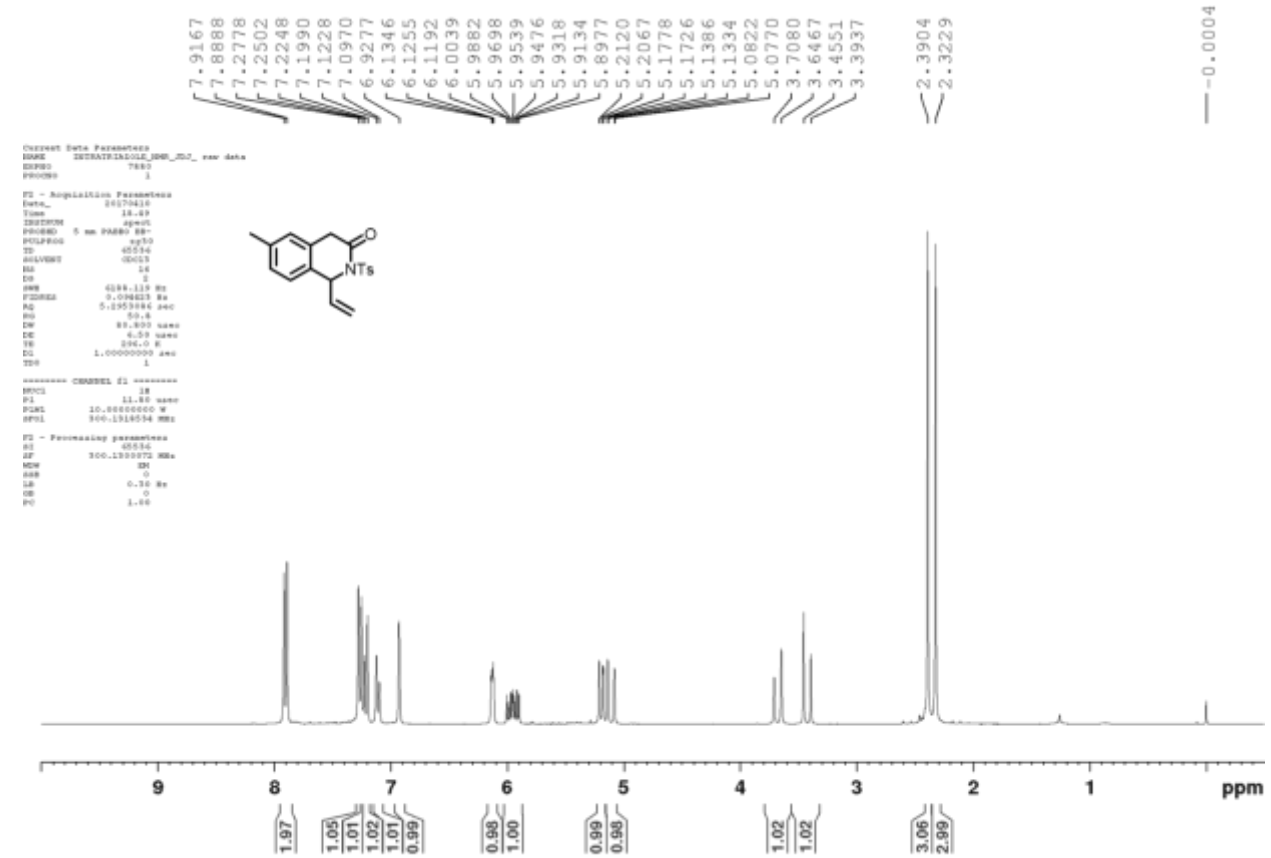
^{1}H spectra of compound **2a**



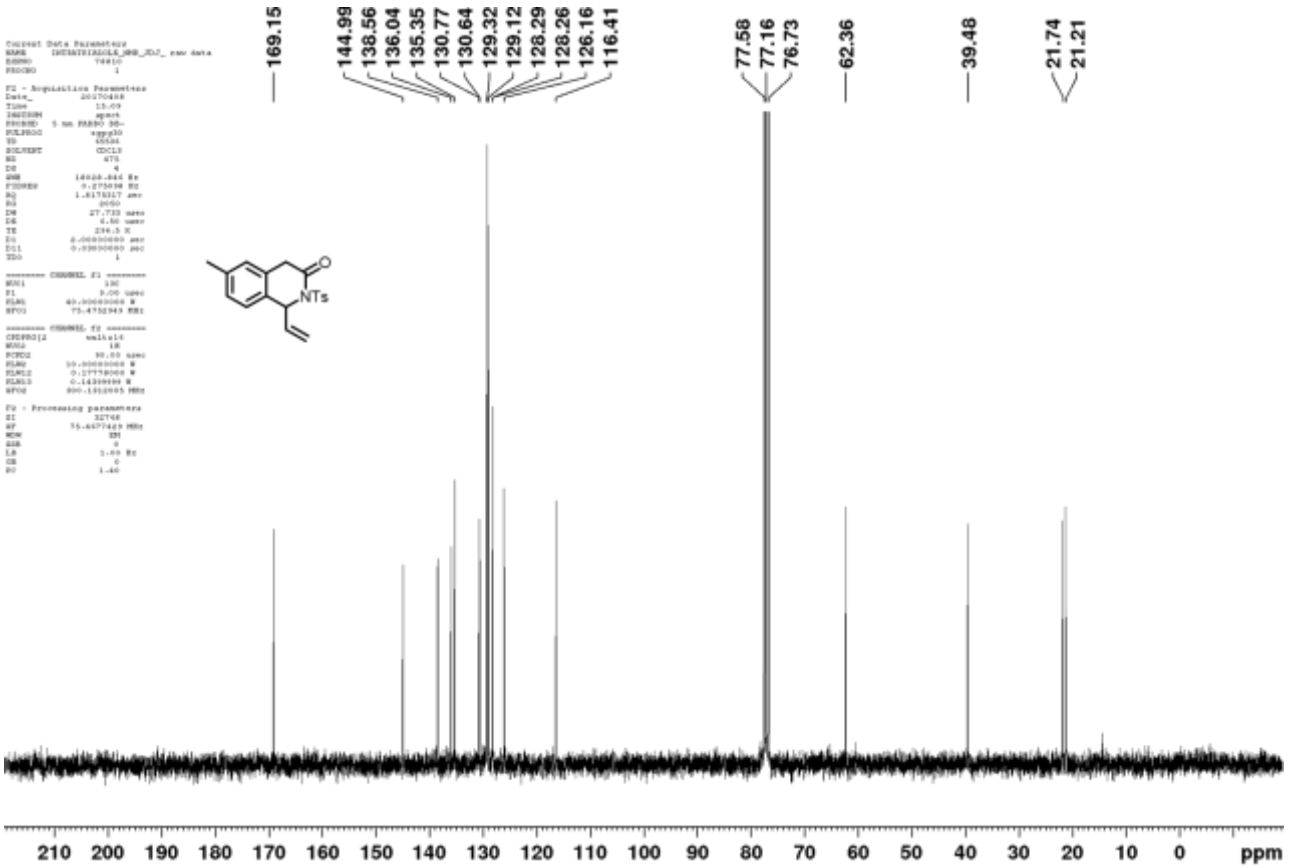
^{13}C spectra of compound **2a**



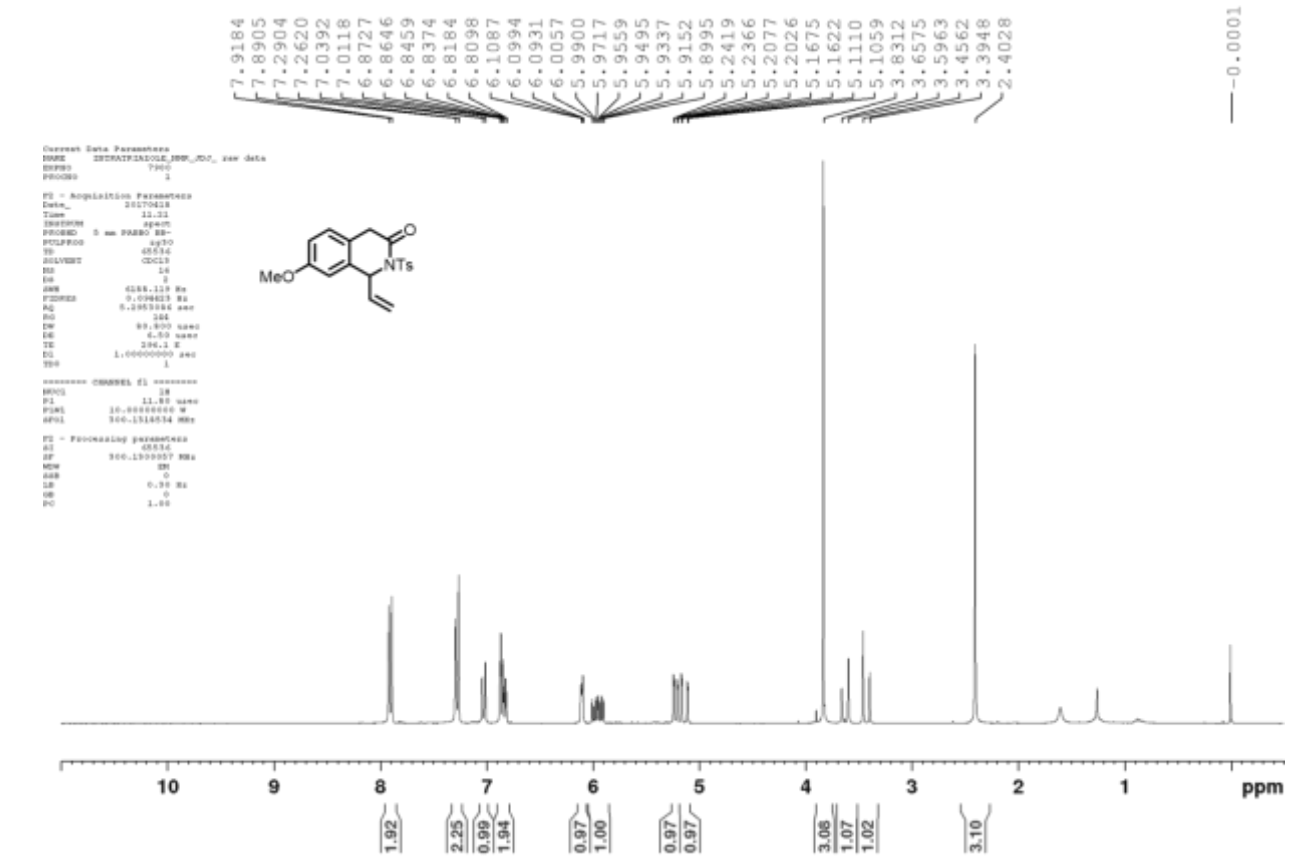
^{1}H spectra of compound **2b**



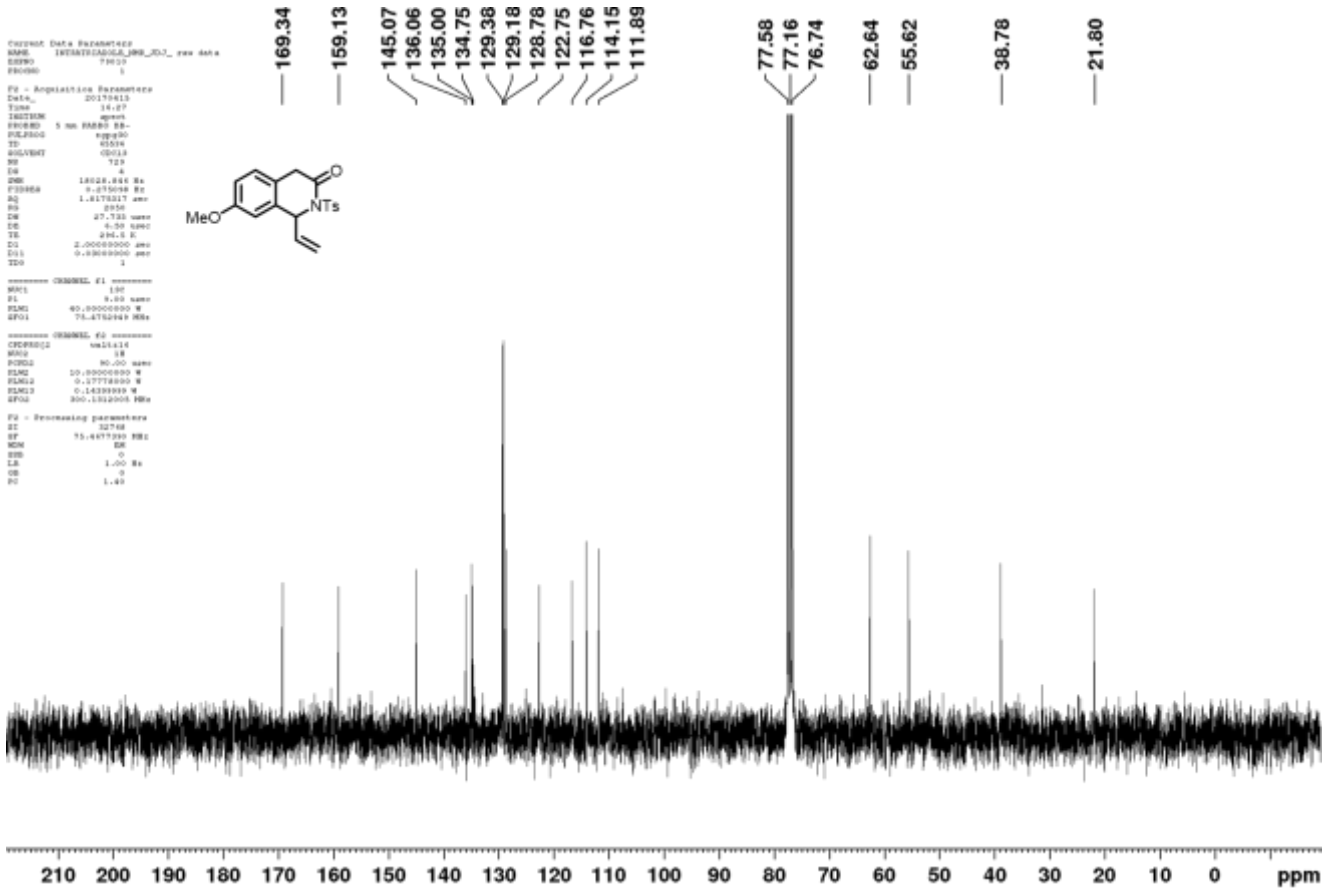
^{13}C spectra of compound **2b**



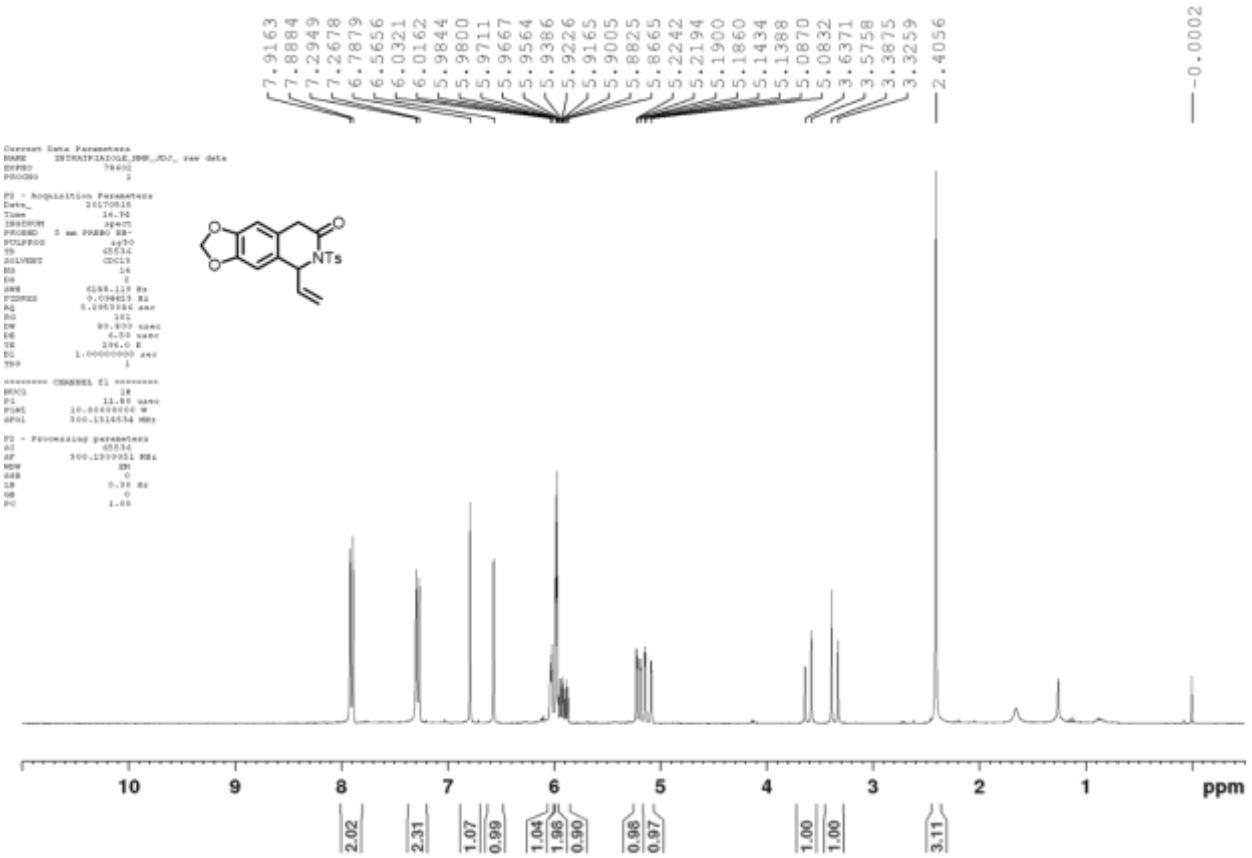
^{1}H spectra of compound **2c**



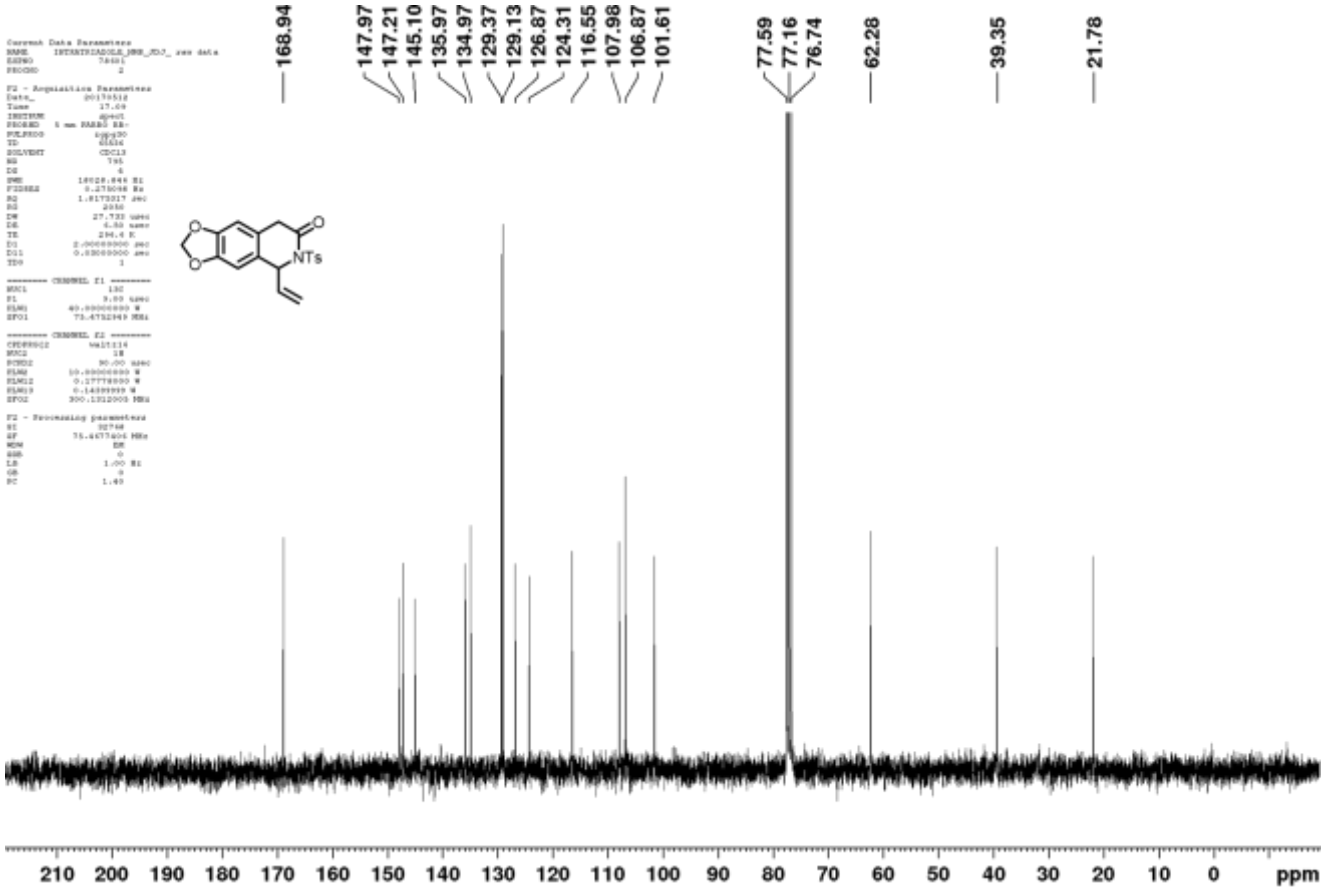
^{13}C spectra of compound **2c**



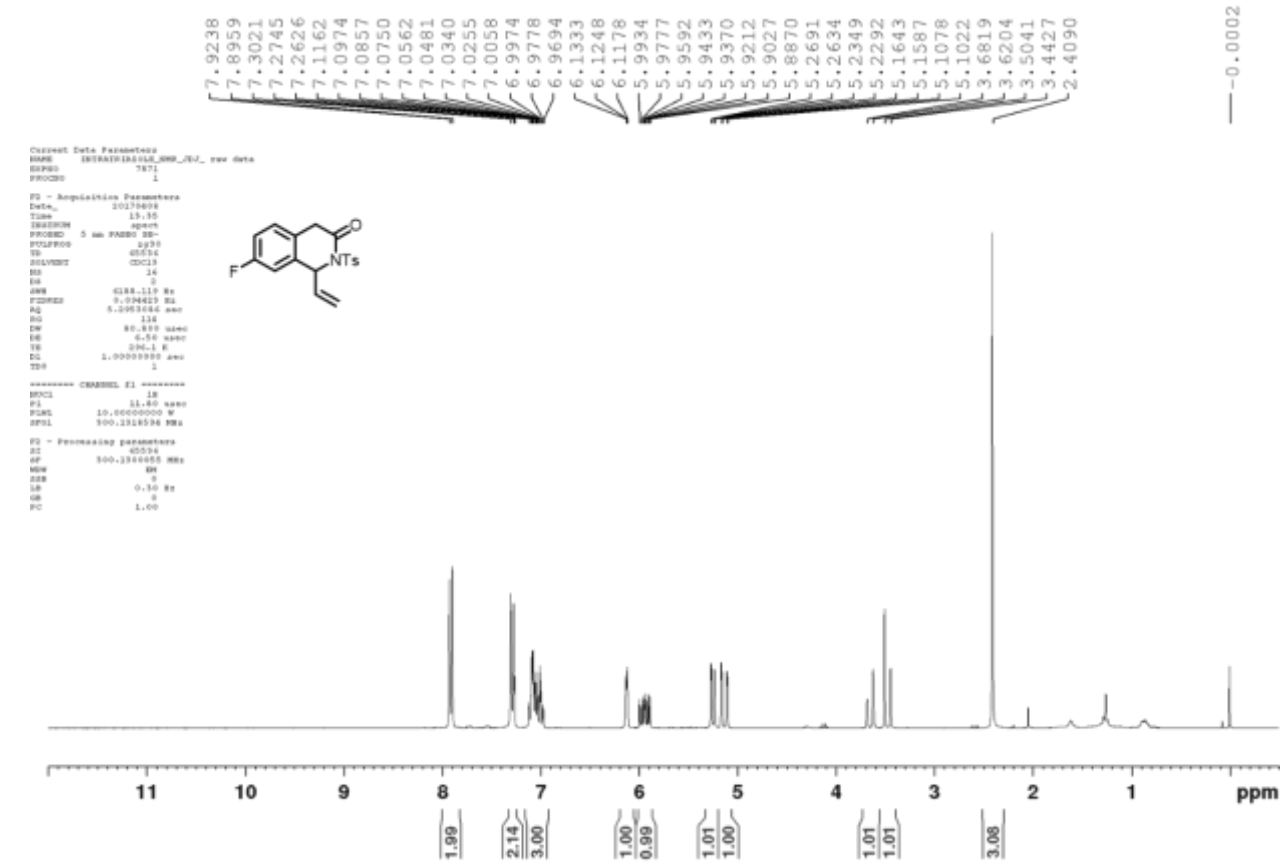
^{1}H spectra of compound **2d**



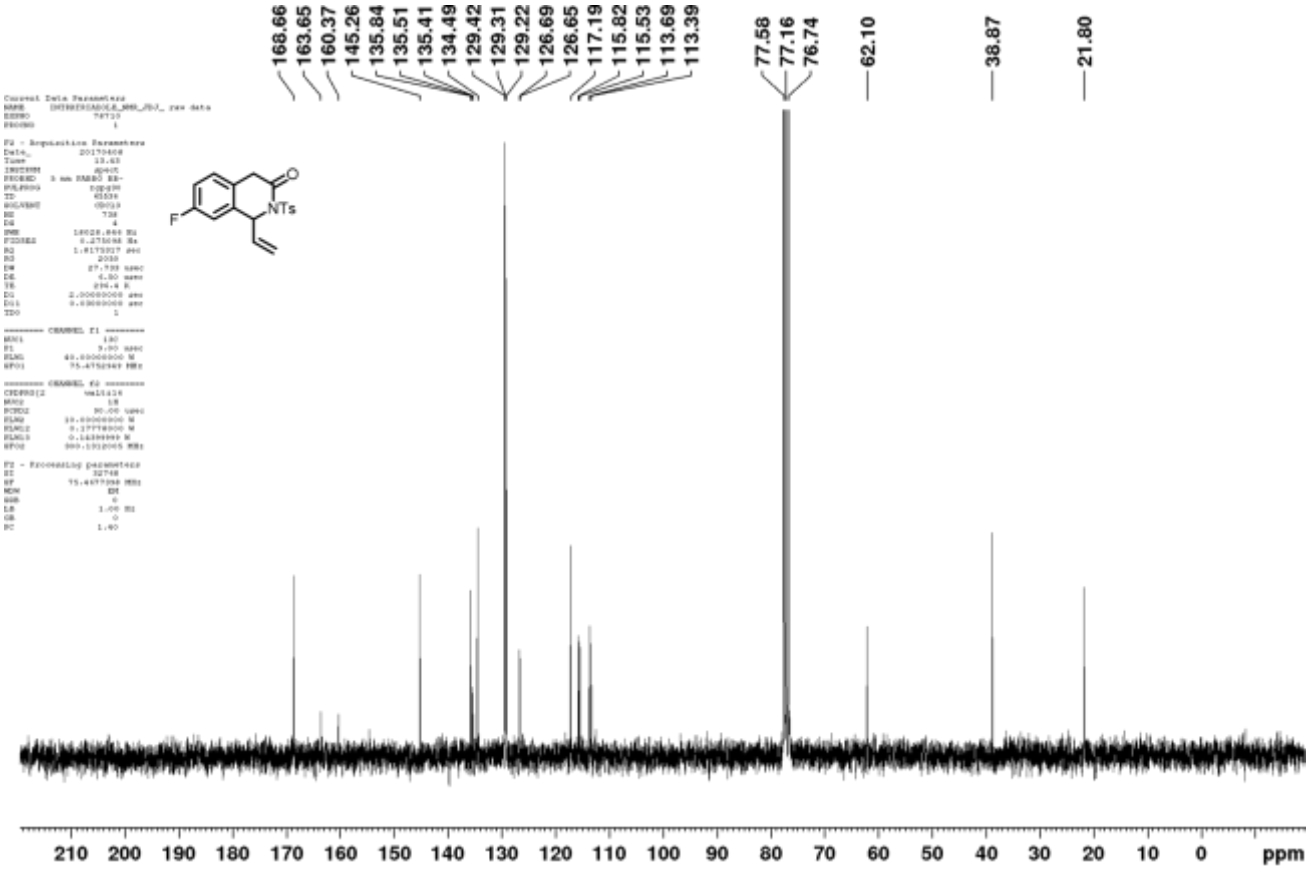
^{13}C spectra of compound **2d**



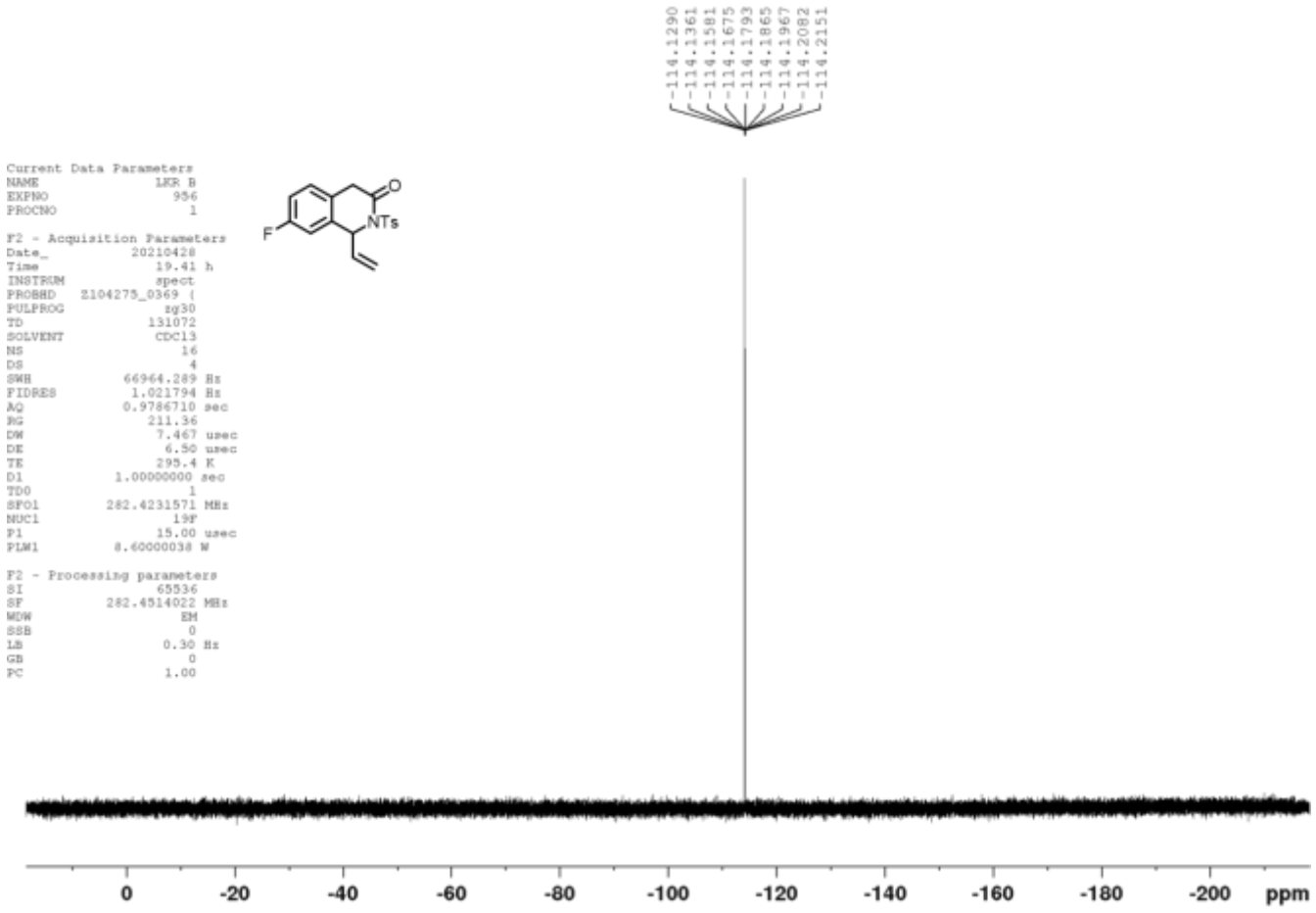
^{1}H spectra of compound **2e**



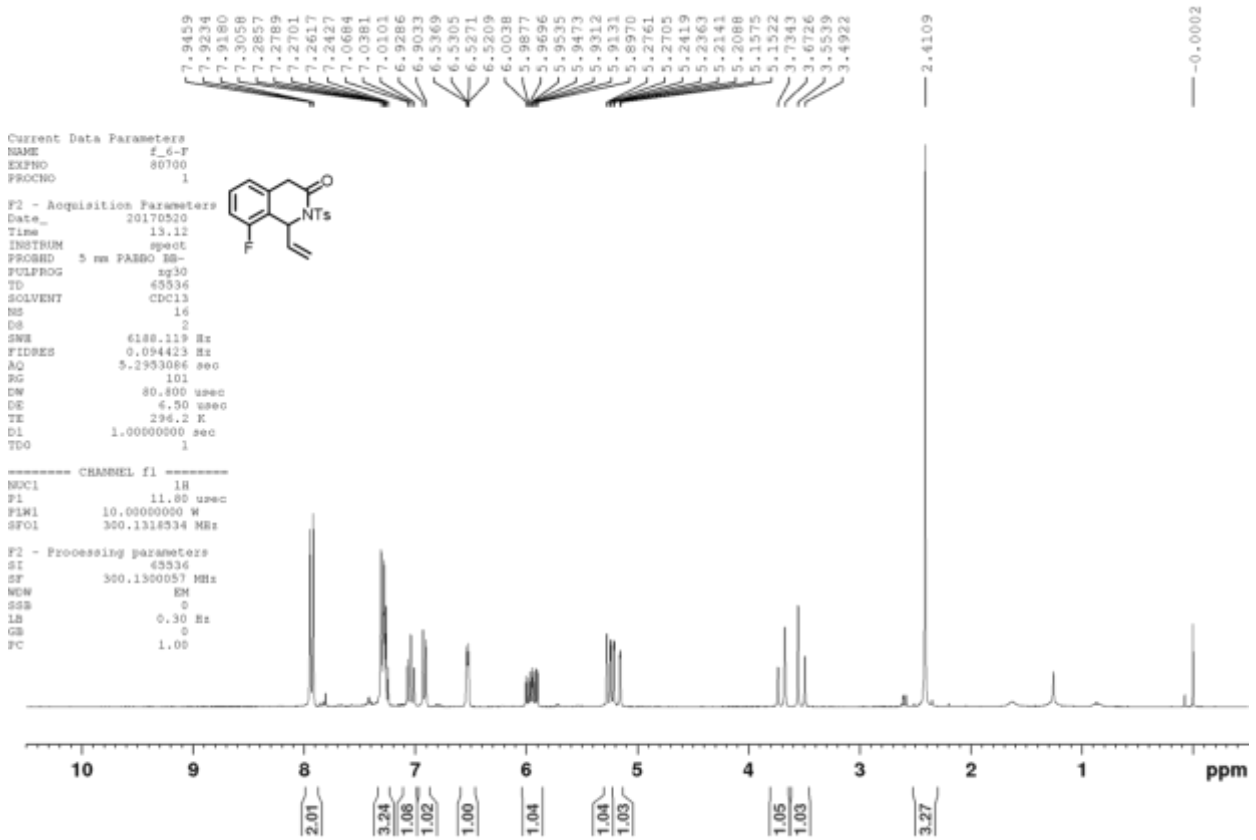
^{13}C spectra of compound **2e**



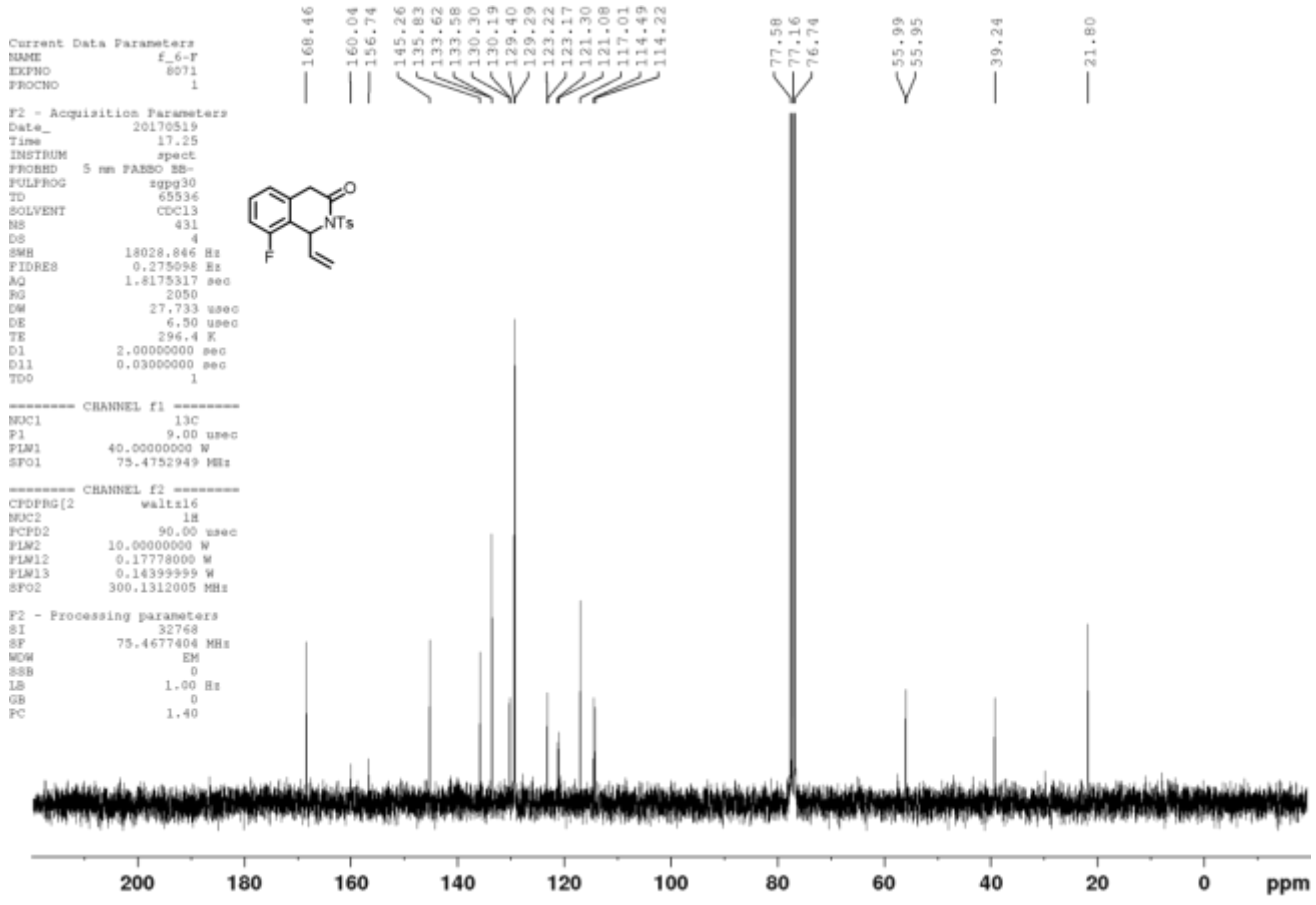
^{19}F spectra of compound **2e**



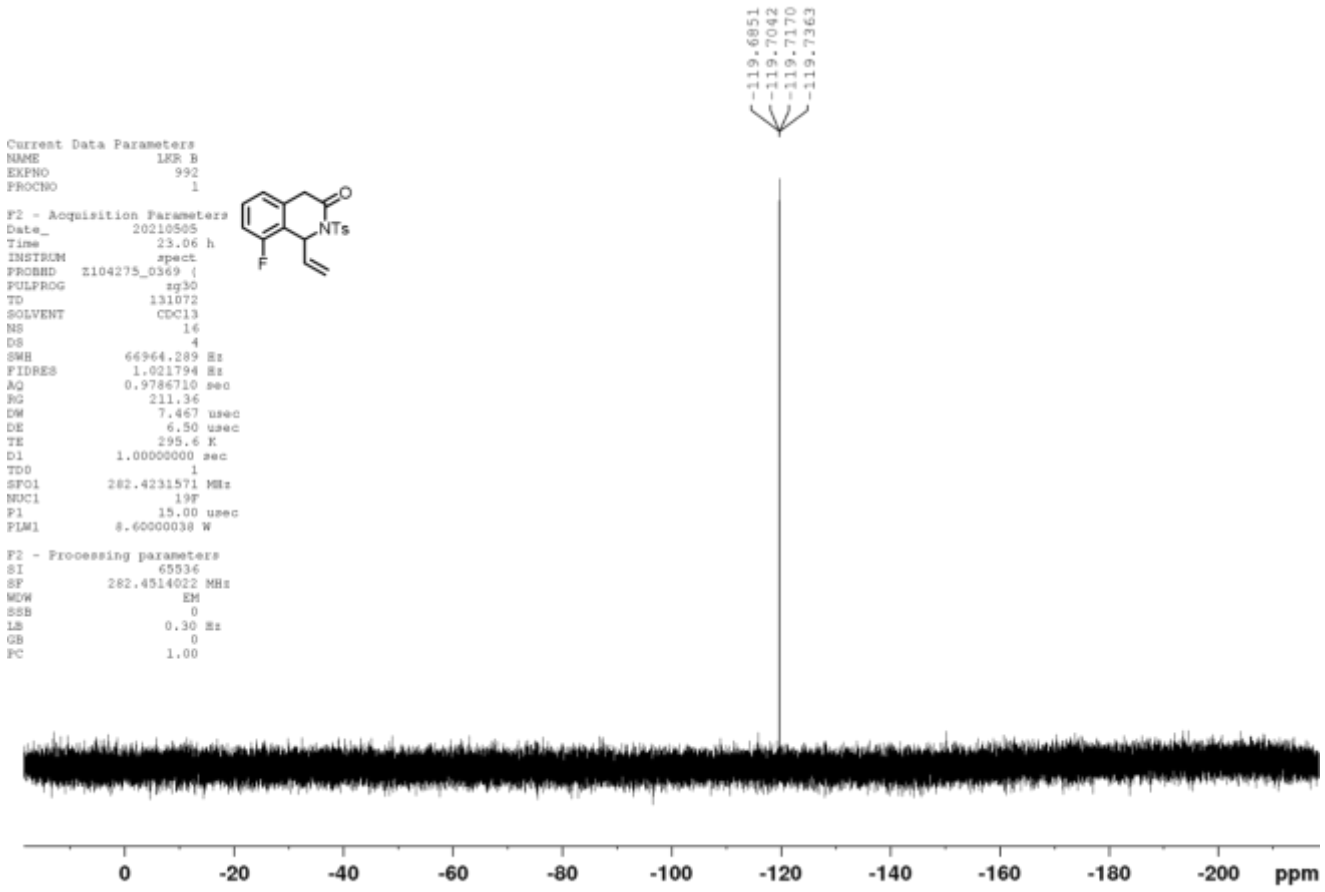
^{1}H spectra of compound **2f**



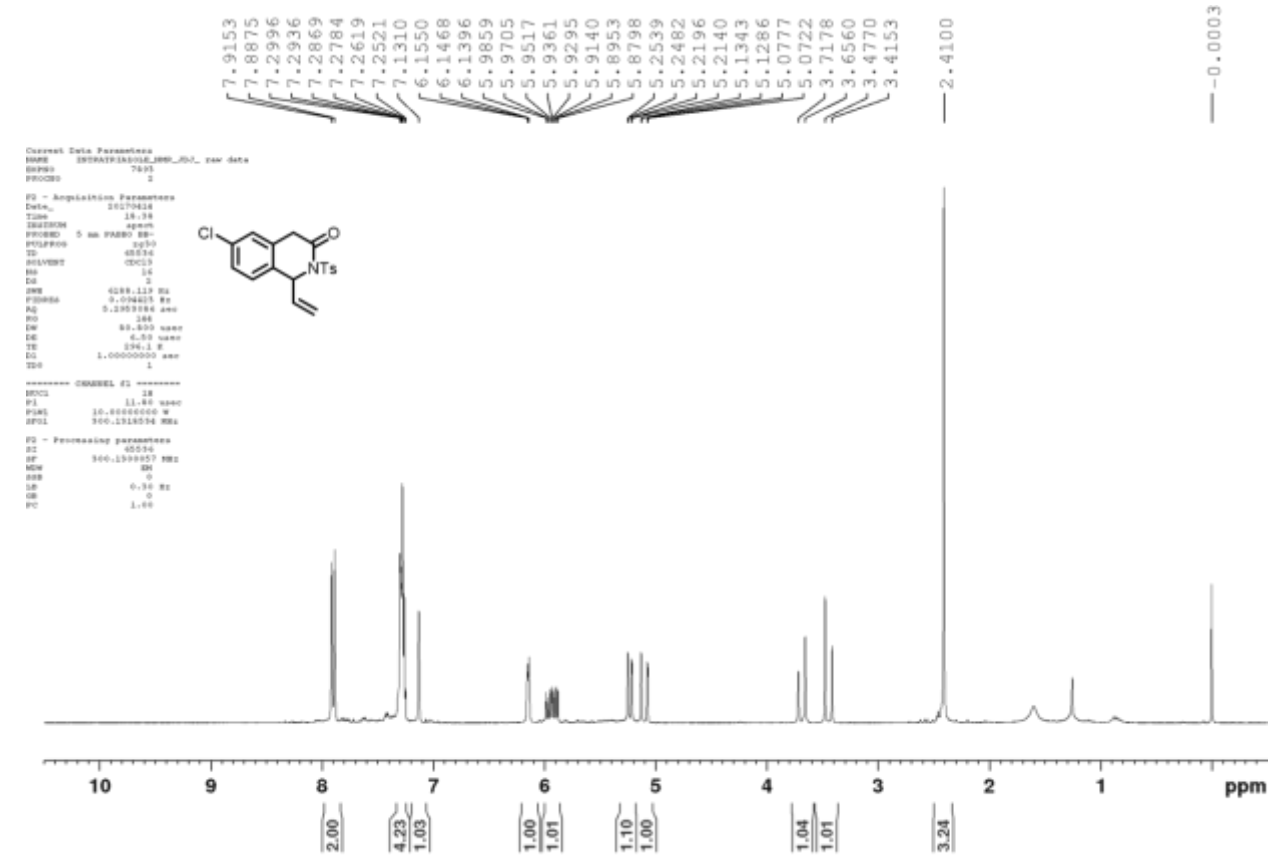
^{13}C spectra of compound **2f**



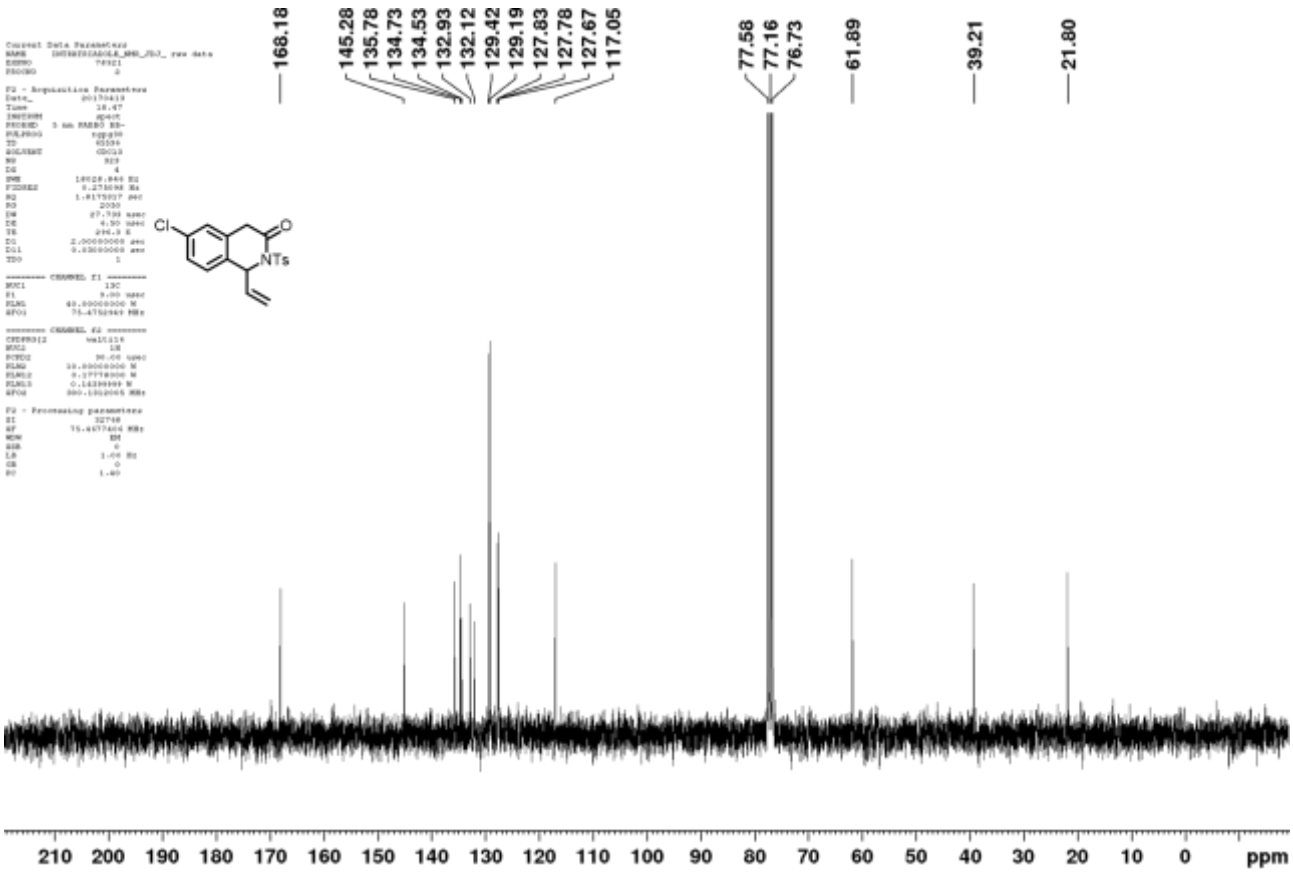
^{19}F spectra of compound **2f**



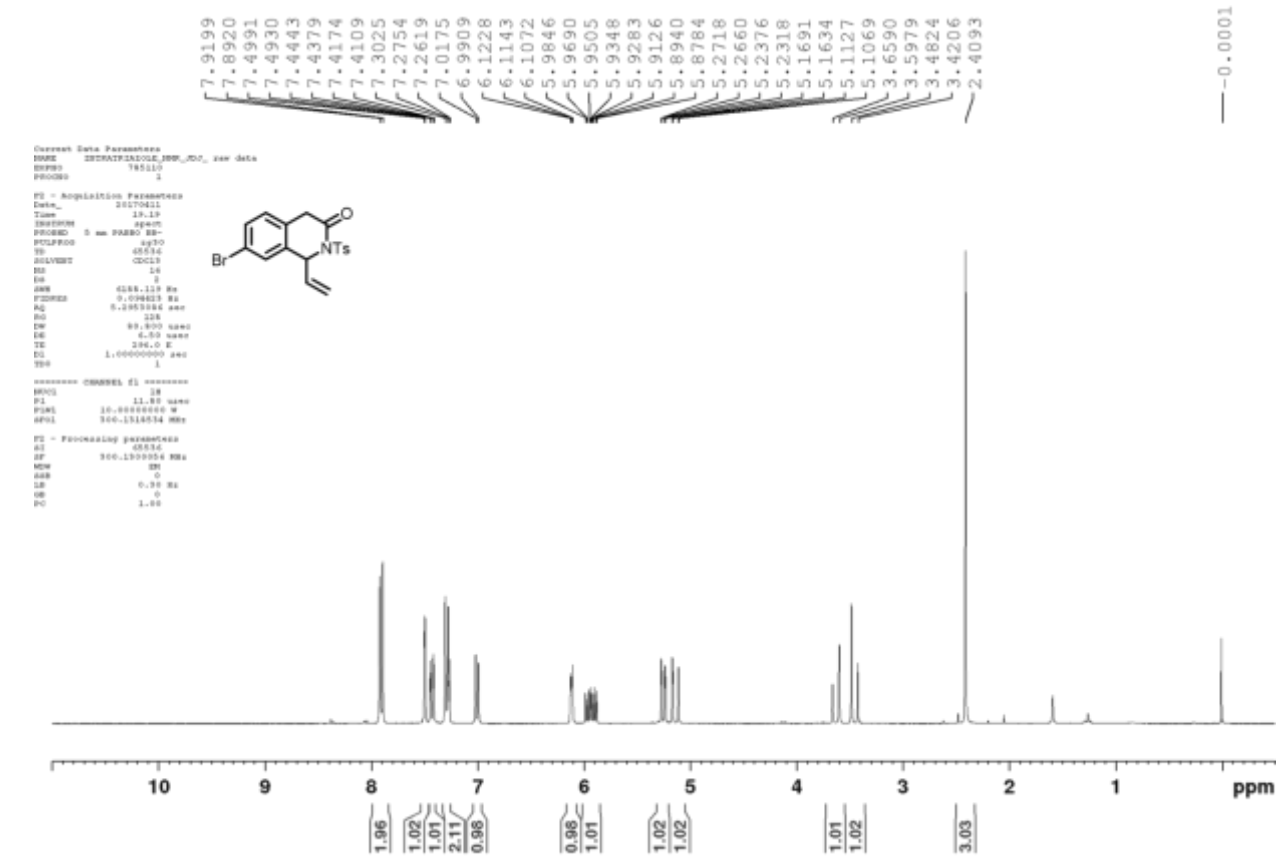
^{1}H spectra of compound **2g**



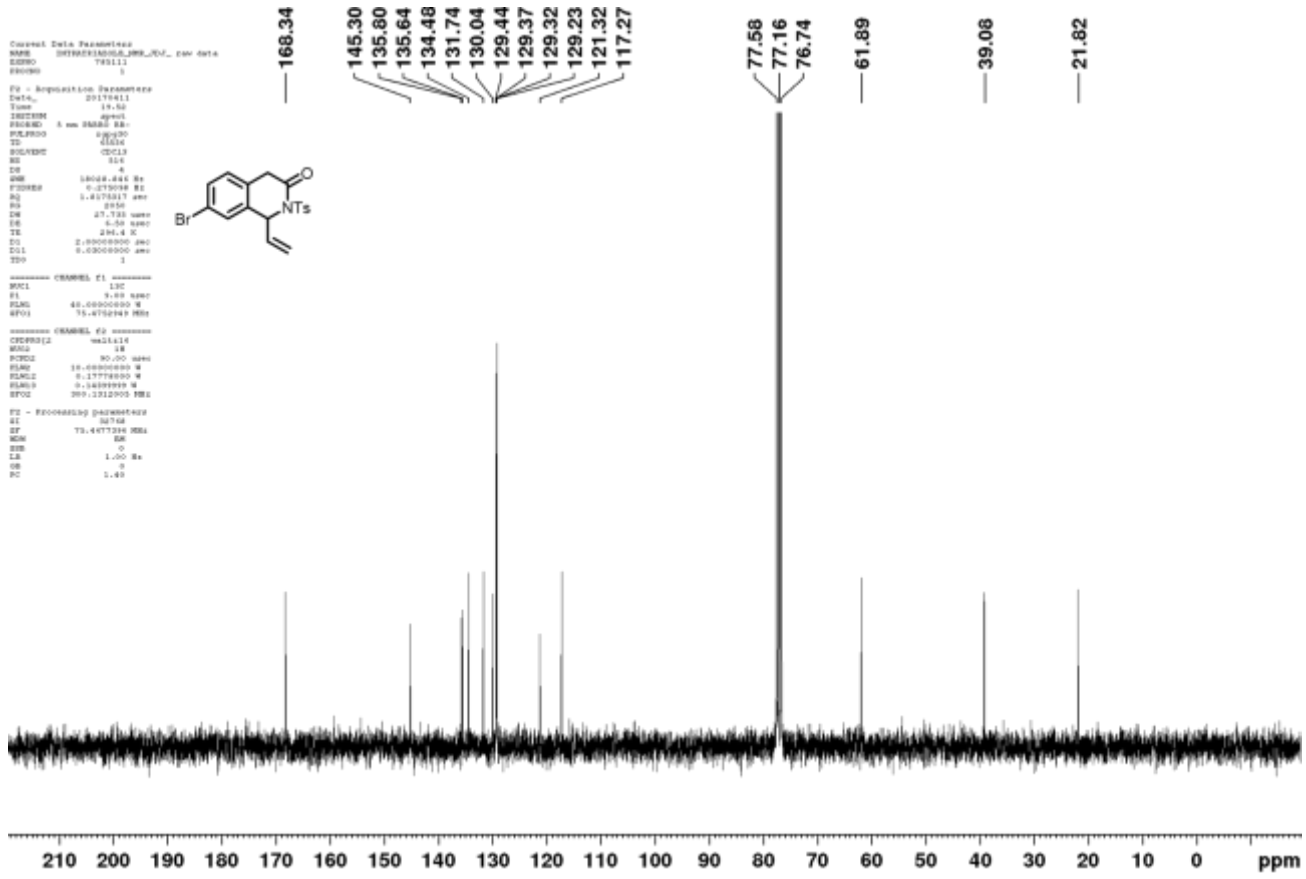
^{13}C spectra of compound **2g**



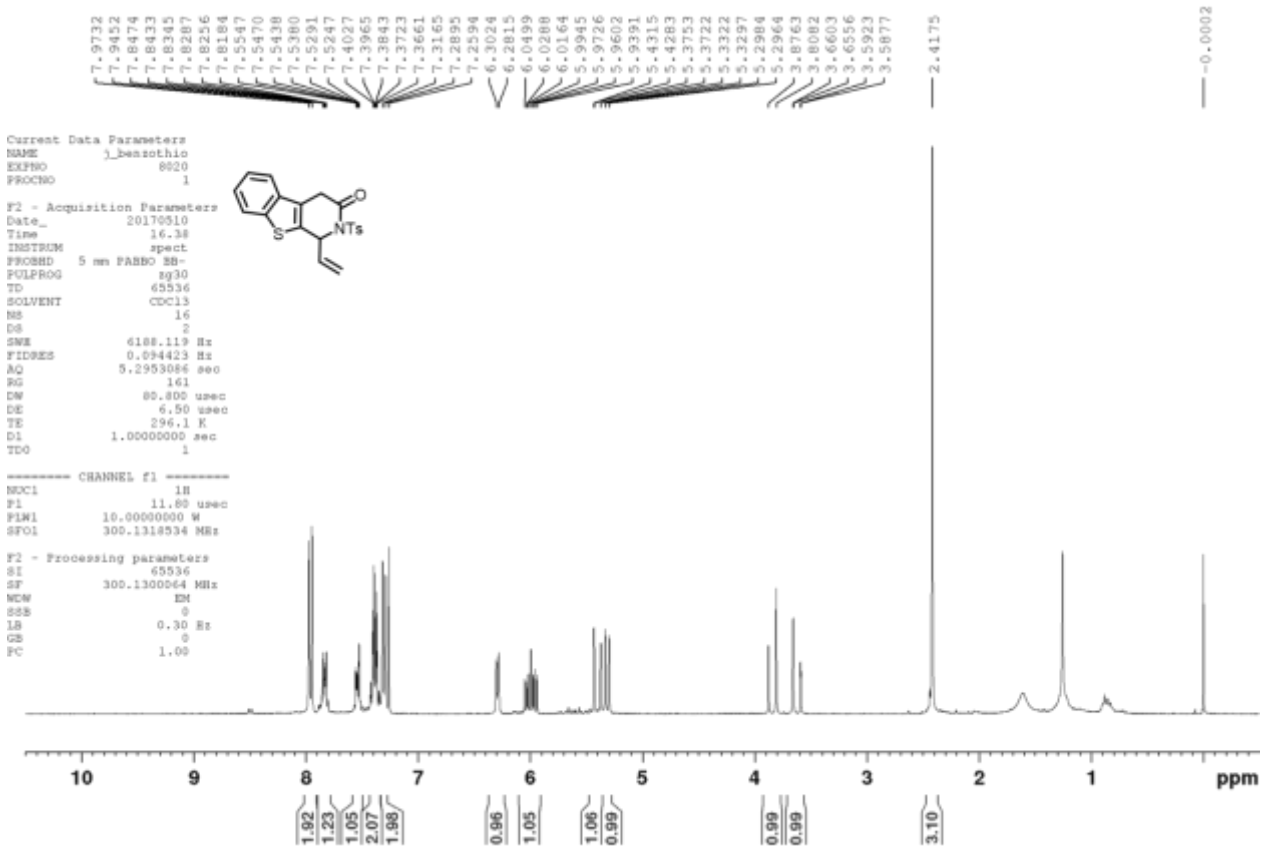
^{1}H spectra of compound **2h**



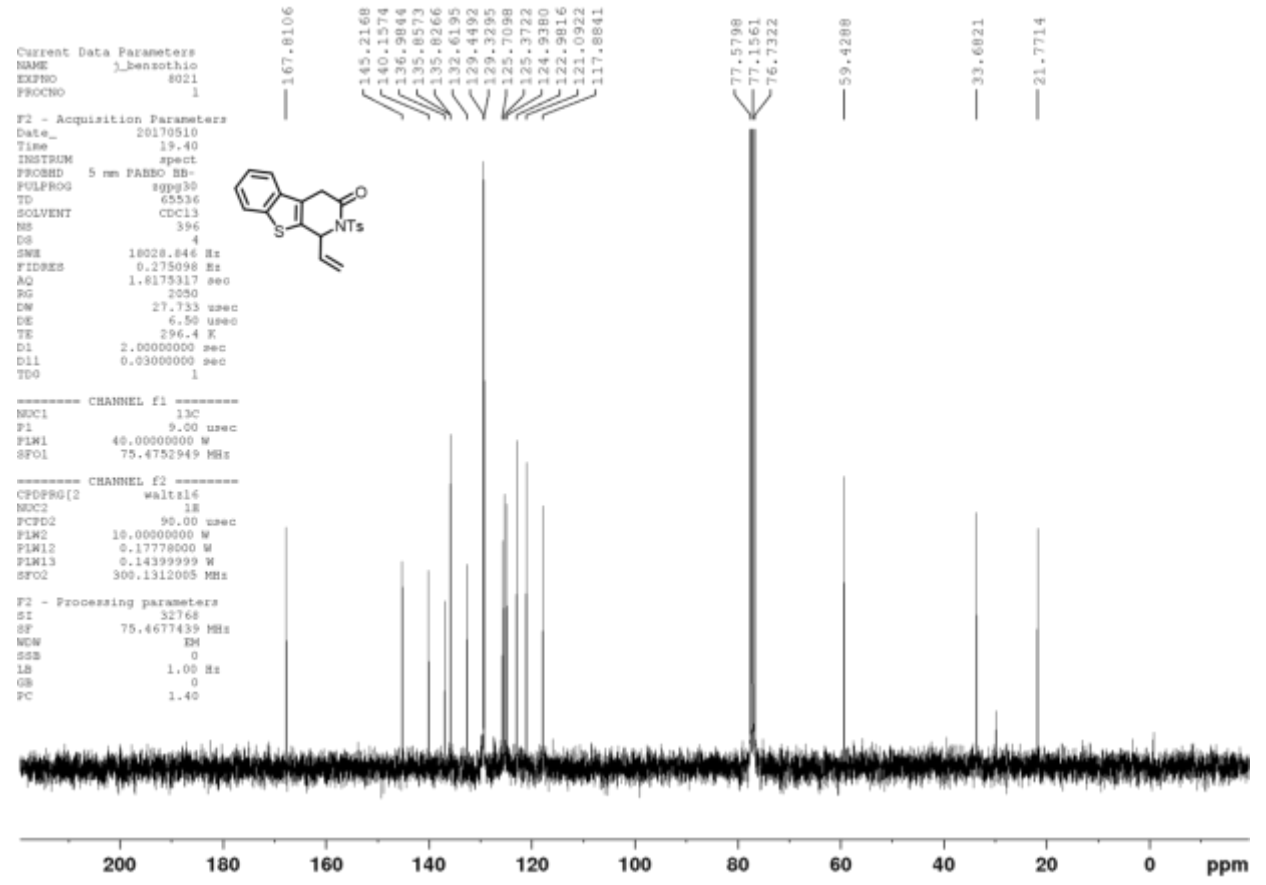
^{13}C spectra of compound **2h**



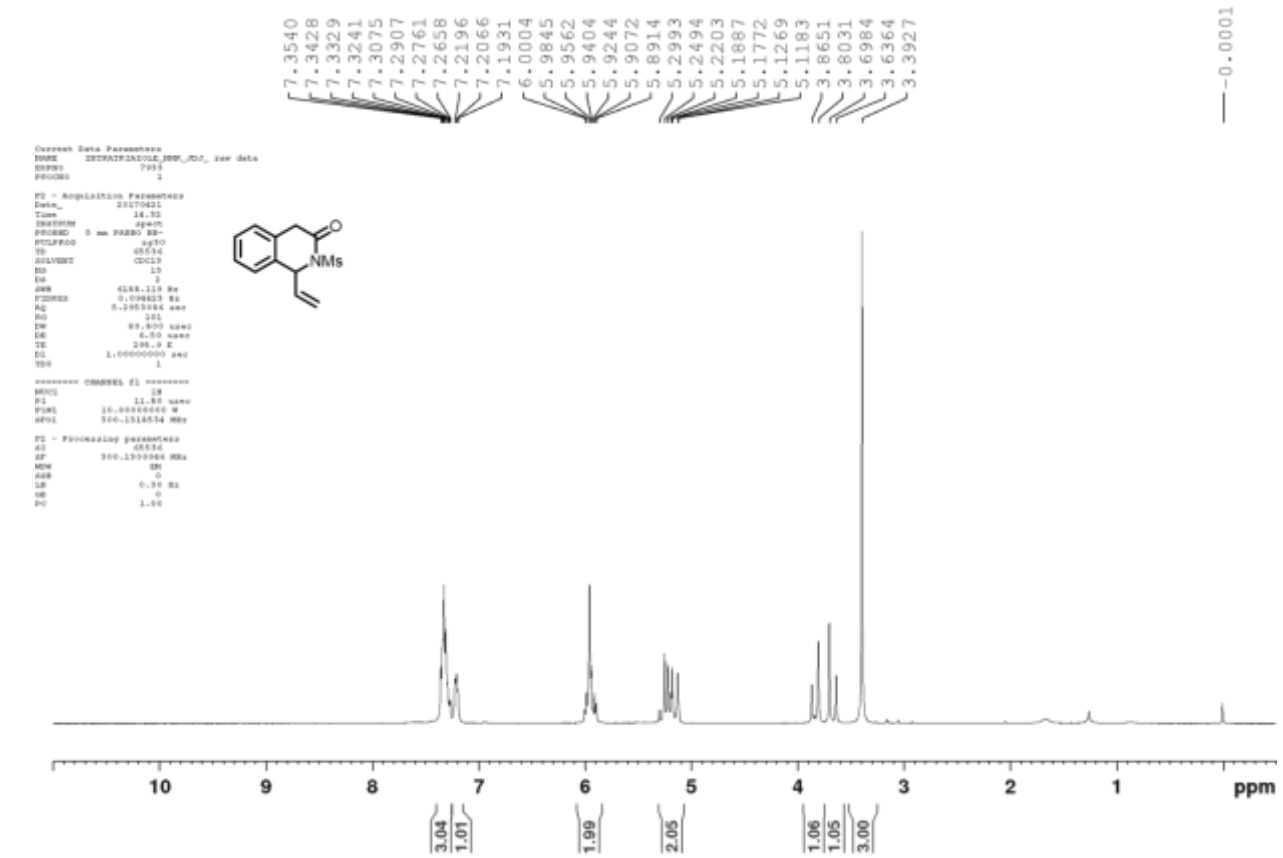
^{1}H spectra of compound **2j**



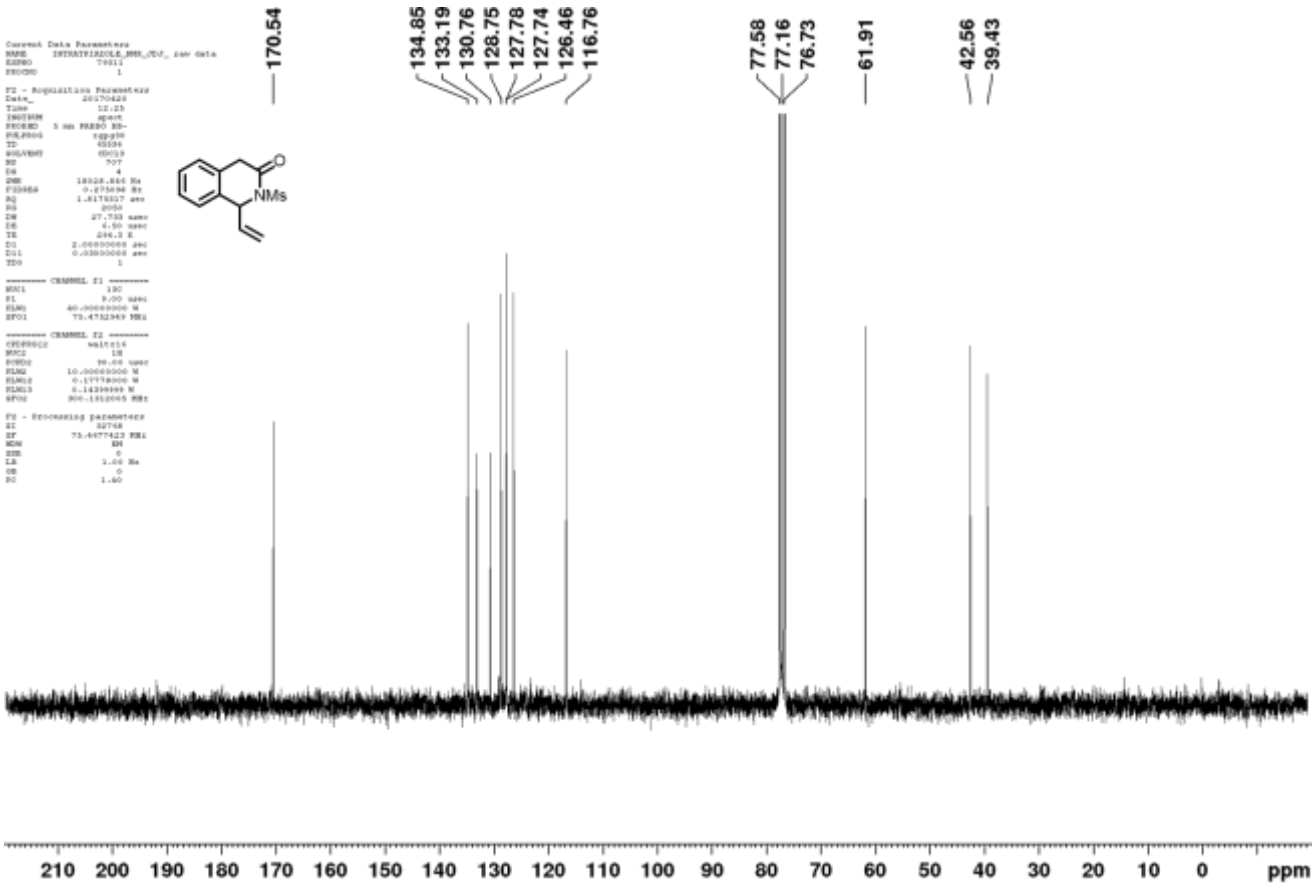
^{13}C spectra of compound **2j**



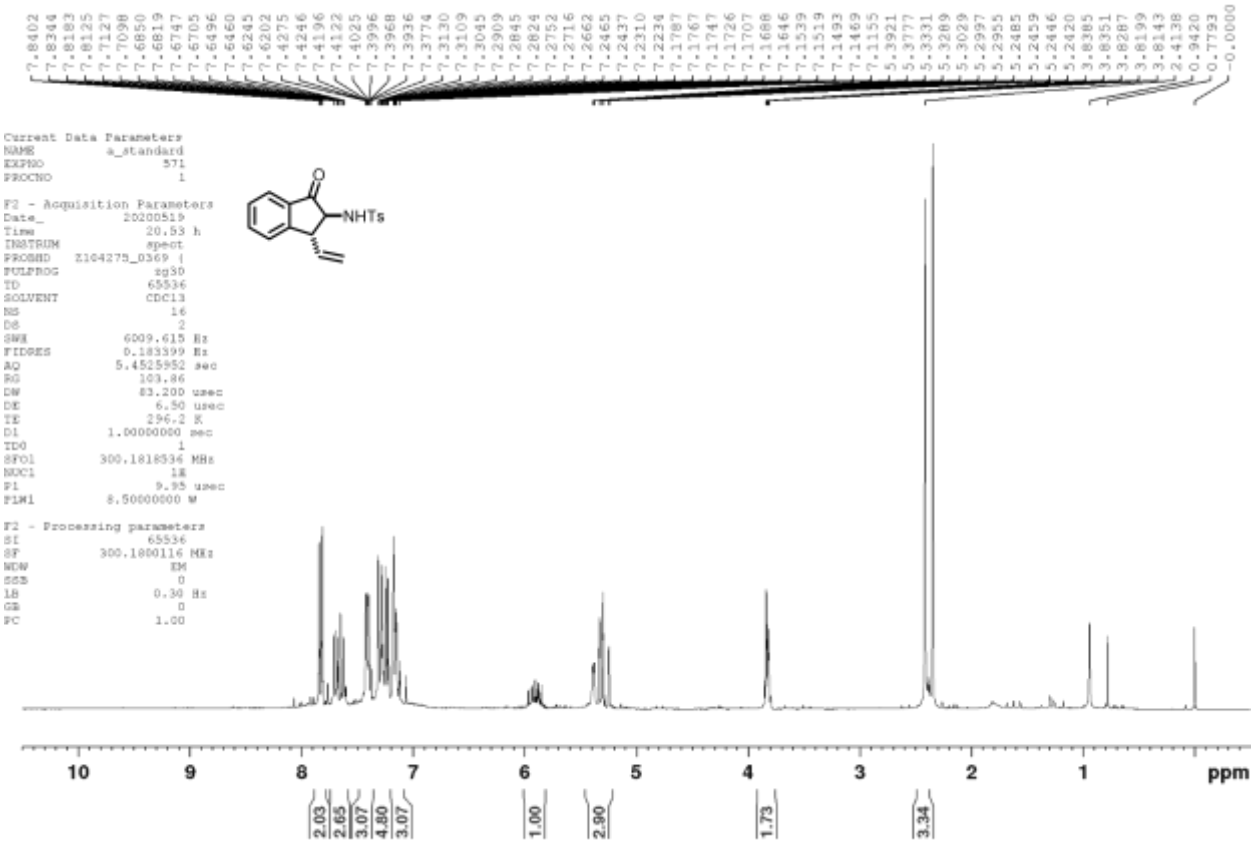
^{1}H spectra of compound **2k**



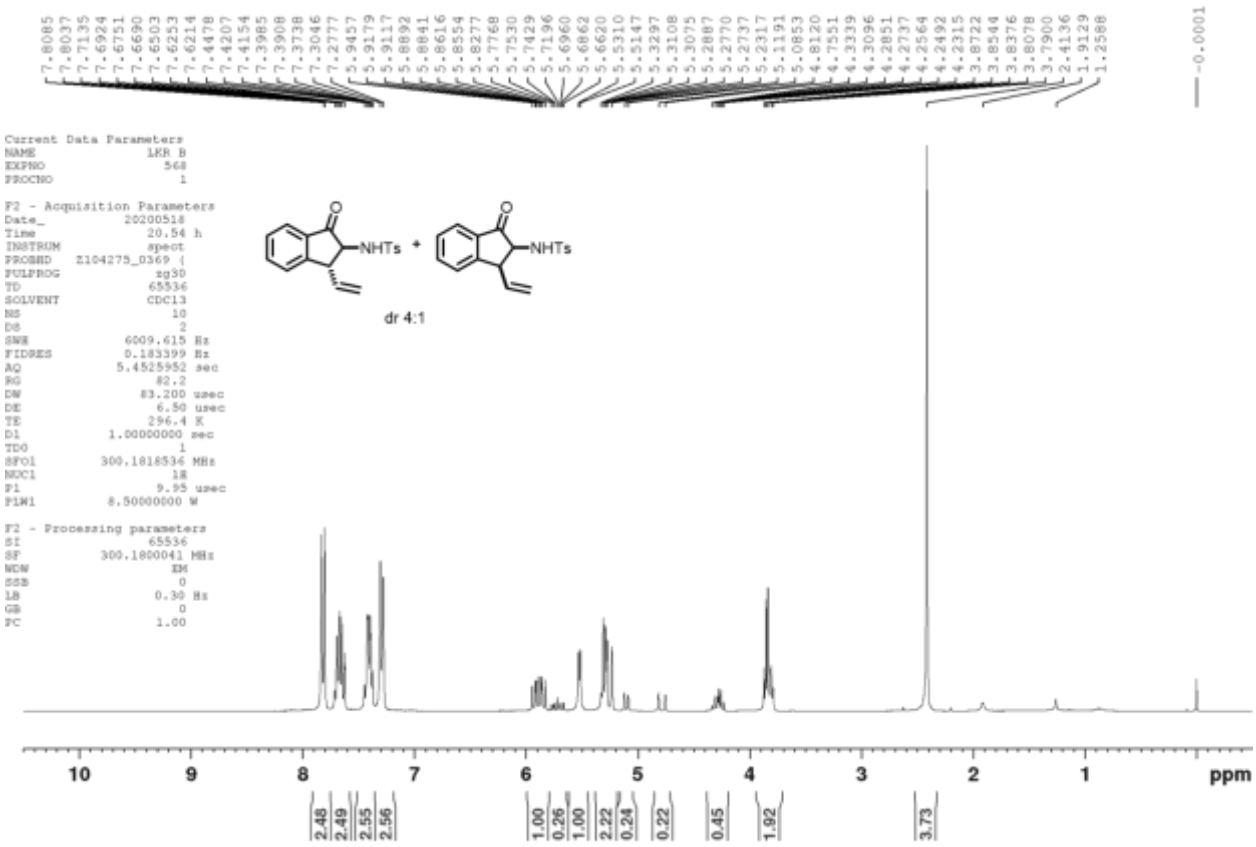
^{13}C spectra of compound **2k**



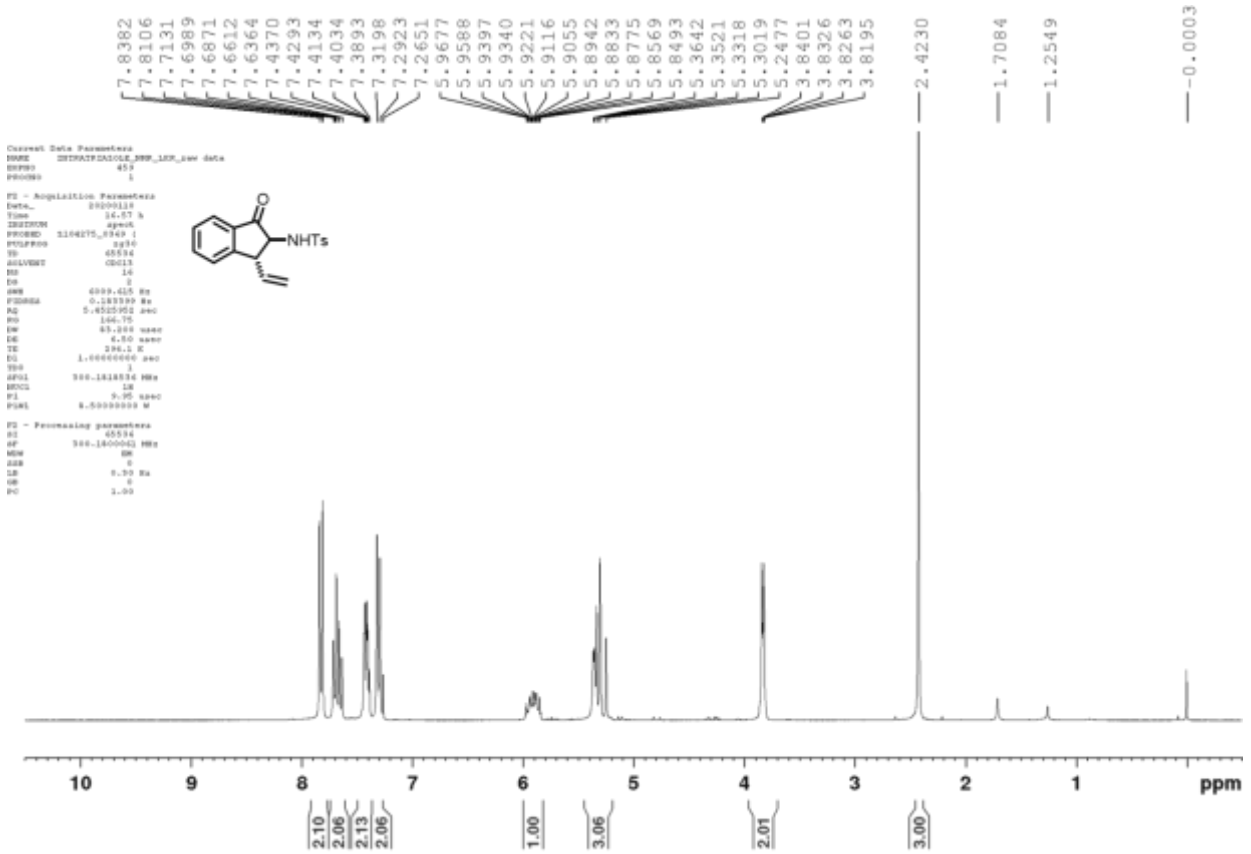
^{1}H spectra of compound **3a** (crude)



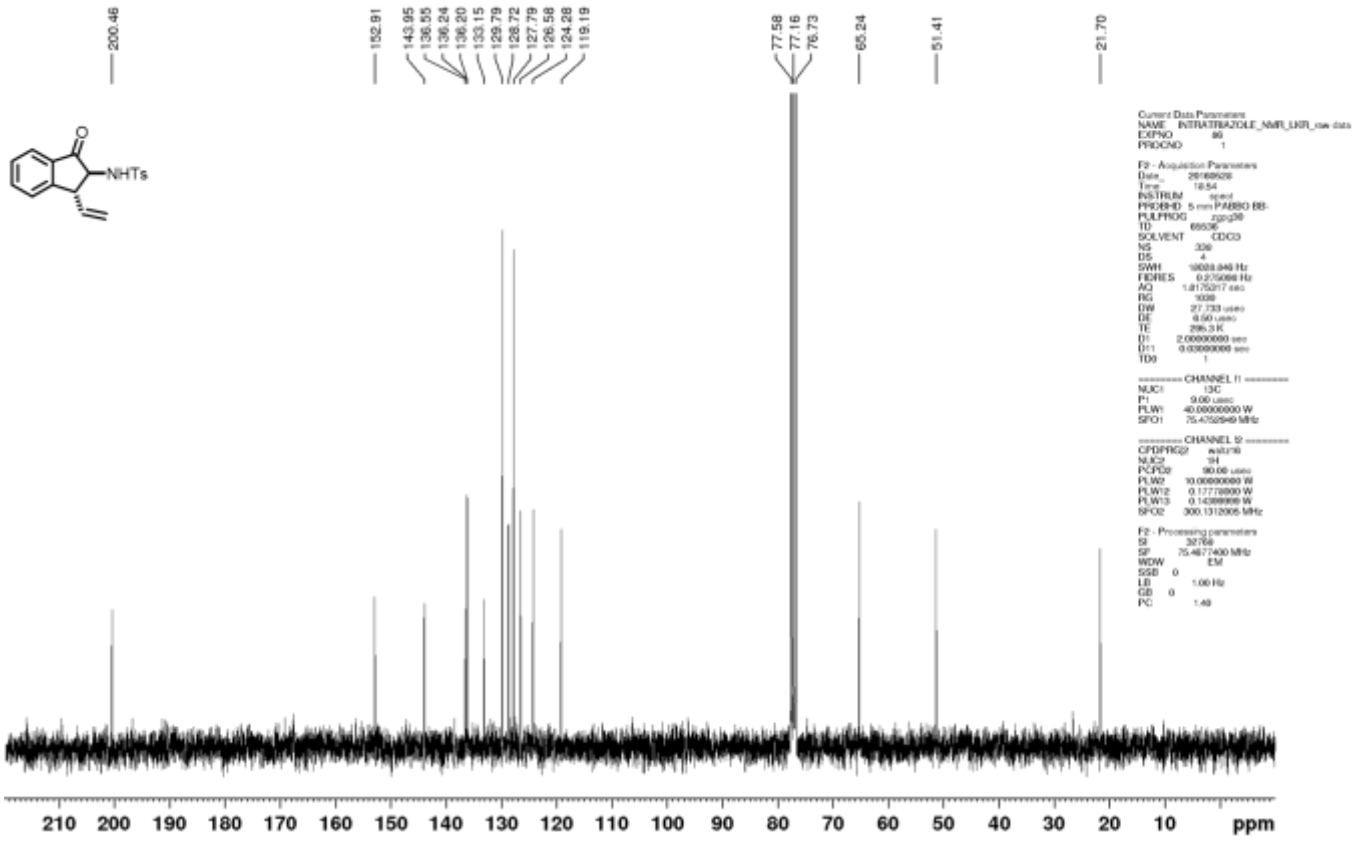
^{1}H spectra of compound **3a** (*cis/trans* mixture after column chromatography)



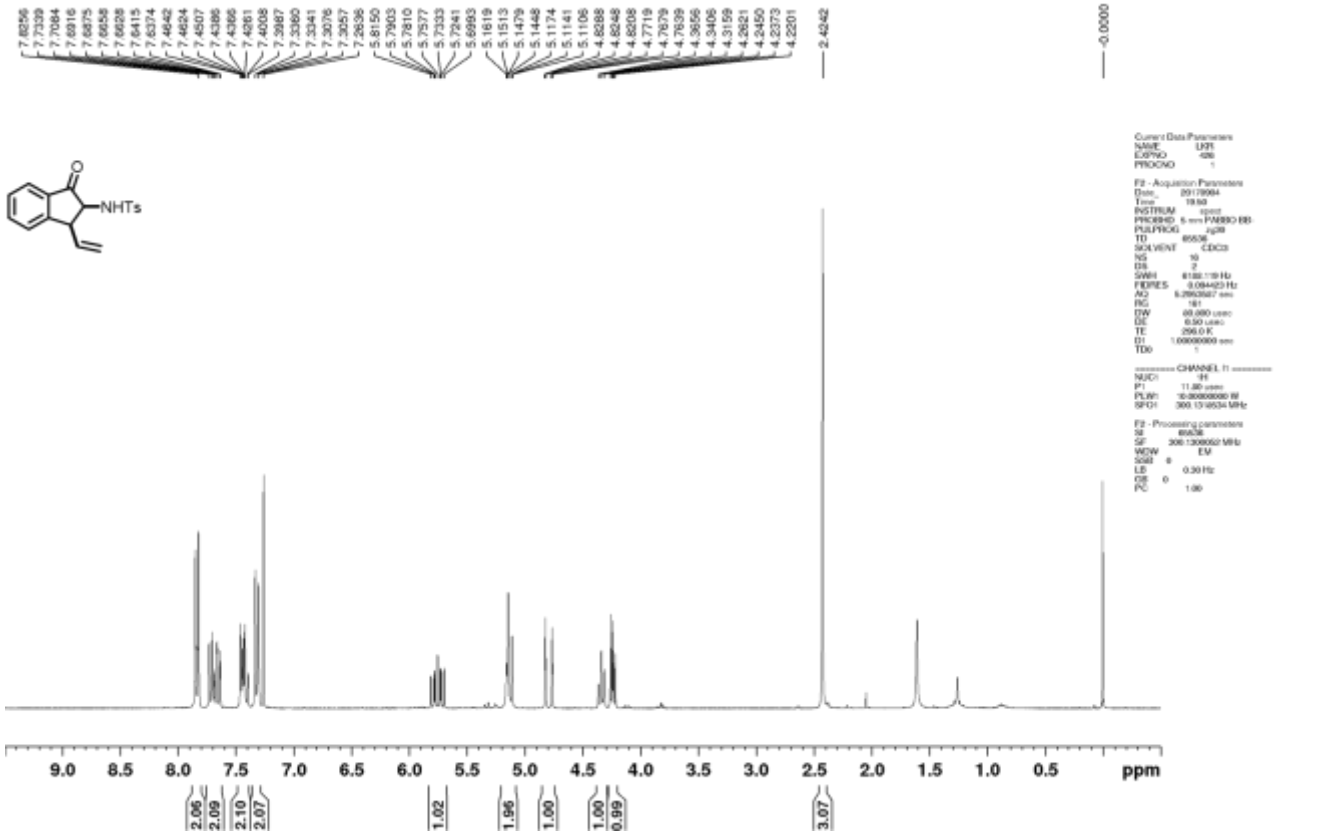
^{1}H spectra of compound **3a** (*trans*)



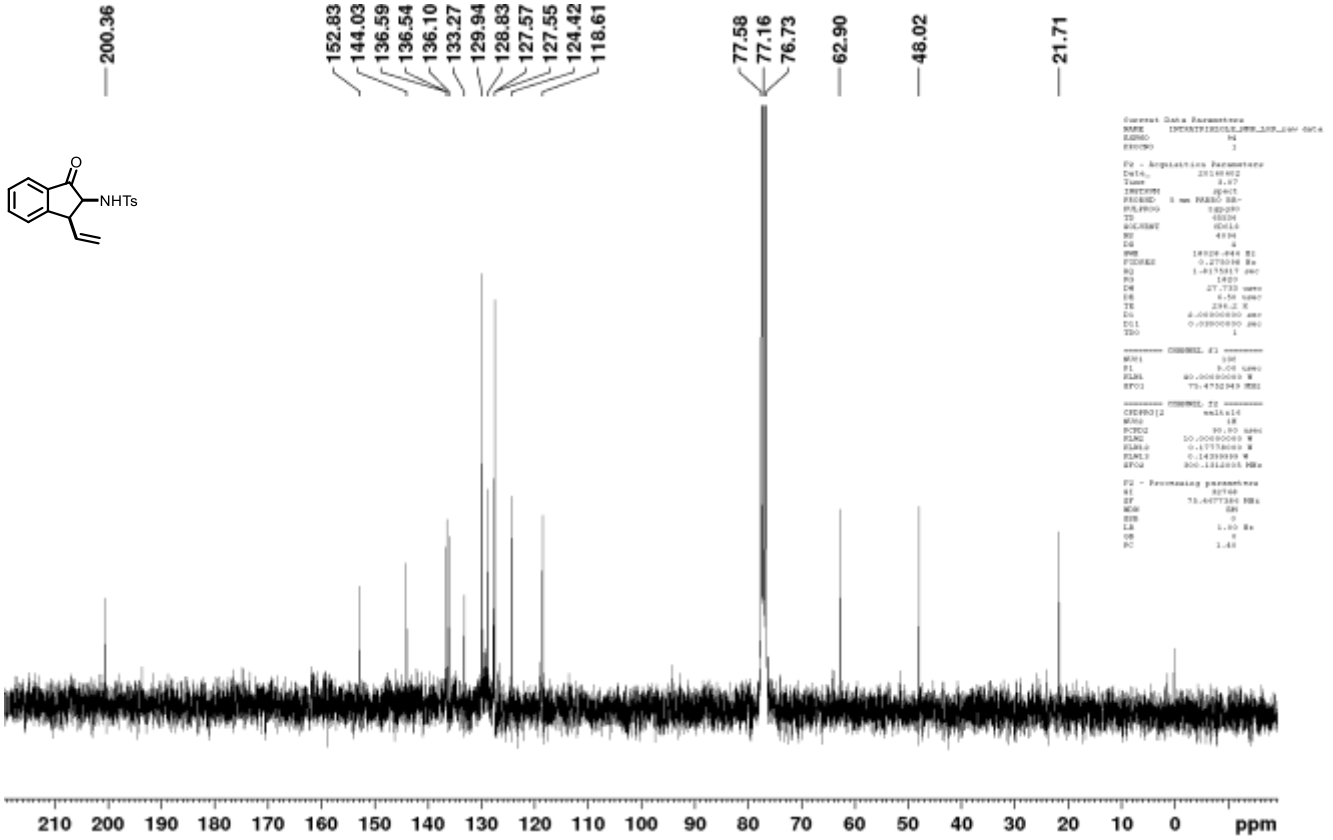
^{13}C spectra of compound **3a** (*trans*)



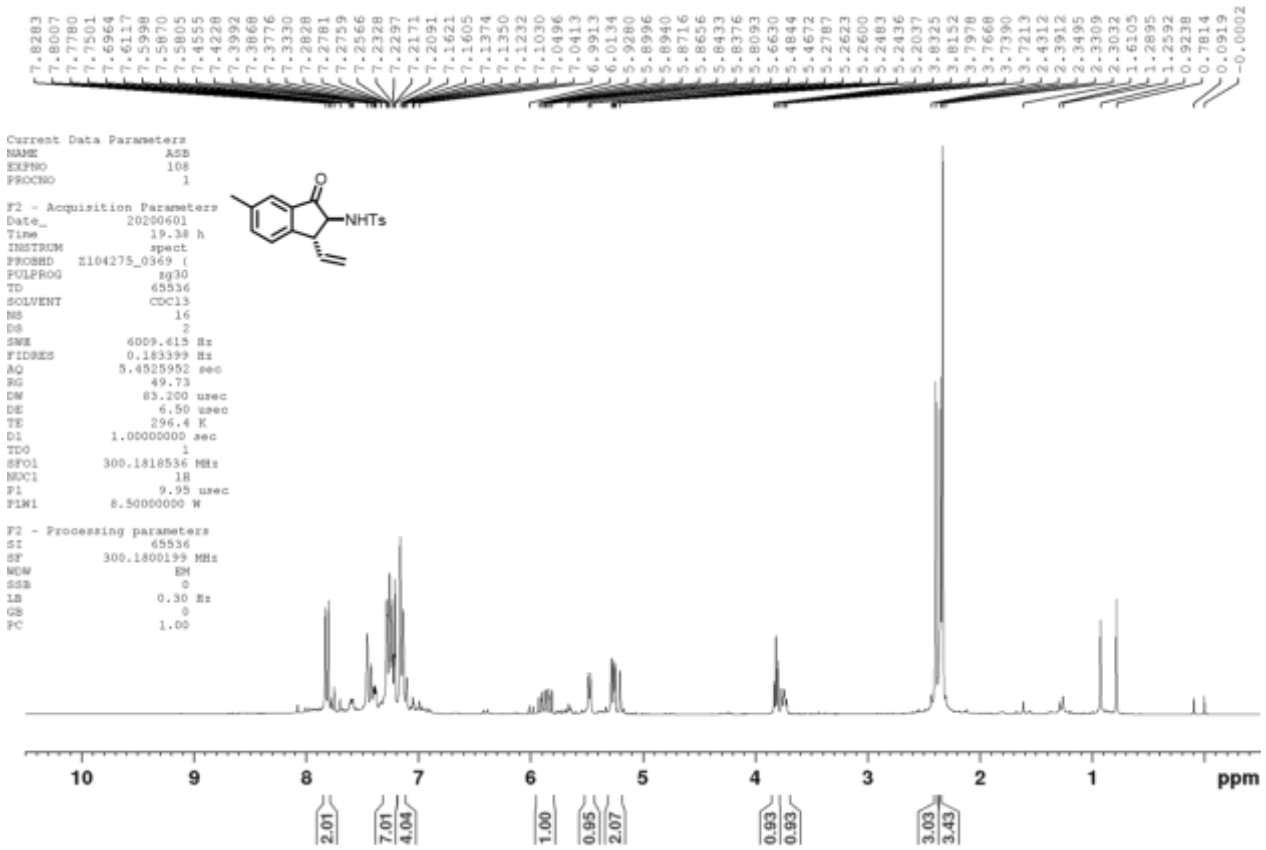
^{1}H spectra of compound **3a'** (*cis*)



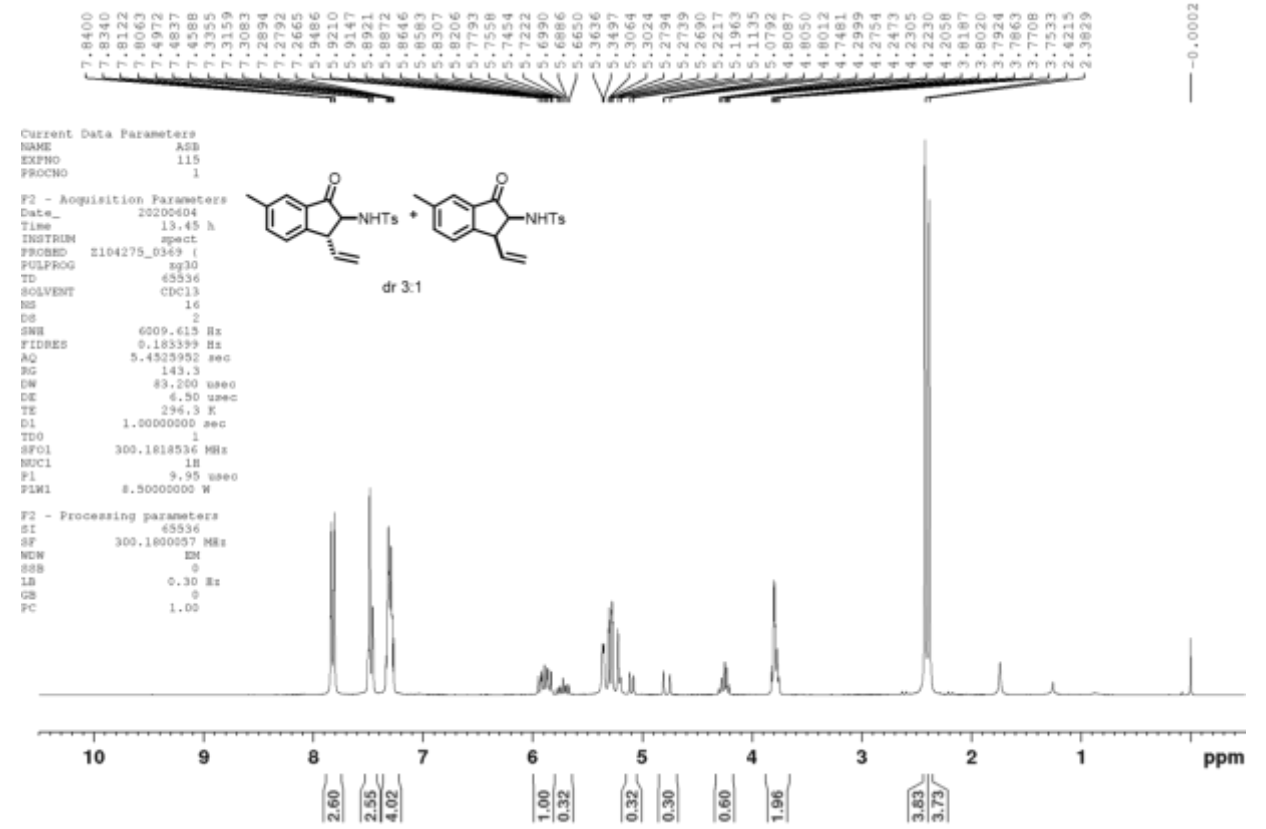
^{13}C spectra of compound **3a'** (*cis*)



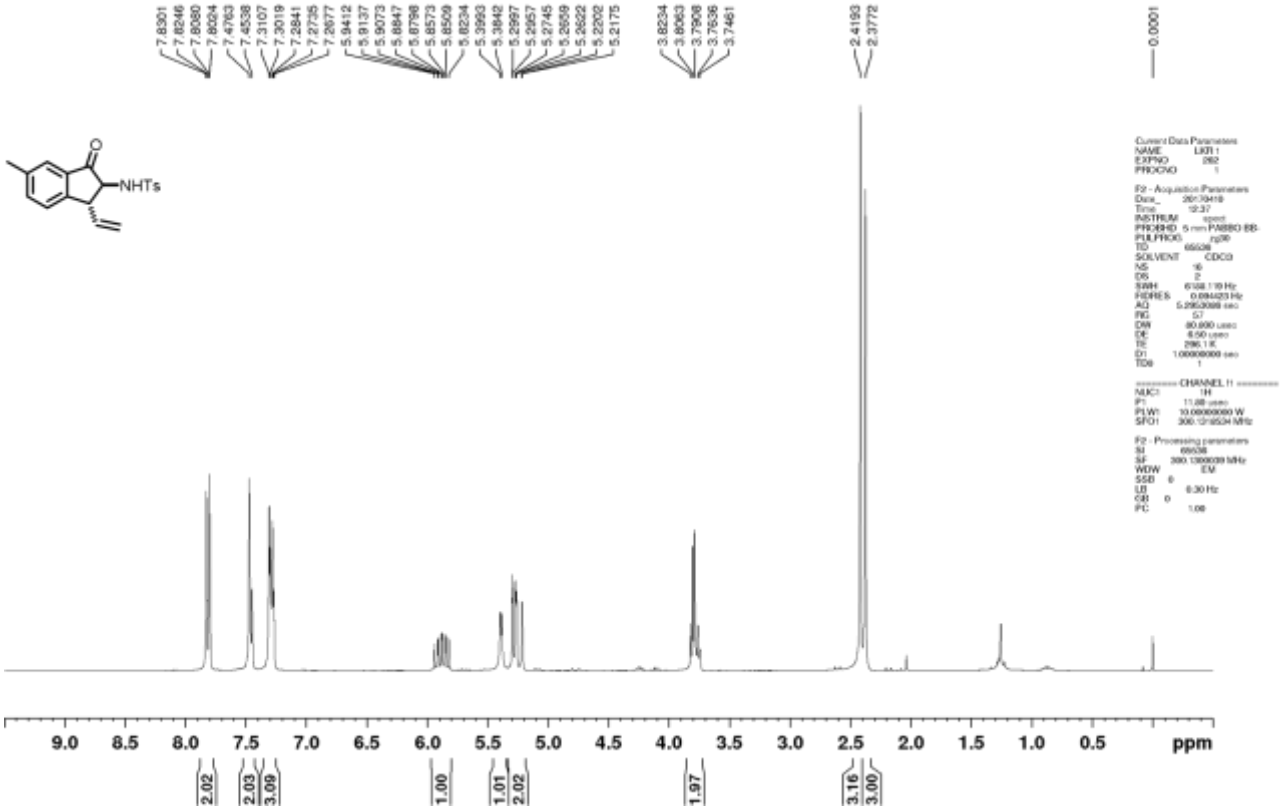
^{1}H spectra of compound **3b** (crude)



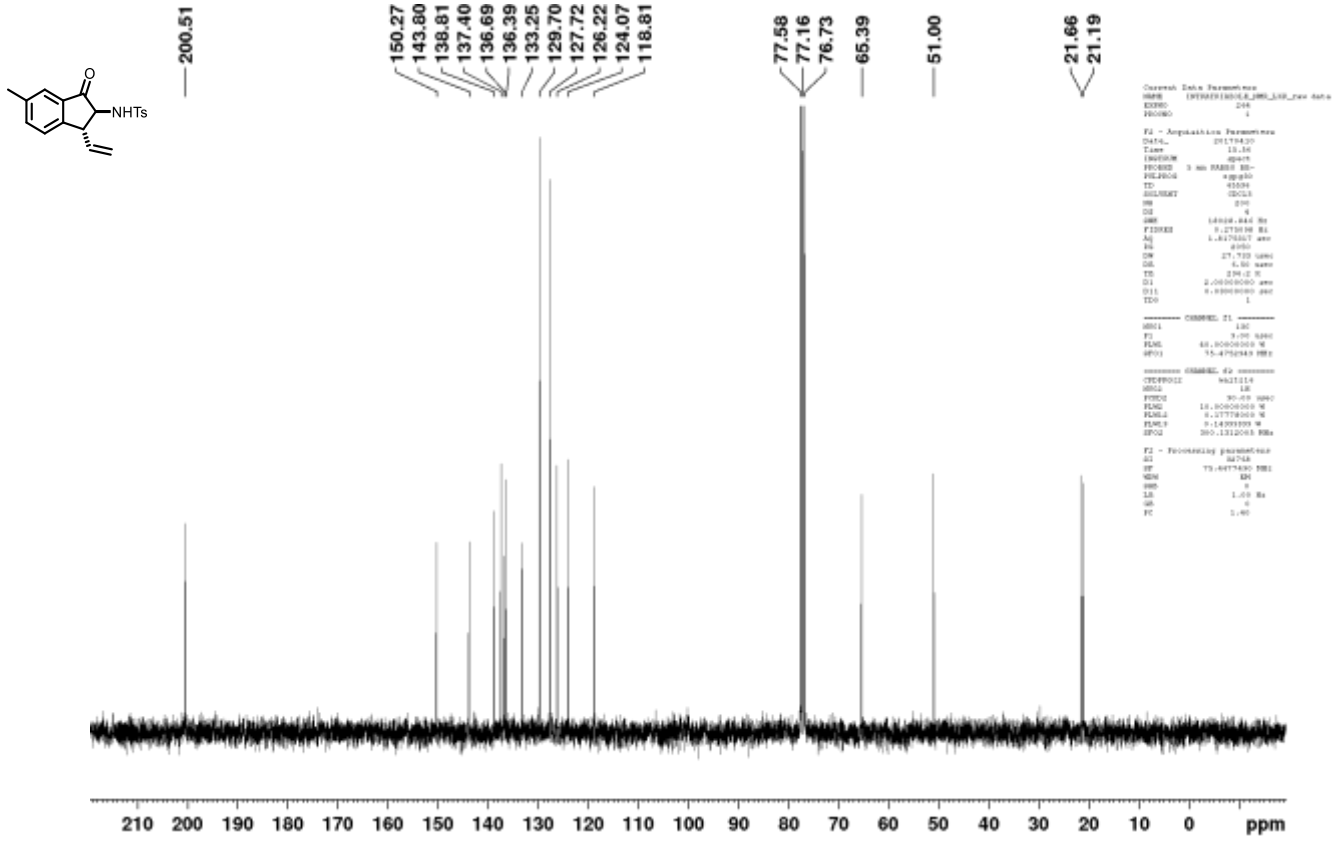
^{1}H spectra of compound **3b** (*cis/trans* mixture after column chromatography)



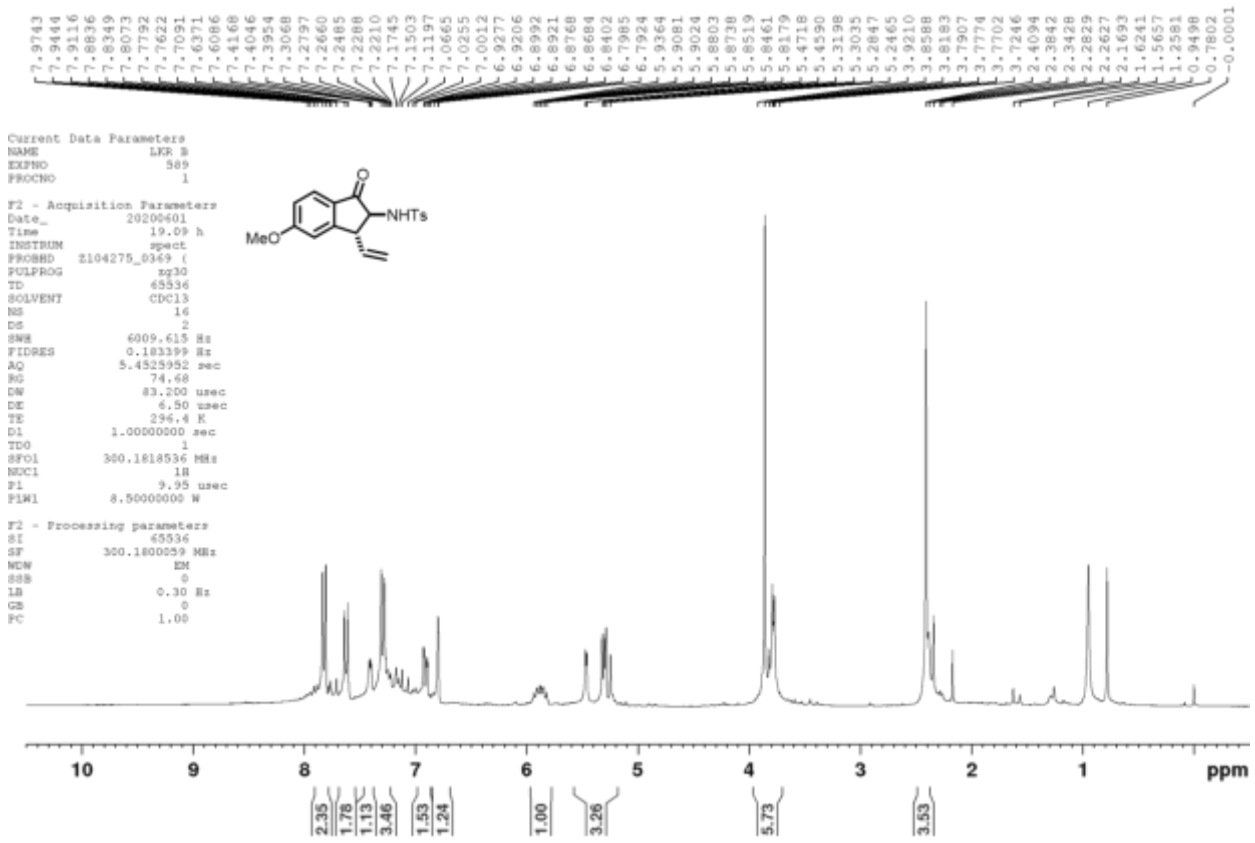
^{1}H spectra of compound **3b** (*trans*)



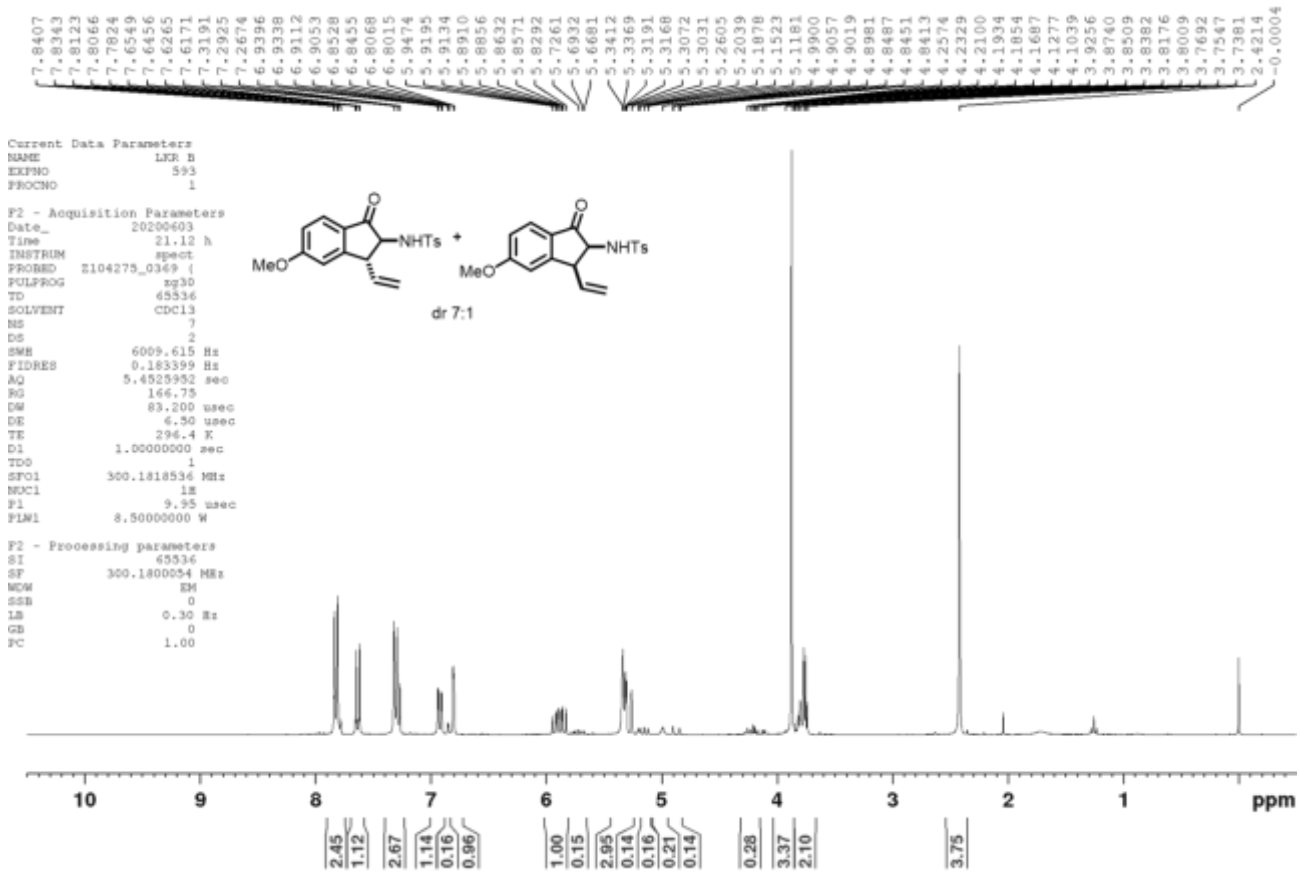
^{13}C spectra of compound **3b** (*trans*)



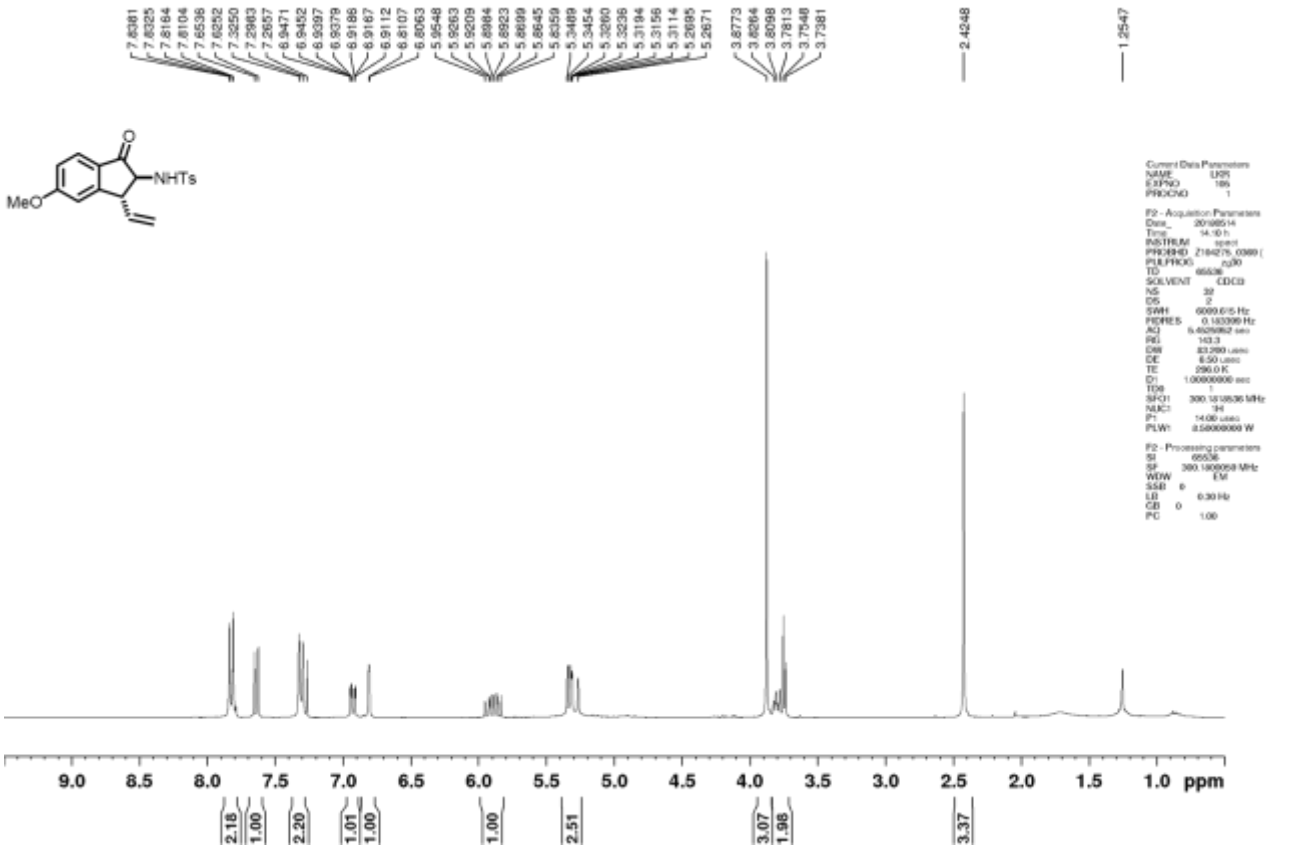
^{1}H spectra of compound **3c** (crude)



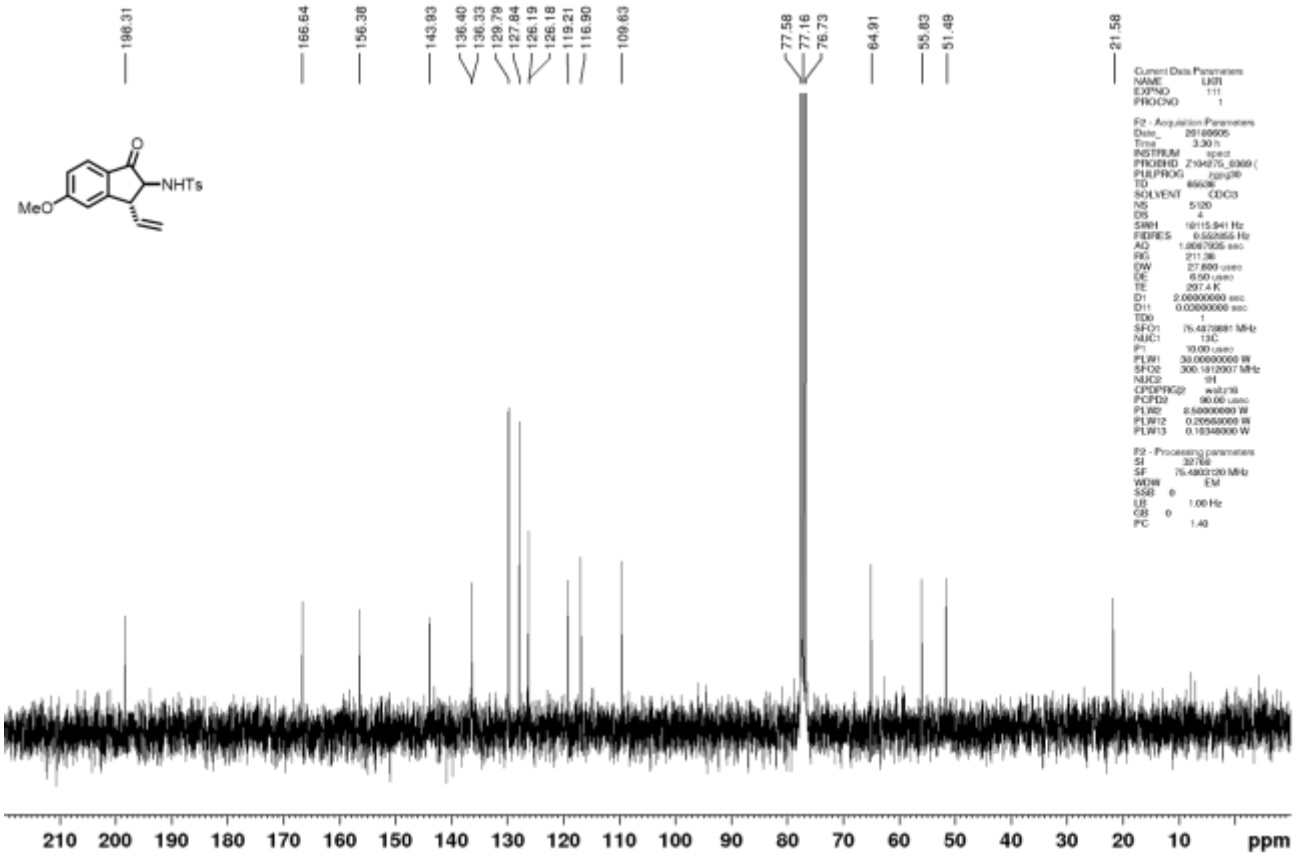
^{1}H spectra of compound **3c** (*cis/trans* mixture after column chromatography)



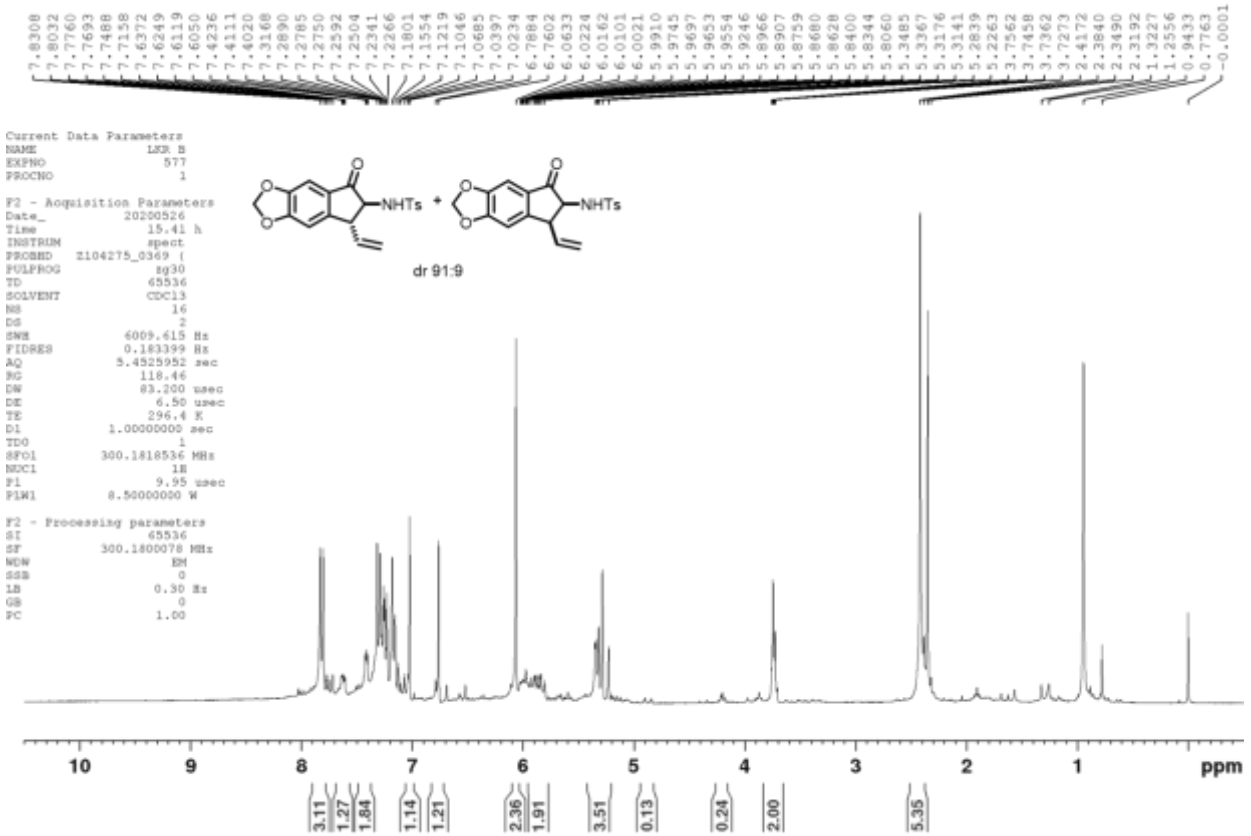
^{1}H spectra of compound **3c** (*trans*)



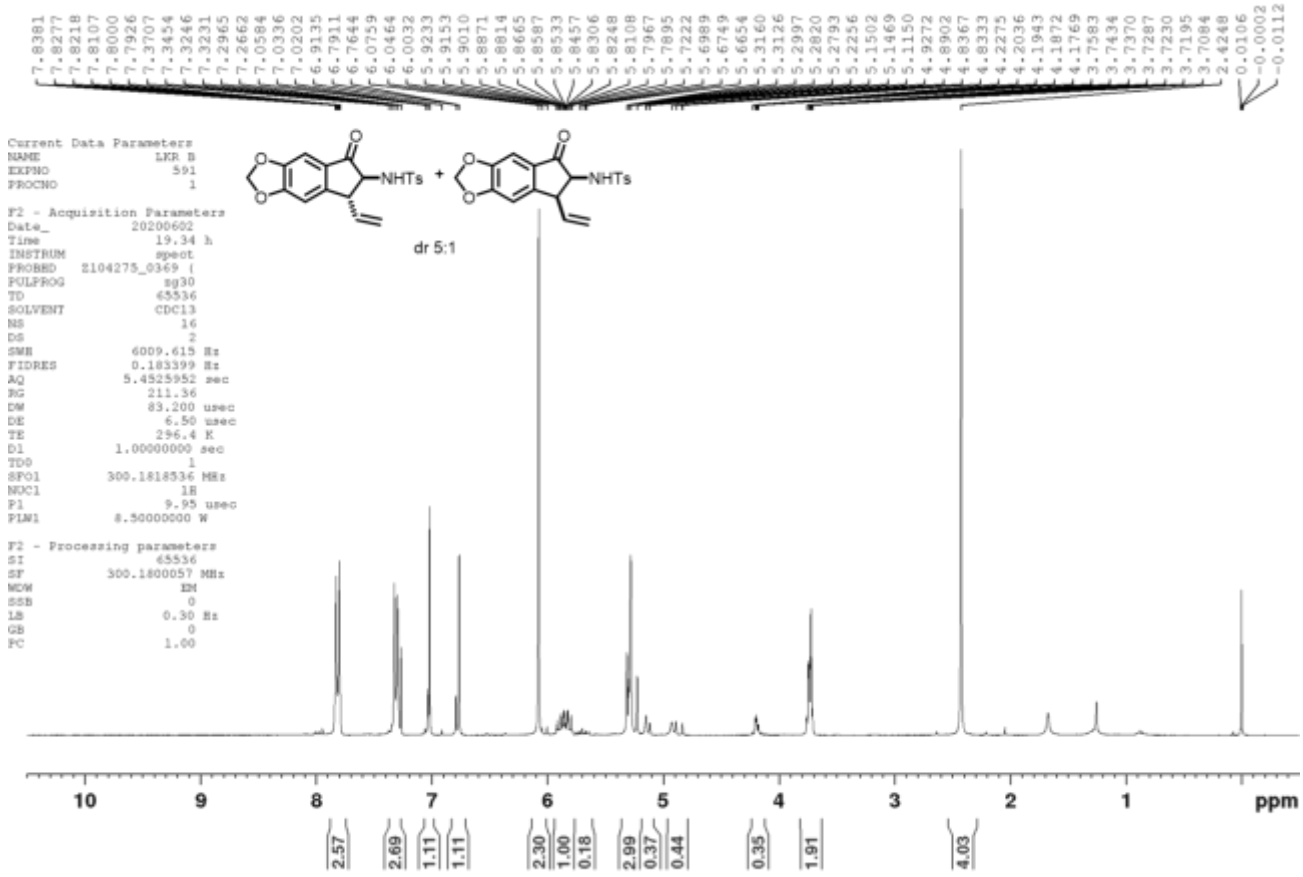
^{13}C spectra of compound **3c** (*trans*)



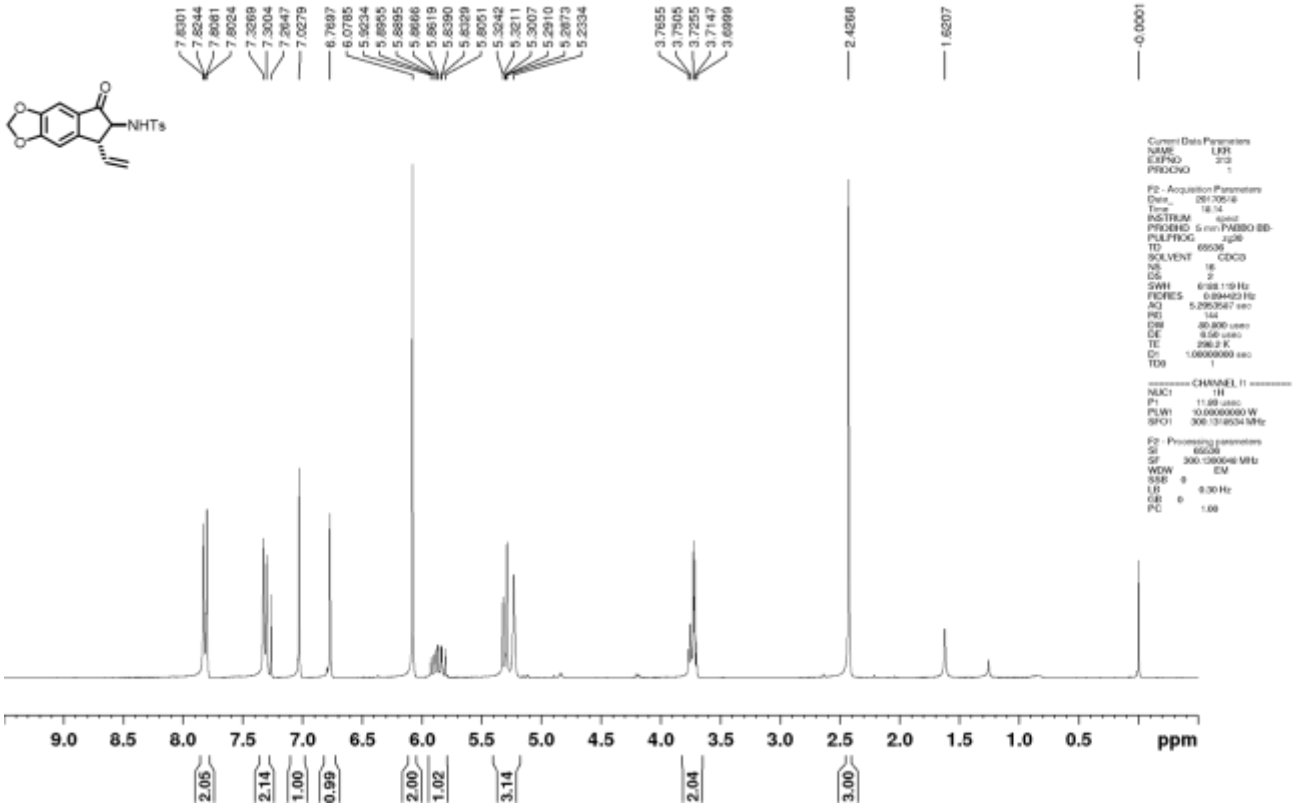
^{1}H spectra of compound **3d** (crude)



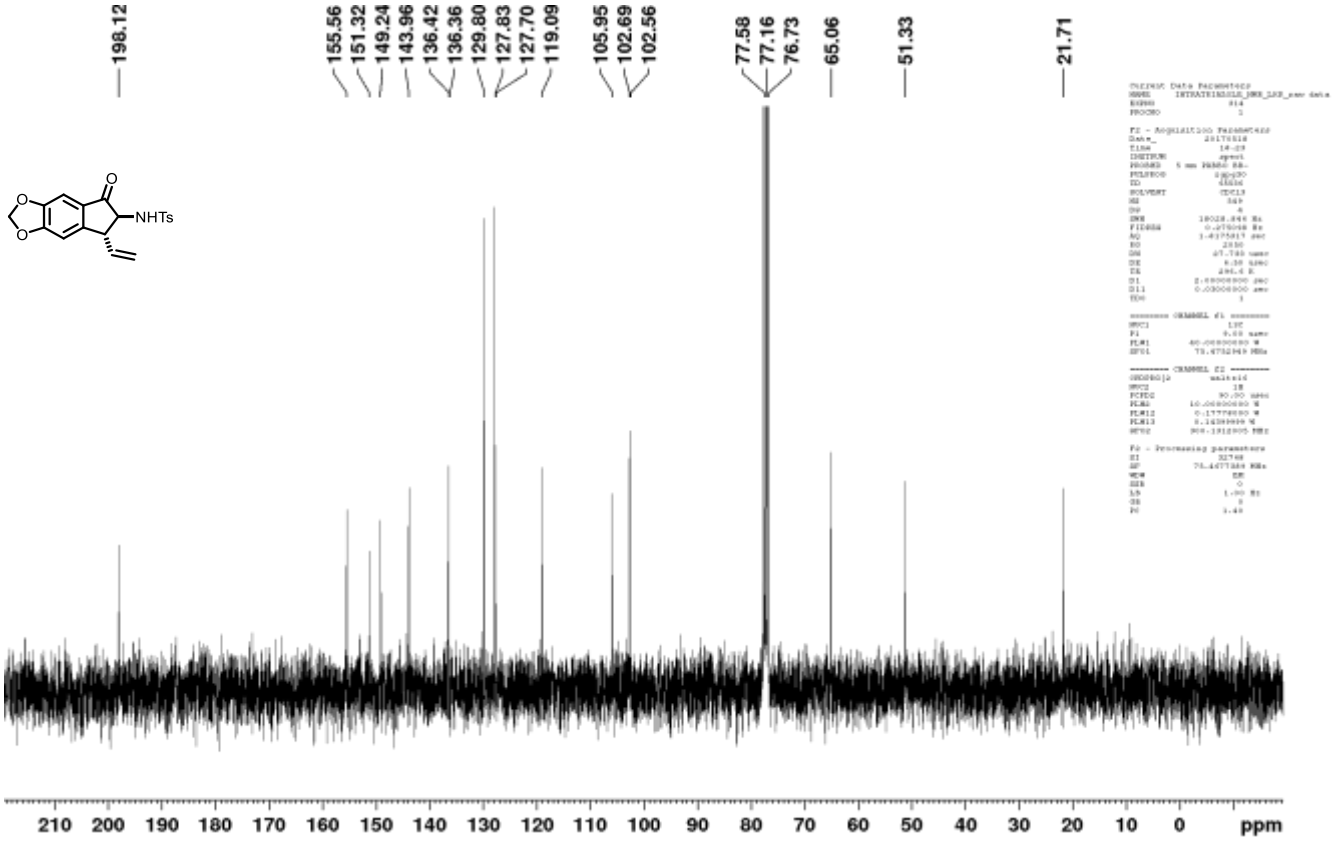
^{1}H spectra of compound **3d** (*cis/trans* mixture after column chromatography)



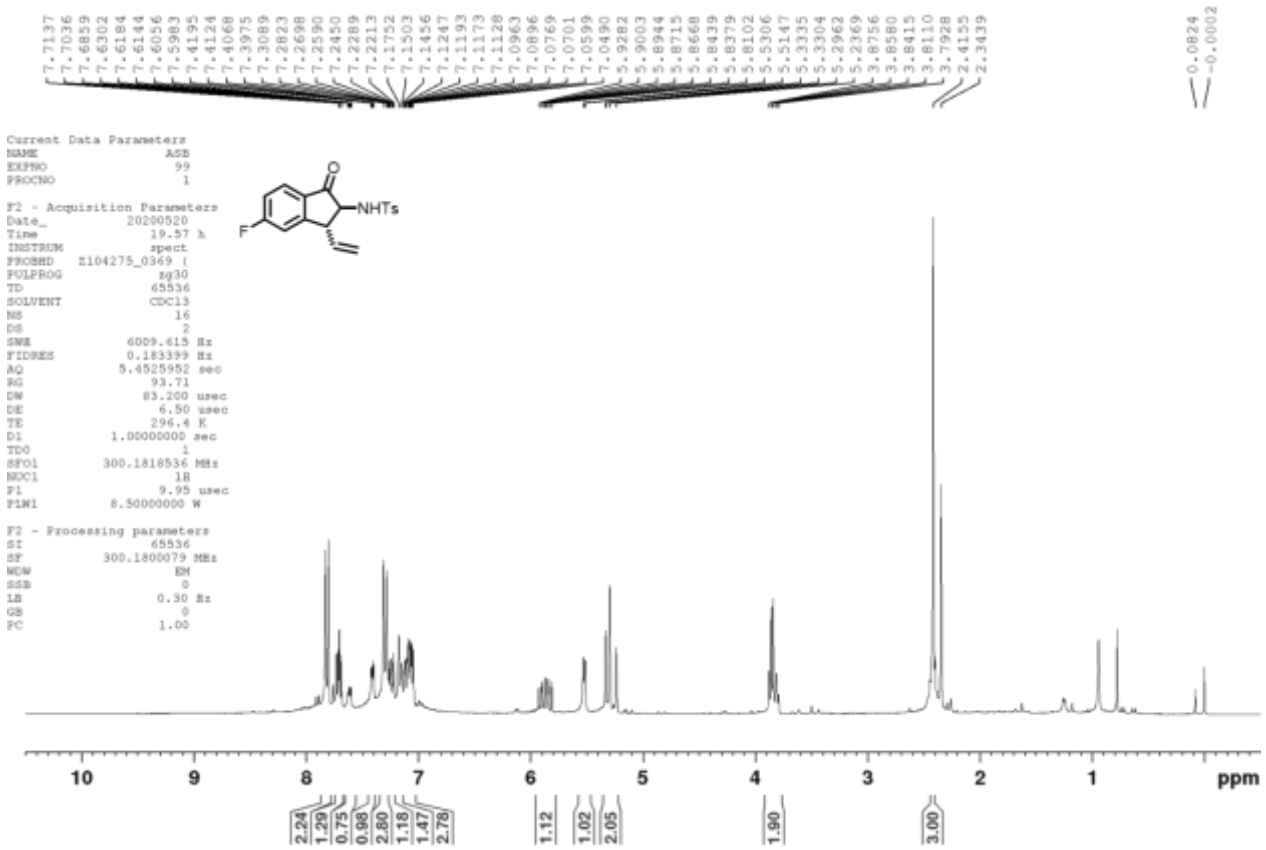
^{1}H spectra of compound **3d** (*trans*)



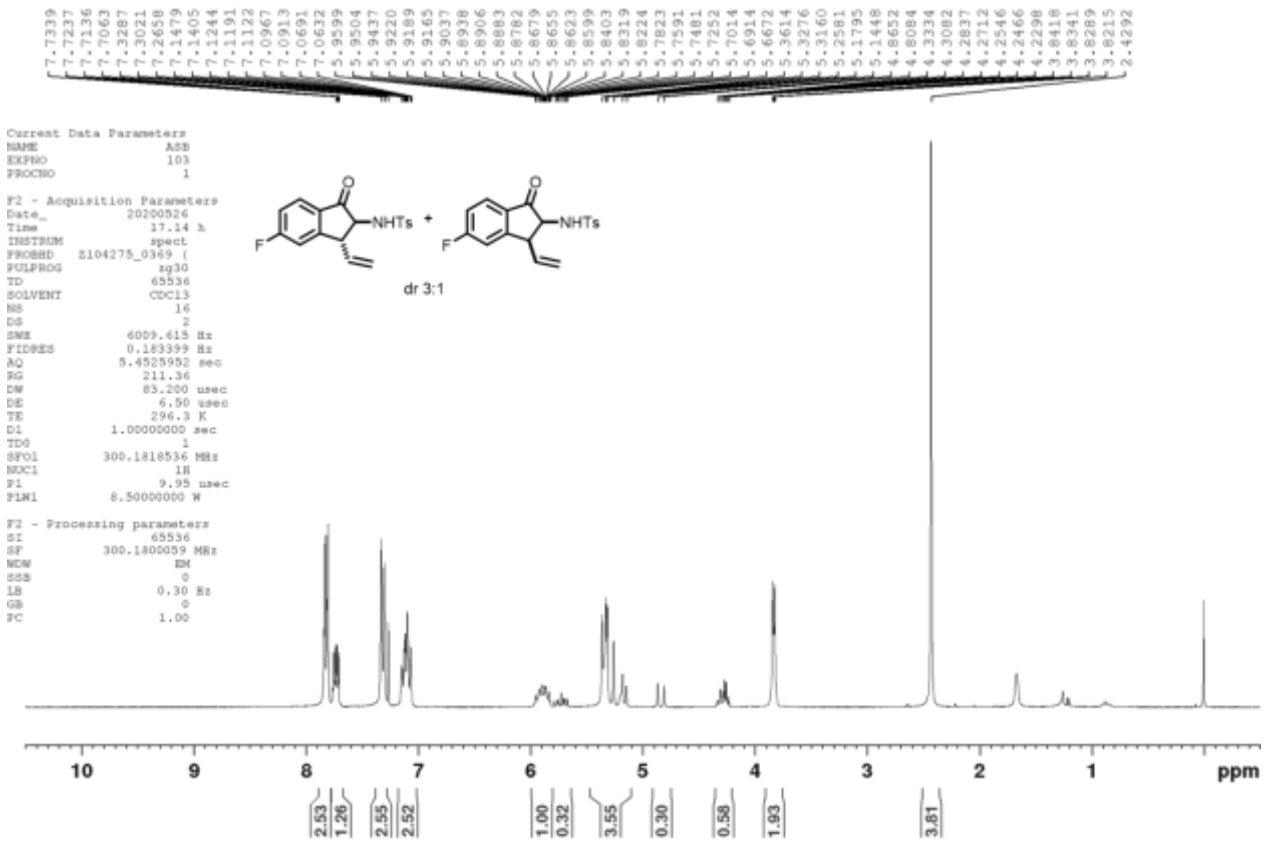
^{13}C spectra of compound **3d** (*trans*)



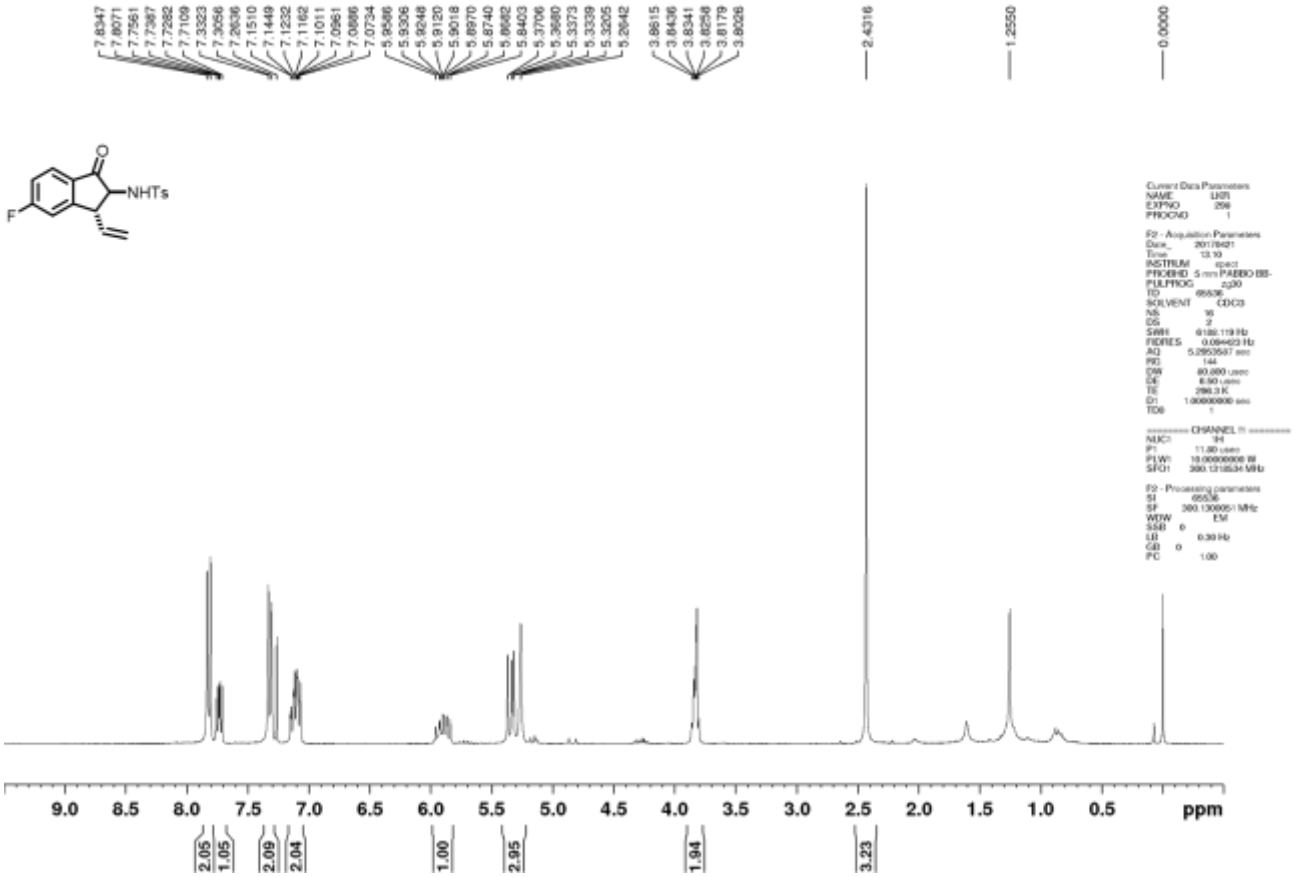
^{1}H spectra of compound **3e** (crude)



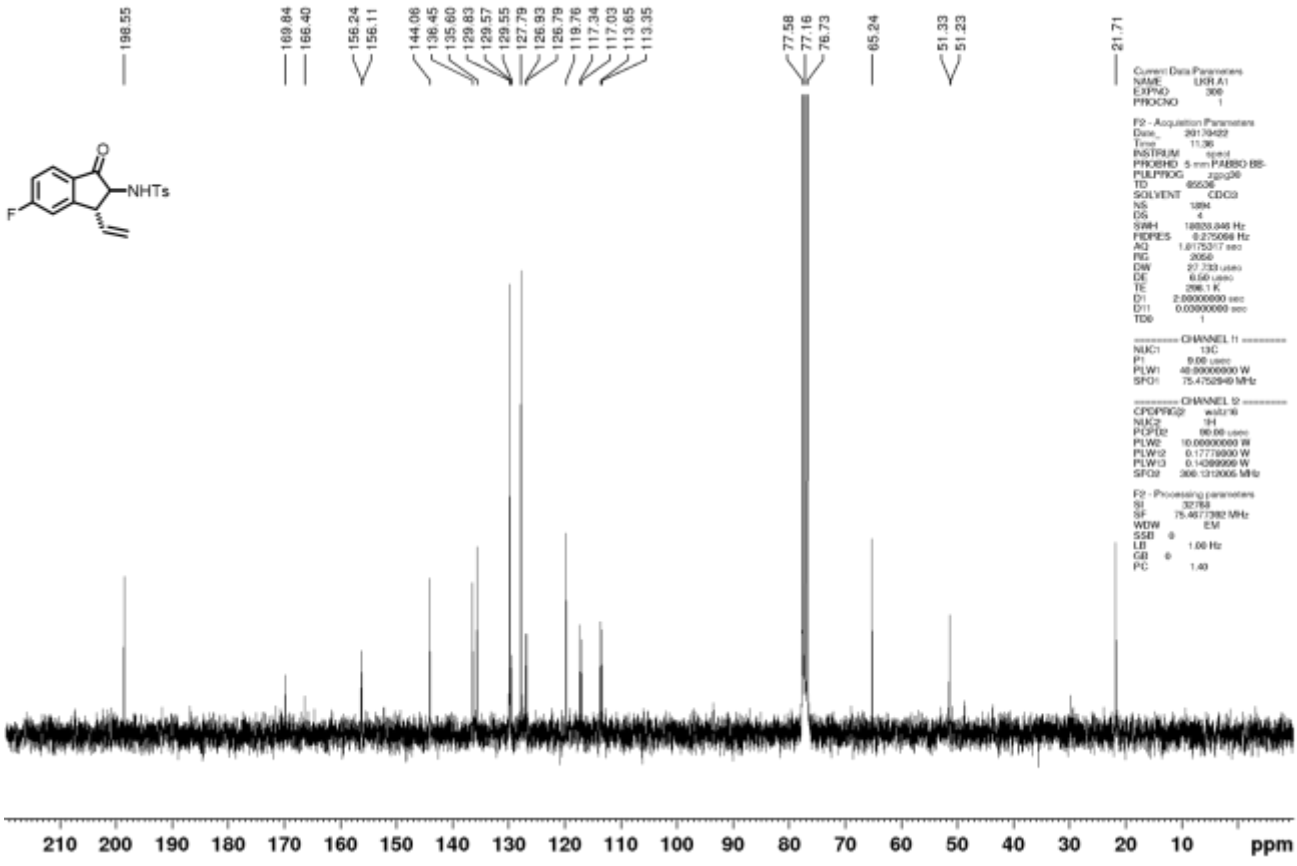
^{1}H spectra of compound **3e** (*cis/trans* mixture after column chromatography)



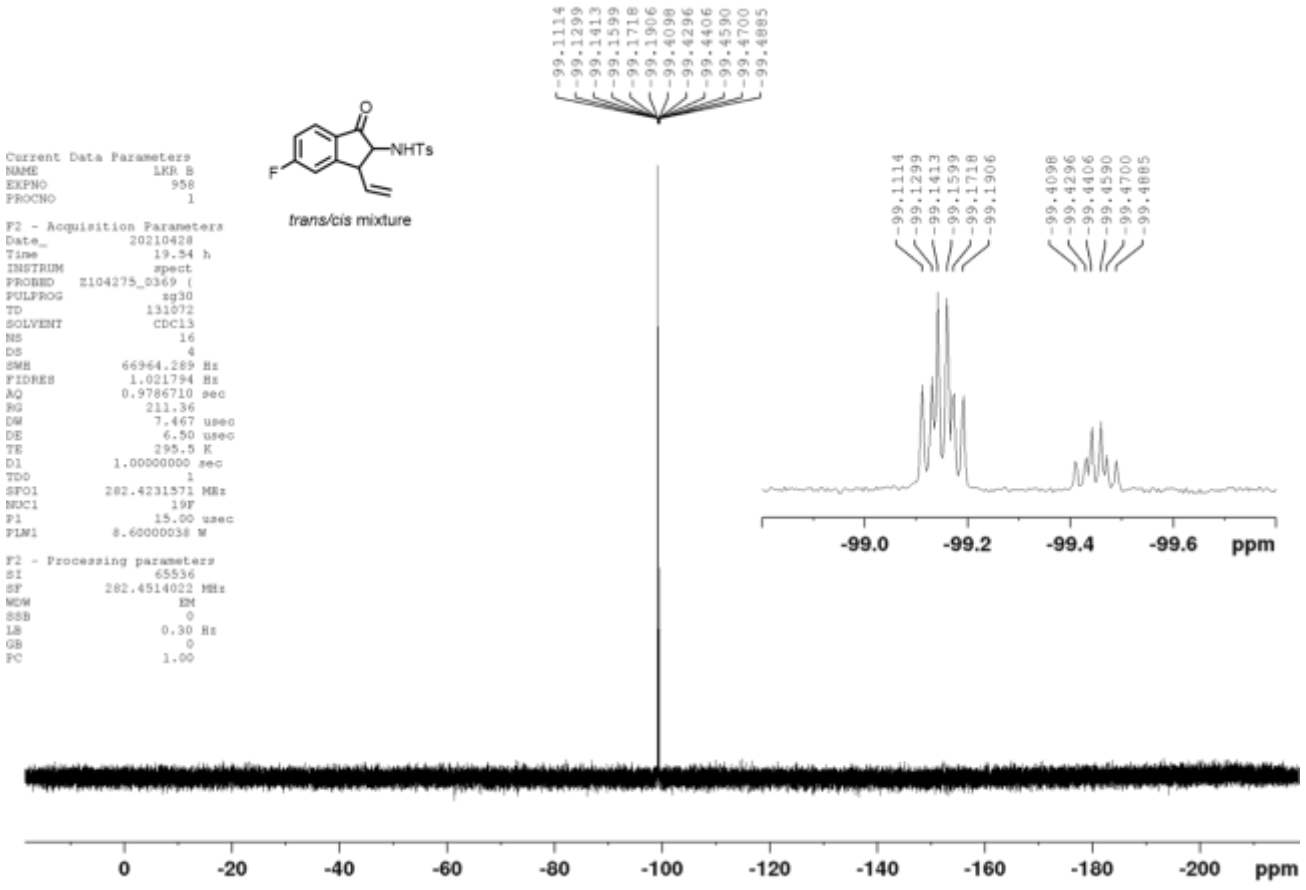
^{1}H spectra of compound **3e** (*trans*)



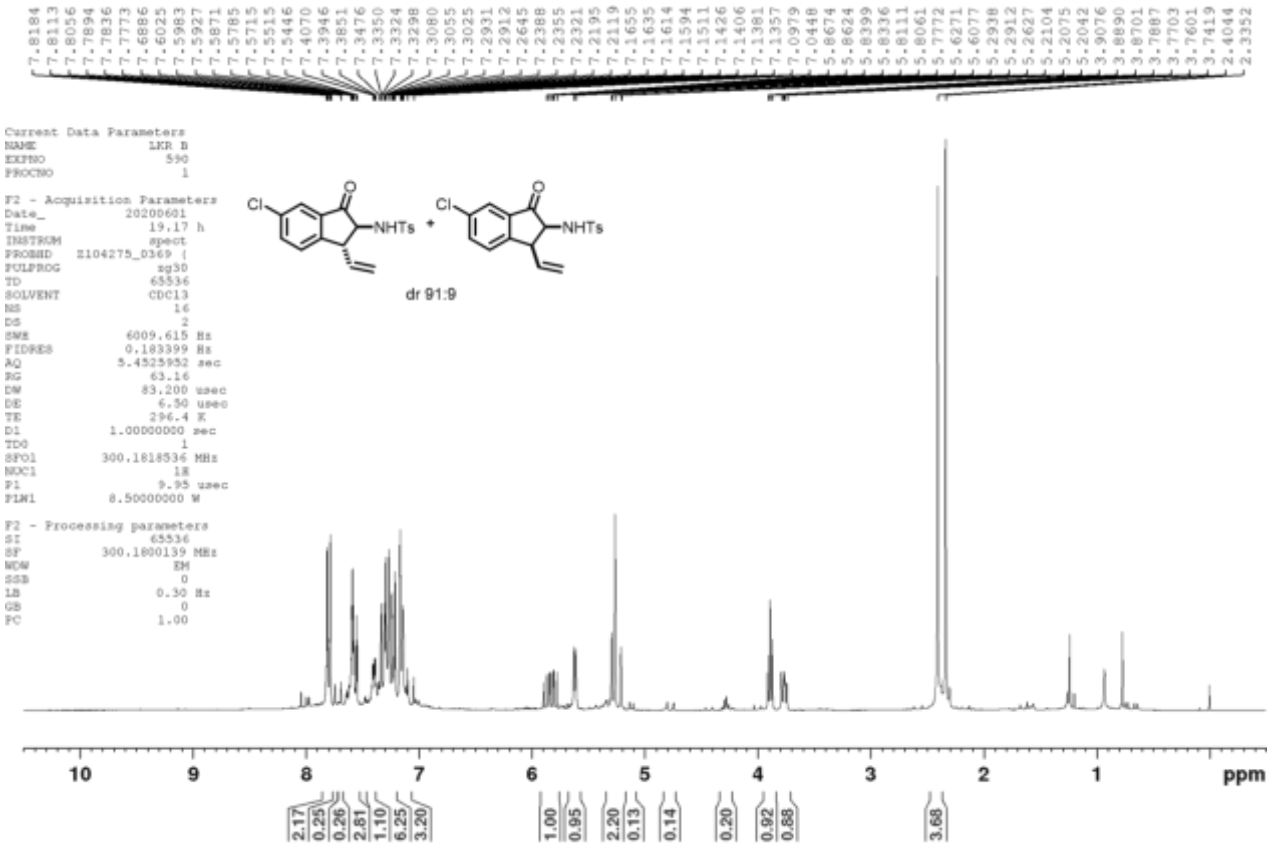
^{13}C spectra of compound **3e** (*trans*)



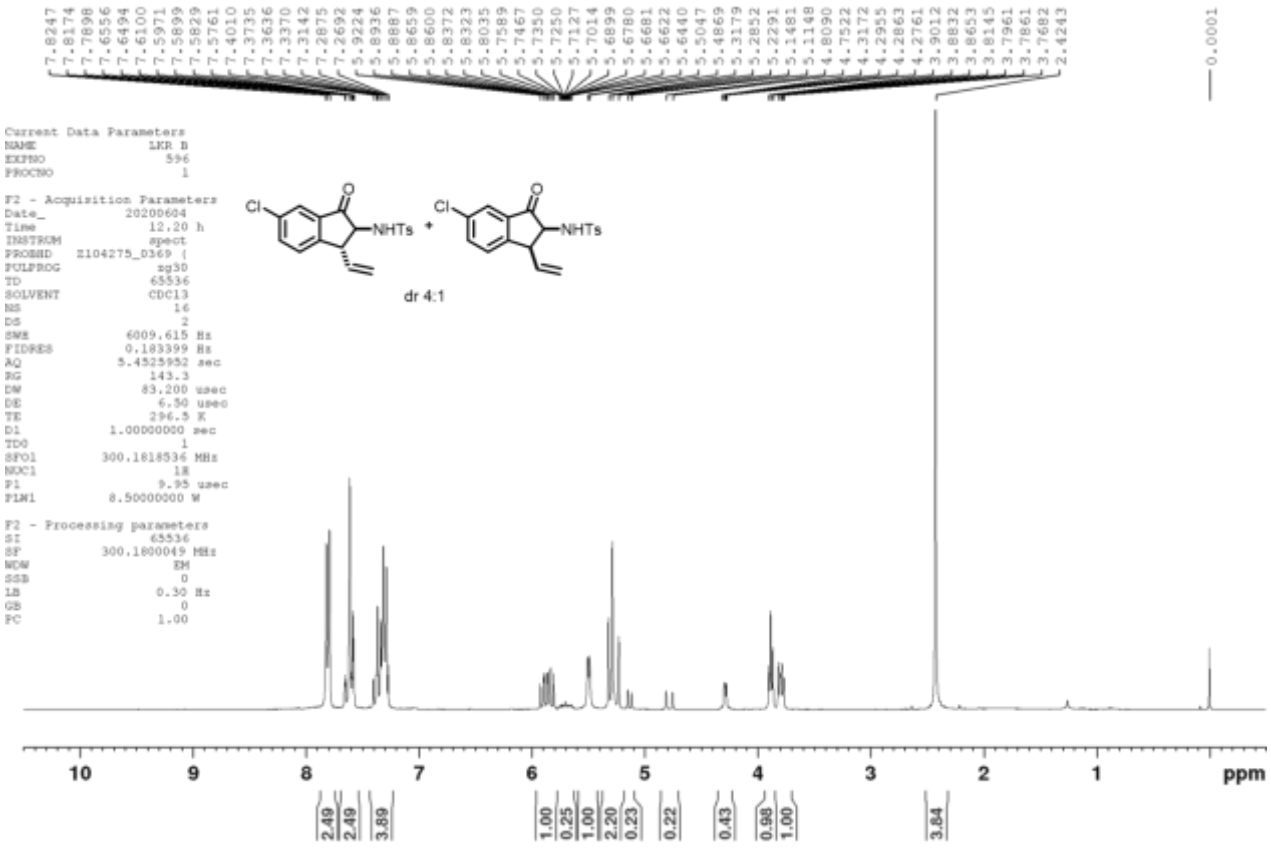
^{19}F spectra of compound **3e**



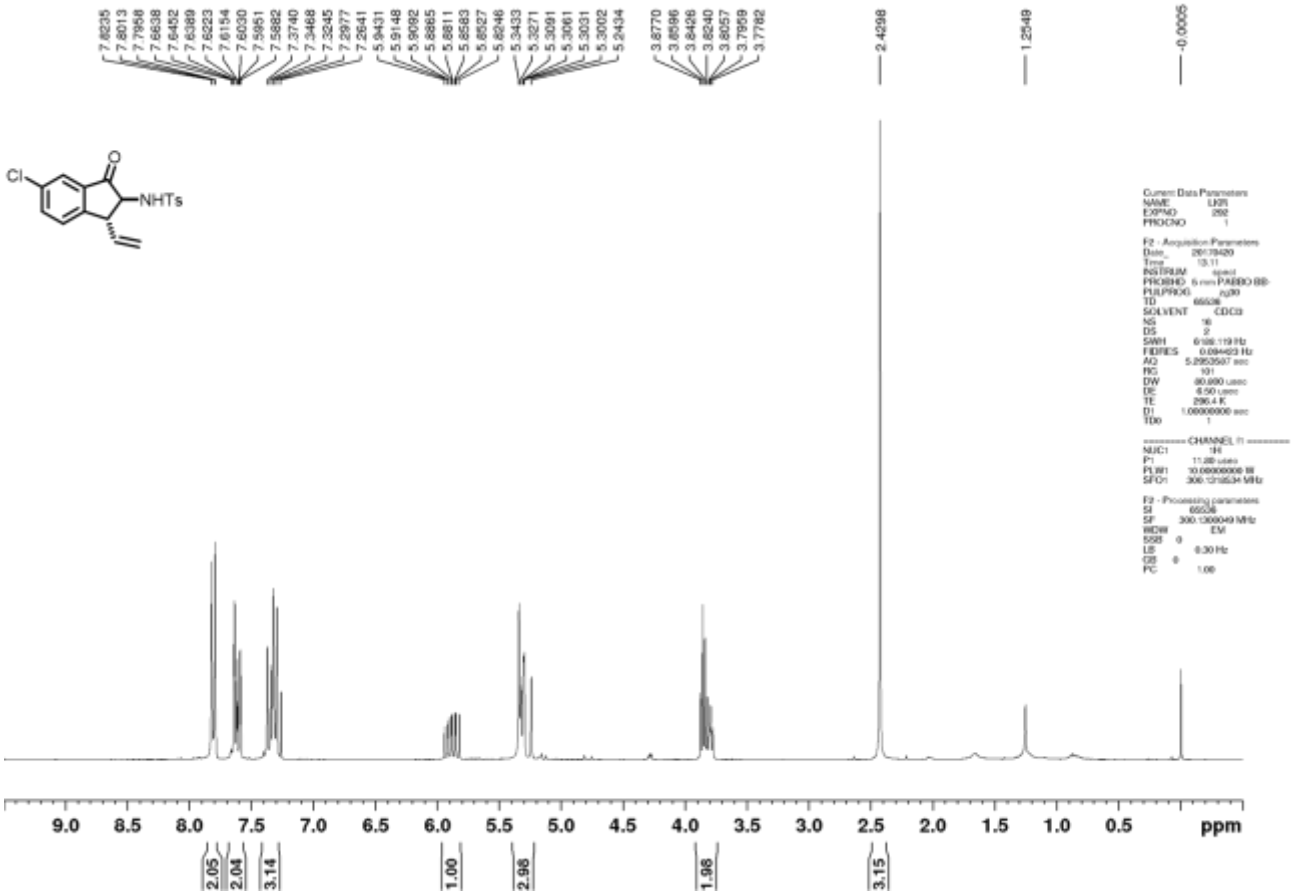
^{1}H spectra of compound **3g** (crude)



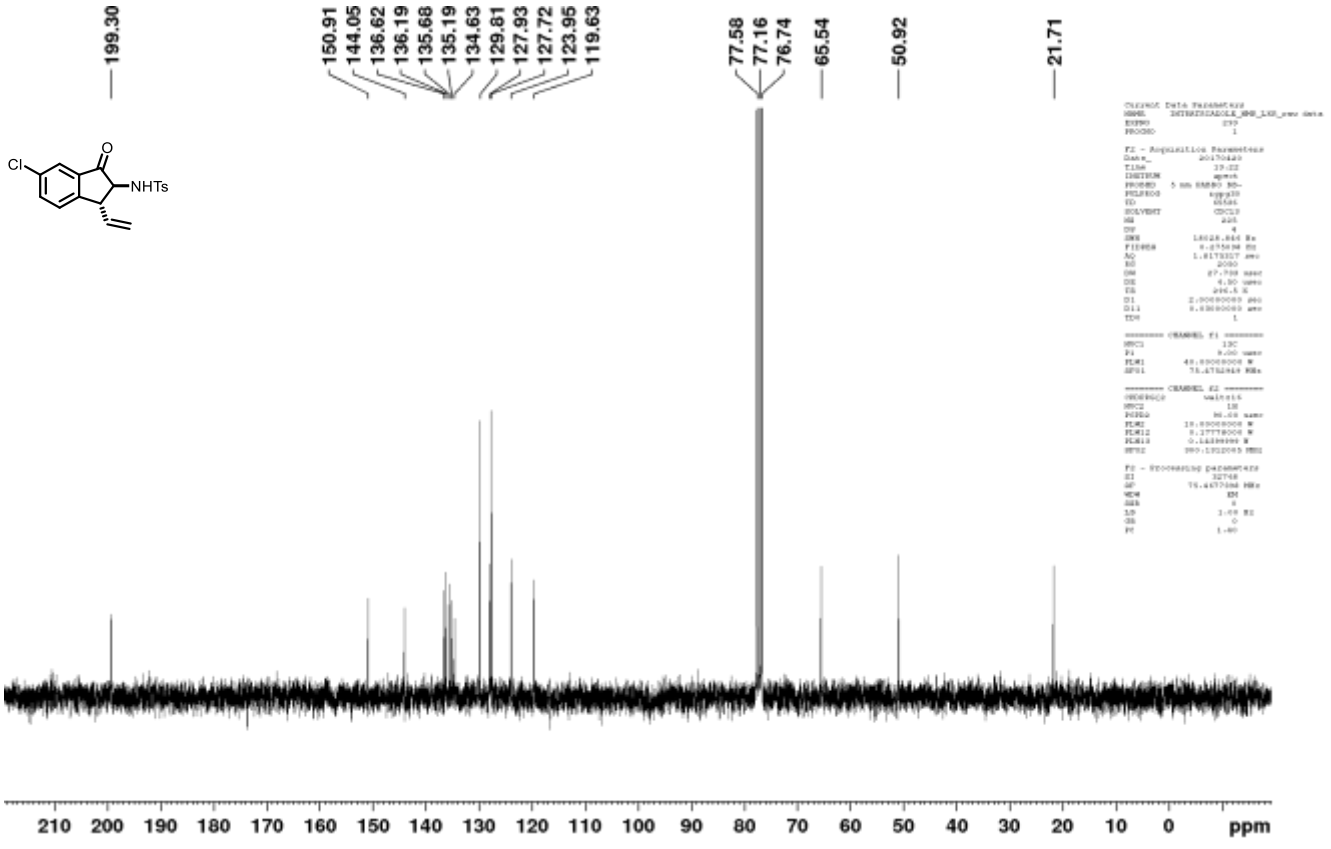
^{1}H spectra of compound **3g** (*cis/trans* mixture after column chromatography)



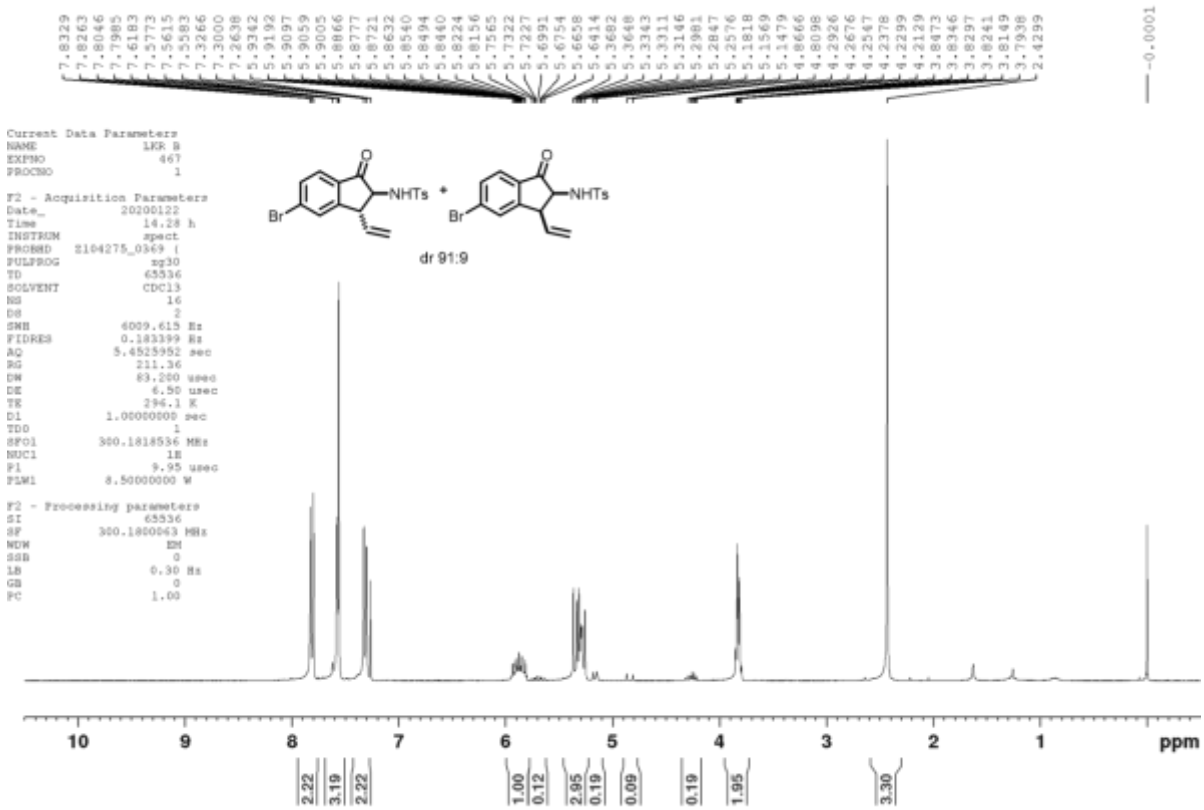
^{1}H spectra of compound **3g** (*trans*)



^{13}C spectra of compound **3g** (*trans*)



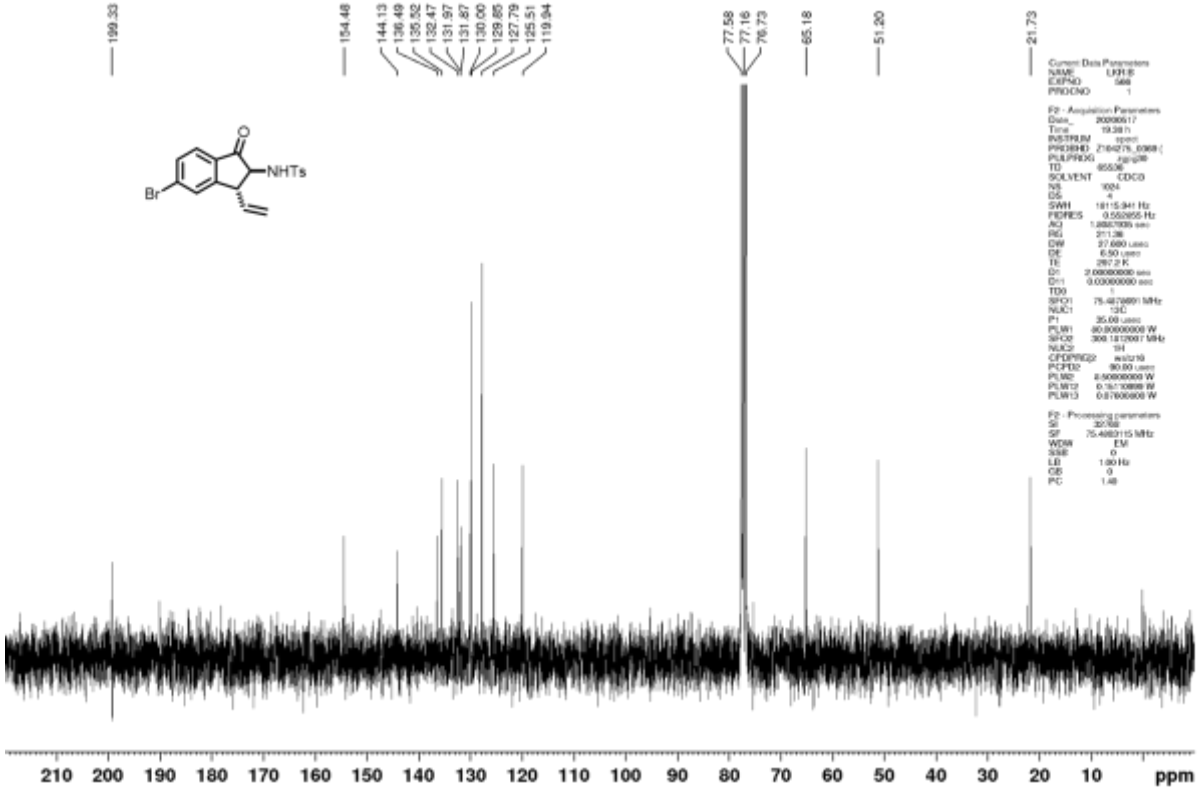
^{1}H spectra of compound **3h** (*cis/trans* mixture after short silica filter)



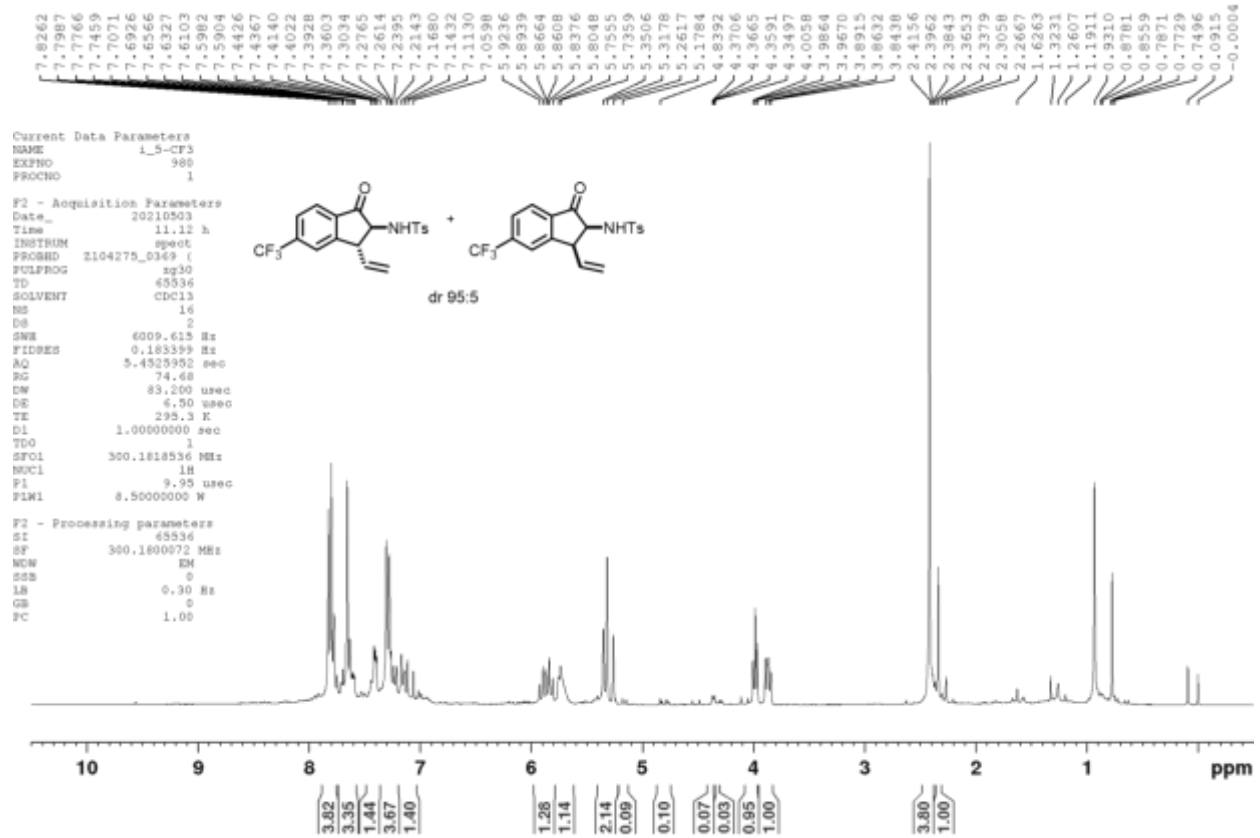
Note.

The ^{1}H NMR spectra of crude mixture of **3h** was too complicated to be identified, in addition, *cis/trans* mixture of **3h** was inseparable. Thus, ^{1}H NMR spectra of *cis/trans* mixture after short silica filter has been attached above.

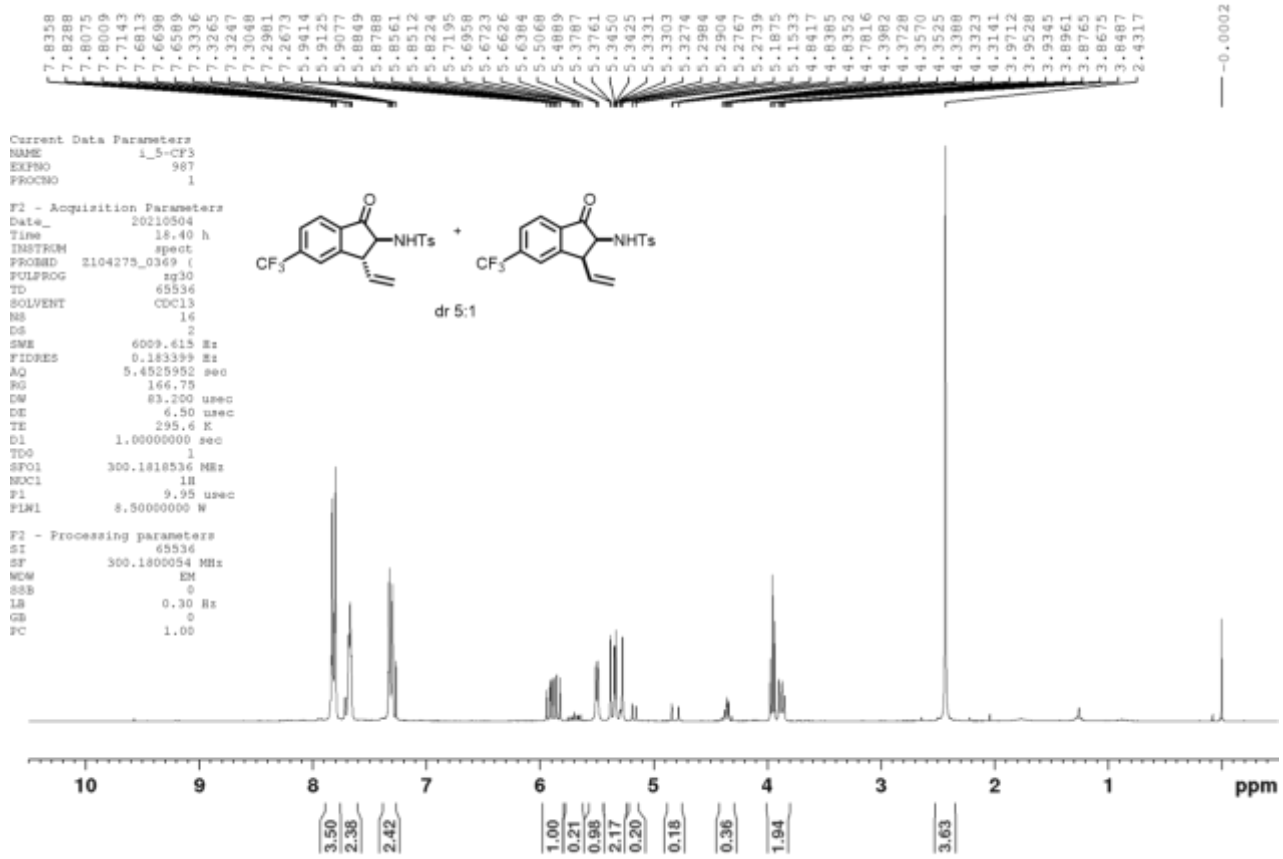
^{13}C spectra of compound **3h** (*trans*)



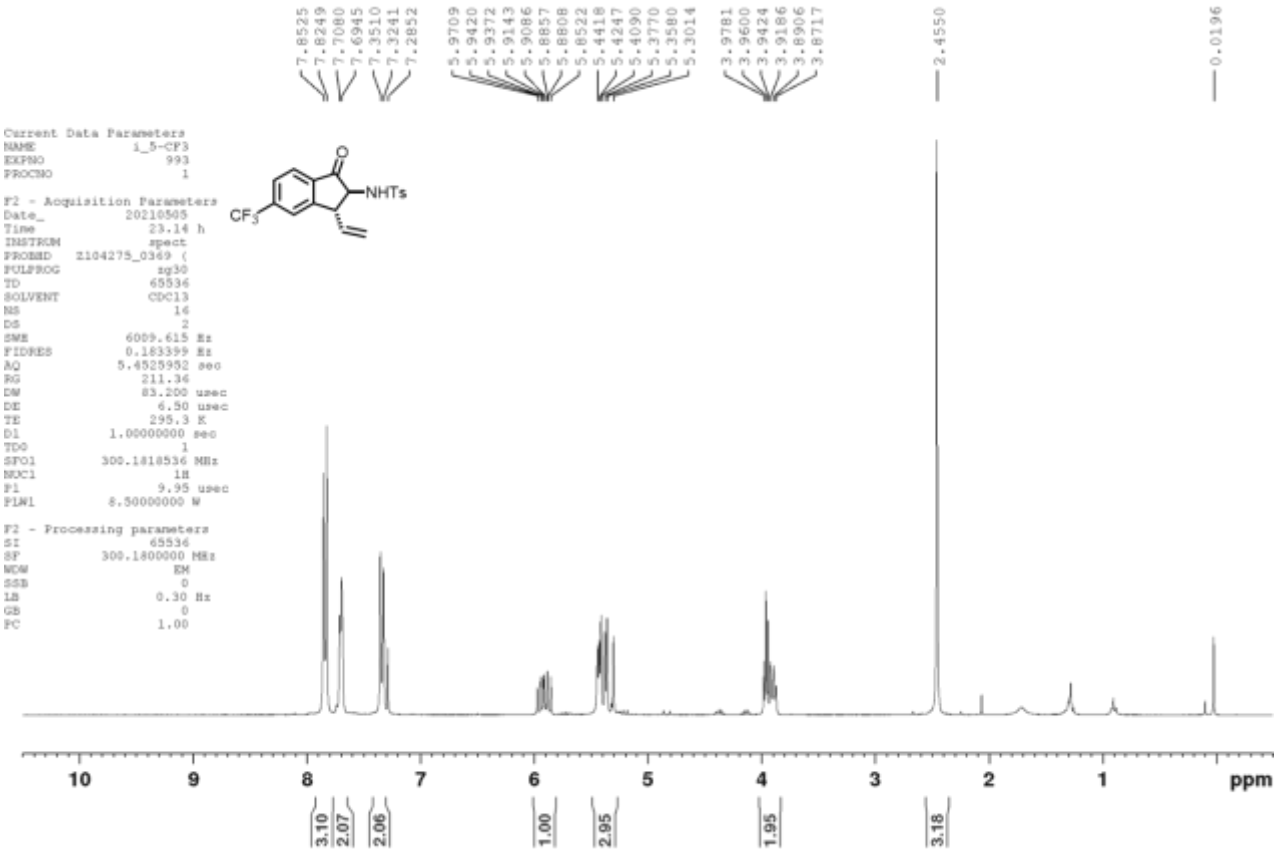
^{1}H spectra of compound **3i** (crude)



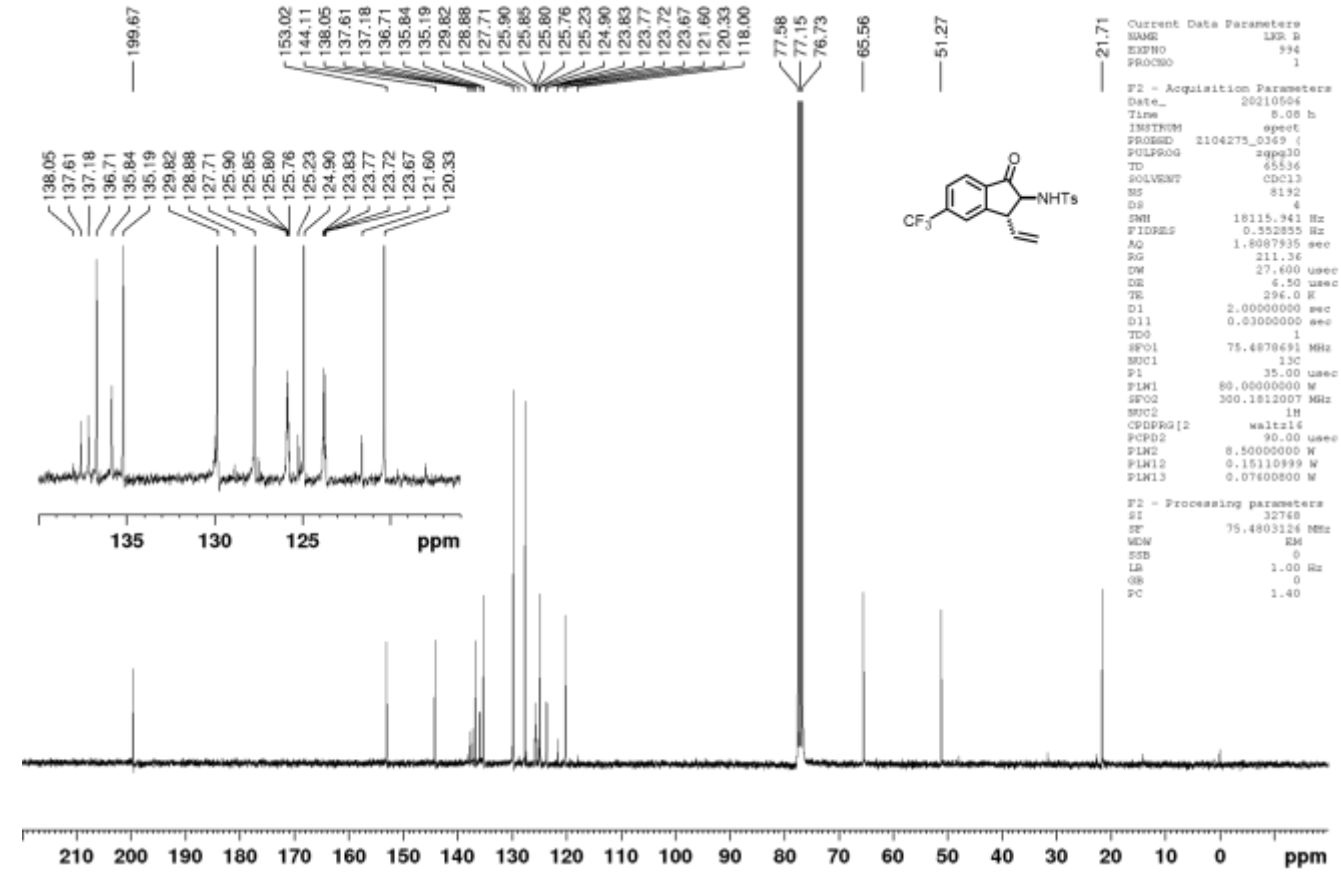
^{1}H spectra of compound **3i** (*cis/trans* mixture after column chromatography)



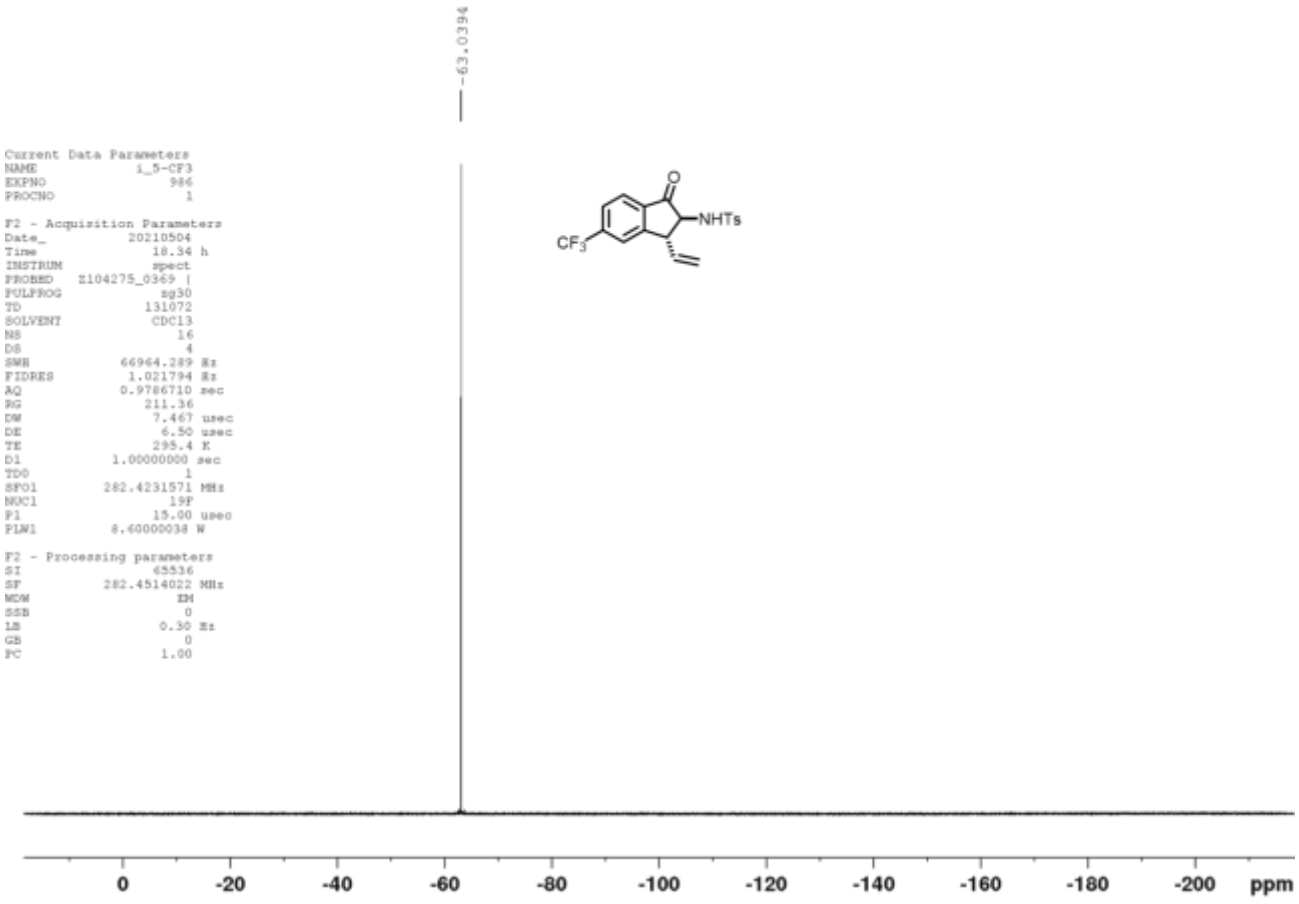
^{1}H spectra of compound **3i** (*trans*)



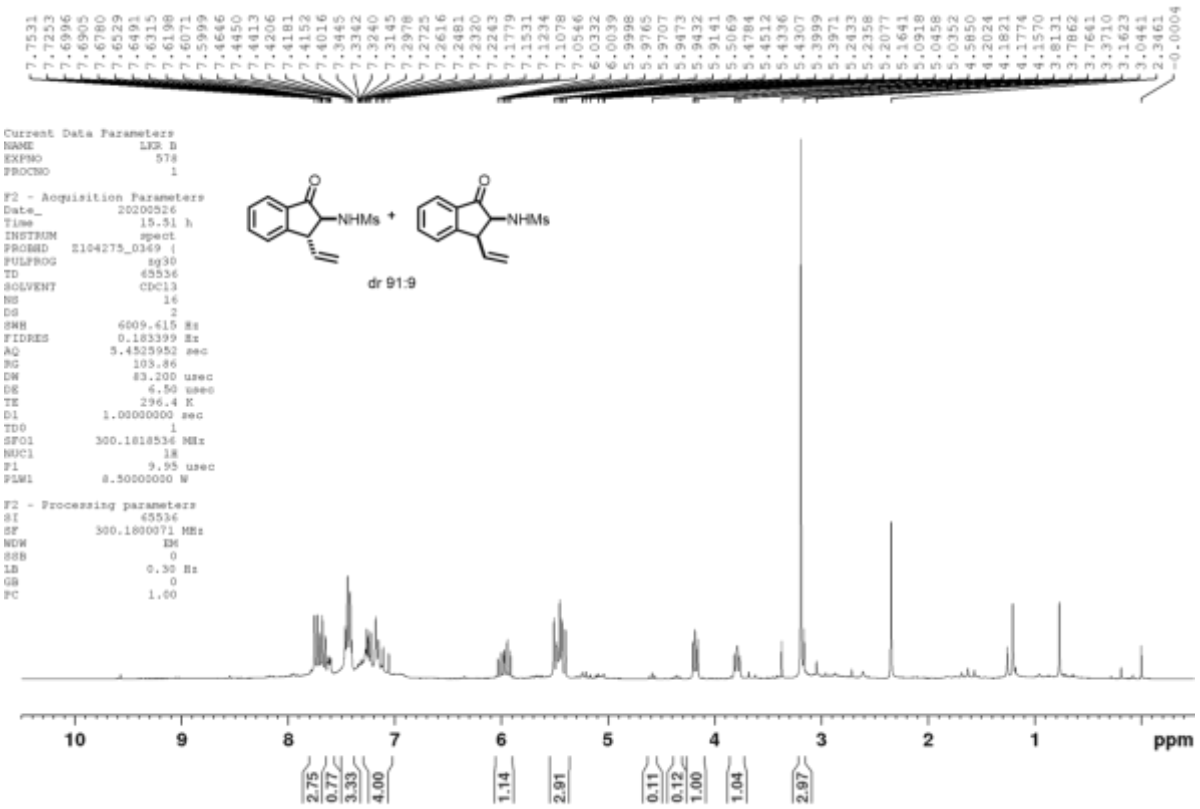
^{13}C spectra of compound **3i** (*trans*)



^{19}F spectra of compound **3i**



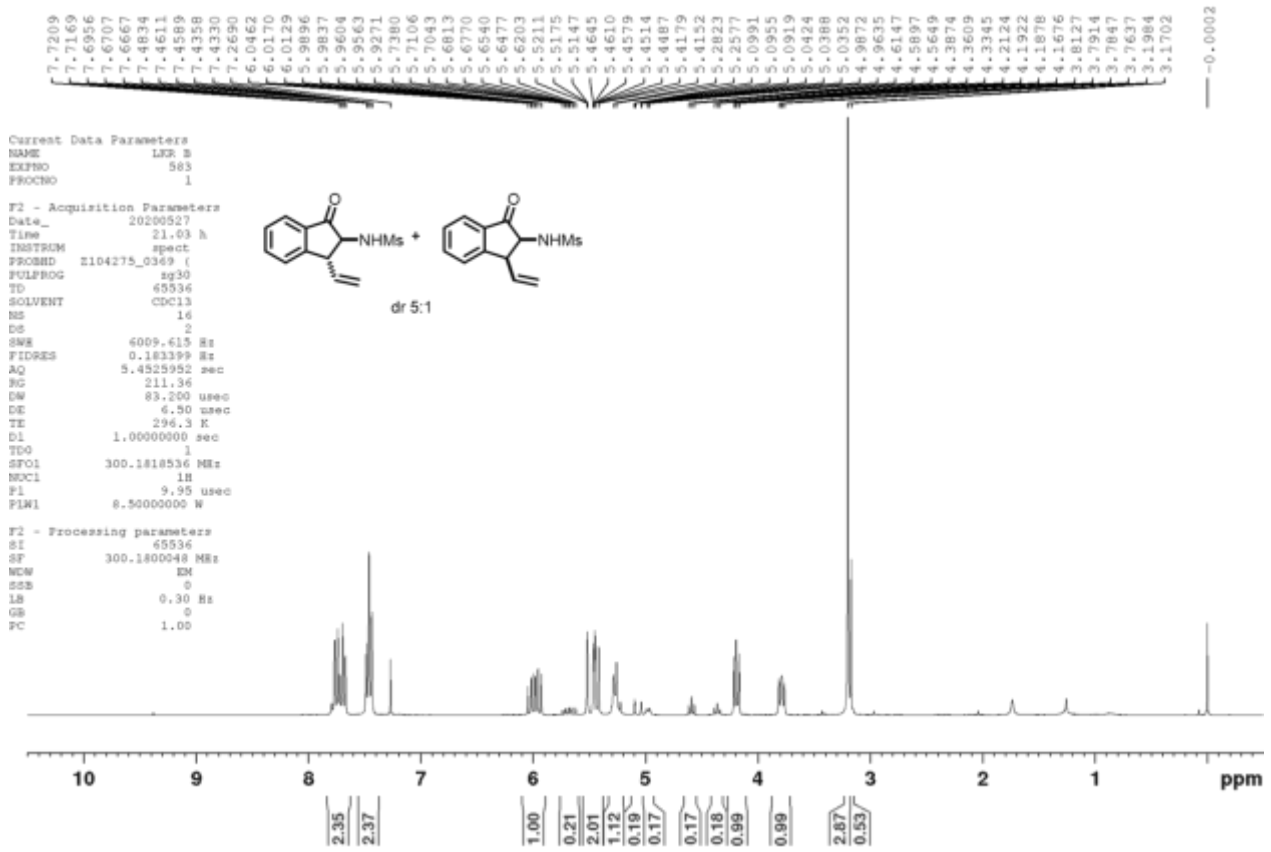
^{1}H spectra of compound **3k** (crude)



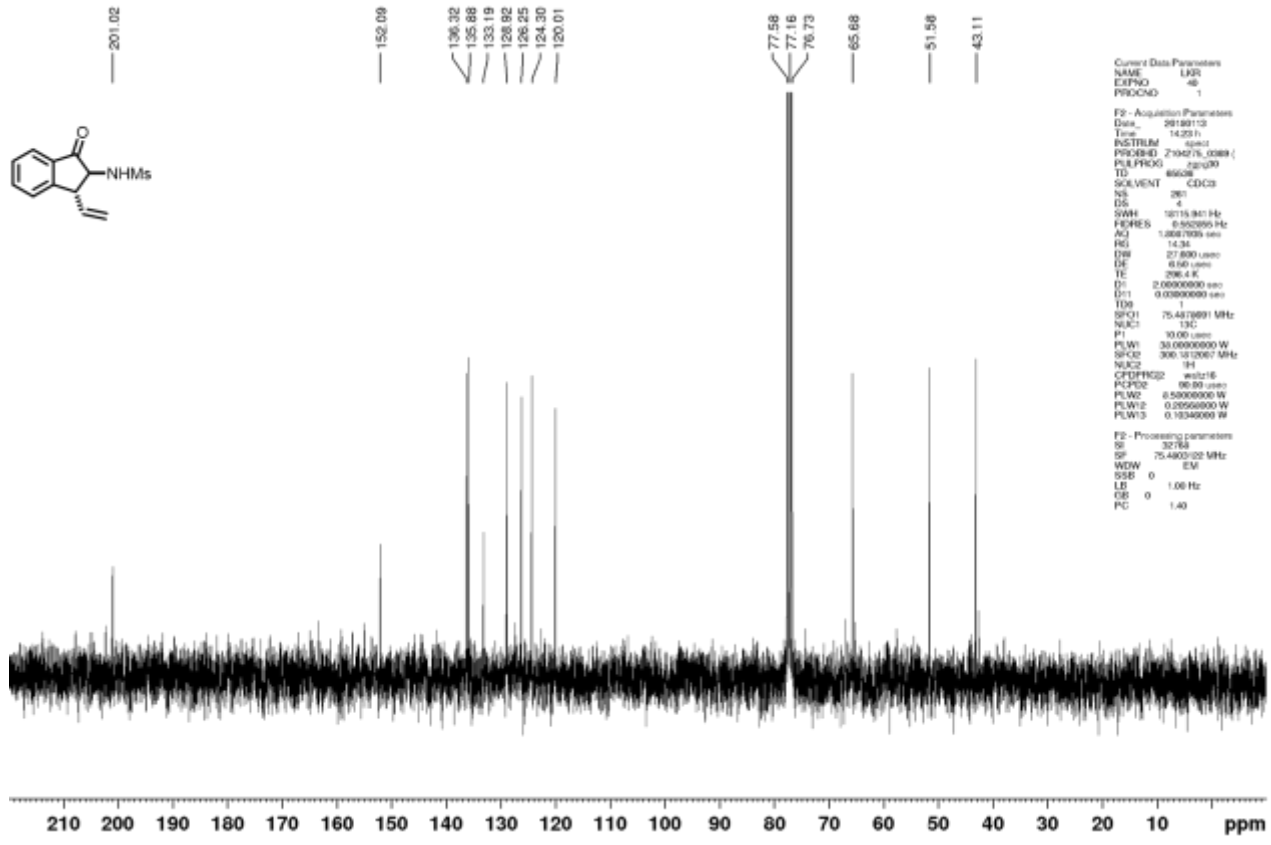
Note.

The *cis/trans* mixture of **3k** was inseparable. Thus, ^{1}H NMR spectra of *cis/trans* mixture after silica column chromatography has been attached below.

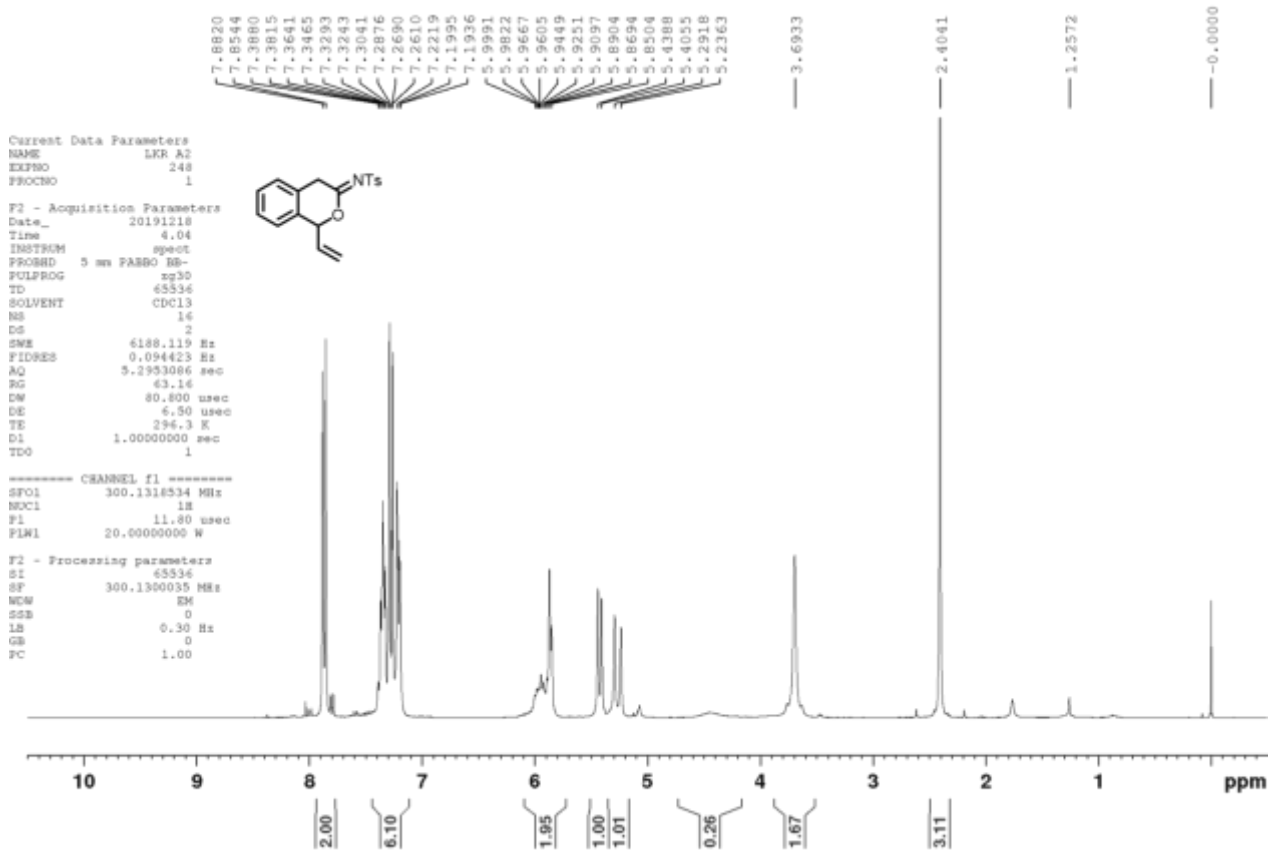
^{1}H spectra of compound **3k** (*cis/trans* mixture after column chromatography)



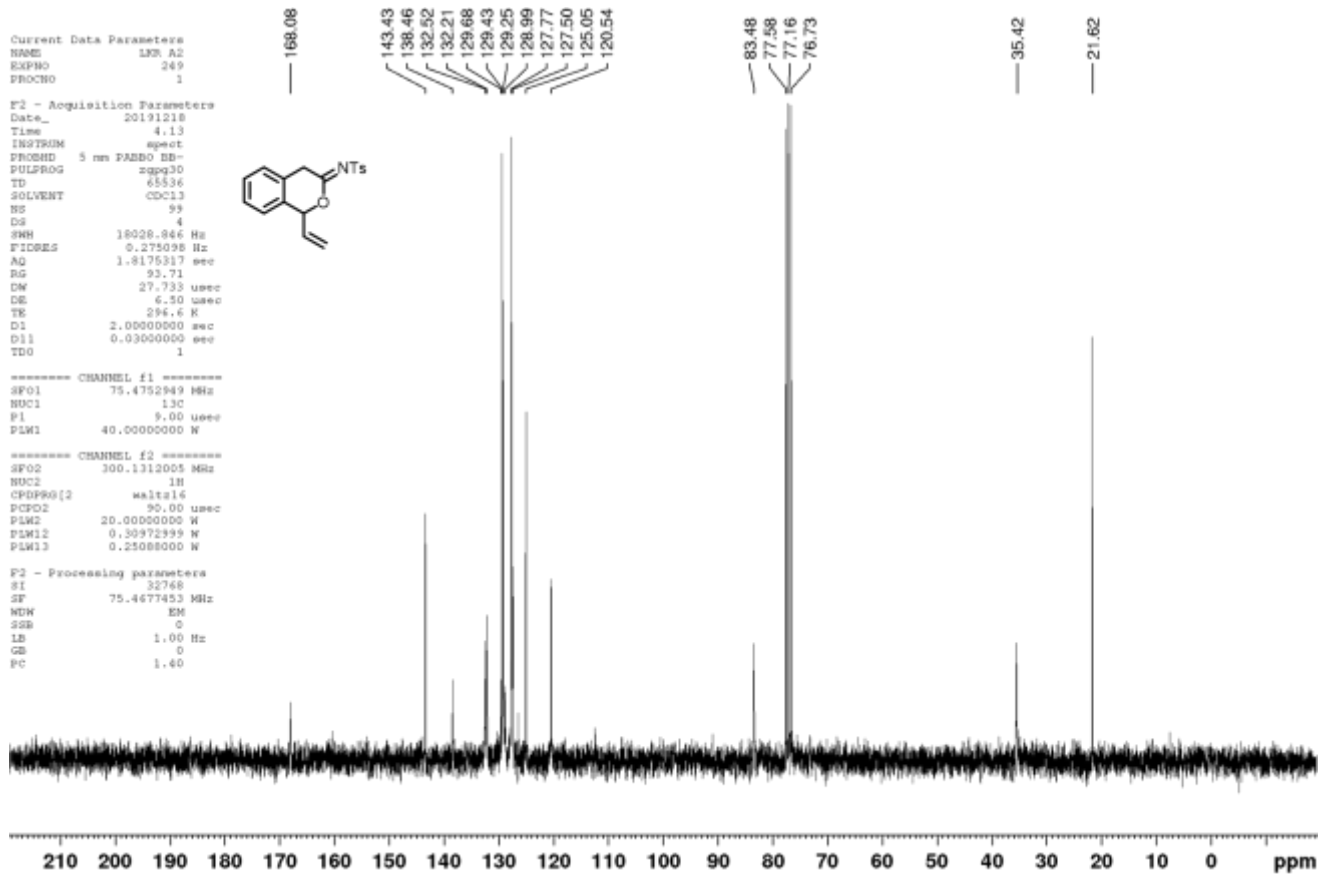
^{13}C spectra of compound **3k** (*trans*)



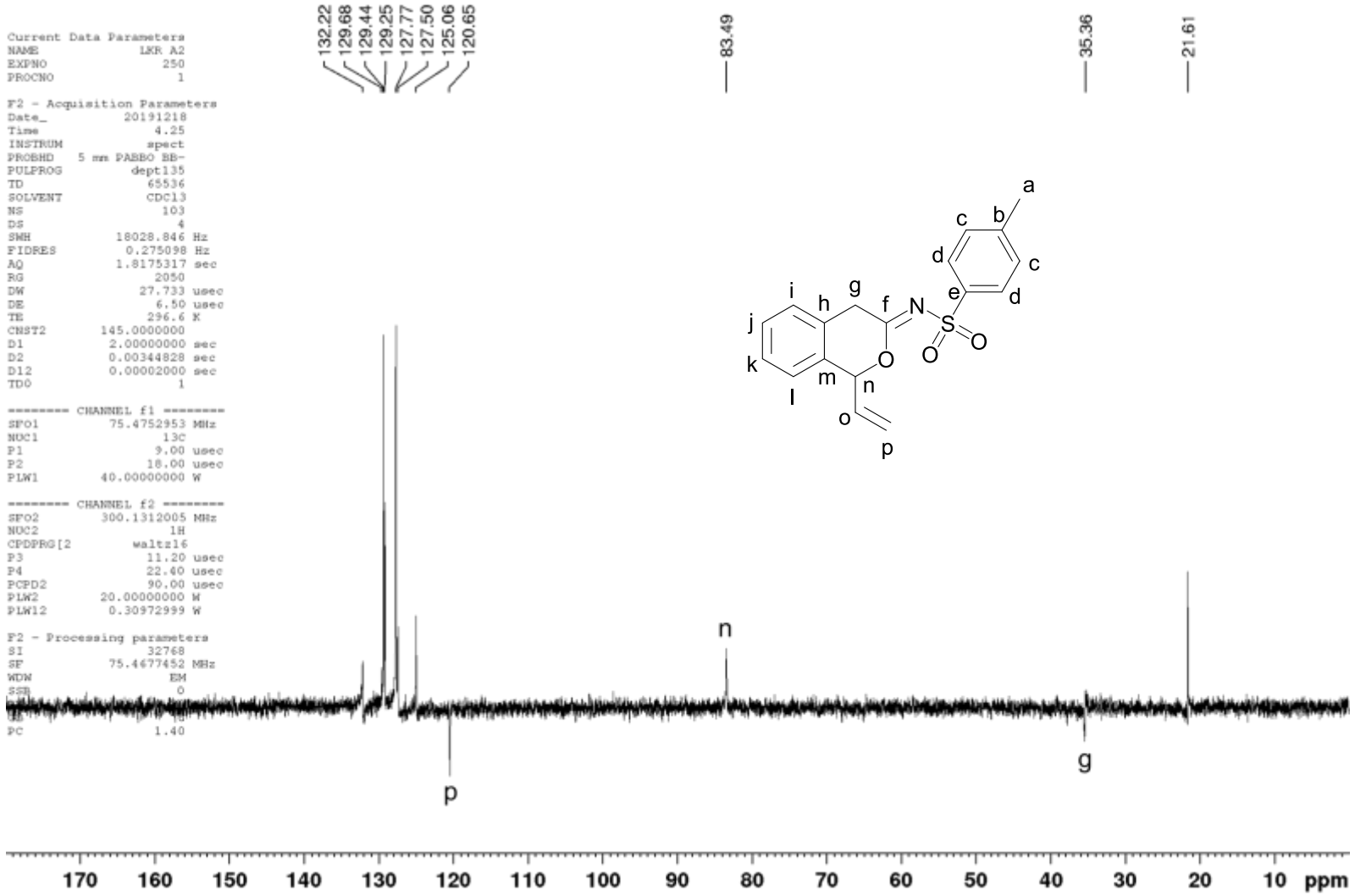
^{1}H spectra of compound **4a**



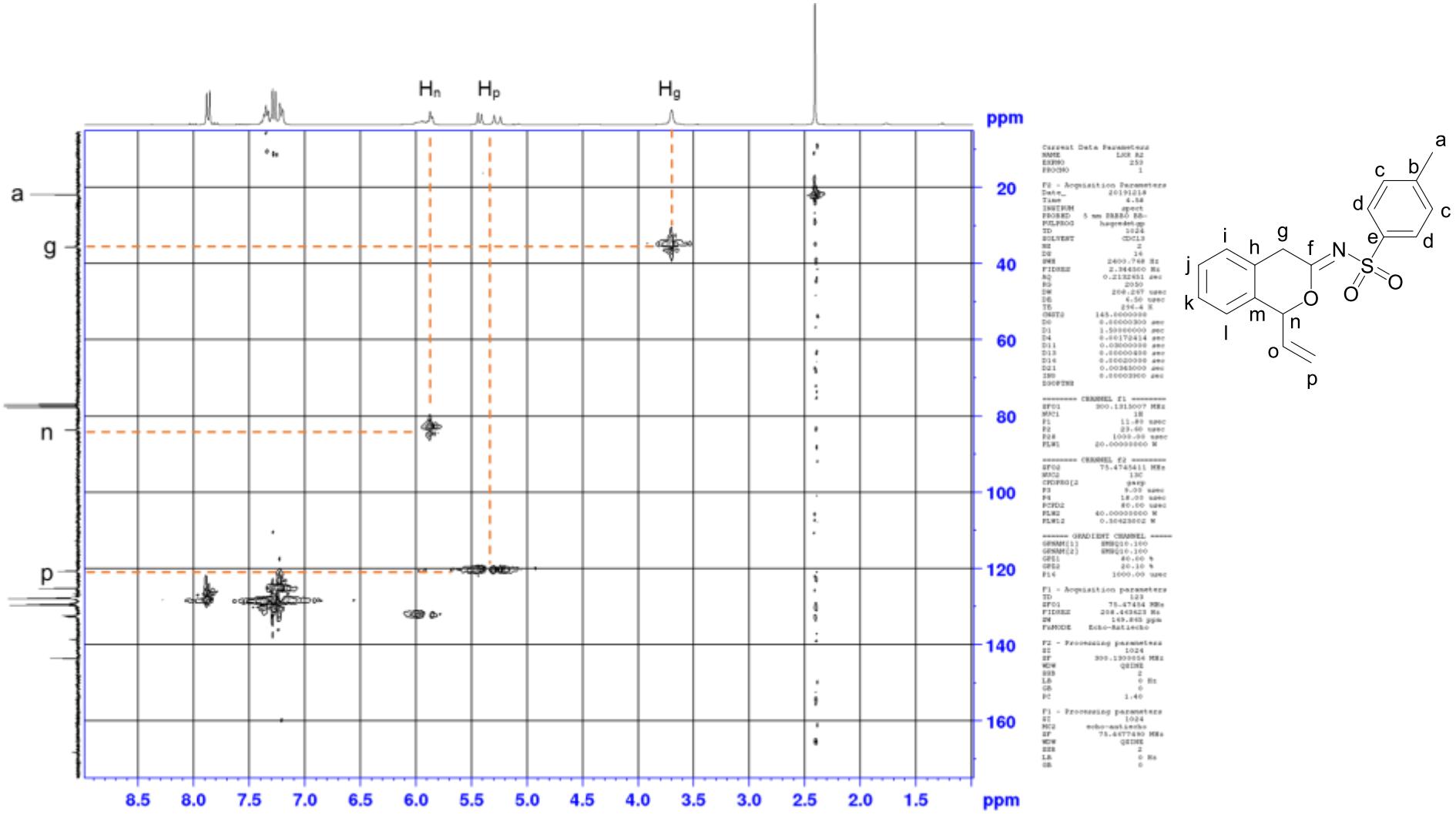
^{13}C spectra of compound **4a**



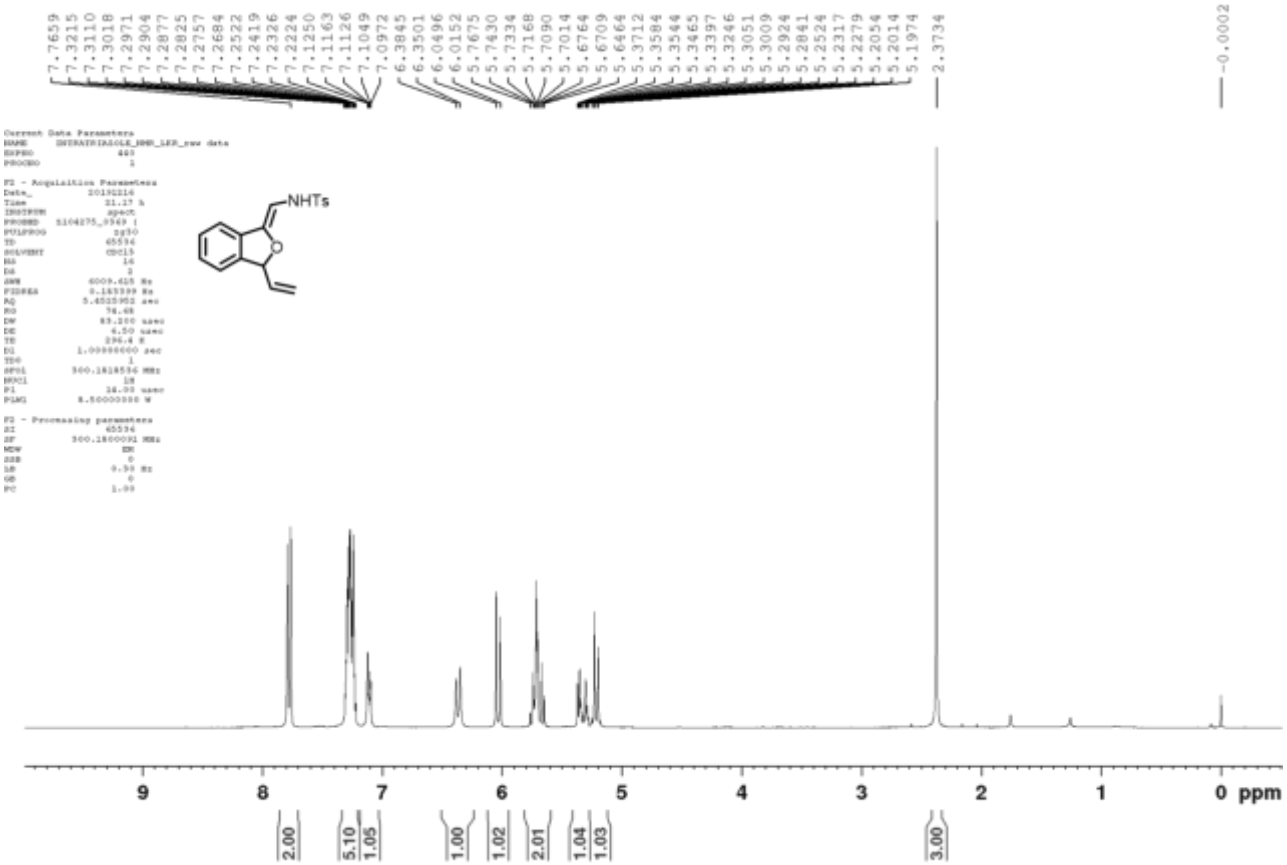
DEPT-135 spectra of compound **4a**



HSQC spectra of compound **4a**



^{1}H spectra of compound **5a**



^{13}C spectra of compound **5a**